# Electronic Supplementary Information

## Synthesis of 1,4-benzoxazine derivatives from *a*-aminocarbonyls under transition-metal-free conditions

Liqiang Hao,[a] Gaorong Wu,[a] Yangyang Wang,[a] Xiaobo Xu,[a] Yafei Ji [a,] *

[a]Engineering Research Center of Pharmaceutical Process Chemistry, Ministry of Education; School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China
E-mail: jyf@ecust.edu.cn (Ji).

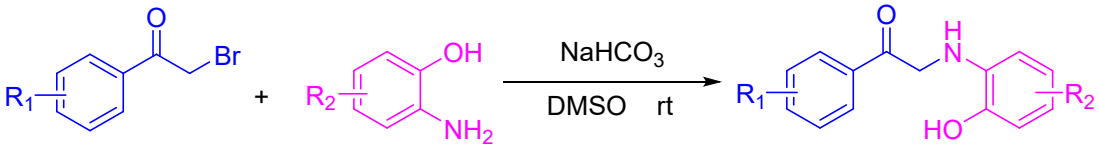
**Table of contents:** **Page**

## 1. General Experiment Information

All reagents were obtained from commercial sources and used as received without further purification unless otherwise stated. NMR spectra were recorded on a BrukerAvanceII 400 spectrometer and BrukerAvanceII 600 spectrometer in DMSO-$d_6$ with tetramethylsilane (TMS) as an internal standard; chemical shifts $\delta$ were given in ppm and coupling constants $J$ in Hz. HRMS were measured on a QSTAR Pulsar I LC/TOF MS mass spectrometer.

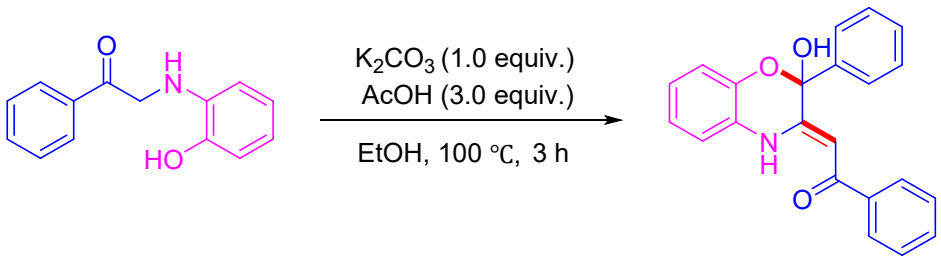
## 2. General Procedures

### 2.1 General procedure for Synthesis of 2-((2-hydroxyphenyl)amino)-1-phenylethan-1-one



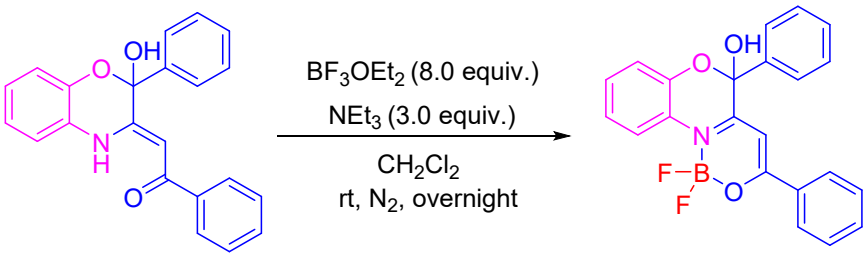

To a solution of 2-bromo-1-phenylethan-1-one (0.5 mmol, 1.0 equiv) and 2-aminophenol (0.55 mmol, 1.1 equiv) in DMSO (10 mL) in a 100 mL round bottom flask, sodium bicarbonate (0.6 mmol, 1.2 equiv) was added. After the mixture was stirred at room temperature for 30 min, then add water (50 ml) into the bottom. Upon completion, the mixture was filtration to afford the desired product.

### 2.2 General procedure for Synthesis of 1,4-benzoxazines derivatives



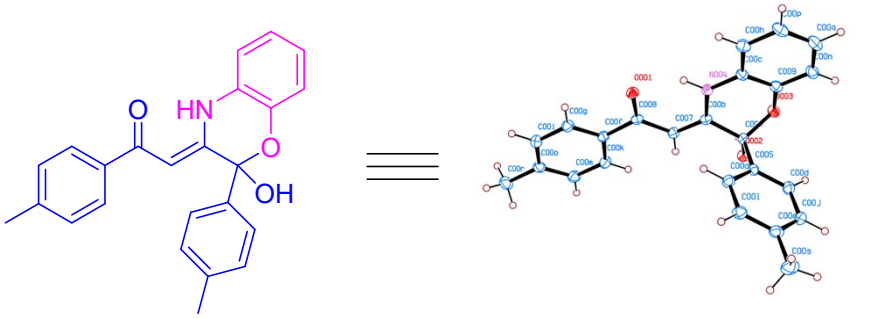

A mixture of the **2a** (0.2 mmol), $K_2CO_3$ (1.0 equiv.) and AcOH (3.0 equiv.) in EtOH (2.0 mL) was stirred at sealed tube under 100 °C for 3 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford the product.

### 2.3 General procedure for Synthesis of 1,4-benzoxazines-$BF_2$ complex 4



The (*Z*)-2-(2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one **2a** (51 mg, 0.15 mmol) was dissolved in anhydrous $CH_2Cl_2$ (2 mL) at room temperature and a solution of triethylamine (3.0 equiv.) in anhydrous $CH_2Cl_2$ (1 mL) was added gradually. After 30 minutes of room temperature stirring, boron trifluoride etherate (8.0 equiv.) was added dropwise into the reaction mixture. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on a short silica gel to afford the product **4** in 85 % yield.

## 2.4 Single crystal structure of 2b



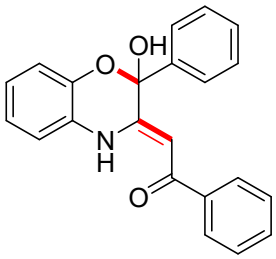

**2b**

X-ray Single crystal structure of **2b**

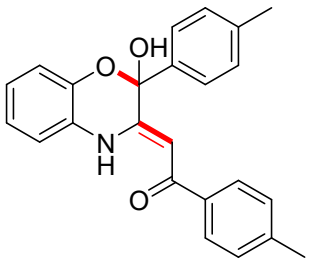
| | | |
|---|---|---|
| Empirical formula | $C_{24}H_{21}NO_3$ | |
| Formula weight | 371.42 | |
| Temperature | 200(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 6.0236(4) Å | a= 79.749(3)°. |
| | b = 9.6327(7) Å | b= 89.873(3)°. |
| | c = 17.0316(12) Å | g = 74.604(3)°. |
| Volume | 936.50(11) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.317 $Mg/m^3$ | |
| Absorption coefficient | 0.695 $mm^{-1}$ | |
| F(000) | 392 | |
| Crystal size | 0.05 x 0.09 x 0.11 $mm^3$ | |
| Theta range for data collection | 4.844 to 68.332°. | |

| | |
|---|---|
| Index ranges | -7<=h<=7, -11<=k<=11, -20<=l<=15 |
| Reflections collected | 11105 |
| Independent reflections | 3350 [R(int) = 0.0415] |
| Completeness to theta = 67.679° | 97.7 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3350 / 0 / 260 |
| Goodness-of-fit on $F^2$ | 1.064 |
| Final R indices [I>2sigma(I)] | R1 = 0.0639, wR2 = 0.1732 |
| R indices (all data) | R1 = 0.0708, wR2 = 0.1761 |
| Extinction coefficient | 0.0274(19) |
| Largest diff. peak and hole | 0.331 and -0.228 e.$Å^{-3}$ |

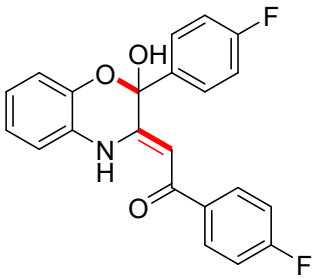
## 3. Characterization of Materials



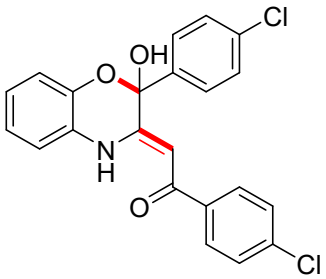

**(*Z*)-2-(2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (2a):** Yellow solid, 27.4 mg, 80 % yield (eluent: ethyl acetate/petroleum ether = 1:25), m.p. 162.3-162.8 °C. $^1$H NMR (400 MHz, DMSO) δ 12.78 (s, 1H), 8.30 (s, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.65 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.51 – 7.39 (m, 5H), 7.38 – 7.31 (m, 1H), 7.11 – 6.93 (m, 3H), 5.73 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 191.41, 153.51, 142.68, 139.00, 138.54, 131.77, 129.71, 128.50, 128.40, 127.28, 126.76, 125.96, 124.02, 123.18, 117.93, 116.33, 96.81, 91.26. HRMS (EI): *m/z* [$M^+$]Calcd. for $C_{22}H_{17}NO_3$: 343.1208. Found 343.1210.



**(*Z*)-2-(2-hydroxy-2-(p-tolyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(p-tolyl)ethan-1-one (2b):** Yellow solid, 28.9 mg, 78 % yield (eluent: ethyl acetate/petroleum ether = 1:25), m.p. 224.5-225.1 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.73 (s, 1H), 8.19 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.99 (td, *J* = 9.6, 5.5 Hz, 3H), 5.76 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.76, 154.54, 143.54, 142.46, 138.95, 137.09, 136.80, 129.73, 129.16, 127.30, 127.16, 126.66, 124.09, 123.03, 117.88, 116.89, 97.12, 90.45, 21.51, 21.25. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{24}H_{21}NO_3$: 371.1521. Found 371.1519.

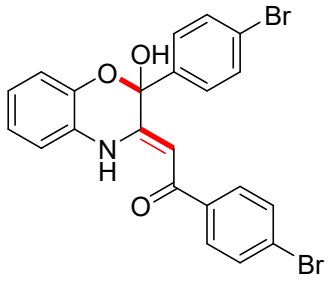



**(*Z*)-1-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2c):** Yellow solid, 31.1 mg, 82 % yield (eluent: ethyl acetate/petroleum ether = 1:20), m.p. 230.4-231.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.72 (s, 1H), 8.37 (s, 1H), 7.79 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.72 – 7.56 (m, 2H), 7.40 – 7.20 (m, 5H), 7.03 (td, *J* = 9.6, 5.3 Hz, 3H), 5.68 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.50, 165.55 (d, *J* = 250.509 Hz), 163.89 (d, *J* = 250.509 Hz), 163.68 (d, *J* = 245.828 Hz), 162.05 (d, *J* = 245.828 Hz), 154.51, 143.34, 136.20 (d, *J* = 2.265 Hz), 136.18 (d, *J* = 2.265 Hz), 135.83 (d, *J* = 2.265 Hz), 135.82 (d, *J* = 2.265 Hz), 130.00 (d, *J* = 8.909 Hz), 129.94 (d, *J* = 8.909 Hz), 129.70 (d, *J* = 8.305 Hz), 129.65 (d, *J* = 8.305 Hz), 126.47, 124.34, 123.23, 117.95, 117.12, 116.24 (d, *J* = 21.895 Hz), 116.10 (d, *J* = 21.895 Hz), 115.63 (d, *J* = 21.744 Hz), 115.49 (d, *J* = 21.744 Hz), 96.70, 90.30. $^{19}$F NMR (565 MHz, DMSO) δ -108.10 – -108.22 (m), -112.53 – -112.66 (m). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{15}F_2NO_3$: 379.1020. Found 379.1025.

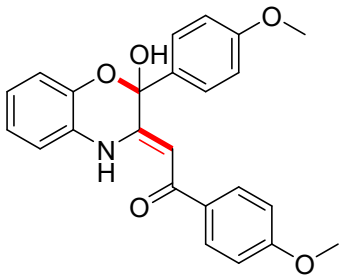



**(*Z*)-1-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2d):** Yellow solid, 30.0 mg, 73 % yield (eluent: ethyl acetate/petroleum ether =

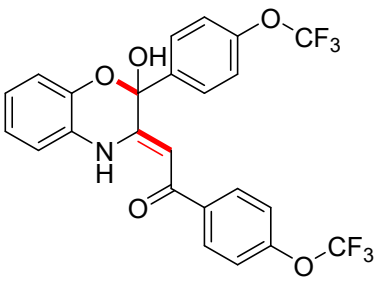
1:25), m.p. 203.4-204.5 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.75 (s, 1H), 8.44 (s, 1H), 7.79 – 7.71 (m, 2H), 7.66 – 7.60 (m, 2H), 7.58 – 7.47 (m, 4H), 7.41 – 7.29 (m, 1H), 7.09 – 6.94 (m, 3H), 5.71 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.54, 154.47, 143.30, 138.84, 137.91, 137.18, 134.39, 129.32, 129.26, 129.15, 128.77, 126.36, 124.50, 123.29, 117.94, 117.24, 96.67, 90.36. HRMS (EI): *m*/*z* [$M^+$]Calcd. for $C_{22}H_{15}Cl_2NO_3$: 411.0429. Found 411.0426.



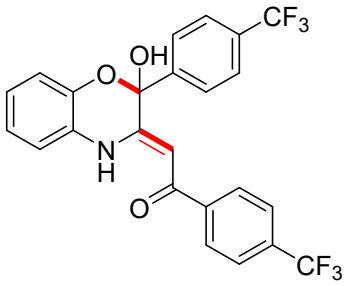

**(*Z*)-1-(4-bromophenyl)-2-(2-(4-bromophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2e):** Yellow solid, 36.9 mg, 74 % yield (eluent: ethyl acetate/petroleum ether = 1:25), m.p. 201.2-202.3 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.78 (s, 1H), 8.47 (s, 1H), 7.71-7.67 (m, 4H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.39 – 7.34 (m, 1H), 7.03 (qt, *J* = 7.0, 3.5 Hz, 3H), 5.74 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.71, 154.44, 143.30, 139.26, 138.26, 132.24, 131.70, 129.53, 129.31, 126.35, 126.25, 124.51, 123.29, 123.15, 117.94, 117.23, 96.75, 90.37. HRMS (EI): *m*/*z* [$M^+$]Calcd. for $C_{22}H_{15}Br_2NO_3$: 498.9419. Found 498.9409.




**(*Z*)-2-(2-hydroxy-2-(4-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-methoxyphenyl)ethan-1-one (2f):** Yellow solid, 29.0 mg, 72 % yield (eluent: ethyl acetate/petroleum ether = 1:15), m.p. 183.2-183.8 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.74 (s, 1H), 8.18 (s, 1H), 7.79 – 7.69 (m, 2H), 7.60 – 7.51 (m, 2H), 7.36 – 7.27 (m, 1H), 7.07 – 6.98 (m, 7H), 5.77 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.01, 162.68, 160.12, 154.34, 143.51, 132.03, 131.98, 129.31, 128.68, 126.78, 123.90, 123.01, 117.89, 116.75, 114.42, 113.87, 97.06, 90.18, 55.87, 55.63. HRMS (EI): *m*/*z* [$M^+$]Calcd. for $C_{24}H_{21}NO_5$: 403.1420. Found 403.1418.

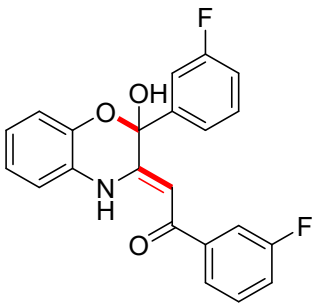


**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethoxy)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one (2g):** Yellow solid, 41.4 mg, 81 % yield (eluent: ethyl acetate/petroleum ether = 1:15), m.p. 180.2-180.9 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.79 (s, 1H), 8.54 (s, 1H), 7.93 – 7.85 (m, 2H), 7.82 – 7.74 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 4H), 7.39 (dt, *J* = 7.1, 3.6 Hz, 1H), 7.12 – 6.97 (m, 3H), 5.76 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.33, 154.47, 151.11, 149.28, 143.30, 139.13, 138.14, 129.55, 129.50, 126.33, 124.52, 123.29, 123.05 (q, *J* = 256.851 Hz), 122.95 (q, *J* = 257.153 Hz), 121.35 (q, *J* = 256.851 Hz), 121.28, 121.25 (q, *J* = 257.153 Hz), 121.09, 119.64 (q, *J* = 256.851 Hz), 119.55 (q, *J* = 257.153 Hz), 117.94 (q, *J* = 256.851 Hz), 117.93, 117.84 (q, *J* = 257.153 Hz), 117.26, 96.60, 90.50. $^{19}$F NMR (565 MHz, DMSO) δ -56.81 (d, *J* = 6.6 Hz), -56.88 (d, *J* = 5.2 Hz). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{24}H_{15}F_6NO_5$: 511.0854. Found 511.0859.

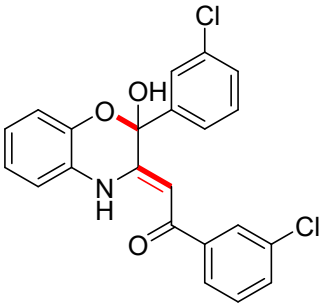


**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (2h):** Yellow solid, 39.8 mg, 83 % yield (eluent: ethyl acetate/petroleum ether = 1:15), m.p. 181.0-181.6 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.88 (s, 1H), 8.70 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.84 (dd, *J* = 8.5, 3.1 Hz, 4H), 7.43 (dt, *J* = 7.0, 3.1 Hz, 1H), 7.19 – 6.87 (m, 3H), 5.81 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.52, 154.57, 144.15, 143.27, 142.62, 132.19 (d, *J* = 31.861 Hz), 131.98 (d, *J* = 31.861 Hz), 131.77 (d, *J* = 31.861 Hz), 131.56 (d, *J* = 31.861 Hz), 130.53 (d, *J* = 32.012 Hz), 130.32 (d, *J* = 32.012 Hz), 130.10 (d, *J* = 32.012 Hz), 129.89 (d, *J* = 32.012 Hz), 128.26, 128.04, 127.17 (d, *J* = 272.857 Hz), 127.04 (d, *J* = 273.159 Hz), 126.18, 126.17 (d, *J* = 3.473 Hz),126.14 (d, *J* = 3.473 Hz), 126.13 (d, *J* = 3.473 Hz), 126.10 (d, *J* = 3.473 Hz), 125.76 (d, *J* = 3.171 Hz), 125.74 (d, *J* = 3.171 Hz), 125.72 (d, *J* = 3.171 Hz), 125.70 (d, *J* = 3.171

Hz), 125.36 (d, $J$ = 272.857 Hz), 125.23 (d, $J$ = 273.159 Hz), 124.77, 123.56 (d, $J$ = 272.857 Hz), 123.43 (d, $J$ = 273.159 Hz), 123.40, 121.76 (d, $J$ = 272.857 Hz), 121.63 (d, $J$ = 273.159 Hz), 117.96, 117.44, 96.61, 90.82. $^{19}$F NMR (565 MHz, DMSO) δ -61.24 (d, $J$ = 4.1 Hz), -61.53 (d, $J$ = 4.3 Hz). HRMS (EI): $m/z$ [M$^+$]Calcd. for $C_{24}H_{15}F_6NO_3$: 479.0956. Found 479.0956.

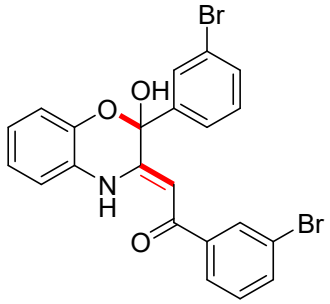



**(*Z*)-1-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2i):** Yellow solid, 30.7 mg, 81 % yield (eluent: ethyl acetate/petroleum ether = 1:25), m.p. 189.7-190.2 °C. $^1$H NMR (400 MHz, DMSO) δ 12.75 (s, 1H), 8.52 (s, 1H), 7.56 – 7.48 (m, 4H), 7.48 – 7.35 (m, 4H), 7.33 – 7.25 (m, 1H), 7.11 – 6.97 (m, 3H), 5.73 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.27, 163.58 (d, $J$ = 245.526 Hz), 163.15 (d, $J$ = 244.016 Hz), 161.96 (d, $J$ = 245.546 Hz), 161.53 (d, $J$ = 244.016 Hz), 154.47, 143.30, 142.65 (d, $J$ = 6.946 Hz), 142.61 (d, $J$ = 6.946 Hz), 141.69 (d, $J$ = 5.587 Hz), 141.65 (d, $J$ = 5.587 Hz), 131.41 (d, $J$ = 8.003 Hz), 131.36 (d, $J$ = 8.003 Hz), 130.89 (d, $J$ = 8.154 Hz), 130.83 (d, $J$ = 8.154 Hz), 126.29, 124.59, 123.53, 123.36, 123.32, 119.25 (d, $J$ = 21.14 Hz), 119.11 (d, $J$ = 21.14 Hz), 117.97, 117.28, 116.75 (d, $J$ = 20.687 Hz), 116.61 (d, $J$ = 20.687 Hz), 114.34 (d, $J$ = 23.254 Hz), 114.18 (d, $J$ = 23.254 Hz), 113.80 (d, $J$ = 22.197 Hz), 113.65 (d, $J$ = 22.197 Hz), 96.49, 90.53. $^{19}$F NMR (565 MHz, DMSO) δ -112.13 – -112.25 (m), -112.56 (dd, $J$ = 15.4, 9.8 Hz). HRMS (EI): $m/z$ [M$^+$]Calcd. for $C_{22}H_{15}F_2NO_3$: 379.1020. Found 379.1023.

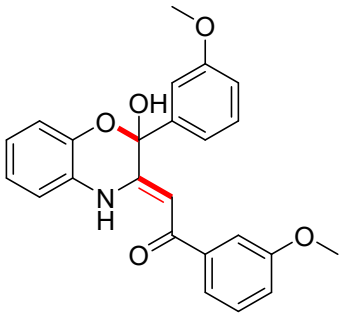



**(*Z*)-1-(3-chlorophenyl)-2-(2-(3-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2j):** Yellow solid, 29.2 mg, 71 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 186.2-187.2 °C. $^1$H NMR (400 MHz, DMSO) δ 12.70 (s, 1H), 8.52 (s, 1H), 7.75 (s, 1H), 7.67

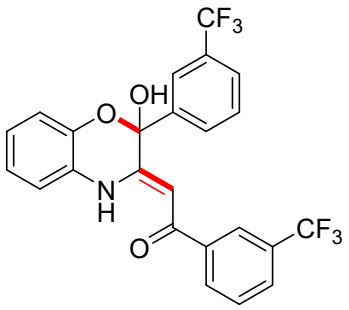
– 7.56 (m, 4H), 7.55 – 7.44 (m, 3H), 7.38 (dd, *J* = 5.4, 3.8 Hz, 1H), 7.12 – 6.94 (m, 3H), 5.73 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.13, 154.37, 143.26, 142.18, 141.18, 134.13, 133.43, 132.08, 131.26, 130.77, 129.80, 127.04, 126.93, 126.26, 126.17, 125.92, 124.65, 123.36, 117.95, 117.36, 96.48, 90.52. HRMS (EI): *m*/*z* [M$^+$]Calcd. for $C_{22}H_{15}Cl_2NO_3$: 411.0429. Found 411.0428.



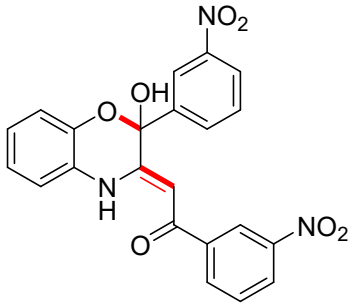

**(*Z*)-1-(3-bromophenyl)-2-(2-(3-bromophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2k):** Yellow solid, 35.9 mg, 72 % yield (eluent: ethyl acetate/petroleum ether = 1:50) , m.p. 187.9-188.5 °C. $^1$H NMR (400 MHz, DMSO) δ 12.71 (s, 1H), 8.54 (s, 1H), 7.94 – 7.85 (m, 1H), 7.82-7.77 (m, 1H), 7.73 (ddd, *J* = 14.3, 7.7, 4.5 Hz, 2H), 7.68 – 7.57 (m, 2H), 7.53 – 7.32 (m, 3H), 7.16 – 6.90 (m, 3H), 5.74 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 188.05, 154.35, 143.27, 142.35, 141.36, 134.96, 132.69, 131.48, 131.03, 129.89, 129.88, 126.54, 126.26, 124.65, 123.36, 122.67, 121.94, 117.95, 117.36, 96.41, 90.51. HRMS (EI): *m*/*z* [M$^+$]Calcd. for $C_{22}H_{15}Br_2NO_3$: 498.9419. Found 498.9414.




**(*Z*)-2-(2-hydroxy-2-(3-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-methoxyphenyl)ethan-1-one (2l):** Yellow solid, 30.6 mg, 76 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 195.6-196.3 °C. $^1$H NMR (600 MHz, DMSO) δ 12.76 (s, 1H), 8.32 (s, 1H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.27 (dd, *J* = 6.0, 3.8 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.09 (m, 1H), 7.06 (dt, *J* = 7.4, 3.7 Hz, 1H), 7.04 – 6.96 (m, 3H), 5.76 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.59, 159.89, 159.47, 154.50, 143.49, 141.48, 140.86, 130.34, 129.83, 126.56, 124.29, 123.15, 119.64, 119.51, 117.97, 117.95, 117.04, 114.88, 113.06, 112.25, 96.94, 90.70, 55.63, 55.59. HRMS (EI): *m*/*z* [M$^+$]Calcd. for $C_{24}H_{21}NO_5$: 403.1420. Found 403.1426.

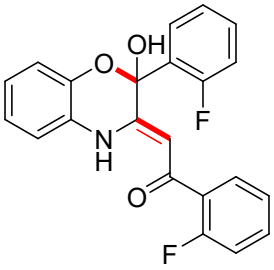



**(*Z*)-2-(2-hydroxy-2-(3-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-(trifluoromethyl)phenyl)ethan-1-one (2m):** Yellow solid, 33.5 mg, 70 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 197.8-198.6 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.74 (s, 1H), 8.67 (s, 1H), 8.05 – 7.89 (m, 5H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 2H), 7.42 (dt, *J* = 7.1, 3.6 Hz, 1H), 7.15 – 6.98 (m, 3H), 5.69 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 187.93, 154.43, 143.21, 141.12, 139.92, 131.66, 131.15, 130.63, 130.25 (q, *J* = 31.861 Hz), 130.16, 130.04 (q, *J* = 31.861 Hz), 129.83 (q, *J* = 31.861 Hz), 129.80 (q, *J* = 32.163 Hz), 129.62 (q, *J* = 31.861 Hz), 129.58 (q, *J* = 32.163 Hz), 129.37 (q, *J* = 32.163 Hz), 129.16 (q, *J* = 32.163 Hz), 128.77 (q, *J* = 2.869 Hz), 128.75 (q, *J* = 2.869 Hz), 128.74 (q, *J* = 2.869 Hz), 128.716 (q, *J* = 2.869 Hz), 127.21 (q, *J* = 273.008 Hz), 127.04 (q, *J* = 272.857 Hz), 126.67 (q, *J* = 3.624 Hz)，126.65 (q, *J* = 3.624 Hz), 126.62 (q, *J* = 3.624 Hz), 126.60 (q, *J* = 3.624 Hz)，126.24, 125.40 (q, *J* = 273.008 Hz), 125.23 (q, *J* = 272.857 Hz), 124.76, 123.765 (q, *J* = 3.624 Hz)，123.74 (q, *J* = 3.624 Hz), 123.765 (q, *J* = 3.624 Hz), 123.72 (q, *J* = 3.624 Hz), 123.69 (q, *J* = 3.624 Hz), 123.60 (q, *J* = 273.008 Hz), 123.51 (q, *J* = 3.775 Hz), 123.48 (q, *J* = 3.775 Hz), 123.46 (q, *J* = 3.775 Hz), 123.43 (q, *J* = 3.775 Hz), 123.47, 123.43 (q, *J* = 272.857 Hz), 121.79 (q, *J* = 273.008 Hz), 121.62 (q, *J* = 272.857 Hz), 118.03, 117.46, 96.50, 90.49. $^{19}$F NMR (565 MHz, DMSO) δ -61.21 (s), -61.50 (s). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{24}H_{15}F_6NO_3$: 479.0956. Found 479.0961.

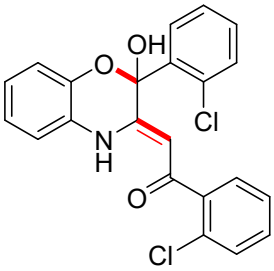



**(*Z*)-2-(2-hydroxy-2-(3-nitrophenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-nitrophenyl)ethan-1-one (2n):** Yellow solid, 30.8 mg, 71 % yield (eluent: ethyl acetate/petroleum ether = 1:50) , m.p. 262.8-263.4 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.82 (s, 1H), 8.83 (s, 1H), 8.49 (s, 1H),

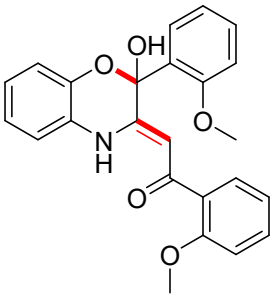
8.45 (s, 1H), 8.36 (dd, *J* = 10.0, 4.0 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.66 (m, 2H), 7.50 – 7.39 (m, 1H), 7.21 – 6.98 (m, 3H), 5.73 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 187.20, 154.45, 148.57, 148.15, 143.11, 141.79, 140.30, 134.21, 133.58, 131.01, 130.68, 126.65, 126.12, 124.94, 124.90, 123.59, 121.95, 121.81, 118.05, 117.62, 96.30, 90.62. HRMS (EI): *m*/*z* [M$^+$]Calcd. for $C_{22}H_{15}N_3O_7$: 433.0910. Found 433.0908.



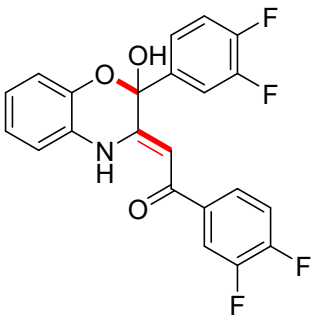

**(*Z*)-1-(2-fluorophenyl)-2-(2-(2-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2o):** Yellow solid, 30.7 mg, 81 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 252.8-253.6°C. $^1$H NMR (400 MHz, DMSO) δ 12.79 (s, 1H), 8.57 (s, 1H), 7.84 (td, *J* = 7.8, 1.6 Hz, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.61 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H), 7.36 (td, *J* = 7.6, 0.9 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.18 (dd, *J* = 11.4, 8.3 Hz, 1H), 7.11 – 6.97 (m, 3H), 5.39 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 186.60 (d, *J* = 3.02 Hz), 186.58 (d, *J* = 3.02 Hz), 161.04 (d, *J* = 251.113 Hz), 161.01 (d, *J* = 249.754 Hz), 159.38 (d, *J* = 251.113 Hz), 159.36 (d, *J* = 249.754 Hz), 154.12, 142.98, 133.90 (d, *J* = 8.607 Hz), 133.84 (d, *J* = 8.607 Hz), 132.50 (d, *J* = 8.305 Hz), 132.45 (d, *J* = 8.305 Hz), 130.40, 128.92, 127.66 (d, *J* = 12.533 Hz), 127.58 (d, *J* = 12.533 Hz), 127.52 (d, *J* = 11.476 Hz), 127.44 (d, *J* = 11.476 Hz), 125.86, 125.29 (d, *J* = 2.718 Hz), 125.27 (d, *J* = 2.718 Hz), 124.62, 124.38 (d, *J* = 2.265 Hz), 124.36 (d, *J* = 2.265 Hz), 123.20, 117.93, 117.43, 117.05 (d, *J* = 7.905 Hz), 116.89 (d, *J* = 7.905 Hz), 116.78 (d, *J* = 21.442 Hz), 116.64 (d, *J* = 21.442 Hz), 95.19, 93.88 (d, *J* = 10.872 Hz), 93.80 (d, *J* = 10.872 Hz). $^{19}$F NMR (565 MHz, DMSO) δ -109.99 (d, *J* = 11.3 Hz), -112.60 – -112.72 (m). HRMS (EI): *m*/*z* [M$^+$]Calcd. for $C_{22}H_{15}F_2NO_3$: 379.1020. Found 379.1014.



**(*Z*)-1-(2-chlorophenyl)-2-(2-(2-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2p):** Yellow solid, 32.1 mg, 78 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 228.4-228.9 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.63 (s, 1H), 8.60 (s, 1H), 8.09 – 7.82 (m, 1H), 7.53 (dt, *J* = 5.7, 3.1 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.12 – 6.90 (m, 3H), 4.97 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.78, 153.28, 142.83, 140.42, 137.39, 133.40, 131.77, 131.64, 131.36, 130.62, 130.04, 129.54, 129.20, 127.86, 127.20, 125.28, 124.65, 123.07, 117.88, 117.48, 95.75, 94.12. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{15}Cl_2NO_3$: 411.0429. Found 411.0437.

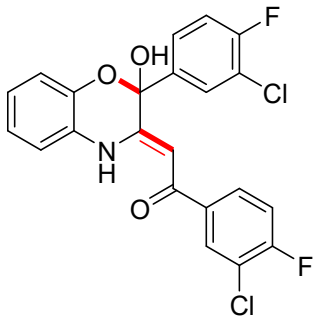



**(*Z*)-2-(2-hydroxy-2-(2-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(2 .methoxyphenyl)ethan-1-one (2q):** Yellow solid, 27.4 mg, 68 % yield (eluent: ethyl acetate/petroleum ether = 1:50) , m.p. 185.6-186.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.84 (s, 1H), 8.01 (s, 1H), 7.75 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (td, *J* = 8.2, 1.7 Hz, 1H), 7.37 (td, *J* = 8.1, 1.8 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.10 – 7.04 (m, 1H), 7.02 – 6.87 (m, 5H), 5.50 (s, 1H), 3.64 (s, 3H), 3.47 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.64, 157.94, 157.62, 154.55, 143.40, 132.64, 131.25, 129.90, 129.53, 128.79, 127.90, 125.93, 123.81, 122.51, 120.90, 120.13, 117.62, 116.82, 113.26, 112.74, 95.53, 94.41, 56.34, 55.49. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{24}H_{21}NO_5$: 403.1420. Found 403.1415.

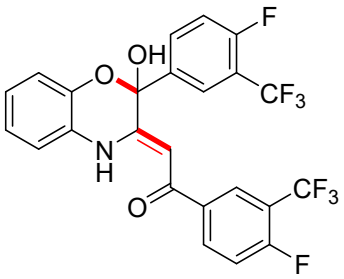



**(*Z*)-1-(3,4-difluorophenyl)-2-(2-(3,4-difluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2s):** Yellow solid, 29.9 mg, 72 % yield (eluent: ethyl acetate/petroleum ether =

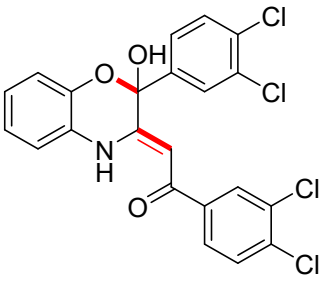
1:50), m.p. 248.8-249.3 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.74 (s, 1H), 8.54 (s, 1H), 7.80 (ddd, *J* = 11.3, 7.9, 2.0 Hz, 1H), 7.70 – 7.58 (m, 2H), 7.58 – 7.41 (m, 3H), 7.41 – 7.33 (m, 1H), 7.13 – 6.97 (m, 3H), 5.69 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 187.20, 154.38, 153.05 (dd, *J* = 251.717, 12.533 Hz), 152.97, 151.38, 151.30, 151.23 (dd, *J* = 257.304, 22.348 Hz), 151.08, 150.85 (dd, *J* = 249.942, 13.288 Hz), 150.76, 150.42 (dd, *J* = 245.073, 11.174 Hz), 150.34, 149.53, 149.38, 149.21, 149.12, 148.79, 148.72, 143.16, 137.56 (d, *J* = 7.55 Hz), 137.53, 137.51, 136.75 (d, *J* = 10.872 Hz), 136.72, 136.68, 126.22, 124.86 (dd, *J* = 5.587, 2.265 Hz), 124.84, 124.81, 124.79, 124.60 124.57 (dd, *J* = 6.946, 3.775 Hz), 124.55, 124.52, 124.50, 123.38, 118.35 (dd, *J* = 65.685, 17.365 Hz), 118.24, 117.98, 117.92, 117.80, 117.29, 116.90 (dd, *J* = 51.038, 18.724 Hz), 116.78, 116.57, 116.45, 96.19, 90.24. $^{19}$F NMR (565 MHz, DMSO) δ -133.54 (dt, *J* = 22.2, 8.0 Hz), -137.38 (dd, *J* = 21.8, 9.5 Hz), -137.43 – -137.61 (m), -137.73 – -137.99 (m). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{13}F_4NO_3$: 415.0832. Found 415.0829.



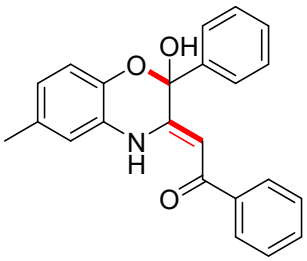

**(*Z*)-1-(3-chloro-4-fluorophenyl)-2-(2-(3-chloro-4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2t):** Yellow solid, 29.9 mg, 67 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 261.2-262.3 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.73 (s, 1H), 8.59 (s, 1H), 7.95 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.83 – 7.71 (m, 2H), 7.63 (ddd, *J* = 8.4, 4.6, 2.2 Hz, 1H), 7.49 (dd, *J* = 12.9, 4.9 Hz, 2H), 7.38 (dt, *J* = 7.0, 3.5 Hz, 1H), 7.14 – 6.97 (m, 3H), 5.74 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 187.10, 160.55 (d, *J* = 257.13 Hz), 158.87 (d, *J* = 257.378 Hz), 158.84 (d, *J* = 257.13 Hz), 157.19 (d, *J* = 257.378 Hz), 154.30, 143.16, 137.69 (d, *J* = 2.718 Hz), 137.67 (d, *J* = 2.718 Hz), 136.87 (d, *J* = 3.624 Hz), 136.85 (d, *J* = 3.624 Hz), 129.78, 129.59, 128.57 (d, *J* = 8.305 Hz), 128.52 (d, *J* = 8.305 Hz), 128.46 (d, *J* = 7.701 Hz), 128.41 (d, *J* = 7.701 Hz), 126.21, 124.65, 123.41, 120.72 (d, *J* = 17.969 Hz), 120.60 (d, *J* = 17.969 Hz), 119.97 (d, *J* = 2.718 Hz), 119.85 (d, *J* = 2.718 Hz), 117.95, 117.80 (d, *J* = 21.14 Hz), 117.66 (d, *J* = 2.718 Hz), 117.40 (d, *J* = 21.14 Hz), 117.35, 117.26 (d, *J* = 21.14 Hz), 96.19, 90.32. $^{19}$F NMR (565 MHz, DMSO) δ -111.40 (d, *J* = 11.9 Hz), -115.26 (dd, *J* = 12.1, 7.4 Hz). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{13}Cl_2F_2NO_3$: 447.0241. Found 447.0239.



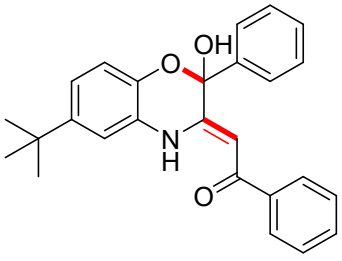

**(*Z*)-1-(4-fluoro-3-(trifluoromethyl)phenyl)-2-(2-(4-fluoro-3-(trifluoromethyl)phenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2u):** Yellow solid, 40.2 mg, 78 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 215.5-216.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.76 (s, 1H), 8.74 (s, 1H), 8.15 – 8.08 (m, 1H), 8.09 – 7.96 (m, 3H), 7.68 – 7.55 (m, 2H), 7.48 – 7.34 (m, 1H), 7.21 – 7.01 (m, 3H), 5.69 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 186.79, 162.03 (d, *J* = 259.871 Hz), 160.54 (d, *J* = 256.7 Hz), 160.31 (d, *J* = 259.871 Hz), 158.84 (d, *J* = 256.7 Hz), 154.31, 143.08, 136.91 (d, *J* = 3.473 Hz), 136.89 (d, *J* = 3.473 Hz), 135.85 (d, *J* = 2.567 Hz), 135.83 (d, *J* = 2.567 Hz), 134.69 (d, *J* = 9.211 Hz), 134.63 (d, *J* = 9.211 Hz), 134.46 (d, *J* = 9.664 Hz), 134.39 (d, *J* = 9.664 Hz), 126.36 (dq, *J* = 29.143, 3.624 Hz), 126.33 (dq, *J* = 29.143, 3.624 Hz), 126.31 (dq, *J* = 29.143, 3.624 Hz), 126.29 (dq, *J* = 29.143, 3.624 Hz),127.18 (dq, *J* = 29.143, 3.624 Hz), 126.17, 126.14 (dq, *J* = 29.143, 3.624 Hz), 126.11 (dq, *J* = 29.143, 3.624 Hz), 126.08 (dq, *J* = 29.143, 3.624 Hz), 125.59 (dq, *J* = 272.253 Hz), 125.42 (dq, *J* = 272.555 Hz), 124.75, 123.79 (dq, *J* = 272.253 Hz), 123.61 (dq, *J* = 272.555 Hz), 123.51, 121.98 (dq, *J* = 272.253 Hz), 121.81 (dq, *J* = 272.555 Hz), 120.18 (dq, *J* = 272.253 Hz), 120.00 (dq, *J* = 272.555 Hz), 118.32, 118.18, 118.01, 117.86, 117.72 (qd, *J* = 32.918, 13.288 Hz), 117.63 (qd, *J* = 29.143, 3.624 Hz), 117.50 (qd, *J* = 32.918, 13.288 Hz), 117.45, 117.42 (qd, *J* = 32.918, 13.288 Hz), 117.29 (qd, *J* = 32.918, 13.288 Hz), 117.26 (qd, *J* = 33.069, 12.231 Hz), 117.20 (qd, *J* = 32.918, 13.288 Hz), 117.18 (qd, *J* = 33.069, 12.231 Hz), 117.07 (qd, *J* = 32.918, 13.288 Hz), 117.04 (qd, *J* = 33.069, 12.231 Hz), 116.99 (qd, *J* = 32.918, 13.288 Hz), 116.95 (qd, *J* = 33.069, 12.231 Hz), 116.82 (qd, *J* = 33.069, 12.231 Hz), 116.74 (qd, *J* = 33.069, 12.231 Hz), 116.61 (qd, *J* = 33.069, 12.231 Hz), 116.52 (qd, *J* = 33.069, 12.231 Hz), 96.17, 90.31. $^{19}$F NMR (565 MHz, DMSO) δ -60.26 (t, *J* = 12.0 Hz), -60.64 (t, *J* = 12.6 Hz), -111.22 – -111.68 (m), -114.82 – -115.22 (m). HRMS (EI): *m/z* [M$^{+}$]Calcd. for $C_{24}H_{13}F_8NO_3$: 515.0768. Found 515.0770.




**(*Z*)-1-(3,4-dichlorophenyl)-2-(2-(3,4-dichlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2v):** Yellow solid, 31.1 mg, 65 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 265.4-266.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.74 (s, 1H), 8.65 (s, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.82 (s, 1H), 7.73 (t, *J* = 9.5 Hz, 3H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.32 (m, 1H), 7.15 – 6.95 (m, 3H), 5.78 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 187.13, 154.25, 143.12, 140.73, 139.44, 135.06, 132.58, 132.21, 131.56, 131.13, 129.28, 129.19, 127.81, 127.52, 126.11, 124.80, 123.48, 117.95, 117.46, 96.16, 90.46. HRMS (EI): *m/z* [M$^{+}$]Calcd. for $C_{22}H_{13}Cl_4NO_3$: 478.9650. Found 478.9651.

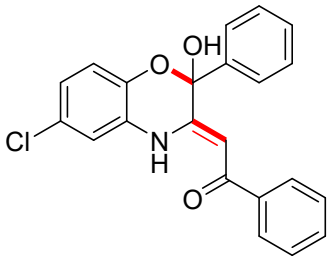



**(*Z*)-2-(2-hydroxy-6-methyl-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3a):** Yellow solid, 26.8 mg, 75 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 183.6-184.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.75 (s, 1H), 8.25 (s, 1H), 7.75 – 7.68 (m, 2H), 7.66 – 7.58 (m, 2H), 7.56 – 7.50 (m, 1H), 7.50 – 7.39 (m, 5H), 7.12 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.80 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.75 (s, 1H), 2.25 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.92, 154.77, 141.38, 139.97, 139.36, 132.29, 132.23, 129.62, 129.17, 128.63, 127.25, 127.18, 126.15, 124.75, 117.64, 117.27, 97.03, 90.57, 20.88. HRMS (EI): *m/z* [M$^{+}$]Calcd. for $C_{23}H_{19}NO_3$: 357.1365. Found 357.1367.

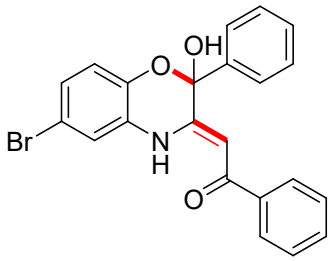



**(*Z*)-2-(6-(tert-butyl)-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3b):** Yellow solid, 30.3 mg, 76 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 215.0-

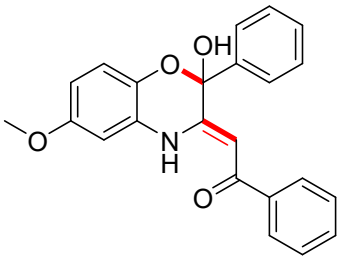
215.4 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.80 (s, 1H), 8.22 (s, 1H), 7.72 – 7.67 (m, 2H), 7.66 – 7.62 (m, 2H), 7.54 – 7.50 (m, 1H), 7.49 – 7.42 (m, 5H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.67 (s, 1H), 1.28 (s, 9H). $^{13}$C NMR (151 MHz, DMSO) δ 189.70, 154.70, 145.81, 141.23, 140.10, 139.39, 132.24, 129.63, 129.17, 128.64, 127.34, 127.12, 125.87, 120.99, 117.23, 114.28, 97.06, 90.53, 34.67, 31.73. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{26}H_{25}NO_3$: 399.1834. Found 399.1836.



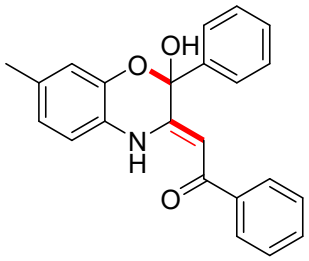

**(*Z*)-2-(6-chloro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3c):** Yellow solid, 27.9 mg, 74 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 231.9-232.4 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.58 (s, 1H), 8.43 (s, 1H), 7.78 – 7.70 (m, 2H), 7.66 (dt, *J* = 5.1, 3.1 Hz, 2H), 7.63-7.60 (m, 1H), 7.60 – 7.54 (m, 1H), 7.50 (dd, *J* = 9.2, 4.7 Hz, 5H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.79 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.14, 153.69, 142.34, 139.58, 139.16, 132.51, 129.78, 129.22, 128.71, 128.11, 127.28, 127.26, 126.64, 123.42, 119.34, 116.81, 97.29, 91.56. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{16}ClNO_3$: 377.0819. Found 377.0821.



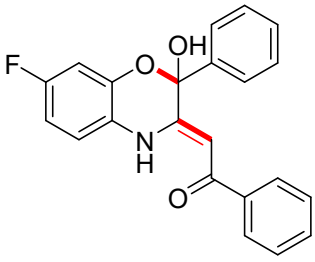

**(*Z*)-2-(6-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3d):** Yellow solid, 30.7 mg, 73 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 244.3-245.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.53 (s, 1H), 8.39 (s, 1H), 7.75 – 7.66 (m, 3H), 7.66 – 7.59 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (dd, *J* = 10.1, 4.7 Hz, 5H), 7.13 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 5.76 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.10, 153.64, 142.79, 139.57, 139.16, 132.51, 129.78, 129.22, 128.71, 128.49, 127.28, 127.26, 126.31, 119.78, 119.58, 114.29, 97.26, 91.58. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{16}BrNO_3$: 421.0314. Found 421.0316.



**(*Z*)-2-(2-hydroxy-6-methoxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3e):** Yellow solid, 28.0 mg, 75 % yield (eluent: ethyl acetate/petroleum ether = 1:50) , m.p. 233.7-234.5 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.67 (s, 1H), 8.18 (s, 1H), 7.74 – 7.67 (m, 2H), 7.62 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.53 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.49 – 7.38 (m, 5H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.55 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.75 (s, 1H), 3.73 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.89, 155.23, 154.63, 140.00, 139.34, 137.27, 132.33, 129.60, 129.19, 128.62, 127.29, 127.18, 127.03, 118.36, 109.67, 102.52, 97.00, 90.80, 55.95. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{23}H_{19}NO_4$: 373.1314. Found 373.1317.

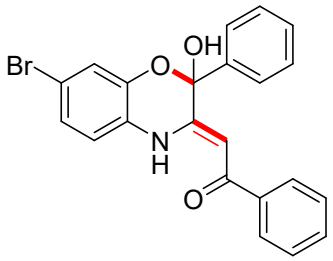


**(*Z*)-2-(2-hydroxy-7-methyl-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3f):** Yellow solid, 28.9 mg, 81 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 189.6-190.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.81 (s, 1H), 8.27 (s, 1H), 7.74 – 7.67 (m, 2H), 7.66 – 7.59 (m, 2H), 7.52 (ddd, *J* = 6.3, 3.6, 1.3 Hz, 1H), 7.49 – 7.39 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.81 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.73 (s, 1H), 2.26 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 189.92, 154.77, 141.38, 139.97, 139.36, 132.29, 132.23, 129.62, 129.17, 128.63, 127.25, 127.18, 126.15, 124.75, 117.64, 117.27, 97.03, 90.57, 20.88. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{23}H_{19}NO_3$: 357.1365. Found 357.1369.



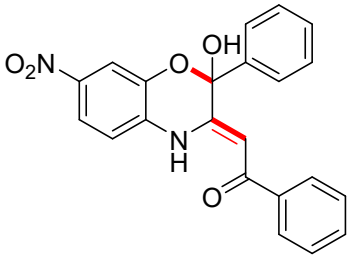
**(*Z*)-2-(7-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one**

**(3g):** Yellow solid, 29.2 mg, 81 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 185.4-186.3 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.78 (s, 1H), 8.48 (s, 1H), 7.74 – 7.67 (m, 2H), 7.68 – 7.59 (m, 2H), 7.54 – 7.40 (m, 7H), 7.03 – 6.97 (m, 1H), 6.87 (td, *J* = 8.7, 2.8 Hz, 1H), 5.72 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 189.83, 159.52 (d, *J* = 240.543 Hz), 157.92 (d, *J* = 240.543 Hz), 154.05, 144.41 (d, *J* = 12.533 Hz), 144.33 (d, *J* = 12.533 Hz), 139.56, 139.29, 132.31, 129.79, 129.17, 128.71, 127.28, 127.16, 123.48 (d, *J* = 2.114 Hz), 123.46 (d, *J* = 2.114 Hz), 117.95 (d, *J* = 9.664 Hz), 117.89 (d, *J* = 9.664 Hz), 109.72 (d, *J* = 23.103 Hz), 109.57 (d, *J* = 23.103 Hz), 105.80 (d, *J* = 25.67 Hz), 105.63 (d, *J* = 25.67 Hz), 97.51, 90.55. $^{19}$F NMR (565 MHz, DMSO) δ -117.68 – -117.79 (m). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{16}FNO_3$: 361.1114. Found 361.1088.




**(*Z*)-2-(7-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one**

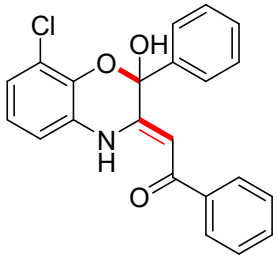
**(3h):** Yellow solid, 28.6 mg, 68 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 245.7-246.3 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.64 (s, 1H), 8.44 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.60 (m, 2H), 7.56 – 7.52 (m, 1H), 7.50 – 7.44 (m, 5H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 7.20 – 7.15 (m, 1H), 5.74 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.04, 153.80, 144.44, 139.48, 139.18, 132.47, 129.83, 129.22, 128.74, 127.27, 127.22, 126.35, 125.86, 120.66, 118.70, 114.88, 97.46, 91.24. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{16}BrNO_3$: 421.0314. Found 421.0311.



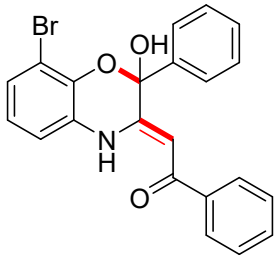

**(*Z*)-2-(2-hydroxy-7-nitro-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one**

**(3i):** Yellow solid, 25.2 mg, 65 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 213.2-214.1 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.57 (s, 1H), 8.64 (s, 1H), 7.98 – 7.87 (m, 1H), 7.84 (d, *J* = 2.2 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 3H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.53 – 7.43 (m, 5H), 5.85

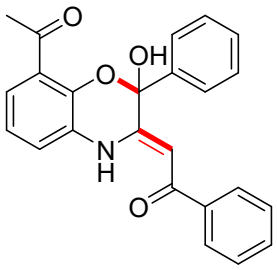
(s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.75, 152.46, 142.98, 142.57, 139.06, 138.81, 133.53, 132.95, 130.02, 129.33, 128.85, 127.44, 127.36, 119.43, 117.06, 113.34, 97.64, 93.53. HRMS (EI): *m/z* [M$^+$]Calcd. for $C_{22}H_{16}N_2O_5$: 388.1059. Found 388.1063.




**(*Z*)-2-(8-chloro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3j):** Yellow solid, 28.3 mg, 75 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 99.2-100.3 °C. $^1$H NMR (400 MHz, DMSO) δ 12.63 (s, 1H), 8.60 (s, 1H), 7.82 – 7.71 (m, 2H), 7.66 – 7.59 (m, 2H), 7.59 – 7.52 (m, 1H), 7.52 – 7.41 (m, 5H), 7.33 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 5.94 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.27, 153.68, 139.63, 139.28, 139.13, 132.57, 129.91, 129.25, 128.80, 128.28, 127.35, 127.05, 124.22, 123.51, 121.65, 115.89, 98.18, 91.26. HRMS (EI): *m/z* [M$^+$]Calcd. for $C_{22}H_{16}ClNO_3$: 377.0819. Found 377.0816.

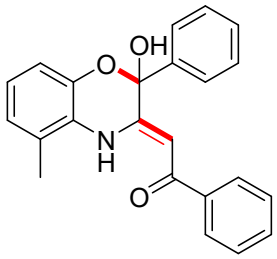



**(*Z*)-2-(8-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3k):** Yellow solid, 29.0 mg, 69 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 103.8-104.5 °C. $^1$H NMR (400 MHz, DMSO) δ 12.62 (s, 1H), 8.59 (s, 1H), 7.84 – 7.75 (m, 2H), 7.67 – 7.60 (m, 2H), 7.58 – 7.54 (m, 1H), 7.53 – 7.48 (m, 2H), 7.48 – 7.42 (m, 3H), 7.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.23 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 5.98 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 190.25, 153.68, 140.68, 139.29, 139.14, 132.57, 129.89, 129.25, 128.78, 128.20, 127.37, 127.08, 127.06, 124.10, 116.50, 110.96, 98.32, 91.18. HRMS (EI): *m/z* [M$^+$]Calcd. for $C_{22}H_{16}BrNO_3$: 421.0314. Found 421.0318.



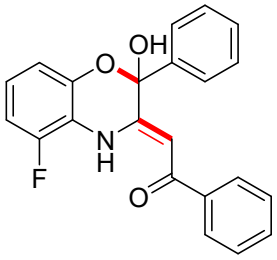
**(*Z*)-2-(8-acetyl-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one**

**(3l):** Red solid, 27.4 mg, 71 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 72.3-72.8 °C. $^{1}$H NMR (400 MHz, DMSO) δ 12.75 (s, 1H), 8.54 (s, 1H), 7.74 – 7.69 (m, 2H), 7.69 – 7.65 (m, 2H), 7.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 – 7.43 (m, 6H), 7.37 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 5.62 (s, 1H), 2.56 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 197.69, 190.11, 153.88, 143.27, 139.39, 139.15, 132.46, 129.92, 129.21, 128.84, 128.55, 127.74, 127.27, 127.17, 123.92, 122.73, 121.01, 97.55, 90.74, 32.39. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{24}H_{19}NO_4$: 385.1314. Found 386.1351.



**(Z)-2-(2-hydroxy-5-methyl-2-phenyl-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)-1-phenylethan-1-one**

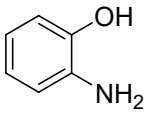
**(3m):** Yellow solid, 23.9 mg, 67 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 240.4-241.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 13.23 (s, 1H), 8.30 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.67 – 7.58 (m, 2H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.52 – 7.40 (m, 5H), 6.93 (dt, *J* = 10.1, 5.0 Hz, 3H), 5.72 (s, 1H), 2.38 (s, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 190.25, 155.12, 143.43, 139.85, 139.21, 132.35, 129.69, 129.20, 128.68, 127.28, 127.20, 124.83, 124.38, 123.85, 115.90, 96.71, 90.61, 16.52. HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{23}H_{19}NO_3$: 357.1365. Found 357.1370.



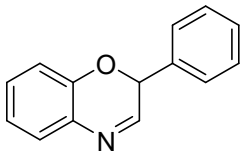
***Z*-2-(5-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one**

**(3n):** Yellow solid, 22.0 mg, 61 % yield (eluent: ethyl acetate/petroleum ether = 1:25), m.p. 216.2-216.7

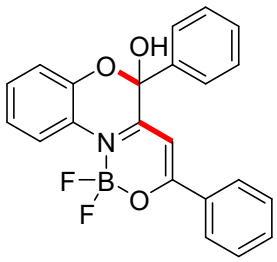
°C. $^{1}$H NMR (400 MHz, DMSO) δ 13.09 (s, 1H), 8.59 (s, 1H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.67 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.52 – 7.44 (m, 5H), 7.10 – 7.01 (m, 2H), 6.98 (dd, *J* = 9.1, 5.0 Hz, 1H), 5.79 (s, 1H). $^{13}$C NMR (101 MHz, DMSO) δ 190.83, 153.89, 151.69 (d, *J* = 244.1 Hz), 149.27 (d, *J* = 244.1 Hz), 144.92 (d, *J* = 4.0 Hz), 144.88 (d, *J* = 4.0 Hz), 139.35, 138.90, 132.69, 129.92, 129.28, 128.78, 127.34, 123.66 (d, *J* = 8.9 Hz), 123.57 (d, *J* = 8.9 Hz), 115.74 (d, *J* = 14.8 Hz), 115.59 (d, *J* = 14.8 Hz), 114.22, 109.74 (d, *J* = 17.5 Hz), 109.56 (d, *J* = 17.5 Hz), 97.46, 91.72. $^{19}$F NMR (565 MHz, DMSO) δ -134.11 – -134.98 (m). HRMS(ESI+): Calculated for $C_{22}H_{16}FNO_3$, $[M+H]^+$ 362.1187. Found 362.1212.




**2-aminophenol (E):** Red brown solid, 0.15 g, 56 % yield (eluent: ethyl acetate/petroleum ether = 1:5), m.p. 235.4-236.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 8.95 (s, 1H), 6.64 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.56 (dtd, *J* = 8.9, 7.7, 1.5 Hz, 2H), 6.39 (td, *J* = 7.5, 1.8 Hz, 1H), 4.48 (s, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 144.43, 136.99, 119.95, 116.86, 114.87, 114.80. HRMS (EI): *m/z* $[M^+]$Calcd. for $C_6H_7NO$: 109.0528. Found 109.0526.



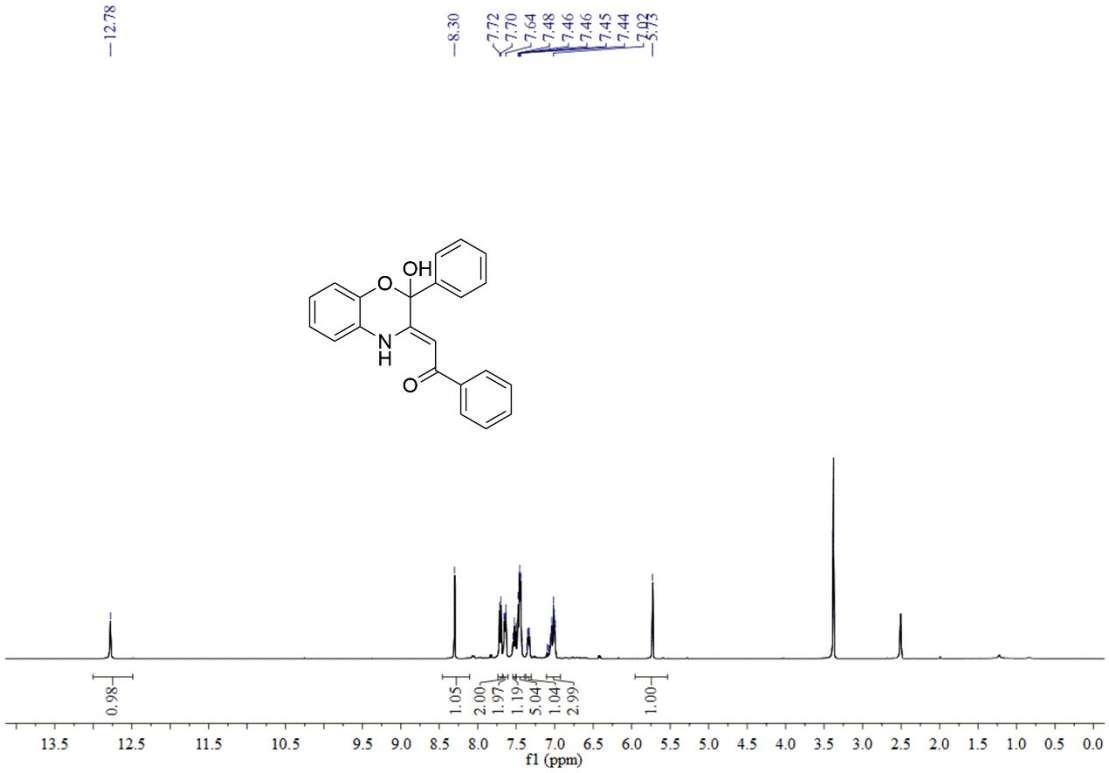

**2-phenyl-2*H*-benzo[b][1,4]oxazine (F):** Yellow solid, 28.4 mg, 68 % yield (eluent: ethyl acetate/petroleum ether = 1:50), m.p. 216.8-217.3 °C. $^{1}$H NMR (400 MHz, DMSO) δ 8.05 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.83 (d, *J* = 6.8 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.27 (td, *J* = 7.7, 1.5 Hz, 1H), 7.16 – 7.00 (m, 2H), 6.41 (d, *J* = 6.8 Hz, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 157.10, 144.37, 135.29, 132.99, 131.45, 129.21, 129.17, 127.90, 127.43, 122.55, 117.24, 84.78. HRMS (EI): *m/z* $[M^+]$Calcd. for $C_{14}H_{11}NO$: 209.0841. Found 209.0838.



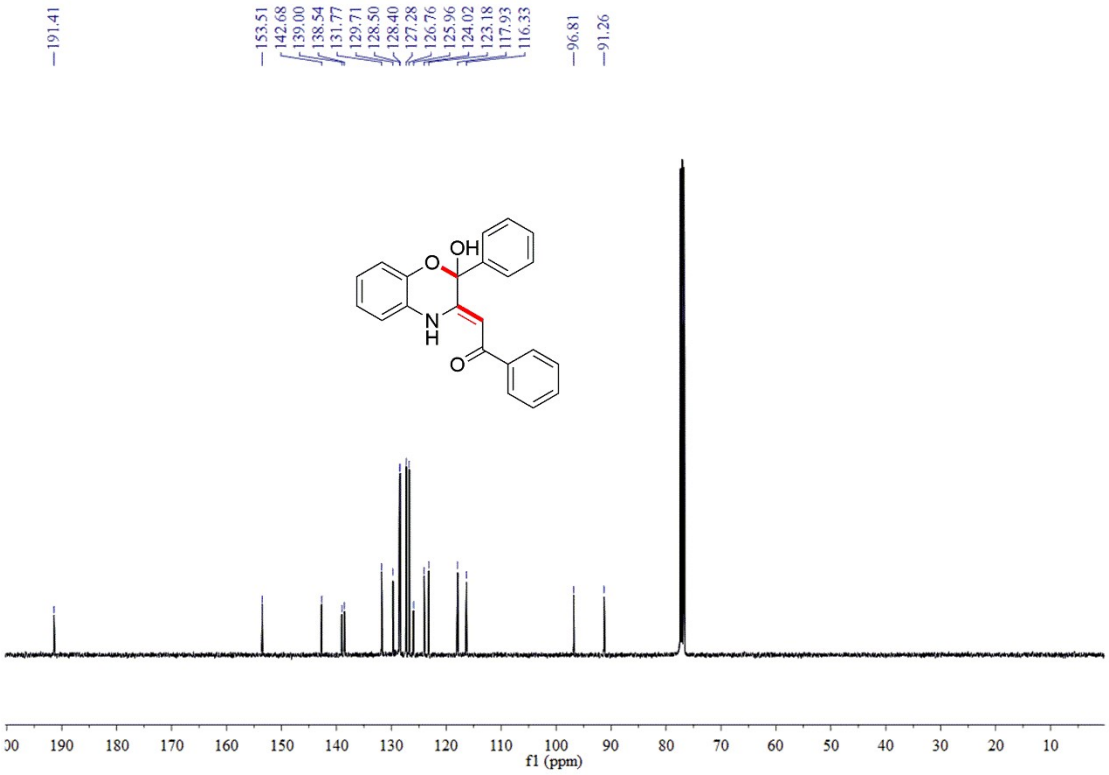
**(*Z*)-3-(2-((difluoroboranyl)oxy)-2-phenylvinyl)-2-phenyl-2*H*-benzo[b][1,4]oxazin-2-ol (4):** Red solid, 49.8 mg, 85 % yield (eluent: ethyl acetate/petroleum ether = 1:50) , m.p. 78.3-79.2 °C. $^{1}$H NMR (400 MHz, DMSO) δ 8.93 (s, 1H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.69 – 7.61 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.19 (ddd, *J* = 15.6, 8.2, 4.1 Hz, 2H), 6.24 (s, 1H). $^{13}$C NMR (151 MHz, DMSO) δ 172.61, 162.26, 145.88, 138.37, 134.16, 132.39, 130.35, 129.81, 129.20, 129.08, 127.73, 127.10, 125.59, 123.40, 121.72 (t, *J* = 4.53 Hz), 121.69 (t, *J* = 4.53 Hz), 121.66 (t, *J* = 4.53 Hz), 118.66, 96.31, 92.30. $^{11}$B NMR (193 MHz, DMSO) δ 1.49 (s). HRMS (EI): *m*/*z* [M$^{+}$]Calcd. for $C_{22}H_{16}BF_2NO_3$: 391.1191. Found 391.1196.

## 4. Copies of NMR Spectra

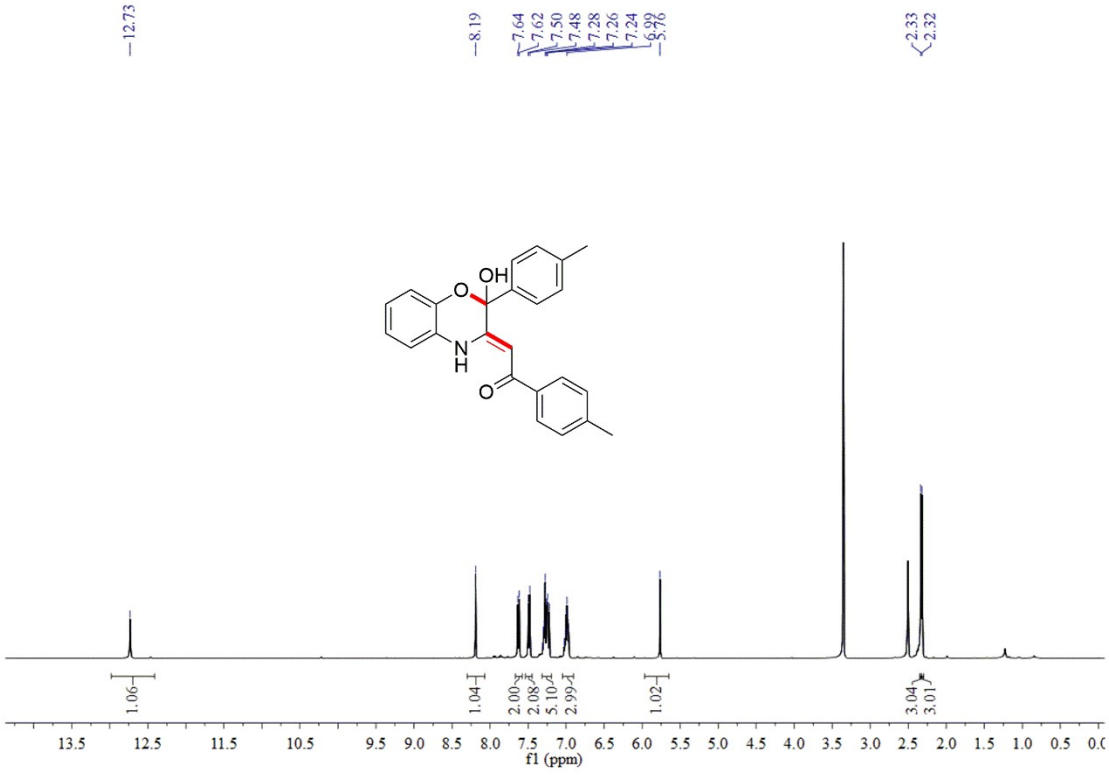
**(*Z*)-2-(2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (2a): $^{1}$H NMR**



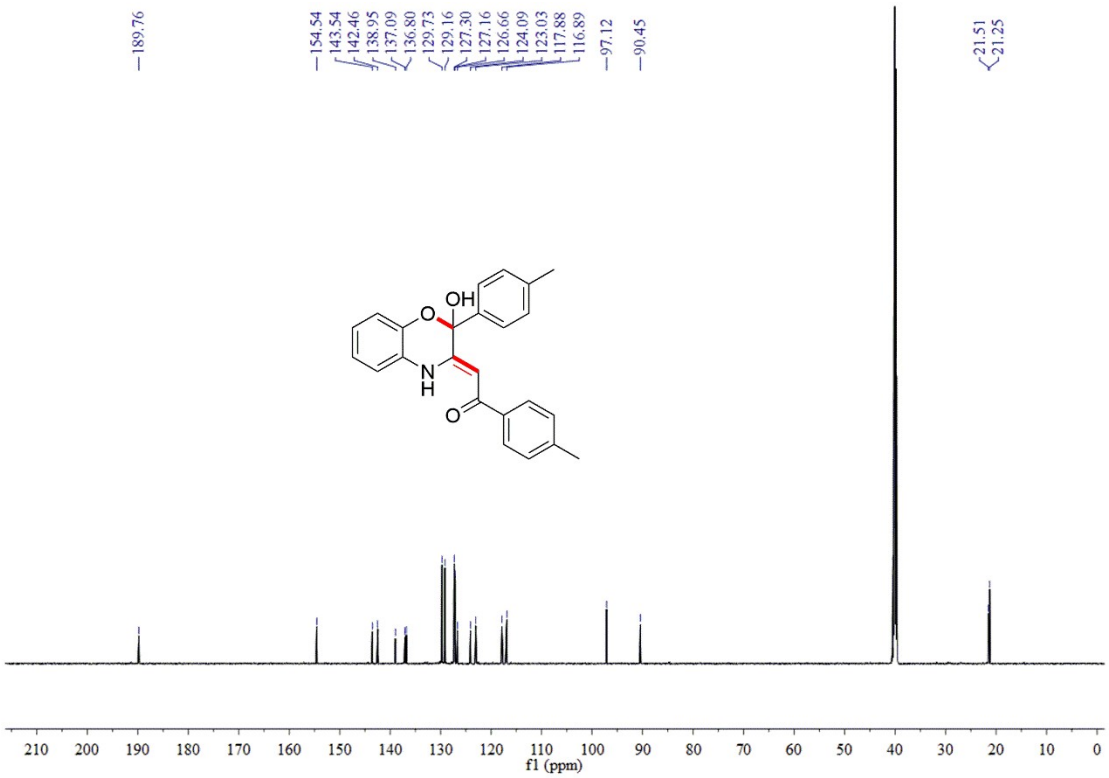
**(*Z*)-2-(2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (2a): $^{13}$C NMR**



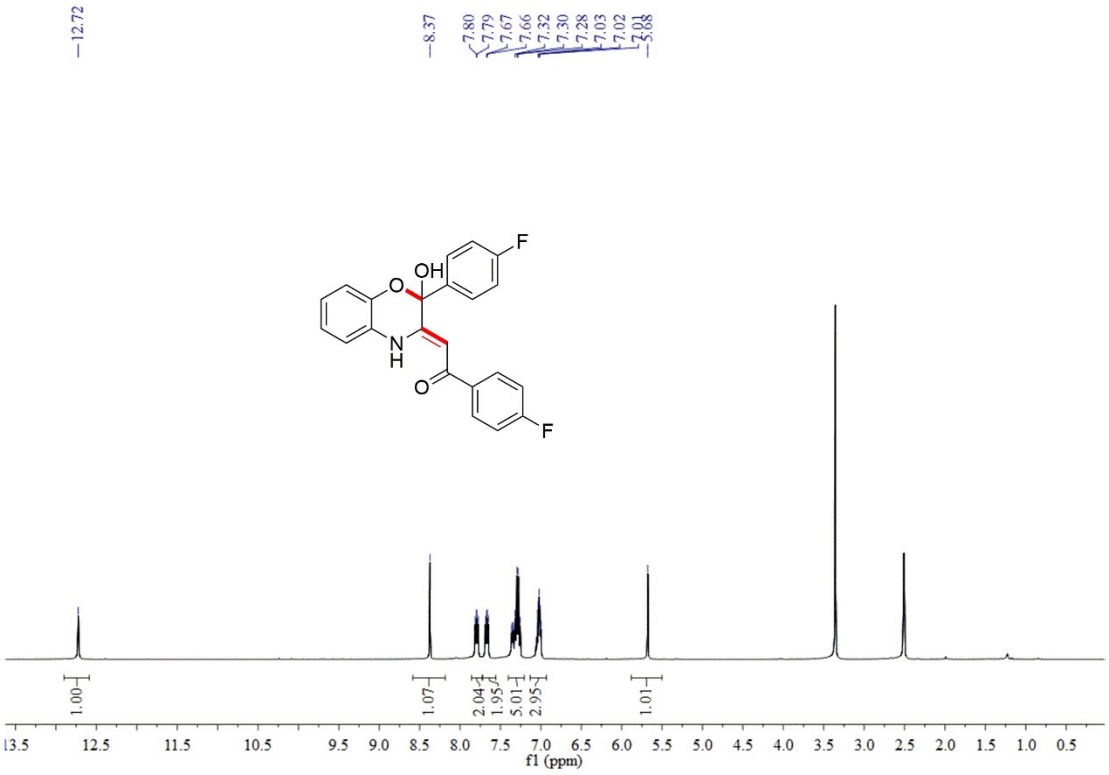

**(*Z*)-2-(2-hydroxy-2-(p-tolyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(p-tolyl)ethan-1-one (2b): $^{1}$H NMR**



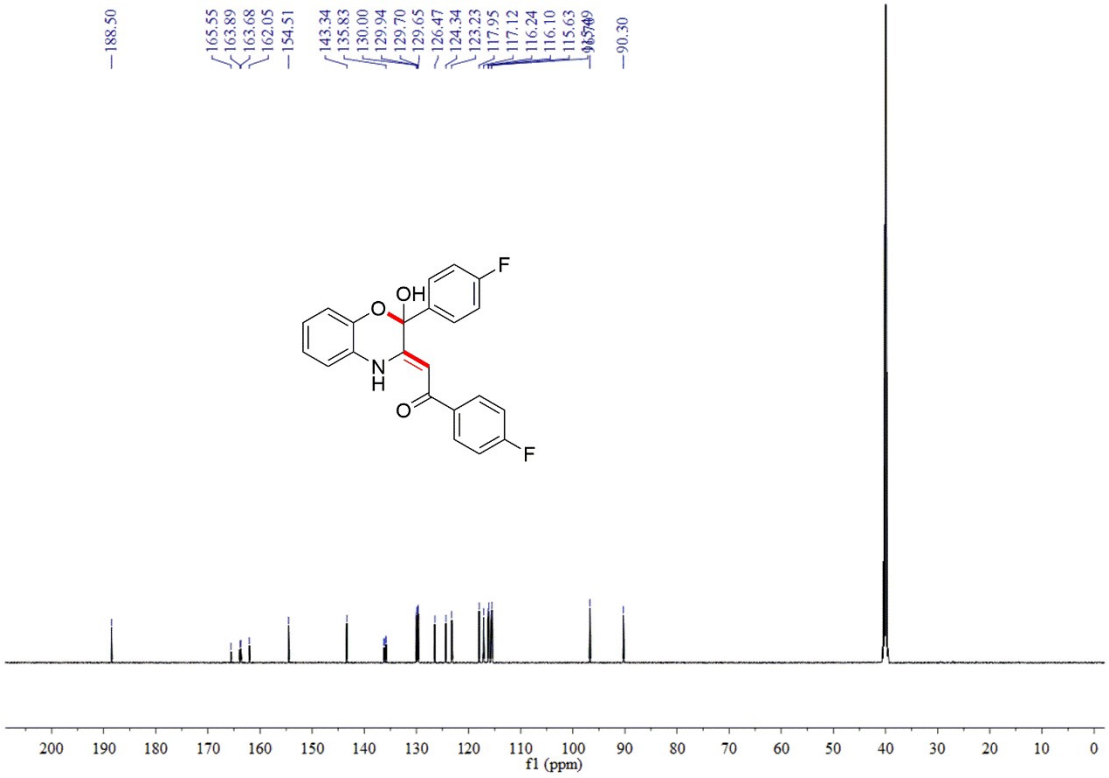
**(*Z*)-2-(2-hydroxy-2-(p-tolyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(p-tolyl)ethan-1-one (2b): $^{13}$C NMR**



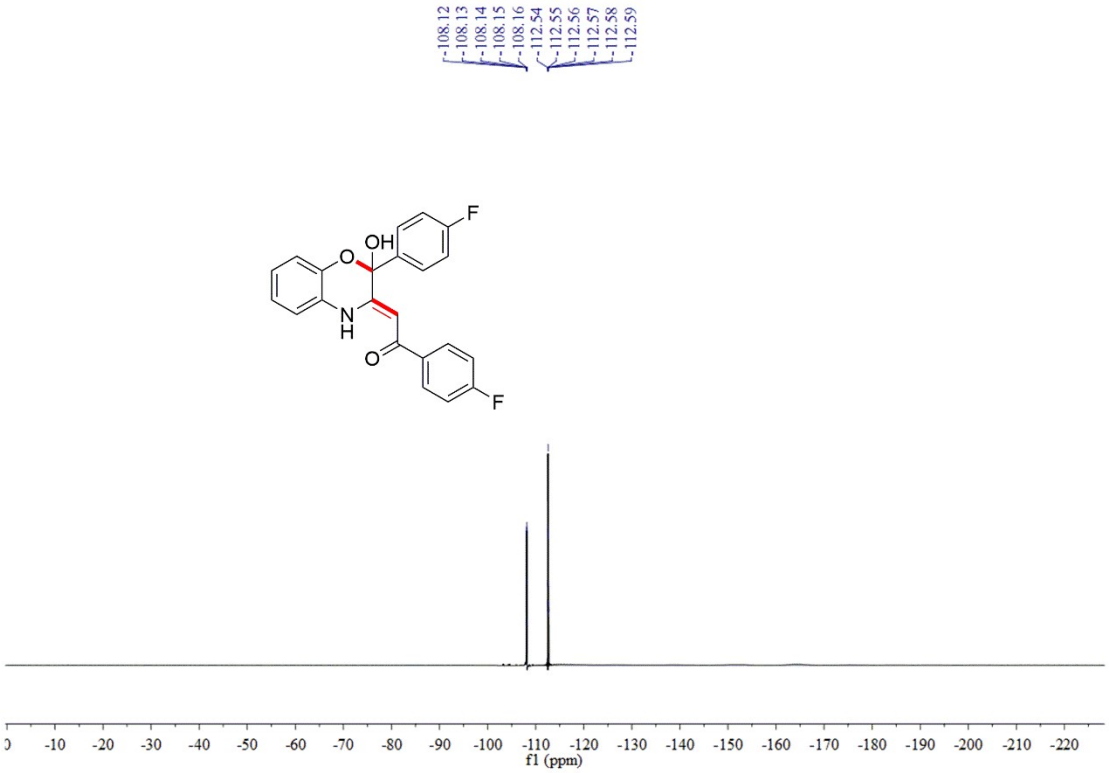

**(*Z*)-1-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2c): $^{1}$H NMR**



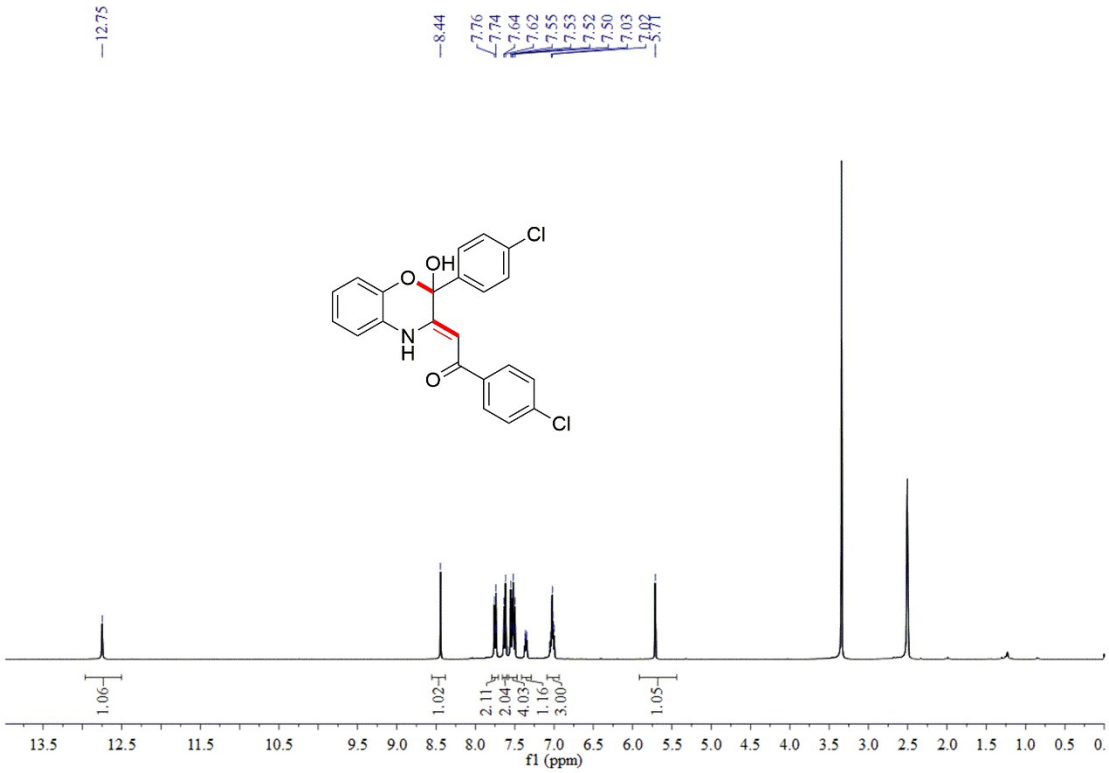
**(*Z*)-1-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2c): $^{13}$C NMR**



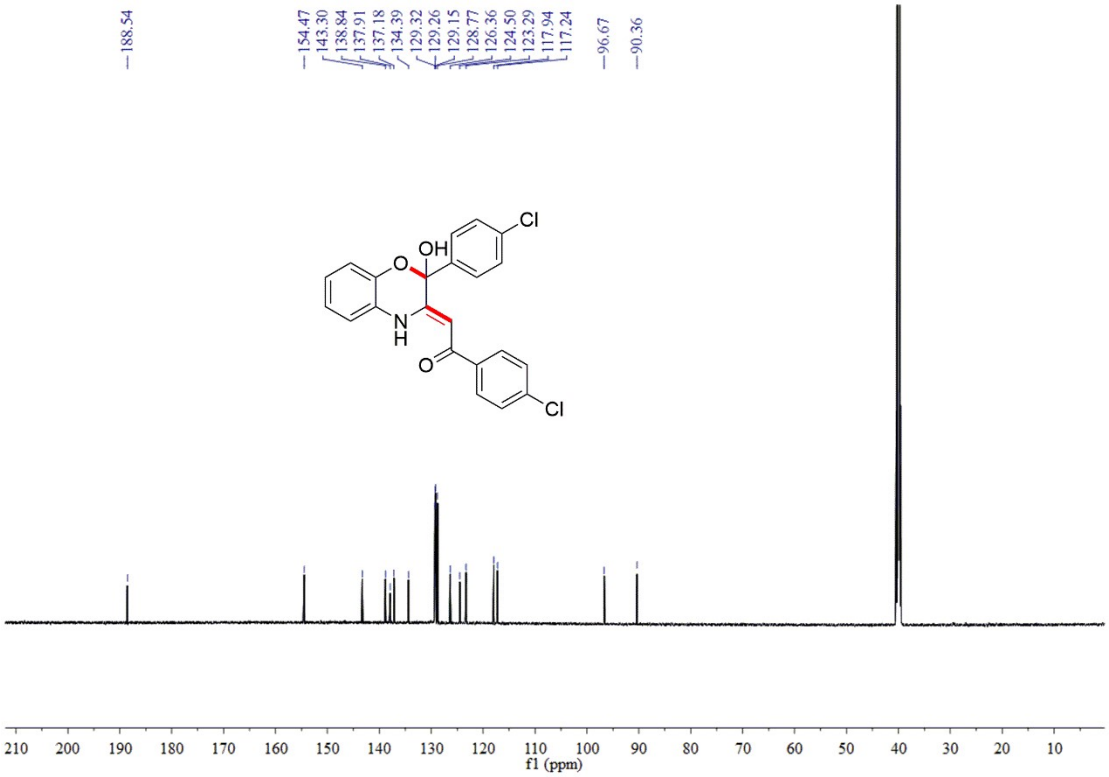

**(*Z*)-1-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2c): $^{19}$F NMR**



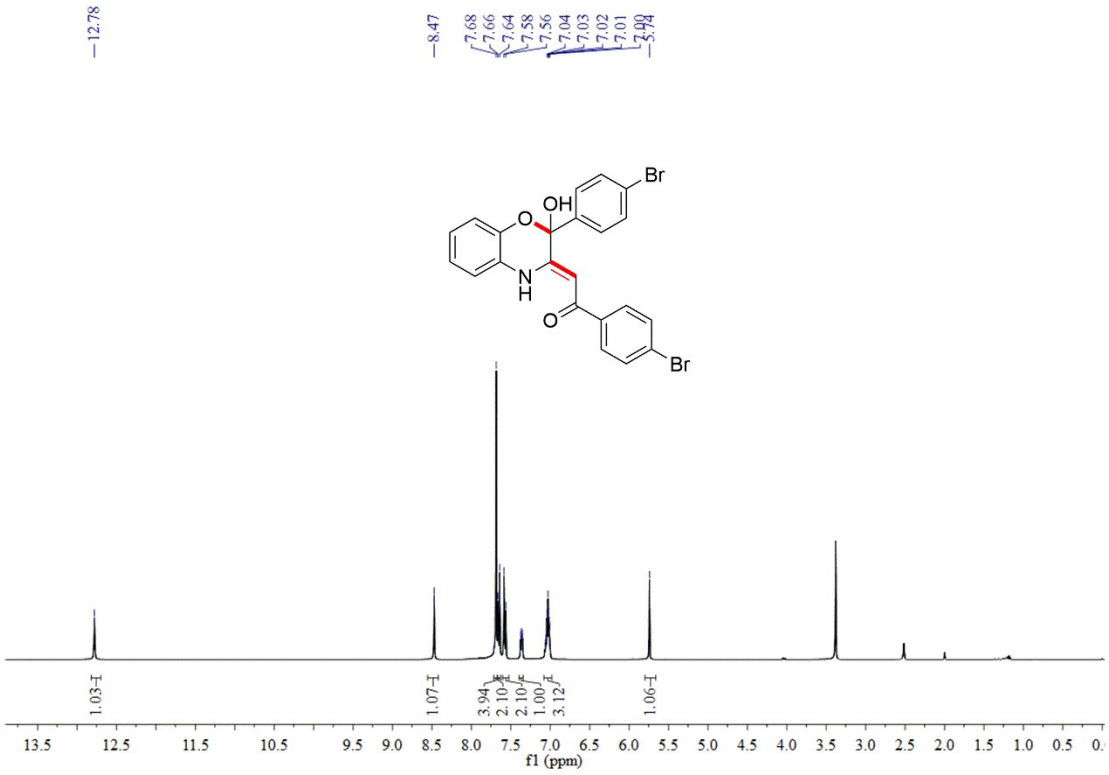
**(*Z*)-1-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2d): $^{1}$H NMR**



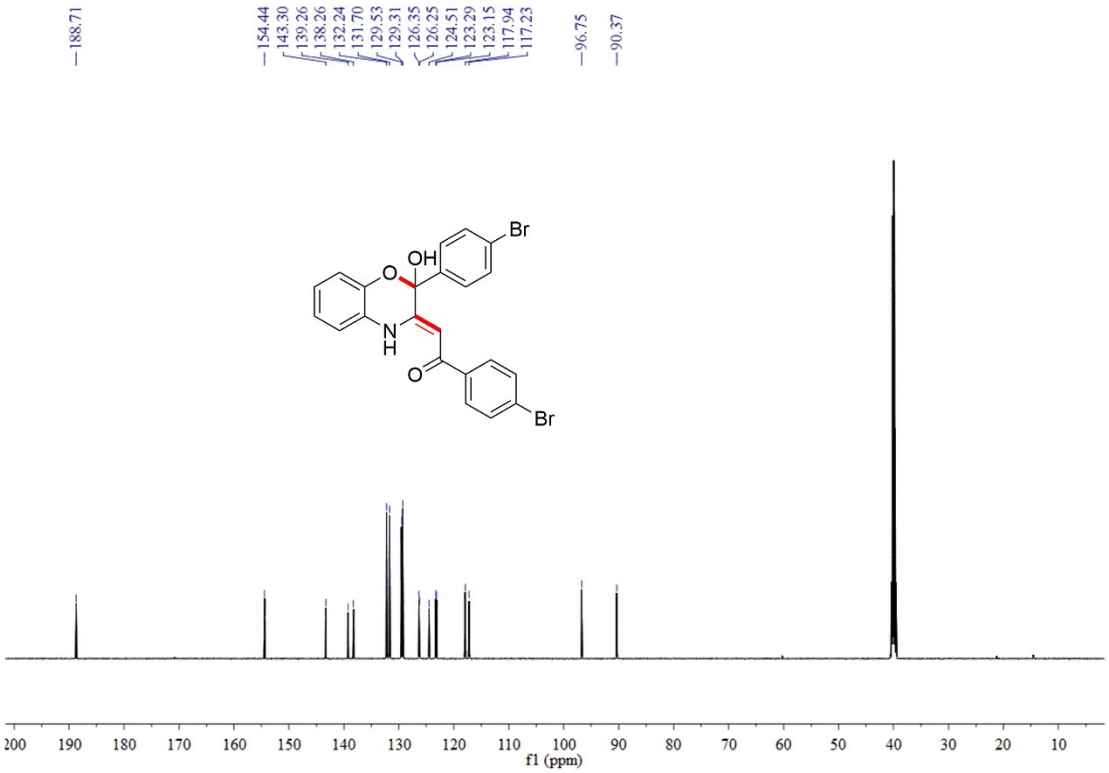

**(*Z*)-1-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2d): $^{13}$C NMR**



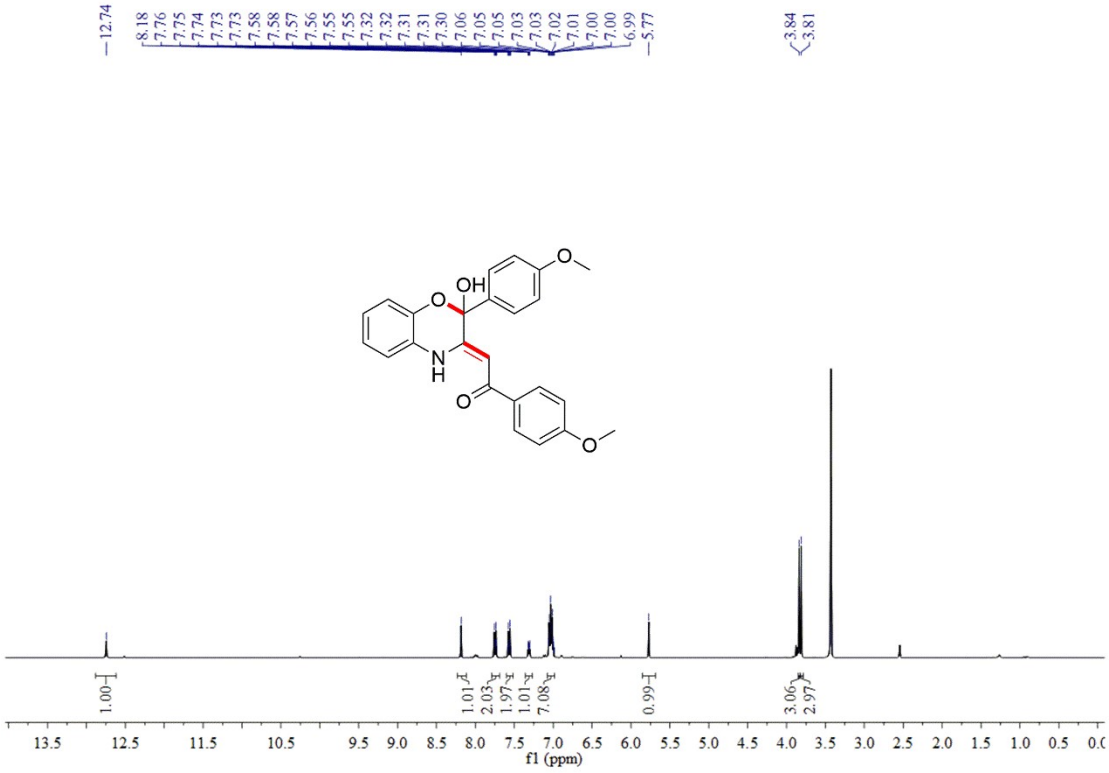
**(*Z*)-1-(4-bromophenyl)-2-(2-(4-bromophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2e): $^{1}$H NMR**



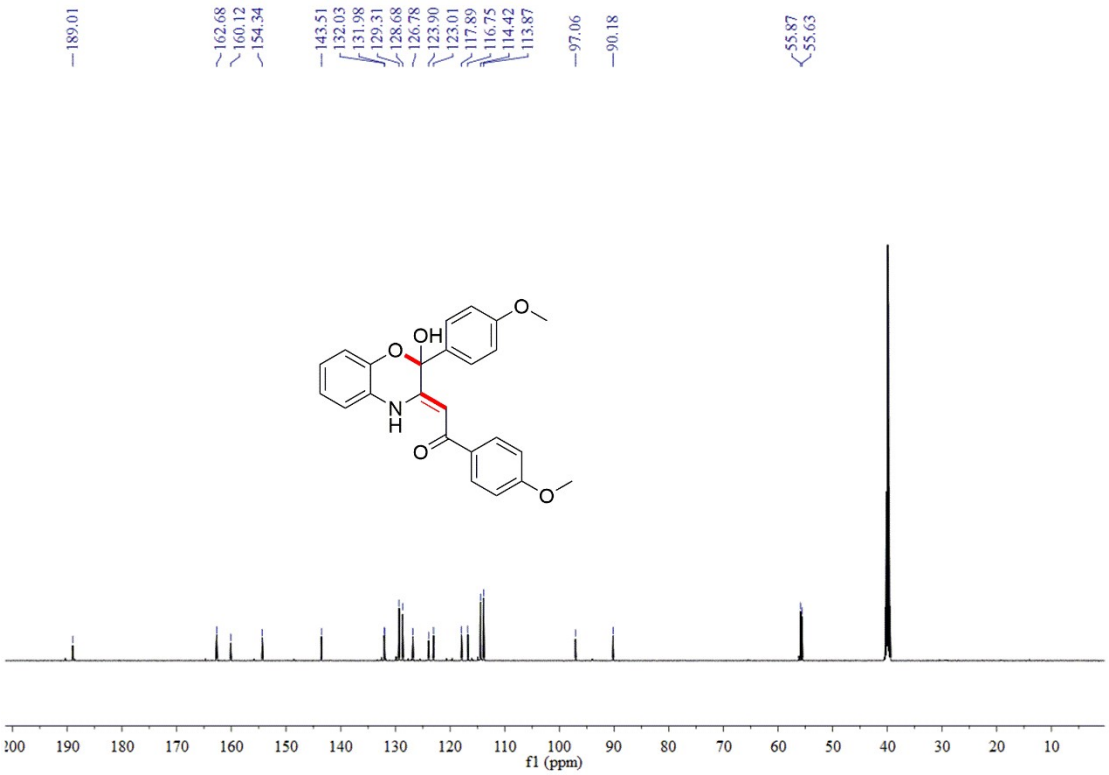

**(*Z*)-1-(4-bromophenyl)-2-(2-(4-bromophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2e): $^{13}$C NMR**



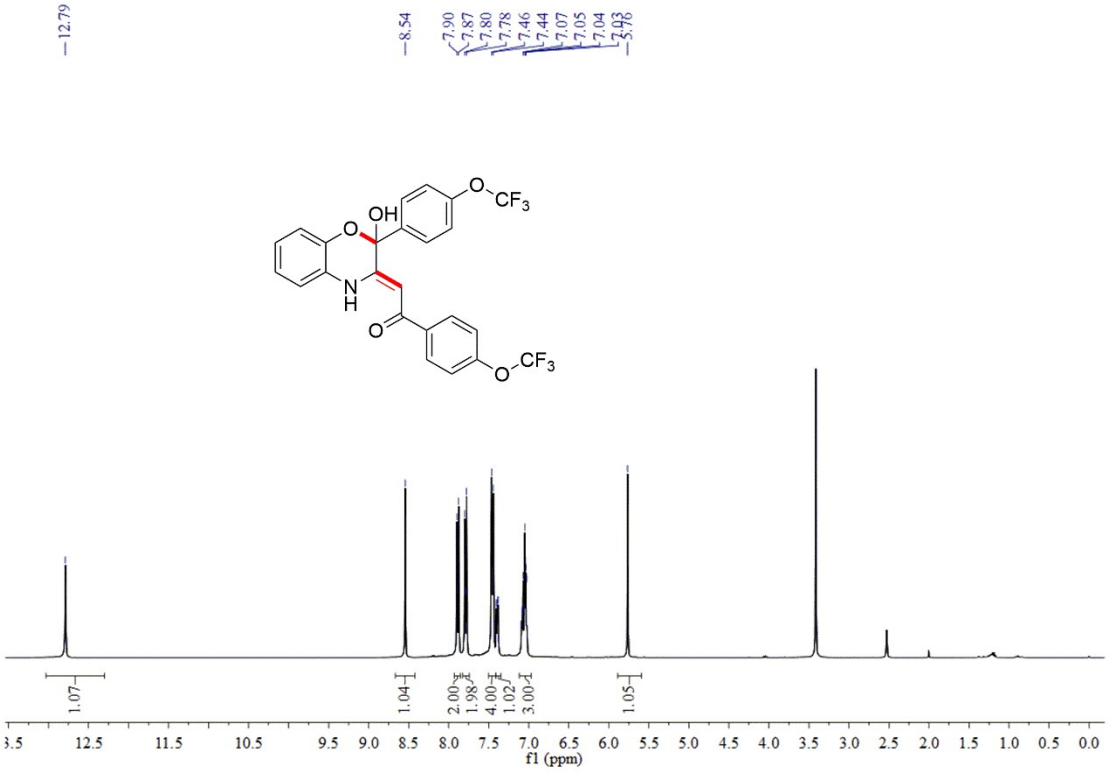
**(*Z*)-2-(2-hydroxy-2-(4-methoxyphenyl)-2H-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-methoxyphenyl)ethan-1-one (2f): $^{1}$H NMR**



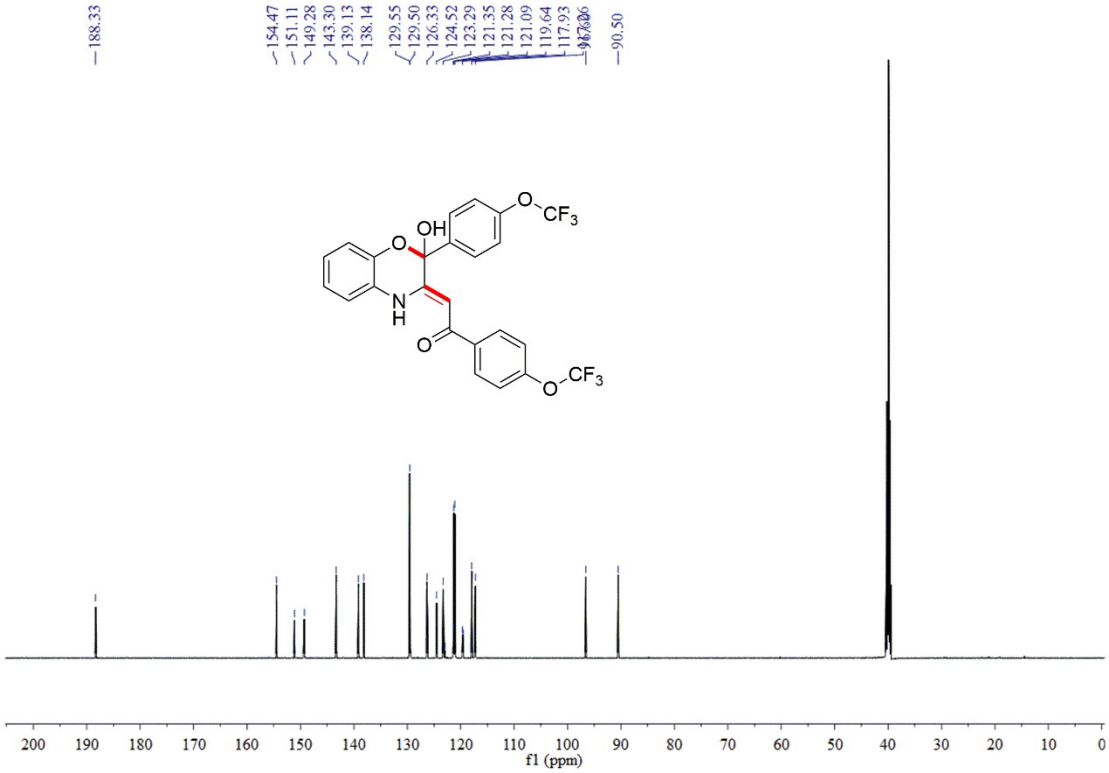

**(*Z*)-2-(2-hydroxy-2-(4-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-methoxyphenyl)ethan-1-one (2f): $^{13}$C NMR**



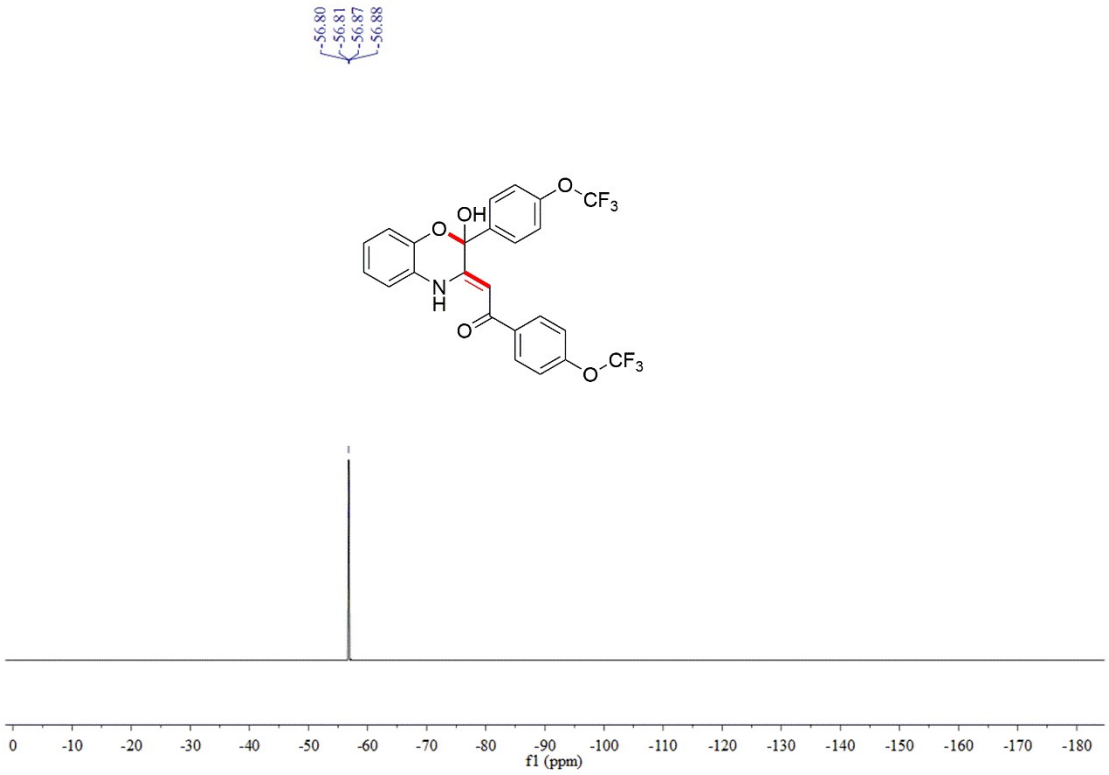
**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethoxy)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one (2g): $^{1}$H NMR**



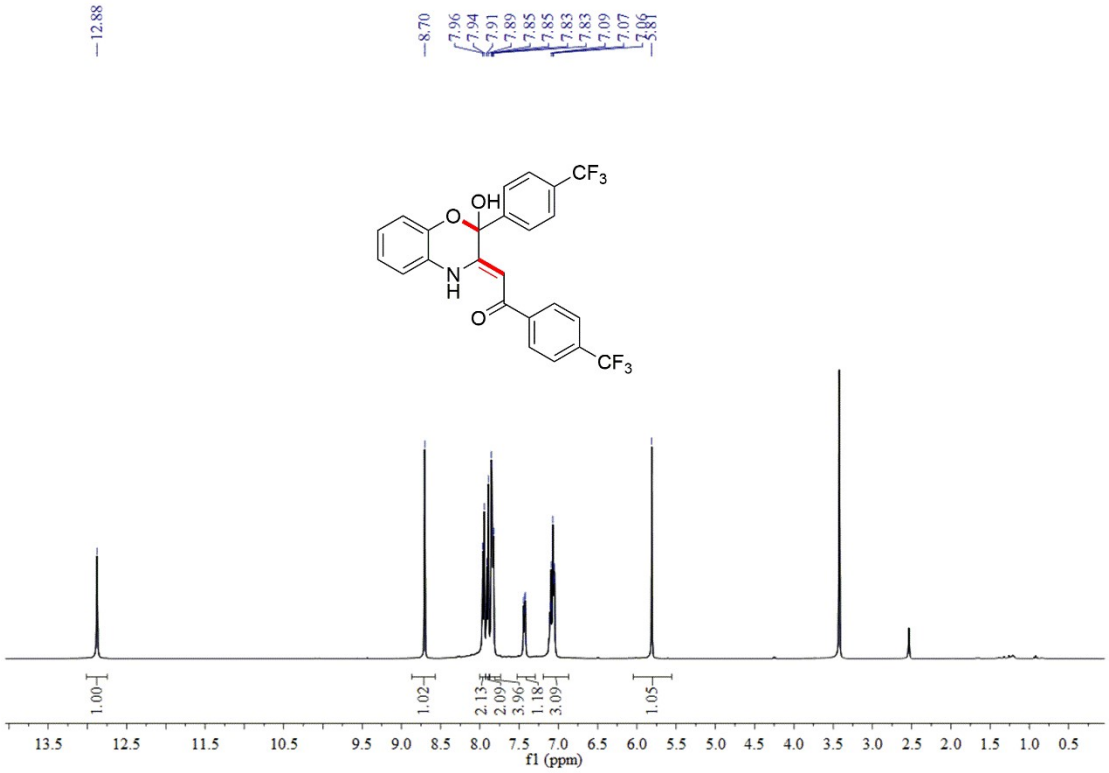

**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethoxy)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one(2g): $^{13}$C NMR**



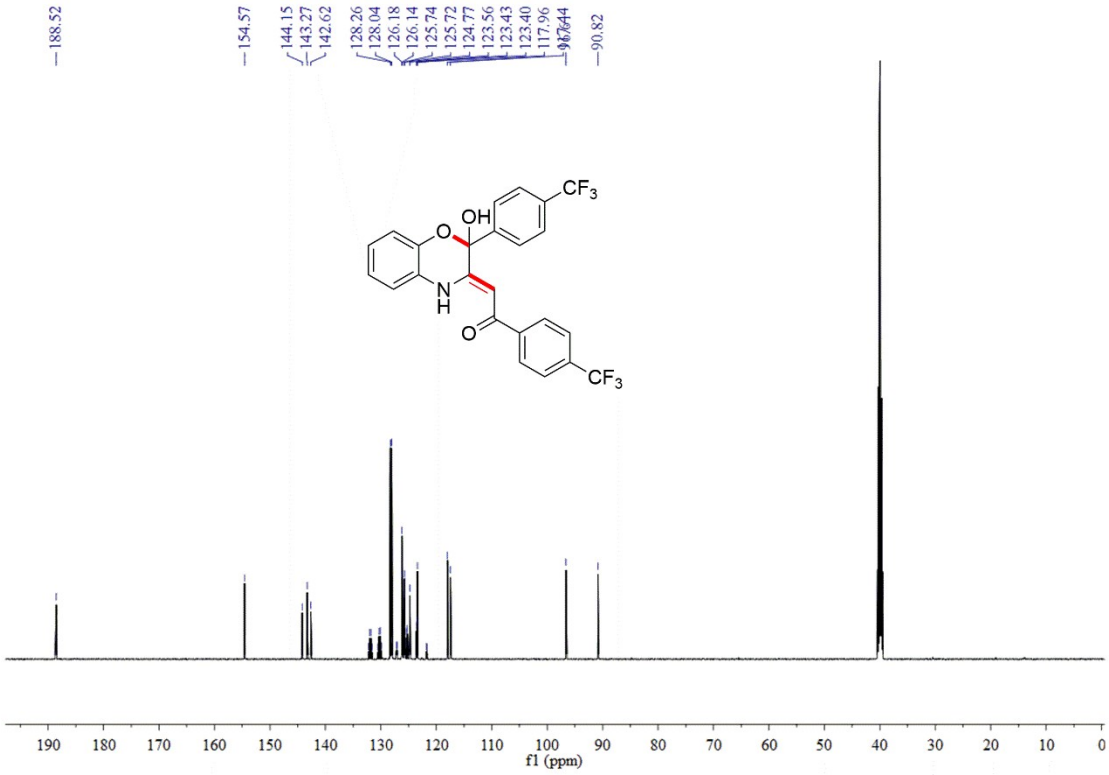
**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethoxy)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one (2g): $^{19}$F NMR**



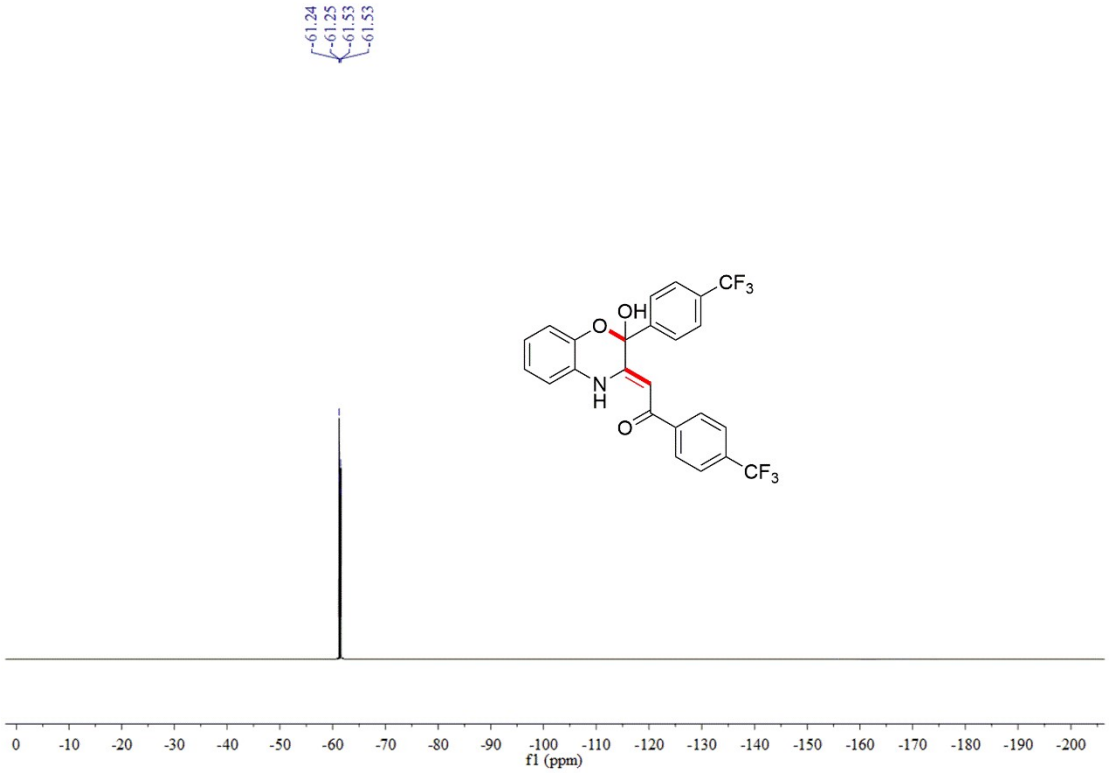

**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (2h): $^{1}$H NMR**



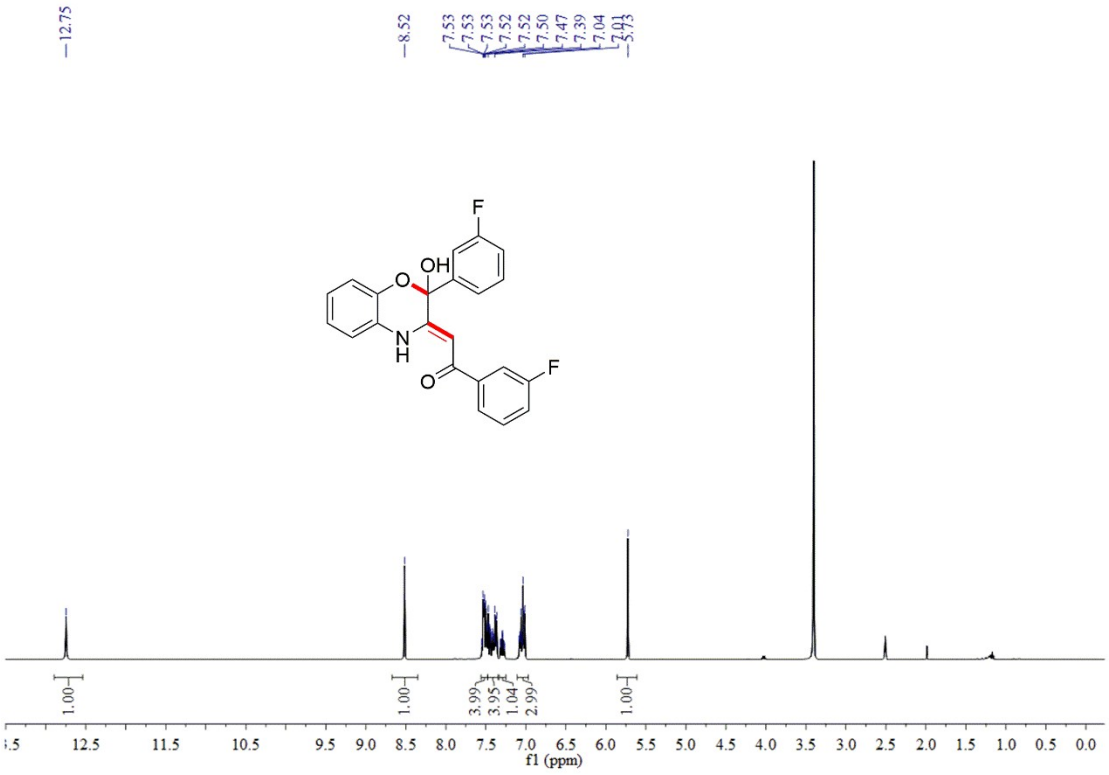
**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (2h): $^{13}$C NMR**



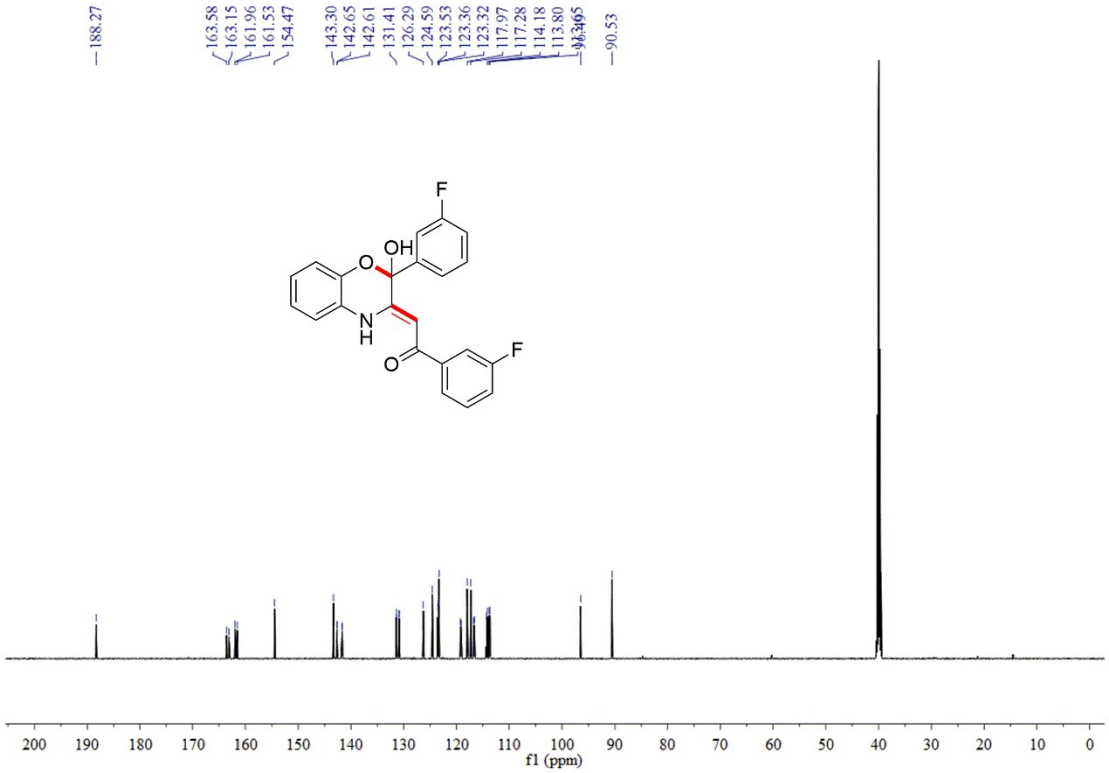

**(*Z*)-2-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (2h): $^{19}$F NMR**



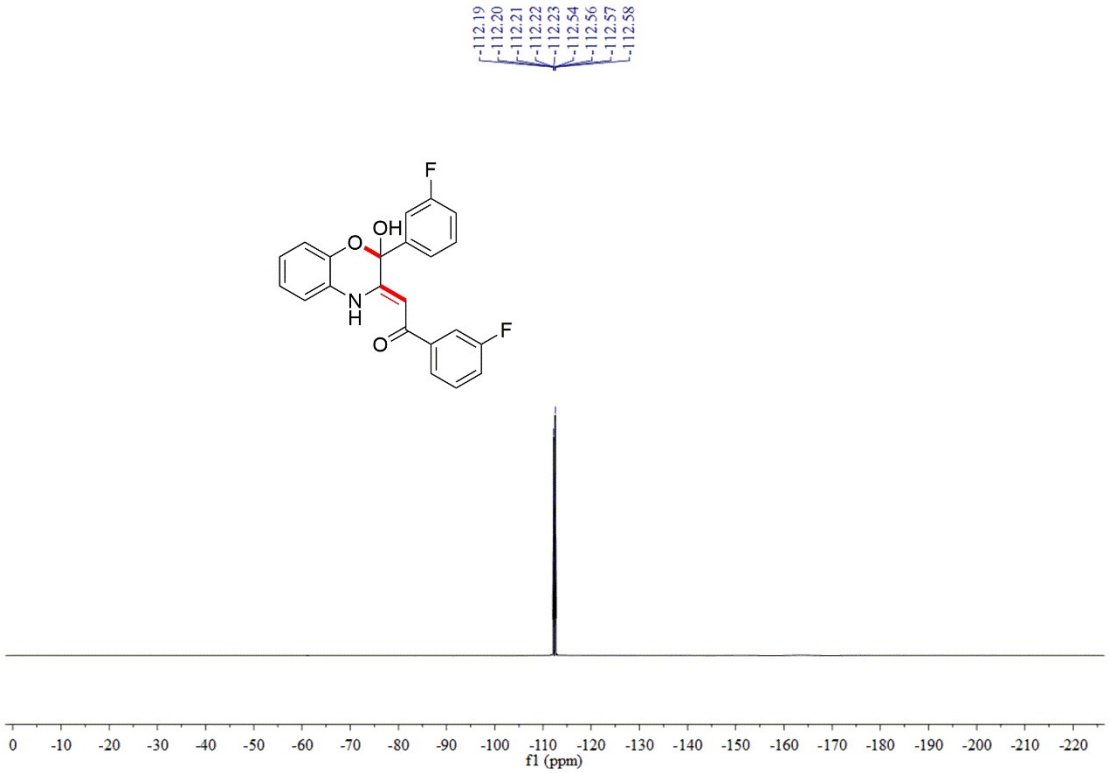
**(*Z*)-1-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2i): $^{1}$H NMR**



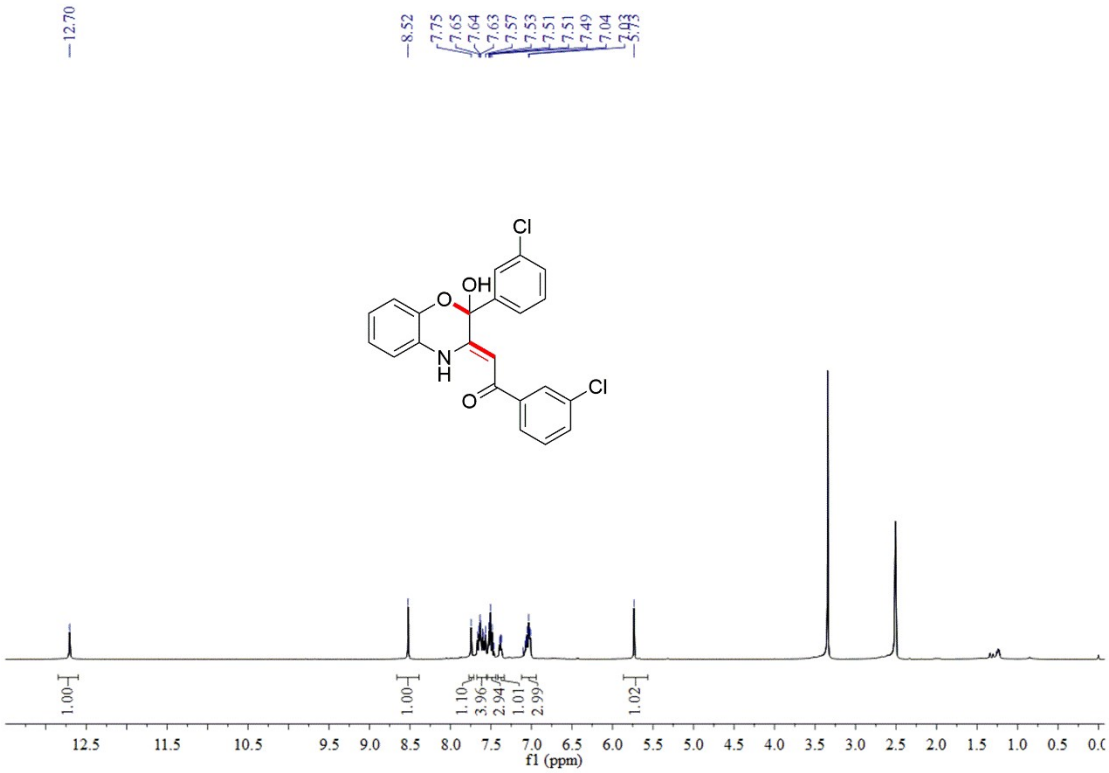

**(*Z*)-1-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2i): $^{13}$C NMR**



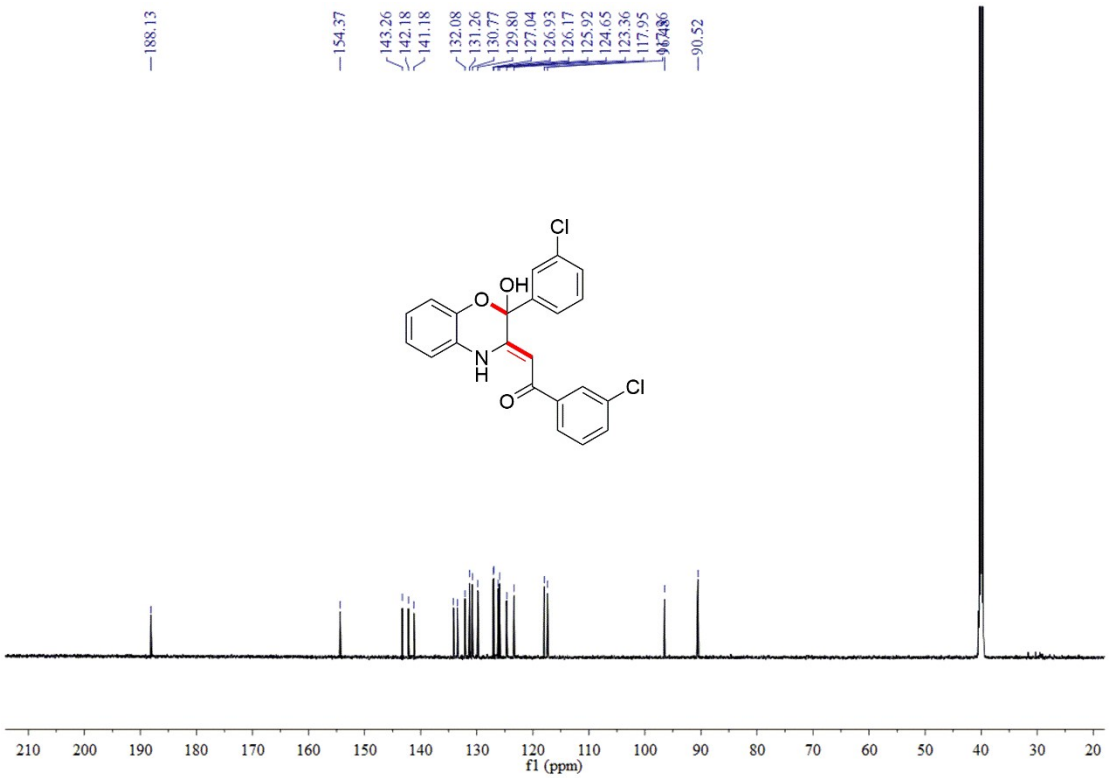
**(*Z*)-1-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one(2i): $^{19}$F NMR**



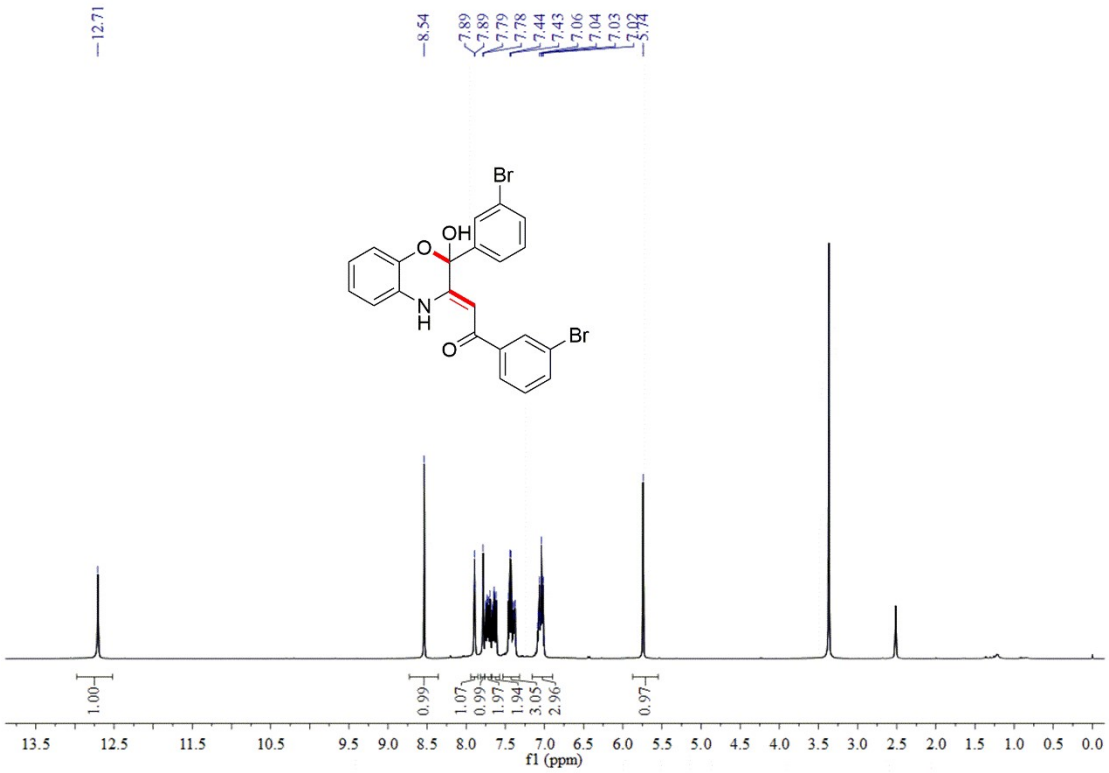

**(*Z*)-1-(3-chlorophenyl)-2-(2-(3-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2j): $^{1}$H NMR**



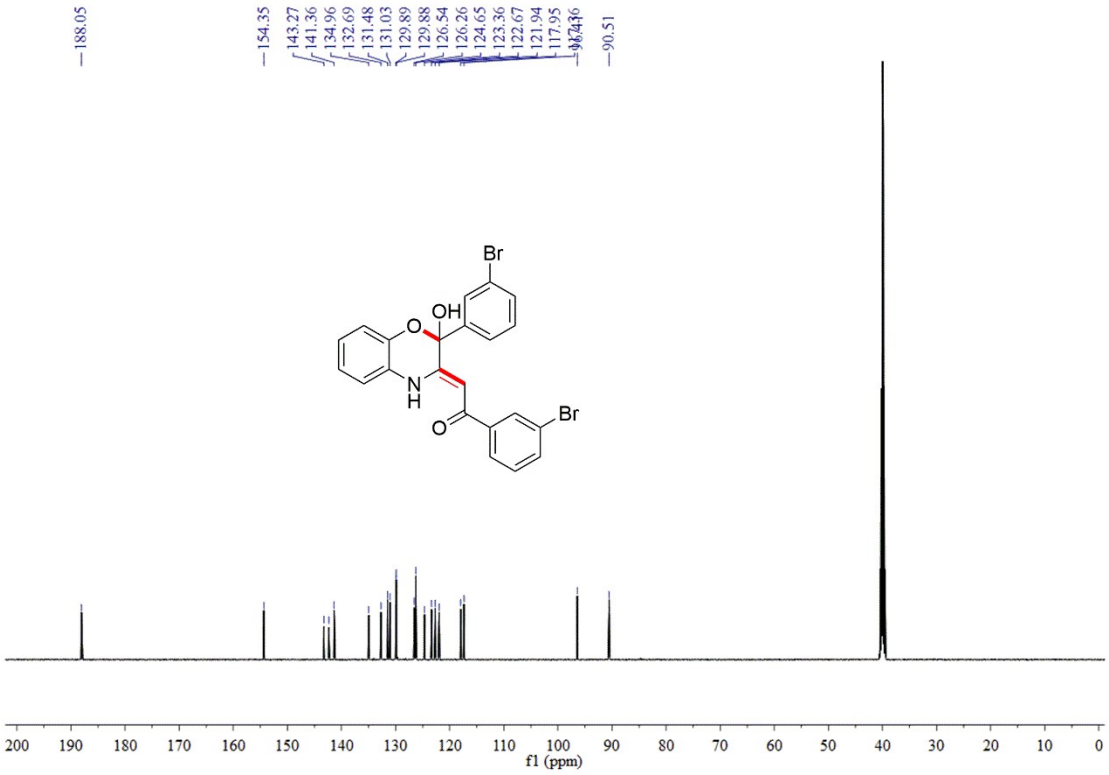
**(*Z*)-1-(3-chlorophenyl)-2-(2-(3-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2j): $^{13}$C NMR**



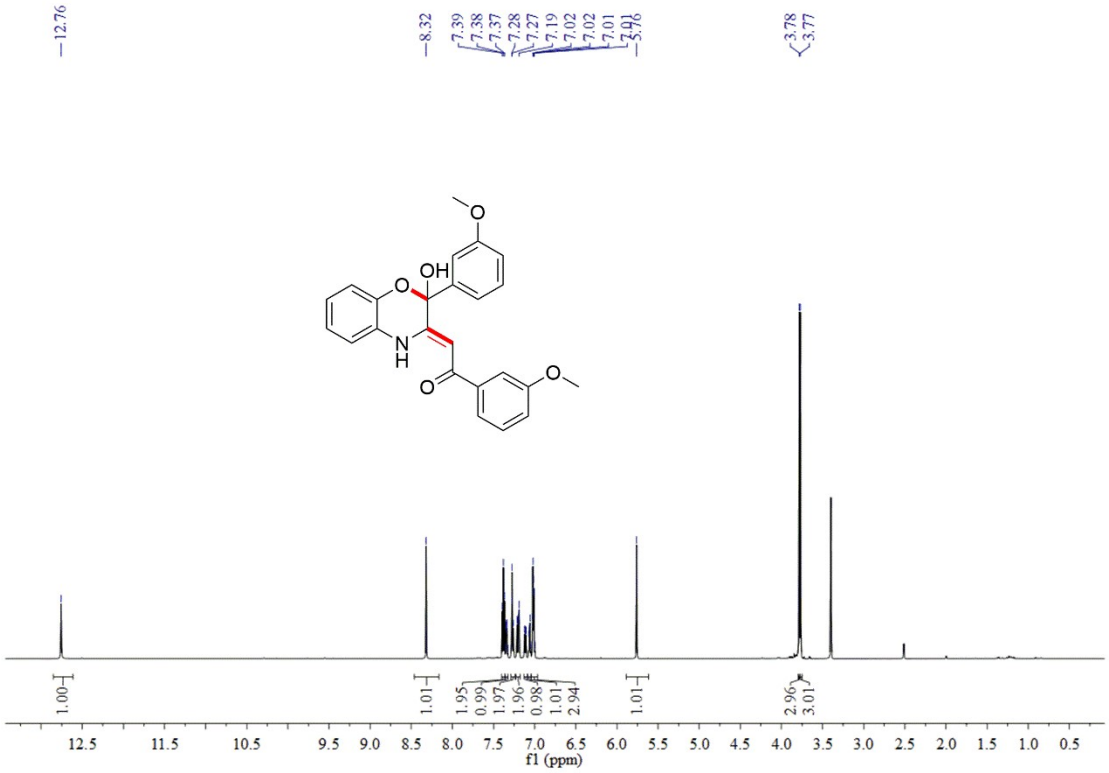

**(*Z*)-1-(3-bromophenyl)-2-(2-(3-bromophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2k): $^{1}$H NMR**



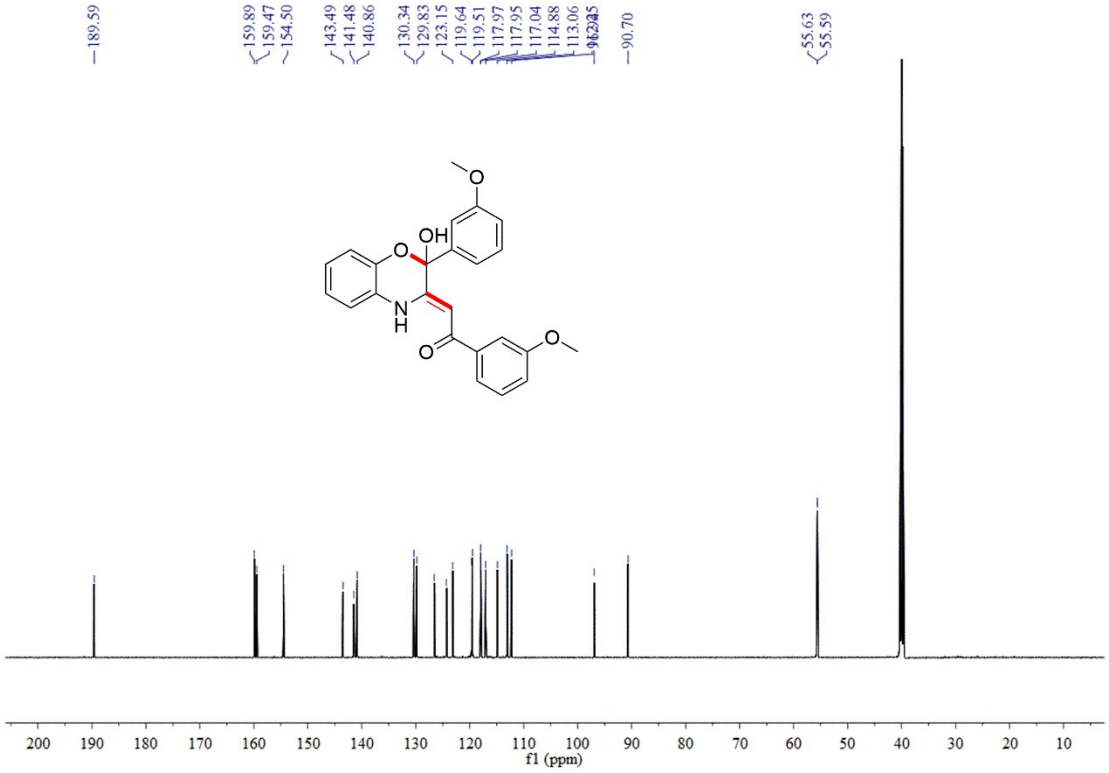
**(*Z*)-1-(3-bromophenyl)-2-(2-(3-bromophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2k): $^{13}$C NMR**



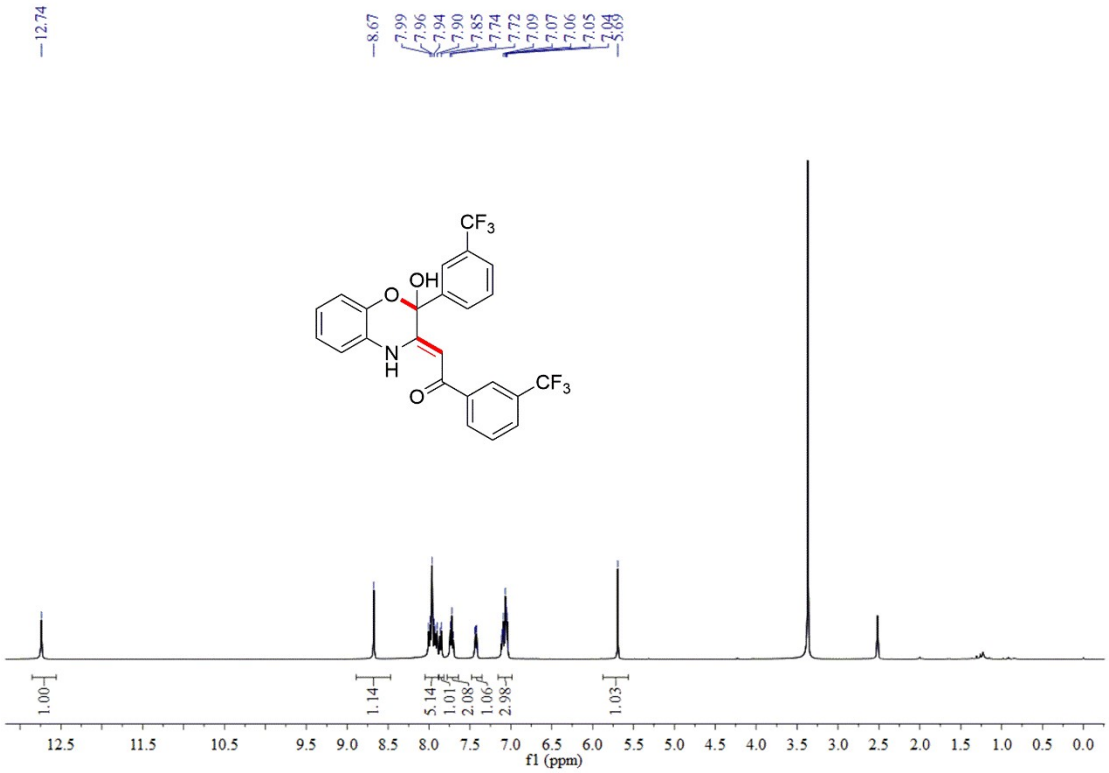

**(*Z*)-2-(2-hydroxy-2-(3-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-methoxyphenyl)ethan-1-one (2l): $^{1}$H NMR**



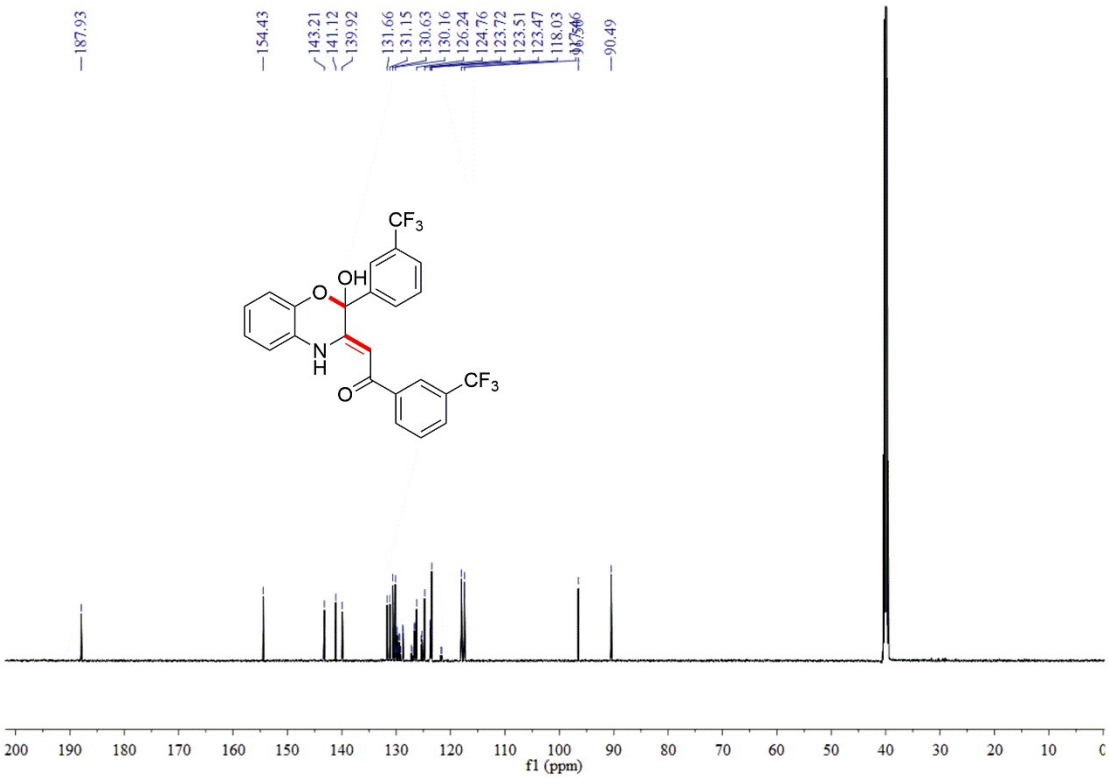
**(*Z*)-2-(2-hydroxy-2-(3-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-methoxyphenyl)ethan-1-one (2l): $^{13}$C NMR**



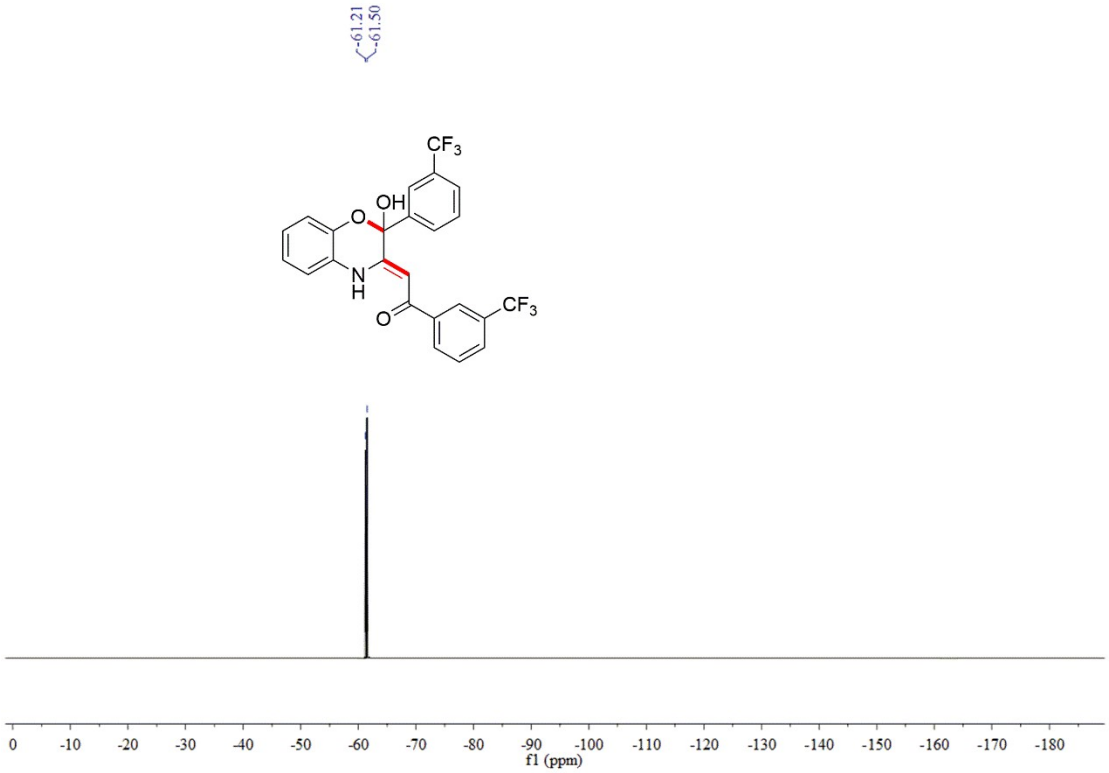

**(*Z*)-2-(2-hydroxy-2-(3-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-(trifluoromethyl)phenyl)ethan-1-one (2m): $^{1}$H NMR**



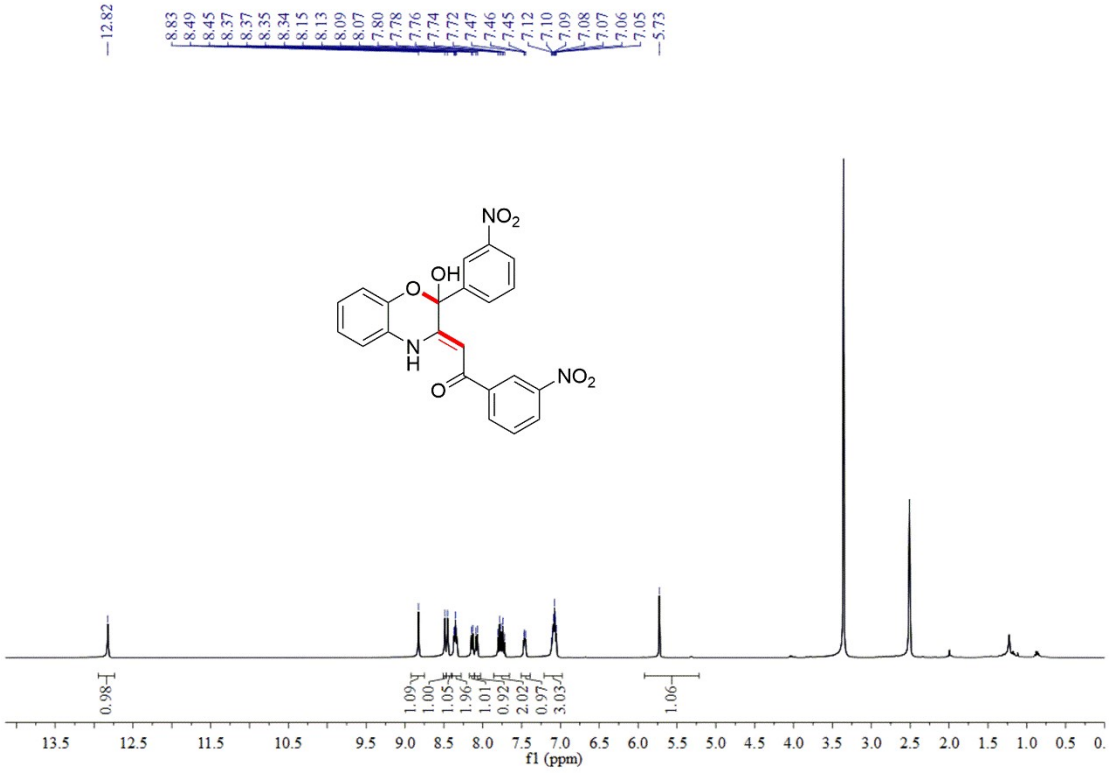
**(*Z*)-2-(2-hydroxy-2-(3-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-(trifluoromethyl)phenyl)ethan-1-one (2m): $^{13}$C NMR**



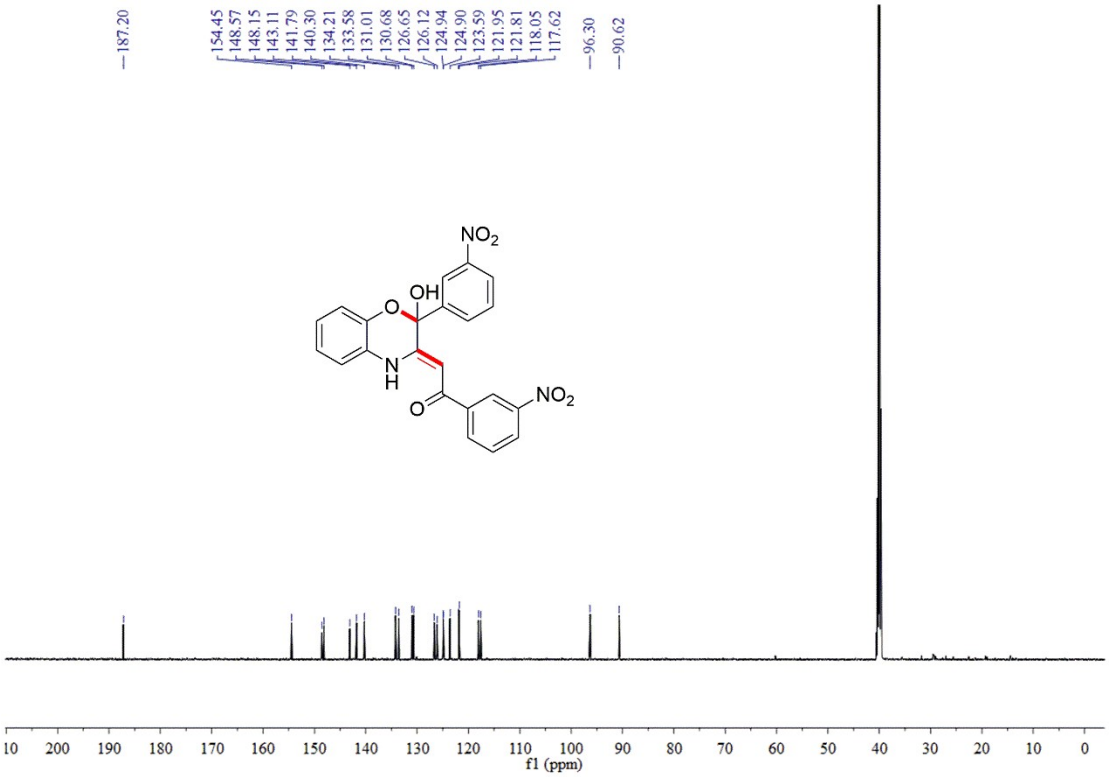

**(*Z*)-2-(2-hydroxy-2-(3-(trifluoromethyl)phenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-(trifluoromethyl)phenyl)ethan-1-one (2m): $^{19}$F NMR**



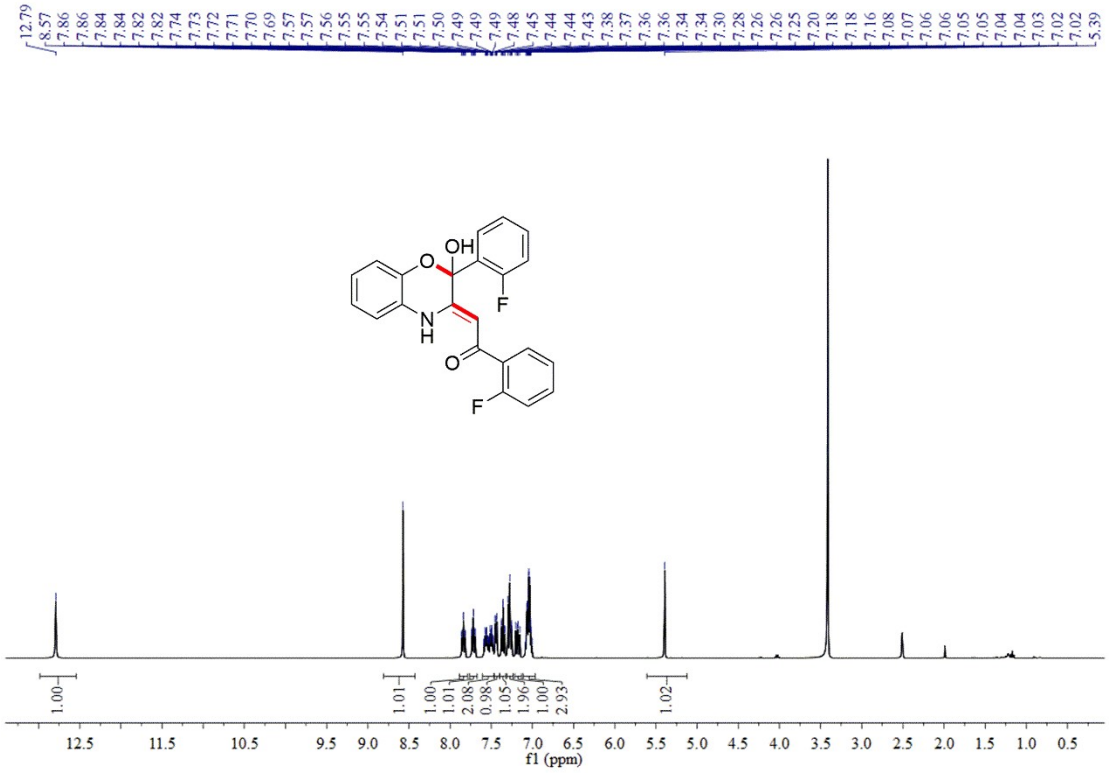
**(*Z*)-2-(2-hydroxy-2-(3-nitrophenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-nitrophenyl)ethan-1-one (2n): $^{1}$H NMR**



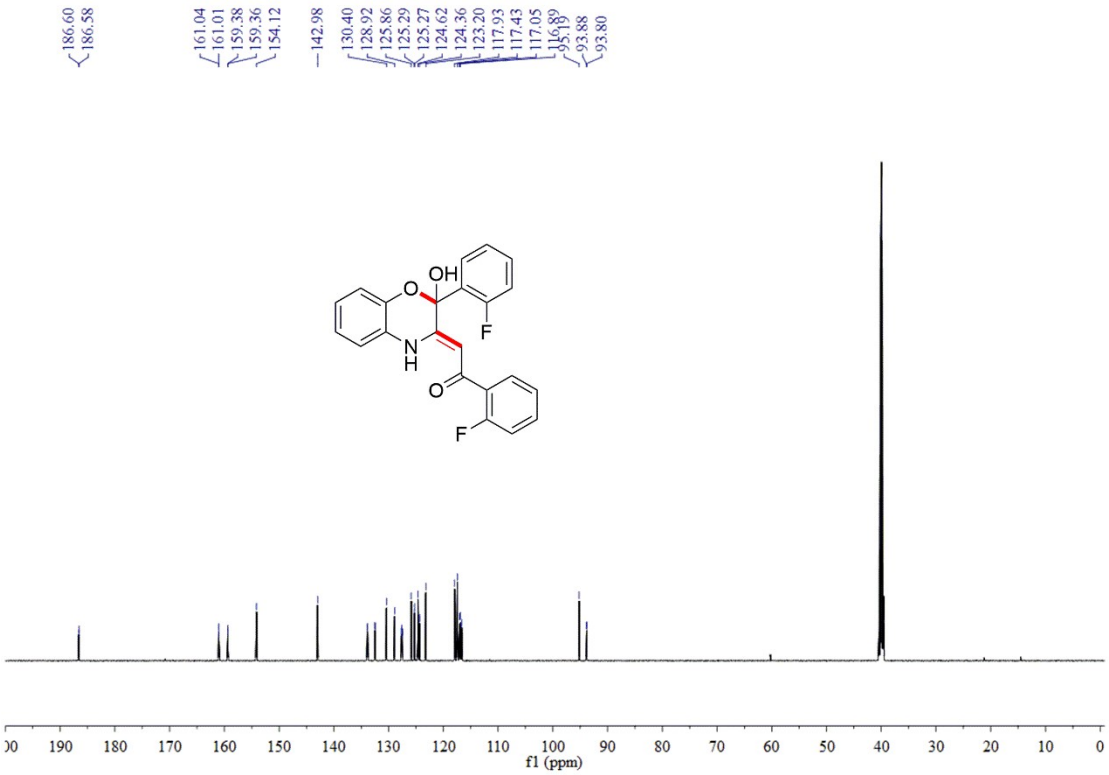

**(*Z*)-2-(2-hydroxy-2-(3-nitrophenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(3-nitrophenyl)ethan-1-one (2n): $^{13}$C NMR**



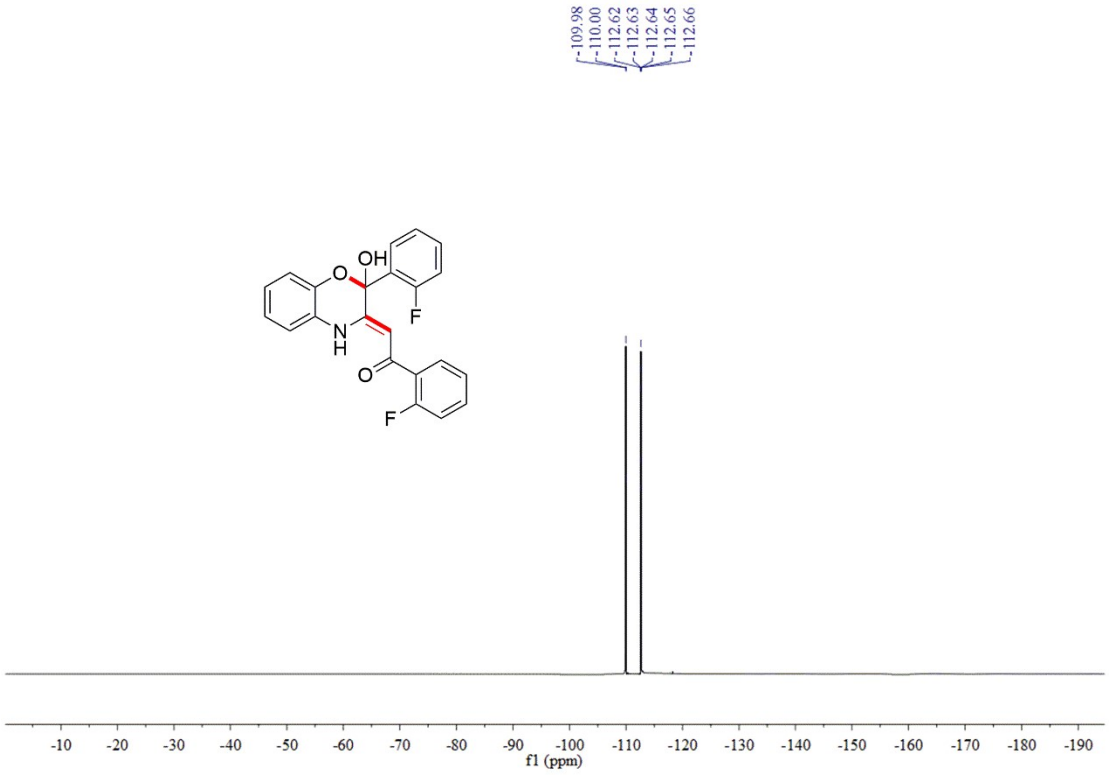
**(*Z*)-1-(2-fluorophenyl)-2-(2-(2-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2o): $^{1}$H NMR**



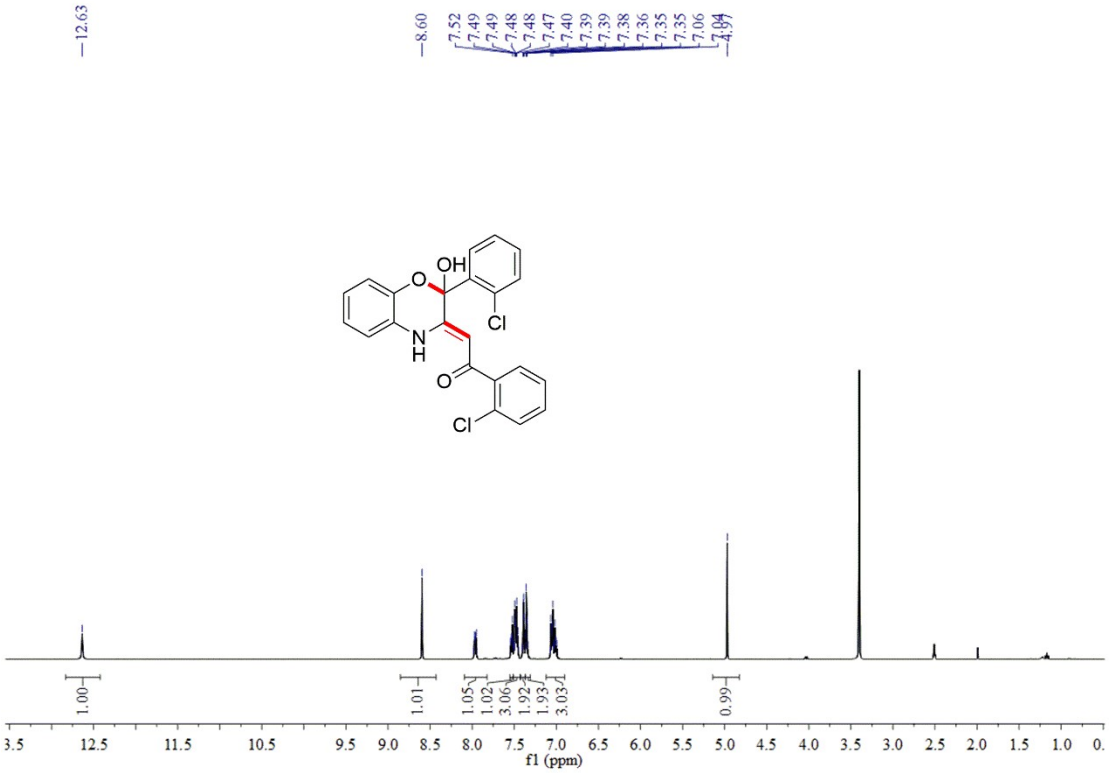

**(*Z*)-1-(2-fluorophenyl)-2-(2-(2-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2o): $^{13}$C NMR**



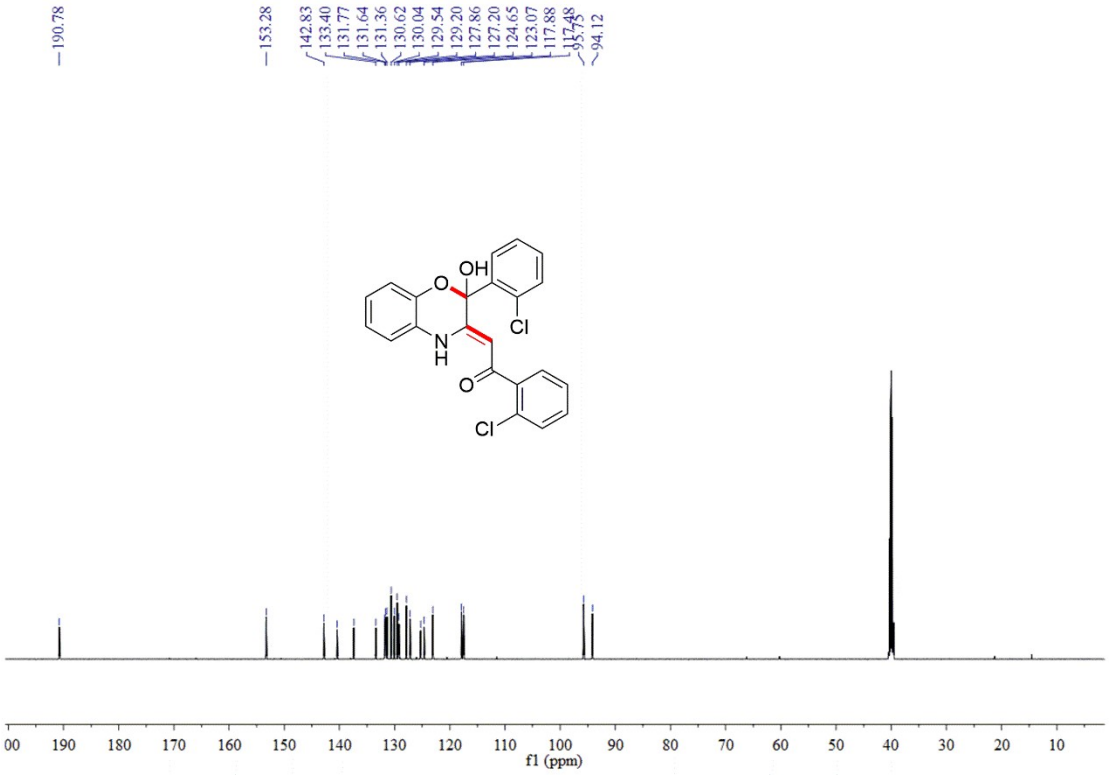
**(*Z*)-1-(2-fluorophenyl)-2-(2-(2-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2o): $^{19}$F NMR**



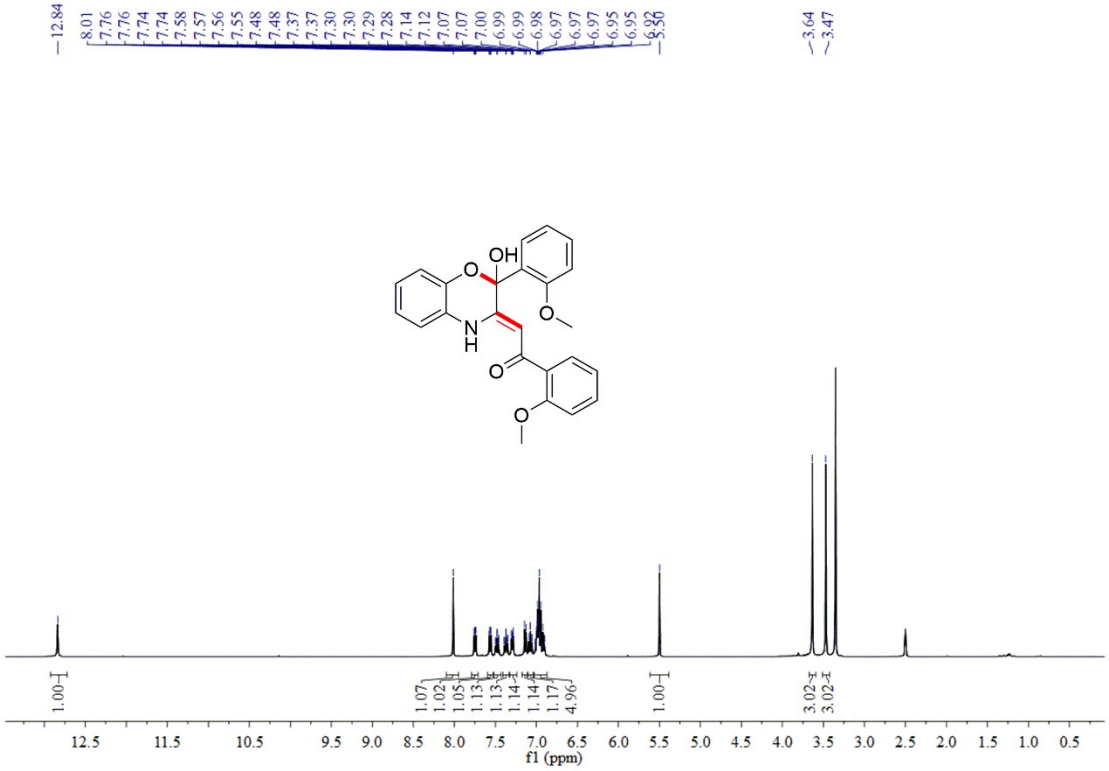

**(*Z*)-1-(2-chlorophenyl)-2-(2-(2-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2p): $^{1}$H NMR**



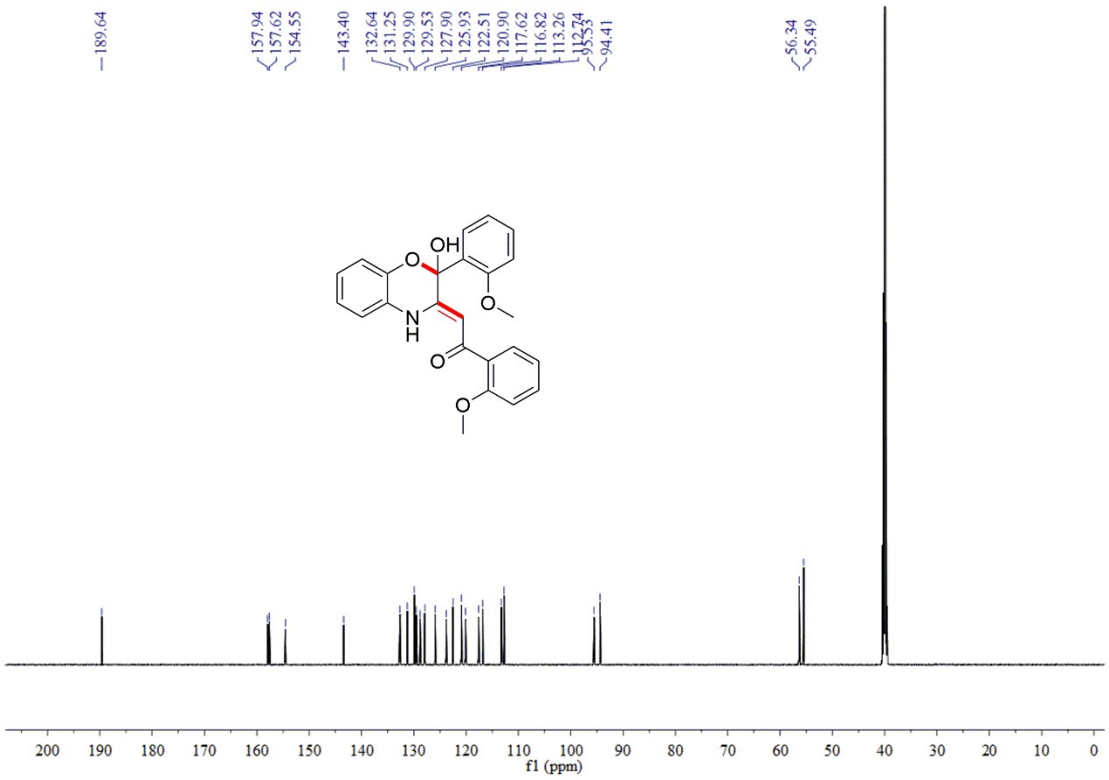
**(*Z*)-1-(2-chlorophenyl)-2-(2-(2-chlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2p): $^{13}$C NMR**



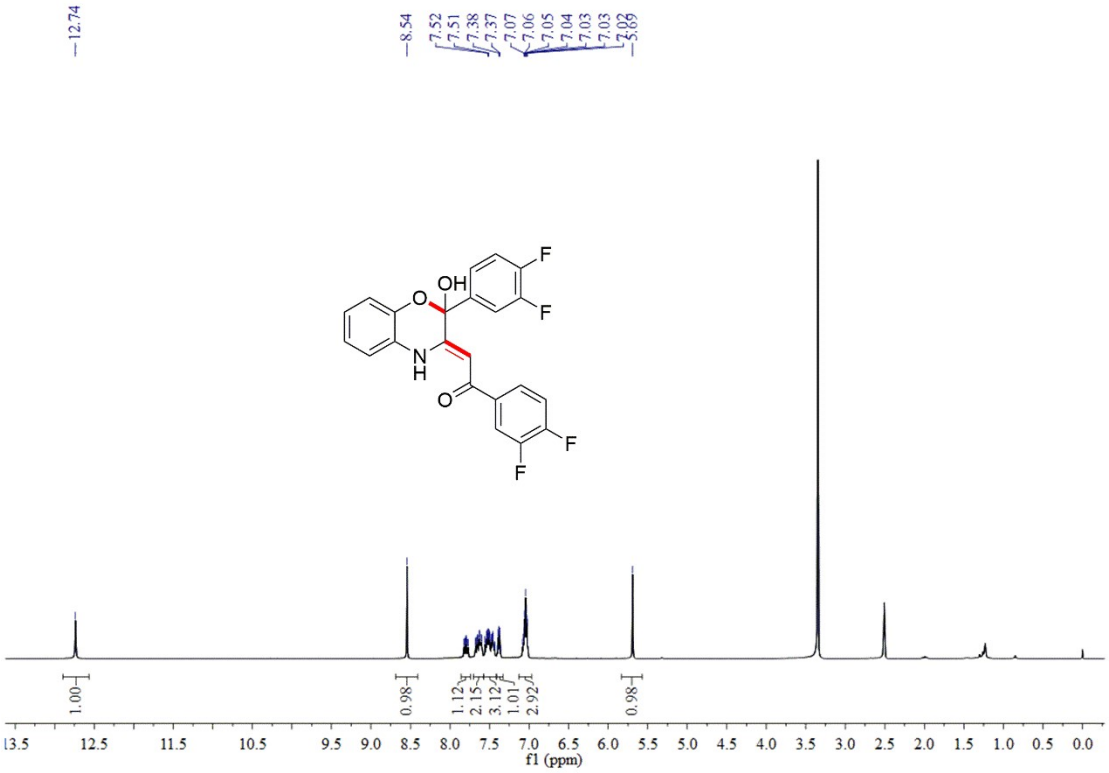

**(*Z*)-2-(2-hydroxy-2-(2-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(2-methoxyphenyl)ethan-1-one (2q): $^{1}$H NMR**



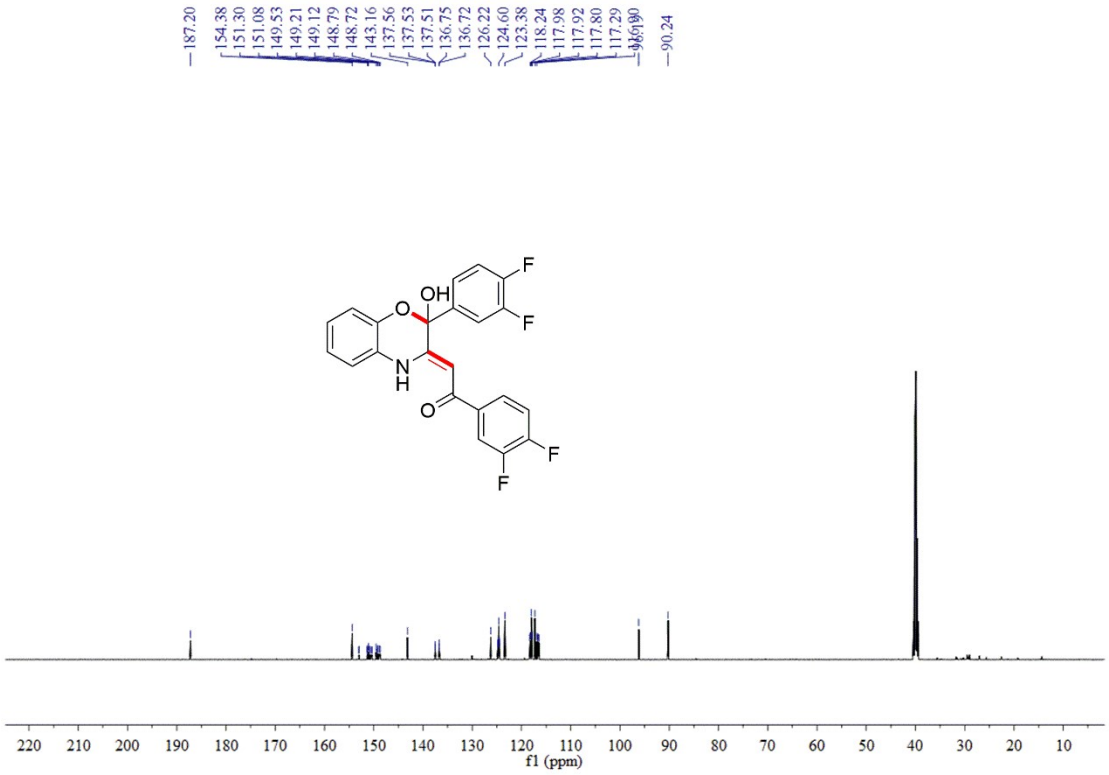
**(*Z*)-2-(2-hydroxy-2-(2-methoxyphenyl)-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-(2-methoxyphenyl)ethan-1-one (2q): $^{13}$C NMR**



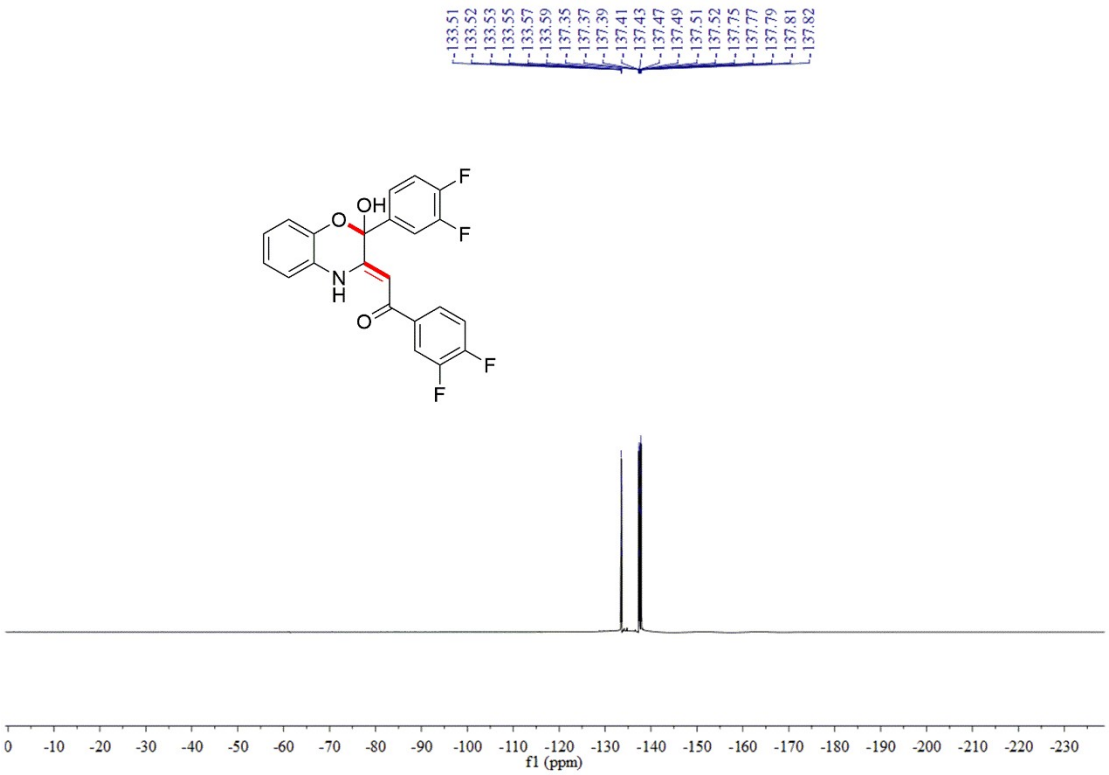

**(*Z*)-1-(3,4-difluorophenyl)-2-(2-(3,4-difluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2s): $^{1}$H NMR**



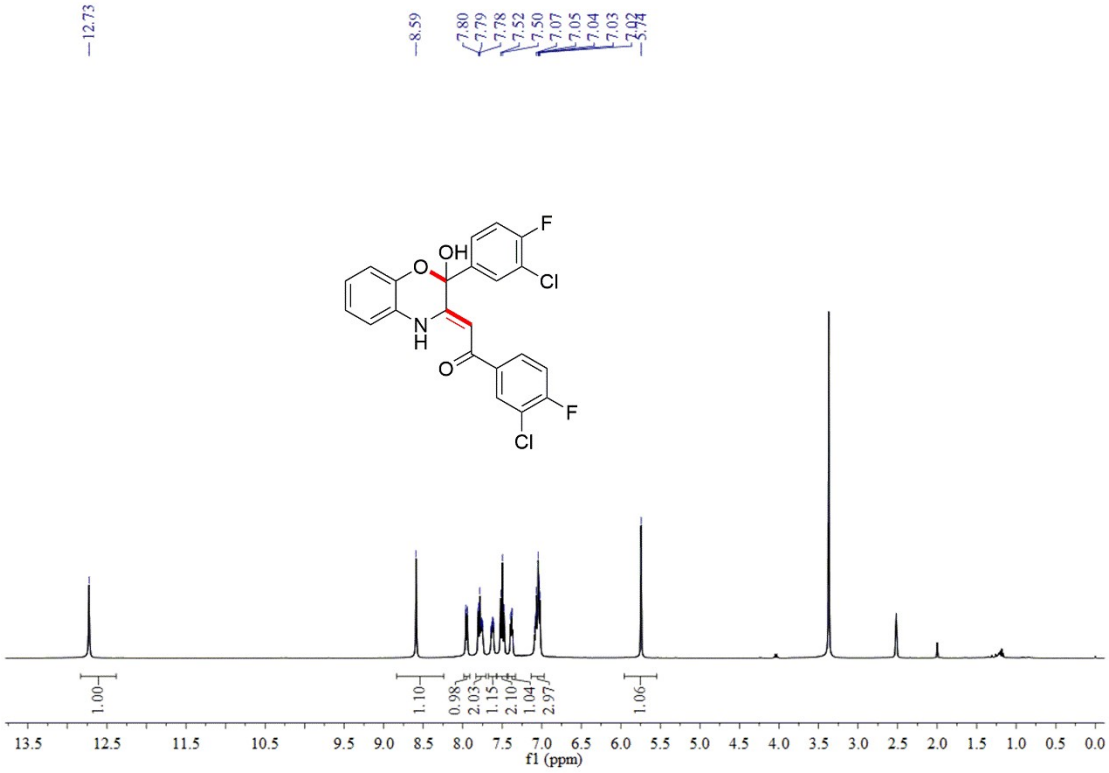
**(*Z*)-1-(3,4-difluorophenyl)-2-(2-(3,4-difluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2s): $^{13}$C NMR**



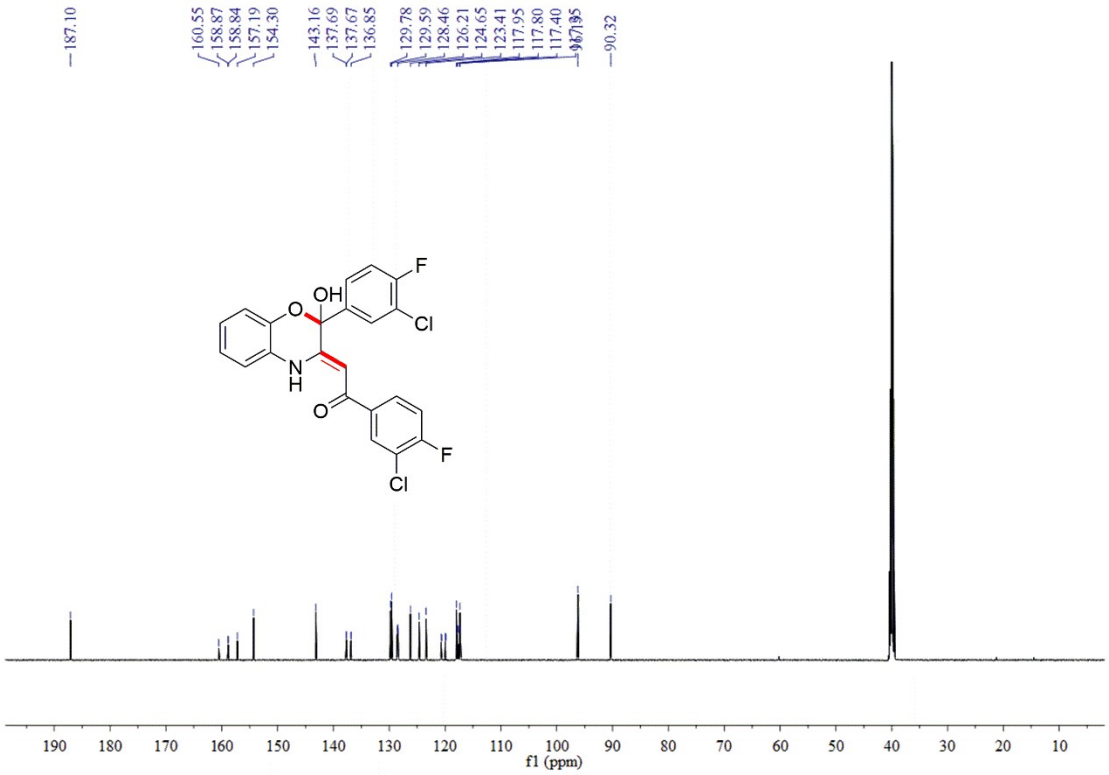

**(*Z*)-1-(3,4-difluorophenyl)-2-(2-(3,4-difluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2s): $^{19}$F NMR**



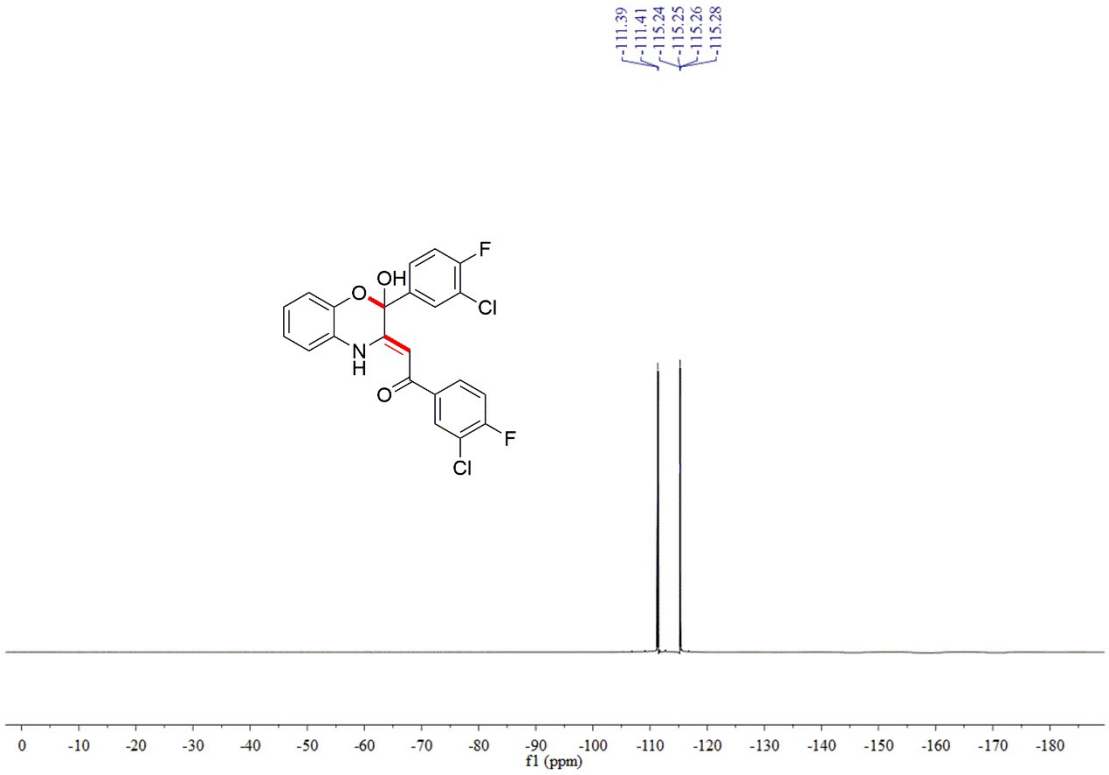
**(*Z*)-1-(3-chloro-4-fluorophenyl)-2-(2-(3-chloro-4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2t): $^{1}$H NMR**



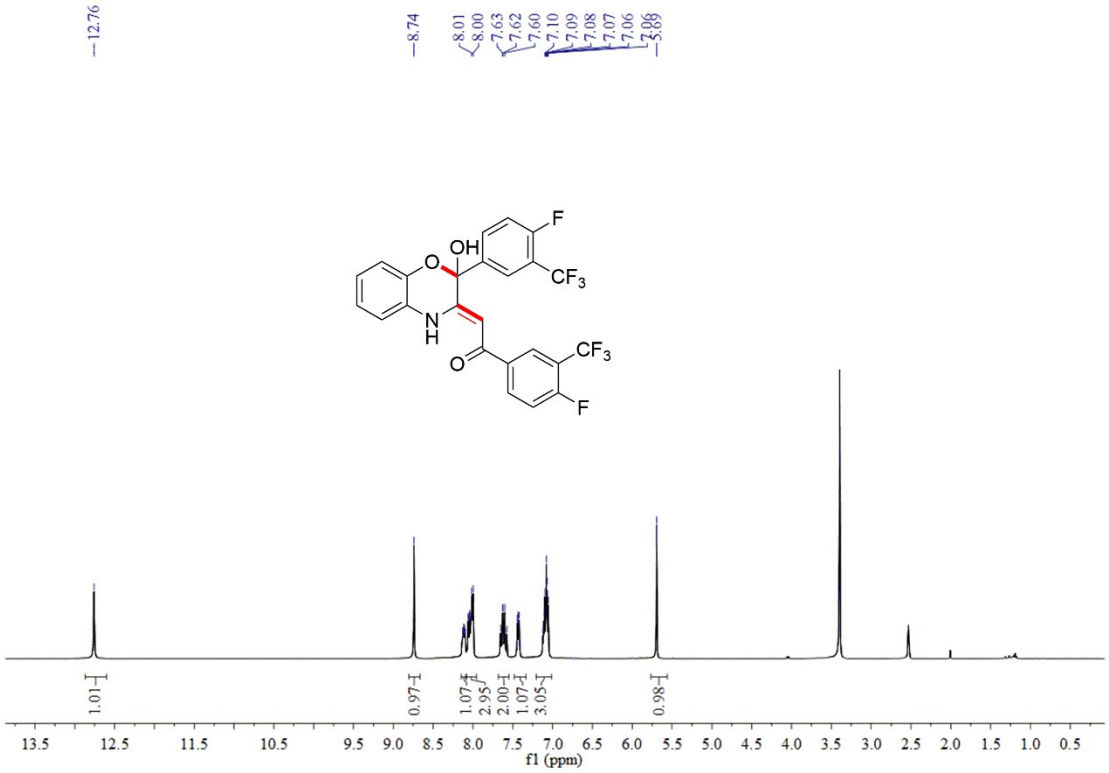

**(*Z*)-1-(3-chloro-4-fluorophenyl)-2-(2-(3-chloro-4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2t): $^{13}$C NMR**



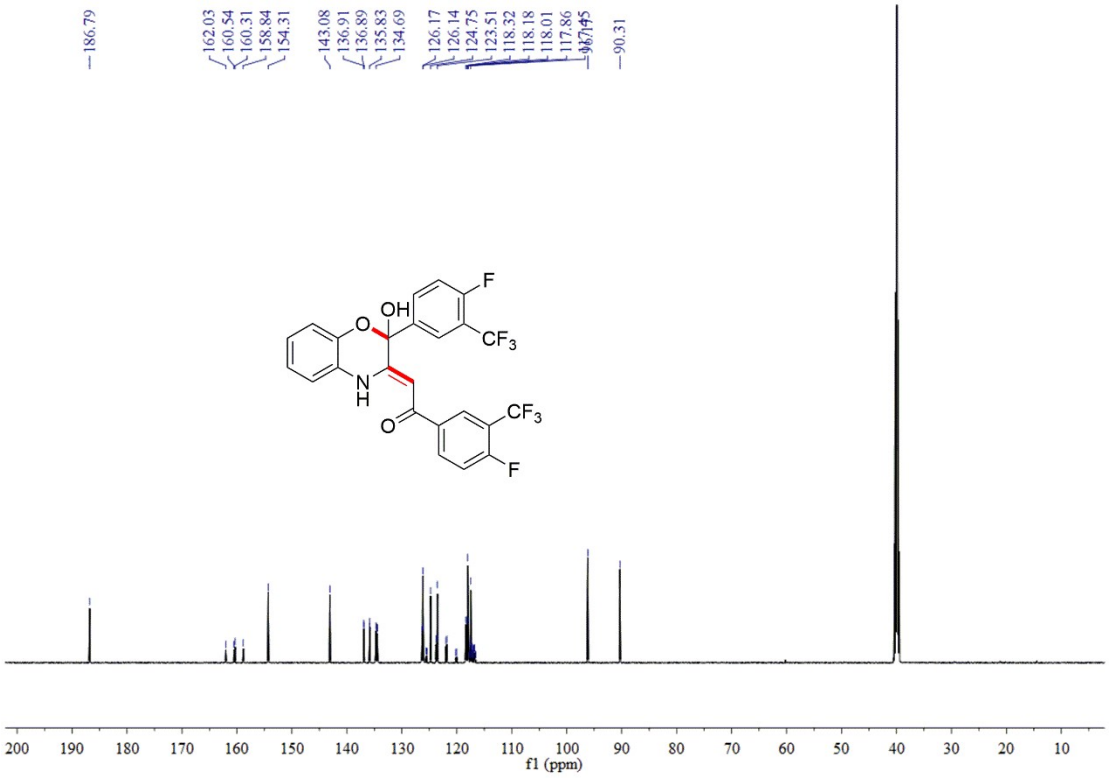
**(*Z*)-1-(3-chloro-4-fluorophenyl)-2-(2-(3-chloro-4-fluorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2t): $^{19}$F NMR**



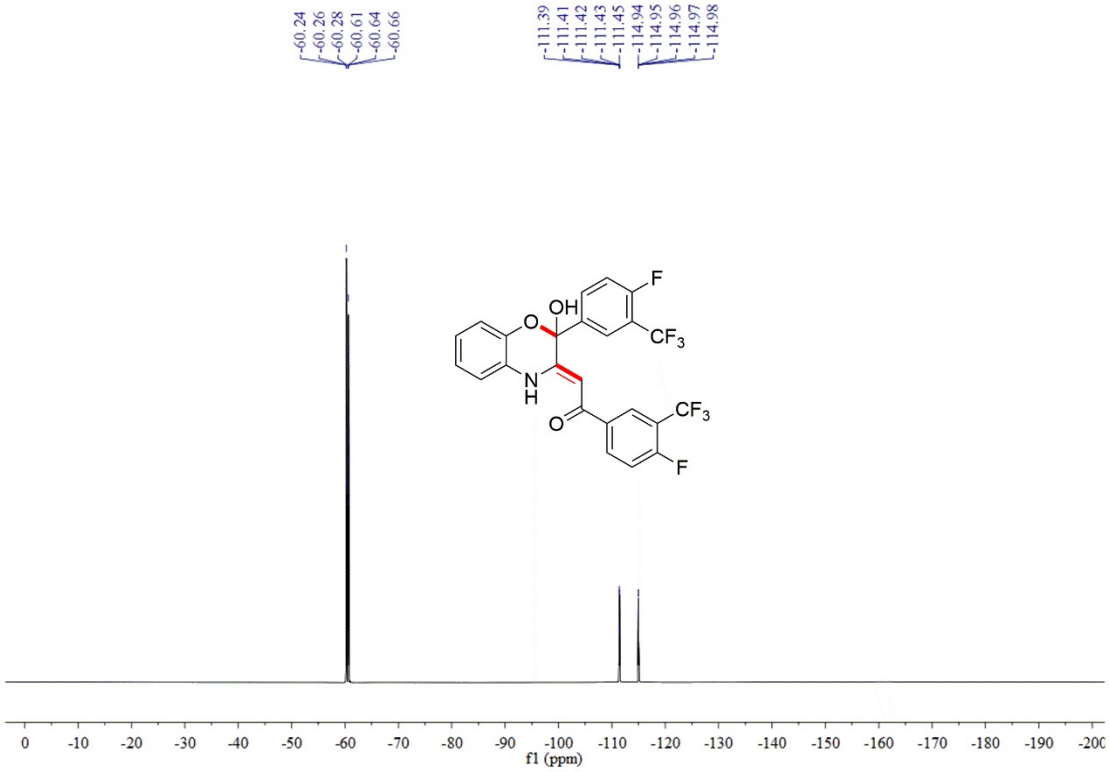

**(*Z*)-1-(4-fluoro-3-(trifluoromethyl)phenyl)-2-(2-(4-fluoro-3-(trifluoromethyl)phenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2u): $^{1}$H NMR**



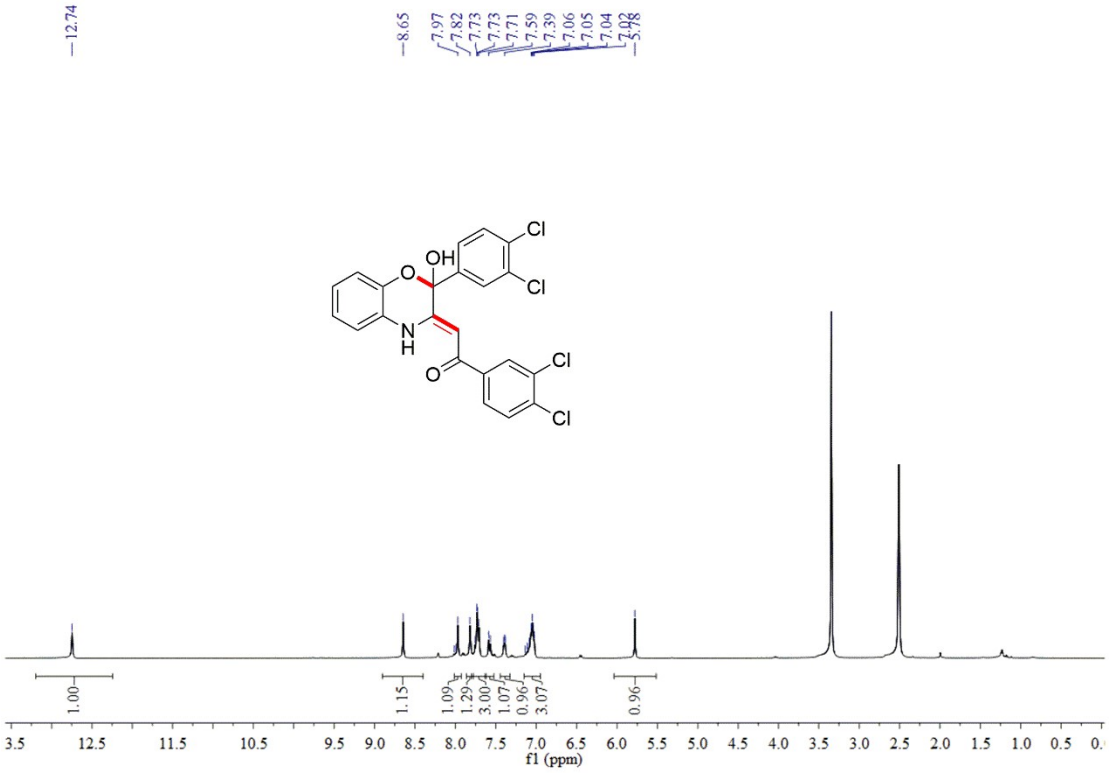
**(*Z*)-1-(4-fluoro-3-(trifluoromethyl)phenyl)-2-(2-(4-fluoro-3-(trifluoromethyl)phenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2u): $^{13}$C NMR**



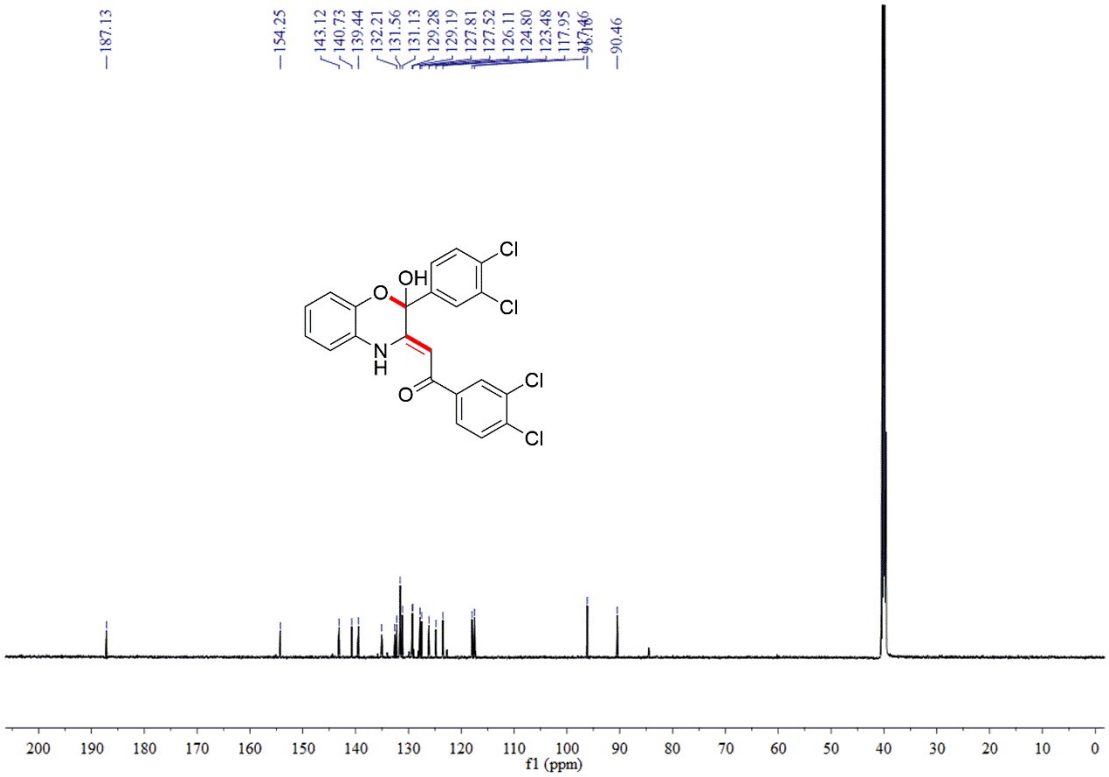

**(*Z*)-1-(4-fluoro-3-(trifluoromethyl)phenyl)-2-(2-(4-fluoro-3-(trifluoromethyl)phenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2u): $^{19}$F NMR**



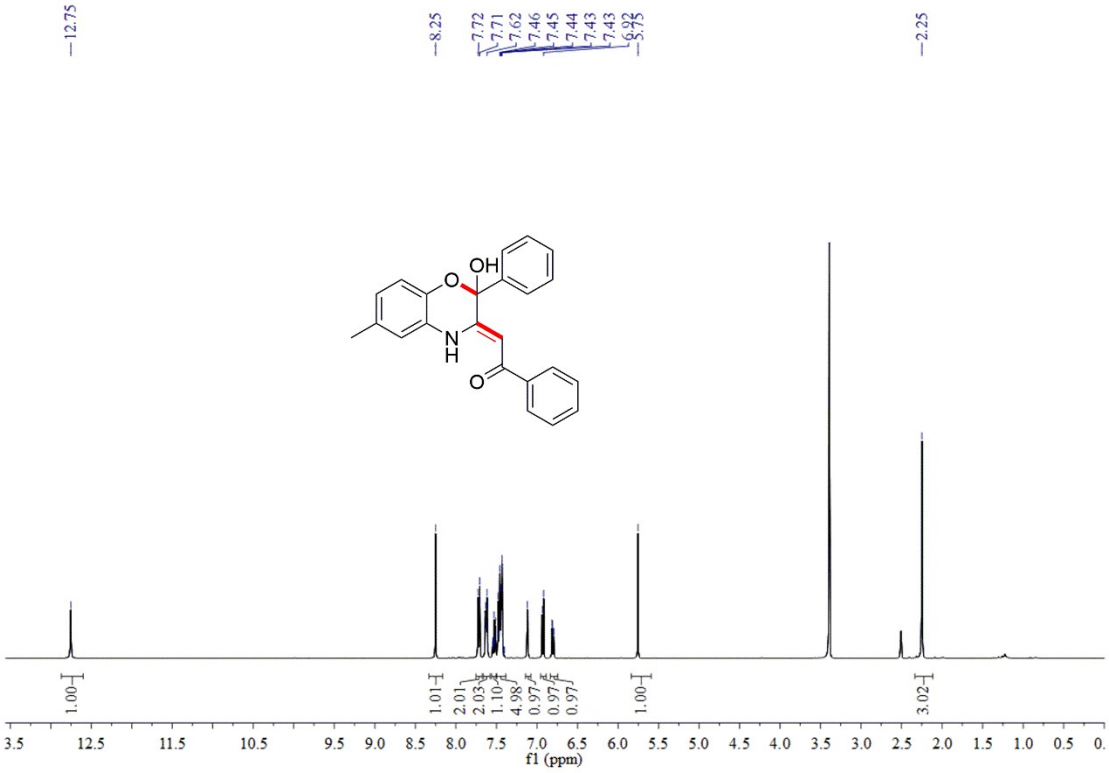
**(*Z*)-1-(3,4-dichlorophenyl)-2-(2-(3,4-dichlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2v): $^{1}$H NMR**



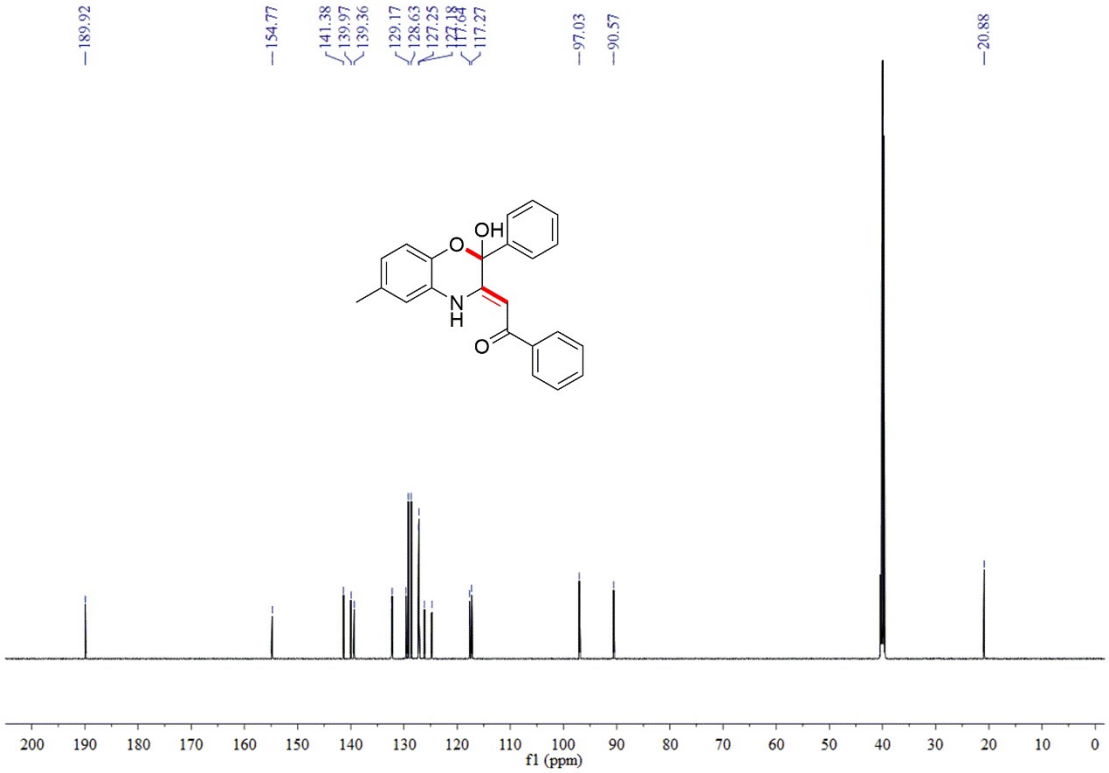

**(*Z*)-1-(3,4-dichlorophenyl)-2-(2-(3,4-dichlorophenyl)-2-hydroxy-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)ethan-1-one (2v): $^{13}$C NMR**



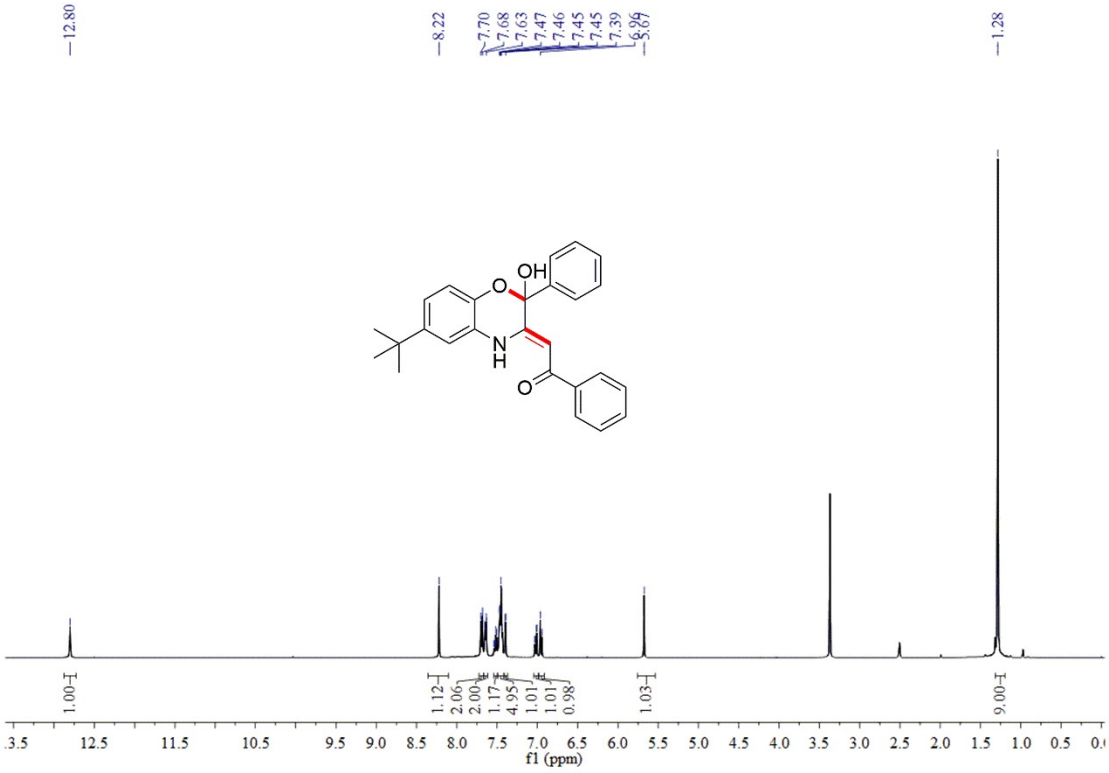
**(*Z*)-2-(2-hydroxy-6-methyl-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3a): $^{1}$H NMR**



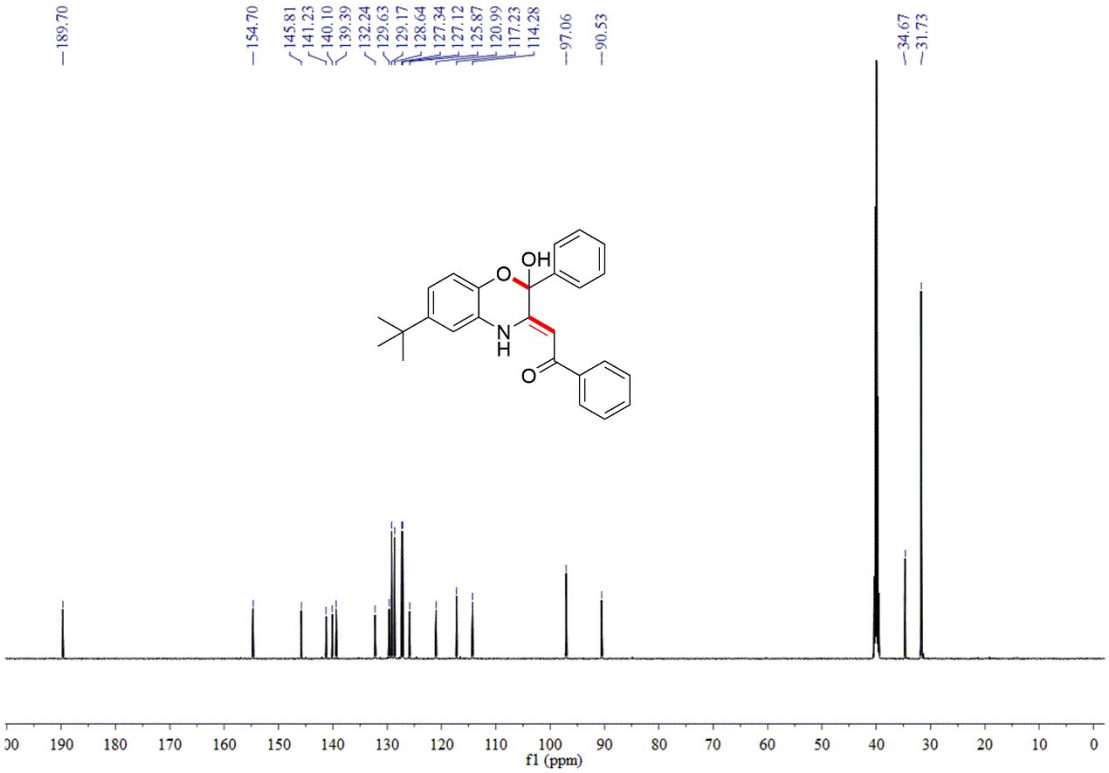

**(*Z*)-2-(2-hydroxy-6-methyl-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3a): $^{13}$C NMR**



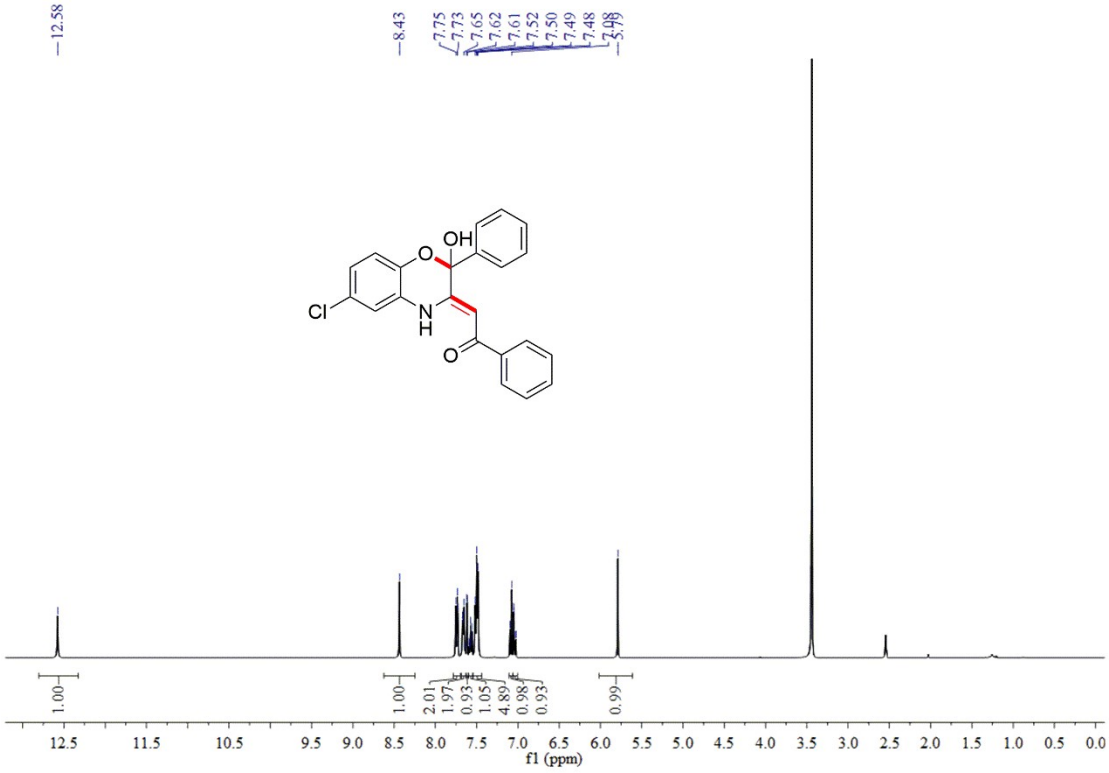
**(*Z*)-2-(6-(tert-butyl)-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3b): $^{1}$H NMR**



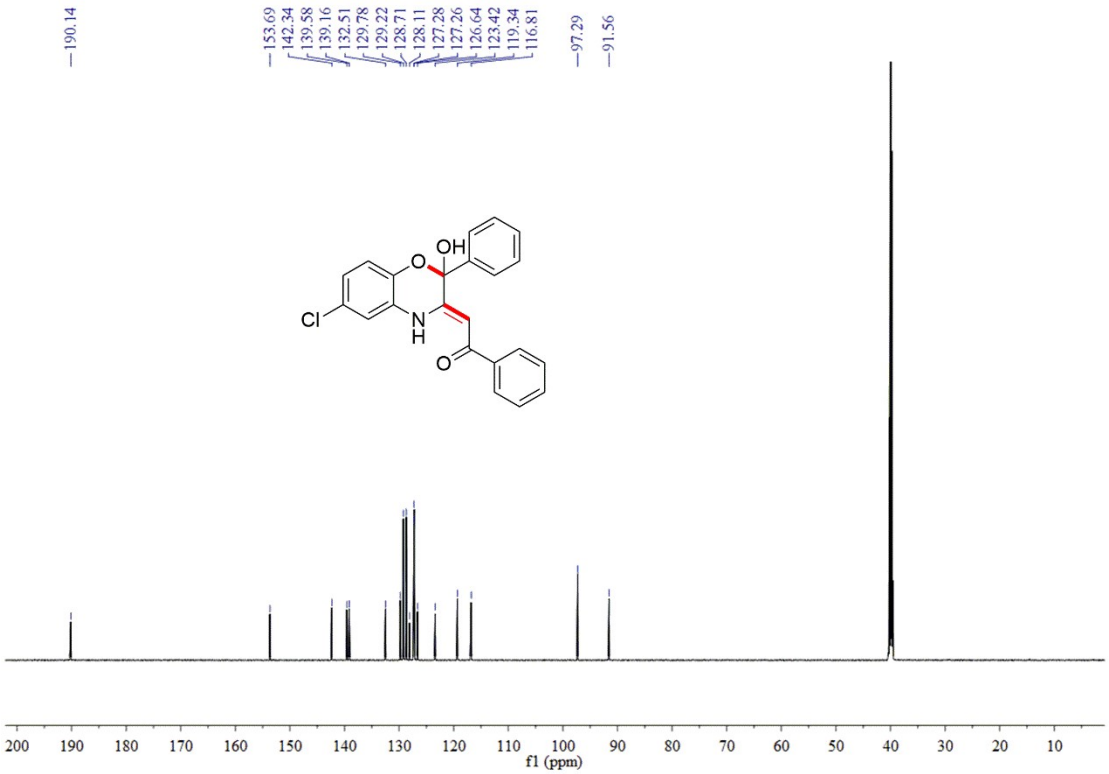

**(*Z*)-2-(6-(tert-butyl)-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3b): $^{13}$C NMR**



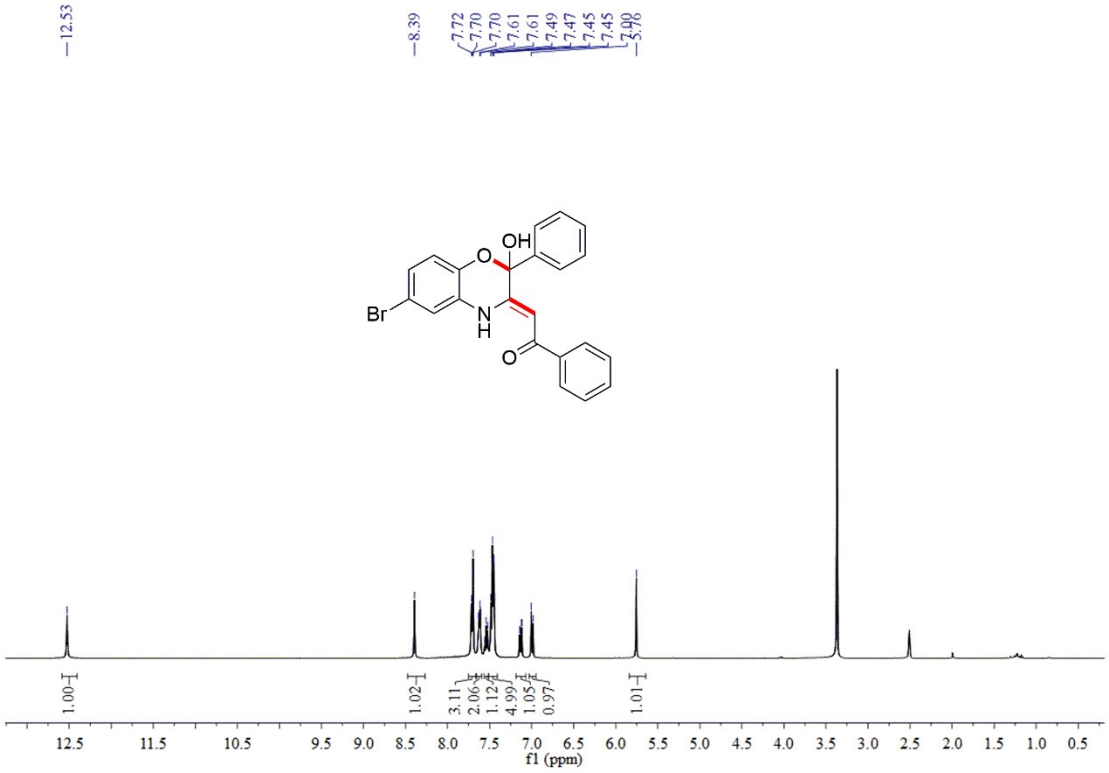
**(*Z*)-2-(6-chloro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3c): $^{1}$H NMR**



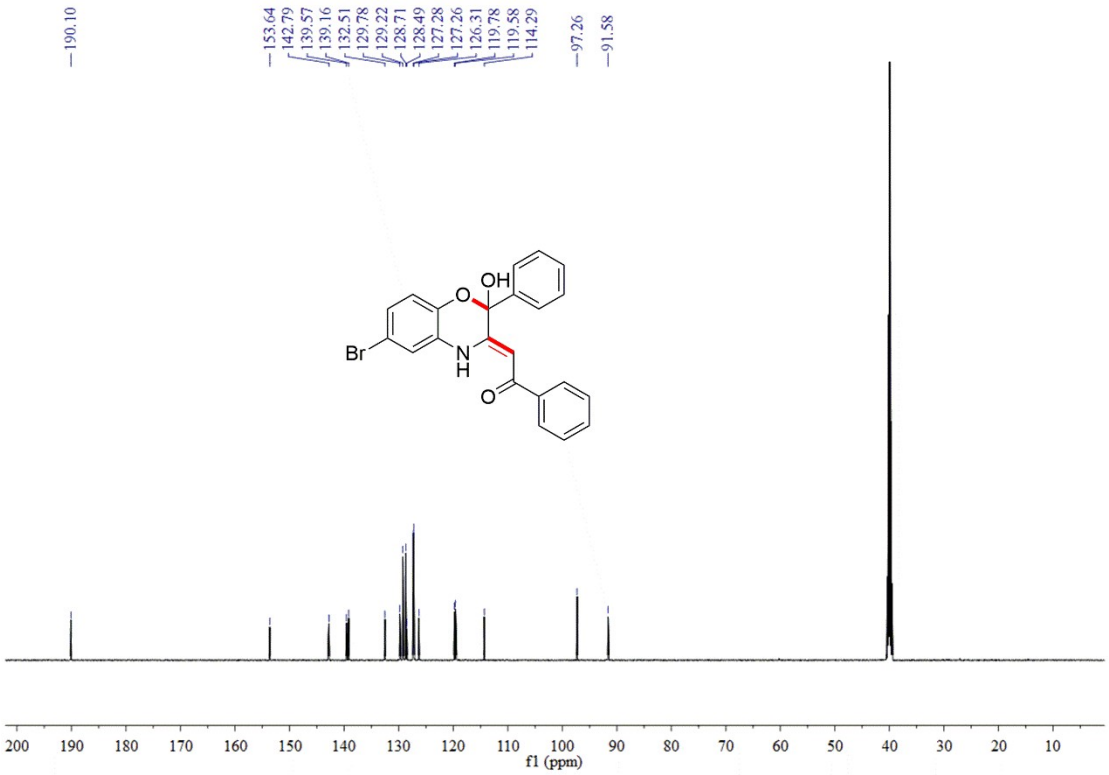

**(*Z*)-2-(6-chloro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3c): $^{13}$C NMR**



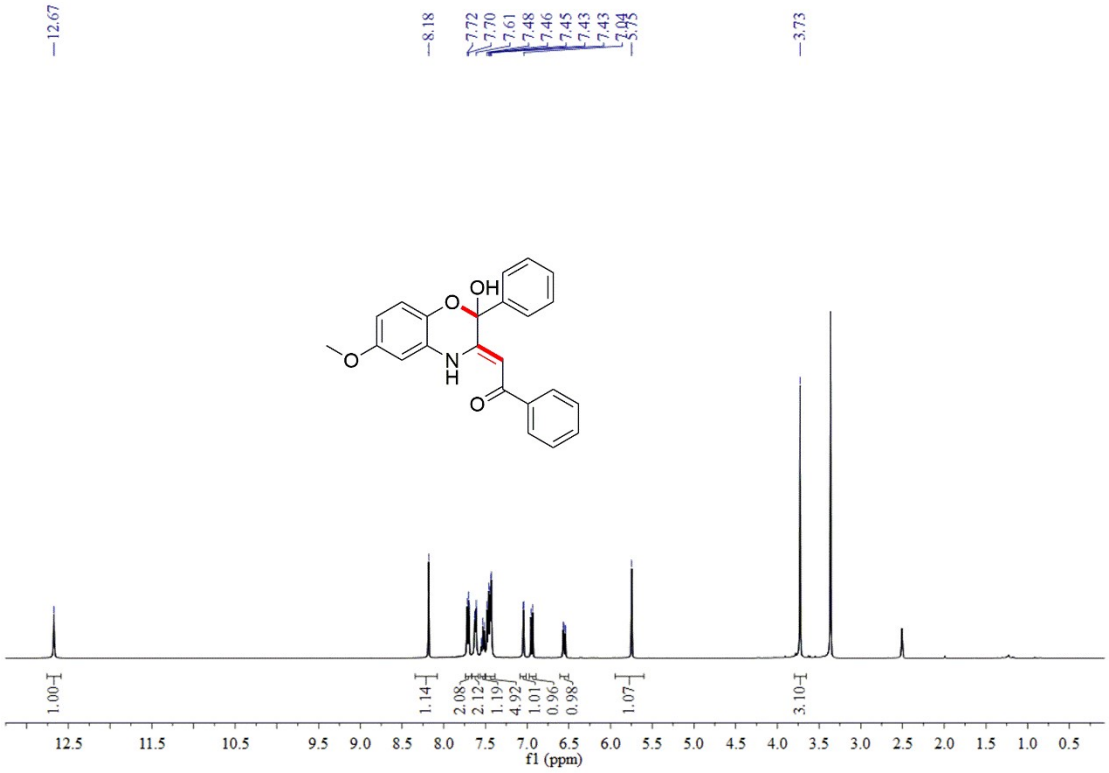
**(*Z*)-2-(6-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3d): $^{1}$H NMR**



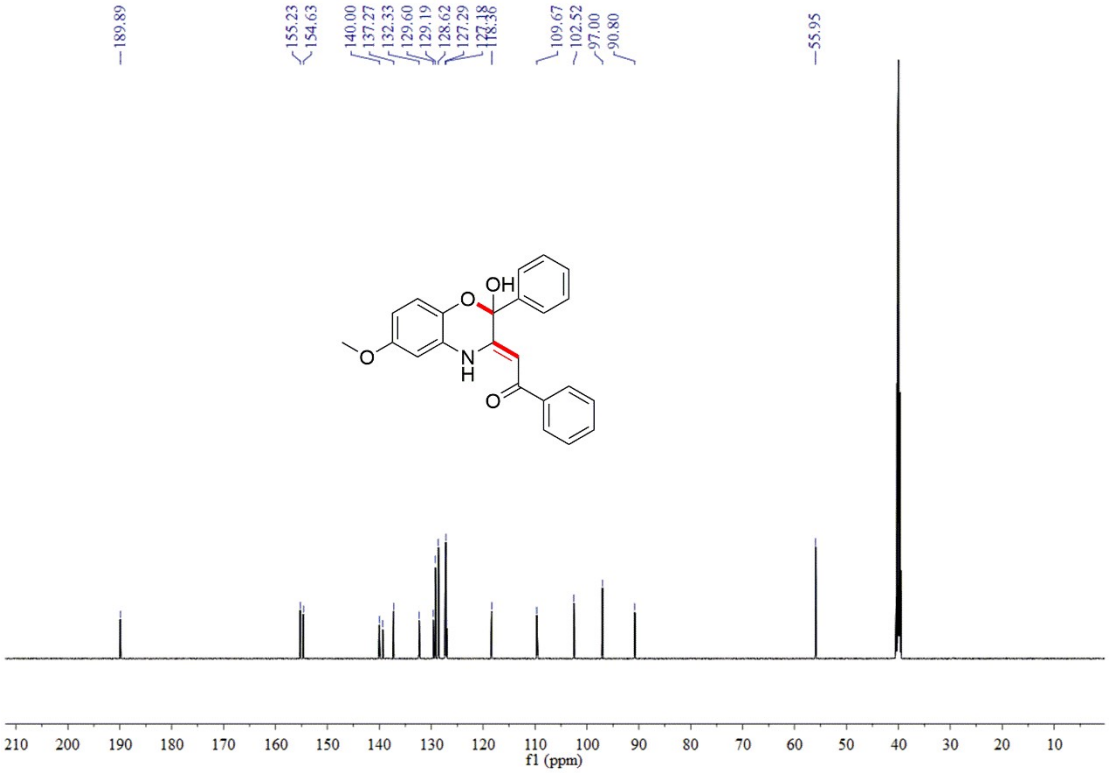

**(*Z*)-2-(6-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3d): $^{13}$C NMR**



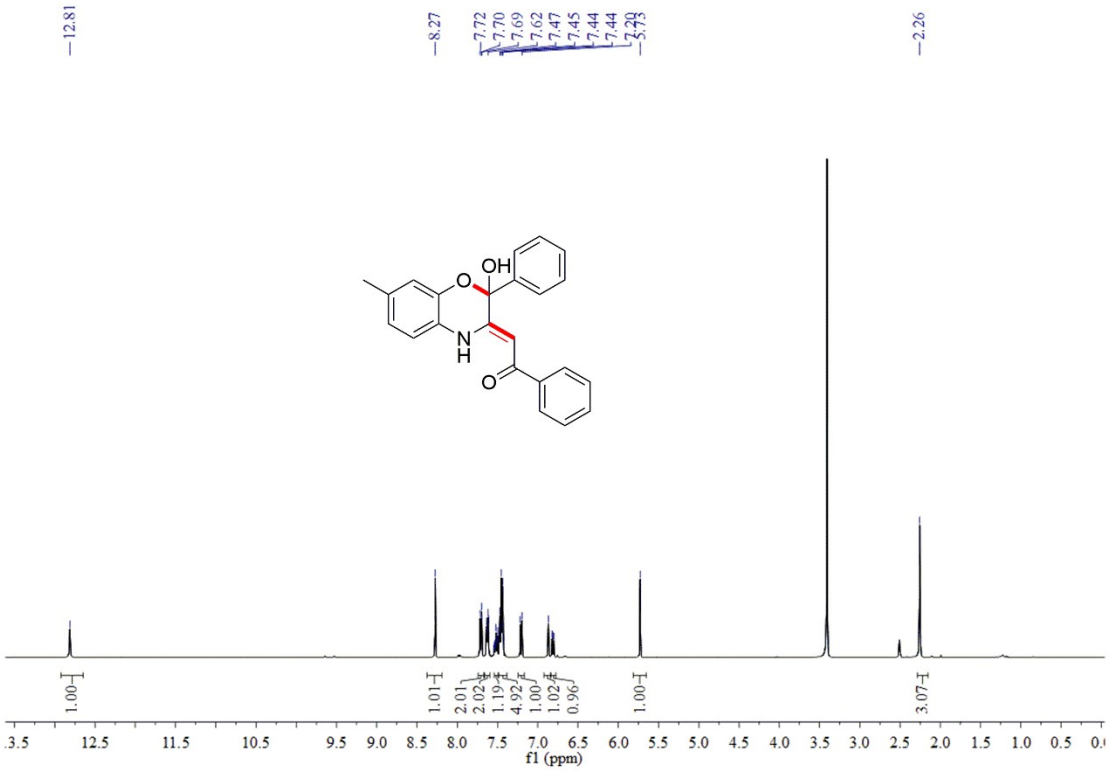
**(*Z*)-2-(2-hydroxy-6-methoxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3e): $^{1}$H NMR**



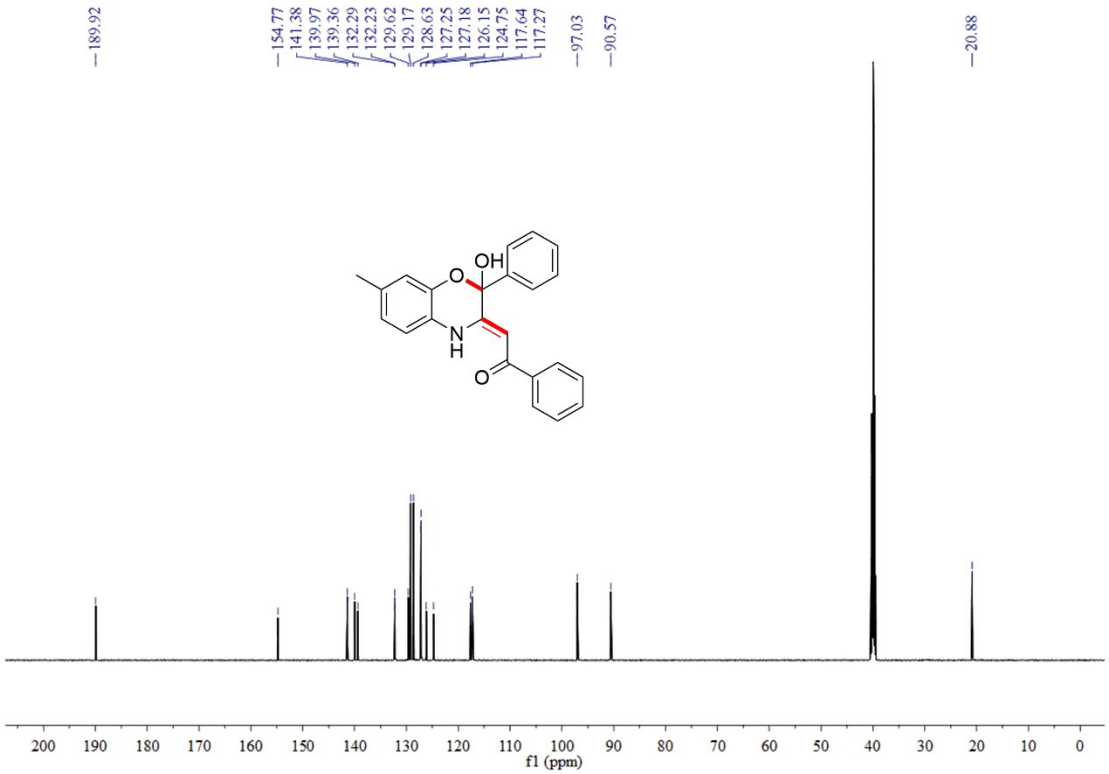

**(*Z*)-2-(2-hydroxy-6-methoxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3e): $^{13}$C NMR**



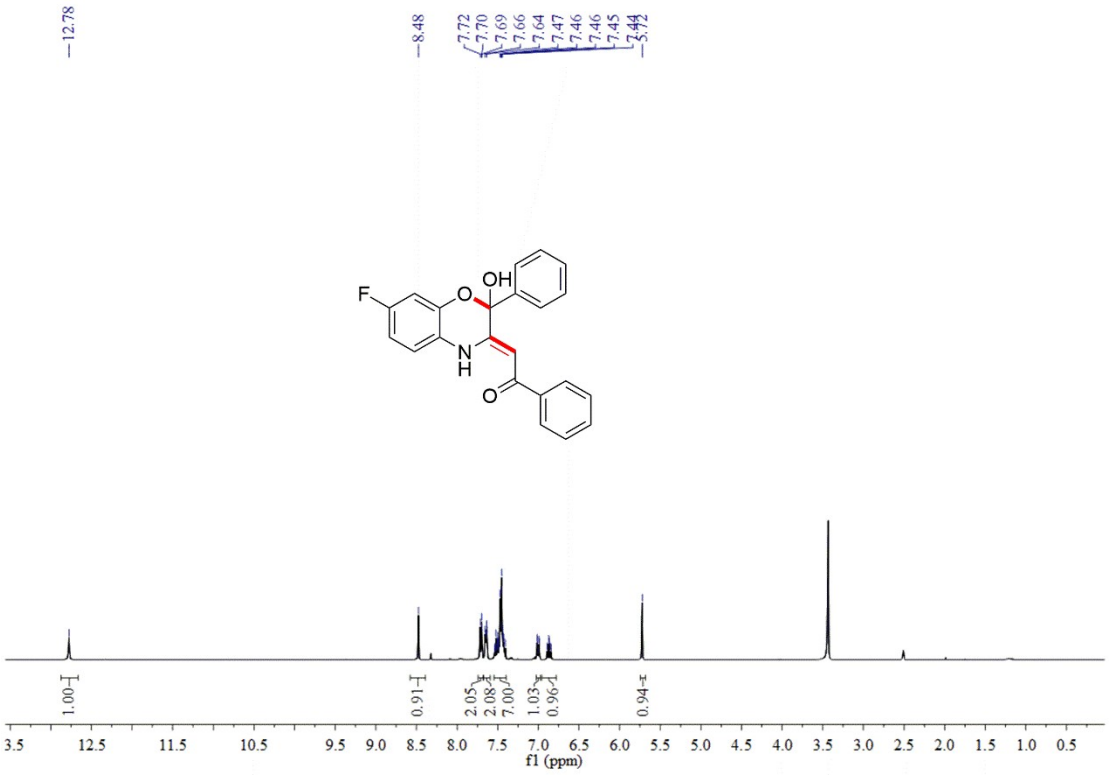
**(*Z*)-2-(2-hydroxy-7-methyl-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3f): $^{1}$H NMR**



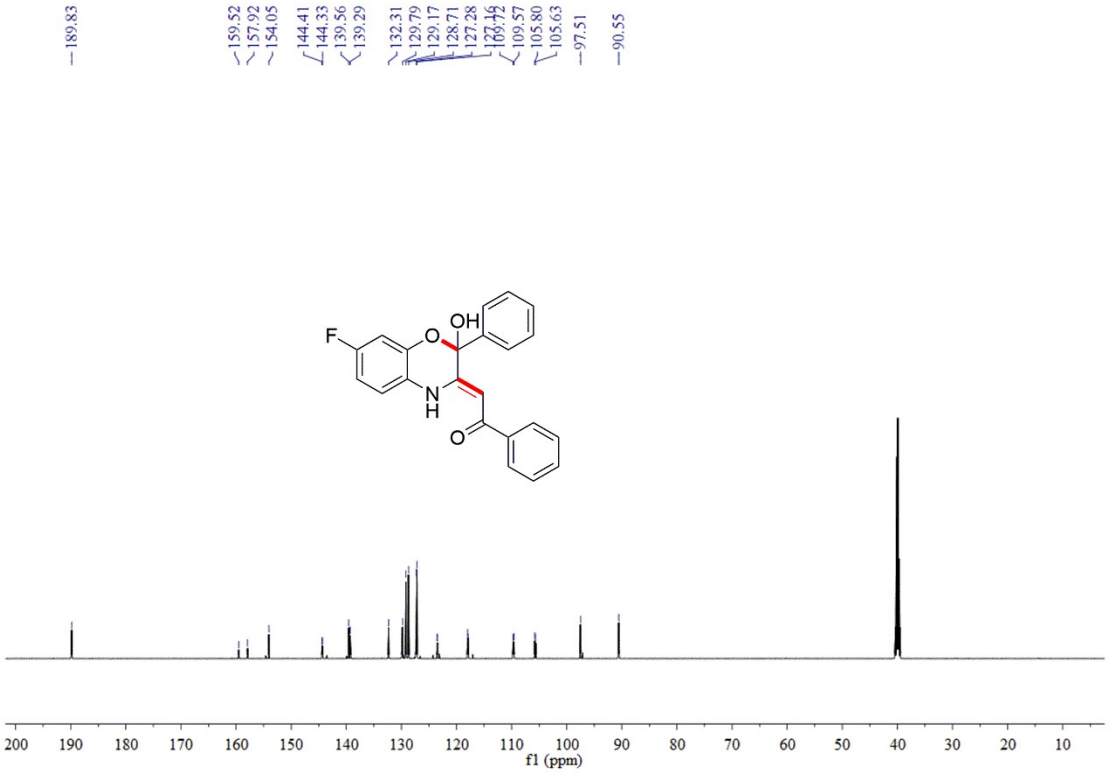

**(*Z*)-2-(2-hydroxy-7-methyl-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3f): $^{13}$C NMR**



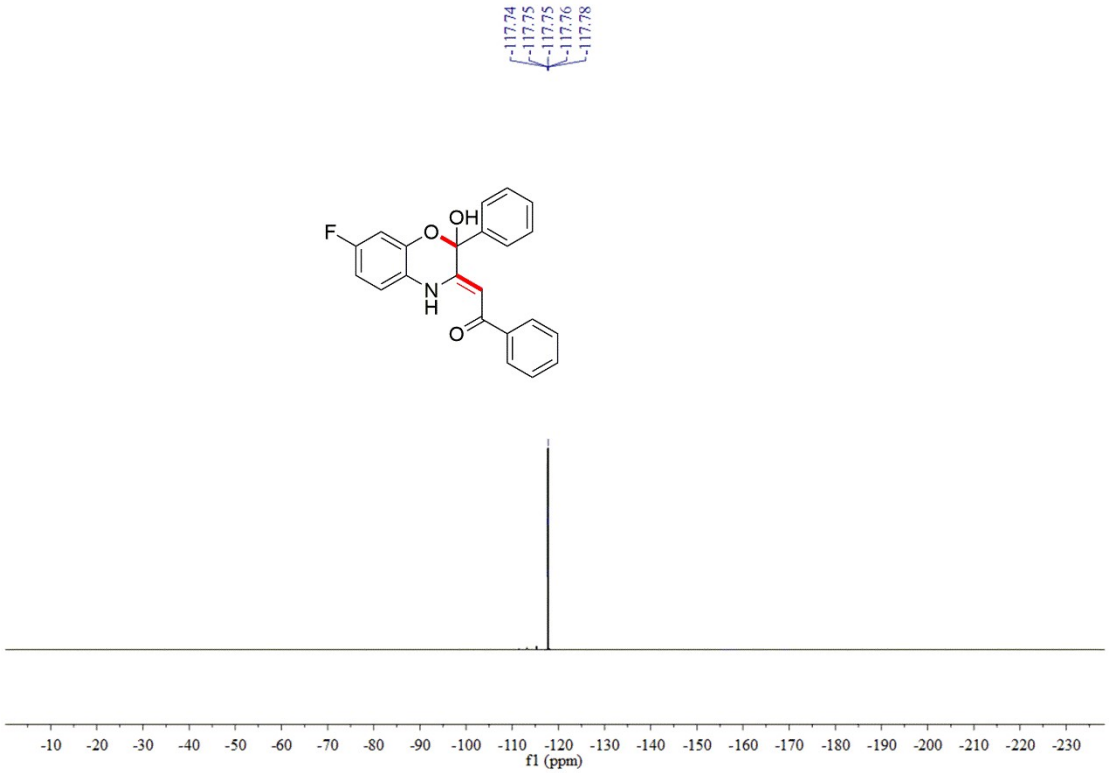
**(*Z*)-2-(7-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3g): $^{1}$H NMR**



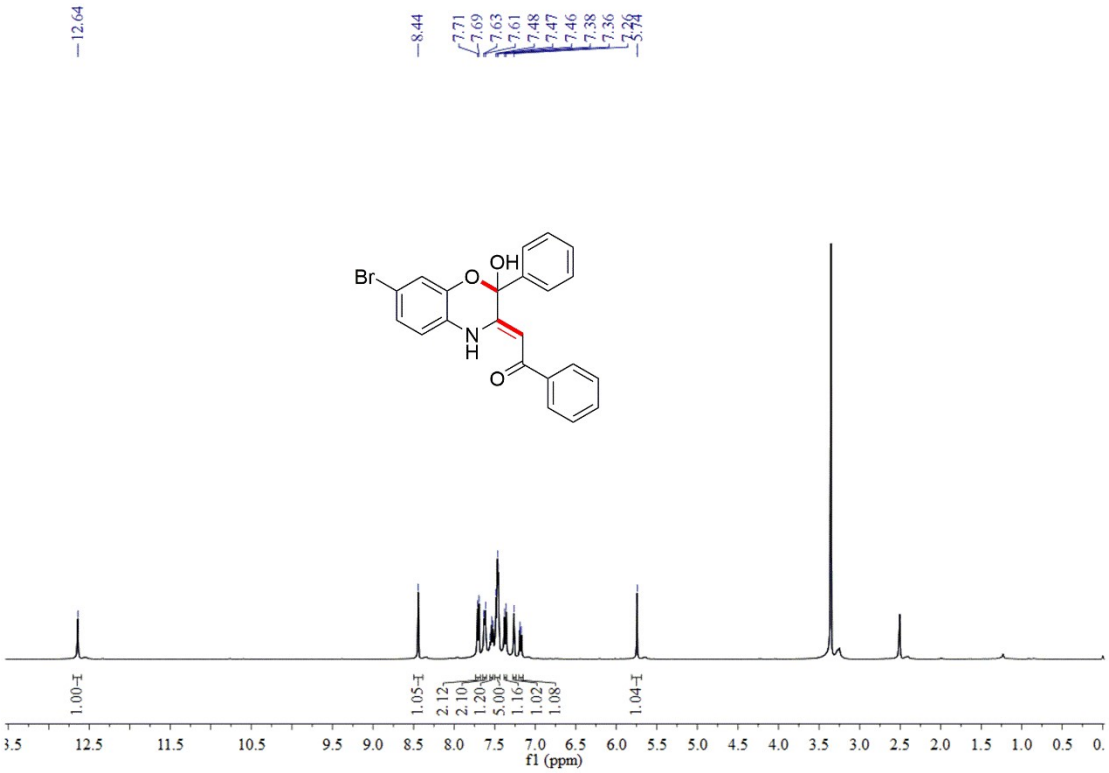

**(*Z*)-2-(7-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3g): $^{13}$C NMR**



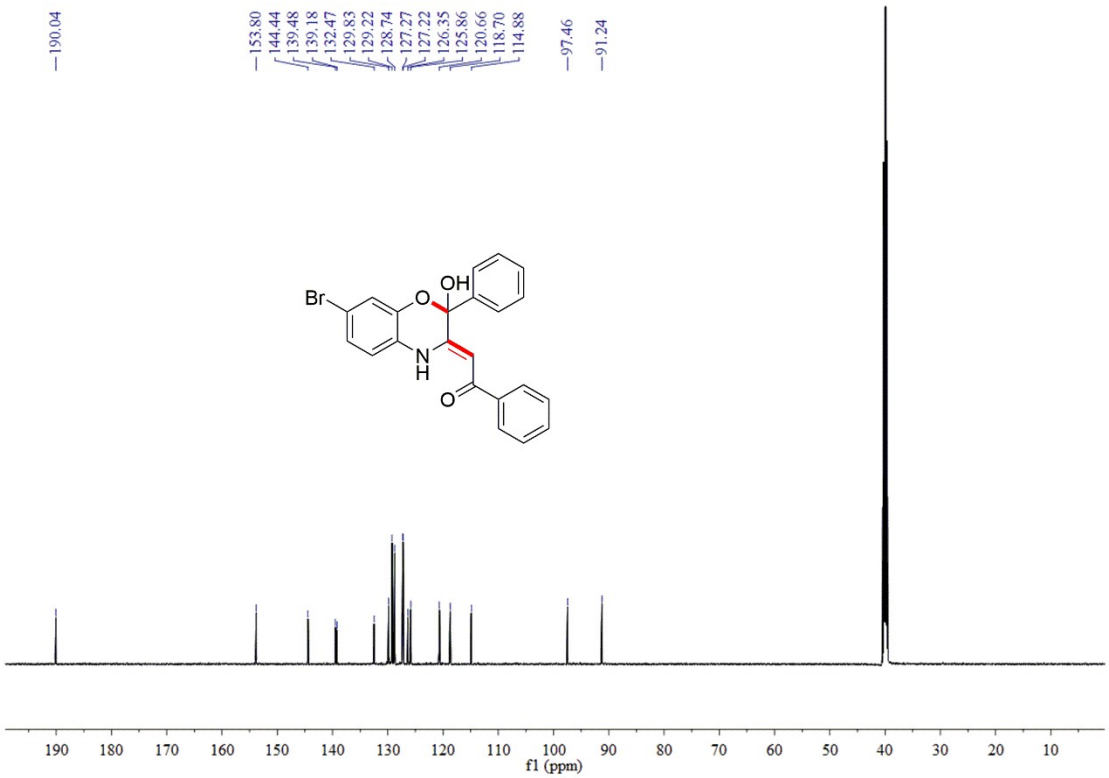
**(*Z*)-2-(7-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3g): $^{19}$F NMR**



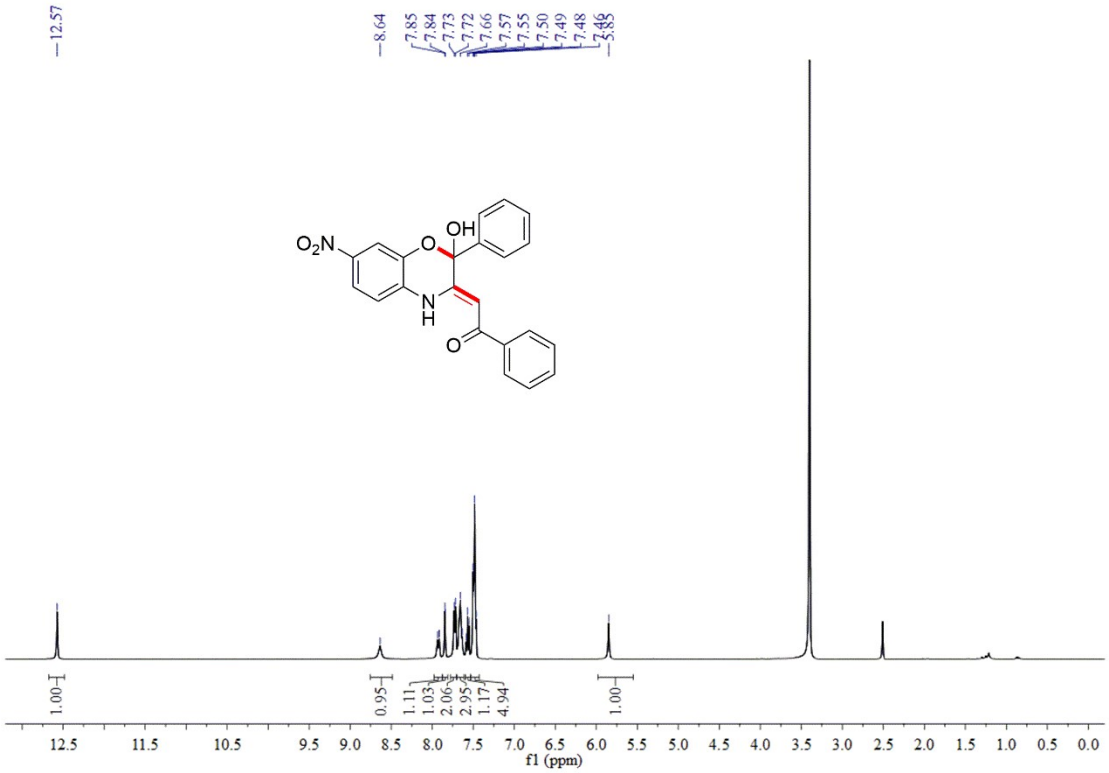

**(*Z*)-2-(7-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3h): $^{1}$H NMR**



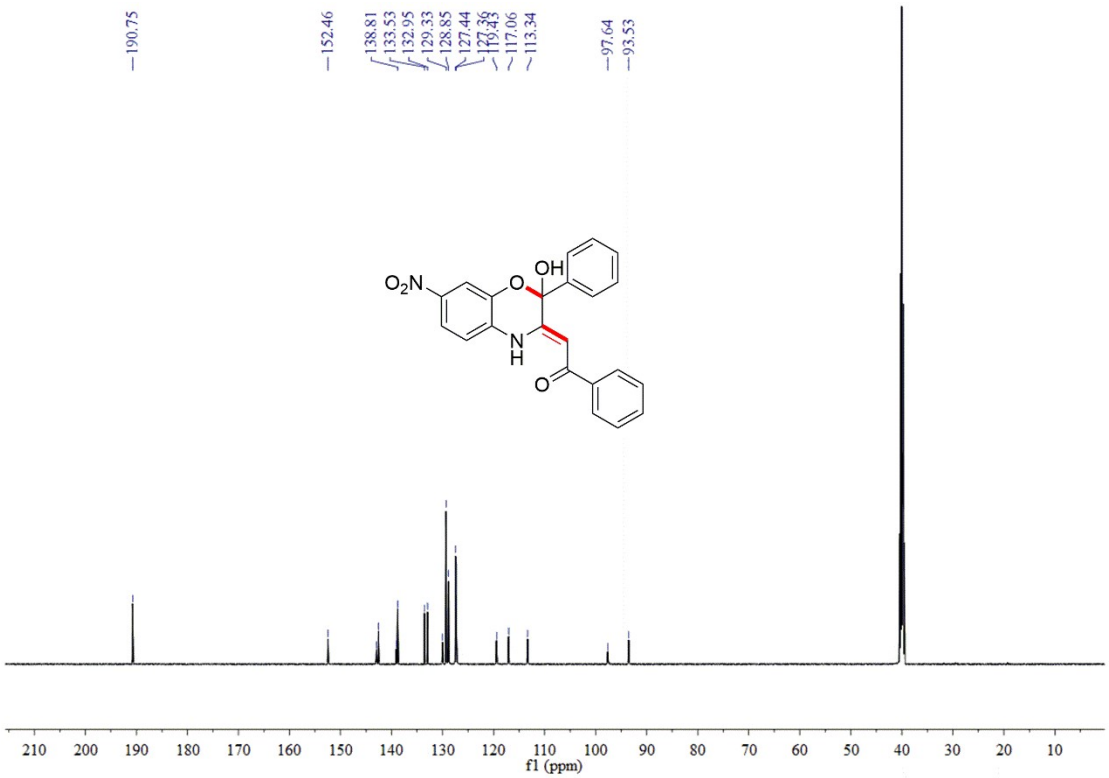
**(*Z*)-2-(7-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3h): $^{13}$C NMR**



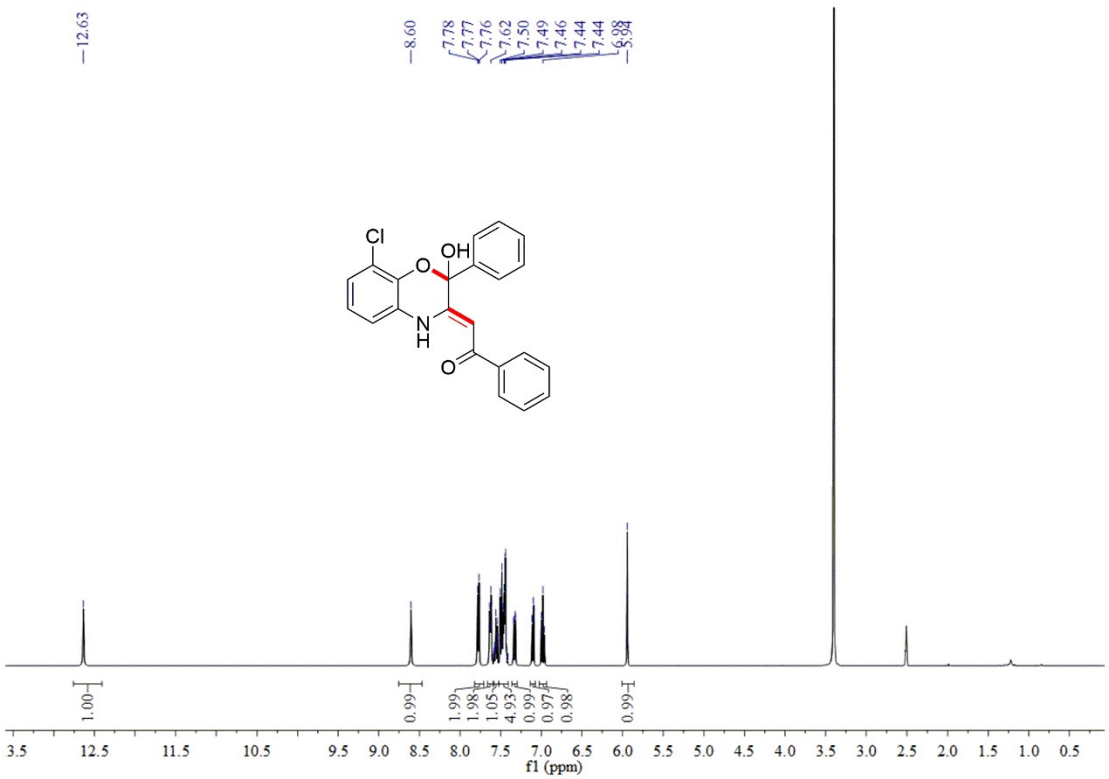

**(*Z*)-2-(2-hydroxy-7-nitro-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3i): $^{1}$H NMR**



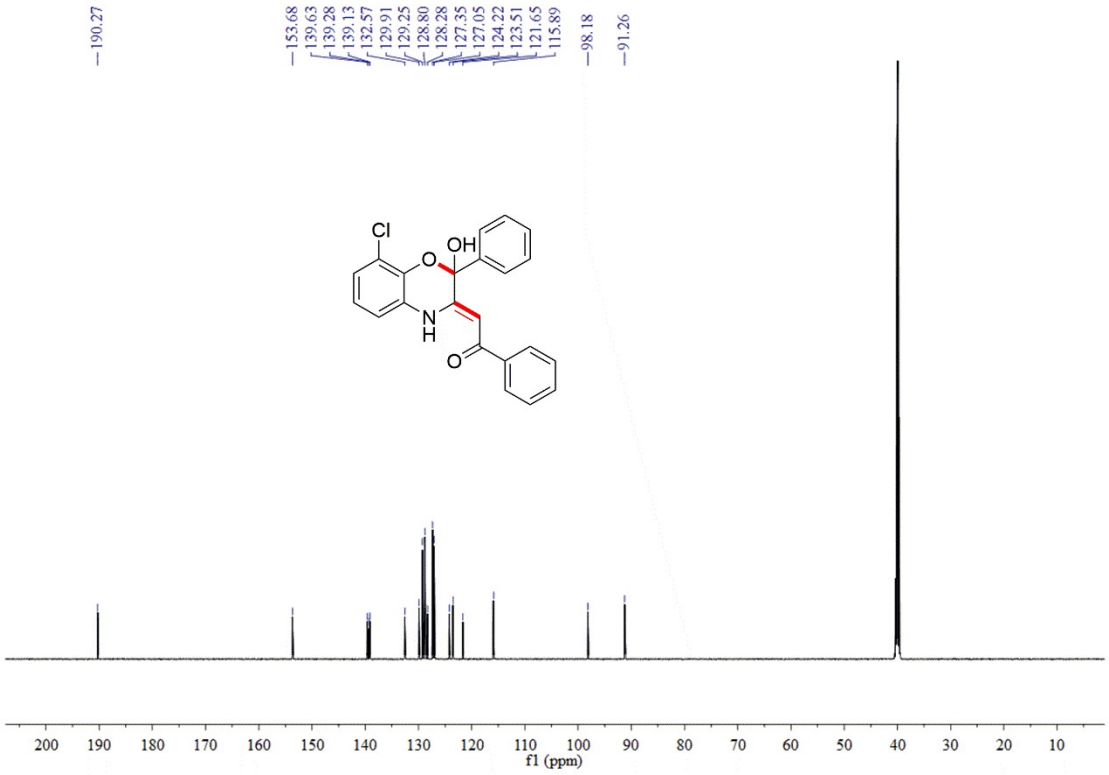
**(*Z*)-2-(2-hydroxy-7-nitro-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3i): $^{13}$C NMR**



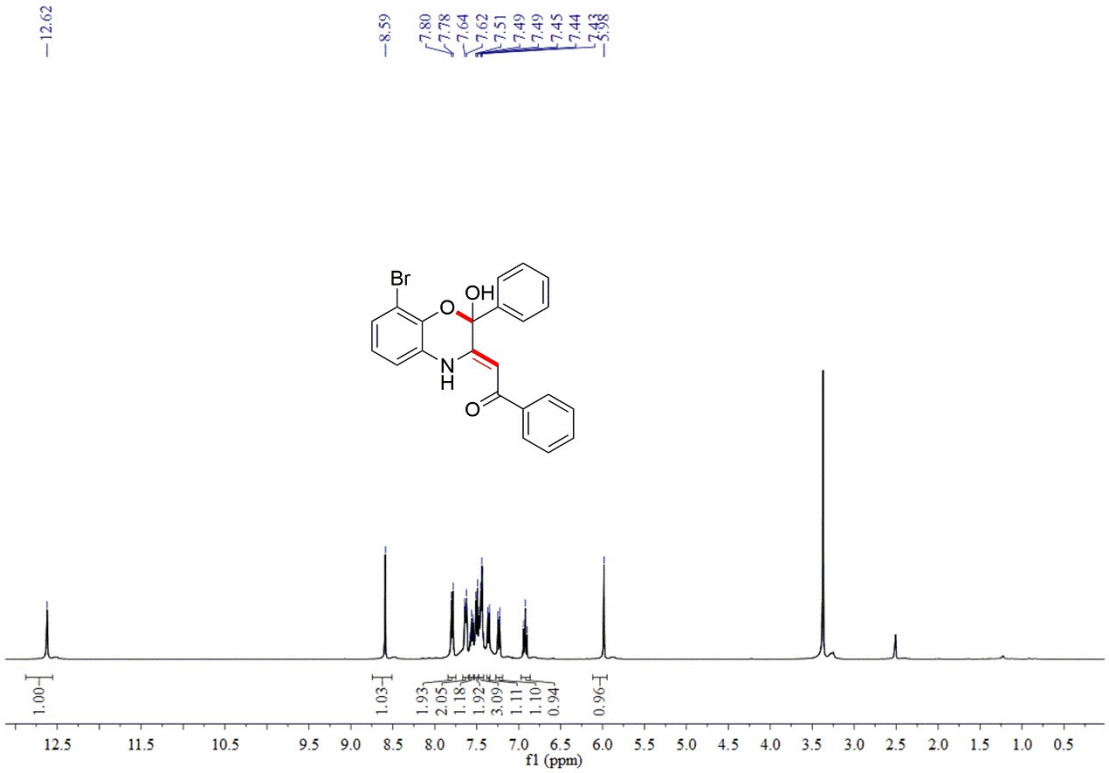

**(*Z*)-2-(8-chloro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3j): $^{1}$H NMR**



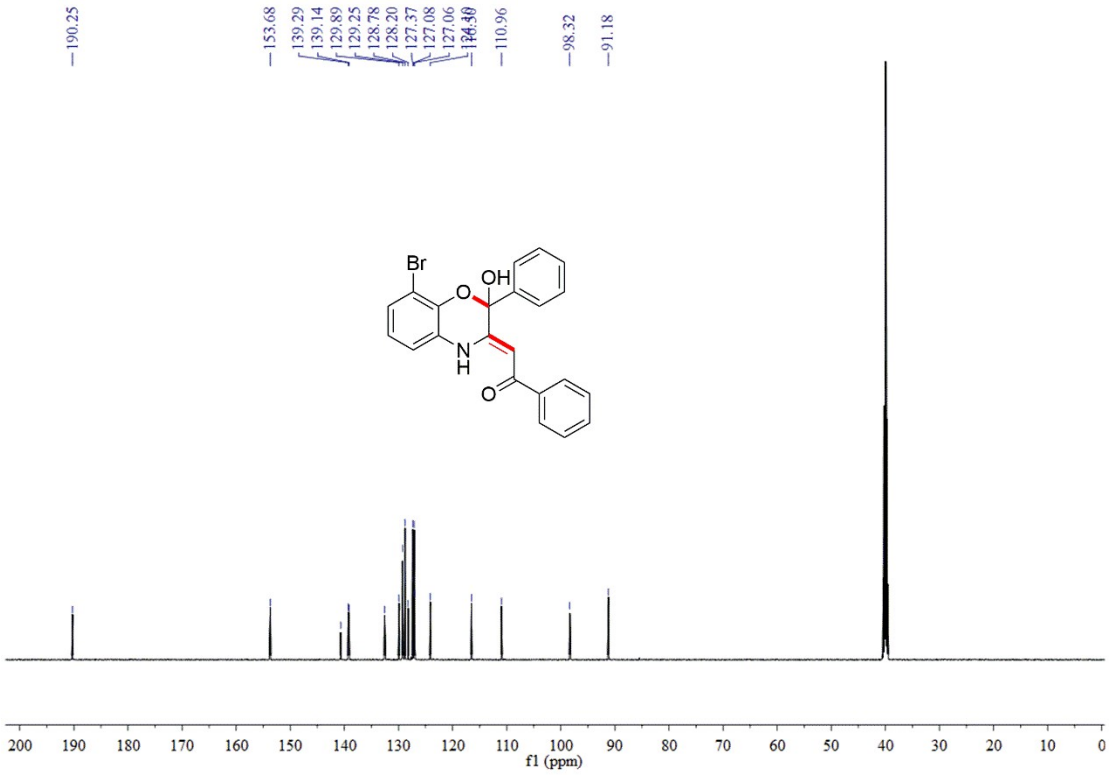
**(*Z*)-2-(8-chloro-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3j): $^{13}$C NMR**



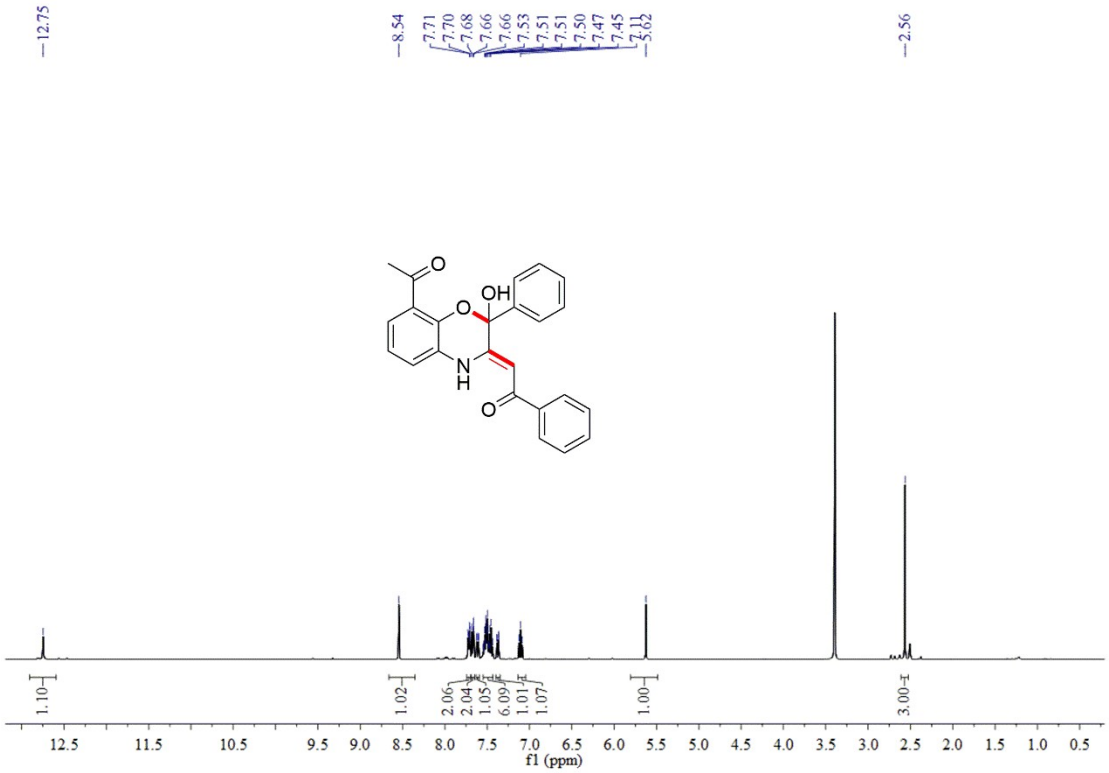

**(*Z*)-2-(8-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3k): $^{1}$H NMR**



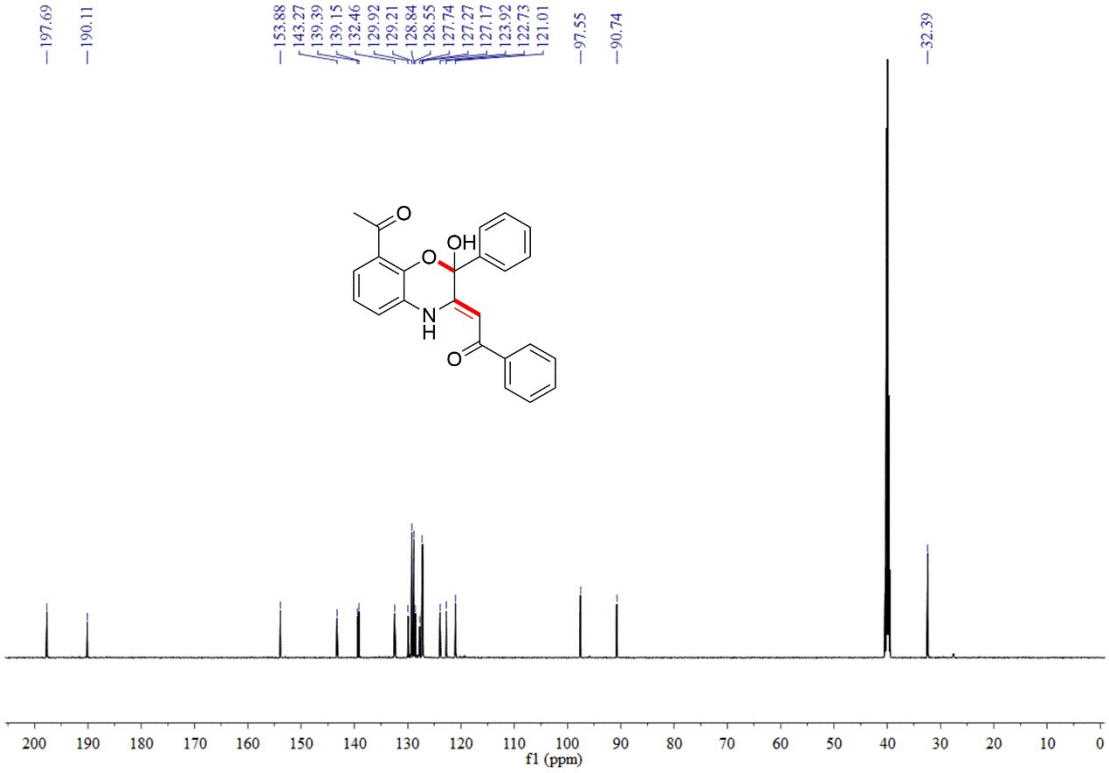
**(*Z*)-2-(8-bromo-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3k): $^{13}$C NMR**



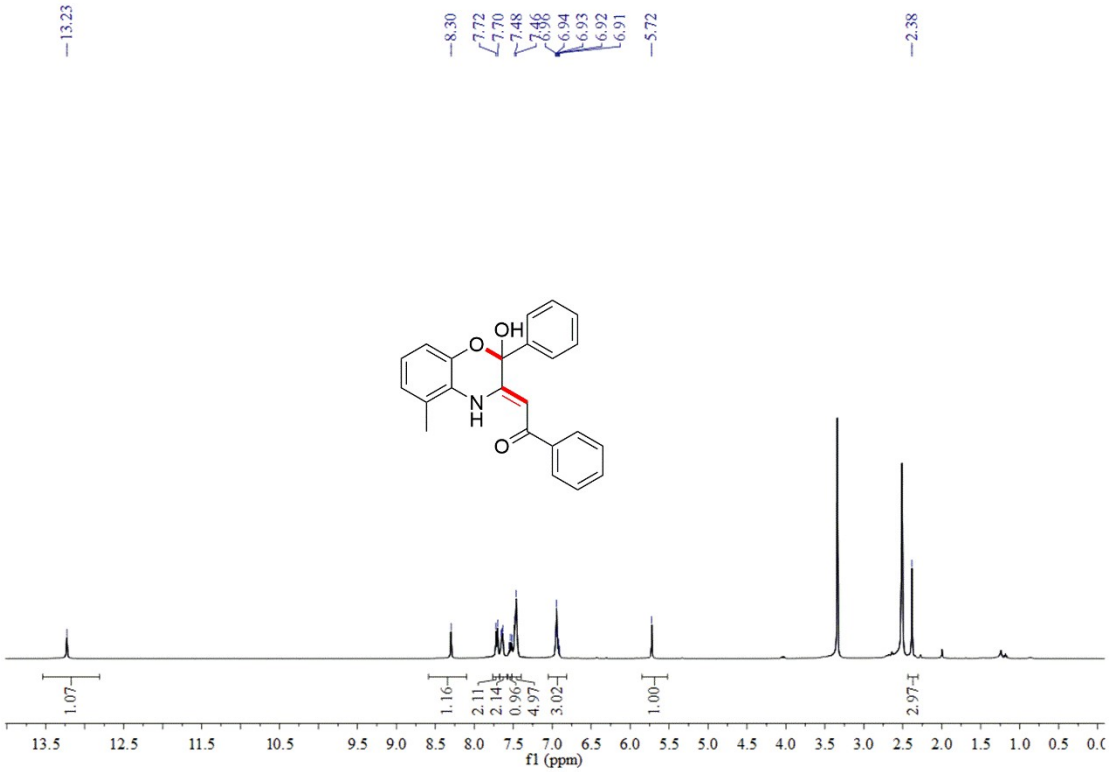

**(*Z*)-2-(8-acetyl-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3l): $^{1}$H NMR**



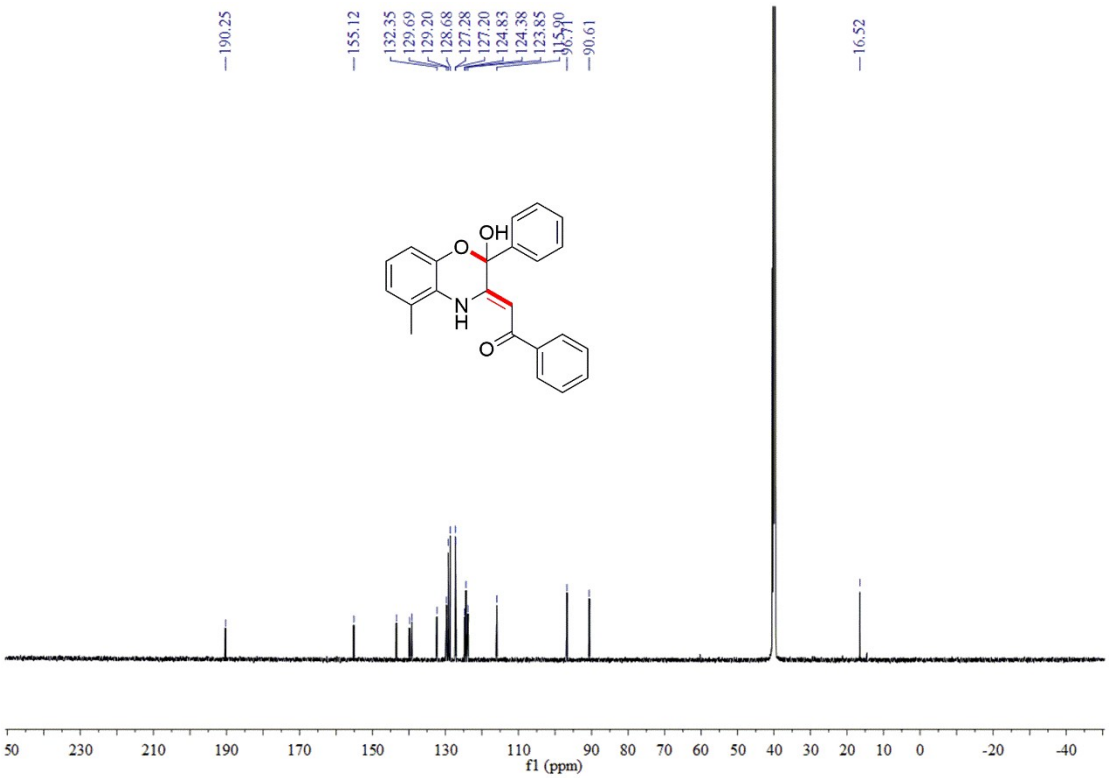
**(*Z*)-2-(8-acetyl-2-hydroxy-2-phenyl-2*H*-benzo[b][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3l): $^{13}$C NMR**



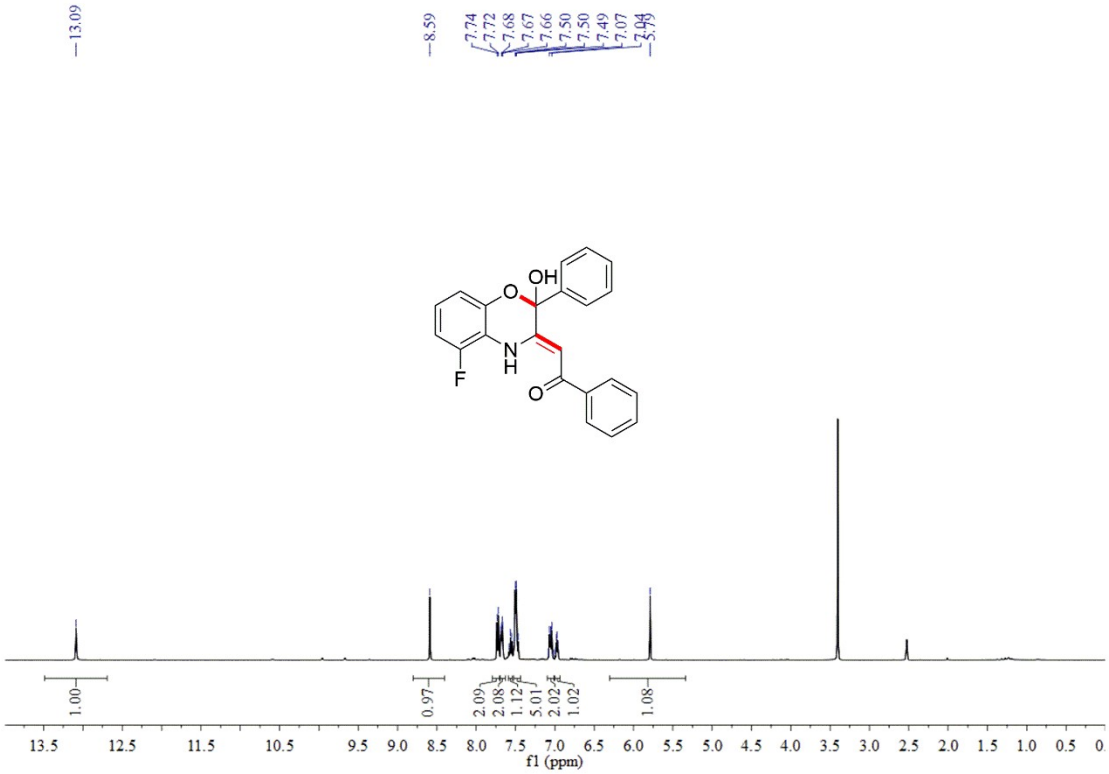

**(Z)-2-(2-hydroxy-5-methyl-2-phenyl-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)-1-phenylethan-1-one (3m): $^{1}$H NMR**



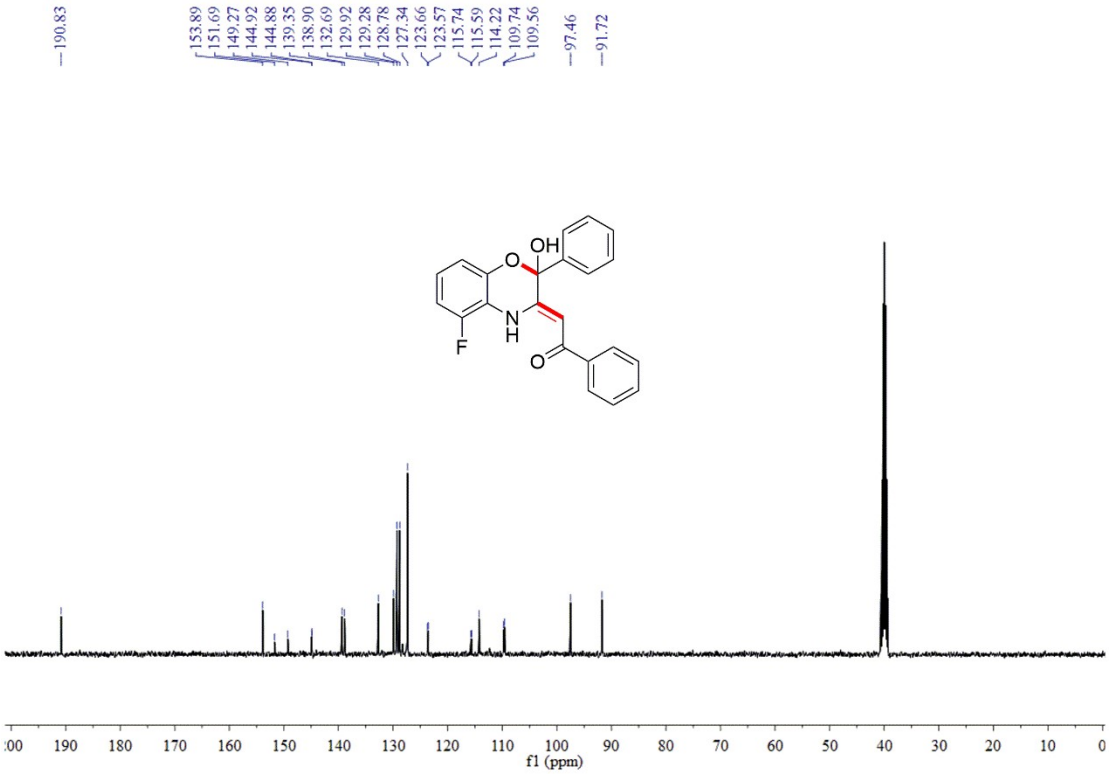
**(Z)-2-(2-hydroxy-5-methyl-2-phenyl-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)-1-phenylethan-1-one (3m): $^{13}$C NMR**



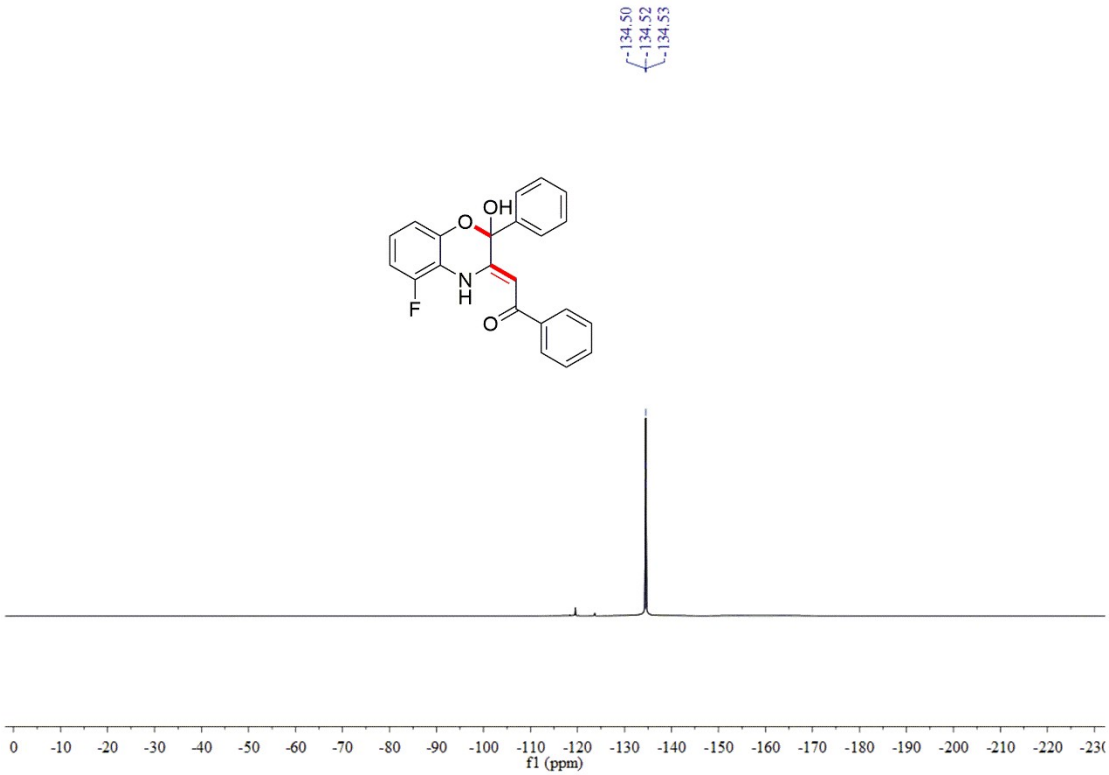

***Z*-2-(5-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3n): $^{1}$H NMR**



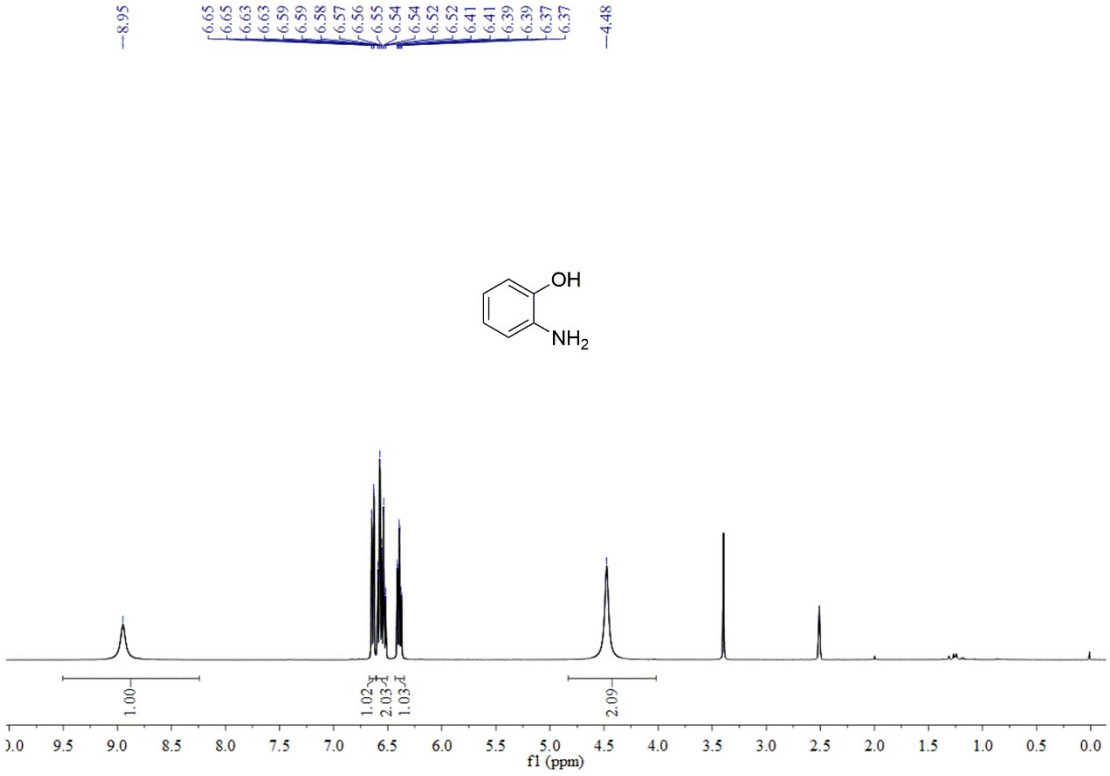
***Z*-2-(5-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3n): $^{13}$C NMR**



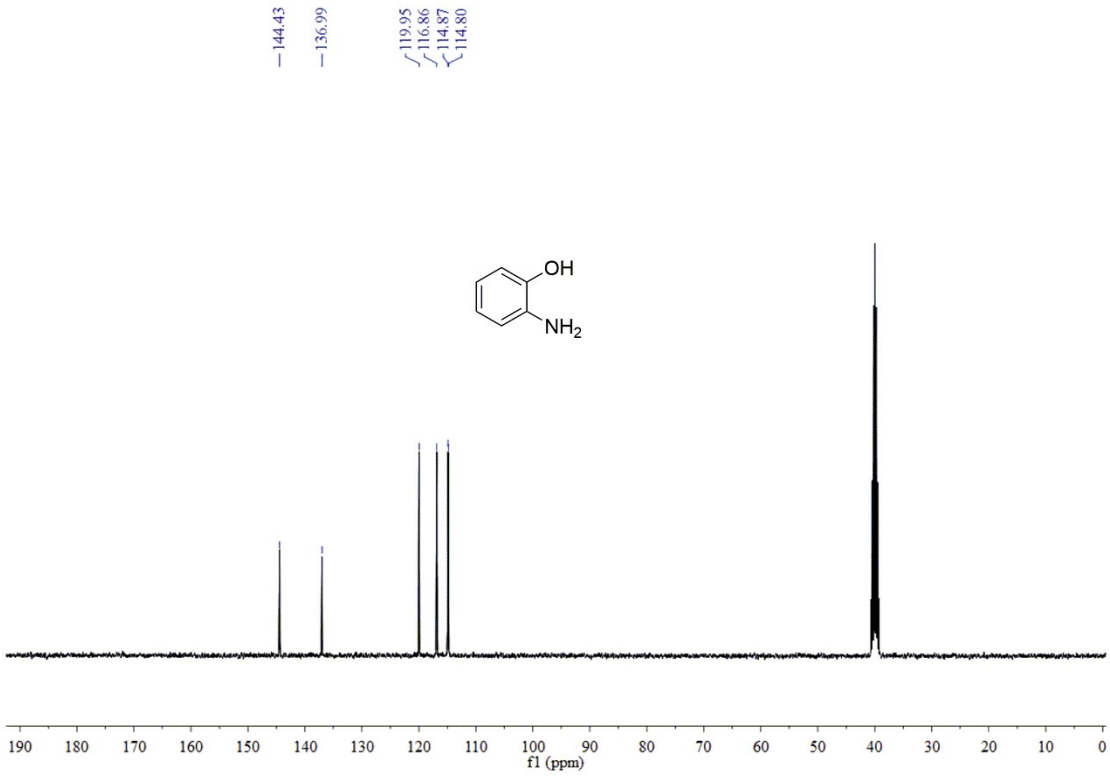

***Z*-2-(5-fluoro-2-hydroxy-2-phenyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-ylidene)-1-phenylethan-1-one (3n): $^{19}$F NMR**



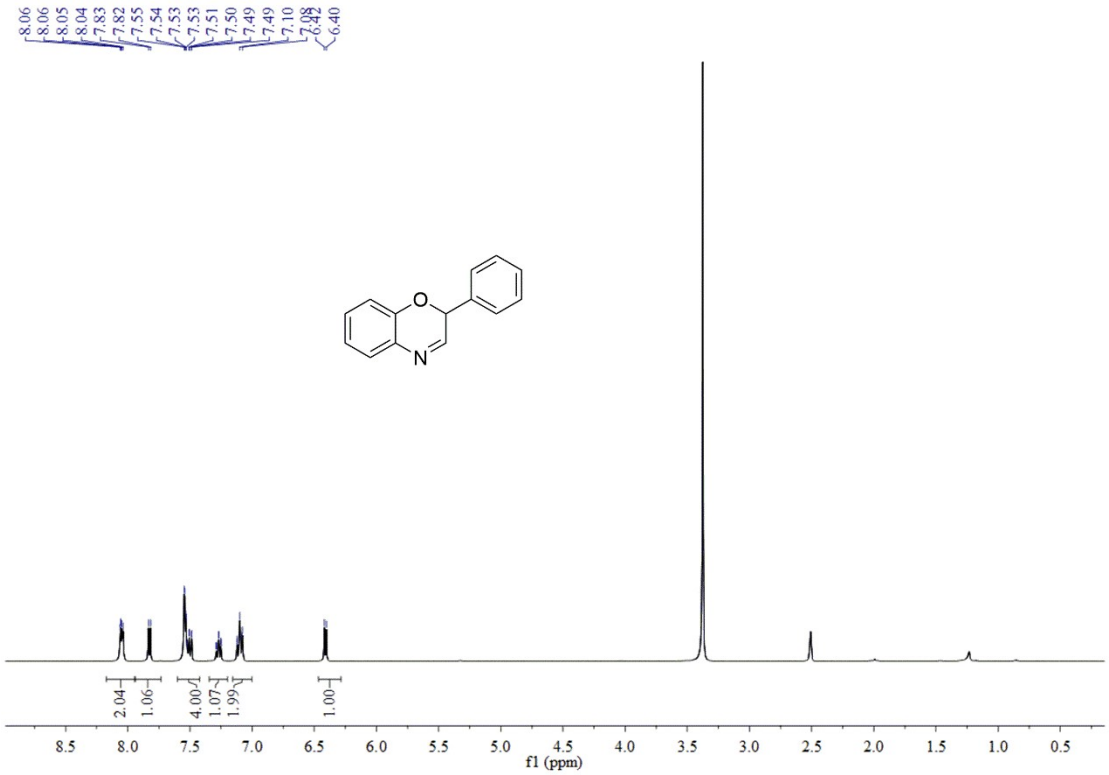
**2-aminophenol (E): $^{1}$H NMR**



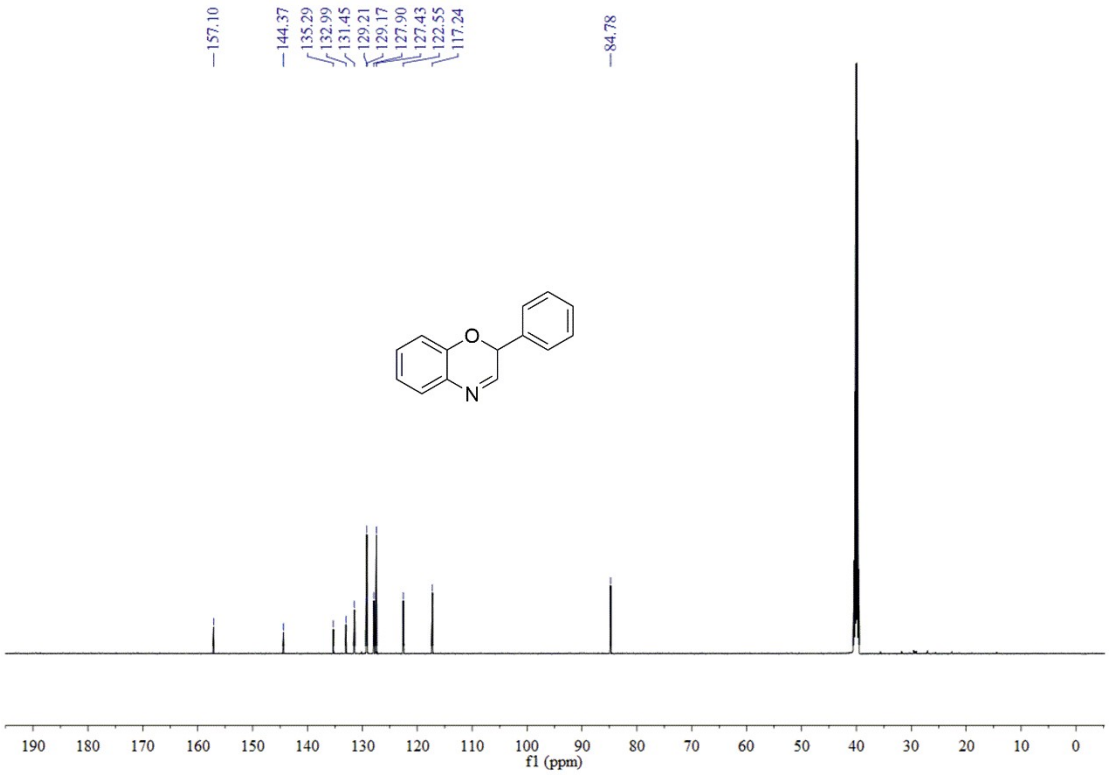

**2-aminophenol (E): $^{13}$C NMR**



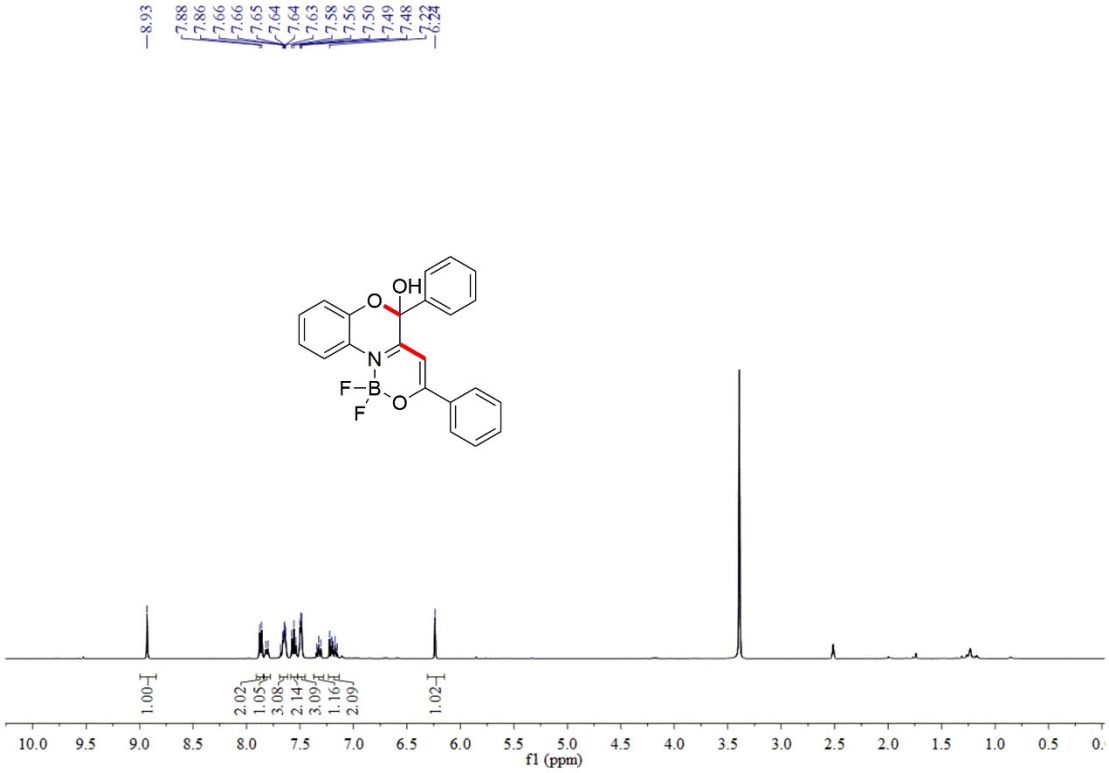
**2-phenyl-2*H*-benzo[b][1,4]oxazine (F): $^{1}$H NMR**



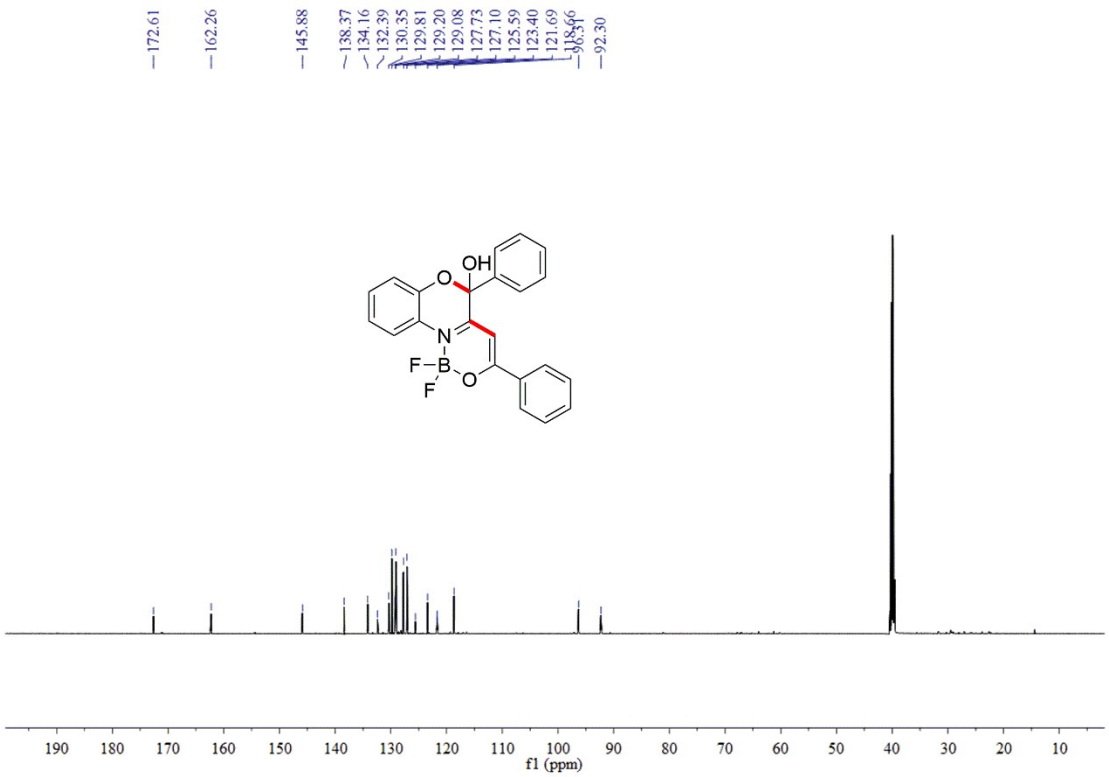

**2-phenyl-2*H*-benzo[b][1,4]oxazine (F): $^{13}$C NMR**



**(*Z*)-3-(2-((difluoroboranyl)oxy)-2-phenylvinyl)-2-phenyl-2*H*-benzo[b][1,4]oxazin-2-ol: $^{1}$H NMR**




**(*Z*)-3-(2-((difluoroboranyl)oxy)-2-phenylvinyl)-2-phenyl-2*H*-benzo[b][1,4]oxazin-2-ol: $^{13}$C NMR**



**(*Z*)-3-(2-((difluoroboranyl)oxy)-2-phenylvinyl)-2-phenyl-2*H*-benzo[b][1,4]oxazin-2-ol: $^{11}$B NMR**