Supporting Information

Access to 2-Substitued-2*H*-Inzazoles via Copper-Catalyzed Regioselective Cross-Coupling Reaction with Diaryliodonium Salts

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Contents

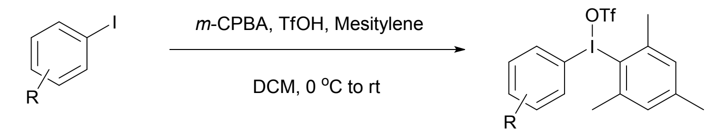
1. General information and materials

Reagent: All the reactions were carried out under inert atmosphere. All the solvents used for the reactions were dried according to standard procedures. All commercial materials were used as received unless otherwise noted. All the hypervalent iodine reagents were synthesized according to the literature procedure [1, 2]. The indazoles, iodides, *m*-CPBA, TfOH, CuCl were purchased from Adamas-beta. All the reactions were monitored by thin layer chromatography; the spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel.

Instruments: NMR spectra were recorded on Bruker Ultrashield™ 500 MHz. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR), DMSO-d_6 (2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR); For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), t (triplet), td (triple doublet), q (quartet), m (multiplet), as well as br (broad); High resolution ESI mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument.

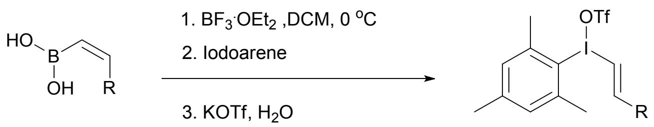
2. Procedures for the Preparation of Starting Materials

General Procedure A for the Preparation of Hypervalent Iodine Reagents[1]



To a solution of iodides (10.00 mmol, 1.0 eq), *m*-chloroperbenzoic acid (*m*-CPBA, 11.00 mmol, 1.1 eq) and mesitylene (11.00 mmol, 1.1 eq) in DCM (50.0 mL) was added TfOH (25.00 mmol, 2.5 eq) dropwise at 0 °C. The mixture was stirred at room temperature for 3~12 h. The reaction mixture was evaporated, and the residue was dissolved in cold diethyl ether (50.0 mL), and stirred at -20 °C for 1.5 h. White precipitates was formed and collected, washed with cold diethyl ether and dried under vacuum to give the desired hypervalent iodine reagents (**8a-q, 8av**).

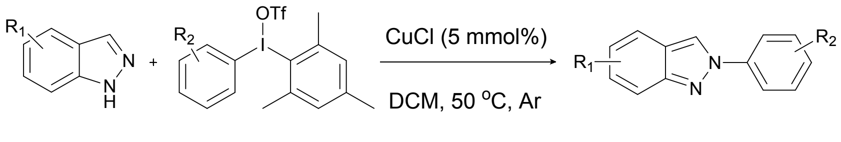
General Procedure B for the Preparation of Hypervalent Iodine Reagents[2]



The corresponding alkenyl boronic acid (5.00 mmol, 1.0 eq.) was suspended in dry CH_2Cl_2 (25.0 mL) at 0 °C to which boron trifluoride diethyl etherate (6.00 mmol, 1.2 eq) was added dropwise via syringe and stirred at this temperature for 15 minutes or until all the boronic acid had dissolved.

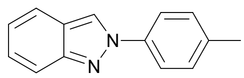
Iodoarene diacetate (6.00 mmol, 1.2 eq.) was then added as a solution in CH_2Cl_2 (25.0 mL) via cannula under a positive pressure of nitrogen. The reaction mixture was stirred for 1 hour or until complete consumption of the iodoarene diacetate, at which point potassium trifluoromethanesulphonate (12.50 mmol, 2.5 eq) dissolved in H_2O (25.0 mL) was added by the syringe. The aqueous phase was extracted with CH_2Cl_2 (3 × 50.0 mL) and the combined organic phases dried ($MgSO_4$), filtered, then concentrated in vacuo. The crude residue was then recrystallized from CH_2Cl_2/Et_2O or triturated with Et_2O to obtain the desired compound (**8as-u, 8aw**).

3. Preparation and characterization Data of Products



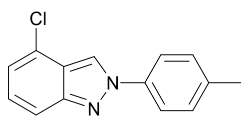
General Procedure for synthesis of 2-substituted-2*H*-indazoles. A sealed tube was charged with 1*H*-indazole substrates **7** (0.20 mmol), hypervalent iodine reagents **8** (0.24 mmol), CuCl (0.01 mmol). The tube was evacuated and backfilled with argon before 1.0 mL dichloromethane was added. The reaction mixture was stirred at 50-120 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane, filtered through a plug of diatomite, concentrated under vacuum and the residue was purified by chromatography on silica with a gradient eluent of petroleum ether and ethyl acetate to give the corresponding products.

2-(*p*-Tolyl)-2*H*-indazole (10aa)



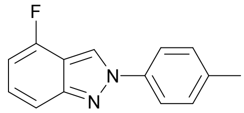
White solid in 92 % yield (38.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.81-7.77 (m, 3H), 7.71 (d, J = 8.5 Hz, 1H), 7.34-7.31 (m, 3H), 7.11 (t, J = 7.3 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 138.3, 137.9, 130.1, 126.74, 126.72, 122.7, 122.4, 120.9, 120.4, 117.9, 21.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}N_2$ $(M + H)^+$ 209.1079, found 209.1076.

4-Chloro-2-(*p*-tolyl)-2*H*-indazole (10ba)



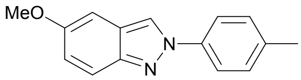
Light yellow solid in 92 % yield (44.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.7 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.1 Hz, 1H); 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 138.4, 138.0, 130.2, 126.9, 125.4, 123.0, 121.4, 120.9, 120.0, 116.6, 21.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}ClN_2$ $(M + H)^+$ 243.0689, found 243.0687.

4-Fluoro-2-(*p*-tolyl)-2*H*-indazole (10ca)



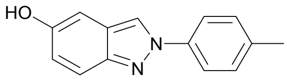
White solid in 88 % yield (39.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.25-7.21 (m, 1H), 6.74-6.70 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}F}$ = 252.6 Hz), 151.9 (d, $J_{C\text{-}F}$ = 5.5 Hz), 138.4, 138.0, 130.2, 126.7 (d, $J_{C\text{-}F}$ = 7.0 Hz), 120.9, 117.7 (d, $J_{C\text{-}F}$ = 4.1 Hz), 114.7 (d, $J_{C\text{-}F}$ = 19.7 Hz), 113.9 (d, $J_{C\text{-}F}$ = 4.6 Hz), 104.9 (d, $J_{C\text{-}F}$ = 17.3 Hz), 21.0; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}FN_2$ $(M + H)^+$ 227.0985, found 227.0986.

5-Methoxy-2-(*p*-tolyl)-2*H*-indazole (10da)



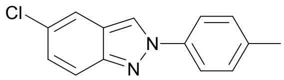
White solid in 95 % yield (45.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 9.3 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.04 (dd, J = 9.4 Hz, 2.4 Hz, 1H), 6.89 (d, J = 2.2 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 146.6, 138.4, 137.5, 130.1, 122.7, 121.8, 120.5, 119.3, 119.2, 96.3, 55.4, 21.0; HRMS (ESI) *m/z* calculated for $C_{15}H_{15}N_2O$ $(M + H)^+$ 239.1184, found 239.1181.

2-(*p*-Tolyl)-2*H*-indazol-5-ol (10ea)



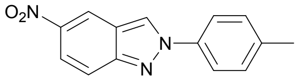
7e (0.20 mmol, 26.8 mg), **8a** (0.24 mmol, 116.7 mg) and CuCl (0.01 mmol, 5.00 mmol%, 1.0 mg) were weighed into a pressure tube, to which was added THF (1.0 mL) under N_2. The reaction mixture was stirred for 12 h at 50 ^{o}C. The crude residue was filtered through celite, evaporated, and then recrystallized from $CHCl_3$ to obtain the desired compound as a yellow solid **10ea** in 82 % yield (36.9 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.37 (s, 1H), 8.71 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 9.2 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 6.96 (dd, J = 9.2 Hz, 1.9Hz, 1H), 6.89 (d, J = 1.7 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.7, 145.9, 138.4, 137.2, 130.5, 123.5, 121.9, 120.1, 119.4, 119.1, 99.9, 20.9; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}N_2O$ $(M + H)^+$ 225.1028, found 225.1023.

5-Chloro-2-(*p*-tolyl)-2*H*-indazole (10fa)



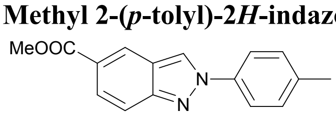
White solid in 88 % yield (42.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.75-7.71 (m, 3H), 7.65 (d, J = 1.7 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.25 (dd, J = 9.2 Hz, 1.7 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 138.3, 138.0, 130.2, 128.0, 127.9, 123.0, 120.7, 119.9, 119.4, 119.0, 21.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}ClN_2$ $(M + H)^+$ 243.0689, found 243.0687.

5-Nitro-2-(*p*-tolyl)-2*H*-indazole (10ga)



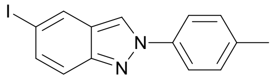
Yellow solid in 81 % yield (41.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, J = 1.6 Hz, 1H), 8.65 (s, 1H), 8.14 (dd, J = 9.5 Hz, 2.0 Hz, 1H), 7.84 (d, J = 9.5 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 143.5, 139.3, 137.5, 130.4, 124.3, 121.04, 120.98, 120.9, 119.5, 118.9, 21.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}N_3O_2$ $(M + H)^+$ 254.0930, found 254.0932.

Methyl 2-(*p*-tolyl)-2*H*-indazole-5-carboxylate (10ha)



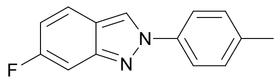
White solid in 84 % yield (44.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.46 (s, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.77-7.74 (m, 3H), 7.30 (d, J = 8.1 Hz, 2H), 3.93 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 150.7, 138.6, 137.8, 130.2, 126.4, 125.1, 124.3, 122.7, 122.0, 120.9, 117.7, 52.1, 21.1; HRMS (ESI) *m/z* calculated for $C_{16}H_{15}N_2O_2$ $(M + H)^+$ 267.1134, found 267.1130.

5-Iodo-2-(*p*-tolyl)-2*H*-indazole (10ia)



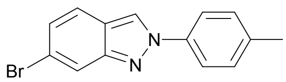
White solid in 87 % yield (58.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.04 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.55-7.48 (m, 2H), 7.29 (d, J = 8.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 138.3, 137.8, 135.2, 130.2, 129.3, 124.9, 120.8, 119.8, 119.2, 86.6, 21.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}IN_2$ $(M + H)^+$ 335.0045, found 335.0043.

6-Fluoro-2-(*p*-tolyl)-2*H*-indazole (10ja)



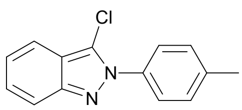
White solid in 85 % yield (38.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.67-7.64 (m, 1H), 7.38 (d, J = 9.9 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 6.94-6.89 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 242.6 Hz), 149.6 (d, $J_{C\text{-}F}$ = 13.1 Hz), 138.08, 138.05, 130.1, 122.3 (d, $J_{C\text{-}F}$ = 10.7 Hz), 120.8, 120.7, 120.0, 114.2 (d, $J_{C\text{-}F}$ = 28.3 Hz), 101.0 (d, $J_{C\text{-}F}$ = 23.6 Hz), 21.0; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}FN_2$ $(M + H)^+$ 227.0985, found 227.0986.

6-Bromo-2-(*p*-tolyl)-2*H*-indazole (10ka)



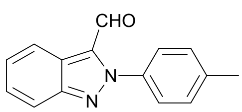
White solid in 89 % yield (51.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.96 (s, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.9 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 138.3, 137.9, 130.2, 126.1, 121.80, 121.78, 121.2, 120.8, 120.7, 120.2, 21.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}BrN_2$ $(M + H)^+$ 287.0184, found 287.0185.

3-Chloro-2-(*p*-tolyl)-2*H*-indazole (10la)



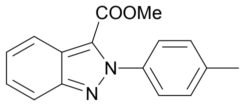
White solid in 86 % yield (41.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.37-7.33 (m, 3H), 7.18-7.14 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 139.3, 136.1, 129.7, 127.5, 125.5, 122.7, 119.8, 119.5, 119.0, 118.2, 21.3; HRMS (ESI) *m/z* calculated for $C_{14}H_{12}ClN_2$ $(M + H)^+$ 243.0689, found 243.0687.

2-(*p*-Tolyl)-2*H*-indazole-3-carbaldehyde (10ma)



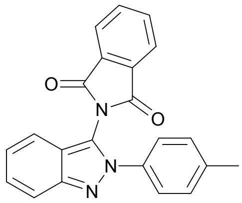
White solid in 45 % yield (21.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.32 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.49-7.40 (m, 4H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 148.4, 140.4, 136.3, 132.2, 130.1, 127.7, 127.0, 126.2, 123.3, 121.0, 118.6, 21.3; HRMS (ESI) *m/z* calculated for $C_{15}H_{13}N_2O$ $(M + H)^+$ 237.1028, found 237.1025.

Methyl 2-(*p*-tolyl)-2*H*-indazole-3-carboxylate (10na)



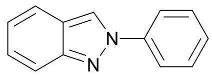
White solid in 92 % yield (49.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.43-7.40 (m, 3H), 7.36-7.32 (m, 3H), 3.92 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 148.4, 139.5, 138.5, 129.3, 127.0, 126.0, 125.5, 124.8, 123.9, 121.5, 118.6, 51.9, 21.3; HRMS (ESI) *m/z* calculated for $C_{16}H_{15}N_2O_2$ $(M + H)^+$ 267.1134, found 267.1130.

2-(2-(*p*-Tolyl)-2*H*-indazol-3-yl) isoindoline-1, 3-dione (10oa)



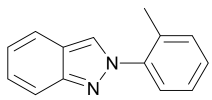
Yellow solid in 82 % yield (58.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.78-7.77 (m, 2H), 7.47-7.44 (m, 3H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 148.4, 139.4, 136.2, 135.0, 131.5, 130.0, 127.1, 124.7, 124.4, 123.7, 121.4, 119.4, 118.7, 118.3, 21.2; HRMS (ESI) *m/z* calculated for $C_{22}H_{16}N_3O_2$ $(M + H)^+$ 354.1243, found 354.1240.

2-Phenyl-2*H*-indazole (10ab)



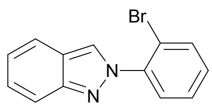
White solid in 88 % yield (34.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 140.6, 129.6, 127.9, 126.9, 122.8, 122.5, 121.0 (2C), 120.4, 118.0; HRMS (ESI) *m/z* calculated for $C_{13}H_{11}N_2$ $(M + H)^+$ 195.0922, found 195.0920.

2-(*o*-Tolyl)-2*H*-indazole (10ac)



White solid in 84 % yield (35.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.47-7.36 (m, 5H), 7.18 (t, *J* = 7.7 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 140.4, 134.0, 131.3, 129.2, 126.64, 126.60, 126.4, 124.4, 122.2, 122.0, 120.3, 117.9, 17.9; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}N_2$ $(M + H)^+$ 209.1079, found 209.1076.

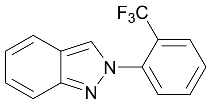
2-(2-Bromophenyl)-2*H*-indazole (10ad)



Light yellow liquid in 54 % yield (29.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.77-7.75 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38-7.34 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 140.3, 133.8, 130.5, 128.9, 128.3, 126.9, 125.2, 122.5, 121.9, 120.6, 119.0, 118.0; HRMS (ESI) *m/z* calculated for $C_{13}H_{10}BrN_2$

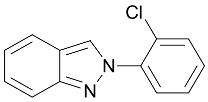
$(M + H)^+$ 273.0027, found 273.0025.

2-(2-(Trifluoromethyl) phenyl)-2*H*-indazole (10ae)



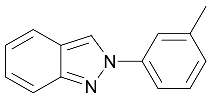
White solid in 15 % yield (7.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.75-7.70 (m, 2H), 7.66-7.63 (m, 2H), 7.36 (t, J = 8.5 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 139.0 (q, $J_{C\text{-}F}$ = 1.4 Hz), 132.7, 129.6, 127.2 (q, $J_{C\text{-}F}$ = 5.0 Hz), 127.0, 126.4, 126.2, 125.8 (q, $J_{C\text{-}F}$ = 1.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 271.7 Hz), 122.6, 122.1, 120.4, 117.9; HRMS (ESI) *m/z* calculated for $C_{14}H_{10}F_3N_2$ $(M + H)^+$ 263.0796, found 263.0792.

2-(2-Chlorophenyl)-2*H*-indazole (10af)



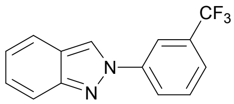
Colorless liquid in 47 % yield (21.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.71-7.69 (m, 1H), 7.60-7.58 (m, 1H), 7.46-7.41 (m, 2H), 7.36 (t, J = 7.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 138.4, 130.7, 130.1, 129.0, 128.6, 127.8, 127.2, 125.4, 122.6, 121.9, 120.6, 117.8; HRMS (ESI) *m/z* calculated for $C_{13}H_{10}N_2Cl$ $(M + H)^+$ 229.0533, found 229.0531.

2-(*m*-Tolyl)-2*H*-indazole (10ag)



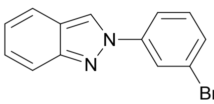
Light yellow liquid in 91 % (37.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.77 (s, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.1 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 140.5, 139.8, 129.4, 128.7, 126.8, 122.7, 122.4, 121.8, 120.5, 120.4, 118.0, 117.9, 21.5; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}N_2$ $(M + H)^+$ 209.1079, found 209.1076.

2-(3-(Trifluoromethyl) phenyl)-2*H*-indazole (10ah)



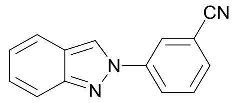
White solid in 86 % yield (45.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.22 (s, 1H), 8.10-8.09 (m, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.65-7.64 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 140.9, 132.6 (q, $J_{C\text{-}F}$ = 32.9 Hz), 130.2, 127.4, 124.7 (q, $J_{C\text{-}F}$ = 270.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.7, 123.02, 122.99, 120.5, 120.4, 118.0, 117.9 (q, $J_{C\text{-}F}$ = 3.8Hz); HRMS (ESI) *m/z* calculated for $C_{14}H_{10}F_3N_2$ $(M + H)^+$ 263.0796, found 263.0792.

2-(3-Bromophenyl)-2*H*-indazole (10ai)



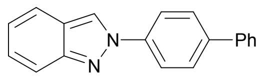
White solid in 87 % yield (47.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.12 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.38-7.32 (m, 2H), 7.12 (t, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 141.5, 130.9, 130.8, 127.34, 127.32, 124.0, 123.3, 122.9, 120.5, 120.4, 119.2, 118.0; HRMS (ESI) *m/z* calculated for $C_{13}H_{10}N_2Br$ $(M + H)^+$ 273.0027, found 273.0029.

3-(2*H*-Indazol-2-yl) benzonitrile (10aj)



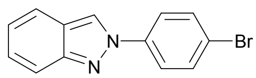
White solid in 56 % yield (24.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.24 (s, 1H), 8.16 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.66-7.61 (m, 2H), 7.34 (t, J = 6.9 Hz, 1H), 7.13 (t, J = 7.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 141.0, 131.1, 130.6, 127.7, 124.6, 124.0, 123.3, 123.1, 120.5, 120.3, 118.0, 117.8, 113.9; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}N_2$ $(M + H)^+$ 220.0875, found 220.0870.

2-([1, 1'-Biphenyl]-4-yl)-2*H*-indazole (10ak)



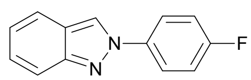
White solid in 72 % yield (38.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.00 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.7 Hz, 1H), 7.76-7.72 (m, 3H), 7.66 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 140.9, 139.9, 139.6, 129.0, 128.2, 127.8, 127.1, 127.0, 122.9, 122.6, 121.2, 120.42, 120.37, 118.0; HRMS (ESI) *m/z* calculated for $C_{19}H_{15}N_2$ $(M + H)^+$ 271.1235, found 271.1231.

2-(4-Bromophenyl)-2*H*-indazole (10al)



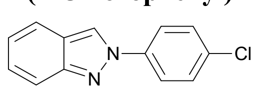
White solid in 84 % yield (45.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.78 (d, J = 8.8 Hz, 3H), 7.69 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 139.5, 132.7, 127.2, 122.9, 122.8, 122.3, 121.5, 120.4, 120.3, 117.9; HRMS (ESI) *m/z* calculated for $C_{13}H_{10}BrN_2$ $(M + H)^+$ 273.0027, found 273.0025.

2-(4-Fluorophenyl)-2*H*-indazole (10am)



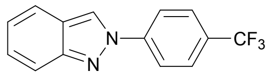
White solid in 85 % yield (36.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.87-7.84 (m, 2H), 7.79 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 8.3 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 246.1 Hz), 149.8, 136.9, 127.0, 122.85, 122.80 (d, $J_{C\text{-}F}$ = 8.5 Hz), 122.6, 120.5, 120.4, 117.9, 116.6 (d, $J_{C\text{-}F}$ = 22.9 Hz);. HRMS (ESI) *m/z* calculated for $C_{13}H_{10}N_2F$ $(M + H)^+$ 213.0828, found 213.0829.

2-(4-Chlorophenyl)-2*H*-indazole (10an)



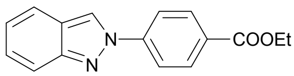
White solid in 85 % yield (38.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.49 (d, J = 8.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 139.0, 133.6, 129.7, 127.2, 122.9, 122.8, 122.0, 120.4, 120.4, 117.9; HRMS (ESI) *m/z* calculated for $C_{13}H_{10}N_2Cl$ (M + H)$^+$ 229.0533, found 229.0531.

2-(4-(Trifluoromethyl) phenyl)-2*H*-indazole (10ao)



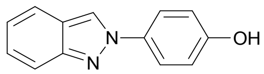
White solid in 89 % yield (46.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 3H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.35 (t. *J* = 6.9 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 142.9, 129.9 (q, $J_{C\text{-}F}$ = 33.3 Hz), 127.5, 126.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.9 (q, $J_{C\text{-}F}$ = 270.4 Hz), 123.09, 123.06, 120.8, 120.5, 120.4, 118.1; HRMS (ESI) *m/z* calculated for $C_{14}H_{10}F_3N_2$ (M + H)$^+$ 263.0796, found 263.0792.

Ethyl 4-(2*H*-indazol-2-yl) benzoate (10ap)



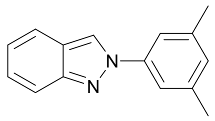
White solid in 70 % yield (37.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 150.2, 143.5, 131.1, 129.6, 127.5, 123.00, 122.98, 120.53, 120.51, 120.2, 118.0, 61.3, 14.4; HRMS (ESI) *m/z* calculated for $C_{16}H_{15}N_2O_2$ (M + H)$^+$ 267.1134, found 267.1130.

4-(2*H*-Indazol-2-yl) phenol (10aq)



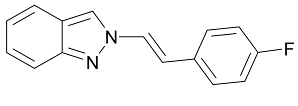
White solid in 83 % yield (34.9 mg).^{1}H NMR (500 MHz, DMSO-d_6) δ 9.86 (s, 1H), 8.90 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.7, 149.0, 132.7, 126.7, 122.8, 122.3, 122.2, 121.4, 121.2, 117.7, 116.4; HRMS (ESI) *m/z* calculated for $C_{13}H_{11}N_2O$ (M + H)$^+$ 211.0871, found 211.0867.

2-(3, 5-Dimethylphenyl)-2*H*-indazole (10ar)



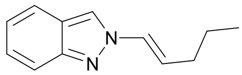
White solid in 88 % yield (39.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.52 (s, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 1H), 2.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 140.4, 139.5, 129.6, 126.8, 122.7, 122.3, 120.5, 120.4, 118.8, 117.9, 21.4; HRMS (ESI) *m/z* calculated for $C_{15}H_{15}N_2$ (M + H)$^+$ 223.1235, found 223.1232.

(*E*)-2-(4-Fluorostyryl)-2*H*-indazole (10as)



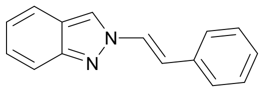
White solid in 85 % yield (40.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.67-7.65 (m, 2H), 7.50-7.47 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.12-7.07 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (d, $J_{C\text{-}F}$ = 247.1 Hz), 149.6, 130.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.4, 126.3, 122.7, 122.3, 121.9, 120.4, 120.2, 117.5, 116.1 (d, $J_{C\text{-}F}$ = 21.7 Hz); HRMS (ESI) *m/z* calculated for $C_{15}H_{12}FN_2$ (M + H)$^+$ 239.0985, found 239.0985.

(*E*)-2-(Pent-1-en-1-yl)-2*H*-indazole (10at)



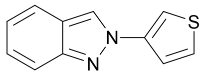
White solid in 87 % yield (32.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.09-7.05 (m, 2H), 6.55-6.50 (m, 1H), 2.24 (q, J = 7.2 Hz, 2H), 1.59-1.52 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 127.7, 126.8, 122.9, 122.2, 122.0, 120.9, 120.2, 117.5, 31.8, 22.4, 13.7; HRMS (ESI) *m/z* calculated for $C_{12}H_{15}N_2$ $(M + H)^+$ 187.1235, found 187.1236.

(*E*)-2-Styryl-2*H*-indazole (10au)



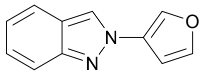
White solid in 86 % yield (37.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.75-7.71 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.52-7.49 (m, 3H), 7.40 (t, J = 7.4 Hz, 2H), 7.33-7.31 (m, 2H), 7.10 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 134.4, 129.0, 128.3, 127.3, 126.7, 126.6, 122.6, 122.3, 121.9, 121.3, 120.3, 117.5; HRMS (ESI) *m/z* calculated for $C_{15}H_{13}N_2$ $(M + H)^+$ 221.1079, found 221.1070.

2-(Thiophen-3-yl)-2*H*-indazole (10av)



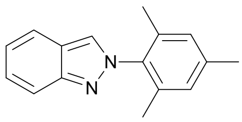
White solid in 72 % yield (28.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.69-7.67 (m, 2H), 7.57 (d, J = 5.1 Hz, 1H), 7.45-7.44 (m, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 140.0, 127.0, 126.9, 122.6, 122.4, 121.0, 120.9, 120.3, 117.7, 113.7; HRMS (ESI) *m/z* calculated for $C_{11}H_9N_2S$ $(M + H)^+$ 201.0486, found 201.0486.

2-(Furan-3-yl)-2*H*-indazole (10aw)



White solid in 42 % yield (15.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.03 (s, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 1.6 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 143.8, 133.4, 130.3, 126.9, 122.5, 122.3, 121.2, 120.1, 117.5, 105.1; HRMS (ESI) *m/z* calculated for $C_{11}H_9N_2O$ $(M + H)^+$ 185.0715, found 185.0714.

2-Mesityl-2*H*-indazole (11)

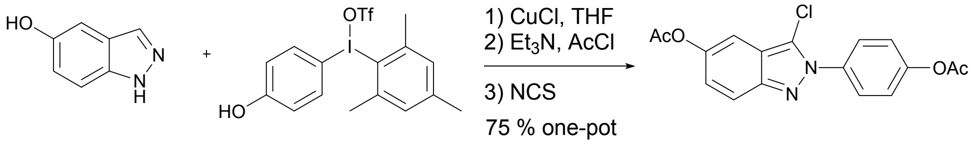


White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.00 (s, 2H), 2.37 (s, 3H), 1.96 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 139.3, 137.3, 135.2, 128.8, 126.1, 124.7, 122.0, 121.9, 120.4, 118.1, 21.2, 17.1; HRMS (ESI) *m/z* calculated for $C_{16}H_{17}N_2$ $(M + H)^+$ 237.1392, found 237.1391.

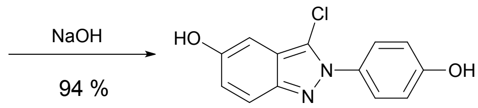
4. Application: Synthesis of Selective Ligand for Estrogen Receptor β

The procedure mainly contains two-step independent reactions from the starting material 1*H*-indazol-5-ol **(7p)**.

General synthetic route to Selective Ligand for Estrogen Receptor β



7p **8r** **12**



4

Step 1: A sealed tube was charged with 1*H*-indazol-5-ol **7p** (26.8 mg, 0.20 mmol), hypervalent iodine reagents **8** (117.2 mg, 0.24 mmol), CuCl (1.0 mg, 0.01 mmol). The tube was evacuated and backfilled with argon before 1.0 mL THF was added. The reaction mixture was stirred at 80 ^{o}C for 12 h. After cooling to room temperature, trimethylamine (70.0 µl, 0.50 mmol) and acetyl chloride (35.6 µl, 0.50 mmol) were directly added in the reaction by syringe. The reaction mixture was stirred at room temperature for 4 h before *N*-Chlorosuccinimide (26.8 mg, 0.20 mmol) was weighed into the reaction system and stirred at room temperature for another 4 h. After that, the mixture was diluted with EtOAc, filtered through a plug of diatomite, concentrated under vacuum and the residue was purified by chromatography on silica with a gradient eluent of petroleum ether and ethyl acetate (20:1~5:1) to give the corresponding product **12** as a white solid in 75% yield.

Step 2: To a 68.9 mg of **12** (0.20 mmol, 1.0 eq) in 6.0 mL of THF/H_2O (2:1) was added 75.2 mg of NaOH (2.00 mmol, 10.0 equiv) in 1.0 mL of water. After 0.5 h, 1M HCl was added to make the pH ≈ 4.0. The aqueous layer was extracted with DCM (20 ml × 3). The combined organic layer was dried over Na_2SO_4, filtered and evaporated. The crude residue was then recrystallized from $CHCl_3$ to obtain the desired compound **4** as a pale pink solid in 94% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.00 (s, 1H), 9.62 (s, 1H), 7.56-7.54 (d, J = 9.2 Hz, 1H), 7.47-7.45 (d, J = 8.8 Hz, 2H), 7.00-6.98 (dd, J = 9.2 Hz, 1H), 6.95-6.94 (d, J = 8.8 Hz, 2H), 6.71-6.71 (d, J = 1.6 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.5, 153.4, 144.4, 130.2, 127.4, 122.6, 119.9, 119.8, 116.3, 116.0, 97.5; HRMS (ESI) *m/z* calculated for $C_{13}H_{10}ClN_2O_2$ $(M + H)^+$ 261.0431, found 261.0424.

5. Computational Calculations

Computational Details

All DFT calculations at the level of B3LYP/6-31+g(d,p) with the SMD solvation model of CH_2Cl_2 at 323.15 K were performed by Gaussian09 suite of Programs, Revision A.01.[3] The key word "5d" was specified to use 5 pure d functions. Geometry optimizations were carried out without any constraint. Frequency calculations were performed for each stationary structure at the same level to make sure that it is an equilibrium structure or a transition state and to provide free energies and enthalpies at 323.15 K. All the free energies correspond to the reference state of 1 mol/L, 323.15 K, dissolved in dichloromethane.

Cartesian Coordinates and Output Energies

CuOTf

0 1

Cu	-2.36058300	-0.31129300	-0.00211000
O	-0.77267500	0.54097300	-0.74442500
S	0.48517200	0.91399100	0.02156600
O	1.33088300	1.85240500	-0.72971100
O	0.25486000	1.18041100	1.45188700
C	1.44503700	-0.70180200	-0.00119400
F	0.75680000	-1.67120100	0.63422000
F	1.67280700	-1.10819300	-1.26159100
F	2.62810500	-0.55125800	0.61640300

Sum of electronic and thermal Enthalpies= -2601.811099

Sum of electronic and thermal Free Energies= -2601.864008

1H-indazole

0 1

C	1.64098800	1.10646900	-0.00002200
C	0.26384000	-0.67433900	-0.00005000
C	0.25823000	0.74657900	-0.00003500
H	2.08471000	2.09375000	-0.00007700
C	-0.92391100	-1.42965200	-0.00005600
C	-0.97085100	1.44029800	0.00001500
C	-2.11706100	-0.72007600	0.00001000
H	-0.90706100	-2.51538900	-0.00007700
C	-2.14415000	0.69973500	0.00003800
H	-0.99500900	2.52655900	-0.00001900
H	-3.05744900	-1.26443100	0.00004200
H	-3.10384600	1.20861500	0.00007900
N	1.57981100	-1.04276800	-0.00004300
N	2.41545000	0.03029300	0.00006000
H	1.96932100	-1.97585300	0.00053200

Sum of electronic and thermal Enthalpies= -379.752079

Sum of electronic and thermal Free Energies= -379.793580

2H-indazole

0 1

C	-1.61869900	1.09215600	0.00000000
C	-0.27097100	-0.70072900	0.00001300
C	-0.26188800	0.73814000	-0.00005500
H	-2.12416800	2.04714700	0.00010400
C	0.94786500	-1.43058400	0.00009700
C	0.96836600	1.44802700	-0.00003900
C	2.12577900	-0.71277600	0.00011200
H	0.94215700	-2.51693200	0.00005900
C	2.13892600	0.71786500	0.00004400
H	0.98418100	2.53451800	-0.00005200
H	3.07476500	-1.24246300	0.00012400
H	3.09584100	1.23247200	0.00005500
N	-1.53527000	-1.18451900	-0.00028400
N	-2.29918800	-0.07165100	0.00007200
H	-3.30783500	-0.17415000	0.00016400

Sum of electronic and thermal Enthalpies= -379.746162

Sum of electronic and thermal Free Energies= -379.787472

int0

0 1

Cu	-0.43094500	-0.30910100	-0.16940600
C	0.55640900	1.37212000	-0.11880400
C	0.86895600	1.90618100	-1.34186200
C	0.78491500	1.89304400	1.13264500
C	1.47816200	3.17621300	-1.28303200
H	0.66329800	1.42398700	-2.29124000
C	1.38931300	3.16232400	1.13265300
H	0.53523300	1.38701100	2.05867700
C	1.74144000	3.81190600	-0.06187100
H	1.73702300	3.65862000	-2.22202100
H	1.59020700	3.63107900	2.09305700
C	2.39623300	5.17273900	-0.02124900
H	1.71888200	5.91888200	0.41026300
H	3.29879900	5.15583800	0.59972800
H	2.67737000	5.50878100	-1.02278600
O	-2.28300800	-1.73402000	-0.19245900
S	-3.04830700	-0.55288500	-0.68786800
O	-3.95522100	-0.69771600	-1.81823500
O	-2.01439000	0.58328800	-0.82783000
C	-4.10941600	0.01151000	0.76020100

F	-4.98773200	-0.94965900	1.06050800
F	-3.33409300	0.24927400	1.82471800
F	-4.76577800	1.12873300	0.43492300
O	0.98197400	-1.22047500	0.62919300
S	2.01673800	-2.08717000	-0.13917000
O	1.89554900	-1.94194300	-1.59229800
O	2.11023600	-3.41962300	0.45690400
C	3.61789800	-1.22468700	0.33832600
F	3.63280100	0.03298900	-0.12009700
F	3.75722500	-1.20396400	1.67011800
F	4.64836800	-1.89332700	-0.19734000

Sum of electronic and thermal Enthalpies= -3834.028428

Sum of electronic and thermal Free Energies= -3834.126069

int1-1

0 1

Cu	0.26317200	-0.00090200	-0.08297100
C	1.15523600	1.69092800	0.30009300
C	1.76747100	2.36496300	-0.73195100
C	1.17157100	2.04237200	1.63395400
C	2.51774800	3.49635900	-0.36386900
H	1.70771400	2.05339500	-1.76917400
C	1.93401300	3.17640900	1.95713600
H	0.64861300	1.48527800	2.40439200
C	2.61173100	3.91264500	0.97164500
H	3.03326400	4.04871000	-1.14539600
H	1.98711200	3.48102600	2.99961100
C	-1.58930100	1.89820000	-1.36834900
C	-3.30564900	1.85982500	0.09023300
C	-2.87758200	2.43760200	-1.13594500
H	-0.89040400	2.08664700	-2.17091100
C	-4.56748900	2.13372300	0.64919500
C	-3.72240500	3.33568300	-1.82857200
C	-5.37420500	3.01387800	-0.05342900
H	-4.88698300	1.67965500	1.58124500
C	-4.95939700	3.61217300	-1.27628900
H	-3.40526600	3.78744900	-2.76321500
H	-6.35648400	3.25814800	0.34063400
H	-5.63484800	4.29658700	-1.78042800
C	3.43102900	5.12355000	1.35059600
H	2.85161600	5.81626000	1.97079200
H	4.31481800	4.83059400	1.93014300
H	3.77454800	5.66278800	0.46357700
O	-0.76148900	-1.80629300	-0.22213900

S	-1.51895700	-2.44457600	0.92071600
O	-0.89470600	-3.64420200	1.48540700
O	-2.03082400	-1.43884100	1.88794000
C	-3.05628400	-3.06140600	0.03806200
F	-2.73536300	-3.96341800	-0.90028200
F	-3.88924800	-3.63613500	0.92033100
F	-3.70027000	-2.03929500	-0.55165400
N	-2.29219300	1.05934300	0.53120000
N	-1.28185000	1.06086700	-0.38082600
H	-2.32803400	0.29996800	1.21903300
O	1.89354500	-0.91568900	0.31126800
S	2.72028100	-1.69055900	-0.72649600
O	2.80671900	-3.12043400	-0.42028700
O	2.43305100	-1.27294800	-2.10559200
C	4.43455600	-1.02027500	-0.34796400
F	4.48334100	0.30492900	-0.54982200
F	4.77373000	-1.27415200	0.92419900
F	5.32923900	-1.60883900	-1.15769400

Sum of electronic and thermal Enthalpies= -4213.814674

Sum of electronic and thermal Free Energies= -4213.931655

int1-2

0 1

Cu	-0.06691200	-0.07493800	-0.01225800
C	-1.21807900	1.35699900	-0.66972400
C	-2.11496400	1.96752600	0.17876400
C	-1.13936000	1.54635900	-2.03625800
C	-3.05900500	2.81654700	-0.42586500
H	-2.12655500	1.80349200	1.25033700
C	-2.10041800	2.39884300	-2.60113600
H	-0.39636100	1.06189200	-2.66148300
C	-3.06587000	3.04160100	-1.80989000
H	-3.79755500	3.30069600	0.20802900
H	-2.07950100	2.56072400	-3.67625400
C	-4.08777400	3.95460900	-2.44529800
H	-3.60359000	4.73724200	-3.04030900
H	-4.74576100	3.39518400	-3.12096000
H	-4.71300600	4.43787400	-1.68967000
O	1.29911500	-1.66157900	0.11642200
S	2.24491500	-2.02374800	-1.00140100
O	2.13752300	-3.40764800	-1.47273400
O	2.32594800	-0.96866700	-2.04807600
C	3.90755100	-1.93396900	-0.13201800
F	3.96037200	-2.81024500	0.88143900

F	4.89833000	-2.21495900	-0.99391500
F	4.11081900	-0.69826700	0.36033000
O	-1.51790800	-1.30782800	-0.26597000
S	-1.92416200	-2.35286200	0.78180400
O	-1.71324500	-3.73010100	0.32722000
O	-1.51360400	-1.98284400	2.14447100
C	-3.78881300	-2.12483000	0.74965200
F	-4.12485300	-0.88690400	1.14762500
F	-4.27319900	-2.32363000	-0.48527200
F	-4.36079400	-3.00955200	1.58249400
C	1.31423300	2.36744600	1.01173800
C	2.23509400	3.31392900	0.47090000
C	0.68038100	2.58448900	2.25018000
C	2.66357900	2.75315700	-0.74935700
H	2.19312300	0.85510000	-1.59015100
C	2.54094600	4.50029300	1.17757800
C	0.99061100	3.75809700	2.91602500
H	-0.01374500	1.86203100	2.66536600
H	3.38610200	3.08777100	-1.48088600
C	1.90935200	4.70879900	2.38899000
H	3.25431600	5.21448900	0.77844900
H	0.52193100	3.96013100	3.87480900
H	2.11848200	5.60873400	2.95915100
N	2.02718700	1.59174200	-0.89337100
N	1.22524600	1.29620000	0.16507900

Sum of electronic and thermal Enthalpies= -4213.812227

Sum of electronic and thermal Free Energies= -4213.928502

ts-1

0 1

Cu	0.34411000	-0.11656900	-0.03422700
C	0.74805000	1.73571000	0.58189900
C	1.65462500	2.46199100	-0.17333700
C	0.50682400	1.90004900	1.93309500
C	2.46847400	3.35130800	0.53467900
H	1.76448400	2.33330500	-1.24433000
C	1.35002900	2.79906800	2.60457900
H	-0.26517100	1.36019100	2.46947700
C	2.33194000	3.53250200	1.92405200
H	3.22040400	3.91252100	-0.01415100
H	1.21520200	2.93031200	3.67475200
C	-1.19259000	1.84651100	-1.58001000
C	-3.12255700	1.87995700	-0.42074500
C	-2.52689200	2.29413900	-1.64552300

H	-0.37628600	1.98261700	-2.27488300
C	-4.47659000	2.12184300	-0.12723600
C	-3.29242300	2.99628000	-2.60768300
C	-5.20062500	2.80577600	-1.08968700
H	-4.92439400	1.79072100	0.80350900
C	-4.61906000	3.24315500	-2.31423900
H	-2.84556400	3.32218300	-3.54143300
H	-6.24953600	3.01915000	-0.90585800
H	-5.23962700	3.77719800	-3.02711200
C	3.22754400	4.49919800	2.65795300
H	4.24830300	4.10293900	2.72655800
H	3.28836400	5.45943700	2.13466400
H	2.86924000	4.68079600	3.67487700
O	-0.81084700	-1.89097600	0.09929400
S	-1.68993500	-2.23285400	1.27319200
O	-1.22708300	-3.35426900	2.09797200
O	-2.15482500	-1.02356500	2.00831400
C	-3.23454600	-2.86991300	0.41780300
F	-2.95702000	-3.96072300	-0.31128700
F	-4.16873600	-3.18965700	1.32860700
F	-3.74354900	-1.92968400	-0.39844900
N	-2.15655800	1.25226500	0.31078000
N	-1.00586300	1.19838000	-0.42124300
O	2.11021700	-1.00396400	0.11067600
S	2.84350700	-1.61323600	-1.07351000
O	3.00272700	-3.07020600	-0.97918200
O	2.42229500	-1.04734900	-2.36872600
C	4.57162500	-0.93334000	-0.79422600
F	4.57017500	0.41055300	-0.84689100
F	5.40335500	-1.39182600	-1.74528500
F	5.04828800	-1.30969300	0.40333800
H	-2.28027300	0.56855900	1.06951800

Sum of electronic and thermal Enthalpies= -4213.808054

Sum of electronic and thermal Free Energies= -4213.922919

ts-2

0 1

Cu	0.04611300	-0.14907100	-0.19875000
C	0.86994200	1.23507000	0.99994900
C	2.04767400	1.84178800	0.60197300
C	0.48410100	1.02376900	2.31371800
C	2.95318900	2.16558800	1.61993300
H	2.29698900	2.03534100	-0.43344600
C	1.42147900	1.36049000	3.30106800

H	-0.47181200	0.59531500	2.59340600
C	2.66060600	1.93009300	2.97401300
H	3.90442200	2.61031200	1.33856800
H	1.16193800	1.17686200	4.34027400
C	-2.43329600	3.02483000	0.15428500
C	3.66551400	2.27088900	4.04634000
H	3.19108900	2.34454100	5.02885900
H	4.43882100	1.49450100	4.10671400
H	4.17172600	3.21773500	3.83240000
O	-1.70391000	-1.48547600	-0.06672300
S	-2.75092800	-1.63538200	0.99139300
O	-2.65013200	-2.83876000	1.82636100
O	-3.01479100	-0.36051900	1.72487300
C	-4.30781400	-1.88854100	-0.02465400
F	-4.19772500	-2.98675800	-0.78799400
F	-5.37429400	-2.03375100	0.77963800
F	-4.52603200	-0.83127800	-0.82800000
N	-1.90225200	1.84987700	0.46904500
N	-0.79875200	1.55682400	-0.28447500
O	1.32112200	-1.65265300	-0.14091800
S	2.11389200	-2.16301200	-1.33415900
O	1.89837400	-3.59070700	-1.60330700
O	2.10391500	-1.23542500	-2.48098400
C	3.86743300	-2.07323100	-0.66820600
F	4.19401700	-0.80748700	-0.35193900
F	4.73238800	-2.51209700	-1.59898900
F	4.00386400	-2.83306800	0.43023900
H	-2.31974800	1.10671300	1.06279400
C	-0.61731800	2.63849600	-1.12278600
C	-1.63909900	3.59557100	-0.86373100
C	0.34368100	2.84726700	-2.12661900
C	-1.70552300	4.79633000	-1.60385500
C	0.26250900	4.03816200	-2.83345900
H	1.10096600	2.10559400	-2.35485600
C	-0.74431100	5.00615500	-2.57597300
H	-2.49400600	5.51844600	-1.41762200
H	0.98594200	4.23163800	-3.61989800
H	-0.76214600	5.91684700	-3.16620400
H	-3.34102100	3.36857000	0.63204000

Sum of electronic and thermal Enthalpies= -4213.808783

Sum of electronic and thermal Free Energies= -4213.925558

P-1

0 1

C	3.16934800	1.32947600	0.12290700
C	2.75871000	-0.87642500	-0.09274200
C	3.80678300	0.07800600	0.05236900
H	3.56625500	2.32403500	0.26389900
C	3.01418700	-2.25782500	-0.20265100
C	5.15589300	-0.35031900	0.10160200
C	4.34183800	-2.64278100	-0.15735700
H	2.20963400	-2.97594000	-0.31608900
C	5.40340300	-1.70387600	-0.00528000
H	5.96086000	0.36840600	0.21657400
H	4.58668400	-3.69779800	-0.23872200
H	6.42502900	-2.06963100	0.02566900
O	-1.72269000	-3.51995100	0.25205300
S	-1.69969500	-2.04517300	0.30512800
O	-1.64349100	-1.43309500	1.65029600
O	-0.78316100	-1.40350600	-0.69366800
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Sum of electronic and thermal Enthalpies= -1612.045160

Sum of electronic and thermal Free Energies= -1612.133770

P-2

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Sum of electronic and thermal Enthalpies= -1612.045271

Sum of electronic and thermal Free Energies= -1612.135886

6. References

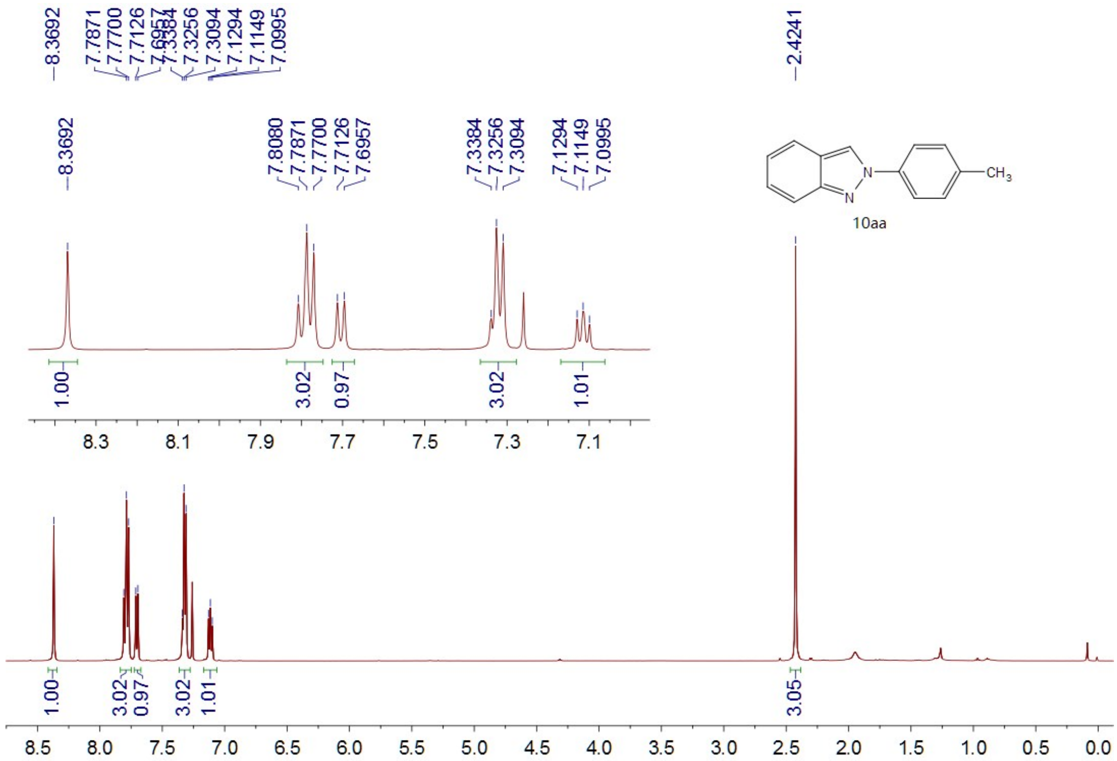
[1] M. Bielawski, B. Olofsson, *Chem. Commun.,* **2007,** 2521-2523.

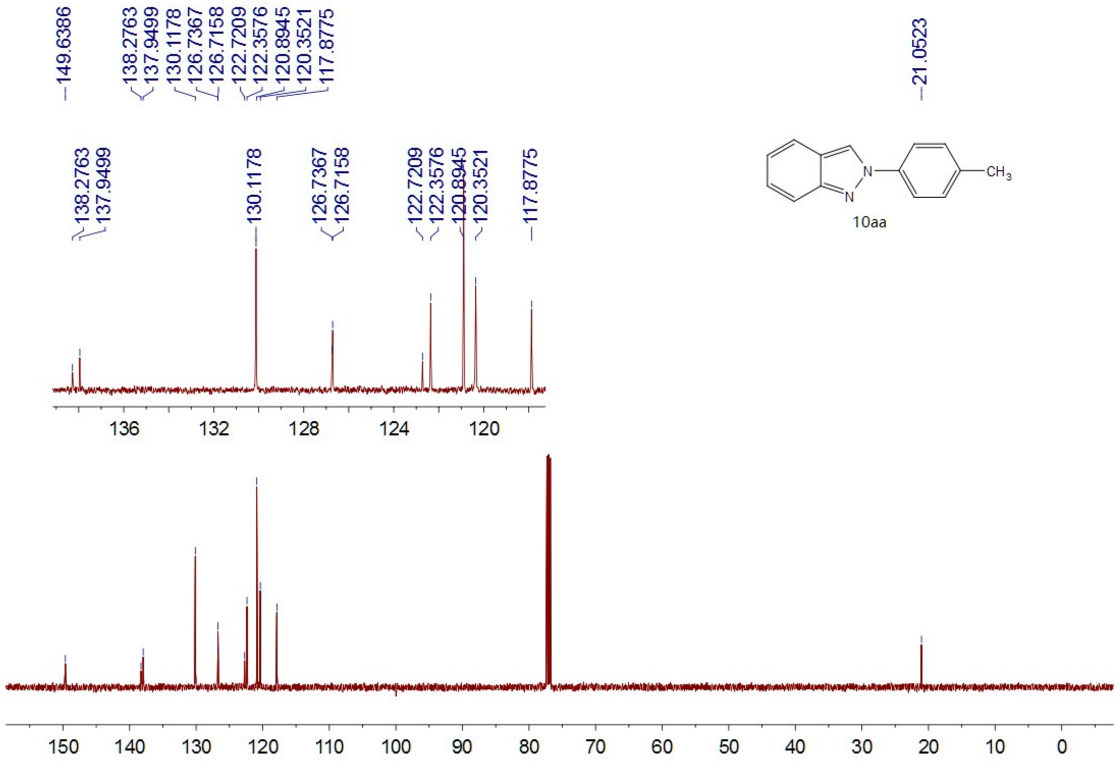
[2] D. Holt, M. J. Gaunt, *Angew. Chem. Int. Ed.,* **2015,** *54*, 7857-7861.

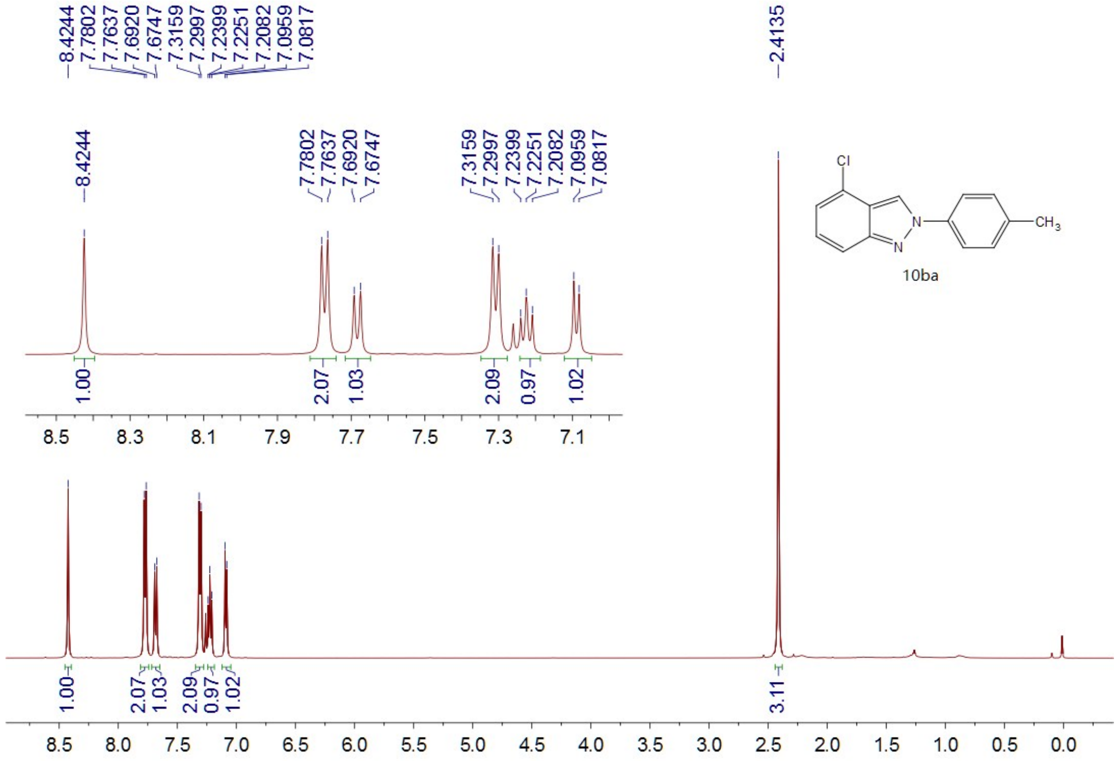
[3] Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman,

G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

7. Copies of ^{1}H and ^{13}C NMR spectrum of products



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1.02
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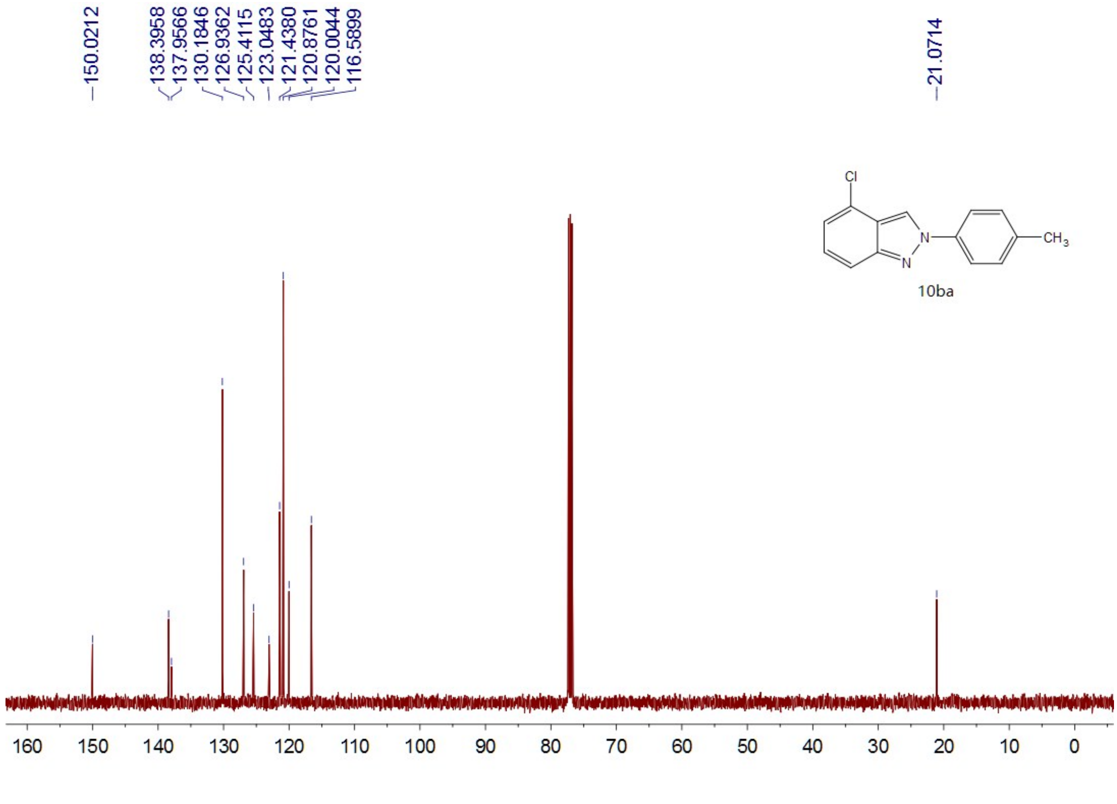
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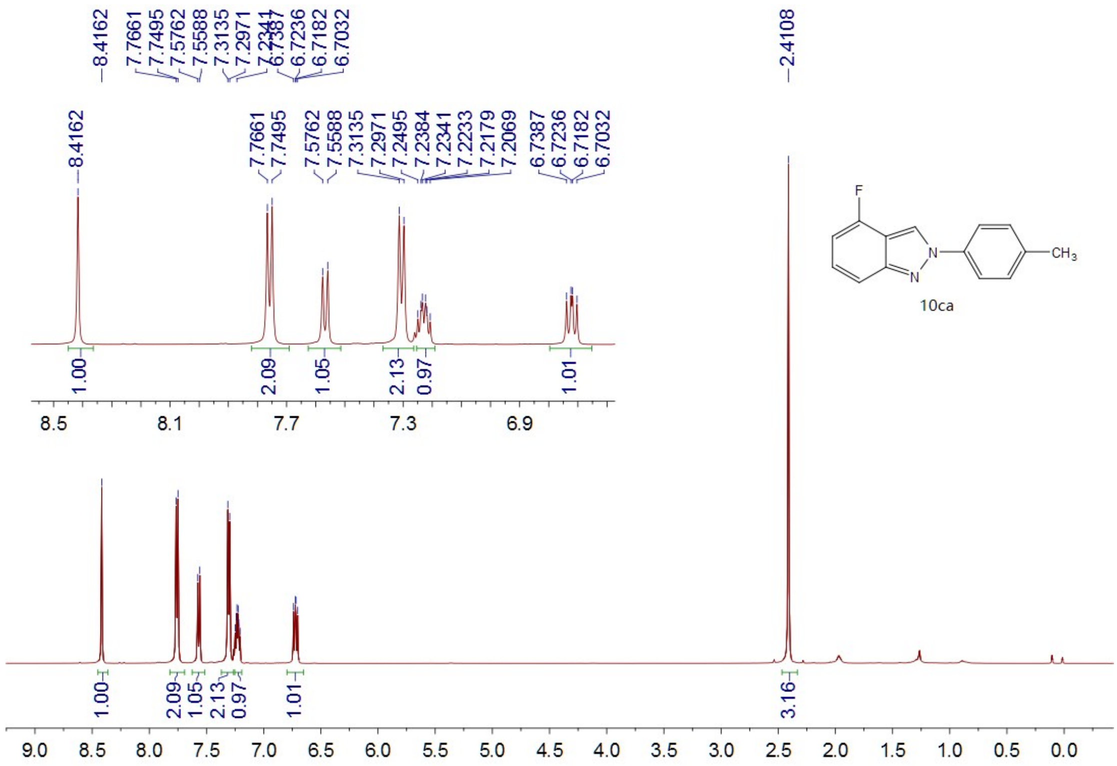

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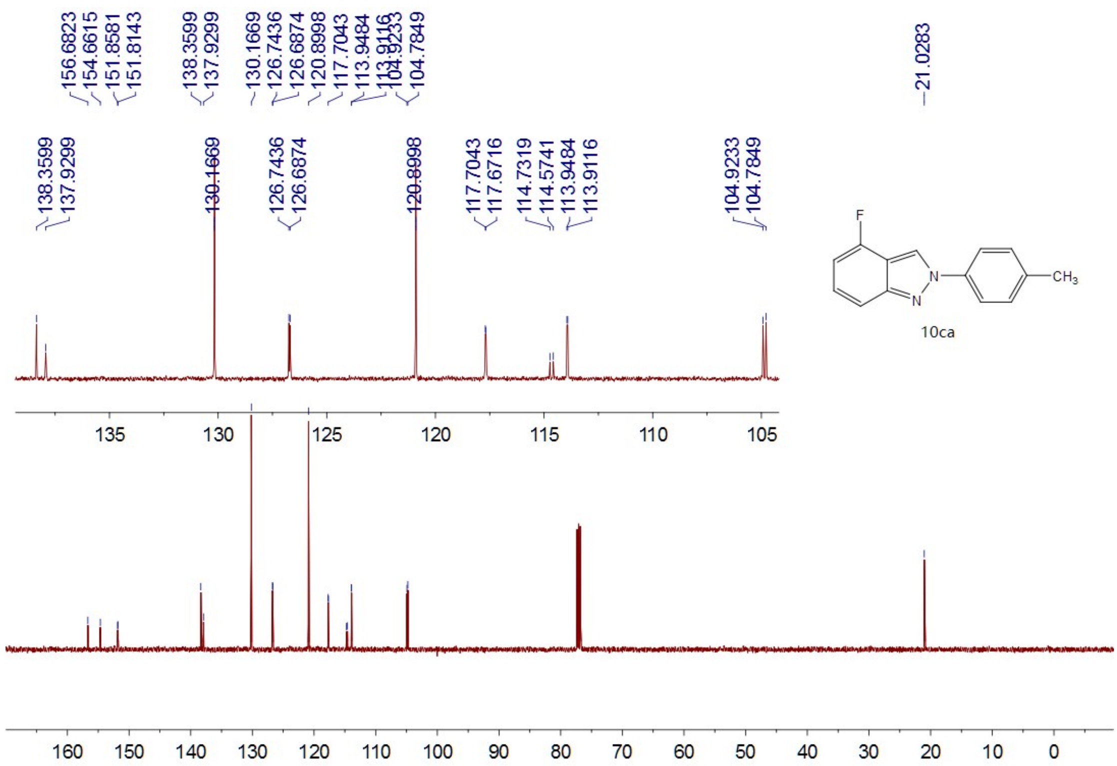

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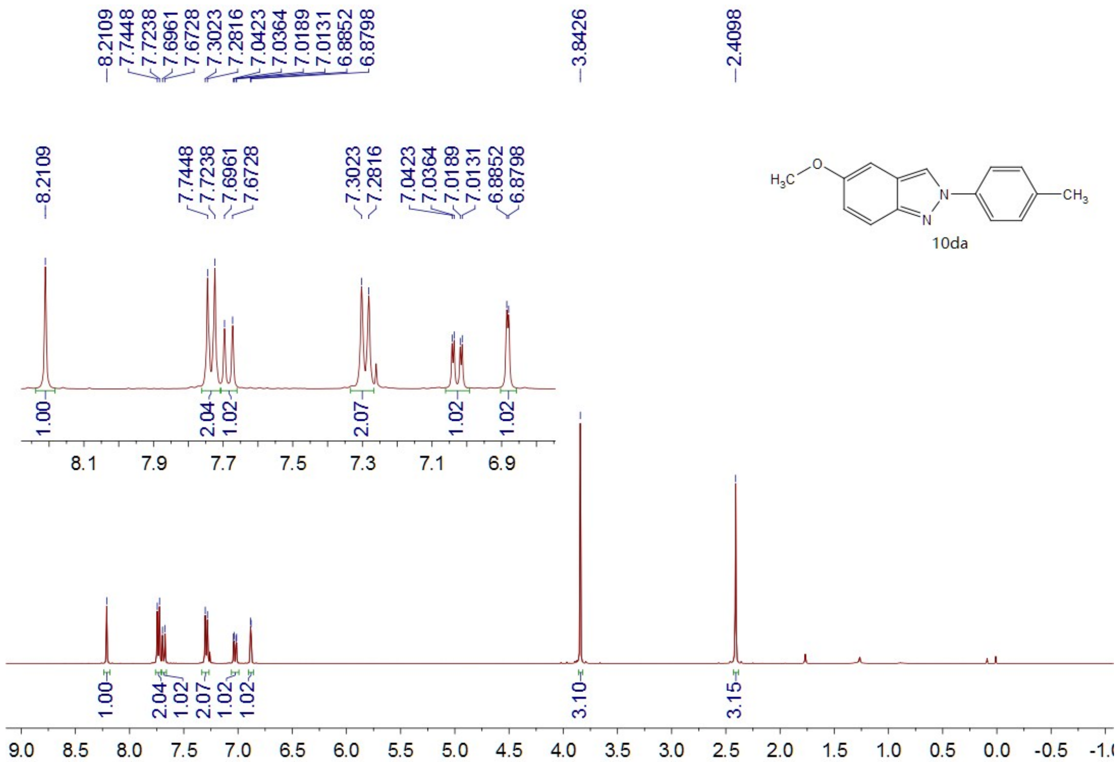
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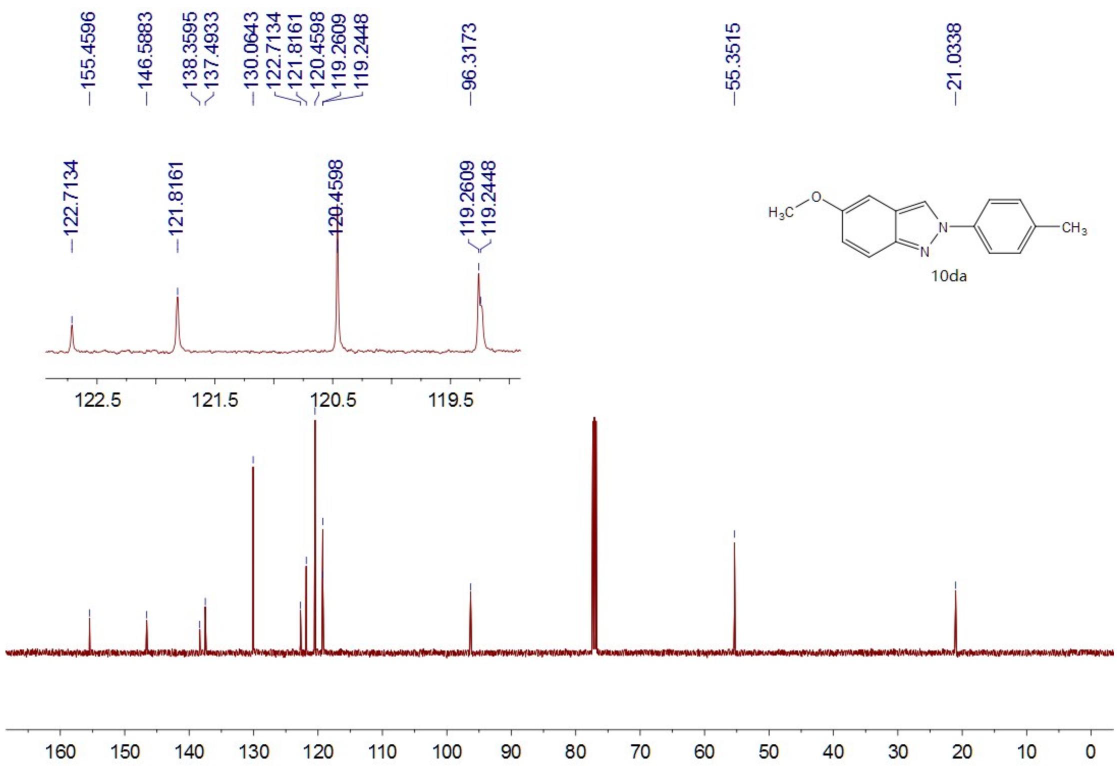
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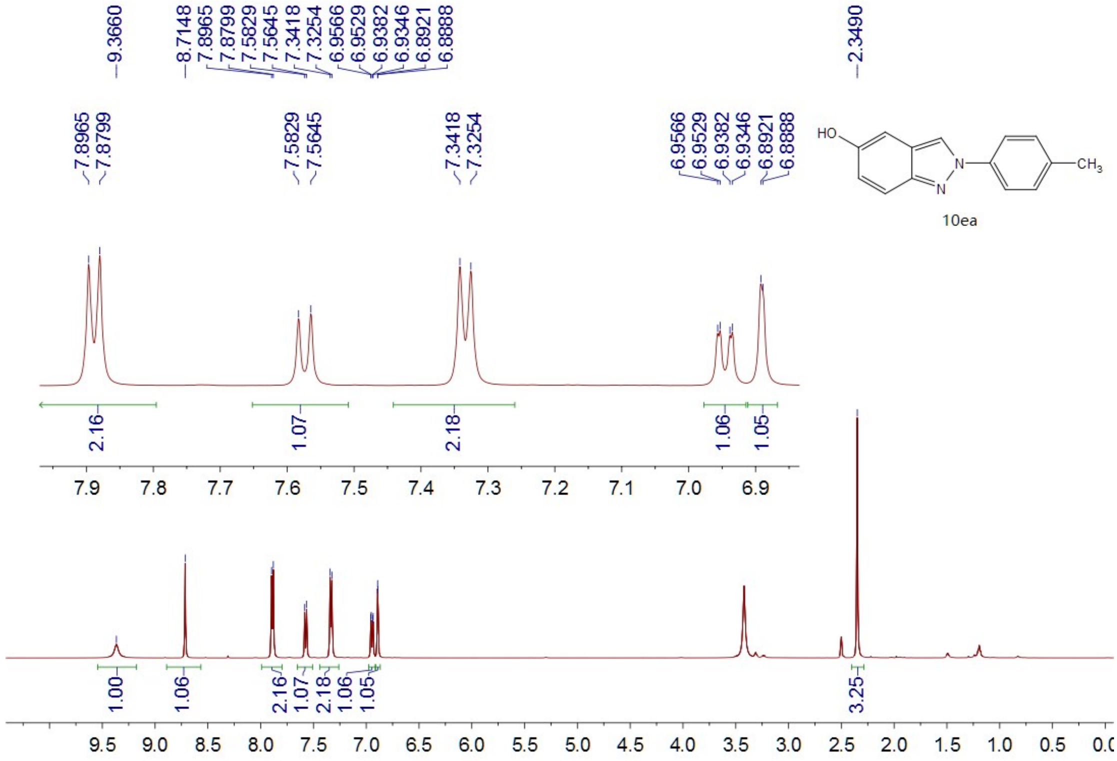
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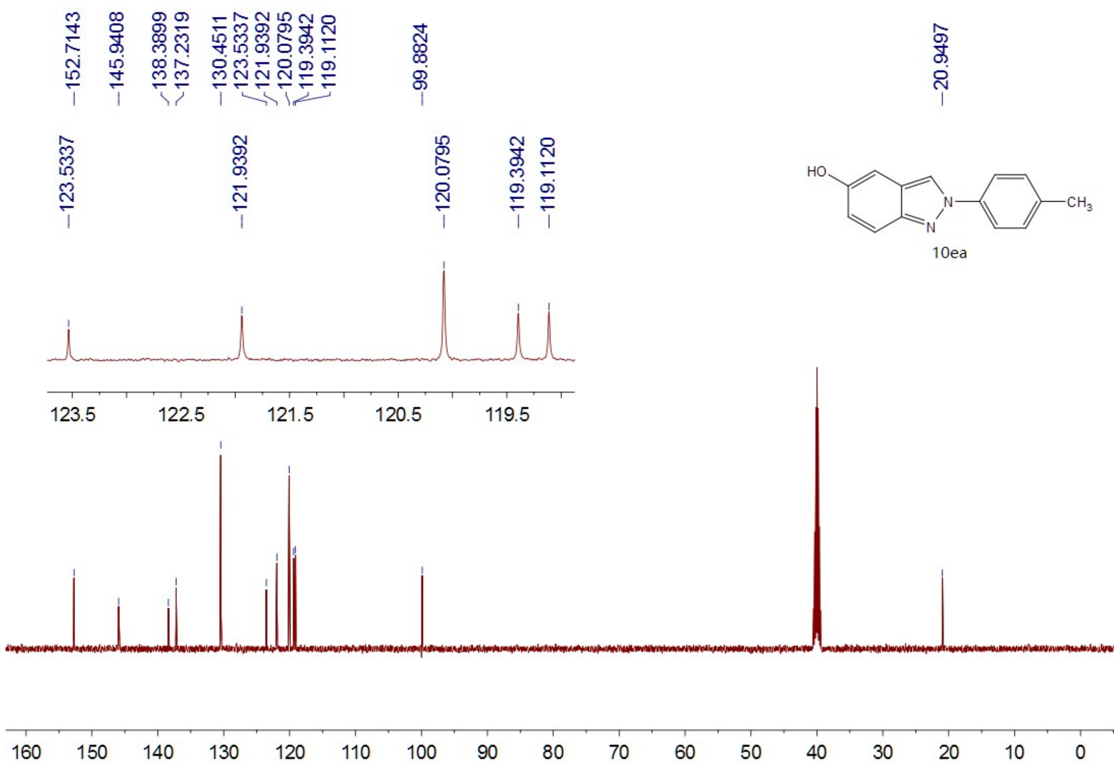
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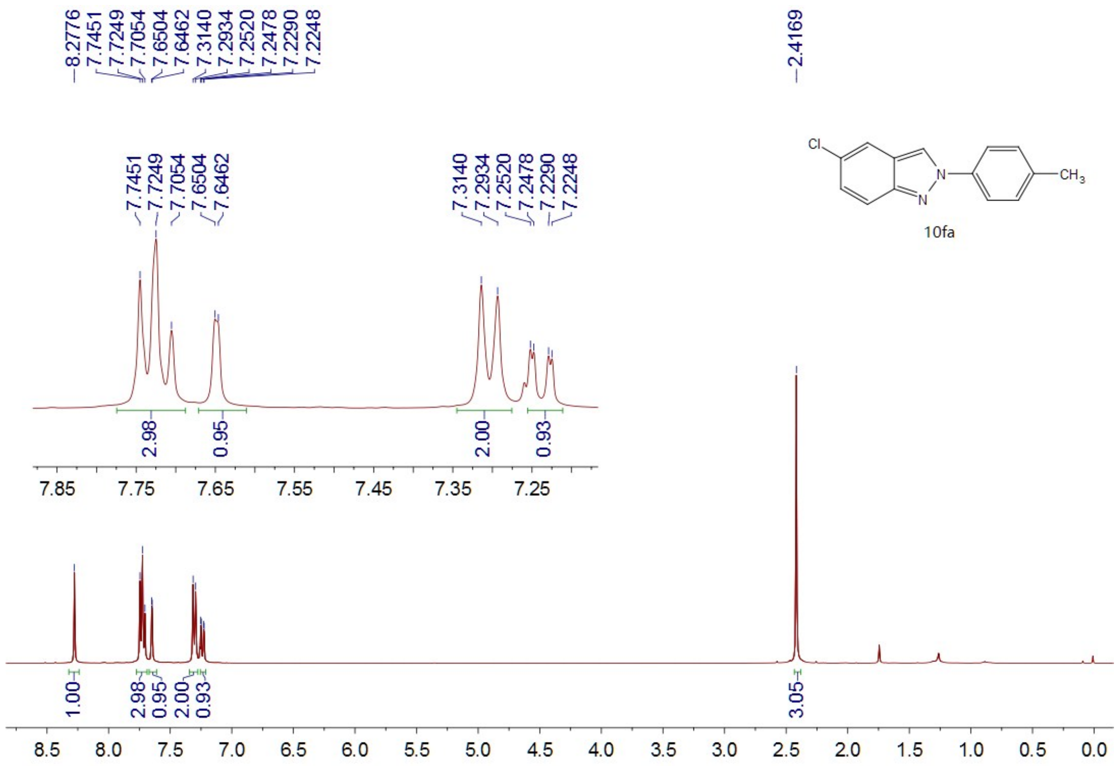
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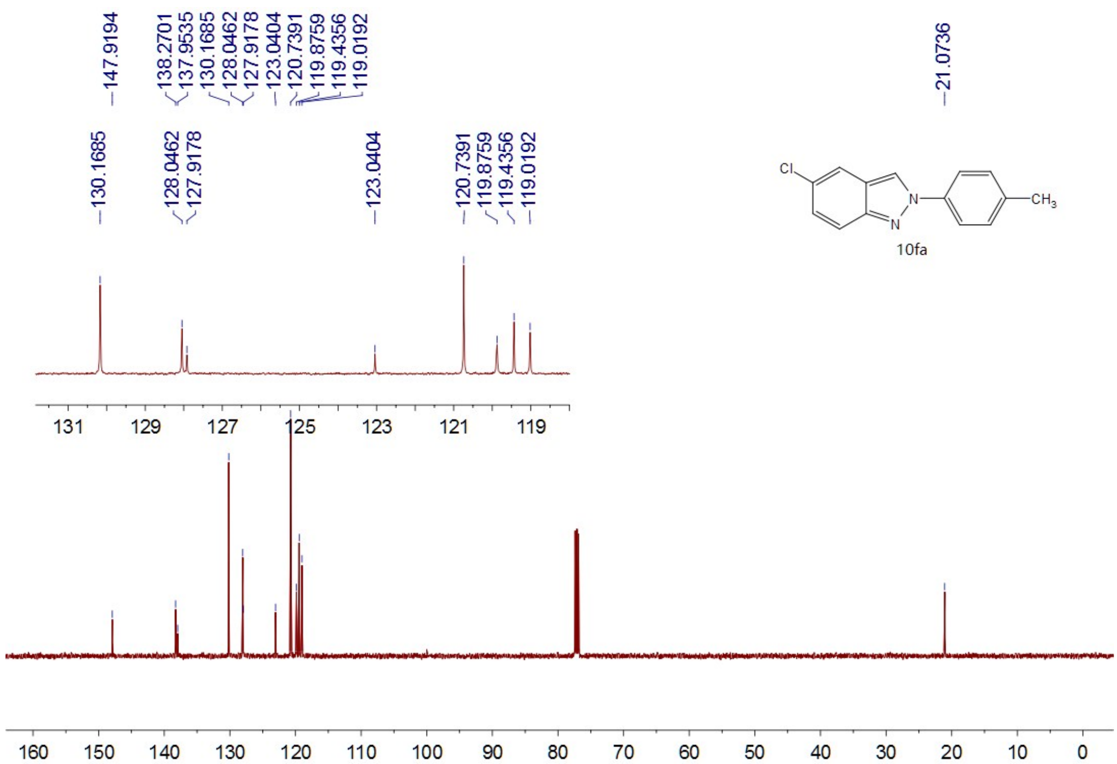
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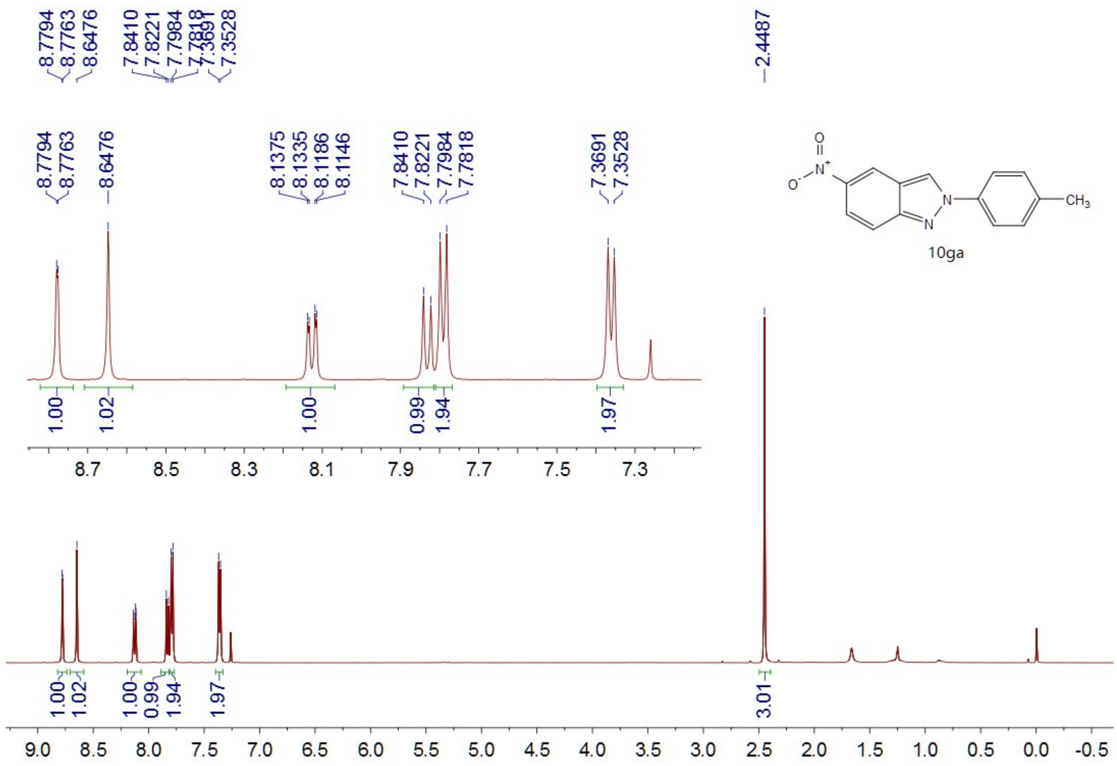
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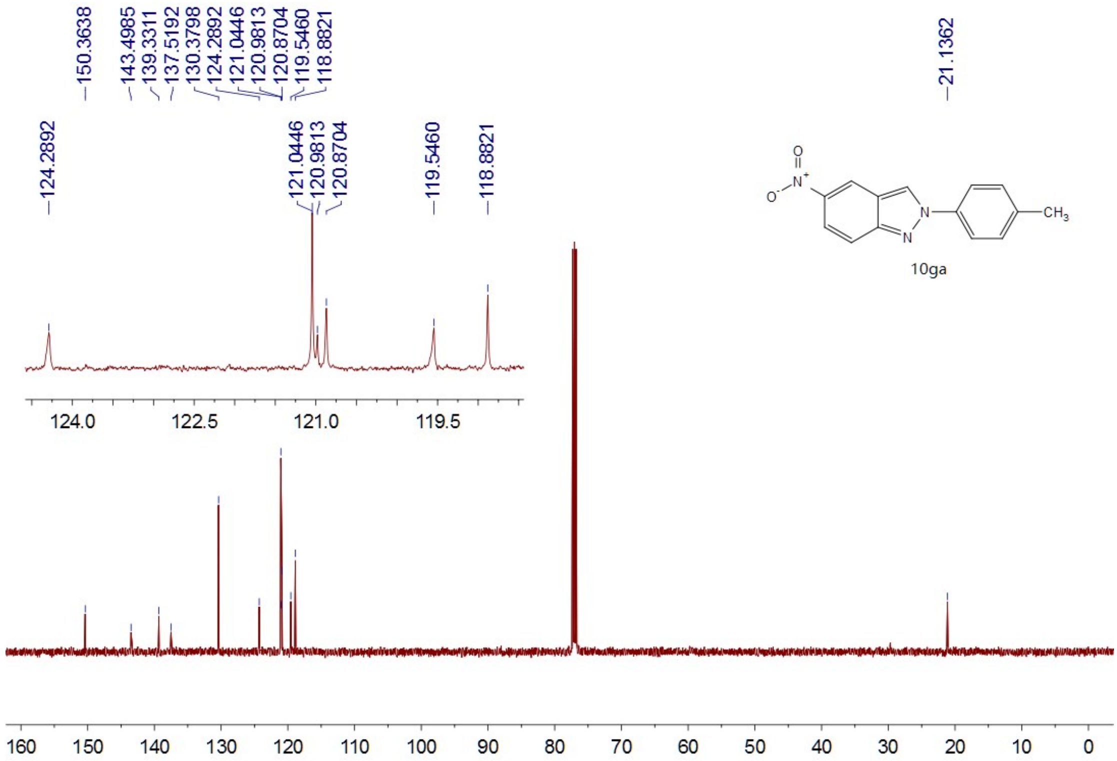
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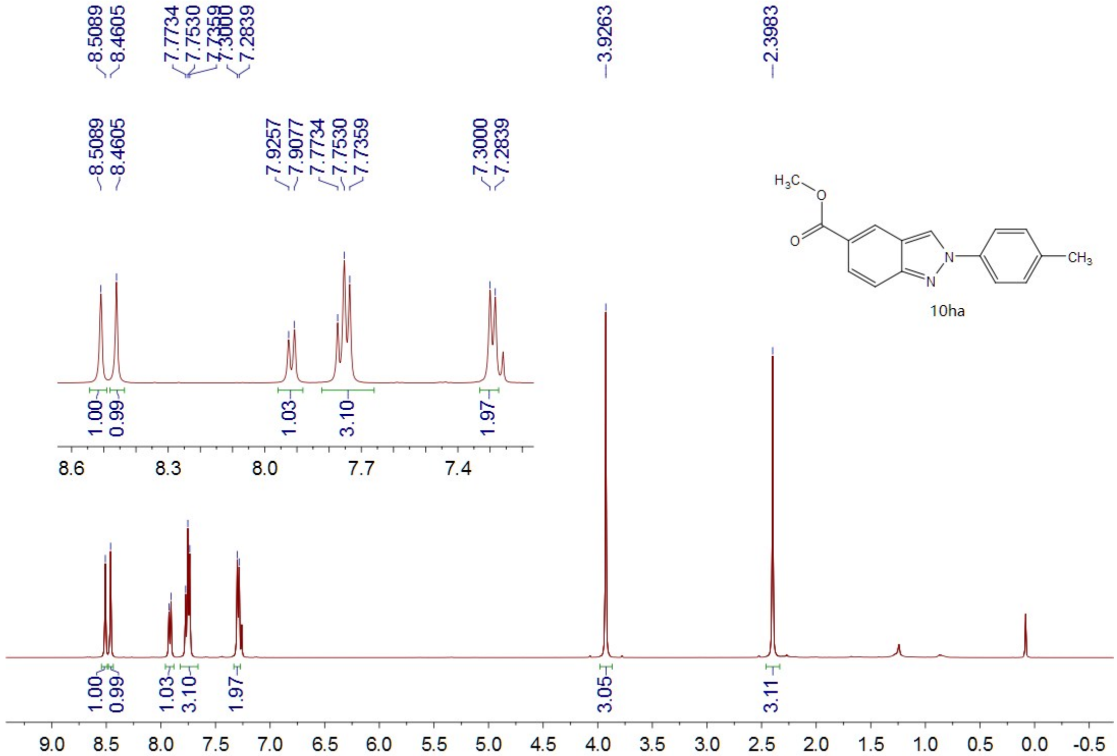
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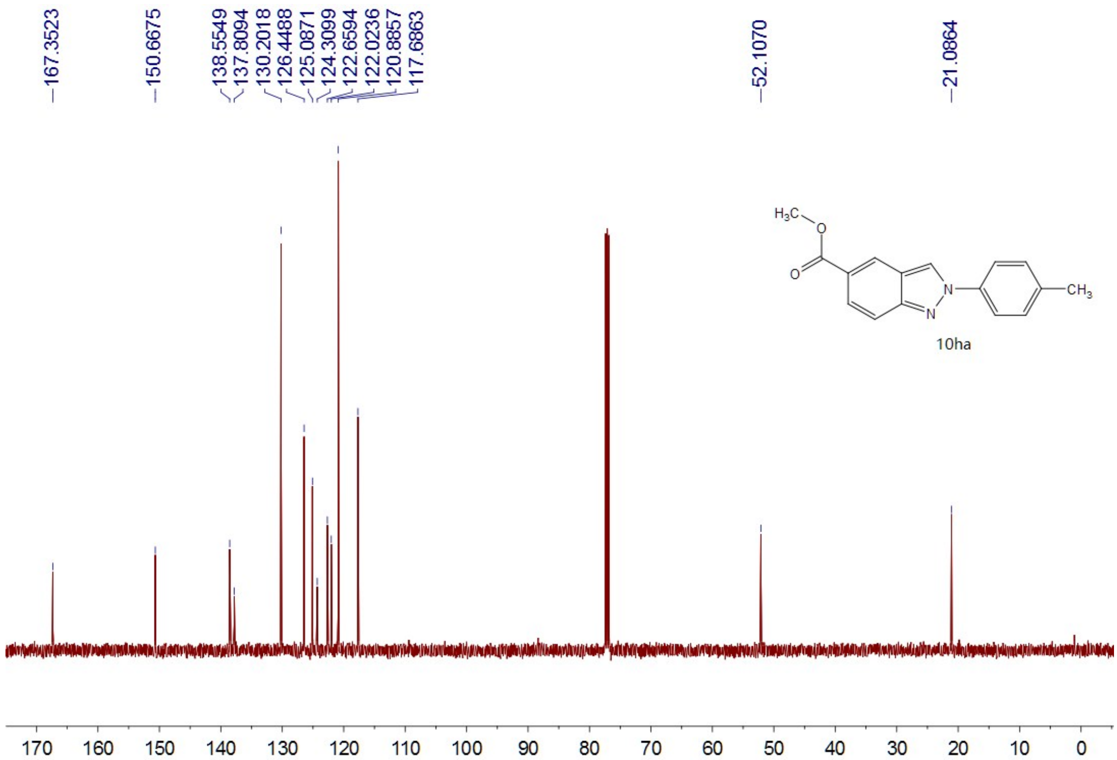
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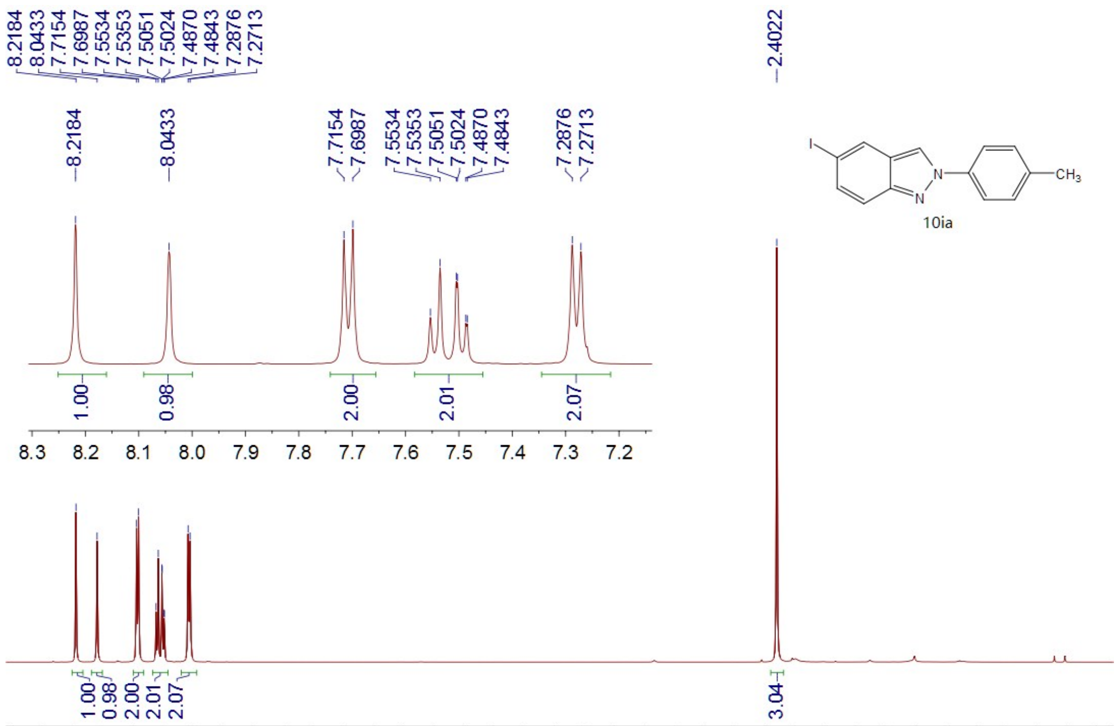

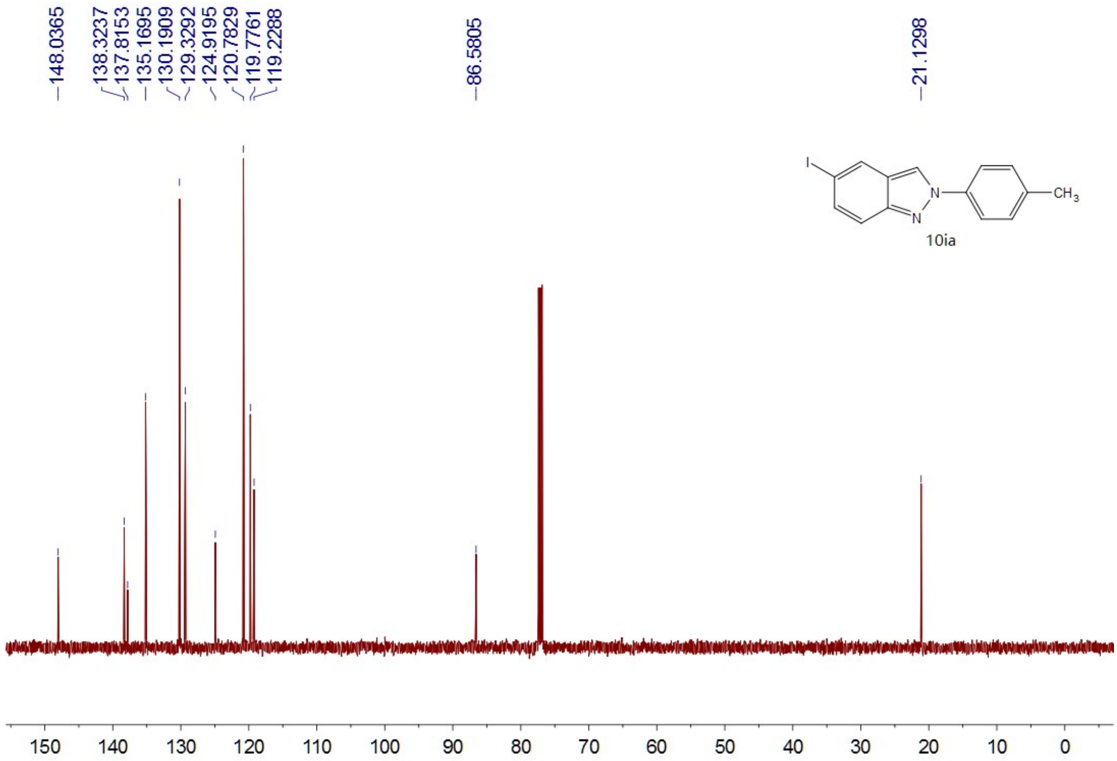

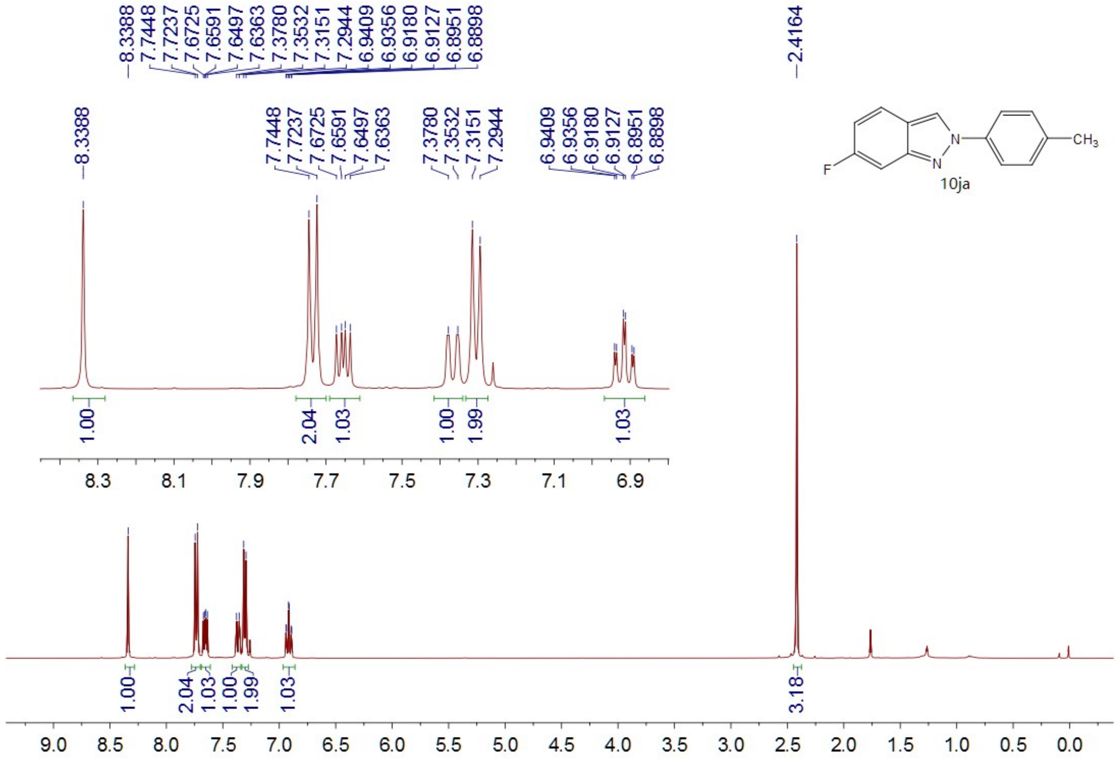
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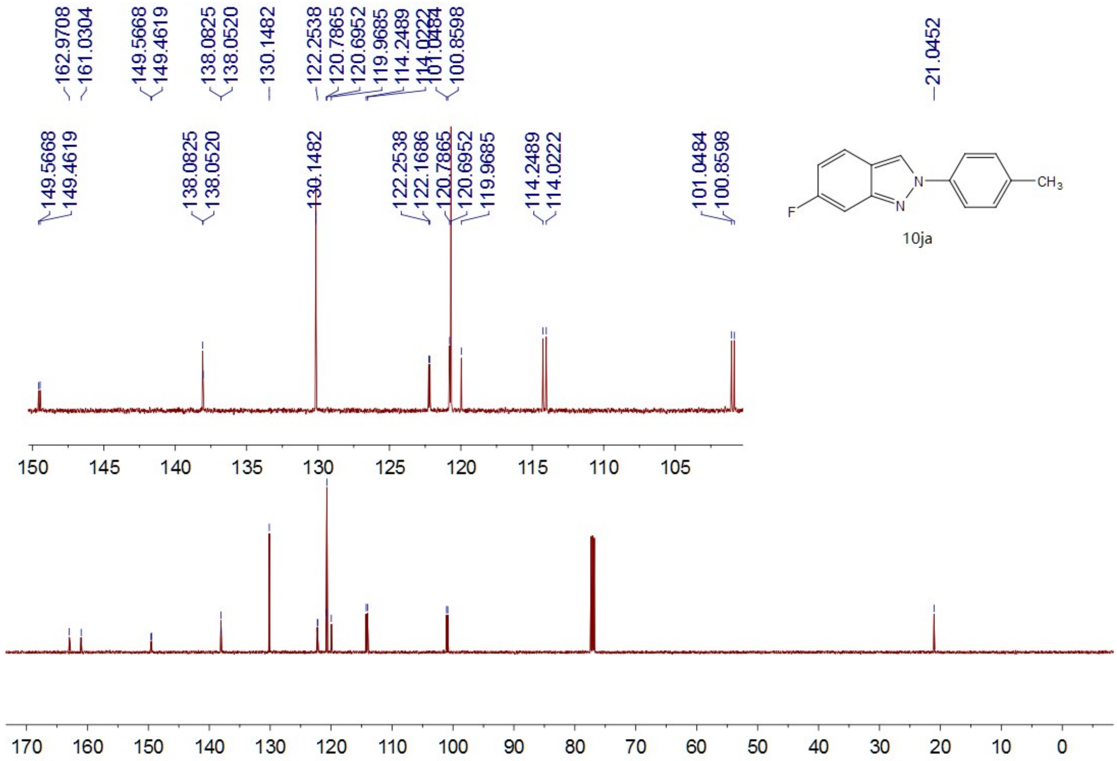
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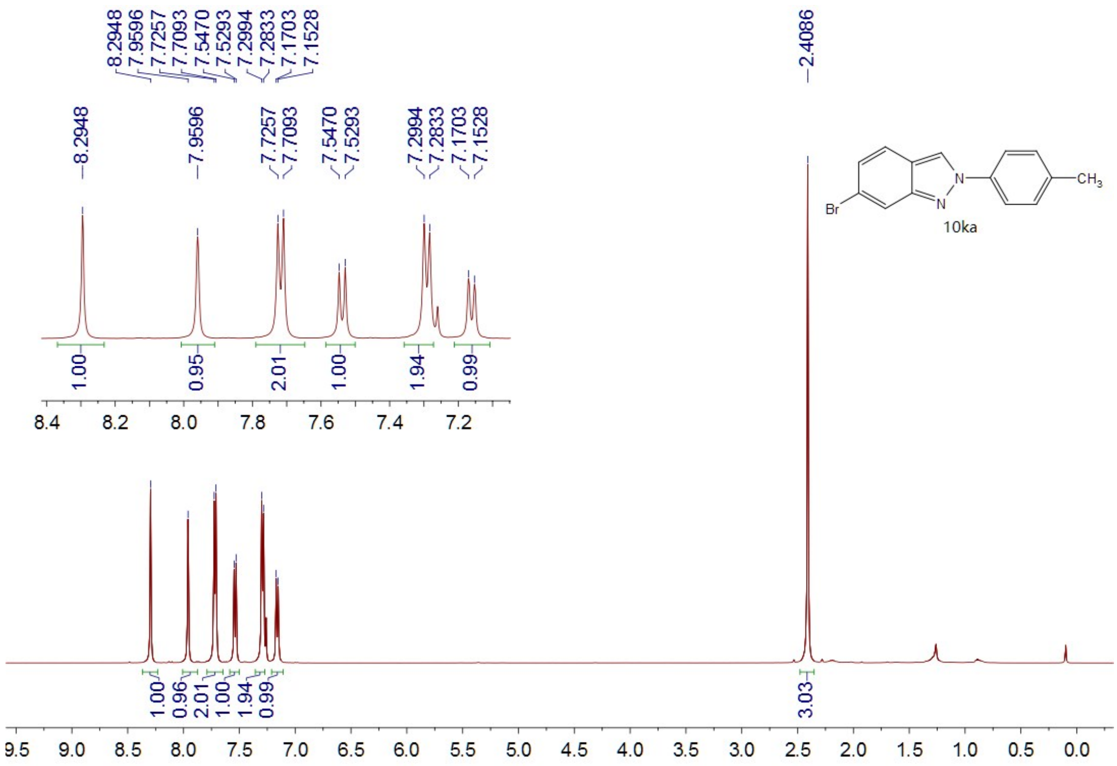

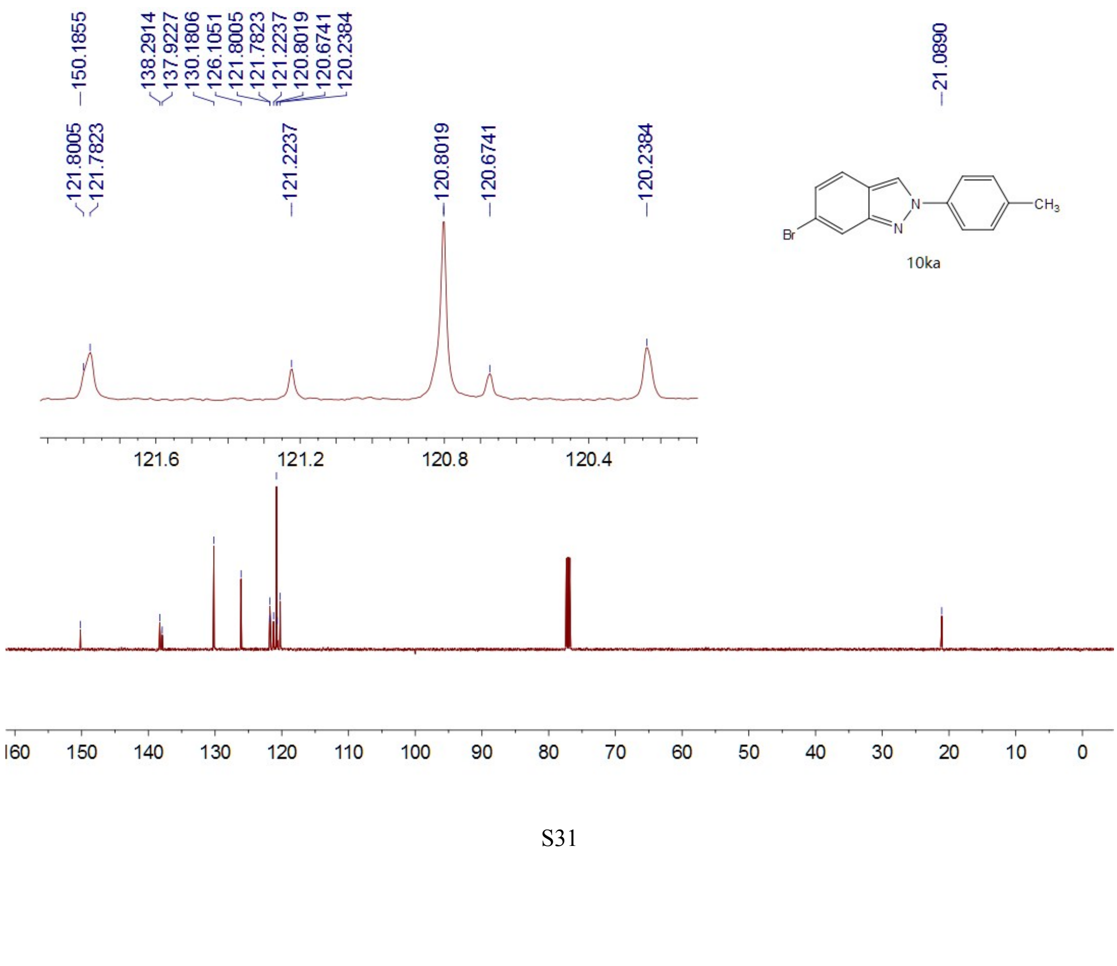

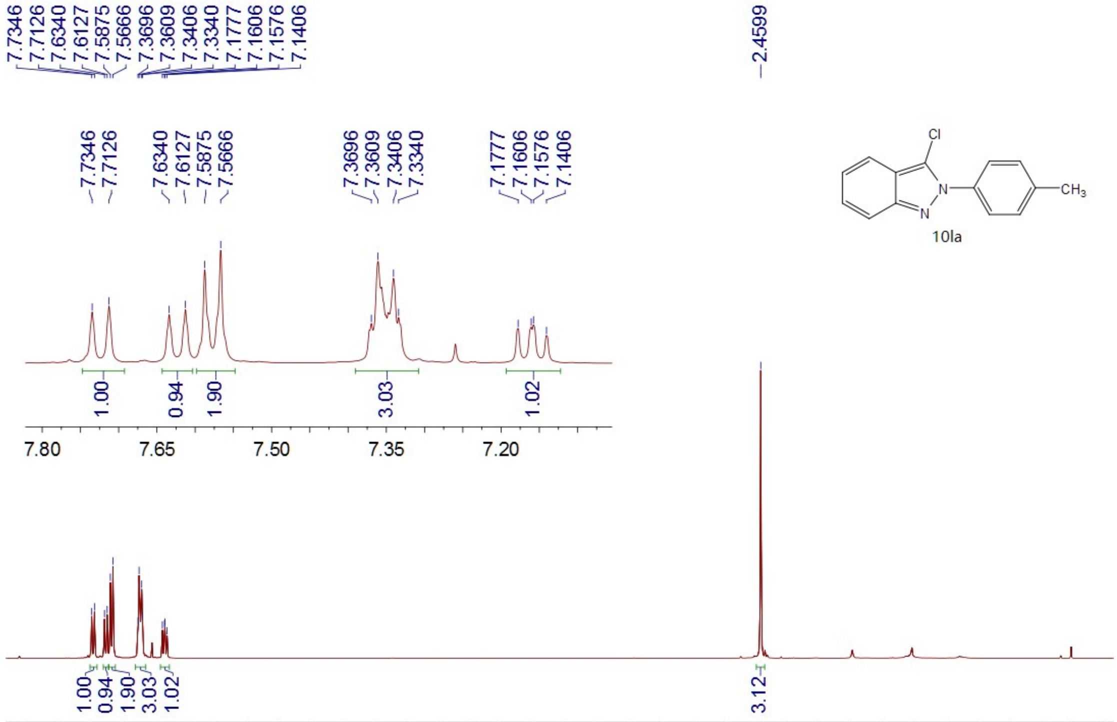
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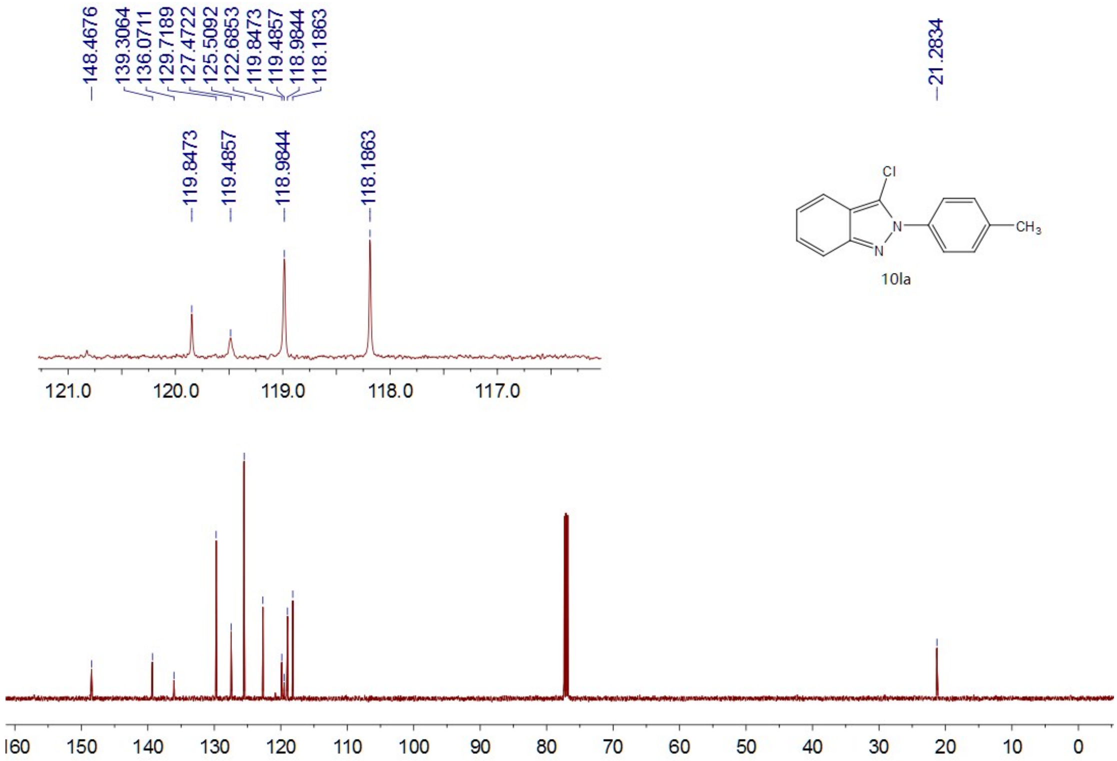
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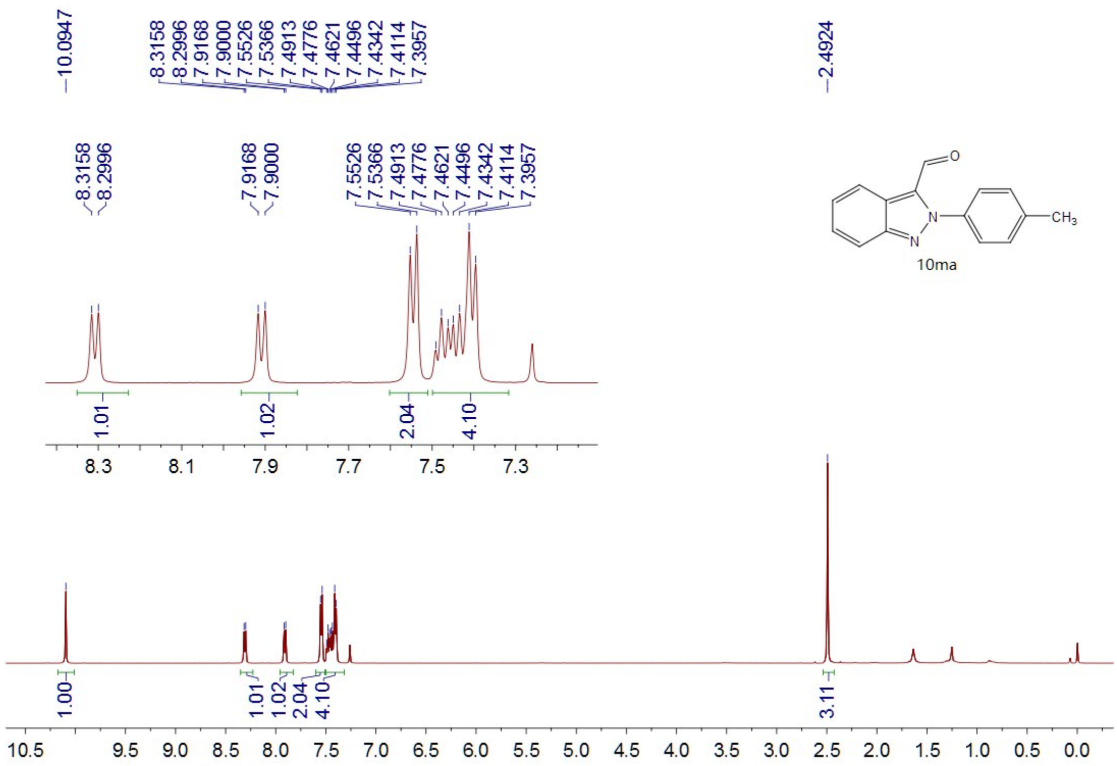
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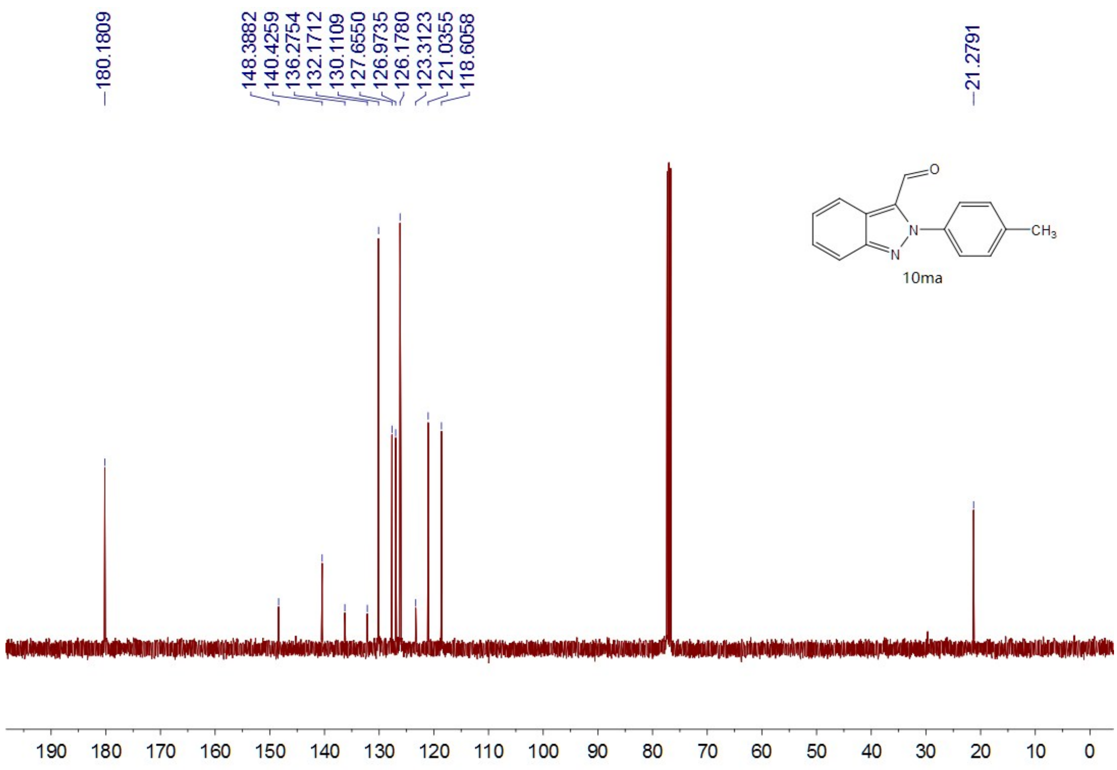
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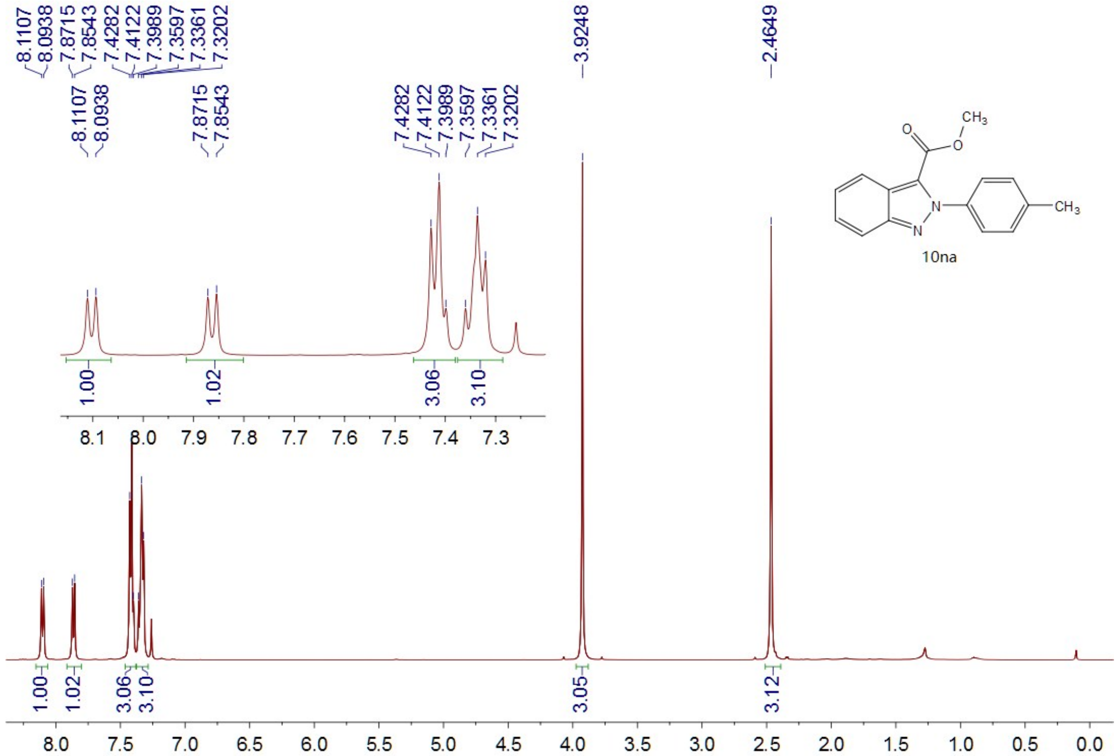
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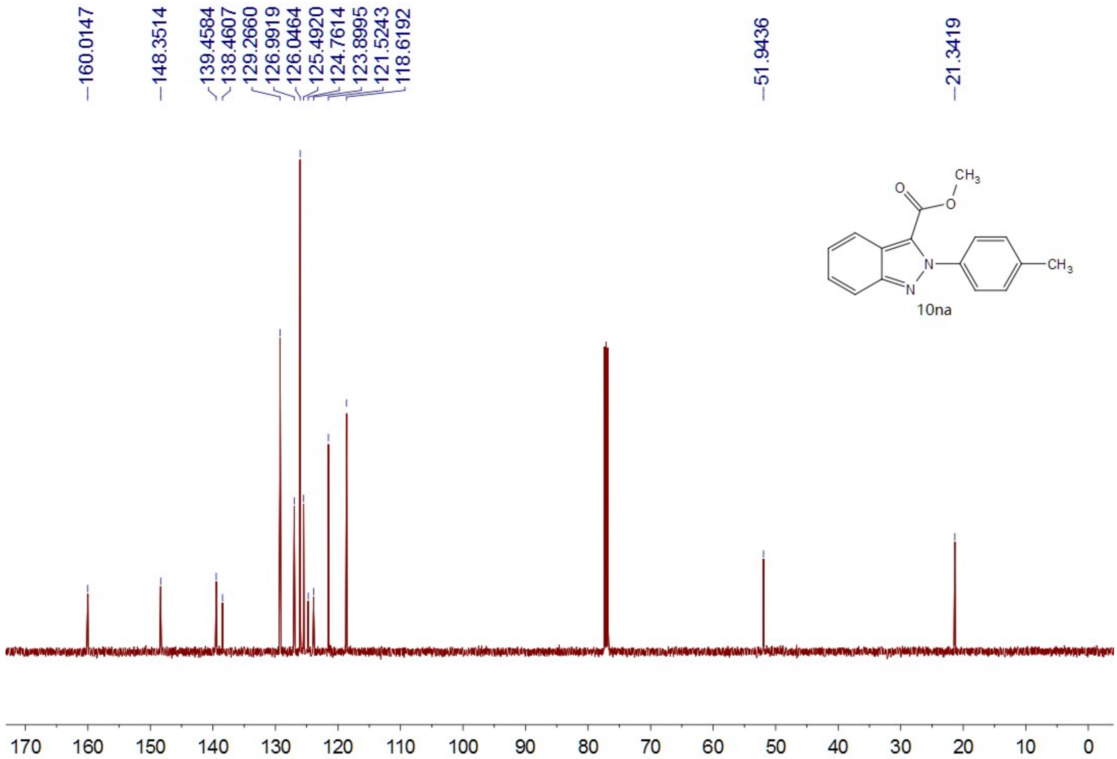
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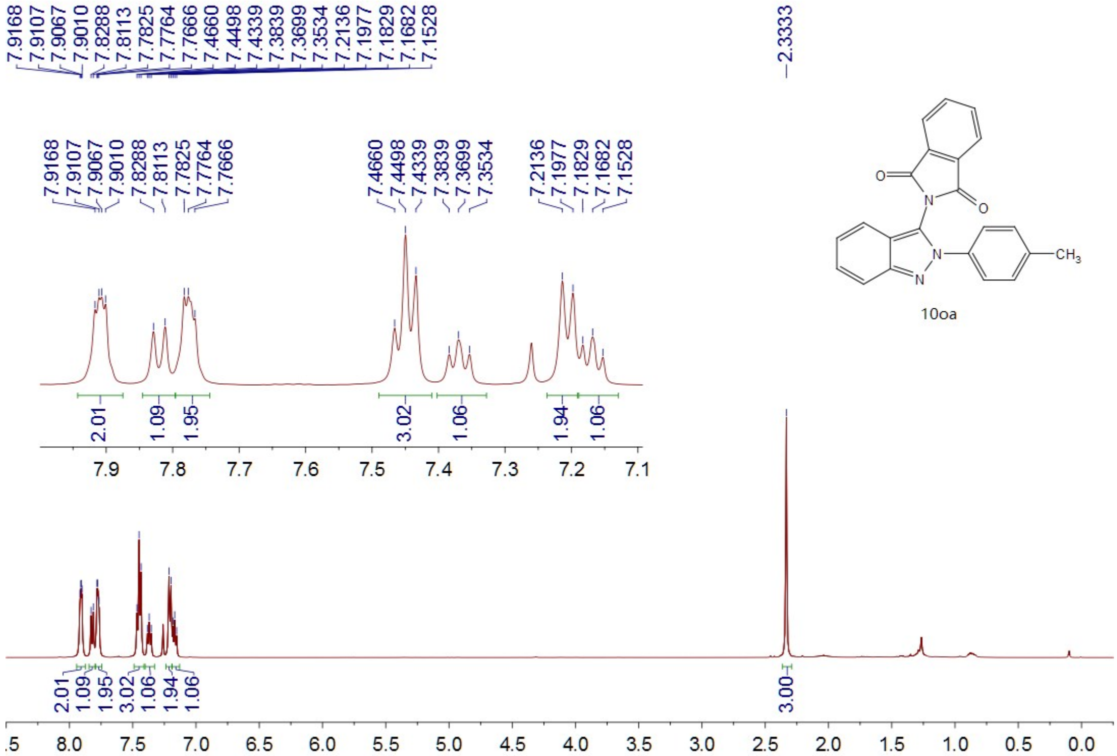
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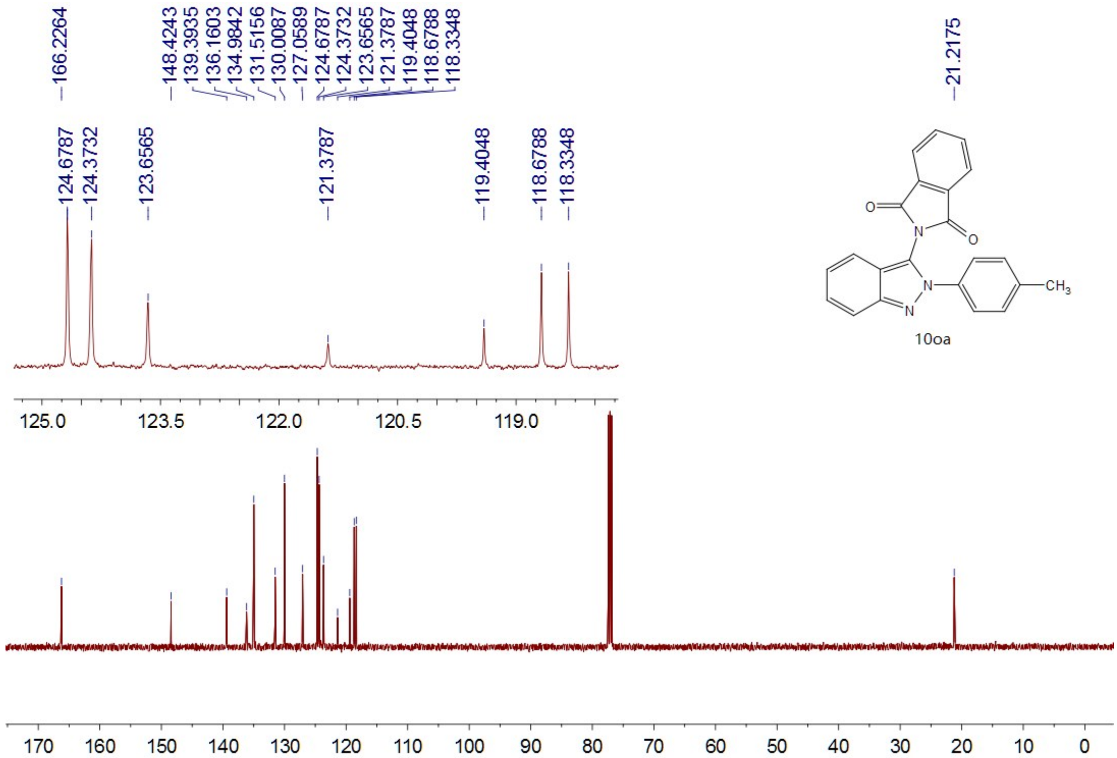
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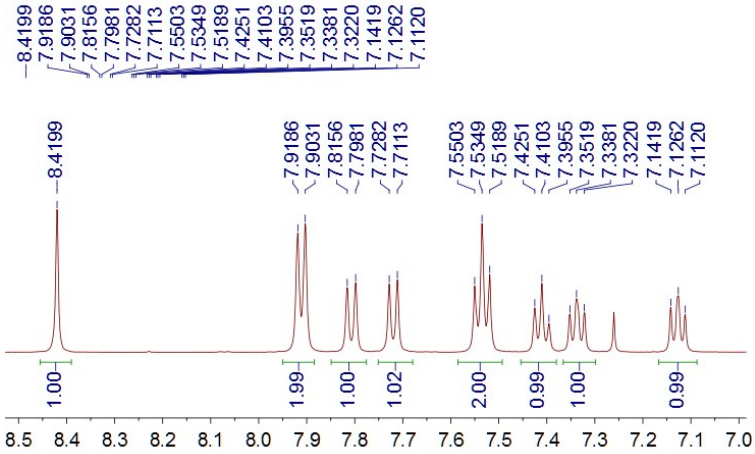
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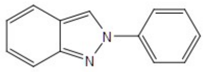
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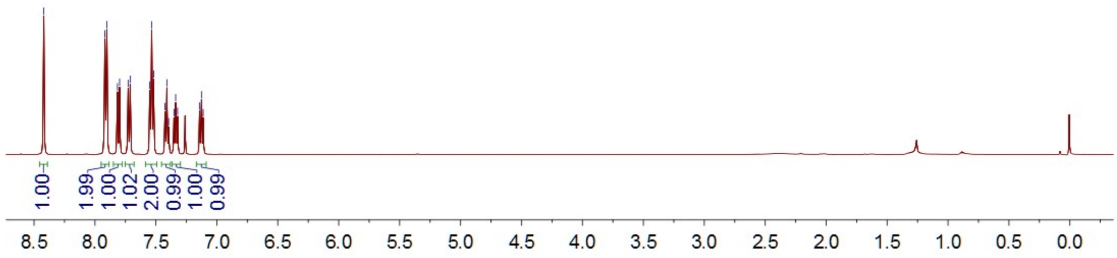
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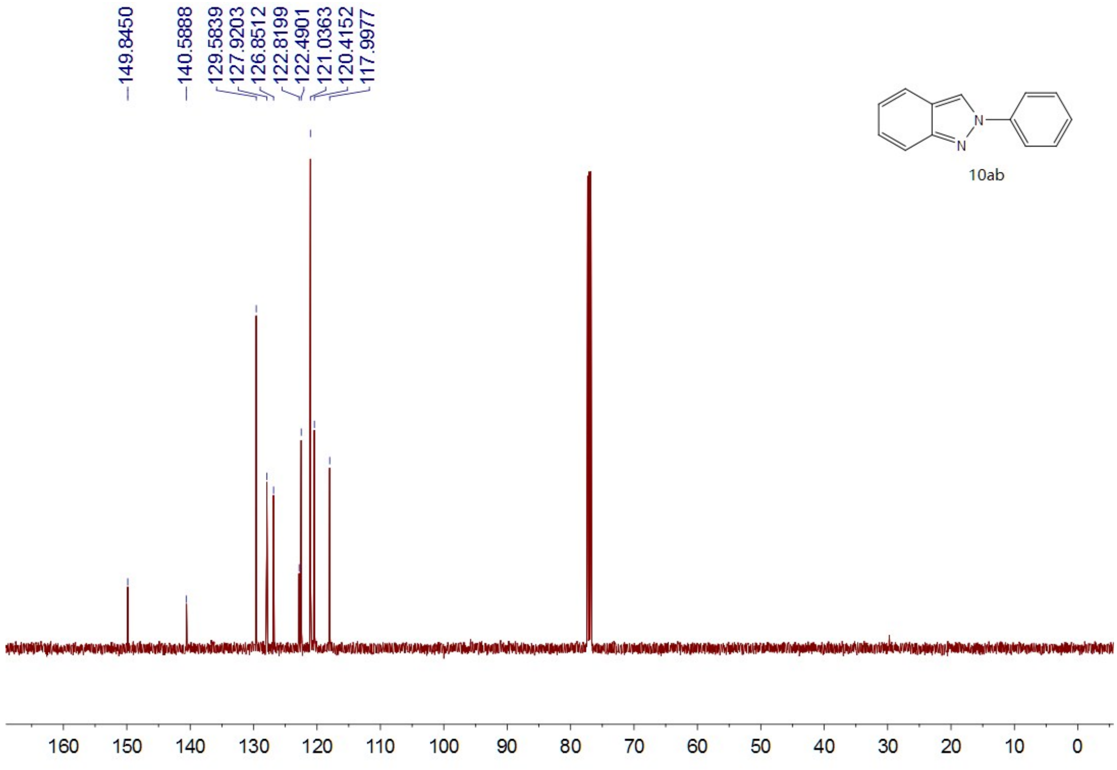
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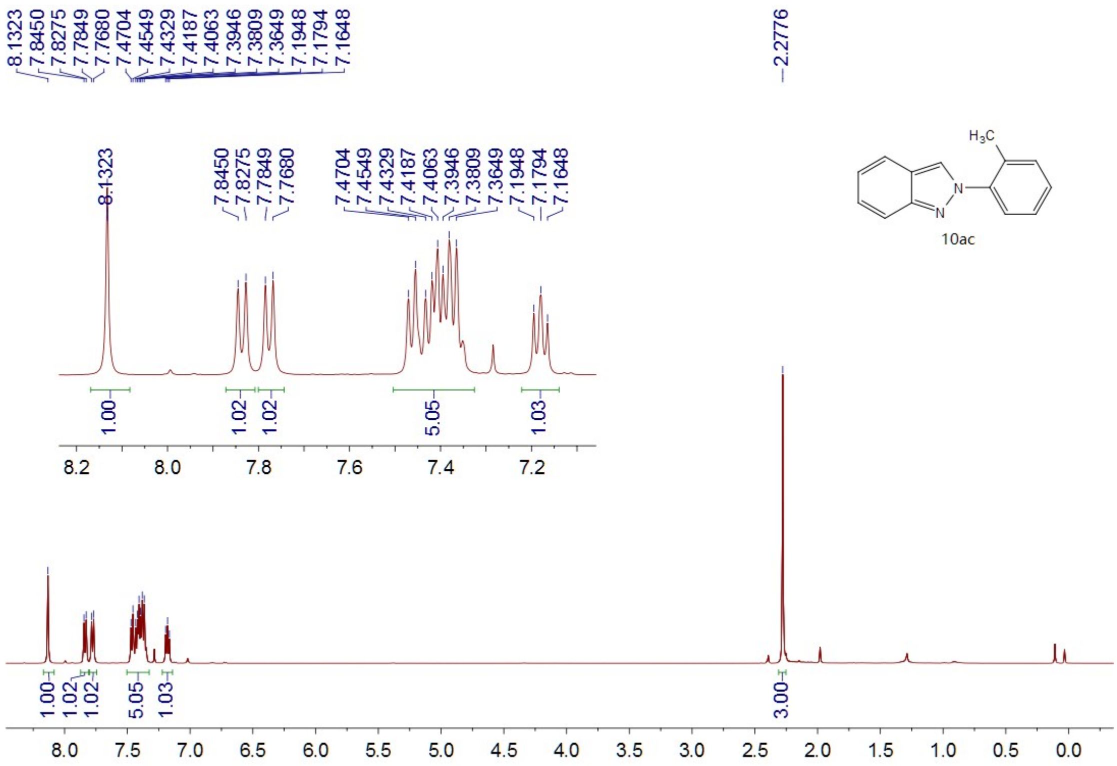
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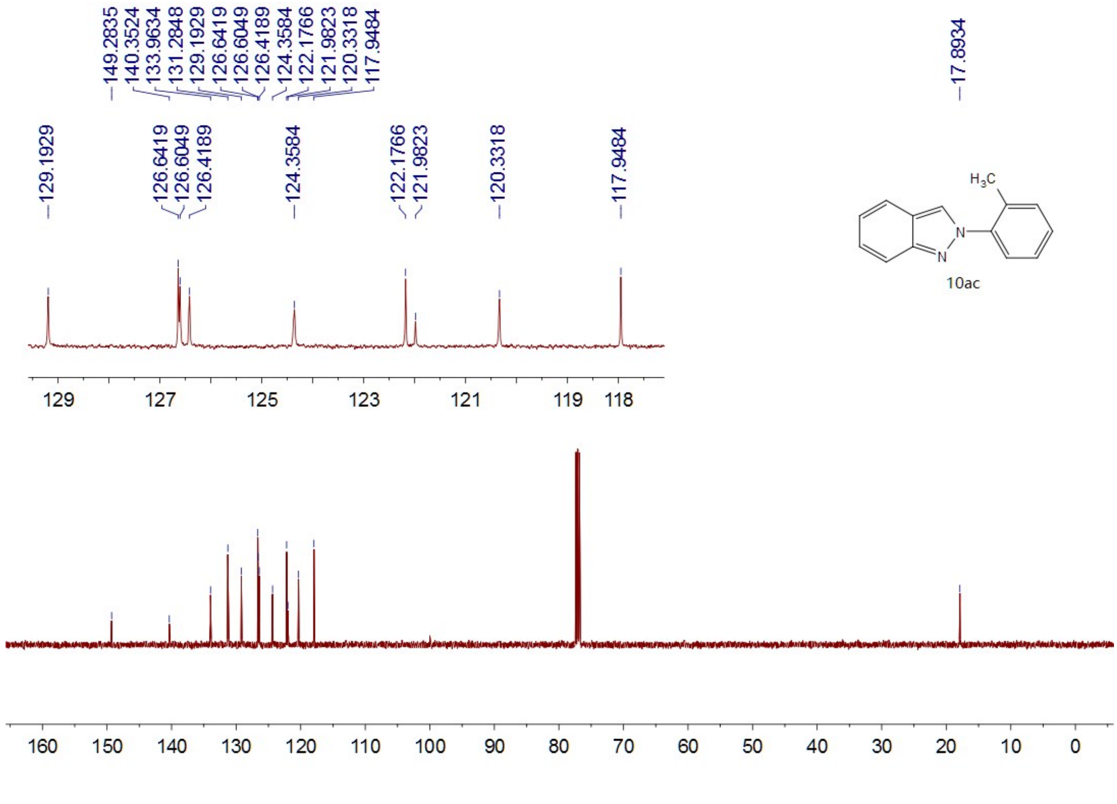
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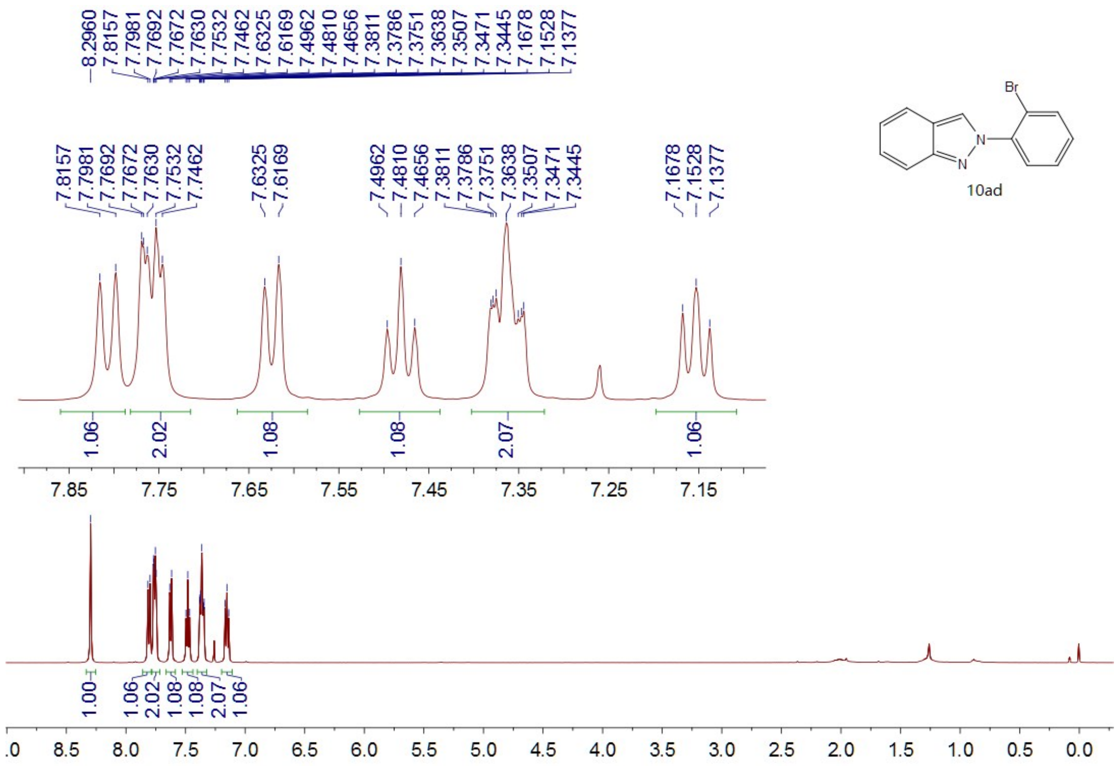

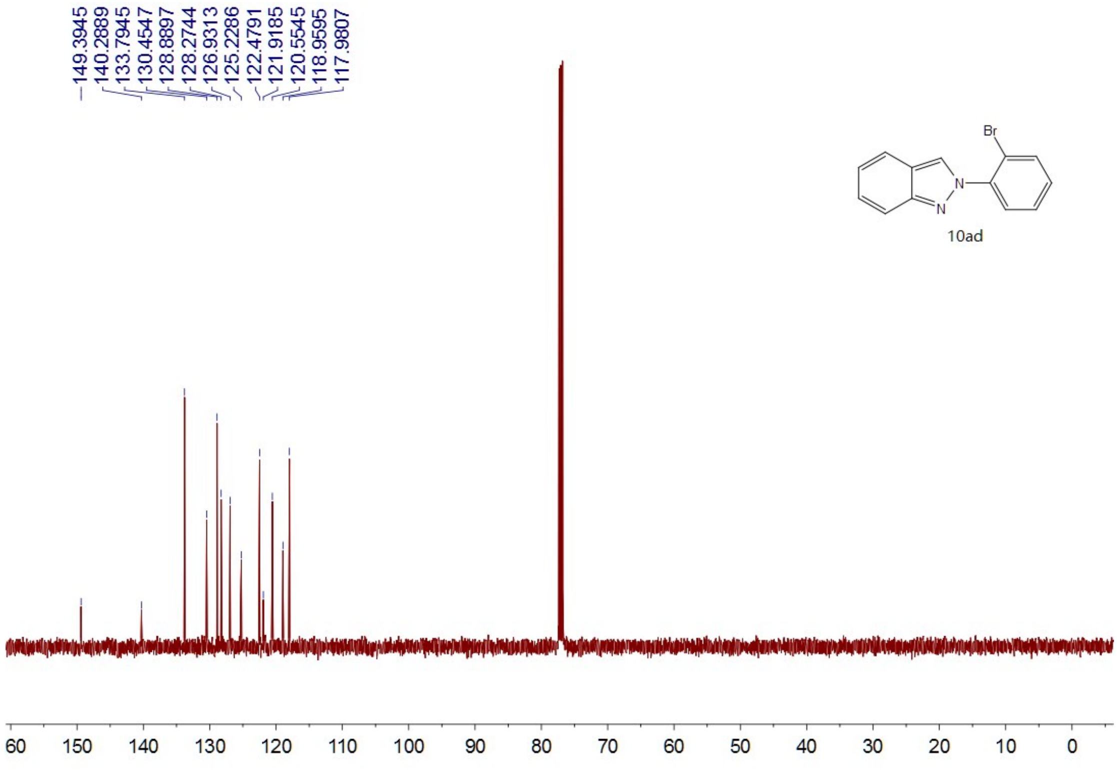

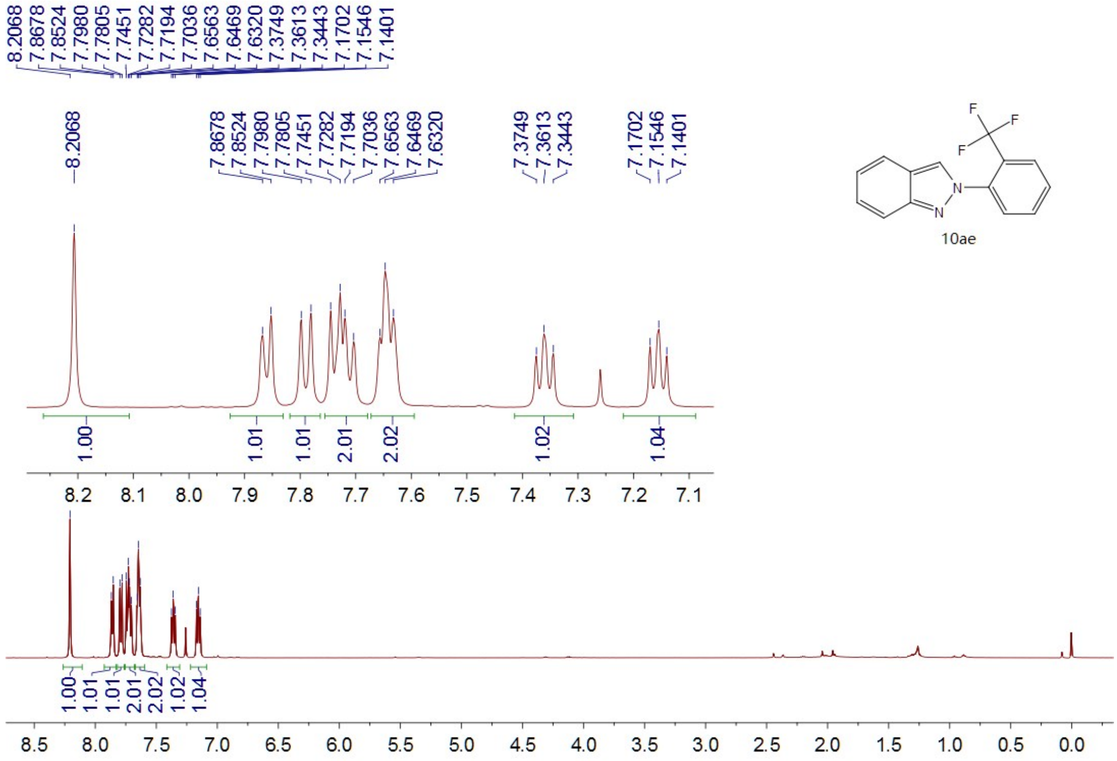

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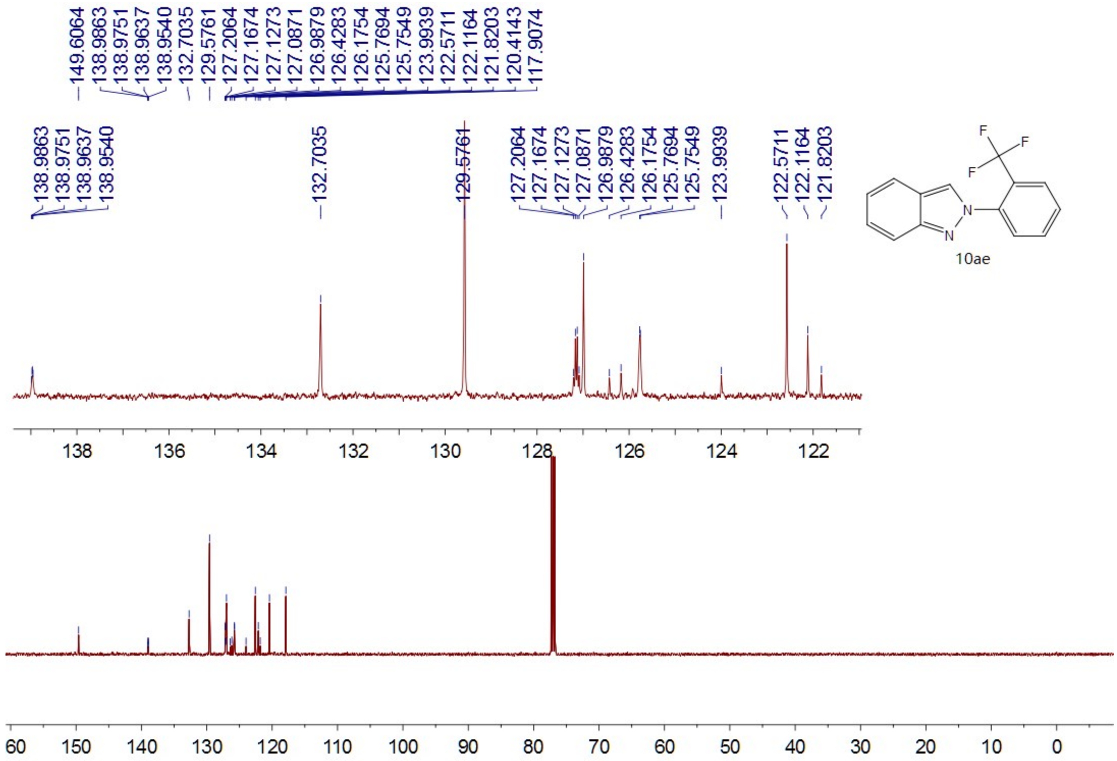

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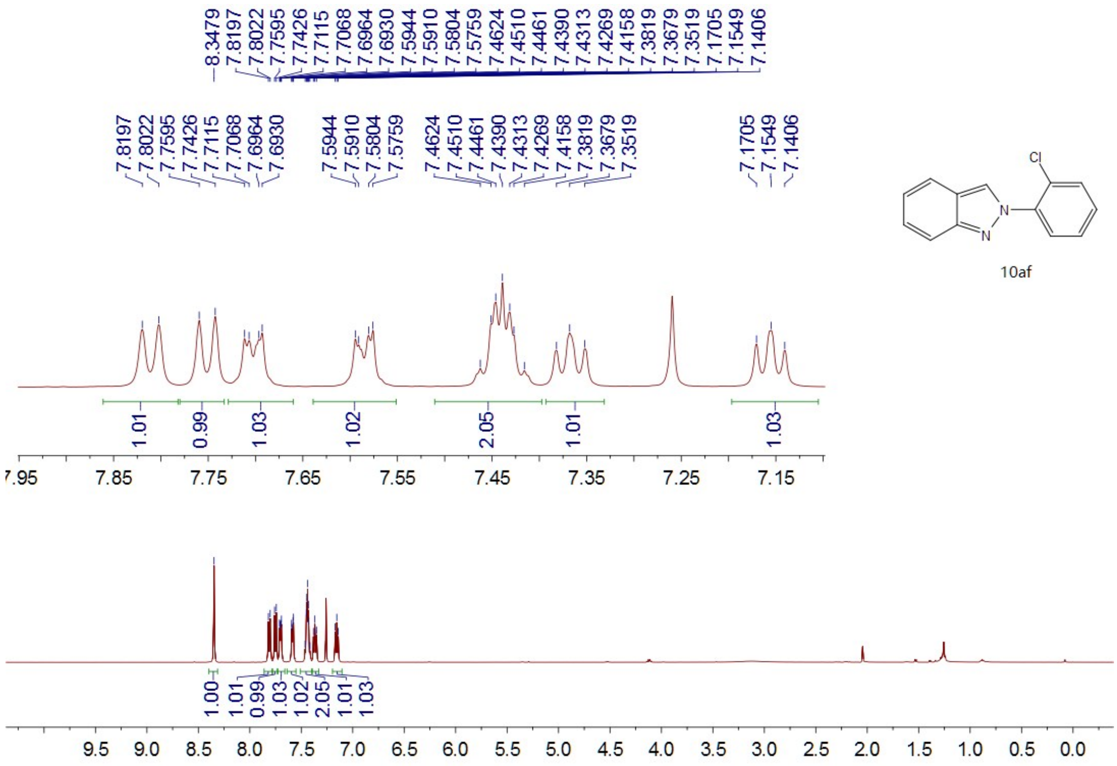
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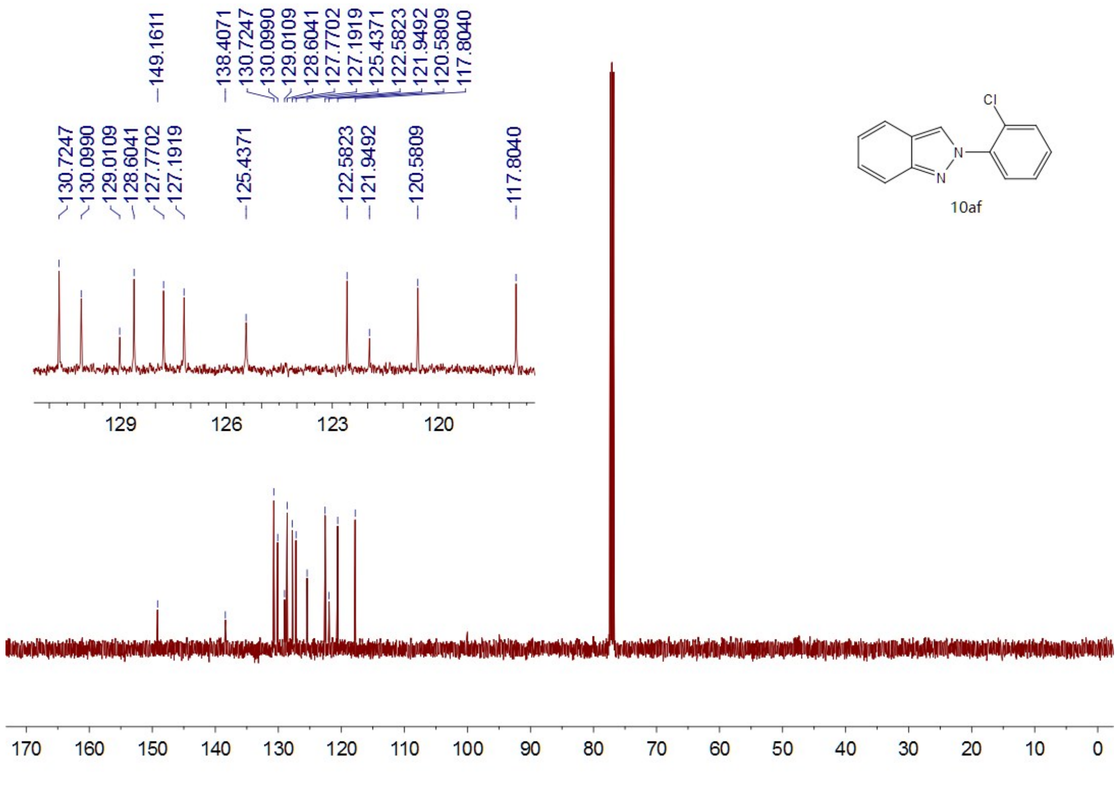
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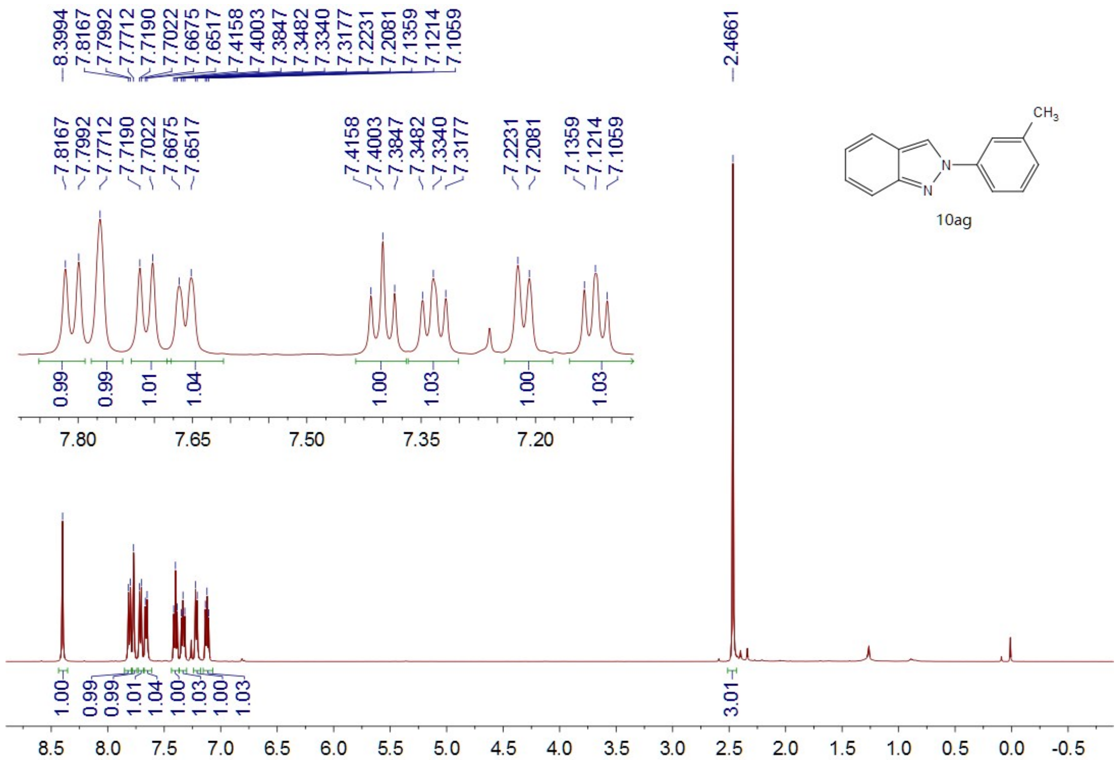
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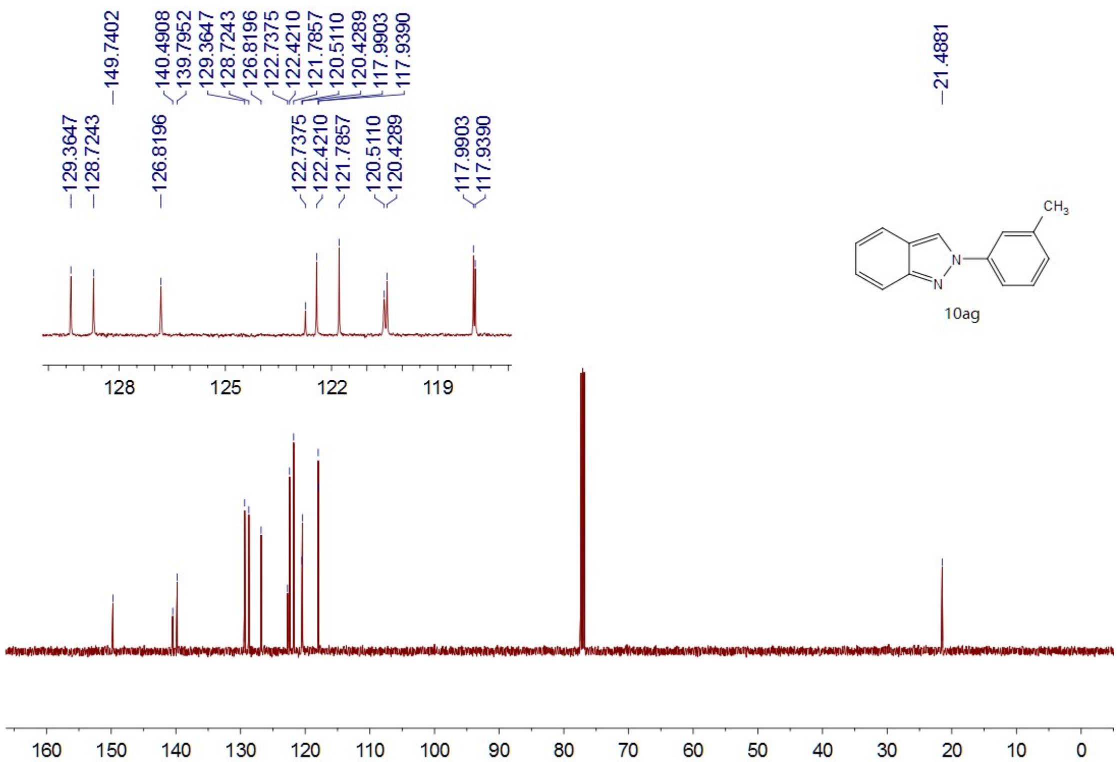
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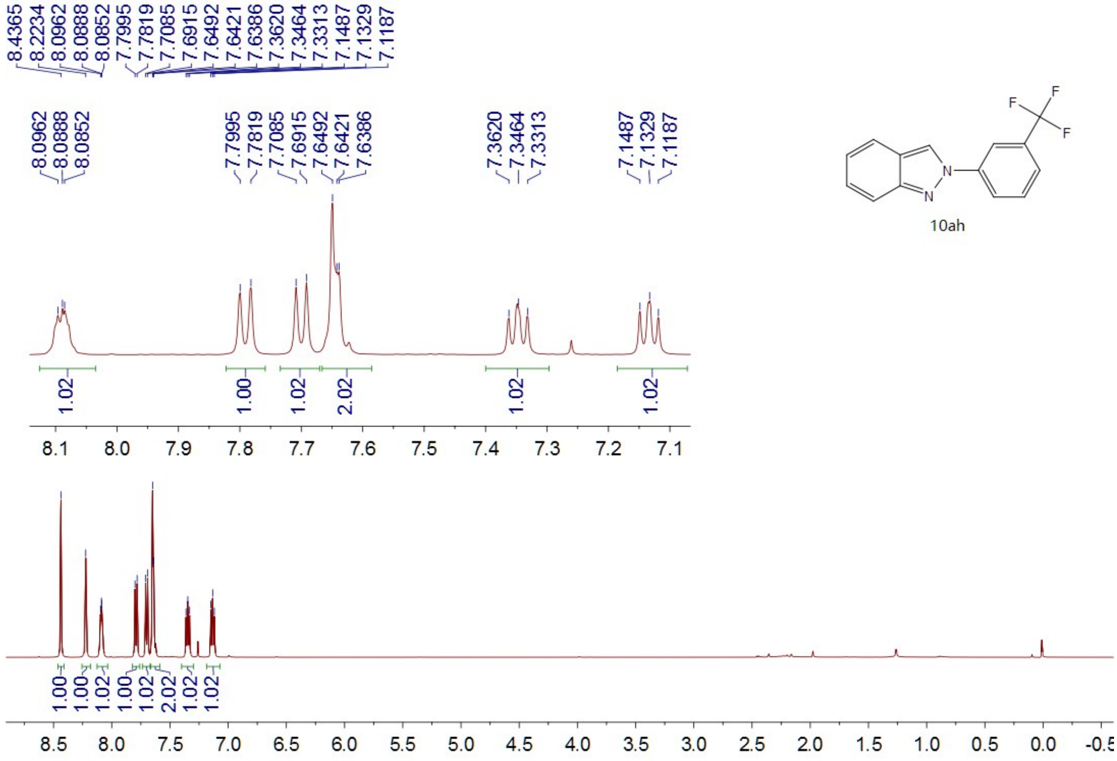
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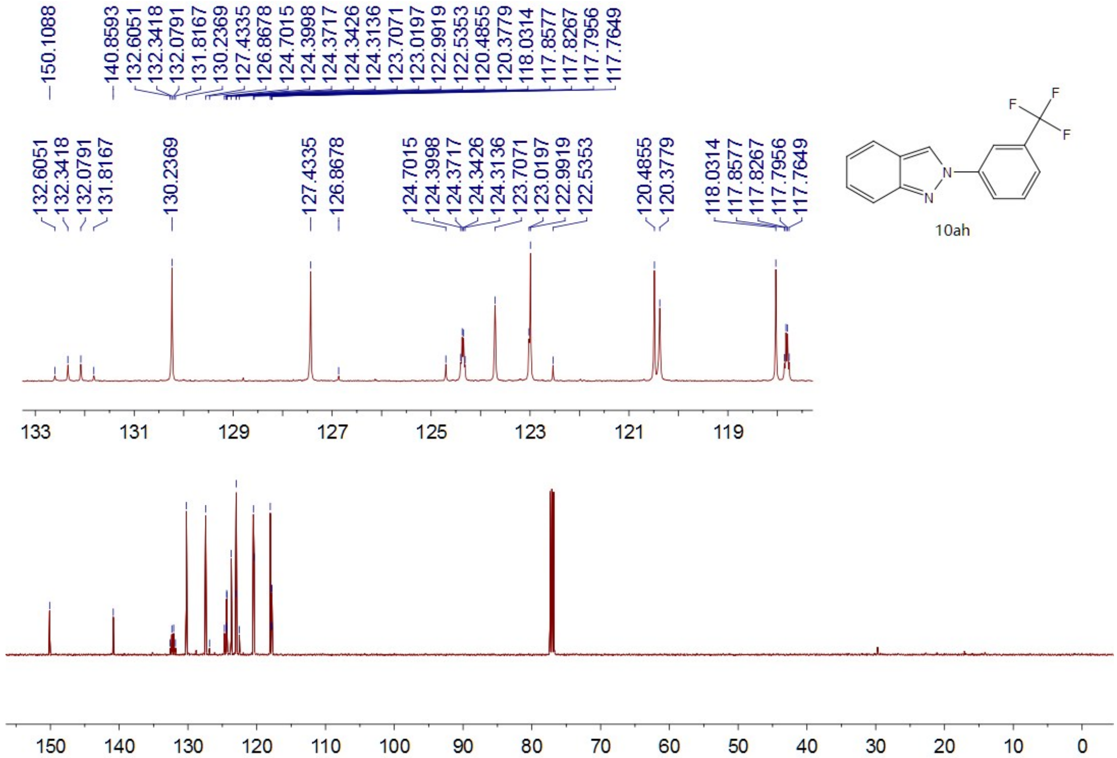
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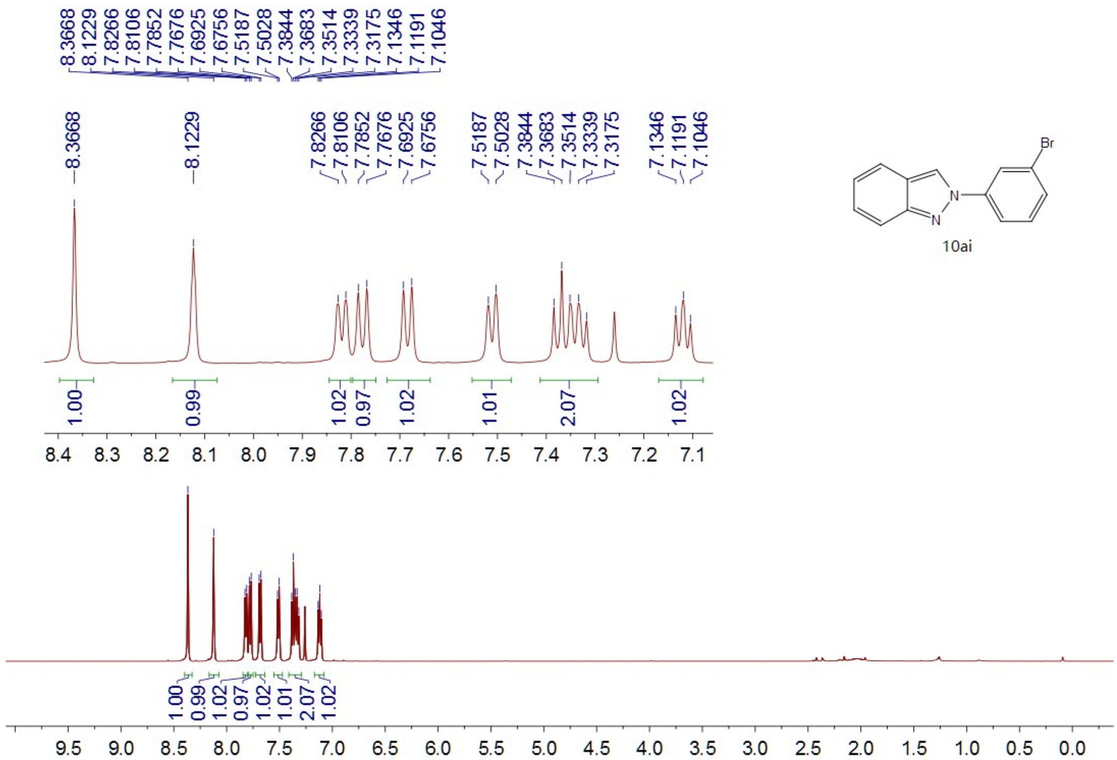
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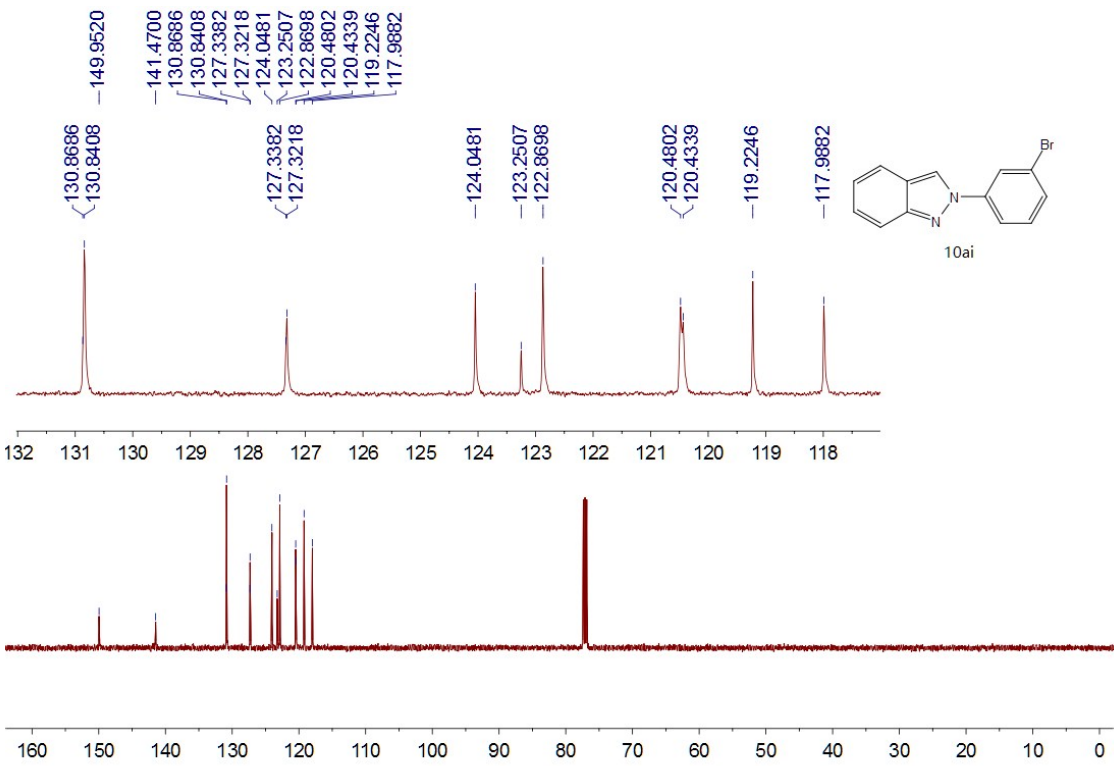
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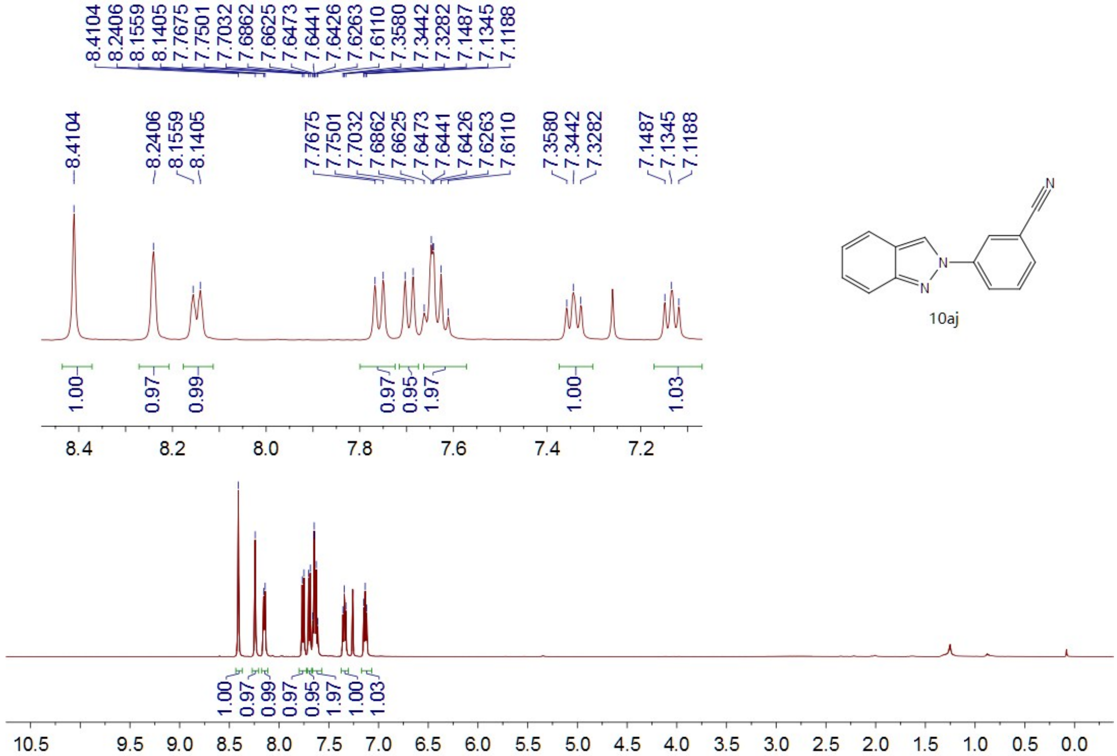

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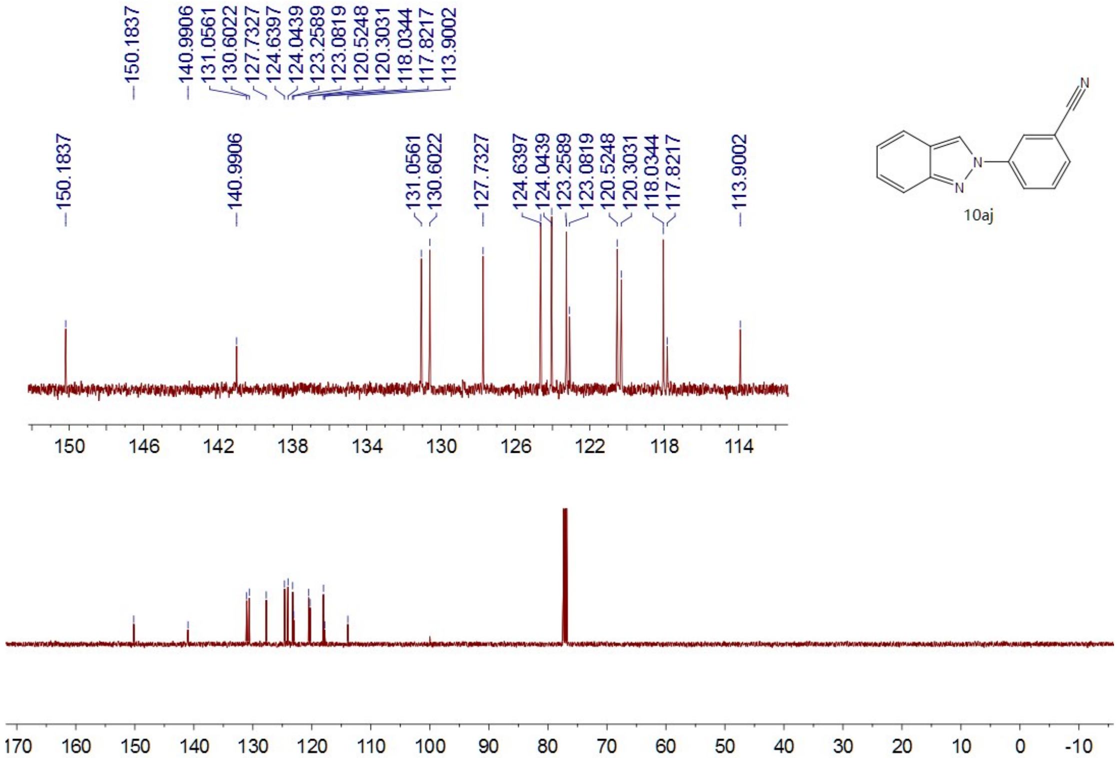

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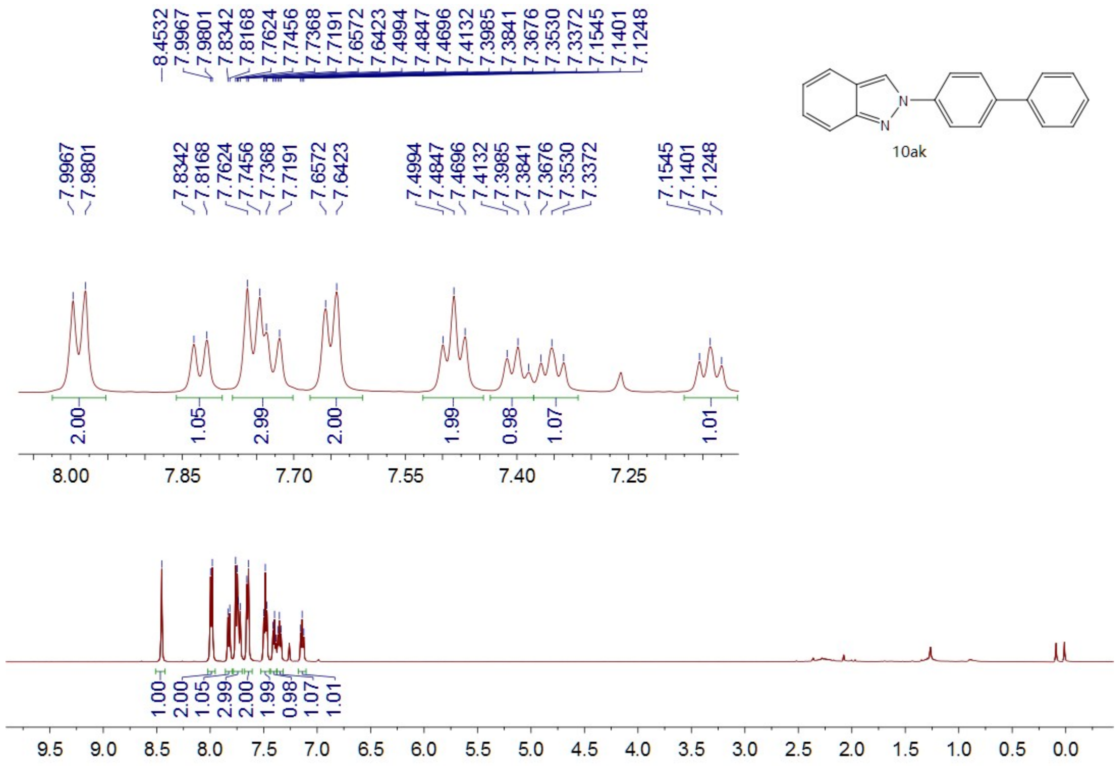

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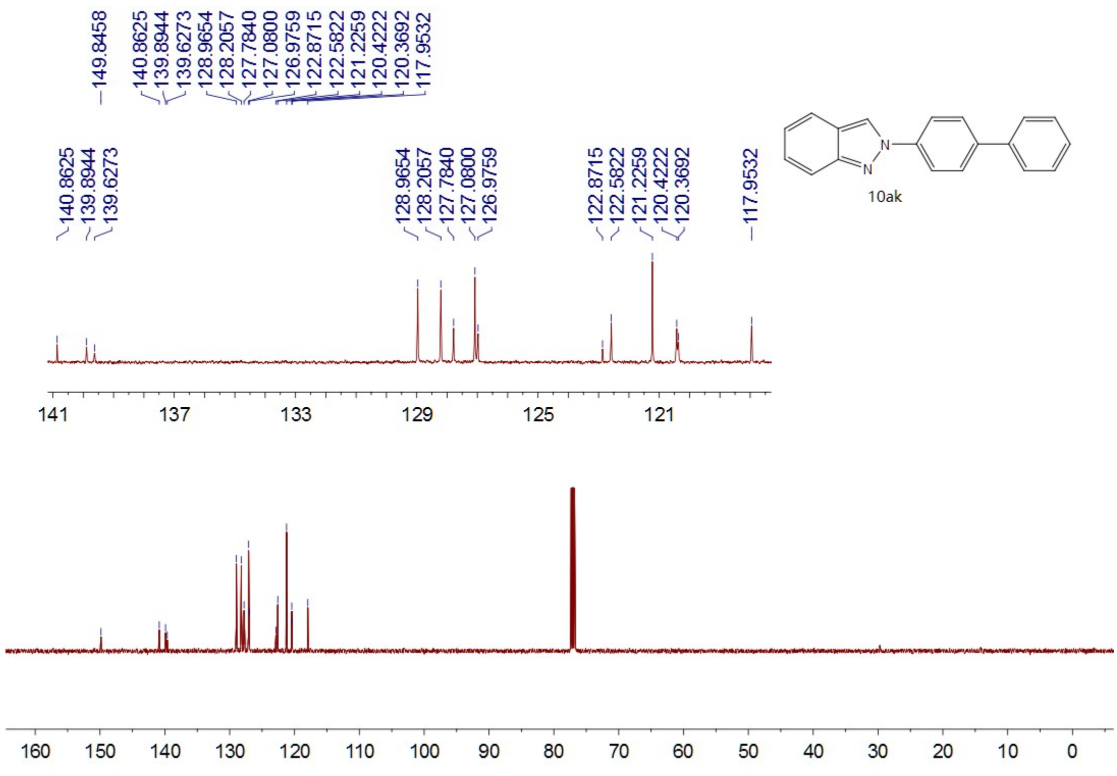

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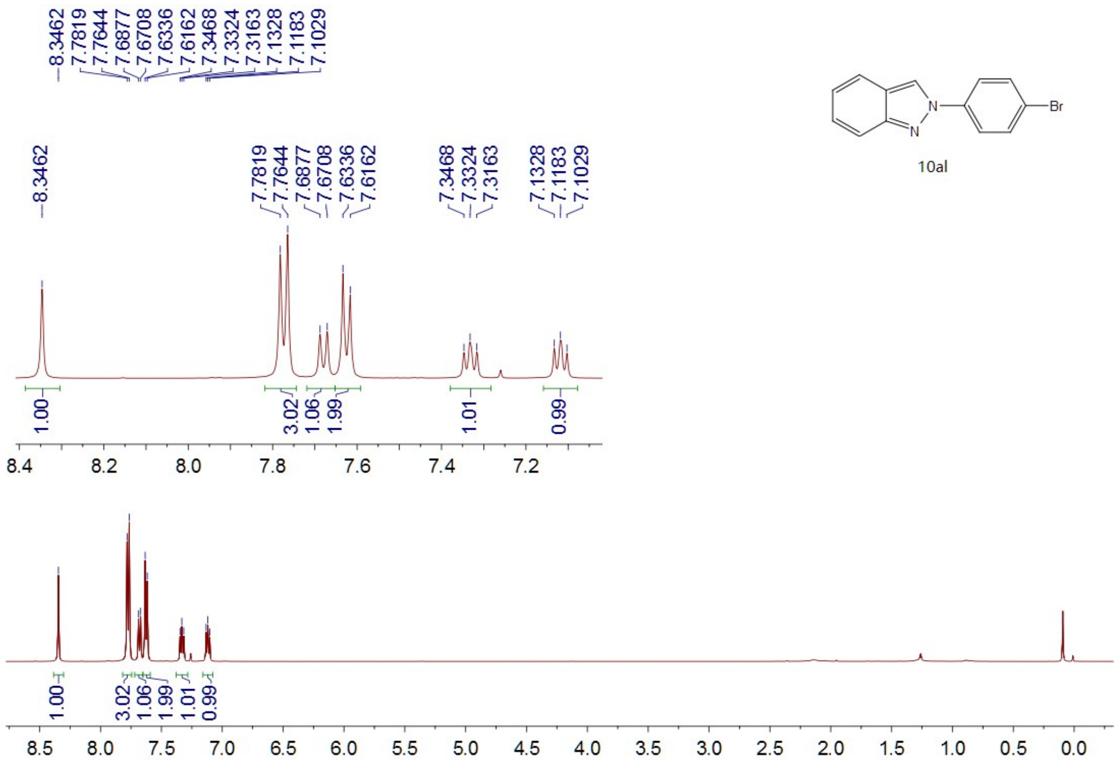
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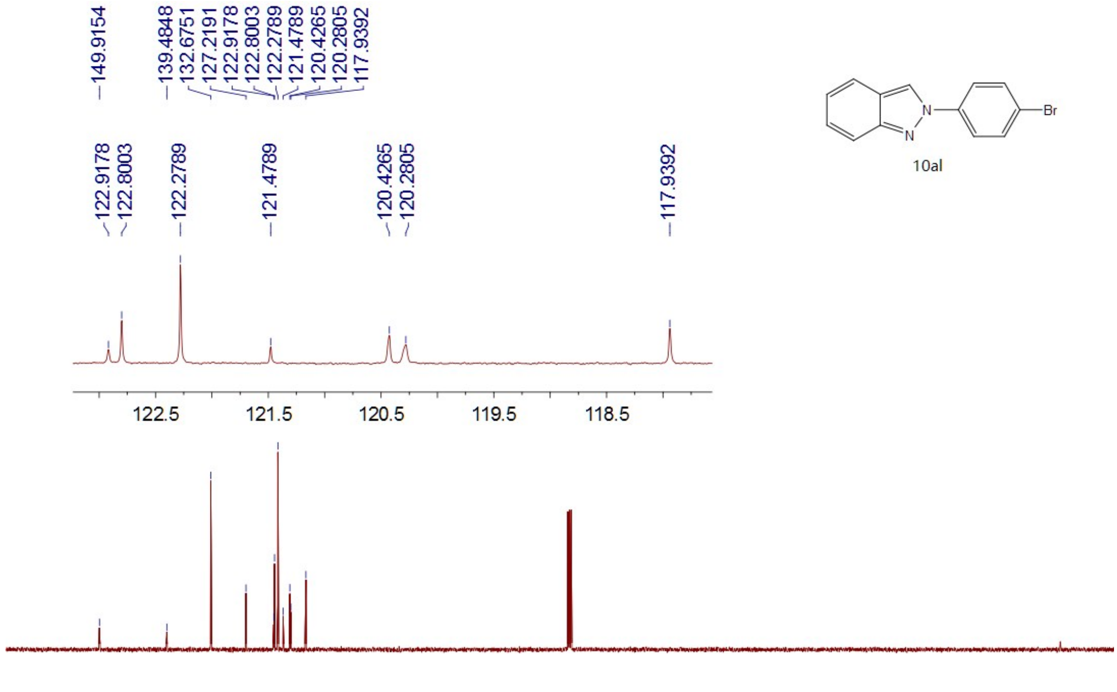
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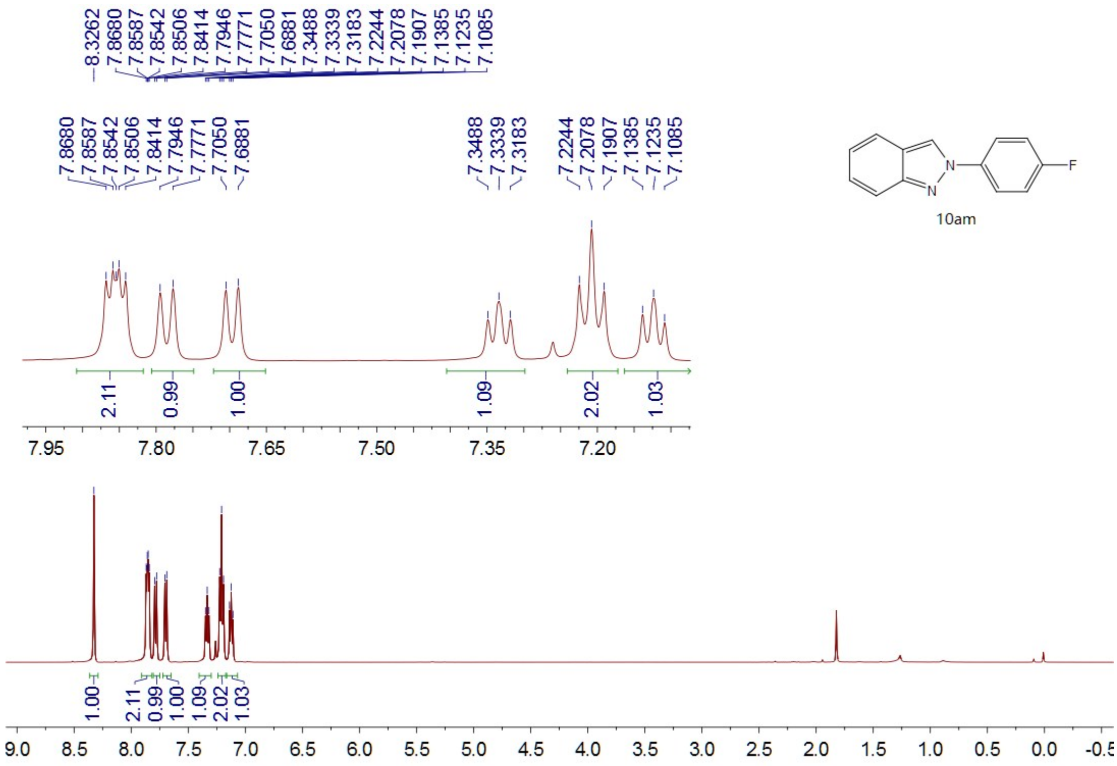
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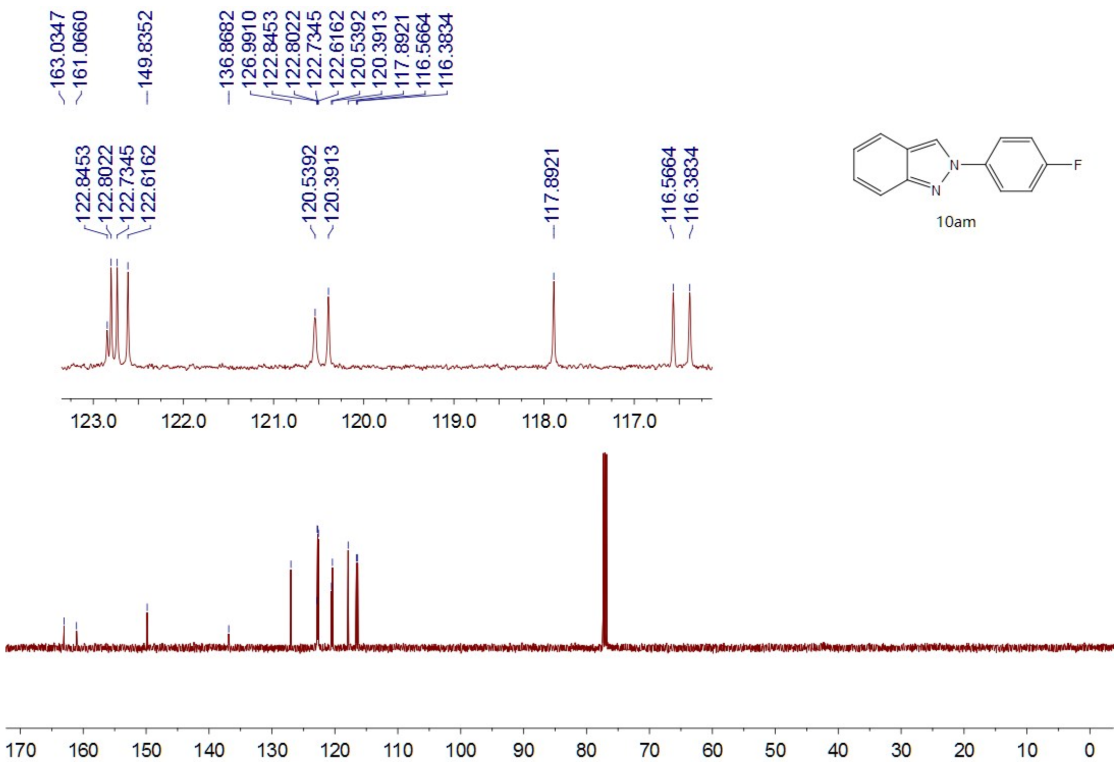
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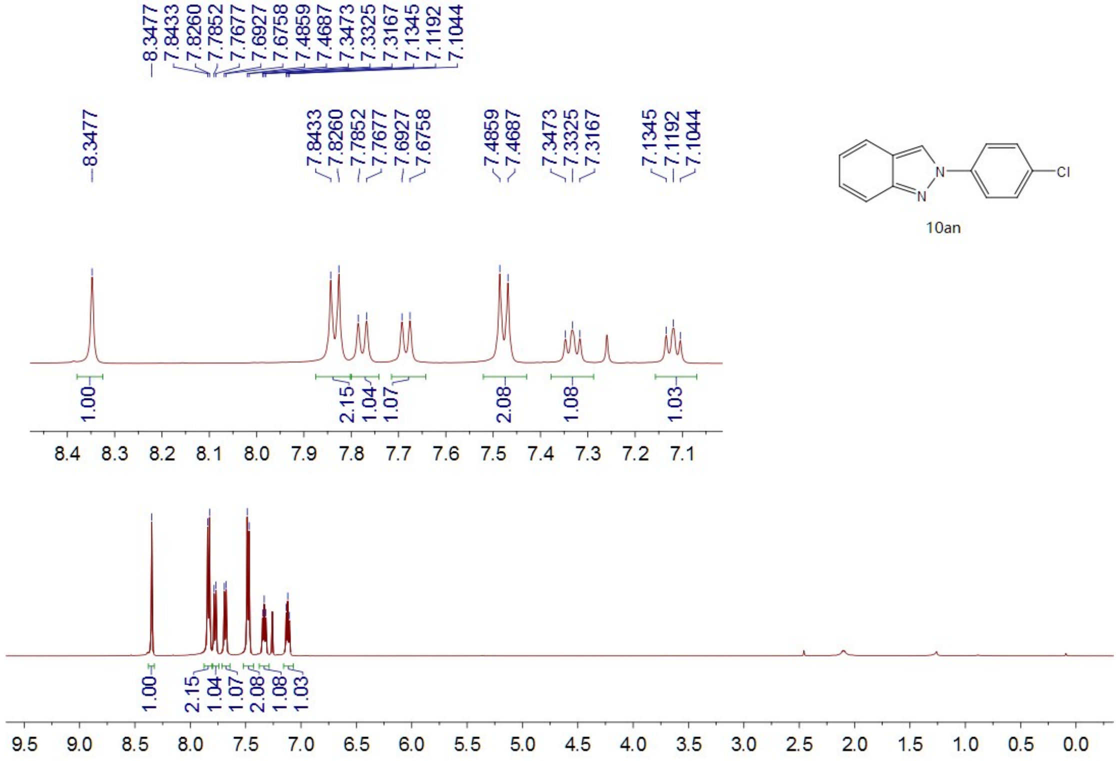
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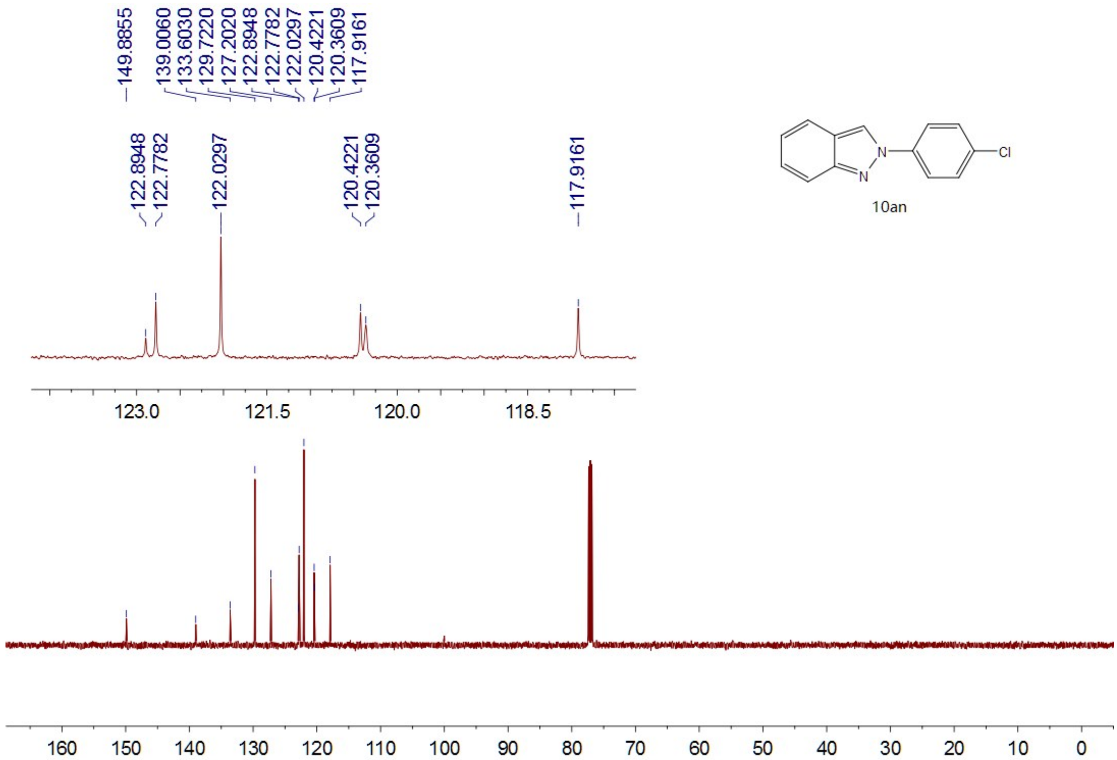
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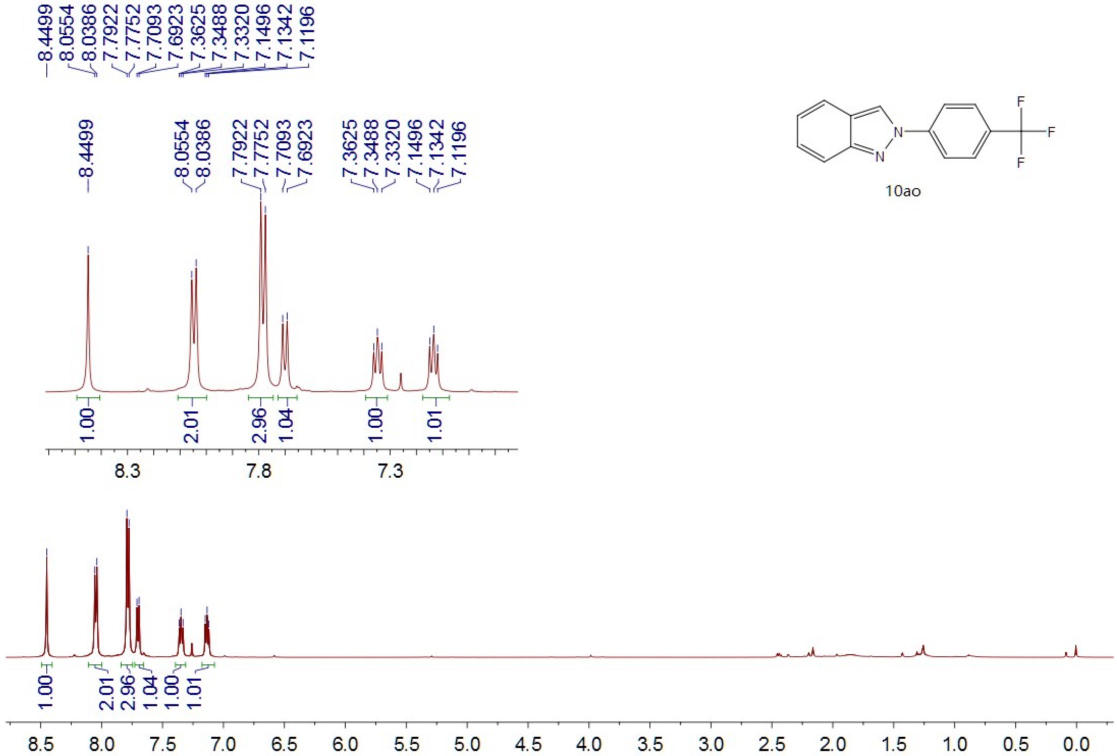
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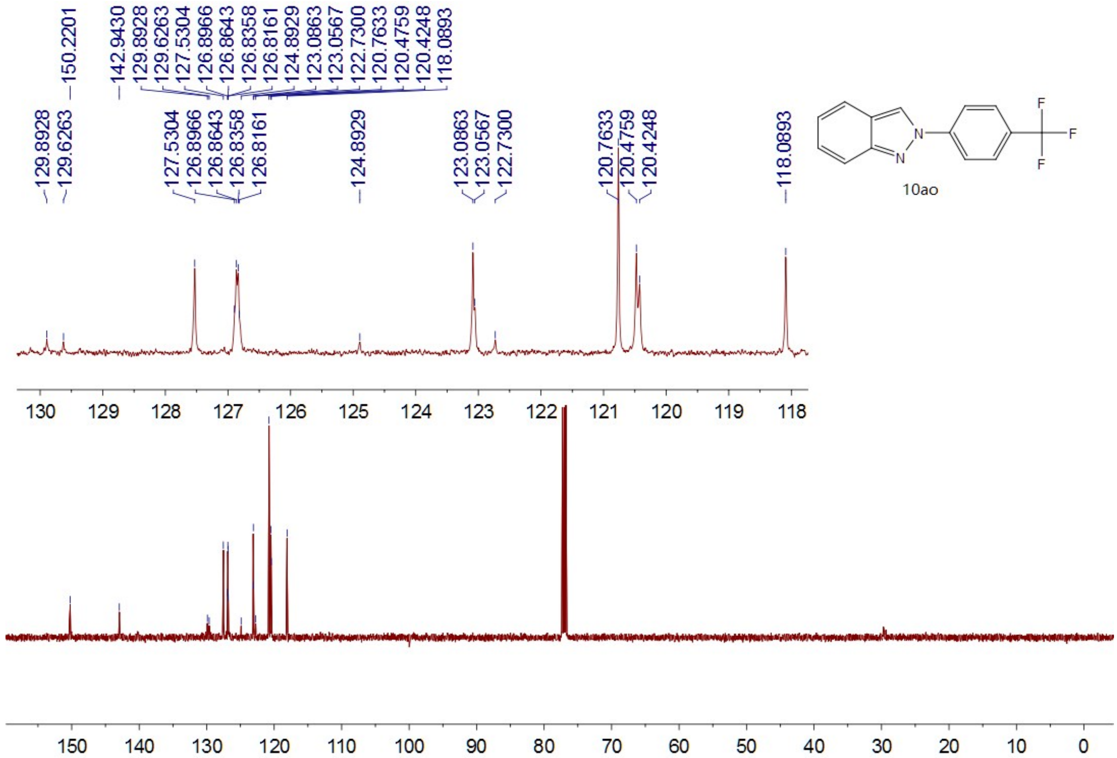
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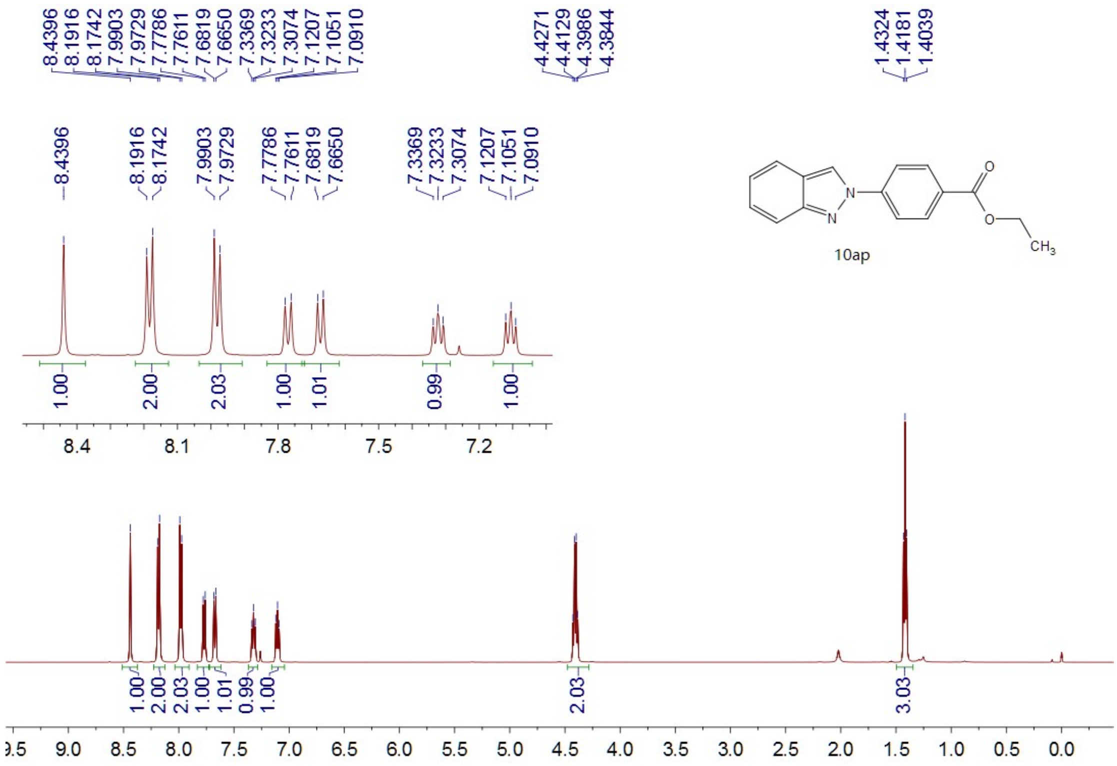

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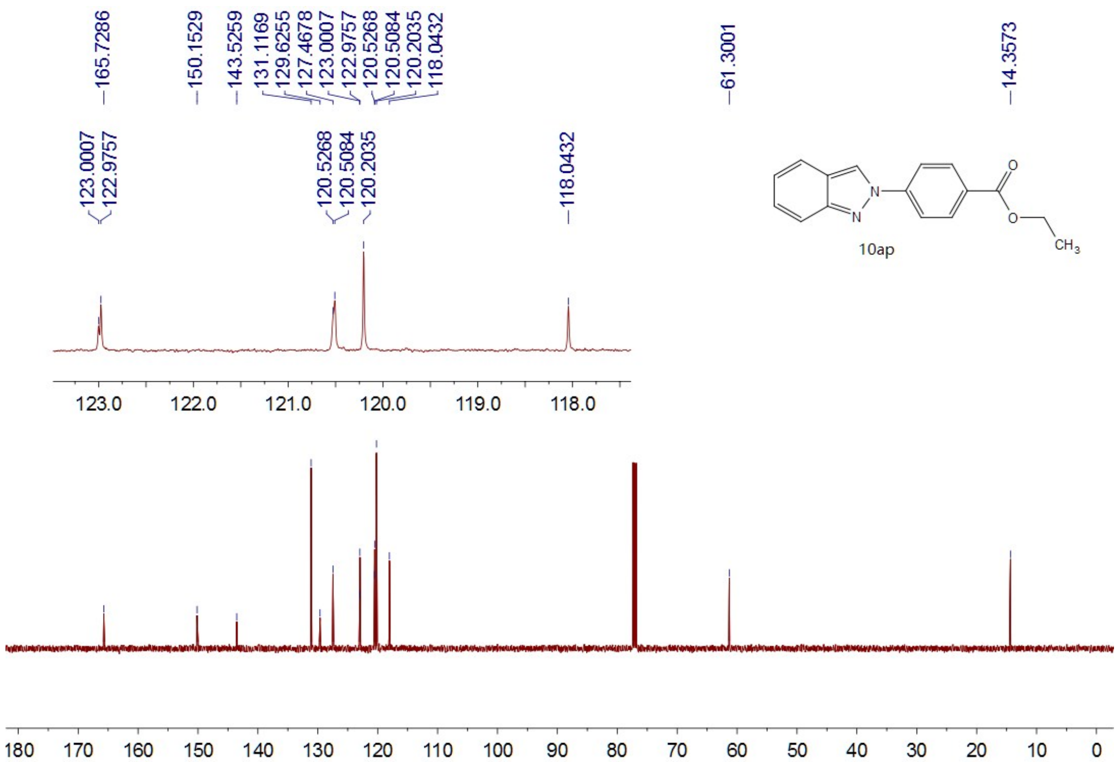

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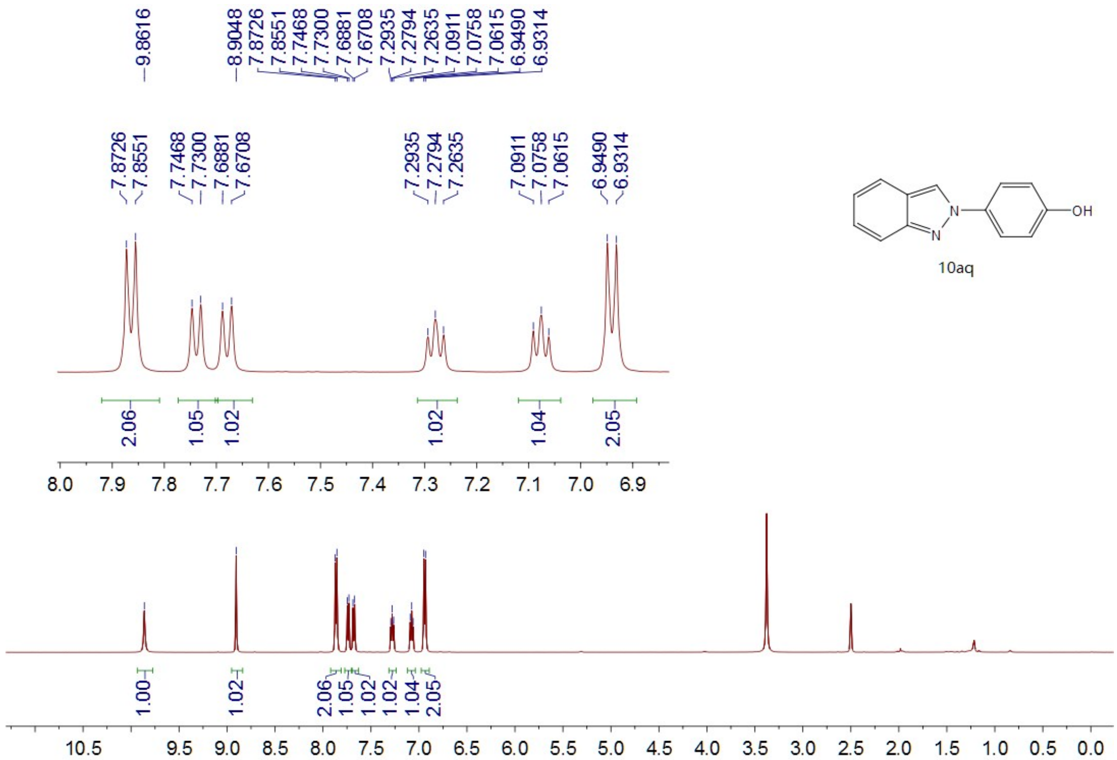

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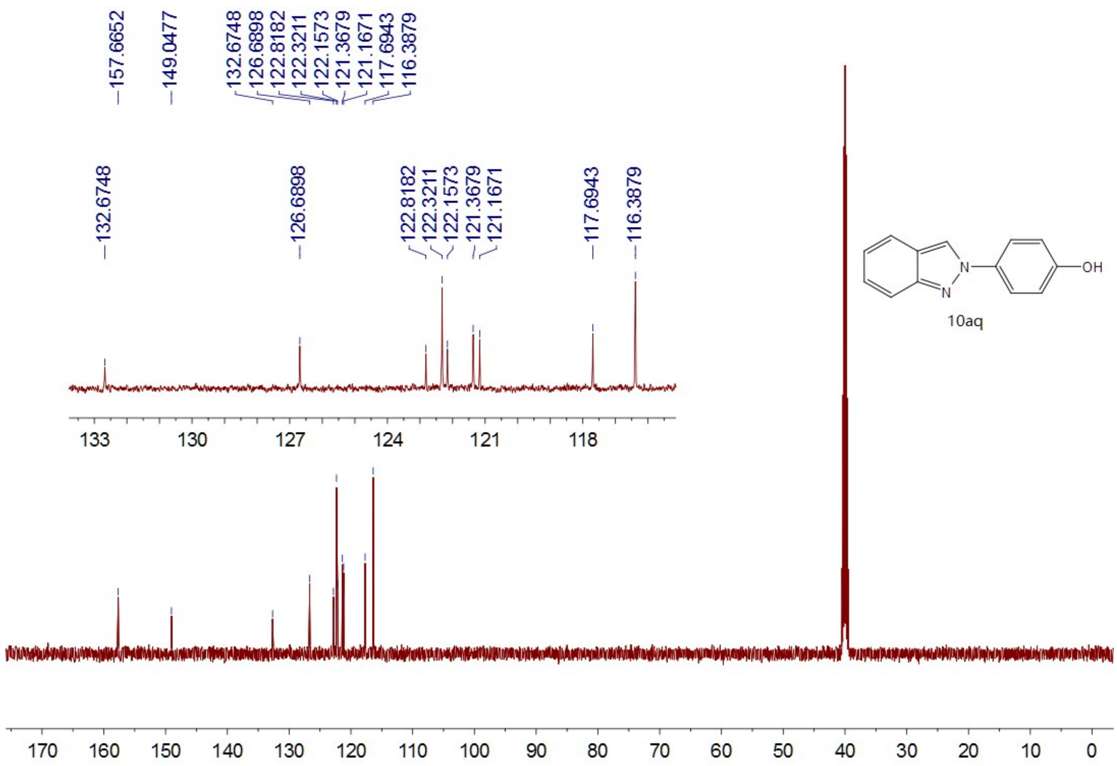

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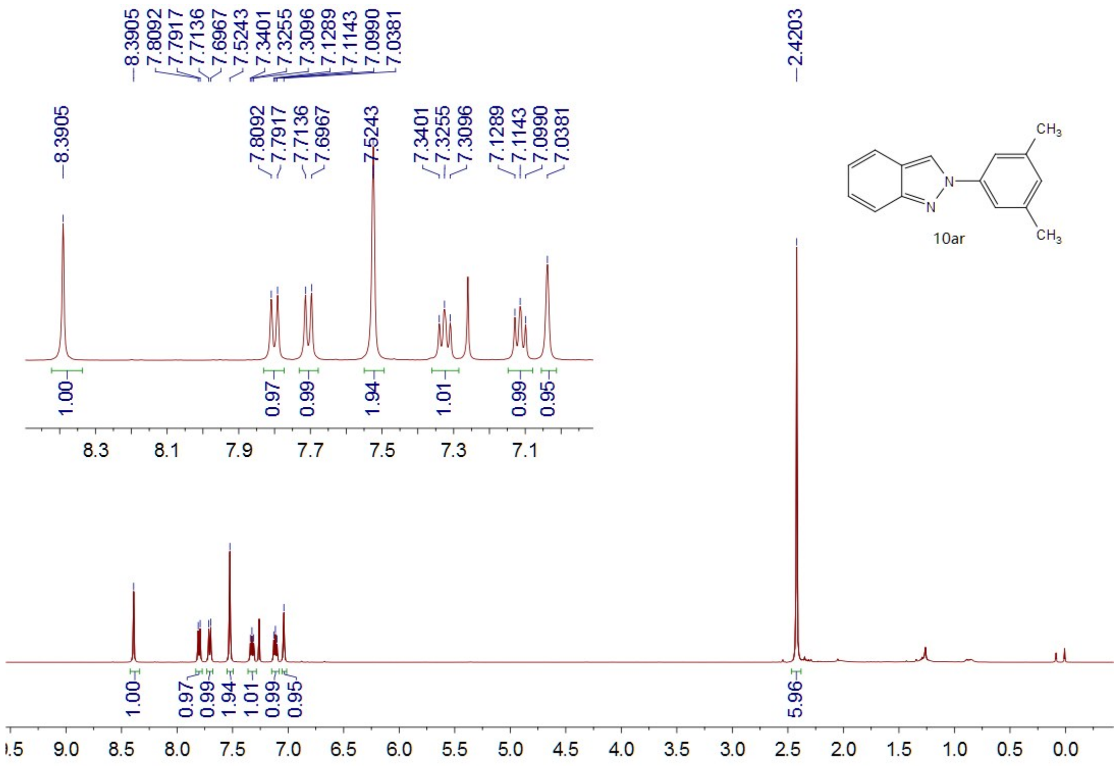
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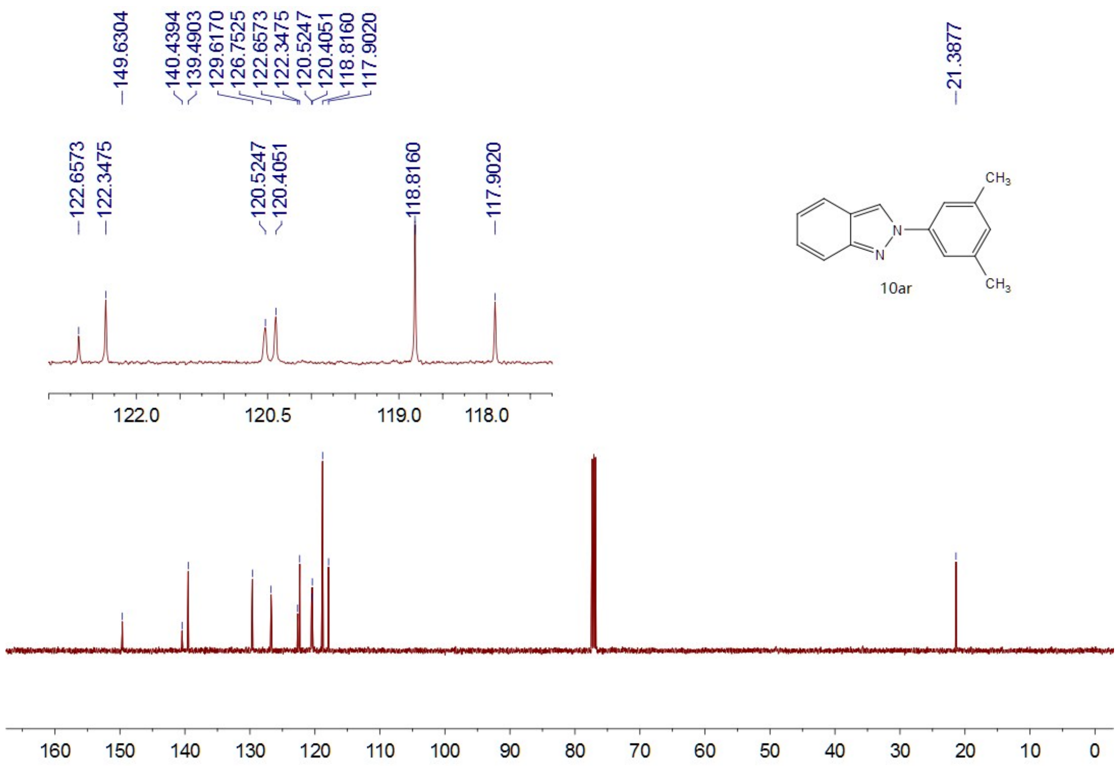
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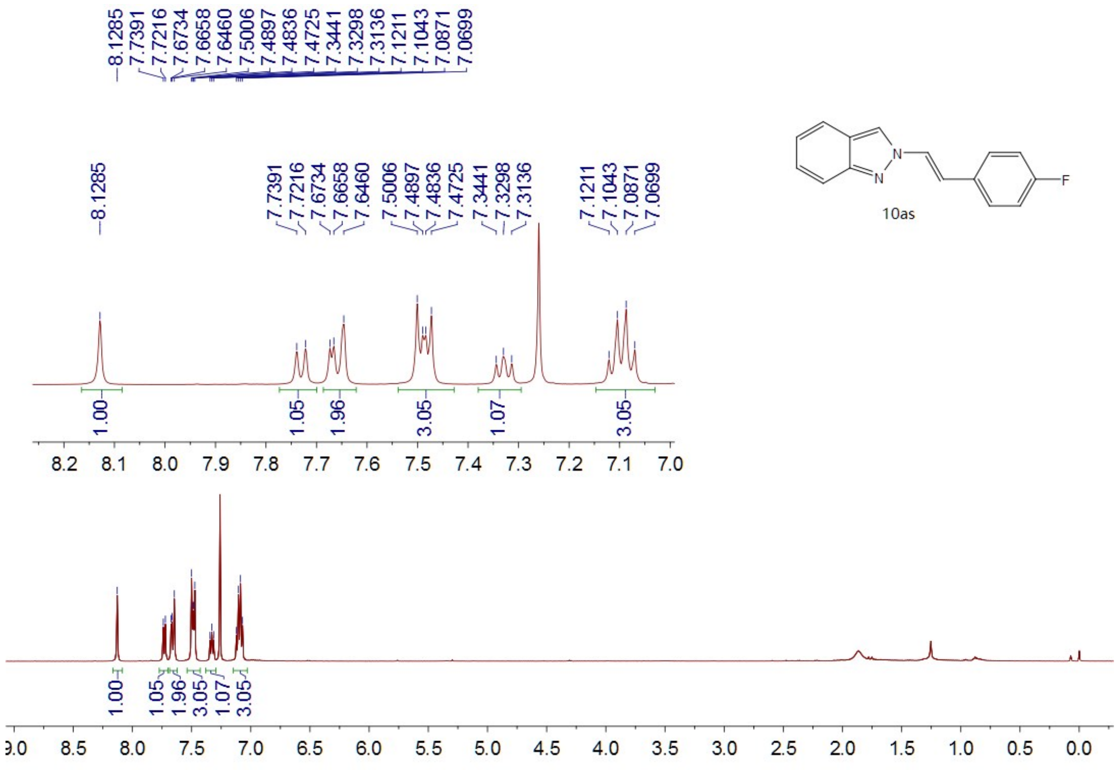
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1.07
3.05
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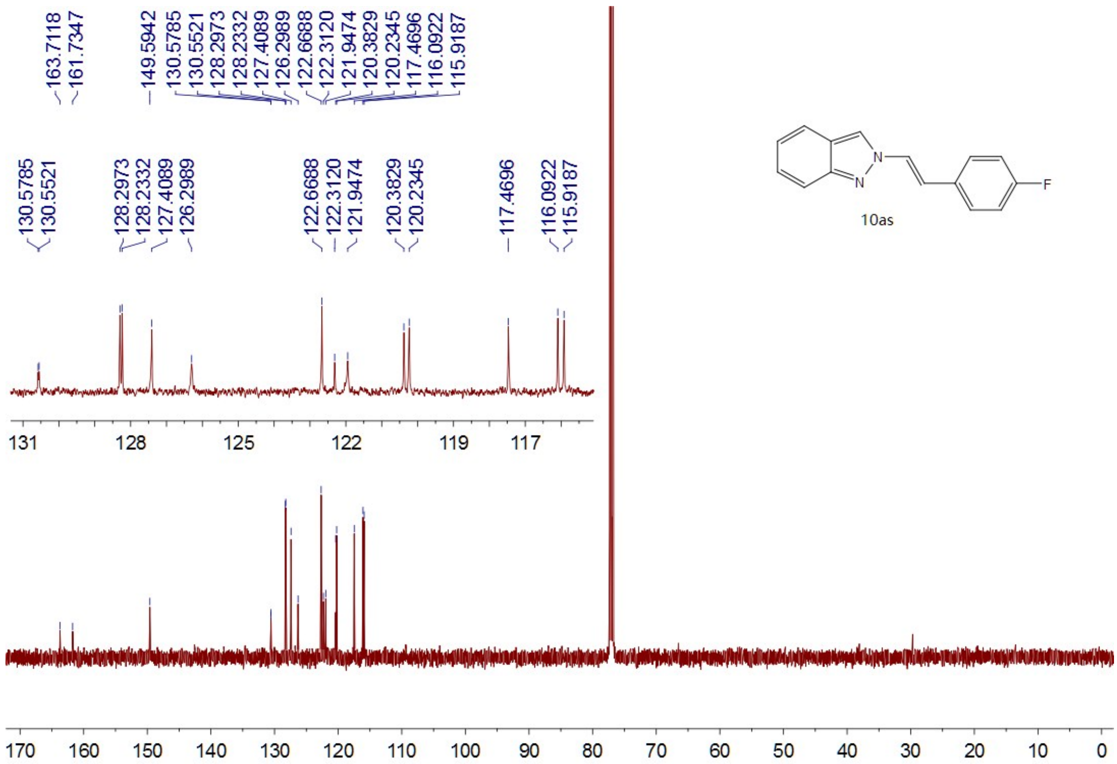
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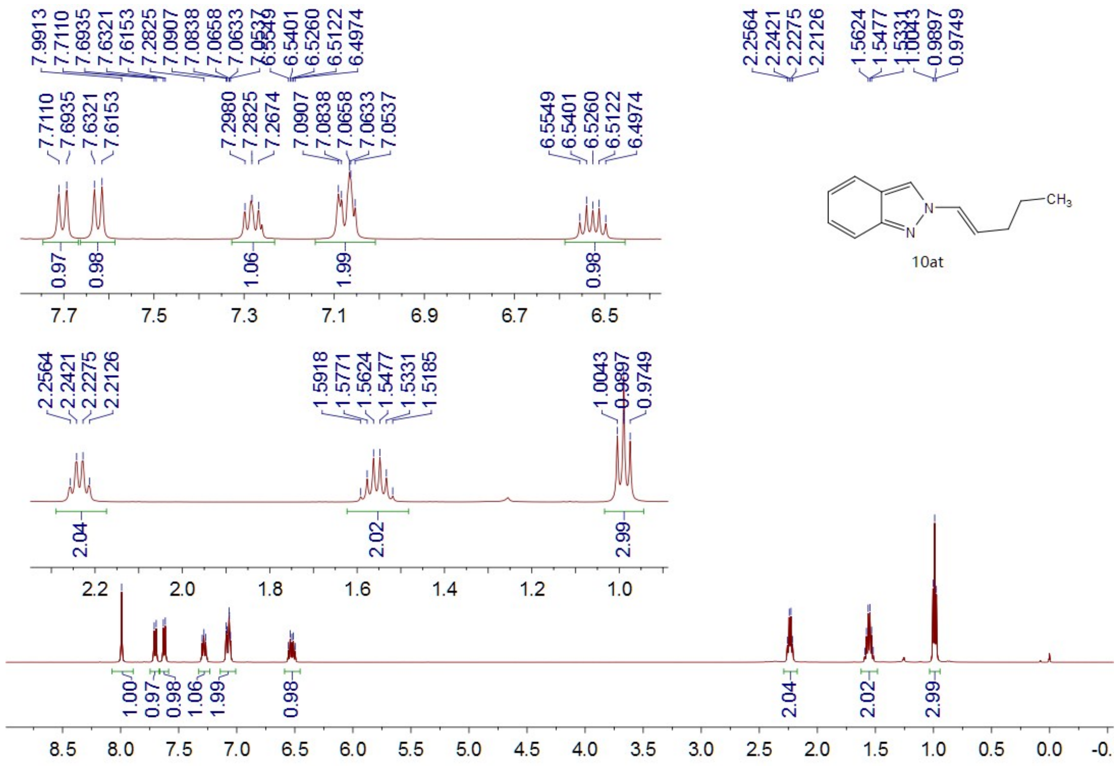
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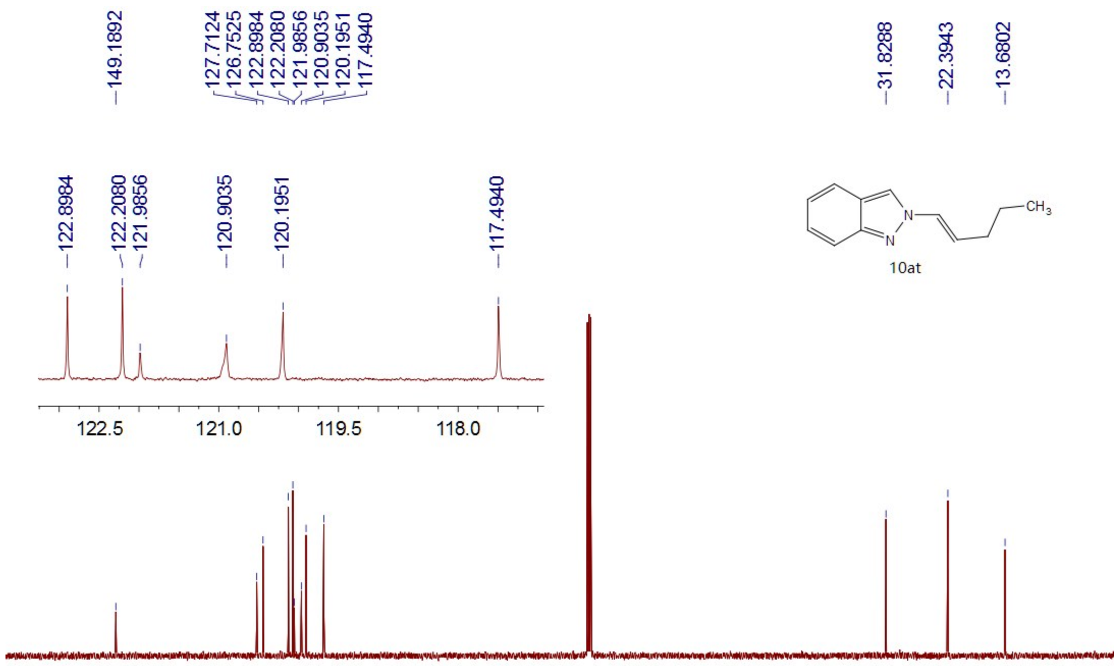
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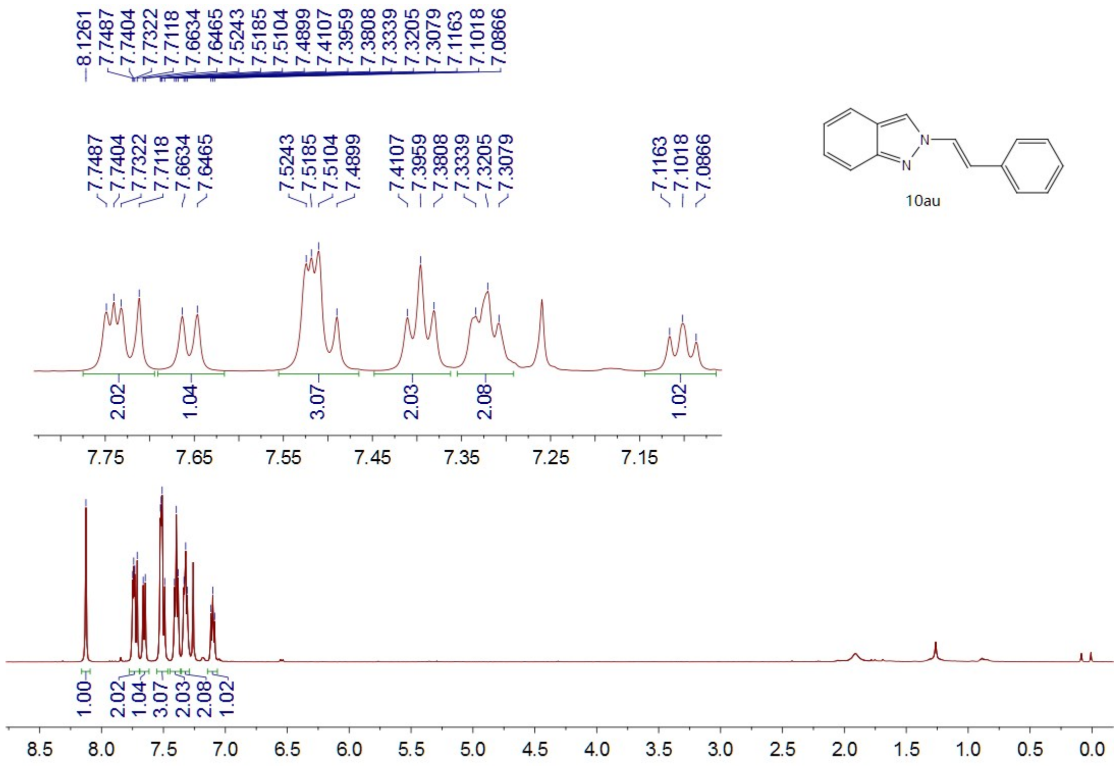
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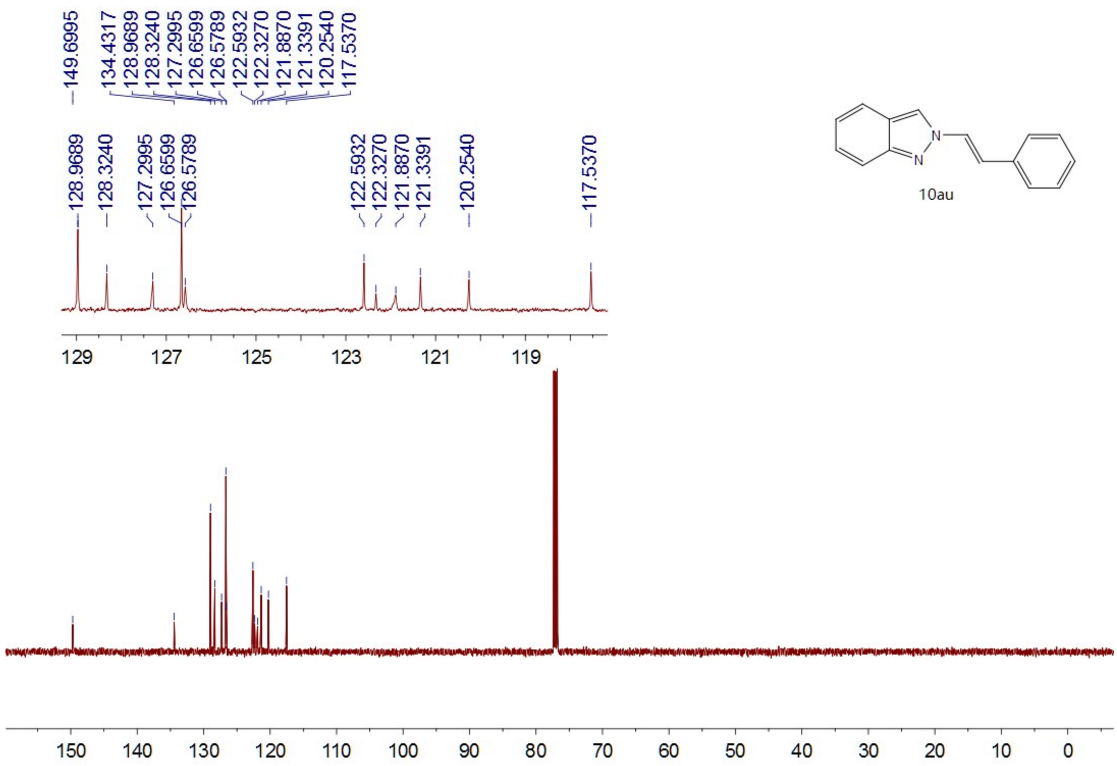
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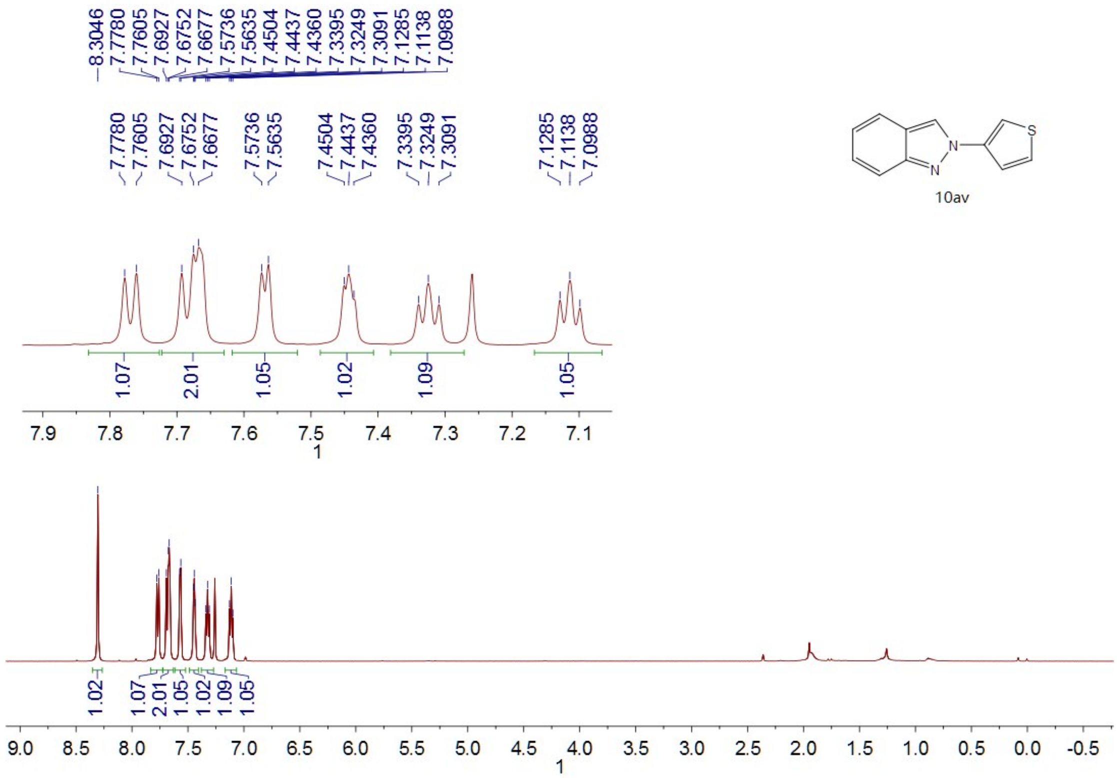
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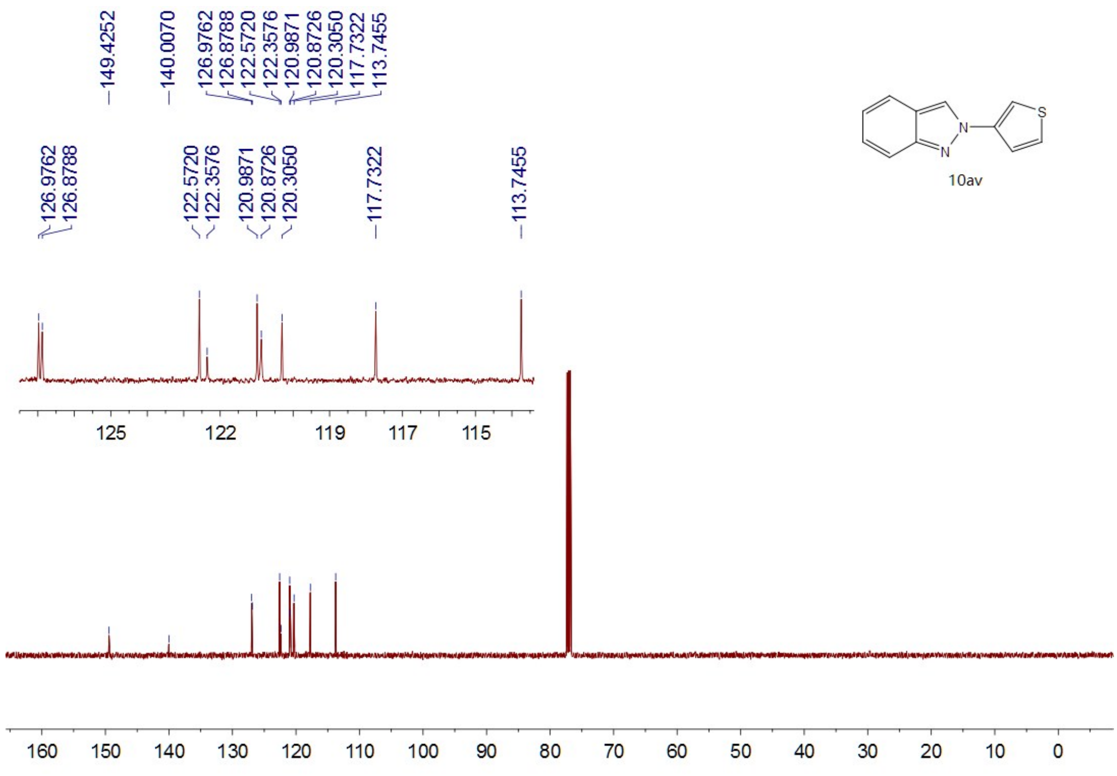
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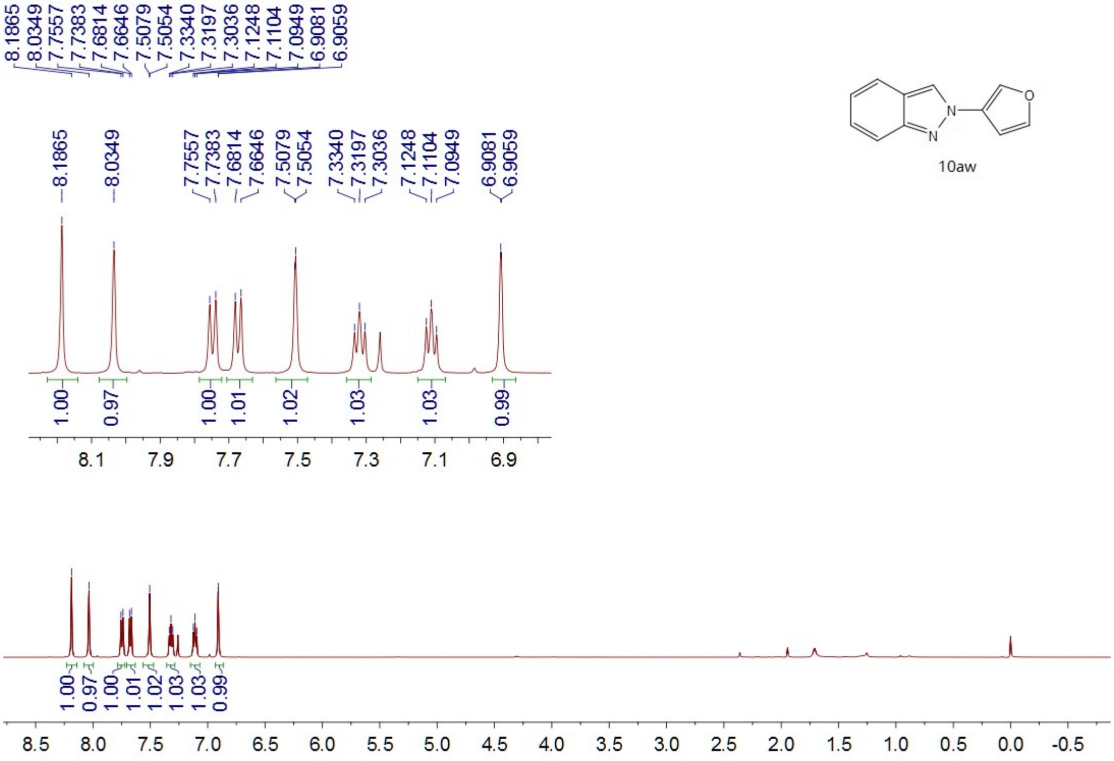
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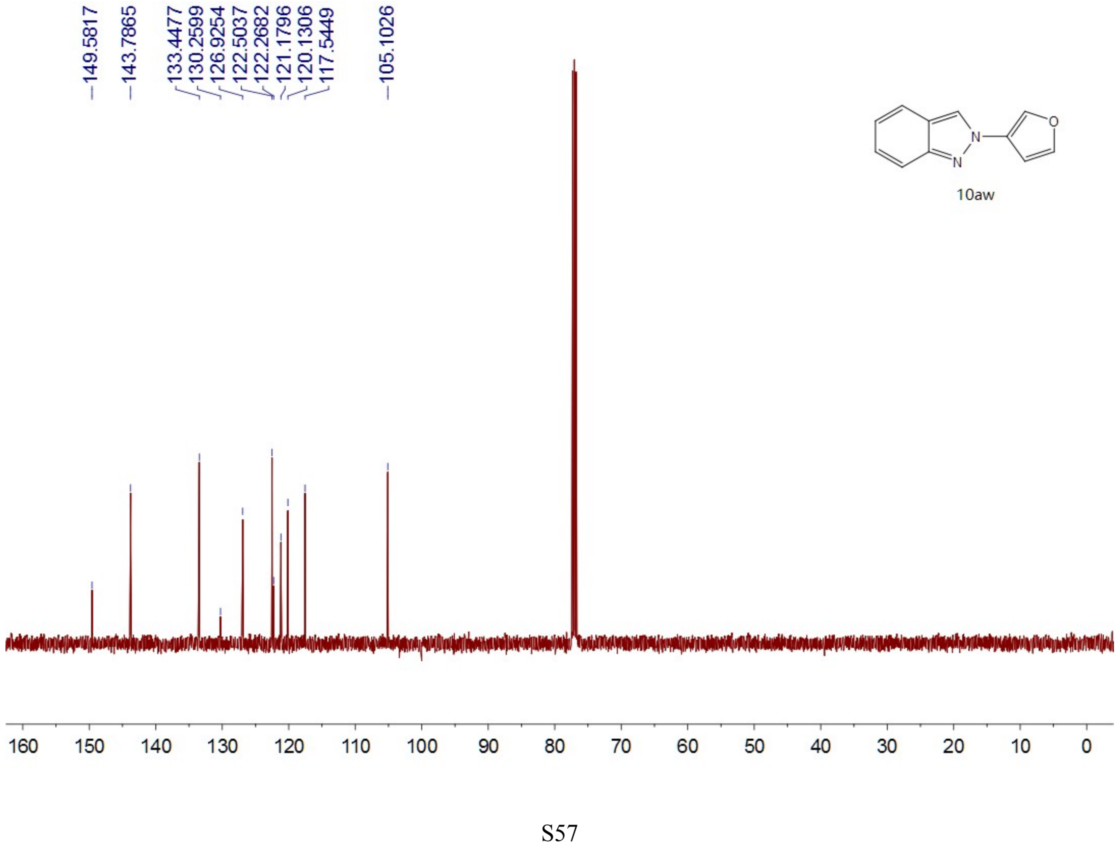
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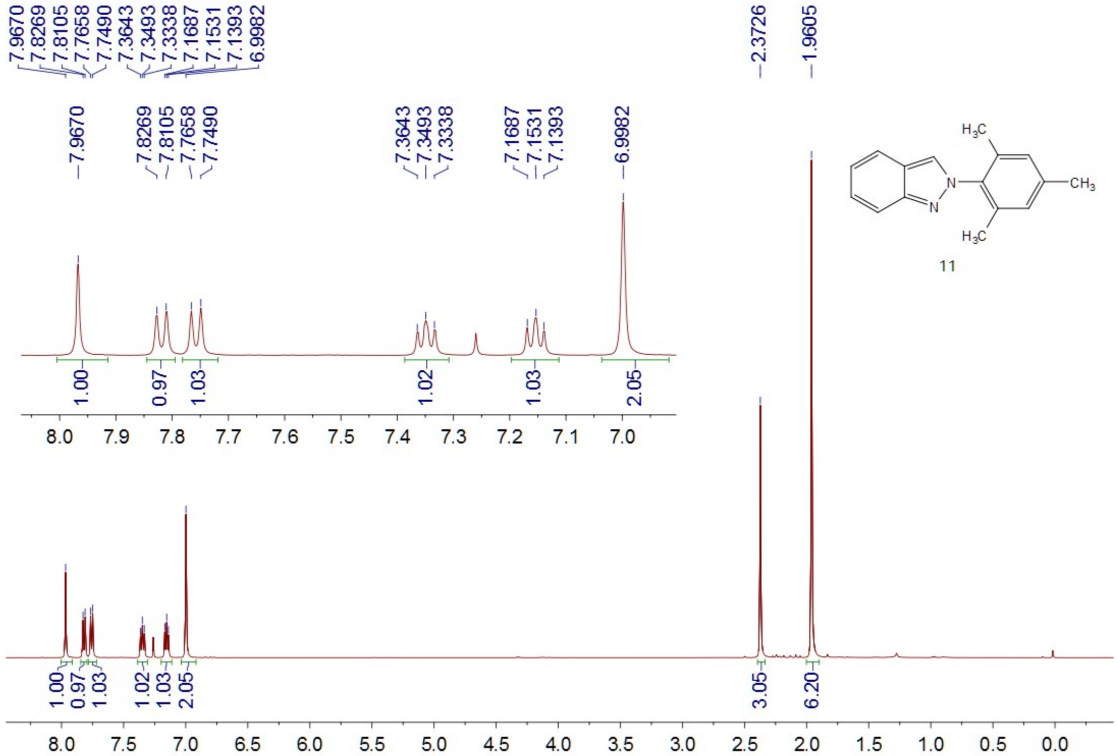
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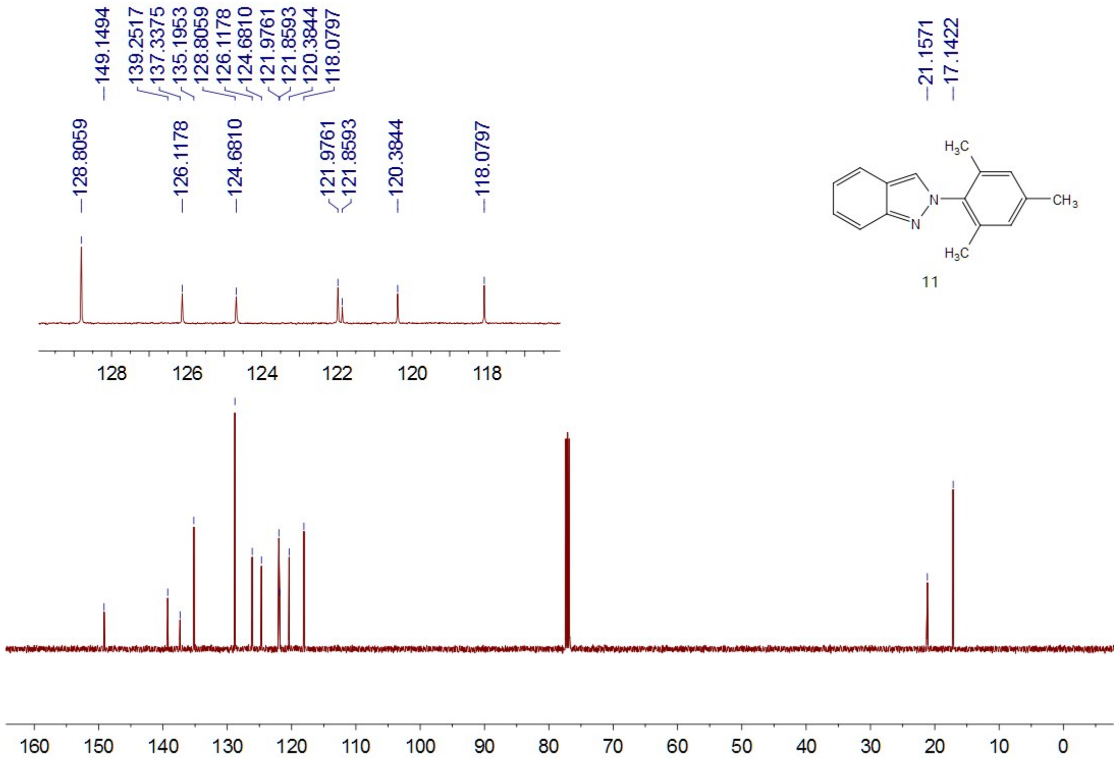
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