Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh-catalyzed C–H bond alkylation of indoles with *α,α*-difluorovinyl tosylate via indolyl group migration

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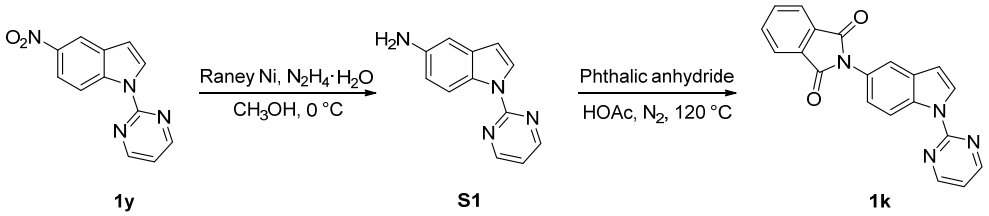
General Information

All reactions were carried out under nitrogen atmosphere unless otherwise stated. Reactions were monitored through thin layer chromatography. Flash chromatography was performed using silica gel with distilled solvents. HRMS spectra were recorded on a Waters Q-Tof Permier Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00, singlet). Multiplicities were given as: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), m (multiplets) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $CHCl_3$ (δ 7.26) and relative to the signal of chloroform-d (δ 77.00, triplet). Unless otherwise noted, commercial reagents were used as received. Compounds **1a**–**1j**, **1l**–**1w**, **1y**–**1z**,[1-4] **D_1-1a**[5] and **2**[6] were prepared according to literature methods.

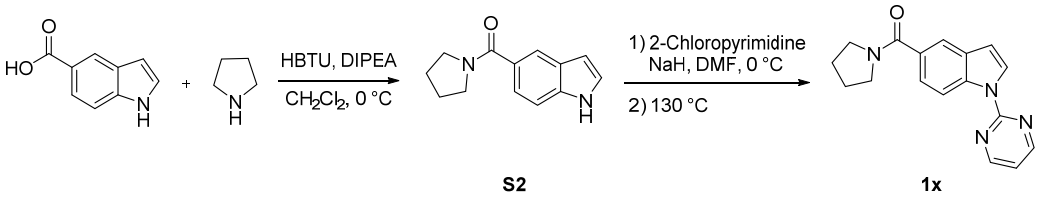
Procedure for synthesis of 1k



To a solution of 5-nitro-1-(pyrimidin-2-yl)-1*H*-indole **1y** (480 mg, 2 mmol, 1.0 equiv) in CH_3OH (10 mL) was added hydrazine hydrate (375 mg, 6 mmol, 3.0 equiv), Raney Ni (20 mg) at 0 °C, and the mixture was stirred for 2 h at room temperature. After the consumption of starting material, the mixture was filtered through celite and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10 : 1 v/v) to give **S1** (282 mg, 1.3 mmol) as a pale yellow oil in 67% yield.

A solution of **S1** (244 mg, 1.2 mmol, 1.0 equiv), phthalicanhydride (151 mg, 1.0 mmol, 0.85 equiv) in glacial acetic acid (10 mL) was stirred at 120 °C for 2 h. After the mixture was cooled 30 mL of cold water was added, a white colour solid precipitated out. The precipitate was filtered, washed with cold water and dried under vacuum to afford **1k** (245 mg, 0.72 mmol) as an off-white solid in 60% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.96 (d, *J* = 8.9 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.36 (d, *J* = 3.6 Hz, 1H), 7.99 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.81 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.37 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.76 (d, *J* = 3.7 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 167.9, 158.2, 157.5, 134.7, 134.3, 131.9, 131.7, 126.9, 125.7, 123.7, 122.2, 119.3, 116.9, 116.5, 107.0; **HRMS (ESI, m/z):** calcd. for $C_{20}H_{13}N_4O_2$ $[M+H]^+$: 341.1039, found: 341.1036.

Procedure for the synthesis of 1x



S2 **1x**

To a solution of in 50 mL of CH_2Cl_2 was added 1*H*-indole-5-carboxylic acid (806 mg, 5.0 mmol, 1.0 equiv), DIPEA (4.5 mL, 25.0 mmol, 5.0 equiv) and pyrrolidine (3.8 mL, 50.0 mmol, 10.0 equiv). HBTU (280 mg, 7.5 mmol, 1.5 equiv) was added at 0 °C. The resulting mixture was stirred at room temperature for 18 h. The mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (eluent = petroleum ether/ethyl acetate = 10 : 1 v/v) to afford **S2** (900 mg, 4.2 mmol) as a pale yellow solid in 84% yield.

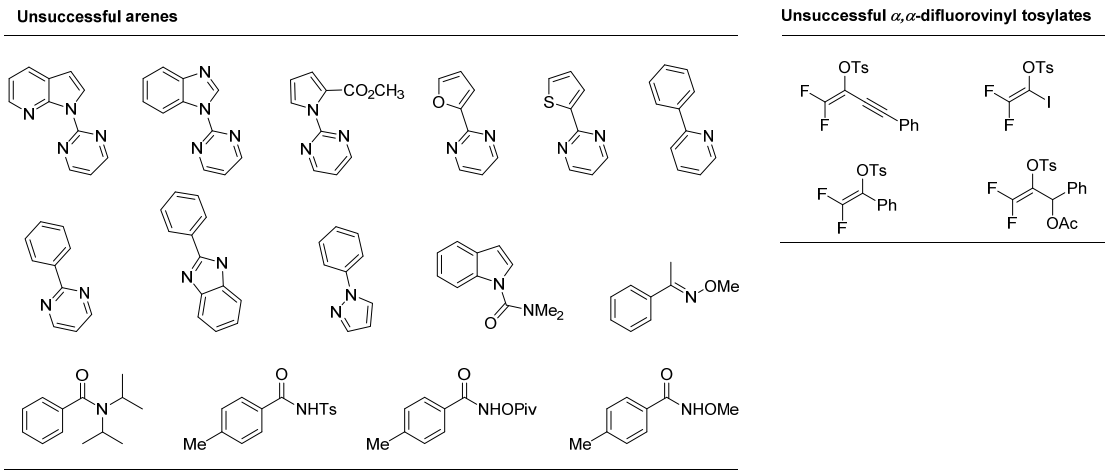
Following a procedure from Ackermann et al.,[1] to a stirred solution of **S2** (2.0 mmol, 1.0 eqiuv) in DMF (50 mL) was added NaH (88 mg, 2.2 mmol, 1.1 eqiuv) by portions at 0 °C. After stirring for 30 min at 0 °C, 2-chloropyrimidine (274 mg, 2.4 mmol, 1.2 eqiuv) was added and the mixture was heated to 130 °C and stirred for 24 h. Then the mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4, concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10 : 1) to afford **1x** (537 mg, 1.8 mmol) as a gray solid in 92% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.81 (dt, *J* = 8.6, 0.8 Hz, 1H), 8.71 (d, *J* = 4.8 Hz, 2H), 8.32 (d, *J* = 3.6 Hz, 1H), 7.82 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.53

(dd, *J* = 8.7, 1.7 Hz, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.73 (dd, *J* = 3.7, 0.8 Hz, 1H), 3.70 (t, *J* = 7.0 Hz, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.03–1.93, (m, 2H), 1.91–1.83 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.5, 158.2, 157.5, 135.9, 131.0, 130.8, 126.8, 122.9, 120.2, 116.5, 115.8, 107.1, 49.9, 46.3, 26.5, 24.5; **HRMS (ESI, m/z):** calcd. for $C_{17}H_{17}N_4O$ $[M+H]^+$: 293.1402, found: 293.1405.

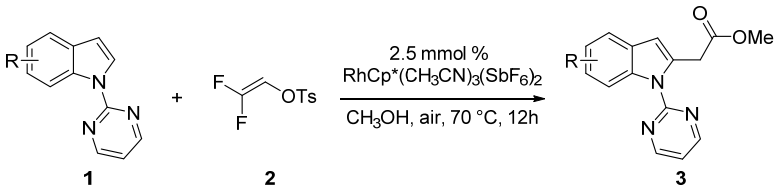
Procedure for synthesis of D_1-2

To a solution of 2,2,2-trifluoroethyl sulfonate (1.27 g, 5.0 mmol, 1.0 equiv) in THF (29 mL) at -78 °C was added dropwise 2.5 M *n*-BuLi in hexanes (4.6 mL, 11.5 mmol, 2.3 equiv). After stirring at -78°C for 1 h, the solution was quenched with a mixture of THF/D_2O (1:1, 5 mL) at -78 °C. Water (~10 mL) was added, and the organic phase was extracted with ethyl acetate, dried over Na_2SO_4, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (eluent = petroleum ether / ethyl acetate v/v = 50:1) to give product (1.04 g, 4.4 mmol, 88%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.82 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H). **^{19}F NMR (396 MHz, $CDCl_3$)**: δ = -90.70 (dt, *J* = 51.2, 2.2 Hz), -109.19 (d, *J* = 51.2 Hz). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 156.9 (ddt, *J* = 294.7, 284.5, 2.1 Hz), 146.1, 131.0, 130.0 , 128.3, 100.5 (dtd, *J* = 59.5, 31.2, 15.3 Hz), 21.6.

Unsuccessful substrates



General procedure for the Rh(III)-catalyzed alkylation reaction



To an oven-dried Schlenk tube was added $RhCp^*(CH_3CN)_3(SbF_6)_2$ (2.1 mg, 0.0025 mmol, 2.5 mol %), substrate **1** (0.1 mmol, 1.0 equiv), *gem*-difluoroalkene **2** (28 mg, 0.12 mmol, 1.2 equiv) and CH_3OH (1 mL) and sealed with a teflon cap. After stirring at 70 °C for 12 h or more (monitored by TLC), the reaction mixture was cooled to room temperature and put through a celite plug. The filtrate was concentrated under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 9:1 v/v) to afford the product **3**.

Procedure for synthesis of 3b

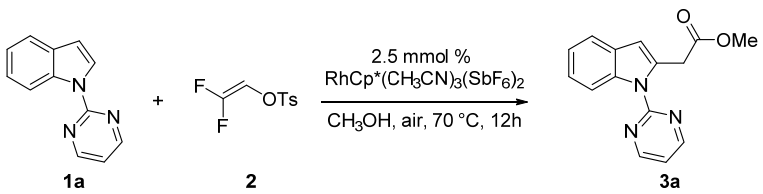
$[IrCp^*Cl_2]_2$(4.0 mg, 0.0050 mmol, 5 mol %), $AgSbF_6$ (7.0 mg, 0.02 mmol, 20 mol %), substrate **1b** (21 mg, 0.1 mmol, 1 equiv), *gem*-difluoroalkene **2** (28 mg, 0.12 mmol, 1.2 equiv) and in CH_3OH (1 mL) were stirred at

100 °C for 12 h under N_2 in a closed Schlenk tube. The reaction mixture was cooled to room temperature and put through a celite plug. The solvent was removed under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 9:1 v/v) to afford the product **3b** (12 mg, 0.044 mmol) as a white solid in 44%.

Procedure for synthesis of 3x

$RhCp^*(CH_3CN)_3(SbF_6)_2$ (2.1 mg, 0.0025 mmol, 2.5 mol %), substrate **1x** (29 mg, 0.1 mmol, 1.0 equiv), *gem*-difluoroalkene **2** (28 mg, 0.12 mmol, 1.2 equiv) and CH_3OH (32 mg, 1.0 mmol, 10.0 equiv) in DCE (1 mL) were stirred at 70 °C for 12 h under air in a closed Schlenk tube. The reaction mixture was cooled to room temperature and put through a celite plug. The solvent was removed under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ ethyl acetate = 9:1 v/v) to afford the product **3x** (34 mg, 0.094 mmol) in 94% yield.

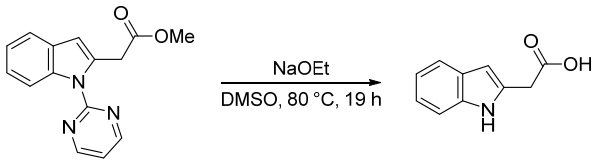
Reaction of 1a on 4.0 mmol scale:



An oven-dried Schlenk tube was added **1a** (781 mg, 4.0 mmol, 1.0 equiv), $RhCp^*(MeCN)_3(SbF_6)_2$ (86 mg, 0.1 mmol, 0.025 equiv), **2** (112 mg, 4.8 mmol, 1.2 equiv) and solvent CH_3OH (40 mL). Then the tube was sealed with a teflon cap. After stirring at 70 °C for 12 h, the mixture was put through a celite plug. The solvent was removed in vacuo and the residual

mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product **3a** (786.9 mg, 2.94 mmol) in 74% yield.

Removal of the directing group

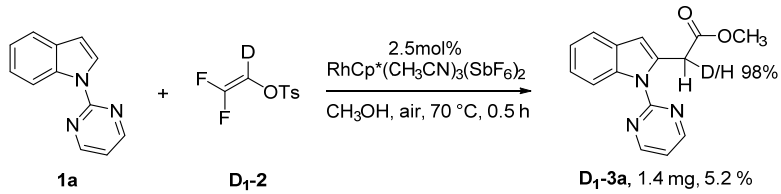


3a **4**, 65%

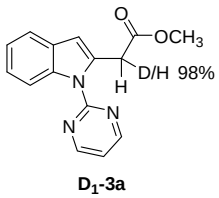
An oven-dried Schlenk tube was added **3a** (781 mg, 0.2 mmol, 1.0 equiv), NaOEt (68 mg, 1.0 mmol, 5.0 equiv) and DMSO (1 mL). Then the tube was sealed with a teflon cap. After stirring at 80 °C for 19 h, the mixture was cooled to room temperature and then quenched with 2 M HCl (5 mL). The aqueous layer was extracted with Et_2O (5 × 5 mL) and the combined organic layers was dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (eluent = dichloromethane/MeOH/acetic acid = 10:1:0.01 v/v/v) to afford the product **4** (22 mg, 0.13 mmol, 65%). **^{1}H NMR (400 MHz, acetone-d_6):** δ = 10.15 (brs, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.07-7.02 (m, 1H), 6.99-6.94 (m, 1H), 6.34 (s, 1H), 3.84 (s, 2H).; **^{13}C NMR (101 MHz, acetone-d_6)** δ = 172.4, 138.4, 133.7, 130.2, 122.5, 121.2, 120.6, 112.4, 102.7, 35.0.; **HRMS (ESI, m/z)**: calcd. for $C_{10}H_{10}NO_2$ $[M+H]^+$: 176.0712, found: 176.0707.

Mechanistic study

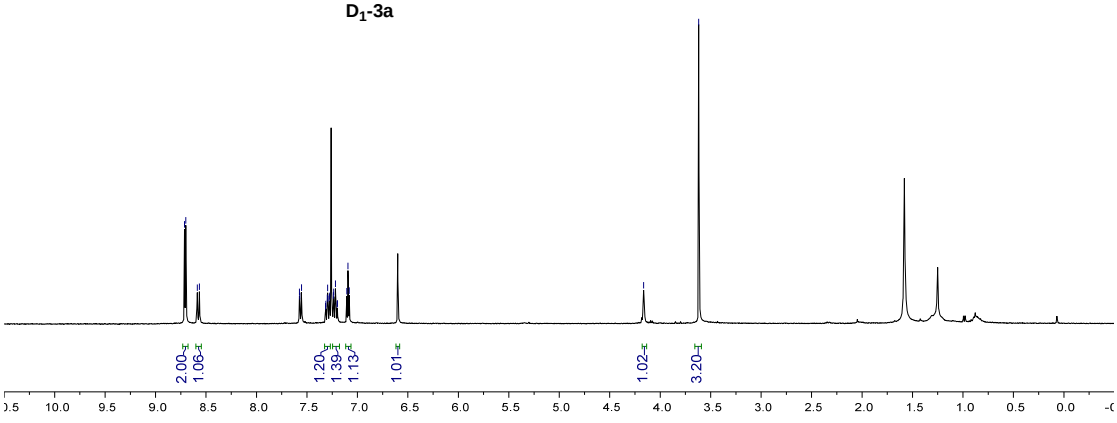
Deuterium labeled experiment



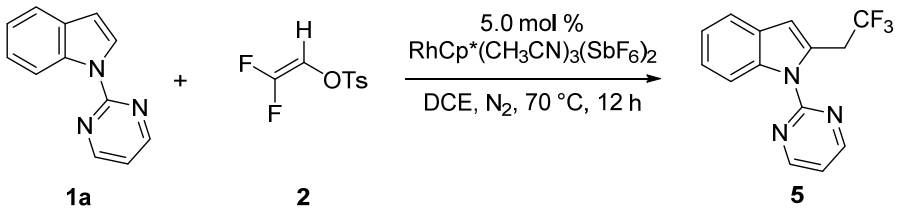
To an oven-dried Schlenk tube was added **1a** (20 mg, 0.1 mmol, 1.0 equiv), RhCp*$(MeCN)_3(SbF_6)_2$ (2.1 mg, 0.0025 mmol, 0.025 equiv), **D_1-2** (28 mg, 0.12 mmol, 1.2 equiv) and CH_3OH (1 mL) under air and the tube was sealed with a teflon cap. After stirring at 70 °C for 0.5 h, the mixture was put through a celite plug. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product **D_1-3a** (1.4 mg, 0.005 mmol) in 5.2% yield.



D_1-3a



Preparation of 1-(pyrimidin-2-yl)-2-(2,2,2-trifluoroethyl)-1*H*-indole

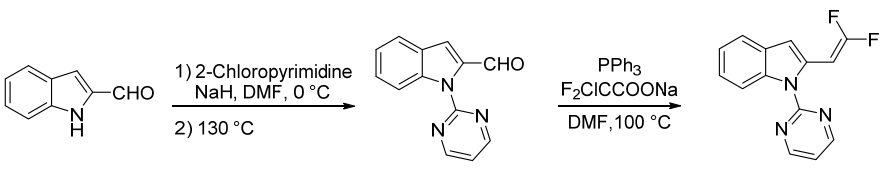


1a **2** **5**

To an oven-dried Schlenk tube was added **1a** (40 mg, 0.2 mmol, 1.0 equiv), $RhCp^*(MeCN)_3(SbF_6)_2$ (8.4 mg, 0.01 mmol, 0.05 equiv), **2** (28 mg, 0.24 mmol, 1.2 equiv) and DCE (1 mL) under air and the tube was sealed with a teflon cap. After stirring at 50 °C for 12 h, the mixture was put through a silica gel plug. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product **5** (10 mg, 0.036 mmol) as a pale yellow oil in 18% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.81 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.30 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.26-7.20 (m, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 6.76 (s, 1H), 4.30 (q, *J* = 10.4 Hz, 2H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ = -65.02 (t, *J* = 10.5 Hz); **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 158.2, 158.1, 137.2, 129.1 (q, *J* = 3.5 Hz), 128.5, 125.3 (q, *J* = 277.4 Hz), 123.8, 122.2, 120.4, 117.4, 114.2, 110.2, 33.9 (q, *J* = 31.0 Hz). All the data is in accordance with the literature values.[7]

Investigation of the intermediacy of 6

Procedure for the synthesis of 6

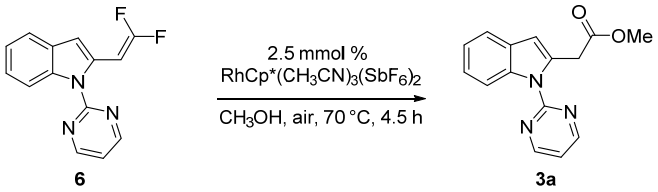


S3 **6**

Following a procedure from Ackermann et al.,[1-4] to a stirred solution of 1-(pyrimidin-2-yl)-1*H*-indole-2-carbaldehyde (1.60 g, 11.0 mmol, 1.0 equiv) in DMF (50 mL) was added NaH (484 mg, 12.1 mmol, 1.1 eqiuv) by portions at 0 °C. After stirring for 30 min at 0 °C, 2-chloropyrimidine (1.37 g, 12 mmol, 1.2 eqiuv) was added and the mixture was heated to 130 °C and stirred for 24 h. Then the mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4, concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10 : 1 v/v) to afford **S3** (490 mg, 2.2 mmol) as a gray solid in 20% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 10.39 (s, 1H), 8.83 (d, *J* = 4.8 Hz, 2H), 8.54 (dd, *J* = 8.6, 0.9 Hz, 1H), 7.76 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.54-7.46 (m, 2H), 7.32 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H), 7.24 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)：** δ = 183.6, 158.3, 157.4, 138.3, 137.6, 127.7, 127.5, 123.2, 123.1, 117.5, 115.5, 115.3. **HRMS (ESI, m/z):** calcd. for $C_{13}H_{10}N_3O$ $[M+H]^+$: 224.0824, found: 224.0821. A solution of **S3** (223 mg, 1.0 mmol, 1.0 equiv) and PPh_3 (524 mg, 2.0 mmol, 2.0 equiv) in DMF (5 mL) was heated to 100 °C. To the reaction mixture at 100 °C was added $F_2ClCCOONa$ (305 mg, 2.0 mmol, 2.0 equiv) slowly. After the reaction finished according to the TLC (about 3 min), the reaction mixture was cooled to room temperature, quenched with water and extracted with ethyl acetate. The combined organic layers were washed with H_2O_2 (30 wt% in water, 5 mL), brine and dried over Na_2SO_4. After solvent was removed under reduced pressure, the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford **6** (62 mg, 0.24 mmol) as a pale yellow solid in 24% yield. **^{1}H NMR**

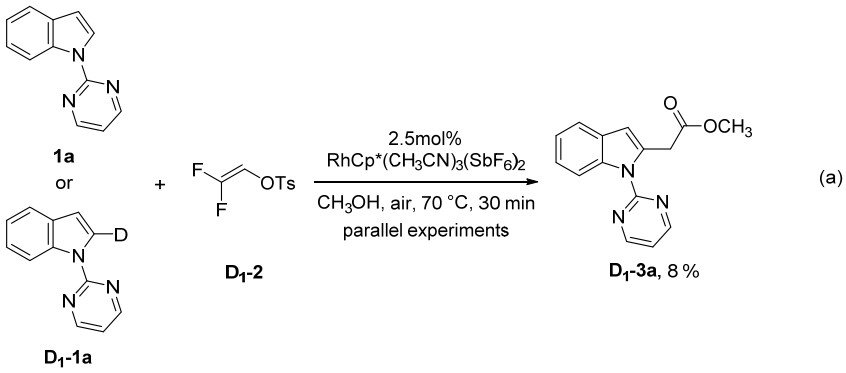
(400 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 4.8 Hz, 2H), 8.28 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.28 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.24 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.21 (d, *J* = 4.8 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.35 (dd, *J* = 25.2, 3.0 Hz, 1H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ = -79.96 (t, *J* = 24.0 Hz), -83.14 (d, *J* = 23.2 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 158.2, 157.7, 156.5 (dd, *J* = 297.7, 286.1 Hz), 136.4, 129.2, 128.9 (dd, *J* = 10.0, 7.9 Hz), 123.5, 122.3, 120.2, 117.3, 114.0, 107.7(d, *J* = 9.9 Hz), 75.7(dd, *J* = 36.8, 12.2 Hz). **HRMS (ESI, m/z):** calcd. for $C_{14}H_{10}F_2N_3$ $[M+H]^+$: 258.0843, found: 258.0846.

Procedure for the control reaction with 5



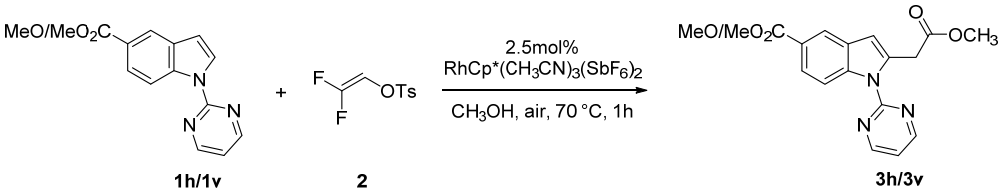
To an oven-dried Schlenk tube was added $RhCp^*(CH_3CN)_3(SbF_6)_2$ (2.1 mg, 0.0025 mol, 2.5 mol%), *gem*-difluoroalkene **6** (25.7 mg, 0.1 mmol, 1.0 equiv) and CH_3OH (1 mL) and sealed with a teflon cap. After stirring at 70 °C for 4.5 h, the mixture was put through a celite plug. The solvent was removed under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ ethyl acetate = 9:1 v/v) to afford the product **3a** (2.0 mg, 0.08 mmol) as a white solid in 8% yield.

Kinetic isotope effect study



To an oven-dried Schlenk tube was added **1a** or **D_1-1a** (0.1 mmol, 1.0 equiv), $RhCp^*(MeCN)_3(SbF_6)_2$ (2.1 mg, 0.0025 mmol, 0.025 equiv), **2** (28 mg, 0.12 mmol, 1.2 equiv) and CH_3OH (1 mL) under air and the tube was sealed with a teflon cap. The reaction mixtures were stirred side-by-side in a preheated oil bath at 70 °C for 30 min. Then the mixture were put through a celite plug and concentrated under reduced pressure separately. The crude residue were purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product **3a** (2.3 mg from **1a**, 2.3 mg from **D_1-1a**).

Intermolecular competition experiments

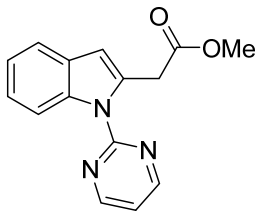


To an oven-dried Schlenk tube was added **1h** (22.5 mg, 0.1 mmol, 1.0 equiv), **1v** (25.3 mg, 0.1 mmol, 1.0 equiv), $RhCp^*(MeCN)_3(SbF_6)_2$ (2.1 mg, 0.0025 mmol, 0.025 equiv), **2** (28 mg, 0.12 mmol, 1.2 equiv) and CH_3OH (1 mL) under air and the tube was sealed with a teflon cap. The reaction

mixtures were stirred side-by-side in a preheated oil bath at 70 °C for 12 h. Then the mixture were put through a celite plug and concentrated under reduced pressure separately. The crude residue were purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product **3h** (15.4 mg, 0.05 mmol, 52%) and **3v** (8.8 mg, 0.03 mmol, 27%).

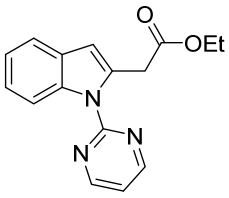
Characterization of products

Methyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3a



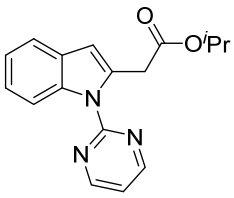
Following the general procedure, **3a** was obtained as a white solid (25 mg, 0.095 mmol, 95%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.70 (d, *J* = 4.8 Hz, 2H), 8.58 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.34-7.27 (m, 1H), 7.25-7.19 (m, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.60 (s, 1H), 4.18 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.1, 158.0, 157.6, 136.7, 133.2, 128.9, 123.3 , 122.0, 120.0, 116.5, 115.31, 109.6, 51.8, 36.9; **HRMS (ESI, m/z)**: calcd. for $C_{15}H_{14}N_3O_2$ $[M+H]^+$: 268.1086, found: 268.1087. The spectral data were in accordance with those reported in the literature.[8]

Ethyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3a'



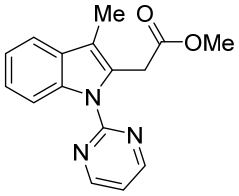
Following the general procedure, **3a'** was obtained as a colorless oil (22 mg, 0.078 mmol, 78%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.70 (d, *J* = 4.8 Hz, 2H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.33-7.27 (m, 1H), 7.25-7.19 (m, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.60 (s, 1H), 4.20 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.7, 158.2, 157.7, 136.8, 133.5, 129.0, 123.3, 122.0, 120.1, 116.5, 115.3, 109.6, 60.5, 37.1, 14.1; **HRMS (ESI, m/z)**: calcd. for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243, found: 282.1247.

Isopropyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3a''



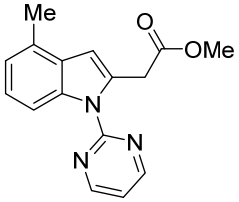
Following the general procedure, **3a''** was obtained as a colorless oil (17 mg, 0.058 mmol, 58%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.71 (d, *J* = 4.8 Hz, 2H), 8.56 (d, *J* = 8.3 Hz, 1H), 7.56 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.29 (td, *J* = 7.4, 1.1Hz, 1H), 7.22 (td, *J* = 7.4, 1.1 Hz, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.62-6.56 (m, 1H), 4.96 (hept, *J* = 6.2 Hz, 1H), 4.18 (s, 2H), 1.12 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.3, 158.3, 157.7, 136.8, 133.6, 129.0, 123.2, 122.0, 120.1, 116.5, 115.3, 109.6, 67.9, 37.4, 21.7; **HRMS (ESI, m/z)**: calcd. for $C_{17}H_{18}N_3O_2$ $[M+H]^+$: 296.1399, found: 296.1399.

Methyl 2-(3-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3b



3b was obtained as a colorless oil (12 mg, 0.044 mmol, 44%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.68 (d, *J* = 4.8 Hz, 2H), 8.55 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.34-7.27 (m, 1H), 7.26 – 7.22 (m, 1H), 7.05 (t, *J* = 4.8 Hz, 1H), 4.14 (s, 2H), 3.63 (s, 3H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.4, 158.2, 157.7, 136.0 , 130.3, 128.9, 123.6, 121.8, 118.3, 116.2, 115.9, 115.0, 51.9, 33.9, 8.9; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243, found: 282.1242. The spectral data were in accordance with those reported in the literature.[8]

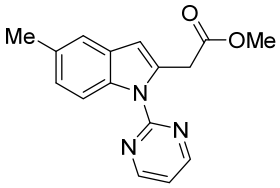
Methyl 2-(4-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3c



Following the general procedure, **3c** was obtained as a white solid (23 mg, 0.082 mmol, 82%). **^{1}H NMR (400 MHz, $CDCl_3$):**δ= 8.70 (d, *J* = 4.8 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.08 (t, *J* = 4.8 Hz,

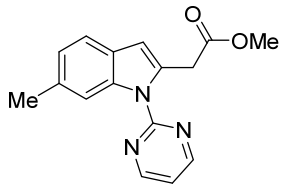
1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.64 (s, 1H), 4.19 (s, 2H), 3.62 (s, 3H), 2.55 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 158.2, 157.7, 136.6, 132.7, 129.4, 128.6, 123.5, 122.5, 116.5, 112.9, 108.2, 51.9, 37.1, 18.5; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243, found: 282.1241.

Methyl 2-(5-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3d



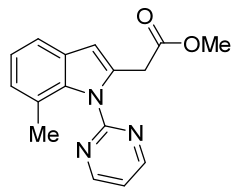
Following the general procedure, **3d** was obtained as a white solid (26 mg, 0.092 mmol, 92%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.50 (d, *J* = 8.6 Hz, 1H), 7.40-7.36 (m, 1H), 7.14 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.06 (t, *J* = 4.8 Hz, 1H), 6.55 (s, 1H), 4.19 (s, 2H), 3.65 (s, 3H), 2.48 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 158.1, 157.6, 135.0, 133.3, 131.4, 129.2, 124.7, 119.9, 116.2, 115.2, 109.5, 51.8, 37.1, 21.2; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243, found: 282.1242. The spectral data were in accordance with those reported in the literature.[8]

Methyl 2-(6-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3e



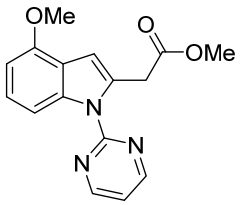
Following the general procedure, **3e** was obtained as a white solid (23 mg, 0.083 mmol, 83%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.71 (d, *J* = 4.8 Hz, 2H), 8.38 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 4.8, 1H), 7.06 (d, *J* =7.9Hz, 1H) 6.55 (s, 1H), 4.16 (s, 2H), 3.61 (s, 3H), 2.51 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 158.2, 157.7, 137.1, 133.2, 132.7, 126.7, 123.6, 119.7, 116.4, 115.3, 109.6, 51.8, 37.0, 22.1; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243, found: 282.1241. The spectral data were in accordance with those reported in the literature.[8]

Methyl 2-(7-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3f



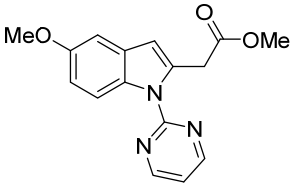
Following the general procedure, **3f** was obtained as a white solid (11 mg, 0.039 mmol, 39%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.82 (d, *J* = 4.8 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 4.8 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.59 (s, 1H), 3.94 (s, 2H), 3.52 (s, 3H), 2.06 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.5, 158.3, 158.2, 136.5, 133.6, 129.4, 126.0, 122.5, 121.7, 118.5, 118.3, 107.3, 52.0, 34.4, 20.7.; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243, found: 282.1242. The spectral data were in accordance with those reported in the literature.[8]

Methyl 2-(4-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3g



Following the general procedure, **3g** was obtained as a white solid (24 mg, 0.082 mmol, 82%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.70 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.72 (s, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 4.16 (s, 2H), 3.95 (s, 3H), 3.60 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 158.2, 157.7, 152.5, 138.1, 131.8, 124.1, 119.4, 116.6, 108.6, 106.6, 102.4, 55.4, 51.9, 37.0.; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_3$ $[M+H]^+$: 298.1192, found: 298.1192. The spectral data were in accordance with those reported in the literature.[8]

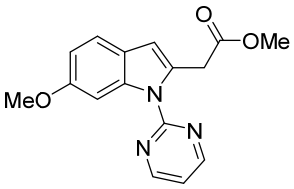
Methyl 2-(5-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3h



Following the general procedure, **3h** was obtained as a white solid (21 mg, 0.07mmol, 70%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.66 (d, *J* = 4.8 Hz, 2H), 8.52 (d, *J* = 9.1 Hz, 1H), 7.04 (t, *J* = 4.8 Hz, 1H),7.03 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* =

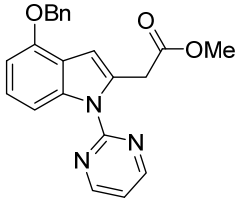
9.1, 2.7 Hz, 1H), 6.53 (s, 1H), 4.16 (s, 2H), 3.87 (s, 3H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 158.1, 157.7, 155.5, 134.0, 131.7, 129.8, 116.6, 116.3, 112.4, 109.8, 102.5, 55.7, 51.9, 37.3.; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_3$ $[M+H]^+$: 298.1192, found: 298.1192. The spectral data were in accordance with those reported in the literature.[8]

Methyl 2-(6-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3i



Following the general procedure, **3i** was obtained as a white solid (23 mg, 0.077 mmol, 77%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.70 (d, *J* = 4.8 Hz, 2H), 8.23 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.52 (s, 1H), 4.14 (s, 2H), 3.89 (s, 3H), 3.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.4, 158.2, 157.6, 157.1, 137.6, 132.2, 123.0, 120.4, 116.4, 110.9, 109.6, 100.3, 55.7, 51.8, 37.1.; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{16}N_3O_3$ $[M+H]^+$: 298.1192, found: 298.1189. The spectral data were in accordance with those reported in the literature.[8]

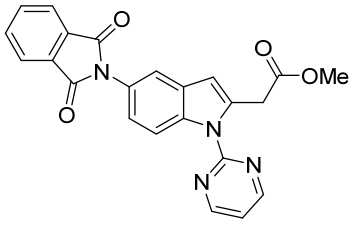
Methyl 2-(4-(benzyloxy)-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3j



Following the general procedure, **3j** was obtained as a white solid (25 mg, 0.067 mmol, 67%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.70 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.55-7.46 (m, 2H), 7.45-7.37 (m, 2H), 7.37-7.29 (m, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.80 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.22 (s, 2H), 4.17 (s, 2H), 3.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 158.2, 157.7, 151.6, 138.2, 137.4, 131.9, 128.5, 127.8, 127.3, 124.1, 119.8, 116.6, 108.9, 106.9, 103.9, 70.0, 51.9, 37.0;

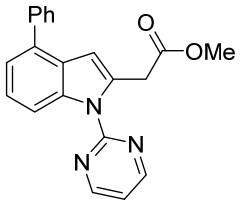
HRMS (ESI, m/z): calcd. for $C_{22}H_{20}N_3O_3$ $[M+H]^+$: 374.1505, found: 374.1500.

Methyl2-(5-(1,3-dioxoisoindolin-2-yl)-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3k



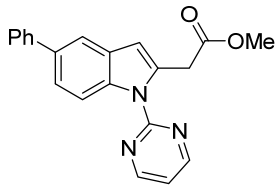
Following the general procedure, **3k** was obtained as a white solid (30 mg, 0.072 mmol, 72%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.83-8.65 (m, 3H), 7.96 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.12 (t, *J* = 4.8 Hz, 1H), 6.65 (s, 1H), 4.20 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 167.8, 158.0, 157.8, 136.2, 134.7, 134.2, 131.9, 129.3, 125.8, 123.6, 122.0, 118.6, 116.9, 116.1, 109.8, 51.9, 37.1. **HRMS (ESI, m/z):** calcd. for $C_{23}H_{17}N_4O_4$ $[M+H]^+$: 413.1250, found: 413.1246.

Methyl 2-(4-phenyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3l



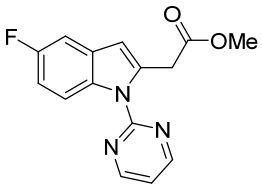
Following the general procedure, **3l** was obtained as a white solid (30 mg, 0.087 mmol, 87%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.72 (d, *J* = 4.8 Hz, 2H), 8.59 (d, *J* = 8.4, Hz, 1H), 7.70 – 7.63 (m, 2H), 7.52-7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.30 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.11 (t, *J* = 4.8 Hz, 1H), 6.78 (s, 1H), 4.18 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.2, 158.1, 157.7, 140.7, 137.2, 134.0, 133.6, 128.9, 128.4, 127.2, 127.0, 123.7, 122.2, 116.7, 114.3, 109.0, 51.9, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{21}H_{18}N_3O_2$ $[M+H]^+$: 344.1399, found: 344.1395.

Methyl 2-(5-phenyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3m



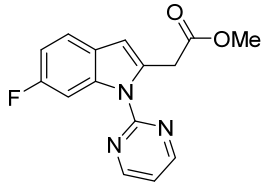
Following the general procedure, **3m** was obtained as a white solid (24 mg, 0.069 mmol, 69%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.72 (d, *J* = 4.8 Hz, 2H), 8.65 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.55 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.66 (s, 1H), 4.21 (s, 2H), 3.63 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.2, 158.1, 157.7， 141.9, 136.3, 135.4, 134.1, 129.5, 128.7, 127.3, 126.6, 123.0, 118.6, 116.6, 115.7, 110.0, 51.9, 37.2; **HRMS (ESI, m/z):** calcd. for $C_{21}H_{18}N_3O_2$ $[M+H]^+$: 344.1399, found: 344.1397.

Methyl 2-(5-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3n



Following the general procedure, **3n** was obtained as a white solid (28 mg, 0.098 mmol, 98%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.56 (dd, *J* = 9.2, 4.7 Hz, 1H), 7.20 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 7.01 (td, *J* = 9.2, 2.7 Hz, 1H), 6.55 (s, 1H), 4.17 (s, 2H), 3.63 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 159.0 (d, *J* = 220.8 Hz), 157.8, 157.7, 135.0, 133.2, 129.7 (d, *J* = 10.2 Hz), 116.7, 116.6 (d, *J* = 8.9 Hz), 111.08 (d, *J* = 24.8 Hz), 109.5 (d, *J* = 4.0 Hz), 105.3 (d, *J* = 23.5 Hz), 51.9, 37.1; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}FN_3O_2$ $[M+H]^+$: 286.0992, found: 286.0992. The spectral data were in accordance with those reported in the literature.[8]

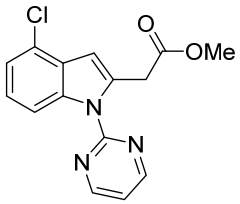
Methyl 2-(6-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3o



Following the general procedure, **3o** was obtained as a white solid (28 mg, 0.097 mmol, 97%). **^{1}H NMR**

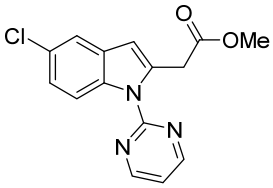
(400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.38 (dd, *J* = 11.3, 2.4 Hz, 1H), 7.46 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.98 (td, *J* = 8.9, 2.4 Hz, 1H), 6.56 (s, 1H), 4.16 (s, 2H), 3.63 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ =171.2, 160.4 (d, *J* = 237.6 Hz), 158.0, 157.7, 136.8 (d, *J* = 13.1 Hz), 133.8 (d, *J* = 4.0 Hz), 125.3, 120.5 (d, *J* = 9.9 Hz), 116.7, 110.4 (d, *J* = 24.3 Hz), 109.5, 102.9 (d, *J* = 29.3 Hz), 51.9, 37.1; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}FN_3O_2$ $[M+H]^+$: 286.0992, found: 286.0998.

Methyl 2-(4-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3p



Following the general procedure, **3p** was obtained as a white solid (25 mg, 0.084 mmol, 84%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.72 (d, *J* = 4.8 Hz, 2H), 8.58 – 8.39 (m, 1H), 7.25 – 7.17 (m, 2H), 6.73(s, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 4.20 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.9, 157.9, 157.8, 137.4, 134.1, 127.7, 125.3, 124.0, 121.9, 117.0, 114.0, 107.8, 52.0, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$: 302.0696, found: 302.0697.

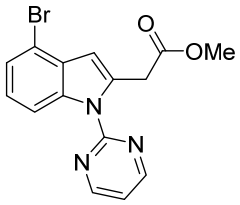
Methyl 2-(5-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3q



Following the general procedure, **3q** was obtained as a white solid (22 mg, 0.074 mmol, 74%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.52 (d, *J* = 8.9 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.23 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.53 (s, 1H), 4.17 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 157.9, 157.7, 135.1, 134.8, 130.1, 127.6, 123.4, 119.5, 116.8, 116.7, 109.0, 51.9, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}ClN_3O_2$

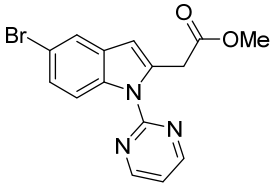
[M+H]$^+$: 302.0696, found: 302.0697. The spectral data were in accordance with those reported in the literature.[8]

Methyl 2-(4-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3r



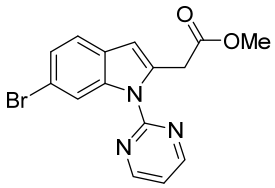
Following the general procedure, **3r** was obtained as a white solid (23 mg, 0.067 mmol, 67%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.73 (d, *J* = 4.8 Hz, 2H), 8.53 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 4.8 Hz, 1H), 6.69 (s, 1H), 4.21 (s, 2H), 3.63 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.9, 158.0, 157.8, 137.1, 134.1, 129.5, 125.0, 124.3, 117.1, 114.5, 113.9, 109.5, 52.0, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}BrN_3O_2$ [M+H]$^+$: 346.0191, found: 346.0193.

Methyl 2-(5-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3s



Following the general procedure, **3s** was obtained as a white solid (28 mg, 0.082 mmol, 82%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.47 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.36 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.52 (s, 1H), 4.17 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 157.8, 157.7, 135.5, 134.6, 130.7, 126.1, 122.6, 117.1, 116.9, 115.3, 108.9, 52.0, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}BrN_3O_2$ [M+H]$^+$: 346.0191, found: 346.0190. The spectral data were in accordance with those reported in the literature.[8]

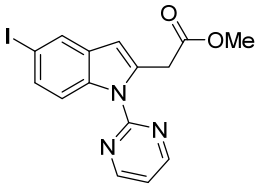
Methyl 2-(6-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3t



Following the general procedure, **3t** was obtained as a white solid (30 mg, 0.086 mmol, 86%). **^{1}H NMR**

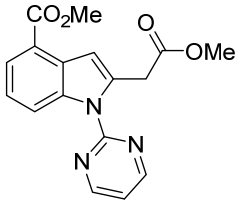
(400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 1.7 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.11 (t, *J* = 4.8 Hz, 1H), 6.56 (s, 1H), 4.16 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 157.80, 157.78, 137.4, 134.0, 127.8, 125.3, 121.1, 118.5, 117.0, 116.9, 109.5, 51.9, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}BrN_3O_2$ $[M+H]^+$: 346.0191, found: 346.0188.

Methyl 2-(5-iodo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate 3u



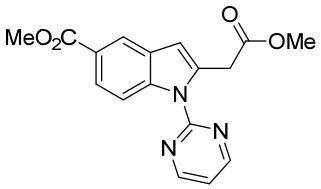
Following the general procedure, **3u** was obtained as a white solid (31 mg, 0.079 mmol, 79%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.36 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.51 (d, *J* = 0.8 Hz, 1H), 4.17 (s, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 157.9, 157.7, 136.0, 134.3, 131.7, 131.3, 128.8, 117.5, 116.9, 108.7, 86.0, 51.9, 36.9; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}IN_3O_2$ $[M+H]^+$: 394.0052, found: 394.0050.

Methyl 2-(2-methoxy-2-oxoethyl)-1-(pyrimidin-2-yl)- 1*H*-indole-4-carboxylate 3v



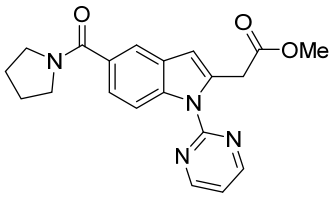
Following the general procedure, **3v** was obtained as a white solid (26 mg, 0.081 mmol, 81%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.79 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 4.7 Hz, 2H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.31 (s, 1H), 7.13 (t, *J* = 4.7 Hz, 1H), 4.23 (s, 2H), 3.98 (s, 3H), 3.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.9, 167.7, 157.9, 157.8, 137.5 , 135.5, 128.9, 125.2, 122.7, 121.0, 120.0, 117.1, 110.4, 52.0, 51.8, 37.0; **HRMS (ESI, m/z):** calcd. for $C_{17}H_{16}N_3O_4$ $[M+H]^+$: 326.1141, found: 326.1140.

Methyl 2-(2-methoxy-2-oxoethyl)-1-(pyrimidin-2-yl)-1*H*-indole-5-carboxylate 3w



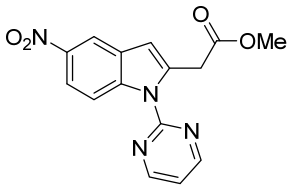
Following the general procedure, **3w** was obtained as a white solid (32 mg, 0.098 mmol, 98%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.73 (d, *J* = 4.8 Hz, 2H), 8.56 (dt, *J* = 8.8, 0.7 Hz, 1H), 8.29 (d, *J* = 1.4 Hz, 1H), 7.98 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.14 (t, *J* = 4.8 Hz, 1H), 6.67 (d, *J* = 0.8 Hz, 1H), 4.19 (s, 2H), 3.94 (s, 3H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.3, 168.1, 158.3(overlap), 139.8, 135.2, 129.0, 125.1, 124.3, 123.0, 117.6, 115.4, 110.5, 52.4, 52.3, 37.2; **HRMS (ESI, m/z):** calcd. for $C_{17}H_{16}N_3O_4$ $[M+H]^+$: 326.1141, found: 326.1141. The spectral data were in accordance with those reported in the literature.[8]

Methyl2-(1-(pyrimidin-2-yl)-5-(pyrrolidine-1-carbonyl)-1*H*-indol-2-yl)acetate 3x



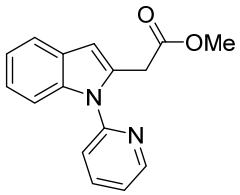
3x was obtained as a white solid (34 mg, 0.094 mmol, 94%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.70 (t, *J* = 4.8 Hz, 2H), 8.55 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.45 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.11 (t, *J* = 4.8 Hz, 1H), 6.61(s, 1H), 4.31 (s, 2H), 3.80 (t, *J* = 7.0 Hz, 2H), 3.75 (s, 3H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.09 (m, 2H), 1.85 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.0, 170.5, 157.9, 157.8, 137.4, 134.4, 130.7, 128.4, 122.6, 119.5, 116.9, 115.0, 109.9, 51.9, 49.9, 46.3, 36.9, 26.4, 24.4; **HRMS (ESI, m/z):** calcd. for $C_{20}H_{21}N_4O_3$ $[M+H]^+$: 365.1614, found: 365.1601.

Methyl 2-(5-nitro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3y



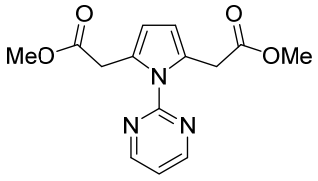
Following the general procedure, **3y** was obtained as a white solid (16 mg, 0.050 mmol, 50%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.77 (d, *J* = 4.8 Hz, 2H), 8.63 (d, *J* = 9.3 Hz, 1H), 8.49 (d, *J* = 2.3 Hz, 1H), 8.17 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 6.75 (s, 1H), 4.22 (s, 2H), 3.64 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.6, 158.1, 157.6, 143.2, 139.8, 136.7, 128.6, 118.7, 117.9, 116.6, 115.5, 110.3, 52.1, 36.8; **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}N_4O_4$ $[M+H]^+$: 313.0937, found: 313.0935.

Methyl 2-(1-(pyridin-2-yl)-1*H*-indol-2-yl)acetate 3z



Following the general procedure, **3z** was obtained as a colorless oil (13 mg, 0.047 mmol, 47%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.58 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.89 (td, *J* = 7.7, 2.0 Hz, 1H), 7.63−7.59 (m, 1H), 7.55 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.43 (ddd, *J* = 7.1, 2.2, 0.8 Hz, 1H), 7.29 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.22-7.12 (m, 2H). 6.61 (d, *J* = 0.9 Hz, 1H), 4.04 (s, 2H), 3.56 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.7, 151.3, 149.4, 138.4, 136.9, 133.0, 128.4, 122.5, 121.8, 121.0, 120.6, 120.2, 110.3, 105.7, 52.0, 34.1; **HRMS (ESI, m/z):** calcd. for $C_{16}H_{15}N_2O_2$ $[M+H]^+$: 267.1134, found: 267.1143.

Dimethyl 2,2'-(1-(pyrimidin-2-yl)-1H-pyrrole-2,5-diyl)diacetate 3aa



Following the general procedure, **3aa** was obtained as a colorless oil (16 mg, 0.055 mmol, 55%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.60 (d, *J* = 4.8 Hz, 2H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.14 (s, 2H), 3.96 (s, 4H), 3.59 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 171.8, 157.6, 127.6, 117.3, 112.4, 99.9,

51.8, 36.0; **HRMS (ESI, m/z):** calcd. for $C_{14}H_{16}N_3O_4$ $[M+H]^+$: 290.1141, found: 290.1147.

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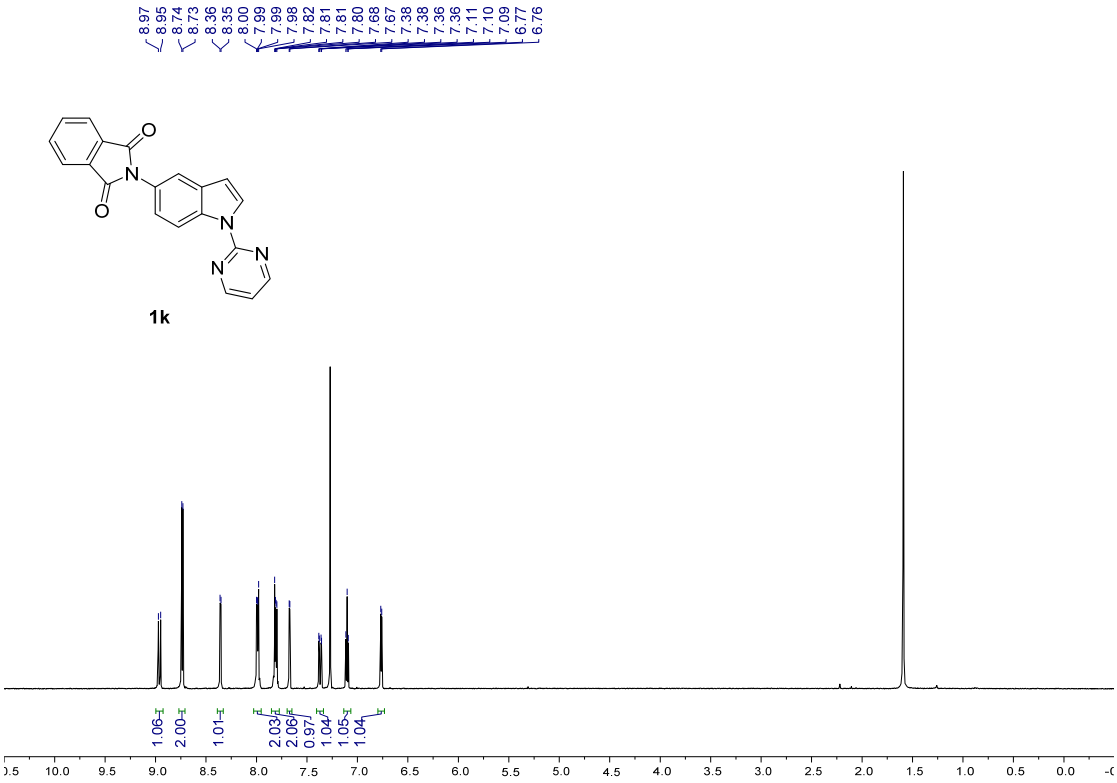
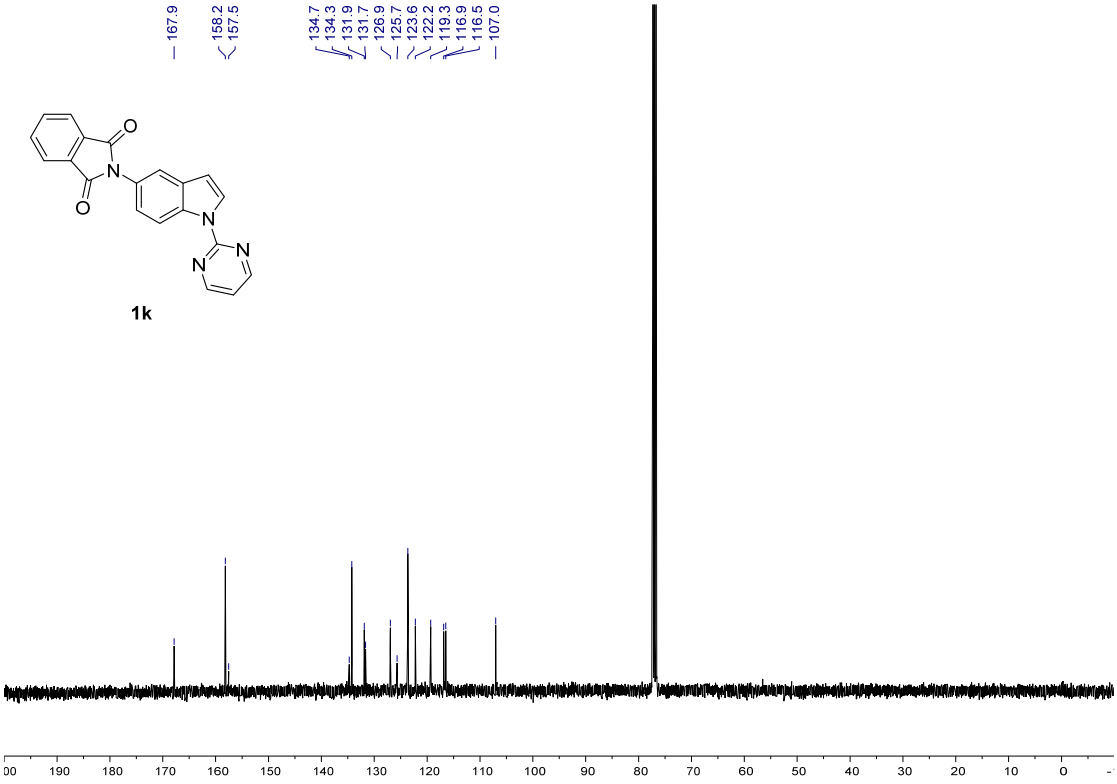
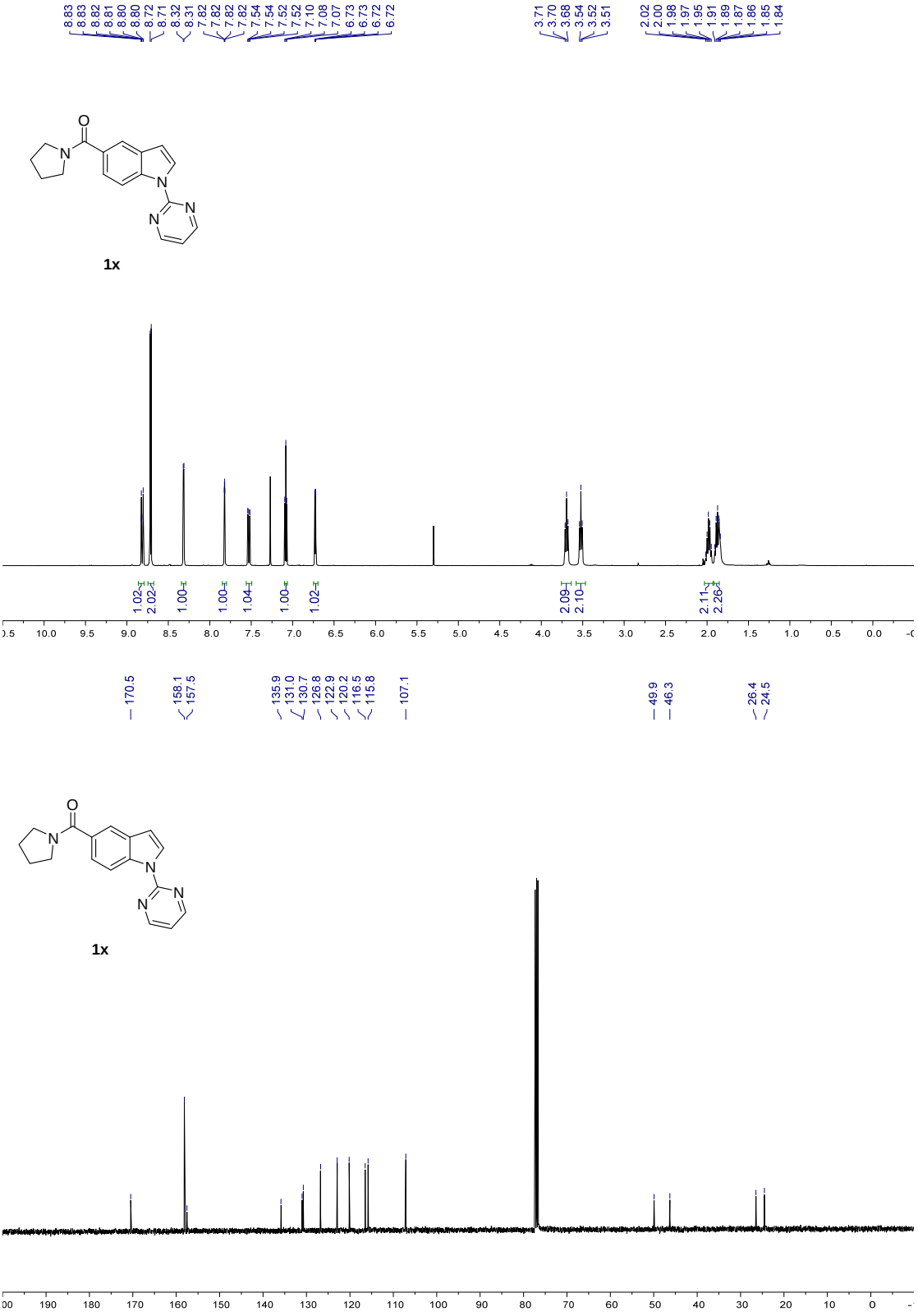
^{1}H, ^{13}C NMR spectra of products



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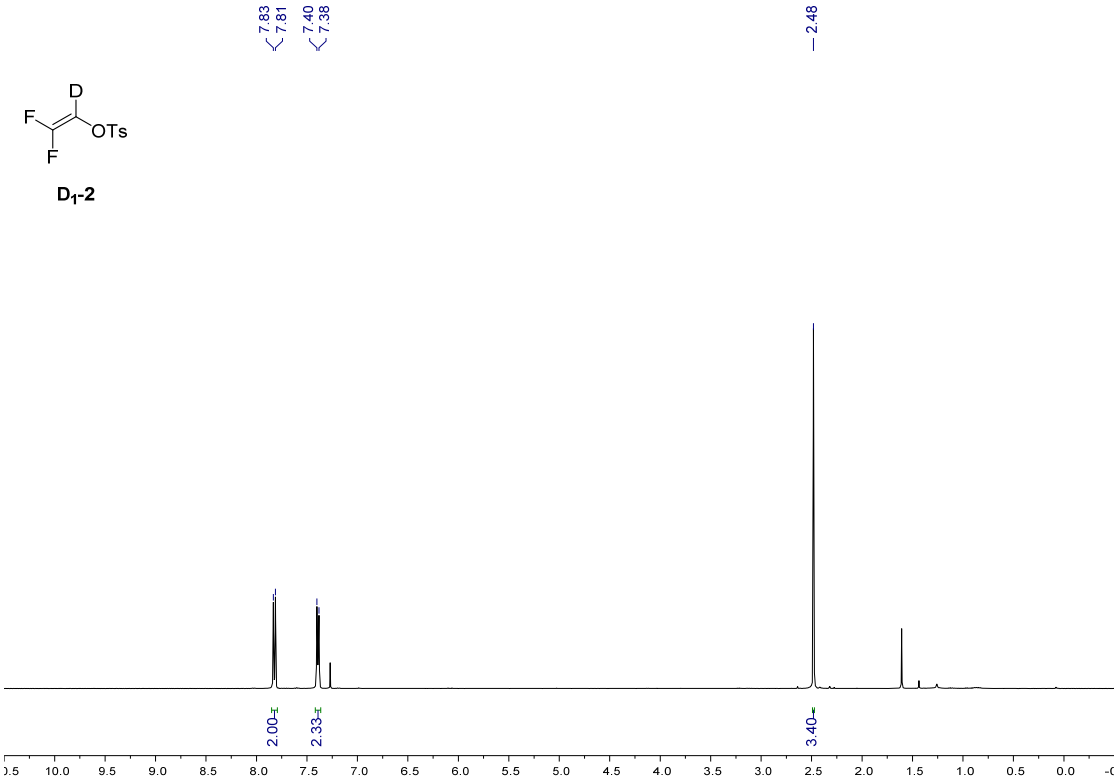
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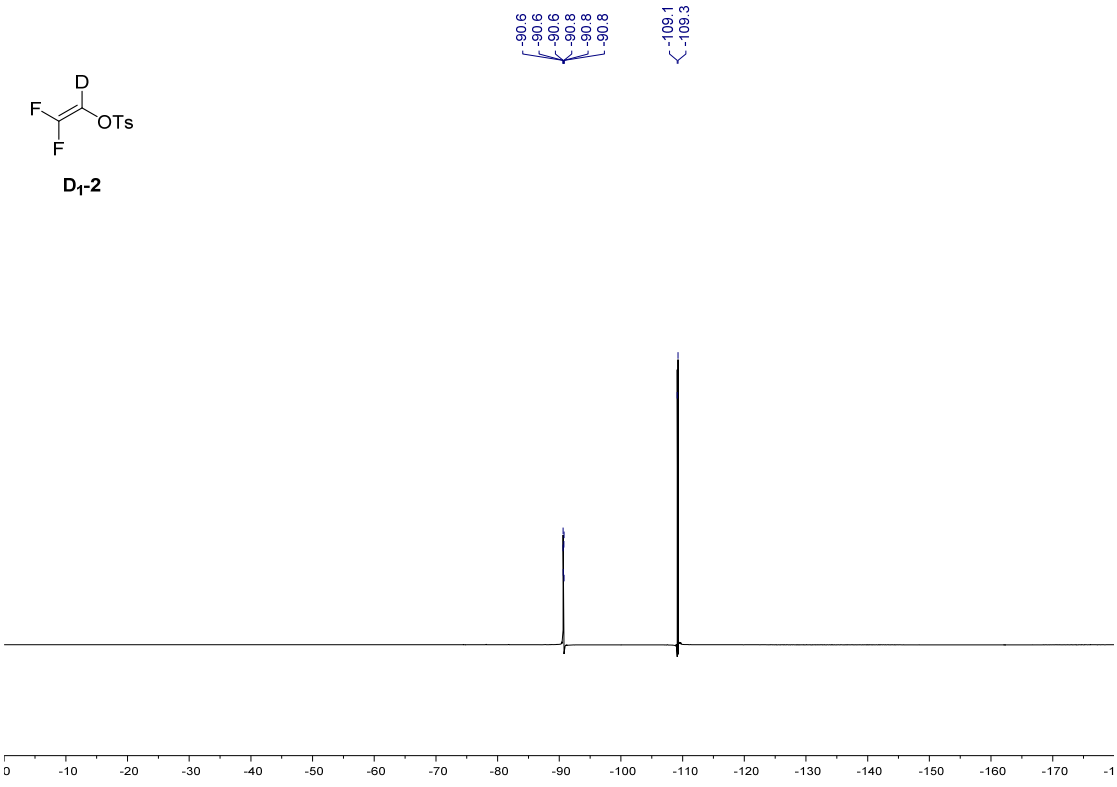
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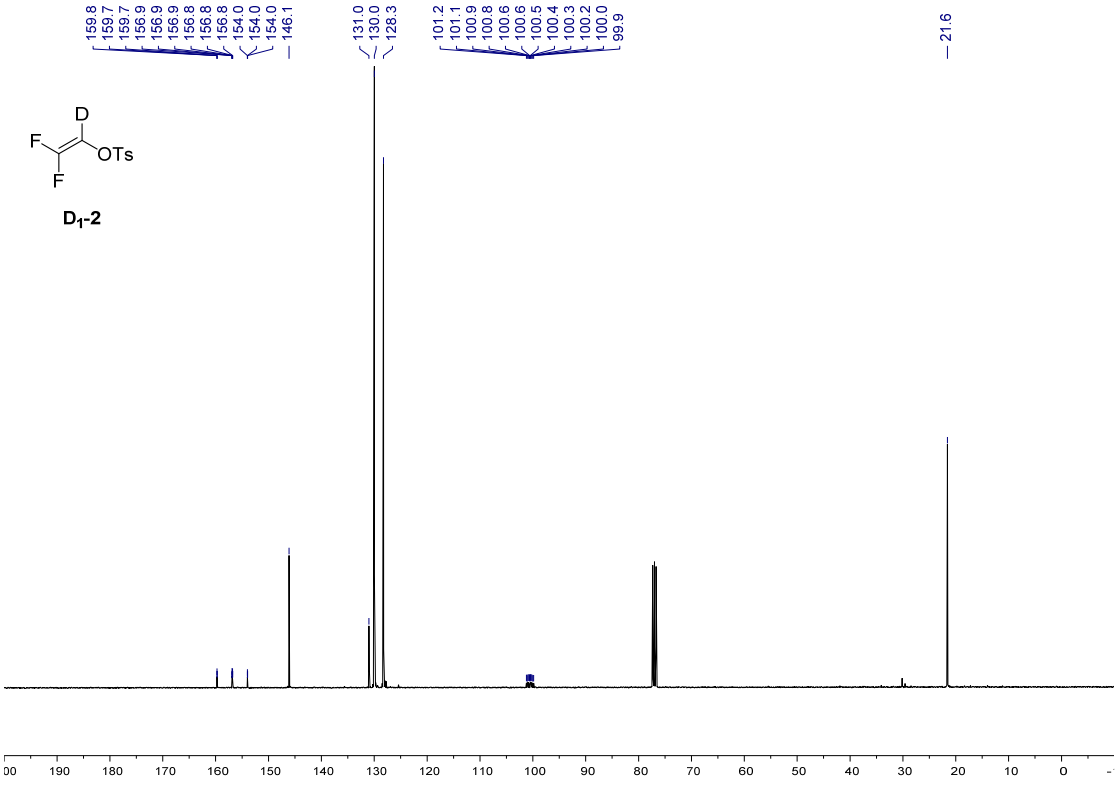
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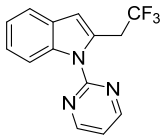
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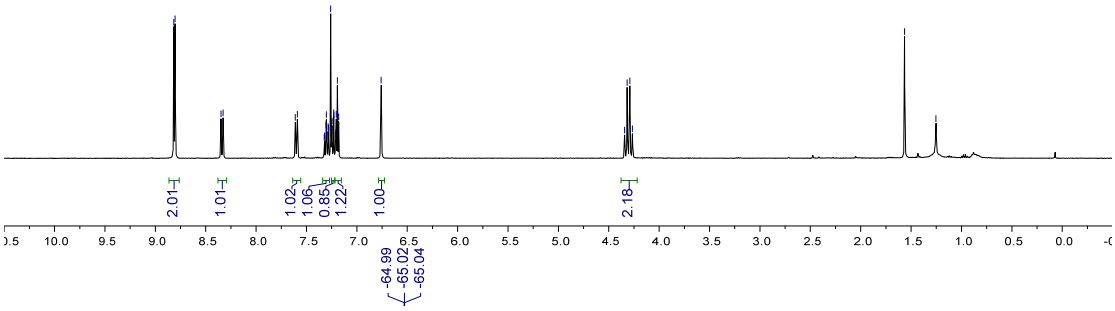
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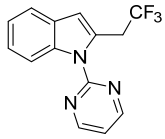
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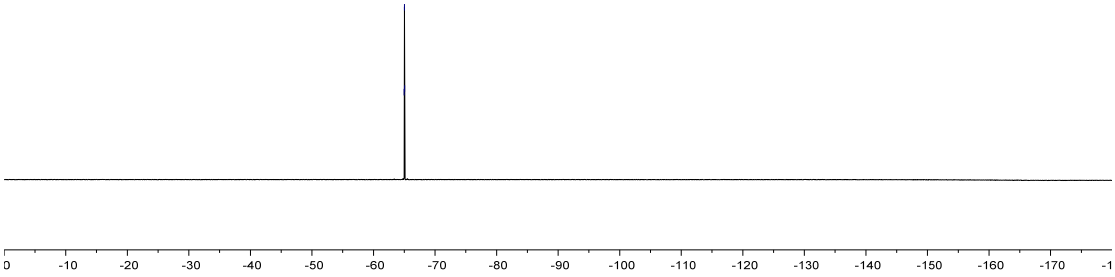
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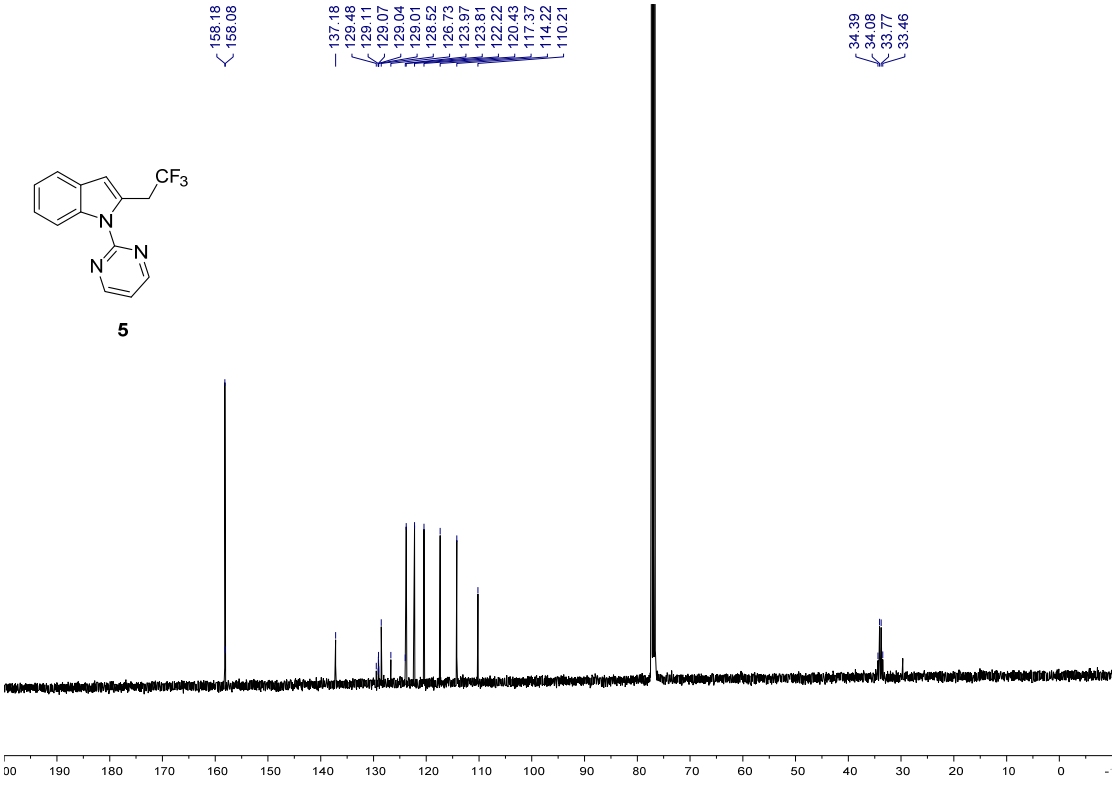
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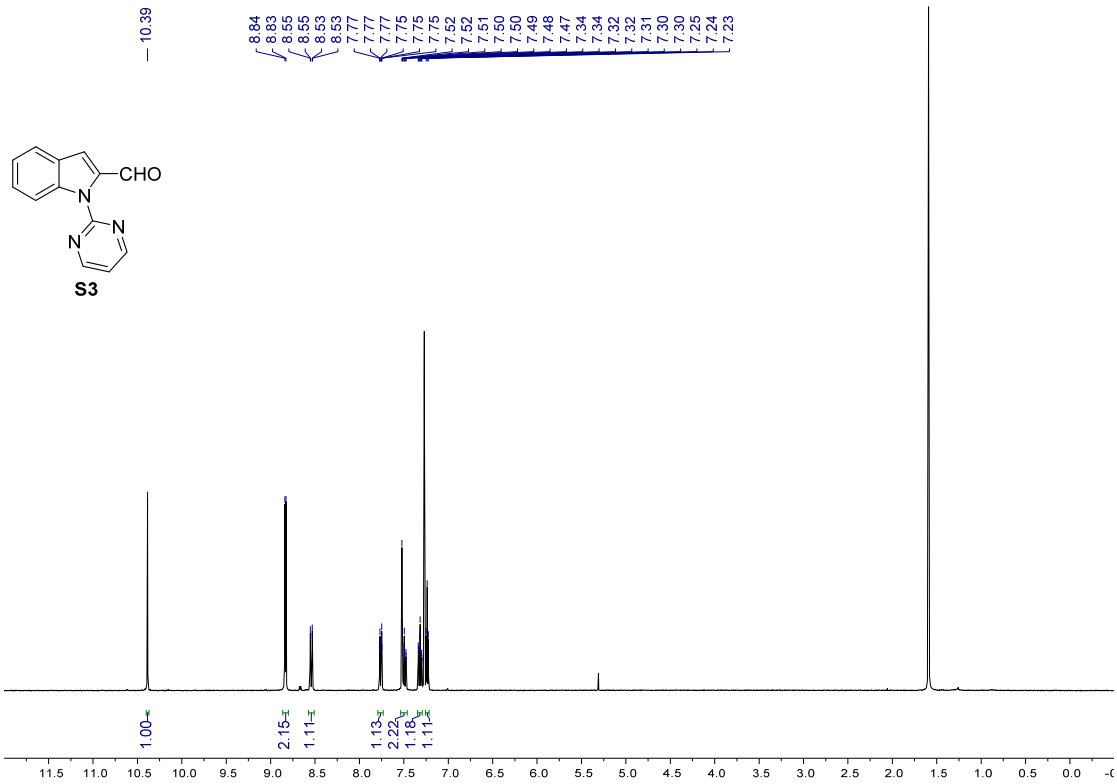
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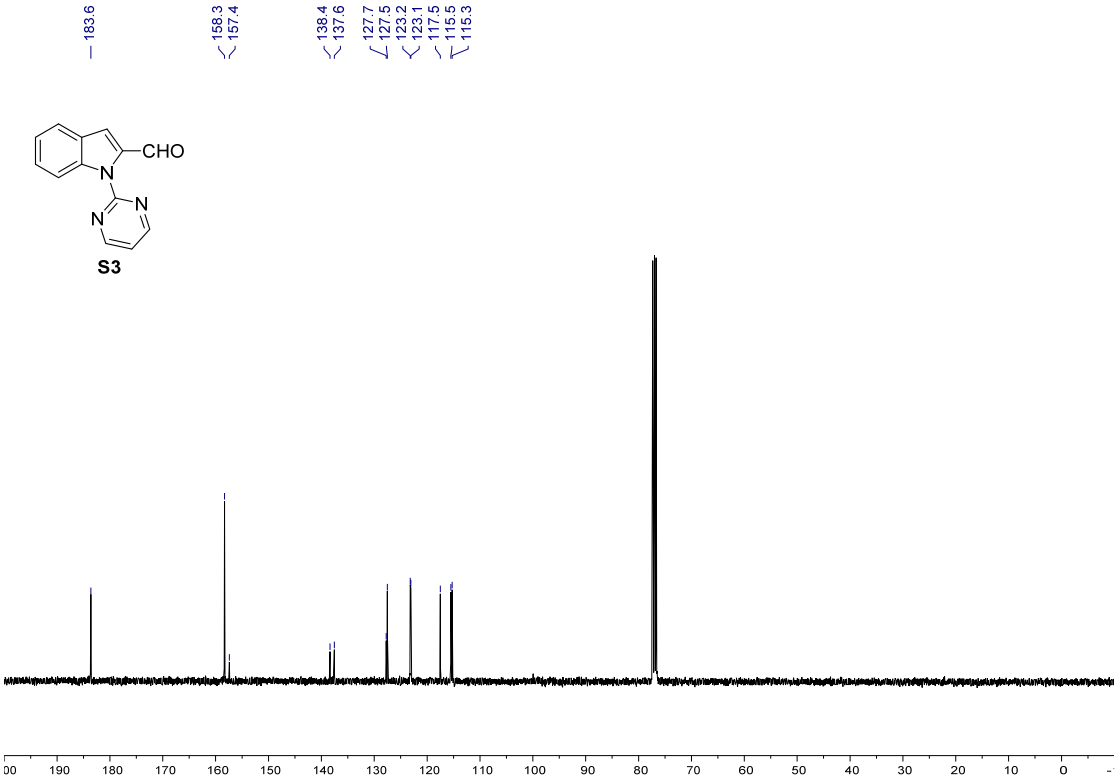
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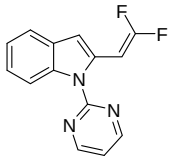
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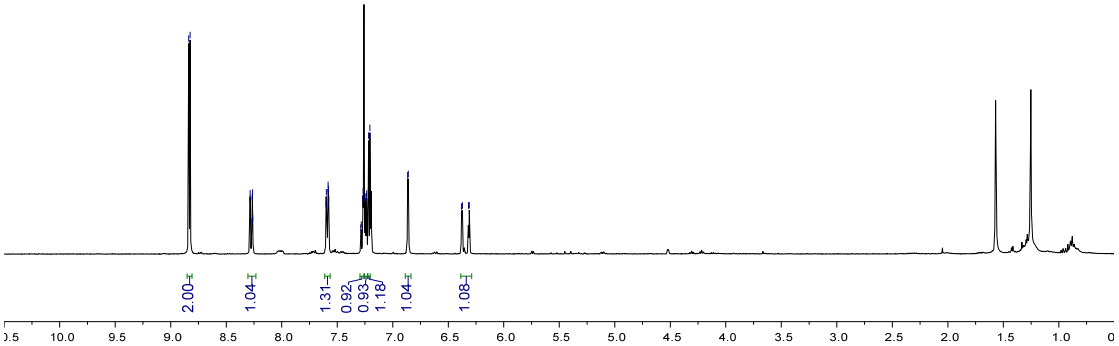
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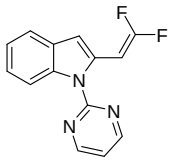
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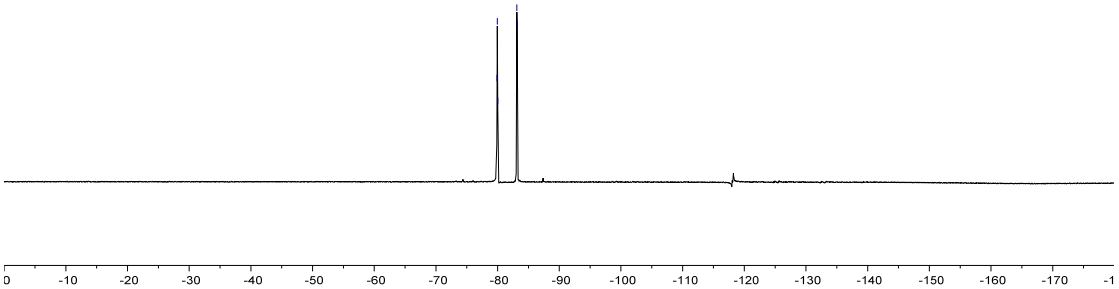
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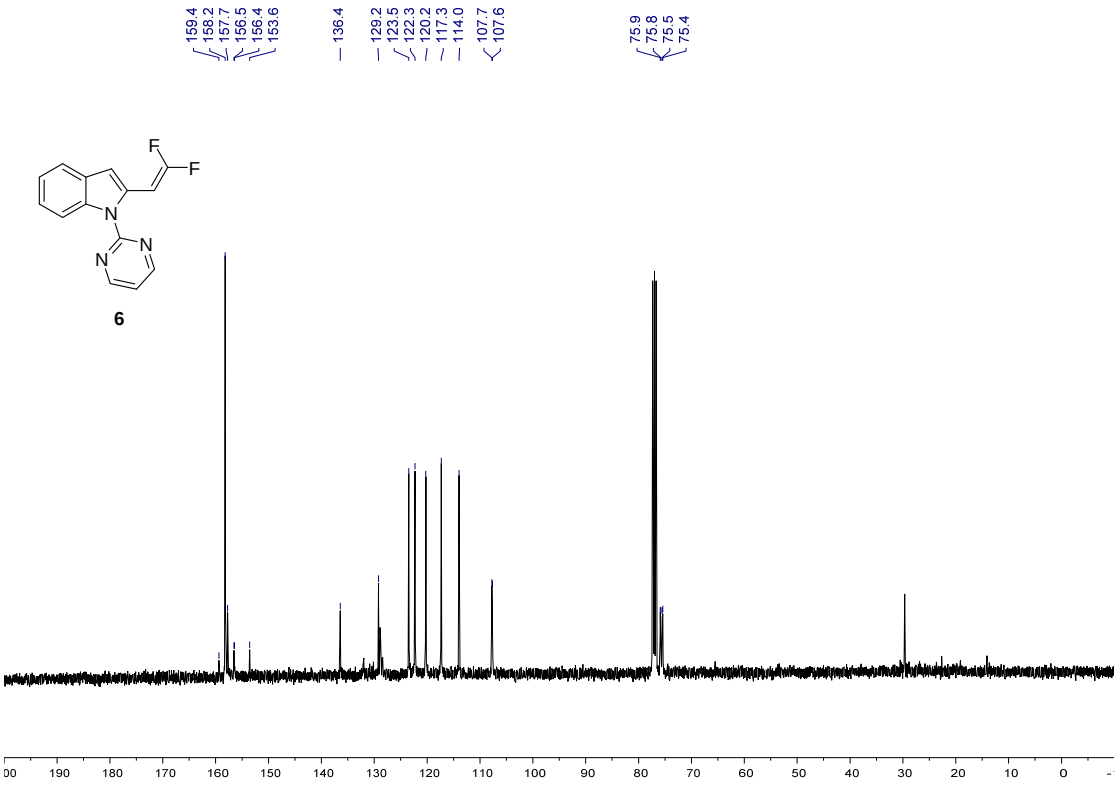
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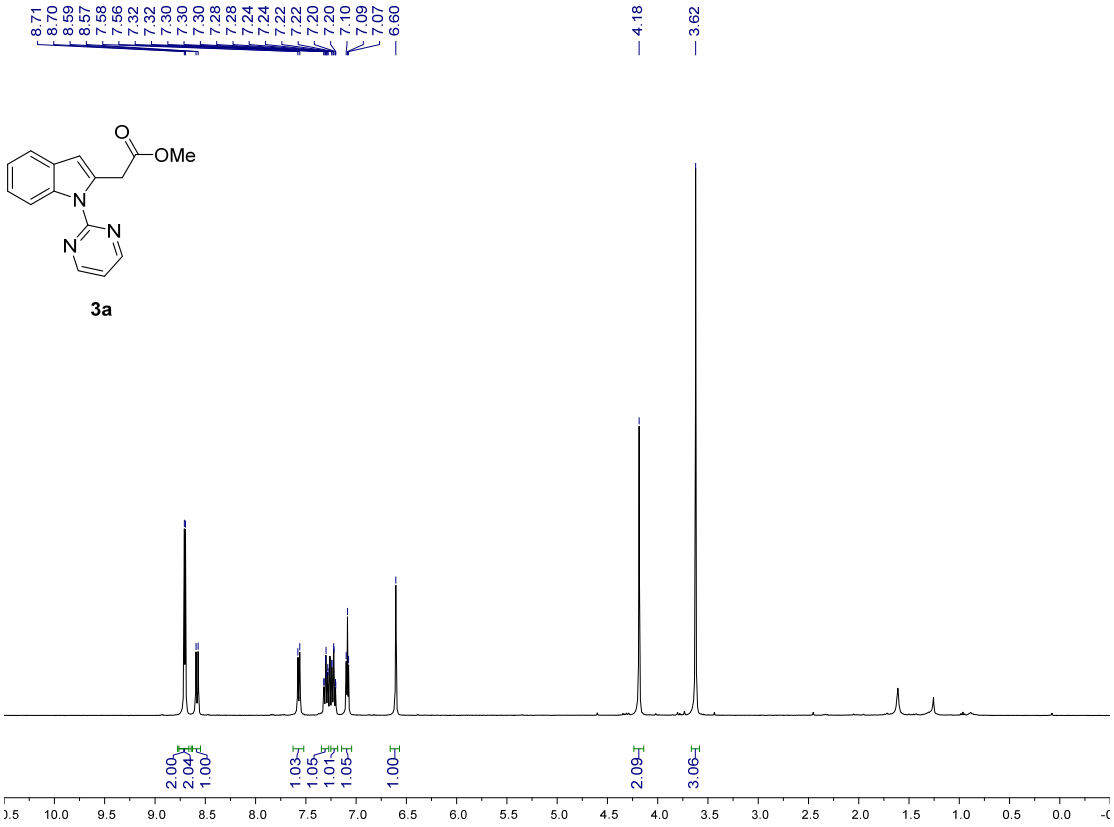
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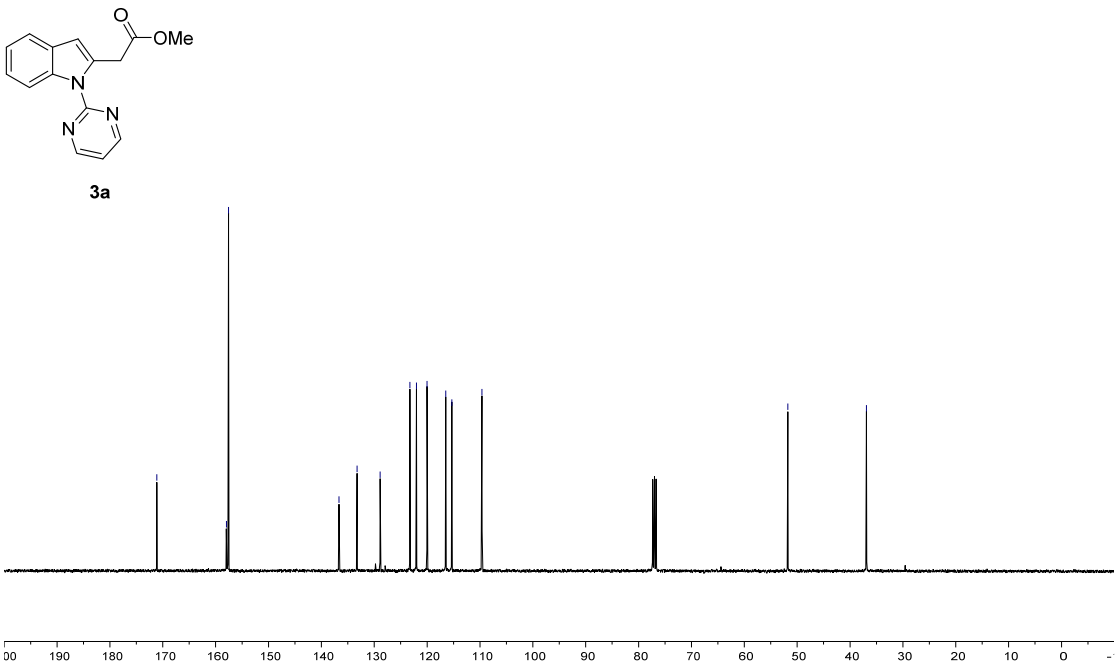
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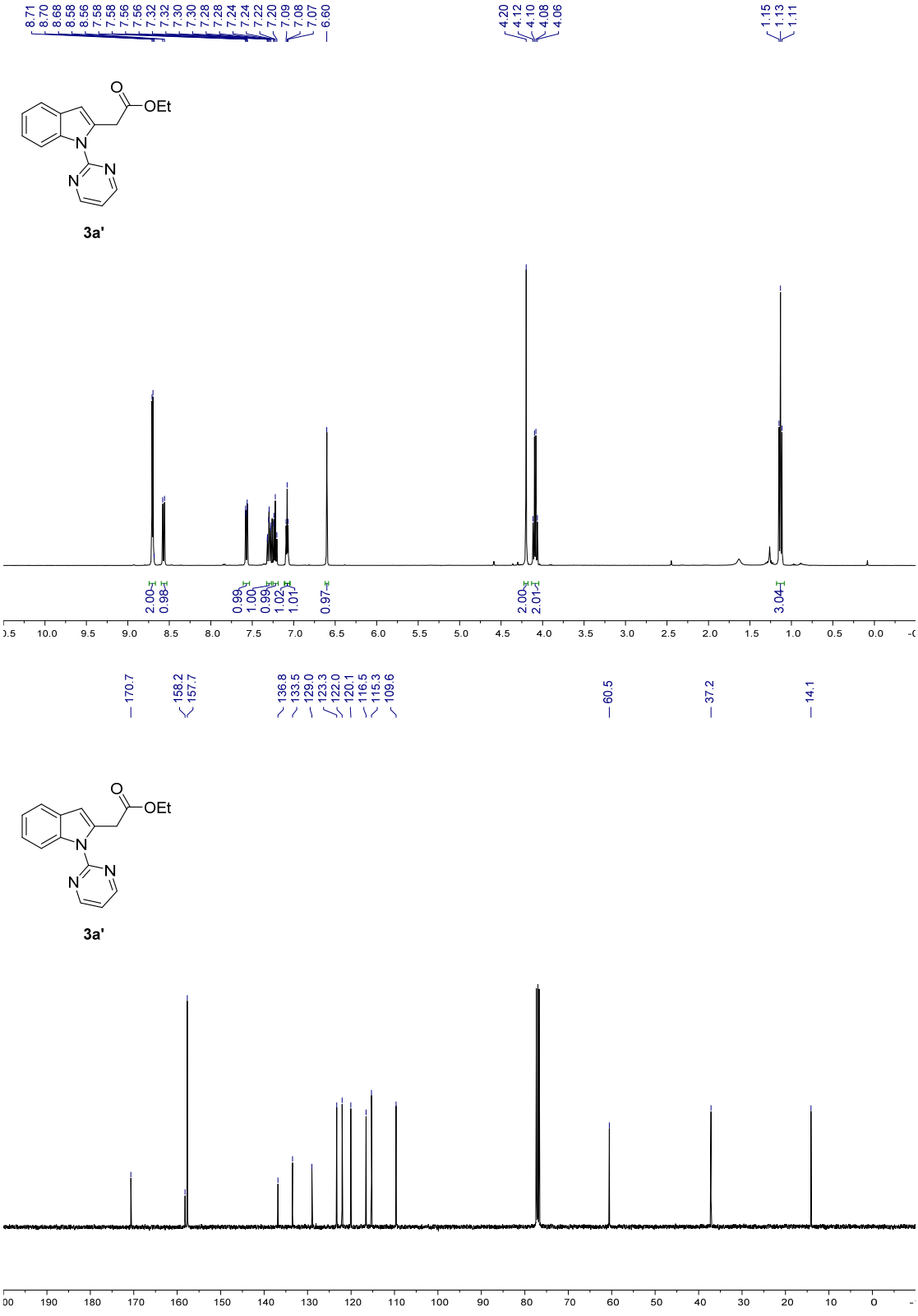
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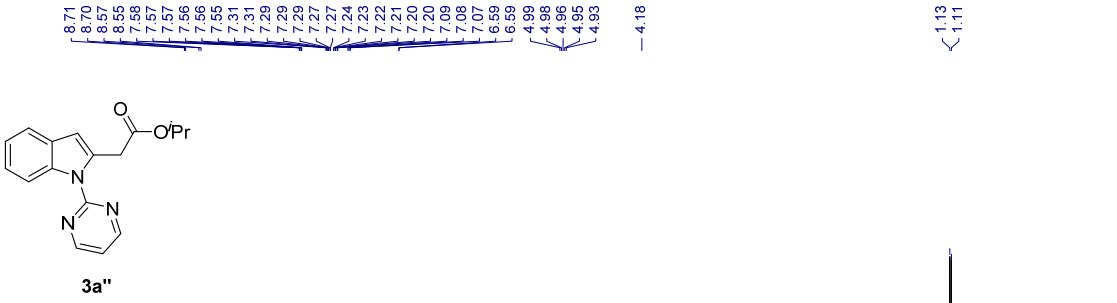
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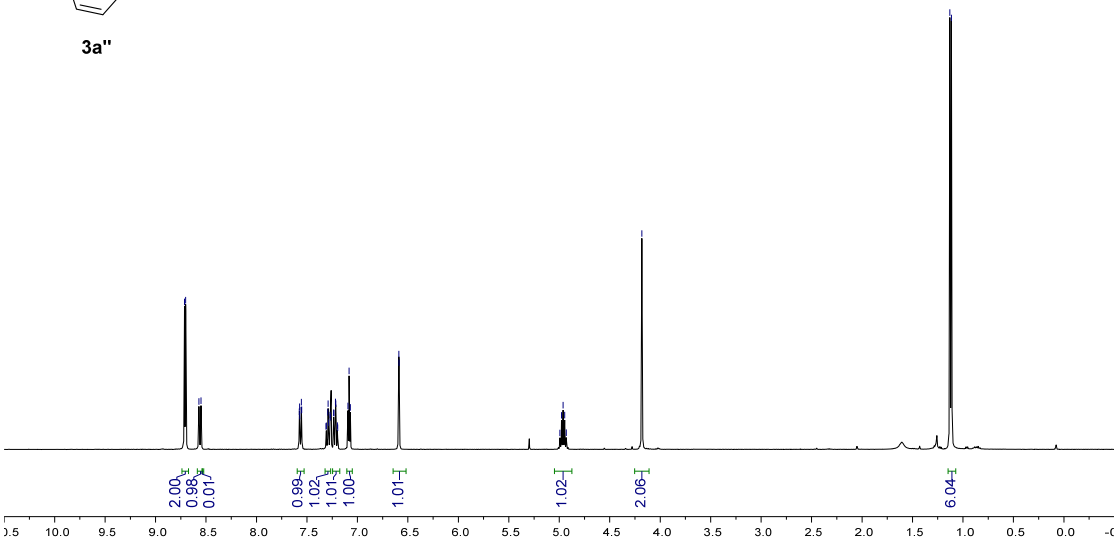
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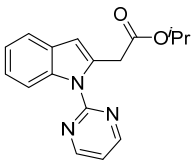

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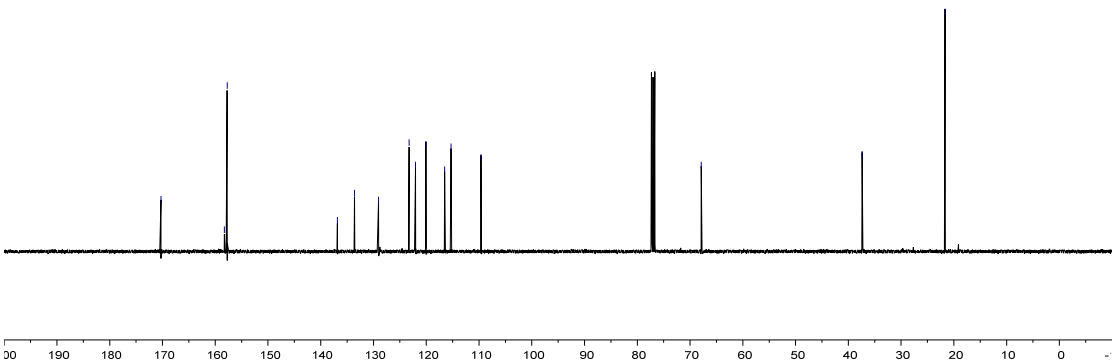

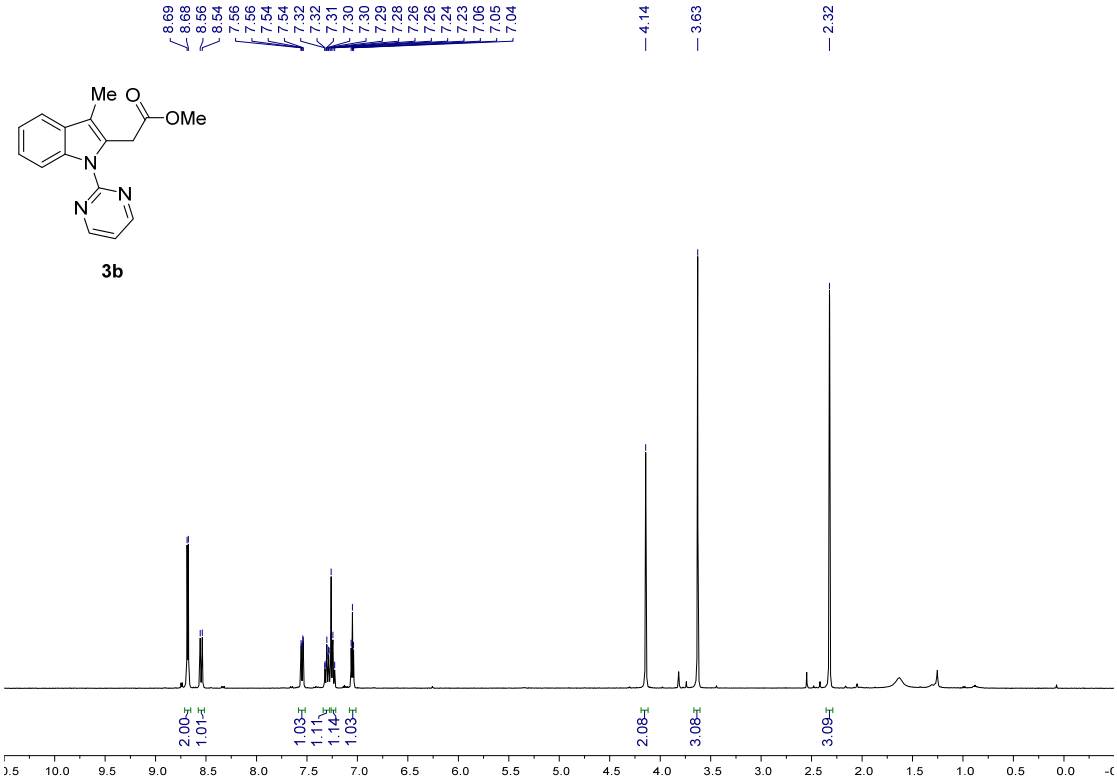
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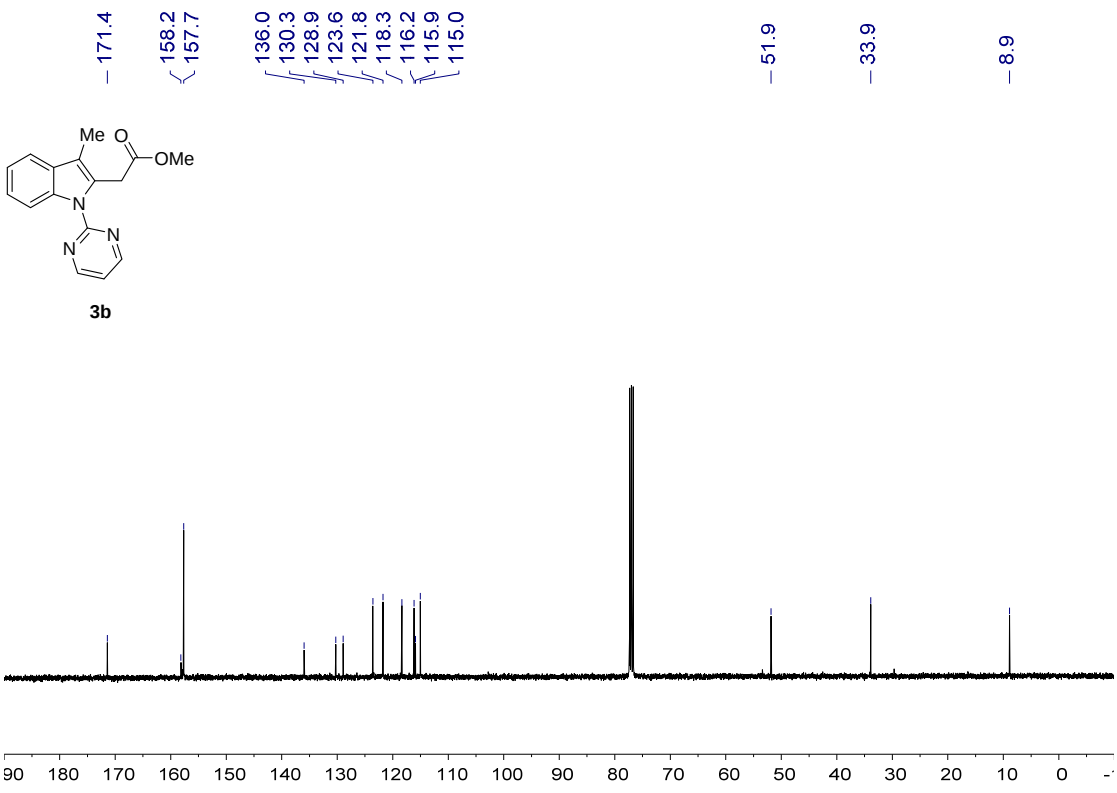
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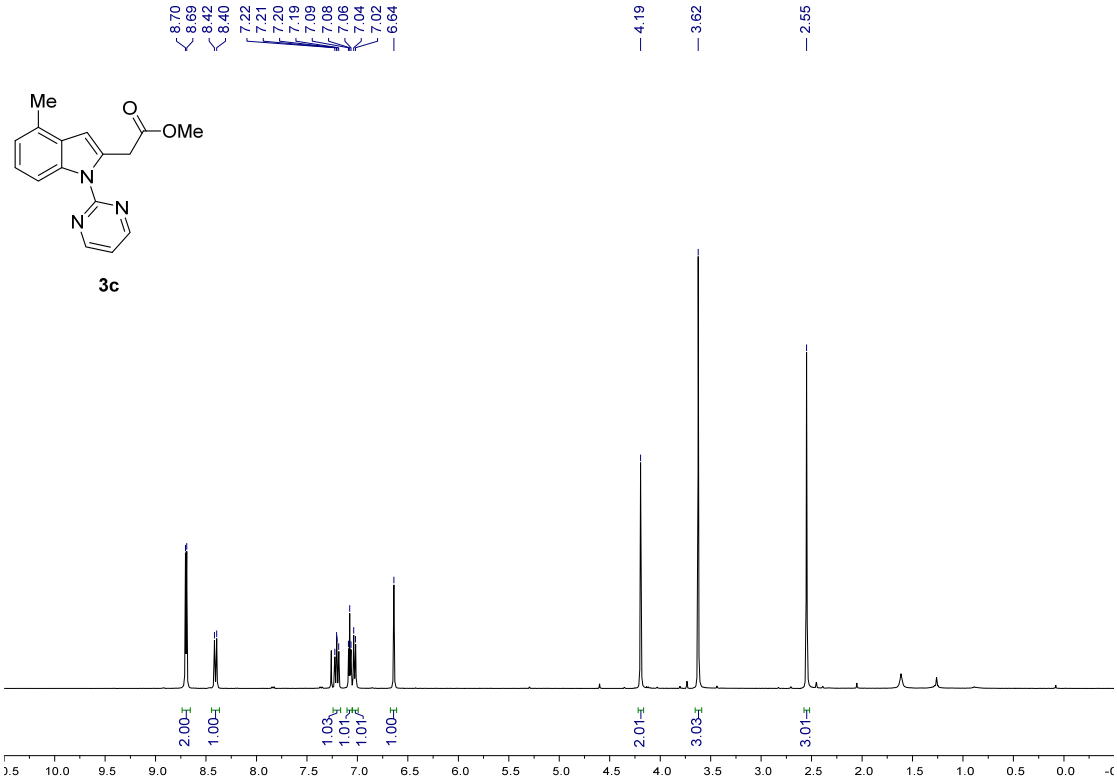
N

3b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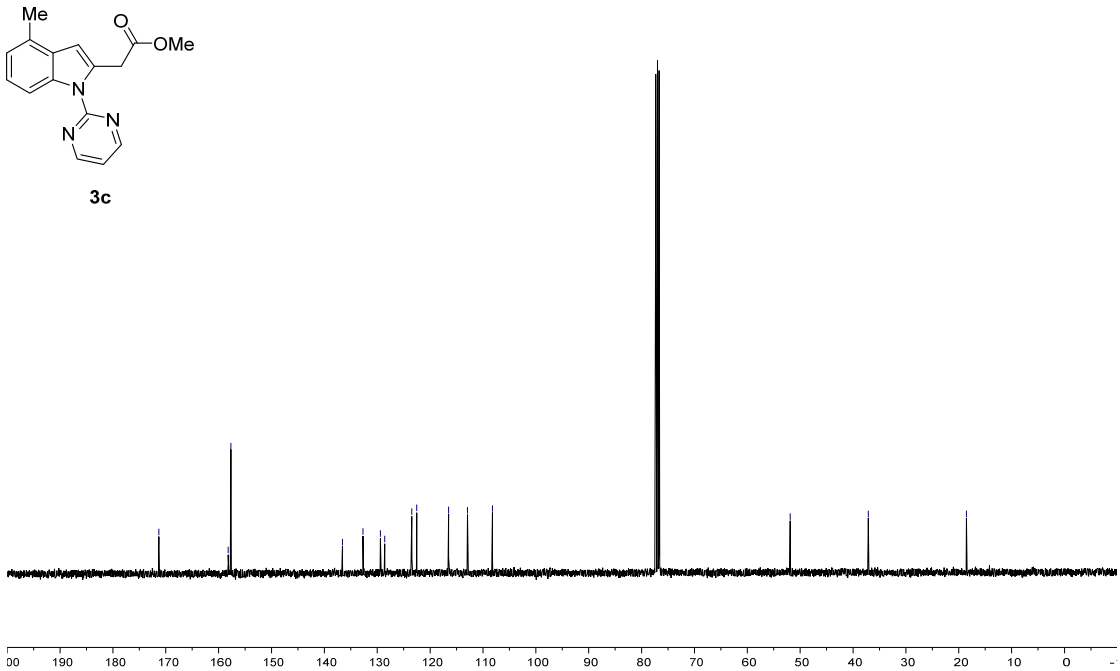
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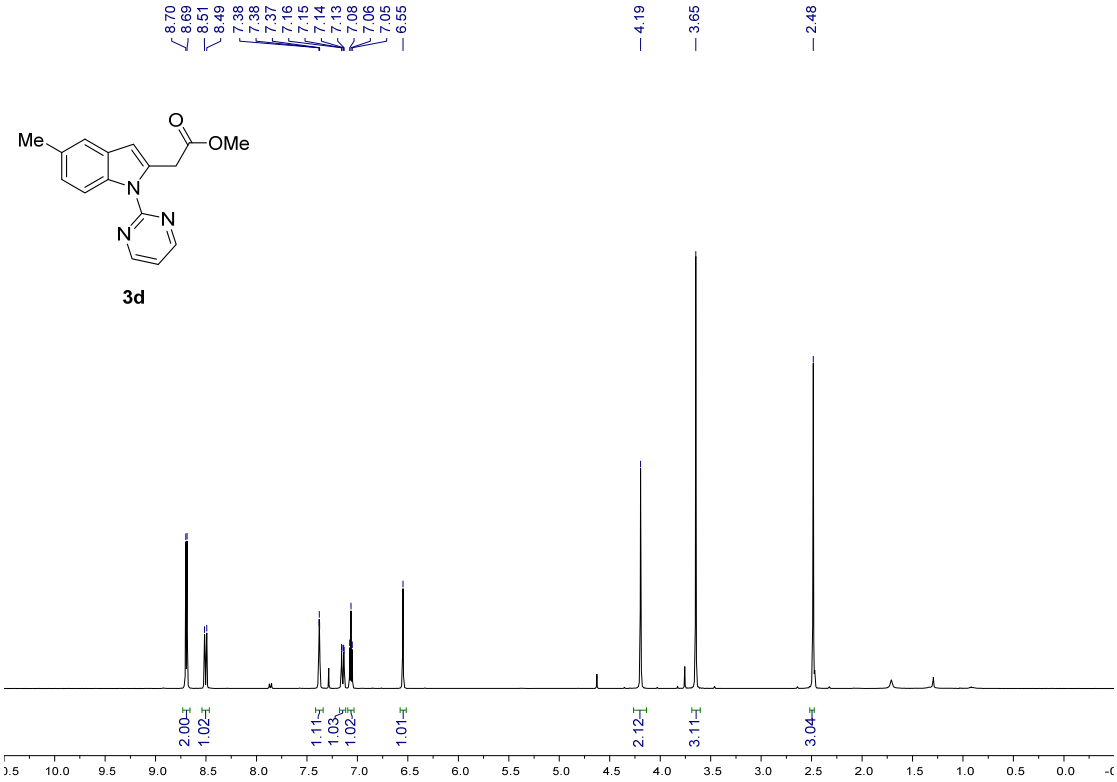
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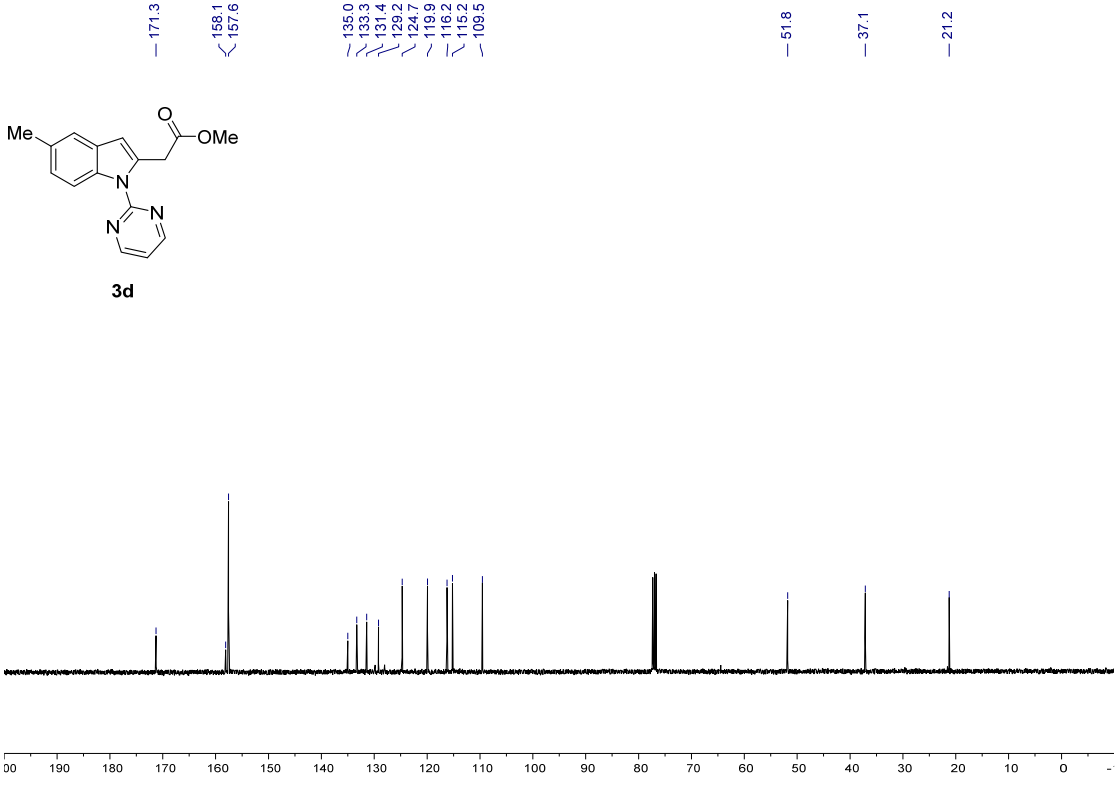
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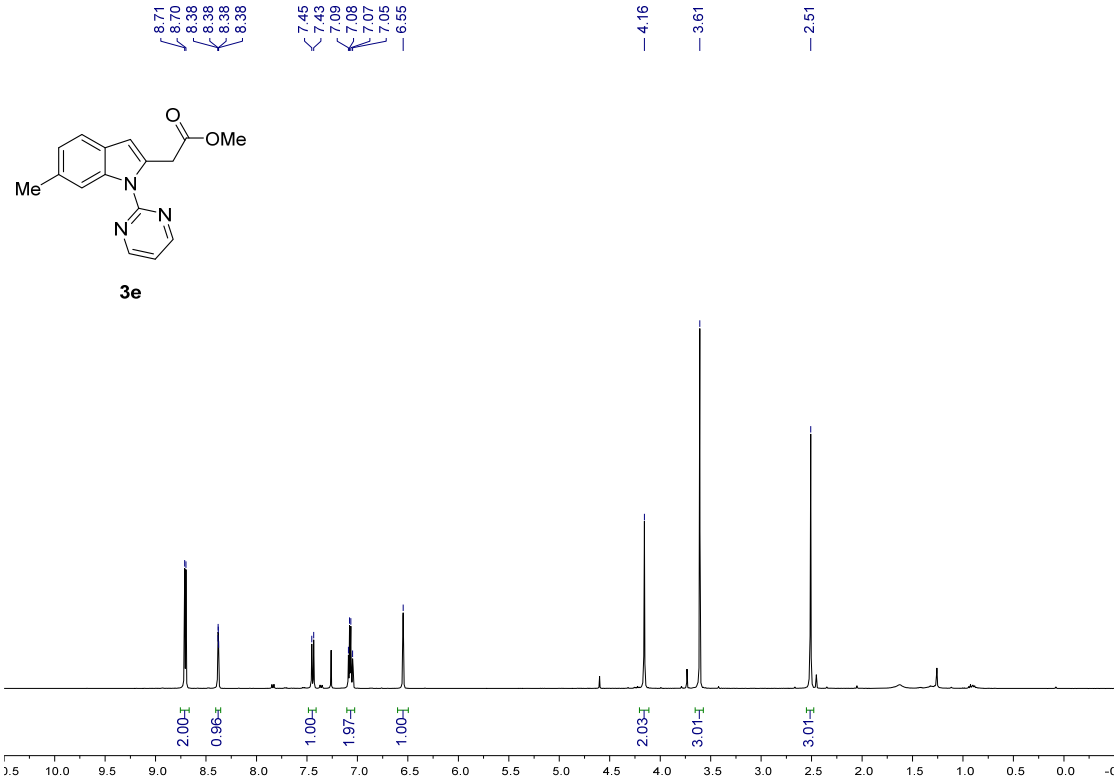
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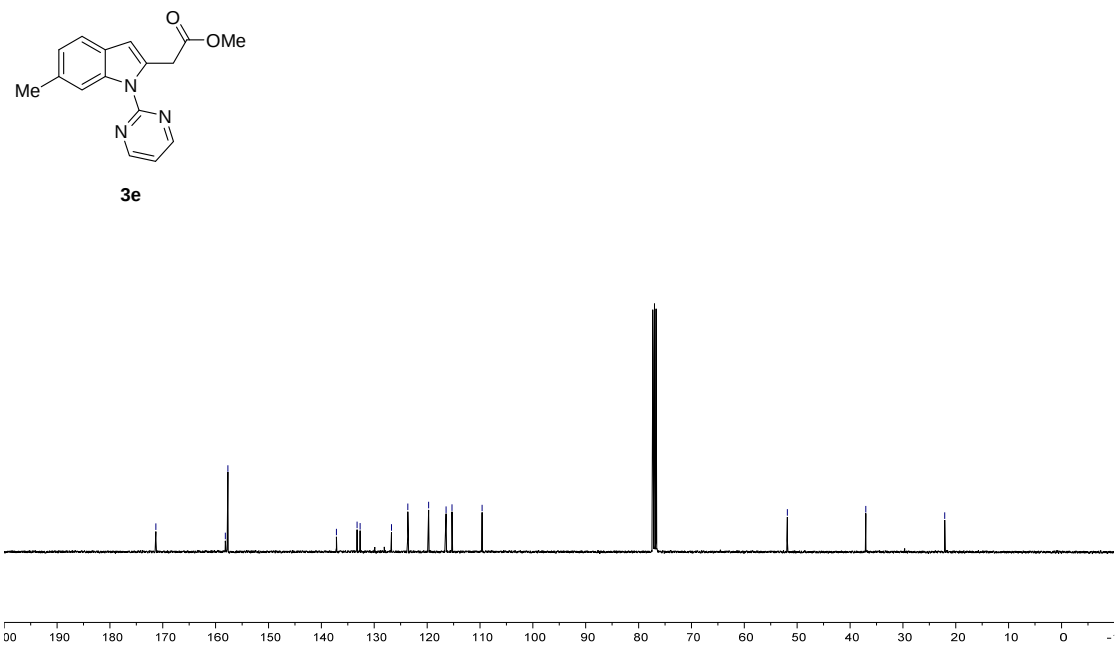
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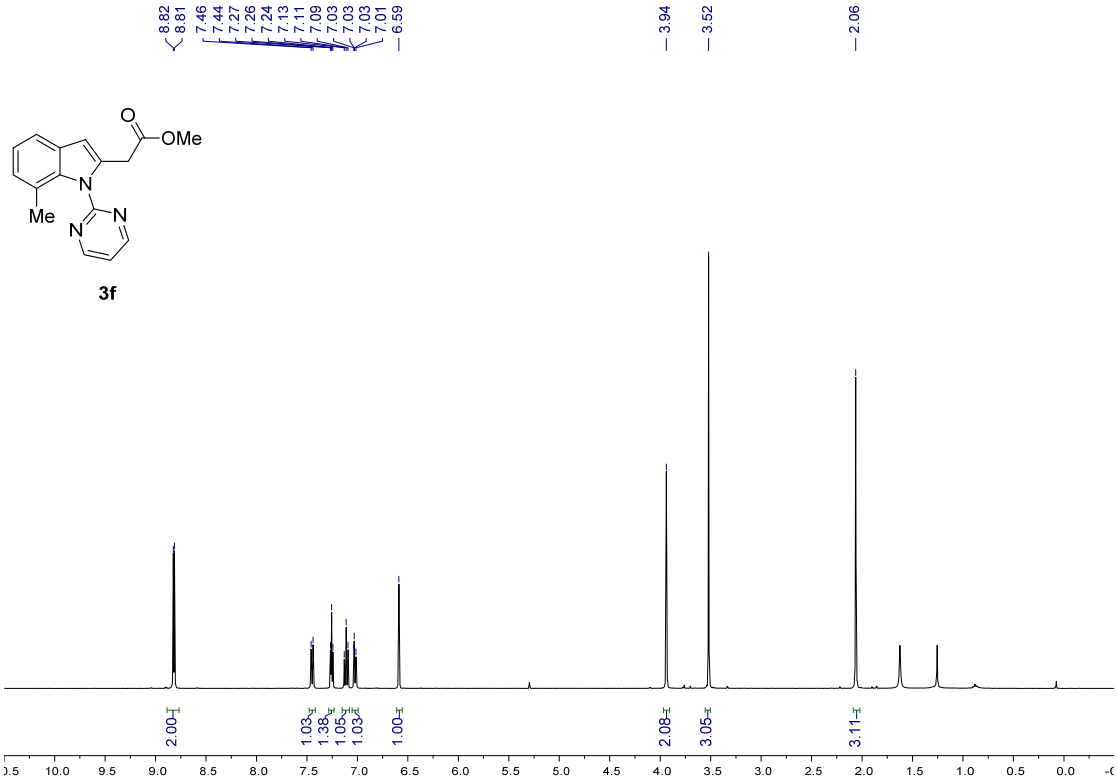
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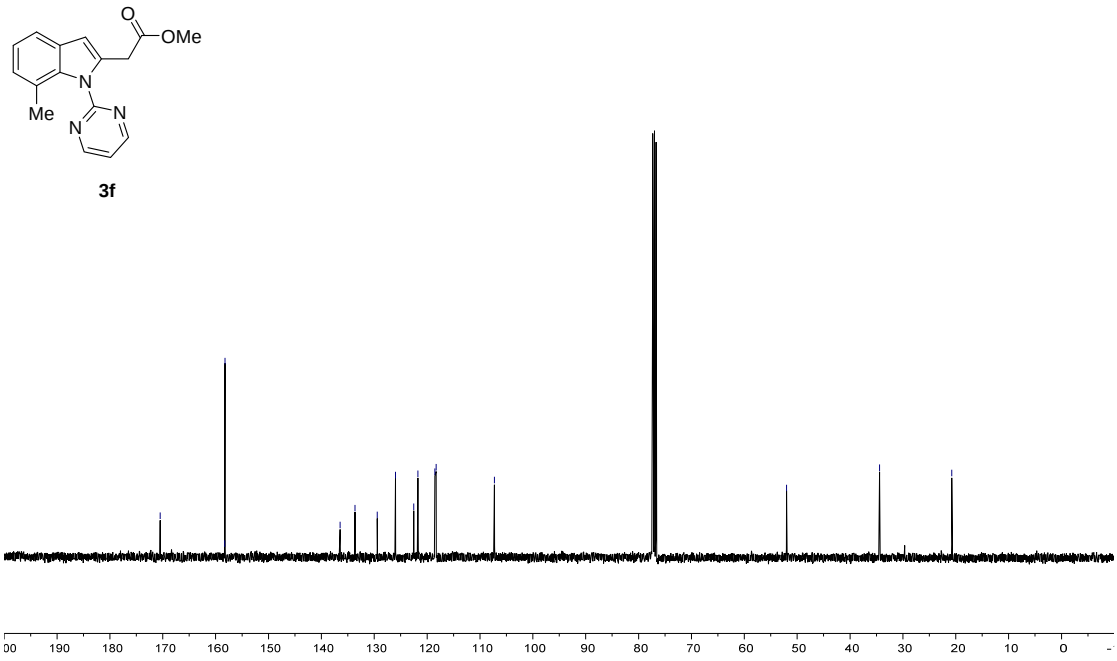
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OMe
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Me
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N

3f


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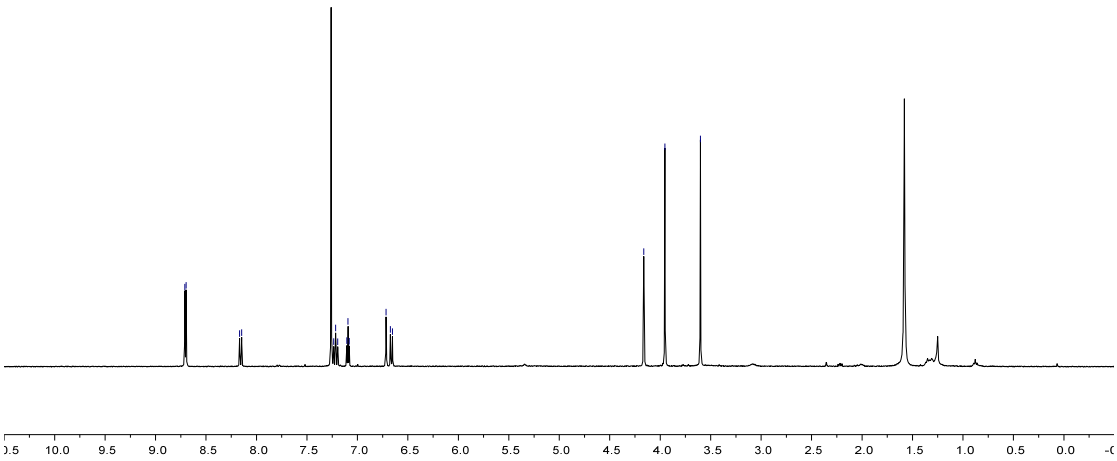

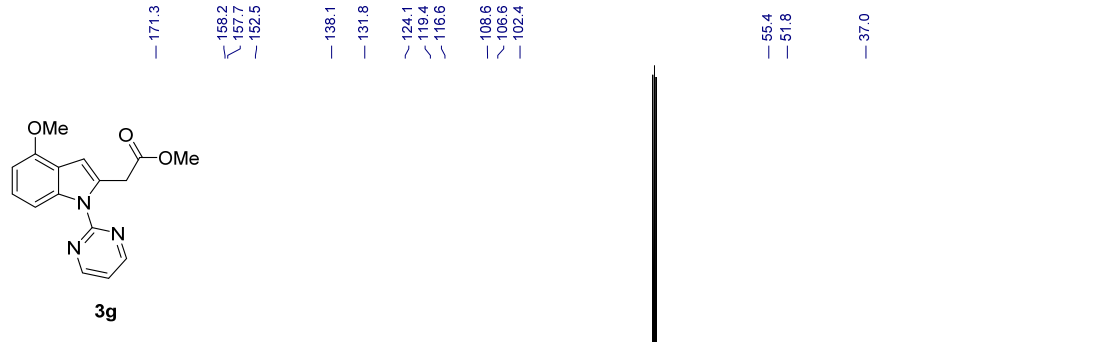
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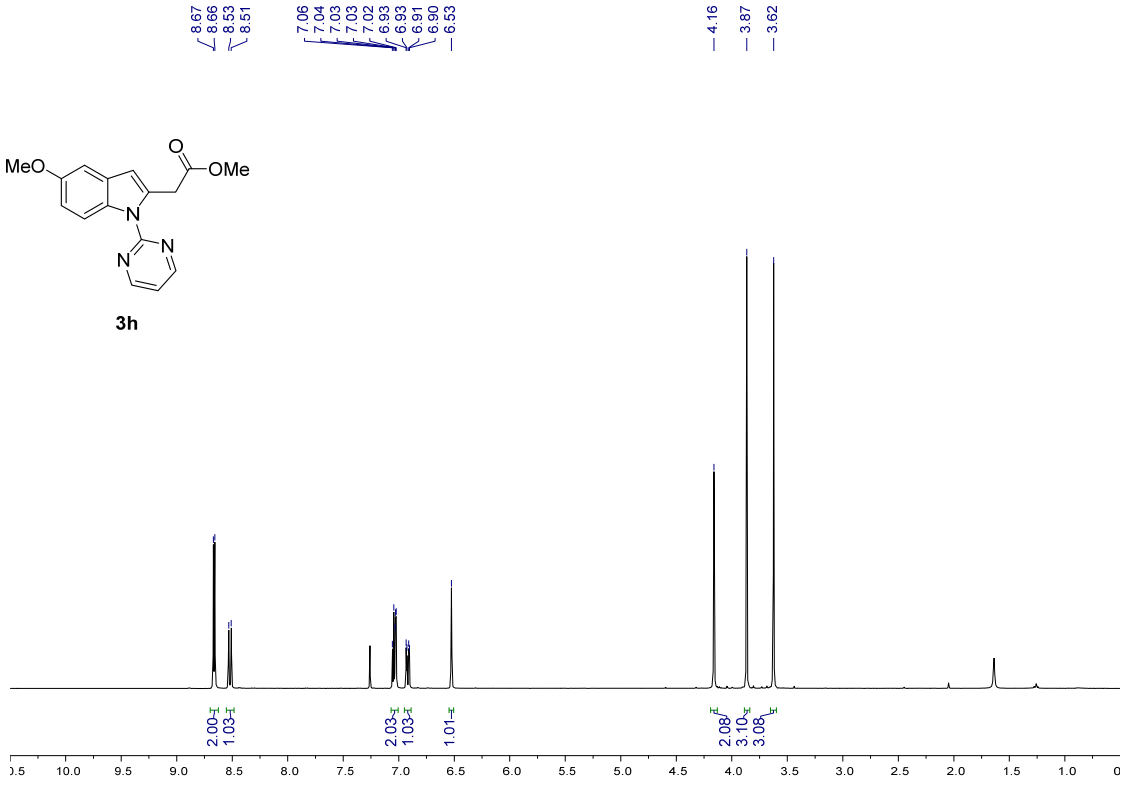
3g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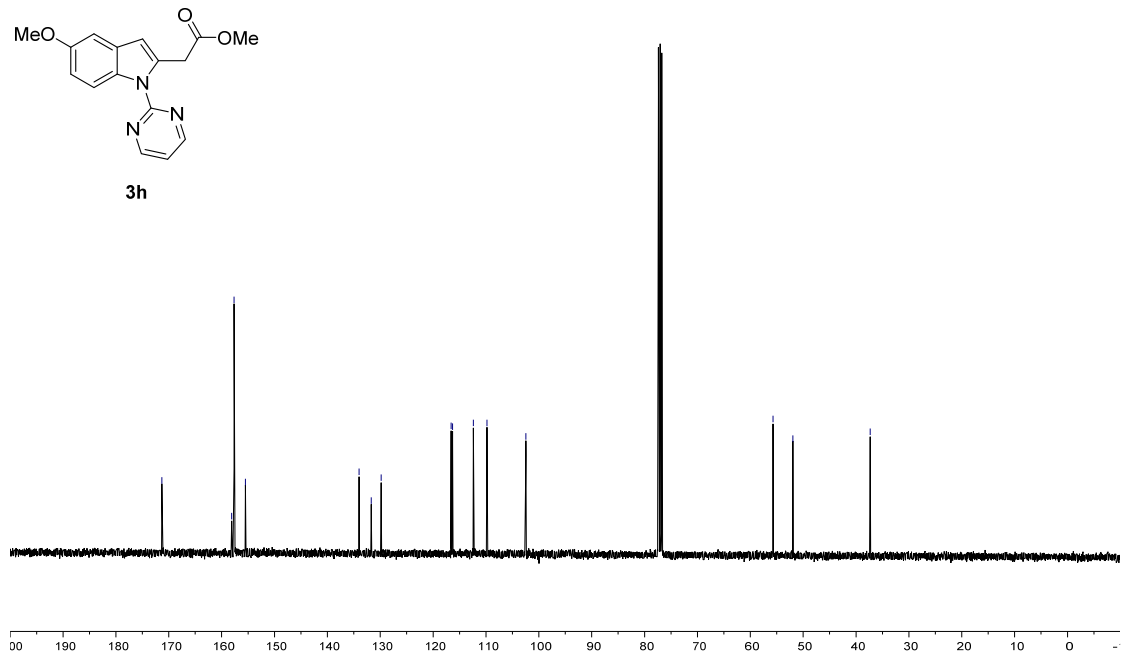
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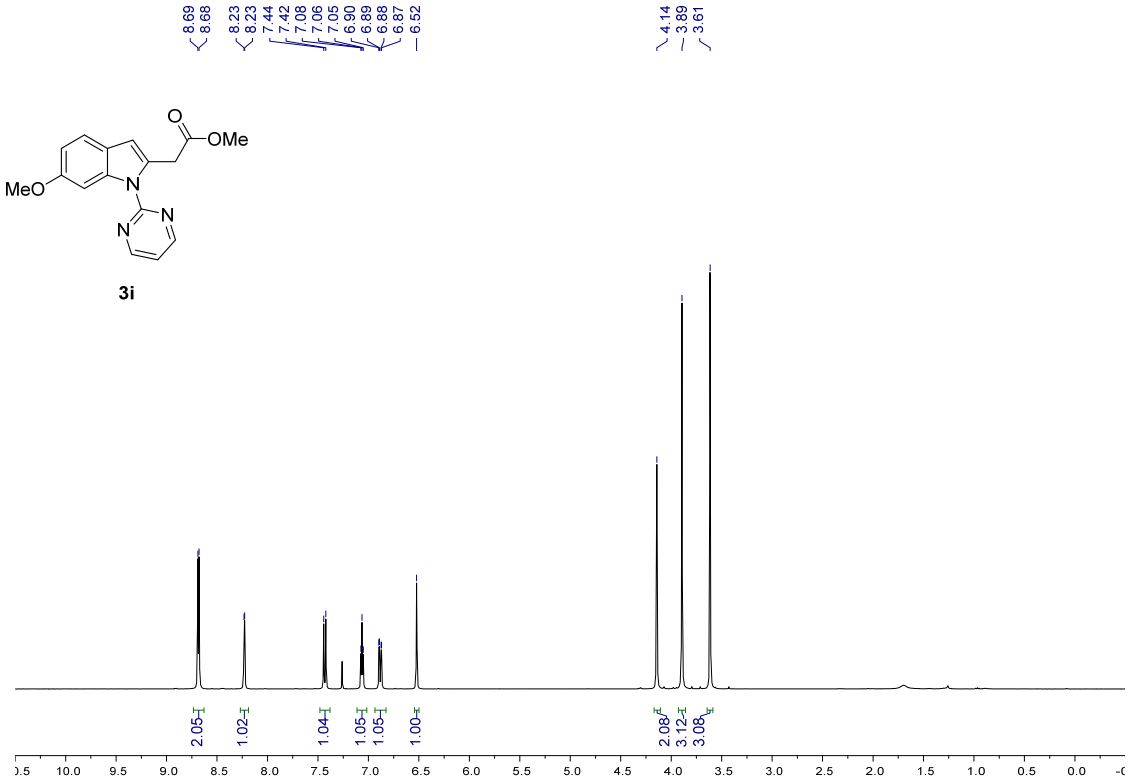
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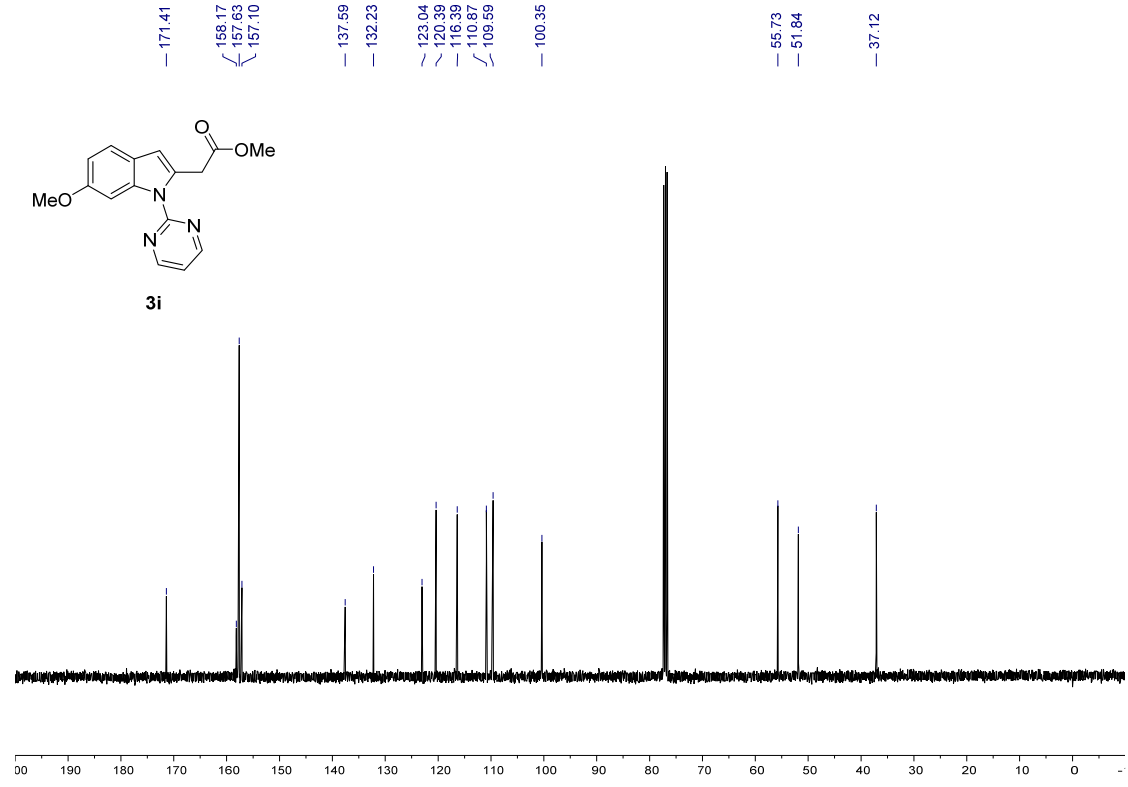
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MeO
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N

3i


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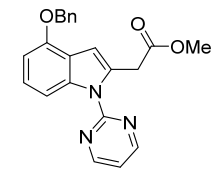
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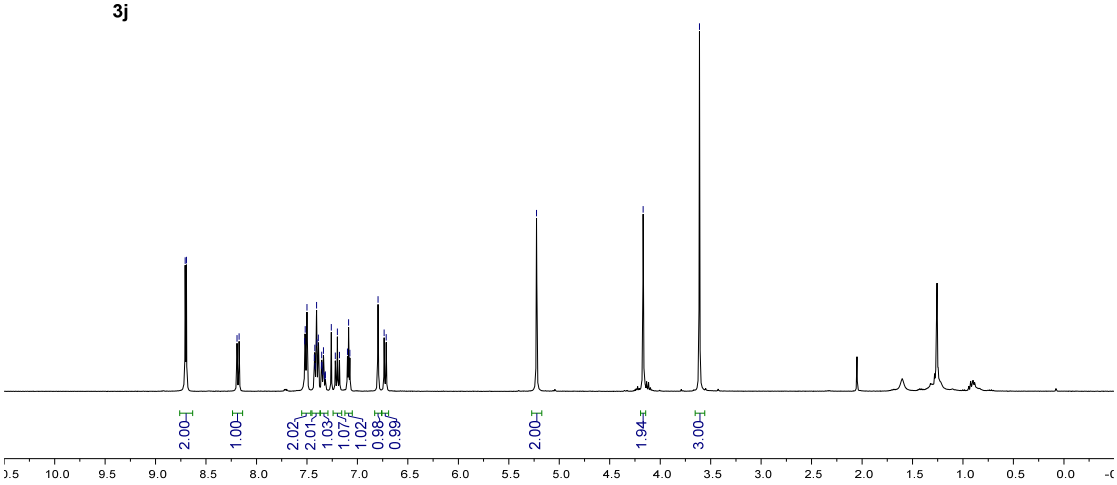
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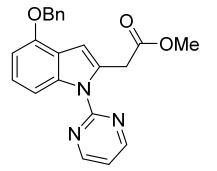
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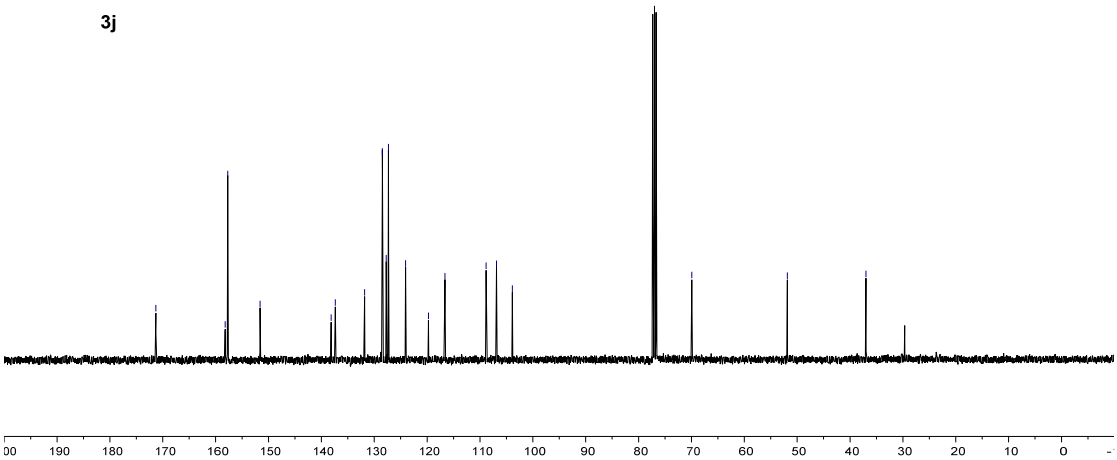
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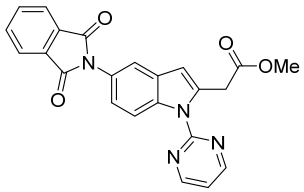
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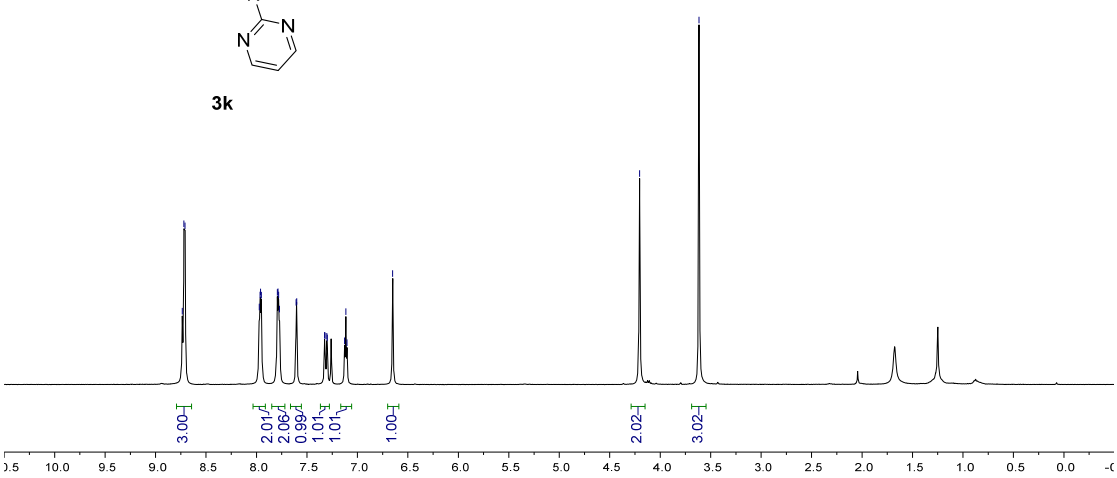
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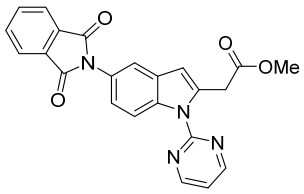
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3k

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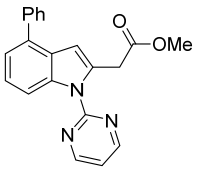
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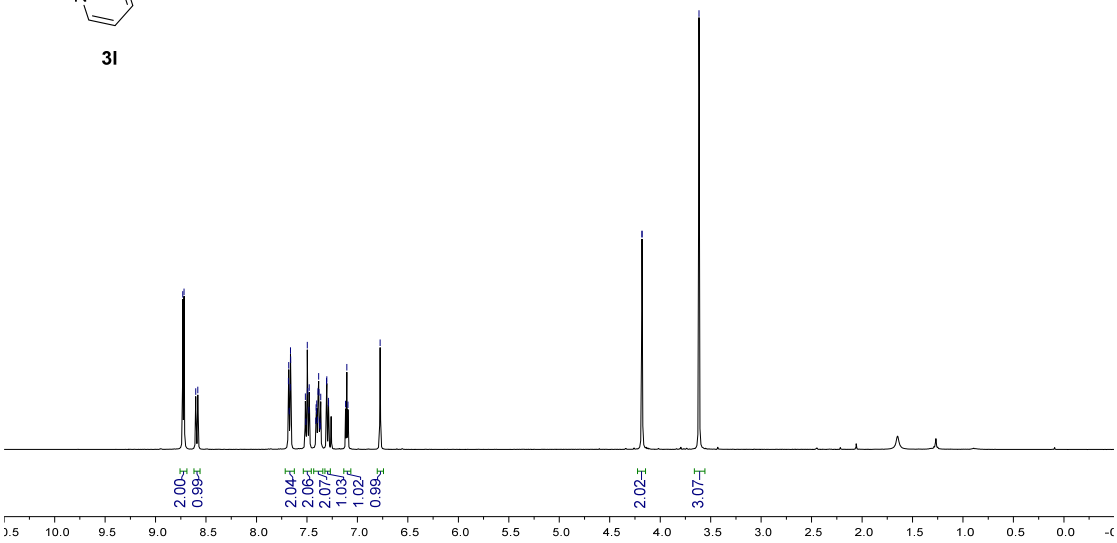
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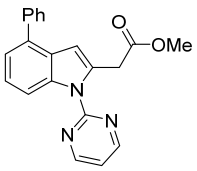
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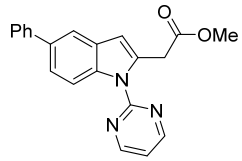
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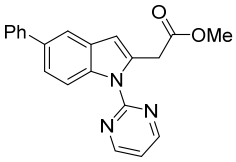
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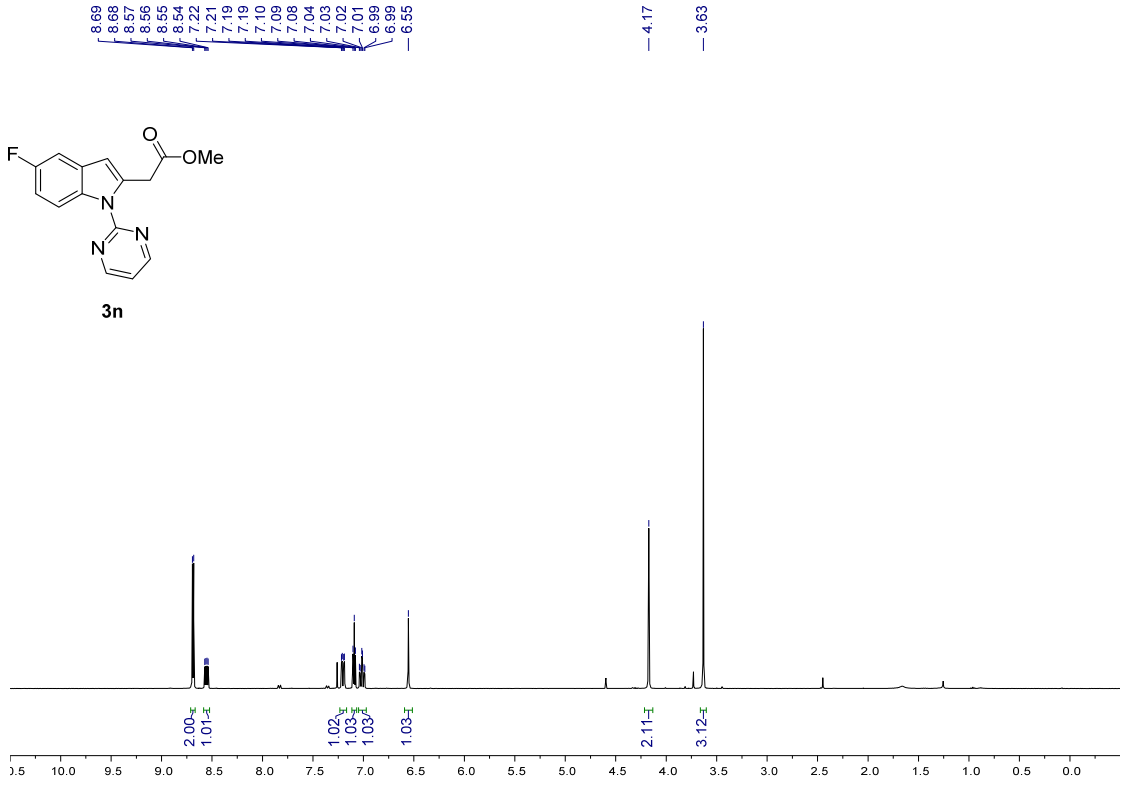
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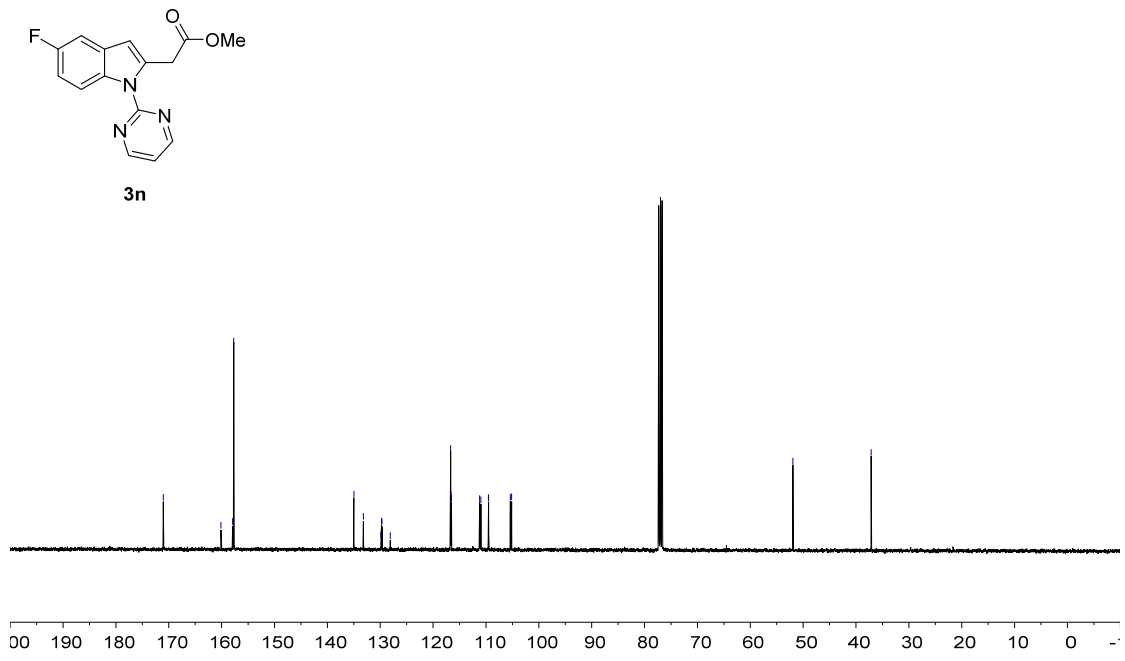
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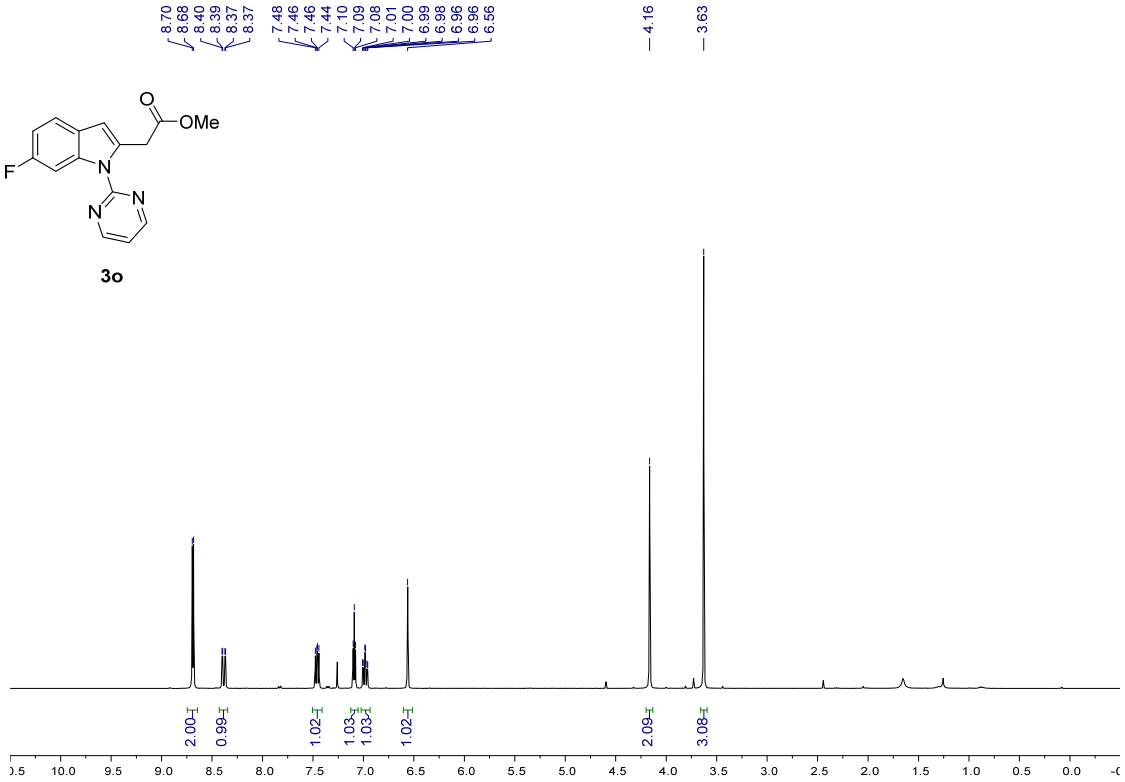
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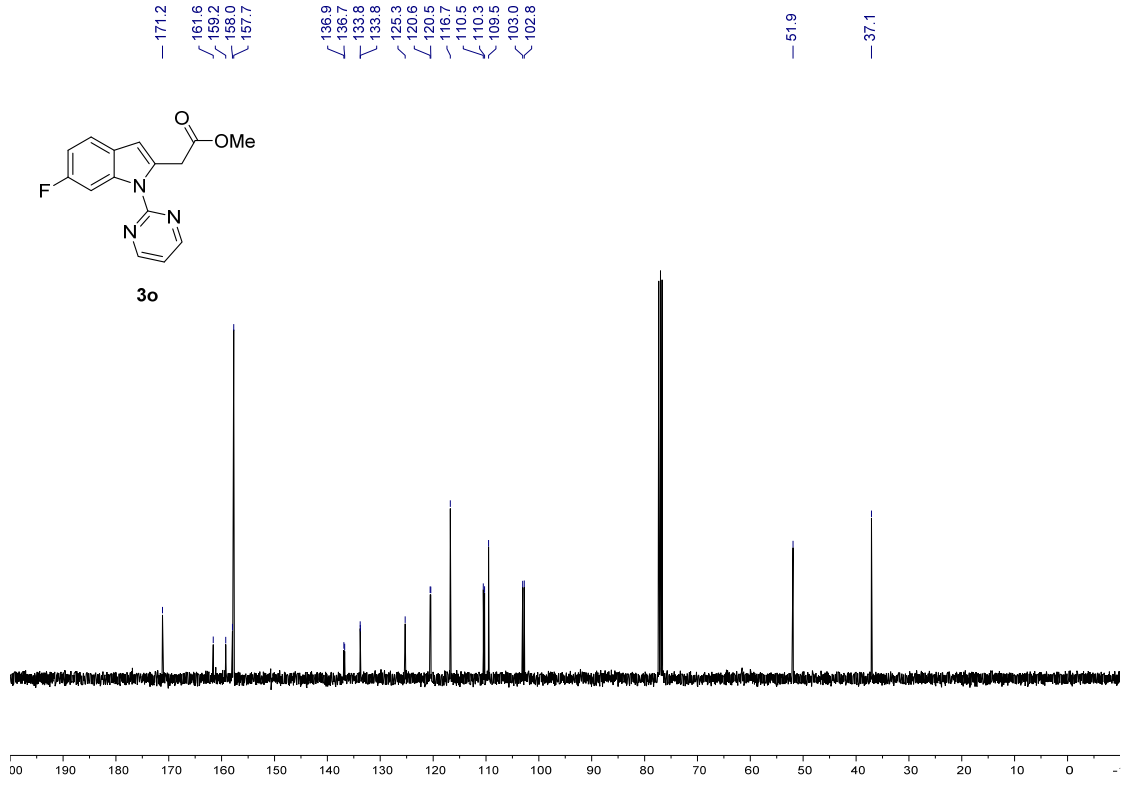
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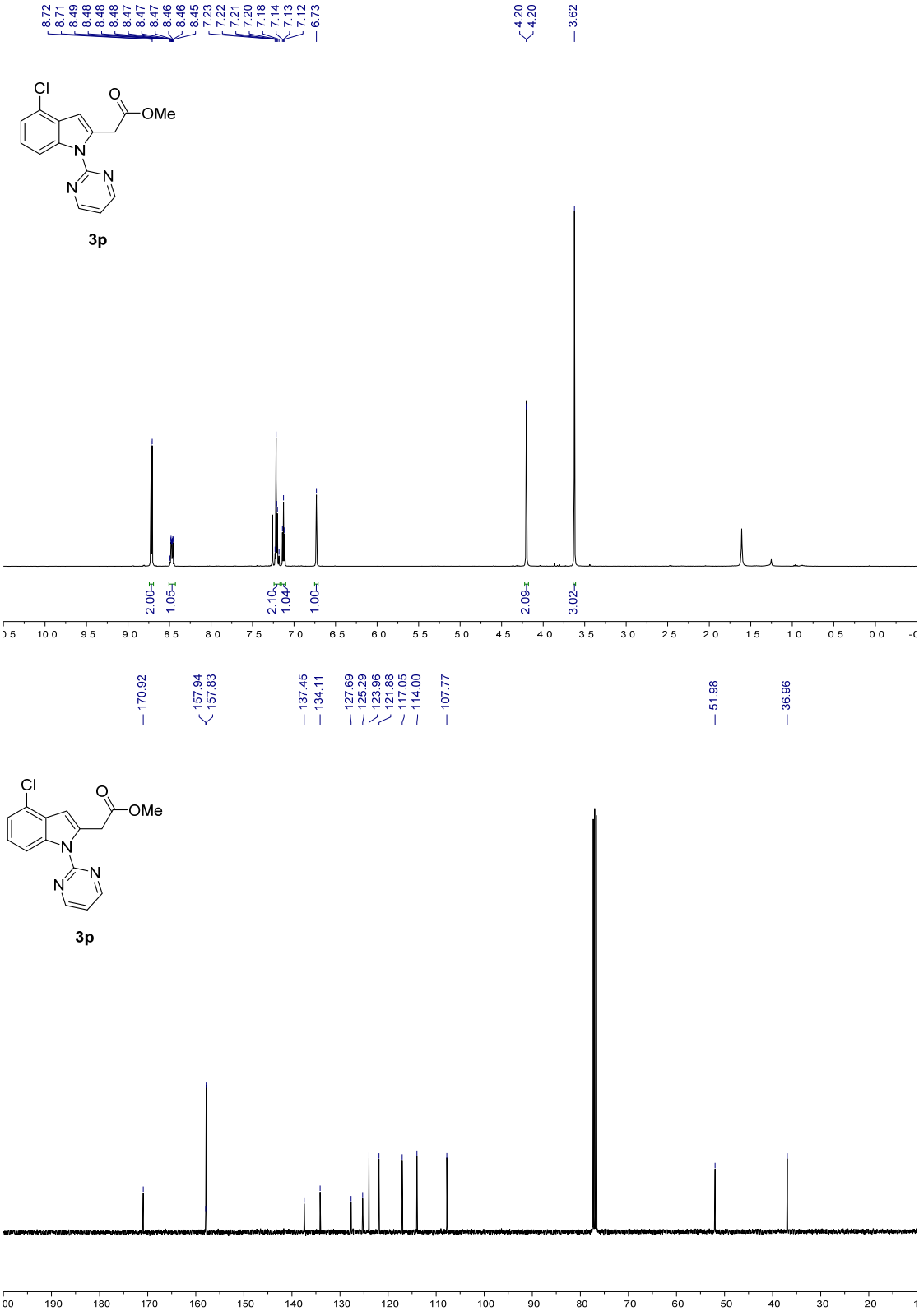
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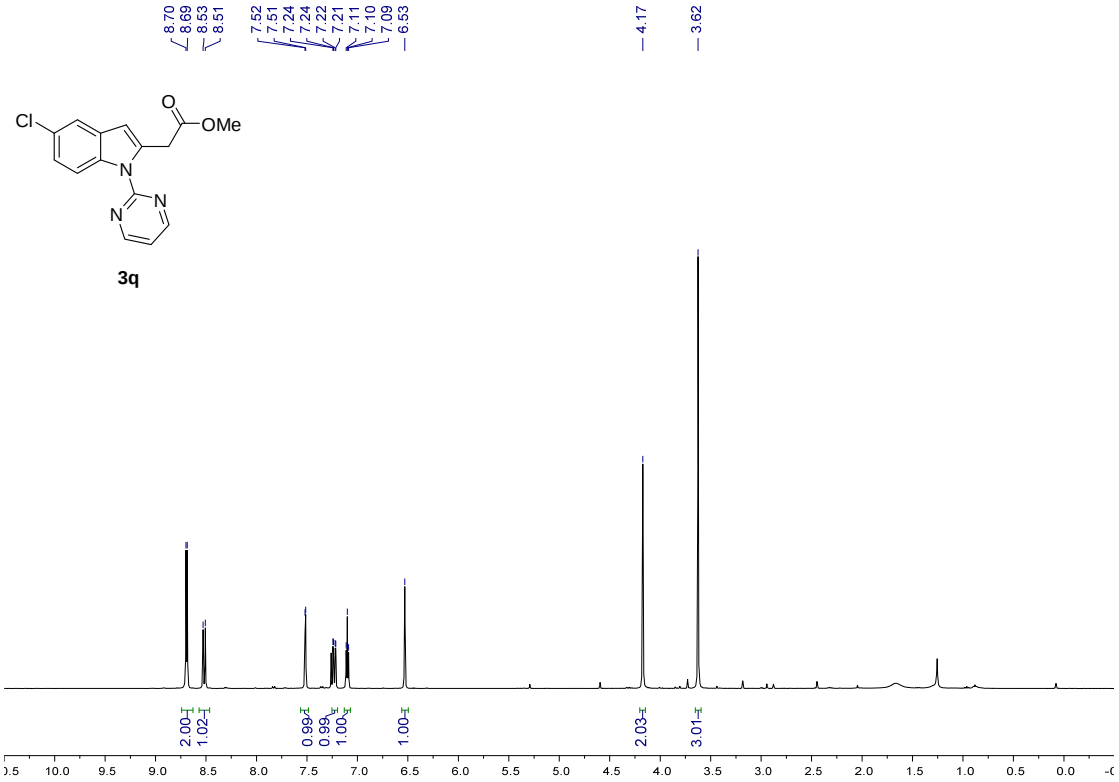
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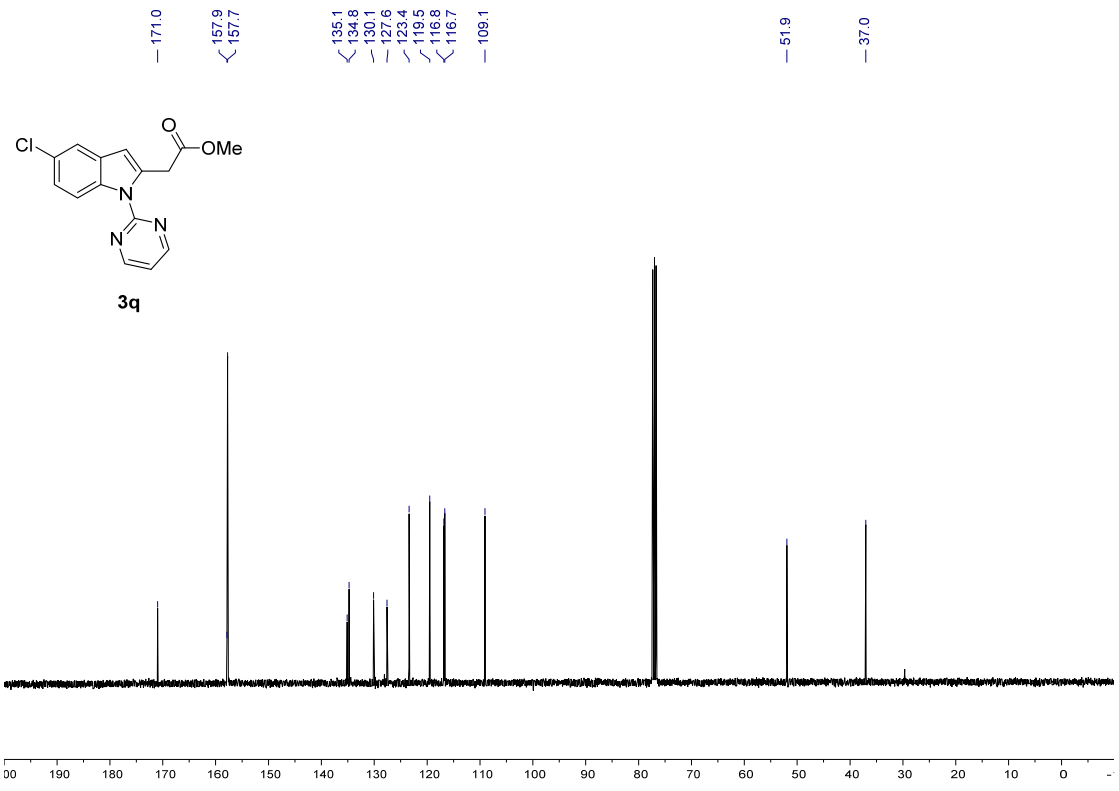
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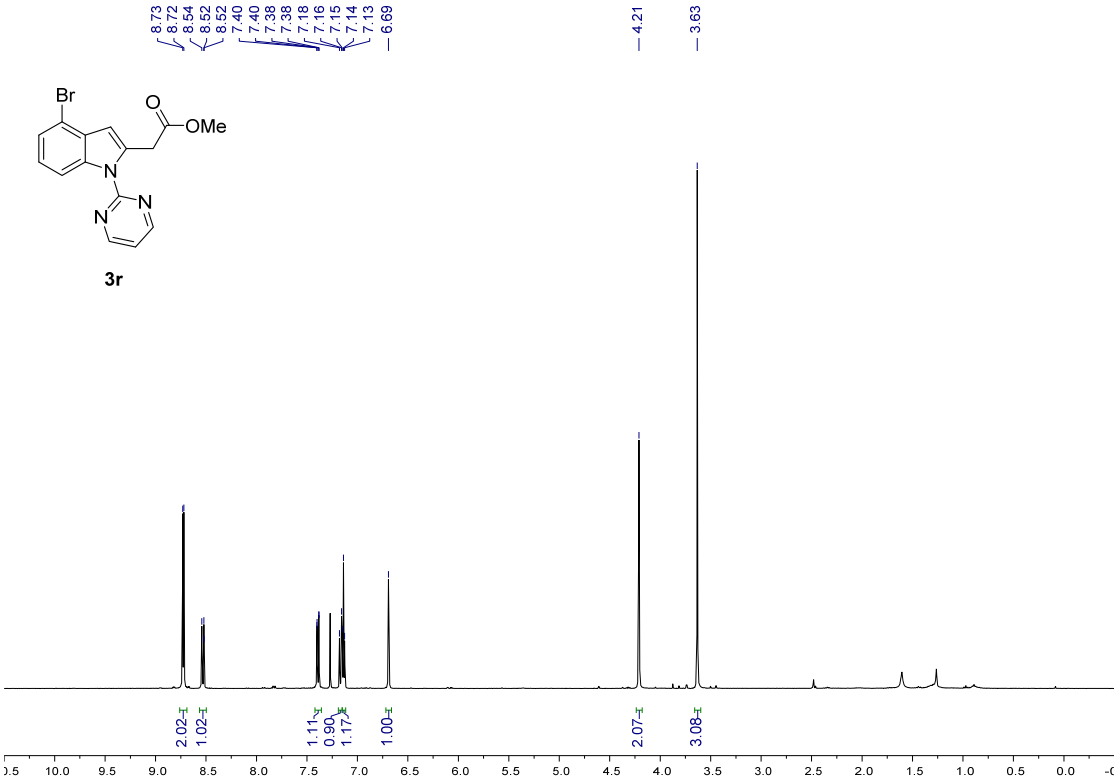
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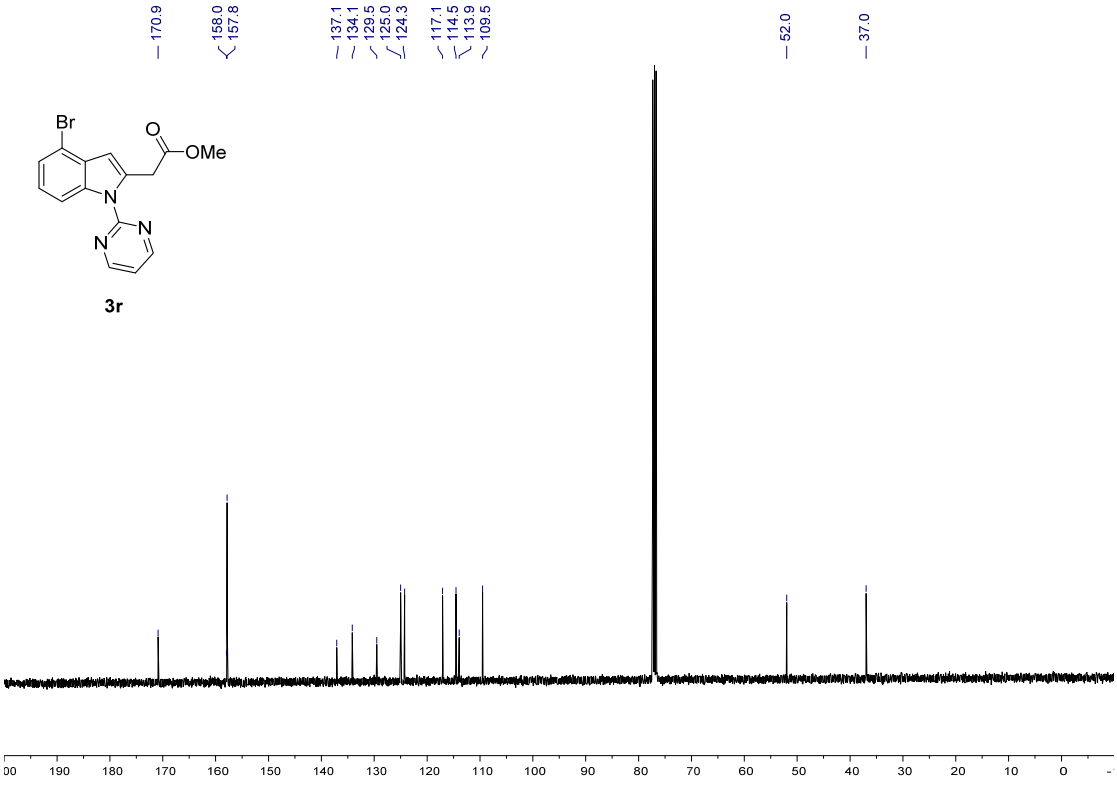
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N

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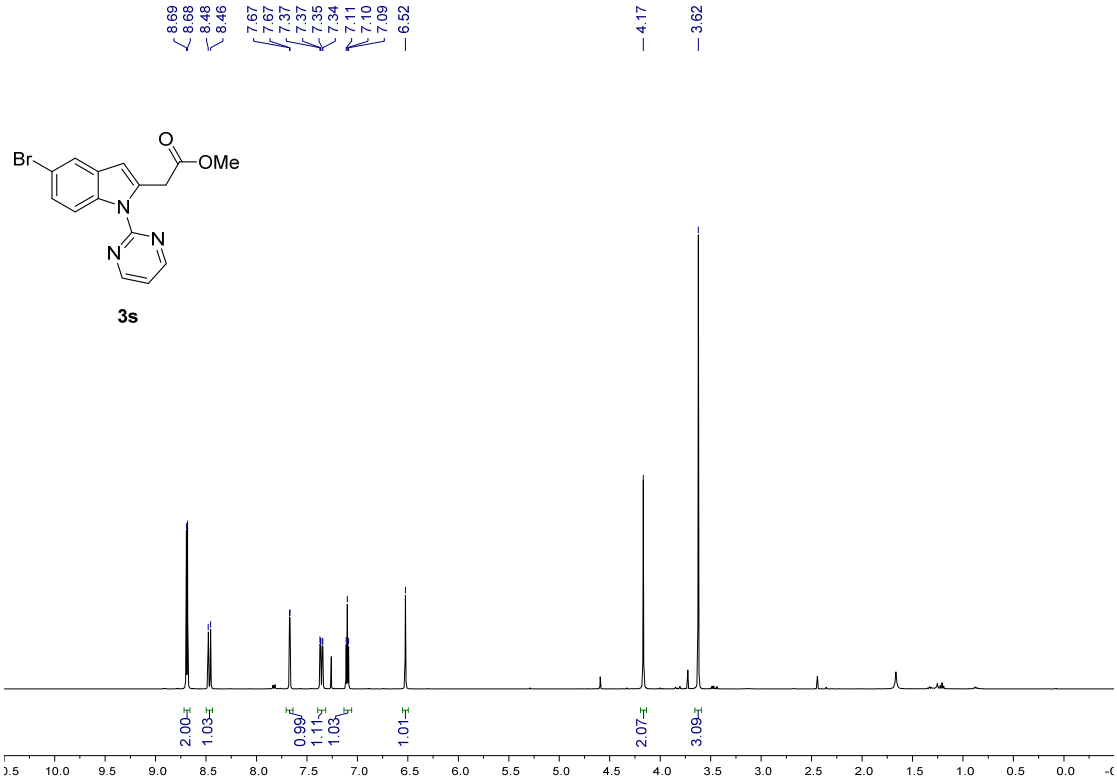
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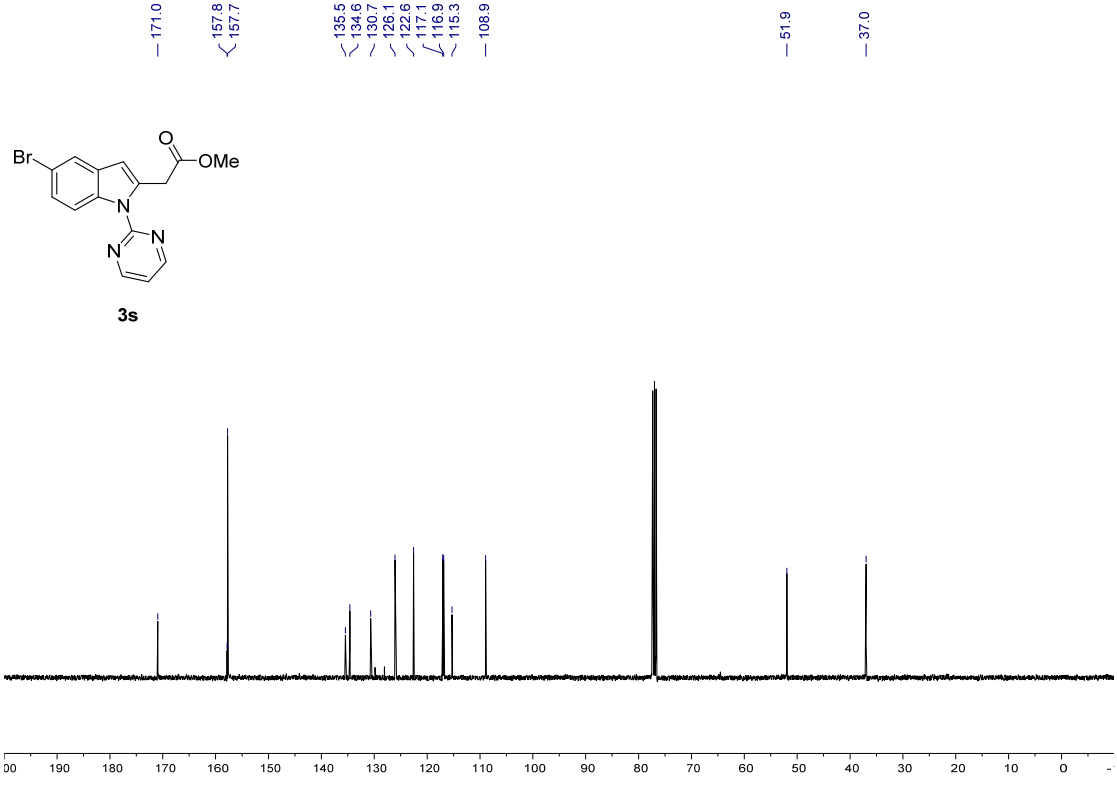
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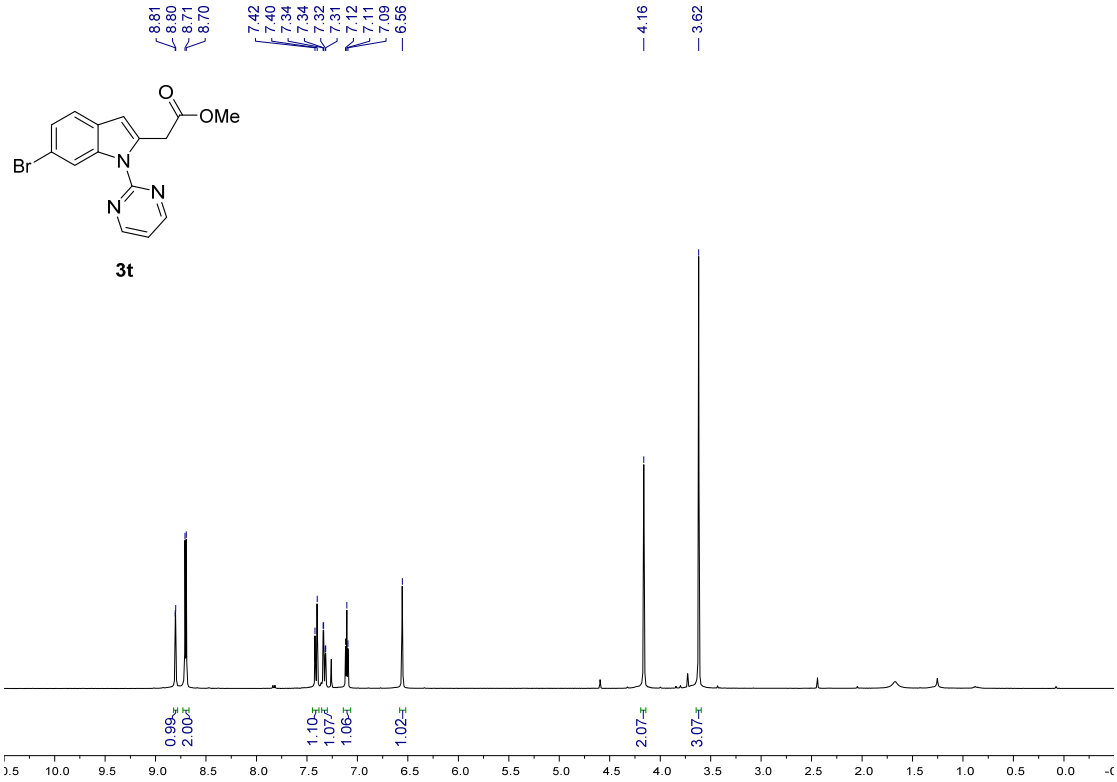
OMe
N
N
N

3s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7.09
6.56
4.16
3.62
O
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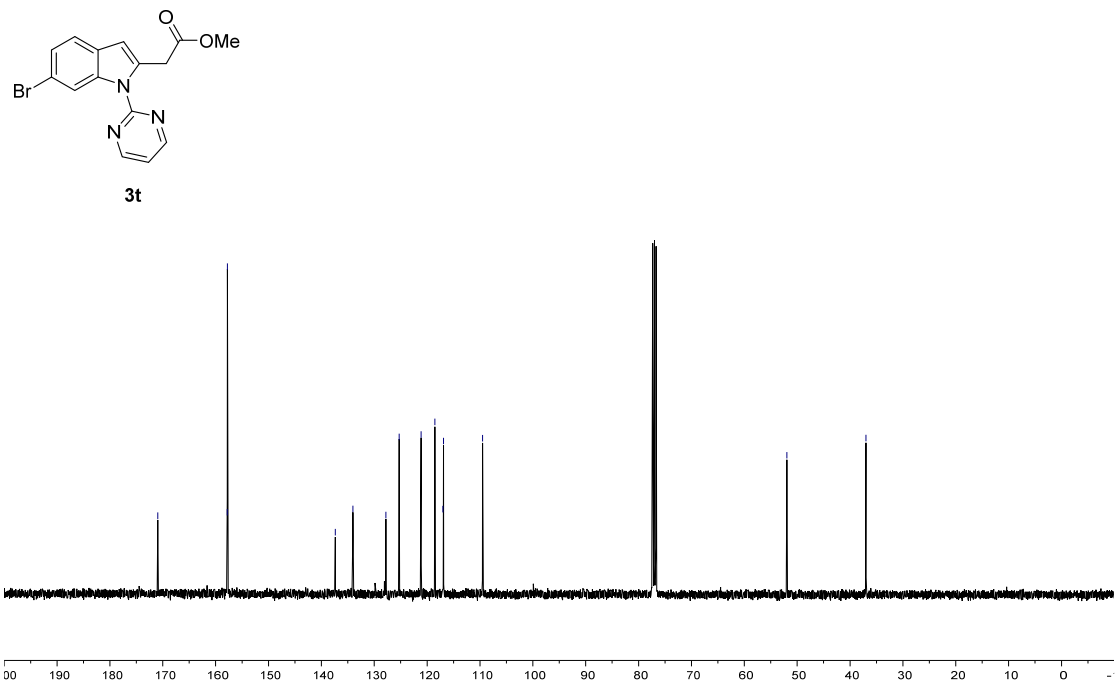
1.06
1.02
2.07
3.07

3t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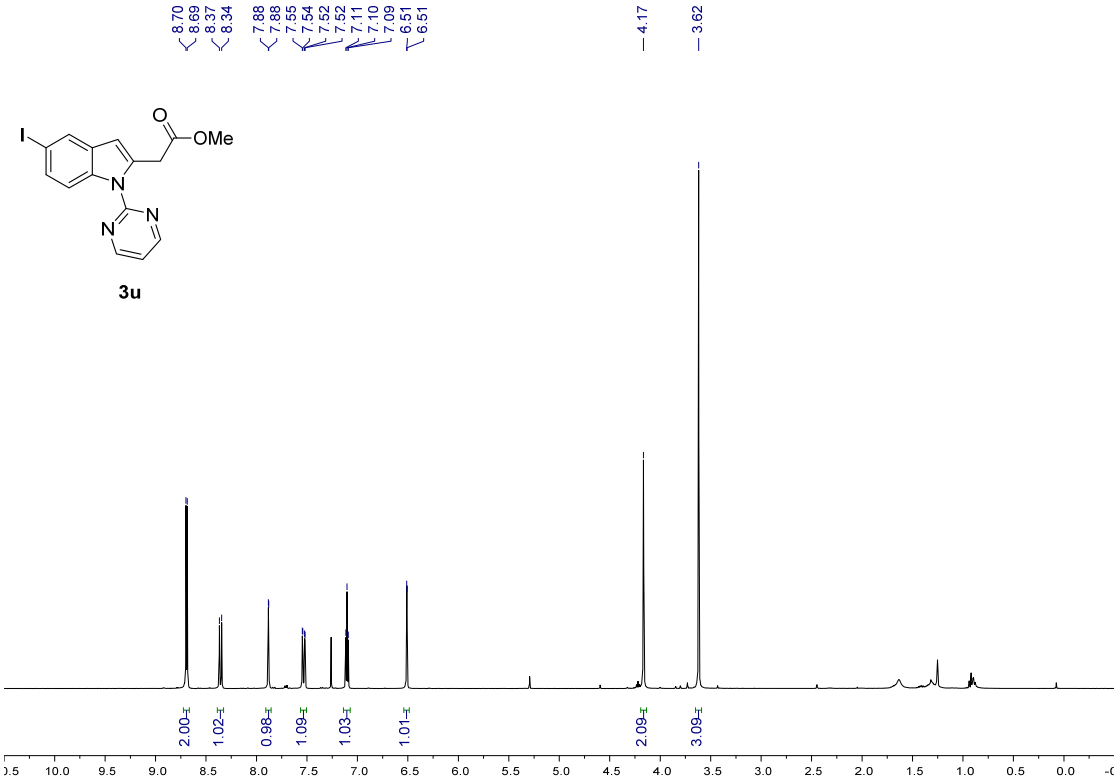
OMe
Br
N
N
N

3t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7.54
7.52
7.52
7.11
7.10
7.09
6.51
6.51
4.17
3.62
I
O
OMe
N
N
N
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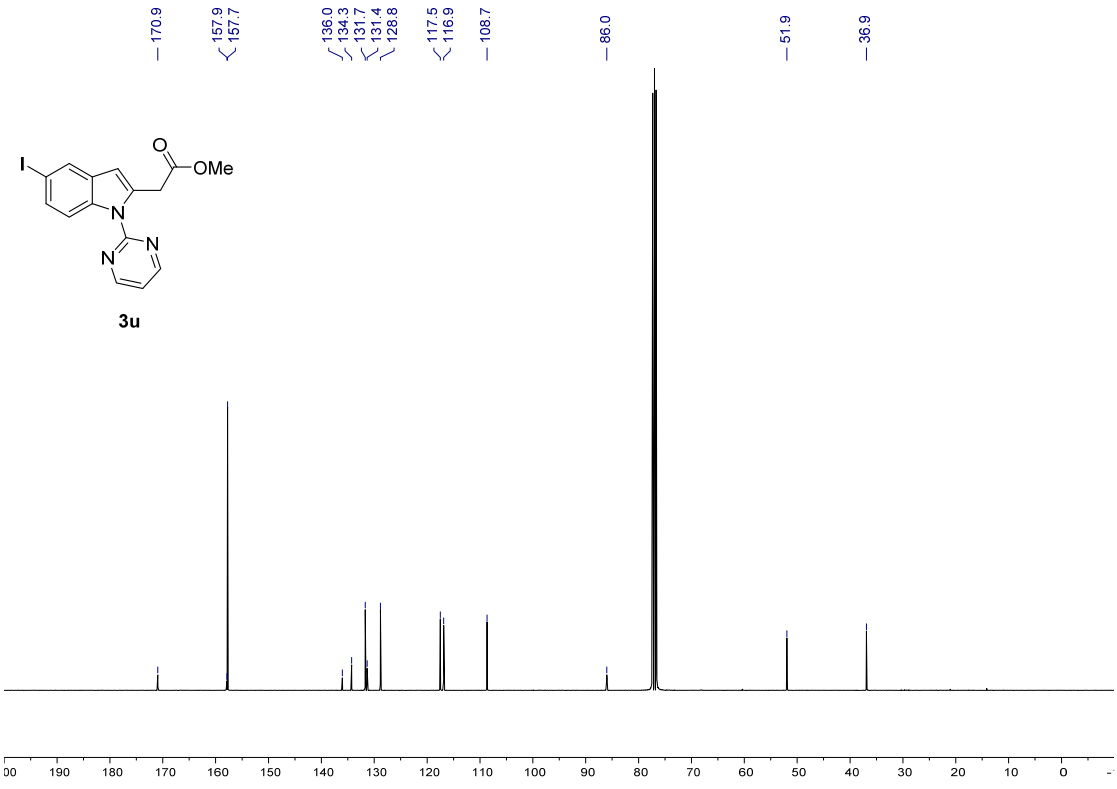
1.02
0.98
1.09
1.03
1.01
2.09
3.09

3u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I
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N
N

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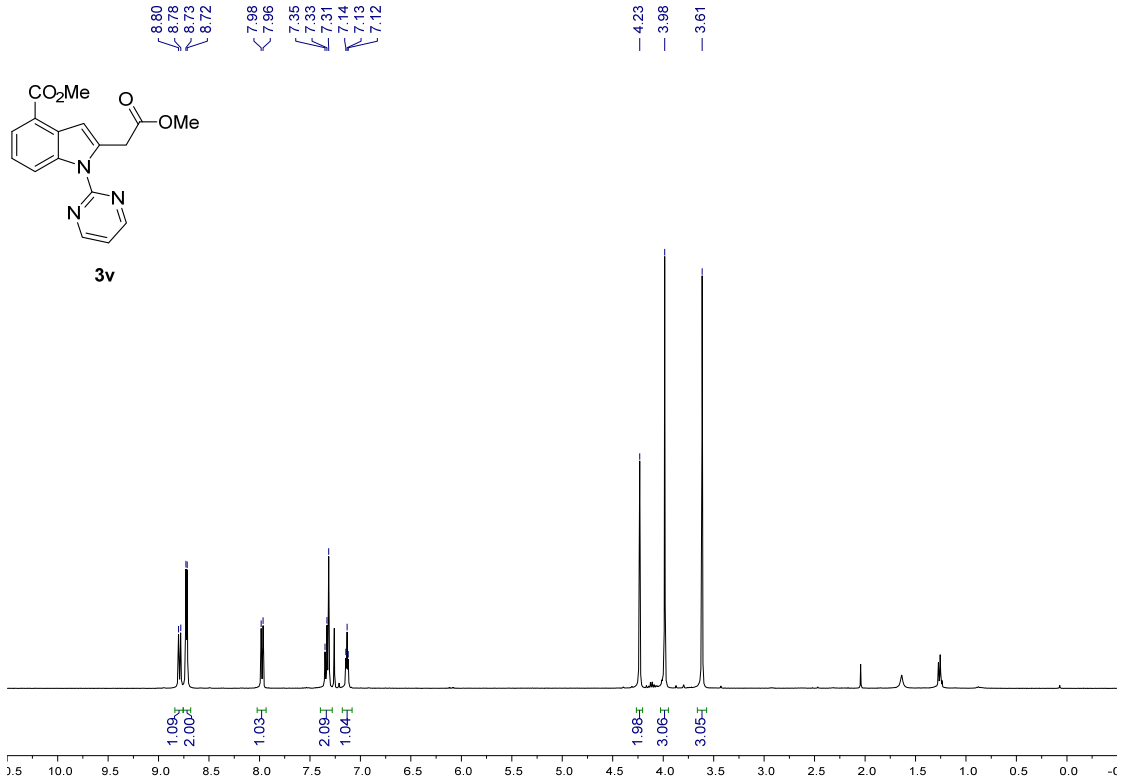
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7.12
4.23
3.98
3.61
CO2Me
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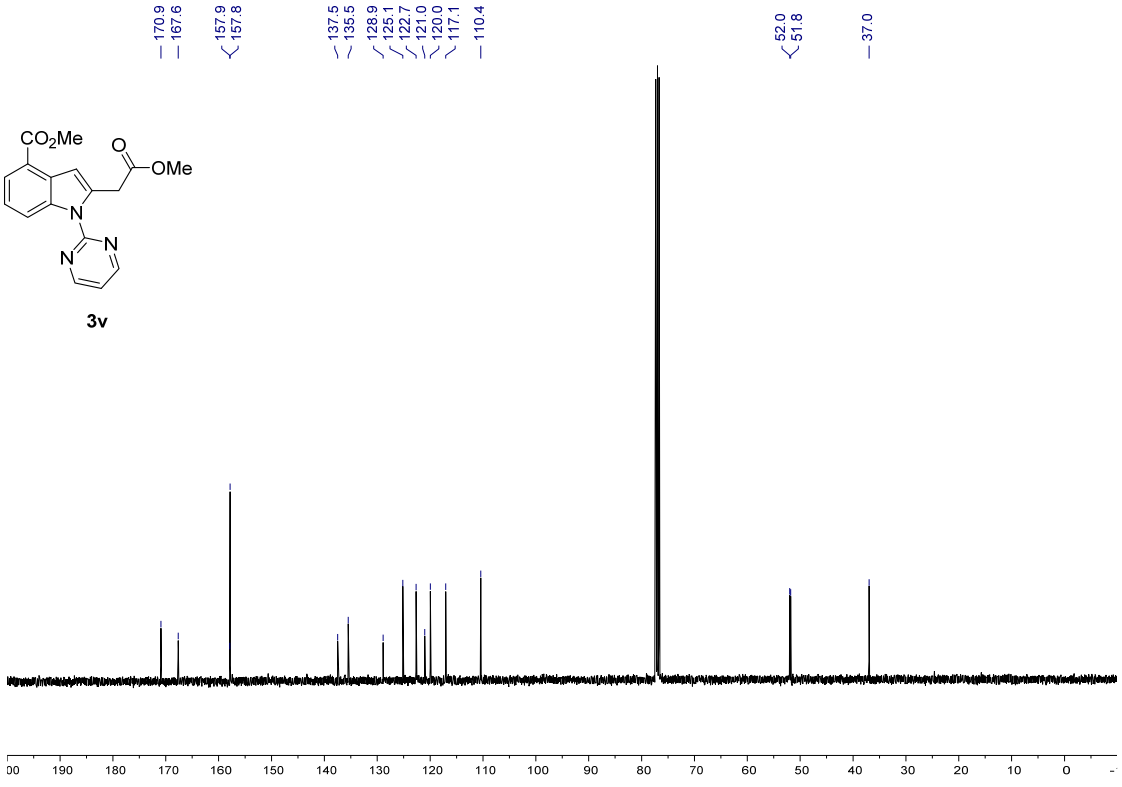
N
1.09
2.00
1.03
2.09
1.04
1.98
3.06
3.05

3v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110.4
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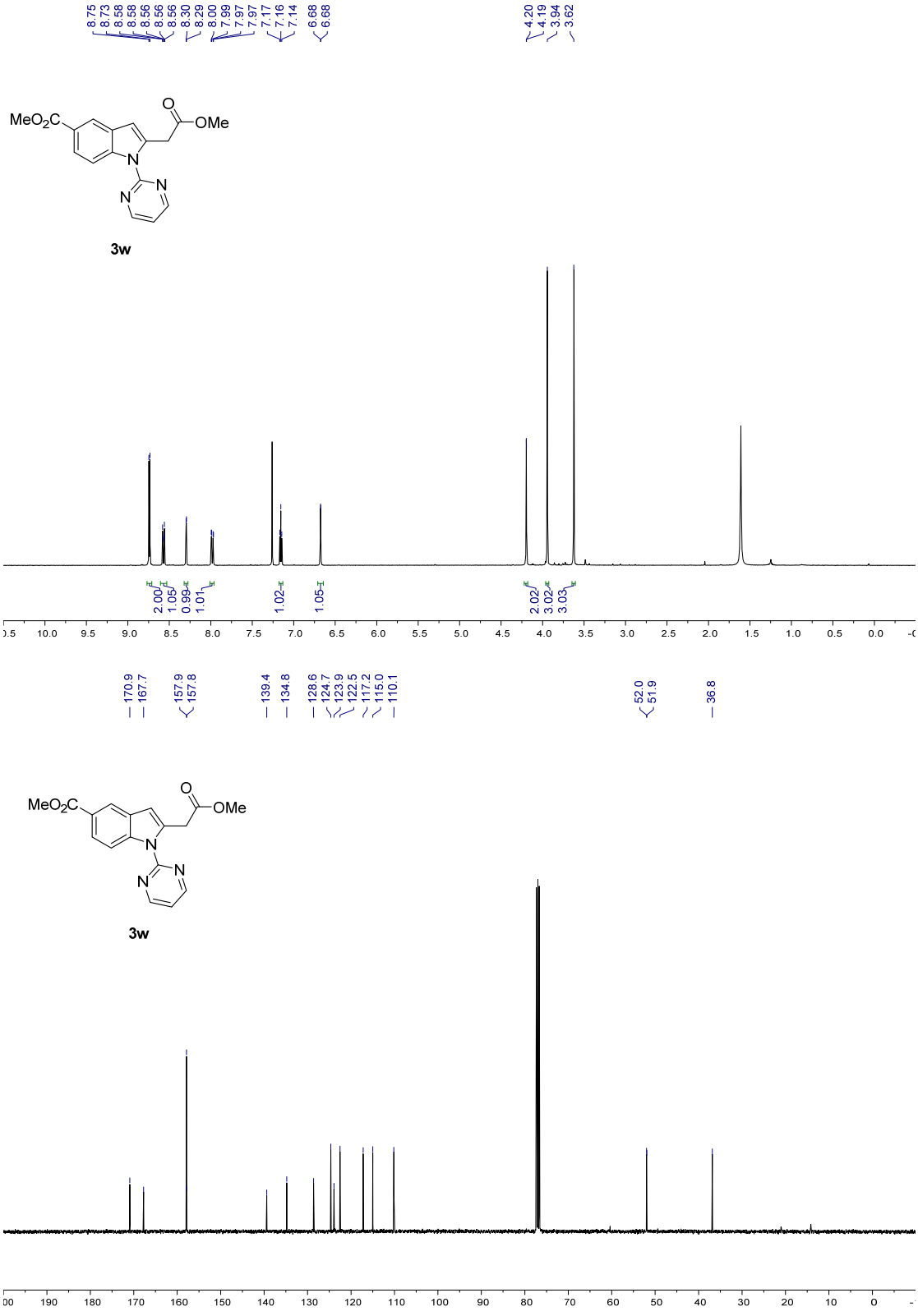
51.8
37.0
CO2Me
O
OMe
N
N
N

3v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6.68
4.20
4.19
3.94
3.62
MeO2C
O
OMe
N
N
N
3w
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1.05
0.99
1.01
1.02
1.05
2.02
3.02
3.03
170.9
167.7
157.9
157.8
139.4
134.8
128.6
124.7
123.9
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110.1
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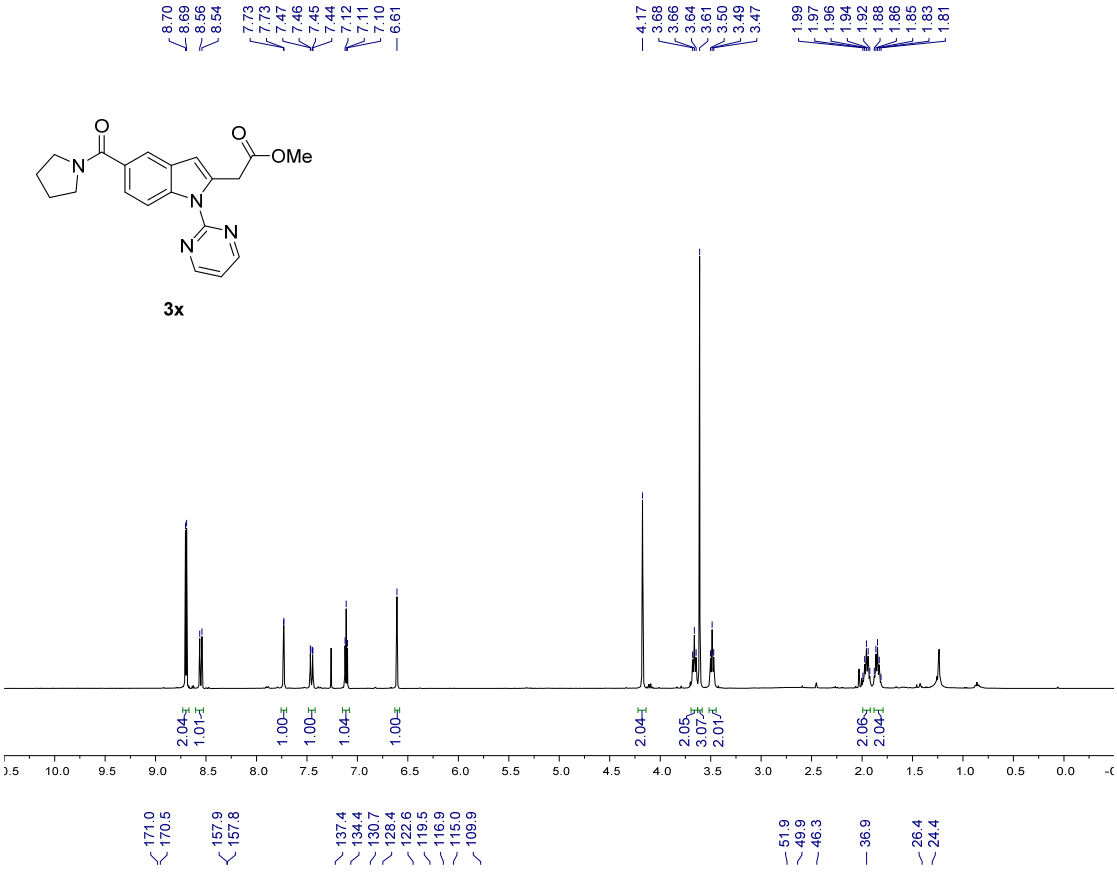
51.9
36.8
MeO2C
O
OMe
N
N
N
3w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7.10
6.61
4.17
3.68
3.66
3.64
3.61
3.50
3.49
3.47
1.99
1.97
1.96
1.94
1.92
1.88
1.86
1.85
1.83
1.81
O
N
O
OMe
N
N
N
2.04
1.01
1.00
1.00
1.04
1.00
2.04
2.05
3.07
2.01
2.06
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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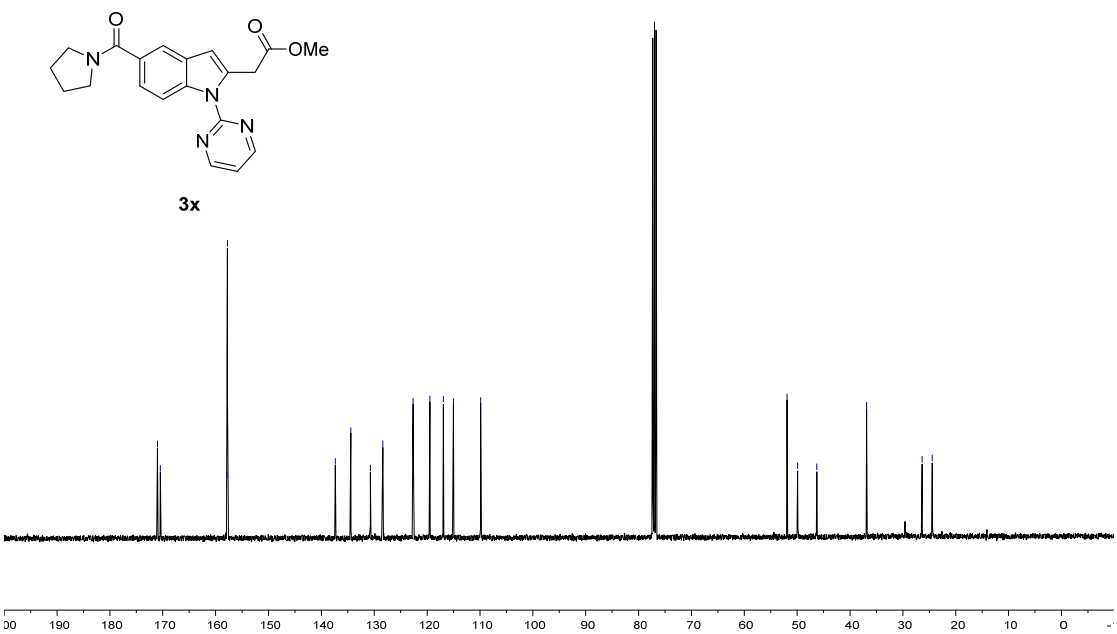
1.5
1.0
0.5
0.0

3x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116.9
115.0
109.9
51.9
49.9
46.3
36.9
26.4
24.4
190
180
170
160
150
140
130
120
110
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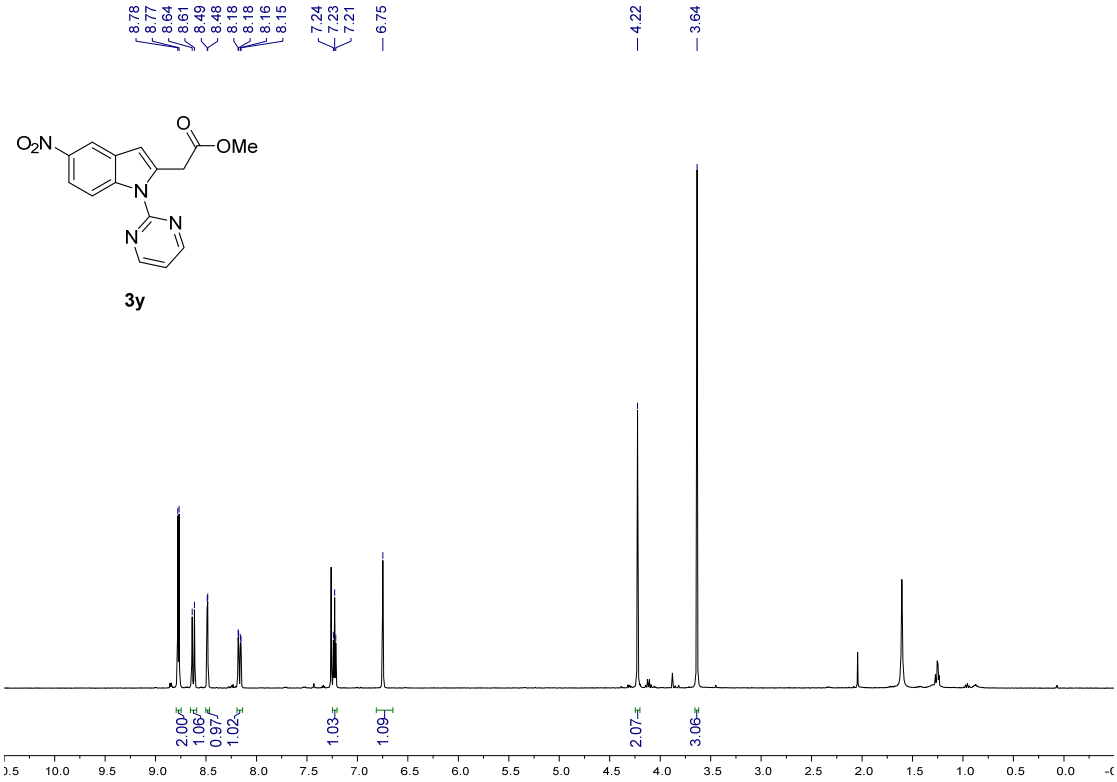
60
50
40
30
20
10
0

O
N
O
OMe
N
N
N

3x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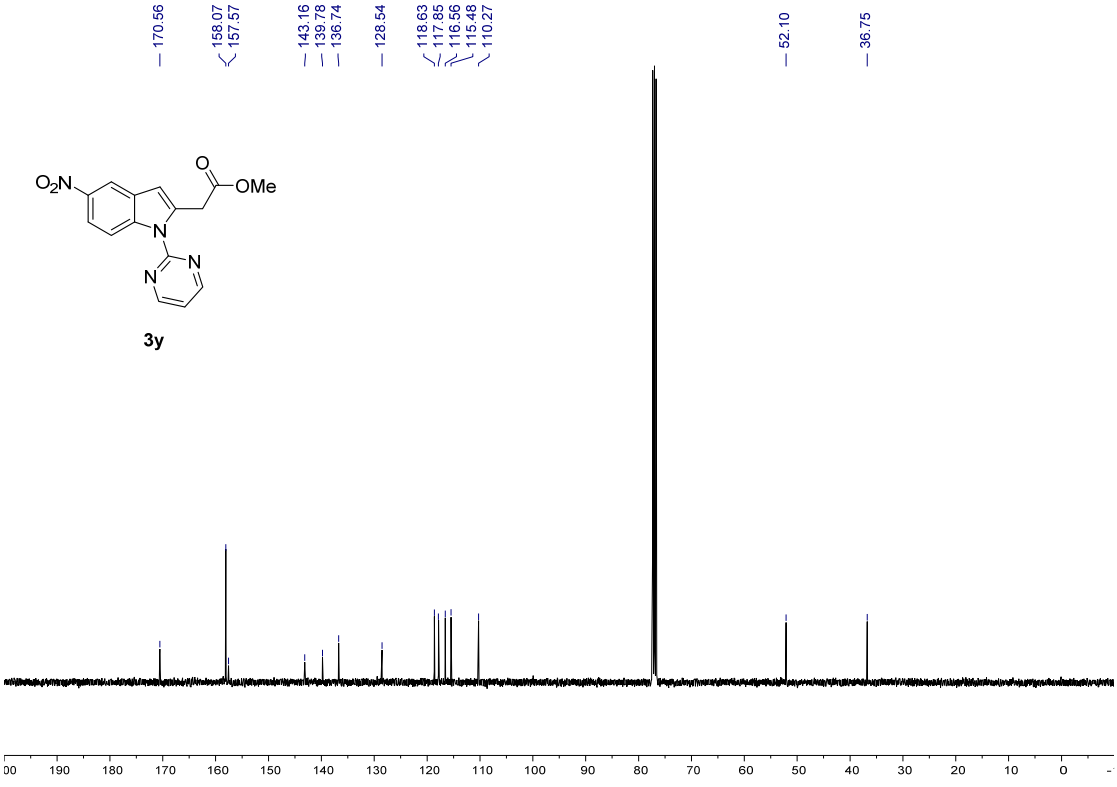
8.18
8.16
8.15
7.24
7.23
7.21
6.75
4.22
3.64
O2N
O
OMe
N
N
N
2.00
1.06
0.97
1.02
1.03
1.09
2.07
3.06

3y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157.57
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136.74
128.54
118.63
117.85
116.56
115.48
110.27
52.10
36.75
O2N
O
OMe
N
N
N

3y


8.59
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8.59
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8.58
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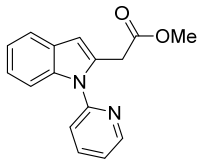
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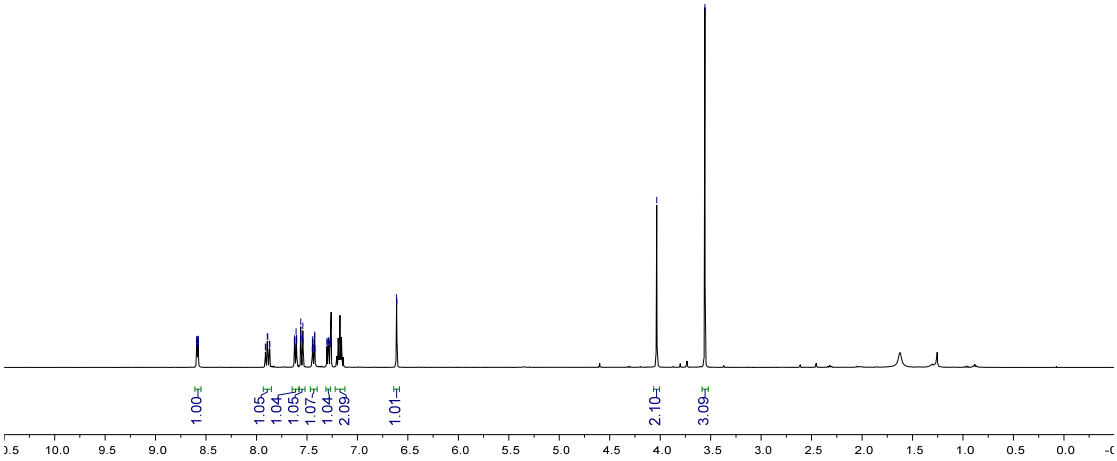
N
N

3z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1.04
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1.04
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1.01
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3.09
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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


170.7
151.3
149.4
138.4
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122.5
121.7
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120.2
110.3
105.7
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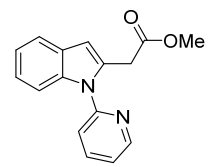
34.1


O
OMe
N
N

3z

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180
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100
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30
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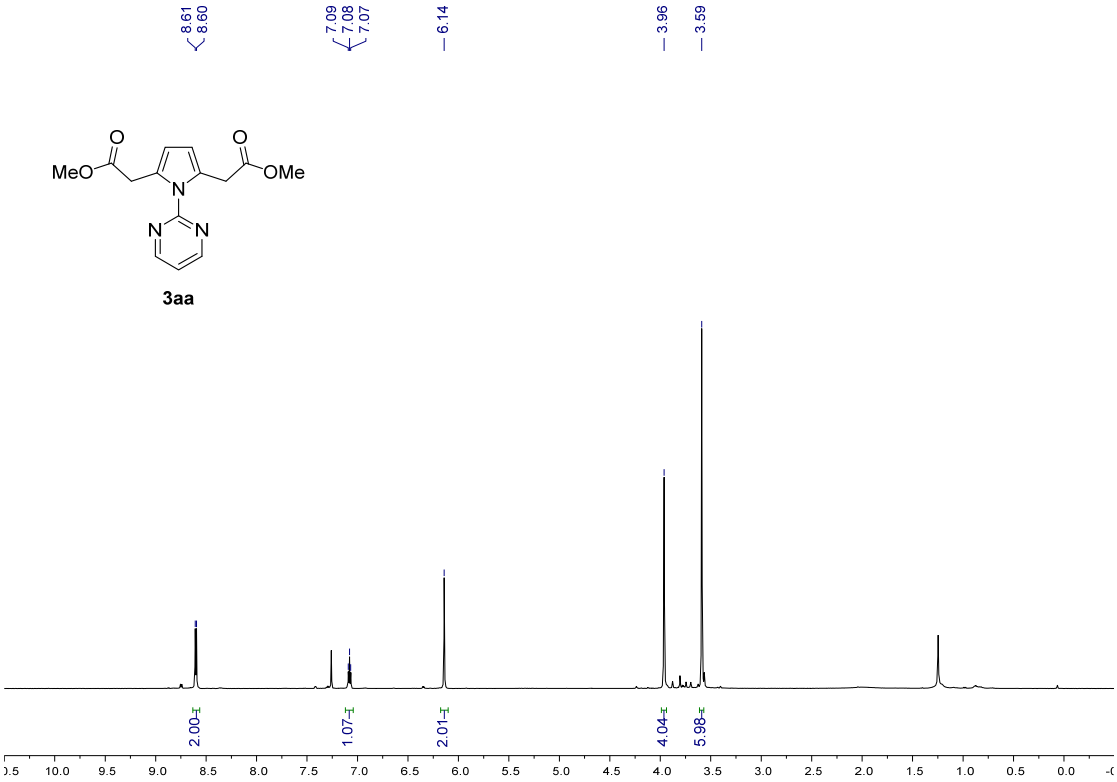
10
0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7.07
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OMe
O
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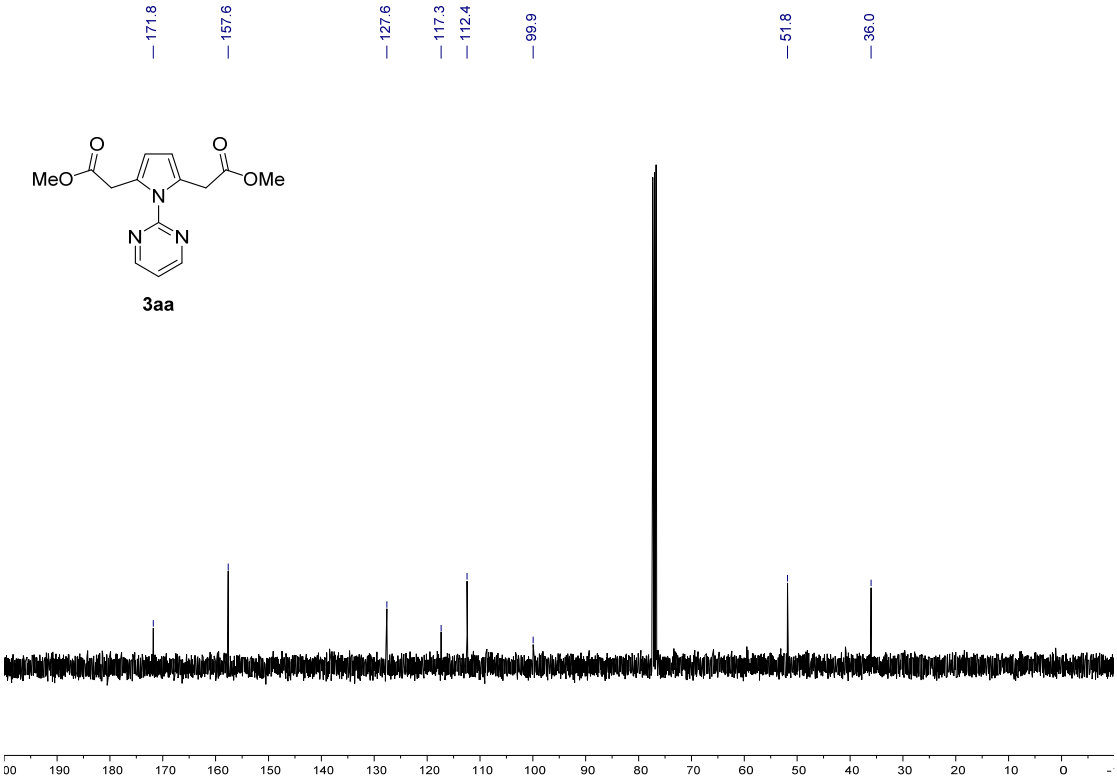
1.07
2.01
4.04
5.98

3aa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36.0
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N

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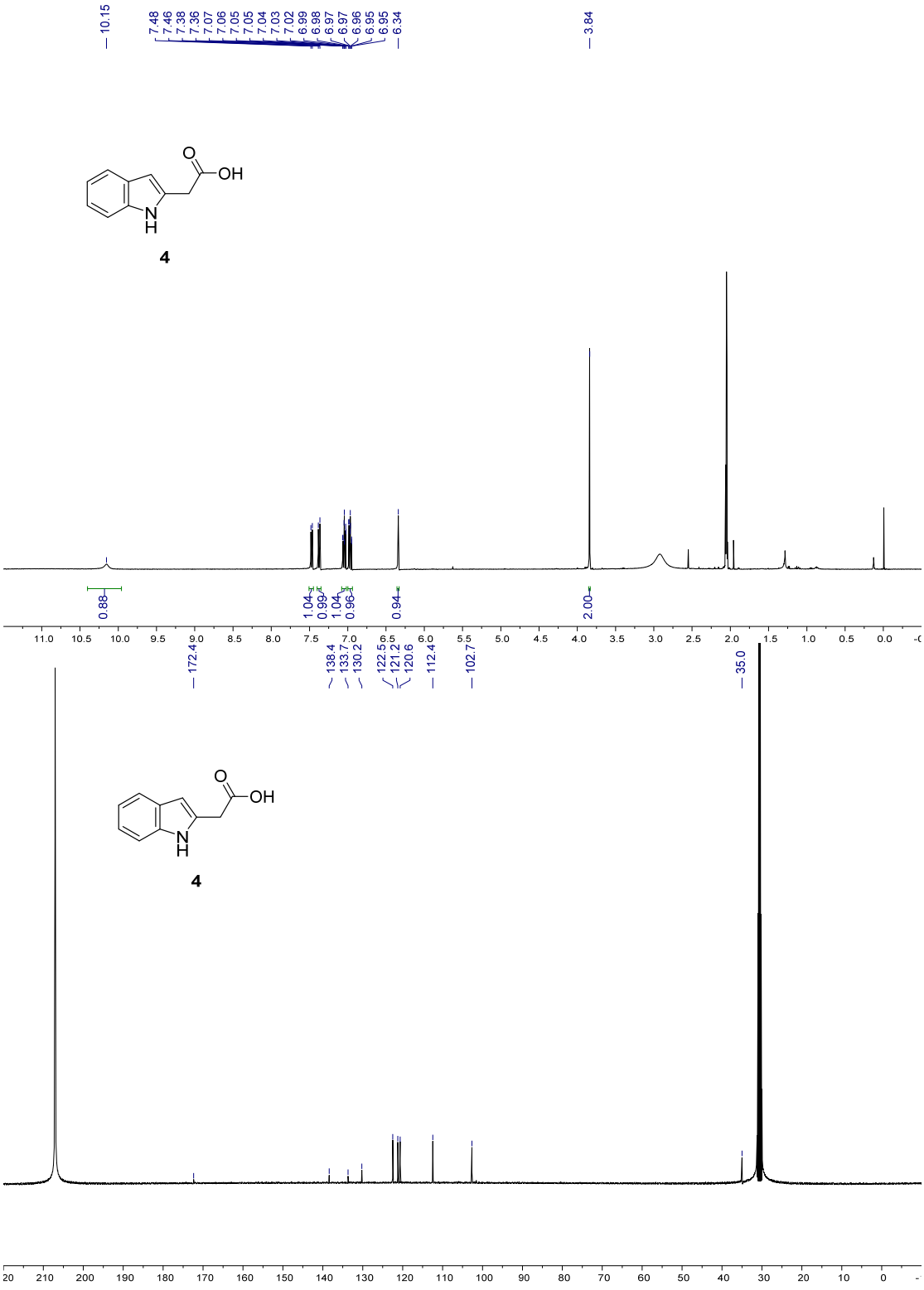
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