

Supporting Information

Radical-mediated remote migration of quinoxalinones

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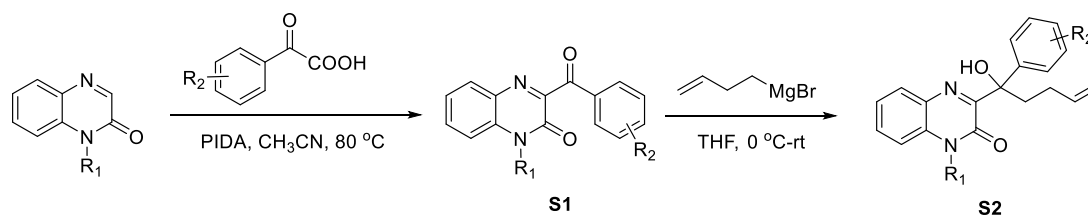
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1. General experimental details

All reactions were maintained under a nitrogen atmosphere unless otherwise stated. Commercially available reagents were used without further purification. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70, $\nu_{\max}$ in cm^{-1} . ^1H -NMR spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard (CDCl_3 : δ 7.26, $\text{DMSO-}d_6$: δ 2.50, CD_3OD : δ 3.31, acetone- d_6 : δ 2.05). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C -NMR spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16). ^{19}F -NMR spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer. Mass spectra were measured with an Agilent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT PremierTM and BRUKER micrOTF-Q III. Melting points were measured using INESA WRR and values are uncorrected.

2. General procedures for synthesis of starting materials

Starting materials **1a-1k** were prepared according to the following procedures:



Step 1: To a dry round bottom flask was added 2-quinoxalinone (1.0 equiv.), benzoylformic acid (2.0 equiv.) and PIDA (1.5 equiv.) in CH_3CN (20 mL) at rt under N_2 . The reaction mixture was stirred at $80\text{ }^\circ\text{C}$ overnight and quenched with saturated NaHCO_3 solution. The reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over MgSO_4 , filtered, concentrated in vacuum, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/ petroleum ether) to give **S1** with 50-60% yield as yellow solid.

Step 2: To a dry round bottom flask was added **S1** (1.0 equiv.) in dry THF (20 mL), then 3-butenylmagnesium bromide in THF (10 mL) was added dropwise at $0\text{ }^\circ\text{C}$ under N_2 . The reaction mixture was stirred at room temperature for 3h and quenched with saturated NH_4Cl solution. The reaction was extracted with ethyl acetate, concentrated in vacuum, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/ petroleum ether) to give **S2** with 40-50% yield as yellow solid.

3. General procedures for radical-mediated migration of quinoxalinones



Light off



Light on

Figure S1 Reaction apparatus

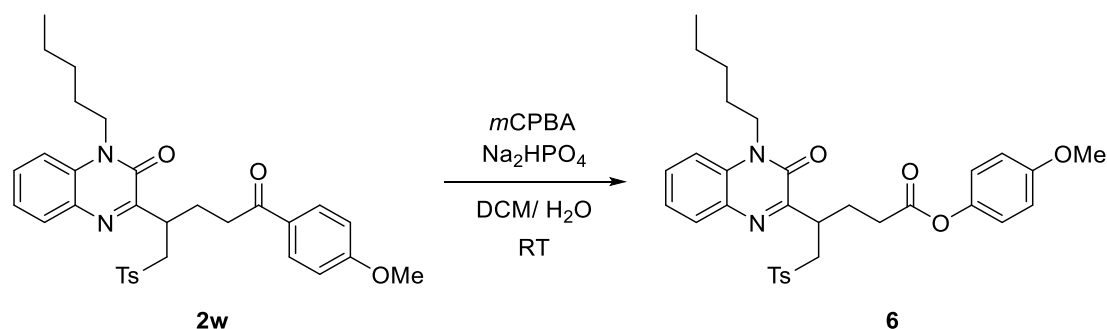
Formation of product 2: To a reaction flask was added **1** (0.2 mmol), TsCl (1.5 equiv.), Na₂CO₃ (1.0 equiv.) and *fac*-Ir-(ppy)₃ (3 mol %) under N₂, then CH₃CN (2.0 mL) was added to the mixture via syringe and the mixture was stirred under 18W blue LEDs irradiation for 12h. The reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over MgSO₄, filtered, concentrated in vacuum, and purified by flash column chromatography on silica gel to give product **2**.

Formation of product 3: To a reaction flask was added **1** (0.2 mmol), Togni's reagent II (2.0 equiv.) and CuI (20 mol %) under N₂, then CHCl₃ (2.0 mL) was added to the mixture via syringe and the mixture was stirred at rt for 12h. The reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over MgSO₄, filtered, concentrated in vacuum, and purified by flash column chromatography on silica gel to give product **3**.

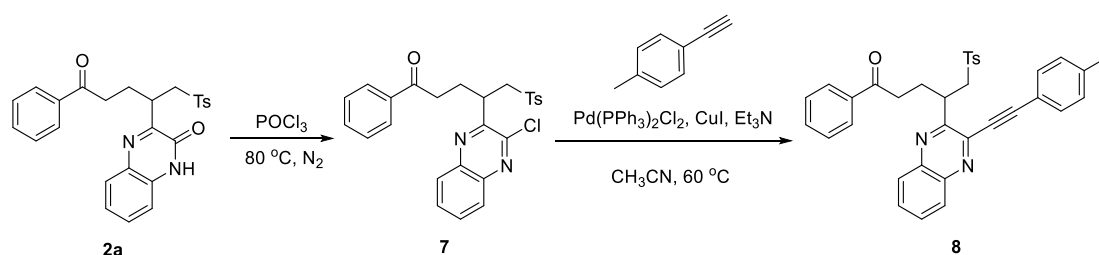
Formation of product 4: To a reaction flask was added **1** (0.2 mmol), BrCF₂CO₂Et or BrCHF₂CO₂Et (2.0 equiv.), K₂CO₃ (1.0 equiv.) and *fac*-Ir(ppy)₃ (3 mol %) under N₂, then CH₃CN (2.0 mL) was added to the mixture via syringe and the mixture was stirred under 30W blue LEDs irradiation for 12h. The reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over MgSO₄, filtered, concentrated in vacuum, and purified by flash column chromatography on silica gel to give product **4**.

Formation of product 5: To a reaction flask was added **1** (0.2 mmol) and PIFA (2.0 equiv.) under N₂, then CH₃CN (2.0 mL) was added to the mixture via syringe, and then TMSN₃ (4.0 equiv.) was added to the reaction in the mixing state. The mixture was stirred at rt for 4h. The reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over MgSO₄, filtered, concentrated in vacuum, and purified by flash column chromatography on silica gel to give product **5**.

4. General procedures for product transformations



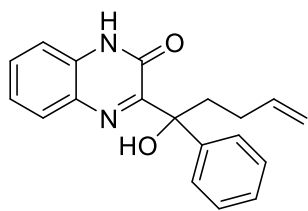
To a reaction flask was added **2w** (90.0 mg, 1.0 equiv.), *m*CPBA (41.0 mg, 1.5 equiv.) and Na₂HPO₄ (34.0 mg, 1.5 equiv.) followed by co-solvent DCM/ H₂O (1.0 mL/ 0.1 mL) at RT under N₂. The reaction mixture was stirred overnight and quenched with saturated NH₄Cl solution. The reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over MgSO₄, filtered, concentrated in vacuum, and purified by flash column chromatography on silica gel to give **6** with 80% yield.



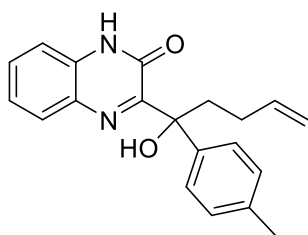
Step 1: To a reaction flask was added **2a** (70.0 mg, 0.15 mmol) and POCl₃ (0.45 mL) under N₂, and the mixture was stirred at 80 °C for 3h. After ambient temperature was reached, the reaction mixture was quenched by water, and extracted with DCM. The combined organic layer was washed with 1M KHSO₄ solution, saturated NaHCO₃ solution, and brine, dried over anhydrous Na₂SO₄, filtered, concentrated, and purified by flash column chromatography on silica gel to afford product **7** as a yellow solid with 85% yield.

Step 2: To a reaction flask was added **7** (47.8 mg, 0.1 mmol), 4-ethynyl toluene (13.9 μ L, 0.11 mmol), CuI (1.0 mg, 5 mol %), Pd(PPh₃)₂Cl₂ (3.5 mg, 5 mol %), Et₃N (0.25 mL) and CH₃CN (0.4 mL) at rt under N₂. The mixture was stirred overnight. The resulting mixture was extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous Na₂SO₄, filtered, concentrated, and purified by flash column chromatography on silica gel to give **8** with 82% yield.

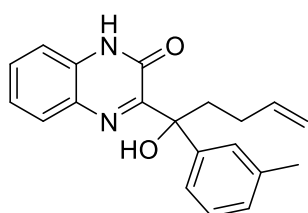
5. Characterization of starting materials



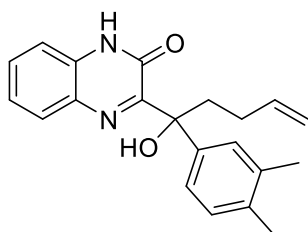
1a: 453.1 mg, 74%, yellow solid, m.p. 122-123 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 12.2 (s, 1H), 7.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.58-7.49 (m, 3H), 7.46-7.38 (m, 1H), 7.30 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.24-7.18 (m, 1H), 7.06 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.14 (s, 1H), 5.93-5.81 (m, 1H), 5.05-4.84 (m, 2H), 2.76-2.66 (m, 1H), 2.51-2.41 (m, 1H), 2.27-2.05 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 156.2, 144.0, 139.0, 131.9, 130.8, 130.8, 129.5, 128.1, 127.1, 125.6, 124.9, 115.6, 114.3, 79.3, 38.4, 27.9. FT-IR: ν (cm⁻¹) 3171, 2973 1659, 1612, 1934. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₁₉H₁₈N₂O₂Na 329.1260; found 329.1278.



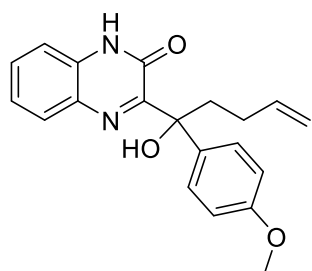
1b: 408.3 mg, 64%, yellow solid, m.p. 135-136 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 11.4 (s, 1H), 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.48 (m, 1H), 7.44-7.38 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 3H), 5.96-5.77 (m, 1H), 5.03-4.95 (m, 1H), 4.93-4.87 (m, 1H), 2.73-2.63 (m, 1H), 2.49-2.38 (m, 1H), 2.28 (s, 3H), 2.24-2.05 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 155.7, 140.9, 139.1, 136.7, 131.9, 130.8, 130.6, 129.5, 128.8, 125.6, 124.8, 115.4, 114.2, 79.2, 38.4, 28.0, 21.0. FT-IR: ν (cm⁻¹) 3424, 3070, 2850, 1651, 1382. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₀H₂₀N₂O₂Na 343.1417; found 343.1424.



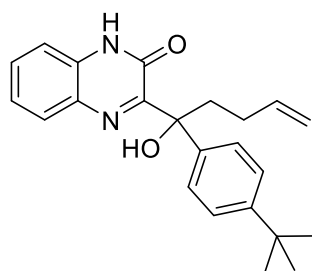
1c: 122 mg, 47%, yellow solid, m.p. 130-131 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 12.0 (s, 1H), 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.49 (m, 1H), 7.46-7.38 (m, 1H), 7.37-7.30 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10-6.99 (m, 2H), 6.09 (s, 1H), 5.93-5.81 (m, 1H), 5.04-4.86 (m, 2H), 2.76-2.64 (m, 1H), 2.50-2.38 (m, 1H), 2.32 (s, 3H), 2.26-2.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 156.0, 143.9, 139.1, 137.6, 131.9, 130.9, 130.7, 129.5, 127.9, 126.2, 124.8, 122.8, 115.5, 114.2, 79.3, 38.5, 29.7, 28.0, 21.7. FT-IR: ν (cm⁻¹) 3423, 3141, 2915, 1676, 1554. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₀H₂₀N₂O₂Na 343.1417; found 343.1428.



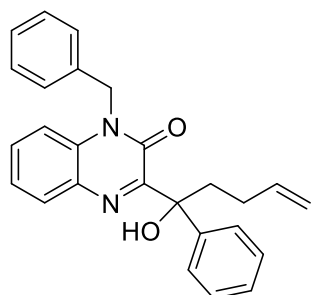
1d: 350 mg, 52%, yellow solid, m.p. 142-143 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 12.3 (s, 1H), 7.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.58-7.48 (m, 1H), 7.44-7.39 (m, 1H), 7.31-7.26 (m, 2H), 7.14-7.03 (m, 2H), 6.10 (s, 1H), 5.95-5.81 (m, 1H), 5.03-4.89 (m, 2H), 2.75-2.65 (m, 1H), 2.50-2.38 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 2.17-2.06 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 156.2, 141.4, 139.2, 136.2, 135.4, 132.0, 130.9, 130.6, 129.5, 129.4, 126.8, 124.8, 123.1, 115.6, 114.2, 79.1, 38.4, 28.0, 20.0, 19.4. FT-IR: ν (cm⁻¹) 3423, 2969, 1648, 1553, 1380. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₁H₂₂N₂O₂Na 357.1573; found 357.1572.



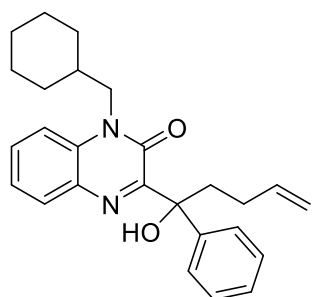
1e: 355.8 mg, 53%, yellow solid, m.p. 124-125 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ^1H NMR (400 MHz, CDCl_3) δ 11.8 (s, 1H), 7.94 (dd, J = 8.0, 1.2 Hz, 1H), 7.55-7.50 (m, 1H), 7.49-7.44 (m, 2H), 7.43-7.38 (m, 1H), 7.08 (dd, J = 8.0, 1.2 Hz, 1H), 6.85-6.80 (m, 2H), 6.12 (s, 1H), 5.92-5.80 (m, 1H), 5.03-4.95 (m, 1H), 4.92-4.86 (m, 1H), 3.74 (s, 3H), 2.76-2.65 (m, 1H), 2.49-2.38 (m, 1H), 2.24-2.06 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 158.7, 155.6, 139.1, 135.9, 131.8, 130.9, 130.7, 129.5, 126.9, 124.8, 115.3, 114.2, 113.4, 78.9, 55.2, 38.4, 28.0. FT-IR: ν (cm^{-1}) 3447, 3076, 2836, 1651, 1652, 1253. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3\text{Na}$ 359.1366; found 359.1364.



1f: 195.7 mg, 27%, yellow solid, m.p. 193-195 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ^1H NMR (400 MHz, CDCl_3) δ 12.2 (s, 1H), 7.95 (dd, J = 8.4, 1.2 Hz, 1H), 7.57-7.51 (m, 1H), 7.50-7.45 (m, 2H), 7.44-7.38 (m, 1H), 7.33-7.27 (m, 2H), 7.15 (dd, J = 8.0, 0.8 Hz, 1H), 6.20 (s, 1H), 5.94-5.81 (m, 1H), 5.03-4.96 (m, 1H), 4.94-4.86 (m, 1H), 2.79-2.68 (m, 1H), 2.51-2.40 (m, 1H), 2.25-2.07 (m, 2H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 156.2, 149.9, 140.8, 139.1, 131.9, 130.9, 130.7, 129.4, 125.4, 124.9, 124.8, 115.6, 114.2, 79.2, 38.4, 34.4, 31.3, 28.0. FT-IR: ν (cm^{-1}) 3275, 3168, 3101, 2857, 1638, 1370. FT-IR: ν (cm^{-1}) 3453, 3300, 2965, 1650, 1610, 1379. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_2\text{Na}$ 385.1886; found 385.1869.

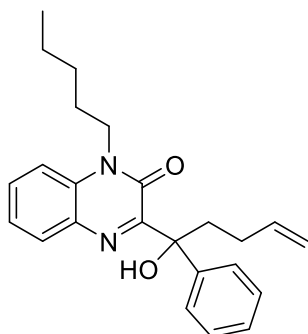


1g: 158.2 mg, 23%, yellow solid, m.p. 103-104 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (dd, J = 7.6, 1.2 Hz, 1H), 7.58-7.52 (m, 2H), 7.50-7.43 (m, 1H), 7.42-7.35 (m, 1H), 7.35-7.29 (m, 2H), 7.29-7.26 (m, 2H), 7.25-7.22 (m, 3H), 7.13-7.07 (m, 2H), 6.23 (s, 1H), 5.94-5.82 (m, 1H), 5.52-5.28 (m, 2H), 5.04-4.97 (m, 1H), 4.93-4.88 (m, 1H), 2.76-2.63 (m, 1H), 2.56-2.38 (m, 1H), 2.32-2.20 (m, 1H), 2.14-2.02 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 154.5, 144.2, 139.2, 134.7, 132.4, 132.1, 130.7, 130.6, 129.0, 128.1, 127.8, 127.1, 126.7, 125.4, 124.2, 114.5, 114.2, 79.6, 45.7, 38.8, 28.0. FT-IR: ν (cm^{-1}) 3422, 2975, 1636, 1598, 1395, 1314. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2\text{Na}$ 419.1730; found 419.1738.

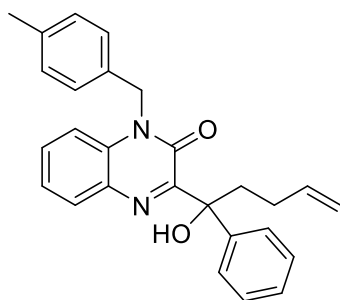


1h: 80 mg, 24%, yellow solid, m.p. 128-129 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (dd, J = 8.0, 1.6 Hz, 1H), 7.62-7.54 (m, 1H), 7.53-7.47 (m, 2H), 7.44-7.37 (m, 1H), 7.36-7.27 (m, 3H), 7.23-7.16 (m, 1H), 6.27 (s, 1H), 5.93-5.81 (m, 1H), 5.06-4.86 (m, 2H), 4.13-3.93 (m, 2H), 2.71-2.61 (m, 1H), 2.47-2.37 (m, 1H), 2.27-2.18 (m, 1H), 2.10-2.01 (m, 1H), 1.86-1.76 (m, 1H), 1.69-1.59 (m, 3H), 1.50-1.44 (m, 1H), 1.30-1.22 (m, 2H), 1.16-1.05 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 154.6, 144.2, 139.3, 132.6, 132.1, 130.8, 130.4, 128.0,

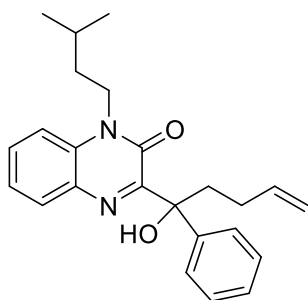
126.9, 125.4, 123.9, 114.2, 114.1, 79.5, 47.7, 38.7, 36.4, 30.7, 28.0, 26.1, 25.7. FT-IR: ν (cm⁻¹) 3365, 2921, 1635, 1599, 1396, 1276, 1145. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₆H₃₀N₂O₂Na 425.2199; found 425.2181.



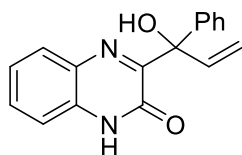
1i: 572.8 mg, 52%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 10/1). ¹H NMR (400 MHz, CDCl₃) δ 8.0 (dd, J = 8.0, 1.6 Hz, 1H), 7.61-7.56 (m, 1H), 7.55-7.51 (m, 2H), 7.44-7.39 (m, 1H), 7.35-7.27 (m, 3H), 7.24-7.18 (m, 1H), 6.33 (s, 1H), 5.94-5.80 (m, 1H), 5.04-4.95 (m, 1H), 4.93-4.86 (m, 1H), 4.24-4.05 (m, 2H), 2.71-2.60 (m, 1H), 2.49-2.38 (m, 1H), 2.30-2.18 (m, 1H), 2.12-2.00 (m, 1H), 1.72-1.63 (m, 2H), 1.48-1.15 (m, 4H), 0.90-0.84 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 154.2, 144.3, 139.3, 132.3, 132.2, 130.8, 130.6, 128.0, 127.0, 125.4, 123.9, 114.1, 113.8, 79.6, 42.2, 38.9, 29.0, 28.0, 26.9, 22.3, 13.9. FT-IR: ν (cm⁻¹) 3402, 3081, 2857, 1634, 1600, 1489, 1384. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₄H₂₈N₂O₂Na 399.2043; found 399.2050.



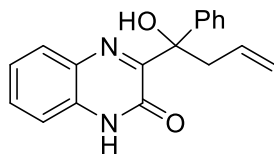
1j: 242.9 mg, 33%, yellow solid, m.p. 147-148 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 10/1). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, J = 8.0, 1.2 Hz, 1H), 7.52 (d, J = 6.8 Hz, 2H), 7.47-7.40 (m, 1H), 7.37-7.26 (m, 3H), 7.26-7.16 (m, 2H), 7.08-6.92 (m, 4H), 6.22 (s, 1H), 5.92-5.79 (m, 1H), 5.44-5.21 (m, 2H), 5.02-4.83 (m, 2H), 2.72-2.61 (m, 1H), 2.50-2.38 (m, 1H), 2.25 (s, 3H), 2.31-2.18 (m, 1H), 2.11-1.99 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 154.5, 144.2, 139.2, 137.6, 132.4, 132.1, 131.7, 130.6, 130.6, 129.6, 128.1, 127.1, 126.8, 125.5, 124.1, 114.6, 114.2, 79.6, 45.5, 38.8, 28.0, 21.1. FT-IR: ν (cm⁻¹) 3446, 2976, 1637, 1599, 1588, 1373. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₇H₂₆N₂O₂Na 433.1886; found 433.1882.



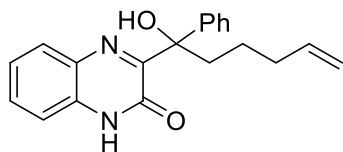
1k: 293.2 mg, 43%, yellow solid, m.p. 81-82 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 10/1). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, J = 8.0, 1.2 Hz, 1H), 7.62-7.56 (m, 1H), 7.55-7.50 (m, 2H), 7.44-7.38 (m, 1H), 7.33-7.26 (m, 3H), 7.24-7.18 (m, 1H), 6.31 (s, 1H), 5.92-5.80 (m, 1H), 5.02-4.95 (m, 1H), 4.93-4.86 (m, 1H), 4.26-4.17 (m, 1H), 4.15-4.05 (m, 1H), 2.69-2.59 (m, 1H), 2.47-2.37 (m, 1H), 2.28-2.17 (m, 1H), 2.09-2.01 (m, 1H), 1.74-1.65 (m, 1H), 1.29-1.22 (m, 2H), 0.98 (dd, J = 6.8, 1.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 154.1, 144.3, 139.3, 132.2, 132.2, 130.8, 130.6, 128.0, 127.0, 125.4, 123.9, 114.1, 113.7, 79.6, 40.9, 38.9, 35.6, 28.0, 26.5, 22.4. FT-IR: ν (cm⁻¹) 3372, 2956, 2926, 2868, 1633, 1598, 1397. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₄H₂₈N₂O₂Na 399.2043; found 399.2052.



9: 280.0 mg, 70%, yellow solid, m.p. 175-177 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 12.5 (s, 1H), 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52-7.45 (m, 3H), 7.41-7.35 (m, 1H), 7.33-7.26 (m, 2H), 7.25-7.20 (m, 1H), 7.07-6.98 (m, 1H), 6.95 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.11 (s, 1H), 5.67 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.38 (dd, *J* = 10.8, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 155.7, 143.2, 138.8, 131.4, 131.3, 130.9, 129.2, 128.2, 127.5, 126.4, 124.8, 115.8, 115.5, 78.9. FT-IR: ν (cm⁻¹) 3447, 3060, 2961, 2849, 1650, 1551, 1379. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₁₇H₁₄N₂NaO₂ 301.0947; found 301.0956.

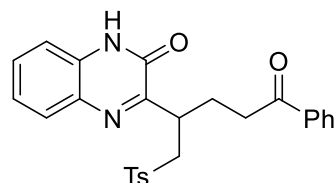


10: 290.2 mg, 67%, yellow solid, m.p. 171-174 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 12.5 (s, 1H), 7.99-7.91 (m, 1H), 7.60-7.48 (m, 3H), 7.45-7.38 (m, 1H), 7.34-7.26 (m, 2H), 7.25-7.18 (m, 1H), 7.08-7.02 (m, 1H), 6.15 (s, 1H), 5.94-5.80 (m, 1H), 5.19-5.09 (m, 1H), 5.05-4.95 (m, 1H), 3.53-3.43 (m, 1H), 3.18-3.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 156.2, 143.7, 133.8, 131.8, 130.9, 130.9, 129.4, 128.1, 127.3, 125.7, 124.9, 118.1, 115.7, 79.0, 43.6. FT-IR: ν (cm⁻¹) 3447, 3062, 2962, 2847, 1652, 1597, 1495, 1361. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₁₈H₁₆N₂O₂Na 315.1104; found 315.1112.

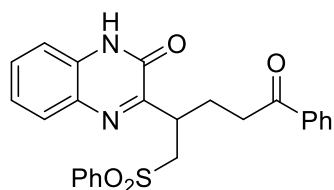


11: 272.7 mg, 57%, yellow solid, m.p. 105-107 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 12.6 (s, 1H), 7.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.60-7.48 (m, 3H), 7.45-7.39 (m, 1H), 7.34-7.27 (m, 2H), 7.24-7.18 (m, 1H), 7.09 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.17 (s, 1H), 5.88-5.75 (m, 1H), 5.06-4.90 (m, 2H), 2.69-2.59 (m, 1H), 2.43-2.33 (m, 1H), 2.18-2.06 (m, 2H), 1.58-1.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 156.3, 144.2, 139.0, 132.0, 130.9, 130.8, 129.5, 128.0, 127.1, 125.7, 124.8, 115.8, 114.4, 79.5, 38.8, 34.1, 22.8. FT-IR: ν (cm⁻¹) 3447, 3060, 2961, 2849, 1650, 1551, 1379. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₀H₂₀N₂O₂Na 343.1417; found 343.1428.

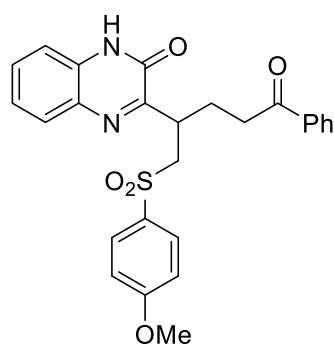
6. Characterization of products



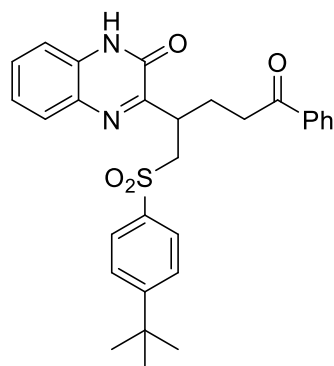
2a: 68.0 mg, 74%, yellow solid, m.p. 161-167 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.3 (s, 1H), 7.85-7.76 (m, 2H), 7.73-7.61 (m, 3H), 7.55-7.42 (m, 2H), 7.40-7.26 (m, 4H), 7.06 (d, *J* = 10.8 Hz, 2H), 4.41-4.30 (m, 1H), 4.22-4.12 (m, 1H), 3.52-3.40 (m, 1H), 3.16-2.90 (m, 2H), 2.39-2.22 (m, 2H), 2.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.9, 159.3, 156.0, 144.6, 136.6, 136.1, 133.1, 132.4, 130.8, 130.5, 129.6, 128.9, 128.5, 128.2, 127.9, 124.2, 115.6, 58.7, 36.2, 35.4, 28.3, 21.4. FT-IR: ν (cm⁻¹) 2919, 1661, 1495, 1449, 1288, 1210. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₆H₂₄N₂O₄SNa 483.1349; found 483.1355.



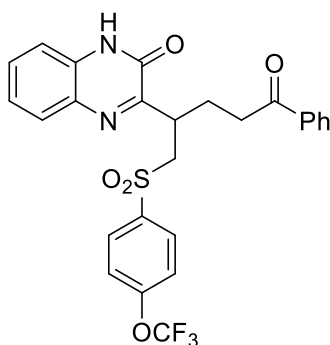
2b: 60.0 mg, 67%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.5 (s, 1H), 7.85-7.78 (m, 4H), 7.70-7.66 (m, 1H), 7.54-7.37 (m, 3H), 7.37-7.27 (m, 6H), 4.42-4.34 (m, 1H), 4.24-4.14 (m, 1H), 3.50 (dd, J = 14.0, 2.8 Hz, 1H), 3.15-2.91 (m, 2H), 2.37-2.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 159.4, 156.1, 139.1, 136.6, 133.4, 133.1, 132.4, 130.8, 130.5, 129.0, 128.9, 128.5, 128.2, 127.9, 124.2, 115.7, 58.7, 36.1, 35.4, 28.2. FT-IR: ν (cm^{-1}) 3060, 2902, 2253, 1659, 1497, 1368, 1209. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_4\text{SNa}$ 469.1192; found 469.1208.



2c: 38.2 mg, 40%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.2 (s, 1H), 7.83-7.79 (m, 2H), 7.75-7.65 (m, 3H), 7.53-7.43 (m, 2H), 7.38-7.26 (m, 4H), 6.74-6.69 (m, 2H), 4.39-4.31 (m, 1H), 4.19-4.10 (m, 1H), 3.66 (s, 3H), 3.46 (dd, J = 14.0, 2.8 Hz, 1H), 3.14-3.04 (m, 1H), 3.02-2.91 (m, 1H), 2.36-2.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 163.5, 159.5, 155.9, 136.6, 133.1, 132.4, 130.7, 130.6, 130.4, 128.9, 128.5, 127.9, 124.2, 115.5, 114.1, 58.9, 55.5, 36.3, 35.5, 28.3. FT-IR: ν (cm^{-1}) 2963, 2921, 2253, 1659, 1594, 1496, 1315, 1208. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_5\text{SNa}$ 499.1298; found 499.1284.

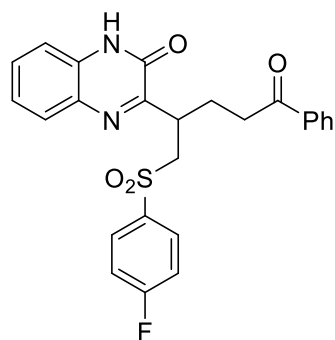


2d: 27.7 mg, 30%, yellow solid, m.p. 103-104 $^{\circ}\text{C}$. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.2 (s, 1H), 8.17-8.15 (m, 1H), 7.86-7.81 (m, 2H), 7.78-7.69 (m, 3H), 7.54-7.48 (m, 4H), 7.38-7.31 (m, 3H), 4.47-4.38 (m, 1H), 4.21-4.14 (m, 1H), 3.52-3.45 (m, 1H), 3.13-2.97 (m, 2H), 2.34-2.22 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 157.4, 156.0, 136.6, 135.9, 133.6, 133.1, 132.4, 130.4, 130.1, 128.5, 128.4, 128.2, 127.9, 125.9, 124.4, 115.7, 58.3, 36.2, 35.5, 35.0, 30.9, 28.3. FT-IR: ν (cm^{-1}) 3065, 2924, 2558, 1671, 1583, 1495, 1421, 1290. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4\text{SNa}$ 525.1818; found 525.1820.

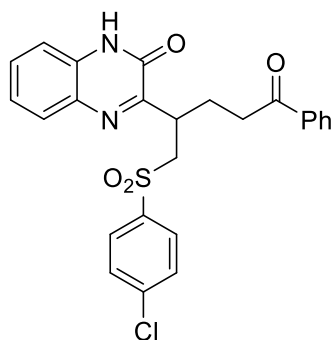


2e: 76.3 mg, 72%, yellow solid, m.p. 137-140 $^{\circ}\text{C}$. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 12.3 (s, 1H), 7.94-7.89 (m, 2H), 7.86-7.79 (m, 2H), 7.62-7.57 (m, 2H), 7.51-7.40 (m, 5H), 7.28-7.21 (m, 2H), 4.26-4.16 (m, 1H), 3.93-3.81 (m, 2H), 3.14-2.90 (m, 2H), 2.14-2.00 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 199.5, 160.7, 154.7, 152.1 (q, $J_{\text{C-F}}$ = 1.6 Hz), 138.3, 137.0, 133.4, 132.1, 131.6, 131.0, 130.4, 129.0, 128.6, 128.2, 123.5, 121.5, 120.1 (q, $J_{\text{C-F}}$ = 257.1 Hz), 115.6, 57.4, 36.1, 35.4, 27.7; ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -56.8 (s). FT-IR: ν (cm^{-1}) 3395, 2919, 2849, 1612, 1560, 1469,

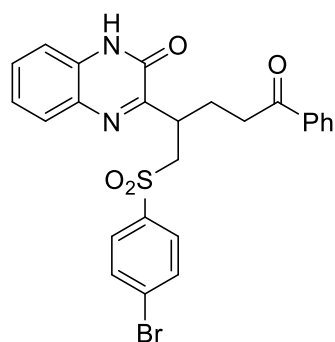
1373, 1288, 1206. HRMS [ESI] m/z: [M+Na]⁺ calcd for C₂₆H₂₁N₂O₅SF₃Na 553.1015; found 553.1011.



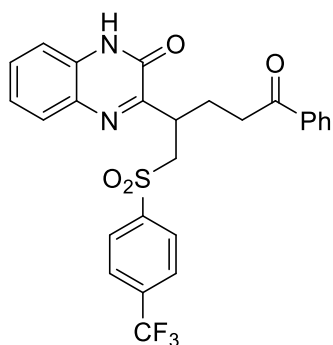
2f: 39.6 mg, 45%, yellow solid, m.p. 128-135 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.4 (s, 1H), 7.86-7.80 (m, 4H), 7.62-7.57 (m, 2H), 7.51-7.44 (m, 3H), 7.31-7.23 (m, 4H), 4.21-4.11 (m, 1H), 3.88-3.78 (m, 2H), 3.13-3.03 (m, 1H), 3.00-2.91 (m, 1H), 2.13-2.01 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 199.6, 165.3 (d, *J*_{C-F} = 251.3 Hz), 160.8, 154.7, 137.0, 135.9 (d, *J*_{C-F} = 2.7 Hz), 133.5, 132.1, 131.7, 131.5 (d, *J*_{C-F} = 9.9 Hz), 130.4, 129.0, 128.7, 128.2, 123.5, 116.8 (d, *J*_{C-F} = 22.6 Hz), 115.6, 57.7, 36.2, 35.4, 27.7. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -104.96 (s). FT-IR: ν (cm⁻¹) 3395, 2919, 2256, 1683, 1589, 1433, 1369, 1225. HRMS [ESI] m/z: [M+Na]⁺ calcd for C₂₅H₂₁FN₂O₄SNa 487.1098; found 487.1096.



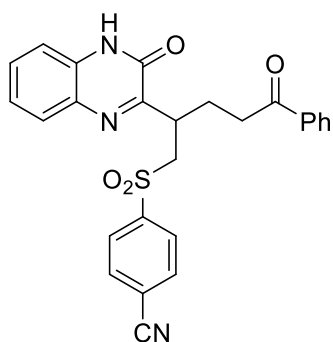
2g: 26.2 mg, 40%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.3 (s, 1H), 7.87-7.80 (m, 2H), 7.78-7.73 (m, 2H), 7.62-7.56 (m, 2H), 7.52-7.43 (m, 5H), 7.29-7.23 (m, 2H), 4.23-4.14 (m, 1H), 3.89-3.80 (m, 2H), 3.15-2.89 (m, 2H), 2.13-2.01 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 199.5, 160.6, 154.7, 139.2, 138.3, 137.0, 133.4, 132.1, 131.7, 130.4, 130.1, 129.7, 129.0, 128.6, 128.2, 123.5, 115.6, 57.6, 36.2, 35.4, 27.8. FT-IR: ν (cm⁻¹) 3404, 2921, 2851, 1685, 1579, 1470, 1411, 1370, 1243. HRMS [ESI] m/z: [M+Na]⁺ calcd for C₂₅H₂₁N₂O₄SClNa 503.0803; found 503.0819.



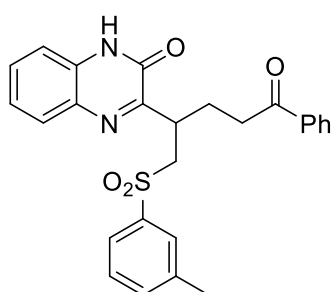
2h: 48.6 mg, 47%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.3 (s, 1H), 7.84-7.79 (m, 2H), 7.69-7.53 (m, 6H), 7.51-7.42 (m, 3H), 7.34-7.21 (m, 2H), 4.25-4.11 (m, 1H), 3.86-3.77 (m, 2H), 3.16-2.84 (m, 2H), 2.12-1.98 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 199.6, 160.6, 154.6, 138.7, 137.0, 133.5, 132.7, 132.1, 131.6, 130.4, 130.2, 129.0, 128.6, 128.3, 128.2, 123.5, 115.7, 57.5, 36.2, 35.4, 27.7. FT-IR: ν (cm⁻¹) 3374, 2924, 1682, 1573, 1503, 1448, 1371, 1245. HRMS [ESI] m/z: [M+Na]⁺ calcd for C₂₅H₂₁N₂O₄SBrNa 547.0298; found 547.0289.



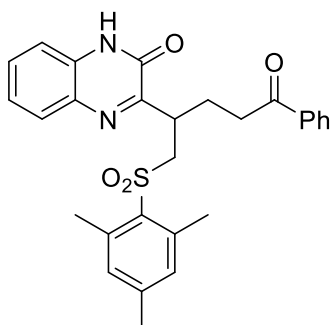
2i: 49.6 mg, 50%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, DMSO- d_6) δ 12.3 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.85-7.81 (m, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.62-7.56 (m, 1H), 7.54-7.51 (m, 1H), 7.49-7.43 (m, 3H), 7.25-7.18 (m, 2H), 4.31-4.22 (m, 1H), 3.96-3.83 (m, 2H), 3.16-2.90 (m, 2H), 2.15-2.01 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 199.5, 160.4, 154.6, 143.3 (q, $J_{\text{C-F}}$ = 0.9 Hz), 137.0, 133.5 (q, $J_{\text{C-F}}$ = 32.1 Hz), 133.5, 132.0, 131.5, 130.4, 129.3, 129.0, 128.5, 128.2, 126.7 (q, $J_{\text{C-F}}$ = 3.6 Hz), 125.8 (q, $J_{\text{C-F}}$ = 271.5 Hz), 123.5, 115.6, 57.3, 36.1, 35.4, 27.8; ^{19}F NMR (376 MHz, DMSO- d_6) δ -61.86 (s). FT-IR: ν (cm^{-1}) 3397, 2918, 2852, 1674, 1402, 1232, 1211. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{N}_2\text{O}_4\text{SF}_3\text{Na}$ 537.1066; found 537.1072.



2j: 28.3 mg, 30%, yellow solid, m.p. 189-191 $^{\circ}\text{C}$. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, DMSO- d_6) δ 12.3 (s, 1H), 7.94-7.81 (m, 6H), 7.62-7.43 (m, 5H), 7.29-7.23 (m, 2H), 4.29-4.19 (m, 1H), 3.97-3.82 (m, 2H), 3.16-2.92 (m, 2H), 2.16-2.02 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 199.5, 160.4, 154.7, 143.6, 137.0, 133.6, 133.5, 132.1, 131.5, 130.6, 129.0, 129.0, 128.7, 128.2, 123.5, 117.8, 116.2, 115.6, 57.4, 36.1, 35.4, 27.7. FT-IR: ν (cm^{-1}) 3405, 2958, 2851, 1669, 1486, 1399, 1284, 1209. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_4\text{SNa}$ 494.1145; found 494.1148.

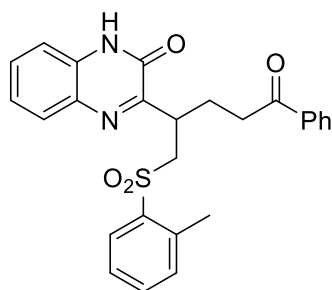


2k: 56.3 mg, 61%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.83-7.79 (m, 2H), 7.69-7.59 (m, 2H), 7.56 (s, 1H), 7.53-7.43 (m, 2H), 7.38-7.26 (m, 4H), 7.18-7.09 (m, 2H), 4.43-4.34 (m, 1H), 4.23-4.13 (m, 1H), 3.48 (dd, J = 14.4, 2.8 Hz, 1H), 3.16-3.05 (m, 1H), 3.02-2.92 (m, 1H), 2.35-2.21 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 159.3, 156.0, 139.3, 138.9, 136.6, 134.1, 133.1, 132.3, 130.7, 130.5, 128.9, 128.9, 128.6, 128.5, 127.9, 125.3, 124.2, 115.6, 58.7, 36.1, 35.4, 28.3, 21.0. FT-IR: ν (cm^{-1}) 2921, 2850, 1659, 1561, 1368, 1209. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4\text{SNa}$ 483.1349; found 483.1334.

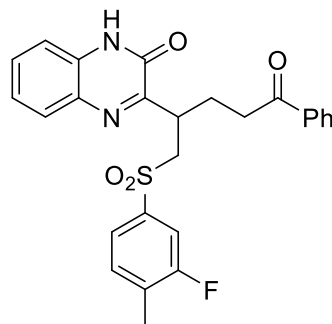


2l: 34.3 mg, 35%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.85-7.80 (m, 2H), 7.68-7.64 (m, 1H), 7.51-7.44 (m, 2H), 7.38-7.29 (m, 3H), 7.26-7.23 (m, 1H), 6.53 (s, 2H), 4.57-4.49 (m, 1H), 4.30-4.21 (m, 1H), 3.41-3.35 (m, 1H), 3.21-3.10 (m, 1H), 3.04-2.95 (m, 1H), 2.57 (s, 6H), 2.34-2.24 (m, 2H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 159.2, 155.8, 143.2, 140.1, 136.7, 133.1, 132.6, 132.2, 132.0, 130.8,

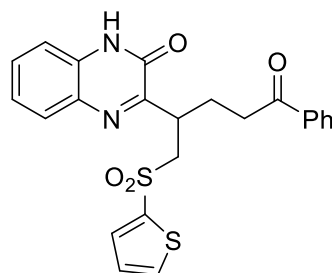
130.3, 128.8, 128.5, 127.9, 124.2, 115.5, 58.4, 36.0, 35.5, 28.6, 22.9, 20.8. FT-IR: ν (cm⁻¹) 3674, 2972, 2901, 1978, 1596, 1307, 1277. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₈H₂₈N₂O₄SNa 511.1662; found 511.1672.



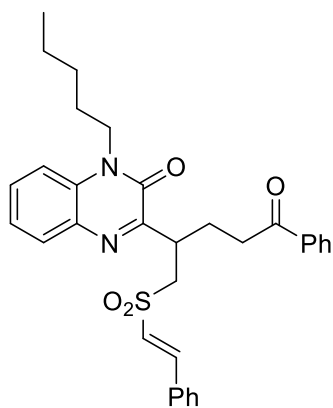
2m: 42.2 mg, 48%, yellow solid, m.p. 153-155 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.4 (s, 1H), 7.87-7.83 (m, 3H), 7.70-7.68 (m, 1H), 7.57-7.45 (m, 3H), 7.38-7.33 (m, 3H), 7.22-7.17 (m, 1H), 7.09-7.04 (m, 1H), 6.94-6.90 (m, 1H), 4.54-4.45 (m, 1H), 4.27-4.21 (m, 1H), 3.53-3.48 (m, 1H), 3.18-3.11 (m, 1H), 3.05-2.98 (m, 1H), 2.64 (s, 3H), 2.34-2.27 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 159.3, 156.0, 138.3, 136.9, 136.6, 133.3, 133.1, 132.3, 132.2, 130.8, 130.5, 130.2, 128.7, 128.5, 127.9, 126.3, 124.2, 115.7, 57.6, 35.8, 35.5, 28.5, 20.4; FT-IR: ν (cm⁻¹) 2971, 2917, 2359, 1698, 1521, 1287, 1210. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₆H₂₄N₂O₄SNa 483.1349; found 483.1339.



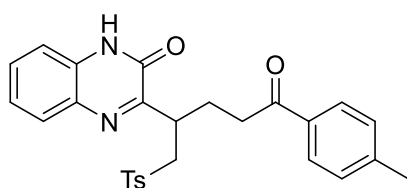
2n: 52.6 mg, 55%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.5 (s, 1H), 7.86-7.78 (m, 2H), 7.68-7.63 (m, 1H), 7.55-7.42 (m, 4H), 7.37-7.28 (m, 4H), 7.12-7.04 (m, 1H), 4.43-4.32 (m, 1H), 4.24-4.14 (m, 1H), 3.47 (dd, J = 14.4, 2.8 Hz, 1H), 3.16-2.88 (m, 2H), 2.34-2.22 (m, 2H), 2.08 (d, J = 1.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 160.6 (d, J_{C-F} = 249.1 Hz), 159.1, 156.1, 138.3 (d, J_{C-F} = 6.5 Hz), 136.6, 133.1, 132.3, 132.1 (d, J_{C-F} = 4.8 Hz), 131.8 (d, J_{C-F} = 17.2 Hz), 130.7, 130.6, 128.9, 128.5, 127.9, 124.3, 123.8 (d, J_{C-F} = 3.6 Hz), 115.7, 115.2 (d, J_{C-F} = 25.2 Hz), 58.7, 36.0, 35.3, 28.4, 14.6 (d, J_{C-F} = 3.5 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -113.67 (s). FT-IR: ν (cm⁻¹) 3064, 2925, 1664, 1582, 1449, 1317, 1231. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₆H₂₃N₂O₄FSNa 501.1255; found 501.1246.



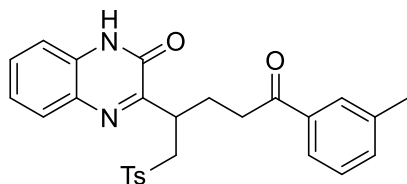
2o: 60.0 mg, 66%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.4 (s, 1H), 7.85-7.78 (m, 2H), 7.74-7.69 (m, 1H), 7.62 (dd, J = 3.6, 1.2 Hz, 1H), 7.53-7.44 (m, 3H), 7.38-7.28 (m, 4H), 6.90 (dd, J = 4.8, 3.6 Hz, 1H), 4.51-4.43 (m, 1H), 4.27-4.18 (m, 1H), 3.58 (dd, J = 14.4, 3.2 Hz, 1H), 3.17-2.93 (m, 2H), 2.38-2.24 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 159.2, 156.1, 140.2, 136.6, 134.6, 134.1, 133.1, 132.4, 130.8, 130.5, 129.0, 128.5, 127.9, 127.7, 124.3, 115.7, 59.9, 36.4, 35.4, 28.2. FT-IR: ν (cm⁻¹) 3090, 2917, 2850, 2252, 1658, 1504, 1448, 1312, 1211. HRMS [ESI] m/z : [M+Na]⁺ calcd for C₂₃H₂₀N₂O₄S₂Na 475.0757; found 475.0760.



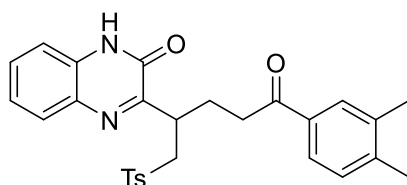
2p: 45.5 mg, 42%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.80 (m, 3H), 7.55-7.49 (m, 2H), 7.43-7.32 (m, 5H), 7.28-7.23 (m, 2H), 7.23-7.18 (m, 2H), 7.13 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 15.6 Hz, 1H), 4.33-4.24 (m, 1H), 4.23-4.16 (m, 1H), 4.07-3.87 (m, 2H), 3.47-3.40 (m, 1H), 3.16-2.96 (m, 2H), 2.42-2.24 (m, 2H), 1.59-1.47 (m, 2H), 1.39-1.32 (m, 4H), 0.94-0.89 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.9, 159.5, 154.2, 144.6, 136.7, 133.1, 132.7, 132.2, 132.1, 131.1, 130.3, 130.1, 128.9, 128.5, 128.4, 128.0, 125.1, 123.5, 113.7, 57.7, 42.3, 37.0, 35.8, 29.0, 28.1, 26.7, 22.3, 14.0. FT-IR: ν (cm^{-1}) 3058, 2924, 2854, 2251, 1683, 1489, 1398, 1244. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_4\text{SNa}$ 565.2131; found 565.2134.



2q: 51.0 mg, 60%, yellow solid, m.p. 174-176 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.74-7.64 (m, 5H), 7.52-7.47 (m, 1H), 7.34-7.27 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 4.39-4.32 (m, 1H), 4.18-4.11 (m, 1H), 3.46 (dd, J = 14.4, 2.8 Hz, 1H), 3.09-3.01 (m, 1H), 2.98-2.89 (m, 1H), 2.31 (s, 3H), 2.30-2.19 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 159.4, 156.0, 144.6, 143.9, 136.1, 134.1, 132.3, 130.8, 130.4, 129.6, 129.2, 128.9, 128.2, 128.0, 124.2, 115.6, 58.7, 36.2, 35.3, 28.4, 21.6, 21.4. FT-IR: ν (cm^{-1}) 2924, 2854, 2253, 1669, 1404, 1285, 1208. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_4\text{SNa}$ 497.1505; found 497.1490.

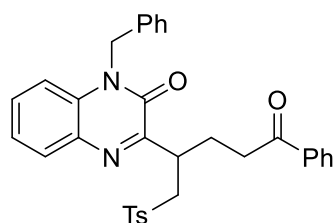


2r: 56.2 mg, 60%, yellow solid, m.p. 146-148 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.4 (s, 1H), 7.69-7.58 (m, 5H), 7.53-7.47 (m, 1H), 7.35-7.27 (m, 3H), 7.25-7.20 (m, 1H), 7.08-7.03 (m, 2H), 4.40-4.32 (m, 1H), 4.21-4.13 (m, 1H), 3.47 (dd, J = 14.0, 2.8 Hz, 1H), 3.12-2.90 (m, 2H), 2.37-2.31 (m, 1H), 2.30 (s, 3H), 2.27-2.21 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 159.3, 156.0, 144.6, 138.3, 136.7, 136.1, 133.8, 132.3, 130.8, 130.4, 129.6, 128.9, 128.4, 128.2, 125.1, 124.2, 115.6, 58.6, 36.2, 35.5, 28.3, 21.4, 21.3. FT-IR: ν (cm^{-1}) 3629, 2959, 2360, 1672, 1488, 1286, 1232. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_4\text{SNa}$ 497.1505; found 497.1502.

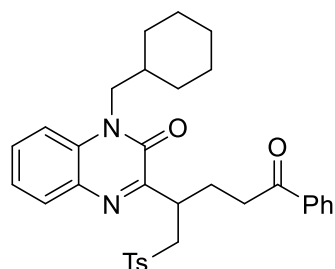


2s: 33.5 mg, 40%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.4 (s, 1H), 7.69-7.63 (m, 3H), 7.58-7.46 (m, 3H), 7.34-7.27 (m, 2H), 7.10-7.02 (m, 3H), 4.40-4.32 (m, 1H), 4.19-4.11 (m, 1H), 3.46 (dd, J = 14.4, 2.8 Hz, 1H), 3.11-2.87 (m, 2H), 2.35-2.23 (m, 2H), 2.21 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 159.4, 156.0, 144.6, 142.6, 136.8, 136.1, 134.6, 132.3, 130.8, 130.4, 129.7, 129.6, 129.0, 128.9, 128.2, 125.7, 124.1, 115.6, 58.6, 36.3, 35.3, 28.4, 21.4, 19.9, 19.7. FT-IR: ν (cm^{-1}) 2922, 2853, 1662, 1501, 1431, 1360, 1284, 1206. HRMS [ESI] m/z :

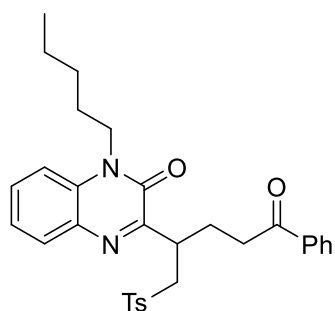
$[M+Na]^+$ calcd for $C_{28}H_{28}N_2O_4SNa$ 511.1662; found 511.1671.



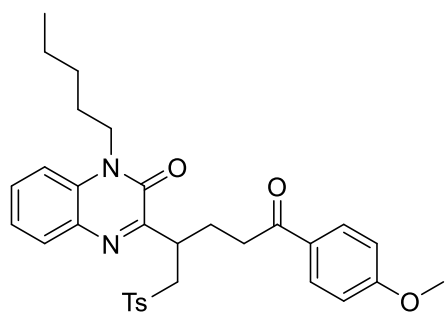
2t: 88.0 mg, 80%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). 1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 2H), 7.73-7.63 (m, 3H), 7.53-7.48 (m, 1H), 7.41-7.26 (m, 8H), 7.25-7.18 (m, 2H), 7.06 (d, J = 8.0 Hz, 2H), 5.49-5.37 (m, 2H), 4.39-4.32 (m, 1H), 4.18-4.09 (m, 1H), 3.46-3.39 (m, 1H), 3.11-2.90 (m, 2H), 2.37-2.18 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 159.2, 154.6, 144.3, 136.6, 136.2, 135.2, 133.1, 132.5, 132.2, 130.2, 130.0, 129.6, 129.0, 128.5, 128.3, 127.9, 127.7, 127.0, 123.6, 114.3, 58.6, 45.9, 36.8, 35.6, 28.3, 21.4. FT-IR: ν (cm^{-1}) 3061, 2924, 1683, 1600, 1449, 1367, 1288, 1207. HRMS [ESI] m/z : $[M+Na]^+$ calcd for $C_{33}H_{30}N_2O_4SNa$ 573.1818; found 573.1819.



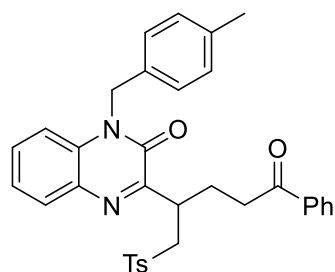
2u: 80.1 mg, 72%, yellow solid, m.p. 136-138 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). 1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.76 (m, 2H), 7.71-7.65 (m, 3H), 7.53-7.45 (m, 2H), 7.42-7.34 (m, 2H), 7.32-7.26 (m, 1H), 7.25-7.20 (m, 1H), 7.09 (d, J = 8.4 Hz, 2H), 4.38-4.28 (m, 1H), 4.19-3.93 (m, 3H), 3.43-3.34 (m, 1H), 3.08-2.97 (m, 1H), 2.93-2.83 (m, 1H), 2.20 (s, 3H), 2.17-2.11 (m, 1H), 1.78-1.56 (m, 6H), 1.26-1.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 159.0, 154.6, 144.3, 136.6, 136.2, 133.0, 132.5, 132.5, 130.2, 130.0, 129.5, 128.5, 128.4, 127.9, 123.3, 113.9, 58.6, 48.1, 36.6, 35.7, 30.9, 30.8, 28.4, 26.2, 25.8, 21.4. FT-IR: ν (cm^{-1}) 2922, 2850, 1684, 1488, 1399, 1288, 1208. HRMS [ESI] m/z : $[M+Na]^+$ calcd for $C_{33}H_{36}N_2O_4SNa$ 579.2288; found 579.2296.



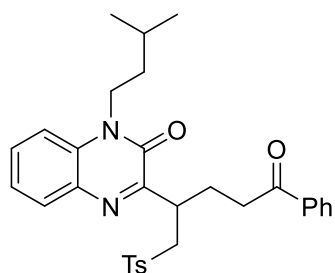
2v: 84.5 mg, 81%, yellow solid, m.p. 97-98 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). 1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.76 (m, 2H), 7.68-7.63 (m, 3H), 7.52-7.47 (m, 2H), 7.41-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.25-7.19 (m, 1H), 7.04 (d, J = 8.0 Hz, 2H), 4.38-4.29 (m, 1H), 4.17-4.02 (m, 3H), 3.42-3.36 (m, 1H), 3.09-2.85 (m, 2H), 2.33-2.19 (m, 1H), 2.16 (s, 3H), 2.14-2.04 (m, 1H), 1.74-1.61 (m, 2H), 1.46-1.36 (m, 4H), 0.96-0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 158.8, 153.9, 144.2, 136.6, 136.2, 133.0, 132.4, 132.1, 130.2, 130.1, 129.5, 128.5, 128.3, 127.9, 123.3, 113.4, 58.4, 42.4, 36.8, 35.7, 29.1, 28.2, 26.9, 22.4, 21.4, 14.0. FT-IR: ν (cm^{-1}) 2924, 2852, 1684, 1600, 1468, 1301, 1245, 1208. HRMS [ESI] m/z : $[M+Na]^+$ calcd for $C_{31}H_{34}N_2O_4SNa$ 553.2131; found 553.2134.



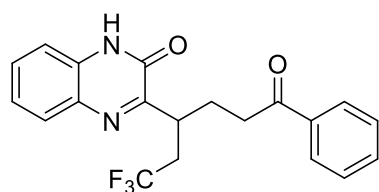
2w: 46.3 mg, 43%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.82-7.77 (m, 2H), 7.69-7.64 (m, 3H), 7.54-7.47 (m, 1H), 7.31-7.27 (m, 1H), 7.72-7.20 (m, 1H), 7.05 (d, J = 8.0 Hz, 2H), 6.89-6.82 (m, 2H), 4.33 (dd, J = 14.4, 10.0 Hz, 1H), 4.20-4.09 (m, 2H), 4.09-4.01 (m, 1H), 3.84 (s, 3H), 3.39 (dd, J = 14.4, 3.2 Hz, 1H), 3.03-2.81 (m, 2H), 2.48-2.32 (m, 1H), 2.17 (s, 3H), 2.14-2.00 (m, 1H), 1.76-1.66 (m, 2H), 1.50-1.34 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 163.4, 158.9, 153.9, 144.2, 136.2, 132.5, 132.1, 130.2, 130.2, 130.1, 129.7, 129.5, 128.4, 123.3, 113.6, 113.4, 58.3, 55.4, 42.4, 36.9, 35.3, 29.1, 28.4, 26.9, 22.4, 21.4, 14.0. FT-IR: ν (cm^{-1}) 3064, 2933, 1599, 1652, 1143. HRMS [ESI] m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_5\text{S}$ 561.2418; found 561.2413.



2x: 76.5 mg, 70%, yellow solid, m.p. 160-161 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.77 (m, 2H), 7.73-7.62 (m, 3H), 7.54-7.48 (m, 1H), 7.43-7.33 (m, 3H), 7.26-7.15 (m, 4H), 7.14-7.09 (m, 2H), 7.08-7.03 (m, 2H), 5.47-5.29 (m, 2H), 4.40-4.31 (m, 1H), 4.18-4.09 (m, 1H), 3.46-3.39 (m, 1H), 3.12-2.88 (m, 2H), 2.30 (s, 3H), 2.28-2.18 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.9, 159.1, 154.5, 144.3, 137.5, 136.6, 136.2, 133.1, 132.5, 132.3, 132.2, 130.2, 130.0, 129.6, 129.6, 128.5, 128.4, 128.0, 127.0, 123.5, 114.3, 58.6, 45.7, 36.8, 35.7, 28.3, 21.4, 21.1. FT-IR: ν (cm^{-1}) 2923, 2252, 1683, 1599, 1469, 1368, 1288, 1207. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_4\text{SNa}$ 587.1975; found 587.1977.

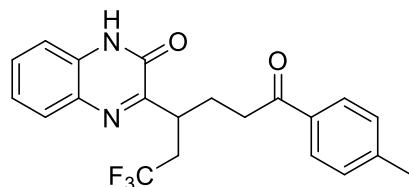


2y: 59.7 mg, 60%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.77 (m, 2H), 7.68-7.63 (m, 3H), 7.54-7.46 (m, 2H), 7.42-7.34 (m, 2H), 7.31-7.26 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 4.38-4.29 (m, 1H), 4.20-4.02 (m, 3H), 3.43-3.36 (m, 1H), 3.07-2.85 (m, 2H), 2.27-2.18 (m, 1H), 2.16 (s, 3H), 2.14-2.02 (m, 1H), 1.79-1.75 (m, 1H), 1.61-1.48 (m, 2H), 1.03 (t, J = 5.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.9, 158.8, 153.9, 144.2, 136.6, 136.2, 133.0, 132.5, 132.1, 130.2, 129.5, 128.5, 128.4, 127.9, 123.3, 113.3, 58.3, 41.0, 36.9, 35.7, 35.7, 28.2, 26.5, 22.5, 22.5, 21.4. FT-IR: ν (cm^{-1}) 2923, 2851, 1684, 1488, 1398, 1366, 1288, 1208. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4\text{SNa}$ 553.2131; found 553.2114.

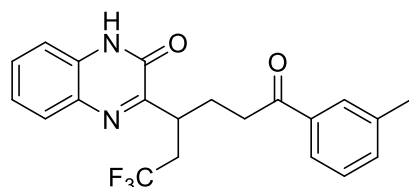


3a: 53.8 mg, 72%, yellow solid, m.p. 105-106 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.8 (s, 1H), 7.86-7.78 (m, 3H), 7.54-7.49 (m, 1H), 7.46-7.40 (m, 1H), 7.37-7.29 (m, 4H), 4.07-3.98 (m, 1H), 3.15-2.95 (m, 3H), 2.62-2.46 (m, 1H), 2.41-2.29 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 160.5, 156.5,

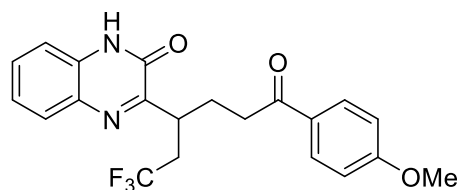
136.7, 133.0, 132.6, 130.8, 130.5, 129.0, 128.5, 127.9, 126.7 (q, $J_{\text{C-F}} = 266.0$ Hz), 124.3, 115.8, 36.6 (q, $J_{\text{C-F}} = 27.7$ Hz), 35.6, 34.7 (q, $J_{\text{C-F}} = 2.5$ Hz), 28.0; ^{19}F NMR (376 MHz, CDCl_3) δ -64.18 (s). FT-IR: ν (cm^{-1}) 2925, 1659, 1598, 1484, 1373, 1251, 1208. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_2\text{Na}$ 397.1134; found 397.1123.



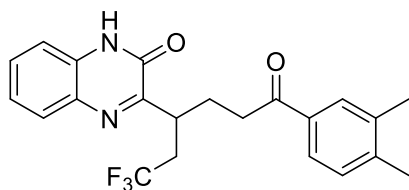
3b: 52.6 mg, 67%, yellow solid, m.p. 105-106 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.86-7.78 (m, 1H), 7.77-7.72 (m, 2H), 7.54-7.48 (m, 1H), 7.37-7.28 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 4.02-3.91 (m, 1H), 3.16-2.90 (m, 3H), 2.58-2.46 (m, 1H), 2.42-2.34 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 160.4, 156.4, 143.8, 134.2, 132.7, 130.6, 130.4, 129.2, 129.1, 128.0, 126.8 (q, $J_{\text{C-F}} = 275.4$ Hz), 124.4, 115.8, 36.6 (q, $J_{\text{C-F}} = 27.8$ Hz), 35.5, 34.8 (q, $J_{\text{C-F}} = 3.0$ Hz), 28.1, 21.5; ^{19}F NMR (376 MHz, CDCl_3) δ -64.18 (s). FT-IR: ν (cm^{-1}) 2920, 2850, 1681, 1558, 1504, 1325, 1293, 1249. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_2\text{Na}$ 411.1291; found 411.1281.



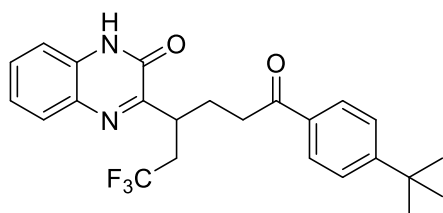
3c: 59.8 mg, 77%, yellow solid, m.p. 107-109 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.80 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.65-7.59 (m, 2H), 7.54-7.48 (m, 1H), 7.37-7.28 (m, 2H), 7.26-7.18 (m, 2H), 4.06-3.96 (m, 1H), 3.14-2.90 (m, 3H), 2.60-2.49 (m, 1H), 2.42-2.30 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 160.6, 156.2, 138.3, 136.8, 133.7, 132.6, 130.8, 130.4, 129.0, 128.4, 128.3, 126.8 (q, $J_{\text{C-F}} = 275.6$ Hz), 125.1, 124.3, 115.7, 36.7 (q, $J_{\text{C-F}} = 27.8$ Hz), 35.6, 34.8 (q, $J_{\text{C-F}} = 2.0$ Hz), 28.1, 21.2; ^{19}F NMR (376 MHz, CDCl_3) δ -64.15 (s). FT-IR: ν (cm^{-1}) 2905, 2852, 1659, 1586, 1498, 1485, 1252. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_2\text{Na}$ 411.1291; found 411.1281.



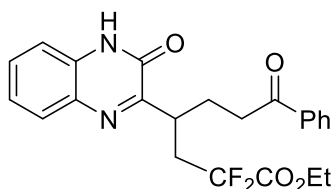
3d: 38.8 mg, 48%, yellow solid, m.p. 113-114 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.85-7.79 (m, 3H), 7.54-7.48 (m, 1H), 7.38-7.28 (m, 2H), 6.83-6.77 (m, 2H), 4.02-3.93 (m, 1H), 3.78 (s, 3H), 3.15-2.90 (m, 3H), 2.60-2.48 (m, 1H), 2.38-2.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 163.4, 160.5, 156.3, 141.8, 132.7, 130.5, 130.2, 129.8, 129.1, 126.8 (q, $J_{\text{C-F}} = 275.3$ Hz), 124.4, 115.8, 113.6, 55.4, 36.8 (q, $J_{\text{C-F}} = 27.9$ Hz), 35.3, 34.9, 28.3; ^{19}F NMR (376 MHz, CDCl_3) δ -64.18 (s). FT-IR: ν (cm^{-1}) 3013, 2955, 2849, 1662, 1576, 1467, 1374, 1294, 1205. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_3\text{Na}$ 427.1240; found 427.1251.



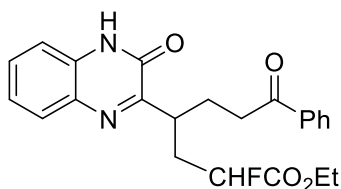
3e: 76.4 mg, 95%, yellow solid, m.p. 108-109 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 10.9 (s, 1H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61-7.56 (m, 2H), 7.51-7.46 (m, 1H), 7.35-7.31 (m, 1H), 7.20-7.17 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 3.98-3.91 (m, 1H), 3.08-2.90 (m, 3H), 2.55-2.48 (m, 1H), 2.35-2.27 (m, 2H), 2.23 (s, 3H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 142.5, 141.8, 136.8, 134.7, 133.3, 131.8, 130.5, 129.7, 129.1, 129.1, 127.8, 126.6 (q, *J*_{C-F} = 265.9 Hz), 125.7, 124.5, 115.8, 36.4 (q, *J*_{C-F} = 28.1 Hz), 35.5, 34.9 (q, *J*_{C-F} = 2.6 Hz), 29.7, 28.2, 19.8 (q, *J*_{C-F} = 23.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -64.18 (s). FT-IR: ν (cm⁻¹) 2962, 2924, 1662, 1608, 1498, 1408, 1375, 1258. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₂H₂₁F₃N₂O₂Na 425.1447; found 425.1451.



3f: 64.2 mg, 74%, yellow solid, m.p. 157-158 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.4 (s, 1H), 8.08-7.99 (m, 1H), 7.83-7.77 (m, 3H), 7.54-7.49 (m, 1H), 7.39-7.34 (m, 3H), 4.03-3.96 (m, 1H), 3.12-2.94 (m, 3H), 2.59-2.49 (m, 1H), 2.38-2.27 (m, 2H), 1.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 198.9, 160.5, 156.8, 141.8, 134.2, 132.7, 131.8, 130.5, 129.1, 127.9, 126.8 (q, *J*_{C-F} = 275.3 Hz), 125.5, 124.5, 115.8, 36.6 (q, *J* = 27.9 Hz), 35.5, 34.90 (q, *J* = 1.7 Hz), 35.0, 31.0, 28.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -64.17 (s). FT-IR: ν (cm⁻¹) 2962, 2852, 1683, 1605, 1503, 1324, 1259. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₄H₂₅F₃N₂O₂Na 453.1760; found 453.1770.

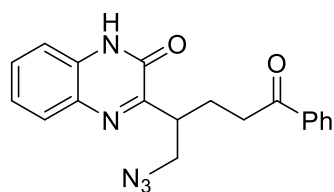


4a: 52.2 mg, 61%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.38 (s, 1H), 7.89-7.75 (m, 3H), 7.52-7.42 (m, 2H), 7.37-7.29 (m, 4H), 4.21-4.13 (m, 2H), 4.05-3.95 (m, 1H), 3.17-2.93 (m, 3H), 2.58-2.44 (m, 1H), 2.41-2.25 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 163.9 (t, *J*_{C-F} = 31.8 Hz), 161.0, 156.1, 136.6, 132.7, 132.4, 130.6, 130.1, 128.7, 128.3, 127.7, 124.0, 115.6 (t, *J*_{C-F} = 256.5 Hz), 115.6, 62.7, 37.2 (t, *J*_{C-F} = 22.6 Hz), 35.6, 34.1, 28.4, 13.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -103.24 (d, *J* = 260.6 Hz), -104.53 (d, *J* = 260.6 Hz). FT-IR: ν (cm⁻¹) 2922, 2852, 1763, 1664, 1449, 1233. HRMS [ESI] *m/z*: [M+Na]⁺ calcd for C₂₃H₂₂F₂N₂NaO₄ 451.1440; found 451.1444.

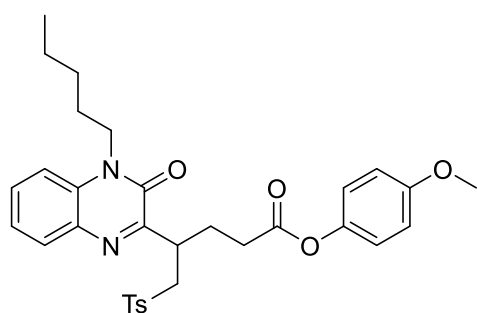


4b: 57.4 mg, 70%, *d.r.* = 1:1, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 12.5 (s, 1H, two isomers), 7.97-7.75 (m, 3H, two isomers), 7.57-7.41 (m, 2H, two isomers), 7.38-7.28 (m, 4H, two isomers), 5.20-4.84 (m, 1H, two isomers), 4.27-4.11 (m, 2H, two isomers), 3.97-3.83 (m, 1H, two isomers), 3.10-2.98 (m, 2H, two isomers), 2.84-2.57 (m, 1H, two isomers), 2.46-2.22 (m, 3H, two isomers), 1.30-1.22 (m, 3H, two isomers); ¹³C NMR (100 MHz, CDCl₃) δ 199.6 & 199.6 (two isomers), 169.9 (d, *J* = 234.0 Hz) & 169.8 (d, *J* = 234.0 Hz) (two isomers), 161.8 & 161.3 (two isomers), 156.6 & 156.5 (two isomers),

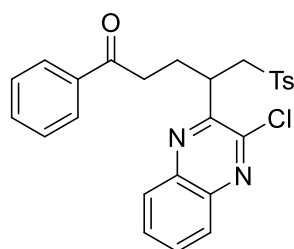
136.8 & 136.8 (two isomers), 132.9 & 132.9 (overlap, two isomers), 132.7 & 132.7 (overlap, two isomers), 130.8 & 130.8 (two isomers), 130.3 & 130.2 (two isomers), 129.0 & 128.9 (two isomers), 128.5 & 128.5 (overlap, two isomers), 128.0 & 128.0 (two isomers), 124.2 & 124.2 (two isomers), 115.8 & 115.8 (two isomers), 88.1 (d, $J = 183.2$ Hz) & 87.5 (d, $J = 182.9$ Hz) (two isomers), 61.6 & 61.6 (overlap, two isomers), 36.6 & 36.5 (two isomers), 36.0 (d, $J = 144.0$ Hz) & 35.9 (d, $J = 105.0$ Hz) (two isomers), 35.4 & 35.2 (two isomers), 28.1 & 27.4 (two isomers), 14.1 & 14.1 (two isomers); ^{19}F NMR (376 MHz, CDCl_3) δ -189.39 (s), -191.03 (s). FT-IR: ν (cm^{-1}) 2925, 2853, 2255, 1737, 1664, 1598, 1261. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{FN}_2\text{NaO}_4$ 433.1534; found 433.1524.



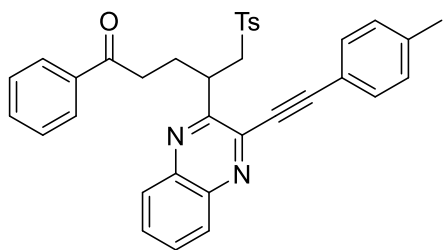
5: 38.2 mg, 55%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 12.3 (s, 1H), 7.92-7.86 (m, 2H), 7.84 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.54-7.43 (m, 2H), 7.39-7.28 (m, 4H), 3.99-3.83 (m, 2H), 3.77-3.65 (m, 1H), 3.14-2.99 (m, 2H), 2.43-2.23 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 160.1, 156.4, 136.8, 133.0, 132.7, 130.8, 130.5, 129.2, 128.5, 128.0, 124.3, 115.8, 53.9, 40.7, 35.9, 25.4. FT-IR: ν (cm^{-1}) 3082, 2103, 1682, 1656, 1596. HRMS [ESI] m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{N}_5\text{O}_2\text{Na}$ 370.1274; found 370.1279.



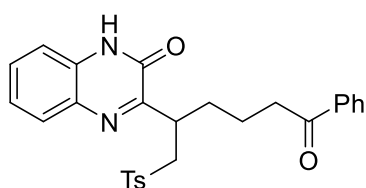
6: 74.5 mg, 80%, yellow oil. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 3/1). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.55-7.49 (m, 1H), 7.35-7.28 (m, 1H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.87-6.77 (m, 4H), 4.30 (dd, $J = 14.3, 10.0$ Hz, 1H), 4.14 (t, $J = 8.0$ Hz, 2H), 4.10-4.02 (m, 1H), 3.76 (s, 3H), 3.39 (dd, $J = 14.4, 3.2$ Hz, 1H), 2.61-2.41 (m, 2H), 2.29-2.21 (m, 1H), 2.20 (s, 3H), 2.18-2.10 (m, 1H), 1.77-1.63 (m, 2H), 1.49-1.34 (m, 4H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 158.4, 157.2, 153.9, 144.3, 144.0, 136.2, 132.5, 132.2, 130.3, 130.2, 129.5, 128.4, 123.4, 122.2, 114.3, 113.5, 58.2, 55.6, 42.4, 36.7, 31.3, 29.1, 28.6, 26.9, 22.4, 21.4, 14.0. FT-IR: ν (cm^{-1}) 2931, 2858, 1753, 1648, 1300. HRMS [ESI] m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_6\text{S}$ 577.2367; found 577.2365.



7: 53.4 mg, 85%, yellow solid, m.p. 173-175 $^{\circ}\text{C}$. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 5/1). ^1H NMR (400 MHz, CDCl_3) δ 7.96-7.88 (m, 1H), 7.85-7.76 (m, 3H), 7.75-7.67 (m, 2H), 7.57-7.49 (m, 3H), 7.44-7.36 (m, 2H), 6.89 (d, $J = 8.0$ Hz, 2H), 4.41 (dd, $J = 14.4, 10.4$ Hz, 1H), 4.32-4.21 (m, 1H), 3.49 (dd, $J = 14.4, 2.0$ Hz, 1H), 3.14-3.00 (m, 1H), 2.94-2.80 (m, 1H), 2.25 (dd, $J = 14.4, 7.2$ Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 153.7, 147.2, 144.3, 140.8, 140.3, 136.4, 136.0, 133.2, 130.7, 130.1, 129.5, 128.6, 128.0, 127.9, 127.8, 59.2, 37.7, 34.9, 29.6, 21.2. FT-IR: ν (cm^{-1}) 2922, 1682, 1596, 1326. HRMS [ESI] m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{ClN}_2\text{O}_3\text{S}$ 479.1191; found 479.1203.

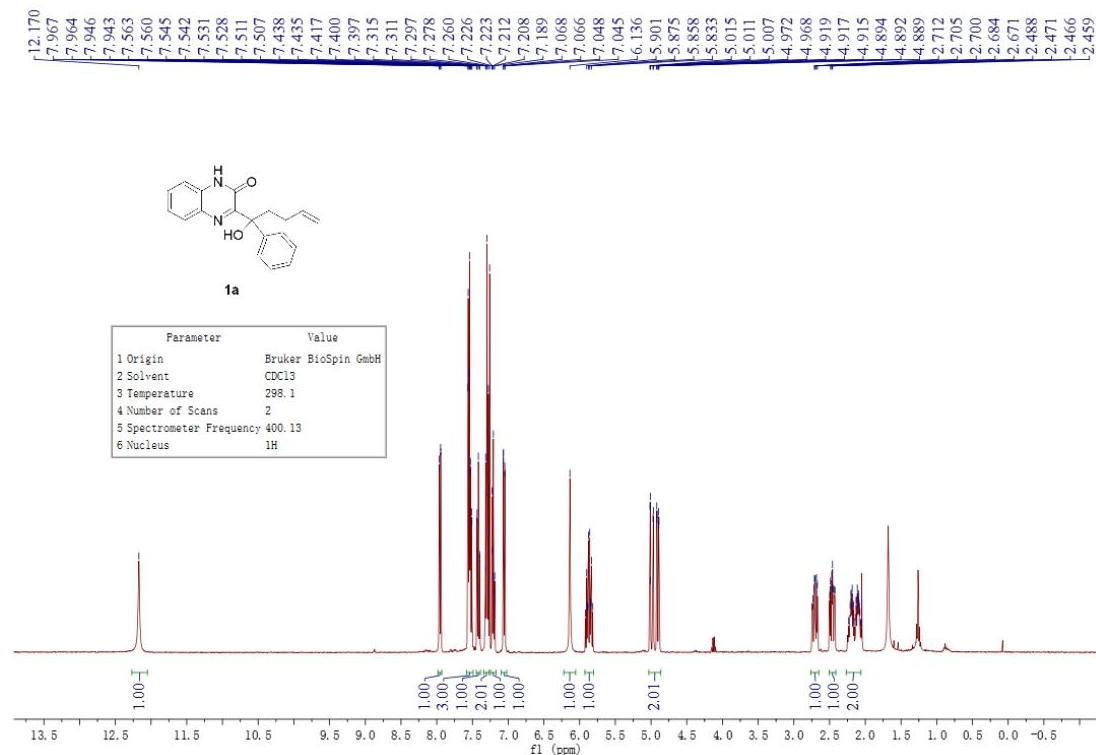


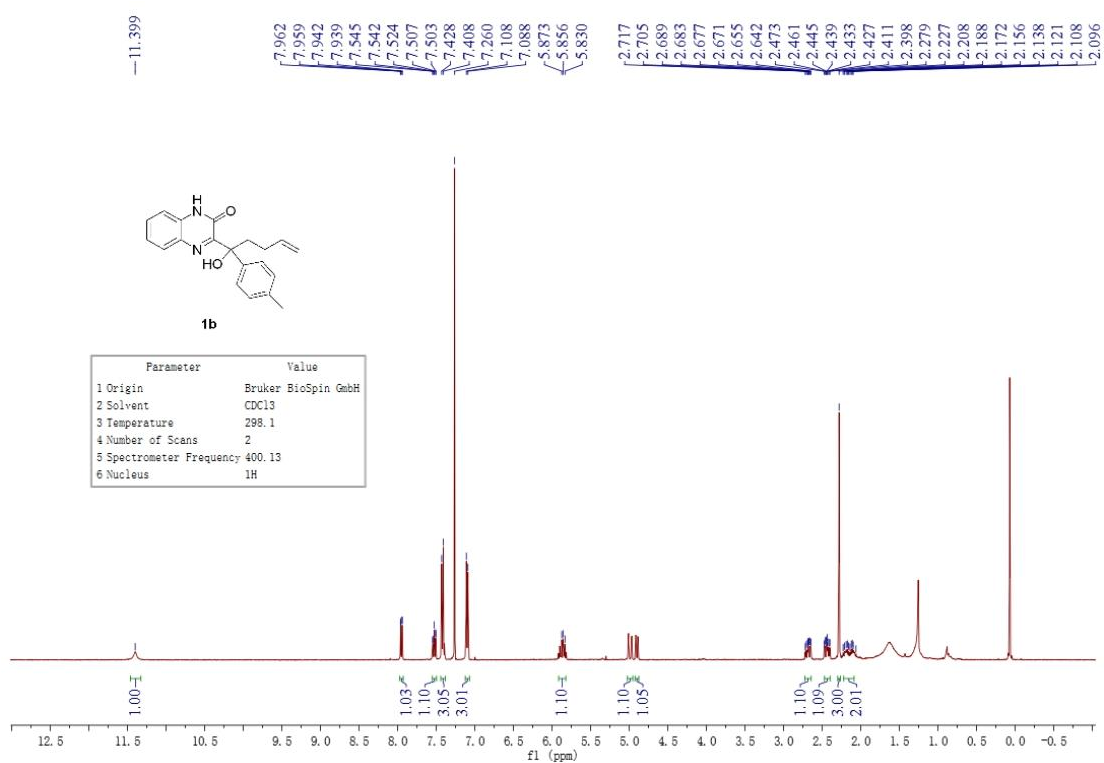
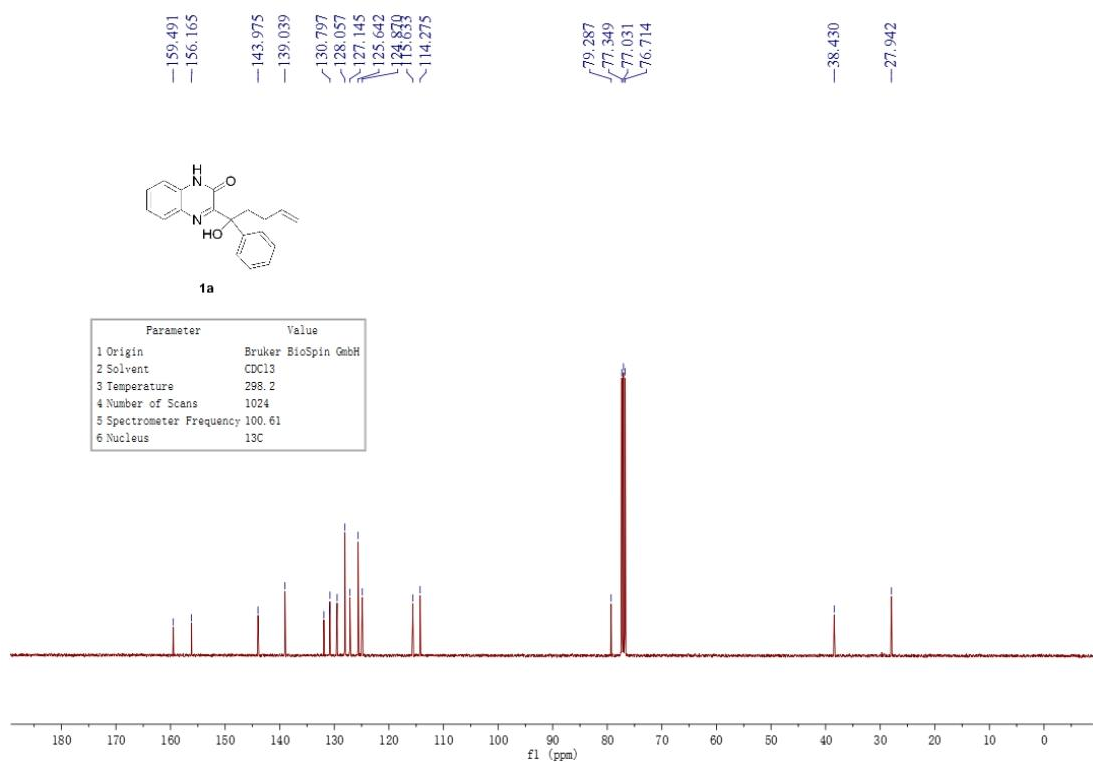
8: 34.3 mg, 82%, white solid, m.p. 166-167 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 2/1). ¹H NMR (400 MHz, CDCl₃) δ 8.04-7.95 (m, 1H), 7.83-7.76 (m, 1H), 7.74-7.63 (m, 4H), 7.60-7.50 (m, 4H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.34-7.26 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 4.50-4.36 (m, 2H), 3.61-3.50 (m, 1H), 3.09-2.95 (m, 1H), 2.88-2.76 (m, 1H), 2.42 (s, 3H), 2.39-2.31 (m, 1H), 2.30-2.19 (m, 1H), 2.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.3, 156.5, 144.1, 140.8, 140.4, 140.2, 139.7, 136.4, 135.9, 133.0, 132.4, 130.2, 130.1, 129.4, 129.3, 128.7, 128.7, 128.4, 127.9, 127.9, 118.2, 97.0, 85.8, 59.7, 38.4, 35.0, 30.2, 21.7, 21.2. FT-IR: ν (cm⁻¹) 3059, 2204, 1677, 1301. HRMS [ESI] *m/z*: [M+H]⁺ calcd for C₃₅H₃₁N₂O₃S 559.2050; found 559.2059.

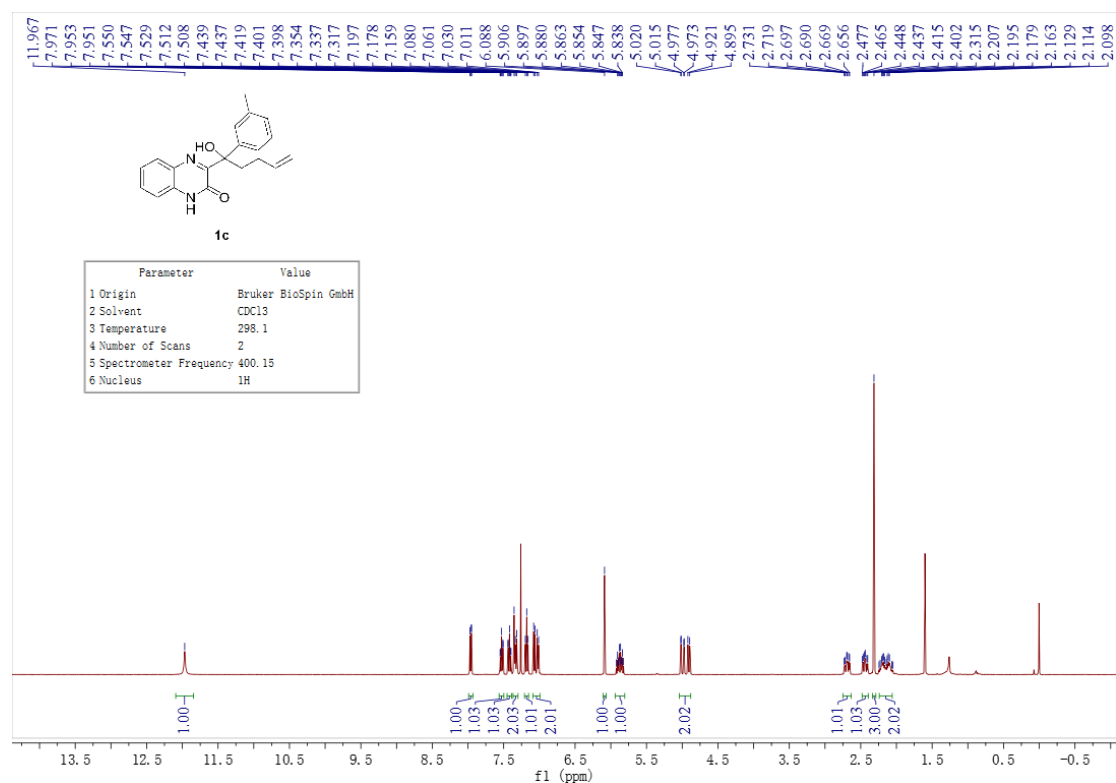
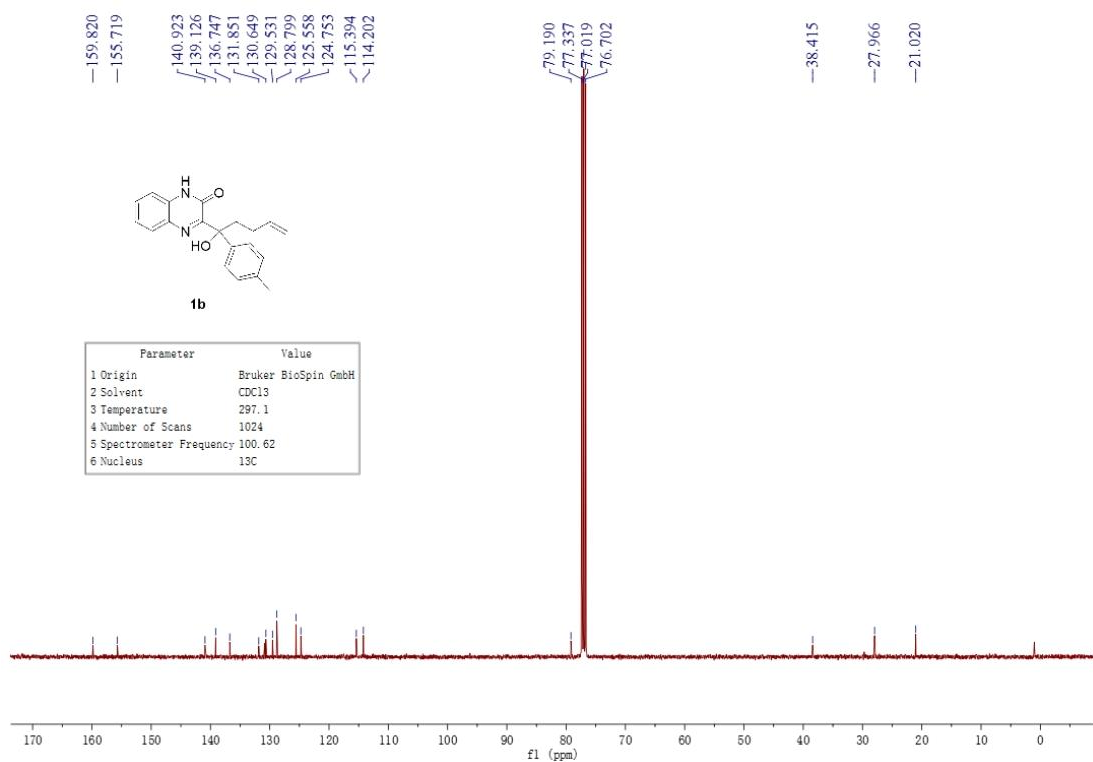


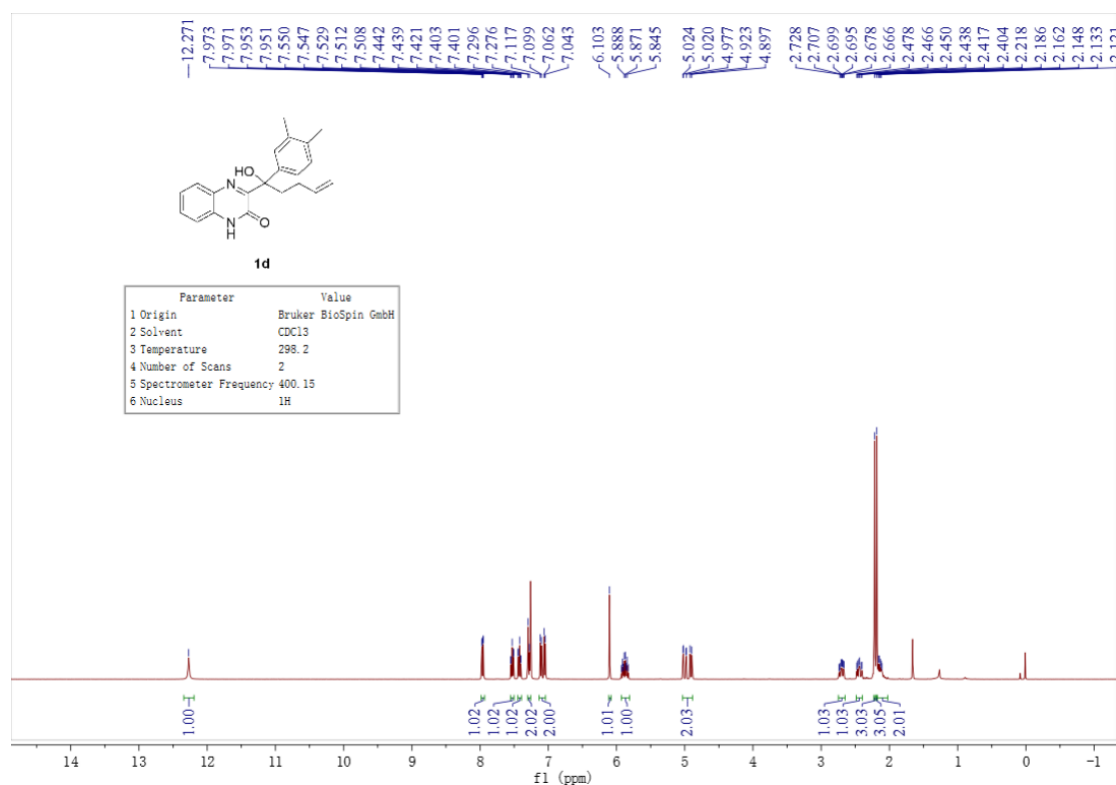
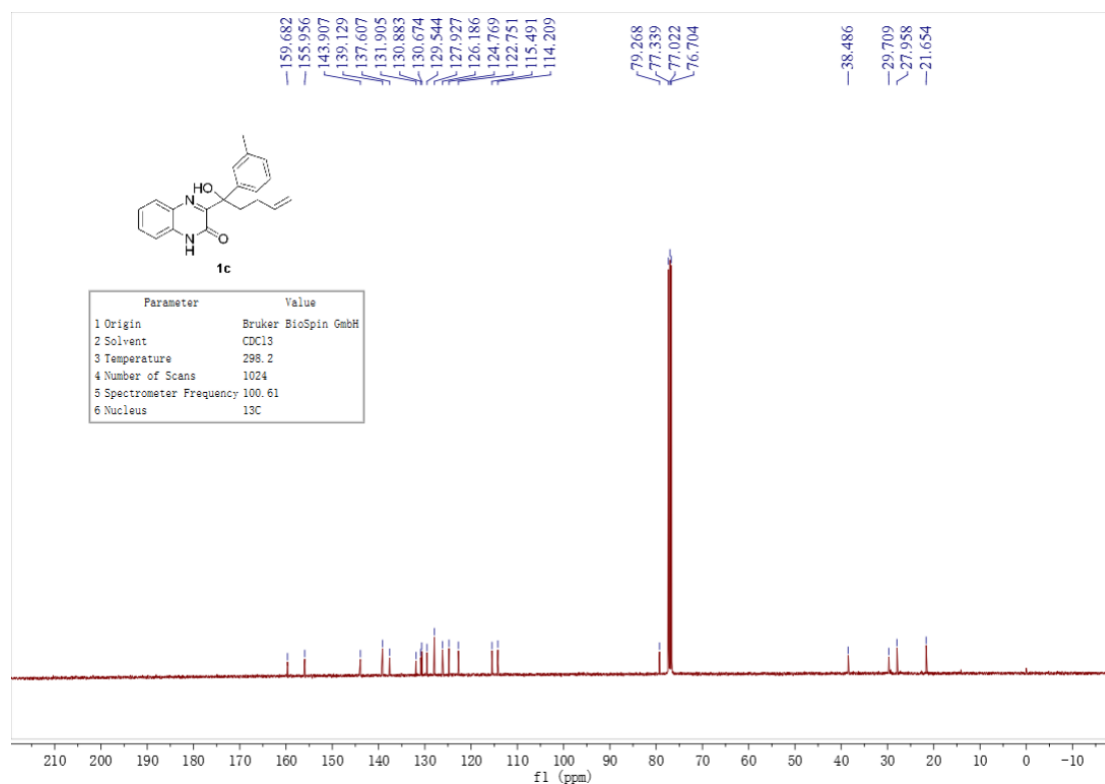
14: 37.8 mg, 82%, white solid, m.p. 72-74 °C. Purification by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1/1). ¹H NMR (400 MHz, CDCl₃) δ 11.8 (s, 1H), 7.92-7.88 (m, 2H), 7.73-7.66 (m, 3H), 7.55-7.39 (m, 4H), 7.35-7.30 (m, 1H), 7.28-7.26 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.35-4.26 (m, 1H), 4.14-4.06 (m, 1H), 3.46-3.39 (m, 1H), 3.04-2.91 (m, 2H), 2.18 (s, 3H), 1.98-1.90 (m, 1H), 1.84-1.74 (m, 2H), 1.32-1.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 199.5, 159.8, 155.7, 144.5, 136.8, 136.2, 133.0, 132.4, 130.7, 130.3, 129.6, 129.0, 128.6, 128.3, 128.0, 124.2, 115.4, 58.3, 37.8, 36.2, 33.5, 21.4, 21.1. FT-IR: ν (cm⁻¹) 3447, 3060, 2961, 2849, 1650, 1483, 1379. HRMS [ESI] *m/z*: [M+H]⁺ calcd for C₂₇H₂₆N₂O₄SNa 497.1505; found 497.1507.

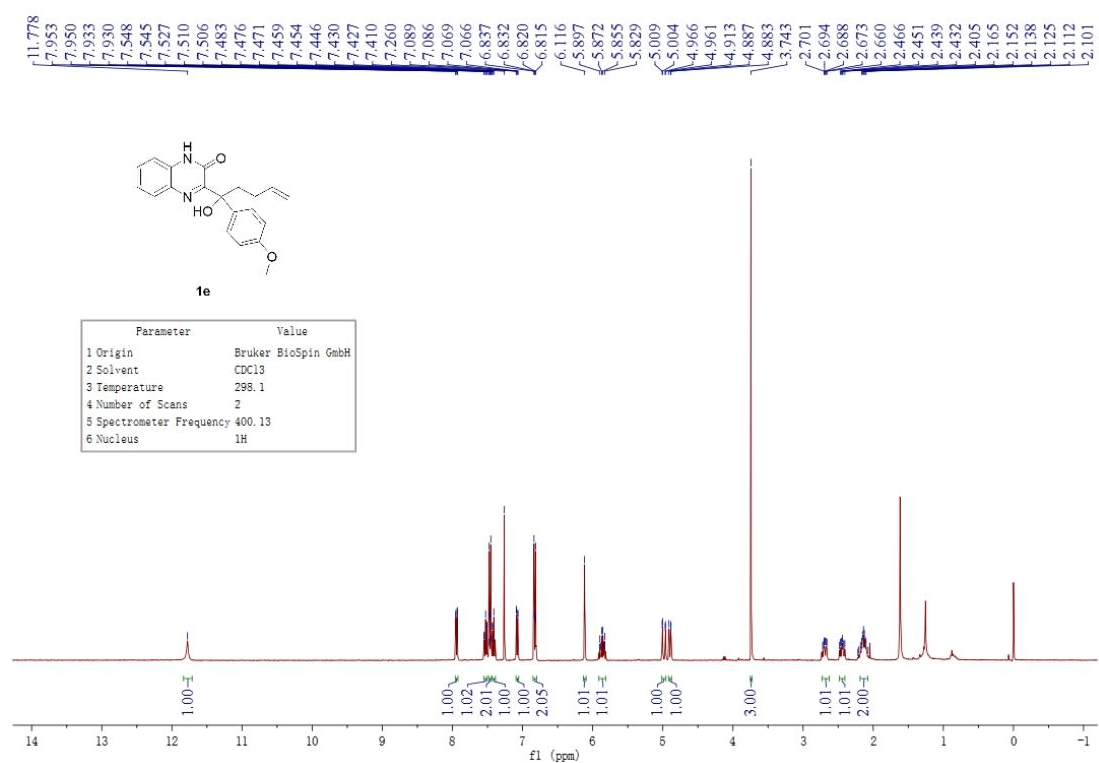
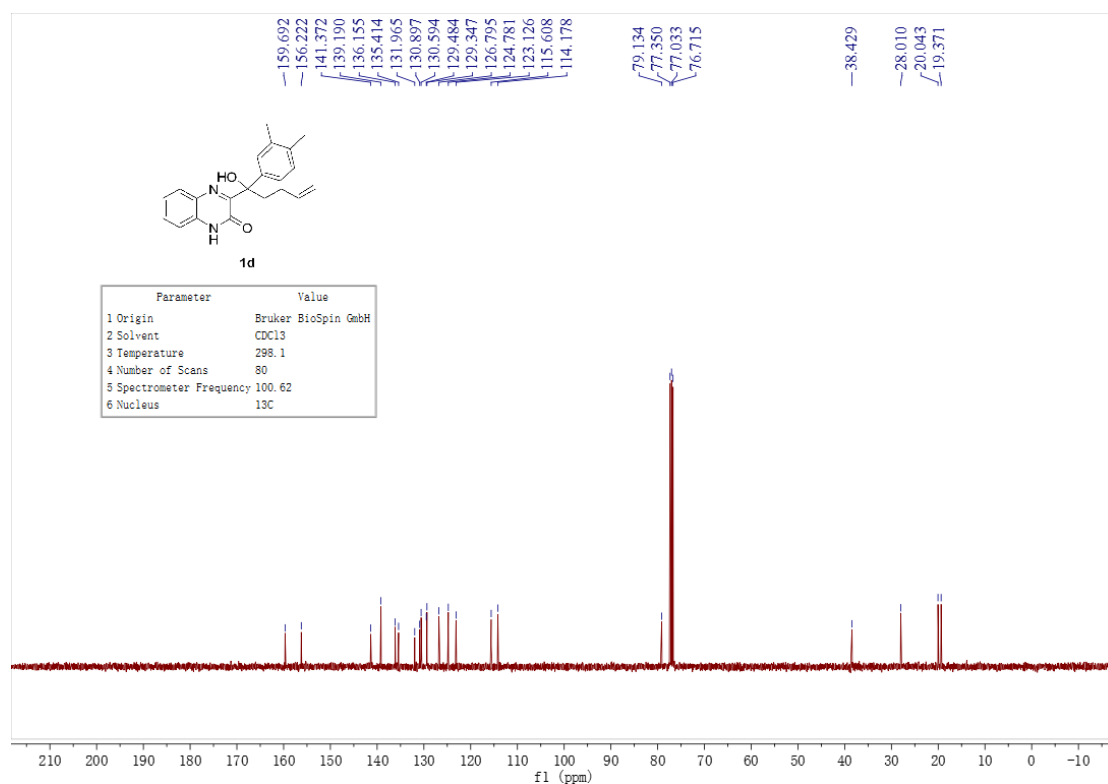
7. ¹H, ¹³C, ¹⁹F NMR spectra

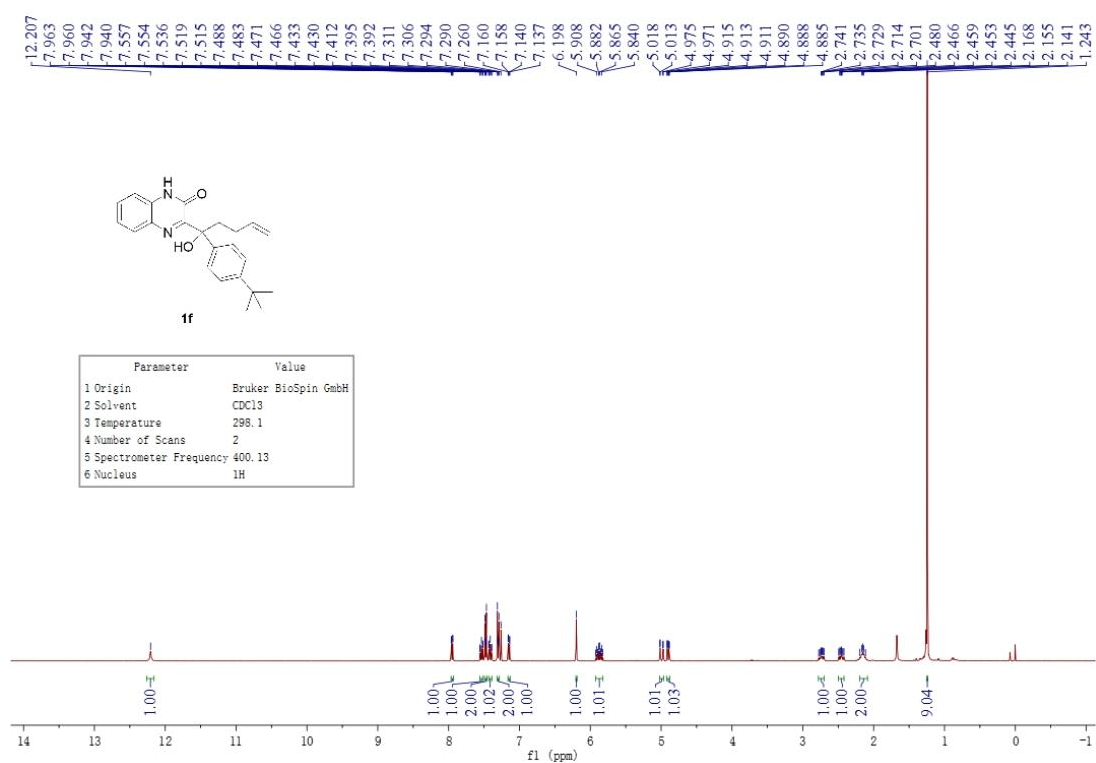
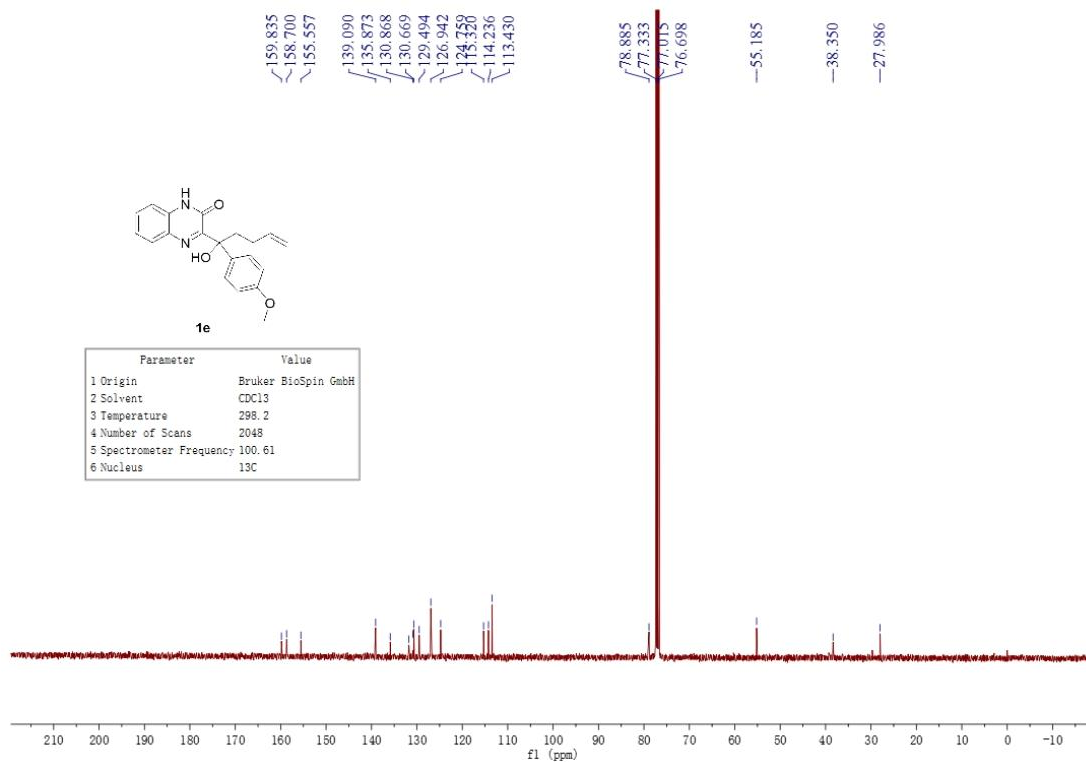


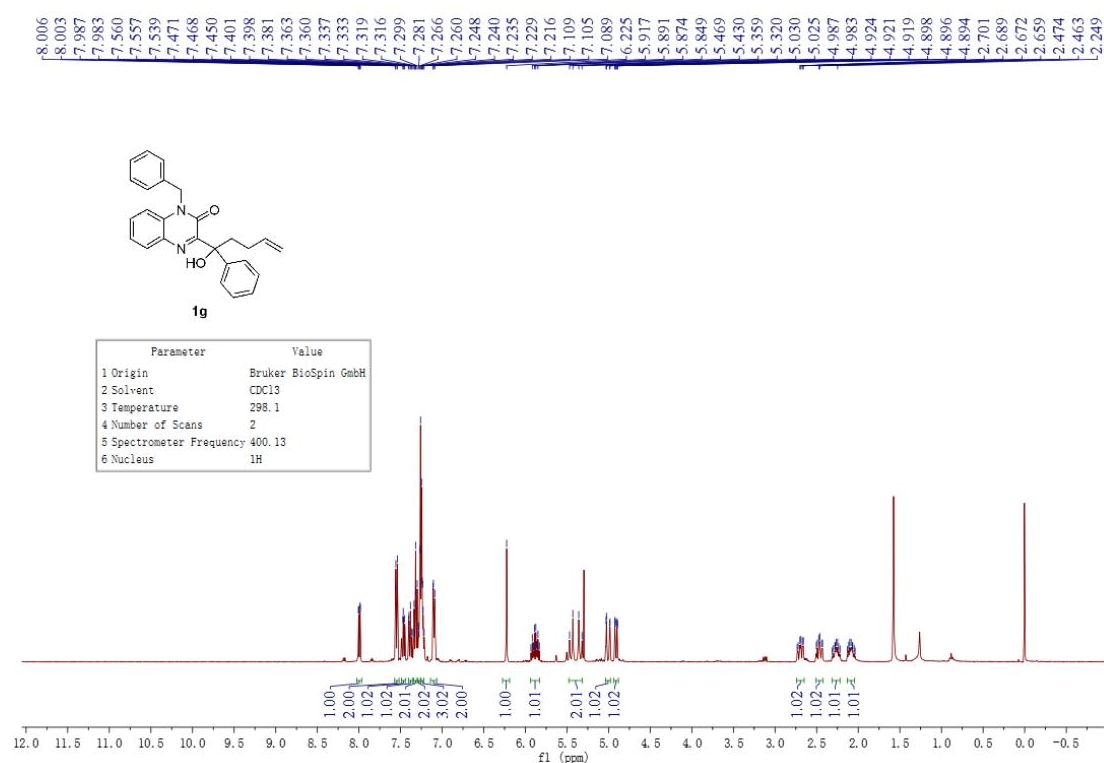
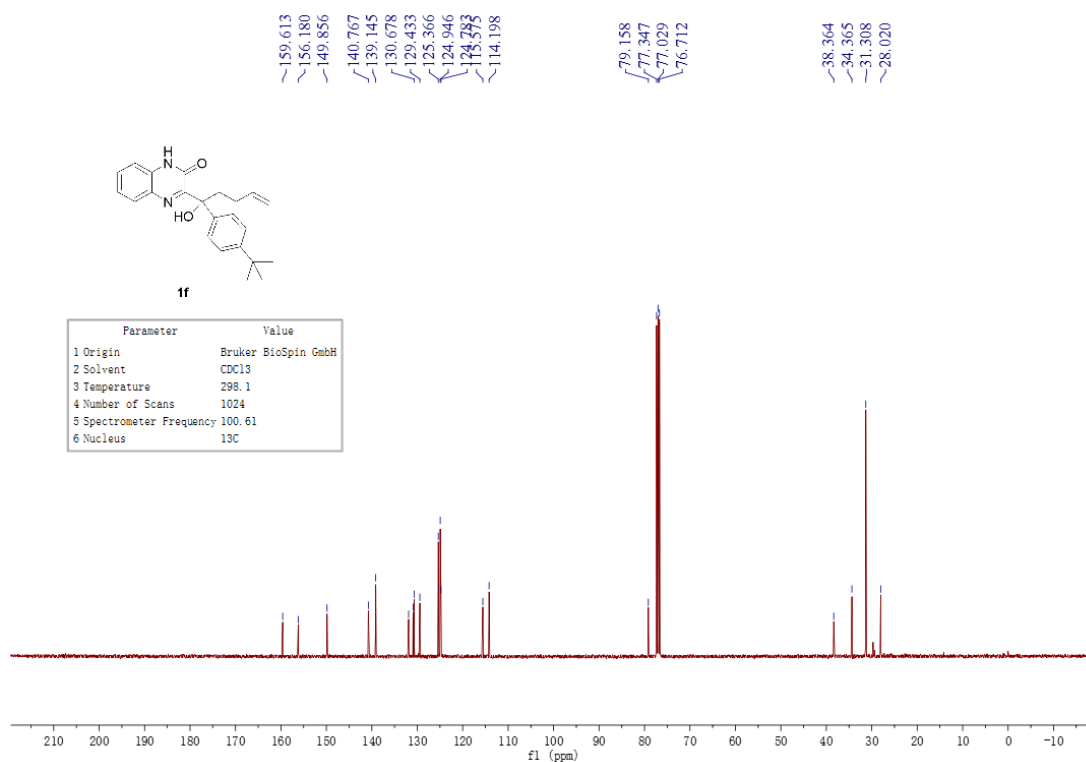


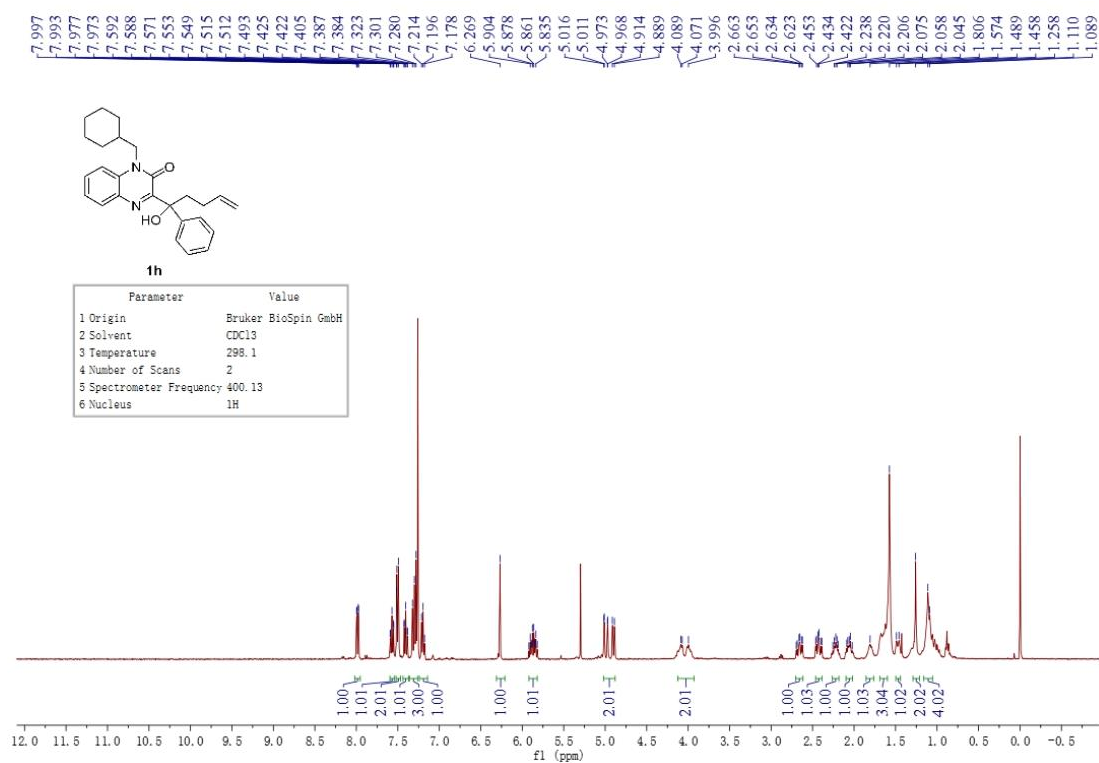
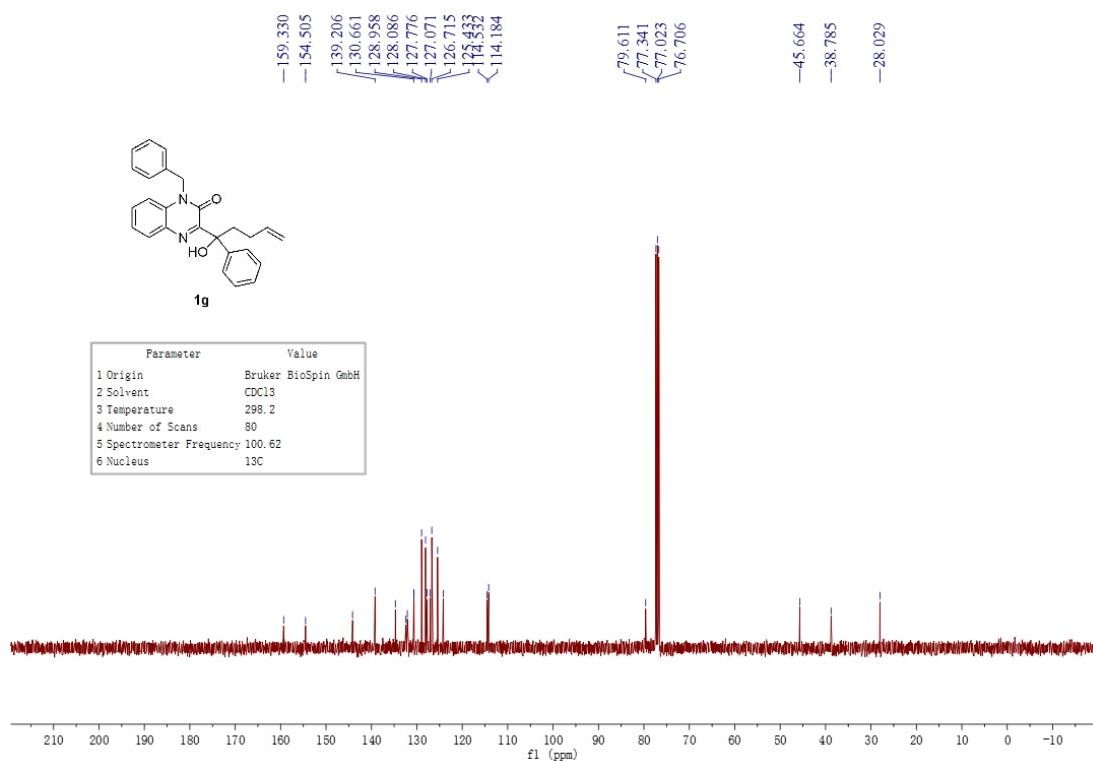






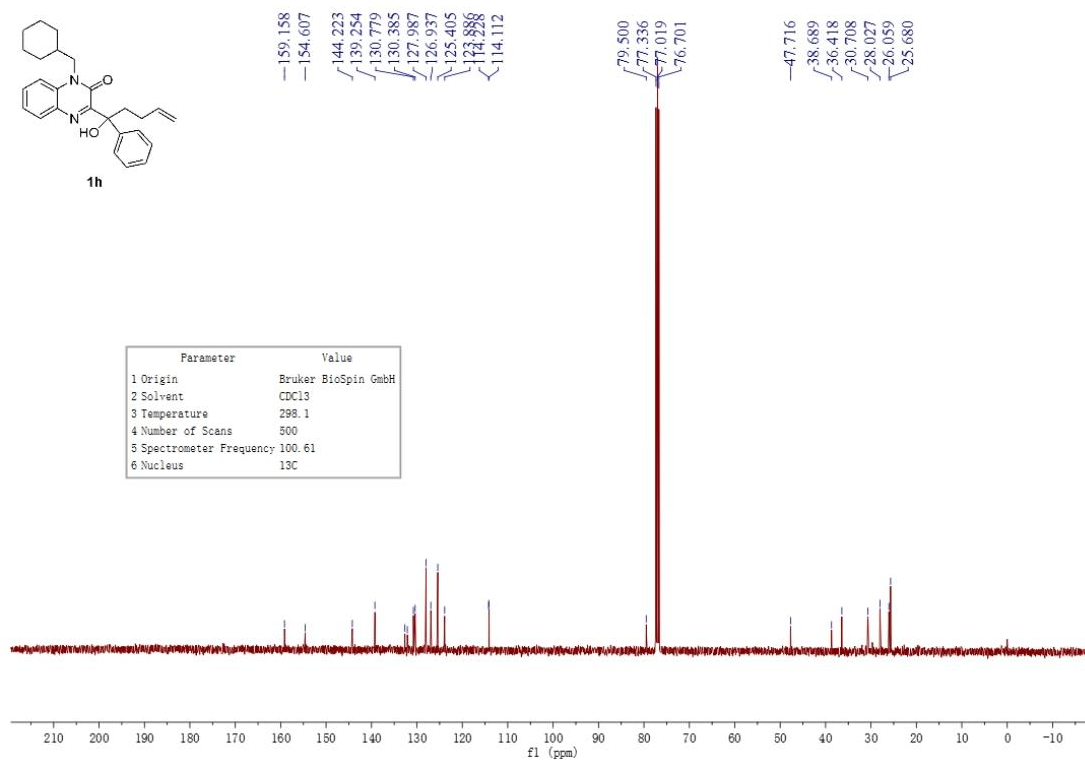








Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.1
4 Number of Scans	500
5 Spectrometer Frequency	100.61
6 Nucleus	¹³ C



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	¹ H

