Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Rhodium(III)-catalyzed C-H/C-F Activation Sequence: Expedient and Divergent Synthesis of 2-Benzylated Indoles and 2,2′-Bis(indolyl)methanes

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Supporting Information

Table of content

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates 1, 2, 3, 4

The substrates of 9-isopropyl-6-phenyl-9*H*-purine **1**, 2-phenylpyridine **2**, *N*,*N*-dimethyl-1*H*-indole-1-carboxamide **3**, and (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4** were prepared accroding to the previous procedure.[1-4] All the characteristic data are consistent with the data reported before.[1-4]

3. General procedure and characterization of products

General procedure A

In an oven-dried Schlenk tube under atmosphere of N_2, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02mmol, 10.0 mmol%), $AgBF_4$ (19.4 mg, 0.1mmol, 0.5 equiv), AgF (12.6 mg, 0.1mmol, 0.5 equiv), $Ca(OH)_2$ (14.8 mg, 0.2 mmol, 1.0 equiv), and DCE (1.0 mL) was stirred at 120 °C for 1 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5**.

General procedure B

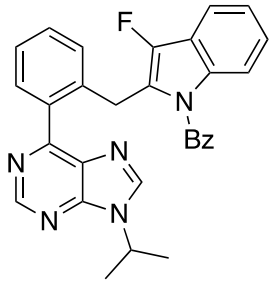
In an oven-dried Schlenk tube under atmosphere of N_2, a mixture of the substrates **2** (0.2 mmol, 1.0 equiv), (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4a** (0.30 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgBF_4$ (38.9 mg, 0.2 mmol, 1.0 equiv), $Ca(OH)_2$ (14.8 mg, 0.2 mmol, 1.0 equiv), and DCE (1.0 mL) was stirred at 80 °C for 2 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **6**.

General procedure C

In an oven-dried Schlenk tube under atmosphere of N_2, a mixture of the substrates **3** (0.2 mmol, 1.0 equiv), (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4a** (0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10.0 mmol%), $AgBF_4$ (19.4 mg, 0.1 mmol, 0.5 equiv), AgF (12.6 mg, 0.1mmol, 0.5 equiv), $Ca(OH)_2$ (29.6 mg, 0.4 mmol, 2.0 equiv), and toluene (2.0 mL) was stirred at 150 ºC for 1 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **7**.

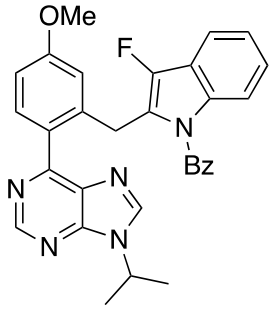
Characterization of products

(3-fluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (5a)



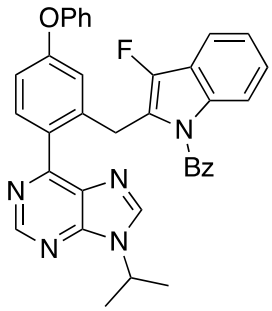
Following the general procedure A, the product **5a** was obtained in 89% yield (87.1 mg, 0.178 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.00 (s, 1H), 7.63 – 7.57 (m, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 2.9 Hz, 3H), 7.22 – 7.15 (m, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.72 (dd, J = 8.5, 2.1 Hz, 1H), 4.90 (p, J = 6.8 Hz, 1H), 4.52 (s, 2H), 1.65 (d, J = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.51. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.8, 151.7, 151.2, 147.4 (d, *J* = 251.7 Hz), 142.12, 137.0, 135.2, 135.0, 133.7, 133.7, 132.7, 132.3, 130.8, 129.8, 129.5, 128.6, 126.8, 124.3, 122.5, 121.7 (d, *J* = 23.4 Hz), 119.1 (d, *J* = 18.7 Hz), 116.2 (d, *J* = 2.4 Hz), 114.0, 47.4, 29.5, 22.6. ESI-MS: calculated $C_{30}H_{25}FN_5O$ $[M+H]^+$ 490.2038; Found 490.2036.

3-fluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)-5-methoxybenzyl)-1*H*-indol-1-yl)(phenyl)methanone (5b)



Following the general procedure A, the product **5b** was obtained in 45% yield (46.7 mg, 0.09 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.17. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.7 Hz, 1H), 8.03 (d, *J* = 2.6 Hz, 1H), 7.69 (dd, *J* = 8.4, 2.7 Hz, 1H), 7.50 (d, *J* = 6.5 Hz, 2H), 7.42 (d, *J* = 6.4 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.00 (s, 1H), 6.88 – 6.80 (m, 2H), 6.68 (s, 1H), 4.97 – 4.86 (m, 1H), 4.54 (s, 2H), 3.72 (d, *J* = 2.7 Hz, 3H), 1.65 (dd, *J* = 6.7, 2.7 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.58. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 160.5, 157.5, 151.6, 151.1, 147.5 (d, *J* = 251.6 Hz), 141.8, 139.2, 135.0, 133.7 (d, *J* = 5.3 Hz), 132.8, 132.6, 132.2, 129.8, 128.5, 127.5, 124.4, 122.6, 121.5 (d, *J* = 23.4 Hz), 119.2 (d, *J* = 18.5 Hz), 116.5, 116.3, 114.1, 111.7, 55.3, 47.3, 29.6, 22.64. ESI-MS: calculated $C_{31}H_{27}FN_5O_2$ $[M+H]^+$ 520.2144; Found 520.2143.

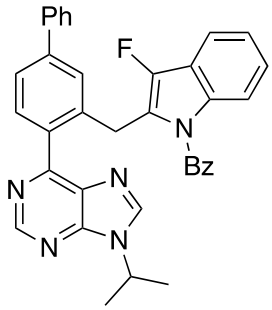
(3-fluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)-5-phenoxybenzyl)-1*H*-indol-1-yl)(phenyl)methanone (5c)



Following the general procedure A, the product **5c** was obtained in 61% yield (71.0 mg, 0.122 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.02 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.22 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.07 (dt, *J* = 14.8, 4.0 Hz, 2H), 7.00 – 6.95 (m, 1H), 6.88 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.85 (dd, *J* = 3.1, 1.8 Hz, 2H), 6.83 (d, *J* = 0.8 Hz, 1H), 6.74 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.91 (dt, *J* = 13.6, 6.8 Hz, 1H), 4.54 (s, 2H), 1.66 (d, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.43. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 158.1, 157.2, 156.7, 151.8, 151.2, 147.5 (d, *J* = 251.9 Hz), 142.0, 139.6, 134.9, 133.7, 132.8, 132.6, 132.3, 130.2, 129.9, 129.7, 128.7, 124.4, 123.5, 122.6, 121.3 (d, *J* = 23.5 Hz), 121.2, 119.1, 119.1 (d, *J* = 18.6 Hz), 116.8, 116.3, 114.0, 47.4, 29.5, 22.6. ESI-MS: calculated $C_{36}H_{29}FN_5O_2$ $[M+H]^+$ 582.2300; Found 582.2304.

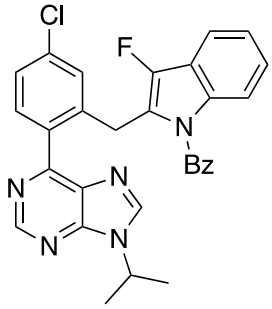
(3-fluoro-2-((4-(9-isopropyl-9*H*-purin-6-yl)-[1,1'-biphenyl]-3-yl)methyl)-1*H*-indol-1-yl)(phen

yl)methanone (5d)



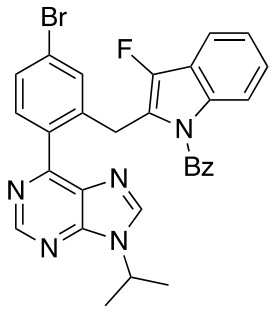
Following the general procedure A, the product **5d** was obtained in 46% yield (52.0 mg, 0.092 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.03 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 3H), 7.45 (t, *J* = 8.9 Hz, 3H), 7.41 – 7.36 (m, 3H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.91 (dt, *J* = 13.5, 6.8 Hz, 1H), 4.60 (s, 2H), 1.66 (d, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.46. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.5, 151.8, 151.2, 147.3 (d, *J* = 251.7 Hz), 142.3, 142.2, 140.7, 137.6, 134.9, 134.1, 133.7 (d, *J* = 5.3 Hz), 132.9, 132.3, 131.3, 129.9, 129.7, 128.8, 128.6, 127.5, 127.3, 125.6, 124.3, 122.5, 121.7 (d, *J* = 23.3 Hz), 119.0 (d, *J* = 18.6 Hz), 116.3, 113.9, 47.4, 29.6, 22.6. ESI-MS: calculated $C_{36}H_{29}FN_5O$ $[M+H]^+$ 566.2351; Found 566.2352.

(2-(5-chloro-2-(9-isopropyl-9*H*-purin-6-yl)benzyl)-3-fluoro-1*H*-indol-1-yl)(phenyl)methanone (5e)



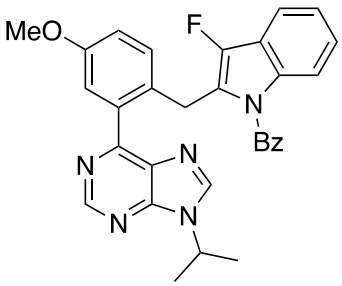
Following the general procedure A, the product **5e** was obtained in 54% yield (56.6 mg, 0.108 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 – 8.77 (m, 1H), 8.08 – 7.99 (m, 1H), 7.63 – 7.57 (m, 1H), 7.57 – 7.50 (m, 3H), 7.43 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.28 (s, 1H), 7.11 (s, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 4.90 (d, *J* = 3.9 Hz, 1H), 4.52 (s, 2H), 1.66 (dd, *J* = 9.1, 6.5 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.10. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 156.5, 151.7, 151.3, 147.6 (d, *J* = 252.0 Hz), 142.3, 139.3, 135.5, 134.8, 133.7, 133.6, 133.6, 133.0, 132.3, 130.4, 129.8, 128.7, 126.9, 124.6, 122.7, 120.8 (d, *J* = 23.2 Hz), 119.1 (d, *J* = 18.6 Hz), 116.4, 114.2, 47.5, 29.4, 22.6. ESI-MS: calculated $C_{30}H_{24}ClFN_5O$ $[M+H]^+$ 524.1648; Found 524.1647.

(2-(5-bromo-2-(9-isopropyl-9*H*-purin-6-yl)benzyl)-3-fluoro-1*H*-indol-1-yl)(phenyl)methanone (5f)



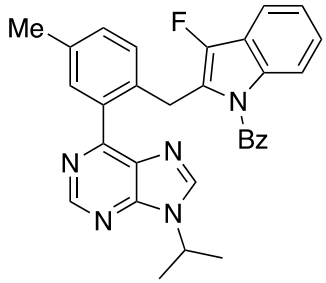
Following the general procedure A, the product **5f** was obtained in 66% yield (75.0 mg, 0.132 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.03 (s, 1H), 7.53 (dd, *J* = 9.6, 7.8 Hz, 4H), 7.46 – 7.35 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.88 (h, *J* = 6.8 Hz, 1H), 4.52 (s, 2H), 1.64 (d, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.05. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 156.5, 151.7, 151.3, 147.6 (d, *J* = 252.3 Hz), 142.4, 139.4, 134.8, 134.1, 133.7, 133.6, 133.2, 133.0, 132.4, 132.2, 129.9 (d, *J* = 3.5 Hz), 128.7, 124.6, 123.9, 122.7, 120.7 (d, *J* = 23.2 Hz), 119.0 (d, *J* = 18.4 Hz), 116.4, 114.1, 47.5, 29.4, 22.6. ESI-MS: calculated $C_{30}H_{24}BrFN_5O$ $[M+H]^+$ 569.1143; Found 568.1142.

(3-fluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)-4-methoxybenzyl)-1*H*-indol-1-yl)(phenyl)methanone (5g)



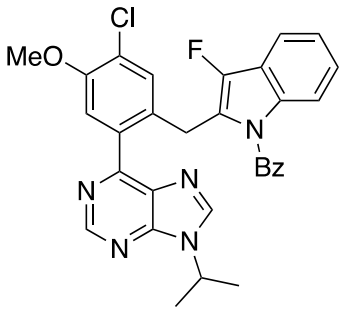
Following the general procedure A, the product **5g** was obtained in 51% yield (53.0 mg, 0.102 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.00 (s, 1H), 7.59 – 7.51 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.74 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.95 – 4.81 (m, 1H), 4.40 (d, *J* = 1.9 Hz, 2H), 3.74 (s, 3H), 1.64 (dd, *J* = 12.6, 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.84. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 158.1 (d, *J* = 6.8 Hz), 157.5, 151.7, 151.2, 147.2 (d, *J* = 251.9 Hz), 142.1, 136.2, 135.1 (d, *J* = 4.8 Hz), 133.7 (d, *J* = 5.4 Hz), 132.7 (d, *J* = 7.2 Hz), 132.2, 132.0, 129.9, 129.1, 128.6, 124.3, 122.5, 120.7 (d, *J* = 22.6 Hz), 119.0 (d, *J* = 18.0 Hz), 116.2, 115.9, 115.3, 113.9, 55.4, 47.4, 28.8, 22.6. ESI-MS: calculated $C_{31}H_{27}FN_5O_2$ $[M+H]^+$ 520.2144; Found 520.2142.

(3-fluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)-4-methylbenzyl)-1*H*-indol-1-yl)(phenyl)methanone (5h)



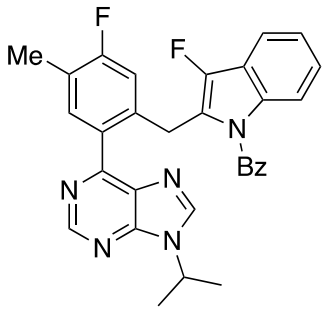
Following the general procedure A, the product **5h** was obtained in 23% yield (23.2 mg, 0.046 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.00 (s, 1H), 7.56 – 7.50 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 4.7 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (s, 2H), 7.13 – 7.01 (m, 3H), 6.96 (td, *J* = 7.7, 7.2, 1.3 Hz, 1H), 6.79 – 6.72 (m, 1H), 4.89 (p, *J* = 6.8 Hz, 1H), 4.42 (s, 2H), 2.29 (s, 3H), 1.65 (d, *J* = 6.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 158.0, 151.8, 151.1, 147.4 (d, *J* = 251.8 Hz), 142.0, 136.3, 135.1, 135.0, 133.9, 132.7, 132.3, 131.2, 130.7, 130.2, 129.9, 128.6, 124.3, 122.5, 120.7 (d, *J* = 24.6 Hz), 119.0 (d, *J* = 17.9 Hz), 116.2, 114.0, 100.1, 47.4, 29.2, 22.6, 21.0. ESI-MS: calculated $C_{31}H_{27}FN_5O$ $[M+H]^+$ 504.2194; Found 504.2197.

(2-(5-chloro-2-(9-isopropyl-9*H*-purin-6-yl)-4-methoxybenzyl)-3-fluoro-1*H*-indol-1-yl)(phenyl) methanone (5i)



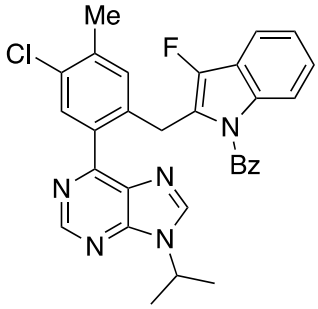
Following the general procedure A, the product **5i** was obtained in 97% yield (107.5 mg, 0.194 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.06 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.20 (s, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 4.90 (dt, *J* = 13.4, 6.7 Hz, 1H), 4.40 (s, 2H), 3.86 (s, 3H), 1.66 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -167.37 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 156.5, 153.5, 151.8, 151.3, 147.4 (d, *J* = 251.8 Hz), 142.4, 134.9, 134.7, 133.7 (d, *J* = 4.9 Hz), 133.0, 132.2, 132.1, 130.3, 129.9, 128.7, 124.5, 123.5, 122.7, 121.2 (d, *J* = 23.0 Hz), 119.0 (d, *J* = 18.6 Hz), 116.3 (d, *J* = 1.7 Hz), 114.5, 114.2, 56.3, 47.5, 28.8, 22.6. ESI-MS: calculated $C_{31}H_{26}ClFN_5O_2$ $[M+H]^+$ 554.1754; Found 554.1762.

(3-fluoro-2-(5-fluoro-2-(9-isopropyl-9*H*-purin-6-yl)-4-methylbenzyl)-1*H*-indol-1-yl)(phenyl) methanone (5j)



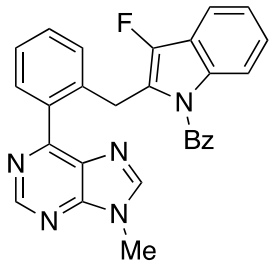
Following the general procedure A, the product **5j** was obtained in 51% yield (53.2 mg, 0.102 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.03 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.35 (dd, *J* = 17.1, 8.1 Hz, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 10.0 Hz, 2H), 4.90 (dt, *J* = 13.1, 6.7 Hz, 1H), 4.46 (s, 2H), 2.23 (s, 3H), 1.65 (d, *J* = 6.6 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.21, -167.39. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 161.8 (d, *J* = 247.9 Hz), 157.0, 151.7, 151.2, 147.5 (d, *J* = 251.9 Hz), 142.2, 137.1 (d, *J* = 7.7 Hz), 134.9, 134.1 (d, *J* = 5.9 Hz), 133.7 (d, *J* = 5.4 Hz), 132.8, 132.3, 130.9 (d, *J* = 3.5 Hz), 129.8, 128.6, 124.5, 123.2 (d, *J* = 17.7 Hz), 122.7, 121.2 (d, *J* = 23.1 Hz), 119.1 (d, *J* = 18.5 Hz), 117.0 (d, *J* = 23.4 Hz), 116.3 (d, *J* = 2.3 Hz), 114.2, 47.4, 29.1, 22.6, 14.2 (d, *J* = 3.0 Hz). ESI-MS: calculated $C_{31}H_{26}F_2N_5O$ $[M+H]^+$ 522.2100; Found 522.2102.

(2-(4-chloro-2-(9-isopropyl-9*H*-purin-6-yl)-5-methylbenzyl)-3-fluoro-1*H*-indol-1-yl)(phenyl) methanone (5k)



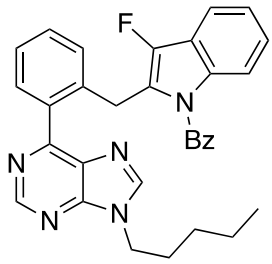
Following the general procedure A, the product **5k** was obtained in 38% yield (40.9 mg, 0.076 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.03 (s, 1H), 7.61 (s, 1H), 7.57 – 7.46 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.81 – 6.74 (m, 1H), 4.89 (p, *J* = 6.8 Hz, 1H), 4.45 (d, *J* = 1.7 Hz, 2H), 2.26 (s, 3H), 1.65 (d, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.42. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 156.2, 151.7, 151.2, 147.3 (d, *J* = 252.1 Hz), 142.3, 137.2, 135.6, 134.9, 134.2, 133.7 (d, *J* = 5.4 Hz), 133.1, 132.9, 132.6, 132.2, 131.2, 129.9, 128.6, 124.4, 122.6, 121.3 (d, *J* = 22.9 Hz), 119.0 (d, *J* = 18.8 Hz), 116.3, 114.0, 47.4, 29.0, 22.5, 19.9. ESI-MS: calculated $C_{31}H_{26}ClFN_5O$ $[M+H]^+$ 538.1805; Found 538.1807.

3-fluoro-2-(2-(9-methyl-9*H*-purin-6-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (5m)



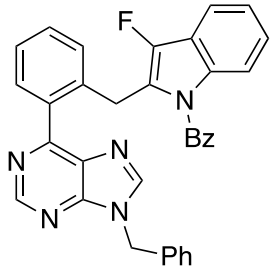
Following the general procedure A, the product **5m** was obtained in 97% yield (89.5 mg, 0.194 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.17. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.85 (s, 1H), 7.61 (dd, *J* = 6.6, 2.5 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (dd, *J* = 6.9, 2.5 Hz, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.79 – 6.72 (m, 1H), 4.50 (s, 2H), 3.83 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.10. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 157.7, 152.1, 151.8, 147.3 (d, *J* = 251.7 Hz), 144.8, 137.0 (d, *J* = 1.7 Hz), 134.9 (d, *J* = 2.7 Hz), 133.6 (d, *J* = 5.4 Hz), 132.7, 132.1, 132.0, 131.7, 130.6 (d, *J* = 6.0 Hz), 129.7, 129.5, 128.5, 126.7, 124.2, 122.4, 121.6 (d, *J* = 23.4 Hz), 119.0 (d, *J* = 18.6 Hz), 116.2 (d, *J* = 2.3 Hz), 113.9 (d, *J* = 1.4 Hz), 29.7, 29.3. ESI-MS: calculated $C_{28}H_{21}FN_5O$ $[M+H]^+$ 462.1725; Found 462.1723.

(3-fluoro-2-(2-(9-pentyl-9*H*-purin-6-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (5n)



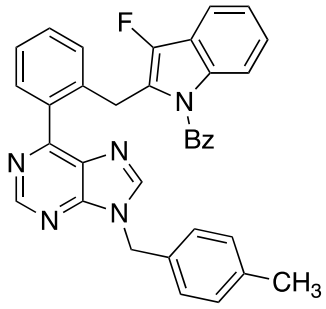
Following the general procedure A, the product **5n** was obtained in 91% yield (94.2 mg, 0.182 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.2 Hz, 1H), 7.91 (s, 1H), 7.61 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 3.4 Hz, 3H), 7.19 (d, *J* = 5.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 4.52 (s, 2H), 4.21 (t, *J* = 7.3 Hz, 2H), 1.93 (p, *J* = 7.3 Hz, 2H), 1.40 (dq, *J* = 10.1, 6.0, 5.2 Hz, 4H), 0.98 – 0.90 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.47. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.7, 152.0, 151.6, 147.4 (d, *J* = 251.5 Hz), 144.4, 137.1 (d, *J* = 1.6 Hz), 135.1, 135.0, 133.7 (d, *J* = 5.1 Hz), 132.7, 131.9, 130.8, 130.7, 129.8, 129.5, 128.6, 126.7, 124.3, 122.5, 121.7 (d, *J* = 23.2 Hz), 119.1 (d, *J* = 18.6 Hz), 116.2 (d, *J* = 2.4 Hz), 114.0, 44.0, 29.7, 29.4, 28.9, 22.3, 14.0. ESI-MS: calculated $C_{32}H_{29}FN_5O$ $[M+H]^+$ 518.2351; Found 518.2356.

(2-(2-(9-benzyl-9*H*-purin-6-yl)benzyl)-3-fluoro-1*H*-indol-1-yl)(phenyl)methanone (5o)



Following the general procedure A, the product **5o** was obtained in 91% yield (97.8 mg, 0.182 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 5.7 Hz, 1H), 7.89 (s, 1H), 7.64 – 7.59 (m, 1H), 7.51 – 7.46 (m, 2H), 7.42 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.40 – 7.34 (m, 5H), 7.31 – 7.26 (m, 4H), 7.24 (s, 1H), 7.21 – 7.16 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.75 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.39 (s, 2H), 4.52 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.53. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.9, 152.3, 151.6, 147.3 (d, *J* = 251.7 Hz), 144.2, 137.1, 135.2, 134.9 (d, *J* = 6.0 Hz), 133.7 (d, *J* = 5.3 Hz), 132.7, 131.8, 130.8, 130.6, 129.8, 129.6, 129.2, 128.7, 128.5, 128.1, 126.7, 124.3, 122.5, 121.7 (d, *J* = 23.4 Hz), 119.1 (d, *J* = 18.6 Hz), 116.3 (d, *J* = 2.1 Hz), 114.0, 47.3, 29.3. ESI-MS: calculated $C_{34}H_{25}FN_5O$ $[M+H]^+$ 538.2038; Found 538.2037.

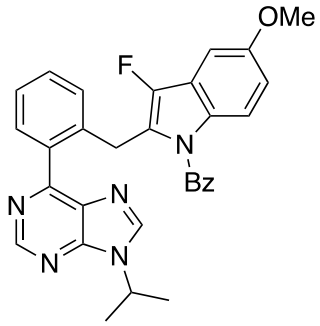
(3-fluoro-2-(2-(9-(4-methylbenzyl)-9*H*-purin-6-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (5p)



Following the general procedure A, the product **5p** was obtained in 59% yield (65.1 mg, 0.118 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.88 (s, 1H), 7.63 – 7.59 (m, 1H), 7.52 – 7.46 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 (s, 1H), 7.28 (d, *J* = 3.9 Hz, 4H), 7.25 (s, 2H), 7.22 – 7.17 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.1 Hz, 1H), 5.35 (s, 2H), 4.51 (d, *J* = 1.7 Hz, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.52. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.8, 152.2, 151.6, 147.4 (d, *J* = 251.6 Hz), 144.2, 138.6, 137.1, 134.9 (d, *J* = 6.2 Hz), 133.7 (d, *J* = 5.3 Hz), 132.7, 132.1, 131.8, 130.8, 130.6, 129.9, 129.8, 129.6, 128.5, 128.1, 126.7, 124.3, 122.5, 121.7 (d, *J* = 23.4 Hz), 119.1 (d, *J* = 18.7 Hz), 116.3 (d, *J* = 2.3 Hz), 114.0, 47.2, 29.3, 21.2. ESI-MS: calculated $C_{35}H_{27}FN_5O$ $[M+H]^+$ 552.2194; Found 552.2190.

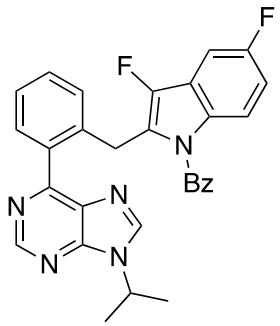
(3-fluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)benzyl)-5-methoxy-1*H*-indol-1-yl)(phenyl)methano

ne (5q)



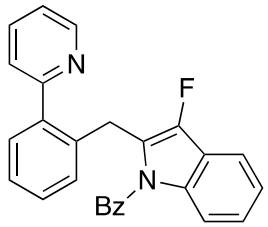
Following the general procedure A, the product **5q** was obtained in 78% yield (81.0 mg, 0.156 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.17. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.01 (s, 1H), 7.65 – 7.58 (m, 1H), 7.53 – 7.46 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.20 – 7.14 (m, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.58 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.93 – 4.85 (m, 1H), 4.48 (s, 2H), 3.78 (s, 3H), 1.65 (d, *J* = 6.7 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.00. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 157.8, 155.7, 151.7, 151.2, 147.5 (d, *J* = 251.3 Hz), 142.1, 137.1 (d, *J* = 1.7 Hz), 135.1, 135.0, 132.6, 132.2, 130.8, 130.6, 129.7, 129.5, 128.5, 128.5, 126.7, 122.3 (d, *J* = 23.1 Hz), 119.9 (d, *J* = 17.9 Hz), 115.2 (d, *J* = 1.5 Hz), 113.6, 98.2 (d, *J* = 2.1 Hz), 55.7, 47.4, 29.7, 22.5. ESI-MS: calculated $C_{31}H_{27}FN_5O_2$ $[M+H]^+$ 520.2144; Found 520.2143.

(3,5-difluoro-2-(2-(9-isopropyl-9*H*-purin-6-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (5r)



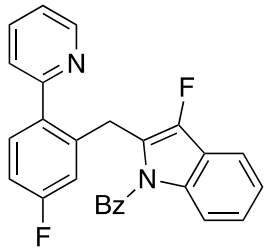
Following the general procedure A, the product **5r** was obtained in 95% yield (96.4 mg, 0.19 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.99 (s, 1H), 7.59 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.18 – 7.14 (m, 1H), 6.92 – 6.88 (m, 1H), 6.70 (d, *J* = 6.3 Hz, 2H), 4.90 (p, *J* = 6.8 Hz, 1H), 4.48 (d, *J* = 1.7 Hz, 2H), 1.65 (d, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.28 – -120.60 (m), -166.89. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 158.8 (d, *J* = 240.3 Hz), 157.7, 151.8, 151.2, 146.9 (d, *J* = 251.7 Hz), 142.1, 136.7, 135.2, 134.7, 132.9, 132.2, 130.8 (d, *J* = 5.4 Hz), 130.0 (d, *J* = 4.6 Hz), 129.8, 129.5, 128.6, 126.9, 123.6 (d, *J* = 22.8 Hz), 119.7 (d, *J* = 18.2 Hz), 115.2 (d, *J* = 8.9 Hz), 112.3 (d, *J* = 25.3 Hz), 102.0 (d, *J* = 1.9 Hz), 101.7 (d, *J* = 2.0 Hz), 47.4, 29.7, 22.5. ESI-MS: calculated $C_{30}H_{24}F_2N_5O$ $[M+H]^+$ 508.1944; Found 508.1942.

(3-fluoro-2-(2-(pyridin-2-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (6a)



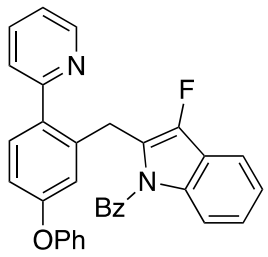
Following the general procedure B, the product **6a** was obtained in 88% yield (71.5 mg, 0.176 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). RF (Petroleum ether/EtOAc 8:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.57 (m, 1H), 7.61 – 7.56 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25 (s, 1H), 7.23 – 7.18 (m, 3H), 7.17 – 7.12 (m, 2H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.92 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.38 (d, *J* = 1.9 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.71. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 159.4, 149.0, 147.7 (d, *J* = 251.3 Hz), 140.4, 136.2, 135.9 (d, *J* = 1.7 Hz), 135.1, 133.8 (d, *J* = 5.3 Hz), 132.9, 129.9, 129.7, 129.3, 128.6, 128.4, 126.7, 124.5, 123.9, 122.8, 121.8, 121.6 (d, *J* = 23.3 Hz), 119.7 (d, *J* = 18.6 Hz), 116.5 (d, *J* = 2.5 Hz), 114.3 (d, *J* = 1.8 Hz), 28.8. ESI-MS: calculated $C_{27}H_{20}FN_2O$ $[M+H]^+$ 407.1554; Found 407.1551.

(3-fluoro-2-(5-fluoro-2-(pyridin-2-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (6b)



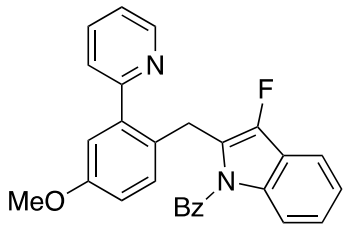
Following the general procedure B, the product **6b** was obtained in 86% yield (73.0 mg, 0.172 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.58 (m, 1H), 7.64 – 7.58 (m, 1H), 7.57 – 7.54 (m, 1H), 7.52 – 7.47 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 1H), 7.17 (q, *J* = 6.8, 5.9 Hz, 2H), 7.06 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 6.92 (td, *J* = 8.3, 2.7 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.70 (dd, *J* = 10.1, 2.6 Hz, 1H), 4.40 (d, *J* = 1.9 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.89 (dt, *J* = 9.5, 4.7 Hz), -167.56. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 162.7 (d, *J* = 247.1 Hz), 158.6, 149.1, 147.9 (d, *J* = 252.0 Hz), 138.8, 136.5, 136.4, 135.0, 133.7, 133.1, 131.6 (d, *J* = 8.3 Hz), 129.6, 128.8, 124.6, 124.0, 122.9, 121.9, 120.8 (d, *J* = 23.4 Hz), 119.6 (d, *J* = 18.6 Hz), 116.6, 116.0 (d, *J* = 22.5 Hz), 114.5, 113.5 (d, *J* = 21.3 Hz), 28.8. ESI-MS: calculated $C_{27}H_{18}F_2N_2ONa$ $[M+Na]^+$ 447.1279; Found 447.1286.

(3-fluoro-2-(5-phenoxy-2-(pyridin-2-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (6c)



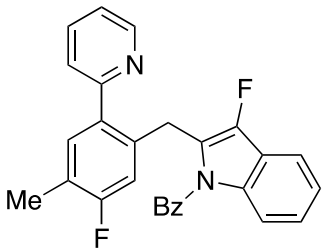
Following the general procedure B, the product **6c** was obtained in 54% yield (53.8 mg, 0.108 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 10:1 v/v). RF (Petroleum ether/EtOAc 10:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.61 (td, *J* = 7.7, 1.8 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 8.7, 6.9 Hz, 3H), 7.19 – 7.13 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.90 – 6.81 (m, 4H), 6.72 (d, *J* = 2.5 Hz, 1H), 4.42 (d, *J* = 1.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.56. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 158.9, 157.1, 157.0, 149.0, 147.8 (d, *J* = 251.8 Hz), 138.2, 136.3, 135.7, 135.0, 133.7, 133.7, 133.0, 131.4, 129.7, 128.7, 124.4, 123.9, 123.2, 122.8, 121.7, 121.2 (d, *J* = 23.3 Hz), 120.0, 119.6 (d, *J* = 18.5 Hz), 118.7, 116.8, 116.5 (d, *J* = 2.3 Hz), 114.3, 28.8. ESI-MS: calculated $C_{33}H_{24}FN_2O_2$ $[M+H]^+$ 499.1817; Found 499.1815.

(3-fluoro-2-(2-methoxy-6-(pyridin-2-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (6d)



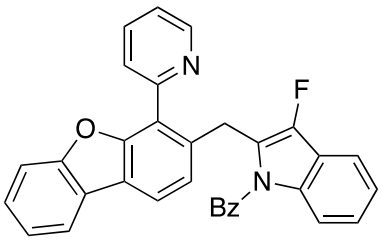
Following the general procedure B, the product **6d** was obtained in 66% yield (57.6 mg, 0.132 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). RF (Petroleum ether/EtOAc 8:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.9 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.50 – 7.42 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.15 (q, *J* = 7.2, 6.6 Hz, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 2.8 Hz, 1H), 6.73 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.28 (d, *J* = 1.9 Hz, 2H), 3.75 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.79. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 159.2, 158.1, 149.0, 147.5 (d, *J* = 251.0 Hz), 141.4, 136.2, 135.1, 133.8, 133.7, 132.9, 130.6, 129.7, 128.6, 127.9, 124.4, 123.8, 122.8, 121.9, 121.9 (d, *J* = 23.1 Hz), 119.7 (d, *J* = 18.6 Hz), 116.4 (d, *J* = 2.4 Hz), 115.3, 114.3, 113.9, 28.1. ESI-MS: calculated $C_{28}H_{22}FN_2O_2$ $[M+H]^+$ 437.1660; Found 437.1661.

(3-fluoro-2-(5-fluoro-4-methyl-2-(pyridin-2-yl)benzyl)-1*H*-indol-1-yl)(phenyl)methanone (6e)



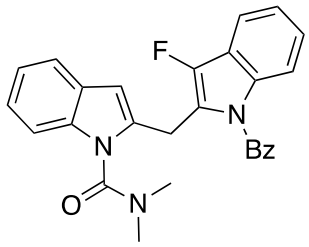
Following the general procedure B, the product **6e** was obtained in 75% yield (65.8 mg, 0.15 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). RF (Petroleum ether/EtOAc 8:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.9 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.50 (dd, *J* = 13.3, 7.8 Hz, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.21 – 7.12 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.64 (d, *J* = 10.7 Hz, 1H), 4.36 (s, 2H), 2.22 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.38 (t, *J* = 9.4 Hz), -167.73. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 161.2 (d, *J* = 245.9 Hz), 158.7, 149.1, 147.8 (d, *J* = 251.8 Hz), 136.2, 136.1 (d, *J* = 3.5 Hz), 135.7 (d, *J* = 1.9 Hz), 135.6 (d, *J* = 1.8 Hz), 135.0, 133.7 (d, *J* = 5.3 Hz), 133.1 (d, *J* = 5.7 Hz), 133.0, 129.7, 128.7, 124.5, 123.9, 122.9 (d, *J* = 17.4 Hz), 121.8, 121.1 (d, *J* = 23.3 Hz), 119.6 (d, *J* = 18.4 Hz), 116.6 (d, *J* = 2.4 Hz), 115.5 (d, *J* = 23.4 Hz), 114.4 (d, *J* = 1.6 Hz), 28.4, 14.2 (d, *J* = 3.0 Hz). ESI-MS: calculated $C_{28}H_{21}F_2N_2O$ $[M+H]^+$ 439.1617; Found 439.1616.

(3-fluoro-2-((4-(pyridin-2-yl)dibenzo[b,d]furan-3-yl)methyl)-1*H*-indol-1-yl)(phenyl)methanone (6h)



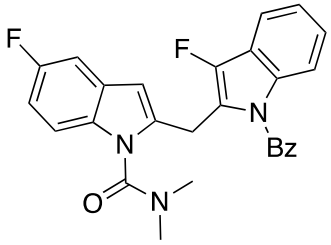
Following the general procedure B, the product **6h** was obtained in 59% yield (58.6 mg, 0.118 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 10:1 v/v). RF (Petroleum ether/EtOAc 10:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.46 (m, 4H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 (q, *J* = 8.2 Hz, 4H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.90 (dd, *J* = 8.5, 2.1 Hz, 1H), 4.48 (d, *J* = 1.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.45. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 156.5, 154.4, 154.1, 149.5, 147.7 (d, *J* = 251.6 Hz), 136.2, 135.9, 135.1, 133.8, 133.0, 129.7, 128.7, 127.0, 125.9, 124.7, 124.5, 124.1 (d, *J* = 4.5 Hz), 123.2, 122.8 (d, *J* = 8.2 Hz), 122.5, 121.6 (d, *J* = 23.1 Hz), 120.6, 120.2, 119.7 (d, *J* = 18.5 Hz), 116.5, 114.4, 111.8, 28.8. ESI-MS: calculated $C_{33}H_{22}FN_2O_2$ $[M+H]^+$ 497.1660; Found 497.1662.

2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (7a)



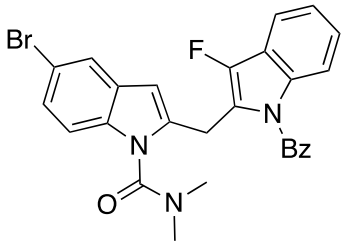
Following the general procedure C, the product **7a** was obtained in 53% yield (46.6 mg, 0.106 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.1, 5.2 Hz, 2H), 7.54 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 19.8 Hz, 2H), 7.17 – 7.10 (m, 1H), 7.05 – 6.99 (m, 2H), 6.70 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.43 (d, *J* = 1.8 Hz, 2H), 2.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.53. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 155.0, 146.8 (d, *J* = 250.0 Hz), 135.9, 135.0, 133.7 (d, *J* = 5.4 Hz), 133.2, 129.7, 128.8, 128.7, 124.5, 124.3, 123.8, 122.8, 121.9 (d, *J* = 24.1 Hz), 121.76, 119.7 (d, *J* = 18.6 Hz), 118.8 (d, *J* = 1.2 Hz), 116.8 (d, *J* = 2.5 Hz), 115.4 (d, *J* = 2.0 Hz), 114.1 (d, *J* = 1.5 Hz), 113.7, 38.2, 20.0. ESI-MS: calculated $C_{27}H_{22}FN_3O_2Na$ $[M+Na]^+$ 462.1588; Found 462.1585.

2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-5-fluoro-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (7b)



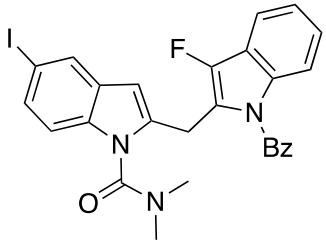
Following the general procedure C, the product **7b** was obtained in 74% yield (67.7 mg, 0.148 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 3H), 7.46 – 7.41 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.08 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.03 (d, *J* = 6.1 Hz, 2H), 6.96 (td, *J* = 9.1, 2.6 Hz, 1H), 6.69 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.39 – 4.35 (m, 2H), 2.84 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.46 (td, *J* = 9.3, 4.7 Hz), -168.78. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 158.8 (d, *J* = 238.0 Hz), 154.8, 146.9 (d, *J* = 250.4 Hz), 135.0, 133.8 (d, *J* = 5.5 Hz), 133.3 132.4, 129.7, 129.4 (d, *J* = 9.7 Hz), 128.9, 126.0, 124.5, 122.9, 121.5 (d, *J* = 24.0 Hz), 119.6 (d, *J* = 18.6 Hz), 117.0 (d, *J* = 2.4 Hz), 115.3, 114.8 (d, *J* = 9.3 Hz), 114.2 (d, *J* = 1.6 Hz), 112.0 (d, *J* = 25.7 Hz), 104.2 (d, *J* = 24.2 Hz), 38.3, 20.0. ESI-MS: calculated $C_{27}H_{21}F_2N_3O_2Na$ $[M+Na]^+$ 480.1494; Found 480.1498.

2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-5-bromo-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (7c)



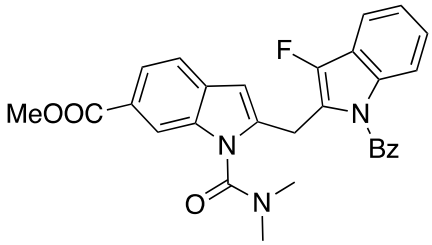
Following the general procedure C, the product **7c** was obtained in 76% yield (78.8 mg, 0.152 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.17. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.43 (m, 2H), 7.40 – 7.29 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.00 (s, 1H), 6.75 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.36 (s, 2H), 2.84 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.66. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 154.5, 146.9 (d, *J* = 247.0 Hz), 134.9, 134.7, 133.8 (d, *J* = 5.4 Hz), 133.3, 130.4, 129.7, 128.9, 126.8, 125.6, 124.6, 123.0, 121.6 (d, *J* = 1.4 Hz), 121.3 (d, *J* = 24.0 Hz), 119.7 (d, *J* = 18.4 Hz), 117.0 (d, *J* = 2.3 Hz), 115.3, 115.1, 115.0 (d, *J* = 2.0 Hz), 114.3 (d, *J* = 1.4 Hz), 38.3, 19.9. ESI-MS: calculated $C_{27}H_{21}BrFN_3O_2Na$ $[M+Na]^+$ 540.0693; Found 540.0706.

2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-5-iodo-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (7d)



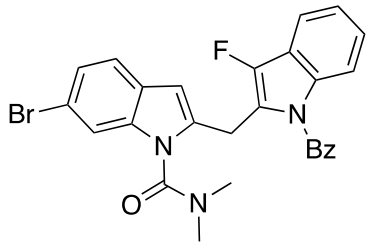
Following the general procedure C, the product **7d** was obtained in 39% yield (44.1 mg, 0.078 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.8 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.48 (ddd, *J* = 16.1, 8.5, 1.6 Hz, 3H), 7.42 – 7.32 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.7, 7.0, 1.2 Hz, 1H), 6.95 (s, 1H), 6.78 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.34 (s, 2H), 2.84 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.67. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 154.5, 146.9 (d, *J* = 250.3 Hz), 135.2, 134.9, 133.8 (d, *J* = 5.0 Hz), 133.3, 132.3, 131.0, 129.7, 128.9, 127.8, 125.1, 124.6, 123.0, 121.3 (d, *J* = 23.9 Hz), 119.7 (d, *J* = 18.8 Hz), 117.0 (d, *J* = 2.1 Hz), 115.7, 114.8 (d, *J* = 1.7 Hz), 114.3 (d, *J* = 0.9 Hz), 85.6, 38.3, 19.9. ESI-MS: calculated $C_{27}H_{21}FIN_3O_2Na$ $[M+Na]^+$ 588.0554; Found 588.0563.

Methyl 2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-1-(dimethylcarbamoyl)-1*H*-indole-6-carboxylate (7f)



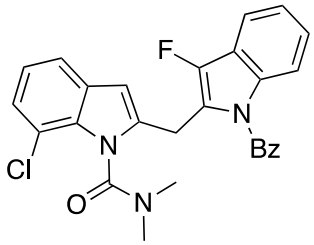
Following the general procedure C, the product **7f** was obtained in 76% yield (75.6 mg, 0.152 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.82 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.15 (m, 2H), 7.02 (t, *J* = 7.9 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.44 (s, 2H), 3.90 (s, 43H), 2.86 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.71. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 167.7, 154.3, 146.9 (d, *J* = 250.4 Hz), 135.2, 134.9, 133.7 (d, *J* = 5.4 Hz), 133.3, 132.2, 129.6, 128.9, 127.6, 125.6, 124.5, 122.9 (d, *J* = 5.7 Hz), 121.4 (d, *J* = 24.0 Hz), 119.6 (d, *J* = 18.6 Hz), 118.6, 116.9 (d, *J* = 2.4 Hz), 115.5, 115.5 (d, *J* = 1.9 Hz), 114.2 (d, *J* = 1.3 Hz), 100.0, 52.1, 38.2, 20.0. ESI-MS: calculated $C_{29}H_{24}FN_3O_4Na$ $[M+Na]^+$ 520.1643; Found 520.1640.

2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-6-bromo-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (7g)



Following the general procedure C, the product **7g** was obtained in 54% yield (56.0 mg, 0.108 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.4 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.41 (d, *J* = 2.5 Hz, 2H), 7.36 (dd, *J* = 7.5, 3.6 Hz, 2H), 7.30 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.19 (td, *J* = 7.4, 3.9 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.67 (d, *J* = 7.3 Hz, 1H), 4.40 (s, 2H), 2.83 (d, *J* = 4.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.84. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 154.4, 146.9 (d, *J* = 250.3 Hz), 136.6, 134.9, 133.7 (d, *J* = 5.5 Hz), 133.3, 129.7, 128.9, 127.5, 125.1, 125.0, 124.5, 122.9, 121.5 (d, *J* = 24.0 Hz), 120.0 (d, *J* = 1.3 Hz), 119.6 (d, *J* = 18.5 Hz), 117.7, 116.9, 116.9, 115.4 (d, *J* = 2.0 Hz), 114.2 (d, *J* = 1.5 Hz), 38.2, 19.9. ESI-MS: calculated $C_{27}H_{21}BrFN_3O_2Na$ $[M+Na]^+$ 540.0693; Found 540.0699.

2-((1-benzoyl-3-fluoro-1*H*-indol-2-yl)methyl)-7-chloro-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (7h)

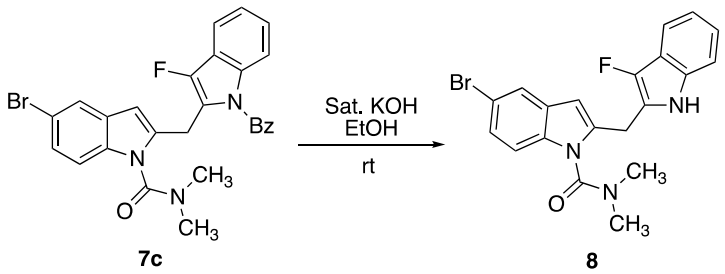


Following the general procedure C, the product **7h** was obtained in 73% yield (69.2 mg, 0.146 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 18.8, 7.7 Hz, 2H), 7.44 (s, 2H), 7.36 (q, *J* = 7.9 Hz, 3H), 7.19 (dt, *J* = 7.6, 3.7 Hz, 2H), 7.02 (q, *J* = 7.3 Hz, 2H), 6.92 (s, 1H), 6.68 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.43 (s, 2H), 3.05 (s, 3H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.95. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 153.5, 146.8 (d, *J* = 250.2 Hz), 134.9, 133.7 (d, *J* = 5.4 Hz), 133.3, 131.9, 130.4, 129.8, 128.8, 125.5, 124.4, 124.3, 122.8, 122.0, 121.7 (d, *J* = 23.9 Hz), 119.6 (d, *J* = 18.6 Hz), 117.8 (d, *J* = 1.0 Hz), 117.5, 116.9 (d, *J* = 2.5 Hz), 115.0 (d, *J* = 2.0 Hz), 114.1 (d, *J* = 1.6 Hz), 37.8, 36.7, 20.1. ESI-MS: calculated $C_{27}H_{21}ClFN_3O_2Na$ $[M+Na]^+$ 496.1198; Found 496.1198.

4. Synthetic application of the product

4.1 Gram- Scale Synthesis

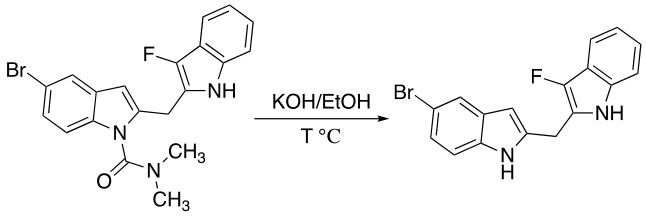
In an oven-dried Schlenk tube under atmosphere of N_2, a mixture of the substrates **1a** (1.0 mmol, 1.0 equiv), (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4a** (325.2 mg, 1.2 mmol, 1.1 equiv), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol, 2.5 mmol%), $AgSbF_6$ (34.3 mg, 0.1 mmol, 10.0 mmol%), AgF (63.0 mg, 0.5 mmol, 0.5 equiv), $AgBF_4$ (98.0 mg, 0.5 mmol, 0.5 equiv) , $Ca(OH)_2$ (74 mg, 1.0 mmol, 1.0 equiv) and DCE (5.0 mL) was stirred at 120 °C for 2 h. The reaction mixture was then diluted with DCM (30 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (petroleum ether : ethyl acetate = 2:1) to give **5a** (427.2 mg, 87%).



7c **8**

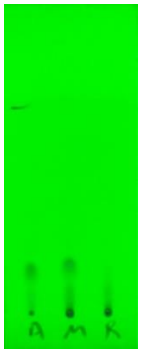
Preparation of a complex **8** was carried out according to the reported Li's procedure:[6] Compound **7c** (0.2 mmol) was charged to an oven-dried Schlenk tube. To the vial was then added 5.6 mL of Ethanol (99%) and 1.8 mL of saturated aqueous KOH solution. The mixture stirred at room temperature for 1 hour. The solution was then diluted with NH_4Cl solution and DCM. The phases were separated and the aqueous phase was reextracted with DCM. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica (petroleum ether : ethyl acetate = 4:1) to afford the pure product **8** as a brown solid. (69.1 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.55 – 7.50 (m, 1H), 7.20 (s, 2H), 7.14 – 7.09 (m, 1H), 7.08 – 7.03 (m, 2H), 7.01 (s, 1H), 4.16 (s, 2H), 2.90 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.71 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 135.2, 131.6 (d, J = 6.1 Hz), 128.8, 124.9, 124.1 (d, J = 16.6 Hz), 121.8, 121.1, 119.5, 119.3, 118.2 (d, J = 13.3 Hz), 117.6 (d, J = 16.2 Hz), 116.1 (d, J = 2.5 Hz), 112.8 (d, J = 5.0 Hz), 112.6, 111.5, 111.0, 49.3 (dp, J = 42.9, 21.4 Hz), 20.1. ESI-MS: calculated $C_{20}H_{17}BrFN_3ONa$ $[M+Na]^+$ 436.0437; Found 436.0483.

Note: we have also tried the removal of *N*,*N*-dimethyl-carboxamide substituent in **7c**. The results are shown in the table below, we repeated similar reaction conditions reported in the literature, unfortunately, the substituent of *N*,*N*-dimethyl-carboxamide in **7c** cannot be removed.



A **B**

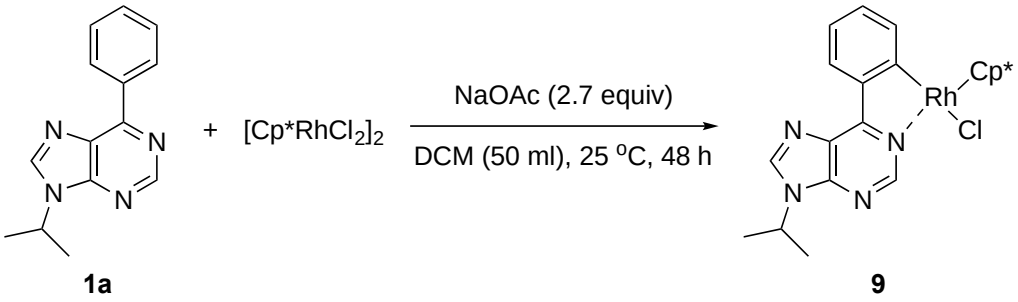
	Reaction conditions	Mw (A)	mmol	m(mg)	V (Base)	T (℃)	results
1	Sat. KOH/EtOH = 1/3	414.28	0.1	41.4	3.6 mL	60 ℃	fail
2	Sat. KOH/EtOH = 1/3	414.28	0.1	41.4	3.6 mL	35 ℃	fail
3	Sat. KOH/EtOH = 1/3	414.28	0.1	41.4	3.6 mL	25 ℃	fail
4	1 mol/L KOH/EtOH = 1/3	414.28	0.1	41.4	3.6 mL	35 ℃	fail



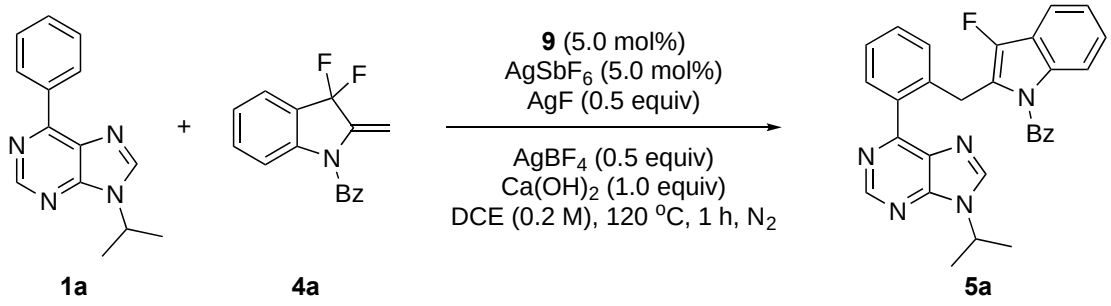
PE:EA = 4/1

PE:EA = 2/1

5. Mechanistic experiments



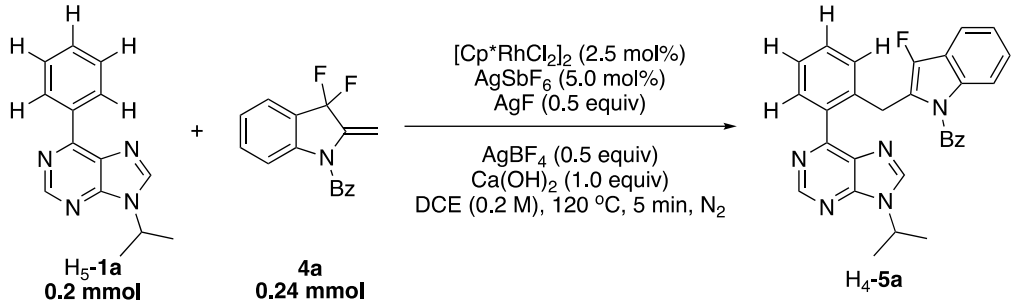
Preparation of a complex **9** was carried out according to the reported Kim's procedure:[5] A solution of 6-arylpurine **1a** (47.6 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol, 0.5 equiv) and NaOAc (44.3 mg, 0.54 mmol, 2.7 equiv) in CH_2Cl_2 (50 mL) was stirred at room temperature under atmosphere of N_2 for 48 h. The crude mixture was filtered through a pad of celite washing with CH_2Cl_2 (10 mL x 2) and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 4:1) to give the desired product (51.4 mg, 69% yield).

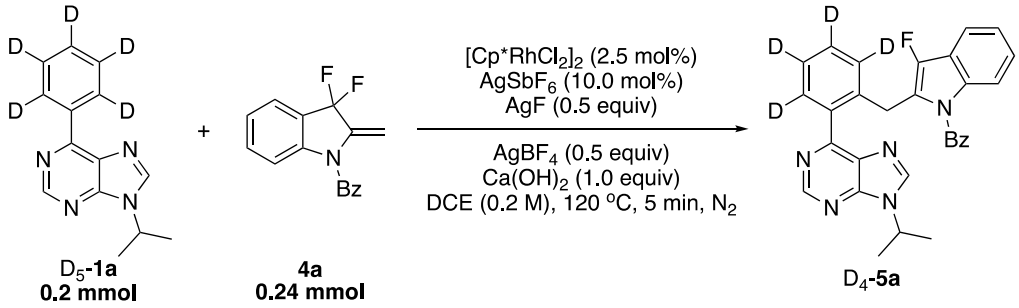


In an oven-dried Schlenk tube under atmosphere of N_2, a mixture of the substrates **1a** (0.2 mmol, 1.0 equiv), (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4a** (59.6 mg, 0.22 mmol, 1.2 equiv), rhodium complex **9** (3.8 mg, 0.01 mmol, 5.0 mmol%), $AgSbF_6$ (3.43 mg, 0.01 mmol, 5.0 mmol%), $AgBF_4$ (19.4 mg, 0.1mmol, 0.5 equiv), AgF (12.6 mg, 0.1mmol, 0.5 equiv), $Ca(OH)_2$ (14.8 mg, 0.2 mmol, 1.0 equiv), and DCE (1.0 mL) was stirred at 120 °C for 1 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried

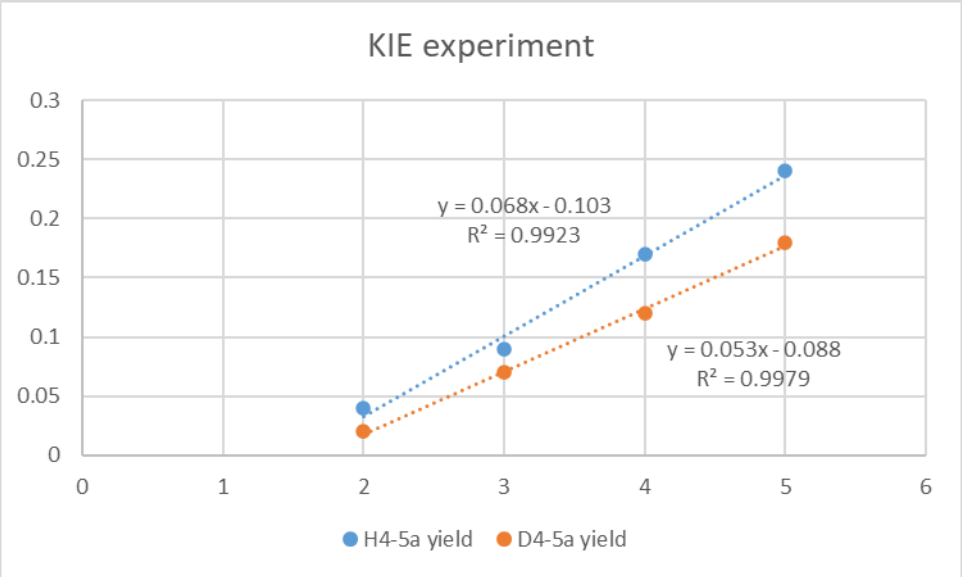
over Na_2SO_4. The pure product was purified by flash column chromatography on silica (petroleum ether : ethyl acetate = 2:1) to afford the pure product **5a** (55.8 mg, 57%).

Kinetic isotope effect experiments

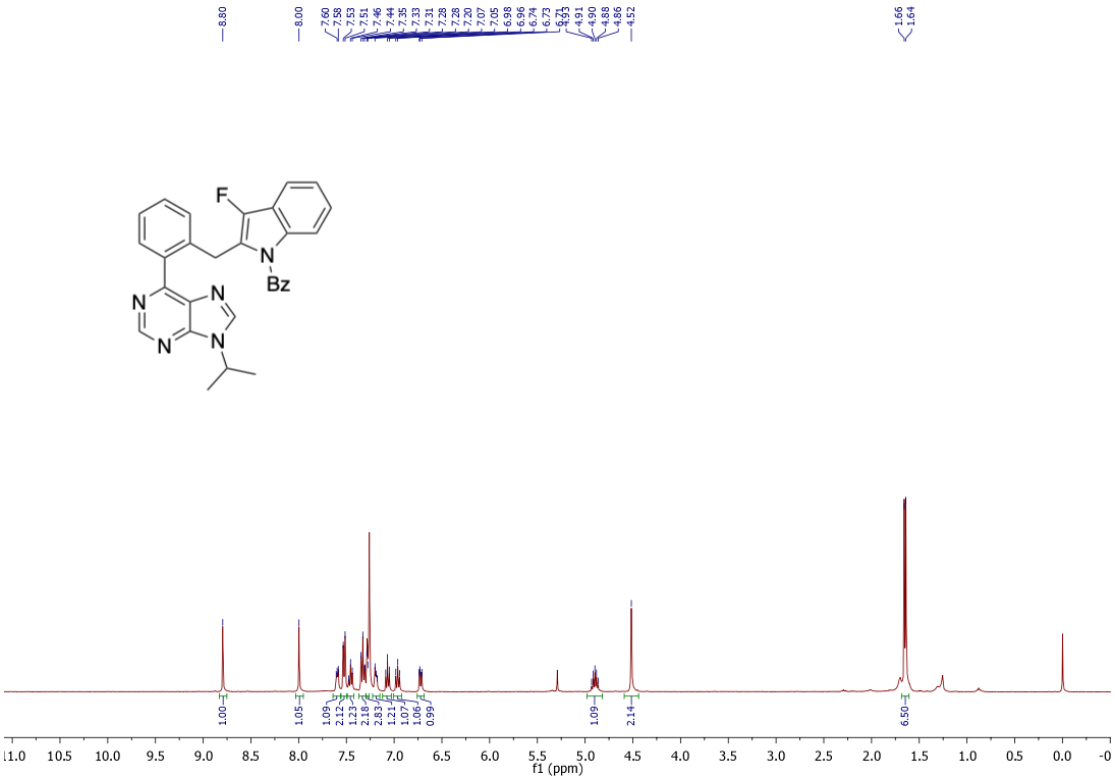


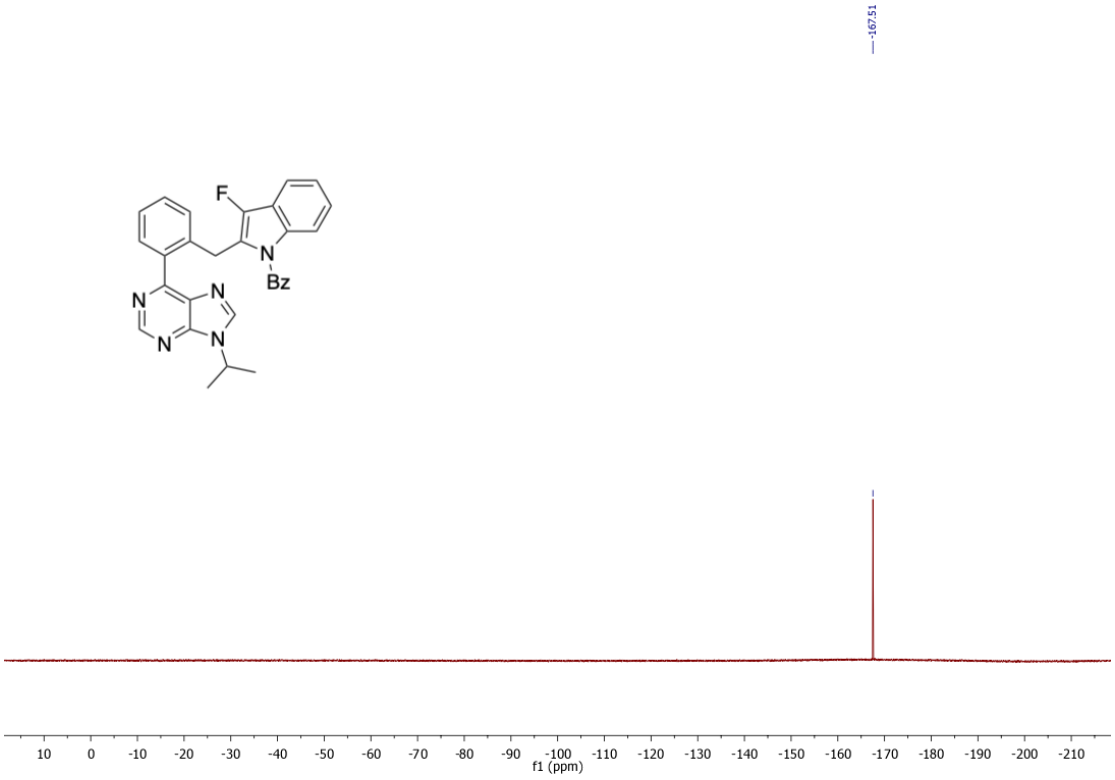


Following general procedure A, to a 15 mL-schlenk tube charged with a stirring bar under atmosphere of N_2, were added 6-arylpurine **1a** (47.6 mg, 0.2 mmol, 1.0 equiv), (3,3-difluoro-2-methyleneindolin-1-yl)(phenyl)methanone **4a** (65.0 mg, 0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.86 mg, 0.02 mmol, 10.0 mmol%), $AgBF_4$ (19.4 mg, 0.1mmol, 0.5 equiv), AgF (12.6 mg, 0.1mmol, 0.5 equiv), $Ca(OH)_2$ (14.8 mg, 0.2 mmol, 1.0 equiv), and DCE (1.0 mL). In another reaction vessel, (D_5)-**1a** (48.6 mg, 0.2 mmol, 1.0 equiv) was used instead of **1a**. The two reactions were allowed to stir at 120 °C. An aliquot of each reaction mixture was taken at the time of 2 min, 3 min, 4 min, and 5 min. The corresponding yield of each product was determined by ^1H NMR. A kinetic isotope effect value K^H/K^D = 0.068/0.053 = 1.3 was obtained

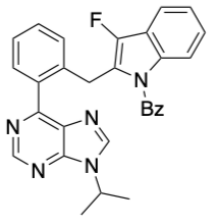

KIE experiment
0.3
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
y = 0.068x - 0.103
R² = 0.9923
y = 0.053x - 0.088
R² = 0.9979
H4-5a yield
D4-5a yield

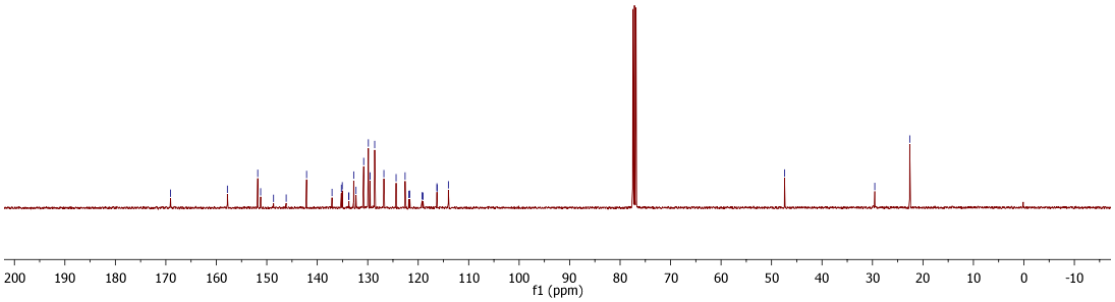
6. NMR Spectra for New Compounds



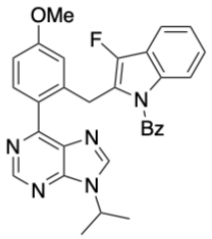


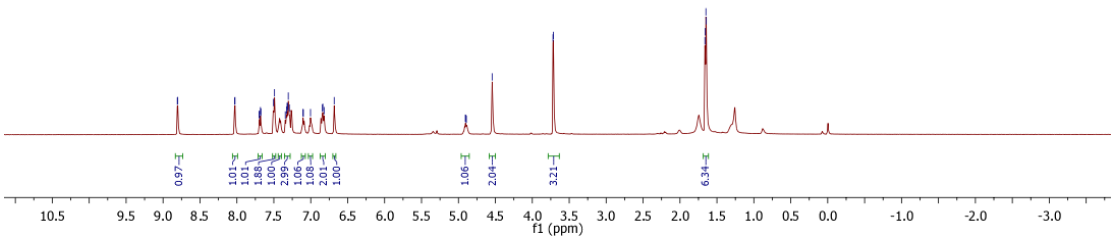

169.06
157.81
151.79
151.21
148.66
146.16
142.12
137.07
135.23
135.04
133.77
133.72
132.78
132.32
130.80
129.87
128.53
126.62
126.60
124.38
122.59
121.88
121.65
119.23
119.04
116.29
116.27
114.02
47.42
29.54
22.62


F
N
Bz
N
N
N
N


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.81
8.80
8.03
8.03
7.70
7.69
7.68
7.68
7.50
7.49
7.33
7.32
7.30
7.29
7.10
7.10
7.00
6.84
6.82
6.88
6.87
4.90
4.89
4.54
3.72
3.71
1.66
1.66
1.65
1.64


OMe
F
N
Bz
N
N
N
N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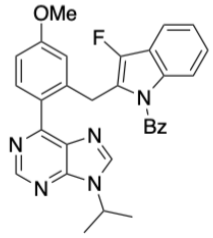
1.01
1.88
1.00
2.99
1.06
1.08
1.01
1.00
1.06
2.04
3.21
6.34
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)


OMe
F
N
Bz
N
N
N
N

167.58
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.01
160.58
157.55
151.65
151.16
148.77
146.23
141.85
139.20
135.04
133.78
133.73
132.81
132.69
132.25
129.82
128.55
127.55
124.47
122.68
121.67
121.44
119.35
119.17
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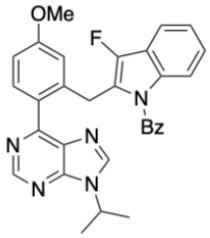
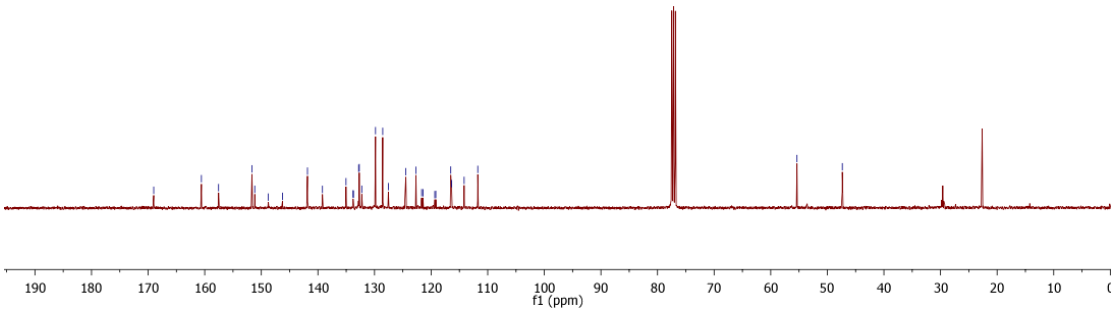
116.38
114.16
111.76
55.36
47.35


OMe
F
N
Bz
N
N
N
N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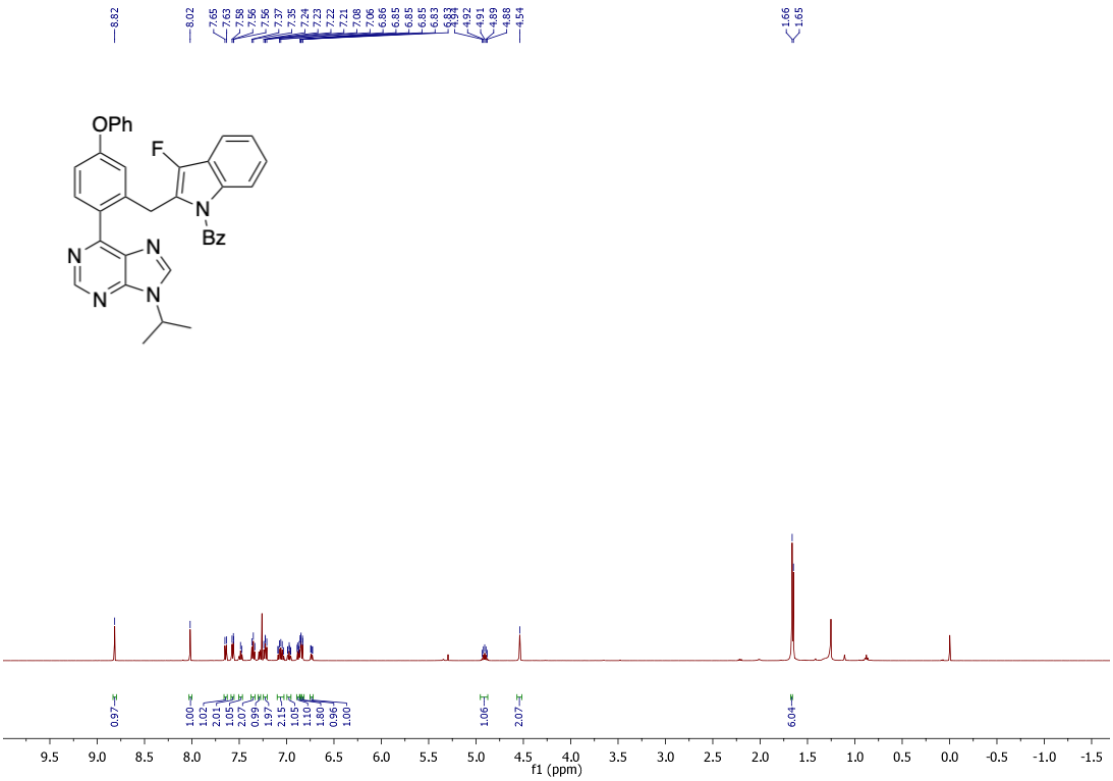
f1 (ppm)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7.56
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7.35
7.24
7.23
7.22
7.21
7.08
7.06
6.86
6.85
6.85
6.85
6.83
4.94
4.92
4.91
4.89
4.88
4.54
1.66
1.65
OPh
F
N
Bz
N
N
N
0.97
1.00
1.02
2.01
1.05
2.07
0.99
1.97
2.15
1.05
1.10
1.80
0.96
1.00
1.06
2.07
6.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
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1.5
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0.5
0.0
-0.5
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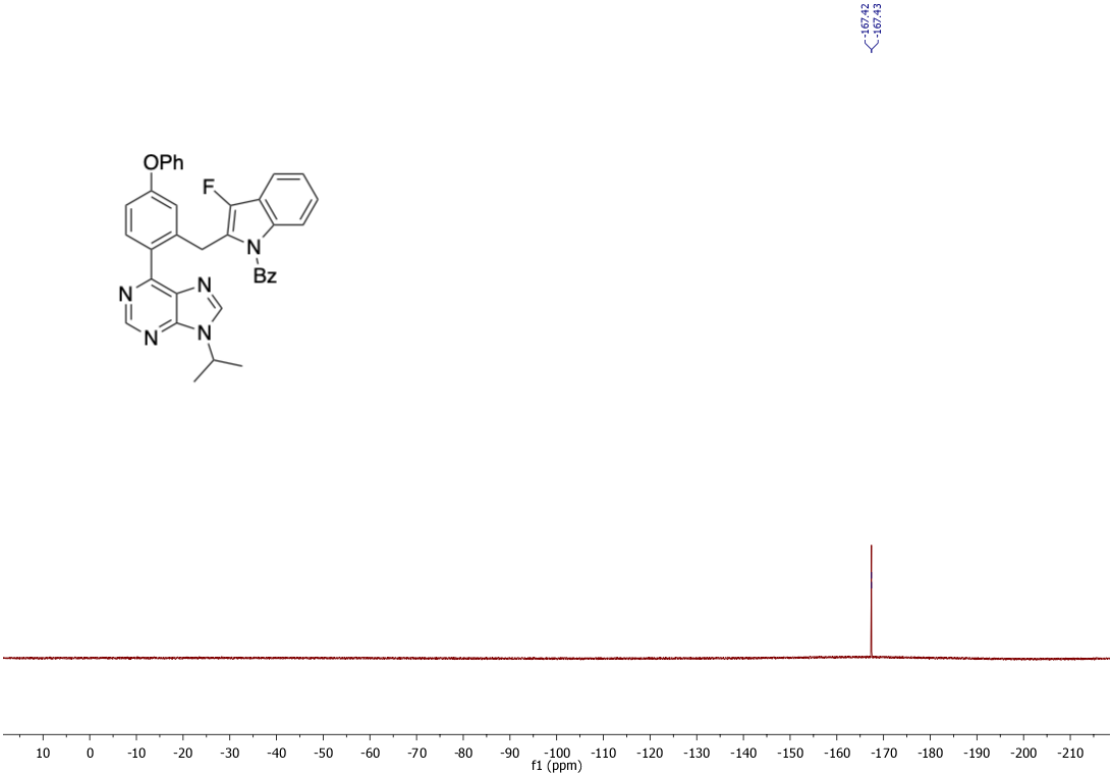
-1.5
f1 (ppm)


-167.42
-167.43
OPh
F
N
Bz
N
N
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


168.91
158.16
157.27
156.75
151.80
151.26
148.79
146.28
142.05
139.61
134.98
133.78
132.89
132.69
131.60
130.23
129.99
129.77
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124.42
123.50
122.60
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114.02
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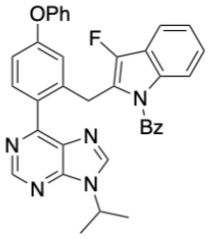
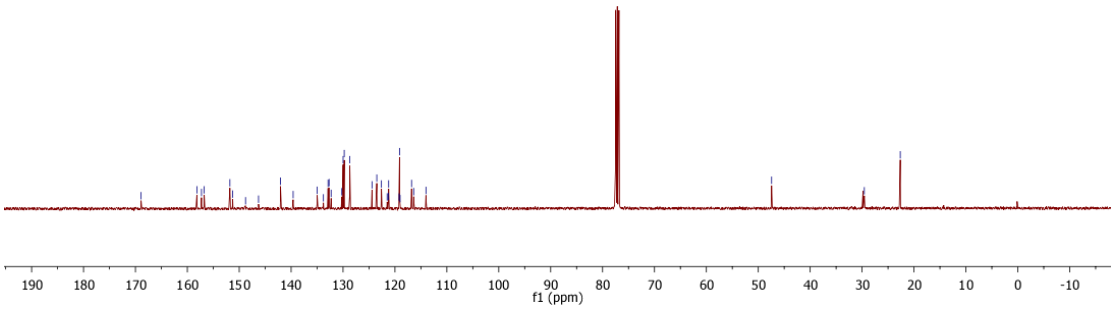
29.57
22.64


OPh
F
N
Bz
N
N
N
N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100
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80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.83
8.03
7.70
7.69
7.51
7.50
7.46
7.45
7.40
7.38
7.37
7.32
7.30
7.29
7.28
7.27
7.26
7.07
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6.94
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4.91
4.90
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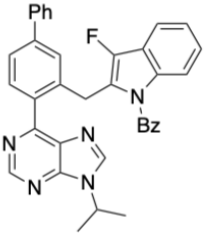
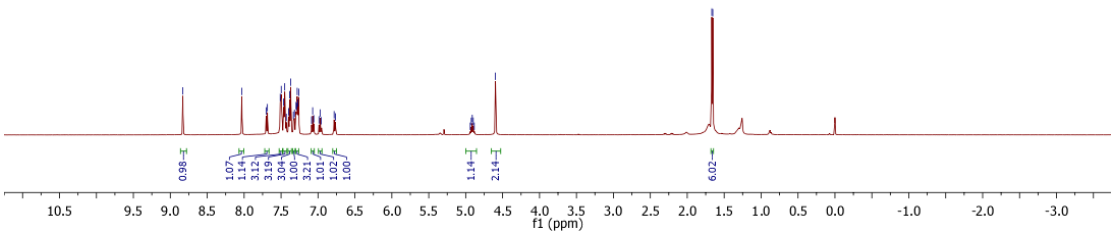
4.60
1.67
1.65


Ph
F
N
Bz
N
N
N
N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1.00
1.14
2.14
6.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
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0.0
-1.0
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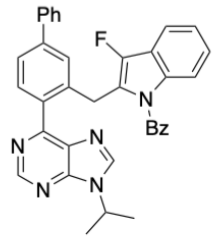
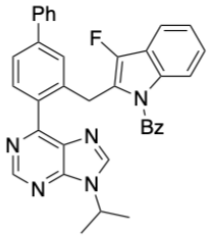
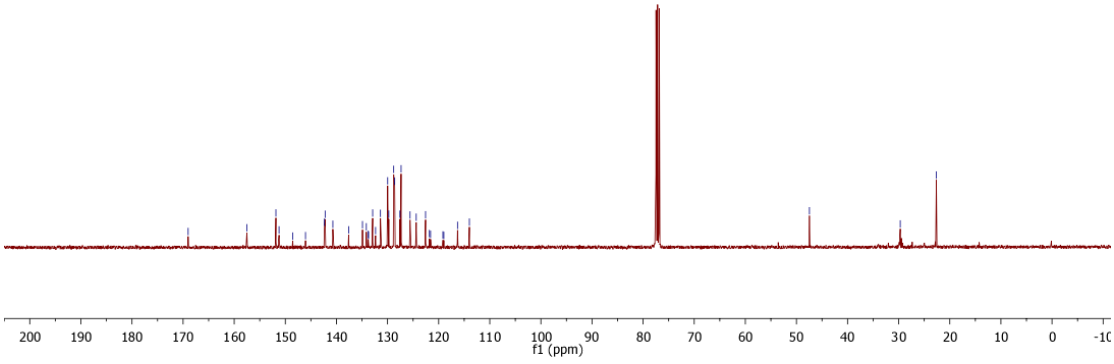
-3.0
f1 (ppm)

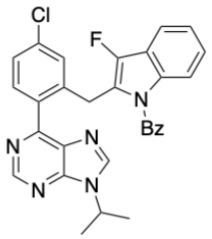

Ph
F
N
Bz
N
N
N
N

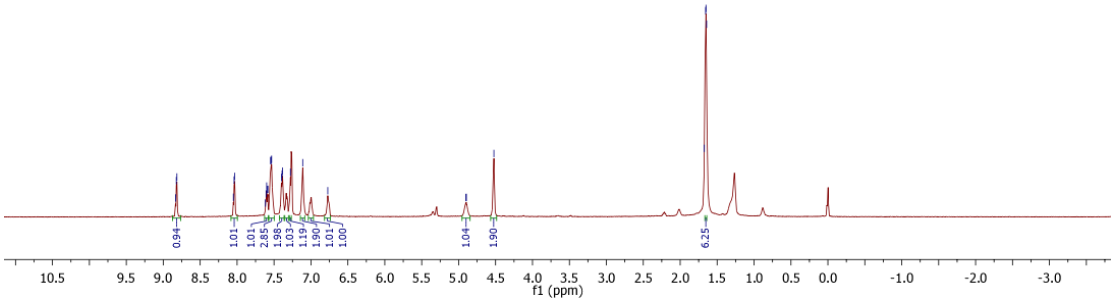
167.46
0.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.01
157.52
151.84
151.23
148.55
146.05
142.35
142.21
140.70
137.61
134.90
134.15
133.78
133.72
132.91
132.34
131.39
129.97
129.76
128.80
128.60
127.58
127.35
125.60
124.39
122.56
121.81
121.58
119.17
118.99
116.31
113.99
47.46
29.69
22.63


Ph
F
N
Bz
N
N
N
N

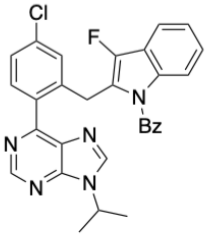

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

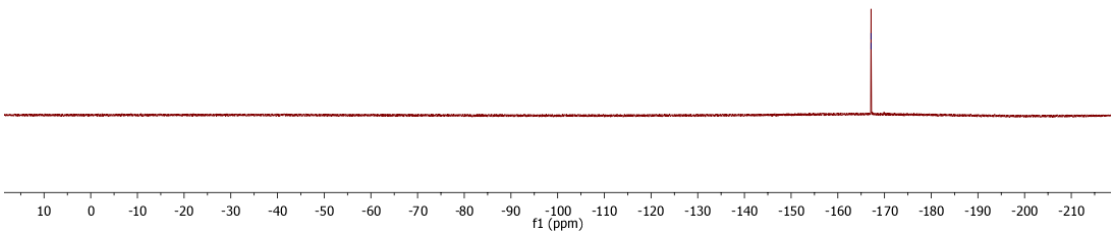

8.83
8.82
8.82
8.05
8.04
8.03
7.62
7.61
7.60
7.59
7.58
7.55
7.54
7.53
7.40
7.39
7.38
7.28
7.11
6.77
4.90
4.90
4.52
1.67
1.66
1.65
1.64


Cl
F
N
Bz
N
N
N
N

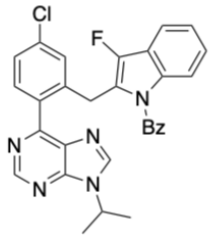

0.94
1.01
1.01
2.85
1.98
1.03
1.19
1.90
1.01
1.00
1.04
1.90
6.25
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

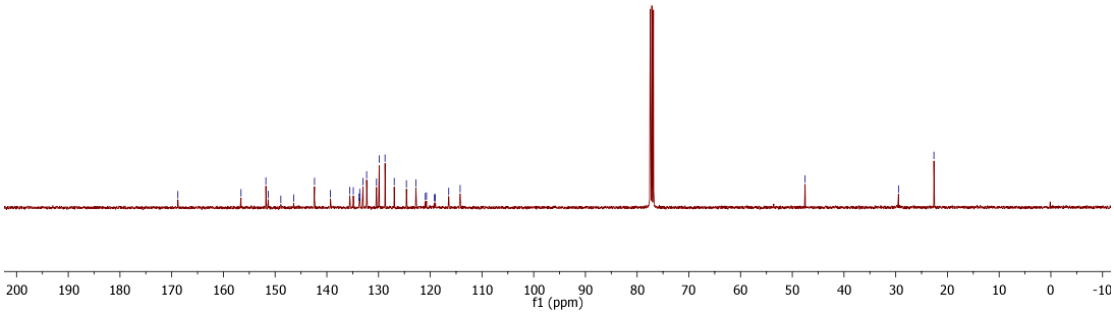

-167.10
-167.10


Cl
F
N
Bz
N
N
N
N

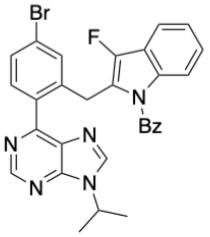

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

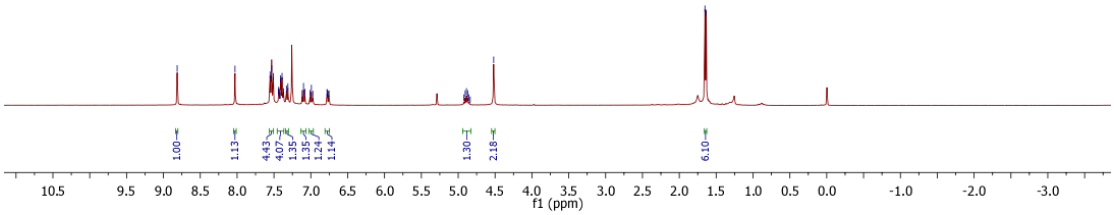

168.81
156.59
151.79
151.33
148.90
146.39
142.39
139.30
135.56
134.86
133.73
133.68
133.65
133.01
132.30
130.40
129.87
128.75
126.97
124.61
122.77
120.96
120.73
119.20
119.01
116.43
114.22
47.53
29.46
22.62

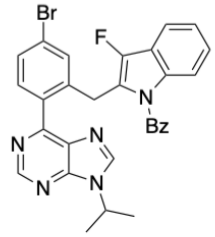

Cl
F
N
Bz
N
N
N
N


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

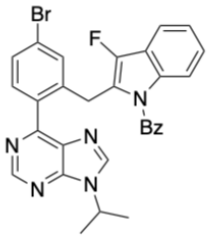

8.81
8.03
7.55
7.54
7.53
7.51
7.44
7.43
7.41
7.39
7.37
7.33
7.31
7.10
7.08
6.99
6.92
4.91
4.89
4.87
4.85
4.84
4.52
1.65
1.64

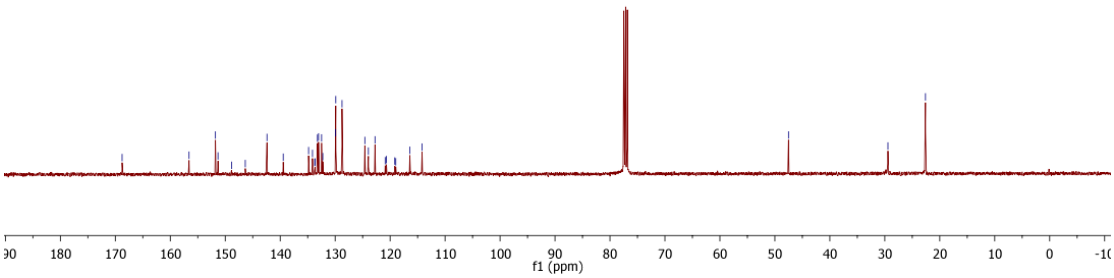

Br
F
N
Bz
N
N
N
N

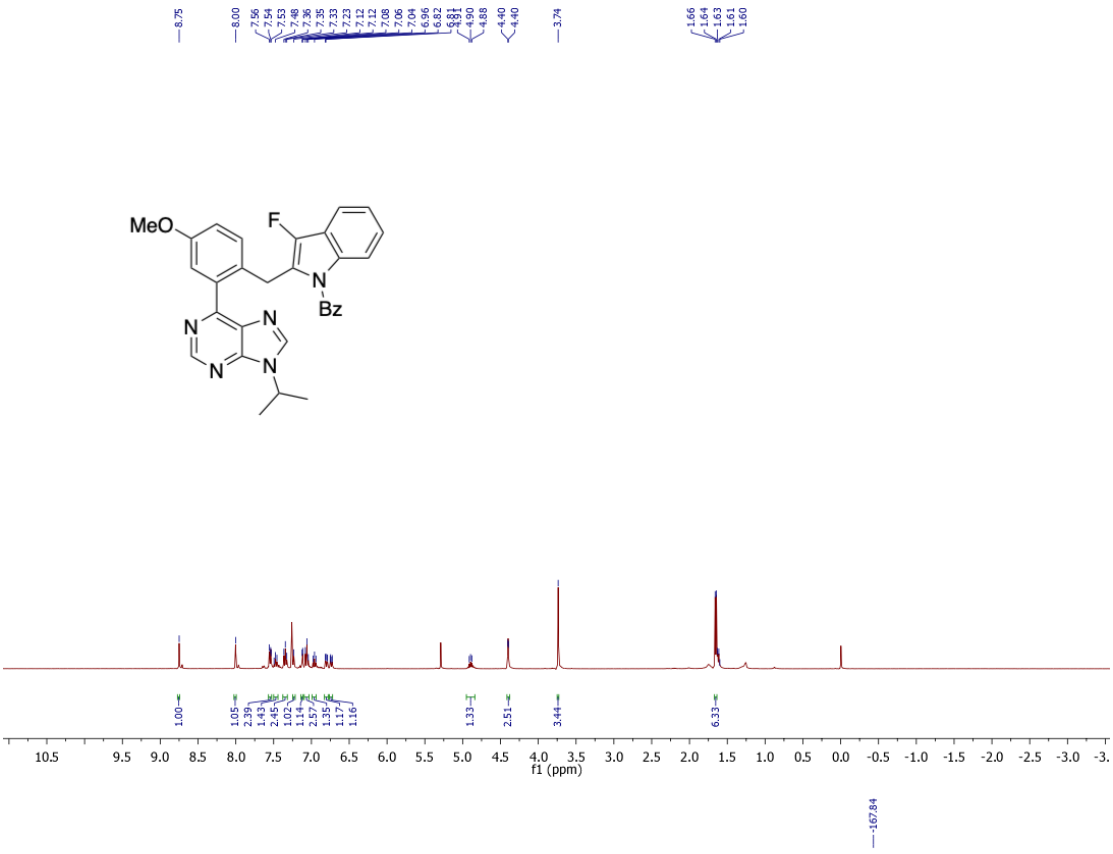

1.00
1.13
4.43
4.07
1.35
1.35
1.24
1.14
1.30
2.18
6.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

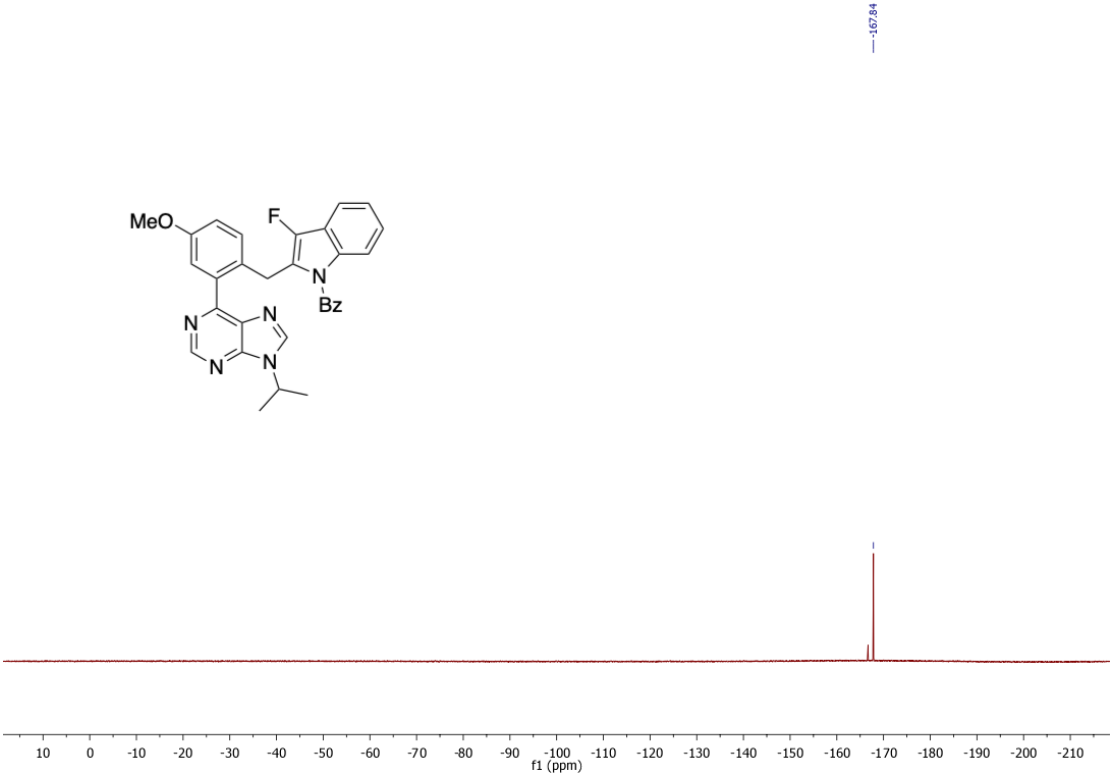

Br
F
N
Bz
N
N
N
N

-167.05
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
168.76
156.59
151.78
151.32
148.86
146.35
142.40
139.45
134.84
134.12
133.71
133.66
133.22
133.02
132.47
132.25
129.92
129.89
128.75
124.60
122.95
122.35
120.90
120.67
119.15
118.97
116.41
114.19
47.52
29.42
22.60

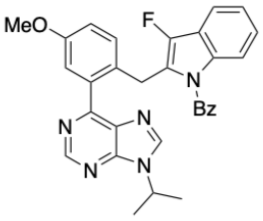

Br
F
N
Bz
N
N
N

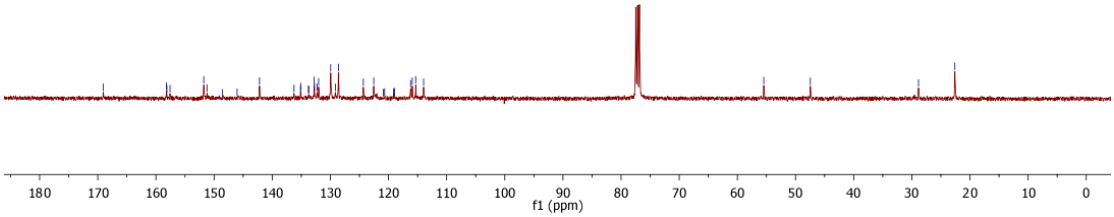

90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.75
8.00
7.56
7.54
7.53
7.48
7.36
7.35
7.33
7.23
7.12
7.12
7.08
7.06
7.04
6.96
6.82
4.91
4.90
4.88
4.40
4.40
3.74
1.66
1.64
1.63
1.61
1.60
MeO
F
N
Bz
N
N
N
N
1.00
1.05
2.39
1.43
2.45
1.02
1.14
2.57
1.35
1.17
1.16
1.33
2.51
3.44
6.33
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f1 (ppm)

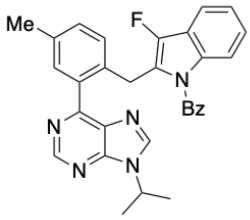

-167.84
MeO
F
N
Bz
N
N
N
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

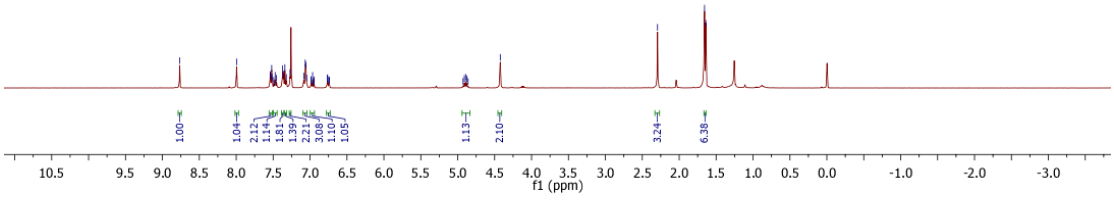

169.06
158.18
158.12
157.58
151.77
151.22
148.54
146.04
142.19
136.25
135.14
133.69
133.26
133.71
132.79
132.72
132.28
132.02
129.94
129.13
128.61
124.33
122.54
120.89
120.66
119.13
118.86
116.20
115.91
115.32
113.97
55.46
47.45
28.85
22.60

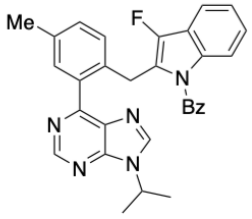

MeO
F
N
Bz
N
N
N
N


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

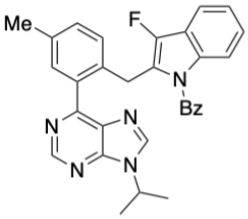

8.77
8.00
7.54
7.54
7.52
7.52
7.52
7.47
7.37
7.36
7.34
7.32
7.27
7.08
7.07
7.06
6.87
6.83
4.91
4.89
4.88
4.86
4.42
2.29
1.66
1.64

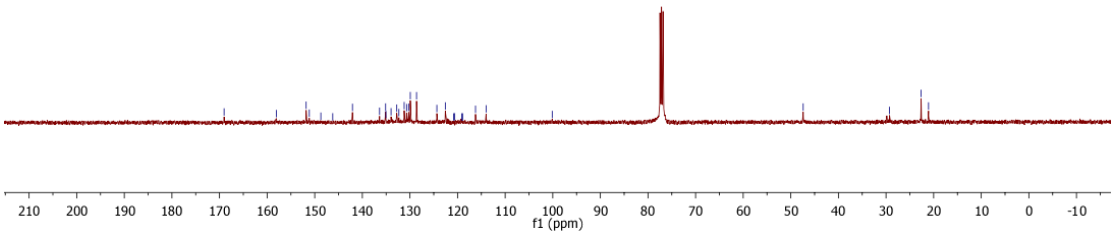

Me
F
N
Bz
N
N
N
N

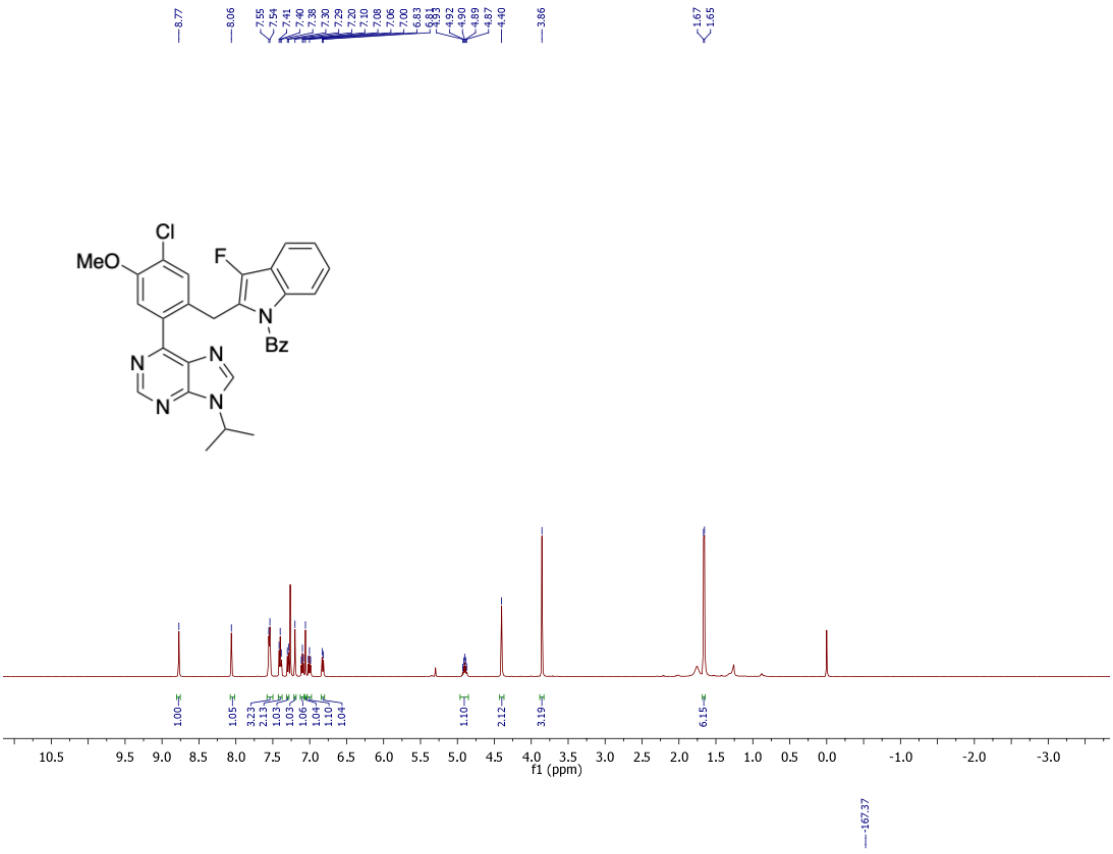

1.00
1.04
2.12
1.14
1.81
1.39
2.21
3.08
1.10
1.05
1.13
2.10
3.24
6.38
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

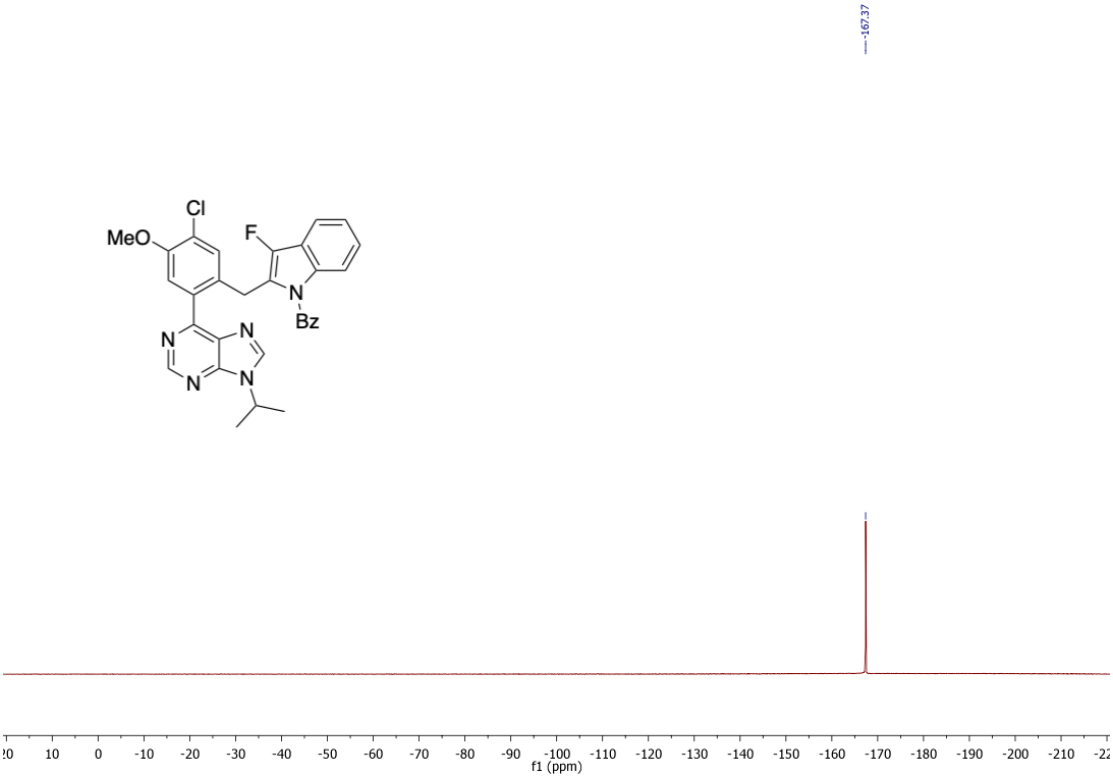

Me
F
N
Bz
N
N
N
N

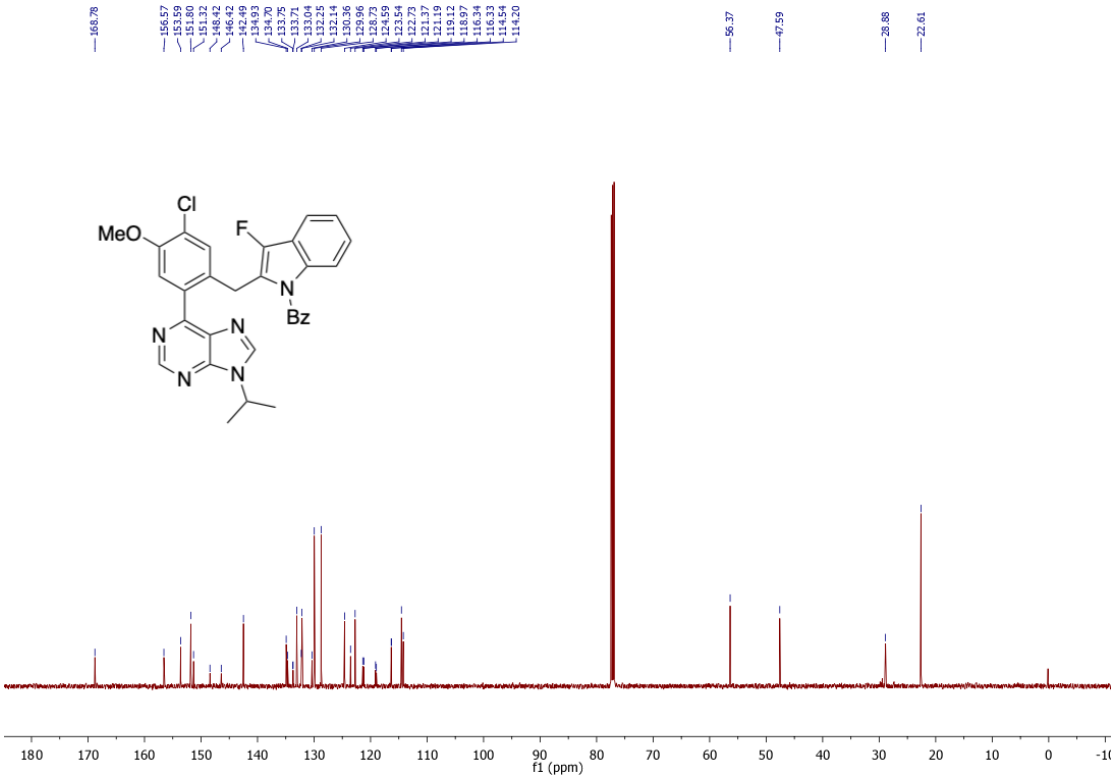
-167.64
-167.65
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.04
158.04
151.80
151.14
148.72
146.22
142.07
136.38
135.11
133.97
132.77
132.32
131.21
130.70
130.26
129.92
128.61
124.34
123.57
116.23
114.01
100.11
47.40
29.36
22.63
21.07

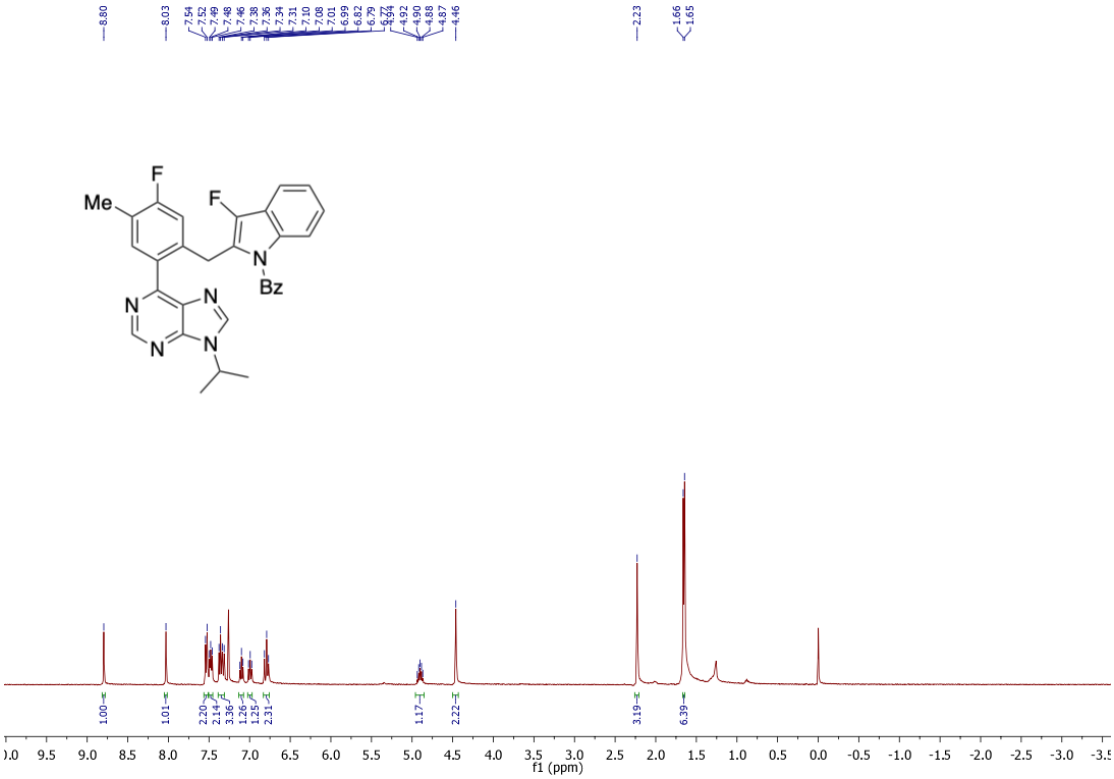

Me
F
N
Bz
N
N
N
N

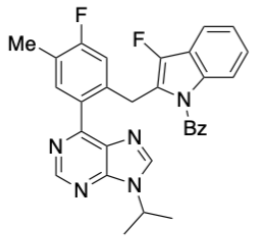

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.77
8.06
7.55
7.54
7.41
7.40
7.38
7.30
7.29
7.20
7.10
7.08
7.06
7.00
6.83
6.81
4.93
4.92
4.90
4.89
4.87
4.40
3.86
1.67
1.65
Cl
MeO
F
N
Bz
N
N
N
N
1.00
1.05
3.23
2.13
1.03
1.03
1.06
1.04
1.10
1.04
1.10
2.12
3.19
6.15
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

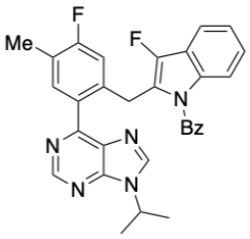

-167.37
Cl
MeO
F
N
Bz
N
N
N
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

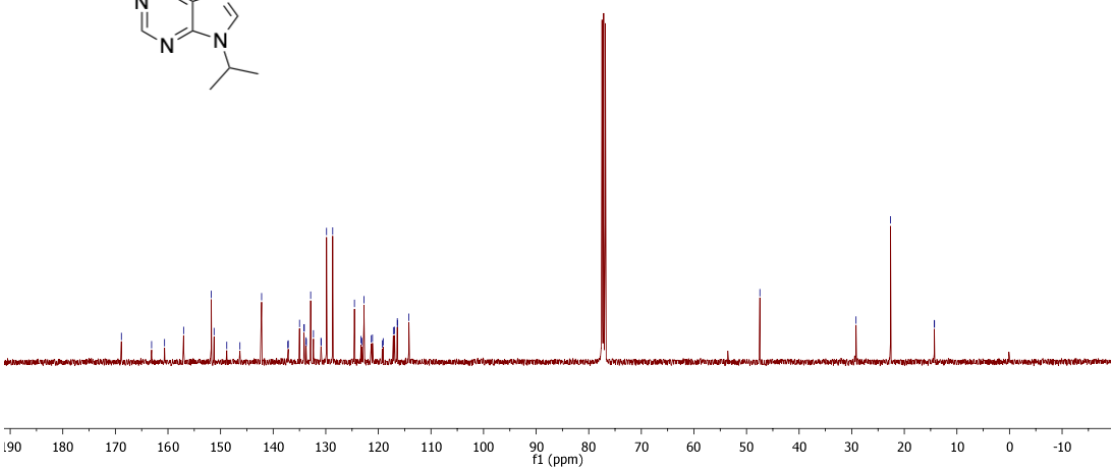

168.78
156.57
153.59
151.80
151.32
148.42
146.42
142.49
134.93
134.70
134.25
133.71
133.04
132.25
132.14
130.36
129.96
128.73
124.59
123.54
122.73
121.37
121.19
118.12
116.97
116.54
116.33
114.54
114.20
56.37
47.59
28.88
22.61
Cl
MeO
F
N
Bz
N
N
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.80
8.03
7.54
7.52
7.49
7.48
7.46
7.38
7.36
7.34
7.31
7.10
7.08
7.01
6.99
6.82
6.79
4.92
4.90
4.88
4.87
4.46
2.23
1.66
1.65
F
Me
F
N
Bz
N
N
N
N
1.00
1.01
2.20
2.14
3.36
1.26
1.25
2.31
1.17
2.22
3.19
6.39
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f1 (ppm)

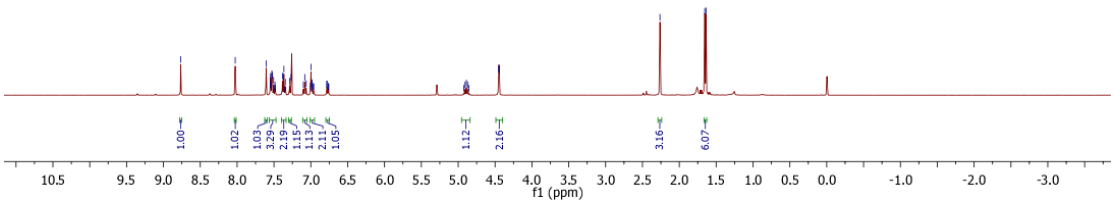

F
Me
F
N
Bz
N
N
N
N

-116.21
-167.39
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
168.86
163.11
160.65
157.03
151.77
151.23
148.82
146.32
142.20
137.20
137.13
134.99
134.14
134.08
133.74
133.69
132.97
132.34
130.91
130.88
129.85
128.68
124.54
123.30
123.12
122.74
121.34
121.11
119.26
119.08
117.45
116.52
116.40
116.38
114.20
67.46
29.18
22.62
14.30
14.27

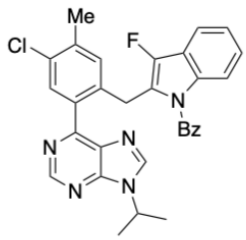

F
Me
F
N
Bz
N
N
N
N

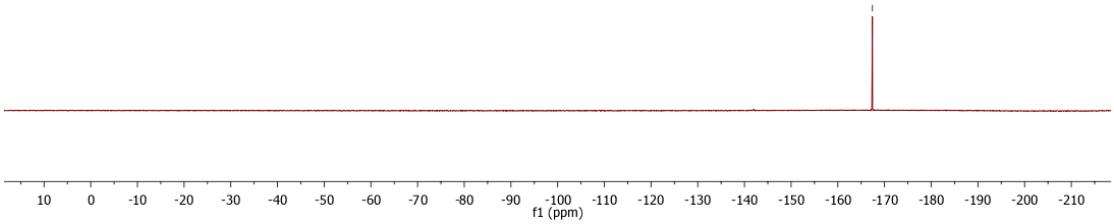

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

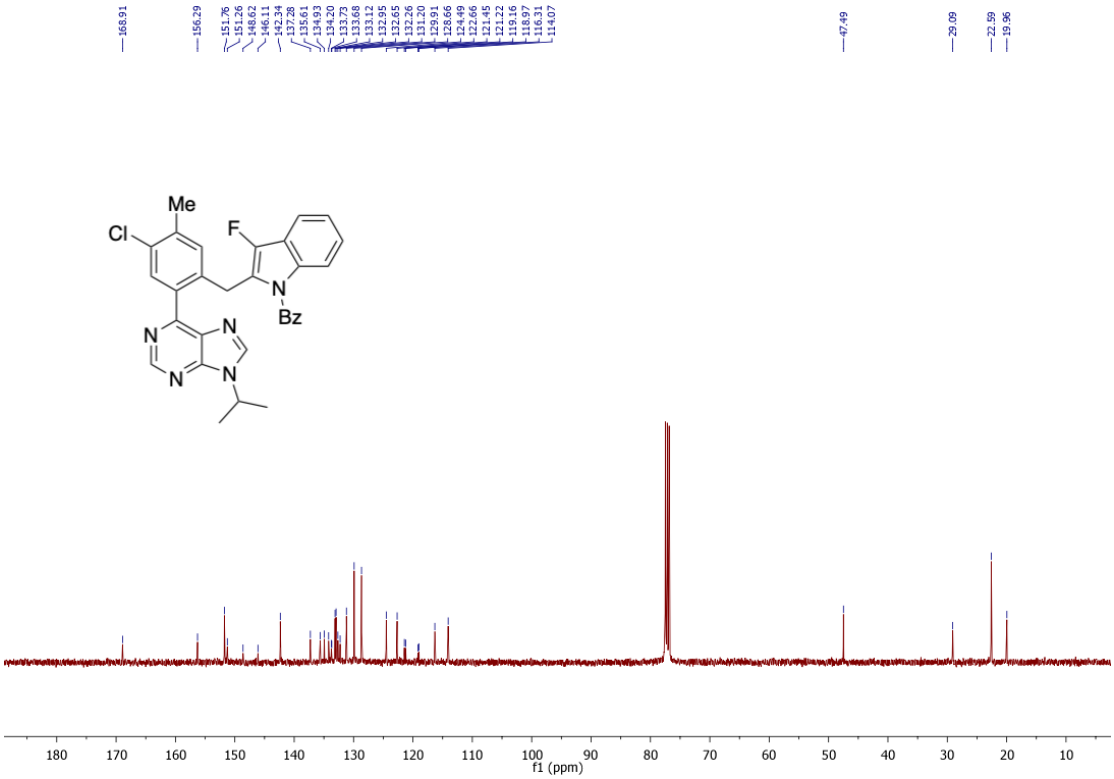

8.77
8.03
7.61
7.55
7.53
7.52
7.50
7.38
7.37
7.35
7.29
7.27
7.08
7.00
4.92
4.91
4.89
4.87
4.66
4.45
4.45
2.26
1.65
1.64
Me
Cl
F
N
Bz
N
N
N
N

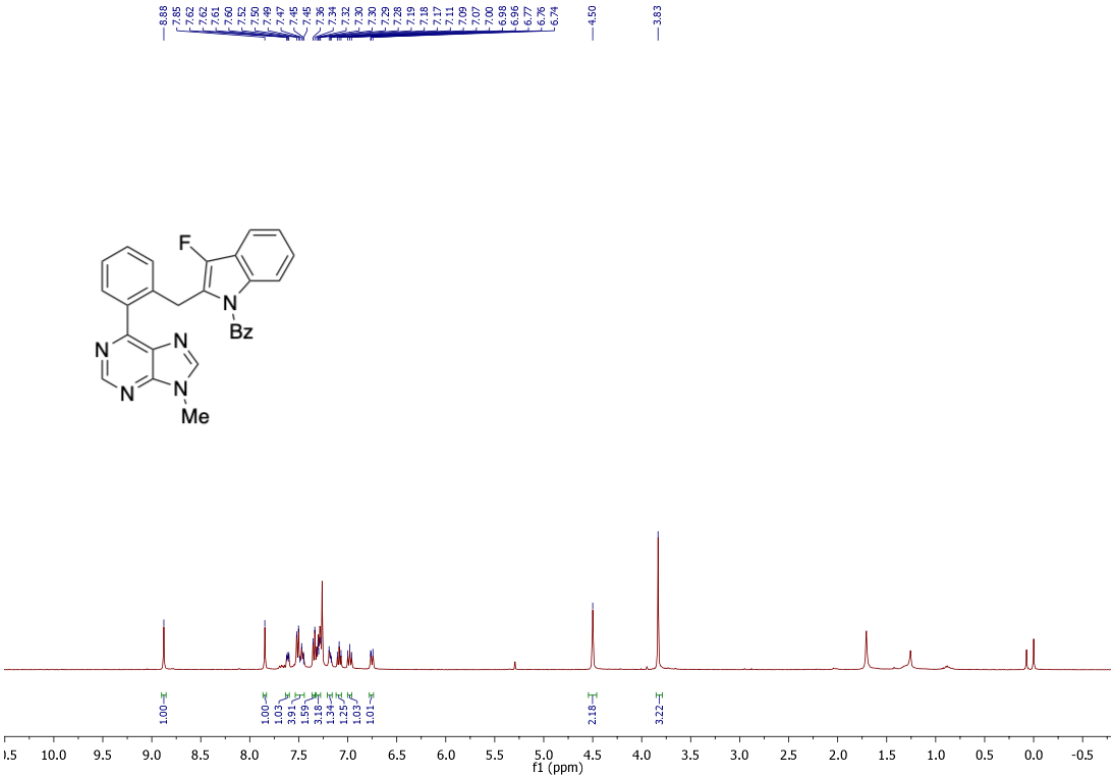

1.00
1.02
1.03
3.29
2.19
1.15
1.13
2.11
1.05
1.12
2.16
3.16
6.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

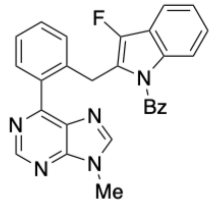
-167.42


Me
Cl
F
N
Bz
N
N
N
N

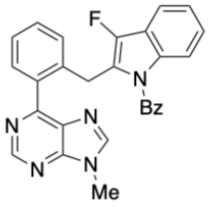

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

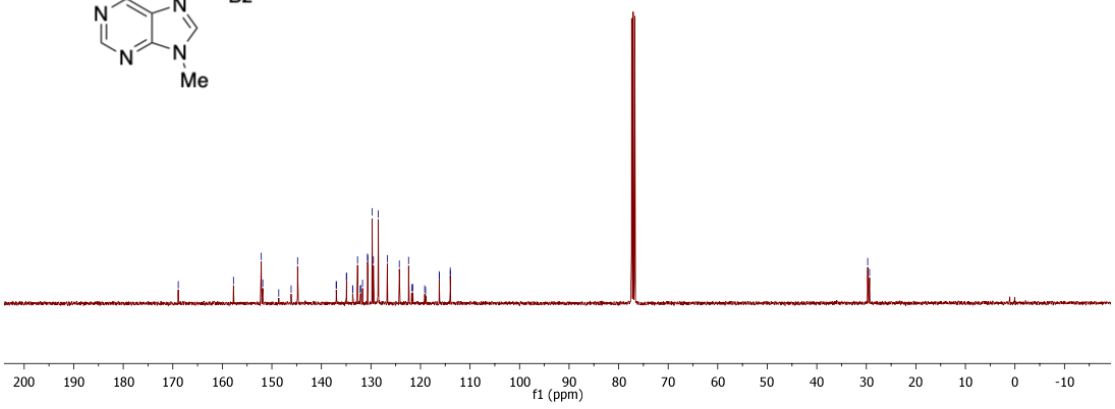

168.91
156.29
151.76
151.26
148.62
146.11
142.34
137.28
135.61
134.93
134.20
133.73
133.68
133.12
132.95
132.65
132.26
131.70
129.91
128.66
124.49
122.66
121.45
121.22
119.16
118.97
116.31
114.07
47.49
29.09
22.59
19.96
Me
Cl
F
N
Bz
N
N
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.88
7.85
7.62
7.62
7.61
7.60
7.52
7.50
7.49
7.47
7.45
7.36
7.34
7.32
7.30
7.30
7.29
7.28
7.19
7.18
7.17
7.11
7.09
7.07
7.00
6.98
6.96
6.77
6.76
6.74
4.50
3.83
F
N
Bz
N
N
N
N
Me
1.00
1.00
1.03
3.91
1.59
3.18
1.34
1.25
1.03
1.01
2.18
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

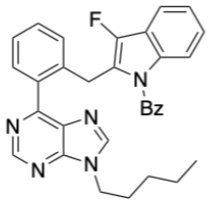

F
N
Bz
N
N
N
N
Me

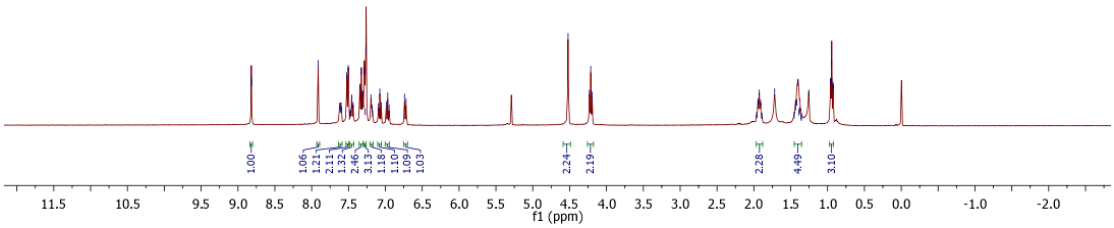
167.10
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
168.90
157.75
152.14
151.84
148.61
146.11
144.81
137.01
136.99
134.96
134.93
133.70
133.65
132.71
132.16
132.06
131.70
131.70
130.64
129.75
129.50
128.51
126.70
124.27
122.40
121.78
121.55
119.15
118.97
116.22
116.20
113.99
113.98
29.72
29.35

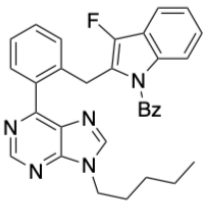

F
N
Bz
N
N
N
N
Me

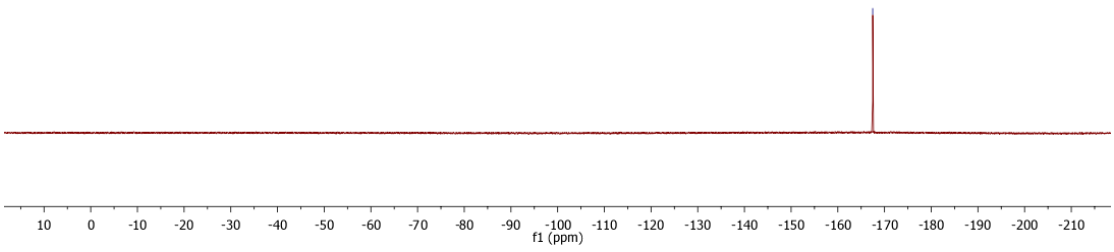

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.82
8.82
7.91
7.62
7.61
7.52
7.50
7.46
7.44
7.34
7.33
7.31
7.29
7.26
7.20
7.18
7.08
7.06
6.99
6.97
6.95
6.74
5.42
4.23
4.21
4.20
1.96
1.94
1.93
1.91
1.89
1.77
1.45
1.43
1.42
1.40
1.39
1.38
1.36
1.36
1.26
0.96
0.94
0.94
0.93


F
N
Bz
N
N
N


1.00
1.06
1.21
2.11
1.32
2.46
3.13
1.18
1.00
1.09
1.03
2.24
2.19
2.28
4.49
3.10
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
f1 (ppm)


F
N
Bz
N
N
N


-167.47
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


169.06
157.79
152.06
151.62
148.65
146.15
144.41
137.11
137.10
135.14
135.03
133.80
133.75
132.79
131.97
130.83
130.76
129.86
129.57
128.61
126.79
124.37
122.56
121.91
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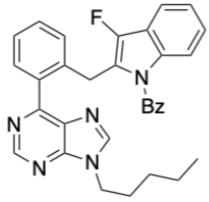
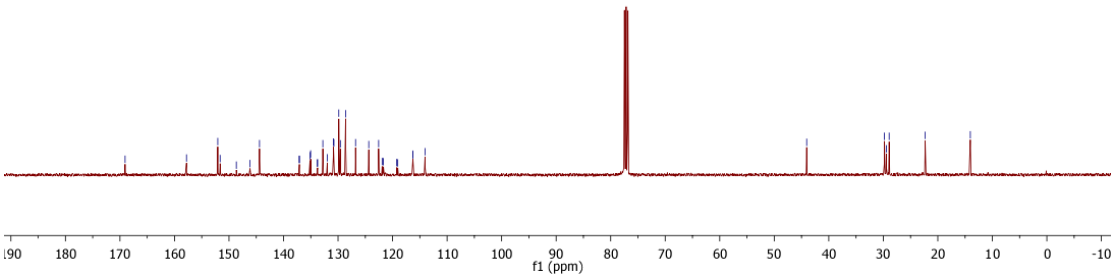
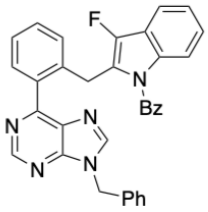
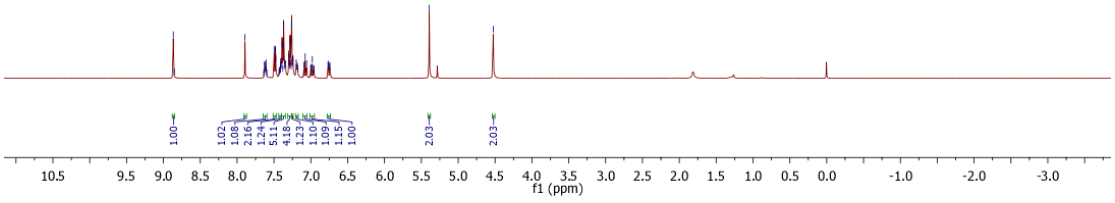
44.05
29.78
29.44
28.93
22.32
14.04

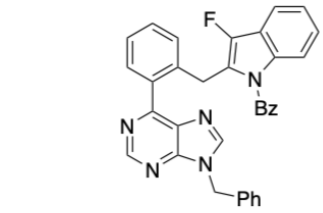

F
N
Bz
N
N
N
N


f1 (ppm)

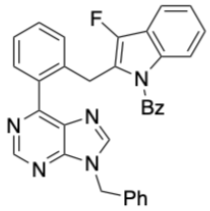

8.87
8.85
7.89
7.61
7.50
7.48
7.48
7.39
7.39
7.37
7.30
7.28
7.28
7.26
7.26
7.24
7.20
7.08
7.06
5.38
4.52

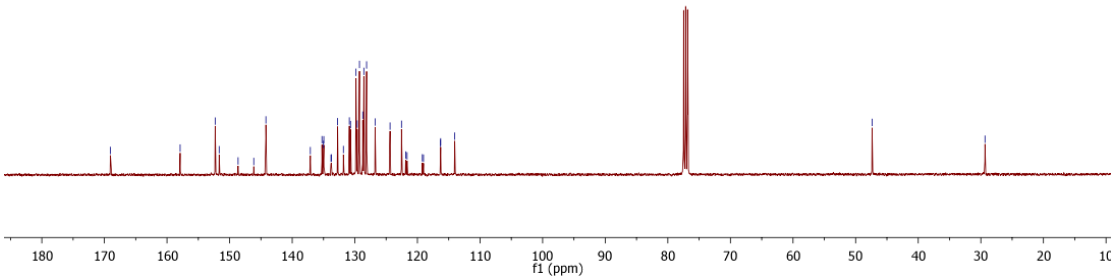

F
N
Bz
N
N
N
N
Ph


1.00
1.02
1.08
2.16
1.24
5.11
4.18
1.23
1.10
1.09
1.15
1.00
2.03
2.03
f1 (ppm)

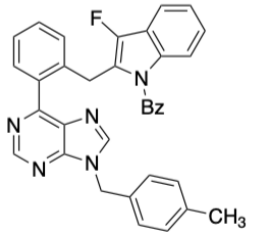

F
N
Bz
N
N
N
Ph

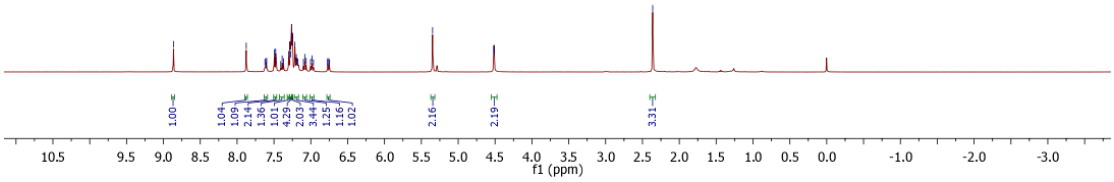
167.53
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.04
157.90
152.30
151.67
148.65
146.14
144.20
137.10
135.25
135.01
134.95
133.81
133.75
132.75
131.82
130.87
130.69
129.81
129.62
129.36
128.73
128.56
128.12
126.76
124.37
122.54
121.88
121.65
119.21
119.03
116.31
116.29
114.04
47.37
29.34


F
N
Bz
N
N
N
Ph

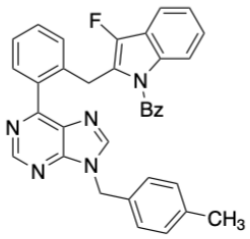

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

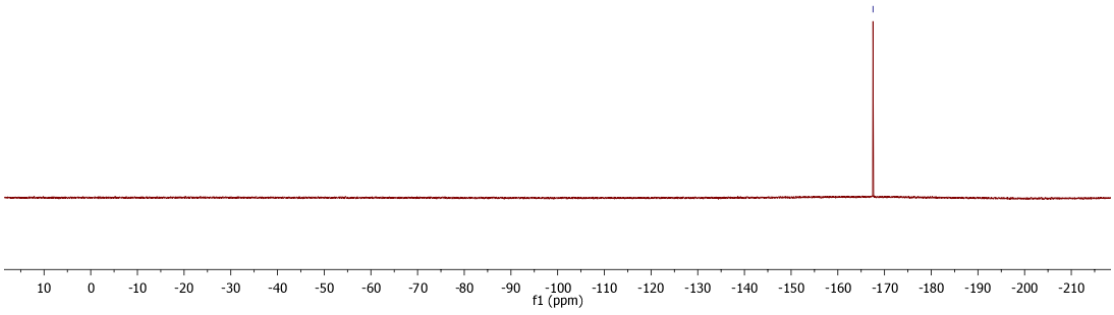

8.86
7.88
7.60
7.49
7.48
7.47
7.39
7.37
7.30
7.28
7.27
7.26
7.25
7.22
7.20
7.08
7.06
6.98
6.37
6.35
4.52
4.51
2.36

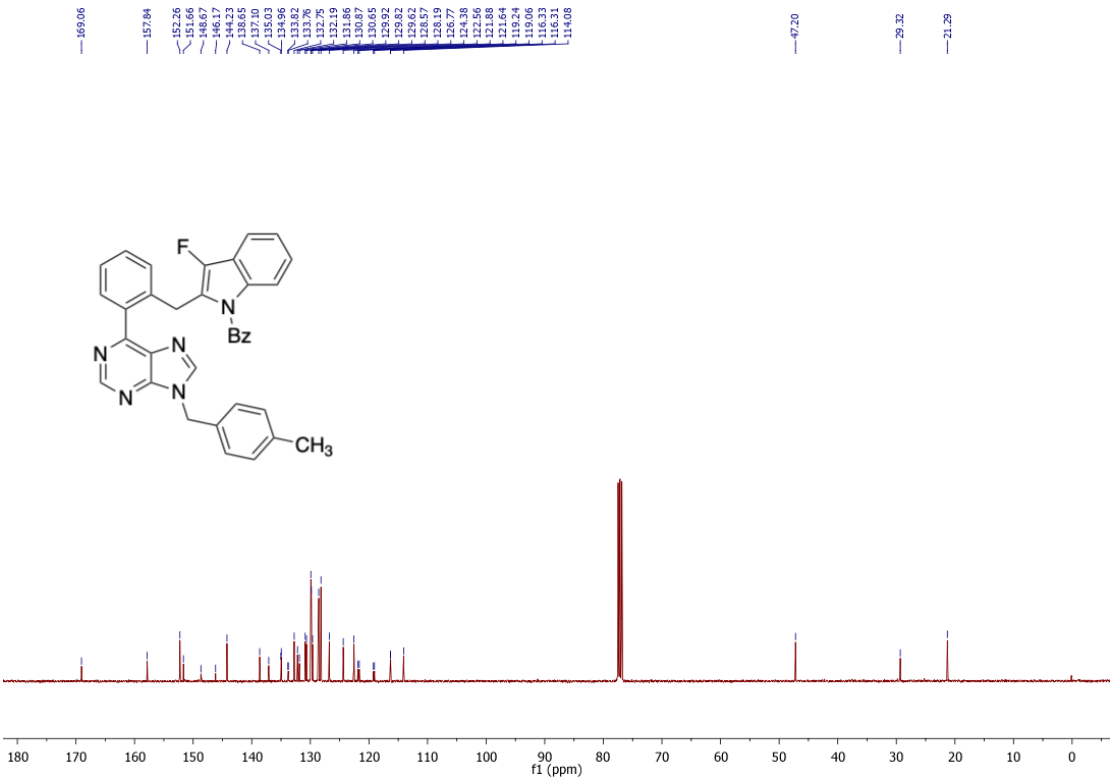

F
N
Bz
N
N
N
N
CH3

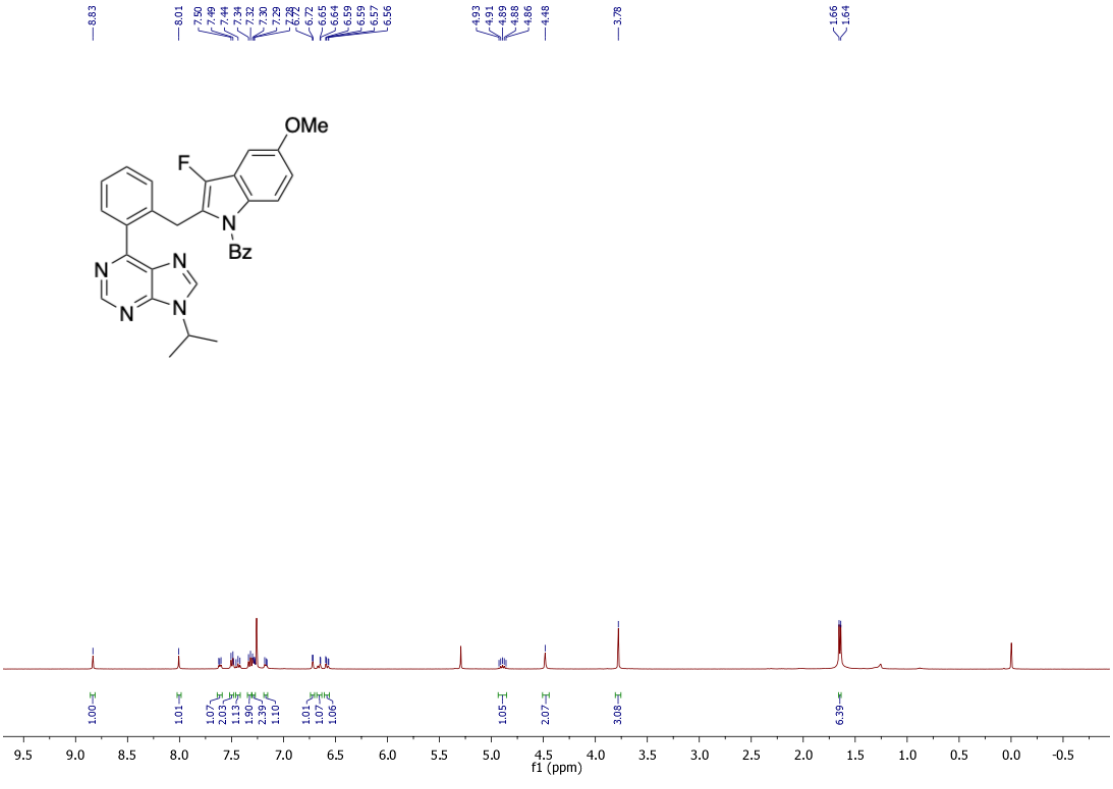

1.00
1.04
1.09
2.14
1.36
1.01
4.29
2.03
3.44
1.25
1.16
1.02
2.16
2.19
3.31
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

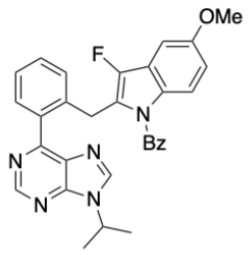
-167.52


F
N
Bz
N
N
N
N
CH3

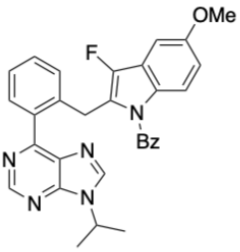

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

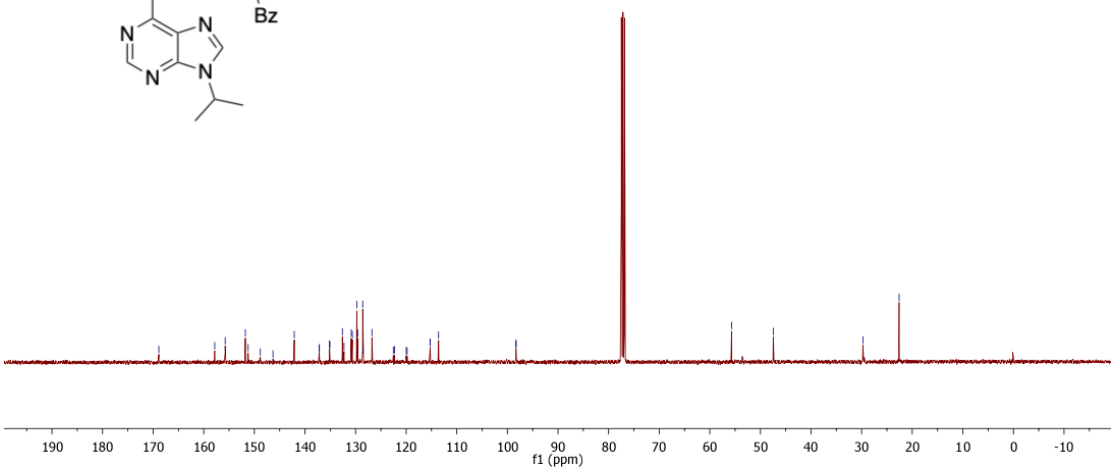

169.06
157.84
152.26
151.66
148.67
146.17
144.23
138.65
137.10
135.03
134.96
133.92
133.76
132.75
132.19
131.86
130.87
130.65
129.92
129.82
129.62
128.57
128.19
126.77
124.38
121.56
121.88
121.64
119.24
119.06
116.33
116.31
114.08
47.20
29.32
21.29
F
N
Bz
N
N
N
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

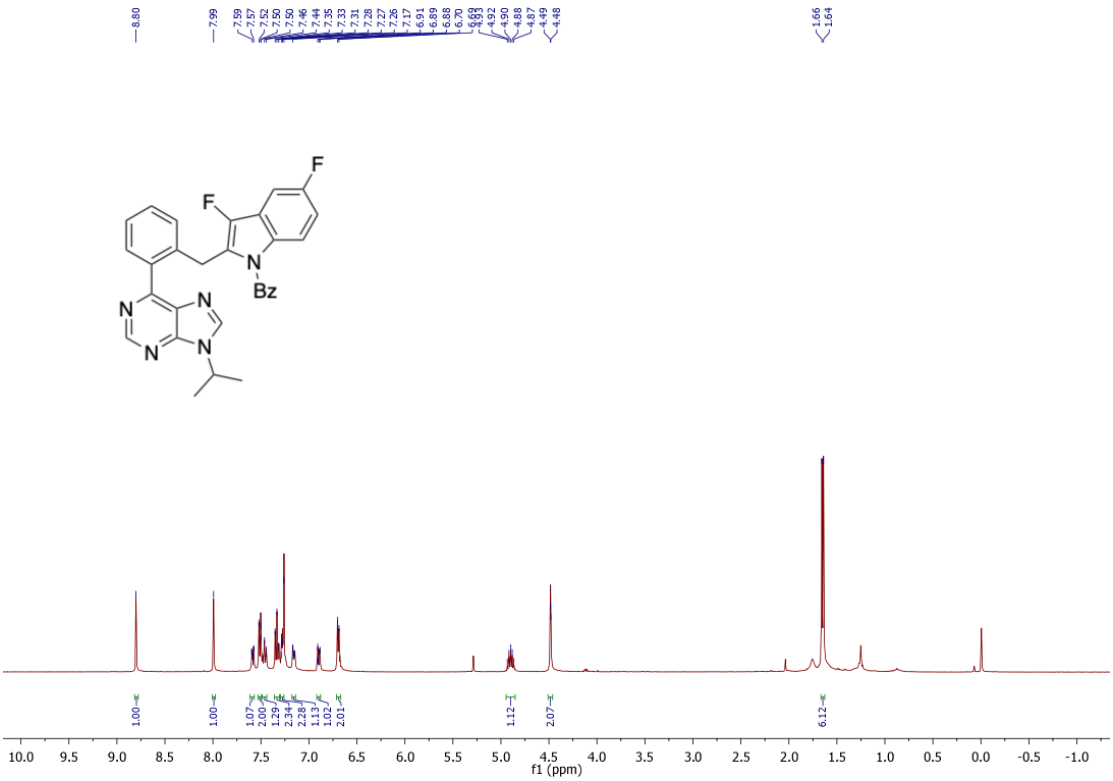

8.83
8.01
7.50
7.49
7.44
7.34
7.32
7.30
7.29
6.72
6.65
6.64
6.59
6.57
6.56
4.93
4.91
4.89
4.88
4.86
4.48
3.78
1.66
1.64
OMe
F
N
Bz
N
N
N
1.00
1.01
1.07
2.03
1.13
1.90
2.39
1.10
1.01
1.07
1.06
1.05
2.07
3.08
6.39
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

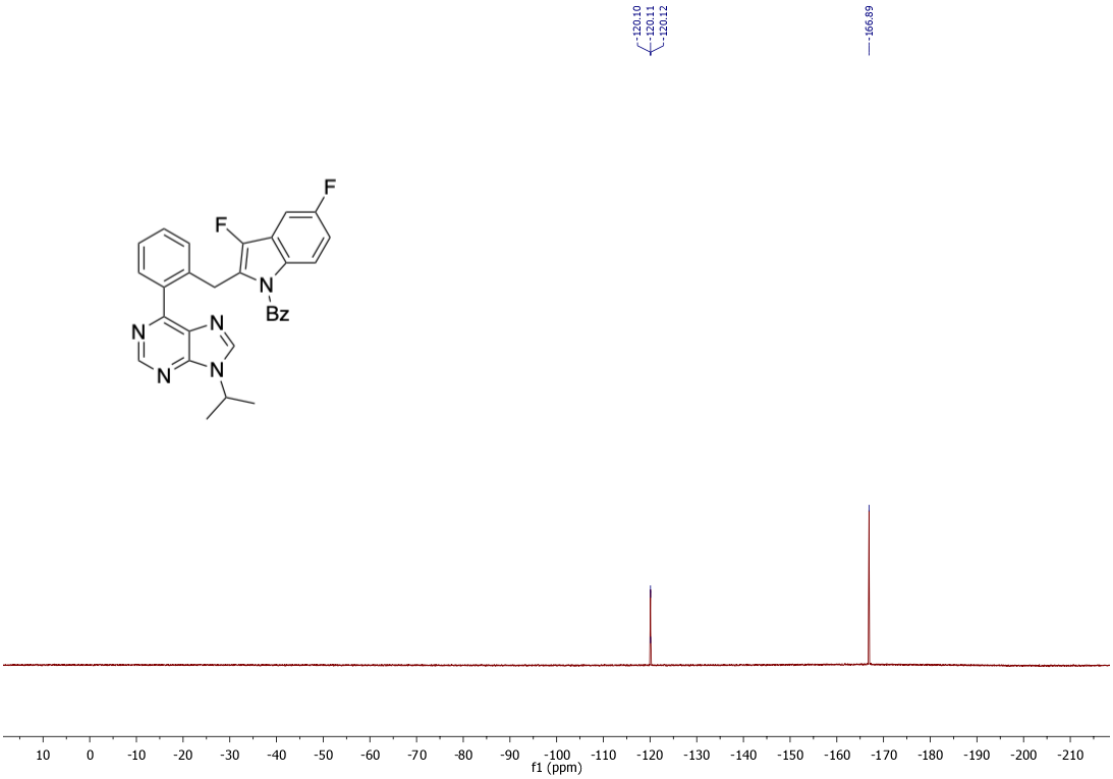

OMe
F
N
Bz
N
N
N
N

-167.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
168.88
157.83
155.77
151.78
151.24
142.11
137.17
137.15
135.08
132.61
132.29
130.86
130.64
129.75
129.58
128.59
128.51
126.77
122.54
122.31
119.99
119.81
115.26
115.24
113.60
98.30
98.28
55.70
47.45
29.75
22.59


OMe
F
N
Bz
N
N
N
N

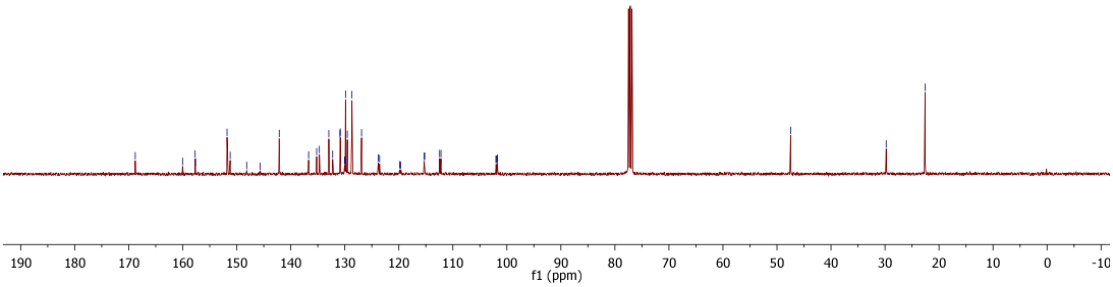

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.80
7.99
7.59
7.57
7.52
7.50
7.50
7.46
7.44
7.35
7.33
7.31
7.28
7.27
7.26
7.17
6.91
6.84
6.88
6.70
4.93
4.92
4.90
4.88
4.87
4.49
4.48
1.66
1.64
F
F
N
Bz
N
N
N
N
1.00
1.00
1.07
2.00
1.29
2.34
2.28
1.13
1.02
2.01
1.12
2.07
6.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

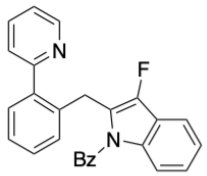

120.10
120.11
120.12
166.89
F
F
N
Bz
N
N
N
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

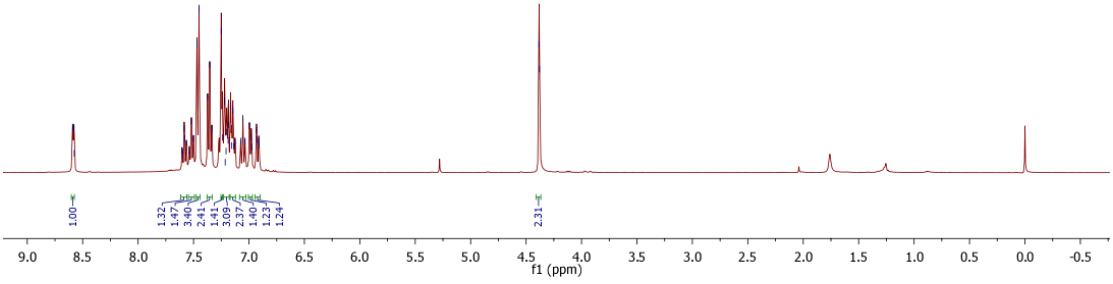

168.79
160.03
157.70
157.64
151.80
151.21
148.47
148.46
142.14
136.70
135.21
134.71
132.96
132.25
130.90
130.84
129.86
129.53
128.68
126.90
115.30
112.45
101.91
101.76
101.74
47.47
29.78
22.58

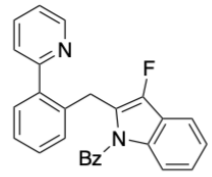
F
F
N
Bz
N
N
N
N


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

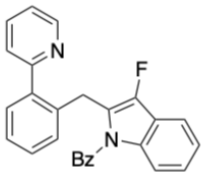

8.59
8.58
8.58
7.60
7.58
7.58
7.56
7.54
7.52
7.50
7.47
7.45
7.37
7.35
7.33
7.25
7.24
7.22
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.07
7.05
7.04
7.00
6.98
6.98
6.93
6.93
6.91
4.38

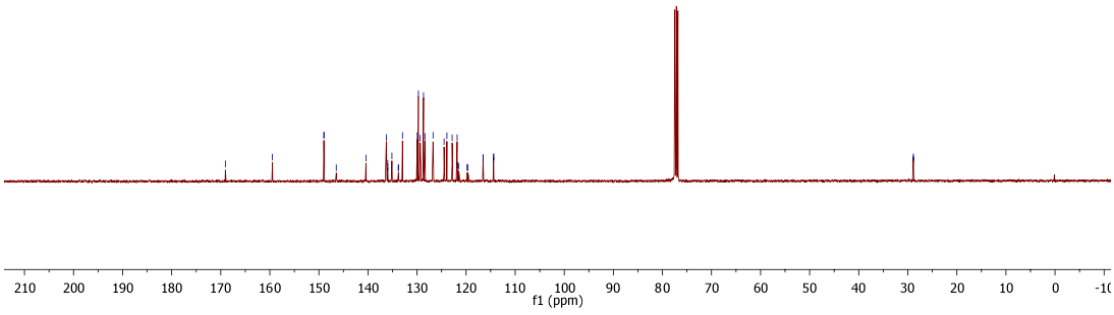

N
F
N
Bz


1.00
1.32
1.47
3.40
2.41
1.41
3.09
2.37
1.49
2.31
1.24
2.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

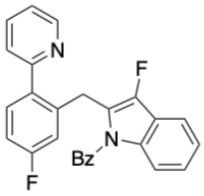

N
F
N
Bz

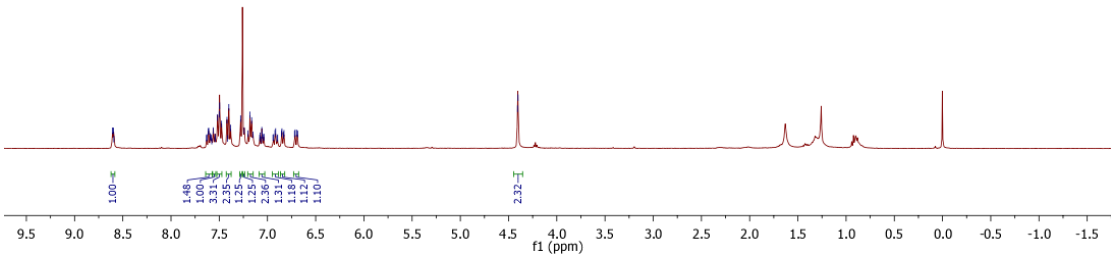
-167.71
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.06
159.47
149.00
148.96
146.46
140.41
136.26
135.97
135.96
135.12
133.83
133.78
132.96
129.95
129.72
129.35
128.68
128.40
126.74
124.50
123.92
122.84
121.83
121.71
121.48
119.80
119.61
116.55
116.53
114.40
114.38
28.87
28.85


N
F
N
Bz

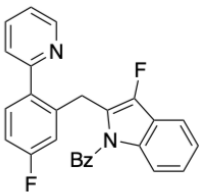

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

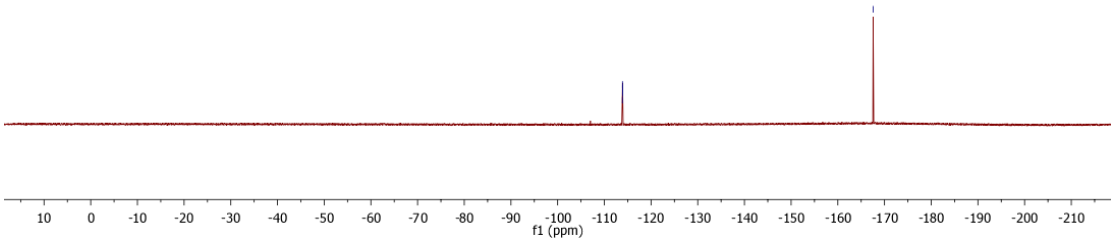

8.61
8.60
8.59
7.61
7.61
7.56
7.52
7.50
7.50
7.48
7.42
7.40
7.38
7.28
7.24
7.20
7.18
7.16
7.15
7.06
7.06
6.92
6.92
6.86
6.85
6.83
6.83
6.72
6.71
6.69
6.69
4.41
4.40


N
F
N
Bz
F

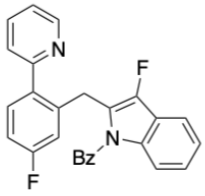

1.00
1.48
1.00
3.31
2.35
2.25
2.36
1.31
1.18
1.12
1.10
2.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

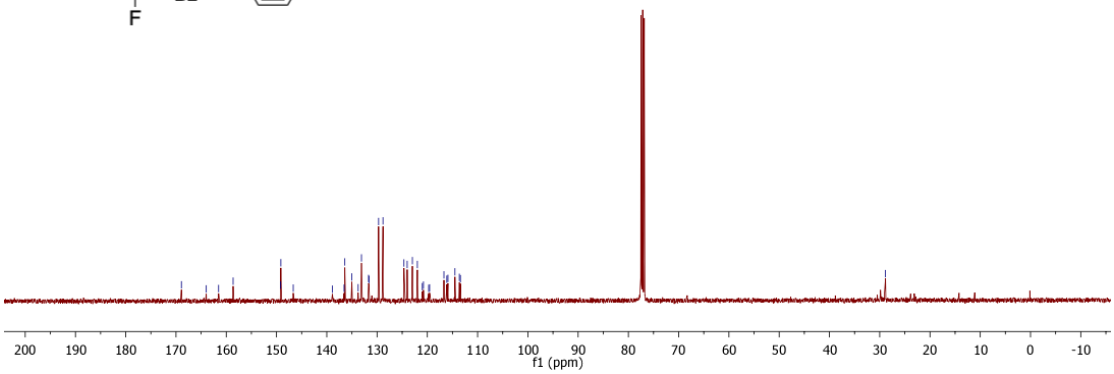

-113.87
-113.88
-113.89
-113.90
-113.92
-167.56


N
F
N
Bz
F

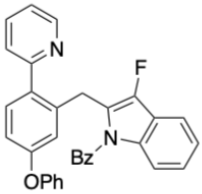

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

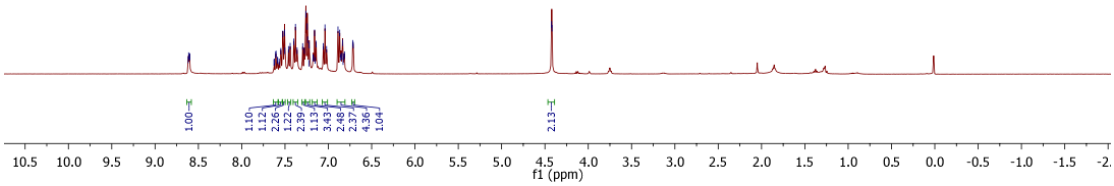

168.92
163.98
161.52
158.64
149.18
149.14
146.68
138.88
136.56
136.42
135.02
133.76
133.10
131.69
131.61
129.69
128.82
124.65
124.00
122.97
121.98
121.00
120.77
119.73
118.65
116.69
116.12
115.90
114.51
113.63
113.42
28.85

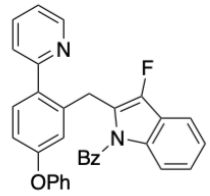

N
F
N
Bz
F


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

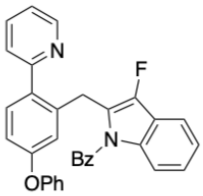

8.62
8.61
8.60
8.60
7.53
7.51
7.50
7.46
7.44
7.40
7.38
7.36
7.30
7.28
7.26
7.24
7.24
7.22
7.16
7.14
7.06
7.04
7.02
6.89
6.87
6.83
6.72
4.47
4.44
4.442

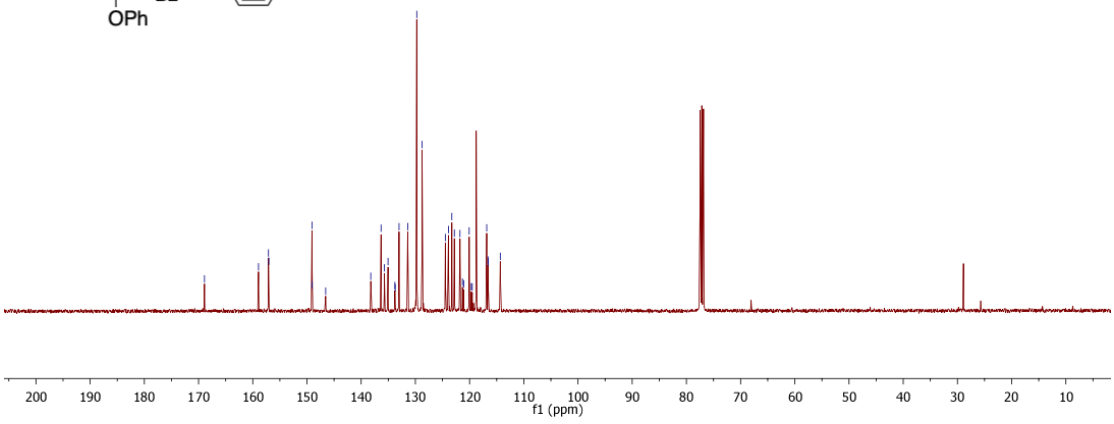

N
F
N
Bz
OPh


1.00
1.10
1.12
2.26
1.22
2.39
1.13
3.43
2.48
2.37
4.06
1.04
2.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

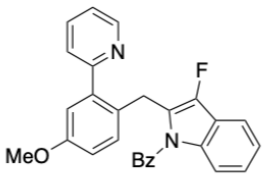

N
F
N
Bz
OPh

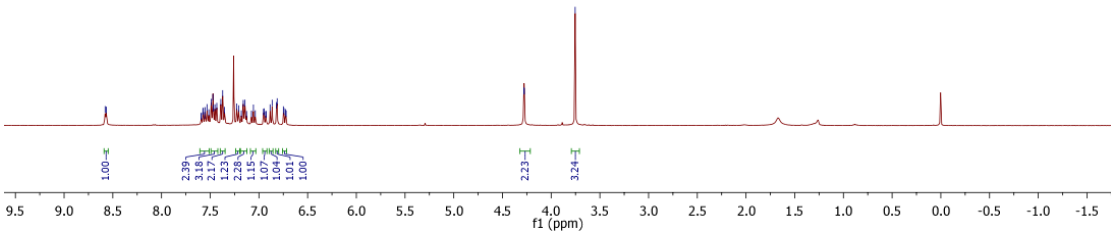
167.56
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
168.91
158.94
157.10
157.04
149.08
149.05
146.55
138.23
136.33
135.73
135.04
133.78
133.73
133.01
131.44
129.75
128.77
124.47
123.90
123.27
122.81
121.77
121.32
121.08
120.07
119.69
119.51
116.84
116.60
116.58
114.33


N
F
N
Bz
OPh

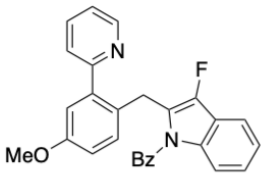

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

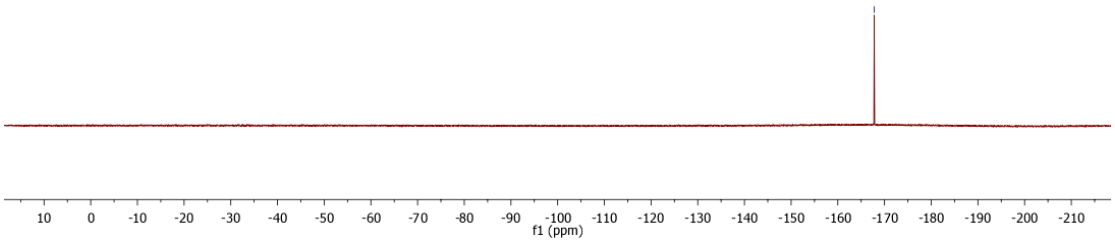

8.58
8.57
7.58
7.57
7.55
7.53
7.51
7.49
7.47
7.47
7.45
7.43
7.39
7.37
7.35
7.23
7.21
7.18
7.16
7.14
7.06
7.04
6.95
6.91
6.89
6.86
6.82
6.81
6.75
6.74
6.73
4.28
3.75


N
F
MeO
N
Bz

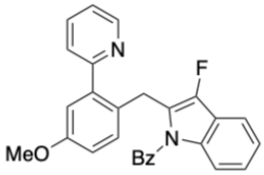

1.00
2.39
3.16
2.17
1.23
2.28
1.15
1.07
1.04
1.01
1.00
2.23
3.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

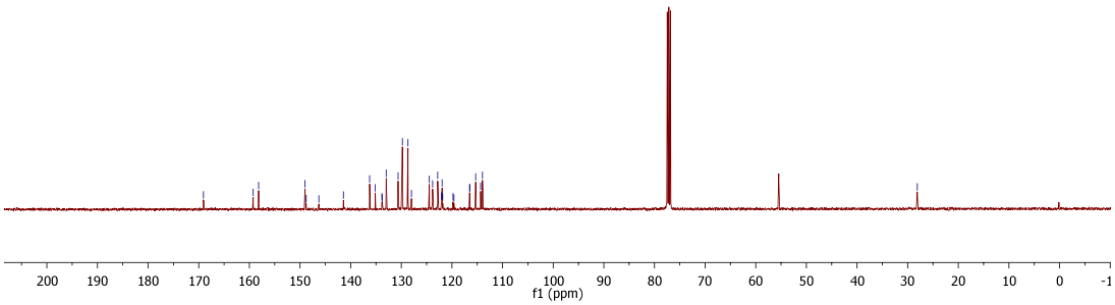
-167.79


N
F
MeO
N
Bz

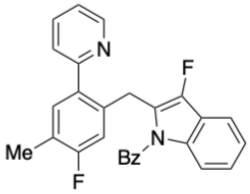

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

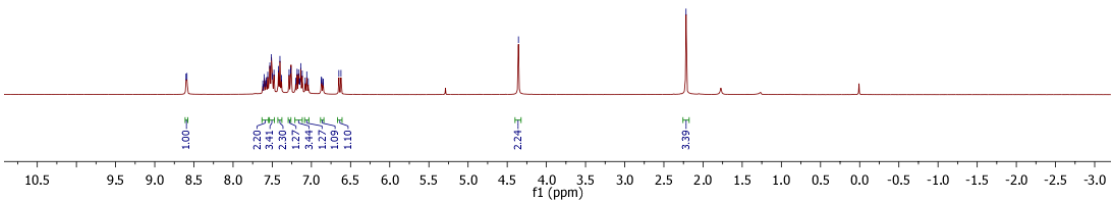

169.07
159.25
158.18
149.02
148.78
146.28
141.43
136.25
135.14
133.83
133.78
132.98
130.63
129.28
128.68
127.99
124.46
123.82
122.81
122.05
121.94
121.82
119.79
119.60
116.51
116.48
115.31
115.34
113.97
28.10

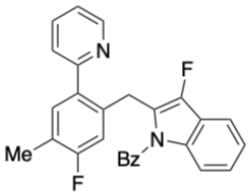

N
F
MeO
N
Bz


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

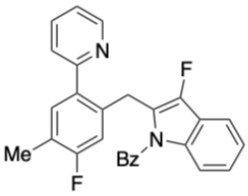

8.60
8.59
7.60
7.58
7.56
7.53
7.51
7.50
7.48
7.42
7.40
7.38
7.28
7.26
7.20
7.18
7.16
7.14
7.12
7.08
7.06
6.87
6.65
6.62
6.58
2.22

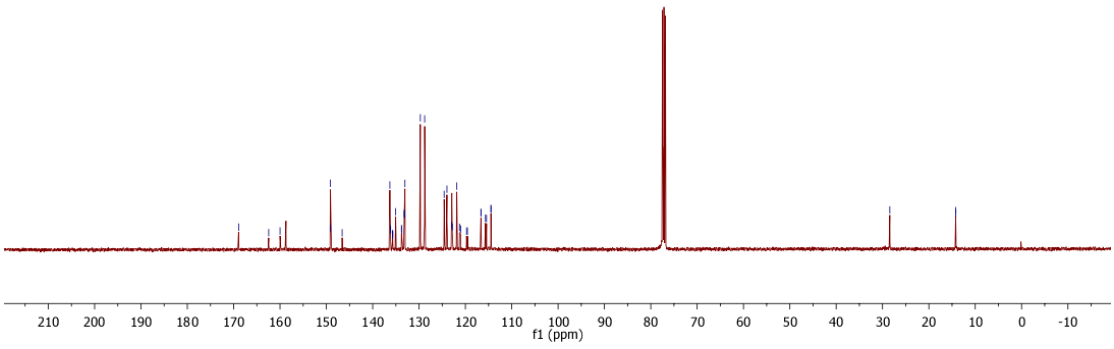

N
F
Me
F
N
Bz


1.00
2.20
3.41
2.39
2.77
3.44
1.27
1.09
1.10
2.24
3.39
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f1 (ppm)

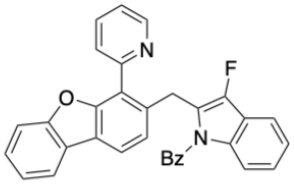

N
F
Me
Bz
N
F

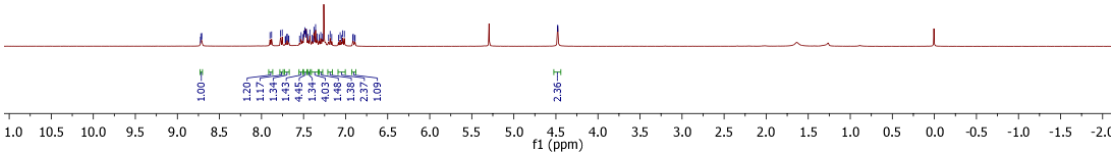
118.35
118.38
118.40
-167.73
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
168.93
162.44
159.99
149.12
149.09
146.59
136.29
136.17
136.13
135.76
135.74
135.68
135.66
135.05
133.80
133.74
133.21
133.15
133.05
129.72
128.79
124.58
123.98
123.00
122.83
121.86
121.26
121.03
119.75
119.57
116.65
116.63
116.67
115.44
114.49
114.47
28.43
14.22
14.19


N
F
Me
Bz
N
F

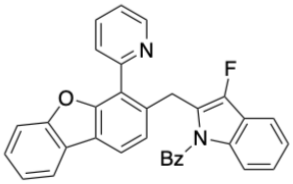

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

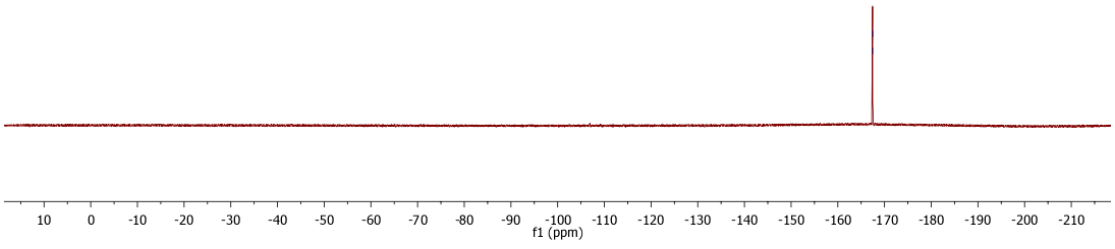

8.73
8.72
8.71
7.90
7.88
7.77
7.75
7.70
7.69
7.53
7.49
7.48
7.47
7.45
7.43
7.38
7.36
7.34
7.30
7.27
7.18
7.07
7.03
7.01
6.91
4.48

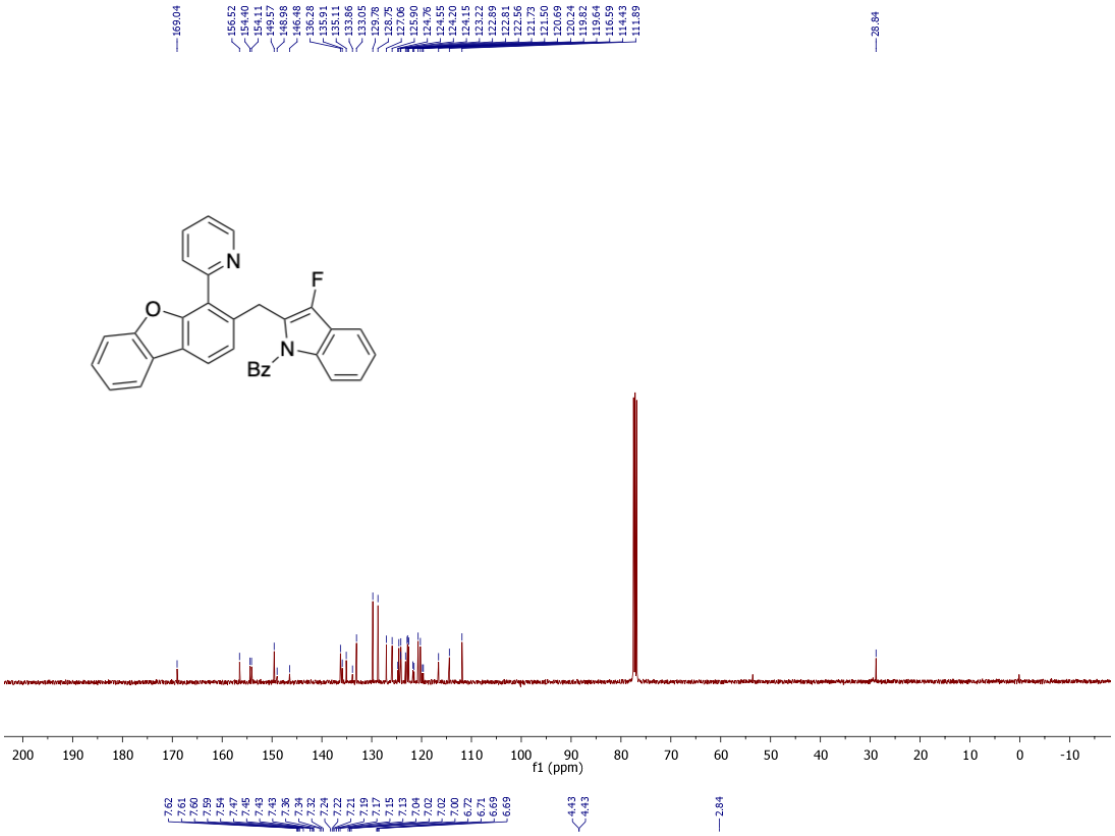

N
F
O
N
Bz

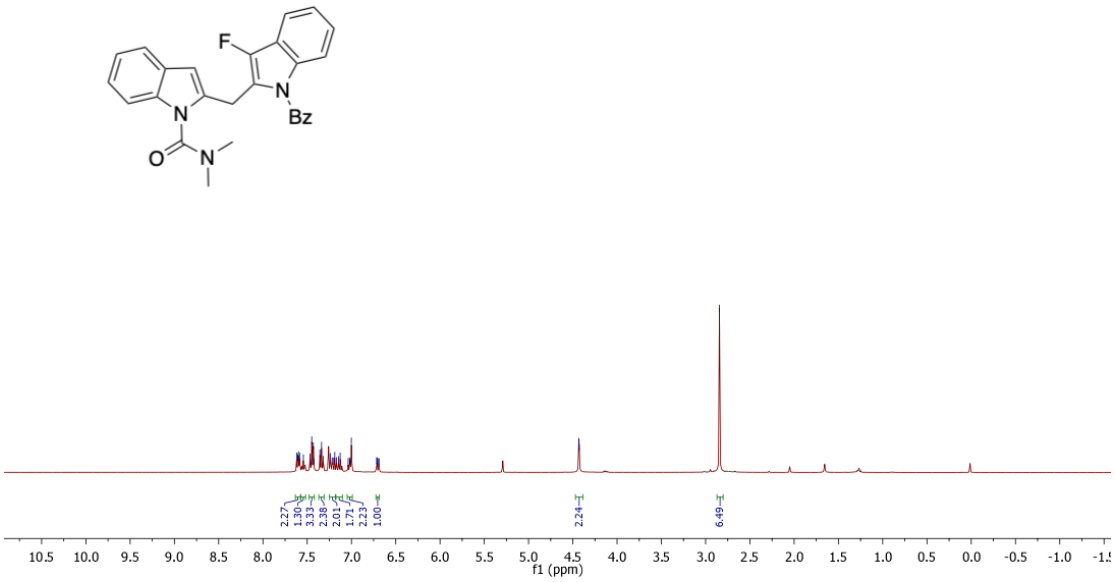

1.00
1.20
1.17
1.34
1.43
4.45
1.34
4.03
4.48
1.38
2.37
1.09
2.36
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

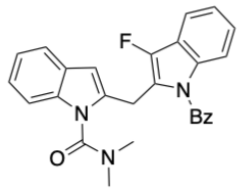

-167.45
-167.45


N
F
O
N
Bz

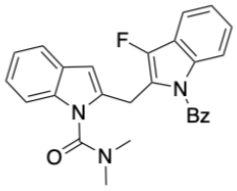

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

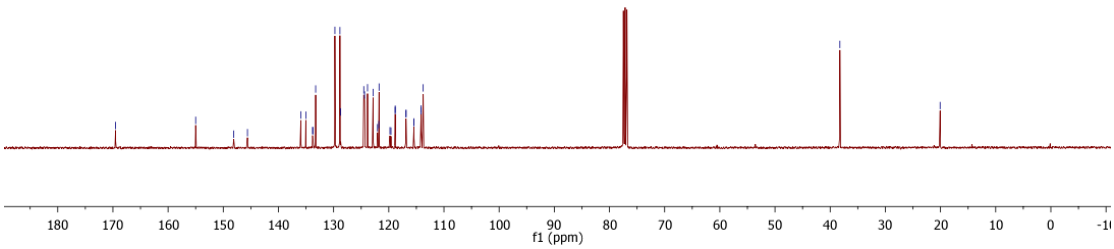

169.04
156.52
154.40
154.11
149.57
148.98
146.48
136.28
135.91
135.11
133.86
133.05
129.78
128.75
127.06
125.90
124.76
124.55
124.20
124.15
123.22
122.89
122.81
122.56
121.73
121.50
120.69
120.24
119.82
119.64
116.59
114.43
111.89
28.84
N
F
O
N
Bz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
7.62
7.61
7.60
7.59
7.54
7.47
7.45
7.43
7.43
7.36
7.34
7.32
7.24
7.22
7.21
7.19
7.17
7.15
7.13
7.04
7.02
7.02
7.00
6.72
6.71
6.69
6.69
4.43
4.43
2.84


F
N
Bz
N
O
N
2.27
1.30
3.33
3.38
2.01
1.71
2.23
1.00
2.24
6.49
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


F
N
Bz
O
N

167.53
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.52
155.00
148.10
145.61
135.93
135.03
133.81
133.76
133.25
129.76
129.55
128.73
124.53
124.39
123.85
122.84
122.04
121.80
121.76
119.79
119.60
118.84
118.83
116.89
116.66
115.45
115.43
114.16
114.14
113.77
38.24
20.07


F
N
Bz
O
N


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.61
7.59
7.58
7.56
7.55
7.54
7.54
7.53
7.44
7.43
7.42
7.37
7.35
7.33
7.21
7.19
7.17
7.09
7.09
7.07
7.06
7.04
7.02
7.00
6.99
6.98
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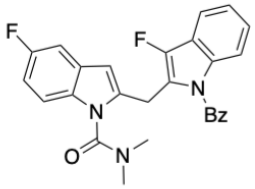
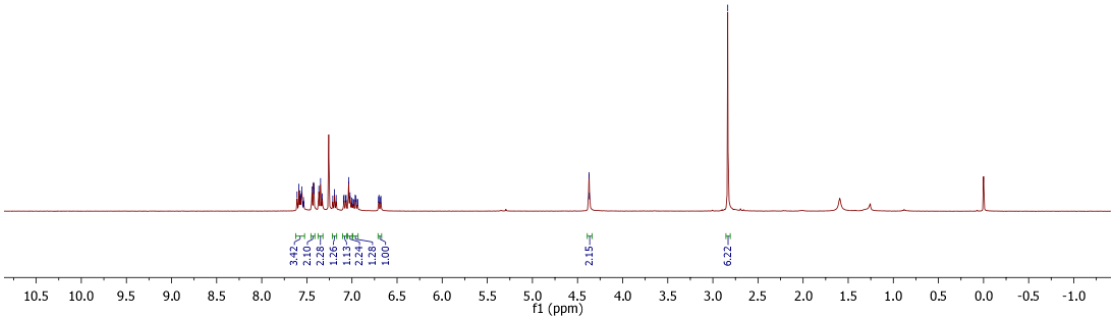
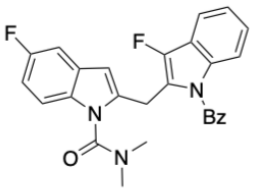
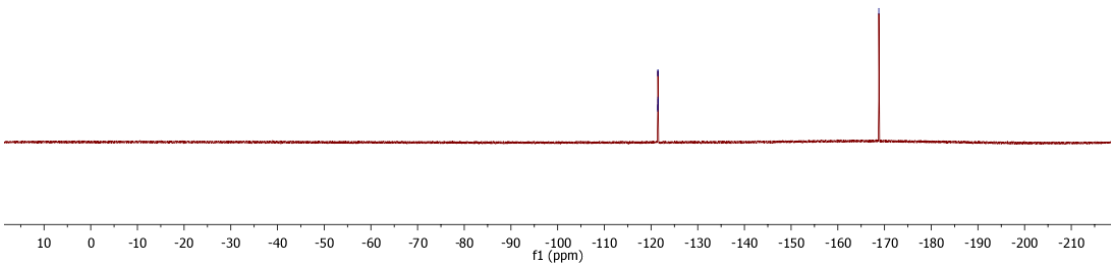
6.96
6.94
6.71
6.70
6.68
6.68
4.37
4.37
2.84

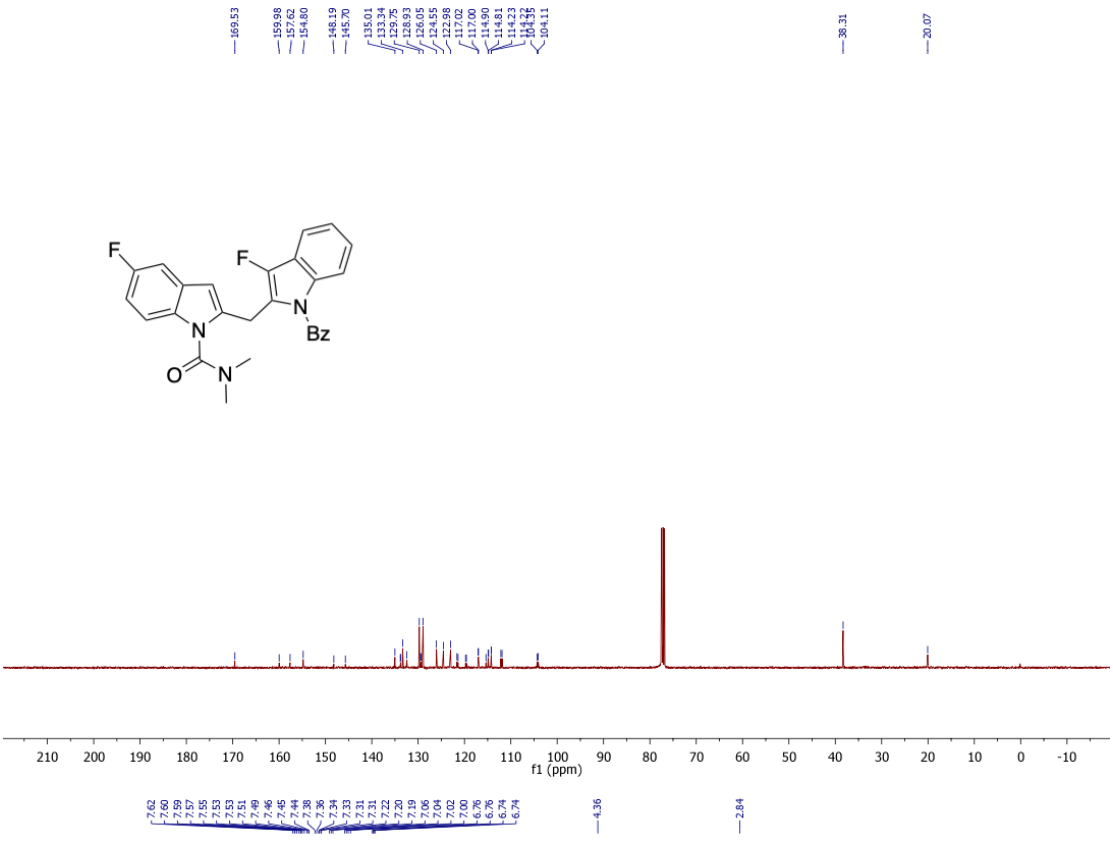

F
F
N
Bz
N
O
N

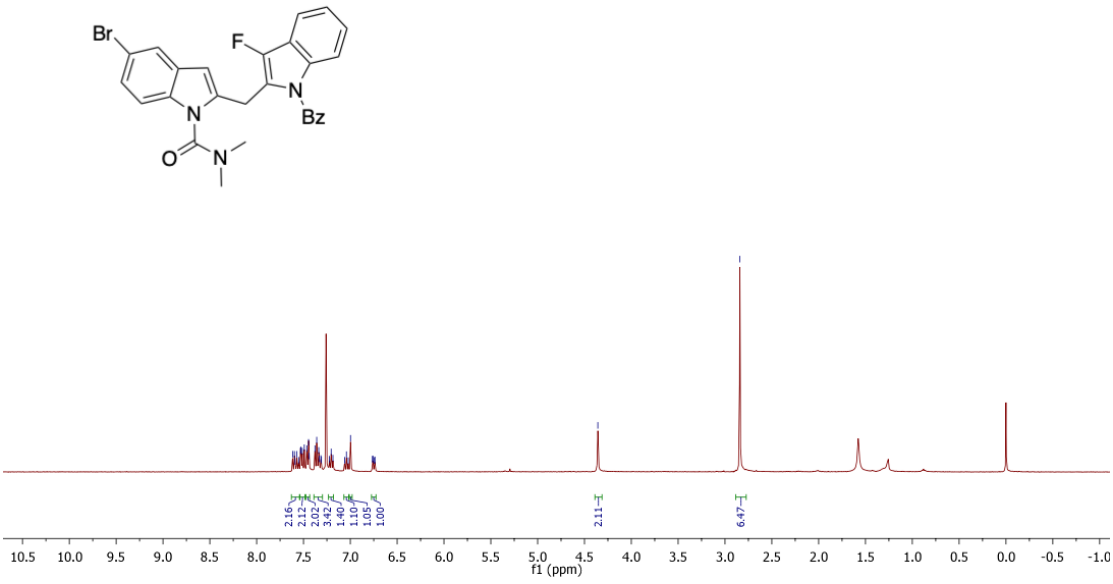

3.42
2.10
2.28
1.26
1.13
2.24
1.28
1.00
2.15
6.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

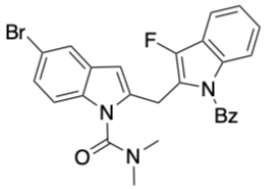

-121.43
-121.45
-121.46
-121.47
-121.48
-121.50
-168.78


F
F
N
Bz
N
O
N

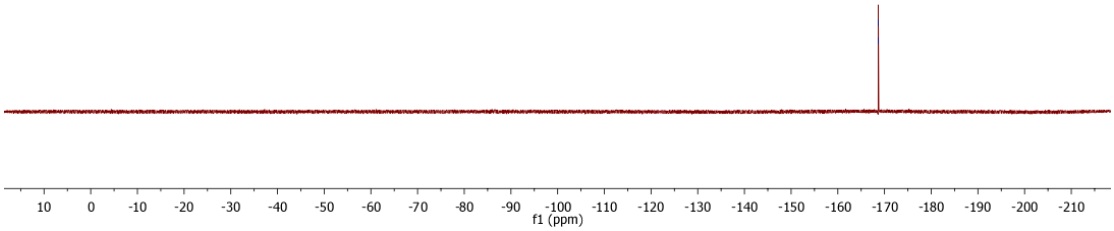

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


169.53
159.98
157.62
154.80
148.19
145.70
135.01
133.34
129.75
129.53
126.05
124.55
122.98
117.02
117.00
114.90
114.81
114.23
104.11
38.31
20.07
F
F
N
Bz
N
O
N
f1 (ppm)
7.62
7.60
7.59
7.57
7.55
7.53
7.53
7.51
7.49
7.46
7.45
7.44
7.38
7.36
7.34
7.33
7.31
7.31
7.22
7.20
7.19
7.06
7.04
7.02
7.00
6.76
6.76
6.74
6.74
4.36
2.84

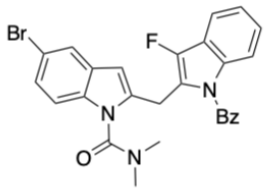

Br
F
N
Bz
N
O
N
2.16
2.12
2.02
3.42
1.40
1.10
1.05
1.00
2.11
6.47
f1 (ppm)

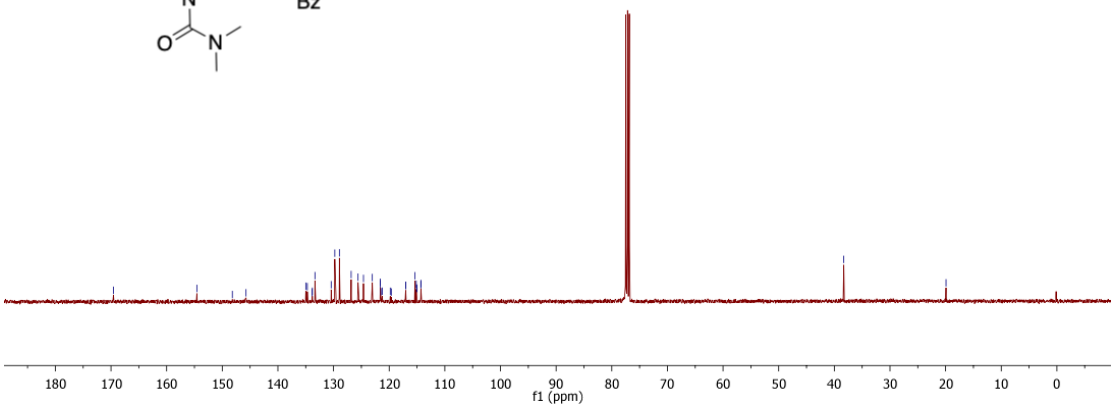


168.66
168.66

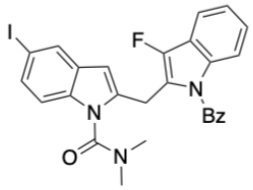


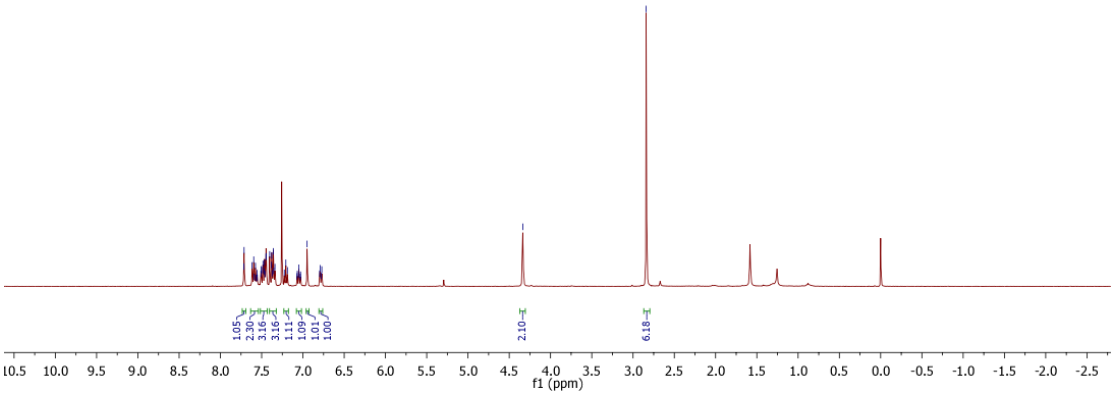
169.56
154.57
148.19
145.73
134.99
134.71
133.86
133.81
133.34
130.42
129.77
128.95
126.83
125.60
124.62
123.04
121.61
121.59
121.49
121.26
119.81
119.62
117.04
117.01
115.36
115.13
115.06
115.04
114.31
114.30
38.31
19.93



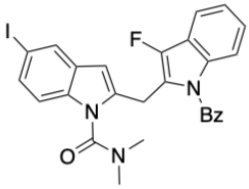


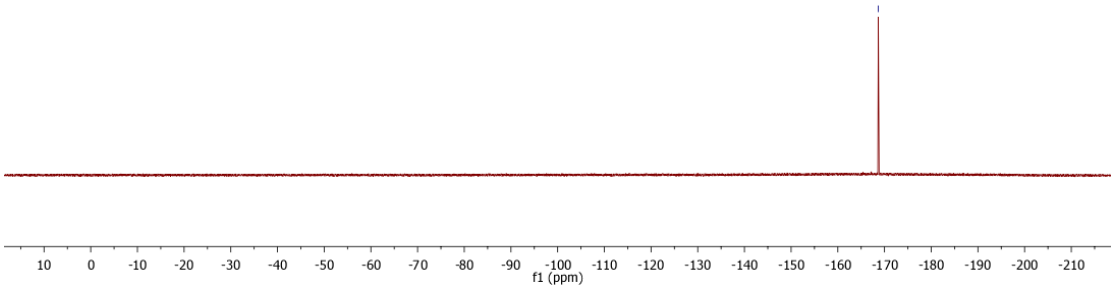

7.72
7.71
7.62
7.60
7.59
7.57
7.57
7.57
7.56
7.55
7.51
7.51
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.40
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.23
7.21
7.19
7.07
7.07
7.05
7.05
7.03
7.03
6.95
6.80
6.79
6.78
6.77
4.34
2.84

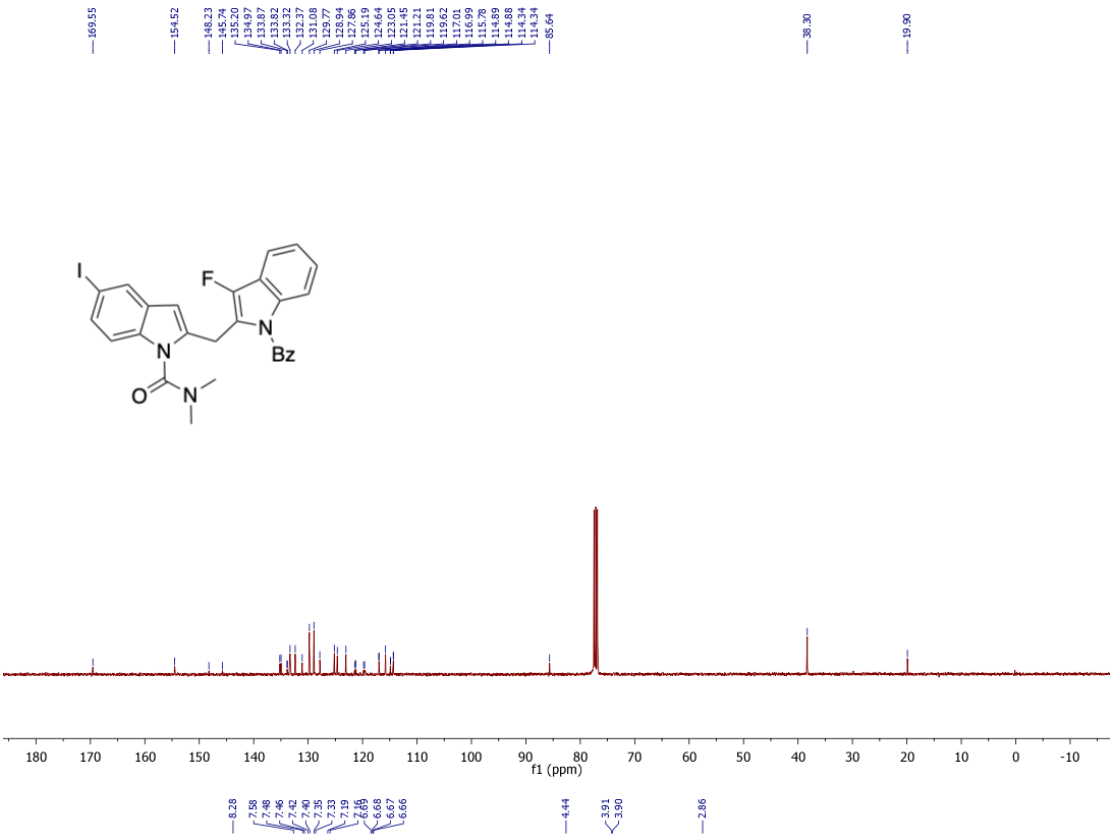

I
F
N
Bz
N
O
N

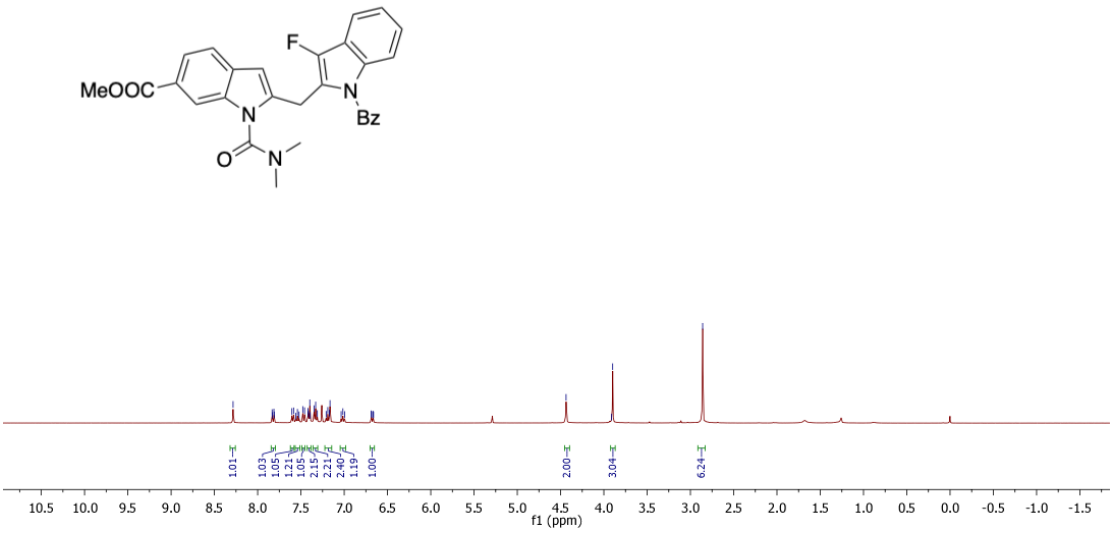

1.05
2.30
3.16
3.16
1.11
1.09
1.01
1.00
2.10
6.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)

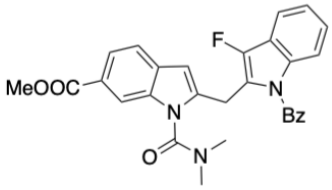
168.67


I
F
N
Bz
N
O
N

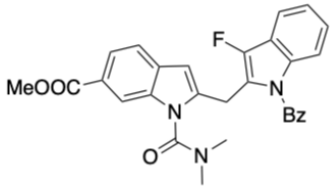

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

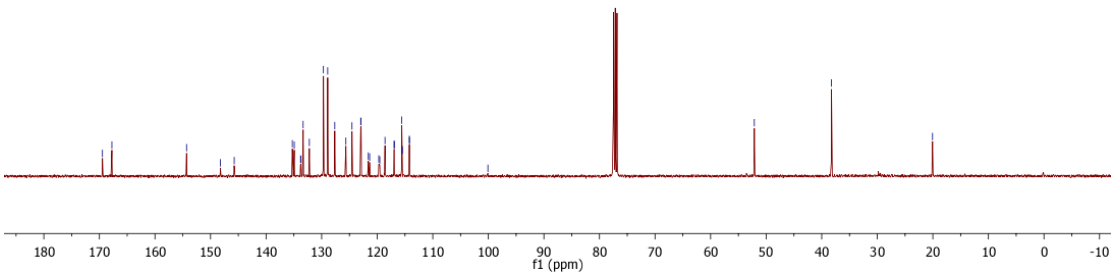

169.55
154.52
148.23
145.74
135.20
134.97
133.87
133.82
133.32
132.37
131.08
129.77
128.94
127.86
125.19
124.64
123.05
121.45
121.21
119.81
119.62
117.01
116.99
115.78
114.89
114.88
114.34
114.34
85.64
38.30
19.90
I
F
N
Bz
N
O
N
f1 (ppm)
8.28
7.58
7.48
7.46
7.42
7.40
7.35
7.33
7.19
6.68
6.67
6.66
4.44
3.91
3.90
2.86

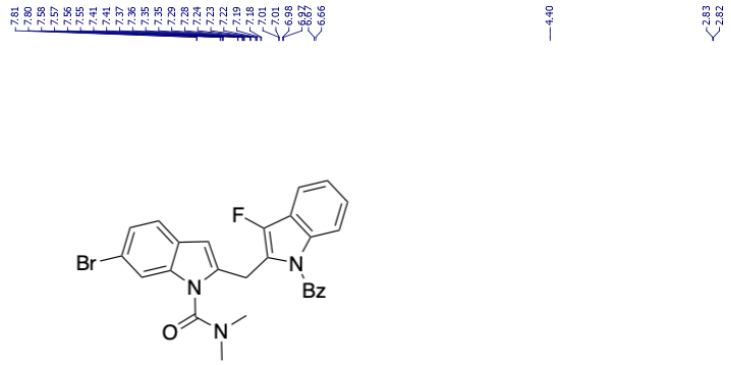

MeOOC
F
N
Bz
N
O
N
f1 (ppm)
1.01
1.03
1.05
1.21
1.05
2.15
2.21
2.40
1.19
1.00
2.00
3.04
6.24


F
MeOOC
N
N
Bz
O
N

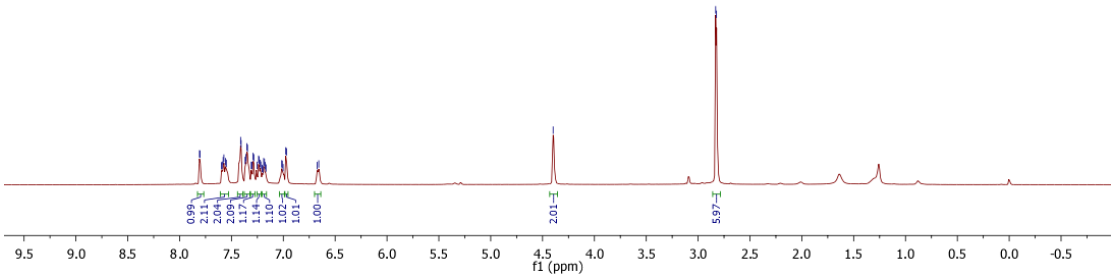
168.71
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.45
167.75
154.31
148.23
145.74
135.28
134.93
133.33
132.21
129.68
128.91
127.64
125.64
124.54
122.97
122.91
118.60
116.96
116.93
115.58
115.53
114.22
52.13
38.24
20.06


F
MeOOC
N
N
Bz
O
N

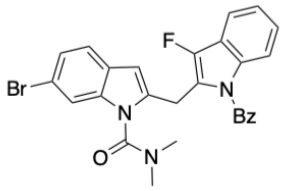

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

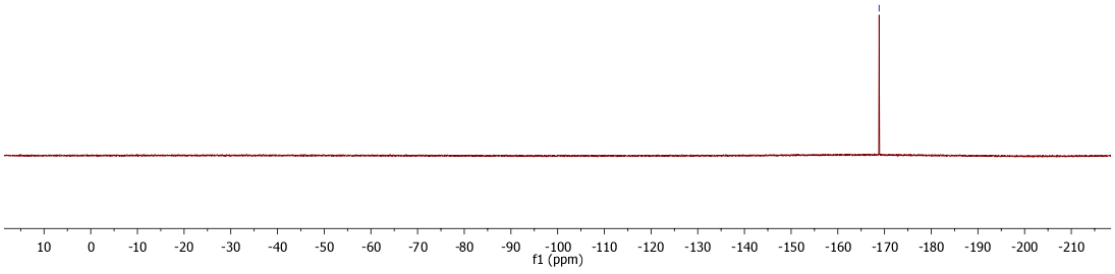

7.81
7.80
7.58
7.57
7.56
7.55
7.41
7.41
7.37
7.36
7.35
7.35
7.29
7.28
7.24
7.23
7.22
7.19
7.18
7.01
7.01
6.98
6.97
6.87
6.66
4.40
2.83
2.82

F
Br
N
N
Bz
O
N

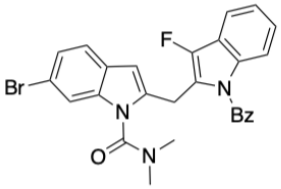

0.99
2.11
2.04
2.09
1.17
1.14
1.10
1.02
1.01
1.00
2.01
5.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

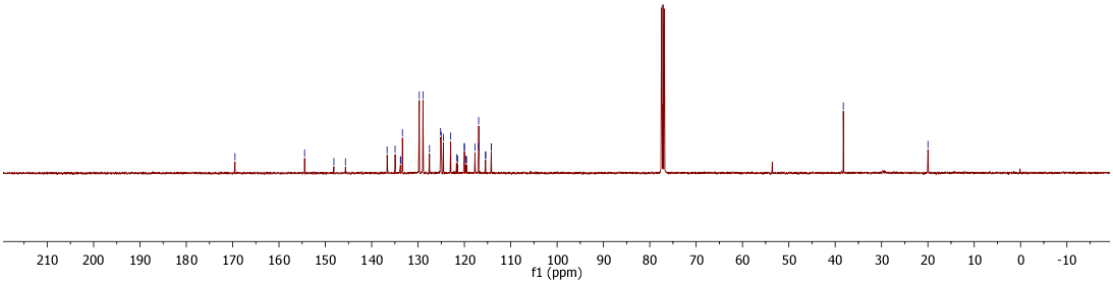
-168.84


F
Br
N
N
Bz
O
N

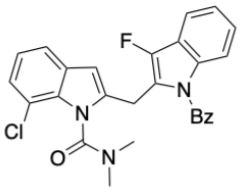

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

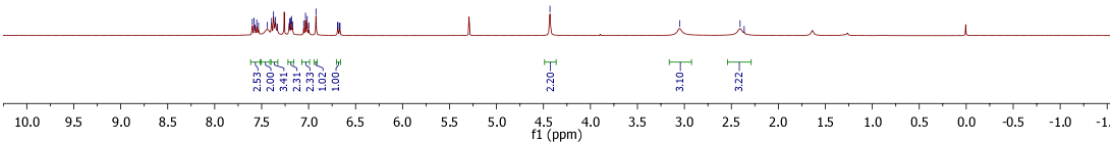

169.49
154.48
148.15
145.67
136.68
134.95
133.80
133.75
133.37
129.73
128.94
127.53
125.54
125.00
124.53
122.96
121.70
121.47
120.01
120.00
119.71
119.52
117.70
116.95
116.92
115.43
115.41
114.21
114.20
38.24
19.99

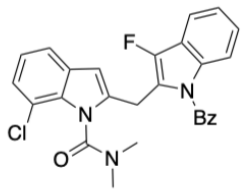

F
Br
N
N
Bz
O
N


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

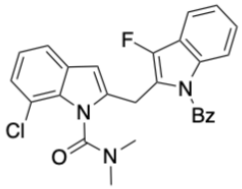

7.60
7.58
7.57
7.55
7.53
7.44
7.39
7.37
7.35
7.33
7.21
7.20
7.19
7.18
7.17
7.05
7.03
7.02
7.00
6.92
6.69
6.67
6.67
4.43
3.05
2.41
2.36

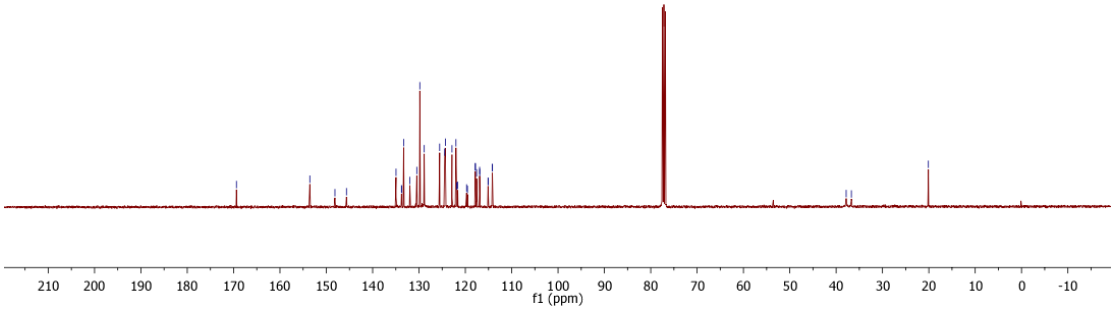

F
N
Bz
Cl
N
O

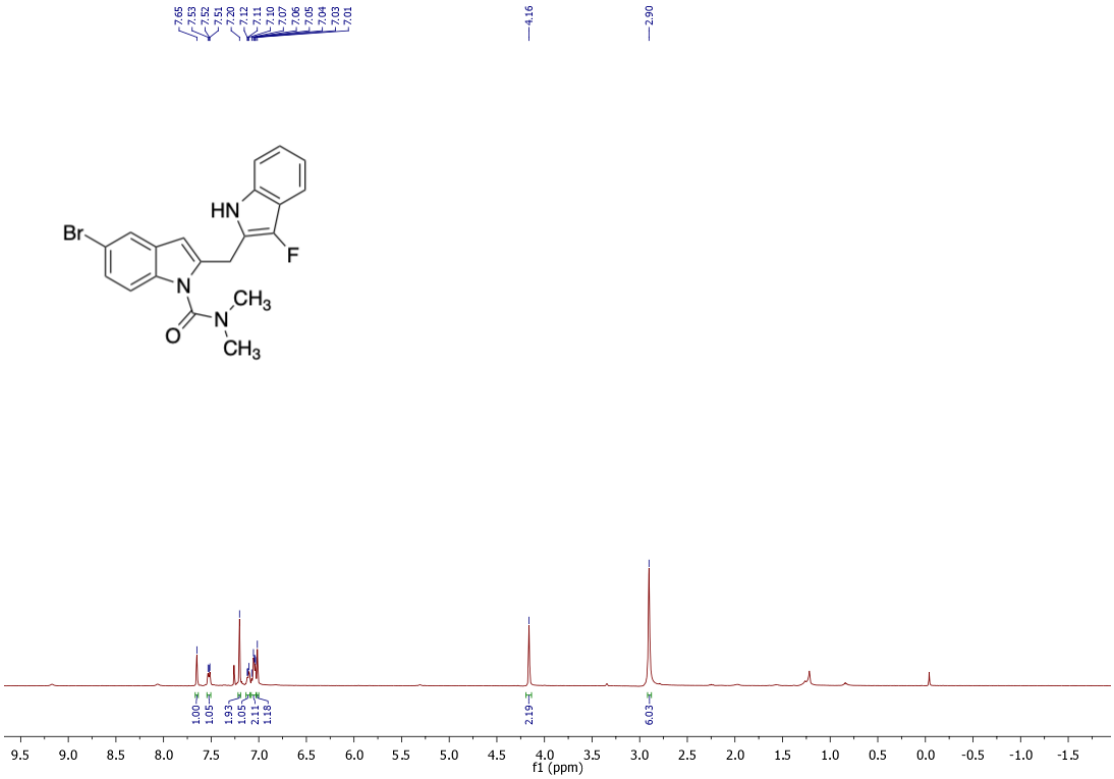

2.53
2.00
3.41
2.31
2.33
1.07
1.00
2.20
3.10
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

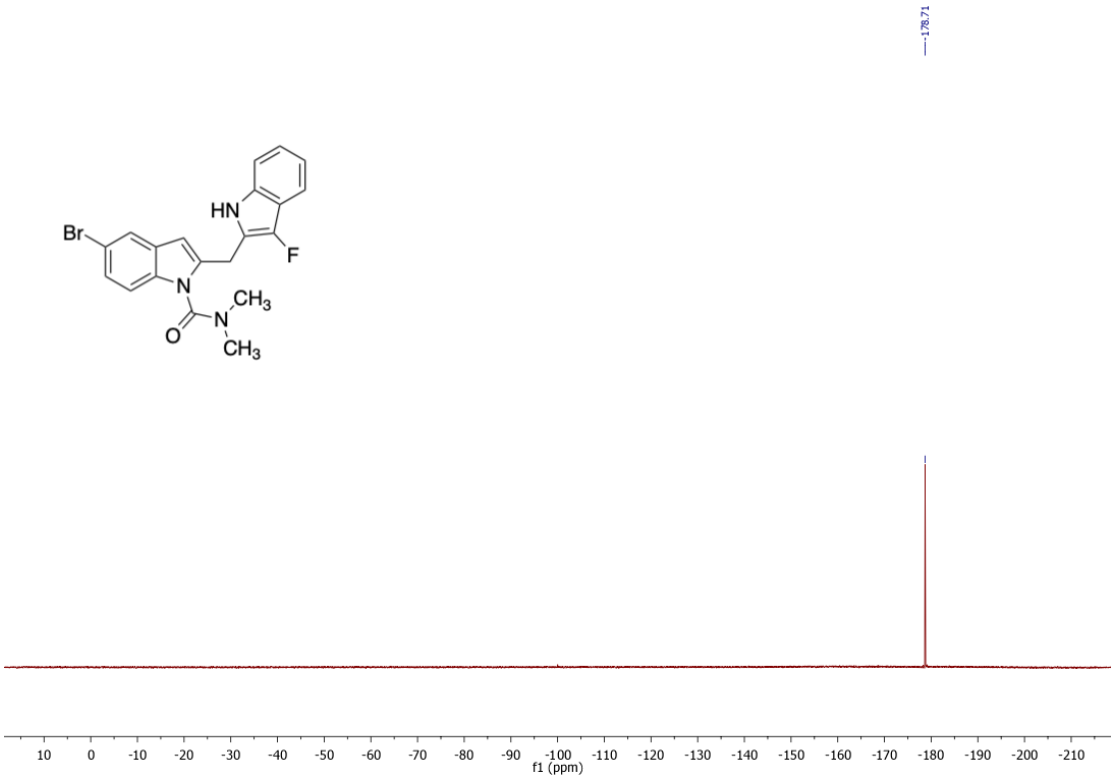

F
N
Bz
Cl
N
O
N

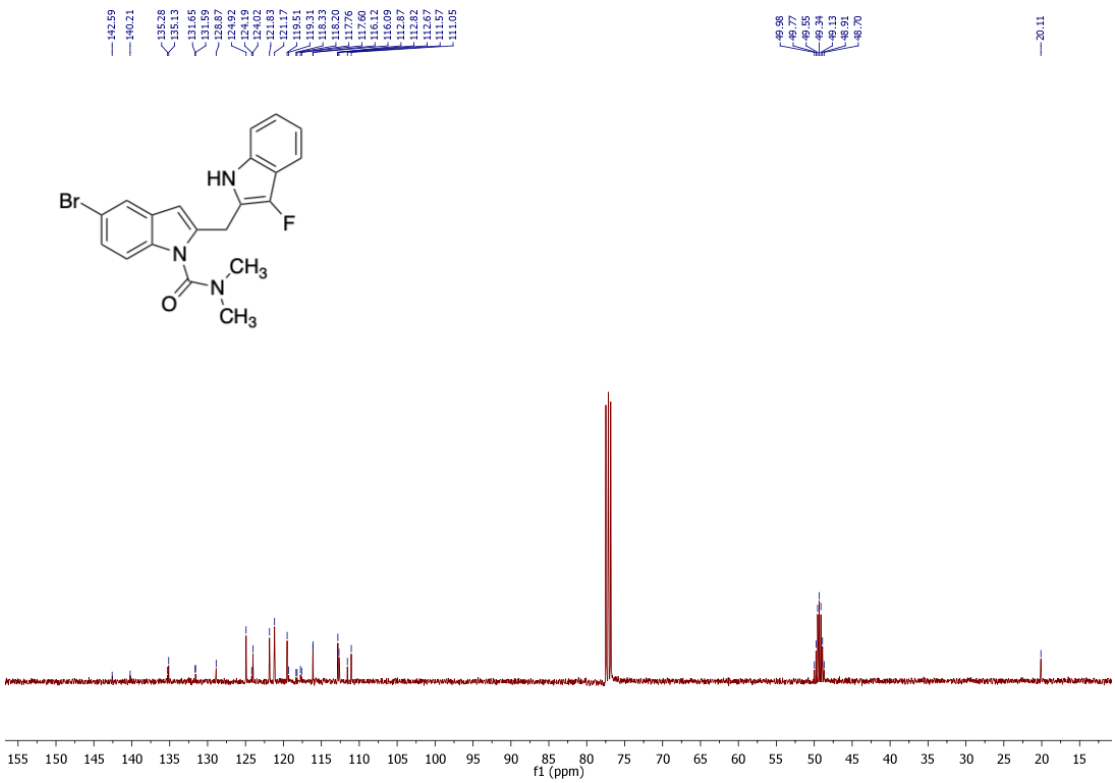
168.95
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.39
153.55
148.14
145.65
134.96
133.78
133.73
133.31
131.97
130.48
129.83
128.87
125.54
124.45
124.31
122.88
122.03
121.87
121.63
119.73
119.55
117.86
117.84
117.58
116.92
116.90
115.10
115.08
114.17
114.15
37.83
36.71
20.10


F
N
Bz
Cl
N
O
N


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.65
7.53
7.52
7.51
7.20
7.12
7.11
7.10
7.07
7.06
7.05
7.04
7.03
7.01
4.16
2.90
HN
Br
F
N
CH3
O
N
CH3
1.00
1.05
1.93
1.05
2.11
1.18
2.19
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


-178.71
HN
Br
F
N
CH3
O
N
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


142.59
140.21
135.28
135.13
131.65
131.59
128.87
124.92
124.19
124.02
121.83
121.17
121.01
119.31
118.33
118.20
117.76
117.60
116.12
116.09
112.87
112.82
112.67
111.57
111.05
49.98
49.77
49.55
49.34
49.13
48.91
48.70
20.11
Br
HN
F
N
O
N
CH3
CH3
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

7. Reference

[1] M. Yoshida, K. Kawai, R. Tanaka, T. Yoshino, S. Matsunaga, *Chem Commun*., **2017**, *53*, 5974-5977.

[2] J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim, S. Chang, *J Am Chem Soc*., **2012**, *134*, 9110-9113.

[3] D.J. Schipper, M. Hutchinson, K. Fagnou, *J. Am. Chem. Soc*., **2010**, *132*, 6910-6911.

[4] N. Zeidan, M. Zambri, S. Unger, C. Dank, A. Torelli, B. Mirabi, M. Lautens, *Org Lett*., **2020**, *22*, 3688-3691.

[5] H. J. Kim, M. J. Ajitha, Y. Lee, J. Ryu, J. Kim, Y. Lee, Y. Jung, S. Chang, *J. Am. Chem. Soc*. **2014**, *136*, 1132-1140.

[6] B. Zhou, Y. Yang, S. Lin, Y. Li, Advanced Synthesis & Catalysis **2013**, *355*, 360-364.