Electronic Supplementary Information

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Transition-metal-free synthesis of trifluoromethylated benzoxazines via a visible-light-promoted tandem difunctionalization of o-vinylanilides with trifluoromethylsulfinate

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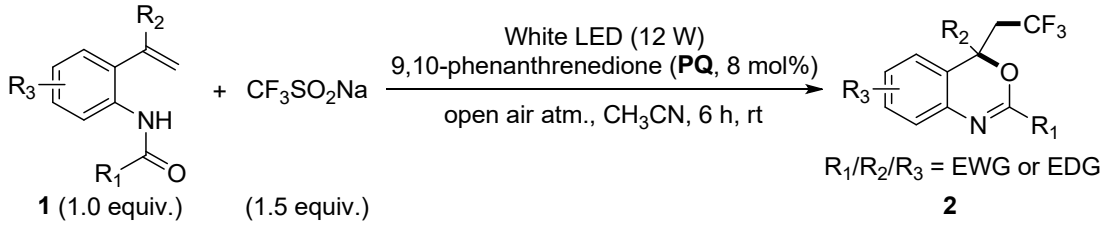
General Information

Unless otherwise stated, all reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. All solvents were distilled according to the established procedures.[1] All reactions were carried out in an open-air atmosphere. The column chromatography was performed using silica gel with 100-200 mesh size. Reactions were monitored by analytical thin layer chromatography on silica gel and visualization was accomplished by irradiation with short wave UV light at 254 nm and near UV 366 nm lights. All products are known and were characterized by their ^{1}H- and ^{13}C NMR followed by a comparison with authentic samples spectra. Chemical shifts are expressed as δ-value in parts per million (ppm) and were calibrated using the residual protinated solvent as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; and so on. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectra were collected by positive mode electrospray ionization (ESI) using Waters-Q-TOF-Premier mass spectrometer.

Experimental Section

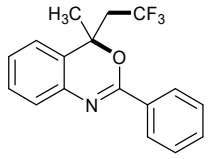
General procedure for the synthesis of trifluoromethylated benzoxazines



1 (1.0 equiv.) (1.5 equiv.) **2**

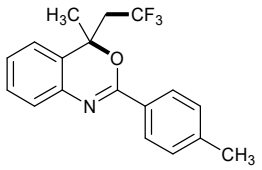
To a vial (20 mL) equipped with a magnetic stir bar was charged under open-air atmosphere with *N*-(2-vinylphenyl)amides (1.0 mmol, 1.0 equiv.), sodium trifluoromethanesulfinate (1.5 mmol, 1.5 equiv.), 9,10-phenanthrenedione (8 mol%) and 5-7 mL of a freshly distilled CH_3CN. Under open-air atmosphere, the mixture was stirred few minutes to mix well and then vial was irradiated through the plane bottom side of the vial using 12W white LED at a distance of 2 cm at ambient conditions. After the completion (as indicated by TLC, ≈6 h) volatiles were evaporated under reduced pressure and then admixed with aqueous NaCl solution (10 mL). The organic matters were extracted with ethyl acetate (3 × 10 mL), dried over Na_2SO_4 and evaporated under reduced pressure to yield pale-yellow gummy materials, which was purified by a filtration through short-pad of silica-gel column chromatography using a mixture of ethyl acetate and *n*-hexane. The identity and purity of the product was confirmed by spectroscopic analysis as well as by a comparison with authentic samples spectra, vide infra.

Experimental characterization data for products



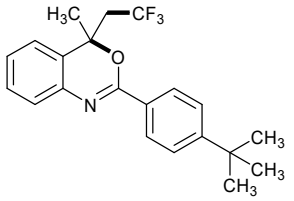
2a, 93%

4-(2,2,2-trifluoroethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (2a):[2] By following the typical procedure, the product (**2a**) was isolated as a white solid, 285 mg (93% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.21 (petroleum ether/ ethyl acetate 7:3); mp 65-67 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.16 (d, J = 7.2 Hz, 2H), 7.52-7.42 (m, 3H), 7.34-7.30 (m, 2H), 7.23-7.19 (m, 1H), 7.12 (d, J = 7.4 Hz, 1H), 2.90-2.79 (m, 1H), 2.65-2.54 (m, 1H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.9, 155.6, 138.2, 132.2, 131.5, 129.4, 128.2, 128.1 (q, J = 276.0 Hz), 126.8, 125.5, 122.6, 76.7 (q, J = 2.0 Hz), 43.2 (q, J = 27.2 Hz), 26.6 (d, J = 1.4 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -60.19 (t, J = 10.5 Hz, 3F). HRMS (ESI), m/z calcd for $C_{17}H_{14}F_3NO$ $[M+H]^+$ 306.1100, found 306.1097.



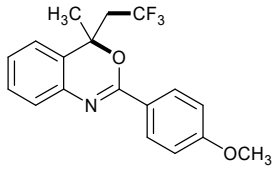
2b, 86%

4-(2,2,2-trifluoroethyl)-4-methyl-2-*p*-tolyl-4H-benzo[d][1,3]oxazine (2b):[2] By following the typical procedure, the product (**2b**) was isolated as a colorless waxy compound, 275 mg (86% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.21 (petroleum ether/ ethyl acetate 7:3). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.07 (d, J = 8.2 Hz, 2H), 7.34-7.30 (m, 2H), 7.25-7.18 (m, 3H), 7.10 (d, J = 7.6 Hz, 1H), 2.89-2.77 (m, 1H), 2.64-2.54 (m, 1H), 2.39 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.8, 142.0, 138.3, 129.4, 129.4, 129.0, 128.2, 128.1, 126.7, 125.6, 125.2 (q, J = 278.2 Hz), 122.3, 76.5 (q, J = 2.0 Hz), 43.4 (q, J = 27.2 Hz), 26.3 (d. J = 1.6 Hz), 21.5. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.6 (t, J = 10.3 Hz, 3F). HRMS (ESI), m/z calcd for $C_{18}H_{16}F_3NO$ $[M+H]^+$ 320.1257, found 320.1262.



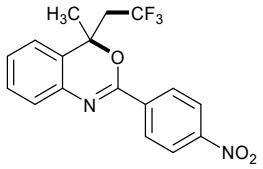
2c, 84%

2-(4-*tert*-butylphenyl)-4-(2,2,2-trifluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (2c):[2] By following the typical procedure, the product (**2c**) was isolated as a colorless waxy compound, 305 mg (84% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.22 (petroleum ether/ ethyl acetate 7:2). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.06 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.35-7.29 (m, 2H), 7.22-7.17 (m, 1H), 7.10 (d, J = 7.6 Hz, 1H), 2.91-2.77 (m, 1H), 2.65-2.54 (m, 1H), 1.92 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.6, 155.0, 138.6, 129.5, 129.2, 128.2, 127.6, 126.6, 125.7, 125.2, 125.1 (q, J = 278.6 Hz), 122.4, 76.4 (q, J = 2.2 Hz), 43.5 (q, J = 27.0 Hz), 34.8, 31.2, 26.3 (d, J = 1.5 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.6 (t, J = 10.6 Hz, 3F). HRMS (ESI), m/z Calcd for $C_{21}H_{22}F_3NO$ $[M+H]^+$ 362.1726, found 362.1744.



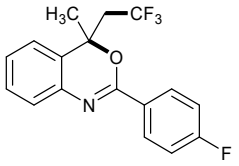
2d, 89%

4-(2,2,2-trifluoroethyl)-2-(4-methoxyphenyl)-4-methyl-4H-benzo[d][1,3]oxazine (2d):[2] By following the typical procedure, the product (**2d**) was isolated as a colorless waxy compound, 300 mg (89% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.19 (petroleum ether/ ethyl acetate 7:3). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.07 (d, J = 8.6 Hz, 2H), 7.35-7.28 (m, 2H), 7.21-7.16 (m, 1H), 7.09 (d, J = 7.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.87-2.76 (m, 1H), 2.64-2.53 (m, 1H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.5, 155.6, 138.6, 129.7, 129.3, 128.2, 126.5, 125.4, 125.1 (q, J = 279.0 Hz), 124.5, 122.4, 113.7, 76.4 (q, J = 2.1 Hz), 55.3, 43.6 (q, J = 27.0 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.7 (t, J = 10.4 Hz, 3F). HRMS (ESI), m/z calcd for $C_{18}H_{16}F_3NO_2$ $[M+H]^+$ 336.1206, found 336.1213.



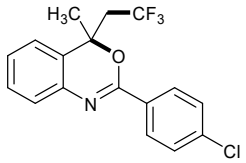
2e, 82%

4-(2,2,2-trifluoroethyl)-4-methyl-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazine (2e):[2] By following the typical procedure, the product (**2e**) was isolated as a pale yellow-solid, 290 mg (82% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.19 (petroleum ether/ethyl acetate 7:3); mp 72-74 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.25 (q, J = 8.8 Hz, 4H), 7.37-7.32 (m, 2H), 7.29-7.26 (m, 1H), 7.15 (d, J = 7.4 Hz, 1H), 2.90-2.78 (m, 1H), 2.67-2.57 (m, 1H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.3, 149.6, 138.0, 137.6, 129.5, 128.7, 128.2, 128.0, 126.2, 125.1 (q, J = 278.2 Hz), 123.5, 122.6, 77.3 (q, J = 2.2 Hz), 43.7 (q, J = 26.9 Hz), 26.6 (d, J = 1.5 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.9 (t, J = 10.4 Hz). HRMS (ESI), m/z calcd for $C_{17}H_{13}F_3N_2O_3$ $[M+H]^+$ 351.0951, found 351.0969.



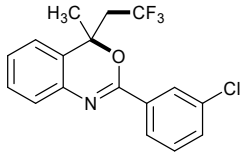
2f, 76%

4-(2,2,2-trifluoroethyl)-2-(4-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (2f):[2] By following the typical procedure, the product (**2f**) was isolated as a white solid, 248 mg (76% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.20 (petroleum ether/ ethyl acetate 7:3); mp 97-100 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.17-8.14 (m, 2H), 7.36-7.29 (m, 2H), 7.23-7.19 (m, 1H), 7.11 (t, J = 7.4 Hz, 3H), 2.91-2.77 (m, 1H), 2.65-2.52 (m, 1H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 166.2, 163.5, 154.9, 138.2, 130.4 (d, J = 8.6 Hz), 129.2, 128.3 (d, J = 2.8 Hz), 128.2, 127.1, 125.4, 125.0 (q, J = 278.2 Hz), 122.4, 115.4 (d, J = 21.8 Hz), 76.5 (q, J = 2.2 Hz), 43.4 (q, J = 27.0 Hz), 26.1 (d, J = 1.6 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.8 (t, J = 10.4 Hz, 3F), -107.9 to -108.1 (m, F). HRMS (ESI), m/z calcd for $C_{17}H_{13}F_4NO$ $[M+H]^+$ 324.1006, found 324.1024.



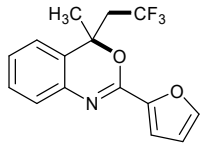
2g, 80%

2-(4-chlorophenyl)-4-(2,2,2-trifluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (2g):[2] By following the typical procedure, the product (**2g**) was isolated as a white solid, 273 mg (80% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.22 (petroleum ether/ethyl acetate 8:2); mp 65-67 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.09 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.35-7.29 (m, 2H), 7.24-7.20 (m, 1H), 7.10 (d, J = 7.4 Hz, 1H), 2.87-2.78 (m, 1H), 2.63-2.51 (m, 1H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.6, 138.1, 137.7, 130.6, 129.4, 129.2, 128.4, 128.2, 127.3, 125.6, 125.1 (q, J = 278.4 Hz), 122.4, 76.6 (q, J = 2.1 Hz), 43.6 (q, J = 27.1 Hz), 26.2 (d, J = 1.6 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.8 (t, J = 10.4 Hz, 3F). HRMS (ESI), m/z calcd for $C_{17}H_{13}ClF_3NO$ $[M+H]^+$ 340.0711, found 340.0719.



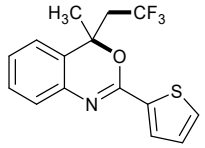
2h, 84%

2-(3-chlorophenyl)-4-(2,2,2-trifluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (2h):[2] By following the typical procedure, the product (**2h**) was isolated as a colorless waxy compound, 286 mg (84% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.23 (petroleum ether/ ethyl acetate 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.14-8.13 (m, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.49-7.42 (m, 1H), 7.39-7.31 (m, 3H), 7.25-7.21 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 2.87-2.78 (m, 1H), 2.67-2.56 (m, 1H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.2, 137.8, 134.5, 134.0, 131.4, 129.6, 129.4, 128.2, 127.9, 127.4, 126.1, 125.9, 125.1 (q, J = 278.2 Hz), 122.7, 76.8 (q, J = 2.2 Hz), 43.7 (q, J = 27.2 Hz), 26.4 (d, J = 1.6 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.7 (t, J = 10.3 Hz, 3F). HRMS (ESI), m/z calcd for $C_{17}H_{13}ClF_3NO$ $[M+H]^+$ 340.0711, found 340.0721.



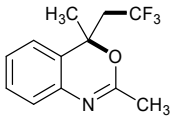
2i, 79%

4-(2,2,2-trifluoroethyl)-2-(furan-2-yl)-4-methyl-4H-benzo[d][1,3]oxazine (2i):[2] By following the typical procedure, the product (**2i**) was isolated as a white solid, 235 mg (79% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.23 (petroleum ether/ ethyl acetate 8:2); mp 81-83 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.38-7.32 (m, 2H), 7.27-7.18 (m, 2H), 7.14-7.07 (m, 2H), 6.91 (dd, J = 11.2, 3.4 Hz, 1H), 2.88-2.76 (m, 1H), 2.61-2.51 (m, 1H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 147.4, 137.2, 129.7, 128.1 (d, J = 29.0 Hz), 127.9, 126.2, 125.0 (q, J = 278.8 Hz), 122.7, 120.5, 117.2, 114.8, 113.0 (q, J = 2.8 Hz), 77.2 (q, J = 2.2 Hz), 43.4 (q, J = 27.0 Hz), 26.2 (d, J = 1.6 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.9 (t, J = 10.2 Hz, 3F). HRMS (ESI), m/z calcd for $C_{15}H_{12}F_3NO_2$ $[M+H]^+$ 296.0893, found 296.0903.



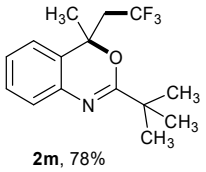
2j, 81%

4-(2,2,2-trifluoroethyl)-4-methyl-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine (2j):[2] By following the typical procedure, the product (**2j**) was isolated as a pale yellow waxy compound, 254 mg (81% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.22 (petroleum ether/ ethyl acetate 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.71 (d, J = 3.8 Hz, 1H), 7.47 (dd, J = 4.8, 1.0 Hz, 1H), 7.32-7.25 (m, 2H), 7.19 (td, J = 7.2, 1.4 Hz, 1H), 7.11-7.07 (m, 2H), 2.87-2.79 (m, 1H), 2.62-2.54 (m, 1H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.3, 138.2, 136.7, 130.5, 130.4, 129.3, 127.6, 126.7, 125.1 (q, J = 278.8 Hz), 122.4, 76.8 (q, J = 2.1 Hz), 43.2 (q, J = 27.1 Hz), 25.8 (d, J = 1.5 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.9 (t, J = 10.4 Hz, 3F). HRMS (ESI), m/z Calcd for $C_{15}H_{12}F_3NOS$ $[M+H]^+$ 312.0664, found 312.0673.



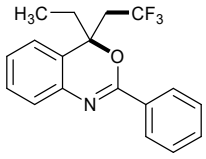
2l, 77%

4-(2,2,2-trifluoroethyl)-2,4-dimethyl-4H-benzo[d][1,3]oxazine (2l):[2] By following the typical procedure, the product (**2l**) was isolated as a pale yellow waxy compound, 190 mg (77% yield), from a column chromatography (petroleum ether/ethyl acetate = 9/1), R_f=0.19 (petroleum ether/ ethyl acetate 9:1). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.28-7.24 (m, 1H), 7.18-7.12 (m, 2H), 7.06-7.01 (m, 1H), 2.78-2.65 (m, 1H), 2.52-2.41 (m, 1H), 2.11 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.1, 137.7, 129.2, 127.4, 126.6, 125.0 (q, J = 277.8 Hz), 124.5, 122.6, 76.2 (q, J = 2.1 Hz), 44.2 (q, J = 26.9 Hz), 26.8 (d, J = 1.6 Hz), 21.4. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -60.2 (t, J = 10.2 Hz, 3F). HRMS (ESI), m/z calcd for $C_{12}H_{12}F_3NO$ $[M+H]^+$ 244.0944, found 244.0951.



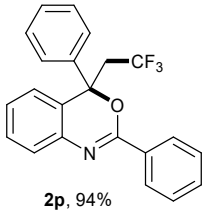
2m, 78%

2-*tert*-butyl-4-(2,2,2-trifluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (2m):[2] By following the typical procedure, the product (**2m**) was isolated as a pale yellow waxy compound, 224 mg (78% yield), from a column chromatography (petroleum ether/ethyl acetate = 9/1), R_f=0.2 (petroleum ether/ ethyl acetate 9:1). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.29-7.23 (m, 1H), 7.19-7.13 (m, 2H), 7.03 (d, J = 7.4 Hz, 1H), 2.78-2.69 (m, 1H), 2.68-2.59 (m, 1H), 1.72 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 166.4, 138.1, 129.0, 127.5, 126.4, 125.4, 125.0 (q, J = 278.6 Hz), 122.4, 75.7 (q, J = 2.1 Hz), 43.5 (q, J = 26.9 Hz), 37.2, 27.3, 27.1 (d, J = 1.5 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.6 (t, J = 10.4 Hz, 3F). HRMS (ESI), m/z calcd for $C_{15}H_{18}F_3NO$ $[M+H]^+$ 286.1413, found 286.1422.



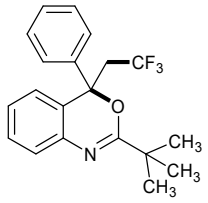
2o, 89%

4-ethyl-4-(2,2,2-trifluoroethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (2o):[2] By following the typical procedure, the product (**2o**) was isolated as a pale yellow waxy compound, 285 mg (89% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.20 (petroleum ether/ ethyl acetate 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.12 (d, J = 7.0 Hz, 2H), 7.49-7.41 (m, 3H), 7.30 (d, J = 4.2 Hz, 2H), 7.21-7.18 (m, 1H), 7.02 (d, J = 7.4 Hz, 1H), 2.88-2.67 (m, 2H), 2.27-2.16 (m, 1H), 2.15-2.07 (m, 1H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.4, 139.2, 132.3, 131.4, 129.2, 128.3, 127.8, 126.7, 125.8, 125.2, 125.1 (q, J = 278.4 Hz), 123.3, 79.7 (q, J = 2.2 Hz), 43.7 (q, J = 26.6 Hz), 33.8 (d, J = 0.9 Hz), 7.3. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.3 (t, J = 10.4 Hz, 3F). HRMS (ESI), m/z calcd for $C_{18}H_{16}F_3NO$ $[M+H]^+$ 320.1257, found 320.1272.



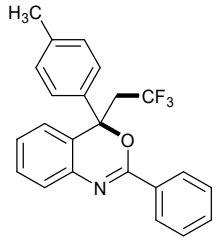
2p, 94%

4-(2,2,2-trifluoroethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (2p):[2] By following the typical procedure, the product (**2p**) was isolated as a white solid, 347 mg (94% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.19 (petroleum ether/ ethyl acetate 7:3); mp 96-98 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.27 (d, J = 8.2 Hz, 2H), 7.55-7.45 (m, 3H), 7.38-7.33 (m, 4H), 7.30-7.19 (m, 5H), 3.34-3.29 (m, 1H), 3.28-3.23 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.3, 141.7, 138.6, 132.1, 131.6, 129.5, 128.6, 128.3, 128.2, 127.9, 126.6, 126.3, 125.8, 125.4, 125.1 (q, J = 278.9 Hz), 124.1, 79.9 (q, J = 2.1 Hz), 43.3 (q, J = 26.9 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -58.4 (t, J = 10.0 Hz, 3F). HRMS (ESI), m/z calcd for $C_{22}H_{16}F_3NO$ $[M+H]^+$ 368.1257, found 368.1266.



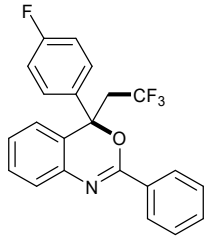
2q, 92%

2-*tert*-butyl-4-(2,2,2-trifluoroethyl)-4-phenyl-4H-benzo[d][1,3]oxazine (2q):[2] By following the typical procedure, the product (**2q**) was isolated as a colorless waxy compound, 320 mg (92% yield), from a column chromatography (petroleum ether/ethyl acetate = 8/2), R_f=0.18 (petroleum ether/ ethyl acetate 8:2). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.35-7.30 (m, 4H), 7.28-7.18 (m, 4H), 7.07 (d, J = 7.4 Hz, 1H), 3.26-3.21 (m, 1H), 3.20-3.16 (m, 1H), 1.22 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 166.0, 142.8, 138.6, 129.3, 128.5, 128.3, 125.9, 125.7, 125.6, 124.9 (q, J = 277.4 Hz), 124.1, 79.2, 43.4 (q, J = 26.9 Hz), 37.2, 27.3. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.5 (t, J = 10.2 Hz, 3F). HRMS (ESI), m/z calcd for $C_{20}H_{20}F_3NO$ $[M+H]^+$ 348.1498, found 348.1504.



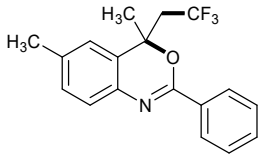
2r, 90%

4-(2,2,2-trifluoroethyl)-2-phenyl-4-*p*-tolyl-4H-benzo[d][1,3]oxazine (2r):[2] By following the typical procedure, the product (**2r**) was isolated as a white solid, 345 mg (90% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.19 (petroleum ether/ ethyl acetate 7:3); mp 87-89 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.97 (d, J = 8.2 Hz, 2H), 7.54-7.45 (m, 3H), 7.39-7.34 (m, 4H), 7.30-7.18 (m, 4H), 3.35-3.29 (m, 1H), 3.28-3.22 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.1, 141.6, 138.6, 132.2, 131.6, 129.4, 128.5, 128.4, 128.2, 127.9, 126.7, 126.3, 125.7, 125.4, 125.0 (q, J = 278.8 Hz), 124.2, 79.9 (q, J = 2.2 Hz), 43.2 (q, J = 26.8 Hz), 21.0. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -58.5 (t, J = 10.1 Hz, 3F). HRMS (ESI), m/z calcd for $C_{23}H_{18}F_3NO$ $[M+H]^+$ 382.1419, found 382.1415.



2t, 87%

4-(2,2,2-trifluoroethyl)-4-(4-fluorophenyl)-2-phenyl-4H-benzo[d][1,3]oxazine (2t): By following the typical procedure, the product (**2t**) was isolated as a pale yellow solid, 337 mg (87% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.2 (petroleum ether/ ethyl acetate 7:3); mp 99-101 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.17-8.14 (m, 2H), 7.55-7.45 (m, 3H), 7.36-7.29 (m, 4H), 7.23-7.19 (m, 1H), 7.11 (t, J = 7.4 Hz, 3H), 3.34-3.29 (m, 1H), 3.28-3.23 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 163.4, 154.9, 141.7, 138.2, 132.1, 131.6, 130.4 (d, J = 8.6 Hz), 129.1, 128.4 (d, J = 2.8 Hz), 128.2, 127.2, 126.6, 125.5, 125.0 (q, J = 278.2 Hz), 122.3, 115.3 (d, J = 21.8 Hz), 76.4 (q, J = 2.1 Hz), 43.5 (q, J = 27.1 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -59.6 (t, J = 10.3 Hz, 3F), -106.8 to -107.1 (m, F). HRMS (ESI), m/z calcd for $C_{22}H_{15}F_4NO$ $[M+H]^+$ 386.1168, found 386.1176.



2u, 74%

4-(2,2,2-trifluoroethyl)-4,6-dimethyl-2-phenyl-4H-benzo[d][1,3]oxazine (2u): By following the typical procedure, the product (**2u**) was isolated as a colorless waxy compound, 240 mg (74% yield), from a column chromatography (petroleum ether/ethyl acetate = 7/3), R_f=0.2 (petroleum ether/ ethyl acetate 7:3). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.12 (d, J = 7.2 Hz, 2H), 7.50-7.41 (m, 2H), 7.32-7.28 (m, 2H), 7.21-7.17 (m, 1H), 7.11 (d, J = 7.4 Hz, 1H), 2.87-2.78 (m, 1H), 2.63-2.52 (m, 1H), 2.31 (s, 3H). 1.90 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.7, 155.6, 138.2, 132.1, 131.5, 129.3, 128.2, 128.1 (q, J = 276.2 Hz), 126.7, 125.5, 122.6, 76.6 (q, J = 2.0 Hz), 43.2 (q, J = 27.2 Hz), 26.4 (d, J = 1.4 Hz), 21.5. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -60.1 (t, J = 10.3 Hz, 3F). HRMS (ESI), m/z calcd for $C_{18}H_{16}F_3NO$ $[M+H]^+$ 320.1262, found 320.1273.

References

1. B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, in Vogel's Textbook of Practical Organic Chemistry, Pearson Education, 5th edn, 1989, ISBN: 978-81-7758-957-3.

2. S. Jana, A. Ashokan, S. Kumar, A. Verma, S. Kumar, *Org. Biomol. Chem.* **2015**, *13*, 8411–8415.

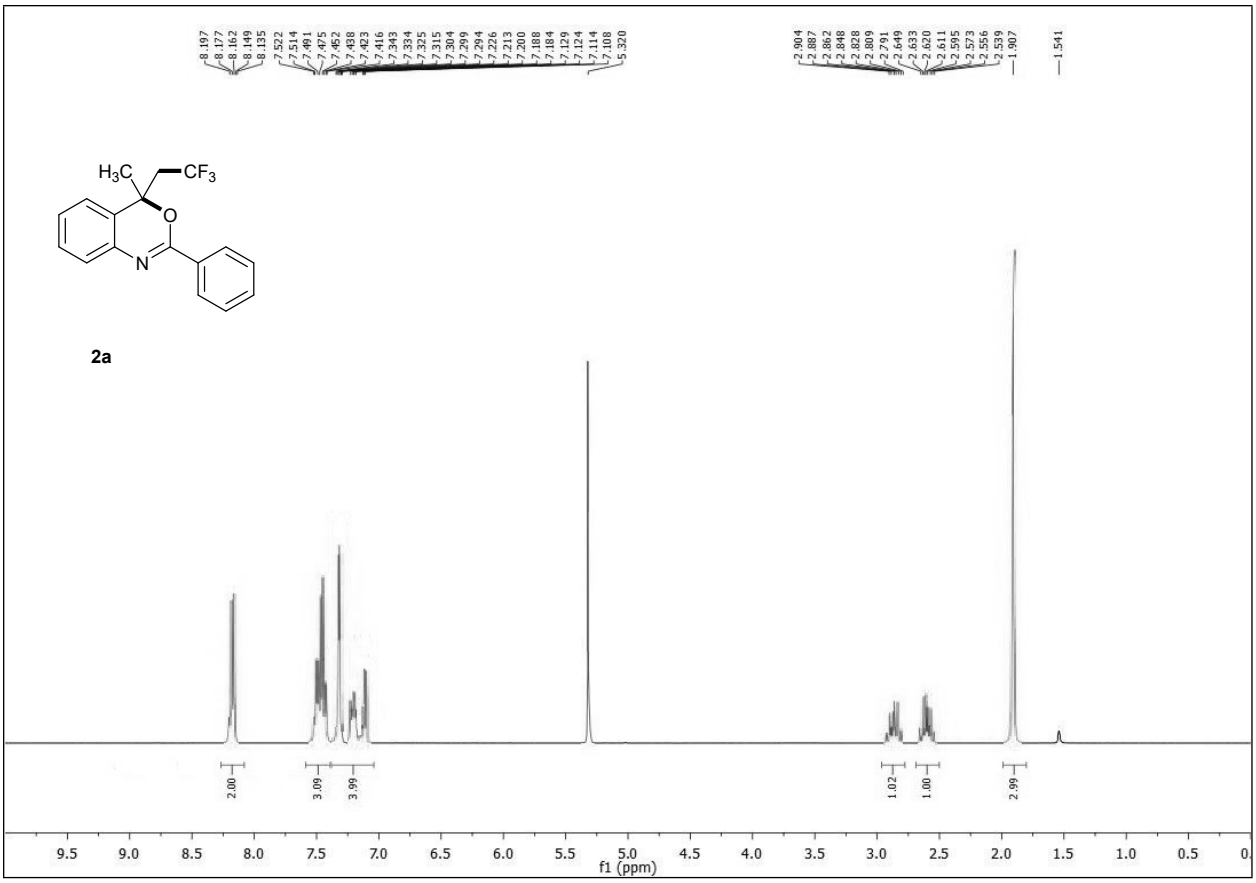


Figure S1. ^{1}H NMR spectra of **2a** in CD_2Cl_2

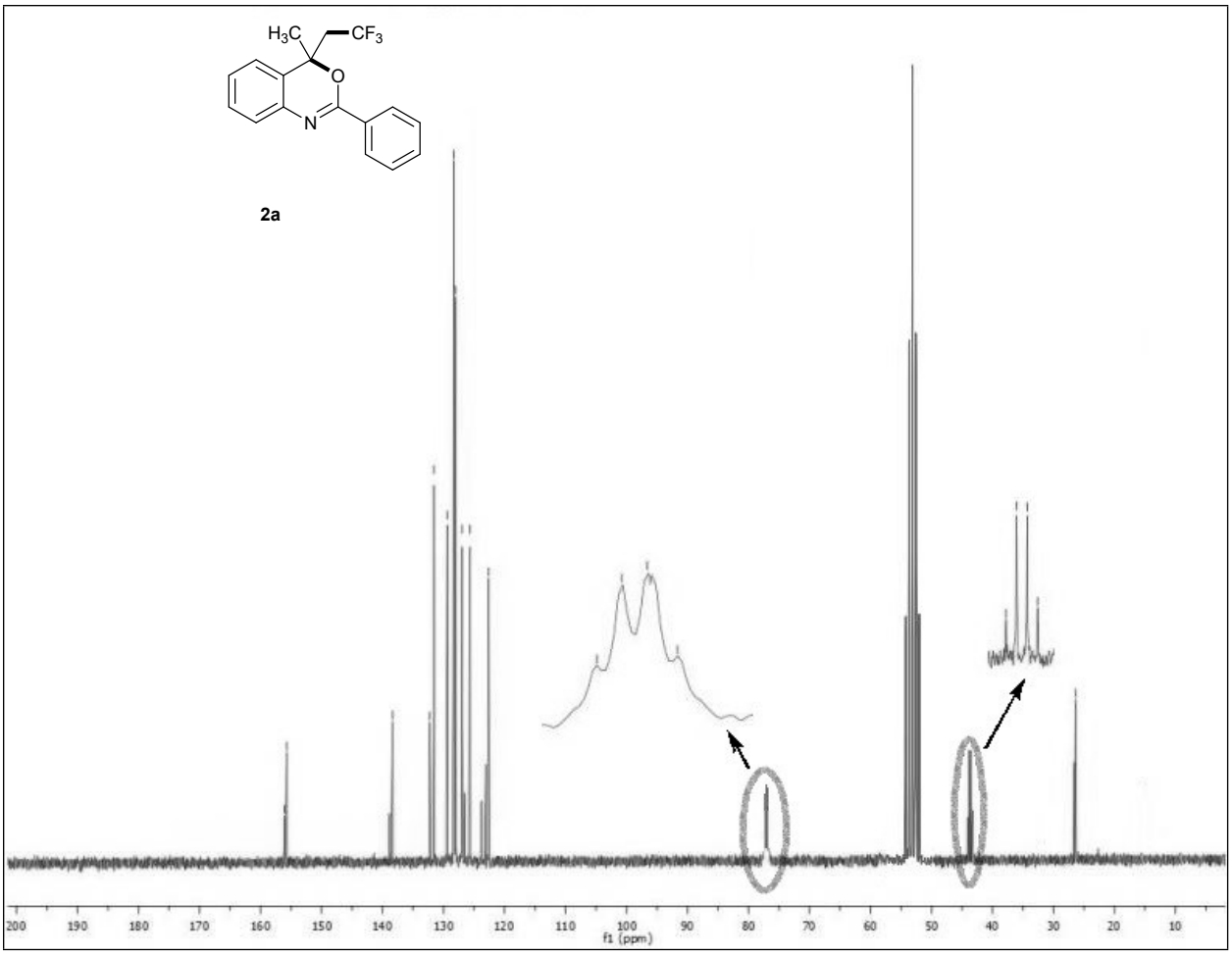


Figure S2. ^{13}C NMR spectra of **2a** in CD_2Cl_2

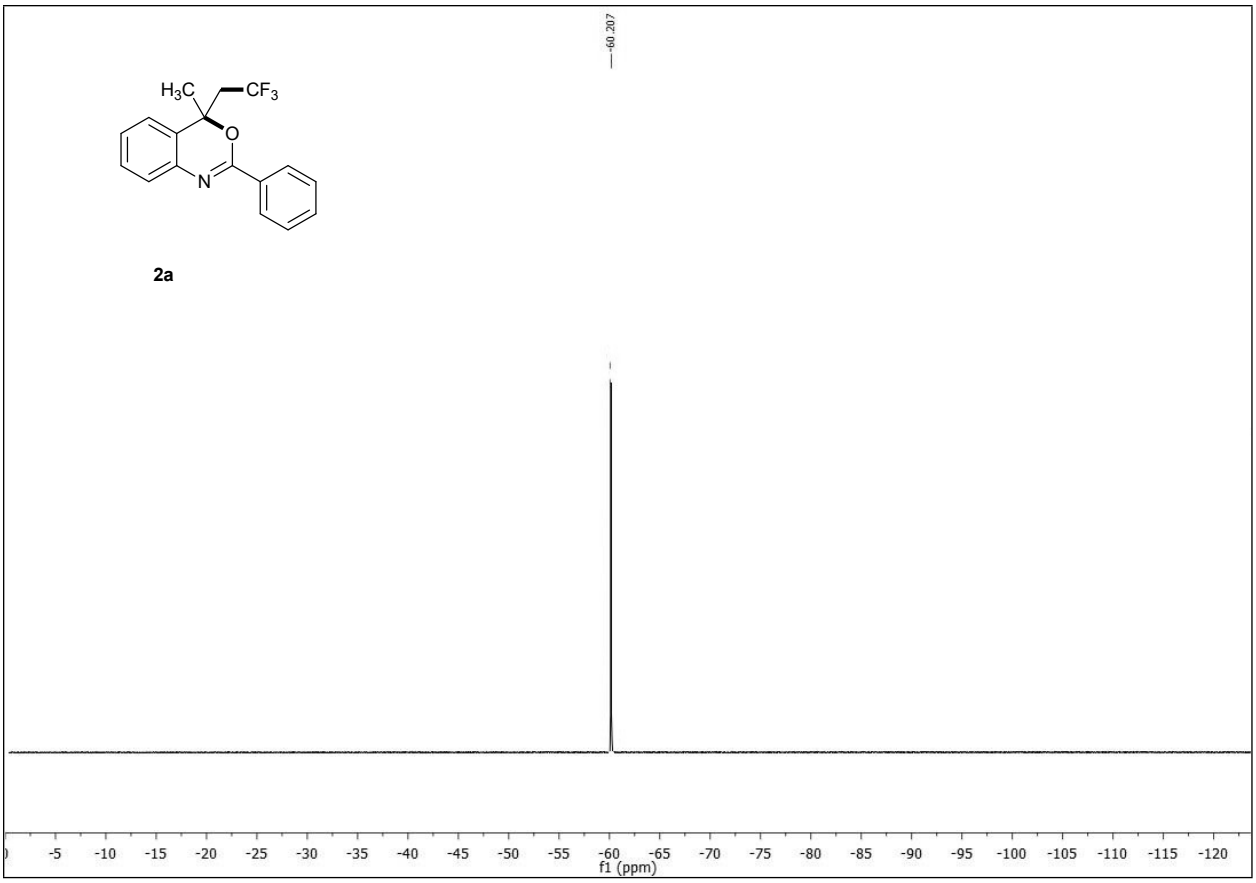


Figure S3. ^{19}F NMR spectra of **2a** in CD_2Cl_2

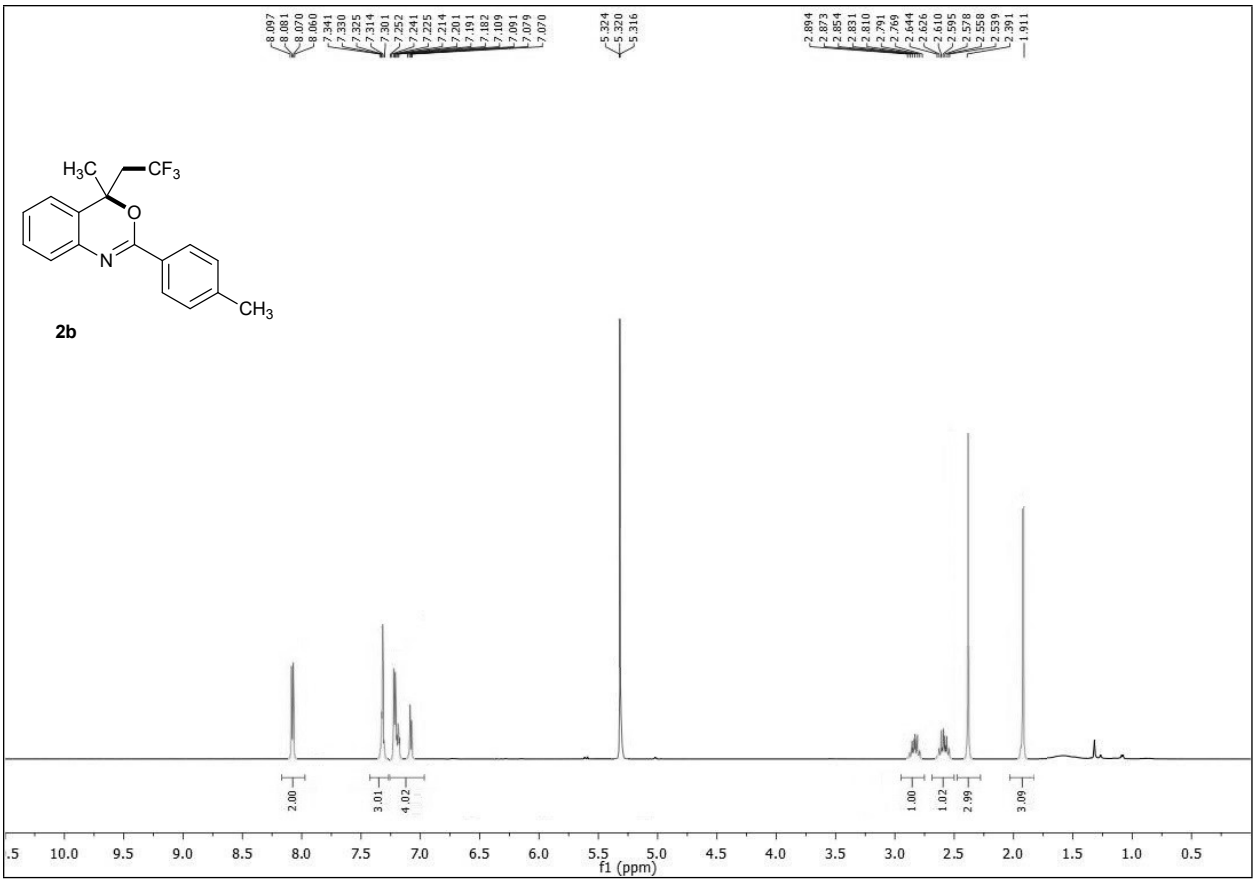


Figure S4. ^{1}H NMR spectra of **2b** in CD_2Cl_2

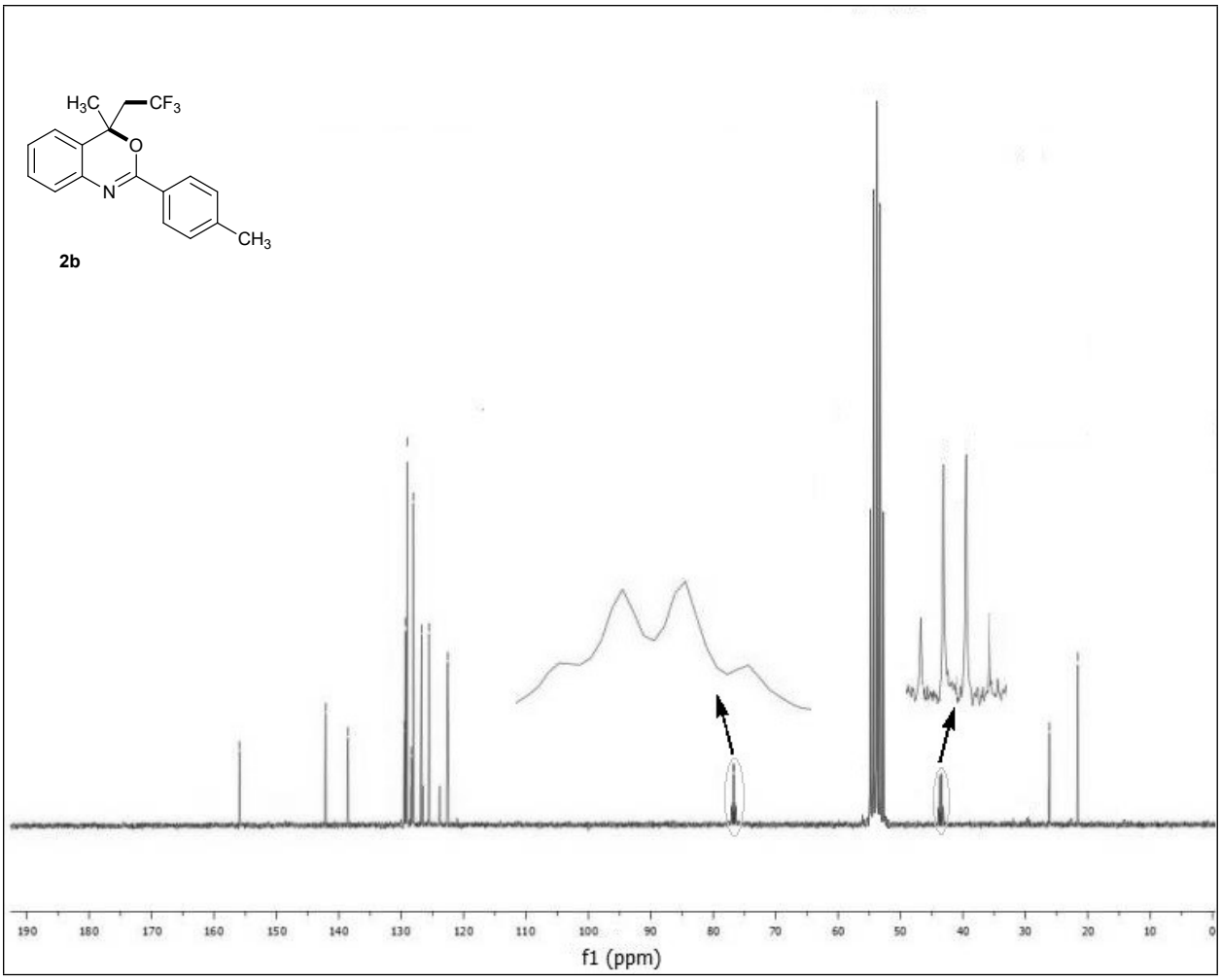


Figure S5. ^{13}C NMR spectra of **2b** in CD_2Cl_2

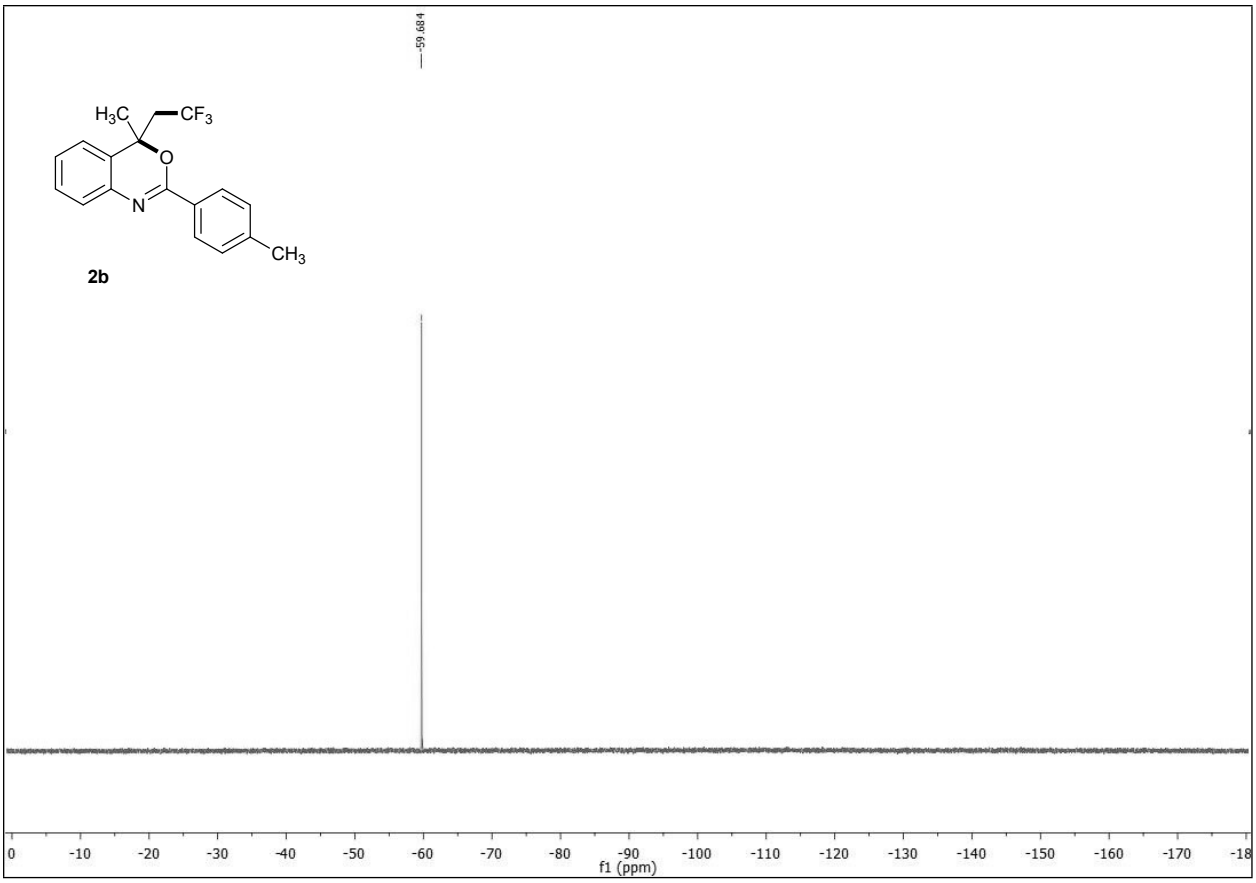


Figure S6. ^{19}F NMR spectra of **2b** in CD_2Cl_2

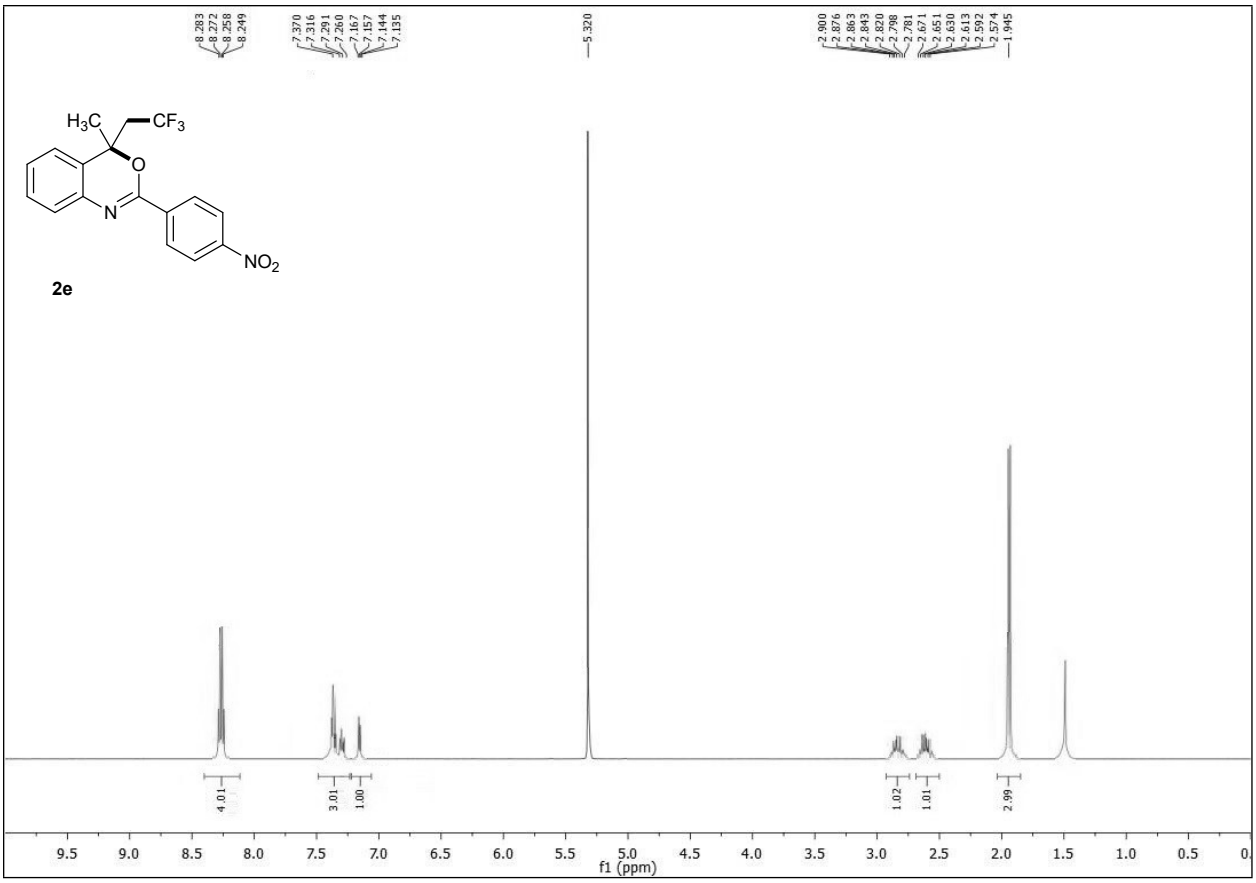


Figure S7. ^{1}H NMR spectra of **2e** in CD_2Cl_2

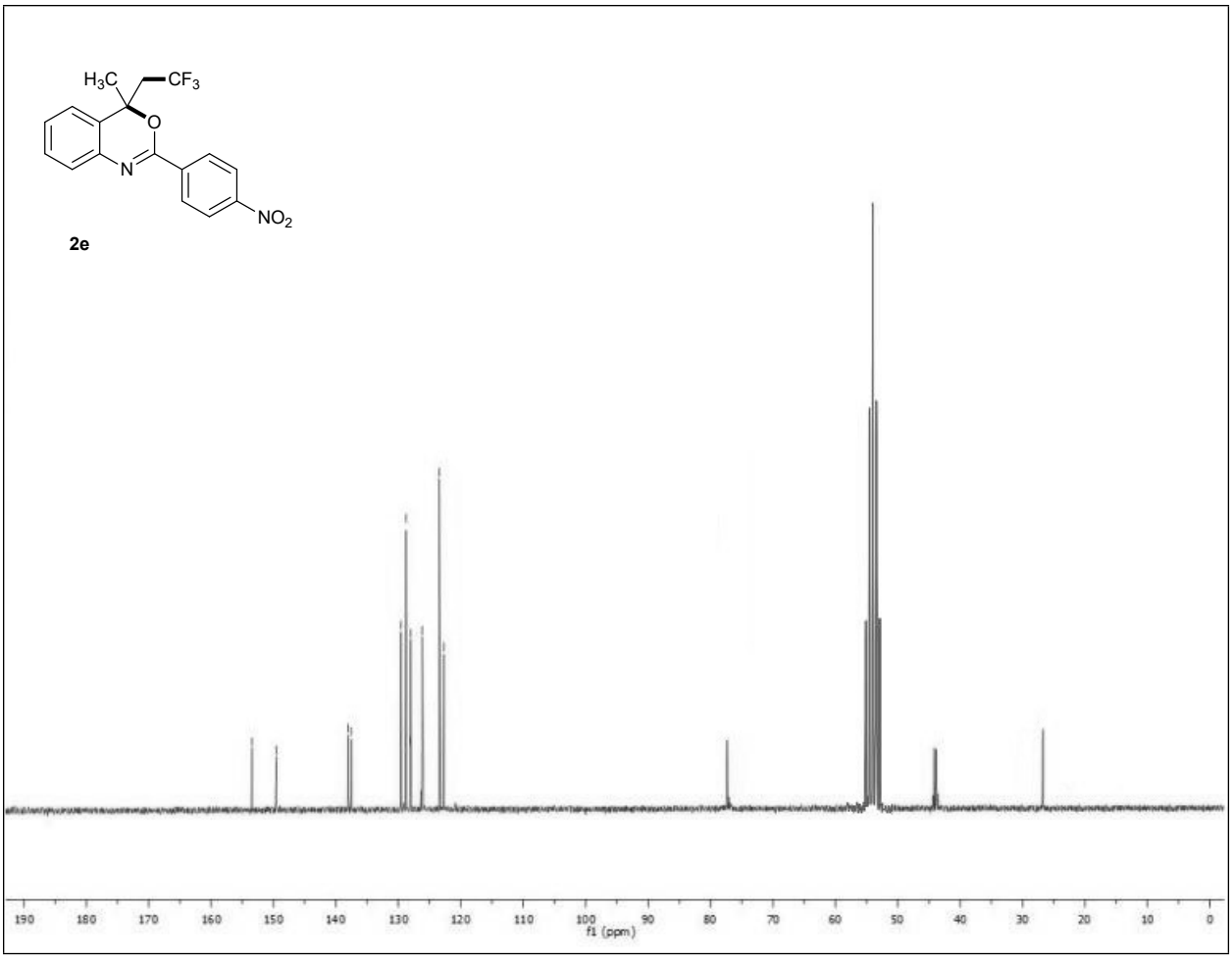


Figure S8. ^{13}C NMR spectra of **2e** in CD_2Cl_2

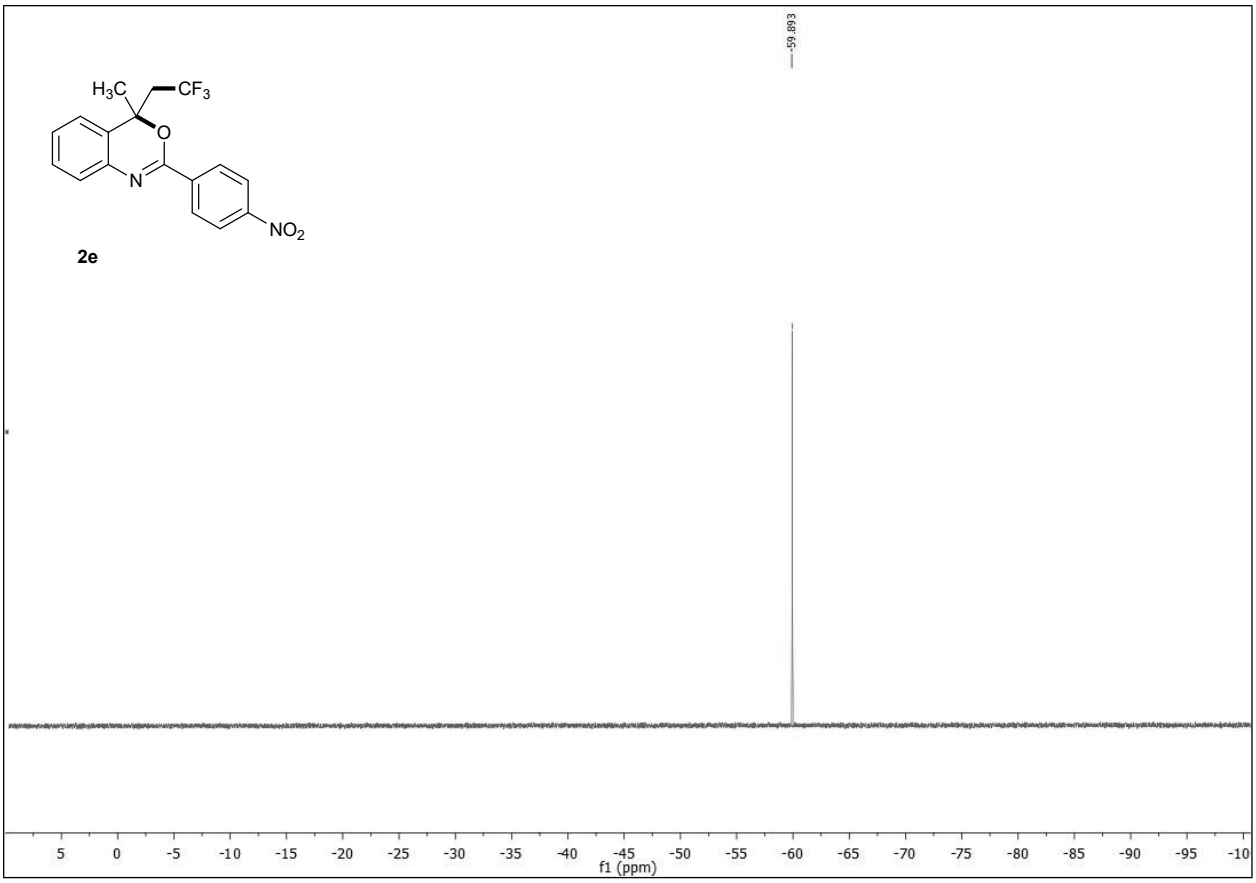


Figure S9. ^{19}F NMR spectra of **2e** in CD_2Cl_2

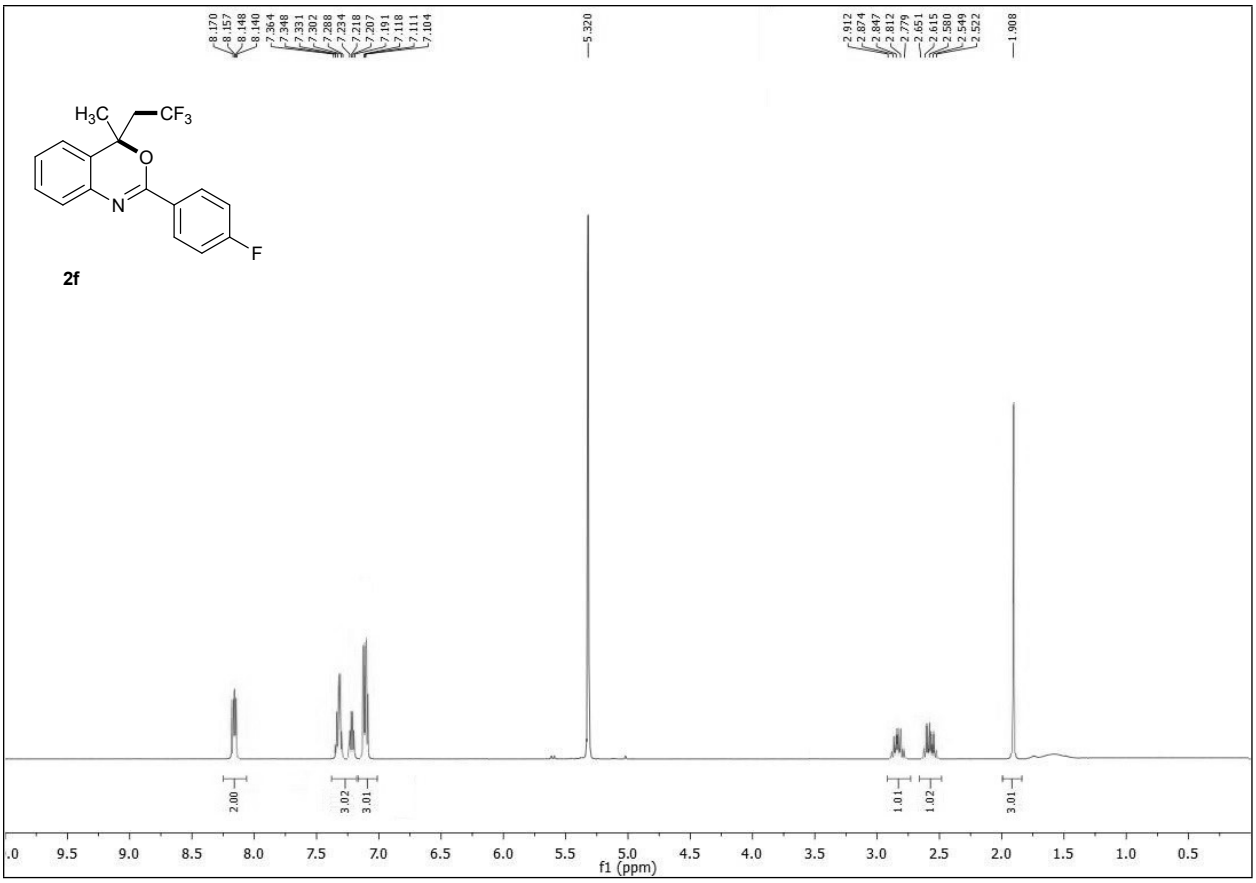


Figure S10. ^{1}H NMR spectra of **2f** in CD_2Cl_2

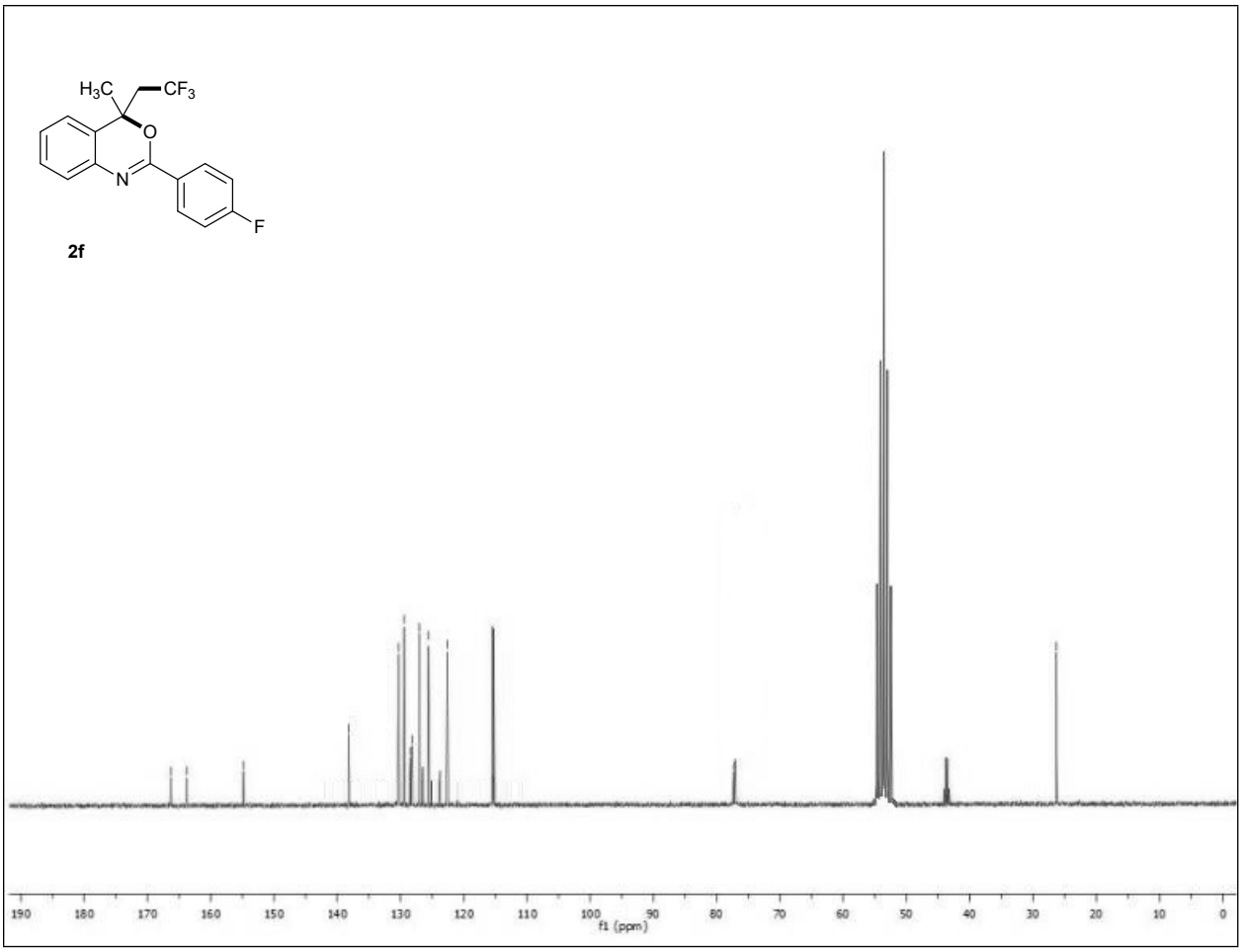


Figure S11. ^{13}C NMR spectra of **2f** in CD_2Cl_2

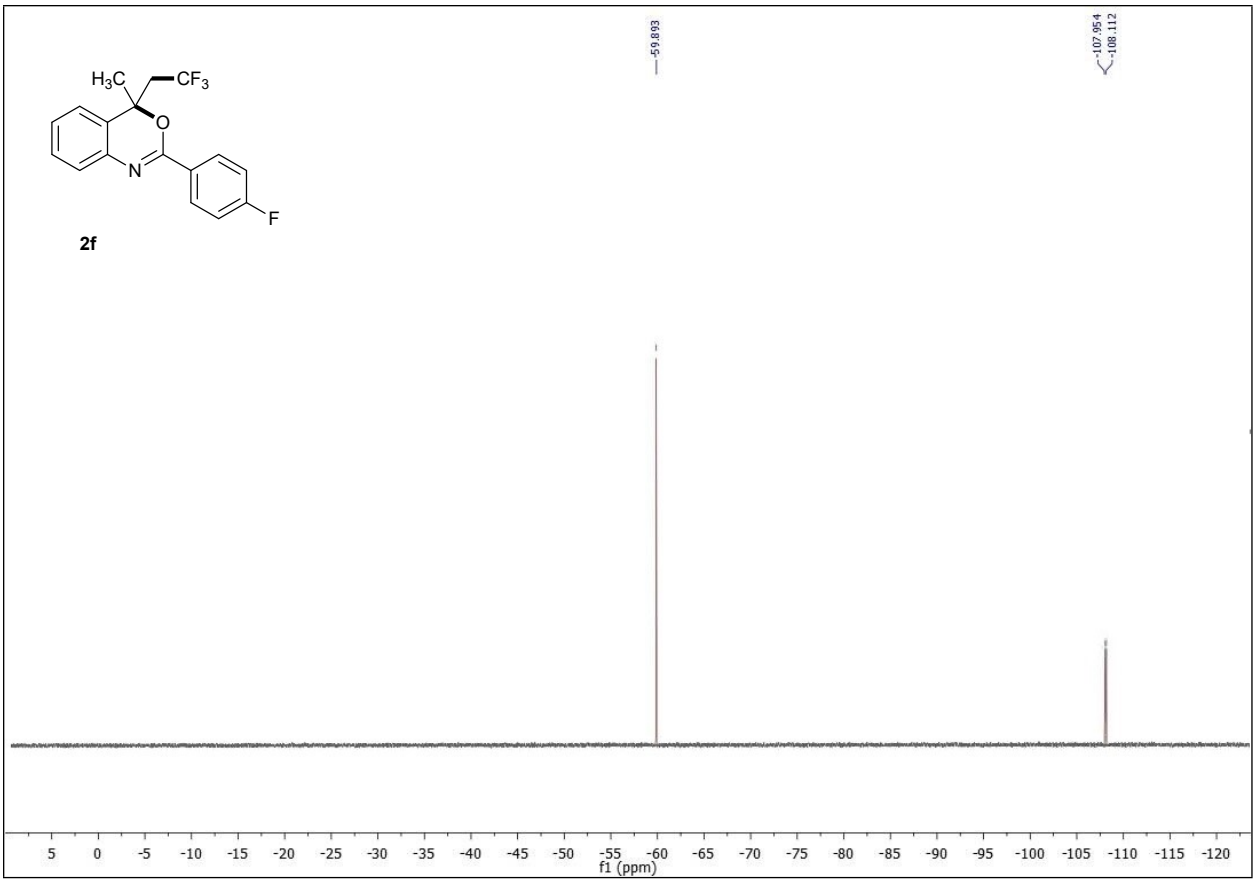


Figure S12. ^{19}F NMR spectra of **2f** in CD_2Cl_2

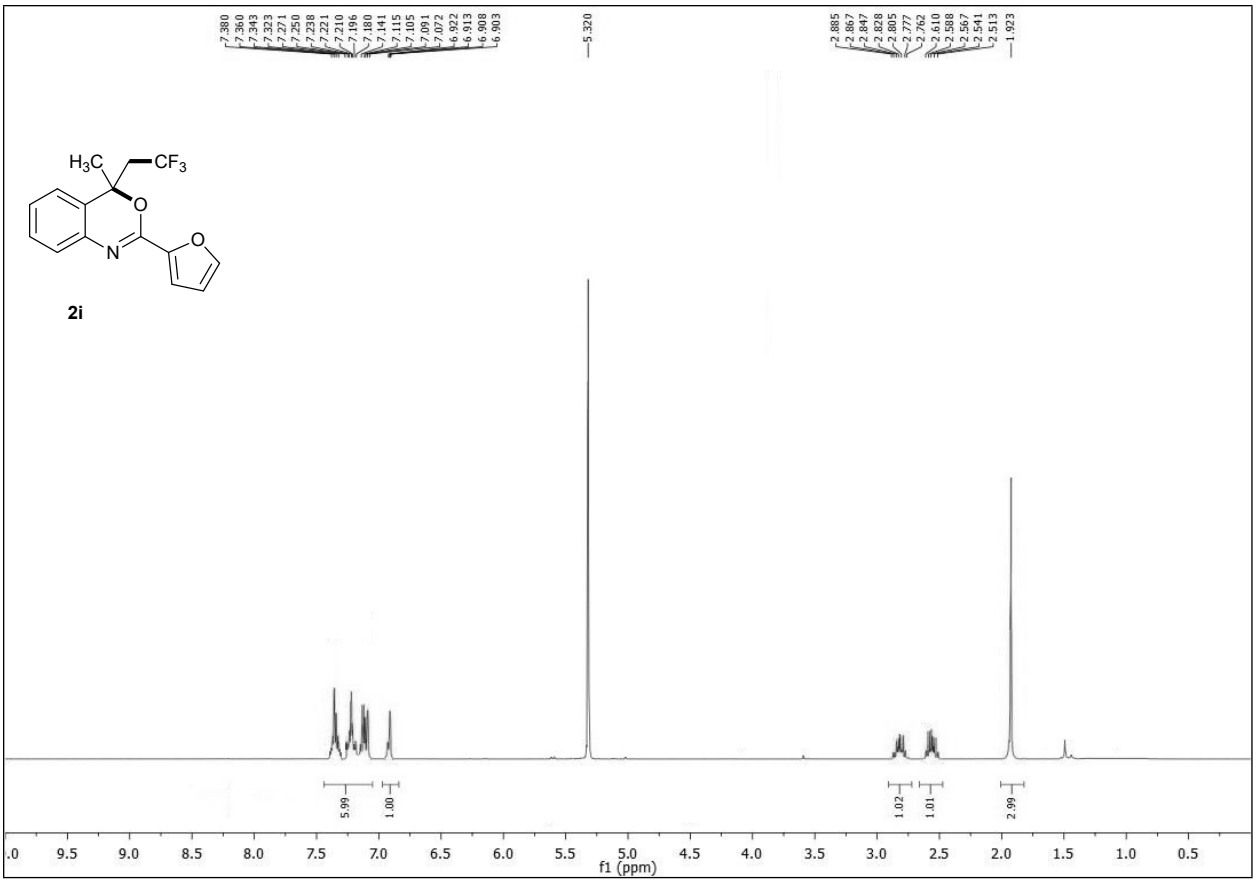


Figure S13. ^{1}H NMR spectra of **2i** in CD_2Cl_2

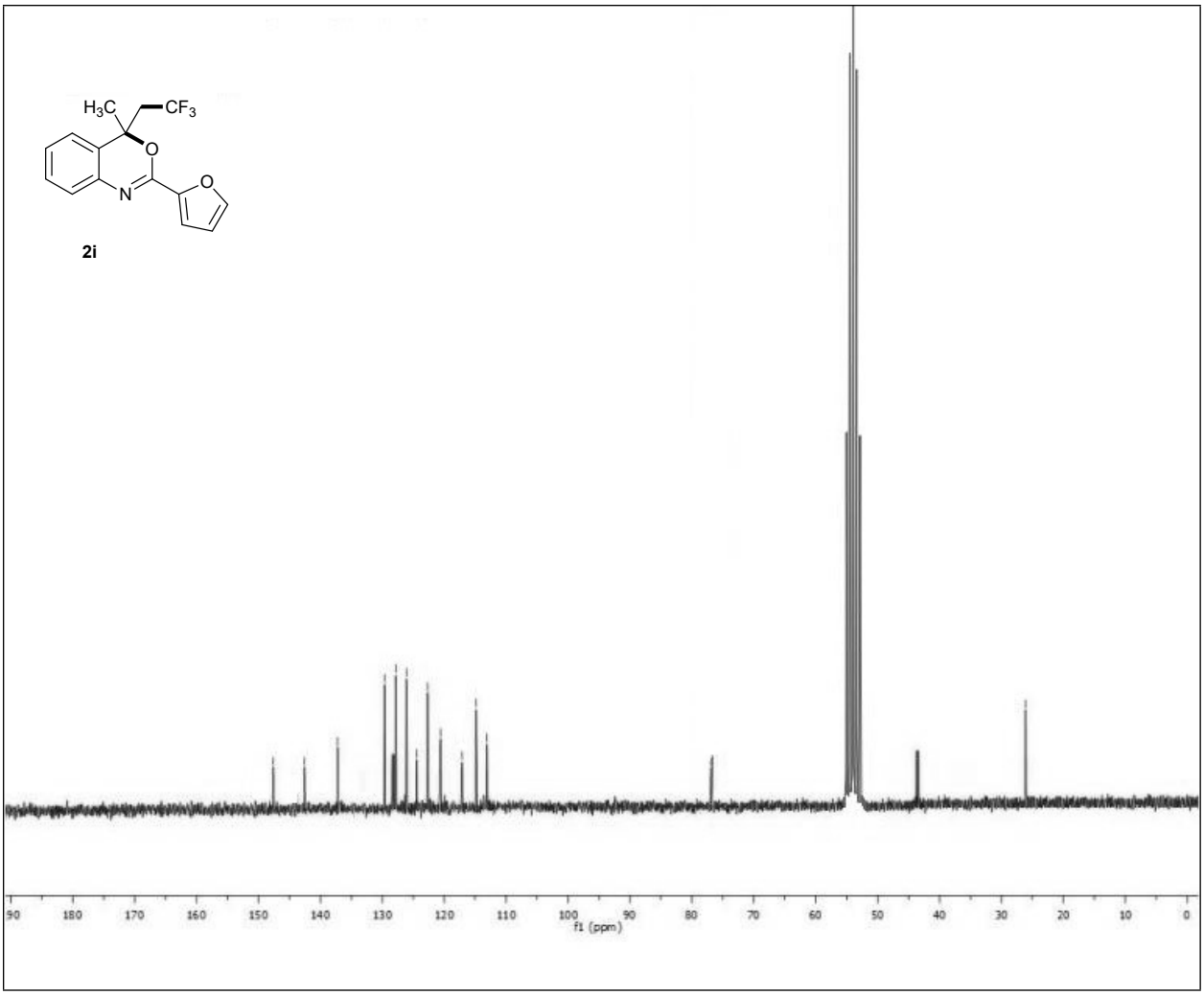


Figure S14. ^{13}C NMR spectra of **2i** in CD_2Cl_2

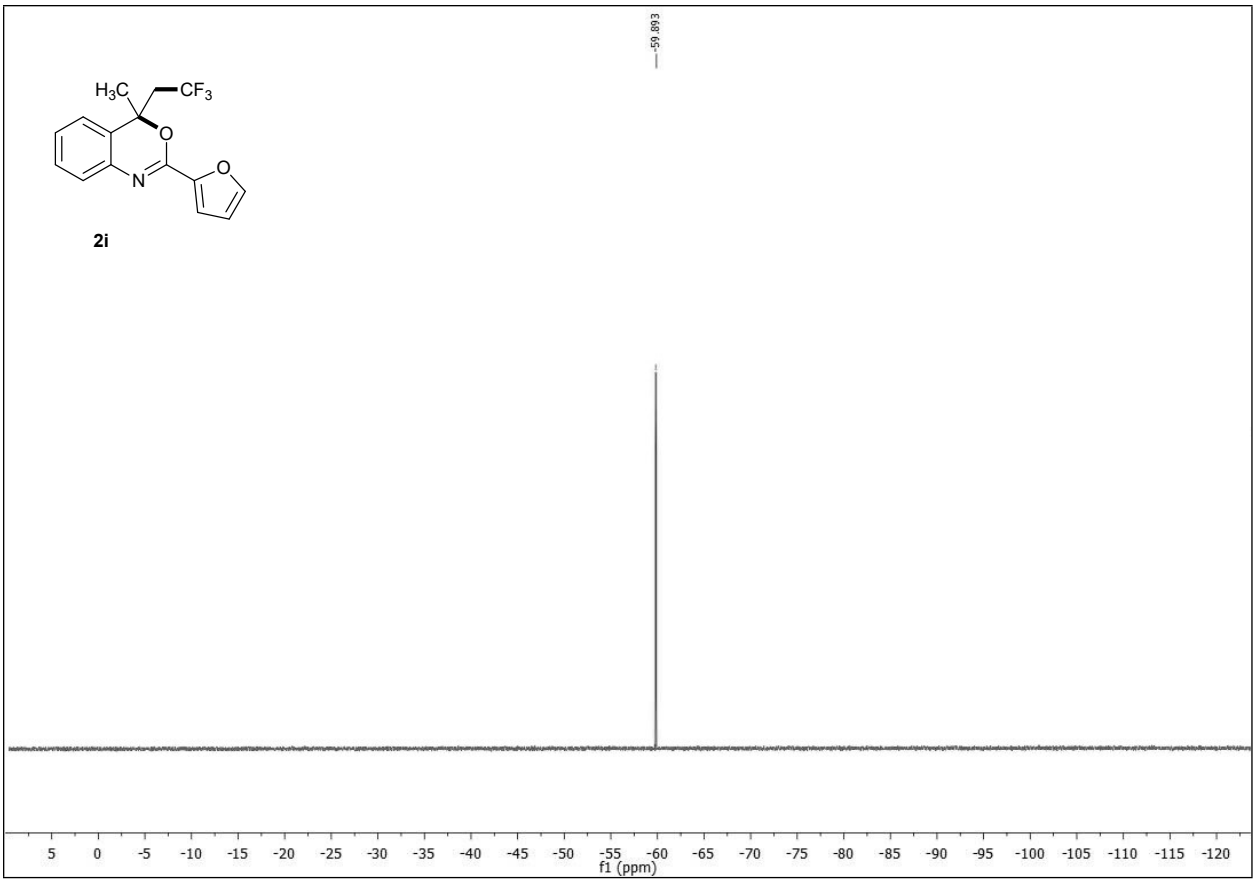


Figure S15. ^{19}F NMR spectra of **2i** in CD_2Cl_2

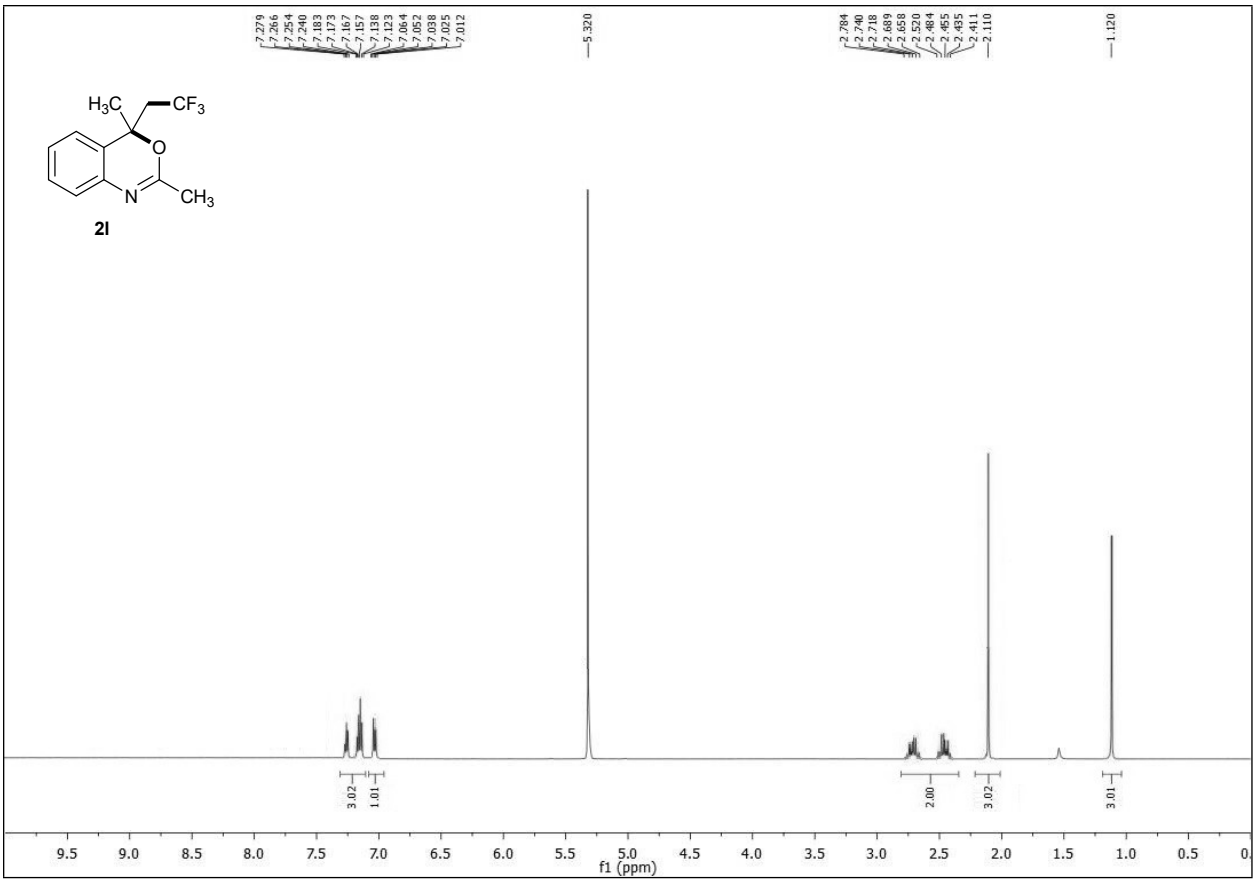


Figure S16. ^{1}H NMR spectra of **2l** in CD_2Cl_2

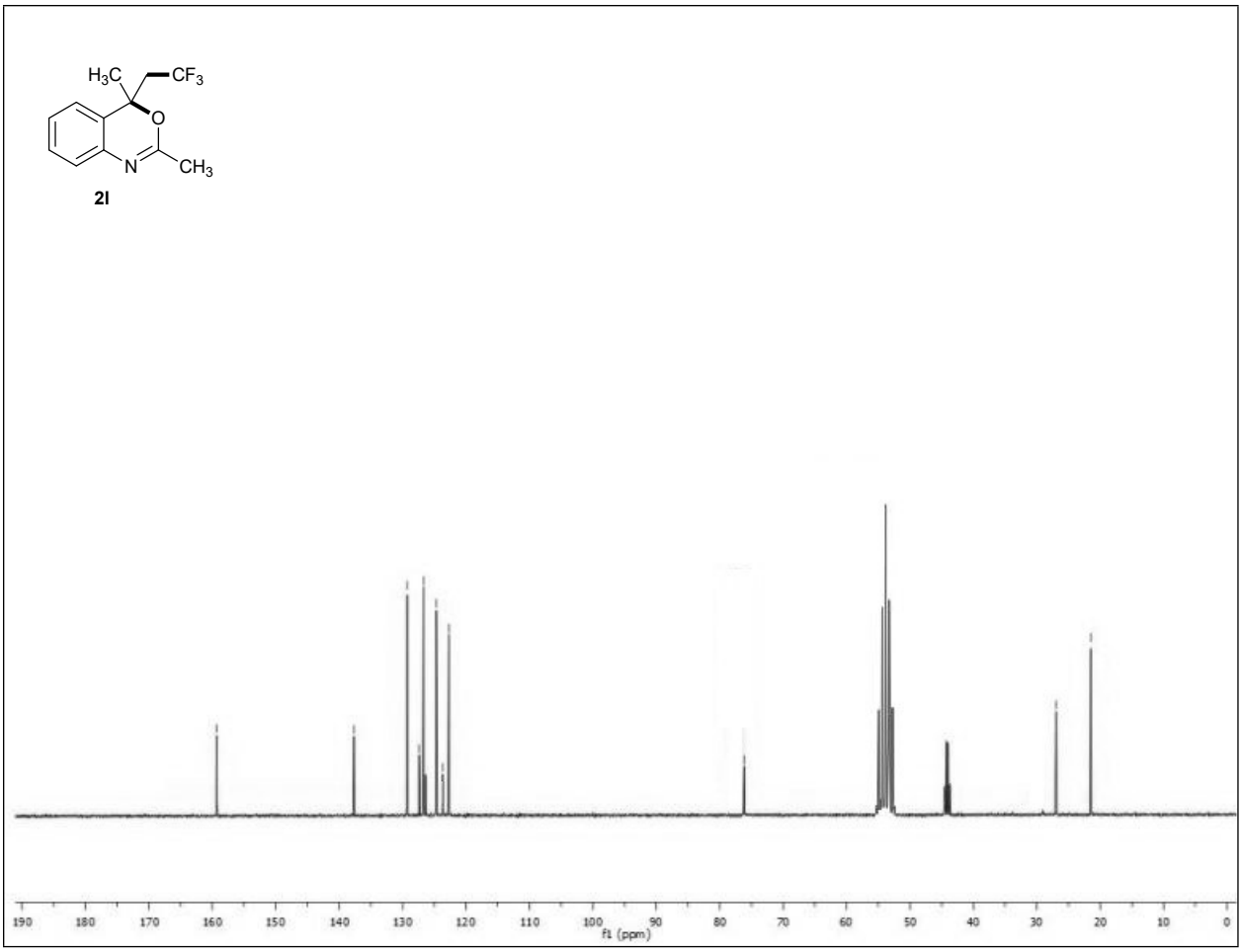


Figure S17. ^{13}C NMR spectra of **2l** in CD_2Cl_2

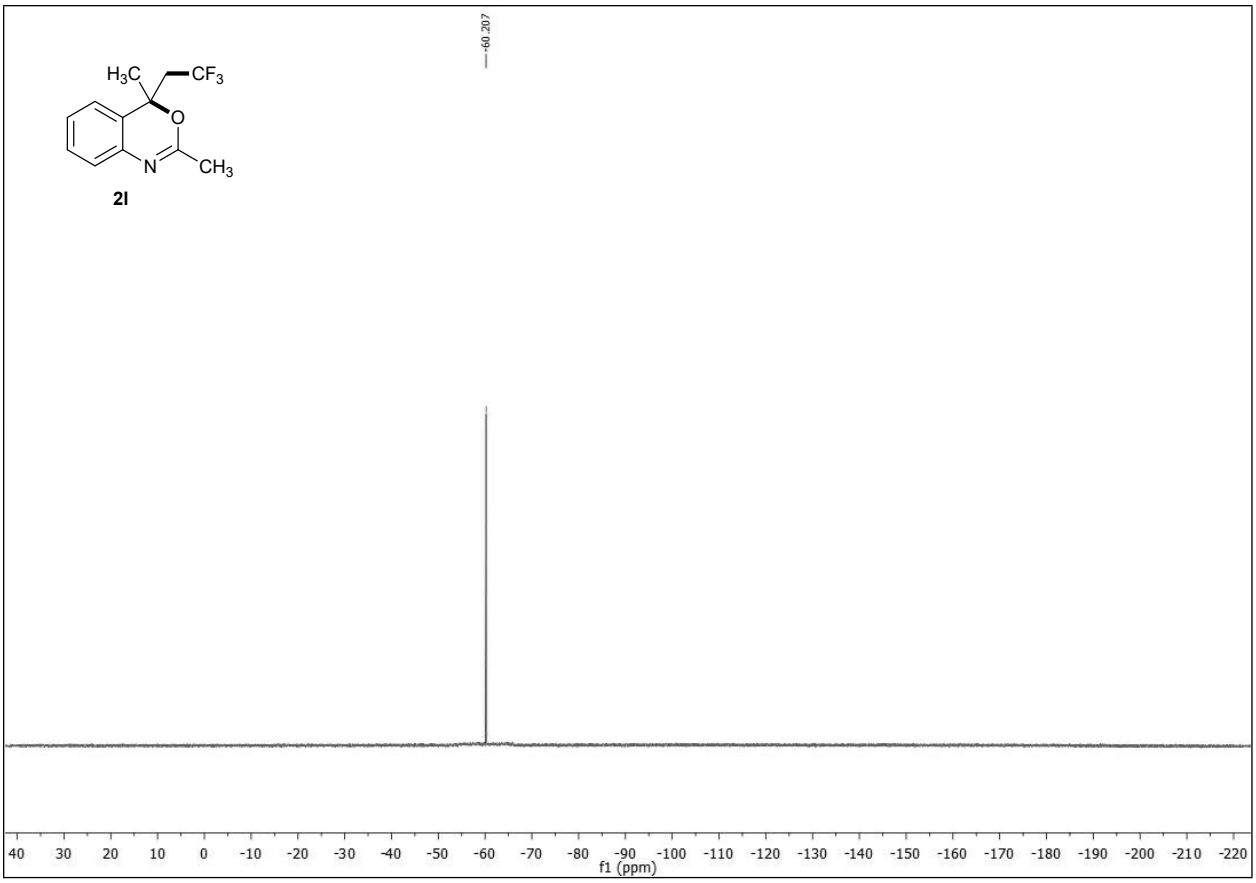


Figure S18. ^{19}F NMR spectra of **2l** in CD_2Cl_2