Electronic Supplementary Information
(File. 1)

Chemical generation of *o*-quinone monoimines for the rapid construction of 1,4-benzoxazine derivatives

Naganjaneyulu Bodipati and Rama Krishna Peddinti*

Department of Chemistry, Indian Institute of Technology, Roorkee-247 667, Uttarakhand, India.

Table of Contents

General Information

Unless otherwise noted, chemicals were purchased from Sigma-Aldrich and Acros Organics at the highest purity grade available and were used without further purification. Solvents were distilled by using P_2O_5 and sodium benzophenone ketyl radical. All Diels-Alder reactions were carried out under dry conditions employing oven- and flame-dried glassware with dry solvents.

NMR spectra were recorded on Brüker AMX-500 instrument using TMS as the internal standard with chemical shifts given in ppm relative to TMS. High-resolution mass spectra (HRMS) were recorded on Waters-HAB213, microOTOF-Q II-10262 and Jeol JMS600H spectrometers. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dt = doublet of triplet, qd = quartet of doublet, m = multiplet, br = broad.

Experimental Procedures

General procedure for compounds 7a-10a

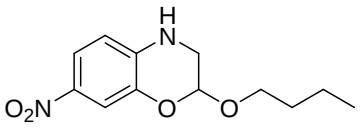
A solution of DAIB (1.2 equiv.) in dichloromethane (2 mL) was added drop wise to a solution of 5-nitro-2-aminophenol (**1a,** 1 mmol) and alkyl vinyl ether **3** or **4** or **6** (5 mmol) or phenyl vinyl sulphide (**5**, 2 mmol) in dichloromethane (6 mL) at 0 ^{o}C. The reaction mixture was stirred at the same temperature. After completion the reaction the solvent was removed under reduced pressure and the crude reaction mixture was loaded directly on silica gel column (100-200 mesh). The product was eluted by using ethyl acetate in hexanes.

General procedure for compounds 7b-f - 10b-f

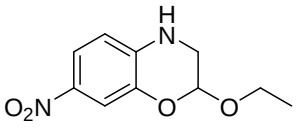
A solution of DAIB (1.2 equiv.) in tetrahydrfuran (4 mL) was added drop wise to a mixture of 2-aminophenol derivative **1b-1f** (1 mmol), potassium bicarbonate (3 mmol) and alkyl vinyl ether **3** or **4** or **6** (5 mmol) or phenyl vinyl sulphide (**5**, (2 mmol) in tetrahydrfuran (2 mL) at 0 ^{o}C. The reaction mixture was stirred at the same temperature. After completion the reaction the solvent was removed under reduced pressure and the crude reaction mixture was loaded directly on silica gel column (100-200 mesh). The product was eluted by using ethyl acetate in hexanes.

Characterization of benzoxazine derivatives

Benzoxazine derivative 7a: Reaction time 3 h; m.p. 62-63 ^{o}C; IR (film) ν_{max}: 3324, 3050, 2947, 1669, 1602, 1515, 1453, 1288, 1160, 966, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.77 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.72 (d, *J* = 2.5 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 5.27 (t, *J* = 2.0 Hz, 1H), 4.53 (br, 1H), 3.85 (td, *J* = 3.0, 6.5 Hz, 1H), 3.62 (td, *J* = 3.0, 6.5 Hz 1H), 3.52 (td, *J* = 2.5, 12.5 Hz, 1H), 3.47 (qd, *J* = 2.0, 12.0 Hz, 1H), 1.56-1.51 (m, 2H), 1.31-1.24 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.1, 138.9, 138.4, 119.3, 113.5, 112.5, 93.6, 68.3, 44.2, 31.3, 19.0, 13.6; HRMS (ES+, *m/z*), calcd for $C_{12}H_{16}N_2O_4$ $[M+Na]^+$: 275.1008, found 275.1002.

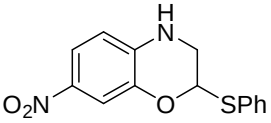


Benzoxazine derivative 8a: Reaction time 2 h; IR (film) ν_{max}: 3386, 3080, 2963, 2868, 1664, 1599, 1537, 1414, 1269, 1111, 1021, 967, 874 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 6.52 (d, *J* = 9.0 Hz, 1H), 5.25 (t, *J* = 2.0 Hz, 1H), 4.93 (br, 1H), 3.87 (dq, *J* = 3.0, 7.0 Hz, 1H), 3.67 (dq, *J* = 2.5, 7.0 Hz, 1H), 3.49 (dt, *J* = 2.0, 14.5 Hz, 1H), 3.43 (dq, *J* = 2.5, 14.0 Hz, 1H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125

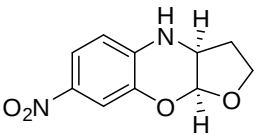


MHz): δ 140.3, 138.7, 138.1, 119.3, 113.3, 112.4, 93.5, 64.1, 44.0, 14.8; HRMS (ES+, *m/z*), calcd for $C_{10}H_{12}N_2O_4$ $[M+Na]^+$: 247.0695, found 247.0699.

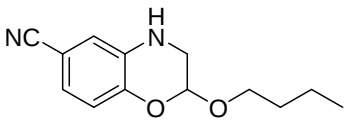
Benzoxazine derivative 9a: Reaction time 4 h; IR (film) ν_{max}: 3382, 3021, 2804, 1610, 1517, 1478, 1438, 1264, 1169, 971, 827, 708 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.81 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.75 (d, *J* = 2.5 Hz, 1H), 7.53-7.52 (m, 2H), 7.37-7.33 (m, 3H), 6.61 (d, *J* = 9.0 Hz, 1H), 5.69 (t, *J* = 3.0 Hz, 1H), 4.68 (br, 1H), 3.86 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.66 (dt, *J* = 3.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.9, 142.3, 133.1, 117.0, 115.1, 110.4, 95.0, 64.4, 44.0, 15.0; HRMS (ES+, *m/z*), calcd for $C_{14}H_{12}N_2O_3S$ $[M+Na]^+$: 311.0467, found 311.0468.



Benzoxazine derivative 10a:[1] Reaction time 0.5 h; m.p. 86-87 °C; IR (film) ν_{max}: 3356, 3051, 2935, 2869, 1673, 1600, 1529, 1485, 1421, 1254, 1020, 972, 878 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 6.26 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.07 (d, *J* = 2.5 Hz, 1H), 5.23 (d, *J* = 9.0 Hz, 1H), 3.90 (d, *J* = 3.5 Hz, 1H), 2.67-2.59 (m, 2H), 2.52-2.49 (m, 1H), 0.86-0.80 (m, 1H), 0.32-0.25 (m, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 140.6, 138.9, 136.4, 120.2, 112.5, 112.0, 96.1, 67.7, 52.9, 30.5; HRMS (ES+, *m/z*), calcd for $C_{10}H_{10}N_2O_4$ $[M+Na]^+$: 245.0539, found 245.0537.

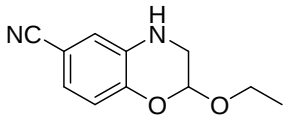


Benzoxazine derivative 7b: Reaction time 3 h; IR (film) ν_{max}: 3380, 3054, 2871, 2958, 2224, 1606, 1586, 1505, 1461, 1308, 1214, 1089, 1023, 897, 808 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.97 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.24 (t, *J* = 2.5 Hz, 1H), 4.02 (br, 1H), 3.84 (td, *J* = 6.5, 9.5 Hz, 1H), 3.62 (td, *J* = 6.5, 9.5 Hz, 1H), 3.39-3.32 (m, 2H), 1.57 1.51 (m, 2H), 1.33-1.24 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C

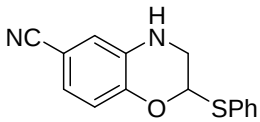


NMR ($CDCl_3$, 125 MHz): δ 145.2, 133.7, 123.4, 119.5, 118.5, 117.9, 104.6, 94.9, 68.6, 44.1, 31.4, 19.0, 13.7; HRMS (FAB+, *m/z*), calcd for $C_{13}H_{16}N_2O_2$ $[M]^+$: 232.1212, found 232.1216.

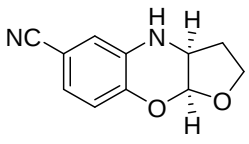
Benzoxazine derivative 8b:[1] Reaction time 2 h; IR(film) ν_{max}: 3387, 3064, 2977, 2917, 2223, 1606, 1504, 1449, 1373, 1313, 1207, 1119, 1087, 937, 881 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.97 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.26 (t, *J* = 2.5 Hz, 1H), 3.92 (qd, *J* = 7.0, 9.5 Hz, 1H), 3.69 (qd, *J* = 7.0 10.0 Hz, 1H), 3.91-3.32 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.2, 133.7, 123.4, 119.5, 118.5, 117.9, 104.6, 94.8, 64.4, 44.1, 15.0; HRMS (FAB+, *m/z*), calcd for $C_{11}H_{12}N_2O_2$ $[M+H]^+$: 205.0977, found 205.0972.



Benzoxazine derivative 9b:[1] Reaction time 4 h; IR (film) ν_{max}: 3391, 3054, 2923, 1588, 1500, 1445, 1338, 1299, 1028, 932, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.52-7.51 (m, 2H), 7.37-7.31 (m, 3H), 7.01 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.70 (t, *J* = 3.0 Hz,1H), 3.75 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.57 (dd, *J* = 3.5, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.0, 133.5, 132.8, 132.5, 129.1, 128.1, 123.6, 119.4, 118.5, 118.5, 105.3, 81.9, 29.4; HRMS (FAB+, *m/z*), calcd for $C_{15}H_{12}N_2OS$ $[M+H]^+$: 269.0749, found 269.0746.

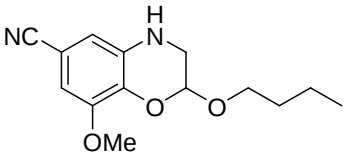


Benzoxazine derivative 10b: Reaction time 1 h; IR (film) ν_{max}: 3357, 3062, 2916, 1602, 1585, 1502, 1316, 1291, 1259, 1108, 902, 851 cm^{-1} ; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.98 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 5.37 (d, *J* = 4.0 Hz, 1H), 4.30 (dt, *J* =



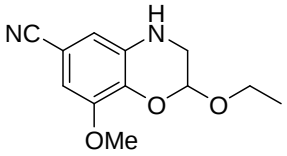
4.0, 9.0 Hz, 1H), 4.20 (br, 1H), 4.09-4.04 (m, 2H), 2.25- 2.18 (m, 1H), 1.89 (qd, *J* = 9.0, 12.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.1, 131.2, 123.2, 119.4, 117.8, 117.3, 104.6, 96.4, 68.0, 53.8, 29.3; HRMS (ESI, *m/z*), calcd for $C_{11}H_{10}N_2O_2$ $[M+Na]^+$: 225.064, found 225.0652.

Benzoxazine derivative 7c:[1] Reaction time 3 h; IR (film) ν_{max}: 3369, 3073, 2961, 2933, 2221, 1652, 1602, 1595, 1495, 1456, 1372 ,1362, 1223, 1030, 936, 862, 765 cm^{-1}; ^{1}H NMR



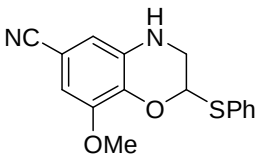
($CDCl_3$, 500 MHz): δ 6.58 (s, 2H), 5.34 (t, *J* = 2.5 Hz, 1H), 3.85-3.82 (m, 1H), 3.84 (s, 3H), 3.64 (td, *J* = 6.5, 10.0 Hz, 1H), 3.38-3.32 (m, 2H), 1.56-1.48 (m, 2H), 1.27-1.21 (m, 2H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.2, 134.2, 134.1, 119.5, 113.0, 105.7, 103.9, 94.4, 68.5, 56.1, 44.0, 31.3, 19.0, 13.6; HRMS (FAB+, *m/z*), calcd for $C_{14}H_{18}N_2O_3$ $[M+H]^+$: 263.1396, found 263.1398.

Benzoxazine derivative 8c:[1] Reaction time 2 h; IR (film) ν_{max}: 3365, 3037, 2958, 2930, 2221, 1658, 1602, 1588, 1496, 1465, 1377 ,1352, 1241, 1211, 1176, 1083, 1029, 936, 877, 796 cm^{-1};



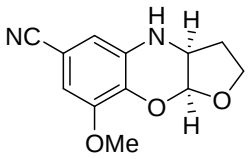
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.56 (s, 2H), 5.33 (t, *J* = 2.5 Hz, 1H), 3.88 (qd, *J* = 7.0, 10.0 Hz, 1H), 3.82 (s, 3H), 3.69 (qd, *J* = 7.0, 10.0 Hz, 1H), 3.35-3.28 (m, 2H), 1.17 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.1, 134.2, 134.0, 119.5, 112.9, 105.6, 103.8, 94.4, 64.3, 56.1, 43.9, 14.9; HRMS (FAB+, *m/z*), calcd for $C_{12}H_{14}N_2O_3$ $[M+H]^+$: 235.1083, found 235.1088.

Benzoxazine derivative 9c:[1] Reaction time 4 h; IR (film) ν_{max}: 3381, 3063, 2954, 1593, 1500, 1454, 1331, 1295, 1021, 932, 800



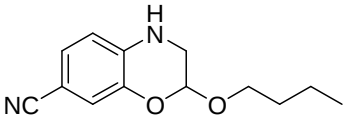
cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55-7.52(m, 2H), 7.32-7.18 (m, 2H), 6.62-6.59 (m, 2H), 5.75 (t, *J* = 2.5 Hz, 1H), 4.23 (br, 1H), 3.83 (s, 3H), 3.71 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.56 (dd, *J* = 2.5, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.7, 134.0, 133.8, 132.8, 132.6, 129.0, 128.0, 119.4, 112.6, 106.0, 104.5, 81.9, 56.2, 45.0; HRMS (FAB+, *m/z*), calcd for $C_{16}H_{14}N_2O_2S$ $[M+H]^+$: 299.0854, found 299.0852.

Benzoxazine derivative 10c:[1] Reaction time 1 h; IR (film) ν_{max}:



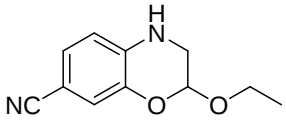
3398, 3087, 2988, 2223, 1595, 1521, 1493, 1352, 1239, 1123, 1053, 907, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.58 (d, *J* = 1.5 Hz, 1H), 6.55 (d, *J* = 1.5 Hz, 1H), 5.33 (d, *J* = 3.5 Hz, 1H), 4.28 (dt, *J* = 4.0, 9.0 Hz, 1H), 4.11-4.00 (m, 2H), 3.82 (s, 3H), 2.22-2.16 (m, 1H), 1.86 (qd, *J* =9.0, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.9, 133.8, 131.9, 119.5, 111.5, 105.2, 104.0, 96.1, 67.9, 56.0, 53.8, 29.3; HRMS (FAB+, *m/z*), calcd for $C_{12}H_{12}N_2O_3$ $[M+H]^+$: 233.0926, found 233.0921.

Benzoxazine derivative 7d: Reaction time 8 h; IR (film) ν_{max}:

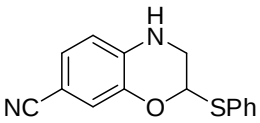


3380, 3054, 2871, 2958, 2224, 1606, 1586, 1505, 1461, 1308, 1214, 1089, 1023, 897, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.24 (t, *J* = 2.5 Hz, 1H), 4.02 (br, 1H), 3.84 (td, *J* = 6.5, 9.5 Hz, 1H), 3.62 (td, *J* = 6.5, 9.5 Hz, 1H), 3.39-3.32 (m, 2H), 1.57 1.51 (m, 2H), 1.33-1.24 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.2, 133.7, 123.4, 119.5, 118.5, 117.9, 104.6, 94.9, 68.6, 44.1, 31.4, 19.0, 13.7; HRMS (FAB+, *m/z*), calcd for $C_{13}H_{16}N_2O_2$ $[M+H]^+$: 233.129, found 233.1294.

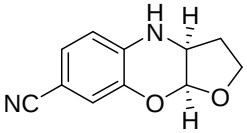
Benzoxazine derivative 8d: Reaction time 7 h; IR(film) ν_{max}: 3387, 3064, 2977, 2917, 2223, 1606, 1504, 1449, 1373, 1313, 1207, 1119, 1087, 937, 881 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.26 (t, *J* = 2.5 Hz, 1H), 3.92 (qd, *J* = 7.0, 9.5 Hz, 1H), 3.69 (qd, *J* = 7.0, 10.0 Hz, 1H), 3.91-3.32 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.2, 133.7, 123.4, 119.5, 118.5, 117.9, 104.6, 94.8, 64.4, 44.1, 15.0; HRMS (FAB+, *m/z*), calcd for $C_{11}H_{12}N_2O_2$ $[M+H]^+$: 205.0977, found 205.0972.



Benzoxazine derivative 9d:[1] Reaction time 8 h; IR (film) ν_{max}: 3391, 3054, 2923, 1588, 1500, 1445, 1338, 1299, 1028, 932, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52-7.51 (m, 2H), 7.37-7.31 (m, 3H), 7.01 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.70 (t, *J* = 3.0 Hz,1H), 3.75 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.57 (dd, *J* = 3.5, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.0, 133.5, 132.8, 132.5, 129.1, 128.1, 123.6, 119.4, 118.5, 118.5, 105.3, 81.9, 29.4; HRMS (FAB+, *m/z*), calcd for $C_{15}H_{12}N_2OS$ $[M+H]^+$: 269.0749, found 269.0752.

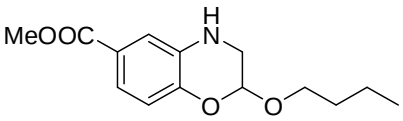


Benzoxazine derivative 10d: Reaction time 4 h; IR (film) ν_{max}: 3357, 3062, 2916, 1602, 1585, 1502, 1316, 1291, 1259, 1108, 902, 851 cm^{-1} ; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.98 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 5.37 (d, *J* = 4.0 Hz, 1H), 4.30 (dt, *J* = 4.0, 9.0 Hz, 1H), 4.20 (br, 1H), 4.09-4.04 (m, 2H), 2.25- 2.18 (m, 1H), 1.89 (qd, *J* = 9.0, 12.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.1, 131.2, 123.2, 119.4, 117.8, 117.3,

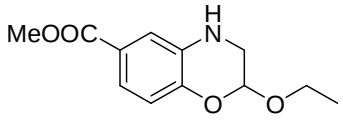


104.6, 96.4, 68.0, 53.8, 29.3; HRMS (FAB+, *m/z*), calcd for $C_{11}H_{10}N_2O_2$ $[M+H]^+$: 203.0821, found 203.0826.

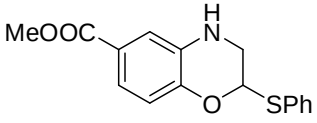
Benzoxazine derivative 7e:[1] Reaction time 3 h; IR (film) ν_{max}: 3356, 2988, 2943, 2360, 1699, 1597, 1488, 1439, 1307, 1208, 1113, 1050, 983, 846, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.40 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.23 (t, *J* = 3.0 Hz, 1H), 3.87-3.83 (m, 1H), 3.83 (s, 3H), 3.61 (td, *J* = 7.0, 10.0 Hz, 1H), 3.37-3.30 (m, 2H), 1.57-1.52 (m, 2H), 1.31-1.24 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.1, 145.8, 132.7, 123.4, 121.3, 117.2, 116.9, 95.1, 68.4, 51.8, 44.4, 31.4, 19.1, 13.7; HRMS (FAB+, *m/z*), calcd for $C_{14}H_{19}NO_4$ $[M+H]^+$: 266.1392, found 266.1398.



Benzoxazine derivative 8e: Reaction time 2 h; IR (film) ν_{max}: 3365, 2992, 2363, 1696, 1592, 1479, 1438, 1208, 1113, 1050, 983, 846, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.41 (dd, *J* = 2.0, 9.5 Hz, 1H), 7.33 (dd, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.25 (t, *J* = 2.5 Hz, 1H), 3.95-3.89 (m, 1H), 3.84 (s, 3H), 3.72-3.65 (m, 1H), 3.38-3.31 (m, 2H), 1.24 (br, 1H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 145.8, 132.6, 123.5, 121.3, 117.2, 116.9, 95.0, 64.2, 51.8, 44.4, 15.0; HRMS (FAB+, *m/z*), calcd for $C_{12}H_{15}NO_4$ $[M+H]^+$: 238.1079, found 238.1081.

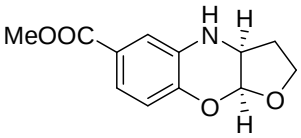


Benzoxazine derivative 9e:[1] Reaction time 5 h; IR (film) ν_{max}: 3355, 2982, 2361, 1699, 1597, 1421, 1208, 1052, 974, 841, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.59-7.55 (m, 2H),

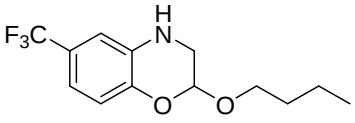


7.48 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.38-7.32 (m, 4H), 6.90 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.77 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.59 (dd, *J* = 3.5, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 145.3, 133.2, 132.5, 132.3, 129.0, 127.8, 123.9, 121.3, 117.5, 117.2, 82.0, 51.8, 45.2; HRMS (FAB+, *m/z*), calcd for $C_{16}H_{15}NO_3S$ $[M+H]^+$: 302.0851, found 302.0855.

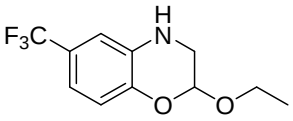
Benzoxazine derivative 10e:[1] Reaction time 1 h; IR (film) ν_{max}: 3362, 2991, 1721, 1696, 1594, 1479, 1438, 1208, 1050, 983, 846, 726 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 5.37 (d, *J* = 4.0 Hz, 1H), 4.26 (dt, *J* = 4.0, 9.0 Hz, 1H), 4.06-4.00 (m, 2H), 3.83 (s, 3H), 2.19-2.10 (m, 1H), 1.87 (qd, *J* = 9.0, 12.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.03, 145.5, 130.3, 123.6, 120.8, 116.7, 115.8, 96.5, 67.9, 54.0, 51.8, 29.2; HRMS (FAB+, *m/z*), calcd for $C_{12}H_{13}NO_4$ $[M+H]^+$: 236.0923, found 236.0924.



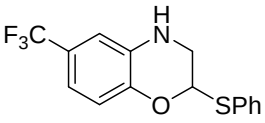
Benzoxazine derivative 7f:[1] Reaction time 3 h; IR (film) ν_{max}: 3398, 3087, 2988, 2853, 2223, 1595, 1521, 1493, 1407, 1372, 1352, 1239, 1172, 1123, 1053, 955, 907, 803 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.94 (dd, *J* = 1.5, 7.0 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 5.23 (t, *J* = 2.5 Hz, 1H), 3.86 (td, *J* = 7.0, 10.0 Hz, 1H), 3.63 (td, *J* = 7.0, 10.0 Hz, 1H), 3.39-3.32 (m, 2H), 1.60-1.54 (m, 2H), 1.34-1.27 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.0, 133.0, 125.4, 123.6, 117.3, 116.1, 112.6, 94.8, 68.5, 44.3, 31.5, 19.1, 13.7; HRMS (FAB+, *m/z*), calcd for $C_{13}H_{16}F_3NO_2$ $[M+H]^+$: 276.1211, found 276.1216.



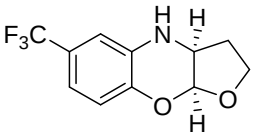
Benzoxazine derivative 8f:[1] Reaction time 3 h; IR (film) ν_{max}: 3387, 3066, 2983, 1618, 1594, 1498, 1334, 1207, 1118, 939, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.94 (dd, *J* = 1.5, 8.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 5.25 (t, *J* = 2.5 Hz, 1H), 3.92 (qd, *J* = 7.5, 10.0 Hz, 1H), 3.69 (qd, *J* = 7.0, 9.5 Hz, 1H), 3.37-3.31 (m, 2H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.0, 133.0, 125.4, 123.6, 117.2, 116.1, 112.6, 94.6, 64.2, 44.3, 15.0; HRMS (FAB+, *m/z*), calcd for $C_{11}H_{12}F_3NO_2$ $[M+H]^+$: 248.0898, found 248.0892.



Benzoxazine derivative 9f: Reaction time 6 h; IR (film) ν_{max}: 3362, 3073, 2940, 2841, 1613, 1486, 1465, 1211, 1062, 865, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.56-7.53 (m, 2H), 7.36-7.31 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.92 (s, 1H), 6.90-6.88 (m, 1H), 5.71 (t, *J* = 3.0 Hz, 1H), 4.04 (br, 1H), 7.50 (dd, *J* = 3.0, 12.5 Hz, 1H), 3.57 (dd, *J* = 3.5, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.8, 133.2, 132.8, 132.4, 129.1, 127.9, 124.5, 123.2, 117.9, 116.3, 112.4, 81.8, 45.3; HRMS (FAB+, *m/z*), calcd for $C_{15}H_{12}F_3NOS$ $[M+H]^+$: 312.067, found 312.0679.



Benzoxazine derivative 10f:[1] Reaction time 2 h; IR (film) ν_{max}: 3373, 3083, 2920, 2847, 1610, 1496, 1453, 1411, 1341, 1211, 1053, 894, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.93-6.89 (m, 2H), 6.83 (d, *J* = 1.0 Hz, 1H), 5.37 (d, *J* = 3.5 Hz, 1H), 4.29 (dt, *J* = 4.0, 9.0 Hz, 1H), 4.08-4.03 (m, 2H), 2.23-2.16 (m, 1H), 1.91 (qd, *J* = 8.5, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.8, 130.8, 125.4, 124.2, 117.1, 115.7, 111.2, 96.3, 67.9, 54.0, 29.5; HRMS (FAB+, *m/z*), calcd for $C_{11}H_{10}F_3NO_2$ $[M+H]^+$: 246.0742, found 246.0744.



X-ray Crystallographic Data

Formula	$C_{12}H_{16}N_2O_4$
Formula Wt.	252.27
Crystal habit	Blocks
Crystal color	Orange
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.418(2)
b (Å)	8.861(2)
c (Å)	9.944(2)
α (deg)	64.890(10)
β (deg)	88.070(10)
γ (deg)	71.110(10)
V (Å^3)	630.8(2)
Z	2
D_{calc} (g cm^{-3})	1.328
T (K)	298(2)
λ (Mo-Kα)	0.71073
μ (mm^{-1})	0.101
2θ range (deg)	50.52
Limiting indices	$-10 \le h \ge 10$ $-10 \le k \ge 10$ $-11 \le l \ge 11$
F(000)	268
No. of Reflns. Measured	6142
No. Unique Reflns. [*R*(*int*)]	2271
No.of Reflns. used	2092
No. of Parameters	197
GOF on F^2	1.055
R1 [I>2σ(I)]	0.0474

wR2	0.1258
Final diff. Fourier map ($e^{-}.Å^{-3}$) max, min	0.229, -0.207

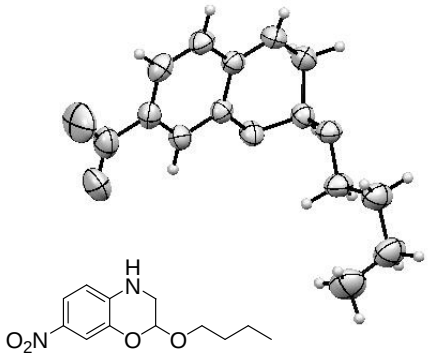
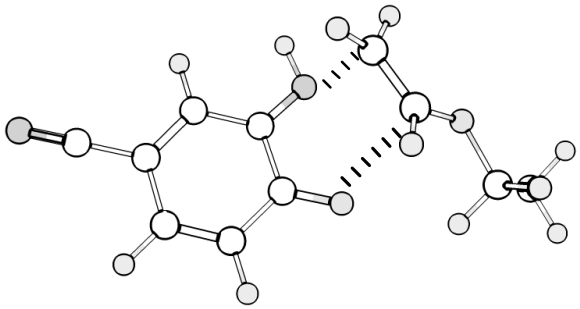


Figure 1. ORTEP diagram of X-ray crystal structure of **7a**

Computational Studies

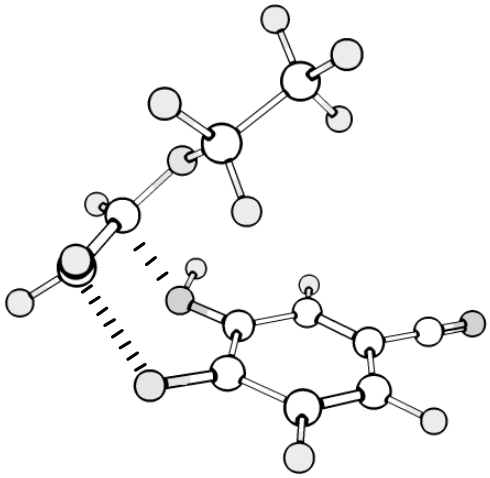
All computations were performed using the Gaussian 09[2] program package, at the B3LYP/6-31-G(d) level of theory[3]. Reactants and products structures were optimized using the B3LYP functional and the 6-31-G(d) basis set. The stationary points were characterized by frequency calculations in order to verify that TSs had one and only one imaginary frequency. Distances and bond lengths are given in Å. The relative energies are given in kcal mol^{-1}.



Total energy -686.226814 au.

Relative energy relative to **1b + 4** 12.70 Kcal/mol

Figure 2. Transition structure of **8b**



Total energy -686.2145657 au.

Relative energy relative to **1b + 4** 20.39 Kcal/mol

Figure 3. Transition structure of counter regio isomer **of 8b**

Cartesian coordinates with the computed total energies

TS-1 of **8b**

-686.226814 au.

C	-3.123186000	-0.150768000	-0.031744000
C	-2.672221000	-1.492515000	0.245684000
C	-1.347076000	-1.807887000	0.219054000
C	-0.340239000	-0.826814000	-0.144209000
C	-0.822383000	0.529357000	-0.485958000
C	-2.210493000	0.836062000	-0.341375000
O	0.884310000	-1.073430000	-0.125536000
C	2.194371000	0.828454000	0.902557000

C	1.415265000	1.946854000	0.687067000
N	0.105493000	1.401112000	-0.885879000
O	3.272897000	0.619411000	0.163741000
C	3.943754000	-0.650991000	0.343980000
C	4.993877000	-0.777644000	-0.741449000
C	-4.520414000	0.147656000	0.028762000
N	-5.659416000	0.383846000	0.085357000
H	-3.416756000	-2.243942000	0.491841000
H	-0.998230000	-2.810117000	0.448027000
H	-2.552351000	1.849079000	-0.541052000
H	1.984572000	0.115256000	1.694413000
H	1.822241000	2.748553000	0.081955000
H	0.681404000	2.209714000	1.439869000
H	-0.331524000	2.326417000	-0.994176000
H	3.190119000	-1.439841000	0.279607000
H	4.397397000	-0.662037000	1.344203000
H	5.530612000	-1.725478000	-0.626997000
H	5.719342000	0.040094000	-0.684026000
H	4.525443000	-0.760834000	-1.729865000

TS-2 of regio isomer of **8b**

-686.2145657 au.

C	-2.334524000	-0.087423000	0.064705000
C	-2.113092000	-0.684052000	-1.222276000
C	-0.932054000	-1.316805000	-1.501338000
C	0.067377000	-1.500019000	-0.483906000
C	-0.168427000	-0.909153000	0.834747000
C	-1.365084000	-0.157114000	1.047025000
O	1.173814000	-2.079612000	-0.712127000
C	2.843526000	-0.949519000	-0.147289000
C	2.511479000	-0.010361000	0.826314000
N	0.822124000	-1.058451000	1.714839000
C	-3.564872000	0.601786000	0.314899000
N	-4.564477000	1.166025000	0.508568000
O	2.079368000	1.247621000	0.582362000
C	1.861586000	1.667361000	-0.778497000
C	1.234700000	3.048249000	-0.732314000
H	-2.894927000	-0.608534000	-1.971628000
H	-0.739779000	-1.753302000	-2.476559000
H	-1.533452000	0.310550000	2.013508000
H	2.947306000	-0.686375000	-1.190548000
H	3.329273000	-1.856697000	0.181256000
H	2.907722000	-0.101164000	1.829579000
H	0.644445000	-0.447645000	2.523520000
H	1.208226000	0.954600000	-1.292796000
H	2.828352000	1.687028000	-1.300621000
H	1.076630000	3.420053000	-1.750128000

H	1.885506000	3.751056000	-0.202933000
H	0.268027000	3.015652000	-0.220803000

Benzoxazine derivative **8b**

-686.3243273 au.

C	-3.337514000	0.796308000	0.035613000
C	-3.110069000	-0.558135000	0.327789000
C	-1.805779000	-1.039686000	0.359083000
C	-0.729371000	-0.192658000	0.098062000
C	-0.944889000	1.170423000	-0.209181000
C	-2.255211000	1.650034000	-0.233386000
O	0.527752000	-0.730664000	0.132430000
C	1.647163000	0.179847000	0.118197000
C	1.384880000	1.325760000	-0.852566000
N	0.160566000	1.992828000	-0.438208000
O	2.762583000	-0.508386000	-0.309110000
C	3.255079000	-1.494758000	0.609395000
C	4.539328000	-2.065768000	0.035985000
C	-4.672537000	1.313623000	0.002962000
N	-5.757354000	1.734909000	-0.024755000
H	-3.946431000	-1.217550000	0.531250000
H	-1.596501000	-2.080281000	0.585090000
H	-2.439821000	2.695622000	-0.463275000
H	1.771868000	0.560323000	1.144790000
H	1.339681000	0.904149000	-1.868853000
H	2.219165000	2.030764000	-0.805153000
H	-0.047258000	2.849802000	-0.935220000
H	2.500488000	-2.278192000	0.746464000
H	3.433980000	-1.020928000	1.587195000
H	4.947636000	-2.825926000	0.710639000
H	5.289204000	-1.279298000	-0.096680000
H	4.351890000	-2.531035000	-0.936843000

Regio isomer of **8b**

-686.3181633 au.

C	-2.009947000	0.828416000	1.739235000
C	-2.079863000	-0.536933000	2.057138000
C	-0.920404000	-1.306058000	2.012515000
C	0.293014000	-0.731605000	1.645252000
C	0.377946000	0.638939000	1.314190000
C	-0.784278000	1.410695000	1.374750000
O	1.399086000	-1.535490000	1.558446000
C	2.651862000	-0.857260000	1.704786000
C	2.785452000	0.363900000	0.787490000

N	1.610126000	1.179901000	0.962316000
C	-3.190272000	1.639117000	1.784512000
N	-4.149229000	2.297805000	1.820168000
O	3.113099000	0.056784000	-0.558055000
C	2.162650000	-0.689678000	-1.328217000
C	2.682968000	-0.747793000	-2.755138000
H	-3.027569000	-0.981561000	2.339301000
H	-0.936355000	-2.364285000	2.252714000
H	-0.742652000	2.468234000	1.130512000
H	3.420134000	-1.590683000	1.456112000
H	2.777334000	-0.540842000	2.749578000
H	3.660239000	0.934170000	1.121984000
H	1.608097000	2.079294000	0.500920000
H	1.180794000	-0.198102000	-1.295985000
H	2.042596000	-1.699588000	-0.915493000
H	1.990285000	-1.313173000	-3.388169000
H	3.662013000	-1.236644000	-2.789430000
H	2.789270000	0.260177000	-3.169116000

4-cyano-*o*-quinone monoimine (**2b**)

-453.8138318 au.

C	-1.019196000	0.758972000	0.000755000
C	-1.028743000	-0.710378000	-0.000825000
C	0.108714000	-1.437911000	-0.006522000
C	1.419610000	-0.779423000	-0.011428000
C	1.424168000	0.751579000	-0.008564000
C	0.146329000	1.457243000	-0.002765000
C	-2.281511000	1.438202000	0.006849000
N	-3.317790000	1.966475000	0.011874000
O	2.481916000	-1.386785000	-0.014888000
N	2.522520000	1.414328000	-0.011403000
H	-1.997940000	-1.200701000	0.002106000
H	0.096803000	-2.523044000	-0.008144000
H	0.170356000	2.541852000	-0.001109000
H	3.301464000	0.737038000	-0.015585000

Ethyl vinyl ether (**4**)

-232.4332375 au.

C	-1.910221000	-1.047404000	0.003021000
C	-1.678859000	0.269543000	0.002703000
O	-0.487921000	0.920137000	0.001565000
C	0.693871000	0.118053000	0.000959000
C	1.890770000	1.052352000	0.000001000
H	-2.935252000	-1.399697000	0.003566000
H	-1.127315000	-1.796657000	0.002413000

H	-2.489185000	0.994225000	0.002885000
H	0.693474000	-0.531055000	-0.886451000
H	0.694597000	-0.530691000	0.888632000
H	2.821092000	0.473991000	-0.000479000
H	1.881134000	1.693226000	0.887309000
H	1.879991000	1.692859000	-0.887559000

Notes & References:

1) The proton attached to the nitrogen atom is merged with the base line.

2) Frisch, M. J.; et al. *Gaussian 09, revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.

3) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785–789.