Structure and Reactivity of Highly Twisted *N*-Acyl Imidazoles

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Supporting Information

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I. GENERAL SYNTHESIS INFORMATION

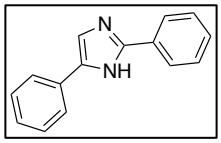
All reactions were carried out under ambient atmosphere unless otherwise noted. Room temperature (rt) is defined as 21–23 °C. Tetrahydrofuran (THF), dimethylformamide (DMF), dichloromethane (DCM), and toluene (PhMe) were obtained from Glass Contour Seca Solvent Purification System in which the solvent was dried over alumina and dispensed under an atmosphere of argon. All reagents were obtained from commercial sources and used without further purification.

Infrared spectra were recorded on a Nicolet 6700 ATR/FT-IR spectrometer with ν_{max} partially reported in cm^{-1}. High-resolution liquid chromatography-mass spectrometry (HRMS) was performed by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign using a Waters Synapt G2-Si instrument equipped with an electrospray ionization (ESI) detector. For crude data analysis, ultra high-performance liquid chromatography-mass spectrometry (UPLC/MS) was performed with a Waters Acquity UPLC/MS instrument equipped with a reversed-phase BEH C18 column (1.7 mm particle size, 2.1 x 50 mm), a dual atmospheric pressure chemical ionization (API)/electrospray ionization (ESI) mass spectrometry detector, and a photodiode array detector. Analytical thin-layer chromatography (TLC) was performed using 60 Å Silica Gel F_{254} pre-coated plates (0.25 mm thickness). TLC plates were visualized by irradiation with a UV lamp. Flash chromatography was performed using a Biotage Isolera One purification system equipped with a 10, 25, 50, or 100 g SNAP Ultra (HP Sphere, 25 μm silica) cartridge and an appropriate ethyl acetate (EtOAc)/hexanes (Hex), or methanol (MeOH)/dichloromethane (DCM) linear gradient in the mobile phase for normal-phase column chromatography, and 12, 30, 60, or 120 g SNAP-C18 columns with an appropriate methanol (MeOH)/H_2O linear gradient in the mobile phase for reverse-phase column chromatography.

Routine ^1H NMR spectra were recorded on Agilent 500 or 600 MHz spectrometers at ambient temperature. NMR solvents, *d*-chloroform ($CDCl_{3)}$, d_4-methanol (CD_3OD), and d_6-dimethylsulfoxide (DMSO-d_6), were purchased from Cambridge Isotope Laboratories and used without further purification. *d*-Chloroform was stored at ambient temperature over 4 Å molecular sieves, and fresh DMSO-d_6 and CD_3OD ampules were used immediately after opening. Spectra were processed using MestReNova 10.0.1 using the automatic phasing and polynomial baseline correction capabilities. Splitting was determined using the automatic multiplet analysis function with intervention as necessary. Spectral data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplet of doublets (dtd), doublet of doublet of doublet of doublets (dddd), doublet of triplets (dt), triplet of doublets (td), complex (comp), etc.], coupling constant, integration). Chemical shifts are reported in ppm (δ), and coupling constants are reported in Hz. ^1H Resonances are referenced to solvent residual peaks for $CDCl_3$ (7.26 ppm), CD_3OD (3.31 ppm), or DMSO-d_6 (2.50 ppm). Routine ^{13}C NMR spectra were recorded on Agilent 500 or 600 MHz spectrometers with protons fully decoupled. ^{13}C Resonances are reported in ppm relative to solvent residual peaks for $CDCl_3$ (77.2 ppm), CD_3OD (49.0 ppm), or DMSO-d_6 (39.5 ppm). ^{19}F-NMR spectra were recorded on Agilent 500 MHz spectrometers, and resonances are reported in ppm relative to solvent residual peaks for $CDCl_3$ (77.2 ppm), CD_3OD (49.0 ppm), or DMSO-d_6 (39.5 ppm).

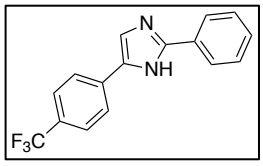
II. SUBSTITUTED-IMIDAZOLE SYNTHESIS

2-5-Diphenyl-1-*H*-imiazoles (6a)



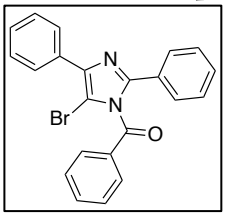
This procedure was adapted from O'Keefe and co-workers.[1] To a 100 mL round bottom flask equipped with a stir bar, 2-bromoacetophenone (1.00 g, 5.0 mmol, 1.0 equiv.) was added and dissolved in DMF (50 mL). Benzamidine (1.20 g, 10.0 mmol, 2.0 equiv.) was then added and the solution was stirred at rt for 13 h (reaction rates can be increased by heating the solution to 40 °C for 2 h). The mixture was diluted with 50% EtOAc in Hex, then poured into a solution of sat. $NaHCO_3$. The aqueous layer was rinsed with EtOAc (3x), then the combined organic layers were rinsed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified *via* reversed-phase column chromatography (SNAP Ultra C18 120g; gradient = 40–80% MeOH/H_2O for 10 CV then 80–100% MeOH/H_2O for 3 CV) to afford a pale-yellow solid (1.08 g, 4.92 mmol 98% yield). TLC: R_f (20% EtOAc/Hex) = 0.15. IR (FT-ATR, neat): 1488, 1463, 1024, 754, 692 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ 8.02 (d, J = 7.4 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H), 7.68 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (comp, 3H), 7.20 (t, J = 7.3 Hz, 1H); *N-H not observed*. $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 146.4, 139.5, 134.1, 131.0, 128.6, 128.5, 127.8, 126.1, 124.9, 124.3, 117.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}N_2$ 221.1079, found 221.1075.

2-Phenyl-5-(4-trifluoromethyl)phenyl)-1-*H*-imiazoles (6b)



This procedure was adapted from O'Keefe and co-workers.[1] To a 100 mL round bottom flask equipped with a stir bar, 2-bromo-4′-(trifluoromethyl)acetophenone (2.67 g, 10.0 mmol, 1.0 equiv.) was added and dissolved in DMF (50 mL). Benzamidine (2.40 g, 20.0 mmol, 2.0 equiv.) was then added and the solution was stirred at 45 °C for 5 h. The mixture was poured into cold water, inducing precipitation of an orange solid (2.50 g, 8.7 mmol 87% yield). TLC: R_f (20% EtOAc/Hex) = 0.13. IR (FT-ATR, neat): 1618, 1328, 1110, 1065, 834, 712 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ 12.90 (bs, 1H), 8.07 (d, J = 7.7 Hz, 2H), 8.02 (d, J = 7.3 Hz, 2H), 7.96 (s, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 6.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 146.4, 139.6, 138.7, 130.3, 128.8, 128.4, 126.3 (q, J = 31.6 Hz), 125.5 (q, J = 3.8 Hz), 125.0, 124.7, 124.6 (q, J = 271.6 Hz), 116.3. ^{19}F NMR (471 MHz, DMSO-d_6) δ –60.61. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}N_2F_3$ 289.0953, found 289.0951.

(5-Bromo-2,4-diphenyl-1*H*-imidazol-1-yl)(phenyl)methanone (7a)

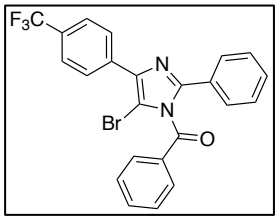


This procedure was adapted from O'Keefe and co-workers.[1] Sodium hydride (60% dispersion in mineral oil; 0.45 g, 11.3 mmol, 1.2 equiv.) was added to an oven-dried 250 mL round bottom flask under an atmosphere of N_2 equipped with a stir bar and dissolved in THF (94 mL). The slurry was cooled to 0 °C using an ice bath, then **6a** (2.07 g, 9.4 mmol, 1.0 equiv.) was added slowly while stirring. After 10 mins, benzoyl chloride (1.10 mL, 9.4 mmol, 1.0 equiv.) was added, and the reaction was allowed to proceed while warming to rt over 2 h. The mixture was then diluted with EtOAc and Hex, inducing formation of a white precipitate (unreacted starting material). The solid was removed *via* vacuum filtration, rinsing with hexanes, and the mother liquor containing the product was then concentrated *in vacuo* to afford a pale yellow solid, which was used crude in the subsequent step.

This procedure was adapted from Huang *et al.*[2] To a 100 mL round bottom flask equipped with a stir bar, the crude, pale yellow solid was added and dissolved in DCM (50 mL). *N*-Bromosuccinimide (2.18 g, 12.2 mmol, 1.3 equiv.) was then added and the solution was allowed to stir at 45 °C for 3 h, monitoring conversion with UPLC/MS. Once complete, the mixture was concentrated *in vacuo* and subjected to purification *via* normal-phase column chromatography (SNAP Ultra 100g; gradient = 0–30% EtOAc/Hex for 6 CV), affording a yellow oil (2.81 g, 7.0 mmol, 74% yield over 2 steps). TLC: R_f (20% EtOAc/Hex) = 0.22. IR (FT-ATR, neat): 1714, 1446, 1348, 1278, 917, 773, 692 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 8.03 (dd, J = 8.4, 1.2 Hz, 2H), 7.81 (dd, J = 8.4, 1.2 Hz, 2H), 7.79 – 7.74 (tt, J = 7.4, 1.2 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.56 – 7.53 (m, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.41 (tt, J =

7.1, 1.2 Hz, 1H), 7.38 (comp, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 168.6, 148.0, 138.5, 136.2, 131.9, 131.4, 131.0, 129.8, 129.7, 129.2, 128.8, 128.6, 128.0, 127.6, 126.7, 99.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{16}N_2OBr$ 403.0446, found 403.0443. X-ray characterization: recrystallized from MeOH.

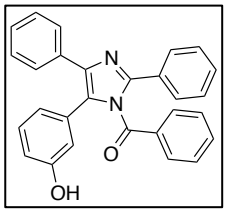
(5-bromo-2-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-1-yl)(phenyl)methanone (7b)



This procedure was adapted from O'Keefe and co-workers.[1] Sodium hydride (60% dispersion in mineral oil; 0.15 g, 3.7 mmol, 1.2 equiv.) was added to an oven-dried 100 mL round bottom flask under an atmosphere of N_2 equipped with a stir bar and dissolved in THF (30 mL). The slurry was cooled to 0 °C using an ice bath, then **6b** (0.88 g, 3.1 mmol, 1.0 equiv.) was added slowly while stirring. After 10 mins, benzoyl chloride (0.36 mL, 3.1 mmol, 1.0 equiv.) was added, and the reaction was allowed to proceed while warming to rt overnight. The mixture was then diluted with EtOAc and Hex, inducing formation of a white precipitate (unreacted starting material). The mixture was then concentrated *in vacuo*, affording a yellow solid, which was used crude in the subsequent step.

This procedure was adapted from Huang *et al.*[2] To a 50 mL round bottom flask equipped with a stir bar, the crude yellow solid was added and dissolved in DCM (15 mL). *N*-Bromosuccinimide (0.72 g, 4.0 mmol, 1.3 equiv.) was then added and the solution was allowed to stir at 45 °C for 3 h, monitoring conversion with UPLC/MS. Once complete, the mixture was concentrated *in vacuo* and subjected to purification *via* normal-phase column chromatography (SNAP Ultra 50g; gradient = 0–3% EtOAc/Hex for 3 CV, then 3% EtOAc/Hex for 3 CV), affording a yellow oil (1.03 g, 2.2 mmol, 71% yield over 2 steps). TLC: R_f (20% EtOAc/Hex) = 0.50. IR (FT-ATR, neat): 1715, 1323, 1279, 1167, 1109, 1064, 902, 858, 771, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.56 (comp, 3H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.27 (comp, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 168.4, 148.3, 137.0, 136.3, 136.0, 131.2, 131.1, 129.9, 129.8, 128.9, 128.9, 128.0 (q, *J* = 31.7 Hz), 127.6, 127.1, 125.6 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 271.9 Hz), 100.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.59. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{15}N_2OBrF_3$ 471.0320, found 471.0324. X-ray characterization: recrystallized from DCM in Hex.

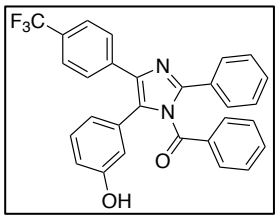
(5-(3-hydroxyphenyl)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-1-yl)(phenyl)methanone (8a)



This procedure was adapted from Kolundzic *et al.*[3] An oven-dried 15 mL sealed-tube flask, which was equipped with a stir bar, was charged with **7a** (0.20 g, 0.50 mmol, 1.0 equiv), 3-(*tert*-butyldimethyl-siloxy)benzene boronic acid (0.19 g, 0.74 mmol, 1.5 equiv), tris(dba)dipalladium (11.0 mg, 2.5 mol%), XPhos (24.0 mg, 10 mol%), anhydrous potassium phosphate tribasic (0.21 g, 1.00 mmol, 2.0 equiv). The vial was sealed with a septum, then evacuated and backfilled with N_2 (3x). A solution of toluene (5.0 mL) and deionized water (0.5 mL), which had been sparged with N_2, was then added using a Teflon cannula. The septum was replaced with a Teflon screw cap and the red solution was stirred at 110 °C for 6 hours. Once cooled to room temperature, the aqueous layer was removed, rinsing with EtOAc (3x). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo.* The crude material was stirred with TBAF (0.6 mL, 1 M in THF) for 1 hr. Completion of the deprotection was confirmed by UPLC/MS. The solution was then quenched with water and further diluted with EtOAc. The aqueous layer was rinsed with EtOAc (3x), then the combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by normal-phase column chromatography (SNAP Ultra-25g column; gradient = 0–50% EtOAc/Hex over 8 CV, then 50–100% EtOAc/Hex over 3 CV). The desired fractions were pooled and concentrated *in vacuo* to afford a solid that was then redissolved in a small amount of EtOAc and precipitated with Hex. The pale yellow solid was isolated *via* vacuum filtration, washing with Hex (0.11 g, 0.27 mmol, 54% yield over 2 steps). R_f (20% EtOAc/Hex) = 0.28. IR (FT-ATR, neat): 3031 (br), 1713, 1359, 1276, 1226, 920, 693 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ 9.55 (s, 1H), 7.68–7.46 (comp, 7H), 7.45–7.27 (comp, 7H), 7.25 (q, *J* = 6.1 Hz, 1H), 7.10 (t, *J* = 6.5 Hz, 1H), 6.73 – 6.63 (comp, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 169.6, 157.3, 146.4, 137.1, 135.2, 133.4, 132.3, 130.5, 130.4,

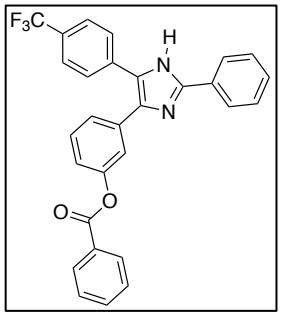
129.9, 129.8, 129.7, 129.2, 129.1, 128.6, 128.3, 127.9, 127.1, 126.7, 121.0, 117.0, 115.9. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{28}H_{21}N_2O_2$ 417.1603, found 417.1597. X-ray characterization: recrystallized from methanol.

(5-(3-hydroxyphenyl)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-1-yl)(phenyl)methanone (8b)



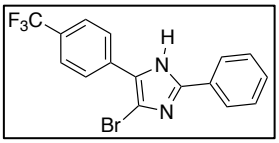
This procedure was adapted from Kolundzic *et al.*[3] An oven-dried 15 mL sealed-tube flask, which was equipped with a stir bar, was charged with **7b** (0.19 g, 0.41 mmol, 1.0 equiv), 3-(*tert*-butyldimethyl-siloxy)benzene boronic acid (0.16 g, 0.62 mmol, 1.5 equiv), tris(dba)dipalladium (9.0 mg, 2.5 mol%), XPhos (19.0 mg, 10 mol%), anhydrous potassium phosphate tribasic (0.17 g, 0.82 mmol, 2.0 equiv). The vial was sealed with a septum, then evacuated and backfilled with N_2 (3x). A solution of toluene (4.0 mL) and deionized water (0.4 mL), which had been sparged with N_2, was then added using a Teflon cannula. The septum was replaced with a Teflon screw cap and the red solution was stirred at 110 °C for 17 hours. Once cooled to room temperature, the aqueous layer was removed, rinsing with EtOAc (3x). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo.* The crude material was stirred with TBAF (0.4 mL, 1 M in THF) for 1 hr. Completion of the deprotection was confirmed by UPLC/MS. The solution was then quenched with water and further diluted with EtOAc. The aqueous layer was rinsed with EtOAc (3x), then the combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by normal-phase column chromatography (SNAP Ultra-25g column; gradient = 0–50% EtOAc/Hex over 10 CV, then 50–100% EtOAc/Hex over 3 CV). The desired fractions were pooled and concentrated *in vacuo* to afford a pale yellow solid (67.5 mg, 0.14 mmol, 34% yield over 2 steps). TLC: R_f (20% EtOAc/Hex) = 0.18. IR (FT-ATR, neat): 3000 (br), 1719, 1447, 1324, 1279, 1161, 1114, 1066, 912, 691cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.61 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.21 (comp, 5H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.71 – 6.66 (m, 2H); *O-H not observed.* ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 170.1, 156.7, 148.3, 137.9, 137.3, 135.4, 133.3, 131.3, 131.2, 131.2, 130.7, 130.4, 129.9, 129.4, 129.1,129.1 (q, *J* = 32.2 Hz), 128.9, 127.9, 125.7 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 271.8 Hz), 123.3, 117.9, 116.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.49. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{29}H_{20}N_2O_2F_3$ 485.1477, found 485.1475.

3-(2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-4-yl)phenyl benzoate (9)



An oven-dried 45 mL sealed-tube flask, which was equipped with a stir bar, was charged with **7b** (1.31 g, 2.79 mmol, 1.0 equiv), 3-(*tert*-butyldimethyl-siloxy)benzene boronic acid (1.05 g, 4.18 mmol, 1.5 equiv), tris(dba)dipalladium (64.0 mg, 2.5 mol%), XPhos (0.13 g, 10 mol%), anhydrous potassium phosphate tribasic (0.59 g, 2.79 mmol, 1.0 equiv). The vial was sealed with a septum, then evacuated and backfilled with N_2 (3x). A solution of toluene (28.0 mL) and deionized water (2.8 mL), which had been sparged with N_2, was then added using a Teflon cannula. The septum was replaced with a Teflon screw cap and the red solution was stirred at 110 °C for 16 hours. Once cooled to room temperature, the aqueous layer was removed, rinsing with EtOAc (3x). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo.* The crude material was stirred with TBAF (3.1 mL, 1 M in THF) for 6 min at 0 °C. Completion of the deprotection was confirmed by UPLC/MS. The solution was then quenched with water (30 mL) and citric acid (10% m/v; 1 mL), then further diluted with EtOAc. The aqueous layer was rinsed with EtOAc (3x), then the combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by normal-phase column chromatography (SNAP Ultra-100g column; gradient = 0–30% EtOAc/Hex over 8 CV). The desired fractions were pooled and concentrated *in vacuo.* The solid was then redissolved in DCM followed by a small amount of Hex to precipitate out a white solid (0.11 g, 0.23 mmol, 8% yield over 2 steps). TLC: R_f (100% DCM) = 0.70. (FT-ATR, neat): 1740, 1717, 1618, 1483, 1323, 1247, 1164, 1114, 1104, 1062, 1022, 846 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.95 – 7.86 (m, 2H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.45 – 7.41 (m, 2H), 7.39 – 7.34 (comp, 3H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.17 – 7.13 (m, 1H); *N-H*

not observed. $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 165.8, 151.6, 147.2, 134.2, 130.6, 130.3, 129.8, 129.5, 129.3, 129.0, 128.1, 126.0, 125.8 (q, J = 3.9 Hz), 125.8, 125.8, 124.6 (q, J = 272.2 Hz), 121.6, 121.5 (*remaining sp² carbons not observed*). ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.46. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{29}H_{20}N_2O_2F_3$ 485.1477, found 485.1474. X-ray characterization: recrystallized from DCM in Hex.



4-Bromo-2-phenyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (10)

To a solution of benzylamine (4 µL, 33 µmol, 2.0 equiv) in toluene/chloroform (4:1 v/v; 100 µL, 0.16 M), **7b** (7.8 mg, 16 µmol, 1.0 equiv) was added and stirred at rt for 15 h. Full conversion was visualized *via* UPLC/MS. The solution was concentrated in vacuo, then subjected to normal-phase column chromatography (SNAP Ultra-10g column; gradient = 0–40% EtOAc/Hex over 10 CV). The desired fractions were pooled and concentrated *in vacuo*, affording a white solid (4.7 mg, 13 µmol, 80% yield).

This product exists as a 6:1 ratio of 1,3-H-imidazole isomers detectable by observable ^{1}H NMR resonances; purity was confirmed by UPLC/MS (Figure S1).

TLC: R_f (50% EtOAc/Hex) = 0.72. IR (FT-ATR, neat): 1620, 1620, 1325, 1163, 1153, 1122, 1111, 1066, 840 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6; major isomer) δ 13.12 (s, 1H), 8.04 (comp, 4H), 7.89 (d, J = 8.3 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H). ^{1}H NMR (500 MHz, DMSO-d_6; minor isomer) δ 13.52 (s, 1H), 8.21 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H); *remaining protons overlap with major isomer*. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6; only major isomer observed) δ 146.8, 132.7, 129.2, 129.1, 128.8, 127.6 (q, J = 31.8 Hz), 127.2, 127.1, 125.6 (q, J = 3.7 Hz), 125.4, 124.2 (d, J = 271.9 Hz), 114.8. ^{19}F NMR (471 MHz, DMSO-d_6) δ –60.98. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}N_2BrF_3$ 367.0058, found 367.0052.

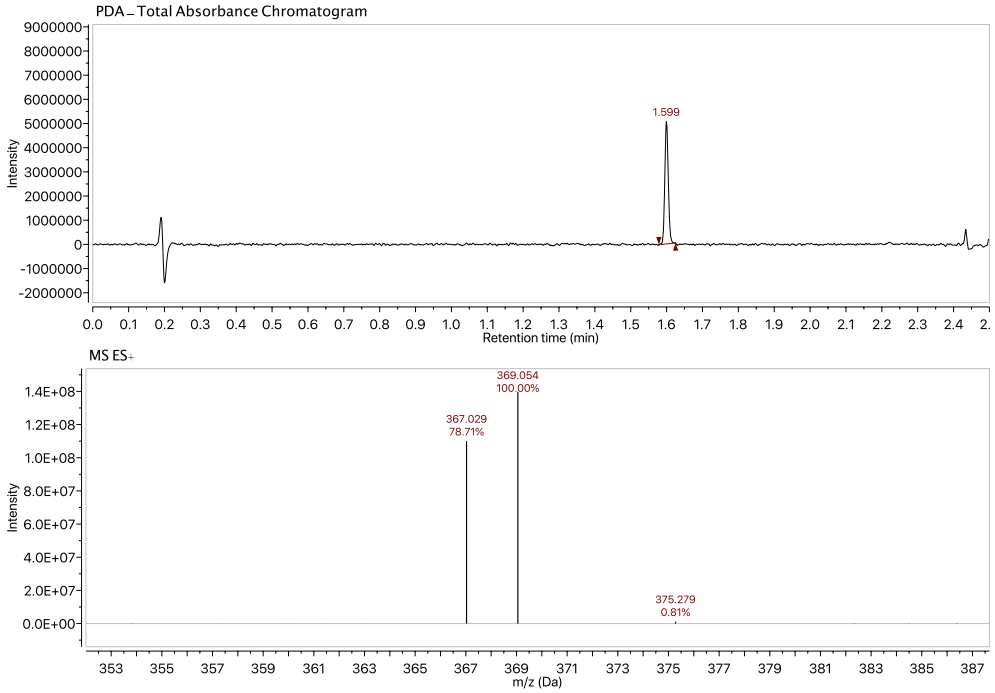
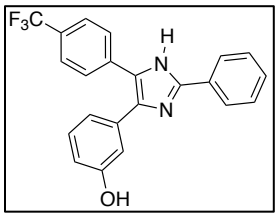


Figure S1. UPLC/MS trace of **10** with photodiode array (PDA) total absorbance chromatogram on top and mass spectrum (ES^+) on bottom, indicating the purity of this compound.

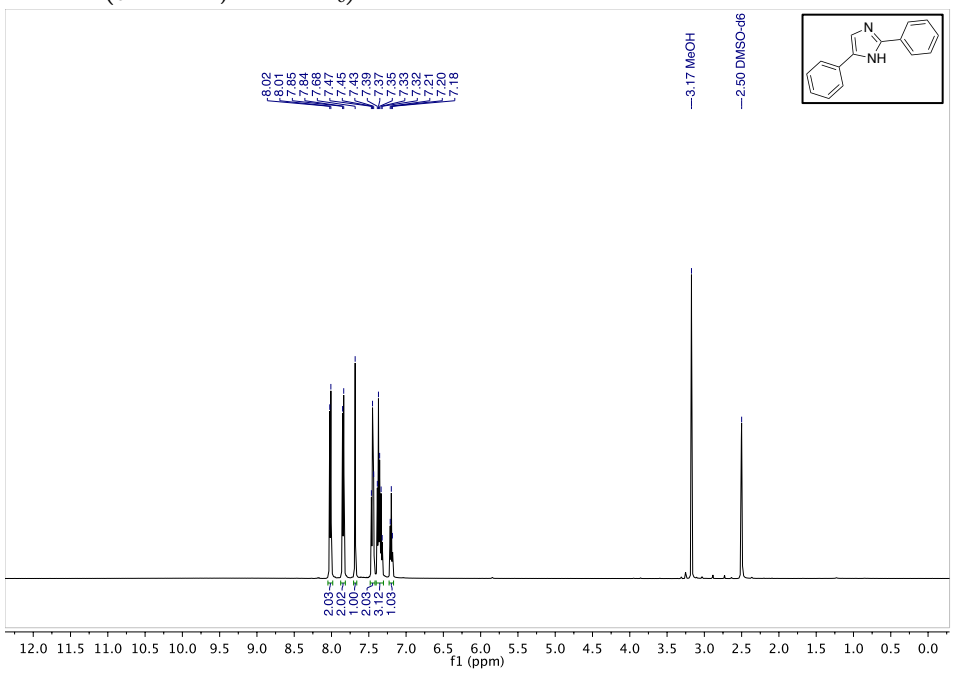


3-(2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-4-yl)phenol (11)

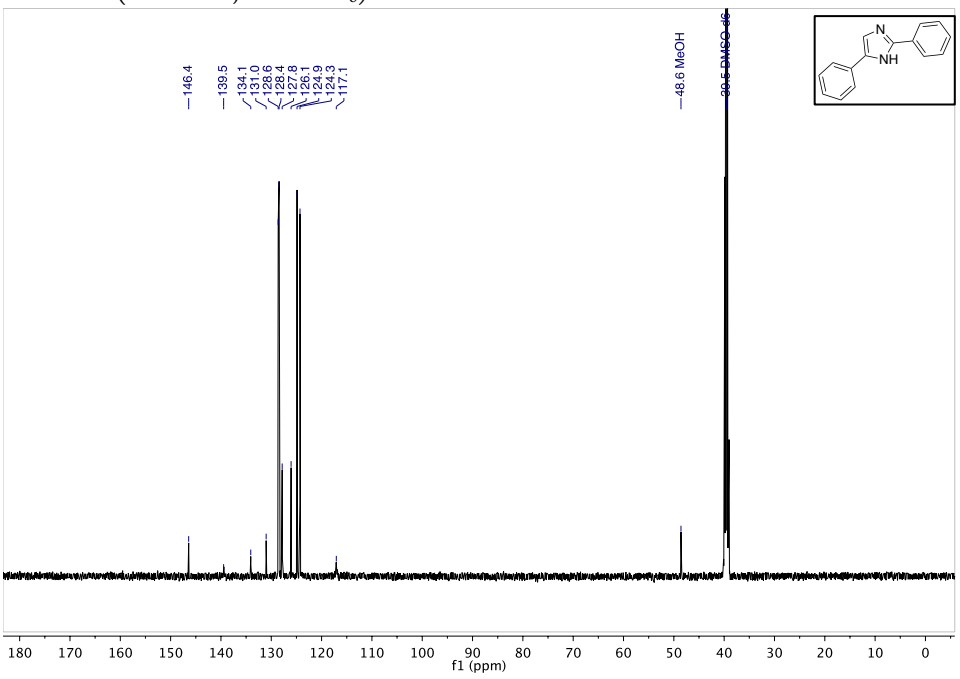
To a solution of benzylamine (4 μL, 33 μmol, 2.0 equiv) in toluene/chloroform (4:1 v/v; 100 μL, 0.16 M), **8b** (7.9 mg, 16 μmol, 1.0 equiv) was added and stirred at rt for 15 h. Conversion was monitored *via* UPLC/MS. The solution was concentrated in vacuo, then subjected to normal-phase column chromatography (SNAP Ultra-10g column; gradient = 0–10% MeOH/DCM over 10 CV). The desired fractions were pooled and concentrated *in vacuo*. The solid was resuspended in EtOAc (1 mL), then rinsed with citric acid solution (1 mL, 10% m/v) followed by saturated bicarbonate (1 mL). The organic layer was extracted, dried over Na_2SO_4, then concentrated *in vacuo*, azeotroping with DCM in Hex, to afford a white solid (4.1 mg, 11 μmol, 67% yield). TLC: R_f (10% MeOH/DCM) = 0.67. IR (FT-ATR, neat): 3000 (b), 1618, 1586, 1460, 1324, 1165, 1122, 1063 cm^{-1}. ^1H NMR (500 MHz, CD_3OD) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 158.9, 148.6, 147.0, 131.1, 131.0, 130.2, 130.1, 130.0, 129.9, 129.6, 129.4, 128.9 (d, *J* = 32.3 Hz), 127.0, 126.3 (q, *J* = 3.7 Hz), 125.8 (q, *J* = 271.5 Hz), 120.9, 116.5, 116.2. ^{19}F NMR (376 MHz, CD_3OD) δ –64.01. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{16}NOF_3$ 381.1215, found 381.1211.

IV. ^{1}H, ^{13}C, and ^{19}F NMR CHARACTERIZATION DATA

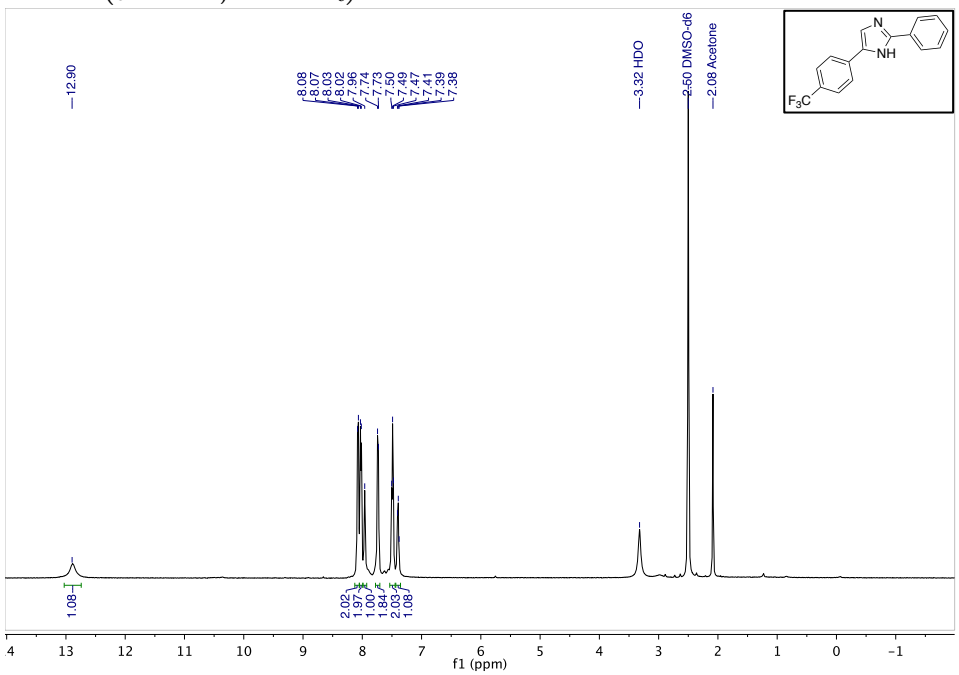
^{1}H NMR (500 MHz, DMSO-d_6)- **6a**



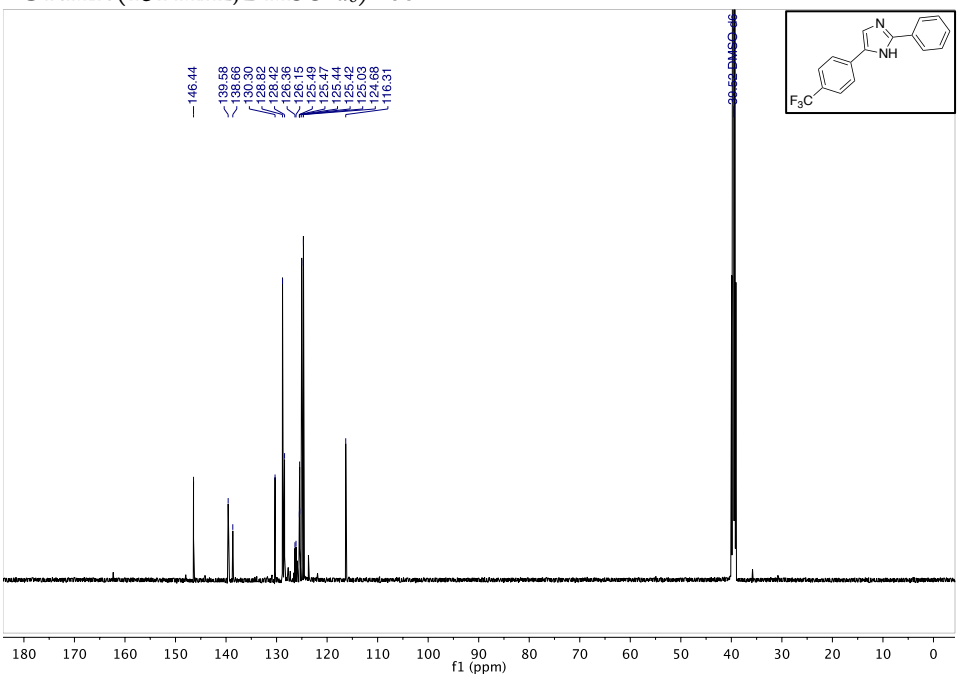
^{13}C NMR (126 MHz, DMSO-d_6)- **6a**



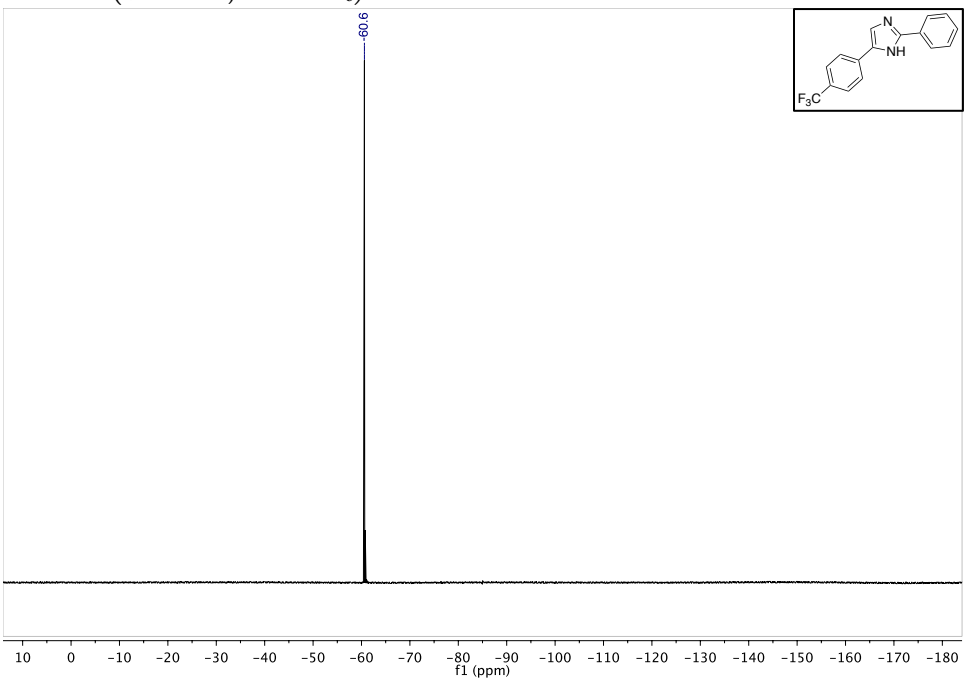
^{1}H NMR (500 MHz, DMSO-d_6)- **6b**



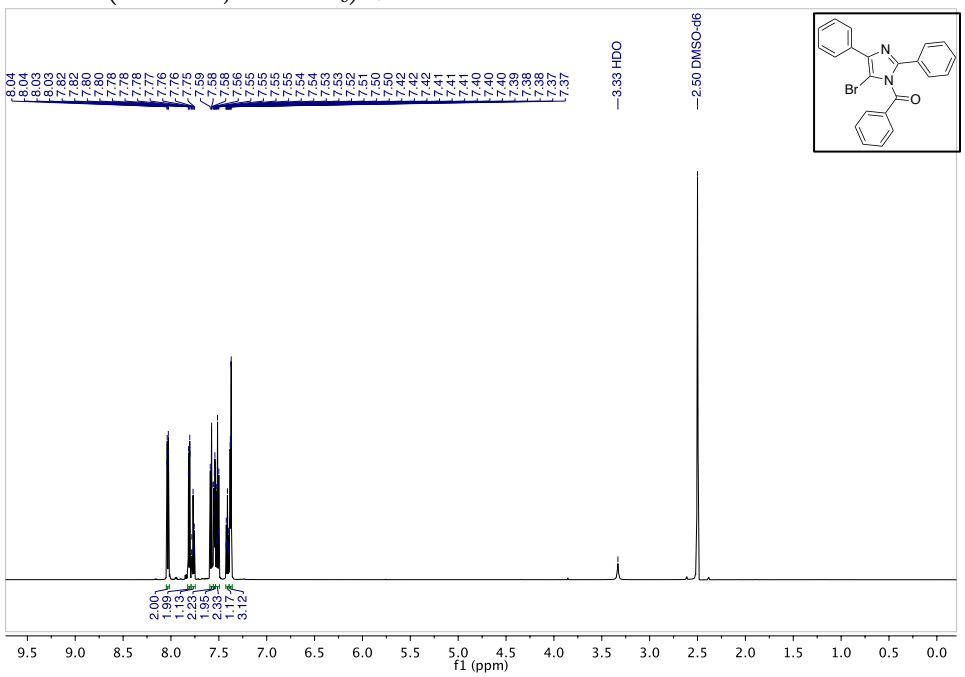
^{13}C NMR (151 MHz, DMSO-d_6)- **6b**



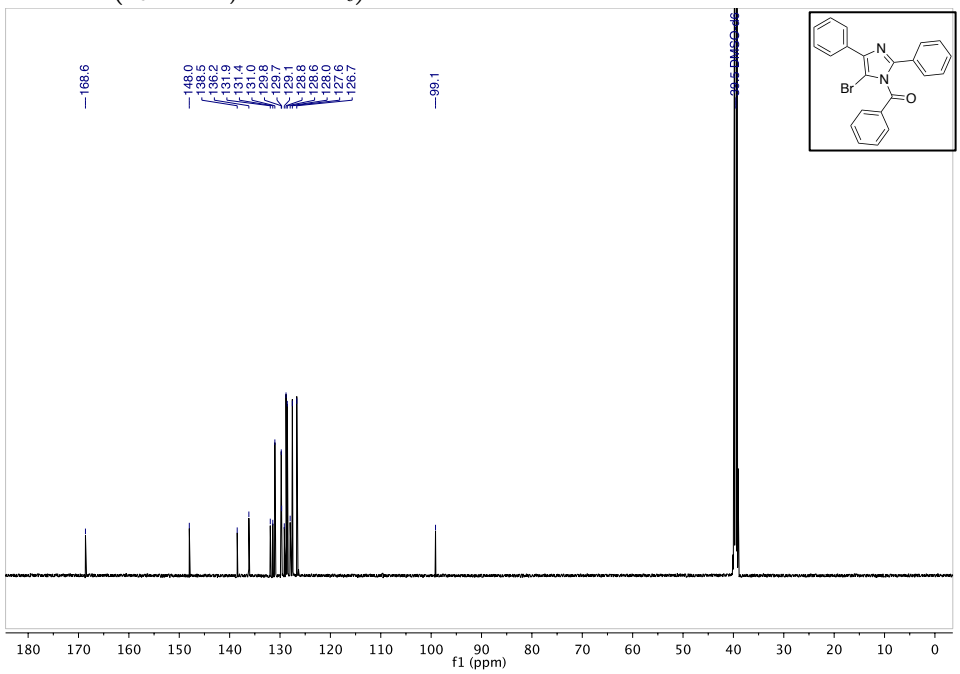
^{19}F NMR (471 MHz, DMSO-d_6)- **6b**



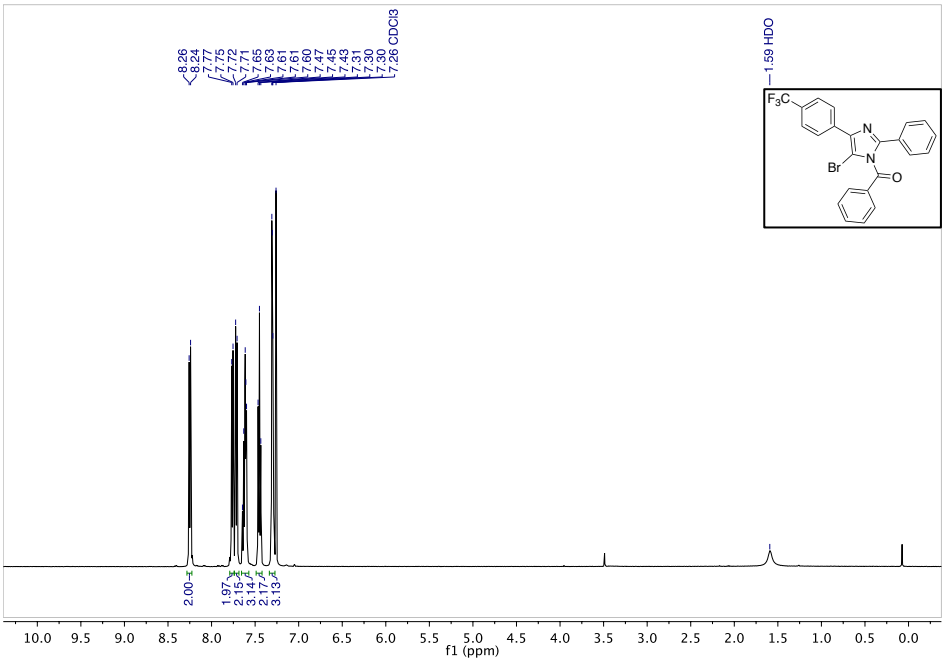
^{1}H NMR (600 MHz, DMSO-d_6)- **7a**



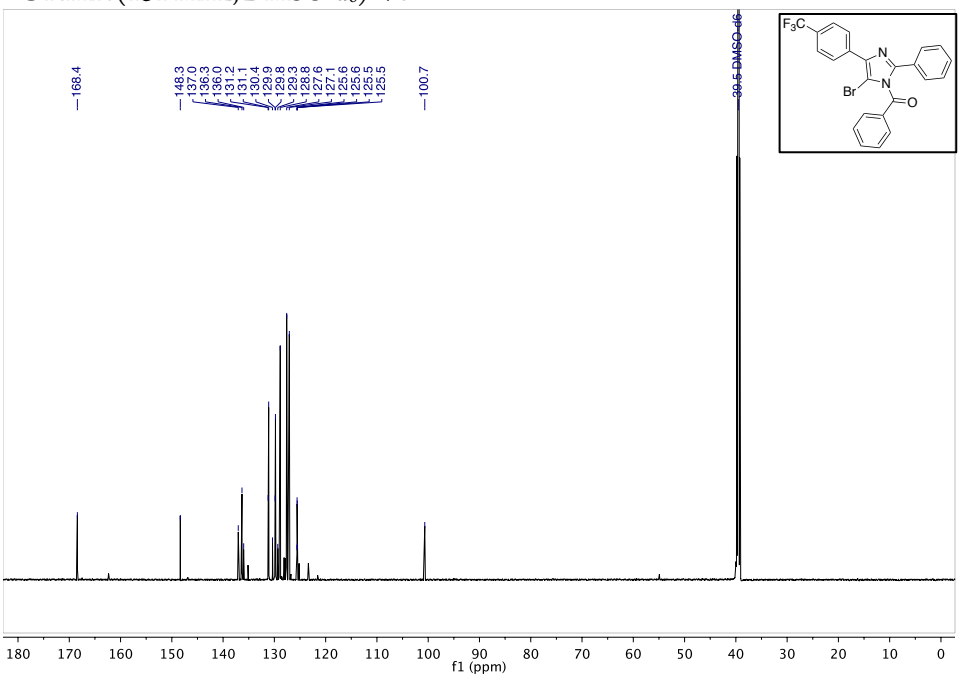
^{13}C NMR (151 MHz, DMSO-d_6) - **7a**



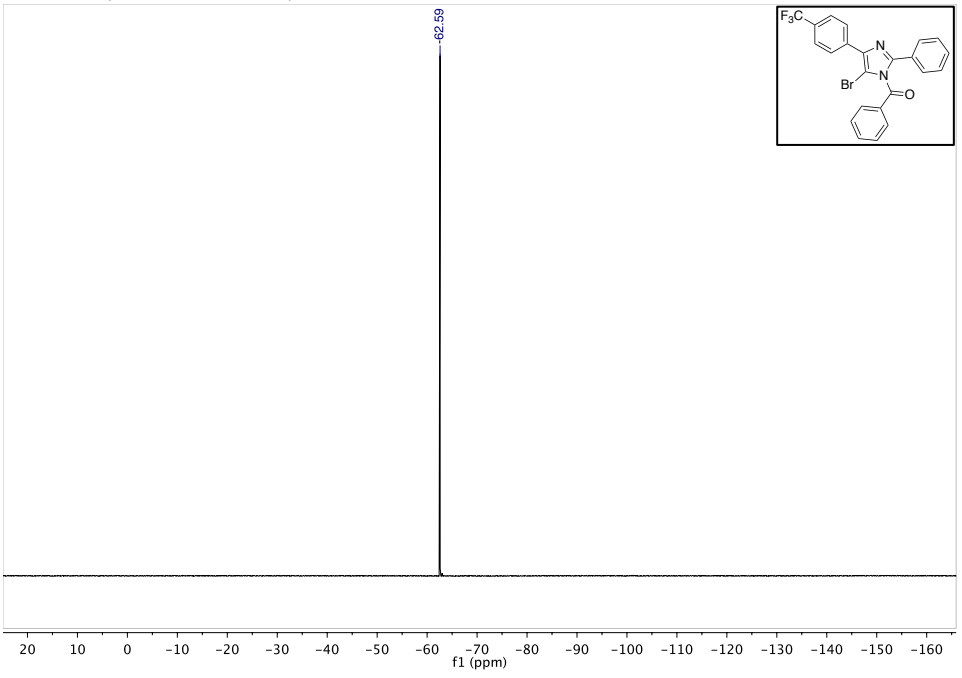
^{1}H NMR (600 MHz, DMSO-d_6) - **7b**



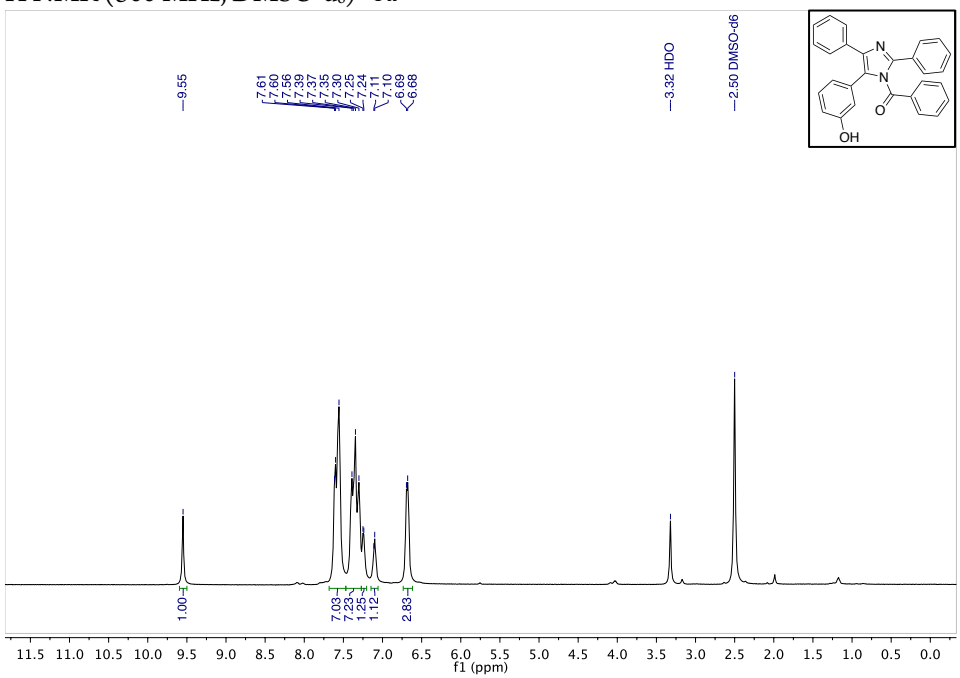
^{13}C NMR (151 MHz, DMSO-d_6)- **7b**



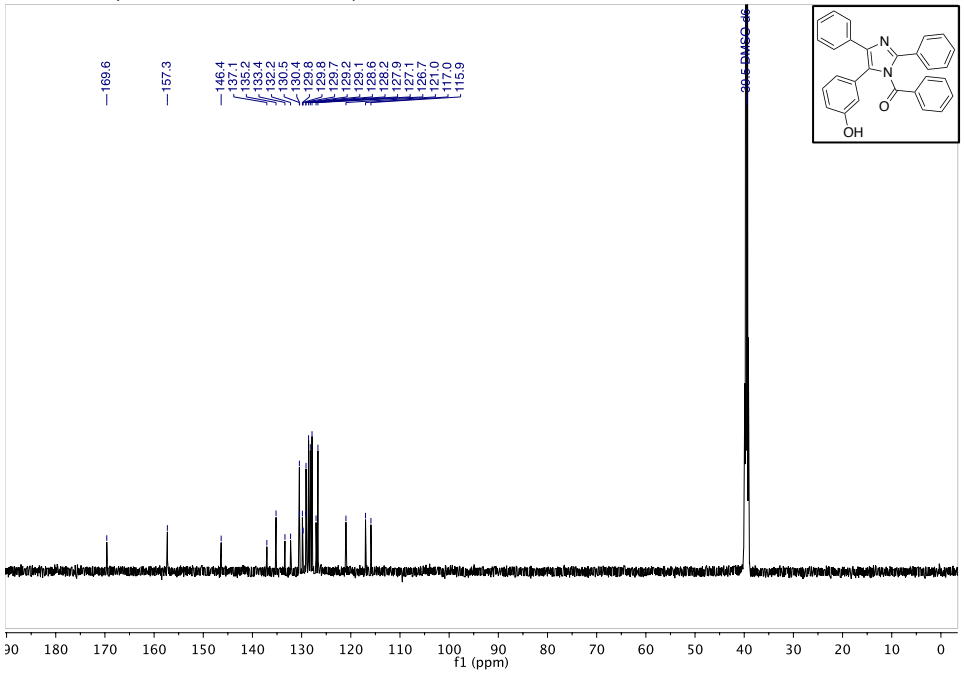
^{19}F NMR (470 MHz, $CDCl_3$)- **7b**



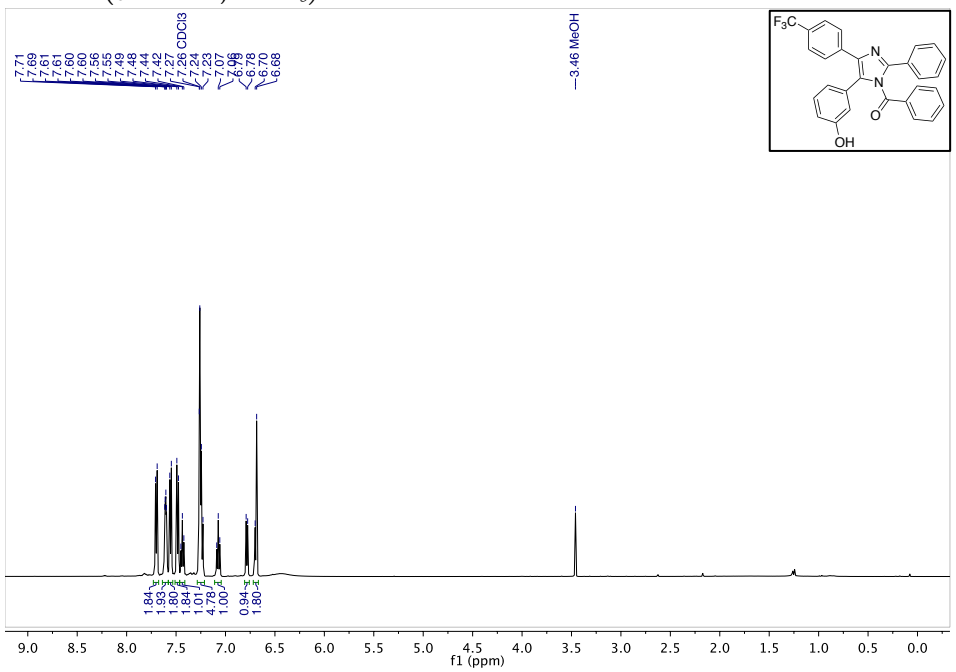
^{1}H NMR (500 MHz, DMSO-d_6)- **8a**



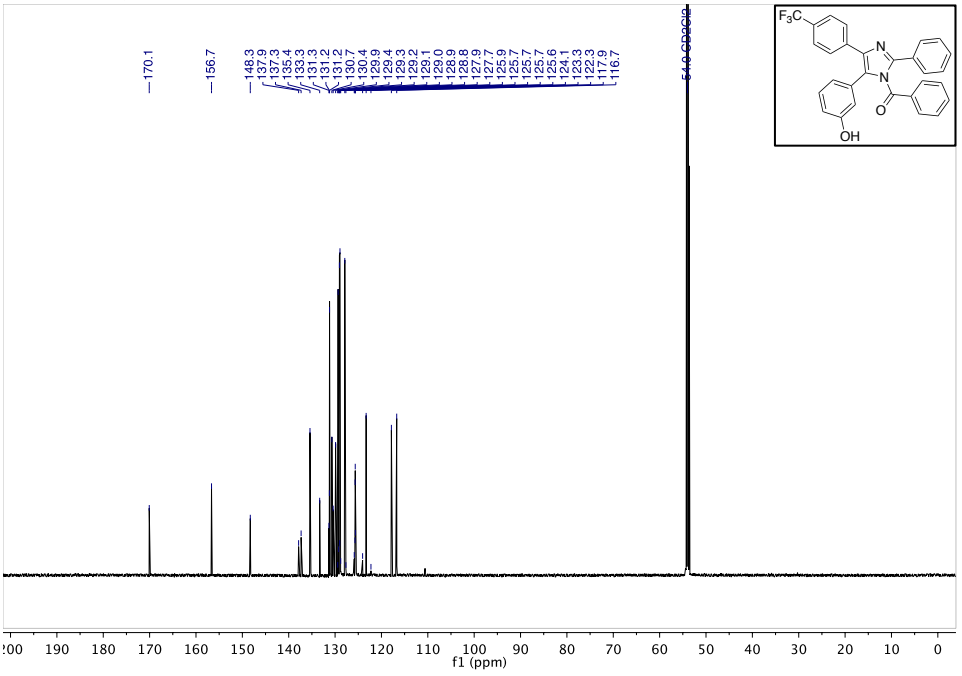
^{13}C NMR (126 MHz, DMSO-d_6)- **8a**



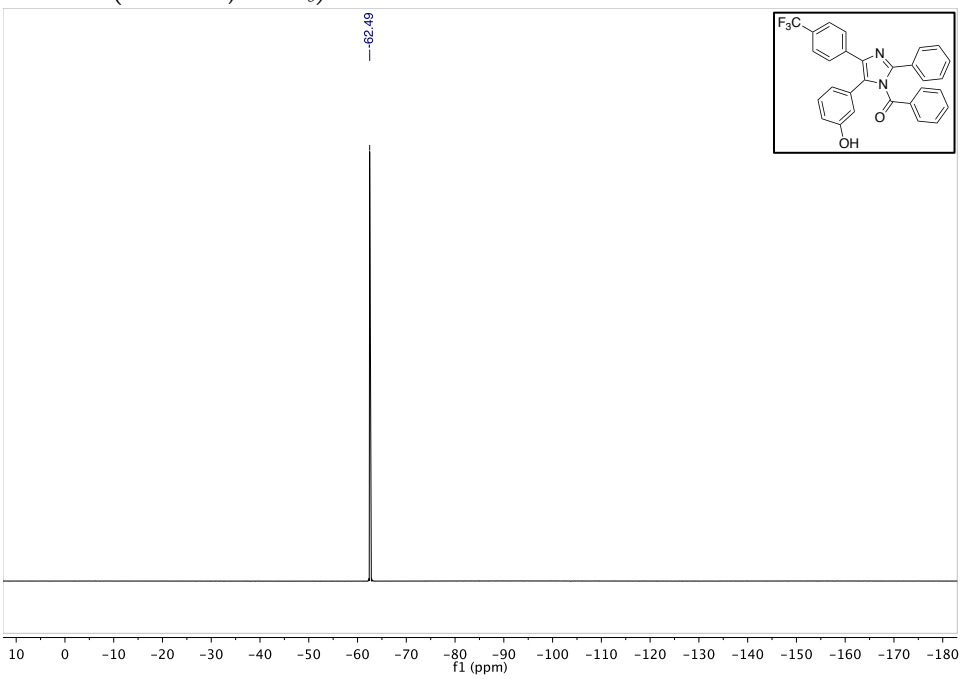
^{1}H NMR (500 MHz, $CDCl_3$)- **8b**



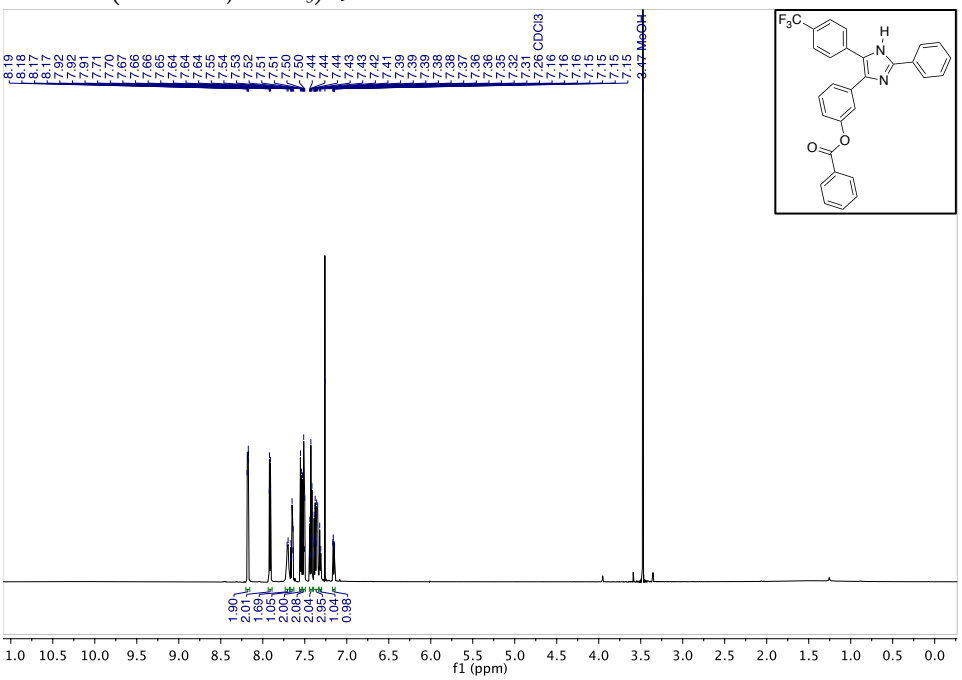
^{13}C NMR (151 MHz, CD_2Cl_2)- **8b**



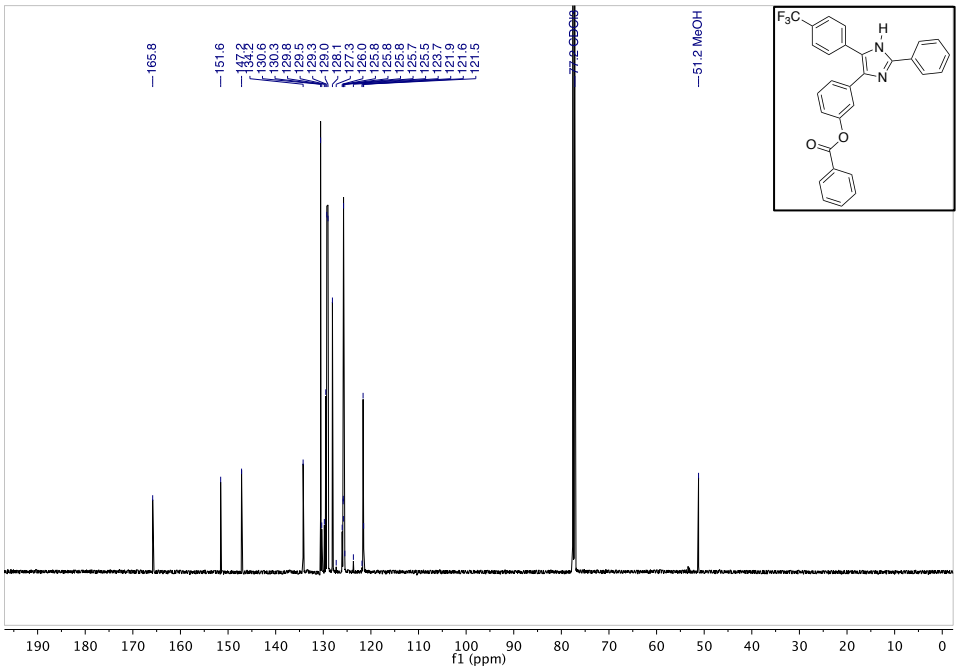
^{19}F NMR (471 MHz, $CDCl_3$)- **8b**



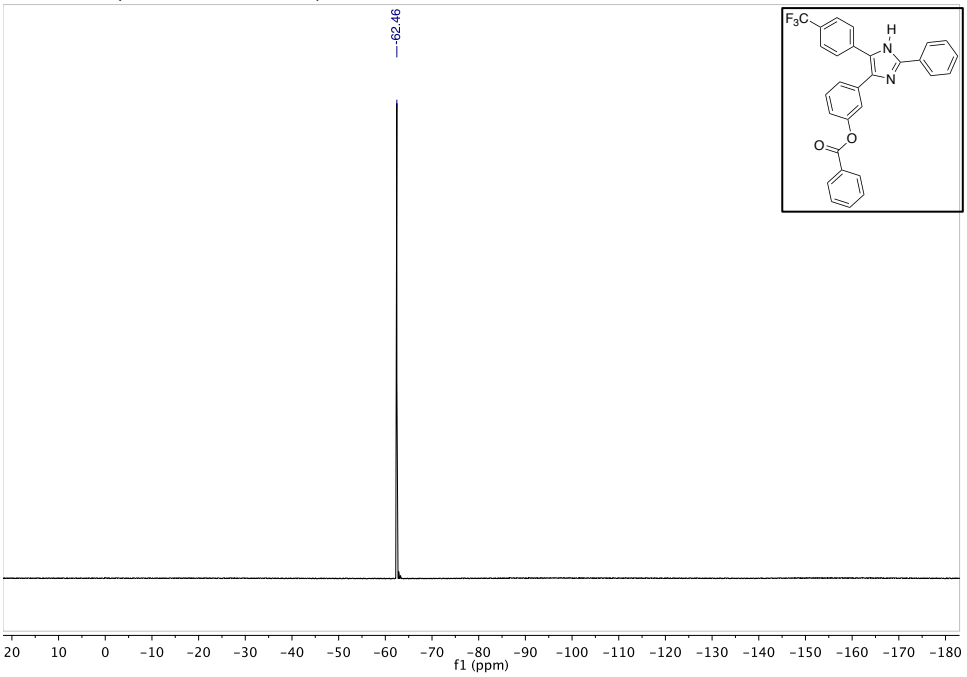
^{1}H NMR (600 MHz, $CDCl_3$)- **9**



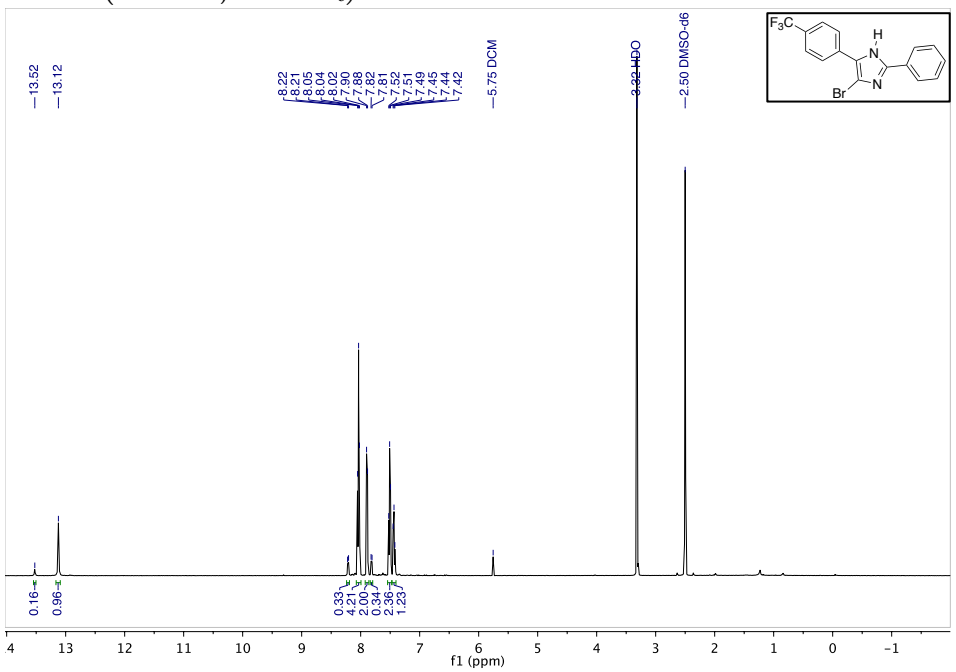
^{13}C NMR (151 MHz, $CDCl_3$)- **9**



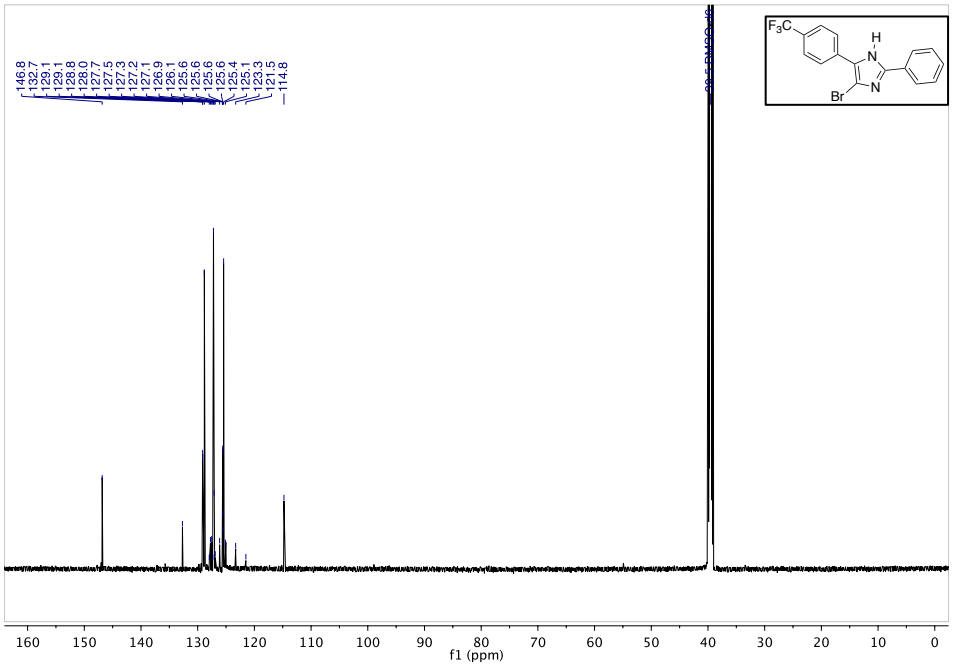
^{19}F NMR (470 MHz, $CDCl_3$)- **9**



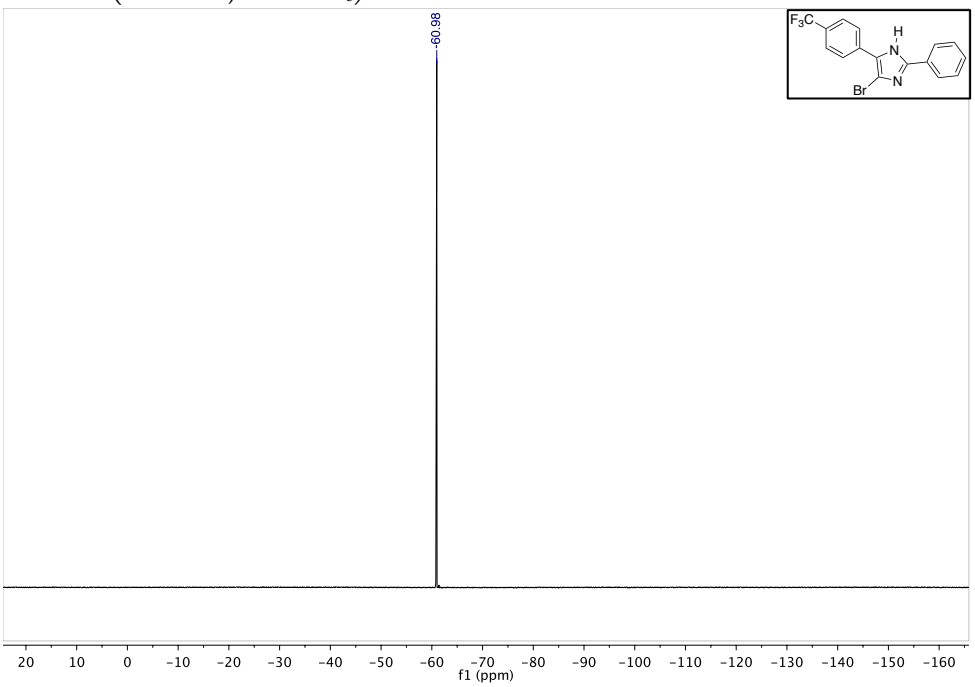
^{1}H NMR (600 MHz, DMSO-d_6)- **10**



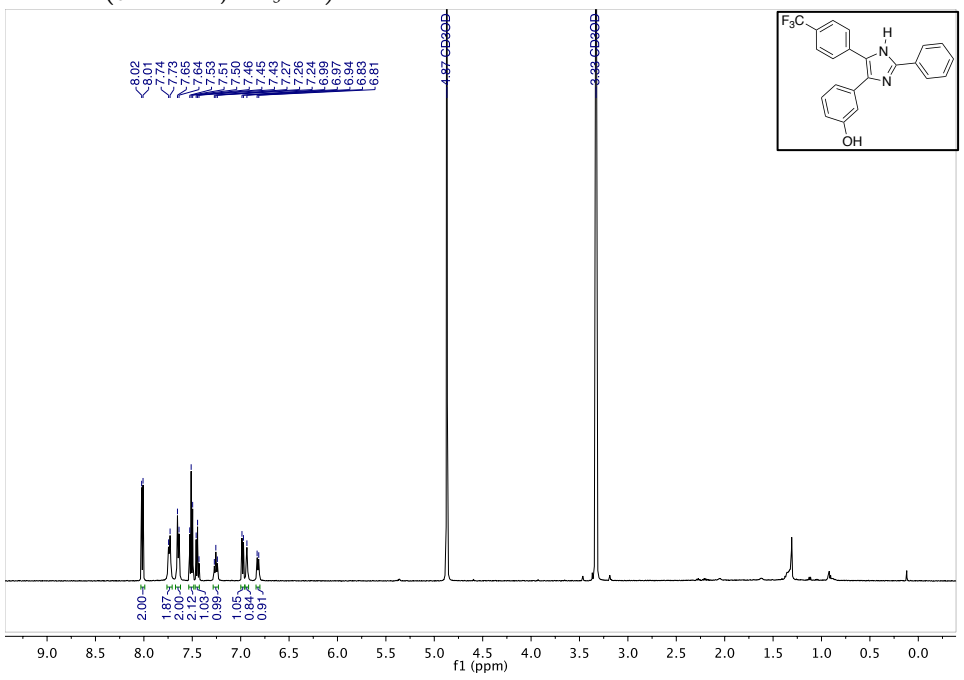
^{13}C NMR (151 MHz, DMSO-d_6)- **10**



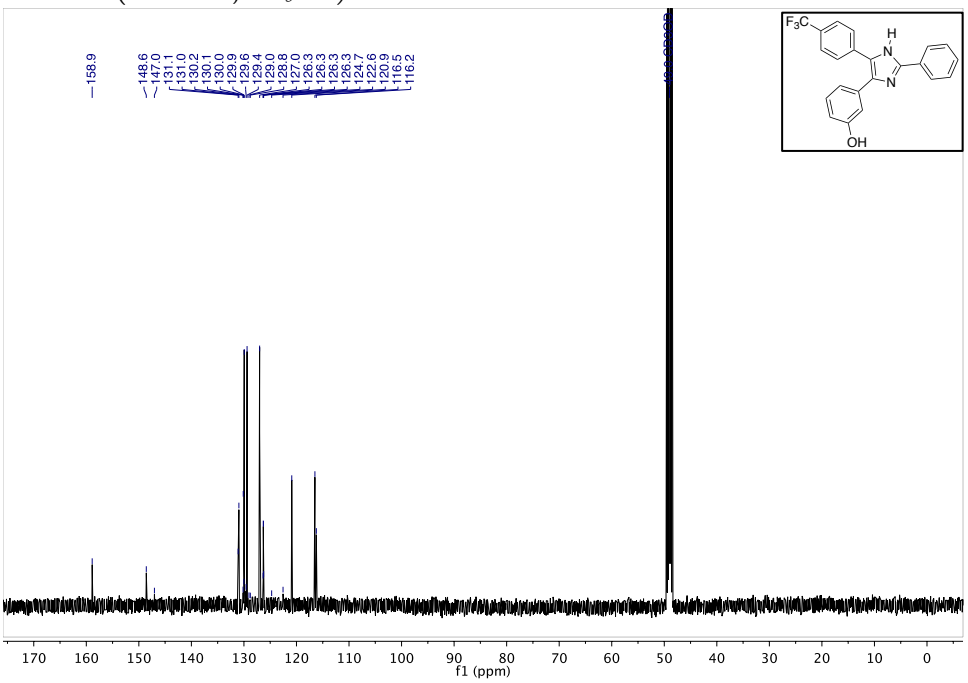
^{19}F NMR (471 MHz, DMSO-d_6)- **10**



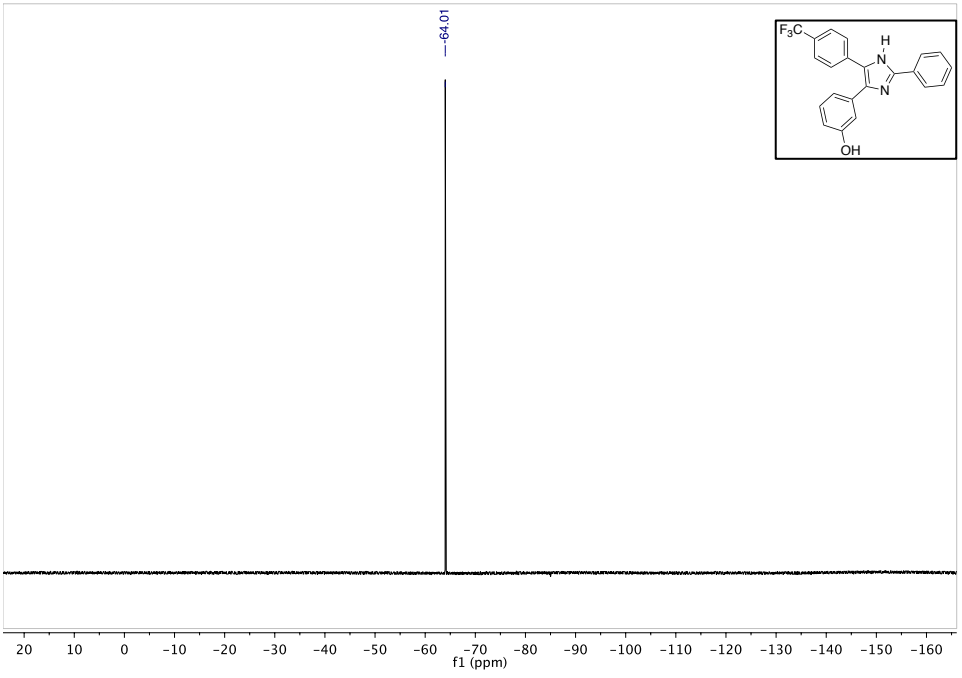
^{1}H NMR (500 MHz, CD_3OD)- **11**



^{13}C NMR (126 MHz, CD_3OD)- **11**



^{19}F NMR (471 MHz, CD_3OD)- **11**



VI. CRYSTALLOGRAPHY DATA

i. Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of amides **7a**, **7b**, **8a**, and **9**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[4] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

For **9**, the N-H was semi-freely refined with a distance restraint of 0.88(2) Å. Several reflections were improperly recorded and omitted from the refinement. The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (120.5 e/Å^3), it is likely that ~2.5 THF molecules, 10 waters, or some combination of these solvents are present in the unit cell. See "_platon_squeeze_details" in this .cif for more information.

Full numbering schemes and additional refinement details for **7a**, **7b**, **8a**, and **9** can be found in the crystallographic information files (.cif), which are provided as supplementary information. The CCDC numbers for **7a** (1897303), **7b** (1895220), **8a** (1895221), and **9** (1895222) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

ii. X-ray Crystal Structure of 7a

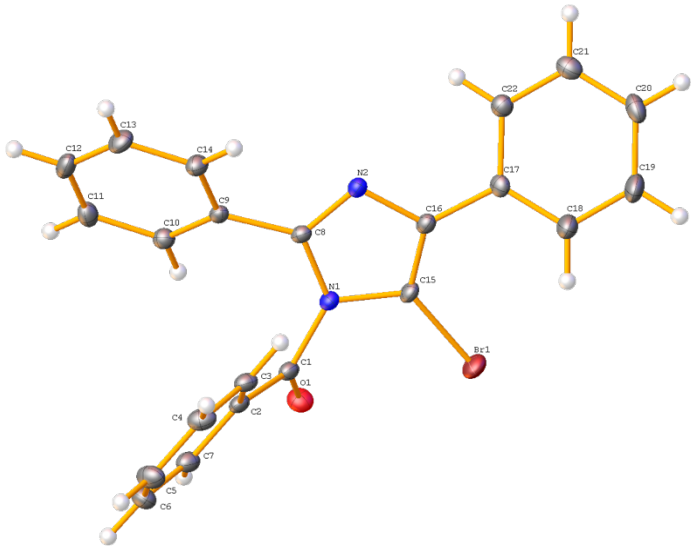


Figure S1. The complete numbering scheme of **7a** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S1. Crystal data and structure refinement for **7a**.

Identification code	007c-19018	
Empirical formula	C22 H15 Br N2 O	
Formula weight	403.27	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.1665(4) Å	α= 90°
	b = 9.7005(3) Å	β= 92.260(3)°
	c = 14.0951(4) Å	γ = 90°
Volume	1798.85(9) $Å^3$	
Z	4	
Density (calculated)	1.489 Mg/m^3	
Absorption coefficient	2.298 mm^{-1}	
F(000)	816	
Crystal size	0.200 x 0.200 x 0.120 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.953 to 27.484°.	
Index ranges	-17<=h<=17, -12<=k<=12, -18<=l<=18	
Reflections collected	41455	
Independent reflections	4125 [R(int) = 0.0294]	
Observed reflections (I > 2sigma(I))	3704	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.36603	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4125 / 0 / 235	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0230, wR2 = 0.0575	
R indices (all data)	R1 = 0.0272, wR2 = 0.0591	
Largest diff. peak and hole	0.350 and -0.313 $e.Å^{-3}$	

Table S2. Atomic coordinates ($x\ 10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for **7a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	5568(1)	3334(1)	4396(1)	21(1)
O(1)	3351(1)	2414(1)	4883(1)	20(1)
N(1)	3582(1)	3616(1)	3510(1)	14(1)
N(2)	3839(1)	4274(1)	2022(1)	14(1)
C(1)	3101(1)	3395(2)	4408(1)	14(1)
C(2)	2367(1)	4464(2)	4693(1)	14(1)
C(3)	2328(1)	5776(2)	4280(1)	16(1)
C(4)	1676(1)	6763(2)	4627(1)	20(1)
C(5)	1057(1)	6444(2)	5375(1)	24(1)
C(6)	1086(1)	5136(2)	5777(1)	22(1)
C(7)	1744(1)	4148(2)	5445(1)	18(1)
C(8)	3144(1)	3955(1)	2630(1)	13(1)
C(9)	2049(1)	3860(2)	2372(1)	13(1)
C(10)	1413(1)	2884(2)	2774(1)	16(1)
C(11)	398(1)	2789(2)	2462(1)	19(1)
C(12)	8(1)	3653(2)	1754(1)	21(1)
C(13)	635(1)	4630(2)	1354(1)	21(1)
C(14)	1652(1)	4728(2)	1659(1)	17(1)
C(15)	4631(1)	3733(2)	3410(1)	14(1)
C(16)	4779(1)	4160(2)	2503(1)	14(1)
C(17)	5714(1)	4496(2)	2007(1)	15(1)
C(18)	6583(1)	5034(2)	2476(1)	24(1)
C(19)	7422(1)	5411(2)	1965(1)	27(1)
C(20)	7411(1)	5256(2)	983(1)	22(1)
C(21)	6552(1)	4729(2)	514(1)	20(1)
C(22)	5712(1)	4354(2)	1019(1)	17(1)

Table S3. Bond lengths [Å] and angles [°] for **7a**.

Br(1)-C(15)	1.8624(14)	C(18)-C(19)	1.391(2)
O(1)-C(1)	1.2026(18)	C(18)-H(18)	0.9500
N(1)-C(8)	1.3871(17)	C(19)-C(20)	1.392(2)
N(1)-C(15)	1.3998(18)	C(19)-H(19)	0.9500
N(1)-C(1)	1.4520(18)	C(20)-C(21)	1.385(2)
N(2)-C(8)	1.3143(19)	C(20)-H(20)	0.9500
N(2)-C(16)	1.3922(18)	C(21)-C(22)	1.387(2)
C(1)-C(2)	1.484(2)	C(21)-H(21)	0.9500
C(2)-C(3)	1.400(2)	C(22)-H(22)	0.9500
C(2)-C(7)	1.400(2)		
C(3)-C(4)	1.388(2)	C(8)-N(1)-C(15)	105.48(12)
C(3)-H(3)	0.9500	C(8)-N(1)-C(1)	129.37(12)
C(4)-C(5)	1.392(2)	C(15)-N(1)-C(1)	124.50(12)
C(4)-H(4)	0.9500	C(8)-N(2)-C(16)	107.00(12)
C(5)-C(6)	1.390(2)	O(1)-C(1)-N(1)	118.86(13)
C(5)-H(5)	0.9500	O(1)-C(1)-C(2)	124.67(13)
C(6)-C(7)	1.385(2)	N(1)-C(1)-C(2)	116.38(12)
C(6)-H(6)	0.9500	C(3)-C(2)-C(7)	120.05(14)
C(7)-H(7)	0.9500	C(3)-C(2)-C(1)	122.40(13)
C(8)-C(9)	1.4760(19)	C(7)-C(2)-C(1)	117.42(13)
C(9)-C(14)	1.397(2)	C(4)-C(3)-C(2)	119.60(14)
C(9)-C(10)	1.398(2)	C(4)-C(3)-H(3)	120.2
C(10)-C(11)	1.393(2)	C(2)-C(3)-H(3)	120.2
C(10)-H(10)	0.9500	C(3)-C(4)-C(5)	120.14(15)
C(11)-C(12)	1.386(2)	C(3)-C(4)-H(4)	119.9
C(11)-H(11)	0.9500	C(5)-C(4)-H(4)	119.9
C(12)-C(13)	1.392(2)	C(6)-C(5)-C(4)	120.27(15)
C(12)-H(12)	0.9500	C(6)-C(5)-H(5)	119.9
C(13)-C(14)	1.394(2)	C(4)-C(5)-H(5)	119.9
C(13)-H(13)	0.9500	C(7)-C(6)-C(5)	120.09(15)
C(14)-H(14)	0.9500	C(7)-C(6)-H(6)	120.0
C(15)-C(16)	1.365(2)	C(5)-C(6)-H(6)	120.0
C(16)-C(17)	1.476(2)	C(6)-C(7)-C(2)	119.84(14)
C(17)-C(22)	1.400(2)	C(6)-C(7)-H(7)	120.1
C(17)-C(18)	1.400(2)	C(2)-C(7)-H(7)	120.1

N(2)-C(8)-N(1)	111.34(12)	N(1)-C(15)-Br(1)	122.32(11)
N(2)-C(8)-C(9)	123.53(12)	C(15)-C(16)-N(2)	108.86(12)
N(1)-C(8)-C(9)	124.94(13)	C(15)-C(16)-C(17)	131.52(13)
C(14)-C(9)-C(10)	119.13(13)	N(2)-C(16)-C(17)	119.62(12)
C(14)-C(9)-C(8)	118.25(13)	C(22)-C(17)-C(18)	118.43(14)
C(10)-C(9)-C(8)	122.51(13)	C(22)-C(17)-C(16)	118.73(13)
C(11)-C(10)-C(9)	120.00(14)	C(18)-C(17)-C(16)	122.71(13)
C(11)-C(10)-H(10)	120.0	C(19)-C(18)-C(17)	120.30(15)
C(9)-C(10)-H(10)	120.0	C(19)-C(18)-H(18)	119.8
C(12)-C(11)-C(10)	120.69(14)	C(17)-C(18)-H(18)	119.8
C(12)-C(11)-H(11)	119.7	C(18)-C(19)-C(20)	120.64(15)
C(10)-C(11)-H(11)	119.7	C(18)-C(19)-H(19)	119.7
C(11)-C(12)-C(13)	119.64(14)	C(20)-C(19)-H(19)	119.7
C(11)-C(12)-H(12)	120.2	C(21)-C(20)-C(19)	119.33(14)
C(13)-C(12)-H(12)	120.2	C(21)-C(20)-H(20)	120.3
C(12)-C(13)-C(14)	120.01(14)	C(19)-C(20)-H(20)	120.3
C(12)-C(13)-H(13)	120.0	C(20)-C(21)-C(22)	120.38(14)
C(14)-C(13)-H(13)	120.0	C(20)-C(21)-H(21)	119.8
C(13)-C(14)-C(9)	120.53(14)	C(22)-C(21)-H(21)	119.8
C(13)-C(14)-H(14)	119.7	C(21)-C(22)-C(17)	120.90(14)
C(9)-C(14)-H(14)	119.7	C(21)-C(22)-H(22)	119.5
C(16)-C(15)-N(1)	107.30(12)	C(17)-C(22)-H(22)	119.5
C(16)-C(15)-Br(1)	130.39(11)		

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	17(1)	28(1)	18(1)	4(1)	-6(1)	2(1)
O(1)	23(1)	19(1)	18(1)	5(1)	1(1)	2(1)
N(1)	12(1)	17(1)	12(1)	0(1)	-2(1)	1(1)
N(2)	12(1)	16(1)	13(1)	-1(1)	-1(1)	1(1)
C(1)	14(1)	17(1)	12(1)	0(1)	-2(1)	-3(1)
C(2)	14(1)	16(1)	11(1)	-1(1)	-3(1)	-2(1)
C(3)	19(1)	18(1)	12(1)	0(1)	-2(1)	-2(1)

C(4)	27(1)	18(1)	16(1)	0(1)	-2(1)	4(1)
C(5)	25(1)	27(1)	19(1)	-3(1)	1(1)	9(1)
C(6)	20(1)	29(1)	16(1)	0(1)	4(1)	1(1)
C(7)	20(1)	19(1)	14(1)	1(1)	-1(1)	-4(1)
C(8)	14(1)	13(1)	11(1)	-1(1)	-1(1)	1(1)
C(9)	12(1)	15(1)	12(1)	-3(1)	0(1)	1(1)
C(10)	16(1)	16(1)	15(1)	0(1)	0(1)	1(1)
C(11)	15(1)	19(1)	22(1)	-3(1)	4(1)	-3(1)
C(12)	13(1)	26(1)	23(1)	-7(1)	-3(1)	1(1)
C(13)	19(1)	25(1)	18(1)	1(1)	-6(1)	3(1)
C(14)	17(1)	20(1)	14(1)	2(1)	-1(1)	-2(1)
C(15)	11(1)	18(1)	14(1)	-1(1)	-3(1)	2(1)
C(16)	12(1)	16(1)	14(1)	-2(1)	-1(1)	2(1)
C(17)	12(1)	16(1)	17(1)	1(1)	1(1)	4(1)
C(18)	15(1)	36(1)	19(1)	1(1)	-1(1)	-2(1)
C(19)	13(1)	42(1)	27(1)	4(1)	-3(1)	-3(1)
C(20)	14(1)	27(1)	26(1)	7(1)	6(1)	3(1)
C(21)	22(1)	19(1)	18(1)	2(1)	4(1)	3(1)
C(22)	16(1)	16(1)	17(1)	-1(1)	1(1)	1(1)

Table S5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **7a**.

	x	y	z	U(eq)
H(3)	2746	5989	3766	19
H(4)	1653	7658	4354	25
H(5)	613	7124	5611	28
H(6)	654	4919	6280	26
H(7)	1772	3259	5728	21
H(10)	1673	2287	3259	19
H(11)	-31	2124	2738	22
H(12)	-685	3578	1544	25
H(13)	370	5230	872	25
H(14)	2080	5391	1379	21
H(18)	6600	5144	3146	28
H(19)	8008	5777	2289	33

H(20)	7987	5511	637	27
H(21)	6539	4623	-156	24
H(22)	5126	3996	689	20

Table S6. Torsion angles [°] for **7a**.

C(8)-N(1)-C(1)-O(1)	134.54(15)
C(15)-N(1)-C(1)-O(1)	-56.1(2)
C(8)-N(1)-C(1)-C(2)	-48.8(2)
C(15)-N(1)-C(1)-C(2)	120.59(15)
O(1)-C(1)-C(2)-C(3)	159.72(14)
N(1)-C(1)-C(2)-C(3)	-16.77(19)
O(1)-C(1)-C(2)-C(7)	-16.2(2)
N(1)-C(1)-C(2)-C(7)	167.33(12)
C(7)-C(2)-C(3)-C(4)	0.6(2)
C(1)-C(2)-C(3)-C(4)	-175.21(13)
C(2)-C(3)-C(4)-C(5)	-0.7(2)
C(3)-C(4)-C(5)-C(6)	-0.1(2)
C(4)-C(5)-C(6)-C(7)	1.0(2)
C(5)-C(6)-C(7)-C(2)	-1.1(2)
C(3)-C(2)-C(7)-C(6)	0.3(2)
C(1)-C(2)-C(7)-C(6)	176.32(13)
C(16)-N(2)-C(8)-N(1)	-0.42(16)
C(16)-N(2)-C(8)-C(9)	-175.62(13)
C(15)-N(1)-C(8)-N(2)	-0.65(16)
C(1)-N(1)-C(8)-N(2)	170.25(13)
C(15)-N(1)-C(8)-C(9)	174.47(13)
C(1)-N(1)-C(8)-C(9)	-14.6(2)
N(2)-C(8)-C(9)-C(14)	-32.0(2)
N(1)-C(8)-C(9)-C(14)	153.47(14)
N(2)-C(8)-C(9)-C(10)	144.16(15)
N(1)-C(8)-C(9)-C(10)	-30.4(2)
C(14)-C(9)-C(10)-C(11)	-0.1(2)
C(8)-C(9)-C(10)-C(11)	-176.18(14)
C(9)-C(10)-C(11)-C(12)	0.0(2)

C(10)-C(11)-C(12)-C(13)	-0.3(2)
C(11)-C(12)-C(13)-C(14)	0.5(2)
C(12)-C(13)-C(14)-C(9)	-0.6(2)
C(10)-C(9)-C(14)-C(13)	0.3(2)
C(8)-C(9)-C(14)-C(13)	176.61(14)
C(8)-N(1)-C(15)-C(16)	1.48(15)
C(1)-N(1)-C(15)-C(16)	-170.00(13)
C(8)-N(1)-C(15)-Br(1)	-178.28(10)
C(1)-N(1)-C(15)-Br(1)	10.25(19)
N(1)-C(15)-C(16)-N(2)	-1.78(16)
Br(1)-C(15)-C(16)-N(2)	177.95(11)
N(1)-C(15)-C(16)-C(17)	177.88(14)
Br(1)-C(15)-C(16)-C(17)	-2.4(3)
C(8)-N(2)-C(16)-C(15)	1.38(16)
C(8)-N(2)-C(16)-C(17)	-178.32(13)
C(15)-C(16)-C(17)-C(22)	153.71(16)
N(2)-C(16)-C(17)-C(22)	-26.7(2)
C(15)-C(16)-C(17)-C(18)	-30.5(3)
N(2)-C(16)-C(17)-C(18)	149.12(15)
C(22)-C(17)-C(18)-C(19)	-0.3(2)
C(16)-C(17)-C(18)-C(19)	-176.07(15)
C(17)-C(18)-C(19)-C(20)	-0.1(3)
C(18)-C(19)-C(20)-C(21)	0.3(3)
C(19)-C(20)-C(21)-C(22)	-0.2(2)
C(20)-C(21)-C(22)-C(17)	-0.2(2)
C(18)-C(17)-C(22)-C(21)	0.4(2)
C(16)-C(17)-C(22)-C(21)	176.40(14)

iii. X-ray Crystal Structure of 7b

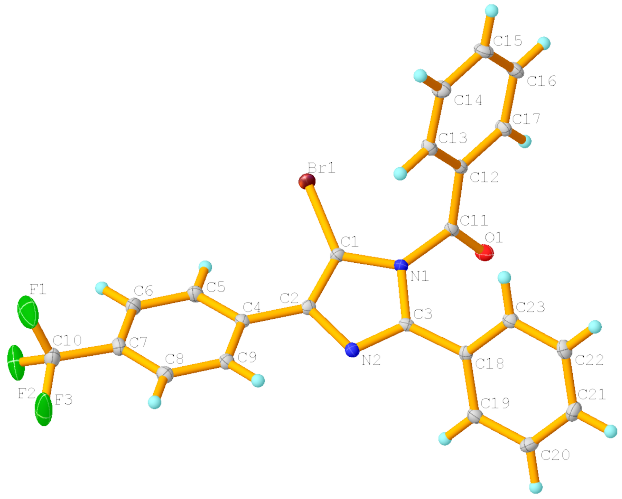


Figure S2. The complete numbering scheme of **7b** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S7. Crystal data and structure refinement for **7b**.

Identification code	007c-18060	
Empirical formula	$C_{23}H_{14}BrF_3N_2O$	
Formula weight	471.27	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7260(3) Å	α= 89.849(3)°
	b = 10.3996(4) Å	β= 83.645(3)°
	c = 10.9045(4) Å	γ = 63.084(4)°
Volume	976.02(7) $Å^3$	
Z	2	
Density (calculated)	1.604 Mg/m^3	
Absorption coefficient	2.151 mm^{-1}	
F(000)	472	
Crystal size	0.200 x 0.200 x 0.160 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.931 to 27.479°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	26563	

Independent reflections	4484 [R(int) = 0.0330]
Observed reflections (I > 2sigma(I))	4134
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.82615
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	4484 / 0 / 271
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0660
R indices (all data)	R1 = 0.0296, wR2 = 0.0674
Largest diff. peak and hole	0.478 and -0.373 e.Å^{-3}

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **7b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7096(1)	7711(1)	3834(1)	17(1)
Br(1)	5583(1)	6036(1)	1096(1)	19(1)
N(1)	6550(2)	5832(1)	3496(1)	12(1)
F(1)	6622(2)	-1233(2)	-313(2)	49(1)
C(1)	6544(2)	5081(2)	2441(1)	13(1)
N(2)	7821(2)	3483(1)	3809(1)	12(1)
C(2)	7328(2)	3639(2)	2642(1)	12(1)
F(2)	8908(2)	-1753(2)	-1118(1)	39(1)
C(3)	7371(2)	4794(2)	4286(1)	11(1)
F(3)	8568(2)	-2611(1)	597(1)	61(1)
C(4)	7560(2)	2350(2)	1914(2)	12(1)
C(5)	7635(2)	2291(2)	621(2)	16(1)
C(6)	7797(2)	1062(2)	-12(2)	18(1)
C(7)	7901(2)	-128(2)	643(2)	17(1)
C(8)	7861(2)	-98(2)	1923(2)	16(1)
C(9)	7692(2)	1136(2)	2552(2)	14(1)
C(10)	7999(2)	-1424(2)	-37(2)	21(1)
C(11)	6103(2)	7371(2)	3659(1)	12(1)

C(12)	4442(2)	8379(2)	3654(1)	12(1)
C(13)	3302(2)	7907(2)	3713(2)	14(1)
C(14)	1750(2)	8912(2)	3757(2)	17(1)
C(15)	1332(2)	10379(2)	3743(2)	18(1)
C(16)	2466(2)	10851(2)	3688(2)	19(1)
C(17)	4020(2)	9860(2)	3646(2)	16(1)
C(18)	7585(2)	5110(2)	5547(1)	11(1)
C(19)	9018(2)	4295(2)	5978(2)	14(1)
C(20)	9218(2)	4522(2)	7186(2)	18(1)
C(21)	7990(2)	5557(2)	7978(2)	18(1)
C(22)	6562(2)	6370(2)	7555(2)	17(1)
C(23)	6353(2)	6152(2)	6343(2)	14(1)

Table S9. Bond lengths [Å] and angles [°] for **7b**.

O(1)-C(11)	1.201(2)	C(7)-C(10)	1.500(2)
Br(1)-C(1)	1.8621(16)	C(8)-C(9)	1.390(2)
N(1)-C(3)	1.383(2)	C(8)-H(8)	0.9500
N(1)-C(1)	1.395(2)	C(9)-H(9)	0.9500
N(1)-C(11)	1.461(2)	C(11)-C(12)	1.476(2)
F(1)-C(10)	1.331(2)	C(12)-C(13)	1.397(2)
C(1)-C(2)	1.370(2)	C(12)-C(17)	1.404(2)
N(2)-C(3)	1.317(2)	C(13)-C(14)	1.388(2)
N(2)-C(2)	1.392(2)	C(13)-H(13)	0.9500
C(2)-C(4)	1.473(2)	C(14)-C(15)	1.390(2)
F(2)-C(10)	1.336(2)	C(14)-H(14)	0.9500
C(3)-C(18)	1.472(2)	C(15)-C(16)	1.391(3)
F(3)-C(10)	1.330(2)	C(15)-H(15)	0.9500
C(4)-C(9)	1.401(2)	C(16)-C(17)	1.386(2)
C(4)-C(5)	1.404(2)	C(16)-H(16)	0.9500
C(5)-C(6)	1.390(2)	C(17)-H(17)	0.9500
C(5)-H(5)	0.9500	C(18)-C(19)	1.398(2)
C(6)-C(7)	1.396(2)	C(18)-C(23)	1.402(2)
C(6)-H(6)	0.9500	C(19)-C(20)	1.390(2)
C(7)-C(8)	1.392(2)	C(19)-H(19)	0.9500

C(20)-C(21)	1.394(2)	C(8)-C(9)-C(4)	120.83(15)
C(20)-H(20)	0.9500	C(8)-C(9)-H(9)	119.6
C(21)-C(22)	1.390(3)	C(4)-C(9)-H(9)	119.6
C(21)-H(21)	0.9500	F(3)-C(10)-F(1)	106.92(17)
C(22)-C(23)	1.394(2)	F(3)-C(10)-F(2)	105.82(17)
C(22)-H(22)	0.9500	F(1)-C(10)-F(2)	105.16(15)
C(23)-H(23)	0.9500	F(3)-C(10)-C(7)	112.87(15)
		F(1)-C(10)-C(7)	112.40(15)
C(3)-N(1)-C(1)	106.00(13)	F(2)-C(10)-C(7)	113.06(16)
C(3)-N(1)-C(11)	124.78(13)	O(1)-C(11)-N(1)	117.88(14)
C(1)-N(1)-C(11)	127.97(13)	O(1)-C(11)-C(12)	125.32(15)
C(2)-C(1)-N(1)	106.95(13)	N(1)-C(11)-C(12)	116.73(13)
C(2)-C(1)-Br(1)	131.36(12)	C(13)-C(12)-C(17)	120.17(15)
N(1)-C(1)-Br(1)	121.69(11)	C(13)-C(12)-C(11)	122.21(14)
C(3)-N(2)-C(2)	106.79(13)	C(17)-C(12)-C(11)	117.56(14)
C(1)-C(2)-N(2)	108.96(14)	C(14)-C(13)-C(12)	119.56(15)
C(1)-C(2)-C(4)	131.32(15)	C(14)-C(13)-H(13)	120.2
N(2)-C(2)-C(4)	119.40(14)	C(12)-C(13)-H(13)	120.2
N(2)-C(3)-N(1)	111.27(14)	C(13)-C(14)-C(15)	120.29(16)
N(2)-C(3)-C(18)	124.06(14)	C(13)-C(14)-H(14)	119.9
N(1)-C(3)-C(18)	124.42(14)	C(15)-C(14)-H(14)	119.9
C(9)-C(4)-C(5)	118.85(15)	C(14)-C(15)-C(16)	120.19(16)
C(9)-C(4)-C(2)	117.97(14)	C(14)-C(15)-H(15)	119.9
C(5)-C(4)-C(2)	123.18(15)	C(16)-C(15)-H(15)	119.9
C(6)-C(5)-C(4)	120.50(16)	C(17)-C(16)-C(15)	120.20(16)
C(6)-C(5)-H(5)	119.7	C(17)-C(16)-H(16)	119.9
C(4)-C(5)-H(5)	119.7	C(15)-C(16)-H(16)	119.9
C(5)-C(6)-C(7)	119.76(16)	C(16)-C(17)-C(12)	119.58(15)
C(5)-C(6)-H(6)	120.1	C(16)-C(17)-H(17)	120.2
C(7)-C(6)-H(6)	120.1	C(12)-C(17)-H(17)	120.2
C(8)-C(7)-C(6)	120.46(15)	C(19)-C(18)-C(23)	119.56(15)
C(8)-C(7)-C(10)	119.95(16)	C(19)-C(18)-C(3)	119.26(14)
C(6)-C(7)-C(10)	119.55(16)	C(23)-C(18)-C(3)	121.08(14)
C(9)-C(8)-C(7)	119.58(15)	C(20)-C(19)-C(18)	120.14(15)
C(9)-C(8)-H(8)	120.2	C(20)-C(19)-H(19)	119.9
C(7)-C(8)-H(8)	120.2	C(18)-C(19)-H(19)	119.9

C(19)-C(20)-C(21)	120.24(16)	C(21)-C(22)-C(23)	120.27(15)
C(19)-C(20)-H(20)	119.9	C(21)-C(22)-H(22)	119.9
C(21)-C(20)-H(20)	119.9	C(23)-C(22)-H(22)	119.9
C(22)-C(21)-C(20)	119.87(16)	C(22)-C(23)-C(18)	119.92(15)
C(22)-C(21)-H(21)	120.1	C(22)-C(23)-H(23)	120.0
C(20)-C(21)-H(21)	120.1	C(18)-C(23)-H(23)	120.0

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	15(1)	14(1)	22(1)	2(1)	-4(1)	-7(1)
Br(1)	27(1)	14(1)	13(1)	3(1)	-8(1)	-5(1)
N(1)	13(1)	9(1)	12(1)	1(1)	-3(1)	-3(1)
F(1)	30(1)	41(1)	77(1)	-28(1)	-5(1)	-18(1)
C(1)	14(1)	13(1)	10(1)	1(1)	-3(1)	-5(1)
N(2)	13(1)	11(1)	12(1)	0(1)	-2(1)	-4(1)
C(2)	12(1)	13(1)	10(1)	1(1)	-1(1)	-6(1)
F(2)	48(1)	38(1)	33(1)	-20(1)	11(1)	-26(1)
C(3)	10(1)	10(1)	12(1)	2(1)	-1(1)	-4(1)
F(3)	131(2)	18(1)	37(1)	7(1)	-42(1)	-30(1)
C(4)	10(1)	11(1)	14(1)	-1(1)	-2(1)	-3(1)
C(5)	20(1)	13(1)	14(1)	2(1)	-3(1)	-6(1)
C(6)	23(1)	17(1)	12(1)	0(1)	-4(1)	-7(1)
C(7)	18(1)	14(1)	18(1)	-2(1)	-4(1)	-6(1)
C(8)	18(1)	13(1)	17(1)	2(1)	-3(1)	-7(1)
C(9)	15(1)	14(1)	12(1)	1(1)	-2(1)	-6(1)
C(10)	29(1)	18(1)	18(1)	-1(1)	-7(1)	-10(1)
C(11)	15(1)	10(1)	10(1)	1(1)	-1(1)	-4(1)
C(12)	13(1)	10(1)	10(1)	1(1)	-1(1)	-3(1)
C(13)	16(1)	11(1)	14(1)	1(1)	0(1)	-6(1)
C(14)	13(1)	17(1)	20(1)	2(1)	-1(1)	-7(1)
C(15)	13(1)	15(1)	20(1)	1(1)	-2(1)	-1(1)
C(16)	19(1)	9(1)	25(1)	1(1)	-4(1)	-3(1)
C(17)	16(1)	12(1)	20(1)	0(1)	-3(1)	-6(1)

C(18)	14(1)	10(1)	11(1)	1(1)	-1(1)	-6(1)
C(19)	14(1)	12(1)	15(1)	0(1)	-1(1)	-4(1)
C(20)	16(1)	20(1)	17(1)	3(1)	-6(1)	-6(1)
C(21)	23(1)	21(1)	12(1)	0(1)	-4(1)	-11(1)
C(22)	18(1)	16(1)	14(1)	-3(1)	2(1)	-7(1)
C(23)	13(1)	13(1)	15(1)	1(1)	-2(1)	-6(1)

Table S11. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **7b**.

	x	y	z	U(eq)
H(5)	7576	3097	174	19
H(6)	7836	1032	-886	22
H(8)	7949	-915	2364	19
H(9)	7666	1156	3425	17
H(13)	3586	6904	3722	17
H(14)	971	8596	3797	21
H(15)	269	11062	3772	22
H(16)	2175	11854	3678	23
H(17)	4794	10183	3611	19
H(19)	9856	3585	5443	17
H(20)	10195	3970	7474	21
H(21)	8129	5707	8805	22
H(22)	5726	7076	8094	20
H(23)	5376	6710	6057	17

Table S12. Torsion angles [°] for **7b**.

C(3)-N(1)-C(1)-C(2)	0.99(17)
C(11)-N(1)-C(1)-C(2)	168.58(14)
C(3)-N(1)-C(1)-Br(1)	-179.31(11)
C(11)-N(1)-C(1)-Br(1)	-11.7(2)
N(1)-C(1)-C(2)-N(2)	0.05(18)
Br(1)-C(1)-C(2)-N(2)	-179.62(12)
N(1)-C(1)-C(2)-C(4)	173.30(16)
Br(1)-C(1)-C(2)-C(4)	-6.4(3)
C(3)-N(2)-C(2)-C(1)	-1.12(18)
C(3)-N(2)-C(2)-C(4)	-175.31(14)
C(2)-N(2)-C(3)-N(1)	1.79(18)
C(2)-N(2)-C(3)-C(18)	176.33(14)
C(1)-N(1)-C(3)-N(2)	-1.77(18)
C(11)-N(1)-C(3)-N(2)	-169.86(14)
C(1)-N(1)-C(3)-C(18)	-176.28(14)
C(11)-N(1)-C(3)-C(18)	15.6(2)
C(1)-C(2)-C(4)-C(9)	-148.39(18)
N(2)-C(2)-C(4)-C(9)	24.3(2)
C(1)-C(2)-C(4)-C(5)	30.9(3)
N(2)-C(2)-C(4)-C(5)	-156.47(15)
C(9)-C(4)-C(5)-C(6)	1.7(2)
C(2)-C(4)-C(5)-C(6)	-177.53(16)
C(4)-C(5)-C(6)-C(7)	-0.7(3)
C(5)-C(6)-C(7)-C(8)	-0.7(3)
C(5)-C(6)-C(7)-C(10)	177.10(16)
C(6)-C(7)-C(8)-C(9)	1.0(3)
C(10)-C(7)-C(8)-C(9)	-176.80(16)
C(7)-C(8)-C(9)-C(4)	0.1(2)
C(5)-C(4)-C(9)-C(8)	-1.4(2)
C(2)-C(4)-C(9)-C(8)	177.87(15)
C(8)-C(7)-C(10)-F(3)	-21.9(3)
C(6)-C(7)-C(10)-F(3)	160.31(18)
C(8)-C(7)-C(10)-F(1)	99.1(2)
C(6)-C(7)-C(10)-F(1)	-78.6(2)
C(8)-C(7)-C(10)-F(2)	-141.98(17)

C(6)-C(7)-C(10)-F(2)	40.2(2)
C(3)-N(1)-C(11)-O(1)	50.9(2)
C(1)-N(1)-C(11)-O(1)	-114.54(18)
C(3)-N(1)-C(11)-C(12)	-126.30(16)
C(1)-N(1)-C(11)-C(12)	68.3(2)
O(1)-C(11)-C(12)-C(13)	-165.88(16)
N(1)-C(11)-C(12)-C(13)	11.1(2)
O(1)-C(11)-C(12)-C(17)	11.3(2)
N(1)-C(11)-C(12)-C(17)	-171.79(14)
C(17)-C(12)-C(13)-C(14)	0.3(2)
C(11)-C(12)-C(13)-C(14)	177.32(15)
C(12)-C(13)-C(14)-C(15)	0.0(3)
C(13)-C(14)-C(15)-C(16)	-0.1(3)
C(14)-C(15)-C(16)-C(17)	0.0(3)
C(15)-C(16)-C(17)-C(12)	0.3(3)
C(13)-C(12)-C(17)-C(16)	-0.4(2)
C(11)-C(12)-C(17)-C(16)	-177.59(15)
N(2)-C(3)-C(18)-C(19)	45.1(2)
N(1)-C(3)-C(18)-C(19)	-141.04(16)
N(2)-C(3)-C(18)-C(23)	-131.06(17)
N(1)-C(3)-C(18)-C(23)	42.8(2)
C(23)-C(18)-C(19)-C(20)	-0.2(2)
C(3)-C(18)-C(19)-C(20)	-176.44(15)
C(18)-C(19)-C(20)-C(21)	0.3(3)
C(19)-C(20)-C(21)-C(22)	-0.3(3)
C(20)-C(21)-C(22)-C(23)	0.1(3)
C(21)-C(22)-C(23)-C(18)	0.0(2)
C(19)-C(18)-C(23)-C(22)	0.0(2)
C(3)-C(18)-C(23)-C(22)	176.18(15)

iii. Crystallographic Data for 8a

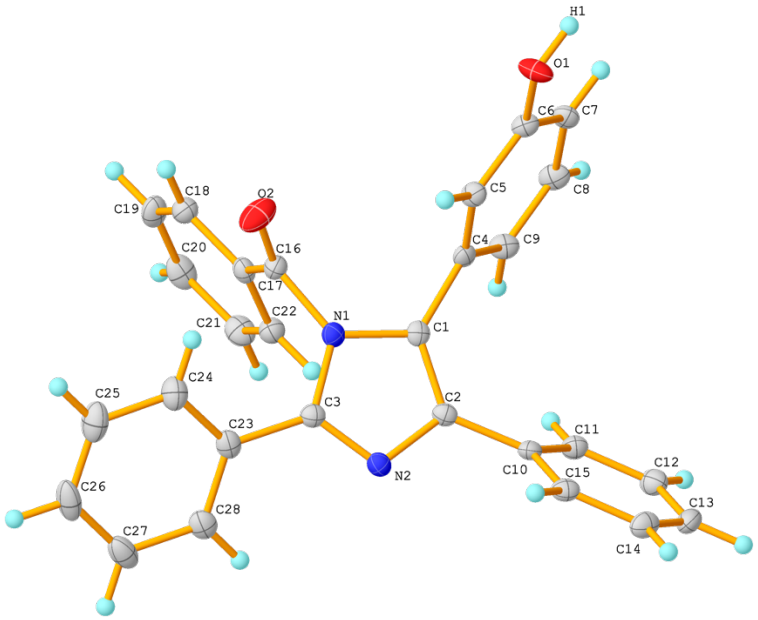


Figure S3. The complete numbering scheme of **8a** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S13. Crystal data and structure refinement for **8a**.

Identification code	007c-18041	
Empirical formula	$C_{28}H_{20}N_2O_2$	
Formula weight	416.46	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 18.8189(6) Å	α= 90°
	b = 6.4080(2) Å	β= 90°
	c = 17.3173(7) Å	γ = 90°
Volume	2088.32(13) $Å^3$	
Z	4	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	872	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Dectris Pilatus 3R	

Theta range for data collection	3.197 to 27.484°.
Index ranges	-24<=h<=17, -8<=k<=8, -22<=l<=21
Reflections collected	14429
Independent reflections	4623 [R(int) = 0.0216]
Observed reflections (I > 2sigma(I))	4310
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.69220
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	4623 / 1 / 293
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0788
R indices (all data)	R1 = 0.0349, wR2 = 0.0802
Absolute structure parameter	0.2(4)
Largest diff. peak and hole	0.203 and -0.193 e.Å^{-3}

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **8a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4566(1)	6857(2)	7406(1)	23(1)
O(2)	6724(1)	8245(2)	5734(1)	32(1)
N(1)	6312(1)	5617(3)	4937(1)	16(1)
N(2)	5914(1)	4089(2)	3873(1)	16(1)
C(1)	5812(1)	4134(3)	5175(1)	15(1)
C(2)	5575(1)	3212(3)	4504(1)	15(1)
C(3)	6360(1)	5499(3)	4145(1)	16(1)
C(4)	5581(1)	3897(3)	5988(1)	16(1)
C(5)	5229(1)	5535(3)	6358(1)	17(1)
C(6)	4936(1)	5247(3)	7093(1)	17(1)
C(7)	5015(1)	3319(3)	7464(1)	18(1)
C(8)	5380(1)	1722(3)	7101(1)	21(1)
C(9)	5664(1)	1985(3)	6364(1)	19(1)
C(10)	5004(1)	1651(3)	4387(1)	16(1)

C(11)	5041(1)	-339(3)	4712(1)	18(1)
C(12)	4502(1)	-1782(3)	4584(1)	22(1)
C(13)	3923(1)	-1255(3)	4124(1)	22(1)
C(14)	3888(1)	710(3)	3792(1)	21(1)
C(15)	4423(1)	2165(3)	3920(1)	18(1)
C(16)	6834(1)	6546(3)	5466(1)	17(1)
C(17)	7464(1)	5249(3)	5622(1)	17(1)
C(18)	8004(1)	6086(3)	6091(1)	21(1)
C(19)	8603(1)	4908(4)	6249(1)	25(1)
C(20)	8670(1)	2916(4)	5944(1)	26(1)
C(21)	8137(1)	2074(3)	5486(1)	25(1)
C(22)	7532(1)	3229(3)	5321(1)	19(1)
C(23)	6843(1)	6770(3)	3666(1)	19(1)
C(24)	7011(1)	8828(3)	3865(1)	26(1)
C(25)	7476(1)	9972(4)	3406(2)	31(1)
C(26)	7768(1)	9106(4)	2749(1)	31(1)
C(27)	7589(1)	7086(4)	2535(1)	28(1)
C(28)	7125(1)	5912(3)	2991(1)	21(1)

Table S15. Bond lengths [Å] and angles [°] for **8a**.

O(1)-C(6)	1.358(2)	C(6)-C(7)	1.401(3)
O(2)-C(16)	1.201(2)	C(7)-C(8)	1.384(3)
N(1)-C(3)	1.376(2)	C(8)-C(9)	1.393(3)
N(1)-C(1)	1.399(2)	C(10)-C(11)	1.396(3)
N(1)-C(16)	1.469(2)	C(10)-C(15)	1.399(3)
N(2)-C(3)	1.321(3)	C(11)-C(12)	1.391(3)
N(2)-C(2)	1.385(3)	C(12)-C(13)	1.391(3)
C(1)-C(2)	1.377(3)	C(13)-C(14)	1.385(3)
C(1)-C(4)	1.482(3)	C(14)-C(15)	1.390(3)
C(2)-C(10)	1.482(2)	C(16)-C(17)	1.473(3)
C(3)-C(23)	1.475(3)	C(17)-C(22)	1.401(3)
C(4)-C(9)	1.396(3)	C(17)-C(18)	1.407(3)
C(4)-C(5)	1.396(3)	C(18)-C(19)	1.385(3)
C(5)-C(6)	1.400(3)	C(19)-C(20)	1.387(3)

C(20)-C(21)	1.387(3)	C(7)-C(8)-C(9)	121.11(18)
C(21)-C(22)	1.388(3)	C(8)-C(9)-C(4)	119.44(18)
C(23)-C(28)	1.397(3)	C(11)-C(10)-C(15)	119.15(18)
C(23)-C(24)	1.399(3)	C(11)-C(10)-C(2)	121.68(17)
C(24)-C(25)	1.390(3)	C(15)-C(10)-C(2)	119.15(17)
C(25)-C(26)	1.381(4)	C(12)-C(11)-C(10)	120.48(18)
C(26)-C(27)	1.388(4)	C(11)-C(12)-C(13)	120.07(19)
C(27)-C(28)	1.397(3)	C(14)-C(13)-C(12)	119.67(18)
		C(13)-C(14)-C(15)	120.63(19)
C(3)-N(1)-C(1)	107.47(16)	C(14)-C(15)-C(10)	120.00(19)
C(3)-N(1)-C(16)	126.80(16)	O(2)-C(16)-N(1)	119.55(18)
C(1)-N(1)-C(16)	122.79(16)	O(2)-C(16)-C(17)	125.34(19)
C(3)-N(2)-C(2)	106.79(16)	N(1)-C(16)-C(17)	115.11(16)
C(2)-C(1)-N(1)	105.15(16)	C(22)-C(17)-C(18)	120.02(17)
C(2)-C(1)-C(4)	131.48(17)	C(22)-C(17)-C(16)	121.79(17)
N(1)-C(1)-C(4)	123.12(17)	C(18)-C(17)-C(16)	118.19(18)
C(1)-C(2)-N(2)	109.98(16)	C(19)-C(18)-C(17)	119.65(19)
C(1)-C(2)-C(10)	129.82(18)	C(18)-C(19)-C(20)	119.99(19)
N(2)-C(2)-C(10)	119.99(17)	C(21)-C(20)-C(19)	120.70(19)
N(2)-C(3)-N(1)	110.57(17)	C(20)-C(21)-C(22)	120.2(2)
N(2)-C(3)-C(23)	124.65(18)	C(21)-C(22)-C(17)	119.47(19)
N(1)-C(3)-C(23)	124.78(17)	C(28)-C(23)-C(24)	119.36(19)
C(9)-C(4)-C(5)	119.90(18)	C(28)-C(23)-C(3)	119.19(18)
C(9)-C(4)-C(1)	120.06(18)	C(24)-C(23)-C(3)	121.44(19)
C(5)-C(4)-C(1)	119.84(17)	C(25)-C(24)-C(23)	119.9(2)
C(4)-C(5)-C(6)	120.28(17)	C(26)-C(25)-C(24)	120.7(2)
O(1)-C(6)-C(5)	117.71(17)	C(25)-C(26)-C(27)	119.8(2)
O(1)-C(6)-C(7)	122.74(18)	C(26)-C(27)-C(28)	120.2(2)
C(5)-C(6)-C(7)	119.51(17)	C(27)-C(28)-C(23)	119.9(2)
C(8)-C(7)-C(6)	119.72(19)		

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) **8a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	34(1)	21(1)	15(1)	1(1)	6(1)	7(1)
O(2)	27(1)	24(1)	46(1)	-15(1)	-7(1)	5(1)
N(1)	13(1)	18(1)	17(1)	1(1)	0(1)	1(1)
N(2)	15(1)	18(1)	14(1)	2(1)	0(1)	1(1)
C(1)	13(1)	14(1)	18(1)	1(1)	-1(1)	2(1)
C(2)	16(1)	16(1)	14(1)	1(1)	-1(1)	2(1)
C(3)	16(1)	17(1)	15(1)	-1(1)	-1(1)	2(1)
C(4)	14(1)	20(1)	14(1)	0(1)	-3(1)	-3(1)
C(5)	21(1)	15(1)	16(1)	2(1)	-2(1)	-1(1)
C(6)	20(1)	16(1)	16(1)	-1(1)	-3(1)	1(1)
C(7)	22(1)	21(1)	12(1)	3(1)	-1(1)	-2(1)
C(8)	28(1)	18(1)	17(1)	3(1)	-5(1)	2(1)
C(9)	20(1)	19(1)	19(1)	-2(1)	-2(1)	4(1)
C(10)	17(1)	19(1)	11(1)	-3(1)	1(1)	-1(1)
C(11)	19(1)	20(1)	15(1)	0(1)	-2(1)	0(1)
C(12)	27(1)	19(1)	20(1)	-1(1)	1(1)	-2(1)
C(13)	20(1)	24(1)	22(1)	-8(1)	1(1)	-6(1)
C(14)	16(1)	26(1)	22(1)	-5(1)	-3(1)	3(1)
C(15)	19(1)	18(1)	16(1)	-3(1)	-1(1)	4(1)
C(16)	16(1)	18(1)	18(1)	-2(1)	1(1)	-2(1)
C(17)	15(1)	21(1)	16(1)	4(1)	1(1)	-2(1)
C(18)	22(1)	21(1)	19(1)	0(1)	-1(1)	-3(1)
C(19)	18(1)	34(1)	22(1)	6(1)	-6(1)	-6(1)
C(20)	18(1)	34(1)	27(1)	10(1)	0(1)	6(1)
C(21)	26(1)	22(1)	26(1)	1(1)	4(1)	4(1)
C(22)	19(1)	21(1)	18(1)	0(1)	0(1)	-1(1)
C(23)	15(1)	22(1)	18(1)	5(1)	-2(1)	0(1)
C(24)	23(1)	23(1)	31(1)	3(1)	2(1)	-3(1)
C(25)	26(1)	26(1)	40(1)	12(1)	-4(1)	-6(1)
C(26)	21(1)	43(1)	29(1)	21(1)	-2(1)	-7(1)
C(27)	20(1)	45(1)	19(1)	9(1)	1(1)	1(1)
C(28)	19(1)	26(1)	19(1)	5(1)	-3(1)	2(1)

Table S17. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **8a**.

	x	y	z	U(eq)
H(1)	4399(15)	6570(40)	7896(19)	35(7)
H(5)	5189	6851	6109	21
H(7)	4819	3109	7964	22
H(8)	5439	423	7358	25
H(9)	5911	874	6120	23
H(11)	5437	-710	5023	22
H(12)	4529	-3129	4811	26
H(13)	3553	-2238	4037	27
H(14)	3494	1067	3475	26
H(15)	4395	3508	3690	21
H(18)	7957	7452	6298	25
H(19)	8969	5465	6566	30
H(20)	9085	2120	6049	32
H(21)	8187	703	5284	30
H(22)	7167	2655	5008	23
H(24)	6808	9443	4312	31
H(25)	7593	11363	3547	37
H(26)	8091	9891	2444	37
H(27)	7783	6500	2078	34
H(28)	7000	4534	2841	26

Table S18. Torsion angles [°] for **8a**.

C(3)-N(1)-C(1)-C(2)	-0.9(2)
C(16)-N(1)-C(1)-C(2)	-162.66(16)
C(3)-N(1)-C(1)-C(4)	-175.76(17)
C(16)-N(1)-C(1)-C(4)	22.5(3)
N(1)-C(1)-C(2)-N(2)	-0.1(2)
C(4)-C(1)-C(2)-N(2)	174.21(19)
N(1)-C(1)-C(2)-C(10)	-174.62(17)
C(4)-C(1)-C(2)-C(10)	-0.4(3)
C(3)-N(2)-C(2)-C(1)	1.0(2)
C(3)-N(2)-C(2)-C(10)	176.20(16)

C(2)-N(2)-C(3)-N(1)	-1.6(2)
C(2)-N(2)-C(3)-C(23)	178.37(17)
C(1)-N(1)-C(3)-N(2)	1.6(2)
C(16)-N(1)-C(3)-N(2)	162.42(17)
C(1)-N(1)-C(3)-C(23)	-178.37(17)
C(16)-N(1)-C(3)-C(23)	-17.6(3)
C(2)-C(1)-C(4)-C(9)	64.5(3)
N(1)-C(1)-C(4)-C(9)	-122.1(2)
C(2)-C(1)-C(4)-C(5)	-110.3(2)
N(1)-C(1)-C(4)-C(5)	63.1(2)
C(9)-C(4)-C(5)-C(6)	-2.3(3)
C(1)-C(4)-C(5)-C(6)	172.56(18)
C(4)-C(5)-C(6)-O(1)	-176.38(17)
C(4)-C(5)-C(6)-C(7)	1.7(3)
O(1)-C(6)-C(7)-C(8)	177.87(19)
C(5)-C(6)-C(7)-C(8)	-0.1(3)
C(6)-C(7)-C(8)-C(9)	-0.9(3)
C(7)-C(8)-C(9)-C(4)	0.3(3)
C(5)-C(4)-C(9)-C(8)	1.3(3)
C(1)-C(4)-C(9)-C(8)	-173.57(18)
C(1)-C(2)-C(10)-C(11)	-62.6(3)
N(2)-C(2)-C(10)-C(11)	123.3(2)
C(1)-C(2)-C(10)-C(15)	119.2(2)
N(2)-C(2)-C(10)-C(15)	-54.9(2)
C(15)-C(10)-C(11)-C(12)	-1.0(3)
C(2)-C(10)-C(11)-C(12)	-179.16(19)
C(10)-C(11)-C(12)-C(13)	0.5(3)
C(11)-C(12)-C(13)-C(14)	0.2(3)
C(12)-C(13)-C(14)-C(15)	-0.5(3)
C(13)-C(14)-C(15)-C(10)	0.0(3)
C(11)-C(10)-C(15)-C(14)	0.8(3)
C(2)-C(10)-C(15)-C(14)	178.95(18)
C(3)-N(1)-C(16)-O(2)	102.5(2)
C(1)-N(1)-C(16)-O(2)	-99.4(2)
C(3)-N(1)-C(16)-C(17)	-77.7(2)
C(1)-N(1)-C(16)-C(17)	80.4(2)

O(2)-C(16)-C(17)-C(22)	176.2(2)
N(1)-C(16)-C(17)-C(22)	-3.7(3)
O(2)-C(16)-C(17)-C(18)	-3.5(3)
N(1)-C(16)-C(17)-C(18)	176.68(17)
C(22)-C(17)-C(18)-C(19)	0.4(3)
C(16)-C(17)-C(18)-C(19)	-179.95(18)
C(17)-C(18)-C(19)-C(20)	0.1(3)
C(18)-C(19)-C(20)-C(21)	-0.6(3)
C(19)-C(20)-C(21)-C(22)	0.6(3)
C(20)-C(21)-C(22)-C(17)	-0.1(3)
C(18)-C(17)-C(22)-C(21)	-0.4(3)
C(16)-C(17)-C(22)-C(21)	179.92(19)
N(2)-C(3)-C(23)-C(28)	-32.7(3)
N(1)-C(3)-C(23)-C(28)	147.2(2)
N(2)-C(3)-C(23)-C(24)	145.7(2)
N(1)-C(3)-C(23)-C(24)	-34.3(3)
C(28)-C(23)-C(24)-C(25)	-2.4(3)
C(3)-C(23)-C(24)-C(25)	179.12(19)
C(23)-C(24)-C(25)-C(26)	0.8(3)
C(24)-C(25)-C(26)-C(27)	1.0(3)
C(25)-C(26)-C(27)-C(28)	-1.2(3)
C(26)-C(27)-C(28)-C(23)	-0.4(3)
C(24)-C(23)-C(28)-C(27)	2.2(3)
C(3)-C(23)-C(28)-C(27)	-179.28(19)

Table S19. Hydrogen bonds for **8a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(2)[a]	0.92(3)	1.84(3)	2.764(2)	178(3)

Symmetry transformations used to generate equivalent atoms: [a] -x+1,-y+1,z+1/2

iv. Crystallographic Data for 9

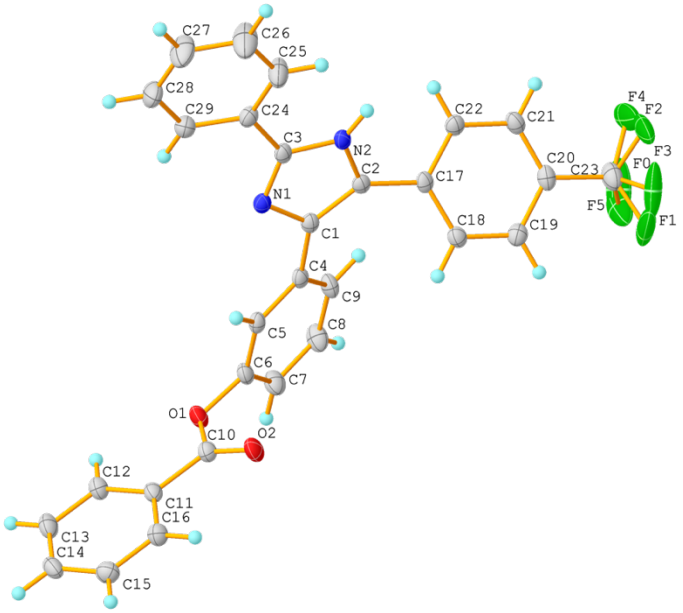


Figure S4. The complete numbering scheme of **9** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S20. Crystal data and structure refinement for **9**.

Identification code	007c-18069	
Empirical formula	C29 H19 F3 N2 O2	
Formula weight	484.46	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 17.1312(5) Å	α= 90°
	b = 8.1191(3) Å	β= 91.392(3)°
	c = 18.3582(5) Å	γ = 90°
Volume	2552.69(14) $Å^3$	
Z	4	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	1000	
Crystal size	0.200 x 0.200 x 0.050 mm^3	
Crystal color and habit	Colorless Plate	

Diffractometer	Dectris Pilatus 3R
Theta range for data collection	2.979 to 27.484°.
Index ranges	-22<=h<=21, -9<=k<=10, -22<=l<=23
Reflections collected	25853
Independent reflections	5777 [R(int) = 0.0276]
Observed reflections (I > 2sigma(I))	4814
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.70203
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	5777 / 32 / 357
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0877
R indices (all data)	R1 = 0.0455, wR2 = 0.0918
Largest diff. peak and hole	0.266 and -0.196 e.$Å^{-3}$

Table S21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(0)	4266(4)	10221(12)	1519(5)	88(2)
F(1)	4873(5)	8064(4)	1318(2)	73(2)
F(2)	5526(2)	10214(7)	1546(1)	52(2)
F(3)	5299(2)	8606(6)	1352(1)	70(2)
F(4)	5184(3)	11129(5)	1674(1)	58(1)
F(5)	4201(2)	9712(7)	1485(3)	51(1)
O(1)	2202(1)	3464(1)	5966(1)	23(1)
O(2)	2913(1)	1439(1)	5454(1)	28(1)
N(1)	4776(1)	6566(1)	5922(1)	18(1)
N(2)	5620(1)	7748(1)	5191(1)	18(1)
C(1)	4417(1)	6840(1)	5250(1)	18(1)
C(2)	4942(1)	7568(1)	4781(1)	18(1)
C(3)	5500(1)	7115(1)	5867(1)	18(1)
C(4)	3589(1)	6382(1)	5144(1)	18(1)

C(5)	3294(1)	5101(1)	5571(1)	19(1)
C(6)	2516(1)	4672(1)	5500(1)	21(1)
C(7)	2005(1)	5457(2)	5021(1)	27(1)
C(8)	2297(1)	6736(2)	4602(1)	28(1)
C(9)	3075(1)	7208(1)	4664(1)	24(1)
C(10)	2452(1)	1887(1)	5905(1)	21(1)
C(11)	2097(1)	788(1)	6451(1)	21(1)
C(12)	1626(1)	1406(2)	6997(1)	23(1)
C(13)	1322(1)	341(2)	7511(1)	26(1)
C(14)	1481(1)	-1331(2)	7471(1)	27(1)
C(15)	1941(1)	-1956(2)	6921(1)	28(1)
C(16)	2254(1)	-899(2)	6412(1)	25(1)
C(17)	4916(1)	8080(1)	4011(1)	18(1)
C(18)	4473(1)	7209(1)	3488(1)	21(1)
C(19)	4469(1)	7681(2)	2762(1)	23(1)
C(20)	4904(1)	9038(2)	2545(1)	23(1)
C(21)	5349(1)	9911(1)	3055(1)	23(1)
C(22)	5358(1)	9429(1)	3783(1)	21(1)
C(23)	4897(1)	9513(2)	1755(1)	33(1)
C(24)	6107(1)	7060(1)	6445(1)	22(1)
C(25)	6889(1)	7353(2)	6297(1)	38(1)
C(26)	7454(1)	7233(3)	6846(1)	55(1)
C(27)	7252(1)	6821(2)	7549(1)	48(1)
C(28)	6478(1)	6538(2)	7702(1)	35(1)
C(29)	5908(1)	6658(2)	7158(1)	26(1)

Table S22. Bond lengths [Å] and angles [°] for **9**.

F(0)-C(23)	1.290(7)	O(1)-C(6)	1.4157(13)
F(1)-C(23)	1.424(3)	O(2)-C(10)	1.2130(13)
F(2)-C(23)	1.286(2)	N(1)-C(3)	1.3252(14)
F(3)-C(23)	1.260(3)	N(1)-C(1)	1.3842(14)
F(4)-C(23)	1.410(3)	N(2)-C(3)	1.3624(14)
F(5)-C(23)	1.290(4)	N(2)-C(2)	1.3773(15)
O(1)-C(10)	1.3549(14)	N(2)-H(2)	0.894(13)

C(1)-C(2)	1.3916(15)	C(22)-H(22)	0.9500
C(1)-C(4)	1.4747(15)	C(24)-C(25)	1.3940(17)
C(2)-C(17)	1.4727(15)	C(24)-C(29)	1.3989(16)
C(3)-C(24)	1.4681(16)	C(25)-C(26)	1.384(2)
C(4)-C(9)	1.4013(16)	C(25)-H(25)	0.9500
C(4)-C(5)	1.4030(15)	C(26)-C(27)	1.385(2)
C(5)-C(6)	1.3814(16)	C(26)-H(26)	0.9500
C(5)-H(5)	0.9500	C(27)-C(28)	1.383(2)
C(6)-C(7)	1.3809(17)	C(27)-H(27)	0.9500
C(7)-C(8)	1.3928(17)	C(28)-C(29)	1.3824(18)
C(7)-H(7)	0.9500	C(28)-H(28)	0.9500
C(8)-C(9)	1.3900(17)	C(29)-H(29)	0.9500
C(8)-H(8)	0.9500		
C(9)-H(9)	0.9500	C(10)-O(1)-C(6)	118.66(8)
C(10)-C(11)	1.4836(15)	C(3)-N(1)-C(1)	105.89(9)
C(11)-C(12)	1.3954(15)	C(3)-N(2)-C(2)	108.30(9)
C(11)-C(16)	1.3976(17)	C(3)-N(2)-H(2)	125.9(10)
C(12)-C(13)	1.3898(16)	C(2)-N(2)-H(2)	125.1(10)
C(12)-H(12)	0.9500	N(1)-C(1)-C(2)	109.88(9)
C(13)-C(14)	1.3866(18)	N(1)-C(1)-C(4)	118.77(9)
C(13)-H(13)	0.9500	C(2)-C(1)-C(4)	131.34(10)
C(14)-C(15)	1.3918(18)	N(2)-C(2)-C(1)	104.85(9)
C(14)-H(14)	0.9500	N(2)-C(2)-C(17)	120.05(9)
C(15)-C(16)	1.3858(17)	C(1)-C(2)-C(17)	135.08(10)
C(15)-H(15)	0.9500	N(1)-C(3)-N(2)	111.05(10)
C(16)-H(16)	0.9500	N(1)-C(3)-C(24)	125.56(10)
C(17)-C(18)	1.4003(16)	N(2)-C(3)-C(24)	123.38(10)
C(17)-C(22)	1.4019(15)	C(9)-C(4)-C(5)	118.51(10)
C(18)-C(19)	1.3857(16)	C(9)-C(4)-C(1)	123.30(10)
C(18)-H(18)	0.9500	C(5)-C(4)-C(1)	118.14(10)
C(19)-C(20)	1.3936(17)	C(6)-C(5)-C(4)	119.60(10)
C(19)-H(19)	0.9500	C(6)-C(5)-H(5)	120.2
C(20)-C(21)	1.3876(17)	C(4)-C(5)-H(5)	120.2
C(20)-C(23)	1.5006(16)	C(7)-C(6)-C(5)	122.59(10)
C(21)-C(22)	1.3916(16)	C(7)-C(6)-O(1)	117.39(10)
C(21)-H(21)	0.9500	C(5)-C(6)-O(1)	119.88(10)

C(6)-C(7)-C(8)	117.78(11)	C(18)-C(19)-C(20)	120.21(11)
C(6)-C(7)-H(7)	121.1	C(18)-C(19)-H(19)	119.9
C(8)-C(7)-H(7)	121.1	C(20)-C(19)-H(19)	119.9
C(9)-C(8)-C(7)	121.10(11)	C(21)-C(20)-C(19)	119.97(10)
C(9)-C(8)-H(8)	119.5	C(21)-C(20)-C(23)	120.79(11)
C(7)-C(8)-H(8)	119.5	C(19)-C(20)-C(23)	119.23(11)
C(8)-C(9)-C(4)	120.41(11)	C(20)-C(21)-C(22)	119.81(11)
C(8)-C(9)-H(9)	119.8	C(20)-C(21)-H(21)	120.1
C(4)-C(9)-H(9)	119.8	C(22)-C(21)-H(21)	120.1
O(2)-C(10)-O(1)	123.50(10)	C(21)-C(22)-C(17)	120.88(11)
O(2)-C(10)-C(11)	124.33(11)	C(21)-C(22)-H(22)	119.6
O(1)-C(10)-C(11)	112.17(9)	C(17)-C(22)-H(22)	119.6
C(12)-C(11)-C(16)	120.27(10)	F(2)-C(23)-F(0)	113.8(4)
C(12)-C(11)-C(10)	121.51(10)	F(3)-C(23)-F(5)	111.1(3)
C(16)-C(11)-C(10)	118.22(10)	F(3)-C(23)-F(4)	106.6(2)
C(13)-C(12)-C(11)	119.79(11)	F(5)-C(23)-F(4)	99.4(3)
C(13)-C(12)-H(12)	120.1	F(2)-C(23)-F(1)	102.1(2)
C(11)-C(12)-H(12)	120.1	F(0)-C(23)-F(1)	99.6(4)
C(14)-C(13)-C(12)	119.72(11)	F(3)-C(23)-C(20)	115.24(16)
C(14)-C(13)-H(13)	120.1	F(2)-C(23)-C(20)	114.58(14)
C(12)-C(13)-H(13)	120.1	F(0)-C(23)-C(20)	115.2(4)
C(13)-C(14)-C(15)	120.70(11)	F(5)-C(23)-C(20)	112.9(3)
C(13)-C(14)-H(14)	119.6	F(4)-C(23)-C(20)	110.31(14)
C(15)-C(14)-H(14)	119.6	F(1)-C(23)-C(20)	109.36(16)
C(16)-C(15)-C(14)	119.88(11)	C(25)-C(24)-C(29)	118.65(11)
C(16)-C(15)-H(15)	120.1	C(25)-C(24)-C(3)	121.30(11)
C(14)-C(15)-H(15)	120.1	C(29)-C(24)-C(3)	120.01(10)
C(15)-C(16)-C(11)	119.64(11)	C(26)-C(25)-C(24)	120.25(13)
C(15)-C(16)-H(16)	120.2	C(26)-C(25)-H(25)	119.9
C(11)-C(16)-H(16)	120.2	C(24)-C(25)-H(25)	119.9
C(18)-C(17)-C(22)	118.47(10)	C(25)-C(26)-C(27)	120.71(13)
C(18)-C(17)-C(2)	121.26(10)	C(25)-C(26)-H(26)	119.6
C(22)-C(17)-C(2)	120.23(10)	C(27)-C(26)-H(26)	119.6
C(19)-C(18)-C(17)	120.65(10)	C(28)-C(27)-C(26)	119.42(13)
C(19)-C(18)-H(18)	119.7	C(28)-C(27)-H(27)	120.3
C(17)-C(18)-H(18)	119.7	C(26)-C(27)-H(27)	120.3

C(29)-C(28)-C(27)	120.38(12)	C(28)-C(29)-C(24)	120.59(11)
C(29)-C(28)-H(28)	119.8	C(28)-C(29)-H(29)	119.7
C(27)-C(28)-H(28)	119.8	C(24)-C(29)-H(29)	119.7

Table S23. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(0)	90(4)	140(6)	33(2)	31(3)	11(3)	79(4)
F(1)	156(4)	46(2)	19(1)	-6(1)	20(2)	-17(2)
F(2)	48(2)	86(4)	23(1)	18(2)	1(1)	-32(2)
F(3)	90(3)	100(4)	21(1)	11(1)	20(1)	59(2)
F(4)	86(2)	60(2)	28(1)	20(1)	-7(1)	-37(2)
F(5)	34(1)	88(2)	30(1)	24(2)	-11(1)	-8(2)
O(1)	24(1)	22(1)	22(1)	3(1)	9(1)	-1(1)
O(2)	29(1)	27(1)	27(1)	0(1)	14(1)	-2(1)
N(1)	23(1)	16(1)	16(1)	-1(1)	2(1)	1(1)
N(2)	21(1)	18(1)	16(1)	-2(1)	4(1)	0(1)
C(1)	24(1)	13(1)	16(1)	-1(1)	3(1)	2(1)
C(2)	23(1)	13(1)	18(1)	-2(1)	4(1)	2(1)
C(3)	24(1)	15(1)	16(1)	-2(1)	5(1)	2(1)
C(4)	23(1)	18(1)	16(1)	-2(1)	5(1)	2(1)
C(5)	23(1)	18(1)	15(1)	-1(1)	4(1)	3(1)
C(6)	25(1)	21(1)	18(1)	1(1)	8(1)	-1(1)
C(7)	21(1)	35(1)	25(1)	4(1)	3(1)	0(1)
C(8)	25(1)	36(1)	24(1)	9(1)	1(1)	5(1)
C(9)	27(1)	24(1)	20(1)	6(1)	6(1)	2(1)
C(10)	20(1)	24(1)	20(1)	-1(1)	3(1)	-1(1)
C(11)	18(1)	25(1)	18(1)	1(1)	2(1)	-3(1)
C(12)	22(1)	26(1)	21(1)	2(1)	4(1)	0(1)
C(13)	22(1)	35(1)	22(1)	2(1)	5(1)	-1(1)
C(14)	26(1)	33(1)	22(1)	7(1)	1(1)	-9(1)
C(15)	33(1)	23(1)	27(1)	1(1)	0(1)	-4(1)
C(16)	25(1)	26(1)	23(1)	-2(1)	4(1)	-1(1)
C(17)	21(1)	16(1)	17(1)	-1(1)	6(1)	4(1)

C(18)	22(1)	20(1)	21(1)	0(1)	4(1)	0(1)
C(19)	23(1)	27(1)	20(1)	-1(1)	1(1)	1(1)
C(20)	25(1)	27(1)	19(1)	4(1)	4(1)	5(1)
C(21)	28(1)	18(1)	23(1)	3(1)	7(1)	1(1)
C(22)	27(1)	16(1)	20(1)	-2(1)	4(1)	1(1)
C(23)	33(1)	43(1)	23(1)	8(1)	2(1)	-1(1)
C(24)	25(1)	21(1)	18(1)	-4(1)	1(1)	0(1)
C(25)	28(1)	67(1)	20(1)	-2(1)	3(1)	-6(1)
C(26)	26(1)	110(2)	30(1)	-2(1)	-1(1)	-11(1)
C(27)	35(1)	82(1)	25(1)	-2(1)	-9(1)	-6(1)
C(28)	39(1)	46(1)	18(1)	0(1)	-2(1)	-7(1)
C(29)	29(1)	27(1)	22(1)	-1(1)	2(1)	-3(1)

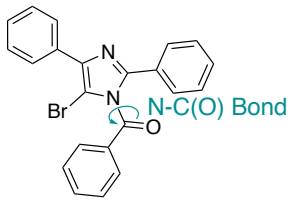
Table S24. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **9**.

	x	y	z	U(eq)
H(2)	6079(8)	8074(18)	5019(8)	34(4)
H(5)	3628	4531	5906	22
H(7)	1473	5135	4979	32
H(8)	1957	7296	4268	34
H(9)	3261	8095	4378	28
H(12)	1515	2550	7018	27
H(13)	1006	757	7887	31
H(14)	1275	-2057	7824	32
H(15)	2039	-3106	6894	33
H(16)	2573	-1319	6039	30
H(18)	4173	6286	3632	25
H(19)	4169	7078	2412	28
H(21)	5647	10834	2908	28
H(22)	5668	10022	4129	25
H(25)	7034	7637	5817	46
H(26)	7985	7434	6739	66
H(27)	7643	6734	7923	57
H(28)	6336	6260	8184	41
H(29)	5377	6465	7270	31

V. DFT CALCULATIONS

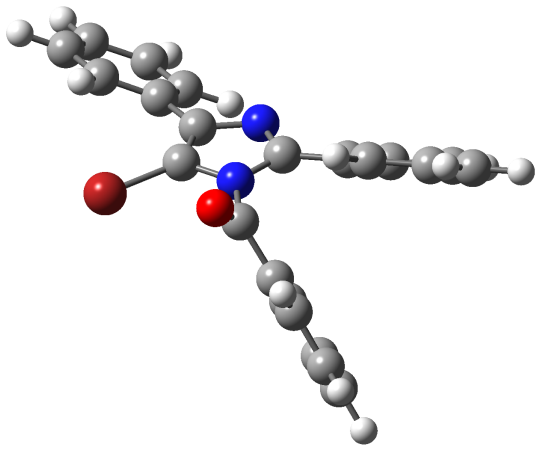
All DFT calculations were performed using the Gaussian16 program package, with visualization of input and output files accomplished using GausView 6.0.16.[6] X-ray crystal structures were used as the starting point for ground state geometry optimization. Rotational barriers were derived from a triple-ζ geometry optimization of the stationary points of a relaxed torsional potential energy scan of the N-C(O) axis at the B3LYP/6-311++G(d,p) level, including D3 version of Grimme's dispersion correction.[7] Gibbs free energies refer to gas phase conditions at standard temperature (298.15 K) and pressure (1 atm). No imaginary frequencies were observed for ground states; transitions states were verified by occurrence of one imaginary frequency (shown below). Their assignment to stationary points was verified by visual inspection and optimization of distorted transition state structures in both directions of the imaginary frequency. In the following sections, the abbreviations GS (ground state) and TS (transition state) are used.

i. (5-Bromo-2,4-diphenyl-1*H*-imidazol-1-yl)(phenyl)methanone (7a)



Entry	GS/TS	Conformer	E (Hartree)	$G^{\ddagger}_{298\ K}$ (Hartree)	$DG^{\ddagger}_{298\ K}$ (kcal/mol)	ν_{imag} (cm^{-1})
1	GS	(a*R*)	–3606.243772	–3606.297384	0.00	none
2	TS	1	–3606.229982	–3606.281036	10.26	–38.68
3	GS	(a*S*)	–3606.243772	–3606.297384	0.00	none
4	TS	2	–3606.229593	–3606.281059	10.24	–46.36

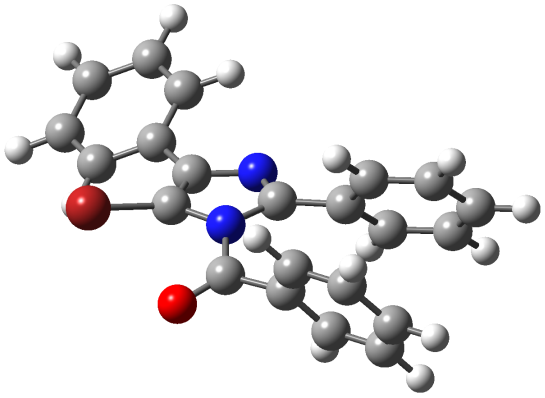
(7a)-1 GS, (a*R*)



C	4.24636200	-0.00635700	-0.37729200
C	3.21663300	0.78862100	0.14540500
C	3.55653000	1.88292100	0.95583800
C	4.88707000	2.15988100	1.25146300
C	1.13818400	-0.65211000	-0.40615400
C	-0.30101000	1.04137000	-0.39922800
C	1.79960000	0.53000500	-0.14342300
N	-0.20943900	-0.33659800	-0.55559800
N	0.87960700	1.55952600	-0.15141400
C	5.57732000	0.27374600	-0.07904200
H	6.36105500	-0.34905200	-0.49571100
C	5.90398400	1.35360600	0.73955500
H	6.94111000	1.56982900	0.96999600
H	5.13155500	3.00748300	1.88213500

C	-1.53763700	1.81539100	-0.55634400
C	-2.52125900	1.46691600	-1.49118200
C	-1.72548100	2.95291800	0.24129500
C	-3.68320800	2.22534700	-1.60442500
H	-2.37181100	0.62055800	-2.15076500
C	-2.88538000	3.70975600	0.12144800
H	-0.95415600	3.22890200	0.94965300
C	-3.87178900	3.34485100	-0.79626800
H	-4.43553900	1.94702700	-2.33347800
H	-3.02283700	4.58439500	0.74713200
H	-4.77691100	3.93459200	-0.88615800
H	2.76560900	2.51292000	1.34327700
H	4.01091100	-0.83364100	-1.03334100
C	-1.28409700	-1.29188500	-0.77060100
O	-1.24967100	-2.01842100	-1.73016100
C	-2.34742900	-1.31044300	0.26100200
C	-2.16819200	-0.74671400	1.53027500
C	-3.55164900	-1.95613100	-0.05192800
C	-3.18856000	-0.82141800	2.47272300
H	-1.23496000	-0.25992100	1.78248600
C	-4.57133000	-2.01801600	0.88797500
H	-3.66867100	-2.39584800	-1.03474600
C	-4.39090100	-1.44966300	2.15124200
H	-3.04617900	-0.38891100	3.45594600
H	-5.50598900	-2.50782100	0.64106200
H	-5.18750300	-1.49943700	2.88501400
Br	1.72897000	-2.43827800	-0.35503200

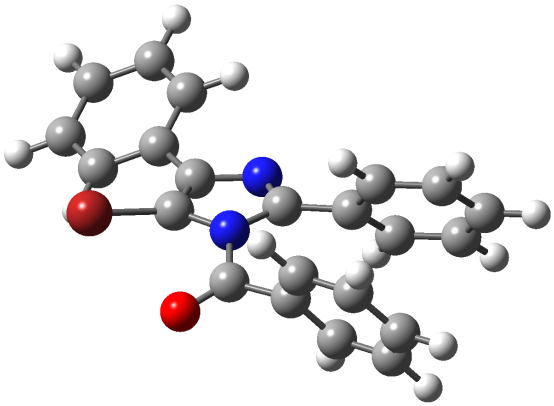
(7a)-2 TS, 1



C	4.27334600	0.10668300	0.66862700
C	3.27012800	0.88336700	0.07164800
C	3.62360700	2.10833000	-0.51521100
C	4.94855700	2.53202500	-0.52411700
C	1.28360400	-0.76802500	0.02232600
C	-0.29061800	0.82445900	-0.01257800
C	1.85985100	0.47344400	0.06781300
N	-0.11851300	-0.58065900	-0.00112100
N	0.85710100	1.43493800	0.04758000
C	5.59763200	0.53531200	0.65951900
H	6.36067900	-0.07471700	1.12985900
C	5.94195100	1.74572700	0.05935000
H	6.97443300	2.07663300	0.05255100
H	5.20622300	3.47823500	-0.98675500
C	-1.55896900	1.56996300	-0.11768800
C	-2.42921300	1.38307400	-1.19668100
C	-1.84694700	2.55081500	0.83698600
C	-3.59314400	2.13692500	-1.29504800
H	-2.19710000	0.64298400	-1.95170600
C	-3.01270400	3.30505800	0.73585000
H	-1.15383800	2.71151600	1.65383400
C	-3.89173100	3.09419000	-0.32539000
H	-4.26655000	1.97779200	-2.12909700
H	-3.23386700	4.05694400	1.48486000

H	-4.80209100	3.67798700	-0.40138300
H	2.84815000	2.72062300	-0.95807400
H	4.01708600	-0.82461300	1.15575000
C	-1.05938300	-1.59523500	0.38480900
O	-0.67525000	-2.67107400	0.76438900
C	-2.52568200	-1.30021700	0.28674000
C	-3.19329200	-0.63238800	1.31343700
C	-3.23778500	-1.81225800	-0.79866600
C	-4.56929300	-0.44253500	1.23280700
H	-2.63899100	-0.24445800	2.15940800
C	-4.61446400	-1.61769900	-0.87600200
H	-2.71628400	-2.35387300	-1.57979700
C	-5.27993400	-0.92736000	0.13561400
H	-5.08448500	0.08996700	2.02344600
H	-5.16602400	-2.00736500	-1.72391200
H	-6.35084600	-0.77211500	0.07235700
Br	2.12178000	-2.41968100	-0.32361500

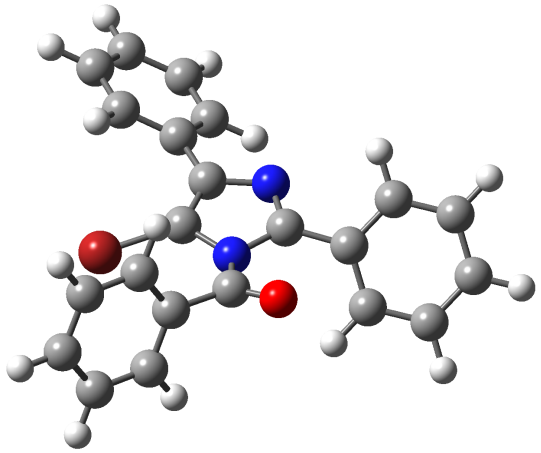
(7a)-3 GS, (a*S*)



C	-4.24635600	-0.00631000	-0.37731000
C	-3.21662400	0.78865300	0.14540400
C	-3.55651300	1.88293800	0.95586100
C	-4.88705200	2.15990000	1.25149100
C	-1.13819700	-0.65210000	-0.40615200
C	0.30102000	1.04136000	-0.39923700
C	-1.79959400	0.53002500	-0.14342700
N	0.20943200	-0.33661000	-0.55560000
N	-0.87958700	1.55953600	-0.15142200
C	-5.57731300	0.27379500	-0.07905400
H	-6.36105200	-0.34899100	-0.49573500
C	-5.90397100	1.35364100	0.73956400
H	-6.94109600	1.56986500	0.97000900
H	-5.13153300	3.00749000	1.88217900
C	1.53766300	1.81535400	-0.55636600
C	1.72556200	2.95285500	0.24129500
C	2.52124700	1.46687100	-1.49124200
C	2.88548100	3.70966100	0.12143500
H	0.95426400	3.22884500	0.94968200
C	3.68321600	2.22527100	-1.60450000
H	2.37175200	0.62053100	-2.15083700
C	3.87185300	3.34475000	-0.79632000
H	3.02298300	4.58428200	0.74713700
H	4.43551900	1.94694800	-2.33358000
H	4.77699100	3.93446500	-0.88622000
H	-2.76558700	2.51292400	1.34331300
H	-4.01090500	-0.83358500	-1.03337200
C	1.28408600	-1.29191200	-0.77057500
O	1.24965400	-2.01848200	-1.73010900
C	2.34742100	-1.31043600	0.26102600
C	3.55165100	-1.95611000	-0.05189500
C	2.16816900	-0.74670000	1.53029500
C	4.57133100	-2.01796900	0.88801200
H	3.66868200	-2.39583600	-1.03470700
C	3.18853600	-0.82138000	2.47274600
H	1.23492800	-0.25991800	1.78249600
C	4.39088900	-1.44960700	2.15127400
H	5.50599900	-2.50776000	0.64110600
H	3.04614400	-0.38886700	3.45596600

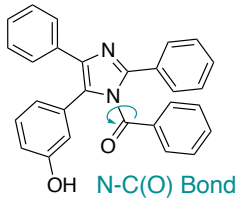
H	5.18749000	-1.49935900	2.88504800
Br	-1.72902100	-2.43825600	-0.35504000

(7a)-4 TS, 2



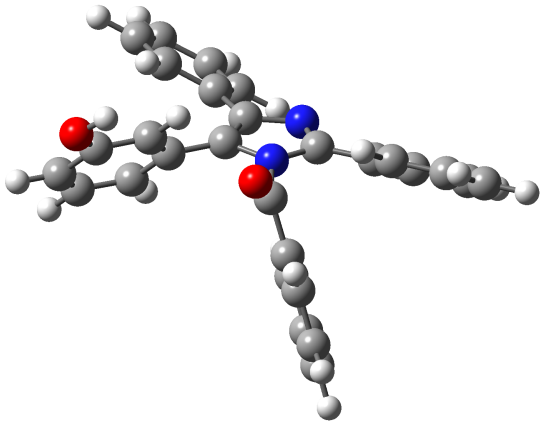
C	3.67887700	-0.45814900	0.63155600
C	2.71679200	-1.32378600	0.09260500
C	3.13225900	-2.56579700	-0.41147600
C	4.47749800	-2.91983200	-0.39834800
C	0.64807000	0.21128000	-0.08826600
C	-0.84363700	-1.45635000	0.06305100
C	1.28602200	-0.99010400	0.06824000
N	-0.74882600	-0.05050500	-0.06314400
N	0.33766100	-1.99903400	0.15021900
C	5.02383200	-0.81690500	0.64510400
H	5.75485600	-0.13846800	1.07049600
C	5.42951400	-2.04557300	0.12595400
H	6.47769200	-2.32256100	0.13672400
H	4.78331200	-3.88067600	-0.79698900
C	-2.07371900	-2.26261900	0.02818500
C	-2.16727200	-3.37245700	0.87588800
C	-3.09214500	-2.02145000	-0.90163300
C	-3.27375800	-4.21489500	0.80851500
H	-1.36851800	-3.56527900	1.58111500
C	-4.19018600	-2.86933700	-0.97319600
H	-3.02336900	-1.17041000	-1.56744300
C	-4.28739100	-3.96584900	-0.11472400
H	-3.34271500	-5.06564200	1.47681900
H	-4.97215200	-2.67574900	-1.69849000
H	-5.14883400	-4.62201400	-0.16768900
H	2.38867000	-3.24585300	-0.80770100
H	3.37463300	0.48869700	1.05770500
C	-1.81644500	0.84316300	0.28073300
O	-2.90133400	0.41541400	0.58158100
C	-1.55439700	2.31738800	0.26716900
C	-1.80788000	3.05545000	-0.88892400
C	-1.16002200	2.95743500	1.44205700
C	-1.63583900	4.43653500	-0.87566100
H	-2.12259600	2.55227000	-1.79598000
C	-0.98767200	4.33880200	1.44925400
H	-0.97660900	2.37801200	2.33967800
C	-1.21887800	5.07843000	0.29015900
H	-1.82575900	5.01096600	-1.77497900
H	-0.67303700	4.83679300	2.35906200
H	-1.08191700	6.15370200	0.29715200
Br	1.43267000	1.84449700	-0.61340200

ii. (5-(3-hydroxyphenyl)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-1-yl)(phenyl)methanone (8a)



Entry	GS/TS	Conformer	E (Hartree)	$G^{\ddagger}_{298\ K}$ (Hartree)	D$G^{\ddagger}_{298\ K}$ (kcal/mol)	ν_{imag} (cm^{-1})
1	GS	(a*R*)	−1338.984139	−1339.043172	0.00	none
2	TS	1	−1338.970222	−1339.02668	10.35	−34.68
3	GS	(a*S*)	−1338.984132	−1339.04275	0.26	none
4	TS	2	−1338.971362	−1339.027262	9.98	−35.38

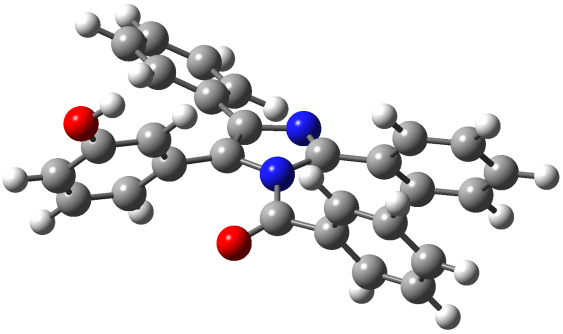
(8a)-1 GS, (a*R*)



C	-3.71738600	-1.48510300	-0.30761800
C	-2.49396900	-2.02377200	0.11759800
C	-2.50224500	-3.24342700	0.81077800
C	-3.70084600	-3.89371200	1.08899100
C	-0.94063600	-0.01282800	-0.34181500
C	0.91544900	-1.25206800	-0.56939400
C	-1.21034100	-1.36076400	-0.16241200
C	-1.78705200	1.17853500	-0.17160500
C	-1.87856700	2.15329200	-1.17320800
C	-2.53239100	1.33107800	1.00549700
C	-2.69508800	3.26858600	-0.99297800
C	-3.35589700	2.44187700	1.16600500
H	-3.93248600	2.55538200	2.07696900
N	0.43121500	0.04798000	-0.61761400
N	-0.05517100	-2.09787600	-0.30693600
C	-3.44256600	3.41595500	0.17588800
H	-4.07261100	4.28924200	0.29138200
O	-2.80680200	4.25097700	-1.93969400
H	-2.21080500	4.06543800	-2.67316500
C	-4.91453200	-2.13706700	-0.02726500
H	-5.85032500	-1.70689000	-0.36667300
C	-4.91323700	-3.34173600	0.67574100
H	-5.84689700	-3.84872900	0.89212900
H	-3.68844900	-4.83454700	1.62833300
C	2.31338300	-1.62078400	-0.81183700
C	3.14049900	-0.88807800	-1.67466900
C	2.83465300	-2.75204800	-0.16648400
C	4.46750800	-1.26455600	-1.86571300
H	2.74508500	-0.04043000	-2.22081900
C	4.15844200	-3.12620700	-0.36440500
H	2.18776100	-3.32466700	0.48643300
C	4.98263000	-2.38045300	-1.20921700
H	5.09499300	-0.69120500	-2.53860600
H	4.55092700	-3.99989400	0.14371200

H	6.01570600	-2.67240800	-1.35984300
H	-2.46950500	0.57510800	1.77773900
H	-1.30304100	2.04246000	-2.08433500
H	-1.55849000	-3.67513300	1.12054300
H	-3.73168300	-0.55749000	-0.86549400
C	1.21999500	1.26733200	-0.61096100
O	1.11767000	2.05586000	-1.51819700
C	2.09565900	1.46020500	0.56750600
C	1.94149700	0.70552100	1.73760200
C	3.07639800	2.46018100	0.50601200
C	2.76608200	0.94648100	2.83152500
H	1.17694400	-0.05871200	1.79572300
C	3.90441200	2.68905900	1.59638900
H	3.17521700	3.03966000	-0.40352300
C	3.74987300	1.93192800	2.76018100
H	2.64235100	0.36552800	3.73777300
H	4.66938500	3.45492900	1.54422000
H	4.39631700	2.11237500	3.61170800

(8a)-2 TS, 1



C	-3.83847600	1.31073100	0.57382600
C	-2.67747600	1.94366000	0.10424200
C	-2.75226700	3.29523500	-0.26608900
C	-3.95817500	3.98575100	-0.19286400
C	-1.10155500	-0.08440100	-0.14549400
C	0.78611700	1.13059600	0.08710600
C	-1.38312100	1.24912100	0.01179100
C	-2.01897200	-1.23128800	-0.26921400
C	-2.04333300	-2.22321800	0.71737800
C	-2.91547600	-1.29952000	-1.33767800
C	-2.94556500	-3.28020100	0.62590600
C	-3.81957900	-2.35669700	-1.41487500
H	-4.51328100	-2.41030900	-2.24618500
N	0.31096600	-0.18977600	-0.09882400
N	-0.20210200	1.97459000	0.12914700
C	-3.84184400	-3.34997900	-0.44213100
H	-4.53611200	-4.17961000	-0.49205900
O	-3.00769100	-4.27855500	1.56243400
H	-2.33183800	-4.13996100	2.23371400
C	-5.04184300	2.00570100	0.64905300
H	-5.92797900	1.50095700	1.01763800
C	-5.10973400	3.34368900	0.26148000
H	-6.04901100	3.88215500	0.32005100
H	-3.99806900	5.02840300	-0.48835000
C	2.18960900	1.56262200	0.24335800
C	2.98185500	1.11273000	1.30406000
C	2.70770400	2.50850800	-0.64700100
C	4.28684500	1.57083500	1.44746900
H	2.57776400	0.39857300	2.01000700
C	4.01438200	2.96690600	-0.50166400
H	2.08075200	2.87548600	-1.45074000
C	4.80907000	2.49337600	0.54111800
H	4.89607000	1.20769900	2.26695300
H	4.41093900	3.69362500	-1.20168300
H	5.82812700	2.84640000	0.65191500
H	-2.90113000	-0.52788500	-2.09669800
H	-1.35560000	-2.16646500	1.55601700
H	-1.85378400	3.79572300	-0.60488200
H	-3.80061800	0.27622700	0.88776200
C	1.01511400	-1.33070500	-0.59681900

O	0.41882900	-2.23295700	-1.12999900
C	2.50176900	-1.40448100	-0.41158600
C	3.37016300	-0.85896800	-1.35685900
C	3.00616300	-2.12965600	0.66854300
C	4.74465300	-1.00677000	-1.19836000
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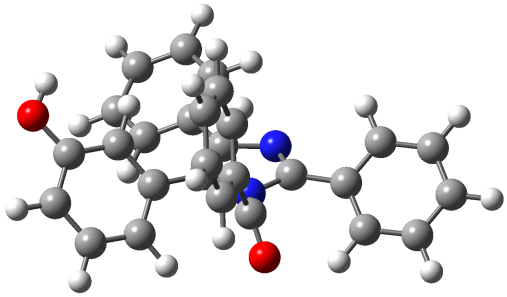
C	4.38230700	-2.27759800	0.82204800
H	2.32566100	-2.57174400	1.38782600
C	5.25259900	-1.71028100	-0.10704400
H	5.41862200	-0.56708600	-1.92403200
H	4.77336400	-2.83569100	1.66510500
H	6.32397500	-1.81951700	0.01613200

(8a)-3 GS, (a*S*)



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C	-2.71181200	4.34670700	1.28370600
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C	1.57820500	1.16904000	-0.35576200
C	-0.53425100	1.63631900	-0.16364000
C	-1.52245200	-0.68988400	-0.83291500
C	-2.57139800	-0.84601400	0.08306400
C	-1.47096500	-1.51560500	-1.96356600
C	-3.55826700	-1.80245300	-0.13514400
C	-2.45793900	-2.48034600	-2.16227500
H	-2.41575400	-3.11629700	-3.03919700
N	0.87410900	0.02709800	-0.72696300
N	0.74405800	2.12754400	-0.01480900
C	-3.50359300	-2.63068700	-1.25932300
H	-4.27914200	-3.37231000	-1.40488700
O	-4.60335500	-1.98703400	0.72870700
H	-4.55855800	-1.33860100	1.43938400
C	-3.98879300	3.17070200	-0.38773000
H	-4.90341800	3.04032300	-0.95563500
C	-3.90298800	4.17264700	0.57915500
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H	-2.63150500	5.13055700	2.02886500
C	3.04103900	1.28907500	-0.28615300
C	3.58968000	2.07053000	0.74345700
C	3.89919000	0.69786200	-1.22401300
C	4.96553500	2.23978000	0.84272400
H	2.92239000	2.54174000	1.45427500
C	5.27740300	0.86953300	-1.11661400
H	3.49088300	0.11928000	-2.04041300
C	5.81574800	1.63509400	-0.08440200
H	5.37620500	2.84239100	1.64508200
H	5.93018000	0.40993600	-1.85010700
H	6.88913900	1.76603900	-0.00563100
H	-0.67355000	-1.39461500	-2.68604400
H	-2.60969500	-0.21358200	0.96353800
H	-0.68941600	3.66088700	1.56849300
H	-2.97070500	1.58046400	-1.40598400
C	1.40075200	-1.32847400	-0.80379300
O	2.03647500	-1.68026400	-1.76472500
C	1.10592400	-2.19400700	0.36273300
C	1.27745500	-3.57742100	0.21943400
C	0.70267200	-1.66520900	1.59552200
C	1.03182200	-4.42279900	1.29334700
H	1.59510200	-3.96778000	-0.73940900
C	0.47231800	-2.51466500	2.67235500

H	0.57586600	-0.59638900	1.71330600
C	0.62992900	-3.89202300	2.52100700
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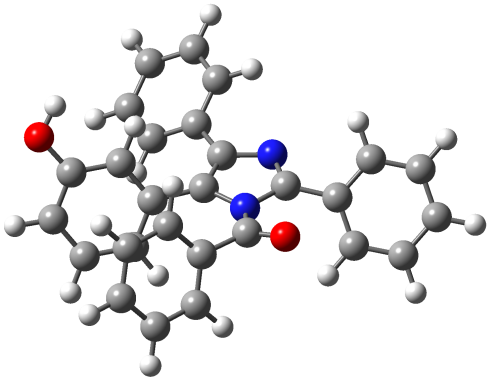
H	0.44047700	-4.55294600	3.35937000

(8a)-4 TS, 2



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C	0.05415300	4.07549700	-0.46561300
C	0.76498200	5.27089200	-0.41392000
C	0.17672200	0.37664600	0.13545900
C	-2.07208900	0.51519800	-0.03800100
C	-0.24626400	1.68221800	0.09876800
C	1.55986100	-0.11603400	0.26441100
C	2.49216700	0.24006700	-0.71673500
C	1.97932600	-0.85599300	1.37349500
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H	3.62928500	-1.84125000	2.32945100
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C	4.23735800	-0.90730500	0.49961400
H	5.27548700	-1.20738600	0.57055800
O	4.77079600	0.17342600	-1.53112000
H	4.38814000	0.75256900	-2.19870000
C	2.43573100	4.21863100	0.96680900
H	3.35520900	4.27220200	1.53916600
C	1.96165400	5.34713800	0.29827300
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H	0.38162400	6.14574100	-0.92739800
C	-3.51271800	0.20794800	-0.02224700
C	-4.36588600	0.96461100	-0.83287900
C	-4.06111000	-0.73337500	0.85642200
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C	-6.28220500	-0.17861600	0.08918700
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H	-7.35454600	-0.33312700	0.12984900
H	1.26631800	-1.12460900	2.14186800
H	2.16896500	0.82953100	-1.56864300
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H	2.10132800	2.15787200	1.45078800
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C	0.12869700	-3.59451800	0.78855000
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H	0.96881400	-2.00878400	-2.09855400
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H	2.84115400	-3.61808400	-1.97279600
H	2.99578700	-5.19919200	-0.06848500

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