Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct Radical Alkylation and Acylation of 2*H*-indazoles Using Substituted Hantzsch Esters as Radical Reservoirs

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Contents

1. General Methods

All reactions were carried out in schlenk tubes. The reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). The crude products were purified by flash column chromatography using silica gel (normal phase, 200-300 mesh. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. Data were reported as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.50 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were reported in ppm from $CDCl_3$ (77.10 ppm), DMSO-d_6 (39.52 ppm). Melting points were obtained on a melting point apparatus and the data are uncorrected. HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source. All commercial materials were used as received unless otherwise noted.

1.1 Synthesis of 2*H*-indazoles

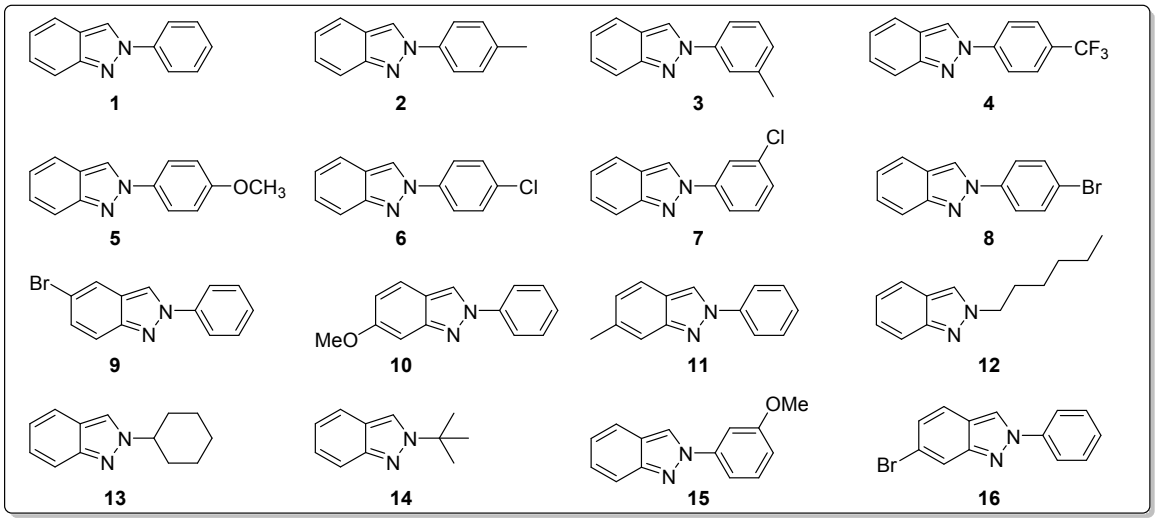


Figure S1 2*H*-indazoles used in this study

Compounds1[1,2], 2-8[2], 9-11[1], 12-14[2], 15-16[1,2]were synthesized via reported procedures.

1.2 Synthesis of 1,4-Dihydropyridines

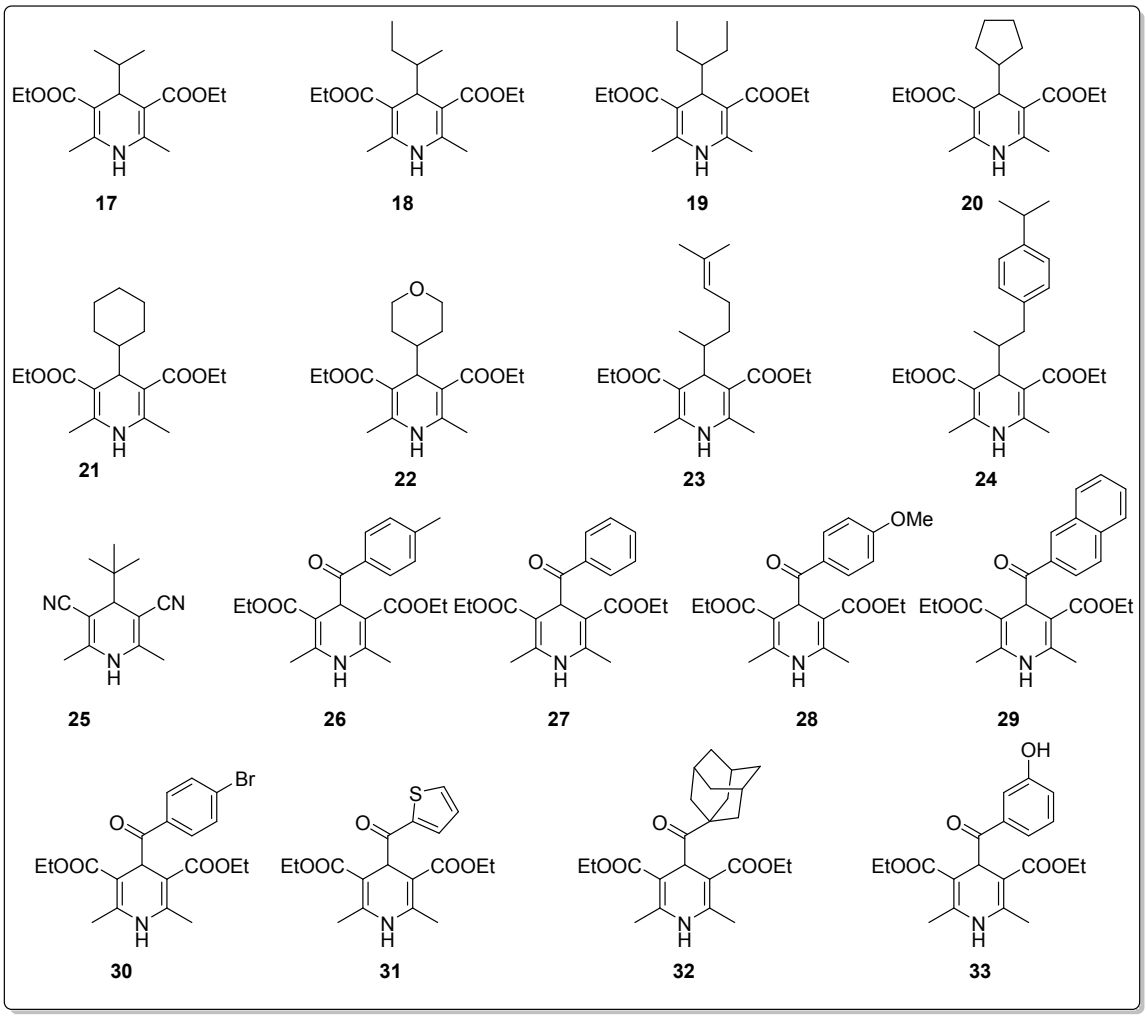
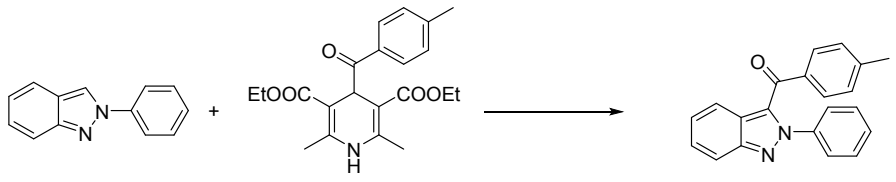


Figure S2 Hantzsch esters used in this study

Compounds 17-19[3], 20[5] 21-24[3], 25[4], 26-33[6] were synthesized via reported procedures.

Table S1. Optimization studies[a]



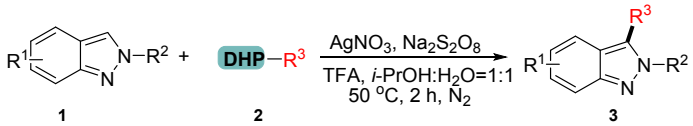
1a 4a 5a

Entry	Catalyst	Oxidant	Additive	Solvent	NMR yield[b]
1	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	75%

2	$AgNO_3$	$Na_2S_2O_8$	TFA	DMSO:H_2O=1:1	45%
3	$AgNO_3$	$Na_2S_2O_8$	TFA	*i*–PrOH:H_2O=1:1	61%
4	$AgNO_3$	$(NH_4)_2S_2O_8$	TFA	acetone:H_2O=1:1	60%
5	$AgNO_3$	$K_2S_2O_8$	TFA	acetone:H_2O=1:1	50%
6[c]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	54%
7[d]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	55%
8[e]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	68%
9[f]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	85%
10[g]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	79%
11[h]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	82%
12[i]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	56%
13[j]	$AgNO_3$	$Na_2S_2O_8$	TFA	acetone:H_2O=1:1	88%(87%[k])

[a]Reaction conditions: **1a** (0.10 mmol), **4a** (0.30 mmol), catalyst (0.03 mmol), oxidant (0.30 mmol) and acid (0.30 mmol) in solvents (v/v = 1:1, 0.1 M) were stirred under N_2 atmosphere for 10 h, RT. [b]Yield was determined by ^1H NMR. [c]1 equiv. $Na_2S_2O_8$ used. [d]2 equiv. $Na_2S_2O_8$ used. [e]4 equiv. $Na_2S_2O_8$ used. [f]25 °C, 4 h. [g]30 °C, 4 h. [h]40 °C, 4 h. [i]80 °C, 4 h. [j]0.4 equiv. $AgNO_3$ used, 25 °C, 4 h. [k]Isolated yields.

2. General Procedure A for the Alkylation of 2*H*-indazoles



The reaction vessel was charged with 2*H*-indazole (**1a**, 0.2 mmol, 39 mg), alkyl-DHP reagent (**2a**, 0.6 mmol, 177 mg), $Na_2S_2O_8$ (3.0 equiv., 143 mg), $AgNO_3$ (30 mol%, 10 mg) and TFA (2.0 equiv., 46 mg) in *i*-PrOH/H_2O (1:1, 4 mL), and the reaction mixture was stirred under nitrogen atmosphere at room temperature for 2 h.

After completion, the reaction mixture was quenched with 20 mL water/ethyl acetate (1:1). Then the reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine, dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents.

When the diethyl 2,6-dimethylpyridine-3,5-dicarboxylate byproduct had a Rf similar to that of products **3**, the pyridine was removed by dissolving the crude product in methyl tert-butyl ether (10 mL) and washing the organic layer with HCl (1 mL) prior to purification by column chromatography.

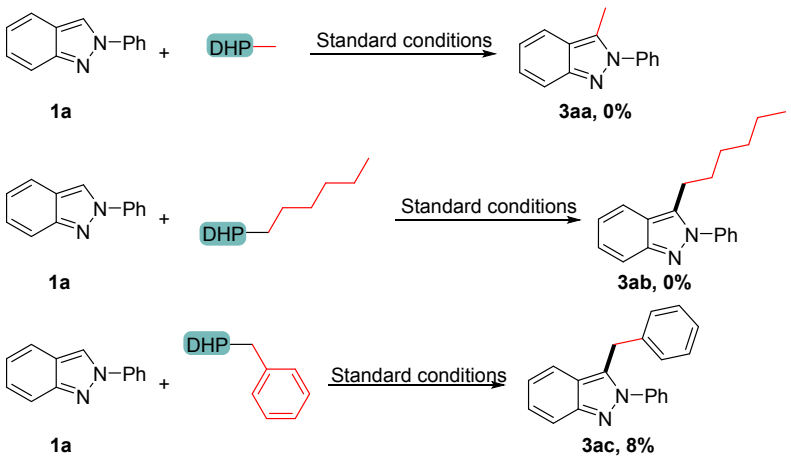
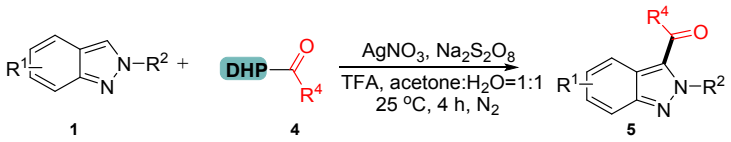


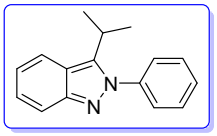
Figure S3 Alkylation of 2*H*-indazoles by 4- primary alkylated DHPs

Unfortunately, primary alkyl radicals did not deliver the expected product because the corresponding DHP does not undergo homolytic C-C cleavage but rather C-H homolysis, resulting in the formation of a 4-alkylated pyridine byproduct (**3aa-3ab**). When 4-benzyl-DHP was used, the produce of **3ac** was low in 8% yield.

3. General procedure B for the Acylation of 2*H*-indazoles



The reaction vessel was charged with 2*H*-indazole (**1a**, 0.2 mmol, 39 mg), acyl-DHP reagent (**4a**, 0.6 mmol, 222 mg), $Na_2S_2O_8$ (3.0 equiv., 143 mg), $AgNO_3$ (40 mol%, 14 mg) and TFA (3.0 equiv., 68 mg) in acetone/H_2O (1:1, 4 mL), and the reaction mixture was stirred under nitrogen atmosphere at 25 °C for 4 h. After completion, the reaction mixture was quenched with 20 mL water/ethyl acetate (1:1). Then the reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine, dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents.



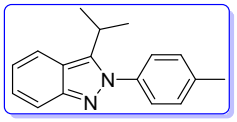
3-isopropyl-2-phenyl-2H-indazole (3a)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **3a** (43 mg, 92% yield) as a yellow solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.55-7.47 (m, 5H), 7.30 (ddd, J = 8.7, 6.6, 0.9 Hz, 1H), 7.05 (ddd, J = 8.5, 6.6, 0.7 Hz, 1H), 3.36 (hept, J = 7.1 Hz, 1H), 1.48 (d, J = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.0, 140.2, 129.2, 129.1, 126.5, 126.4, 121.0, 120.7, 119.2, 117.9, 27.1, 22.5.

HRMS (ESI): Calcd for $C_{16}H_{17}N_2^+$ $[M+H]^+$ 237.1386, found 237.1380.



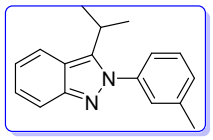
3-isopropyl-2-(p-tolyl)-2H-indazole (3b)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3b** (39 mg, 78% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.36-7.26 (m, 5H), 7.05-7.01 (m, 1H), 3.35 (hept, J = 7.0 Hz, 1H), 2.45 (s, 3H), 1.47 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.9, 139.1, 137.6, 129.7, 126.6, 120.9, 120.5, 119.0, 117.8, 27.1, 22.4, 21.2.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 251.1543, found 251.1435.



3-isopropyl-2-(m-tolyl)-2H-indazole (3c)

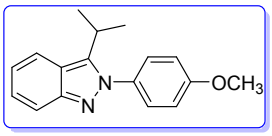
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3c** (44 mg, 89% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.32-7.24 (m, 4H), 7.06-7.02 (m, 1H), 3.37 (hept, J = 7.0 Hz, 1H),

2.44 (s, 3H), 1.48 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.8, 140.0, 139.4, 129.8, 128.8, 127.1, 126.2, 123.4, 120.9, 120.5, 119.1, 117.8, 27.1, 22.5, 21.3.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 251.1543, found 251.1436.



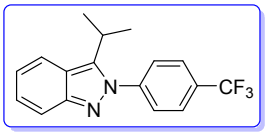
3-isopropyl-2-(4-methoxyphenyl)-2H-indazole (3d)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3d** (50 mg, 95% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.44-7.40 (m, 2H), 7.32 (ddd, J = 8.7, 6.6, 0.9 Hz, 1H), 7.09-7.03 (m, 3H), 3.91 (s, 3H), 3.36 (hept, J = 7.1 Hz, 1H), 1.50 (d, J = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 148.7, 142.1, 133.1, 127.6, 126.2, 120.9, 120.5, 119.0, 117.8, 114.2, 55.6, 27.1, 22.4.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2O^+$ $[M+H]^+$ 267.1492, found 267.1488.



3-isopropyl-2-(4-(trifluoromethyl)phenyl)-2H-indazole (3e)

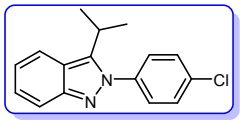
Following the general procedure A, the crude product was purified by silica gel flash

chromatography (PE: EA=15:1 as the eluent) to give **3e** (28 mg, 47% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 3H), 7.71 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.32 (ddd, J = 8.8, 6.6, 0.9 Hz, 1H), 7.07 (ddd, J = 8.5, 6.6, 0.8 Hz, 1H), 3.37 (hept, J = 7.0 Hz, 1H), 1.51 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 143.1, 142.1, 131.2(q, J = 32.8 Hz, 1C), 127.0, 126.9, 126.5(q, J = 3.7 Hz, 1C), 123.8(q, J = 270.8 Hz, 1C), 121.1, 121.0, 119.5, 118.0, 27.2, 22.6.

HRMS (ESI): Calcd for $C_{17}H_{16}F_3N_2^+$ $[M+H]^+$ 305.1260, found 305.1259.



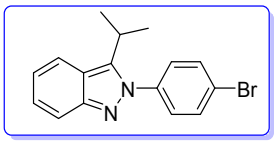
2-(4-chlorophenyl)-3-isopropyl-2H-indazole (3f)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3f** (37 mg, 70% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.44-7.41 (m, 2H), 7.30 (ddd, J = 8.7, 6.6, 0.9 Hz, 1H), 7.05 (ddd, J = 8.4, 6.6, 0.8 Hz, 1H), 3.33 (hept, J = 7.0 Hz, 1H), 1.48 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 142.0, 138.6, 135.0, 129.3, 127.7, 126.6, 120.9, 120.8, 119.2, 117.8, 27.1, 22.4.

HRMS (ESI): Calcd for $C_{16}H_{16}ClN_2^+$ $[M+H]^+$ 271.0997, found 271.0994.



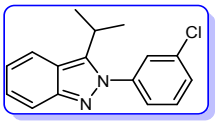
2-(4-bromophenyl)-3-isopropyl-2H-indazole (3g)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3g** (44 mg, 71% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.32 -7.28 (m, 1H), 7.07-7.03 (m, 1H), 3.33 (hept, J = 7.0 Hz, 1H), 1.48 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 142.0, 139.1, 132.3, 128.0, 126.6, 123.0, 120.9, 120.9, 119.2, 117.8, 27.1, 22.5.

HRMS (ESI): Calcd for $C_{16}H_{16}BrN_2^+$ $[M+H]^+$ 315.0491, found 315.0484.



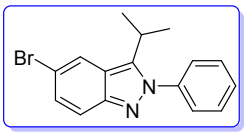
2-(3-chlorophenyl)-3-isopropyl-2H-indazole (3h)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3h** (36 mg, 67% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.53-7.44 (m, 3H), 7.38 (dt, J = 6.9, 1.9 Hz, 1H), 7.31 (ddd, J = 8.7, 6.6, 1.0 Hz, 1H), 7.06 (ddd, J = 8.5, 6.6, 0.8 Hz, 1H), 3.36 (hept, J = 7.0 Hz, 1H), 1.50 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 142.0, 141.1, 134.9, 130.1, 129.2, 126.9, 126.7, 124.6, 120.9, 120.9, 119.2, 117.9, 27.1, 22.5.

HRMS (ESI): Calcd for $C_{16}H_{16}ClN_2^+$ $[M+H]^+$ 271.0997, found 271.0994.



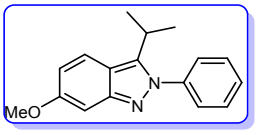
5-bromo-3-isopropyl-2-phenyl-2H-indazole (3i)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3i** (40 mg, 64% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.2 Hz, 1H), 7.60-7.45(m, 6H), 7.34 (dd, J = 9.1, 1.8 Hz, 1H), 3.33 (hept, J = 7.0 Hz, 1H), 1.45 (d, J = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 141.7, 139.8, 130.0, 129.3, 129.3, 126.4, 123.0, 120.3, 119.7, 114.0, 27.1, 22.5.

HRMS (ESI): Calcd for $C_{16}H_{16}BrN_2^+$ $[M+H]^+$ 315.0491, found 315.0490.



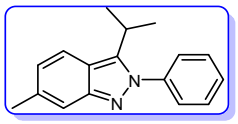
3-isopropyl-6-methoxy-2-phenyl-2H-indazole(3j)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3j** (37 mg, 71% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 9.2 Hz, 1H), 7.53-7.46 (m, 5H), 6.95 (d, J = 1.8 Hz, 1H), 6.75 (dd, J = 9.2, 2.1 Hz, 1H), 3.87 (s, 3H), 3.32 (hept, J = 7.0 Hz, 1H), 1.45 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 150.0, 142.2, 140.2, 129.1, 128.8, 126.5, 121.8, 115.7, 114.9, 94.6, 55.3, 27.0, 22.5.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2O^+$ $[M+H]^+$ 267.1492, found 267.1483.



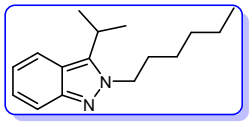
3-isopropyl-6-methyl-2-phenyl-2H-indazole(3k)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3k** (49 mg, 99% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.7 Hz, 1H), 7.54-7.45 (m, 6H), 6.89 (dd, J = 8.7, 0.8 Hz, 1H), 3.33 (hept, J = 7.0 Hz, 1H), 2.45 (s, 3H), 1.46 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 141.8, 140.2, 136.2, 129.1, 128.9, 126.5, 123.5, 120.4, 117.5, 116.1, 27.0, 22.5, 22.1.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 251.1543, found 251.1535.



2-hexyl-3-isopropyl-2H-indazole(3l)

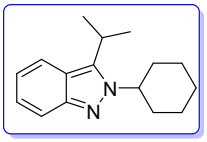
Following the general procedure A, the crude product was purified by silica gel flash

chromatography (PE: EA=15:1 as the eluent) to give **3l** (22 mg, 45% yield) as a yellow oil. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.24-7.20 (m, 1H), 6.97 (dd, J = 8.0, 7.1 Hz, 1H), 4.35 (t, J = 7.5 Hz , 2H), 3.42 (hept, J = 7.0 Hz, 1H), 1.97-1.89 (m, 2H), 1.52 (d, J = 7.0 Hz, 6H), 1.38-1.28 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 140.1, 125.5, 120.7, 119.9, 119.0, 117.4, 50.8, 31.5, 31.1, 27.0, 26.6, 22.5, 22.4, 14.0.

HRMS (ESI): Calcd for $C_{16}H_{25}N_2^+$ $[M+H]^+$ 245.2012, found 245.2006.



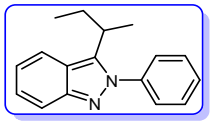
2-cyclohexyl-3-isopropyl-2H-indazole (3m)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3m** (20 mg, 42% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.21 (ddd, J = 8.7, 6.6, 1.0 Hz, 1H), 6.97 (ddd, J = 8.4, 6.6, 0.8 Hz, 1H), 4.35 (tt, J = 11.7, 3.7 Hz, 1H), 3.49 (hept, J = 7.0 Hz, 1H), 2.25-2.14 (m, 2H), 1.99-1.94 (m, 4H), 1.80-1.75 (m, 1H), 1.52 (d, J = 7.1 Hz, 6H), 1.48-1.34 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 139.3, 125.2, 120.8, 119.9, 118.8, 117.5, 59.0, 33.6, 26.7, 25.9, 25.2, 22.5.

HRMS (ESI): Calcd for $C_{16}H_{23}N_2^+$ $[M+H]^+$ 243.1856, found 243.1855.



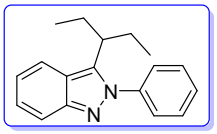
3-(sec-butyl)-2-phenyl-2H-indazole (3n)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3n** (21 mg, 43% yield) as a yellow oil. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.55-7.45 (m, 5H), 7.32-7.28 (m, 1H), 7.04 (dd, J = 7.9, 7.1 Hz, 1H), 3.13-3.03 (m, 1H), 2.03-1.92 (m, 1H), 1.85-1.74 (m, 1H), 1.46 (d, J = 7.1 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.2, 140.2, 129.1, 129.1, 126.8, 126.4, 120.9, 120.6, 119.1, 117.9, 34.2, 29.8, 20.6, 12.5.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 251.1543, found 251.1546.



3-(pentan-3-yl)-2-phenyl-2H-indazole (3o)

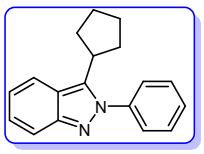
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3o** (33 mg, 62% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.54-7.44 (m, 5H), 7.30 (ddd, J = 8.7, 6.6, 0.9 Hz, 1H), 7.03 (ddd, J = 8.4, 6.6, 0.7 Hz,

1H), 2.92-2.84 (m, 1H), 2.00-1.78 (m, 4H), 0.77 (t, J = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 140.3, 140.2, 129.1, 129.0, 127.3, 126.4, 120.9, 120.6, 119.1, 117.9, 41.5, 28.2, 12.6.

HRMS (ESI): Calcd for $C_{18}H_{21}N_2^+$ $[M+H]^+$ 265.1699, found 265.1691.



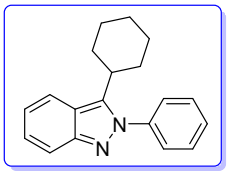
3-cyclopentyl-2-phenyl-2H-indazole (3p)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3p** (42 mg, 81% yield) as a yellow oil. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.55-7.48 (m, 5H), 7.31-7.28 (m, 1H), 7.06-7.02 (m, 1H), 3.36 (p, J = 9.1 Hz, 1H), 2.12-2.07 (m, 4H), 2.00-1.90 (m, 2H), 1.74-1.67 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 140.5, 140.3, 129.2, 128.9, 126.5, 126.4, 120.8, 120.6, 119.0, 118.0, 37.7, 33.5, 26.4.

HRMS (ESI): Calcd for $C_{18}H_{19}N_2^+$ $[M+H]^+$ 263.1543, found 263.1534.



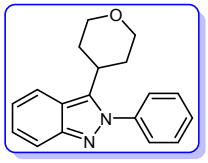
3-cyclohexyl-2-phenyl-2H-indazole (3q)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3q** (41 mg, 74% yield) as a white solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.54-7.45 (m, 5H), 7.30-7.26 (m, 1H), 7.03 (dd, J = 8.1, 7.1 Hz, 1H), 2.97 (tt, J = 11.6, 4.3 Hz, 1H), 2.03-1.90 (m, 4H), 1.85-1.82 (m, 2H), 1.76-1.73 (m, 1H), 1.41-1.19 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.1, 140.2, 129.1, 128.9, 126.4, 126.3, 121.2, 120.5, 119.5, 117.8, 37.3, 32.6, 26.6, 25.9.

HRMS (ESI): Calcd for $C_{19}H_{21}N_2^+$ $[M+H]^+$ 277.1699, found 277.1692.



2-phenyl-3-(tetrahydro-2H-pyran-4-yl)-2H-indazole (3r)

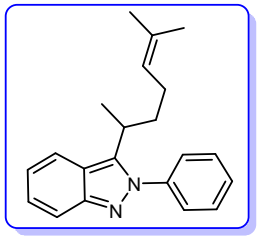
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3r** (30 mg, 55% yield) as a yellow

solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.57-7.45 (m, 5H), 7.33 -7.29 (m, 1H), 7.08 (dd, J = 8.0, 7.1 Hz, 1H), 4.07 (dd, J = 11.6, 4.1 Hz, 2H), 3.40 (t, J = 11.4 Hz, 2H), 3.23 (tt, J = 12.3, 3.8 Hz, 1H), 2.38 (qd, J = 12.7, 4.4 Hz, 2H), 1.78 (dd, J = 13.2, 1.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 140.0, 138.9, 129.3, 129.3, 126.5, 126.4, 121.1, 120.8, 119.6, 118.0, 68.1, 34.6, 32.1.

HRMS (ESI): Calcd for $C_{18}H_{19}N_2O^+$ $[M+H]^+$ 279.1492, found 279.1483.



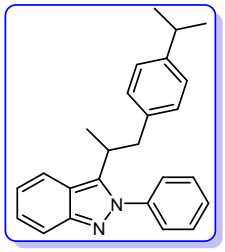
3-(6-methylhept-5-en-2-yl)-2-phenyl-2H-indazole (3s)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3s** (39 mg, 65% yield) as a yellow oil. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.54-7.45 (m, 5H), 7.31-7.27 (m, 1H), 7.04 (dd, J = 7.9, 7.1 Hz, 1H), 4.89-4.88 (m, 1H), 3.24-3.15 (m, 1H), 2.03-1.97 (m, 1H), 1.84-1.76 (m, 3H), 1.56 (s, 3H), 1.46 (d, J = 7.0 Hz, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.1, 140.1, 132.2, 129.1, 129.0, 126.7, 126.3, 123.4, 120.8, 120.6, 119.2, 117.9, 36.6, 31.8, 26.1, 25.6, 20.7, 17.6.

HRMS (ESI): Calcd for $C_{21}H_{25}N_2^+$ $[M+H]^+$ 305.2012, found 305.2004.



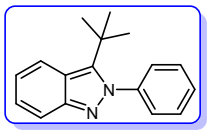
3-(1-(4-isopropylphenyl)propan-2-yl)-2-phenyl-2H-indazole(3t)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3t** (45 mg, 64% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.40-7.36 (m, 1H), 7.333-7.30 (m, 3H), 7.12-7.08 (m, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 7.4 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 3.35-3.26 (m, 1H), 3.20 (dd, J = 12.9, 9.7 Hz, 1H), 2.95 (dd, J = 12.9, 5.5 Hz, 1H), 2.84 -2.77 (m, 1H), 1.54 (d, J = 7.0 Hz, 3H), 1.19 (dd, J = 6.9, 1.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 146.9, 140.1, 139.7, 136.9, 128.9, 128.7, 128.6, 126.7, 126.3, 126.2, 120.8, 119.2, 118.0, 42.7, 35.5, 33.7, 24.1, 24.0, 20.7.

HRMS (ESI): Calcd for $C_{25}H_{27}N_2^+$ $[M+H]^+$ 355.2169, found 355.2160.



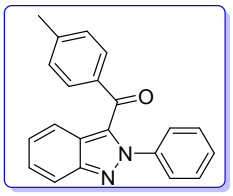
3-(tert-butyl)-2-phenyl-2H-indazole(3u)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3u** (32 mg, 65% yield) as a white solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.51-7.41 (m, 5H), 7.30-7.28(m, 1H), 7.06-7.02 (m, 1H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 144.4, 142.9, 129.4, 128.4, 128.1, 125.9, 122.6, 120.7, 119.7, 117.8, 34.7, 31.8.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 251.1543, found 251.1536.



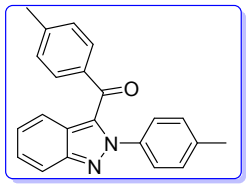
(2-phenyl-2H-indazol-3-yl)(p-tolyl)methanone (5a)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5a** (54 mg, 87% yield) as a yellow solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.55-7.53 (m, 2H), 7.44-7.35 (m, 5H), 7.26 (d, J = 8.2 Hz, 2H), 7.16 (dd, J = 8.2, 7.4 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 148.5, 144.7, 140.5, 135.2, 132.5, 130.2, 129.4, 129.1, 128.9, 127.0, 125.5, 124.8, 123.9, 120.7, 118.5, 21.8.

HRMS (ESI): Calcd for $C_{21}H_{17}N_2O^+$ $[M+H]^+$ 313.1335, found 313.1328.



p-tolyl(2-(p-tolyl)-2H-inden-1-yl)methanone (5b)

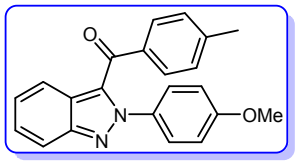
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5b** (60 mg, 92% yield) as a white solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.42

(d, J = 8.3 Hz, 2H), 7.37-7.33 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.16 -7.12 (m, 1H), 2.44 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 148.4, 144.7, 138.9, 138.1, 135.2, 132.3, 130.2, 129.7, 129.4, 126.8, 125.2, 124.6, 123.8, 120.6, 118.4, 21.8, 21.2.

HRMS (ESI): Calcd for $C_{24}H_{21}O^+$ $[M+H]^+$ 327.1492, found 327.1491.



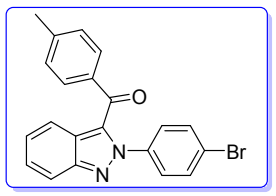
(2-(4-methoxyphenyl)-2H-indazol-3-yl)(p-tolyl)methanone (5c)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5c** (63 mg, 92% yield) as a white solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.38-7.34 (m, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.17-7.13 (m, 1H), 6.93 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 159.8, 148.3, 144.7, 135.3, 133.6, 132.3, 130.2, 129.3, 126.8, 126.6, 124.6, 123.7, 120.6, 118.3, 114.2, 55.5, 21.8.

HRMS (ESI): Calcd for $C_{21}H_{17}N_2O^+$ $[M+H]^+$343.1441, found 343.1433



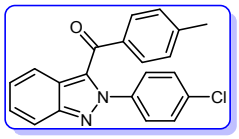
(2-(4-bromophenyl)-2H-indazol-3-yl)(p-tolyl)methanone (5d)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5d** (67 mg, 86% yield) as a white solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.58-7.54 (m, 2H), 7.44-7.41 (m, 2H), 7.38 (ddd, *J* = 8.7, 6.6, 0.9 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (ddd, *J* = 8.6, 6.6, 0.6 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 185.5, 148.7, 145.1, 139.6, 135.1, 132.5, 132.3, 130.2, 129.5, 127.2, 127.0, 125.1, 123.9, 122.9, 120.7, 118.5, 21.9.

HRMS (ESI): Calcd for $C_{21}H_{16}BrN_2O^+$ $[M+H]^+$ 391.0441, found 391.0440.



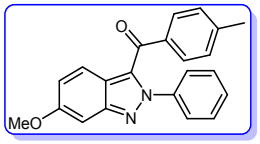
(2-(4-chlorophenyl)-2H-indazol-3-yl)(p-tolyl)methanone (5e)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5e** (50 mg, 73% yield) as a white solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.37-7.35 (m, 1H), 7.29 (dd, *J* = 18.9, 10.9 Hz, 3H), 7.20-7.12 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 185.5, 148.6, 145.0, 139.0, 135.0, 134.8, 132.4, 130.2, 129.5, 129.2, 127.2, 126.6, 125.0, 123.9, 120.6, 118.5, 21.8.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 347.0946, found 347.0940.



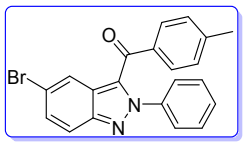
(6-methoxy-2-phenyl-2H-indazol-3-yl)(p-tolyl)methanone (5f)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5f** (55 mg, 81% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.52-7.50 (m, 2H), 7.42-7.35 (m, 3H), 7.25-7.21 (m, 3H), 7.09 (d, J = 1.9 Hz, 1H), 6.85 (dd, J = 9.2, 2.2 Hz, 1H), 3.89 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 159.2, 149.6, 144.7, 140.5, 135.1, 132.4, 130.1, 129.4, 129.0, 128.5, 125.3, 121.4, 119.9, 119.7, 95.0, 55.3, 21.8.

HRMS (ESI): Calcd for $C_{22}H_{19}N_2O_2^+$ $[M+H]^+$ 343.1441, found 343.1432.



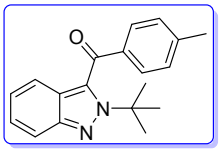
(5-bromo-2-phenyl-2H-indazol-3-yl)(p-tolyl)methanone (5g)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5g** (53 mg, 68% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 3H), 7.59 (d, J = 1.2 Hz, 1H), 7.52-7.50 (m, 2H), 7.45-7.39 (m, 4H), 7.27 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 146.9, 145.2, 140.2, 134.8, 132.0, 130.9, 130.1, 129.6, 129.2, 129.1, 125.3, 124.9, 122.8, 120.2, 118.8, 21.9.

HRMS (ESI): Calcd for $C_{21}H_{16}BrN_2O^+$ $[M+H]^+$ 391.0441, found 391.0443.



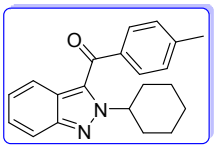
(2-(tert-butyl)-2H-indazol-3-yl)(p-tolyl)methanone (5h)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5h** (25 mg, 43% yield) as a yellow solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 1H), 6.97-6.96 (m, 2H), 2.46 (s, 3H), 1.83 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 145.8, 145.1, 135.7, 132.0, 130.5, 129.6, 125.7, 124.1, 123.1, 120.1, 117.9, 64.1, 30.7, 21.9.

HRMS (ESI): Calcd for $C_{19}H_{21}N_2O^+$ $[M+H]^+$ 293.1648, found 293.1646.



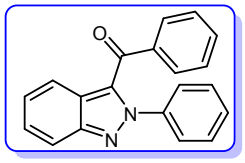
(2-cyclohexyl-2H-indazol-3-yl)(p-tolyl)methanone (5i)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5i** (29 mg, 45% yield) as a white solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.29-7.25 (m, 1H), 7.06-7.05 (m, 2H), 5.15-5.07 (m, 1H), 2.48 (s, 3H), 2.20-2.11 (m, 4H), 1.94 (d, J = 13.2 Hz, 2H), 1.77-1.73 (m, 1H), 1.54-1.42 (m, 2H), 1.41- 1.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 147.3, 144.3, 136.2, 131.2, 130.1, 129.3, 125.7, 124.0, 123.3, 120.6, 118.3, 61.3, 33.8, 25.7, 25.4, 21.8.

HRMS (ESI): Calcd for $C_{21}H_{23}N_2O^+$ $[M+H]^+$ 319.1805, found 319.1797.



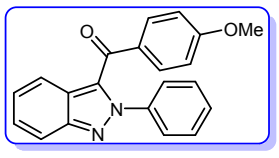
phenyl(2-phenyl-2H-indazol-3-yl)methanone (5j)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5j** (52 mg, 87% yield) as a yellow solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 3H), 7.61 (t, J = 7.4 Hz, 1H), 7.55-7.52 (m, 2H), 7.48-7.36 (m, 7H), 7.18 (dd, J = 8.2, 7.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 148.6, 140.5, 137.9, 133.6, 132.3, 129.9, 129.1, 129.0, 128.7, 127.1, 125.6, 125.1, 124.1, 120.6, 118.6.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 299.1179, found 299.1171.



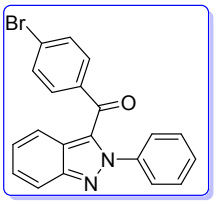
(4-methoxyphenyl)(2-phenyl-2H-indazol-3-yl)methanone(5k)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5k** (33 mg, 51% yield) as a white solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.86 (m, 3H), 7.56-7.54 (m, 2H), 7.45-7.36 (m, 5H), 7.19-7.15 (m, 1H), 6.95 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 164.1, 148.5, 140.5, 132.6, 132.5, 130.5, 129.1, 128.8, 126.9, 125.4, 124.6, 123.7, 120.6, 118.4, 113.9, 55.6.

HRMS (ESI): Calcd for $C_{24}H_{17}N_2O^+$ $[M+H]^+$ 329.1285, found 329.1276.



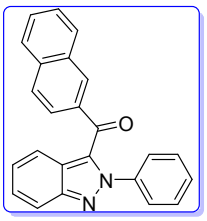
(4-bromophenyl)(2-phenyl-2H-indazol-3-yl)methanone (5l)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5l** (41 mg, 55% yield) as a yellow solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.5, 1.2 Hz, 1H), 7.72-7.70 (m, 2H), 7.60-7.57 (m, 2H), 7.52-7.50 (m, 2H), 7.43-7.36 (m, 5H), 7.21-7.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 148.6, 140.4, 136.5, 132.0, 131.8, 131.3, 129.1, 129.1, 128.8, 127.1, 125.5, 125.3, 124.0, 120.3, 118.7.

HRMS (ESI): Calcd for $C_{20}H_{14}BrN_2O^+$ $[M+H]^+$ 377.0284, found 377.0278.



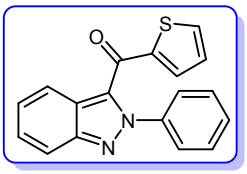
naphthalen-2-yl(2-phenyl-2H-indazol-3-yl)methanone (5m)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5m** (49 mg, 70% yield) as a white solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.99-7.85 (m, 5H), 7.63-7.55 (m, 4H), 7.41-7.36 (m, 5H), 7.15 (dd, J = 8.2, 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 148.6, 140.6, 135.9, 135.1, 132.5, 132.5, 132.3, 129.6, 129.1, 129.0, 129.0, 128.8, 127.9, 127.1, 127.1, 125.5, 125.1, 125.0, 124.1, 120.6, 118.6.

HRMS (ESI): Calcd for $C_{24}H_{17}N_2O^+$ $[M+H]^+$ 349.1335, found 349.1326.



(2-phenyl-2H-indazol-3-yl)(thiophen-2-yl)methanone (5n)

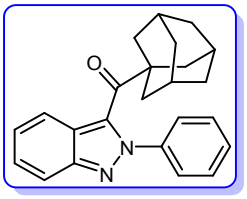
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5n** (47 mg, 78% yield) as a yellow solid. Compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 1H), 7.76 (dd, J = 4.9, 0.7 Hz, 1H), 7.66-7.63 (m, 2H), 7.58-7.56 (m, 2H), 7.47-7.37(m, 4H), 7.24-7.20 (m, 1H),

7.13-7.11 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 148.6, 144.2, 140.4, 135.6, 135.5, 132.1, 129.2, 129.0, 128.3, 127.1, 125.4, 124.9, 123.6, 120.4, 118.5.

HRMS (ESI): Calcd for $C_{17}H_{19}N_2^+$ $[M+H]^+$ 305.0743, found 305.0735.



((1r,3R,5S)-adamantan-1-yl)(2-phenyl-2H-indazol-3-yl)methanone(5o)

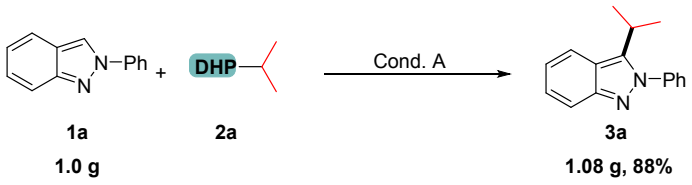
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **5o** (28 mg, 40% yield) as a white solid. New compounds.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.8 Hz, 1H), 7.60-7.55 (m, 3H), 7.52-7.43 (m, 3H), 7.37-7.33 (m, 1H), 7.18-7.14 (m, 1H), 1.92 (s, 3H), 1.68 (d, J = 2.2 Hz, 6H), 1.65-1.62 (m, 3H), 1.54-1.51 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 148.5, 141.1, 133.9, 129.4, 129.0, 127.0, 125.0, 123.3, 121.7, 120.1, 117.9, 48.2, 38.1, 36.1, 27.7.

HRMS (ESI): Calcd for $C_{24}H_{25}N_2O^+$ $[M+H]^+$ 357.1961, found 357.1954.

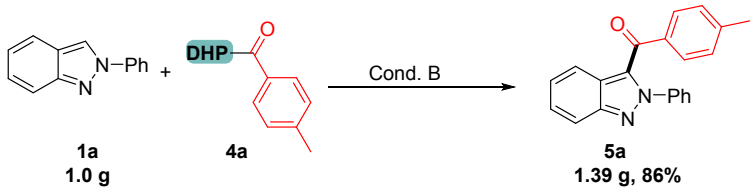
4. Scale-up Synthesis



1a **2a** **3a**

1.0 g **1.08 g, 88%**

The reaction vessel was charged with 2-phenyl-2H-indazole (**1a**, 5.15 mmol, 1 g), diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2a,** 15.45 mmol, 4.56 g), $Na_2S_2O_8$ (3.0 equiv., 3.68 g), $AgNO_3$ (30 mol%, 262.4 mg) and TFA (2.0 equiv., 1.17 g) in *i*-PrOH /H_2O (1:1, 104 mL), and the reaction mixture was stirred under nitrogen atmosphere at room temperature for 2 h. After completion, the reaction mixture was quenched with 100 mL water/ethyl acetate (1:1). Then the reaction mixture was extracted with ethyl acetate and the organic phase was washed with Brine, dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents. The product was obtained as a yellow solid (1.08 g, 88%).



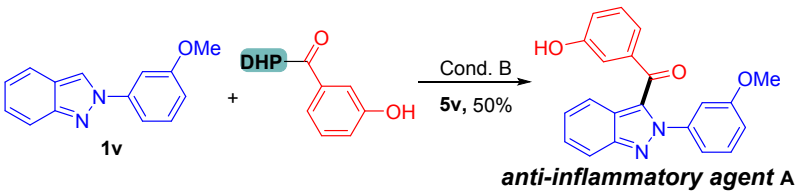
1a
1.0 g

4a

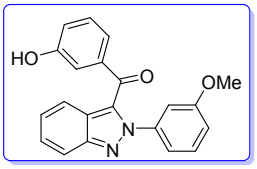
5a
1.39 g, 86%

The reaction vessel was charged with 2*H*-indazole (**1a**, 5.15 mmol, 1g), diethyl 2,6-dimethyl-4-(4-methylbenzoyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4a**, 15.45 mmol, 5.74 g), $Na_2S_2O_8$ (3.0 equiv., 3.68 g), $AgNO_3$ (40 mol%, 350 mg) and TFA (3.0 equiv., 1.76 g) in acetone/H_2O (1:1, 104 mL), and the reaction mixture was stirred under nitrogen atmosphere at 25 ^oC for 4 hours. After completion, the reaction mixture was quenched with 100 mL water/ethyl acetate (1:1). Then the reaction mixture was extracted with ethyl acetate and the organic phase was washed with Brine, dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents. The product was obtained as a yellow solid (1.39 g, 86%).

5. Synthesis of Bioactive Molecules



The reaction vessel was charged with 2-(3-methoxyphenyl)-2H-indazole (**1v**, 0.2 mmol, 44.9 mg), diethyl 4-(3-hydroxybenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.6 mmol, 224 mg), $Na_2S_2O_8$ (3.0 equiv., 143 mg), $AgNO_3$ (40 mol%, 14 mg) and TFA (3.0 equiv., 68 mg) in acetone/H_2O (1:1, 4 mL), and the reaction mixture was stirred under nitrogen atmosphere at 25 °C for 4 hours. After completion, the reaction mixture was quenched with 20 mL water/ethyl acetate (1:1). Then the reaction mixture was extracted with ethyl acetate and the organic phase was washed with Brine, dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents. The product was obtained as a yellow solid (34.4 mg, 50%).



(3-hydroxyphenyl)(2-(3-methoxyphenyl)-2H-indazol-3-yl)methanone (5v)

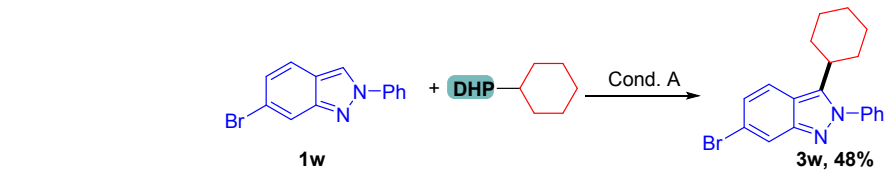
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give **5v** (34mg, 50% yield) as a white solid

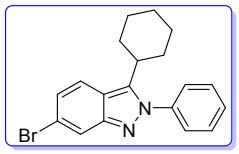
^{1}H NMR (400 MHz, DMSO) δ 9.87 (s, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.45-7.22 (m,

6H), 7.18-7.15 (m, 2H), 7.10-7.02 (m, 3H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 185.5, 159.4, 157.5, 147.7, 141.1, 138.5, 132.2, 129.9, 127.1, 125.0, 123.3, 120.9, 120.5, 120.2, 118.1, 117.6, 115.4, 114.7, 111.1, 55.4.

HRMS (ESI): Calcd for $C_{21}H_{17}N_2O_3^+$ $[M+H]^+$ 345.1234, found 345.1226.





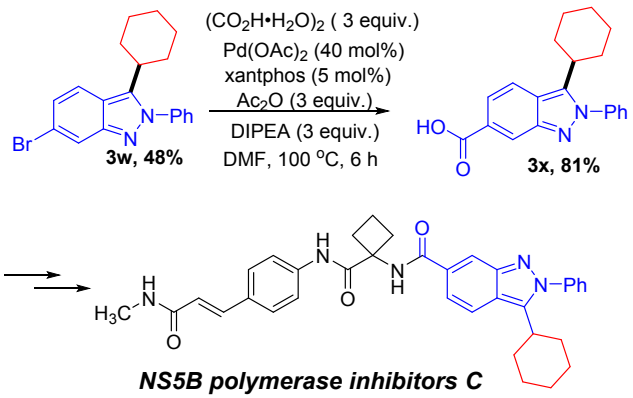
6-bromo-3-cyclohexyl-2-phenyl-2H-indazole (3w)

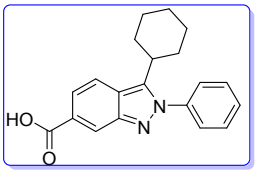
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **3w** (34mg, 48% yield) as a white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.57-7.50 (m, 3H), 7.46-7.44 (m, 2H), 7.11 (dd, J = 9.0, 1.5 Hz, 1H), 2.98-2.90 (m, 1H), 1.93-1.83 (m, 6H), 1.78-1.74 (m, 1H), 1.39-1.19 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 141.8, 139.8, 129.2, 129.2, 126.3, 124.2, 122.6, 120.4, 120.1, 118.1, 37.2, 32.6, 26.4, 25.7.

HRMS (ESI): Calcd for $C_{19}H_{20}BrN_2^+$ $[M+H]^+$ 355.0804, found 355.0797.





3-cyclohexyl-2-phenyl-2H-indazole-6-carboxylic acid (3x)[7]

A 10 mL Schlenk tube equipped with a stir bar was charged with $(CO_2H{\cdot}H_2O)_2$ (3 equiv.), $Pd(OAc)_2$ (40 mol%), xantphos (5 mol%), 6-bromo-3-cyclohexyl-2-phenyl-2H-indazole (**3x**) (0.2 mmol), Ac_2O (3 equiv.), DIPEA(3 equiv.), and DMF (1.0 mL) in air. The tube was quickly sealed with a Teflon® high pressure valve, frozen in liquid nitrogen, evacuated and backfilled with N_2 (5 times). After the reaction mixture was stirred in a preheated oil bath (100 °C) for 6 h, it was allowed to cool down to room temperature. Then the reaction mixture was extracted with ethyl acetate and the organic phase was washed with Brine, dried over anhydrous Na_2SO_4. the crude product was purified by silica gel flash chromatography (PE: EA=5:1 to EA as the eluent) , then recrystallization with $CHCl_3$ to give **3x** (52 mg, 81% yield) as a white solid.

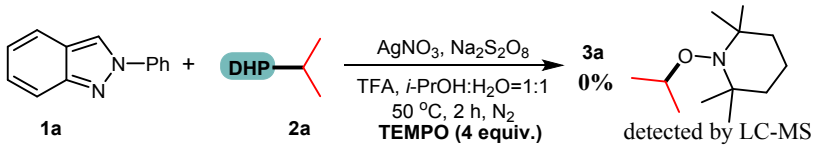
^{1}H NMR (400 MHz, DMSO) δ 12.97 (br, 1H), 8.29 (s, 1H), 8.06 (d, J = 8.9 Hz, 1H), 7.65-7.56 (m, 6H), 2.92-2.87 (m, 1H), 1.97-1.91 (m, 4H), 1.80-1.77 (m, 2H), 1.68-1.65 (m, 1H), 1.42-1.33 (m, 1H), 1.20-1.17 (m, 2H).

^{13}C NMR (100 MHz, DMSO) δ 167.6, 147.3, 141.2, 139.4, 129.4, 129.3, 128.6,

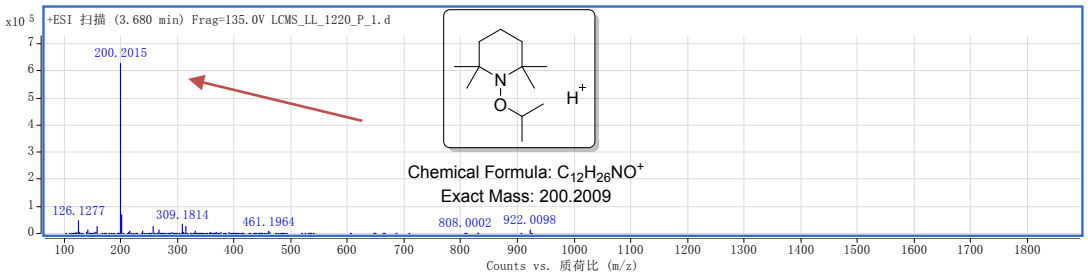
126.3, 121.6, 120.7, 120.5, 119.8, 36.7, 31.7, 26.1, 25.0.

HRMS (ESI): Calcd for $C_{20}H_{21}N_2O_2^+$ $[M+H]^+$ 321.1598, found 321.1591.

6. Control Experiment



The reaction vessel was charged with 2-phenyl-2H-indazole (**1a**, 0.2 mmol), diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2a,** 0.6 mmol, 177 mg), $Na_2S_2O_8$ (3.0 equiv., 143 mg), $AgNO_3$ (30 mol%, 10 mg), TEMPO (4.0 equiv., 125 mg) and TFA (2.0 equiv., 46 mg) in *i*-PrOH /H_2O (1:1, 4 mL), and the reaction mixture was stirred under nitrogen atmosphere at room temperature for 2 h.



HRMS (ESI): Calcd for $C_{12}H_{26}NO^+$ $[M+H]^+$ 200.2009, found 200.2015.

7. References

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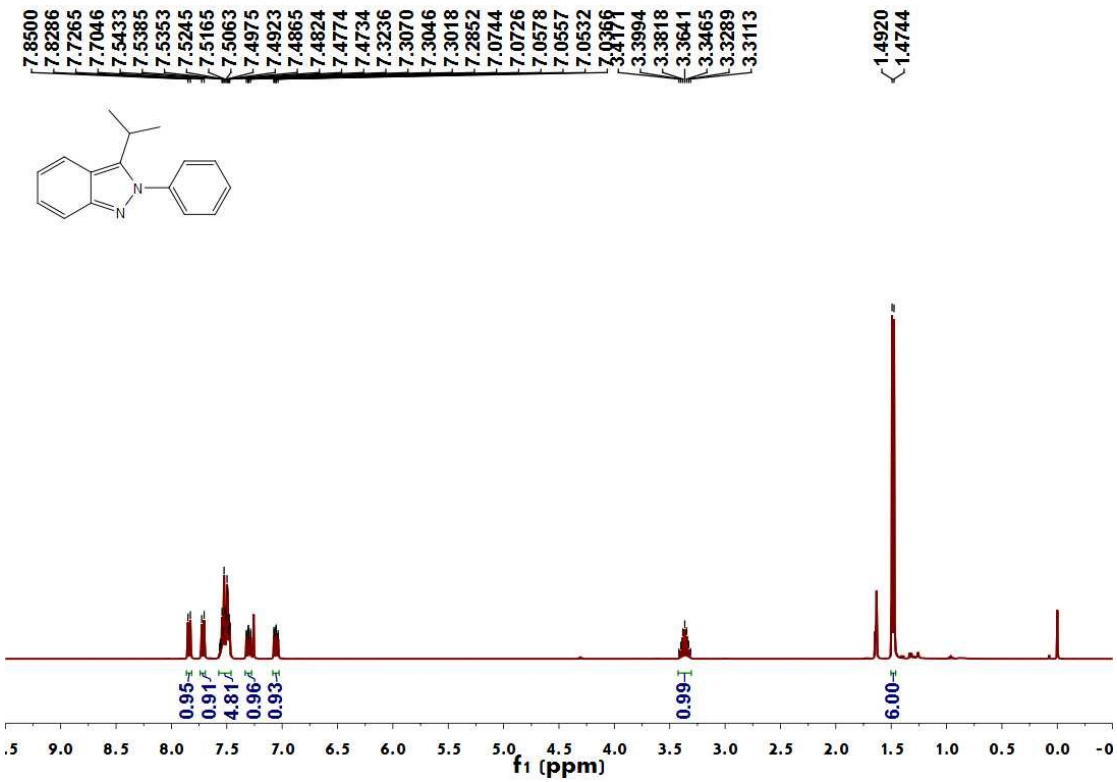
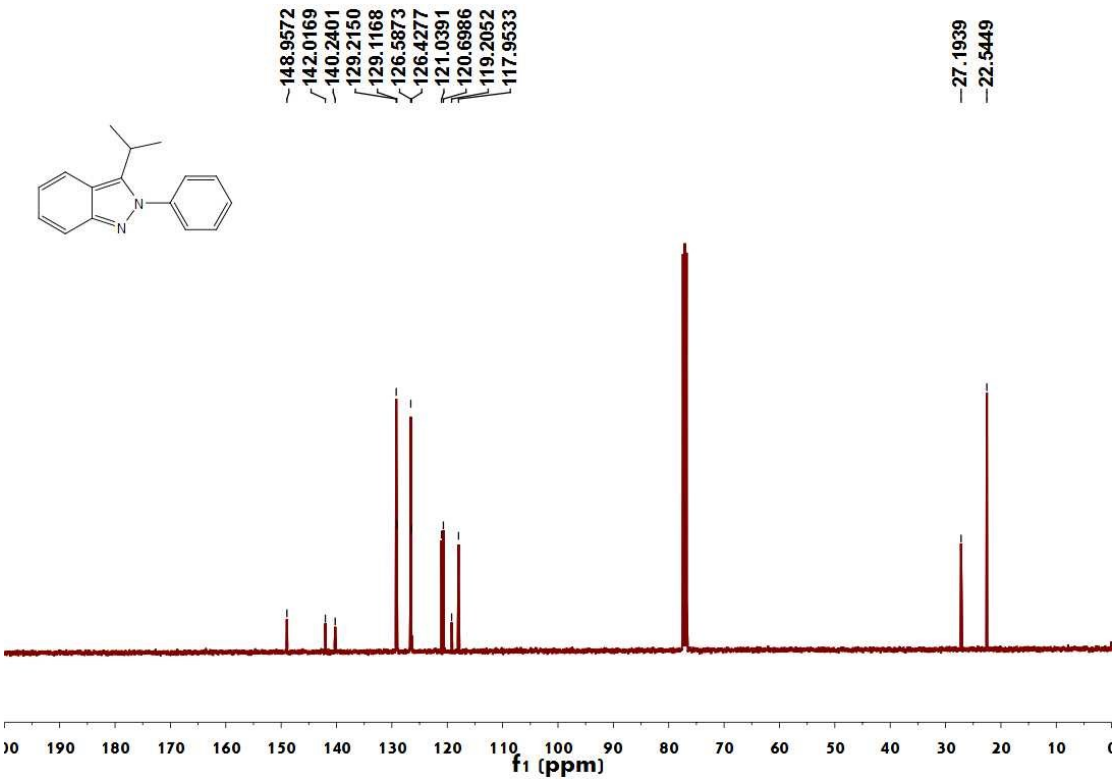
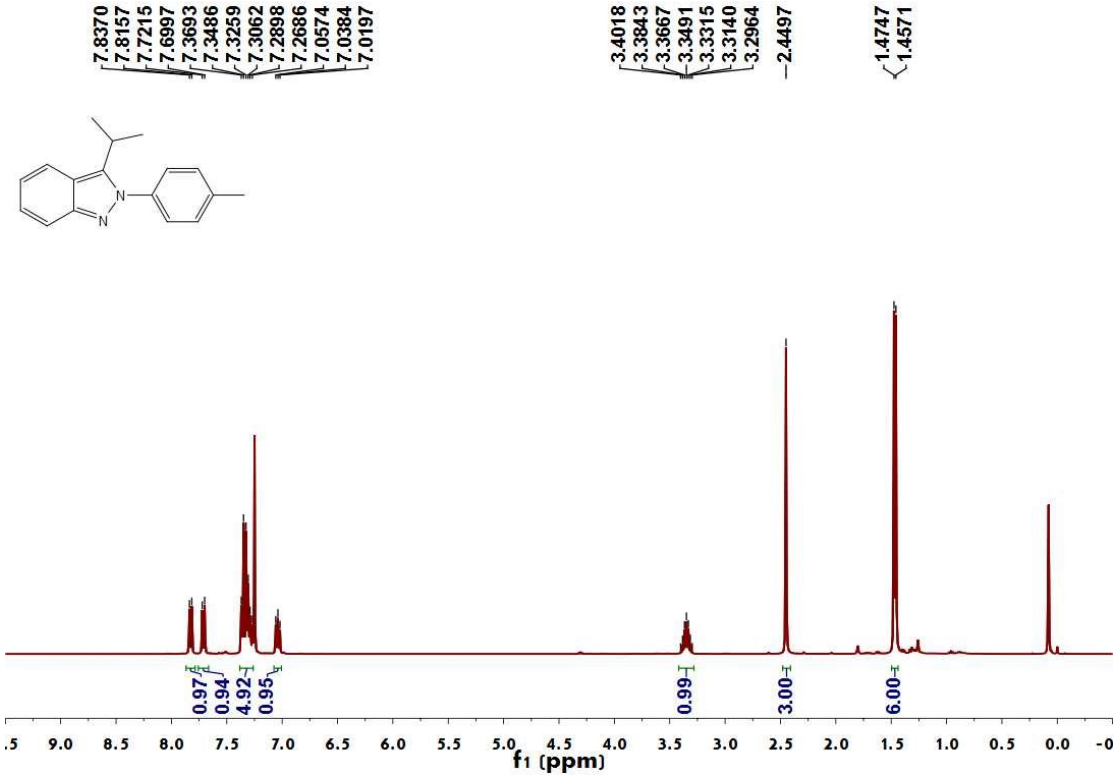
8. ^{1}H NMR and ^{13}C NMR Spectra of the Products

3a





3b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7.3259
7.3062
7.2898
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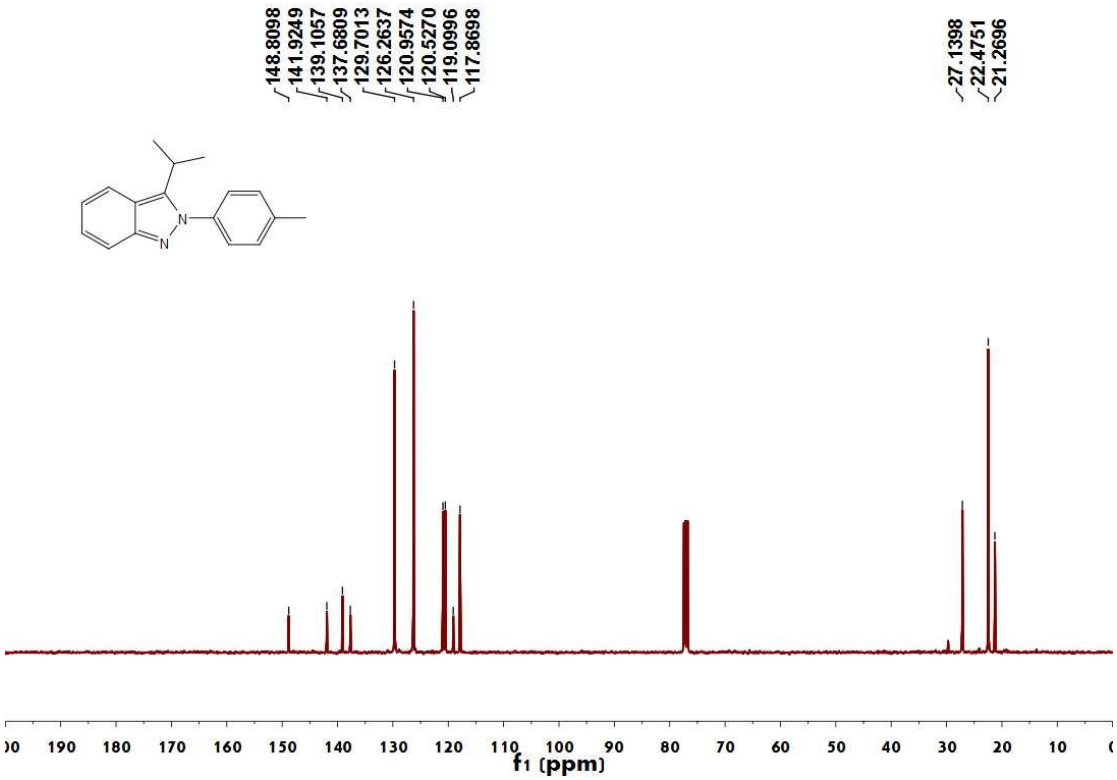
7.0574
7.0384
7.0197
3.4018
3.3843
3.3667
3.3491
3.3315
3.3140
3.2964
2.4497
1.4747
1.4571
0.97
0.94
4.92
0.95
0.99
3.00
6.00
f1 (ppm)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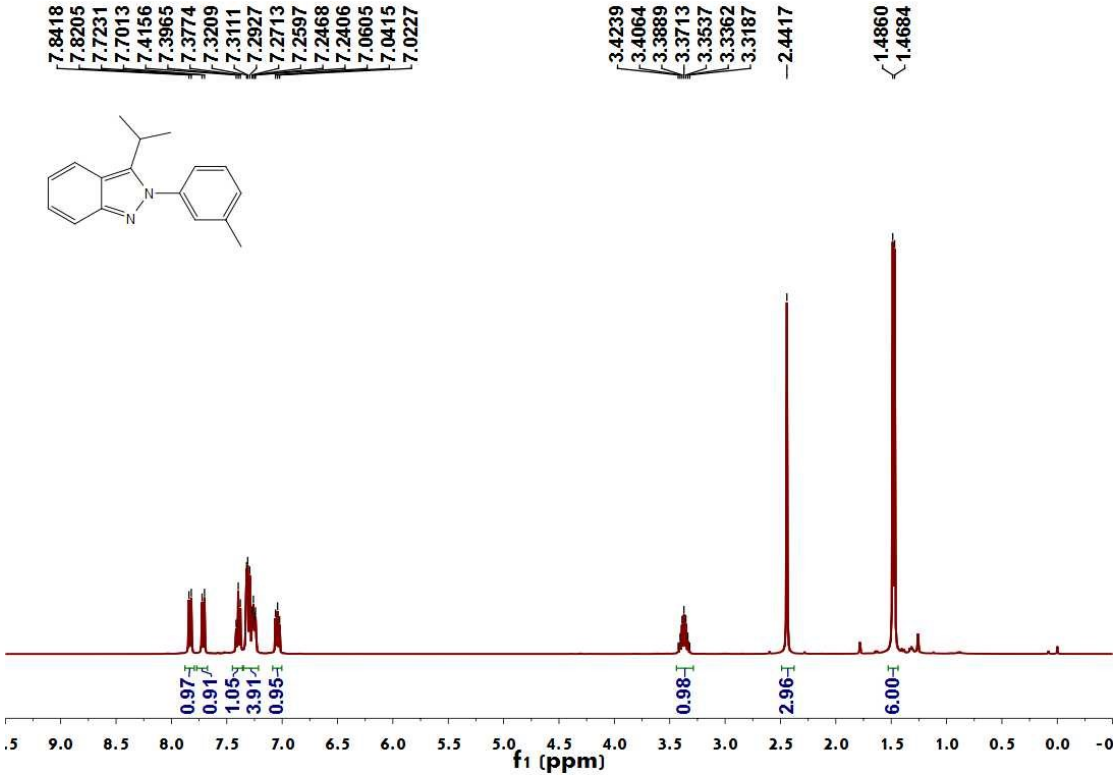
137.6809
129.7013
126.2637
120.9574
120.5270
119.0996
117.8698
27.1398
22.4751
21.2696
f1 (ppm)

3c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7.4156
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7.3774
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7.3111
7.2927
7.2713
7.2597
7.2468
7.2406
7.0605
7.0415
7.0227
3.4239
3.4064
3.3889
3.3713
3.3537
3.3362
3.3187
2.4417
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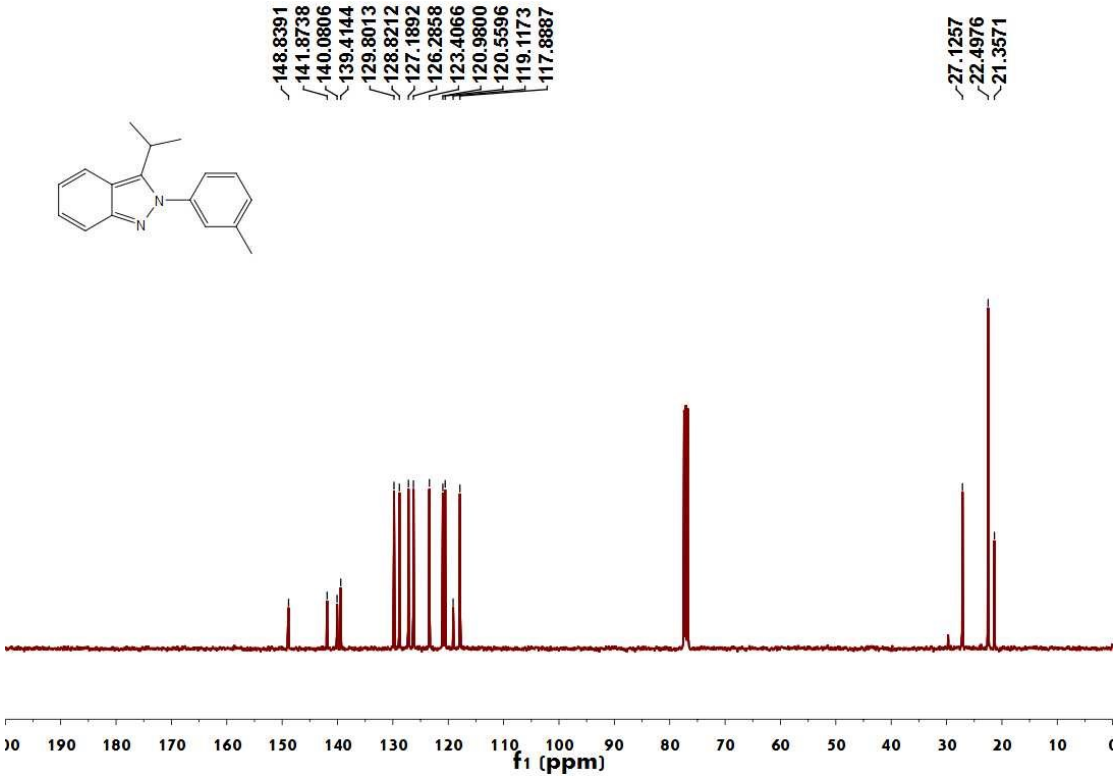
0.91
1.05
3.91
0.95
0.98
2.96
6.00
f1 (ppm)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128.8212
127.1892
126.2858
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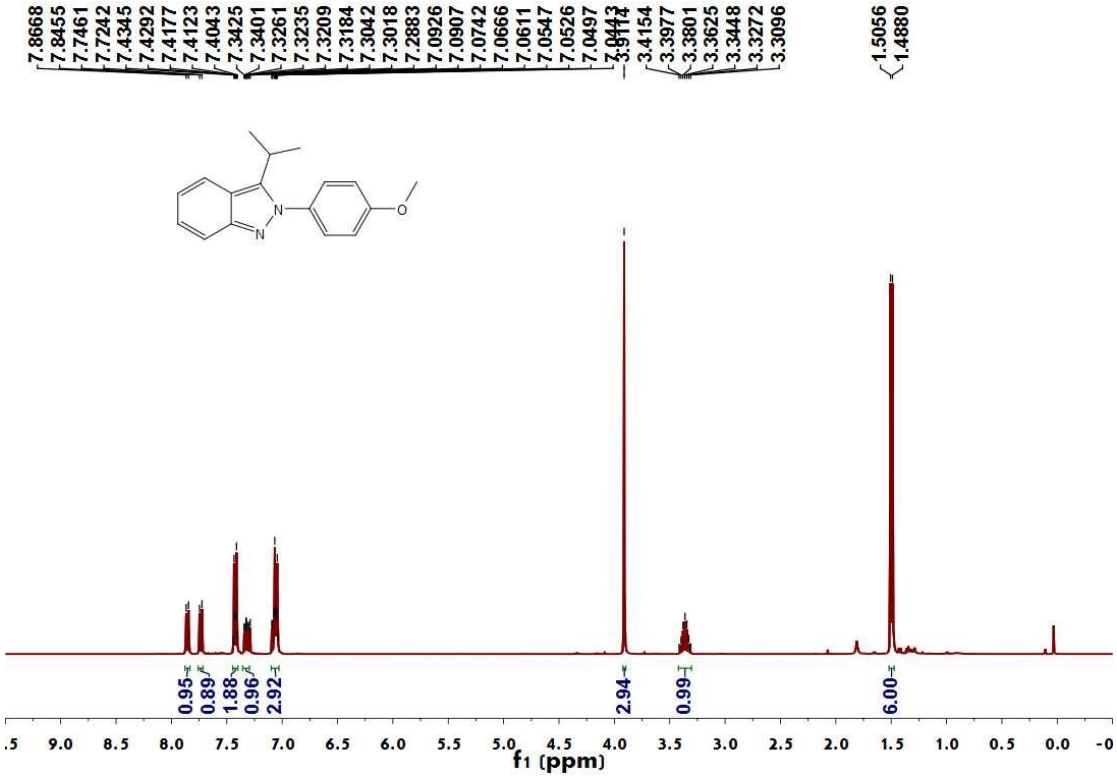
27.1257
22.4976
21.3571
f1 (ppm)

3d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7.4123
7.4043
7.3425
7.3401
7.3261
7.3235
7.3209
7.3184
7.3042
7.3018
7.2883
7.0926
7.0907
7.0742
7.0666
7.0611
7.0547
7.0526
7.0497
3.4154
3.3977
3.3801
3.3625
3.3448
3.3272
3.3096
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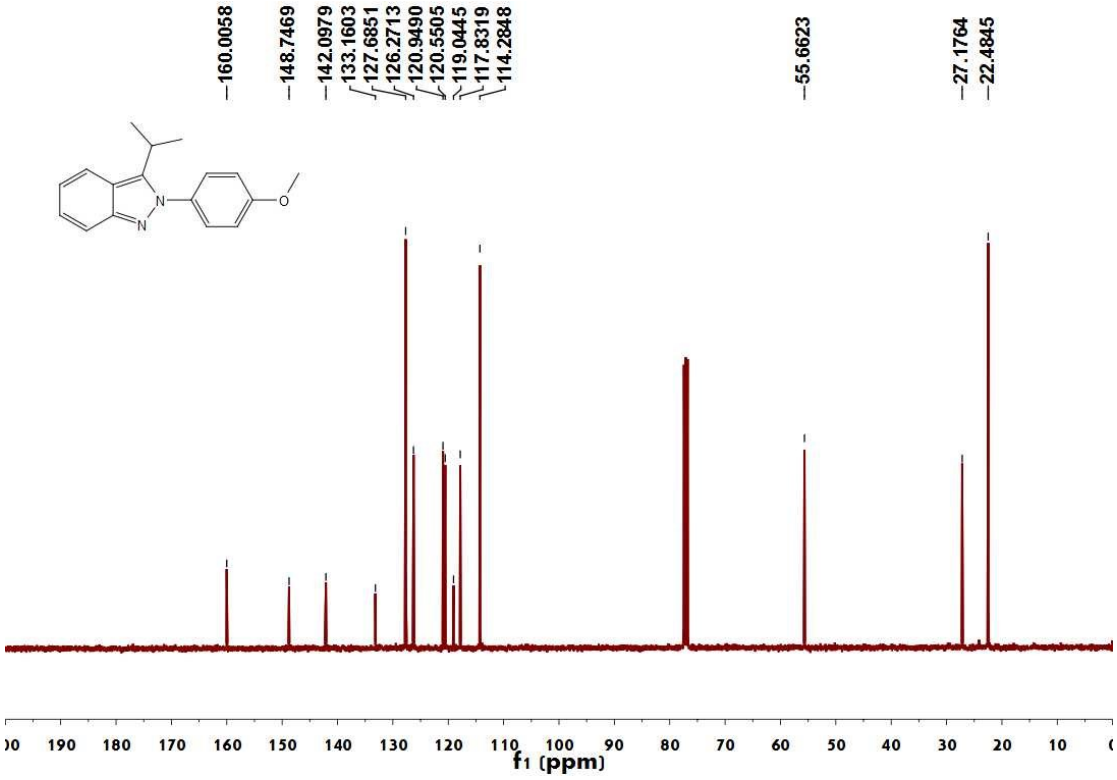
0.95
0.89
1.88
0.96
2.92
2.94
0.99
6.00
f1 (ppm)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142.0979
133.1603
127.6851
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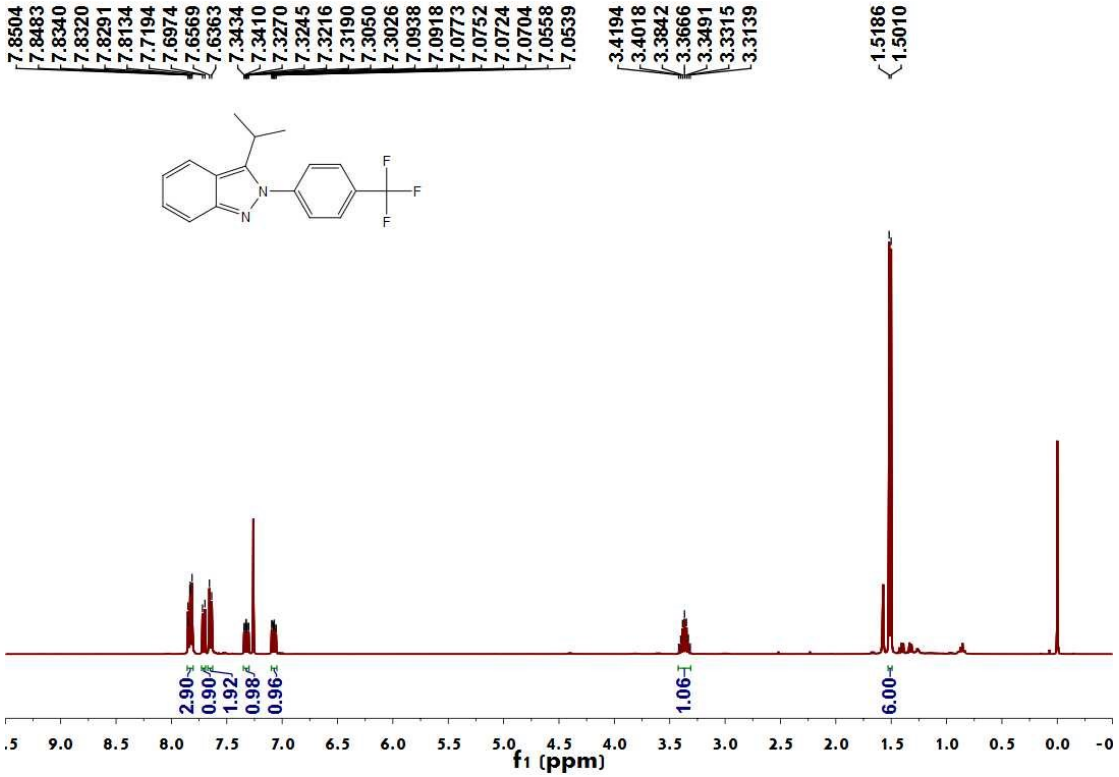
120.5505
119.0445
117.8319
114.2848
55.6623
27.1764
22.4845
f1 (ppm)

3e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7.7194
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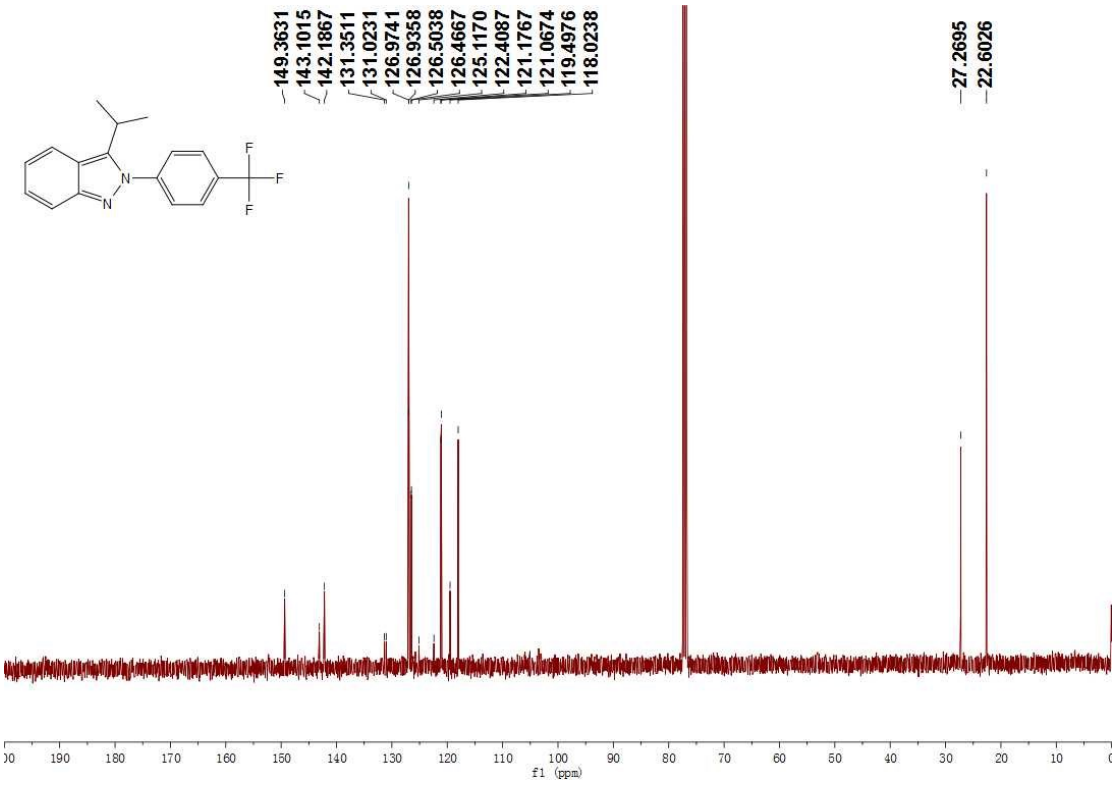
7.6569
7.6363
7.3434
7.3410
7.3270
7.3245
7.3216
7.3190
7.3050
7.3026
7.0938
7.0918
7.0773
7.0752
7.0724
7.0704
7.0558
7.0539
3.4194
3.4018
3.3842
3.3666
3.3491
3.3315
3.3139
1.5186
1.5010
F
F
F
N
N
2.90
0.90
1.92
0.98
0.96
1.06
6.00
f1 (ppm)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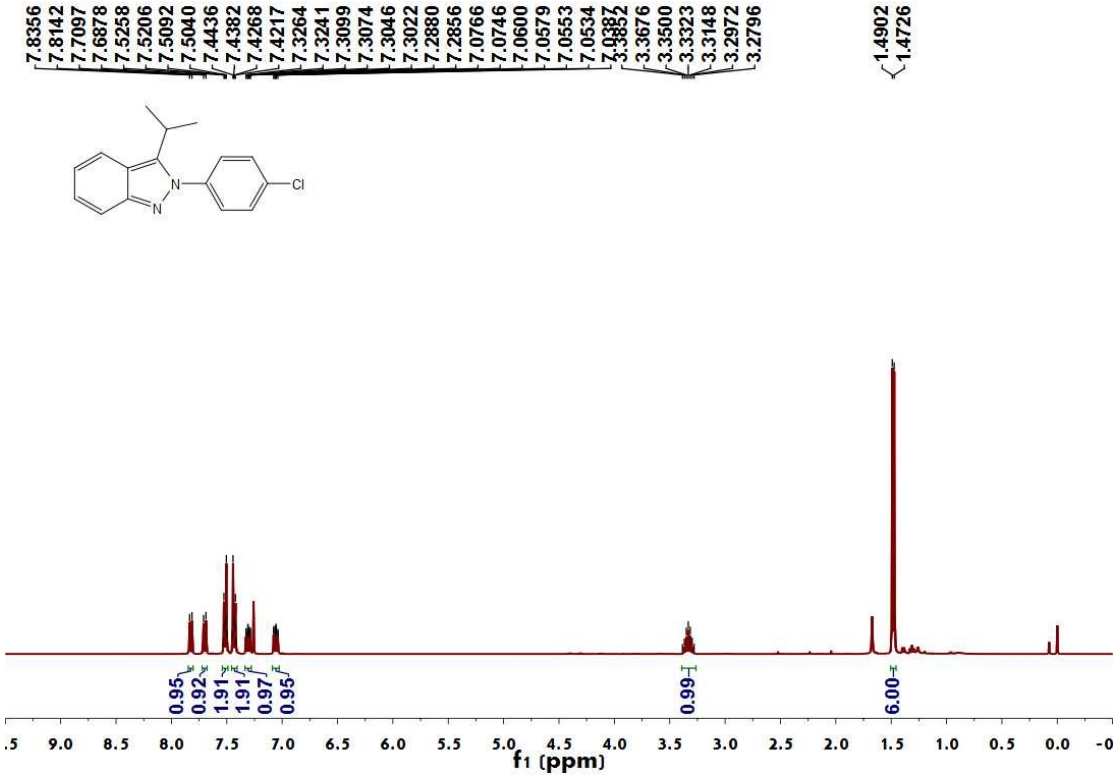
143.1015
142.1867
131.3511
131.0231
126.9741
126.9358
126.5038
126.4667
125.1170
122.4087
121.1767
121.0674
119.4976
118.0238
27.2695
22.6026
F
F
F
N
N
f1 (ppm)

3f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7.7097
7.6878
7.5258
7.5206
7.5092
7.5040
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7.4268
7.4217
7.3264
7.3241
7.3099
7.3074
7.3046
7.3022
7.2880
7.2856
7.0766
7.0746
7.0600
7.0579
7.0553
7.0534
3.3676
3.3500
3.3323
3.3148
3.2972
3.2796
1.4902
1.4726
Cl
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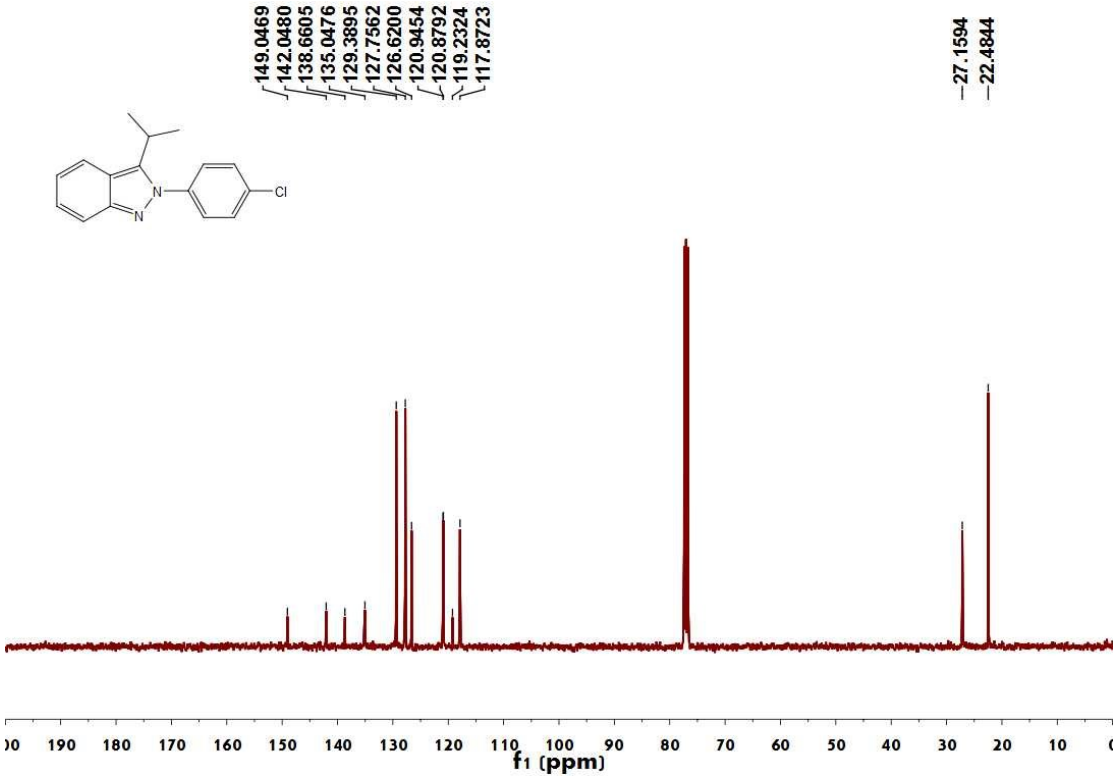
N
0.95
0.92
1.91
1.91
0.97
0.95
0.99
6.00
f1 (ppm)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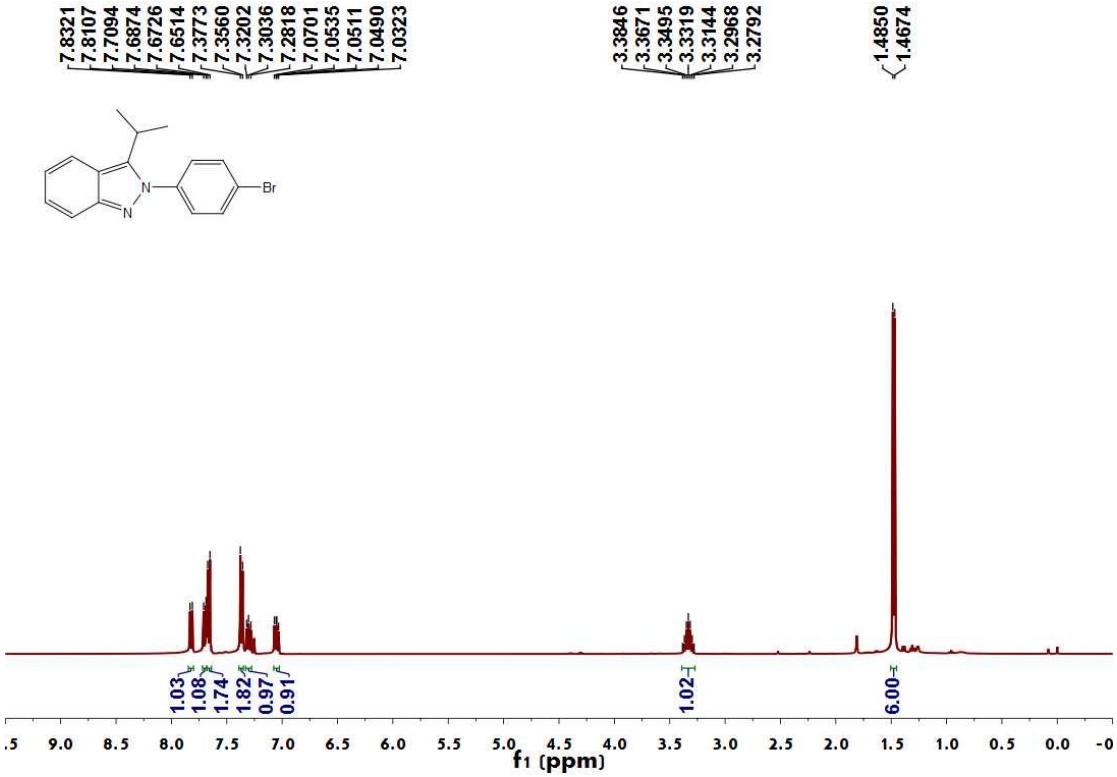
142.0480
138.6605
135.0476
129.3895
127.7562
126.6200
120.9454
120.8792
119.2324
117.8723
27.1594
22.4844
Cl
N
N
f1 (ppm)

3g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7.6726
7.6514
7.3773
7.3560
7.3202
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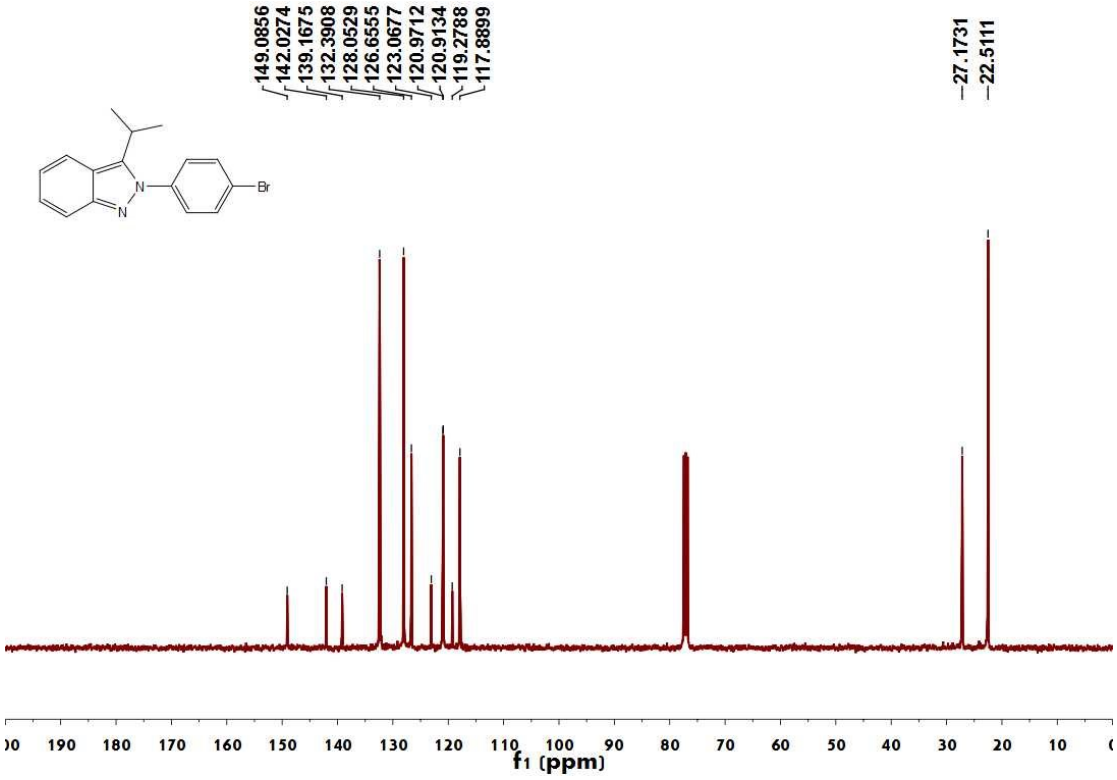
7.2818
7.0701
7.0535
7.0511
7.0490
7.0323
3.3846
3.3671
3.3495
3.3319
3.3144
3.2968
3.2792
1.4850
1.4674
Br
1.03
1.08
1.74
1.82
0.97
0.91
1.02
6.00
f1 (ppm)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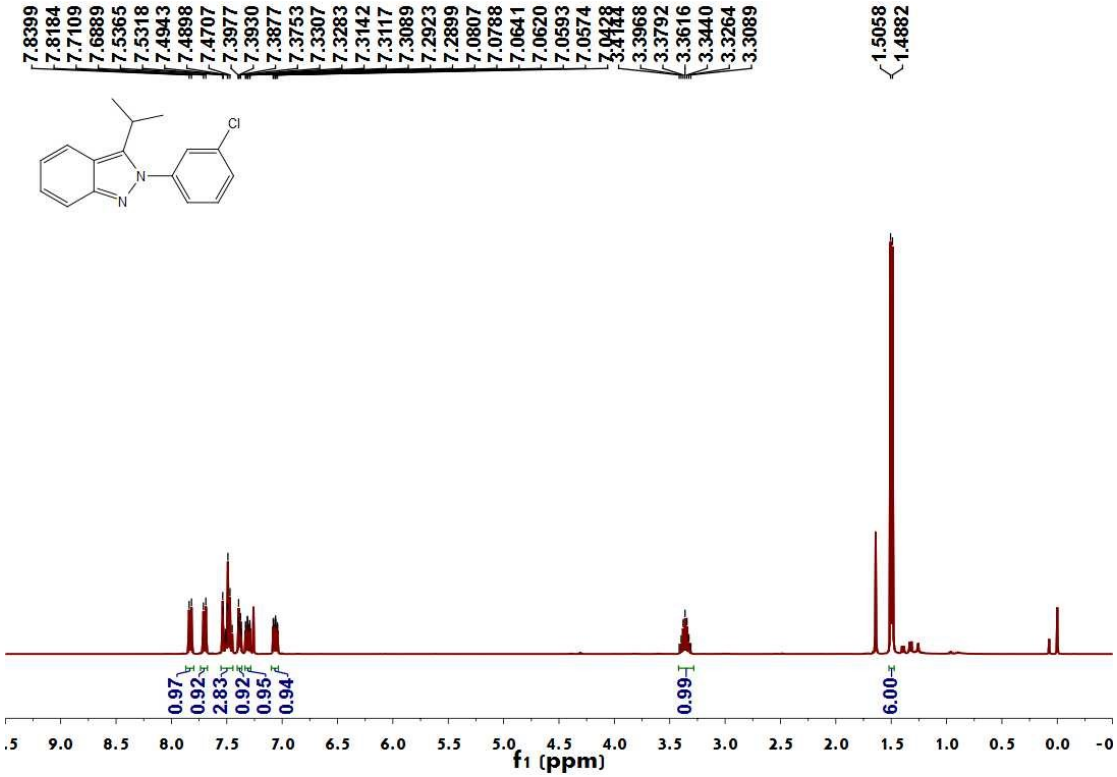
117.8899
27.1731
22.5111
Br
f1 (ppm)

3h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7.5318
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7.4707
7.3977
7.3930
7.3877
7.3753
7.3307
7.3283
7.3142
7.3117
7.3089
7.2923
7.2899
7.0807
7.0788
7.0641
7.0620
7.0593
7.0574
3.3968
3.3792
3.3616
3.3440
3.3264
3.3089
1.5058
1.4882
Cl
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N
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0.92
2.83
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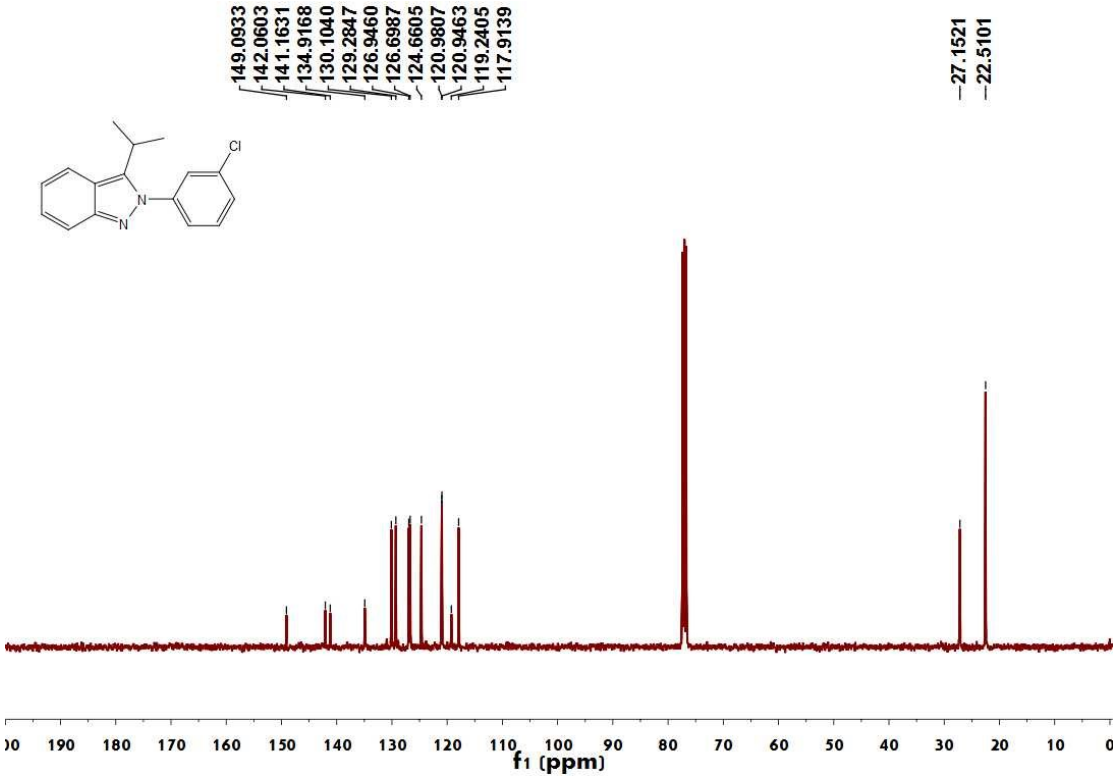
0.95
0.94
0.99
6.00
f1 (ppm)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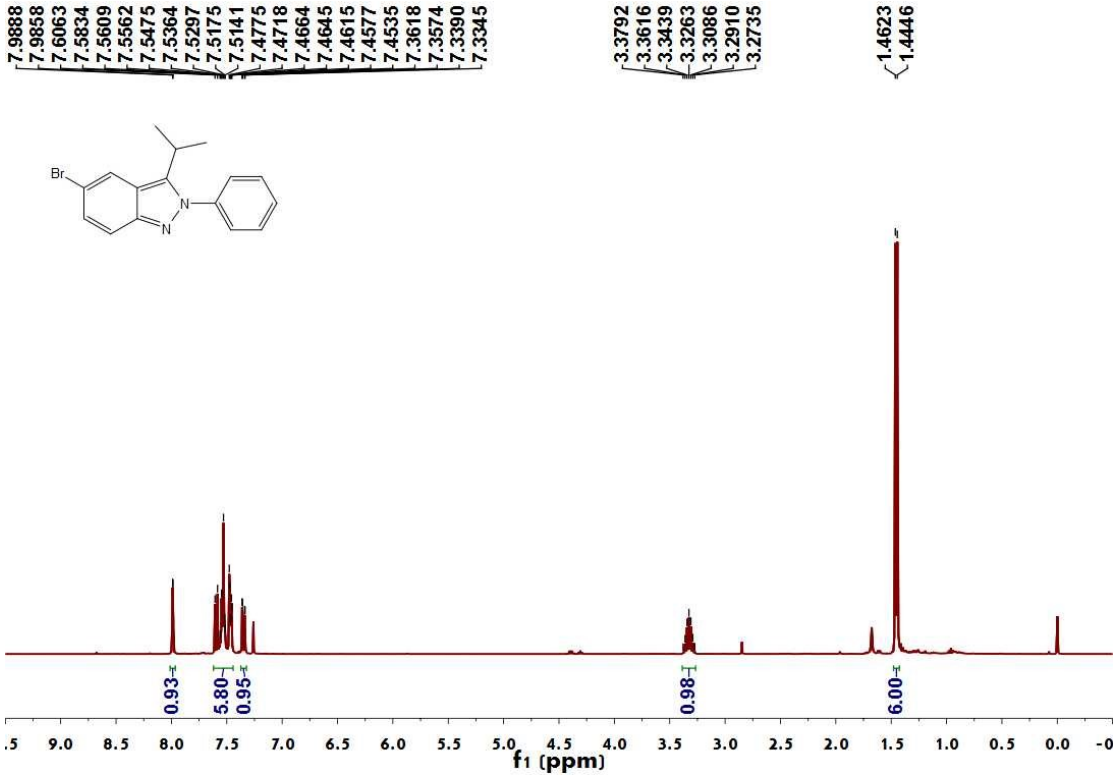
141.1631
134.9168
130.1040
129.2847
126.9460
126.6987
124.6605
120.9807
120.9463
119.2405
117.9139
27.1521
22.5101
Cl
N
N
f1 (ppm)

3i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7.5297
7.5175
7.5141
7.4775
7.4718
7.4664
7.4645
7.4615
7.4577
7.4535
7.3618
7.3574
7.3390
7.3345
3.3792
3.3616
3.3439
3.3263
3.3086
3.2910
3.2735
1.4623
1.4446
Br
N
N
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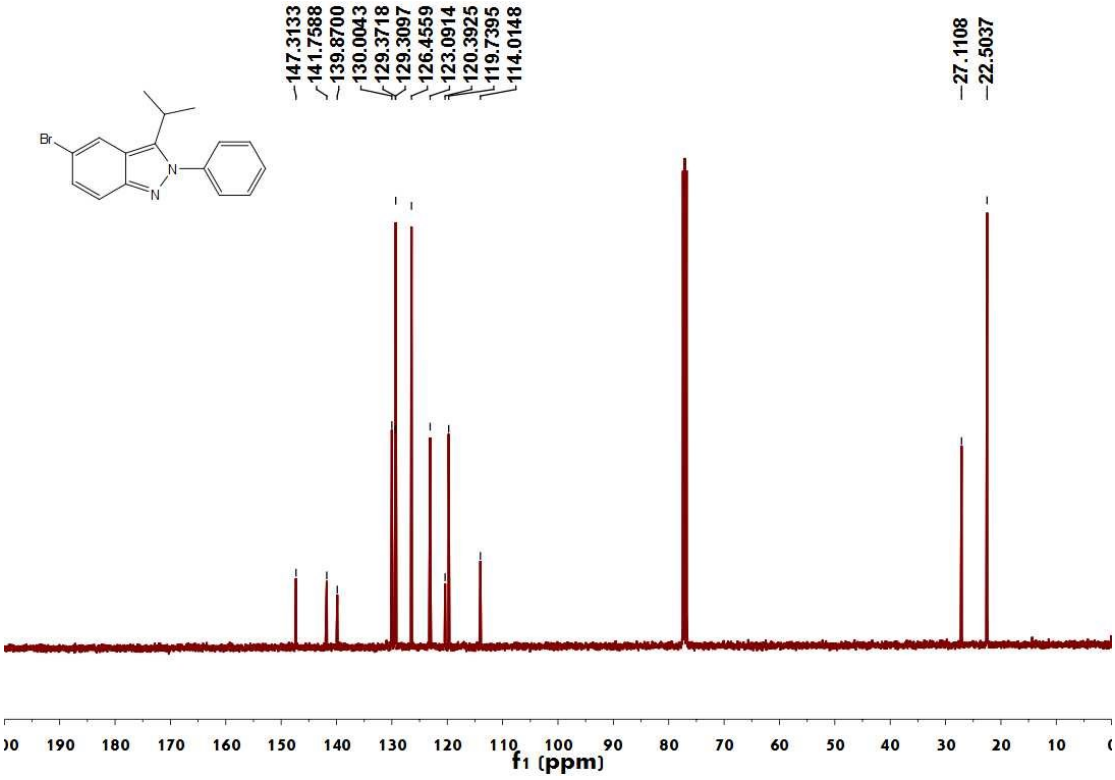
5.80
0.95
0.98
6.00
f1 (ppm)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129.3718
129.3097
126.4559
123.0914
120.3925
119.7395
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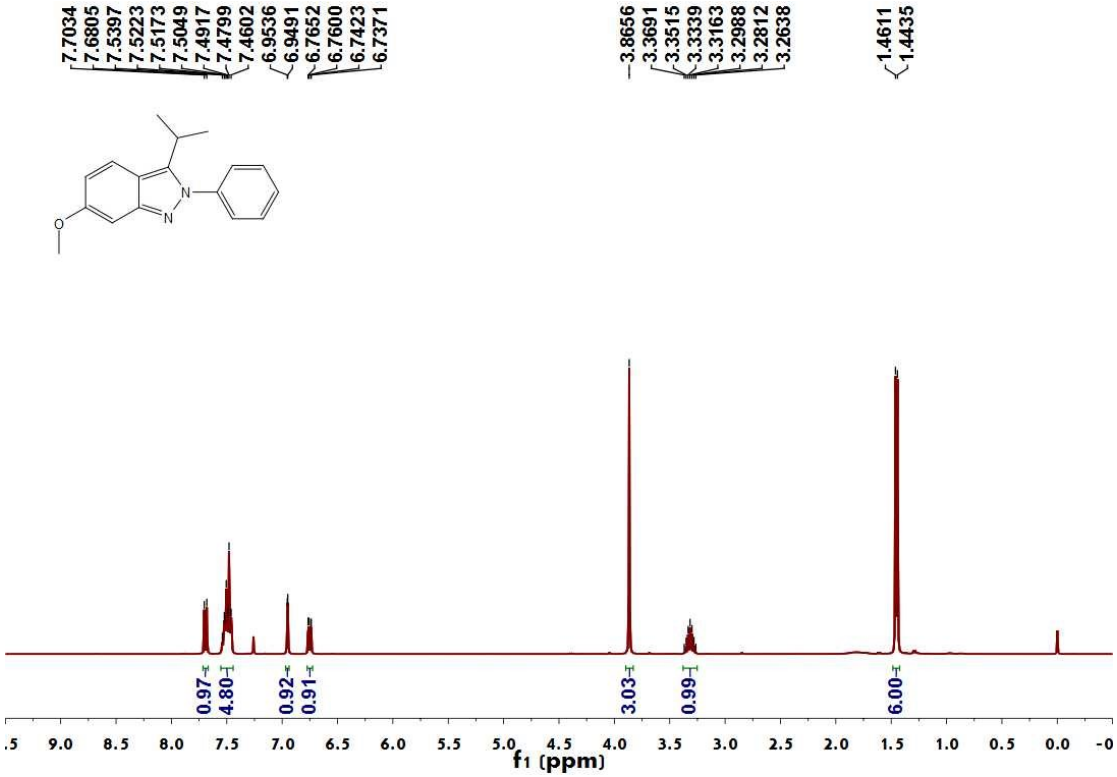
27.1108
22.5037
Br
N
N
f1 (ppm)

3j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7.5173
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7.4917
7.4799
7.4602
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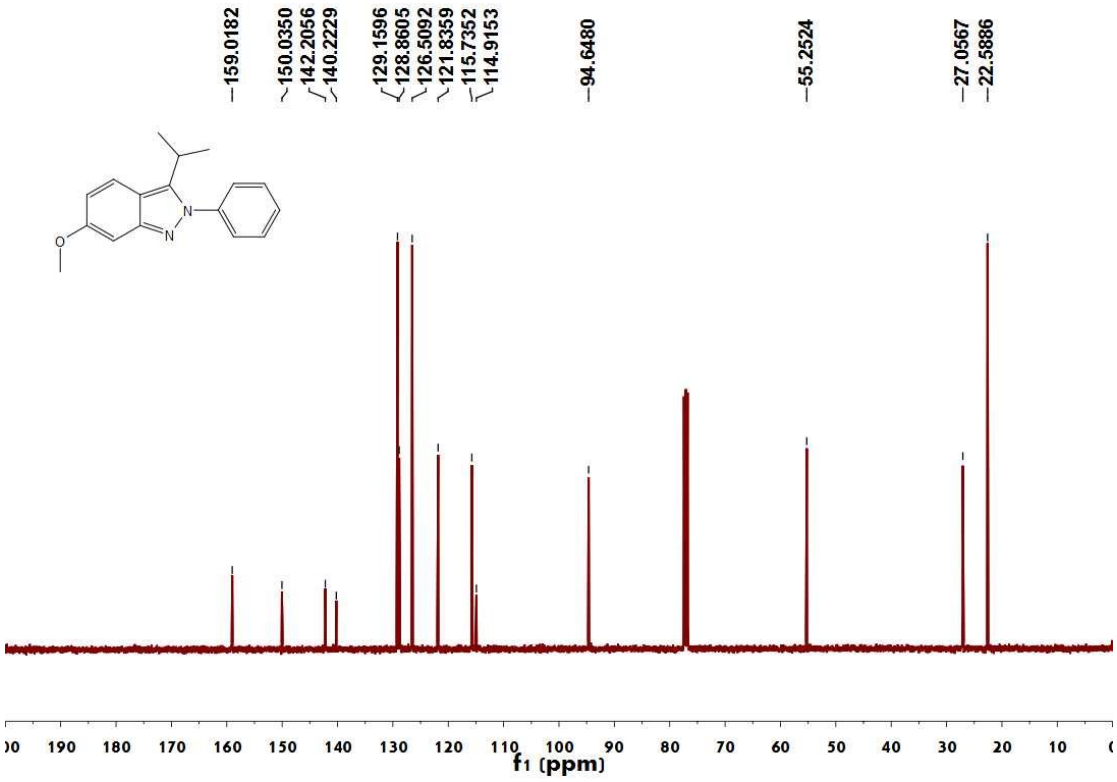
6.9491
6.7652
6.7600
6.7423
6.7371
3.8656
3.3691
3.3515
3.3339
3.3163
3.2988
3.2812
3.2638
1.4611
1.4435
0.97
4.80
0.92
0.91
3.03
0.99
6.00
f1 (ppm)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140.2229
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128.8605
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115.7352
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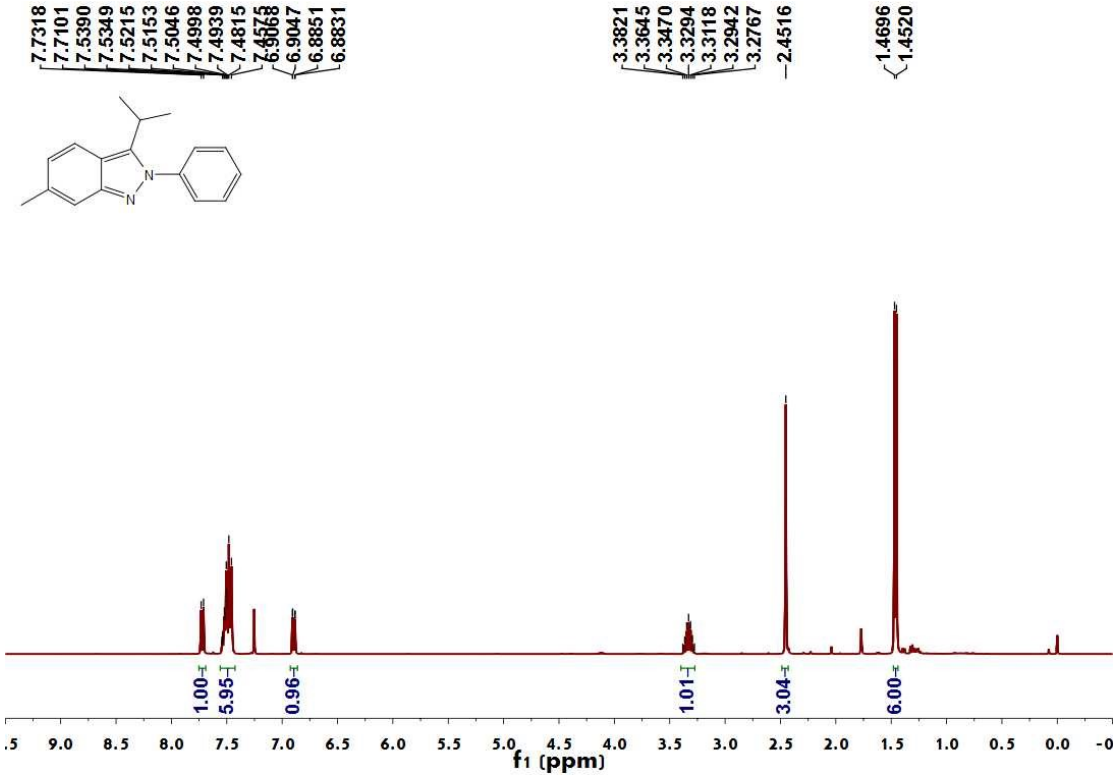
94.6480
55.2524
27.0567
22.5886
f1 (ppm)

3k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7.5153
7.5046
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7.4939
7.4815
7.4575
6.9068
6.9047
6.8851
6.8831
3.3821
3.3645
3.3470
3.3294
3.3118
3.2942
3.2767
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1.4696
1.4520
1.00
5.95
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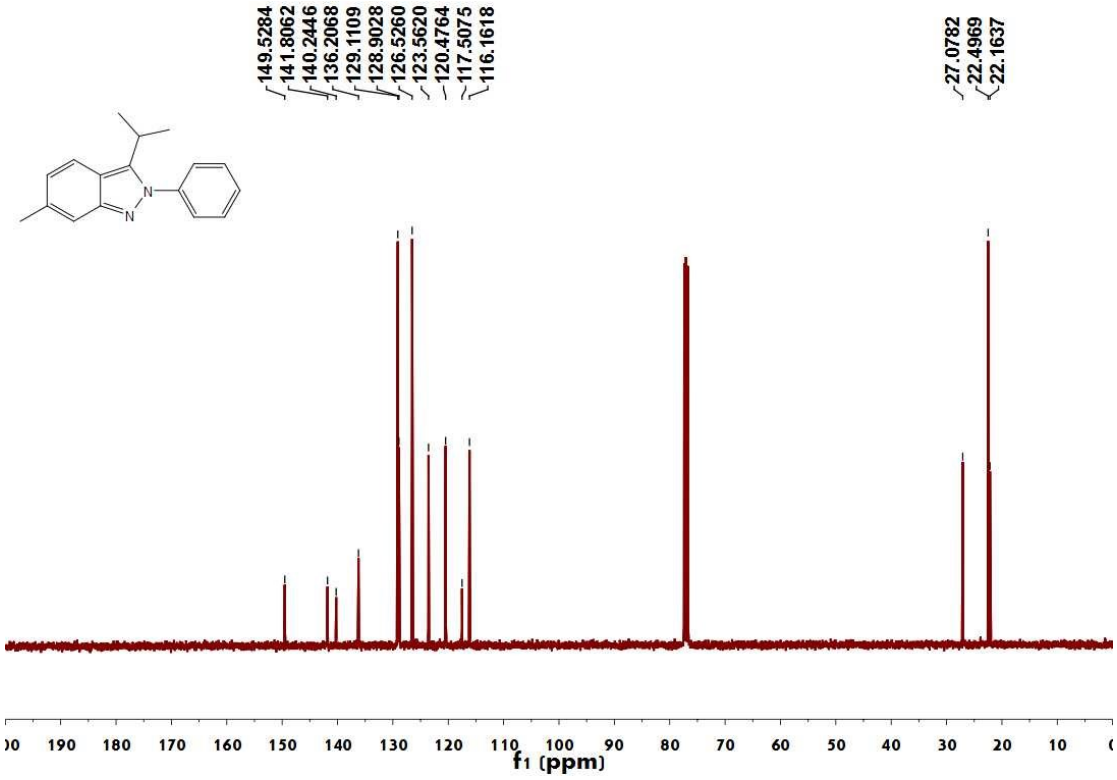
1.01
3.04
6.00
f1 (ppm)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116.1618
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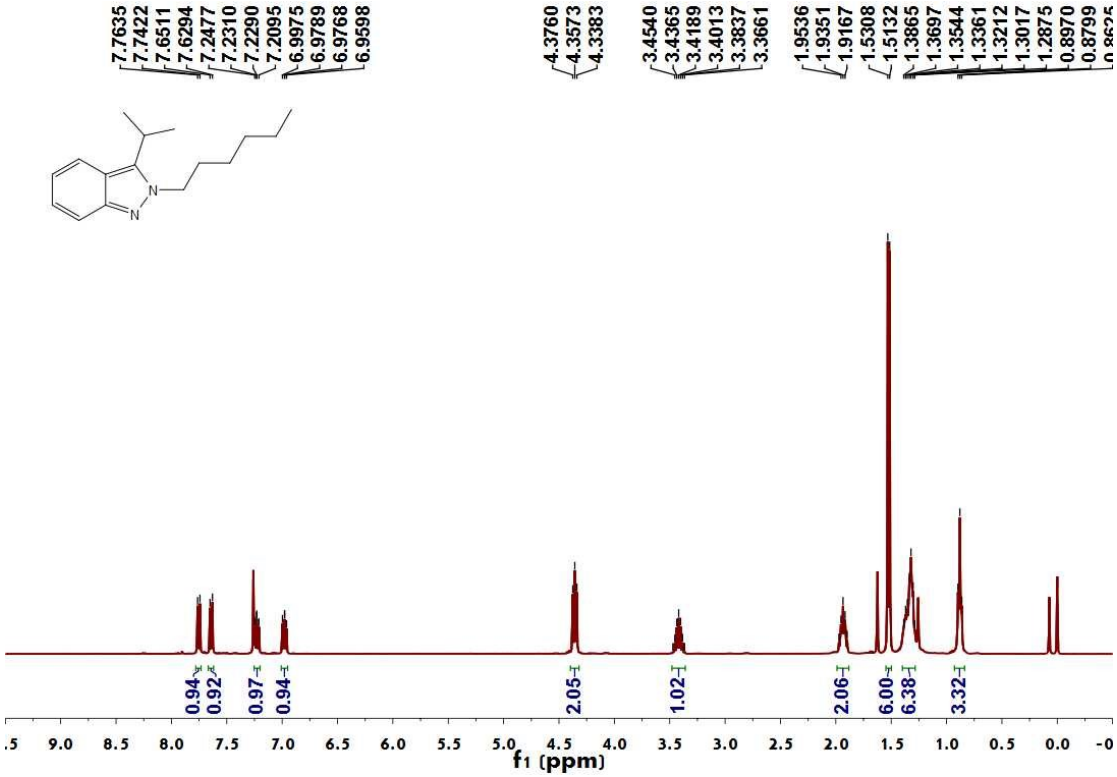
22.4969
22.1637
f1 (ppm)

3l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6.9598
4.3760
4.3573
4.3383
3.4540
3.4365
3.4189
3.4013
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1.5132
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1.3697
1.3544
1.3361
1.3212
1.3017
1.2875
0.8970
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0.97
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2.05
1.02
2.06
6.00
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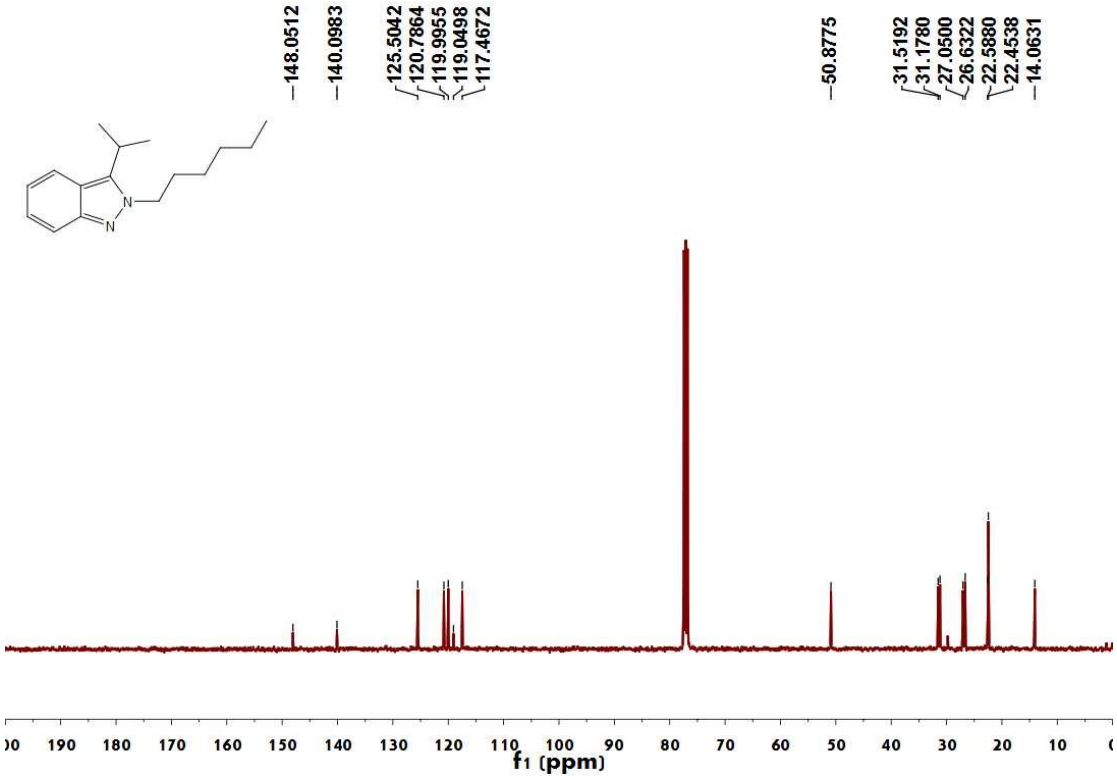
3.32
f1 (ppm)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125.5042
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119.0498
117.4672
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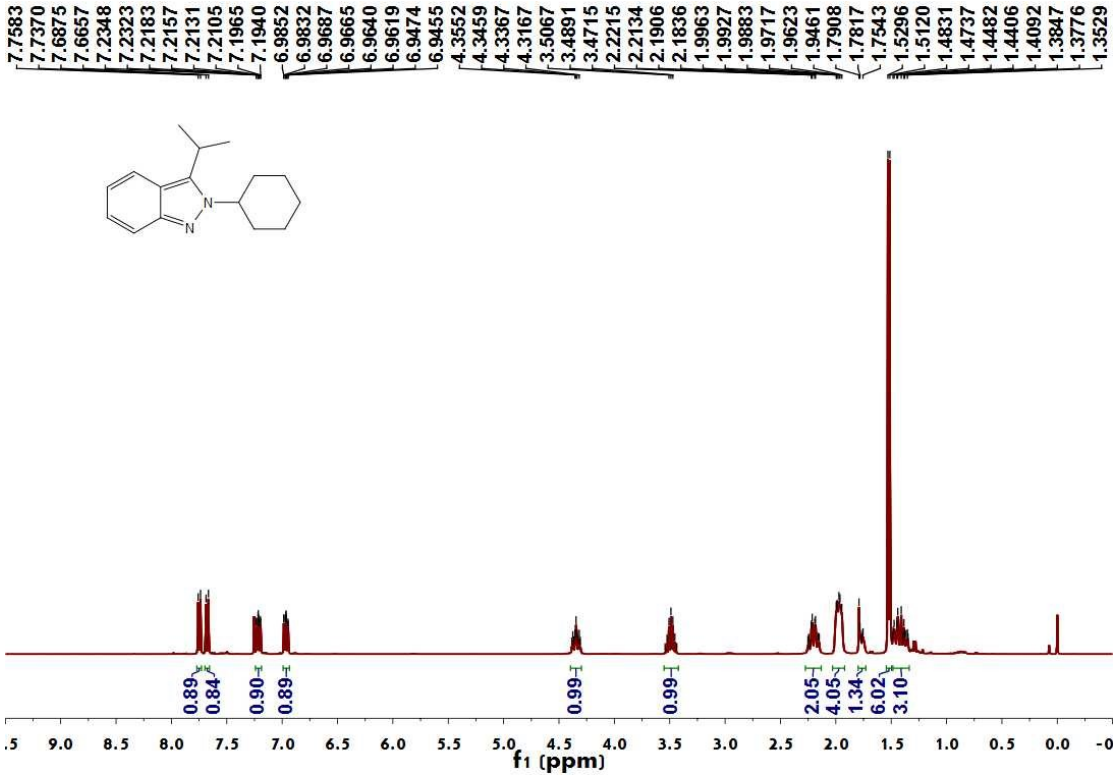
31.1780
27.0500
26.6322
22.5880
22.4538
14.0631
f1 (ppm)

3m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7.2183
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7.2131
7.2105
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7.1940
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6.9832
6.9687
6.9665
6.9640
6.9619
6.9474
6.9455
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4.3367
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3.5067
3.4891
3.4715
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2.2134
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2.1836
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1.7908
1.7817
1.7543
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1.5120
1.4831
1.4737
1.4482
1.4406
1.4092
1.3847
1.3776
1.3529
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0.99
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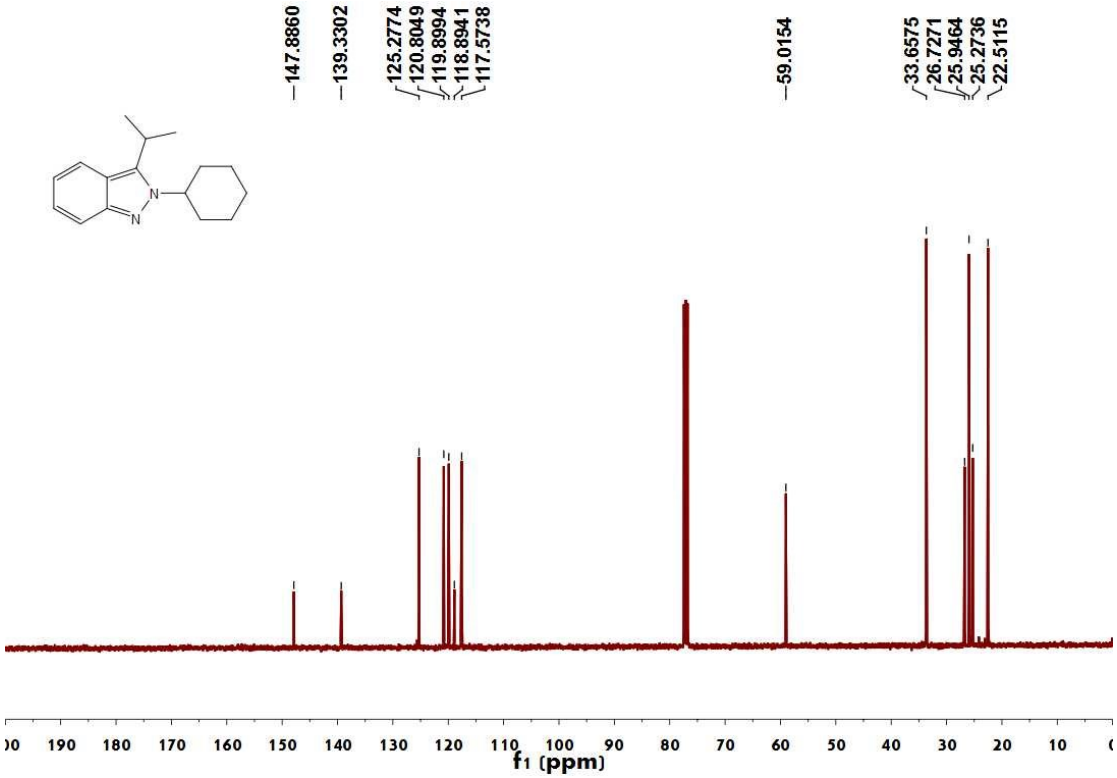
3.10
f1 (ppm)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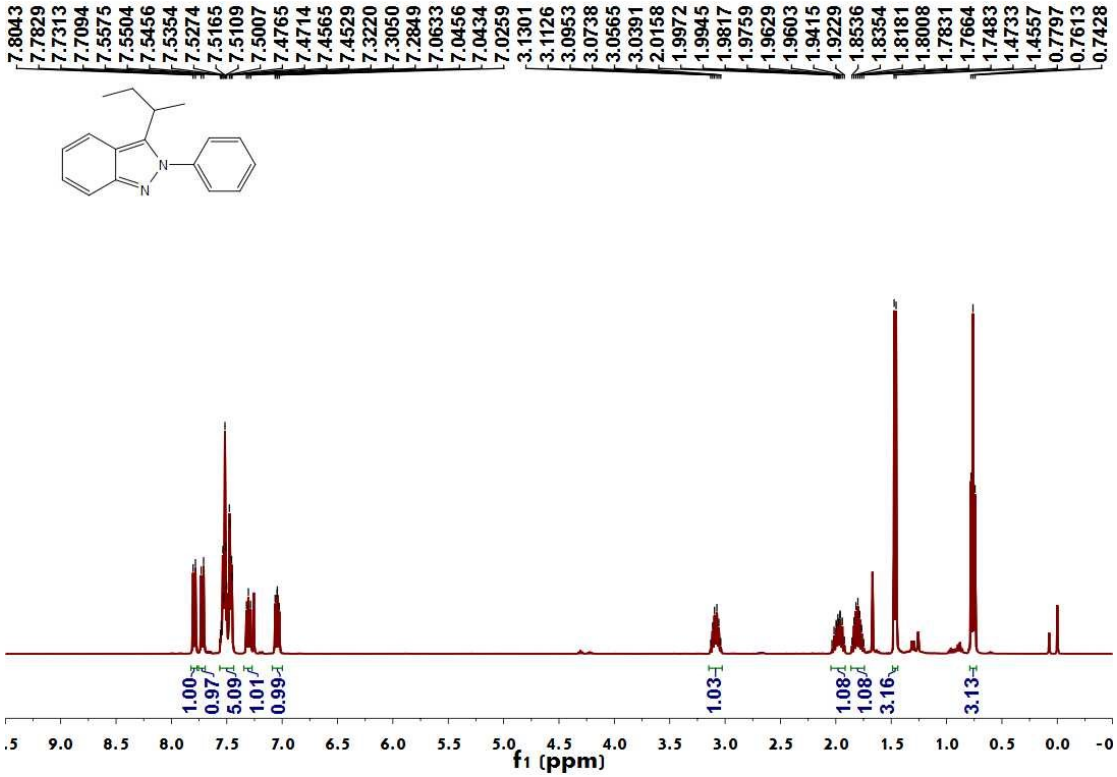
59.0154
33.6575
26.7271
25.9464
25.2736
22.5115
f1 (ppm)

3n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7.5109
7.5007
7.4765
7.4714
7.4565
7.4529
7.3220
7.3050
7.2849
7.0633
7.0456
7.0434
7.0259
3.1301
3.1126
3.0953
3.0738
3.0565
3.0391
2.0158
1.9972
1.9945
1.9817
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1.9415
1.9229
1.8536
1.8354
1.8181
1.8008
1.7831
1.7664
1.7483
1.4733
1.4557
0.7797
0.7613
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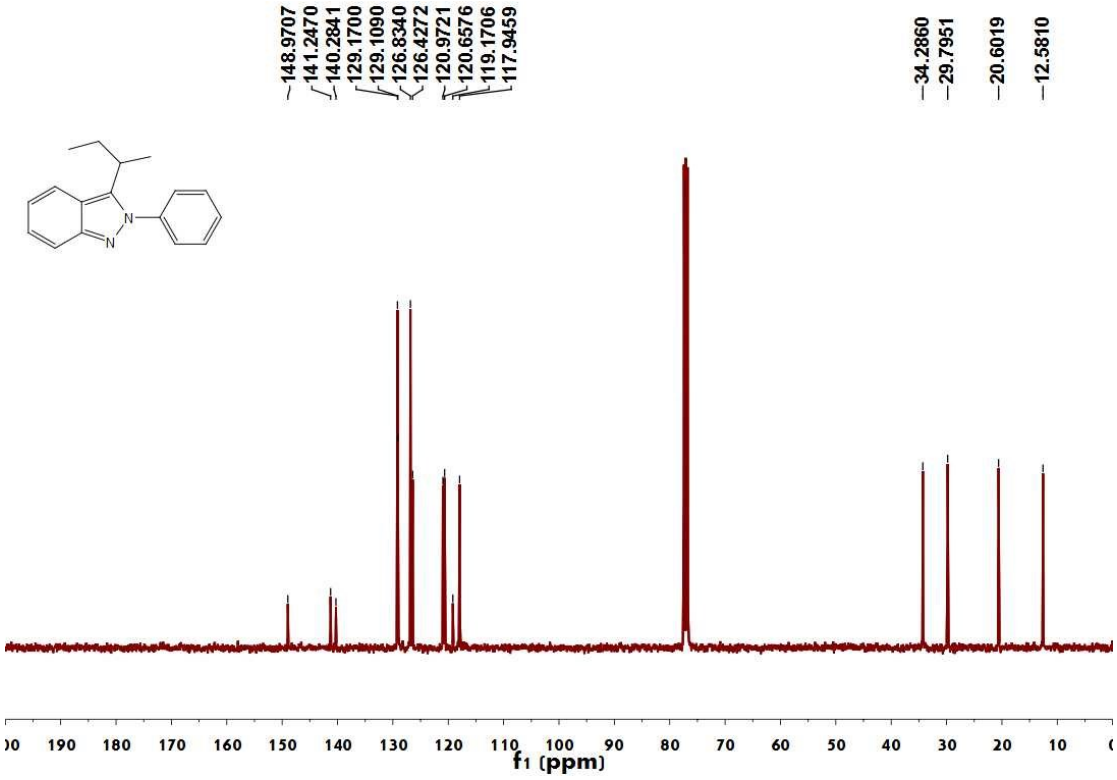
0.97
5.09
1.01
0.99
1.03
1.08
1.08
3.16
3.13
f1 (ppm)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140.2841
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126.4272
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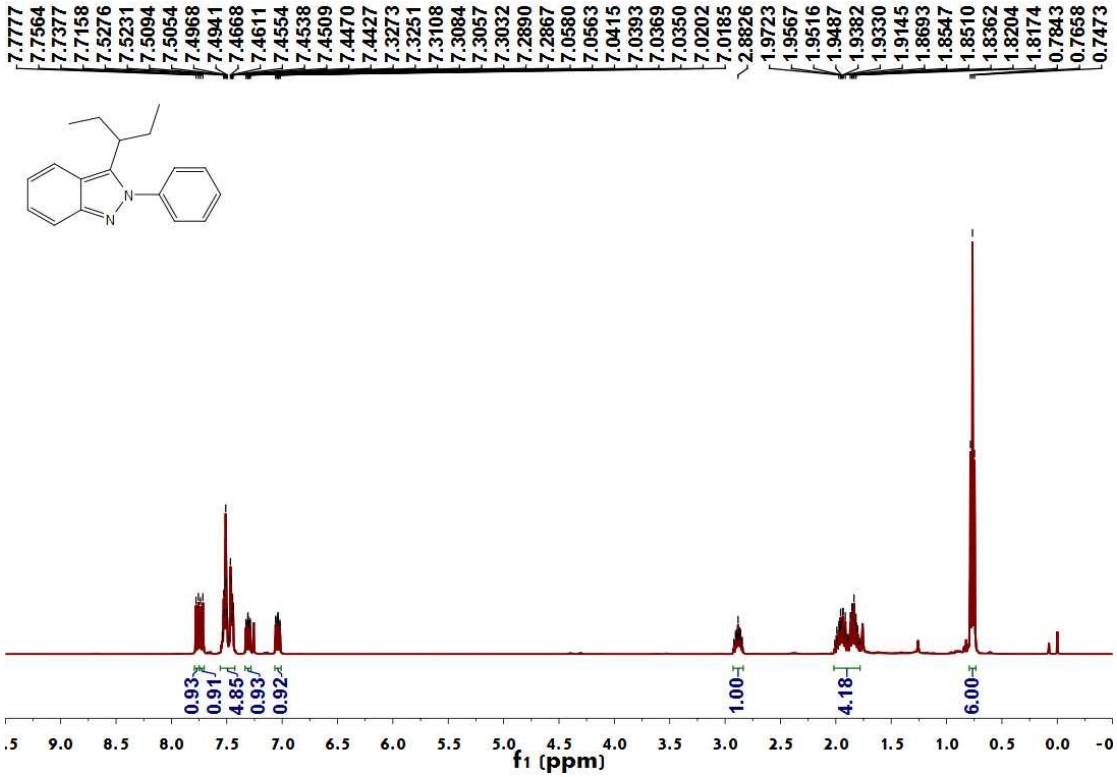
120.6576
119.1706
117.9459
34.2860
29.7951
20.6019
12.5810
f1 (ppm)

3o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7.5094
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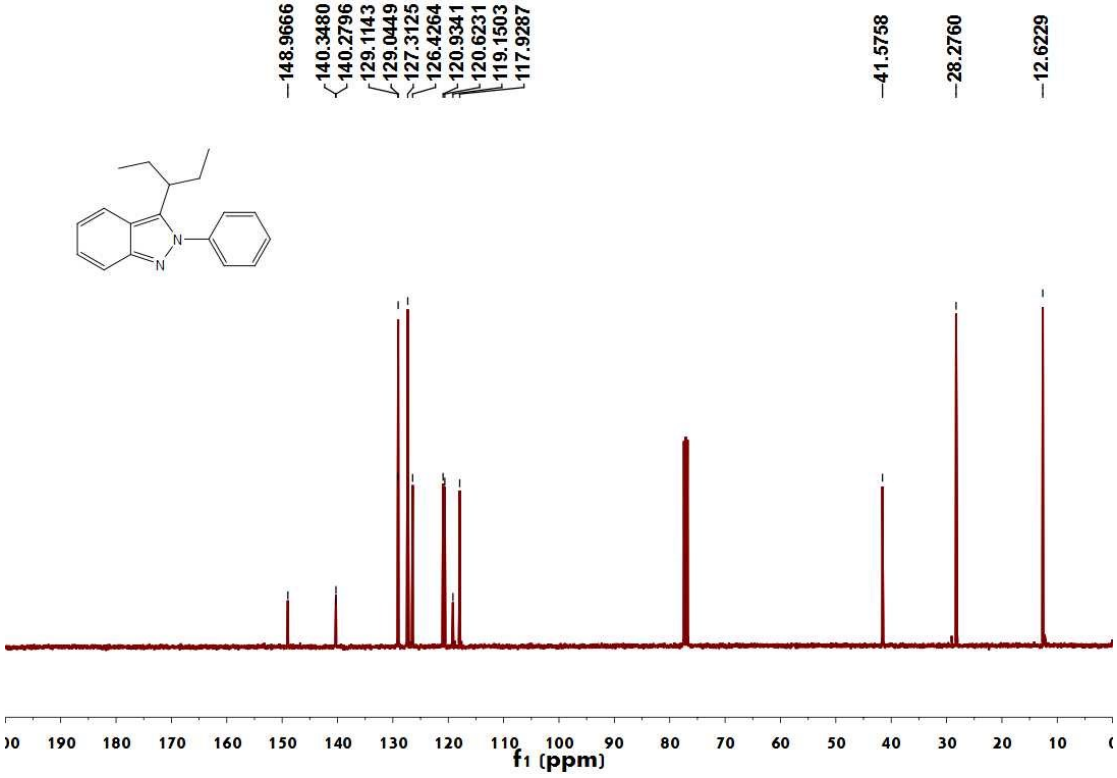
7.4968
7.4941
7.4668
7.4611
7.4554
7.4538
7.4509
7.4470
7.4427
7.3273
7.3251
7.3108
7.3084
7.3057
7.3032
7.2890
7.2867
7.0580
7.0563
7.0415
7.0393
7.0369
7.0350
7.0202
7.0185
2.8826
1.9723
1.9567
1.9516
1.9487
1.9382
1.9330
1.9145
1.8693
1.8547
1.8510
1.8362
1.8204
1.8174
0.7843
0.7658
0.7473
0.93
0.91
4.85
0.93
0.92
1.00
4.18
6.00
f1 (ppm)


148.9666
140.3480
140.2796
129.1143
129.0449
127.3125
126.4264
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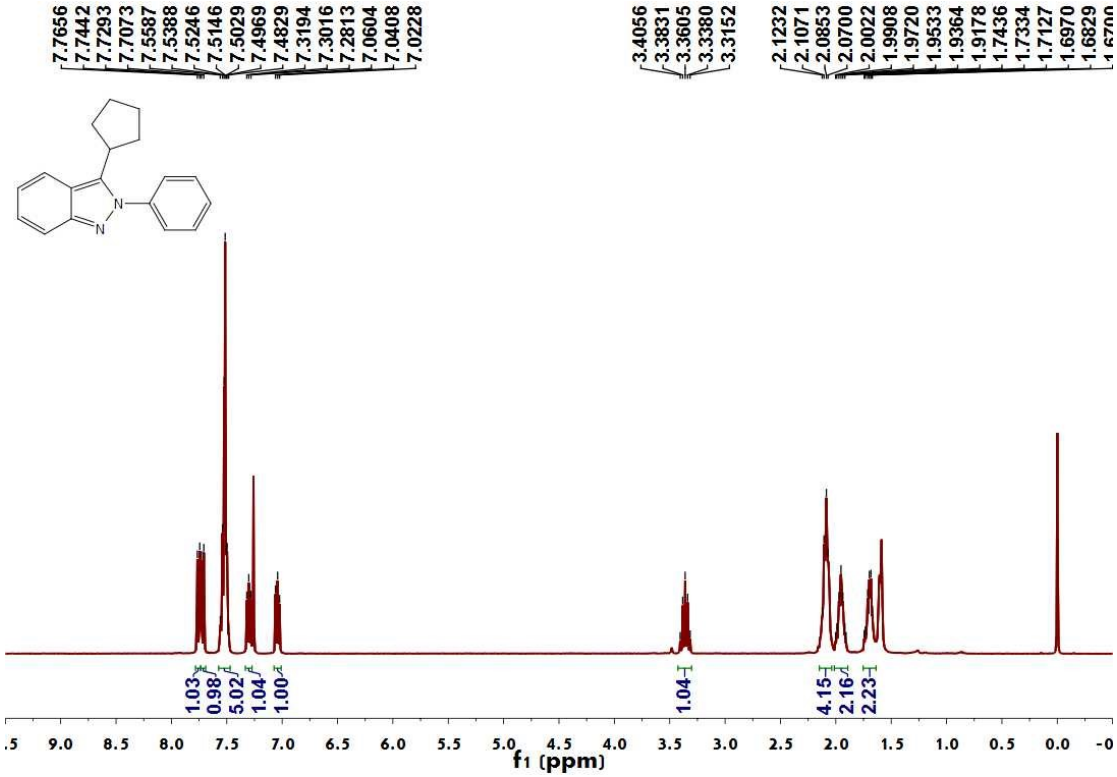
120.6231
119.1503
117.9287
41.5758
28.2760
12.6229
f1 (ppm)

3p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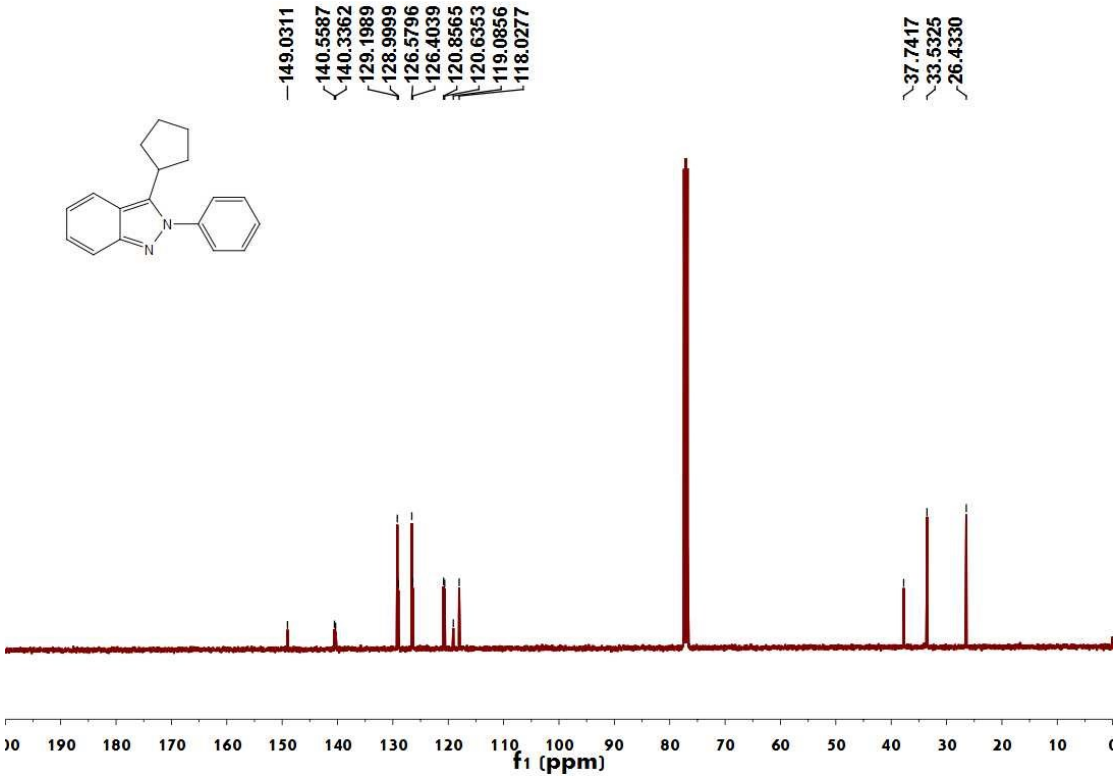
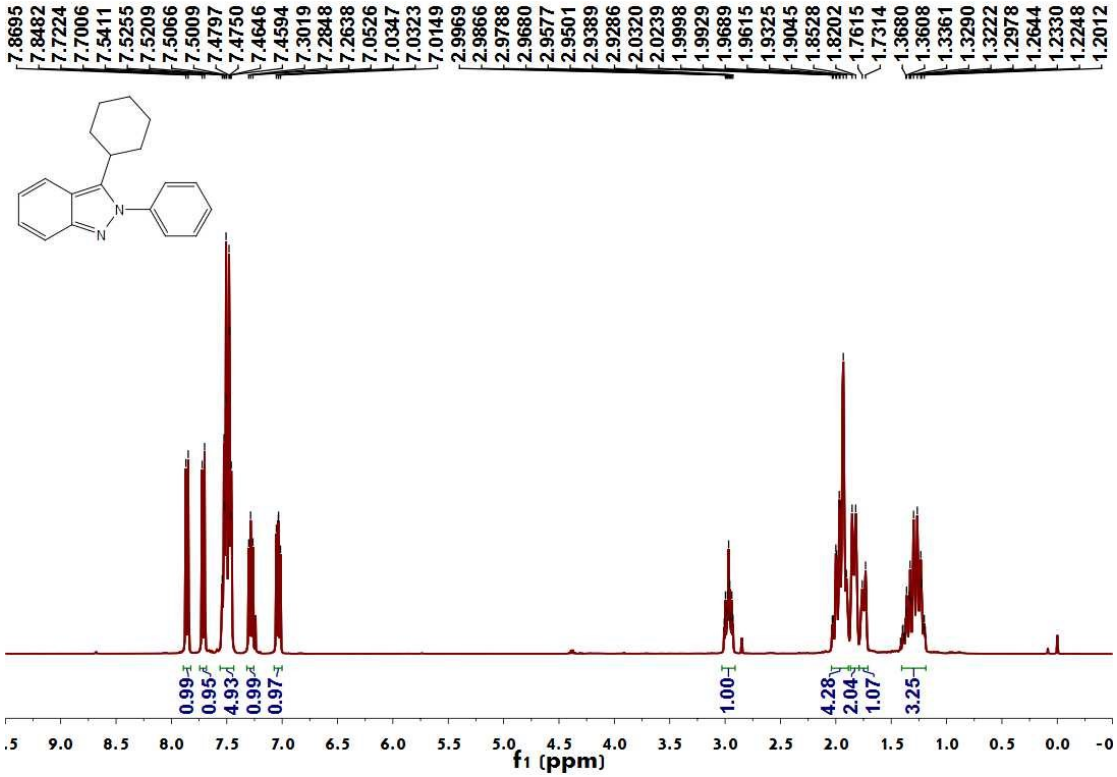
7.7293
7.7073
7.5587
7.5388
7.5246
7.5146
7.5029
7.4969
7.4829
7.3194
7.3016
7.2813
7.0604
7.0408
7.0228
3.4056
3.3831
3.3605
3.3380
3.3152
2.1232
2.1071
2.0853
2.0700
2.0022
1.9908
1.9720
1.9533
1.9364
1.9178
1.7436
1.7334
1.7127
1.6970
1.6829
1.03
0.98
5.02
1.04
1.00
1.04
4.15
2.16
2.23
f1 (ppm)


149.0311
140.5587
140.3362
129.1989
128.9999
126.5796
126.4039
120.8565
120.6353
119.0856
118.0277
37.7417
33.5325
26.4330
f1 (ppm)

3q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7.8482
7.7224
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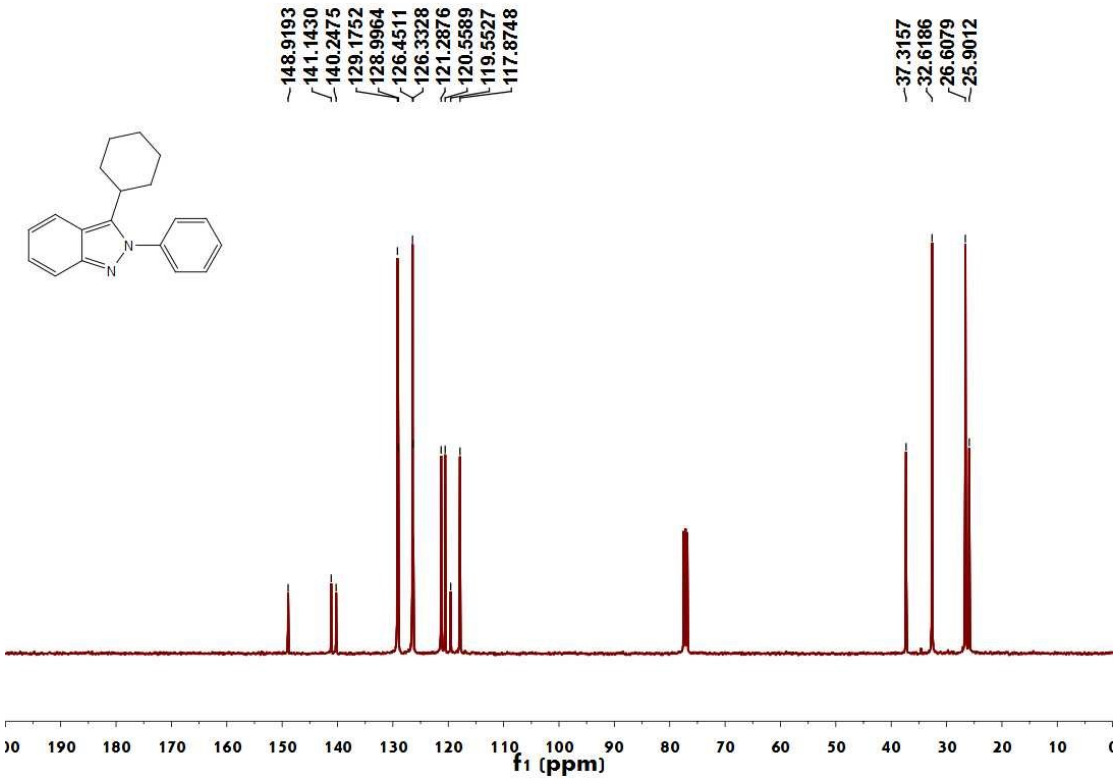
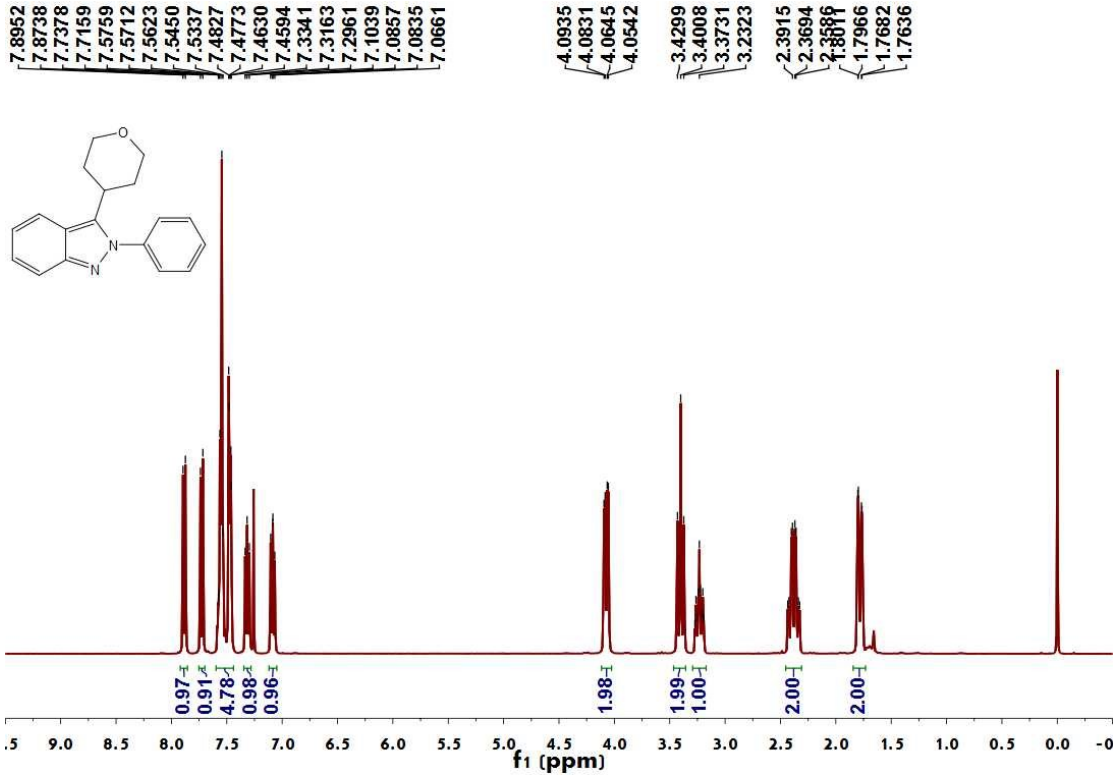
7.5411
7.5255
7.5209
7.5066
7.5009
7.4797
7.4750
7.4646
7.4594
7.3019
7.2848
7.2638
7.0526
7.0347
7.0323
7.0149
2.9969
2.9866
2.9788
2.9680
2.9577
2.9501
2.9389
2.9286
2.0320
2.0239
1.9998
1.9929
1.9689
1.9615
1.9325
1.9045
1.8528
1.8202
1.7615
1.7314
1.3680
1.3608
1.3361
1.3290
1.3222
1.2978
1.2644
1.2330
1.2248
1.2012
0.99
0.95
4.93
0.99
0.97
1.00
4.28
2.04
1.07
3.25
f1 (ppm)


148.9193
141.1430
140.2475
129.1752
128.9964
126.4511
126.3328
121.2876
120.5589
119.5527
117.8748
37.3157
32.6186
26.6079
25.9012
f1 (ppm)

3r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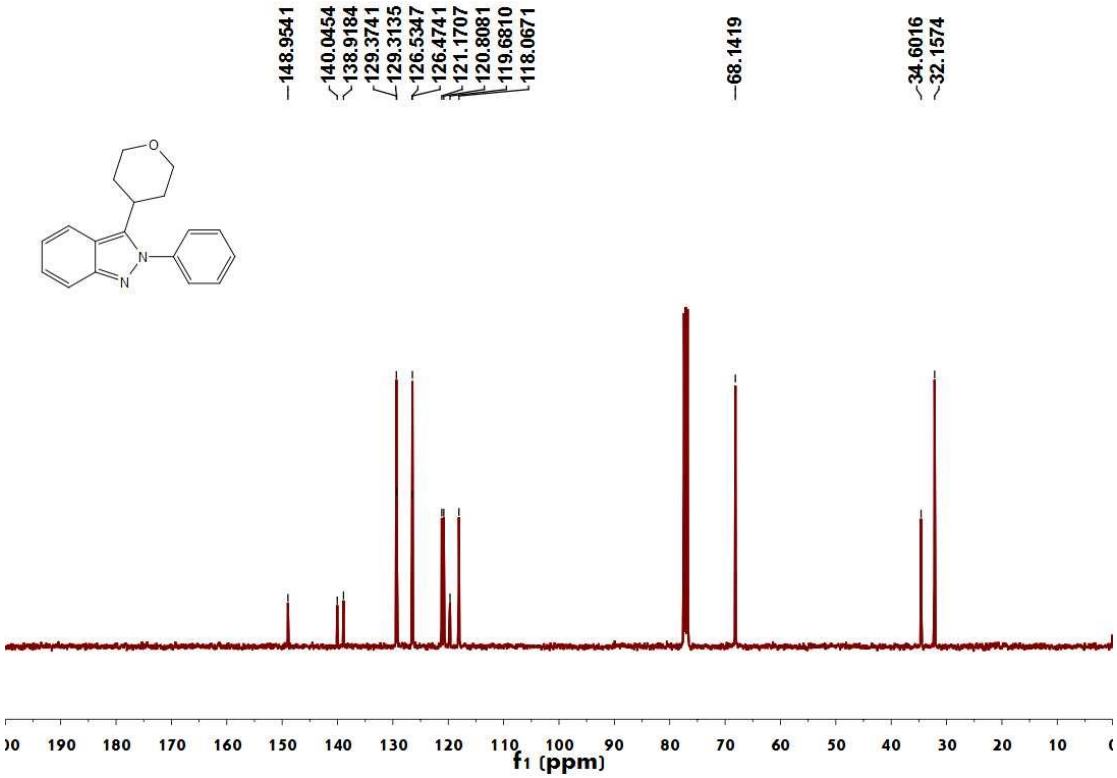
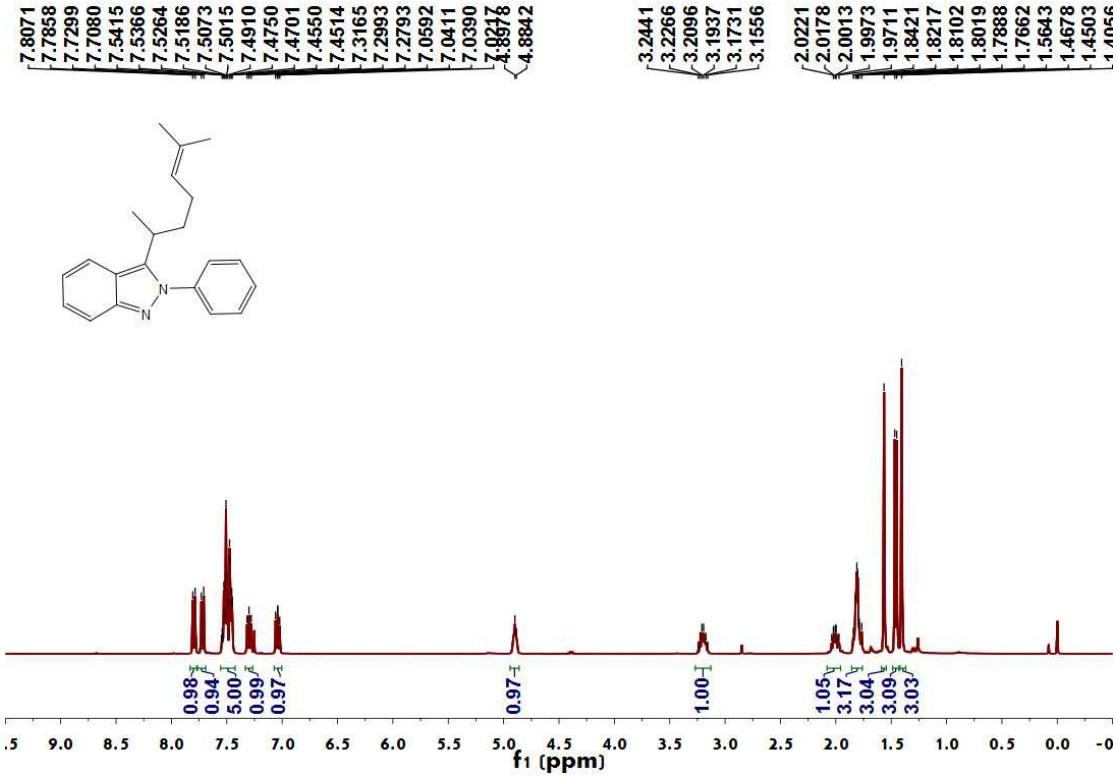
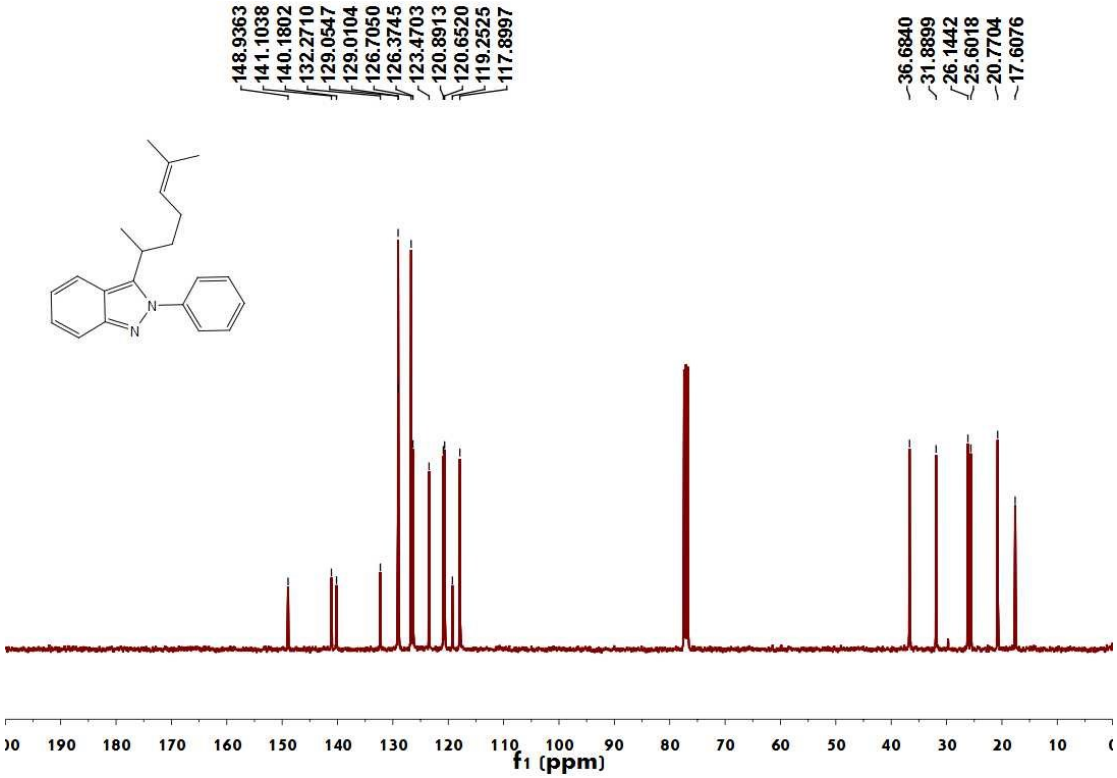
7.8738
7.7378
7.7159
7.5759
7.5712
7.5623
7.5450
7.5337
7.4827
7.4773
7.4630
7.4594
7.3341
7.3163
7.2961
7.1039
7.0857
7.0835
7.0661
4.0935
4.0831
4.0645
4.0542
3.4299
3.4008
3.3731
3.2323
2.3915
2.3694
1.7966
1.7682
1.7636
0.97
0.91
4.78
0.98
0.96
1.98
1.99
1.00
2.00
2.00
f1 (ppm)


148.9541
140.0454
138.9184
129.3741
129.3135
126.5347
126.4741
121.1707
120.8081
119.6810
118.0671
68.1419
34.6016
32.1574
f1 (ppm)

3s


7.8071
7.7858
7.7299
7.7080
7.5415
7.5366
7.5264
7.5186
7.5073
7.5015
7.4910
7.4750
7.4701
7.4550
7.4514
7.3165
7.2993
7.2793
7.0592
7.0411
7.0390
4.8978
4.8842
3.2441
3.2266
3.2096
3.1937
3.1731
3.1556
2.0221
2.0178
2.0013
1.9973
1.9711
1.8421
1.8217
1.8102
1.8019
1.7888
1.7662
1.5643
1.4678
1.4503
0.98
0.94
5.00
0.99
0.97
0.97
1.00
1.05
3.17
3.04
3.09
3.03
f1 (ppm)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140.1802
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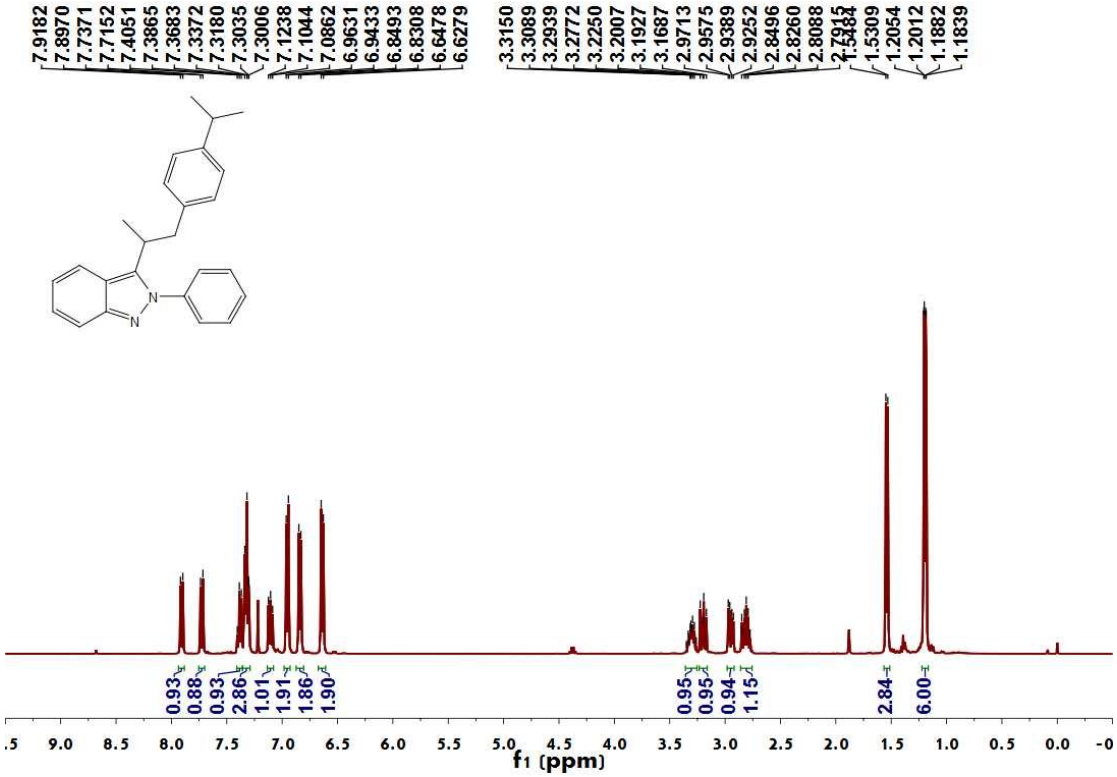
126.7050
126.3745
123.4703
120.8913
120.6520
119.2525
117.8997
36.6840
31.8899
26.1442
25.6018
20.7704
17.6076
f1 (ppm)

3t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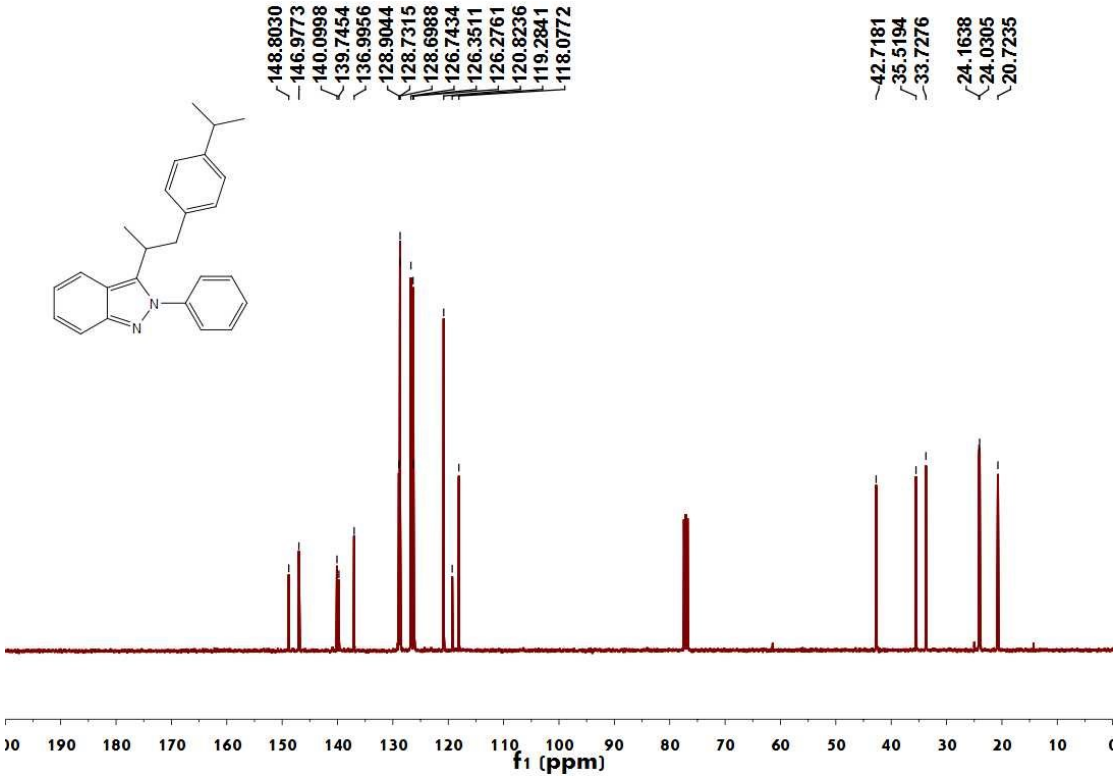
7.4051
7.3865
7.3683
7.3372
7.3180
7.3035
7.3006
7.1238
7.1044
7.0862
6.9631
6.9433
6.8493
6.8308
6.6478
6.6279
3.3150
3.3089
3.2939
3.2772
3.2250
3.2007
3.1927
3.1687
2.9713
2.9575
2.9389
2.9252
2.8496
2.8260
2.8088
1.5309
1.2054
1.2012
1.1882
1.1839
0.93
0.88
0.93
2.86
1.01
1.91
1.86
1.90
0.95
0.95
0.94
1.15
2.84
6.00
f1 (ppm)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140.0998
139.7454
136.9956
128.9044
128.7315
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126.7434
126.3511
126.2761
120.8236
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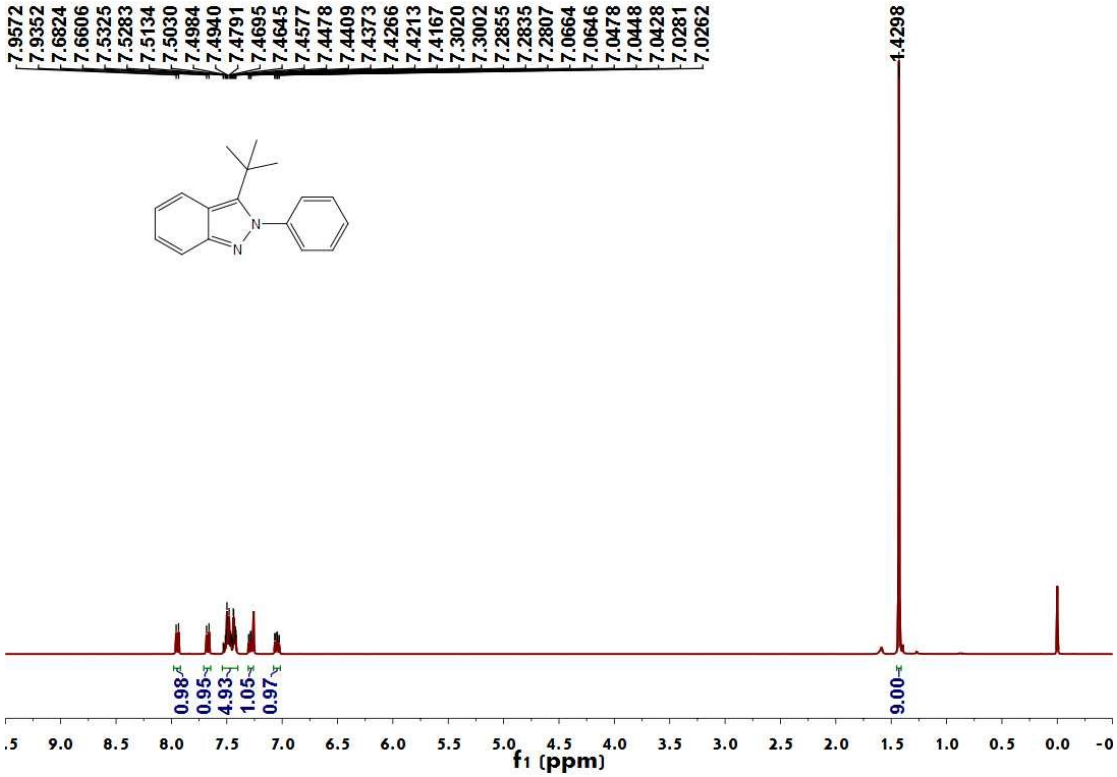
42.7181
35.5194
33.7276
24.1638
24.0305
20.7235
f1 (ppm)

3u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7.9352
7.6824
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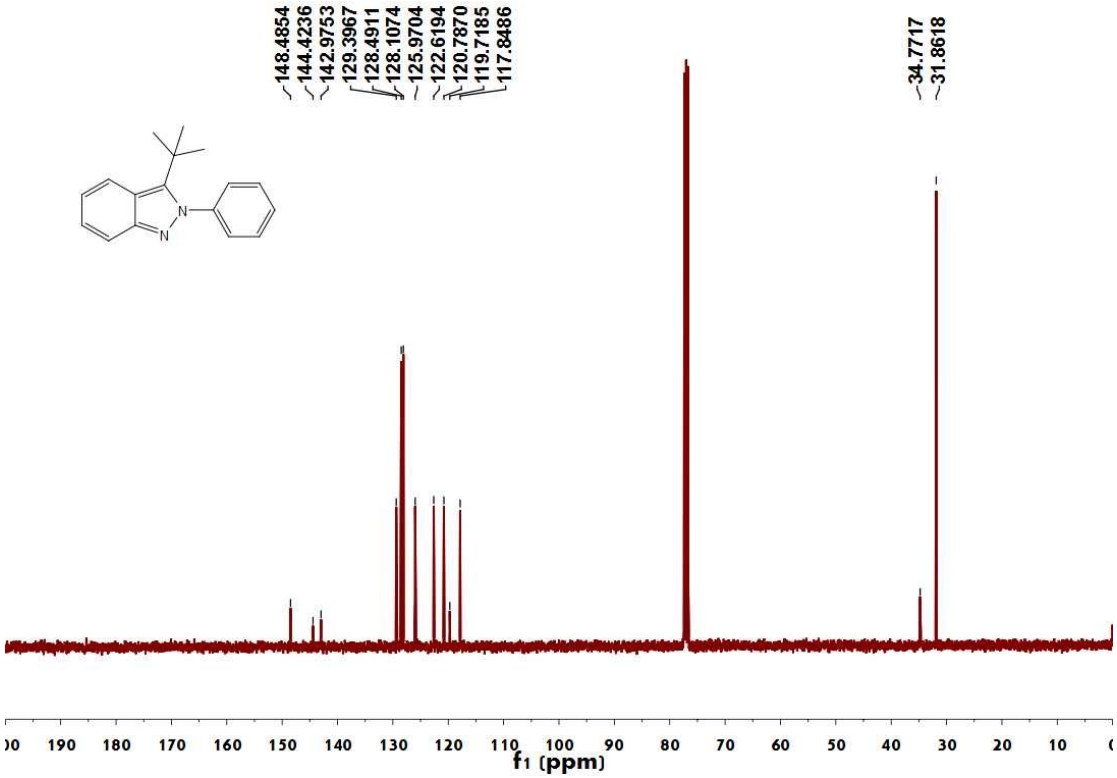
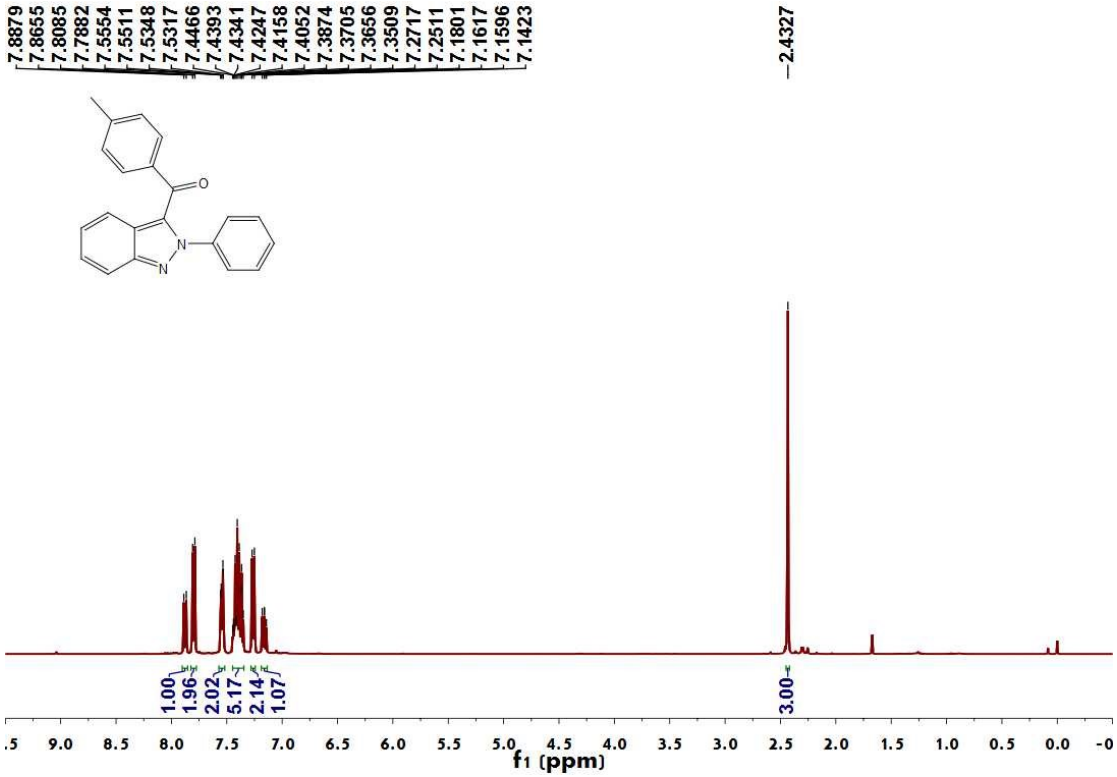
7.5325
7.5283
7.5134
7.5030
7.4984
7.4940
7.4791
7.4695
7.4645
7.4577
7.4478
7.4409
7.4373
7.4266
7.4213
7.4167
7.3020
7.3002
7.2855
7.2835
7.2807
7.0664
7.0646
7.0478
7.0448
7.0428
7.0281
7.0262
1.4298
0.98
0.95
4.93
1.05
0.97
9.00
f1 (ppm)


148.4854
144.4236
142.9753
129.3967
128.4911
128.1074
125.9704
122.6194
120.7870
119.7185
117.8486
34.7717
31.8618
f1 (ppm)

5a


7.8879
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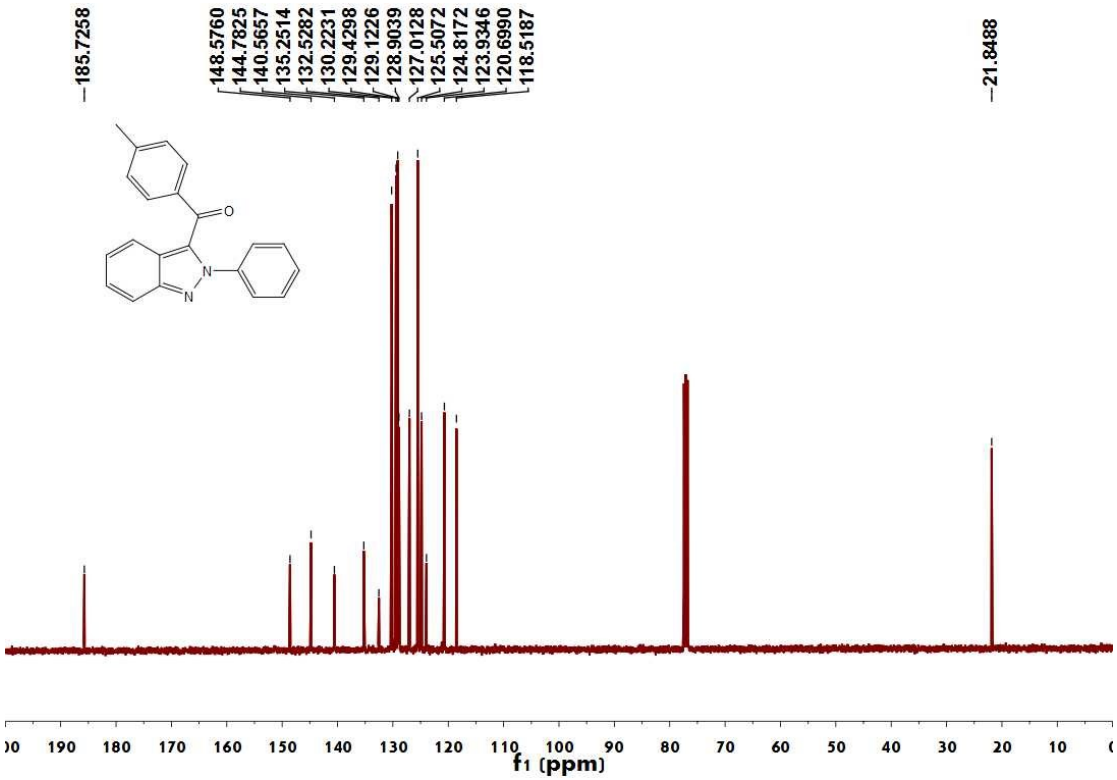
7.7882
7.5554
7.5511
7.5348
7.5317
7.4466
7.4393
7.4341
7.4247
7.4158
7.4052
7.3874
7.3705
7.3656
7.3509
7.2717
7.2511
7.1801
7.1617
7.1596
7.1423
2.4327
1.00
1.96
2.02
5.17
2.14
1.07
3.00
f1 (ppm)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135.2514
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130.2231
129.4298
129.1226
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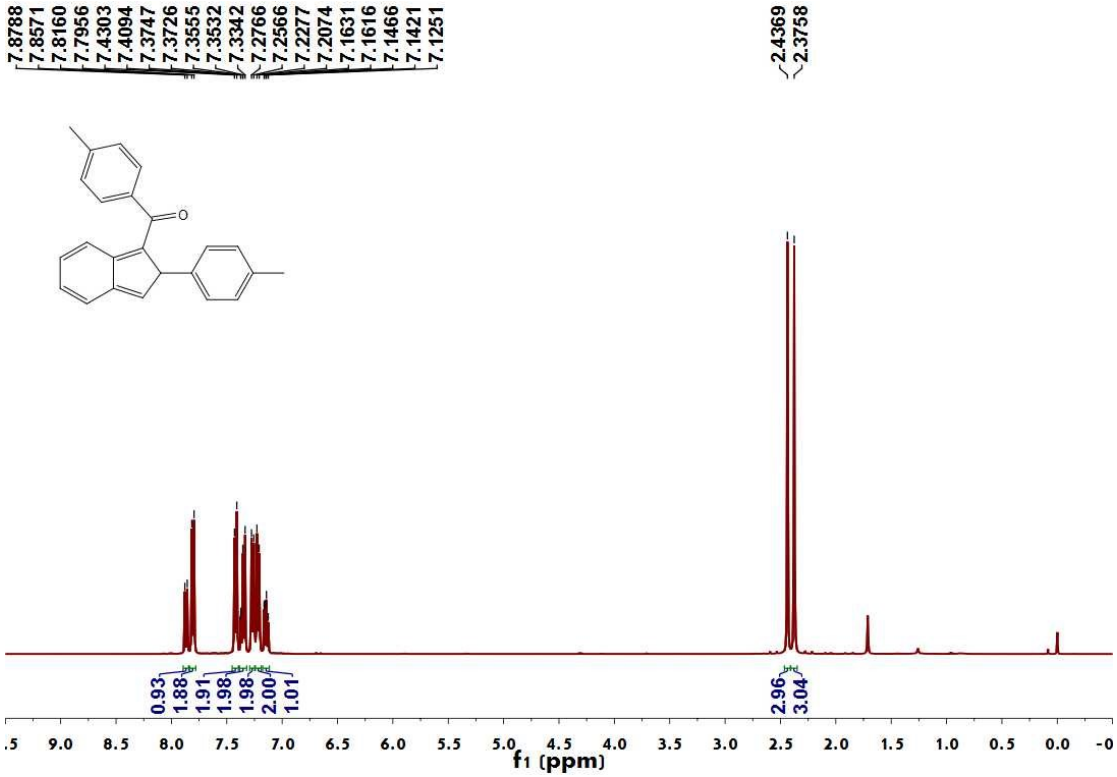
125.5072
124.8172
123.9346
120.6990
118.5187
21.8488
f1 (ppm)

5b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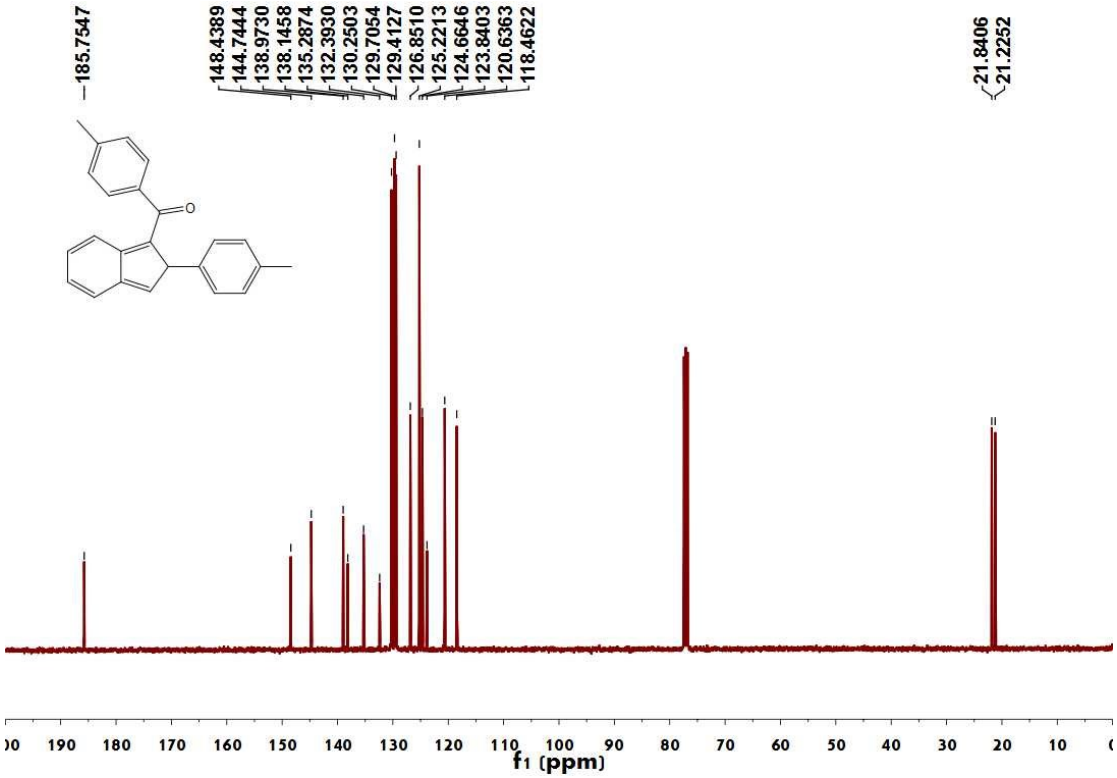
7.8160
7.7956
7.4303
7.4094
7.3747
7.3726
7.3555
7.3532
7.3342
7.2766
7.2566
7.2277
7.2074
7.1631
7.1616
7.1466
7.1421
7.1251
2.4369
2.3758
O
0.93
1.88
1.91
1.98
1.98
2.00
1.01
2.96
3.04
f1 (ppm)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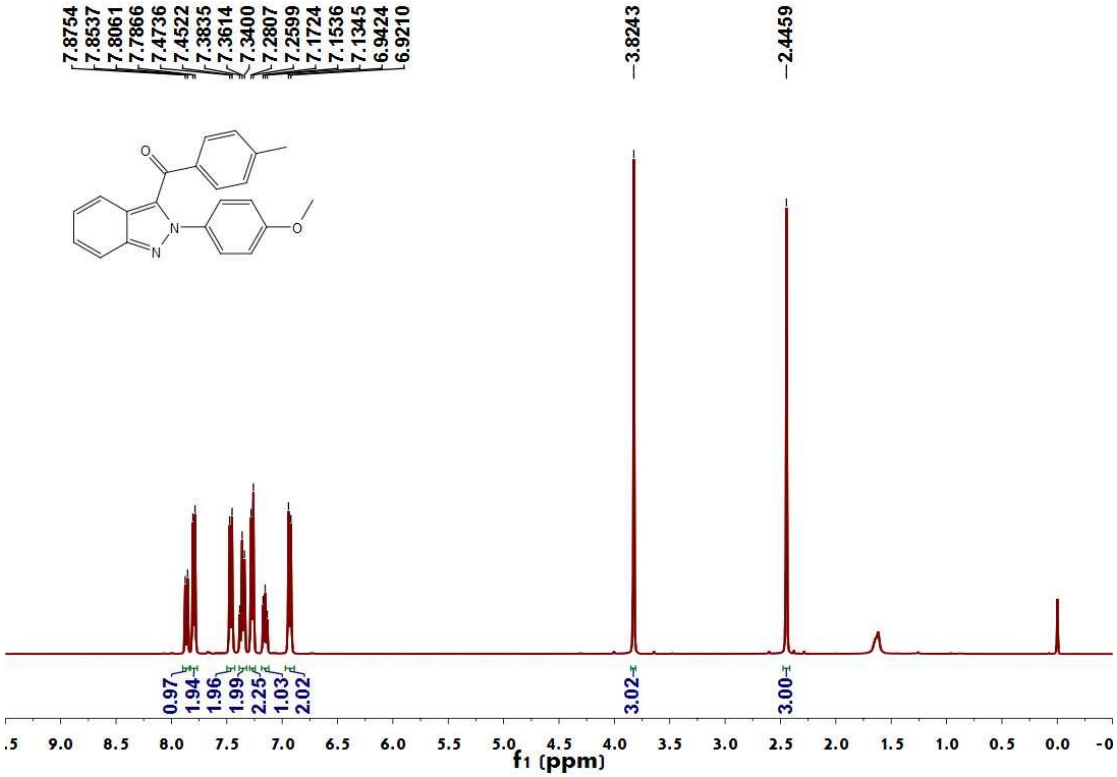
138.9730
138.1458
135.2874
132.3930
130.2503
129.7054
129.4127
126.8510
125.2213
124.6646
123.8403
120.6363
118.4622
21.8406
21.2252
O
f1 (ppm)

5c


7.8754
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7.8061
7.7866
7.4736
7.4522
7.3835
7.3614
7.3400
7.2807
7.2599
7.1724
7.1536
7.1345
6.9424
6.9210
3.8243
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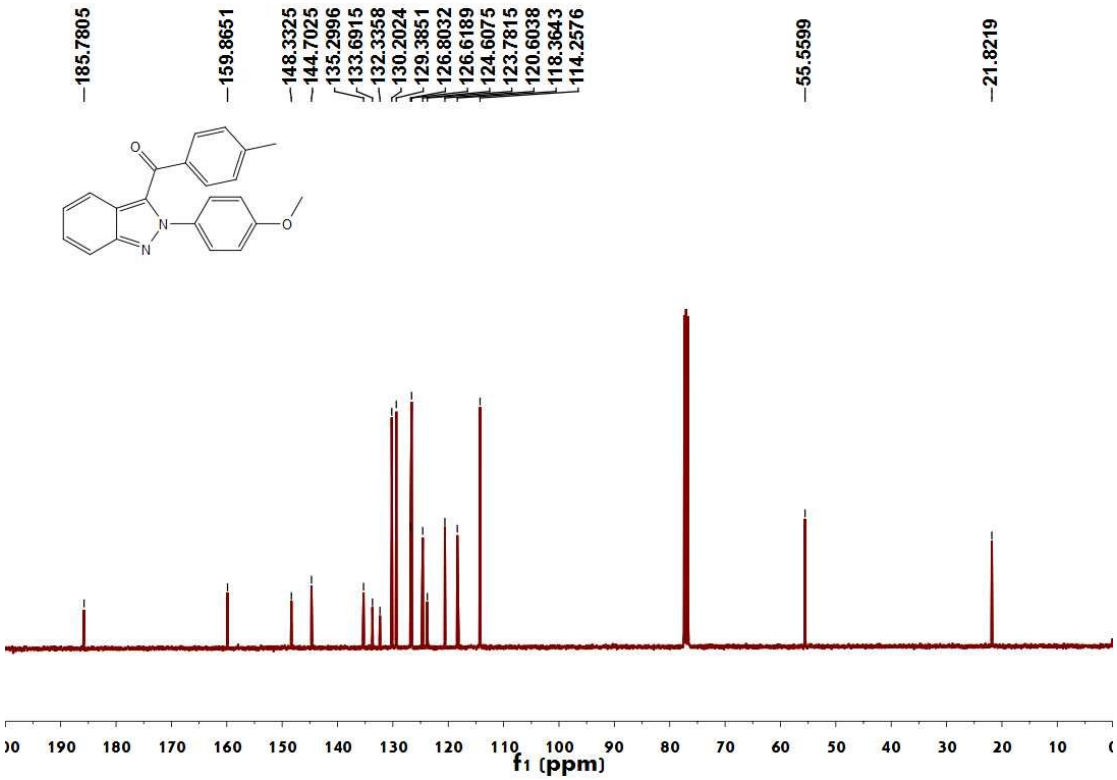
1.94
1.96
1.99
2.25
1.03
2.02
3.02
3.00
f1 (ppm)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132.3358
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126.8032
126.6189
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123.7815
120.6038
118.3643
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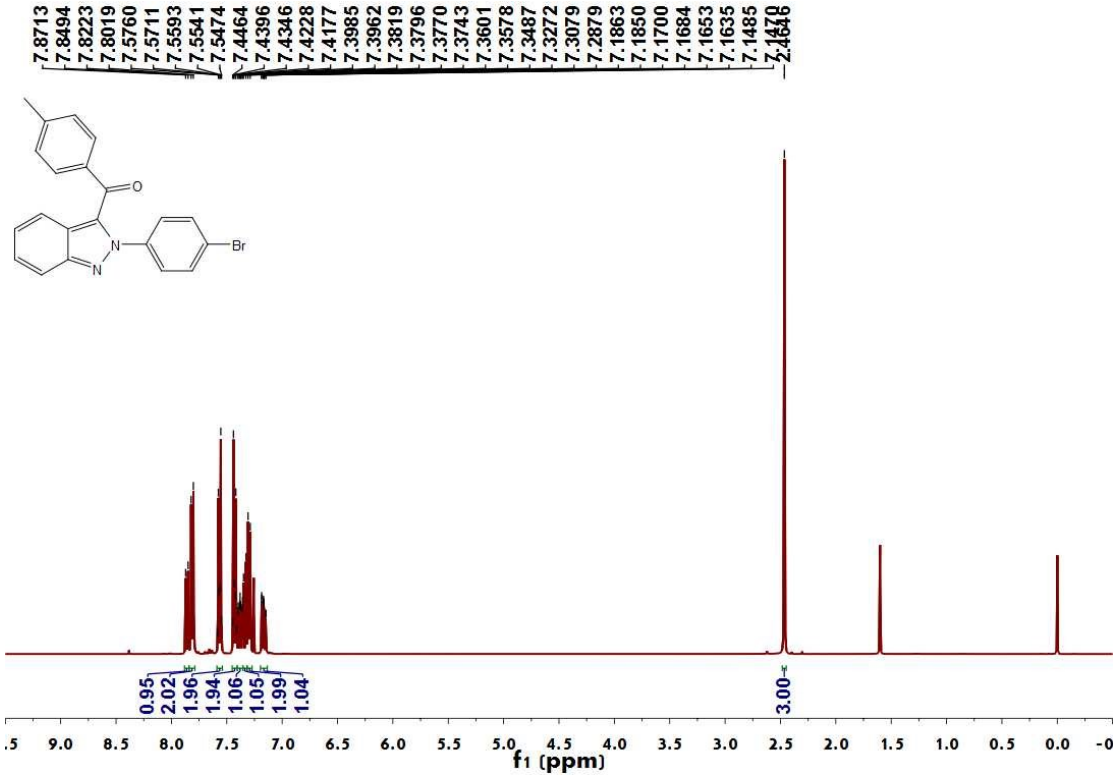
55.5599
21.8219
f1 (ppm)

5d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7.5593
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7.4396
7.4346
7.4228
7.4177
7.3985
7.3962
7.3819
7.3796
7.3770
7.3743
7.3601
7.3578
7.3487
7.3272
7.3079
7.2879
7.1863
7.1850
7.1700
7.1684
7.1653
7.1635
7.1485
2.4646
O
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Br
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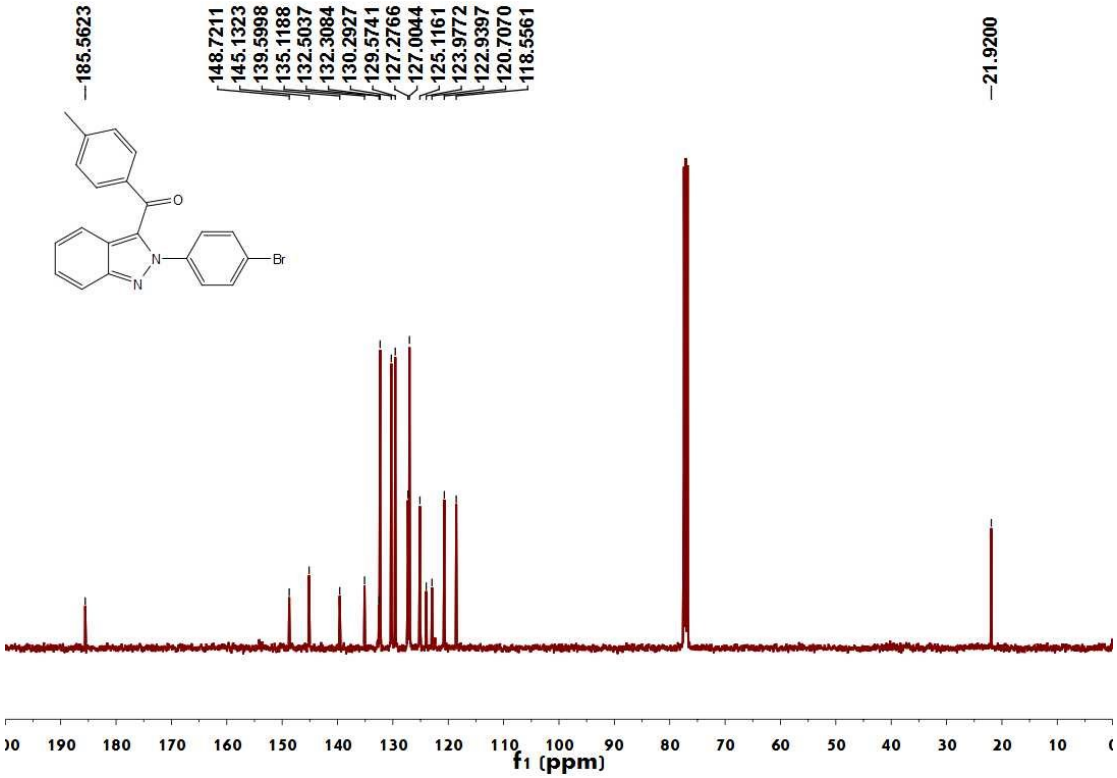
1.94
1.06
1.05
1.99
1.04
3.00
f1 (ppm)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135.1188
132.5037
132.3084
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129.5741
127.2766
127.0044
125.1161
123.9772
122.9397
120.7070
118.5561
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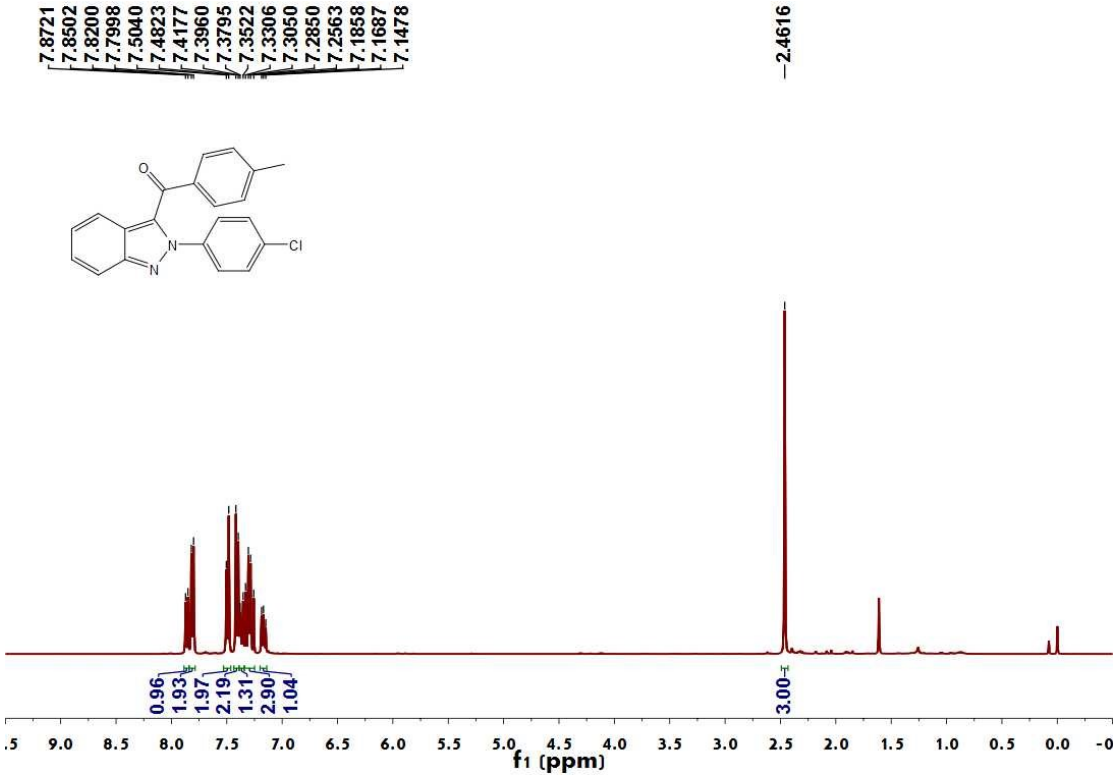
O
N
N
Br
f1 (ppm)

5e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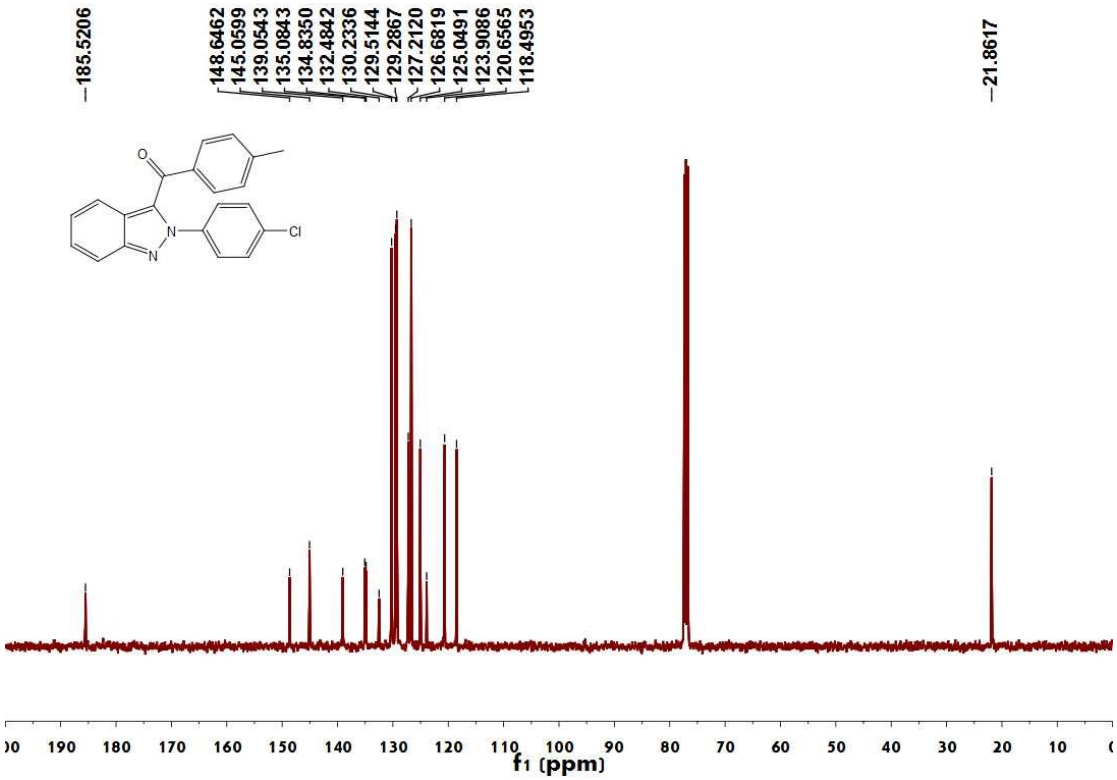
7.8200
7.7998
7.5040
7.4823
7.4177
7.3960
7.3795
7.3522
7.3306
7.3050
7.2850
7.2563
7.1858
7.1687
7.1478
2.4616
O
N
N
Cl
0.96
1.93
1.97
2.19
1.31
2.90
1.04
3.00
f1 (ppm)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127.2120
126.6819
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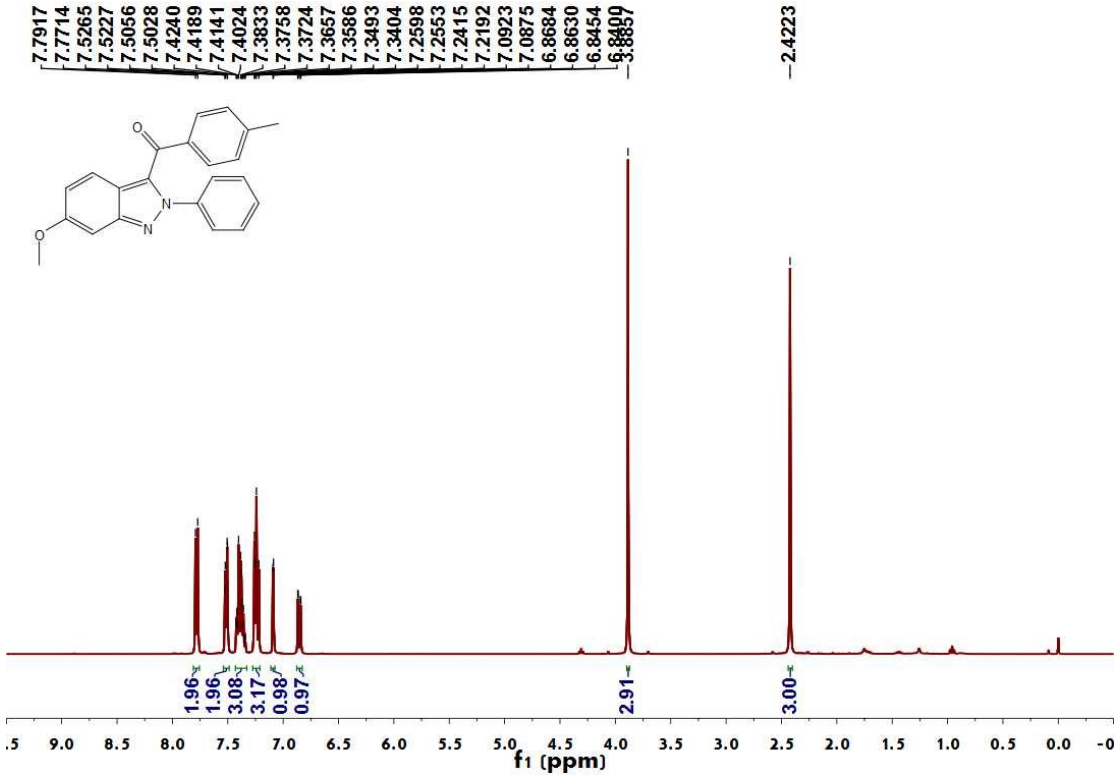
123.9086
120.6565
118.4953
21.8617
O
N
N
Cl
f1 (ppm)

5f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7.5028
7.4240
7.4189
7.4141
7.4024
7.3833
7.3758
7.3724
7.3657
7.3586
7.3493
7.3404
7.2598
7.2553
7.2415
7.2192
7.0923
7.0875
6.8684
6.8630
6.8454
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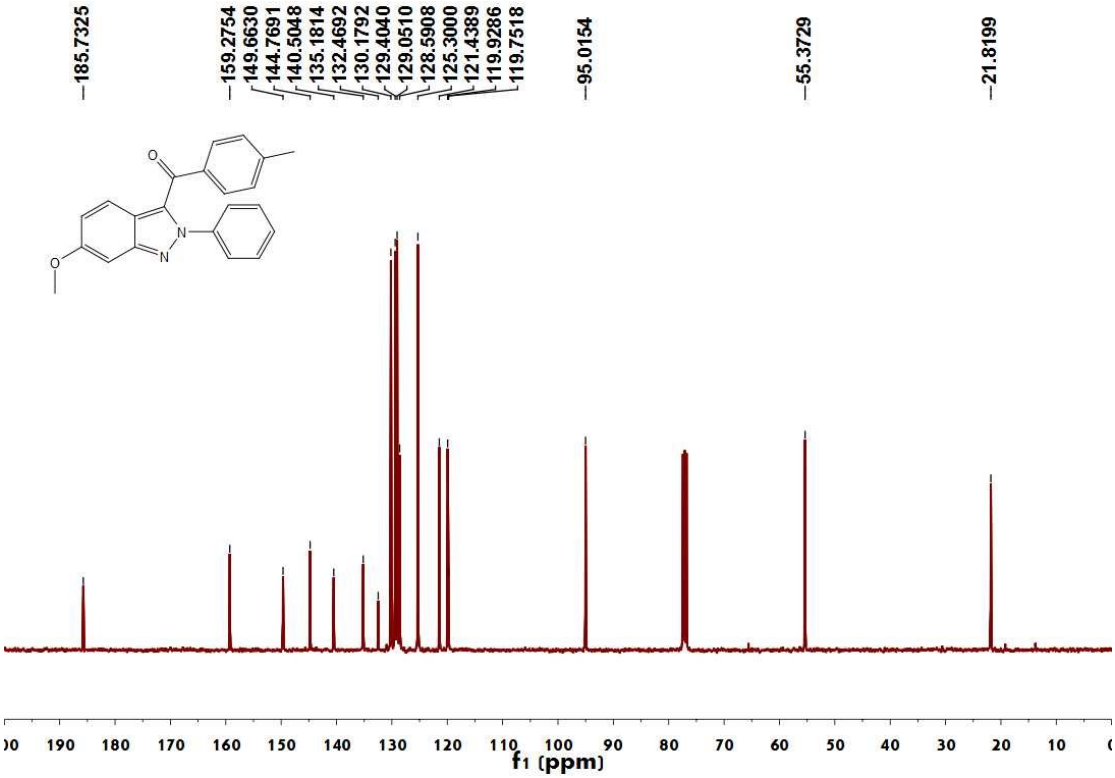
1.96
1.96
3.08
3.17
0.98
0.97
2.91
3.00
f1 (ppm)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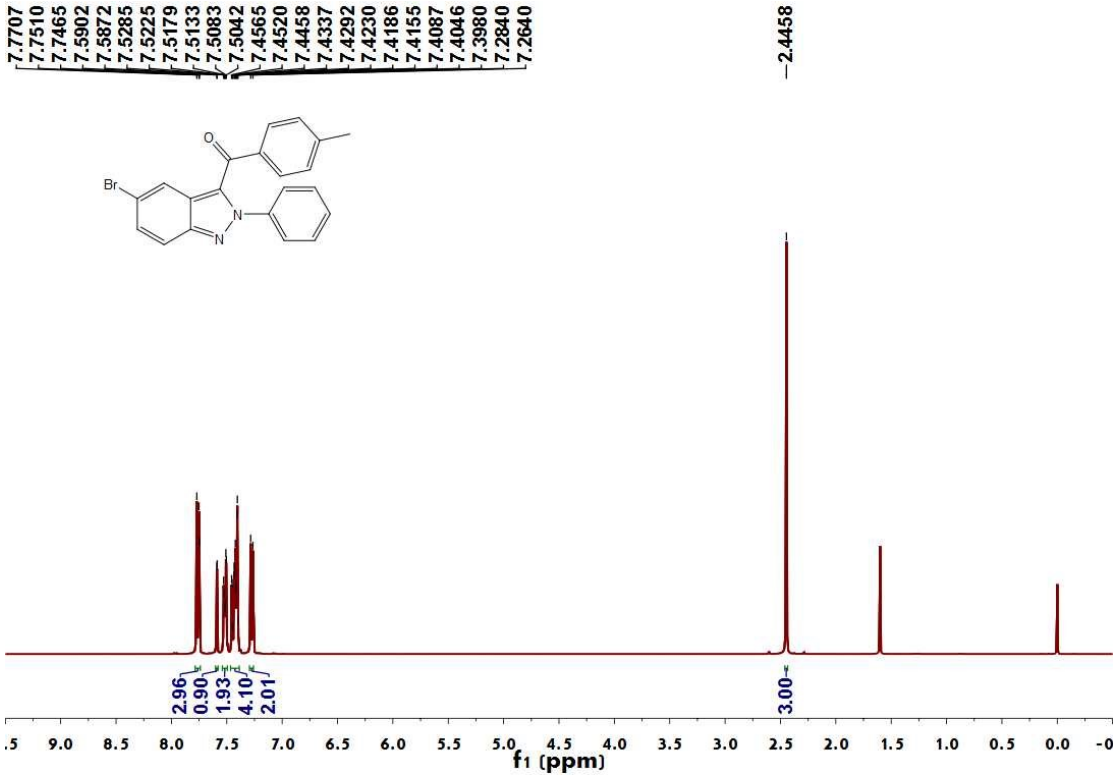
140.5048
135.1814
132.4692
130.1792
129.4040
129.0510
128.5908
125.3000
121.4389
119.9286
119.7518
95.0154
55.3729
21.8199
f1 (ppm)

5g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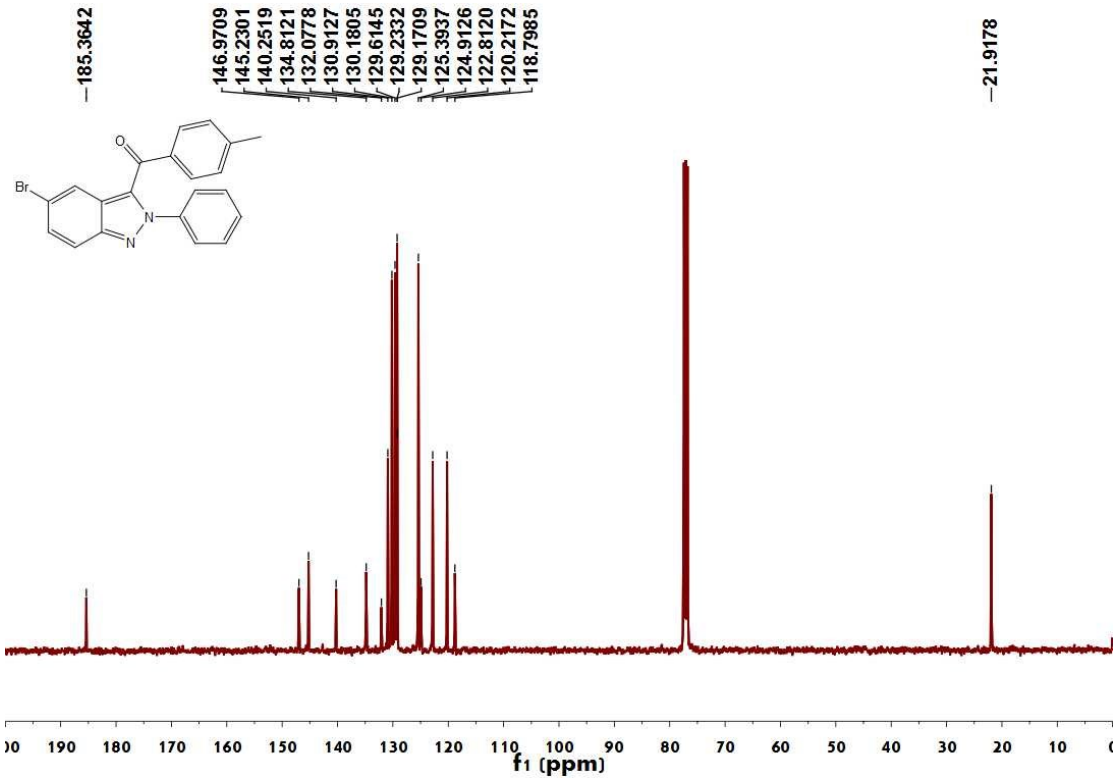
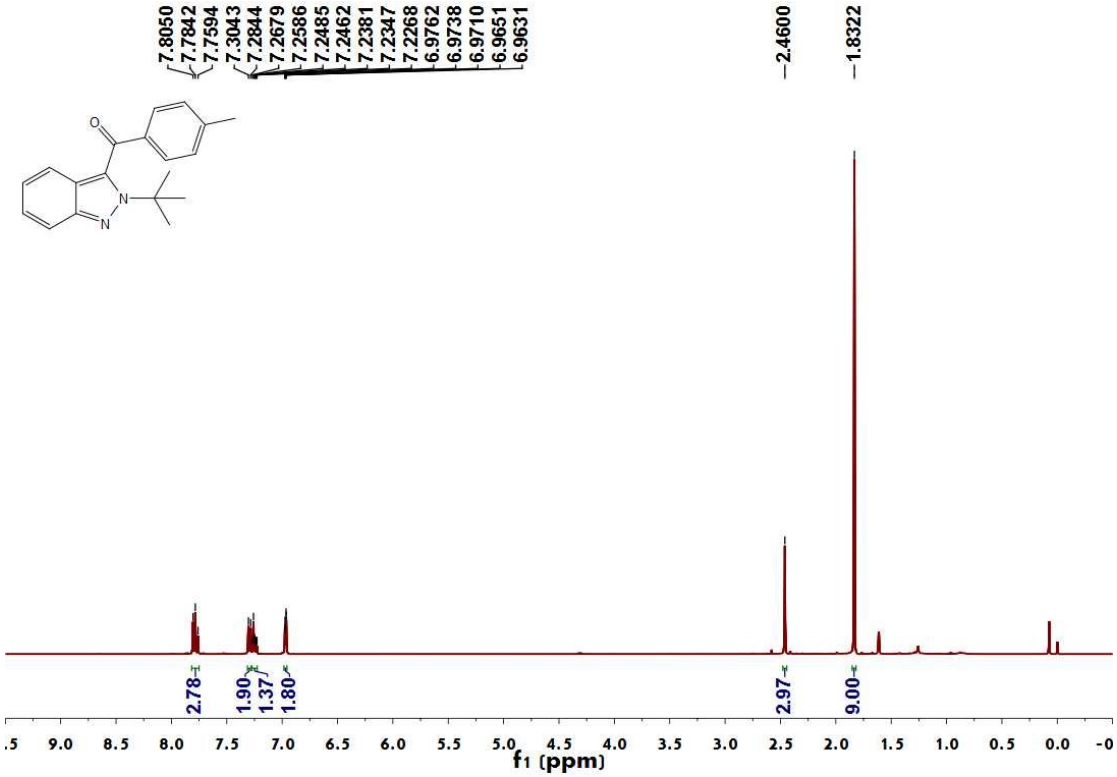
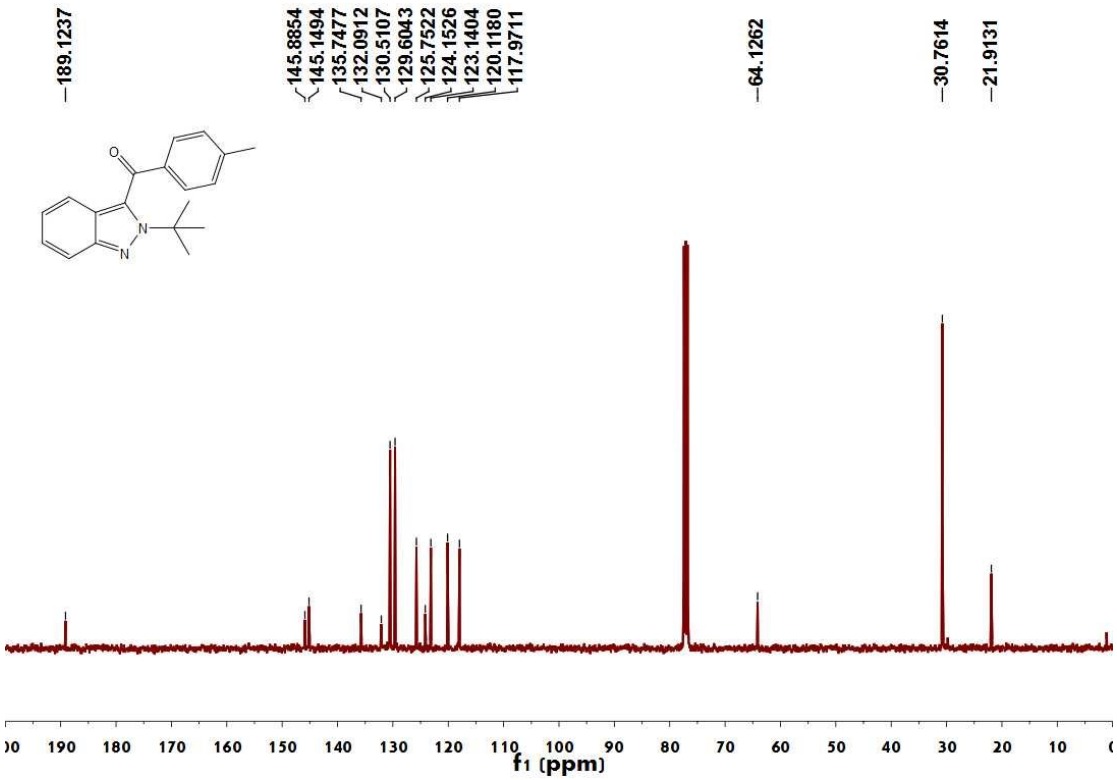
7.7510
7.7465
7.5902
7.5872
7.5285
7.5225
7.5179
7.5133
7.5083
7.5042
7.4565
7.4520
7.4458
7.4337
7.4292
7.4230
7.4186
7.4155
7.4087
7.4046
7.3980
7.2840
7.2640
2.4458
O
Br
N
N
2.96
0.90
1.93
4.10
2.01
3.00
f1 (ppm)

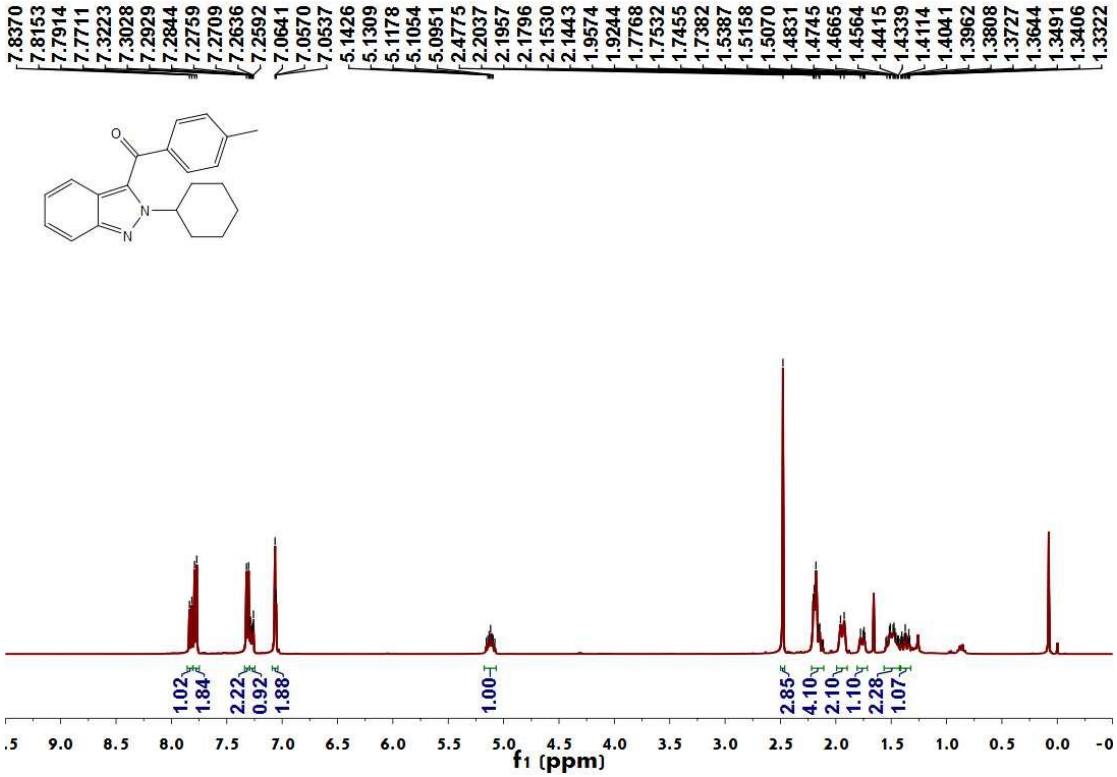

185.3642
146.9709
145.2301
140.2519
134.8121
132.0778
130.9127
130.1805
129.6145
129.2332
129.1709
125.3937
124.9126
122.8120
120.2172
118.7985
21.9178
O
Br
N
N
f1 (ppm)

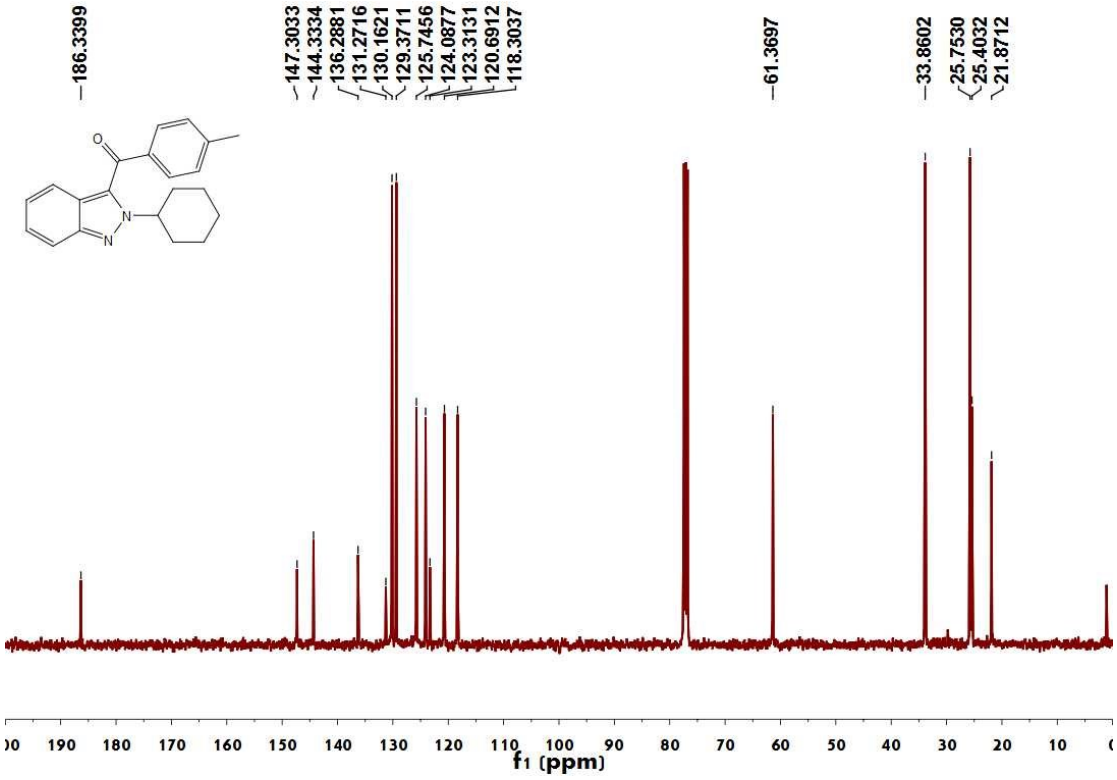
5h


7.8050
7.7842
7.7594
7.3043
7.2844
7.2679
7.2586
7.2485
7.2462
7.2381
7.2347
7.2268
6.9762
6.9738
6.9710
6.9651
6.9631
2.4600
1.8322
2.78
1.90
1.37
1.80
2.97
9.00
f1 (ppm)


189.1237
145.8854
145.1494
135.7477
132.0912
130.5107
129.6043
125.7522
124.1526
123.1404
120.1180
117.9711
64.1262
30.7614
21.9131
f1 (ppm)

5i


7.8370
7.8153
7.7914
7.7711
7.3223
7.3028
7.2929
7.2844
7.2759
7.2709
7.2636
7.2592
7.0641
7.0570
7.0537
5.1426
5.1309
5.1178
5.1054
5.0951
2.4775
2.2037
2.1957
2.1796
2.1530
2.1443
1.9574
1.9244
1.7768
1.7532
1.7455
1.7382
1.5387
1.5158
1.5070
1.4831
1.4745
1.4665
1.4564
1.4415
1.4339
1.4114
1.4041
1.3962
1.3808
1.3727
1.3644
1.3491
1.3406
1.3322
O
N
N
1.02
1.84
2.22
0.92
1.88
1.00
2.85
4.10
2.10
1.10
2.28
1.07
f1 (ppm)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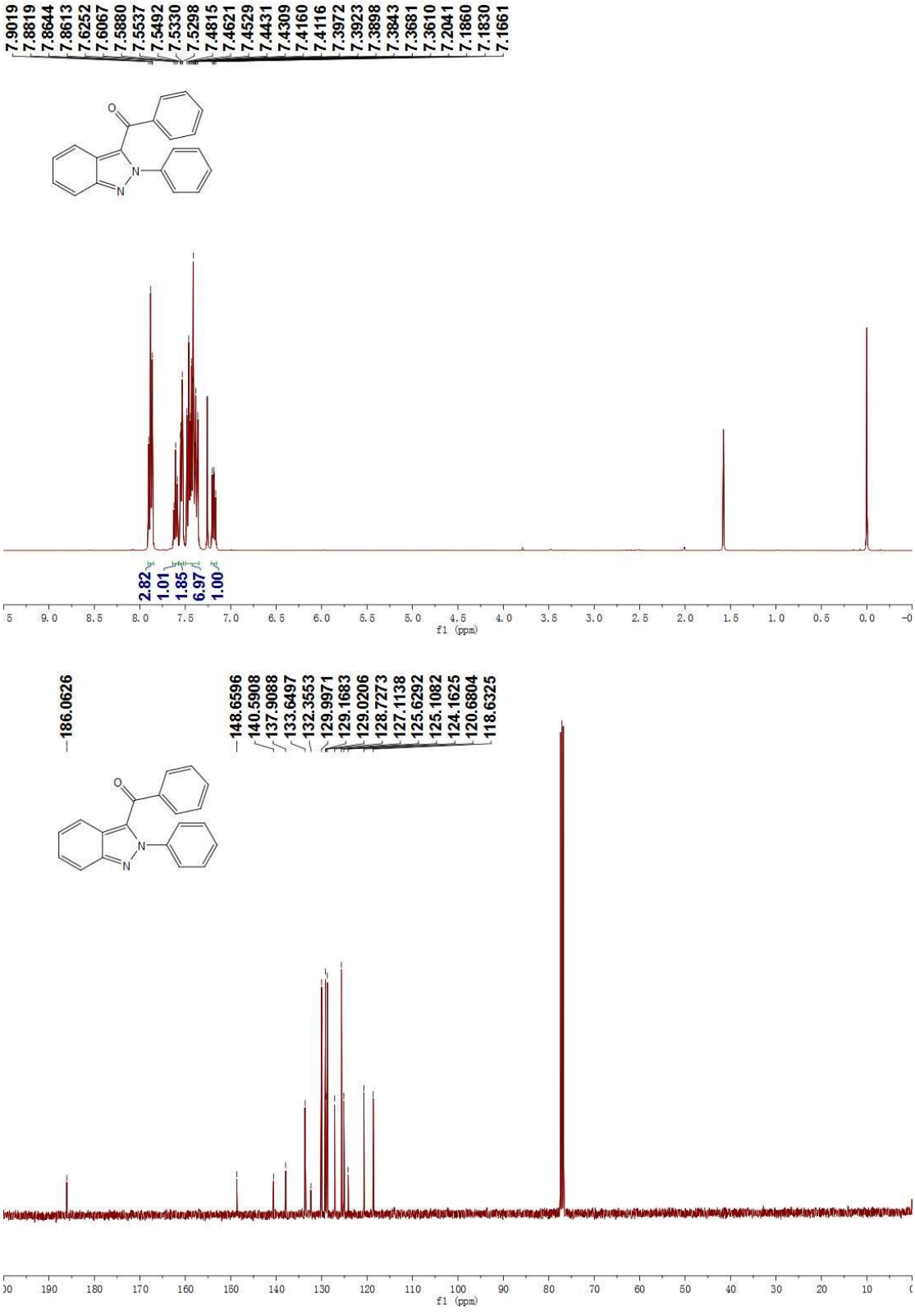
144.3334
136.2881
131.2716
130.1621
129.3711
125.7456
124.0877
123.3131
120.6912
118.3037
61.3697
33.8602
25.7530
25.4032
21.8712
O
N
N
f1 (ppm)

5j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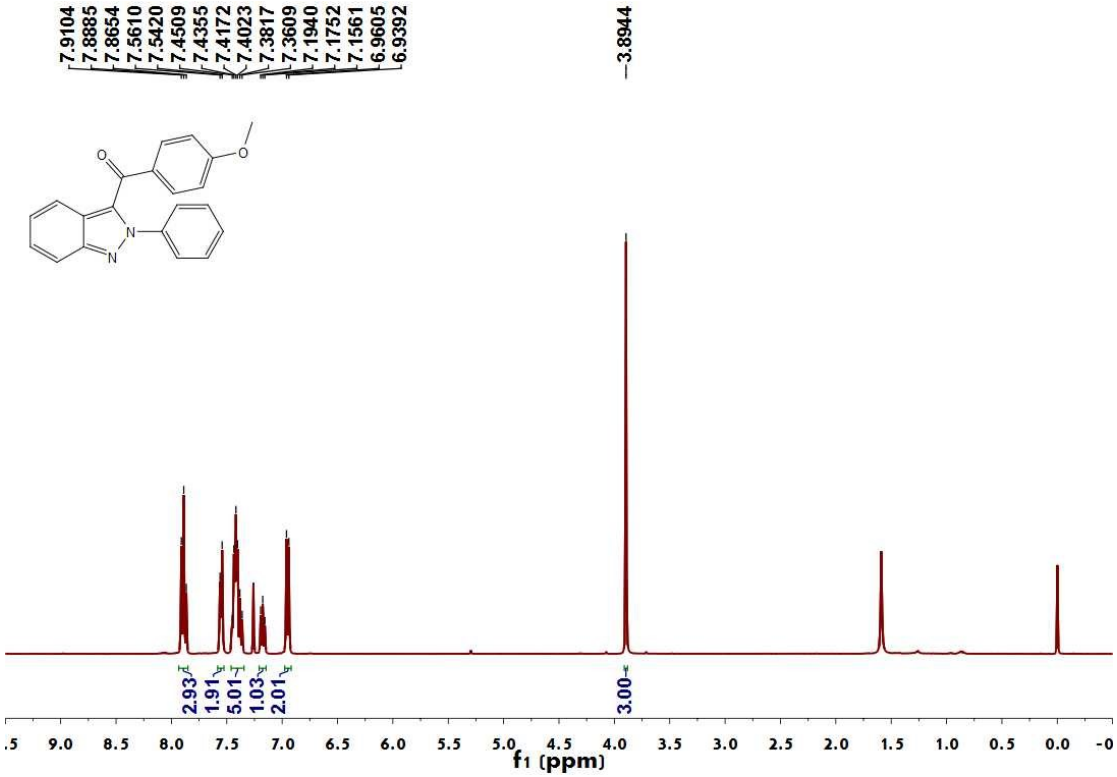
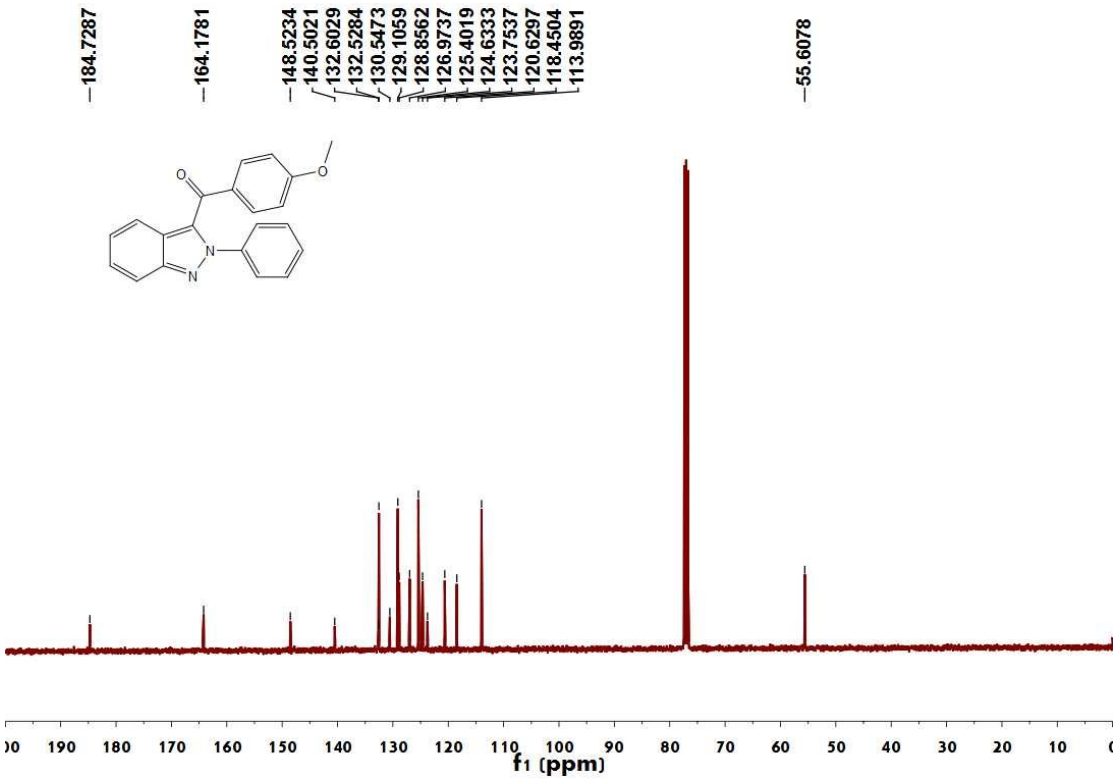
7.8819
7.8644
7.8613
7.6252
7.6067
7.5880
7.5537
7.5492
7.5330
7.5298
7.4815
7.4621
7.4529
7.4431
7.4309
7.4160
7.4116
7.3972
7.3923
7.3898
7.3843
7.3681
7.3610
7.2041
7.1860
7.1830
7.1661
O
N
N
2.82
1.01
1.85
6.97
1.00
f1 (ppm)
186.0626
148.6596
140.5908
137.9088
133.6497
132.3553
129.9971
129.1683
129.0206
128.7273
127.1138
125.6292
125.1082
124.1625
120.6804
118.6325
O
N
N
f1 (ppm)

5k


7.9104
7.8885
7.8654
7.5610
7.5420
7.4509
7.4355
7.4172
7.4023
7.3817
7.3609
7.1940
7.1752
7.1561
6.9605
6.9392
3.8944
2.93
1.91
5.01
1.03
2.01
3.00
f1 (ppm)


184.7287
164.1781
148.5234
140.5021
132.6029
132.5284
130.5473
129.1059
128.8562
126.9737
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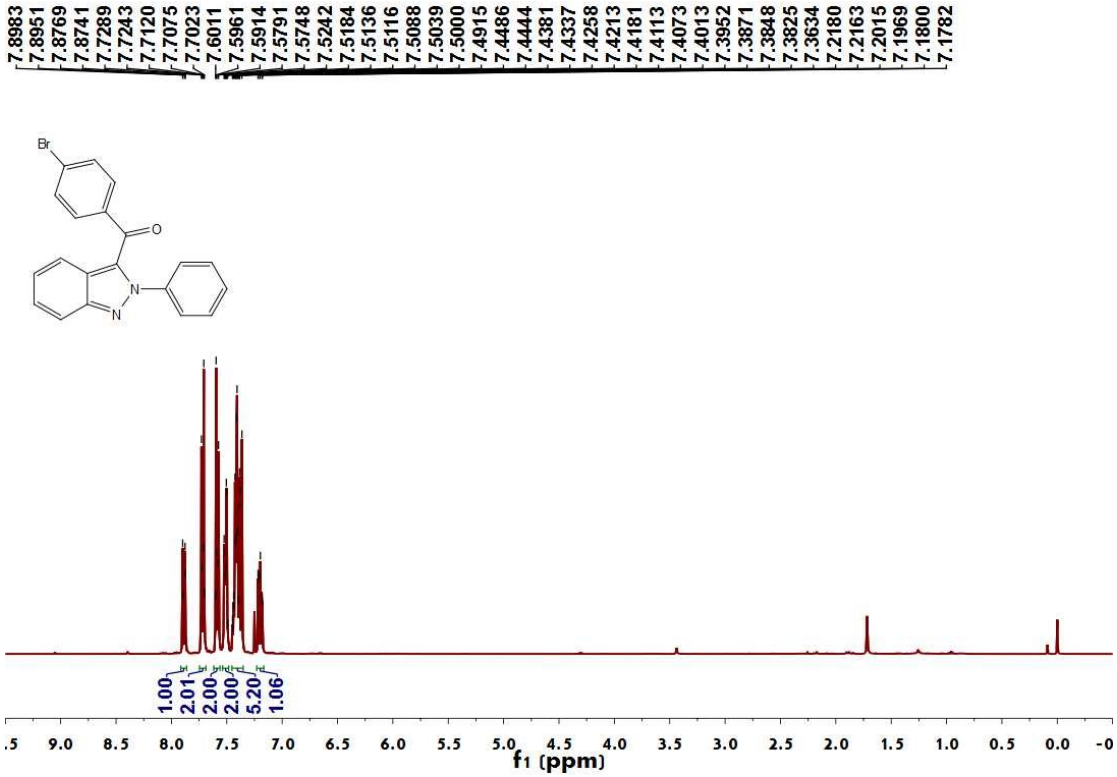
124.6333
123.7537
120.6297
118.4504
113.9891
55.6078
f1 (ppm)

5l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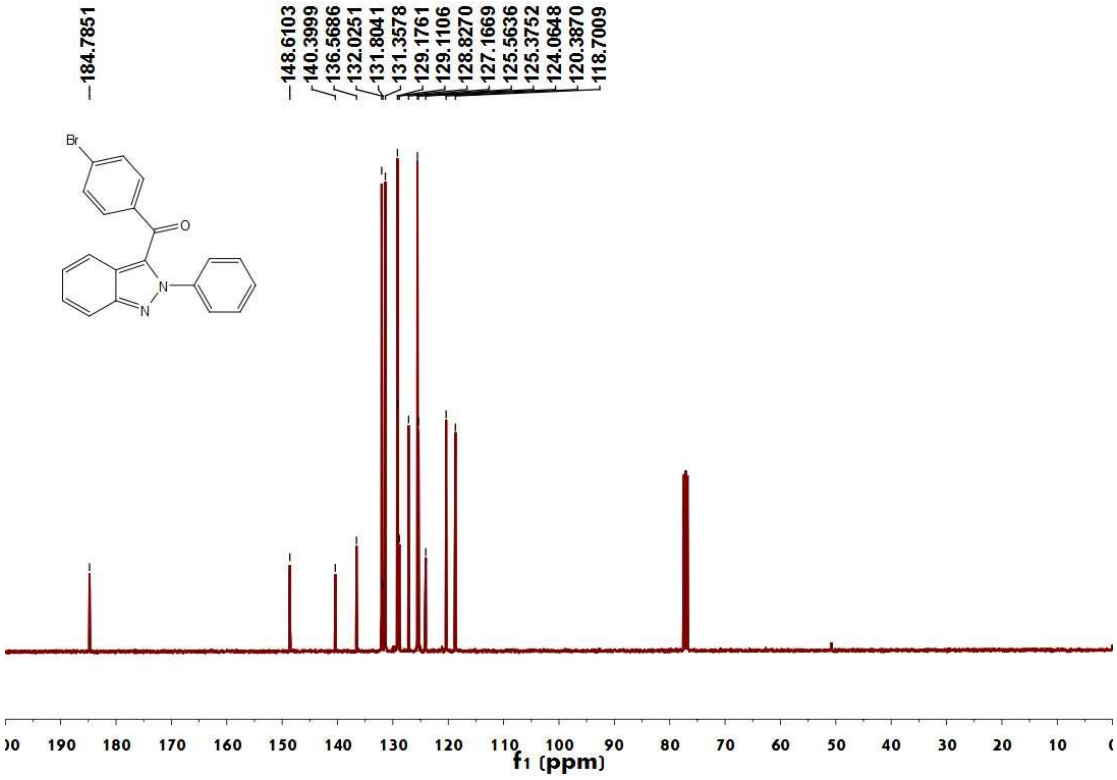
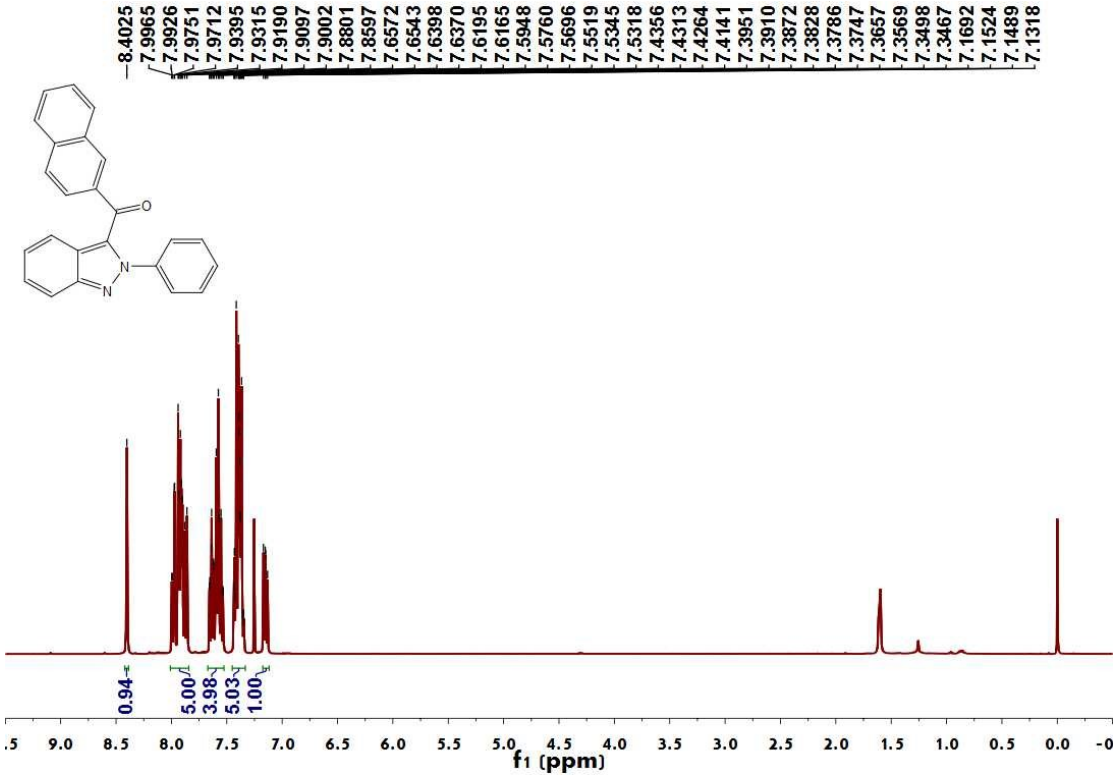
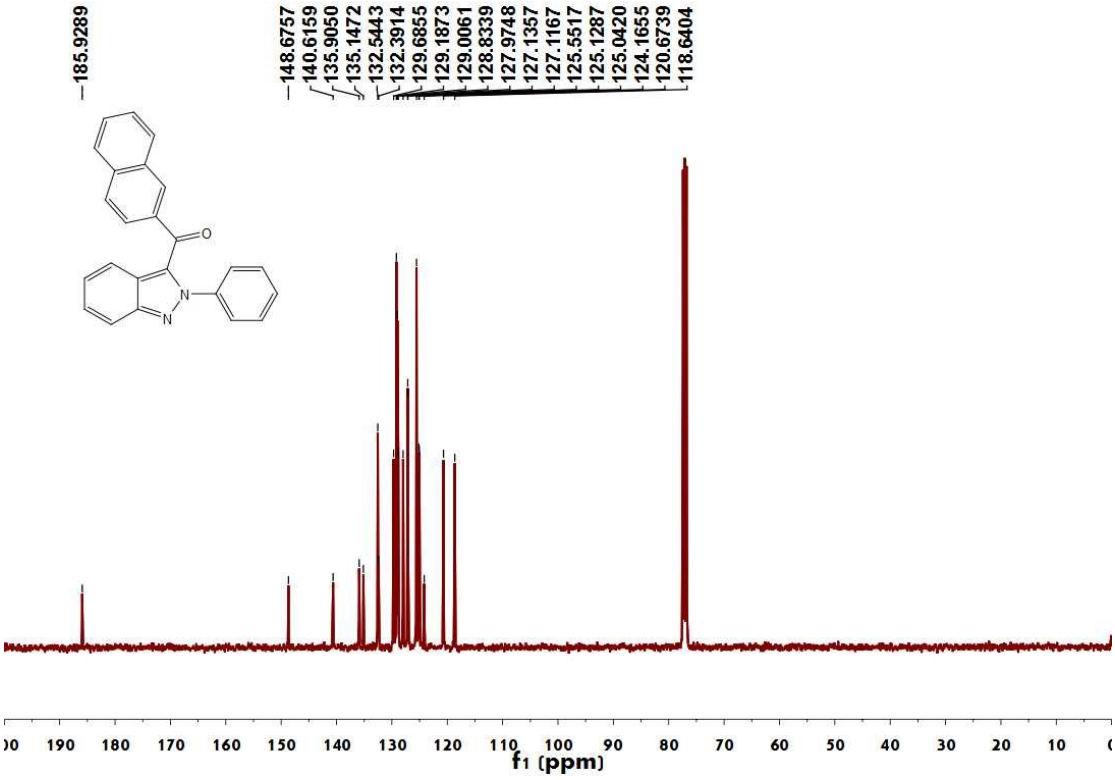
7.8951
7.8769
7.8741
7.7289
7.7243
7.7120
7.7075
7.7023
7.6011
7.5961
7.5914
7.5791
7.5748
7.5242
7.5184
7.5136
7.5116
7.5088
7.5039
7.5000
7.4915
7.4486
7.4444
7.4381
7.4337
7.4258
7.4213
7.4181
7.4113
7.4073
7.4013
7.3952
7.3871
7.3848
7.3825
7.3634
7.2180
7.2163
7.2015
7.1969
7.1800
7.1782
Br
O
N
N
1.00
2.01
2.00
2.00
5.20
1.06
f1 (ppm)

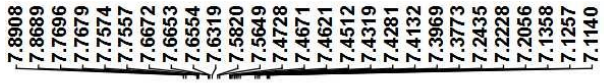

184.7851
148.6103
140.3999
136.5686
132.0251
131.8041
131.3578
129.1761
129.1106
128.8270
127.1669
125.5636
125.3752
124.0648
120.3870
118.7009
Br
O
N
N
f1 (ppm)

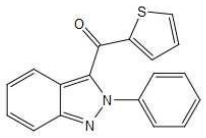
5m

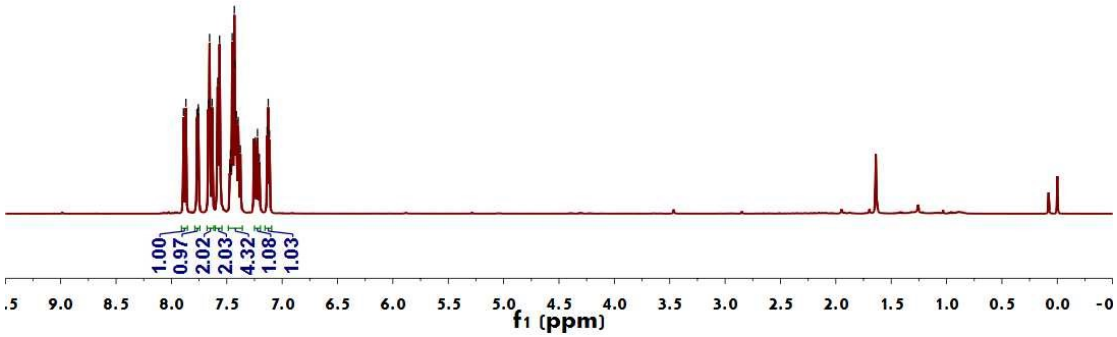

8.4025
7.9965
7.9926
7.9751
7.9712
7.9395
7.9315
7.9190
7.9097
7.9002
7.8801
7.8597
7.6572
7.6543
7.6398
7.6370
7.6195
7.6165
7.5948
7.5760
7.5696
7.5519
7.5345
7.5318
7.4356
7.4313
7.4264
7.4141
7.3951
7.3910
7.3872
7.3828
7.3786
7.3747
7.3657
7.3569
7.3498
7.3467
7.1692
7.1524
7.1489
7.1318
0.94
5.00
3.98
5.03
1.00
f1 (ppm)

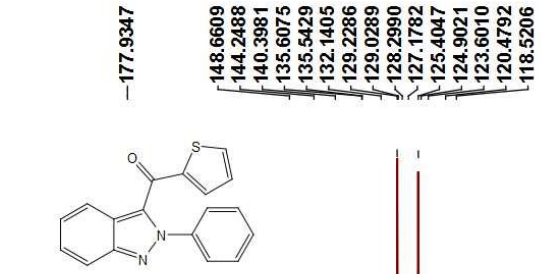

185.9289
148.6757
140.6159
135.9050
135.1472
132.5443
132.3914
129.6855
129.1873
129.0061
128.8339
127.9748
127.1357
127.1167
125.5517
125.1287
125.0420
124.1655
120.6739
118.6404
f1 (ppm)

5n


7.8908
7.8689
7.7696
7.7679
7.7574
7.7557
7.6672
7.6653
7.6554
7.6319
7.5820
7.5649
7.4728
7.4671
7.4621
7.4512
7.4319
7.4281
7.4132
7.3969
7.3773
7.2435
7.2228
7.2056
7.1358
7.1257
7.1140


O
S
N
N


1.00
0.97
2.02
2.03
4.32
1.08
1.03
f1 (ppm)


177.9347
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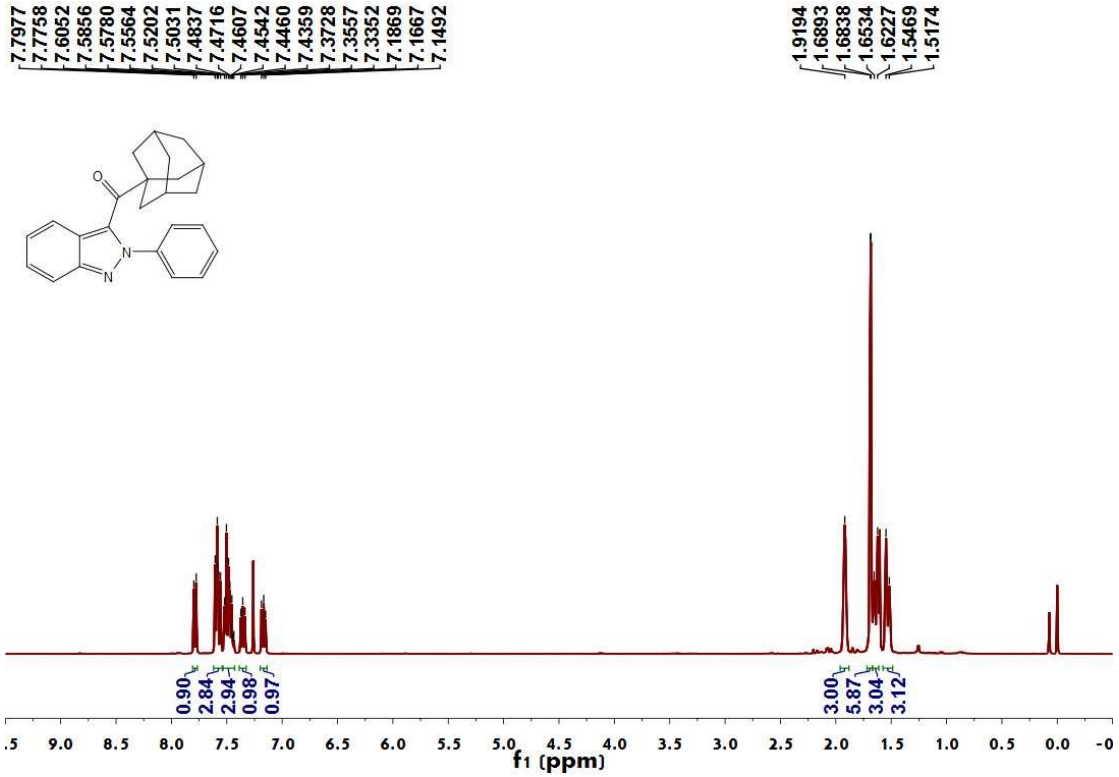
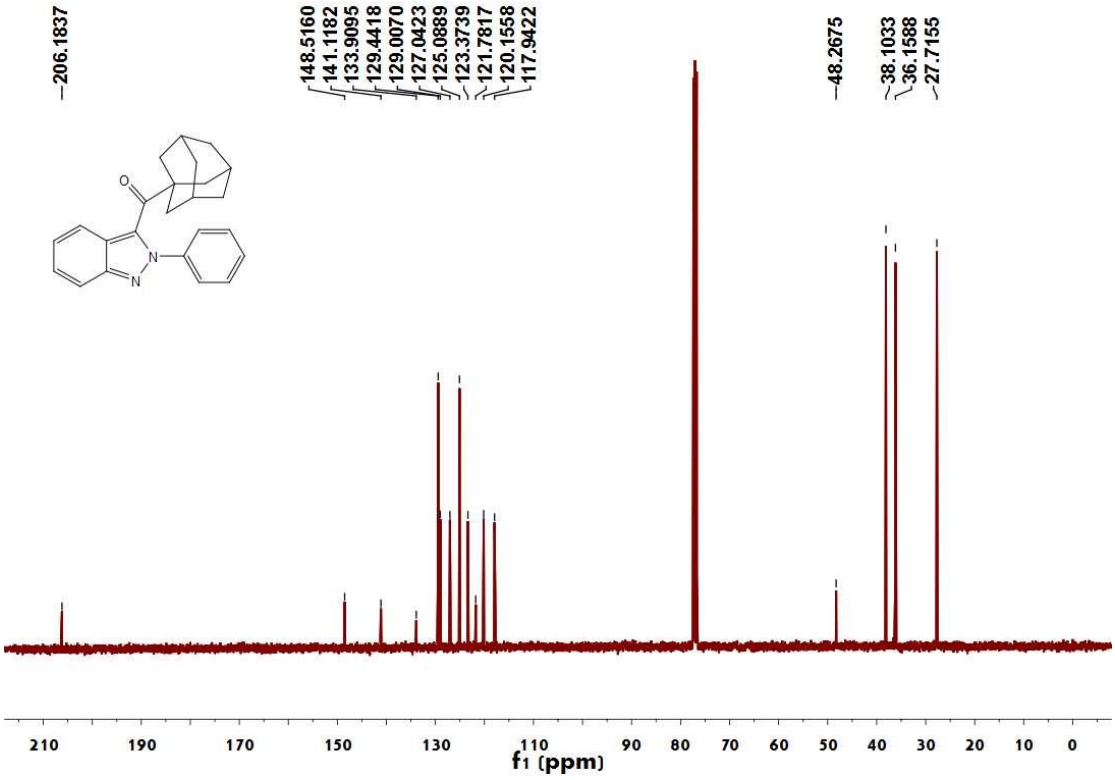
144.2488
140.3981
135.6075
135.5429
132.1405
129.2286
129.0289
128.2990
127.1782
125.4047
124.9021
123.6010
120.4792
118.5206

O
S
N
N

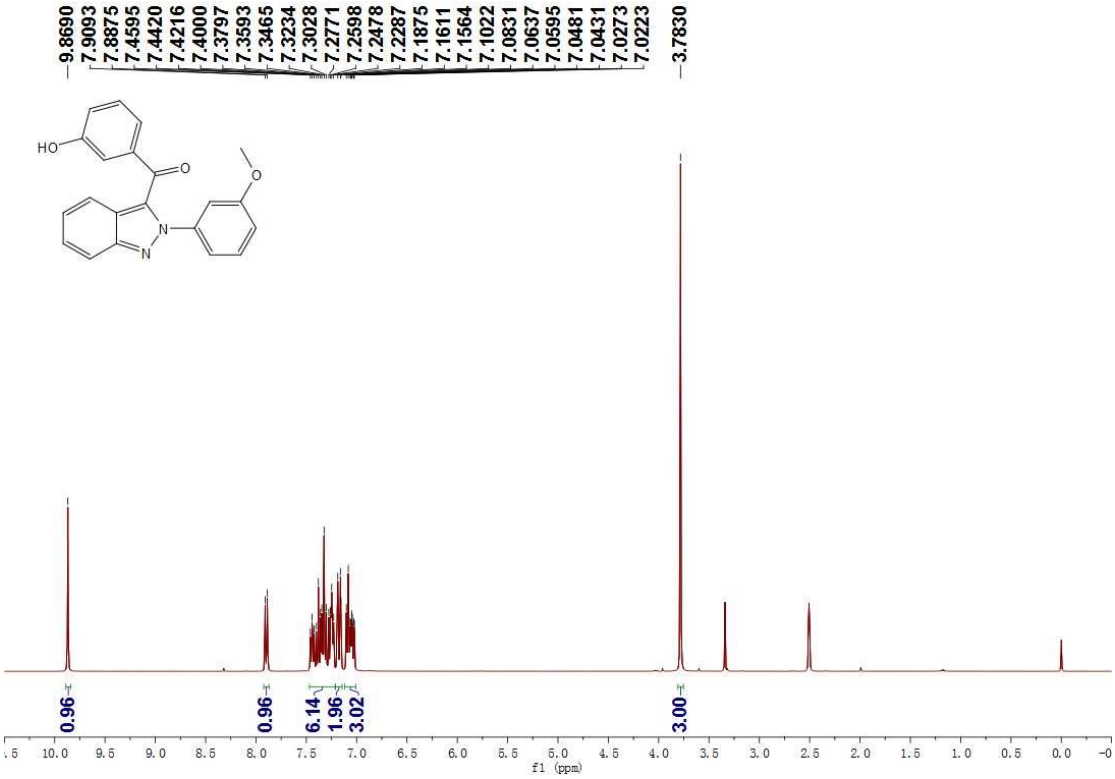
f1 (ppm)

5o


7.7977
7.7758
7.6052
7.5856
7.5780
7.5564
7.5202
7.5031
7.4837
7.4716
7.4607
7.4542
7.4460
7.4359
7.3728
7.3557
7.3352
7.1869
7.1667
7.1492
1.9194
1.6893
1.6838
1.6534
1.6227
1.5469
1.5174
O
N
N
0.90
2.84
2.94
0.98
0.97
3.00
5.87
3.04
3.12
f1 (ppm)


206.1837
148.5160
141.1182
133.9095
129.4418
129.0070
127.0423
125.0889
123.3739
121.7817
120.1558
117.9422
48.2675
38.1033
36.1588
27.7155
O
N
N
f1 (ppm)

5v


9.8690
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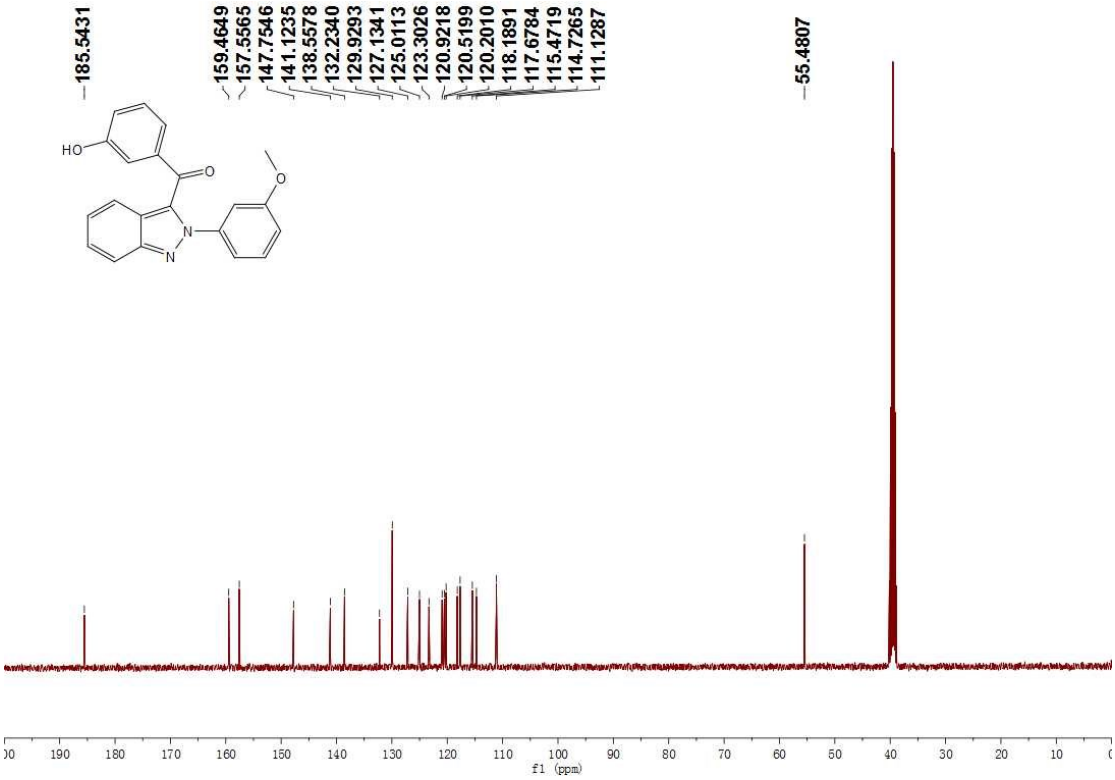
7.8875
7.4595
7.4420
7.4216
7.4000
7.3797
7.3593
7.3465
7.3234
7.3028
7.2771
7.2598
7.2478
7.2287
7.1875
7.1611
7.1564
7.1022
7.0831
7.0637
7.0595
7.0481
7.0431
7.0273
7.0223
3.7830
HO
O
O
N
N
0.96
0.96
6.14
1.96
3.02
3.00
f1 (ppm)


185.5431
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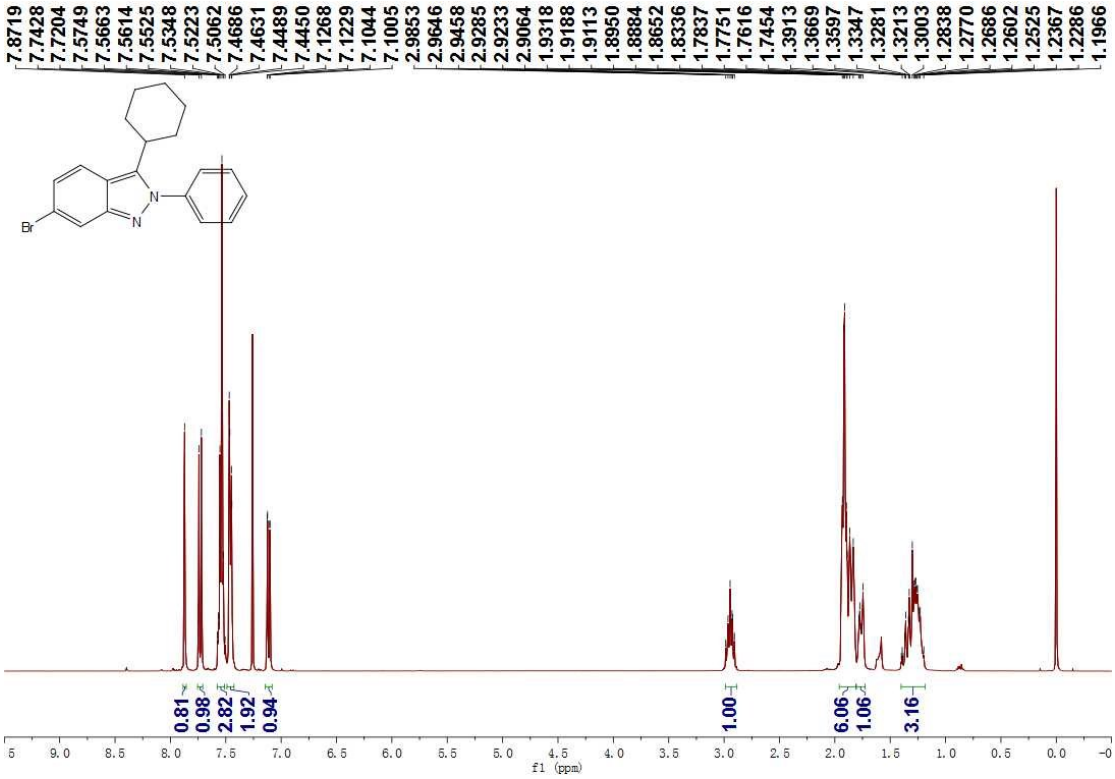
157.5565
147.7546
141.1235
138.5578
132.2340
129.9293
127.1341
125.0113
123.3026
120.9218
120.5199
120.2010
118.1891
117.6784
115.4719
114.7265
111.1287
55.4807
HO
O
O
N
N
f1 (ppm)

3w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7.5525
7.5348
7.5223
7.5062
7.4686
7.4631
7.4489
7.4450
7.1268
7.1229
7.1044
7.1005
2.9853
2.9646
2.9458
2.9285
2.9233
2.9064
1.9318
1.9188
1.9113
1.8950
1.8884
1.8652
1.8336
1.7837
1.7751
1.7616
1.7454
1.3913
1.3669
1.3597
1.3347
1.3281
1.3213
1.3003
1.2838
1.2770
1.2686
1.2602
1.2525
1.2367
1.2286
1.1966
Br
N
N
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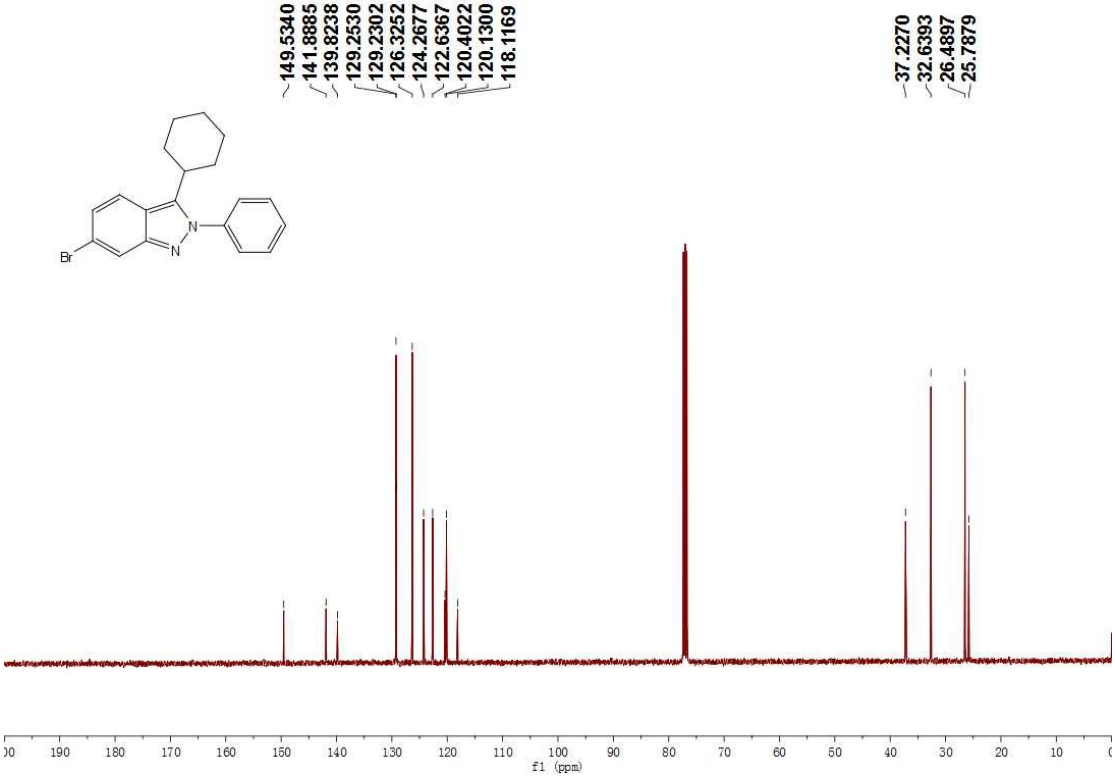
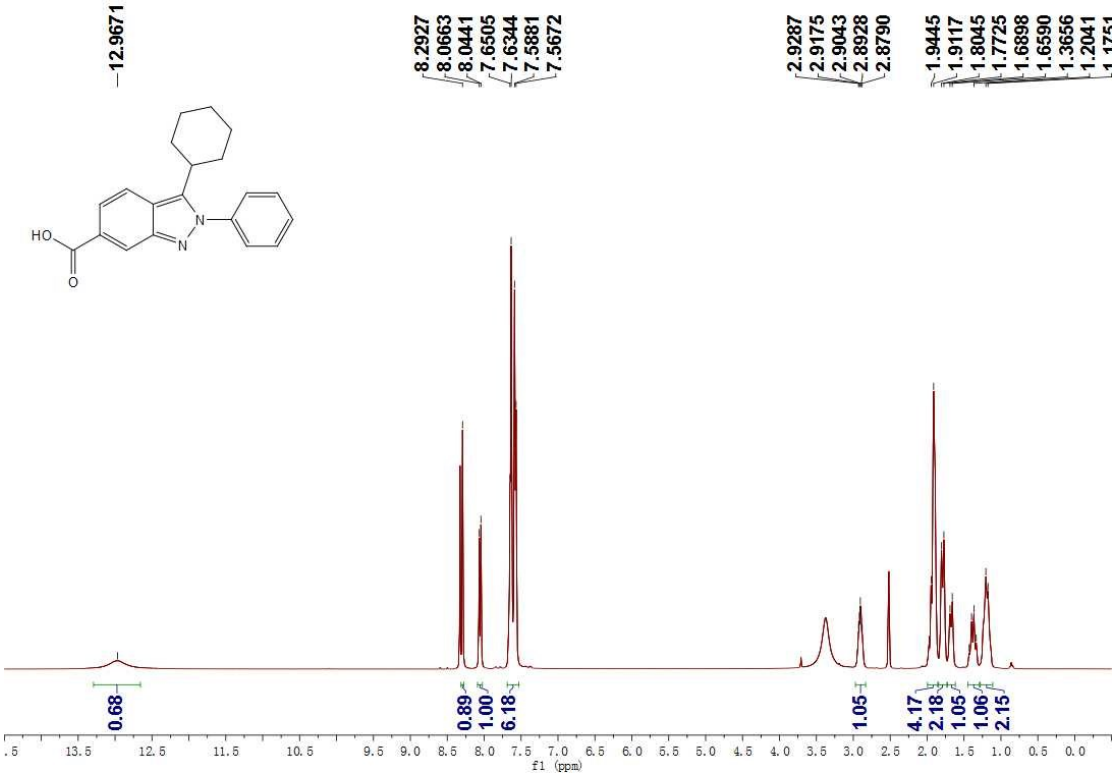
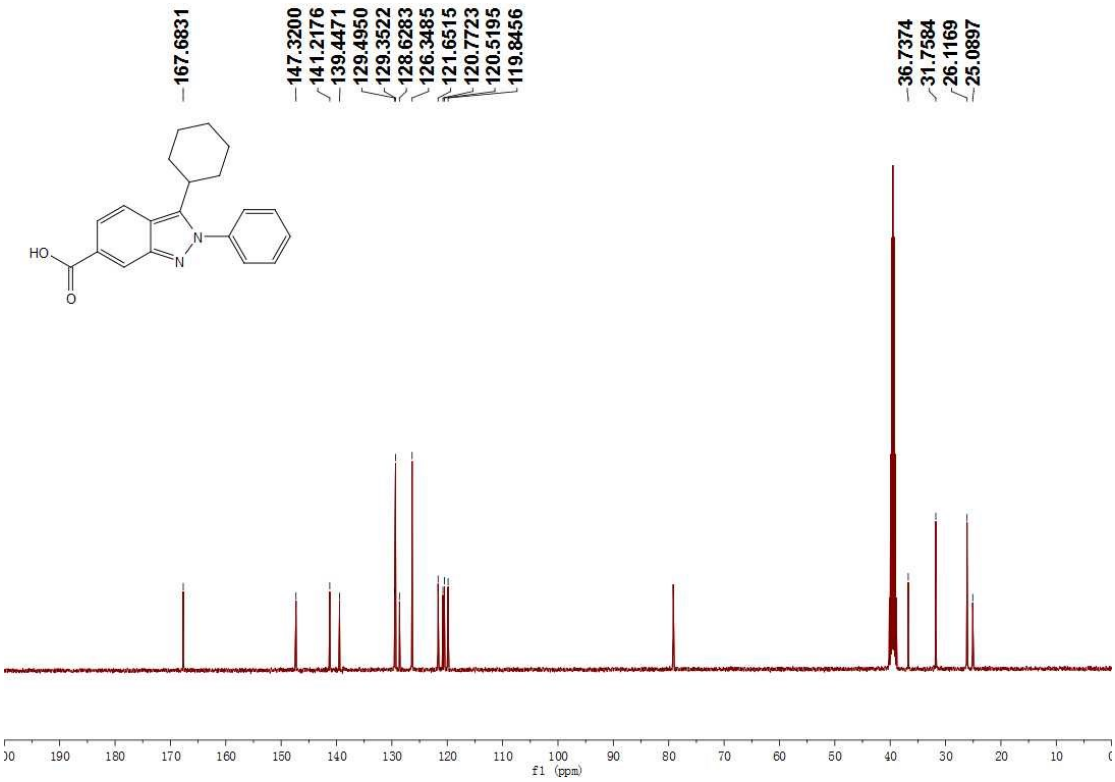
0.98
2.82
1.92
0.94
1.00
6.06
1.06
3.16
f1 (ppm)


149.5340
141.8885
139.8238
129.2530
129.2302
126.3252
124.2677
122.6367
120.4022
120.1300
118.1169
37.2270
32.6393
26.4897
25.7879
Br
N
N
f1 (ppm)

3x


12.9671
8.2927
8.0663
8.0441
7.6505
7.6344
7.5881
7.5672
2.9287
2.9175
2.9043
2.8928
2.8790
1.9445
1.9117
1.8045
1.7725
1.6898
1.6590
1.3656
1.2041
HO
O
N
N
0.68
0.89
1.00
6.18
1.05
4.17
2.18
1.05
1.06
2.15
f1 (ppm)


167.6831
147.3200
141.2176
139.4471
129.4950
129.3522
128.6283
126.3485
121.6515
120.7723
120.5195
119.8456
36.7374
31.7584
26.1169
25.0897
HO
O
N
N
f1 (ppm)