Supporting Information

Catalyst-free C(sp^3)–H functionalization of methyl azaarenes with trifluoromethyl ketone hydrates: "All-water" synthesis of α-trifluoromethyl tertiary alcohols

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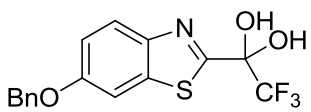
I. General Information

Column chromatography was performed over silica gel (200-300 mesh) purchased from Qindao Puke Co., China. All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using anhydrous solvents. Anhydrous dichloromethane, tetrahydrofuran, and acetonitrile were purchased from Energy Chemical and used as received. ACS grade 2,2,2-trifluoroacetic anhydride (TFA), Et_3N, toluene, and 1,2-dichloroethane (DCE) were purchased from Sinopharm Chemical Reagent Co.,Ltd and used as received. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualisation was by ultraviolet fluorescence, and/or phosphomolybdic acid, and/or $KMnO_4$.

^1H, ^{13}C, and ^{19}F NMR spectra were collected on a Varian INOVA-400 or a Bruker AV-400 NMR spectrometer using peaks of deuterated solvents as an internal standard (^1H NMR: $CDCl_3$ at 7.26 ppm, d_6-acetone at 2.05 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm, d_6-acetone at 206.26 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad), coupling constant *J* (Hz), and integration. High resolution mass spectra were recorded on a Bruker Maxis System. Melting points were measured by a melting point instrument and were uncorrected. IR spectra were collected on a Spectrum QATR-S from SHIMADZU and reported in unit of cm^{-1}.

II. Synthesis of Ketone Hydrate Substrates

Genral Procedure A for the synthesis of ketone hydrate substrates 2. To a solution of substituted benzothiazole (5.0 mmol) in toluene (20 mL) at −20 °C was added dropwise trifluoroacetic anhydride (6.0 mmol) over 10 min. The mixture was stirred for 0.5 h, and triethylamine (6.0 mmol) was slowly added. After stirring at −20 °C overnight, the resulting reaction mixture was spontaneously warmed to room temperature and stirred for 12 h. The solvent was removed in vacuo, and water (5 mL) was added to form white precipitation, which was dissolved in ethyl acetate (40 mL). The organic phase was successively washed with 1 M HCl (20 mL), water (20 mL), and brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford the crude product. The pure ketone hydrate was obtained by recrystallization from petroleum ether/ethyl acetate (5:1). Ketone hydrates **2c** and **2e** are unkown compunds, and others are known. [1,2]



2c

1-(6-(Benzyloxy)benzo[*d*]thiazol-2-yl)-2,2,2-trifluoroethane-1,1-diol (2c) was prepared from 6-(benzyloxy)benzothiazole (1.20 g, 5.0 mmol) according to the above procedure. Yellow solid, m.p. 138.1−139.8 °C; 0.95 g, 54% yield.

^{1}H NMR (400 MHz, d_6-acetone) δ 7.95 (d, J = 9.2 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.59 (s, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H),

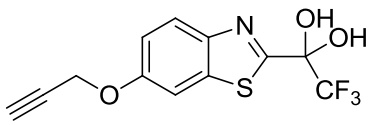
7.25 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 5.22 (s, 2H) ppm.

^{13}C NMR (100 MHz, d_6-acetone) δ 166.0, 157.9, 147.8, 137.9, 137.4, 128.8, 128.3, 128.0, 124.6, 123.2 (q, J = 286.3 Hz), 117.2, 105.7, 92.8 (q, J = 33.0 Hz), 70.6 ppm.

^{19}F NMR (376.5 MHz, d_6-acetone) δ −83.6 ppm.

HRMS (ESI) m/z: Calcd for $C_{16}H_{10}F_3NO_2S$ [M-H_2O] 337.0382; Found 337.0382.

IR (neat, cm^{-1}): 3377, 3081, 3031, 1703, 1596, 1476, 1205, 1167, 953, 834.



2e

2,2,2-Trifluoro-1-(6-(prop-2-yn-1-yloxy)benzo[*d*]thiazol-2-yl)ethane-1,1-diol (2e) was prepared from 6-(prop-2-yn-1-yloxy)benzothiazole (0.95 g, 5.0 mmol) according to the above procedure. Yellow solid, m.p. 115.6−117.8 °C; 0.66 g, 43% yield.

^{1}H NMR (400 MHz, d_6-acetone) δ 7.98 (d, J = 8.8 Hz, 1H), 7.73 (s, 1H), 7.53 (s, 2H), 7.23 (d, J = 9.2 Hz, 1H), 4.91 (s, 2H), 3.12 (s, 1H) ppm.

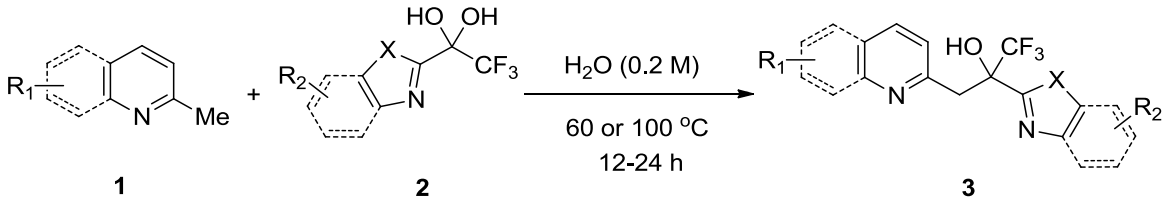
^{13}C NMR (100 MHz, d_6-acetone) δ 166.3, 156.7, 148.2, 137.8, 124.7, 123.2 (q, J = 286.2 Hz), 117.1, 106.1, 92.8 (q, J = 33.0 Hz), 78.9, 76.9, 56.5 ppm.

^{19}F NMR (376.5 MHz, d_6-acetone) δ −83.6 ppm.

HRMS (ESI) m/z: [M-H_2O] Calcd for $C_{12}H_6F_3NO_2S$ 285.0071; Found 285.0074.

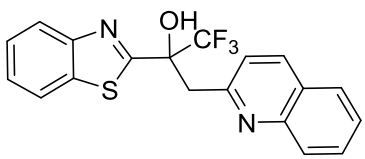
IR (neat, cm^{-1}): 3521, 3307, 3162, 1602, 1520, 1457, 1249, 1187, 1130, 1042, 890.

III. Synthesis of α-Trifluoromethyl Tertiary Alcohols



1 2 3

General Procedure B. To a 4-mL vial equipped with a magnetic stir bar, 2-methylquinoline **1** (0.45 mmol, 1.5 equiv), ketone hydrate **2** (0.30 mmol, 1.0 equiv), and H_2O (1.5 mL) were sequentially added. The vial was then capped and heated at 60 or 100 °C in an oil bath. After stirring for 12~24 h, the reaction mixture was then allowed to cool to room temperature. The crude reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired trifluoromethyl tertiary alcohol **3**.



3aa

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-ol (3aa) was prepared from 2-methylquinoline **1a** and ketone hydrate **2a** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 117.5–119.6 °C; 110.0 mg, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.95 (t, J = 7.6 Hz,

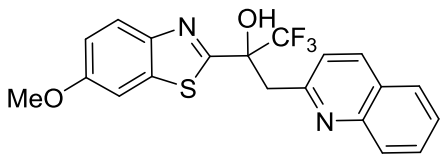
2H), 7.75 (d, *J* = 10.0 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 2H), 7.43–7.36 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 4.22 (d, *J* = 15.2 Hz, 1H), 3.91 (d, *J* = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 157.4, 153.5, 145.8, 137.8, 135.8, 130.3, 127.9, 127.6, 126.8, 126.7, 125.9, 125.3, 123.9 (q, *J* = 284.4 Hz), 123.4, 122.5, 121.6, 78.6 (q, *J* = 29.4 Hz), 38.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −78.8 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{13}F_3N_2OS$ 374.0701; Found 374.0689.

IR (neat, cm^{-1}): 3061, 2924, 1508, 1256, 1176, 1130, 999, 953, 828, 760.



3ab

1,1,1-Trifluoro-2-(6-methoxybenzo[*d*]thiazol-2-yl)-3-(quinolin-2-yl)propan-2-ol (3ab) was prepared from 2-methylquinoline **1a** and ketone hydrate **2b** at 60 °C for 24 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 183.0−185.1 °C; 117.5 mg, 97% yield.

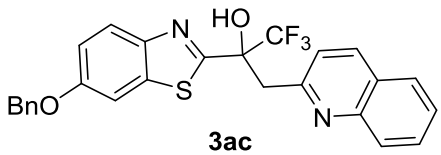
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.70–7.65 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 4.13 (d, *J* = 15.2 Hz, 1H), 3.84 (d, *J* = 15.2 Hz, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 157.8, 157.7, 148.1, 146.0, 137.9, 137.4, 130.4, 128.1, 127.8, 127.0, 126.8, 124.0, 123.9 (q, J = 284.4 Hz), 122.7, 115.8, 103.8, 78.5 (q, J = 29.4 Hz), 55.7, 38.7 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.3 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{20}H_{15}F_3N_2O_2S$ 404.0806; Found 404.0803.

IR (neat, cm^{-1}): 3069, 2930, 1602, 1514, 1256, 1180, 1105, 960, 815, 746.



3ac

2-(6-(Benzyloxy)benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-ol (3ac) was prepared from 2-methylquinoline **1a** and ketone hydrate **2c** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1). White solid, m.p. 119.8−121.6 °C; 140.3 mg, 97% yield.

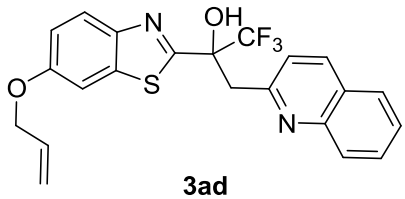
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.67–7.72 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.43–7.33 (m, 6H), 7.29 (s, 1H), 7.11 (d, J = 8.8 Hz, 1H), 5.03 (s, 2H), 4.16 (d, J = 15.2 Hz, 1H), 3.86 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 157.6, 157.0, 148.3, 146.0, 137.9, 137.3, 136.6, 130.4, 128.7, 128.2, 128.1, 127.8, 127.5, 127.0, 126.9, 124.1, 123.9 (q, J = 284.2 Hz), 122.7, 116.3, 105.1, 78.5 (q, J = 29.4 Hz), 70.6, 38.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.0 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{26}H_{19}F_3N_2O_2S$ 480.1119; Found 480.1116.

IR (neat, cm^{-1}): 3062, 2924, 1602, 1501, 1457, 1244, 1155, 997, 815, 733.



3ad

2-(6-(Allyloxy)benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-ol (3ad) was prepared from 2-methylquinoline **1a** and ketone hydrate **2d** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1). White solid, m.p. 125.6−126.8 °C; 123.8 mg, 96% yield.

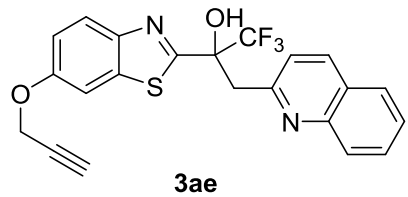
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.68–7.63 (m, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.20 (s, 1H), 7.03 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz), 6.05–5.96 (m, 1H), 5.38 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 4.48 (d, J = 4.8 Hz, 2H), 4.14 (d, J = 15.2 Hz, 1H), 3.85 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 157.6, 156.7, 148.1, 145.9, 137.8, 137.2, 132.8, 130.3, 128.0, 127.7, 126.9, 126.8, 124.0, 123.9 (q, J = 284.3 Hz), 122.7, 117.9, 116.2, 104.9, 78.4 (q, J = 29.4 Hz), 69.3, 38.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.1 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{22}H_{17}F_3N_2O_2S$ 430.0963; Found 430.0966.

IR (neat, cm^{-1}): 3069, 2924, 2143, 1602, 1507, 1457, 1249, 1180, 997, 828, 758.



3ae

1,1,1-Trifluoro-2-(6-(prop-2-yn-1-yloxy)benzo[*d*]thiazol-2-yl)-3-(quinolin-2-yl)propan-2-ol (3ae) was prepared from 2-methylquinoline **1a** and ketone hydrate **2e** at 60 °C for 24 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1). White solid, m.p. 107.5–109.3 °C; 125.5 mg, 98% yield.

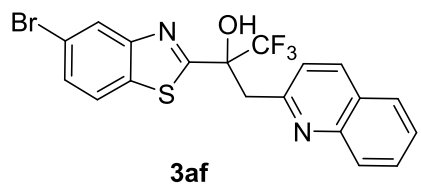
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.69–7.63 (m, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 5.6 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 4.66 (s, 2H), 4.14 (d, J = 15.2 Hz, 1H), 3.84 (d, J = 15.2 Hz, 1H), 2.52 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 157.6, 155.6, 148.6, 145.9, 137.9, 137.2, 130.4, 128.0, 127.7, 126.9, 126.8, 126.7 (q, J = 284.4 Hz), 124.1, 122.7, 116.2, 105.5, 78.5 (q, J = 29.4 Hz), 78.2, 76.1, 58.3, 38.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{22}H_{15}F_3N_2O_2S$ 428.0806; Found 428.0804.

IR (neat, cm^{-1}): 3295, 2930, 1609, 1514, 1451, 1256, 1180, 1029, 954, 828, 765.



3af

2-(5-Bromobenzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-ol (3af)

was prepared from 2-methylquinoline **1a** and ketone hydrate **2f** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 169.0–171.2 °C; 125.0 mg, 92% yield.

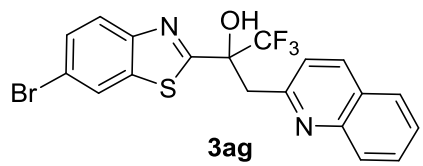
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.14 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.34(d, J = 8.4 Hz, 1H), 4.12 (d, J = 15.2 Hz, 1H), 3.83 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 157.5, 154.7, 146.0, 138.1, 134.9, 130.5, 128.6, 128.1, 127.9, 127.1, 127.0, 126.6, 123.8 (q, J = 284.1 Hz), 122.9, 122.7, 119.7, 78.7 (q, J = 29.5 Hz), 38.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}BrF_3N_2OS$ 451.9806; Found 451.9806.

IR (neat, cm^{-1}): 3069, 2924, 1609, 1501, 1432, 1256, 1187, 960, 822, 752.



3ag

2-(6-Bromobenzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-ol (3ag) was prepared from 2-methylquinoline **1a** and ketone hydrate **2g** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 129.5–131.2 °C; 126.7 mg, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4

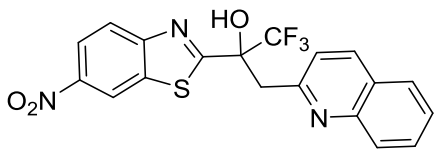
Hz, 1H), 7.91 (s, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.71 (dd, J_1 = 17.6 Hz, J_2 = 8.0 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 4.10 (d, J = 15.2 Hz, 1H), 3.84 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 157.4, 152.5, 146.0, 138.0, 137.7, 130.6, 129.6, 128.2, 127.8, 127.1, 127.0, 124.7, 124.4, 123.8 (q, J = 284.0 Hz), 122.7, 119.2, 78.6 (q, J = 29.6 Hz), 38.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.1 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}BrF_3N_2OS$ 451.9806; Found 451.9804.

IR (neat, cm^{-1}): 3056, 2924, 1596, 1507, 1432, 1256, 1174, 1092, 960, 822, 740.



3ah

1,1,1-Trifluoro-2-(6-nitrobenzo[*d*]thiazol-2-yl)-3-(quinolin-2-yl)propan-2-ol (3ah) was prepared from 2-methylquinoline **1a** and ketone hydrate **2h** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1). White solid, m.p. 153.8–155.1 °C; 112.2 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.65 (s, 1H), 8.23 (d, J = 10.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.72–7.65 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 4.13 (d, J = 15.2 Hz, 1H), 3.87 (d, J = 15.2 Hz, 1H) ppm.

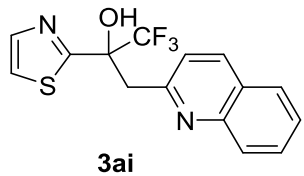
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 157.1, 151.0, 145.9, 145.1, 138.1, 136.3, 130.6,

128.0, 127.8, 127.1, 127.0, 123.9, 123.5 (q, J = 284.2 Hz), 122.5, 121.4, 118.4, 78.8 (q, J = 29.7 Hz), 38.4 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.0 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}F_3N_3O_3S$ 419.0551; Found 419.0545.

IR (neat, cm^{-1}): 3100, 3062, 2168, 1520, 1337, 1256, 1180, 960, 828, 815, 752.



3ai

1,1,1-Trifluoro-3-(quinolin-2-yl)-2-(thiazol-2-yl)propan-2-ol (3ai) was prepared from 2-methylquinoline **1a** and ketone hydrate **2i** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 142.1−144.5 °C; 87.4 mg, 90% yield.

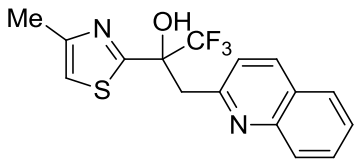
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.74–7.65 (m, 3H), 7.49 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 3.2 Hz, 1H), 4.03 (d, J = 14.8 Hz, 1H), 3.77 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 157.6, 146.0, 143.1, 137.8, 130.4, 128.1, 127.8, 126.9, 126.8, 123.9 (q, J = 283.9 Hz), 122.8, 121.3, 78.2 (q, J = 29.5 Hz), 38.8 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.7 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{15}H_{11}F_3N_2OS$ 324.0544; Found 324.0537.

IR (neat, cm^{-1}): 3075, 2924, 1596, 1507, 1426, 1244, 1167, 954, 815, 733.



3aj

1,1,1-Trifluoro-2-(4-methylthiazol-2-yl)-3-(quinolin-2-yl)propan-2-ol (3aj) was prepared from 2-methylquinoline **1a** and ketone hydrate **2j** at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 124.7−126.5 °C; 89.2 mg, 88% yield.

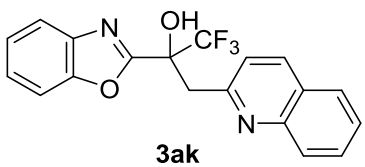
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 6.77 (s, 1H), 4.00 (d, J = 15.2 Hz, 1H), 3.76 (d, J = 14.8 Hz, 1H), 2.36 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 157.8, 153.3, 146.1, 137.7, 130.3, 128.2, 127.8, 127.0, 126.8, 123.9 (q, J = 284.0 Hz), 122.7, 115.8, 78.1 (q, J = 29.4 Hz), 38.8, 17.3 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.5 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{16}H_{13}F_3N_2OS$ 338.0701; Found 338.0699.

IR (neat, cm^{-1}): 3062, 2924, 1609, 1514, 1419, 1256, 1167, 979, 822, 746.



3ak

2-(Benzo[*d*][1,3]oxathiol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-ol (3ak) was prepared from 2-methylquinoline **1a** and ketone hydrate **2k** at 100 °C for 12 h

according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 125.9–126.8 °C; 104.9 mg, 98% yield.

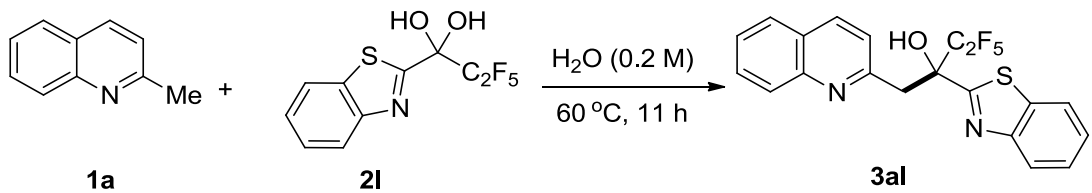
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.66–7.63 (m, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.26–7.19 (m, 2H), 4.14 (d, J = 15.2 Hz, 1H), 3.83 (d, J = 15.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 157.2, 151.1, 145.9, 140.6, 137.8, 130.3, 128.1, 127.5, 126.9, 126.8, 125.8, 124.6, 123.8 (q, J = 284.4 Hz), 122.5, 120.5, 111.1, 76.2 (q, J = 30.3 Hz), 37.8 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{13}F_3N_2O_2S$ 358.0929; Found 358.0925.

IR (neat, cm^{-1}): 3062, 2930, 1609, 1507, 1457, 1249, 1174, 985, 828, 740.



1a **2l** **3al**

2-(Benzo[*d*]thiazol-2-yl)-3,3,4,4,4-pentafluoro-1-(quinolin-2-yl)butan-2-ol (3aa'). To a 4-mL vial equipped with a magnetic stir bar, 2-methylquinoline **1a** (0.45 mmol, 1.5 equiv), ketone hydrate **2l** (0.30 mmol, 1.0 equiv), and H_2O (1.5 mL) were sequentially added. The vial was then capped and heated at 60 °C in an oil bath. After stirring for 11 h, the reaction mixture was then allowed to cool to room temperature. The crude reaction mixture was extracted with ethyl acetate (3 × 5

mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1) to afford the desired product **3al**. White solid, m.p. 170.5−172.3 °C; 121.1 mg, 95% yield.

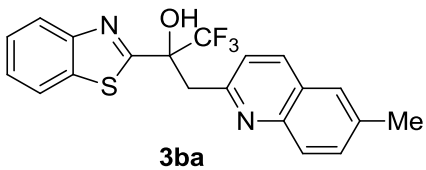
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.02–7.94 (m, 3H), 7.74 (d, J = 8.0 Hz, 1H), 7.70–7.66 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 8.4 Hz, 2H), 4.17 (d, J = 14.8 Hz, 1H), 3.92 (d, J = 14.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 157.6, 153.8, 146.0, 137.9, 135.9, 130.5, 128.1, 127.8, 127.0, 126.9, 126.0, 125.3, 123.6, 122.8, 121.7, 119.3 (qt, J_1 = 286.6 Hz, J_2 = 35.8 Hz), 113.2 (tq, J_1 = 262.6 Hz, J_2 = 35.4 Hz), 79.1 (t, J = 24.3 Hz), 38.9 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −78.2, −121.7, −121.8 ppm.

HRMS (ESI) m/z: [M] Calcd for $C_{20}H_{13}F_5N_2OS$ 424.0669; Found 424.0665.

IR (neat, cm^{-1}): 3069, 2930, 1596, 1507, 1432, 1256, 1350,1174, 1072, 922, 815, 758.



3ba

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(6-methylquinolin-2-yl)propan-2-ol (3ba) was prepared from 2,6-dimethylquinoline **1b** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 129.5−131.7 °C; 112.9 mg, 97% yield.

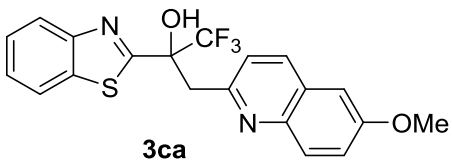
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 13.6 Hz, 2H), 7.19–7.15 (m, 2H), 4.01 (d, J = 15.2 Hz, 1H), 3.73 (d, J = 15.2 Hz, 1H), 2.32 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 158.4, 153.6, 144.6, 137.2, 136.8, 135.9, 132.6, 127.7, 127.0, 126.5, 126.0, 125.3, 123.9 (q, J = 284.4 Hz), 123.5, 122.6, 121.7, 78.6 (q, J = 29.5 Hz), 38.5, 21.5 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −78.9 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{20}H_{15}F_3N_2OS$ 388.0857; Found 388.0873.

IR (neat, cm^{-1}): 3062, 2924, 1602, 1501, 1432, 1256, 1187, 960, 828, 752.



3ca

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(6-methoxyquinolin-2-yl)propan-2-ol (3ca) was prepared from 6-methoxy-2-methylquinoline **1c** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 151.6–153.2 °C; 116.4 mg, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.34–7.31 (m, 2H), 7.27 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 2.4 Hz, 1H), 4.10 (d, J = 15.2

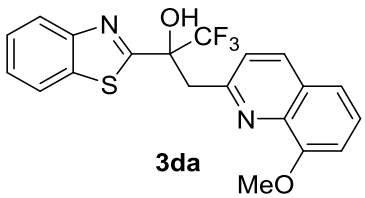
Hz, 1H), 3.85 (s, 3H), 3.83 (d, *J* = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 158.0, 154.6, 153.6, 142.1, 136.6, 135.9, 129.5, 128.1, 126.0, 125.3, 123.9 (q, *J* = 284.4 Hz), 123.5, 123.2, 122.9, 121.8, 105.1, 78.6 (q, *J* = 29.4 Hz), 55.6, 38.4 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{20}H_{15}F_3N_2O_2S$ 404.0806; Found 404.0804.

IR (neat, cm^{-1}): 3062, 2924, 2855, 1602, 1451, 1426, 1256, 1180, 865, 752, 733.



3da

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(8-methoxyquinolin-2-yl)propan-2-ol (3da) was prepared from 8-methoxy-2-methylquinoline **1d** and ketone hydrate **2a** at 100 °C for 16 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 163.7−165.5 °C; 118.8 mg, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.40–7.32 (m, 3H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 4.17 (d, *J* = 15.2 Hz, 1H), 4.02 (s, 3H), 3.89 (d, *J* = 15.2 Hz, 1H) ppm.

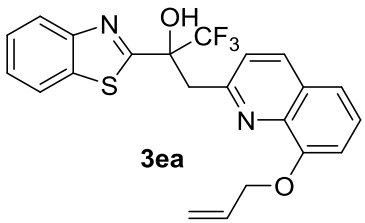
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 155.9, 154.4, 153.5, 137.7, 137.6, 136.0, 127.8, 127.0, 125.9, 125.2, 124.0 (q, *J* = 284.4 Hz), 123.4, 122.9, 121.6, 119.0, 108.4, 78.5 (q, *J* =

29.2 Hz), 56.0, 38.2 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{20}H_{15}F_3N_2O_2S$ 404.0806; Found 404.0804.

IR (neat, cm^{-1}): 3062, 2924, 1571, 1507, 1426, 1256, 1174, 1105, 954, 758.



3ea

3-(8-(Allyloxy)quinolin-2-yl)-2-(benzo[*d*]thiazol-2-yl)-1,1,1-trifluoropropan-2-ol (3ea) was prepared from 8-allyloxy-2-methylquinoline **1e** and ketone hydrate **2a** at 100 °C for 16 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 127.8−129.5 °C; 125.1 mg, 98% yield.

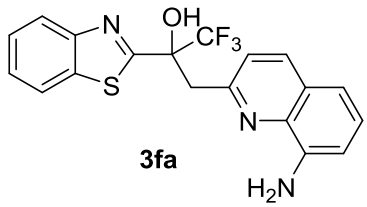
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.42–7.33 (m, 3H), 7.29 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.29–6.22 (m, 1H), 5.67 (d, J = 17.2 Hz, 1H), 5.44 (d, J = 10.8 Hz, 1H), 4.75 (d, J = 4.8 Hz, 2H), 4.25 (d, J = 15.2 Hz, 1H), 3.92 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 156.0, 153.5, 153.2, 137.8, 137.5, 136.0, 132.7, 127.9, 126.8, 125.8, 125.2, 123.4, 122.8, 123.9 (q, J = 284.0 Hz), 121.6, 119.2, 117.6, 109.7, 78.6 (q, J = 29.2 Hz), 69.2, 38.1 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.0 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{22}H_{17}F_3N_2O_2S$ 430.0963; Found 430.0959.

IR (neat, cm^{-1}): 3062, 2924, 1571, 1501, 1426, 1256, 1174, 960, 828, 752.



3fa

3-(8-Aminoquinolin-2-yl)-2-(benzo[*d*]thiazol-2-yl)-1,1,1-trifluoropropan-2-ol (3fa) was prepared from 8-amino-2-methylquinoline **1f** and ketone hydrate **2a** at 100 °C for 16 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 161.6−163.2 °C; 116.7 mg, 95% yield.

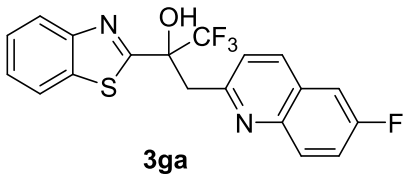
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 4.67 (s, 2H), 4.18 (d, J = 14.8 Hz, 1H) , 3.86 (d, J = 14.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 154.3, 153.5, 142.8, 138.2, 136.5, 135.9, 127.8, 127.7, 126.2, 125.5, 123.9 (q, J = 284.1 Hz), 123.7, 123.0, 121.8, 116.4, 111.7, 78.2 (q, J = 29.4 Hz), 39.4 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.0 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{14}F_3N_3OS$ 389.0810; Found 389.0812.

IR (neat, cm^{-1}): 3069, 2917, 1596, 1507, 1426, 1249, 1174, 960, 834, 746.



3ga

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(6-fluoroquinolin-2-yl)propan-2-ol (3fa) was prepared from 6-fluoro-2-methylquinoline **1g** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 110.0−111.9 °C; 112.8 mg, 96% yield.

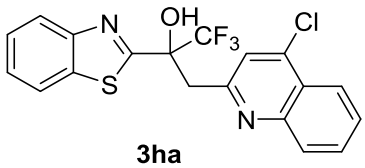
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.01 (d, J = 4.0 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.94 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.46−7.39 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.33−7.29 (m, 2H), 4.17 (d, J = 15.6 Hz, 1H), 3.86 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 160.5 (d, J = 247.8 Hz), 156.9, 153.5, 143.1, 137.2 (d, J = 5.2 Hz), 136.0, 130.5 (d, J = 9.1 Hz), 127.7 (d, J = 10.0 Hz), 126.1, 125.4, 123.9 (q, J = 284.3 Hz), 123.6, 123.5, 121.8, 120.6 (d, J = 25.7 Hz), 110.8 (d, J = 21.7 Hz), 78.6 (q, J = 29.4 Hz), 38.7 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.1, −112.3 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}F_4N_2OS$ 392.0606; Found 392.0597.

IR (neat, cm^{-1}): 3062, 2924, 1602, 1507, 1244, 1174, 960, 834, 758, 727.



3ha

2-(Benzo[*d*]thiazol-2-yl)-3-(4-chloroquinolin-2-yl)-1,1,1-trifluoropropan-2-ol (3ba) was prepared from 4-chloro-2-methylquinoline **1h** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 117.5–119.6 °C; 117.5 mg, 99% yield.

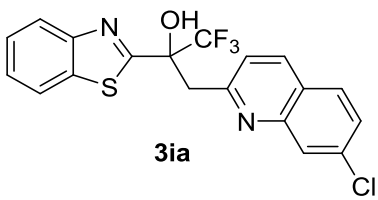
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.47 (s, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 4.15 (d, J = 15.6 Hz, 1H), 3.85 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 157.5, 153.5, 146.8, 144.3, 136.0, 131.3, 128.5, 127.8, 126.1, 125.5, 125.3, 124.2, 123.7, 123.8 (q, J = 284.3 Hz), 122.7, 121.8, 78.6 (q, J = 29.5 Hz), 38.5 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}ClF_3N_2OS$ 408.0311; Found 408.0316.

IR (neat, cm^{-1}): 3062, 2924, 1589, 1501, 1407, 1256, 1167, 954, 758, 720.



3ia

2-(Benzo[*d*]thiazol-2-yl)-3-(7-chloroquinolin-2-yl)-1,1,1-trifluoropropan-2-ol (3ia) was prepared from 7-chloro-2-methylquinoline **1i** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 159.6−162.1 °C; 112.8 mg, 92% yield.

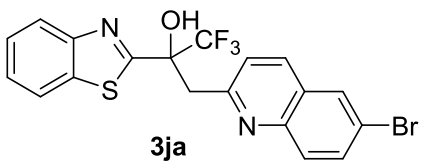
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.01 (d, J = 2.8 Hz, 1H), 7.99 (d, J = 2.4 Hz, 1H), 7.93 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (dd, J_1 = 14.4. Hz, J_2 = 8.0 Hz, 2H), 4.17 (d, J = 15.2 Hz, 1H), 3.85 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 158.8, 153.5, 146.3, 137.7, 136.4, 136.0, 129.0, 128.0, 127.1, 126.1, 125.5, 125.4, 123.6, 123.0, 123.8 (q, J = 284.2 Hz), 121.8, 78.6 (q, J = 29.5 Hz), 38.9 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.1 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}ClF_3N_2OS$ 408.0311; Found 408.0308.

IR (neat, cm^{-1}): 3062, 2924, 1609, 1501, 1419, 1256, 1174, 935, 847, 752.



3ja

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(6-methoxyquinolin-2-yl)propan-2-ol (3ja) was prepared from 6-bromo-2-methylquinoline **1j** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 146.1−148.3 °C; 129.2 mg, 95%

yield.

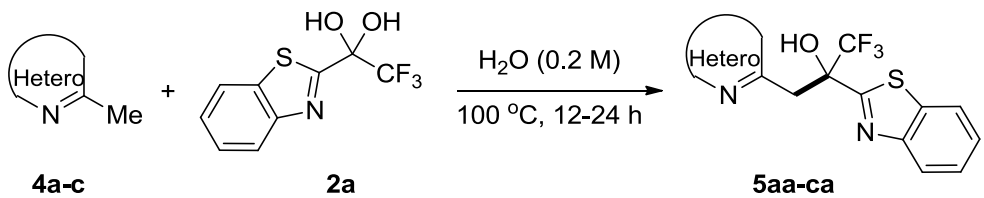
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.00 (dd, J_1 = 8.4 Hz, J_2 = 3.6 Hz, 1H), 7.93 (dd, J_1 = 8.8 Hz, J_2 = 3.6 Hz, 1H), 7.85–7.78 (m, 3H), 7.74–7.70 (m, 1H), 7.45–7.30 (m, 3H), 4.16 (d, J = 15.6 Hz, 1H), 3.85 (d, J = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 158.1, 153.5, 144.6, 136.8, 136.0, 133.9, 129.8, 129.7, 128.1, 126.1, 125.5, 123.8 (q, J = 284.3 Hz), 123.7, 123.6, 121.8, 120.8, 78.6 (q, J = 29.5 Hz), 38.9 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{19}H_{12}BrF_3N_2OS$ 451.9806; Found 451.9812.

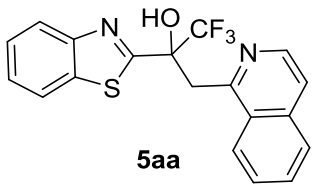
IR (neat, cm^{-1}): 3062, 2924, 1596, 1489, 1249, 1174, 1117, 954, 828, 752.



4a-c **2a** **5aa-ca**

General Procedure C. To a 4-mL vial equipped with a magnetic stir bar, methyl azaarene **4** (0.45 mmol, 1.5 equiv), ketone hydrate **2a** (0.30 mmol, 1.0 equiv), and H_2O (1.5 mL) were sequentially added. The vial was then capped and heated at 100 °C in an oil bath. After stirring for 12~24 h, the reaction mixture was then allowed to cool to room temperature. The crude reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired trifluoromethyl tertiary

alcohol **5**.



5aa

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(isoquinolin-2-yl)propan-2-ol (5aa) was prepared from 1-methylisoquinoline **4a** and ketone hydrate **2a** at 100 °C for 12 h according to the general procedure C (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 159.0–161.3 °C; 95.4 mg, 85% yield.

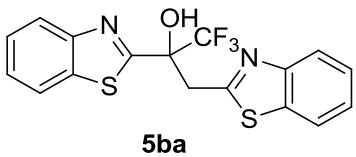
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.33 (d, J = 6.8 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.74–7.63 (m, 3H), 7.47 (d, J = 5.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 4.70 (d, J = 15.6 Hz, 1H), 3.98 (d, J = 16.0 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 157.3, 153.5, 139.4, 136.4, 136.1, 131.0, 128.1, 127.5, 127.4, 125.9, 125.3, 125.1, 124.1 (q, J = 284.3 Hz), 123.5, 121.7, 120.6, 78.6 (q, J = 29.2 Hz), 33.7 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.2 ppm.

HRMS (ESI) m/z: [M] Calcd for $C_{19}H_{13}F_3N_2OS$ 374.0701; Found 374.0699.

IR (neat, cm^{-1}): 3069, 2924, 2855, 1464, 1256, 1180, 967, 822, 752.



5ba

2,3-Bis(benzo[*d*]thiazol-2-yl)-1,1,1-trifluoropropan-2-ol (5ba) was prepared from

2-methylbenzothiazole **4b** and ketone hydrate **2a** at 100 °C for 16 h according to the general procedure C (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 113.9−115.5 °C; 109.4 mg, 96% yield.

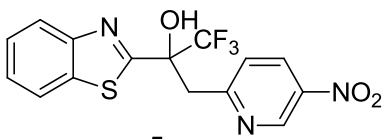
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.49–7.32 (m, 4H), 4.40 (d, J = 15.6 Hz, 1H), 3.98 (d, J = 15.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.8, 153.2, 151.9, 136.2, 134.1, 126.5, 126.3, 125.7, 125.6, 123.8, 123.6 (q, J = 284.5 Hz), 122.7, 121.9, 121.6, 78.0 (q, J = 29.8 Hz), 36.6 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.0 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{17}H_{11}F_3N_2OS_2$ 380.0265; Found 380.0268.

IR (neat, cm^{-1}): 3062, 2924, 1507, 1439, 1256, 1167, 1004, 942, 758, 727.



5ca

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(5-nitropyridin-2-yl)propan-2-ol (5ca) was prepared from 2-methyl-5-nitropyridine **4c** and ketone hydrate **2a** at 100 °C for 24 h according to the general procedure C (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 161.0−162.8 °C; 107.8 mg, 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 7.6

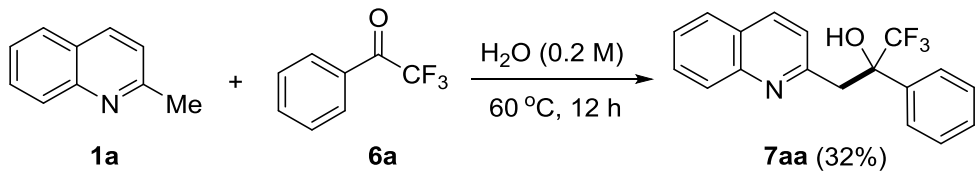
Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 4.15 (d, *J* = 15.2 Hz, 1H), 3.81 (d, *J* = 15.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 162.7, 153.1, 143.6, 143.3, 135.8, 132.5, 126.2, 125.7, 125.5, 123.6 (q, *J* = 284.4 Hz), 123.5, 121.8, 78.2 (q, *J* = 29.7 Hz), 39.2 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −79.1 ppm.

HRMS (ESI) m/z: [M] Calcd for $C_{15}H_{10}F_3N_3O_3S$ 369.0395; Found 369.0391.

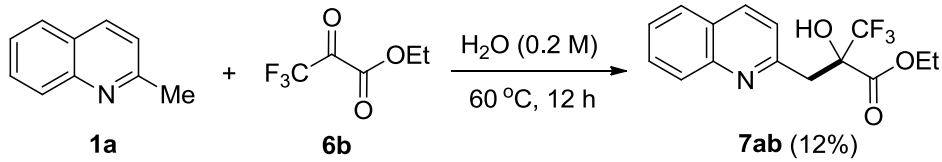
IR (neat, cm^{-1}): 3069, 2924, 1602, 1526, 1344, 1256, 1180, 954, 860, 765.



1a **6a** **7aa** (32%)

1,1,1-Trifluoro-2-phenyl-3-(quinolin-2-yl)propan-2-ol (7aa) was prepared from 2-methylquinoline **1a** (60.9 mg, 0.45 mmol) and trifluoroacetophenone **6a** (52.2 mg, 0.30 mmol) at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 20:1 to 15:1). Known compound,[3] white solid, 30.5 mg, 32% yield.

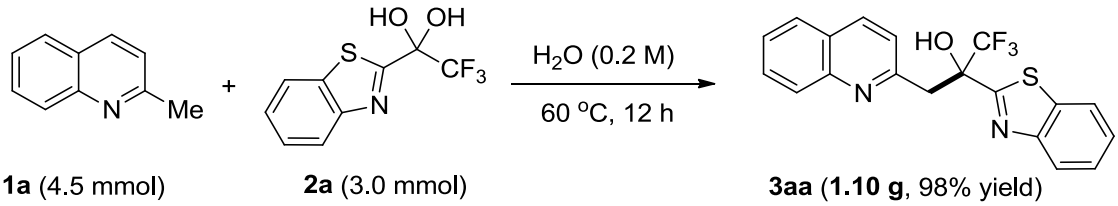
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 3H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 8.4 Hz, 2H), 3.81 (d, *J* = 15.2 Hz, 1H), 3.70 (d, *J* = 14.8 Hz, 1H) ppm.



Ethyl 3,3,3-trifluoro-2-hydroxy-2-(quinolin-2-ylmethyl)propanoate (7ab) was prepared from 2-methylquinoline **1a** (60.9 mg, 0.45 mmol) and ethyl trifluoropyruvate **6b** (51.0 mg, 0.30 mmol) at 60 °C for 12 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 20:1 to 15:1). Known compound,[3] white solid,10.8 mg, 12% yield.

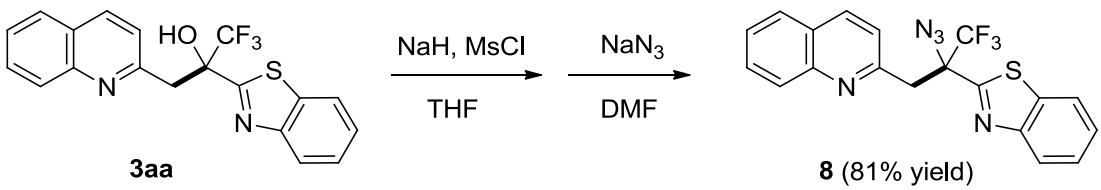
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 6.79 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.76 (d, J = 15.2 Hz, 1H), 3.52 (d, J = 15.2 Hz, 1H), 1.18 (t, J = 7.2 Hz, 3H) ppm.

IV. Gram-Sale Catalytic Reaction and Product Transformations



1a (4.5 mmol) **2a** (3.0 mmol) **3aa** (**1.10 g**, 98% yield)

To a 50-mL round-bottom flask equipped with a magnetic stir bar, 2-methylquinoline **1a** (4.5 mmol, 1.5 equiv), ketone hydrate **2a** (3.0 mmol, 1.0 equiv), and H_2O (15 mL) were sequentially added. The flask was then capped with a rubber plug and heated at 60 °C in an oil bath. After stirring for 12 h, the reaction mixture was then allowed to cool to room temperature. The crude reaction mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1) to afford the desired product **3aa** as a white solid (1.10 g, 98% yield).



3aa **8** (81% yield)

2-(2-Azido-1,1,1-trifluoro-3-(quinolin-2-yl)propan-2-yl)benzo[*d*]thiazole (8). Under N_2, to a suspension of NaH (60 mg, 1.5 mmol, 60% in mineral oil) in anhydrous THF (5 mL) was dropwise added alcohol **3aa** (0.5 mmol, 187 mg) in anhydrous THF (5 mL) at 0 °C**.** The reaction mixture was spontaneously warmed

to room temperature and stirred for 1 h. Then methanesulfonyl chloride (0.12 mL, 1.5 mmol) was added dropwise. After 3 h, the reation was quenched with H_2O (5 mL). The layers were separated, and the aqueous layer was extracted with ethyl acetate (15 mL × 2). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The desired methanesulfonate product was obtained, and it was directly used for the next step without further purification.

The obtained crude product was redissolved in DMF (5 mL) followed by the addition of NaN_3 (2.0 equiv). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the reaction was quenched with water (20 mL) and then was extracted with ethyl acetate three times (20 mL x 3). The combined organic layers were sequentially washed with water (20 mL x 3) and brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate 20:1 to 10:1) to afford the desired product **8**. Yellow solid, m.p. 157.5-159.6 °C, 160 mg, 81% yield**.**

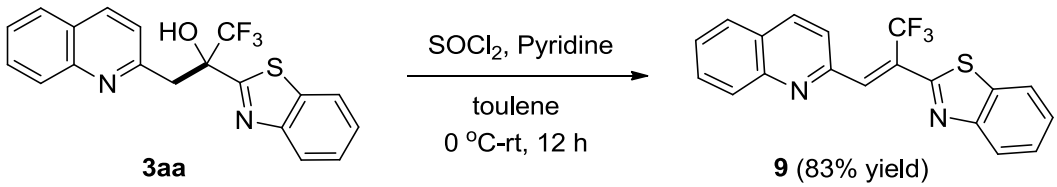
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 9.6 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.70–7.63 (m, 2H), 7.49 (t, J = 7.2 Hz, 2H), 7.42–7.37 (m, 2H), 3.46 (s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 153.1, 135.8, 134.4, 131.6, 130.8, 130.1, 128.3, 127.5, 127.4, 126.3, 125.8, 125.2 (q, J = 285.0 Hz), 123.8, 123.7, 121.8, 116.4, 116.3, 63.4 (q, J = 29.6 Hz) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ –76.0 ppm.

HRMS (ESI) m/z: [M] Calcd for $C_{19}H_{12}F_3N_5S$ 399.0766; Found 399.0769.

IR (neat, cm^{-1}): 3062, 2924, 2848, 1602, 1501, 1269, 1167, 1124, 928, 822, 746.



3aa **9** (83% yield)

(*E*)-2-(3,3,3-Trifluoro-1-(quinolin-2-yl)prop-1-en-2-yl)benzo[*d*]thiazole (9). To a solution of trifluoromethyl tertiary alcohol **3aa** (0.75 g, 2.0 mmol) in toluene (8 mL) were added $SOCl_2$ (6.0 mmol, 3.0 equiv) and pyridine (8.0 mmol, 4.0 equiv) successively at 0 °C in an ice bath. The mixture was stirred for 12 h at room temperature and then was diluted with ethyl acetate (30 mL). The mixture was sequentially washed with water (20 mL) and brine (20 mL). The organic phase was dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate 30:1 to 15:1) to afford the desired product **9**. Yellow solid, m.p. 110.5–112.6 °C; 0.59 g, 83% yield.

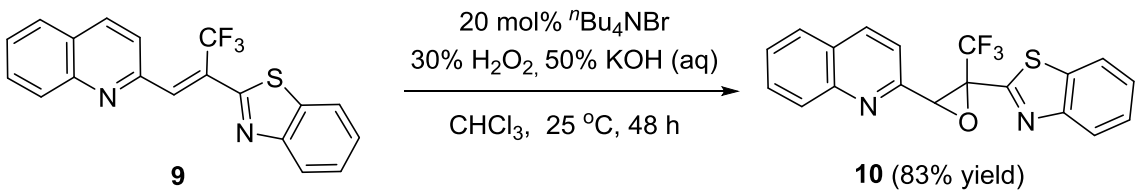
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.86–7.82 (m, 3H), 7.70 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.54–7.49 (m, 2H), 7.46–7.42 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 153.2, 151.8, 147.9, 139.1 (q, J = 5.3 Hz), 136.4, 136.2, 130.2, 129.7, 127.8, 127.5, 127.2, 126.5, 126.2, 124.2, 123.6, 122.5 (q, J = 272.8 Hz), 121.9, 121.7 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −64.9 ppm.

HRMS (ESI) m/z: [M] Calcd for $C_{19}H_{11}F_3N_2S$ 356.0595; Found 356.0594.

IR (neat, cm^{-1}): 3062, 2924, 2854, 1602, 1501, 1362, 1167, 890, 840, 765, 727.



2-(3-(Quinolin-2-yl)-2-(trifluoromethyl)oxiran-2-yl)benzo[*d*]thiazole (10). To a solution of **9** (106.9 mg, 0.30 mmol) and ^{n}BuN$_4$Br (19.3 mg, 0.06 mmol, 20 mol%) in $CHCl_3$ (0.3 mL) were added aqueous hydrogen peroxide (30%, 0.60 mL, 20.0 equiv) and 50% aqueous KOH (105 μL, 3.0 equiv) successively. The reaction mixture was stirred at room temperature for 48 h and then was diluted with ethyl acetate (15 mL). The mixture was sequentially washed with water (10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate 50:1 to 20:1) to afford the desired product **10**. Yellow oil, 92.7

mg, 83% yield, dr >20:1.

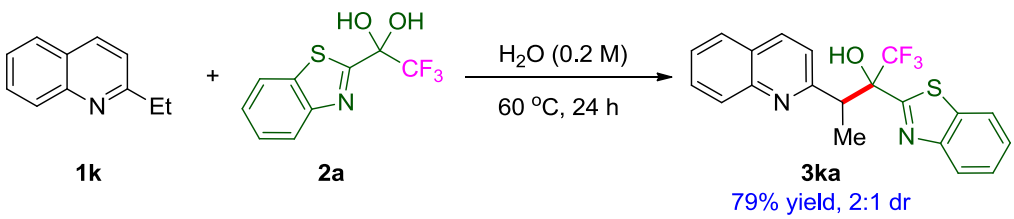
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.57 (q, J = 7.2 Hz, 2H), 7.47 (t, J = 7.9 Hz, 1H), 4.85 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 153.5, 151.3, 147.7, 136.8, 134.7, 130.2, 129.3, 127.9, 127.8, 127.4, 126.8, 126.4, 124.2, 122.2 (q, J = 287.6 Hz), 121.9, 118.7 (q, J = 3.3 Hz), 66.7, 62.8 (q, J = 37.6 Hz) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −66.3 ppm.

HRMS (ESI) m/z: [M] Calcd for $C_{19}H_{11}F_3N_2OS$ 372.0544; Found 372.0548.

IR (neat, cm^{-1}): 3401, 3326, 3062, 1614, 1558, 1249, 1174, 890, 822, 752, 733.



1k **2a** **3ka**

79% yield, 2:1 dr

2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-3-(quinolin-2-yl)butan-2-ol (3ka) was prepared from 2-ethylquinoline **1k** and ketone hydrate **2a** at 60 °C for 11 h according to the general procedure B (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1). White solid, m.p. 110.5−112.6 °C; 91.9 mg, 79% yield, dr = 2:1.

Major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.99 (q, J_1 = 4.0 Hz, J_2 = 8.4 Hz, 2H), 7.70 (t, J = 9.6 Hz, 2H), 7.63–7.57 (m, 1H), 7.49 (q, J_1 = 7.6 Hz, J_2 = 14.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 4.54 (q, J = 7.2 Hz, 1H), 1.73 (d, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 163.8, 153.6, 145.8, 138.2, 135.7, 130.3, 128.1, 127.8, 126.9, 126.8, 125.8, 125.1, 123.8 (q, J = 284.8 Hz), 123.4, 121.9, 121.4, 80.8 (q, J = 28.5 Hz), 43.9, 17.7 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ −74.4 ppm.

Minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 0.5 H), 8.28 (d, J = 8.4 Hz, 0.5 H), 8.20 (d, J = 8.4 Hz, 0.5 H), 8.10 (d, J = 8.4 Hz, 0.5 H), 8.04 (d, J = 8.0 Hz, 0.5 H), 7.99 (q, J_1 = 4.0 Hz, J_2 = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 0.5 H), 7.80 (t, J = 8.0 Hz, 0.5 H), 7.70 (t, J = 9.6 Hz, 1H), 4.25 (q, J = 6.8 Hz, 0.5 H), 1.33 (d, J = 7.2 Hz, 1.5 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 163.2, 153.9, 146.4, 138.6, 135.4, 130.5, 128.4, 127.9, 127.3, 126.9, 126.2, 125.5, 123.8 (q, J = 284.8 Hz), 123.7, 122.0, 121.7, 81.4 (q, J = 27.6 Hz), 42.7, 17.0 ppm.

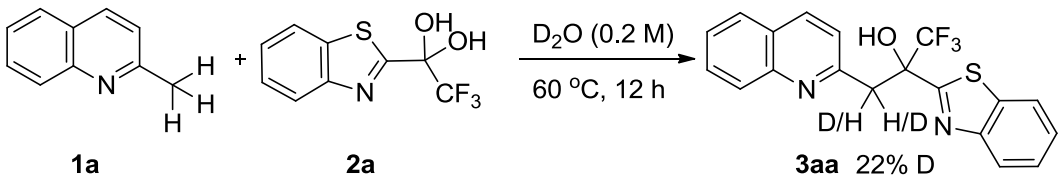
^{19}F NMR (376.5 MHz, $CDCl_3$) δ −75.2 ppm.

HRMS (EI) m/z: [M] Calcd for $C_{20}H_{15}F_3N_2OS$ 388.0857; Found 388.0855.

IR (neat, cm^{-1}): 3062, 2917, 1501, 1256, 1174, 1137, 992, 960, 828, 765.

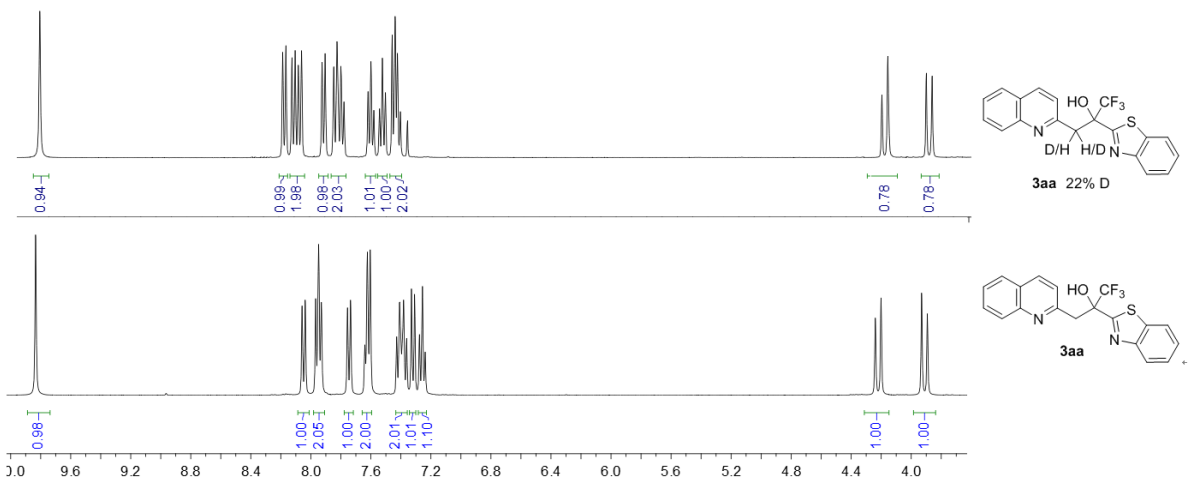
V. Deuterium Experiment and Plausible Reaction Mechanism.

Deuterium experiment

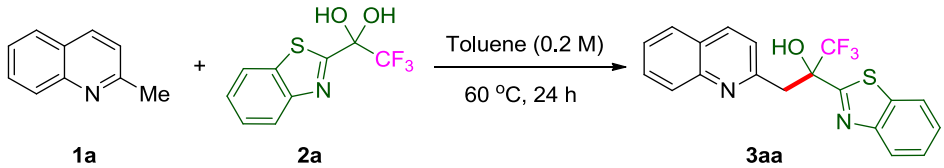


1a **2a** **3aa** 22% D

To a 4-mL vial equipped with a magnetic stir bar, 2-methylquinoline **1a** (0.45 mmol), ketone hydrate **2a** (0.30 mmol), and D_2O (1.5 mL) were sequentially added. The vial was then capped and heated at 60 in an oil bath. After stirring for 12 h, the reaction mixture was then allowed to cool to room temperature. The crude reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired trifluoromethyl tertiary alcohol **3aa** (109.2 mg, 99% yield), and a marked deuterium incorporation of 22% was observed.



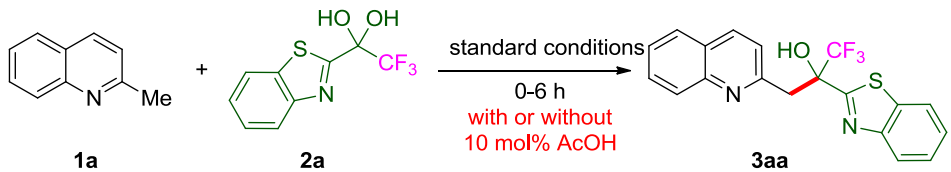
Control experiments



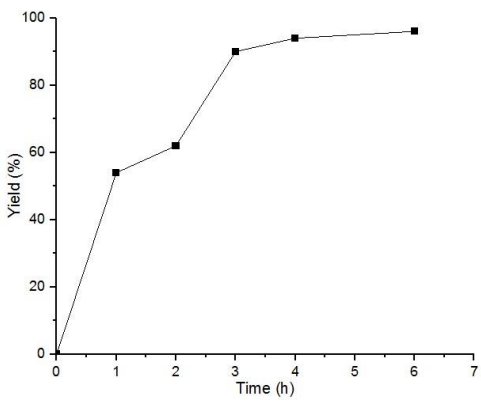
1a **2a** **3aa**

Entry	Additive	Yield (%)
1	None	29
2	100 mg 4 Å MS	trace
3	20 equiv. of H_2O	67

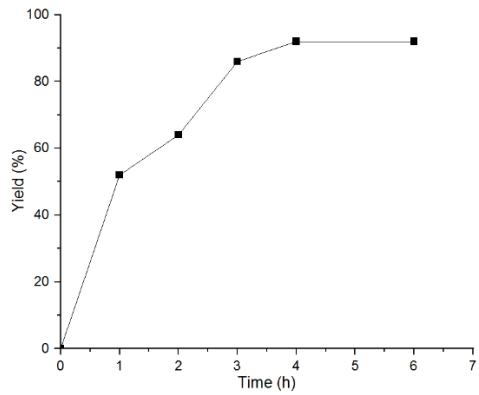
[a] Reactions were performed with **1a** (0.15 mmol) and **2a** (0.10 mmol) in toluene (0.5 mL) at 60 °C for 24 h. [b] Isolated yield.



1a **2a** **3aa**



without 10 mol% AcOH



with 10 mol% AcOH

We carried out the control experiments. When the reaction was performed in toluene, the desired product **3aa** was obtained in 29% yield. The addition of 4 Å MS could shut down the reaction, while the addition of 20 equiv. of H_2O increased the yield to 67%. Moreover, we found that the use of 10 mol% AcOH as the catalyst under the standard conditions could not obviously accelerate this

transformation. The results indicated that water serves as the promoter for the C-C bond formation.

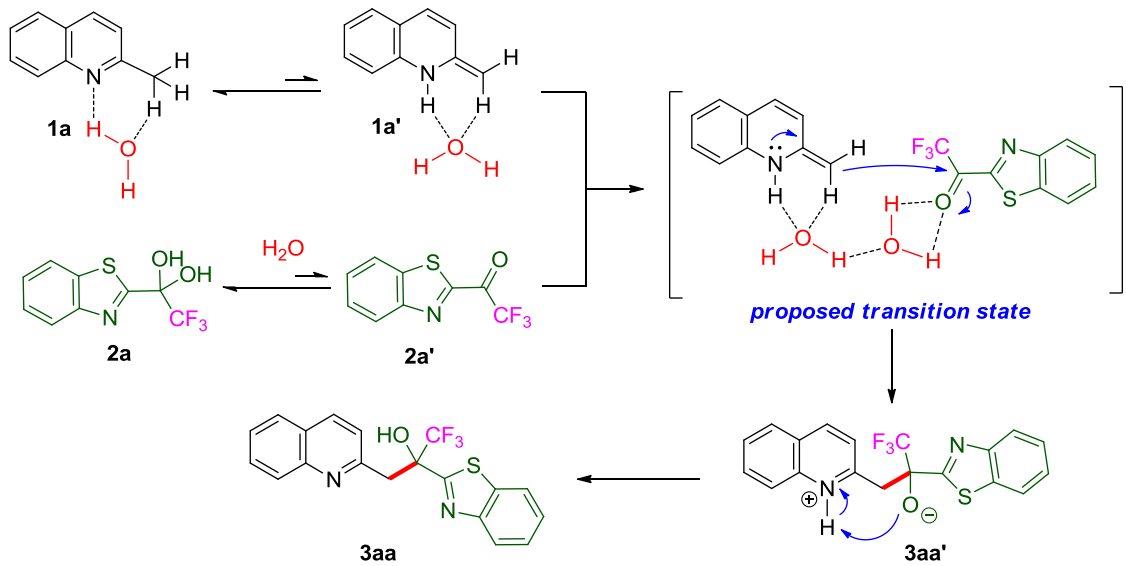


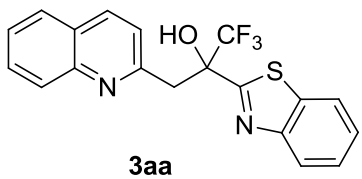
Fig. S1 Plausible reaction mechanism.

As shown in Figure S1, we proposed a plausible reaction mechanism. There is a weak equilibrium between 2-methylquinoline **1a** and its enamine form **1a'** with the action of water, meanwhile there is also a weak equilibrium between hydate **2a** and its ketone form **2a'**. We speculate that water may act as a dual catalyst in this transformation. Water may activate enamine **1a'** and the carbonyl group of **2a'** through hydrogen bonding. The proposed transition state facilitates nucleophilic addition of enamine **1a'** to ketone **2a'** to form the intermediate **3aa'**, which undergoes intramolecular proton transfer to give the desired alcohol **3aa**.

VI. X-ray Crystallographic Analysis of Product 3aa

In a 25 mL round-bottom flask, 50 mg of **3aa** (from the gram-scale preparation) was completely dissolved in DCM (5.0 mL), then 10.0 mL of petroleum ether was added slowly. The round-bottom flask was placed on a stable experimental table. After several days, the crystal was obtained by slow evaporation of the solvents at room temperature. A suitable single crystal was selected for X-ray diffraction on a Brucker D8 Advance X–Ray diffractometer, Eos fitted with Mo Kα radiation (λ = 0.71073 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The absolute configuration was established by anomalous dispersion effects in diffraction measurements on the crystal. The thermal ellipsoids are shown at 50% probability level (Figure S2).

The relative configuration of **3aa** was determined by single-crystal X-ray diffraction analysis. The X-ray data of **3aa** have been deposited at the Cambridge Crystallographic Data Center (CCDC 2246226).



3aa

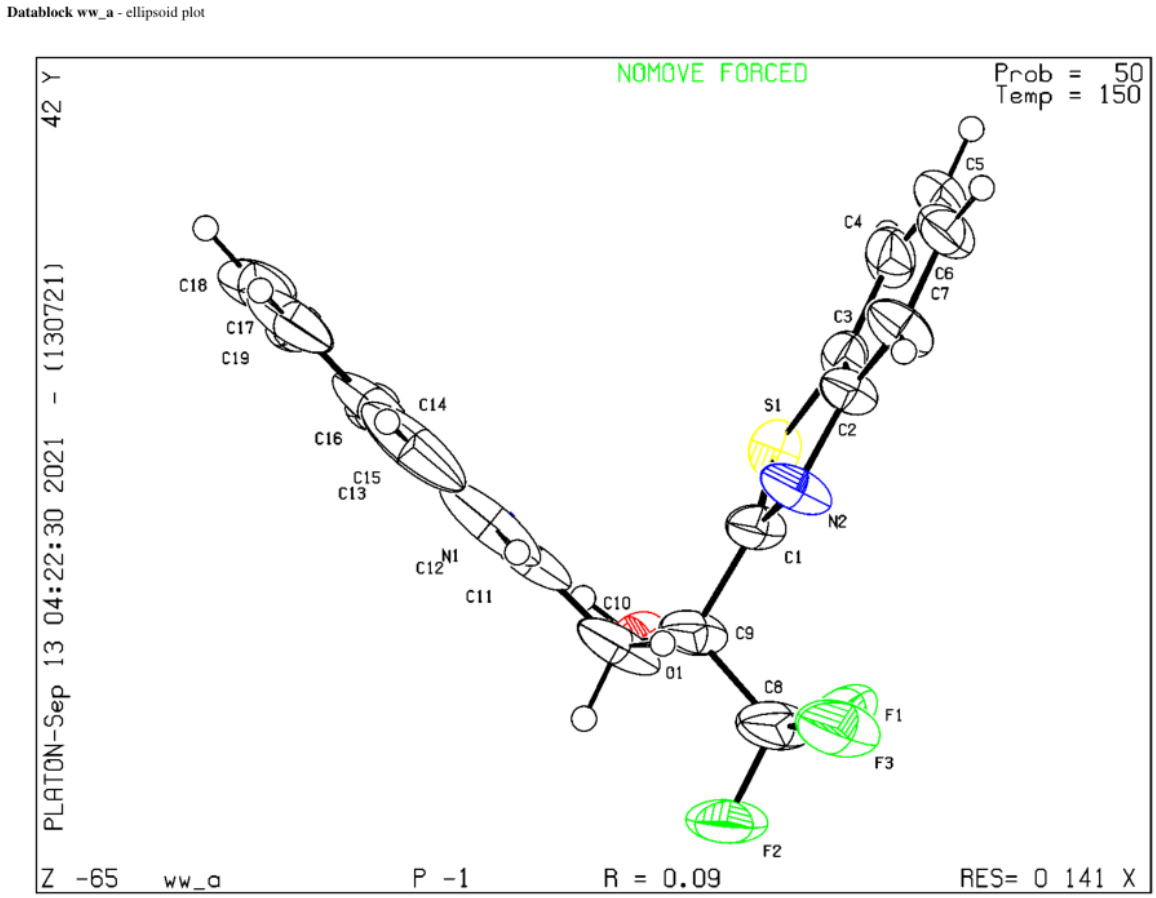


Fig. S2 ORTEP representation of **3aa** (The thermal ellipsoids are shown at 50% probability level.).

Table S1 Crystal data and structure refinement for **3aa**.

Identification code	**3aa**
Empirical formula	$C_{19}H_{13}F_3N_2OS$
Formula weight	374.37
Temperature	150.15 K
Wavelength	0.71073 Å
Crystal system	Triclinic

Space group	P-1
Unit cell dimensions	
a/Å	8.929(3)
b/Å	9.985(3)
c/Å	10.178(3)
α/°	101.361(6)
β/°	92.022(7)
γ/°	108.738(7)
Volume/Å^3	837.7(4)
Z	2
Density (calculated)	1.484 g/cm^3
Absorption coefficient	0.235 mm^{-1}
F(000)	384
Crystal size	0.22 x 0.18 x 0.12 mm^3
Theta range for data collection/°	2.208 to 28.583
Index ranges	-12<=h<=11, -13<=k<=13, -13<=l<=13
Reflections collected	18847
Independent reflections	4194 [R(int) = 0.0329]
Completeness to theta = 25.242	99.8 %
Max. and min. transmission	0.7457 and 0.7056

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4194 / 0 / 236
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R_1 = 0.0932, wR_2 = 0.2208
R indices (all data)	R_1 = 0.1064, wR_2 = 0.2310
Extinction coefficient	n/a
Largest diff. peak and hole/ $Å^{-3}$	0.776 and -0.823

Table S2 Atomic coordinates (Å x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	**x**	**y**	**z**	**U(eq)**
C(1)	4332(4)	8150(5)	1713(3)	44(1)
C(2)	6949(4)	8982(4)	2058(4)	42(1)
C(3)	6632(4)	9880(3)	3161(3)	38(1)
C(4)	7869(5)	10888(4)	4081(4)	53(1)
C(5)	9397(5)	10972(5)	3862(5)	60(1)
C(6)	9725(5)	10097(5)	2762(5)	58(1)

C(7)	8518(4)	9093(5)	1854(5)	56(1)
C(8)	2271(6)	7870(12)	-99(6)	109(3)
C(9)	2656(4)	7246(6)	1075(4)	61(1)
C(10)	2525(5)	5658(6)	585(4)	77(2)
C(11)	2788(4)	4958(5)	1710(5)	62(1)
C(12)	3496(5)	3837(7)	1523(8)	101(3)
C(13)	3725(6)	3240(6)	2541(12)	123(4)
C(14)	3257(5)	3686(4)	3802(7)	81(2)
C(15)	2523(4)	4763(4)	3931(5)	50(1)
C(16)	2024(5)	5228(4)	5177(4)	54(1)
C(17)	2254(7)	4657(5)	6257(6)	84(2)
C(18)	3005(10)	3641(7)	6131(11)	134(5)
C(19)	3468(7)	3143(6)	4991(12)	124(4)
F(1)	2387(4)	9257(6)	308(4)	112(2)
F(2)	815(3)	7144(6)	-709(4)	135(2)
F(3)	3291(4)	7811(5)	-1043(3)	119(2)
N(1)	2304(3)	5378(3)	2878(3)	42(1)
N(2)	5605(3)	7987(4)	1256(3)	55(1)
O(1)	1530(3)	7426(4)	1977(3)	56(1)
S(1)	4604(1)	9489(1)	3173(1)	43(1)

Table S3 Bond lengths [Å] and angles [°] for **3aa**.

Atom-Atom	**Length/ Å**
C(1)-C(9)	1.519(5)
C(1)-N(2)	1.289(4)
C(1)-S(1)	1.743(4)
C(2)-C(3)	1.391(5)
C(2)-C(7)	1.396(5)
C(2)-N(2)	1.392(4)
C(3)-C(4)	1.397(5)
C(3)-S(1)	1.726(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.369(7)
C(5)-H(5)	0.9500
C(5)-C(6)	1.380(7)
C(6)-H(6)	0.9500
C(6)-C(7)	1.375(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.528(8)
C(8)-F(1)	1.334(10)
C(8)-F(2)	1.327(6)

C(8)-F(3)	1.353(7)
C(9)-C(10)	1.530(8)
C(9)-O(1)	1.416(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(10)-C(11)	1.501(8)
C(11)-C(12)	1.438(8)
C(11)-N(1)	1.316(5)
C(12)-H(12)	0.9500
C(12)-C(13)	1.333(12)
C(13)-H(13)	0.9500
C(13)-C(14)	1.398(11)
C(14)-C(15)	1.416(5)
C(14)-C(19)	1.450(11)
C(15)-C(16)	1.401(6)
C(15)-N(1)	1.374(5)
C(16)-H(16)	0.9500
C(16)-C(17)	1.372(6)
C(17)-H(17)	0.9500
C(17)-C(18)	1.373(10)
C(18)-H(18)	0.9500

C(18)-C(19)	1.305(14)
C(19)-H(19)	0.9500
O(1)-H(1)	0.8400

C(9)-C(1)-S(1)	119.5(3)
N(2)-C(1)-C(9)	124.2(3)
N(2)-C(1)-S(1)	116.3(3)
C(3)-C(2)-C(7)	119.9(3)
C(3)-C(2)-N(2)	114.7(3)
N(2)-C(2)-C(7)	125.3(3)
C(2)-C(3)-C(4)	120.7(4)
C(2)-C(3)-S(1)	109.9(3)
C(4)-C(3)-S(1)	129.4(3)
C(3)-C(4)-H(4)	120.9
C(5)-C(4)-C(3)	118.2(4)
C(5)-C(4)-H(4)	120.9
C(4)-C(5)-H(5)	119.2
C(4)-C(5)-C(6)	121.5(4)
C(6)-C(5)-H(5)	119.2
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-C(5)	120.9(4)

C(7)-C(6)-H(6)	119.6
C(2)-C(7)-H(7)	120.6
C(6)-C(7)-C(2)	118.8(4)
C(6)-C(7)-H(7)	120.6
F(1)-C(8)-C(9)	111.5(5)
F(1)-C(8)-F(3)	107.1(6)
F(2)-C(8)-C(9)	112.1(6)
F(2)-C(8)-F(1)	107.9(8)
F(2)-C(8)-F(3)	107.0(5)
F(3)-C(8)-C(9)	111.0(7)
C(1)-C(9)-C(8)	108.2(4)
C(1)-C(9)-C(10)	110.5(4)
C(8)-C(9)-C(10)	110.7(5)
O(1)-C(9)-C(1)	110.5(3)
O(1)-C(9)-C(8)	103.9(4)
O(1)-C(9)-C(10)	112.8(4)
C(9)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
C(11)-C(10)-C(9)	113.1(3)
C(11)-C(10)-H(10A)	109.0

C(11)-C(10)-H(10B)	109.0
C(12)-C(11)-C(10)	121.9(5)
N(1)-C(11)-C(10)	117.6(4)
N(1)-C(11)-C(12)	120.5(6)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-C(11)	120.7(6)
C(13)-C(12)-H(12)	119.6
C(12)-C(13)-H(13)	119.9
C(12)-C(13)-C(14)	120.1(5)
C(14)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	117.3(6)
C(13)-C(14)-C(19)	125.4(6)
C(15)-C(14)-C(19)	117.3(6)
C(16)-C(15)-C(14)	119.0(5)
N(1)-C(15)-C(14)	122.0(5)
N(1)-C(15)-C(16)	119.0(3)
C(15)-C(16)-H(16)	119.8
C(17)-C(16)-C(15)	120.4(5)
C(17)-C(16)-H(16)	119.8
C(16)-C(17)-H(17)	119.9
C(16)-C(17)-C(18)	120.1(7)

C(18)-C(17)-H(17)	119.9
C(17)-C(18)-H(18)	118.8
C(19)-C(18)-C(17)	122.3(7)
C(19)-C(18)-H(18)	118.8
C(14)-C(19)-H(19)	119.6
C(18)-C(19)-C(14)	120.8(5)
C(18)-C(19)-H(19)	119.6
C(11)-N(1)-C(15)	119.3(4)
C(1)-N(2)-C(2)	110.4(3)
C(9)-O(1)-H(1)	109.5
C(3)-S(1)-C(1)	88.68(16)

Symmetry transformations used to generate equivalent atoms:

Table S4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**

C(1)	31(2)	72(2)	25(2)	4(2)	6(1)	14(2)
C(2)	32(2)	46(2)	38(2)	-4(1)	0(1)	9(1)
C(3)	46(2)	32(2)	33(2)	7(1)	4(1)	12(1)
C(4)	69(3)	32(2)	42(2)	1(1)	2(2)	-1(2)
C(5)	56(2)	46(2)	55(2)	10(2)	-13(2)	-11(2)
C(6)	33(2)	52(2)	79(3)	15(2)	-6(2)	2(2)
C(7)	32(2)	57(2)	65(3)	-7(2)	5(2)	9(2)
C(8)	35(2)	214(9)	51(3)	57(5)	-1(2)	-10(4)
C(9)	26(2)	114(4)	32(2)	14(2)	6(1)	9(2)
C(10)	27(2)	117(4)	42(2)	-29(2)	6(2)	-8(2)
C(11)	20(2)	65(3)	68(3)	-37(2)	1(2)	2(2)
C(12)	26(2)	76(4)	150(6)	-75(4)	12(3)	4(2)
C(13)	34(2)	46(3)	254(11)	-48(4)	-20(4)	17(2)
C(14)	32(2)	26(2)	168(6)	-9(3)	-33(3)	9(2)
C(15)	30(2)	27(2)	82(3)	-2(2)	-20(2)	8(1)
C(16)	56(2)	34(2)	63(3)	10(2)	-18(2)	7(2)
C(17)	88(4)	47(2)	91(4)	28(2)	-50(3)	-13(2)
C(18)	110(6)	39(3)	219(10)	48(4)	-114(7)	-17(3)
C(19)	59(3)	27(2)	266(12)	26(4)	-85(5)	2(2)
F(1)	62(2)	200(5)	92(3)	101(3)	7(2)	25(3)
F(2)	40(2)	256(5)	80(2)	90(3)	-20(2)	-19(2)

F(3)	55(2)	223(5)	35(1)	36(2)	4(1)	-18(2)
N(1)	26(1)	41(2)	52(2)	-10(1)	-2(1)	13(1)
N(2)	27(1)	81(2)	35(2)	-17(2)	6(1)	6(1)
O(1)	35(1)	97(2)	52(2)	38(2)	19(1)	30(1)
S(1)	50(1)	45(1)	40(1)	10(1)	17(1)	23(1)

Table S5 Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3aa**.

Atom	x	y	z	U(eq)
H(4)	7656	11498	4839	64
H(5)	10251	11648	4482	72
H(6)	10799	10190	2630	70
H(7)	8748	8487	1103	67
H(10A)	1456	5110	99	92
H(10B)	3319	5601	-60	92
H(12)	3804	3519	665	122
H(13)	4207	2510	2408	147

H(16)	1522	5945	5274	65
H(17)	1894	4965	7094	101
H(18)	3194	3289	6900	160
H(19)	3949	2415	4940	149
H(1)	1552	6968	2582	84

Table S6 Torsion angles [°] for **3aa**.

A B C D	**Angle/°**
C(1)-C(9)-C(10)-C(11)	63.9(4)
C(2)-C(3)-C(4)-C(5)	0.4(6)
C(2)-C(3)-S(1)-C(1)	0.3(3)
C(3)-C(2)-C(7)-C(6)	0.2(7)
C(3)-C(2)-N(2)-C(1)	1.5(5)
C(3)-C(4)-C(5)-C(6)	0.3(6)
C(4)-C(3)-S(1)-C(1)	-177.9(4)
C(4)-C(5)-C(6)-C(7)	-0.9(7)
C(5)-C(6)-C(7)-C(2)	0.6(7)
C(7)-C(2)-C(3)-C(4)	-0.7(6)
C(7)-C(2)-C(3)-S(1)	-179.1(3)

C(7)-C(2)-N(2)-C(1)	179.4(4)
C(8)-C(9)-C(10)-C(11)	-176.3(3)
C(9)-C(1)-N(2)-C(2)	179.7(4)
C(9)-C(1)-S(1)-C(3)	179.7(4)
C(9)-C(10)-C(11)-C(12)	-148.2(4)
C(9)-C(10)-C(11)-N(1)	33.7(4)
C(10)-C(11)-C(12)-C(13)	179.6(4)
C(10)-C(11)-N(1)-C(15)	180.0(3)
C(11)-C(12)-C(13)-C(14)	0.9(8)
C(12)-C(11)-N(1)-C(15)	1.8(5)
C(12)-C(13)-C(14)-C(15)	1.0(7)
C(12)-C(13)-C(14)-C(19)	-178.7(5)
C(13)-C(14)-C(15)-C(16)	179.4(4)
C(13)-C(14)-C(15)-N(1)	-1.5(5)
C(13)-C(14)-C(19)-C(18)	179.2(6)
C(14)-C(15)-C(16)-C(17)	0.5(6)
C(14)-C(15)-N(1)-C(11)	0.1(5)
C(15)-C(14)-C(19)-C(18)	-0.4(8)
C(15)-C(16)-C(17)-C(18)	1.2(7)
C(16)-C(15)-N(1)-C(11)	179.2(3)
C(16)-C(17)-C(18)-C(19)	-2.6(9)

C(17)-C(18)-C(19)-C(14)	2.2(10)
C(19)-C(14)-C(15)-C(16)	-0.9(5)
C(19)-C(14)-C(15)-N(1)	178.2(4)
F(1)-C(8)-C(9)-C(1)	-58.5(6)
F(1)-C(8)-C(9)-C(10)	-179.7(4)
F(1)-C(8)-C(9)-O(1)	59.0(5)
F(2)-C(8)-C(9)-C(1)	-179.6(6)
F(2)-C(8)-C(9)-C(10)	59.3(8)
F(2)-C(8)-C(9)-O(1)	-62.1(8)
F(3)-C(8)-C(9)-C(1)	60.8(8)
F(3)-C(8)-C(9)-C(10)	-60.4(6)
F(3)-C(8)-C(9)-O(1)	178.3(5)
N(1)-C(11)-C(12)-C(13)	-2.3(6)
N(1)-C(15)-C(16)-C(17)	-178.6(4)
N(2)-C(1)-C(9)-C(8)	-81.6(7)
N(2)-C(1)-C(9)-C(10)	39.7(6)
N(2)-C(1)-C(9)-O(1)	165.3(4)
N(2)-C(1)-S(1)-C(3)	0.5(4)
N(2)-C(2)-C(3)-C(4)	177.3(4)
N(2)-C(2)-C(3)-S(1)	-1.1(4)
N(2)-C(2)-C(7)-C(6)	-177.6(4)

O(1)-C(9)-C(10)-C(11)	-60.3(4)
S(1)-C(1)-C(9)-C(8)	99.3(5)
S(1)-C(1)-C(9)-C(10)	-139.4(3)
S(1)-C(1)-C(9)-O(1)	-13.8(5)
S(1)-C(1)-N(2)-C(2)	-1.2(5)
S(1)-C(3)-C(4)-C(5)	178.5(3)

Crystal structure determination of 3aa

Crystal Data for $C_{19}H_{13}F_3N_2OS$ (*M* =374.37 g/mol): orthorhombic, space group P-1, *a* = 8.929 (3) Å, *b* = 9.985 (3) Å, *c* = 10.178 (3) Å, *V* = 837.7(4) Å^3, *Z* = 2, *T* = 150.15 K, μ(MoKα) = 0.235 mm^{-1}, *Dcalc* = 1.484 g/cm^3, 18847 reflections measured (2.208° ≤ 2Θ ≤ 28.583°), 4194 unique (*R*int = 0.0329) which were used in all calculations. The final R_1 was 0.0932 (I > 2σ(I)) and wR_2 was 0.2208 (all data).

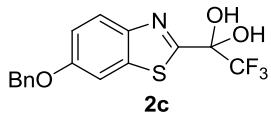
VII. References

1 P. V. Khodakovskiy, D. M. Volochnyuk, D. M. Panov, I. I. Pervak, E. V. Zarudnitskii, O. V. Shishkin, A. A. Yurchenko, A. Shivanyuk and A. A. Tolmachev, *Synthesis*, 2008, **6**, 948–956.

2 W. Wang, W. Xiong, J. Wang, Q.-A. Wang and W. Yang, *J. Org. Chem.*, 2020, **85**, 4398–4407.

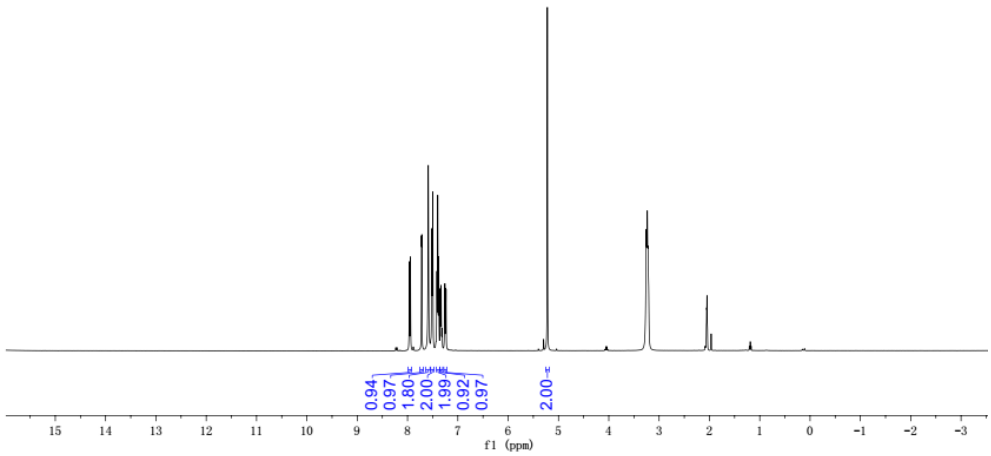
3 Z. Jamal and Y.-C. Teo, *RSC Adv.*, 2015, **5**, 26949–26953.

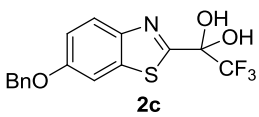
^{1}H, ^{13}C, and ^{19}F NMR Spectra



2c

^{1}H NMR (400 MHz, CD_3COCD_3)





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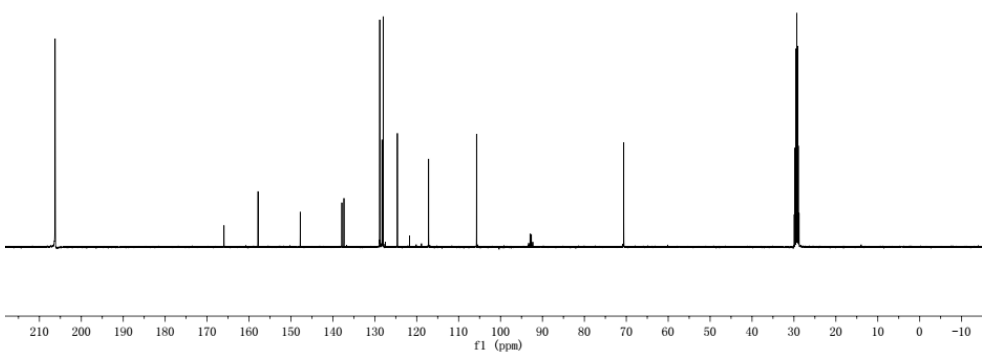
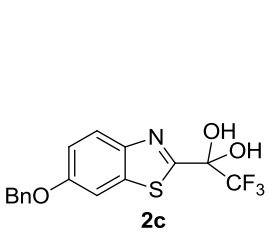
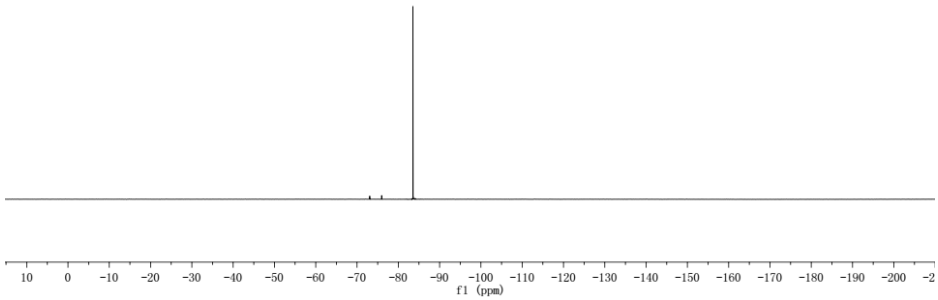
^{13}C NMR (100 MHz, CD_3COCD_3)

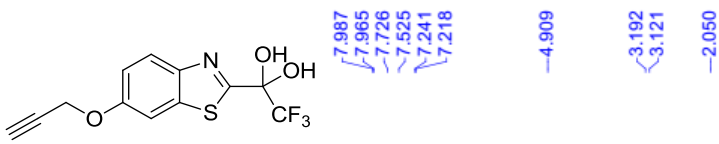




2c

^{19}F NMR (376.5 MHz, CD_3COCD_3)





2e

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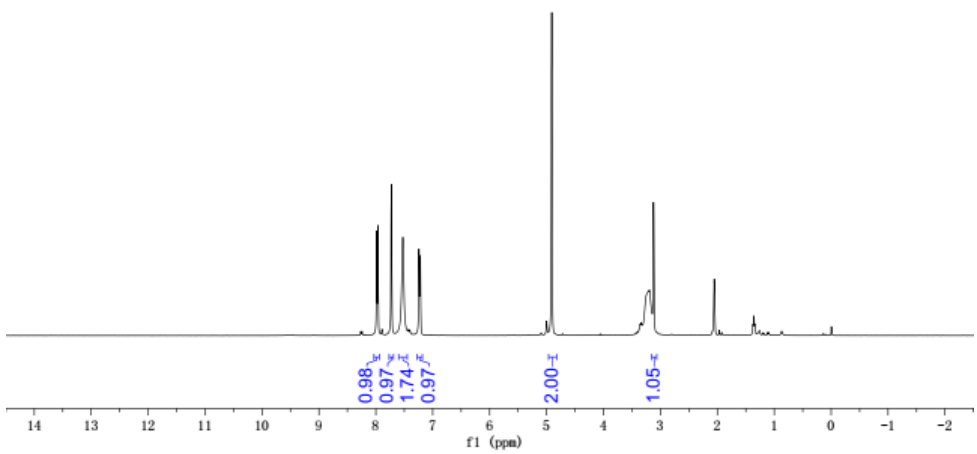

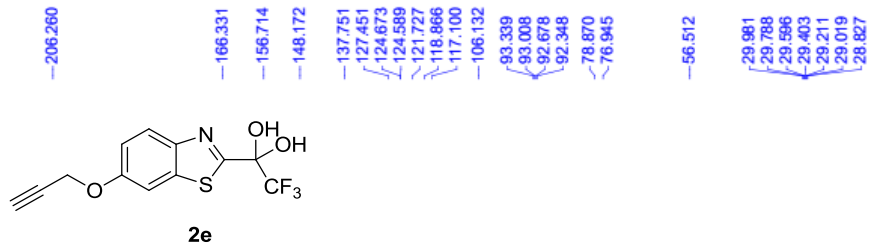

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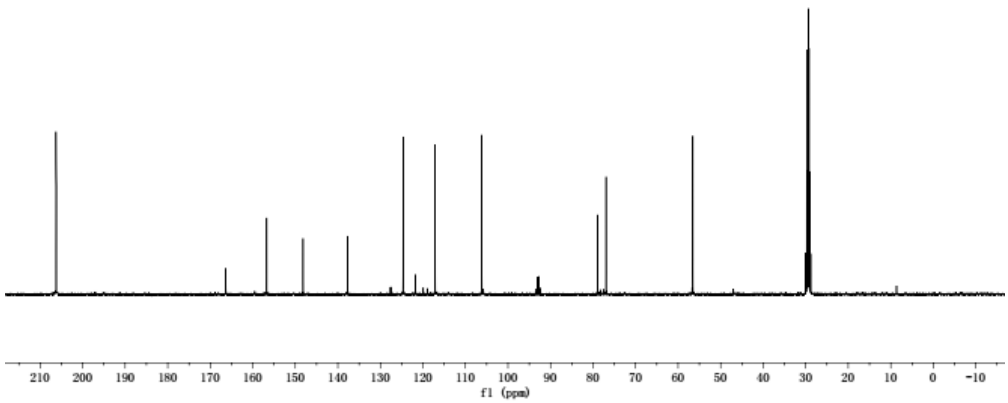
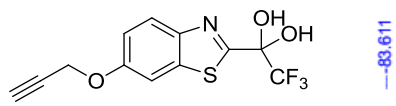
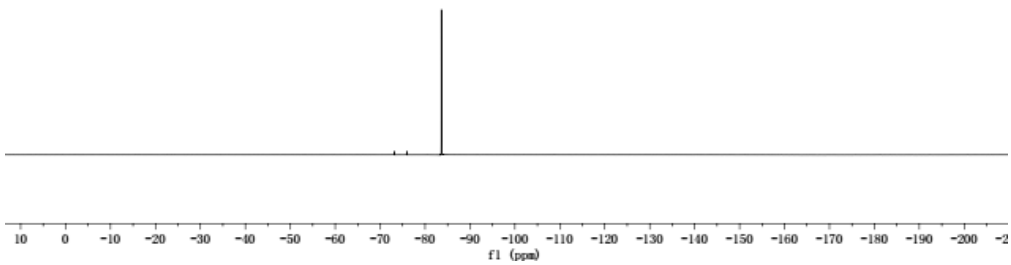
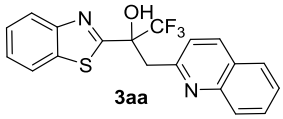




2e

^{19}F NMR (376.5 MHz, CD_3COCD_3)





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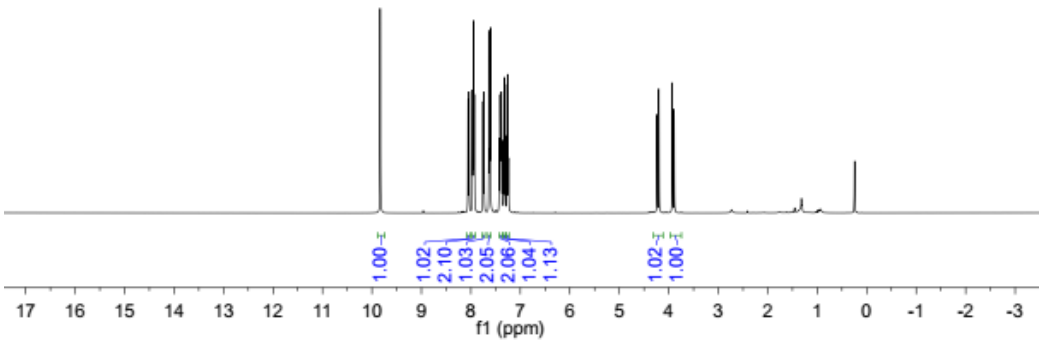

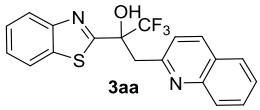

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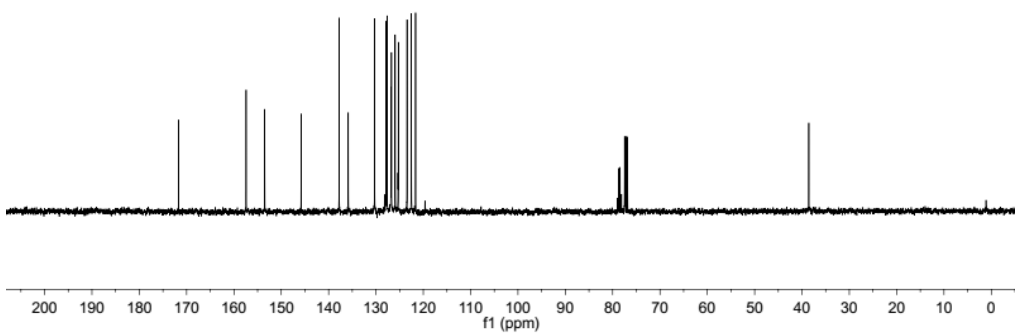
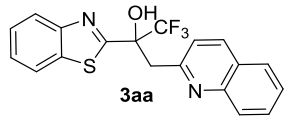
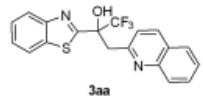
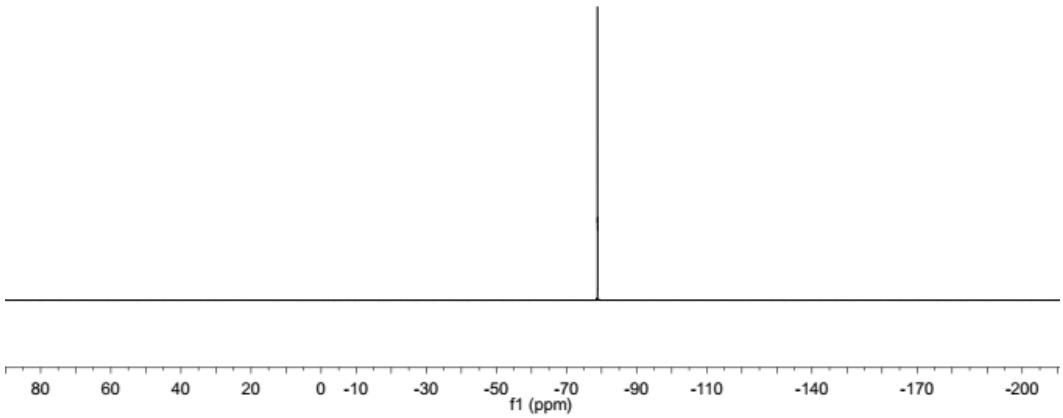
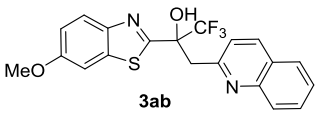






^{19}F NMR (376.5 MHz, $CDCl_3$)





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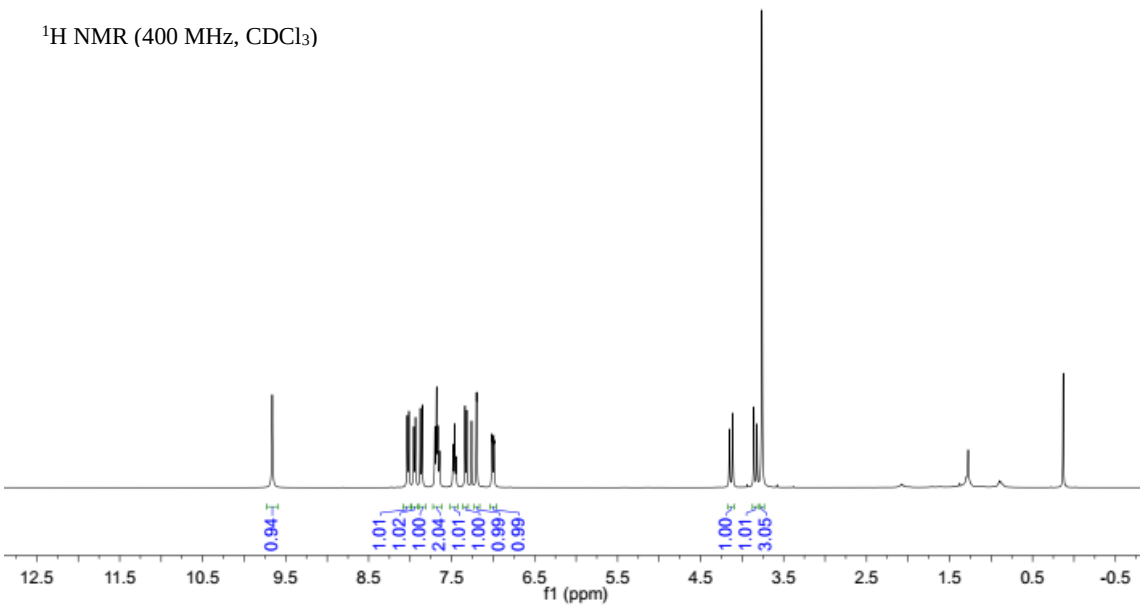
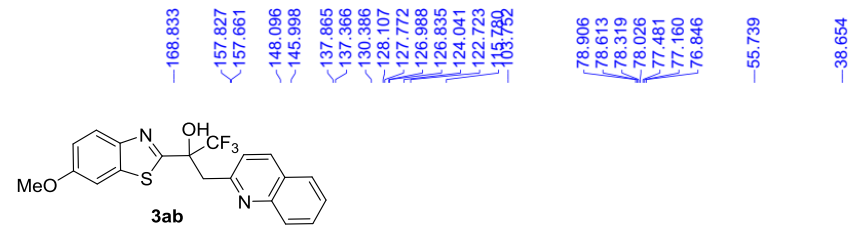
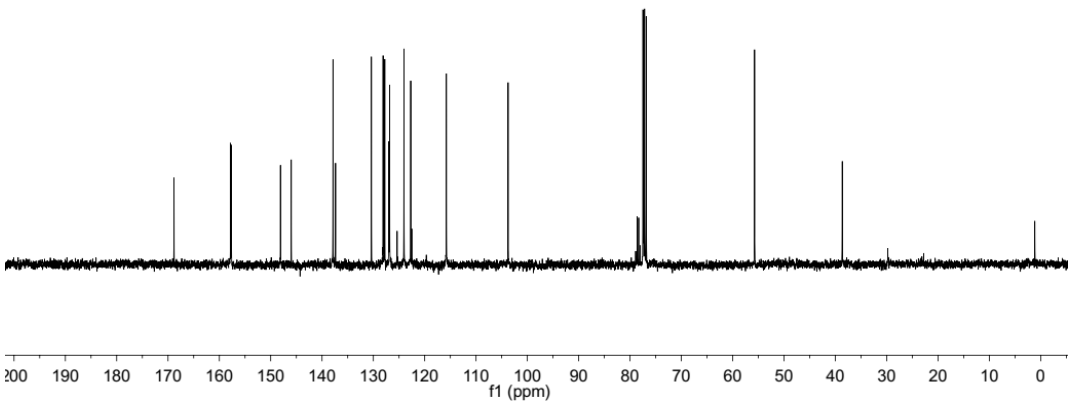
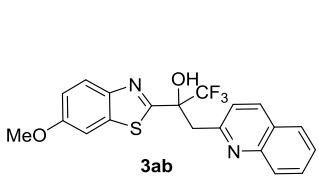


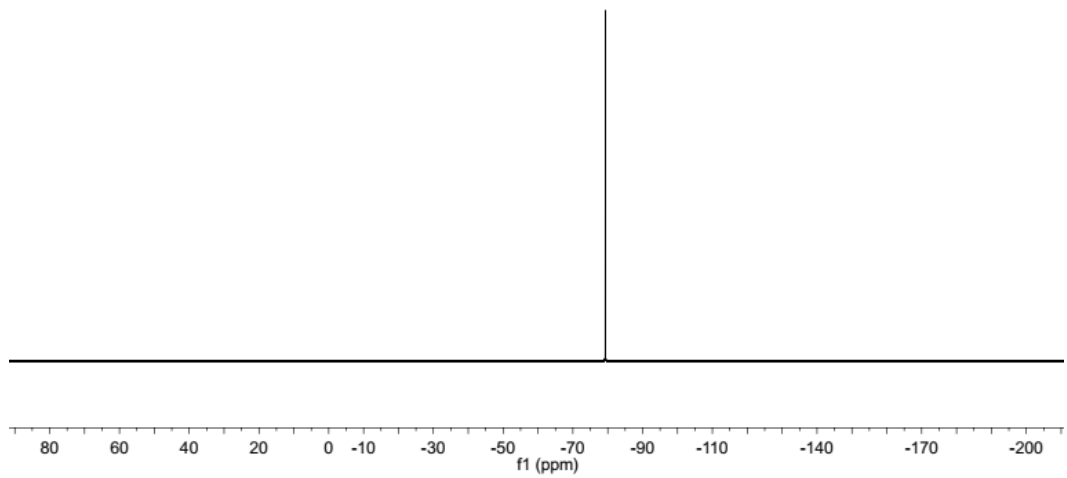


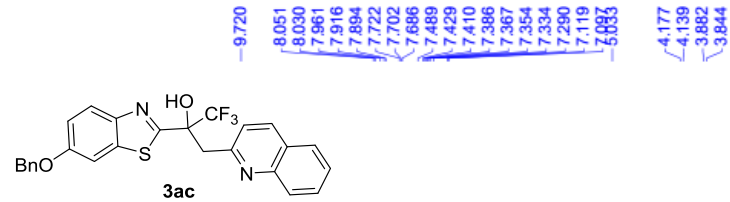
^{13}C NMR (100 MHz, $CDCl_3$)





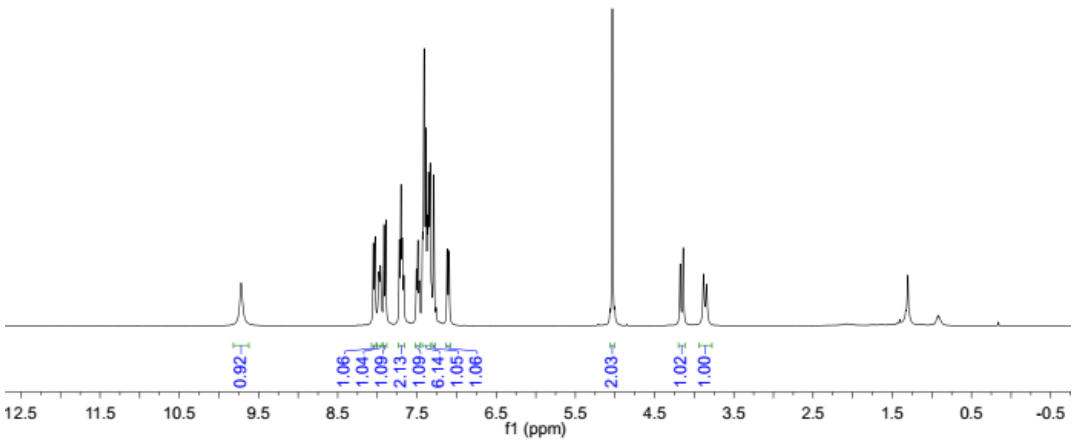
^{19}F NMR (376.5 MHz, $CDCl_3$)

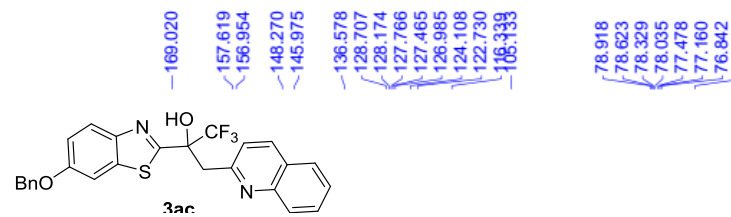




3ac

^{1}H NMR (400 MHz, $CDCl_3$)





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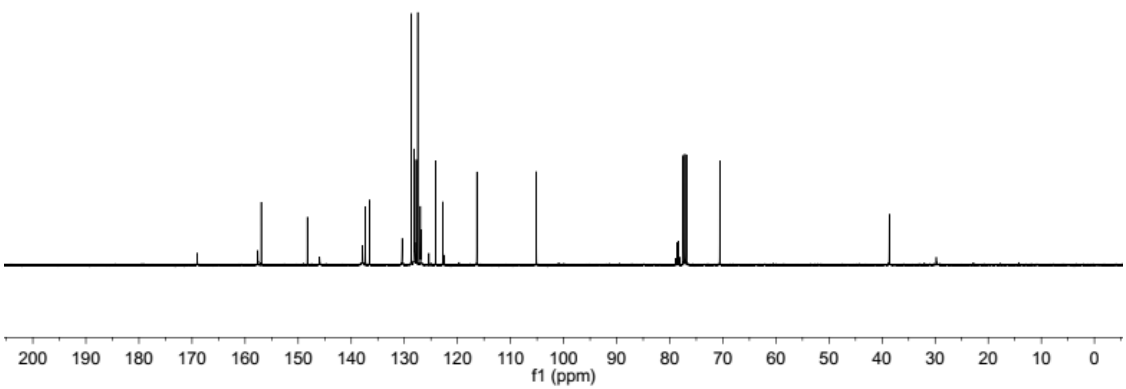

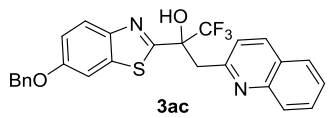

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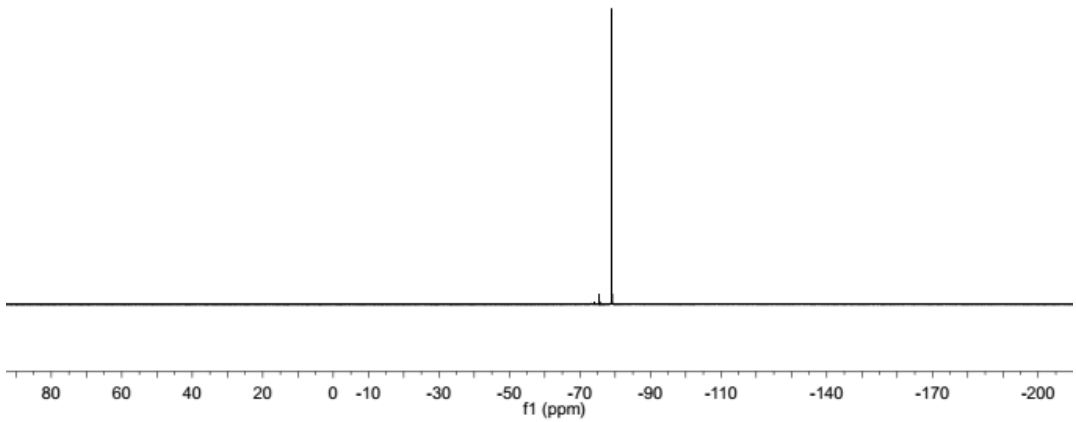
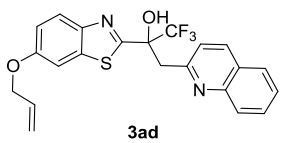
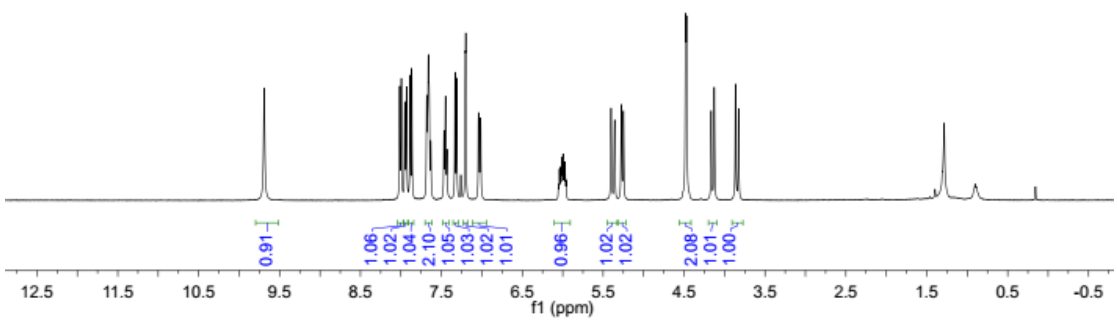
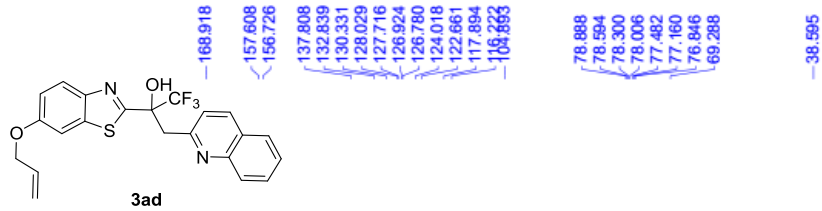




3ad

^{1}H NMR (400 MHz, $CDCl_3$)





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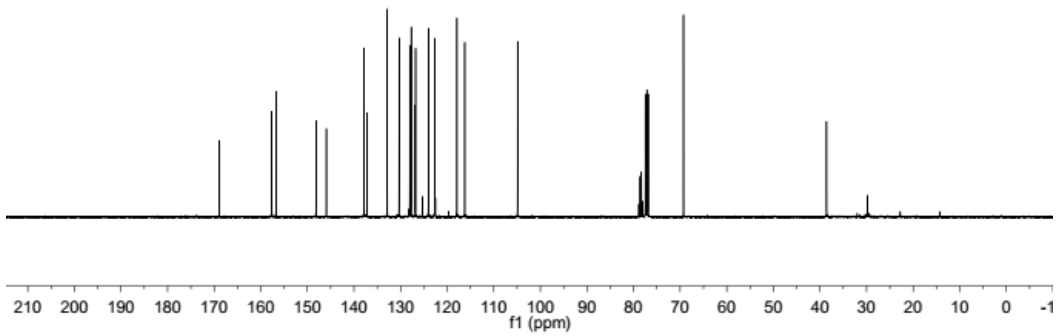

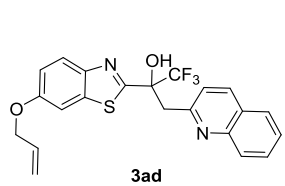

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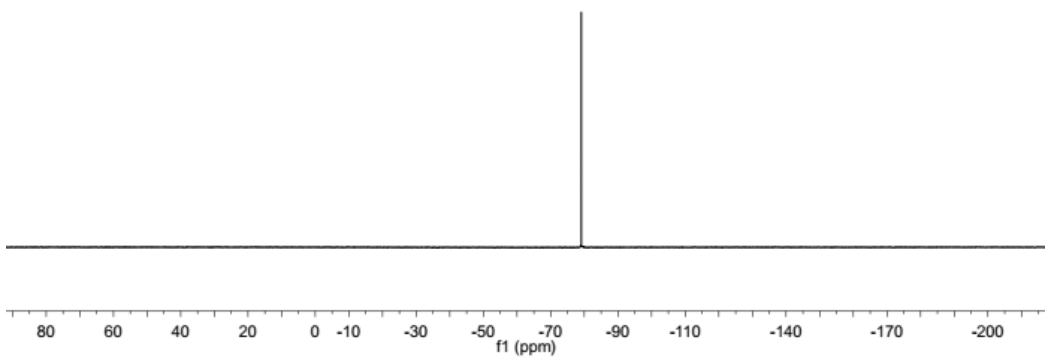

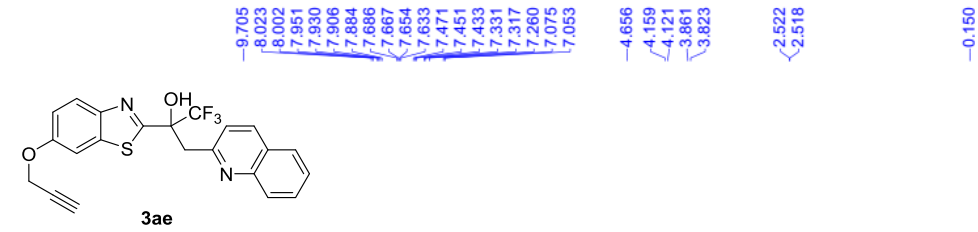

3ae

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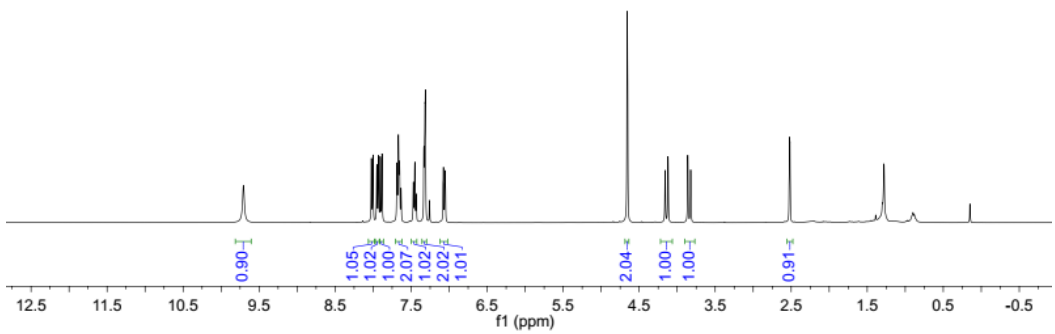

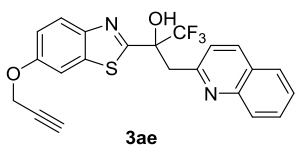

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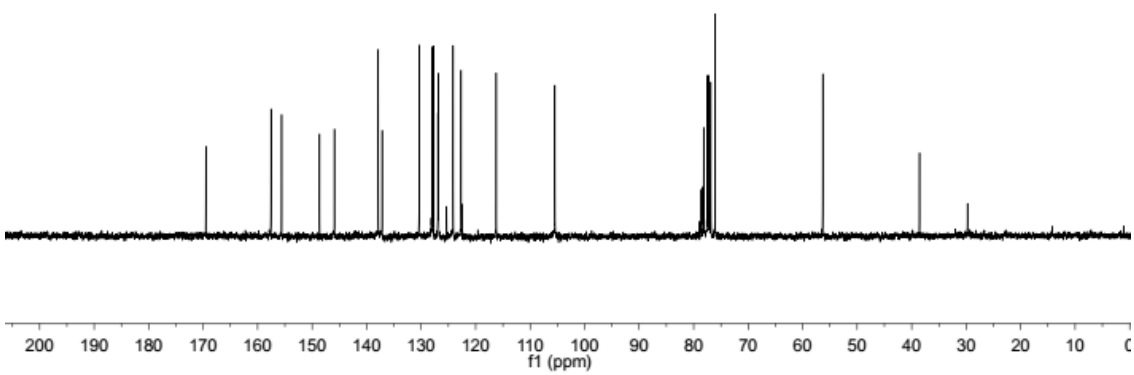

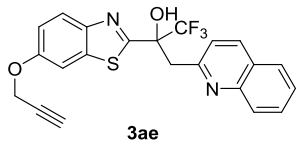

3ae

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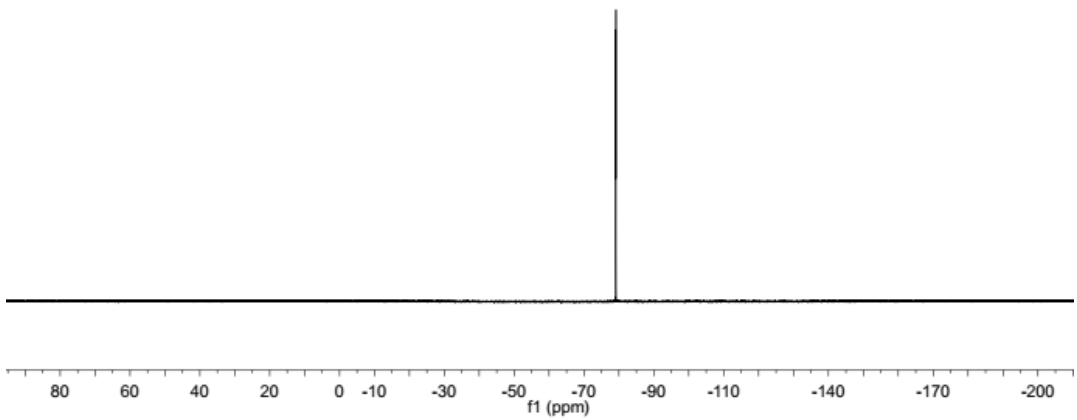

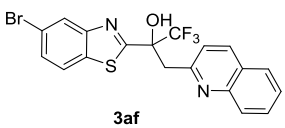

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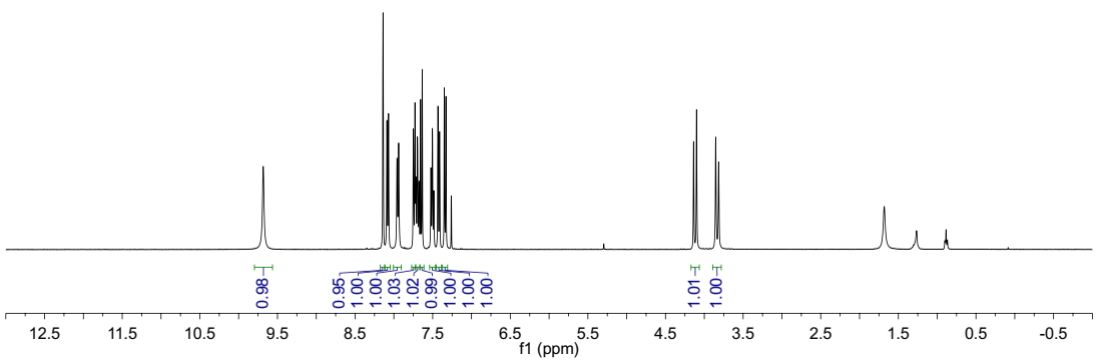

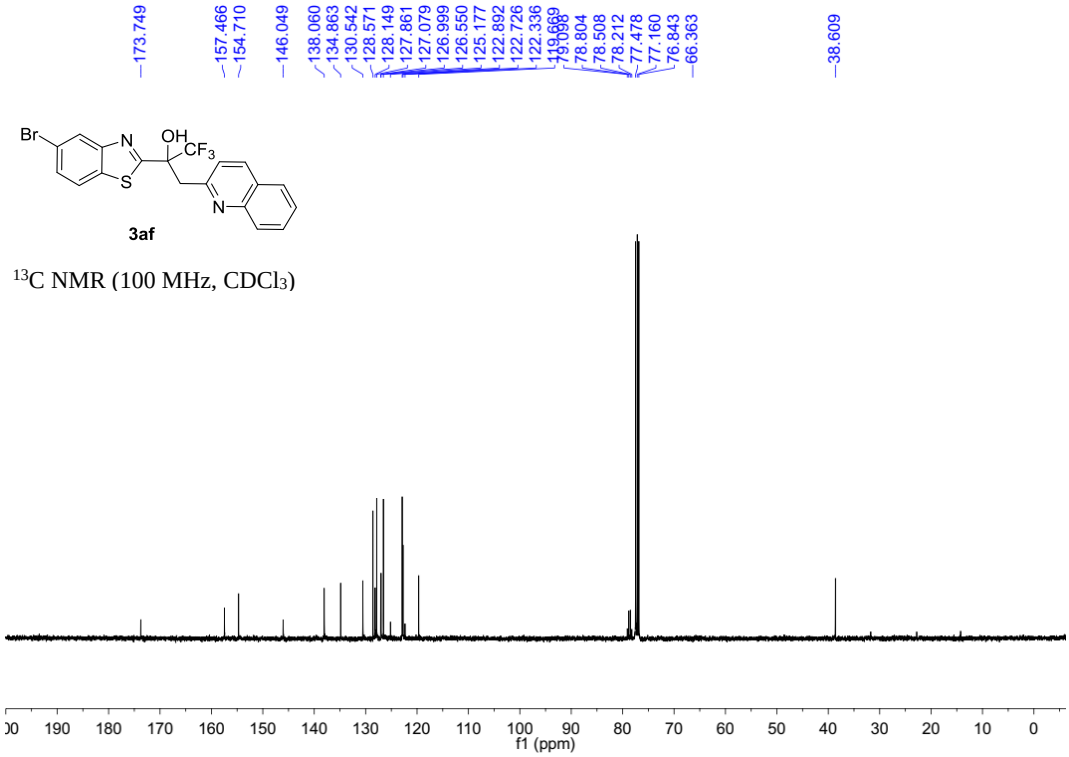

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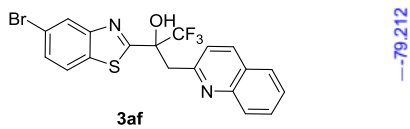

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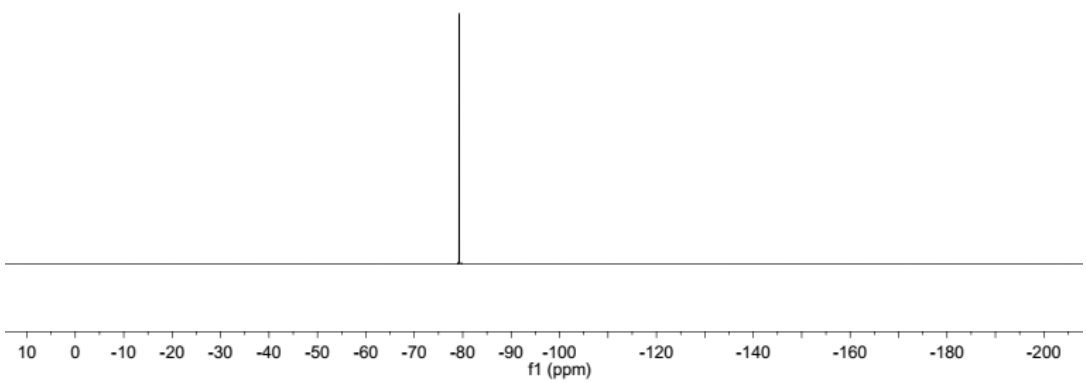

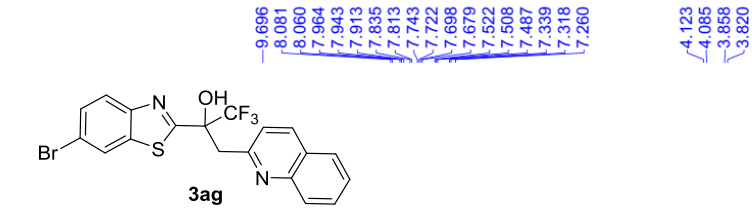

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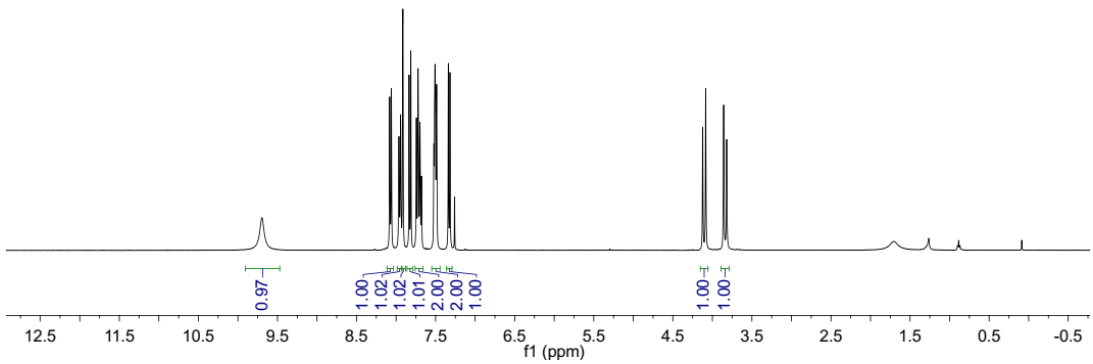

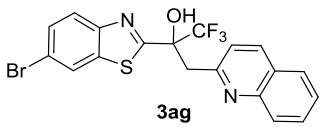

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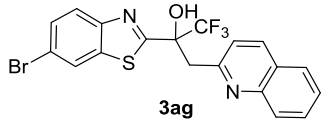
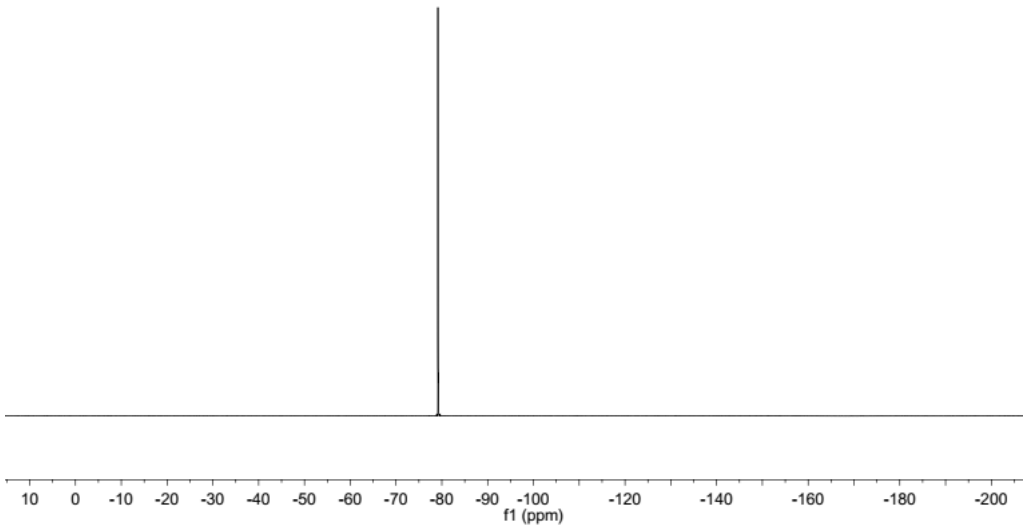
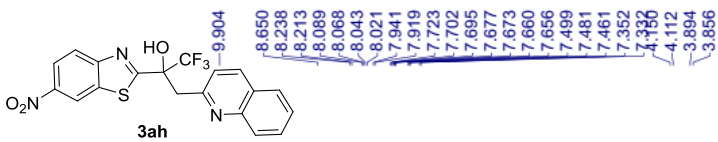


3ag

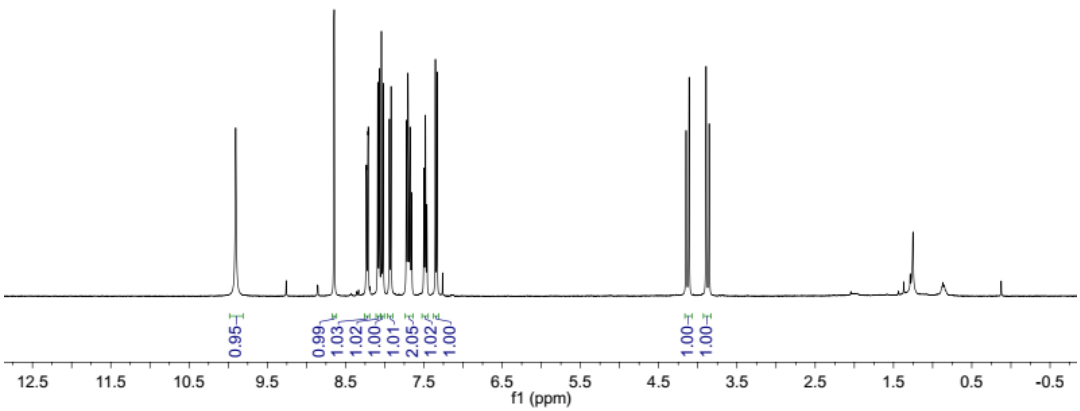
^{19}F NMR (376.5 MHz, $CDCl_3$)

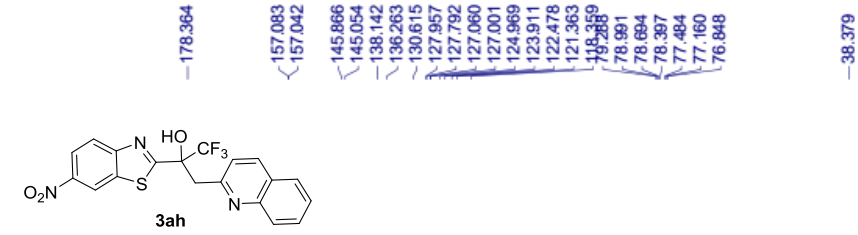




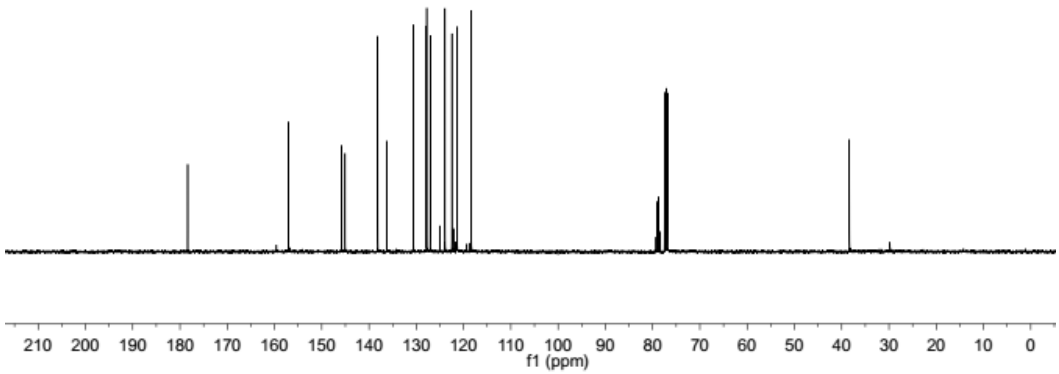
3ah

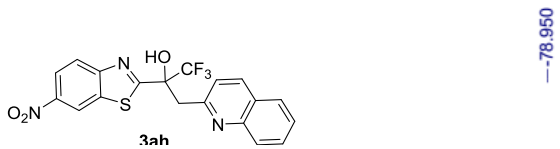
^{1}H NMR (400 MHz, $CDCl_3$)



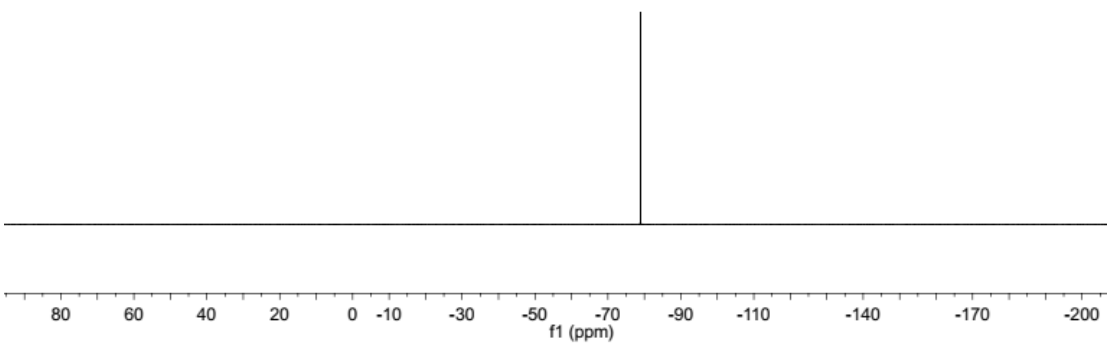


^{13}C NMR (100 MHz, $CDCl_3$)

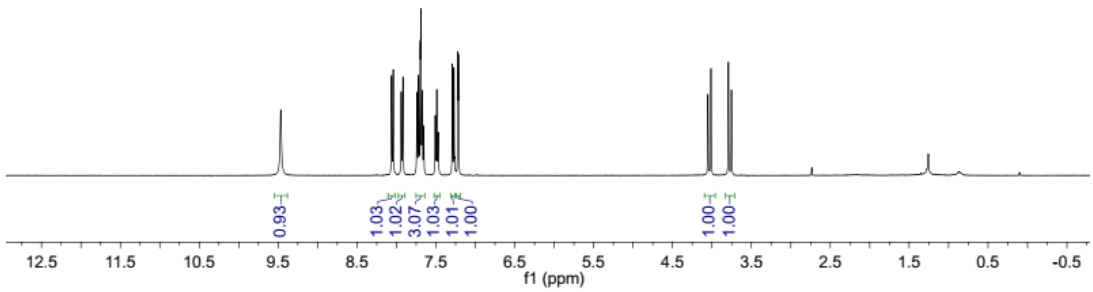


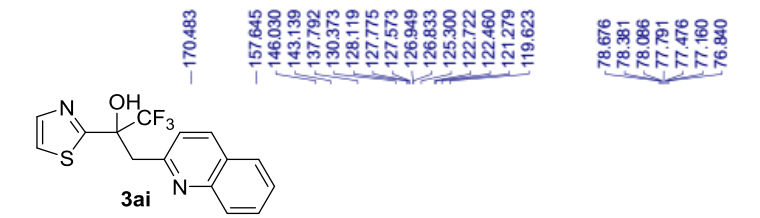


^{19}F NMR (376.5 MHz, $CDCl_3$)

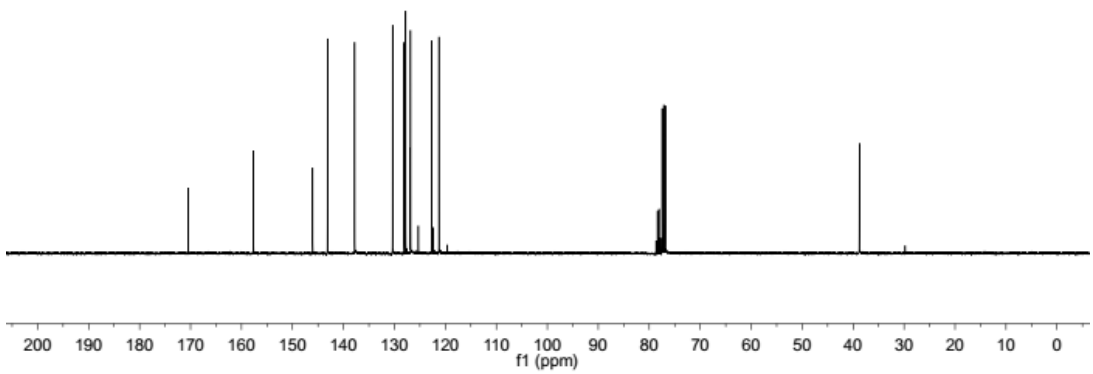


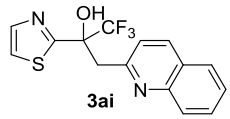
^{1}H NMR (400 MHz, $CDCl_3$)





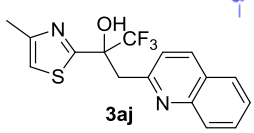
^{13}C NMR (100 MHz, $CDCl_3$)





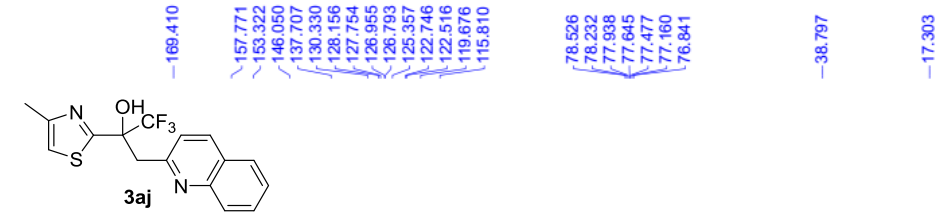
3ai

^{19}F NMR (376.5 MHz, $CDCl_3$)

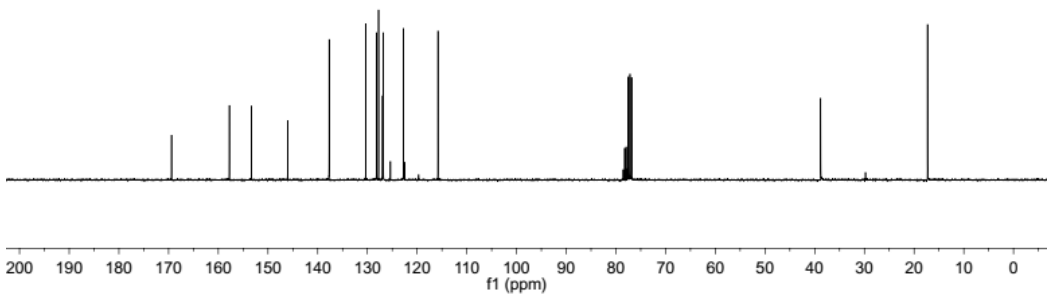


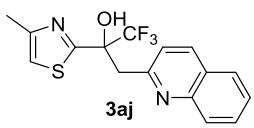
3aj

^{1}H NMR (400 MHz, $CDCl_3$)

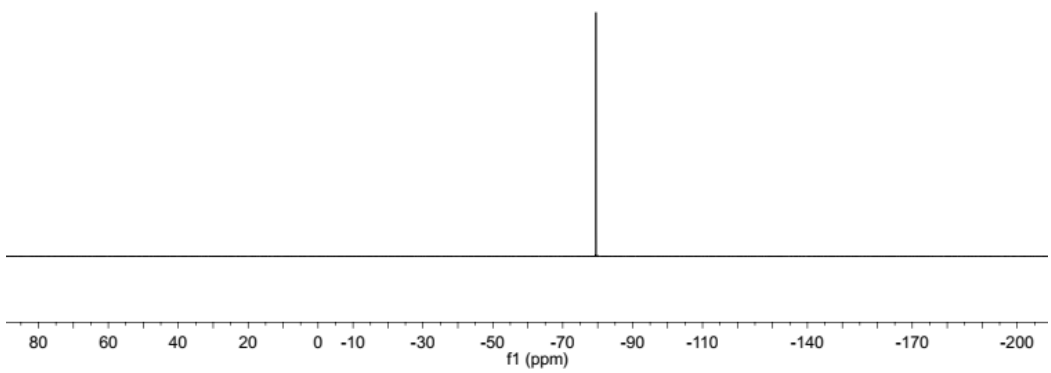


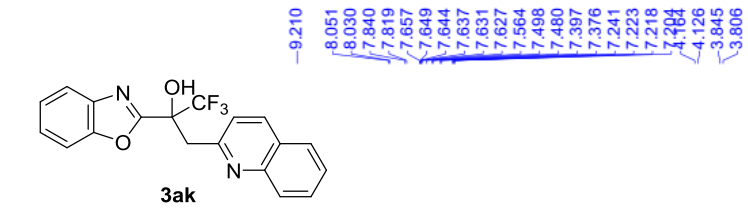
^{13}C NMR (100 MHz, $CDCl_3$)



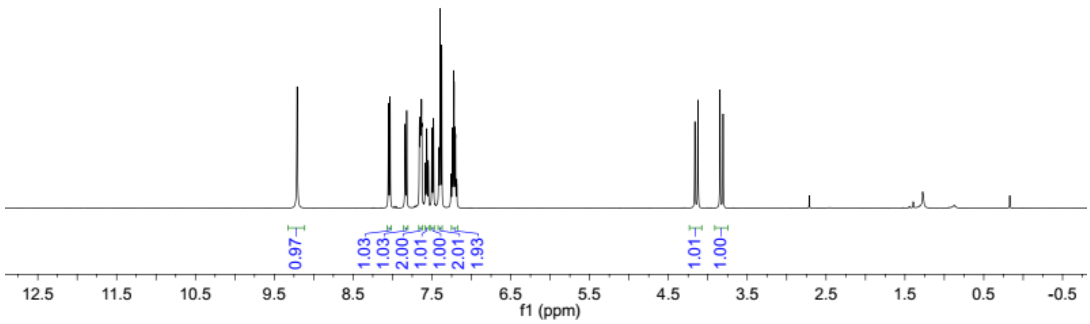


^{19}F NMR (376.5 MHz, $CDCl_3$)

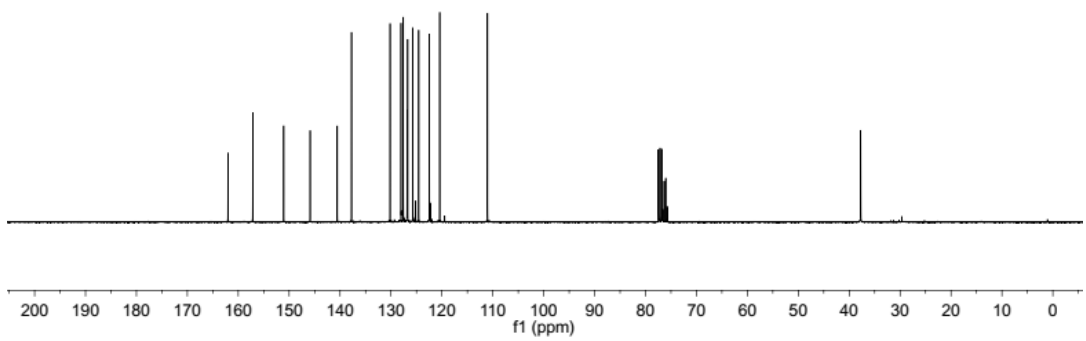


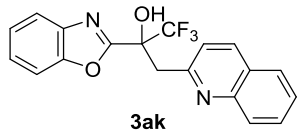


^{1}H NMR (400 MHz, $CDCl_3$)



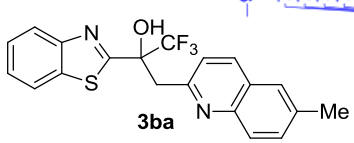
^{13}C NMR (100 MHz, $CDCl_3$)





3ak

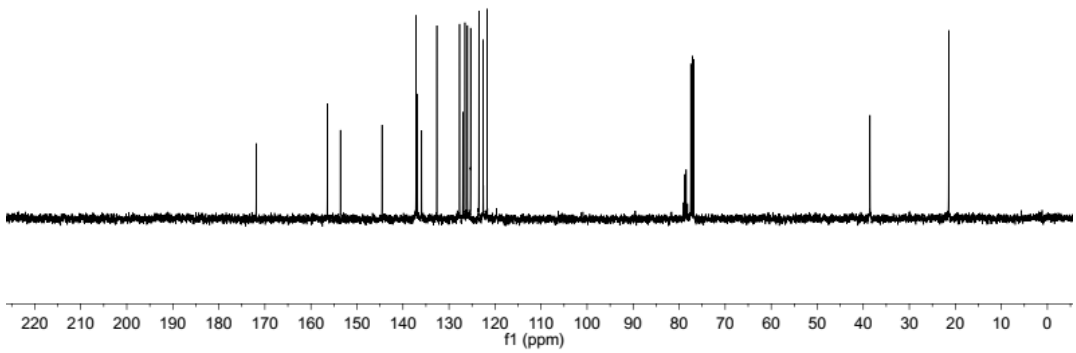
^{19}F NMR (376.5 MHz, $CDCl_3$)

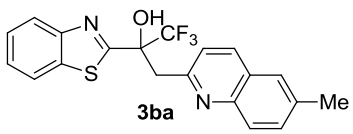


3ba

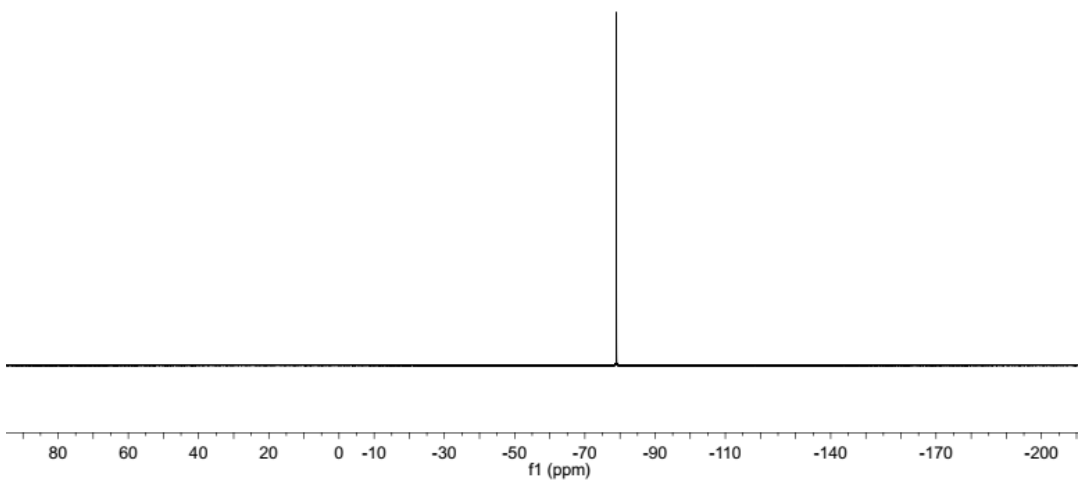
^{1}H NMR (400 MHz, $CDCl_3$)

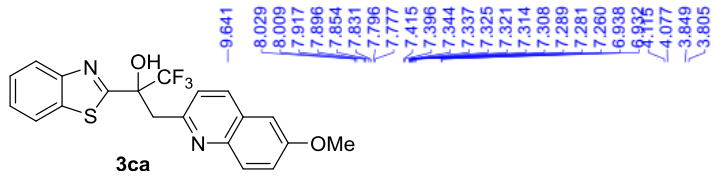
^{13}C NMR (100 MHz, $CDCl_3$)



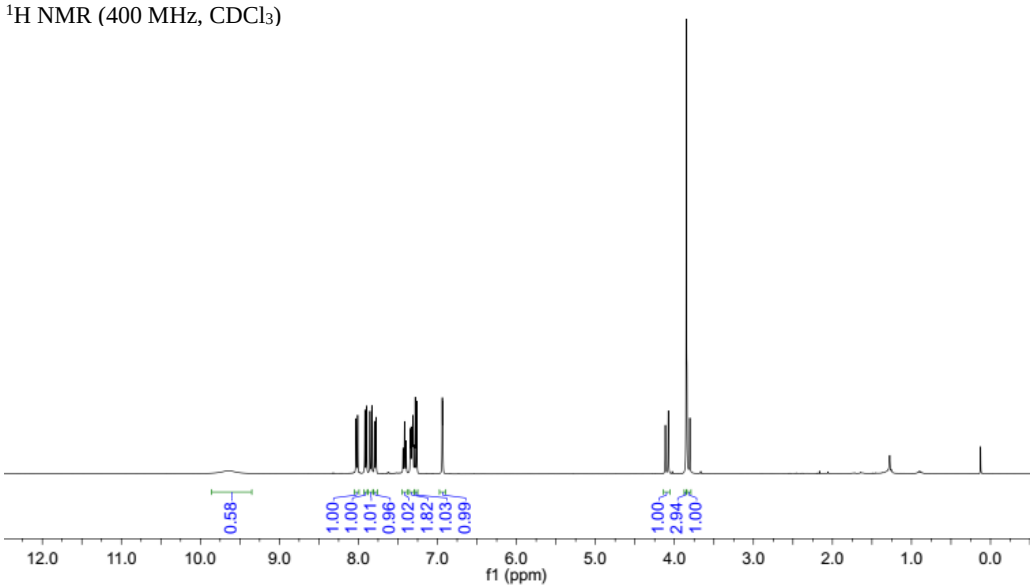


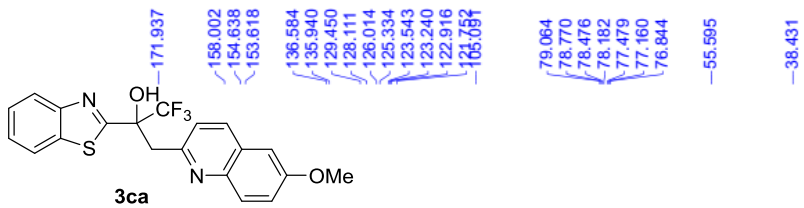
^{19}F NMR (376.5 MHz, $CDCl_3$)



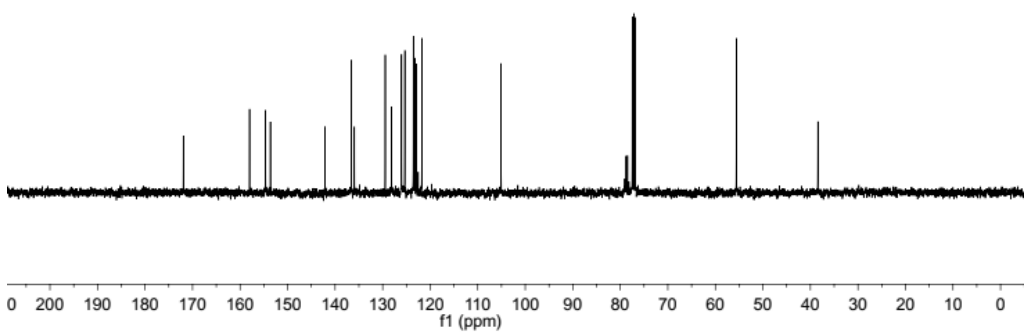


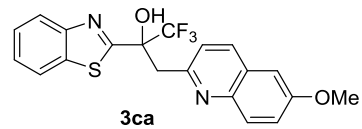
^{1}H NMR (400 MHz, $CDCl_3$)





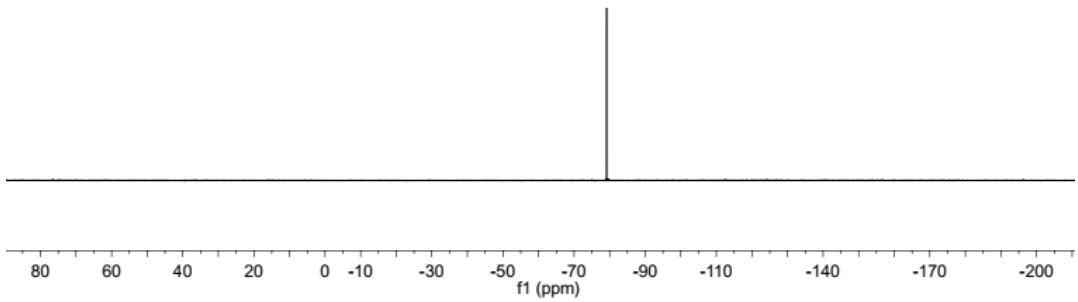
^{13}C NMR (100 MHz, $CDCl_3$)

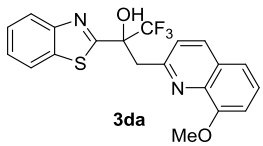




3ca

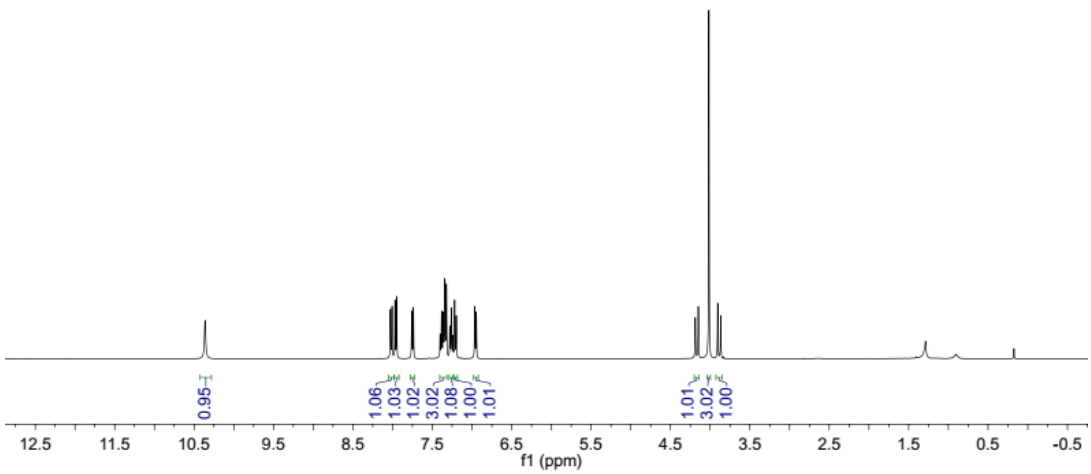
^{19}F NMR (376.5 MHz, $CDCl_3$)

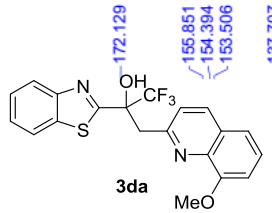




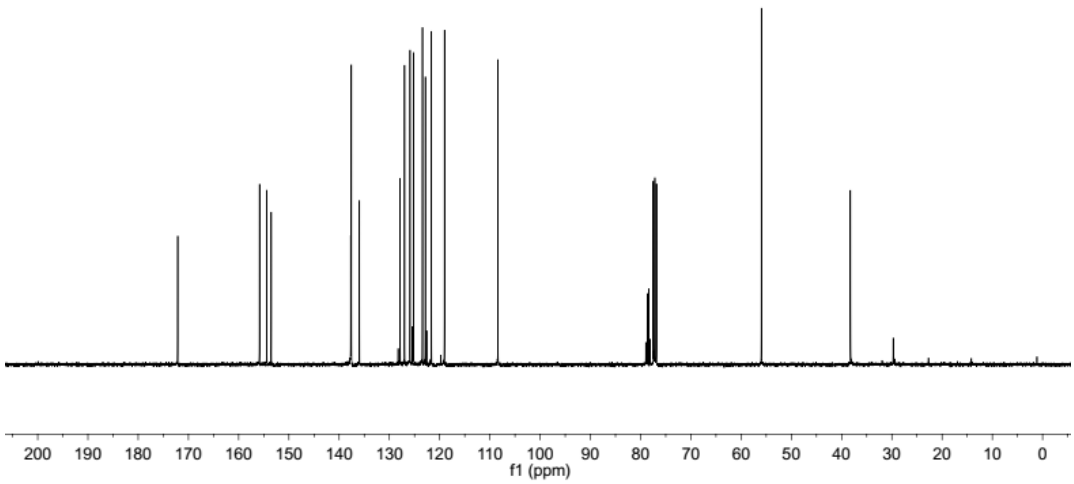
3da

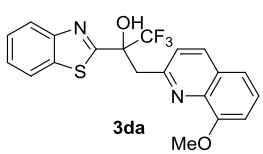
^{1}H NMR (400 MHz, $CDCl_3$)



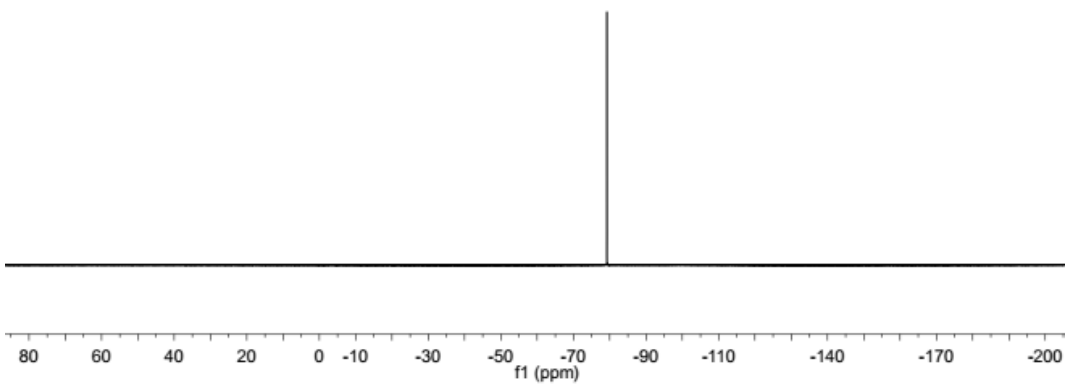


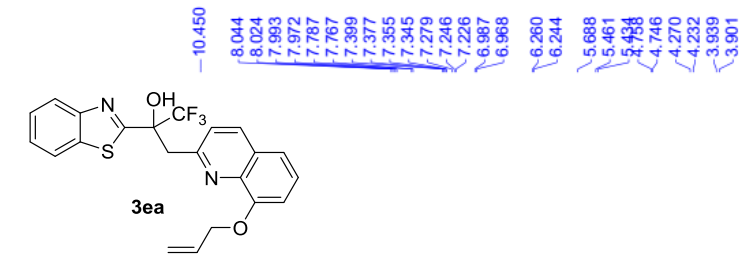
^{13}C NMR (100 MHz, $CDCl_3$)



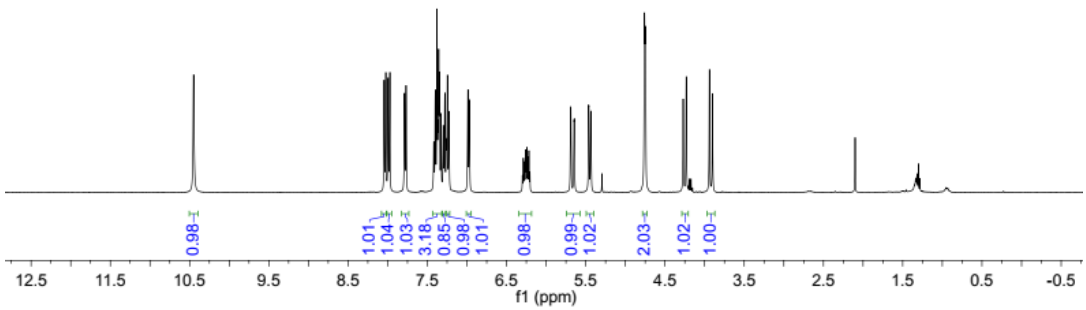


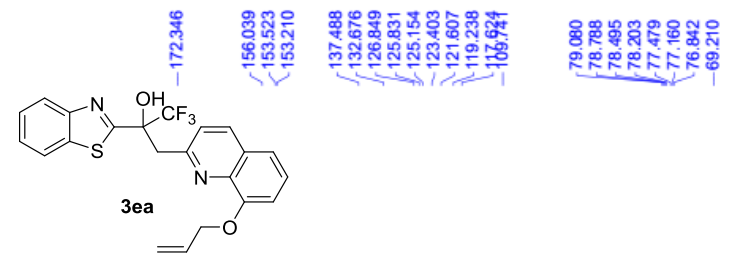
^{19}F NMR (376.5 MHz, $CDCl_3$)



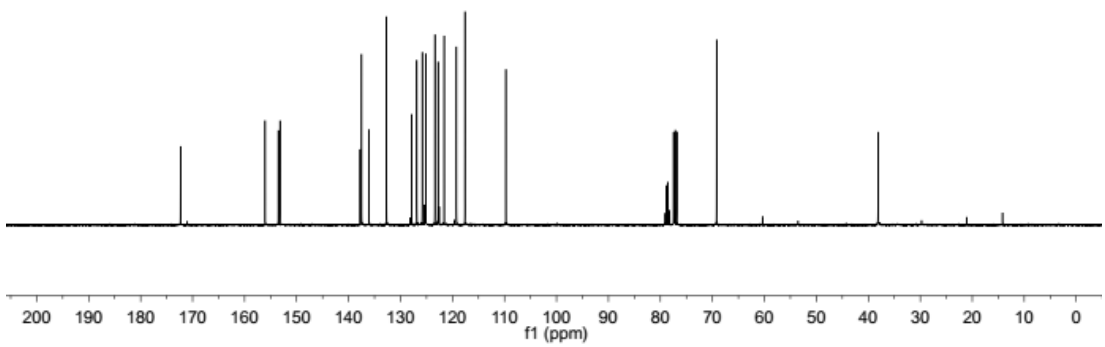


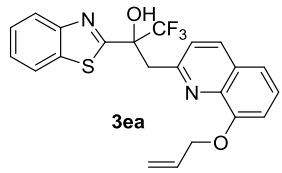
^{1}H NMR (400 MHz, $CDCl_3$)



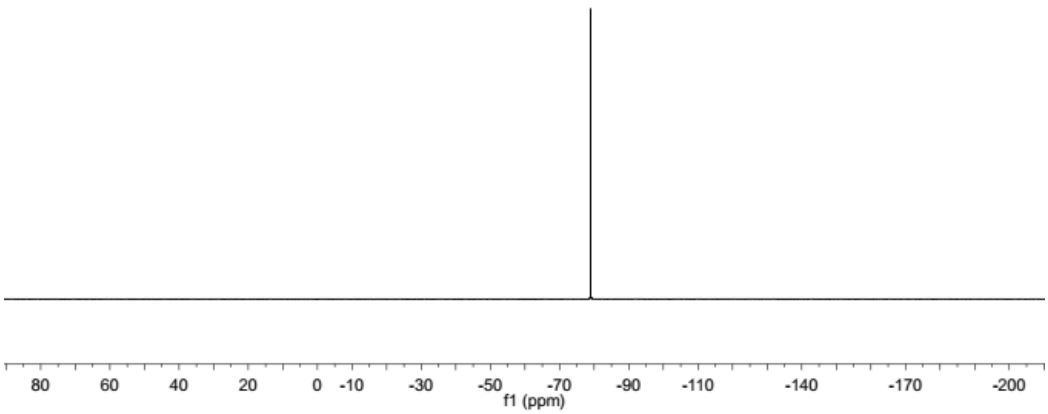


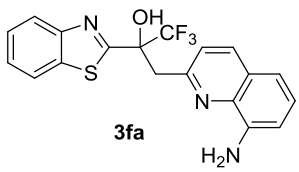
^{13}C NMR (100 MHz, $CDCl_3$)



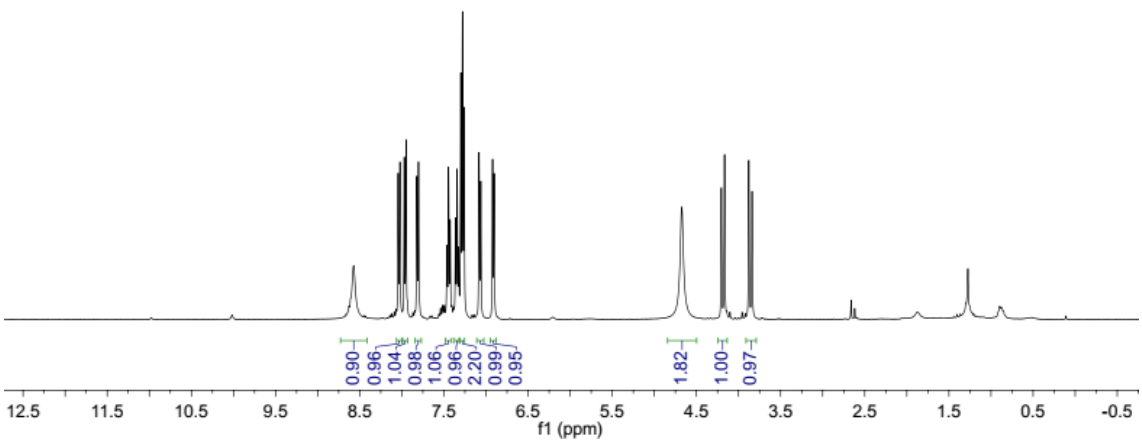


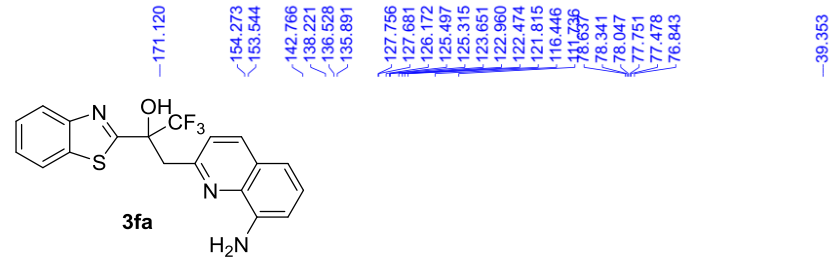
^{19}F NMR (376.5 MHz, $CDCl_3$)



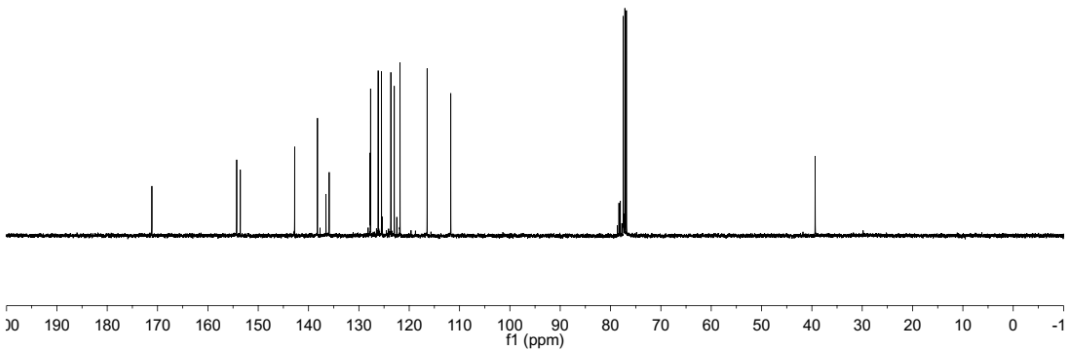


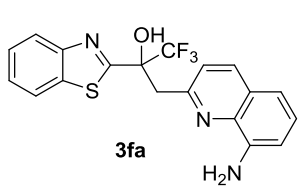
^{1}H NMR (400 MHz, $CDCl_3$)



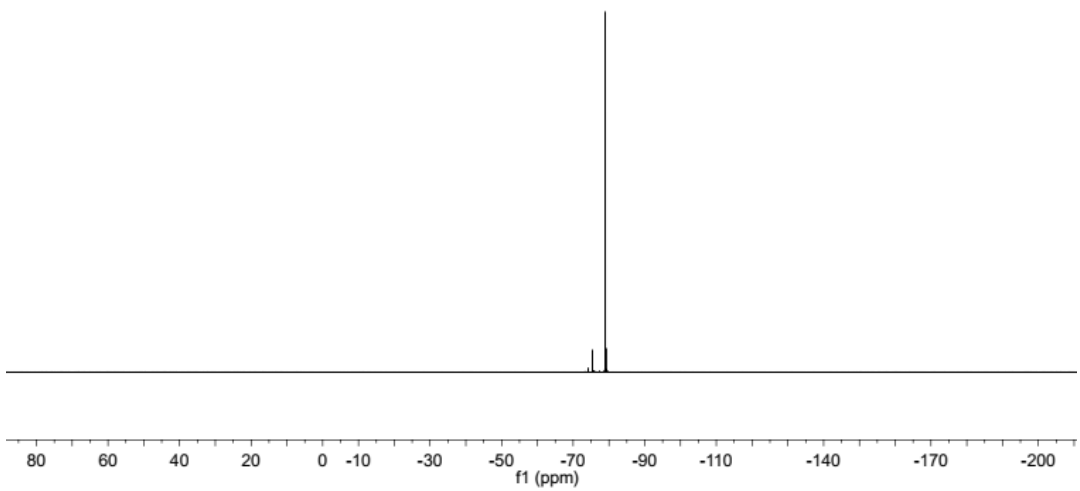


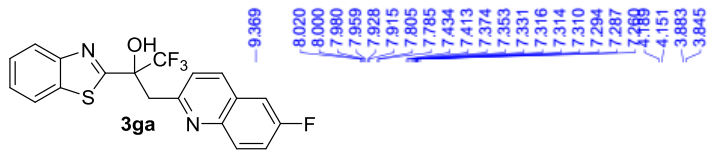
^{13}C NMR (100 MHz, $CDCl_3$)



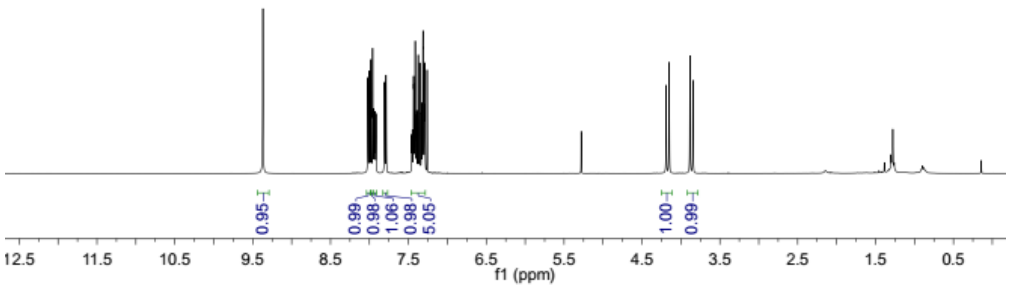


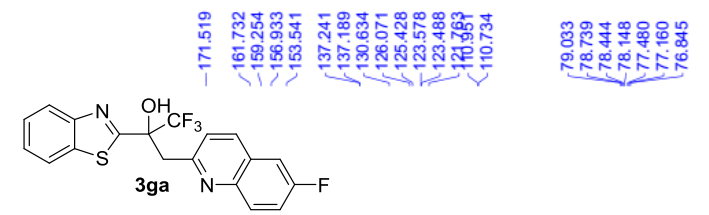
^{19}F NMR (376.5 MHz, $CDCl_3$)



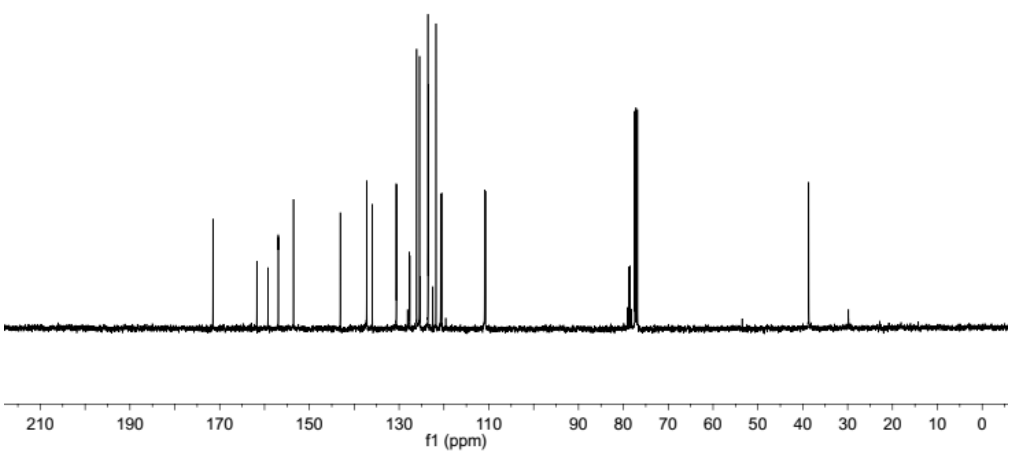


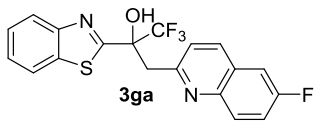
^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (100 MHz, $CDCl_3$)



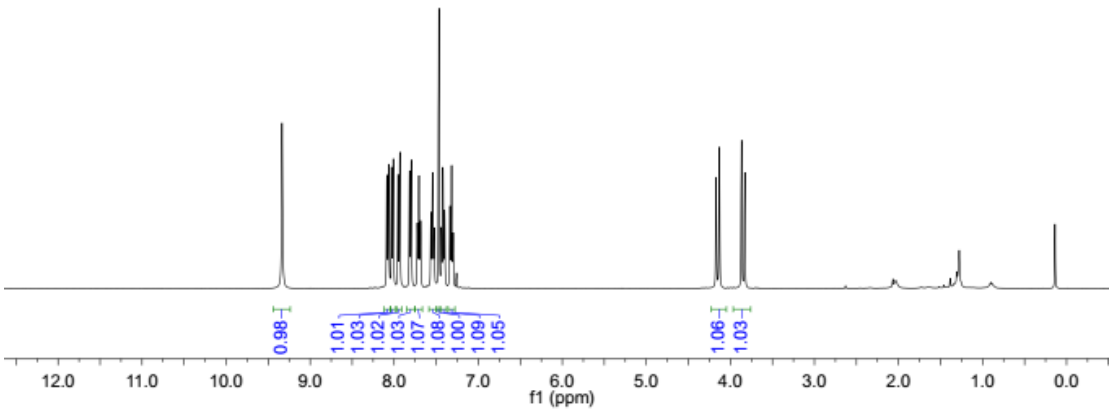


3ga

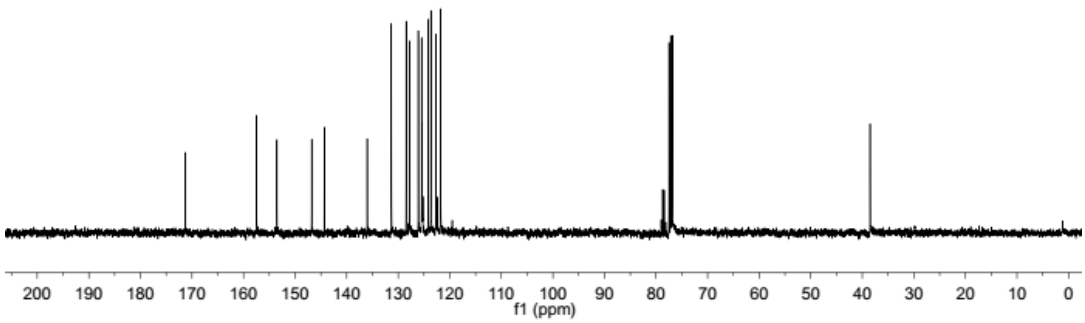
^{19}F NMR (376.5 MHz, $CDCl_3$)

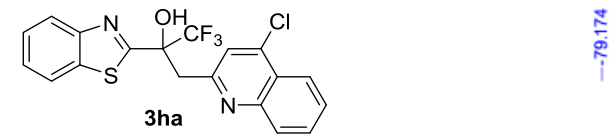
3ha

^{1}H NMR (400 MHz, $CDCl_3$)

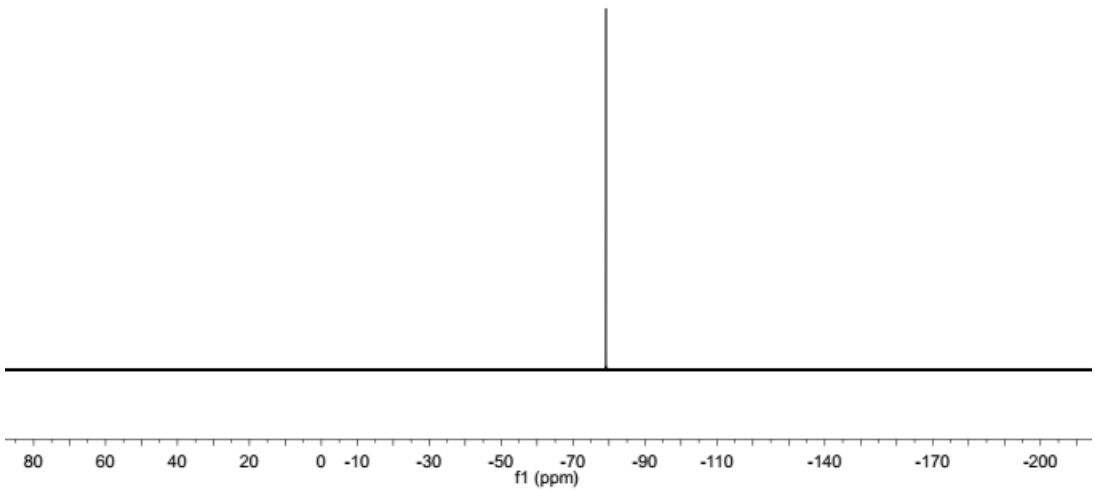


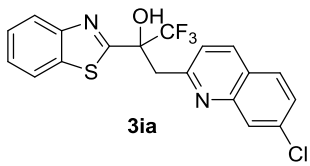
^{13}C NMR (100 MHz, $CDCl_3$)





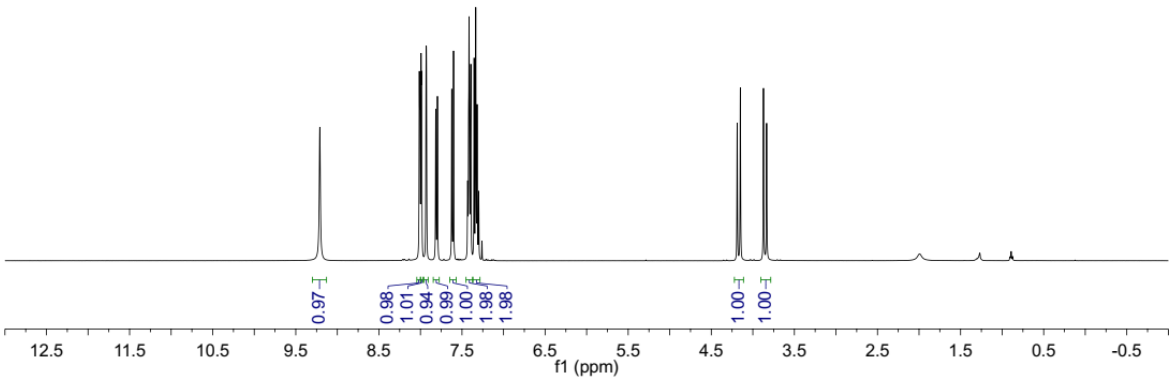
^{19}F NMR (376.5 MHz, $CDCl_3$)

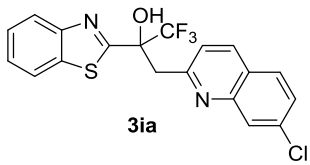




3ia

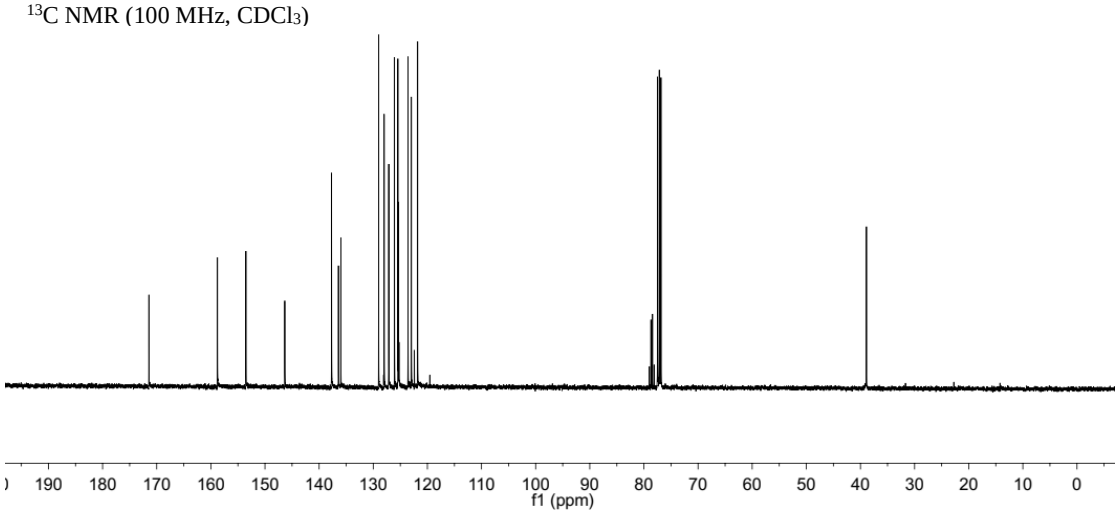
^{1}H NMR (400 MHz, $CDCl_3$)

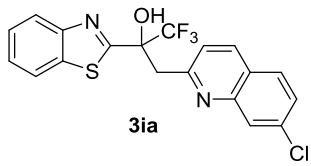




3ia

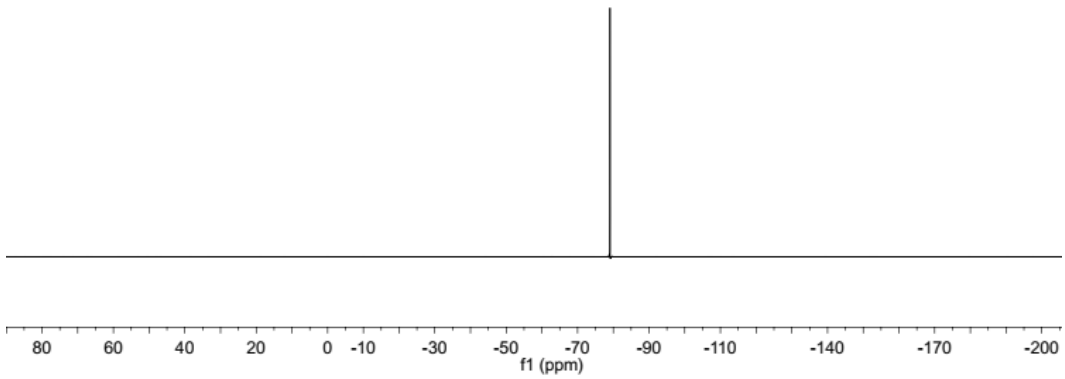
^{13}C NMR (100 MHz, $CDCl_3$)

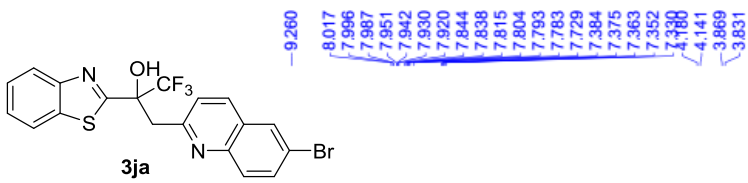




3ia

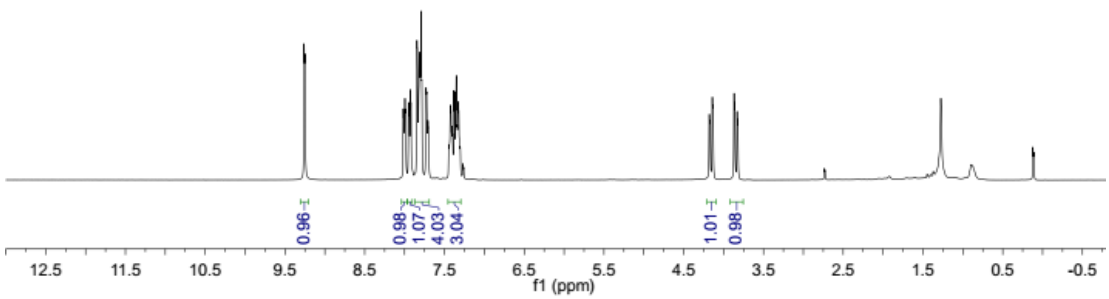
^{19}F NMR (376.5 MHz, $CDCl_3$)

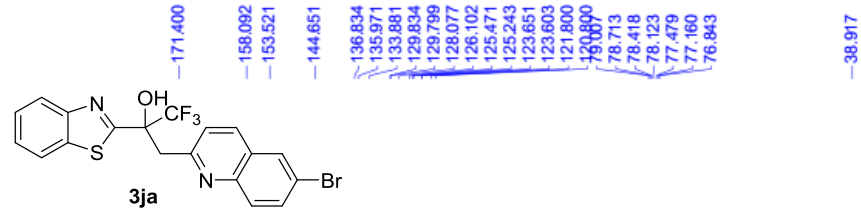




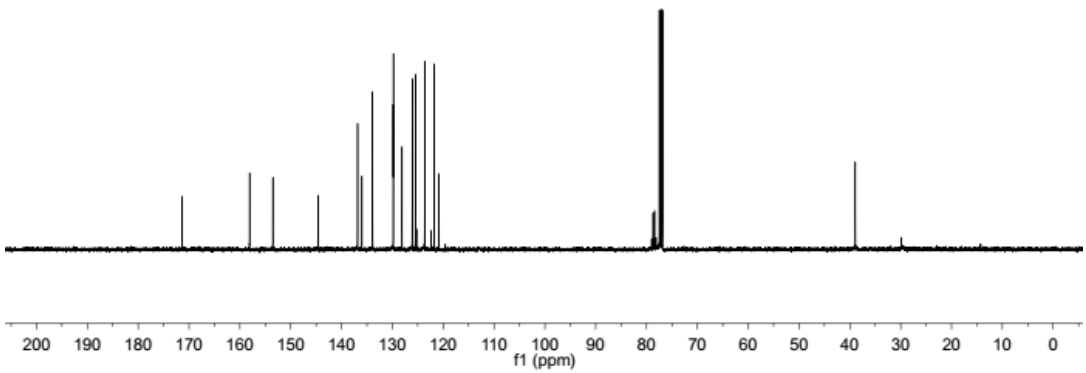
3ja

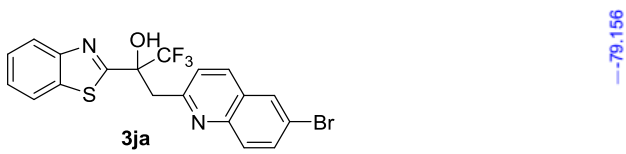
^{1}H NMR (400 MHz, $CDCl_3$)



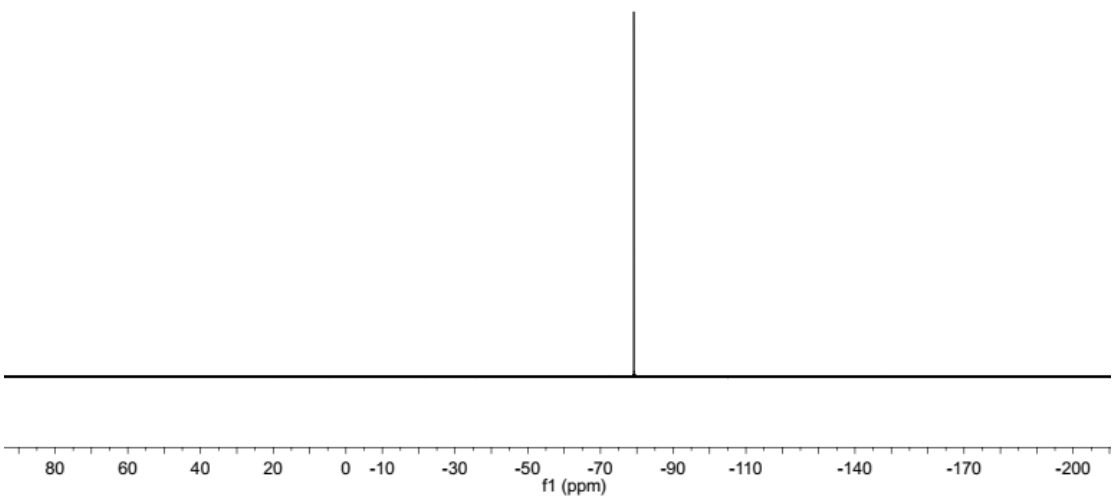


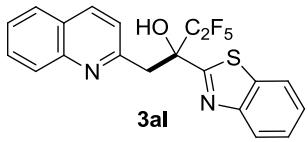
^{13}C NMR (100 MHz, $CDCl_3$)





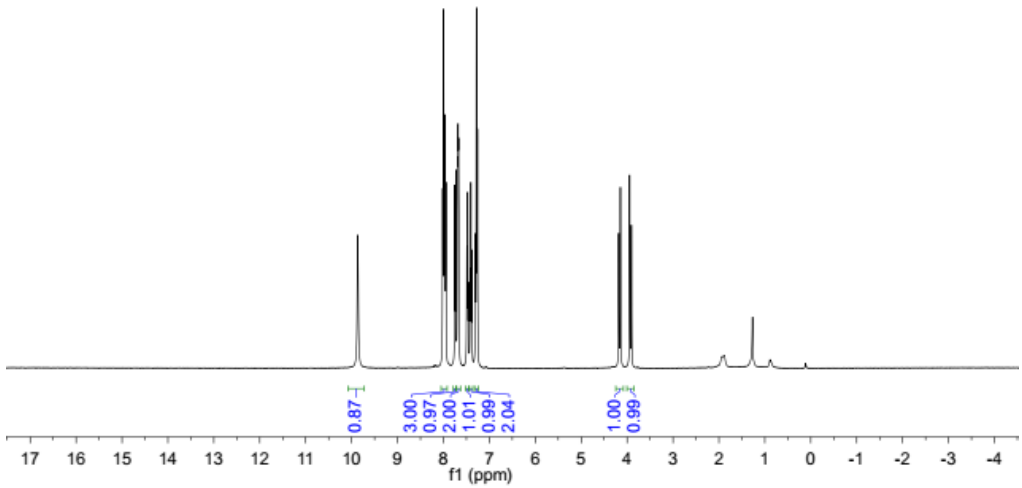
^{19}F NMR (376.5 MHz, $CDCl_3$)

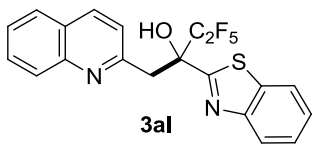




3al

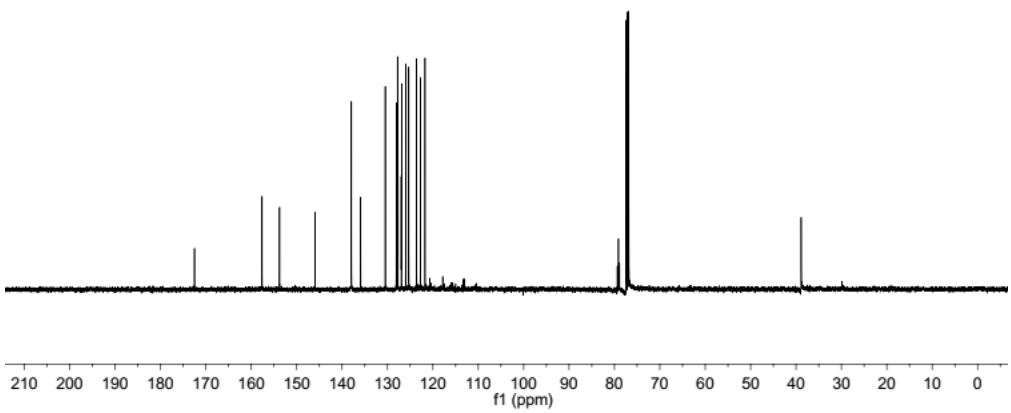
^{1}H NMR (400 MHz, $CDCl_3$)

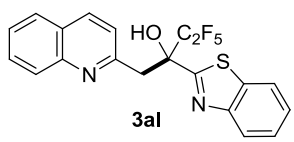


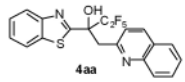


3al

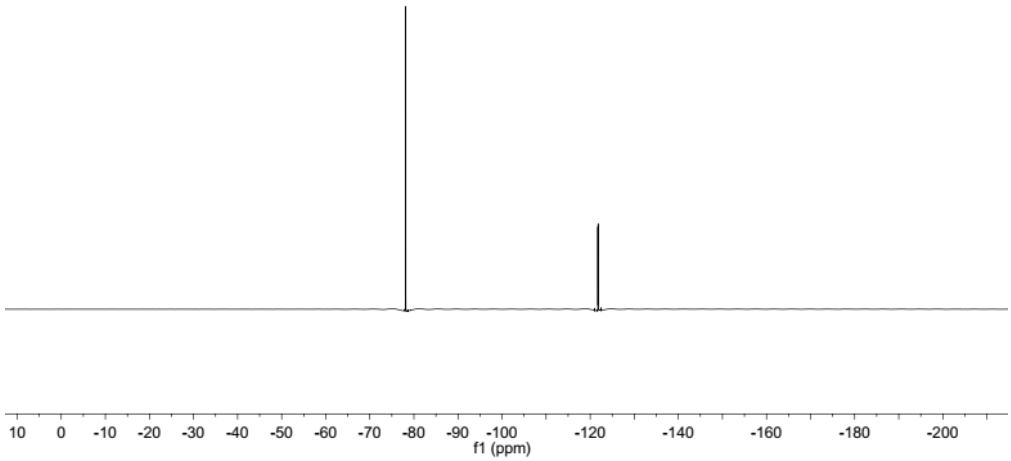
^{13}C NMR (100 MHz, $CDCl_3$)

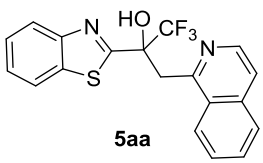


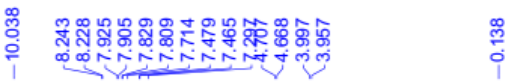




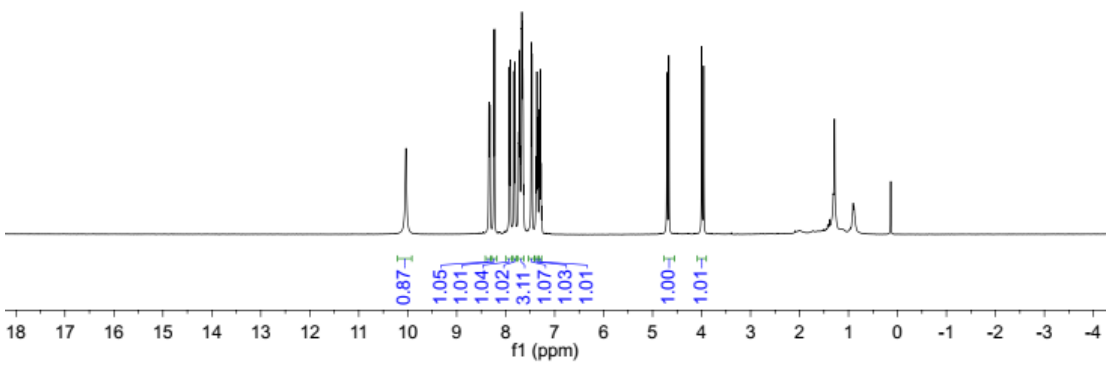
^{19}F NMR (376.5 MHz, $CDCl_3$)

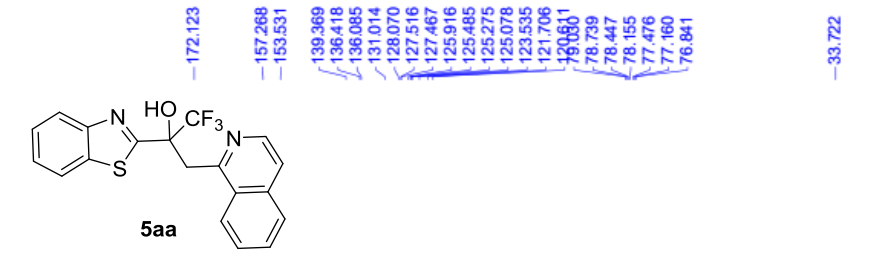




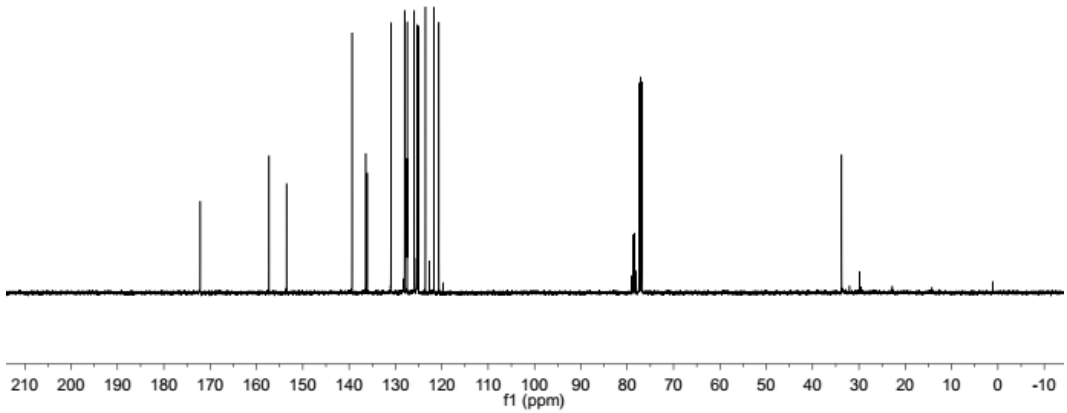


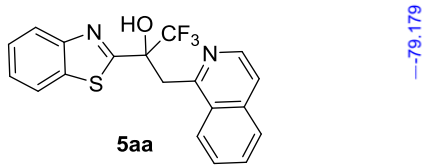
^{1}H NMR (400 MHz, $CDCl_3$)



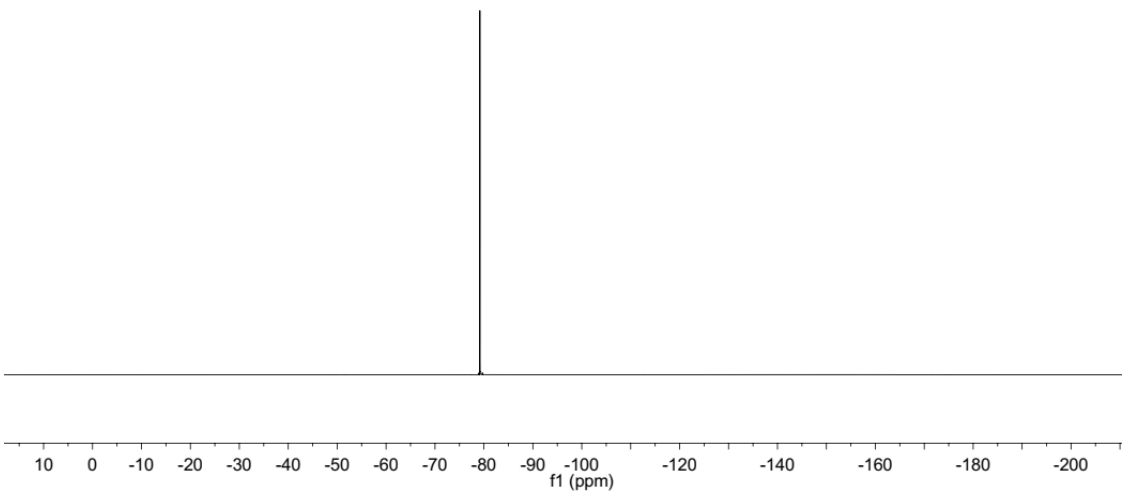


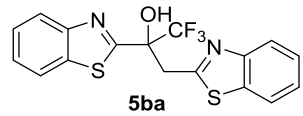
^{13}C NMR (100 MHz, $CDCl_3$)





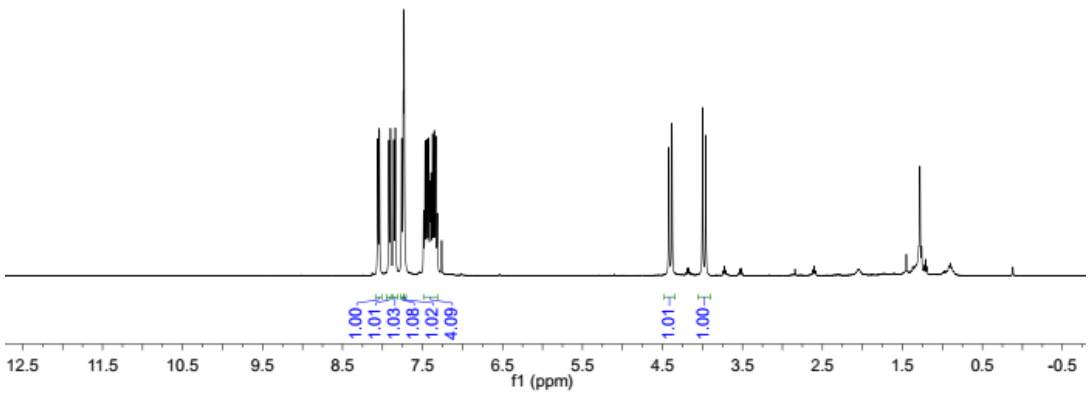
^{19}F NMR (376.5 MHz, $CDCl_3$)

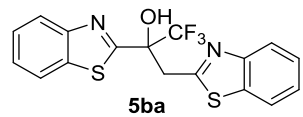




5ba

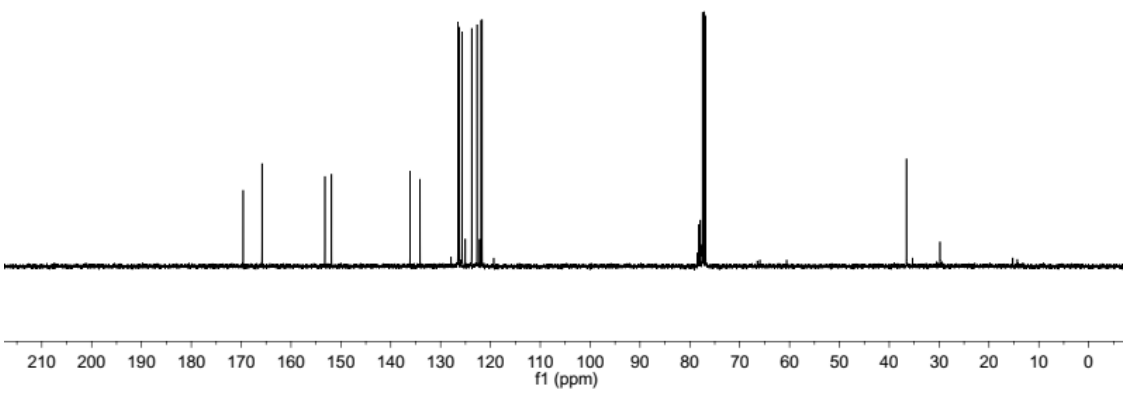
^{1}H NMR (400 MHz, $CDCl_3$)

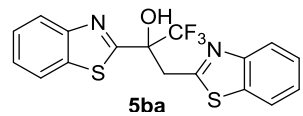




5ba

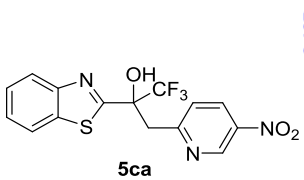
^{13}C NMR (100 MHz, $CDCl_3$)





5ba

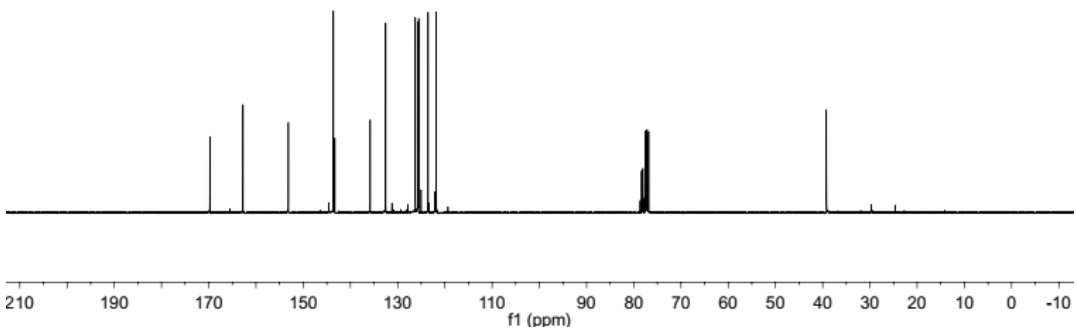
^{19}F NMR (376.5 MHz, $CDCl_3$)

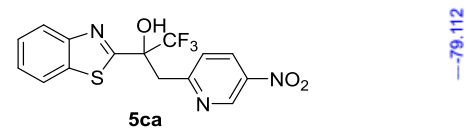


5ca

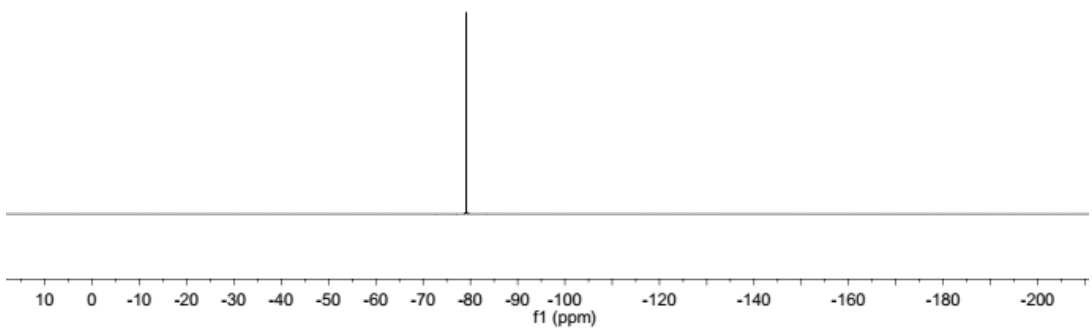
^{1}H NMR (400 MHz, $CDCl_3$)

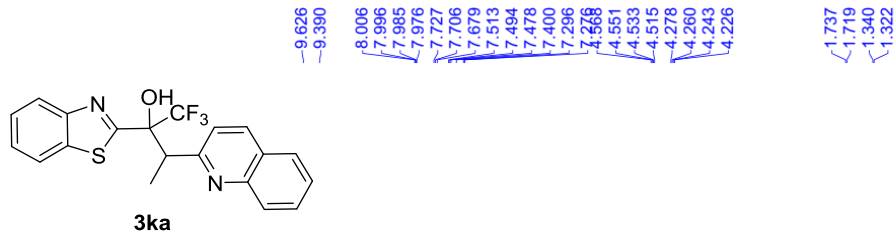
^{13}C NMR (100 MHz, $CDCl_3$)





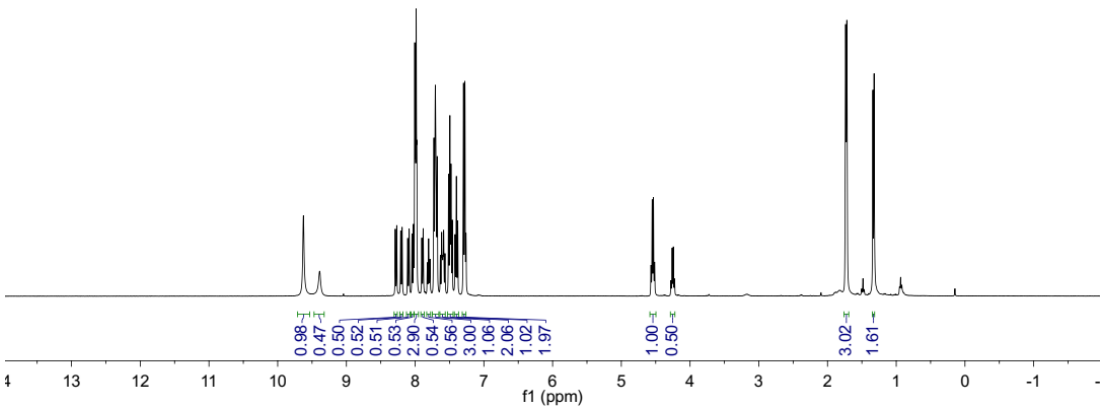
^{19}F NMR (376.5 MHz, $CDCl_3$)

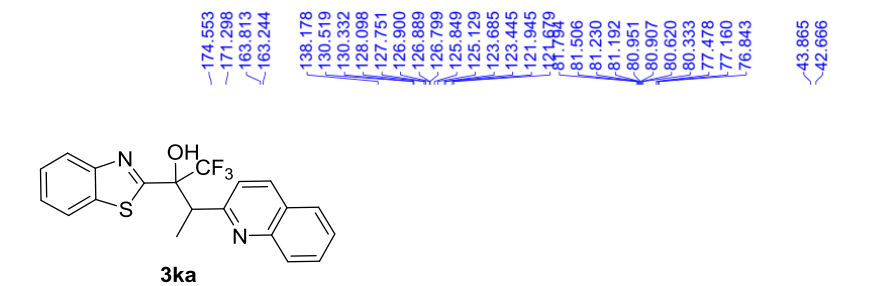




3ka

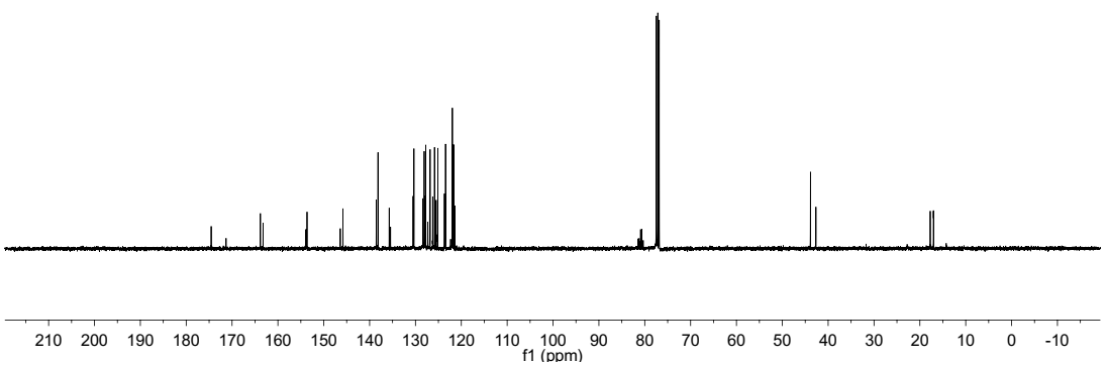
^{1}H NMR (400 MHz, $CDCl_3$)

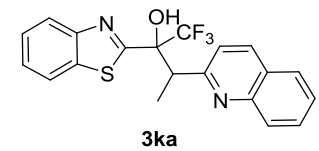




3ka

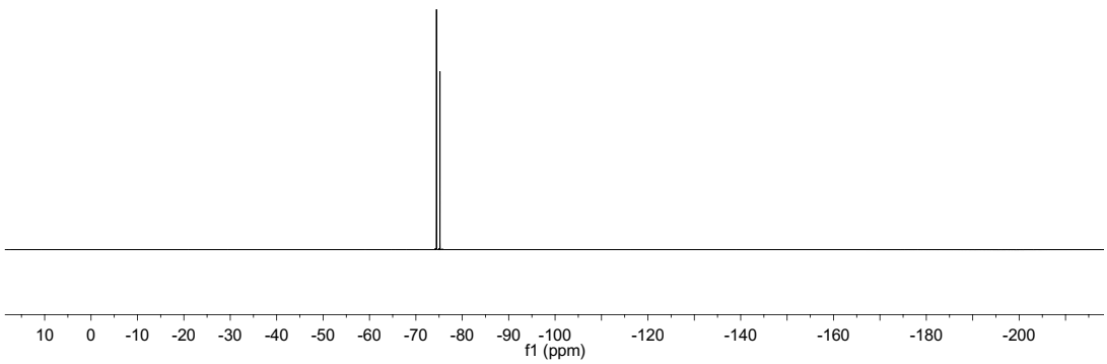
^{13}C NMR (100 MHz, $CDCl_3$)

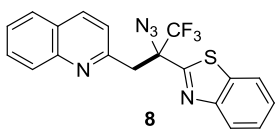




3ka

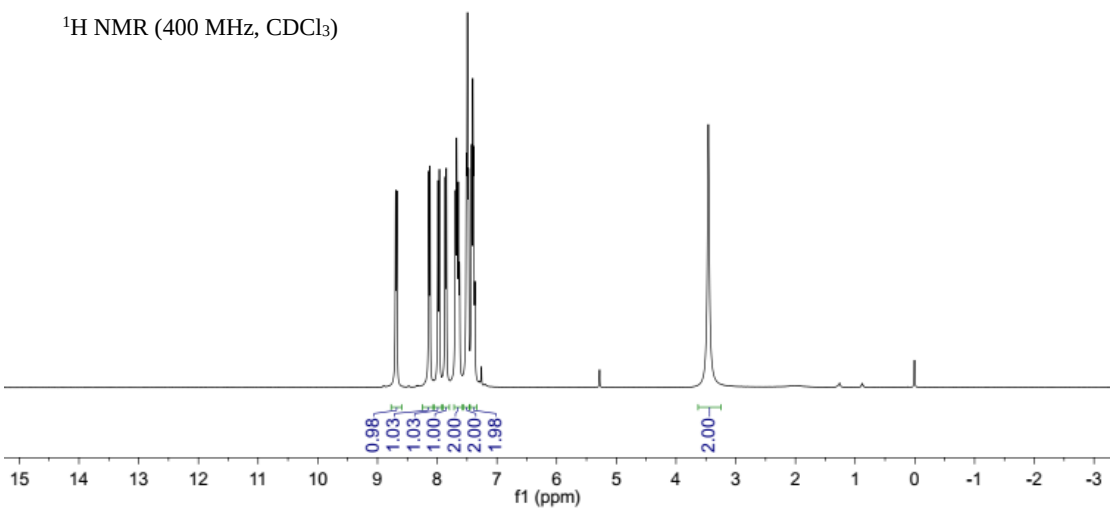
^{19}F NMR (376.5 MHz, $CDCl_3$)

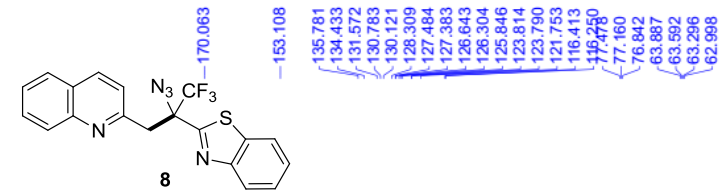




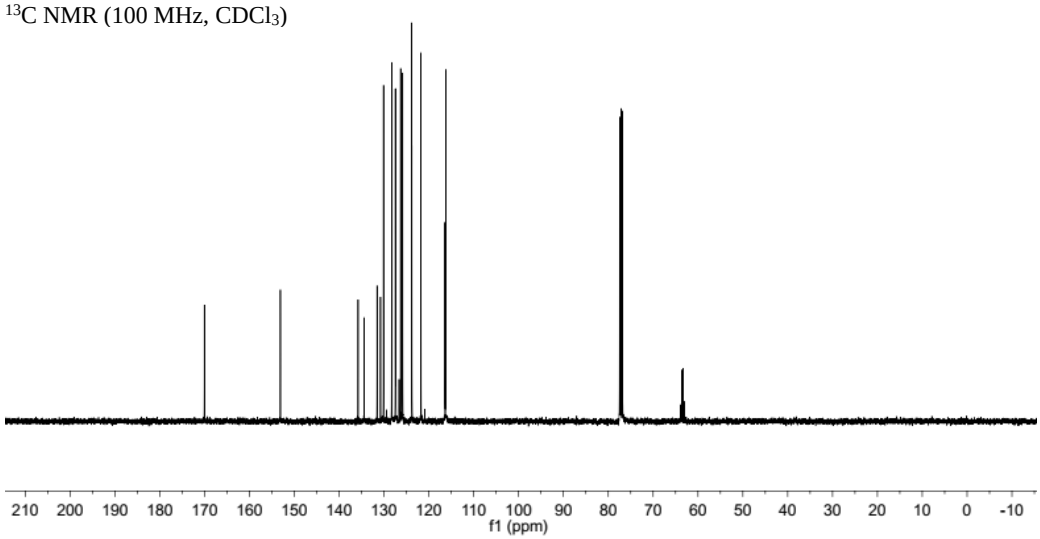
8

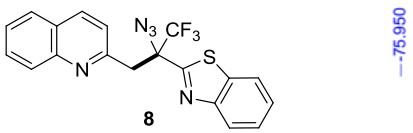
^{1}H NMR (400 MHz, $CDCl_3$)



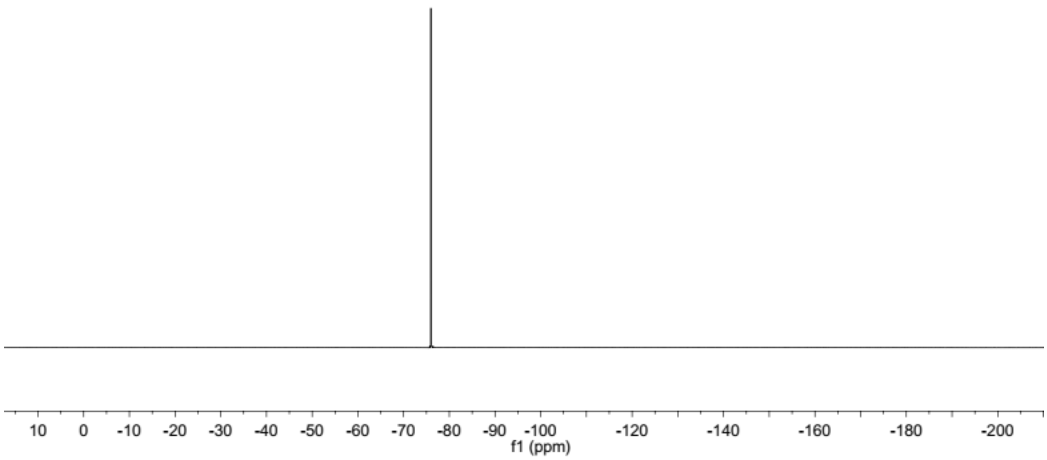


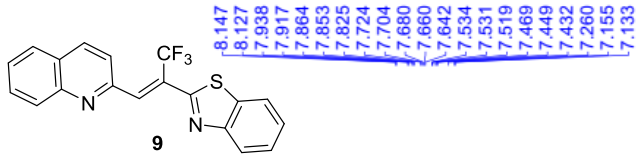
^{13}C NMR (100 MHz, $CDCl_3$)





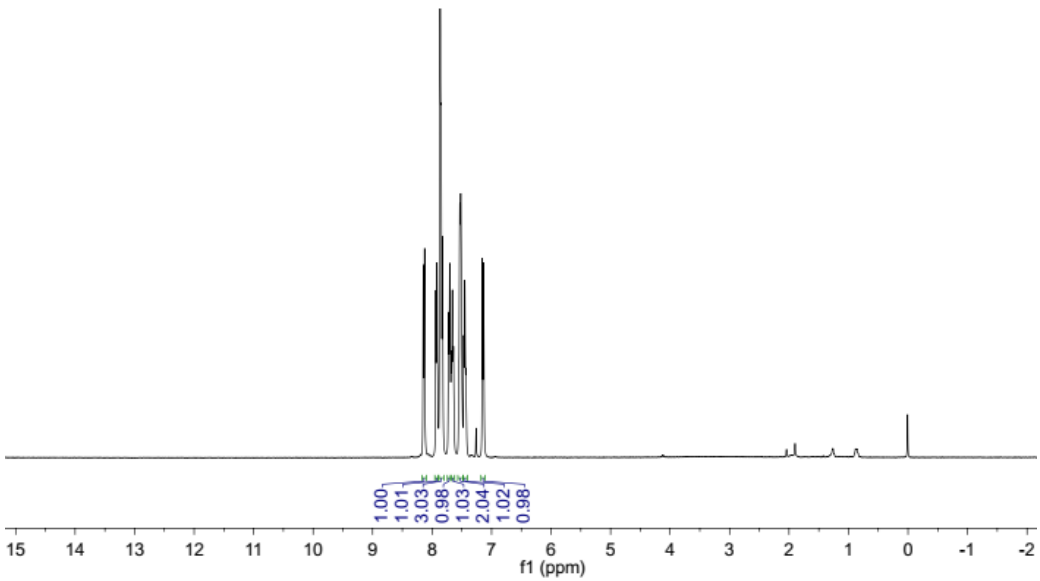
^{19}F NMR (376.5 MHz, $CDCl_3$)

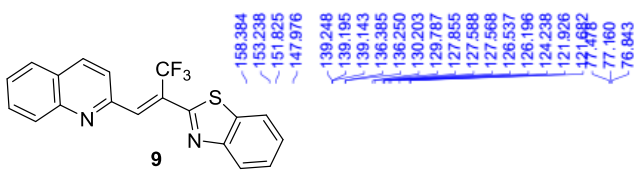




9

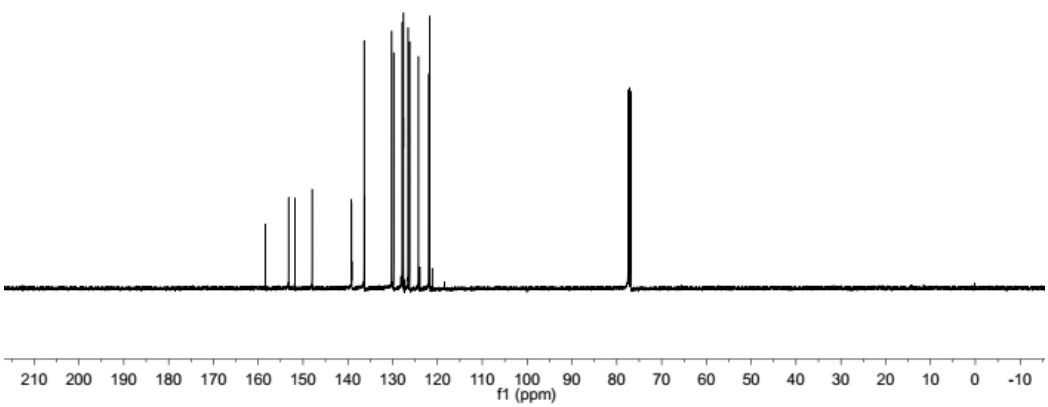
^{1}H NMR (400 MHz, $CDCl_3$)

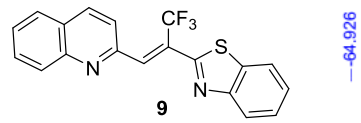




9

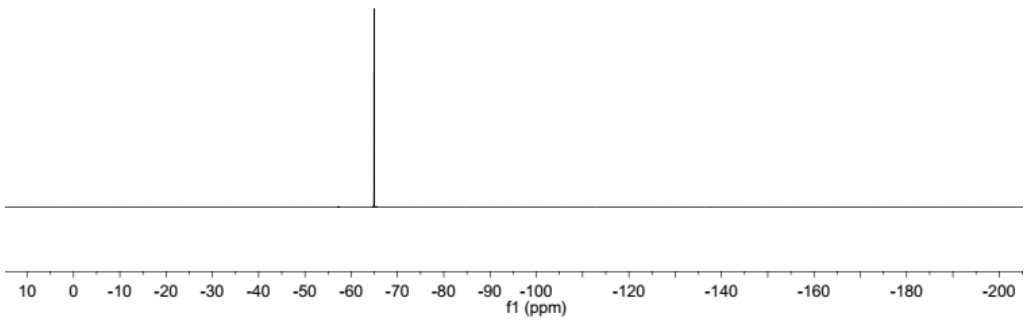
^{13}C NMR (100 MHz, $CDCl_3$)

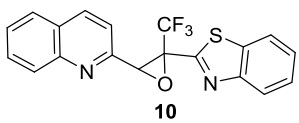




9

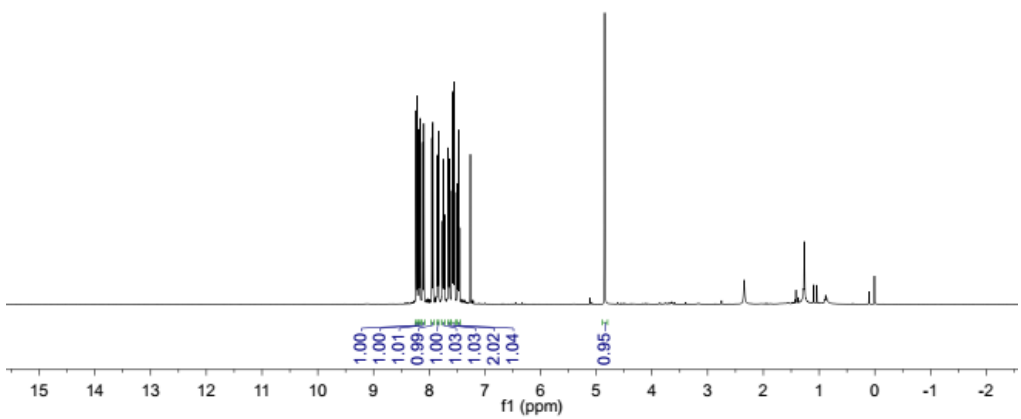
^{19}F NMR (376.5 MHz, $CDCl_3$)

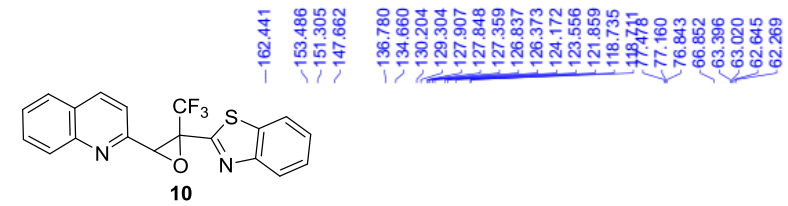




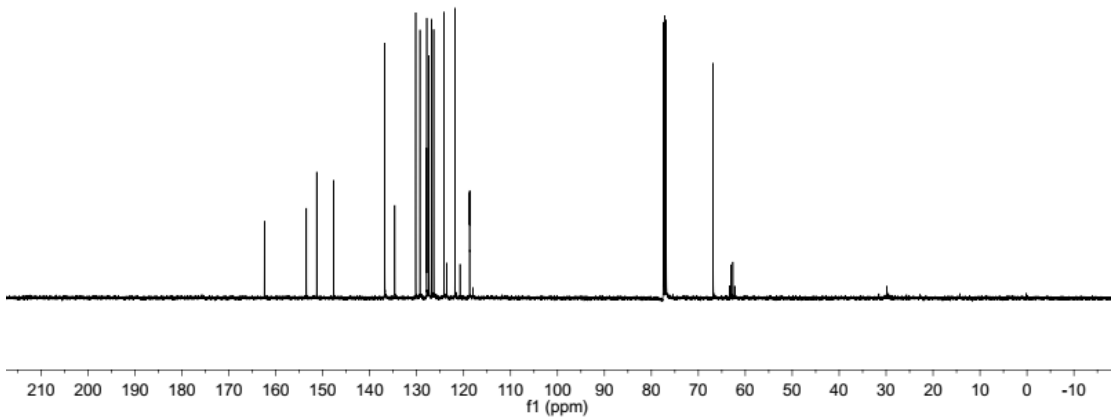
10

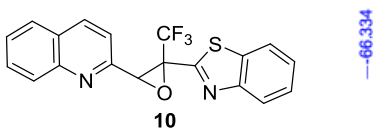
^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (100 MHz, $CDCl_3$)





^{19}F NMR (376.5 MHz, $CDCl_3$)