

Supporting Information

**Rh-catalyzed C-H allylation and annulation of *N*-arylpirazolidinones with MBH adducts**

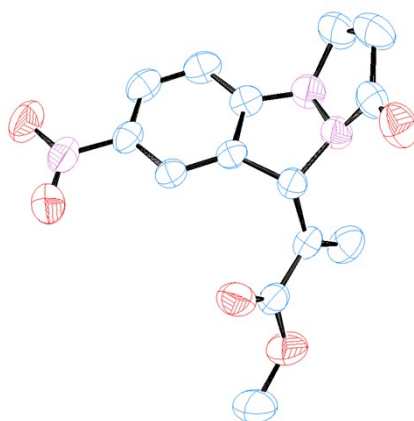
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**General Information.** [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (97%), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (97%), [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (98%), Zn(OAc)<sub>2</sub> (>98%), Cu(OAc)<sub>2</sub> (98%), Ag(OAc) (>99%), Zn(OTf)<sub>2</sub> (>98%), Ag<sub>2</sub>CO<sub>3</sub> (99%), NaOAc (98%), AcOH (98%), LiBH<sub>4</sub> (>95%), BnNH<sub>2</sub> (99%), H<sub>2</sub>O<sub>2</sub> (30%), 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and phenyl hydrazine hydrochlorides of Sigma-Aldrich, BLD Pharm and TCI chemicals were used as received. Toluene, THF, 1,4-dioxane, CHCl<sub>3</sub> and (CH<sub>2</sub>Cl)<sub>2</sub> were dried prior as per the standard procedure. Silica gel-G/GF254 plates (Merck) were used for TLC analysis with a mixture of hexane and EtOAc as the eluent. Column chromatography was carried out using Rankem silica gel (60-120 mesh). Bruker Avance III 400, 500 and 600 MHz NMR spectrometers were used to record (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F) spectra using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations were used when appropriate: s = singlet, d = doublet, t = triplet and m = multiplet. Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Open capillary tubes were used for the measurements and are uncorrected. Mestre nova software was used throughout the spectral analysis. Q-ToF ESI-MS instrument Agilent (model: 6546 LC/Q-TOF) was used for recording HRMS data. Infrared spectra were recorded on Perkin Elmer FT-IR instrument. Single crystal X-ray data of **3oa** was collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/*K*α radiation and the structure was solved by direct method using SHELXL-19 (Göttingen, Germany).

**Sample Preparation for Crystal Growth.** The compound **30a** (10 mg) was dissolved in CHCl<sub>3</sub> (1 mL) and CH<sub>3</sub>CN (1 mL) and kept at room temperature for slow evaporation (2 days). Block shaped colorless crystals were formed. The single crystal was then subjected to X-ray diffraction.

**Crystal Structure and Data of 30a.**

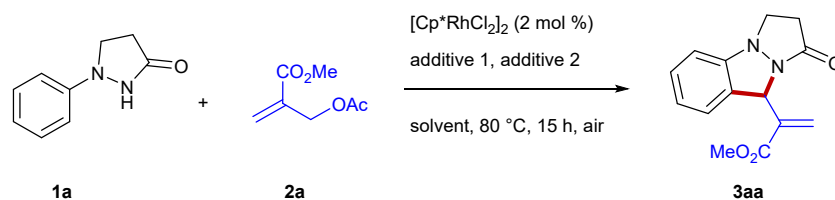


**Figure S1.** ORTEP diagram of Methyl 2-(7-nitro-1-oxo-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-9-yl) acrylate **30a** (CCDC 2516536) with 50% ellipsoid. H-omitted for clarity.

CCDC	2516536
Identification code	<b>30a</b>
Empirical formula	'C <sub>14</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub> '
Formula weight	303.27
Crystal habit, colour	Block/Yellow
Temperature, <i>T</i> /K	297 K
Wavelength, $\lambda$ /Å	0.71073
Crystal system	'monoclinic'
Space group	'P 1 21/c 1'
Unit cell dimensions	a = 8.740(3) Å b = 21.397(7) Å c = 7.686(3) Å $\alpha$ = 90 $\beta$ = 100.897(9) $\gamma$ = 90

Volume, $V/\text{\AA}^3$	1411.5(8)
$Z$	4
Calculated density, $\text{Mg}\cdot\text{m}^{-3}$	1.427
Absorption coefficient, $\mu/\text{mm}^{-1}$	0.111
$F(000)$	632
$\theta$ range for data collection	1.903 to 24.998
Limiting indices	$-10 \leq h \leq 10, -25 \leq k \leq 25, -9 \leq l \leq 9$
Reflection collected / unique	2459/2093
Completeness to $\theta$	99.2%
Absorption correction	Multi-scan
Refinement method	'SHELXL-2019/3 (Sheldrick 2019)'
Data / restraints / parameters	2459/0/ 200
Goodness-of-fit on $F^2$	1.059
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0414, wR2 = 0.0948$
$R$ indices (all data)	$R1 = 0.0503, wR2 = 0.1035$

**Table S1. Optimization of Reaction Conditions<sup>a</sup>**

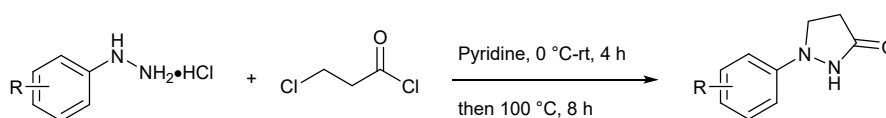


Entry	Additive 1	Additive 2	Solvent	Yield <sup>b</sup> (%)
1	Zn(OAc) <sub>2</sub>	-	(CH <sub>2</sub> Cl) <sub>2</sub>	45
2	Cu(OAc) <sub>2</sub>	-	(CH <sub>2</sub> Cl) <sub>2</sub>	trace
3	Ag(OAc)	-	(CH <sub>2</sub> Cl) <sub>2</sub>	n.d.
4	NaOAc	-	(CH <sub>2</sub> Cl) <sub>2</sub>	33
5	Ag <sub>2</sub> CO <sub>3</sub>	-	(CH <sub>2</sub> Cl) <sub>2</sub>	n.d.
6	Zn(OTf) <sub>2</sub>	-	(CH <sub>2</sub> Cl) <sub>2</sub>	35
7 <sup>c</sup>	Zn(OAc) <sub>2</sub>	-	(CH <sub>2</sub> Cl) <sub>2</sub>	52
8 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	(CH <sub>2</sub> Cl) <sub>2</sub>	73
9 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	toluene	70
10 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	1,4-dioxane	88

11 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	CHCl <sub>3</sub>	57
12 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	TFE	n.d.
13 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	HFIP	trace
14 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	THF	63
15 <sup>d</sup>	Zn(OAc) <sub>2</sub>	AcOH	CH <sub>3</sub> CN	25
16 <sup>e</sup>	Zn(OAc) <sub>2</sub>	AcOH	1,4-dioxane	81
17 <sup>f</sup>	Zn(OAc) <sub>2</sub>	AcOH	1,4-dioxane	trace
18 <sup>g</sup>	Zn(OAc) <sub>2</sub>	AcOH	1,4-dioxane	n.d.
19 <sup>h</sup>	Zn(OAc) <sub>2</sub>	AcOH	1,4-dioxane	n.d.

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (2 mol %), additive 1 (50 mol %), additive 2 (1 equiv), solvent (1 mL), 15 h, 80 °C, air. <sup>b</sup>Isolated yield. <sup>c</sup>Additive 1 (1 equiv) used. <sup>d</sup>Additive 1 (2 equiv) used. <sup>e</sup>At 100 °C. <sup>f</sup>N<sub>2</sub> atm. <sup>g</sup>[Cp\*Co(CO)I<sub>2</sub>] was used. <sup>h</sup>[Cp\*IrCl<sub>2</sub>]<sub>2</sub> was used. n.d.= not detected, HFIP = 1,1,1,3,3,3-Hexafluoro-isopropanol, TFE = 2,2,2-Trifluoroethanol.

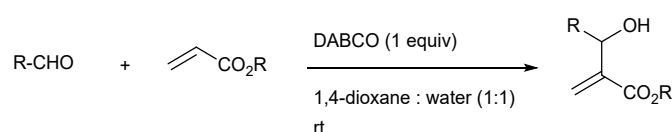
### General Procedure for the Preparation of *N*-Arylpyrazolidinones **1**.<sup>1</sup>



**Scheme S1**

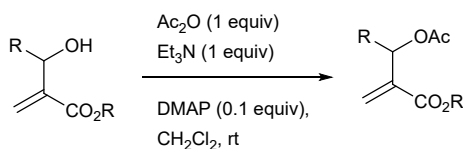
To a stirred solution of aryl hydrazine hydrochloride (5 mmol, 1equiv) in pyridine (15 mL), 3-chloropropionyl chloride (5 mmol, 1 equiv, 0.5 mL) was added dropwise at 0 °C. The resultant mixture was stirred at room temperature for 4 h and further heated at 100 °C in an oil bath for 8 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, acidified with 3M HCl until the pH became 1-2 and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). The combined organic layer was washed with brine (20 mL) and water (10 mL). Drying (Na<sub>2</sub>SO<sub>4</sub>) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate/hexane as eluent to afford *N*-arylpyrazolidinones **1a-s**.

### General Procedure for the Preparation of MBH Adducts **2**.<sup>2</sup>



**Scheme S2**

**Step-I:** To a stirred solution of aldehyde (5 mmol, 1 equiv) in 1,4-dioxane/water (1:1, 10 mL), acrylate (15 mmol, 3 equiv) and DABCO (5 mmol, 1 equiv, 560 mg) were added at room temperature. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate (50 mL) and washed with sat. NaHCO<sub>3</sub> (3 x 15 mL). Drying (Na<sub>2</sub>SO<sub>4</sub>) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford corresponding MBH alcohols.

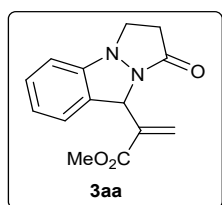


**Scheme S3**

**Step-II:** To a stirred solution of MBH alcohols (2 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), Ac<sub>2</sub>O (2 mmol, 1 equiv, 0.2 mL), Et<sub>3</sub>N (2 mmol, 1 equiv, 0.3 mL) and DMAP (0.2 mmol, 0.1 equiv, 24 mg) were added and stirred for 4 h at room temperature. After completion (monitored by TLC), the reaction mixture was poured into 2M HCl and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). Drying (Na<sub>2</sub>SO<sub>4</sub>) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford MBH acetates **2a-n**.

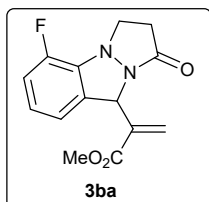
### General Procedure for the Rh-Catalyzed C-H allylation/annulation of *N*-Arylpyrazolidinones with MBH Adducts.

To a stirred solution of *N*-arylpyrazolidinone **1** (0.1 mmol, 1 equiv) and MBH acetate **2** (0.15 mmol, 1.5 equiv) in 1,4-dioxane (1 mL) under air, [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.002 mmol, 0.02 equiv, 1.4 mg), Zn(OAc)<sub>2</sub> (0.2 mmol, 2 equiv, 37 mg) and AcOH (0.1 mmol, 1 equiv, 5.8 μL) were added and the reaction mixture was stirred at 80 °C in an oil bath for 15 h. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **3**.

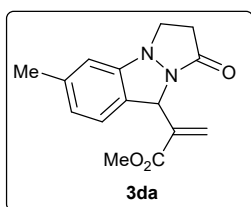


**Methyl 2-(1-oxo-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*] indazol-9-yl)-acrylate **3aa**.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f$  = 0.45; colorless liquid; yield 88% (22 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d,  $J$  = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 6.99

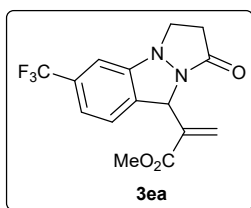
(t,  $J = 7.46$  Hz, 1H), 6.81 (d,  $J = 8.0$  Hz, 1H), 6.26 (s, 1H), 6.23 (s, 1H), 5.91 (s, 1H), 4.14-4.08 (m, 1H), 3.83 (s, 3H), 3.62-3.55 (m, 1H), 3.02-2.93 (m, 1H), 2.69-2.61 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.2, 165.9, 149.0, 137.9, 129.7, 129.1, 125.8, 124.5, 123.1, 110.1, 59.5, 52.2, 50.4, 32.7; FT-IR (neat) 2958, 2926, 2851, 1721, 1655, 1676, 1373, 1261, 1151, 1021, 795  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_3$  259.1077; Found 259.1067.



**Methyl 2-(5-fluoro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-9-yl) acrylate 3ba.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.48$ ; yellow liquid; yield 68% (18 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14-7.12 (m, 1H), 7.00-6.92 (m, 2H), 6.29 (s, 1H), 6.26 (s, 1H), 5.93 (s, 1H), 4.23-4.16 (m, 1H), 3.82 (s, 3H), 3.77-3.71 (m, 1H), 3.06-2.98 (m, 1H), 2.72-2.64 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 165.8, 150.2 ( $J_{\text{C-F}} = 243.1$  Hz), 137.6, 135.8 ( $J_{\text{C-F}} = 12.1$  Hz), 133.2 ( $J_{\text{C-F}} = 3.2$  Hz), 126.3, 124.6 ( $J_{\text{C-F}} = 5.8$  Hz), 120.1 ( $J_{\text{C-F}} = 3.5$  Hz), 116.2 ( $J_{\text{C-F}} = 17.3$  Hz), 59.8, 52.3, 51.0, 33.1;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -132.18. FT-IR (neat) 2941, 2924, 2852, 1713, 1626, 1484, 1266, 1193, 1032  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{FN}_2\text{O}_3$  277.0983; Found 277.0976.

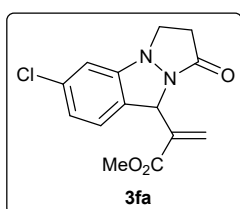


**Methyl 2-(6-methyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl) acrylate 3da.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 81% (22 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (d,  $J = 7.6$  Hz, 1H), 6.79 (d,  $J = 8.2$  Hz, 1H), 6.62 (s, 1H), 6.24 (s, 1H), 6.17 (s, 1H), 5.88 (s, 1H), 4.12-4.05 (m, 1H), 3.82 (s, 3H), 3.59-3.52 (m, 1H), 3.01-2.92 (m, 1H), 2.68-2.60 (m, 1H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 165.9, 149.2, 139.4, 138.1, 127.0, 125.6, 124.1, 123.9, 110.8, 59.4, 52.2, 50.5, 32.7, 21.7; FT-IR (neat) 2953, 2922, 2855, 1726, 1623, 1438, 1266, 1196, 808  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3$  273.1234; Found 273.1218.



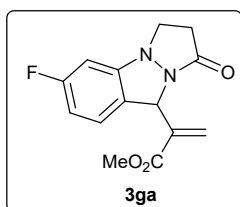
**Methyl 2-(1-oxo-6-(trifluoromethyl)-2,3-dihydro-1H,9H-pyrazolo-**

**[1,2-a]indazol-9-yl) acrylate 3ea.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.35$ ; yellow liquid; yield 82% (20 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 7.5$  Hz, 1H), 7.24 (s, 1H), 7.02 (s, 1H), 6.29 (s, 1H), 6.25 (s, 1H), 5.95 (s, 1H), 4.18-4.12 (m, 1H), 3.83 (s, 3H), 3.70-3.64 (m, 1H), 3.02-2.95 (m, 1H), 2.71-2.65 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 165.7, 149.4, 137.2, 133.4, 131.9 ( $J_{\text{C-F}} = 32.1$  Hz), 126.3, 125.1 ( $J_{\text{C-F}} = 270.7$  Hz), 125.0, 120.2 ( $J_{\text{C-F}} = 3.8$  Hz), 106.8 ( $J_{\text{C-F}} = 3.6$  Hz), 59.6, 52.4, 49.8, 32.3;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.43; FT-IR (neat) 2956, 2917, 2857, 1715, 1631, 1436, 1317, 1269, 1125, 1161, 1062  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_3$  327.0951; Found 327.0947.



**Methyl 2-(6-chloro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

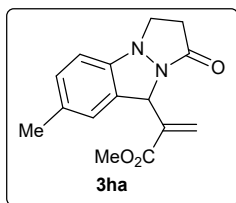
**9-yl) acrylate 3fa.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; yellow liquid; yield 73% (20 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.26 (m, 1H), 6.96-6.94 (m, 1H), 6.79-6.78 (m, 1H), 6.27 (s, 1H), 6.17 (s, 1H), 5.92 (s, 1H), 4.12-4.06 (m, 1H), 3.82 (s, 3H), 3.64-3.57 (m, 1H), 3.00-2.92 (m, 1H), 2.71-2.62 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 165.8, 150.2, 137.5, 134.9, 128.2, 126.0, 125.4, 123.1, 110.5, 59.4, 52.3, 49.9, 32.4; FT-IR (neat) 2965, 2907, 2890, 1718, 1601, 1466, 1307, 1270, 1129, 1169, 1065  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{ClN}_2\text{O}_3$  293.0687; Found 293.0680.



**Methyl 2-(6-fluoro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

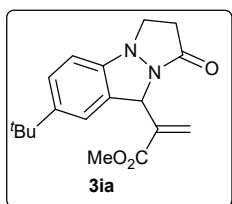
**9-yl) acrylate 3ga.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.45$ ; colorless liquid; yield 75% (20 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.27 (m, 1H), 6.67 (t,  $J = 9$  Hz, 1H), 6.50 (d,  $J = 9$  Hz, 1H), 6.26 (s, 1H), 6.16 (s, 1H), 5.91 (s, 1H), 4.11-4.06 (m, 1H), 3.82 (s, 3H), 3.62-3.56 (m, 1H), 3.00-2.93 (m, 1H), 2.70-2.63 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4,

165.8, 164.7 ( $J_{C-F} = 244.6$  Hz), 150.5 ( $J_{C-F} = 10.8$  Hz), 137.7, 125.8, 125.6 ( $J_{C-F} = 9.8$  Hz), 125.2 ( $J_{C-F} = 2.3$  Hz), 109.8 ( $J_{C-F} = 22.8$  Hz), 98.2 ( $J_{C-F} = 27$  Hz), 59.3, 52.3, 50.0, 32.5;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.27; FT-IR (neat) 2955, 2918, 2880, 1728, 1621, 1426, 1327, 1265, 1141, 1132, 1055, 779  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{FN}_2\text{O}_3$  277.0983; Found 277.0980.



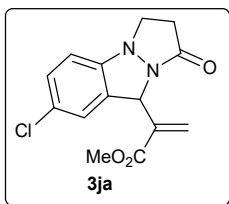
**Methyl 2-(7-methyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

**9-yl) acrylate 3ha.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 72% (19.5 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (s, 1H), 7.04 (d,  $J = 8.0$  Hz, 1H), 6.70 (d,  $J = 8.0$  Hz, 1H), 6.25 (s, 1H), 6.18 (s, 1H), 5.90 (s, 1H), 4.11-4.04 (m, 1H), 3.82 (s, 3H), 3.54-3.47 (m, 1H), 3.00-2.91 (m, 1H), 2.67-2.59 (m, 1H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 165.9, 146.8, 138.1, 132.9, 130.0, 129.6, 125.8, 124.9, 110.0, 59.5, 52.2, 50.9, 32.8, 21.1; FT-IR (neat) 2952, 2923, 2861, 1712, 1631, 1485, 1194, 1157, 816  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3$  273.1234; Found 273.1228.



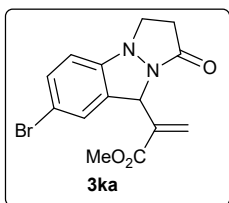
**Methyl 2-(7-(tert-butyl)-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]**

**indazol-9-yl) acrylate 3ia.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.50$ ; yellow liquid; yield 83% (26 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (s, 1H), 7.28-7.26 (m, 1H), 6.73 (d,  $J = 8.2$  Hz, 1H), 6.25 (s, 1H), 6.21 (s, 1H), 5.89 (s, 1H), 4.12-4.06 (m, 1H), 3.83 (s, 3H), 3.57-3.50 (m, 1H), 3.01-2.92 (m, 1H), 2.68-2.60 (m, 1H), 1.27 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.2, 166.0, 146.6, 146.5, 138.0, 129.5, 126.0, 125.7, 121.4, 109.6, 59.6, 52.2, 50.7, 34.7, 32.8, 31.7; FT-IR (neat) 2957, 2934, 1718, 1631, 1486, 1264, 1033  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3$  315.1703; Found 315.1694.



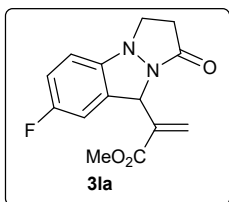
**Methyl 2-(7-chloro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

**9-yl) acrylate 3ja.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 77% (21 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (s, 1H), 7.20 (d,  $J = 8.0$  Hz, 1H), 6.73 (d,  $J = 8.2$  Hz, 1H), 6.29 (s, 1H), 6.18 (s, 1H), 5.93 (s, 1H), 4.13-4.06 (m, 1H), 3.84 (s, 3H), 3.59-3.52 (m, 1H), 3.00-2.92 (m, 1H), 2.69-2.61 (m, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 165.7, 147.6, 137.4, 131.4, 129.1, 128.3, 126.2, 124.8, 110.9, 59.5, 52.3, 50.3, 32.5; FT-IR (neat) 2953, 2926, 2851, 1718, 1630, 1465, 1164, 816  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{ClN}_2\text{O}_3$  293.0687; Found 293.0682.



**Methyl 2-(7-bromo-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

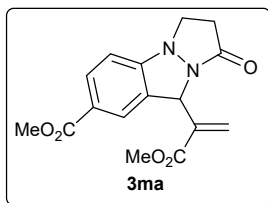
**9-yl) acrylate 3ka.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.45$ ; colorless liquid; yield 80% (27 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (s, 1H), 7.37-7.35 (m, 1H), 6.68 (d,  $J = 8.2$  Hz, 1H), 6.29 (s, 1H), 6.18 (s, 1H), 5.93 (s, 1H), 4.13-4.06 (m, 1H), 3.84 (s, 3H), 3.60-3.53 (m, 1H), 3.00-2.92 (m, 1H), 2.69-2.61 (m, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 165.7, 148.1, 137.4, 132.0, 131.8, 127.6, 126.2, 115.4, 111.4, 59.4, 52.3, 50.2, 32.5; FT-IR (neat) 2958, 2916, 2841, 1728, 1650, 1485, 1255, 1188, 828  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{BrN}_2\text{O}_3$  337.0182; Found 337.0180.



**Methyl 2-(7-fluoro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

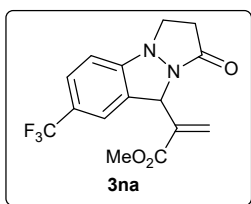
**9-yl) acrylate 3la.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.46$ ; yellow liquid; yield 74% (20 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12-7.09 (m, 1H), 6.98-6.93 (m, 1H), 6.75-6.72 (m, 1H), 6.28 (s, 1H), 6.19 (s, 1H), 5.94 (s, 1H), 4.13-4.06 (m, 1H), 3.83 (s, 3H), 3.56-3.49 (m, 1H), 3.00-2.93 (m, 1H), 2.69-2.61 (m, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 165.8, 160.3 ( $J_{\text{C-F}} = 239.6$  Hz), 145.2, 137.4, 131.3 ( $J_{\text{C-F}} = 8.7$  Hz), 126.1, 115.9 ( $J_{\text{C-F}} = 24.0$

Hz), 112.2 ( $J_{C-F} = 25.5$  Hz), 110.8 ( $J_{C-F} = 8.6$  Hz), 59.6, 52.3, 50.9, 32.6;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.32; FT-IR (neat) 2954, 2928, 1709, 1631, 1478, 1264, 1156, 888  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{FN}_2\text{O}_3$  277.0983; Found 277.0979.



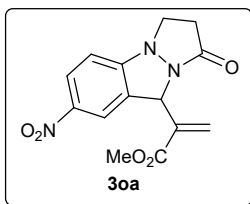
**Methyl 9-(3-methoxy-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-**

**1H,9H-pyrazolo[1,2-a] indazole-7-carboxylate 3ma.** Analytical TLC on silica gel, 1:1 EtOAc/hexane  $R_f = 0.3$ ; colorless liquid; yield 75% (24 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.97 (m, 2H), 6.80 (d,  $J = 8.0$  Hz, 1H), 6.30 (s, 1H), 6.21 (s, 1H), 5.92 (s, 1H), 4.15-4.10 (m, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.73-3.68 (m, 1H), 3.01-2.94 (m, 1H), 2.73-2.66 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 166.7, 165.6, 152.4, 137.5, 131.7, 129.7, 126.5, 126.0, 125.0, 109.1, 59.6, 52.4, 52.2, 49.3, 32.5; FT-IR (neat) 2988, 2943, 2845, 1719, 1651, 1488, 1277, 1188, 898  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_5$  317.1132; Found 317.1125.



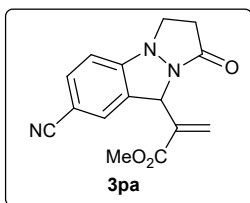
**Methyl 2-(1-oxo-7-(trifluoromethyl)-2,3-dihydro-1H,9H-pyrazolo**

**[1,2-a] indazol-9-yl) acrylate 3na.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; yellow liquid; yield 70% (22 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (s, 1H), 7.51 (d,  $J = 8.0$  Hz, 1H), 6.85 (d,  $J = 8.4$  Hz, 1H), 6.31 (s, 1H), 6.24 (s, 1H), 5.95 (s, 1H), 4.18-4.11 (m, 1H), 3.84 (s, 3H), 3.72-3.65 (m, 1H), 3.02-2.93 (m, 1H), 2.72-2.64 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 165.7, 151.5, 137.3, 130.2, 126.9 ( $J_{C-F} = 3.75$  Hz), 126.3, 125.4 ( $J_{C-F} = 32.6$  Hz), 125.3 ( $J_{C-F} = 270$  Hz), 122.0 ( $J_{C-F} = 3.7$  Hz), 109.6, 59.5, 52.4, 49.5, 32.3;  $^{19}\text{F}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.38; FT-IR (neat) 2986, 2942, 2833, 1706, 1653, 1385, 1293, 1199, 1139, 1088  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_3$  327.0951; Found 327.0946.



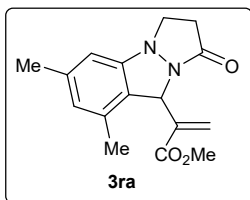
**Methyl 2-(7-nitro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

**9-yl) acrylate 3oa.** Analytical TLC on silica gel, 1:1 EtOAc/hexane  $R_f = 0.45$ ; yellow solid; mp 145-146 °C; yield 72% (21 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21-8.19 (m, 2H), 6.80 (d,  $J = 9.2$ , 1H), 6.34 (s, 1H), 6.23 (s, 1H), 5.97 (s, 1H), 4.20-4.13 (m, 1H), 3.85 (s, 3H), 3.82-3.73 (m, 1H), 3.04-2.95 (m, 1H), 2.78-2.70 (m, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 165.4, 153.3, 143.4, 136.8, 130.4, 126.8, 126.3, 120.9, 108.6, 59.6, 52.5, 48.7, 32.3; FT-IR (neat) 2982, 2949, 2834, 1709, 1661, 1496, 1265, 1179, 857  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_5$  304.0928; Found 304.0918.



**Methyl 2-(7-cyano-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-**

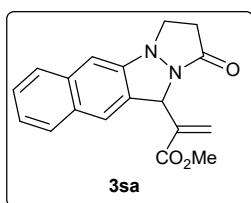
**9-yl) acrylate 3pa.** Analytical TLC on silica gel, 1:1 EtOAc/hexane  $R_f = 0.30$ ; yellow liquid; yield 63% (17 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 1H), 7.56-7.53 (m, 1H), 6.82 (d,  $J = 8.0$  Hz, 1H), 6.31 (s, 1H), 6.20 (s, 1H), 5.95 (s, 1H), 4.18-4.11 (m, 1H), 3.84 (s, 3H), 3.76-3.69 (m, 1H), 3.02-2.94 (m, 1H), 2.74-2.66 (m, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 165.6, 151.9, 136.9, 134.0, 130.5, 128.6, 126.4, 119.1, 109.9, 105.9, 59.4, 52.5, 48.9, 32.2; FT-IR (neat) 2966, 2922, 2876, 1716, 1643, 1325, 1236, 1167, 1135, 1048  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_3$  284.1030; Found 284.1015.



**Methyl 2-(6,8-dimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]**

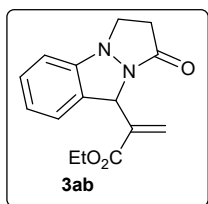
**indazol-9-yl) acrylate 3ra.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.35$ ; yellow liquid; yield 77% (22 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 (s, 1H), 6.62 (s, 1H), 6.24 (s, 1H), 6.16 (s, 1H), 5.89 (s, 1H), 4.10-4.04 (m, 1H), 3.82 (s, 3H), 3.53-3.46 (m, 1H), 3.01-2.92 (m, 1H), 2.67-2.59 (m, 1H), 2.24 (s, 3H), 2.19 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 166.0, 147.1, 138.2, 137.7, 131.5, 127.3, 125.6, 125.2, 111.5, 59.5, 52.2, 51.0, 32.9, 20.3, 19.6;

FT-IR (neat) 2987, 2965, 2865, 1708, 1654, 1487, 1234, 1183, 1194, 891  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3$  287.1390; Found 287.1378.



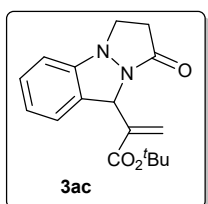
**Methyl-2-(1-oxo-2,3-dihydro-1H,11H-benzo[f]pyrazolo[1,2-a]**

**indazol-11-yl) acrylate 3sa.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f$ = 0.40; yellow liquid; yield 74% (23 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H), 7.75 (d,  $J$  = 8.5 Hz, 1H), 7.72 (d,  $J$  = 8.0 Hz, 1H), 7.44 (t,  $J$  = 7.5 Hz, 1H), 7.34 (t,  $J$  = 7.0 Hz, 1H), 7.10 (s, 1H), 6.34 (s, 1H), 6.30 (s, 1H), 5.99 (s, 1H), 4.23-4.18 (m, 1H), 3.85 (s, 3H), 3.75-3.70 (m, 1H), 3.03-2.96 (m, 1H), 2.74-2.68 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 165.9, 147.3, 137.7, 134.2, 131.3, 130.5, 128.5, 127.0, 126.9, 125.9, 124.4, 123.8, 105.2, 58.8, 52.3, 50.2, 32.7; FT-IR (neat) 2944, 2923, 2819, 1705, 1629, 1428, 1287, 1217, 1125  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3$  309.1234; Found 309.1231.



**Ethyl 2-(1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl) acrylate**

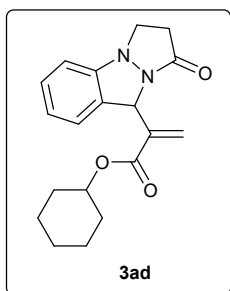
**3ab.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f$ = 0.40; colorless liquid; yield 83% (22 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J$  = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 6.99 (t,  $J$  = 8.0 Hz, 1H), 6.80 (d,  $J$  = 8.0 Hz, 1H), 6.26 (s, 1H), 6.24 (s, 1H), 5.89 (s, 1H), 4.32-4.26 (m, 2H), 4.14-4.08 (m, 1H), 3.61-3.54 (m, 1H), 3.02-2.94 (m, 1H), 2.69-2.61 (m, 1H), 1.34 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 165.4, 148.9, 138.2, 129.8, 129.0, 125.5, 124.4, 123.1, 110.1, 61.2, 59.5, 50.4, 32.7, 14.3; FT-IR (neat) 2968, 2936, 2861, 1723, 1657, 1345, 1281, 1163, 1042  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3$  273.1234; Found 273.1227.



**tert-Butyl 2-(1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-9-yl)**

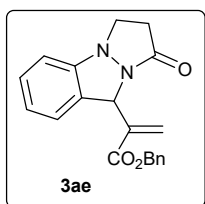
**acrylate 3ac.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f$ = 0.30; colorless liquid; yield

75% (23 mg);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 8.0$  Hz, 1H), 6.99 (t,  $J = 7.5$  Hz, 1H), 6.80 (d,  $J = 7.5$  Hz, 1H), 6.22 (s, 1H), 6.15 (s, 1H), 5.80 (s, 1H), 4.14-4.09 (m, 1H), 3.59-3.53 (m, 1H), 3.02-2.95 (m, 1H), 2.68-2.62 (m, 1H), 1.53 (s, 9H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 164.7, 148.9, 139.5, 130.1, 129.0, 124.4, 123.1, 110.1, 81.8, 59.5, 50.5, 32.8, 28.3, 27.9; FT-IR (neat) 2998, 2966, 2871, 1733, 1647, 1335, 1291, 1143, 1042, 980  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_3$  301.1547; Found 301.1548.



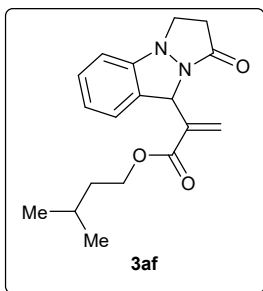
**Cyclohexyl 2-(1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)**

**acrylate 3ad.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 82% (26 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 7.6$  Hz, 1H), 7.23 (d,  $J = 7.2$  Hz, 1H), 6.98 (t,  $J = 7.2$  Hz, 1H), 6.80 (d,  $J = 8.0$  Hz, 1H), 6.25 (s, 1H), 6.23 (s, 1H), 5.87 (s, 1H), 4.94-4.88 (m, 1H), 4.14-4.08 (m, 1H), 3.60-3.53 (m, 1H), 3.03-2.94 (m, 1H), 2.69-2.61 (m, 1H), 1.96-1.86 (m, 2H), 1.79-1.72 (m, 2H), 1.54-1.37 (m, 6H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 164.9, 148.9, 138.6, 129.9, 129.0, 125.2, 124.5, 123.1, 110.1, 73.8, 59.6, 50.5, 32.8, 31.8, 31.7, 25.5, 23.93, 23.90; FT-IR (neat) 2908, 2816, 1730, 1687, 1325, 1271, 1123, 1092  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3$  327.1703; Found 327.1702.



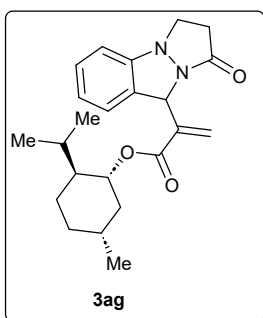
**Benzyl 2-(1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-9-yl)**

**acrylate 3ae.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.4$ ; colorless liquid; yield 84% (28 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.22 (m, 7H), 6.95 (t,  $J = 7.6$  Hz, 1H), 6.79 (d,  $J = 7.6$  Hz, 1H), 6.31 (s, 1H), 6.24 (s, 1H), 5.92 (s, 1H), 5.28 (d,  $J = 12.4$  Hz, 1H), 5.21 (d,  $J = 12.4$  Hz, 1H), 4.11-4.04 (m, 1H), 3.60-3.53 (m, 1H), 3.00-2.91 (m, 1H), 2.68-2.60 (m, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 165.2, 148.9, 137.9, 135.6, 129.6, 129.1, 128.7, 128.5, 128.4, 126.1, 124.5, 123.1, 110.1, 67.0, 59.5, 50.4, 32.7; FT-IR (neat) 2948, 2934, 2807, 1702, 1680, 1321, 1299, 1144, 1012  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3$  335.1390; Found 335.1400.



**Isopentyl 2-(1-oxo-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*] indazol-9-yl)**

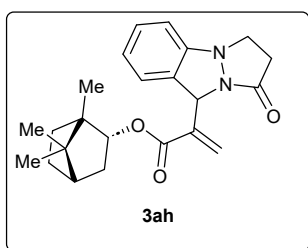
**acrylate 3af.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 80% (35 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 7.6$  Hz, 1H), 7.24 (t,  $J = 7.6$  Hz, 1H), 6.98 (t,  $J = 7.2$  Hz, 1H), 6.80 (d,  $J = 8.0$  Hz, 1H), 6.24-6.23 (m, 2H), 5.88 (s, 1H), 4.24 (t,  $J = 6.8$  Hz, 2H), 4.14-4.08 (m, 1H), 3.60-3.53 (m, 1H), 3.02-2.93 (m, 1H), 2.69-2.61 (m, 1H), 1.74-1.68 (m, 1H), 1.60 (q,  $J = 6.8$  Hz, 2H), 0.92 (d,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 165.5, 148.9, 138.2, 129.8, 129.0, 125.4, 124.5, 123.1, 110.1, 63.9, 59.5, 50.5, 37.4, 32.7, 25.2, 22.6; FT-IR (neat) 2978, 2954, 2832, 1722, 1670, 1421, 1399, 1114, 1014  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3$  315.1703; Found 315.1691.



**(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-(1-oxo-2,3-dihydro-**

**1*H*,9*H*-pyrazolo[1,2-*a*] indazol-9-yl) acrylate 3ag.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.35$ ; colorless liquid; yield 73% (28 mg); 1:0.8 mixture of diastereomers;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.33 (m, 1.8H) (major + minor), 7.22 (d,  $J = 7.6$  Hz, 1.8H) (major + minor), 7.00-6.95 (m, 1.8H) (major + minor), 6.79 (d,  $J = 8.0$  Hz, 2H) (major + minor), 6.22-6.21 (m, 3.6H) (major + minor), 5.88-5.86 (m, 1.8H) (major + minor), 4.87-4.81 (m, 1.8H) (major + minor), 4.14-4.08 (m, 1.8H) (major + minor), 3.59-3.56 (m, 1.8H) (major + minor), 3.02-2.95 (m, 1.8H) (major + minor), 2.70-2.61 (m, 1.8H) (major + minor), 2.04-2.03 (m, 2H) (major + minor), 1.51-1.42 (m, 4.2H) (major + minor), 0.93-0.88 (m, 7.8H) (major + minor), 0.81 (d,  $J = 7.2$  Hz, 3H) (major), 0.77 (d,  $J = 6.8$  Hz, 2.4H) (minor), 0.71 (d,  $J = 7.2$  Hz, 3H) (major);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 172.9, 165.1, 165.0, 149.0, 148.9, 138.5, 138.4, 129.9, 129.0, 128.9, 125.0, 124.9, 124.6, 124.4, 123.05, 123.03, 110.01, 109.99, 75.2, 75.1, 59.7, 59.6, 50.5, 50.4, 47.2, 41.0, 40.9, 34.4, 34.3, 32.8, 32.7, 31.6, 31.5, 26.4, 26.3, 23.5, 22.14,

22.11, 21.0, 20.9, 16.5, 16.4; FT-IR (neat) 2988, 2974, 2852, 1702, 1666, 1442, 1388, 1167, 1050  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_3$  383.2329; Found 383.2327.



**(1R,2R,4R)-1,7,7-Trimethyl bicyclo[2.2.1] heptan-2-yl 2-(1-oxo-**

**2,3-dihydro-1H,9H-pyrazolo[1,2-a] indazol-9-yl) acrylate 3ah.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.50$ ; colorless liquid; yield 78% (29 mg); 1:1 mixture of diastereomers;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.36 (m, 2H), 7.22 (d,  $J = 7.6$  Hz, 2H), 6.98 (t,  $J = 7.6$  Hz, 2H), 6.80 (d,  $J = 7.6$  Hz, 2H), 6.26-6.24 (m, 4H), 5.90-5.88 (m, 2H), 5.01-4.98 (m, 2H), 4.14-4.08 (m, 2H), 3.60-3.52 (m, 2H), 3.03-2.93 (m, 2H), 2.69-2.61 (m, 2H), 2.45-2.36 (m, 2H), 1.98-1.90 (m, 2H), 1.77-1.68 (m, 6H), 1.32-1.20 (m, 4H), 0.92-0.83 (m, 18H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 172.8, 165.74, 165.72, 148.9, 148.8, 138.5, 138.4, 129.9, 129.8, 129.0, 125.1, 125.0, 124.5, 124.4, 123.1, 110.0, 81.0, 59.6, 59.5, 50.54, 50.49, 49.10, 49.08, 48.0, 47.9, 45.0, 44.96, 36.8, 36.7, 32.7, 28.1, 28.0, 27.3, 19.8, 19.0, 13.8, 13.6; FT-IR (neat) 2968, 2924, 1732, 1656, 1484, 1393, 1155, 1070  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_3$  381.2173; Found 381.2177.

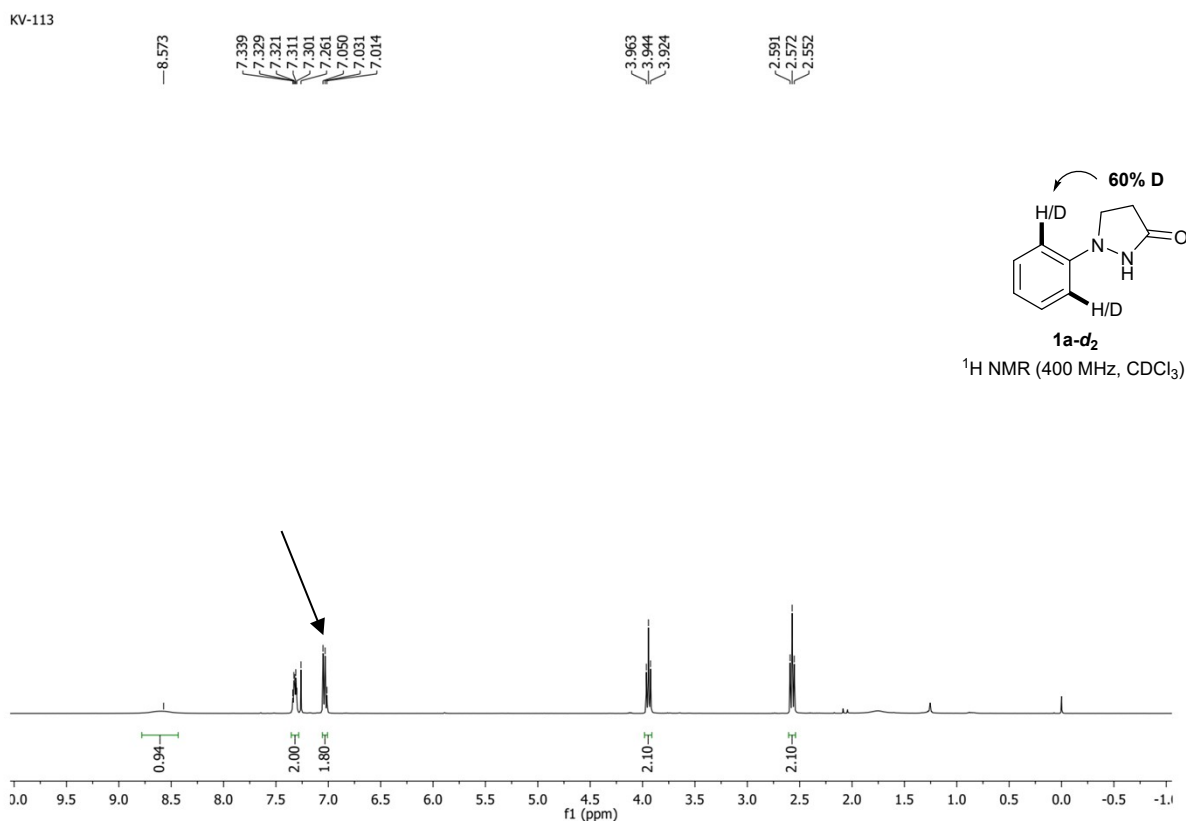
**Scale-up Synthesis of 3aa.** To a stirred solution of **1a** (2 mmol, 1 equiv, 324 mg) and **2a** (3 mmol, 1.5 equiv, 474 mg) in 1,4-dioxane (12 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.04 mmol, 0.02 equiv, 26 mg),  $\text{Zn}(\text{OAc})_2$  (4 mmol, 2 equiv, 732 mg) and AcOH (2 mmol, 1 equiv, 0.1 mL) were added and the reaction mixture was allowed to stir at 80  $^\circ\text{C}$  in an oil bath for 15 h. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate (20 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **3aa** (650 mg) in 68% yield.

## Preliminary Mechanistic Investigations

### H/D Exchange Experiments

**H/D Exchange Experiment of 1a with  $\text{D}_2\text{O}$  in Absence of 2a.** To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) in 1,4-dioxane (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.002 mmol, 0.02 equiv, 1.5 mg),  $\text{Zn}(\text{OAc})_2$  (0.2 mmol, 2 equiv, 36.6 mg), AcOH (0.1 mmol, 1 equiv, 5.7  $\mu\text{L}$ ) and  $\text{D}_2\text{O}$  (1

mmol, 10 equiv, 18  $\mu$ L) were added and the reaction mixture was allowed to stir at 80  $^{\circ}$ C in an oil bath for 2 h. The reaction mixture was diluted with ethyl acetate (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **1a-d<sub>2</sub>**. The deuterium incorporation of **1a-d<sub>2</sub>** was calculated based on its 400 MHz  $^1$ H NMR spectrum (See the following  $^1$ H NMR spectrum).

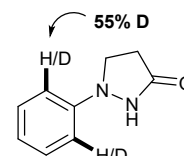


**H/D Exchange Experiment of 1a with D<sub>2</sub>O in Presence of 2a.** To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg), **2a** (0.15 mmol, 1.5 equiv, 24 mg) in 1,4-dioxane (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.002 mmol, 0.02 equiv, 1.5 mg),  $\text{Zn}(\text{OAc})_2$  (0.2 mmol, 2 equiv, 36.6 mg), AcOH (0.1 mmol, 1 equiv, 5.7  $\mu$ L) and D<sub>2</sub>O (1 mmol, 10 equiv, 18  $\mu$ L) were added and the reaction mixture was allowed to stir at 80  $^{\circ}$ C in an oil bath for 2 h. The reaction mixture was diluted with ethyl acetate (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **3a-d** and **1a-d<sub>2</sub>**. The deuterium incorporation of **3a-d** and **1a-d<sub>2</sub>** was

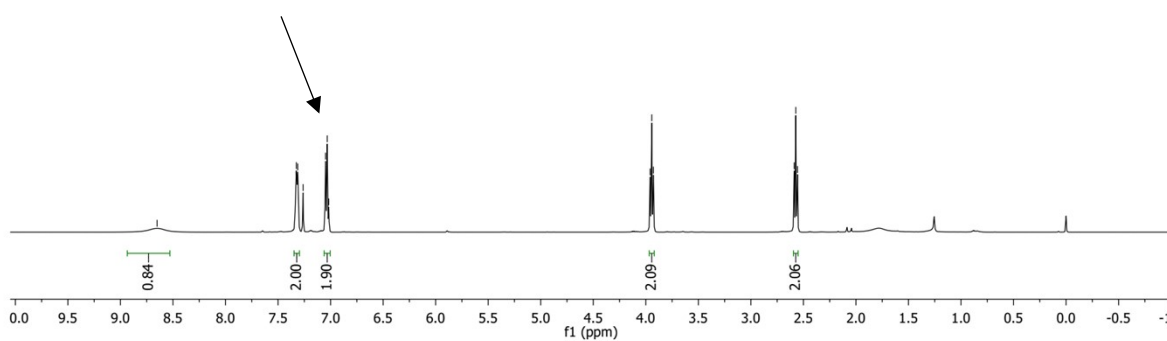
calculated based on their respective  $^1\text{H}$  NMR spectrum (See the following  $^1\text{H}$  NMR spectra).

KV-112-W2a

8.651  
7.326  
7.312  
7.261  
7.048  
7.032  
7.017  
3.959  
3.943  
3.927  
2.588  
2.572  
2.556

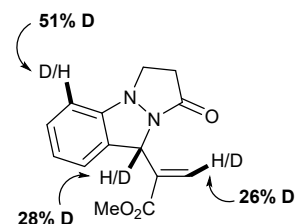


recovered  
**1a-d<sub>2</sub>**  
 $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

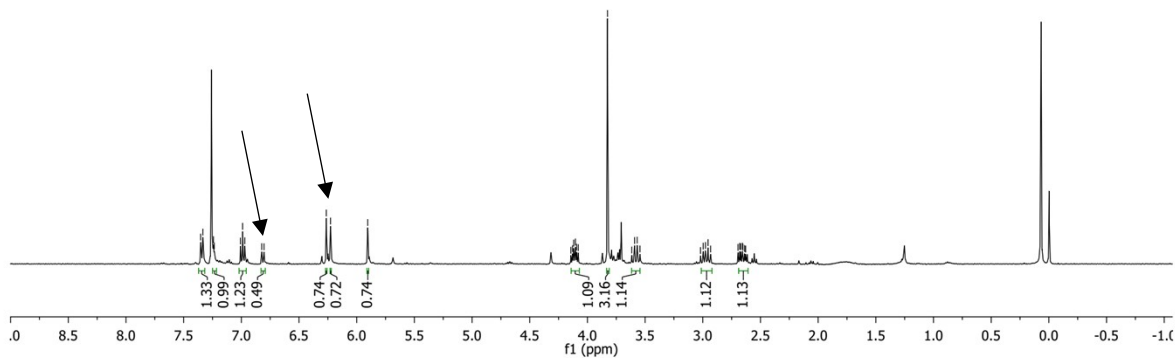


KV-112-D20-1H

7.552  
7.534  
7.242  
7.234  
7.008  
6.989  
6.970  
6.823  
6.803  
6.263  
6.227  
5.904  
4.143  
4.129  
4.119  
4.104  
4.094  
4.080  
3.826  
3.616  
3.591  
3.569  
3.545  
3.020  
2.997  
2.977  
2.955  
2.932  
2.695  
2.680  
2.671  
2.656  
2.653  
2.638  
2.628



**3aa-d**  
 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



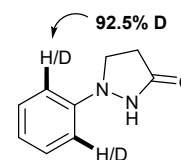
**Preparation of  $1a-d_2$  [92.5% D].**<sup>3</sup> To a stirred solution of **1a** (0.5 mmol, 1 equiv, 81 mg),  $[Cp^*RhCl_2]_2$  (0.015 mmol, 0.03 equiv, 9.2 mg),  $Zn(OAc)_2$  (0.5 mmol, 1 equiv, 91 mg) in  $(CH_2Cl)_2$  (2 mL),  $CD_3OD$  (20 mmol, 40 equiv, 0.88 mL) were added and the reaction mixture was allowed to stir at 100 °C in an oil bath for 12 h. The reaction mixture was diluted with ethyl acetate (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **1a-d<sub>2</sub>**. The deuterium incorporation of **1a-d<sub>2</sub>** was calculated based on its 400 MHz  $^1H$  NMR spectrum (See the following  $^1H$  NMR spectrum).

KV-115-A

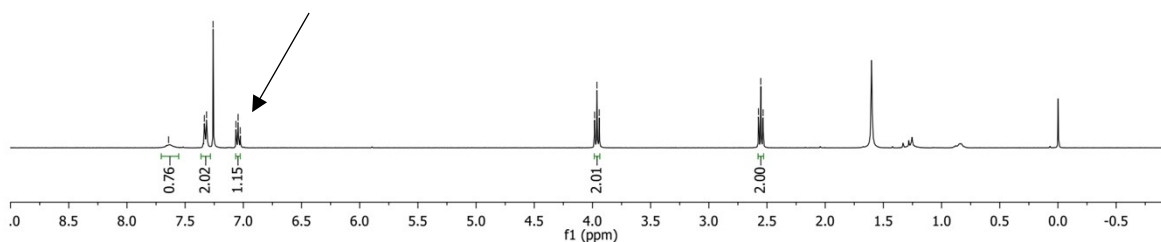
7.642  
7.335  
7.316  
7.260  
7.063  
7.045  
7.027

3.981  
3.962  
3.942

2.573  
2.554  
2.534



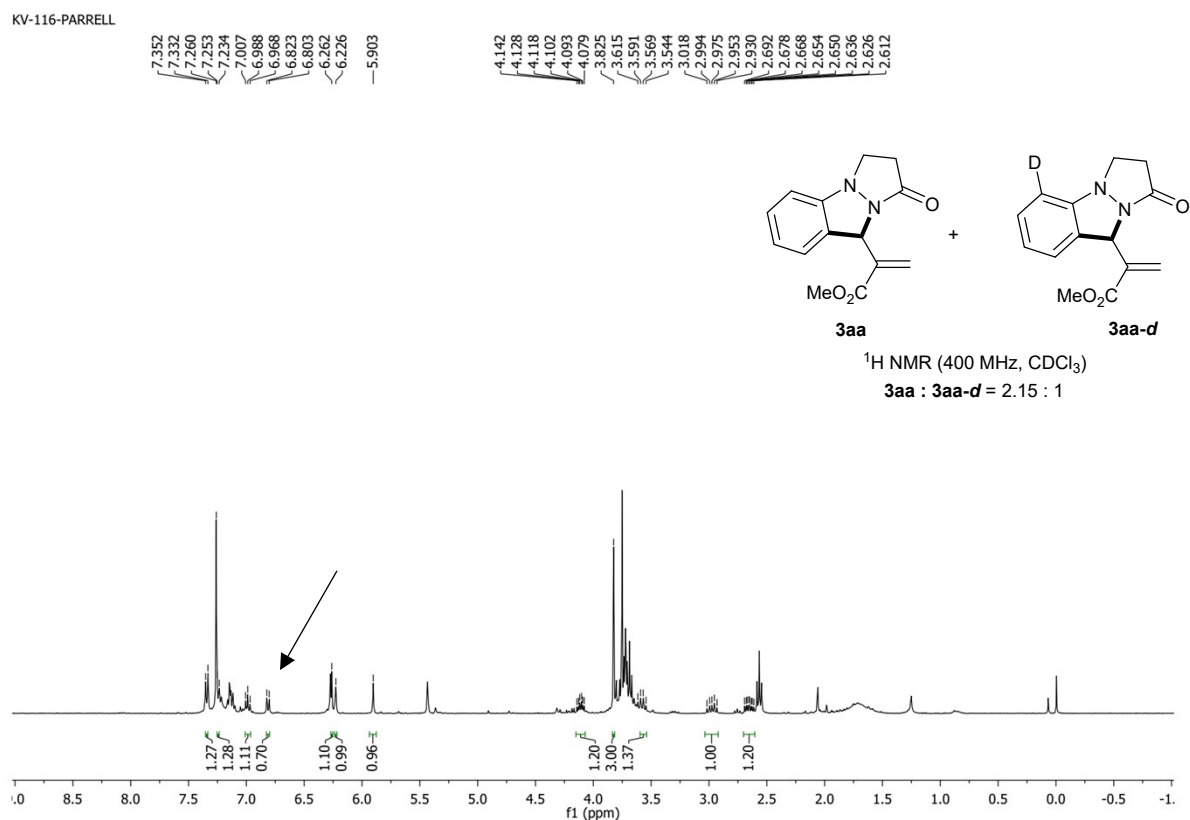
**1a-d<sub>2</sub>**  
 $^1H$  NMR (400 MHz,  $CDCl_3$ )



## Kinetic Isotope Effect Experiments

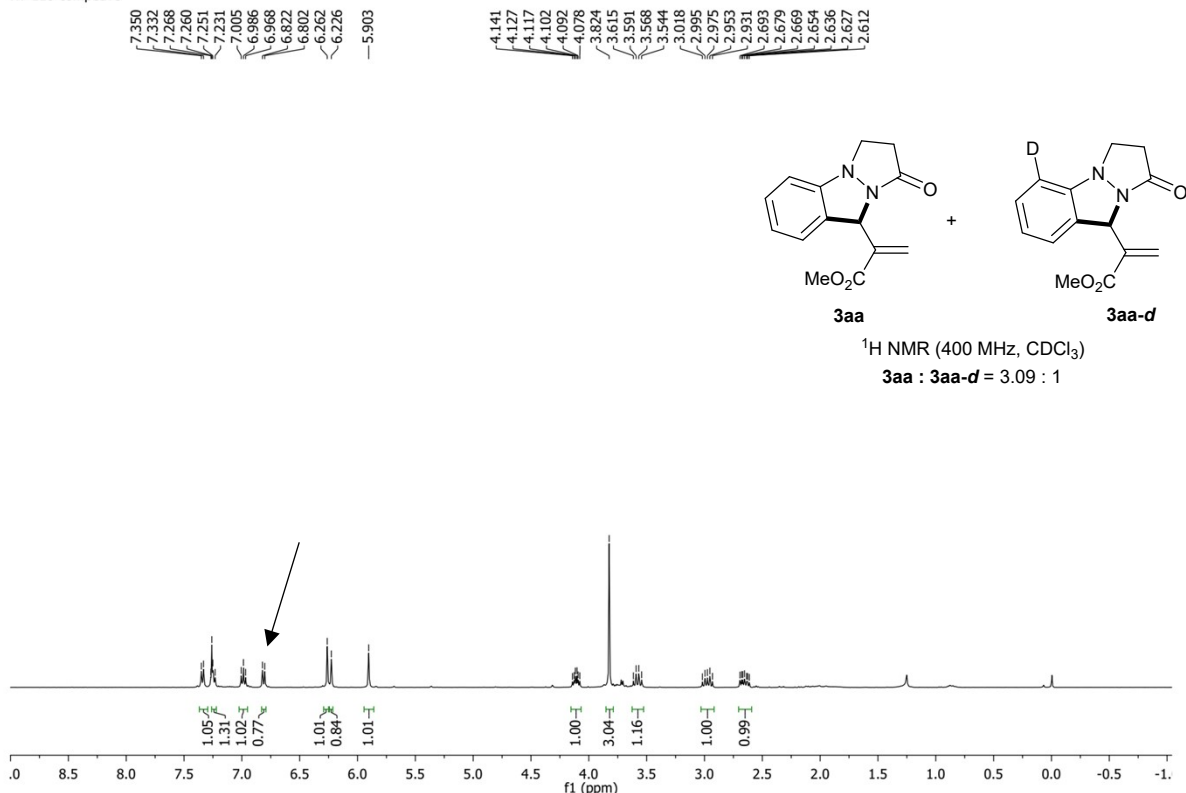
**Parallel Experiment:** To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) and **1a-d<sub>2</sub>** [92.5% D] (0.1 mmol, 1 equiv, 15.4 mg) were separately reacted with **2a** (0.15 mmol, 1.5 equiv, 24 mg) in 1,4-dioxane (1 mL),  $[Cp^*RhCl_2]_2$  (0.002 mmol, 0.02 equiv, 1.5 mg),  $Zn(OAc)_2$  (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7  $\mu$ L) were added and the reaction mixture was allowed to stir at 80 °C in an oil bath for 2 h. Both the reaction mixtures were combined and passed through a short celite pad using ethyl acetate (5 mL). Evaporation of the solvent gave a residue that was purified on silica gel column

chromatography using ethyl acetate and hexane as an eluent to afford a mixture **3aa** and **3aa-d**. The KIE value was determined to be  $k_H/k_D = 2.15$  on the basis of  $^1\text{H}$  NMR analysis.



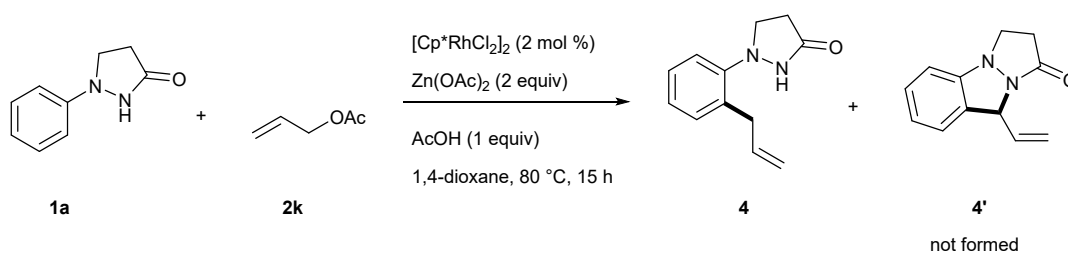
**Competitive Experiment:** To a stirred mixture of **1a** (0.1 mmol, 1 equiv, 16.2 mg), **1a-d<sub>2</sub>** [92.5% D] (0.1 mmol, 1.0 equiv, 15.4 mg) and **2a** (0.3 mmol, 1.5 equiv, 48 mg) in 1,4-dioxane (2 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.004 mmol, 0.02 equiv, 3 mg),  $\text{Zn}(\text{OAc})_2$  (0.4 mmol, 2 equiv, 78 mg) and AcOH (0.2 mmol, 1 equiv, 12  $\mu\text{L}$ ) were added and the resultant mixture was allowed to warm to 80  $^\circ\text{C}$  in an oil bath and stirred for 2 h. The reaction mixture was then passed through a short celite bed using ethyl acetate (5 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford a mixture of **3aa** and **3aa-d**. The KIE value was determined to be  $k_H/k_D = 3.09$  on the basis of  $^1\text{H}$  NMR analysis.

KV-116-competitive



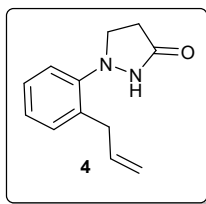
## Control Experiments

(I)



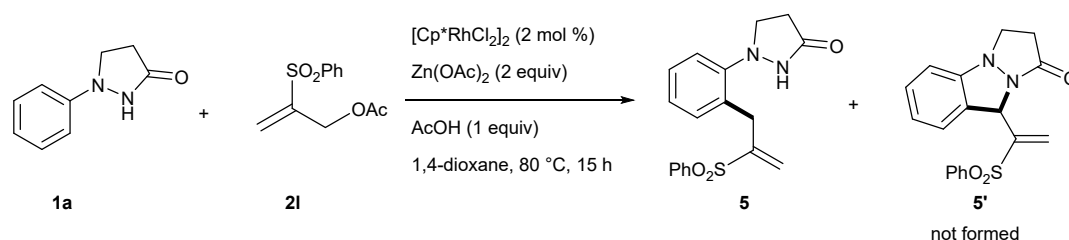
Scheme S4

To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) and **2k** (0.15 mmol, 1.5 equiv, 15 mg) in 1,4-dioxane (1 mL), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.002 mmol, 0.02 equiv, 1.5 mg), Zn(OAc)<sub>2</sub> (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7  $\mu\text{L}$ ) were added and the resultant mixture was allowed to stir at 80 °C in an oil bath for 15 h. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford to afford **4** in 66% yield.



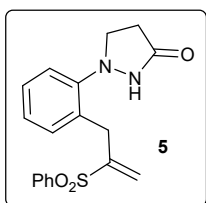
**1-(2-Allylphenyl) pyrazolidin-3-one 4.** Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.35$ ; brown solid; mp 164-165 °C; yield 66% (13 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.4$  Hz, 1H), 7.24-7.20 (m, 2H), 7.15-7.11 (m, 1H), 6.04-5.94 (m, 1H), 5.13-5.06 (m, 2H), 3.69 (t,  $J = 8.0$  Hz, 2H), 3.46 (d,  $J = 6.4$  Hz, 2H), 2.55 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.8, 149.6, 137.0, 132.3, 131.0, 127.2, 125.3, 118.1, 116.5, 56.1, 34.9, 29.2; FT-IR (neat) 2968, 2924, 2914, 1712, 1666, 1476, 1363, 1132, 1082  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}$  203.1179; Found 203.1171.

## (II)



**Scheme S5**

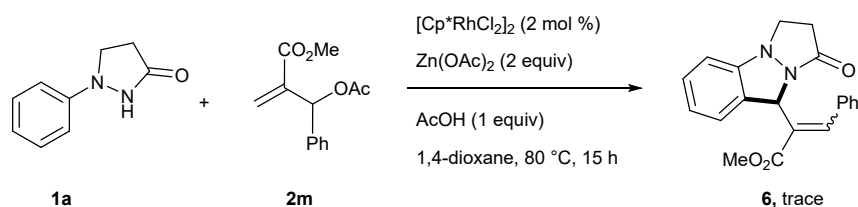
To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) and **2I** (0.15 mmol, 1.5 equiv, 15 mg) in 1,4-dioxane (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.002 mmol, 0.02 equiv, 1.5 mg),  $\text{Zn}(\text{OAc})_2$  (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7  $\mu\text{L}$ ) were added and the reaction mixture was allowed to stir at 80 °C in an oil bath for 15 h. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford to afford **5** in 70% yield.



**1-(2-(2-(Phenylsulfonyl)allyl)phenyl)pyrazolidin-3-one 5.** Analytical TLC on silica gel, 1:1 EtOAc/hexane  $R_f = 0.30$ ; colorless liquid; yield 70% (20 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.0$  Hz, 2H), 7.78 (s, 1H), 7.65 (t,  $J = 7.5$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 2H), 7.29-7.22 (m, 2H), 7.10-7.03 (m, 2H), 6.40 (s, 1H), 5.39 (s, 1H), 3.64 (s, 2H), 3.20 (t,  $J = 8.0$  Hz, 2H), 2.40 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 150.3, 149.9,

138.8, 133.8, 132.0, 129.3, 128.6, 128.5, 128.4, 125.6, 124.6, 118.9, 55.5, 31.0, 29.3; FT-IR (neat) 2988, 2944, 2902, 1710, 1664, 1495, 1388, 1122, 1032  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_3\text{S}$  343.1111; Found 343.1104.

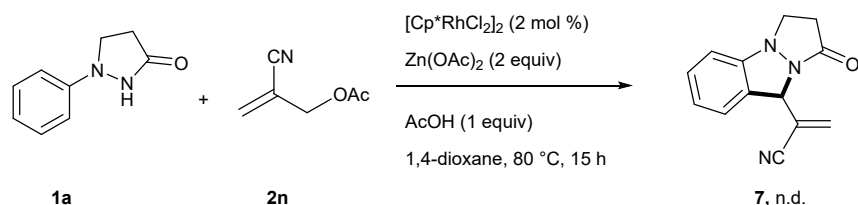
(III)



Scheme S6

To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) and **2m** (0.15 mmol, 1.5 equiv, 35 mg) in 1,4-dioxane (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.002 mmol, 0.02 equiv, 1.5 mg),  $\text{Zn}(\text{OAc})_2$  (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7  $\mu\text{L}$ ) were added and the reaction mixture was allowed to stir at 80 °C in an oil bath for 15 h. The formation of **6** was observed in a trace amount.

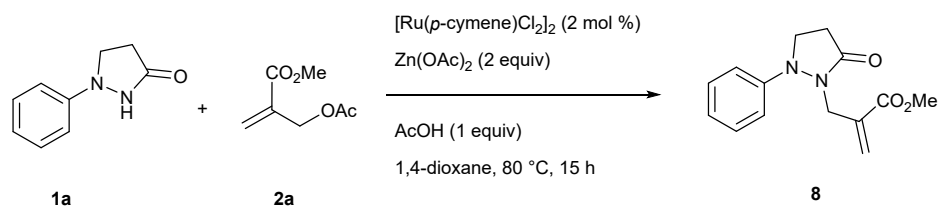
(IV)



Scheme S7

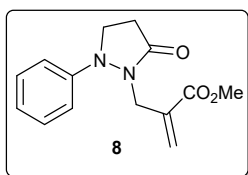
To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) and **2n** (0.15 mmol, 1.5 equiv, 19 mg) in 1,4-dioxane (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.002 mmol, 0.02 equiv, 1.5 mg),  $\text{Zn}(\text{OAc})_2$  (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7  $\mu\text{L}$ ) were added and the reaction mixture was allowed to stir at 80 °C in an oil bath for 15 h. The formation of **7** was not observed.

(V)



Scheme S8

To a stirred solution of **1a** (0.1 mmol, 1 equiv, 16.2 mg) and **2a** (0.15 mmol, 1.5 equiv, 24 mg) in 1,4-dioxane (1 mL), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (0.002 mmol, 0.02 equiv, 1.3 mg), Zn(OAc)<sub>2</sub> (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7 μL) were added and the reaction mixture was allowed to stir at 80 °C in an oil bath for 15 h. After completion (monitored by TLC), the reaction mixture was diluted with EtOAc (5 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford to afford **8** in 55% yield.

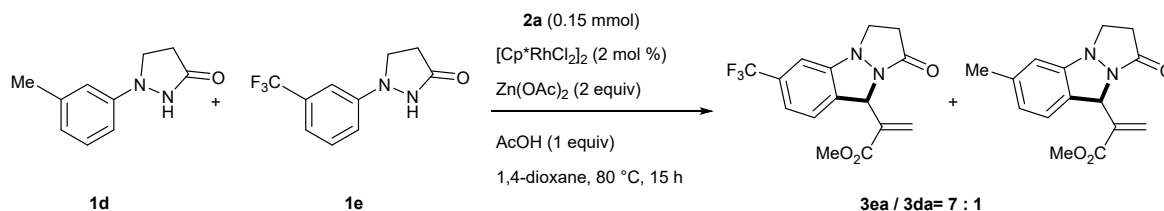


**Methyl 2-((5-oxo-2-phenylpyrazolidin-1-yl)methyl) acrylate **8**.**

Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f$  = 0.35; colorless liquid; yield 55% (14 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33 (t,  $J$  = 7.5 Hz, 2H), 7.10 (t,  $J$  = 7.5 Hz, 1H), 6.94 (d,  $J$  = 8.5 Hz, 2H), 6.30 (s, 1H), 5.68 (s, 1H), 4.31 (s, 2H), 3.79 (d,  $J$  = 7.5 Hz, 2H), 3.70 (s, 3H), 2.55 (t,  $J$  = 7.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.0, 166.2, 149.7, 134.5, 129.5, 127.3, 124.3, 119.1, 56.0, 52.1, 43.6, 29.4; FT-IR (neat) 2998, 2976, 1712, 1622, 1444, 1334, 1168, 1073 cm<sup>-1</sup>; HRMS (ESI-TOF)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> 261.1234; Found 261.1235.

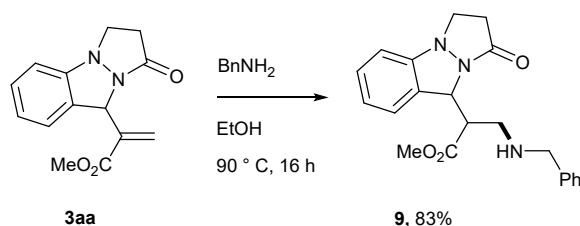
**Intermolecular Competition Experiment**

To a stirred solution of **1d** (0.1 mmol, 1.0 equiv, 17.5 mg), **1e** (0.1 mmol, 1.0 equiv, 23 mg) and **2a** (0.15 mmol, 1.5 equiv, 24 mg) in 1,4-dioxane (1 mL), [Cp\**Rh*Cl<sub>2</sub>]<sub>2</sub> (0.002 mmol, 0.02 equiv, 1.5 mg), Zn(OAc)<sub>2</sub> (0.2 mmol, 2 equiv, 36.6 mg) and AcOH (0.1 mmol, 1 equiv, 5.7 μL) were added and the reaction mixture was allowed to stir at 80 °C in an oil bath for 5 h. The reaction mixture was then passed through a short celite bed using ethyl acetate (5 mL). Evaporation of the solvent gave a mixture of **3ea** and **3da** in 7:1 ratio, calculated from 400 MHz <sup>1</sup>H NMR spectrum.



**Scheme S9**

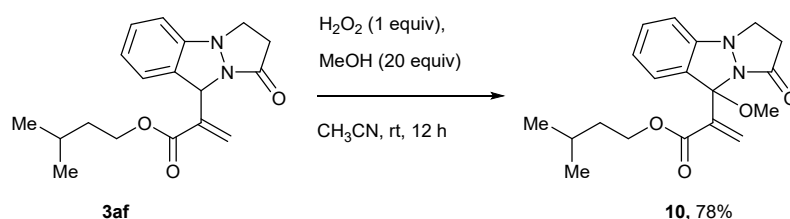
### Synthesis of Methyl 3-(benzylamino)-2-(1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl) propanoate **9**.



**Scheme S10**

To a stirred solution of **3aa** (0.1 mmol, 1 equiv, 25 mg) in EtOH (2 mL), benzyl amine (0.2 mmol, 2 equiv, 22 mg) was added and the reaction mixture was allowed to stir at 90 °C in an oil bath for 16 h. After completion (monitored by TLC), the solvent was evaporated and the residue was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **9** in 83% yield. Analytical TLC on silica gel, 1:1 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 83% (30 mg);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.28 (m, 5H), 7.24-7.23 (m, 1H), 7.16 (d,  $J = 7.6$  Hz, 1H), 6.98 (t,  $J = 7.2$  Hz, 1H), 6.78 (d,  $J = 8.0$  Hz, 1H), 5.65 (d,  $J = 8.8$  Hz, 1H), 4.10-4.04 (m, 1H), 3.76 (s, 2H), 3.72 (s, 3H), 3.52-3.45 (m, 1H), 3.18-3.13 (m, 1H), 2.96-2.80 (m, 3H), 2.63-2.55 (m, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 172.9, 149.8, 140.3, 129.2, 129.1, 128.4, 128.3, 127.0, 124.1, 123.1, 110.0, 59.1, 53.9, 52.0, 50.7, 50.3, 48.5, 32.5; FT-IR (neat) 2958, 2924, 2856, 1730, 1708, 1459, 1254, 1029, 752  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_3$  366.1812; Found 366.1802.

### Synthesis of Isopentyl 2-(9-methoxy-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl) acrylate **10**.

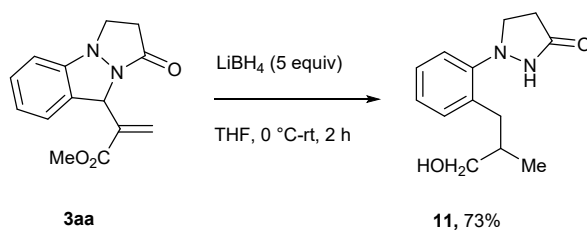


**Scheme S11**

To a stirred solution of **3af** (0.1 mmol, 1 equiv, 30 mg) in  $\text{CH}_3\text{CN}$  (2 mL),  $\text{H}_2\text{O}_2$  (30%, 0.1 mmol, 1 equiv, 5  $\mu\text{L}$ ) and methanol (2 mmol, 20 equiv, 80  $\mu\text{L}$ ) were added and the reaction mixture were allowed to stir at room temperature for 12 h. After completion (monitored by TLC), the solvent was evaporated and the residue was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **10** in 78% yield. Analytical TLC on silica gel, 1:0.25 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 78% (26

mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 8.0$  Hz, 1H), 7.47 (d,  $J = 8.4$  Hz, 1H), 7.39 (t,  $J = 6.8$  Hz, 1H), 7.16 (t,  $J = 7.2$  Hz, 1H), 6.53-6.52 (m, 1H), 6.24-6.23 (m, 1H), 6.68 (t,  $J = 6.8$  Hz, 2H), 4.31 (t,  $J = 6.8$  Hz, 2H), 3.66 (s, 3H), 3.00 (t,  $J = 6.8$  Hz, 2H), 1.74-1.67 (m, 1H), 1.62-1.60 (m, 2H), 0.91 (d,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.8, 166.4, 141.2, 140.7, 134.1, 128.6, 126.6, 122.6, 121.6, 121.2, 109.4, 64.1, 52.1, 44.3, 37.4, 34.4, 25.2, 22.6; FT-IR (neat) 2998, 2984, 2846, 1710, 1705, 1480, 1263, 1092, 754  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_4$  345.1809; Found 345.1808.

### Synthesis of 1-(2-(3-Hydroxy-2-methyl-propyl) phenyl) pyrazolidin-3-one **11**.



**Scheme S12**

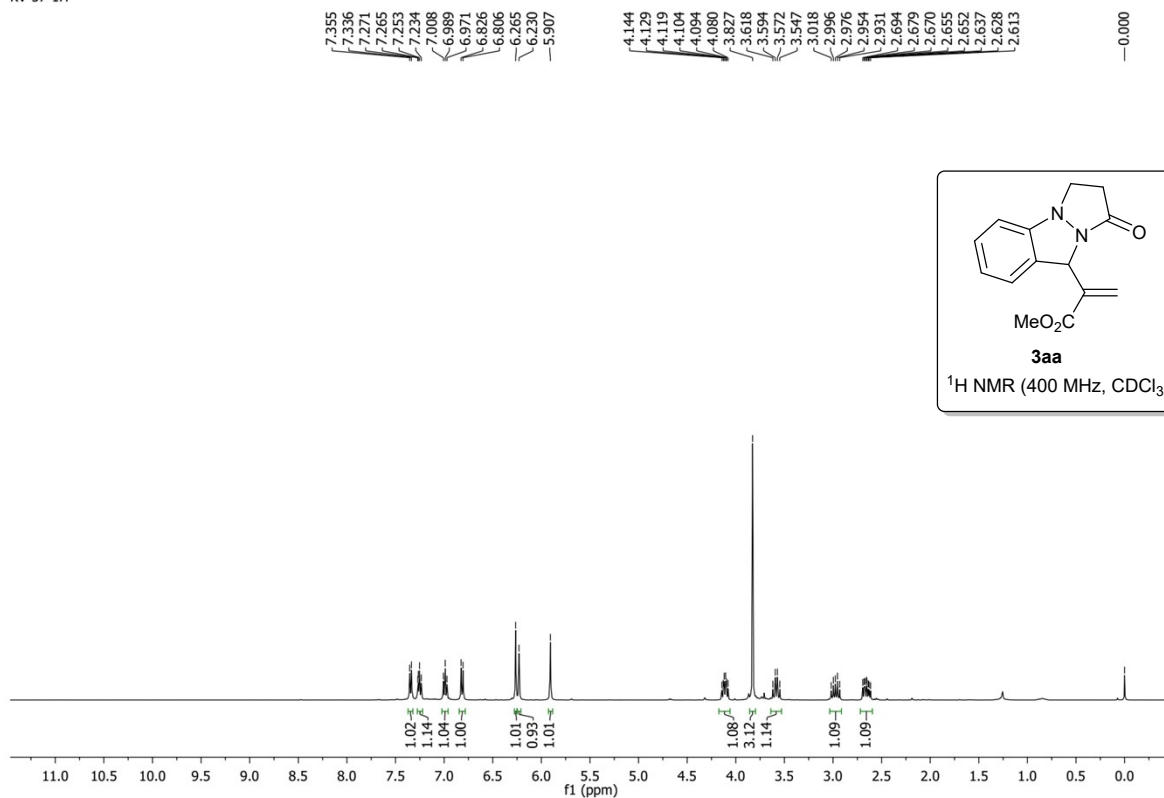
To a stirred solution of **3aa** (0.1 mmol, 1.0 equiv, 25 mg) in THF (1 mL) at 0 °C,  $\text{LiBH}_4$  (0.5 mmol, 11 mg) was added and the reaction was allowed to stir at room temperature for 2 h. After completion (monitored by TLC), the solvent was evaporated and the residue was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **11** in 73% yield. Analytical TLC on silica gel, 1:3 EtOAc/hexane  $R_f = 0.40$ ; colorless liquid; yield 73% (17 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 8.4$  Hz, 1H), 7.42-7.36 (m, 2H), 7.14-7.11 (m, 1H), 4.48 (t,  $J = 6.4$  Hz, 2H), 3.95 (d,  $J = 5.2$  Hz, 2H), 3.60 (t,  $J = 5.6$  Hz, 2H), 3.49-3.44 (m, 1H), 2.13-2.07 (m, 2H), 1.43 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 140.6, 126.8, 122.3, 120.8, 120.2, 109.3, 67.0, 59.9, 45.4, 35.2, 32.3, 17.0; FT-IR (neat) 2966, 2935, 2857, 1715, 1652, 1429, 1317, 1161, 1062  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{13}\text{H}_{18}\text{N}_2\text{NaO}_2$  257.1260; Found 257.1243.

### References

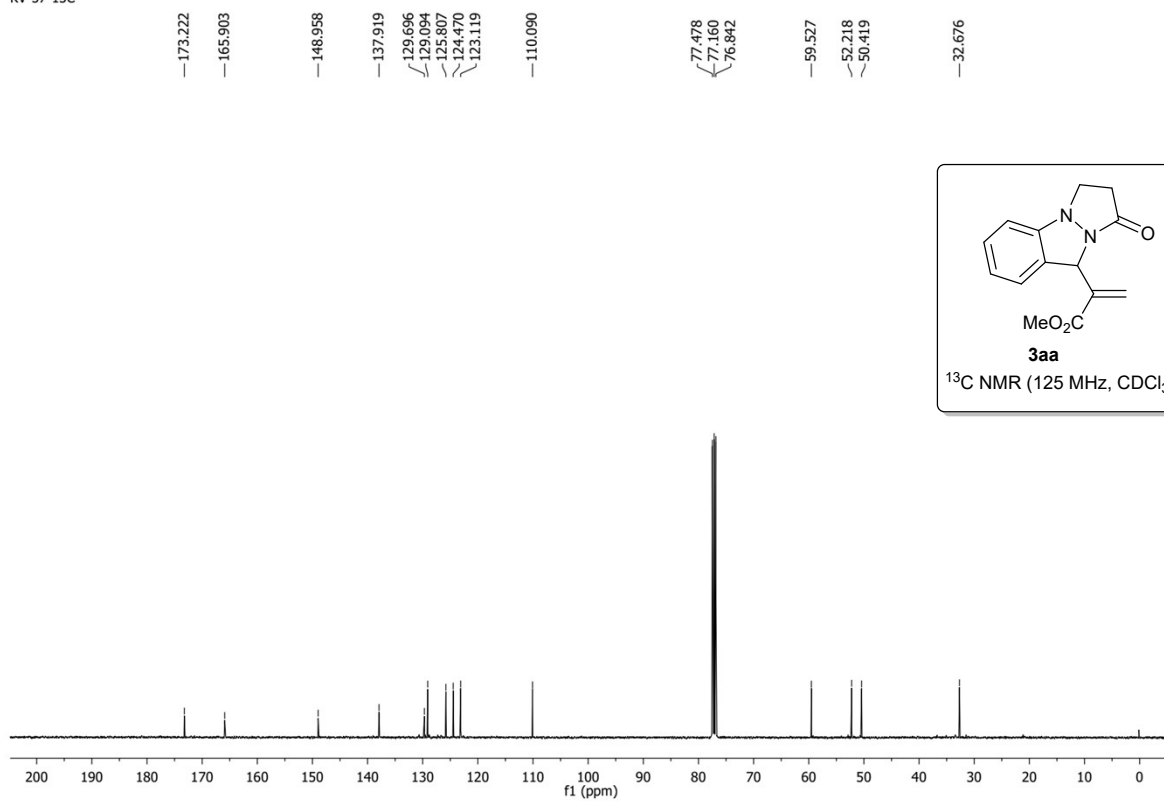
- (a) T. Li, Z. Yang, Z. Song, R. Chauvin and X. Cui, *Org. Lett.*, 2020, **22**, 4078. (b) Y. Li, Y. Wang, X. Huang, Y. Shi, Y. Tang, J. Jiao, J. Li and S. Xu, *Org. Lett.*, 2022, **24**, 435. (c) H. Li, M. Shen, B. Li, X. Zhang and X. Fan, *Org. Lett.*, 2023, **25**, 720.
- (a) X. Mi, S. Luo and J.-P. Cheng, *J. Org. Chem.*, 2005, **70**, 2338. (b) H. Bhattacharyya, S. Saha, K. Verma and T. Punniyamurthy, *Org. Lett.*, 2023, **25**, 6830.
- N. Li, B. Hu, X. Zhang and X. Fan, *J. Org. Chem.*, 2023, **88**, 60.

# NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F) Spectra

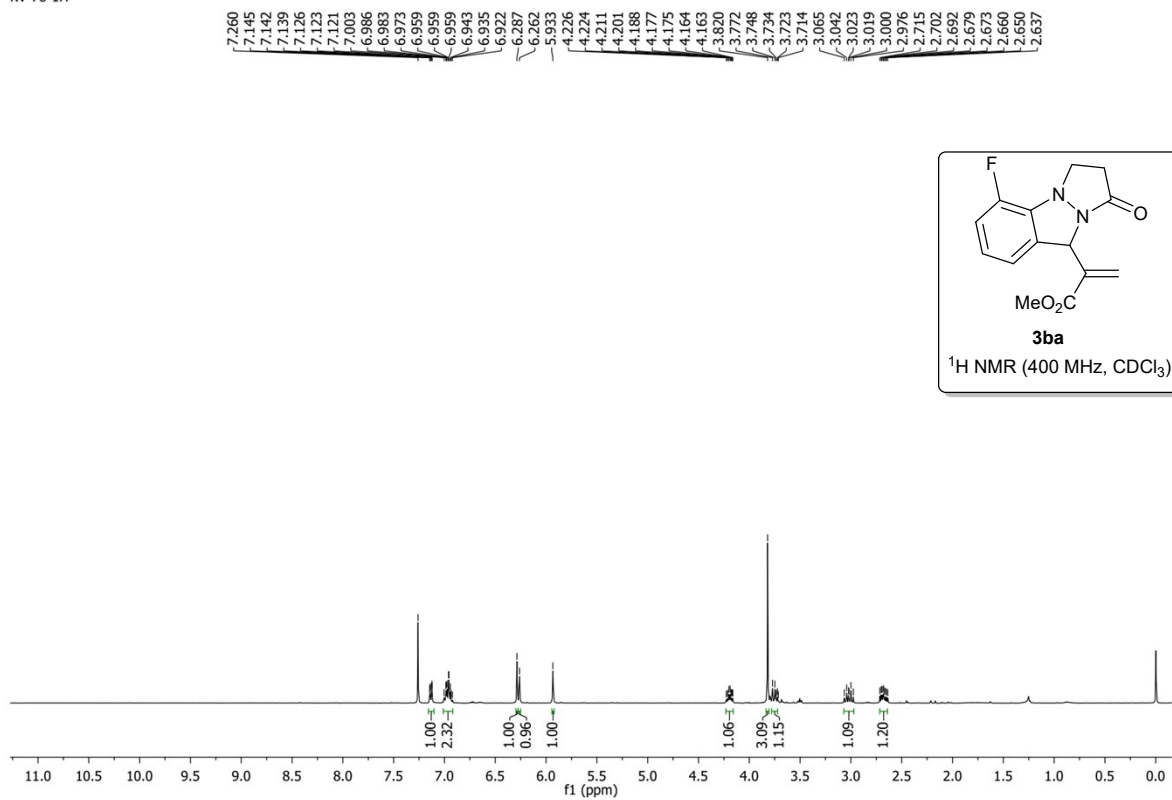
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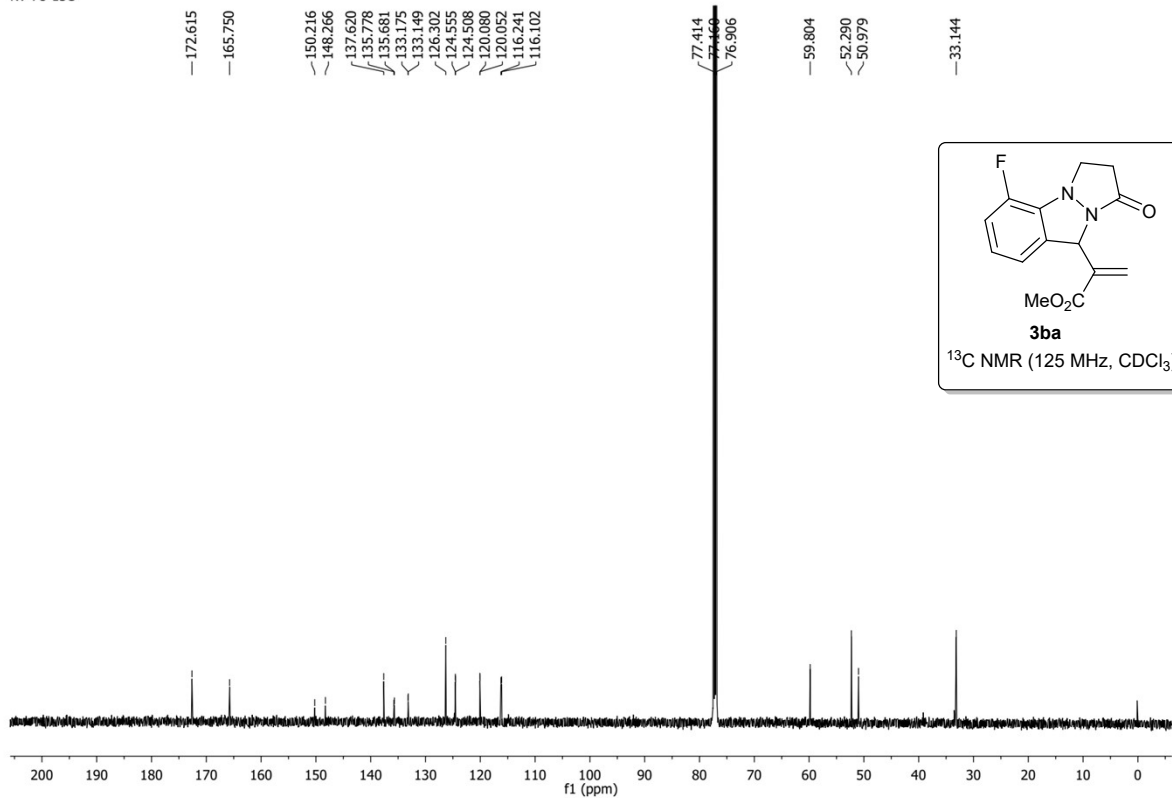
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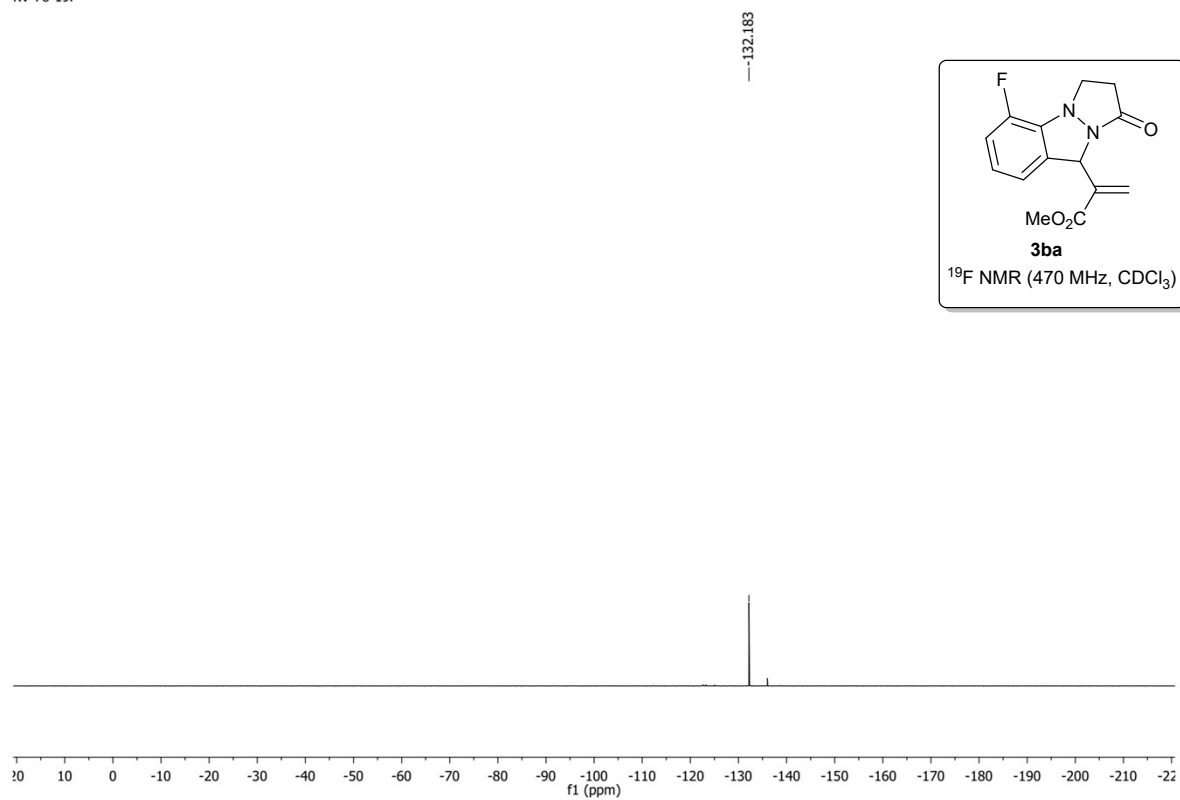
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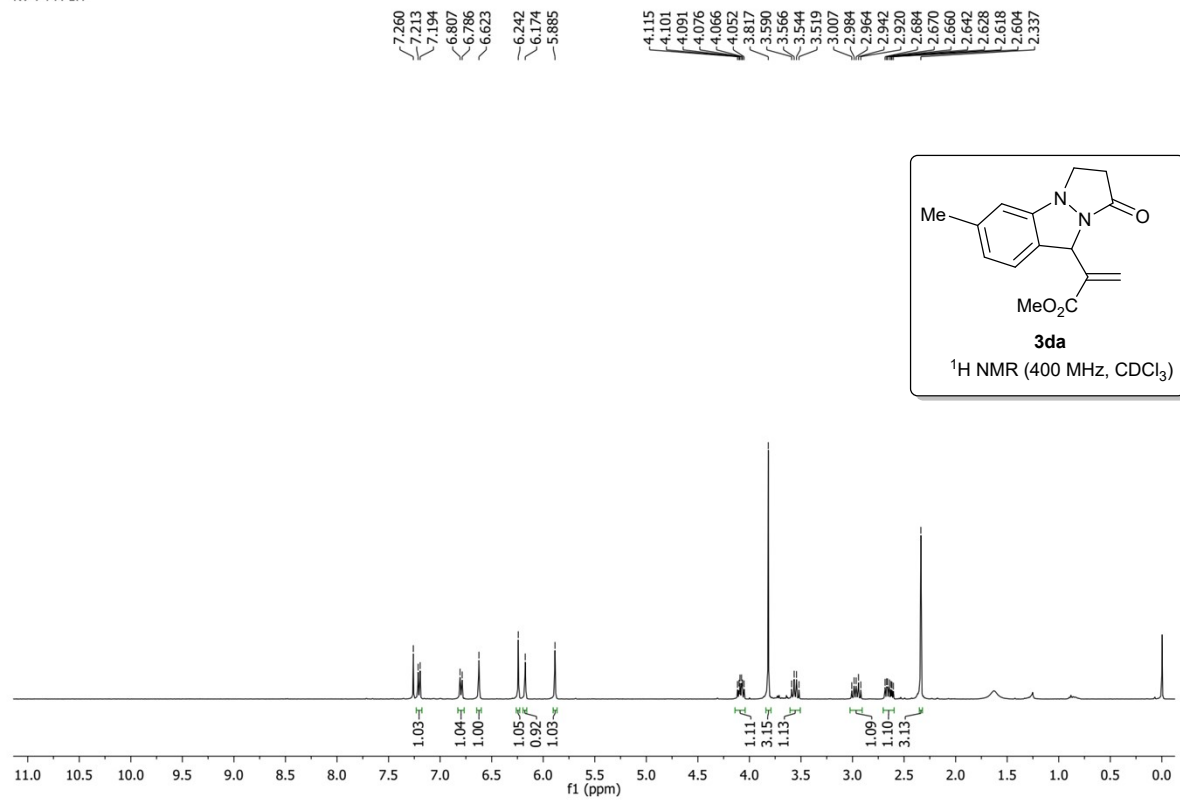
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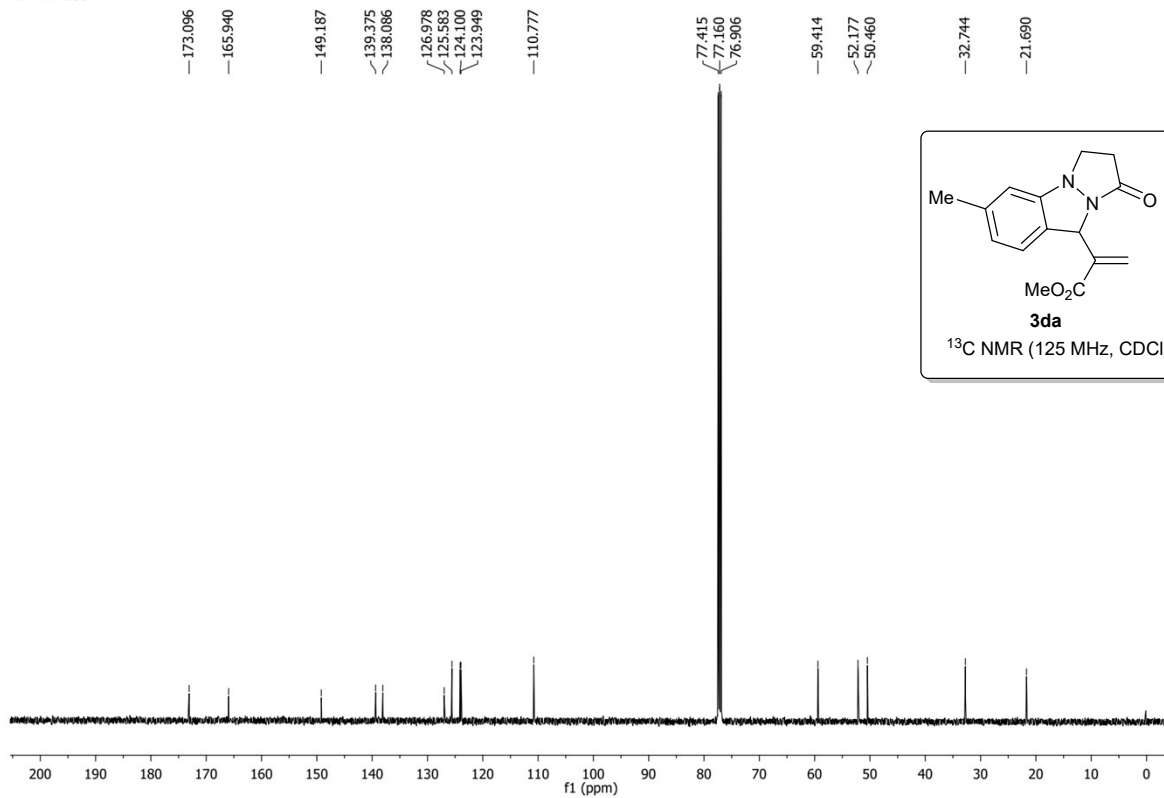
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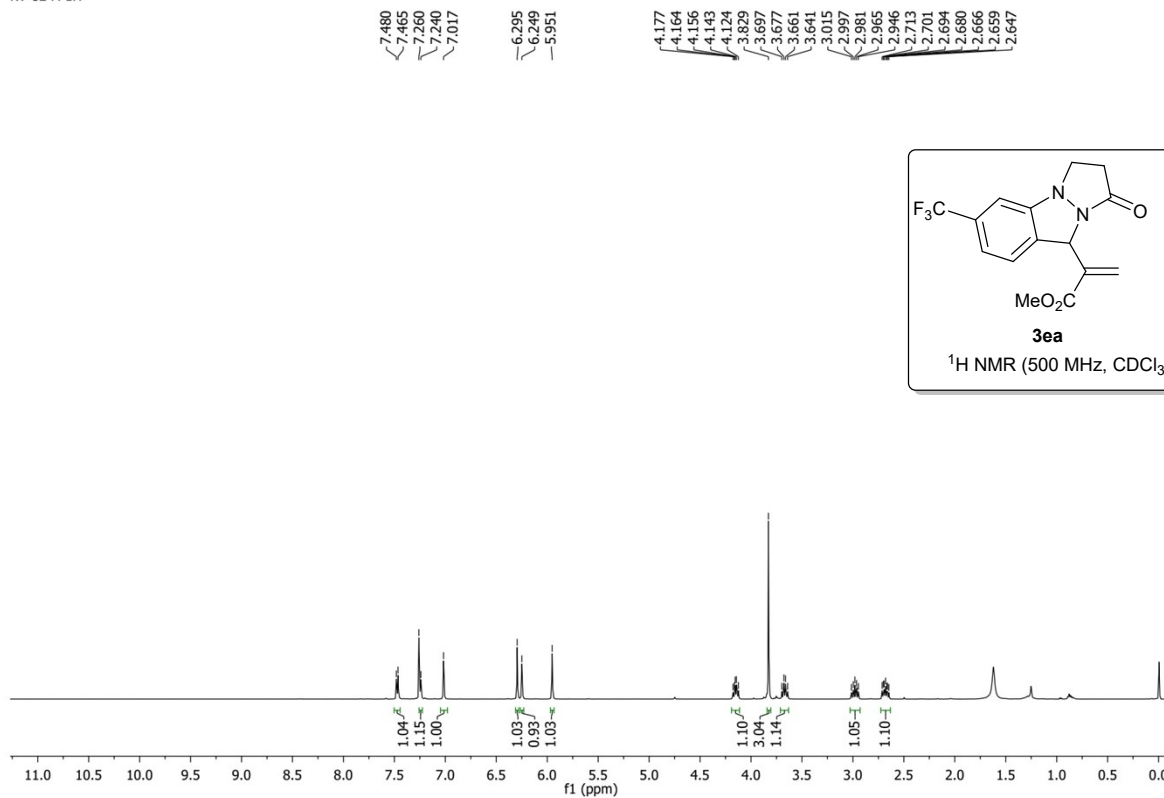
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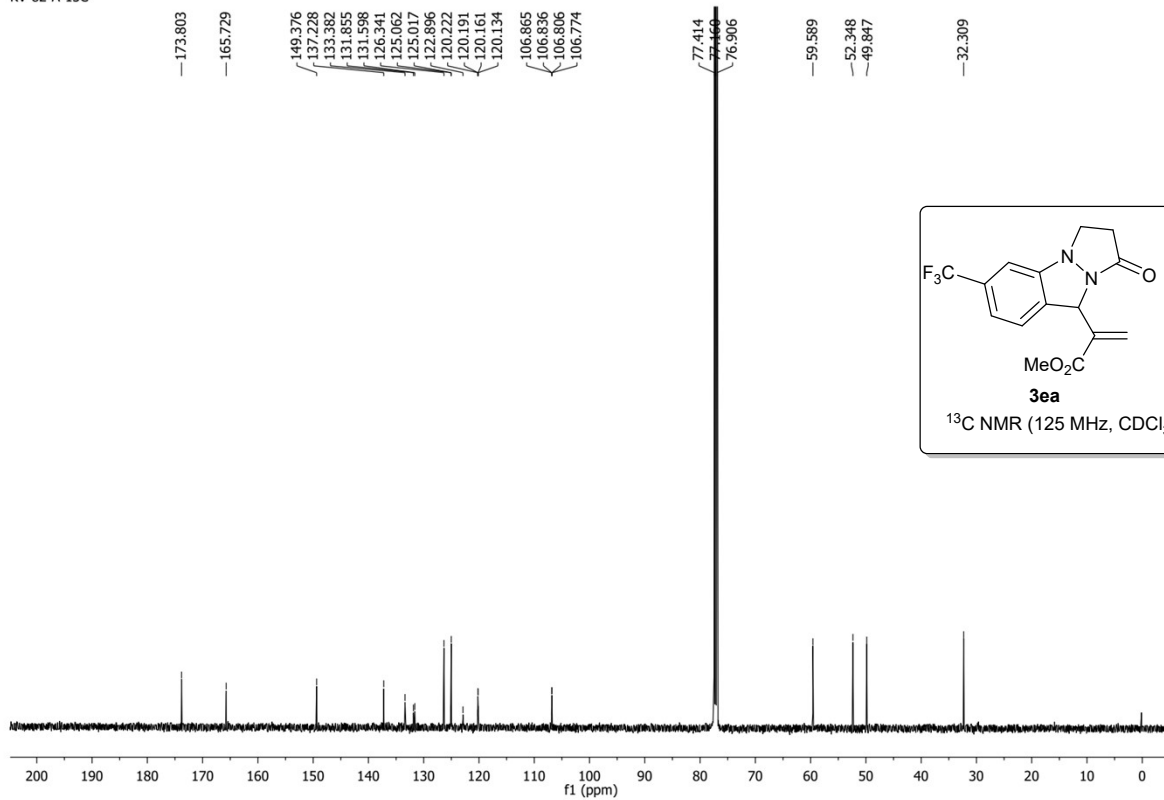
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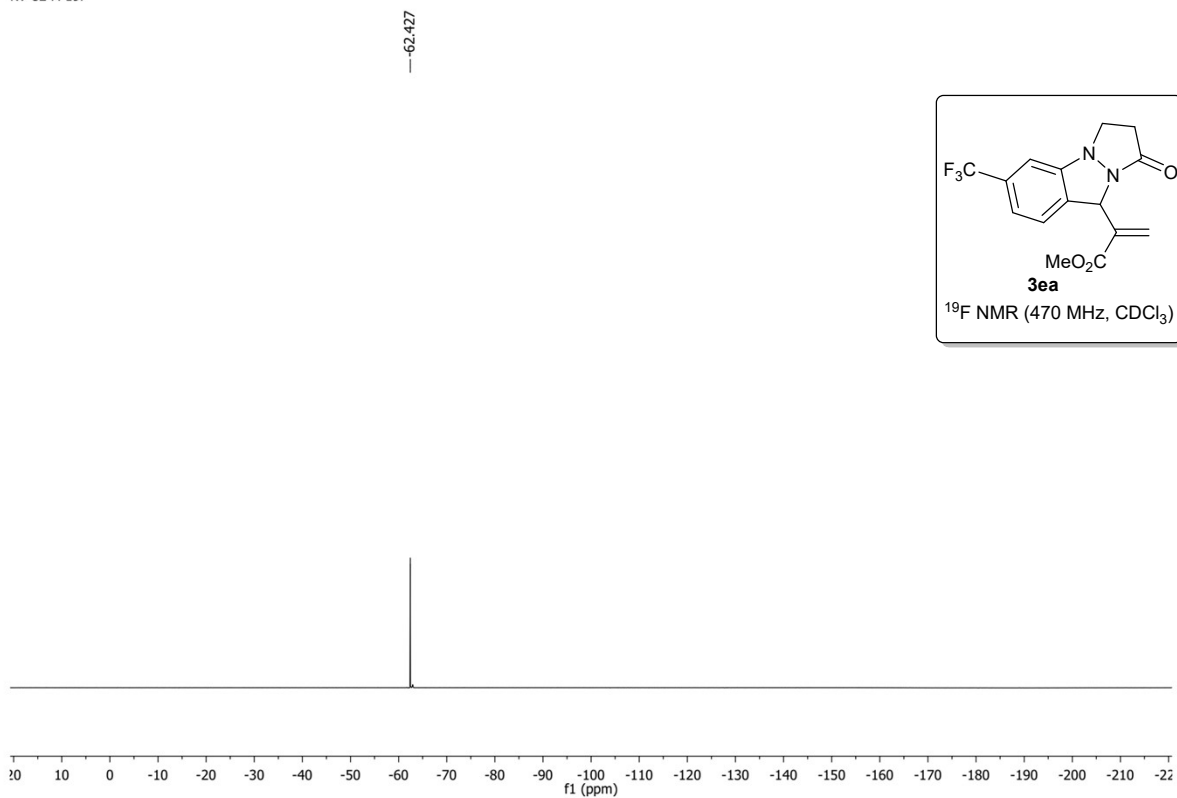
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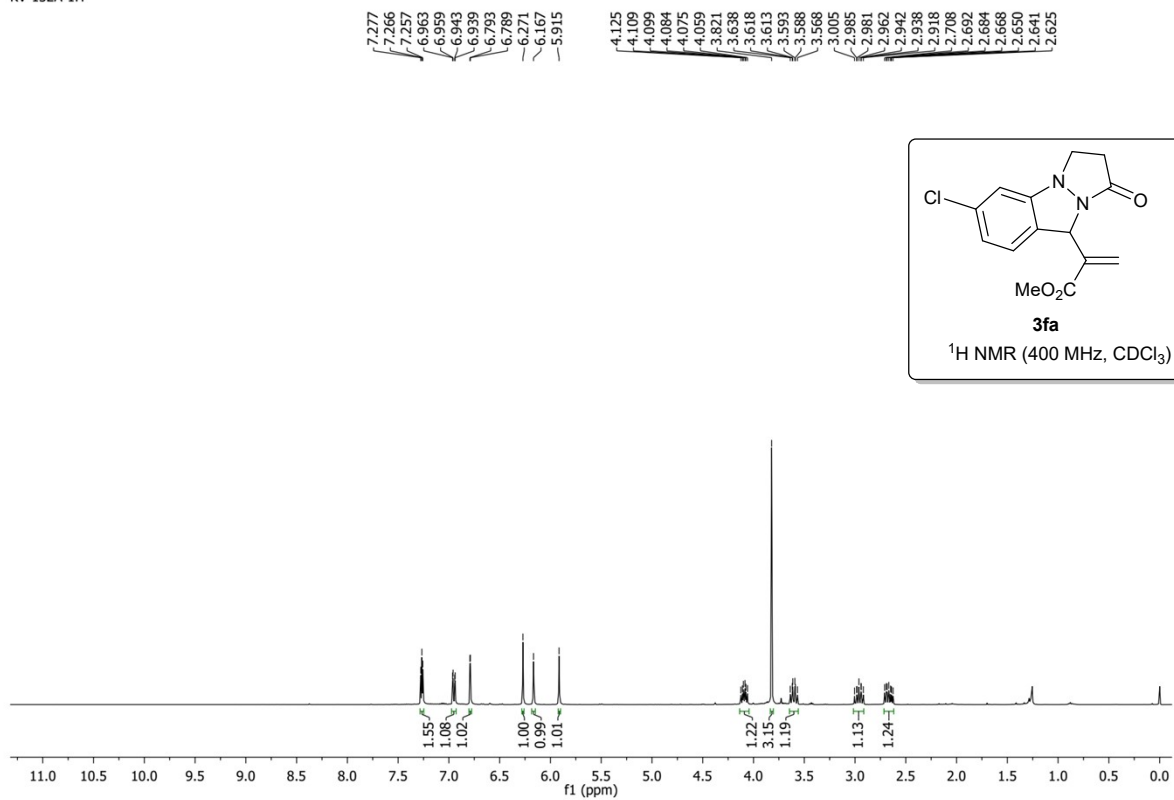
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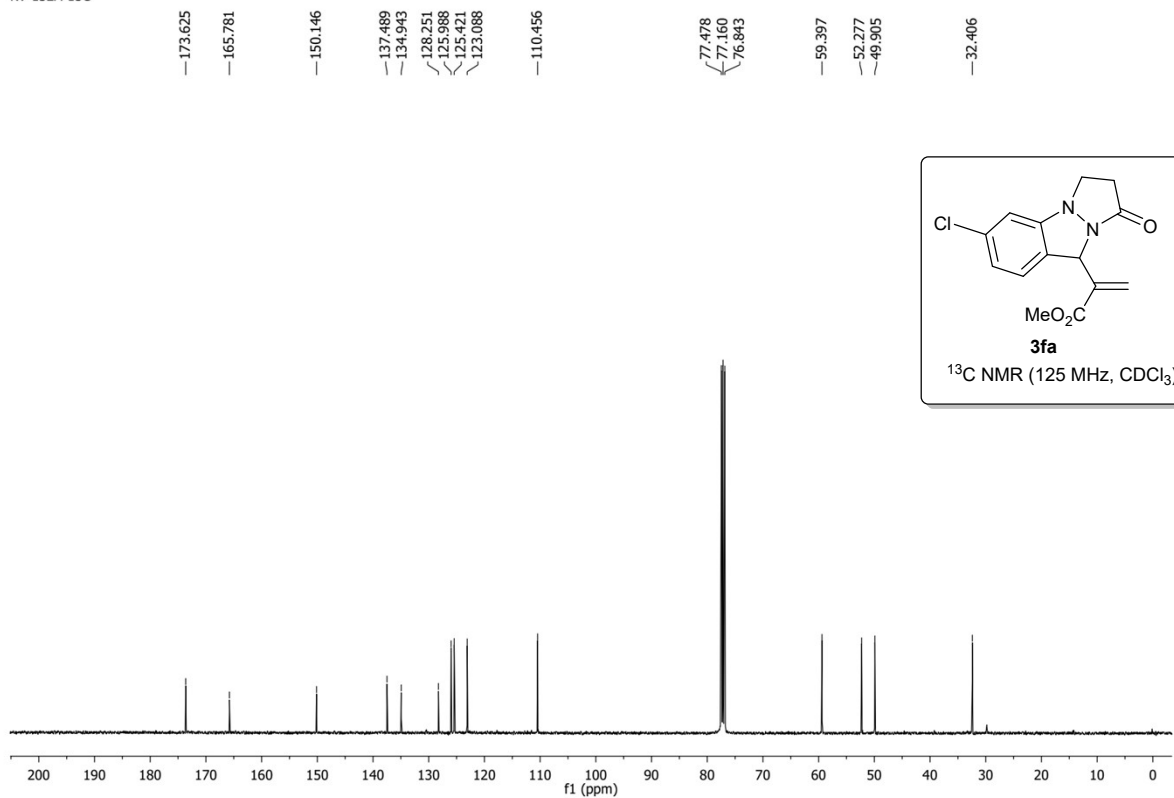
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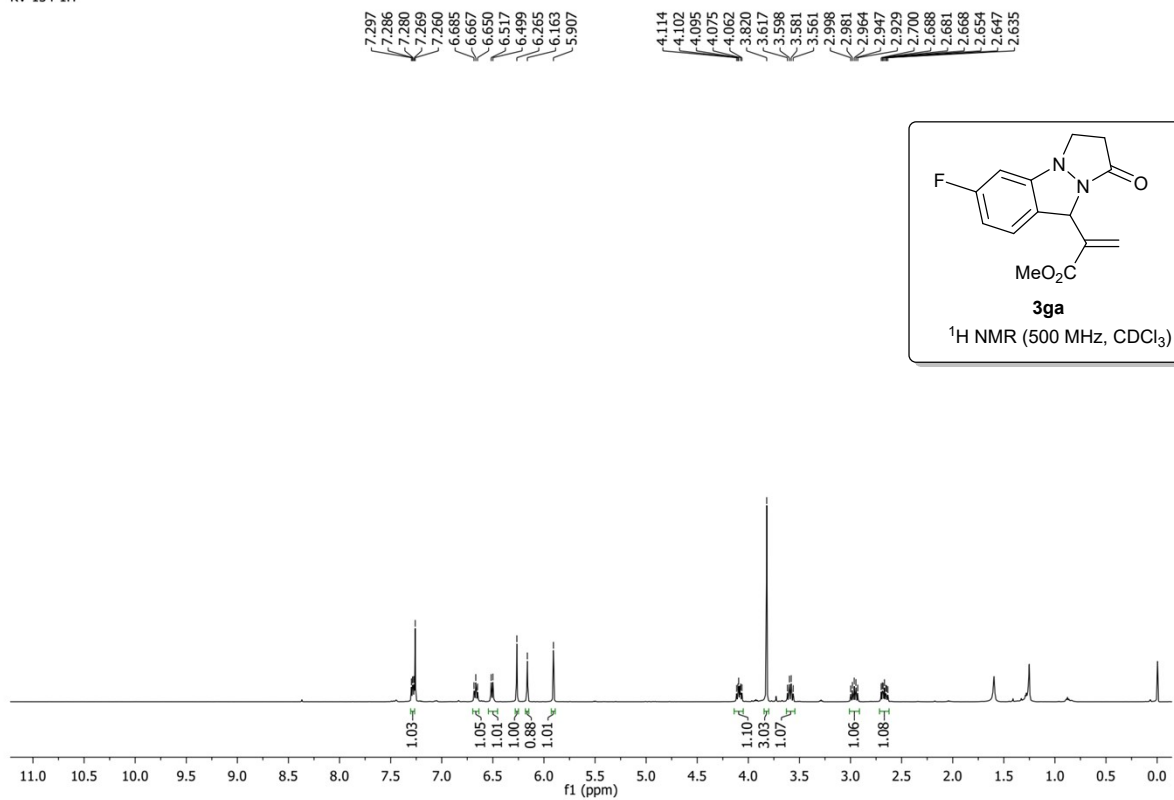
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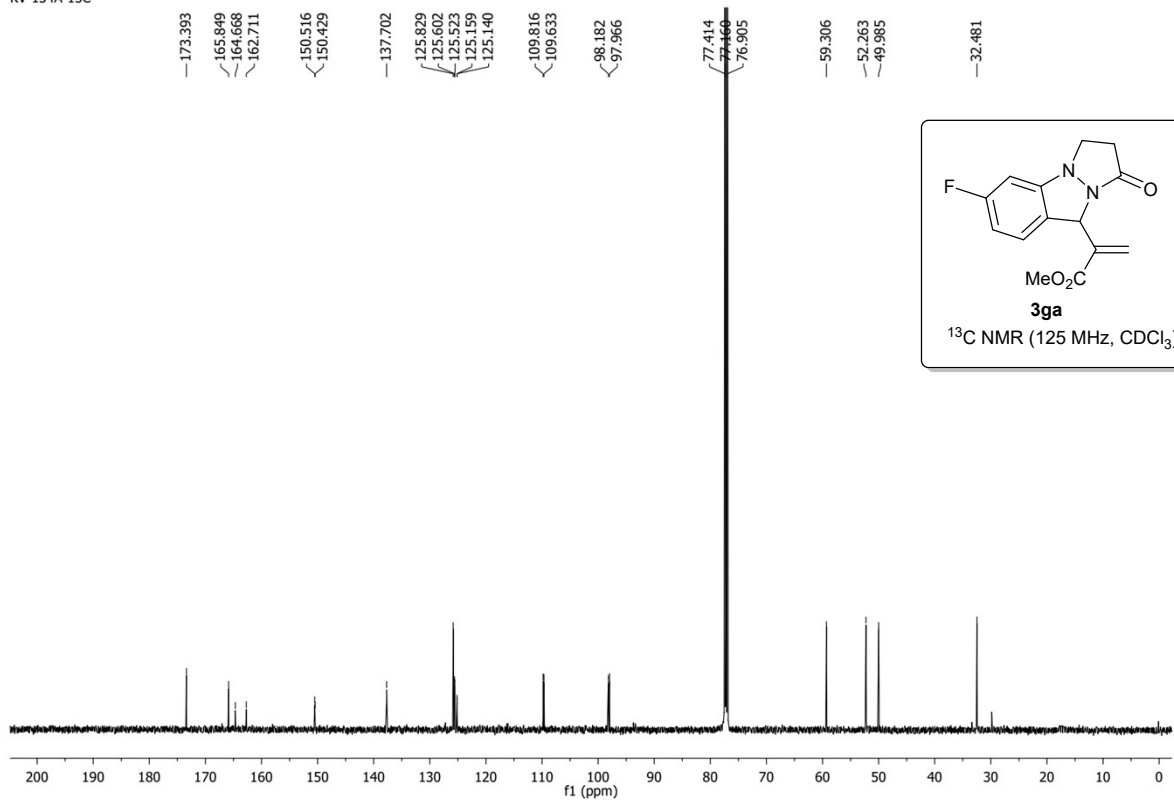
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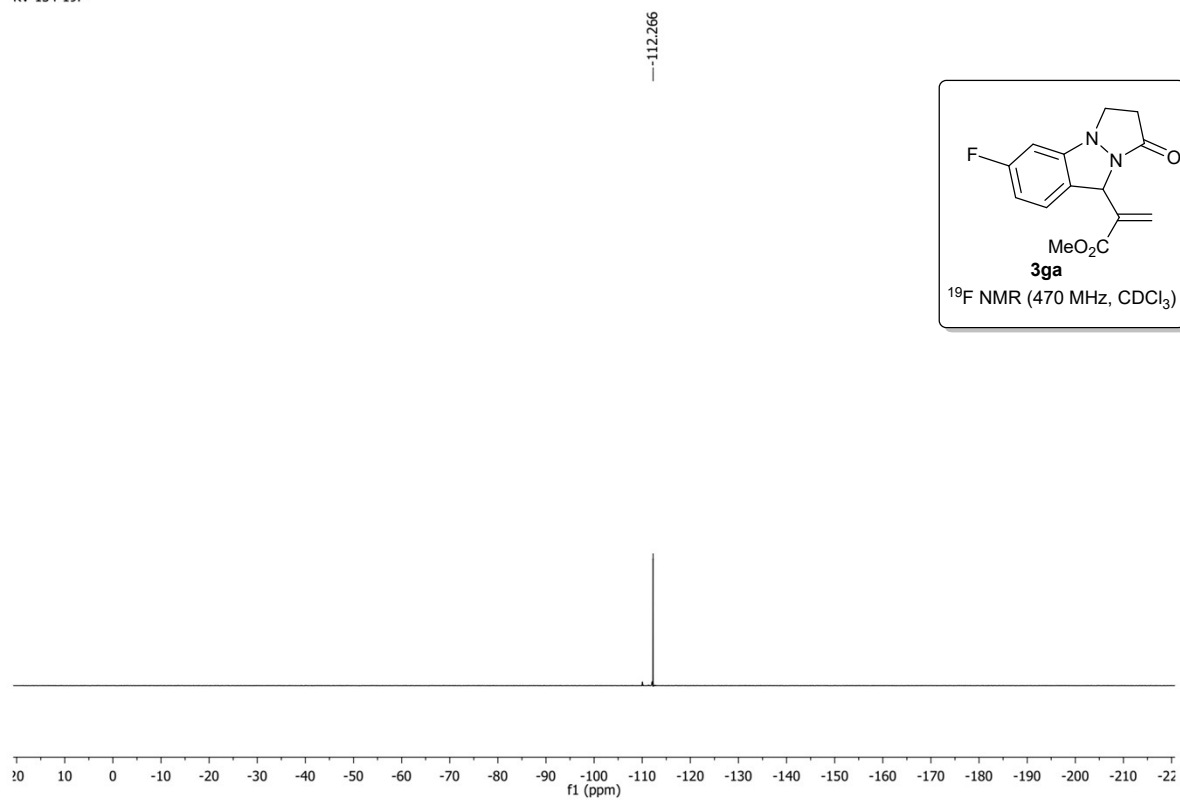
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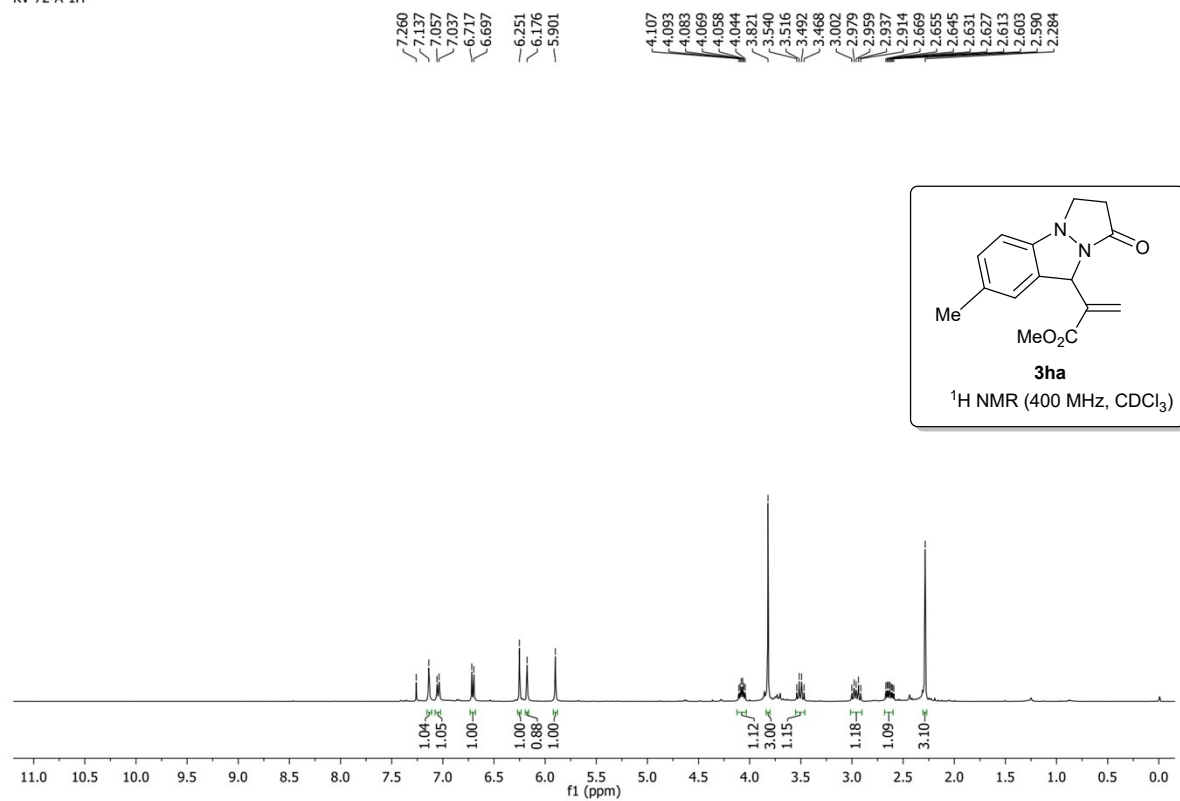
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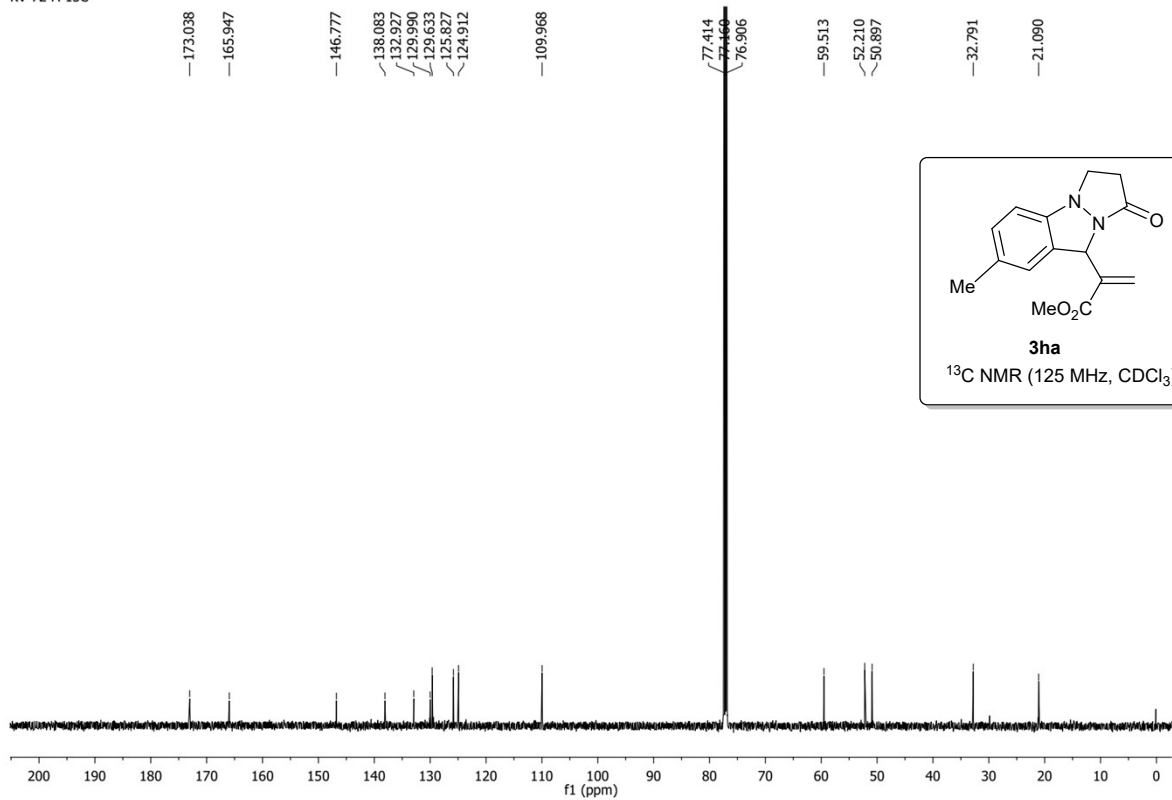
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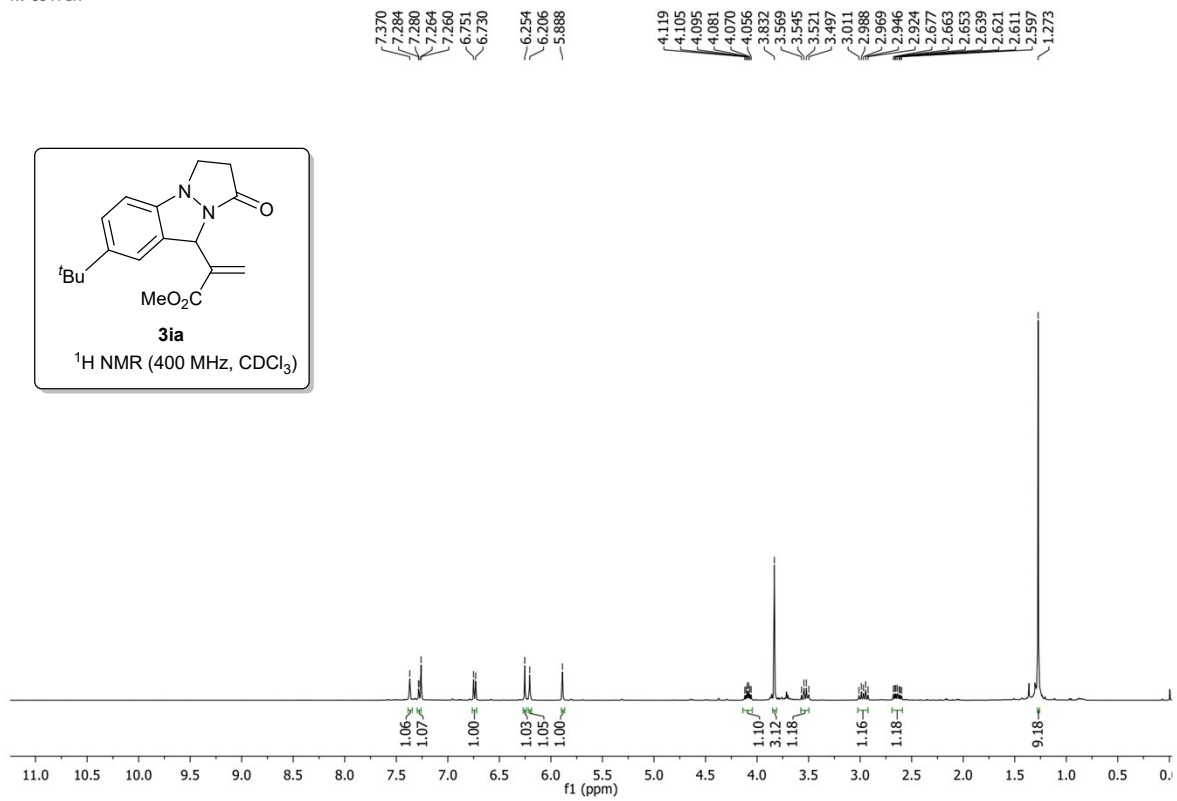
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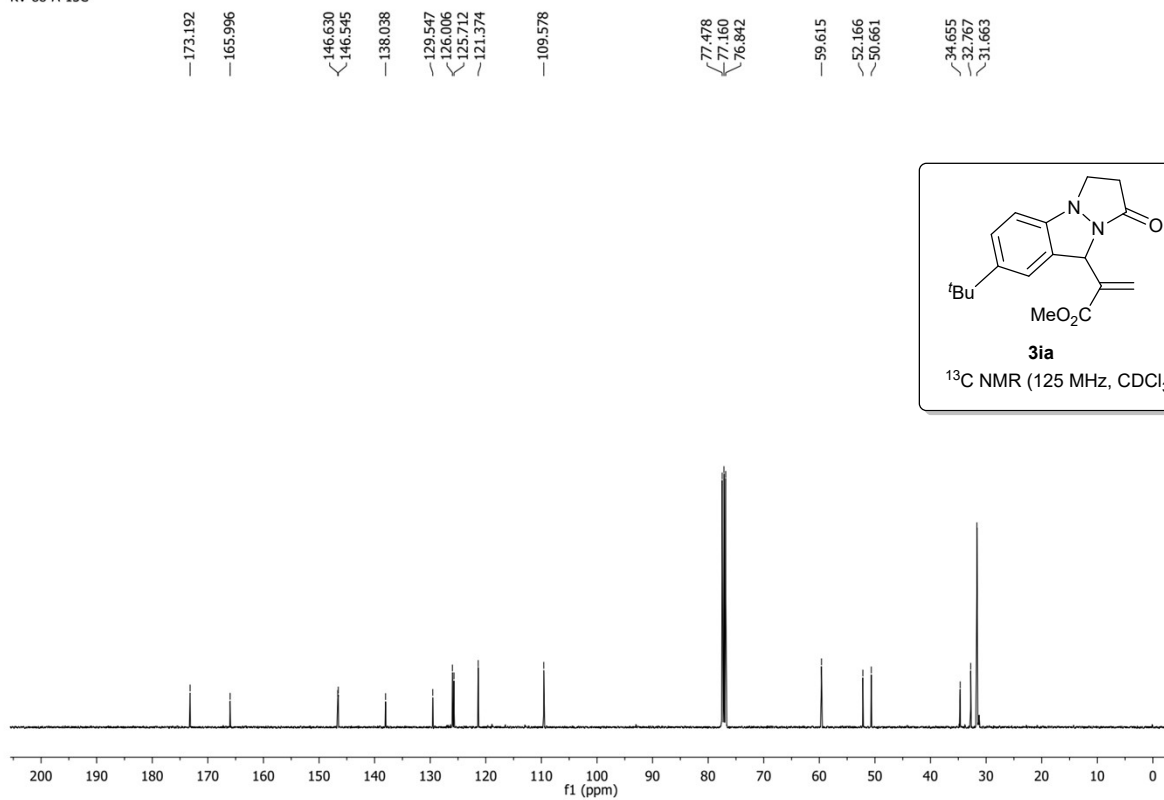
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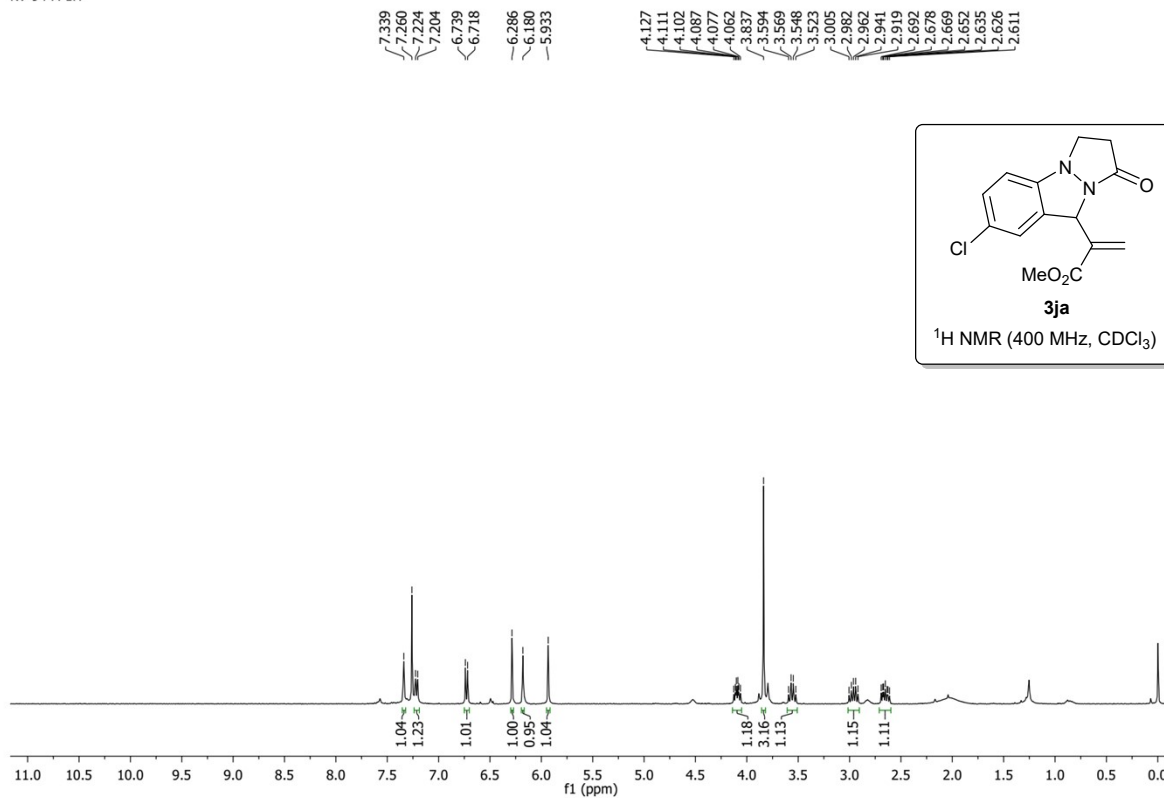
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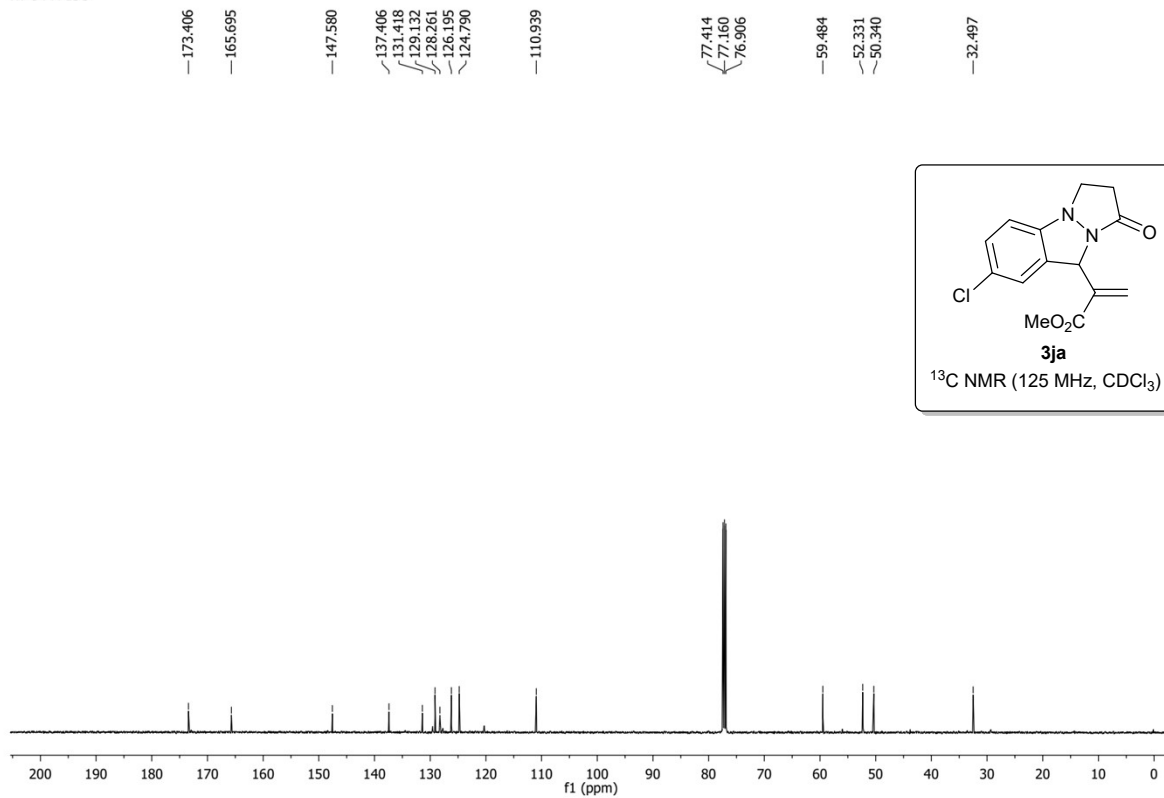
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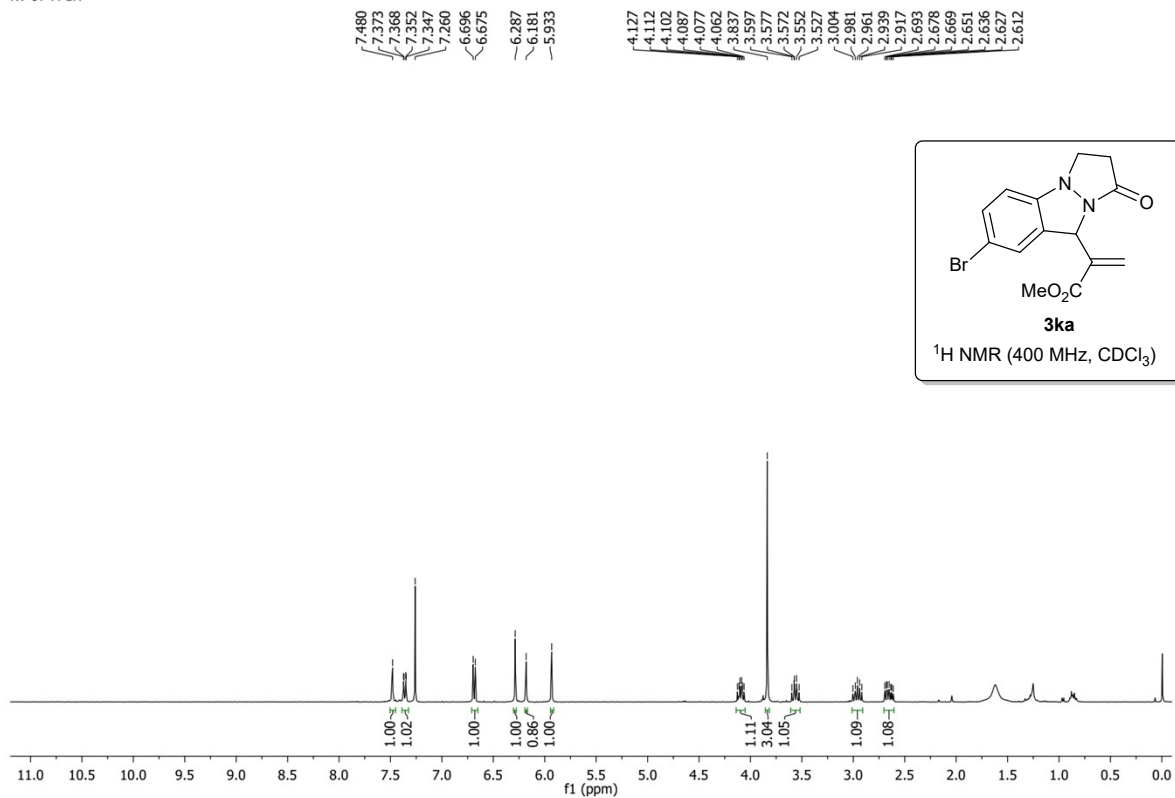
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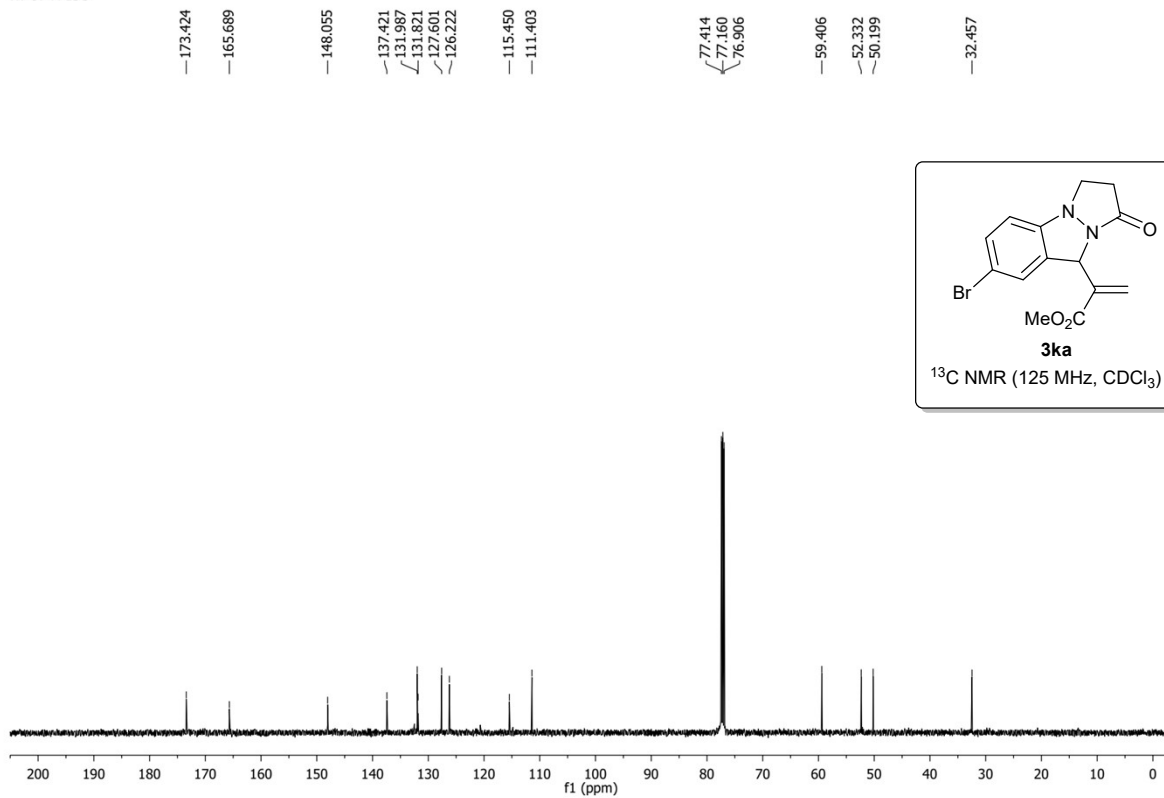
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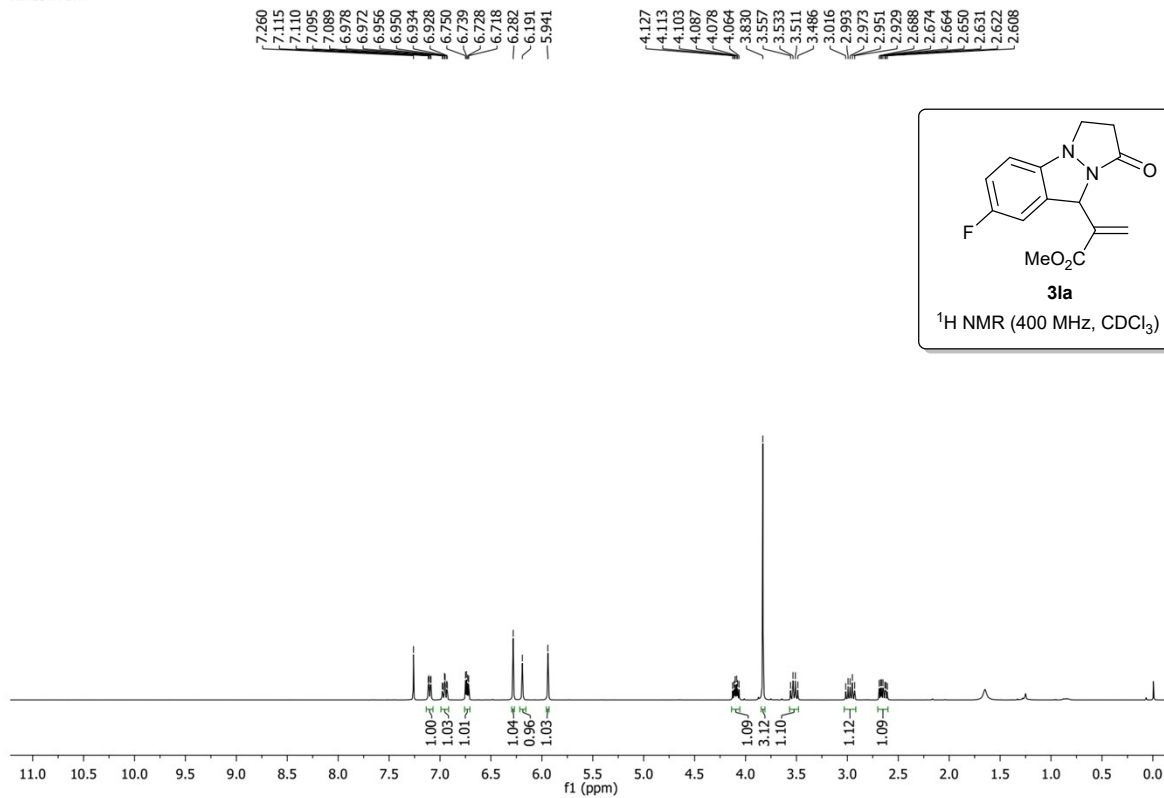
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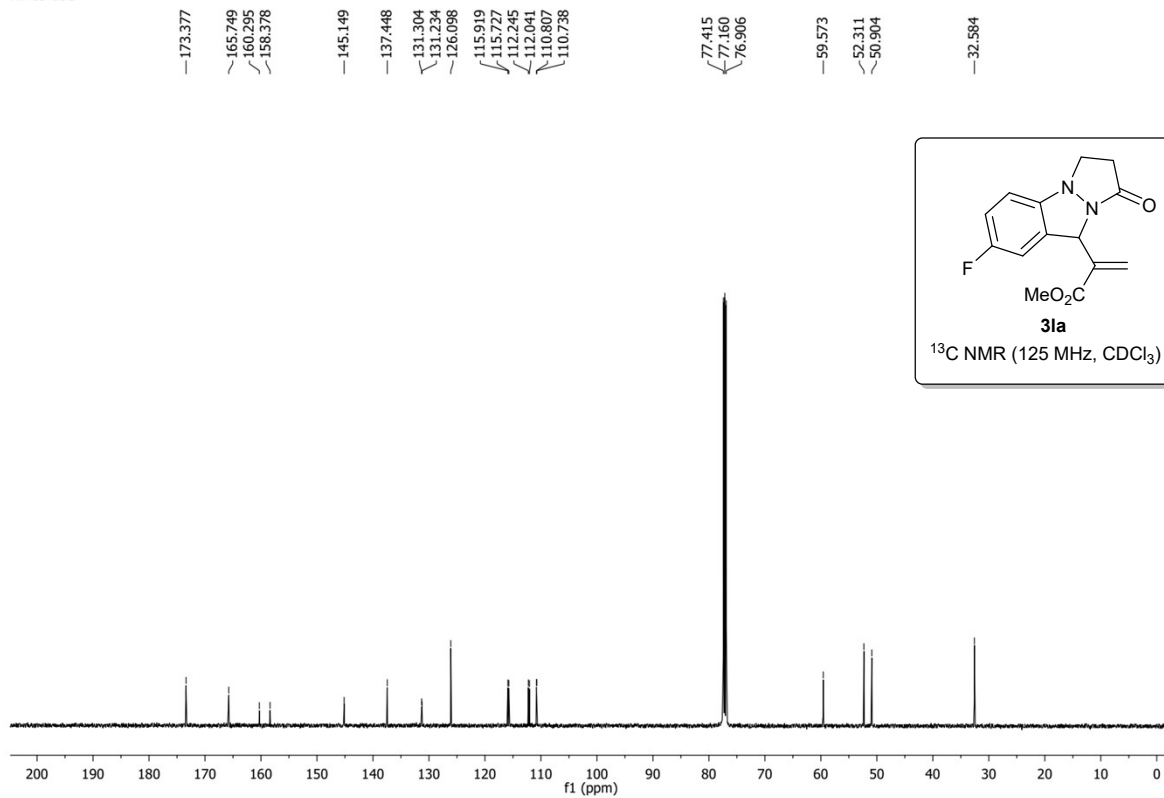
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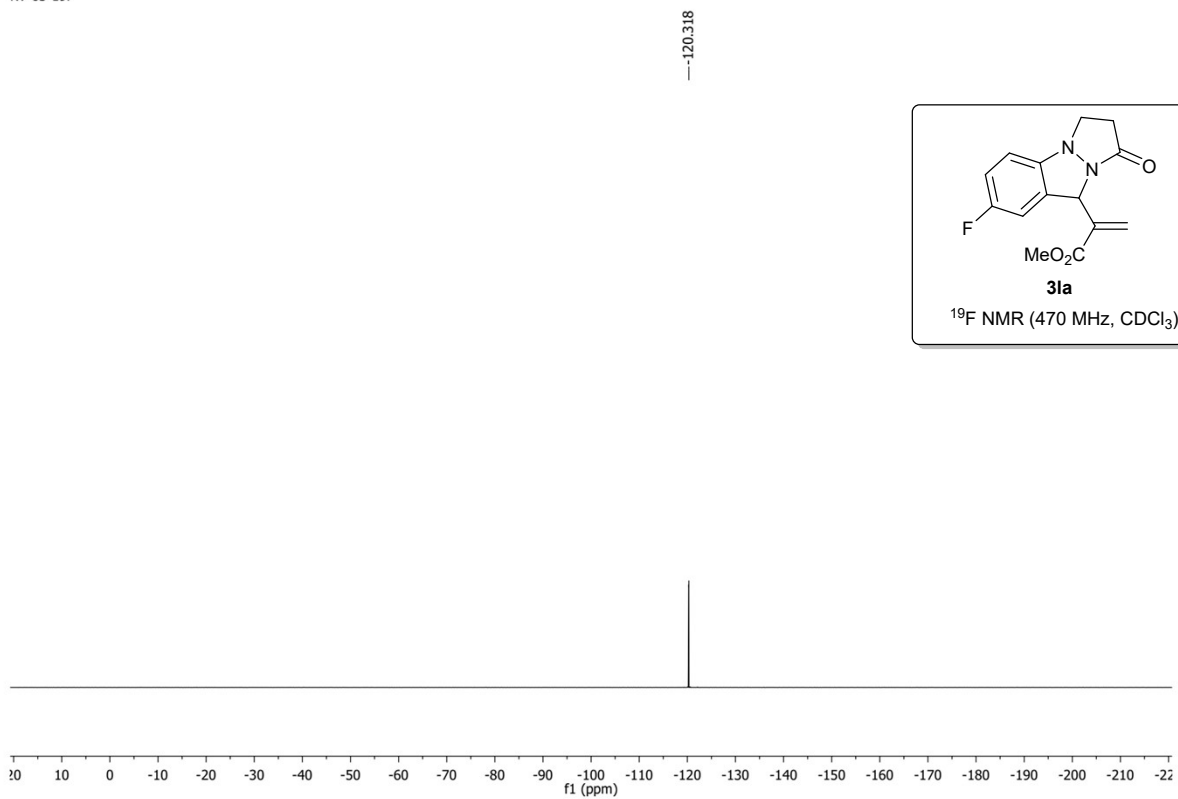
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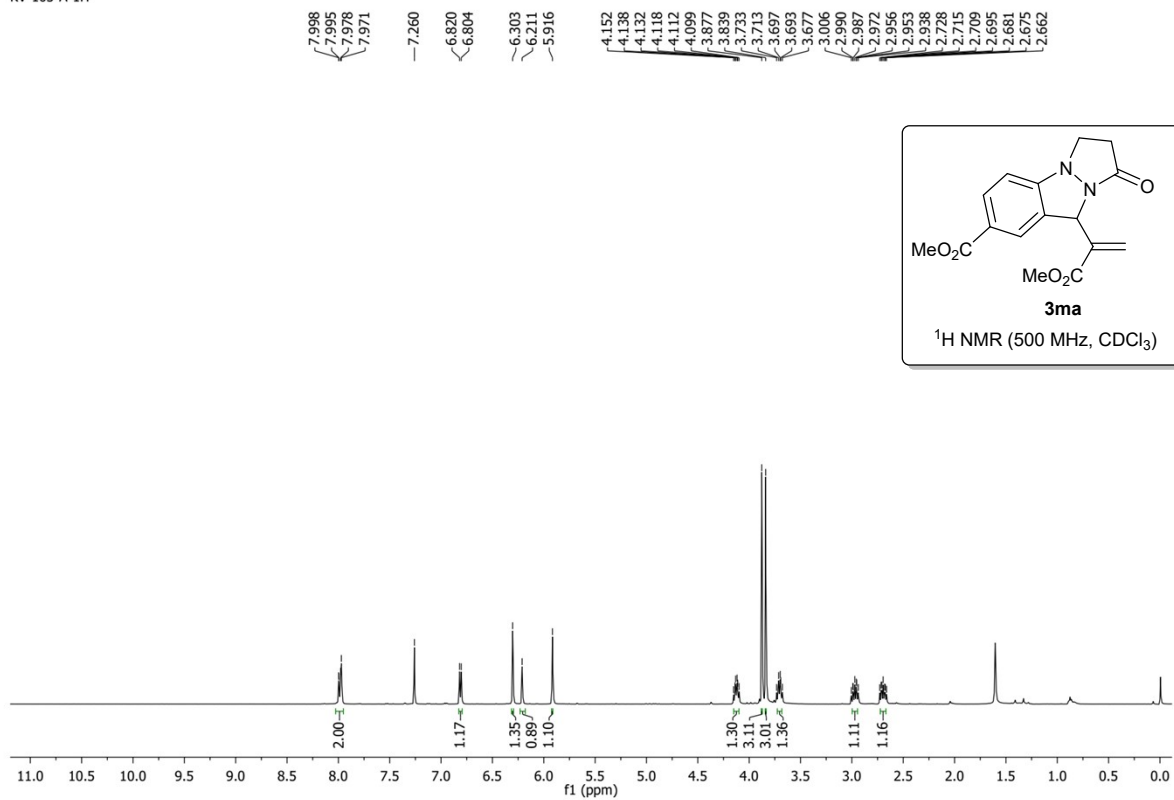
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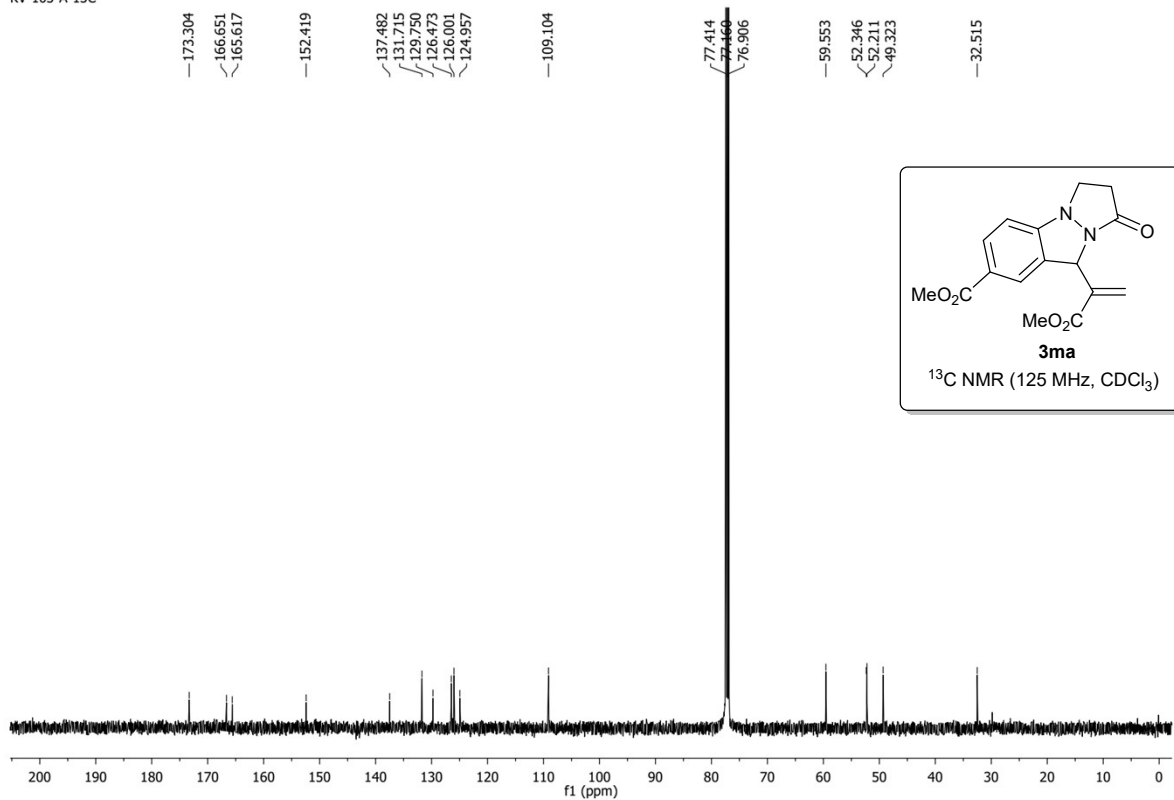
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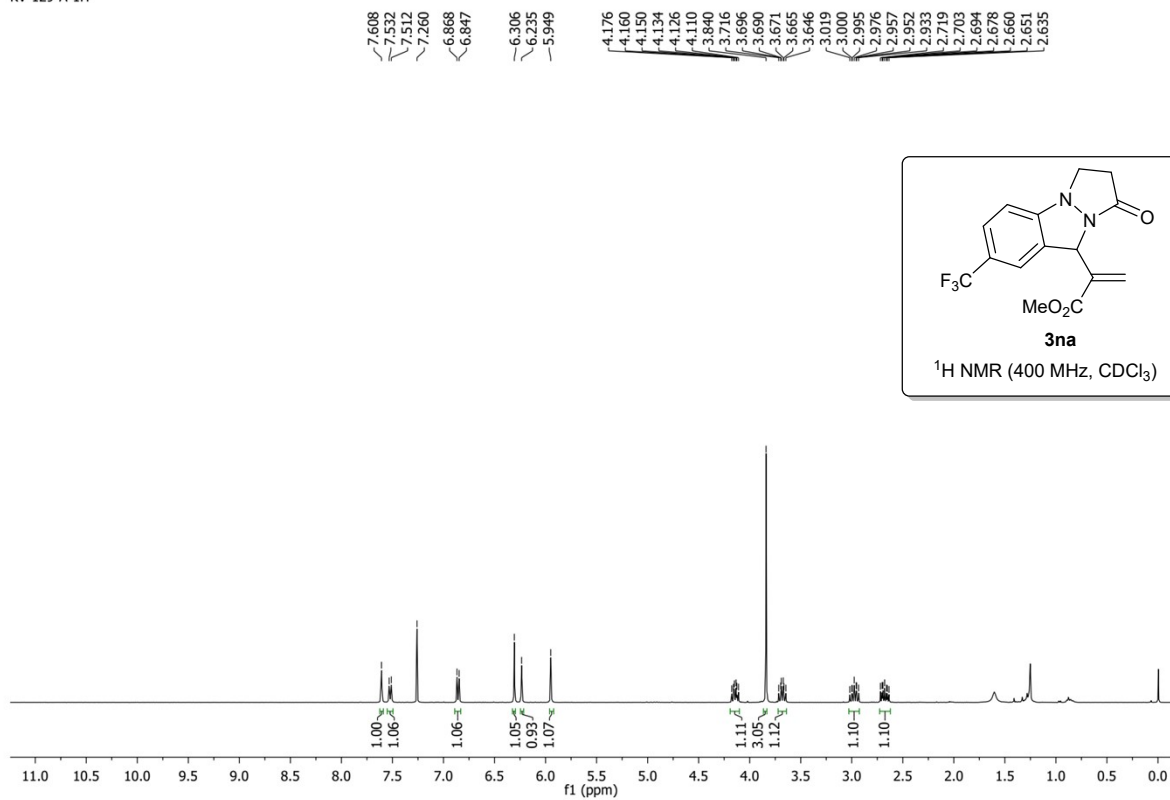
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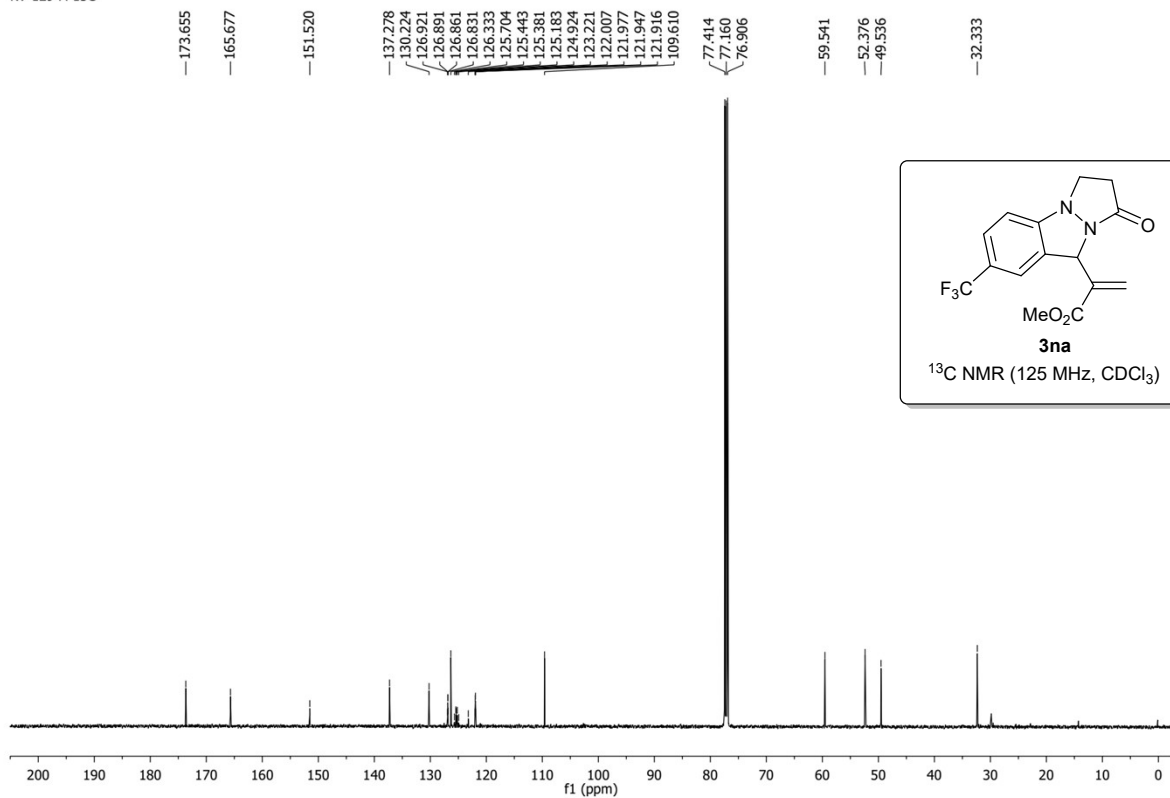
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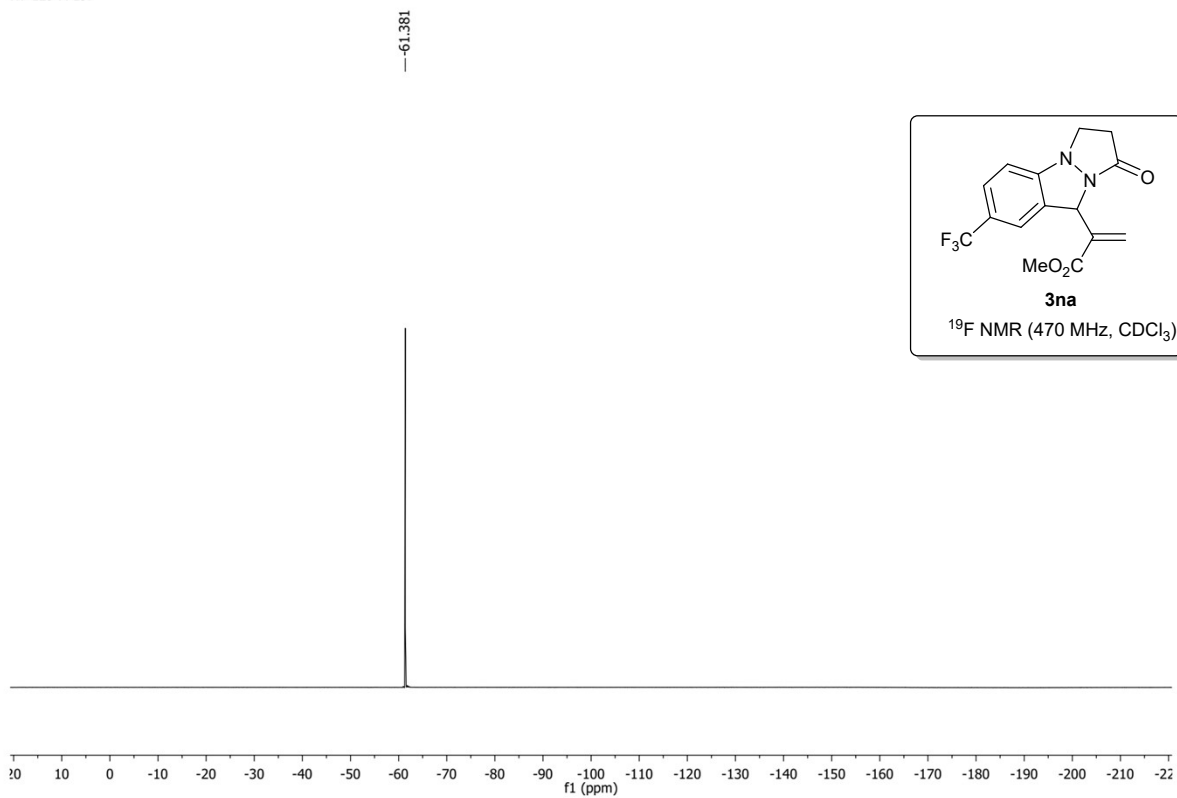
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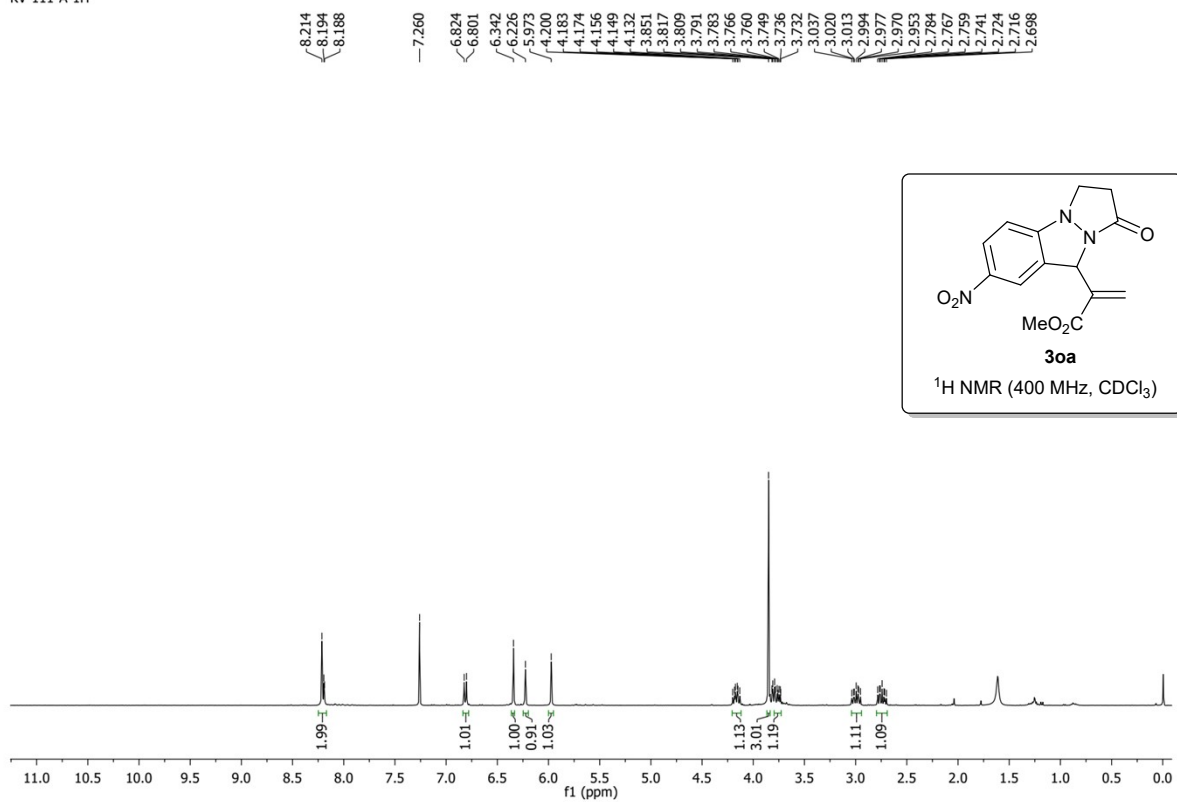
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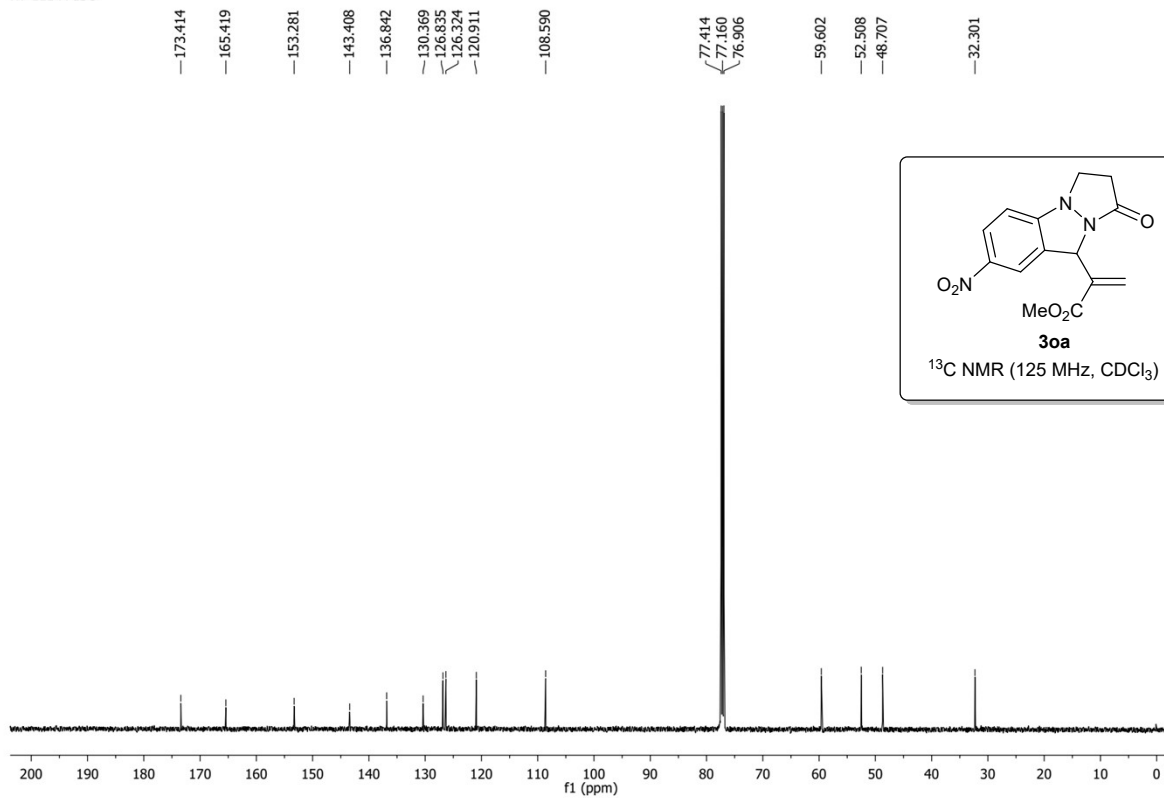
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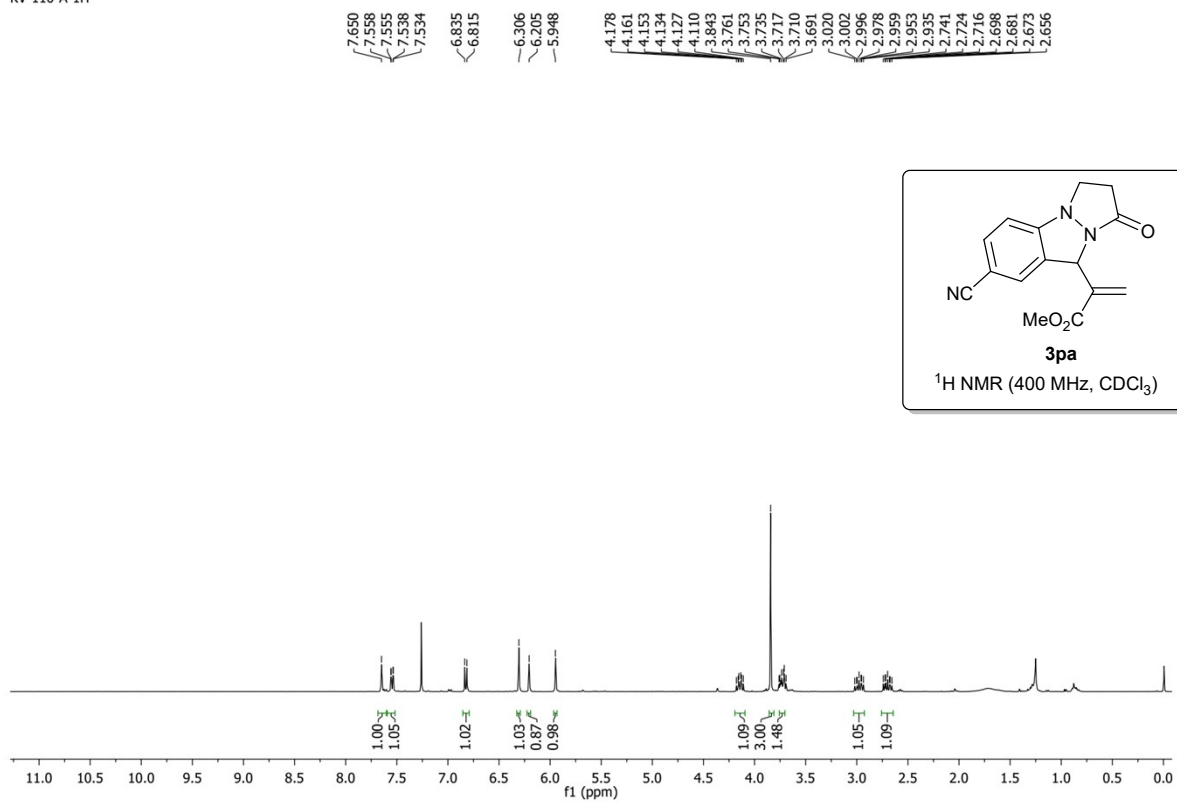
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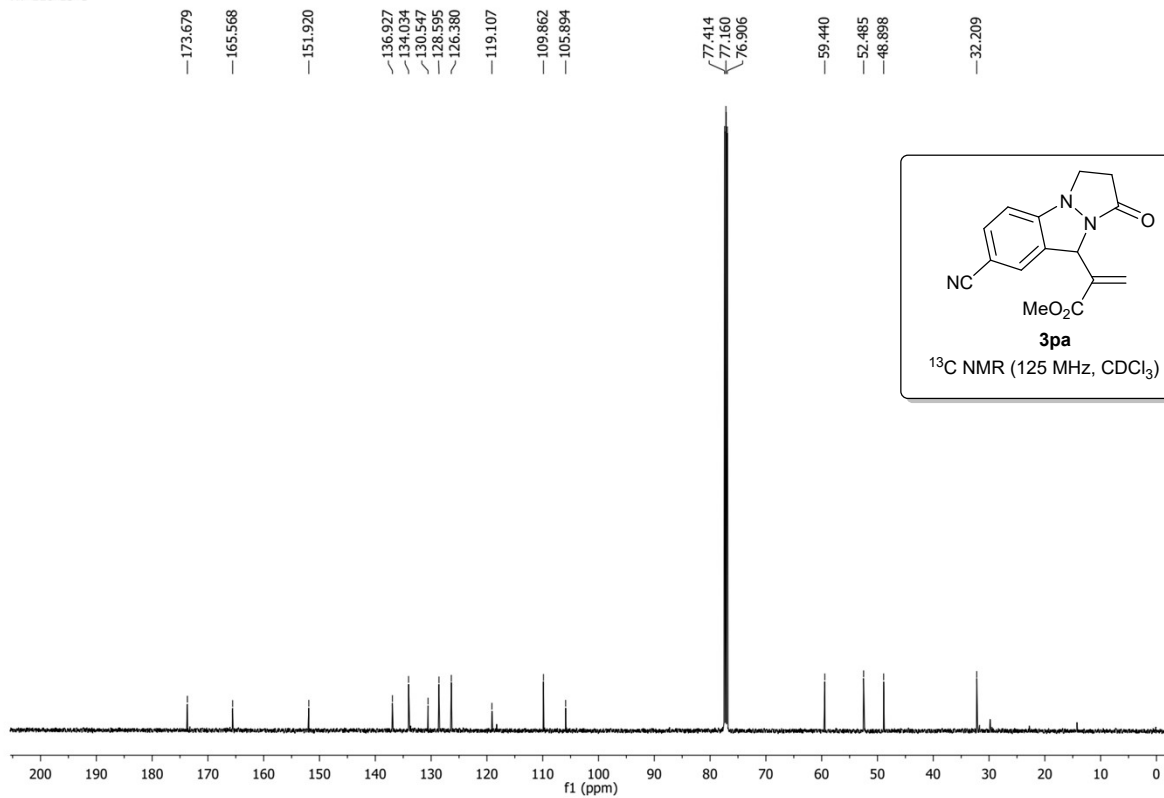
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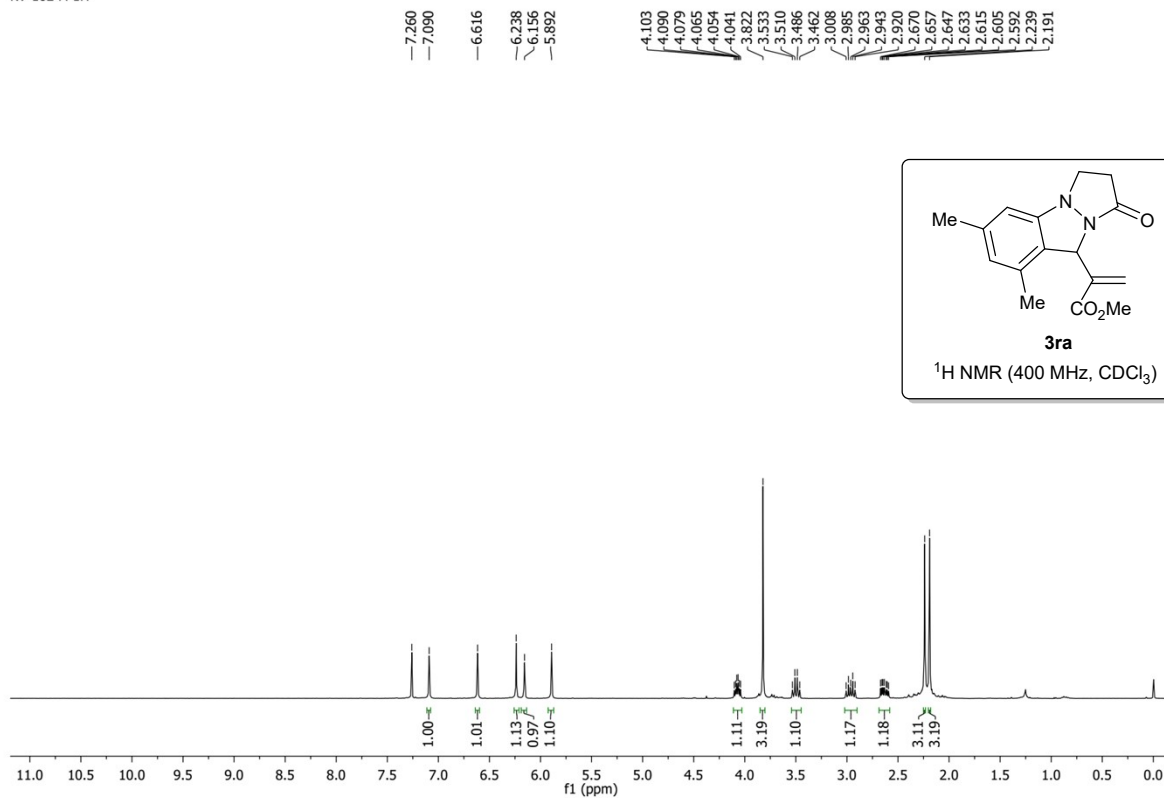
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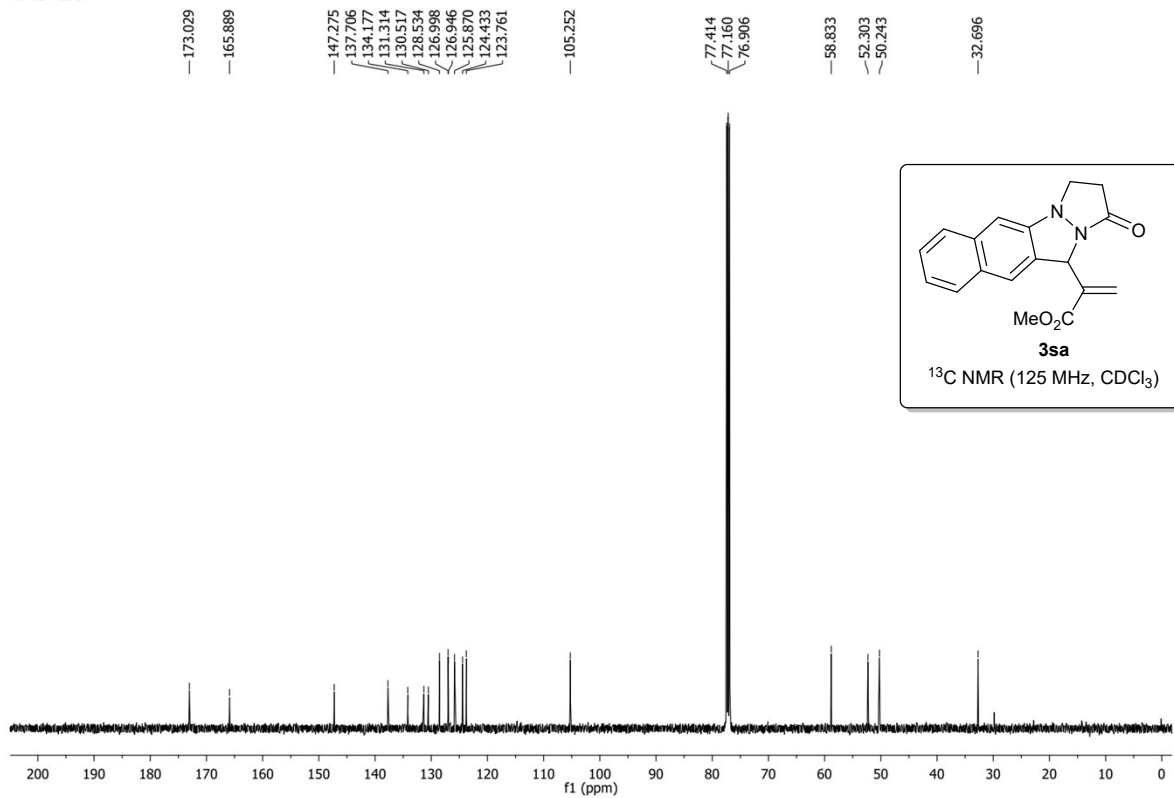


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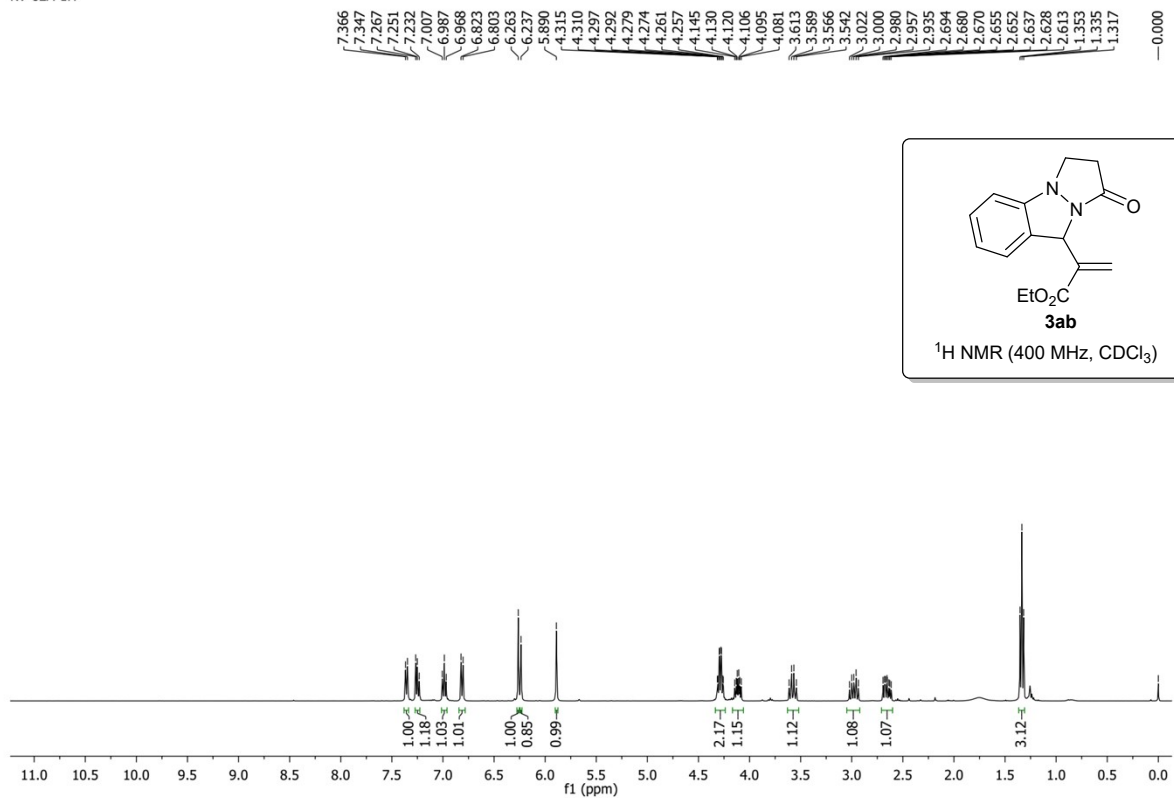




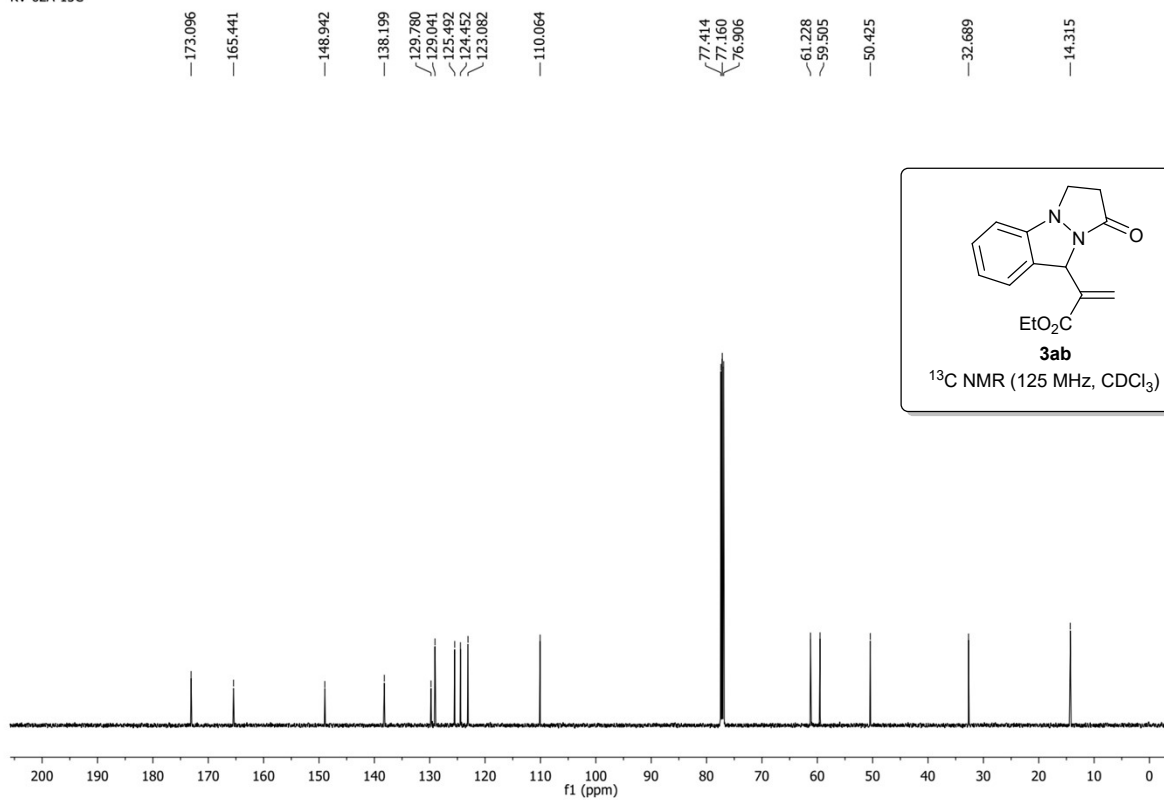
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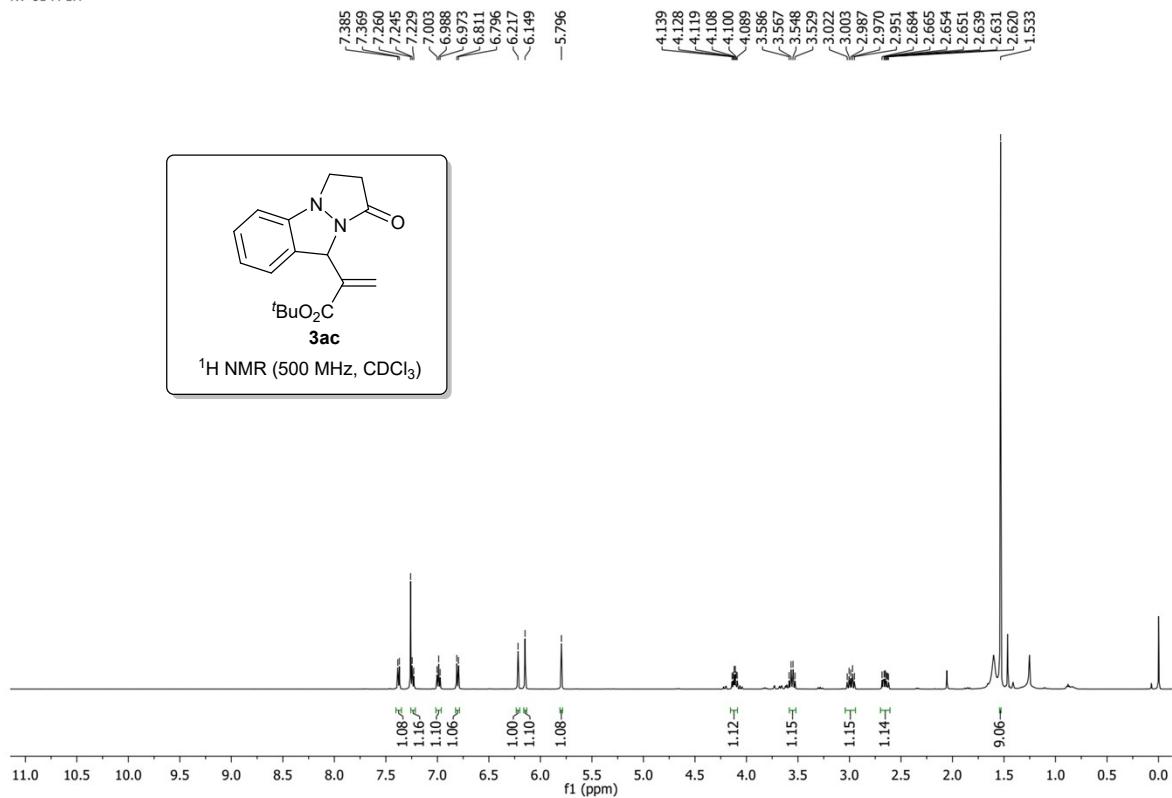
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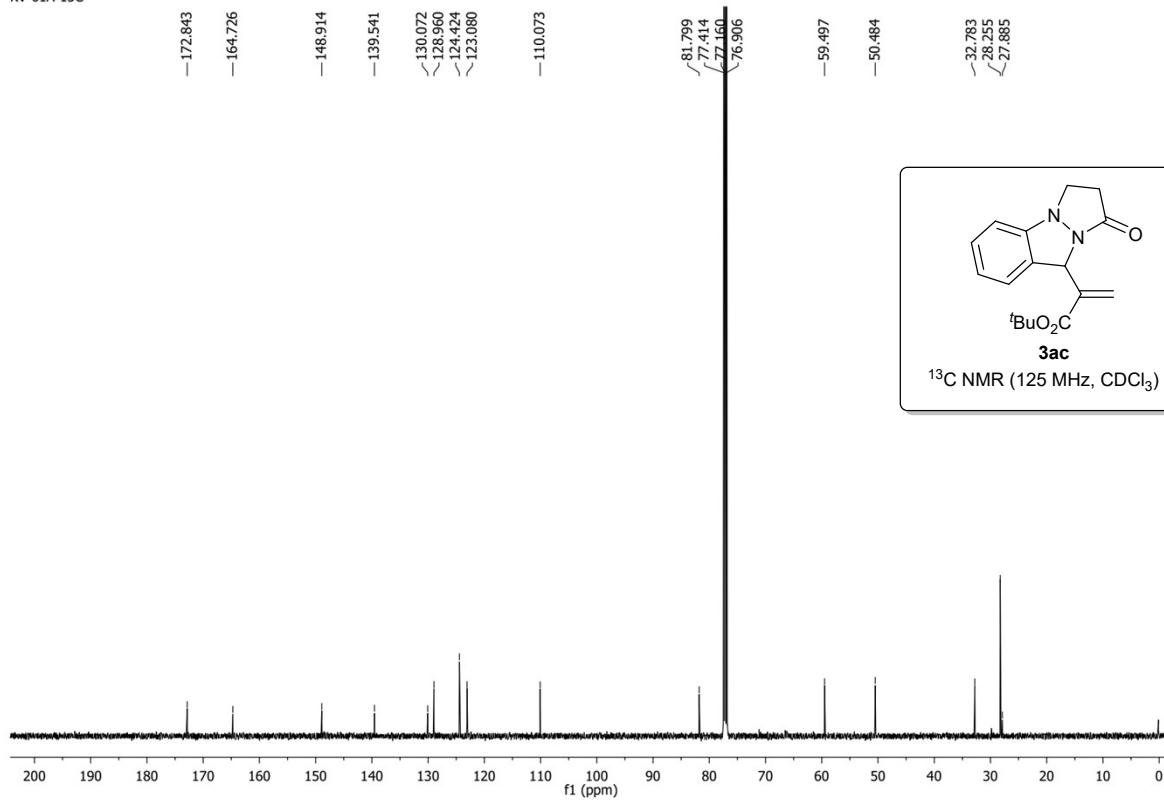
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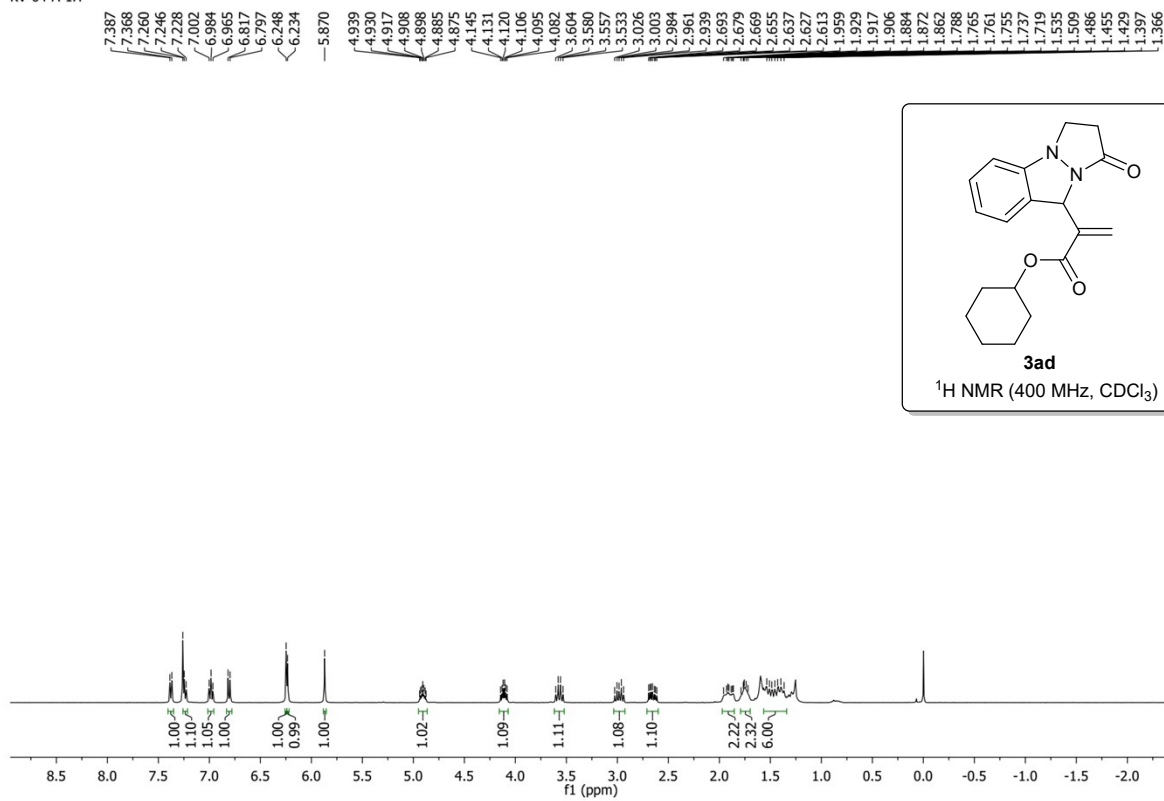
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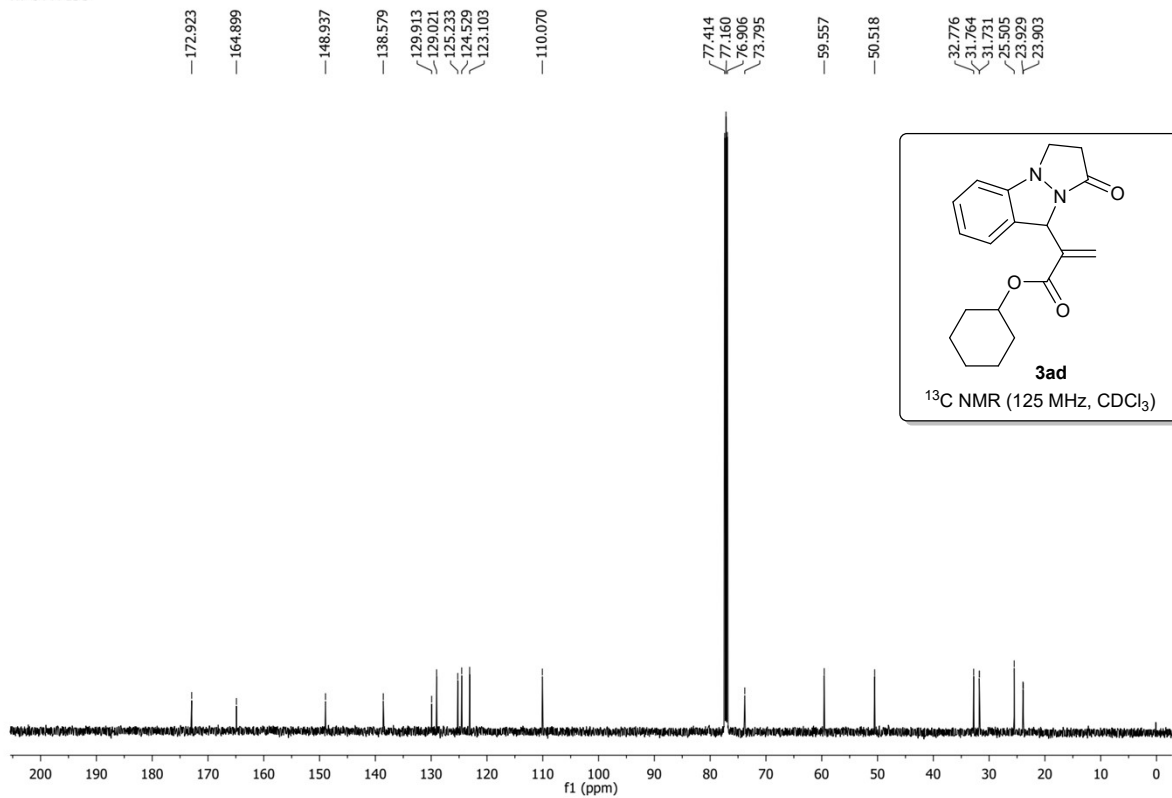
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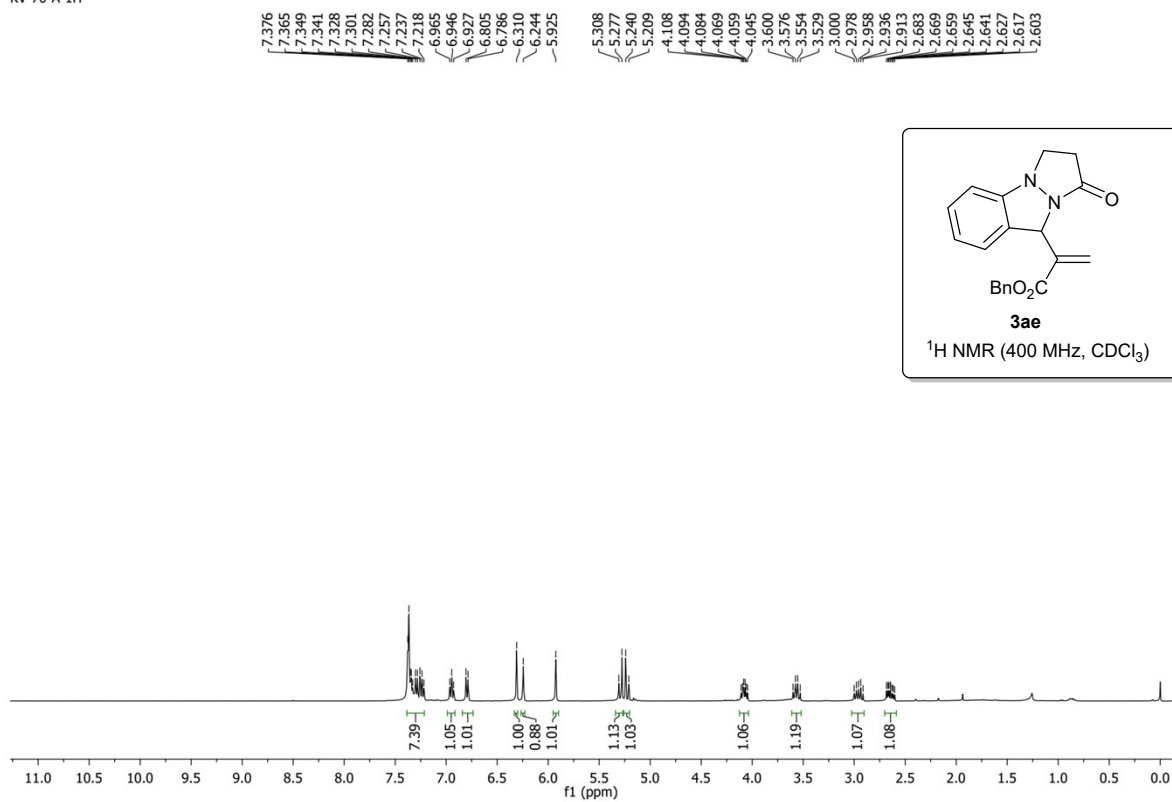
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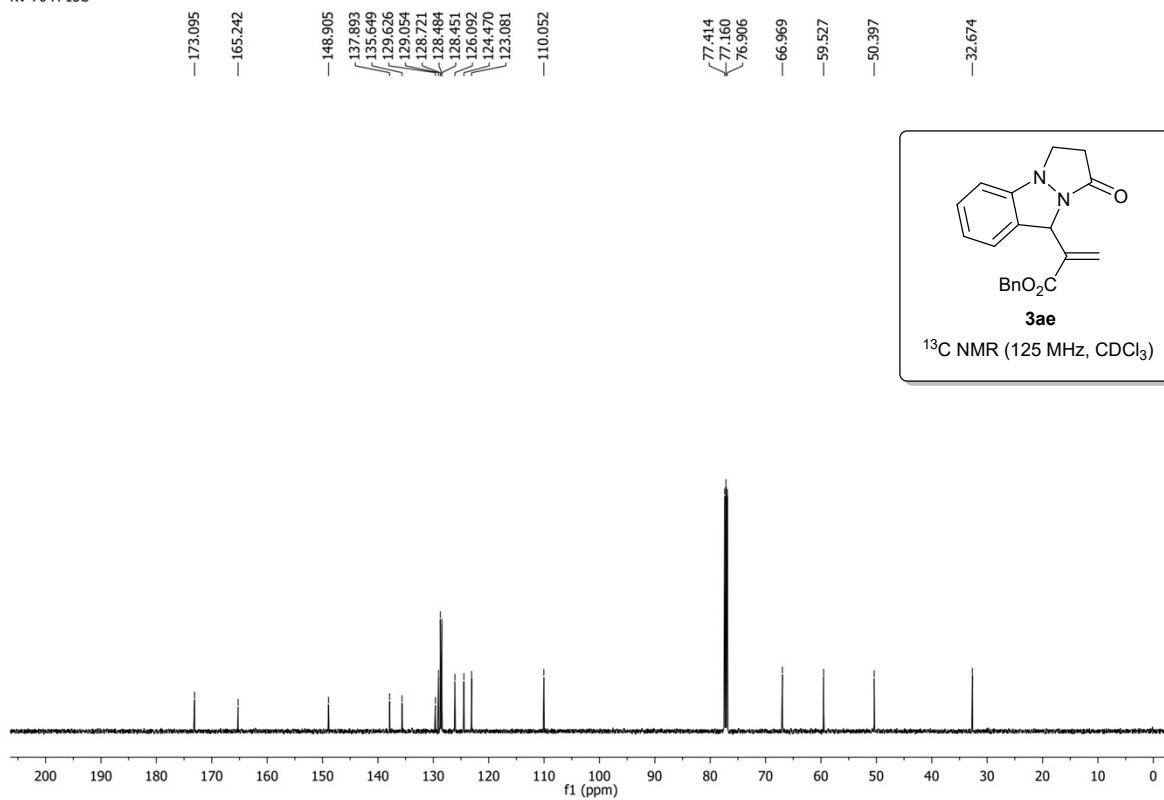
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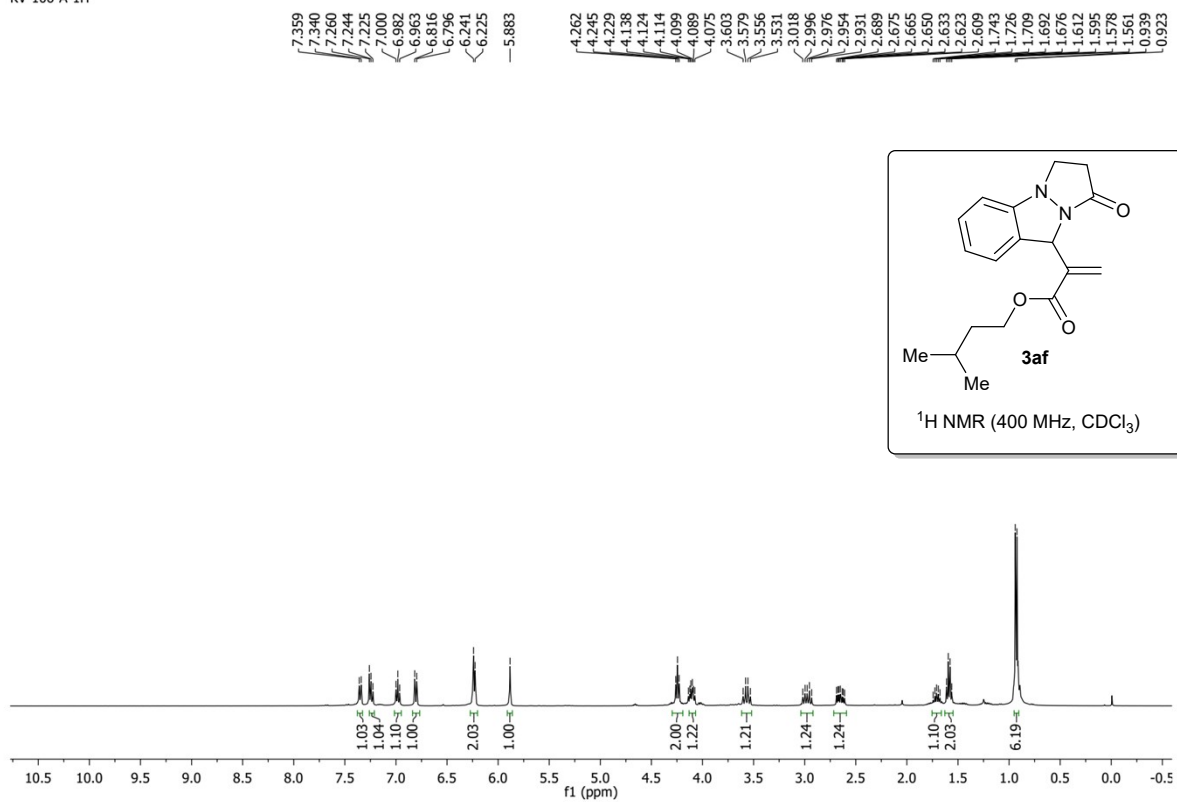
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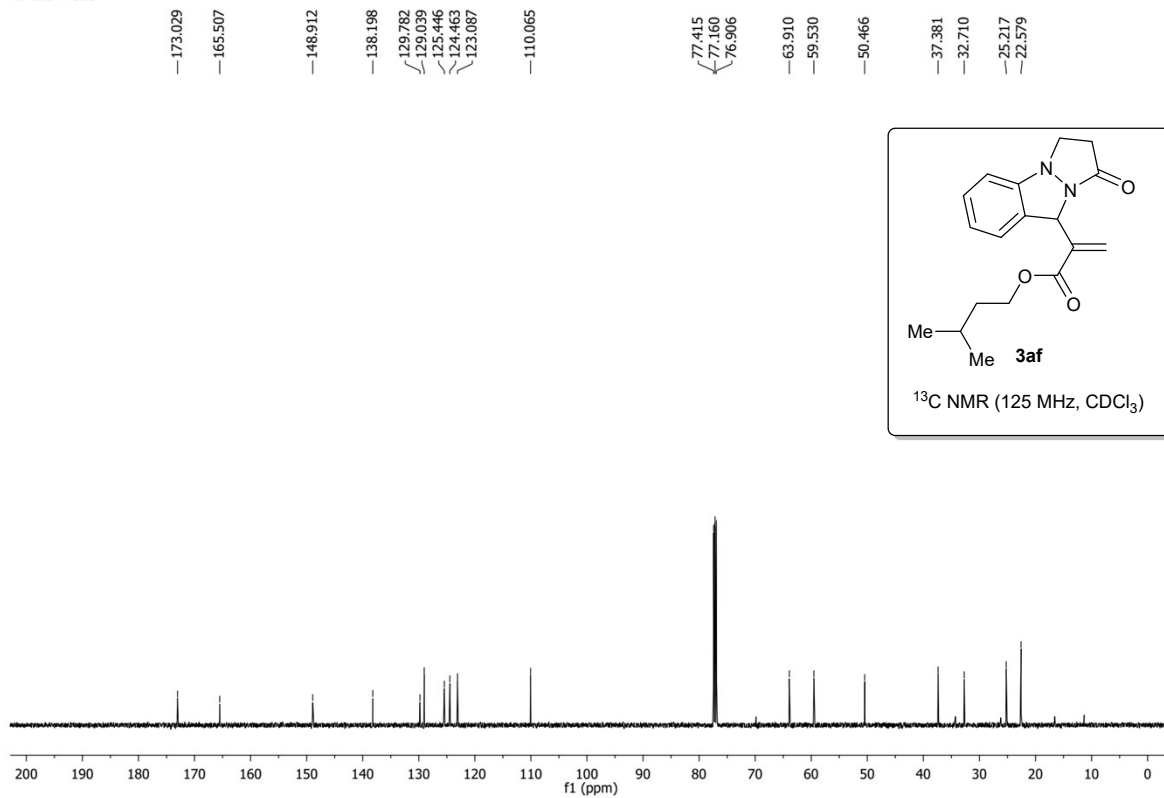
KV-70-A-13C



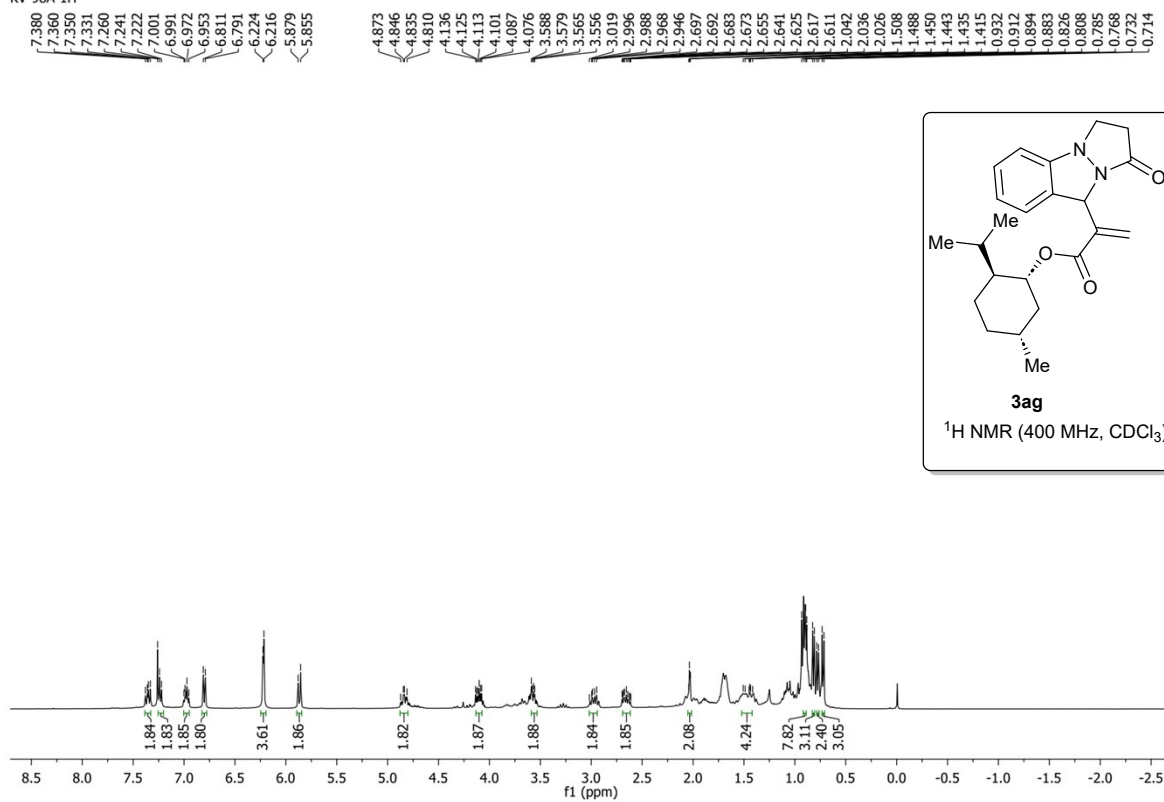
KV-106-A-1H



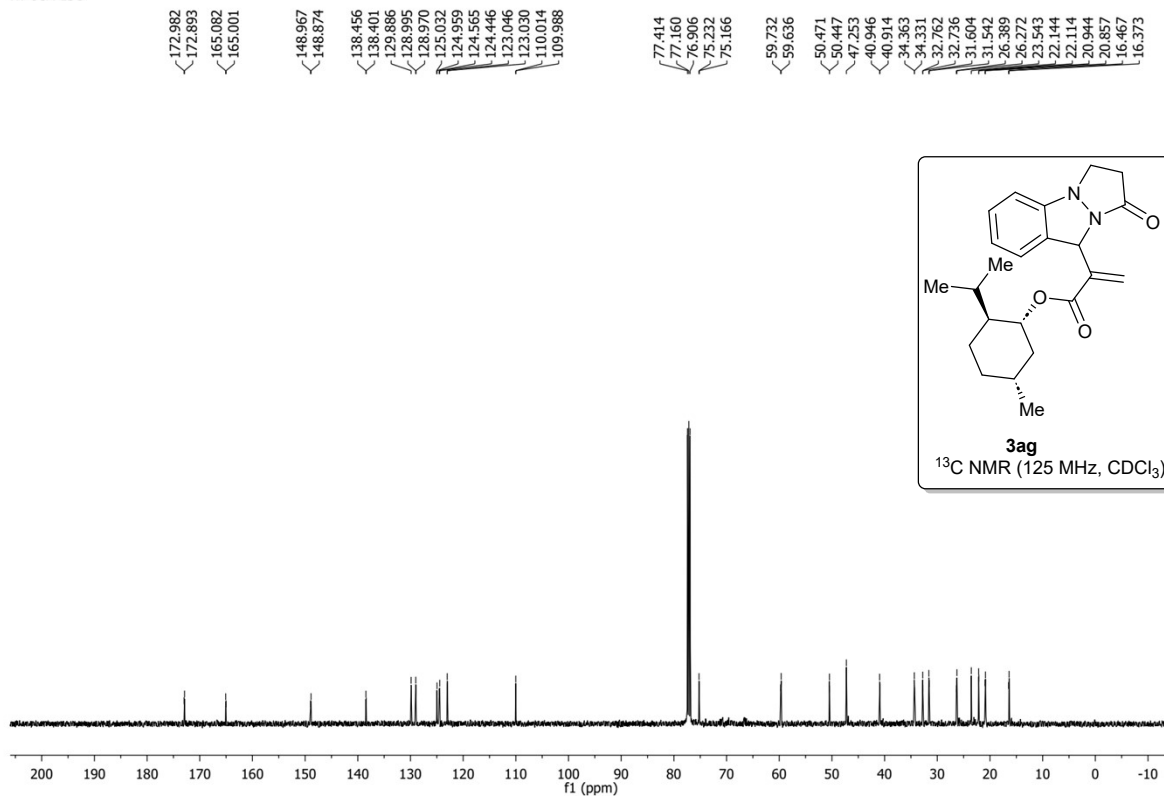
KV-106-A-13C



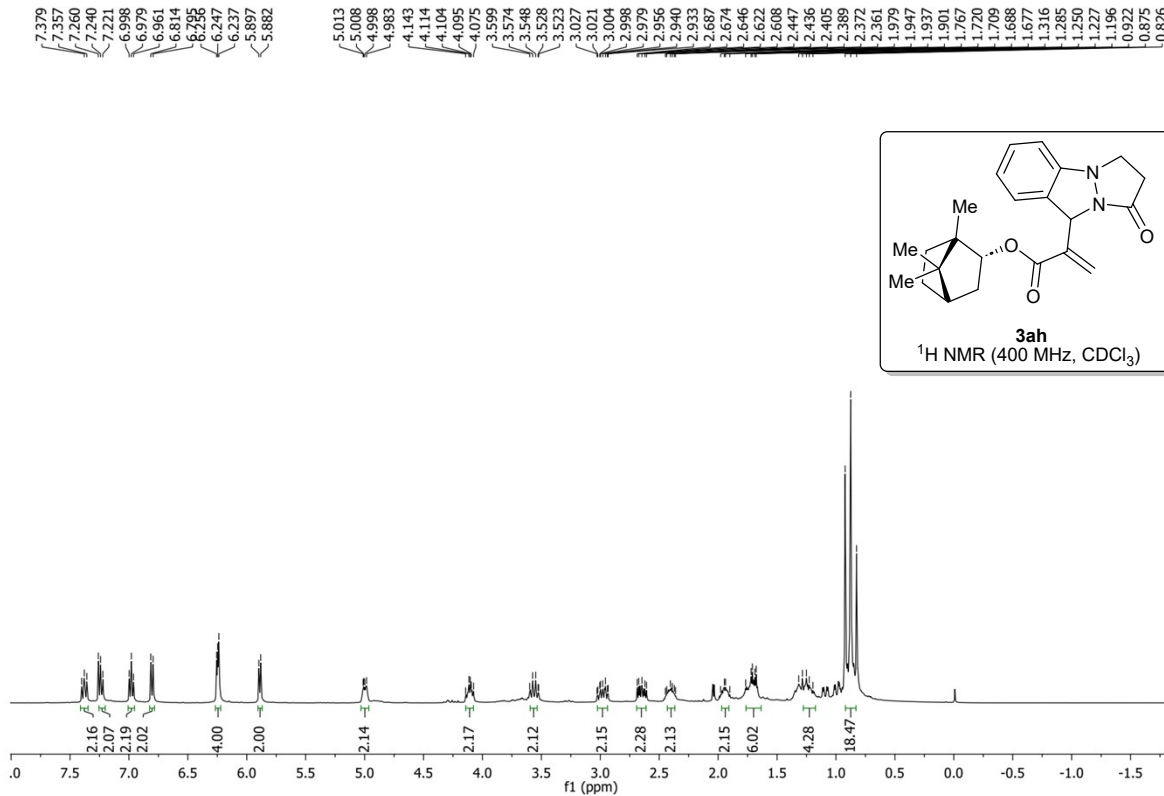
KV-98A-1H



KV-98A-13C

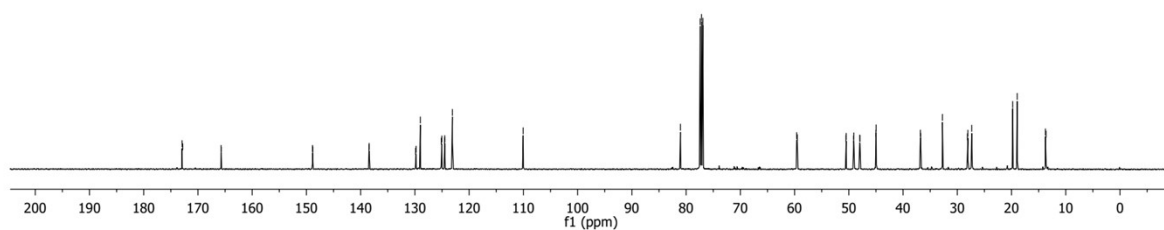
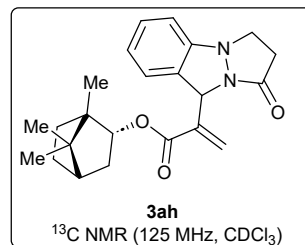


KV-92-A-1H



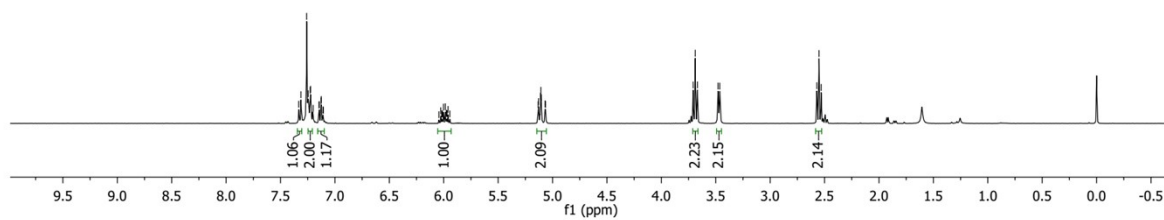
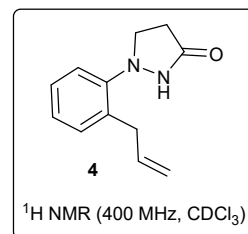
KV-92-A-13C

172.929  
172.809  
165.740  
165.721  
148.872  
148.836  
138.478  
138.445  
129.875  
129.777  
129.000  
125.136  
125.037  
124.531  
124.499  
123.086  
110.039  
81.042  
77.414  
77.160  
76.906  
59.611  
59.498  
50.535  
50.488  
49.105  
49.080  
47.992  
47.947  
44.995  
44.965  
36.810  
36.758  
32.739  
28.138  
28.049  
27.344  
19.787  
18.956  
13.754  
13.641

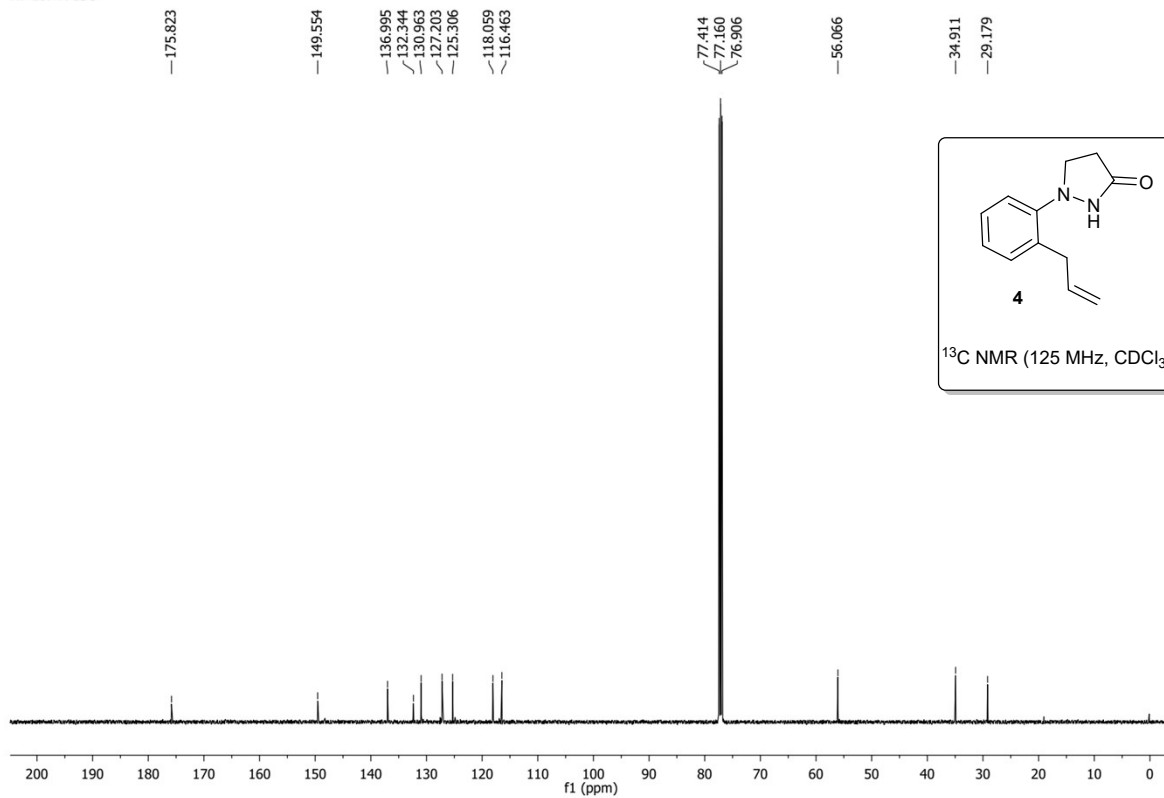


KV-107-A-1H

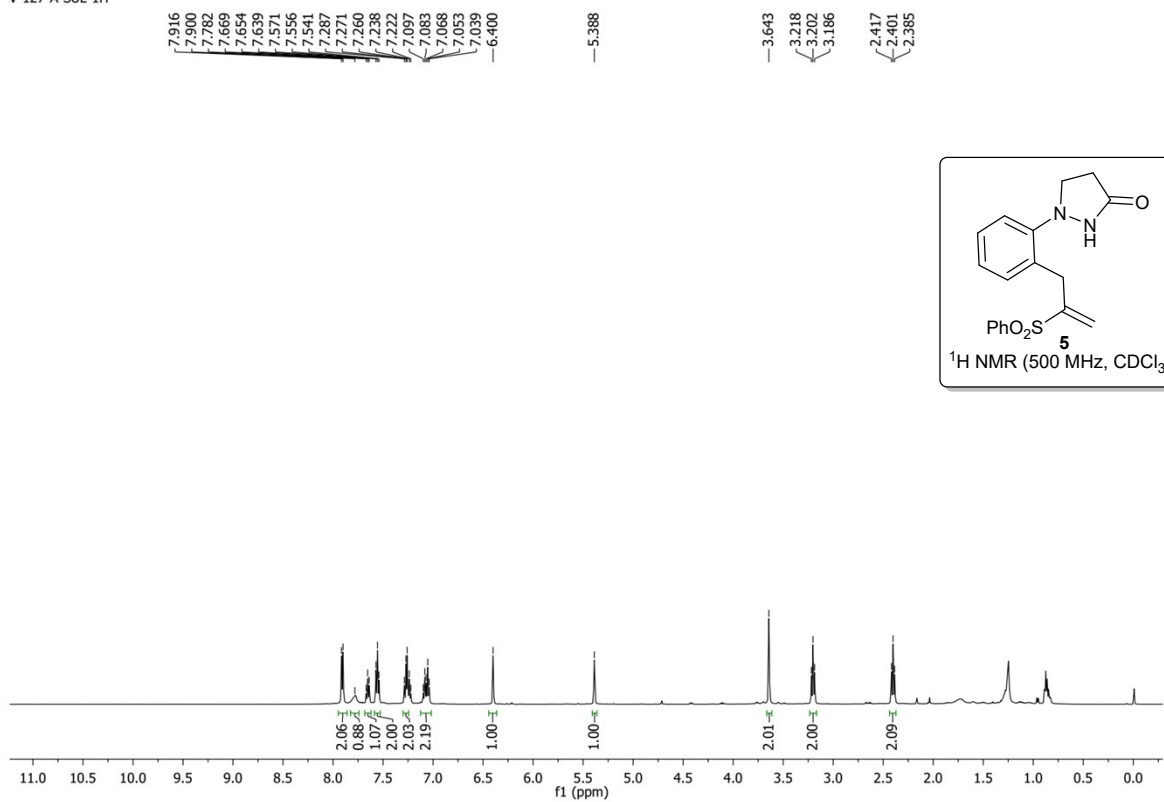
7.333  
7.312  
7.260  
7.245  
7.227  
7.224  
7.200  
7.147  
7.144  
7.128  
7.125  
7.110  
7.107  
6.044  
6.028  
6.019  
6.012  
6.002  
5.986  
5.976  
5.969  
5.960  
5.944  
5.132  
5.128  
5.111  
5.107  
5.103  
5.069  
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3.708  
3.688  
3.668  
3.479  
3.463  
2.571  
2.551  
2.531



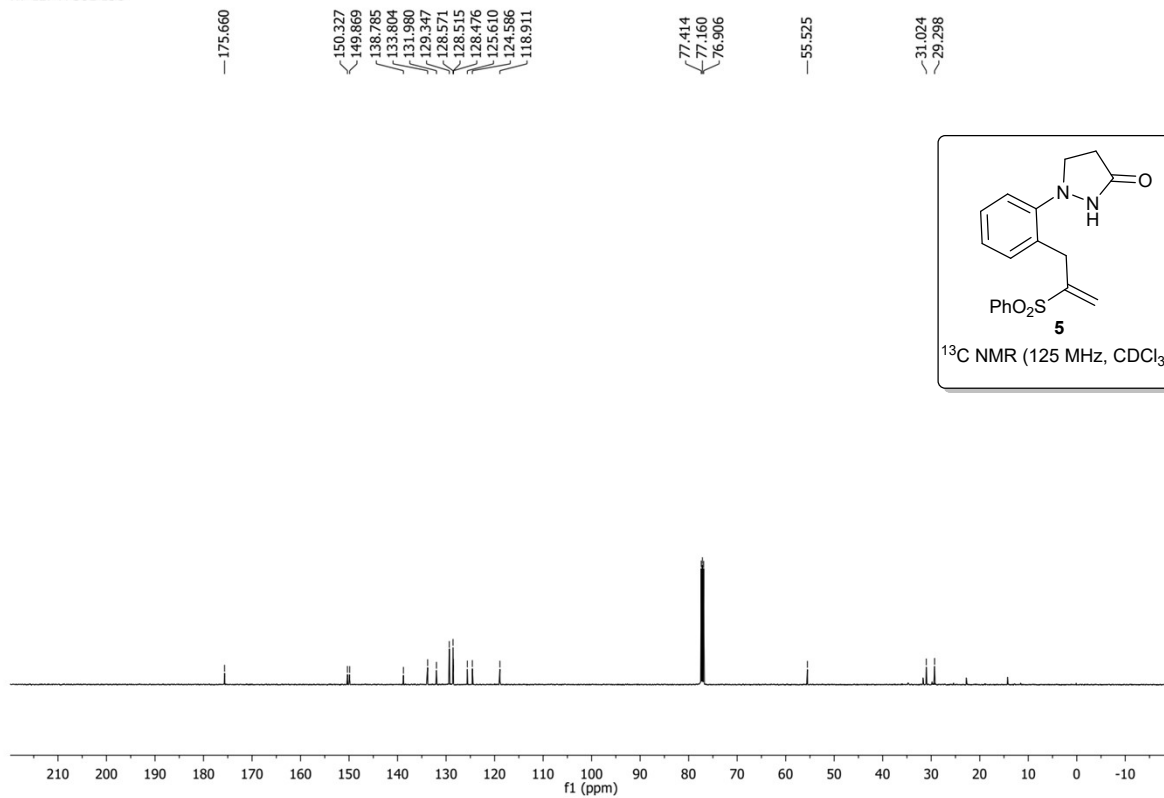
KV-107-A-13C



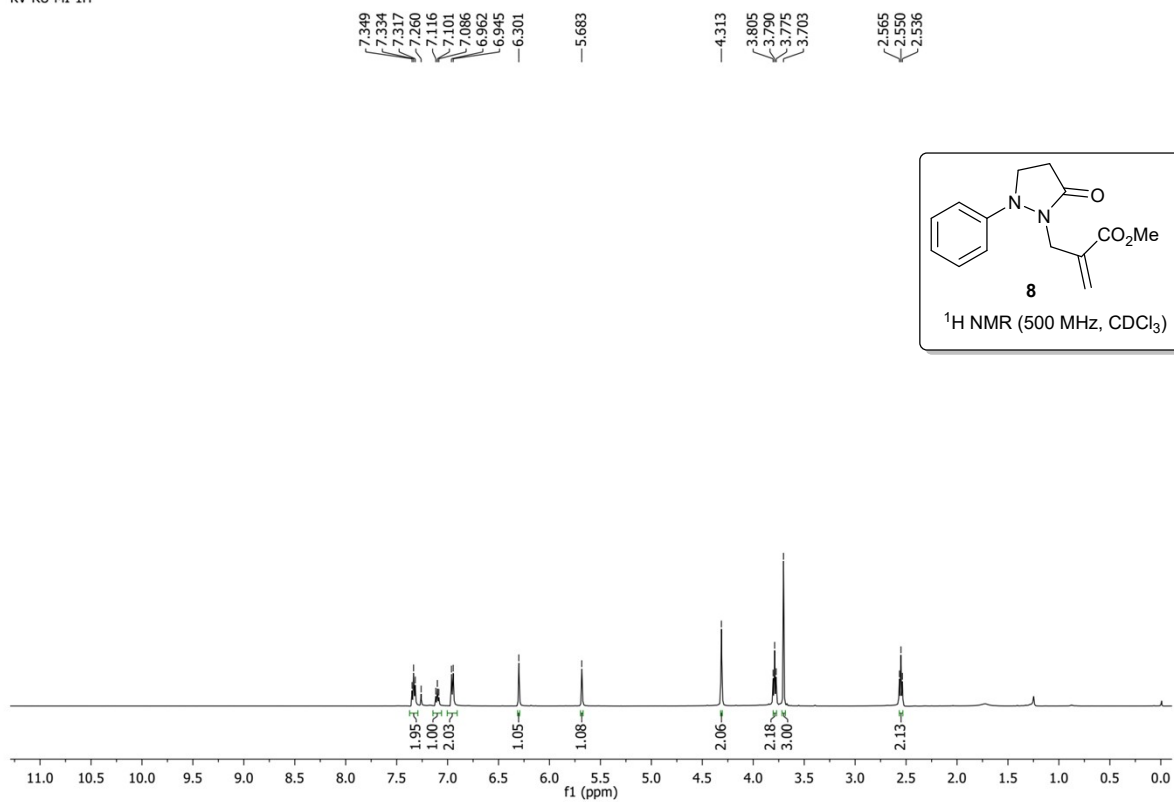
V-127-A-SUL-1H



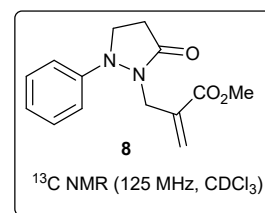
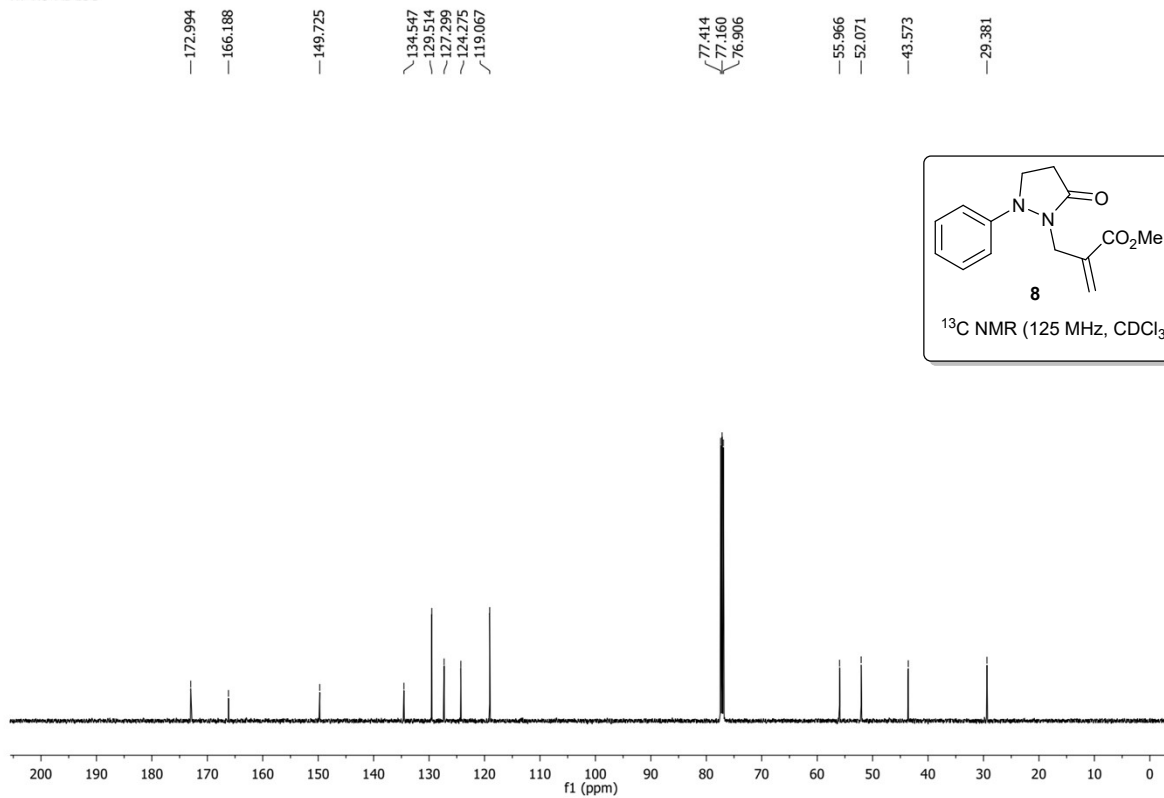
KV-127-A-SUL-13C



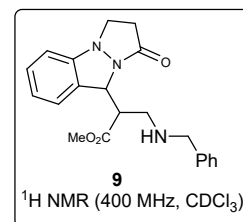
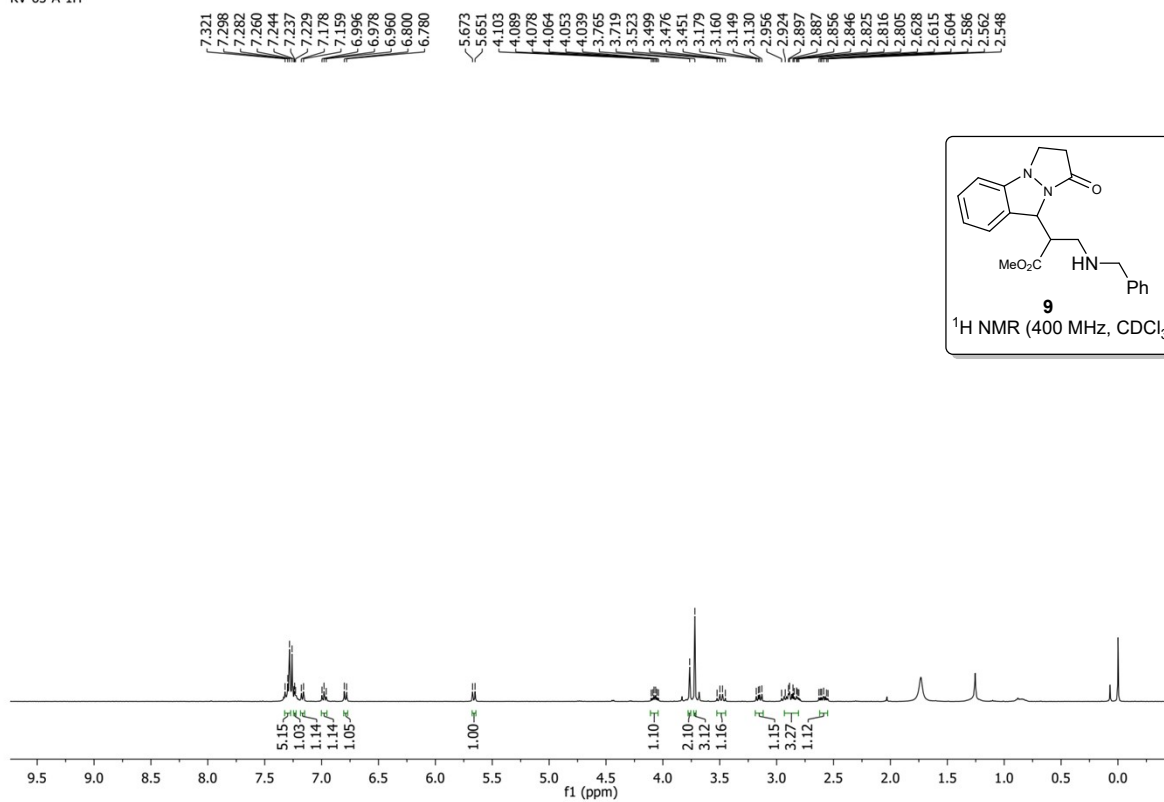
KV-RU-MI-1H



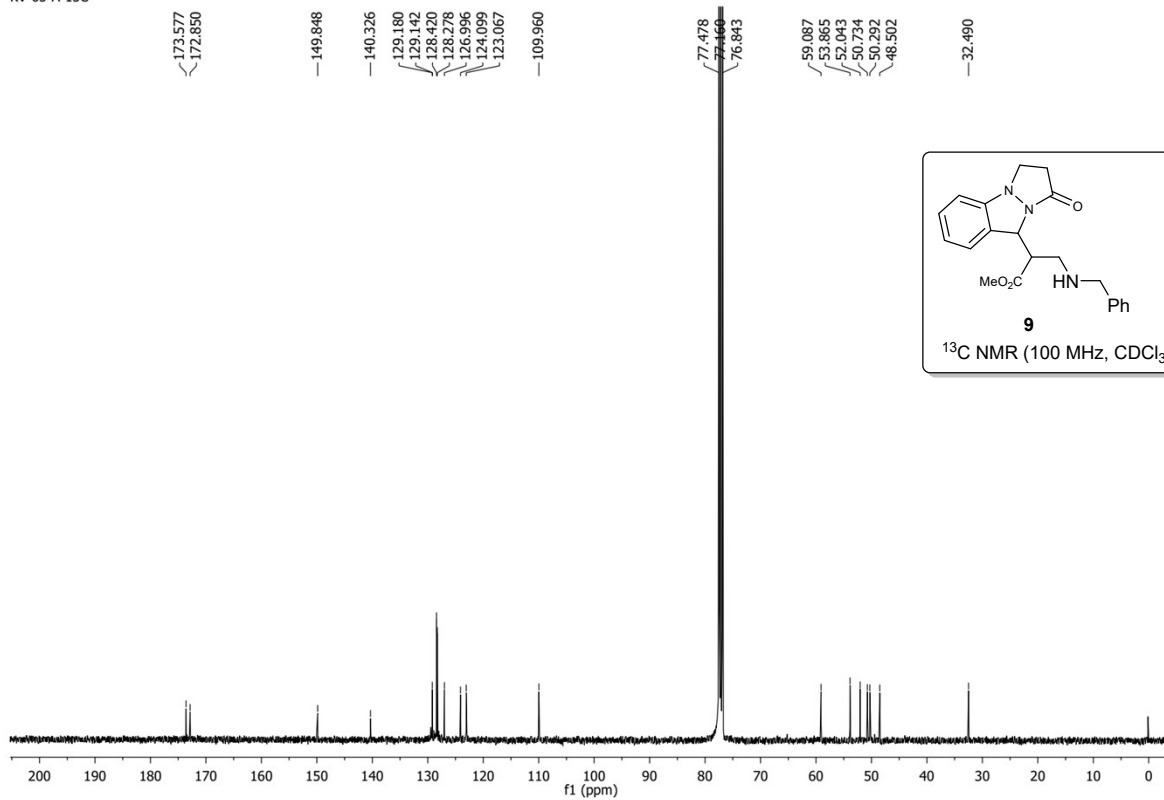
KV-RU-MI-13C



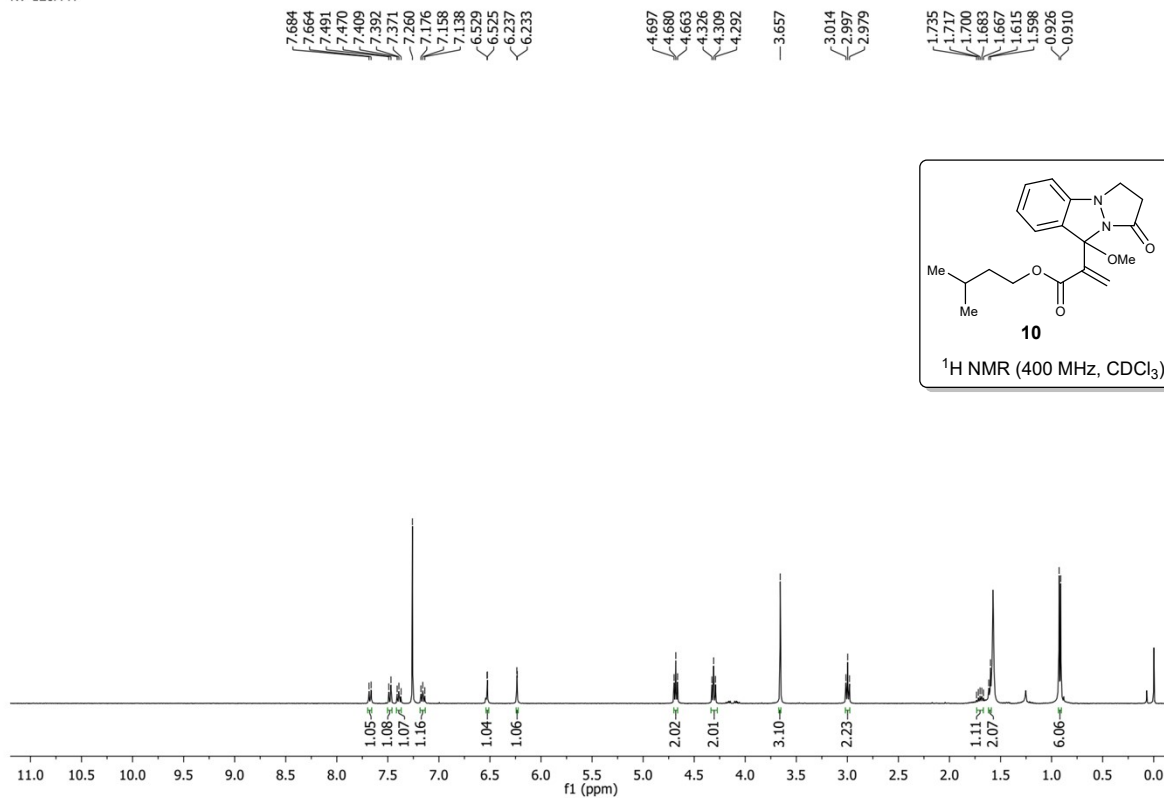
KV-65-A-1H



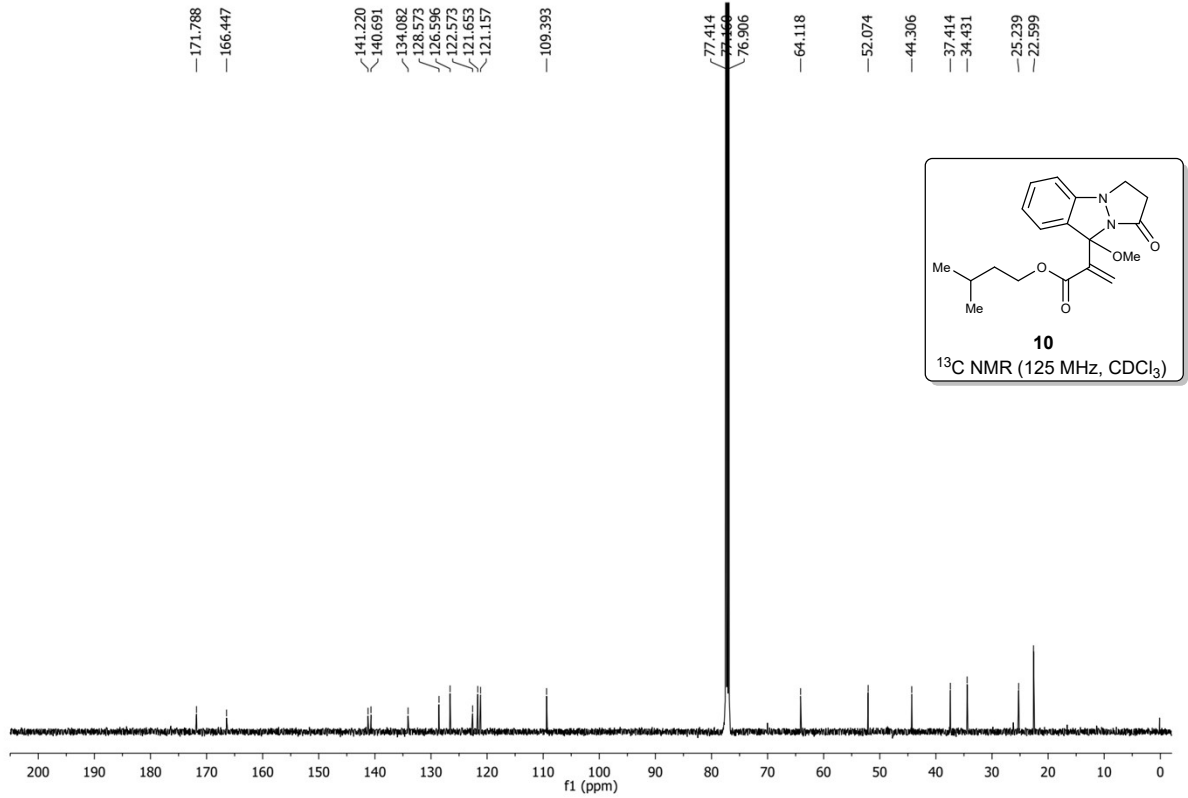
KV-65-A-13C



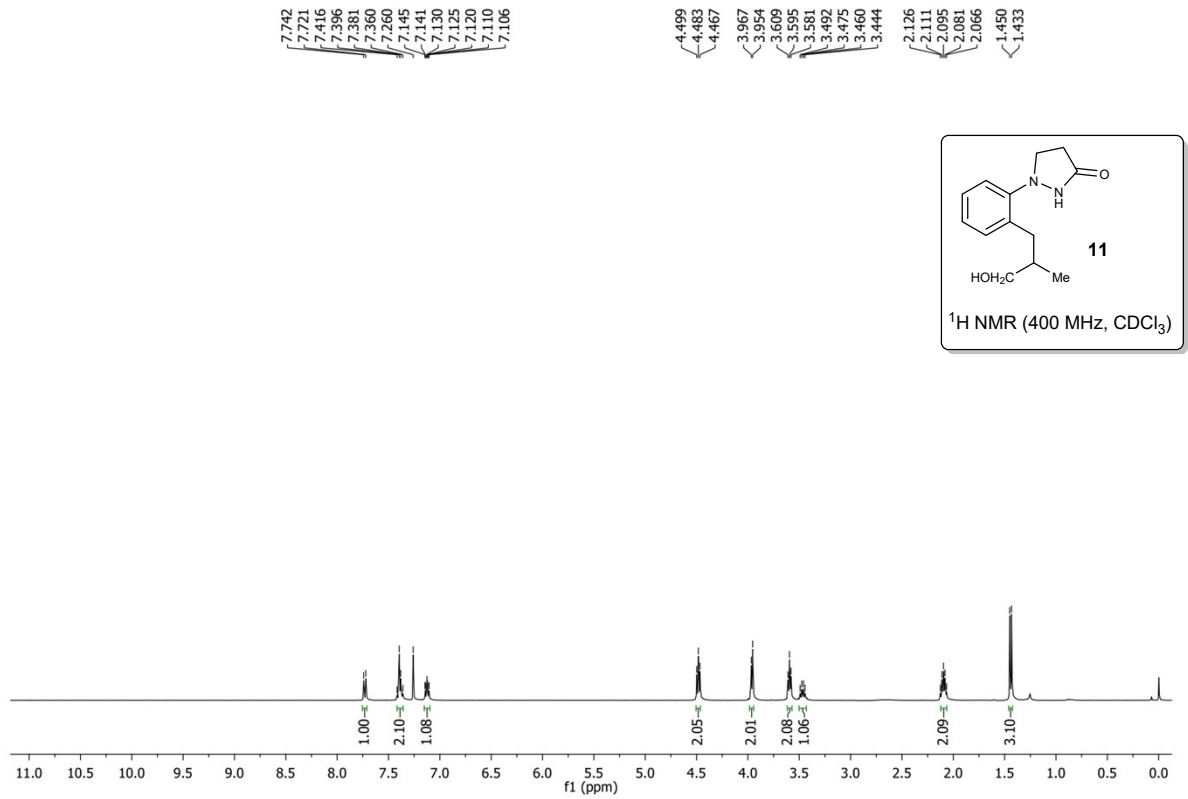
KV-120A-H



KV-120A-13C



KV-124A-1H



KV-124A-13C

