Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-Mediated Domino C-H Iodination and Nitration of Indoles

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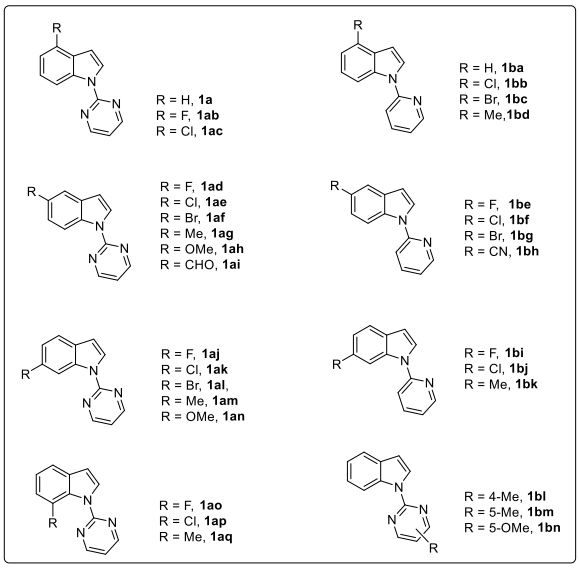
1. General Information.

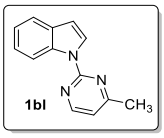
All reagents and metal catalysts were obtained from commercial sources without further purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica plates. Yields of the products refer to purification by silica-gel column chromatography. Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography. Mass spectra were recorded with a TSQ Quantum-LC/MS/MS of Finnigan using Electrospray ionization (ESI) techniques. ^{1}H and ^{13}C NMR spectra were recorded with a Brukers AV-300 and AV-500 spectrometer operating at 300 MHz/500 MHz and 75 MHz/126 MHz, respectively, with chemical shift values being reported in ppm relative to $CDCl_3$ (δ = 7.26 ppm) or DMSO-d_6 (δ = 2.50 ppm) for ^{1}H NMR, and $CDCl_3$ (δ = 77.16 ppm) or DMSO-d_6 (δ = 39.5 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Preparation of Substrates.

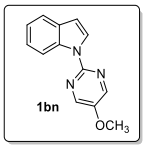


Scheme S1.The scope of substrates

The above substrates were synthesized following the procedure in previous reports,[1] and the spectral data of known compounds can be found in our previous papers or others' paper.[2,3] The spectral data of unreported compounds are shown below:

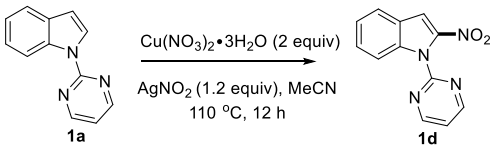


1-(4-methylpyrimidin-2-yl)-1*H*-indole (1bl): white solid. Yield: 85%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 5.0 Hz, 1H), 8.30 (d, *J* = 3.6 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 2.59 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.61, 157.62, 135.52, 131.42, 126.06, 123.59, 122.05, 120.87, 116.53, 115.79, 106.60, 24.33. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{12}N_3$ $[M + H]^+$ 210.1031, found 210.1030.



1-(5-methoxypyrimidin-2-yl)-1*H*-indole (1bn): white powder. Yield: 88%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 2H), 8.19 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 3.6 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.12, 150.00, 144.19, 135.20, 131.02, 126.03, 123.43, 121.73, 120.82, 115.69, 105.97, 56.24. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{12}N_3O$ $[M + H]^+$ 226.0980, found 226.0981.

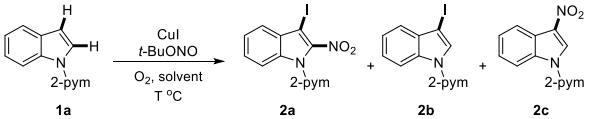
The procedure for the synthesis of substrate (**1d**)



The mixture of **1a** (0.3 mmol, 58.5 mg), $Cu(NO_3)_2 \cdot 3H_2O$ (0.6 mmol, 182.4 mg), $AgNO_2$ (0.36 mmol, 55.4 mg) in MeCN (3 mL) was stirred at 110 °C for 12 h. After the reaction was over, the resulting mixture was cooled to room temperature, filtered through a pad of silica gel and washed with 100 mL 50% EtOAc/ petroleum ether. Then the solvents were evaporated under reduced pressure and purified via chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) to give the 2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (**1d**) as a yellow oil. (Yield: 35%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.12 – 8.04 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.55 – 7.45 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.67, 156.69, 142.91, 137.76, 128.88, 125.02, 124.01, 123.72, 119.02, 113.68, 110.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_9N_4O_2$ $[M + H]^+$ 241.0726, found 241.0722.

3. Procedure for the Optimization of Reaction Conditions

Table S1. Optimization of copper-mediated C-H nitration [a]

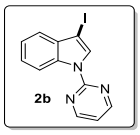


1a **2a** **2b** **2c**

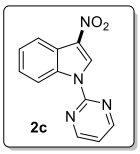
entry	CuI (equiv)	T (°C)	solvent	yield (%)[a] of **2a/2b/2c**
1	0.5	70	CH_3CN	29/40/8
2	1.0	70	CH_3CN	27/62/trace
3	1.5	70	CH_3CN	13/85/0
4	2.0	70	CH_3CN	trace/66/0
5	1.5	80	CH_3CN	28/47/0
6	1.5	90	CH_3CN	31/49/0
7	1.5	100	CH_3CN	29/36/0
8	1.5	90	dioxane	10/38/trace
9	1.5	90	DMF	0/42/0
10	1.5	90	DCE	30/17/trace
11[b]	1.5	90	CH_3CN	75/9/0
12[c]	**1.5**	**90**	**CH_3CN**	**77/0/0 (61/0/7)**[g]
13[d]	1.5	90	CH_3CN	60/0/trace
14[c,e]	1.5	90	CH_3CN	10/69/trace
15[c,f]	1.5	90	CH_3CN	0/52/0
16[c,h]	1.5	90	CH_3CN	66/0/0

[a] Reaction condition: 1a (0.2 mmol), *t*-BuONO (0.4 mmol), solvent (2 ml), stirred under O_2 (1 atm) for 12 h, yields of isolated product are given. [b] 3 equiv of *t*-BuONO used. [c] 4 equiv. of *t*-BuONO used. [d] 5 equiv. of *t*-BuONO used. [e] The reaction was carried out under air (1 atm). [f] The reaction was carried out under nitrogen (1 atm). [g] 1 equiv of CuI instead of 1.5 equiv of CuI. [h] The reaction was carried out at the gram-scale (5 mmol) to afford 1.2 g of **2a**. 2-pym = pyrimidyl.

Procedure: An oven dried 25 mL Schlenk tube, equipped with a stir bar, was charged with substrates **1a** (0.2 mmol, 39.0 mg), CuI (0.5 - 2.0 equiv), *t*-BuONO (2 - 5 equiv), and solvent (2 mL). The tube was capped and back filled with oxygen except for special requirement. Then the reaction mixture was stirred at corresponding temperature for 12 h. Upon completion, EtOAc was added to dilute the mixture and then filtered through a pad of silica gel. The solvents were evaporated under reduced pressure and then purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to obtain the pure product.

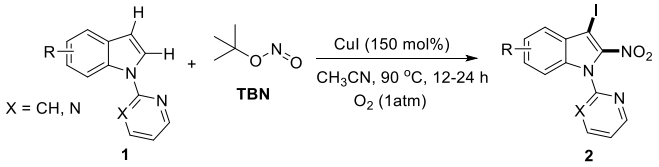


3-iodo-1-(pyrimidin-2-yl)-1*H*-indole (2b): white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.2 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 8.44 (s, 1H), 7.45 (t, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.07 (t, *J* = 4.8 Hz, 1H). The spectral data of the product was in accordance with that reported in the literature.[2b]

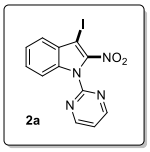


3-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2c): yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.92 – 8.86 (m, 1H), 8.82 (d, *J* = 4.8 Hz, 2H), 8.35 (dd, *J* = 6.5, 2.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.29 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 159.88, 156.26, 134.33, 131.99, 131.46, 129.18, 126.53, 125.77, 121.96, 120.34, 120.25, 117.14. **HRMS** (ESI-TOF) m/z calcd for $C_{12}H_9N_4O_2$ $[M + H]^+$ 241.0726, found 241.0720.

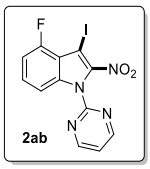
4. General Procedure for the Iodination and Nitration of Indoles



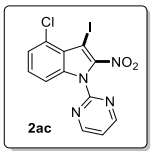
General Procedure: Substrates (**1**, 0.3 mmol), CuI (85.5 mg, 150 mol%), MeCN (3.0 - 4.0 mL) were added to a 25 mL Schlenk tube with a magnetic bar, the resulting mixture was stirred for 5 min at laboratory temperature to obtain a clear solution. TBN (4.0 equiv, 145 ul) was added to the solution, then the tube was sealed with a Teflon-lined cap and back filled with oxygen (about 1 mmol of O_2 in the tube), and the mixture was stirred at 90 °C for 12 - 24 h. After the reaction completed monitoring by Thin Layer Chromatography (TLC), cooling to room temperature, diluted with ethyl acetate, the mixture was filtered through a pad of silica gel and washed with 100 mL ethyl acetate: petroleum ether (1:1). The filtrate was evaporated under reduced pressure to remove the solvents and then purified *via* chromatography on silica gel with ethyl acetate/petroleum ether to provide the corresponding product **2**.



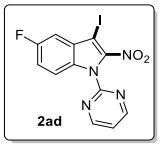
3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2a): Yield: 77%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.68, 156.21, 143.87, 136.28, 129.74, 129.25, 124.93, 124.68, 118.99, 114.18, 70.93. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_8IN_4O_2$ $[M + H]^+$ 366.9692, found 366.9693.



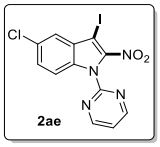
4-fluoro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ab): Yield: 77%, yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.46 (td, *J* = 8.3, 5.2 Hz, 1H), 7.32 (t, *J* = 4.9 Hz, 1H), 7.05 (dd, *J* = 10.5, 8.1 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 159.96, 157.32 (d, $J_{C\text{-}F}$ = 254.23 Hz), 155.37, 144.08, 137.67 (d, *J* = 6.62 Hz), 130.64 (d, *J* = 7.99 Hz), 120.60, 117.56 (d, *J* = 16.44 Hz), 110.64 (d, *J* = 3.82 Hz), 110.06 (d, *J* = 18.34 Hz), 64.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7FIN_4O_2$ $[M + H]^+$ 384.9598, found 384.9596.



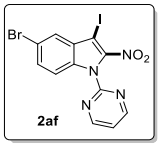
4-chloro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ac): Yield: 55%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.38 (d, 1H), 7.34 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.76, 155.71, 145.16, 136.53, 129.90, 128.76, 125.96, 123.04, 119.30, 113.15, 63.08. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7ClIN_4O_2$ $[M + H]^+$ 400.9302, found 400.9301.



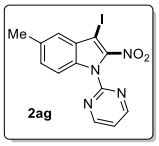
5-fluoro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ad): Yield: 71%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.23 (dd, *J* = 9.2, 4.3 Hz, 1H), 7.35 – 7.26 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.19 (d, $J_{C\text{-}F}$ = 243.84 Hz), 158.70, 155.99, 144.83, 132.44, 130.23 (d, *J* = 10.05 Hz), 119.10, 118.28 (d, *J* = 25.86 Hz), 116.21 (d, *J* = 8.70 Hz), 109.88 (d, *J* = 25.22 Hz), 69.21. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7FIN_4O_2$ $[M + H]^+$ 384.9598, found 384.9597.



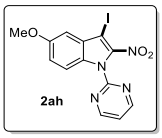
5-chloro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ae): Yield: 70%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.31 (t, *J* = 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 160.00, 155.39, 144.60, 134.62, 130.53, 130.42, 129.72, 124.17, 120.57, 116.54, 73.16. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7ClIN_4O_2$ $[M + H]^+$ 400.9302, found 400.9301.



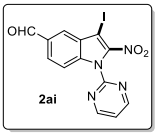
5-bromo-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2af): Yield: 42%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.62 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.31 (t, *J* = 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 160.02, 155.39, 144.41, 134.94, 133.03, 131.02, 127.21, 120.58, 117.57, 116.79, 73.13. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7BrIN_4O_2$ $[M + H]^+$ 444.8797, found 444.8795.



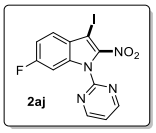
3-iodo-5-methyl-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ag): Yield: 62%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.40 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.27 (t, *J* = 6.3, 3.4 Hz, 1H), 2.51 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.62, 156.28, 143.79, 134.64, 134.56, 131.52, 129.32, 124.27, 118.84, 113.97, 70.80, 21.44. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_2$ $[M + H]^+$ 380.9848, found 380.9846.



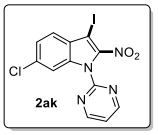
3-iodo-5-methoxy-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ah): Yield: 75%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 7.16 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.63, 157.41, 156.22, 143.89, 131.09, 129.99, 120.58, 118.87, 115.58, 105.06, 70.50, 55.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_3$ $[M + H]^+$ 396.9798, found 396.9799.



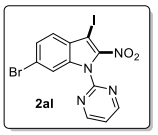
3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole-5-carbaldehyde (2ai): Yield: 56%, yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.85 (d, *J* = 4.8 Hz, 2H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.18 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.37 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 192.57, 160.06, 155.22, 144.73, 139.01, 133.45, 129.46, 129.41, 128.95, 120.83, 115.19, 75.43. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8IN_4O_3$ $[M + H]^+$ 394.9641, found 394.9640.



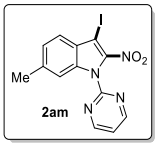
6-fluoro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2aj): Yield: 86%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 7.97 (dd, *J* = 9.8, 2.2 Hz, 1H), 7.61 (dd, *J* = 8.8, 5.3 Hz, 1H), 7.30 (t, *J* = 4.8 Hz, 1H), 7.16 (td, *J* = 8.9, 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 163.70 (d, $J_{C\text{-}F}$ = 245.41 Hz), 159.93, 155.50, 144.20, 136.44 (d, *J* = 13.99 Hz), 127.40 (d, *J* = 10.67 Hz), 126.09, 120.38, 114.33 (d, *J* = 25.08 Hz), 100.99 (d, *J* = 29.08 Hz), 75.07. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7FIN_4O_2$ $[M + H]^+$ 384.9598, found 384.9597.



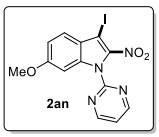
6-chloro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (**2ak**): Yield: 80%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 2H), 8.27 (d, *J* = 1.7 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.31 (t, *J* = 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.75, 155.87, 144.17, 136.17, 135.77, 127.83, 125.87, 125.58, 119.20, 114.33, 70.19. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7ClIN_4O_2$ $[M + H]^+$ 400.9302, found 400.9300.



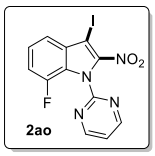
6-bromo-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2al): Yield: 82%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.44 (s, 1H), 7.55 – 7.50 (m, 2H), 7.32 (t, *J* = 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.76, 155.83, 143.98, 136.33, 128.20, 126.06, 123.69, 119.21, 117.27, 70.16. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7BrIN_4O_2$ $[M + H]^+$ 444.8797, found 444.8793.



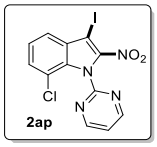
3-iodo-6-methyl-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2am): Yield: 75%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 2H), 7.94 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 2.52 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.68, 156.30, 143.37, 140.88, 136.75, 127.25, 126.56, 124.58, 118.96, 113.58, 71.60, 22.44. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_2$ $[M + H]^+$ 380.9848, found 380.9845.



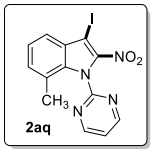
3-iodo-6-methoxy-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2an): Yield: 63%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 2H), 7.63 (d, *J* = 2.1 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.29 (t, *J* = 4.8 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.24, 158.66, 156.46, 142.92, 137.98, 125.98, 123.43, 118.94, 115.45, 96.16, 72.77, 55.90. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_3$ $[M + H]^+$ 396.9798, found 396.9794.



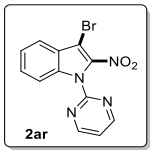
7-fluoro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ao): Yield: 72%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.9 Hz, 2H), 7.49 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.46 (t, *J* = 4.9 Hz, 1H), 7.29 (td, *J* = 8.0, 4.3 Hz, 1H), 7.20 (ddd, *J* = 11.6, 7.9, 0.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.98, 156.82, 149.40 (d, $J_{C\text{-}F}$ = 251.56 Hz), 142.85, 132.06, 124.87 (d, *J* = 11.15 Hz), 123.85 (d, *J* = 6.24 Hz), 121.12 (d, *J* = 4.13 Hz), 120.93, 114.82 (d, *J* = 18.01 Hz), 67.72. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7FIN_4O_2$ $[M + H]^+$ 384.9598, found 384.9595.



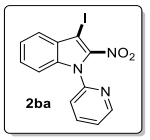
7-chloro-3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ap): Yield: 45%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.9 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 4.9 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.78, 157.15, 142.43, 132.61, 131.31, 130.57, 124.40, 124.07, 121.46, 117.95, 67.16. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_7ClIN_4O_2$ $[M + H]^+$ 400.9302, found 400.9303.



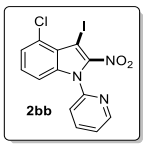
3-iodo-7-methyl-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2aq): Yield: 55%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.9 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.48 (t, *J* = 4.9 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 1.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.84, 158.24, 142.34, 135.87, 132.08, 129.77, 123.89, 123.47, 123.20, 121.29, 68.76, 18.89. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_2$ $[M + H]^+$ 380.9848, found 380.9849.



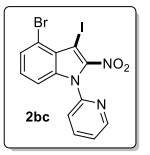
3-bromo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (2ar): Yield: 68%, pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.68, 156.21, 140.19, 135.47, 129.87, 125.97, 124.59, 122.48, 118.95, 114.22, 100.89. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_8BrN_4O_2$ $[M + H]^+$ 318.9831, found 318.9830.



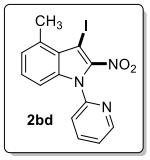
3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2ba): Yield: 77%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 – 8.59 (m, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 (dd, *J* = 7.4, 4.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.98, 149.87, 142.65, 138.95, 137.22, 129.46, 129.19, 125.23, 124.04, 123.66, 120.66, 111.95, 68.18. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_9IN_3O_2$ $[M + H]^+$ 365.9739, found 365.9739.



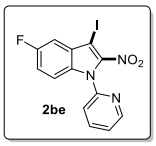
4-chloro-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bb): Yield: 56%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.8, 1.0 Hz, 1H), 7.98 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.35 – 7.28 (m, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 150.25, 148.98, 144.61, 140.37, 137.53, 129.48, 129.21, 125.50, 124.77, 122.72, 121.18, 111.98, 64.77. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8ClIN_3O_2$ $[M + H]^+$ 399.9350, found 399.9347.



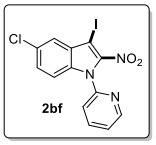
4-bromo-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bc): Yield: 43%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 – 8.54 (m, 1H), 7.97 (td, *J* = 7.8, 1.8 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.34 (dd, *J* = 15.0, 8.5 Hz, 1H), 7.26 – 7.21 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.19, 149.23, 144.45, 139.10, 137.28, 129.12, 128.65, 123.99, 120.60, 118.54, 111.63, 96.66, 62.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8BrIN_3O_2$ $[M + H]^+$ 443.8845, found 443.8845.



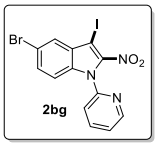
3-iodo-4-methyl-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bd): Yield: 51%, yellow solid. **^{1}H NMR** (500 MHz, DMSO) δ 8.52 (d, *J* = 4.7 Hz, 1H), 8.08 (td, *J* = 7.8, 1.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 7.2, 5.1 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 2.87 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 150.19, 149.46, 143.73, 140.23, 137.32, 134.95, 129.24, 126.02, 125.33, 124.43, 121.17, 110.50, 66.83, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{11}IN_3O_2$ $[M + H]^+$ 379.9896, found 379.9887.



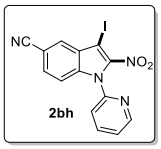
5-fluoro-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2be): Yield: 82%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 – 8.57 (m, 1H), 7.97 (td, *J* = 7.7, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.5, 4.2 Hz, 2H), 7.33 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.29 (dd, *J* = 9.1, 4.2 Hz, 1H), 7.21 (td, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.85 (d, J_{C-F} = 242.77 Hz), 150.04, 149.66, 143.43, 139.09, 133.61, 129.90 (d, *J* = 10.45 Hz), 123.88, 120.59, 118.59 (d, *J* = 26.67 Hz), 113.79 (d, *J* = 9.01 Hz), 109.86 (d, *J* = 24.84 Hz), 66.76. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8FIN_3O_2$ $[M + H]^+$ 383.9645, found 383.9647.



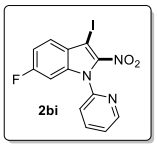
5-chloro-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bf): Yield: 75%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.97 (td, *J* = 7.8, 1.9 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.25 (d, *J* = 3.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.05, 149.48, 143.25, 139.11, 135.40, 130.12, 129.89, 124.40, 123.95, 120.55, 113.51, 66.34. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8ClIN_3O_2$ $[M + H]^+$ 399.9350, found 399.9348.



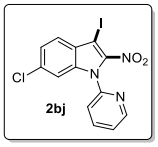
5-bromo-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bg): Yield: 65%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.97 (td, *J* = 7.8, 1.9 Hz, 1H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.54 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.20 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 150.10, 149.22, 143.51, 140.25, 135.69, 132.61, 130.66, 127.14, 124.59, 121.01, 116.84, 114.85, 70.27. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8BrIN_3O_2$ $[M + H]^+$ 443.8845, found 443.8846.



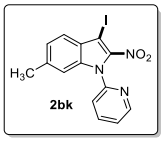
3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole-5-carbonitrile (2bh): Yield: 40%, yellow solid. **^{1}H NMR** (500 MHz, DMSO) δ 8.59 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.20 (d, *J* = 1.0 Hz, 1H), 8.14 (td, *J* = 7.8, 1.9 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.58 (ddd, *J* = 7.5, 4.9, 0.7 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 150.22, 148.87, 144.43, 140.45, 138.47, 131.99, 131.11, 129.12, 124.97, 121.32, 119.12, 114.36, 107.13, 71.56. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_8IN_4O_2$ $[M + H]^+$ 390.9692, found 390.9693.



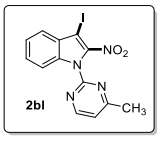
6-fluoro-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bi): Yield: 95%, yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.68 – 8.49 (m, 1H), 7.96 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62 (dd, *J* = 8.9, 5.2 Hz, 1H), 7.49 – 7.34 (m, 2H), 7.11 (td, *J* = 9.0, 2.1 Hz, 1H), 7.00 (dd, *J* = 9.2, 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.97 (d, J_{C-F} = 248.89 Hz), 150.01, 149.63, 142.96, 139.15, 137.40 (d, *J* = 12.92 Hz), 127.06 (d, *J* = 10.48 Hz), 125.76, 123.91, 120.51, 113.74 (d, *J* = 25.43 Hz), 98.42 (d, *J* = 27.88 Hz), 68.35. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8FIN_3O_2$ $[M + H]^+$ 383.9645, found 383.9645.



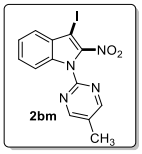
6-chloro-3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bj): Yield: 81%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.99 (td, *J* = 7.8, 1.9 Hz, 1H), 7.60 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.37 – 7.29 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.07, 149.41, 142.93, 139.19, 137.17, 135.59, 127.72, 126.32, 125.08, 123.99, 120.59, 111.93, 67.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_8ClIN_3O_2$ $[M + H]^+$ 399.9350, found 399.9351.



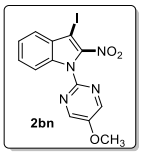
3-iodo-6-methyl-2-nitro-1-(pyridin-2-yl)-1*H*-indole (2bk): Yield: 83%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 3.2 Hz, 1H), 7.96 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.06 (s, 1H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.04, 149.89, 142.15, 140.59, 138.93, 137.71, 127.27, 126.16, 124.83, 123.62, 120.85, 111.41, 68.74, 22.35. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{11}IN_3O_2$ $[M + H]^+$ 379.9896, found 379.9893.



3-iodo-1-(4-methylpyrimidin-2-yl)-2-nitro-1*H*-indole (2bl): Yield: 82%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.1 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.2, 1.2 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.13 (d, *J* = 5.1 Hz, 1H), 2.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.73, 158.09, 155.92, 143.88, 136.33, 129.58, 129.22, 124.86, 124.53, 118.67, 114.18, 70.36, 24.18. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_2$ $[M + H]^+$ 380.9848, found 380.9846.



3-iodo-1-(5-methylpyrimidin-2-yl)-2-nitro-1*H*-indole (2bm): Yield: 88%, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 2H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.53 (ddd, *J* = 8.4, 7.2, 1.1 Hz, 1H), 7.42 – 7.36 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.69, 154.33, 143.68, 136.36, 129.59, 129.17, 128.82, 124.87, 124.48, 113.93, 70.09, 15.30. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_2$ $[M + H]^+$ 380.9848, found 380.9847.



3-iodo-1-(5-methoxypyrimidin-2-yl)-2-nitro-1*H*-indole (2bn): Yield: 73%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (s, 2H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 3.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.04, 149.48, 144.69, 143.41, 136.53, 129.53, 129.10, 124.92, 124.33, 113.48, 69.34, 56.48. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{10}IN_4O_3$ $[M + H]^+$ 396.9798, found 396.9797.

5. Mechanism Studies

5.1 Monitoring the process of reaction.

We monitored the reaction by ^{1}H-NMR at 1 h, 4 h, 8 h, 12 h (**Figure S1**). The starting material **1a** was consumed completely within 1 h with presence of intermediate **2b** and product **2a** in a ratio of 1.2 : 1. Subsequently, all the **2b** were converted into **2a** within 8 -12 hours.

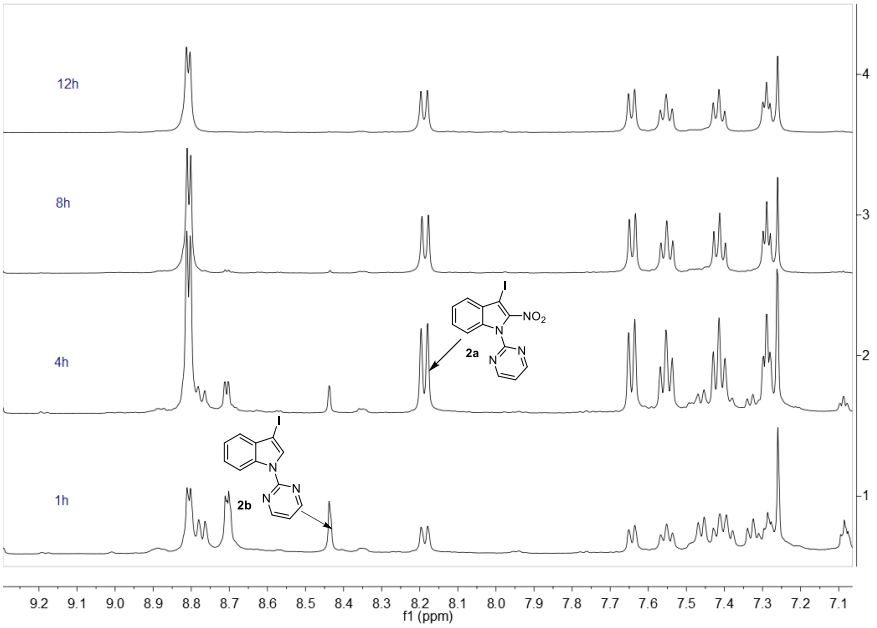
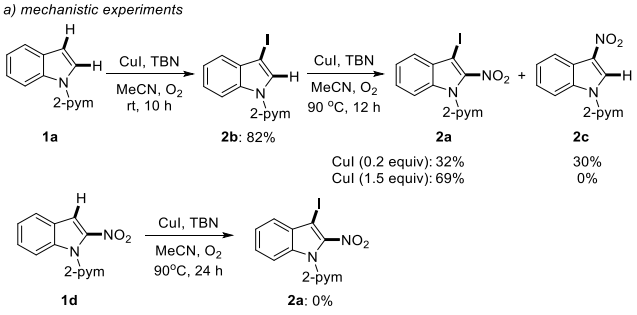


Figure S1. Monitoring the reaction with ^{1}H-NMR (500 M).

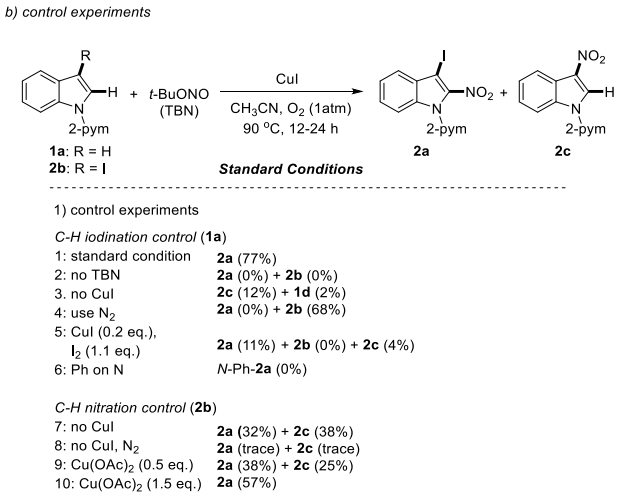
5.2 Mechanistic experiments



Scheme S2. Mechanistic experiments

The Mechnistic experiments were conducted following the **General Procedure** in section 4.

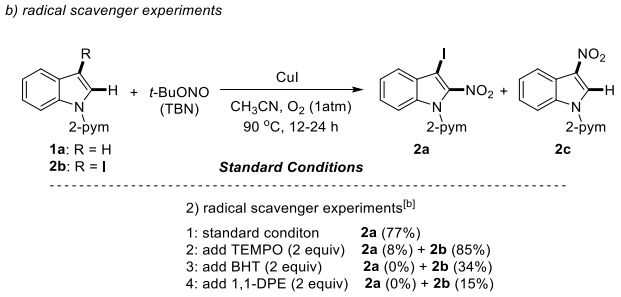
5.3 Control experiments of C-H iodination and nitration



Scheme S3. Control experiments of C-H iodination and nitration

The control experiments were conducted following the **General Procedure** in section 4.

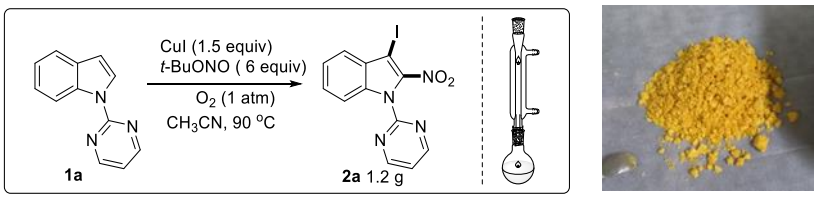
5.4 Radical scavenger experiments



Scheme S4. Radical scavenger experiments

The radical scavenger experiments were conducted following the **General Procedure** in section 4 with radical trapping reagents added.

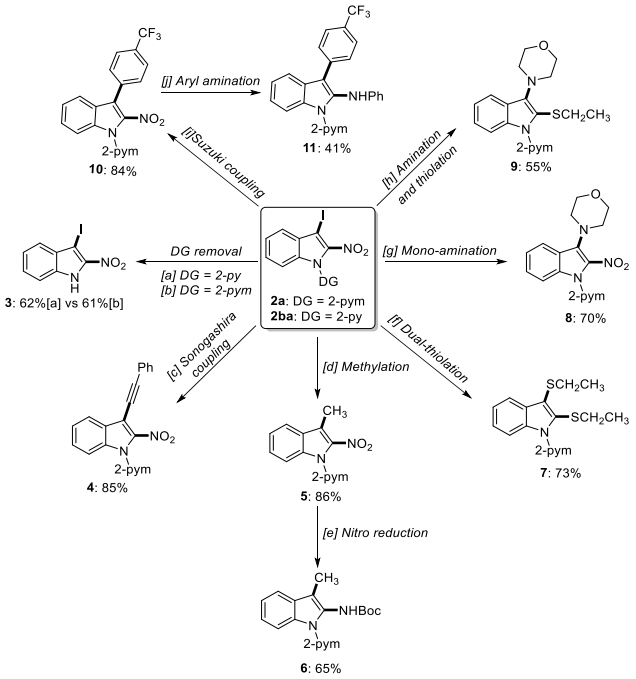
6. Scale up Experiment on Gram Scale



Scheme S5. Gram scale synthesis

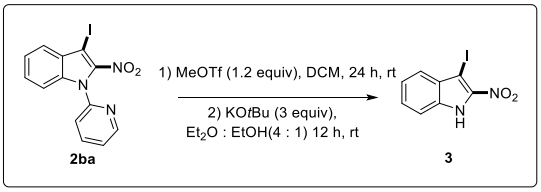
Substrate **1a** (5 mmol, 0.975 g), CuI (7.5 mmol, 1.425 g), and CH_3CN (50 ml) were added in a 100 mL flask under stirring to obtain a clear solution (it is crucial to dissolve all the CuI), and then TBN (30 mmol, 3.6 mL) was added and stirred at 90 °C under O_2 atmosphere for 2 days. The resulting mixture was cooled to room temperature, filtered through a pad of silica gel and washed with 100 mL 50% EtOAc/ petroleum ether. Then the solvents were evaporated under reduced pressure and purified *via* chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) to give the 3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole **2a** as a yellow solid. (1.2 g, Yield : 66%).

7. Derivatization of the C-H Iodination and Nitraion Products

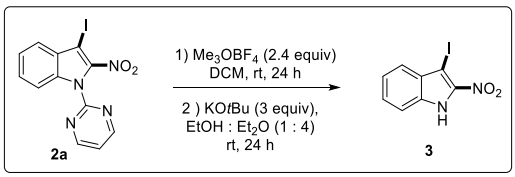


Scheme S6. Derivatization of the C-H iodination and nitraion products.

3-iodo-2-nitro-1*H*-indole (3) [4]

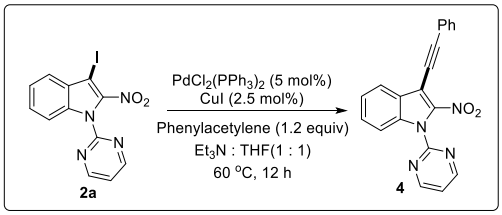


3-iodo-2-nitro-1-(pyridin-2-yl)-1*H*-indole (**2ba**, 0.2 mmol) and CH_2Cl_2 (3 mL) were placed in a dry sealed tube, methy trifluoromethanesulfonate (0.22 mmol) were added. The mixture was stirred at room temperature for 24 h. Volatile materials were evaporated in vacuo, and potassium *tert*-butoxide (0.6 mmol) was added. EtOH (0.4 mL) and Et_2O (1.6 mL) were added, and the resulting suspension was stirred for 12 h at room temperature. The mixture was diluted with CH_2Cl_2 and washed by water. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue purified by flash chromatography afforded **3** as a yellow solid in 62% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.24, 135.73, 130.38, 128.93, 124.34, 122.96, 113.97, 64.58. **HRMS** (ESI-TOF) *m/z* calcd for $C_8H_6IN_2O_2$ $[M + H]^+$ 288.9474, found 288.9473.



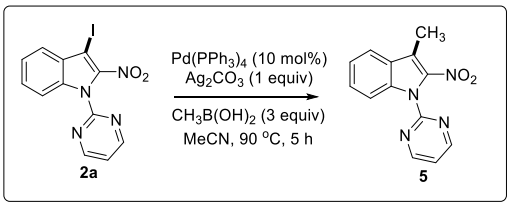
3-iodo-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (**2a**, 0.2 mmol), and CH_2Cl_2 (3 ml) were placed in a 25 mL flask, Me_3OBF_4 (0.48 mmol) were added. The mixture was stirred at room temperature for 24 h. Volatile materials were evaporated in vacuo, and potassium *tert*-butoxide (0.6 mmol) was added. EtOH (0.8 mL) and Et_2O (3.2 mL) were added, and the resulting suspension was stirred for 24 h at room temperature. The mixture solvents were removed under reduced pressure, then diluted with ethyl acetate and washed with saturated brine. The combined organic layer dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue purified by flash chromatography afforded **3** as a yellow solid in 61% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.24, 135.73, 130.38, 128.93, 124.34, 122.96, 113.97, 64.58. **HRMS** (ESI-TOF) *m/z* calcd for $C_8H_6IN_2O_2$ $[M + H]^+$288.9474, found 288.9473.

2-nitro-3-(phenylethynyl)-1-(pyrimidin-2-yl)-1*H*-indole (4)



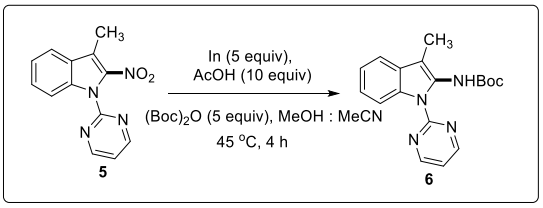
A mixture of **2a** (0.2 mmol, 73.0 mg), $PdCl_2(PPh_3)_2$(5 mol%, 5.0 mg), CuI (5 mol%, 1.0 mg), phenylacetylene (0.24 mmol., 27 ul) in (Et_3N: THF = 1:1) 2 ml was stirred at 60 °C in a 25 ml sealed tube for 12 h. After completed, the solvent were evaporated under reduced pressure and then purified directly *via* chromatography on silica gel to afford **4** as a yellow oil in 85% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.69 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.31 (t, *J* = 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.67, 156.29, 142.35, 136.01, 132.24, 129.55, 129.42, 128.59, 126.55, 124.42, 122.63, 122.44, 119.06, 114.06, 106.54, 100.50, 79.22. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{13}N_4O_2$ $[M+H]^+$ 341.1039, found 341.1037.

3-methyl-2-nitro-1-(pyrimidin-2-yl)-1*H*-indole (5)



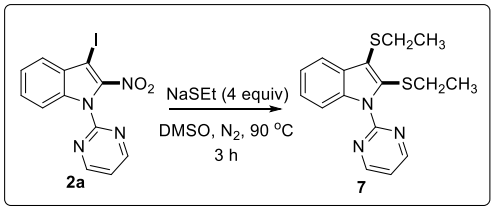
A mixture of **2a** (0.2 mmol, 73.0 mg), Pd (PPh_3)$_4$(10 mol%, 23.1 mg), Ag_2CO_3 (0.2 mmol, 55.0 mg), $CH_3B(OH)_2$ (0.6 mmol, 36.0 mg) in MeCN (3 ml)was stirred at 90 °C in a 25 mL sealed tube for 5 h. After the reaction finished, the resulting mixture was cooled to room temperature, filtered through a pad of silica gel and washed with 100 mL 50% EtOAc/ petroleum ether. Then the solvents were evaporated under reduced pressure and then purified *via* chromatography on silica gel to afford **5** as a yellow solid in 86% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 2.67 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.48, 156.97, 140.12, 136.62, 129.21, 126.94, 123.54, 122.17, 121.85, 118.33, 113.86, 10.07. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{11}N_4O_2$ $[M + H]^+$ 255.0882, found 255.0883.

***tert*-butyl (3-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)carbamate (6)[5]**



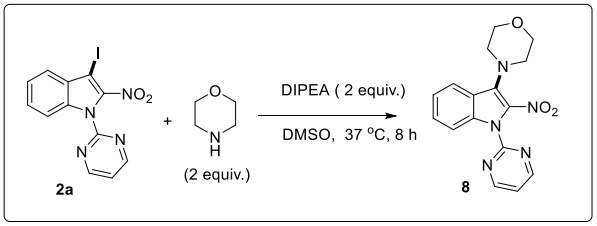
To a stirred mixture of **5** (0.1 mmol, 25.4 mg), AcOH (1 mmol, 60 ul), and di-*tert*-butyl dicarbonate (0.5 mmol, 109 mg) in MeOH: MeCN (3:1) 2 ml at rt was added indium metal (0.5 mmol, 57.5 mg). The reaction mixture was stirred for 4 h at 45 °C. After cooling to rt, the opaque solution was filtered through Celite and the filtrate was concentrated in vacuo. The resulting residue was diluted with ethyl acetate and washed with saturated $NaHCO_3$ to remove the acetic acid. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Column purification (5:1 petroleum ether /ethyl acetate) gave **6** as a white solid (Yield: 65 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.47 – 8.39 (m, 1H), 7.57 – 7.47 (m, 1H), 7.29 – 7.20 (m, 2H), 7.09 (t, *J* = 4.8 Hz, 1H), 2.26 (s, 3H), 1.47 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.95, 152.91, 133.96, 129.65, 129.17, 123.41, 122.17, 118.31, 116.17, 114.30, 109.76, 80.57, 28.30, 9.35; **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{21}N_4O_2$ $[M + H]^+$ 325.1665, found 325.1663.

2,3-bis(ethylthio)-1-(pyrimidin-2-yl)-1*H*-indole (7)



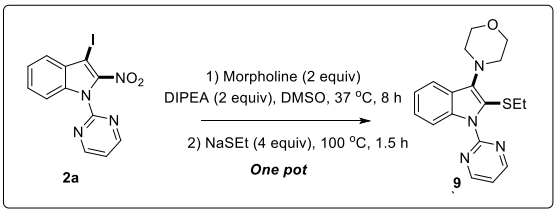
Under nitrogen atmosphere, a mixture of **2a** (0.2 mmol ,73 mg), EtSNa (0.8 mmol, 67.2 mg), and DMSO (2 ml) was stirred in a reaction tube at 90 °C for 3 h. The resulting mixture was then quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried by sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel. The product 2,3-bis(ethylthio)-1-(pyrimidin-2-yl)-1*H*-indole **7** was obtained as a red oil (Yield: 73%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.8 Hz, 2H), 7.91 – 7.85 (m, 1H), 7.83 – 7.76 (m, 1H), 7.33 – 7.25 (m, 3H), 3.02 (q, *J* = 7.4 Hz, 2H), 2.92 (q, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.4 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.36, 157.25, 137.37, 135.58, 130.65, 124.65, 122.24, 119.67, 118.50, 118.41, 112.56, 31.33, 29.88, 15.23, 14.54; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{18}N_3S_2$ $[M + H]^+$ 316.0942, found 316.0944.

4-(2-nitro-1-(pyrimidin-2-yl)-1*H*-indol-3-yl)morpholine (8)



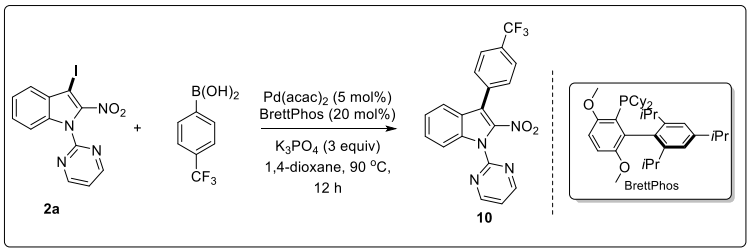
A mixture of **2a** (0.1 mmol, 36.5 mg), Morpholine (0.2 mmol, 17.4 ul), DIPEA (0.2 mmol, 34.8 ul), in DMSO (1.5 ml) was stirred at 37 °C in a 25 ml sealed tube for 8 h. After the reaction finished, the resulting reaction was diluted with ethyl acetate and washed with saturated NaCl, and the combined organic layer was dried by sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel. It is noteworthy that the product **8** is unstable under acidic condition which will degrade slowly, it is critical for column chromatography quickly or using neutral column chromatography for purification.The product 4-(2-nitro-1-(pyrimidin-2-yl)-1*H*-indol-3-yl)morpholine **8** was obtained as a yellow solid (Yield: 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 8.6 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 3.99 (t, *J* = 4.5 Hz, 4H), 3.85 (t, *J* = 4.8 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.27, 157.38, 141.31, 137.71, 130.75, 123.95, 123.04, 121.41, 117.65, 114.19, 67.65, 53.95; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{16}N_5O_3$ $[M + H]^+$ 326.1253, found 326.1250.

4-(2-(ethylthio)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl)morpholine (9)



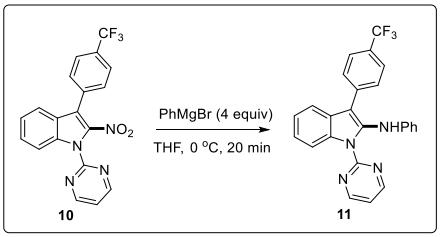
A mixture of **2a** (0.2 mmol, 73.0 mg), Morpholine(0.4 mmol, 35 ul), DIPEA (0.4 mmol, 70 ul), in DMSO (2 ml) was stirred at 37 °C in a 25 mL sealed tube for 8 h, without further purification, NaSEt (0.8 mmol, 67.2 mg) was added to the tube, and raising the temperature to 100 °C for 1.5 h. After the reaction finished, the resulting reaction was diluted with ethyl acetate and washed with saturated NaCl, and the combined organic layer was dried by sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel. The product 4-(2-(ethylthio)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl)morpholine **9** was obtained as a yellow oil (Yield: 55%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.23 (m,1H), 7.16 – 7.21 (m, , 2H), 3.91 (t, *J* = 4.6 Hz, 4H), 3.48 (t, *J* = 4.6 Hz, 4H), 2.92 (q, *J* = 7.4 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.09, 157.32, 137.78, 136.53, 125.43, 124.32, 122.09, 121.38, 119.18, 117.51, 112.75, 68.02, 51.93, 31.24, 14.34; **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{21}N_4OS$ $[M + H]^+$ 341.1436, found 341.1432.

2-nitro-1-(pyrimidin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1*H*-indole (10)



A mixture of **2a** (0.2 mmol, 73.0 mg), Pd (acac)$_2$(5 mol%, 3.4 mg), BrettPhos (20 mol%, 21.5 mg), (4-(trifluoromethyl)phenyl)boronic acid (0.3 mmol, 57.0 mg), K_3PO_4 (0.6 mmol,127.2 mg) in 1,4-dioxane (3 ml) was stirred at 90 °C in a 25 ml sealed tube for 12 h. After completed, cooling to rt, the opaque solution was filtered through Celite and the filtrate was concentrated in vacuo. Column purification (5:1 petroleum ether /ethyl acetate) gave **10** as a yellow oil (Yield: 84%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.70 (m, 4H), 7.63 – 7.53 (m, 2H), 7.40 – 7.32 (m, 1H), 7.30 (t, *J* = 4.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.66, 156.54, 138.86, 135.59, 133.60, 130.96, 129.14, 125.89 (d, *J* = 11.1 Hz), 125.17, 125.47, 124.39, 123.01, 122.28, 121.55, 118.75, 114.23; **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{12}F_3N_4O_2$ $[M + H]^+$ 385.0912, found 385.0910.

***N*-phenyl-1-(pyrimidin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1H-indol-2-amine (11)[6]**



Under N_2 atmosphere, to a solution of 10 (0.1 mmol, 38.4 mg) was addded PhMgBr (1M in THF solution) (0.4 mmol, 0.4 ml) dropwise with the color of the solution changes from yellow to brown slowly. The reaction mixture was stirred at 0 °C for 20 min and then quenched with sat. NH4Cl (0.5 ml), which was extracted with EtOAc (3 × 20 ml). The combined organic layers were washed with brine (2 × 15 ml), dried over Na_2SO_4, and evaporated. Chromatography of the residue on silica gel, eluting with a PE–EtOAc gradient to give 11, as a pale brown oil (Yield: 41%).1H NMR (500 MHz, CDCl3) δ 11.14 (s, 1H), 8.73 (d, J = 4.8 Hz, 2H), 8.45 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.38 – 7.27 (m, 6H), 7.19 – 7.13 (m, 2H), 7.12 (t, J = 4.8 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 167.33, 158.70, 157.56, 148.59, 143.87, 141.20, 133.08, 129.49, 128.86, 128.42, 127.35, 126.13, 125.31, 125.17, 125.14, 124.05, 123.15, 116.63, 115.92, 62.48; HRMS (ESI-TOF) m/z calcd for C25H18F3N4 [M + H]+ 431.1484, found 431.1480.

8. References

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[2] (a) Tu, D.; Cheng, X.; Gao, Y.; Yang, P.; Ding, Y.; Jiang, C. *Org. Biomol. Chem.* **2016**, *14*, 7443 – 7446. (b) Zhao, J.; Cheng, X.; Le, J.; Yang, W.; Xue, F.; Zhang, X.; Jiang, C. *Org. Biomol. Chem.* **2015**, *13*, 9000 – 9004.

[3] (a) Wu, J.-Q. ; Yang, Z. ; Zhang, S.-S.; Jiang, C.-Y. ; Li, Q. , Huang, Z.-S. ; Wang, H. *ACS Catal.* **2015**, *5*, 6453 – 6457. (b) Shi, J.; Zhou, B.; Yang, Y.; Li, Y. *Org. Biomol. Chem.* **2012**, *10*, 8953–8955. (c) Kou, X.; Zhao, M.; Qiao, X.; Zhu, Y.; Tong, X.; Shen, Z. *Chem. Eur. J.* **2013**, *19*, 16880 – 16886.

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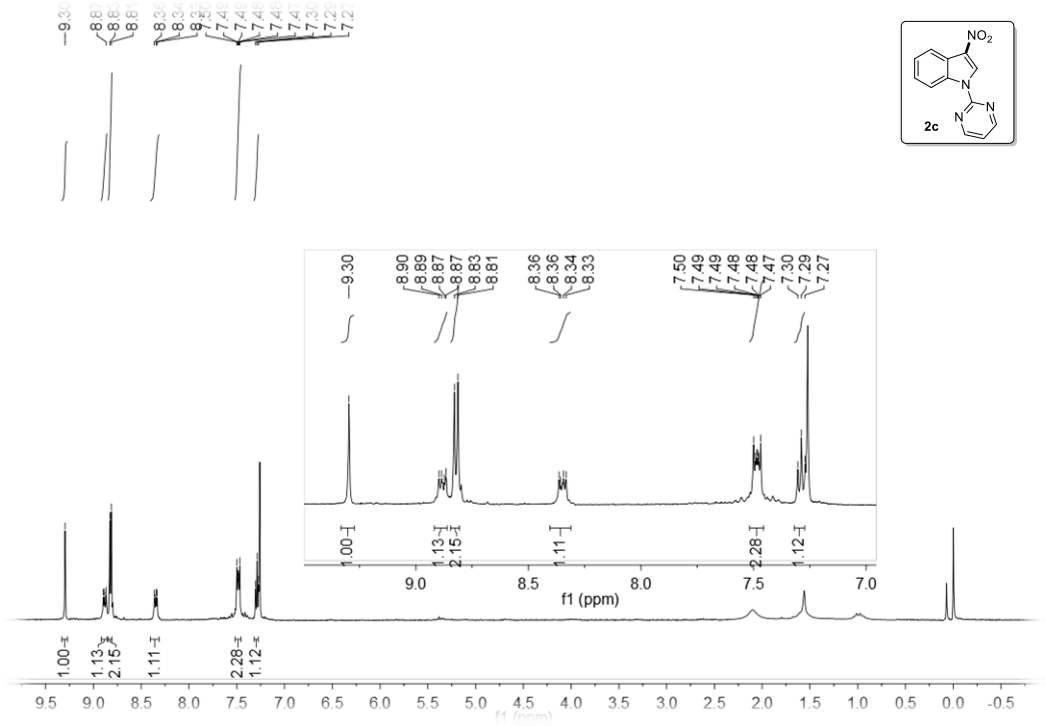
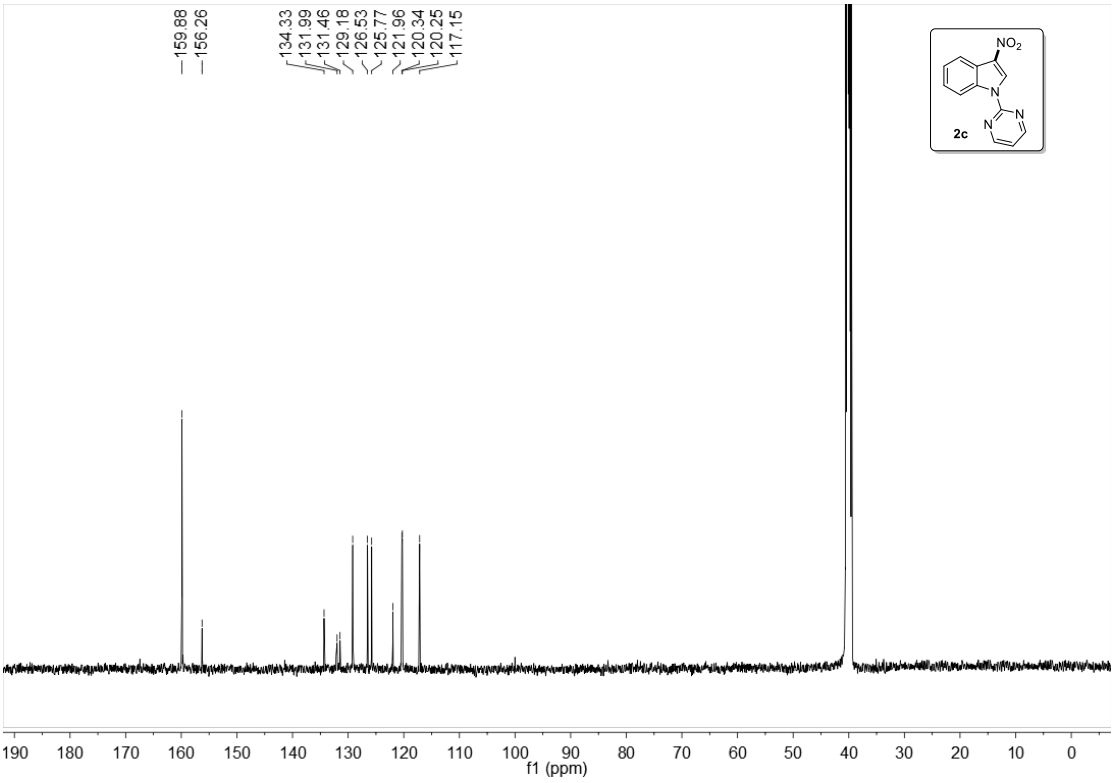
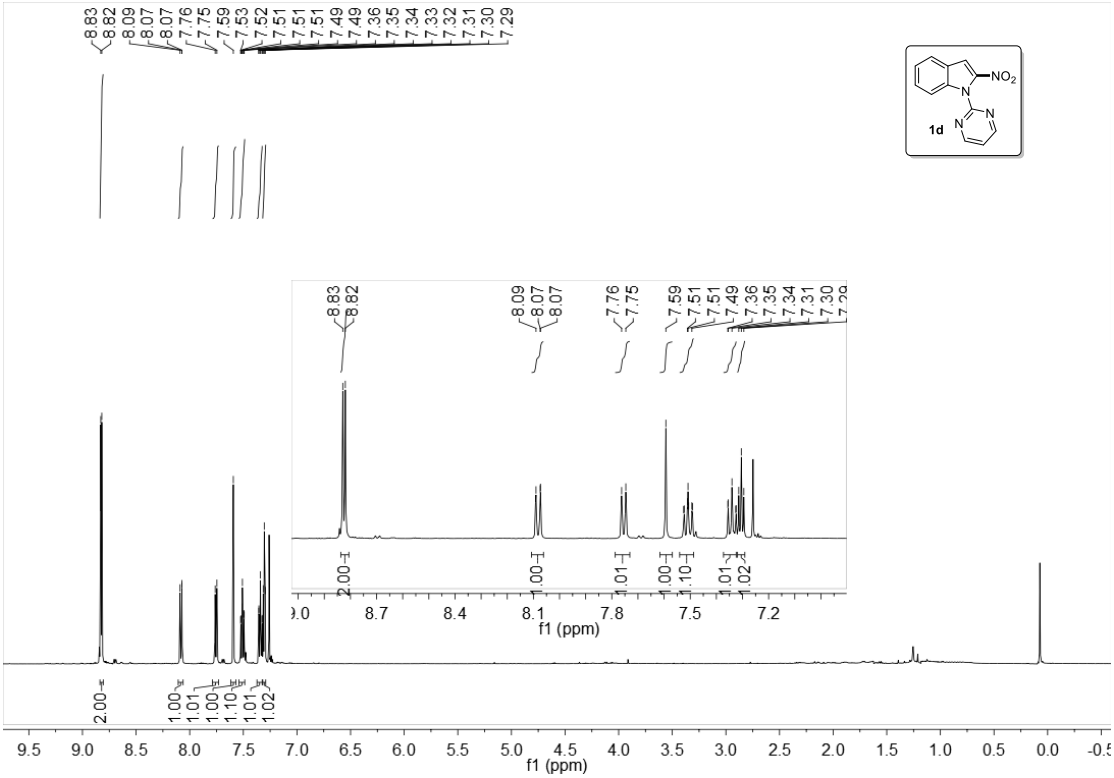
[6] Sánchez ,J. D.; Avendaño, C.; Menéndez, J. C. *Synlett.* **2008**, *9*, 1371–1375.

9. ^{1}H and ^{13}C NMR spectras



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7.49
7.49
7.36
7.35
7.34
7.33
7.32
7.31
7.30
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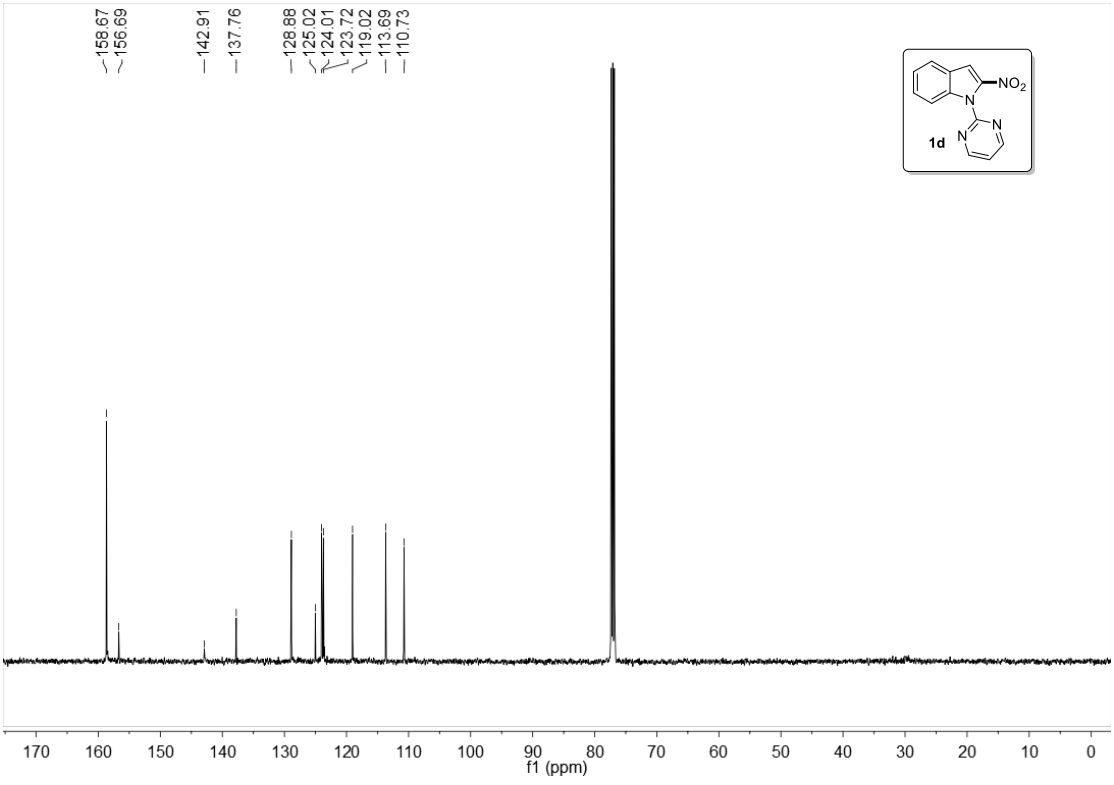
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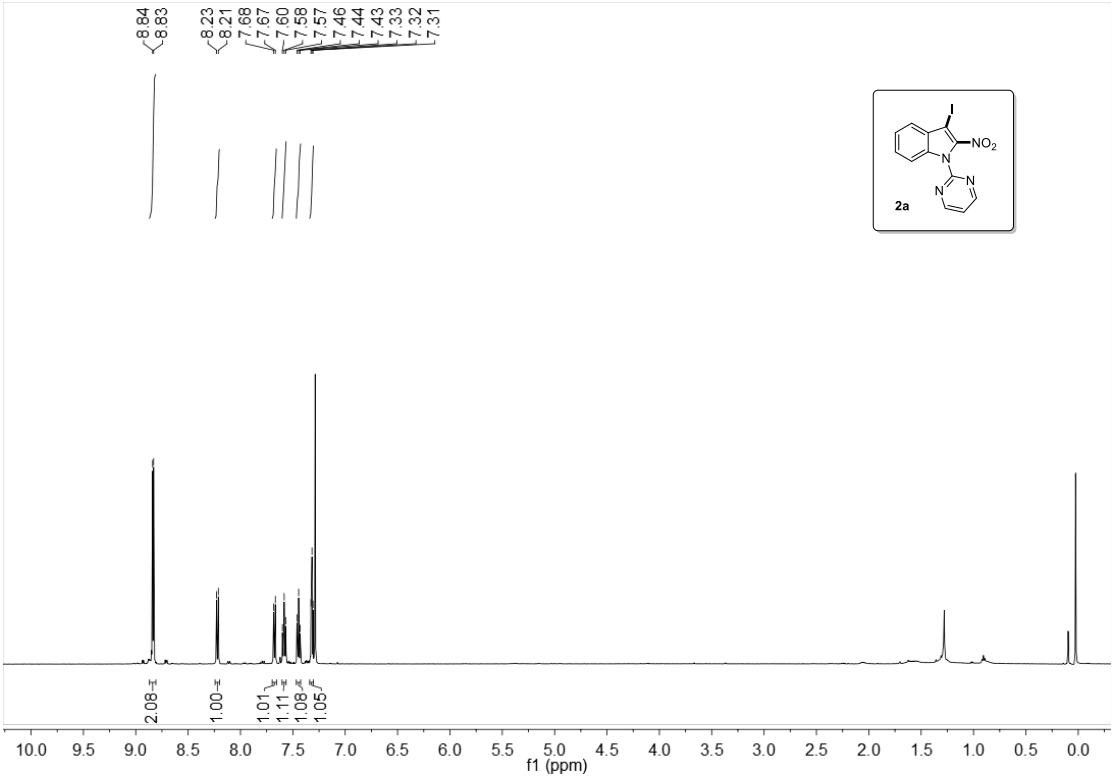
f1 (ppm)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7.32
7.31
I
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N
N
N
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2.08
1.00
1.01
1.11
1.08
1.05
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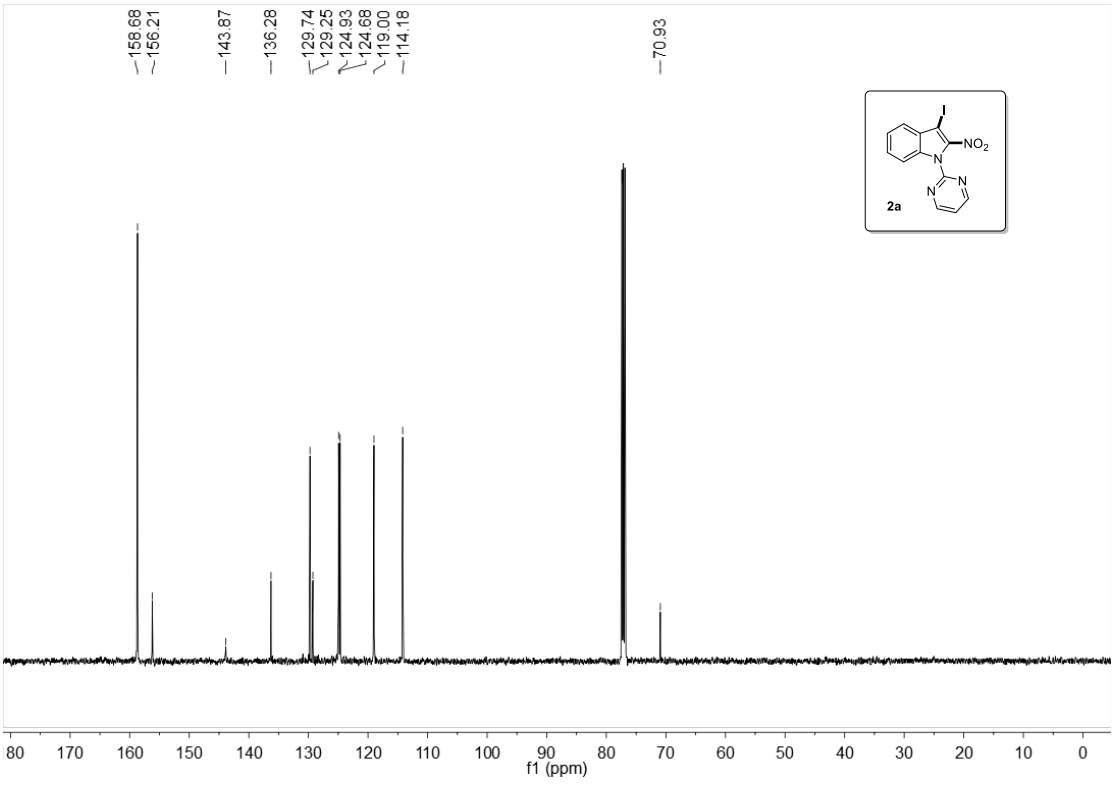
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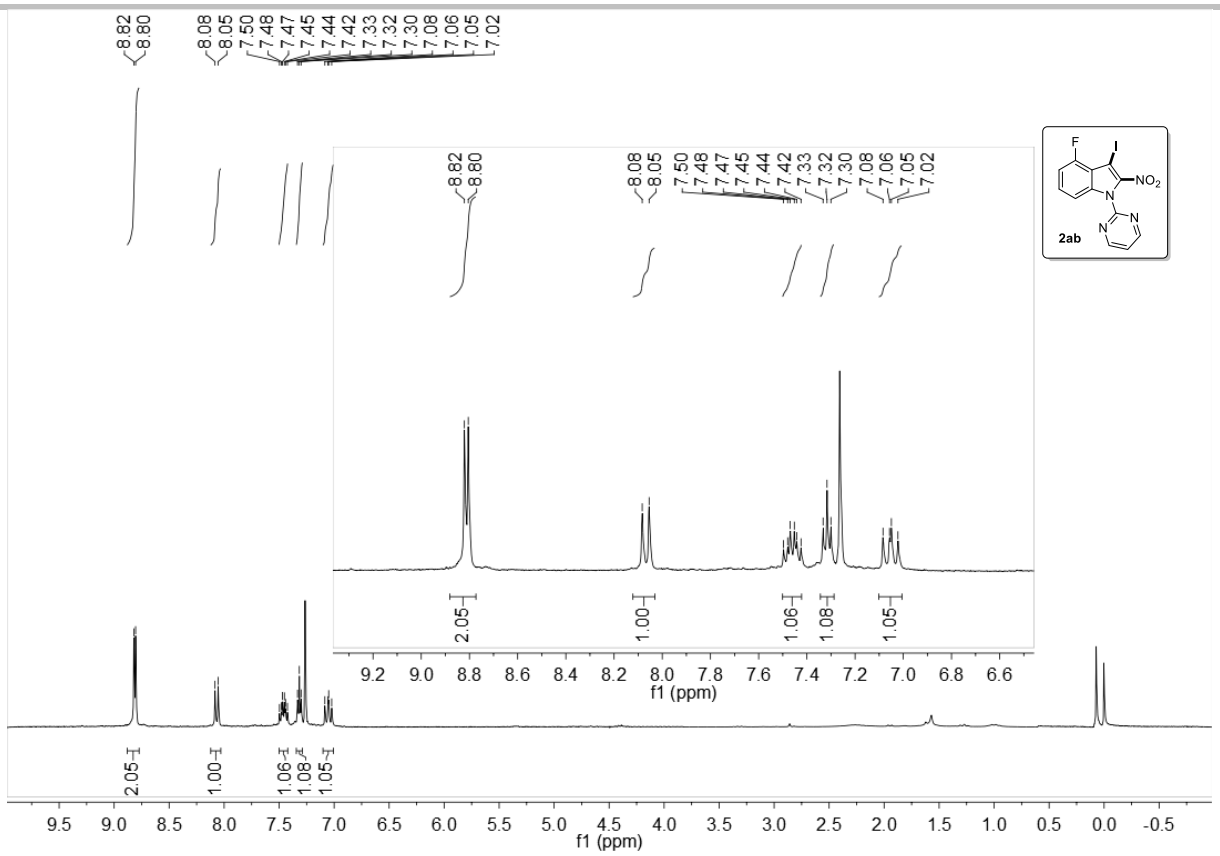
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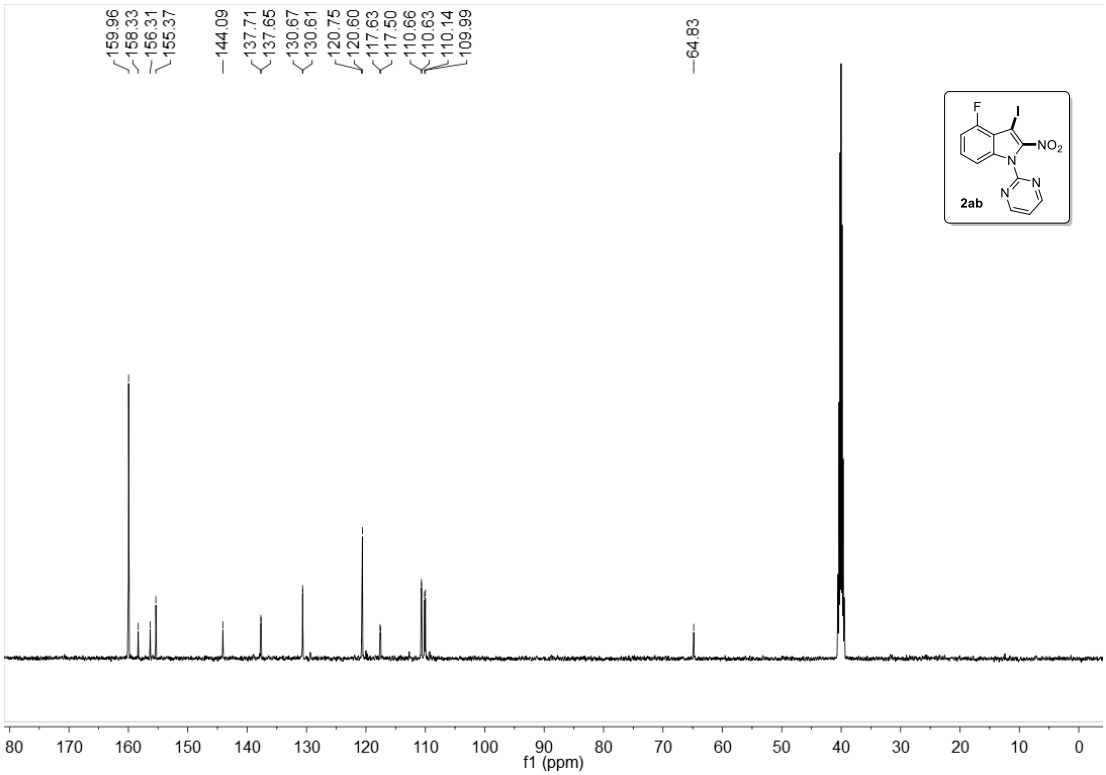
NO2
N
N
2ab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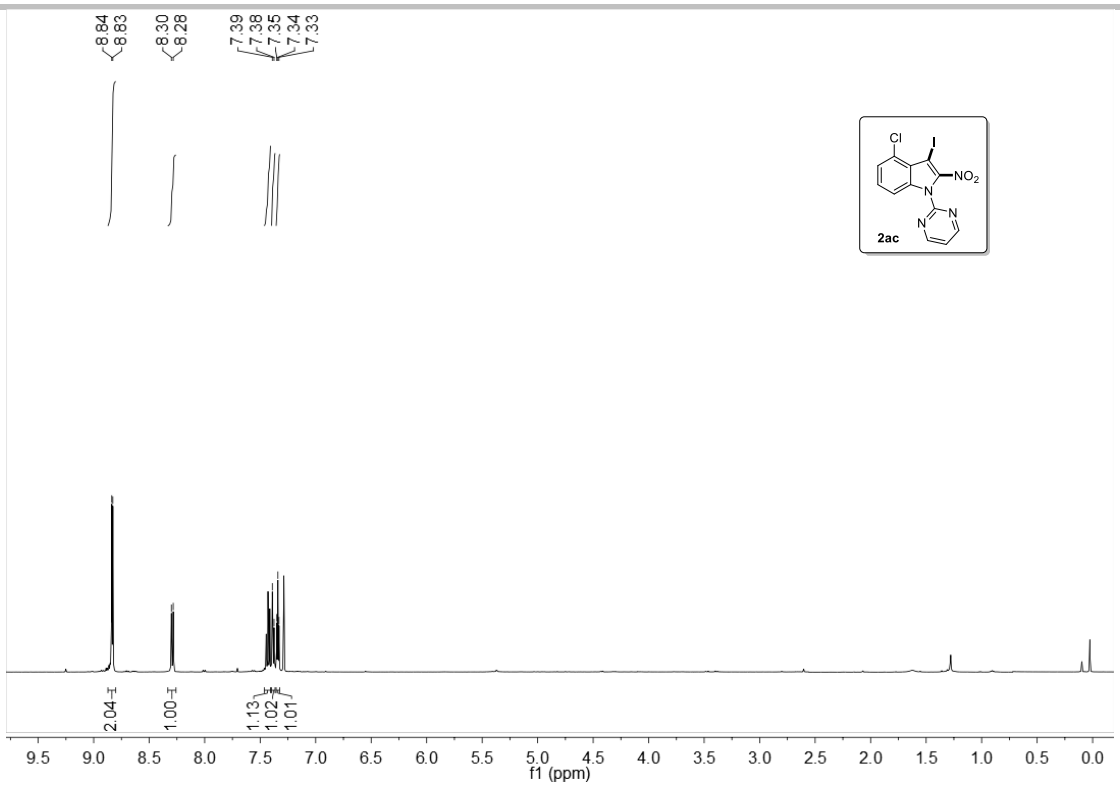
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1.02
1.01
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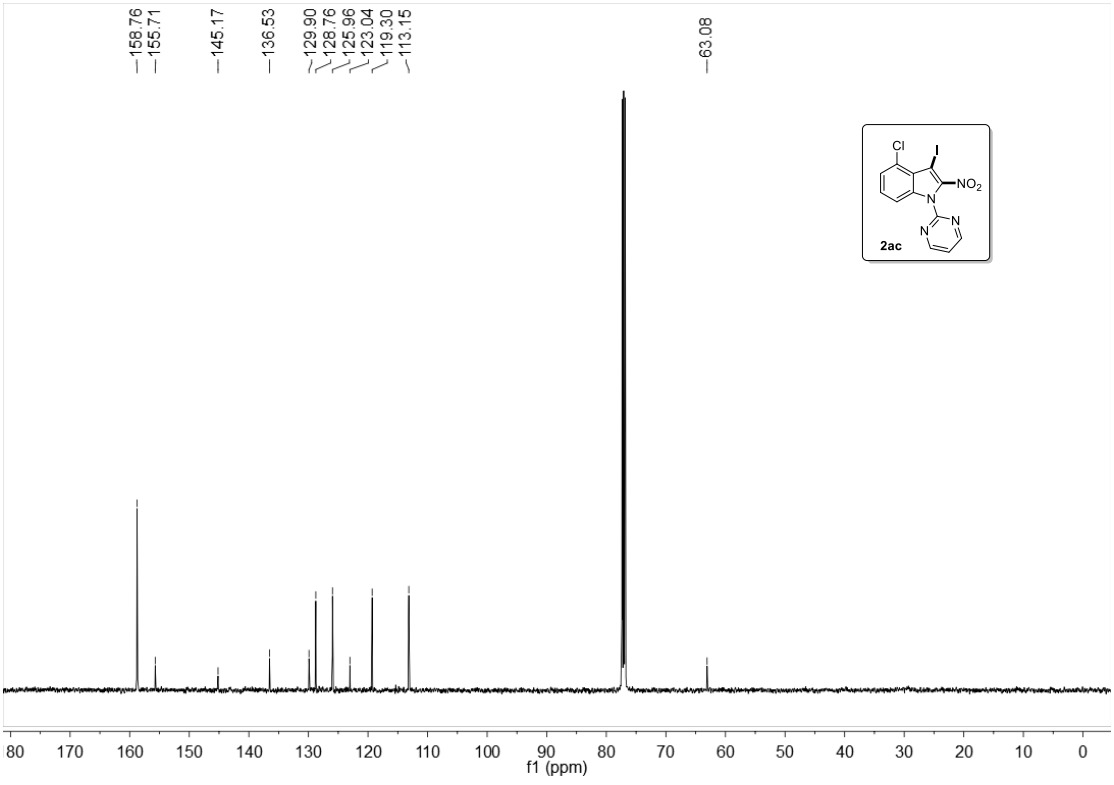
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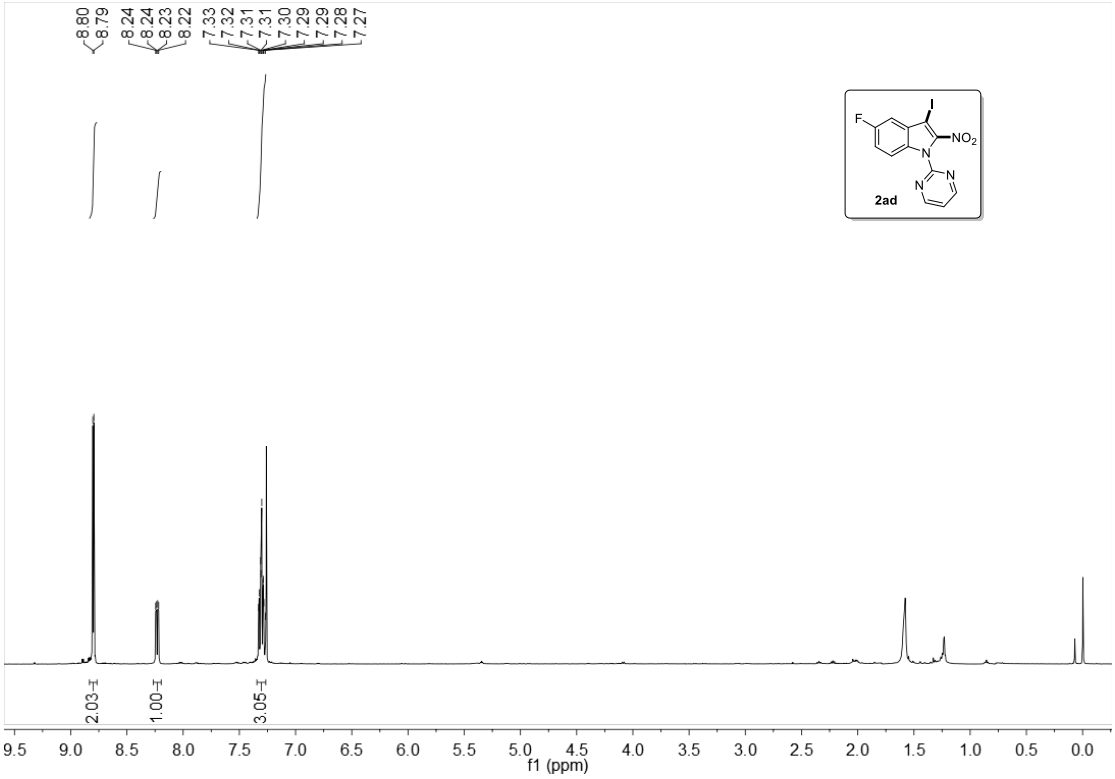
f1 (ppm)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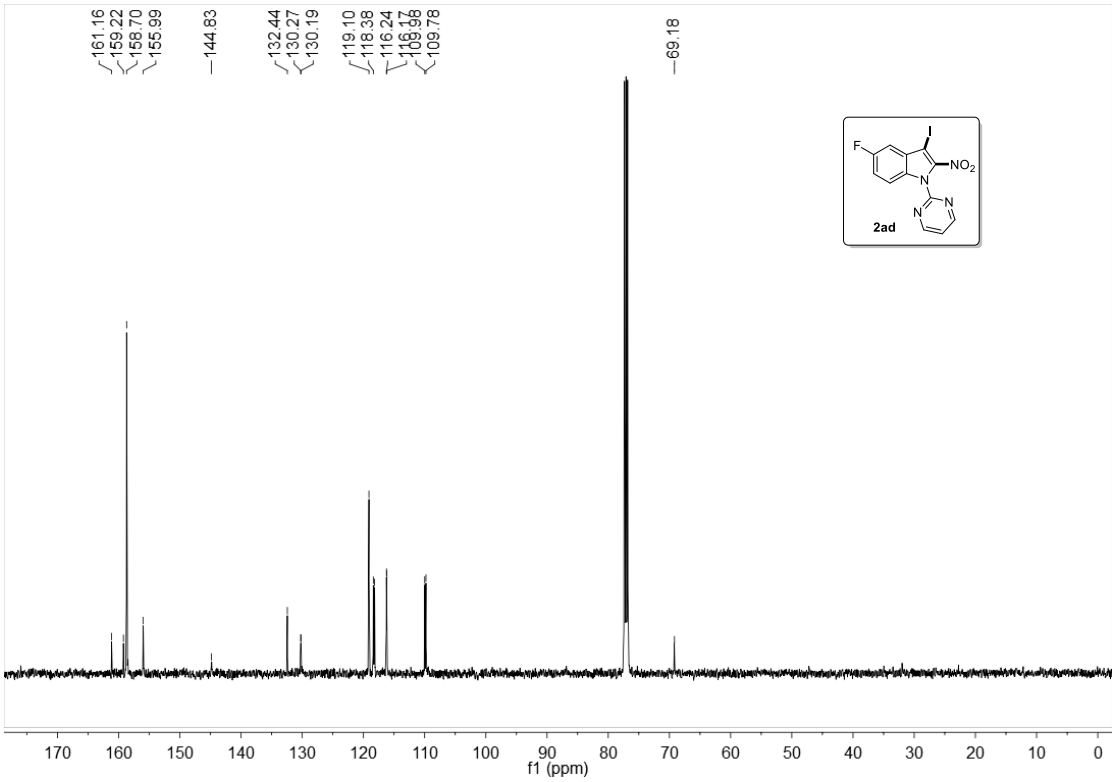
f1 (ppm)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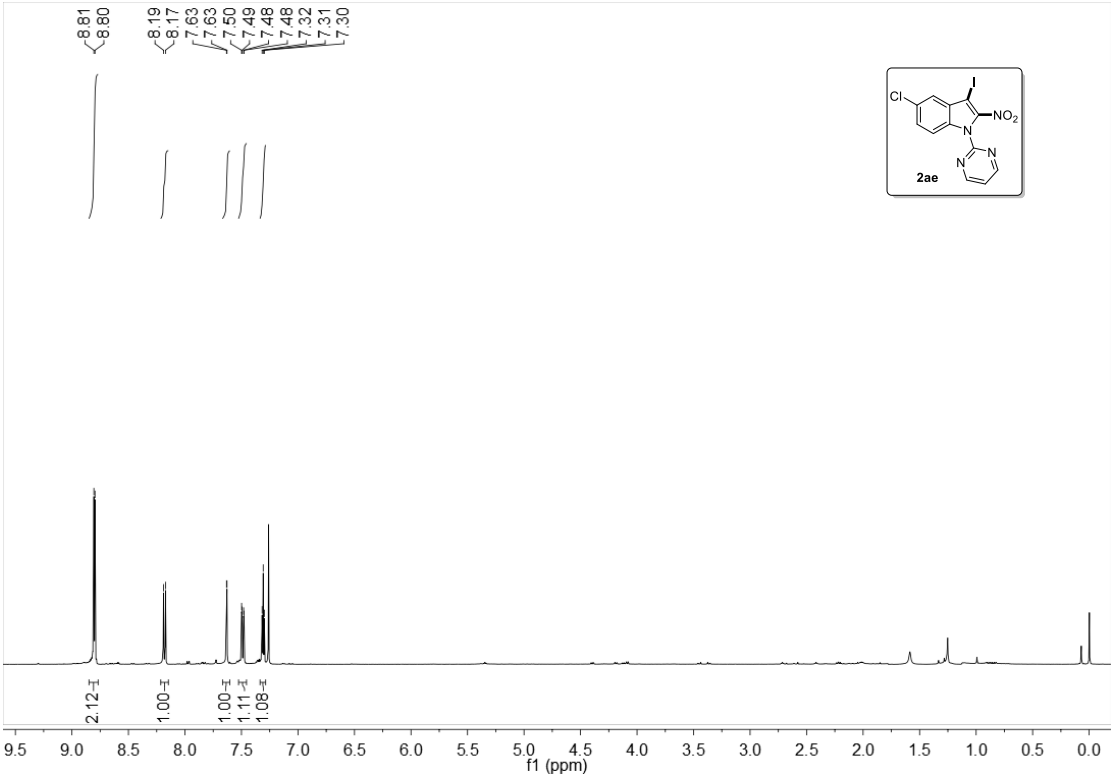
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1.00
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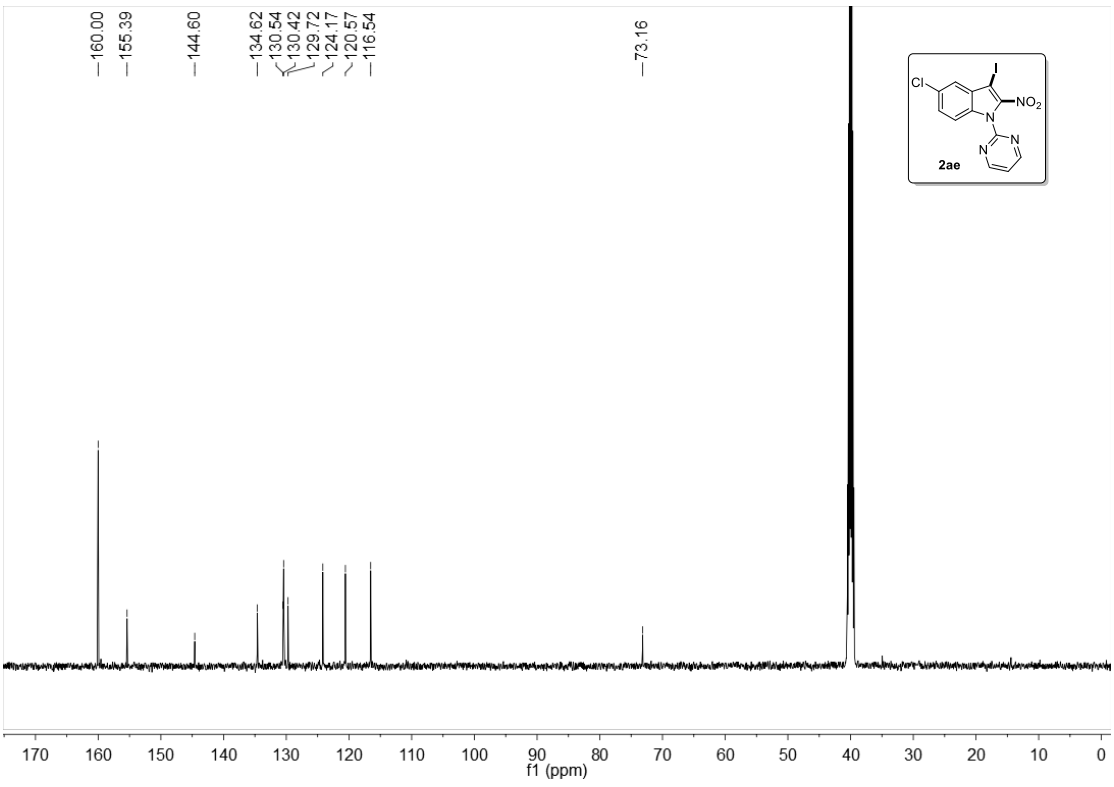
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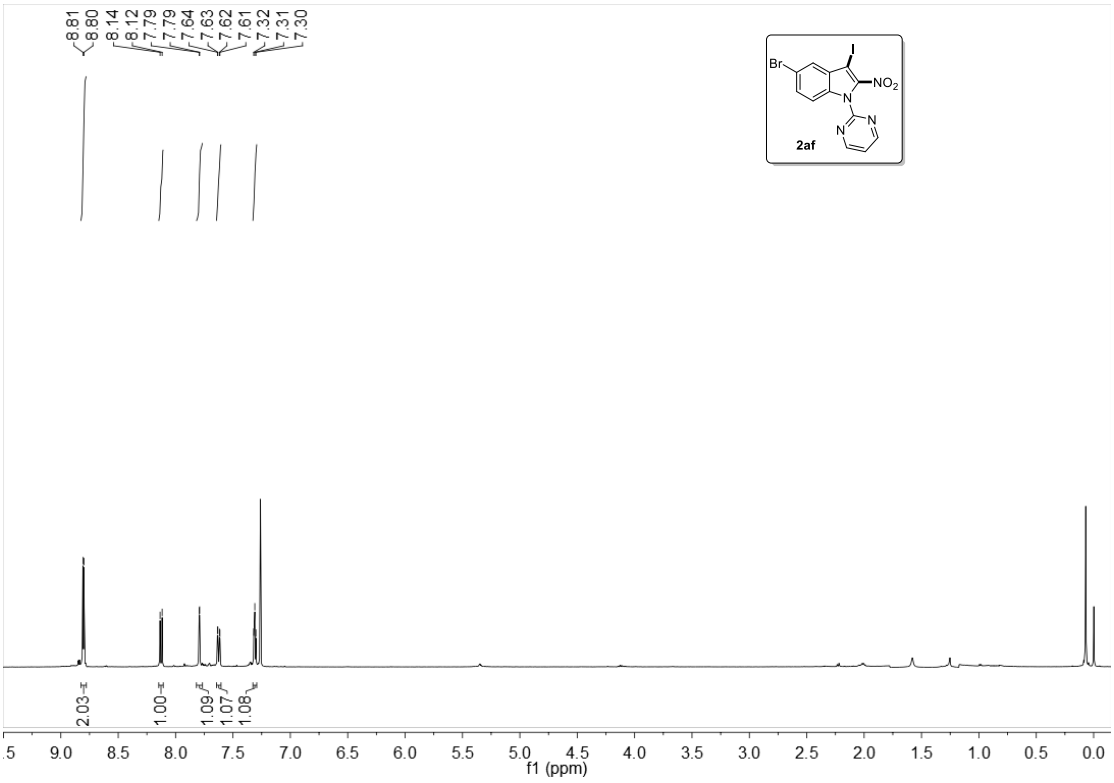
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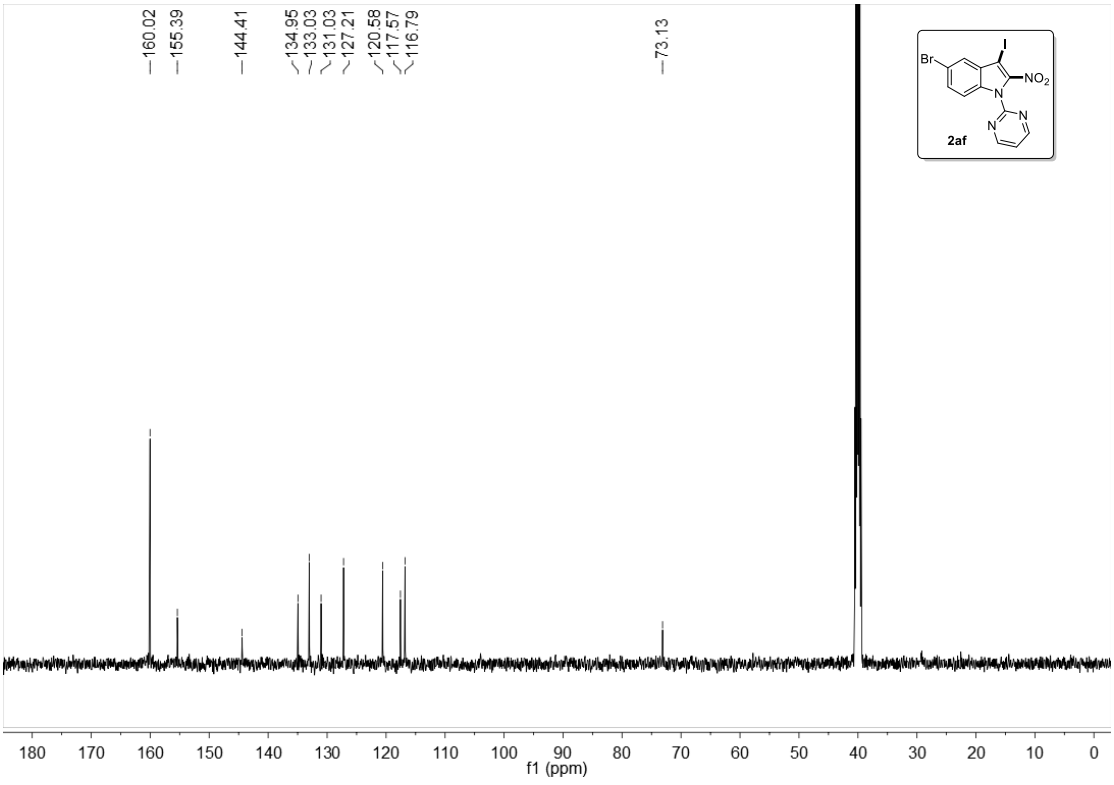
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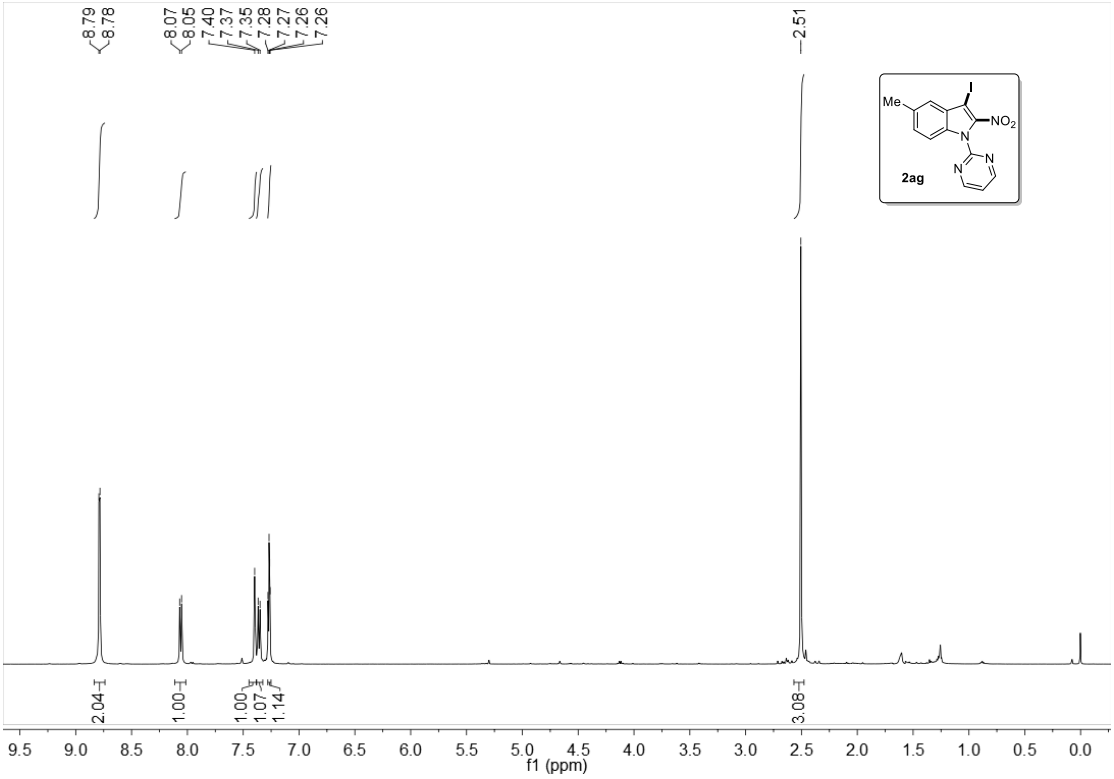
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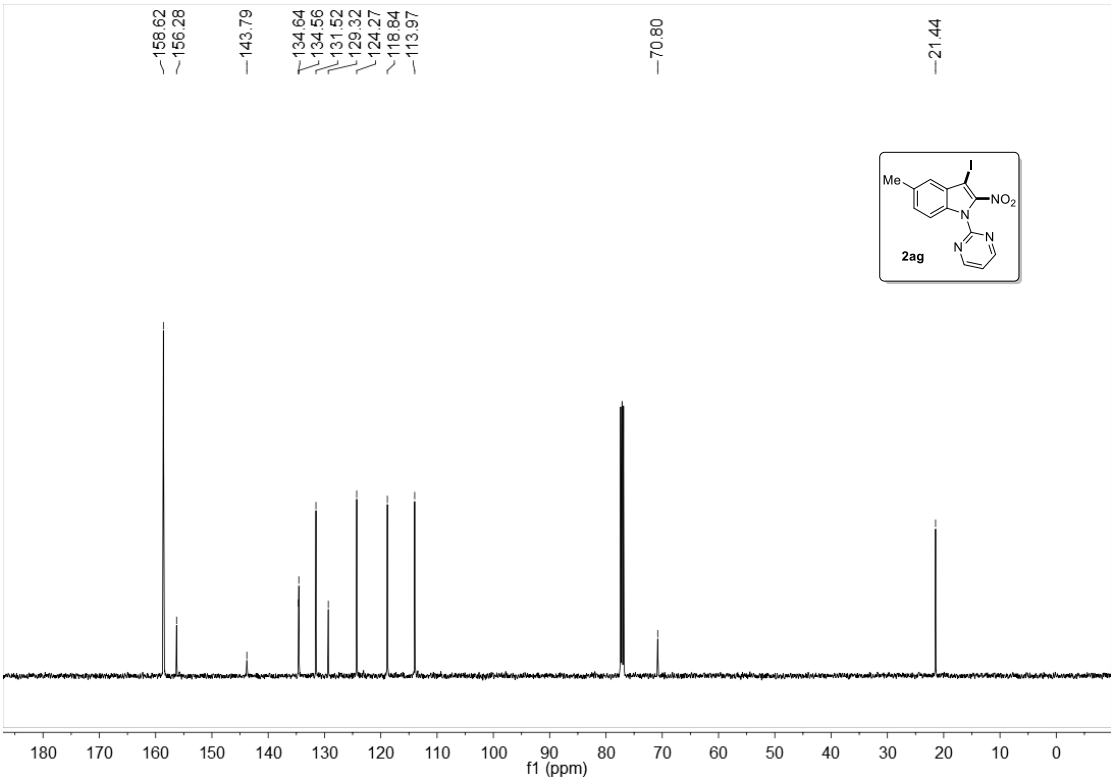
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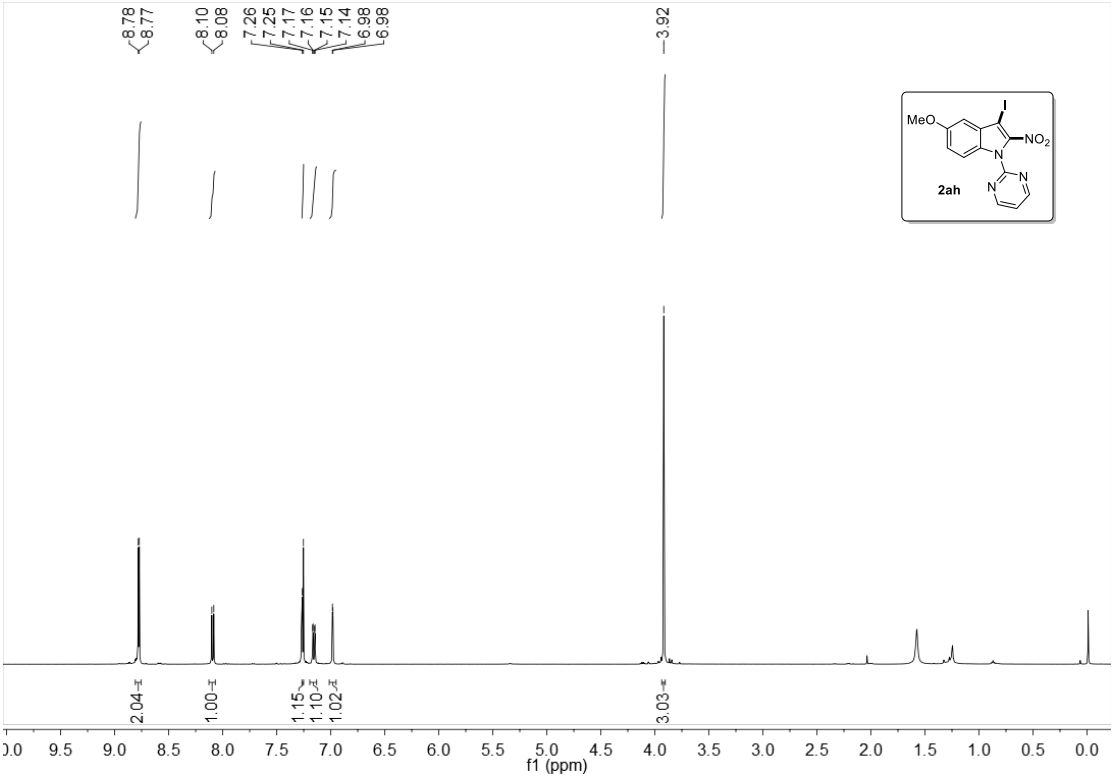
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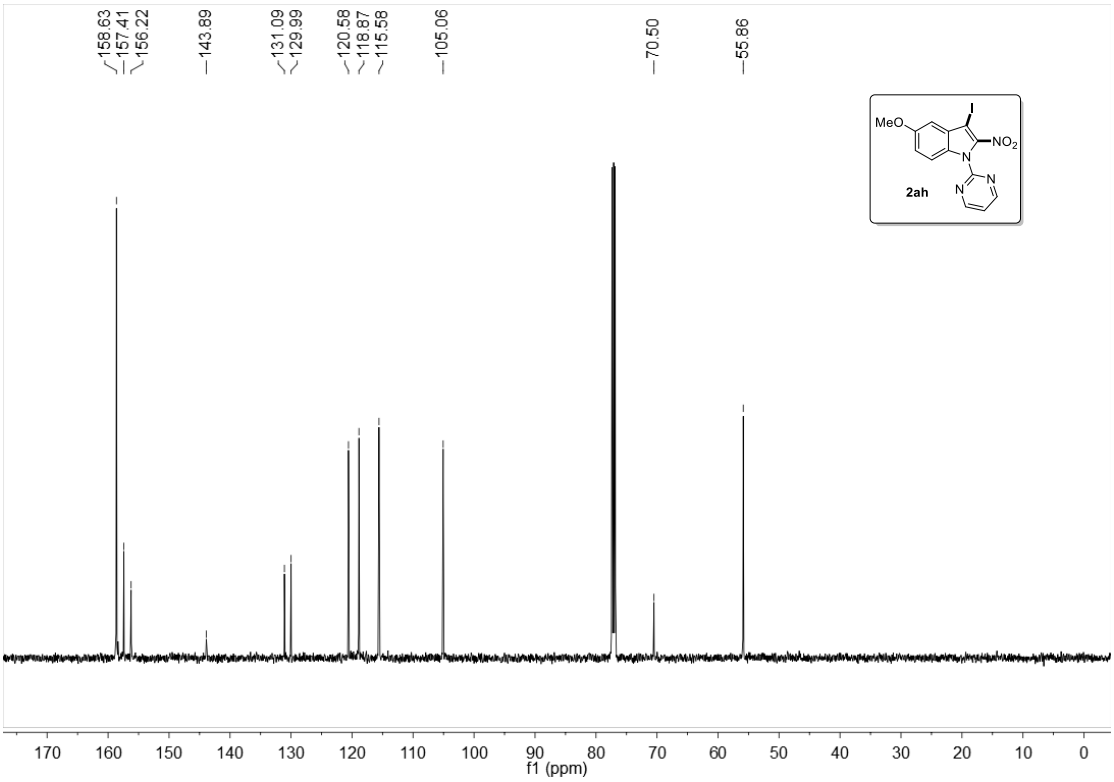
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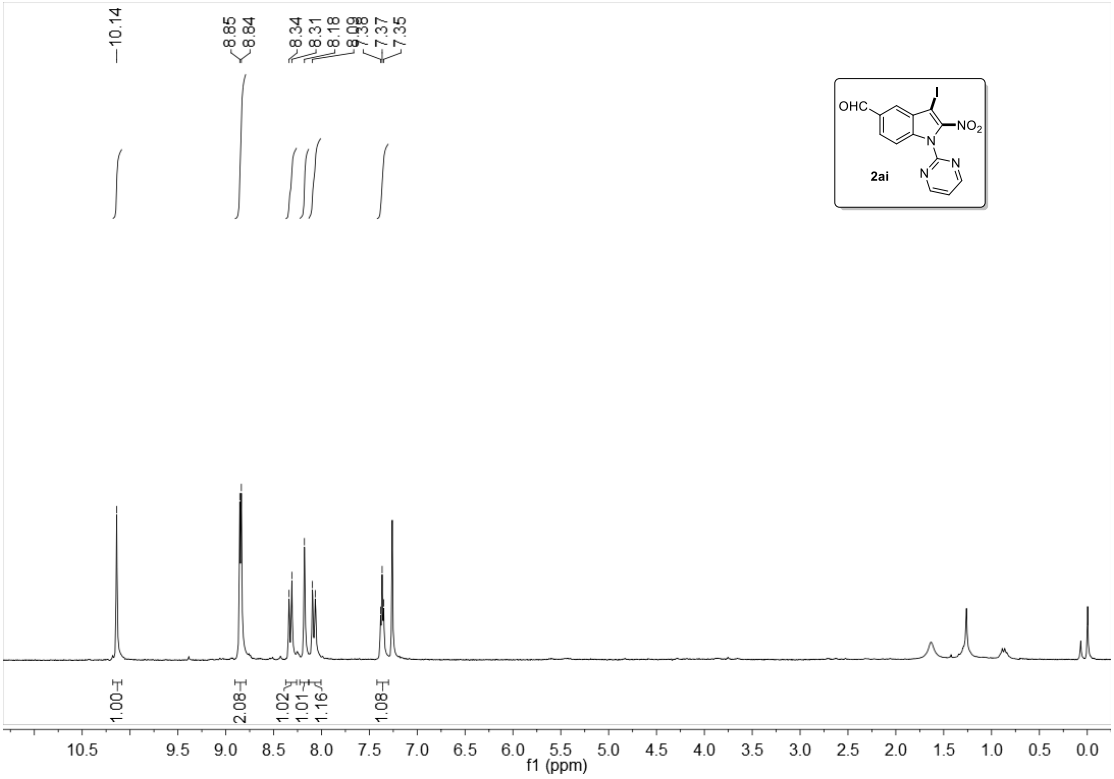
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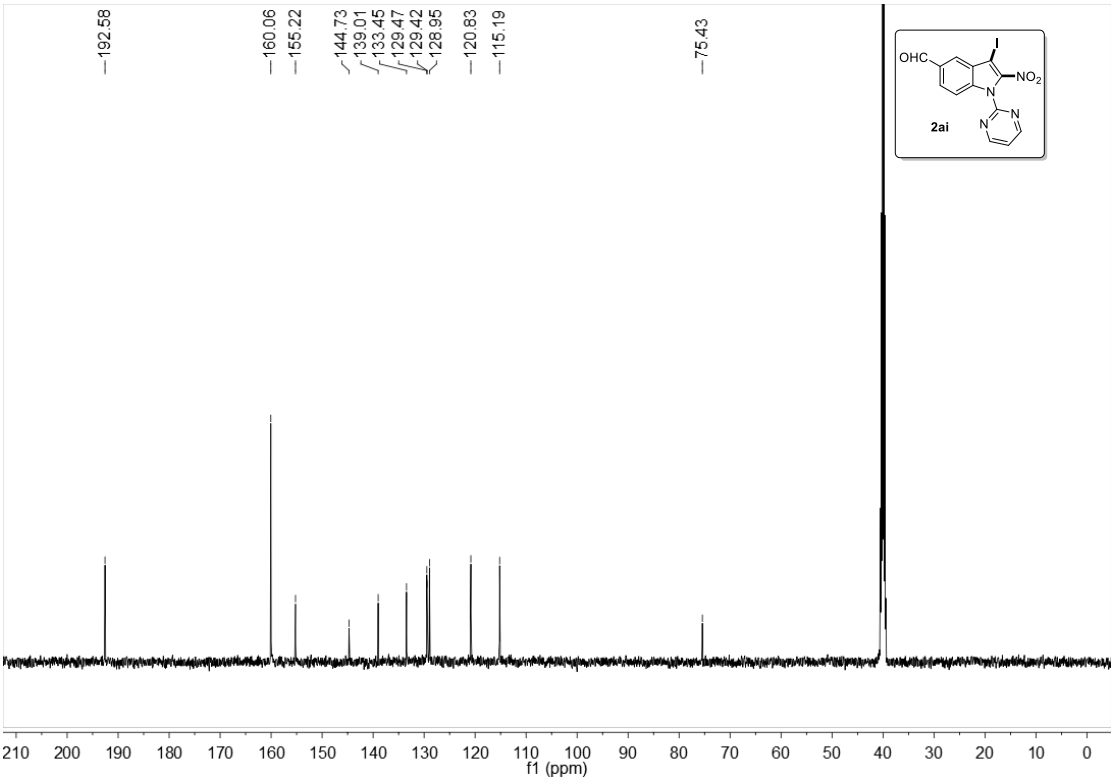
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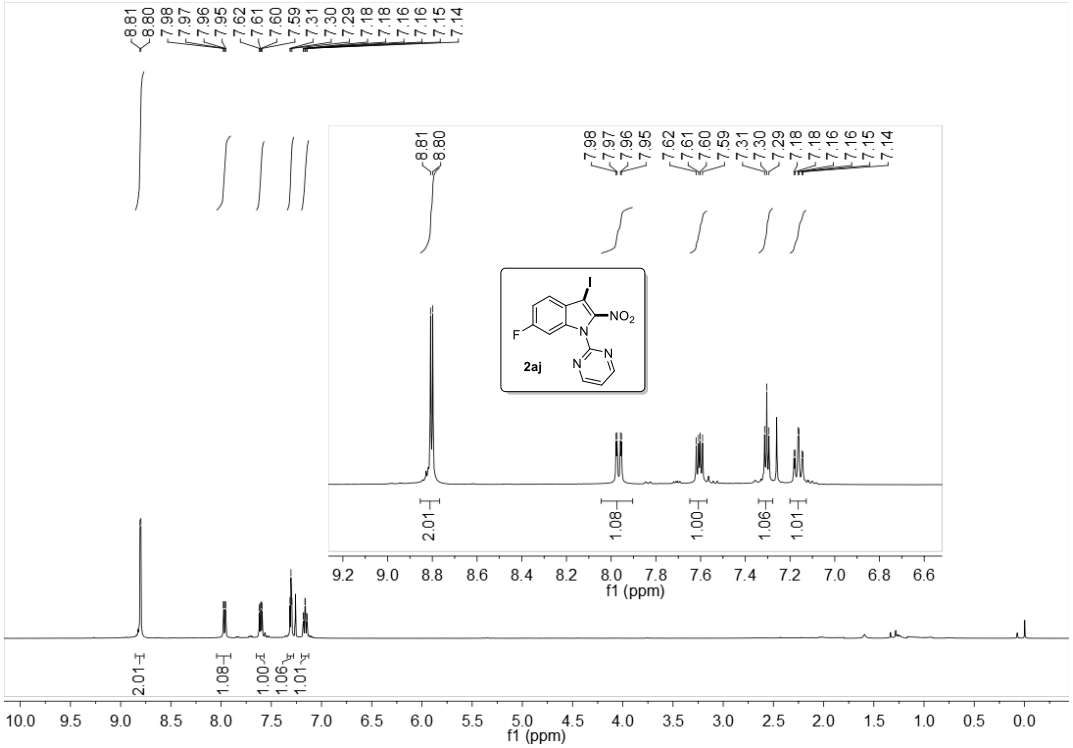
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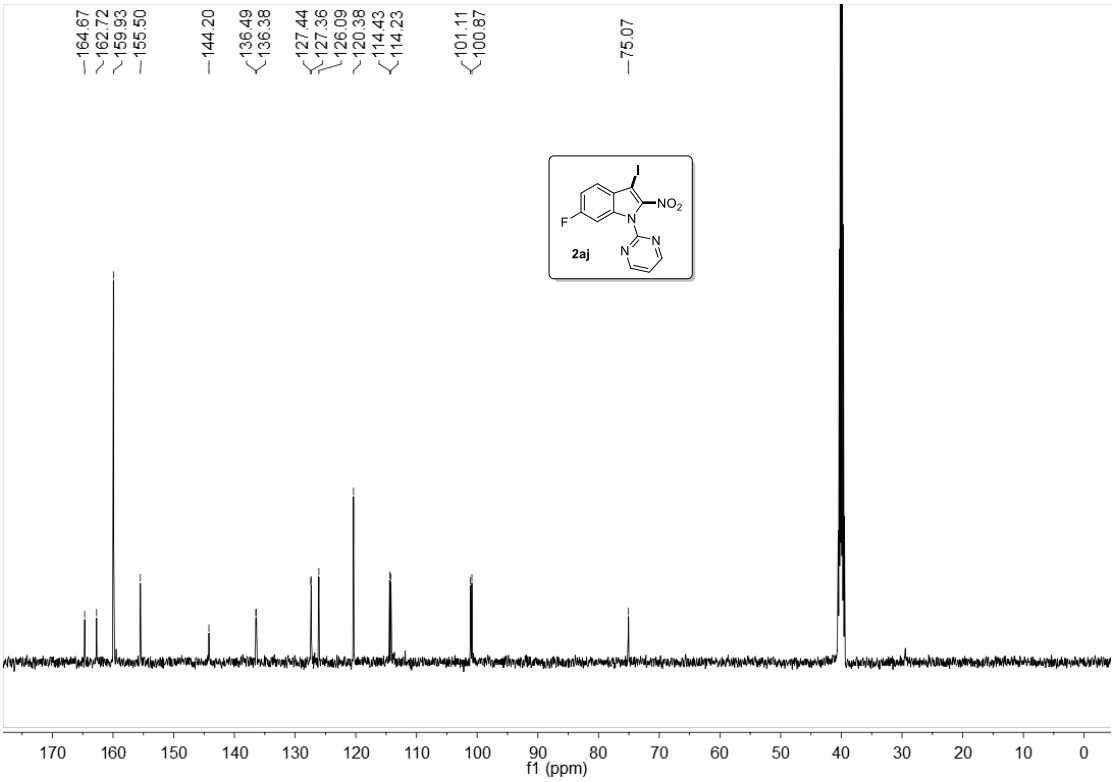
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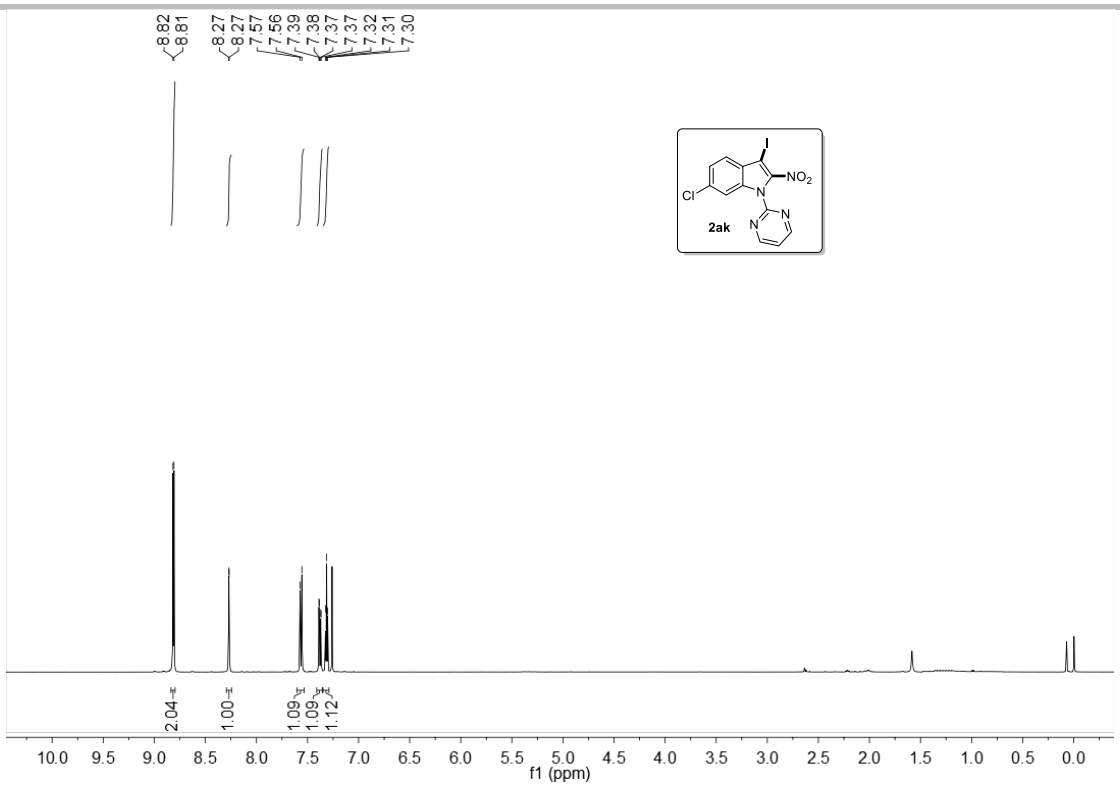
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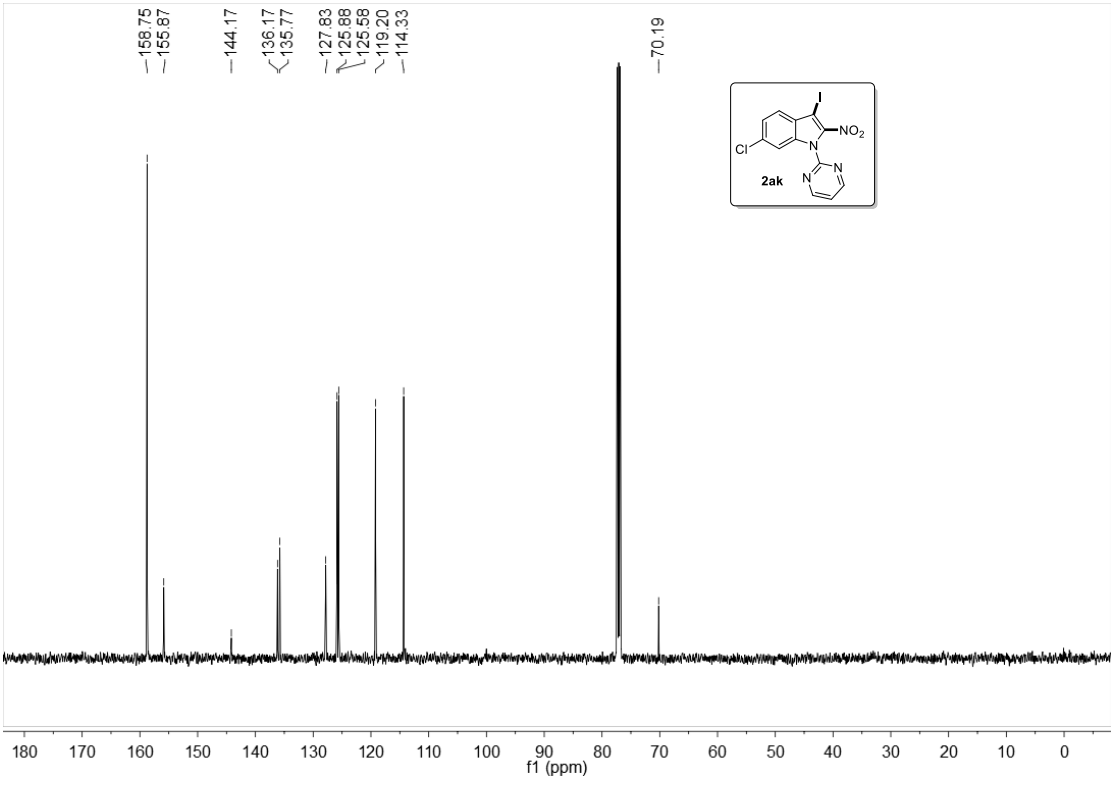
f1 (ppm)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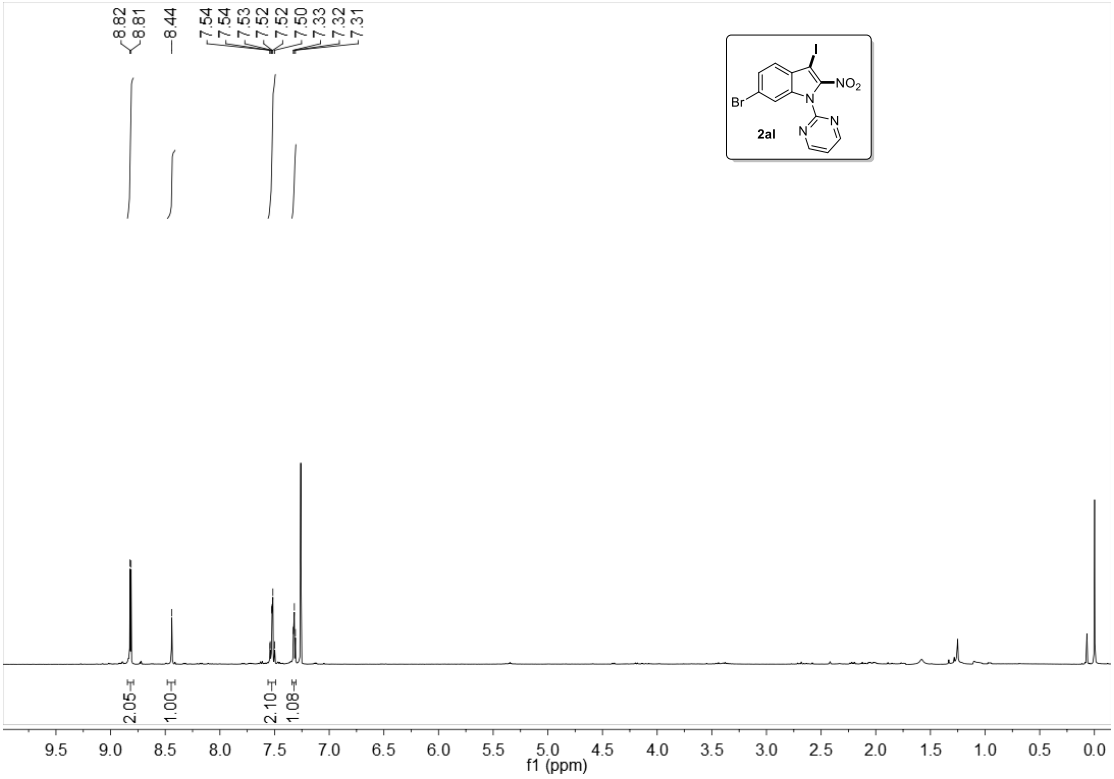
155.87
144.17
136.17
135.77
127.83
125.88
125.58
119.20
114.33
70.19
I
NO2
Cl
N
N
N
2ak
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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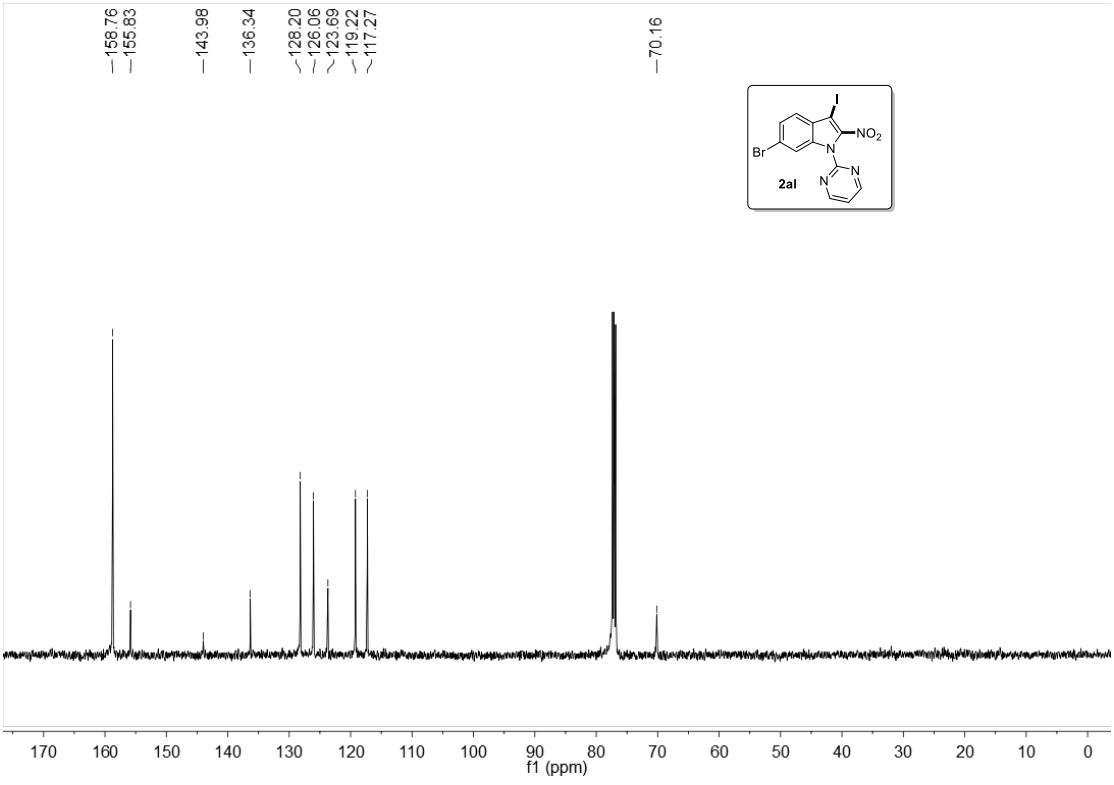
8.81
8.44
7.54
7.54
7.53
7.52
7.52
7.50
7.33
7.32
7.31
2.05
1.00
2.10
1.08
f1 (ppm)
2al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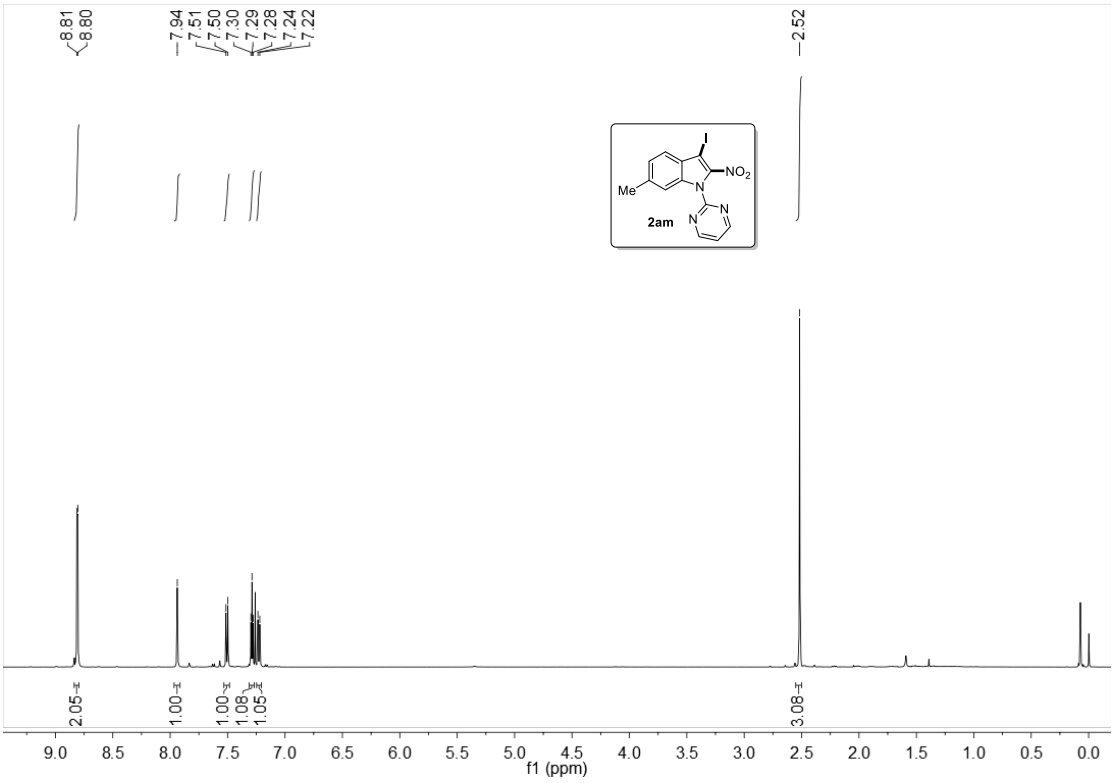
143.98
136.34
128.20
126.06
123.69
119.22
117.27
70.16
f1 (ppm)
2al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8.80
7.94
7.51
7.50
7.30
7.29
7.28
7.24
7.22
2.52
2.05
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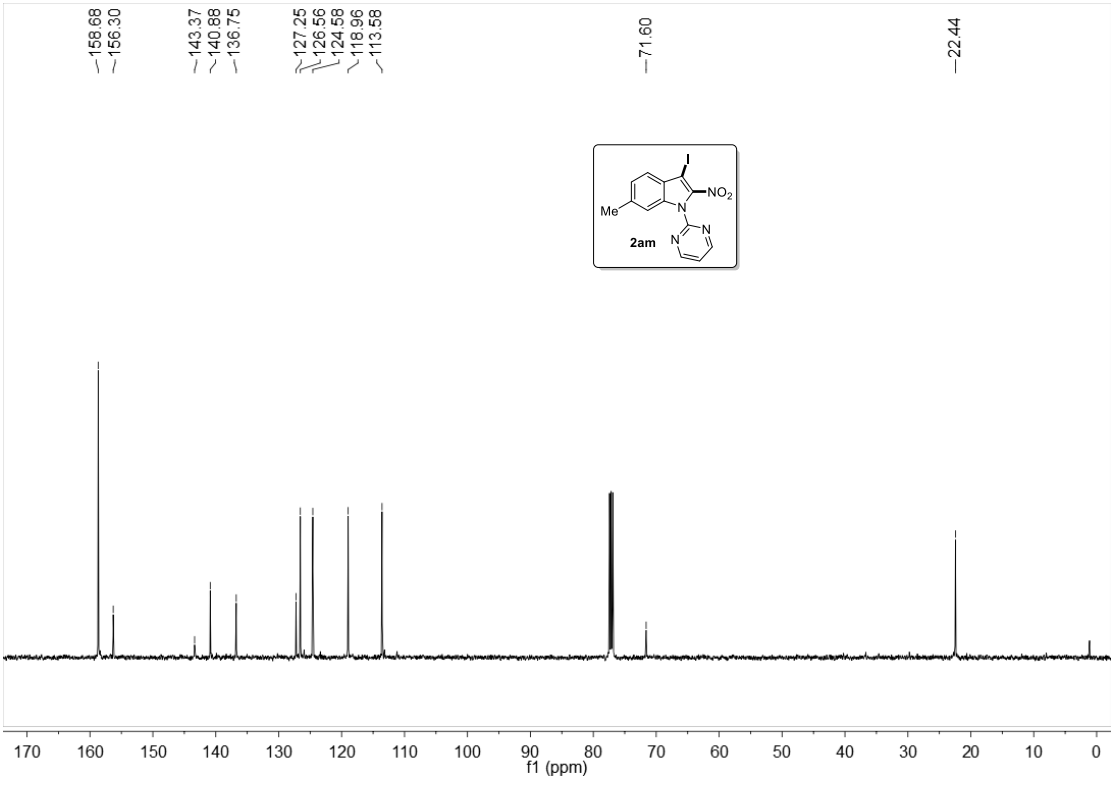
1.08
1.05
3.08
2am
f1 (ppm)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156.30
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127.25
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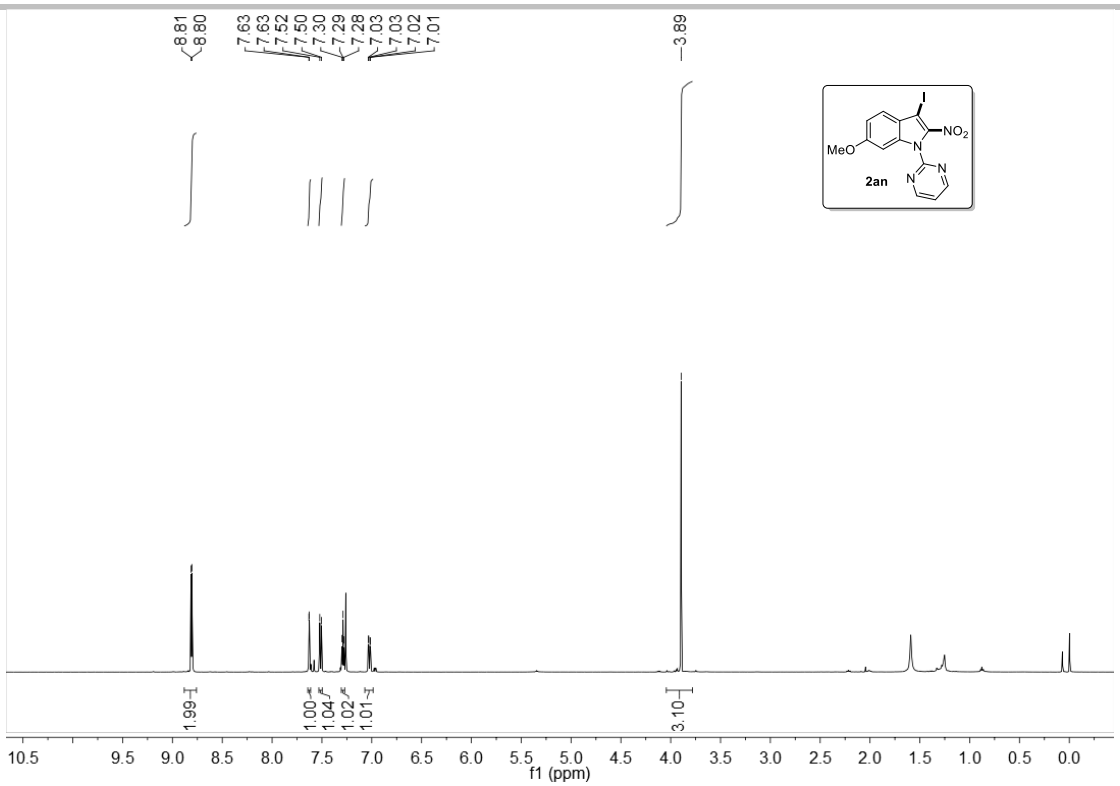
124.58
118.96
113.58
71.60
22.44
2am
f1 (ppm)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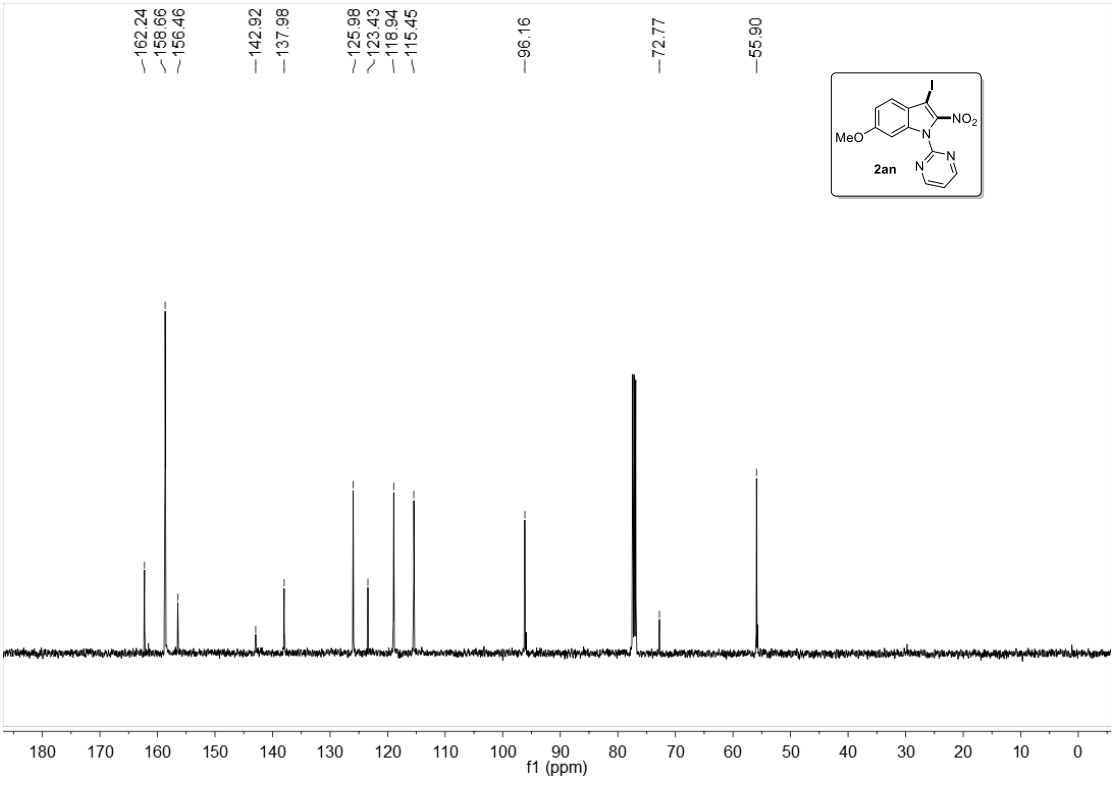
8.80
7.63
7.63
7.52
7.50
7.30
7.29
7.28
7.03
7.03
7.02
7.01
3.89
I
NO2
MeO
N
N
2an
1.99
1.00
1.04
1.02
1.01
3.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.24
158.66
156.46
142.92
137.98
125.98
123.43
118.94
115.45
96.16
72.77
55.90
I
NO2
MeO
N
N
2an
180
170
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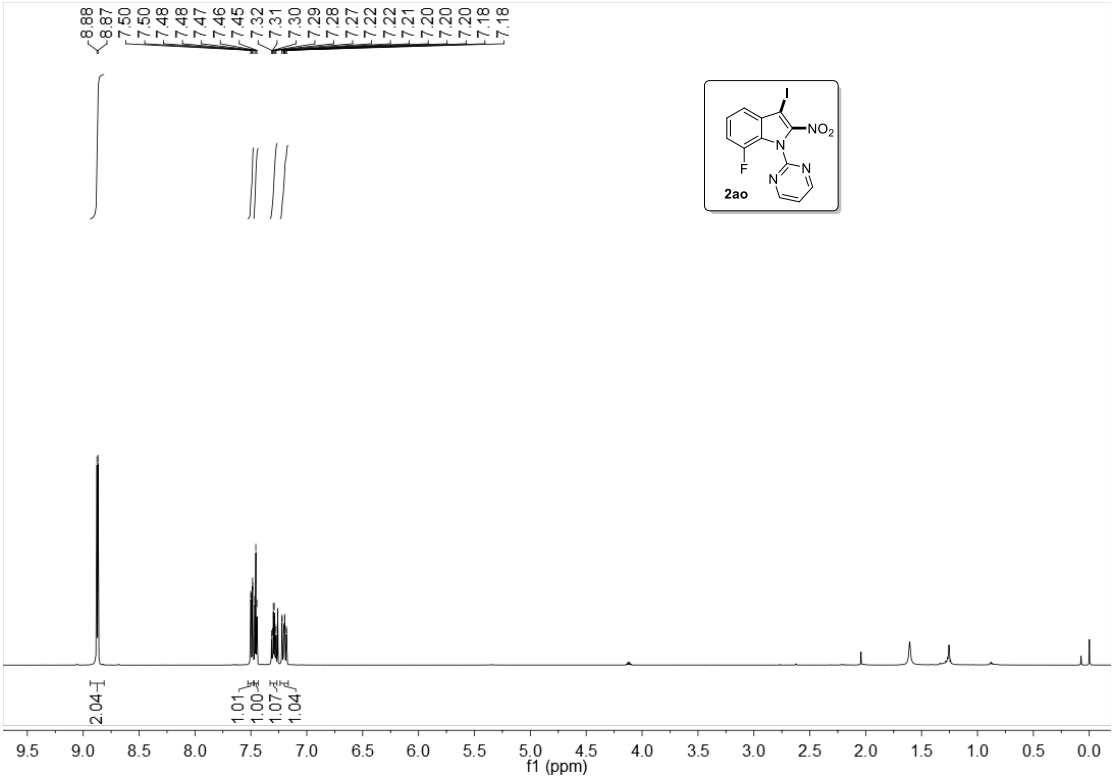
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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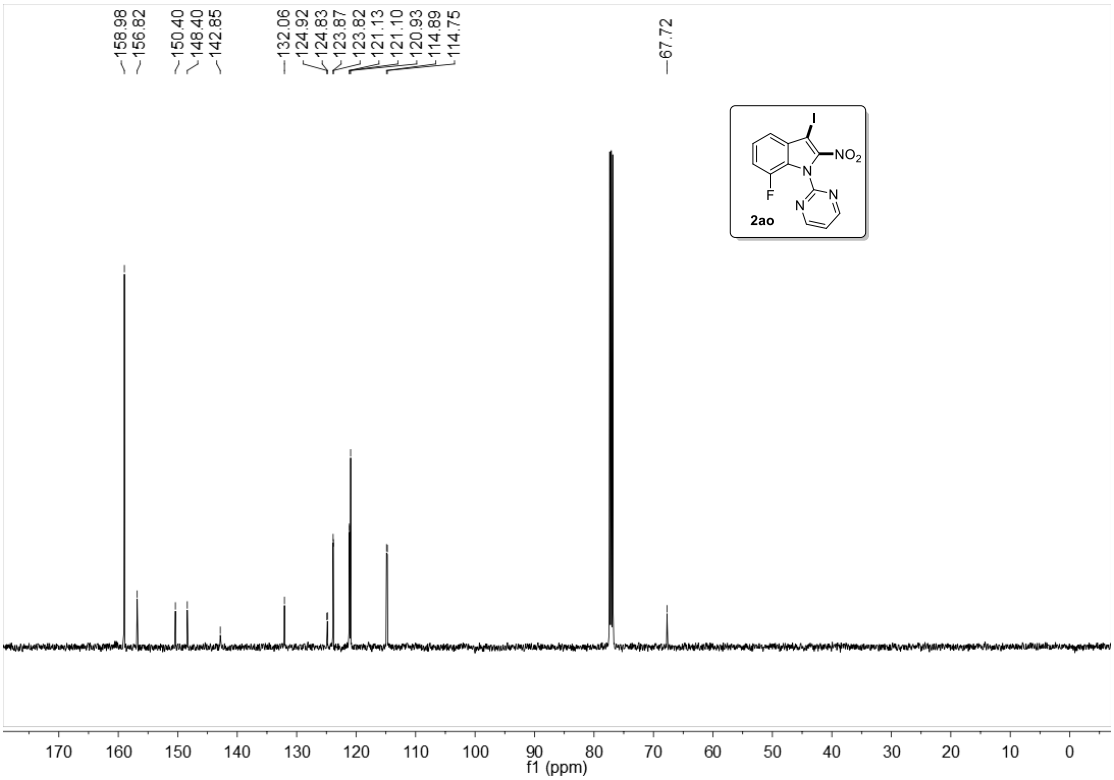
7.48
7.47
7.46
7.45
7.32
7.31
7.30
7.29
7.28
7.27
7.22
7.22
7.21
7.20
7.20
7.20
7.18
7.18
I
NO2
N
F
N
N
2ao
2.04
1.01
1.00
1.07
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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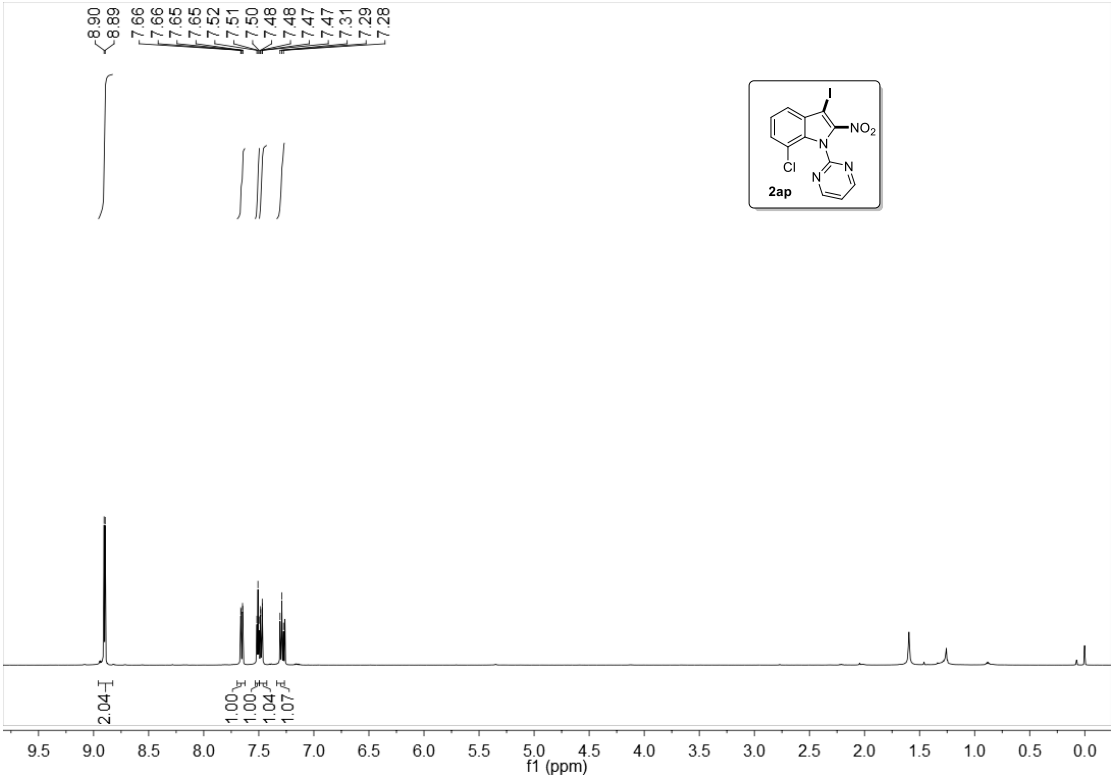
148.40
142.85
132.06
124.92
124.83
123.87
123.82
121.13
121.10
120.93
114.89
114.75
67.72
I
NO2
N
F
N
N
2ao
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.89
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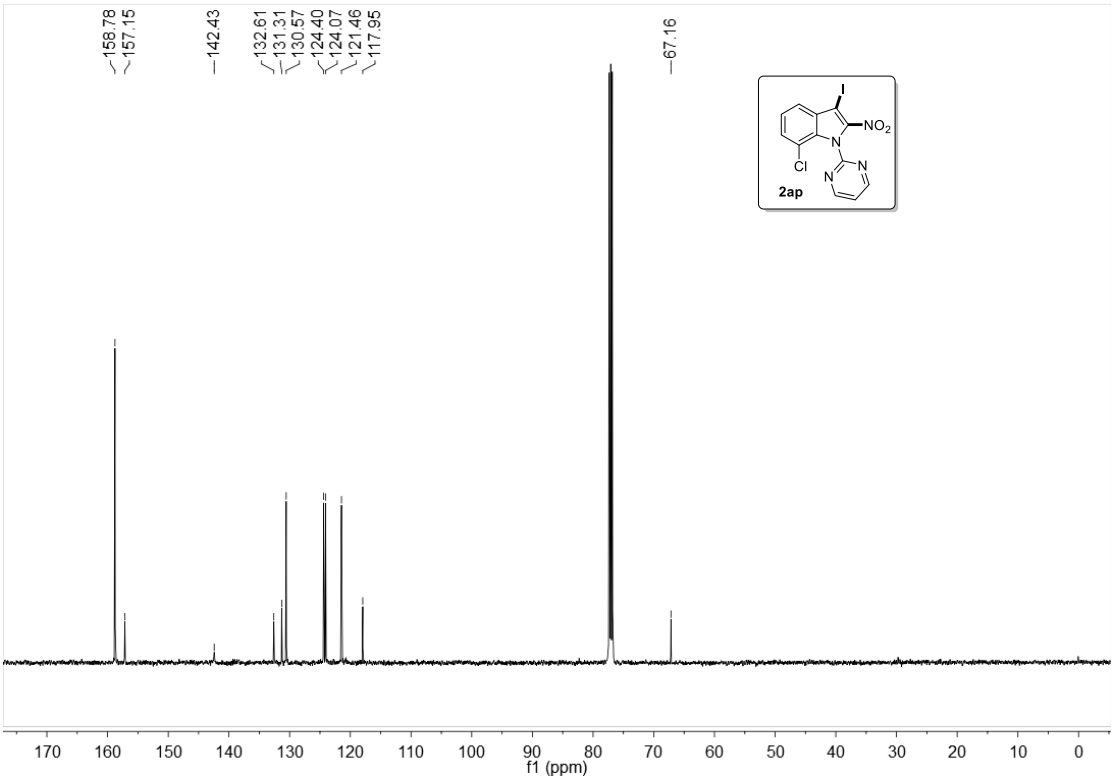
7.66
7.65
7.65
7.52
7.51
7.50
7.48
7.48
7.47
7.47
7.31
7.29
7.28
I
NO2
Cl
N
N
2ap
2.04
1.00
1.00
1.04
1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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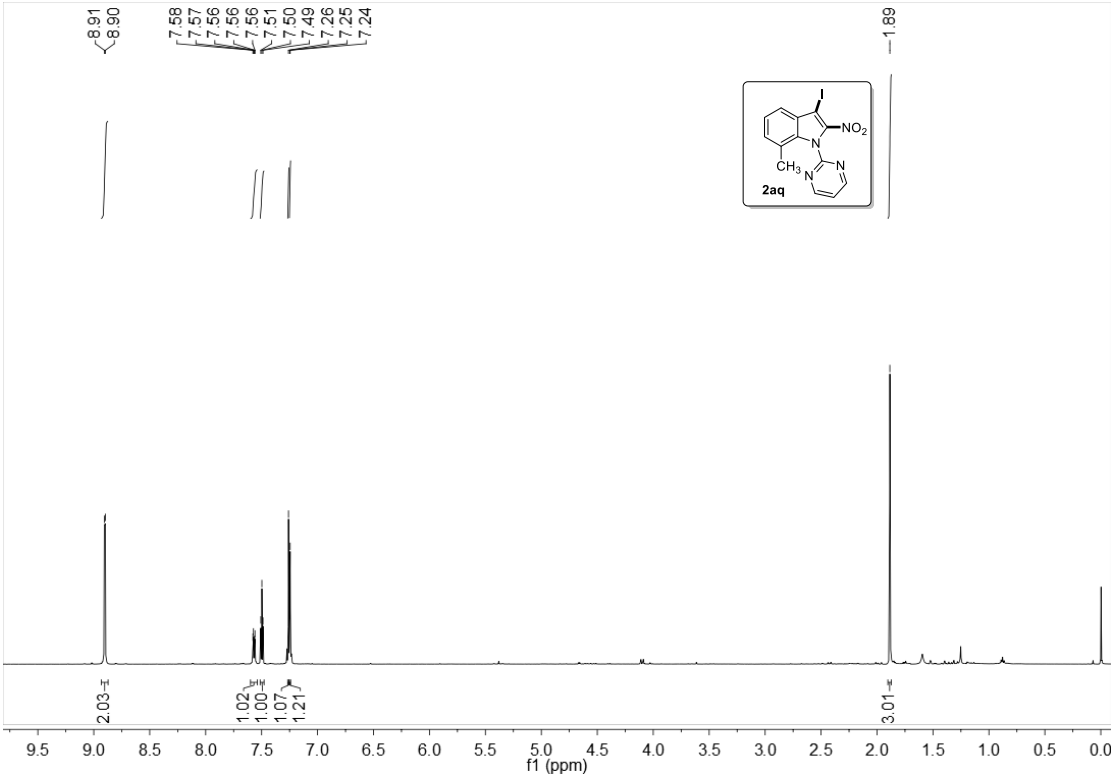
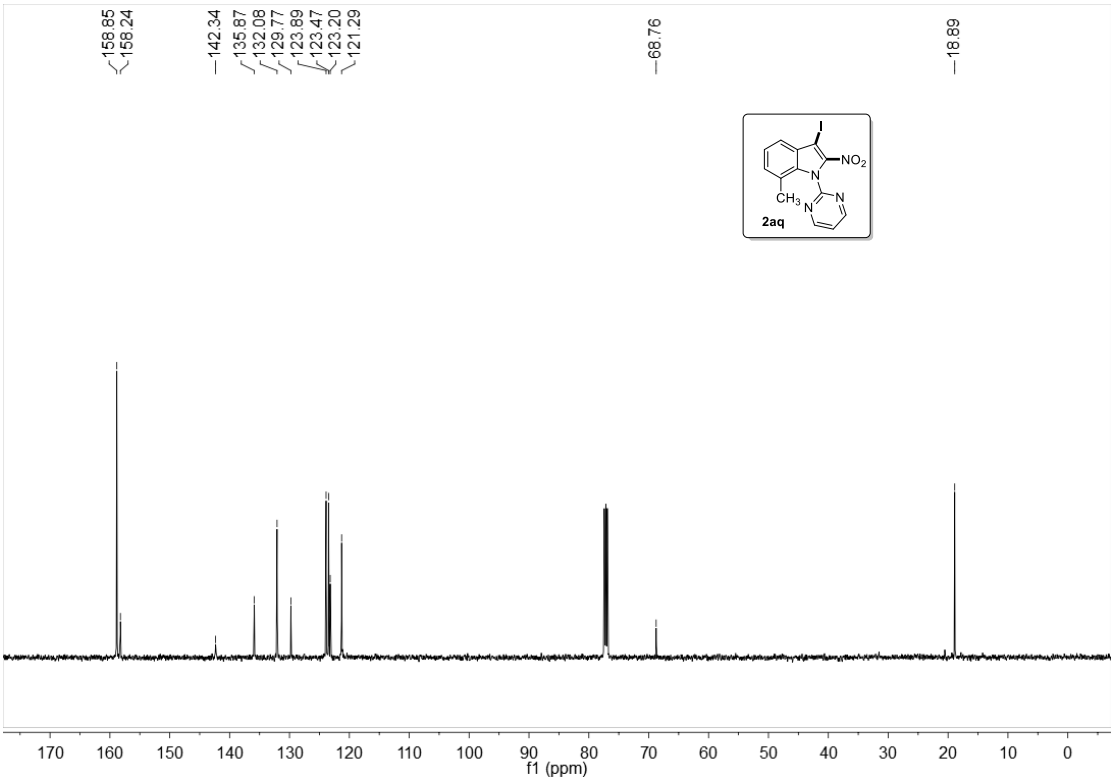
157.15
142.43
132.61
131.31
130.57
124.40
124.07
121.46
117.95
67.16
I
NO2
Cl
N
N
2ap
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.91
8.90
7.58
7.57
7.56
7.56
7.56
7.51
7.50
7.49
7.26
7.25
7.24
1.89
2aq
2.03
1.02
1.00
1.07
1.21
3.01
f1 (ppm)


158.85
158.24
142.34
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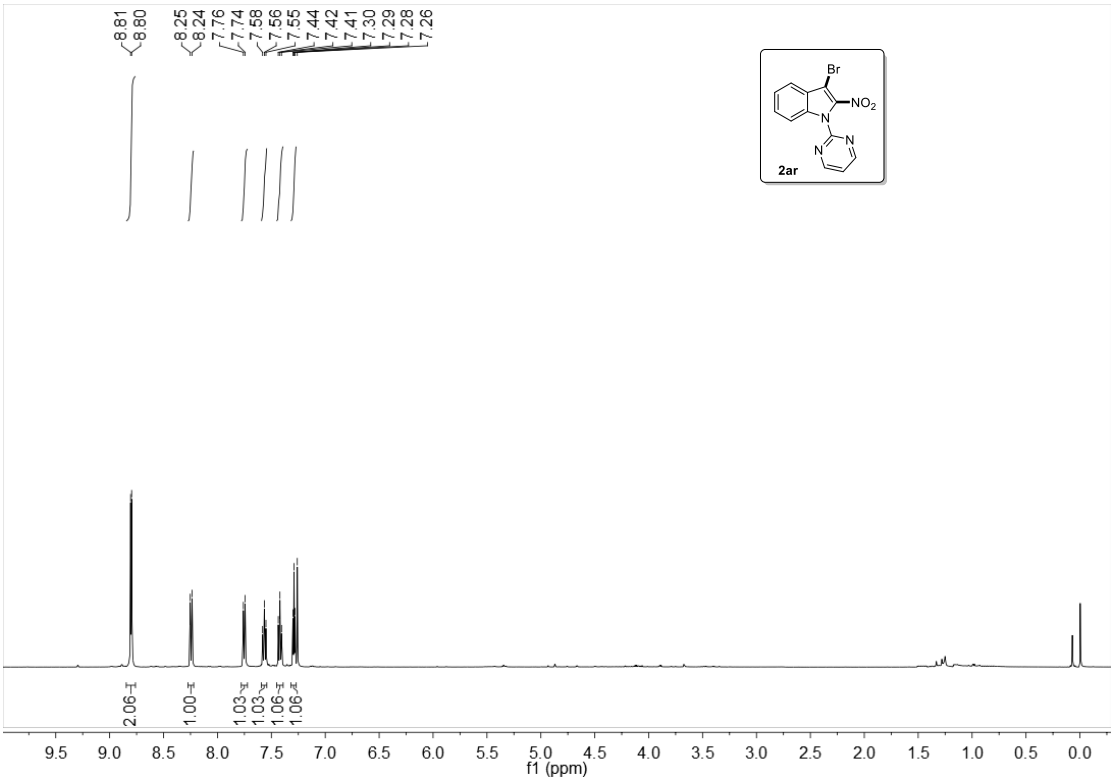
132.08
129.77
123.89
123.47
123.20
121.29
68.76
18.89
2aq
f1 (ppm)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7.58
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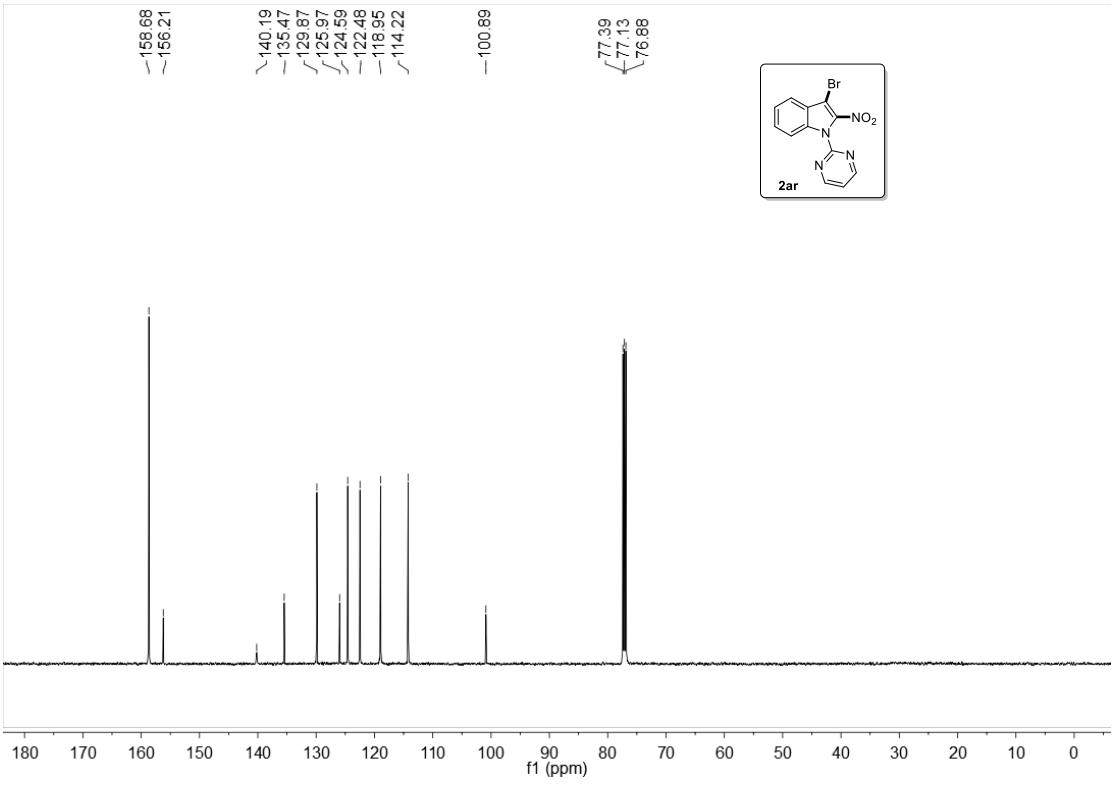
7.55
7.44
7.42
7.41
7.30
7.29
7.28
7.26
Br
NO2
N
N
2ar
2.06
1.00
1.03
1.03
1.06
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.97
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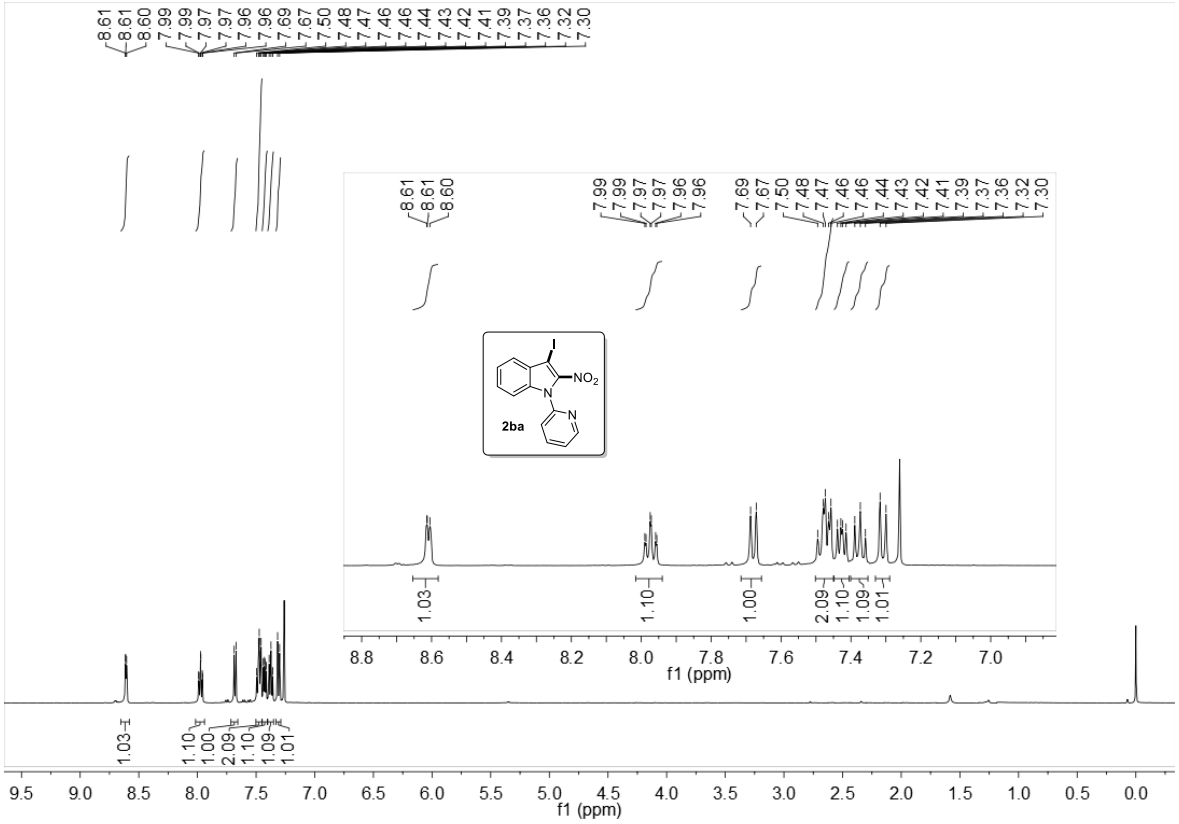
122.48
118.95
114.22
100.89
77.39
77.13
76.88
Br
NO2
N
N
2ar
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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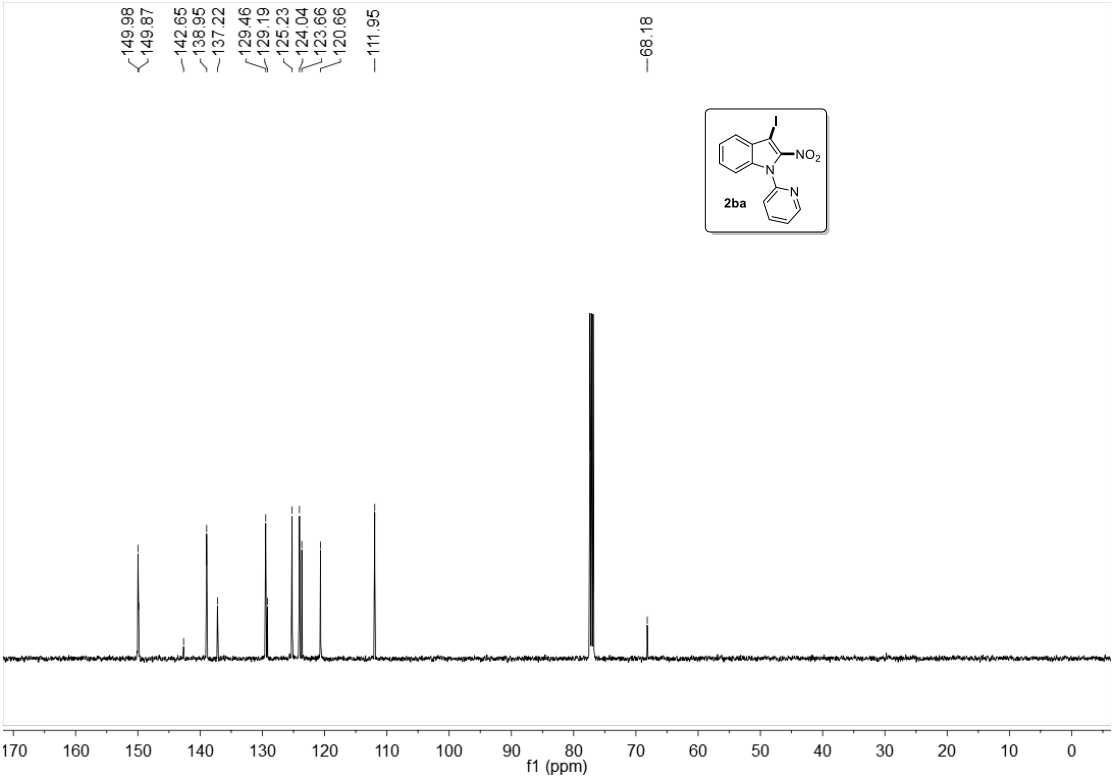
7.99
7.97
7.97
7.96
7.96
7.69
7.67
7.50
7.48
7.47
7.46
7.46
7.44
7.43
7.42
7.41
7.39
7.37
7.36
7.32
7.30
2ba
1.03
1.10
1.00
2.09
1.10
1.09
1.01
f1 (ppm)


149.98
149.87
142.65
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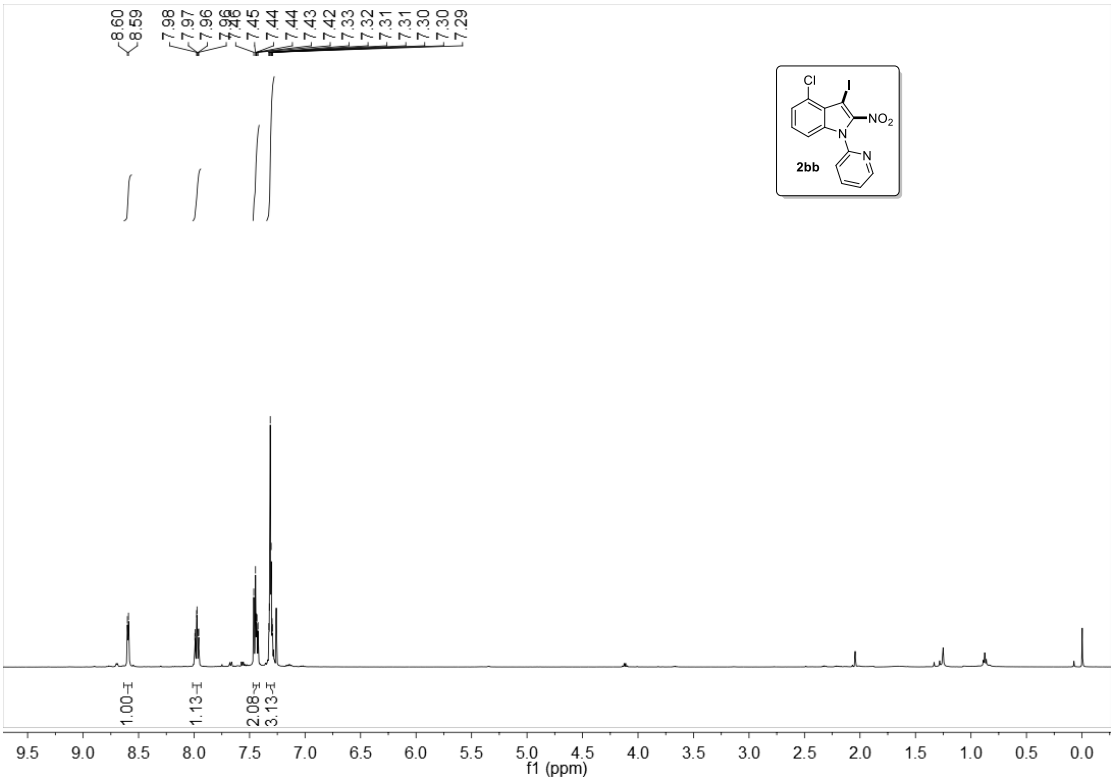
137.22
129.46
129.19
125.23
124.04
123.66
120.66
111.95
68.18
2ba
f1 (ppm)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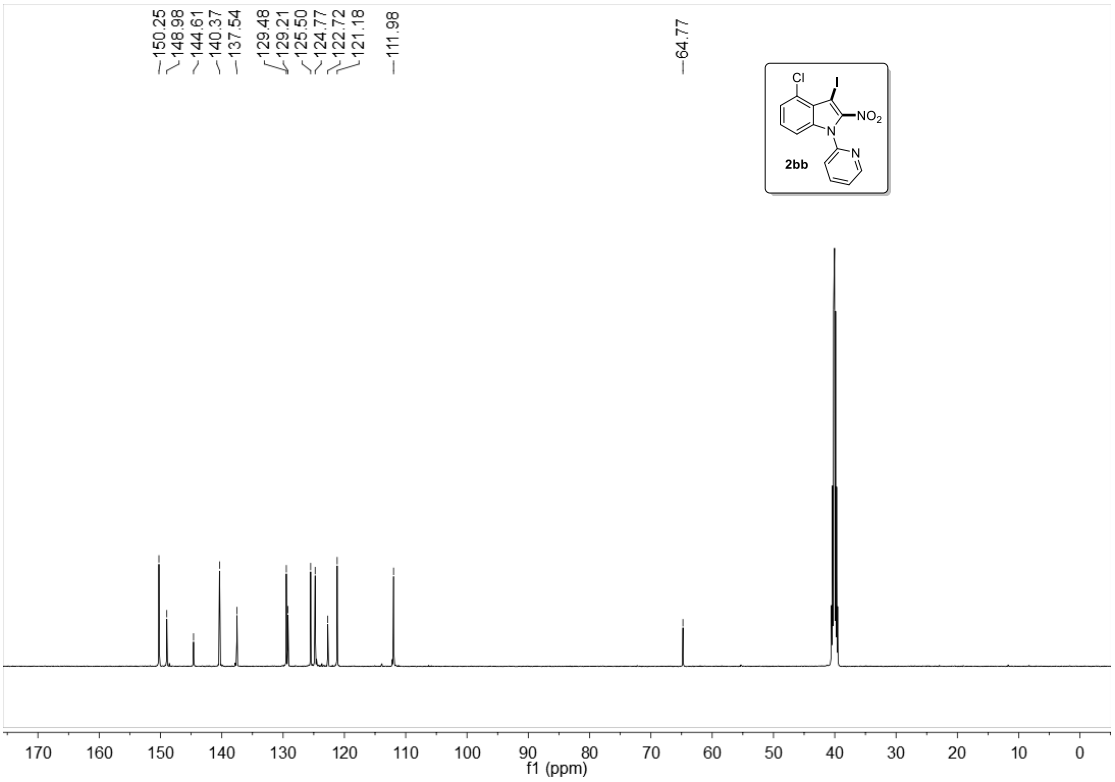
7.97
7.96
7.45
7.44
7.44
7.43
7.42
7.33
7.32
7.31
7.31
7.30
7.30
7.29
Cl
I
NO2
N
N
2bb
1.00
1.13
2.08
3.13
f1 (ppm)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129.48
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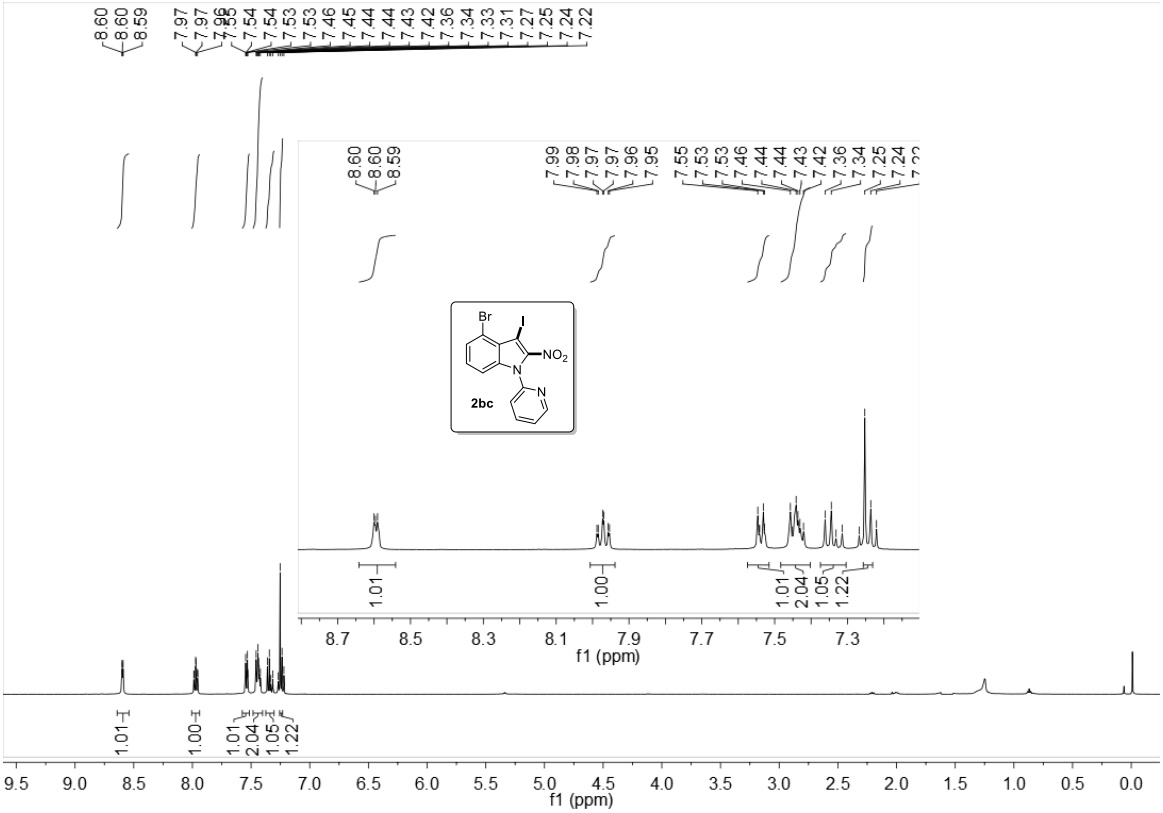
125.50
124.77
122.72
121.18
111.98
64.77
Cl
I
NO2
N
N
2bb
f1 (ppm)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7.97
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7.54
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7.53
7.46
7.45
7.44
7.44
7.43
7.42
7.36
7.34
7.33
7.31
7.27
7.25
7.24
7.22
Br
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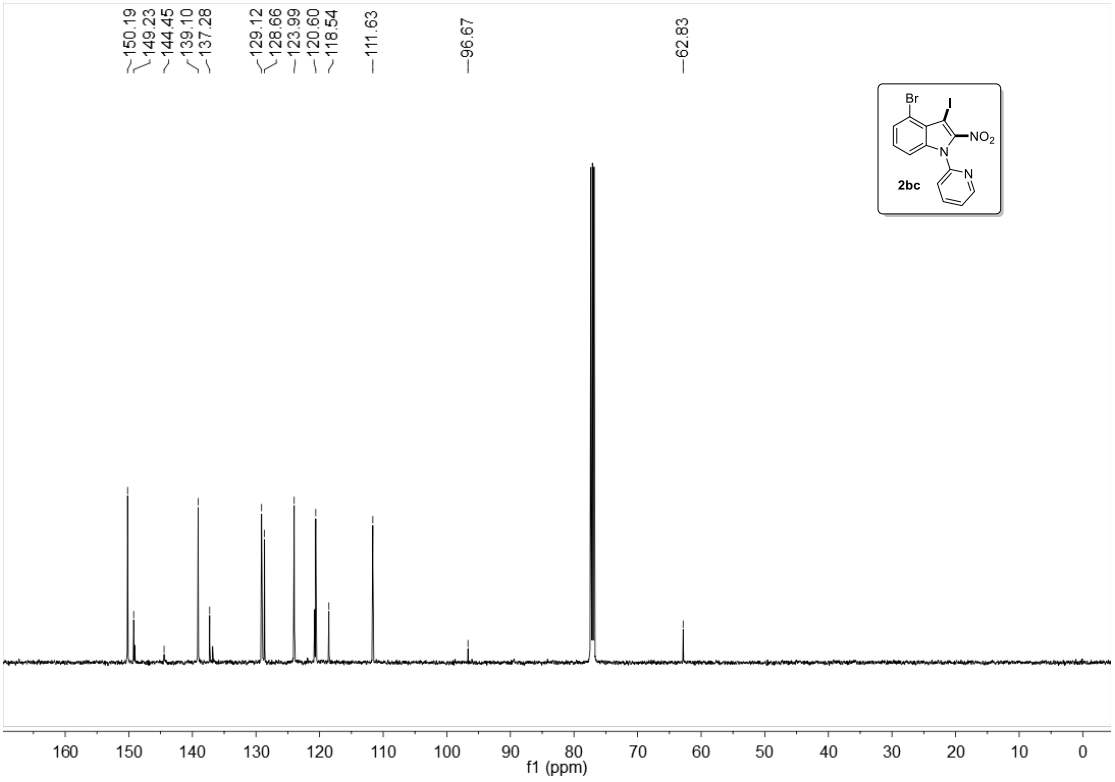
NO2
N
N
2bc
1.01
1.00
1.01
2.04
1.05
1.22
f1 (ppm)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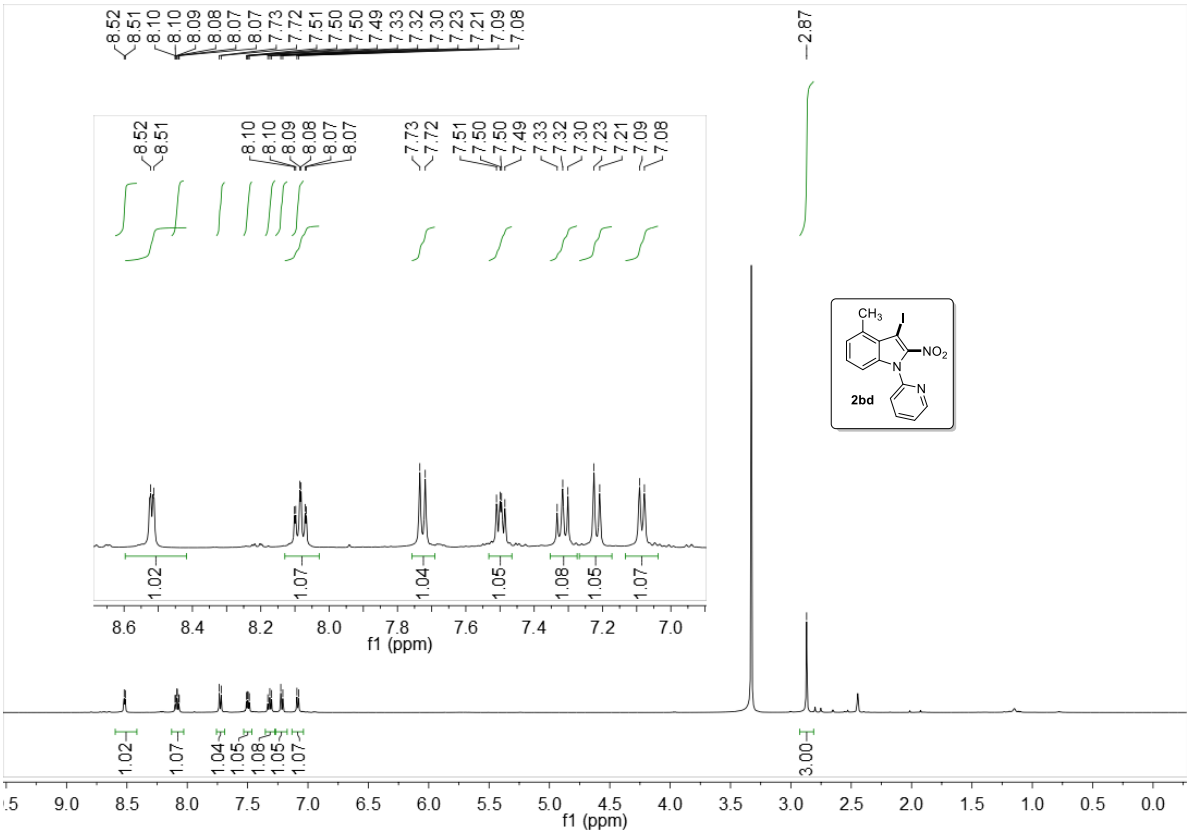
118.54
111.63
96.67
62.83
Br
I
NO2
N
2bc
f1 (ppm)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8.08
8.07
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7.72
7.51
7.50
7.49
7.33
7.32
7.30
7.23
7.21
7.09
7.08
2.87
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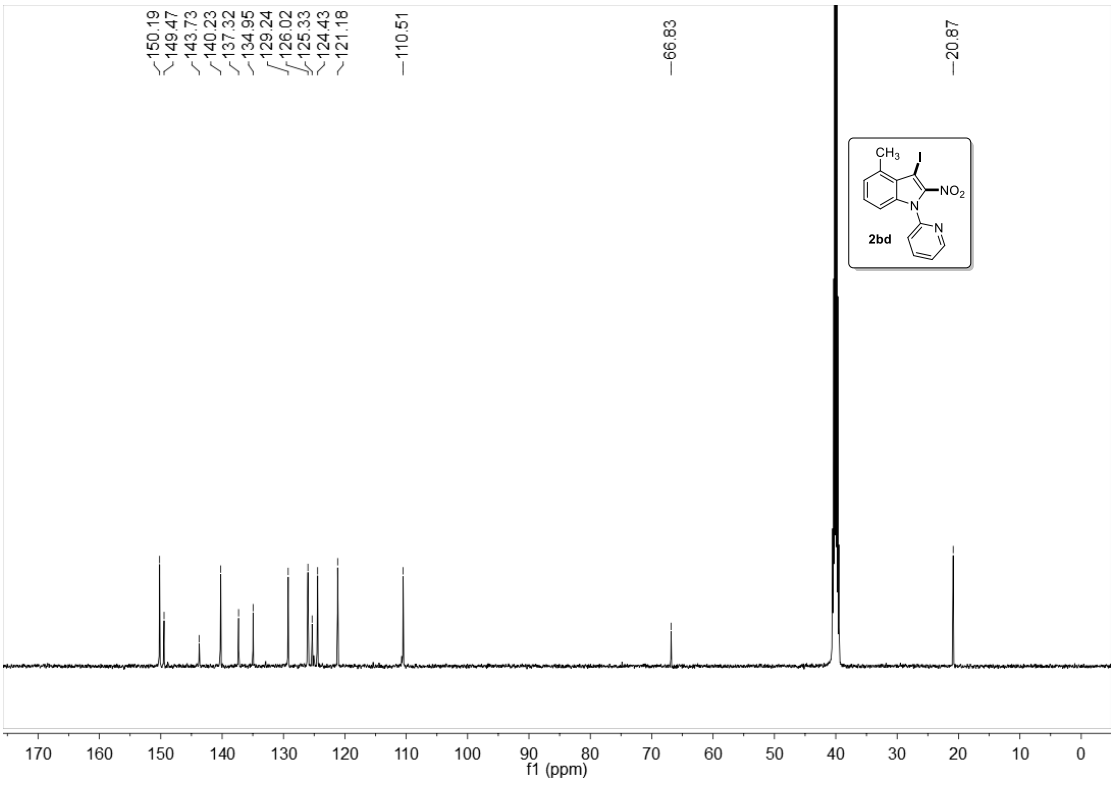
1.07
1.04
1.05
1.08
1.05
1.07
3.00
f1 (ppm)
2bd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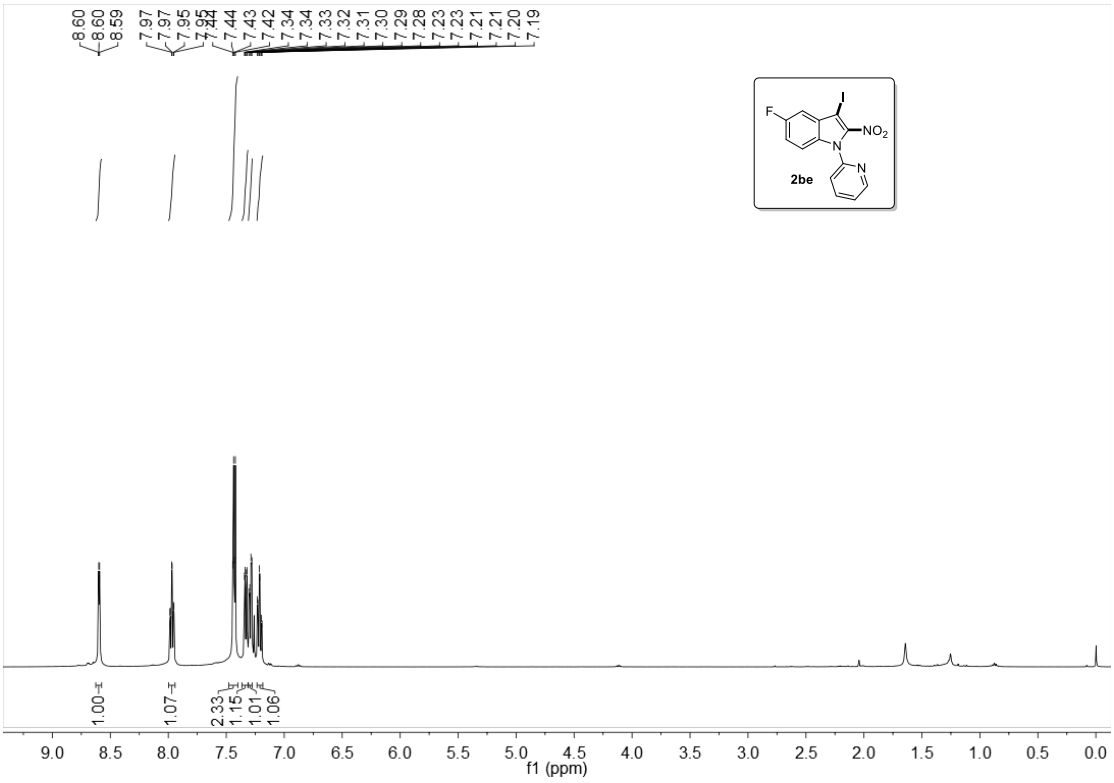
149.47
143.73
140.23
137.32
134.95
129.24
126.02
125.33
124.43
121.18
110.51
66.83
20.87
f1 (ppm)
2bd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8.60
8.59
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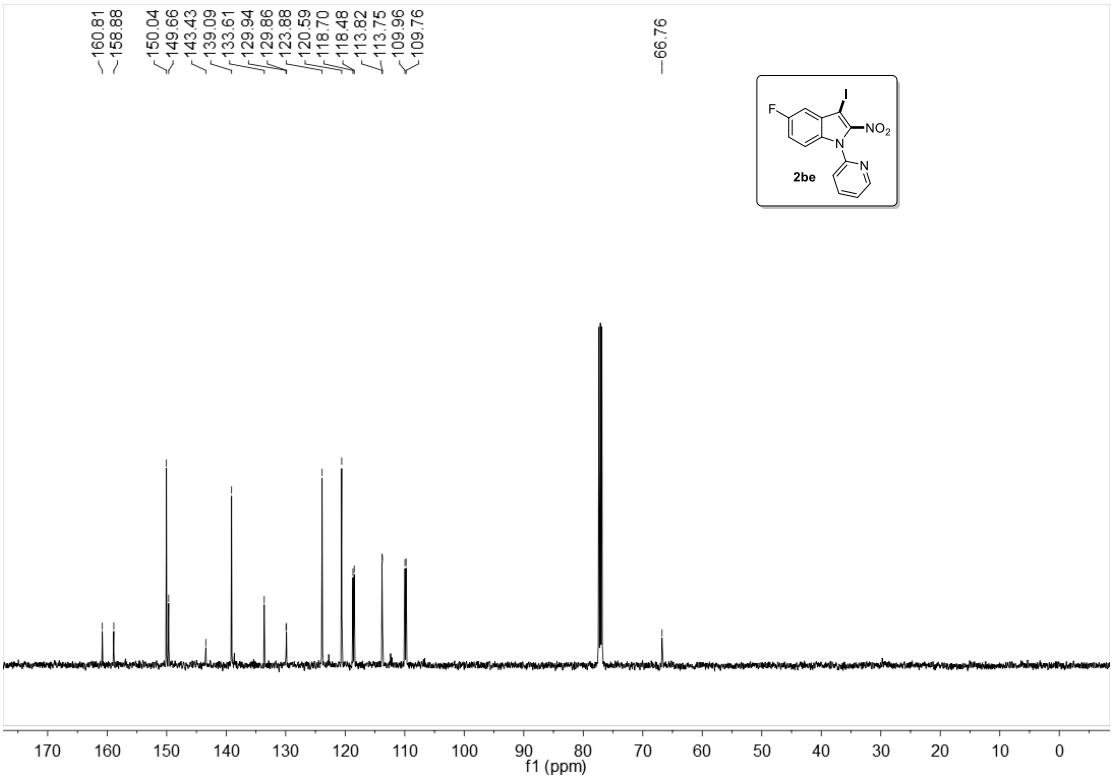
7.97
7.95
7.44
7.43
7.42
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.23
7.21
7.21
7.20
7.19
F
I
NO2
N
N
2be
1.00
1.07
2.33
1.15
1.01
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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120.59
118.70
118.48
113.82
113.75
109.96
109.76
66.76
F
I
NO2
N
N
2be
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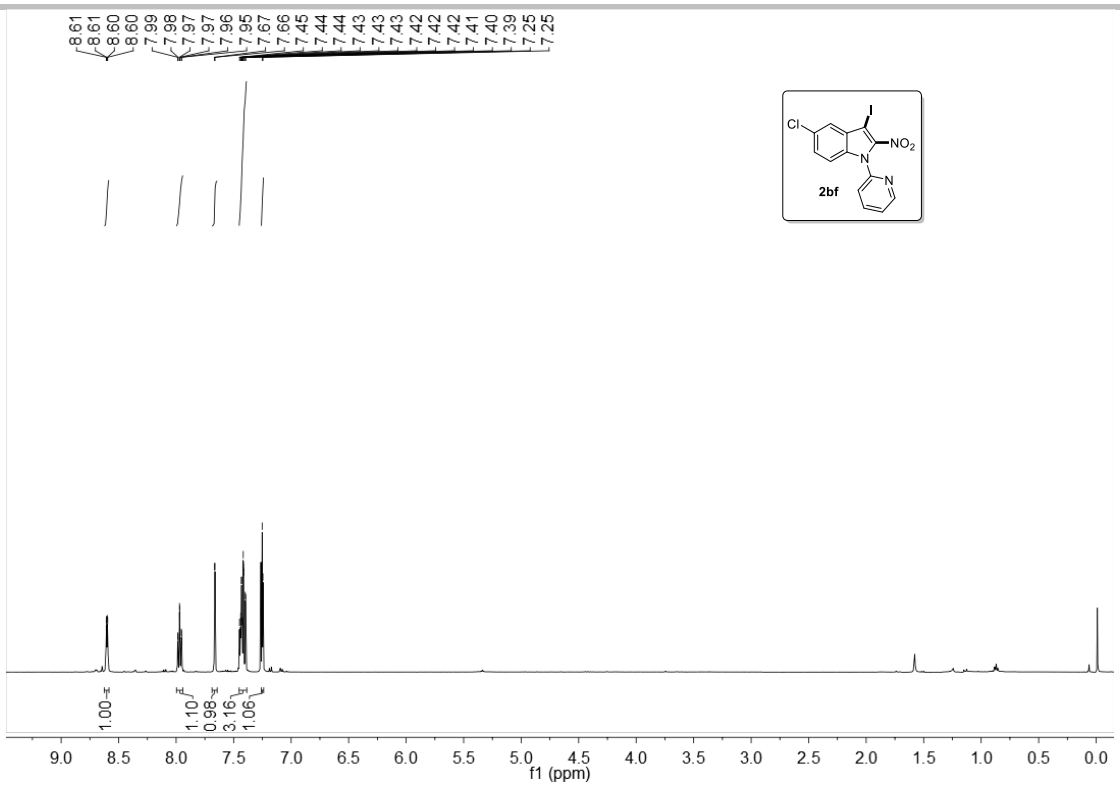
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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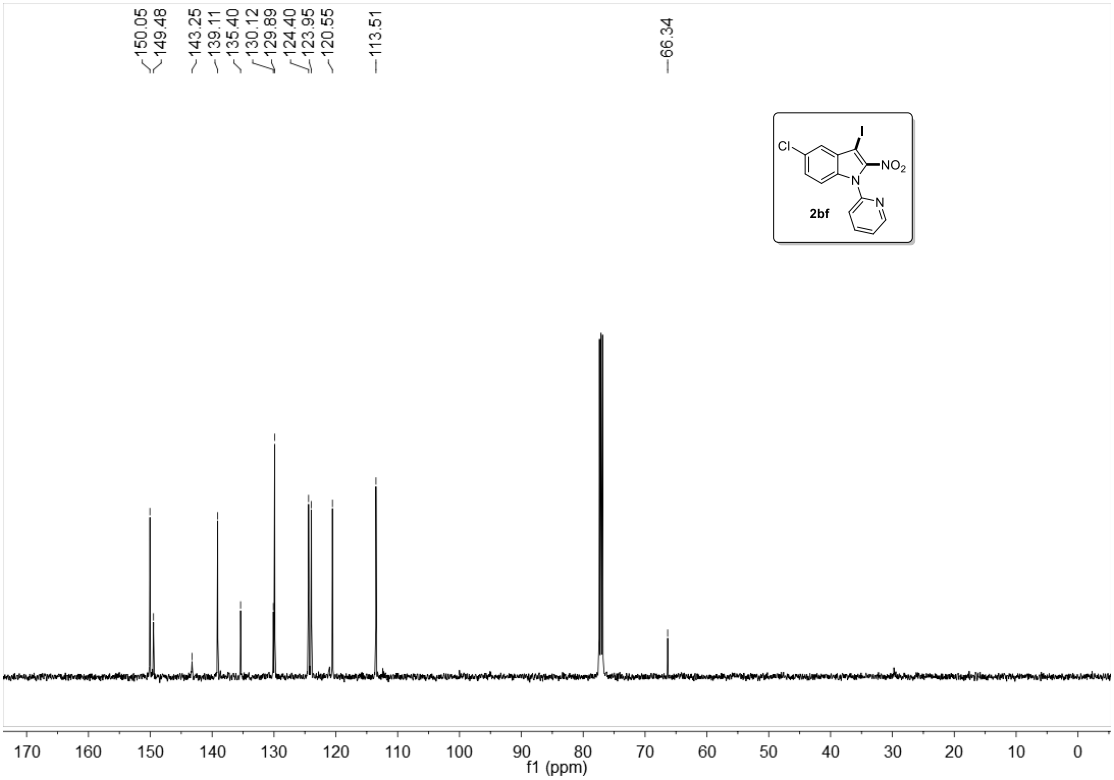
7.97
7.97
7.96
7.95
7.67
7.66
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.40
7.39
7.25
7.25
Cl
I
NO2
N
N
2bf
1.00
1.10
0.98
3.16
1.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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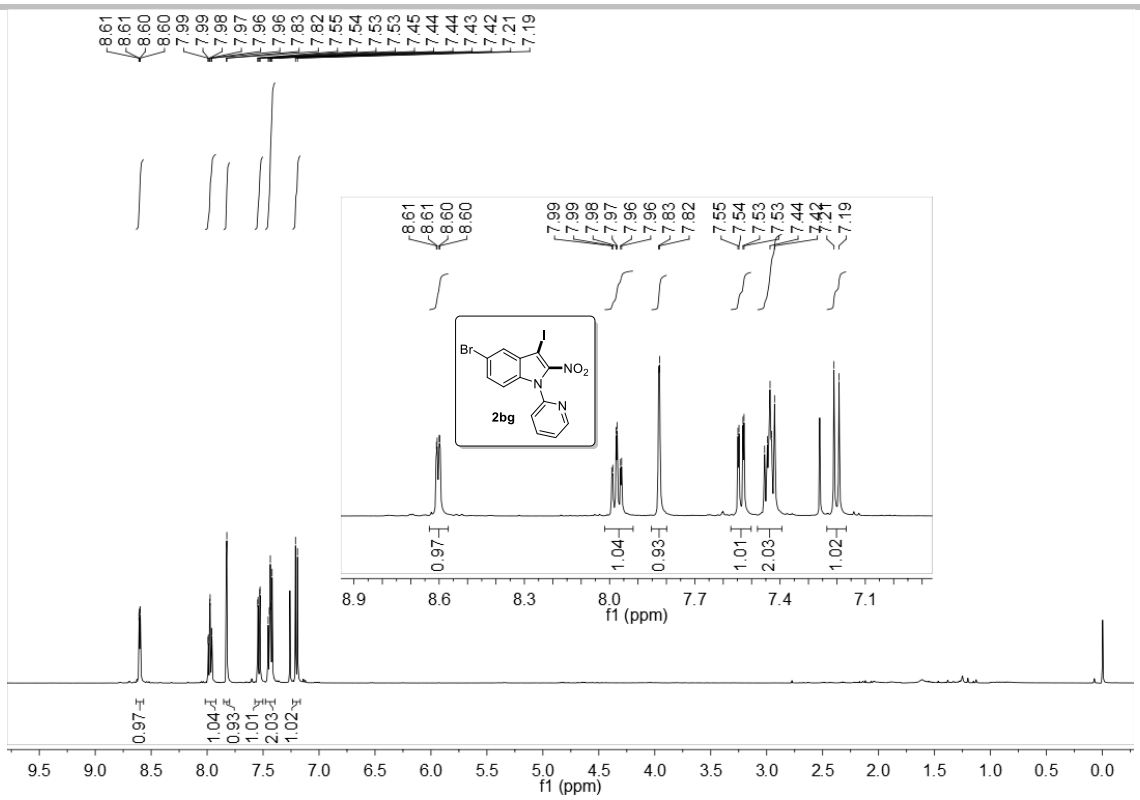
135.40
130.12
129.89
124.40
123.95
120.55
113.51
66.34
Cl
I
NO2
N
N
2bf
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.60
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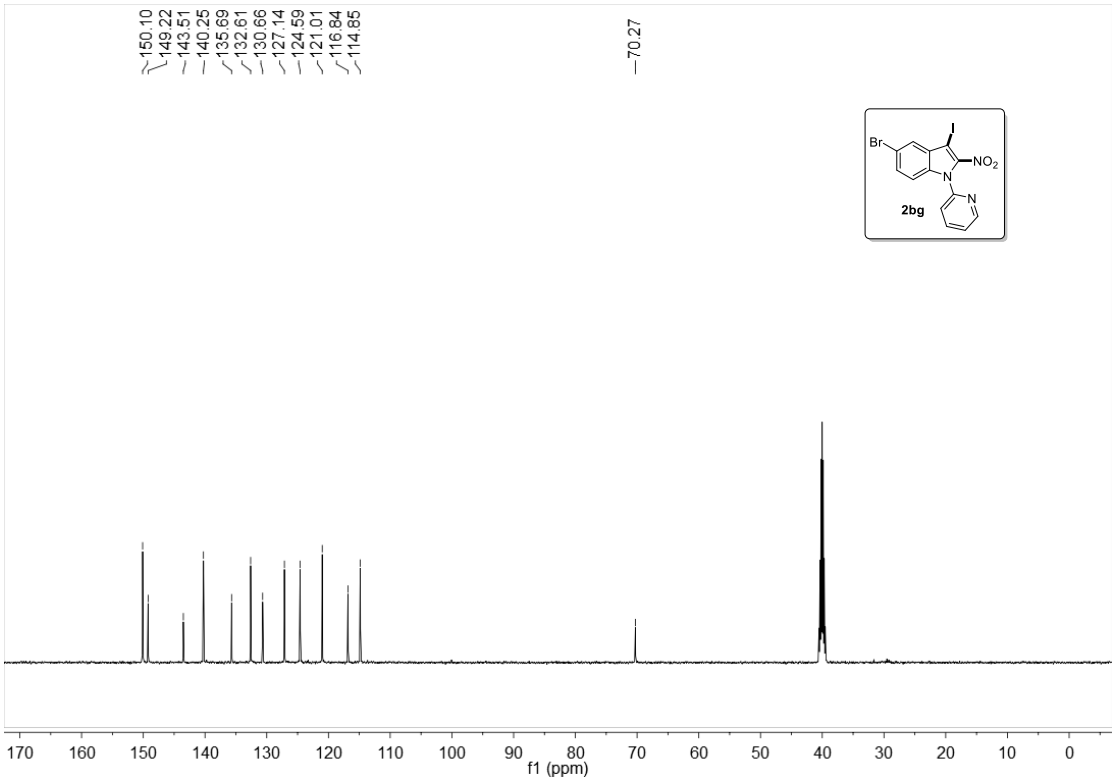
7.99
7.98
7.97
7.96
7.96
7.83
7.82
7.55
7.54
7.53
7.53
7.45
7.44
7.43
7.42
7.21
7.19
Br
I
NO2
N
N
2bg
0.97
1.04
0.93
1.01
2.03
1.02
f1 (ppm)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149.22
143.51
140.25
135.69
132.61
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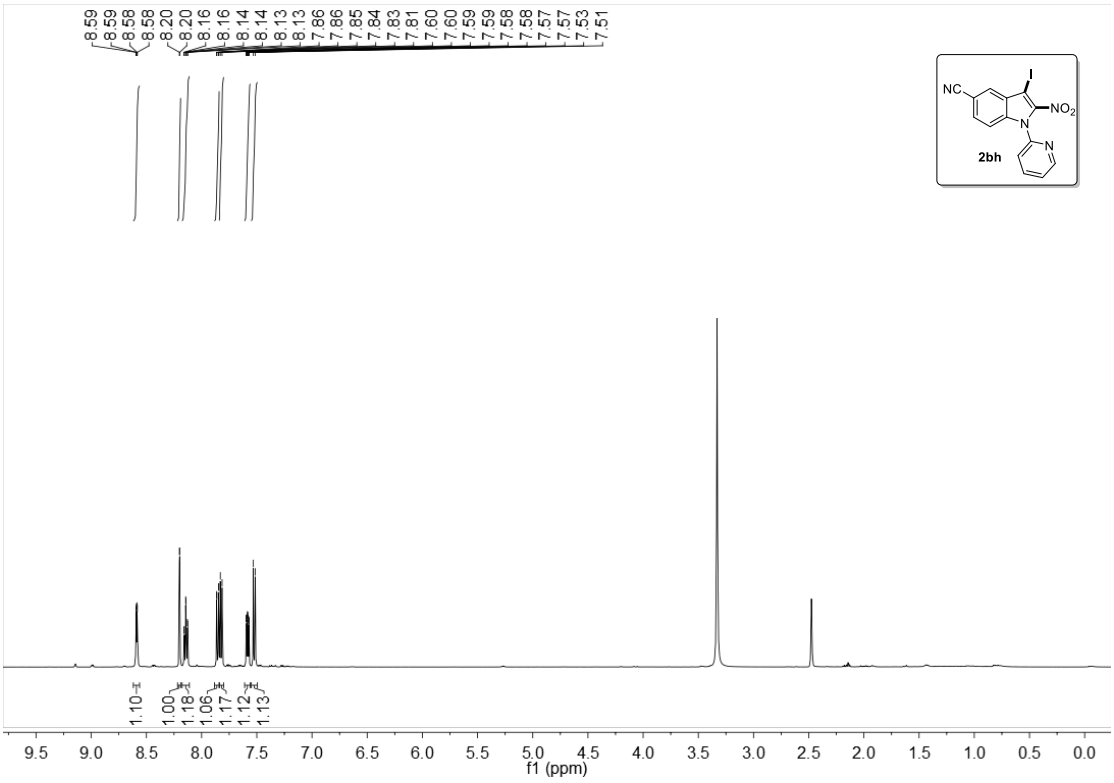
127.14
124.59
121.01
116.84
114.85
70.27
Br
I
NO2
N
N
2bg
f1 (ppm)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8.58
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8.14
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8.13
7.86
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7.85
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7.51
NC
I
NO2
N
N
2bh
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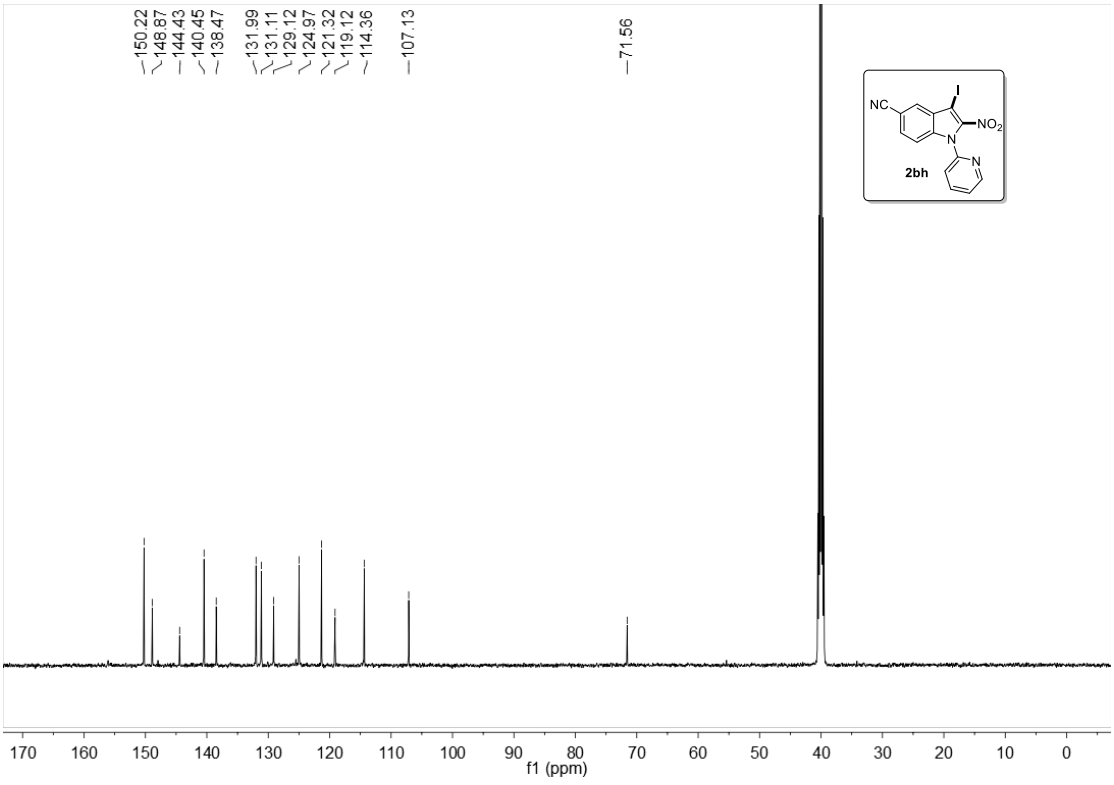
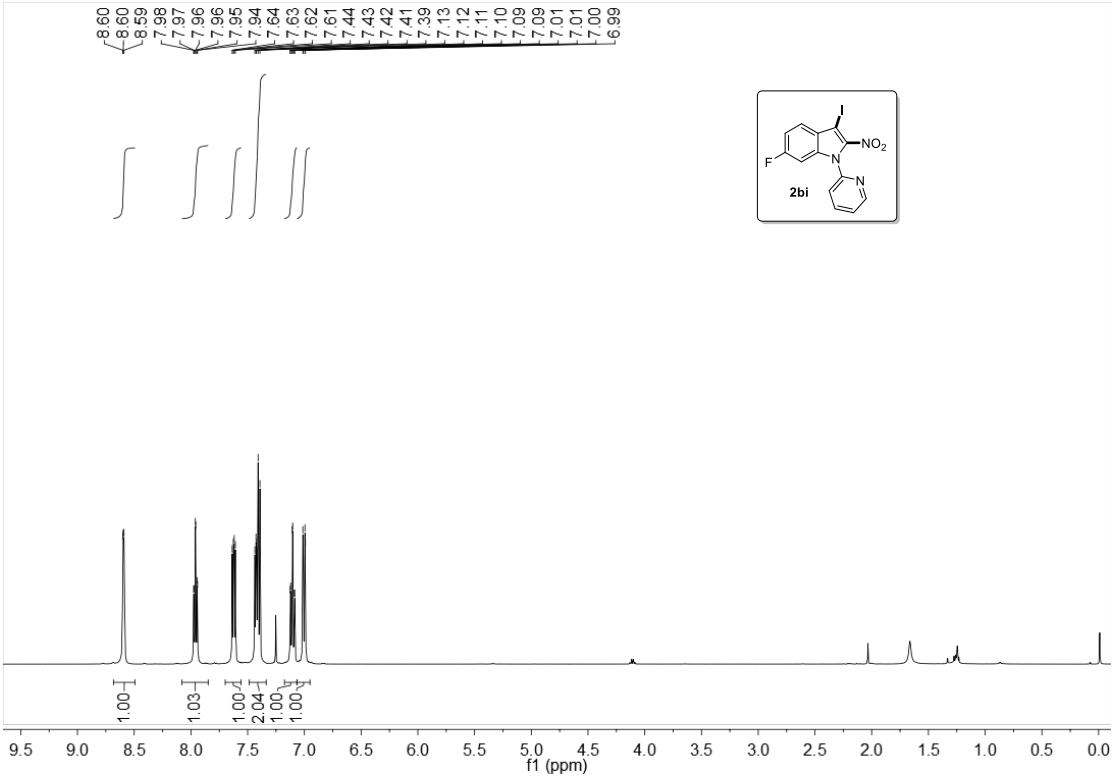
1.00
1.18
1.06
1.17
1.12
1.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.22
148.87
144.43
140.45
138.47
131.99
131.11
129.12
124.97
121.32
119.12
114.36
107.13
71.56
NC
I
NO2
N
N
2bh
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.59
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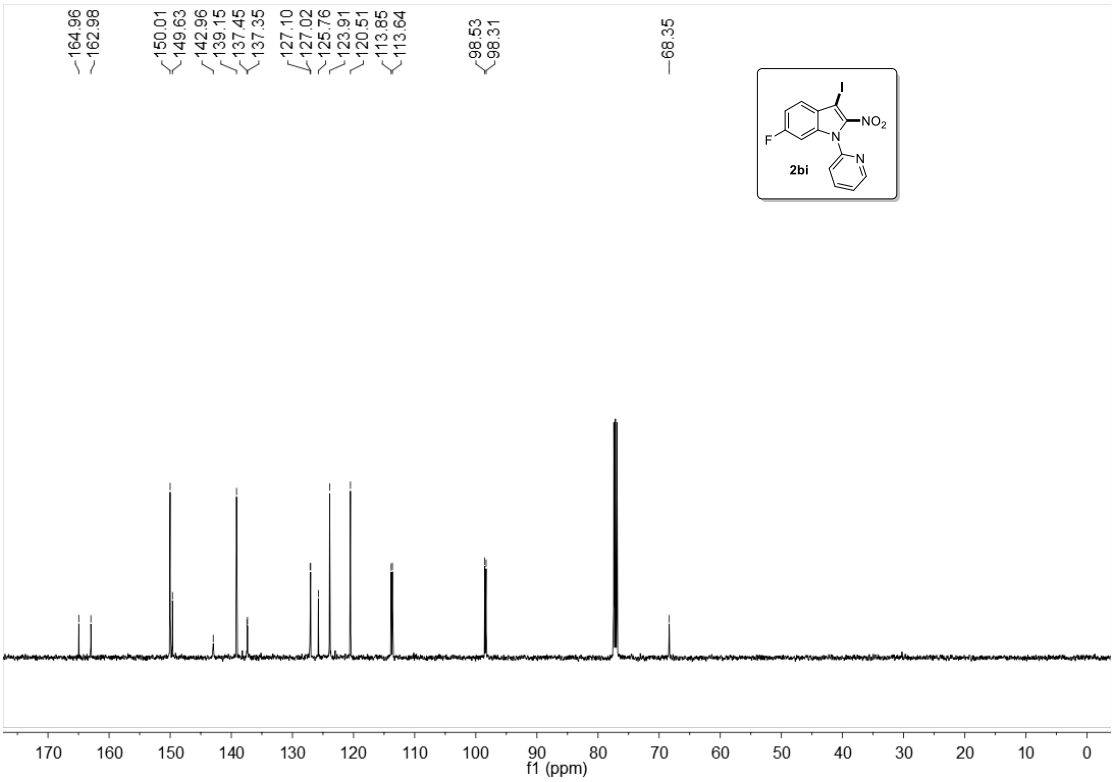
7.96
7.96
7.95
7.94
7.64
7.63
7.62
7.61
7.44
7.43
7.42
7.41
7.39
7.13
7.12
7.11
7.10
7.09
7.09
7.01
7.01
7.00
6.99
I
NO2
F
N
N
2bi
1.00
1.03
1.00
2.04
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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162.98
150.01
149.63
142.96
139.15
137.45
137.35
127.10
127.02
125.76
123.91
120.51
113.85
113.64
98.53
98.31
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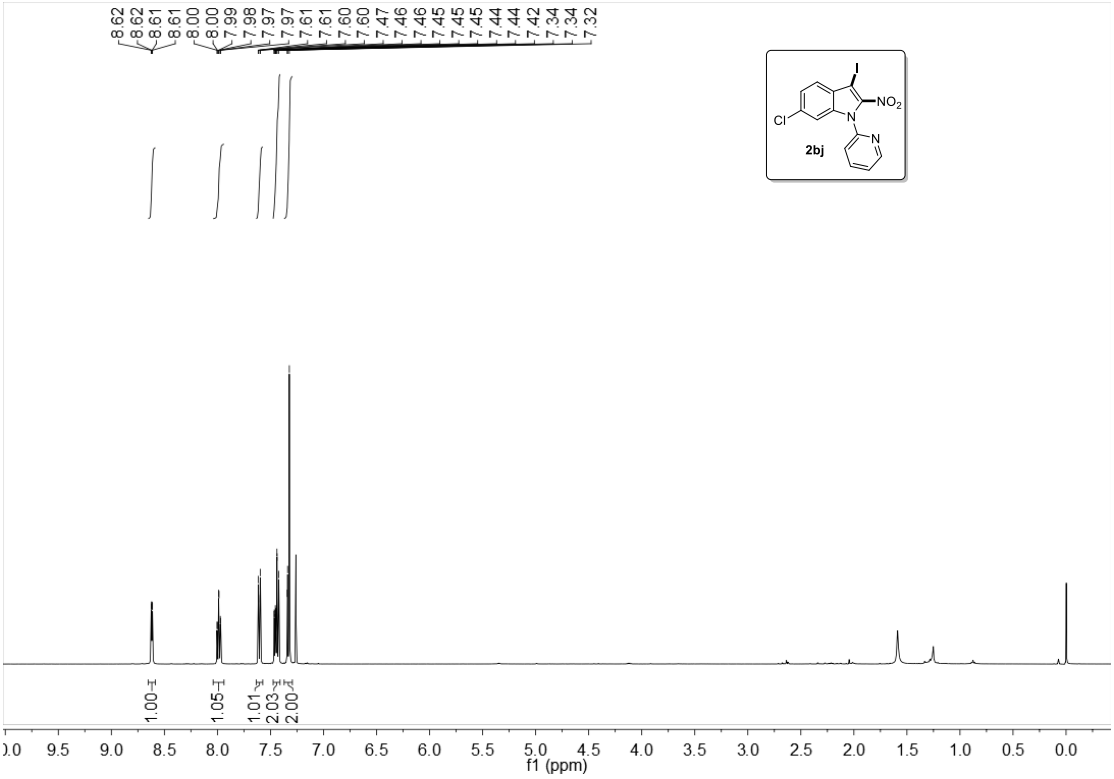
I
NO2
F
N
N
2bi
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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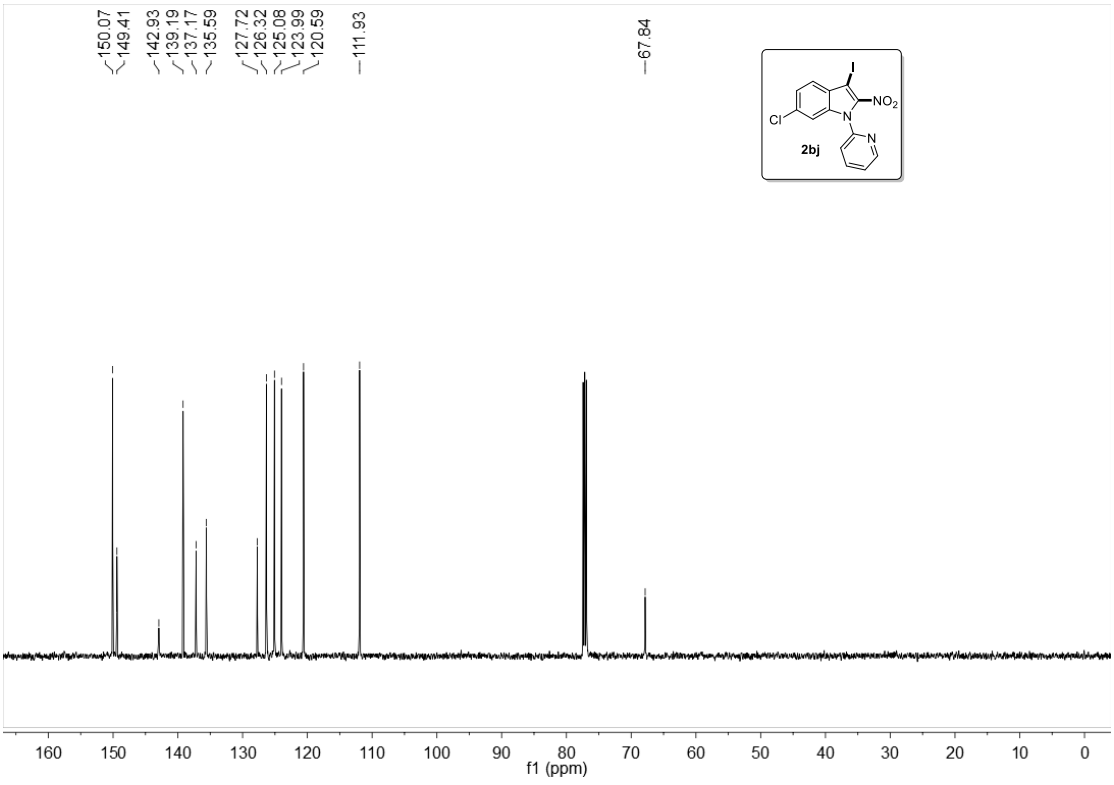
8.62
8.61
8.61
8.00
8.00
7.99
7.98
7.97
7.97
7.61
7.61
7.60
7.60
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.42
7.34
7.34
7.32
I
NO2
Cl
N
N
2bj
1.00
1.05
1.01
2.03
2.00
f1 (ppm)


150.07
149.41
142.93
139.19
137.17
135.59
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126.32
125.08
123.99
120.59
111.93
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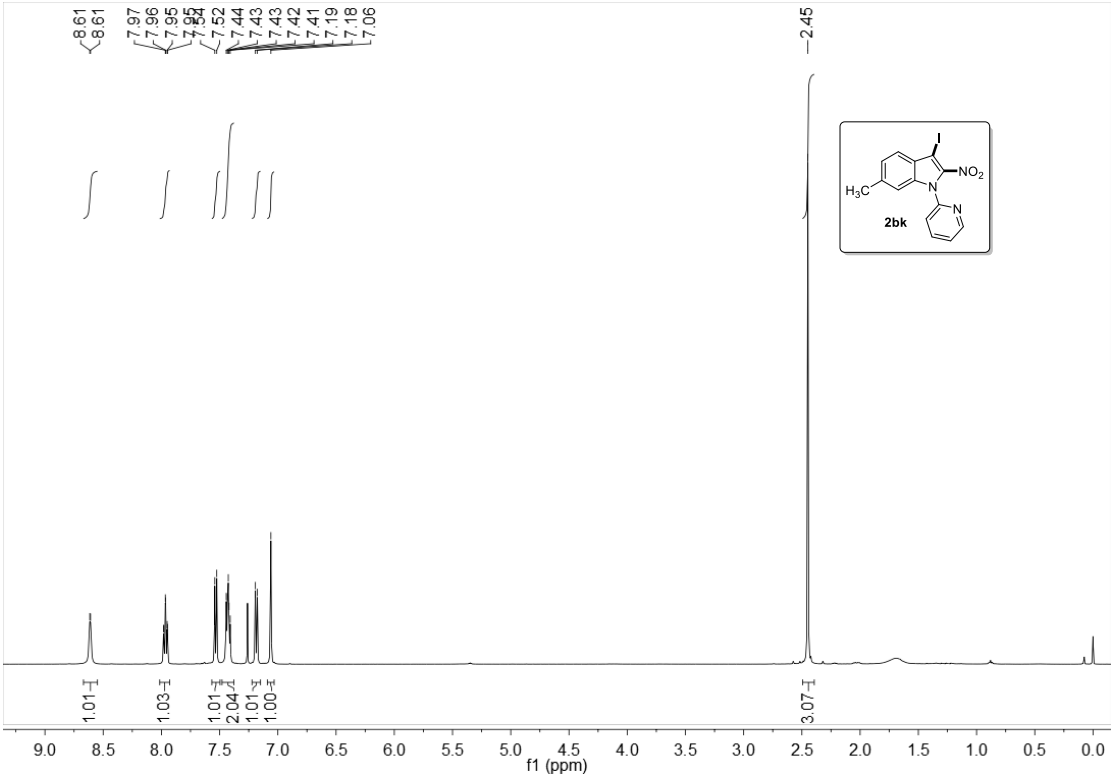
I
NO2
Cl
N
N
2bj
f1 (ppm)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8.61
7.97
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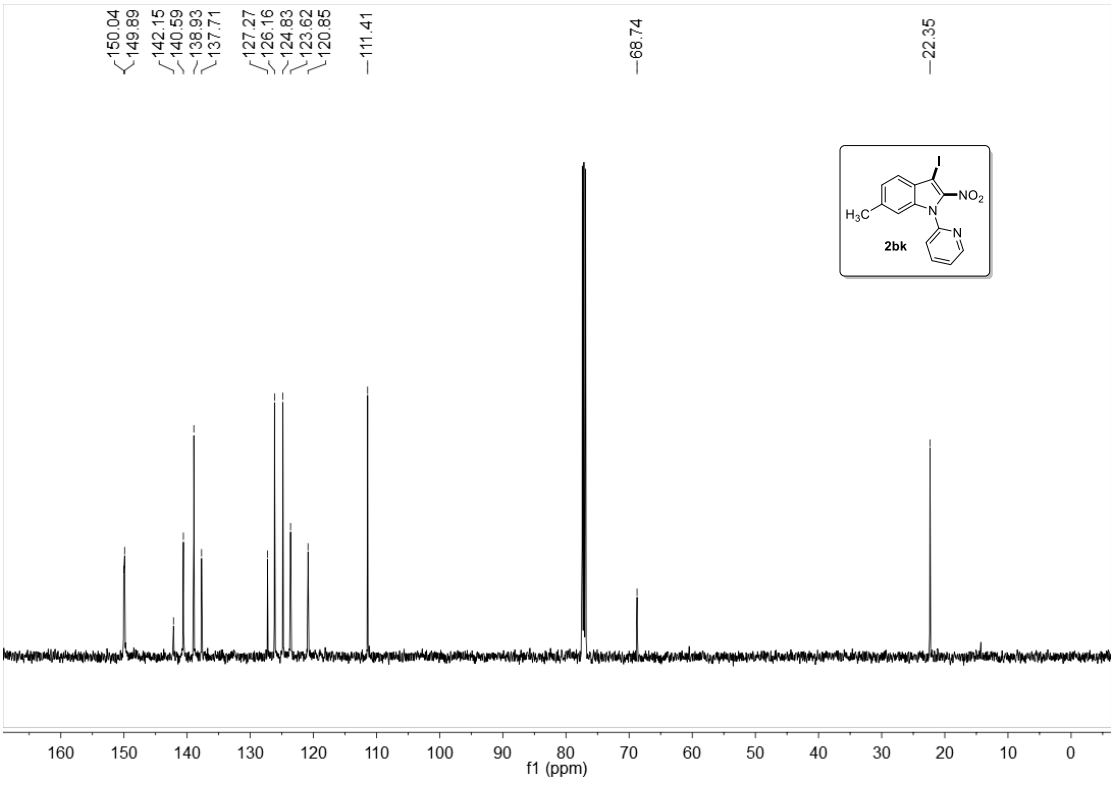
7.95
7.52
7.44
7.43
7.43
7.42
7.41
7.19
7.18
7.06
2.45
1.01
1.03
1.01
2.04
1.01
1.00
3.07
I
NO2
H3C
N
N
2bk
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.93
137.71
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126.16
124.83
123.62
120.85
111.41
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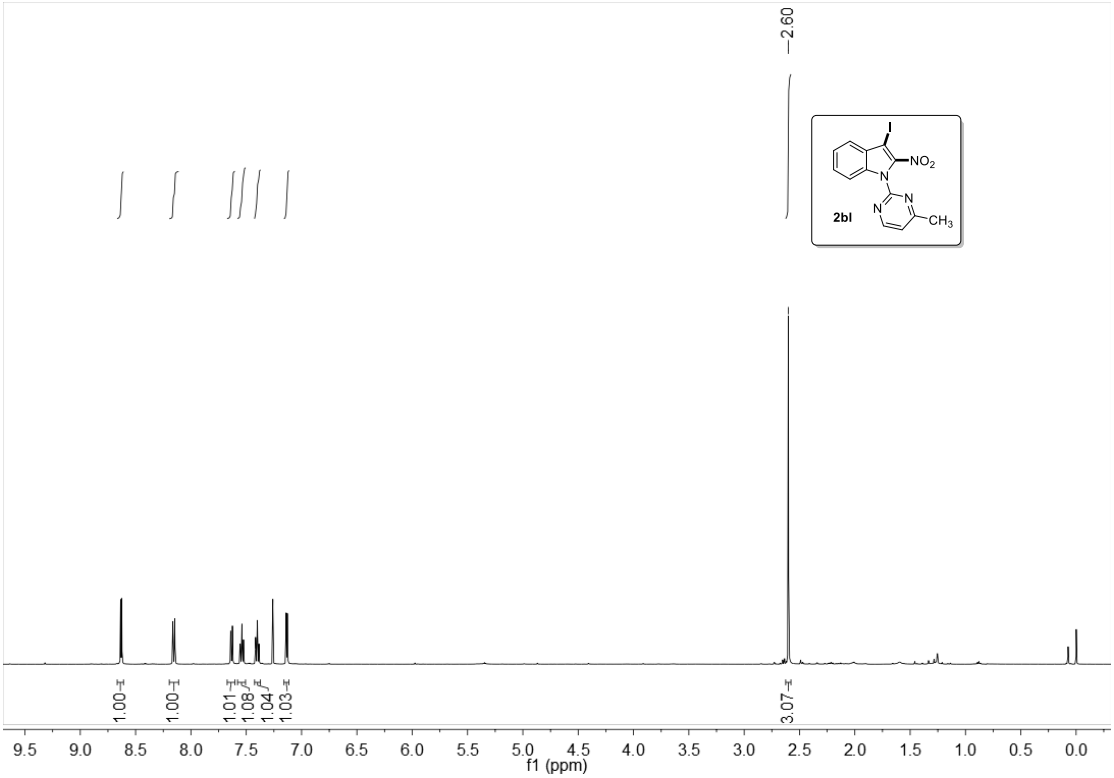
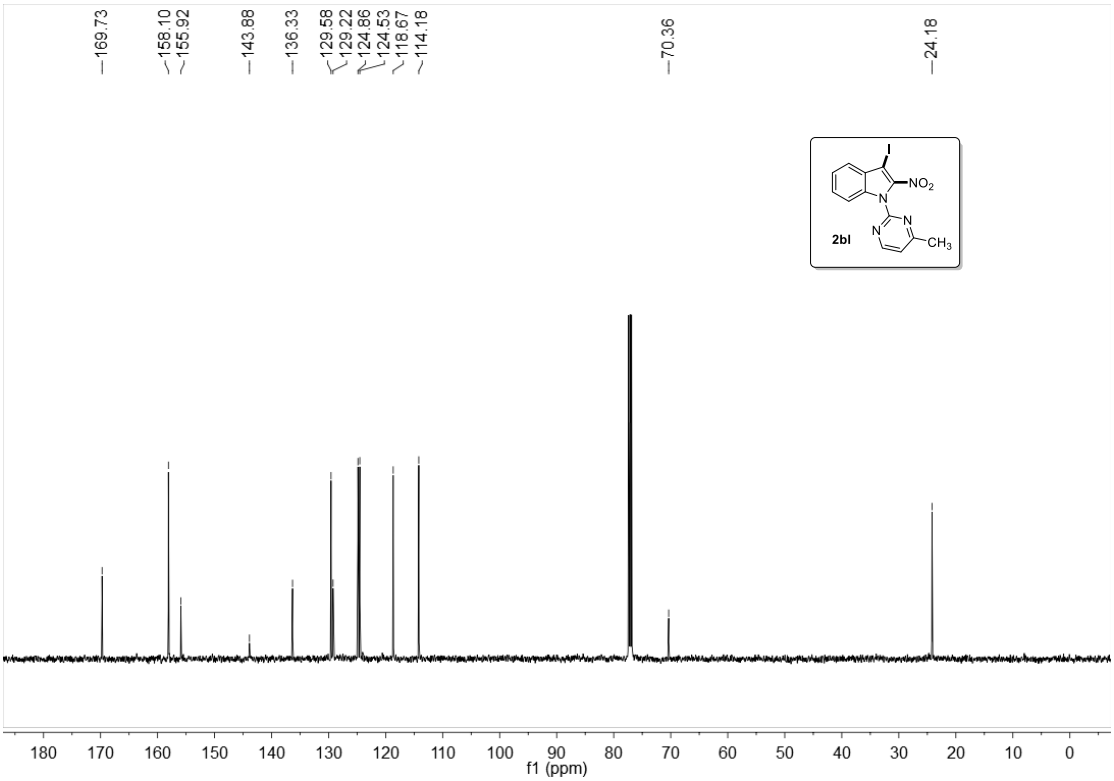
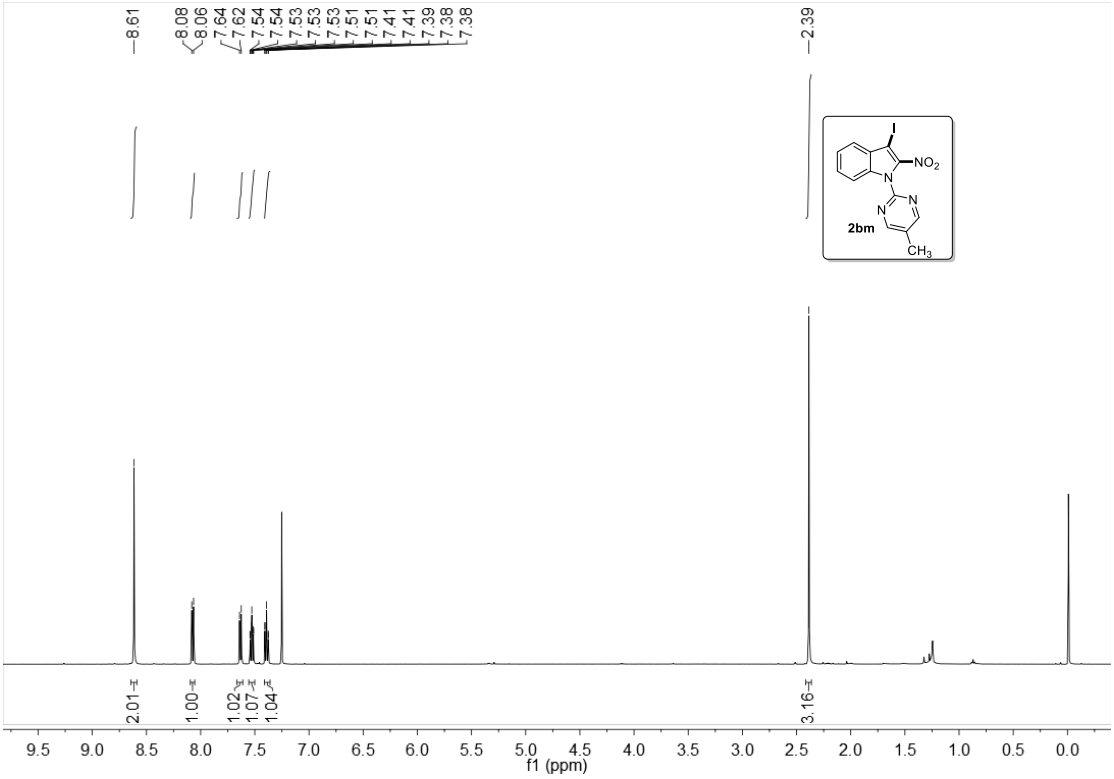
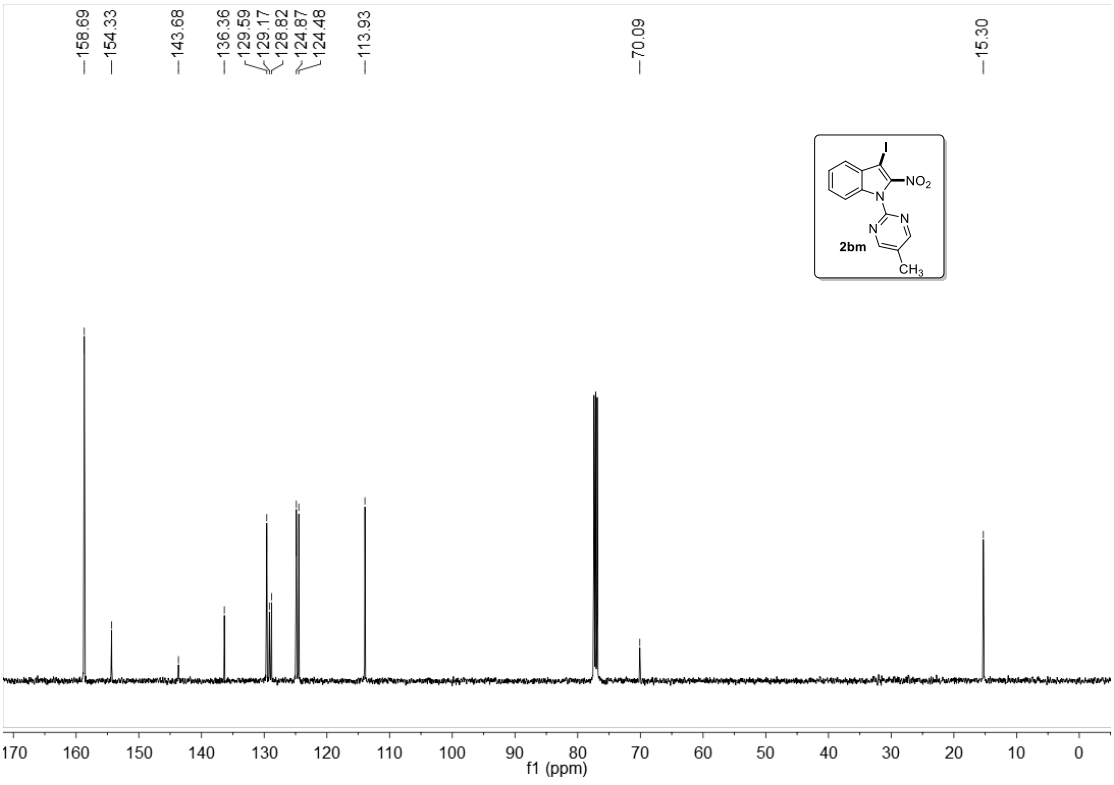
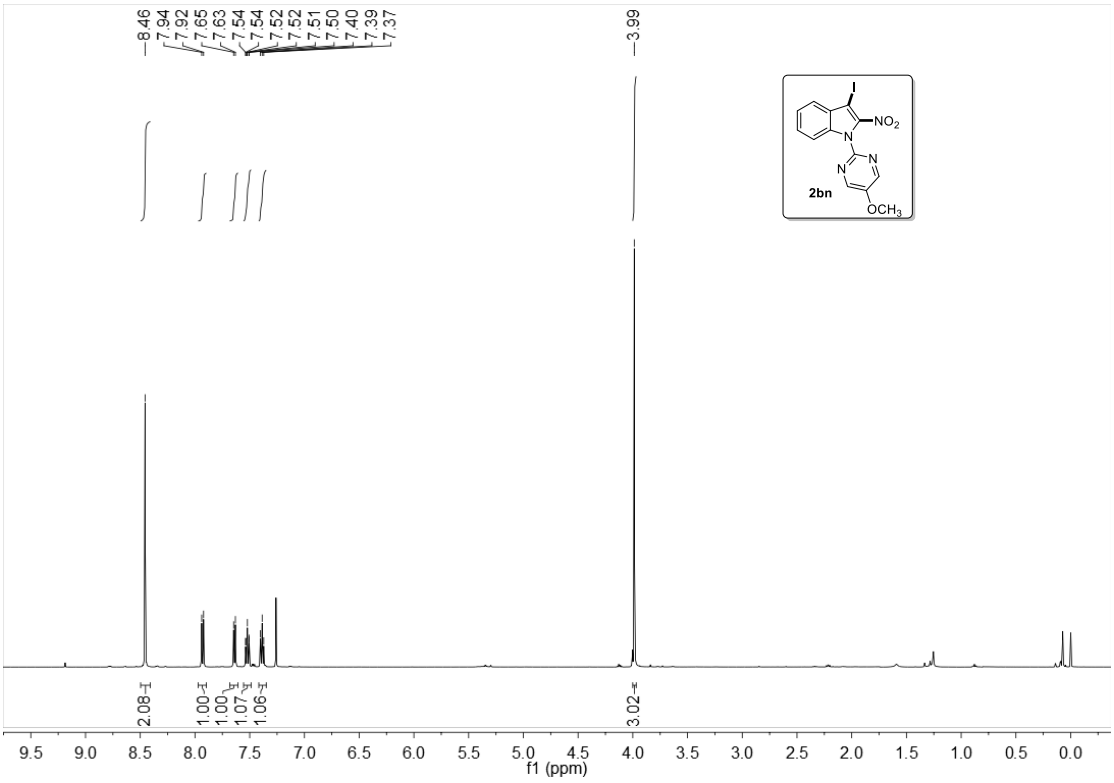
22.35
I
NO2
H3C
N
N
2bk
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2.60
1.00
1.00
1.01
1.08
1.04
1.03
3.07
2bl
f1 (ppm)


169.73
158.10
155.92
143.88
136.33
129.58
129.22
124.86
124.53
118.67
114.18
70.36
24.18
2bl
f1 (ppm)


8.61
8.08
8.06
7.64
7.62
7.54
7.54
7.53
7.53
7.53
7.51
7.51
7.41
7.39
7.38
7.38
2.39
2bm
2.01
1.00
1.02
1.07
1.04
3.16
f1 (ppm)


158.69
154.33
143.68
136.36
129.59
129.17
128.82
124.87
124.48
113.93
70.09
15.30
2bm
f1 (ppm)


8.46
7.94
7.92
7.65
7.63
7.54
7.54
7.52
7.52
7.51
7.50
7.40
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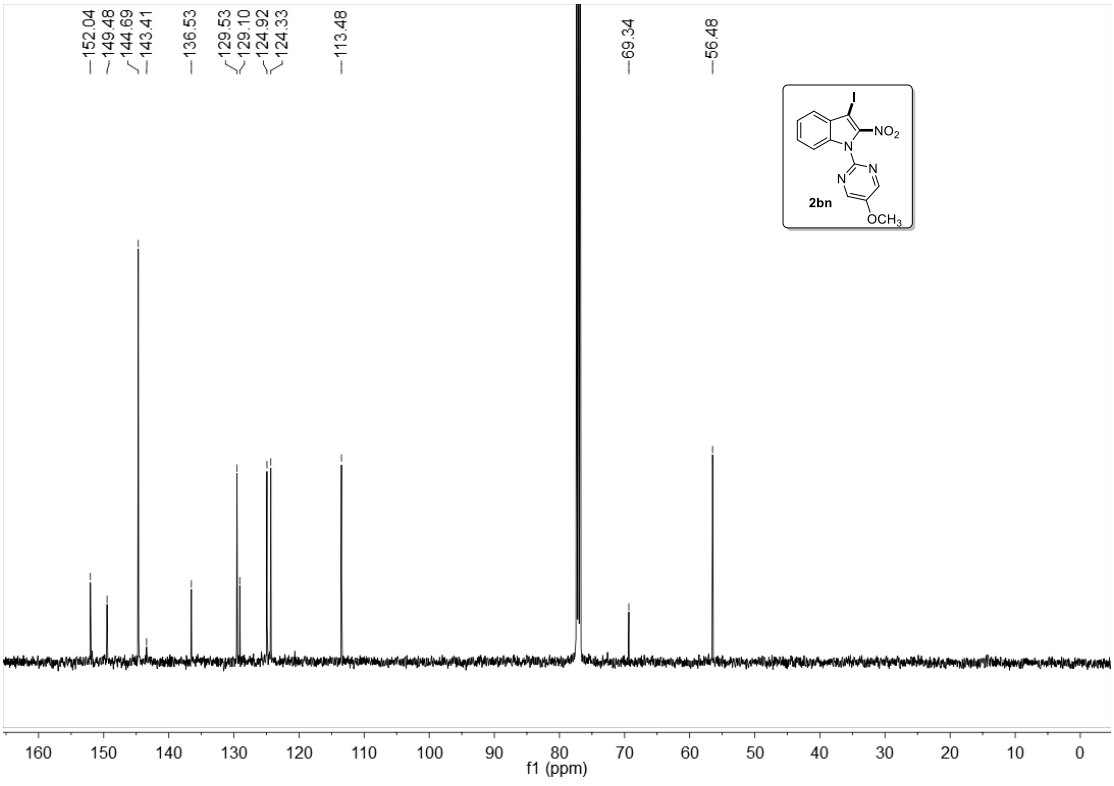
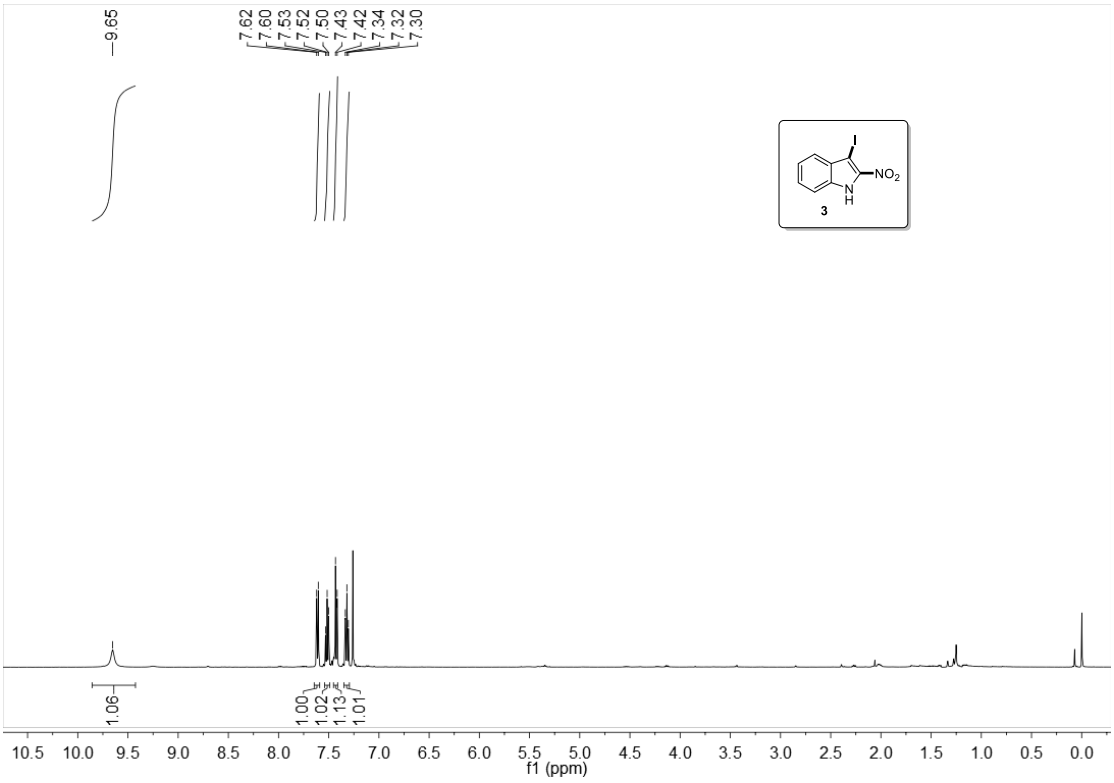
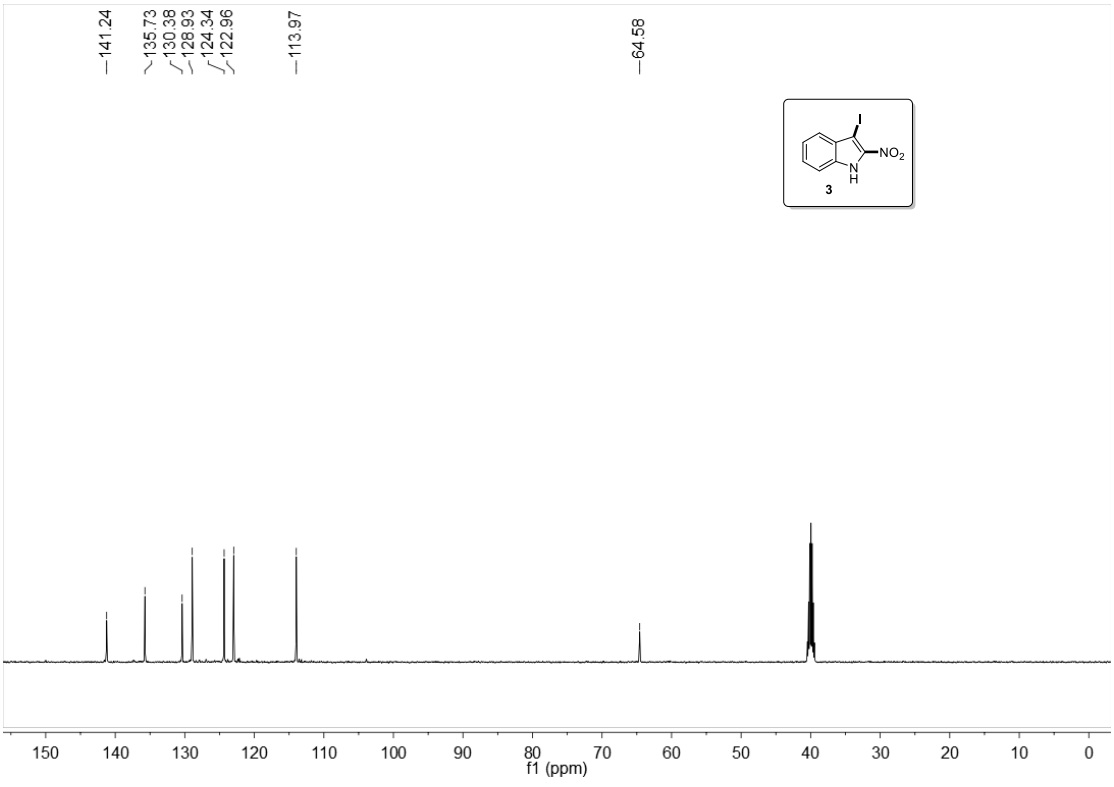
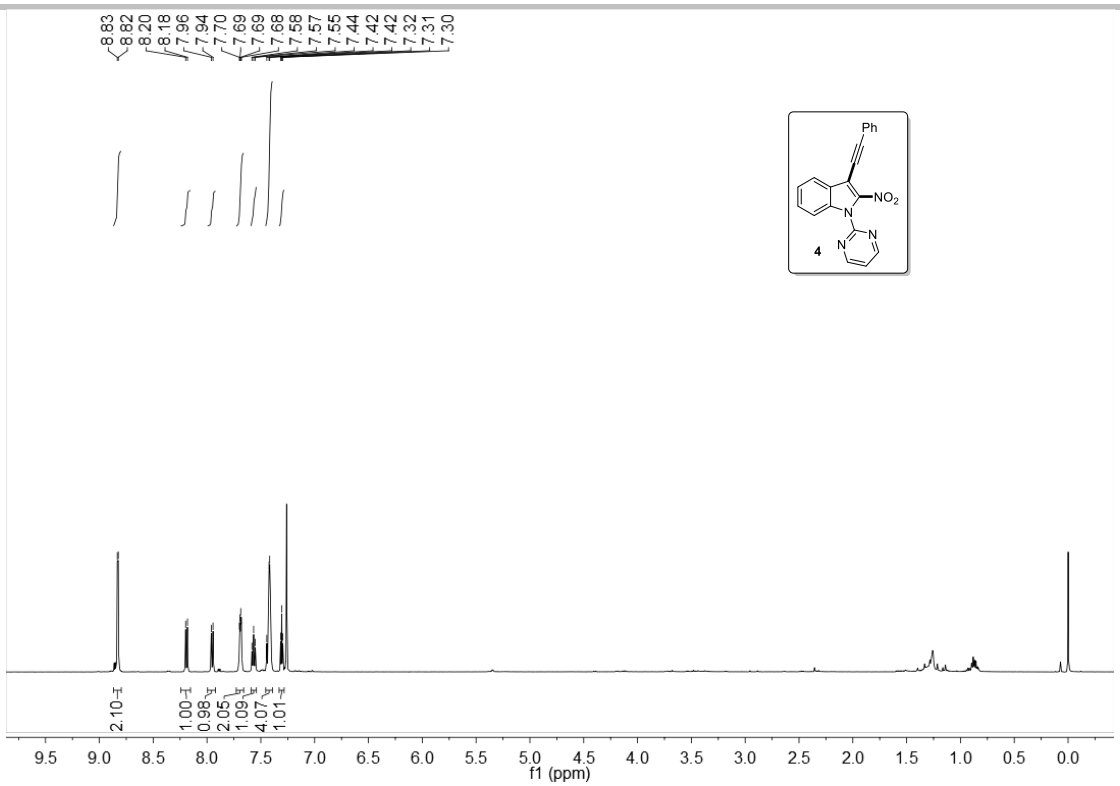
1.07
1.06
3.02
2bn
f1 (ppm)


152.04
149.48
144.69
143.41
136.53
129.53
129.10
124.92
124.33
113.48
69.34
56.48
2bn
f1 (ppm)


9.65
7.62
7.60
7.53
7.52
7.50
7.43
7.42
7.34
7.32
7.30
I
NO2
N
H
3
1.06
1.00
1.02
1.13
1.01
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
f1 (ppm)


141.24
135.73
130.38
128.93
124.34
122.96
113.97
64.58
I
NO2
N
H
3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.82
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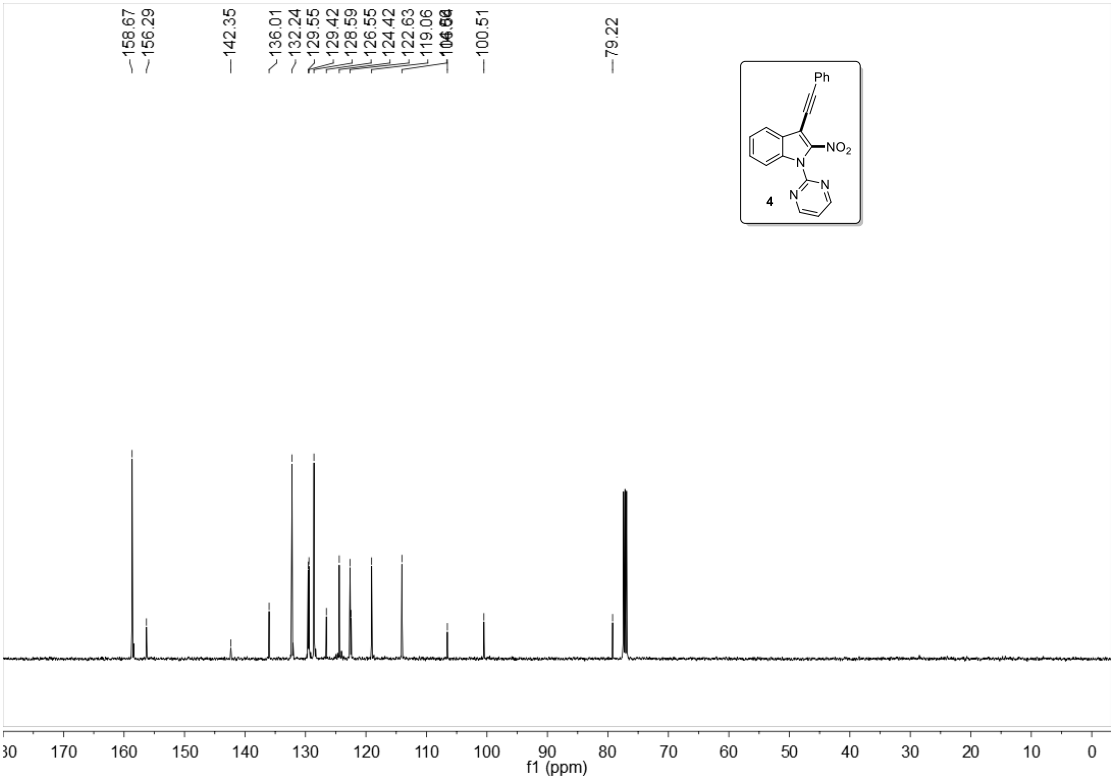
7.94
7.70
7.69
7.69
7.68
7.58
7.57
7.55
7.44
7.42
7.42
7.32
7.31
7.30
Ph
NO2
N
N
N
4
2.10
1.00
0.98
2.05
1.09
4.07
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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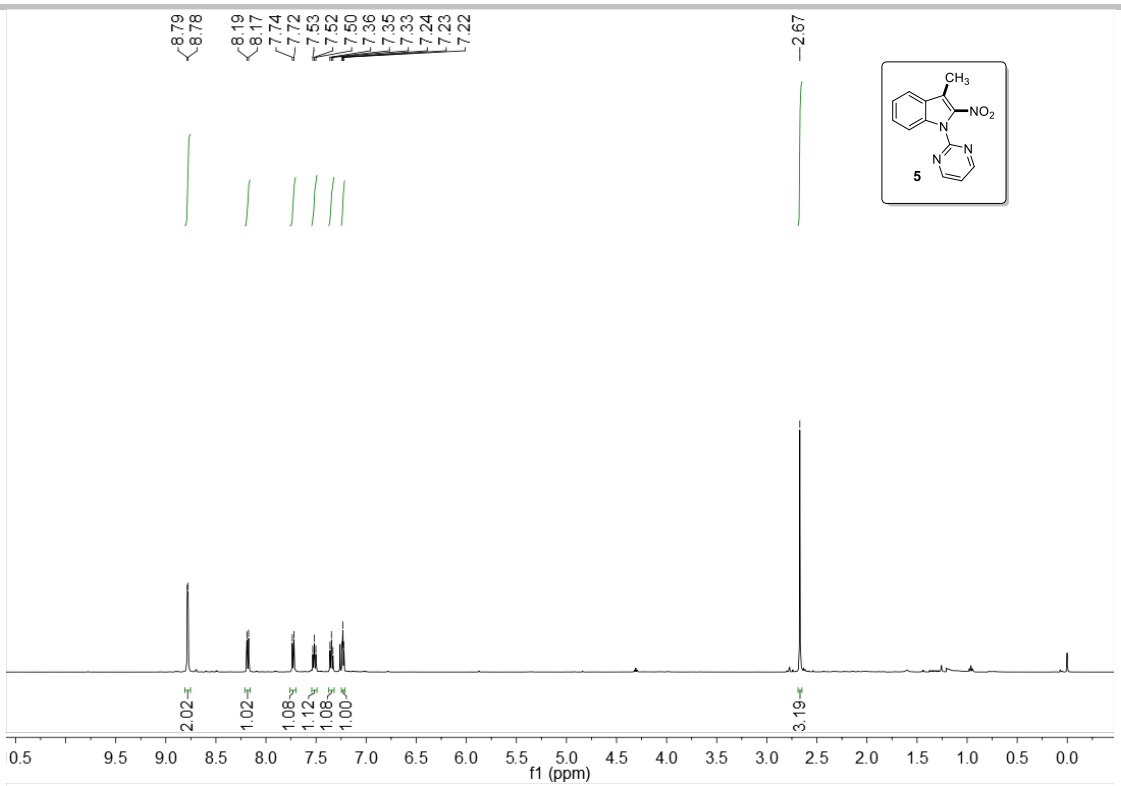
142.35
136.01
132.24
129.55
129.42
128.59
126.55
124.42
122.63
119.06
100.51
79.22
Ph
NO2
N
N
N
4
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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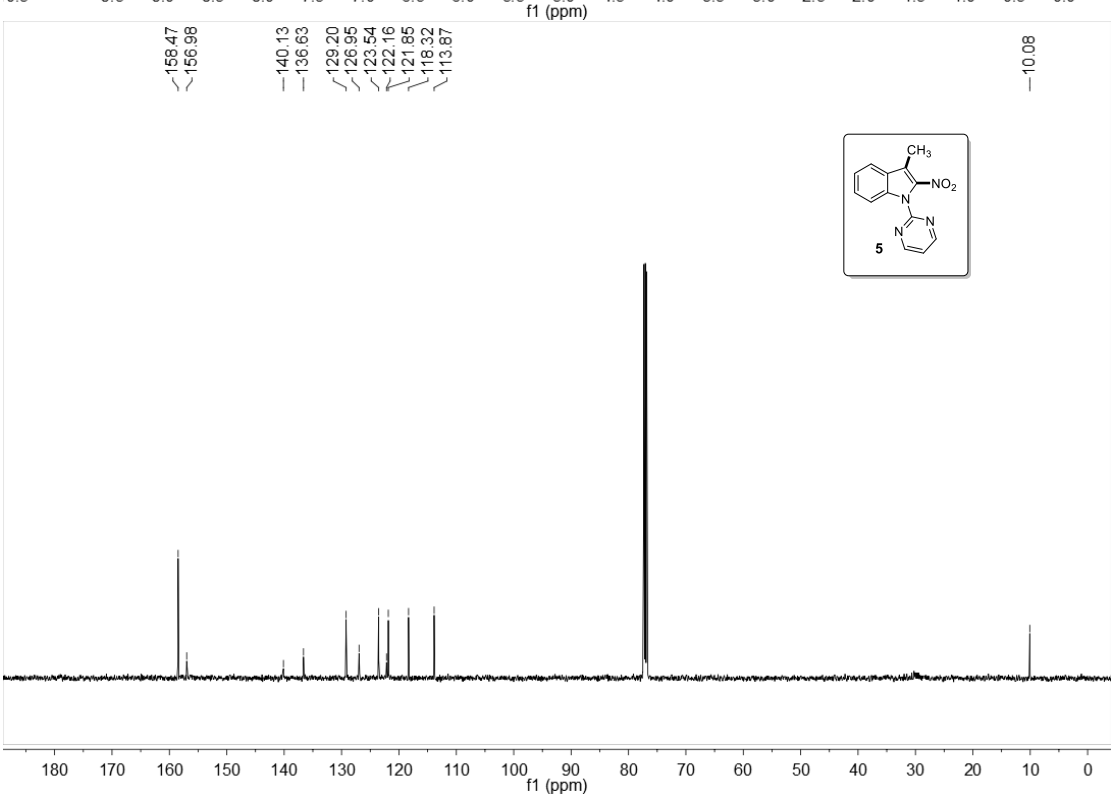
8.78
8.19
8.17
7.74
7.72
7.53
7.52
7.50
7.36
7.35
7.33
7.24
7.23
7.22
2.67
CH3
NO2
N
N
5
2.02
1.02
1.08
1.12
1.08
1.00
3.19
f1 (ppm)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156.98
140.13
136.63
129.20
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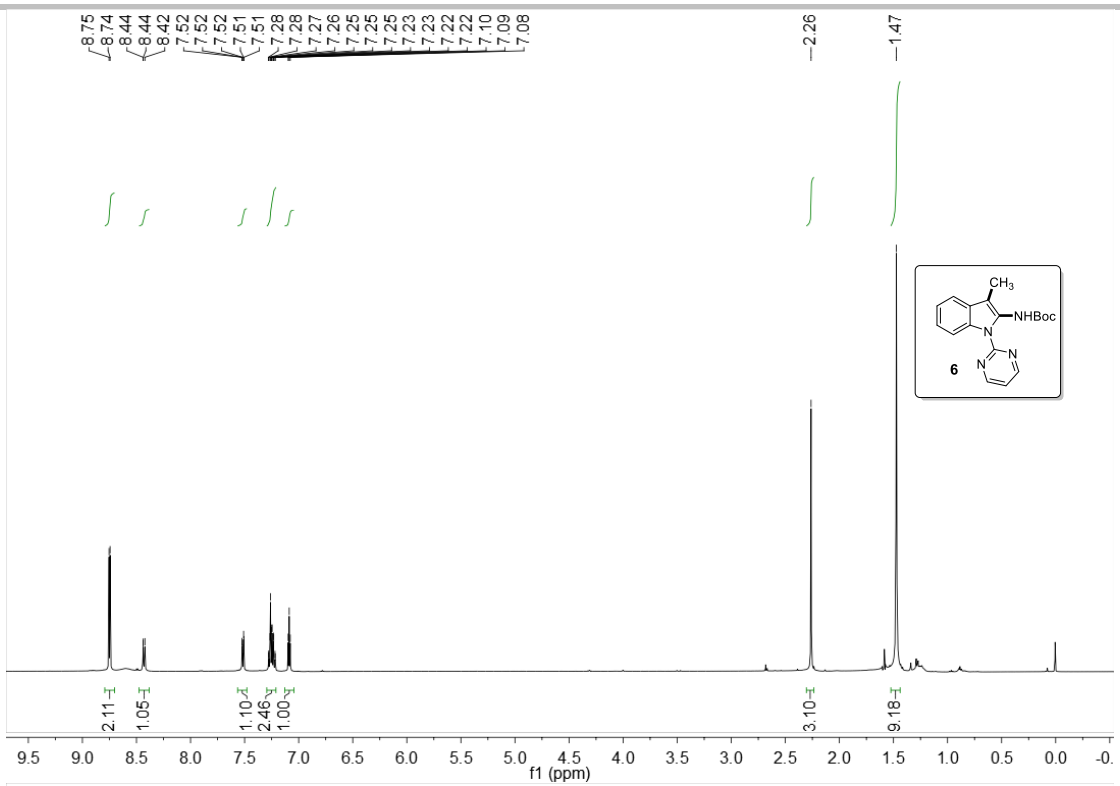
123.54
122.16
121.85
118.32
113.87
10.08
CH3
NO2
N
N
5
f1 (ppm)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8.74
8.44
8.44
8.42
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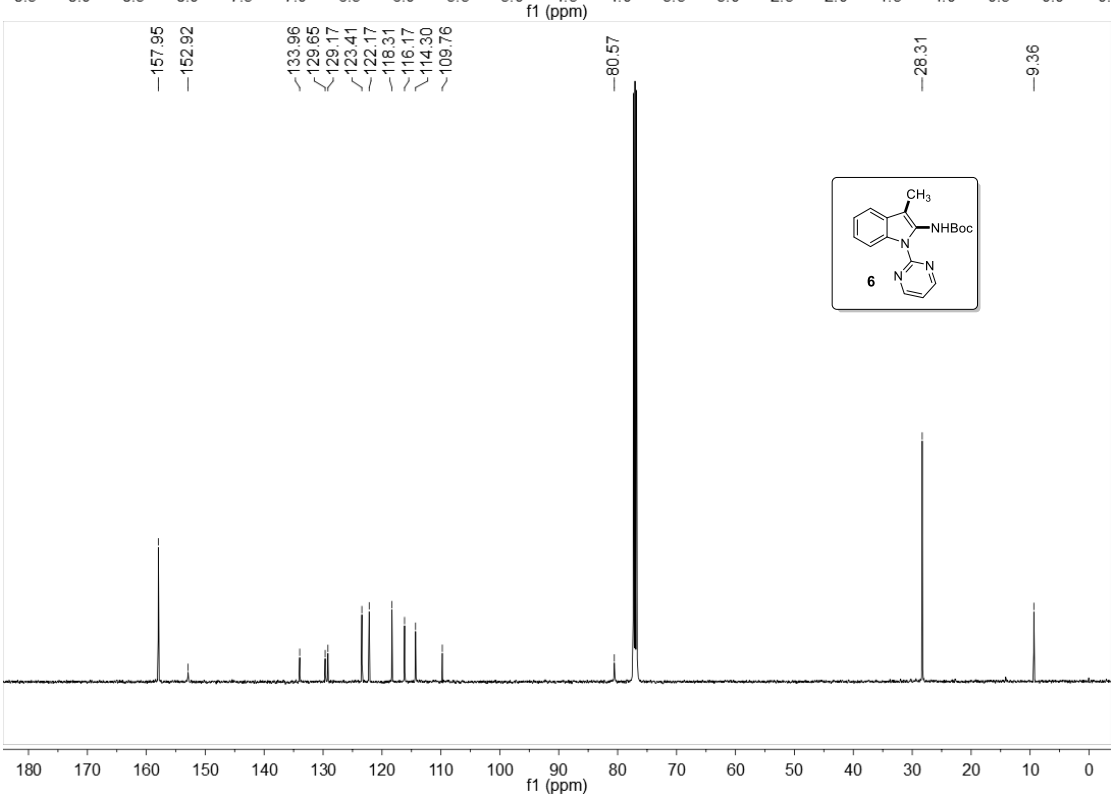
7.52
7.52
7.51
7.51
7.28
7.28
7.27
7.26
7.25
7.25
7.25
7.23
7.23
7.22
7.22
7.10
7.09
7.08
2.26
1.47
CH3
NHBoc
N
N
N
6
2.11
1.05
1.10
2.46
1.00
3.10
9.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.92
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129.65
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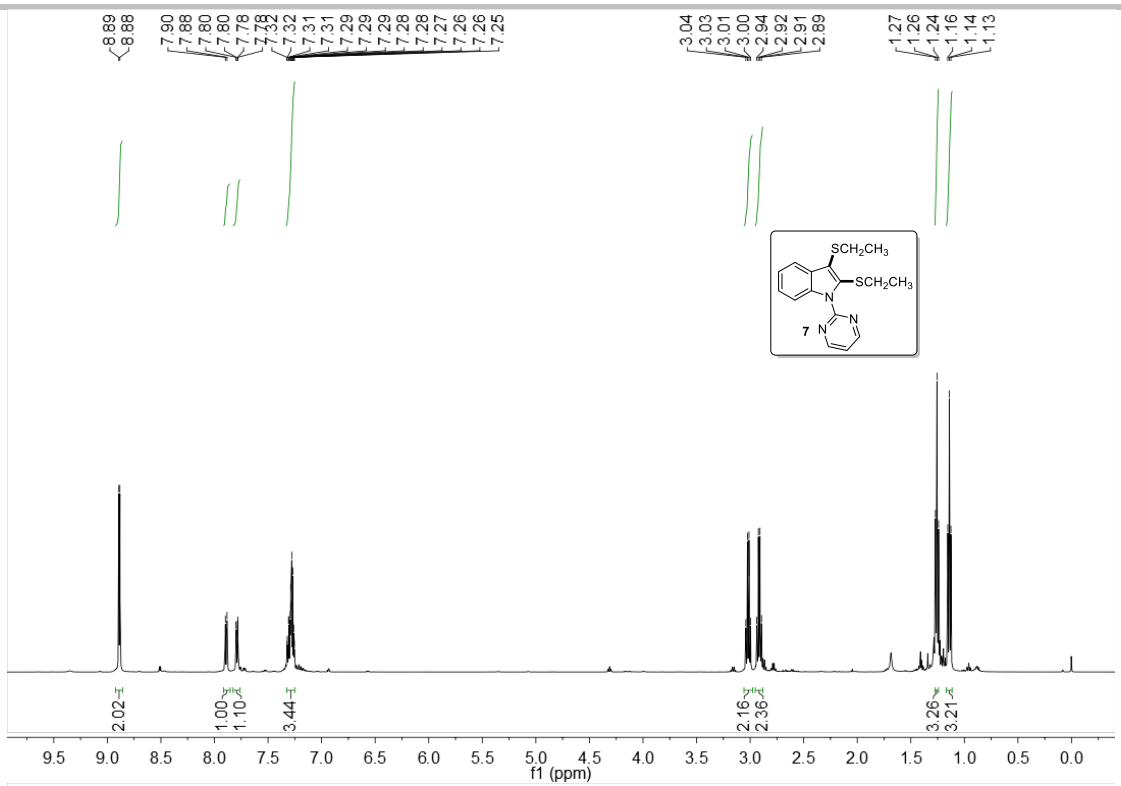
123.41
122.17
118.31
116.17
114.30
109.76
80.57
28.31
9.36
CH3
NHBoc
N
N
N
6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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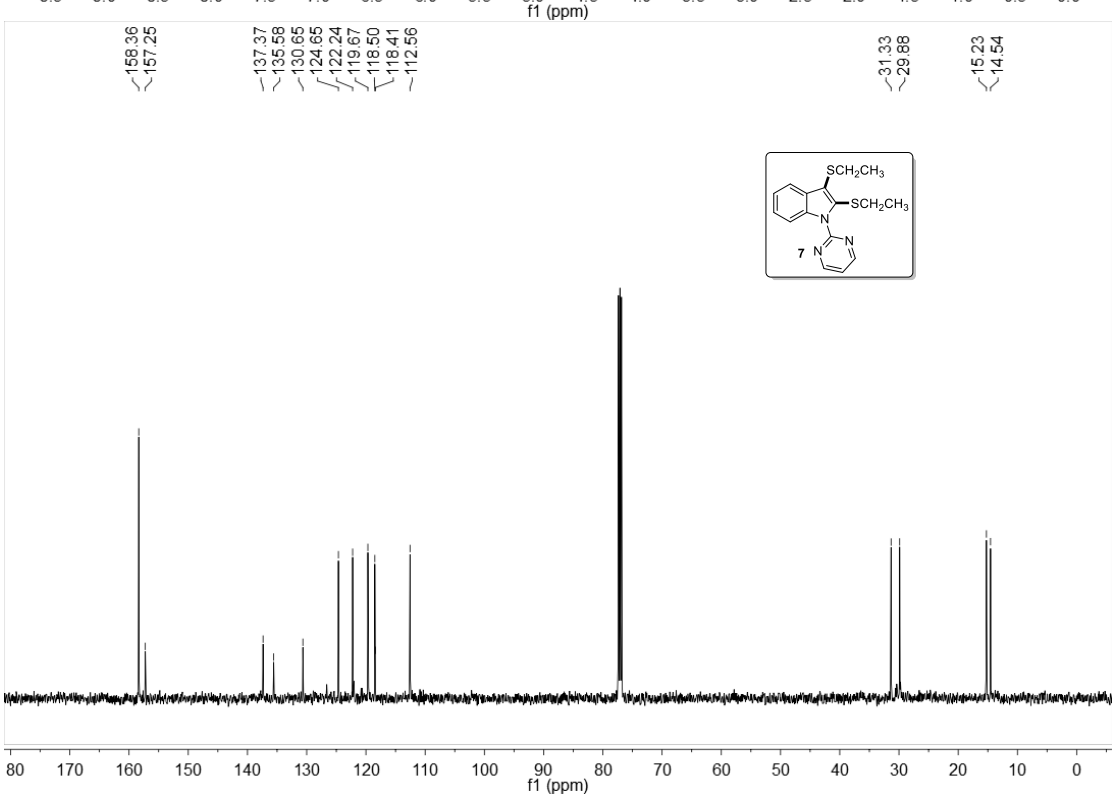
7.31
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
3.04
3.03
3.01
3.00
2.94
2.92
2.91
2.89
1.27
1.26
1.24
1.16
1.14
1.13
SCH2CH3
SCH2CH3
N
N
7
2.02
1.00
1.10
3.44
2.16
2.36
3.26
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.65
122.24
119.67
118.50
118.41
112.56
31.33
29.88
15.23
14.54
SCH2CH3
SCH2CH3
N
N
7
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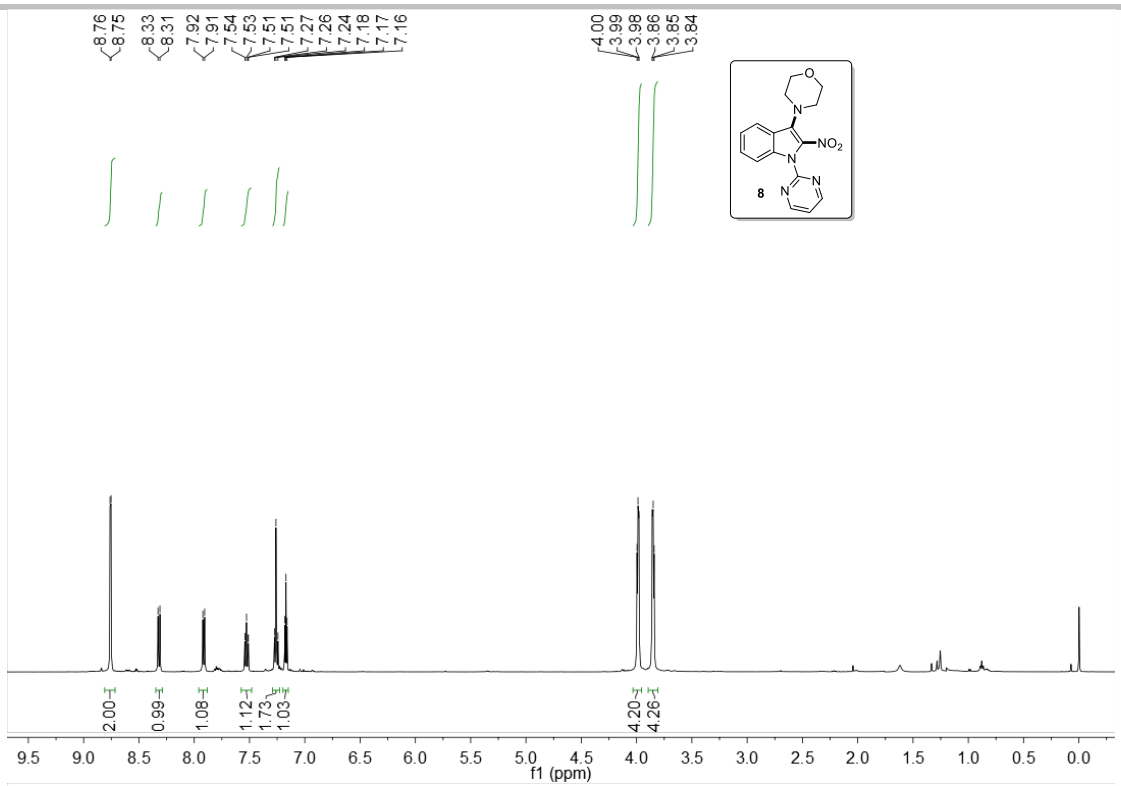
f1 (ppm)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7.91
7.54
7.53
7.51
7.51
7.27
7.26
7.24
7.18
7.17
7.16
4.00
3.99
3.98
3.86
3.85
3.84
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0.99
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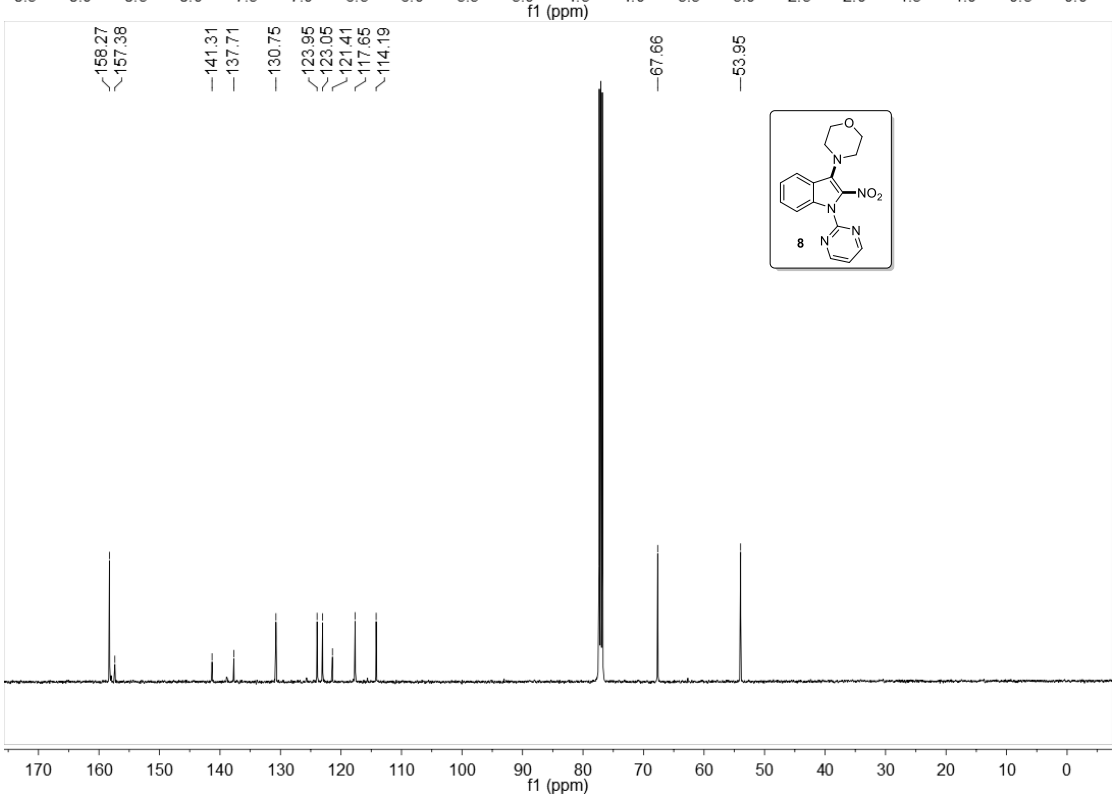
1.12
1.73
1.03
4.20
4.26
f1 (ppm)
8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121.41
117.65
114.19
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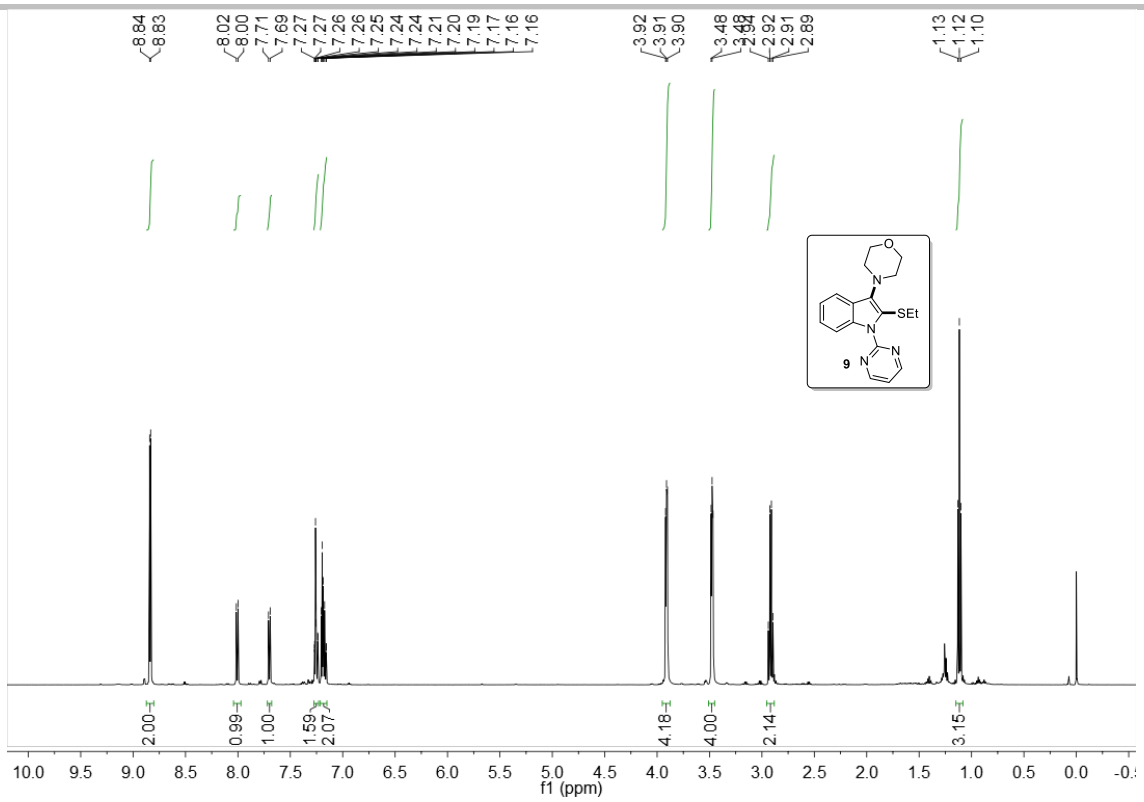
53.95
f1 (ppm)
8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8.83
8.02
8.00
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7.69
7.27
7.26
7.25
7.24
7.21
7.20
7.19
7.17
7.16
3.92
3.91
3.90
3.48
2.92
2.91
2.89
1.13
1.12
1.10
SEt
9
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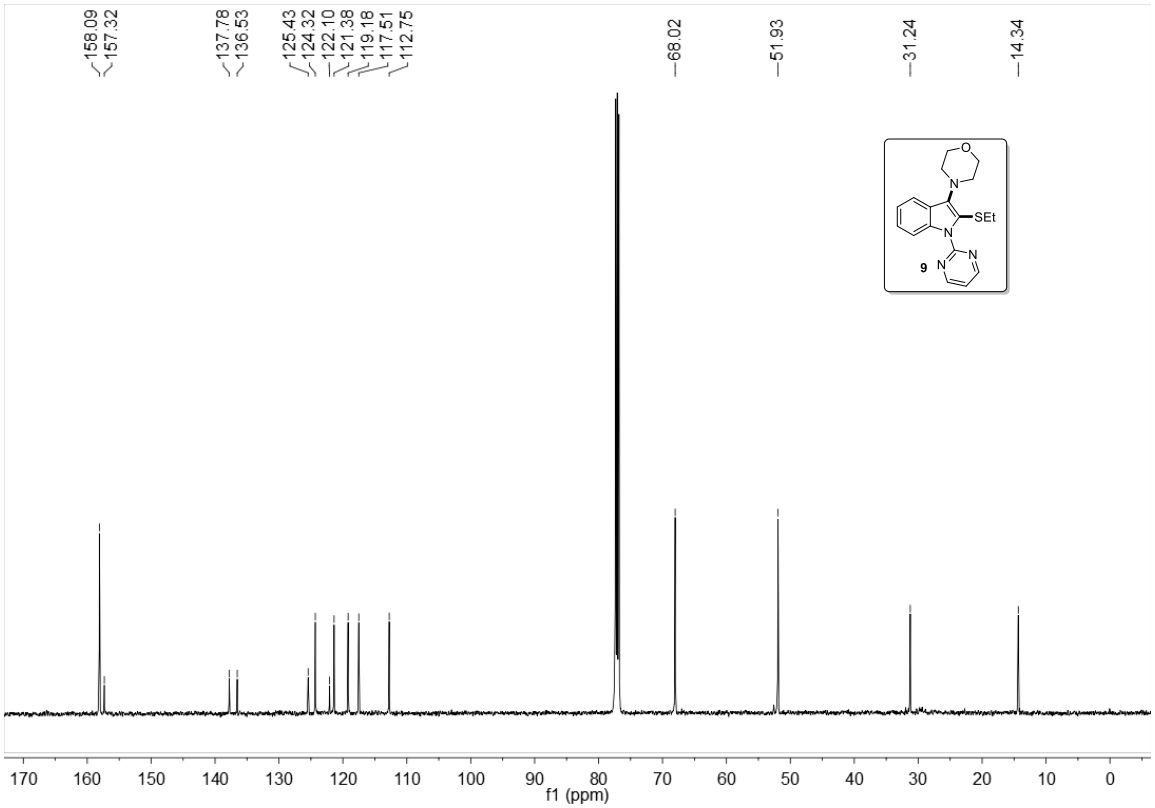
0.99
1.00
1.59
2.07
4.18
4.00
2.14
3.15
f1 (ppm)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124.32
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117.51
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68.02
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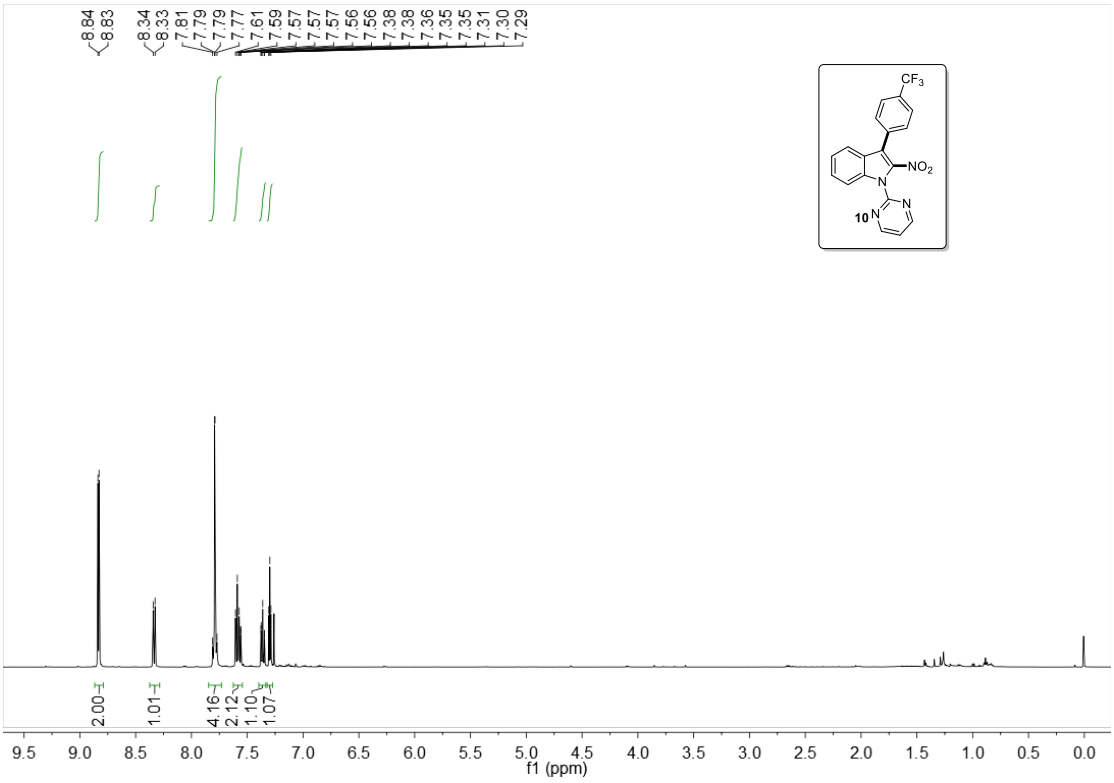
31.24
14.34
SEt
9
f1 (ppm)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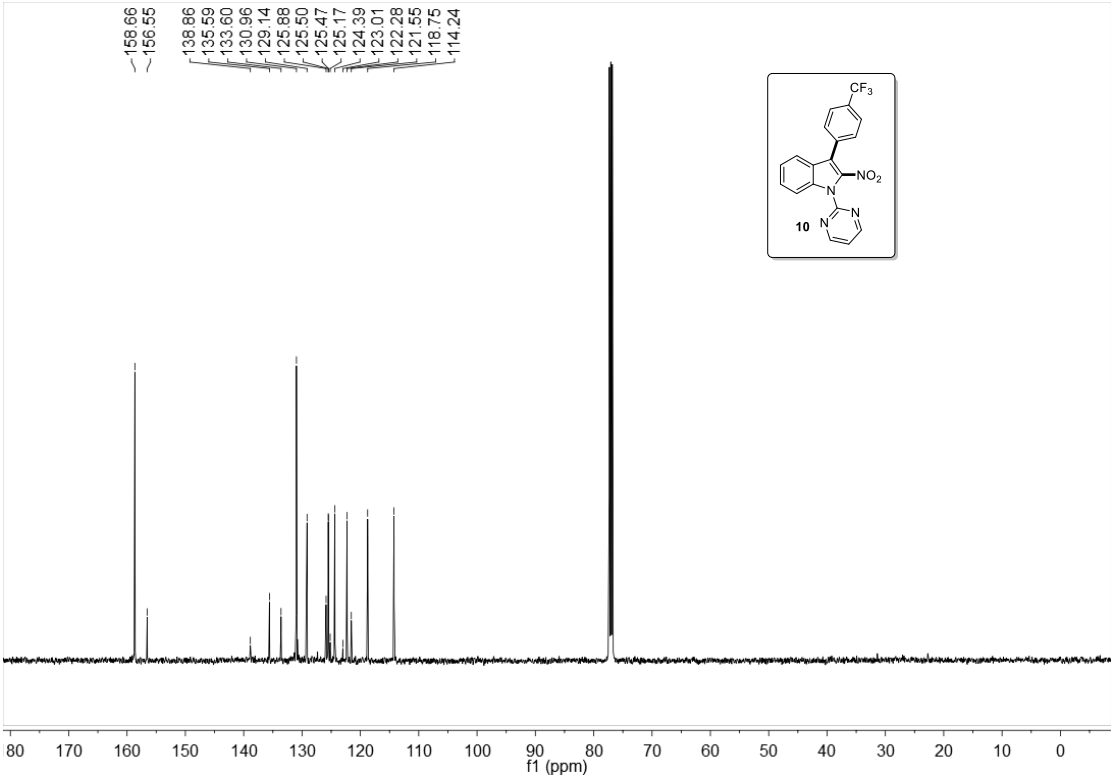
7.57
7.56
7.56
7.38
7.38
7.36
7.35
7.35
7.31
7.30
7.29
CF3
NO2
N
N
N
10
2.00
1.01
4.16
2.12
1.10
1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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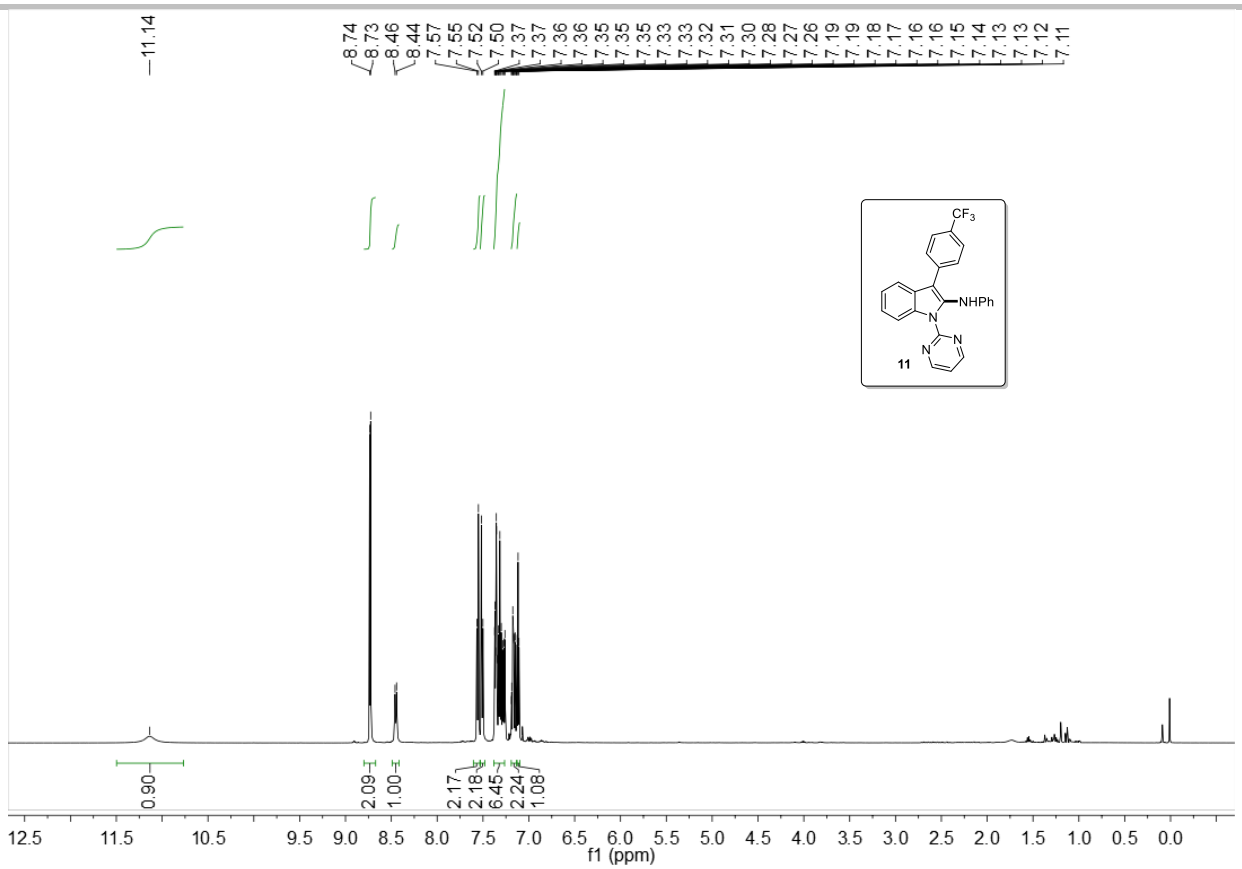
130.96
129.14
125.88
125.50
125.47
125.17
124.39
123.01
122.28
121.55
118.75
114.24
CF3
NO2
N
N
N
10
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.35
7.35
7.35
7.33
7.33
7.32
7.31
7.30
7.28
7.27
7.26
7.19
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.13
7.13
7.12
7.11
CF3
NHPh
N
N
11
0.90
2.09
1.00
2.17
2.18
6.45
2.24
1.08
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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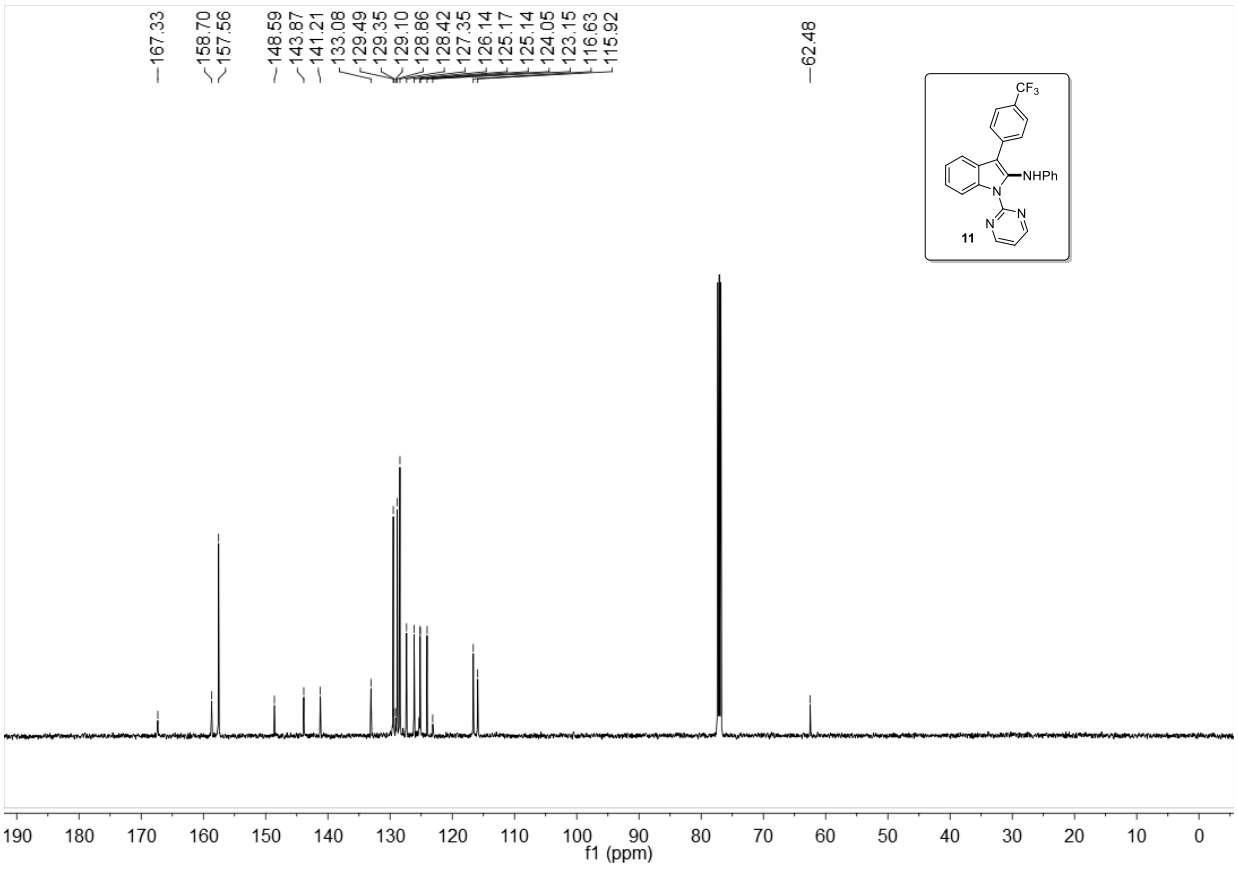
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.08
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129.10
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127.35
126.14
125.17
125.14
124.05
123.15
116.63
115.92
62.48
CF3
NHPh
N
N
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)