

Supporting Information

Visible-light-induced Direct 3-Ethoxycarbonylmethylation of 2-Aryl- 2*H*-Indazoles in Water

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Table of Contents

1. General information	2
2. Experimental procedures	3
3. Procedure and Results of Sensitivity Assessment	7
4. Characterization of compounds.....	8
5. NMR copies of products	26

1. General information

Dilauroyl peroxide (DLP) was purchased from damas-beta, Shanghai, China. Other reagents were purchased from Bidepharm.com. Unless otherwise stated, all commercially available reagents were directly used without further purification. All solvents were purified by standard methods before use. All reactions were monitored by thin-layer chromatography (TLC), and column chromatography was carried out on 100-200 mesh of silica gel purchased from Tansoole, Shanghai, China. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz or 600 MHz in CDCl_3 at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Bruker compact Qq TOF MS/MS system with the ESI technique.

The photochemical reactions were carried out under visible light irradiation by a white LED at r.t. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system (See Figure A). Eight 10 W white LEDs were equipped in this Photo reactor.

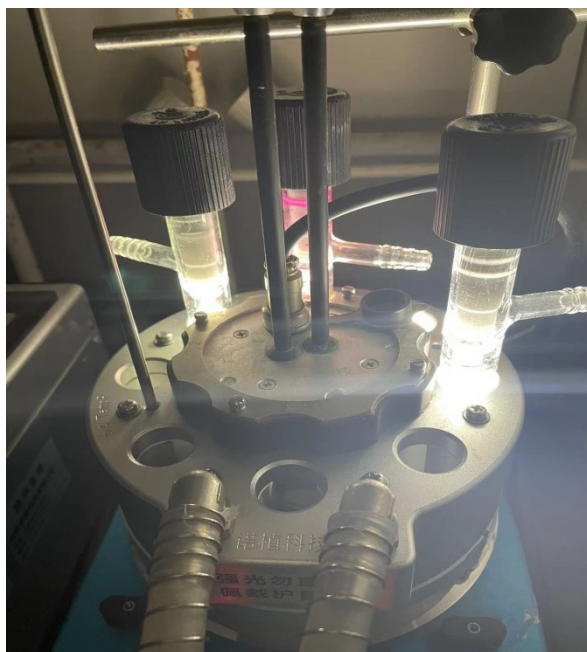
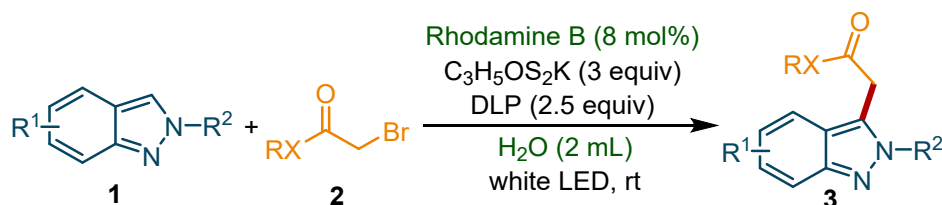


Figure A

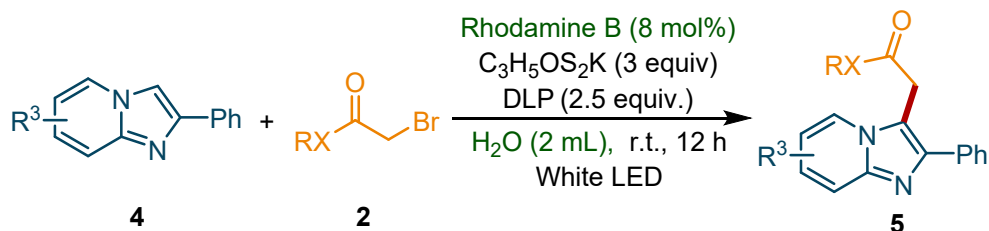
2. Experimental procedures

2.1 General experimental procedures for 3-ethoxycarbonylmethylation of 2-aryl-2*H*-indazoles



In a 10 mL reaction vial with a stirring bar, 2-aryl-2*H*-indazole **1** (0.2 mmol), ethyl 2-bromoacetate **2** (3.0 equiv.), potassium ethylxanthate (3.0 equiv.), DLP (2.5 equiv.) and Rhodamine B (8 mol%) were added, followed by adding H₂O (2 mL). The mixture was stirred at room temperature with 10 W white LED irradiation for 12 h. After the reaction was completed, ethyl acetate (15 mL) was added to the residue for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated. Then dissolved the residue in MeOH, added a few drops of Et₃N and stirred for 10 minutes, the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate=20/1) to provide the desired product **3**.

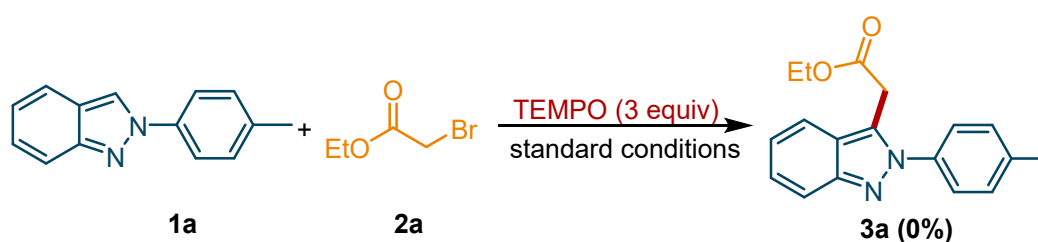
2.2 General experimental procedures for ethoxycarbonylmethylated imidazo[1,2-*a*]pyridines



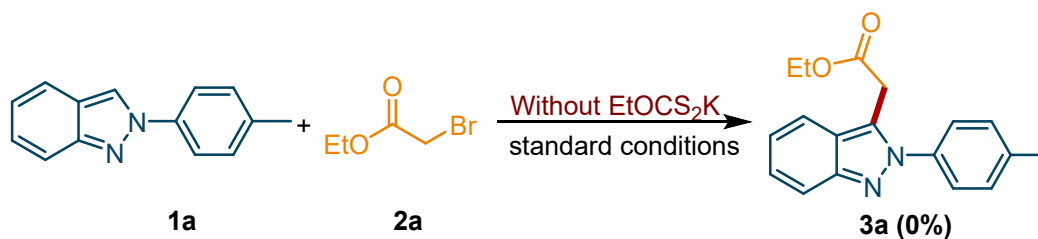
In a 10 mL reaction vial with a stirring bar, ethoxycarbonylmethylated imidazo[1,2-*a*]pyridines **4** (0.2 mmol), ethyl 2-bromoacetate **2** (3.0 equiv.), potassium ethylxanthate (3.0 equiv.), DLP (2.5 equiv.) and Rhodamine B (8 mol%) were added, followed by adding H₂O (2 mL). The mixture was stirred at room temperature with 10

W white LED irradiation for 12 h. After the reaction was completed, ethyl acetate (15 mL) was added to the residue for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated. Then dissolved the residue in MeOH, added a few drops of Et₃N and stirred for 10 minutes, the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate=20/1) to provide the desired product **5**.

2.3 Control experiments

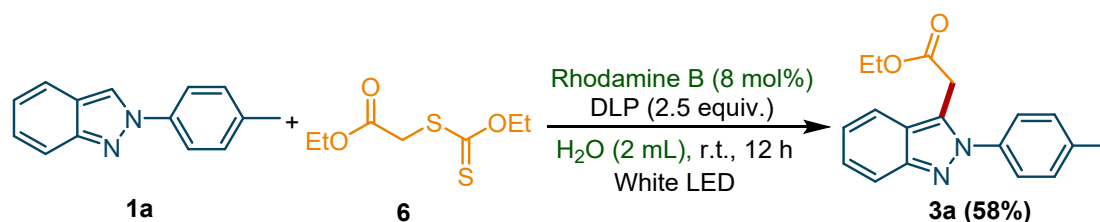


Control experiments with TEMPO: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2*H*-indazole **1a** (0.2 mmol), ethyl 2-bromoacetate **2a** (3.0 equiv.), potassium ethylxanthate (3.0 equiv.), DLP (2.5 equiv.), Rhodamine B (8 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv.) were added, followed by adding H₂O (2 mL). The mixture was stirred at room temperature with 10 W white LED irradiation for 12 h. After the reaction was completed, ethyl acetate (15 mL) was added to the residue for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated. Then dissolved the residue in MeOH, added a few drops of Et₃N and stirred for 10 minutes, the solvent was evaporated under vacuum. No target product **3a** was generated, it indicated that a radical pathway should be involved in this photocatalytic reaction.



Control experiments without EtOCS₂K: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2*H*-indazole **1a** (0.2 mmol), ethyl 2-bromoacetate **2a** (3.0

equiv.), potassium ethylxanthate (3.0 equiv.), DLP (2.5 equiv.) and Rhodamine B (8 mol%) were added, followed by adding H₂O (2 mL). The mixture was stirred at room temperature with 10 W white LED irradiation for 12 h. After the reaction was completed, ethyl acetate (15 mL) was added to the residue for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated. Then dissolved the residue in MeOH, added a few drops of Et₃N and stirred for 10 minutes, the solvent was evaporated under vacuum. No target product **3a** was generated, it indicated that EtOCS₂K is necessary for the photocatalytic reaction.



Control experiments with ethyl 2-((ethoxycarbonothioyl)thio)acetate: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2*H*-indazole **1a** (0.2 mmol), ethyl 2-((ethoxycarbonothioyl)thio)acetate **6** (3.0 equiv.), potassium ethylxanthate (3.0 equiv.), DLP (2.5 equiv.) and Rhodamine B (8 mol%) were added, followed by adding H₂O (2 mL). The mixture was stirred at room temperature with 10 W white LED irradiation for 12 h. After the reaction was completed, ethyl acetate (15 mL) was added to the residue for extraction. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated. Then dissolved the residue in MeOH, added a few drops of Et₃N and stirred for 10 minutes, the solvent was evaporated under vacuum. The yield of the target product **3a** decreased significantly, it indicated that the *in situ* generated xanthate ester **6** probably is a key intermediate in the ethoxycarbonylmethylation reaction.

2.4 Procedure for emission quenching experiment

Stern-Volmer fluorescence quenching experiments were conducted via adding the appropriate amount of 2-phenyl-2*H*-indazole to a freshly prepared solution of Rhodamine B (1×10^{-4} M) in dry MeCN in a screw-top quartz cuvette at room

temperature. After degassing with a stream of N_2 for 10 minutes, the sample was irradiated at 365 nm and the fluorescence was measured from 500 nm to 700 nm.

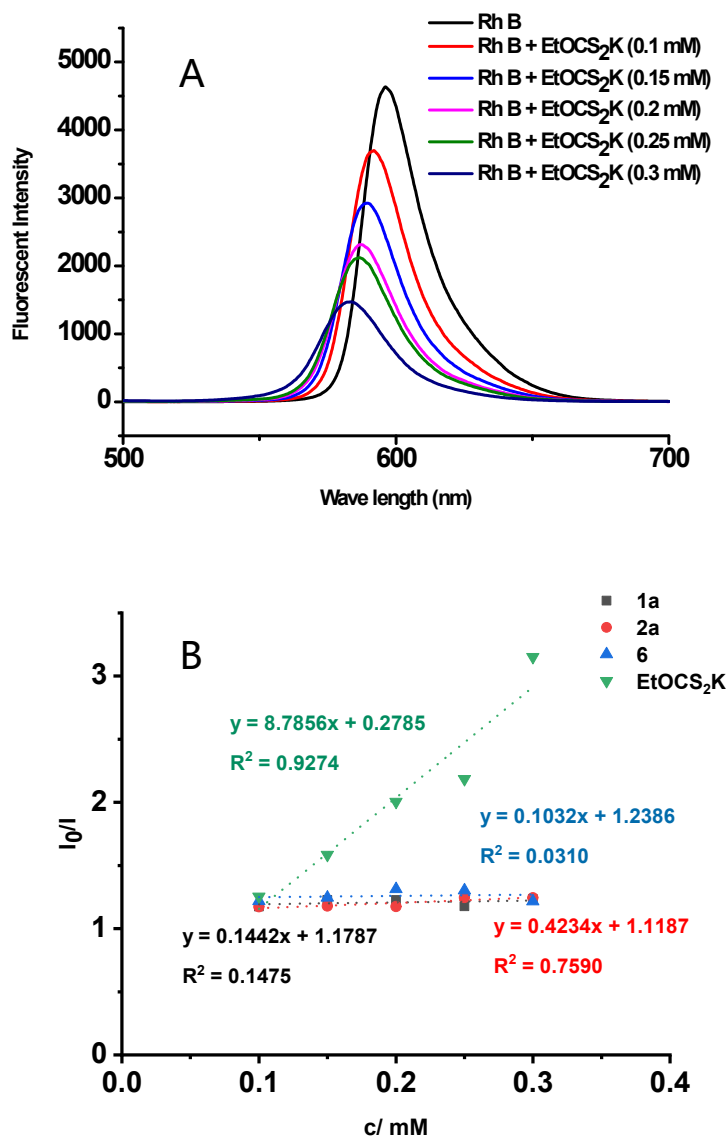


Figure S1. (A) The emission spectra of 1×10^{-4} M solution of Rhodamine B with various concentrations of EtOCS₂K. (B) The linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after adding the different components of various concentrations, respectively) and the concentration.

2.5 Procedure for cyclic voltametric experiment

Cyclic voltammetry analysis of 2*H*-indazole **1a**, ethyl 2-bromoacetate **2a** and EtOCS₂K were conducted by a potentiostat (CH instrument, 660E) with a three-electrode system (Reference electrode: SCE, working electrode: Glassy carbon,

counter electrode: Pt wire). 0.1 M Bu₄NPF₆ in CH₃CN was used as a supporting electrolyte. The Pt disk was polished by using an alumina suspension ($d = 50$ nm) before each CV experiment.

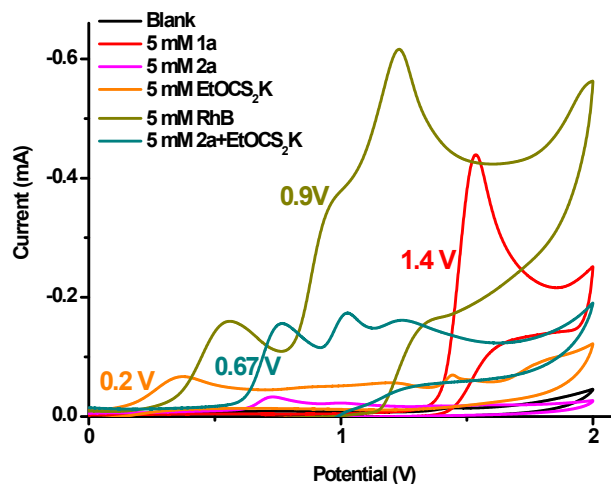


Figure S2. CV of **1a** (5 mM in CH₃CN), **2a** (5 mM in CH₃CN), EtOCS₂K (5 mM in CH₃CN), RhB (5 mM in CH₃CN) and blank (only 0.1 M Bu₄NPF₆) under nitrogen atmosphere at room temperature. The scan rate was 0.10 V/s, ranging from 0 V to 2 V.

3. Procedure and Results of Sensitivity Assessment

General Procedure:

The influence of parameter variations as shown in Table S1 on the reaction was investigated. Only one parameter, such as concentration, water level, oxygen level, light intensity, oxidant dosage and catalyst dosage, was deliberately changed per experiment while maintaining the others at the standard level. Each experiment was carried out twice at the same time in order to reduce the error.

Table S1. Preparation of sensitivity assessment.

#	Experiment	Preparation
1	High c	1.6 mL H ₂ O
2	Low c	2.4 mL H ₂ O
3	High O ₂	Under air
4	Low I	9W white LED
5	High oxidant	3 eq DLP
6	Low oxidant	2 eq DLP

7	High catalyst	10% Rhodamine B
8	Low catalyst	5% Rhodamine B
9	Control	Standard procedure

Results:

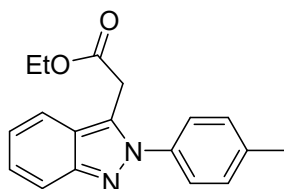
$$\text{Deviation\%} = (\text{Average Y.} - \text{Standard Y.}) / \text{Standard Y.}$$

Table S2. Results of sensitivity assessment.

#	Experiment	Yield 1 / %	Yield 2 / %	Average Y. / %	Deviation / %
1	High <i>c</i>	68	69	69	-15.9%
2	Low <i>c</i>	70	73	72	-12.2%
3	High O ₂	43	45	44	-46.3%
4	Low <i>I</i>	58	56	57	-30.5%
5	High oxidant	71	69	70	-14.6%
6	Low oxidant	73	70	71	-13.4%
7	High catalyst	66	67	67	-18.3%
8	Low catalyst	71	74	73	-11.0%
9	Control	82	81	82	-

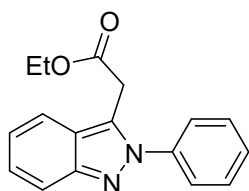
4. Characterization of compounds

ethyl 2-(2-(p-tolyl)-2H-indazol-3-yl)acetate (3a)



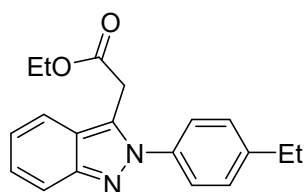
48.0 mg, 82%; Light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.32 (m, 3H), 7.12 (dd, *J* = 8.1, 6.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 2.45 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.0, 148.7, 139.4, 137.1, 130.0, 128.4, 126.9, 126.1, 122.0, 119.9, 117.9, 61.7, 31.8, 21.4, 14.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₁₉N₂O₂⁺ 295.1441, Found: 295.1444.

ethyl 2-(2-phenyl-2H-indazol-3-yl)acetate (3b)^[1]



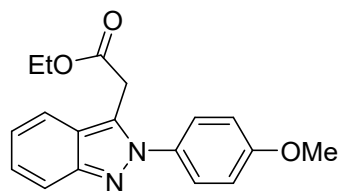
37.0 mg, 62%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.62 – 7.60 (m, 2H), 7.56 – 7.53 (m, 2H), 7.52 – 7.49 (m, 1H), 7.34 (ddd, $J = 8.7, 6.6, 0.9$ Hz, 1H), 7.14 – 7.12 (m, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 2H), 1.20 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.0, 148.8, 139.6, 129.4, 129.3, 128.4, 127.0, 126.3, 122.1, 122.0, 119.9, 118.0, 61.7, 31.8, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2^+$ 281.1285, Found: 281.1287.

ethyl 2-(2-(4-ethylphenyl)-2H-indazol-3-yl)acetate (3c)



41.3 mg, 67%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.50 (d, $J = 8.3$ Hz, 2H), 7.36 – 7.32 (m, 3H), 7.12 (dd, $J = 8.0, 6.9$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 4.03 (s, 2H), 2.75 (q, $J = 7.6$ Hz, 2H), 1.30 (t, $J = 7.6$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.1, 148.7, 145.6, 137.2, 128.8, 128.3, 126.8, 126.2, 121.9, 119.8, 117.9, 61.7, 31.8, 28.7, 15.6, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2^+$ 309.1598, Found: 309.1600.

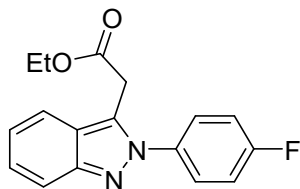
ethyl 2-(2-(4-methoxyphenyl)-2H-indazol-3-yl)acetate (3d)



39.0 mg, 63%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.53 – 7.50 (m, 2H), 7.35 – 7.32 (m, 1H), 7.12 (dd, $J = 8.0, 6.9$ Hz, 1H), 7.04 – 7.02 (m, 2H), 4.14 (t, $J = 7.1$ Hz, 2H), 4.01 (s, 2H), 3.88 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.1, 160.2, 148.6, 132.6, 128.5, 127.6, 126.8, 121.9, 121.8, 119.8, 117.9, 114.5, 61.7, 55.8, 31.8, 14.3.

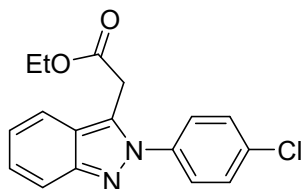
HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_3^+$ 311.1390, Found: 311.1391.

ethyl 2-(2-(4-fluorophenyl)-2H-indazol-3-yl)acetate (3e)



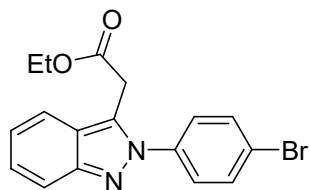
42.0 mg, 70%; Light yellow oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.62 – 7.59 (m, 2H), 7.35 – 7.33 (m, 1H), 7.25 – 7.21 (m, 2H), 7.13 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 4.01 (s, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 162.9 (d, $J = 249.0$ Hz), 148.8, 136.2 (d, $J = 3.0$ Hz), 128.6, 128.2 (d, $J = 9.0$ Hz), 127.1, 122.2, 121.9, 119.8, 117.9, 116.4 (d, $J = 22.5$ Hz), 61.8, 31.7, 14.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.5. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2O_2^+$ 299.1190, Found: 299.1189.

ethyl 2-(2-(4-chlorophenyl)-2H-indazol-3-yl)acetate (3f)



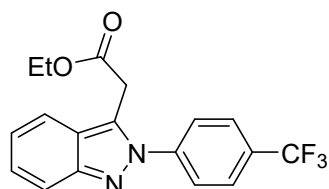
47.8 mg, 76%; Light yellow oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.59 – 7.57 (m, 2H), 7.53 – 7.51 (m, 2H), 7.35 (ddd, $J = 8.6, 6.6, 0.8$ Hz, 1H), 7.13 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.02 (s, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 148.9, 138.1, 135.3, 129.6, 128.5, 127.5, 127.3, 122.3, 122.1, 119.8, 117.9, 61.9, 31.7, 14.2. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{17}H_{16}ClN_2O_2^+$ 315.0895, Found: 315.0893.

ethyl 2-(2-(4-bromophenyl)-2H-indazol-3-yl)acetate (3g)



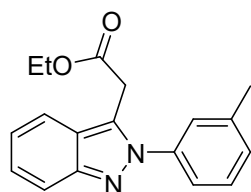
50.8 mg, 71%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.69 – 7.65 (m, 3H), 7.53 – 7.51 (m, 2H), 7.35 (ddd, $J = 8.6, 6.6, 0.7$ Hz, 1H), 7.13 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.02 (s, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 148.9, 138.6, 132.6, 128.4, 127.8, 127.3, 123.3, 122.3, 122.1, 119.8, 117.9, 61.8, 31.7, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}_2^+$ 359.0390, Found: 359.0392.

ethyl 2-(2-(4-(trifluoromethyl)phenyl)-2H-indazol-3-yl)acetate (3h)



30.2 mg, 43%; Light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (t, $J = 5.3$ Hz, 4H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.36 (ddd, $J = 8.7, 6.6, 0.8$ Hz, 1H), 7.17 – 7.13 (m, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.06 (s, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 149.2, 142.5, 131.2 (q, $J = 33.0$ Hz), 128.5, 127.5, 126.7 (q, $J = 4.5$ Hz), 126.6, 123.8 (q, $J = 271.5$ Hz), 122.6, 122.4, 119.9, 118.0, 61.9, 31.8, 14.2. ^{19}F NMR (564 MHz, CDCl_3) δ -62.6. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2^+$ 349.1158, Found: 349.1156.

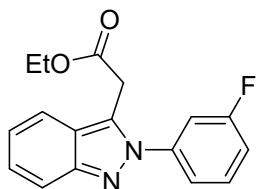
ethyl 2-(2-(m-tolyl)-2H-indazol-3-yl)acetate (3i)



41.8 mg, 71%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.7$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.43 – 7.38 (m, 3H), 7.35 – 7.31 (m, 2H), 7.13 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 2H), 2.45 (s, 3H), 1.22 (t, $J = 7.1$

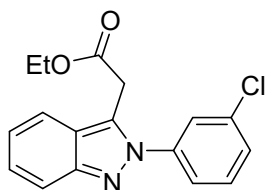
Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.0, 148.7, 139.7, 139.5, 130.0, 129.1, 128.3, 127.0, 126.9, 123.2, 122.01, 121.99, 119.9, 117.9, 61.7, 31.9, 21.5, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2^+$ 295.1441, Found: 295.1442.

ethyl 2-(2-(3-fluorophenyl)-2H-indazol-3-yl)acetate (3j)



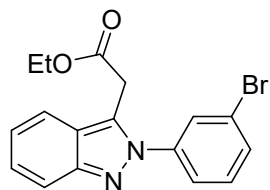
29.9 mg, 50%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.51 (td, $J = 8.1, 6.1$ Hz, 1H), 7.43 (ddd, $J = 9.2, 6.5, 5.0$ Hz, 2H), 7.35 (dd, $J = 7.9, 6.9$ Hz, 1H), 7.22 (td, $J = 8.3, 1.9$ Hz, 1H), 7.14 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.06 (s, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 162.8 (d, $J = 247.5$ Hz), 148.9, 140.9 (d, $J = 10.5$ Hz), 130.7 (d, $J = 9.0$ Hz), 128.4, 127.3, 122.4, 122.2, 121.9 (d, $J = 3.0$ Hz), 119.8, 118.0, 116.3 (d, $J = 21.0$ Hz), 114.0 (d, $J = 25.5$ Hz), 61.8, 31.7, 14.2. ^{19}F NMR (564 MHz, CDCl_3) δ -110.5. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{FN}_2\text{O}_2^+$ 299.1190, Found: 299.1190.

ethyl 2-(2-(3-chlorophenyl)-2H-indazol-3-yl)acetate (3k)



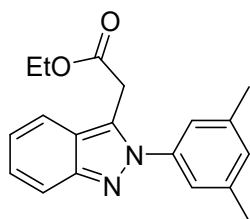
42.8 mg, 68%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 1H), 7.68 (dd, $J = 10.1, 5.1$ Hz, 2H), 7.55 – 7.54 (m, 1H), 7.50 – 7.47 (m, 2H), 7.35 (dd, $J = 8.1, 7.1$ Hz, 1H), 7.14 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.05 (s, 2H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 149.0, 140.6, 135.2, 130.4, 129.5, 128.5, 127.4, 126.7, 124.4, 122.4, 122.2, 119.9, 118.0, 61.9, 31.8, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{O}_2^+$ 315.0895, Found: 315.0894.

ethyl 2-(2-(3-bromophenyl)-2H-indazol-3-yl)acetate (3l)



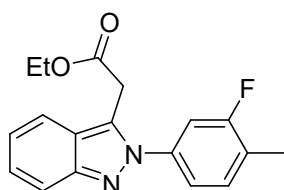
43.0 mg, 60%; Light yellow oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.84 (t, $J = 1.9$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.67 – 7.64 (m, 2H), 7.59 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.36 – 7.34 (m, 1H), 7.14 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 2H), 1.24 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.8, 149.0, 140.7, 132.4, 130.6, 129.5, 128.5, 127.4, 124.8, 122.9, 122.4, 122.1, 119.9, 118.0, 61.9, 31.8, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}_2^+$ 359.0390, Found: 359.0389.

ethyl 2-(2-(3,5-dimethylphenyl)-2H-indazol-3-yl)acetate (3m)



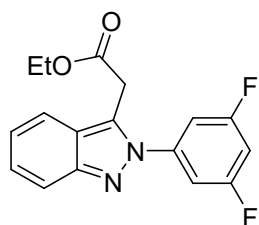
35.2 mg, 57%; Light yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.34 (dd, $J = 11.0, 4.3$ Hz, 1H), 7.21 (s, 2H), 7.13 (d, $J = 6.0$ Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 2H), 2.40 (s, 6H), 1.22 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.1, 148.6, 139.4, 139.3, 130.9, 128.3, 126.9, 123.9, 122.0, 121.9, 119.9, 117.9, 61.7, 31.9, 21.4, 14.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2^+$ 309.1598, Found: 309.1594.

ethyl 2-(2-(3-fluoro-4-methylphenyl)-2H-indazol-3-yl)acetate (3n)



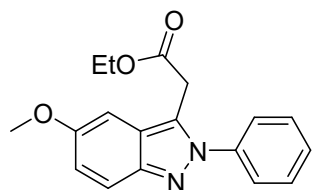
39.3 mg, 63%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.36 – 7.31 (m, 4H), 7.13 (dd, $J = 8.1, 6.9$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 2H), 2.37 (d, $J = 1.6$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.9, 161.0 (d, $J = 246.0$ Hz), 148.8, 138.4 (d, $J = 10.5$ Hz), 131.9 (d, $J = 6.0$ Hz), 128.4, 127.2, 126.4 (d, $J = 16.5$ Hz), 122.2, 122.0, 121.6 (d, $J = 4.5$ Hz), 119.8, 117.9, 113.5 (d, $J = 24.0$ Hz), 61.8, 31.8, 14.6 (d, $J = 4.5$ Hz), 14.2. ^{19}F NMR (564 MHz, CDCl_3) δ -114.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{O}_2^+$ 313.1347, Found: 313.1349.

ethyl 2-(2-(3,5-difluorophenyl)-2H-indazol-3-yl)acetate (3o)



44.6 mg, 71%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.37 – 7.35 (m, 1H), 7.29 (dt, $J = 7.3, 3.6$ Hz, 2H), 7.15 (dd, $J = 8.1, 7.0$ Hz, 1H), 6.98 (tt, $J = 8.7, 2.3$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 4.08 (s, 2H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.7, 163.0 (dd, $J_1 = 249.0$ Hz, $J_2 = 13.5$ Hz), 149.1, 141.6 (t, $J = 13.5$ Hz), 128.5, 127.7, 119.9, 118.0, 110.0 (dd, $J = 21.0, 6.0$ Hz), 104.8 (t, $J = 25.5$ Hz), 62.0, 31.7, 14.2; ^{19}F NMR (564 MHz, CDCl_3) δ -107.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{F}_2\text{N}_2\text{O}_2^+$ 317.1096, Found: 345.1097.

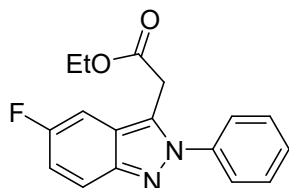
ethyl 2-(5-methoxy-2-phenyl-2H-indazol-3-yl)acetate (3p)



45.1 mg, 73%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.65 (d, $J = 9.3$ Hz, 1H), 7.60 – 7.58 (m, 2H), 7.55 – 7.52 (m, 2H), 7.50 – 7.47 (m, 1H), 7.05 (dd, $J = 9.2,$

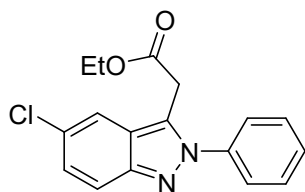
2.4 Hz, 1H), 6.84 (d, $J = 2.2$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.99 (s, 2H), 3.87 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.2, 155.4, 145.7, 139.7, 129.4, 129.1, 127.1, 126.2, 122.1, 121.9, 119.4, 95.8, 61.7, 55.6, 31.8, 14.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_3^+$ 311.1390, Found: 311.1386.

ethyl 2-(5-fluoro-2-phenyl-2H-indazol-3-yl)acetate (3q)



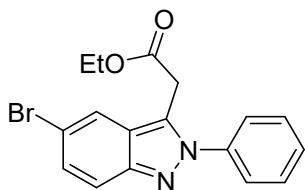
41.2 mg, 69%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.72 (dd, $J = 9.2, 4.5$ Hz, 1H), 7.59 – 7.50 (m, 5H), 7.24 (dd, $J = 8.9, 1.6$ Hz, 1H), 7.14 (td, $J = 9.2, 1.9$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.98 (s, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 158.5 (d, $J = 240.0$ Hz), 146.2, 139.4, 129.5, 129.4, 128.5 (d, $J = 9.0$ Hz), 126.2, 121.3 (d, $J = 12.0$ Hz), 120.1 (d, $J = 9.0$ Hz), 118.6 (d, $J = 28.5$ Hz), 102.4 (d, $J = 24.0$ Hz), 61.8, 31.8, 14.2. ^{19}F NMR (564 MHz, CDCl_3) δ -119.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{FN}_2\text{O}_2^+$ 299.1190, Found: 299.1191.

ethyl 2-(5-chloro-2-phenyl-2H-indazol-3-yl)acetate (3r)



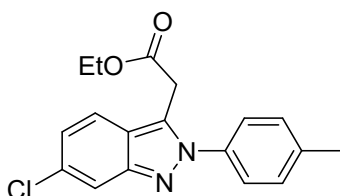
45.8 mg, 73%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.69 (d, $J = 9.2$ Hz, 1H), 7.66 (d, $J = 1.4$ Hz, 1H), 7.60 – 7.51 (m, 5H), 7.28 – 7.26 (m, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.99 (s, 2H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.7, 147.1, 139.3, 129.6, 129.5, 128.4, 128.2, 127.7, 126.2, 122.4, 119.6, 118.7, 61.9, 31.7, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2^+$ 315.0895, Found: 315.0896.

ethyl 2-(5-bromo-2-phenyl-2H-indazol-3-yl)acetate (3s)



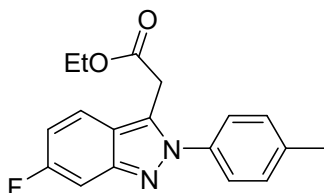
41.6 mg, 58%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 1.1$ Hz, 1H), 7.63 (d, $J = 9.1$ Hz, 1H), 7.59 – 7.51 (m, 5H), 7.39 (dd, $J = 9.1, 1.7$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.99 (s, 2H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.6, 147.2, 139.3, 130.7, 129.6, 129.5, 128.1, 126.3, 123.3, 122.2, 119.8, 115.6, 61.9, 31.8, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}_2^+$ 359.0390, Found: 359.0387.

ethyl 2-(6-chloro-2-(p-tolyl)-2H-indazol-3-yl)acetate (3t)



39.5 mg, 60%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.68 (d, $J = 9.1$ Hz, 1H), 7.65 (d, $J = 1.2$ Hz, 1H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.27 (dd, $J = 9.1, 1.9$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.97 (s, 2H), 2.45 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 147.0, 139.7, 136.8, 130.1, 128.3, 128.2, 127.6, 126.0, 122.4, 119.6, 118.7, 61.9, 31.7, 21.4, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{O}_2^+$ 329.1051, Found: 329.1051.

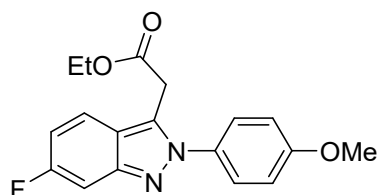
ethyl 2-(6-fluoro-2-(p-tolyl)-2H-indazol-3-yl)acetate (3u)



24.3 mg, 39%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.71 (dd, $J = 9.3, 4.6$ Hz, 1H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.23 (dd, $J = 9.0, 2.2$ Hz, 1H), 7.13 (td, $J = 9.2, 2.4$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.96 (s, 2H), 2.45 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.9, 158.5 (d, $J = 238.5$ Hz),

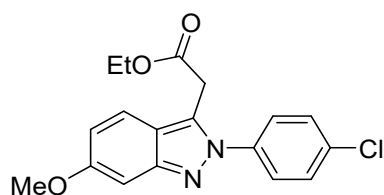
146.1, 139.6, 136.9, 130.0, 128.5 (d, $J = 9.0$ Hz), 126.0, 121.2 (d, $J = 12.0$ Hz), 120.1 (d, $J = 10.5$ Hz), 118.5 (d, $J = 28.5$ Hz), 102.4 (d, $J = 24.0$ Hz), 61.8, 31.8, 21.4, 14.2. ^{19}F NMR (564 MHz, CDCl_3) δ -119.5. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{O}_2^+$ 313.1347, Found: 313.1336.

ethyl 2-(6-fluoro-2-(4-methoxyphenyl)-2H-indazol-3-yl)acetate (3v)



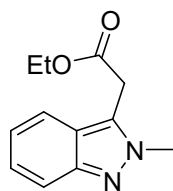
46.0 mg, 70%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.72 – 7.70 (m, 1H), 7.51 – 7.48 (m, 2H), 7.23 (dd, $J = 9.0, 2.2$ Hz, 1H), 7.13 (td, $J = 9.2, 2.4$ Hz, 1H), 7.05 – 7.02 (m, 2H), 4.16 (d, $J = 7.1$ Hz, 2H), 3.95 (s, 2H), 3.89 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.9, 160.3, 158.5 (d, $J = 240.0$ Hz), 146.0, 132.4, 128.7 (d, $J = 9.0$ Hz), 127.5, 121.1 (d, $J = 10.5$ Hz), 120.0 (d, $J = 9.0$ Hz), 118.4 (d, $J = 30.0$ Hz), 114.5, 102.3 (d, $J = 24.0$ Hz), 61.8, 55.8, 31.8, 14.3; ^{19}F NMR (564 MHz, CDCl_3) δ -119.6. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{O}_3^+$ 329.1296, Found: 329.1298.

ethyl 2-(2-(4-chlorophenyl)-6-methoxy-2H-indazol-3-yl)acetate (3w)



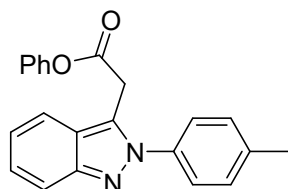
41.2 mg, 60%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.63 (d, $J = 9.3$ Hz, 1H), 7.58 – 7.56 (m, 2H), 7.52 – 7.49 (m, 2H), 7.05 (dd, $J = 9.3, 2.3$ Hz, 1H), 6.82 (d, $J = 2.2$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.97 (s, 2H), 3.87 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.1, 155.5, 145.8, 138.3, 135.0, 129.6, 127.4, 127.1, 122.5, 122.1, 119.4, 95.7, 61.8, 55.6, 31.8, 14.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{O}_3^+$ 345.1000, Found: 345.1001.

ethyl 2-(2-methyl-2H-indazol-3-yl)acetate (**3x**)^[2]



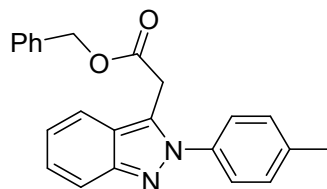
9.2 mg, 21%; White solid, m.p. 66-67 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.08 – 7.03 (m, 1H), 4.17 – 4.12 (m, 5H), 3.99 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 147.8, 127.5, 126.1, 121.5, 121.4, 119.2, 117.2, 61.7, 38.0, 31.0, 14.2. ESI-MS: 218.8 [M + H]⁺

phenyl 2-(2-(*p*-tolyl)-2H-indazol-3-yl)acetate (**3y**)



44.8 mg, 65%; Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (t, *J* = 9.5 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.28 (m, 5H), 7.17 – 7.09 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 4.22 (s, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.6, 150.5, 148.7, 139.6, 137.0, 130.1, 129.6, 127.6, 127.0, 126.3, 126.2, 122.3, 122.0, 121.4, 119.7, 118.1, 31.9, 21.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₁₉N₂O₂⁺ 343.1441, Found: 343.1442.

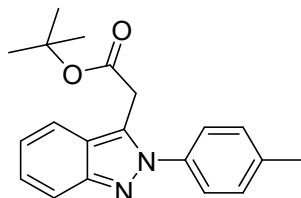
benzyl 2-(2-(*p*-tolyl)-2H-indazol-3-yl)acetate (**3z**)



44.4 mg, 76%; Light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 7.6, 4.5 Hz, 4H), 7.24 (d, *J* = 6.8 Hz, 4H), 7.11 – 7.09 (m, 1H), 5.11 (s, 2H), 4.06 (s, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 168.8, 148.6, 139.4, 137.0, 135.4, 130.0, 128.7, 128.6,

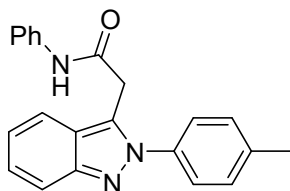
128.5, 127.0, 126.1, 122.1, 122.0, 119.8, 117.9, 67.4, 31.8, 21.4. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{23}H_{21}N_2O_2^+$ 357.1598, Found: 357.1596.

tert-butyl 2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetate (**3aa**)



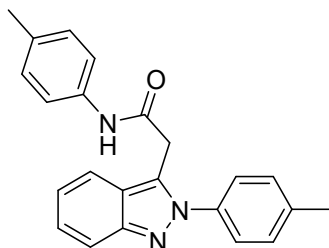
22 mg, 34%; Light yellow oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.7$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.34 – 7.31 (m, 3H), 7.11 (dd, $J = 8.1, 6.9$ Hz, 1H), 3.94 (s, 2H), 2.45 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 148.7, 139.3, 137.2, 129.9, 129.0, 126.8, 126.1, 122.0, 121.8, 120.0, 117.9, 82.1, 33.1, 28.0, 21.4. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_2^+$ 323.1754, Found: 323.1755.

N-phenyl-2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetamide (**3ab**)



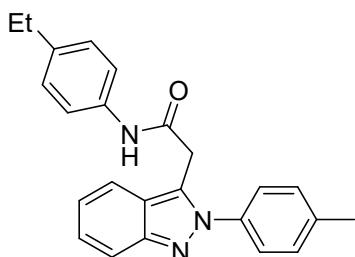
44.2 mg, 65%; Light yellow oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.40 – 7.38 (m, 1H), 7.35 – 7.31 (m, 4H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.19 (dd, $J = 13.9, 6.6$ Hz, 2H), 7.11 (t, $J = 7.3$ Hz, 1H), 4.13 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 148.9, 139.8, 137.2, 136.8, 130.3, 129.2, 128.4, 127.3, 125.8, 125.1, 123.0, 122.0, 120.3, 119.2, 118.4, 34.7, 21.4. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O^+$ 342.1601, Found: 342.1600.

N-(*p*-tolyl)-2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetamide (**3ac**)



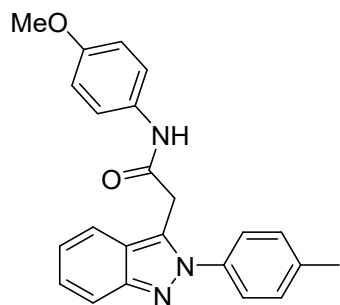
44.2 mg, 62%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.40 – 7.37 (m, 1H), 7.34 (d, $J = 7.9$ Hz, 2H), 7.21 – 7.18 (m, 3H), 7.08 (d, $J = 8.2$ Hz, 3H), 4.12 (s, 2H), 2.45 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 149.0, 139.8, 136.9, 134.8, 134.7, 130.3, 129.7, 128.5, 127.3, 125.9, 123.0, 122.1, 120.4, 119.2, 118.4, 34.7, 29.9, 21.4, 21.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}^+$ 356.1757, Found: 356.1758.

N-(4-ethylphenyl)-2-(2-(*p*-tolyl)-2H-indazol-3-yl)acetamide (**3ad**)



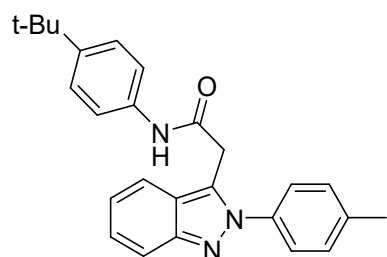
41.1 mg, 56%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, $J = 8.7$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.44 (d, $J = 7.9$ Hz, 2H), 7.39 – 7.37 (m, 1H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 2H), 7.10 (d, $J = 8.1$ Hz, 2H), 4.11 (s, 2H), 2.59 (q, $J = 7.6$ Hz, 2H), 2.44 (s, 3H), 1.19 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.9, 148.9, 141.2, 139.8, 136.8, 134.8, 130.3, 128.53, 128.47, 127.3, 125.8, 122.9, 122.0, 120.5, 119.2, 118.3, 34.6, 28.4, 21.4, 15.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}^+$ 370.1914, Found: 370.1915.

N-(4-methoxyphenyl)-2-(2-(*p*-tolyl)-2H-indazol-3-yl)acetamide (**3ae**)



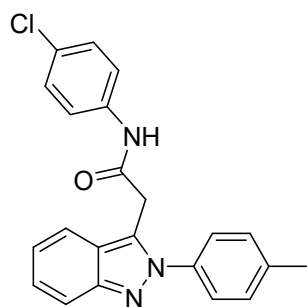
28.3 mg, 38%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.38 (dd, $J = 7.9, 6.8$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.23 – 7.21 (m, 2H), 7.19 (dd, $J = 8.1, 6.9$ Hz, 1H), 7.09 (s, 1H), 6.82 – 6.79 (m, 2H), 4.11 (s, 2H), 3.76 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 157.1, 149.0, 139.8, 136.9, 130.3, 128.6, 127.3, 125.8, 122.9, 122.3, 122.1, 119.2, 118.4, 114.3, 55.6, 34.5, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_2^+$ 372.1707, Found: 372.1707.

N-(4-(*tert*-butyl)phenyl)-2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetamide (**3af**)



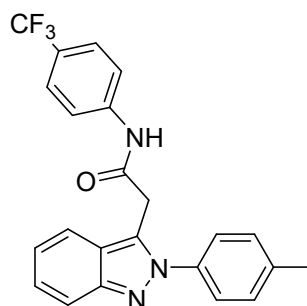
58.0 mg, 73%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.37 (t, $J = 7.3$ Hz, 2H), 7.29 (dd, $J = 15.3, 8.5$ Hz, 5H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.16 (dd, $J = 8.0, 7.0$ Hz, 1H), 4.08 (s, 2H), 2.43 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.0, 148.9, 148.1, 139.7, 136.8, 134.6, 130.2, 128.6, 127.3, 126.0, 125.8, 122.8, 122.0, 120.1, 119.3, 118.2, 34.51, 34.48, 31.4, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}^+$ 398.2227, Found: 398.2229.

N-(4-chlorophenyl)-2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetamide (**3ag**)



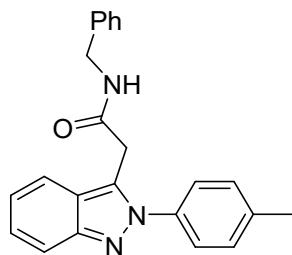
41.2 mg, 55%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.41 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.9$ Hz, 2H), 7.25 – 7.21 (m, 3H), 7.19 (dd, $J = 8.0$, 7.0 Hz, 1H), 4.11 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 149.0, 139.9, 136.8, 135.8, 130.3, 130.1, 129.2, 128.2, 127.3, 125.8, 123.1, 122.0, 121.5, 119.1, 118.4, 34.6, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{ClN}_3\text{O}^+$ 376.1211, Found: 376.1213.

2-(2-(p-tolyl)-2H-indazol-3-yl)-N-(4-(trifluoromethyl)phenyl)acetamide(3ah)



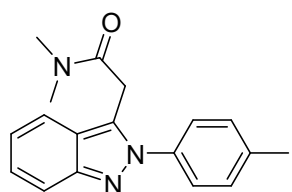
46.7 mg, 57%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.42 – 7.38 (m, 3H), 7.34 (d, $J = 8.1$ Hz, 3H), 7.22 – 7.19 (m, 1H), 4.15 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.2, 149.0, 140.2, 140.0, 136.7, 130.4, 127.9, 127.4, 126.8 (q, $J = 33.0$ Hz), 126.4 (q, $J = 3.0$ Hz), 125.8, 124.1 (q, $J = 240.0$ Hz), 123.2, 122.0, 119.7, 119.0, 118.5, 34.7, 21.2. ^{19}F NMR (564 MHz, CDCl_3) δ -62.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{N}_3\text{O}^+$ 410.1475, Found: 410.1475.

N-benzyl-2-(2-(p-tolyl)-2H-indazol-3-yl)acetamide(3ai)



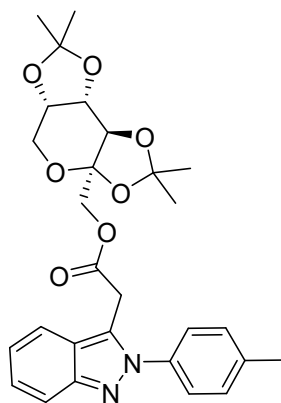
27.0 mg, 38%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.7$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.36 – 7.34 (m, 3H), 7.30 – 7.24 (m, 5H), 7.14 (t, $J = 7.5$ Hz, 3H), 5.80 (s, 1H), 4.38 (d, $J = 5.9$ Hz, 2H), 4.01 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.8, 148.8, 139.6, 137.8, 136.8, 130.2, 128.8, 128.7, 127.84, 127.78, 127.2, 125.7, 122.6, 122.0, 119.4, 118.2, 43.9, 33.6, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}^+$ 356.1757, Found: 356.1755.

N,N-dimethyl-2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetamide (**3aj**)



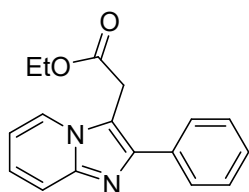
37.0 mg, 63%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.30 (m, 3H), 7.08 (dd, $J = 8.0, 7.0$ Hz, 1H), 4.05 (s, 2H), 2.95 (s, 3H), 2.85 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.2, 148.8, 139.3, 137.3, 130.0, 129.5, 126.8, 126.0, 121.9, 120.0, 117.9, 37.6, 36.0, 31.7, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}^+$ 294.1601, Found: 294.1602.

((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methyl 2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetate (**3ak**)



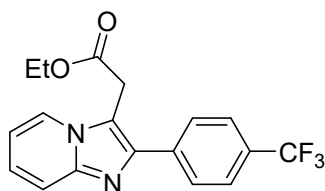
35.6 mg, 35%; Light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.8$ Hz, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.45 – 7.42 (m, 2H), 7.34 – 7.30 (m, 3H), 7.12 (ddd, $J = 8.4, 6.6, 0.6$ Hz, 1H), 4.55 (dd, $J = 7.9, 2.6$ Hz, 1H), 4.38 (d, $J = 11.7$ Hz, 1H), 4.21 (dd, $J = 7.9, 1.1$ Hz, 1H), 4.10 – 4.08 (m, 3H), 4.06 (d, $J = 11.7$ Hz, 1H), 3.87 (dd, $J = 13.0, 1.8$ Hz, 1H), 3.74 (d, $J = 13.0$ Hz, 1H), 2.45 (s, 3H), 1.46 (s, 6H), 1.34 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 148.7, 139.5, 130.1, 127.9, 126.9, 126.1, 122.1, 122.0, 119.6, 118.0, 109.3, 108.9, 101.3, 70.8, 70.5, 70.1, 66.3, 61.4, 31.5, 26.5, 26.0, 24.8, 24.2, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{33}\text{N}_2\text{O}_7^+$ 509.2282, Found: 509.2283.

ethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (5a)^[3]



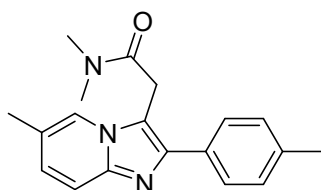
26.3 mg, 47%; Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 8.13 (d, $J = 6.9$ Hz, 1H), 7.85 – 7.84 (m, 2H), 7.67 (d, $J = 9.0$ Hz, 1H), 7.49 – 7.47 (m, 2H), 7.40 – 7.37 (m, 1H), 7.23 (ddd, $J = 9.0, 6.7, 1.2$ Hz, 1H), 6.87 (td, $J = 6.8, 1.1$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 4.05 (s, 2H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.6, 145.2, 144.8, 134.2, 128.8, 128.7, 128.0, 124.6, 123.9, 117.8, 113.1, 112.5, 61.8, 31.0, 14.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2^+$ 281.1285, Found: 281.1285.

ethyl 2-(2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridin-3-yl)acetate (**5b**)^[3]



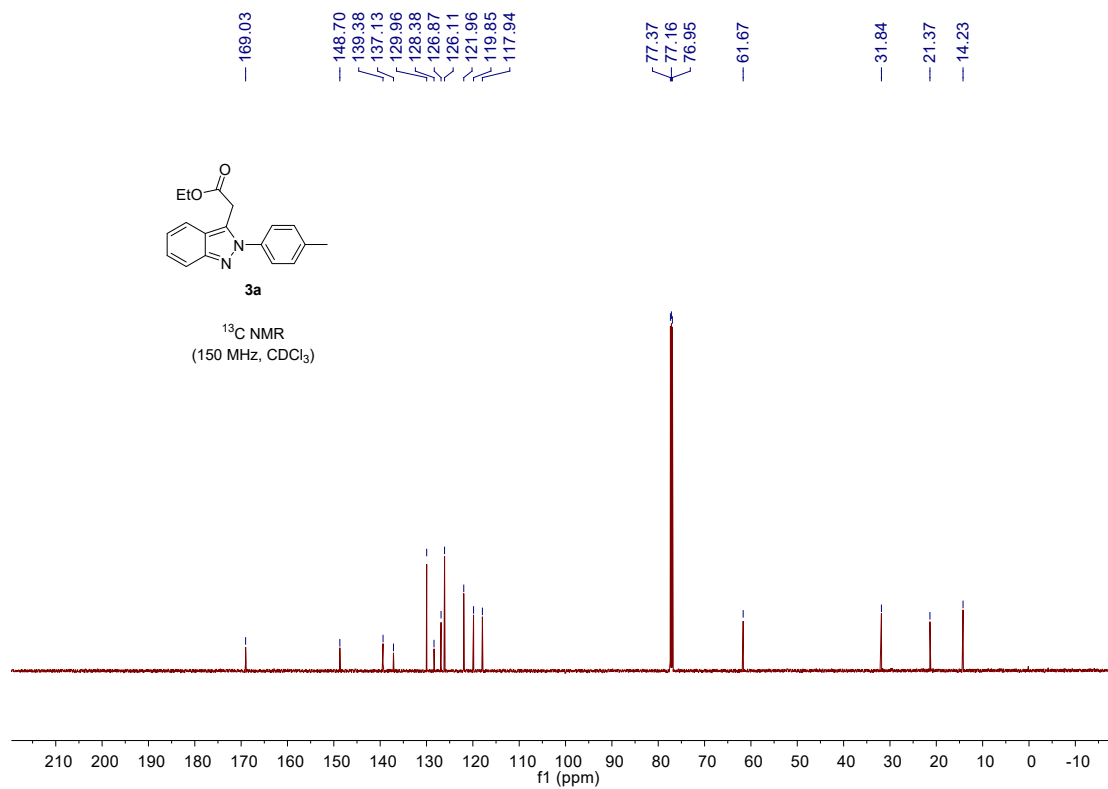
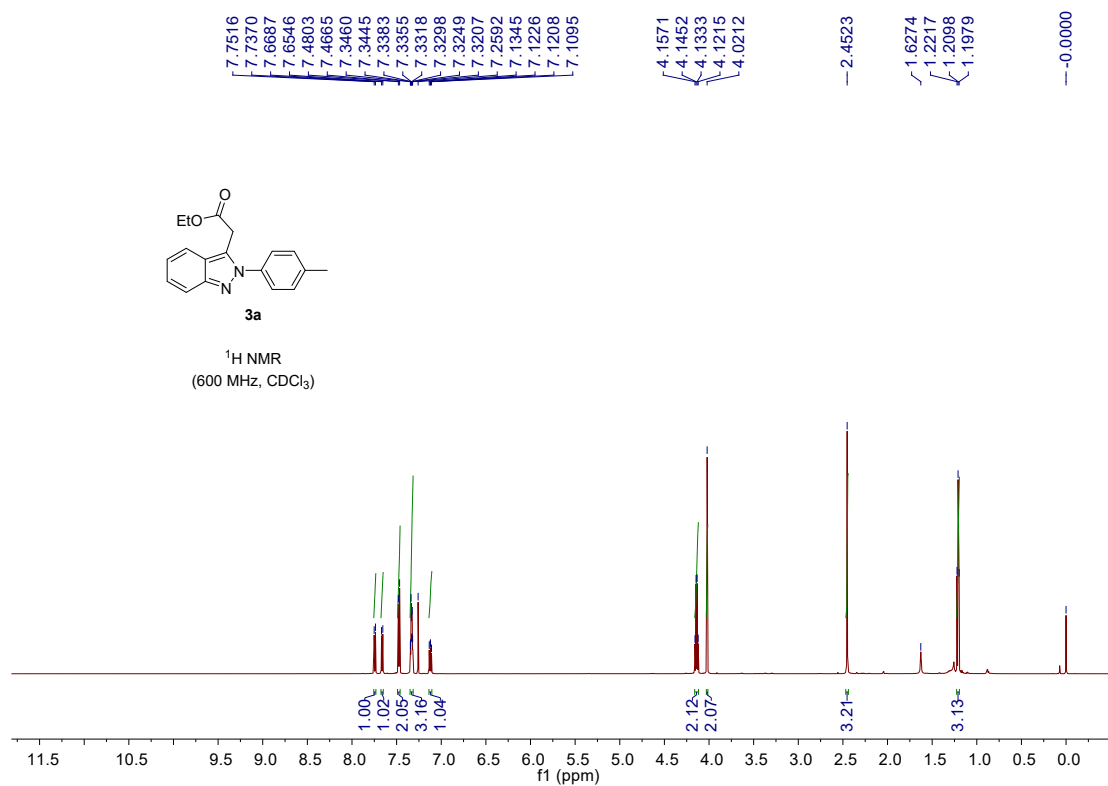
35.6 mg, 51%; Light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 8.17 (d, *J* = 6.9 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.29 – 7.27 (m, 1H), 6.91 (td, *J* = 6.8, 0.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.2, 145.4, 143.3, 137.8, 130.0(q, *J* = 33.0 Hz), 128.9, 125.7 (q, *J* = 3.0 Hz), 125.2, 124.4 (q, *J* = 271.5 Hz), 124.0, 118.0, 113.9, 112.9, 62.0, 31.0, 14.3. ¹⁹F NMR (564 MHz, CDCl₃) δ -62.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₁₆F₃N₂O₂⁺ 349.1158, Found: 349.1157.

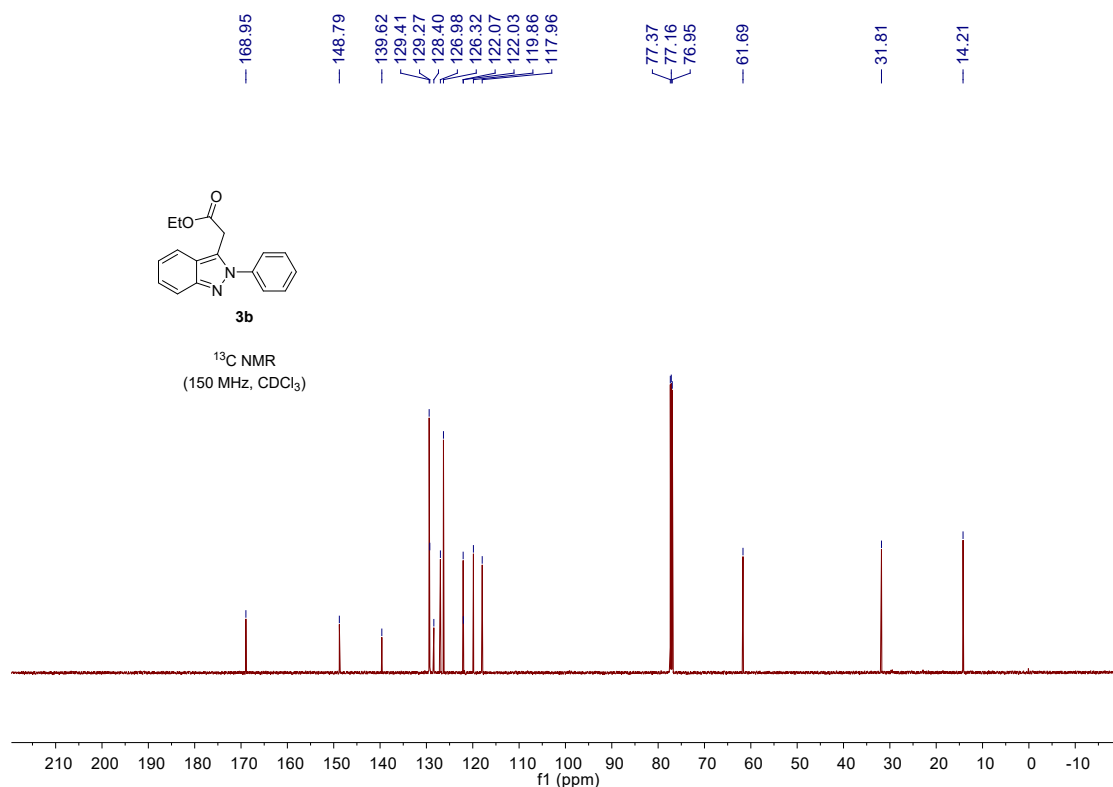
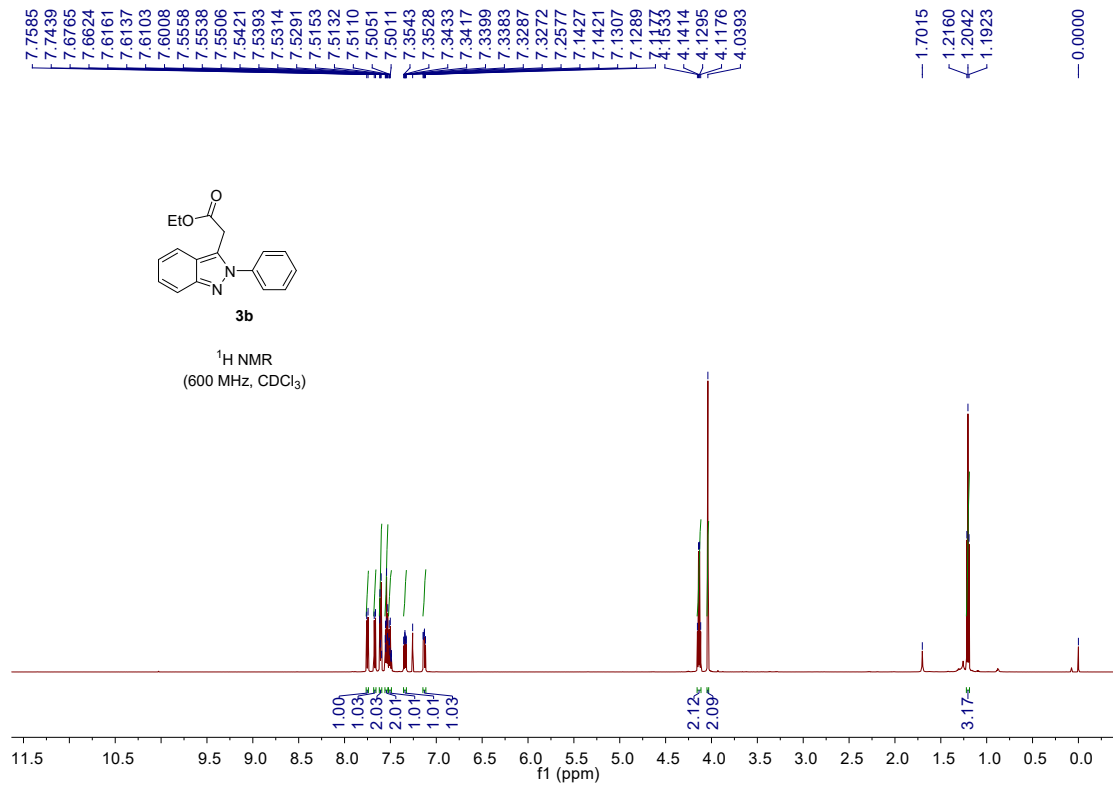
N,N-dimethyl-2-(6-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)acetamide (**5c**)^[4]



31.2 mg, 51%; Light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 8.01 (s, 1H), 7.54 (t, *J* = 9.2 Hz, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.04 (dd, *J* = 9.1, 1.5 Hz, 1H), 4.09 (s, 2H), 2.94 (s, 3H), 2.88 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 168.5, 144.3, 137.6, 131.9, 129.5, 128.6, 127.7, 122.4, 121.9, 116.8, 113.7, 37.7, 36.0, 30.5, 21.4, 18.6. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₂N₃O⁺ 308.1757, Found: 308.1757.

5. NMR copies of products





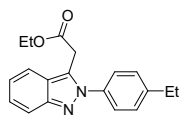
7.7536
7.7390
7.6717
7.6576
7.5094
7.4956
7.3623
7.3482
7.3359
7.3344
7.3327
7.3311
7.3214
7.3200
7.2596
7.1351
7.1236
7.1217
7.1104

4.1591
4.1472
4.1354
4.1235
4.0343

2.7683
2.7556
2.7429
2.7302

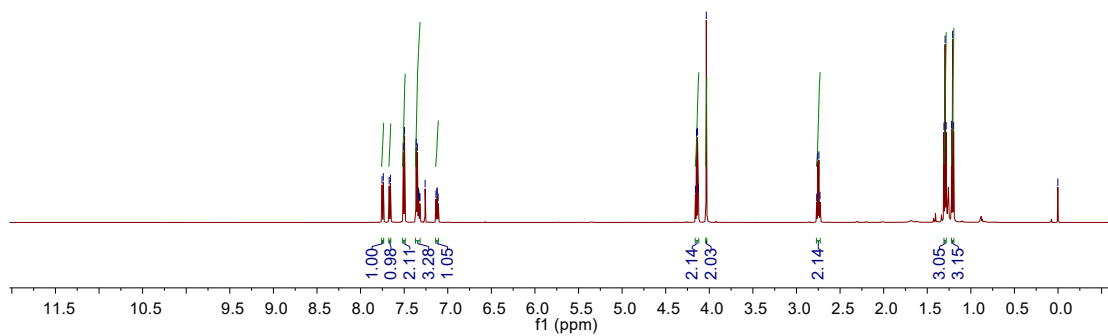
1.3084
1.2957
1.2830
1.2211
1.2093
1.1974

— 0.0020



3c

¹H NMR
(600 MHz, CDCl₃)



169.05

148.66
145.63

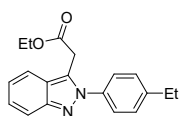
137.23
128.79
128.34
126.84
126.15
121.94
119.84
117.91

77.37
77.16
76.95

61.66

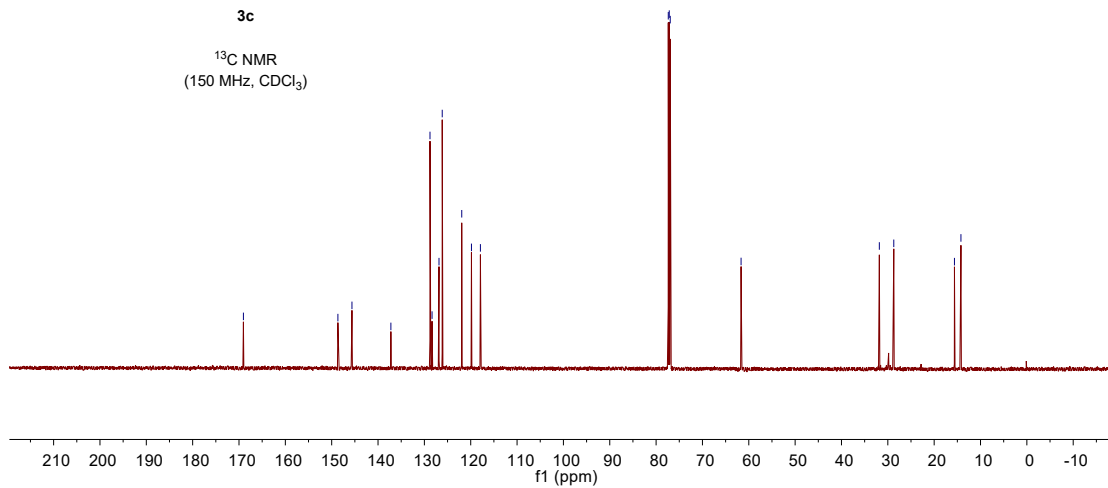
31.83
28.71

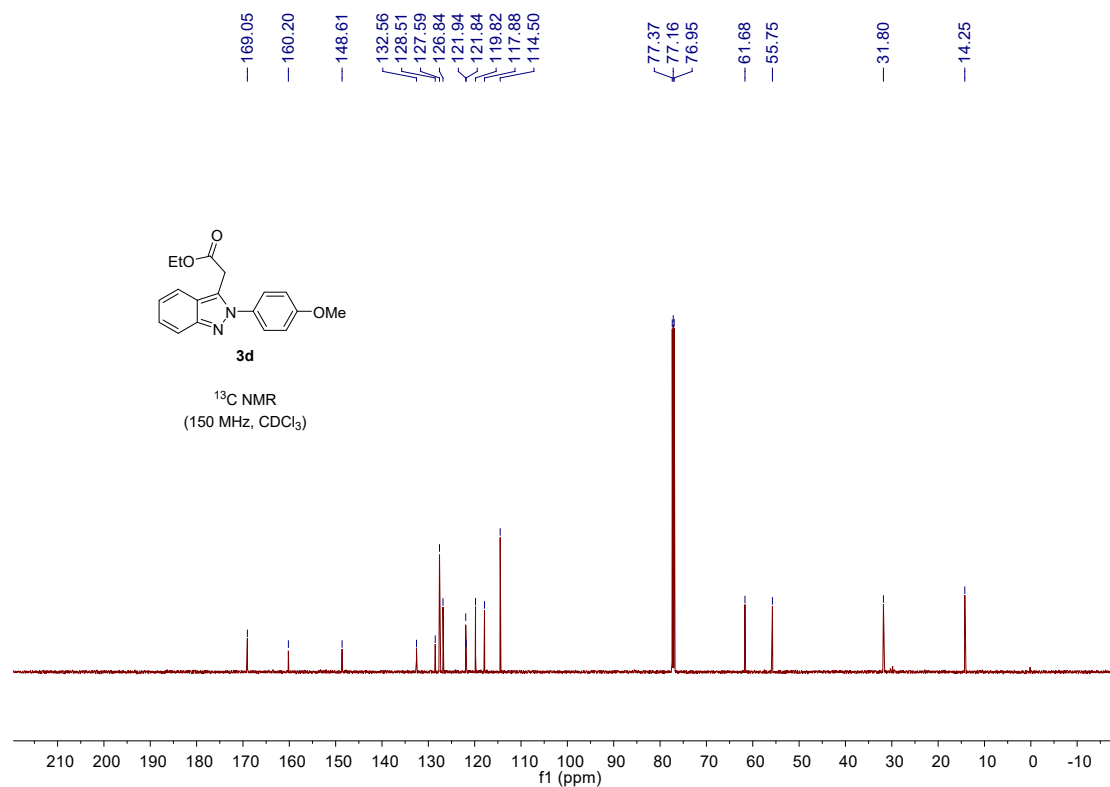
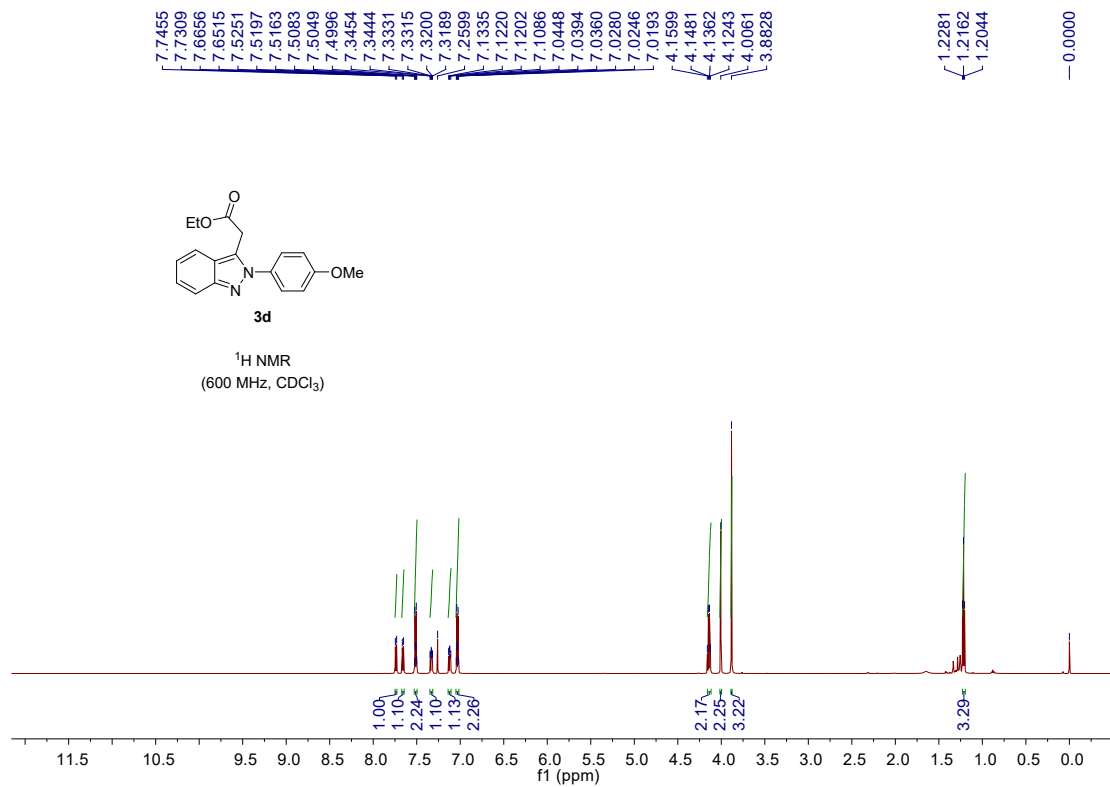
15.62
14.22

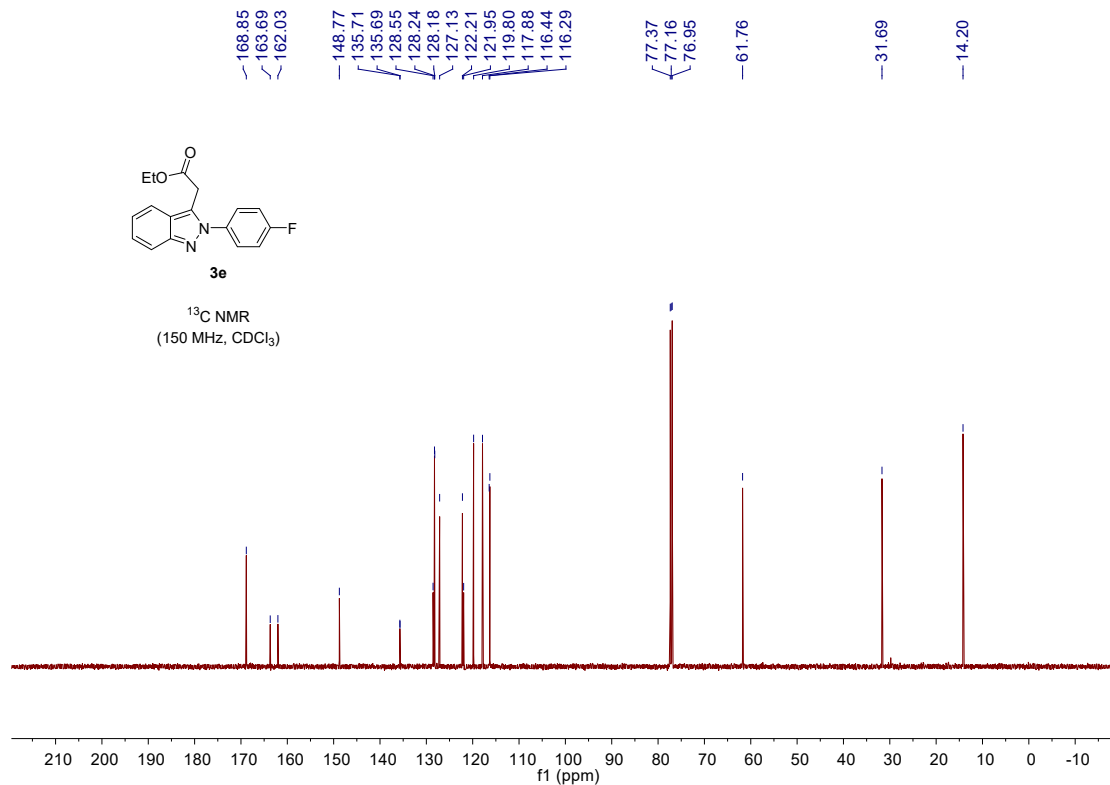
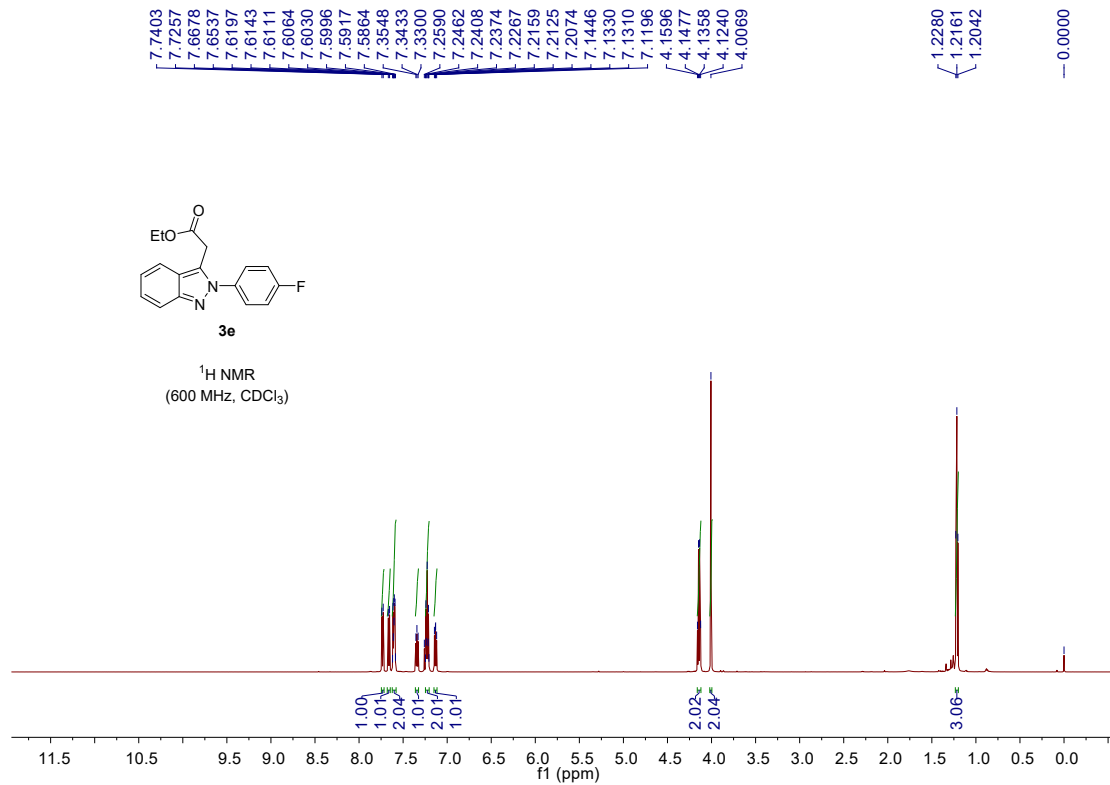


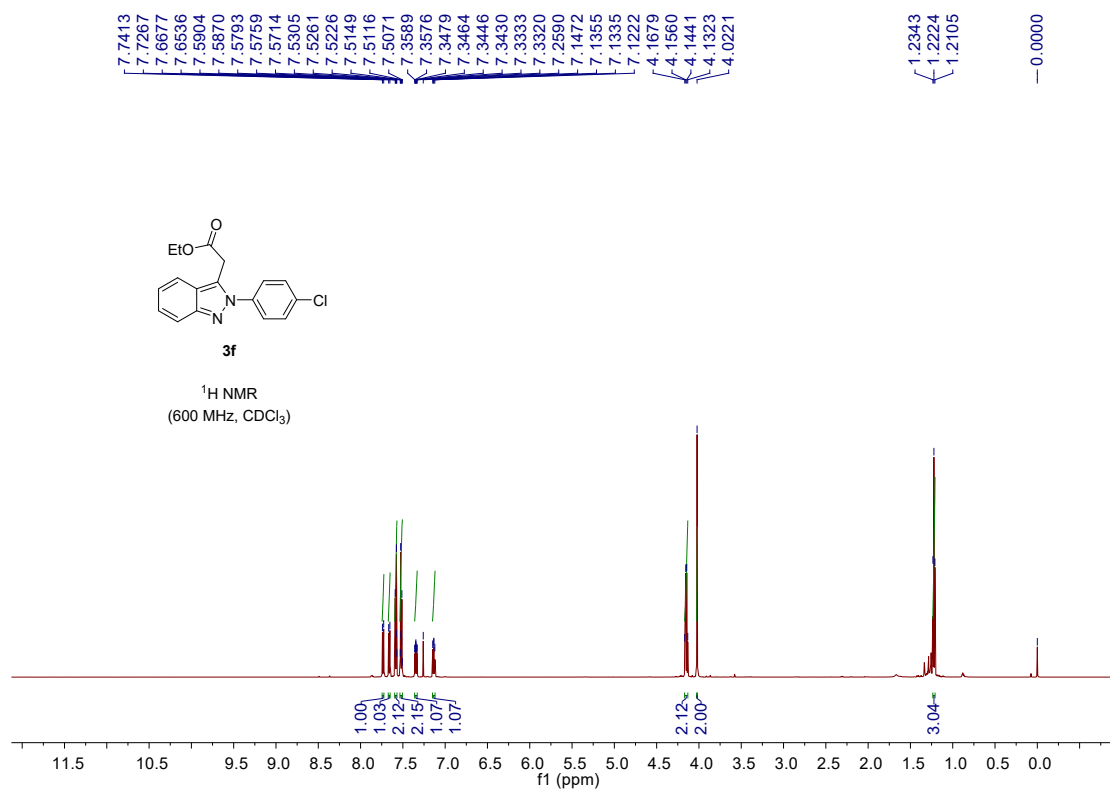
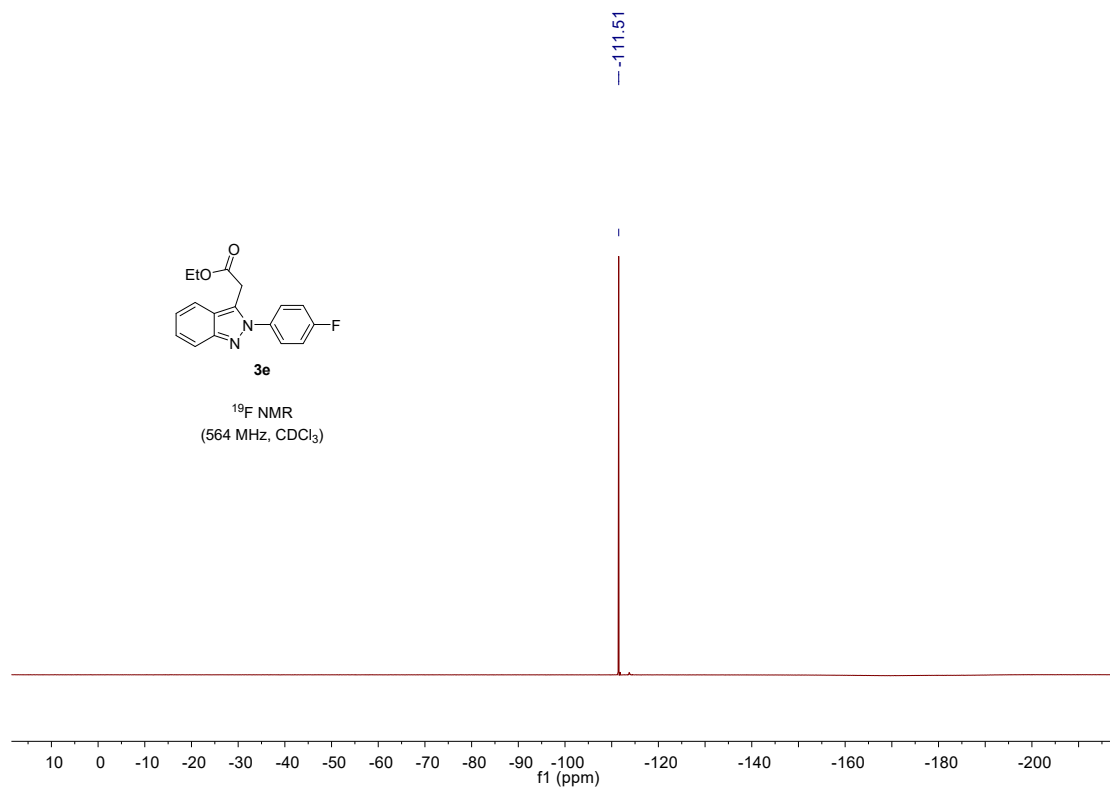
3c

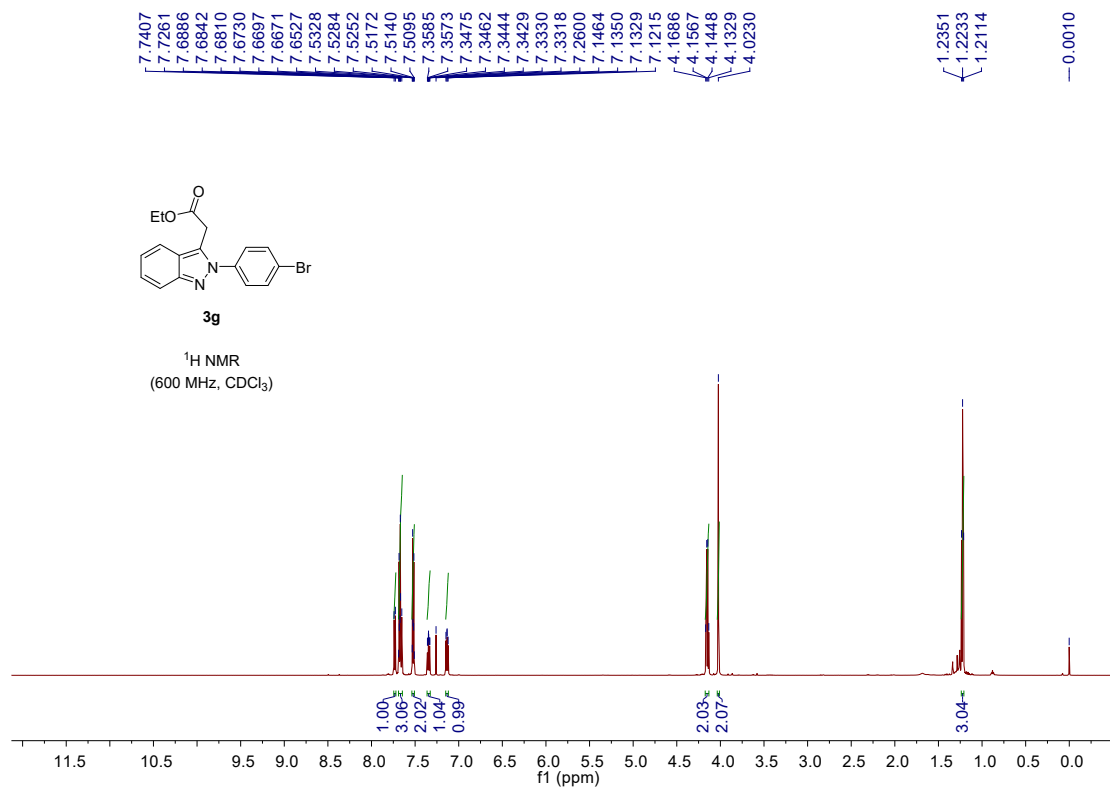
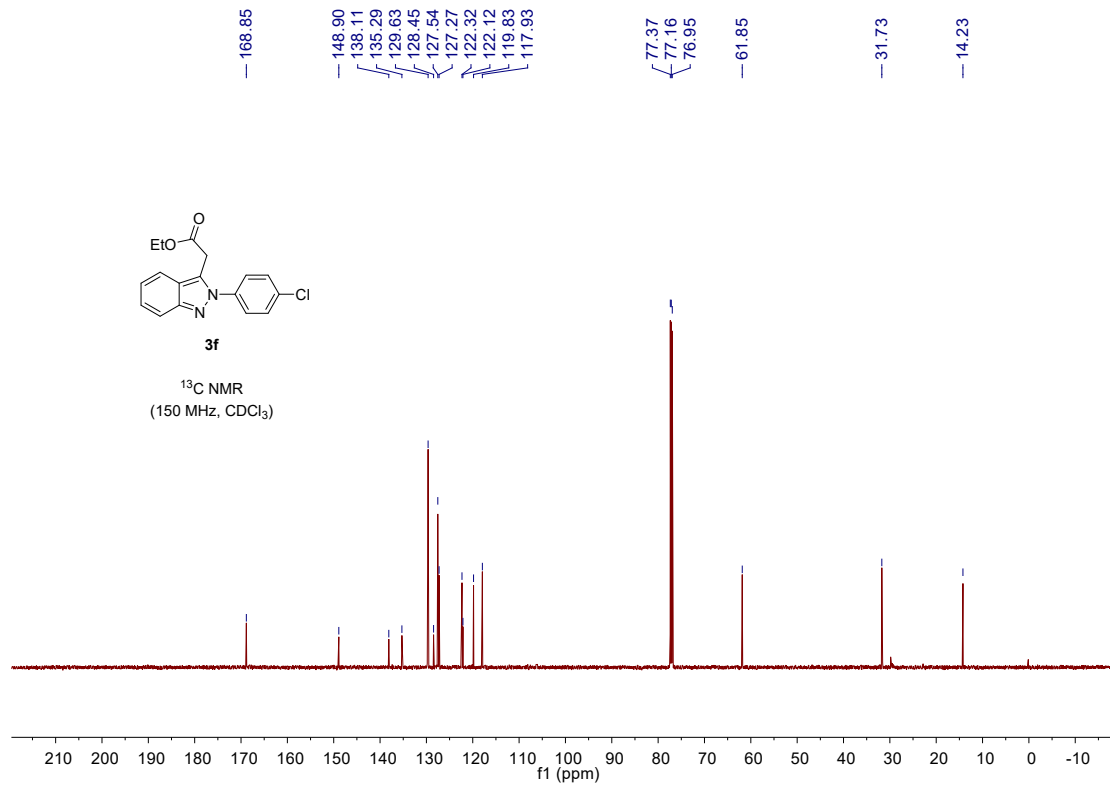
¹³C NMR
(150 MHz, CDCl₃)

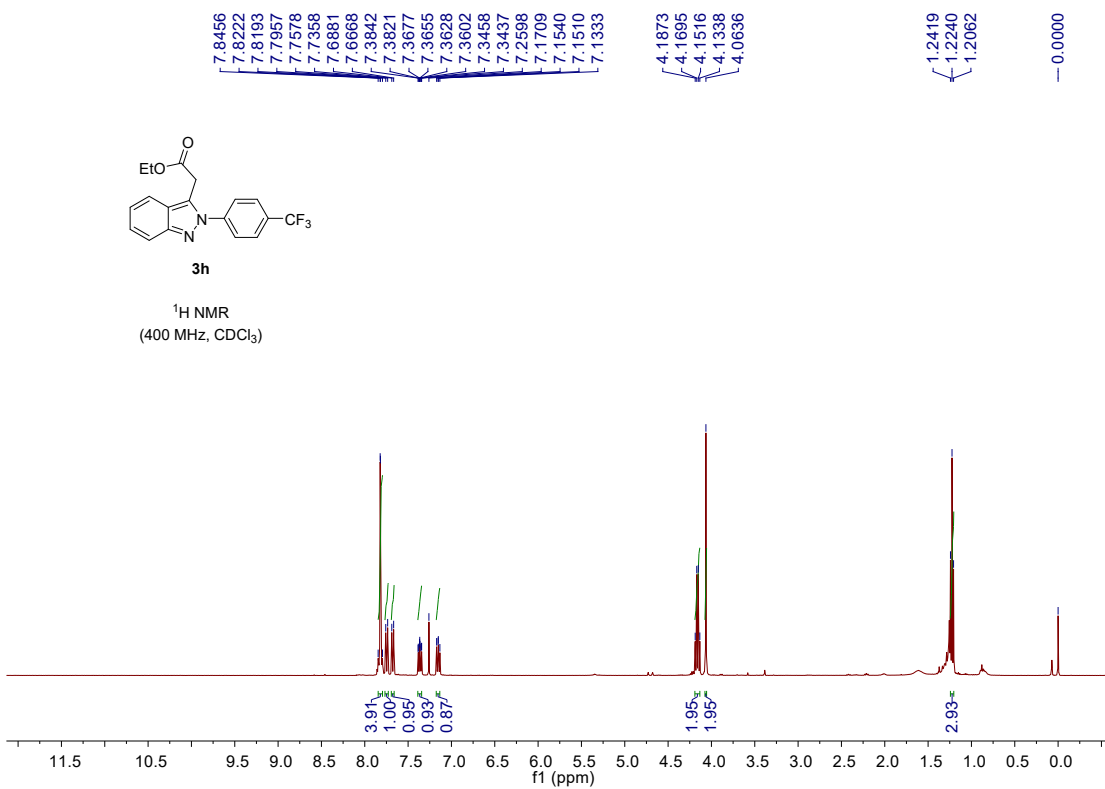
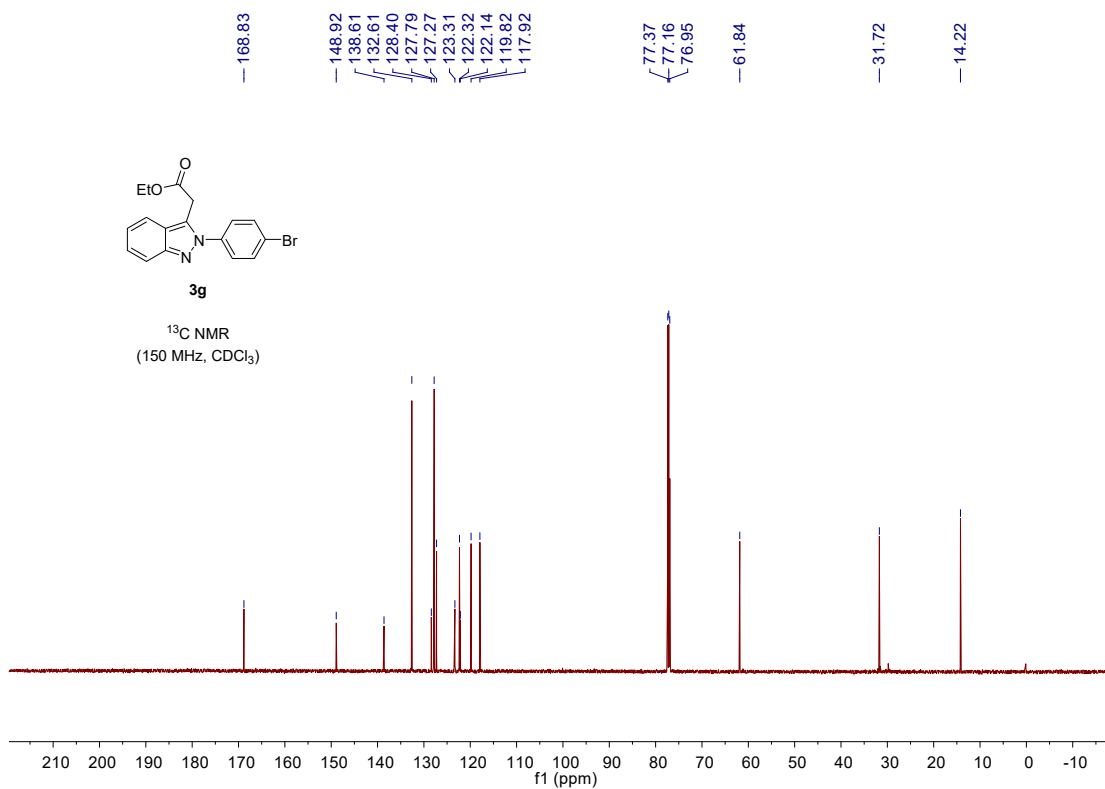


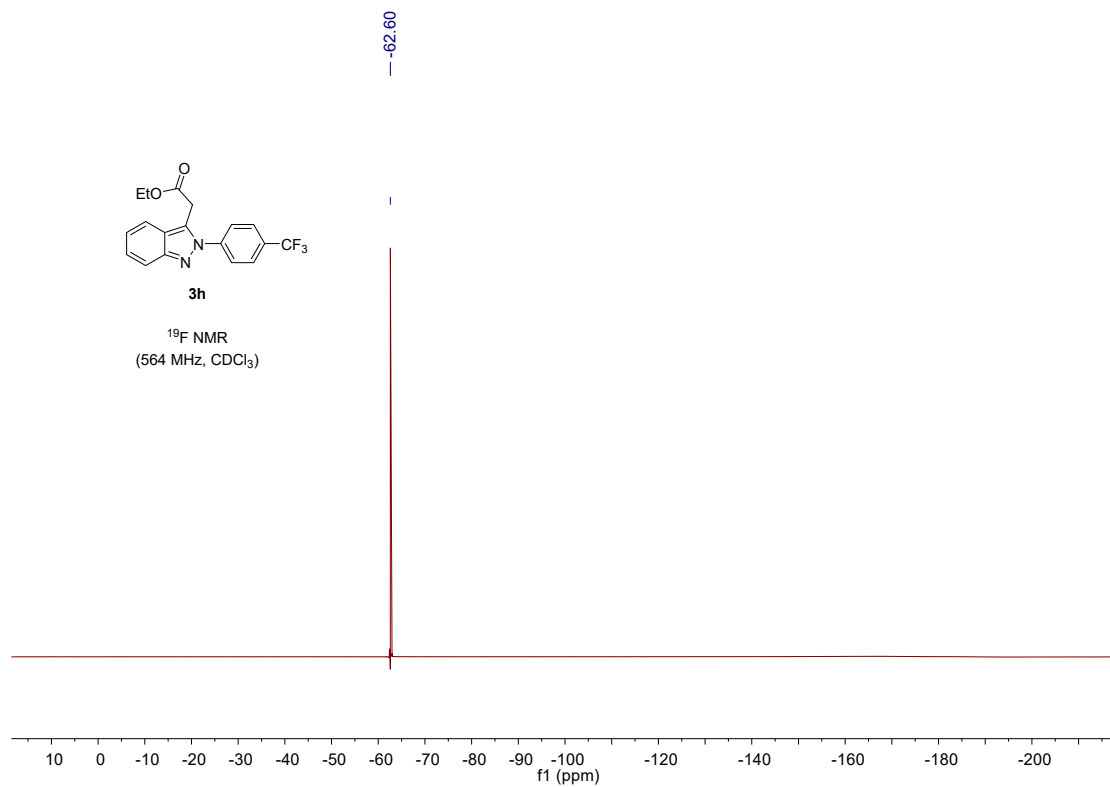
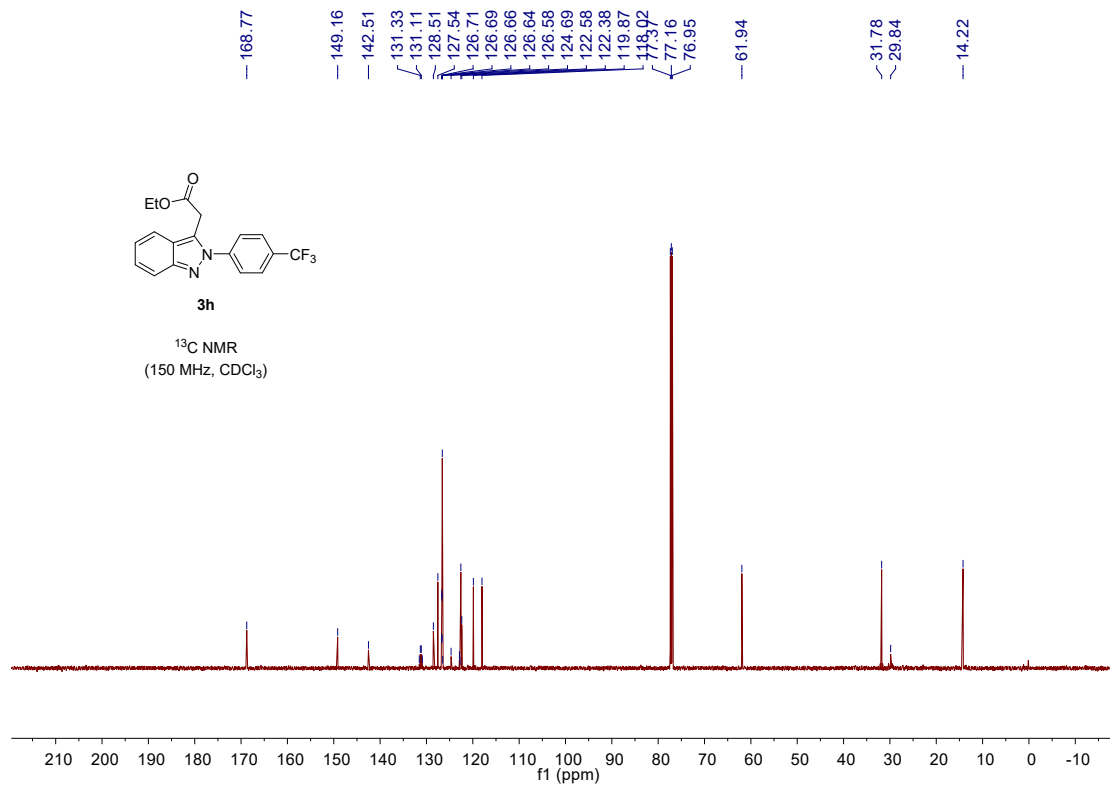


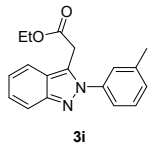




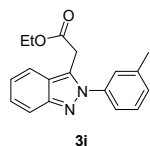
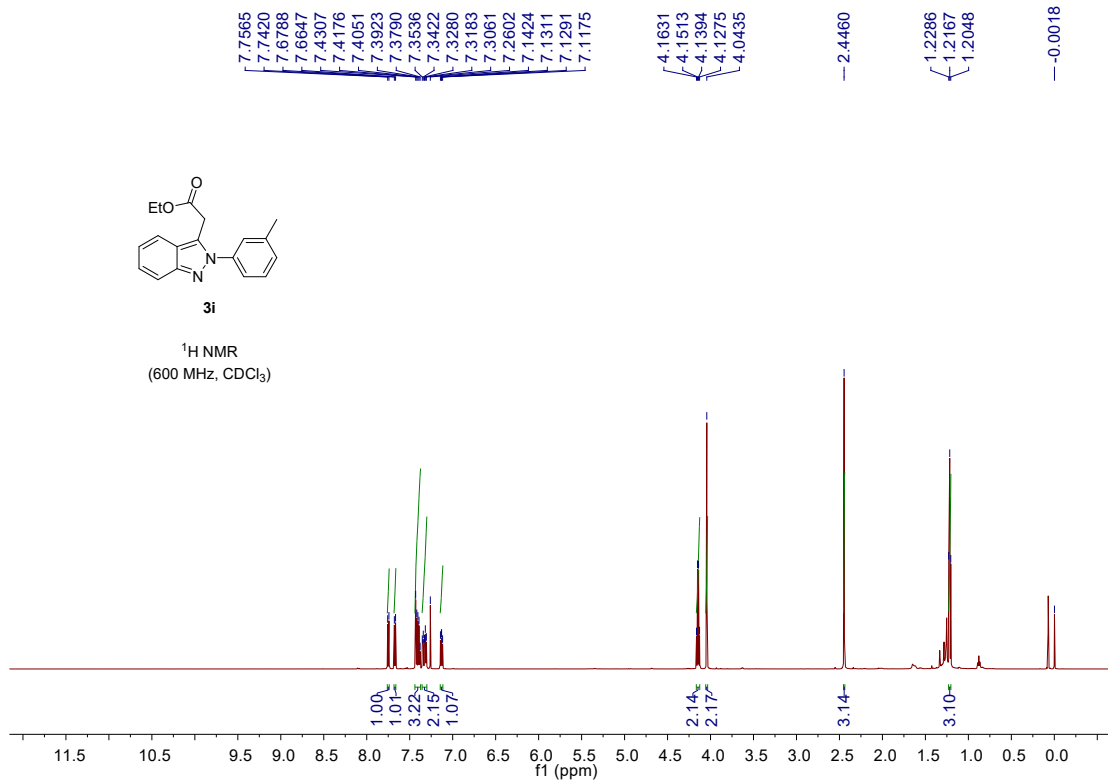




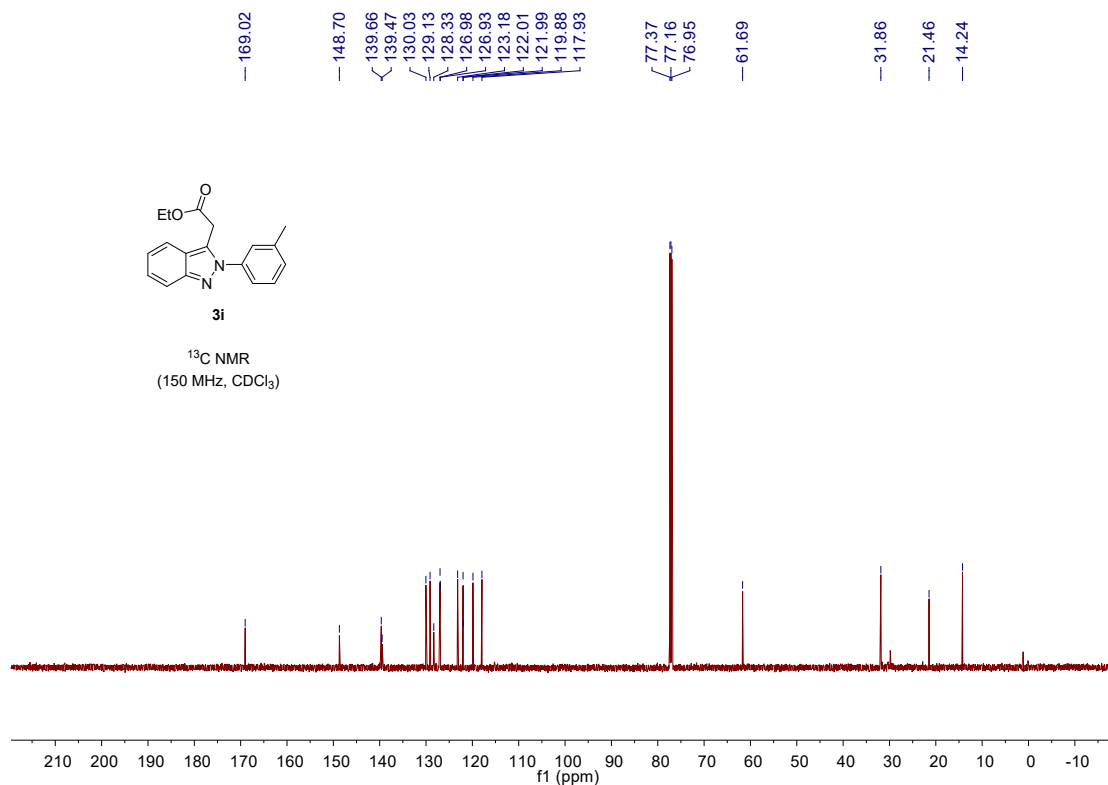


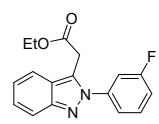
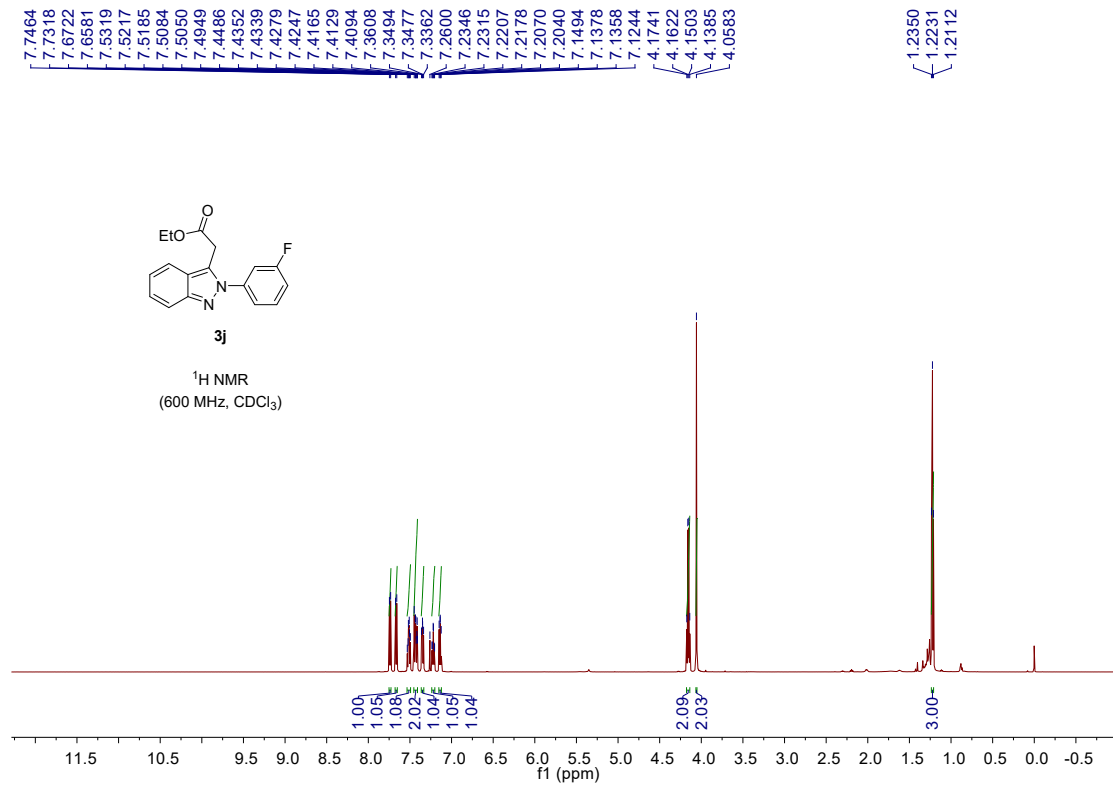


¹H NMR
(600 MHz, CDCl₃)



¹³C NMR
(150 MHz, CDCl₃)

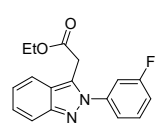
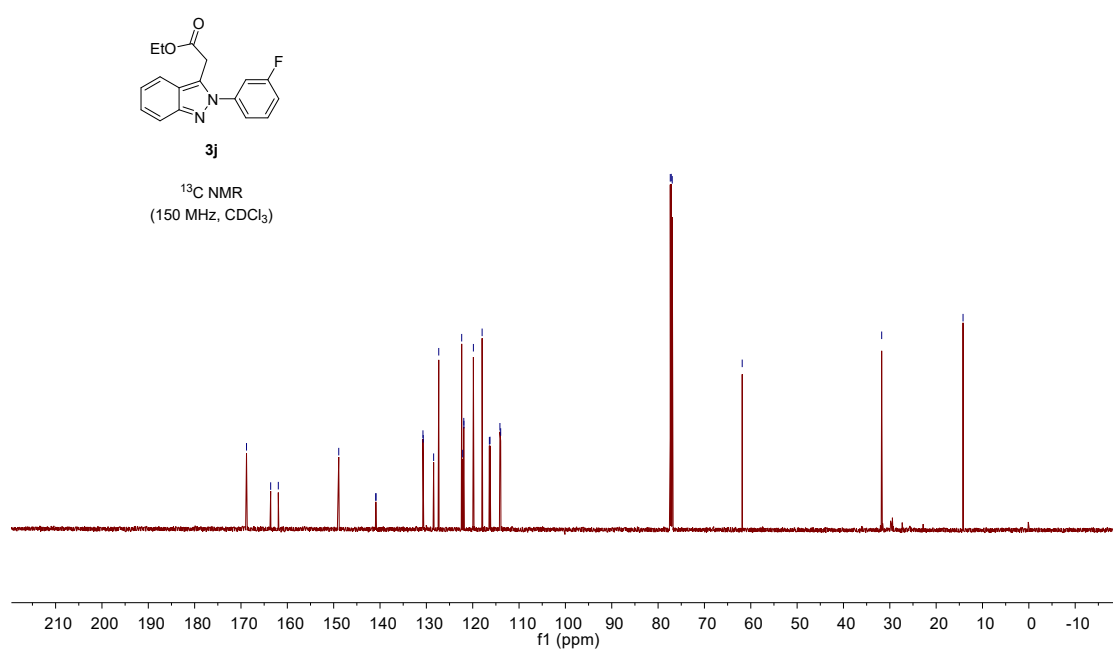




3j

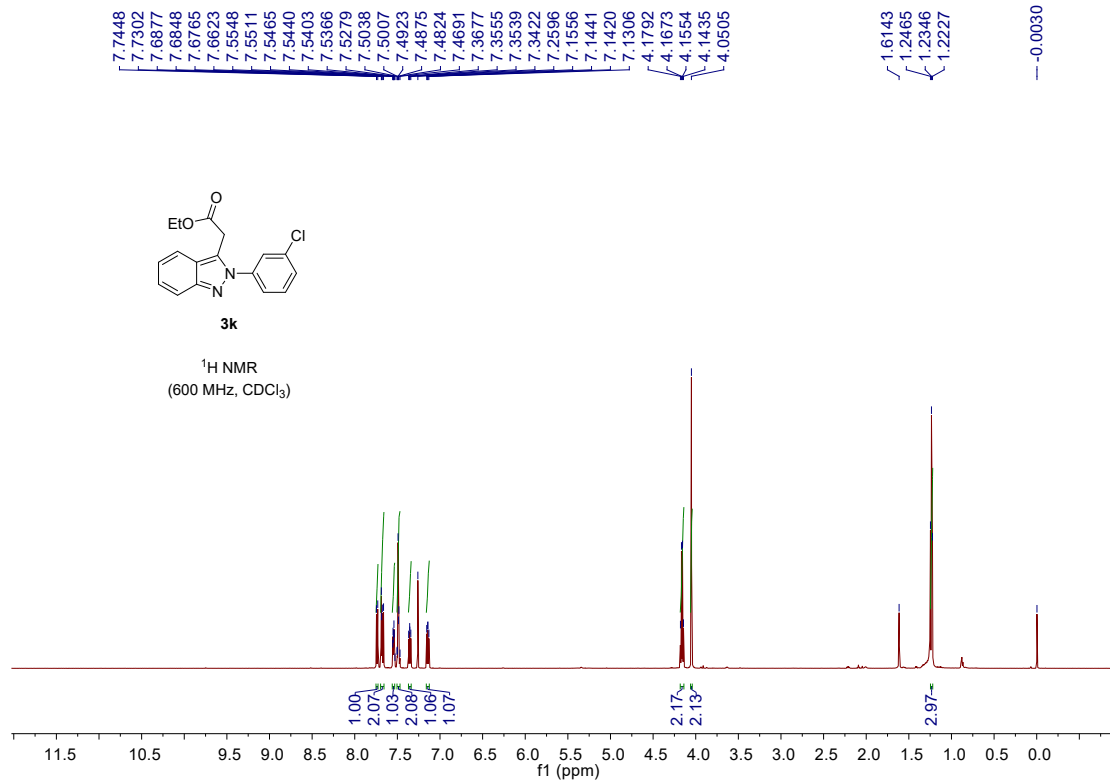
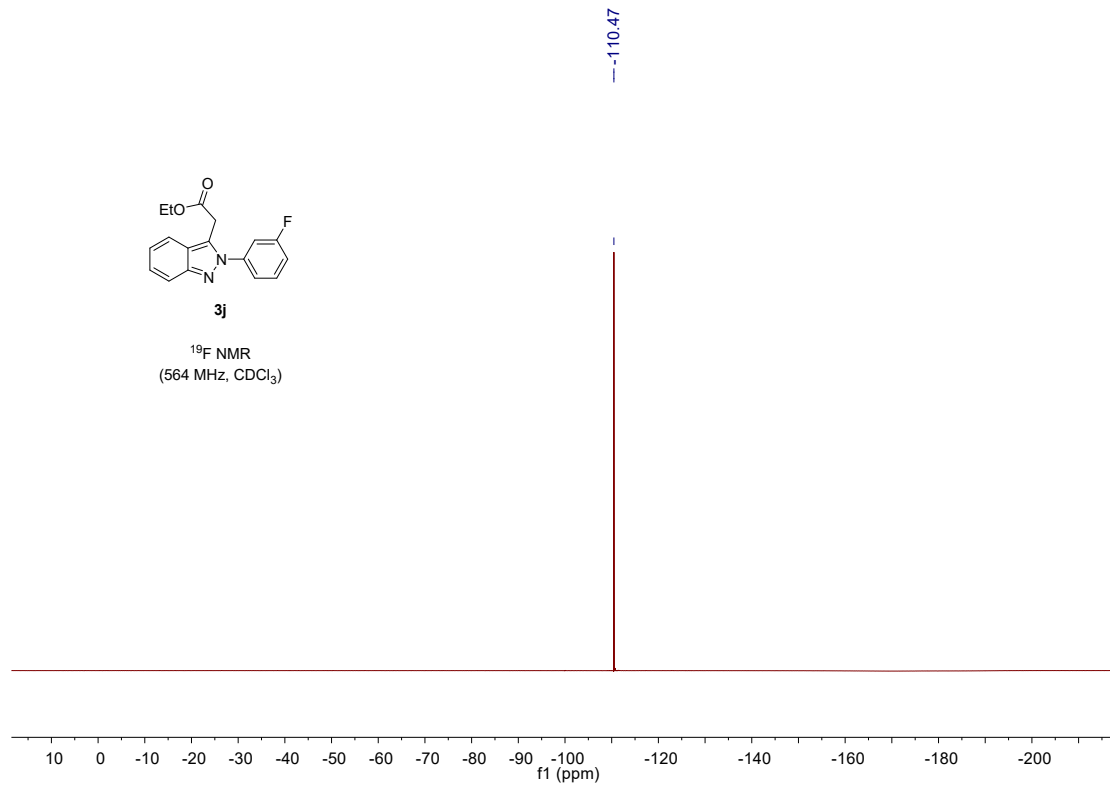
¹H NMR
 (600 MHz, CDCl₃)

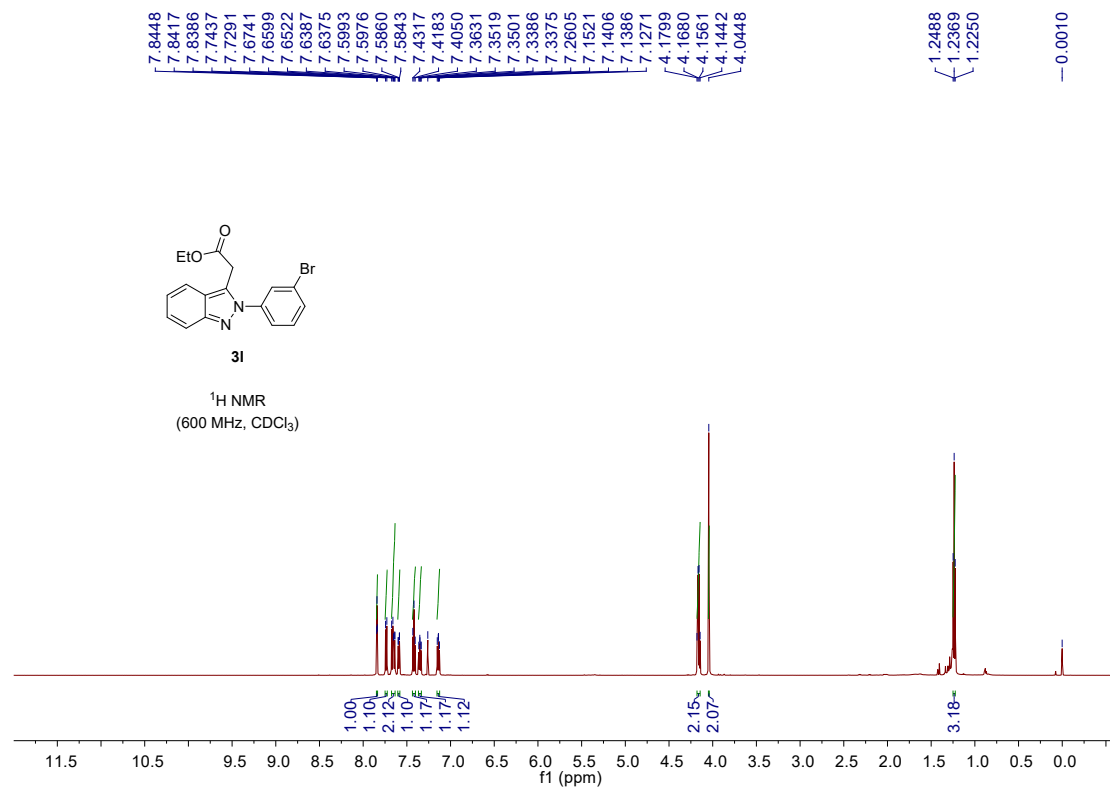
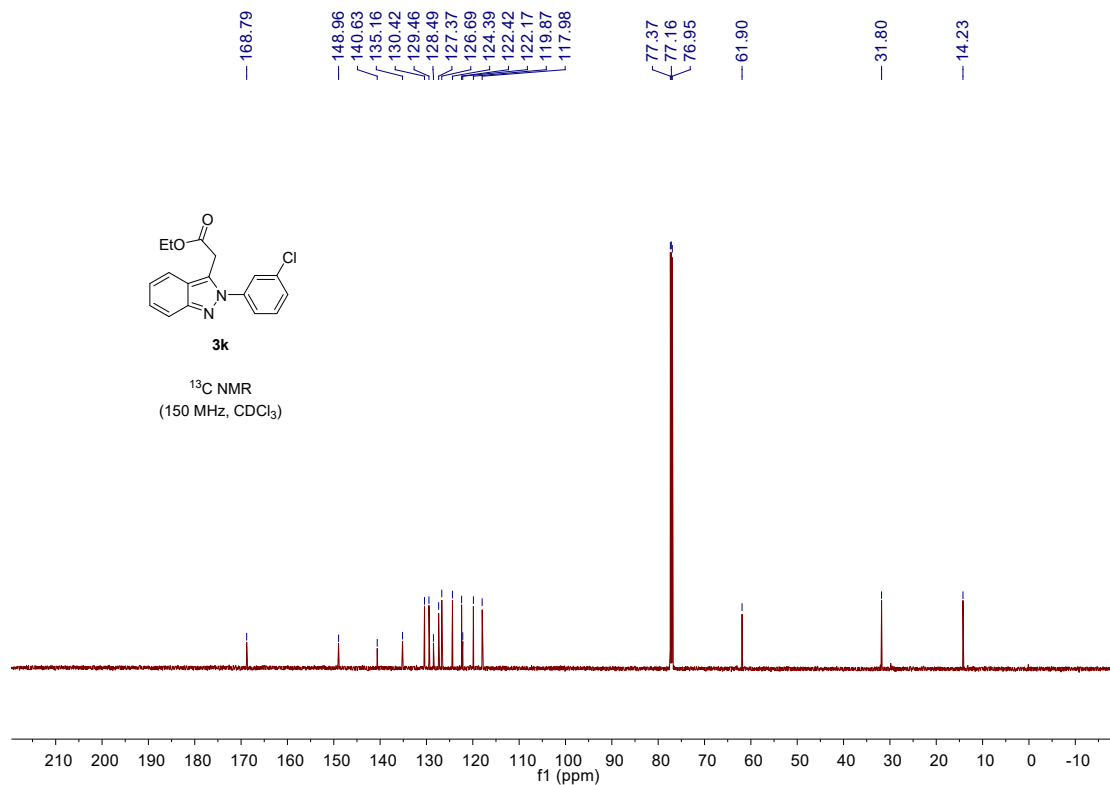
- 168.81
- 163.60
- 161.95
- 148.91
- 140.93
- 140.86
- 130.74
- 130.68
- 127.33
- 122.38
- 122.16
- 121.92
- 121.90
- 119.85
- 117.97
- 116.41
- 114.13
- 113.96
- 77.16
- 76.95
- 61.85
- 31.75
- 14.20

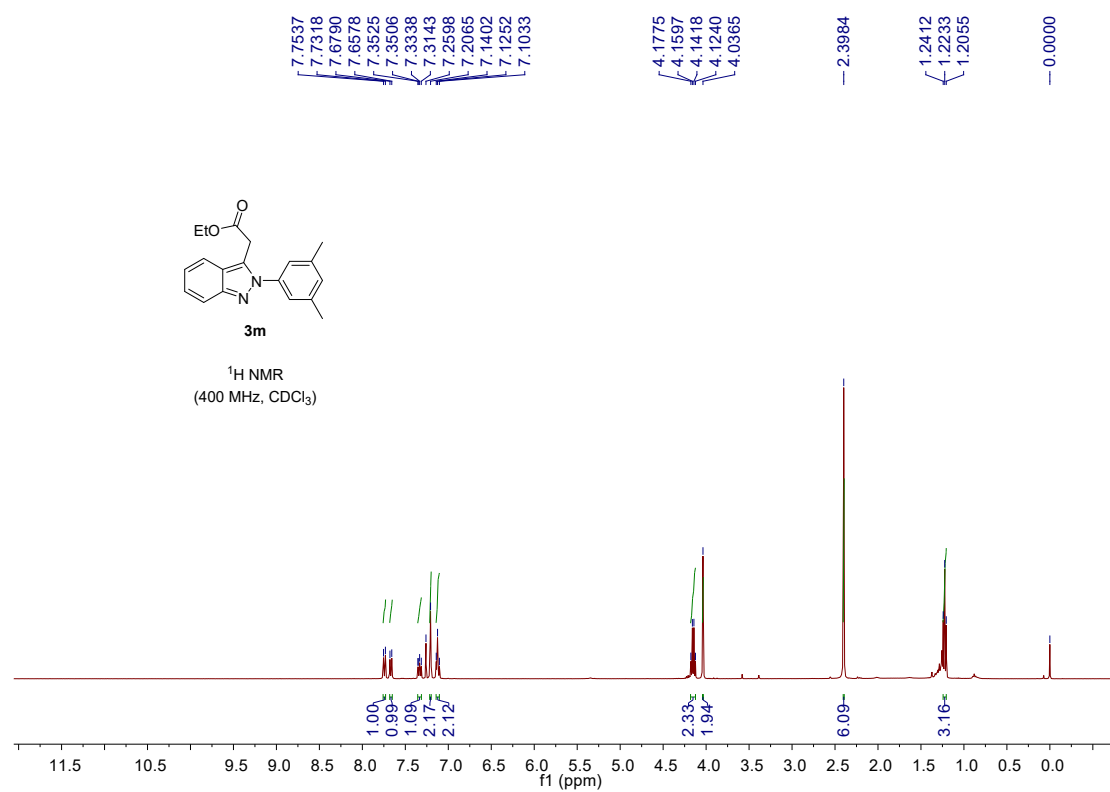
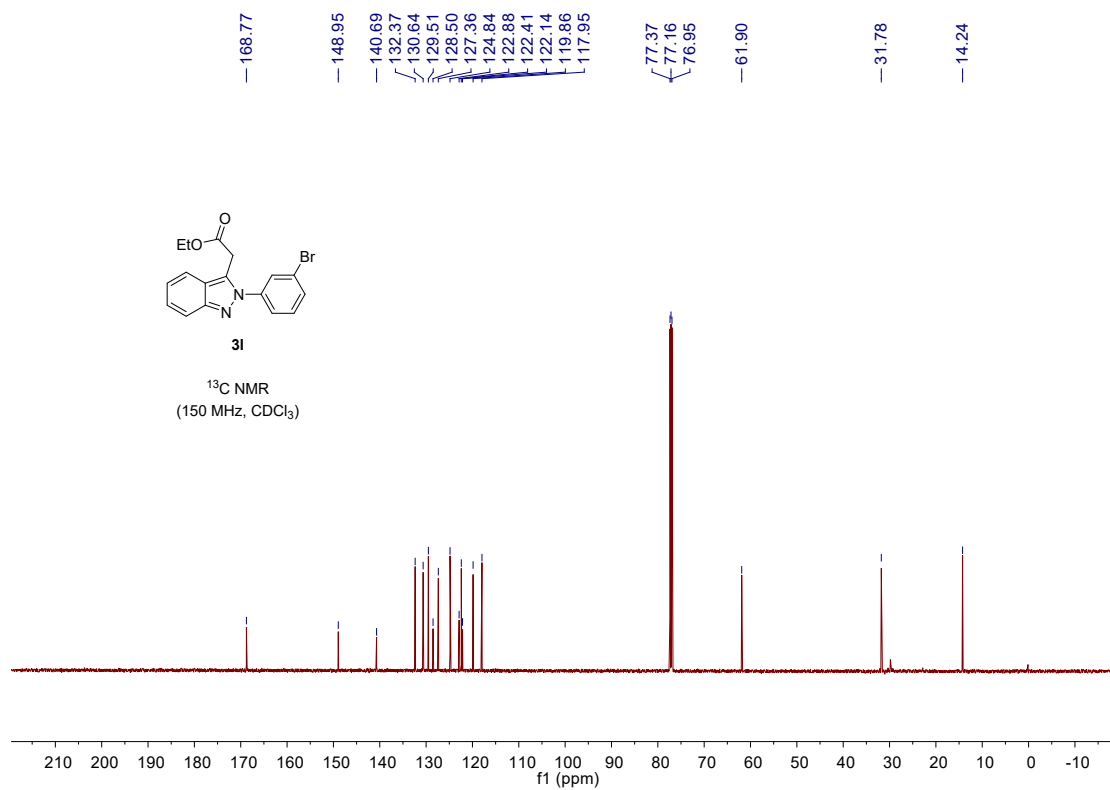


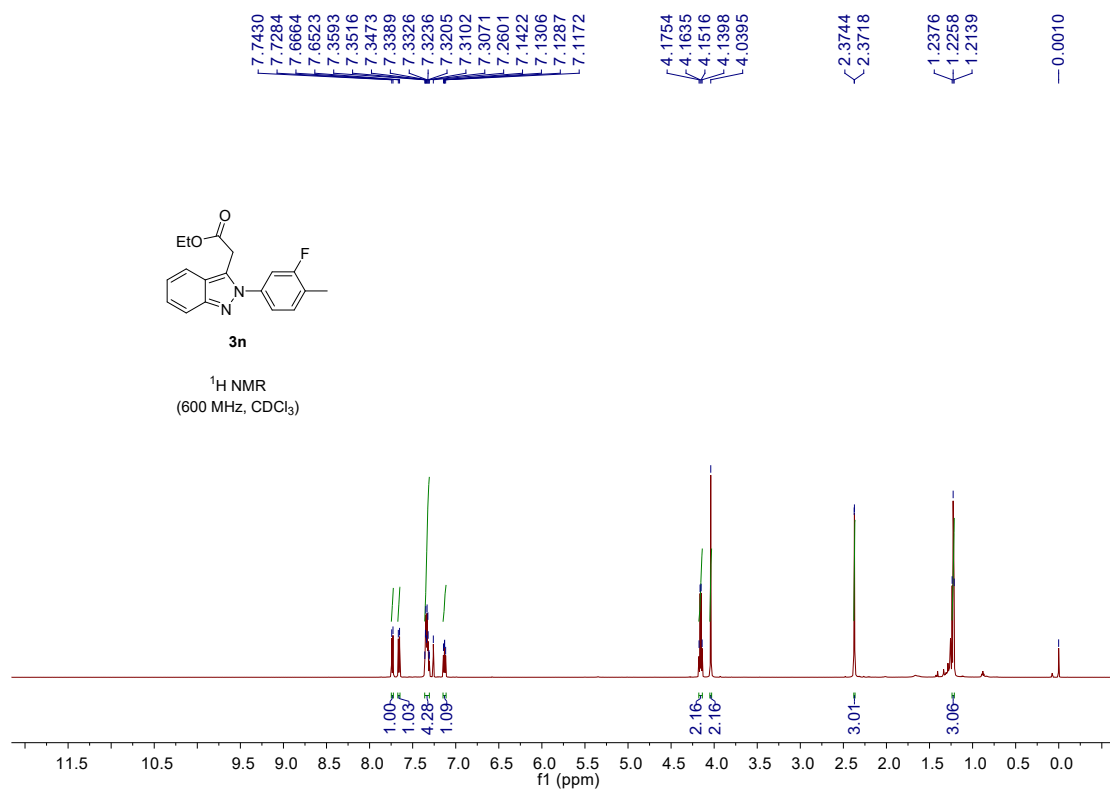
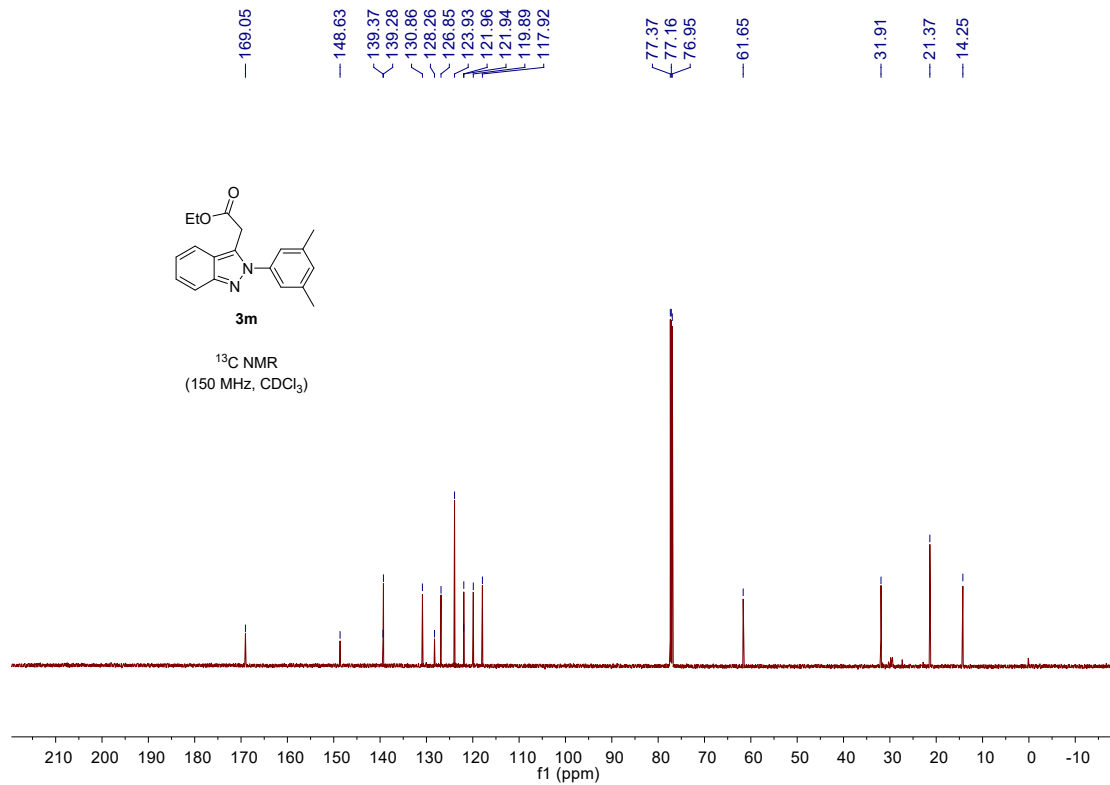
3j

¹³C NMR
 (150 MHz, CDCl₃)

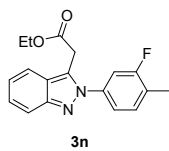




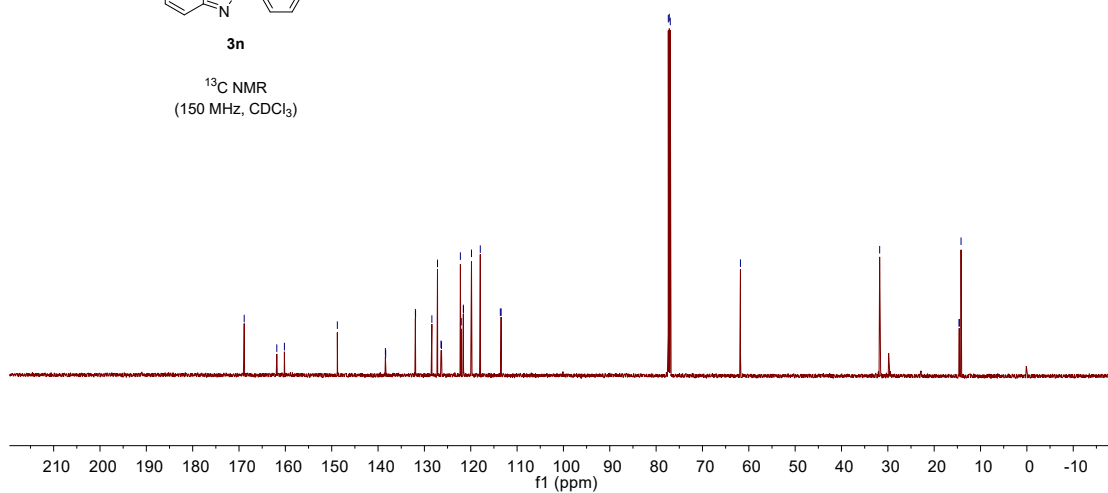




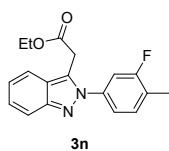
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 138.42
 131.95
 131.91
 128.39
 127.17
 126.42
 126.31
 122.24
 122.05
 121.60
 121.57
 119.84
 117.94
 113.61
 113.45
 77.16
 76.95
 61.81
 31.77
 14.62
 14.59
 14.21



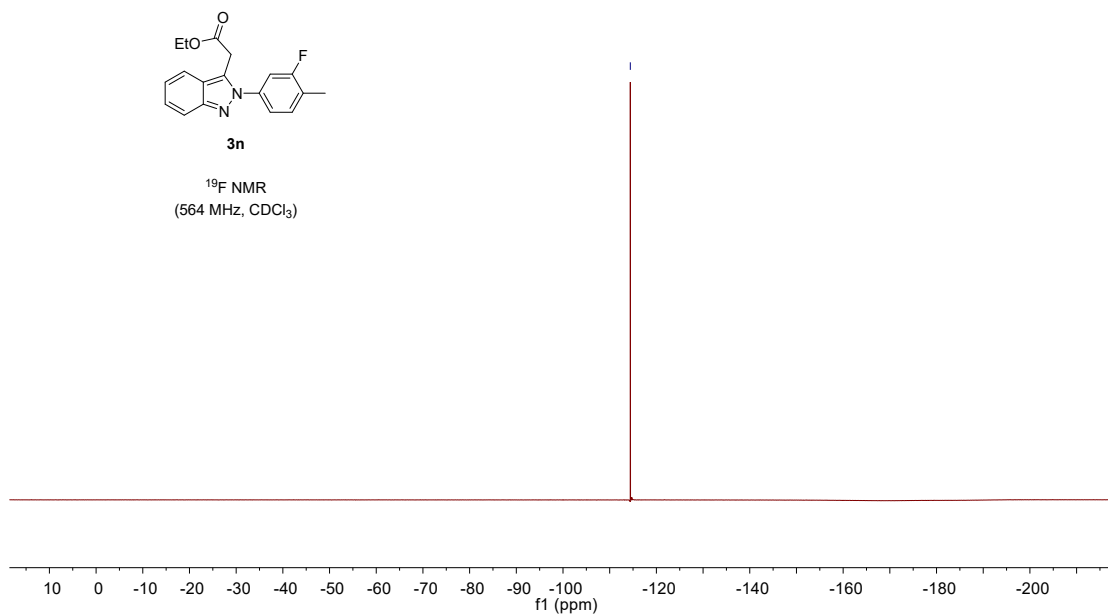
¹³C NMR
(150 MHz, CDCl₃)

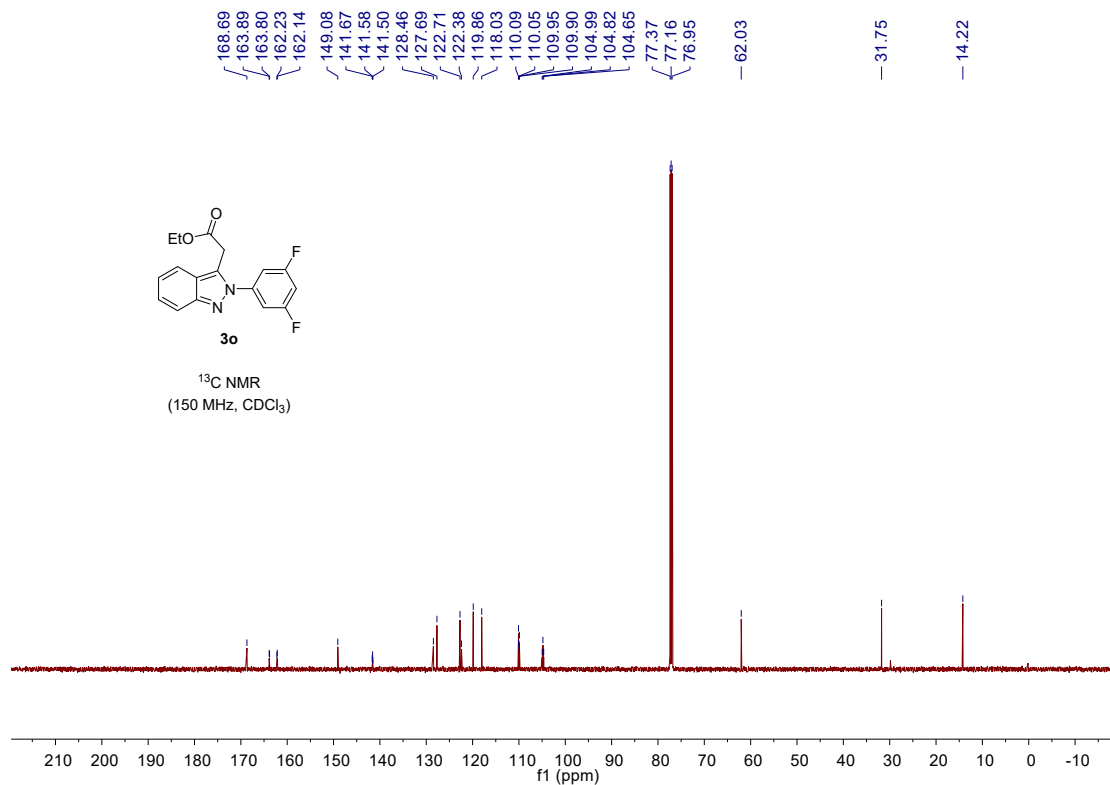
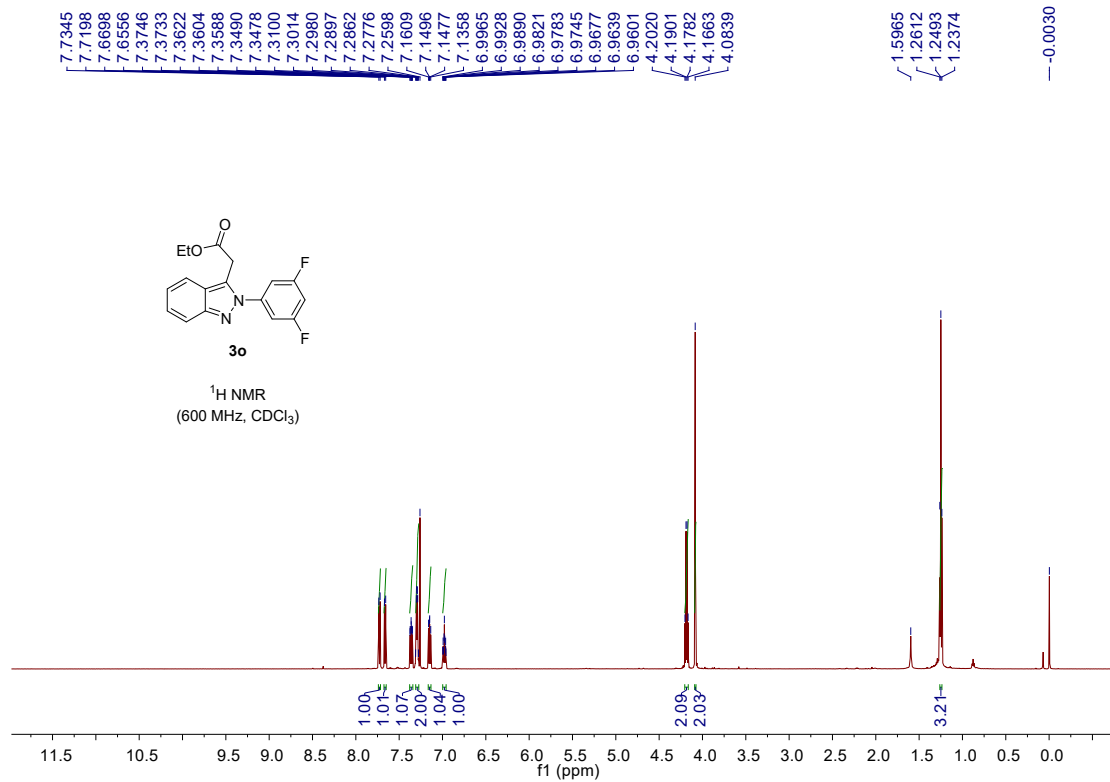


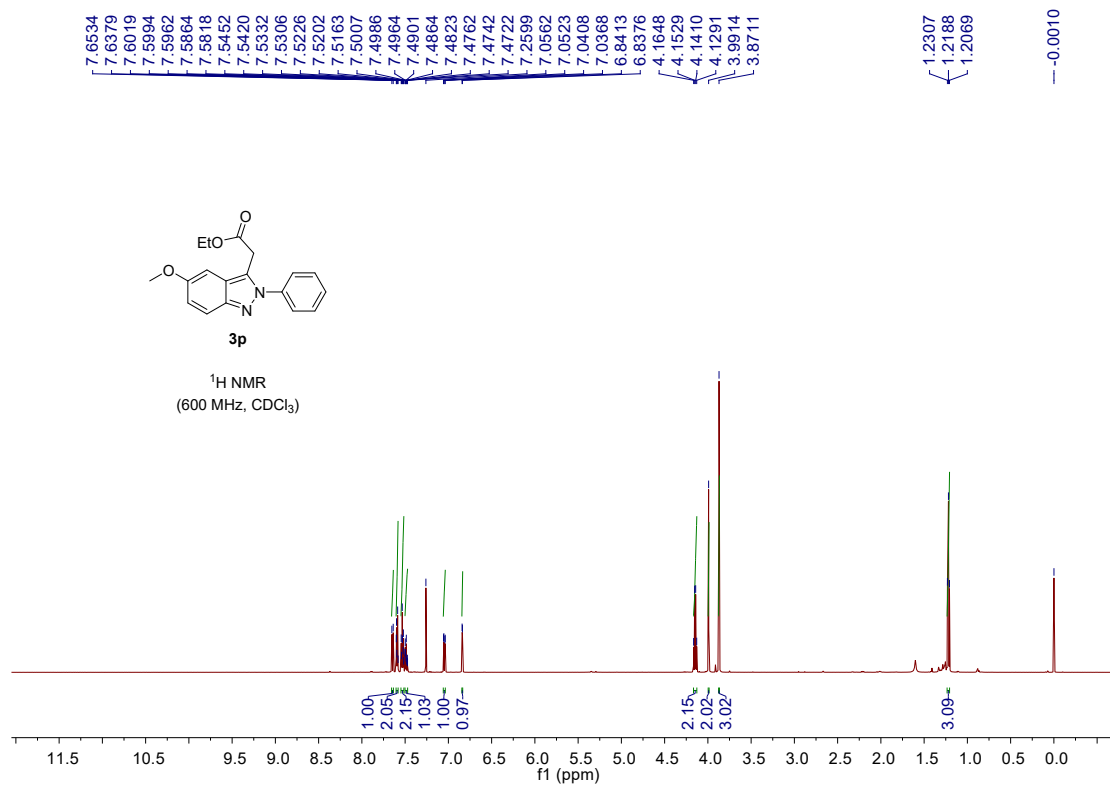
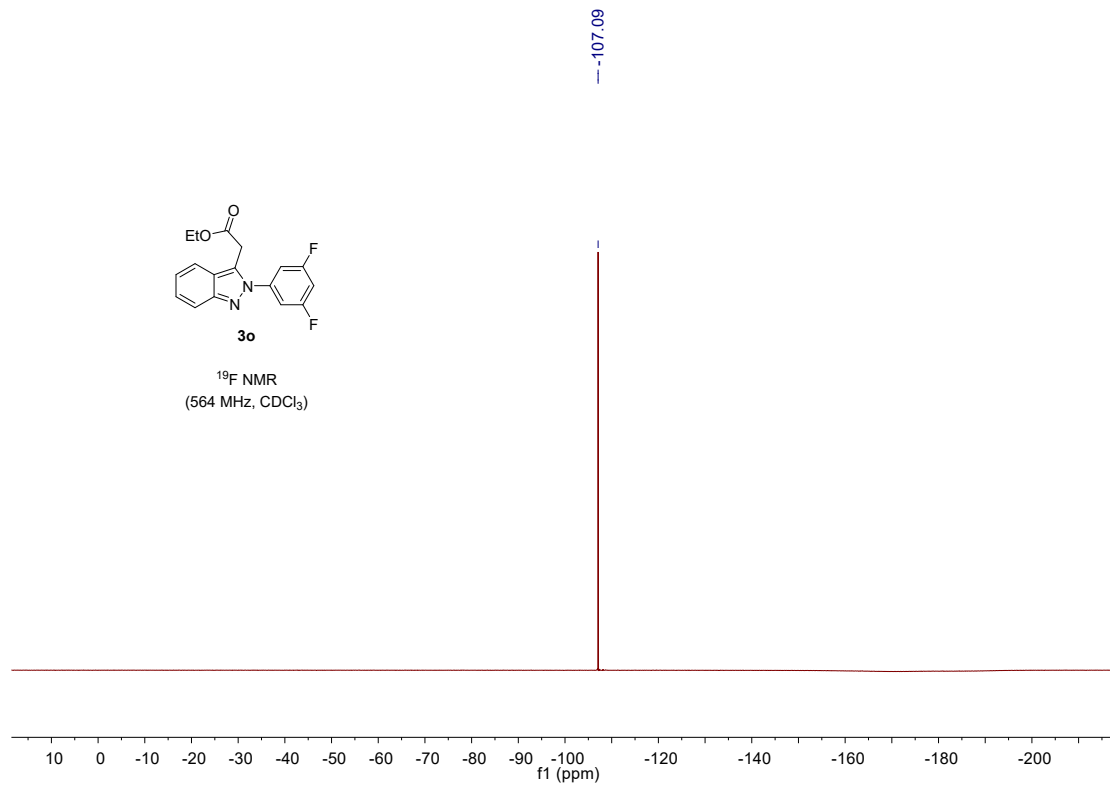
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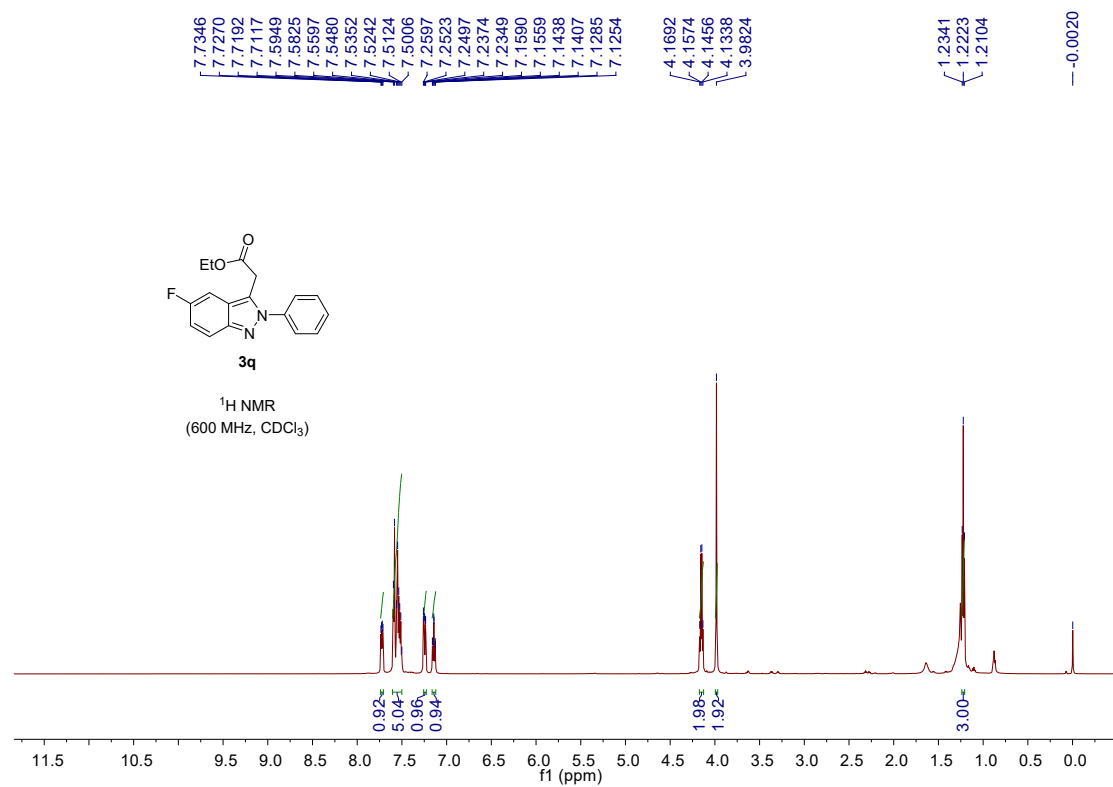
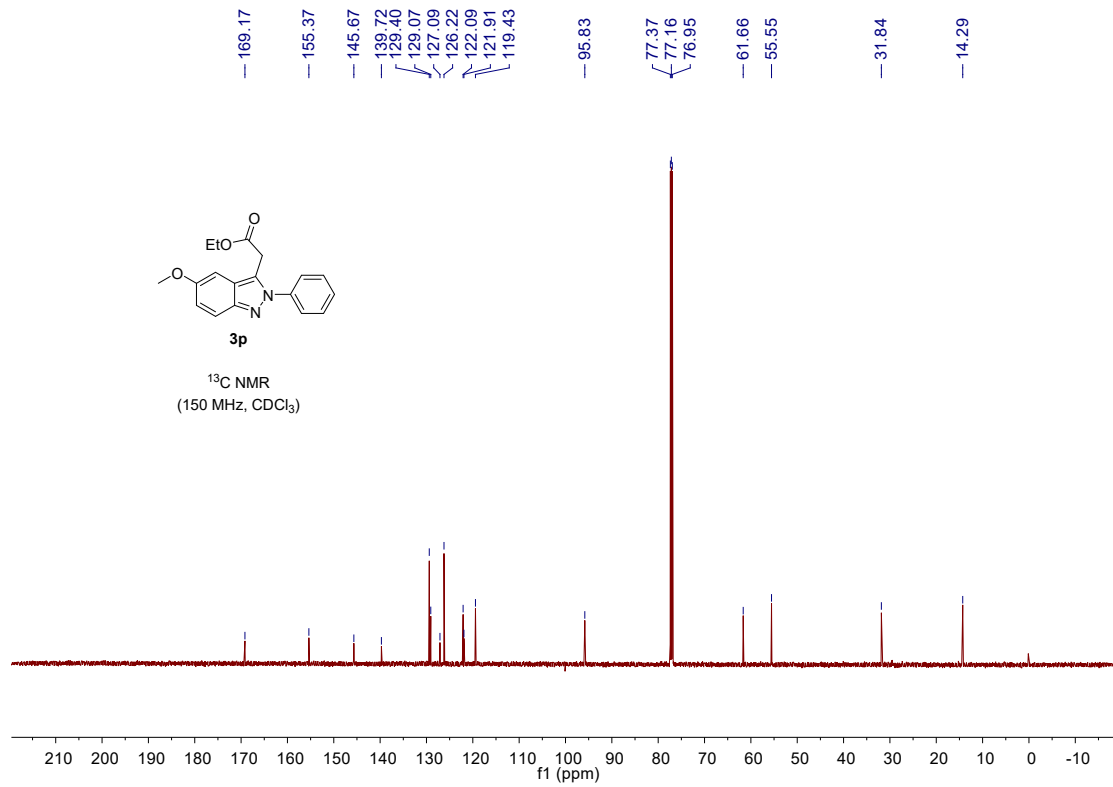


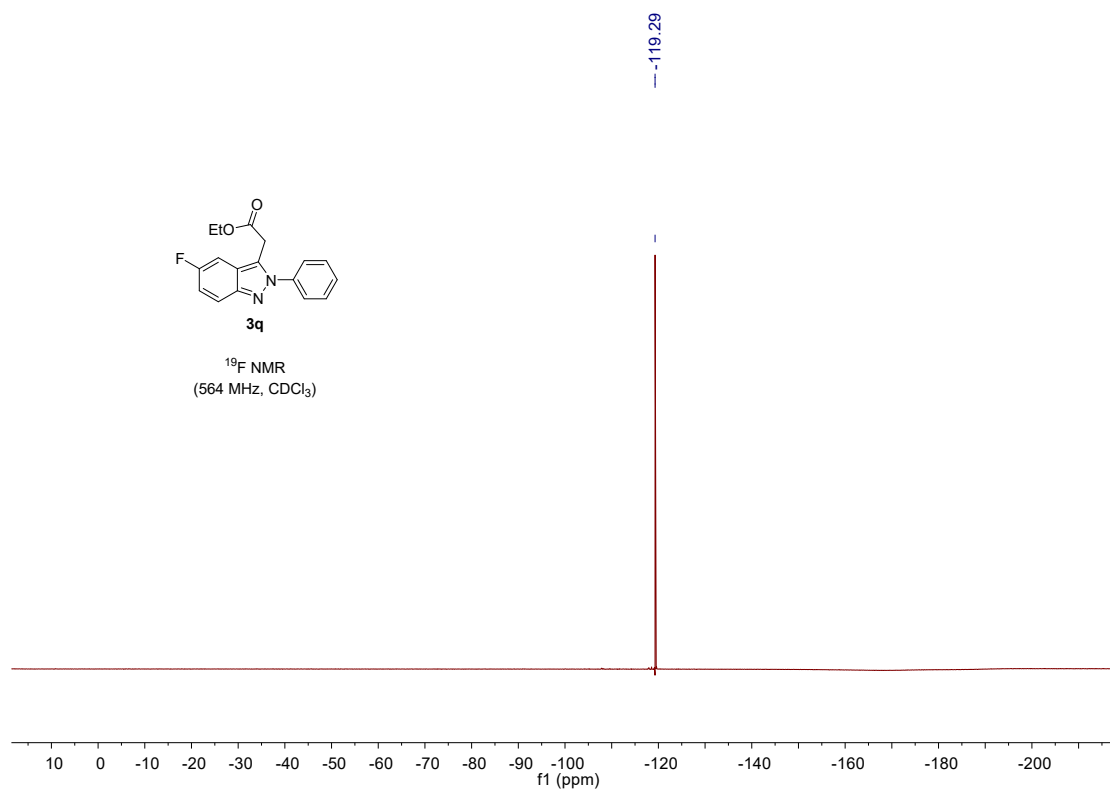
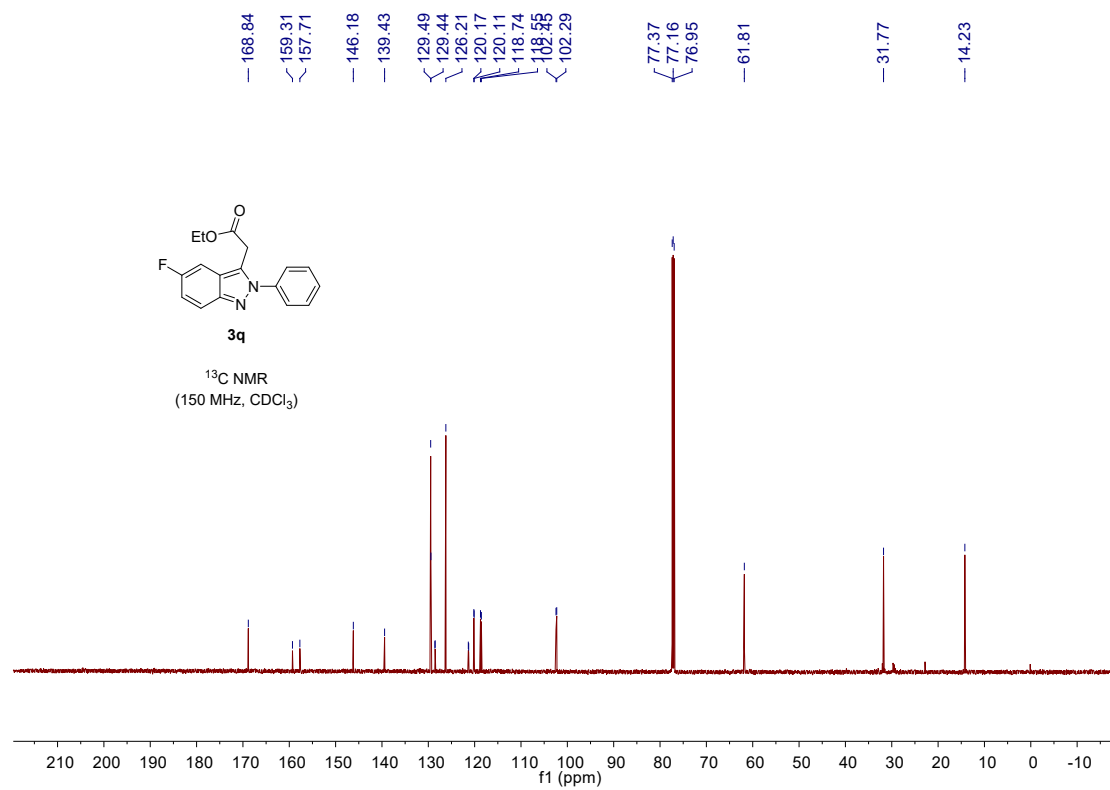
¹⁹F NMR
(564 MHz, CDCl₃)

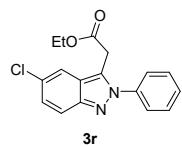




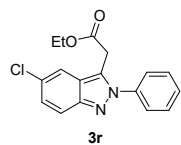
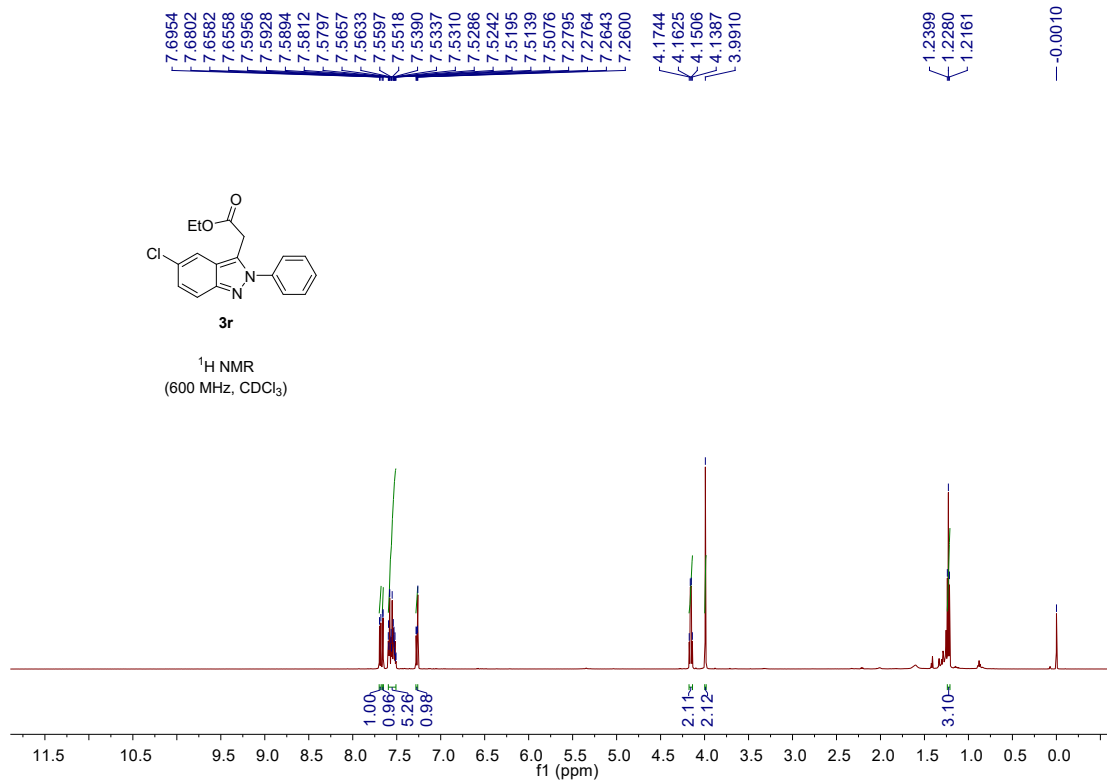




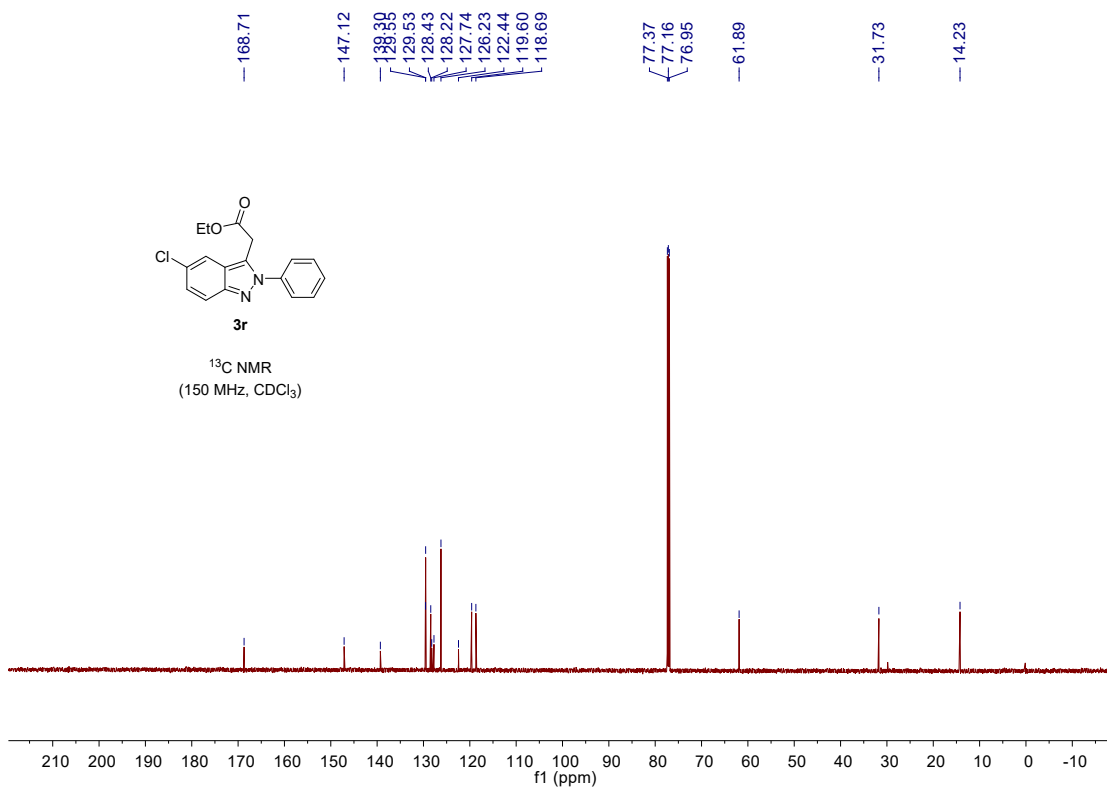


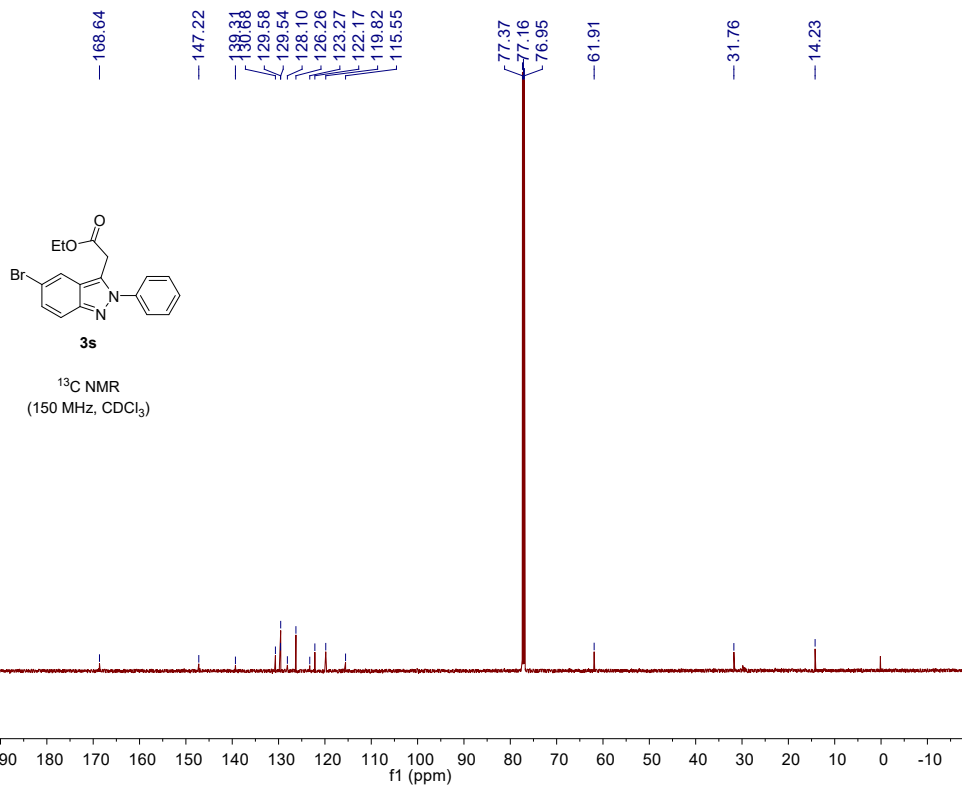
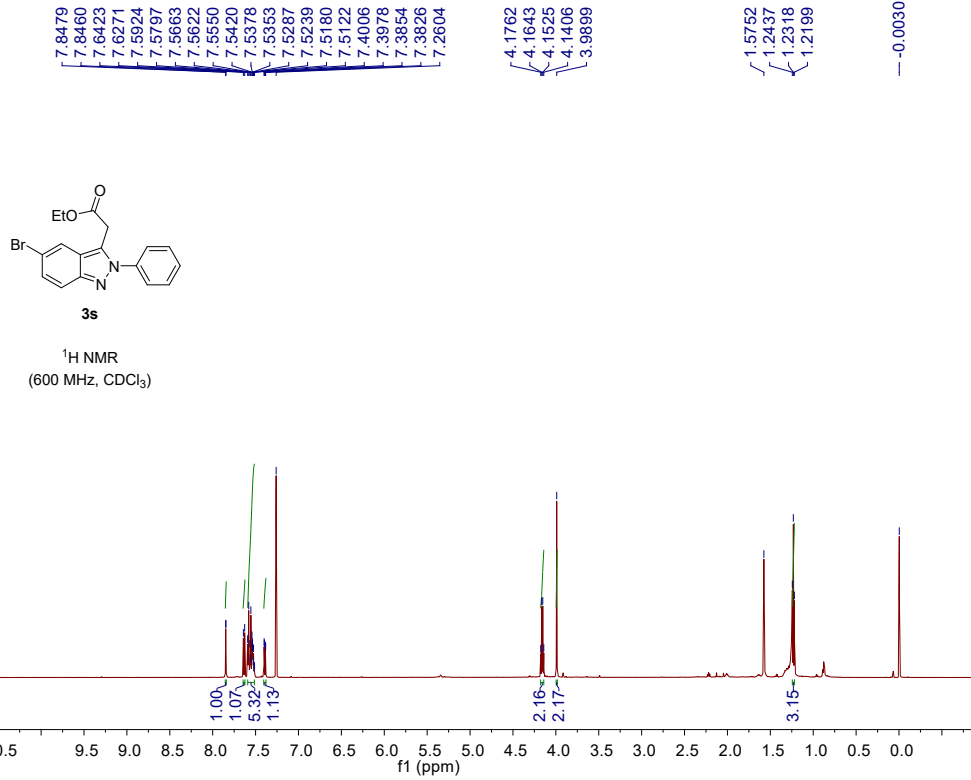


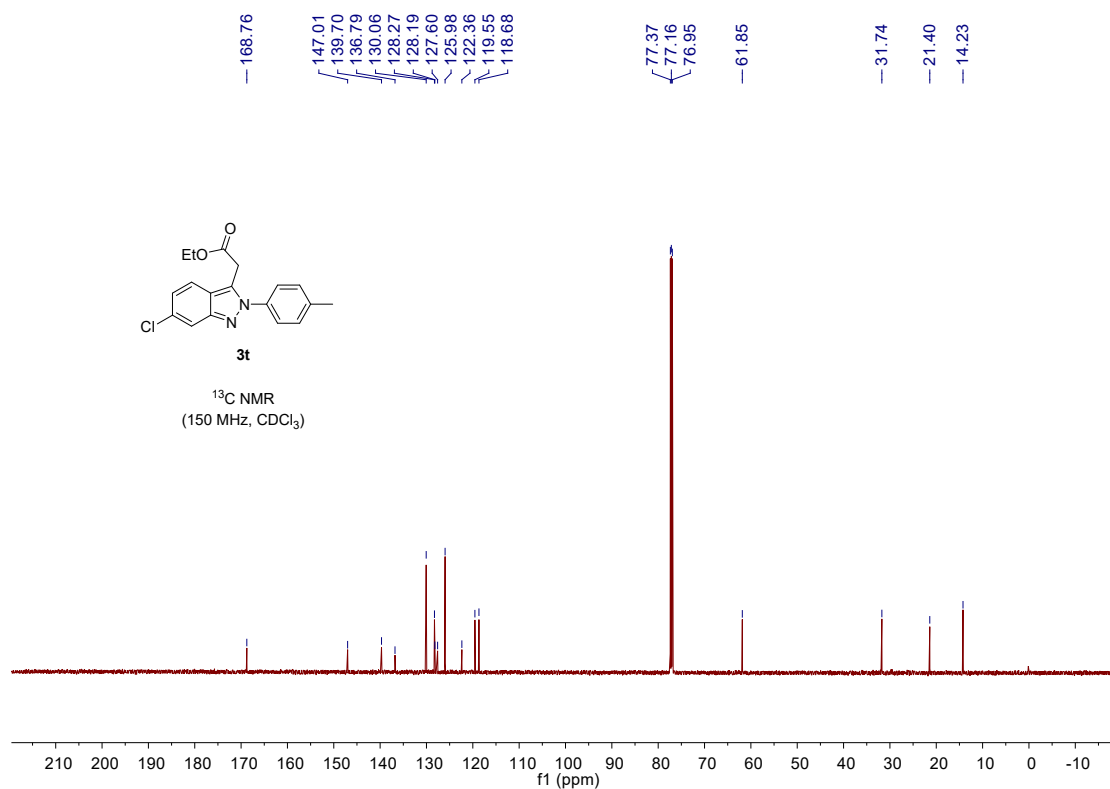
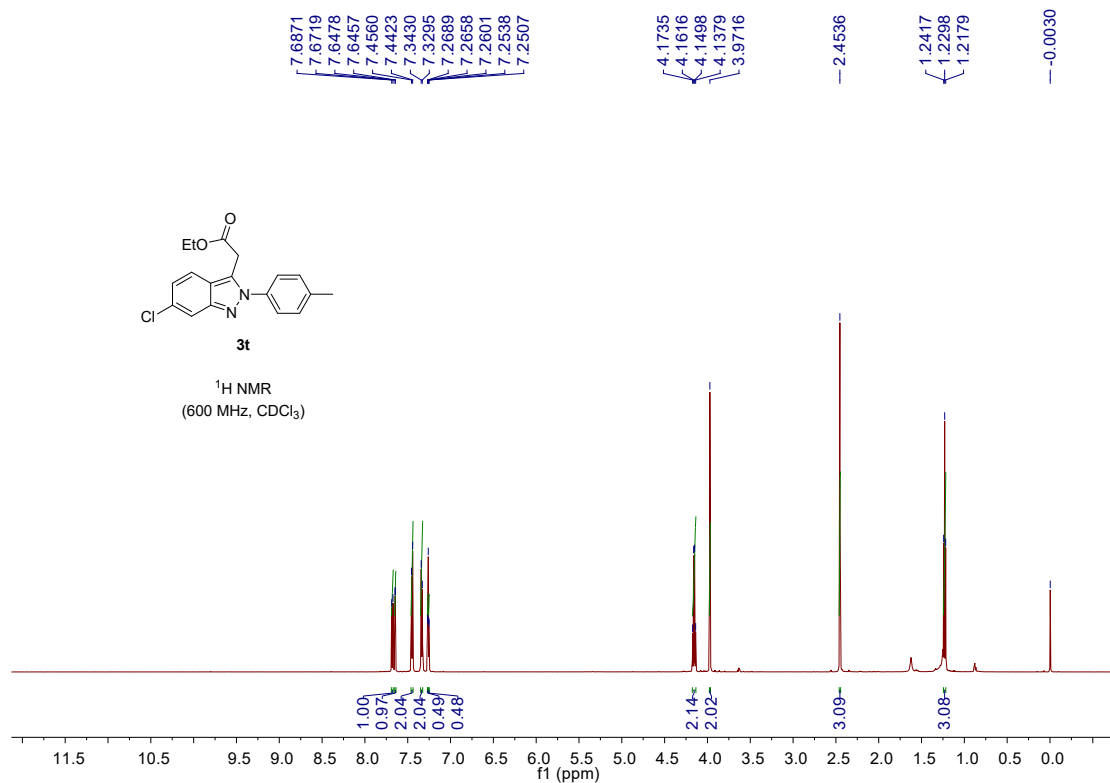
¹H NMR
(600 MHz, CDCl₃)

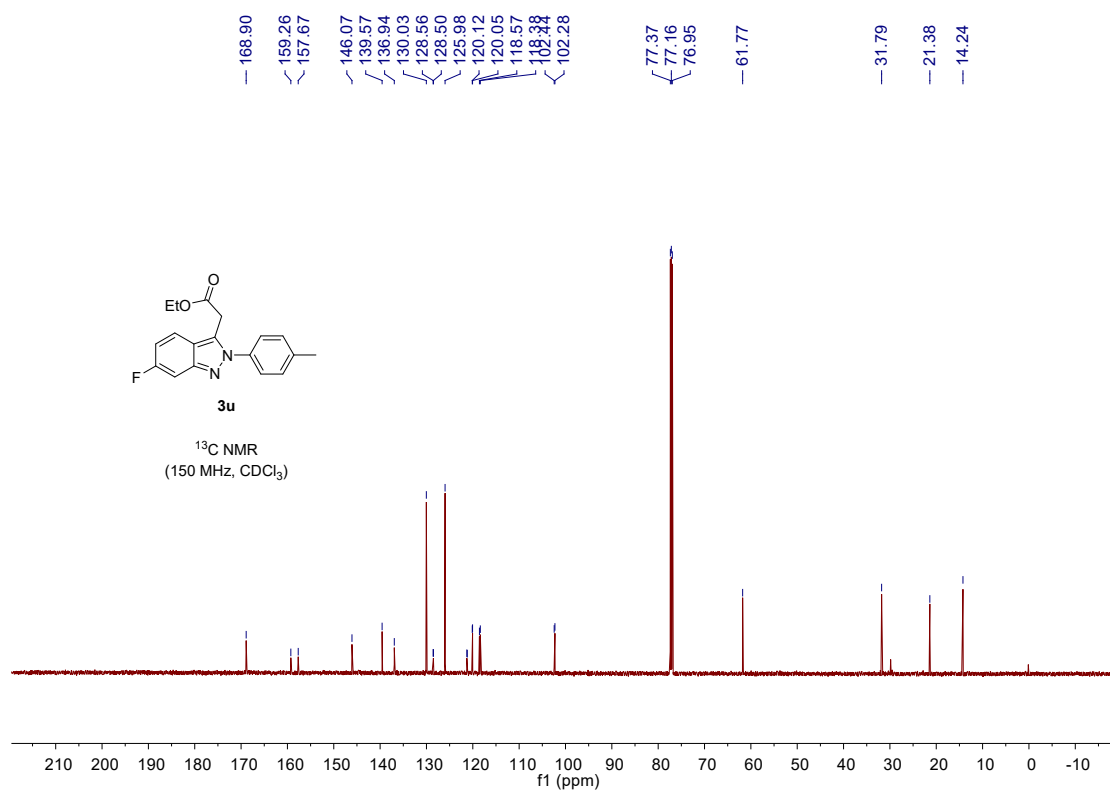
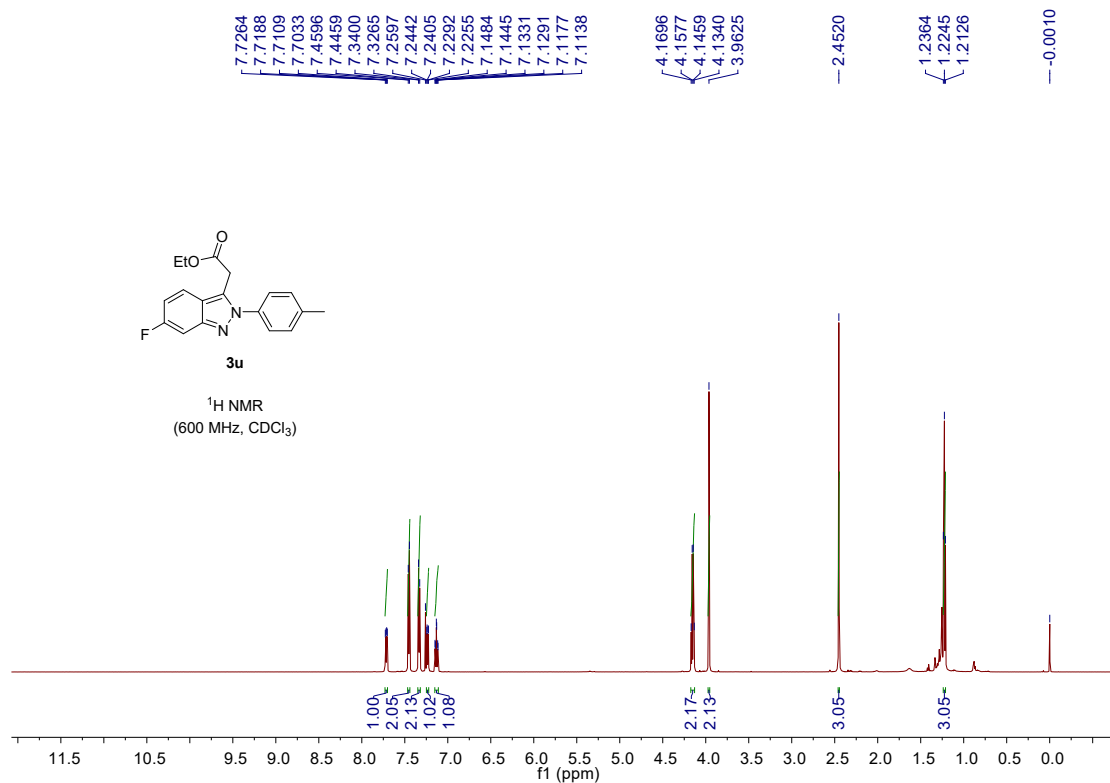


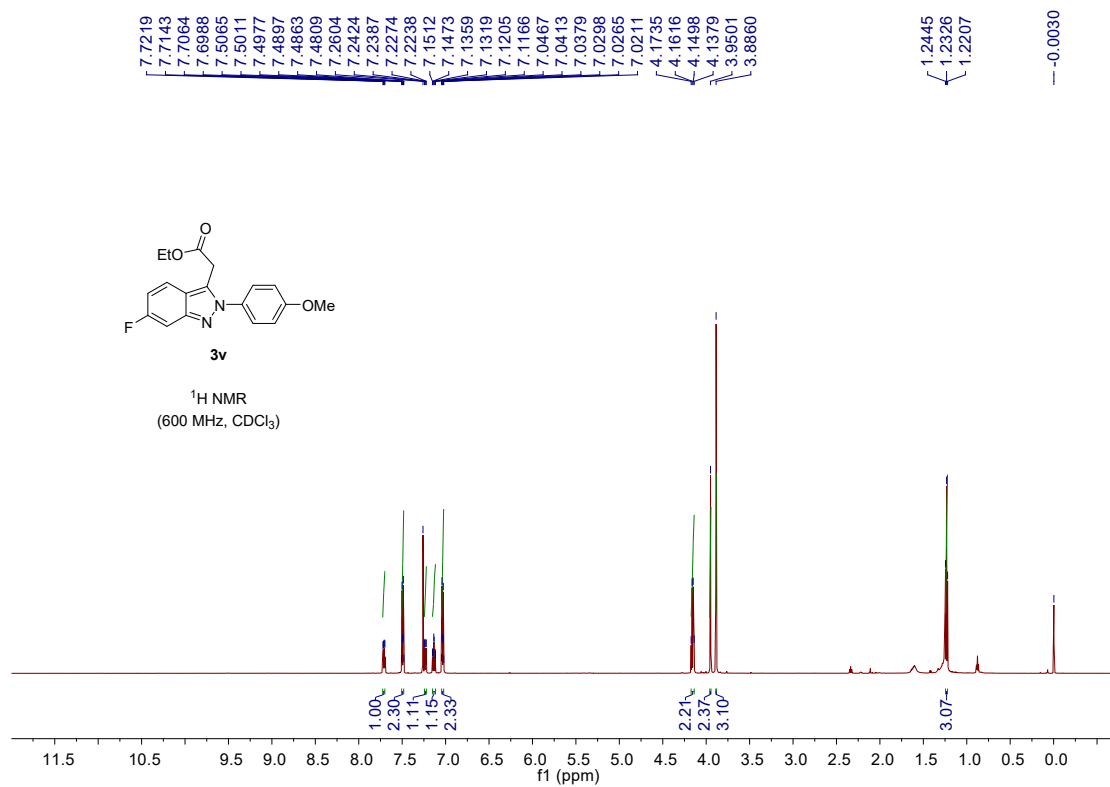
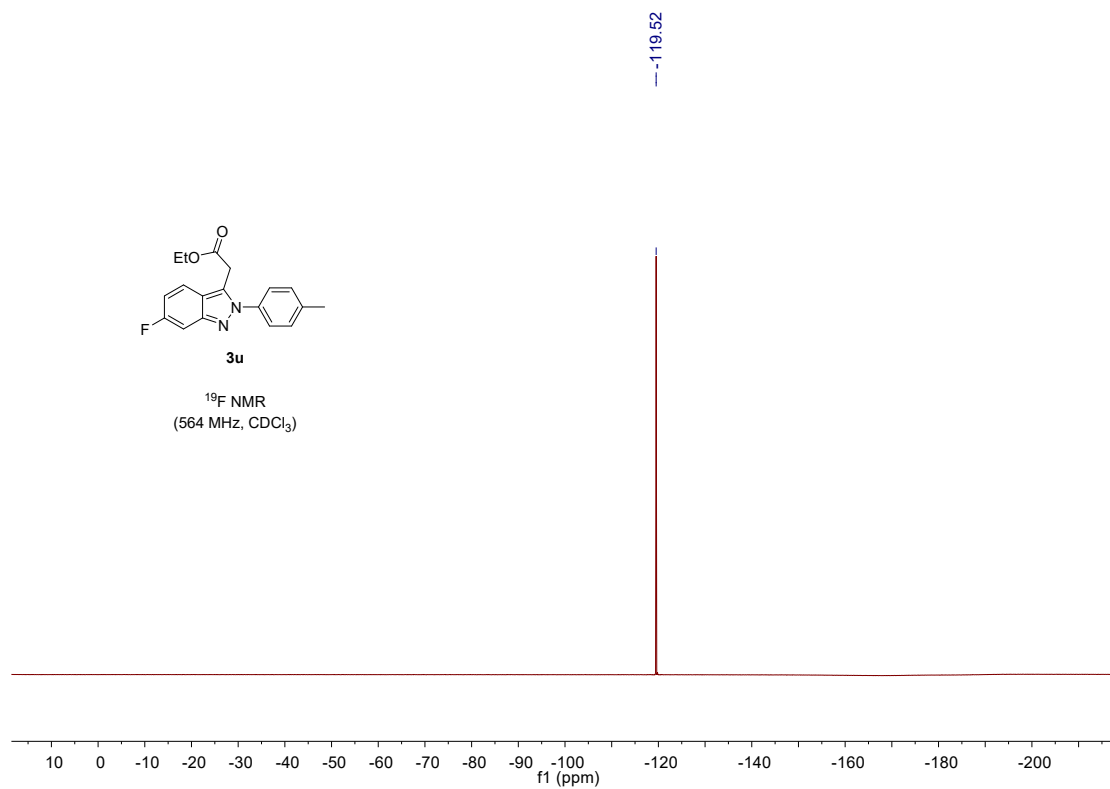
¹³C NMR
(150 MHz, CDCl₃)

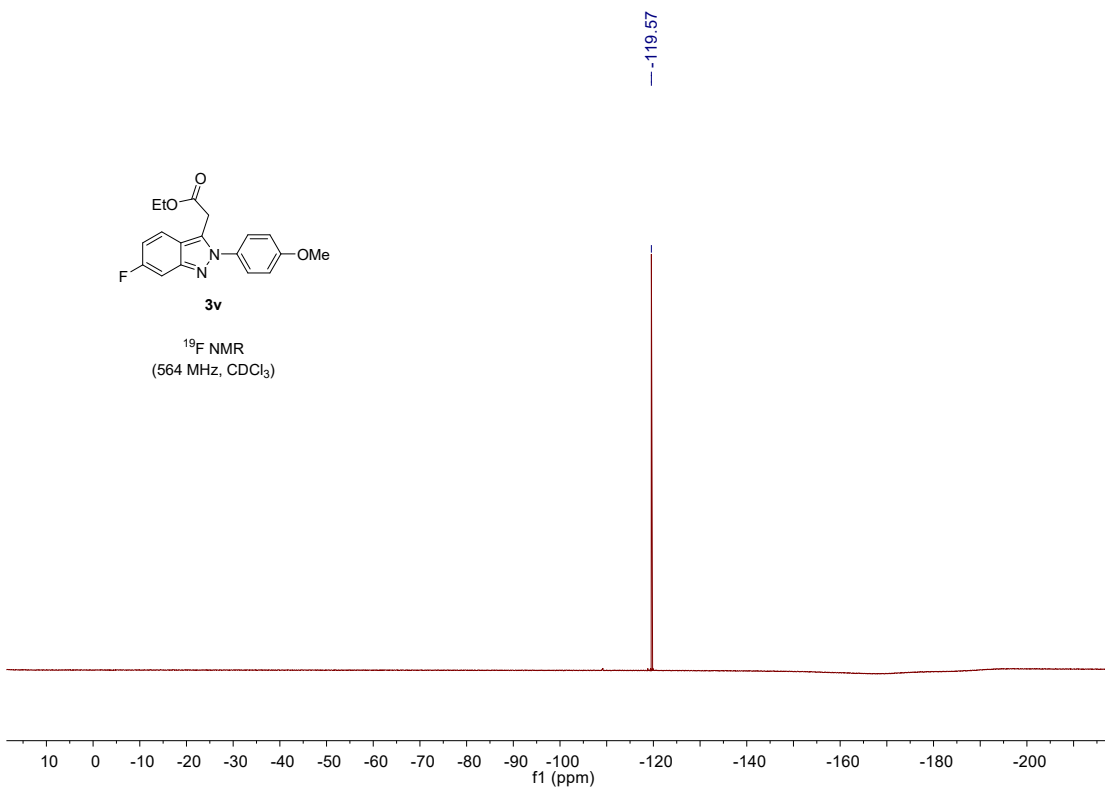
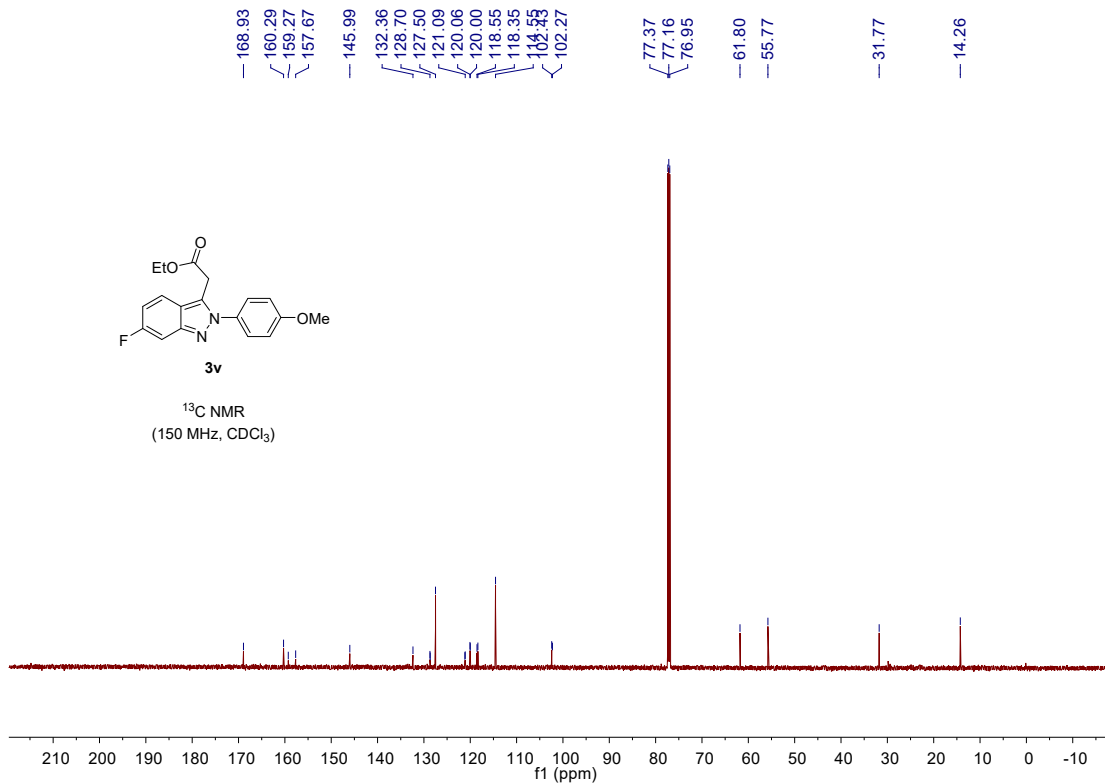


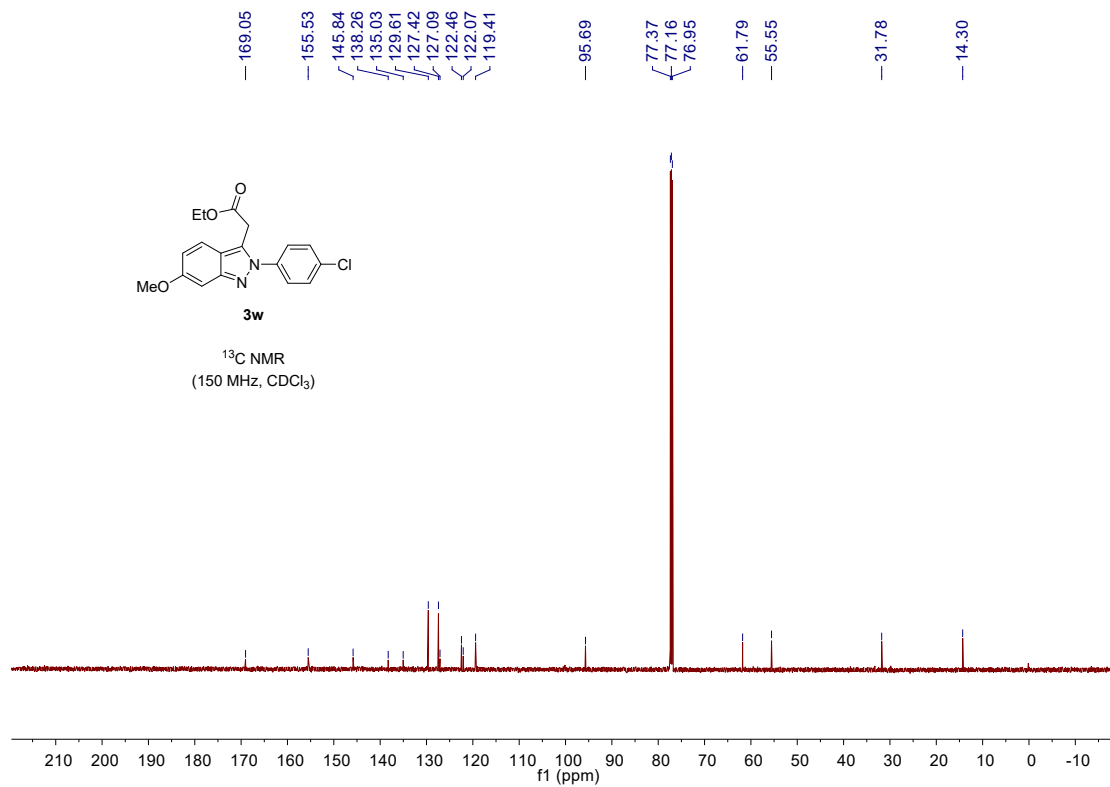
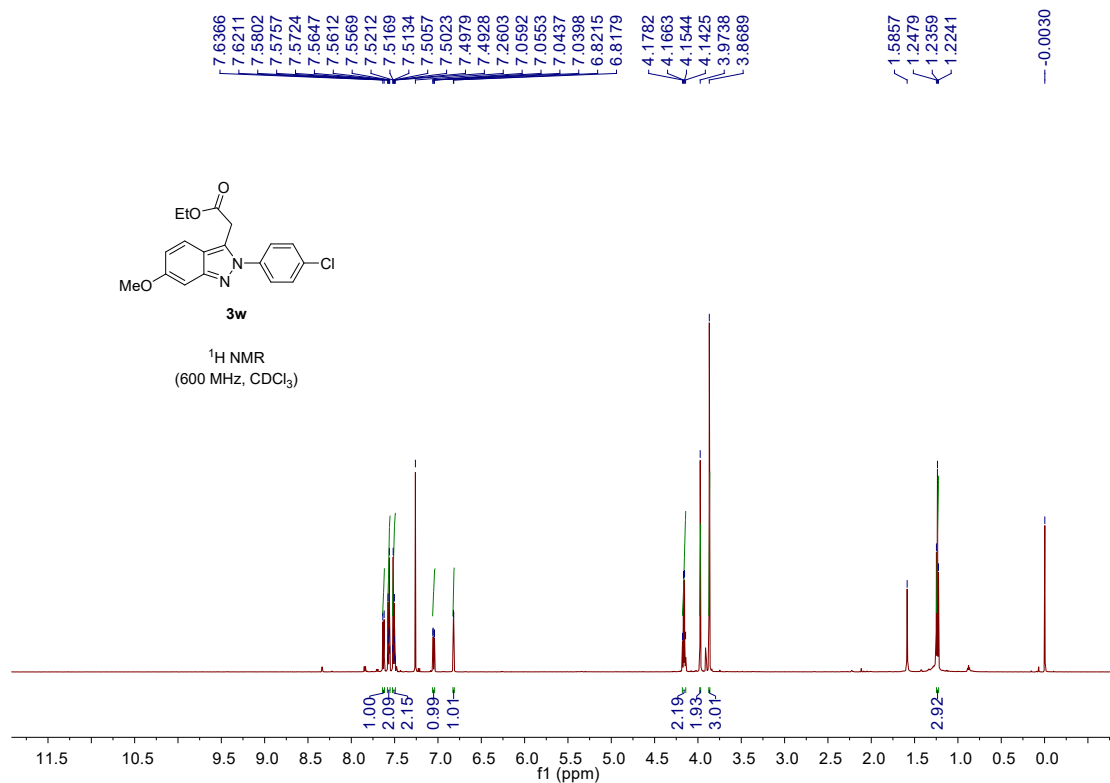


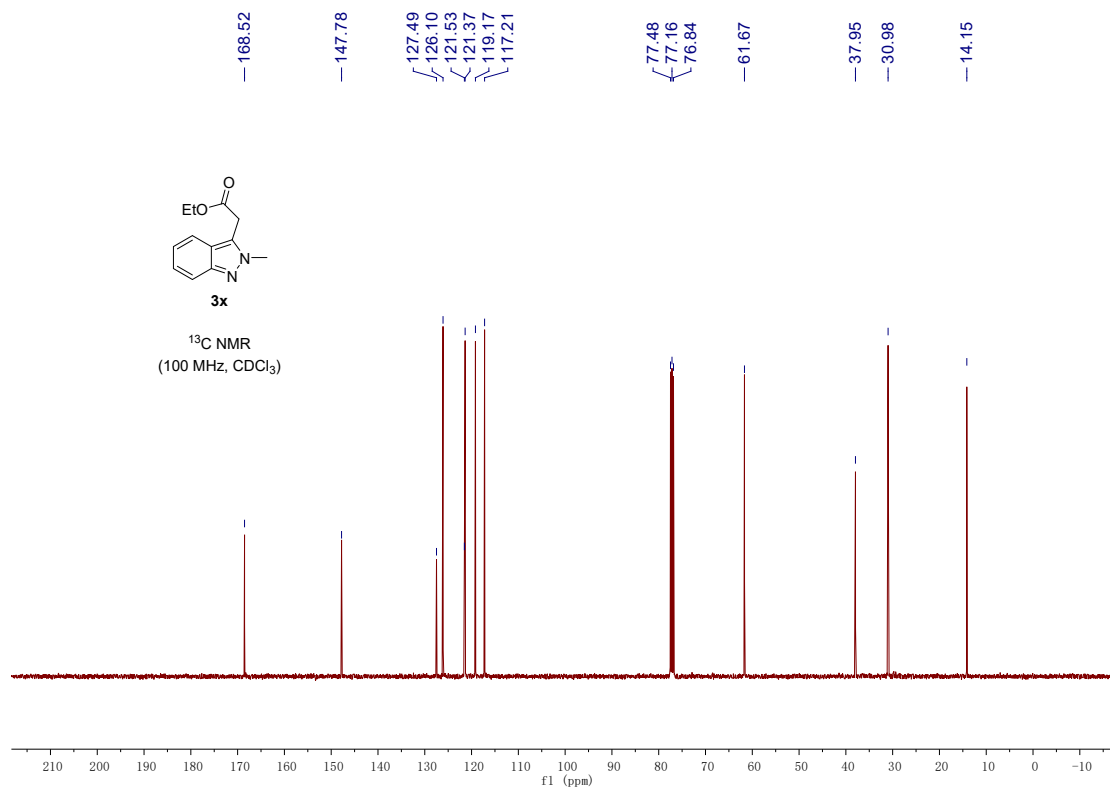
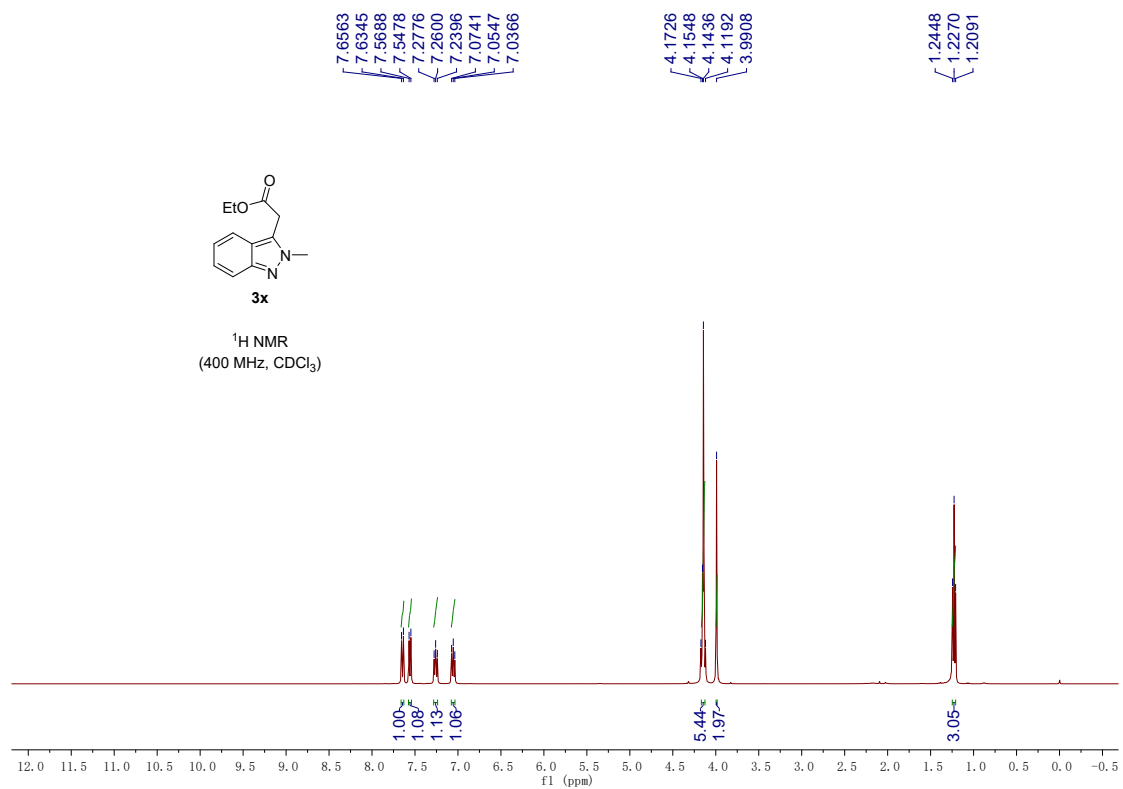


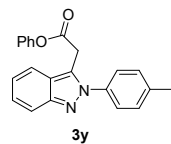




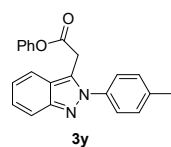
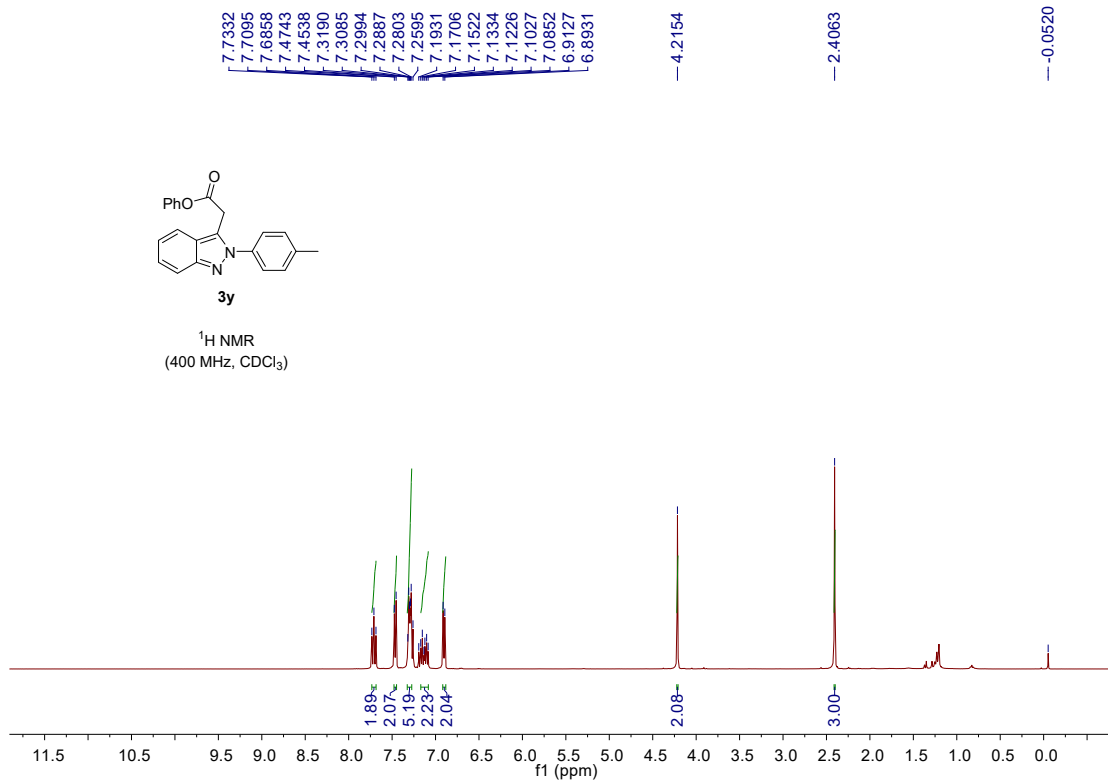




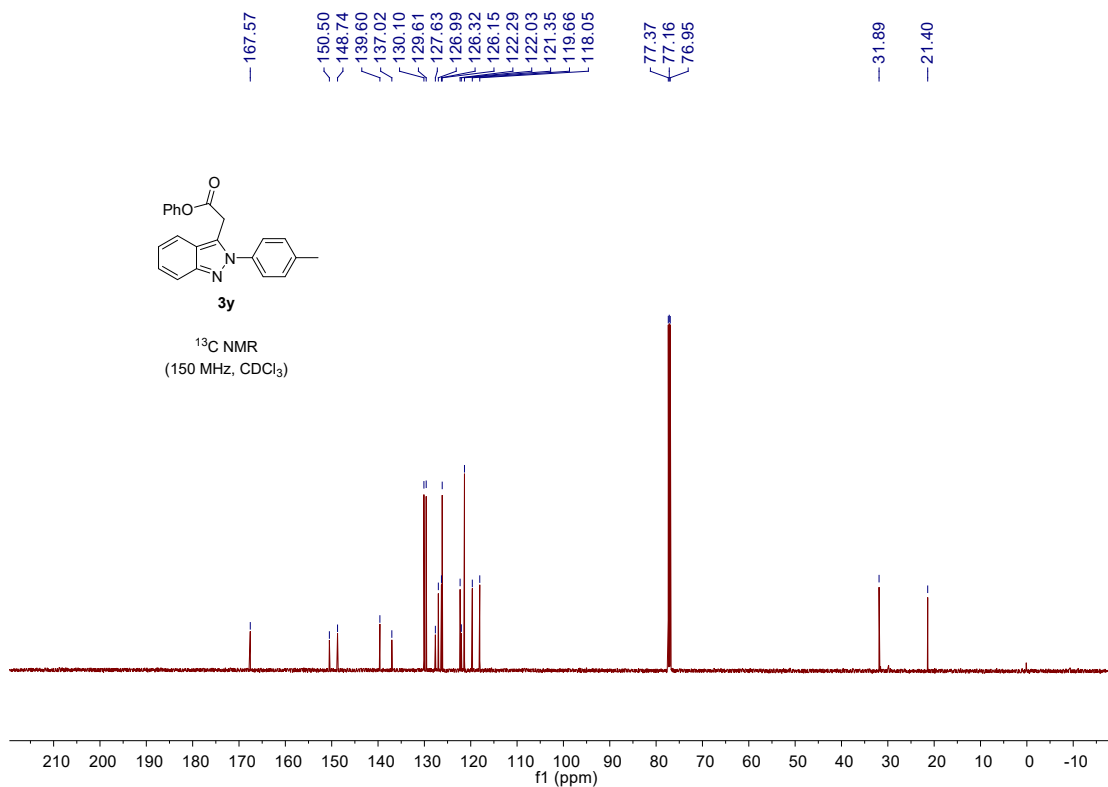


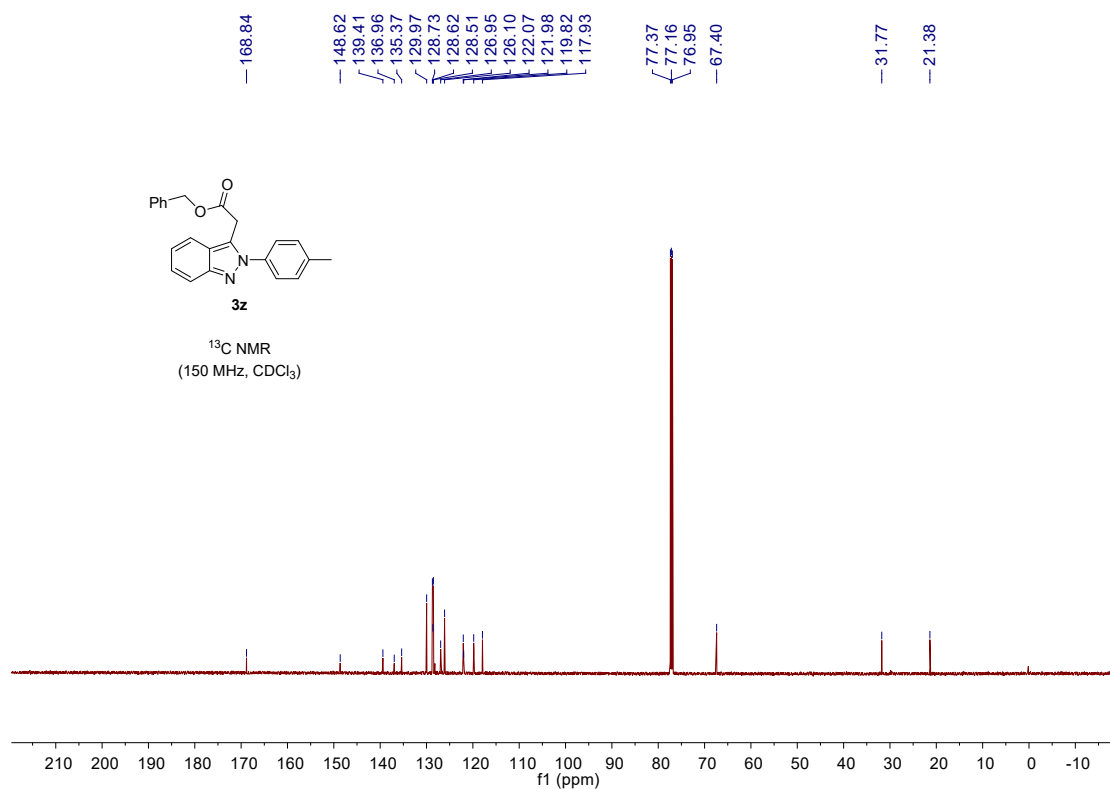
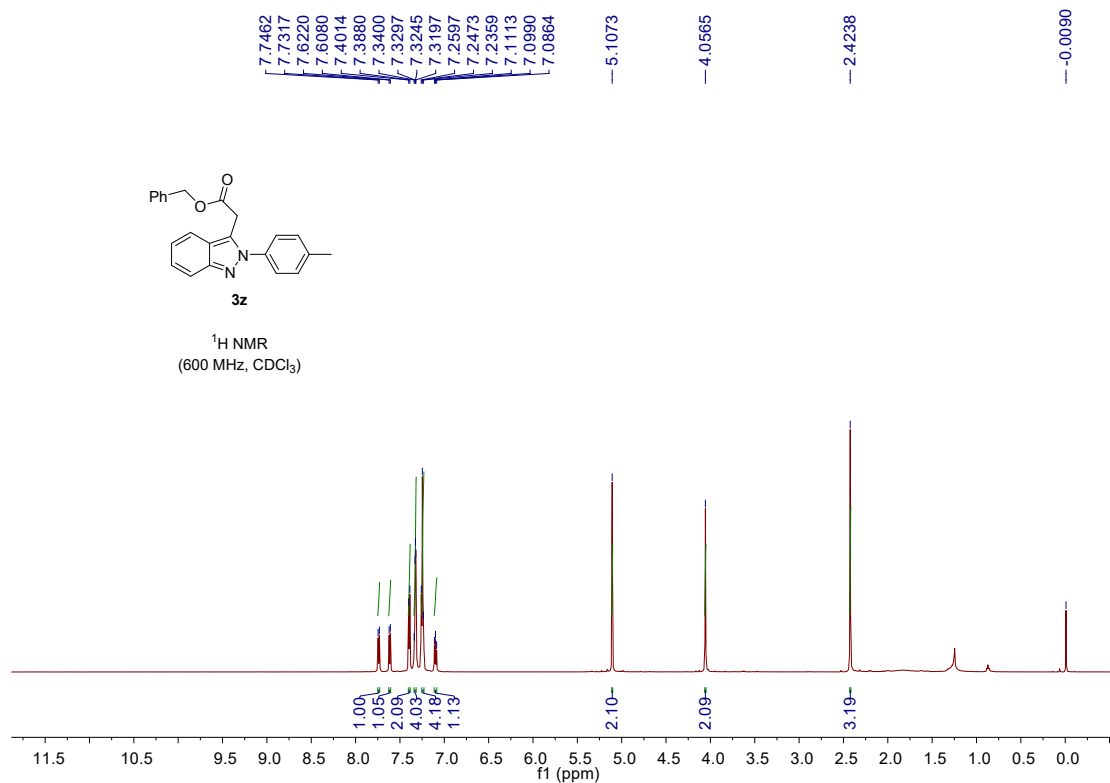


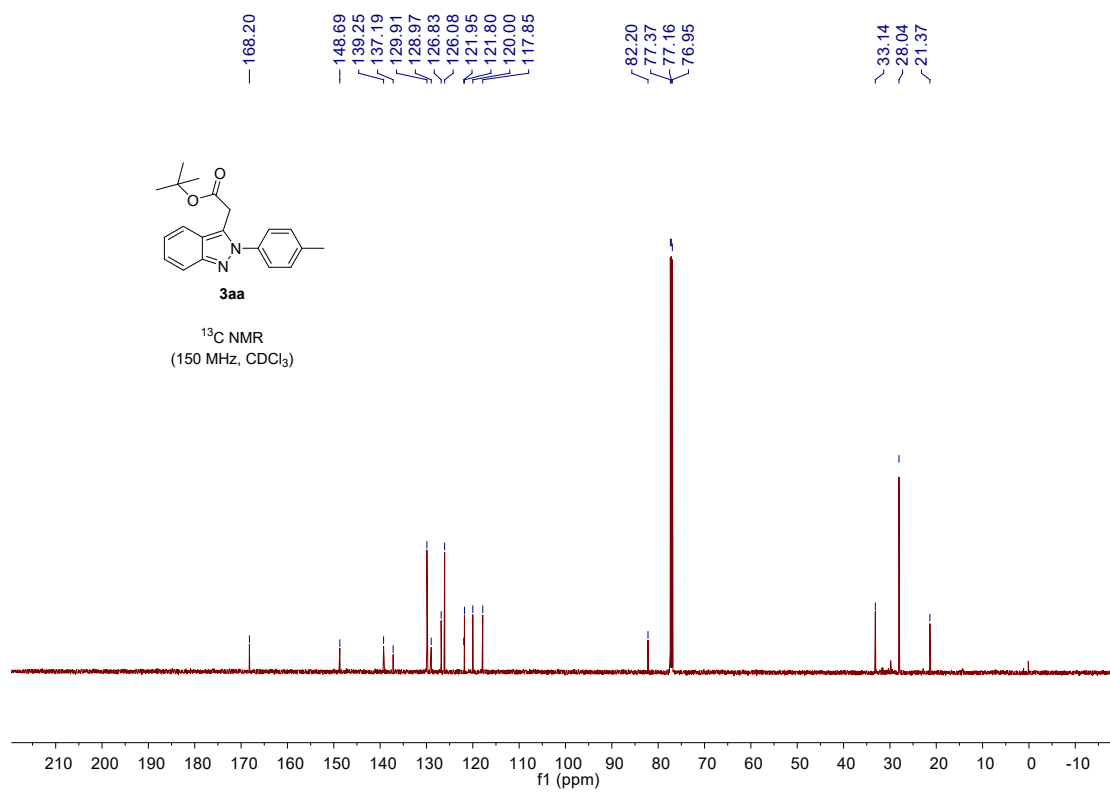
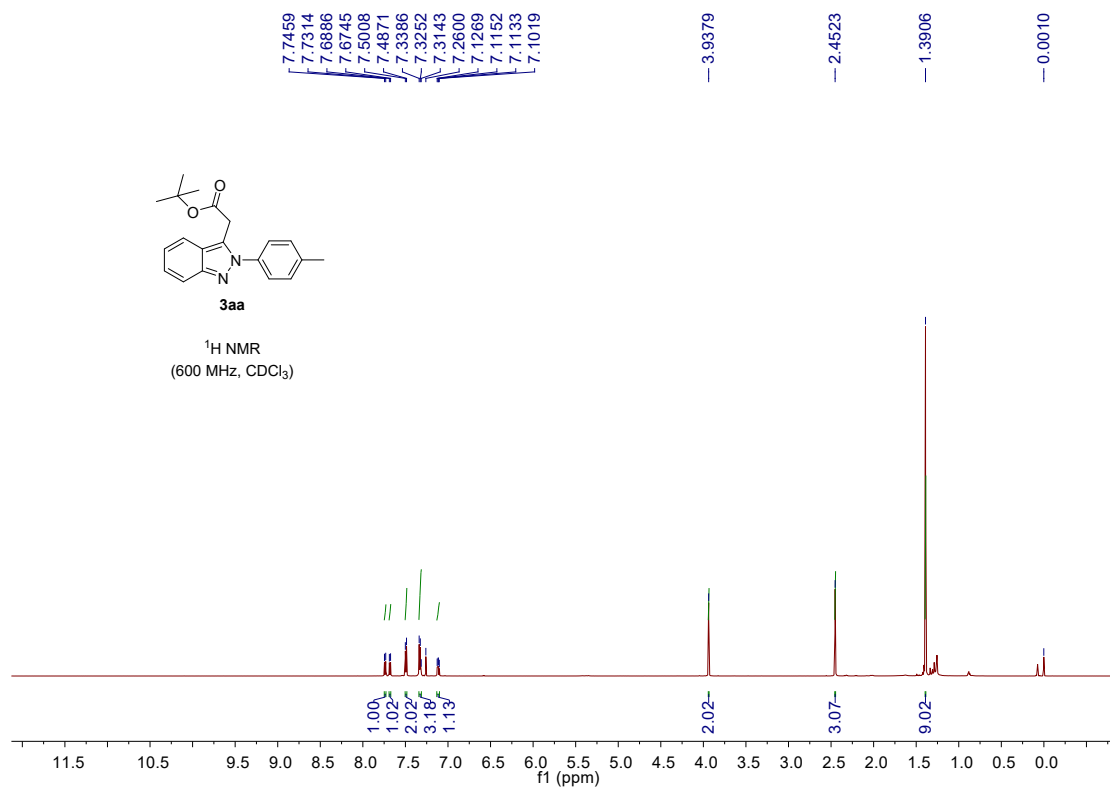
¹H NMR
(400 MHz, CDCl₃)



¹³C NMR
(150 MHz, CDCl₃)

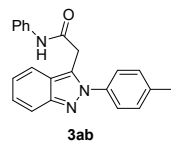




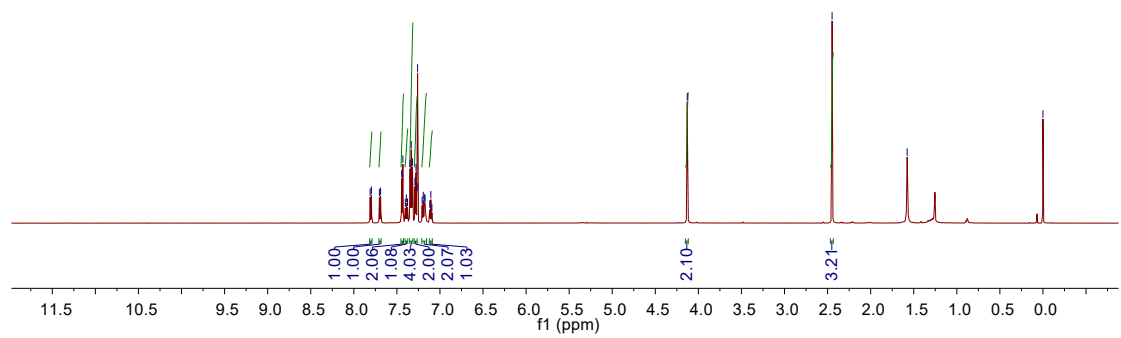


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7.7959
7.7029
7.6888
7.4442
7.4306
7.4018
7.3903
7.3763
7.3467
7.3331
7.3196
7.2904
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7.1937
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7.1727
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7.1057
7.0936

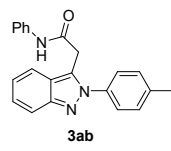
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2.4478
1.5763
0.0000



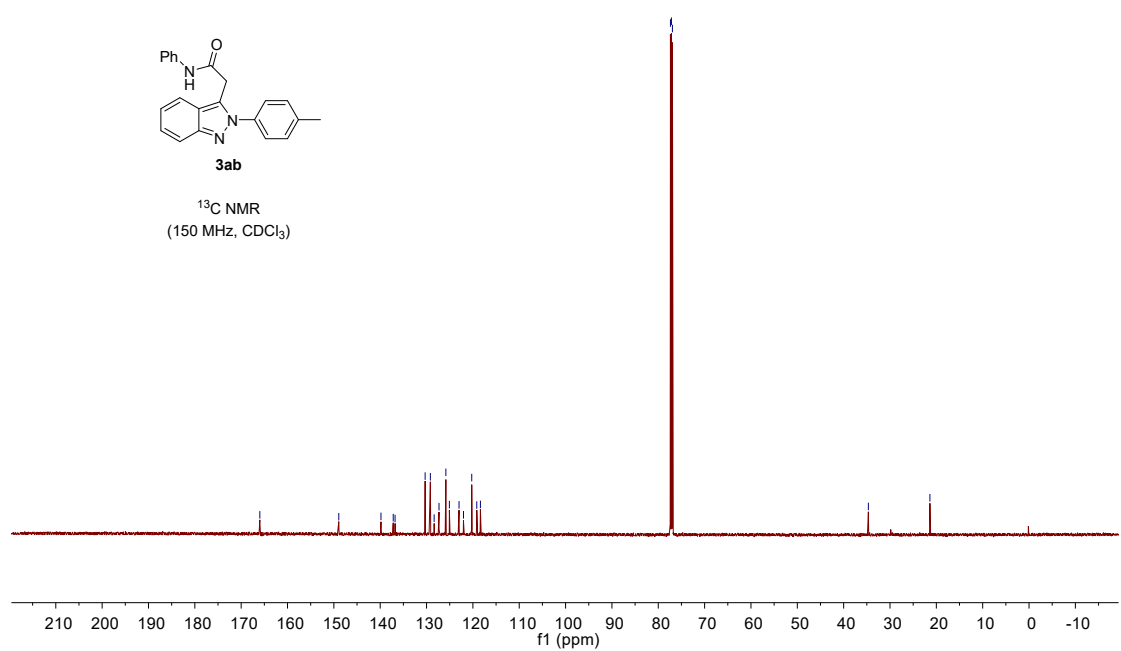
¹H NMR
(600 MHz, CDCl₃)

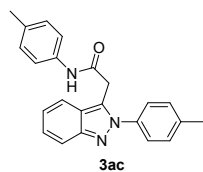


165.97
148.94
139.84
137.19
136.79
130.30
129.18
128.36
127.31
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21.39

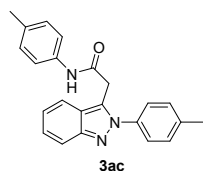
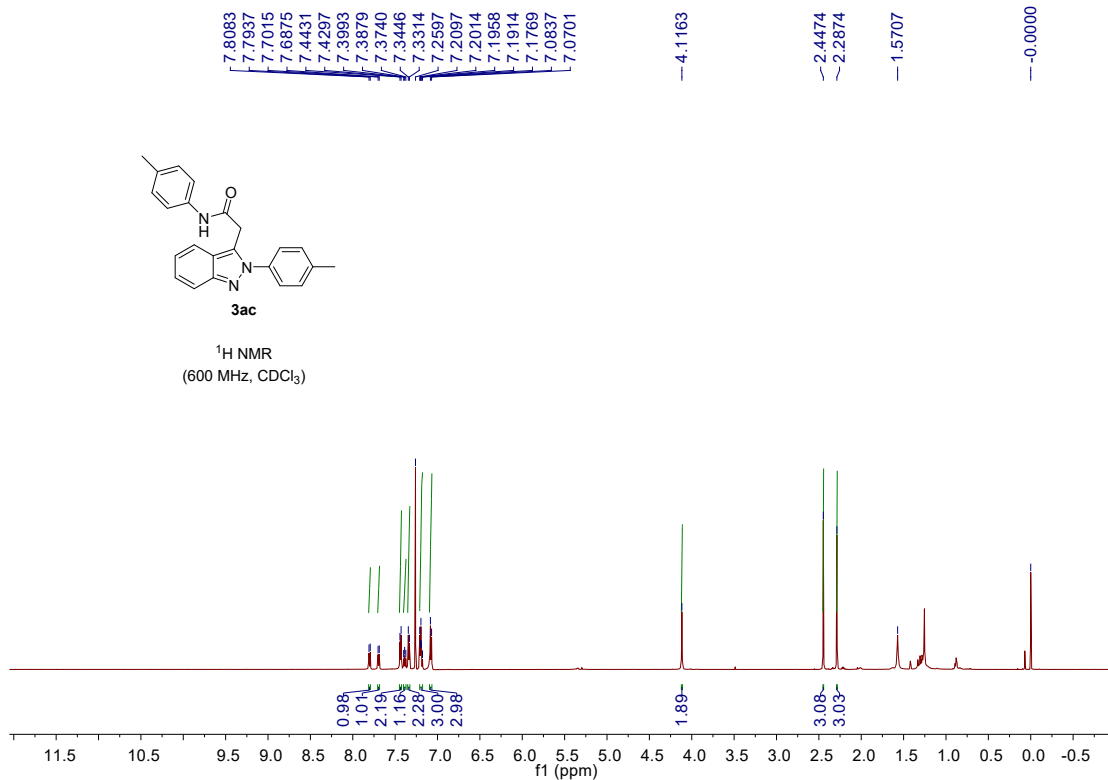


¹³C NMR
(150 MHz, CDCl₃)

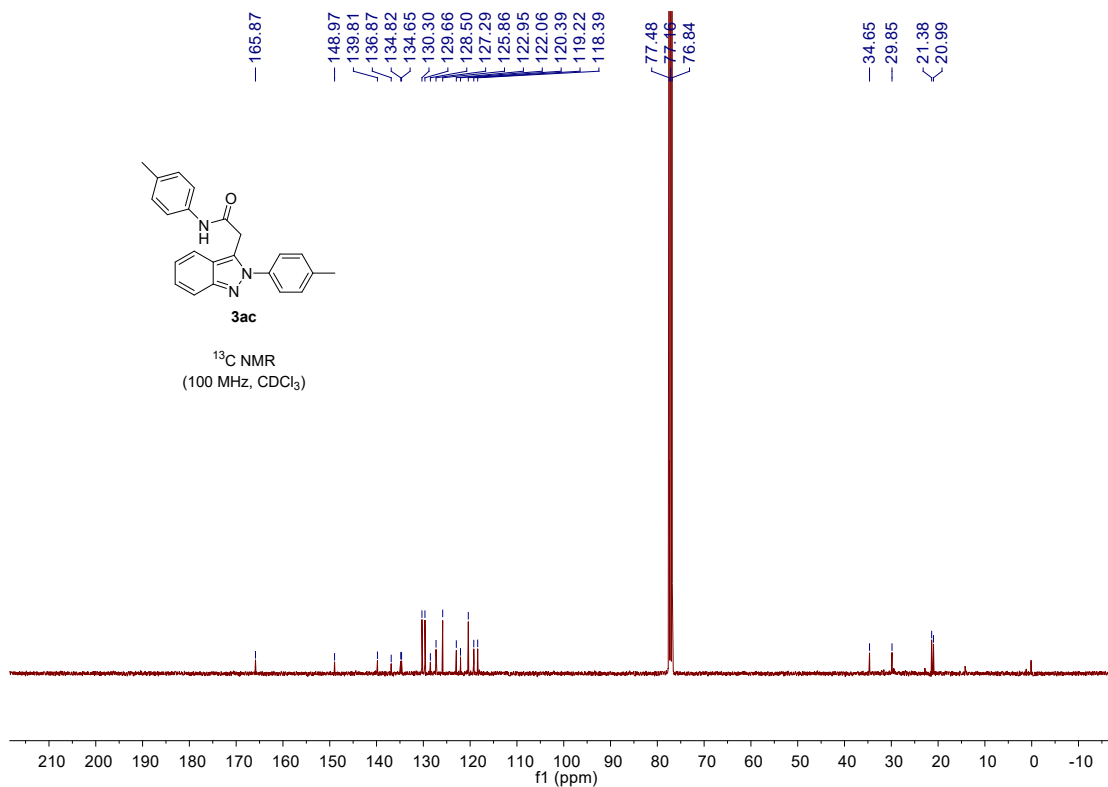


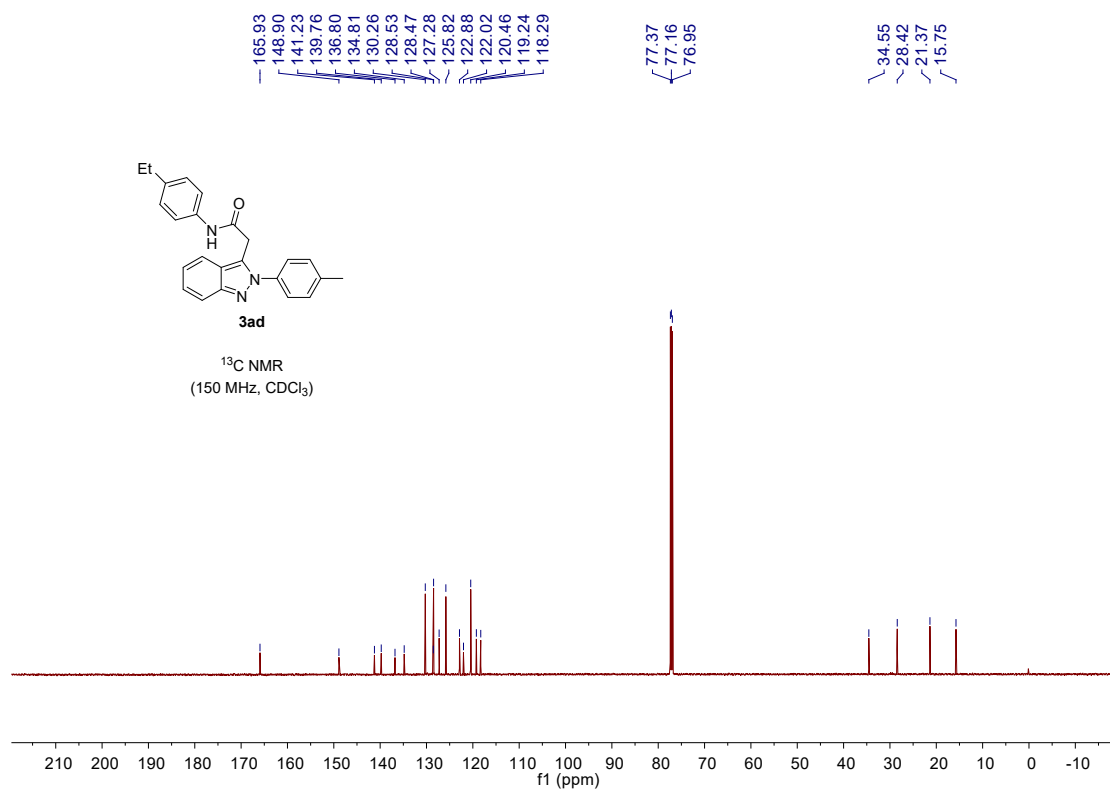
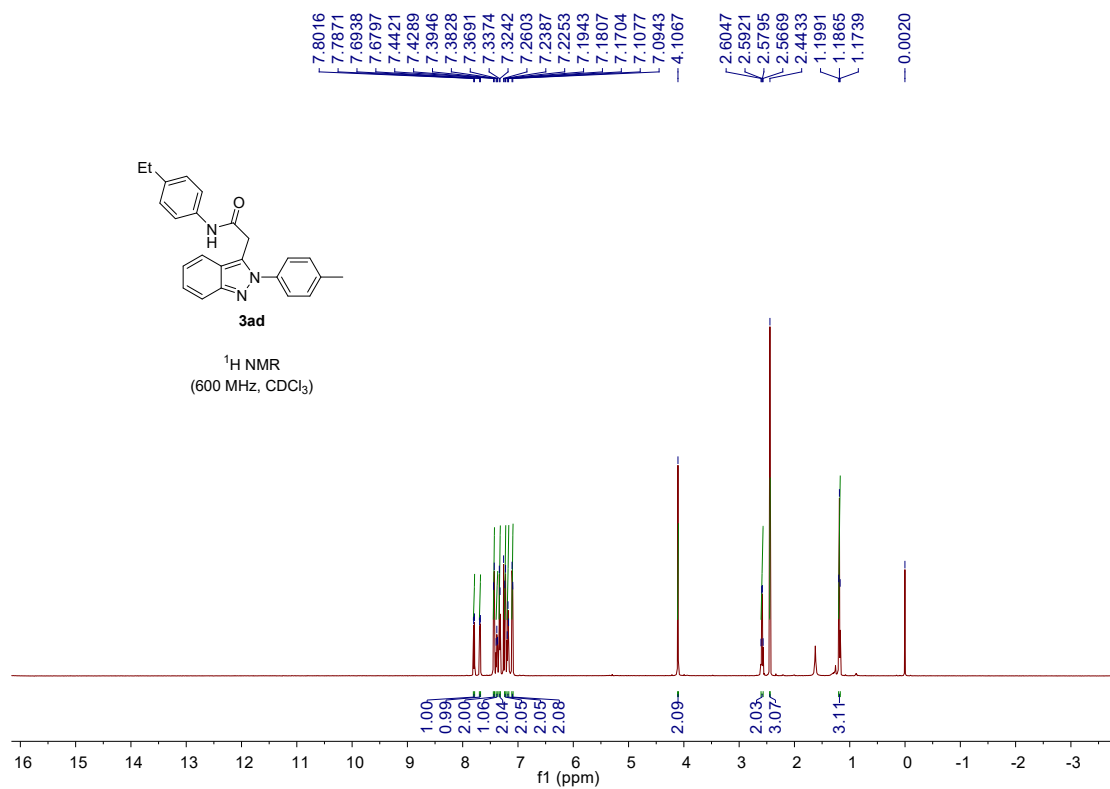


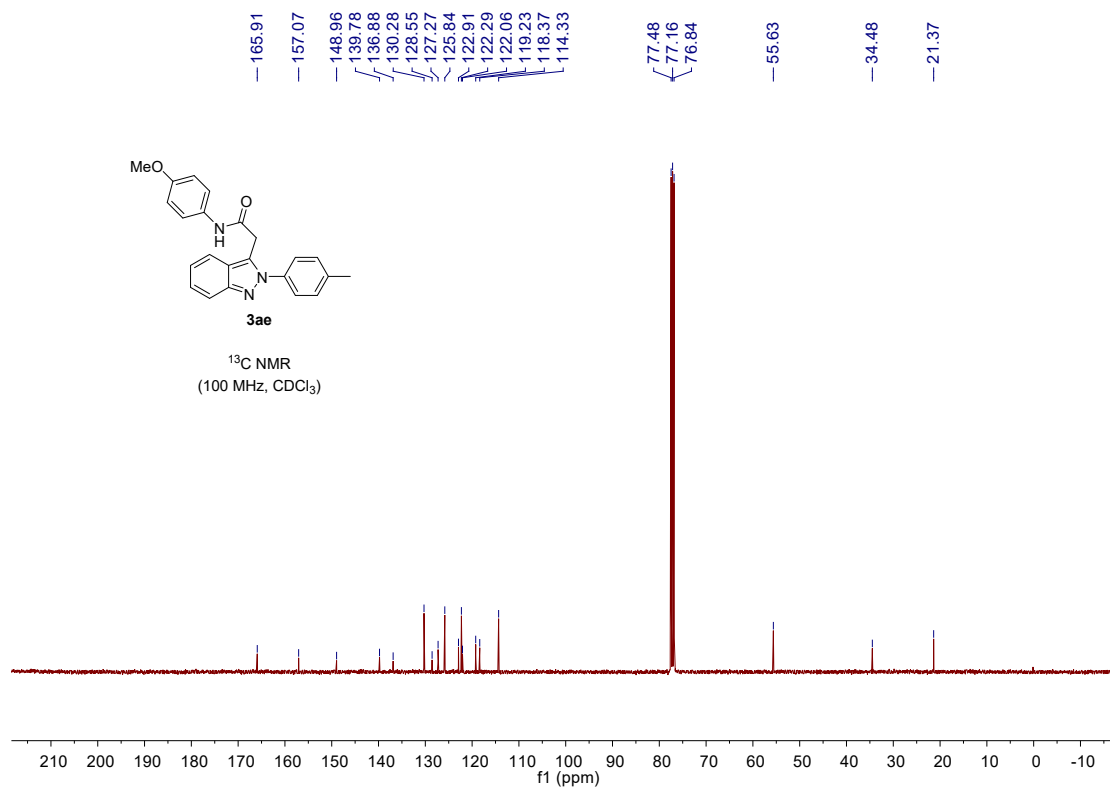
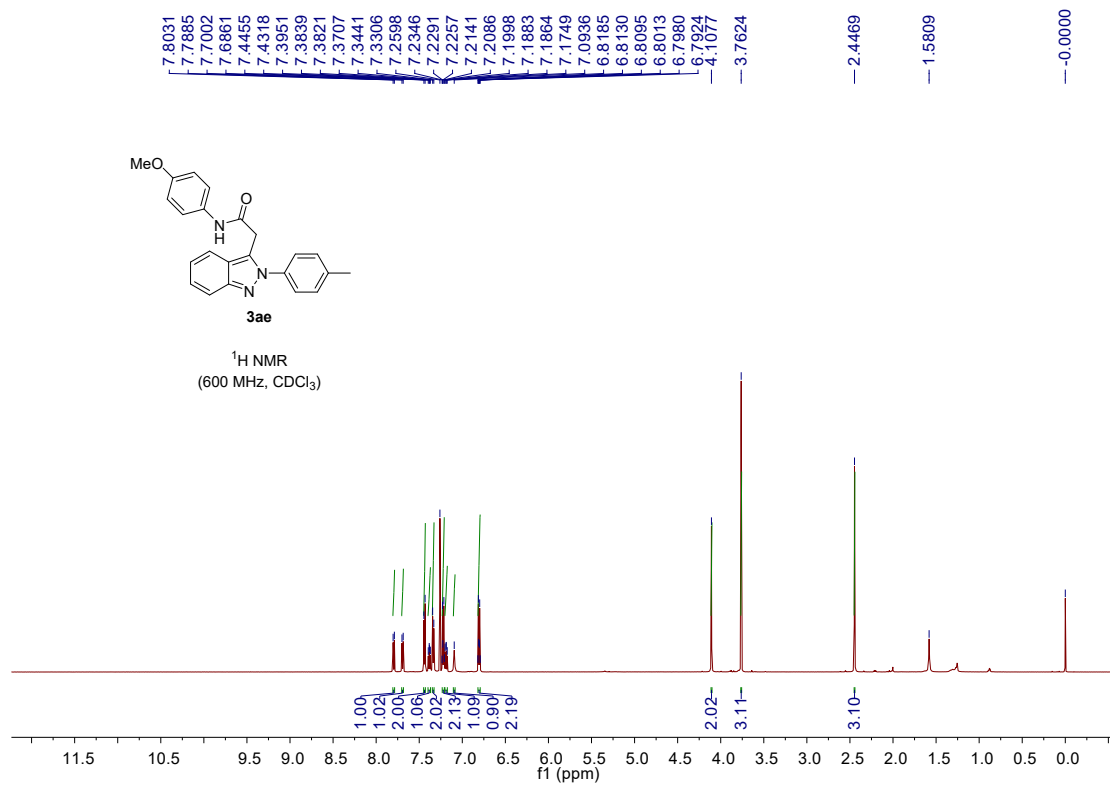
¹H NMR
(600 MHz, CDCl₃)

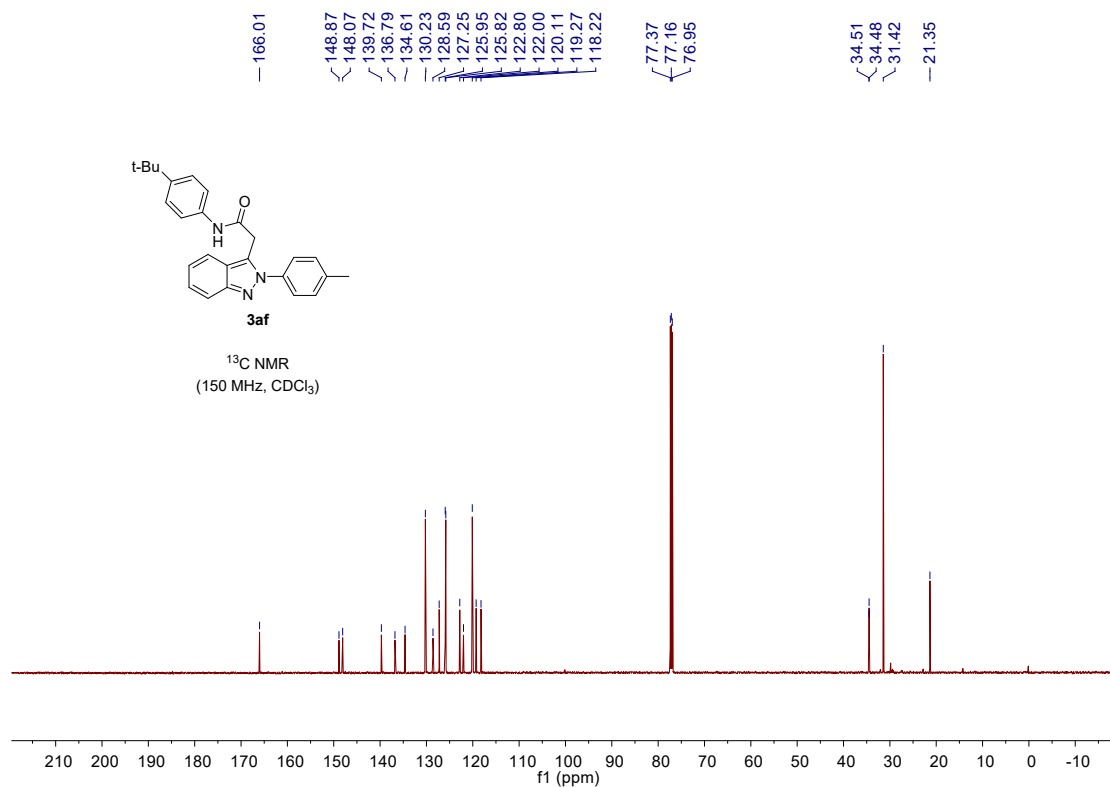
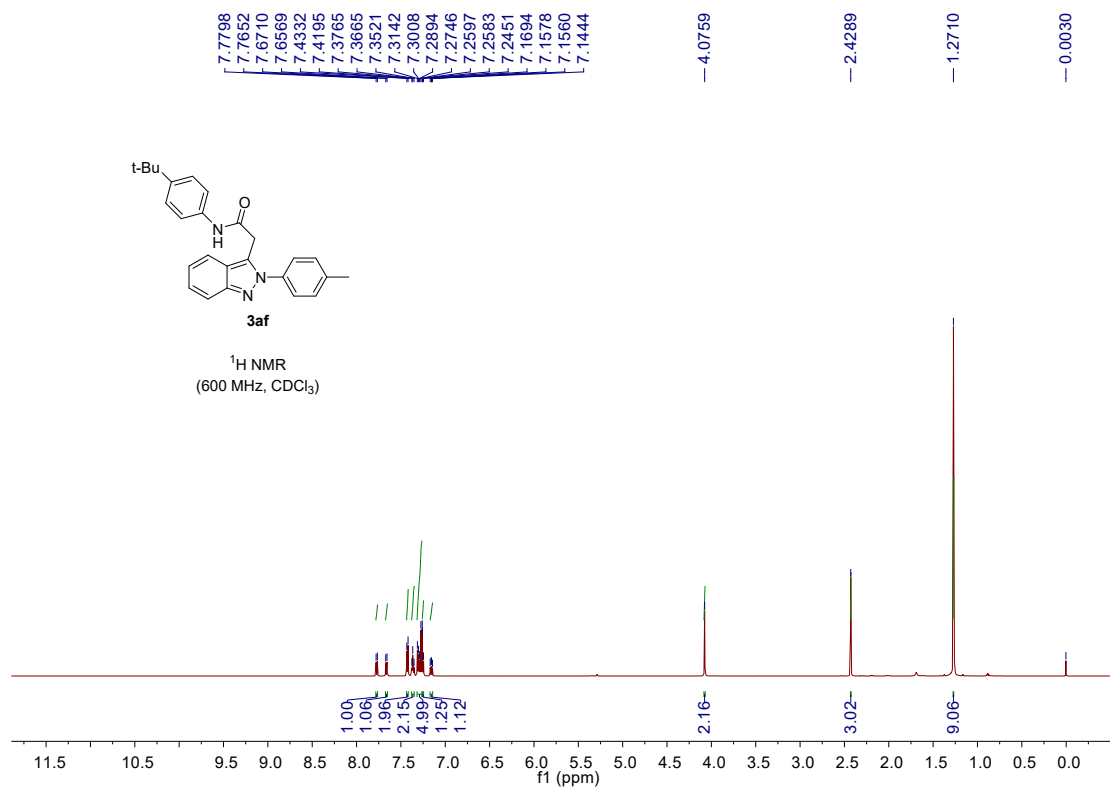


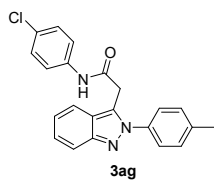
¹³C NMR
(100 MHz, CDCl₃)



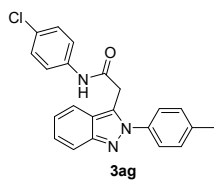
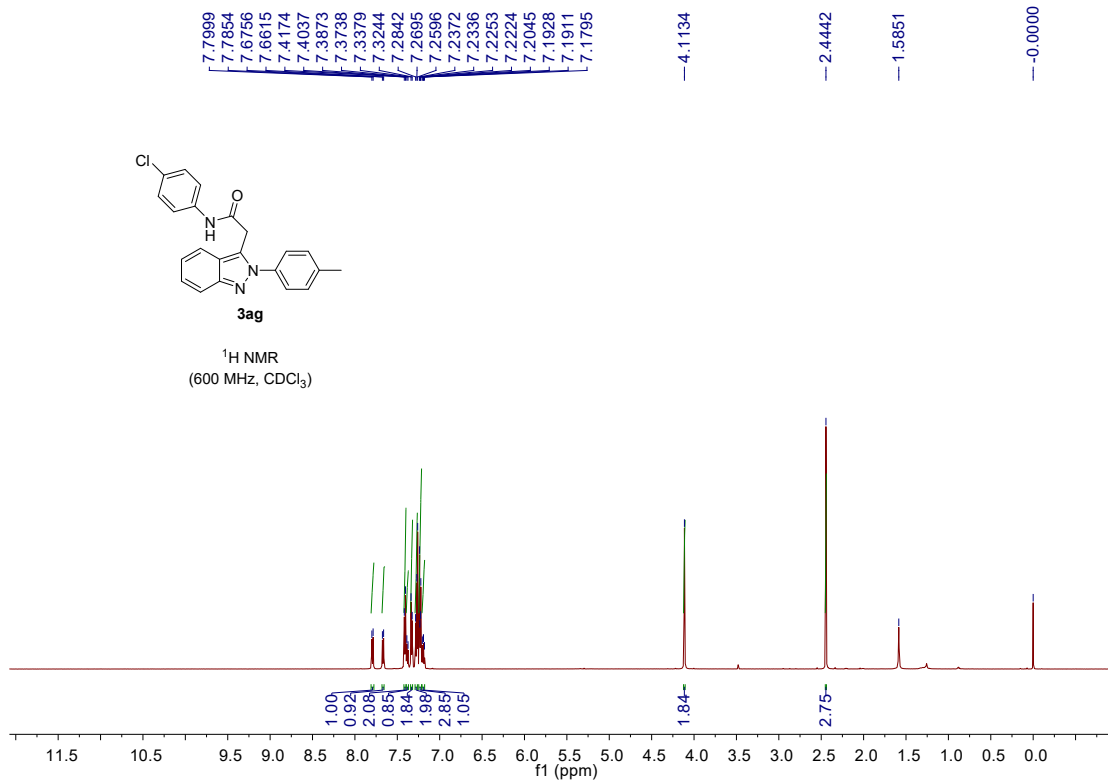




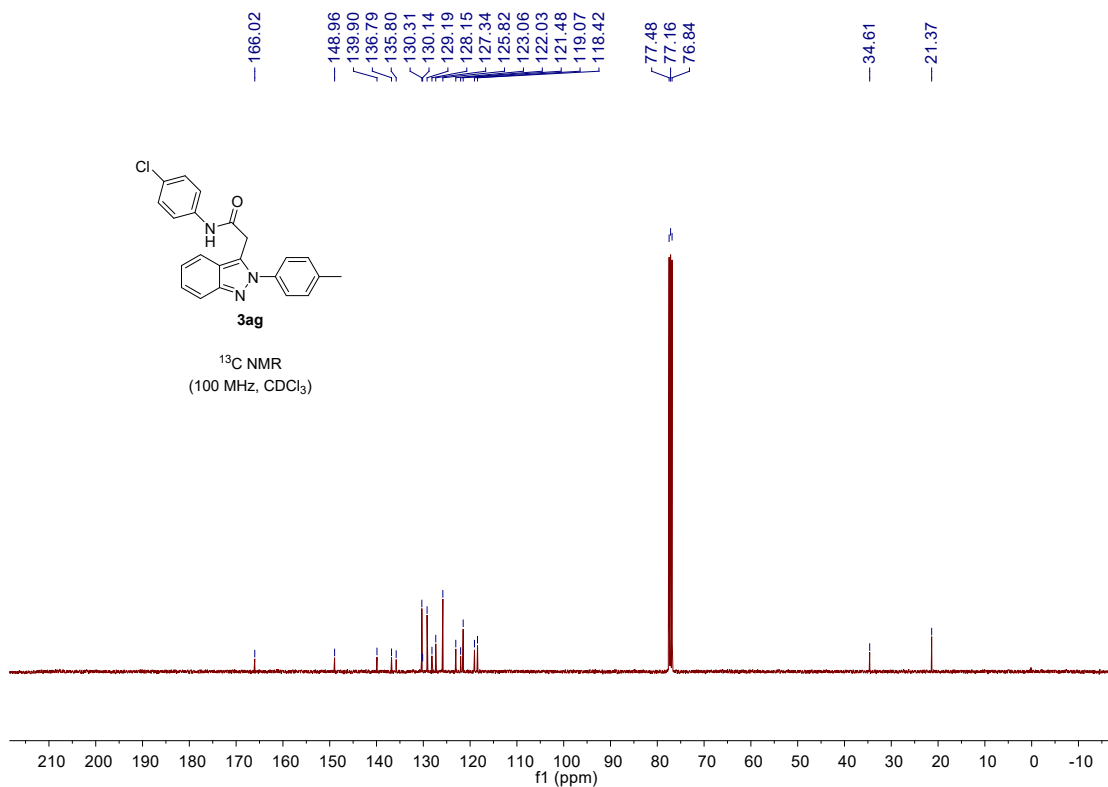




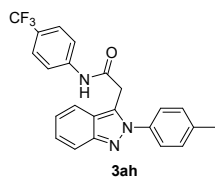
¹H NMR
(600 MHz, CDCl₃)



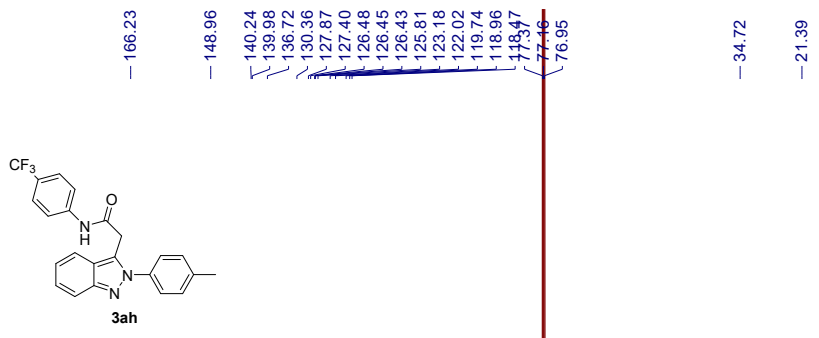
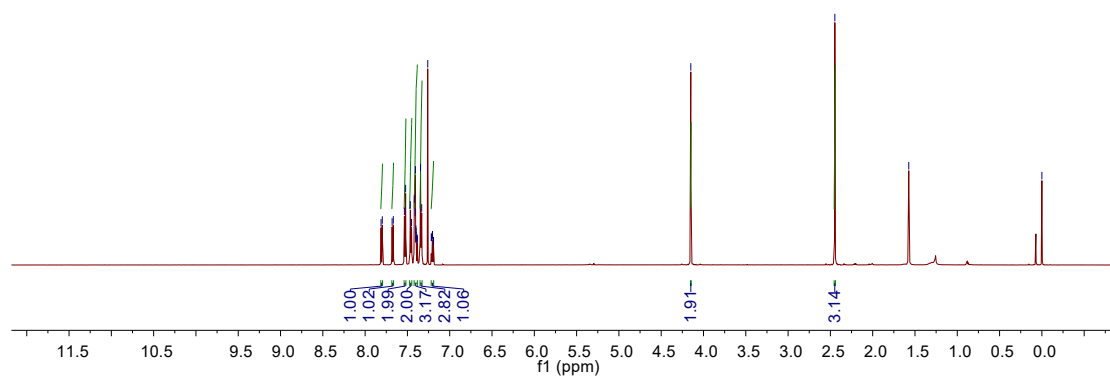
¹³C NMR
(100 MHz, CDCl₃)



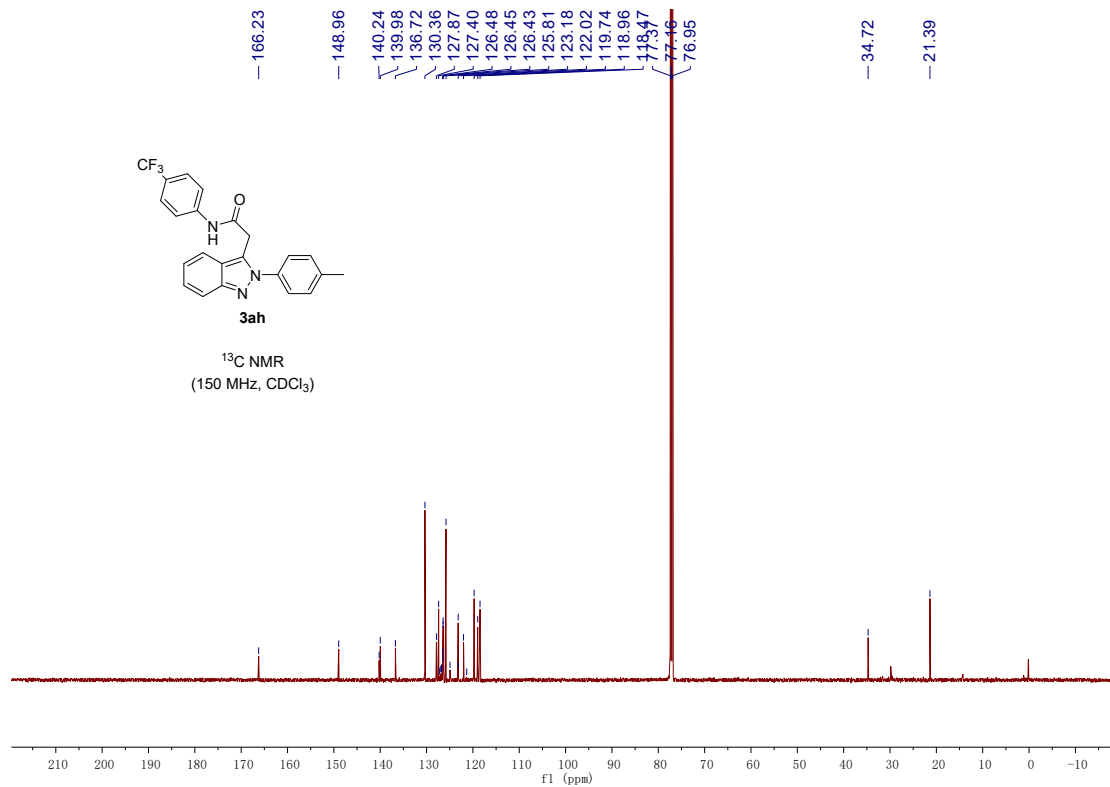
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7.3996
7.3980
7.3961
7.3945
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7.3834
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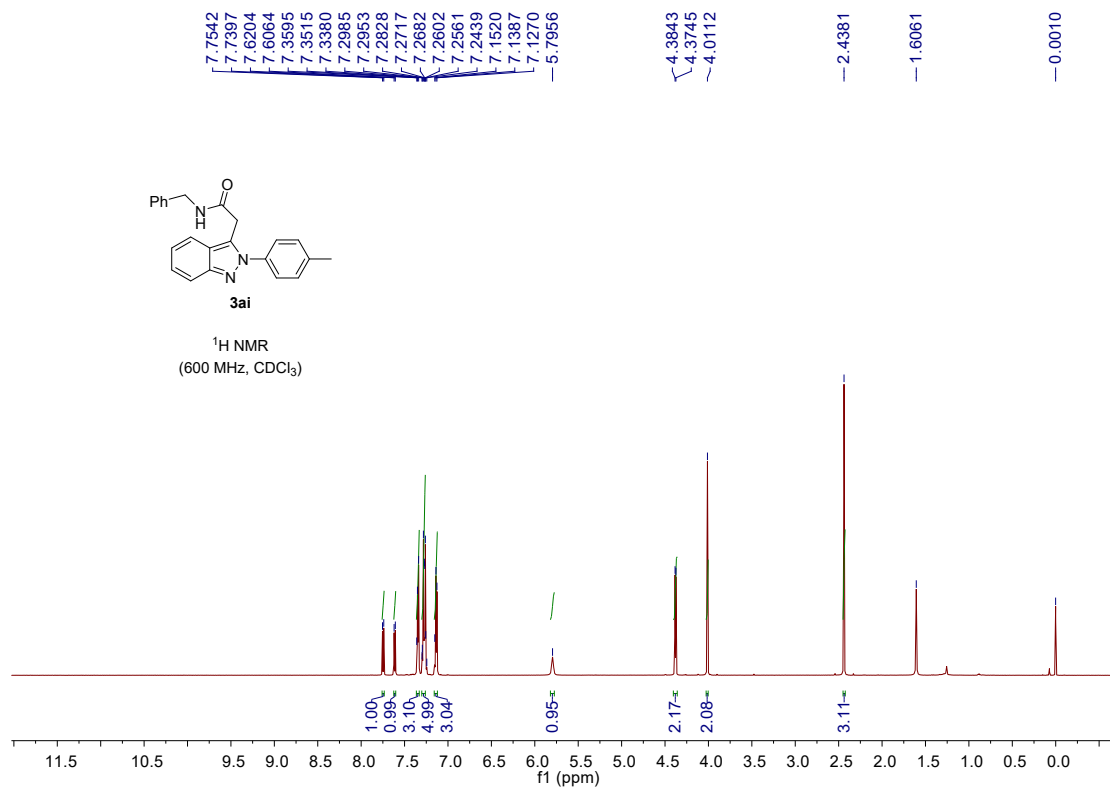
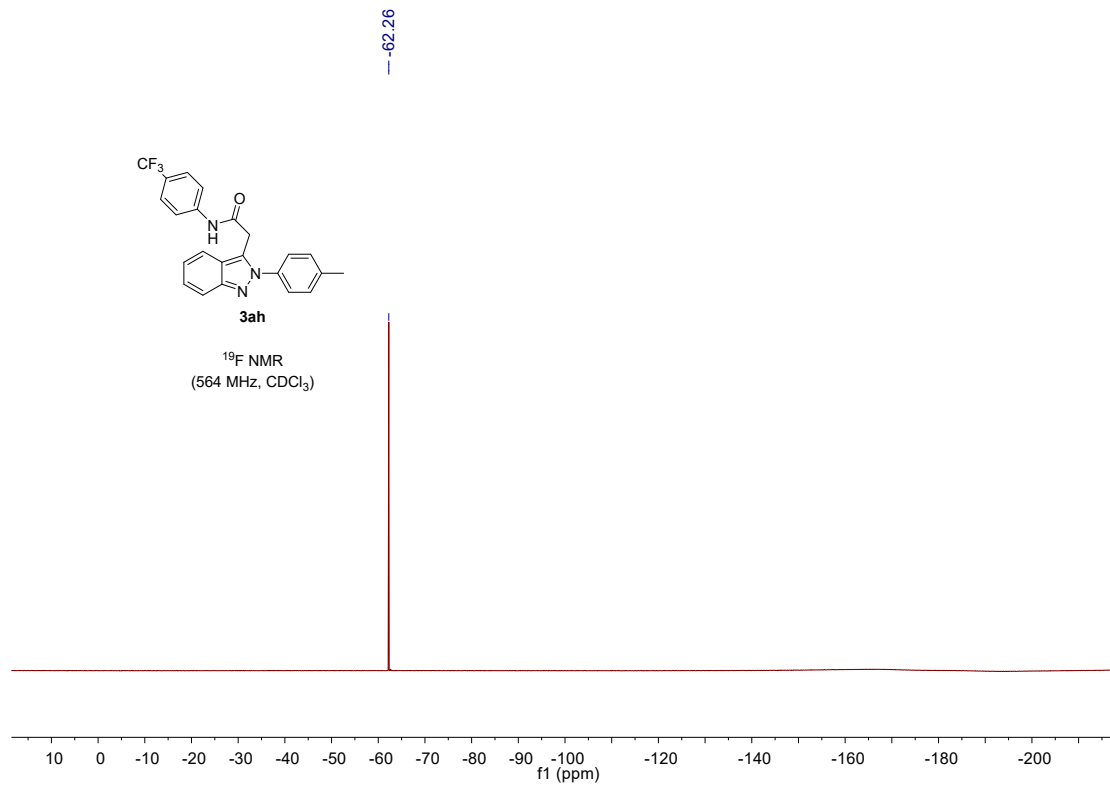


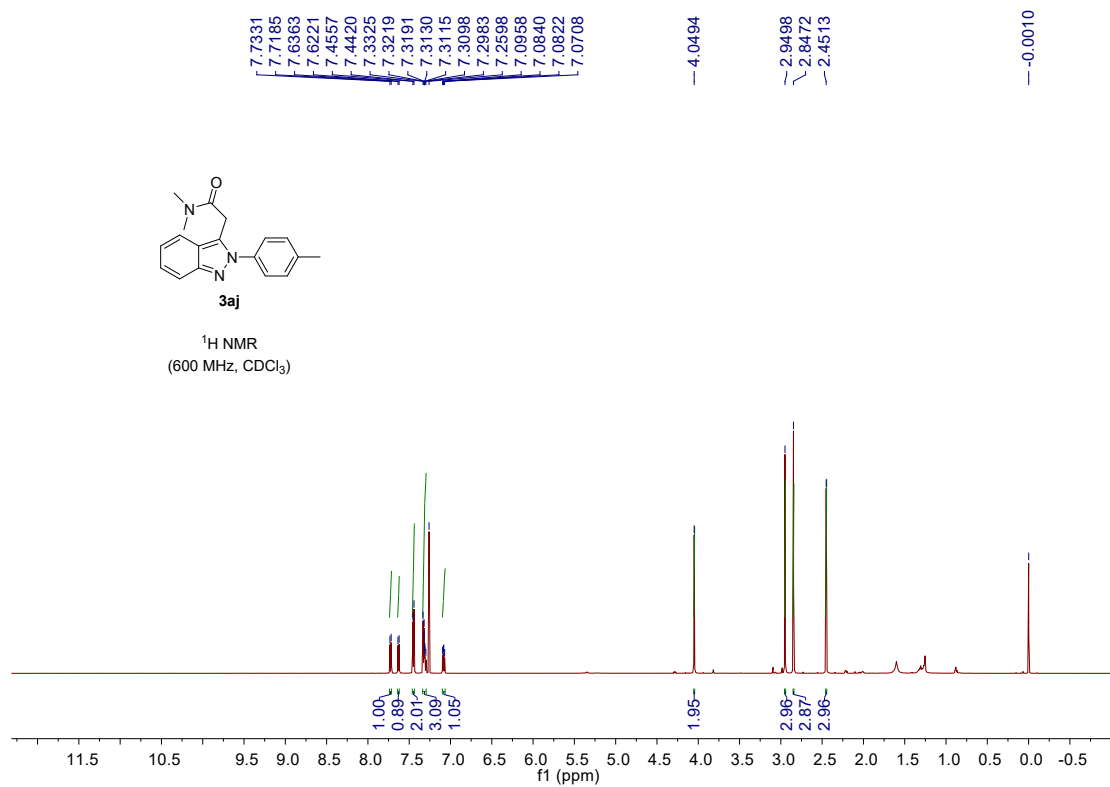
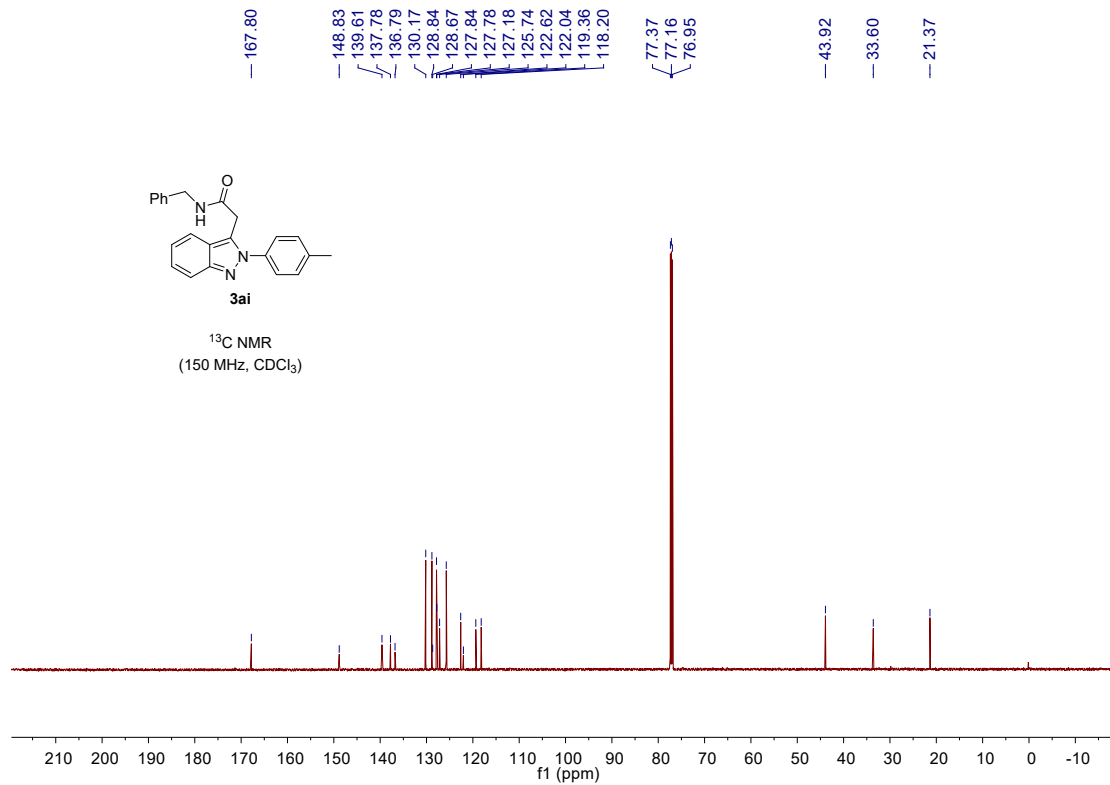
¹H NMR
(600 MHz, CDCl₃)

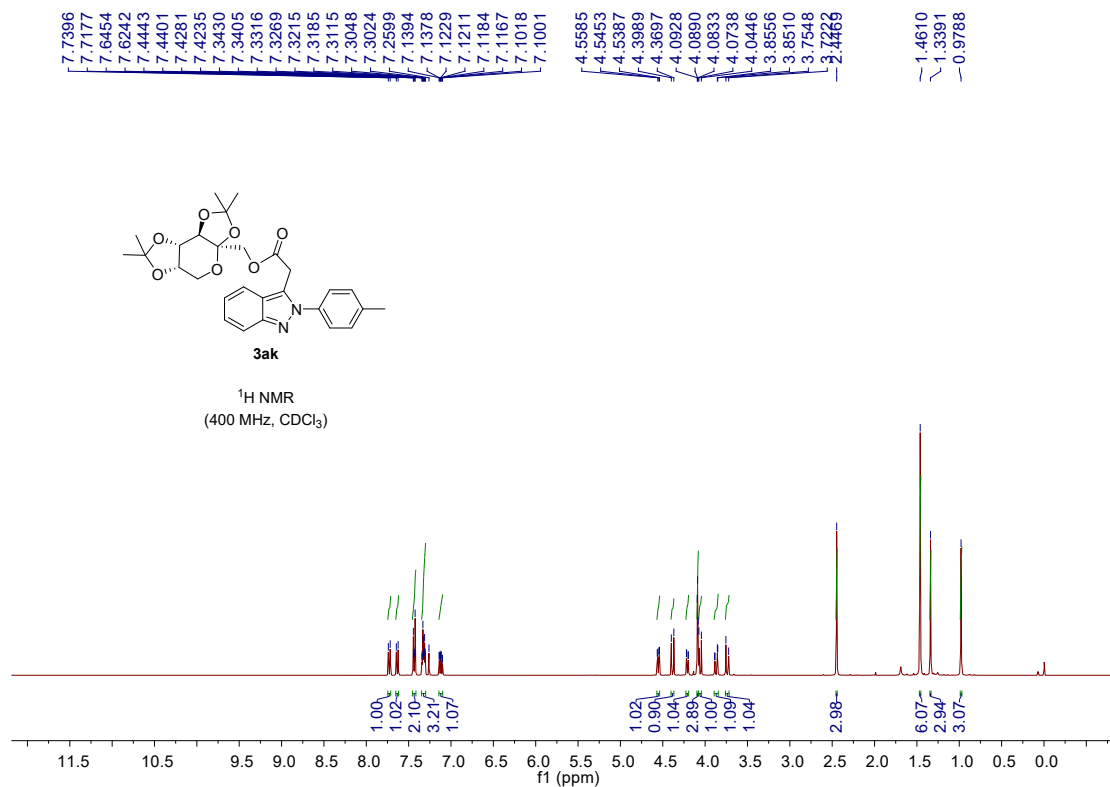
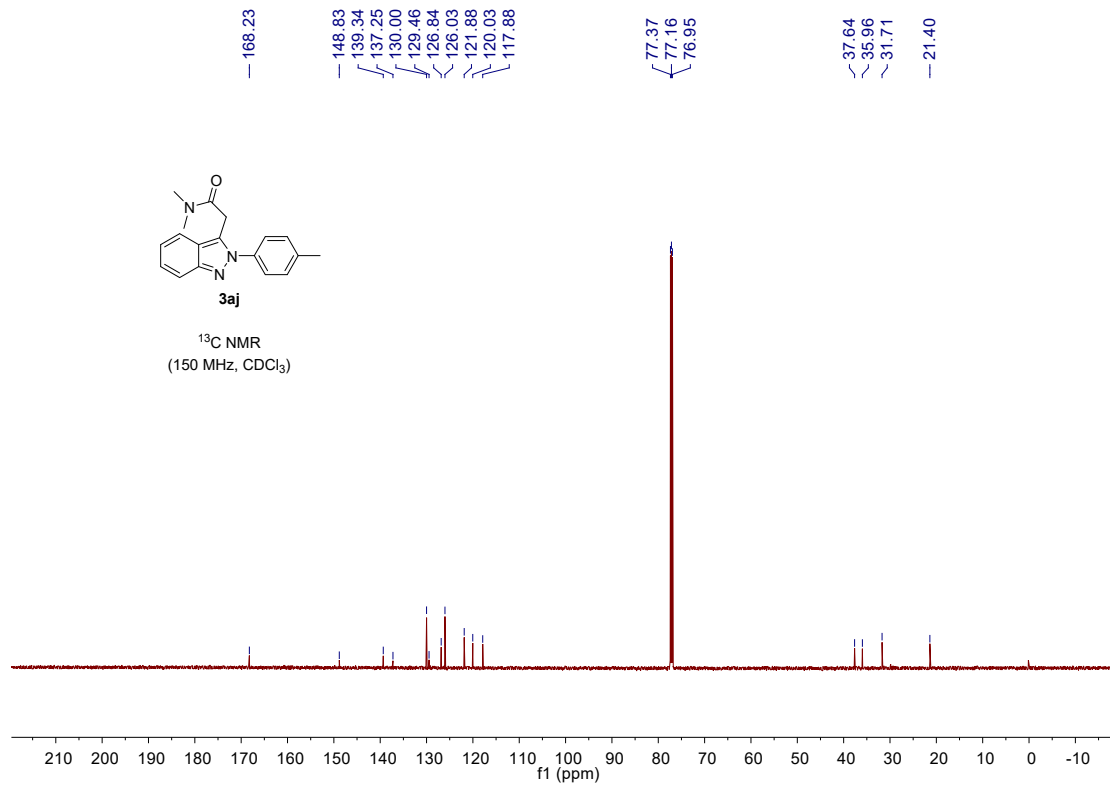


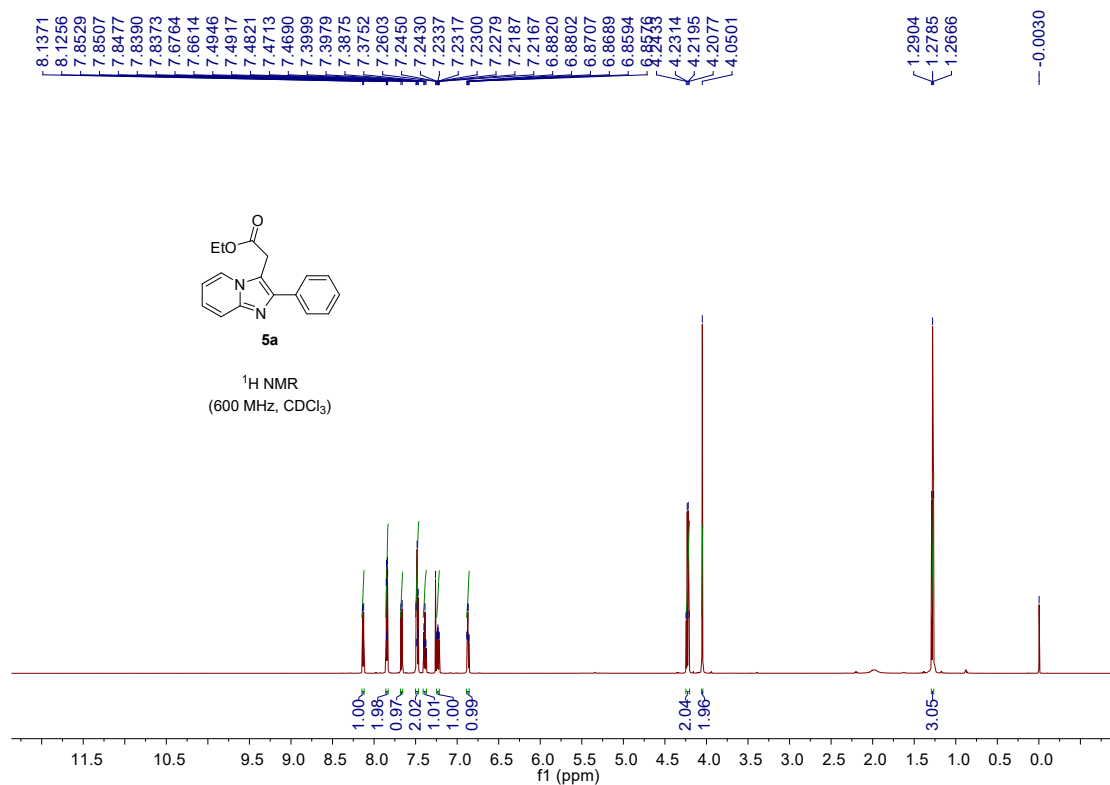
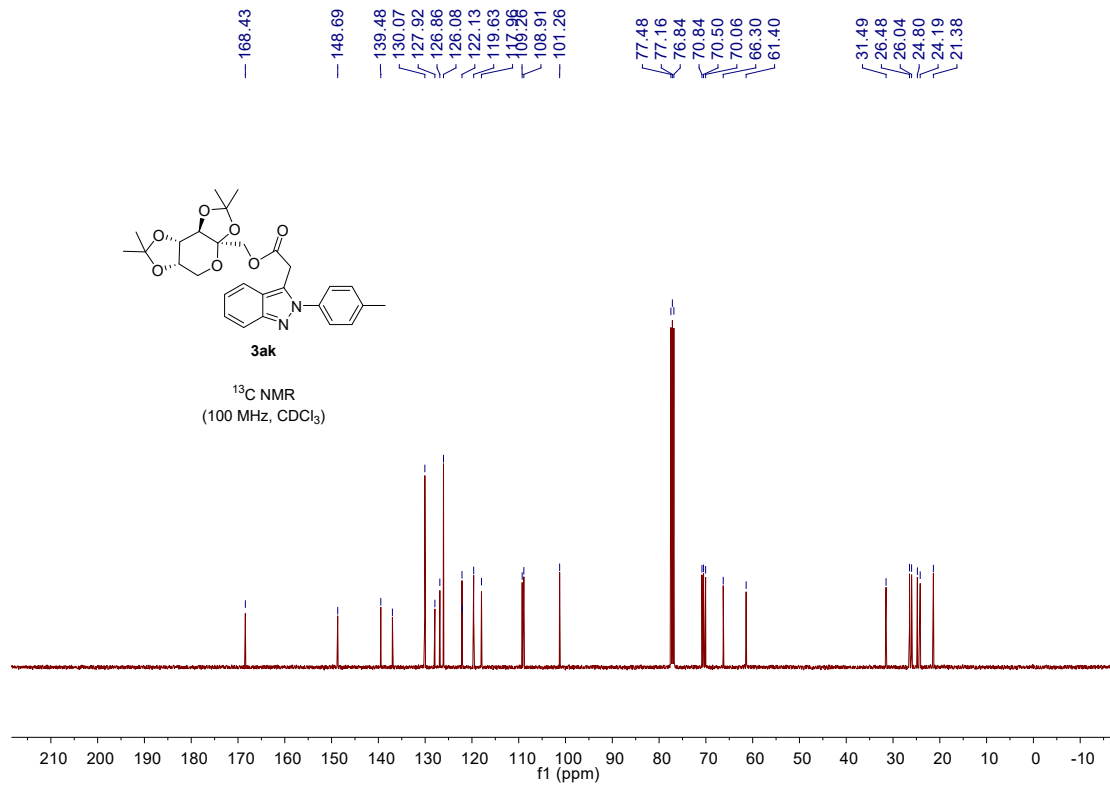
¹³C NMR
(150 MHz, CDCl₃)

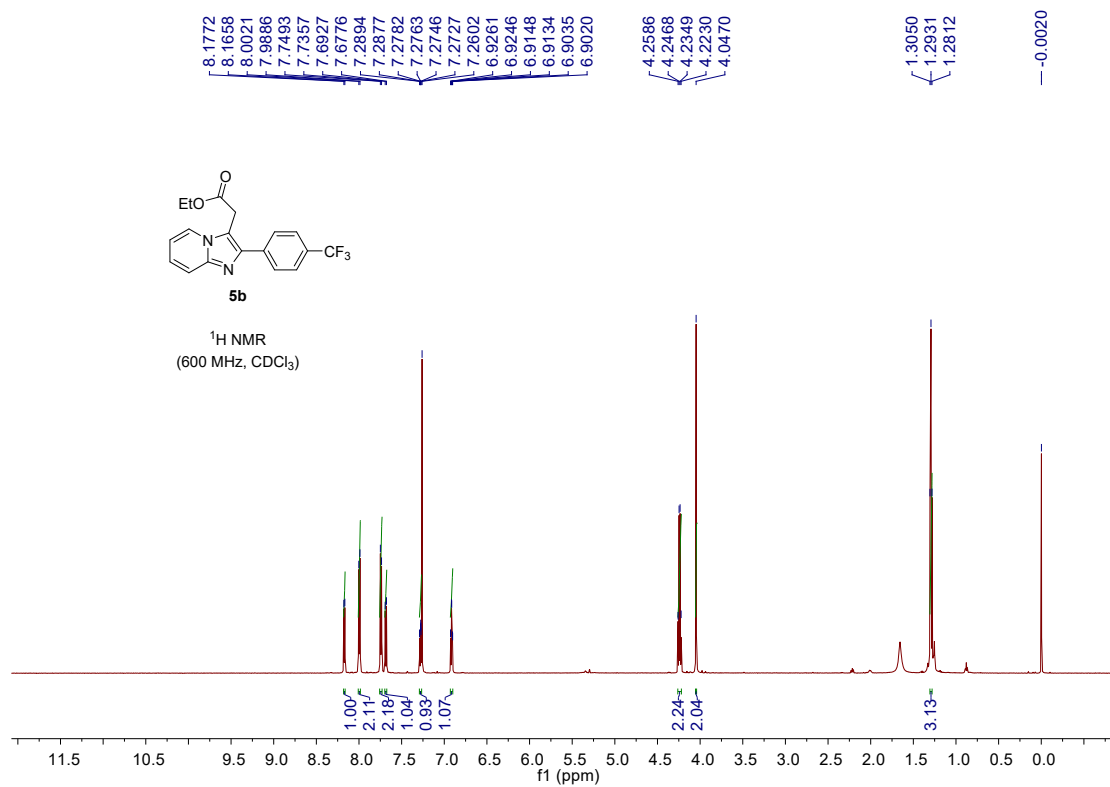
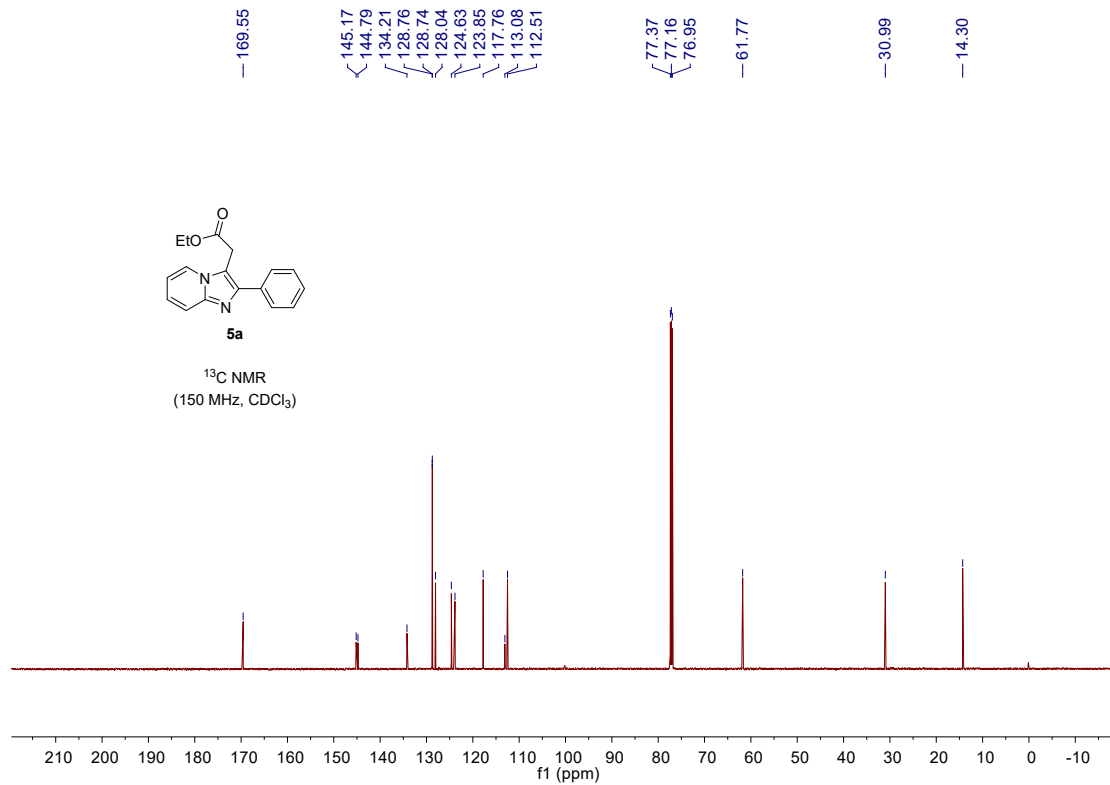


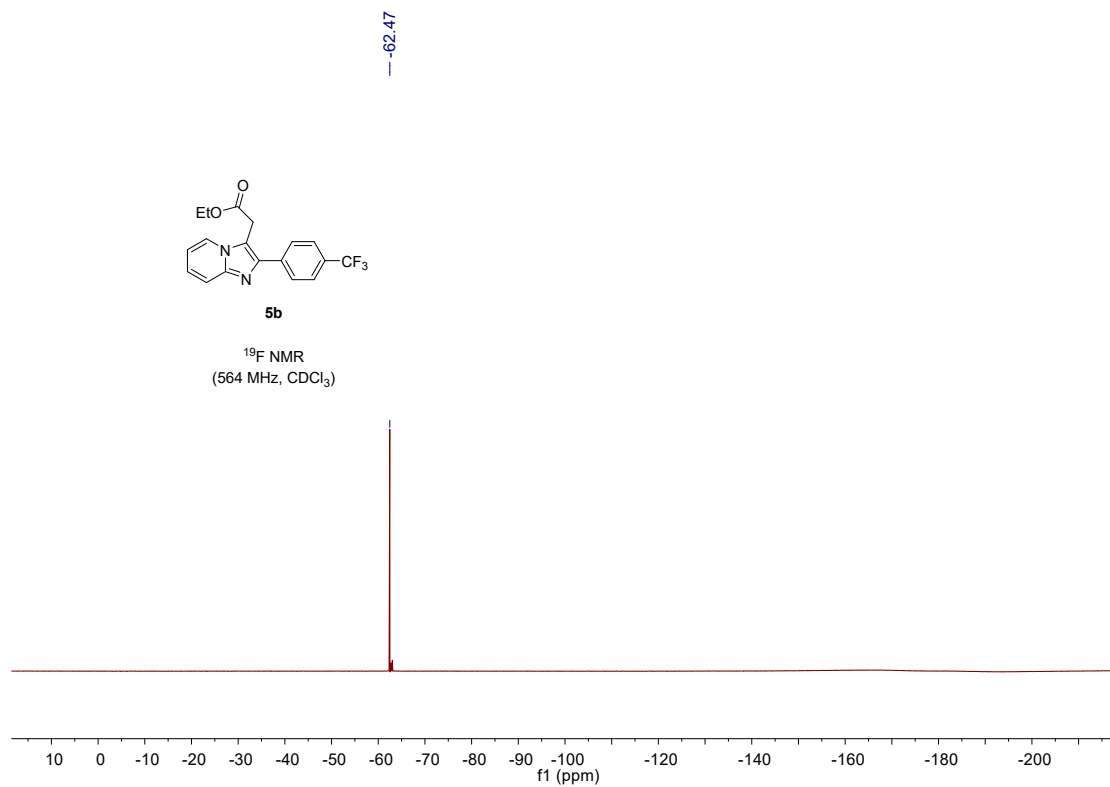
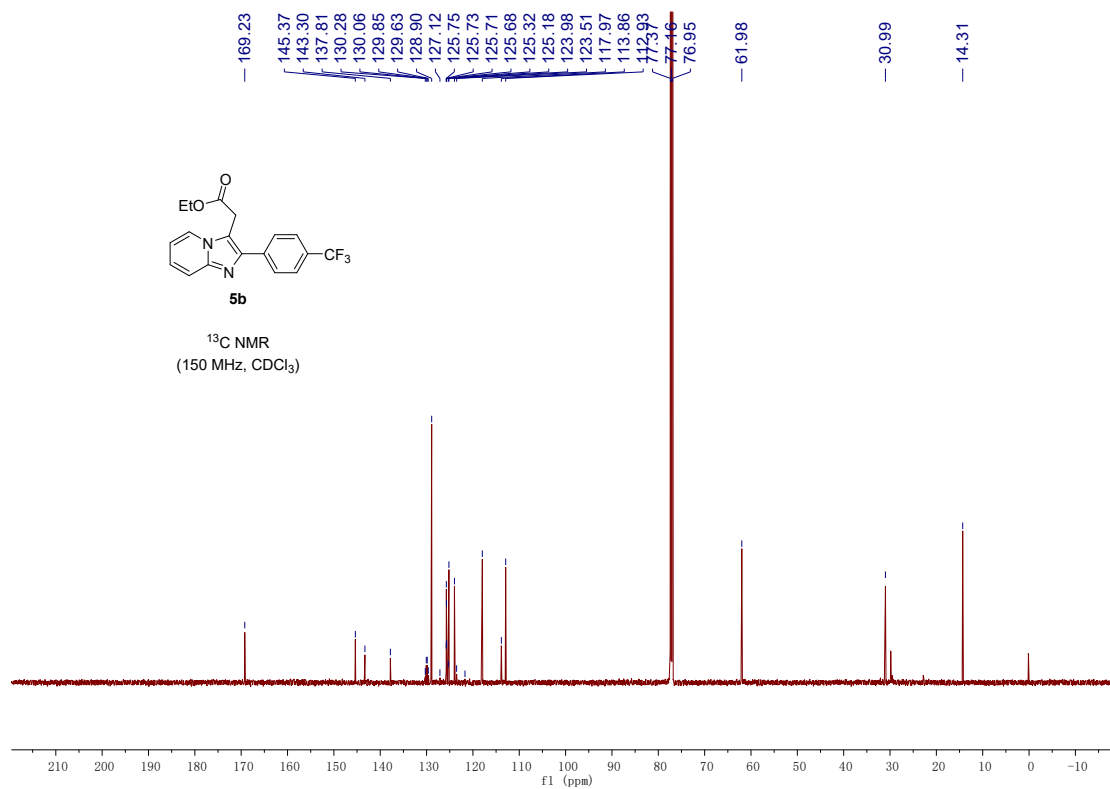


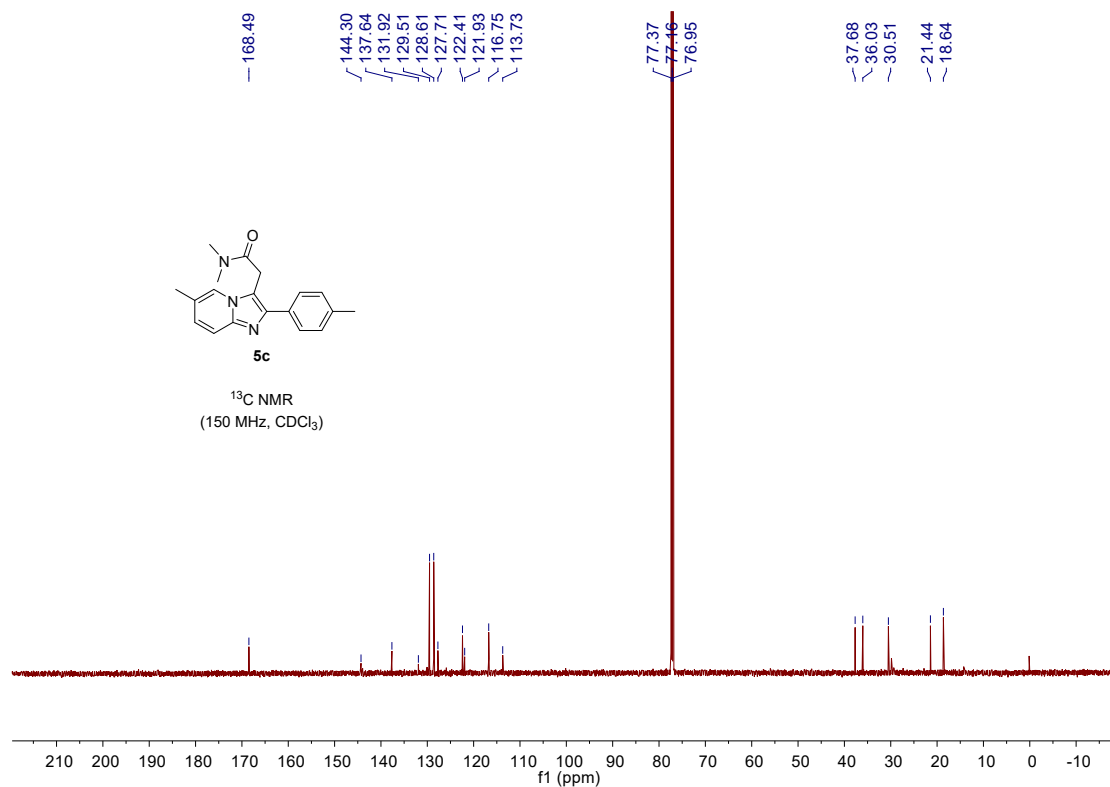
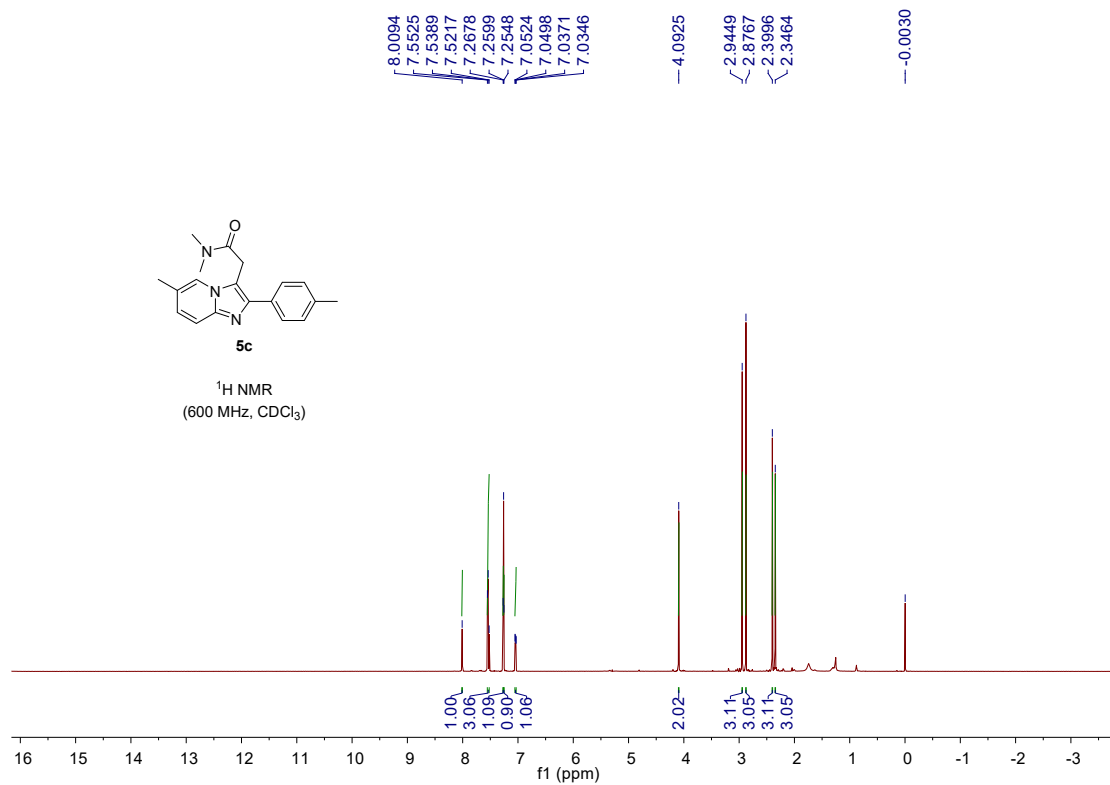












References

- [1] Chanjuan, Cai, Shangjun, et al. Substrate-Controlled Transformation of Azobenzenes to Indazoles and Indoles via Rh(III)-Catalysis[J]. *The Journal of Organic Chemistry*, 2017, 82(1):512-520.
- [2] Kozikowski A, Gaysina I, et al. Inhibitors of Glycogen Synthase Kinase 3. WO 2007008514 A2.
- [3] Bhattacharjee S, Laru S, Samanta S, et al. Visible light-induced photocatalytic C–H ethoxycarbonylmethylation of imidazoheterocycles with ethyl diazoacetate[J]. *RSC Advances*, 2020, 10(47):27984-27988.
- [4] Wang Y, Zhang B, et al. Practical and scalable preparation of Minodronic acid and Zolpidem from 2-chloroimidazole[1,2-a]pyridines[J]. *Tetrahedron*, 2019, 75(8):1064-1071.