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Supporting Information

Visible-Light-Driven photocyclization reaction: Photocatalyst-free mediated intramolecular N-N coupling for synthesis of 2H-indazole-3-carboxamides from aryl azides

Jinni Liu, Na Liu, Qingqing Yang and Long Wang*

College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic

Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang,

Hubei 443002, China.

Email：longwwwang@163.com, Tel./fax: +86 0717 6397505

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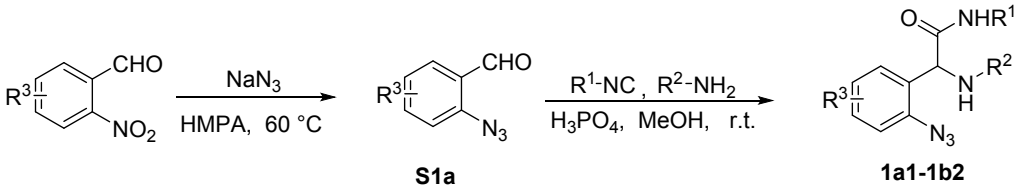
1. General Information

Reactions were monitored by analytical thin-layer chromatography (TLC) on Silica gel plates (GF254). The TLC plates were isualized by shortwave (254 nm) or longwave (365 nm) UV light. Column chromatography was carried out using silica gel (200-300 mesh) to purify the products. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in $CDCl_3$ or DMSO-d6 on Bruker AVANCE III 400 MHz spectrometers using TMS as the internal standard ($CDCl_3$ δ_H = 7.26 ppm, downfield from TMS, δ_C = 77.16 ppm). Chemical shifts are given in ppm downfield from tetramethylsilane (TMS) as an internal reference, and coupling constants (J-values) are in Hertz (Hz). ^{1}H NMR assignment abbreviations are the following; singlet (s), doublet (d), triplet (t), quartet (q), broad singlet (bs), doublet of doublets (dd), triplet of doublets (td), doublet of a triplets (dt) and multiplet (m). The high-resolution mass spectra (HRMS) were recorded in waters G2-Xs qtof mass spectrometer. Melting points were measured using a WRR point instrument and are uncorrected. All reagents and solvents were purchased from commercial sources and used without further purification. All the reactions were carried out with the irradiation of visible light under air atmosphere.

2. Details of experimental procedures

2.1. Typical procedure for the synthesis of 1a1-1b2.

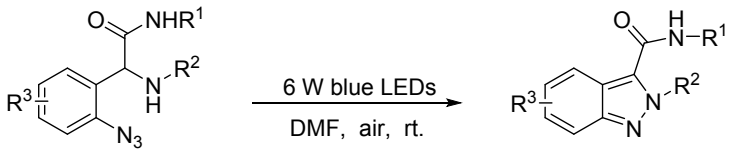


S1a **1a1-1b2**

Procedure for starting materials S1a (S1a-1 as an example): A round bottom flask equipped with a stir bar was charged with the 2-nitrobenzaldehyde (30 mmol, 1.0 equiv) and NaN_3 (60 mmol, 2.0 equiv) in HMPA (2.5 equiv). The flask was not sealed and the reactants in contact with air. The mixture was stirred at 60 ^{o}C for 24 h. When the reaction was complete, the reaction solution was cooled to room temperature and poured into deionised water (0 ^{o}C) with constant stirring. Subsequently, gradual precipitation of a yellowish solid was observed. After all the solids were precipitated, o-azidobenzaldehyde was obtained by simple washing, filtration and drying.

Procedure for starting materials 1a1-1b2: In a round bottom flask, a mixture of substituted for azidobenzaldehyde (3.0 mmol, 1 equiv) was dissolved in 3 mL of MeOH and the amine (3.0 mmol, 1 equiv) was added sequentially, 3 mL of MeOH was added after 5 minutes. Finally, isonitrile (3.0 mmol, 1 equiv) was added and stirred at room temperature for 12-24 h. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether−ethyl acetate = 10:1-3:1, v/v) to afford products **1a1-1b2** as solids.

2.1. Typical procedure for the synthesis of 2aa-2bb.



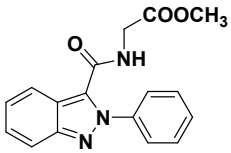
1a1-1b2 **2aa-2bb**

Procedure for 2H-indazole-3-carboxamides 2aa-2bb: In a Schlenk tube, starting materials **1a1-1b2** (1.0 mmol) and 5 mL of CH_3CN was placed with the irradiation of 6 W blue LEDs while stirring at room temperature under air atmosphere for 24 h. The mixture was quenched by NaCl

saturated solution after completion and then extracted with ethyl acetate (3×10 mL). The combined ethyl acetate layer was then dried over anhydrous $NaSO_4$ and concentrated in a vacuum. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether-ethyl acetate = 5:1-3:1, v/v) to afford products **2aa-2bb** as solids.

3. Characterization Data of 2aa-2bb

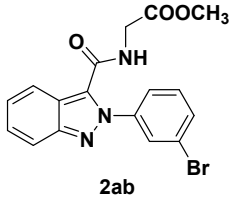
Methyl (2-phenyl-2H-indazole-3-carbonyl)glycinate



2aa

White solid, 278 mg, 90%, mp 144-145 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.52 (m, 5H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 4.21 (d, *J* = 5.1 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.93, 159.54, 148.39, 140.06, 129.46, 129.14, 128.02, 127.11, 125.83, 124.90, 122.47, 119.86, 118.50, 52.52, 41.41. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{17}H_{16}N_3O_3$ 310.1192; found 310.1193.

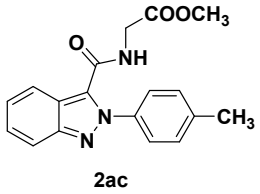
Methyl (2-(3-bromophenyl)-2H-indazole-3-carbonyl)glycinate



2ab

White solid, 348 mg, 90%, mp 146-147 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 4.26 (d, *J* = 5.3 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 170.06, 159.38, 148.51, 141.22, 132.36, 130.12, 128.95, 128.11, 127.44, 125.16, 124.59, 122.45, 122.04, 119.45, 118.60, 52.67, 41.48. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{17}H_{15}BrN_3O_3$ 388.0297; found 388.0300.

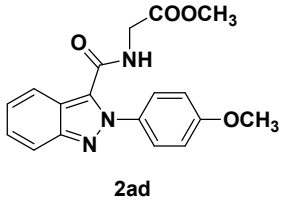
Methyl (2-(p-tolyl)-2H-indazole-3-carbonyl)glycinate



2ac

White solid, 281 mg, 87%, mp 185-186 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.27 (m, 3H), 6.53 (s, 1H), 4.20 (d, *J* = 5.3 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.93, 159.64, 148.31, 139.62, 137.61, 129.72, 127.95, 126.96, 125.61, 124.72, 122.39, 119.87, 118.47, 52.44, 41.49, 21.38. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{18}H_{17}N_3O_3$ 324.1348; found 324.1351.

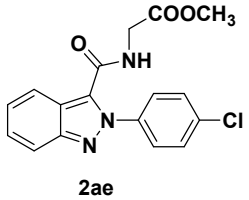
Methyl (2-(4-methoxyphenyl)-2H-indazole-3-carbonyl)glycinate



2ad

Yellow solid, 288 mg, 85%, mp 153-154 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 8.9 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.49 (s, 1H), 4.22 (d, *J* = 5.3 Hz, 2H), 3.88 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.95, 160.20, 159.41, 148.18, 133.00, 127.86, 127.12, 126.98, 124.78, 122.51, 120.00, 118.41, 114.32, 55.50, 52.33, 41.46. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{18}H_{18}N_3O_4$ 340.1297; found 340.1301.

Methyl (2-(4-chlorophenyl)-2H-indazole-3-carbonyl)glycinate

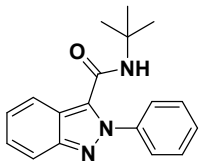


2ae

White solid, 312 mg, 91%, mp 178-179 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.40 (t, *J* = 6.9 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 6.66 (s, 1H), 4.24 (d, *J* = 5.3 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.97, 159.51, 148.45, 138.62, 135.24, 129.18, 127.98, 127.28, 126.96,

125.14, 122.04, 119.39, 118.62, 52.63, 41.41. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{17}H_{15}ClN_3O_3$ 344.0802; found 344.0804.

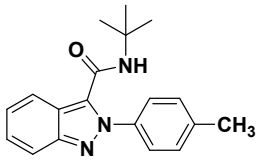
N-(tert-butyl)-2-phenyl-2H-indazole-3-carboxamide



2af

White solid, 281 mg, 96%, mp 147-148 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.64 – 7.51 (m, 5H), 7.38 (t, *J* = 6.7Hz, 1H), 7.28 – 7.24 (m, 1H), 5.58 (s, 1H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.86, 148.39, 140.04, 130.09, 129.44, 129.23, 127.07, 125.74, 124.22, 122.32, 120.19, 118.21, 52.18, 28.64. Known compound.[1]

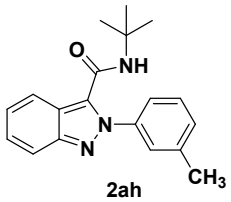
N-(tert-butyl)-2-(p-tolyl)-2H-indazole-3-carboxamide



2ag

White solid, 295 mg, 96%, mp 131-132 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.25 – 7.21 (m, 1H), 5.62 (s, 1H), 2.45 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.92, 148.33, 139.48, 137.68, 129.95, 129.76, 126.80, 125.46, 124.14, 122.57, 120.07, 118.29, 52.07, 28.57, 21.13. Known compound.[1]

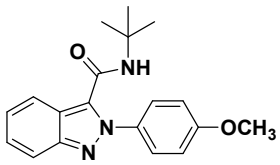
N-(tert-butyl)-2-(m-tolyl)-2H-indazole-3-carboxamide



2ah

White solid, 295 mg, 96%, mp 128-129 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.45 – 7.32 (m, 5H), 7.24 (d, *J* = 7.7 Hz, 1H), 5.55 (s, 1H), 2.45 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.96, 148.33, 139.91, 139.52, 130.18, 130.04, 129.07, 127.04, 126.28, 124.15, 122.84, 122.40, 120.28, 118.15, 52.13, 28.63, 21.23. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{17}H_{15}BrN_3O_3$ 308.1763; found 308.1767.

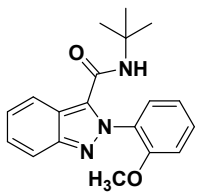
N-(tert-butyl)-2-(4-methoxyphenyl)-2H-indazole-3-carboxamide



2ai

White solid, 307 mg, 95%, mp 113-114 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.25 – 7.22 (m, 1H), 7.04 (d, *J* = 8.9 Hz, 2H), 5.61 (s, 1H), 3.88 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 160.28, 158.91, 148.20, 133.05, 129.94, 126.96, 126.88, 124.07, 122.27, 120.23, 118.10, 114.33, 55.62, 52.10, 28.70. Known compound.[1]

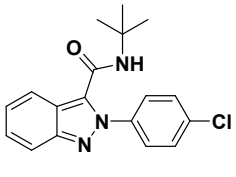
N-(tert-butyl)-2-(2-methoxyphenyl)-2H-indazole-3-carboxamide



2aj

White solid, 307 mg, 95%, mp 112-113 °C, ^{1}H NMR (400 MHz, $CDCl_3$,) δ (ppm) 7.96 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.38 – 7.34 (m, 1H), 7.27 – 7.23 (m, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 5.73 (s, 1H), 3.78 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.87, 153.56, 148.35, 131.58, 131.10, 129.43, 128.10, 126.74, 123.98, 121.51, 121.10, 120.33, 118.24, 111.67, 55.71, 51.71, 28.68. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{19}H_{22}N_3O_2$ 324.1712; found 324.1715.

N-(tert-butyl)-2-(4-chlorophenyl)-2H-indazole-3-carboxamide

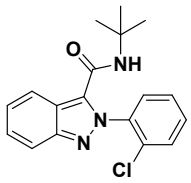


2ak

White solid, 314 mg, 96%, mp 161-162 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 9.4 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.39 – 7.35 (m, 1H), 7.26 – 7.22 (m, 1H), 5.82 (s, 1H), 1.44 (s, 9H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ (ppm) 158.85, 148.42, 138.68, 135.08, 130.00, 129.20, 127.18, 126.63, 124.43, 121.70, 119.49, 118.41, 52.39, 28.76. Known compound.[1]

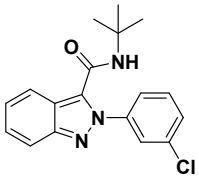
N-(tert-butyl)-2-(2-chlorophenyl)-2H-indazole-3-carboxamide



2al

White solid, 307 mg, 94%, mp 145-146 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.55 (m, 2H,), 7.50 – 7.47 (m, 2H), 7.42 – 7.38 (m, 2H), 7.31 – 7.28 (m, 1H), 5.76 (s, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.44, 148.54, 138.57, 131.36, 131.04, 130.79, 129.99, 128.87, 127.65, 127.09, 124.57, 120.61, 119.78, 118.66, 52.05, 28.57. Known compound.[1]

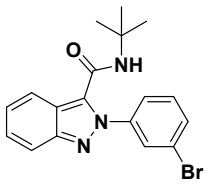
N-(tert-butyl)-2-(3-chlorophenyl)-2H-indazole-3-carboxamide



2am

White solid, 311 mg, 95%, mp 167-168 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 – 7.76 (m, 2H), 7.63 (s, 1H), 7.53 – 7.44 (m, 3H), 7.37 (t, *J* = 6.5 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.87, 148.43, 140.97, 134.72, 130.13, 130.01, 129.20, 127.30, 125.68, 124.43, 123.48, 121.77, 119.60, 118.34, 52.45, 28.69. Known compound.[1]

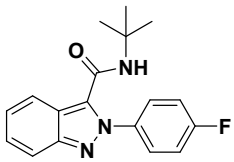
N-(tert-butyl)-2-(3-bromophenyl)-2H-indazole-3-carboxamide



2an

White solid, 349 mg, 94%, mp 172-173 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (t, *J* = 7.7 Hz, 3H), 7.62 – 7.56 (m, 2H), 7.41 – 7.35 (m, 2H), 7.24 (t, *J* = 6.6 Hz, 1H), 5.80 (s, 1H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.83, 148.49, 141.13, 132.13, 130.26, 130.20, 128.56, 127.32, 124.46, 124.00, 122.45, 121.85, 119.64, 118.38, 52.47, 28.75. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{18}H_{18}BrN_3O$ 372.0712; found 372.0713.

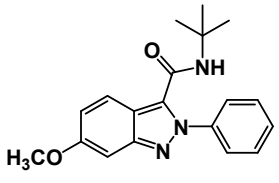
N-(tert-butyl)-2-(4-fluorophenyl)-2H-indazole-3-carboxamide



2ao

White solid, 289 mg, 93%, mp 157-158 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (dd, *J* = 14.9, 8.6 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.20 (m, 3H), 5.77 (s, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 164.04, 161.49, 158.99, 148.25, 127.40, 127.13, 124.38, 121.67, 119.73, 118.34, 116.18, 115.95, 52.45, 28.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -111.40 (s, 1F). Known compound.[1]

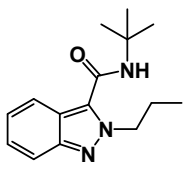
N-(tert-butyl)-6-methoxy-2-phenyl-2H-indazole-3-carboxamide



2ap

White solid, 275 mg, 85%, mp 152-153 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 9.2 Hz, 1H), 7.62 – 7.48 (m, 5H), 6.99 (d, *J* = 1.9 Hz, 1H), 6.93 (dd, *J* = 9.2, 2.2 Hz, 1H), 5.52 (s, 1H), 3.88 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.32, 158.84, 149.46, 139.95, 130.13, 129.20, 125.63, 121.10, 119.38, 118.27, 94.65, 55.26, 52.14, 28.58. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{19}H_{22}N_3O_3$ 324.1712; found 324.1716.

N-(tert-butyl)-2-propyl-2H-indazole-3-carboxamide

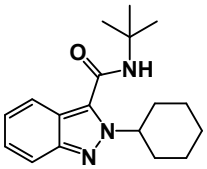


2aq

White solid, 186 mg, 72%, mp 102-103 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.7 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 8.1 Hz, 1H), 6.03 (s, 1H), 4.78 (t, *J* = 7.2 Hz, 2H), 2.06 – 1.96 (m, 2H), 1.55 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.61, 147.06, 128.41, 125.80, 123.79, 119.99, 118.48, 118.44, 54.19,

52.24, 29.01, 24.38, 11.15. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{15}H_{22}N_3O$ 260.1763; found 260.1770.

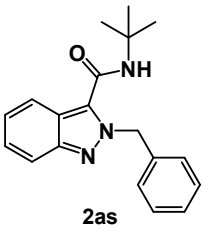
N-(tert-butyl)-2-cyclohexyl-2H-indazole-3-carboxamide



2ar

White solid, 263 mg, 88%, mp 124-125 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 8.7 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 1H), 6.03 (s, 1H), 5.34 – 5.23 (m, 1H), 2.16 – 2.07 (m, 4H), 1.92 (d, *J* = 13.2 Hz, 2H), 1.79 – 1.72 (m, 1H), 1.55 (s, 10H), 1.43 – 1.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.73, 147.00, 128.12, 125.60, 123.61, 119.95, 118.56, 118.47, 60.57, 52.25, 33.55, 29.07, 25.60, 25.31. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{18}H_{26}N_3O$ 300.2076; found 300.2074.

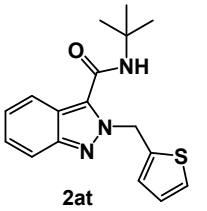
2-benzyl-N-(tert-butyl)-2H-indazole-3-carboxamide



2as

White solid, 233 mg, 76%, mp 109-110 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.26 (m, 5H), 7.22 (t, *J* = 7.6 Hz, 2H), 6.02 (s, 2H), 5.91 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.60, 147.26, 136.62, 128.51, 128.19, 127.91, 126.10, 126.02, 123.92, 120.35, 118.64, 118.57, 55.83, 52.24, 28.89. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{19}H_{22}N_3O$ 308.1763; found 308.1768.

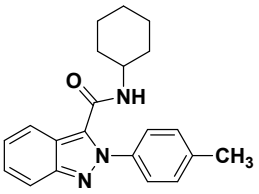
N-(tert-butyl)-2-(thiophen-2-ylmethyl)-2H-indazole-3-carboxamide



2at

White solid, 213 mg, 68%, mp 133-134 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.18 (m, 3H), 6.92 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.23 (s, 2H), 6.00 (s, 1H), 1.55 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.58, 147.31, 138.31, 127.82, 127.73, 126.66, 126.32, 126.11, 124.14, 120.24, 118.78, 118.52, 52.31, 50.34, 29.00. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{17}H_{20}N_3O$ 314.1327; found 314.1333.

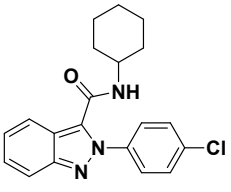
N-cyclohexyl-2-(p-tolyl)-2H-indazole-3-carboxamide



2au

White solid, 283 mg, 85%, mp 215-216 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.25 – 7.22 (m, 1H), 5.71 (s, 1H), 3.95 (s, 1H), 2.45 (s, 3H), 1.91 (d, *J* = 10.2 Hz, 2H), 1.70 – 1.60 (m, 3H), 1.37 (d, *J* = 10.6 Hz, 2H), 1.15 – 1.09 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.67, 148.31, 139.64, 137.60, 129.76, 129.25, 126.91, 125.54, 124.20, 122.42, 120.21, 118.20, 48.39, 32.74, 25.36, 24.47, 21.23. Known compound.[1]

2-(4-chlorophenyl)-N-cyclohexyl-2H-indazole-3-carboxamide

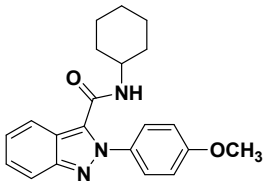


2av

White solid, 293 mg, 83%, mp 248-249 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.47 (m, 4H), 7.38 (t, *J* = 7.0 Hz, 1H), 5.91 (d, *J* = 7.0 Hz, 1H), 3.97 (s, 1H), 2.00 (d, *J* = 9.7 Hz, 2H), 1.73 – 1.65 (m, 4H), 1.45 – 1.36 (m, 2H), 1.25 – 1.20 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.59, 148.45, 138.67, 135.15, 129.28, 129.18, 127.21, 126.79, 124.57, 121.81, 119.48, 118.48, 48.75, 32.96, 25.36, 24.66..

Known compound.[1]

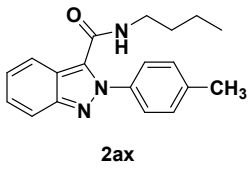
N-cyclohexyl-2-(4-methoxyphenyl)-2H-indazole-3-carboxamide



2aw

White solid, 318 mg, 91%, mp 189-190 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 5.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 2H), 5.72 (s, 1H), 3.88 (s, 4H), 1.92 (d, *J* = 8.5 Hz, 2H), 1.70 – 1.62 (m, 3H), 1.37 (d, *J* = 10.9 Hz, 2H), 1.15 – 1.10 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 160.30, 158.66, 148.24, 133.04, 129.22, 127.03, 126.90, 124.19, 122.40, 120.23, 118.14, 114.33, 55.62, 48.40, 32.80, 25.36, 24.51. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{21}H_{24}N_3O_2$ 350.1869; found 350.1870.

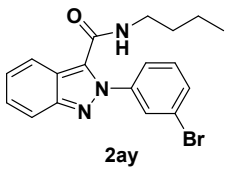
N-butyl-2-(p-tolyl)-2H-indazole-3-carboxamide



2ax

White solid, 246 mg, 80%, mp 163-164 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 8.1 Hz, 1H), 5.87 (s, 1H), 3.37 (q, *J* = 6.9, 2H), 2.44 (s, 3H), 1.50 – 1.42 (m, 2H), 1.30 – 1.21 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.96, 148.22, 139.64, 137.54, 129.77, 129.10, 126.93, 125.47, 124.23, 122.39, 120.16, 118.15, 39.41, 31.36, 21.23, 19.97, 13.65. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{19}H_{22}N_3O$ 308.1763; found 308.1766.

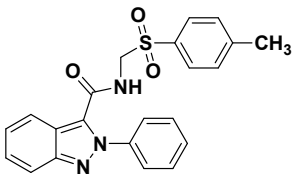
2-(3-bromophenyl)-N-butyl-2H-indazole-3-carboxamide



2ay

Yellow solid, 315 mg, 85%, mp 175-176 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 – 7.77 (m, 3H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.27 – 7.25 (m, 1H), 6.04 (s, 1H), 3.44 (q, *J* = 6.9 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.41 – 1.31 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.46, 148.50, 141.08, 132.25, 130.18, 129.31, 128.71, 127.34, 124.67, 124.23, 122.43, 121.87, 119.57, 118.44, 39.71, 31.53, 19.95, 13.70. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{18}H_{19}N_3O$ 372.0712; found 372.0715.

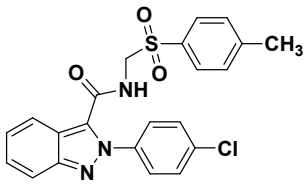
2-phenyl-N-(tosylmethyl)-2H-indazole-3-carboxamide



2az

White solid, 320 mg, 79%, mp 193-194 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 – 7.83 (m, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.41 (m, 6H), 7.36 – 7.29 (m, 3H), 6.79 (t, *J* = 6.6 Hz, 1H), 4.85 (d, *J* = 6.8 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.21, 148.36, 145.51, 139.83, 133.86, 130.08, 129.60, 129.15, 128.69, 127.26, 126.75, 125.73, 125.47, 122.42, 119.35, 118.80, 60.09, 21.73. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{22}H_{20}N_3O_3S$ 406.1225; found 406.1226.

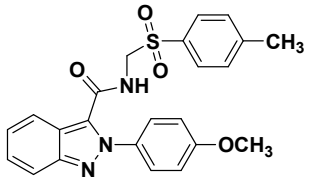
2-(4-chlorophenyl)-N-(tosylmethyl)-2H-indazole-3-carboxamide



2ba

White solid, 334 mg, 76%, mp 217-218 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (t, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.35 (m, 6H), 7.29 (d, *J* = 8.9 Hz, 2H), 6.94 (t, *J* = 6.2 Hz, 1H), 4.90 (d, *J* = 6.7 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.29, 148.43, 145.68, 138.35, 135.35, 133.88, 130.14, 129.11, 128.67, 127.44, 126.90, 125.80, 121.99, 118.96, 118.89, 60.07, 21.75. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{22}H_{19}N_3O_3SCl$ 440.0836; found 440.0840.

methyl (2-(4-methoxyphenyl)-2H-indazole-3-carbonyl)glycinate



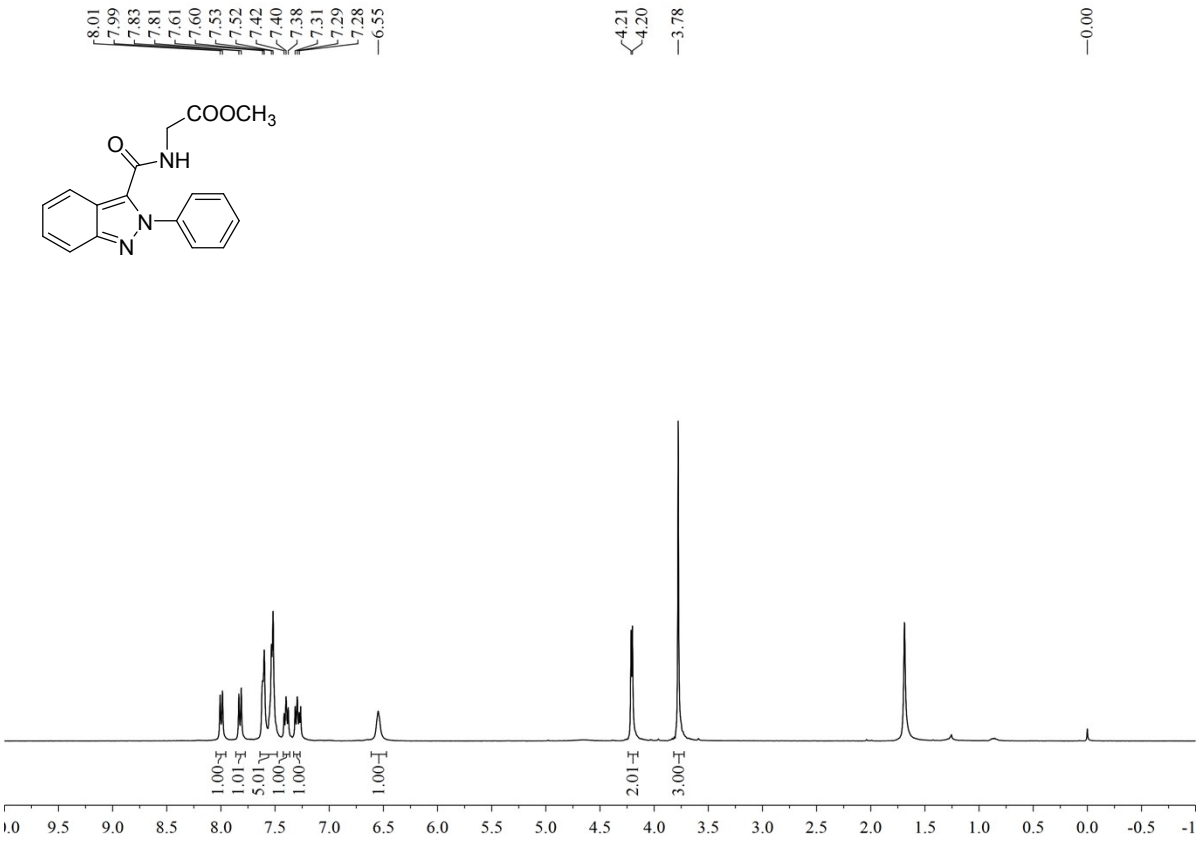
2bb

White solid, 305 mg, 70%, mp 192-193 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.81 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.28 (m, 6H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.78 (t, *J* = 6.6 Hz, 1H), 4.84 (d, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm) 160.35, 158.34, 148.16, 145.51, 133.91, 132.64, 130.05, 128.68, 127.10, 126.96, 126.69, 125.26, 122.50, 119.52, 118.62, 114.31, 60.09, 55.58, 21.69. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{23}H_{21}N_3O_4S$ 436.1331; found 436.1334.

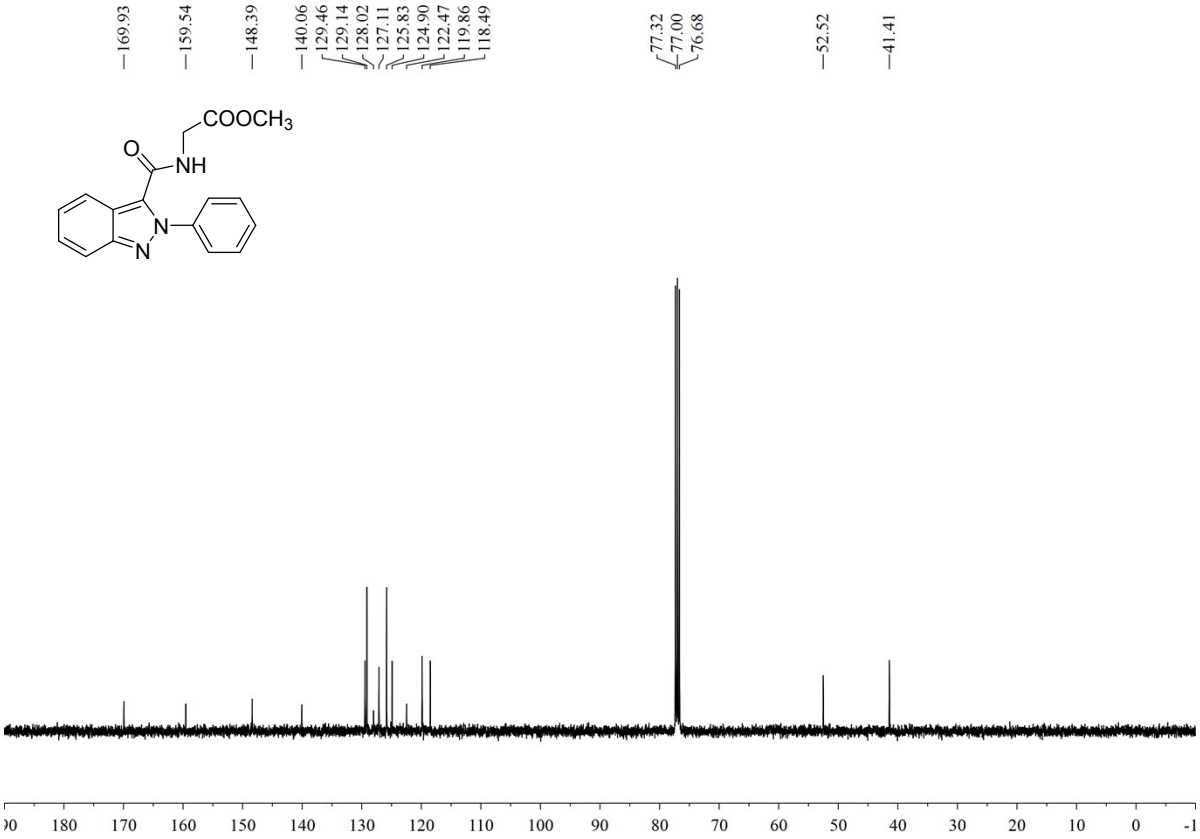
1 M. Chen, Studies on the phosphoric acid catalyzed Ugi-type reaction and its application in heterocyclic synthesis [D], *Central China Normal University.*, 2015. (in Chinese)

4. Copies of ^{1}H and ^{13}C NMR spectras of compounds 2aa-2bb

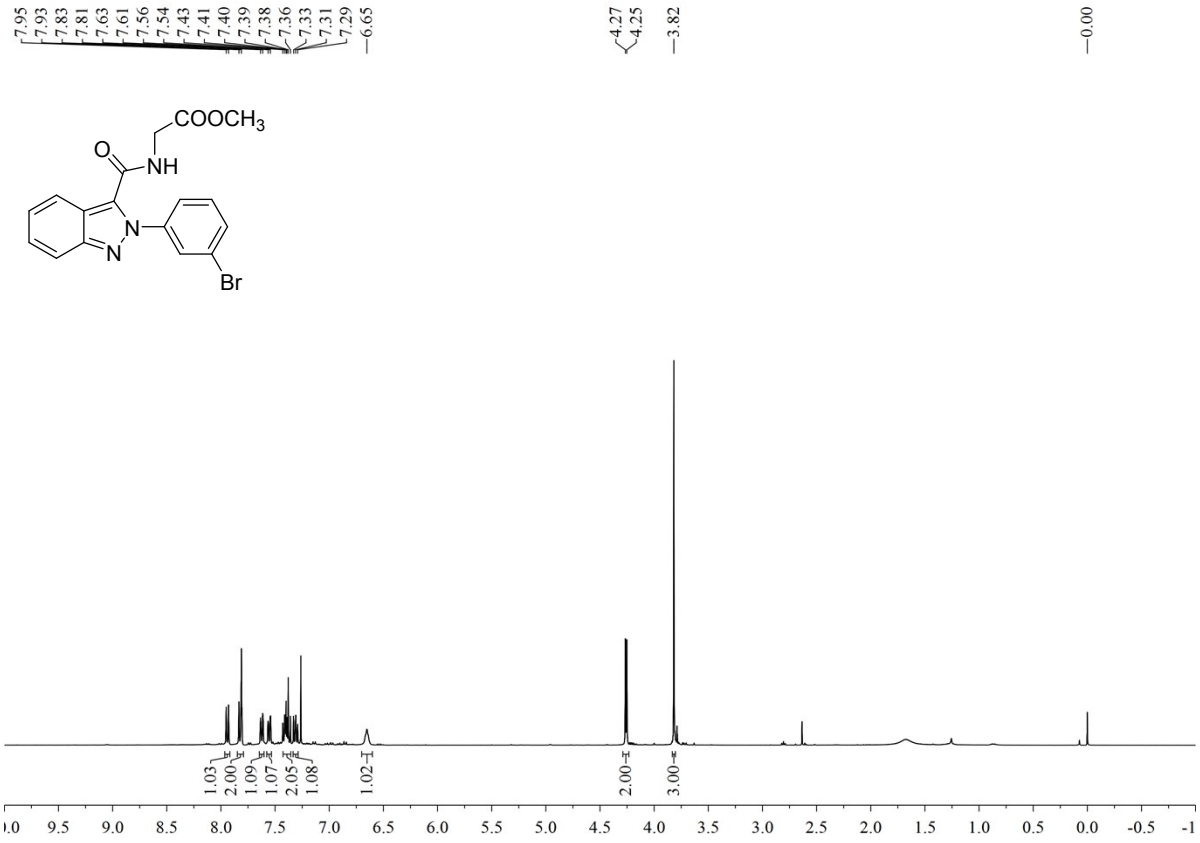
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2aa.



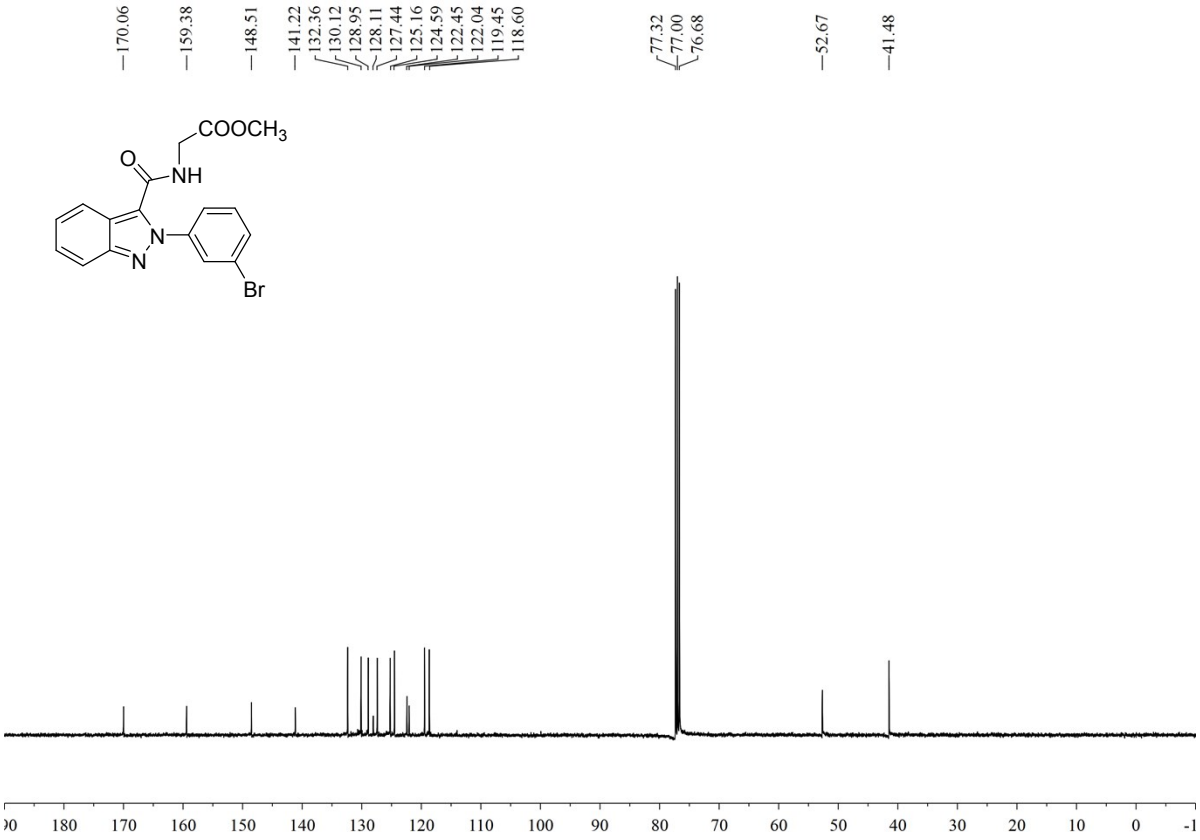
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2aa.



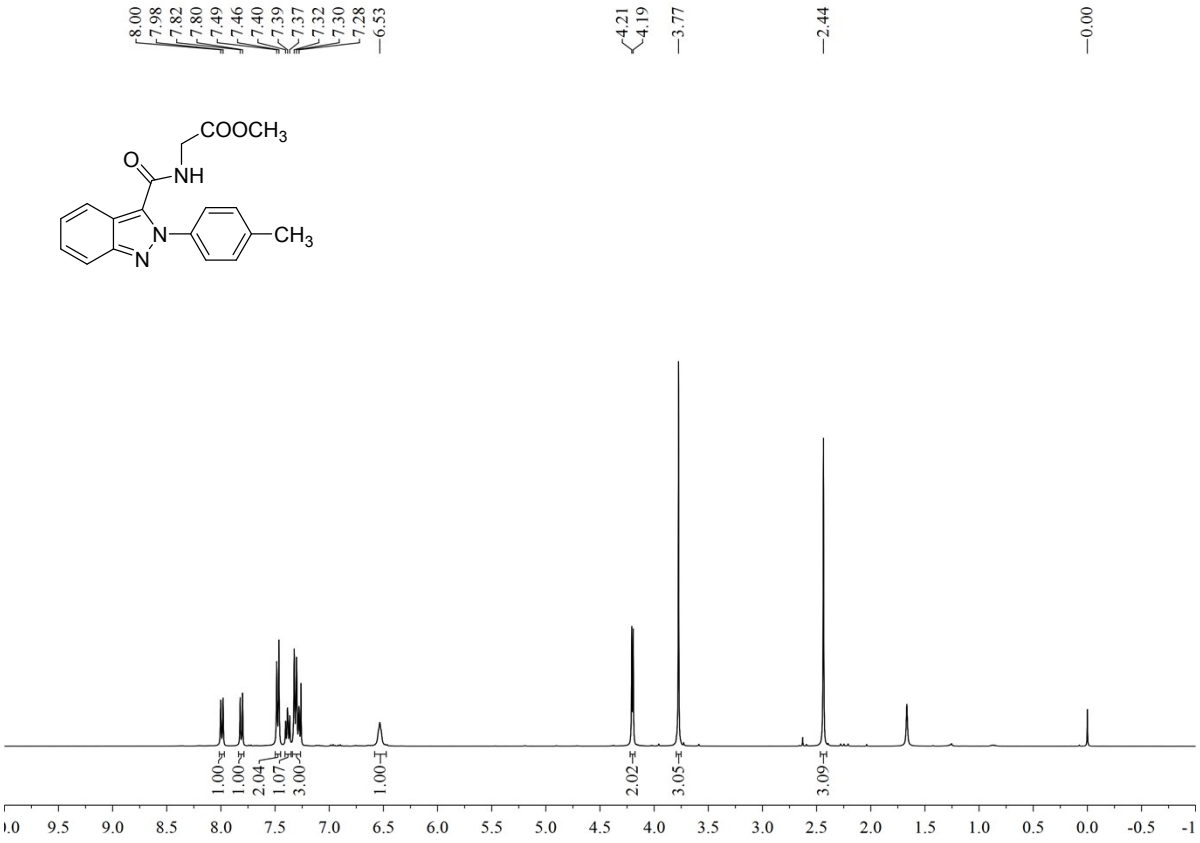
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ab.



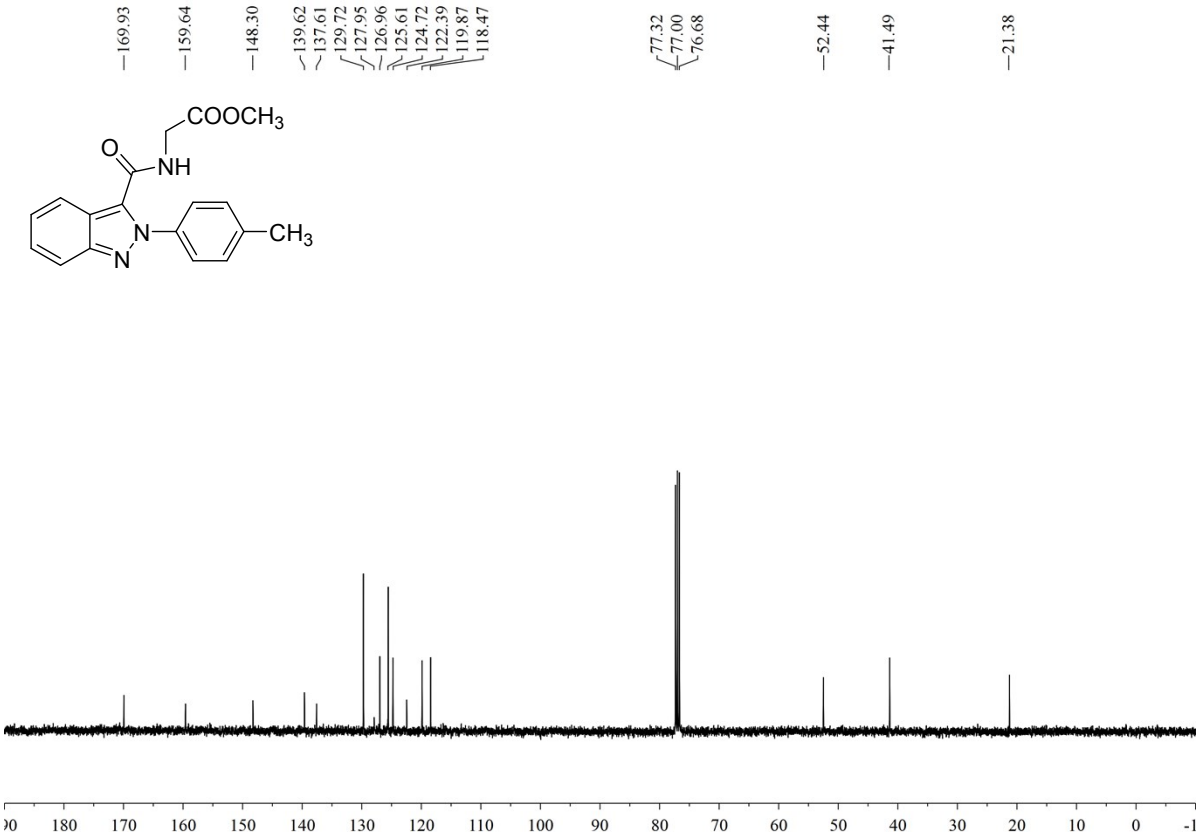
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ab.



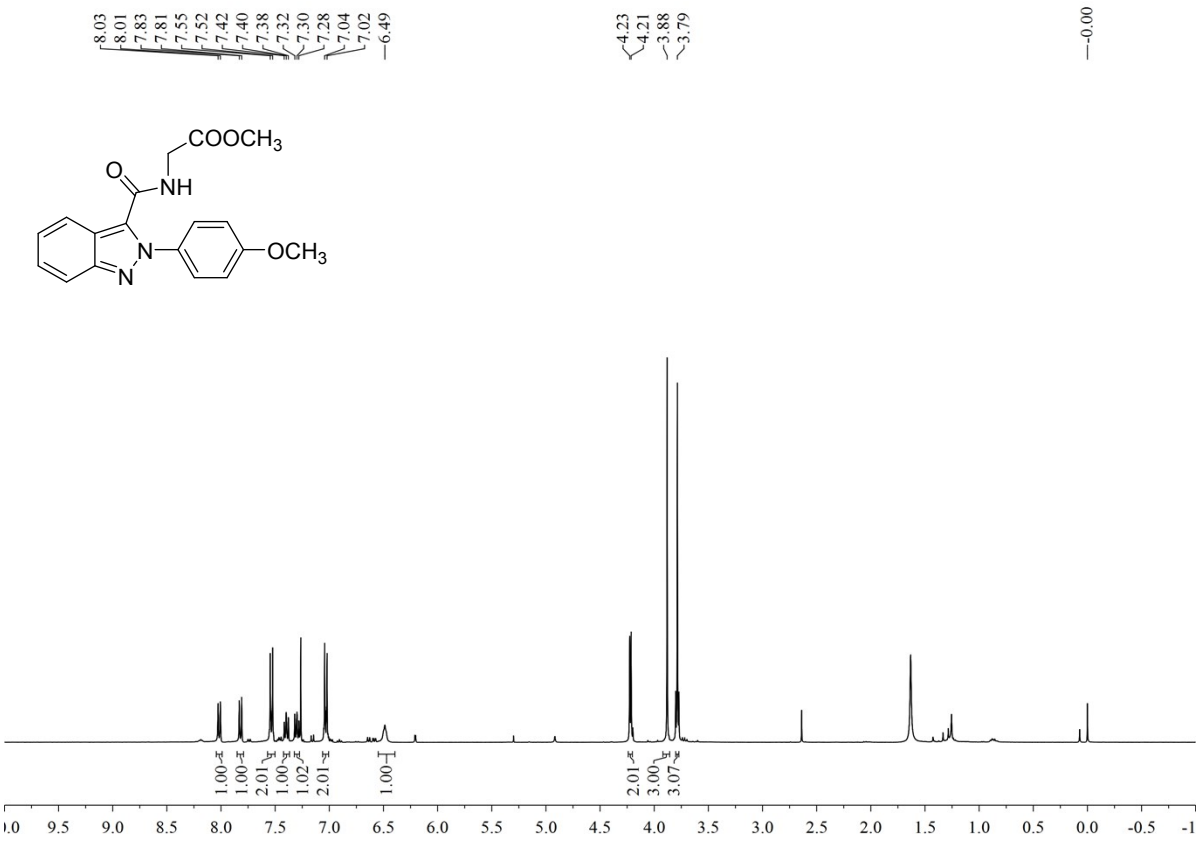
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ac.



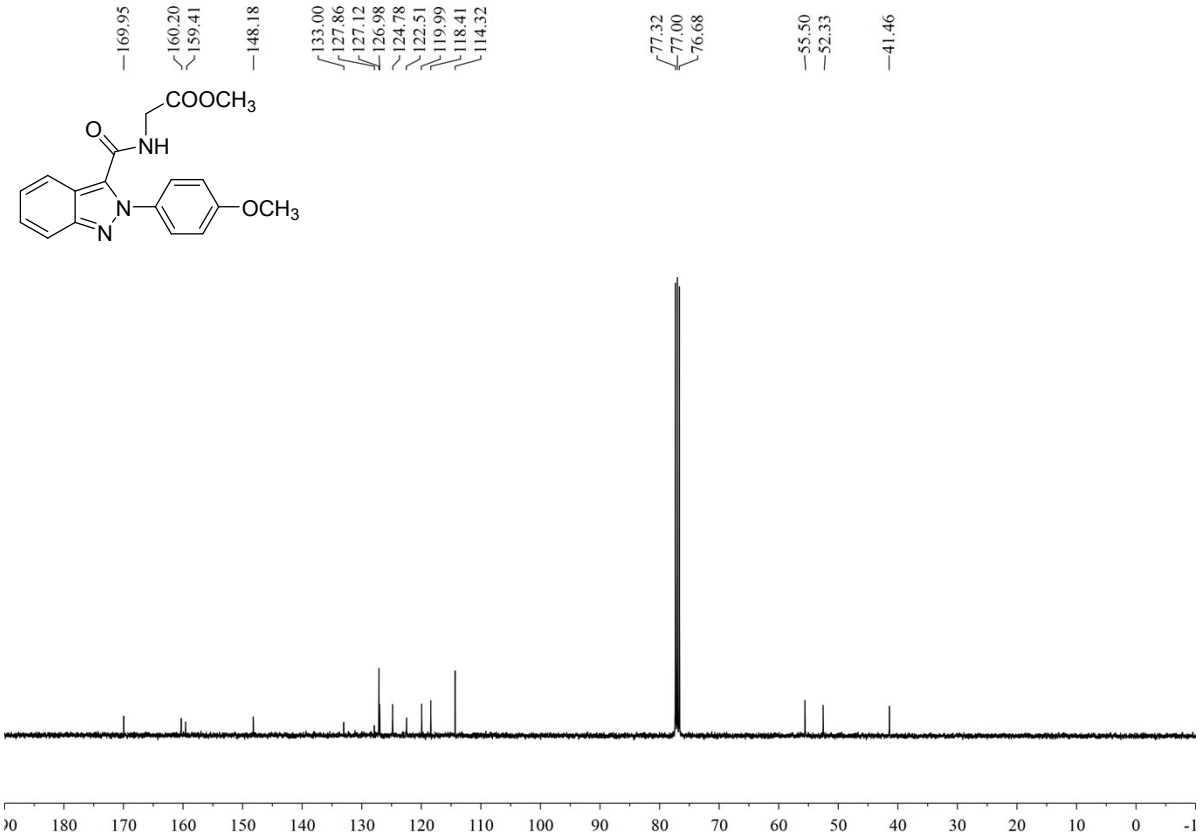
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ac.



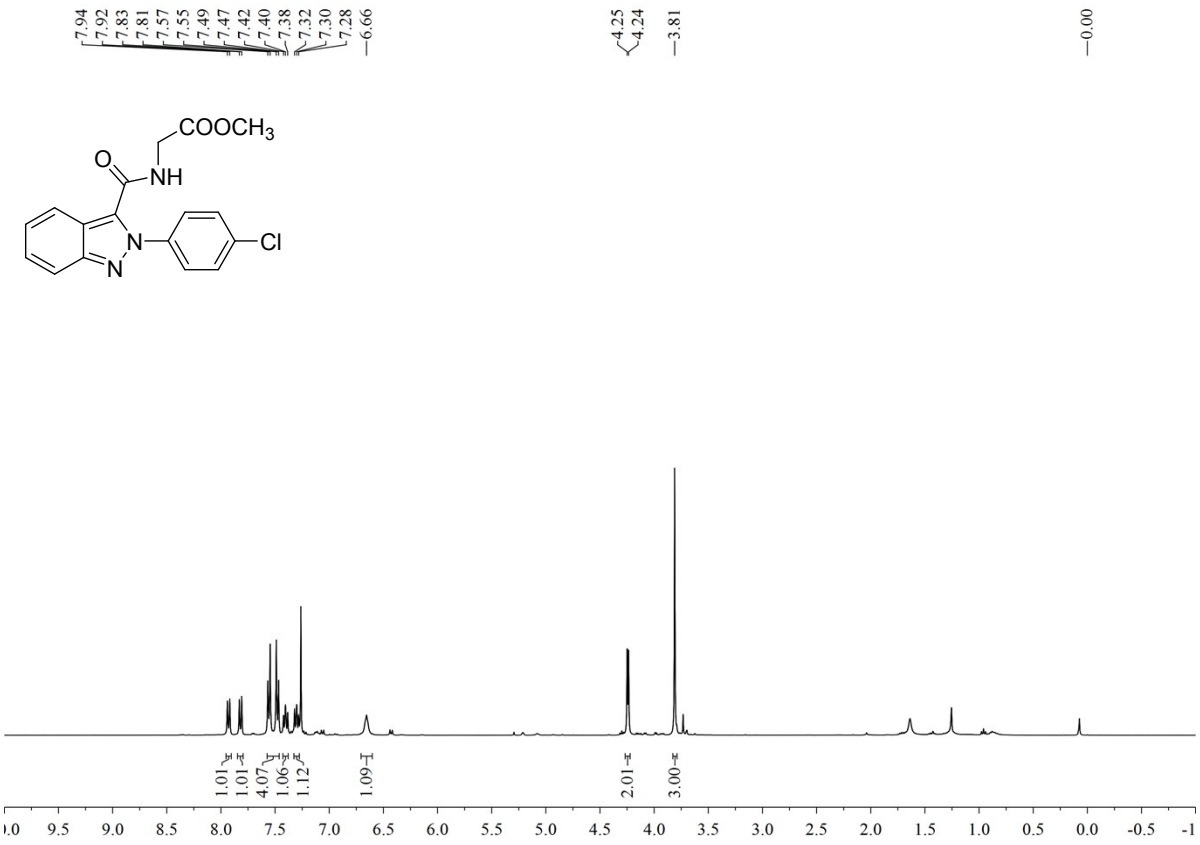
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ad.



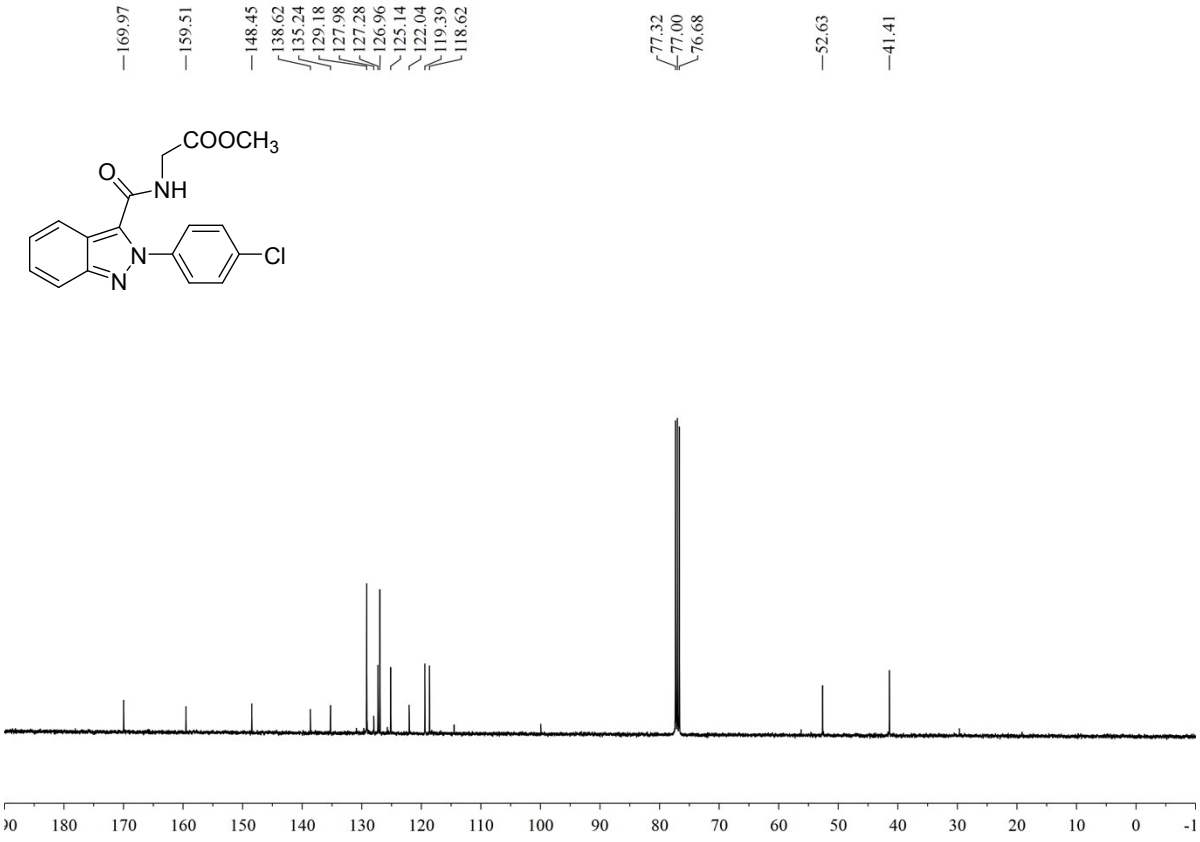
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ad.



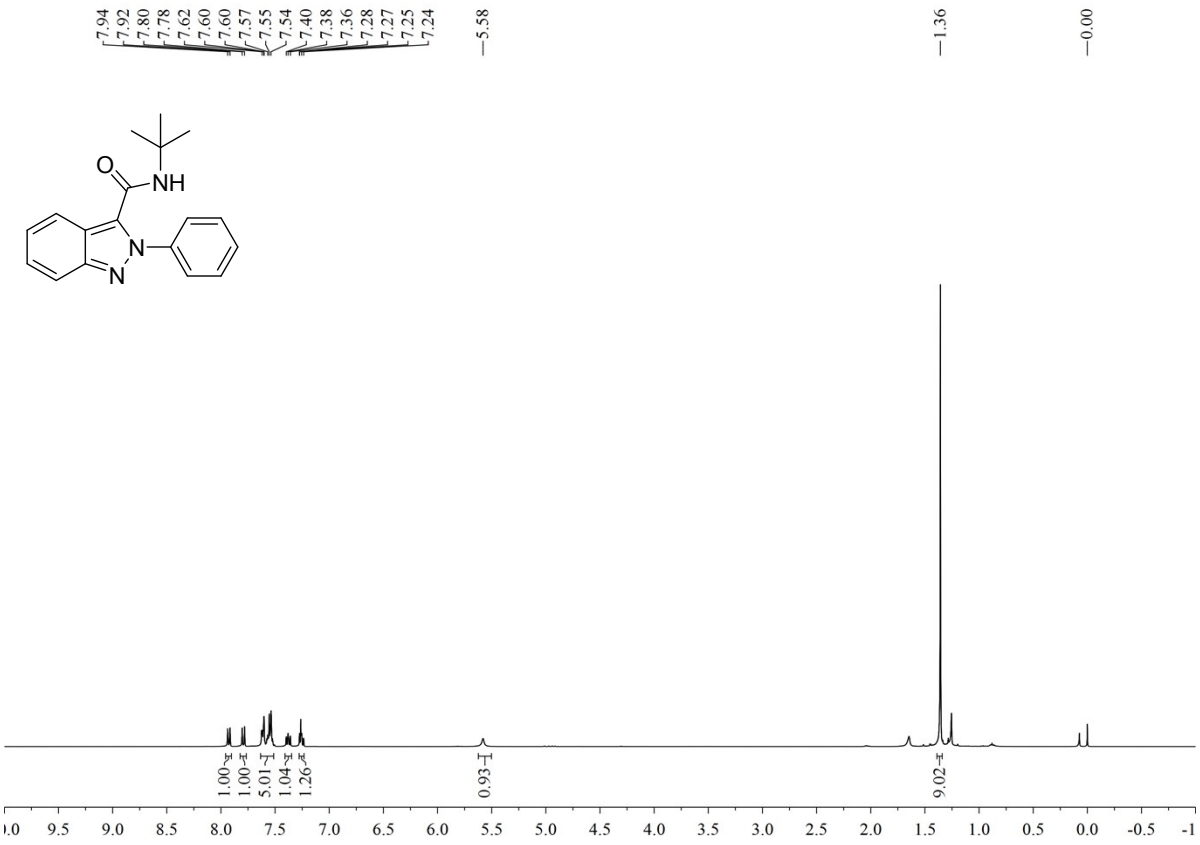
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ae.



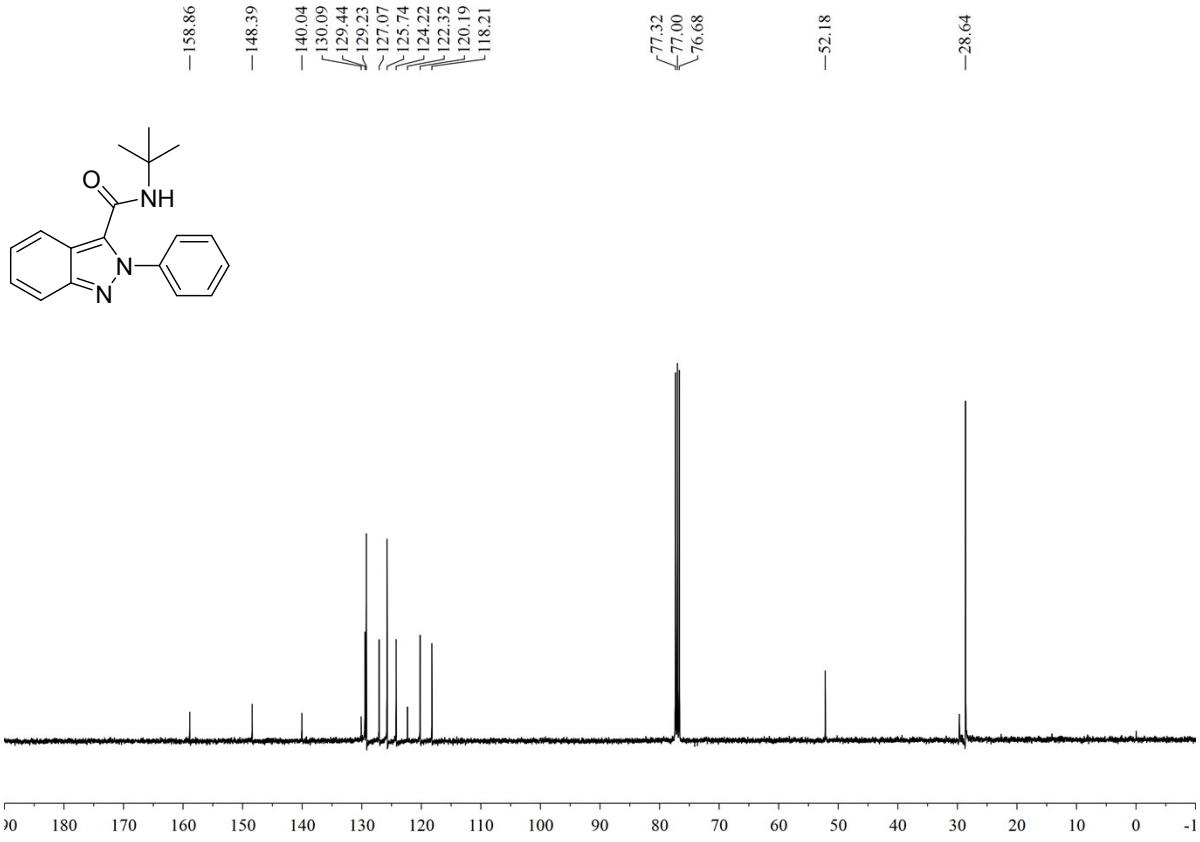
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ae.



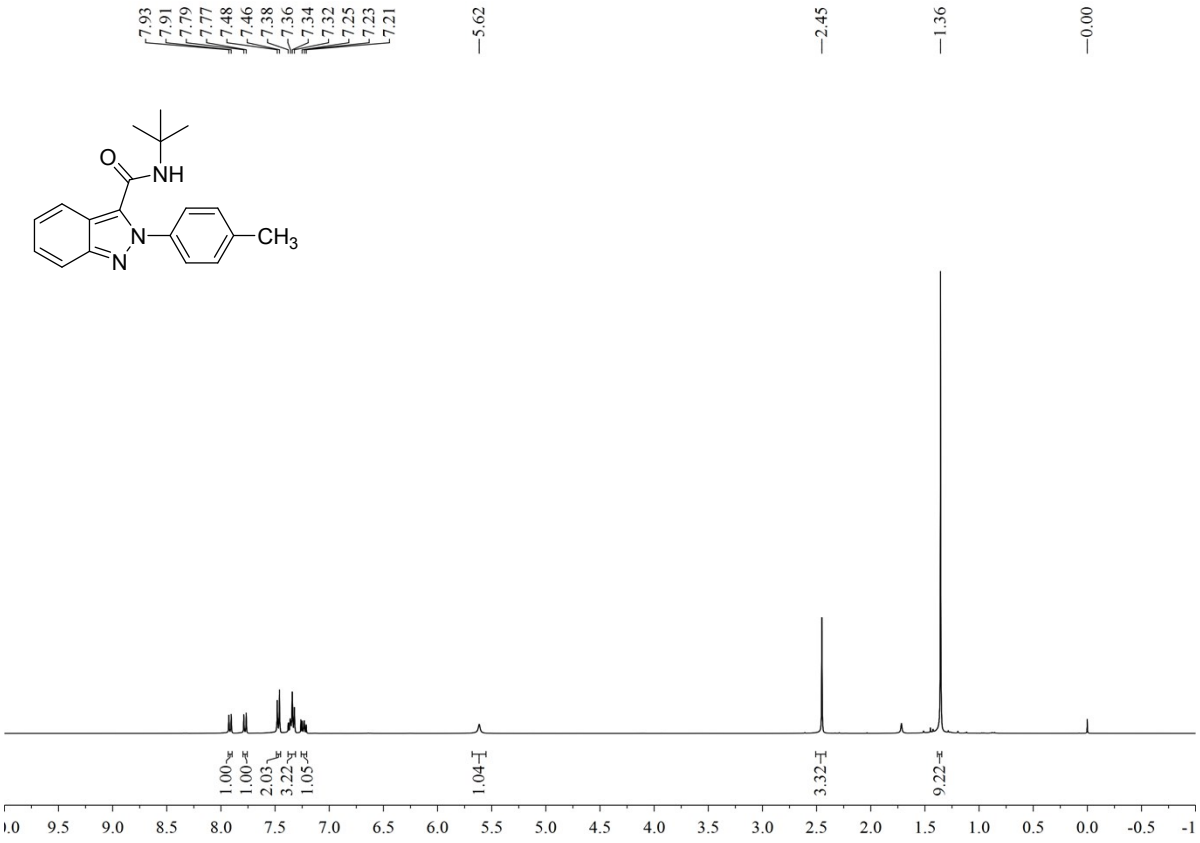
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2af.



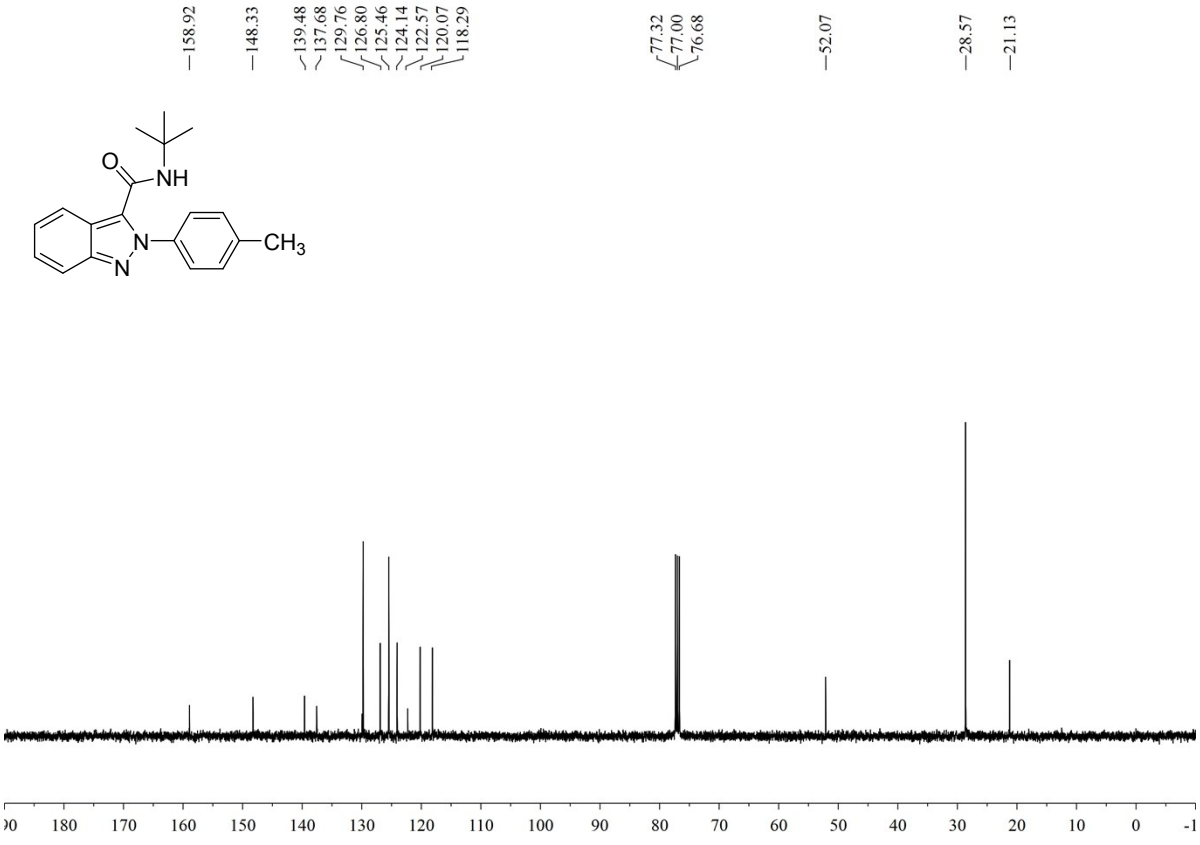
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2af.



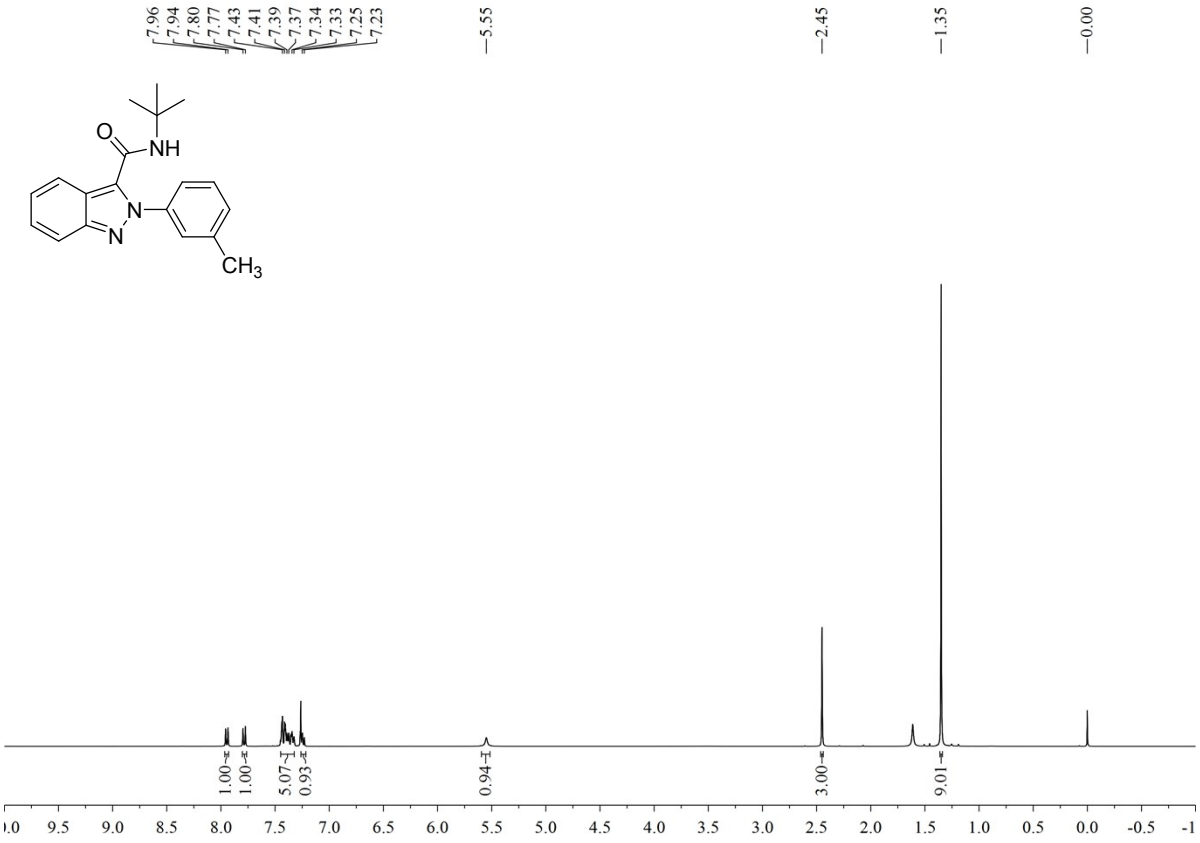
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ag.



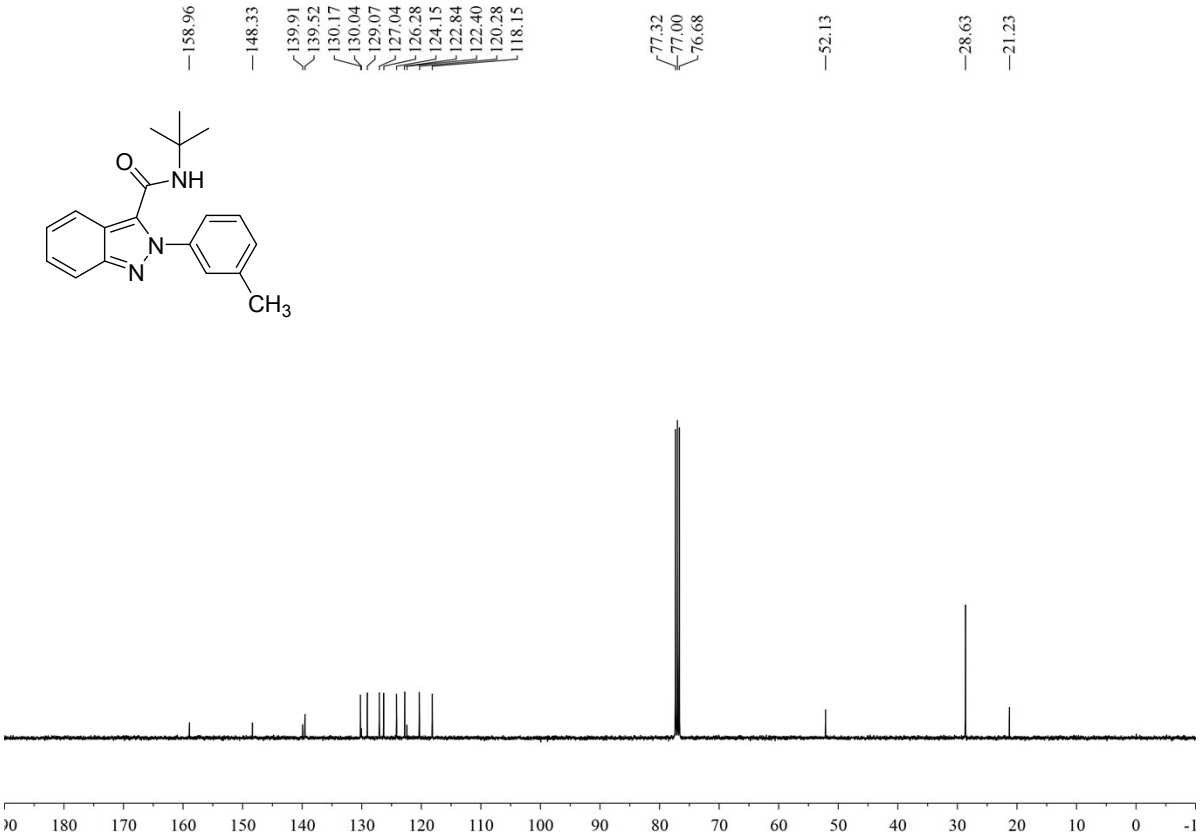
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ag.



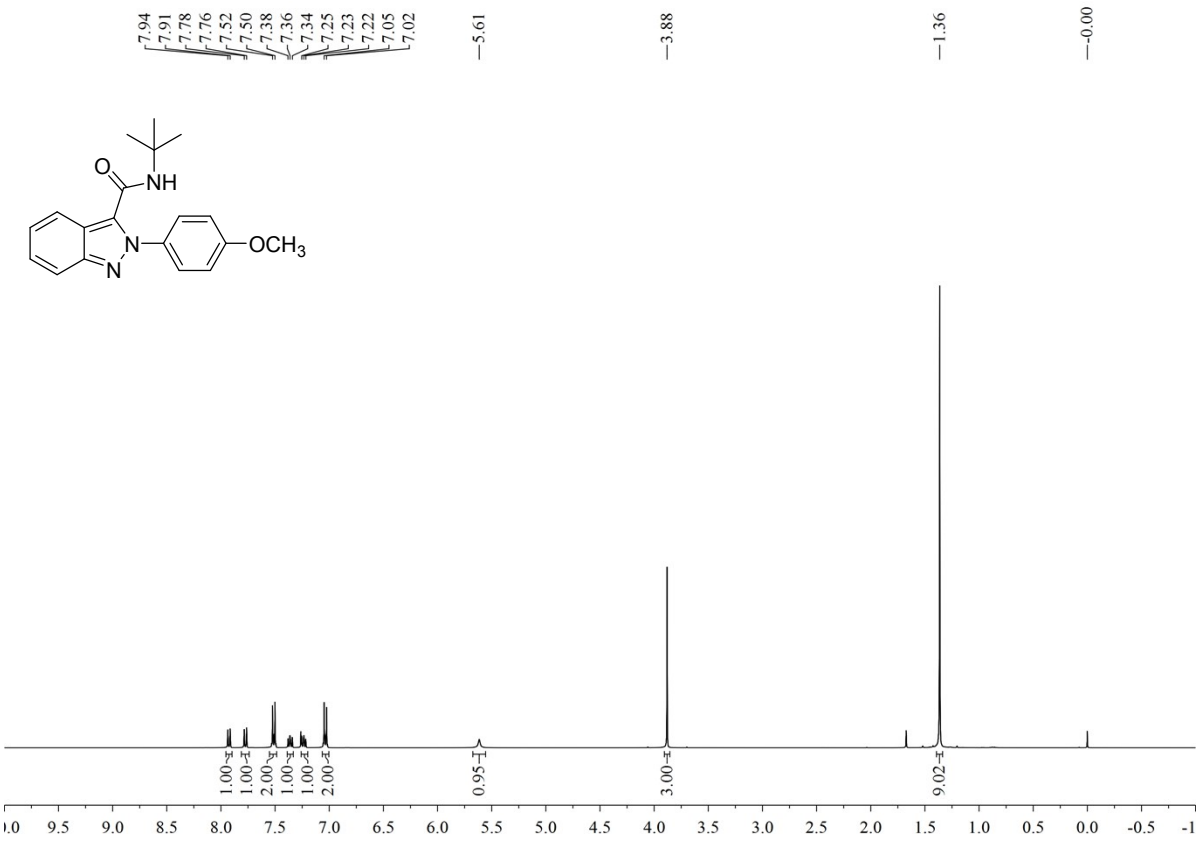
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ah.



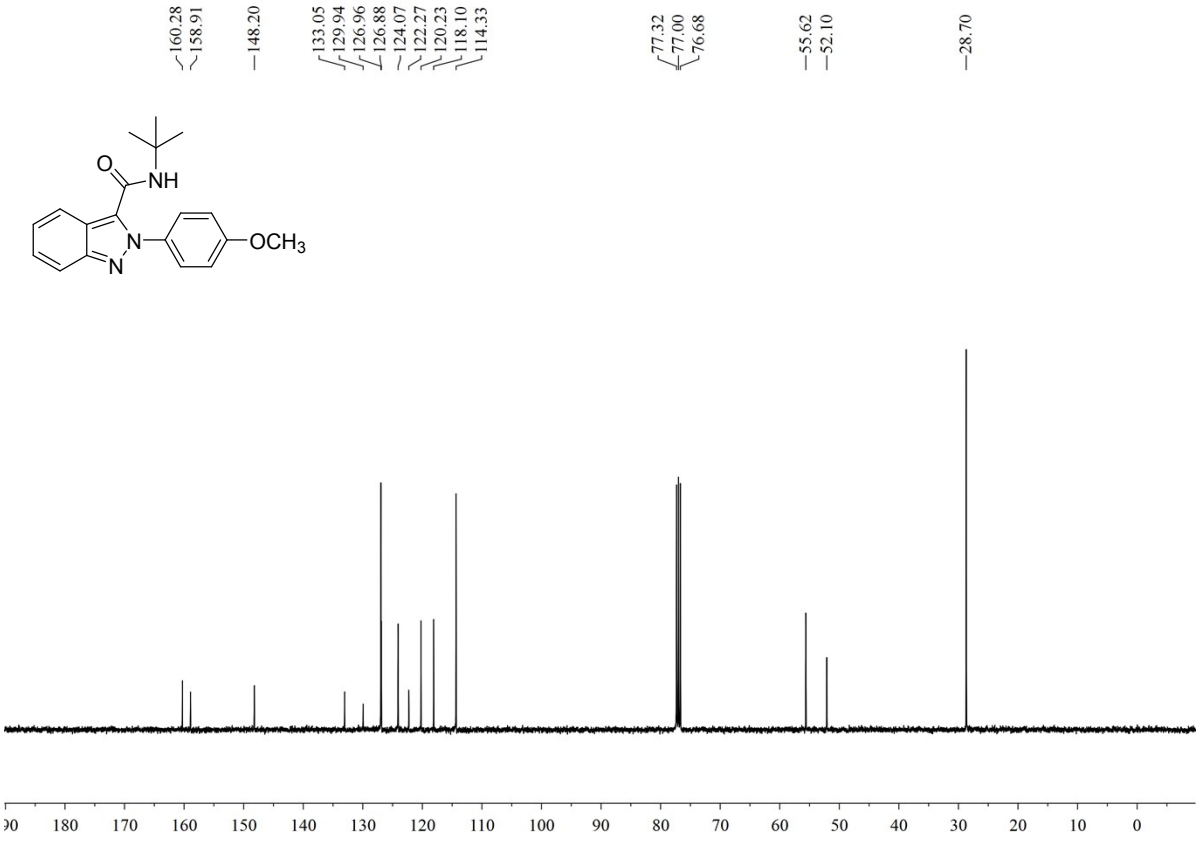
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ah.



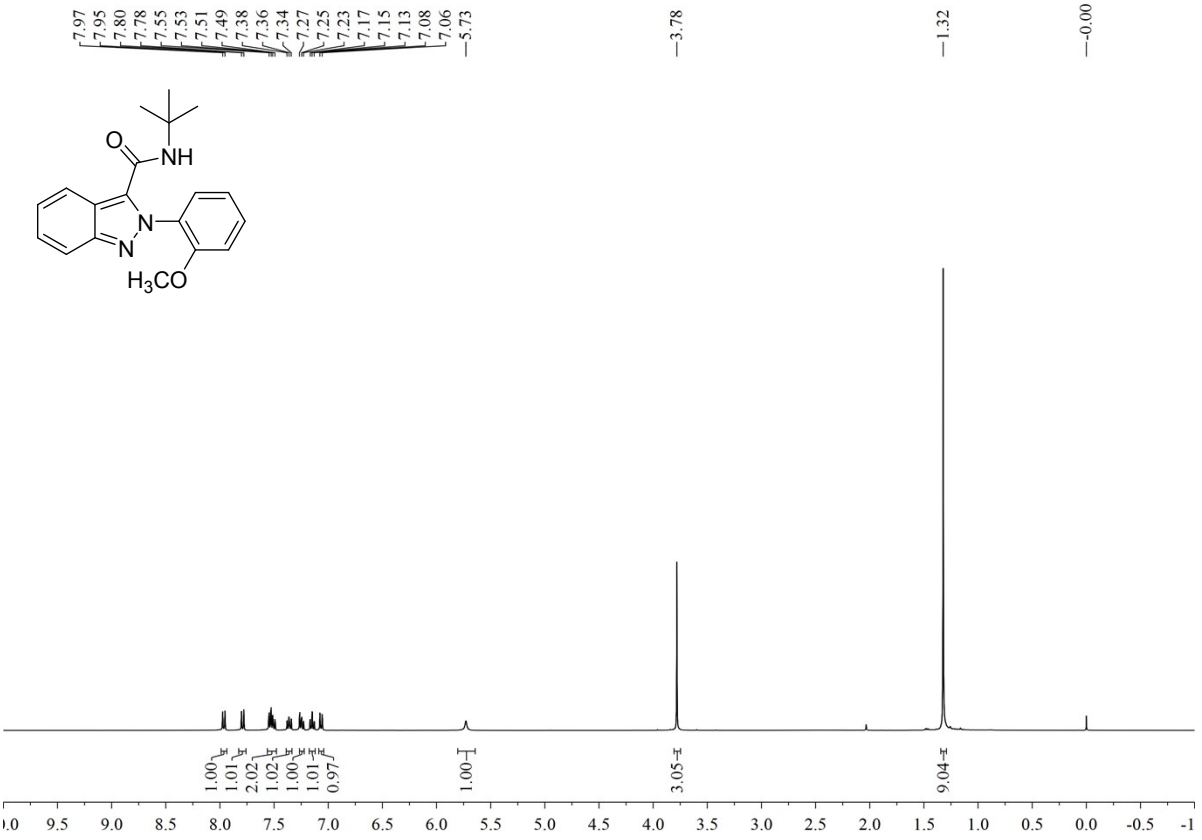
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ai.



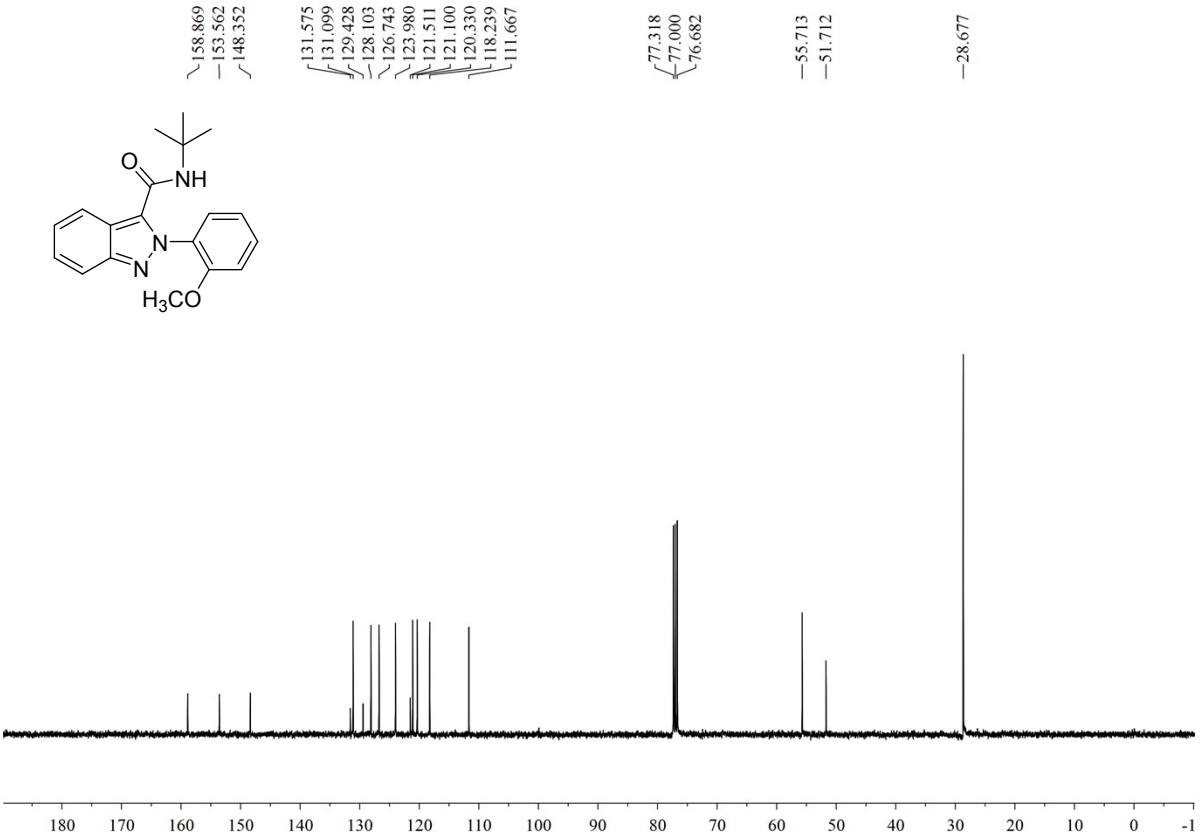
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ai.



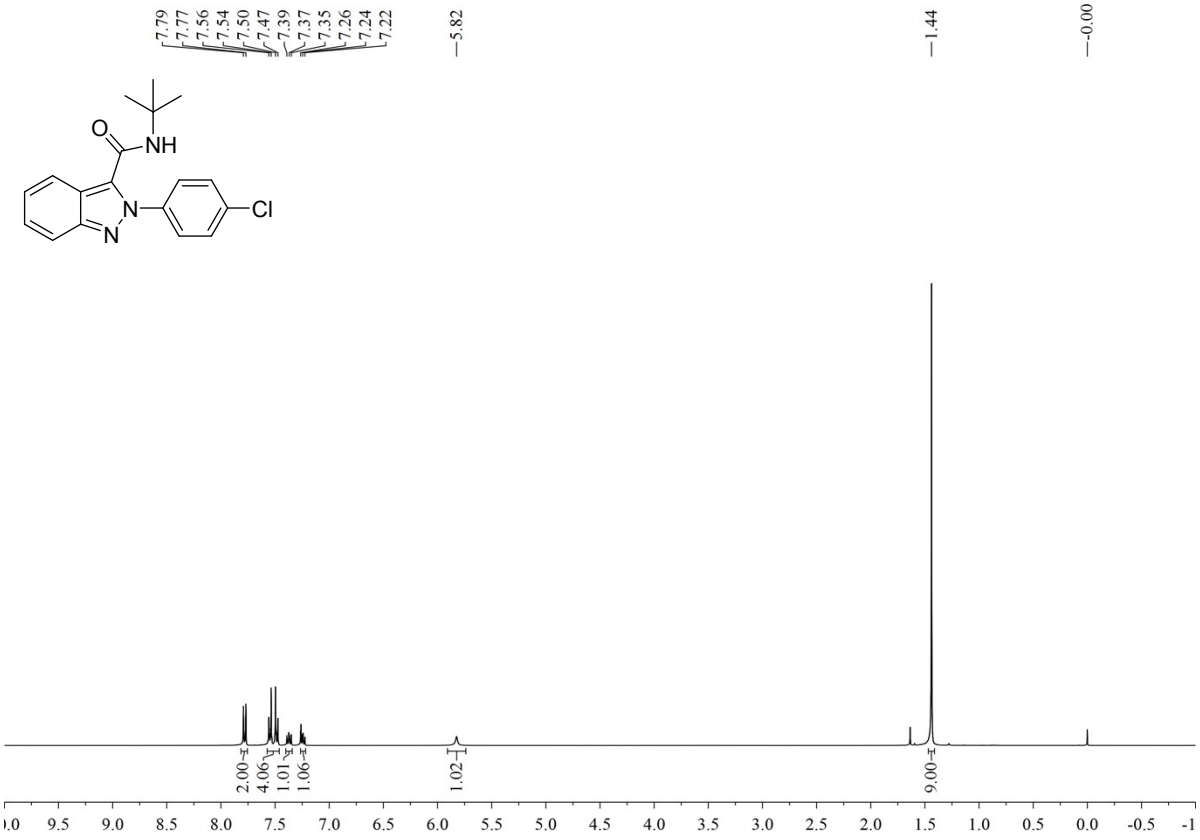
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2aj.



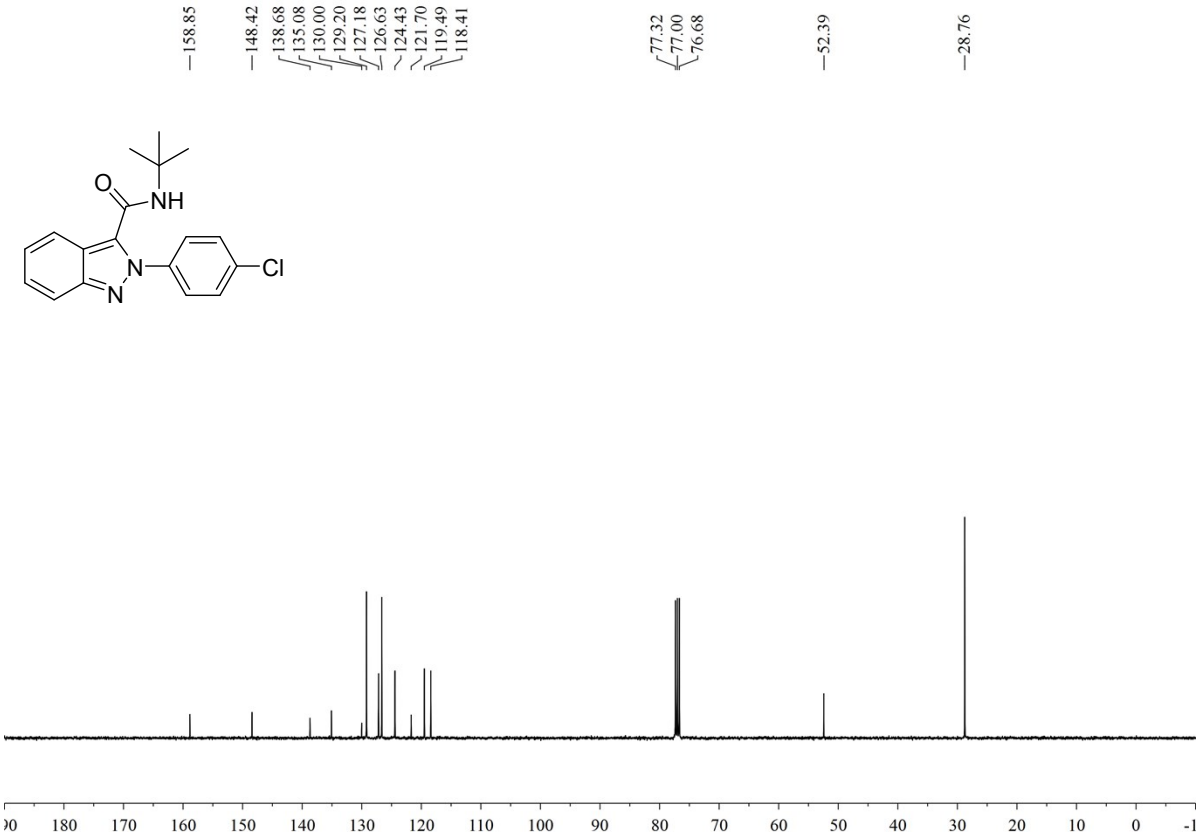
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2aj.



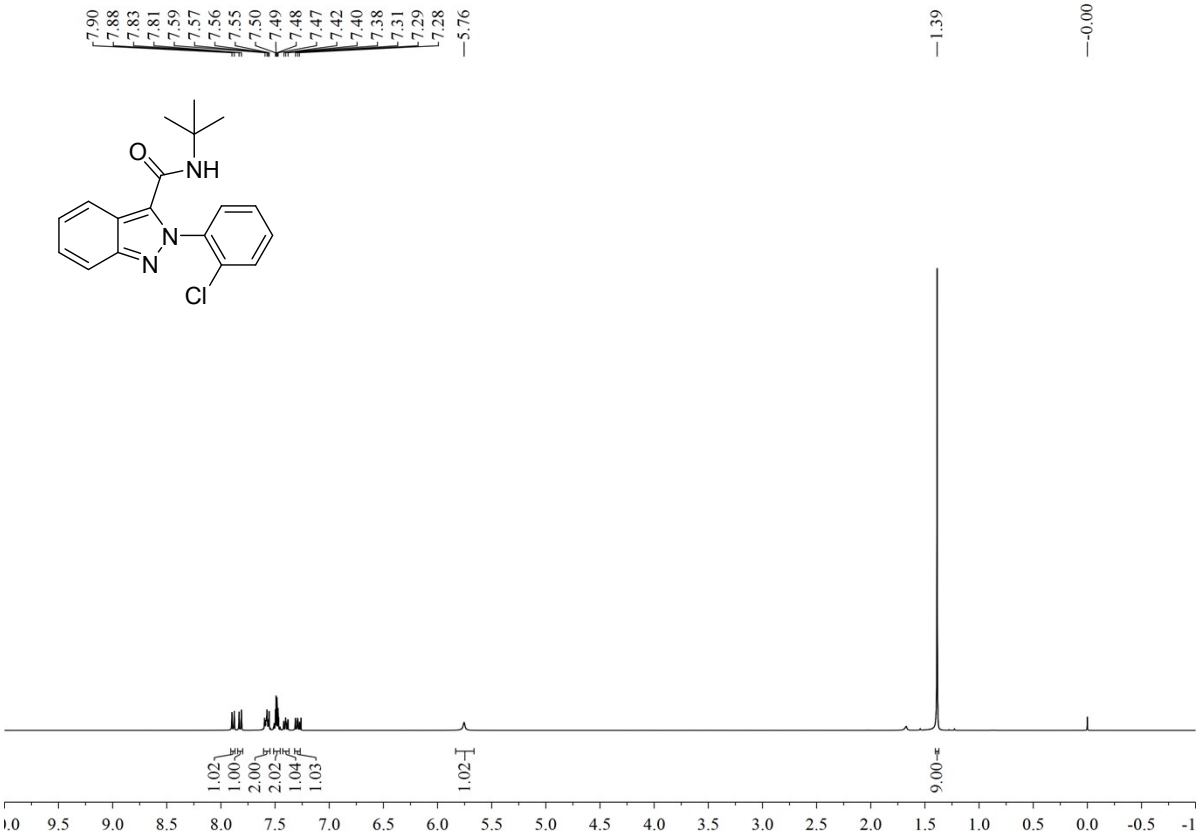
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ak.



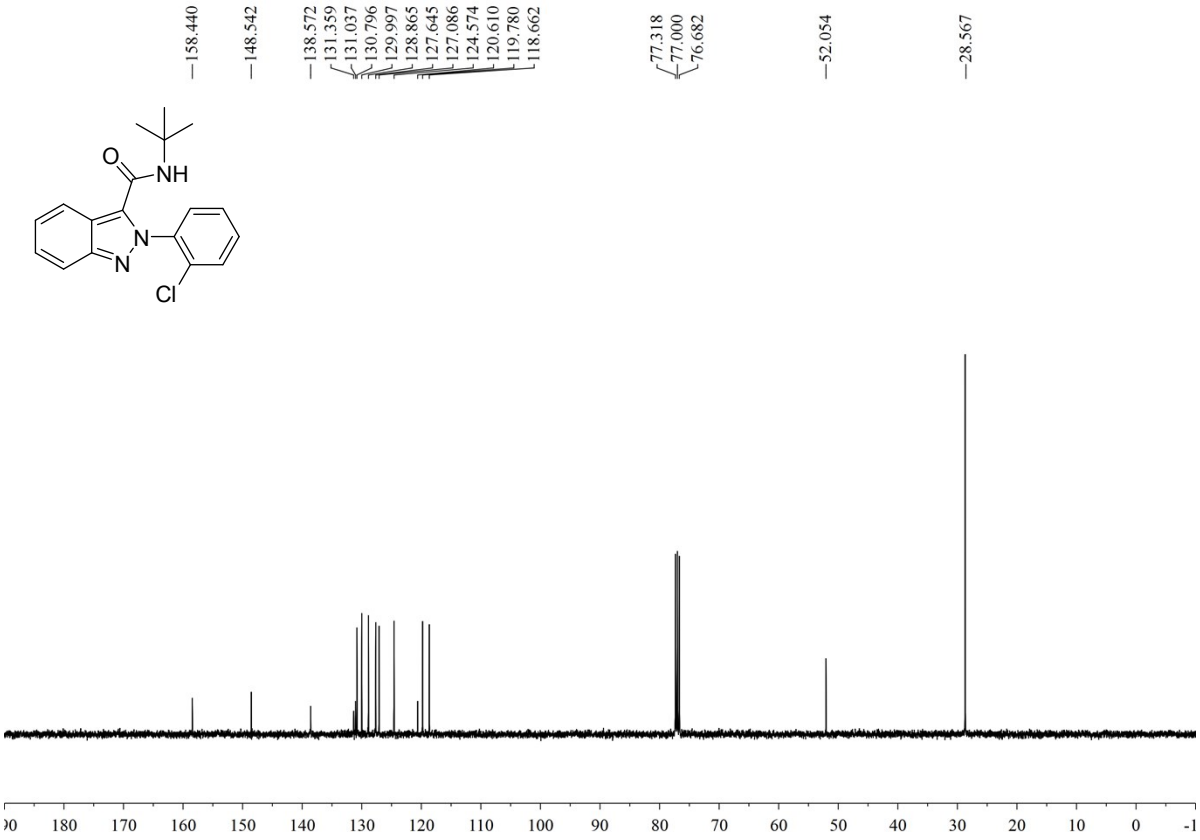
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ak.



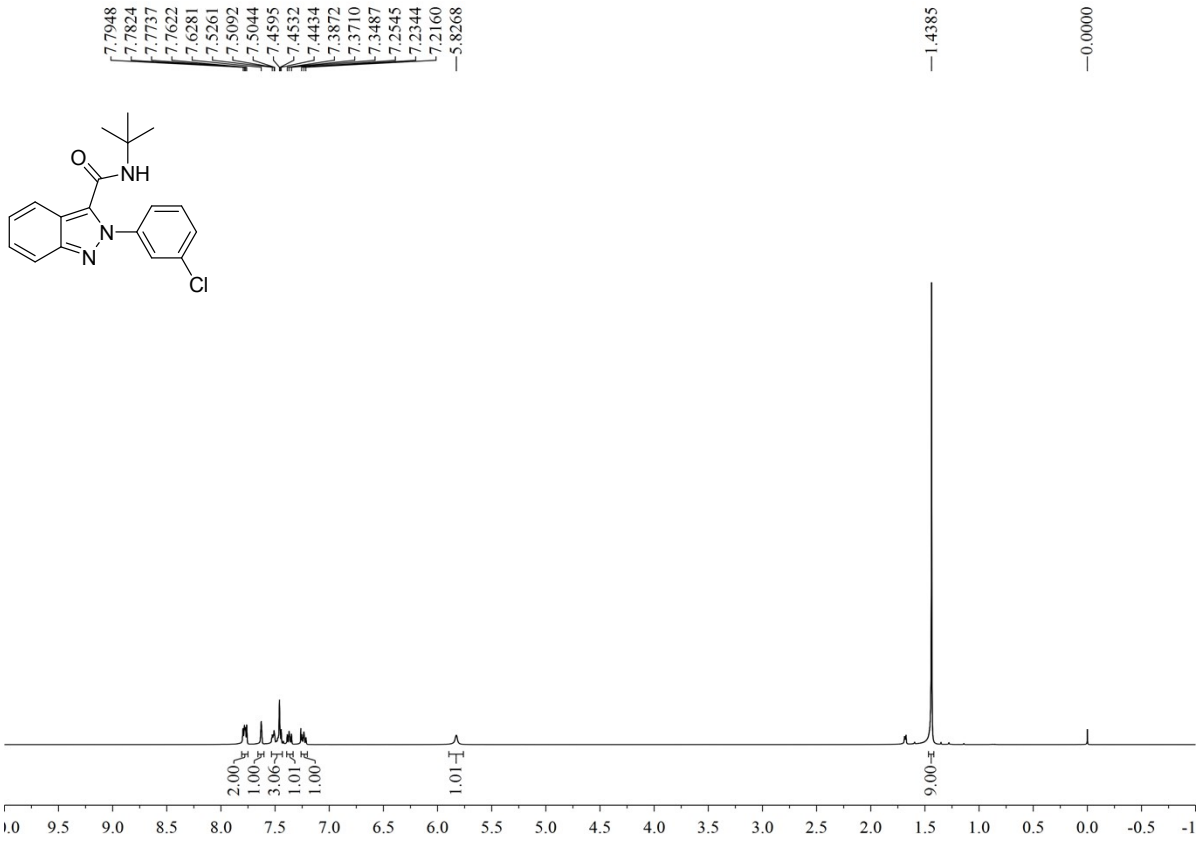
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2al.



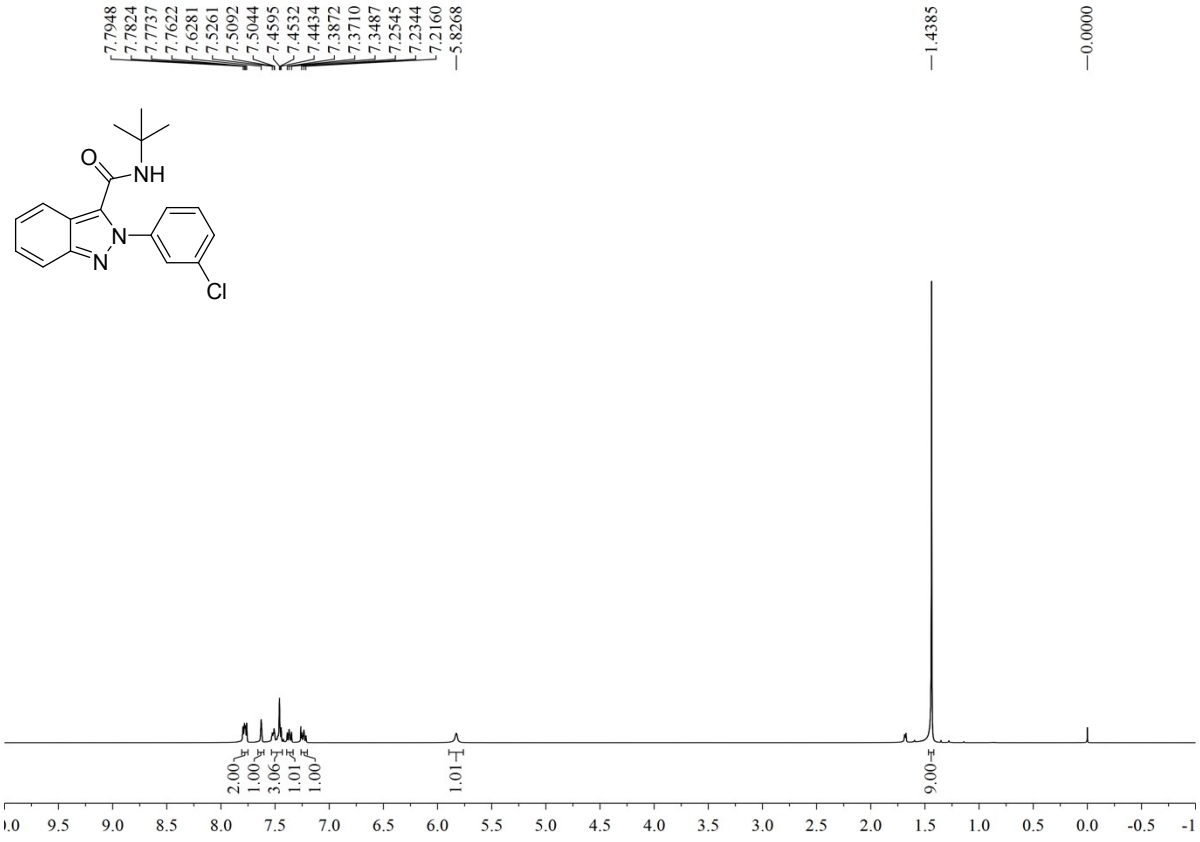
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2al.



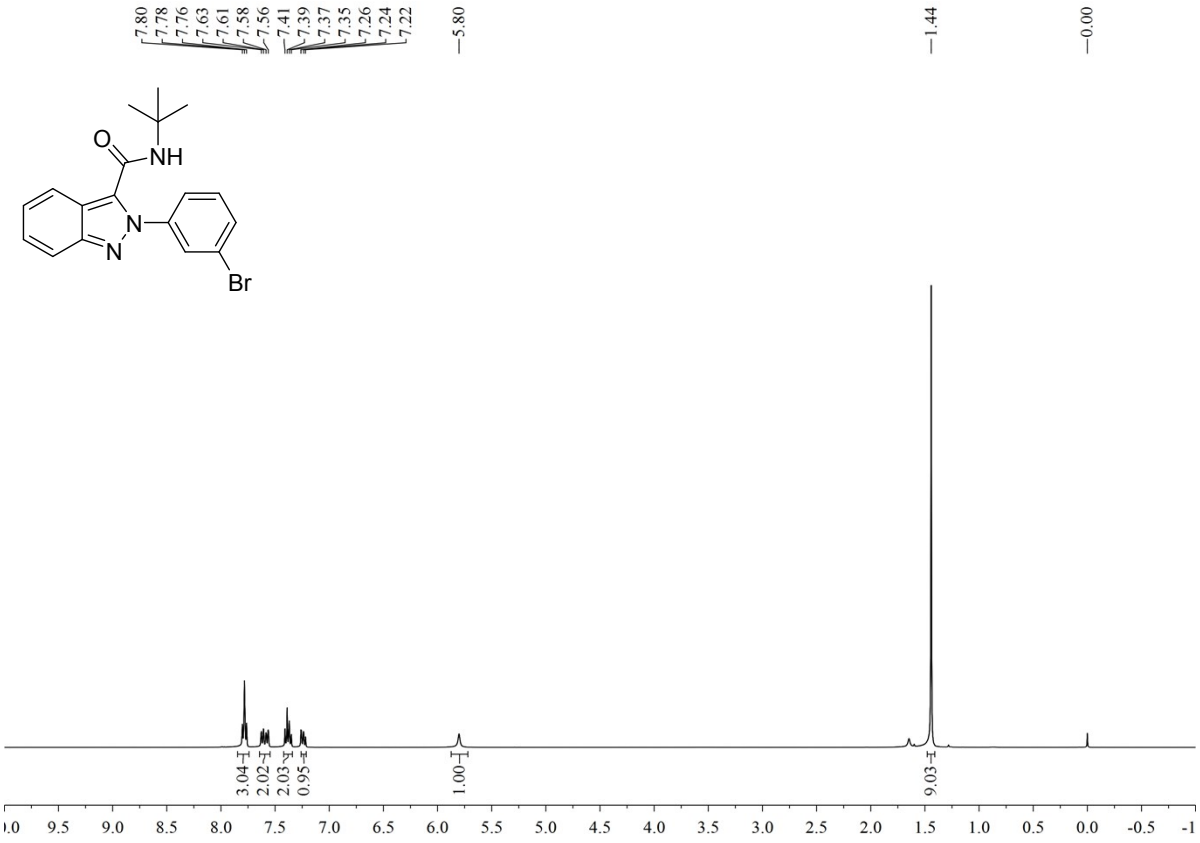
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2am.



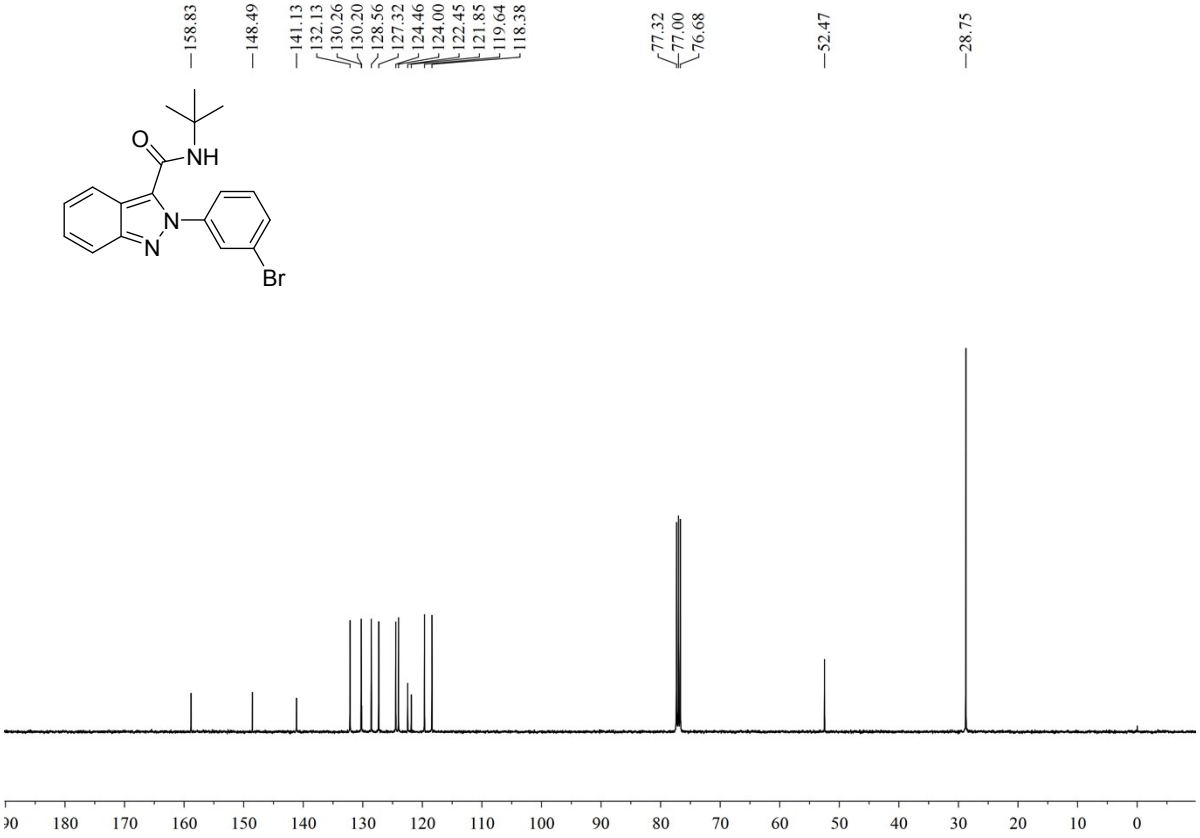
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2am.



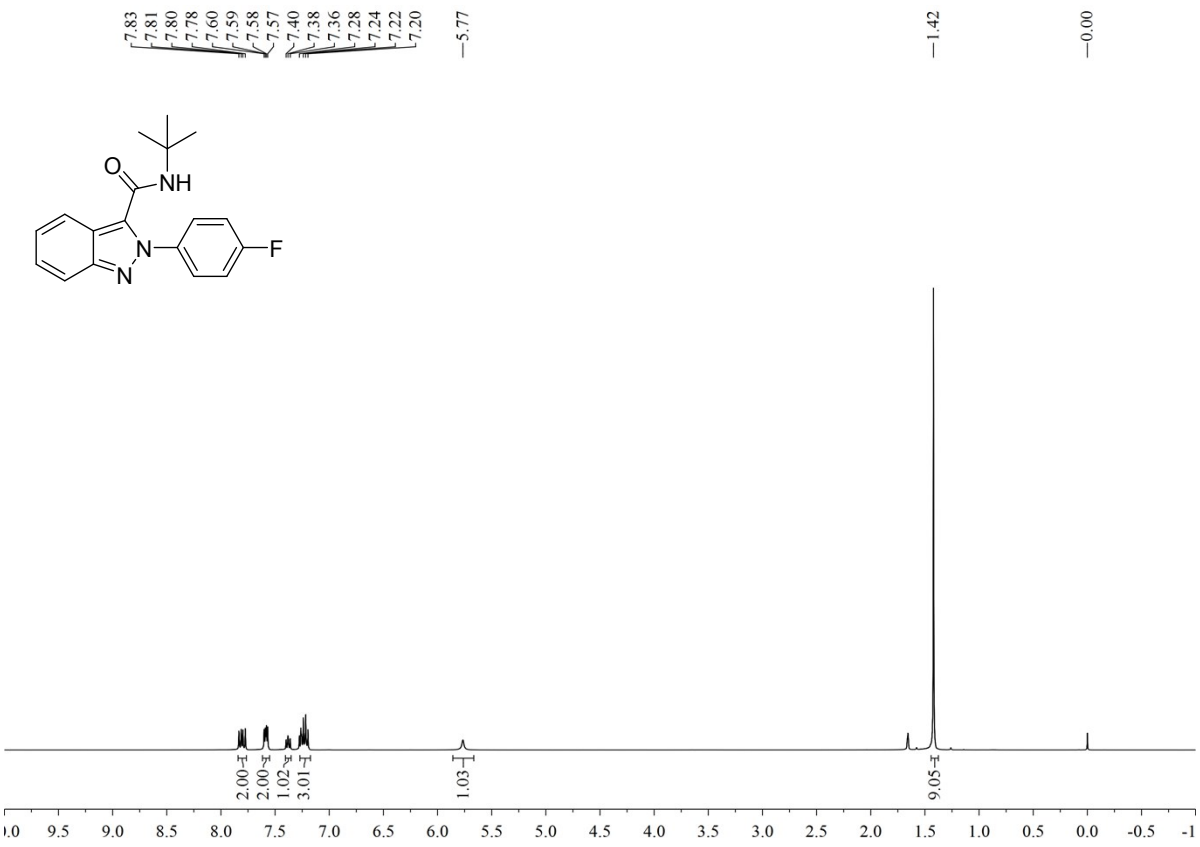
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2an.



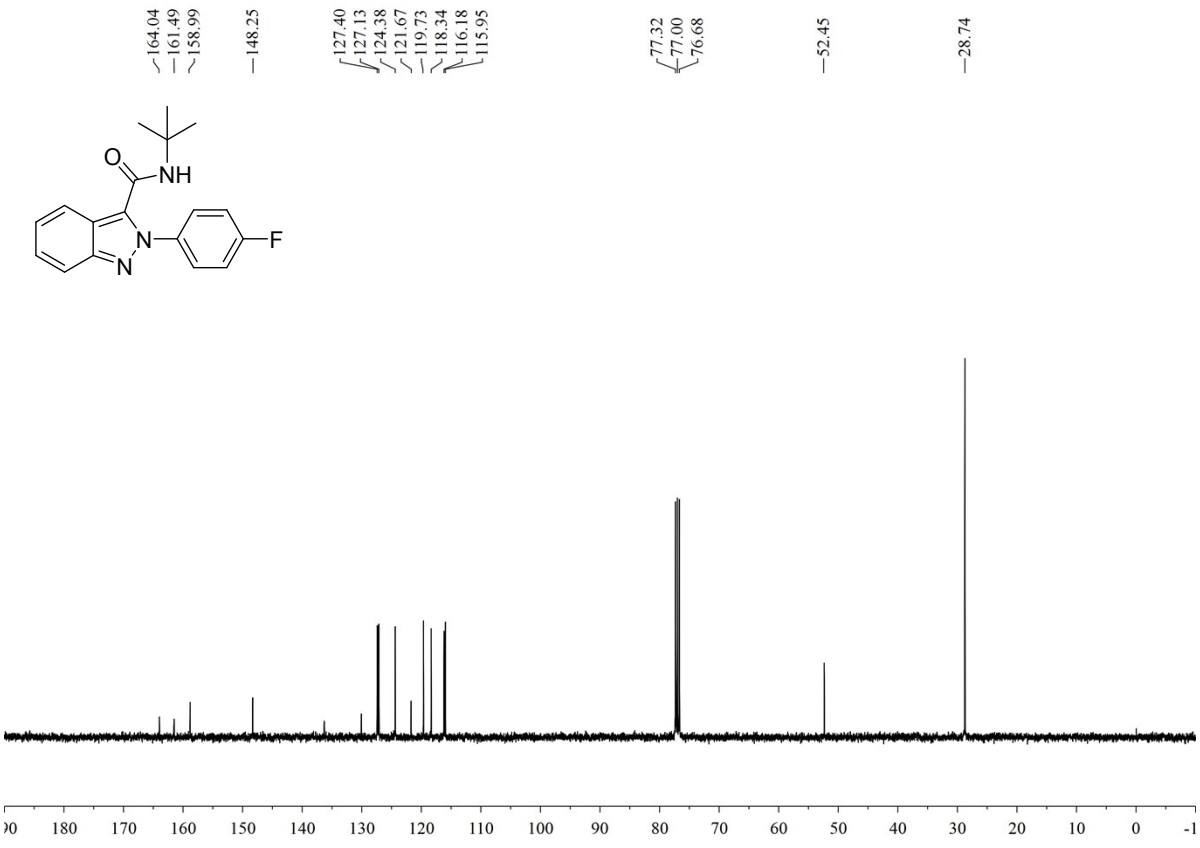
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2an.



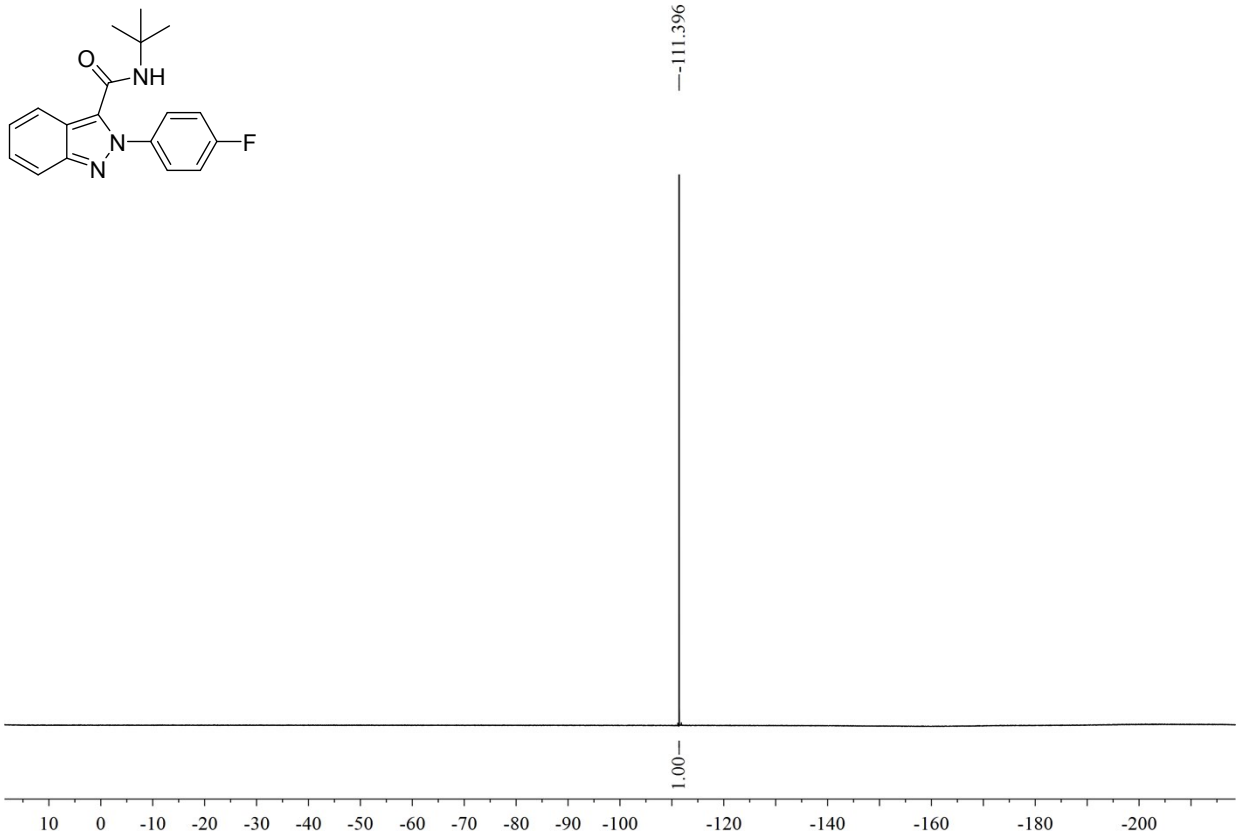
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ao.



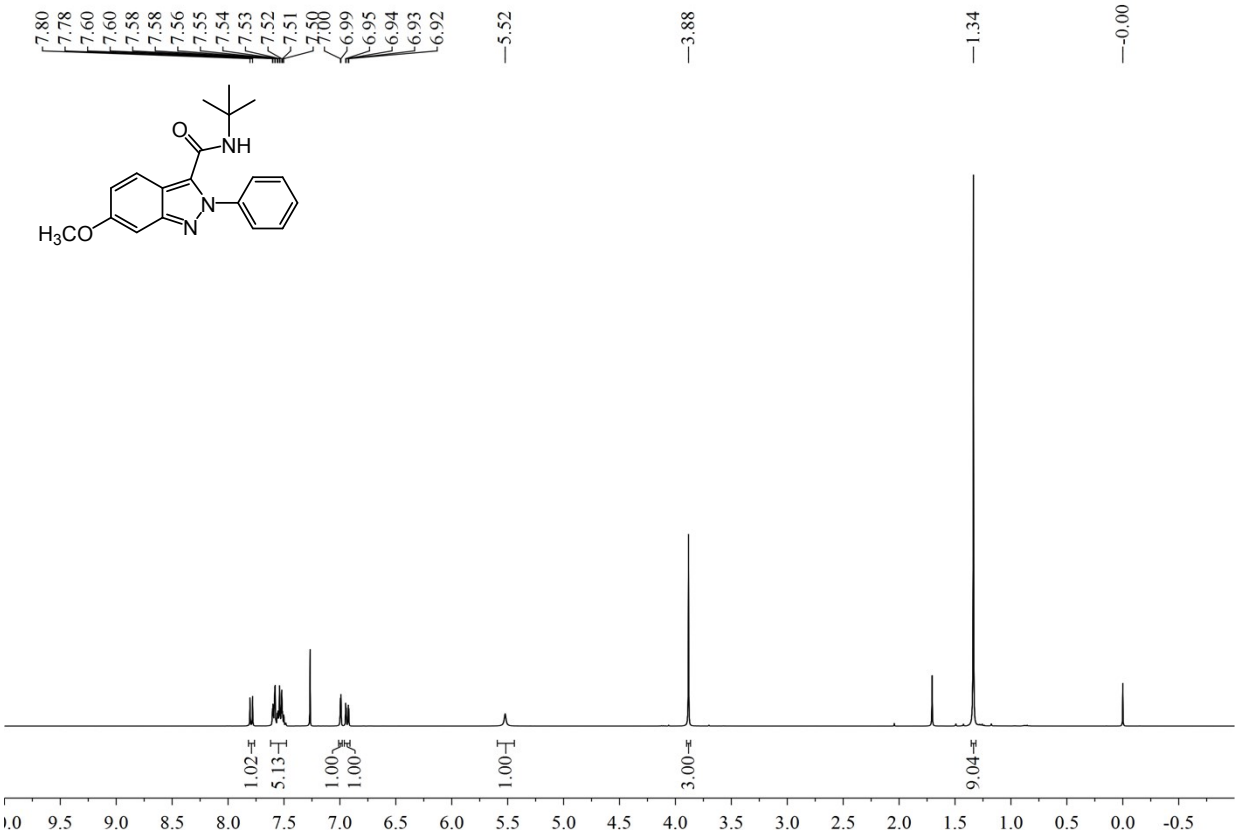
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ao.



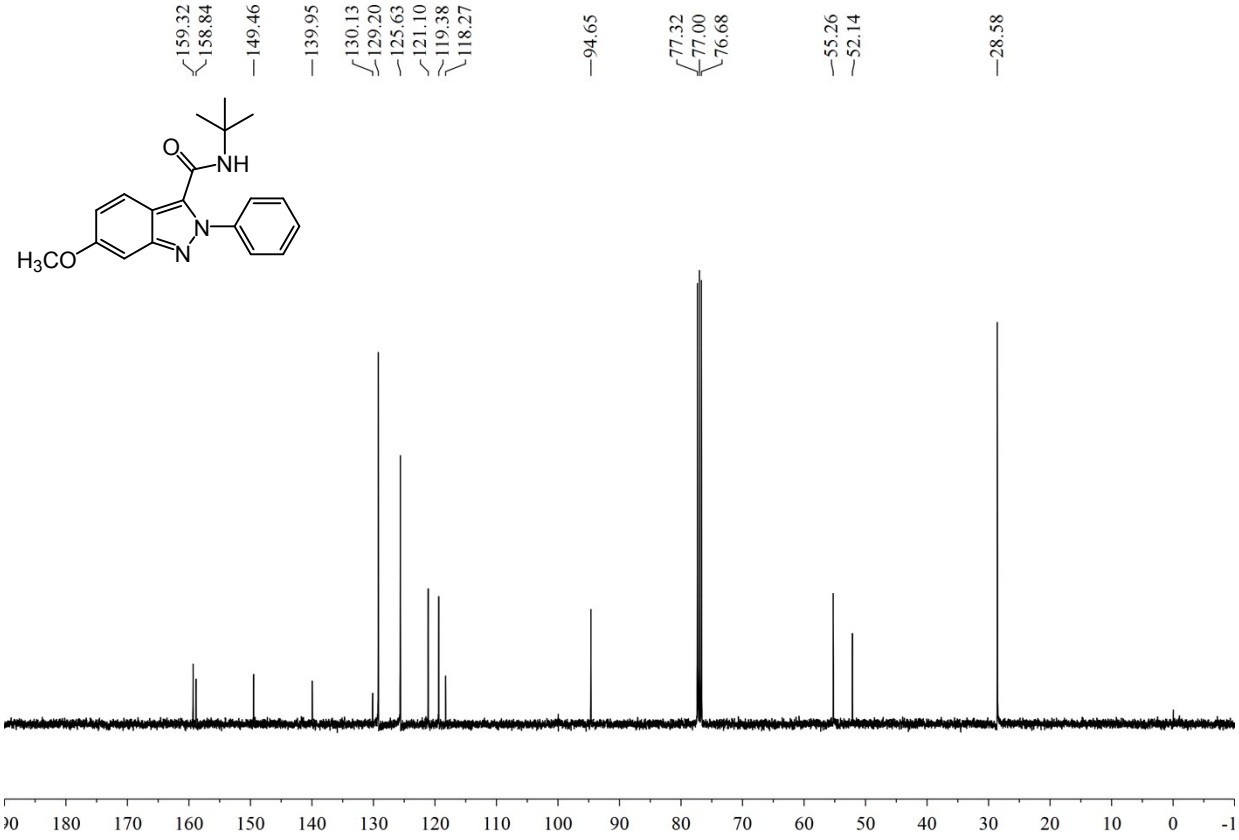
^{19}F NMR (101 MHz, $CDCl_3$) spectra of product 2ao.



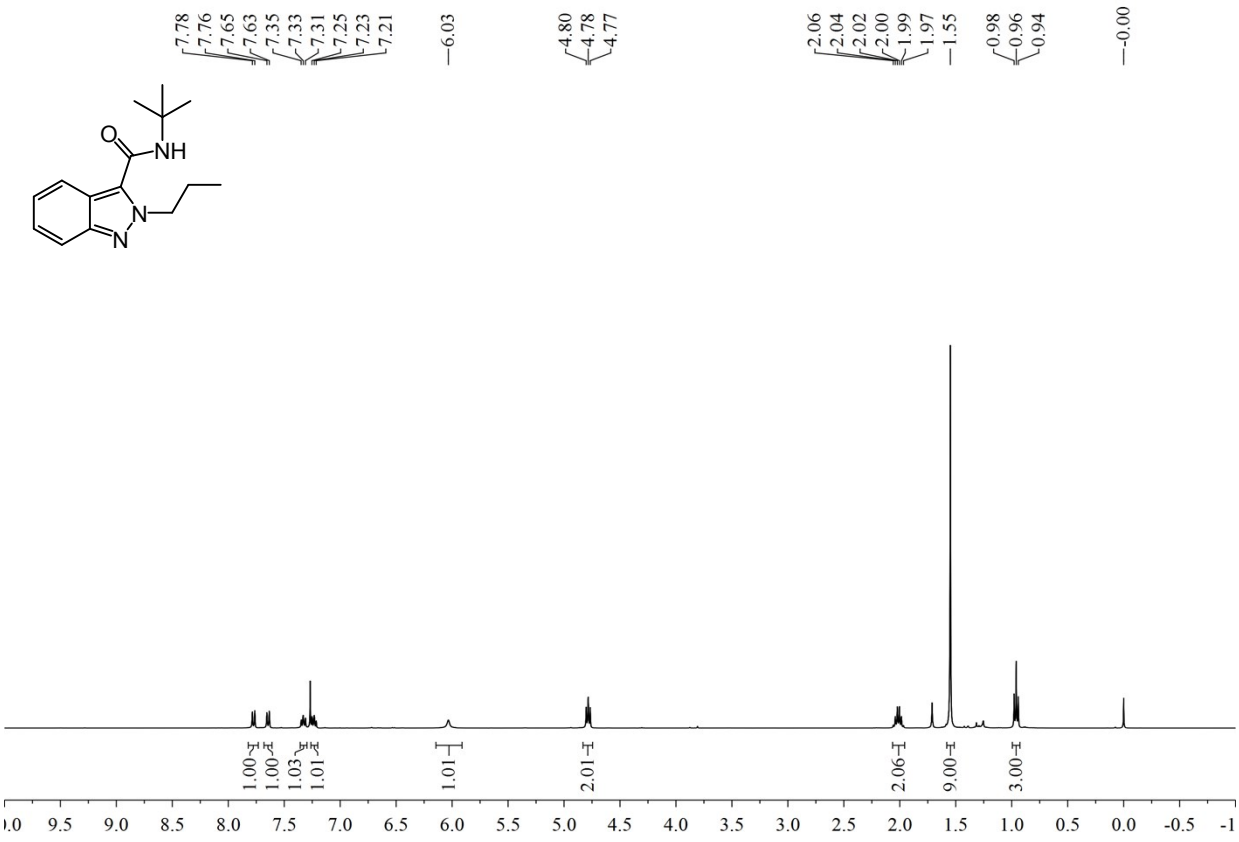
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ap.



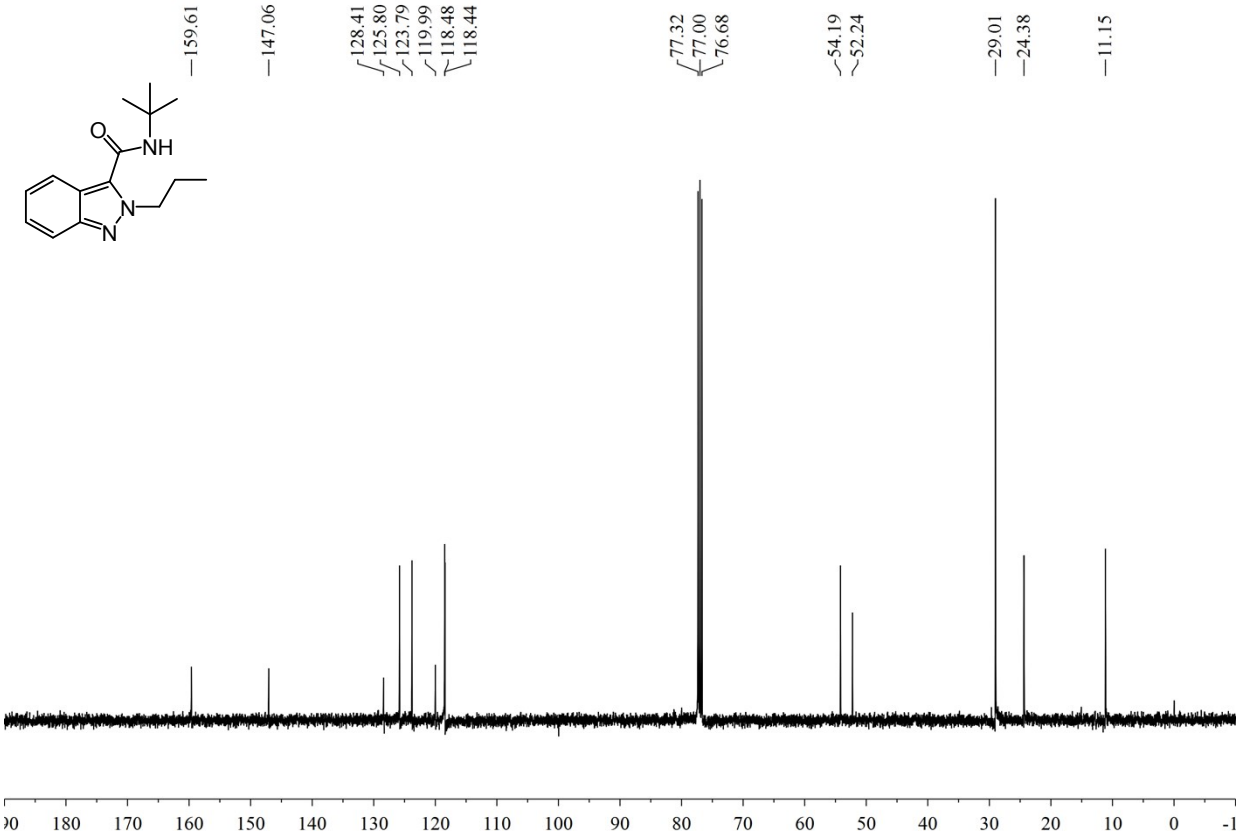
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ap.



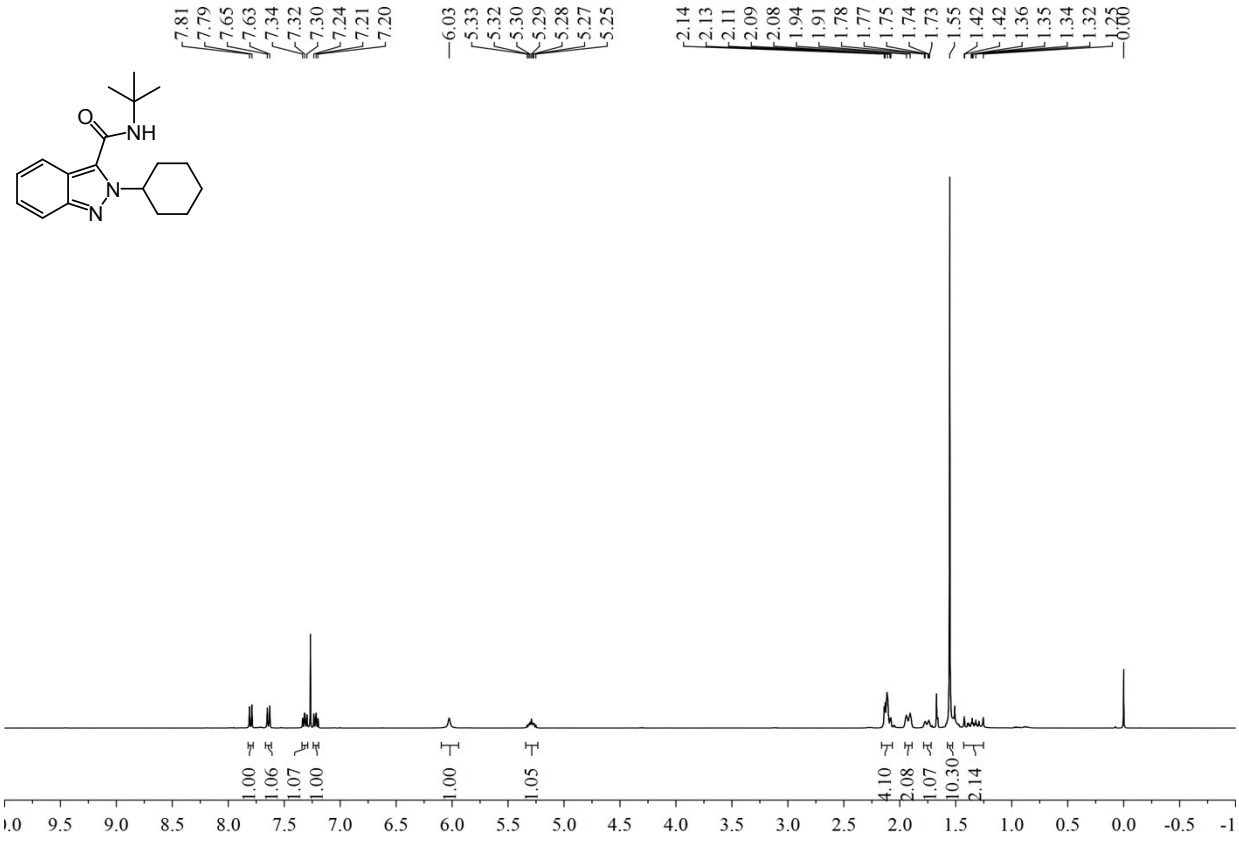
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2aq.



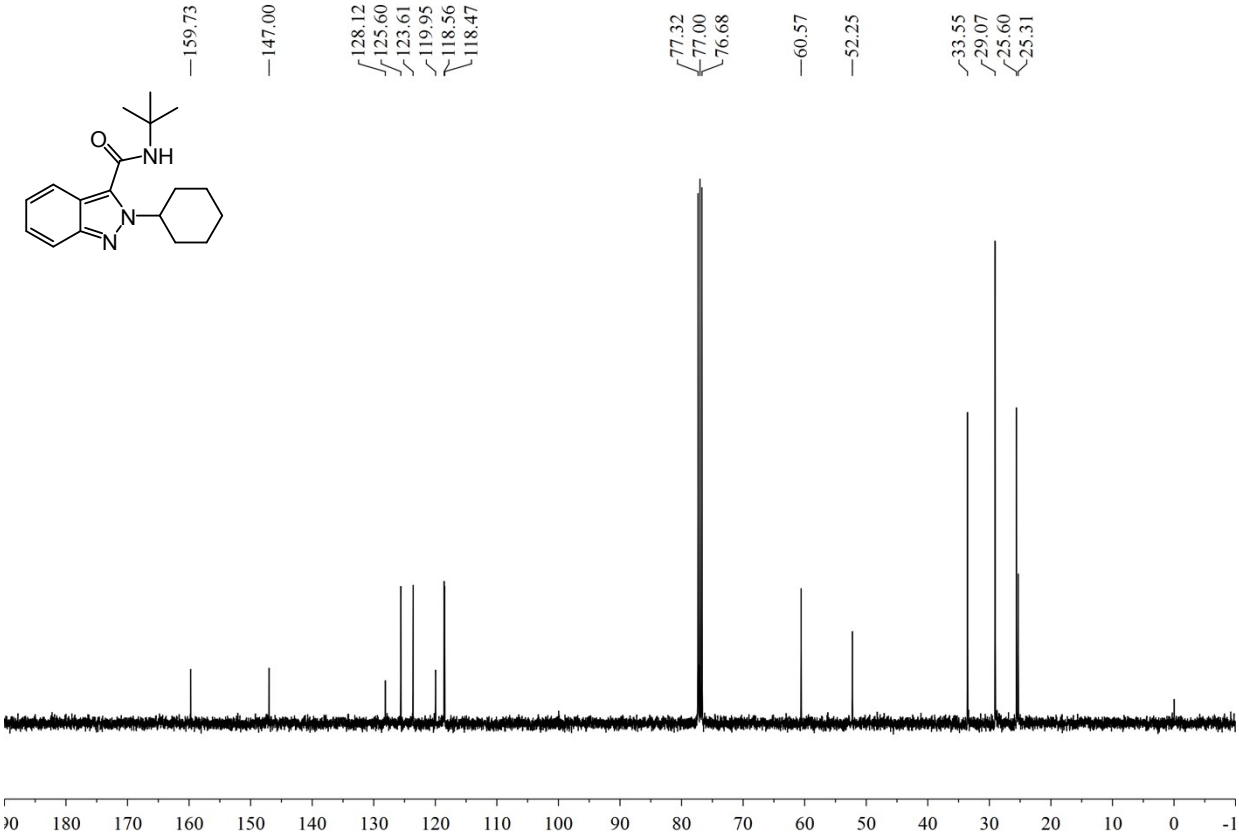
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2aq.



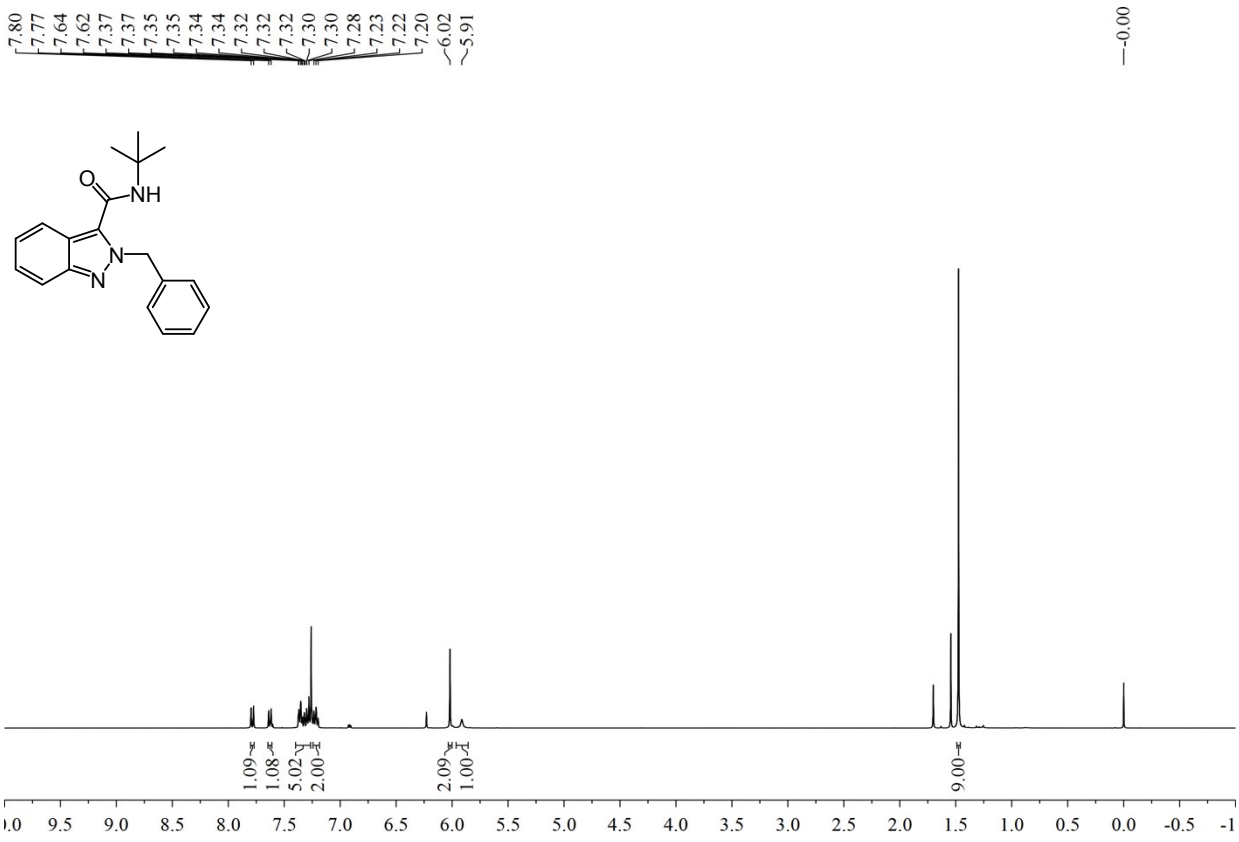
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ar.



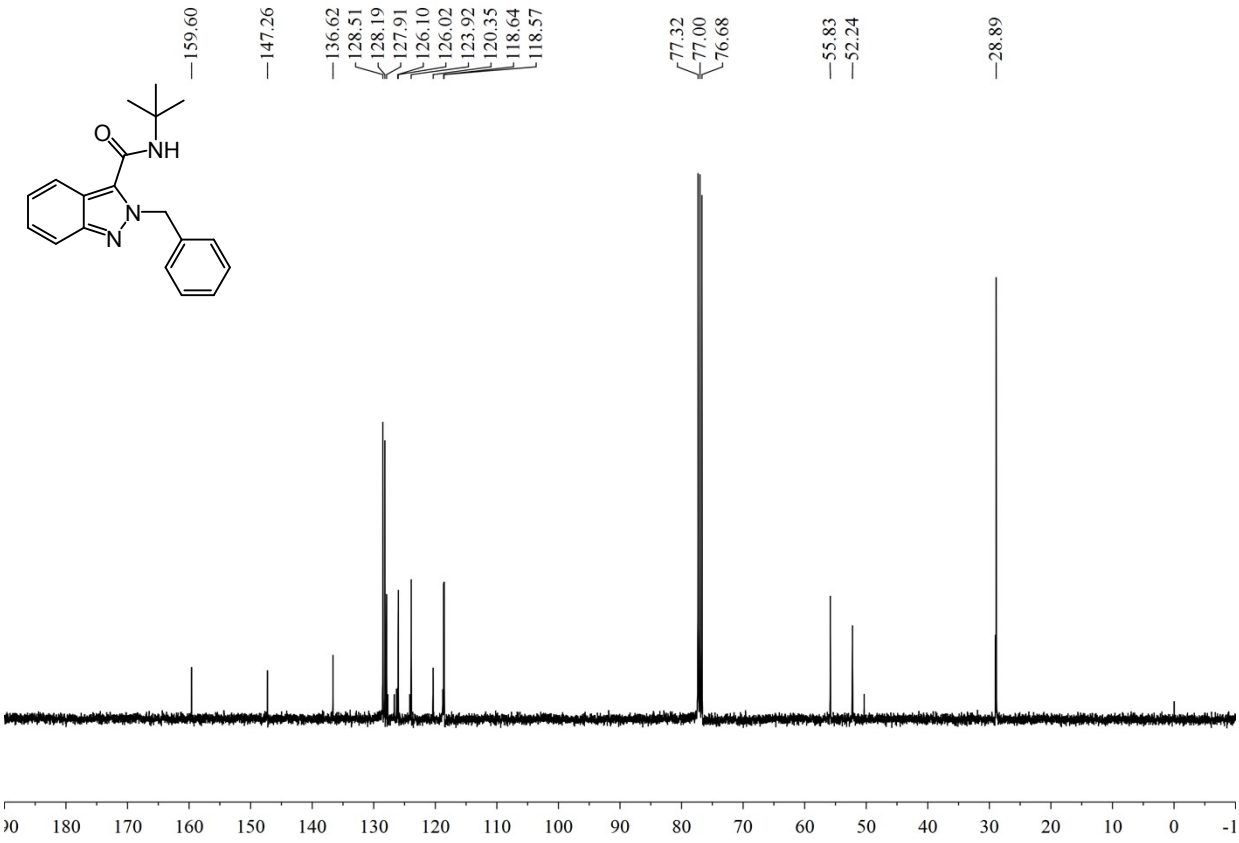
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ar.



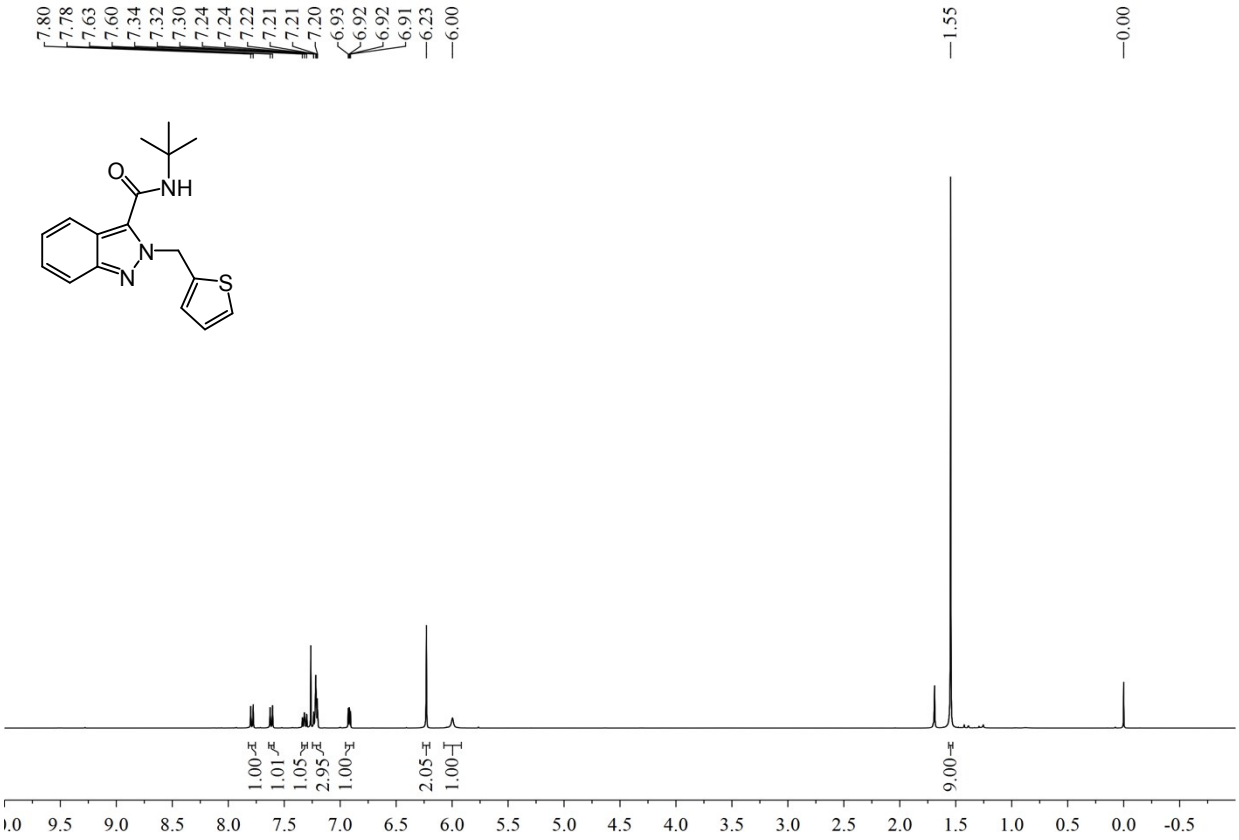
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2as.



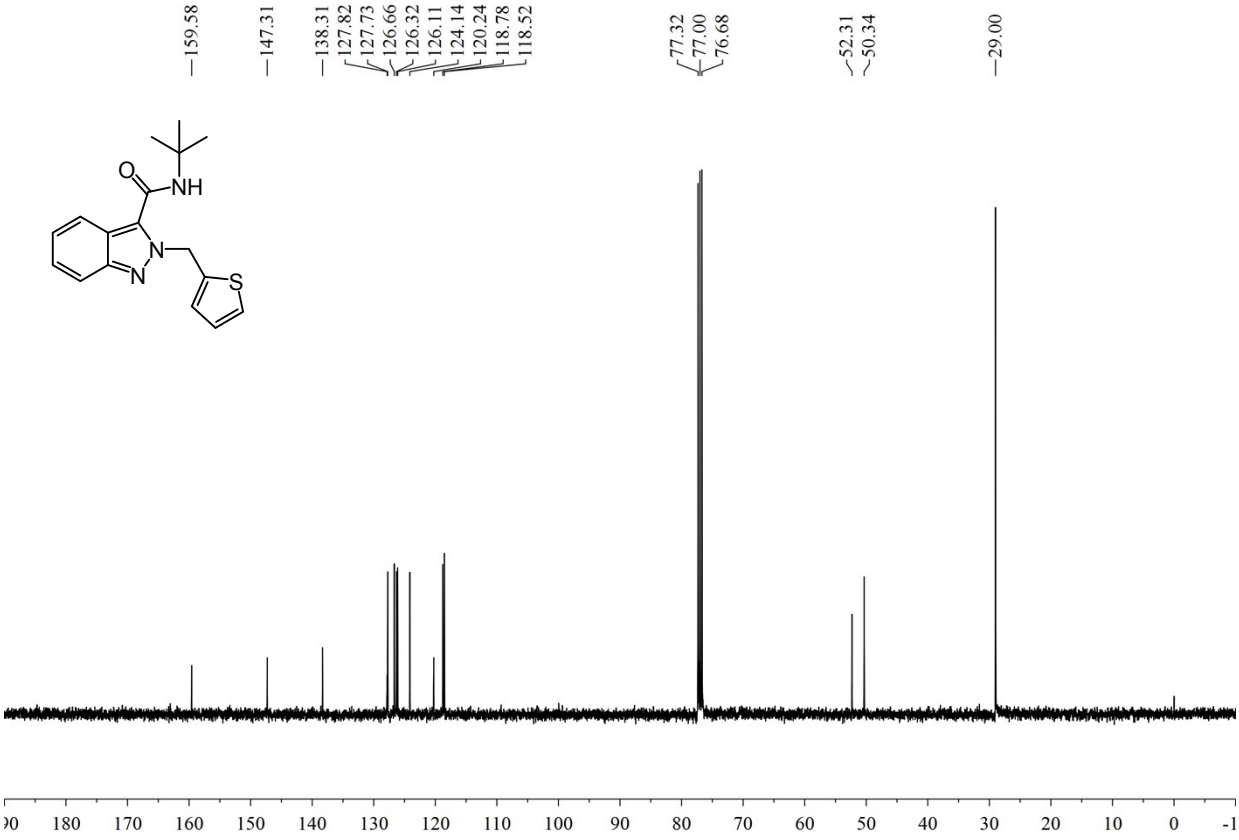
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2as.



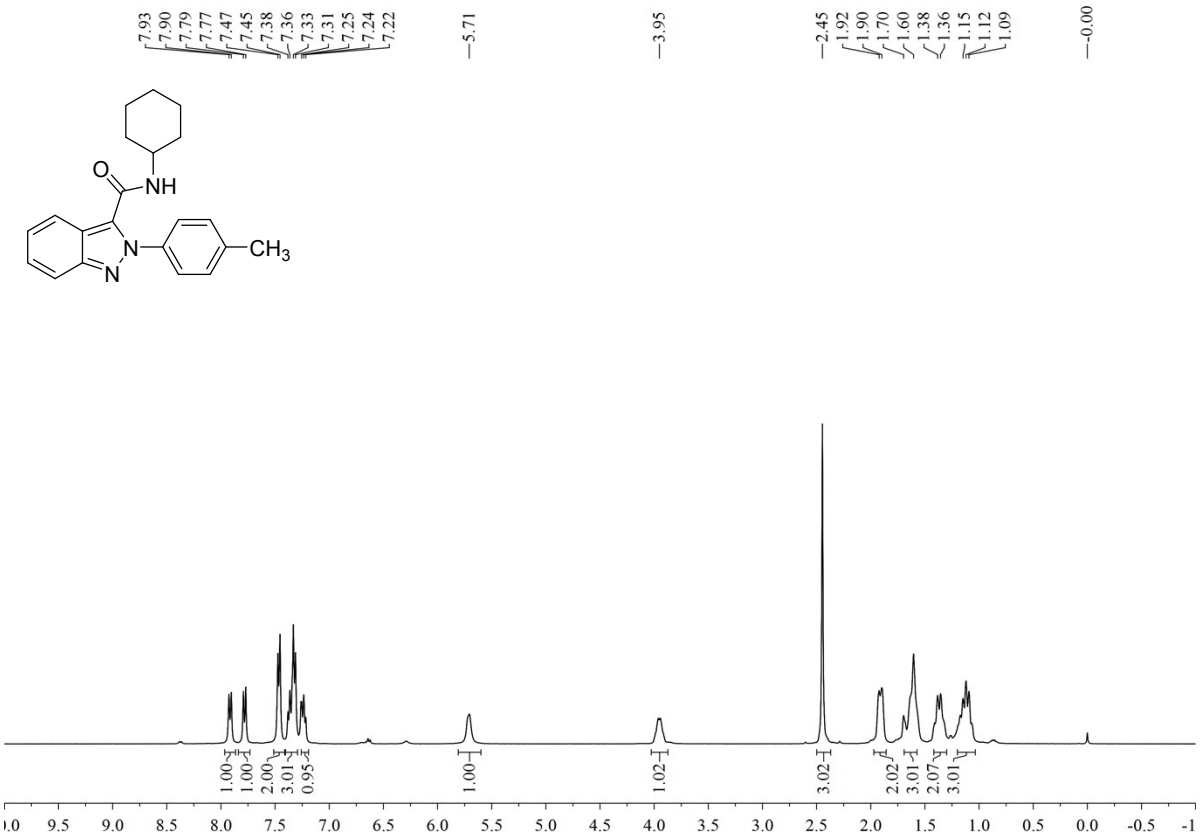
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2at.



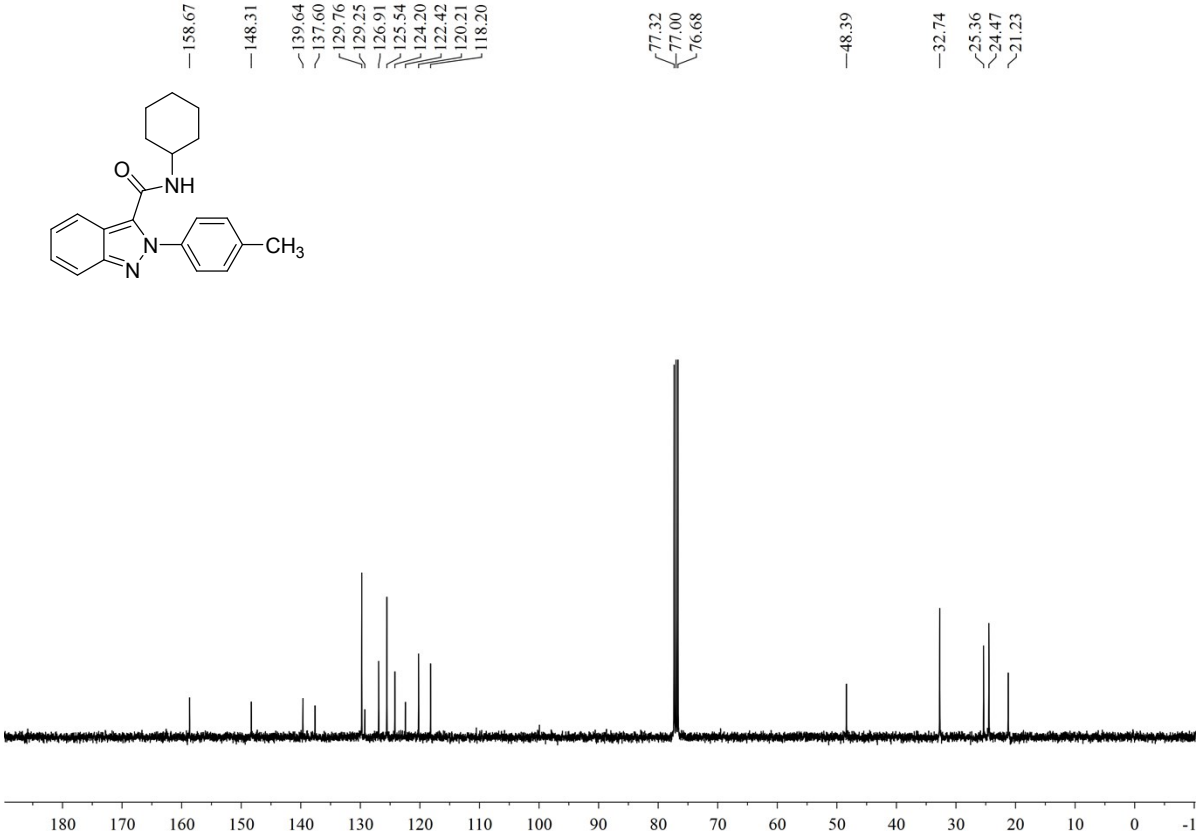
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2at.



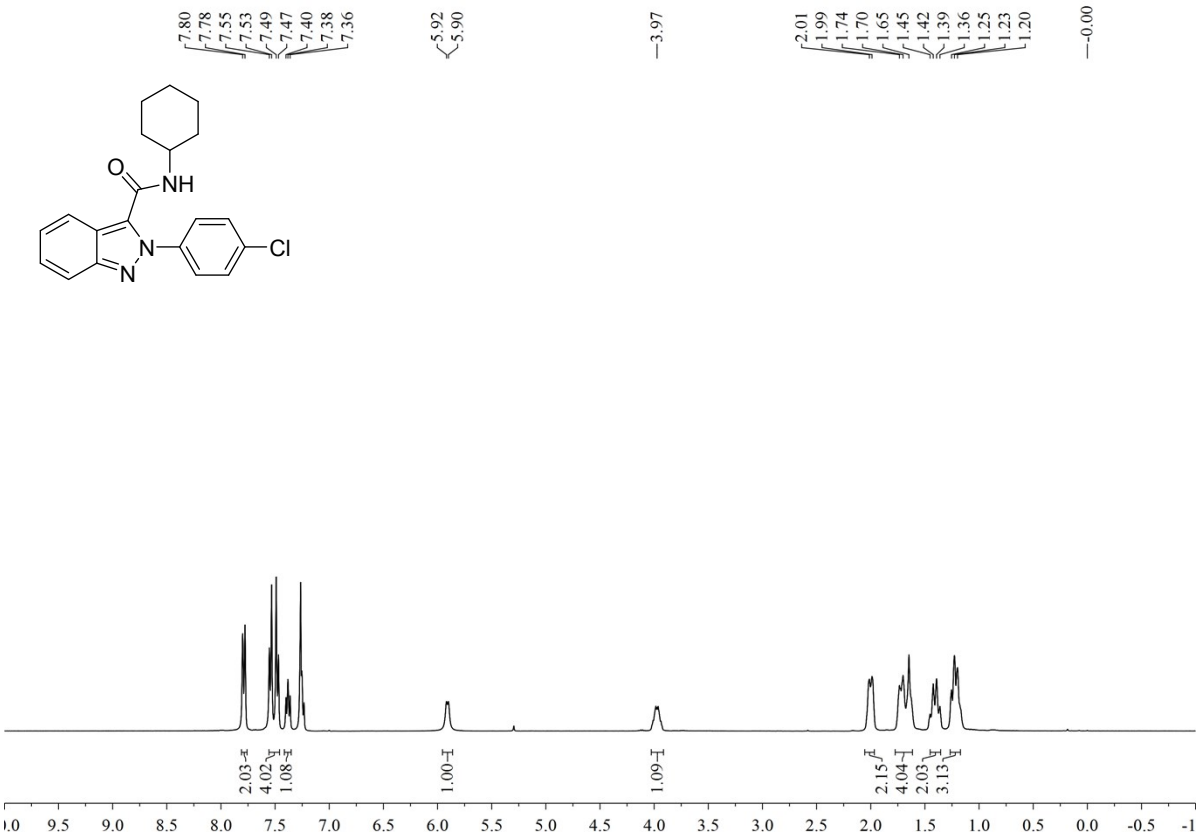
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2au.



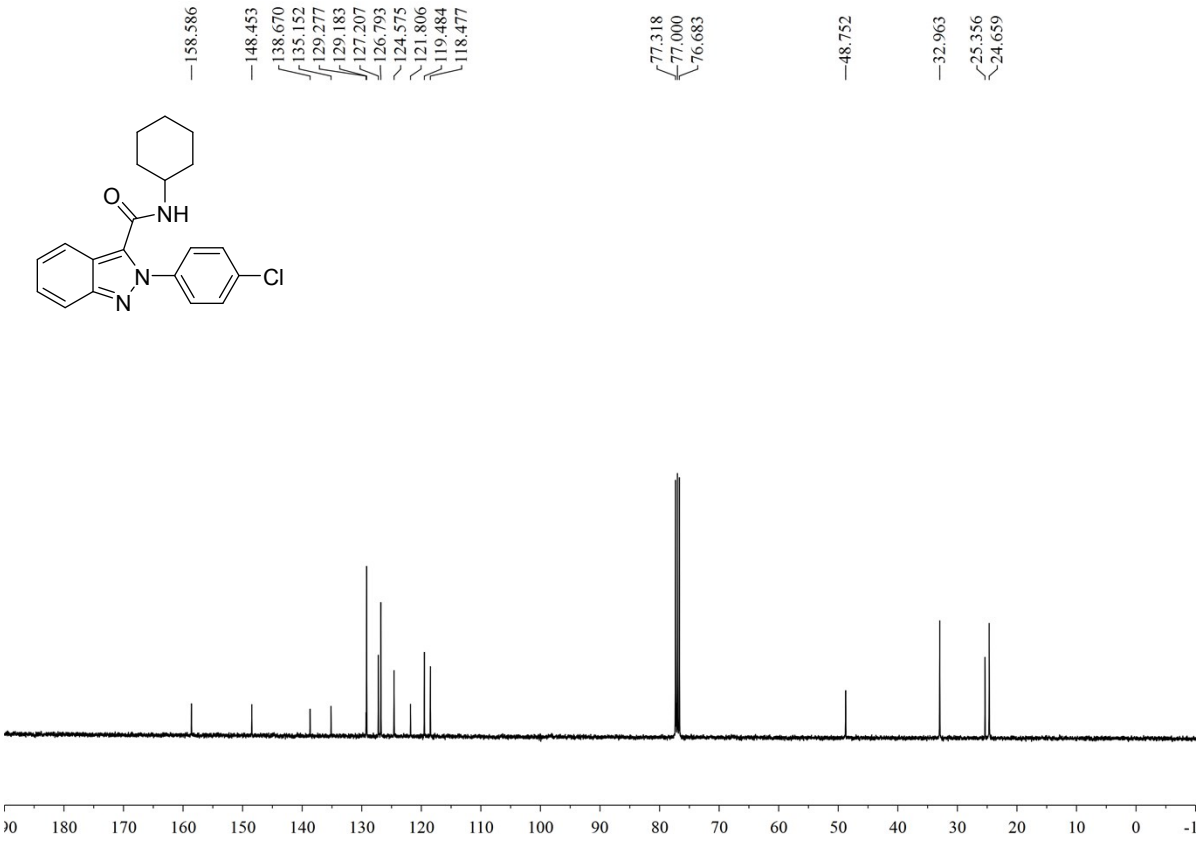
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2au.



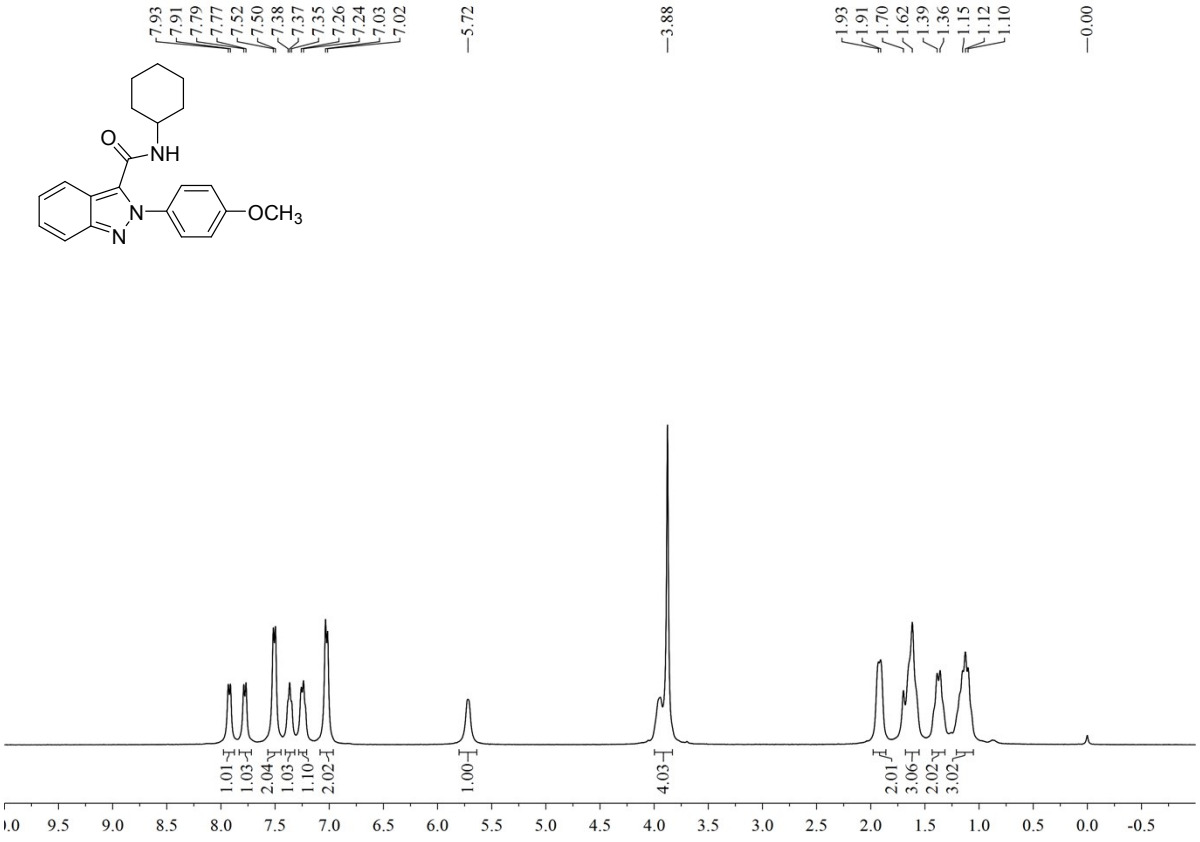
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2av.



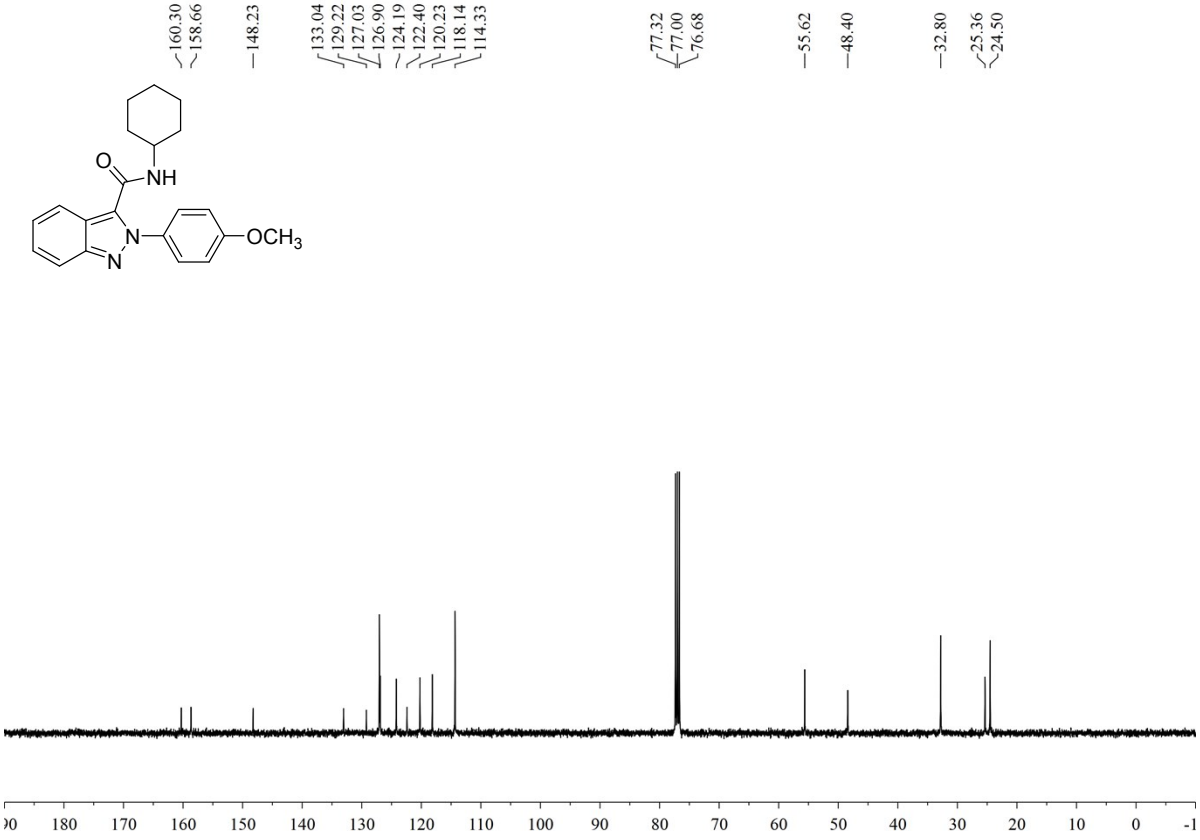
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2av.



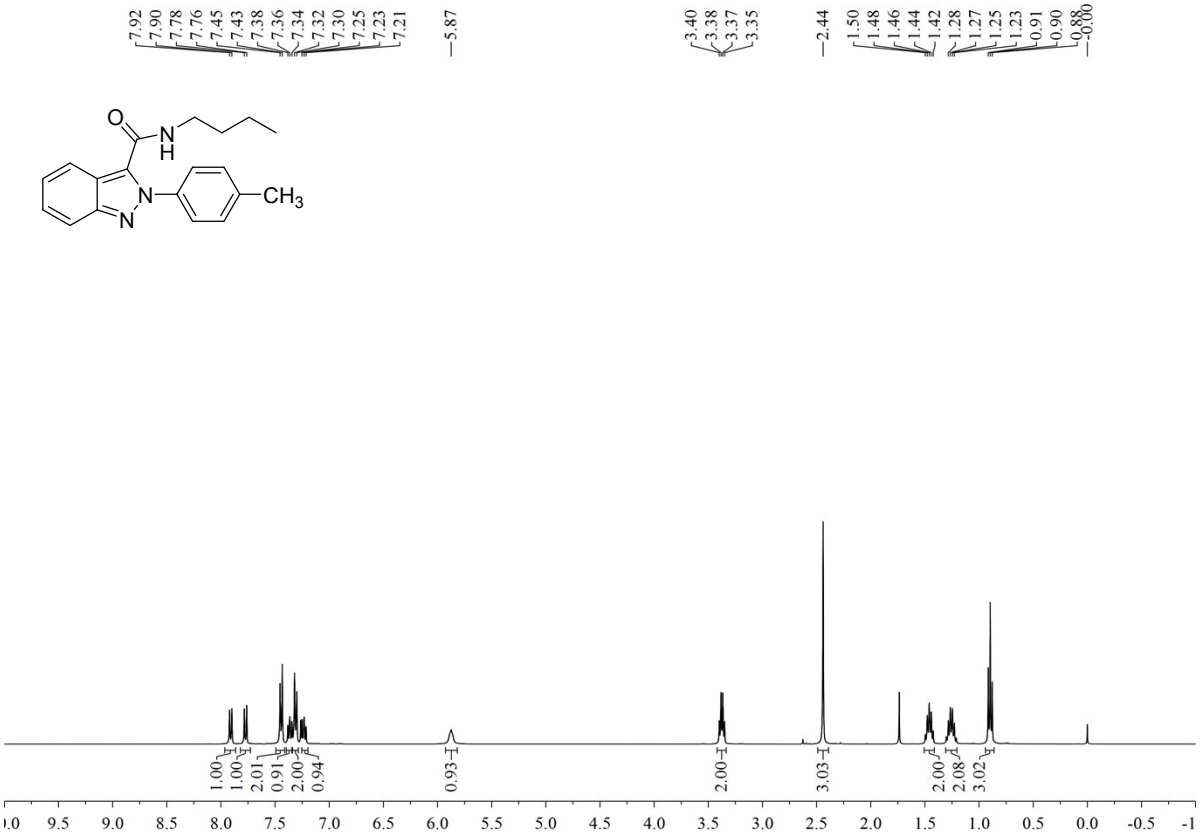
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2aw.



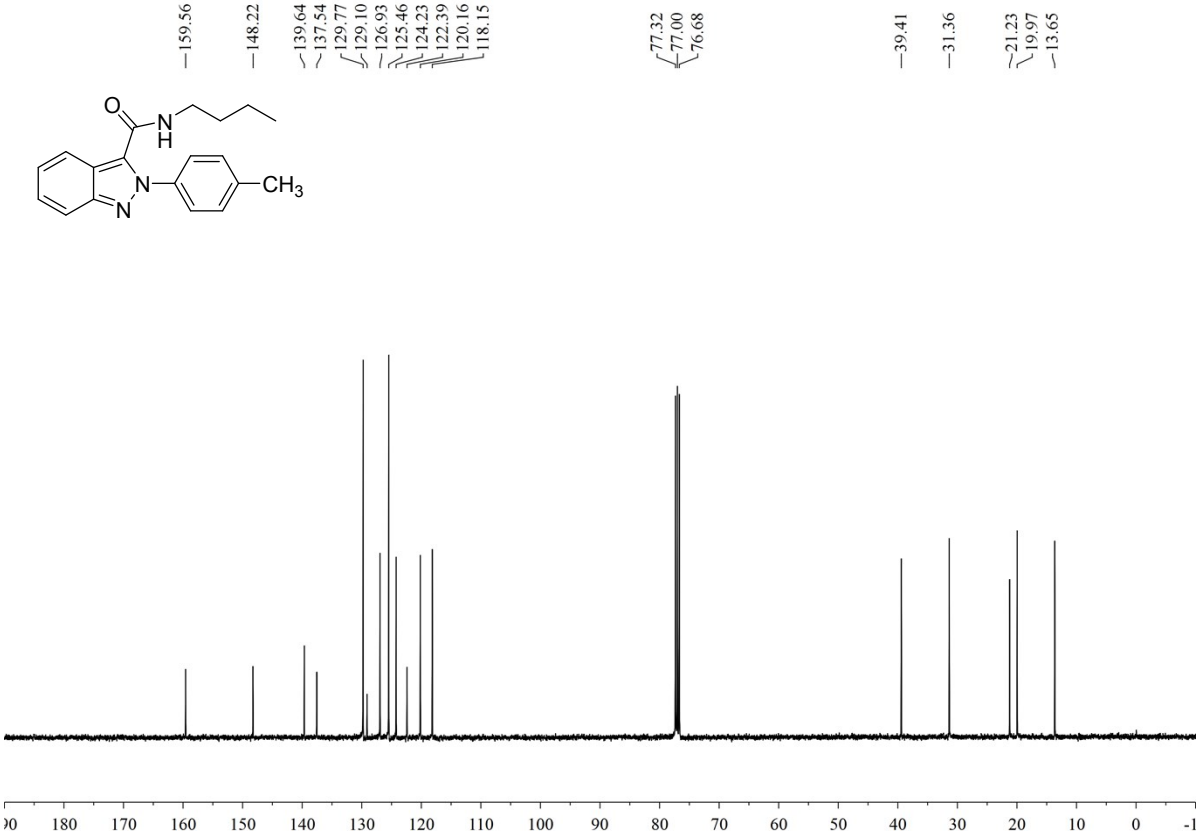
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2aw.



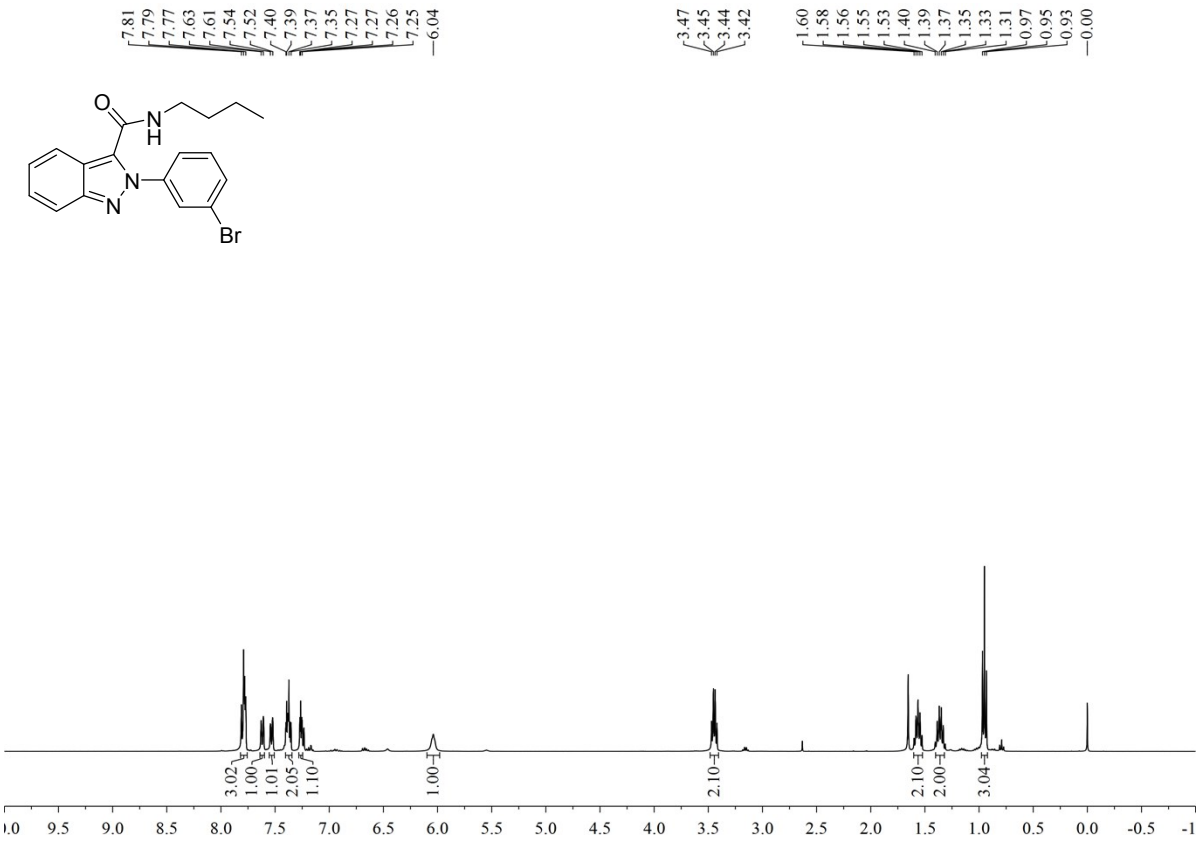
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ax.



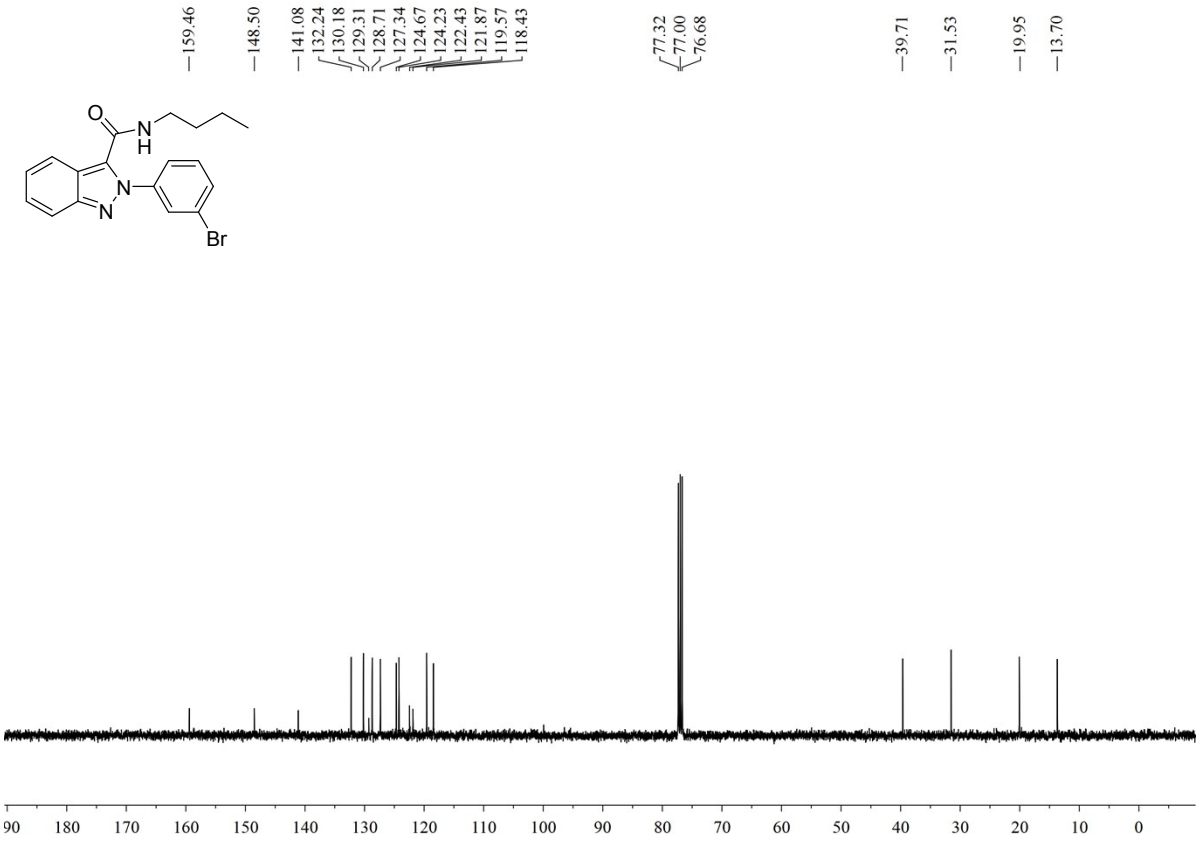
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ax.



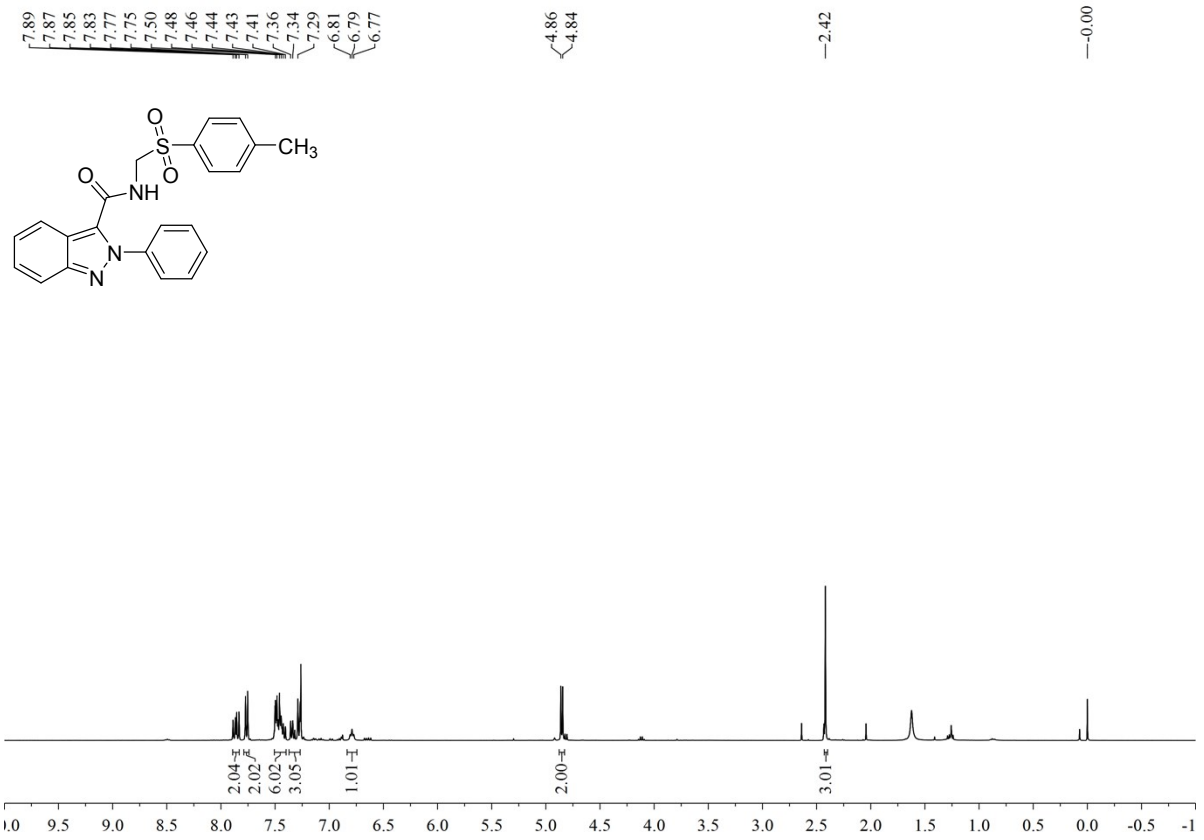
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ay.



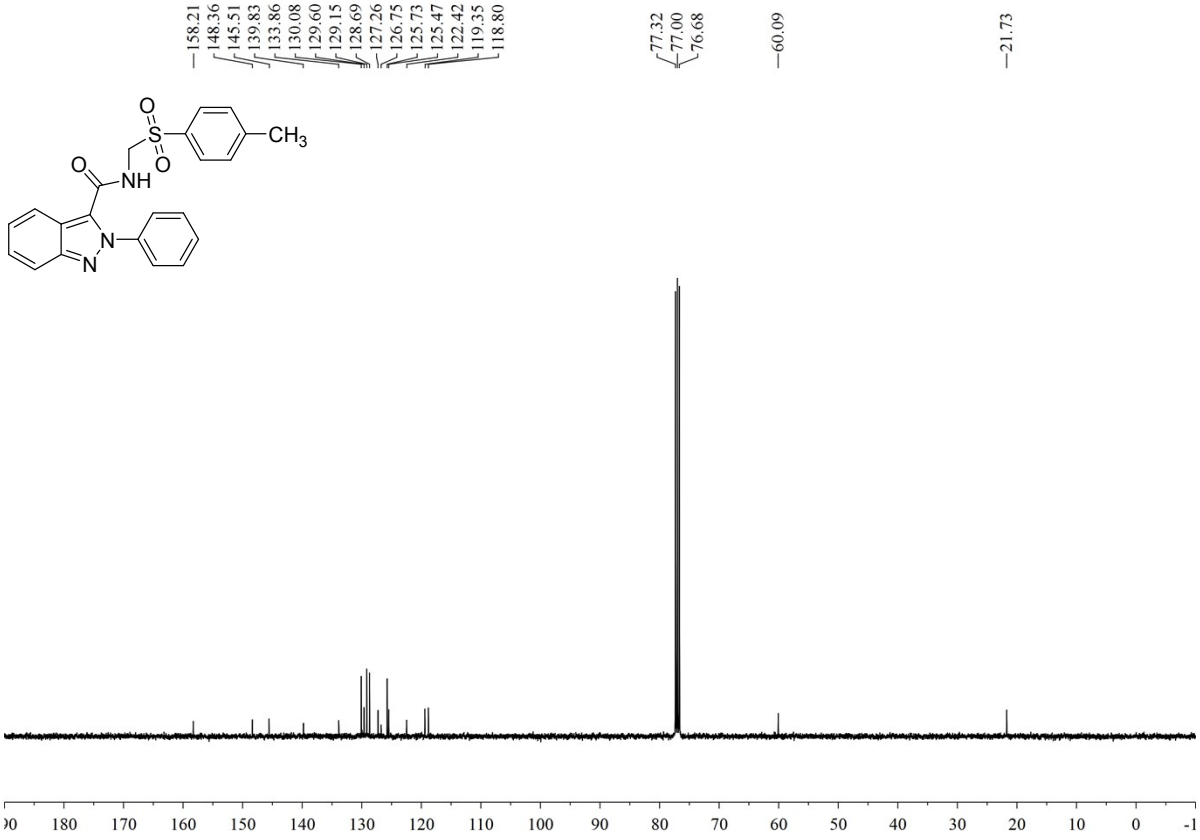
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ay.



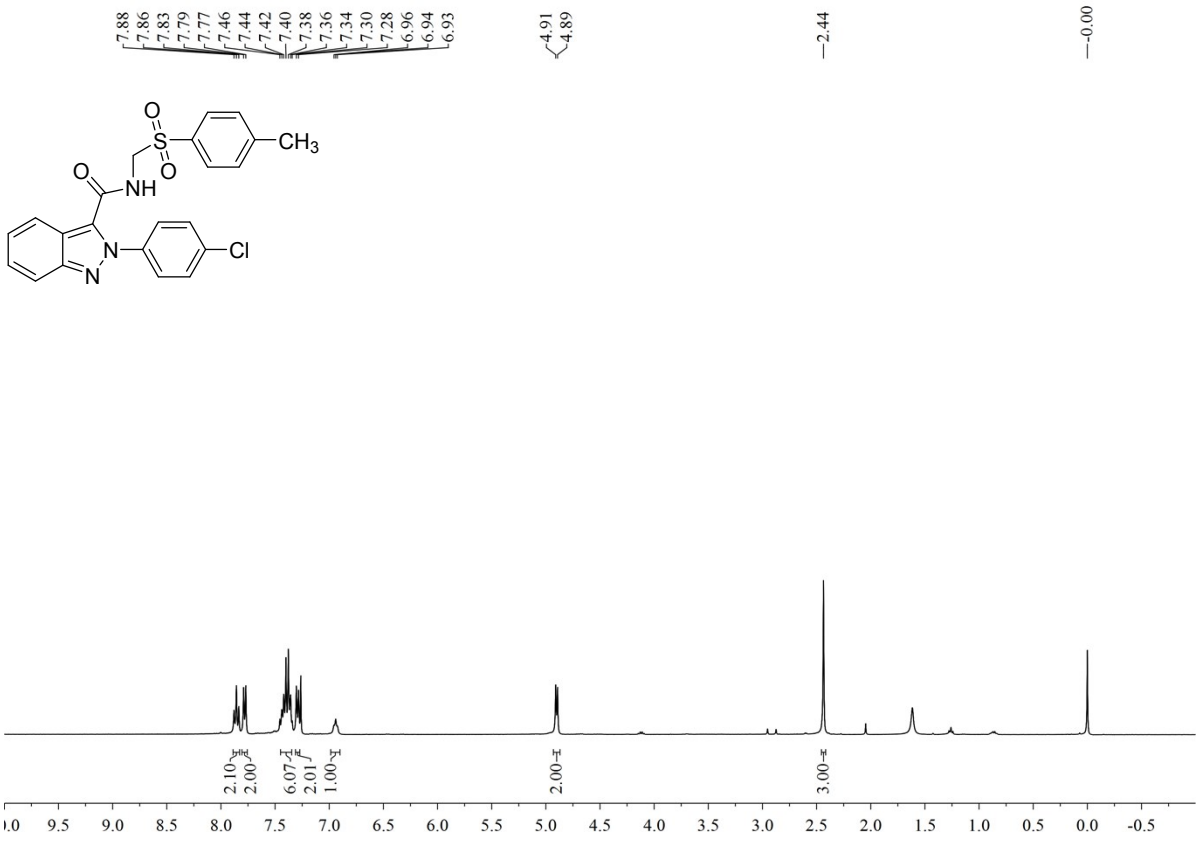
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2az.



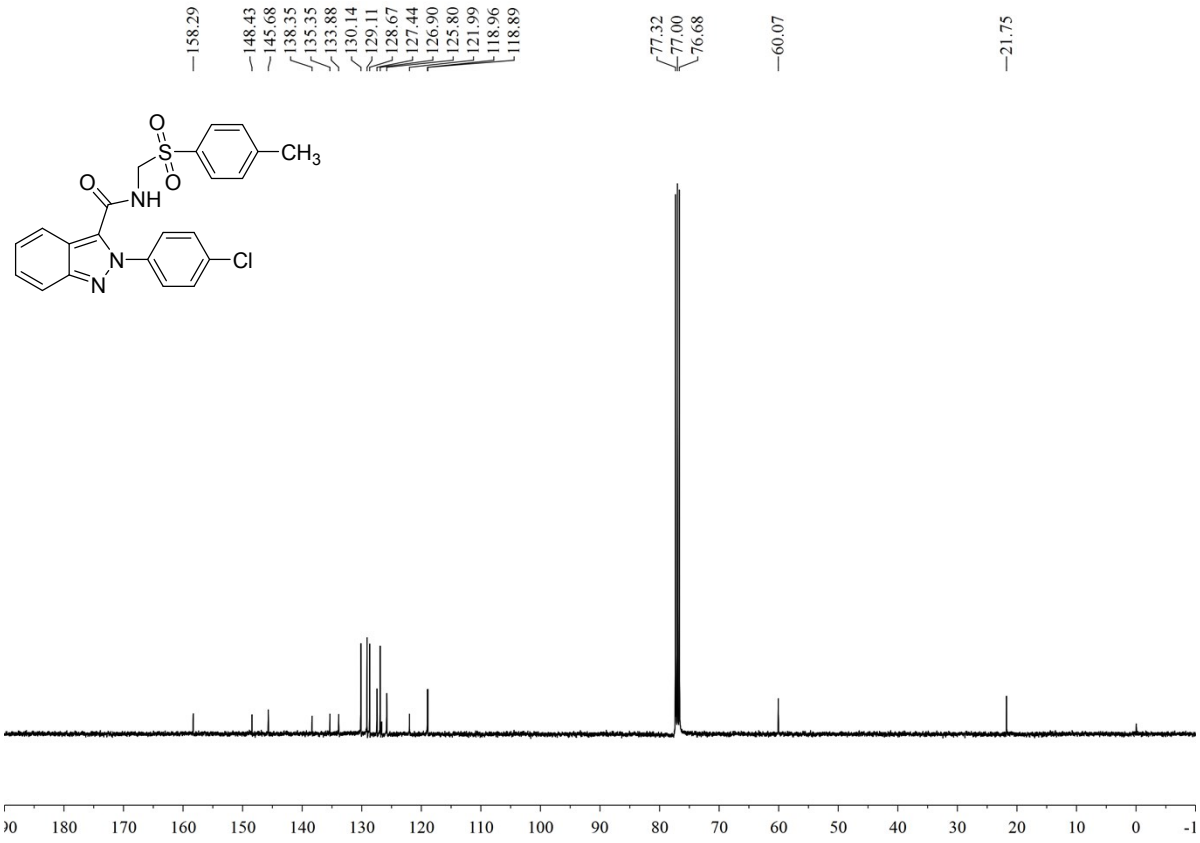
^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2az.



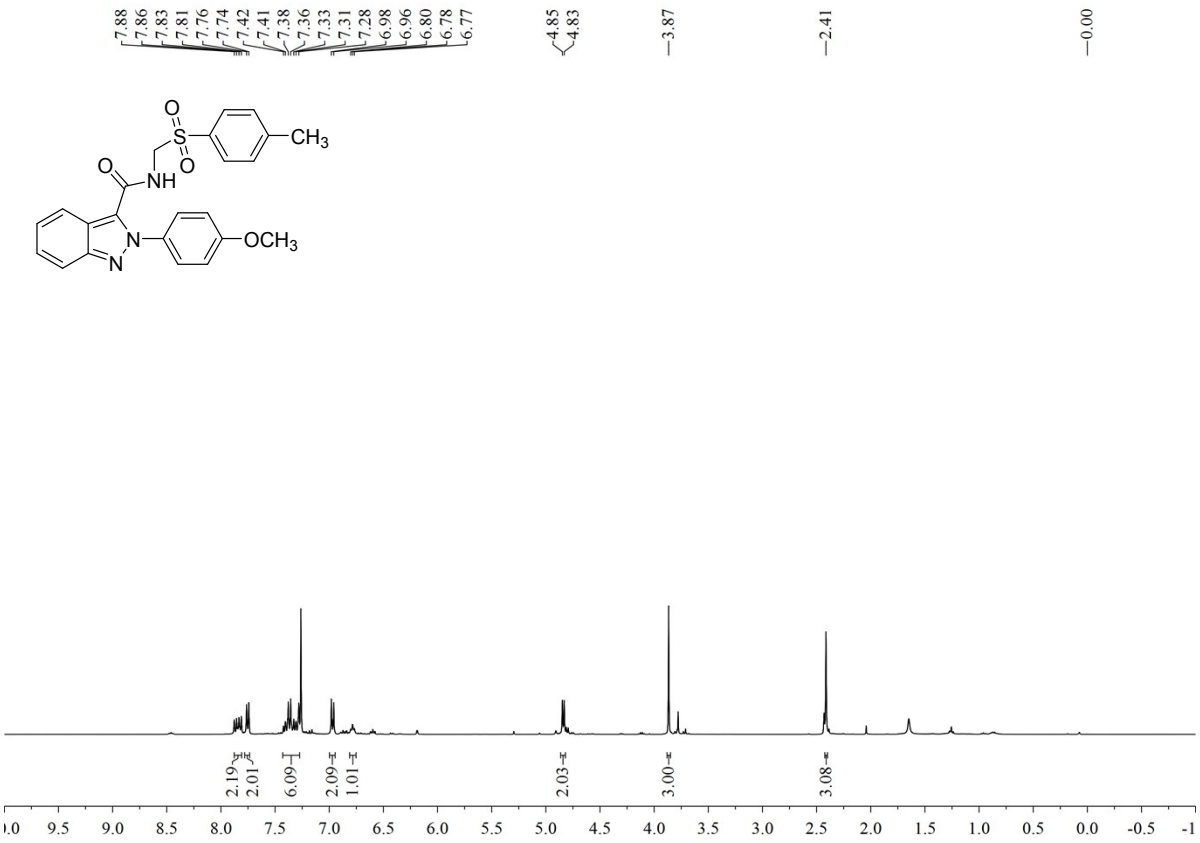
^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2ba.



^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2ba.



^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 2bb.



^{13}C NMR (101 MHz, $CDCl_3$) spectra of product 2bb.