Supporting Information

Synthesis of 1,4-Benzoxazines via $Y(OTf)_3$-Catalyzed Ring Opening/Annulation Cascade Reaction of Benzoxazoles with Propargylic Alcohols

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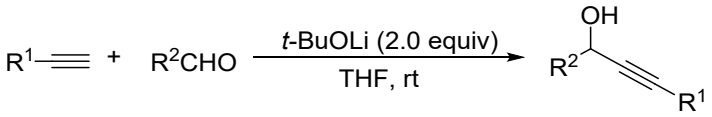
CONTENTS

1. General Information

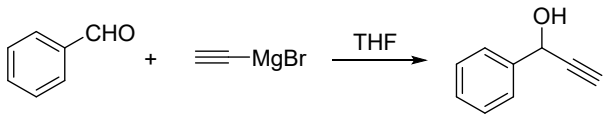
All commercially available reagents were used directly without purification unless otherwise stated. All solvents were purified following standard procedures. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. NMR spectra were recorded on a Bruker advance III 500 (^{1}H NMR: 500 MHz, ^{13}C NMR: 126 MHz) spectrometer. ^{1}H NMR spectra were referenced to the residual solvent signal ($CDCl_3$ = 7.26 ppm) or TMS. ^{13}C NMR spectra were referenced to the residual solvent signal ($CDCl_3$ = 77.0 ppm). Chemical shifts are given in ppm. IR spectra were recorded on a FT-IR instrument. The HRMS analysis was obtained on a QTOF mass spectrometer. Melting points were determined with melting points apparatus and are uncorrected. X-ray diffraction data were collected at 273 K or 293 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Enantiomeric excesses (ee) were determined by HPLC analysis on Shimazu (LC-2020) HPLC or Thermo Fisher HPLC with Daicel chiral columns. Substrates **1**[1,2], compound **8**[3] and (*S*)-**1a**[4] were synthesized in the lab by the reported procedures. Substrates **2** were purchased from commercial sources and used directly without further purification unless otherwise stated.

2. General Procedure for the Preparation of Substrates 1



Scheme S1

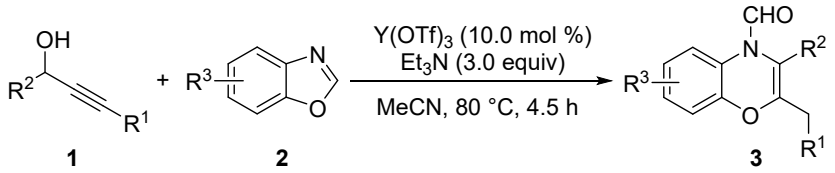
To the solution of aldehydes (1.0 equiv, 10.0 mmol) and alkynes (1.1 equiv, 11.0 mmol) in THF (10.0 mL) was added *t*-BuOLi (1.1 equiv, 11.0 mmol, 1.8 g) at room temperature. The solution was stirred at room temperature for overnight. After the completion of the reaction, the mixture was quenched by the addition of water and extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) afforded the desired products **1** (Scheme S1).



Scheme S2

To a solution of benzaldehyde (10.0 mmol, 1.06 g, 1.0 equiv) in THF (30.0mL) was added dropwise ethynylmagnesium bromide (1.5 equiv, 0.5 M solution in THF, 30.0 mL) at 0 °C under argon. Then the mixture was warmed up to room temperature and stirred for 5 h. The resulting reaction mixture was quenched with saturated NH_4Cl solution, and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to afford the desired product **1j** as a yellow oil (1.2 g, 91% yield) (Scheme S2).

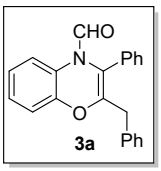
3. General Procedure for the Synthesis of ***Products*** 3



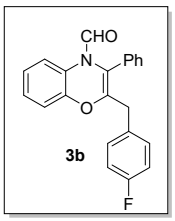
Scheme S3

To a solution of compounds **1** (0.2 mmol, 1.0 equiv), compounds **2** (0.3 mmol, 1.5 equiv), and Et_3N (61.0 mg, 0.6 mmol, 3.0 equiv) in MeCN (2.0 mL) was added $Y(OTf)_3$ (10.7 mg, 10.0 mol %) under an air atmosphere in a sealed tube. The resulting mixture was stirred at 80 °C in an oil bath for the indicated time. After cooling at room temperature, the mixture was concentrated under reduced pressure. The residue was purified on a silica gel column to afford the products **3** (Scheme S3).

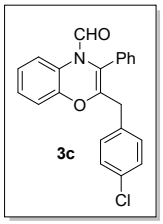
4. Spectral Data for the Compounds 3



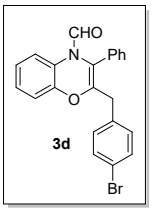
2-Benzyl-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3a)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (44 mg, 68% yield). Mp: 120-123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.99 – 7.94 (m, 1H), 7.48 – 7.38 (m, 5H), 7.33 – 7.19 (m, 5H), 7.12 – 7.05 (m, 2H), 6.87 – 6.81 (m, 1H), 3.53 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.5, 142.4, 137.0, 132.7, 129.9, 129. 4, 129.0, 128.5, 128.3, 126.9, 126.7, 126.5, 123.4, 122.4, 119.7, 116.1, 36.1. IR (KBr): 2783, 1679, 1584, 1495, 1450, 1349, 1301, 1236, 1129, 965, 915, 757, 706, 617 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{17}NO_2Na$ $[M+Na]^+$ 350.1130, found 350.1130.



*2-(4-Fluorobenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3b**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as yellow solid (49 mg, 71% yield). Mp: 123-125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.96 (d, J = 7.0 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.15 – 7.04 (m, 5H), 6.98 – 6.93 (m, 2H), 6.83 (d, J = 7.3 Hz, 1H), 3.48 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 244.8 Hz), 160.2, 148.4, 142.2, 132.6, 132.5, 129.8, 129.8, 129.4, 129.1, 126.9, 123.4, 122.4, 119.7, 116.0, 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz). 35.3. IR (KBr): 2782, 1689, 1584, 1502, 1497, 1350, 1304, 1234, 1149, 1078, 962, 827, 756, 697 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}FNO_2Na$ $[M+Na]^+$ 368.1057, found 368.1050.

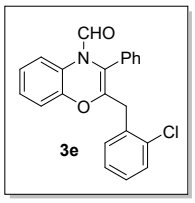


*2-(4-Chlorobenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3c**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (52 mg, 73% yield). Mp: 111-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.45 – 7.36 (m, 5H), 7.28 – 7.20 (m, 2H), 7.12 – 7.07 (m, 4H), 6.83 (d, J = 7.5 Hz, 1H), 3.48 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 148.4, 141.8, 135.4, 132.5, 132.4, 129.8, 129.7, 129.4, 129.1, 128.6, 126.9, 126.5, 123.5, 122.4, 119.9, 116.0, 35.4. IR (KBr): 2789, 1673, 1590, 1489, 1349, 1295, 1233, 1150, 1069, 962, 745, 703, 626 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}ClNO_2Na$ $[M+Na]^+$ 384.0761, found 384.0741.

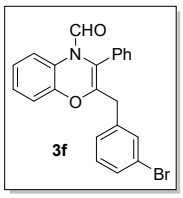


*2-(4-Bromobenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3d**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (59 mg, 73% yield). Mp: 129-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.95 (d, J = 7.3 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.39 (t, J = 7.1 Hz, 5H), 7.11 – 7.03 (m, 4H), 6.83 (d, J = 7.4 Hz, 1H), 3.47 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 148.4, 141.7, 136.0, 132.4, 131.6, 130.1, 129.8, 129.4, 129.2,

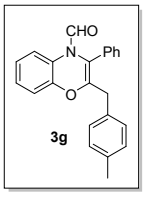
127.0, 123.5, 122.4, 120.6, 119.9, 116.0, 35.5. IR (KBr): 2783, 1685, 1590, 1488, 1406, 1352, 1295, 1242, 1147, 1072, 1000, 965, 837, 754, 703, 620 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}BrNO_2Na$ $[M+2+Na]^+$ 430.0238, found 430.0219.



*2-(2-Chlorobenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3e**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (42 mg, 58% yield). Mp: 118-120 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.30 – 7.25 (m, 1H), 7.23 – 7.17 (m, 1H), 7.10 – 7.05 (m, 3H), 6.99 (t, J = 9.1 Hz, 1H), 6.82 (d, J = 8.6 Hz, 1H), 3.58 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 148.5, 141.1, 132.5, 130.2, 130.2, 129.8, 129.4, 129.1, 128.5, 128.4, 126.9, 124.1, 124.0, 123.9, 123.7, 123.5, 122.4, 120.2, 29.2. IR (KBr): 2884, 1682, 1587, 1492, 1450, 1358, 1304, 1236, 1147, 1078, 757, 703, 629 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}ClNO_2Na$ $[M+Na]^+$ 384.0761, found 384.0749.

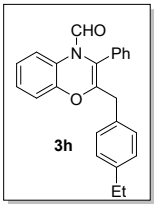


*2-(3-Bromobenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3f**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (55 mg, 68% yield). Mp: 115-117 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.94 (d, J = 7.3 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.4 Hz, 2H), 7.15 – 7.06 (m, 4H), 6.85 (d, J = 7.3 Hz, 1H), 3.50 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 149.3, 142.6, 136.8, 131.9, 131.8, 128.6, 128.3, 127.0, 126.8, 126.4, 123.47, 122.4, 119.0, 116.7, 116.5, 116.1, 36.1. IR (KBr): 2878, 1593, 1498, 1415, 1349, 1304, 1230, 1147, 1084, 971, 831, 751, 700, 599 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}BrNO_2Na$ $[M+2+Na]^+$ 430.0238, found 430.0210.

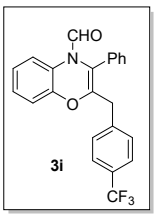


*2-(4-Methylbenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3g**).* Purification by column chromatography on silica gel (petroleum

ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (38 mg, 55% yield). Mp: 63-64 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.08 (d, J = 13.2 Hz, 6H), 6.85 (d, J = 7.4 Hz, 1H), 3.48 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.6, 142.6, 136.2, 133.9, 132.7, 129.9, 129.3, 129.2, 129.0, 128.2, 126.8, 123.3, 122.4, 119.5, 116.1, 35.7, 21.0. IR (KBr): 2966, 2873, 1687, 1580, 1488, 1351, 1298, 1235, 1137, 958, 828, 754, 694, 629 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{23}H_{19}NO_2Na$ $[M+Na]^+$ 364.1308, found 364.1288.

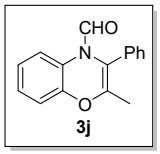


2-(4-Ethylbenzyl)-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3h)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (49 mg, 69% yield). Mp: 67-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.96 (d, J = 7.4 Hz, 1H), 7.45 – 7.34 (m, 5H), 7.14 – 7.04 (m, 6H), 6.89 – 6.83 (m, 1H), 3.49 (s, 2H), 2.61 (d, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.5, 142.6, 134.1, 132.7, 129.8, 129.3, 128.9, 128.2, 128.0, 126.8, 126.5, 123.3, 122.4, 119.5, 116.1, 35.7, 28.4, 15.5. IR (KBr): 2956, 2927, 2870, 1684, 1592, 1491, 1351, 1301, 1235, 1134, 971, 754, 700, 623 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{24}H_{21}NO_2Na$ $[M+Na]^+$ 378.1464, found 378.1445.

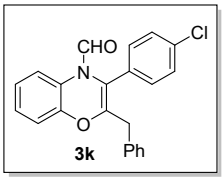


3-Phenyl-2-(4-(trifluoromethyl)benzyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3i)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (64 mg, 81% yield). Mp: 89-94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.97 (d, J = 7.2 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.46 – 7.37 (m, 5H), 7.29 (d, J = 8.0 Hz, 2H), 7.13 – 7.04 (m, 2H), 6.83 (d, J = 7.6 Hz, 1H), 3.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 148.3, 141.2, 141.1, 132.3, 129.8, 129.4, 129.2, 128.9, 128.6, 127.0, 126.4, 125.4 (q, J_{C-F} = 3.8 Hz). 125.3, 125.2, 123.5, 123.0, 122.4, 120.2, 116.0, 35.9. IR (KBr): 2911, 1682, 1575, 1489, 1406, 1340, 1236, 1153,

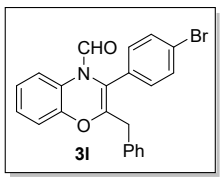
1102, 837, 757, 706, 623 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{23}H_{16}F_3NO_2Na$ $[M+Na]^+$ 418.1025, found 418.1043.



2-Methyl-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3j)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a white solid (18 mg, 36% yield). Mp: 93-94 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.37 (d, J = 6.3 Hz, 3H), 7.12 (dd, J = 18.6, 7.5 Hz, 2H), 6.94 (d, J = 7.8 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.5, 141.0, 133.1, 129.8, 129.2, 128.6, 126.8, 126.5, 123.4, 122. 6, 117.9, 116.0, 16.5. IR (KBr): 2913, 1689, 1584, 1491, 1391, 1343, 1299, 1240, 1202, 1163, 1091, 1017, 948, 856, 754, 702, 622.9, 552, 472 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{16}H_{13}NO_2Na$ $[M+Na]^+$ 274.0838, found 274.0861.

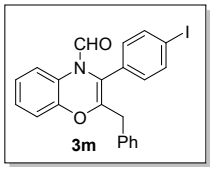


2-Benzyl-3-(4-chlorophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3k)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (49 mg, 68% yield). Mp: 99-101 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.3 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.34 (d, J = 9.7 Hz, 2H), 7.17 – 7.09 (m, 4H), 6.85 (d, J = 7.3 Hz, 1H), 3.49 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 148.3, 141.5, 139.3, 132.4, 131.5, 130.1, 129.9, 129.4, 129.2, 127.0, 126.4, 123.5, 122.5, 122.4, 120.1, 116.1, 35.7. IR (KBr): 2905, 1688, 1581, 1492, 1415, 1352, 1301, 1233, 1135, 1081, 974, 760, 709 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{22}H_{17}ClNO_2$ $[M+H]^+$ 362.0942, found 362.0940.

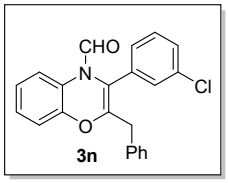


2-Benzyl-3-(4-bromophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3l)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (58 mg, 71% yield). Mp: 97-99 °C. ^1H

NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.92 (d, J = 6.9 Hz, 1H), 7.57 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 6.3 Hz, 4H), 7.23 (d, J = 6.9 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.85 (d, J = 6.9 Hz, 1H), 3.51 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 148.4, 143.0, 136.6, 132.6, 131.7, 131.3, 128.6, 128.2, 127.0, 126.8, 126.3, 123.5, 123.2, 122.5, 118.6, 116.1, 36.1. IR (KBr): 2855, 1685, 1584, 1498, 1387, 1295, 1242, 1141, 1069, 1010, 974, 816, 748, 701 cm^{-1}. HRMS (ESI) calcd for *m*/*z*: $C_{22}H_{16}BrNO_2Na$ $[M+2+Na]^+$ 430.0238, found 430.0221.

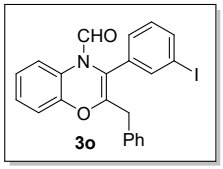


*2-Benzyl-3-(4-iodophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3m**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (58 mg, 64% yield). Mp: 139-142 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, J = 6.9 Hz, 1H), 7.77 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H), 7.23 (d, J = 6.9 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 7.9 Hz, 3H), 7.08 (d, J = 5.9 Hz, 1H), 6.84 (d, J = 6.9 Hz, 1H), 3.51 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 148.4, 143.0, 138.5, 136.6, 132.3, 131.4, 128.6, 128.2, 127.0, 126.8, 126.3, 123.5, 122.5, 118.8, 116.1, 94.9, 36.1. IR (KBr): 2905, 1673, 1587, 1483, 1346, 1236, 1290, 1141, 968, 805, 754, 698 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}INO_2Na$ $[M+Na]^+$ 476.0117, found 476.0149.

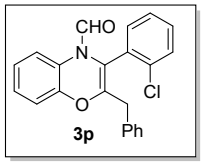


*2-Benzyl-3-(3-chlorophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3n**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid. (46 mg, 64% yield). Mp: 135-137 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.28 (d, J = 7.6 Hz, 3H), 7.24 – 7.22 (m, 1H), 7.18 (d, J = 7.4 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.84 (d, J = 7.5 Hz, 1H), 3.52 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 148.4, 143.4, 136.6, 135.3, 134.6, 131.7, 130.6, 129.7, 129.2, 128.6, 128.3, 128.0, 127.0, 126.8, 123.5, 122.5, 118.4, 116.1, 36.1. IR (KBr): 2902, 1685, 1593, 1486,

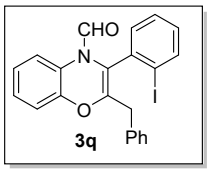
1412, 1349, 1296, 1236, 1141, 1084, 983, 879, 751, 698 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}ClNO_2Na$ *m/z*: $[M+Na]^+$ 384.0761, found 384.0761.



*2-Benzyl-3-(3-iodophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3o**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (62 mg, 68% yield). Mp: 140-141 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.93 (d, J = 7.0 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.36 (d, J = 7.6 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22 (d, J = 7.1 Hz, 1H), 7.18 (d, J = 7.4 Hz, 2H), 7.14 (d, J = 7.7 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.84 (d, J = 7.1 Hz, 1H), 3.50 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 148.3, 143.3, 138.4, 138.0, 136.6, 134.8, 130.8, 129.0, 128.6, 128.3, 127.0, 126.7, 126.2, 123.5, 122.4, 118.1, 116.0, 94.8, 36.1. IR (KBr): 2899, 1682, 1593, 1489, 1415, 1346, 1293, 1236, 1144, 1075, 974, 751, 700 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{22}H_{16}INO_2Na$ $[M+Na]^+$ 476.0117, found 476.0147.

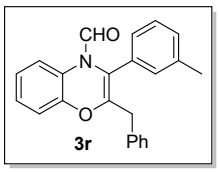


*2-Benzyl-3-(2-chlorophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3p**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (29 mg, 40% yield). Mp: 98-100 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.28 – 7.23 (m, 3H), 7.20 (d, J = 7.1 Hz, 1H), 7.13 (d, J = 7.2 Hz, 3H), 7.09 – 7.06 (m, 2H), 6.86 – 6.81 (m, 1H), 3.47 (d, J = 15.6 Hz, 1H), 3.34 (d, J = 15.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 148.1, 143.8, 136.4, 134.8, 133.2, 130.9, 130.6, 128.5, 128.4, 127.5, 126.8, 126.7, 126.3, 123.6, 122.3, 116.7, 116.1, 36.0. IR (KBr): 2872, 1685, 1593, 1486, 1348, 1301, 1239, 1147, 968, 760, 700 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{22}H_{16}ClNO_2Na$ $[M+Na]^+$ 384.0761, found 384.0749.

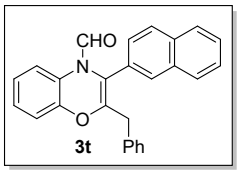


*2-benzyl-3-(2-iodophenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3q**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title

compound as a yellow solid (24 mg, 26% yield). Mp: 96-99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.94 (m, 2H), 7.46 – 7.35 (m, 2H), 7.27 – 7.22 (m, 2H), 7.20 (d, J = 7.0 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.10 – 7.04 (m, 2H), 6.86 – 6.81 (m, 1H), 3.45 (d, J = 15.5 Hz, 1H), 3.31 (d, J = 15.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 147.9, 143.2, 140.4, 136.7, 136.2, 133.1, 130.8, 128.8, 128.5, 128.4, 126.8, 126.6, 126.5, 123.5, 122.4, 120.6, 116.1, 100.8, 36.0. IR (KBr): 2872, 1685, 1593, 1486, 1349, 1301, 1239, 1147, 968, 760, 700 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}INO_2Na$ $[M+Na]^+$ 476.0117, found 476.0131.

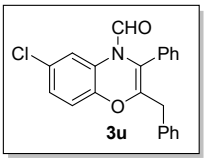


2-Benzyl-3-(m-tolyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3r)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (50 mg, 74% yield). Mp: 113-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.01 – 7.94 (m, 1H), 7.30 – 7.24 (m, 3H), 7.21 – 7.16 (m, 6H), 7.09 – 7.02 (m, 2H), 6.86 – 6.79 (m, 1H), 3.52 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.5, 142.1, 139.1, 137.1, 132.5, 130.3, 129.7, 129.1, 128.4, 128.3, 127.0, 126.8, 126.6, 123.3, 122.3, 119.7, 116.0, 36.1, 21.3. IR (KBr): 2920, 1685, 1593, 1491, 1414, 1313, 1242, 1158, 1114, 1061, 834, 757, 698 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1488, found 342.1479.

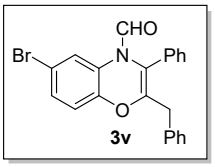


2-Benzyl-3-(naphthalen-2-yl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde ***(3t)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (51 mg, 67% yield). Mp: 102-105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 9.9 Hz, 2H), 7.81 – 7.77 (m, 1H), 7.57 – 7.49 (m, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.23 – 7.20 (m, 3H), 7.13 – 7.06 (m, 2H), 6.87 (d, J = 8.6 Hz, 1H), 3.59 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 148.6, 142.9, 137.1, 133.2, 133.1, 129.9, 129.7, 129.4, 128.5, 128.4, 128.0, 127.8, 127.0, 126.9, 126.7, 126.6, 126.4, 123.4, 122.4, 119.7, 116.1, 36.2. IR (KBr): 2911, 1670,

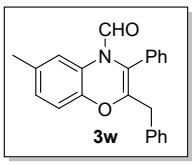
1587, 1489, 1418, 1346, 1287, 1236, 1132, 1087, 751, 695 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{26}H_{19}NO_2Na$ $[M+Na]^+$ 400.1308, found 400.1302.



*2-Benzyl-6-chloro-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3u**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (40 mg, 52% yield). Mp: 106-108 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 50.8 Hz, 2H), 7.49 – 7.37 (m, 5H), 7.31 – 7.26 (m, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 7.2 Hz, 2H), 7.09 – 7.02 (m, 1H), 6.75 (d, J = 8.6 Hz, 1H), 3.51 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 147.1, 142.3, 136.7, 132.2, 129.9, 129.5, 129.2, 128.6, 128.3, 127.4, 126.8, 126.7, 122.4, 119.4, 116.9, 36.0. IR (KBr): 2893, 1688, 1590, 1489, 1426, 1352, 1304, 1233, 1129, 1090, 971, 855, 807, 751, 698 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{17}ClNO_2$ $[M+H]^+$ 384.0761, found 384.0729.

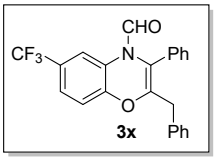


*2-Benzyl-6-bromo-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3v**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (46 mg, 57% yield). Mp: 84-86 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 26.2 Hz, 2H), 7.45 – 7.36 (m, 5H), 7.29 – 7.25 (m, 2H), 7.23 – 7.14 (m, 4H), 6.67 (d, J = 8.6 Hz, 1H), 3.49 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 147.6, 142.2, 136.6, 132.1, 129.8, 129.6, 129.4, 129.2, 128.5, 128.2, 127.6, 126.7, 125.1, 119.4, 117.3, 115.4, 35.9. IR (KBr): 2890, 1682, 1590, 1486, 1423, 1352, 1299, 1230, 1135, 1084, 962, 784, 692 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}BrNO_2Na$ $[M+2+Na]^+$ 430.0238, found 430.0230.

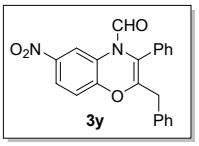


*2-Benzyl-6-methyl-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3w**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (42 mg, 62% yield). Mp: 115-117 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.78 (s, 1H), 7.47 – 7.35 (m, 5H), 7.29 – 7.24 (m, 2H), 7.22 –

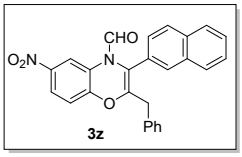
7.16 (m, 3H), 6.88 (d, J = 7.9 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 3.51 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 146.4, 142.6, 137.0, 133.1, 132.8, 129.9, 129.3, 128.9, 128.5, 128.3, 127.3, 126.6, 126.2, 122.7, 119.5, 115.7, 36.1, 20.9. IR (KBr): 2920, 1679, 1599, 1501, 1435, 1355, 1289, 1242, 1131, 1072, 968, 804, 742, 700 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1488, found 342.1460.



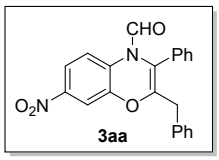
*2-Benzyl-3-phenyl-6-(trifluoromethyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3x**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (40 mg, 51% yield). Mp: 95-98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.14 (s, 1H), 7.46 – 7.39 (m, 5H), 7.34 (d, J = 9.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.17 (d, J = 7.3 Hz, 2H), 6.88 (d, J = 8.4 Hz, 1H), 3.52 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 150.9, 141.9, 136.6, 131.9, 129.8, 129.5, 129.4, 129.1, 128.8, 128.6, 128.4, 128.3, 126.9, 126.8, 124.2 (d, J_{C-F} = 3.4 Hz). 119.9, 119.8, 116.4, 35.9. IR (KBr): 2893, 1697, 1604, 1503, 1441, 1358, 1319, 1251, 1155, 1120, 962, 828, 757, 695, 635 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{23}H_{16}F_3NO_2Na$ $[M+Na]^+$ 418.1025, found 418.1025.



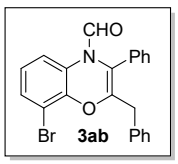
*2-Benzyl-6-nitro-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3y**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (24 mg, 32% yield). Mp: 119-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.16 (s, 1H), 8.04 – 7.98 (m, 1H), 7.53 – 7.40 (m, 5H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.17 (d, J = 7.2 Hz, 2H), 6.90 (d, J = 8.9 Hz, 1H), 3.53 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 153.4, 143.4, 141.5, 136.3, 131.3, 129.8, 129.7, 128.7, 128.3, 127.0, 126.7, 123.0, 119.8, 118.4, 116.2, 35.8. IR (KBr): 2845, 1682, 1584, 1528, 1486, 1444, 1343, 1281, 1239, 1141, 1063, 974, 897, 733, 698 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}N_2O_4Na$ $[M+Na]^+$ 395.1002, found 395.0984.



*2-Benzyl-3-(naphthalen-2-yl)-6-nitro-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3z**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (42 mg, 50% yield). Mp: 90-93 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.19 (s, 1H), 8.05 – 7.95 (m, 2H), 7.89 (d, J = 7.7 Hz, 2H), 7.86 – 7.82 (m, 1H), 7.63 – 7.53 (m, 2H), 7.50 – 7.44 (m, 1H), 7.33 – 7.28 (m, 2H), 7.25 (d, J = 7.0 Hz, 1H), 7.19 (d, J = 7.1 Hz, 2H), 6.93 (d, J = 8.9 Hz, 1H), 3.60 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.94, 153.5, 142.0, 136.4, 133.4, 133.2, 129.9, 129.8, 128.7, 128.3, 128.0, 127.9, 127.5, 127.2, 127.0, 126.0, 123.0, 119.9, 118.4, 116.2, 36.0. IR (KBr): 2914, 1688, 1584, 1518, 1482, 1340, 1242, 1126, 1063, 819, 742, 695 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{26}H_{18}N_2O_4Na$ $[M+Na]^+$ 445.1158, found 445.1158.



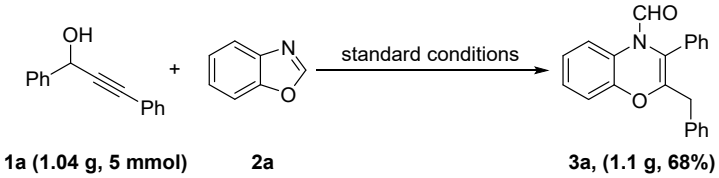
*2-Benzyl-7-nitro-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3aa**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (55 mg, 74% yield). Mp: 174-176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.10 (m, 2H), 7.96 – 7.91 (m, 1H), 7.66 (d, J = 1.9 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.44 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.17 (d, J = 7.1 Hz, 2H), 3.52 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 148.5, 145.7, 142.0, 136.2, 132.4, 131.4, 129.8, 129.7, 128.7, 128.3, 127.0, 122.3, 119.3, 119.1, 111.5, 35.8. IR (KBr): 2922, 1685, 1596, 1506, 1435, 1337, 1278, 1227, 1138, 1087, 885, 757, 695 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}N_2O_4Na$ $[M+Na]^+$ 395.1002, found 395.0983.



*2-Benzyl-8-bromo-3-phenyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**3ab**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (46 mg, 57% yield). Mp: 111-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.32 – 7.21 (m, 6H), 6.93 (s, 1H), 3.54 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 145.9, 143.0, 136.6, 132.1, 130.3, 129.9, 129.4, 129.2, 128.7, 128.5, 127.6, 126.8, 123.9, 121.5, 119.6, 109.6, 36.0. IR (KBr):

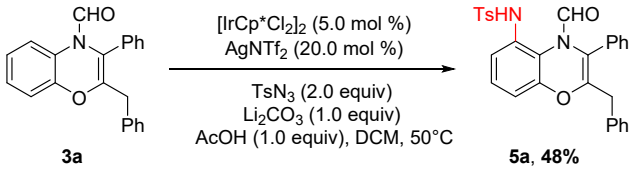
2908, 1688, 1581, 1465, 1346, 1266, 1221, 1105, 968, 754, 698 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{16}BrNO_2Na$ $[M+2+Na]^+$ 430.0238, found 430.0279.

5. Scale-up Reaction and Derivatizations



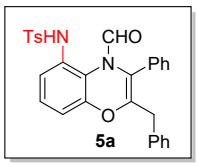
Scheme S4

Scale-up reaction: Compound **1a** (5.0 mmol, 1.04 g, 1.0 equiv), **2a** (7.5 mmol, 893 mg, 1.5 equiv), $Y(OTf)_3$ (0.5 mmol, 268 mg) and Et_3N (15.0 mmol, 1.5 g) were added to a sealed tube, and toluene (50.0 mL) was added via syringe under an air atmosphere. The reaction mixture was stirred at 80 °C until completion (monitored by TLC). After cooling at room temperature, the mixture was concentrated under reduced pressure. The residue was purified on a silica gel column (petroleum ether/ethyl acetate = 10: 1, v/v) to afford the product **3aa** (1.1 g, 68%) (Scheme S4).

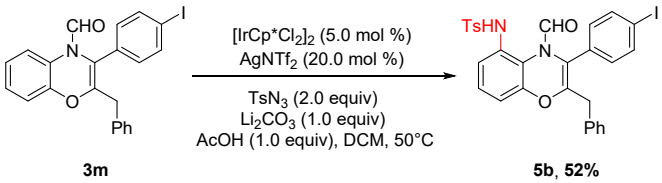


Scheme S5

To a round bottom flask was added **3a** (0.15 mmol, 49 mg, 1.0 equiv), TsN_3 (0.3 mmol, 59 mg, 2.0 equiv), $[IrCp^*Cl_2]_2$ (5.0 mol %, 6 mg), $AgNTf_2$ (20.0 mol %, 11.6 mg) Li_2CO_3 (0.15 mmol, 11 mg, 1.0 equiv) and AcOH (0.15 mmol, 9 mg, 1.0 equiv) in open atmosphere in DCM (2.0 mL). Then, the reaction mixture was refluxed at 50 °C in an oil bath for 5 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, and diluted with 50% EtOAc/hexane (5 mL), passed through a short silica gel (100-200 mesh size) bed, and washed with 50% EtOAc/ hexane. The combined organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) to give the corresponding product **5a** as a yellow solid (Scheme S5).

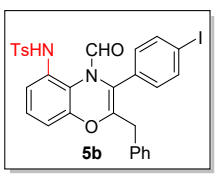


N-(2-benzyl-4-formyl-3-phenyl-4H-benzo[b][1,4]oxazin-5-yl)-4-methylbenzenesulfon-amide ***(5a)***. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded the title compound as a yellow solid (36 mg, 48% yield). Mp: 75-76 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.91 (s, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.3 Hz, 3H), 7.31 – 7.21 (m, 5H), 7.18 (d, J = 8.1 Hz, 1H), 7.16 – 7.11 (m, 3H), 6.99 (d, J = 6.2 Hz, 2H), 6.76 – 6.72 (m, 1H), 3.62 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 151.7, 145.8, 143.6, 138.1, 136.4, 132.6, 130.1, 129.6, 129.2, 129.1, 129.0, 128.6, 128.2, 128.1, 126.9, 126.8, 121.2, 121.1, 114.0, 36.0, 21.5. IR (KBr): 2917, 1670, 1593, 1483, 1349, 1284, 1239, 1153, 1093, 1024, 813, 703, 659 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{29}H_{24}N_2O_4SNa$ $[M+Na]^+$ 519.1348, found 519.1339.



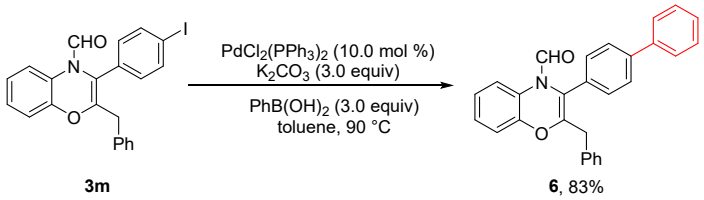
Scheme S6

To a round bottom flask was added **3m** (0.15 mmol, 68 mg, 1.0 equiv), TsN_3 (0.3 mmol, 59 mg, 2.0 equiv), $[IrCp^*Cl_2]_2$ (5.0 mol %, 6 mg), $AgNTf_2$ (20.0 mol %, 11.6 mg) Li_2CO_3 (0.15 mmol, 11 mg, 1.0 equiv) and AcOH (0.15 mmol, 9 mg, 1.0 equiv) in open atmosphere in DCM (2.0 mL). Then, the reaction mixture was refluxed at 50 °C in an oil bath for 5 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, and diluted with 50% EtOAc/hexane (5 mL), passed through a short silica gel (100-200 mesh size) bed, and washed with 50% EtOAc/ hexane. The combined organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) to give the corresponding product **5b** as a yellow solid (Scheme S6).



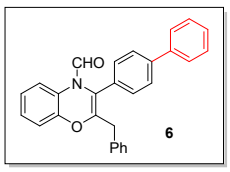
N-(2-benzyl-4-formyl-3-(4-iodophenyl)-4H-benzo[b][1,4]oxazin-

*5-yl)-4-methylbenzenesulfonamide (**5b**)*. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded the title compound as a yellow solid (49 mg, 52% yield). Mp: 93-95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.80 (s, 1H), 7.74 – 7.67 (m, 4H), 7.34 – 7.25 (m, 5H), 7.19 – 7.08 (m, 4H), 6.84 – 6.74 (m, 3H), 3.62 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 151.6, 146.5, 143.7, 138.5, 138.1, 136.2, 132.3, 130.8, 130.1, 129.7, 128.7, 128.2, 127.0, 121.7, 121.5, 121.2, 120.3, 114.3, 95.1, 36.2, 21.3. IR (KBr): 2915, 1670, 1590, 1482, 1352, 1242, 1162, 1099, 1021, 811, 698, 662, 549 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{29}H_{23}IN_2O_4SNa$ $[M+Na]^+$ 645.0315, found 645.0340.



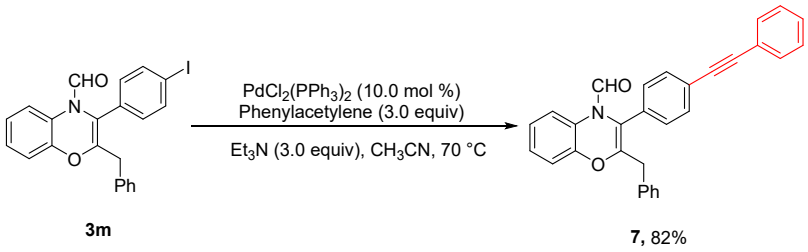
Scheme S7

To a solution of **3m** (0.1 mmol, 1.0 equiv, 45 mg), phenylboronic acid (0.3 mmol, 3.0 equiv, 37 mg) and K_2CO_3 (0.3 mmol, 42 mg, 3.0 equiv) in toluene (2.0 mL) was added $PdCl_2(PPh_3)_2$ (7 mg, 10.0 mol%). The resulting mixture was then heated under a nitrogen atmosphere at 90 °C. in an oil bath for 1 h. After the completion of the reaction, the mixture was cooled to room temperature, and the solid was removed by filtration. Then the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1, v/v) on silica gel to provide the desired product **6** as yellow solid (Scheme S7).



*3-([1,1'-Biphenyl]-4-yl)-2-benzyl-4H-benzo[b][1,4]oxazine-4-carbaldehyde (**6**)*. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (34 mg, 83% yield). Mp: 156-158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.97 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 7.4 Hz, 2H), 7.47 (d, J = 8.2 Hz, 4H), 7.40 – 7.36 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 –

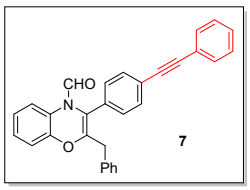
7.22 (m, 3H), 7.12 – 7.07 (m, 2H), 6.86 (d, J = 7.3 Hz, 1H), 3.59 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 148.6, 142.6, 141.8, 140.0, 137.0, 131.5, 130.2, 129.5, 128.9, 128.6, 128.3, 128.0, 127.8, 127.0, 126.9, 126.7, 123.4, 122.5, 119.5, 116.1, 115.3, 36.2. IR (KBr): 2902, 1682, 1587, 1489, 1355, 1292, 1236, 1137, 968, 762, 698 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{28}H_{22}NO_2$ $[M+H]^+$ 404.1645, found 404.1647.



3m **7**, 82%

Scheme S8

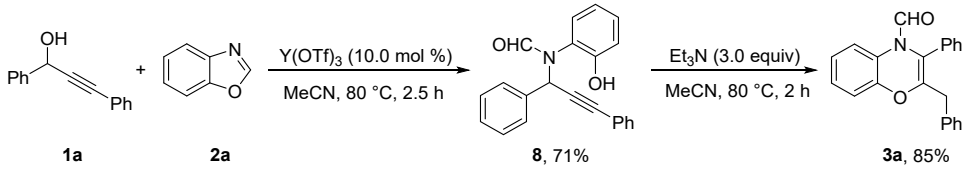
To a solution of **3m** (0.1 mmol, 1.0 equiv, 45 mg), phenyl acetylene (0.3 mmol, 3.0 equiv) and Et_3N (0.3 mmol, 31 mg, 3.0 equiv) in MeCN (2.0 mL) was added $PdCl_2(PPh_3)_2$ (10 % mol, 7 mg). The resulting mixture was then heated under a nitrogen atmosphere at 70 °C in an oil bath for 1 h. After the completion of the reaction, the mixture was cooled to room temperature, and the solid was removed by filtration. Then the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1, v/v) on silica gel to provide the desired product **7** as yellow solid (Scheme S8).



2-Benzyl-3-(4-(phenylethynyl)phenyl)-4H-benzo[b][1,4]oxazine-4-carbaldehyde (7). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow solid (35 mg, 82% yield). Mp: 139-141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.94 (d, J = 6.9 Hz, 1H), 7.59 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 4.2 Hz, 2H), 7.40 – 7.33 (m, 5H), 7.28 (d, J = 7.3 Hz, 2H), 7.23 (d, J = 6.5 Hz, 1H), 7.20 (d, J = 7.7 Hz, 2H), 7.07 (d, J = 11.8 Hz, 2H), 6.85 (d, J = 6.9 Hz, 1H), 3.55 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 148.5, 143.1, 136.8, 132.4, 131.6, 129.7, 128.6, 128.4, 128.3, 126.9, 126.7,

126.4, 124.1, 123.5, 122.8, 122.5, 119.2, 116.1, 91.0, 88.5, 36.2. IR (KBr): 2908, 1679, 1590, 1488, 1355, 1293, 1236, 1143, 965, 831, 757, 688 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{30}H_{22}NO_2$ $[M+H]^+$ 428.1645, found 428.1666.

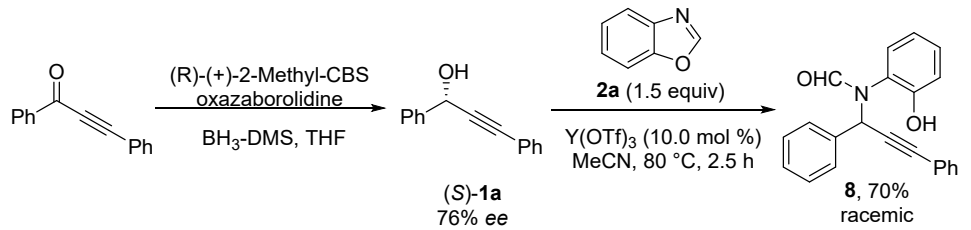
6. Control Experiments



Scheme S9

$Y(OTf)_3$ (11 mg, 10 mol %) was added to a solution of the benzoxazole (1.5 equiv, 0.3 mmol, 36 mg) and propargylic alcohol (1.0 equiv, 0.2 mmol, 42 mg) in MeCN (2.0 mL) under an air atmosphere. The resulting mixture was heated at 80 °C in an oil bath for 2.5 h. After the completion of the reaction, the mixture was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) on silica gel to provide the desired product **8** as white solid (71%, 47 mg).

To a round bottom flask was added **8** (0.1 mmol, 33 mg, 1.0 equiv) and Et_3N (0.3 in open atmosphere in MeCN (2.0 mL). Then, the resulting mixture was heated at 80 °C in an oil bath for 2 h. After the completion of the reaction, the mixture was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) on silica gel to provide the desired product **3a** as yellow solid (85%, 28 mg) (Scheme S9).[3]

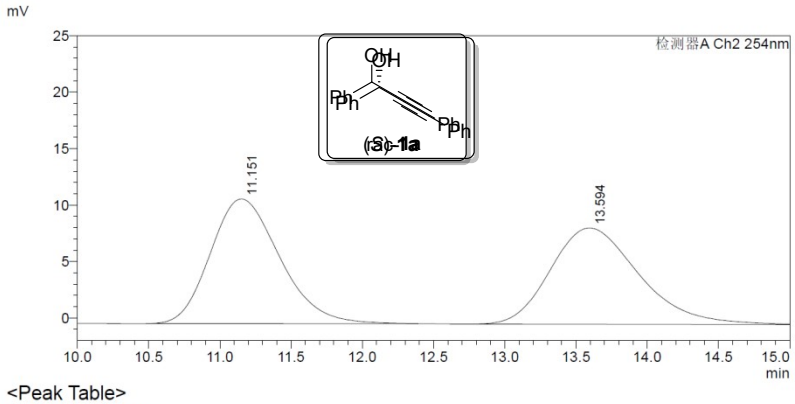


Scheme S10

(*R*)-(+)-2-Methyl-CBS-oxazaborolidine (5.0 mol%) was taken in a clean and dry round bottom flask. High vacuum was applied and released under nitrogen atmosphere. The flask was fitted with clean septa and nitrogen balloon. Dry THF (10 mL, for 1.0

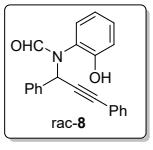
mmol of alkynyl ketone) was added to the flask and cooled to 0 °C. Then BH_3-DMS (1.1 equiv) was added via a syringe dropwise and allowed to stir for 20 min at 0 °C. Alkynyl ketone (1.0 equiv) in 10 mL dry THF was added dropwise at 0 °C and allowed the reaction to stir for less than 20 min at 0 °C. The reaction was quenched with methanol. The solvent was removed under vacuum, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) on silica gel to provide the desired product (*S*)-**1a** as yellow oil (60%, 125 mg, 76% *ee*).[4] The *ee* was measured by HPLC (Chiralpak OD column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 1 = 254 nm).

$Y(OTf)_3$ (11 mg, 10 mol %) was added to a solution of the benzoxazole(1.5 equiv, 0.3 mmol, 36 mg) and (*S*)-**1a** (1.0 equiv, 0.2 mmol, 42 mg) in MeCN (2.0 mL) under an air atmosphere. The resulting mixture was heated at 80 °C in an oil bath for 2.5 h. After the completion of the reaction, the mixture was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) on silica gel to provide the racemic product **8** as white solid (70%, 45 mg) (Scheme S10). The *ee* was measured by HPLC (Chiralpak IA column, hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, 1 = 254 nm).



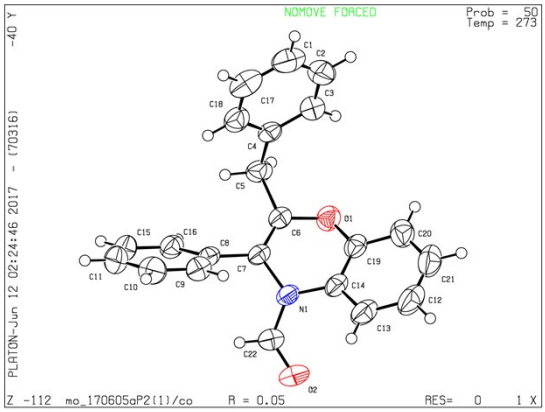
<Peak Table>
检测器A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.151	373918	11041	50.247
2	13.594	370244	8533	49.753
总计		744161	19574	100.000



7. X-Ray Analysis Data of Single Crystal 3a and 3j

The crystal of products **3a** and **3j** were obtained by slow evaporation in *n*-hexane and dichloromethane. The single crystal X-ray analysis determined the structure of products **3a** and **3j** (**Figure S1**) as expected.



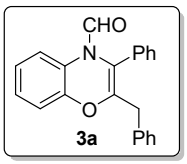


Figure S1. X-ray structure of 3a. Thermal ellipsoids shown at 50% probability.

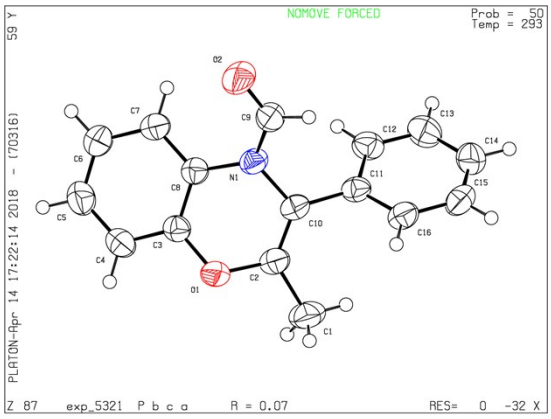
Bond precision	C-C = 0.0023 Å
Wavelength	0.71073
Cell	a=9.6932(5) b=10.1353(5) c=18.2929(8)
Temperature	273 K

	Calculated	Reported
Volume	1707.69(15)	1707.69(14)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C22 H17 N O2	?
Sum formula	C22 H17 N O2	C22 H17 N O2
Mr	327.37	327.37
Dx, g cm^{-3}	1.273	1.273
Z	4	4
Mu (mm^{-1})	0.082	0.082
F000	688.0	688.0
F000’	688.30	-
h, k, lmax	12, 13, 24	12, 13, 24

Nref	4267	4245
Tmin, Tmax	-	0.688, 0.746
Tmin’		

Correction method= # Reported T Limits : Tmin = 0.688 Tmax = 0.746

Data completeness = 0.995	Theta(max) = 28.360
R(reflections) = 0.0466 (3244)	wR_2(reflections) = 0.1235 (4245)
S = 1.020	Npar= 226



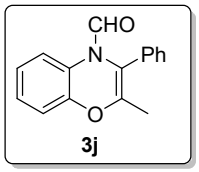


Figure S2. X-ray structure of 3j. Thermal ellipsoids shown at 50% probability.

Bond precision	C-C = 0.0044 Å
Wavelength	0.71073
Cell	a=18.0493(10) b=8.6789(6) c=16.1121(11)
Temperature	293 K

	Calculated	Reported
Volume	2523.9 (3)	1707.69 (14)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C16 H13 N O2	C16 H13 N O2
Sum formula	C16 H13 N O2	C16 H13 N O2
Mr	251.27	251.27
Dx, g cm^{-3}	1.323	1.323
Z	8	8

Mu (mm^{-1})	0.088	0.088
F000	1056.0	1056.0
F000’	1056.48	
h, k, lmax	23, 11, 20	23, 11, 20
Nref	2748	2702
Tmin, Tmax	0.981, 0.982	0.661, 1.000
Tmin’	0,981	

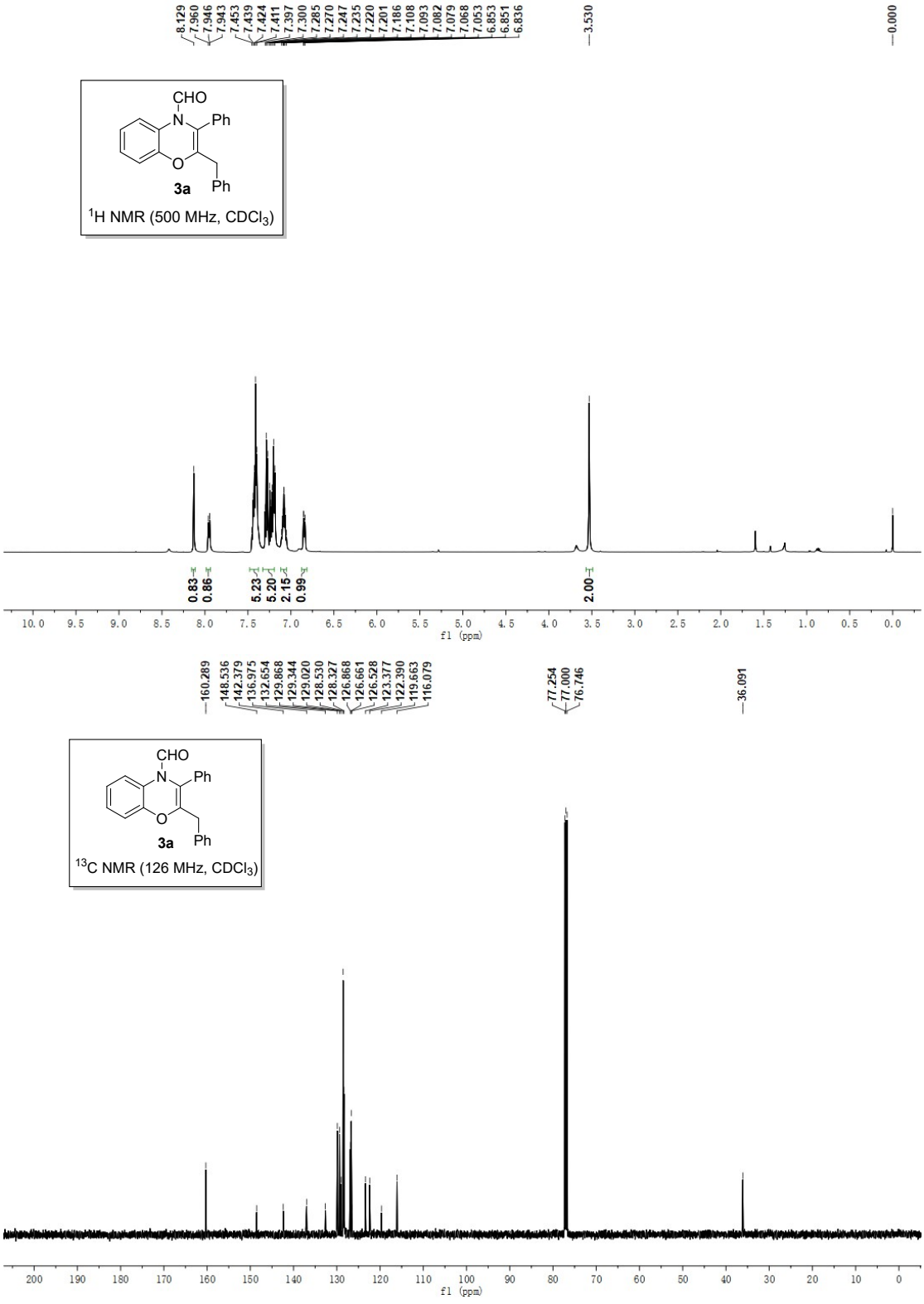
Correction method= # Reported T Limits : Tmin = 0.661 Tmax = 1.000

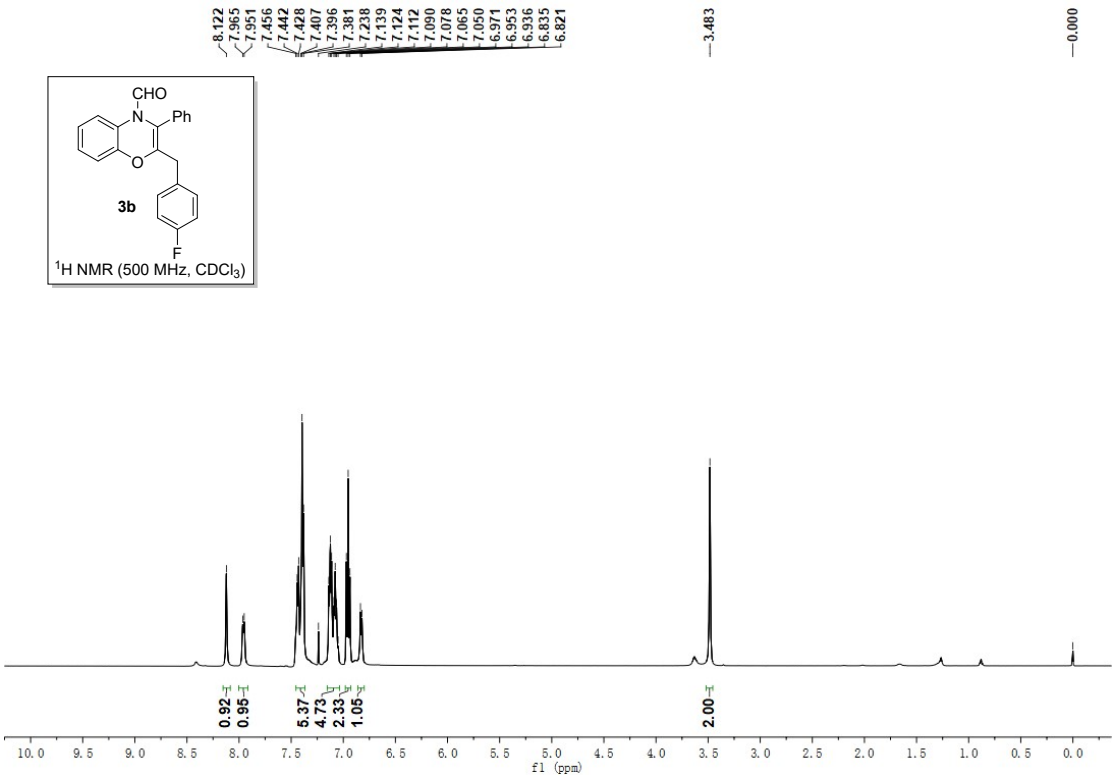
Data completeness = 0.983	Theta(max) = 26.989
R(reflections) = 0.0720 (2039)	wR_2(reflections) = 0.1564 (2702)
S = 1.164	Npar = 173

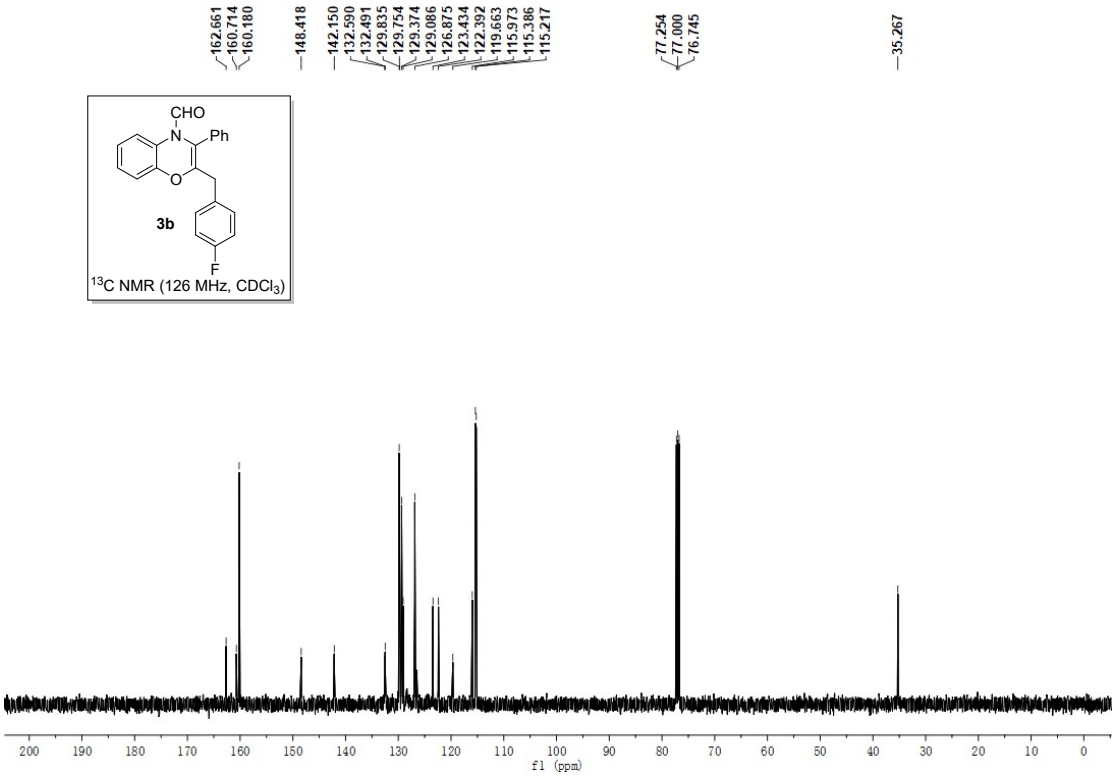
8. References

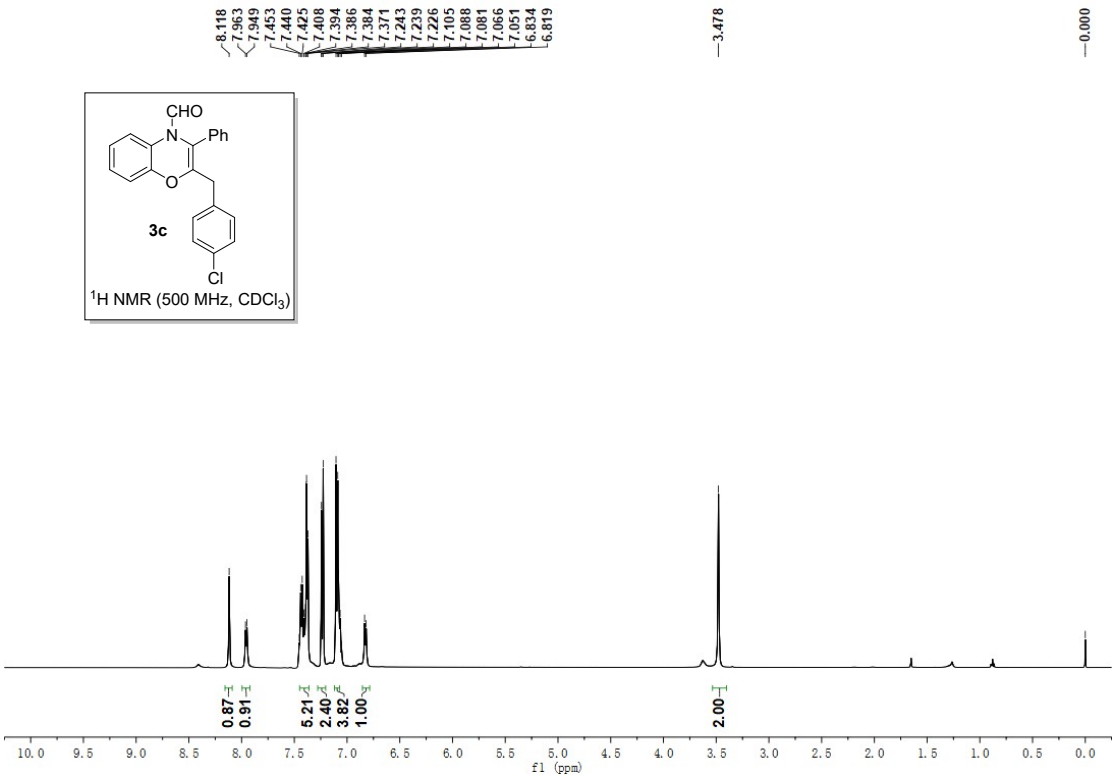
1. S. Chen, F. Yuan, H. Zhao and B. Li, *Res. Chem. Intermed.*, 2013, **39**, 2391-2399.
2. S. González-Granda, D. Méndez-Sánchez, I. Lavandera and V. Gotor-Fernández, *ChemCatChem*, 2020, **12**, 520-527.
3. W. Liu, Y. Sun, H. Zhao, B. Li and S. Chen, *ChemCatChem*, 2016, **8**, 2894-2897.
4. N. Naveen, S. R. Koppolu and R. Balamurugan. *Adv. Synth. Catal.*, 2015, **357**, 1463-1473.

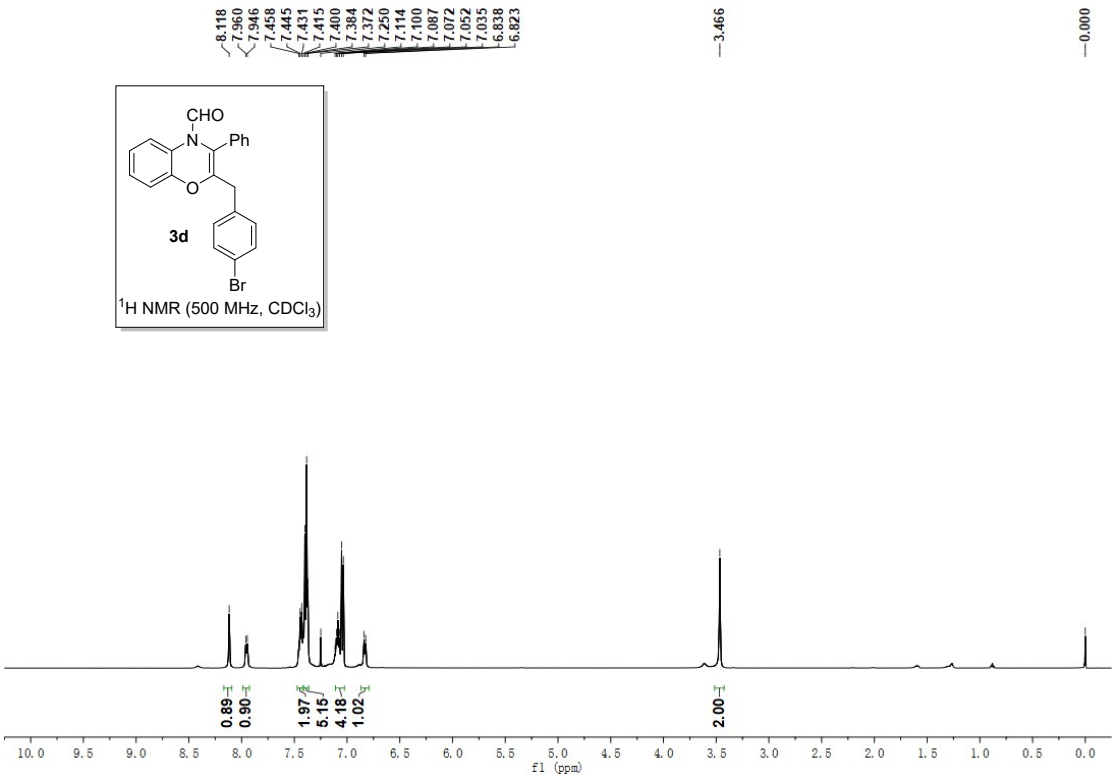
9. ^{1}H and ^{13}C NMR Spectra

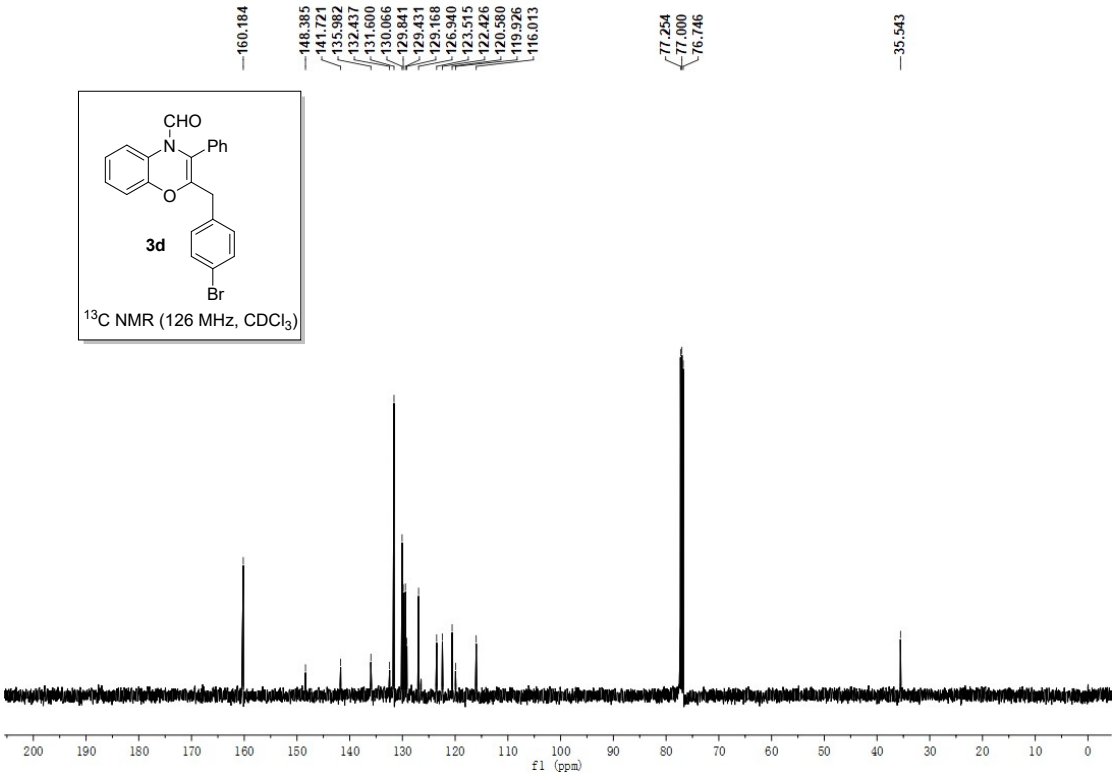


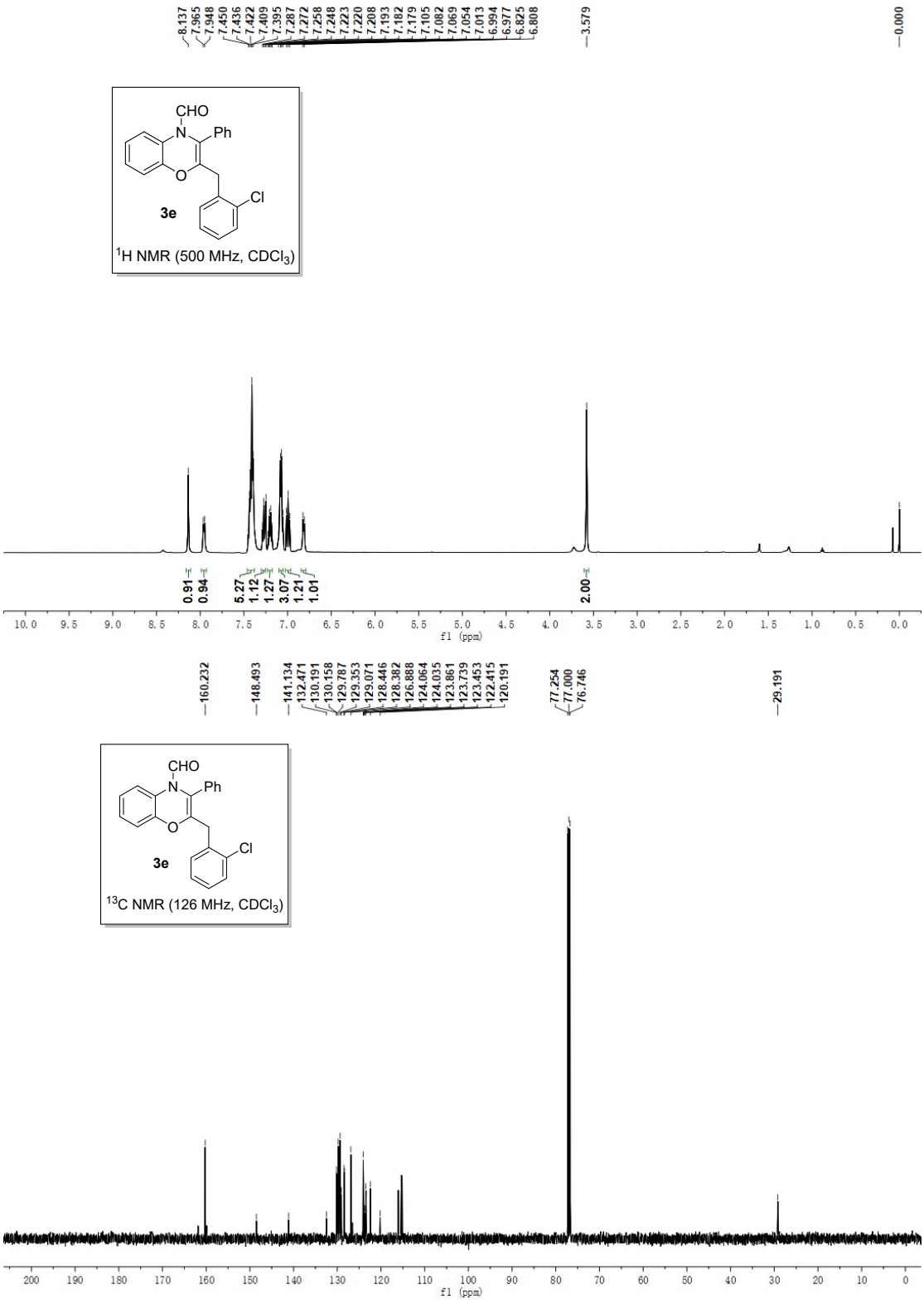

8.122
7.965
7.951
7.456
7.442
7.428
7.407
7.396
7.381
7.238
7.139
7.124
7.112
7.090
7.078
7.065
7.050
6.971
6.953
6.936
6.835
6.821
3.483
0.000
CHO
N
Ph
O
3b
F
1H NMR (500 MHz, CDCl3)
0.92
0.95
5.37
4.73
2.33
1.05
2.00
f1 (ppm)

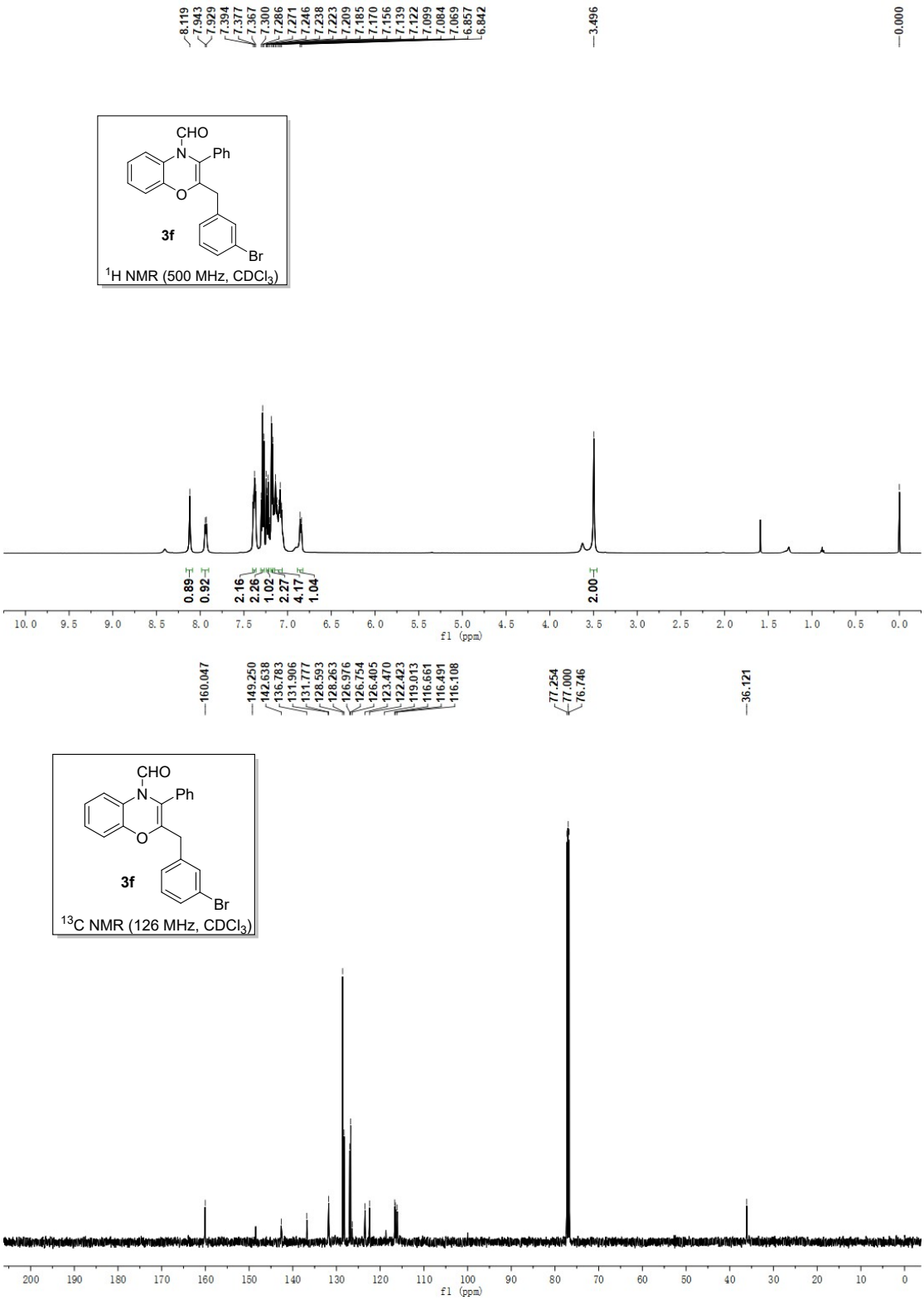

162.661
160.714
160.180
148.418
142.150
132.590
132.491
129.835
129.754
129.374
129.086
126.875
123.434
122.392
119.663
115.973
115.386
115.217
77.254
77.000
76.745
35.267
CHO
N
Ph
O
3b
F
13C NMR (126 MHz, CDCl3)
f1 (ppm)

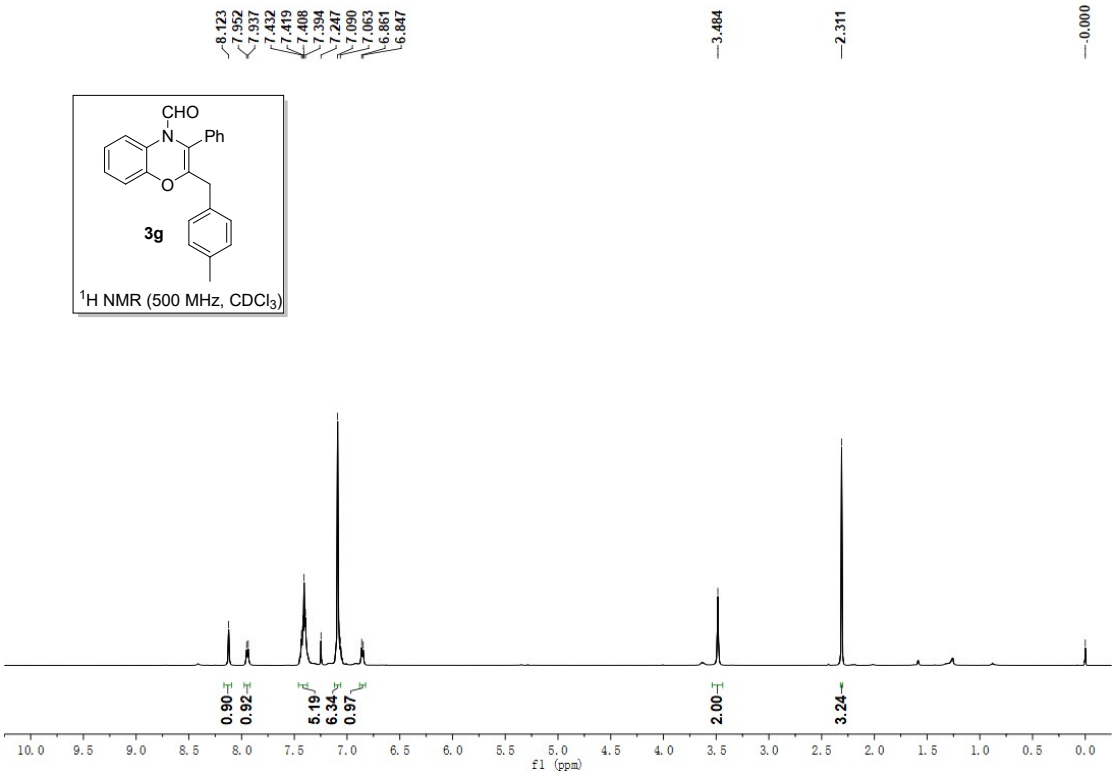

8.118
7.963
7.949
7.453
7.440
7.425
7.408
7.394
7.386
7.384
7.371
7.243
7.239
7.226
7.105
7.088
7.081
7.066
7.051
6.834
6.819
3.478
0.000
CHO
N
Ph
O
3c
Cl
1H NMR (500 MHz, CDCl3)
0.87
0.91
5.21
2.40
3.82
1.00
2.00
f1 (ppm)
160.151
148.358
141.787
135.429
132.482
132.419
129.810
129.660
129.393
129.126
128.614
126.901
126.452
123.472
122.394
119.857
115.976
77.255
77.000
76.746
35.439
13C NMR (126 MHz, CDCl3)

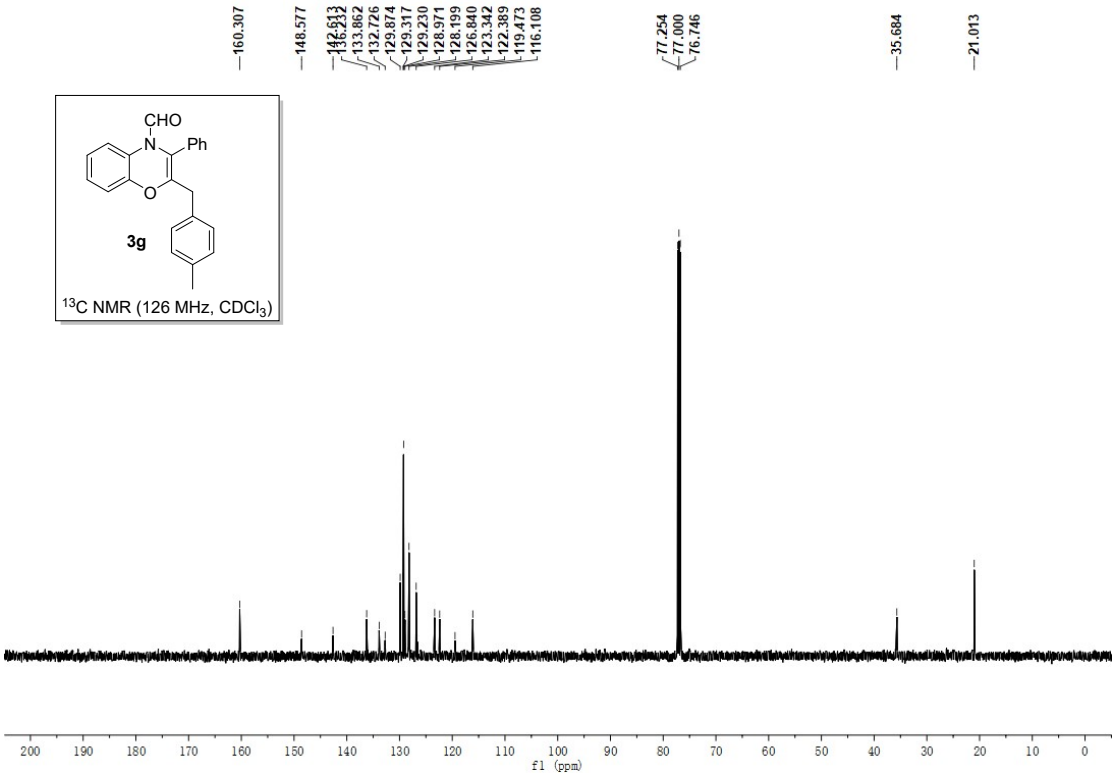

8.118
7.960
7.946
7.458
7.445
7.431
7.415
7.400
7.384
7.372
7.250
7.114
7.100
7.087
7.072
7.052
7.035
6.838
6.823
3.466
0.000
CHO
N
Ph
O
3d
Br
1H NMR (500 MHz, CDCl3)
0.89
0.90
1.97
5.15
4.18
1.02
2.00
f1 (ppm)

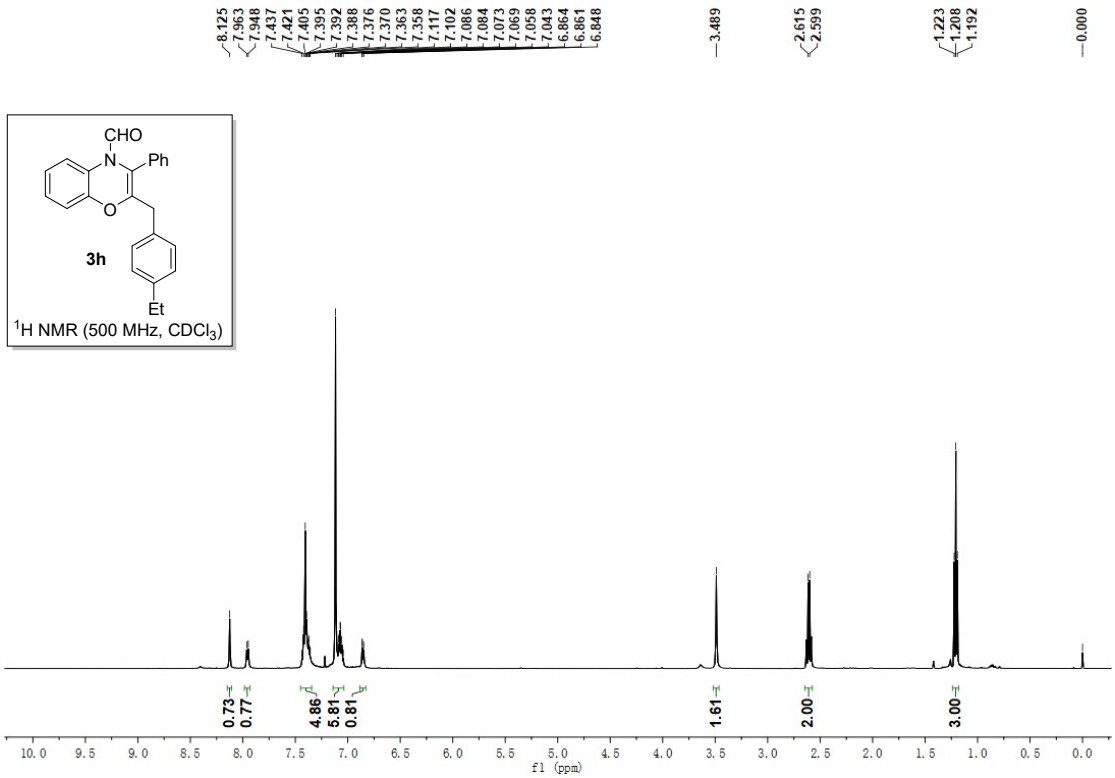

160.184
148.385
141.721
135.982
132.437
131.600
130.066
129.841
129.431
129.168
126.940
123.515
122.426
120.580
119.926
116.013
77.254
77.000
76.746
35.543
CHO
N
Ph
O
3d
Br
13C NMR (126 MHz, CDCl3)
f1 (ppm)

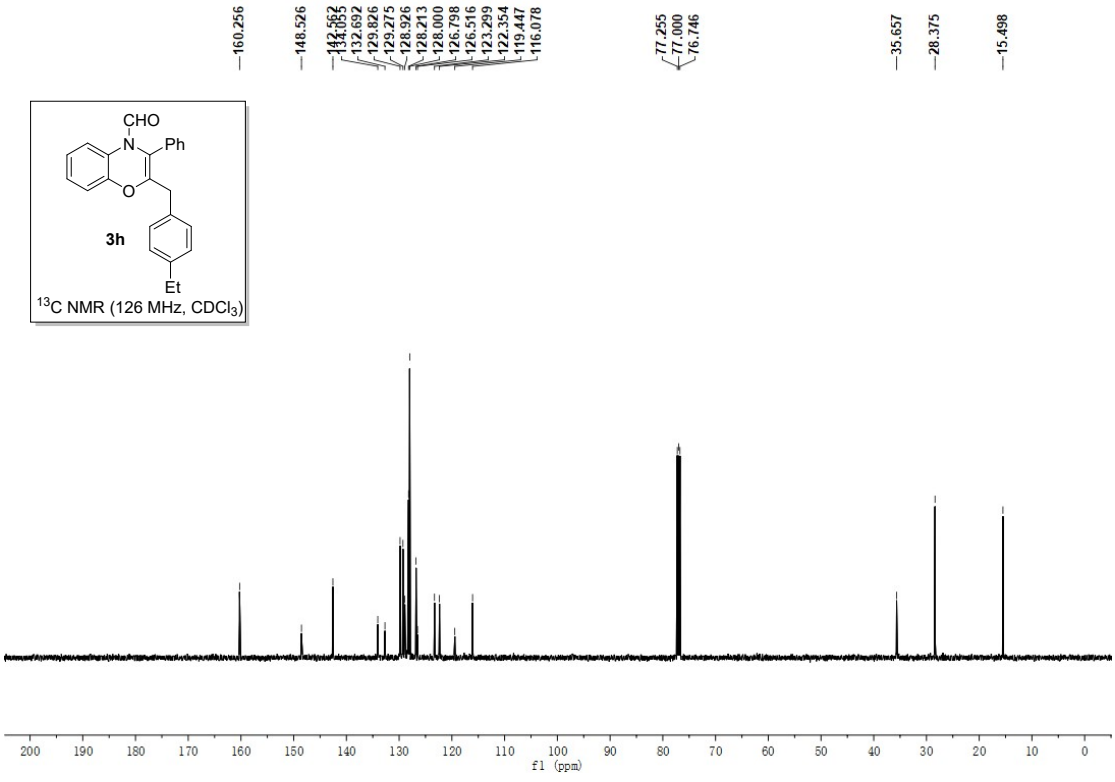

8.137
7.965
7.948
7.450
7.436
7.422
7.409
7.395
7.287
7.272
7.258
7.248
7.223
7.220
7.208
7.193
7.182
7.179
7.105
7.082
7.069
7.054
7.013
6.994
6.977
6.825
6.808
3.579
0.000
CHO
N
Ph
O
Cl
3e
1H NMR (500 MHz, CDCl3)
0.91
0.94
5.27
1.12
1.27
3.07
1.21
1.01
2.00
f1 (ppm)
160.232
148.493
141.134
132.471
130.191
130.158
129.787
129.353
129.071
128.446
128.382
126.888
124.064
124.035
123.861
123.739
123.453
122.415
120.191
77.254
77.000
76.746
29.191
13C NMR (126 MHz, CDCl3)

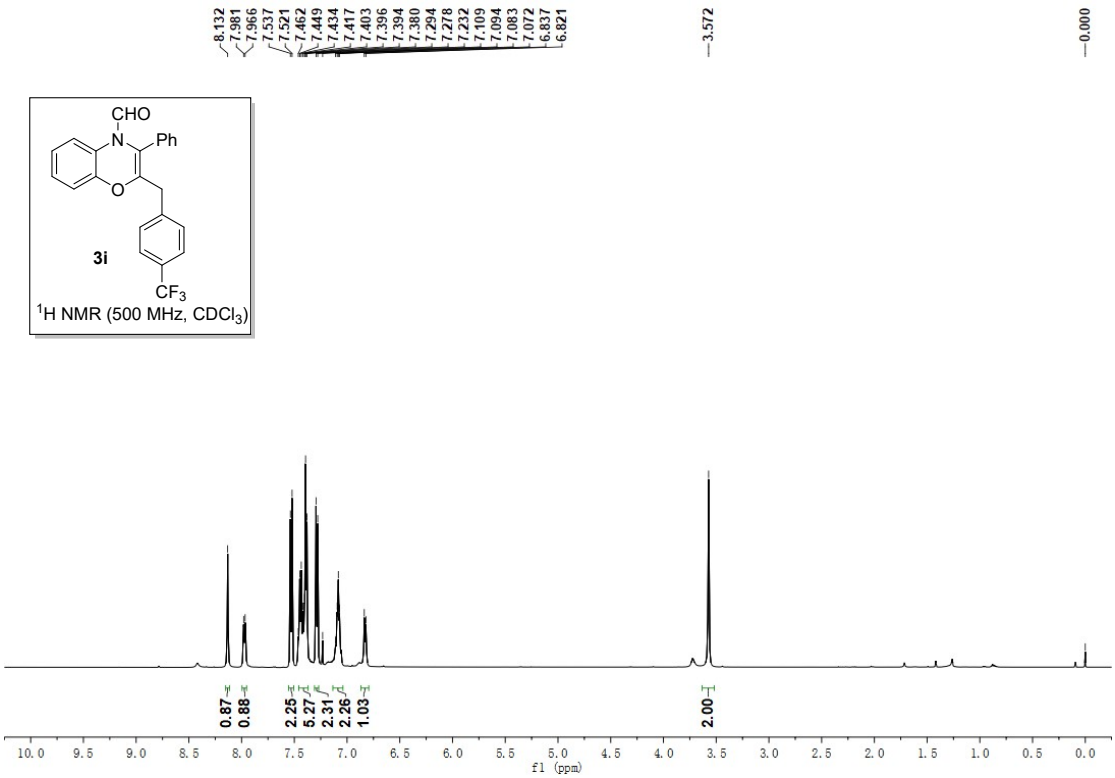

8.119
7.943
7.929
7.394
7.377
7.367
7.300
7.286
7.271
7.246
7.238
7.223
7.209
7.185
7.170
7.156
7.139
7.122
7.099
7.084
7.069
6.857
6.842
3.496
0.000
CHO
N
Ph
O
Br
3f
1H NMR (500 MHz, CDCl3)
0.89
0.92
2.16
2.26
1.02
2.27
4.17
1.04
2.00
f1 (ppm)
160.047
149.250
142.638
136.783
131.906
131.777
128.593
128.263
126.976
126.754
126.405
123.470
122.423
119.013
116.661
116.491
116.108
77.254
77.000
76.746
36.121
13C NMR (126 MHz, CDCl3)

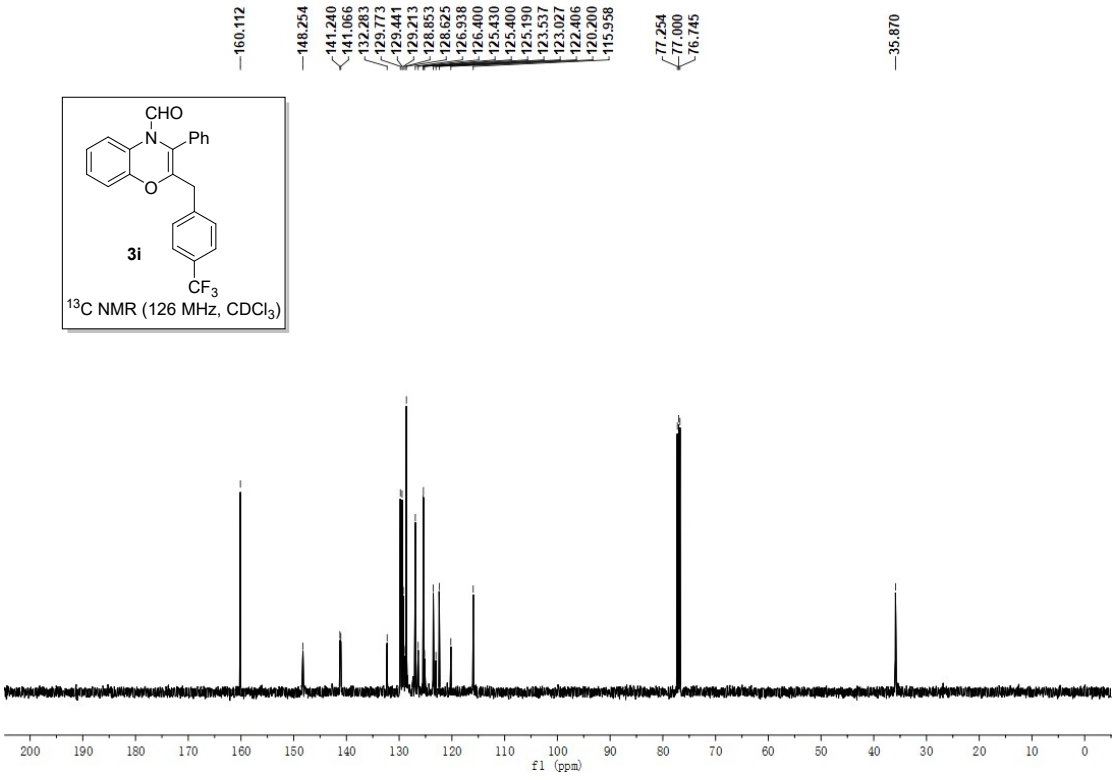

8.123
7.952
7.937
7.432
7.419
7.408
7.394
7.247
7.090
7.063
6.861
6.847
3.484
2.311
0.000
CHO
N
Ph
O
3g
1H NMR (500 MHz, CDCl3)
0.90
0.92
5.19
6.34
0.97
2.00
3.24
f1 (ppm)

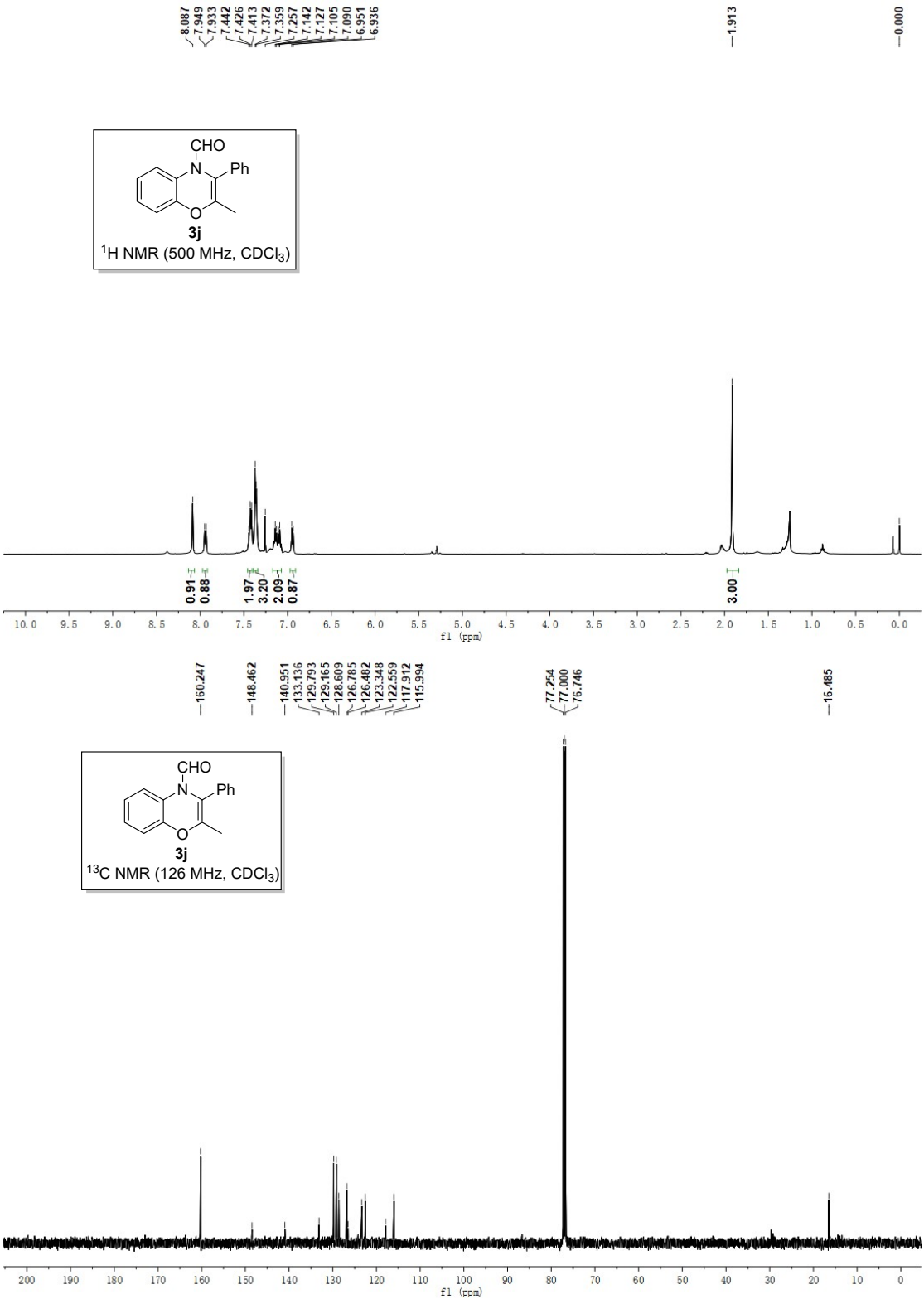

160.307
148.577
142.613
136.232
133.862
132.726
129.874
129.317
129.230
128.971
128.199
126.840
123.342
122.389
119.473
116.108
77.254
77.000
76.746
35.684
21.013
CHO
N
Ph
O
3g
13C NMR (126 MHz, CDCl3)
f1 (ppm)

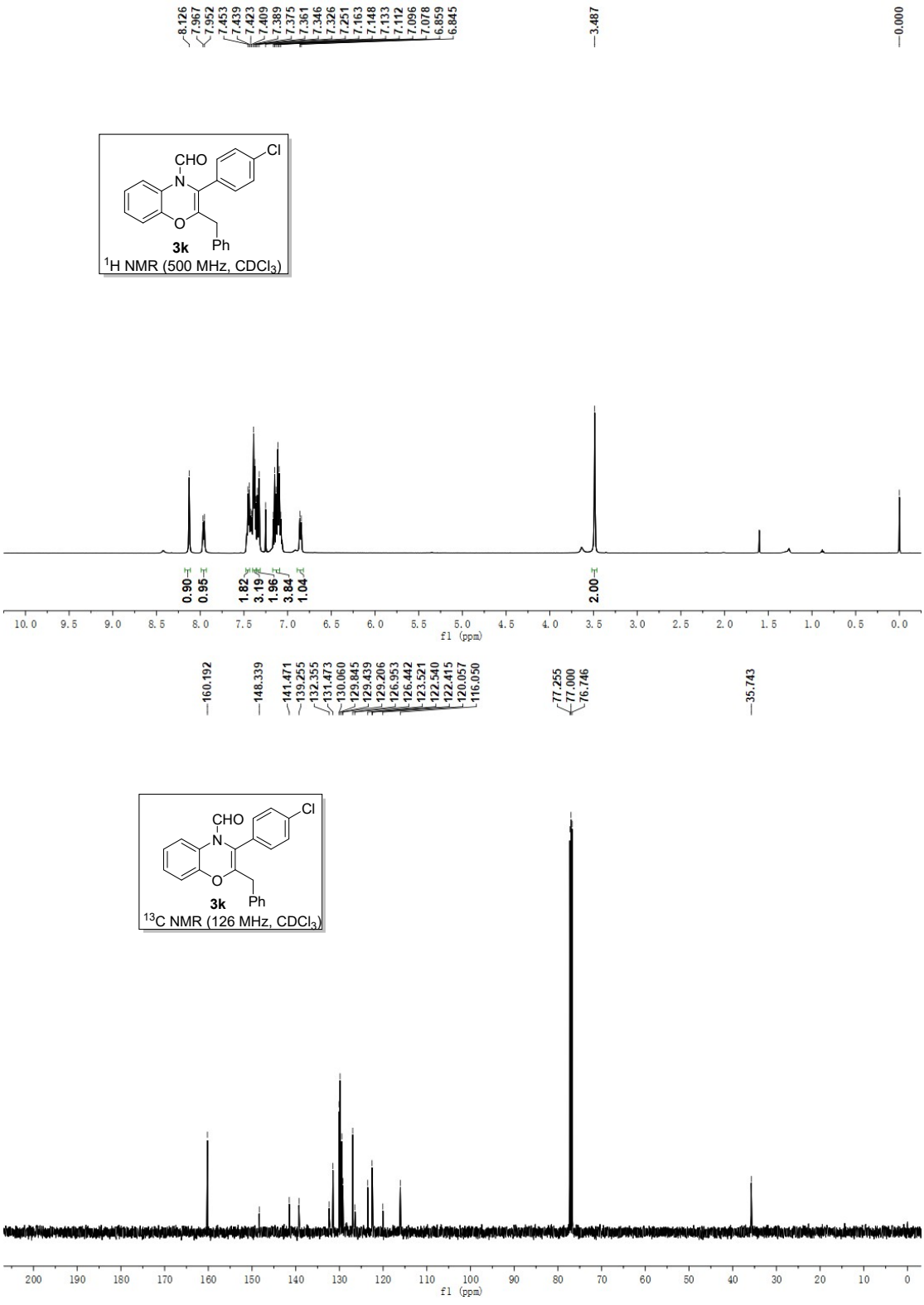

8.125
7.963
7.948
7.437
7.421
7.405
7.395
7.392
7.388
7.376
7.370
7.363
7.358
7.117
7.102
7.086
7.084
7.073
7.069
7.058
7.043
6.864
6.861
6.848
3.489
2.615
2.599
1.223
1.208
1.192
0.000
CHO
N
Ph
O
3h
Et
^{1}H NMR (500 MHz, CDCl$_3$)
0.73
0.77
4.86
5.81
0.81
1.61
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 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 0.0
f1 (ppm)

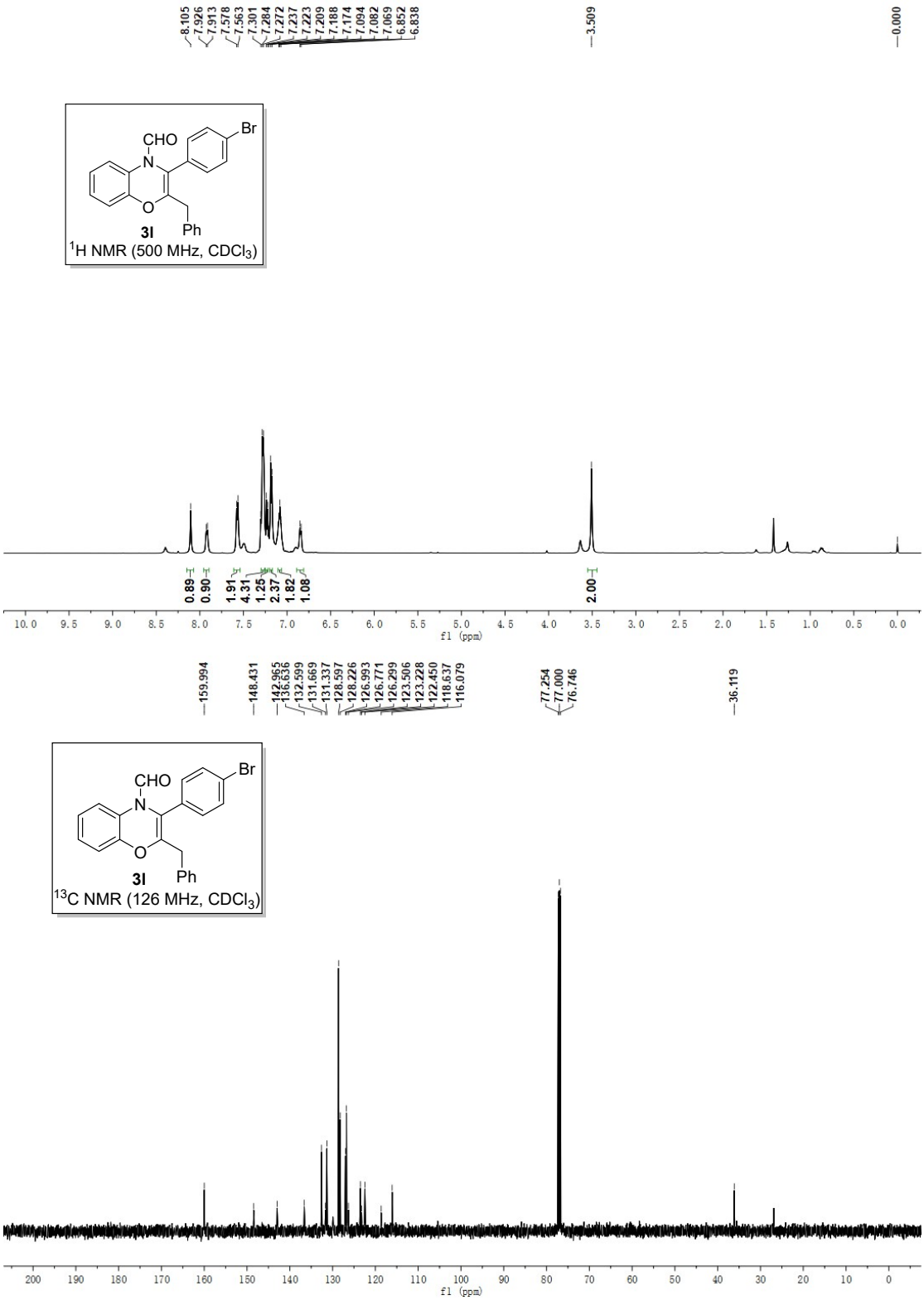

160.256
148.526
142.562
134.055
132.692
129.826
129.275
128.926
128.213
128.000
126.798
126.516
123.299
122.354
119.447
116.078
77.255
77.000
76.746
35.657
28.375
15.498
CHO
N
Ph
O
3h
Et
^{13}C NMR (126 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

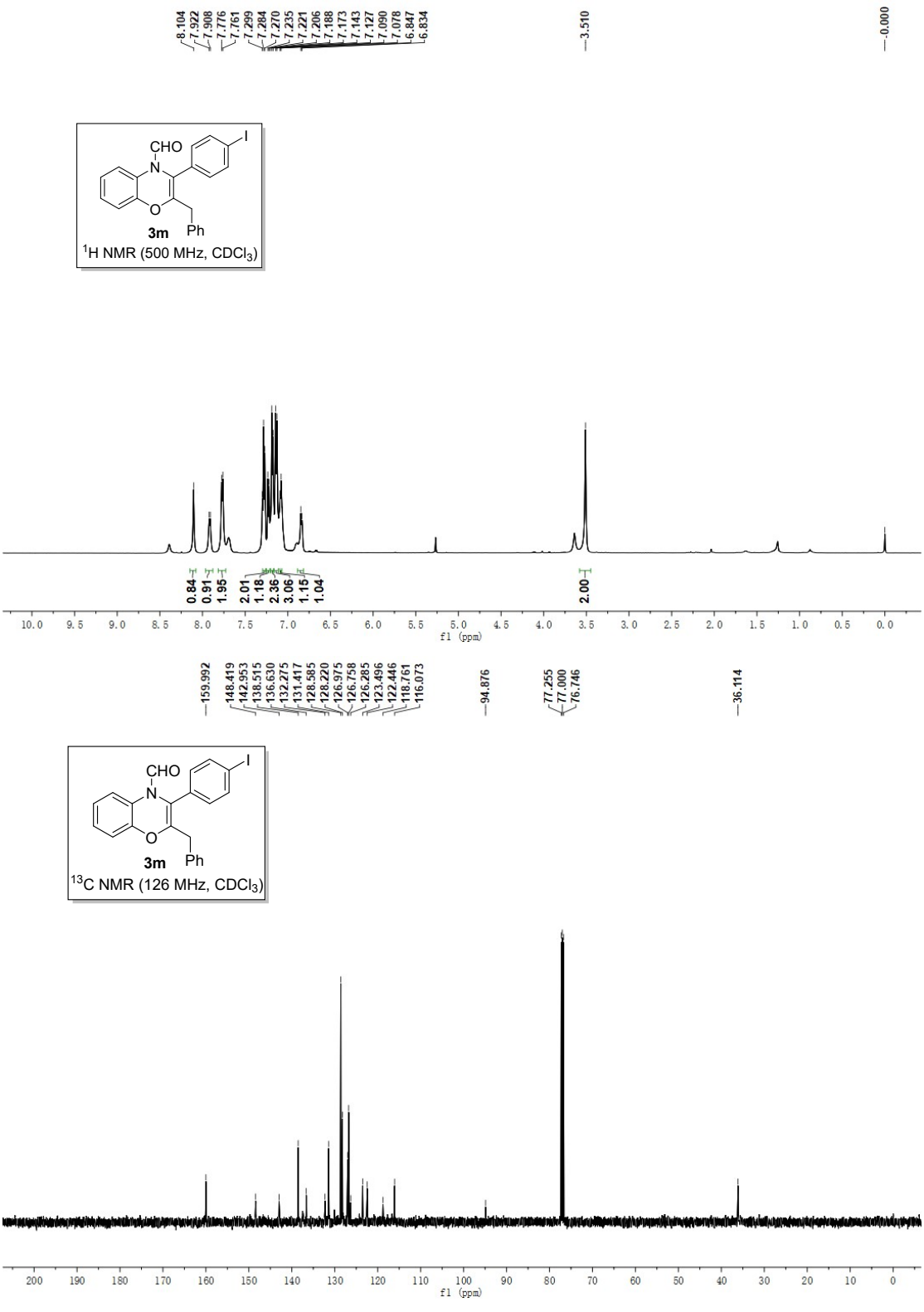

8.132
7.981
7.966
7.537
7.521
7.462
7.449
7.434
7.417
7.403
7.396
7.394
7.380
7.294
7.278
7.232
7.109
7.094
7.083
7.072
6.837
6.821
3.572
0.000
CHO
N
Ph
O
3i
CF3
1H NMR (500 MHz, CDCl3)
0.87
0.88
2.25
5.27
2.31
2.26
1.03
2.00
f1 (ppm)

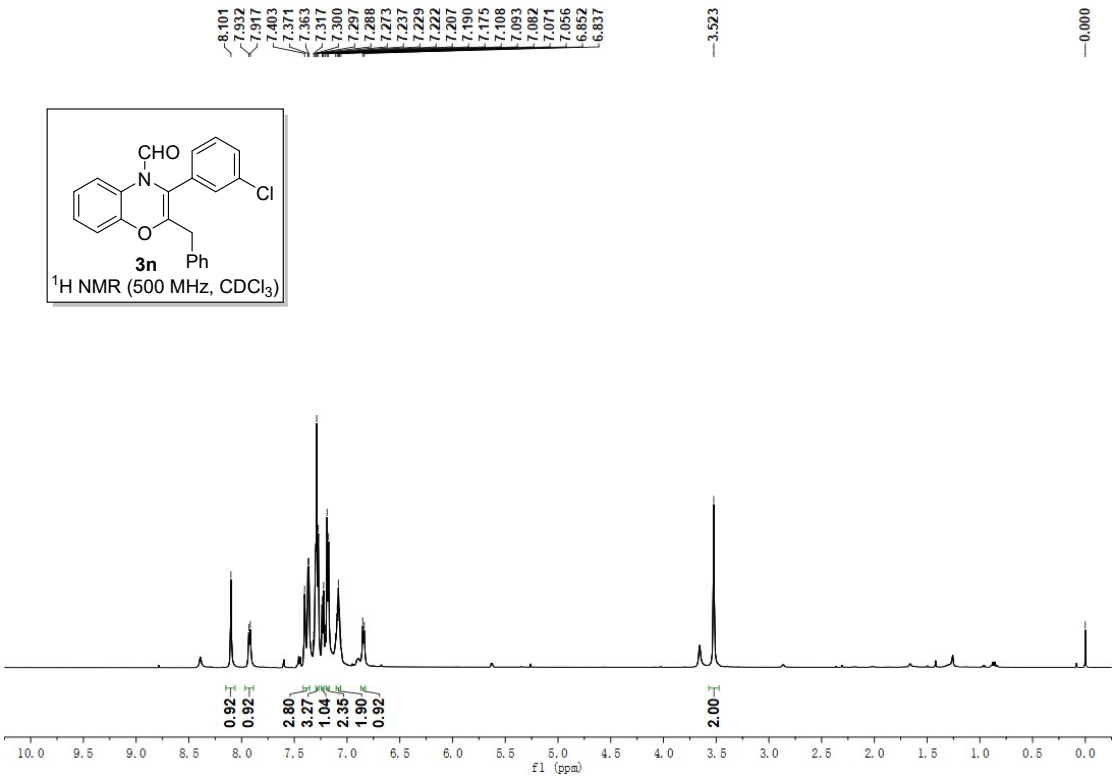

160.112
148.254
141.240
141.066
132.283
129.773
129.441
129.213
128.853
128.625
126.938
126.400
125.430
125.400
125.190
123.537
123.027
122.406
120.200
115.958
77.254
77.000
76.745
35.870
CHO
N
Ph
O
3i
CF3
13C NMR (126 MHz, CDCl3)
f1 (ppm)

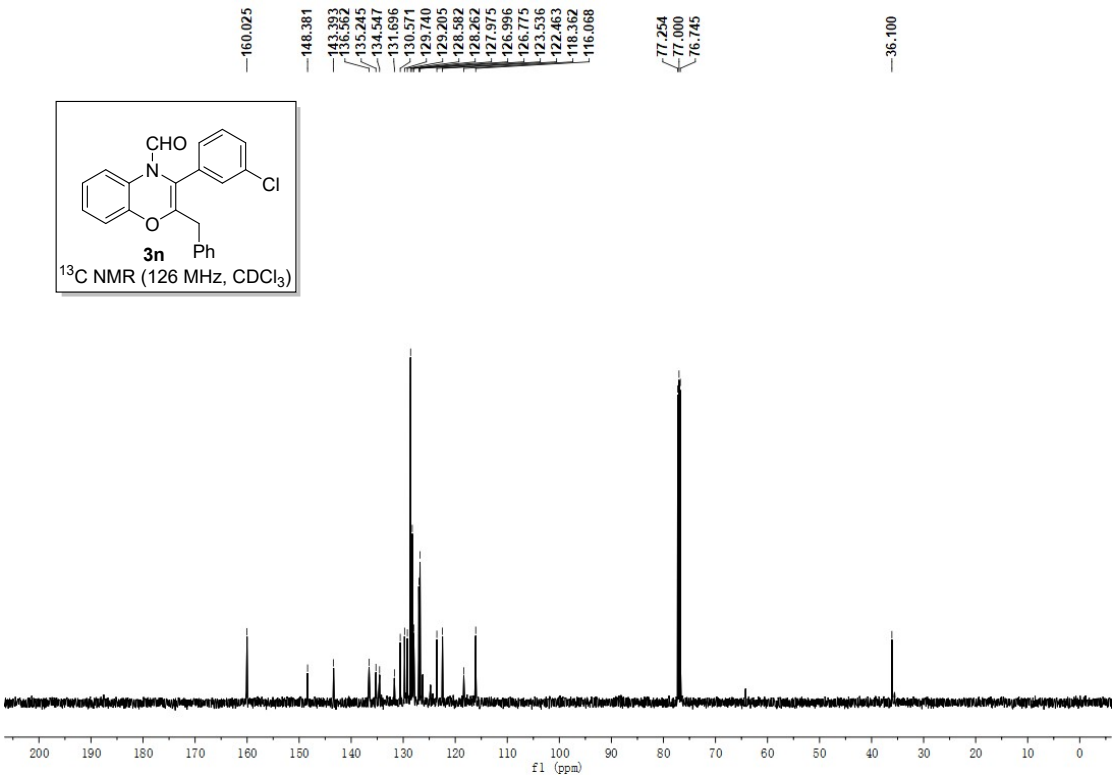

8.087
7.949
7.933
7.442
7.426
7.413
7.372
7.359
7.257
7.142
7.127
7.105
7.090
6.951
6.936
1.913
0.000
CHO
N
Ph
O
3j
1H NMR (500 MHz, CDCl3)
0.91
0.88
1.97
3.20
2.09
0.87
3.00
f1 (ppm)
160.247
148.462
140.951
133.136
129.793
129.165
128.609
126.785
126.482
123.348
122.559
117.912
115.994
77.254
77.000
76.746
16.485
CHO
N
Ph
O
3j
13C NMR (126 MHz, CDCl3)
f1 (ppm)

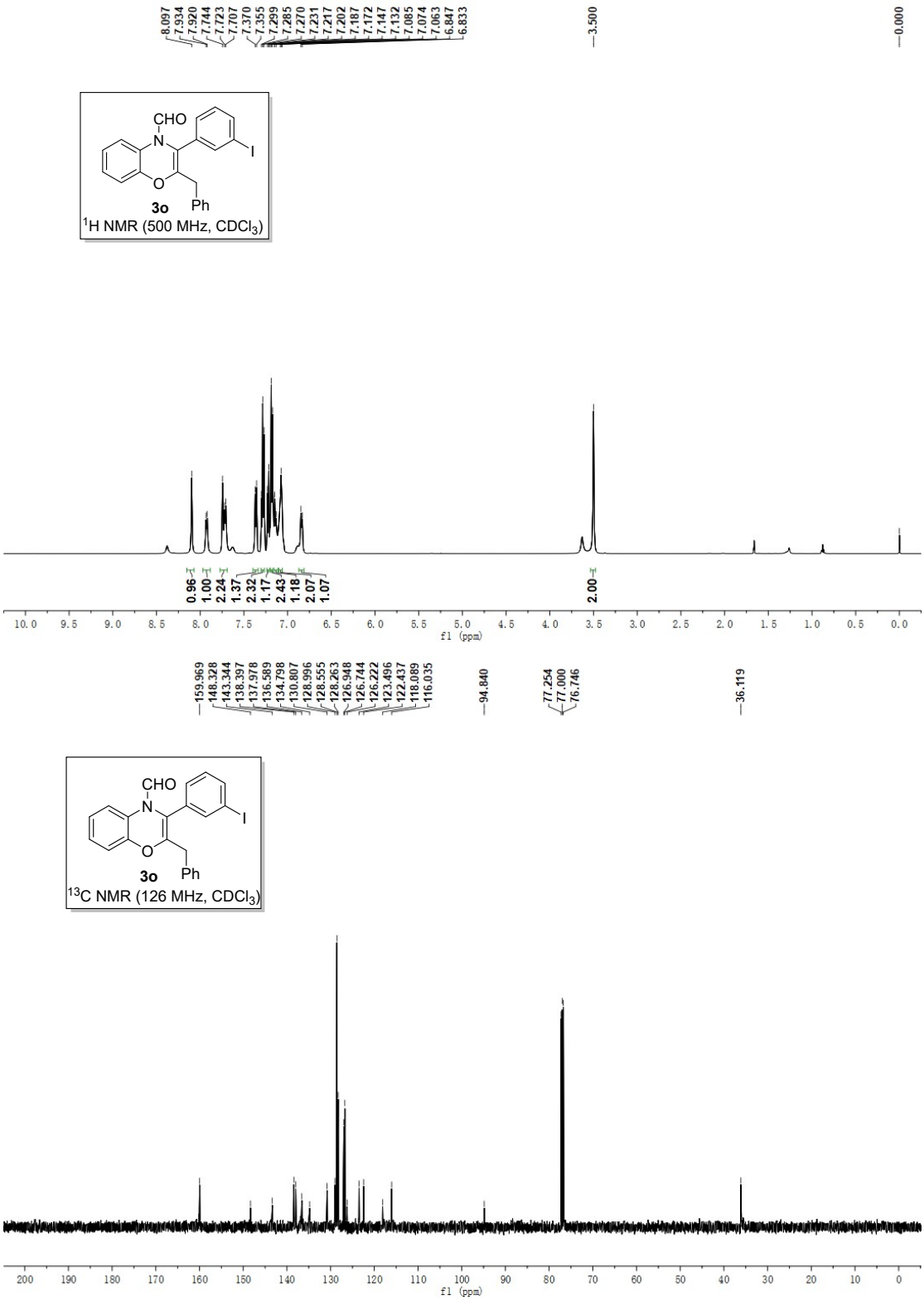

8.126
7.967
7.952
7.453
7.439
7.423
7.409
7.389
7.375
7.361
7.346
7.326
7.251
7.163
7.148
7.133
7.112
7.096
7.078
6.859
6.845
3.487
0.000
CHO
N
O
Cl
Ph
3k
1H NMR (500 MHz, CDCl3)
0.90
0.95
1.82
3.19
1.96
3.84
1.04
2.00
f1 (ppm)
160.192
148.339
141.471
139.255
132.355
131.473
130.060
129.845
129.439
129.206
126.953
126.442
123.521
122.540
122.415
120.057
116.050
77.255
77.000
76.746
35.743
CHO
N
O
Cl
Ph
3k
13C NMR (126 MHz, CDCl3)
f1 (ppm)

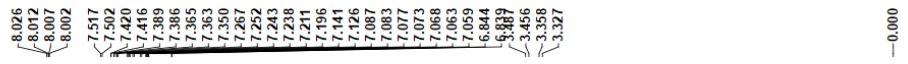

8.105
7.926
7.913
7.578
7.563
7.301
7.284
7.272
7.237
7.223
7.209
7.188
7.174
7.094
7.082
7.069
6.852
6.838
3.509
0.000
CHO
N
O
Br
Ph
3l
1H NMR (500 MHz, CDCl3)
0.89
0.90
1.91
4.31
1.25
2.37
1.82
1.08
2.00
f1 (ppm)
159.994
148.431
142.965
136.636
132.599
131.669
131.337
128.597
128.226
126.993
126.771
126.299
123.506
123.228
122.450
118.637
116.079
77.254
77.000
76.746
36.119
13C NMR (126 MHz, CDCl3)

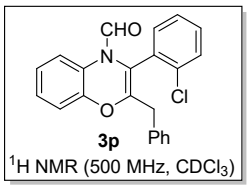

8.104
7.922
7.908
7.776
7.761
7.299
7.284
7.270
7.235
7.221
7.206
7.188
7.173
7.143
7.127
7.090
7.078
6.847
6.834
3.510
0.000
CHO
N
O
I
Ph
3m
1H NMR (500 MHz, CDCl3)
0.84
0.91
1.95
2.01
1.18
2.36
3.06
1.15
1.04
2.00
f1 (ppm)
159.992
148.419
142.953
138.515
136.630
132.275
131.417
128.585
128.220
126.975
126.758
126.285
123.496
122.446
118.761
116.073
94.876
77.255
77.000
76.746
36.114
3m
13C NMR (126 MHz, CDCl3)


8.101
7.932
7.917
7.403
7.371
7.363
7.317
7.300
7.297
7.288
7.273
7.237
7.229
7.222
7.207
7.190
7.175
7.108
7.093
7.082
7.071
7.056
6.852
6.837
3.523
0.000
CHO
N
Cl
O
Ph
3n
^{1}H NMR (500 MHz, $CDCl_3$)
0.92
0.92
2.80
3.27
1.04
2.35
1.90
0.92
2.00
f1 (ppm)


160.025
148.381
143.393
136.562
135.245
134.547
131.696
130.571
129.740
129.205
128.582
128.262
127.975
126.996
126.775
123.536
122.463
118.362
116.068
77.254
77.000
76.745
36.100
CHO
N
Cl
O
Ph
3n
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

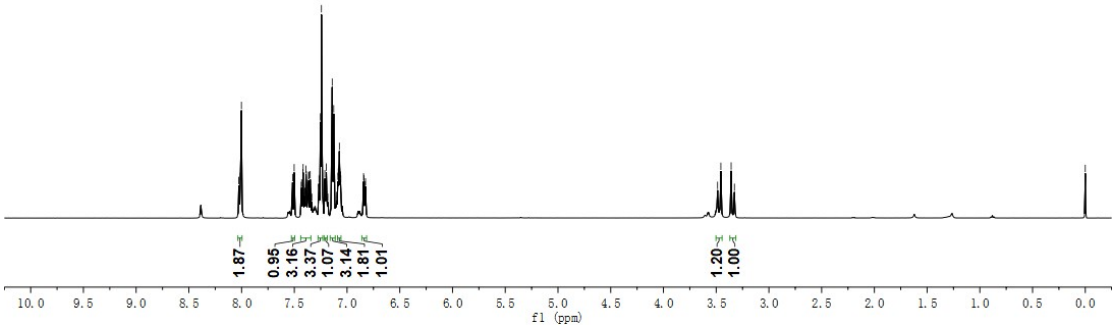

8.097
7.934
7.920
7.744
7.723
7.707
7.370
7.355
7.299
7.285
7.270
7.231
7.217
7.202
7.187
7.172
7.147
7.132
7.085
7.074
7.063
6.847
6.833
3.500
0.000
CHO
N
I
O
Ph
3o
1H NMR (500 MHz, CDCl3)
0.96
1.00
2.24
1.37
2.32
1.17
2.43
1.18
2.07
1.07
2.00
f1 (ppm)
159.969
148.328
143.344
138.397
137.978
136.589
134.798
130.807
128.996
128.555
128.263
126.948
126.744
126.222
123.496
122.437
118.089
116.035
94.840
77.254
77.000
76.746
36.119
3o
13C NMR (126 MHz, CDCl3)
f1 (ppm)

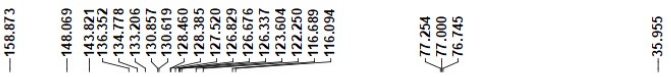


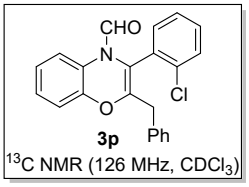


3p

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

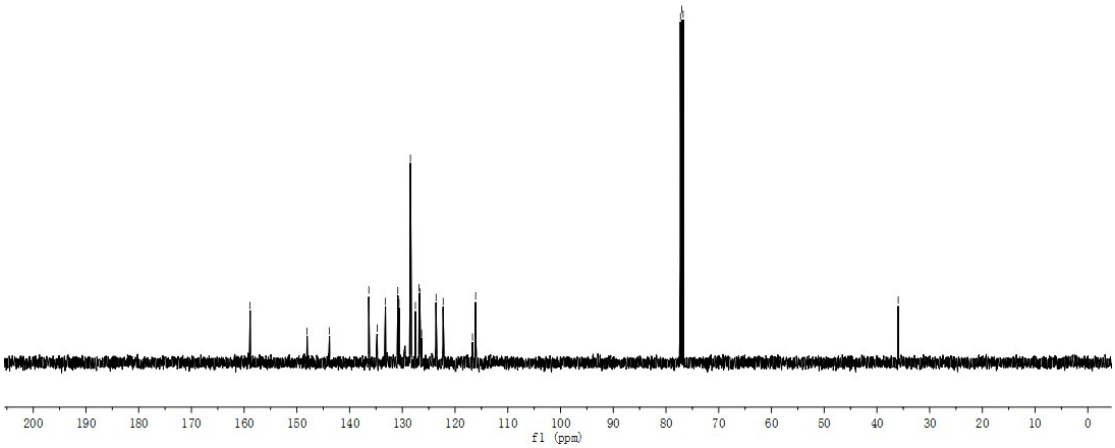


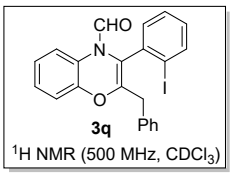




3p

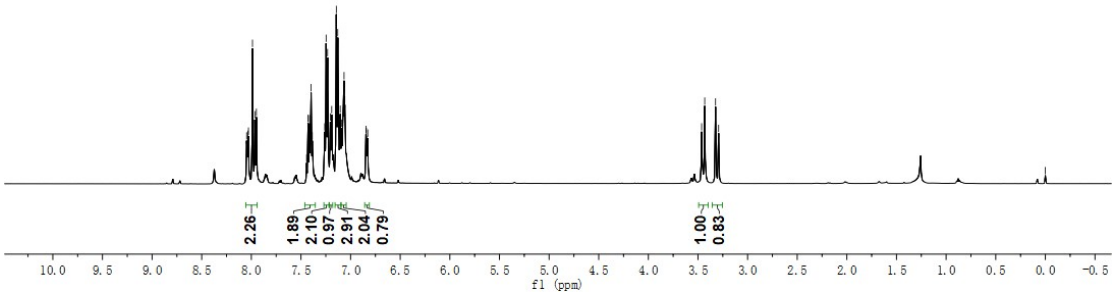
^{13}C NMR (126 MHz, $CDCl_3$)

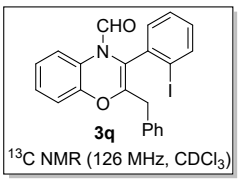




3q

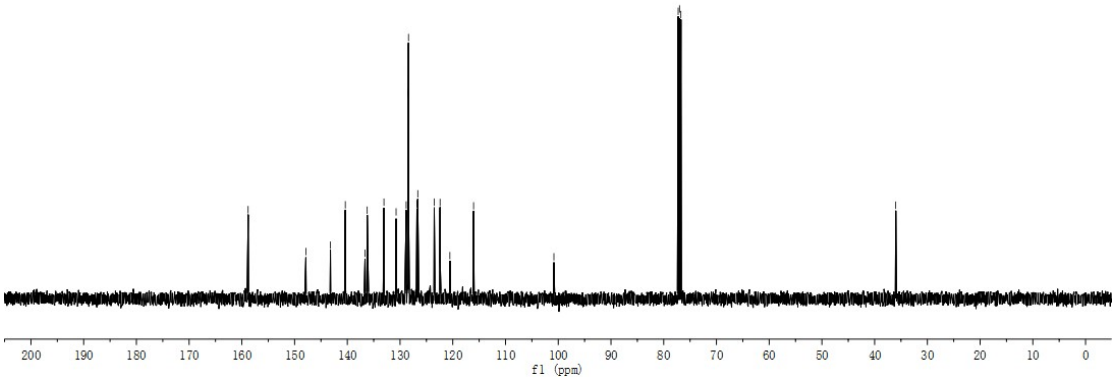
^{1}H NMR (500 MHz, $CDCl_3$)

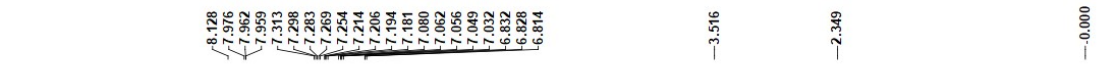


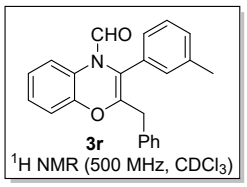


3q

^{13}C NMR (126 MHz, $CDCl_3$)

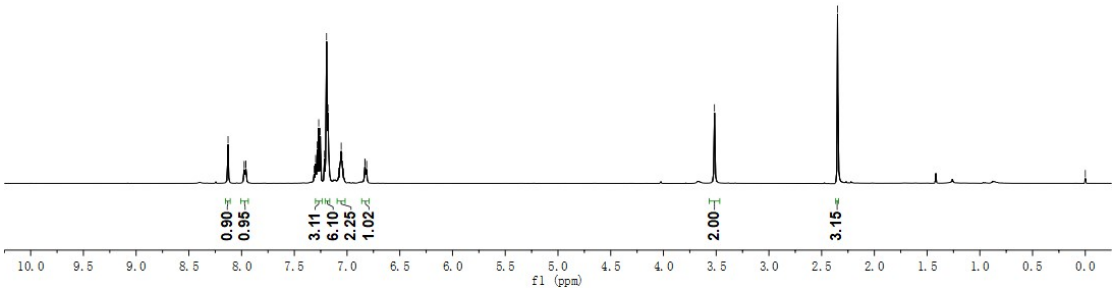


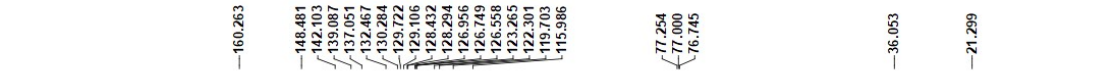


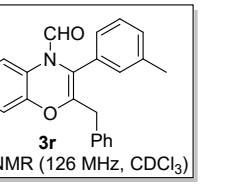


3r

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

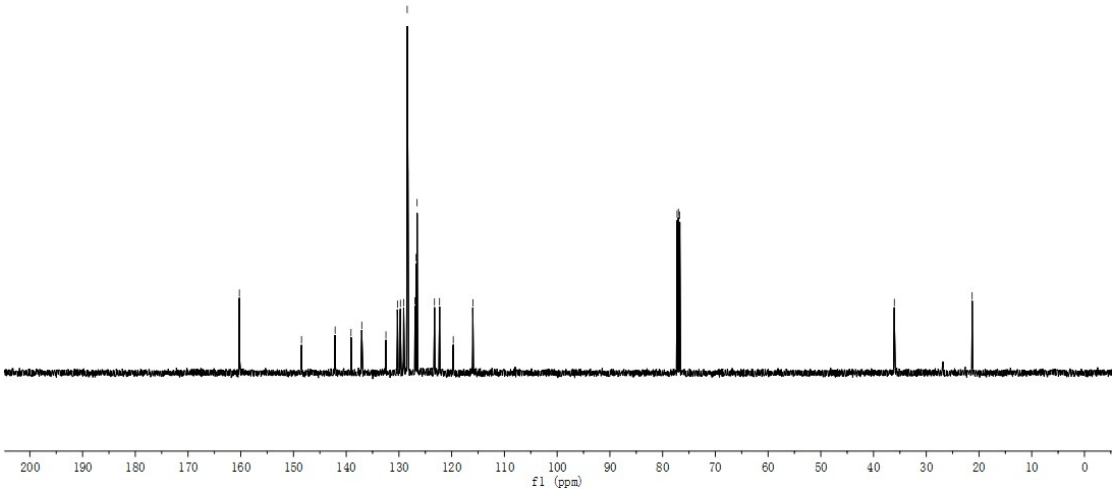


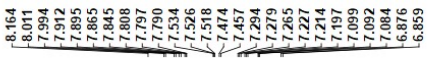


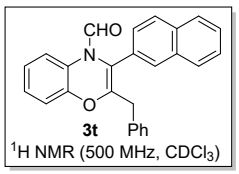


3r

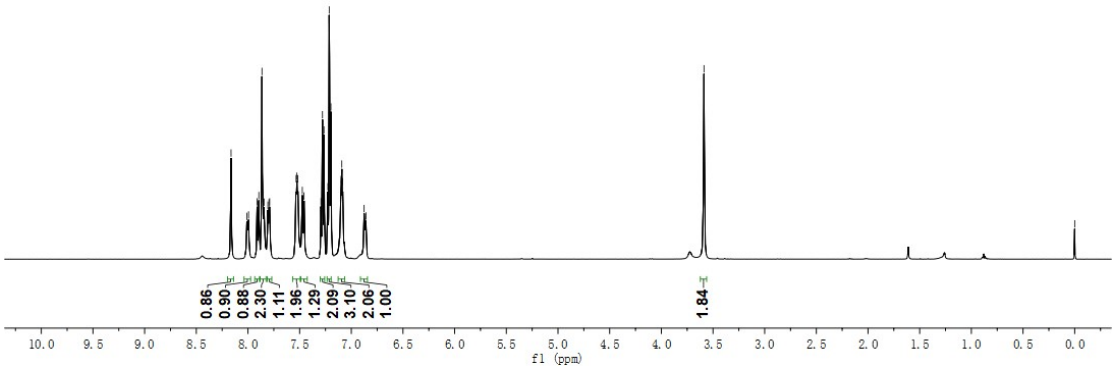
^{13}C NMR (126 MHz, $CDCl_3$)

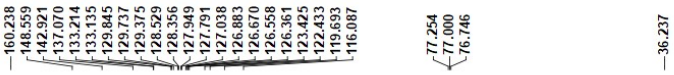


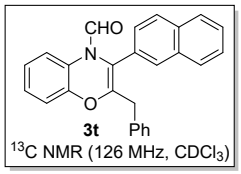




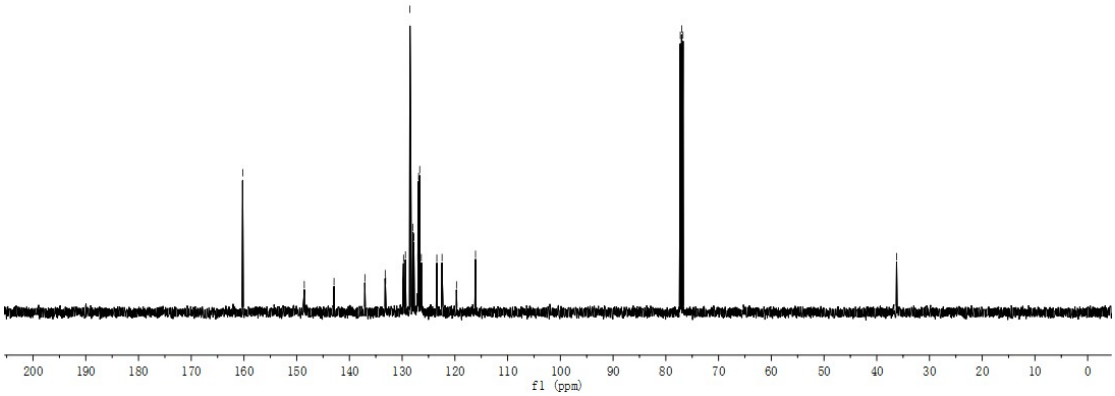
^{1}H NMR (500 MHz, $CDCl_3$)

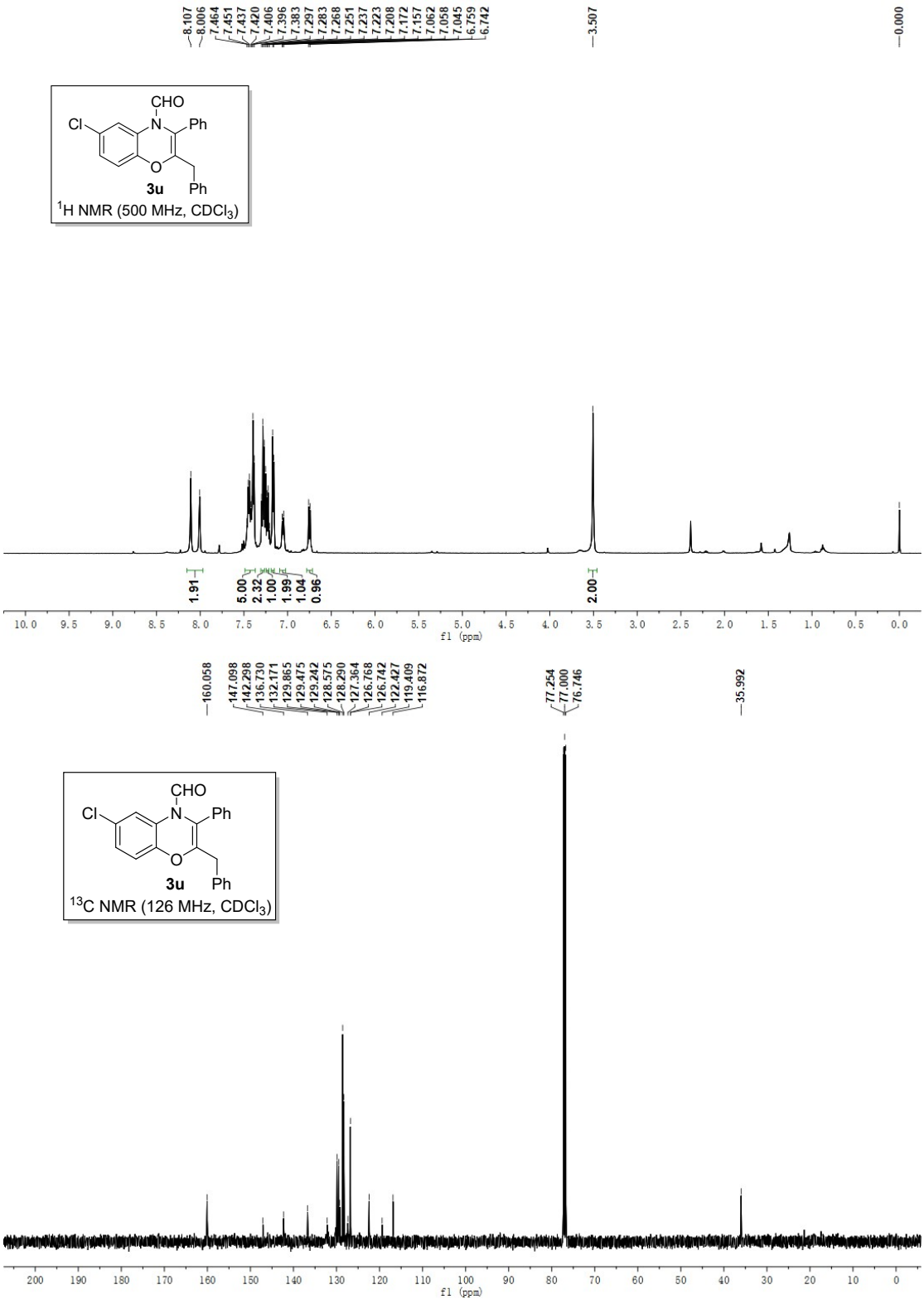




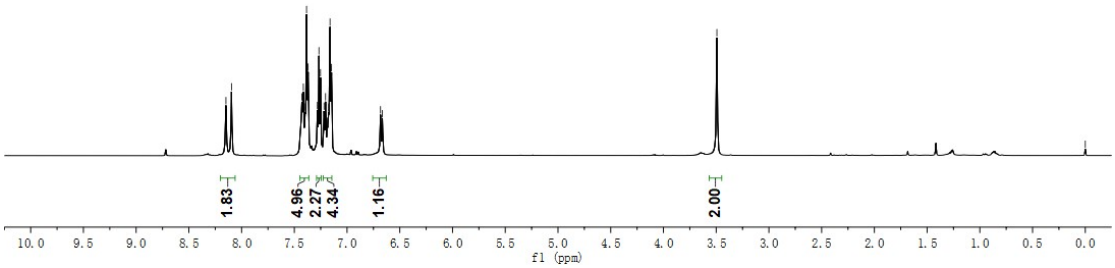


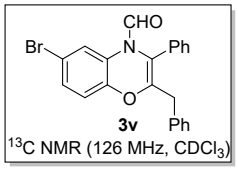
^{13}C NMR (126 MHz, $CDCl_3$)



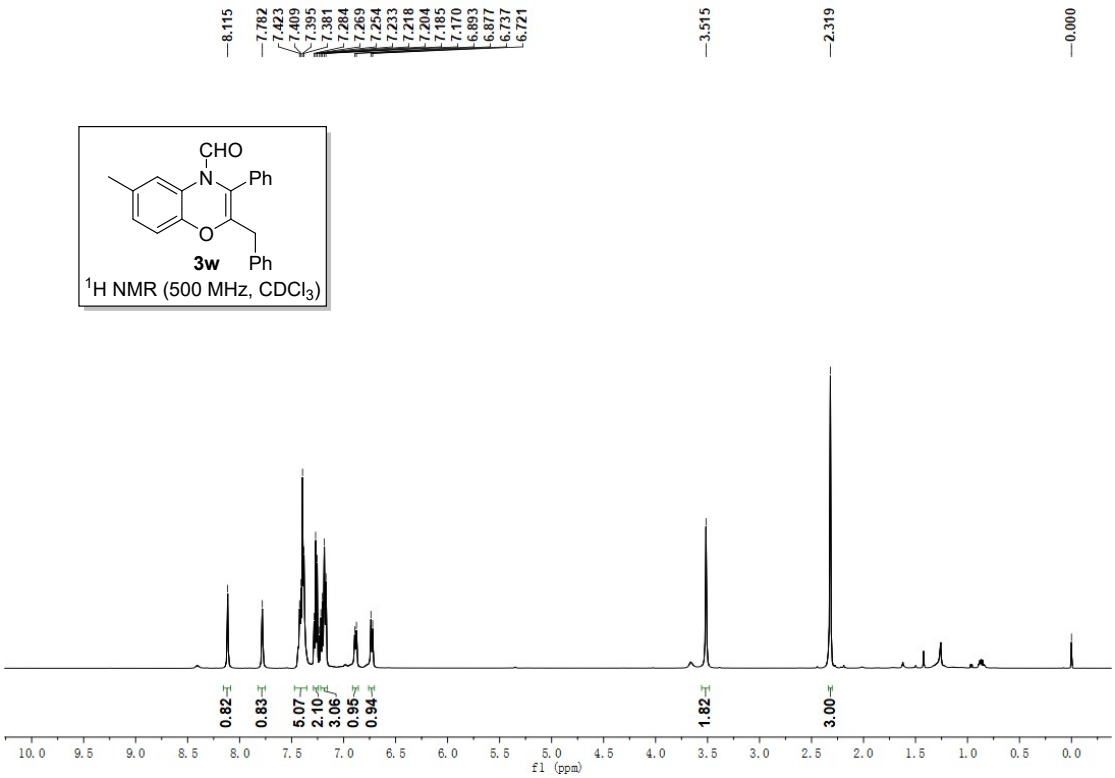

8.107
8.006
7.464
7.451
7.437
7.420
7.406
7.396
7.383
7.297
7.283
7.268
7.251
7.237
7.223
7.208
7.172
7.157
7.062
7.058
7.045
6.759
6.742
3.507
0.000
CHO
Cl
N
Ph
O
3u
Ph
1H NMR (500 MHz, CDCl3)
1.91
5.00
2.32
1.00
1.99
1.04
0.96
2.00
f1 (ppm)
160.058
147.098
142.298
136.730
132.171
129.865
129.475
129.242
128.575
128.290
127.364
126.768
126.742
122.427
119.409
116.872
77.254
77.000
76.746
35.992
CHO
Cl
N
Ph
O
3u
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)

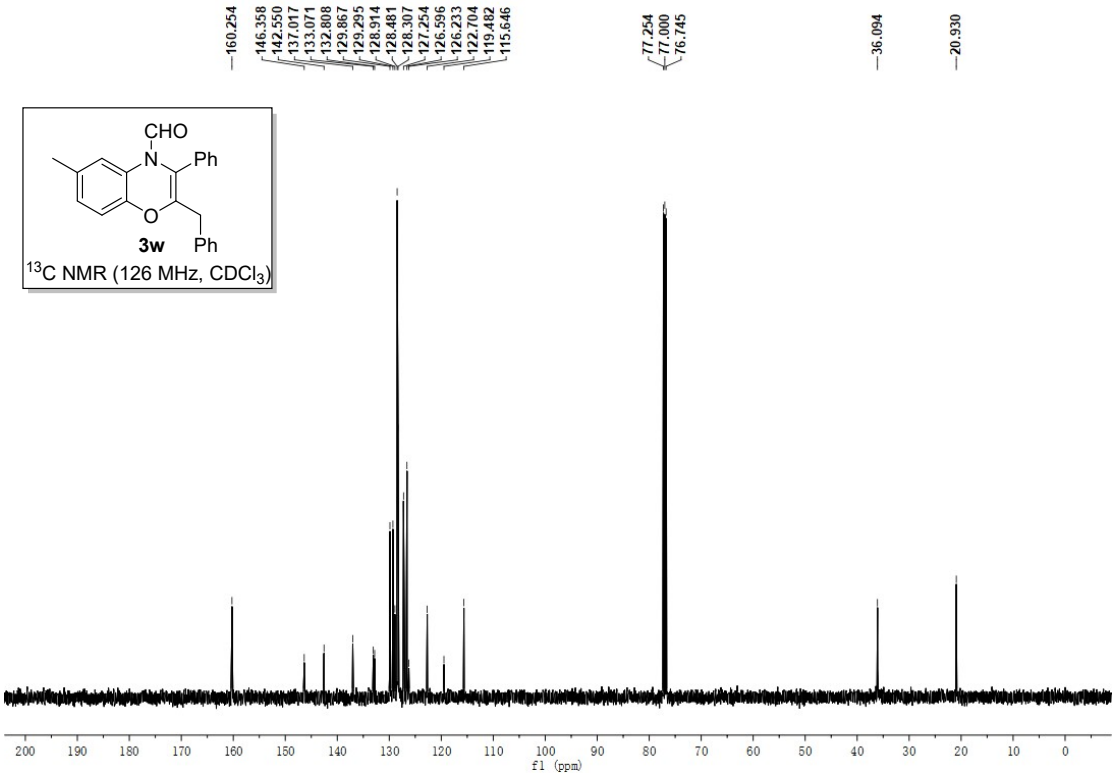
^{1}H NMR (500 MHz, $CDCl_3$)

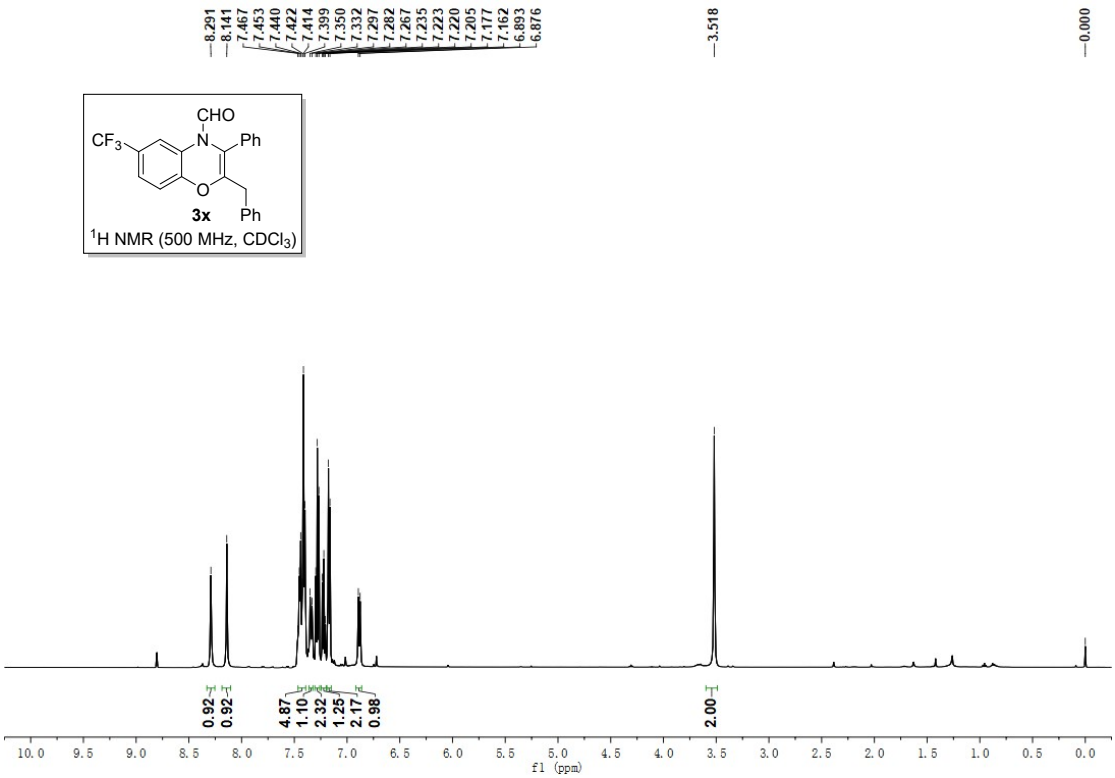


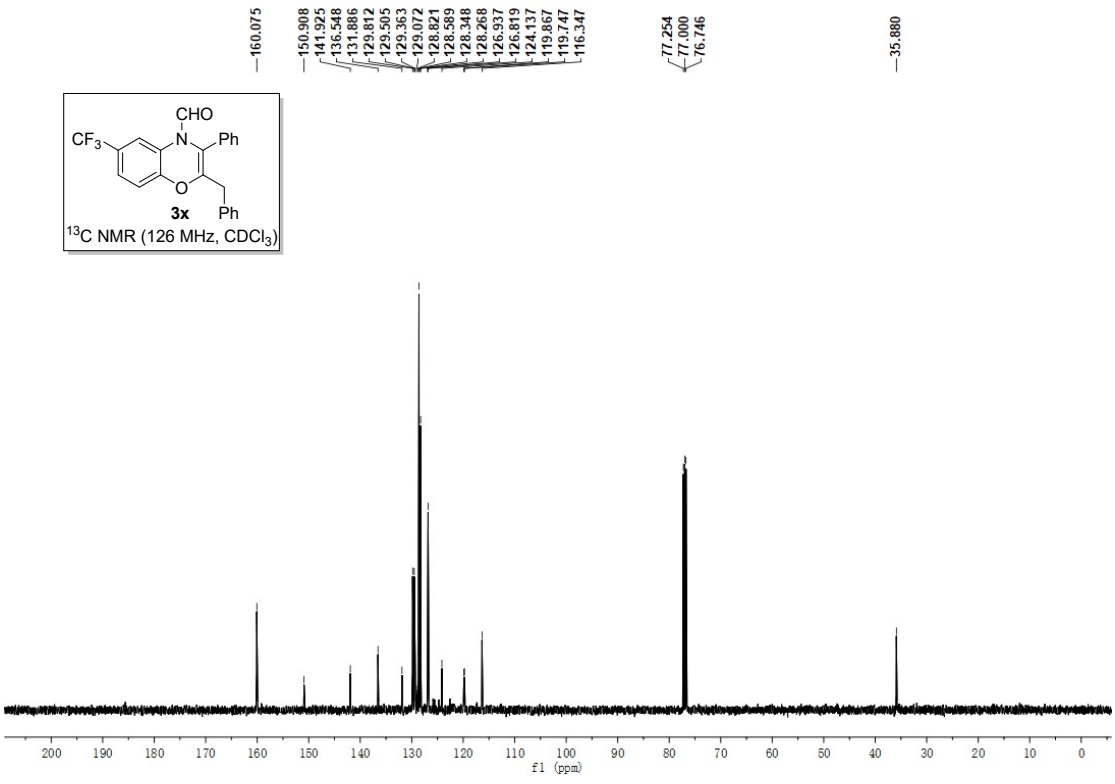


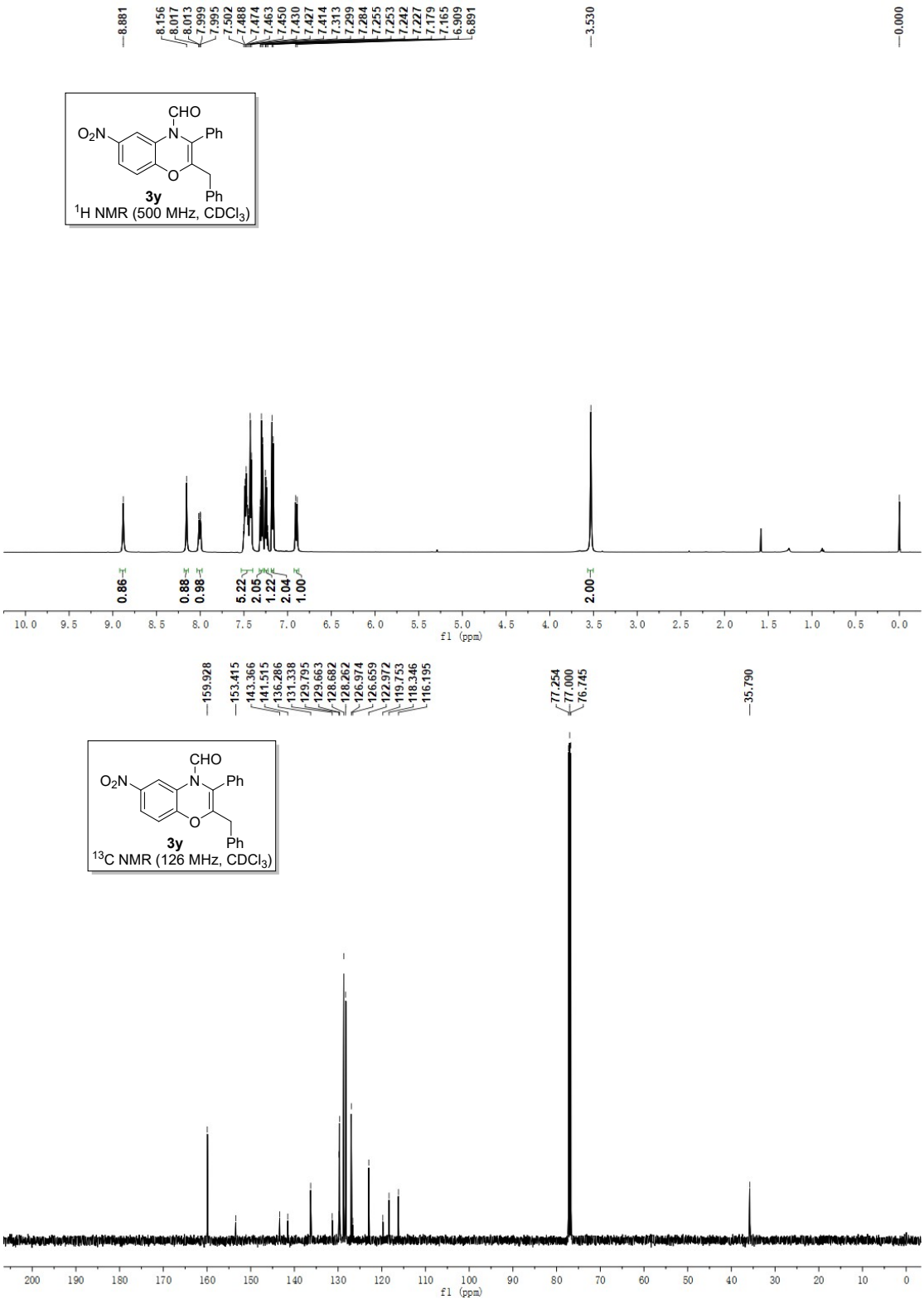
^{13}C NMR (126 MHz, $CDCl_3$)

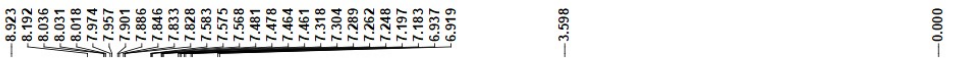

8.115
7.782
7.423
7.409
7.395
7.381
7.284
7.269
7.254
7.233
7.218
7.204
7.185
7.170
6.893
6.877
6.737
6.721
3.515
2.319
0.000
CHO
N
Ph
O
3w
Ph
1H NMR (500 MHz, CDCl3)
0.82
0.83
5.07
2.10
3.06
0.95
0.94
1.82
3.00
f1 (ppm)

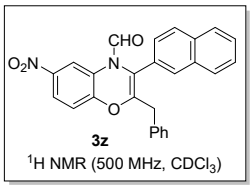

160.254
146.358
142.550
137.017
133.071
132.808
129.867
129.295
128.914
128.481
128.307
127.254
126.596
126.233
122.704
119.482
115.646
77.254
77.000
76.745
36.094
20.930
CHO
N
Ph
O
3w
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)


8.291
8.141
7.467
7.453
7.440
7.422
7.414
7.399
7.350
7.332
7.297
7.282
7.267
7.235
7.223
7.220
7.205
7.177
7.162
6.893
6.876
3.518
0.000
CHO
CF3
N
Ph
O
3x
Ph
1H NMR (500 MHz, CDCl3)
0.92
0.92
4.87
1.10
2.32
1.25
2.17
0.98
2.00
f1 (ppm)


160.075
150.908
141.925
136.548
131.886
129.812
129.505
129.363
129.072
128.821
128.589
128.348
128.268
126.937
126.819
124.137
119.867
119.747
116.347
77.254
77.000
76.746
35.880
CHO
CF3
N
Ph
O
3x
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)

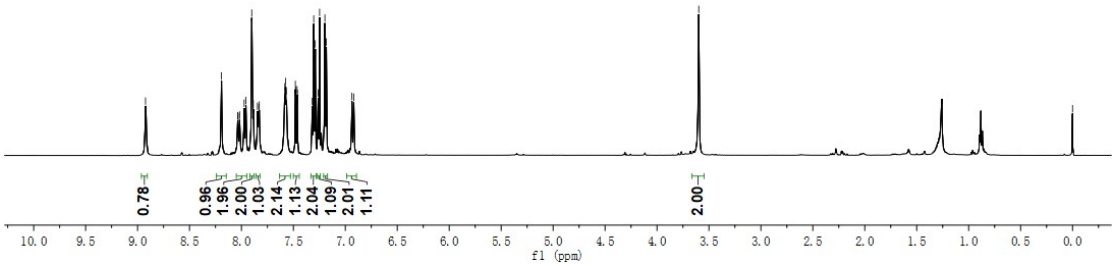

8.881
8.156
8.017
8.013
7.999
7.995
7.502
7.488
7.474
7.463
7.450
7.430
7.427
7.414
7.313
7.299
7.284
7.255
7.253
7.242
7.227
7.179
7.165
6.909
6.891
3.530
0.000
CHO
O2N
N
Ph
O
3y
Ph
1H NMR (500 MHz, CDCl3)
0.86
0.88
0.98
5.22
2.05
1.22
2.04
1.00
2.00
f1 (ppm)
159.928
153.415
143.366
141.515
136.286
131.338
129.795
129.663
128.682
128.262
126.974
126.659
122.972
119.753
118.346
116.195
77.254
77.000
76.745
35.790
13C NMR (126 MHz, CDCl3)

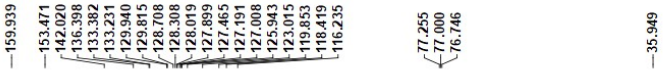


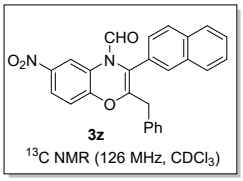


3z

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

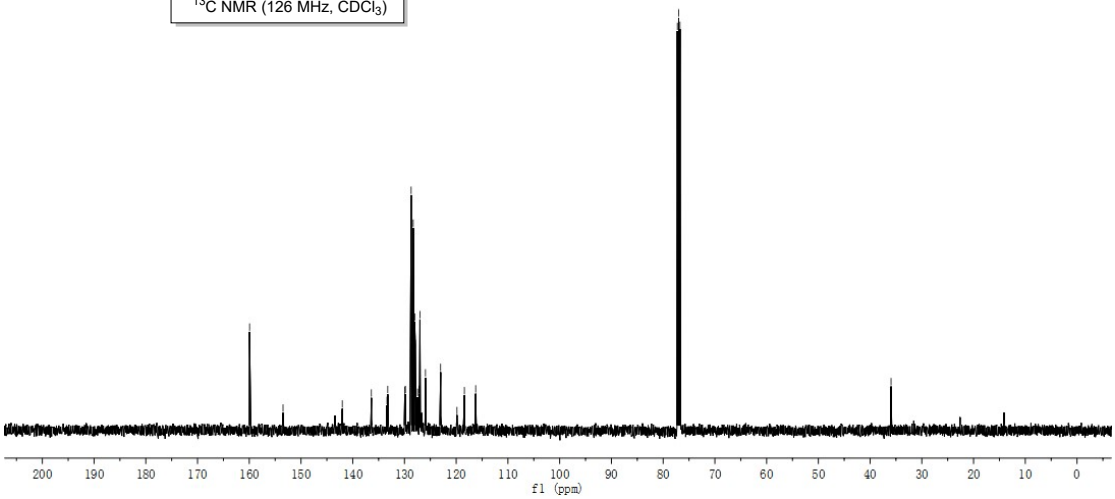


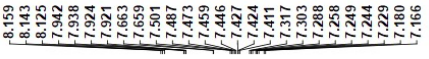


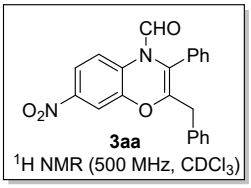


3z

^{13}C NMR (126 MHz, $CDCl_3$)

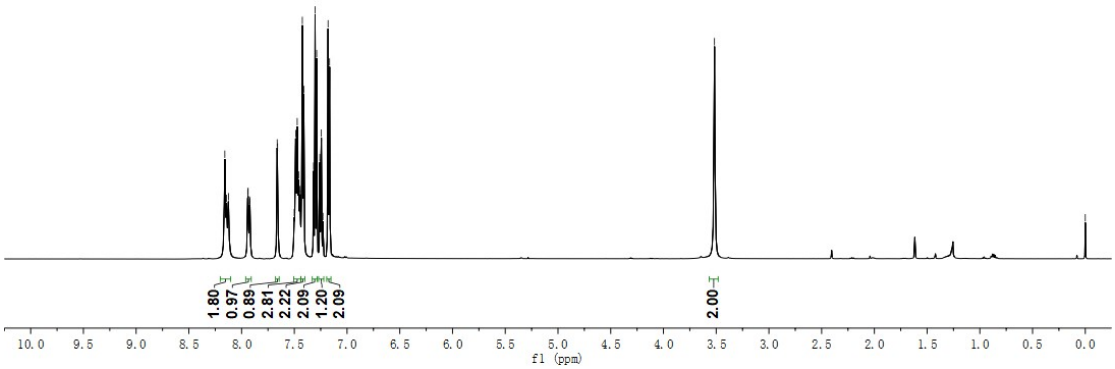


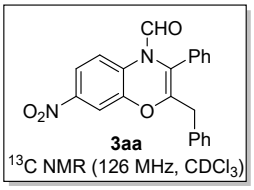




3aa

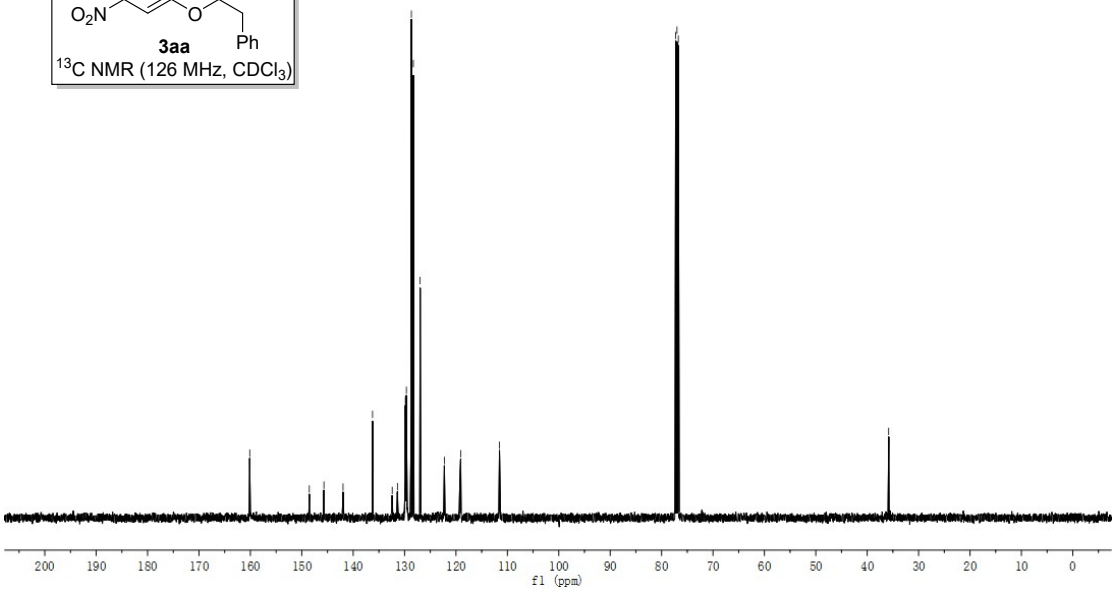
^{1}H NMR (500 MHz, $CDCl_3$)

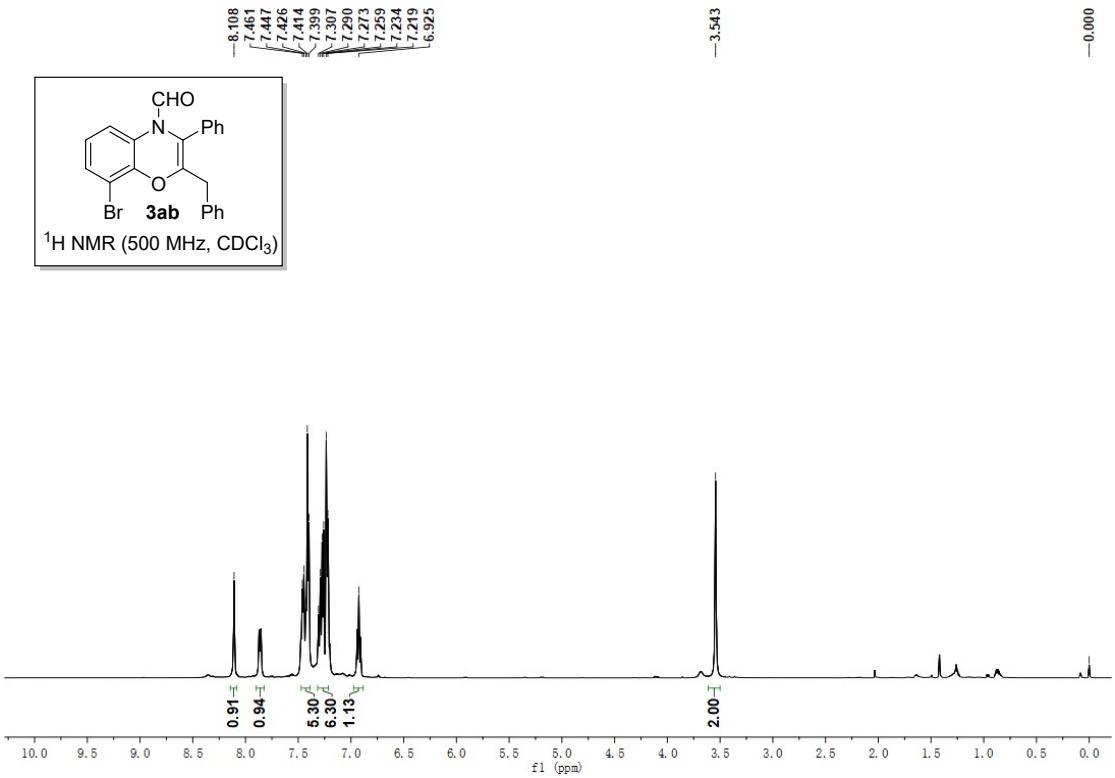


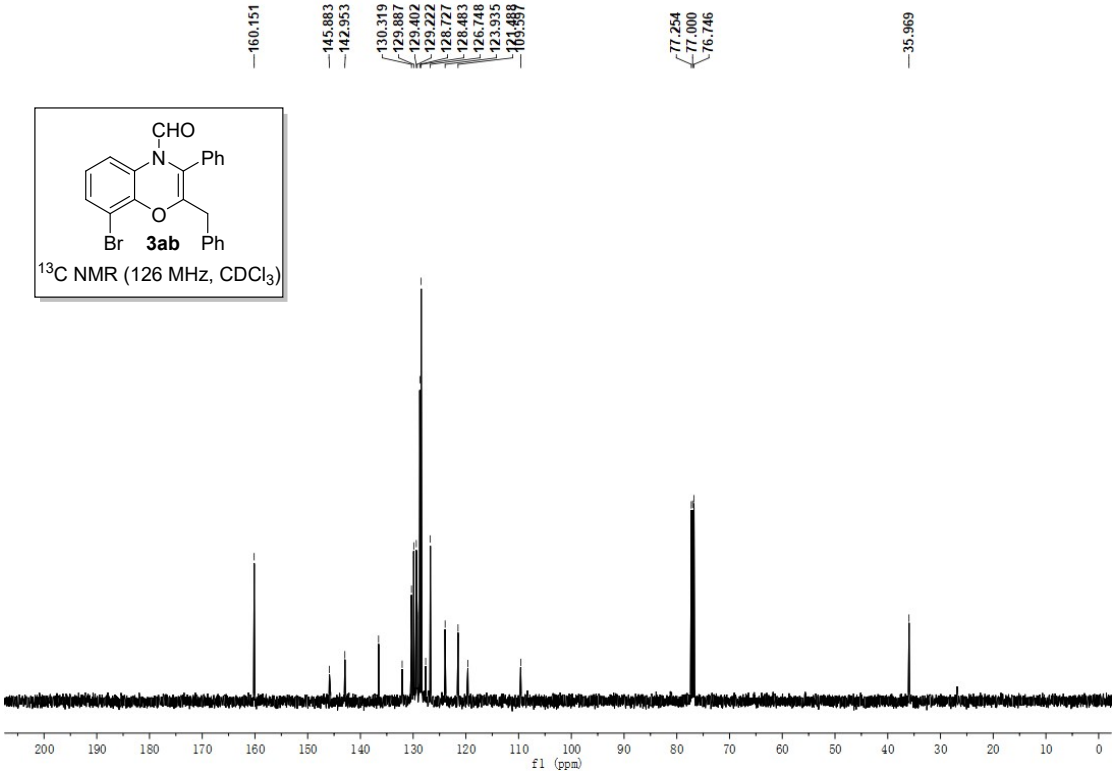


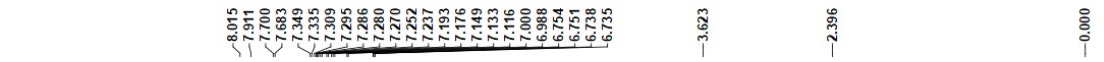
3aa

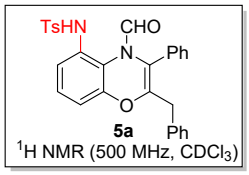
^{13}C NMR (126 MHz, $CDCl_3$)



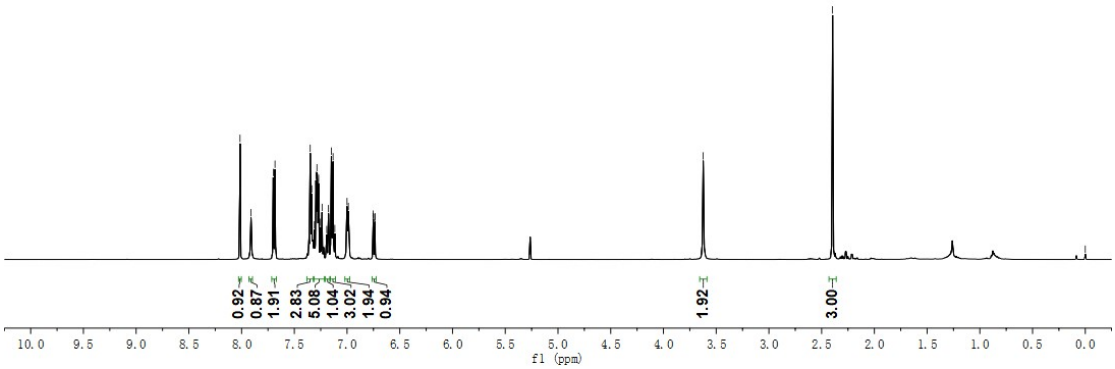

8.108
7.461
7.447
7.426
7.414
7.399
7.307
7.290
7.273
7.259
7.234
7.219
6.925
3.543
0.000
CHO
N
Ph
O
Br
3ab
Ph
1H NMR (500 MHz, CDCl3)
0.91
0.94
5.30
6.30
1.13
2.00
f1 (ppm)

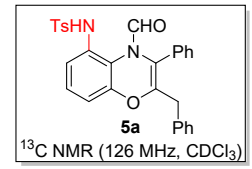

160.151
145.883
142.953
130.319
129.887
129.402
129.222
128.727
128.483
126.748
123.935
77.254
77.000
76.746
35.969
CHO
N
Ph
O
Br
3ab
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)



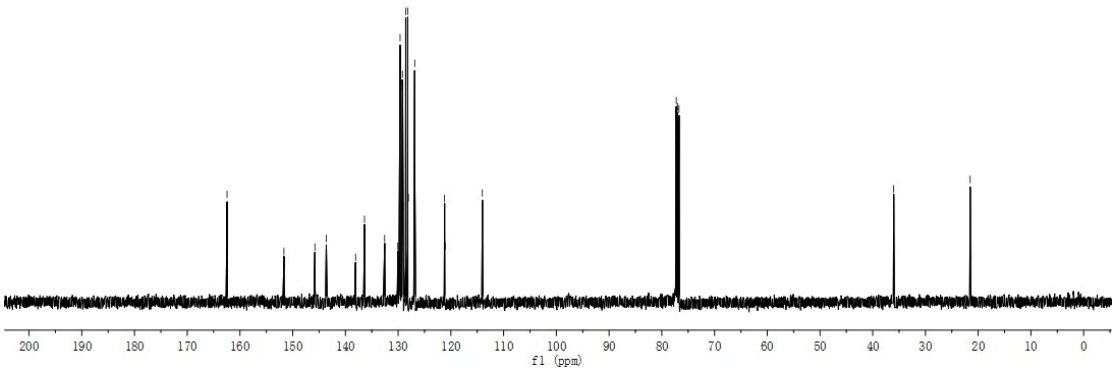


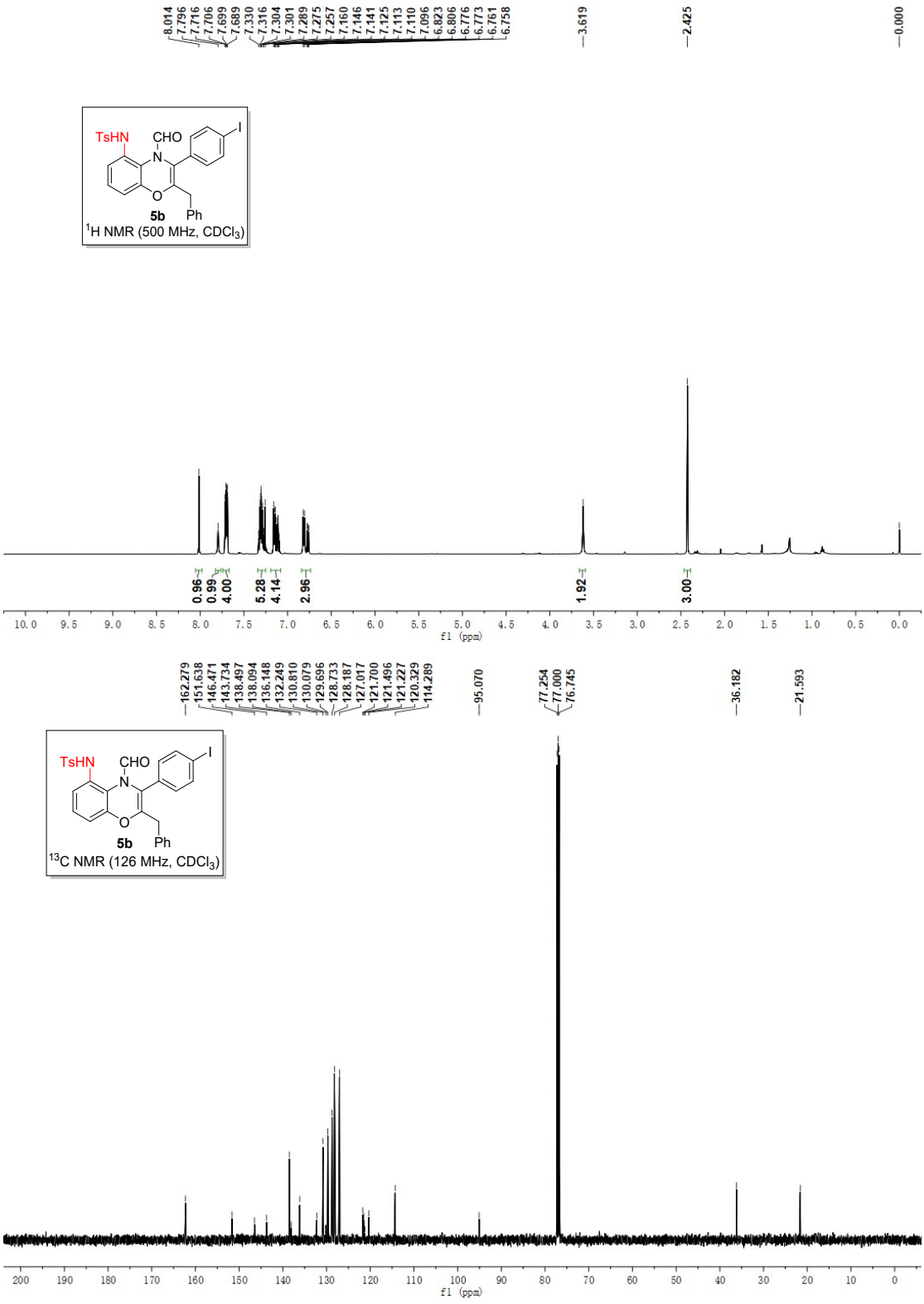
^{1}H NMR (500 MHz, $CDCl_3$)



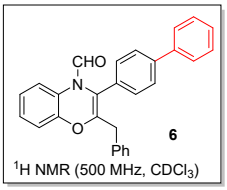


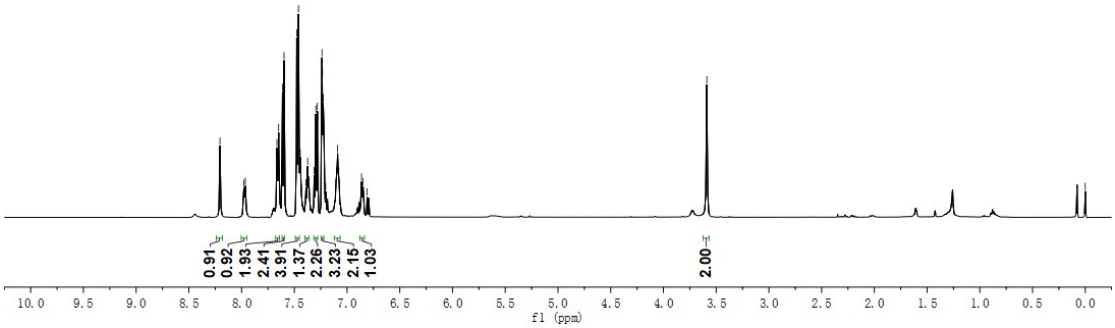
^{13}C NMR (126 MHz, $CDCl_3$)

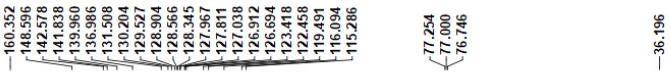


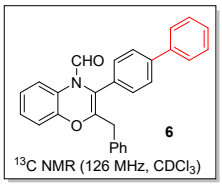

8.014
7.796
7.716
7.706
7.699
7.689
7.330
7.316
7.304
7.301
7.289
7.275
7.257
7.160
7.146
7.141
7.125
7.113
7.110
7.096
6.823
6.806
6.776
6.773
6.761
6.758
3.619
2.425
0.000
TsHN
CHO
N
O
I
Ph
5b
1H NMR (500 MHz, CDCl3)
0.96
0.99
4.00
5.28
4.14
2.96
1.92
3.00
f1 (ppm)
162.279
151.638
146.471
143.734
138.497
138.094
136.148
132.249
130.810
130.079
129.696
128.733
128.187
127.017
121.700
121.496
121.227
120.329
114.289
95.070
77.254
77.000
76.745
36.182
21.593
13C NMR (126 MHz, CDCl3)

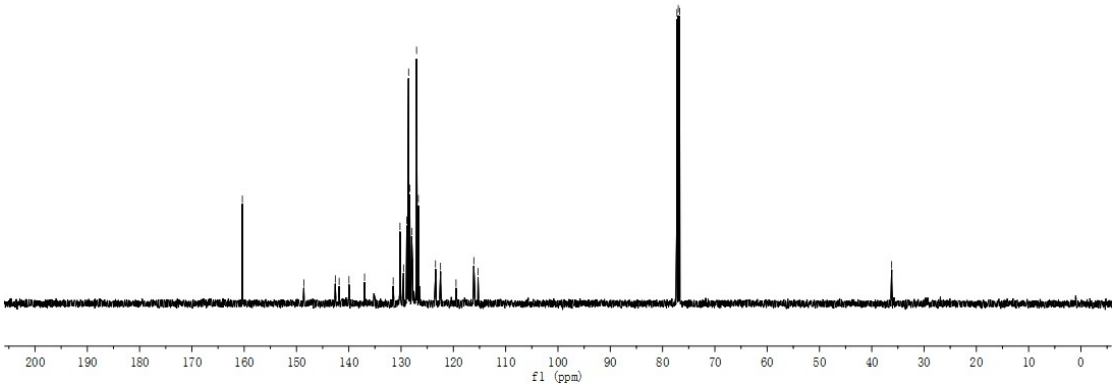

8.205
7.979
7.964
7.665
7.649
7.612
7.597
7.477
7.461
7.444
7.434
7.389
7.374
7.361
7.312
7.296
7.282
7.238
7.233
7.226
7.203
7.100
7.090
7.079
6.863
6.848
6.810
3.589
0.000

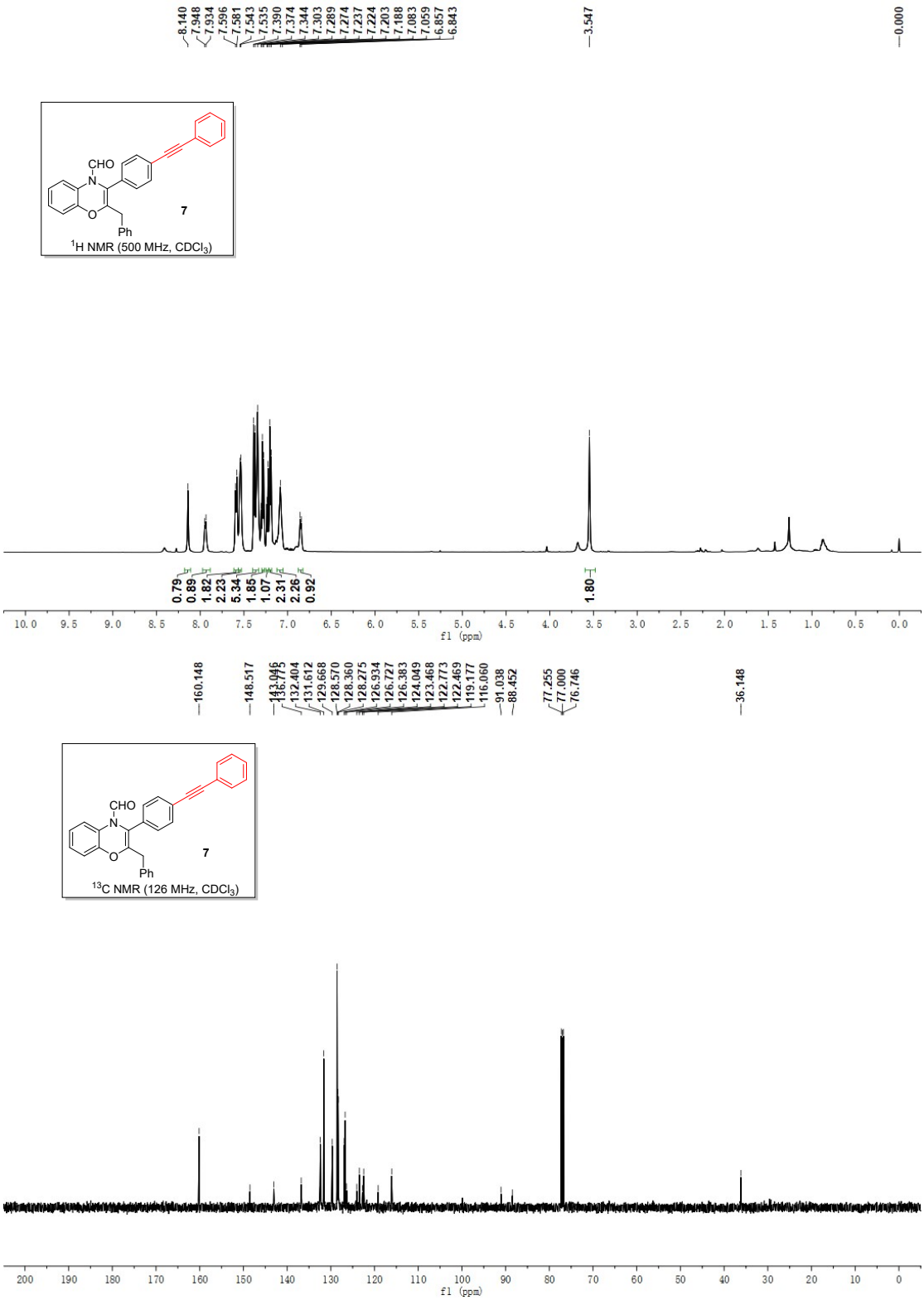

CHO
N
O
Ph
6
^{1}H NMR (500 MHz, CDCl$_3$)


0.91
0.92
1.93
2.41
3.91
1.37
2.26
3.23
2.15
1.03
2.00
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 0.0
f1 (ppm)


160.352
148.596
142.578
141.838
139.960
136.986
131.508
130.204
129.527
128.904
128.566
128.345
127.967
127.811
127.038
126.912
126.694
123.418
122.458
119.491
116.094
115.286
77.254
77.000
76.746
36.196


CHO
N
O
Ph
6
^{13}C NMR (126 MHz, CDCl$_3$)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.140
7.948
7.934
7.596
7.581
7.543
7.535
7.390
7.374
7.344
7.303
7.289
7.274
7.237
7.224
7.203
7.188
7.083
7.059
6.857
6.843
3.547
0.000
CHO
N
O
Ph
7
1H NMR (500 MHz, CDCl3)
0.79
0.89
1.82
2.23
5.34
1.85
1.07
2.31
2.26
0.92
1.80
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 0.0
f1 (ppm)
160.148
148.517
143.046
136.775
132.404
131.612
129.668
128.570
128.360
128.275
126.934
126.727
126.383
124.049
123.468
122.773
122.469
119.177
116.060
91.038
88.452
77.255
77.000
76.746
36.148
CHO
N
O
Ph
7
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)