

Direct Deoxygenative C-N Coupling to Construct Indazole under Visible Light

Xinluo Song, Lingfeng Yin, Subin Hao, Yu Wang, Yanqi Chen, Cheng Ma, Ming-De Li* and Li Dang*

College of Chemistry and Chemical Engineering, Key (Guangdong-Hong Kong Joint) Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Guangdong 515063, P. R. China.

Supporting Information Placeholder

Email: mdli@stu.edu.cn, ldang@stu.edu.cn

Table of contents

1. General information.....	2
2. Experimental procedure	2
3. Mechanistic Studies.....	18
4. Green Chemistry Metrics.....	19
5. Metrics Computational results.....	20
6. NMR spectra.....	25
7. References.....	66

1. General information

Materials:

All photoreactions were carried out in 15 ml quartz tubes (bought from *Synthware*) under nitrogen atmosphere, unless otherwise mentioned. Major reagent B_2cat_2 was purchased from Energy Chemical, and other commercial reagents were purchased from *Energy Chemical*, *Bidepharm* or *J&K Scientific*. Ultra-dry solvents for all reactions were bought from *J&K Scientific*. The Photo Reaction Setup was purchased from *Hefei Hanhaixing Technology*.

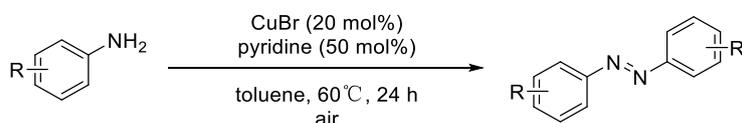
Chromatography and Instrumentation:

All NMR spectra were recorded at 25 °C. Chemical shifts (δ) are given in parts per million (ppm) and referenced to $CDCl_3$ (1H : 7.26 ppm, ^{13}C : 77.16) or $DMSO-d_6$ (1H : 2.50 ppm, ^{13}C : 39.52). Coupling constants (J) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, h = heptet, m = multiplet, dd = doublet of doublets, etc.). The 1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons)

2. Experimental procedure

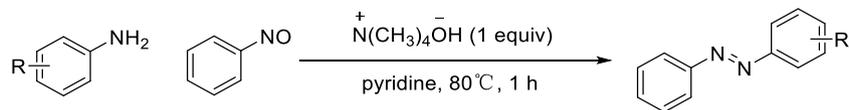
General Procedures for the Synthesis of Azobenzenes.

General Procedure 1 (GP 1): Symmetric Azobenzenes¹.



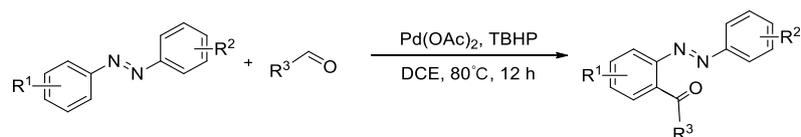
Aniline (1.0 equiv., 5 mmol), $CuBr$ (143 mg, 20 mol%, 1 mmol), pyridine (198 mg, 50 mol%) and toluene (30 mL) were carefully weighed into a 100 mL round-bottom flask under the air. The reaction mixture was refluxed in air at $60^\circ C$ for 24 hours. At the end of the reaction, the flask was cooled to room temperature and most of the solvent was removed by concentrating under vacuum. The reaction mixture was extracted with ethyl acetate, washed with brine, dried over $NaSO_4$, and concentrated under reduced pressure. The crude product is purified by flash column chromatography on silica gel (hexane: ethyl acetate = 150:1 ~ 50:1).

General Procedure 2 (GP 2): Asymmetric Azobenzene².



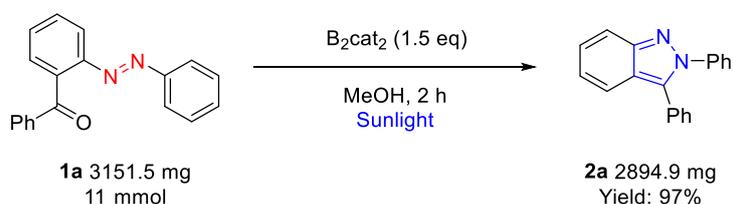
Aniline (1.0 equiv., 5 mmol) and 25% Tetramethylammonium hydroxide (1790 μL , 1.0 equiv., 5.0 mmol) dissolved in pyridine (30 mL) in a 100 mL flask and stirred vigorously for 10 minutes at room temperature. Nitrobenzene (589 mg, 1.1 equiv., 5.5 mmol) was then added to the flask and the reaction was heated to $80^\circ C$ for 1 h. The reaction was cooled to room temperature and extracted with ethyl acetate, washed with brine, dried over $NaSO_4$, and concentrated under reduced pressure. The crude product is purified by flash column chromatography on silica gel (hexane: ethyl acetate = 150:1 ~ 50:1).

General Procedure 3 (GP 3): 2-Acylazobenzenes³.



Azobenzene (2.0 mmol, 1.0 equiv.), aldehyde (2-3.0 mmol, 1.0-1.5 equiv.), Pd(OAc)₂ (5.0 mol %), and tert-butyl hydroperoxide (TBHP, 5.5 mol/L in decane (over molecular sieve 4A), 4.0 mmol, 2.0 equiv.) were stirred in 1,2-dichloroethane (10.0 mL) at 80°C for 12 h under N₂ atmosphere. The resulting mixture was cooled to room temperature, then evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel using hexane: ethyl acetate = 50:1 ~ 20:1.

Gram-Scale Synthesis.



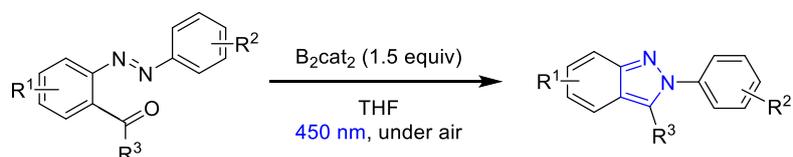
2-Benzoylazobenzene (3151.5 mg, 11 mmol, 1.0 equiv.), B₂cat₂ (3923.9 mg, 16.5 mmol, 1.5 equiv.) were carefully weighed into a 250 mL quartz flask containing a magnetic stirrer bar, then MeOH (150 mL) were added in the air. The flask was tightly sealed and stirred under sunlight irradiation for 2 hours. Irradiation is stopped and MeOH was removed by concentrating under vacuum. The reaction mixture was extracted with ethyl acetate, washed with water, dried over NaSO₄, and concentrated under reduced pressure. The crude product is purified by flash column chromatography on silica gel (hexane: ethyl acetate = 15:1), 2894.9 mg product (97% yield) was obtained as a white solid (**Figures S1**).



Figure S1: Gram-scale reaction under the sunlight.

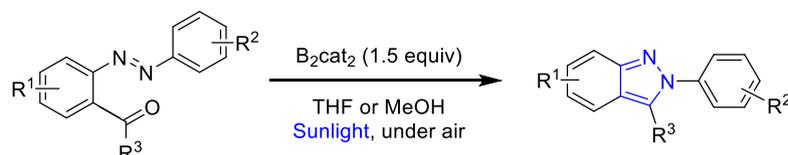
General Procedures for the Synthesis of 2H-Indazoles.

General Procedure 4 (GP 4): Reduction of 2-Acylazobenzenes to 2H-Indazoles under the 450 nm LED.



Azobenzene (1.0 eq., 0.2 mmol), B₂cat₂ (71 mg, 1.5 eq., 3.0 mmol) were carefully weighed into a flame-dried 15mL tube containing a small magnetic stirrer bar. THF (1.5 mL) were added in the air. The tube was tightly sealed and stirred under 450 nm LED irradiation for 0.5-1 hours. Irradiation was stopped and the solvent was removed by concentrating under vacuum. The crude product is purified by flash column chromatography on silica gel (hexane: ethyl acetate = 15:1).

General Procedure 5 (GP 5): Reduction of 2-Acylazobenzenes to 2H-Indazoles under the Sunlight.



Azobenzene (1.0 eq., 0.2 mmol), B₂cat₂ (71 mg, 1.5 eq., 3.0 mmol) were carefully weighed into a flame-dried 15 mL tube containing a small magnetic stirrer bar. THF or MeOH (1.5 mL) were added in the air. The tube was tightly sealed and stirred under sunlight irradiation for 0.5-1.5 hours. Irradiation was stopped and the solvent was removed by concentrating under vacuum. The crude product is purified by flash column chromatography on silica gel (hexane: ethyl acetate = 15:1) (Figures S2).

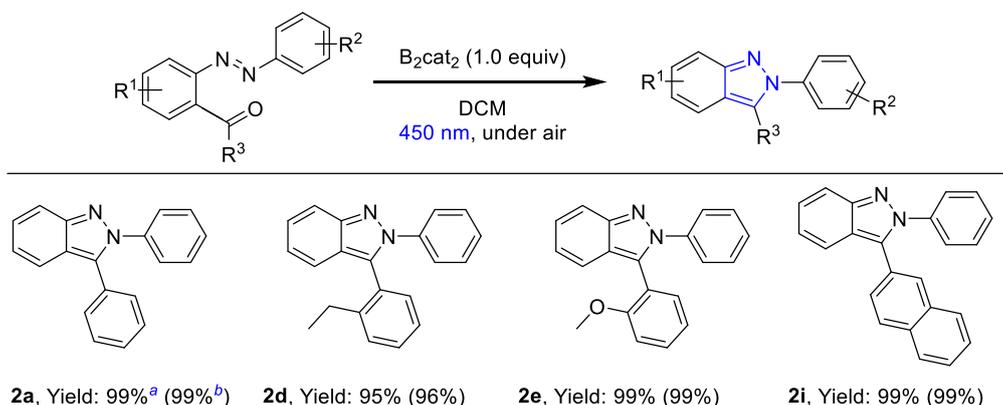


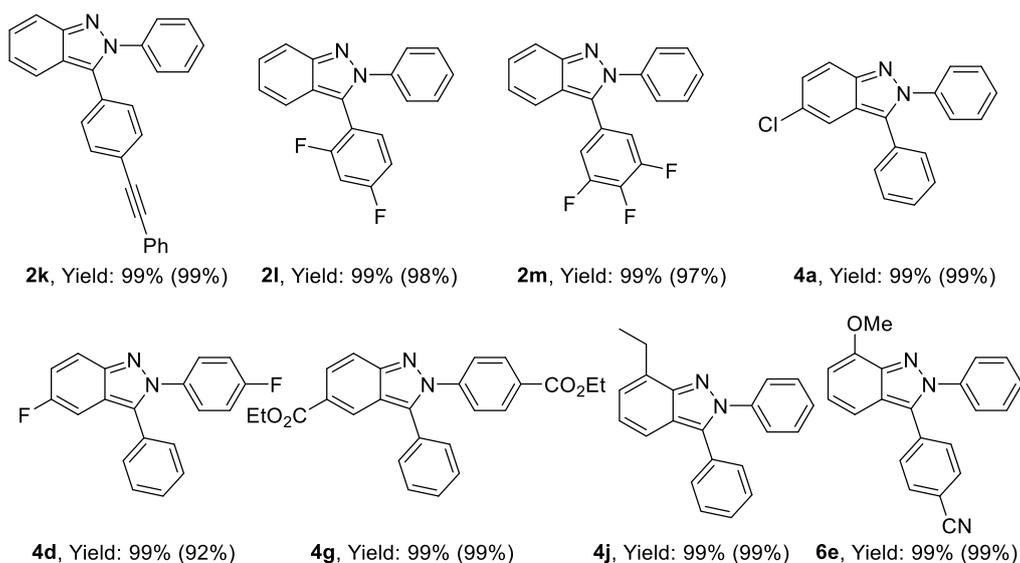
Figure S2: a) Changes in reaction for 30 minutes in MeOH under sunlight; b) Changes in reaction for 60 minutes in THF under sunlight.

General Procedure 6 (GP 6): Reduction of 2-Acylazobenzenes to 2H-Indazoles without column chromatography

2-Benzoylazobenzene (1.0 equiv.), B₂cat₂ (1.0 equiv.) were carefully weighed into quartz tube containing a magnetic stirrer bar, then DCM were added. The tube was tightly sealed and stirred under 450 nm irradiation for 0.5 hours. Irradiation was stopped, the reaction mixture was extracted with DCM, washed with sodium hydroxide solution (three times). Combined organic phases, dried over NaSO₄ and concentrated under reduced pressure. Recrystallization to obtain a purer product.

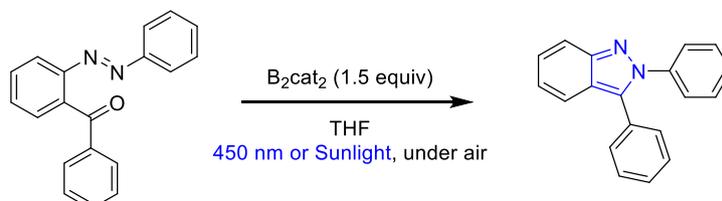
Table S1. Substrates extension for the chromatography-free method.





^a Yield of chromatography-free method according to GP6; ^b Yield of standard condition according to GP4.

(1) Conversion of azobenzene **1a** to 2H-indazole **2a**.

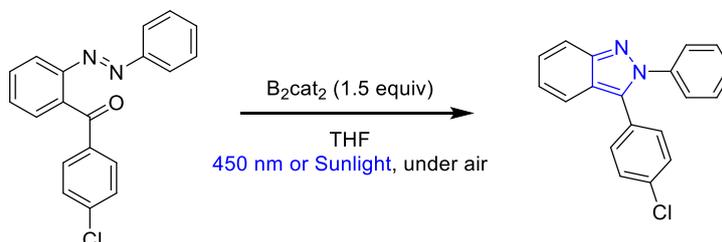


According to GP4/5/6, the reaction is carried out with **1a** (57.3 mg, 0.20 mmol), B₂cat₂ (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2a** (53.9 mg, 99% yield under 450 nm LED; 53.8 mg, 99% yield under sunlight; 99% yield under 450 nm LED without column chromatography).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.36 (m, 11H), 7.20 – 7.14 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 149.02, 140.28, 135.42, 129.96, 129.70, 128.97, 128.76, 128.31, 128.25, 126.98, 126.04, 122.51, 121.77, 120.51, 117.78.

(2) Conversion of azobenzene **1b** to 2H-indazole **2b**.



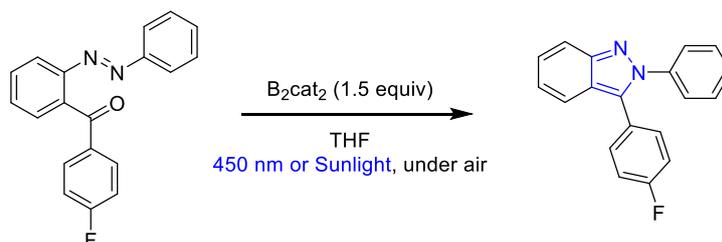
According to GP 4/5, the reaction is carried out with **1b** (64.2 mg, 0.20 mmol), B₂cat₂ (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2b** (59.1 mg, 97% yield under 450 nm LED; 57.3 mg, 94% yield under sunlight).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.35 (m, 8H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.22 – 7.14 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 148.99, 140.00, 134.50, 134.13, 130.86, 129.15, 129.14, 128.51,

128.40, 127.12, 126.04, 122.89, 121.73, 120.12, 117.91.

(3) Conversion of azobenzene **1c** to 2H-indazole **2c**.

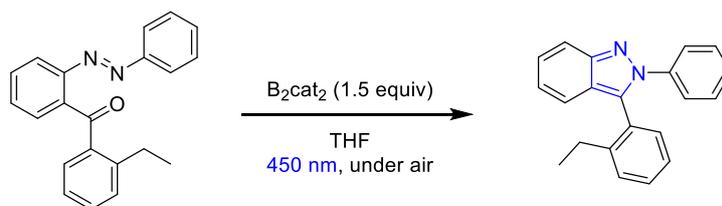


According to GP 4/5, the reaction is carried out with **1c** (60.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2c** (57.5 mg, 99% yield under 450 nm LED; 57.4 mg, 99% yield under sunlight).

1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.8$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.46 – 7.38 (m, 6H), 7.35 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.19 – 7.08 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.85, 161.38, 148.96, 140.05, 134.39, 131.53, 131.45, 129.09, 128.42, 127.08, 126.03, 122.70, 121.73, 120.21, 117.84, 116.13, 115.91.

(4) Conversion of azobenzene **1d** to 2H-indazole **2d**.

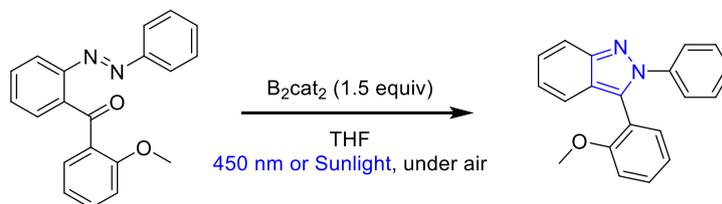


According to GP 4/6, the reaction is carried out with **1d** (62.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2d** (57.3 mg, 96% yield under 450 nm LED; 95% yield under 450 nm LED without column chromatography).

1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.8$ Hz, 1H), 7.50 – 7.29 (m, 11H), 7.14 – 7.08 (m, 1H), 2.32 (dp, $J = 22.1, 7.4$ Hz, 2H), 0.91 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.75, 143.83, 140.37, 135.25, 131.40, 129.55, 128.98, 128.88, 128.84, 127.88, 127.02, 126.02, 124.89, 122.91, 122.09, 120.72, 117.65, 26.00, 14.48.

(5) Conversion of azobenzene **1e** to 2H-indazole **2e**.



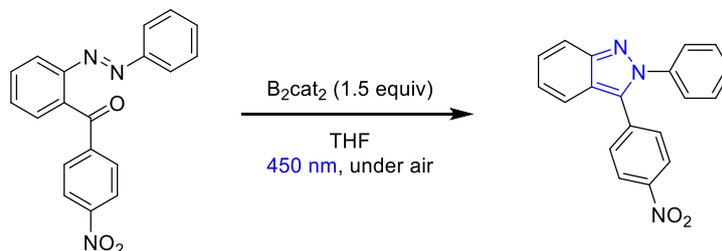
According to GP 4/5/6, the reaction is carried out with **1e** (63.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2e** (60.0 mg, 99% yield under 450 nm LED; 59.9 mg, 99% yield under sunlight; 99% yield under 450 nm LED without column chromatography).

1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, $J = 8.7, 5.5$ Hz, 1H), 7.65 – 7.59 (m, 1H), 7.51 – 7.32 (m,

8H), 7.16 – 7.07 (m, 2H), 6.88 (dd, $J = 7.9, 5.7$ Hz, 1H), 3.37 (d, $J = 5.6$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 156.75, 148.97, 141.41, 132.53, 131.68, 130.64, 128.60, 127.72, 126.74, 124.58, 122.59, 121.99, 120.89, 120.75, 119.15, 117.71, 111.51, 54.83.

(6) Conversion of azobenzene **1f** to 2H-indazole **2f**.

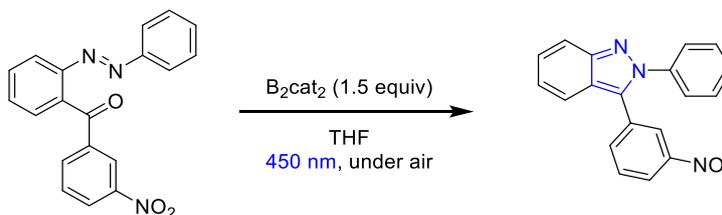


According to GP 4, the reaction is carried out with **1f** (66.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2f** (49.2 mg, 78% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.9$ Hz, 2H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.53 (d, $J = 8.9$ Hz, 2H), 7.48 – 7.40 (m, 6H), 7.27 – 7.21 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.15, 147.16, 139.73, 136.37, 132.73, 130.15, 129.42, 128.99, 127.33, 126.09, 124.06, 123.91, 122.08, 119.58, 118.29.

(7) Conversion of azobenzene **1g** to 2H-indazole **2g**.

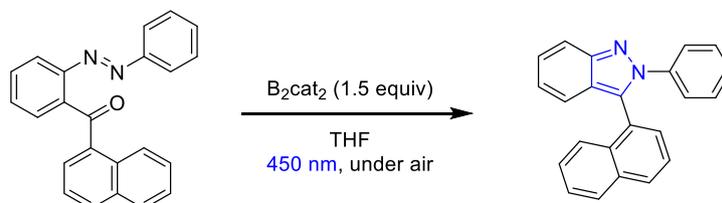


According to GP 4, the reaction is carried out with **1g** (66.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2g** (51.1 mg, 81% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 7.60 (dt, $J = 15.7, 7.8$ Hz, 2H), 7.45 (s, 6H), 7.28 – 7.22 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.06, 148.52, 139.60, 135.31, 132.51, 131.68, 129.84, 129.41, 128.98, 127.32, 126.10, 124.19, 123.70, 122.94, 121.87, 119.53, 118.21.

(8) Conversion of azobenzene **1h** to 2H-indazole **2h**.



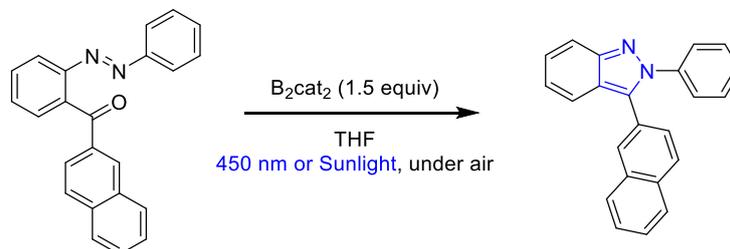
According to GP 4, the reaction is carried out with **1h** (67.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2h** (63.9 mg, 99% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.91 (m, 3H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.55 – 7.37 (m, 8H),

7.26 – 7.21 (m, 3H), 7.10 (dd, $J = 8.2, 6.8$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.91, 140.28, 134.01, 133.77, 132.08, 129.65, 129.53, 128.82, 127.08, 126.84, 126.34, 125.65, 125.32, 125.06, 123.45, 122.33, 120.87, 117.87.

(9) Conversion of azobenzene **1i** to 2H-indazole **2i**

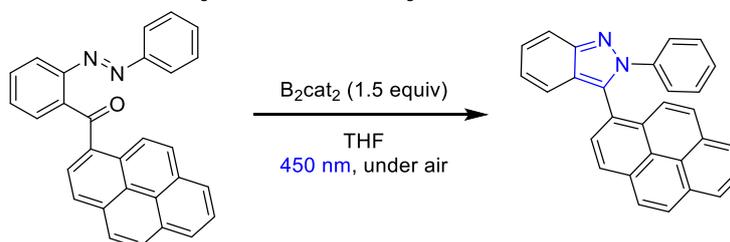


According to GP 4/5/6, the reaction is carried out with **1i** (67.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2i** (64.0 mg, 99% yield under 450 nm LED; 64.0 mg, 99% yield under sunlight; 99% yield under 450 nm LED without column chromatography).

^1H NMR (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.85 (dd, $J = 22.8, 8.2$ Hz, 5H), 7.61 – 7.48 (m, 4H), 7.48 – 7.36 (m, 4H), 7.33 (d, $J = 8.5$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.12, 140.29, 135.38, 133.31, 132.79, 129.08, 129.06, 128.45, 128.33, 128.25, 127.82, 127.39, 127.11, 127.00, 126.89, 126.69, 126.03, 122.70, 122.06, 120.58, 117.87.

(10) Conversion of azobenzene **1j** to 2H-indazole **2j**

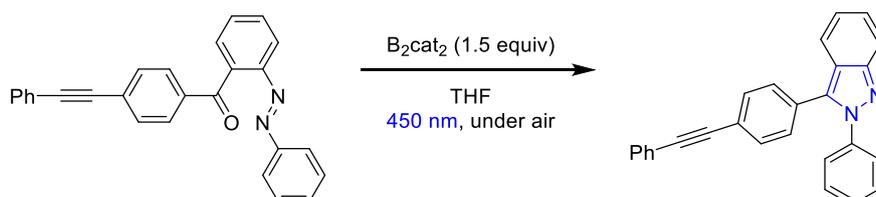


According to GP 4, the reaction is carried out with **1j** (82.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2j** (78.9 mg, 99% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 8.31 – 7.92 (m, 9H), 7.82 (d, $J = 7.7$ Hz, 1H), 7.44 (dd, $J = 17.0, 7.9$ Hz, 4H), 7.16 (d, $J = 30.0$ Hz, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.84, 140.13, 134.54, 131.76, 131.26, 130.85, 130.00, 128.91, 128.51, 128.46, 128.00, 127.29, 127.26, 126.40, 125.80, 125.65, 125.29, 124.97, 124.74, 124.54, 124.44, 123.68, 122.58, 120.95, 117.90.

(11) Conversion of azobenzene **1k** to 2H-indazole **2k**



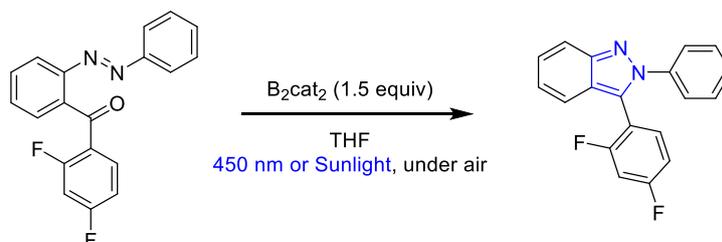
According to GP 4/6, the reaction is carried out with **1k** (77.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1)

give the desired product **2k** (73.9 mg, 99% yield under 450 nm LED; 99% yield under 450 nm LED without column chromatography).

^1H NMR (400 MHz, CDCl_3) δ 7.85 (dd, $J = 8.8, 1.8$ Hz, 1H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.57 (dtd, $J = 5.9, 3.4, 2.0$ Hz, 4H), 7.49 – 7.36 (m, 11H), 7.23 – 7.17 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.07, 140.13, 134.67, 131.97, 131.66, 129.66, 129.53, 129.15, 128.55, 128.46, 128.43, 127.11, 126.06, 123.25, 122.96, 122.88, 121.78, 120.33, 117.92, 90.94, 88.86.

(12) Conversion of azobenzene **1l** to 2H-indazole **2l**

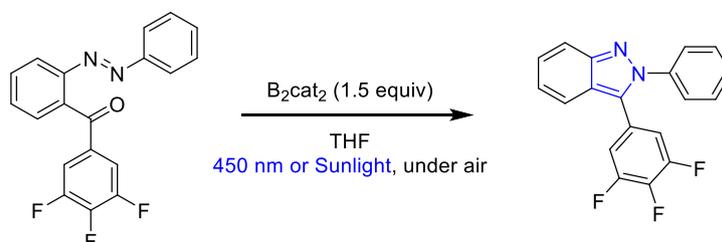


According to GP 4/5/6, the reaction is carried out with **1l** (64.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2l** (64.0 mg, 98% yield under 450 nm LED; 64.1 mg, 98% yield under sunlight; 98% yield under 450 nm LED without column chromatography).

^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 7.48 – 7.35 (m, 7H), 7.18 (t, $J = 7.5$ Hz, 1H), 6.99 (t, $J = 8.2$ Hz, 1H), 6.91 (t, $J = 9.2$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 164.80, 164.66, 162.26, 162.13, 161.27, 161.14, 158.75, 158.63, 148.96, 140.25, 132.84, 132.79, 132.75, 129.08, 128.62, 128.45, 127.05, 125.18, 122.85, 122.72, 120.06, 118.00, 114.46, 114.30, 112.18, 112.15, 111.97, 111.93, 105.22, 104.96, 104.71.

(13) Conversion of azobenzene **1m** to 2H-indazole **2m**

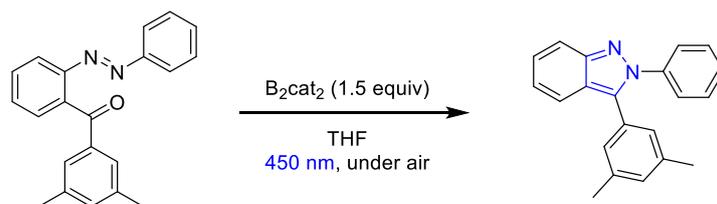


According to GP 4/5/6, the reaction is carried out with **1m** (68.1 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2m** (64.6 mg, 99% yield under 450 nm LED; 64.4 mg, 99% yield under sunlight; 97% yield under 450 nm LED without column chromatography).

^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.80 (m, 1H), 7.69 (t, $J = 7.2$ Hz, 1H), 7.52 – 7.39 (m, 6H), 7.23 (q, $J = 6.9$ Hz, 1H), 6.99 (q, $J = 6.6$ Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 152.74, 152.69, 152.64, 152.59, 150.24, 150.19, 150.14, 150.10, 148.95, 141.01, 139.54, 138.48, 131.92, 129.40, 128.99, 127.27, 125.97, 123.58, 121.74, 119.48, 118.17, 113.97, 113.91, 113.81, 113.74.

(14) Conversion of azobenzene **1n** to 2H-indazole **2n**

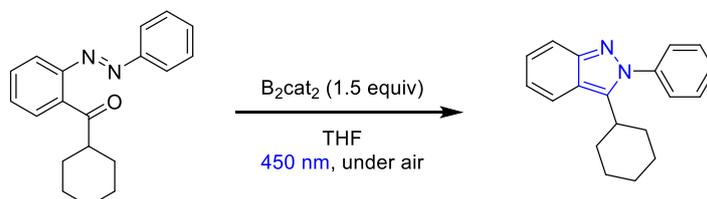


According to GP 4, the reaction is carried out with **1n** (62.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2n** (59.3 mg, 99% yield under 450 nm LED).

1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.7$ Hz, 1H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.52 – 7.46 (m, 2H), 7.45 – 7.37 (m, 4H), 7.16 (s, 1H), 7.02 (d, $J = 13.6$ Hz, 3H), 2.31 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.98, 140.39, 138.30, 135.77, 130.06, 129.75, 128.87, 128.14, 127.46, 126.93, 125.98, 122.26, 121.75, 120.75, 117.70, 21.31.

(15) Conversion of azobenzene **1o** to 2H-indazole **2o**

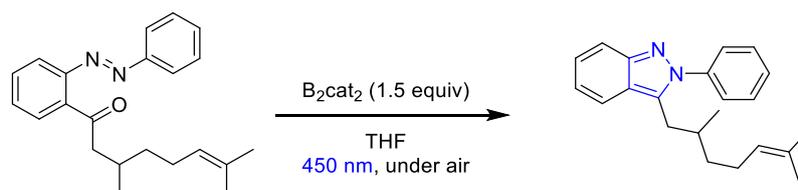


According to GP 4, the reaction is carried out with **1o** (58.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2o** (53.6 mg, 97% yield under 450 nm LED).

1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.6$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.60 – 7.47 (m, 5H), 7.35 – 7.29 (m, 1H), 7.10 – 7.03 (m, 1H), 3.00 (tt, $J = 11.6, 4.2$ Hz, 1H), 2.04 – 1.75 (m, 7H), 1.32 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.88, 141.14, 140.23, 129.14, 128.98, 126.45, 126.32, 121.24, 120.55, 119.53, 117.84, 37.32, 32.60, 26.59, 25.88.

(16) Conversion of azobenzene **1p** to 2H-indazole **2p**

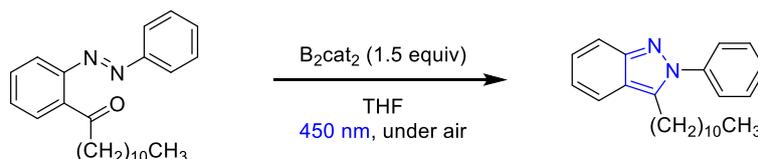


According to GP 4, the reaction is carried out with **1p** (66.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2p** (40.8 mg, 99% yield under 450 nm LED).

1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.7$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.59 – 7.46 (m, 5H), 7.34 (dd, $J = 8.3, 6.4$ Hz, 1H), 7.13 – 7.06 (m, 1H), 4.94 (t, $J = 7.0$ Hz, 1H), 3.15 – 2.78 (m, 2H), 1.84 (ddt, $J = 37.0, 14.1, 6.8$ Hz, 3H), 1.66 (s, 3H), 1.53 (s, 3H), 1.29 – 1.11 (m, 2H), 0.78 (d, $J = 6.6$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.52, 140.22, 136.19, 131.55, 129.13, 128.91, 126.62, 126.46, 124.14, 121.57, 120.96, 120.43, 117.56, 36.87, 33.19, 32.56, 25.69, 25.33, 19.74, 17.65.

(17) Conversion of azobenzene **1q** to 2H-indazole **2q**

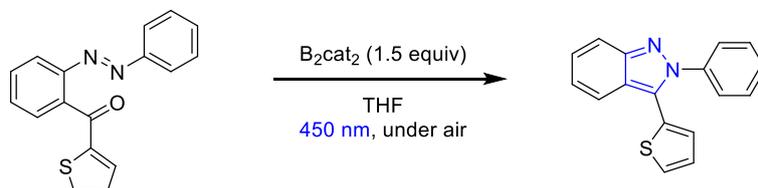


According to GP 4, the reaction is carried out with **1q** (72.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2q** (48.8 mg, 70% yield under 450 nm LED).

1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, $J = 8.8$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.59 – 7.47 (m, 5H), 7.37 – 7.31 (m, 1H), 7.13 – 7.06 (m, 1H), 3.10 – 3.01 (m, 2H), 1.66 (p, $J = 7.5$ Hz, 2H), 1.27 (dd, $J = 23.8, 13.9$ Hz, 16H), 0.91 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.64, 140.16, 136.93, 129.14, 128.85, 126.63, 126.21, 121.09, 120.89, 120.24, 117.62, 31.90, 29.57, 29.55, 29.38, 29.37, 29.31, 29.28, 29.10, 25.29, 22.68, 14.10.

(18) Conversion of azobenzene **1r** to 2H-indazole **2r**

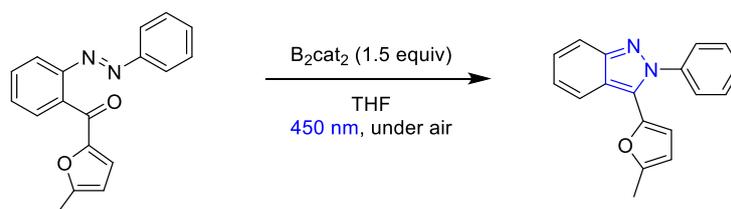


According to GP 4, the reaction is carried out with **1r** (58.4 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2r** (53.5 mg, 97% yield under 450 nm LED).

1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.5$ Hz, 1H), 7.80 – 7.77 (m, 1H), 7.49 (d, $J = 2.6$ Hz, 2H), 7.47 – 7.44 (m, 3H), 7.41 – 7.36 (m, 2H), 7.21 – 7.17 (m, 1H), 7.05 (dd, $J = 5.1, 3.6$ Hz, 1H), 7.01 (dd, $J = 3.6, 1.2$ Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.87, 140.07, 130.42, 129.68, 129.12, 128.98, 128.17, 127.52, 127.41, 127.12, 126.54, 122.90, 121.82, 120.60, 117.86.

(19) Conversion of azobenzene **1s** to 2H-indazole **2s**

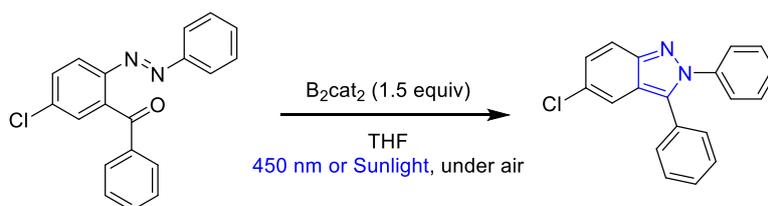


According to GP 4, the reaction is carried out with **1s** (58.1 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **2s** (47.7 mg, 87% yield under 450 nm LED).

1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, $J = 8.5$ Hz, 1H), 7.75 (d, $J = 8.7$ Hz, 1H), 7.57 – 7.48 (m, 5H), 7.39 – 7.32 (m, 1H), 7.18 (dd, $J = 8.5, 6.6$ Hz, 1H), 5.98 (d, $J = 3.3$ Hz, 1H), 5.89 (d, $J = 3.4$ Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.01, 148.86, 143.27, 140.68, 129.23, 129.17, 127.55, 127.12, 126.40, 122.57, 121.57, 120.46, 117.56, 110.59, 107.57, 13.63.

(20) Conversion of azobenzene **3a** to 2H-indazole **4a**

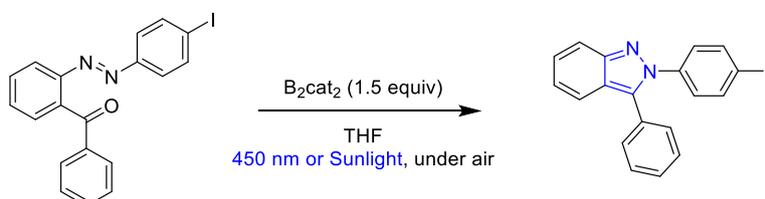


According to GP 4/5/6, the reaction is carried out with **3a** (64.2 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4a** (60.5 mg, 99% yield under 450 nm LED; 60.4 mg, 99% yield under sunlight; 99% yield under 450 nm LED without column chromatography).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 – 7.66 (m, 2H), 7.51 – 7.28 (m, 11H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 147.31, 139.96, 135.22, 129.58, 129.37, 129.07, 128.92, 128.63, 128.51, 128.40, 128.19, 125.91, 122.18, 119.39, 119.26.

(21) Conversion of azobenzene **3b** to 2H-indazole **4b**

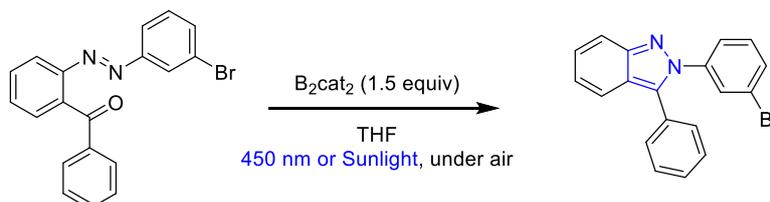


According to GP 4/5, the reaction is carried out with **3b** (82.4 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4b** (79.0 mg, 99% yield under 450 nm LED; 79.2 mg, 99% yield under sunlight).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.76 – 7.68 (m, 3H), 7.48 – 7.36 (m, 6H), 7.19 (ddd, $J = 21.5, 10.6, 4.4$ Hz, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 149.13, 139.91, 138.15, 135.46, 129.70, 129.63, 128.99, 128.61, 127.57, 127.35, 122.79, 121.96, 120.52, 117.73, 93.60.

(22) Conversion of azobenzene **3c** to 2H-indazole **4c**.

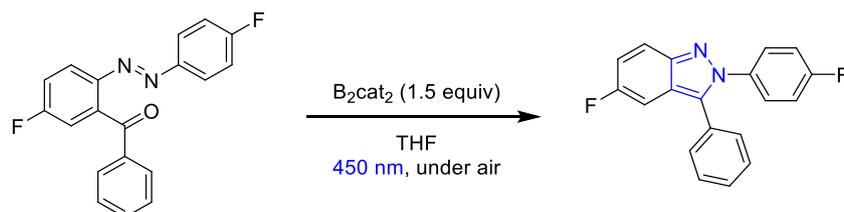


According to GP 4/5, the reaction is carried out with **3c** (73.0 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4c** (69.5 mg, 99% yield under 450 nm LED; 69.2 mg, 99% yield under sunlight).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 – 7.77 (m, 2H), 7.76 – 7.69 (m, 1H), 7.56 – 7.50 (m, 1H), 7.50 – 7.36 (m, 6H), 7.32 – 7.26 (m, 1H), 7.26 – 7.14 (m, 2H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 149.17, 141.31, 135.65, 131.34, 130.08, 129.71, 129.51, 129.05, 128.98, 128.69, 127.42, 124.56, 122.87, 122.54, 121.88, 120.56, 117.78.

(23) Conversion of azobenzene **3d** to 2H-indazole **4d**.

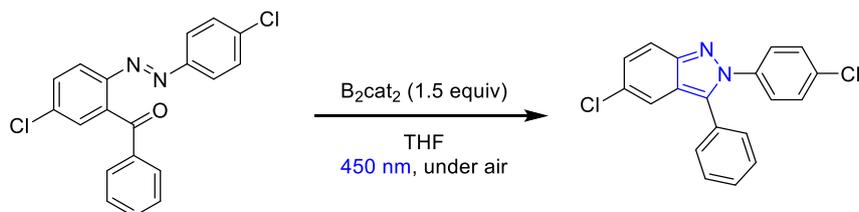


According to GP 4/6, the reaction is carried out with **3d** (64.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4d** (56.4 mg, 92% yield under 450 nm LED; 92% yield under 450 nm LED without column chromatography).

^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 9.3, 4.5$ Hz, 1H), 7.41 (t, $J = 6.1$ Hz, 5H), 7.34 – 7.26 (m, 3H), 7.19 (td, $J = 9.2, 2.2$ Hz, 1H), 7.10 (t, $J = 8.5$ Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 163.44, 160.97, 160.28, 157.88, 146.31, 136.16, 135.80, 135.72, 129.47, 129.35, 128.99, 128.63, 127.67, 127.58, 121.11, 120.99, 119.88, 119.79, 119.00, 118.71, 116.17, 115.94, 103.01, 102.76.

(24) Conversion of azobenzene **3e** to 2H-indazole **4e**.

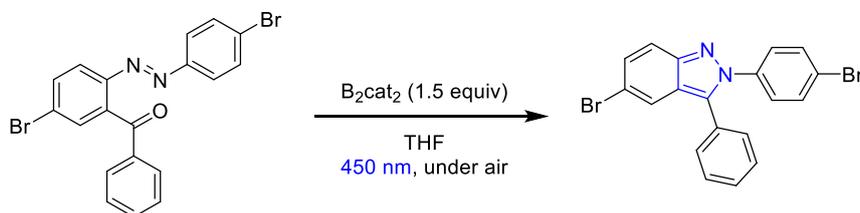


According to GP 4, the reaction is carried out with **3e** (71.0 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4e** (61.7 mg, 91% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 9.1$ Hz, 1H), 7.69 – 7.65 (m, 1H), 7.48 – 7.28 (m, 10H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.36, 138.41, 135.30, 134.42, 129.57, 129.28, 129.10, 129.05, 128.89, 128.73, 128.45, 126.99, 122.27, 119.31, 119.20.

(25) Conversion of azobenzene **3f** to 2H-indazole **4f**.

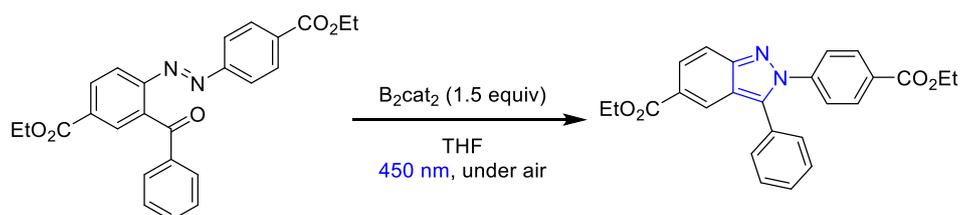


According to GP 4, the reaction is carried out with **3f** (88.8 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4f** (84.9 mg, 99% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.85 (s, 1H), 7.68 (d, $J = 9.1$ Hz, 1H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 7.4$ Hz, 4H), 7.32 (dd, $J = 8.7, 4.4$ Hz, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.44, 138.86, 135.13, 132.26, 130.99, 129.57, 129.13, 129.00, 128.94, 127.26, 123.08, 122.65, 122.46, 119.50, 116.24.

(26) Conversion of azobenzene **3g** to 2H-indazole **4g**.

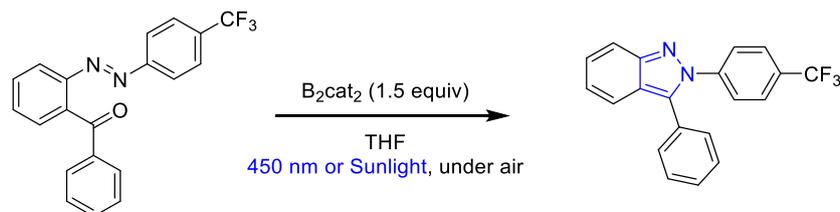


According to GP 4/6, the reaction is carried out with **3g** (86.1 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4g** (82.3 mg, 99% yield under 450 nm LED; 99% yield under 450 nm LED without column chromatography).

1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.09 (d, $J = 8.6$ Hz, 2H), 8.05 – 7.98 (m, 1H), 7.80 (d, $J = 9.1$ Hz, 1H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.49 – 7.43 (m, 3H), 7.38 (d, $J = 3.4$ Hz, 2H), 4.40 (qd, $J = 7.0, 2.8$ Hz, 4H), 1.41 (td, $J = 7.0, 2.2$ Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.76, 165.59, 150.29, 143.19, 138.35, 130.46, 130.43, 129.76, 129.24, 129.20, 128.81, 127.29, 125.66, 125.29, 125.26, 121.55, 117.58, 61.37, 61.00, 14.41, 14.28.

(27) Conversion of azobenzene **3h** to 2H-indazole **4h**.

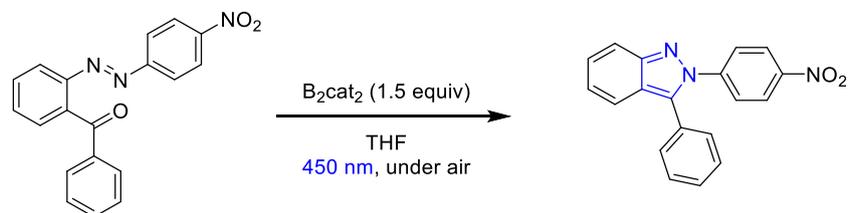


According to GP 4/5, the reaction is carried out with **3h** (70.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4h** (67.3 mg, 99% yield under 450 nm LED; 67.3 mg, 99% yield under sunlight).

1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.70 – 7.59 (m, 4H), 7.48 – 7.37 (m, 6H), 7.18 (t, $J = 7.5$ Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.39, 143.02, 135.74, 130.27, 129.94, 129.73, 129.54, 129.09, 128.79, 127.59, 126.20, 126.17, 126.08, 125.10, 123.02, 122.40, 122.15, 120.56, 117.83.

(28) Conversion of azobenzene **3i** to 2H-indazole **4i**.

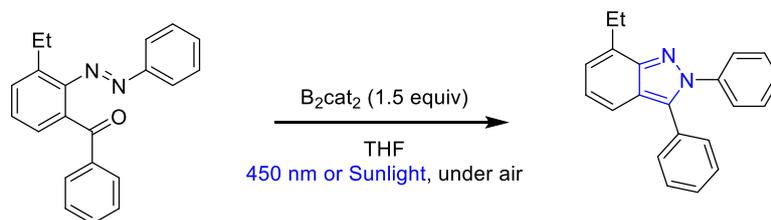


According to GP 4, the reaction is carried out with **3i** (66.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4i** (62.5 mg, 99% yield under 450 nm LED).

1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, $J = 9.0$ Hz, 2H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.67 (t, $J = 9.6$ Hz, 3H), 7.51 – 7.33 (m, 6H), 7.17 (t, $J = 7.5$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.61, 146.79, 145.03, 136.06, 129.72, 129.25, 129.10, 128.04, 126.21, 124.47, 123.38, 122.40, 120.56, 117.82.

(29) Conversion of azobenzene **3j** to 2H-indazole **4j**.

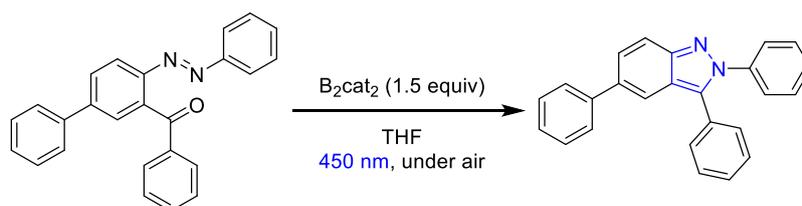


According to GP 4/5/6, the reaction is carried out with **3j** (62.9 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4j** (59.3 mg, 99% yield under 450 nm LED; 59.2 mg, 99% yield under sunlight; 99% yield under 450 nm LED without column chromatography).

^1H NMR (400 MHz, CDCl_3) δ 7.60 (t, $J = 8.1$ Hz, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.33 (m, 8H), 7.25 – 7.08 (m, 2H), 3.19 (q, $J = 7.5$ Hz, 2H), 1.50 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.60, 140.40, 135.62, 133.95, 130.21, 129.72, 129.00, 128.69, 128.19, 128.17, 126.29, 123.86, 122.93, 121.74, 117.92, 24.32, 13.92.

(30) Conversion of azobenzene **3k** to 2H-indazole **4k**.

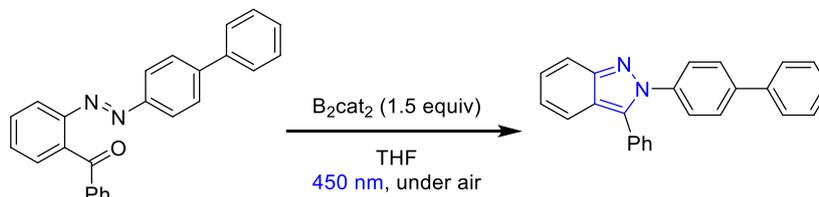


According to GP 4, the reaction is carried out with **3k** (72.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4k** (67.9 mg, 98% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.72 – 7.63 (m, 3H), 7.52 – 7.32 (m, 13H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.41, 141.68, 140.14, 136.01, 135.89, 129.83, 129.74, 129.04, 128.87, 128.75, 128.45, 128.36, 127.83, 127.27, 126.98, 126.00, 122.20, 118.24, 118.10.

(31) Conversion of azobenzene **3l** to 2H-indazole **4l**.

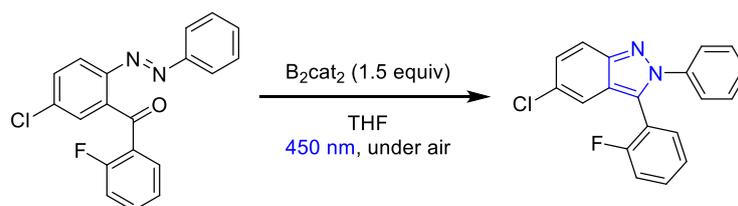


According to GP 4, the reaction is carried out with **3l** (72.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **4l** (64.4 mg, 93% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.8$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.66 – 7.60 (m, 4H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.43 (tq, $J = 14.8, 7.2$ Hz, 9H), 7.21 – 7.14 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.62, 141.05, 139.86, 139.29, 135.43, 129.93, 129.75, 128.88, 128.85, 128.41, 127.76, 127.58, 127.11, 127.06, 126.19, 123.17, 121.86, 120.52, 117.72.

(32) Conversion of azobenzene **5a** to 2H-indazole **6a**.

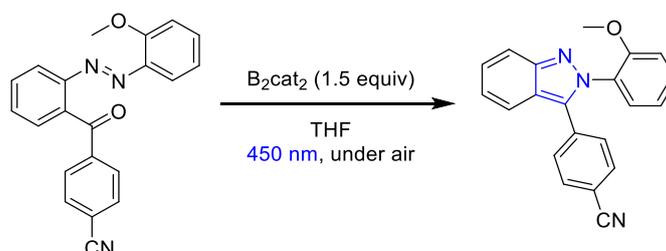


According to GP 4, the reaction is carried out with **5a** (67.8 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **6a** (62.6 mg, 97% yield under 450 nm LED).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 9.2$ Hz, 1H), 7.59 (s, 1H), 7.47 – 7.29 (m, 8H), 7.22 (td, $J = 7.6, 0.9$ Hz, 1H), 7.13 (t, $J = 9.1$ Hz, 1H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 160.79, 158.30, 147.30, 140.14, 131.79, 131.77, 131.31, 131.23, 129.36, 129.07, 128.56, 128.40, 128.34, 125.05, 124.66, 124.62, 123.11, 119.52, 119.11, 117.61, 117.46, 116.60, 116.39.

(33) Conversion of azobenzene **5b** to 2H-indazole **6b**.

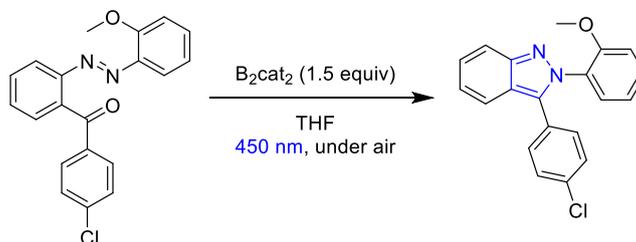


According to GP 4, the reaction is carried out with **5b** (68.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **6b** (57.9 mg, 89% yield under 450 nm LED).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.6$ Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.45 (dd, $J = 19.9, 8.6$ Hz, 4H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 8.3$ Hz, 1H), 3.45 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 153.40, 148.85, 135.19, 134.96, 132.24, 131.16, 128.95, 128.78, 128.60, 127.14, 123.44, 121.19, 120.84, 119.70, 118.49, 118.10, 112.25, 111.50, 55.35.

(34) Conversion of azobenzene **5c** to 2H-indazole **6c**.



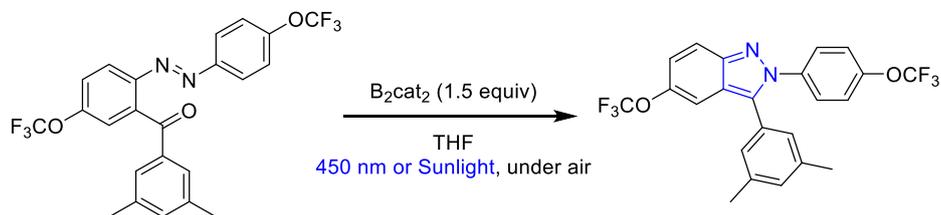
According to GP 4, the reaction is carried out with **5c** (70.2 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **6c** (60.9 mg, 91% yield under 450 nm LED).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.52 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.41 (dtd, $J = 19.1, 8.0, 1.2$ Hz, 2H), 7.32 (q, $J = 8.8$ Hz, 4H), 7.21 – 7.14 (m, 1H),

7.09 (td, $J = 7.7, 1.0$ Hz, 1H), 6.92 (d, $J = 8.3$ Hz, 1H), 3.49 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.71, 148.87, 136.19, 134.09, 130.79, 129.88, 128.92, 128.85, 128.74, 126.82, 122.56, 120.96, 120.63, 120.14, 117.91, 112.19, 99.99, 55.42.

(35) Conversion of azobenzene **5d** to 2H-indazole **6d**.

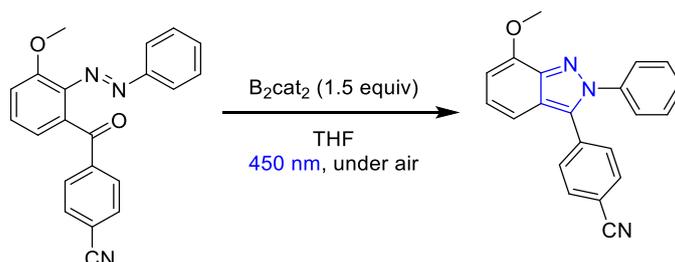


According to GP 4/5, the reaction is carried out with **5d** (96.5 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **6d** (92.6 mg, 99% yield under 450 nm LED; 91.4 mg, 98% yield under sunlight).

^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 9.3$ Hz, 1H), 7.55 – 7.47 (m, 3H), 7.27 (d, $J = 7.3$ Hz, 3H), 7.08 (s, 1H), 6.93 (s, 2H), 2.32 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.79, 147.32, 144.66, 138.83, 138.47, 136.98, 130.75, 128.71, 127.26, 127.21, 122.77, 121.98, 121.65, 121.43, 121.00, 119.64, 119.43, 119.09, 111.94, 21.24.

(36) Conversion of azobenzene **5e** to 2H-indazole **6e**.

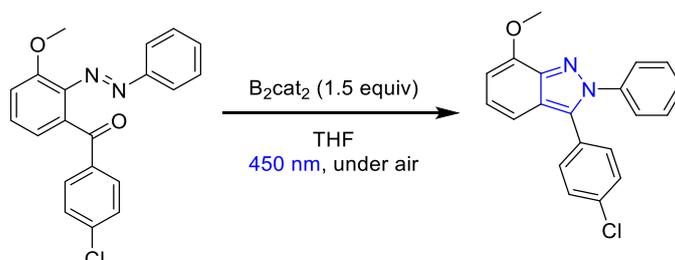


According to GP 4, the reaction is carried out with **5e** (68.3 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1) give the desired product **6e** (64.4 mg, 99% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 24.0$ Hz, 7H), 7.26 (d, $J = 7.9$ Hz, 1H), 7.13 (t, $J = 7.8$ Hz, 1H), 6.66 (d, $J = 7.1$ Hz, 1H), 4.05 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 150.57, 142.60, 139.59, 134.51, 133.24, 132.46, 129.98, 129.19, 128.86, 126.26, 124.52, 123.44, 118.39, 111.71, 111.39, 103.66, 55.58.

(37) Conversion of azobenzene **5f** to 2H-indazole **6f**.



According to GP 4, the reaction is carried out with **5f** (70.2 mg, 0.20 mmol), B_2cat_2 (71 mg, 0.3 mmol) in THF (1.5 mL). Purification by flash column chromatography (hexane: ethyl acetate = 15:1)

give the desired product **6f** (60.9 mg, 91% yield under 450 nm LED).

^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.41 (m, 2H), 7.41 – 7.34 (m, 5H), 7.31 – 7.24 (m, 3H), 7.09 (dd, $J = 8.5, 7.4$ Hz, 1H), 6.65 (d, $J = 7.3$ Hz, 1H), 4.06 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 150.44, 142.51, 139.91, 134.38, 134.25, 130.83, 129.06, 128.96, 128.46, 128.43, 126.24, 123.58, 123.25, 111.93, 103.40, 55.52.

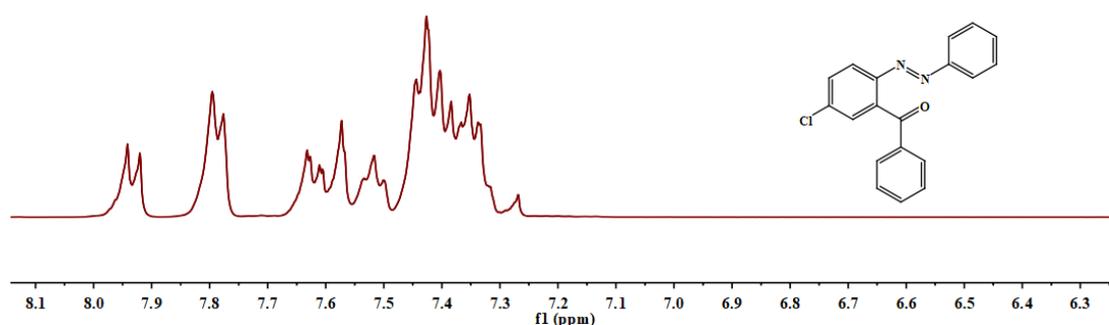
3. Mechanistic Studies

Light/Dark Experiment

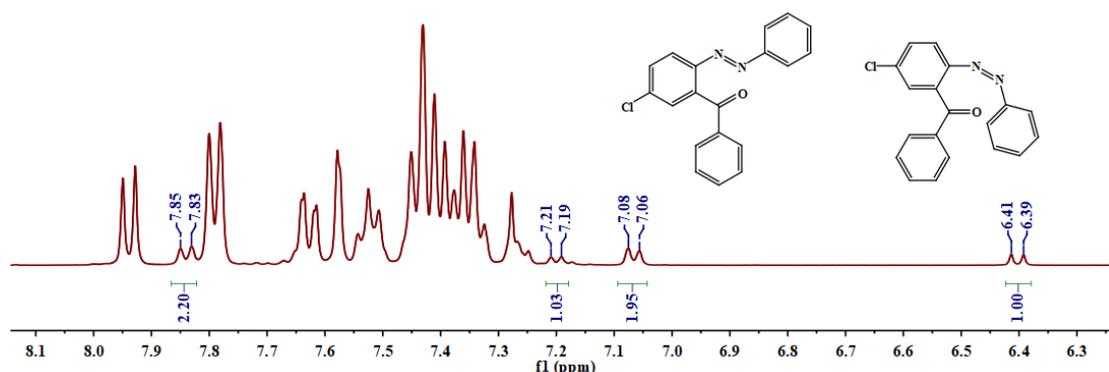


0.1 mmol azobenzene **3a** (^1H -NMR in **Figure S3-a**) was added into a flame-dried 15 mL tube containing a small magnetic stirrer bar. 1.0 mL CDCl_3 were added in the air. The tube was tightly sealed and stirred under 450 nm LED irradiation for 10 minutes. A small amount of **3aa** was isomerized to produce (^1H -NMR in **Figure S3-b**). Irradiation was stopped and the B_2cat_2 (12 mg, 0.5 eq, 0.05 mmol) was added into tube under the air atmosphere. The reaction was stirred for 10 minutes under dark conditions. The reaction ended, and **3aa** were completely generated into **4a** (^1H -NMR in **Figure S3-c**).

a)



b)



c)

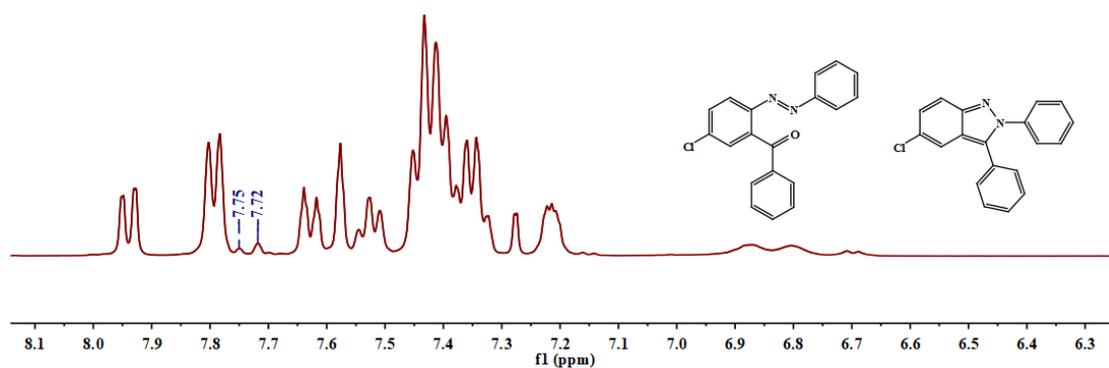


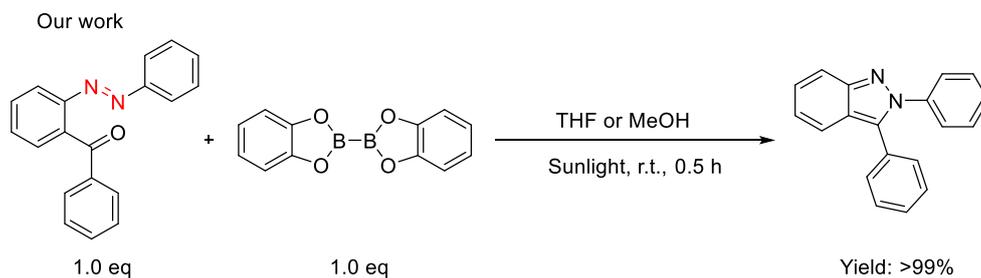
Figure S3: $^1\text{H-NMR}$ of the reaction of light/dark experiment: **a)** $^1\text{H-NMR}$ of trans-azobenzene before reaction; **b)** $^1\text{H-NMR}$ of trans-azobenzene after 450 nm irradiation; **c)** $^1\text{H-NMR}$ of the system after addition of B_2cat_2 .

4. Green Chemistry Metrics^{4,5}

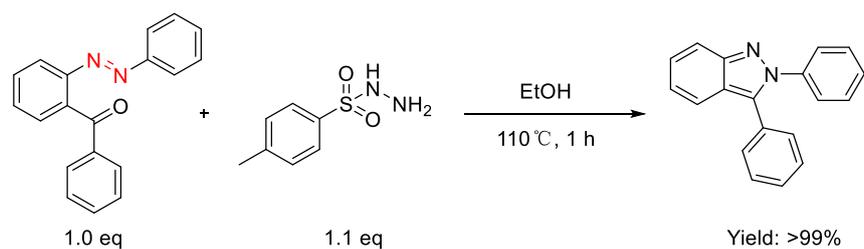
Table S2. 14 green chemistry indicators are selected for comparison of the synthesis method in this paper with similar methods in three literatures.

References Metrics	Our work	<i>Adv. Synth. Catal.</i> 2018, 360 , 4354-4361.	<i>Org. Chem. Front.</i> 2017, 4 , 22-25.	<i>Chem. Eur. J.</i> 2019, 25 , 9866-9869.
Atom Economy	52%	57%	35%	26%
Safe Chemical Synthesis	✓	✓	✗	✗
Safe Solvents and Auxiliaries	✓	✓	✗	✗
Energy Usage	r.t. Sunlight	Heating 110°C	Heating 130°C	r.t.
Renewable Feedstocks	✓	✓	✓	✓
Reaction Time	0.5 h	1 h	15 h	19 h
No Ecotoxicity	✓	✗	✗	✗
Harmless Derivatives	✓	✗	✗	✗
Price of Reaction Components (100 mmol)	\$10-50	\$10-50	> \$50	> \$50
No Chromatography Required	✓	✗	✗	✗
Carbon Efficiency	61%	73%	42%	42%
Reaction Mass Efficiency	52%	61%	26%	17
Environmental Factor ^a	5-50	5-50	5-50	5-50
Eco-Scale ^b	9	21	23	21

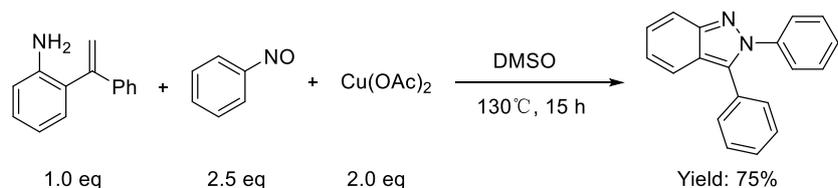
The compared reactions are below:



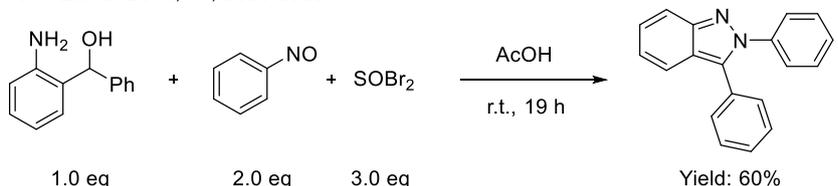
Adv. Synth. Catal. 2018, **360**, 4354-4361.



Org. Chem. Front. 2017, **4**, 22-25.



Chem. Eur. J. 2019, **25**, 9866-9869.



5. Computational Results

Computational Details

All the calculations were carried out via density functional theory (DFT) calculation using Gaussian 16⁸ with the M06-2X⁹ functional. Geometric structures of all species in this work were optimized in gas phase. In addition, free energy corrections were considered at a concentration of 1 M and a temperature of 298.15 K. Frequency calculation were performed to determine all the minima (no imaginary frequency) and transition state structures (only one imaginary frequency). The 6-31G (d) basis set was used for all atoms. In addition, the intrinsic reaction coordinate (IRC) calculations were applied to confirm the connection of each transition state to its corresponding appropriate intermediates, reactants, or products. The solvent effect of Tetrahydrofuran was evaluated through the SMD¹⁰ method, in which a better basis system was used. We employed 6-311++G (d,p) basis sets for all atoms. The molecular orbital of *Z*-**1a**, **1aa** and **B₂cat₂** are drawn by GaussView.

Cartesian coordinates of the optimized structures

1a

E = -916.774973203 a.u.

0 1

C	3.40057300	0.32689300	-1.81814800
C	4.37947700	0.61620100	-0.87335400
C	5.06463300	1.83182600	-0.91802200
C	4.73992800	2.79719700	-1.89004300
C	3.76144900	2.48635100	-2.83566800
C	3.09418500	1.26299300	-2.80516100
H	2.88099500	-0.62565800	-1.78617300
H	4.64825300	-0.09601200	-0.09915900
H	3.52460000	3.22540200	-3.59565000
H	2.33194200	1.04554800	-3.54689900
C	5.35444000	4.17109100	-1.98369200
O	5.78338300	4.56192100	-3.05198100
N	6.07492100	2.00789500	0.06508500
N	6.96586200	2.80368000	-0.28043100
C	5.31303200	5.08240700	-0.79271900
C	6.13555900	6.21261400	-0.80294800
C	4.47773400	4.84213600	0.30123300
C	6.13706100	7.08520600	0.28022600
H	6.77029000	6.38531400	-1.66704400
C	4.47288400	5.72191300	1.38151100
H	3.83062300	3.96886600	0.31207100
C	5.30615700	6.83989000	1.37483900
H	6.78613200	7.95578900	0.27453100
H	3.82031800	5.53354800	2.22864700
H	5.30764000	7.52040700	2.22127600
C	7.95333500	3.08644600	0.70227600
C	8.98468000	3.92617900	0.27973800
C	7.91826100	2.60139000	2.01513300
C	9.99807700	4.27819600	1.16802400
H	8.96990300	4.28884500	-0.74414400
C	8.93258900	2.95734300	2.89474800
H	7.10048000	1.95908600	2.32326400
C	9.97230200	3.79343700	2.47440900
H	10.80338300	4.92930600	0.84261000
H	8.91597500	2.58659200	3.91525600
H	10.75988800	4.06714400	3.17021700

Cis-1a

E = -916.750369357 a.u.

0 1

C	3.87912000	1.66298900	-0.60836900
C	5.06334200	1.38502200	-1.27888600
C	6.09432700	2.32736300	-1.31383500
C	5.89013400	3.61004700	-0.77965600
C	4.68304600	3.87443800	-0.11593400
C	3.69263600	2.90721800	-0.00349000
H	3.09864000	0.90939900	-0.56133200
H	5.21367400	0.42812000	-1.77141500
H	4.53204200	4.85544300	0.32547200
H	2.77424700	3.12764500	0.53067800
C	6.93284200	4.68140600	-0.89734300
O	8.11966000	4.41767700	-0.84954600
C	6.48895200	6.10309300	-1.08066100
C	5.30904100	6.44025700	-1.75241000
C	7.33649000	7.11596500	-0.61872200
C	4.97946100	7.77909500	-1.95416100
H	4.66019700	5.65873300	-2.13741900
C	6.99533000	8.45157500	-0.80220600
H	8.25948900	6.83582200	-0.12015400
C	5.81607500	8.78423100	-1.47132900
H	4.07067200	8.03667300	-2.48942900
H	7.64927300	9.23441600	-0.43025500
H	5.55289700	9.82716200	-1.62130500
N	7.24901900	1.99833600	-2.10889400
N	8.31680700	1.62655100	-1.61036500
C	8.48761700	1.47130900	-0.19089000
C	7.70169100	0.61262600	0.57912500
C	9.59218300	2.11459500	0.37114100
C	8.00427500	0.43115800	1.92840400
H	6.87694000	0.07259200	0.12839300
C	9.86797600	1.95039300	1.72348000
H	10.19988700	2.75607000	-0.25822700
C	9.07596600	1.10737300	2.50603100
H	7.39806700	-0.24334800	2.52559800
H	10.71178200	2.47073300	2.16639900
H	9.30321900	0.96837600	3.55859400

B₂cat₂

E = -812.584128579 a.u.

0 1

C	-4.94592700	-1.14192700	1.30600800
C	-3.54705700	-1.15947000	1.32412400

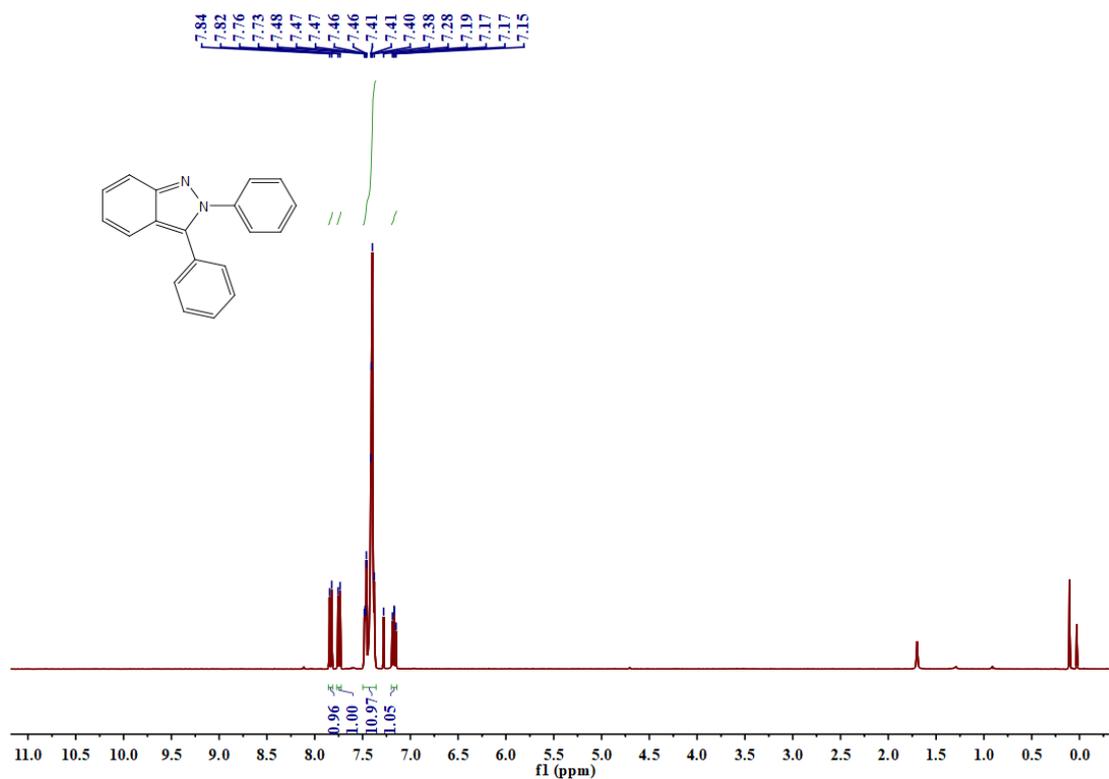
C	-2.91821900	0.07152200	1.34340100	C	5.18465700	6.82370200	-2.18602800
C	-3.63151700	1.26718500	1.34480300	C	5.13212100	6.77598500	0.60869300
C	-5.01343700	1.29874300	1.32703600	H	5.27151800	4.63289100	0.43013700
C	-5.66261600	0.05953600	1.30742400	C	5.10632700	8.01493900	-1.47487900
H	-5.48595400	-2.08310500	1.29038800	H	5.21526900	6.82784000	-3.27191800
H	-2.97881700	-2.08299800	1.32325500	C	5.08156000	7.99051000	-0.07934800
H	-5.55614500	2.23748800	1.32834700	H	5.13325400	6.76308300	1.69421100
H	-6.74738200	0.03148400	1.29299400	H	5.07409400	8.95945600	-2.00899500
O	-1.57536100	0.35517500	1.36347100	H	5.02827300	8.92238600	0.47609300
O	-2.74409400	2.31415200	1.36576700	C	7.75657500	3.05822100	-1.03795900
B	-1.48345900	1.73813700	1.37706100	C	8.35280500	4.28889500	-0.76063200
C	2.11448700	3.07641500	1.43628700	C	7.39899200	2.19377200	0.00766500
C	3.49642400	3.04549500	1.45414200	C	8.53147400	4.67428400	0.56810500
C	4.14504500	4.28499100	1.47399700	H	8.65966300	4.95431900	-1.55657400
C	3.42780300	5.48612300	1.47555200	C	7.59097200	2.58793400	1.32403900
C	2.02893100	5.50302900	1.45729700	H	6.99312400	1.21169500	-0.20918700
C	1.40063400	4.27175200	1.43778100	C	8.14789700	3.83775100	1.61056800
H	4.03952800	2.10698200	1.45271600	H	8.97755800	5.64141900	0.77726000
H	5.22979700	4.31358500	1.48851300	H	7.31888500	1.91109600	2.12787600
H	3.96741200	6.42754100	1.49135500	H	8.29556000	4.14401900	2.64175100
H	1.46031100	6.42632200	1.45825900	B	7.51679900	4.78690500	-3.89015600
O	1.22762000	2.02901200	1.41508700	B	8.50871100	3.27549900	-3.56682400
O	0.05792900	3.98745000	1.41751600	O	7.85352200	6.00813400	-3.21296500
B	-0.03327800	2.60440700	1.40376500	O	7.38018700	5.07361100	-5.27865600
				O	8.57195200	2.40980600	-4.71488300
TS₁				O	9.86331300	3.57854100	-3.15308600
E = -1729.33158136 a.u.				C	7.76695400	6.99277400	-4.15299200
0 1				C	7.91898200	8.35611300	-3.98842100
C	3.58873900	0.62251500	-1.25313600	C	7.47353200	6.42399400	-5.39707900
C	4.80573300	0.64846500	-1.91768800	C	7.77114300	9.15591900	-5.13239500
C	5.45085200	1.87102400	-2.13874200	H	8.14799000	8.77813000	-3.01486800
C	4.81095300	3.08322100	-1.78561200	C	7.33154500	7.20458300	-6.52983200
C	3.57872700	3.03154100	-1.11522100	C	7.48367200	8.59061600	-6.37515700
C	2.97651700	1.81298000	-0.83886300	H	7.88721700	10.23197900	-5.04704100
H	3.10391900	-0.32969400	-1.06097000	H	7.11222100	6.75356100	-7.49166900
H	5.29414300	-0.26352000	-2.24691600	H	7.37755900	9.23425300	-7.24293200
H	3.08041800	3.96053600	-0.85308900	C	9.89067100	2.16680200	-4.92199900
H	2.01767000	1.78465500	-0.33209400	C	10.47210100	1.37977800	-5.89894300
C	5.36179300	4.35799300	-2.27245300	C	10.66772200	2.85875300	-3.98292200
O	5.93286800	4.35135400	-3.38764300	C	11.87268100	1.29397100	-5.90627500
N	6.68144300	1.85941200	-2.80196900	H	9.85968700	0.85527400	-6.62469800
N	7.63881900	2.58043700	-2.39876000	C	12.04751700	2.78558500	-3.98707000
C	5.22249300	5.60307200	-1.50043100	C	12.64463900	1.98153900	-4.97046700
C	5.19382400	5.58080200	-0.09829500	H	12.36191200	0.68154900	-6.65757900

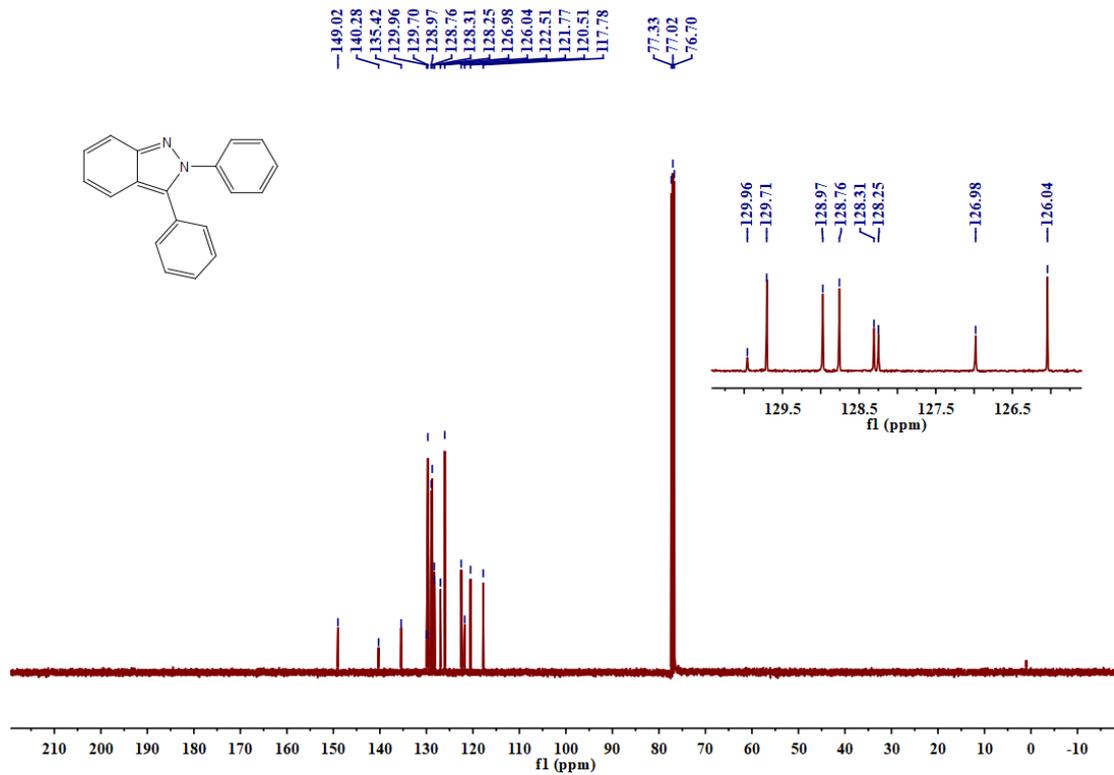
H	12.63543500	3.33241900	-3.25726700	O	7.01063600	6.16072400	-3.12784600
H	13.72663500	1.89793600	-5.00213800	O	7.68274900	4.47374600	-4.53835400
Int1				O	8.56518600	1.60426300	-4.21639400
E = -1729.43520423 a.u.				O	9.84235500	3.00635800	-2.90745300
0 1				C	8.09952600	6.58425200	-3.85869000
C	3.46799300	0.36389800	-1.01115900	C	8.74844600	7.80178100	-3.81336100
C	4.56298300	0.37884700	-1.80040000	C	8.50143100	5.56348800	-4.71861800
C	5.42356700	1.56059900	-1.84419300	C	9.83673300	7.95838200	-4.68242000
C	4.80395000	2.82918100	-1.38895300	H	8.42535900	8.58831400	-3.14027600
C	3.71201100	2.71802000	-0.42701300	C	9.56751800	5.70450700	-5.58349400
C	3.07722600	1.53856300	-0.25013200	C	10.23554800	6.93527800	-5.54649300
H	2.87294500	-0.54041600	-0.92313400	H	10.37990700	8.89795700	-4.68315200
H	4.91145900	-0.50018300	-2.33345900	H	9.87092000	4.89548500	-6.24130900
H	3.36472100	3.61267800	0.07886800	H	11.08414100	7.09383900	-6.20436200
H	2.23224800	1.47214800	0.42798200	C	9.69649400	1.95917400	-4.89941100
C	5.10444100	4.01877700	-1.97939800	C	10.08267400	1.60275800	-6.17679800
O	5.84554800	3.98393300	-3.11871100	C	10.48020800	2.79594400	-4.10333700
N	6.64931500	1.31884300	-2.19638800	C	11.30675400	2.11558600	-6.63062100
N	7.63387700	2.28521800	-2.01510000	H	9.46301000	0.95789400	-6.79010700
C	4.63405800	5.34379700	-1.52308400	C	11.69201200	3.29824800	-4.53173400
C	4.89028700	5.75226900	-0.21020700	C	12.09637100	2.93963200	-5.82523800
C	3.98166700	6.20974300	-2.40678100	H	11.64867600	1.85961400	-7.62850400
C	4.48844400	7.01542900	0.21609400	H	12.28531900	3.94944800	-3.89893600
H	5.42885000	5.08382400	0.45869100	H	13.04146400	3.31268300	-6.20721900
C	3.57458800	7.46826400	-1.97541300	TS₂			
H	3.79038400	5.89065000	-3.42827400	E = -1729.40856823 a.u.			
C	3.82834400	7.87265800	-0.66418200	0 1			
H	4.69905100	7.33337800	1.23283000	C	2.74440200	3.00907500	-3.12175200
H	3.06114900	8.13496900	-2.66149000	C	3.98912200	2.42560200	-3.13372500
H	3.51524700	8.85756000	-0.33056100	C	5.10287200	3.11193900	-2.56305900
C	7.74309100	3.01067400	-0.79367700	C	4.89011800	4.45447100	-2.11870300
C	8.31765200	4.28509500	-0.78002600	C	3.59326300	4.99122900	-2.04815800
C	7.29726200	2.45062600	0.41122600	C	2.51874800	4.28755800	-2.55667100
C	8.44533800	4.98654800	0.41875400	H	1.90440500	2.46408600	-3.54544300
H	8.69561800	4.72511300	-1.69708500	H	4.14787900	1.43175500	-3.53960600
C	7.41826500	3.16135000	1.59899400	H	3.45781300	5.99265000	-1.64386000
H	6.85107900	1.46087900	0.41230200	H	1.52383400	4.71886800	-2.55002200
C	7.99297000	4.43508200	1.61324800	C	6.06954500	5.20046900	-1.73940400
H	8.89401900	5.97546500	0.40558400	O	6.82577100	5.83099900	-2.68963800
H	7.06711300	2.71137700	2.52309500	N	6.25034600	2.48567400	-2.28825300
H	8.08795800	4.98458600	2.54473000	N	7.17322100	3.40733900	-1.71552100
B	6.78865800	4.86020600	-3.54979700	C	6.21265200	5.82458200	-0.42158800
B	8.65147600	2.28577800	-3.01078700	C	5.50118700	5.29333200	0.66614500

H	4.04596700	1.53224300	-3.73046900	H	5.91087200	6.36771400	3.45910800
H	3.75258200	6.31963600	-2.17099000	H	6.53937700	8.87588800	0.02565900
H	2.43728500	5.52312600	-4.10758800	H	6.42724700	8.59745700	2.49212500
C	5.54283900	4.42599600	-0.75188100	C	7.00779600	2.70464900	0.32867500
N	5.57659200	2.28731900	-1.52060600	C	8.14040600	3.46968200	0.60130200
N	6.03972500	3.16396200	-0.61451300	C	6.80597000	1.47195500	0.94569300
C	5.80895100	5.55151400	0.15625000	C	9.06879800	3.00093900	1.52708100
C	5.74038800	5.40389900	1.54844300	H	8.29176000	4.41649300	0.09287700
C	6.09509000	6.81229200	-0.38202500	C	7.74609900	1.00961400	1.86275100
C	5.96603100	6.49452500	2.38209300	H	5.92459500	0.89278700	0.69214800
H	5.50719700	4.43155700	1.97392700	C	8.87402500	1.77407600	2.16065300
C	6.31413600	7.90439400	0.45542000	H	9.95204300	3.59350400	1.74414600
H	6.16224000	6.92640300	-1.46078600	H	7.59442000	0.04979600	2.34678200
C	6.25350200	7.74766000	1.83894900	H	9.60302700	1.41147400	2.87872500

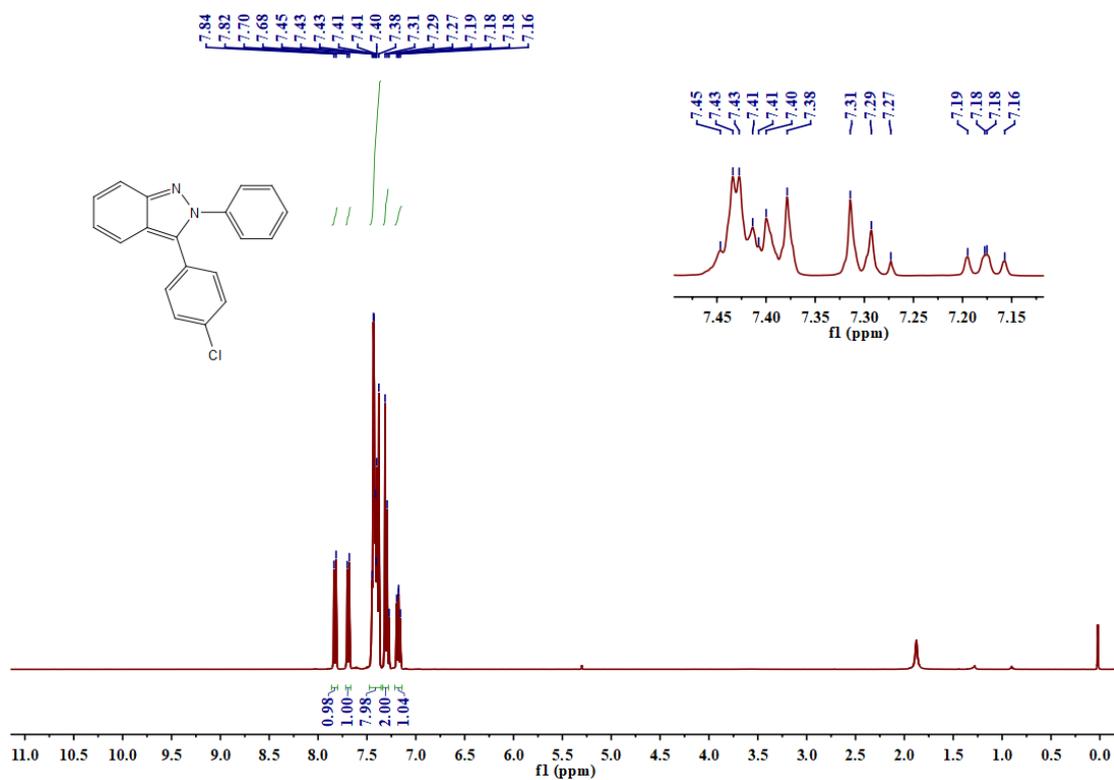
6. NMR spectra

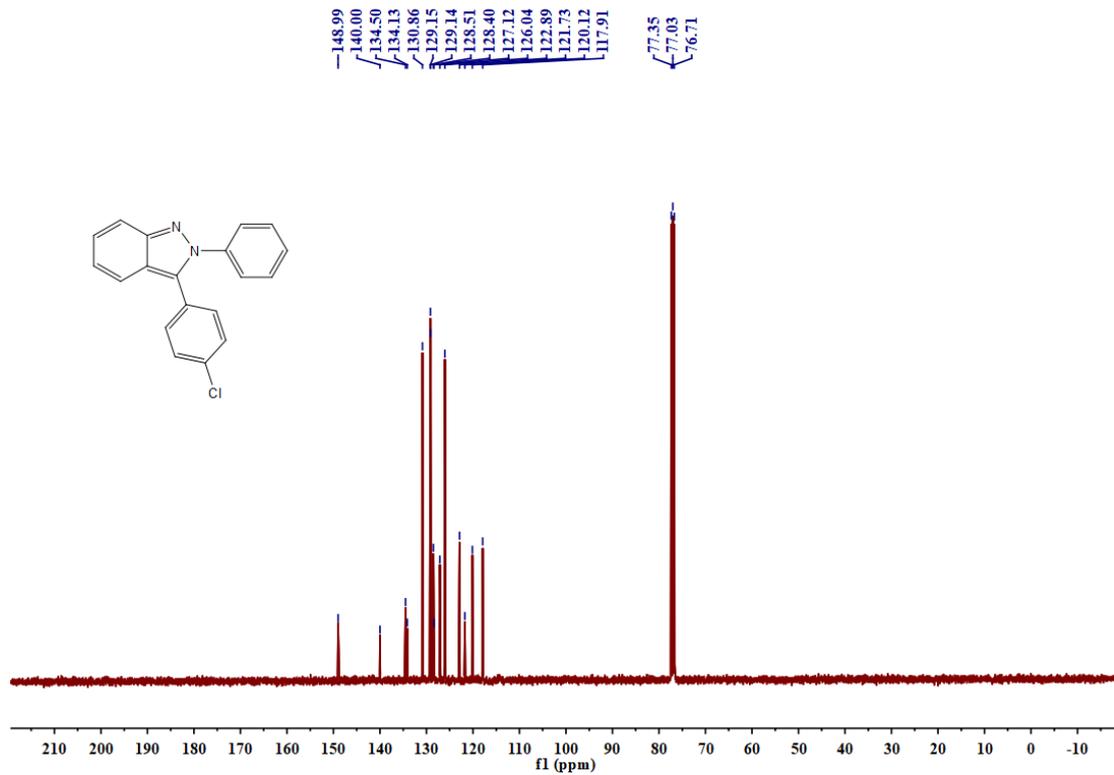
2H-Indazole 2a



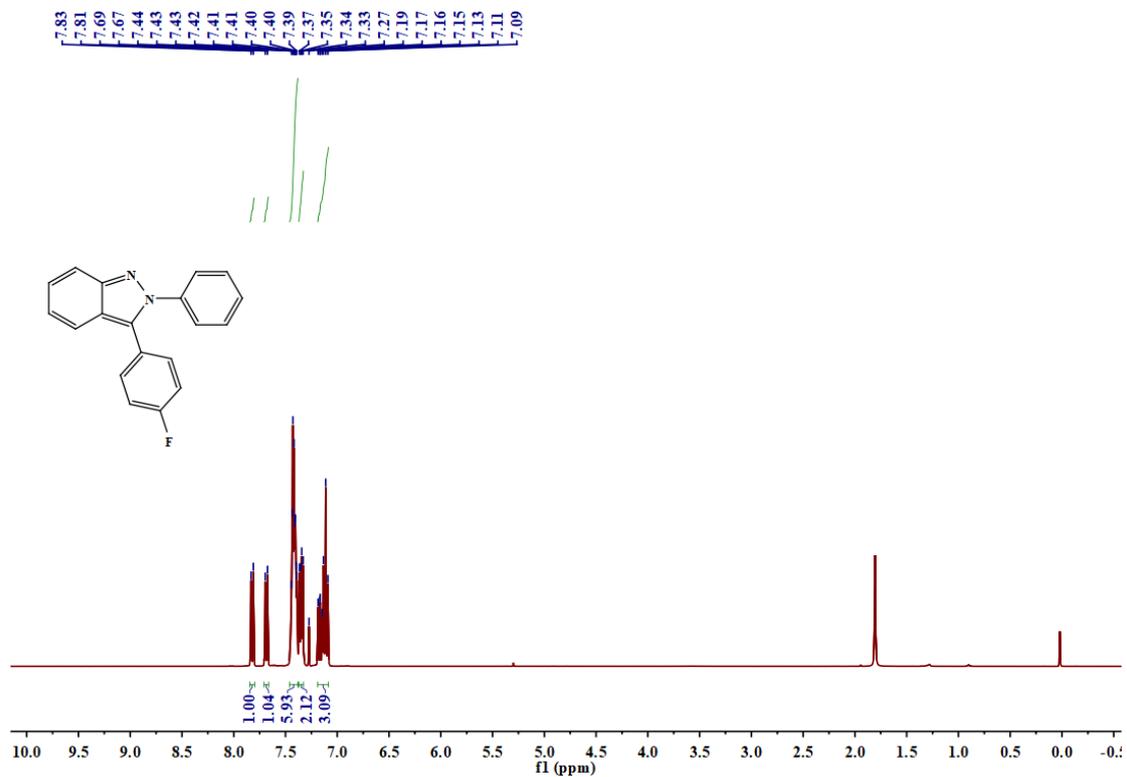


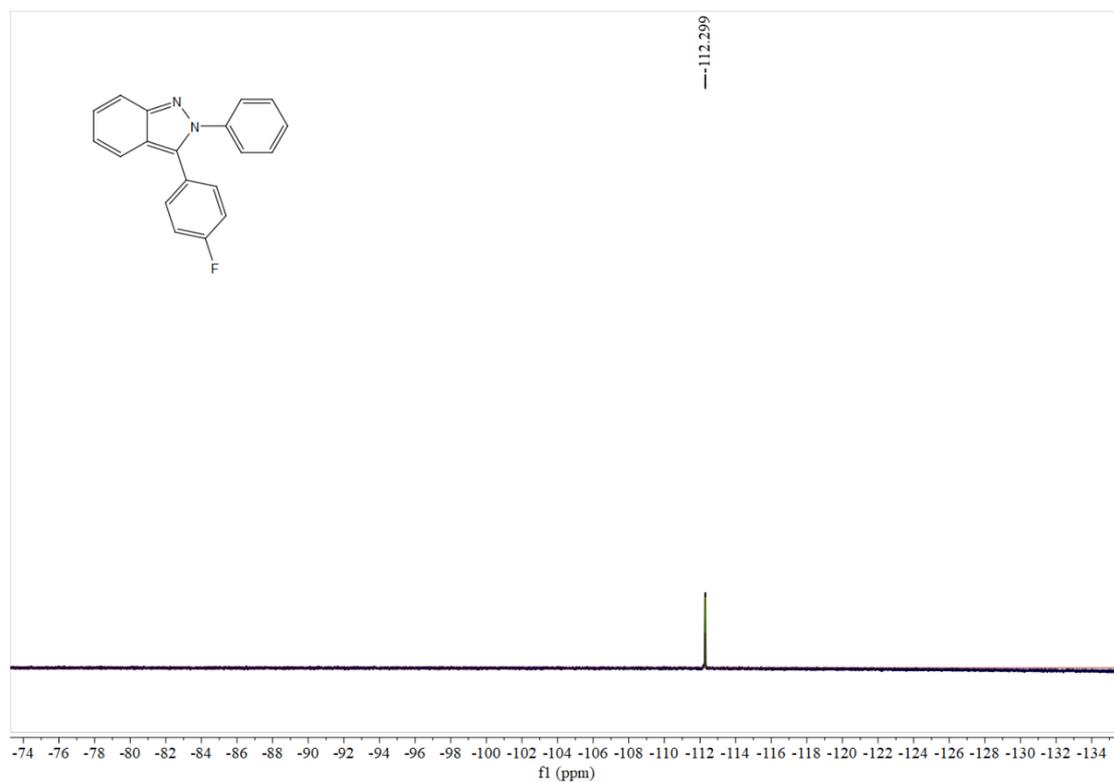
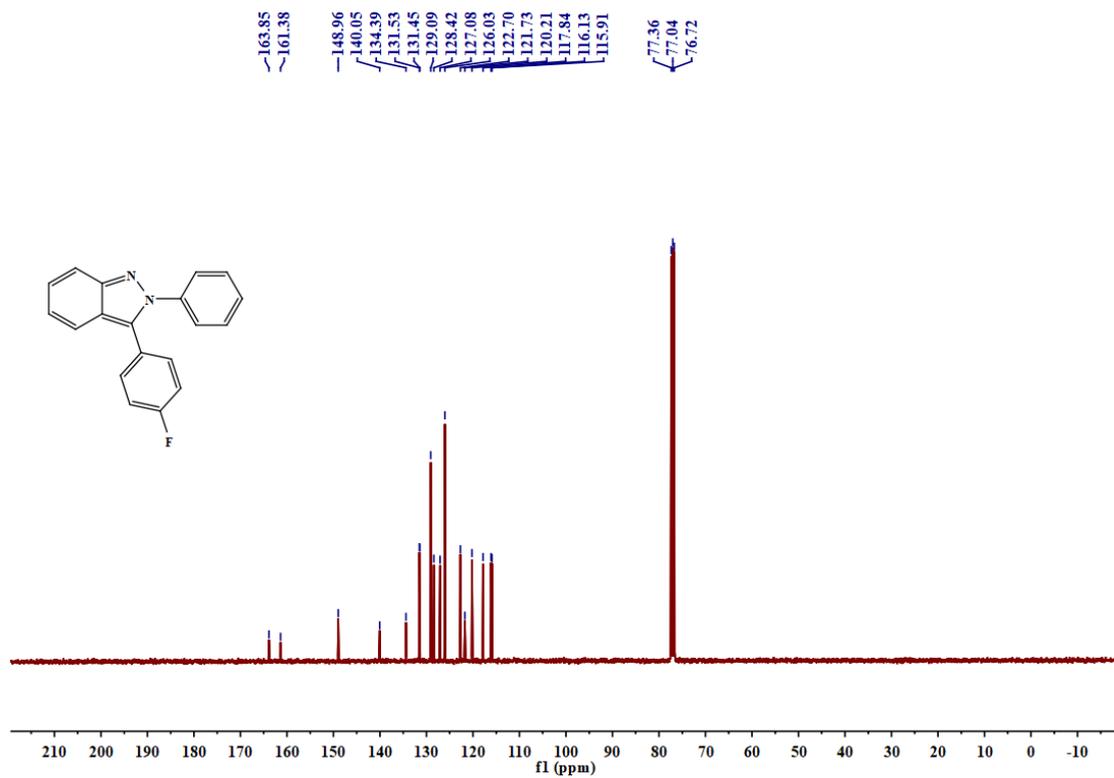
2H-Indazole 2b



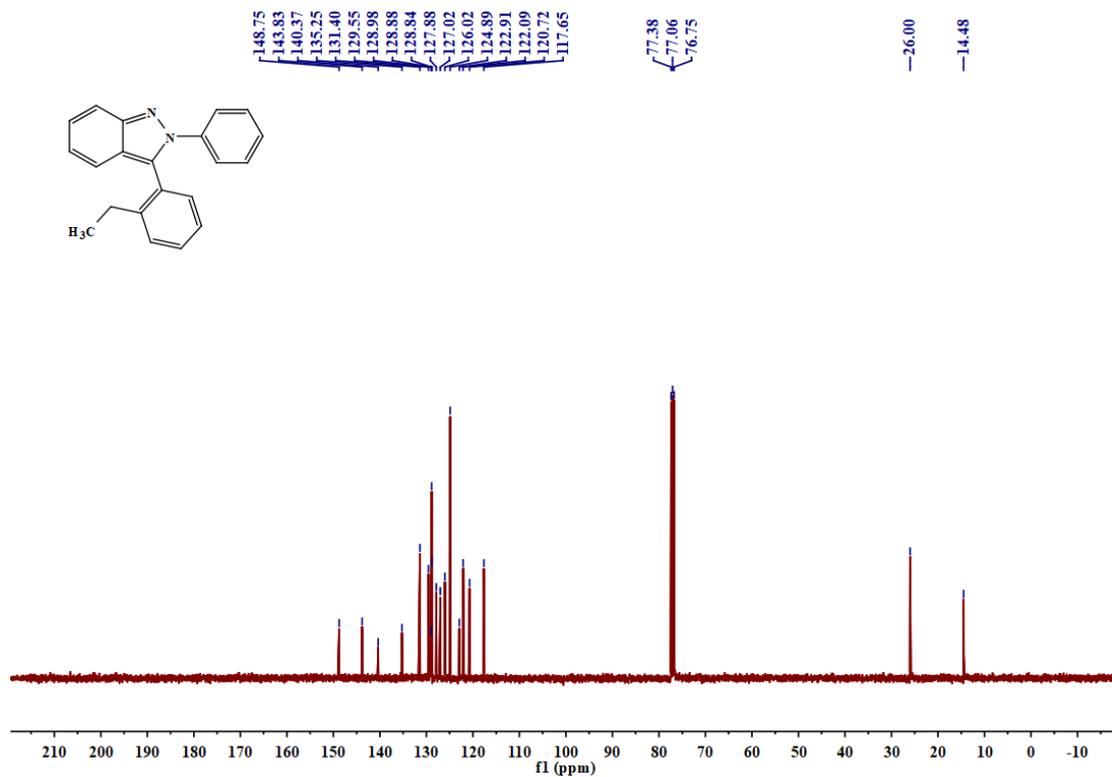
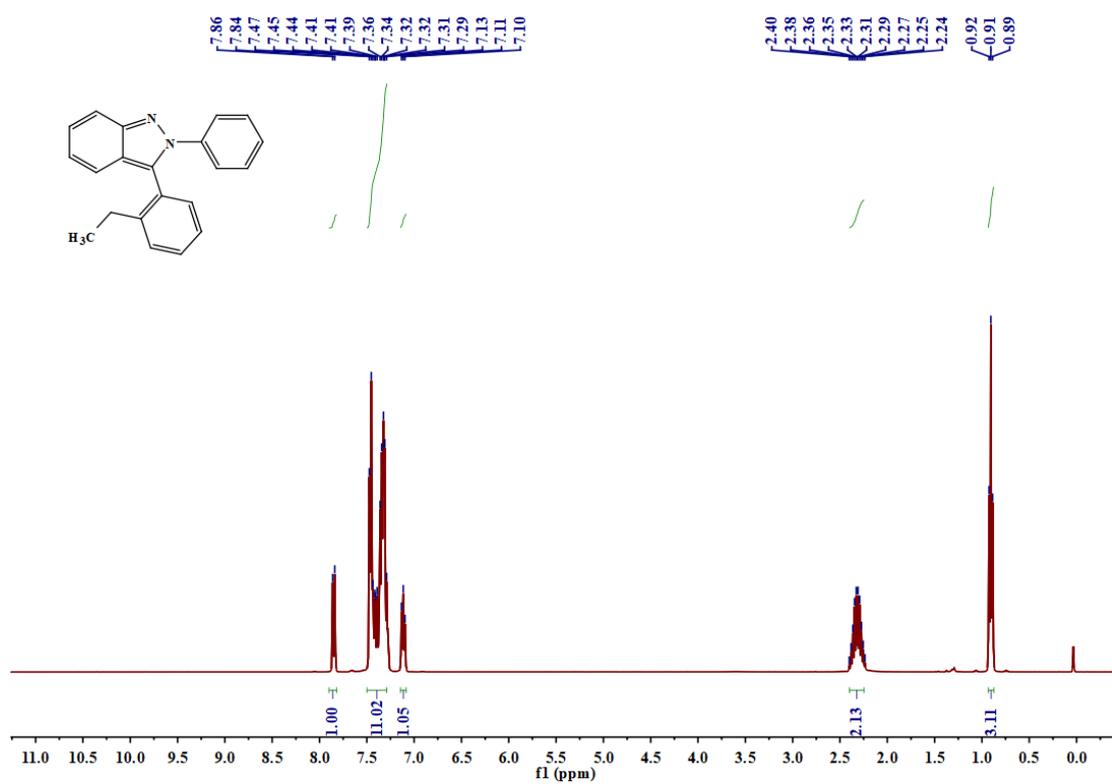


2H-Indazole 2c

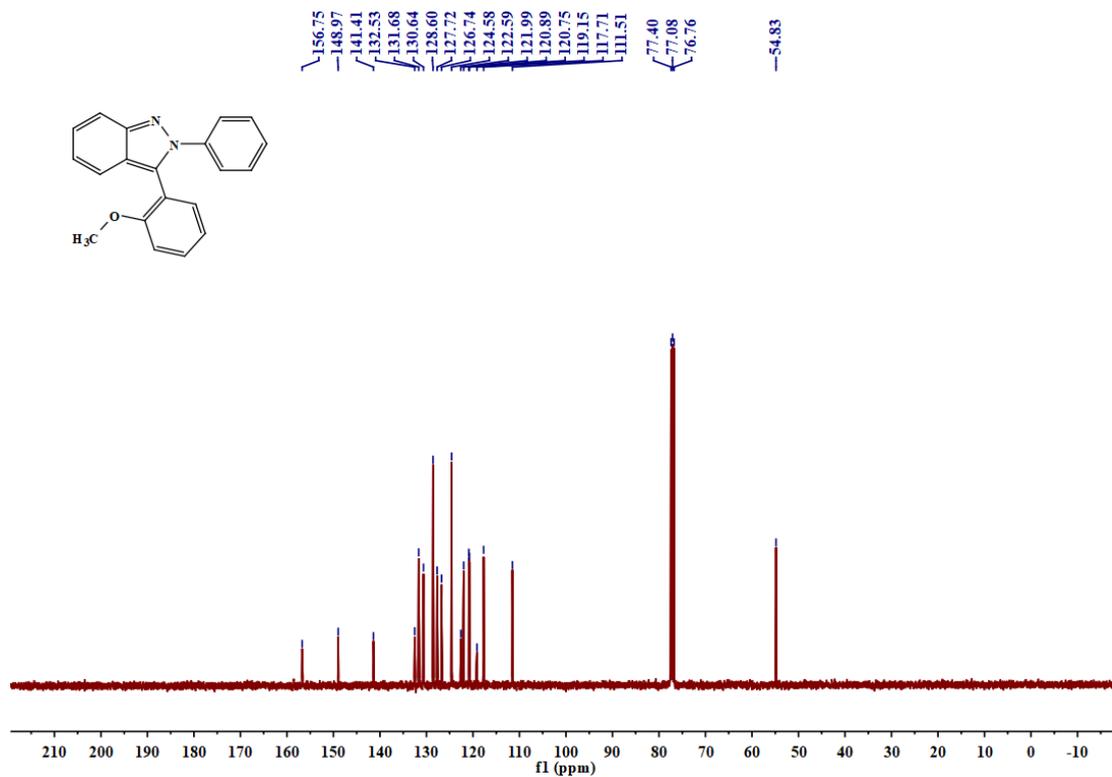
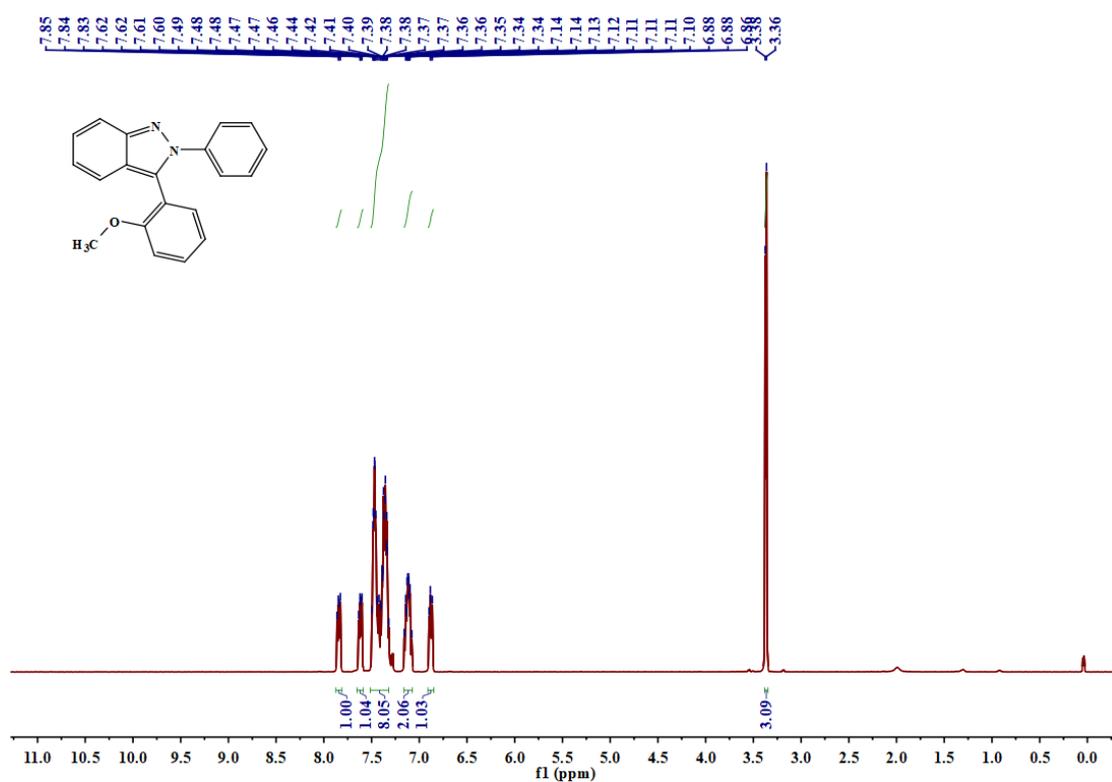




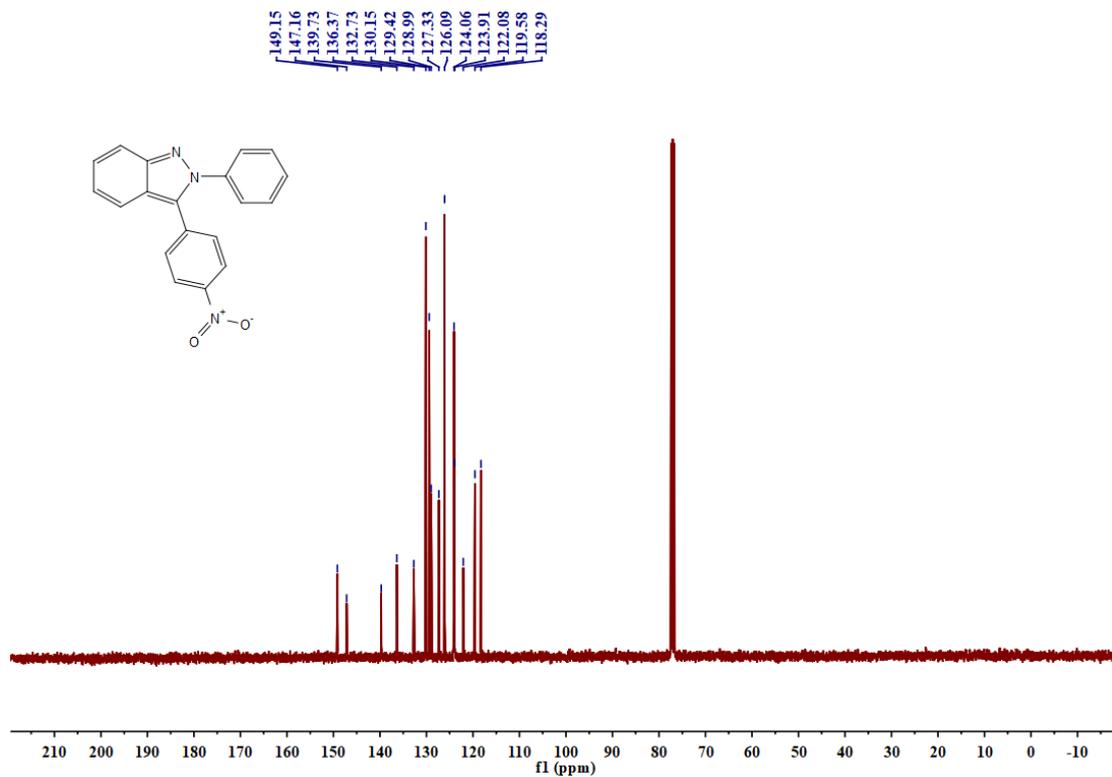
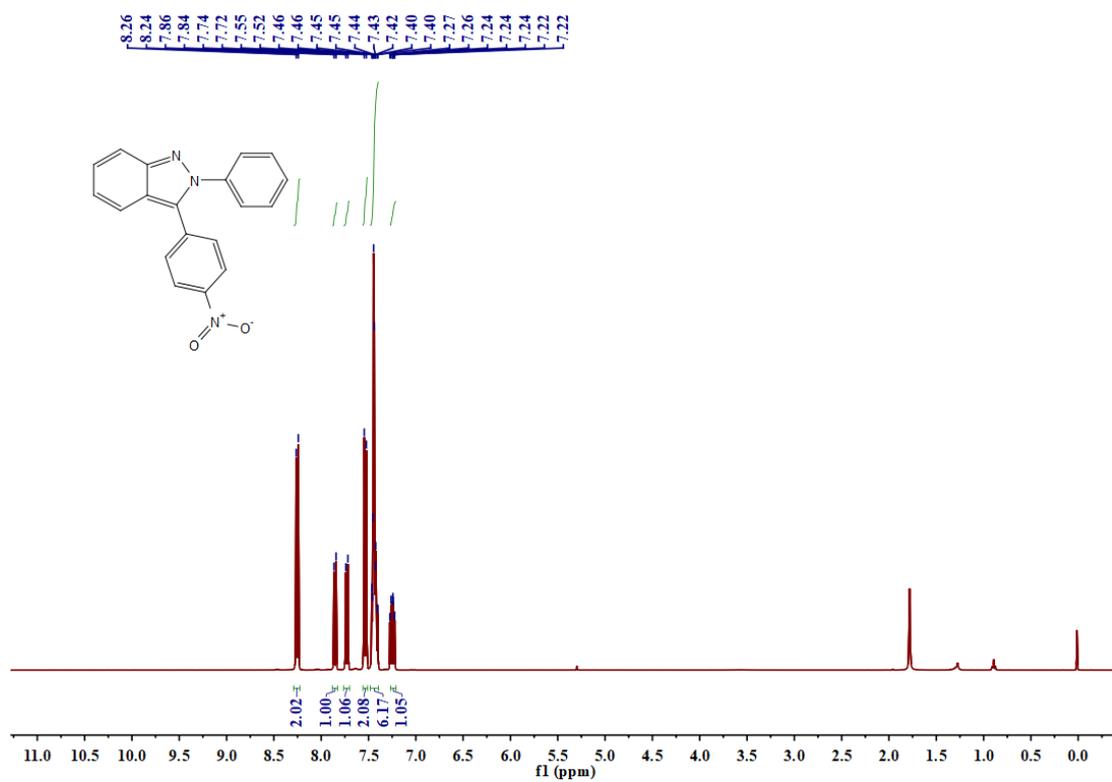
2H-Indazole 2d



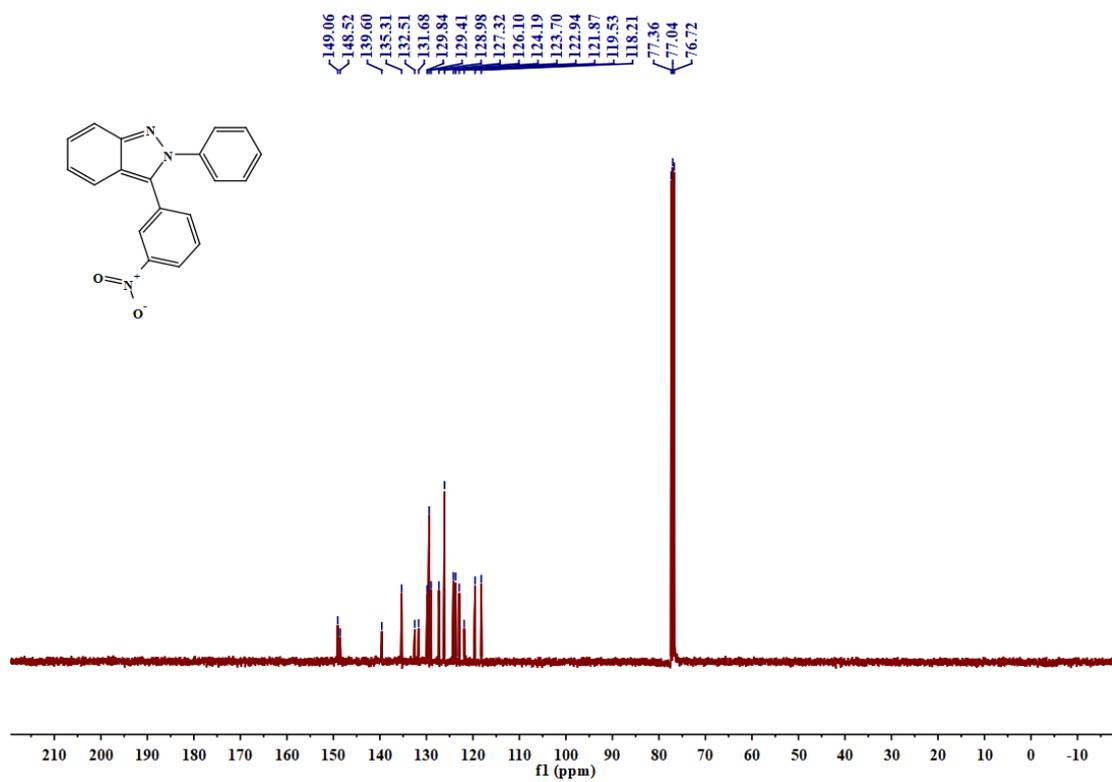
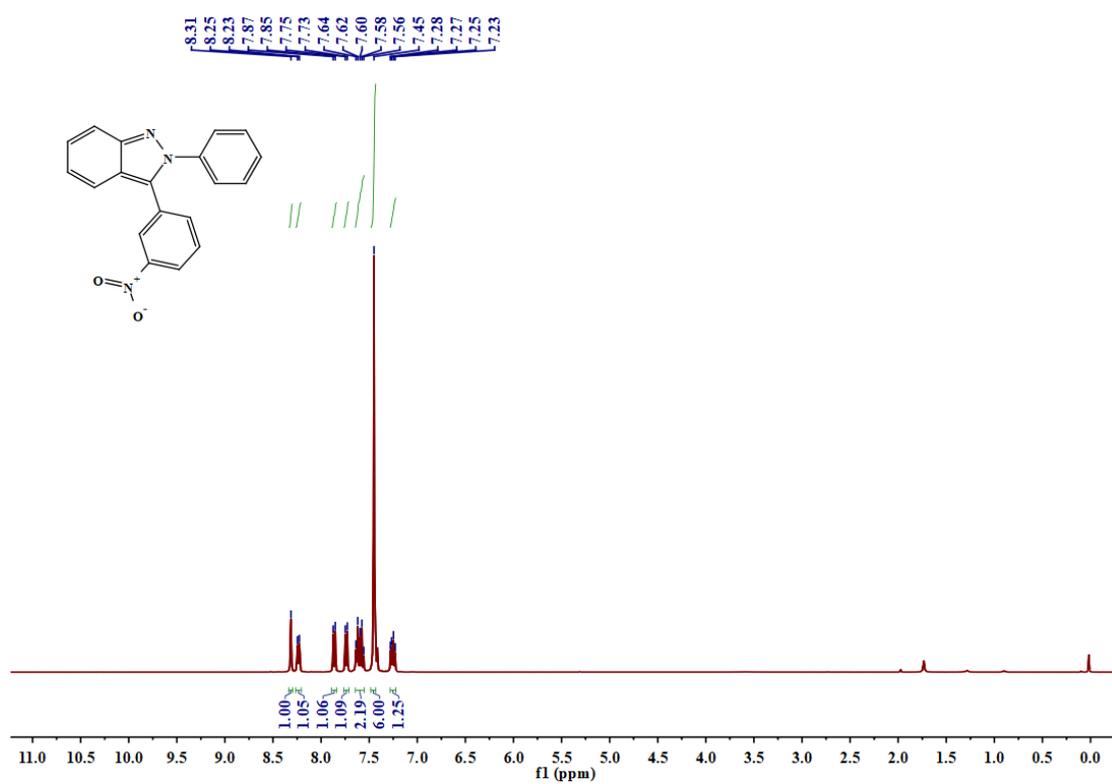
2H-Indazole 2e



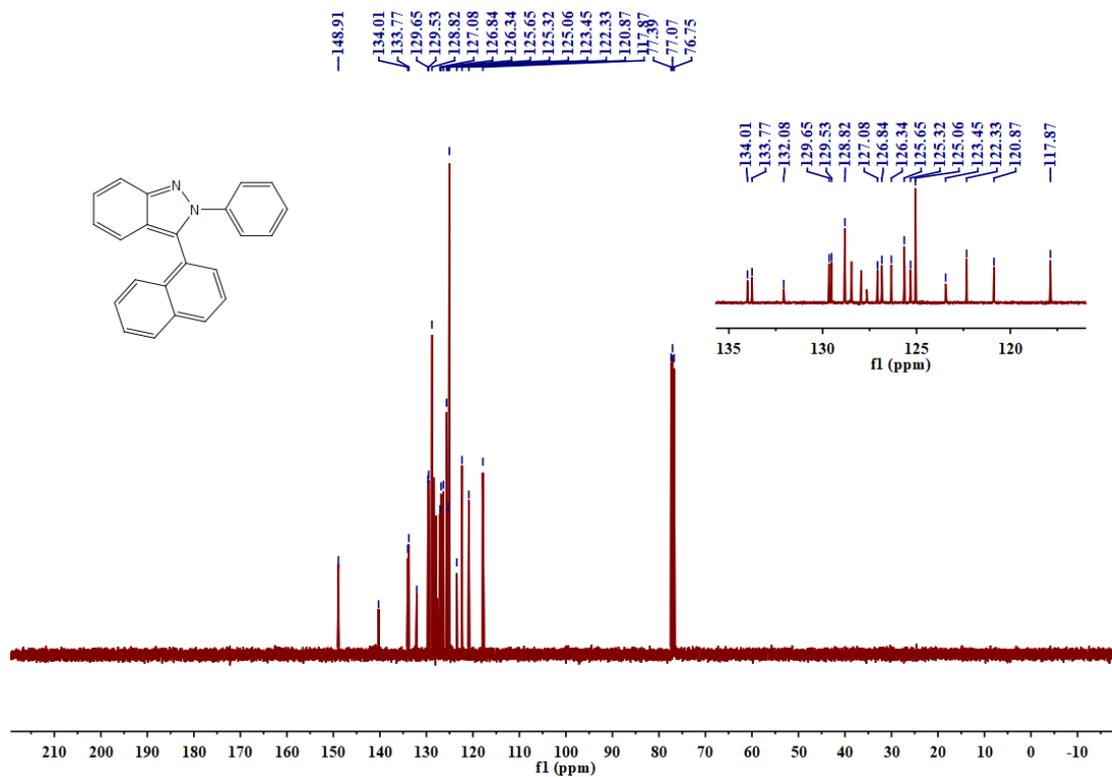
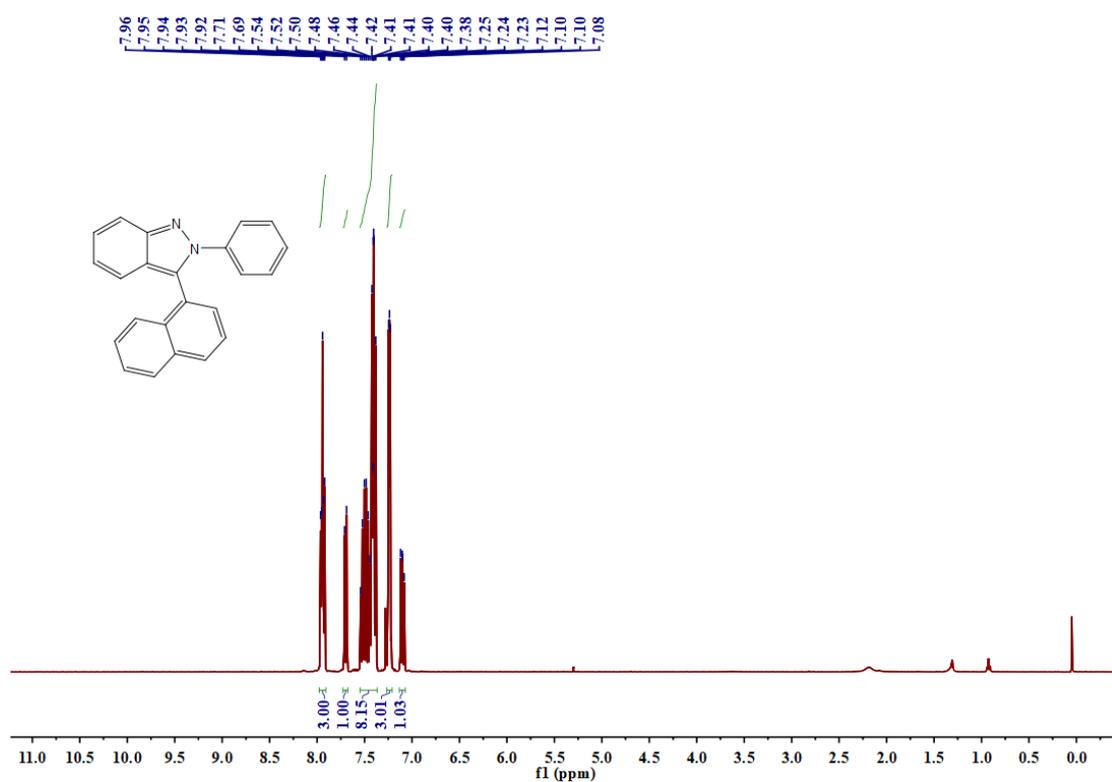
2H-Indazole 2f



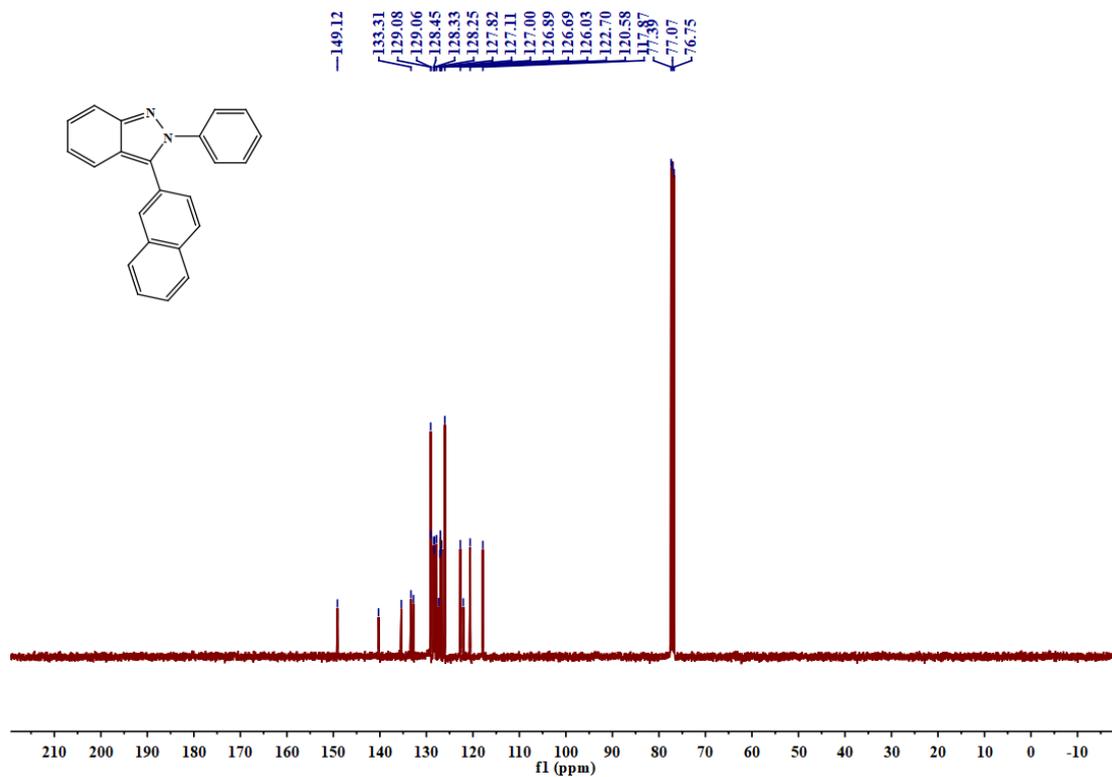
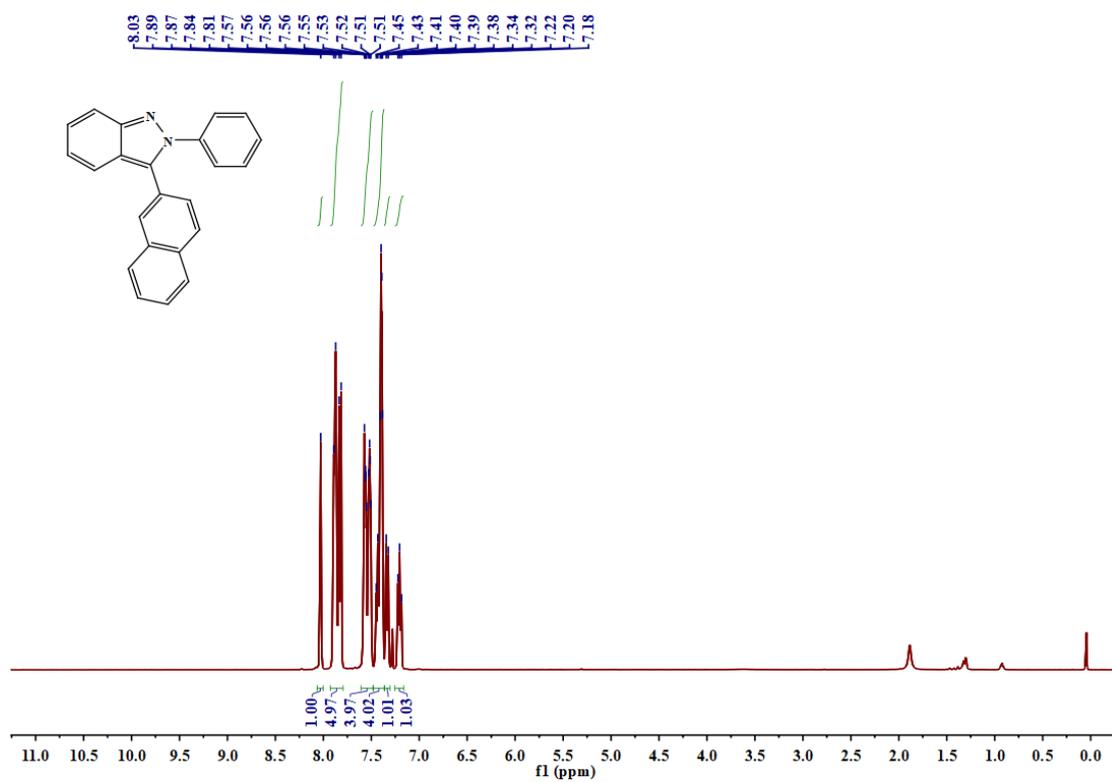
2H-Indazole 2g



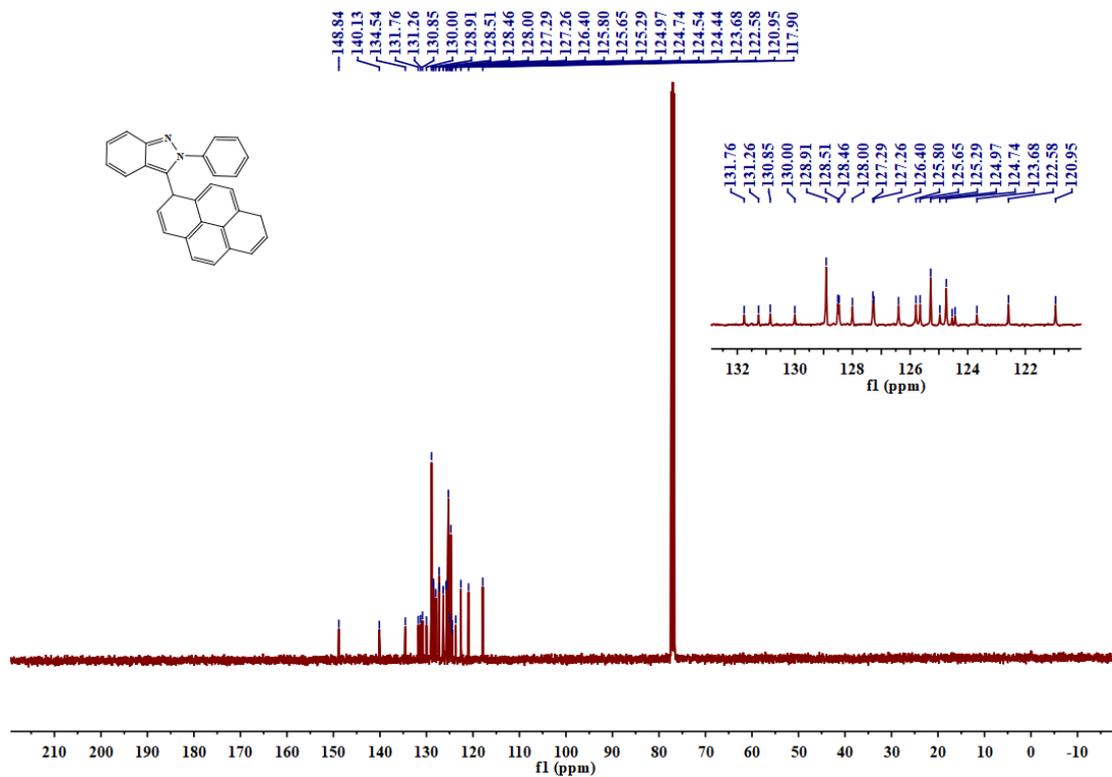
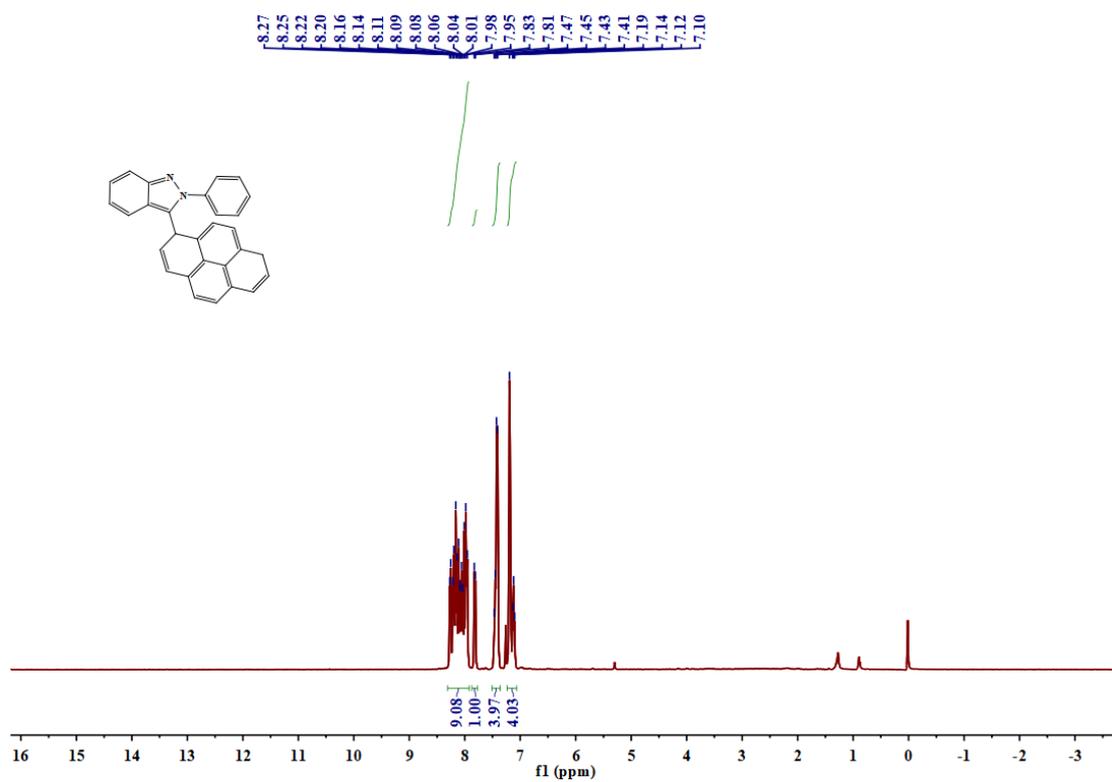
2H-Indazole 2h



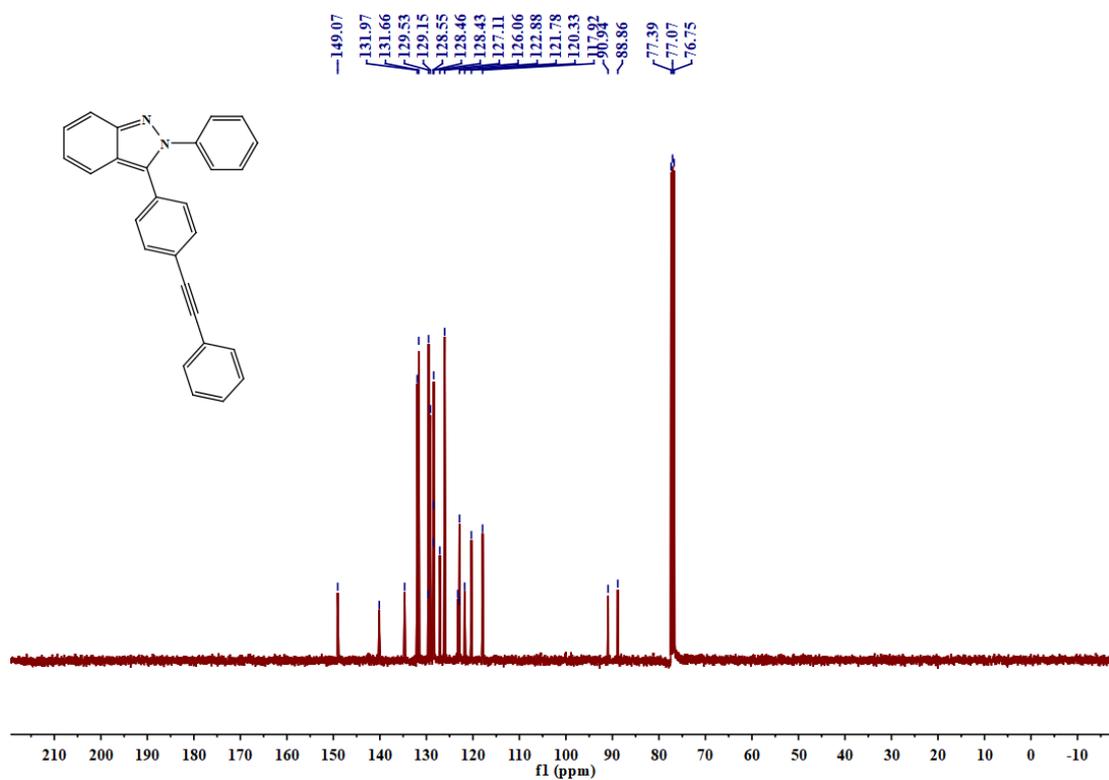
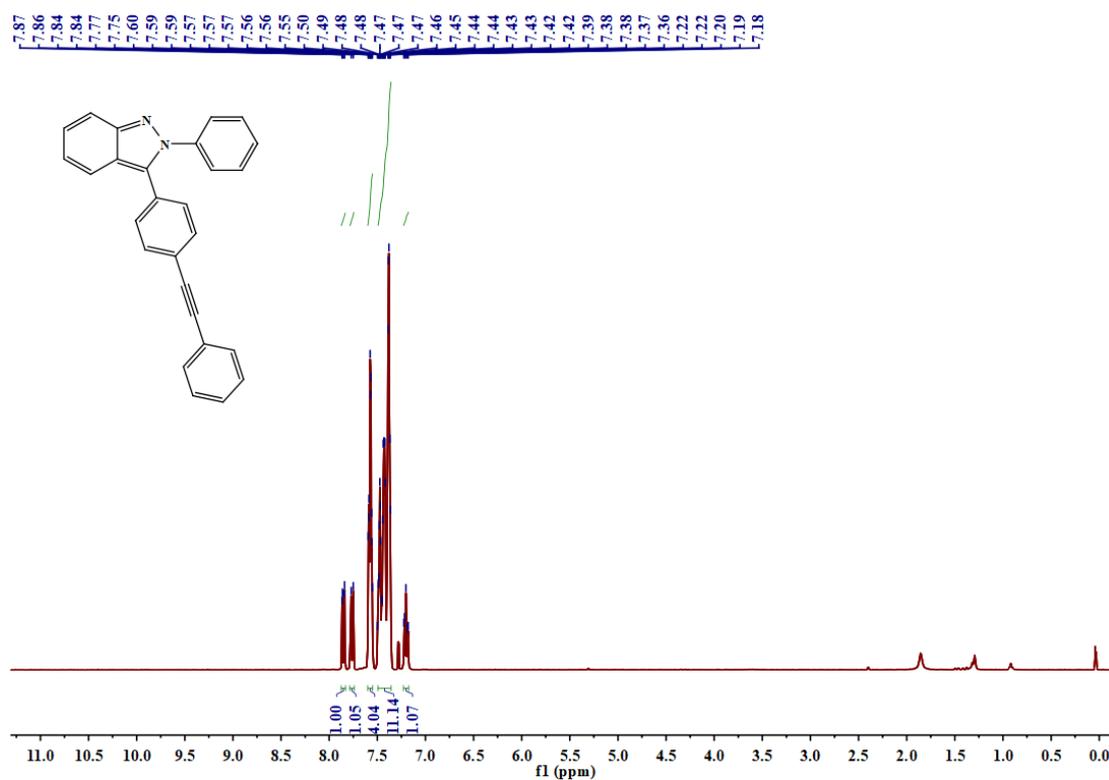
2H-Indazole 2i



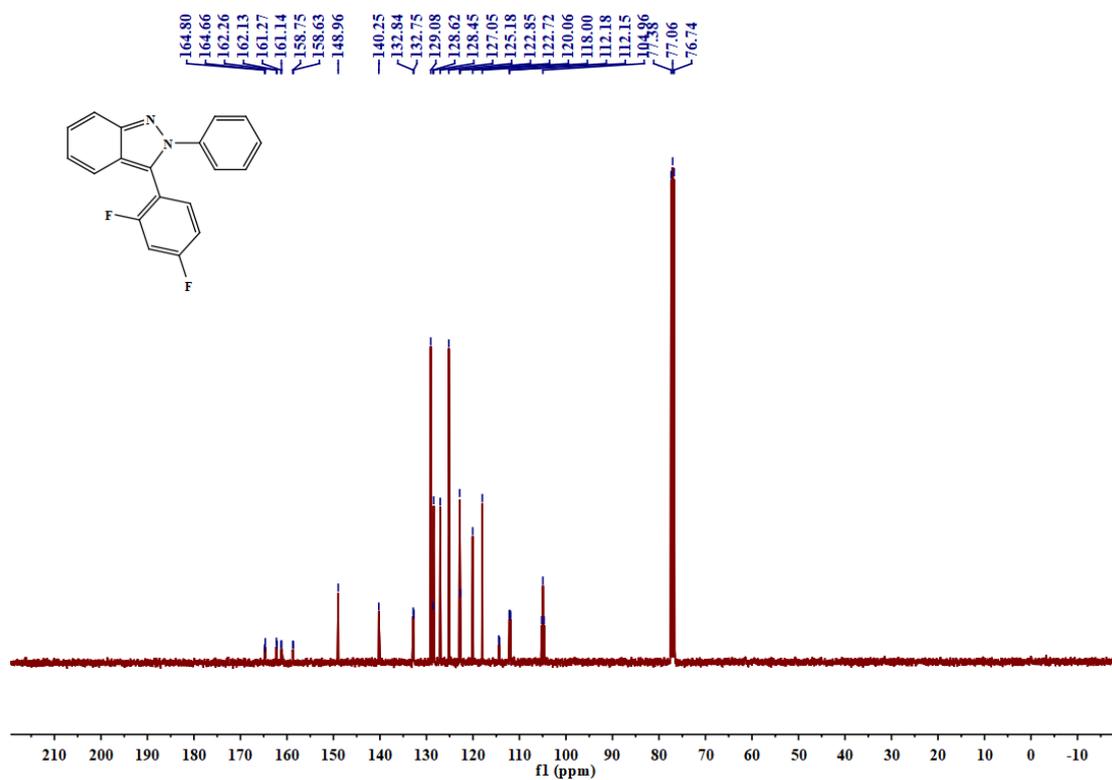
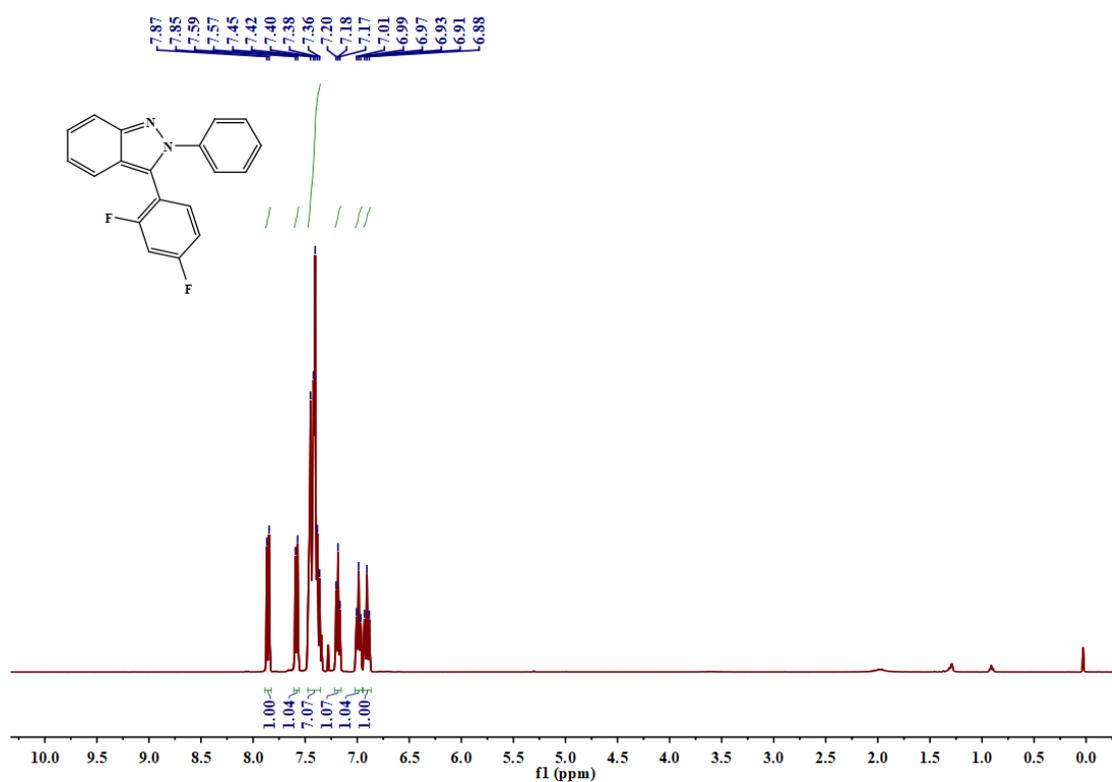
2H-Indazole 2j

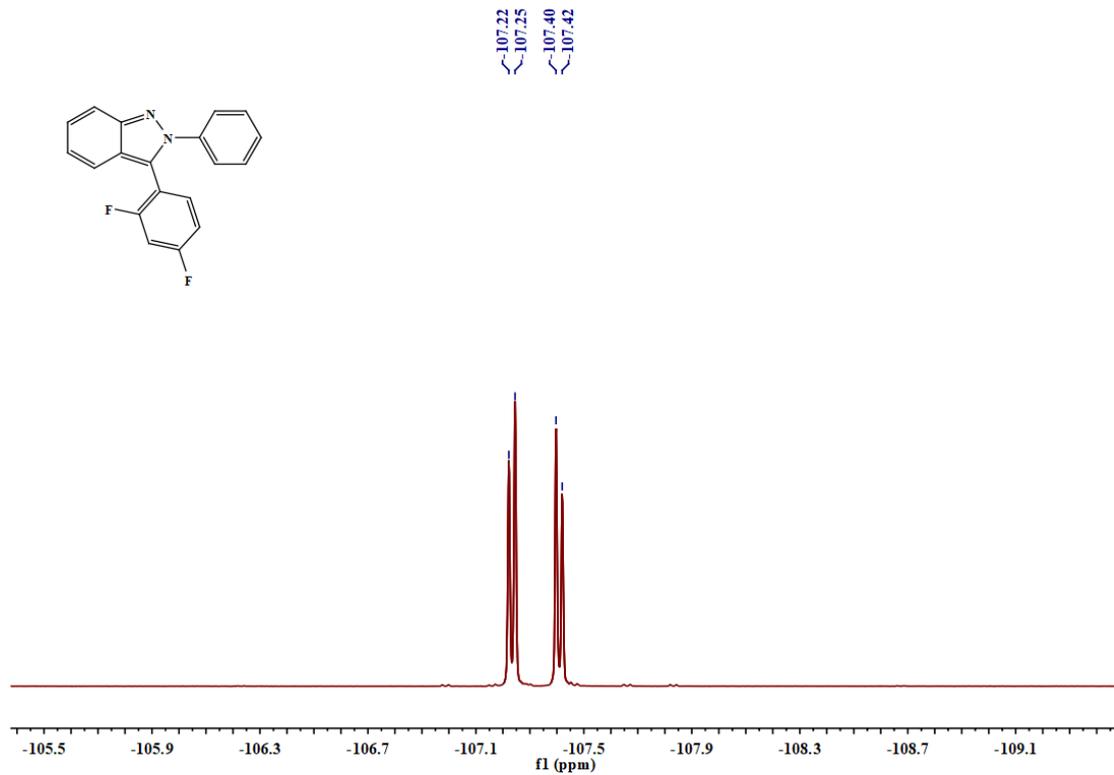


2H-Indazole 2k

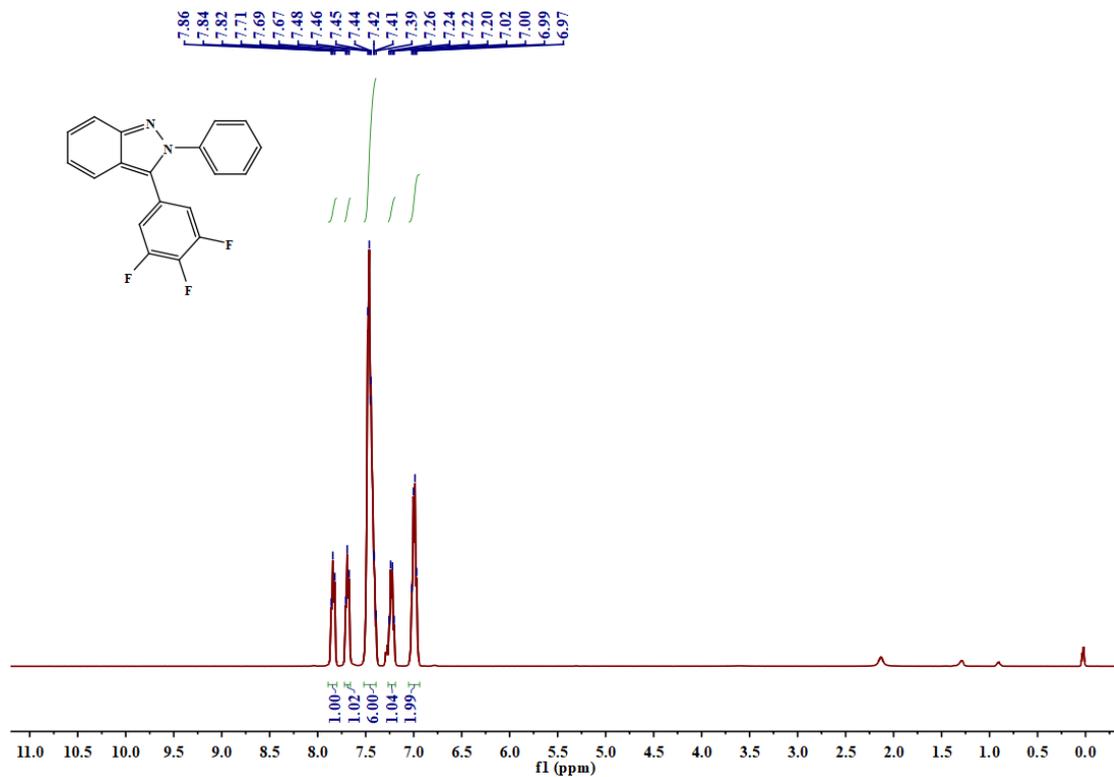


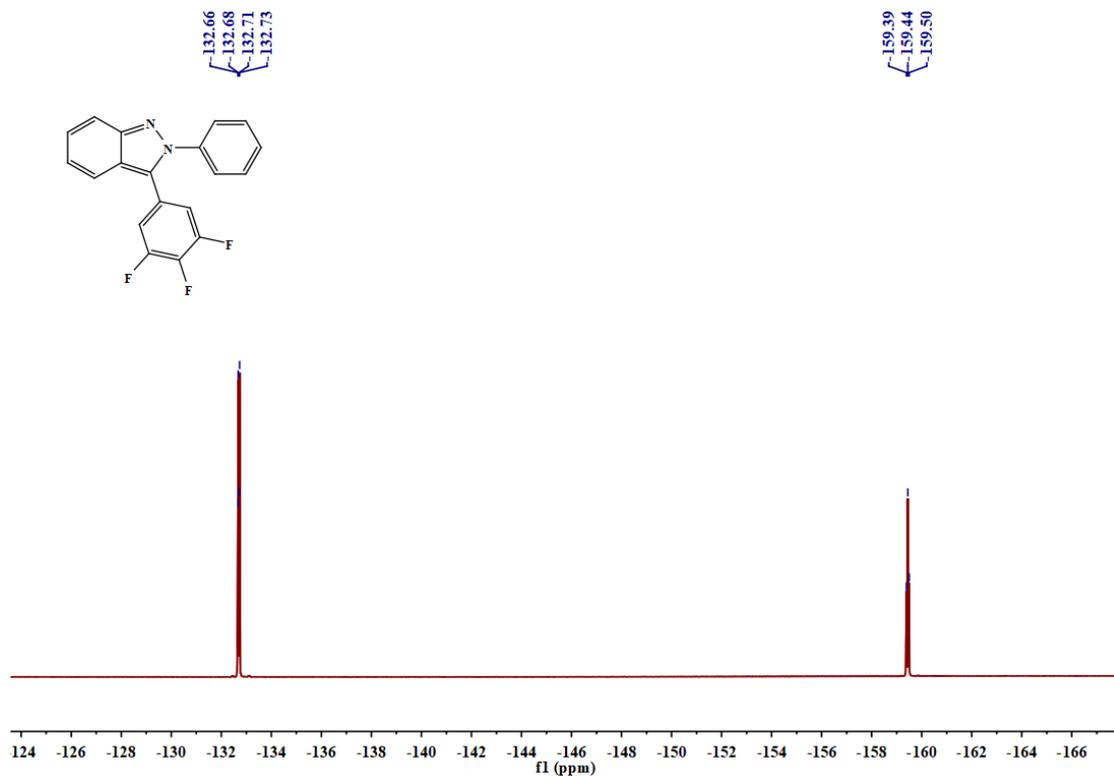
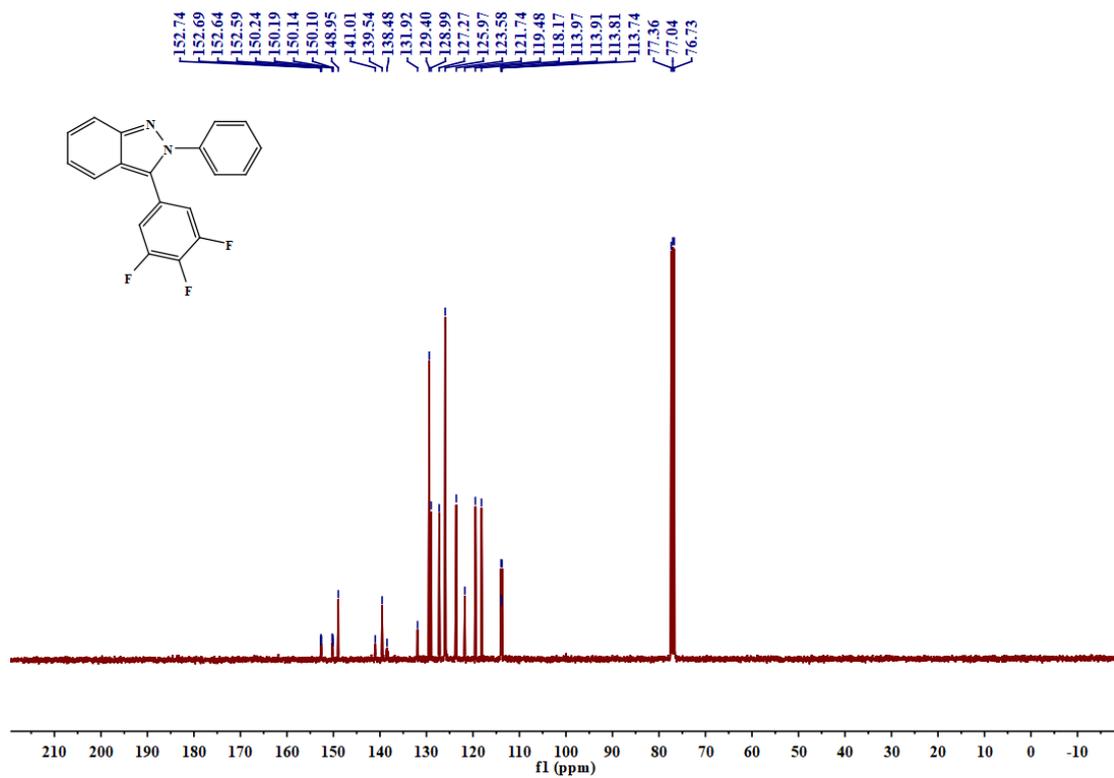
2H-Indazole 21



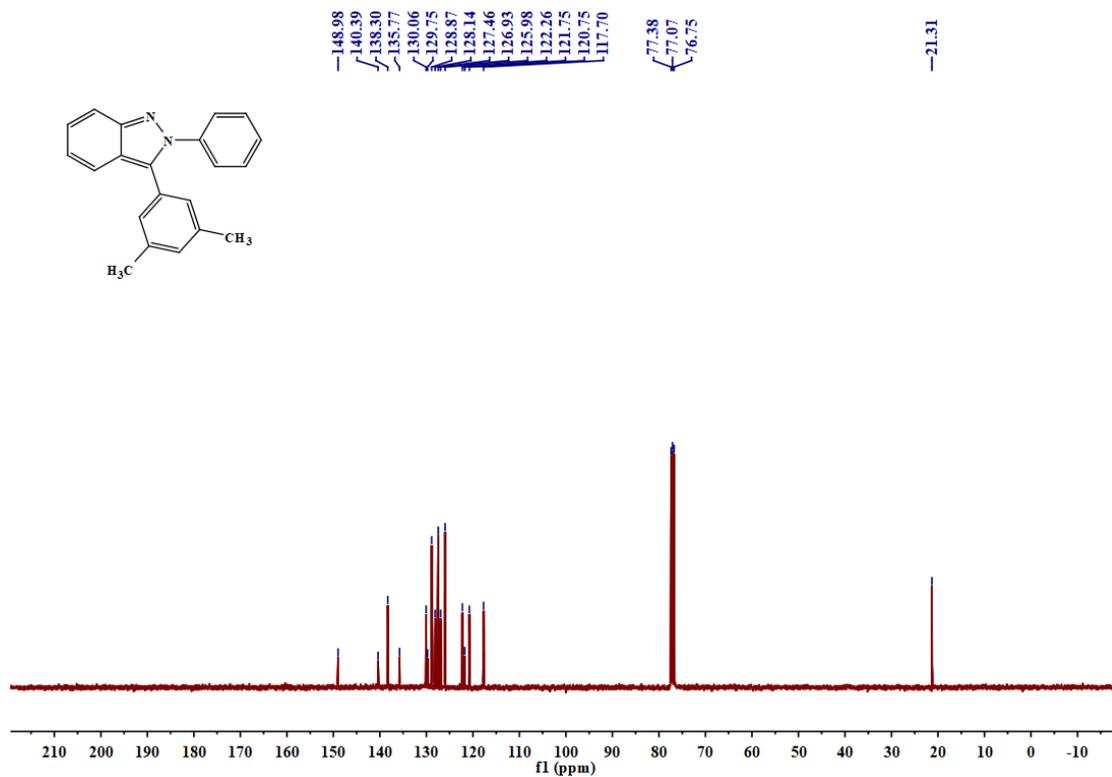
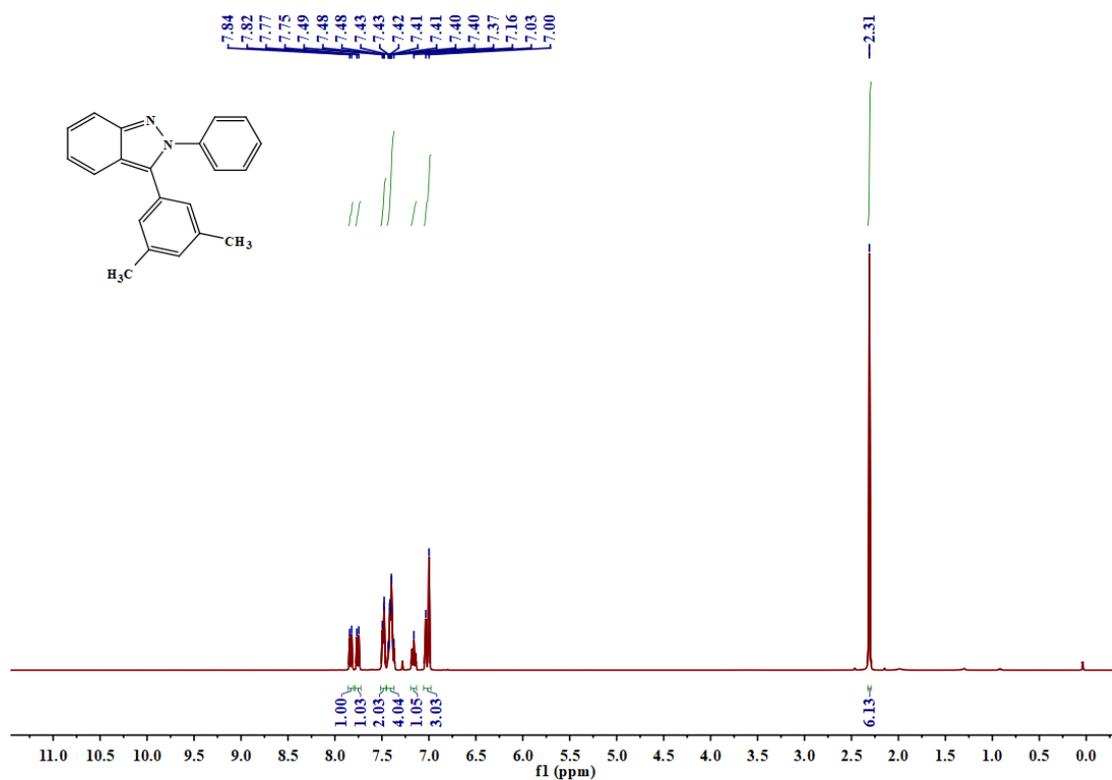


2H-Indazole 2m

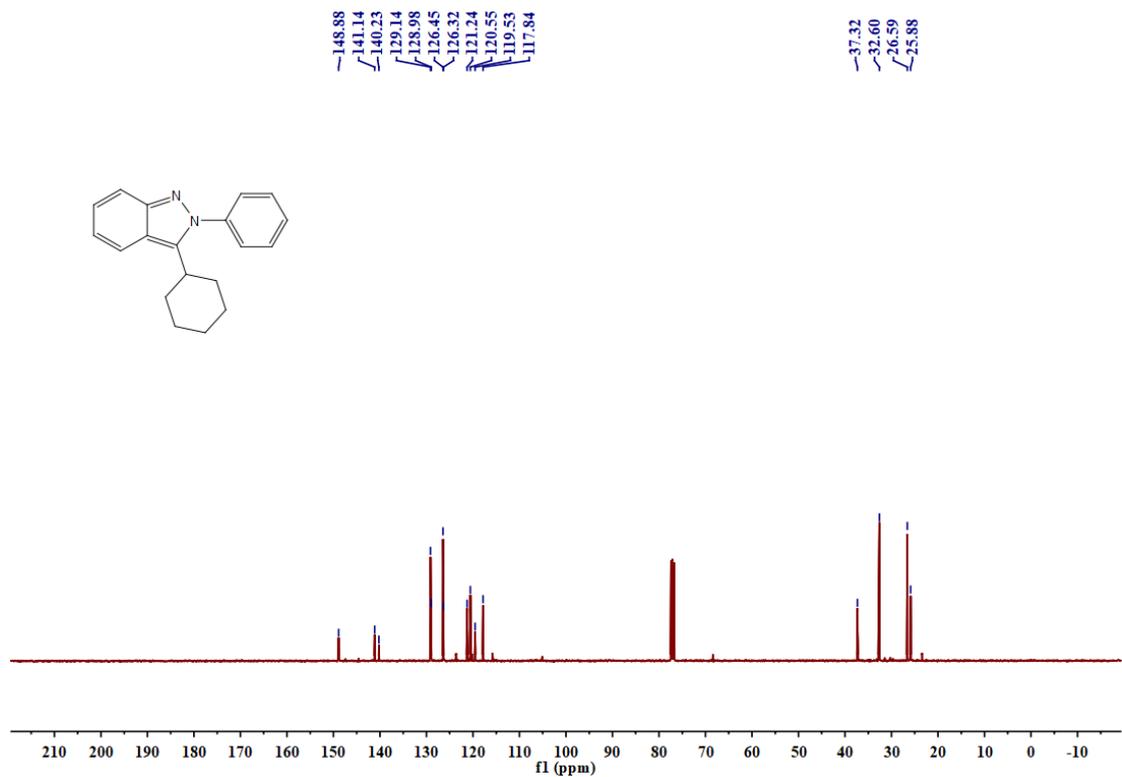
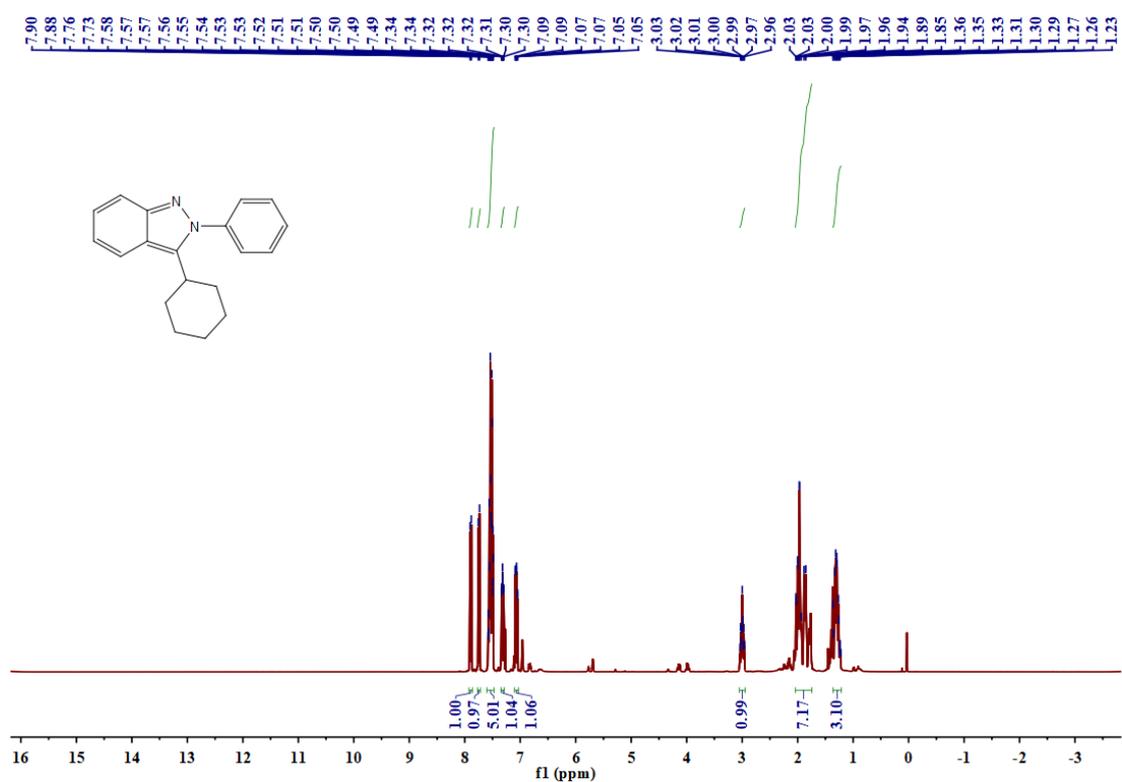




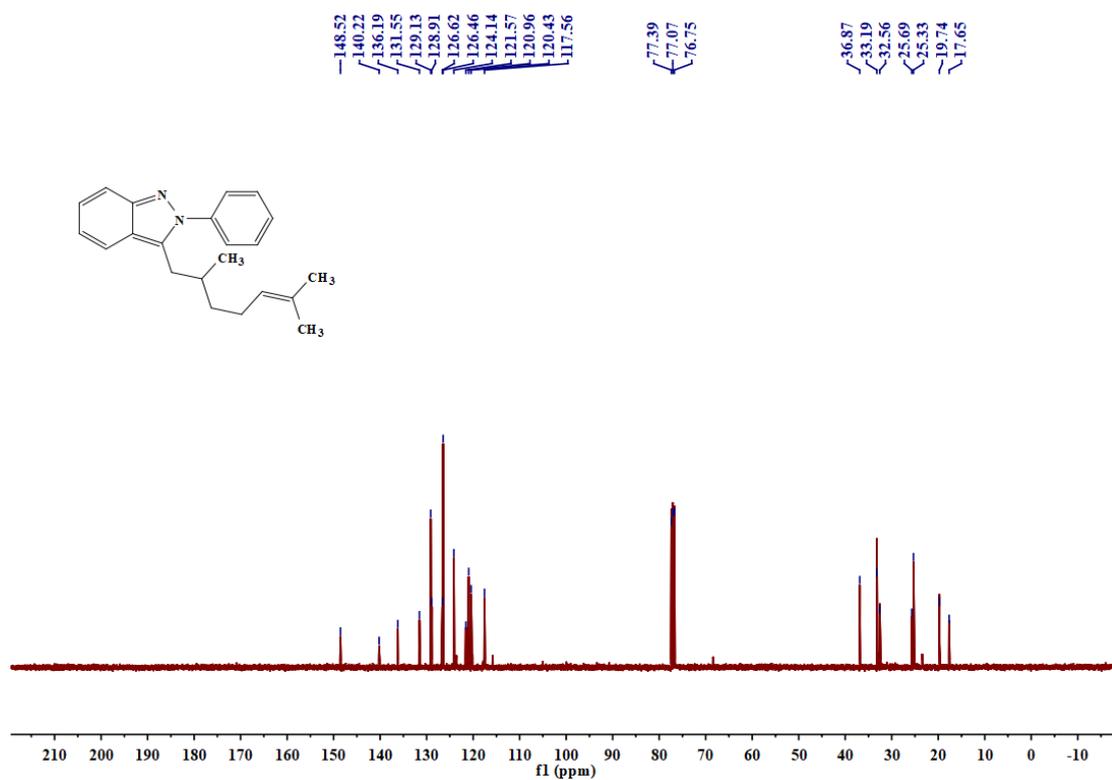
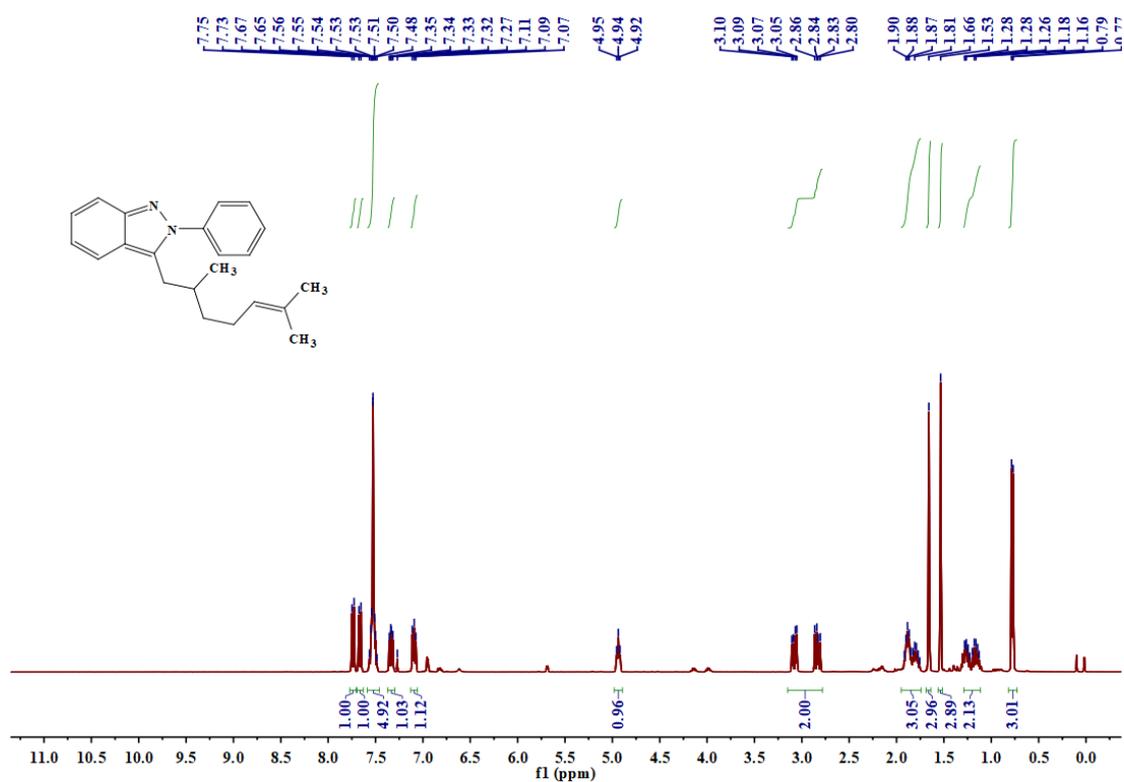
2H-Indazole 2n



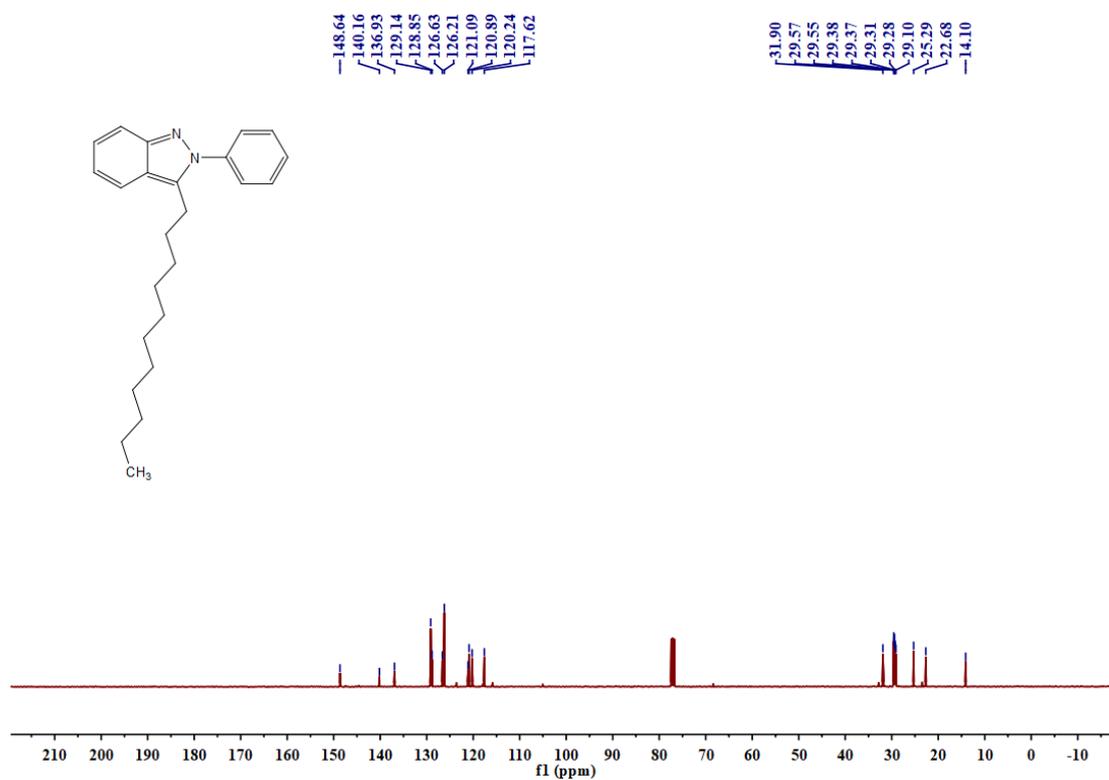
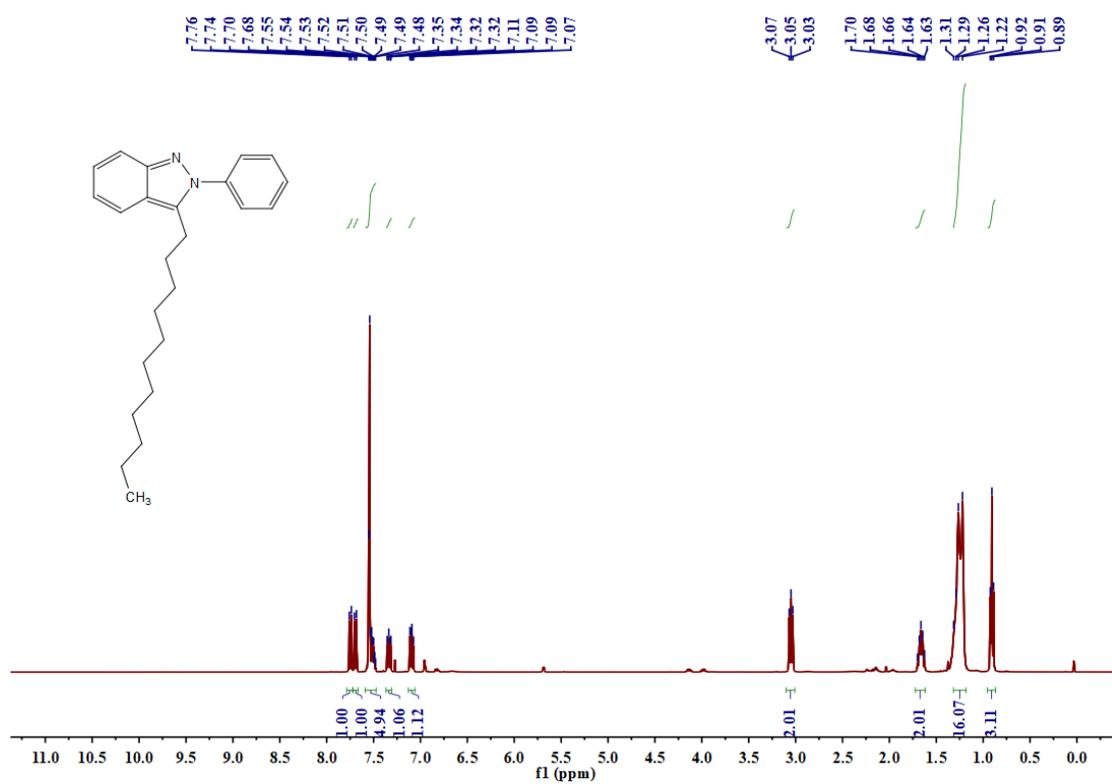
2H-Indazole 2o



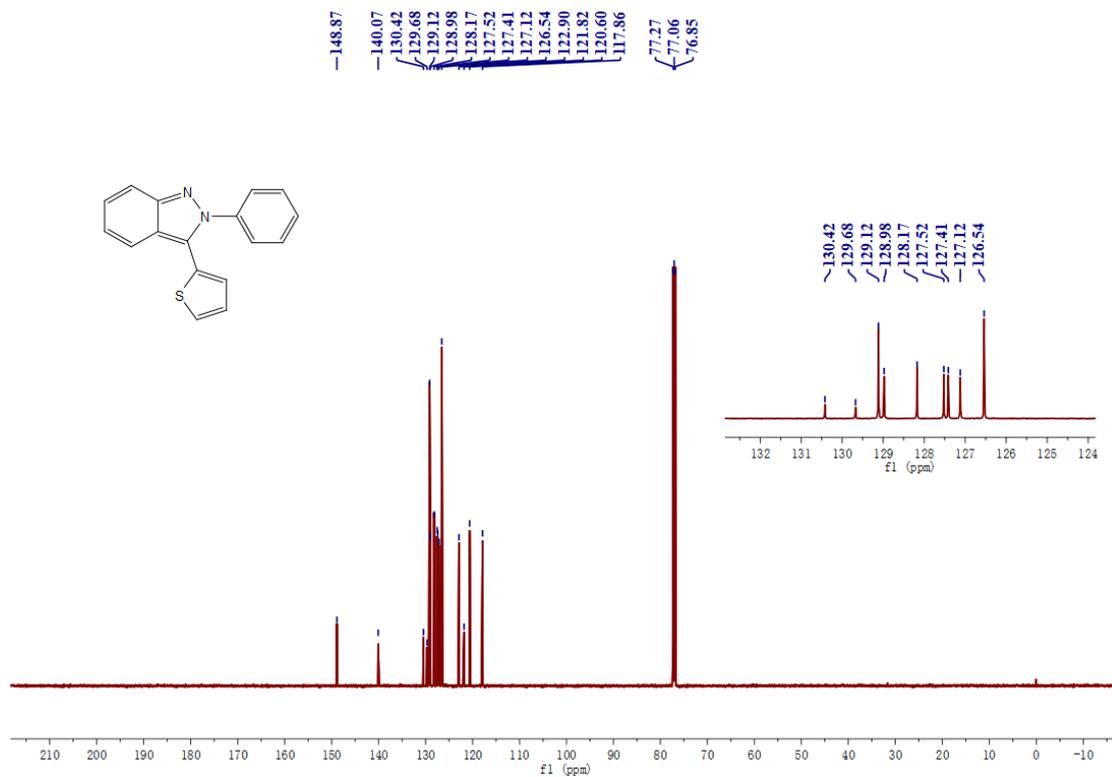
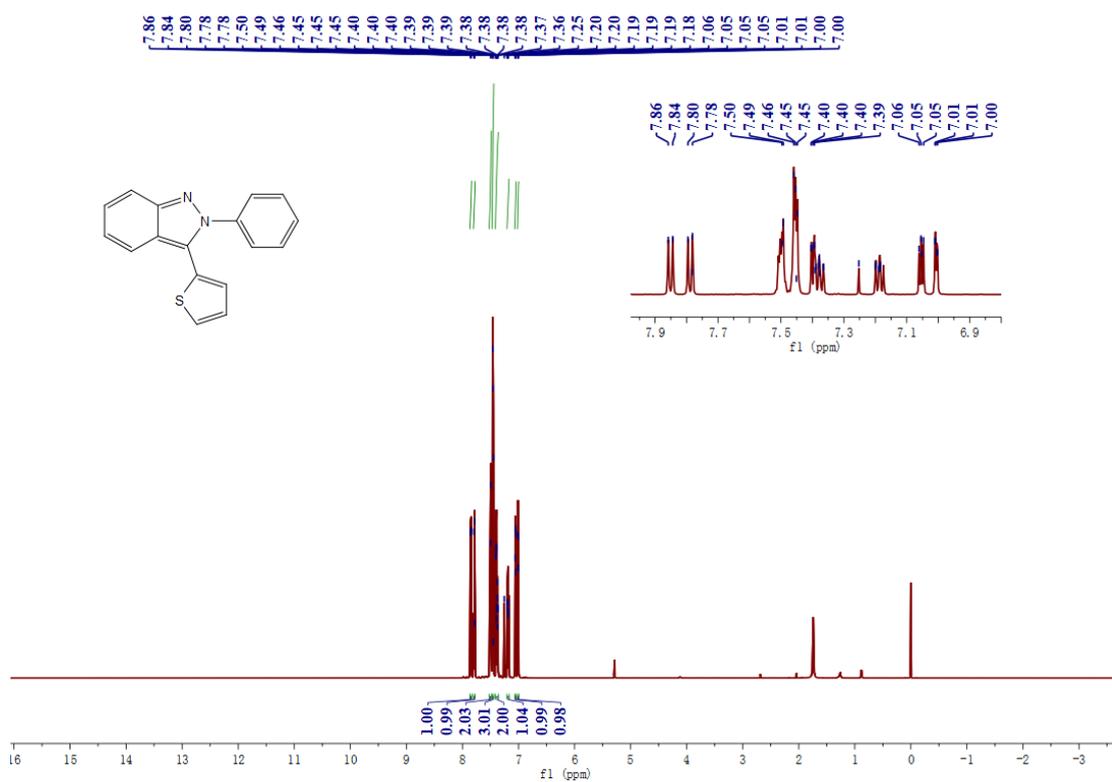
2H-Indazole 2p



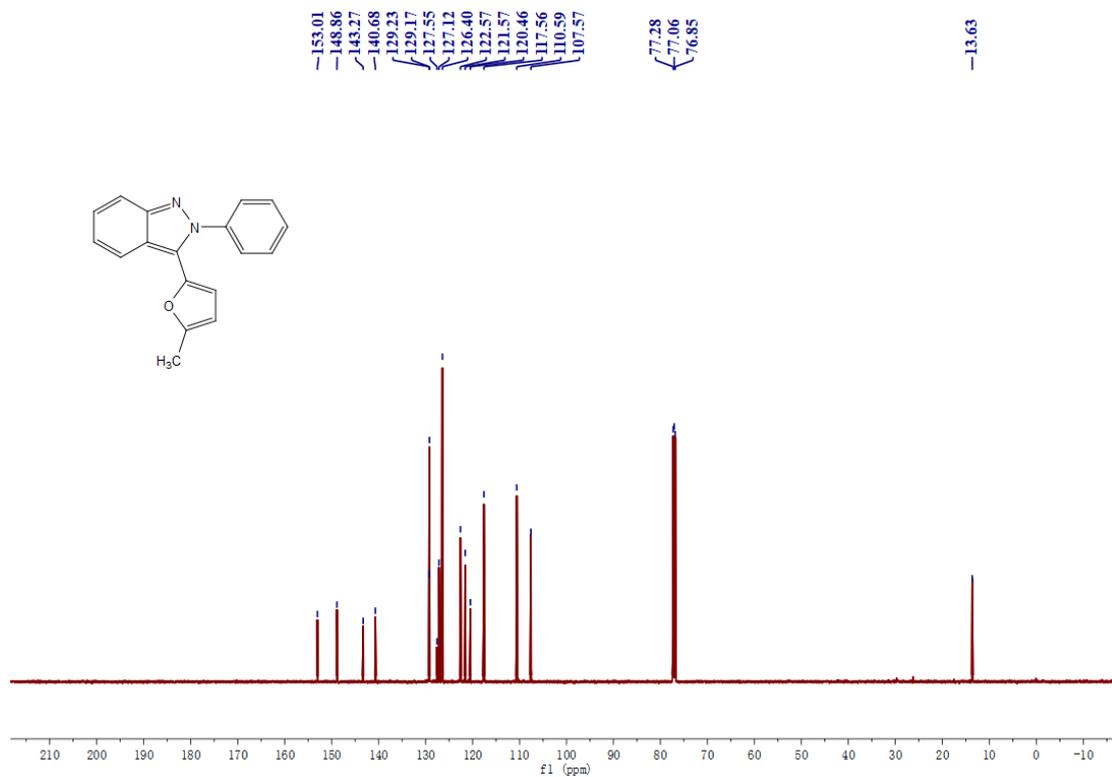
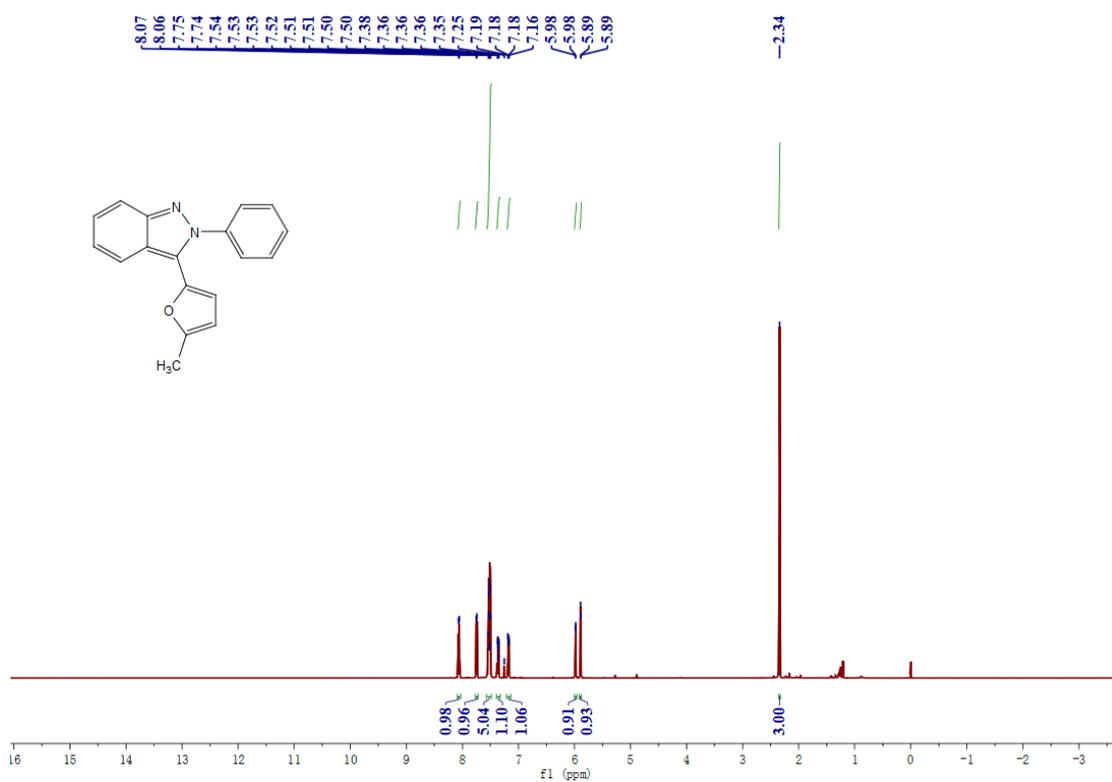
2H-Indazole 2q



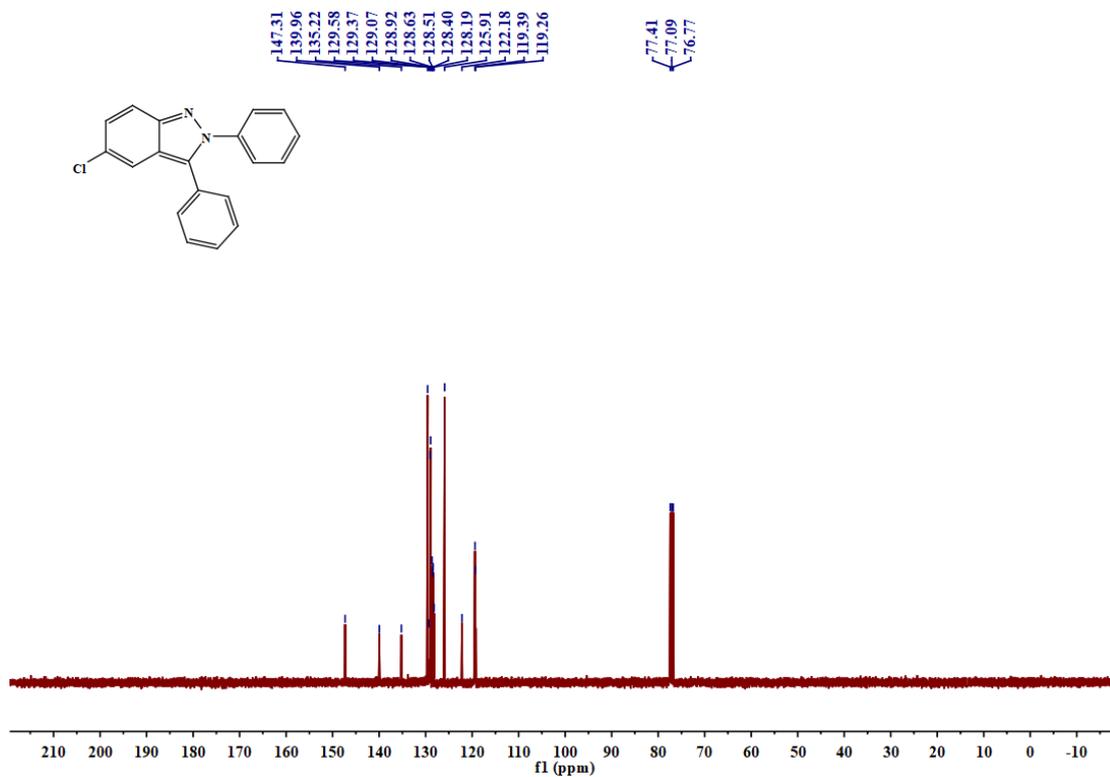
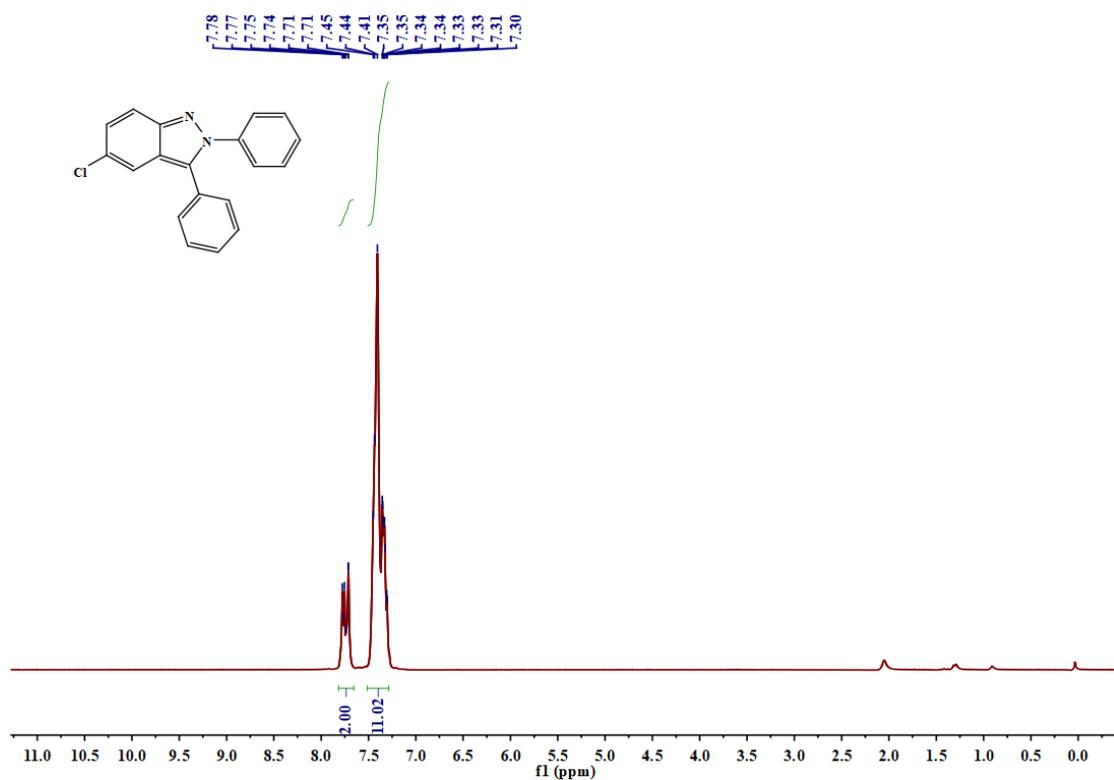
2H-Indazole 2r



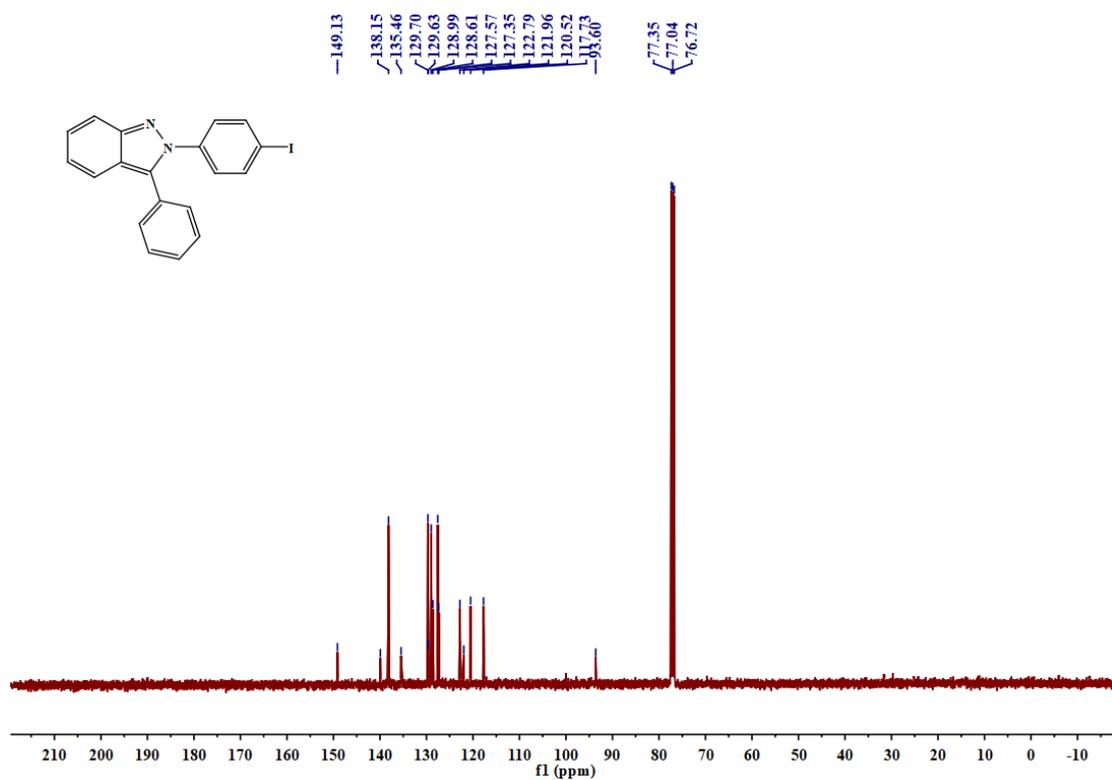
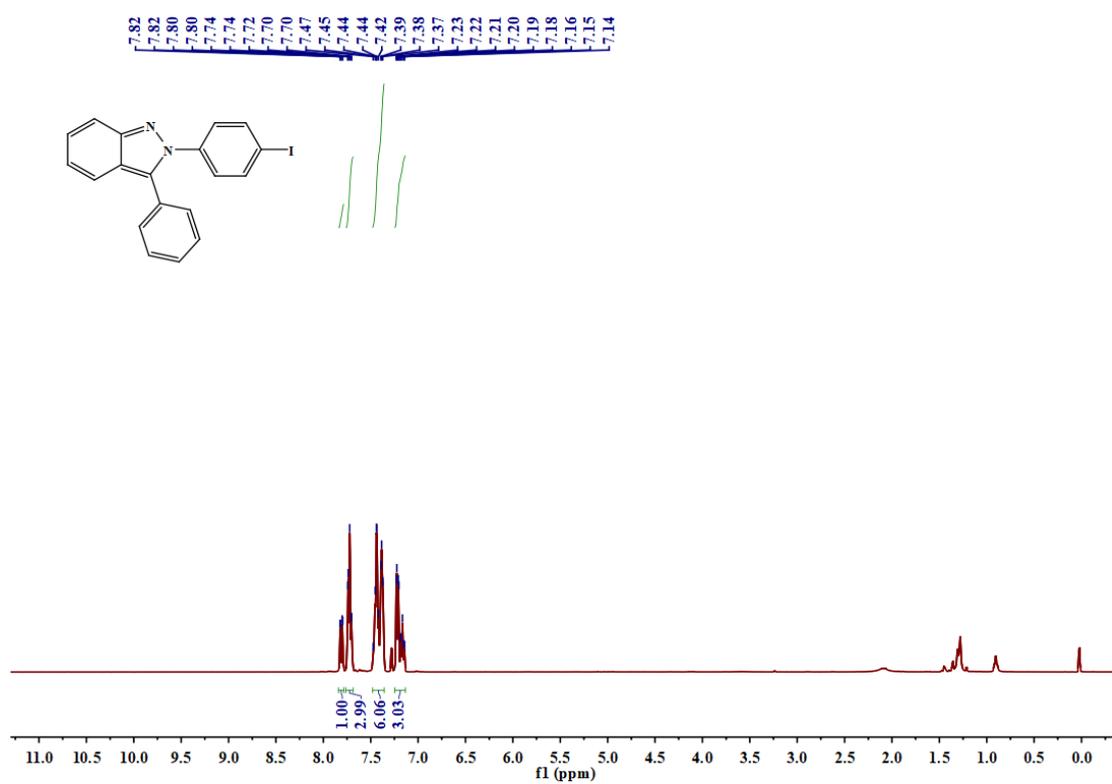
2H-Indazole 2s



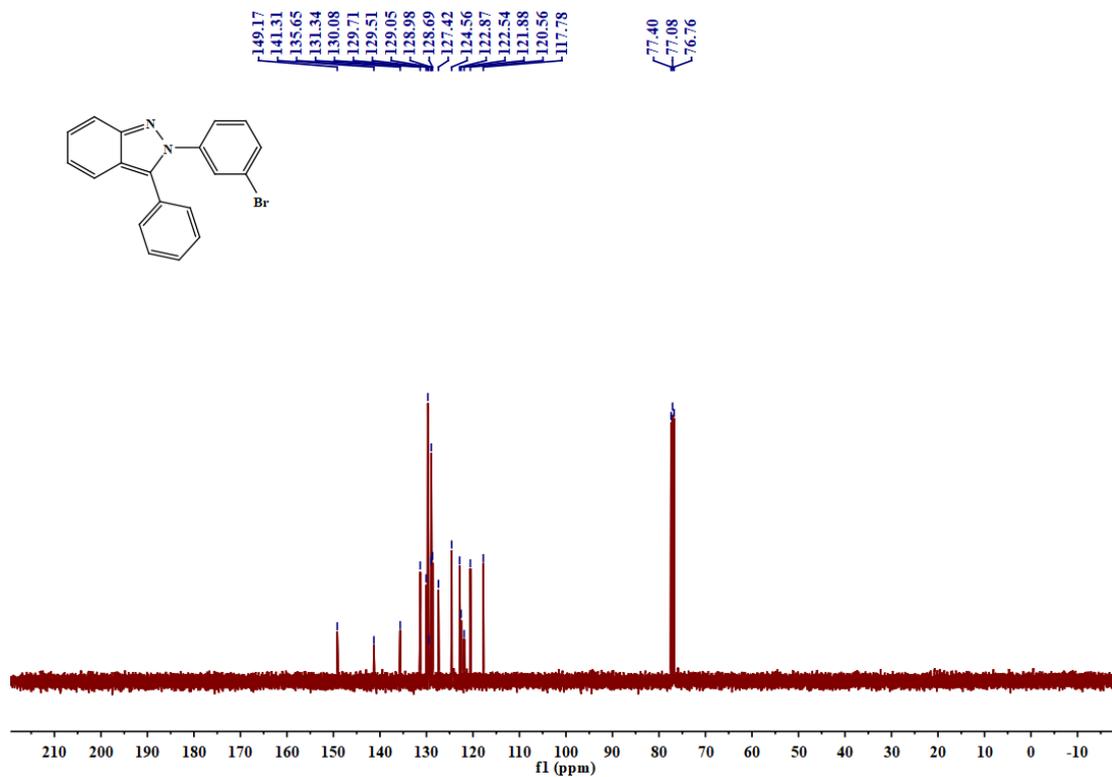
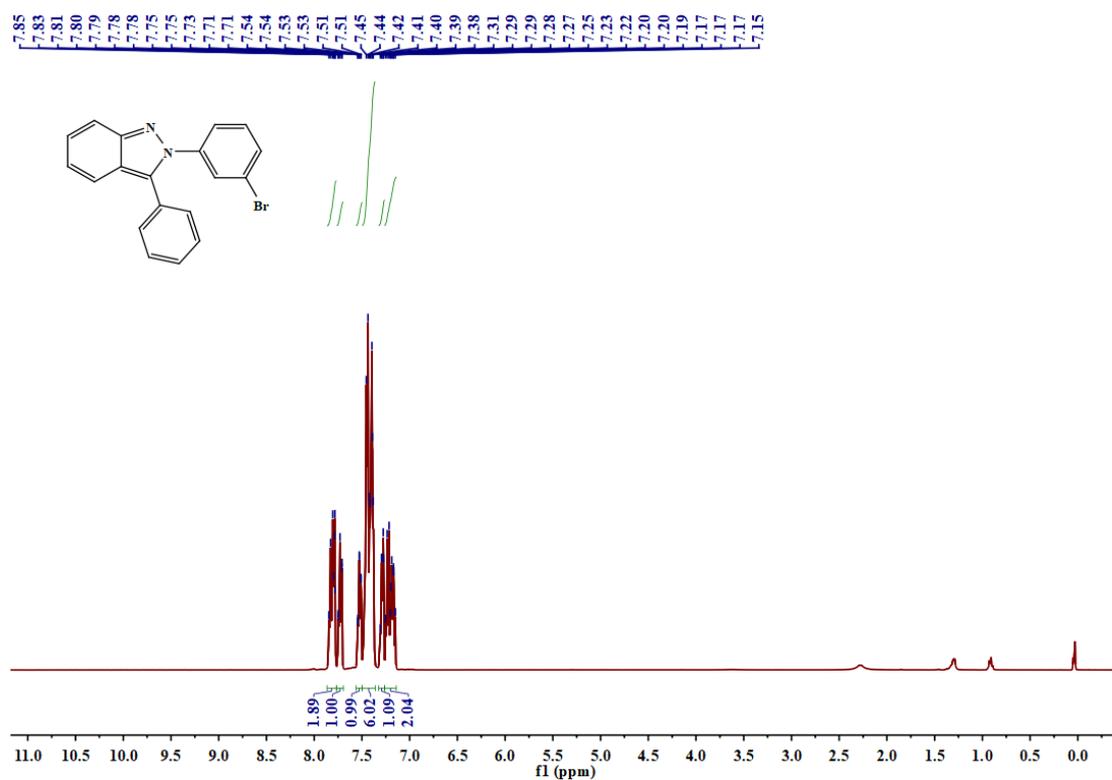
2H-Indazole 4a



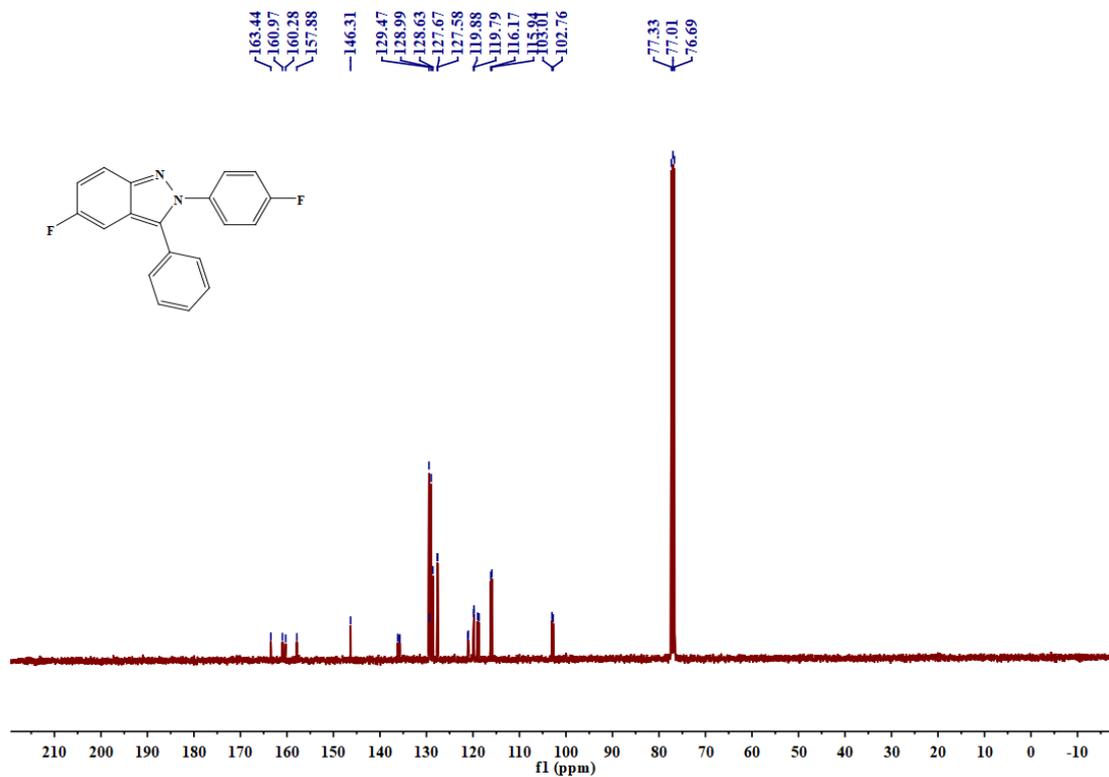
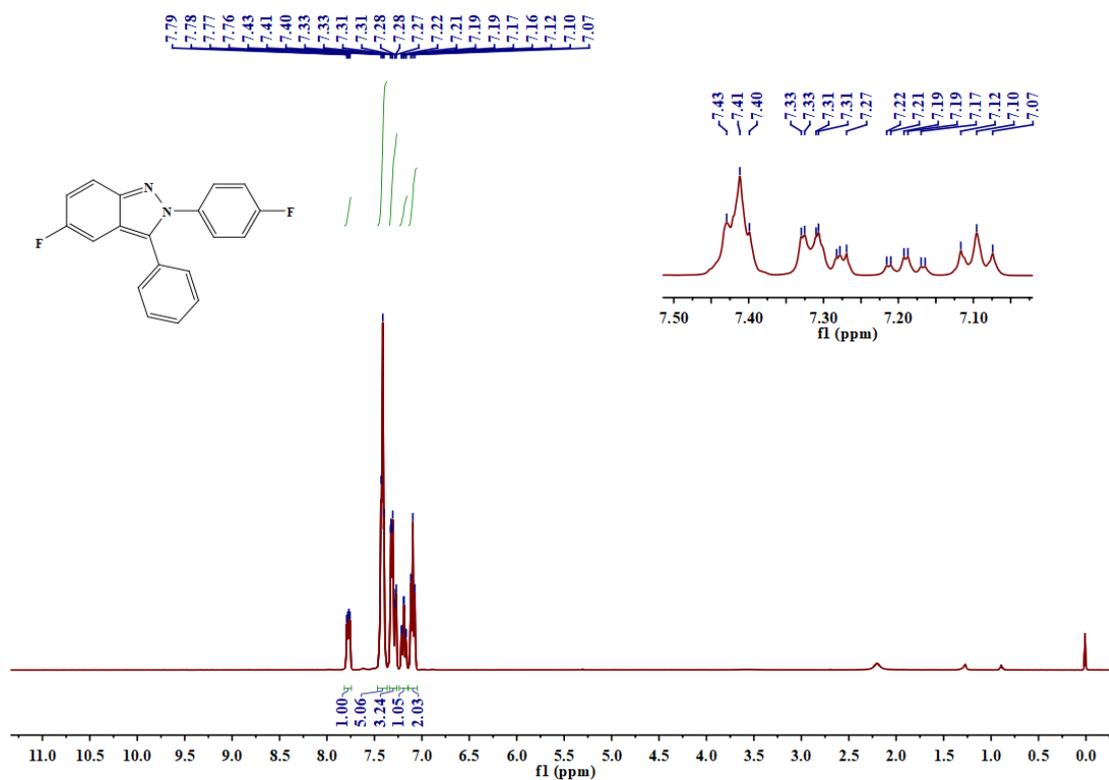
2H-Indazole 4b

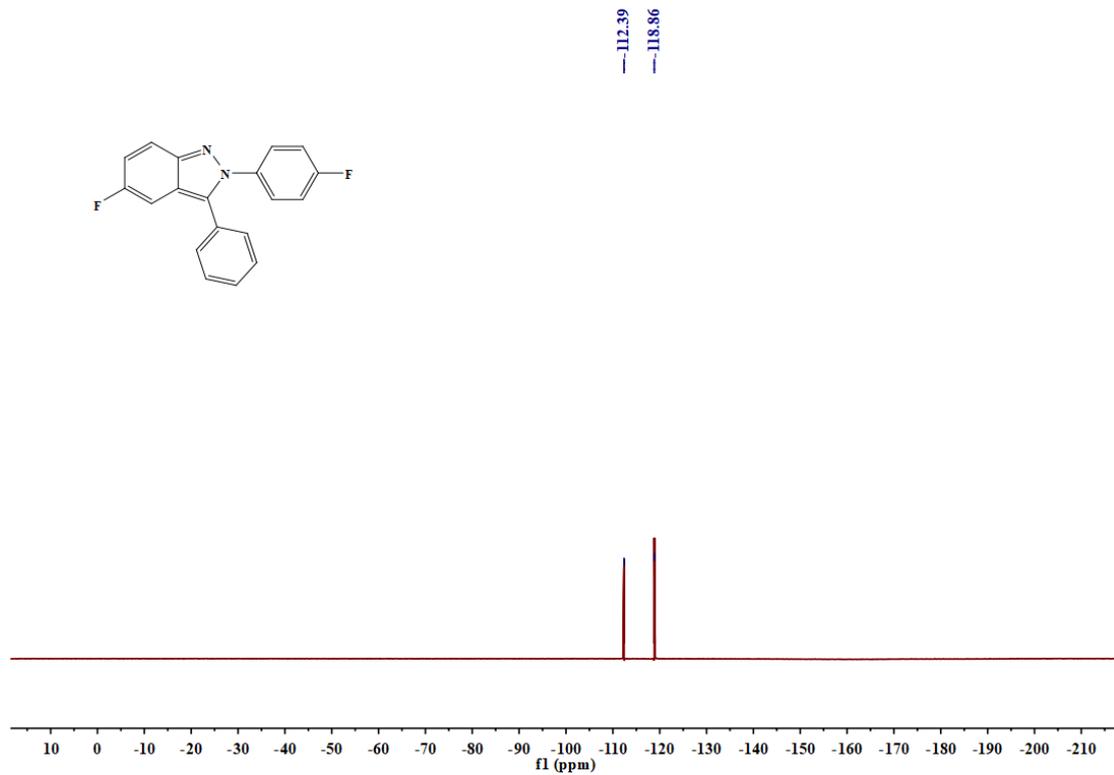


2H-Indazole 4c

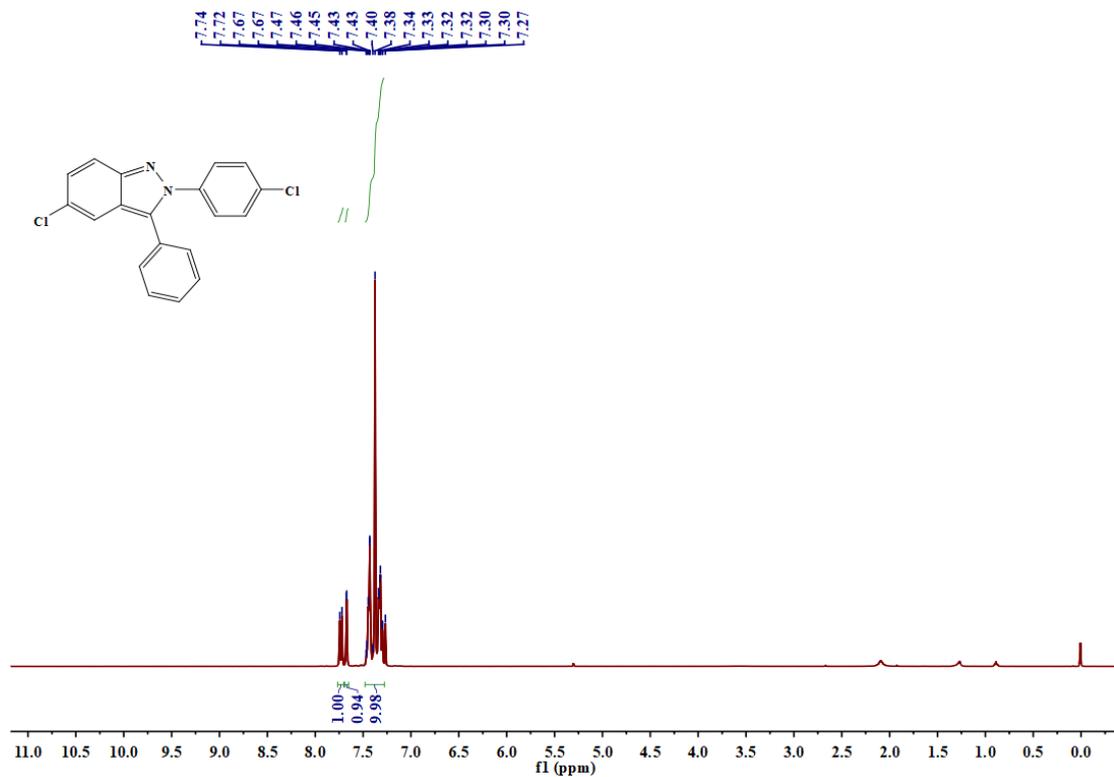


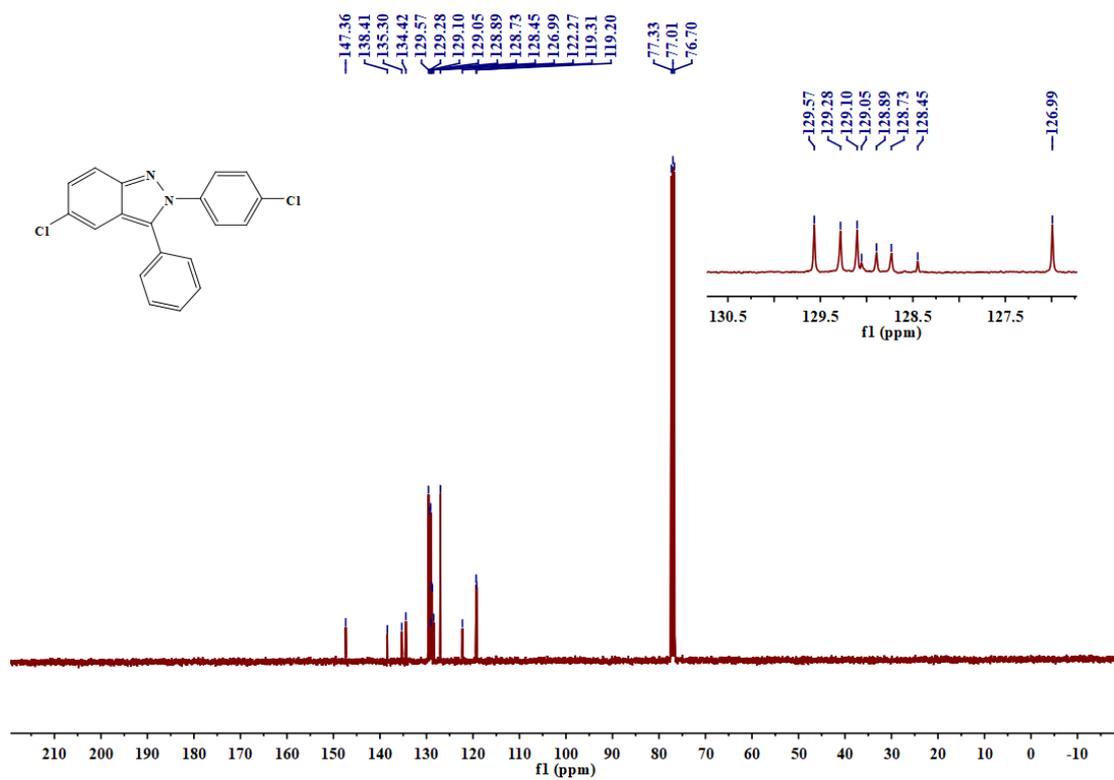
2H-Indazole 4d



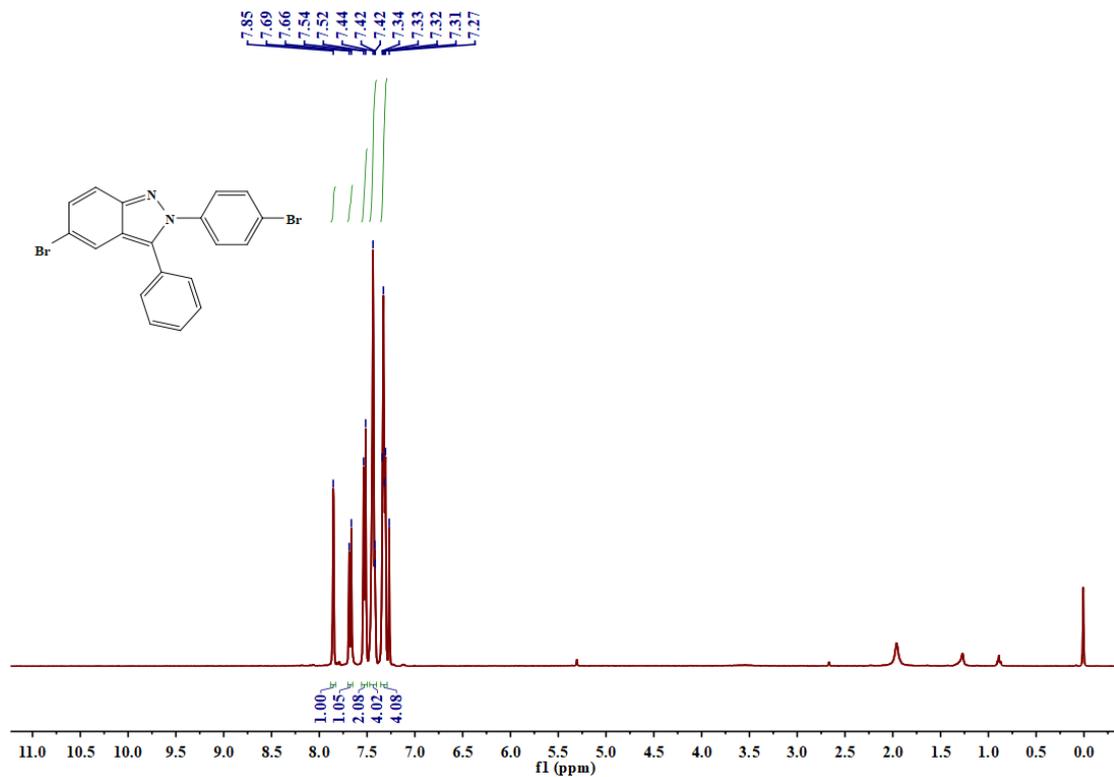


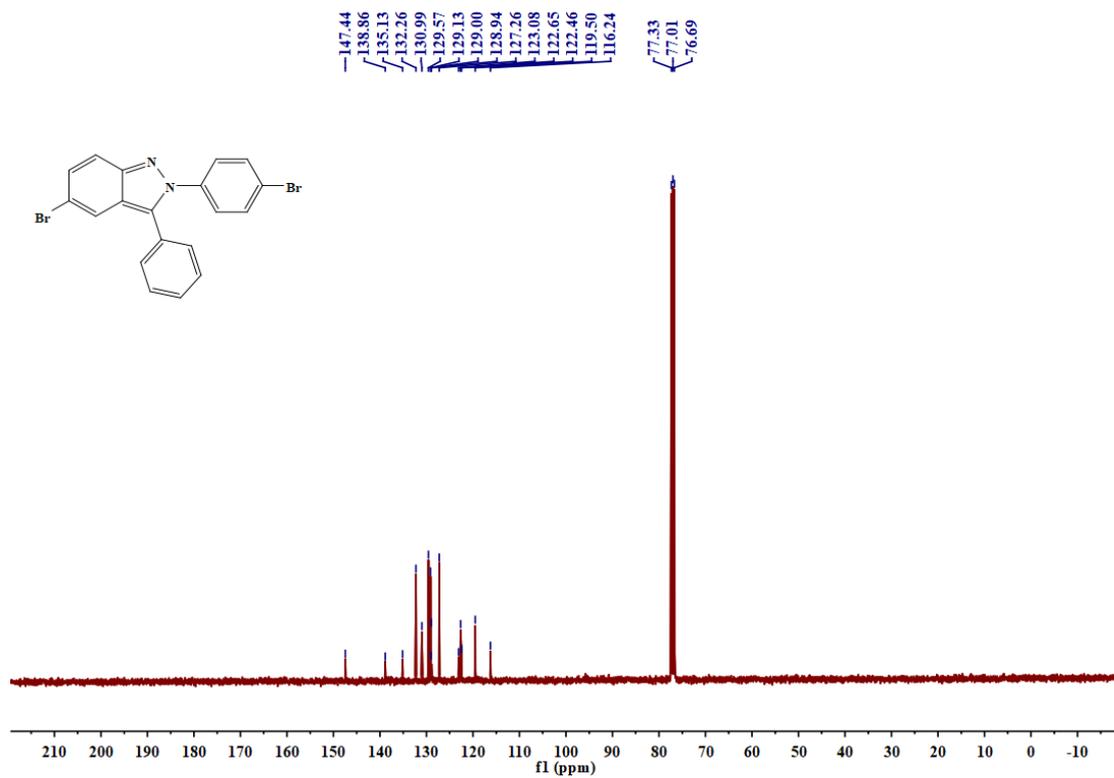
2H-Indazole 4e



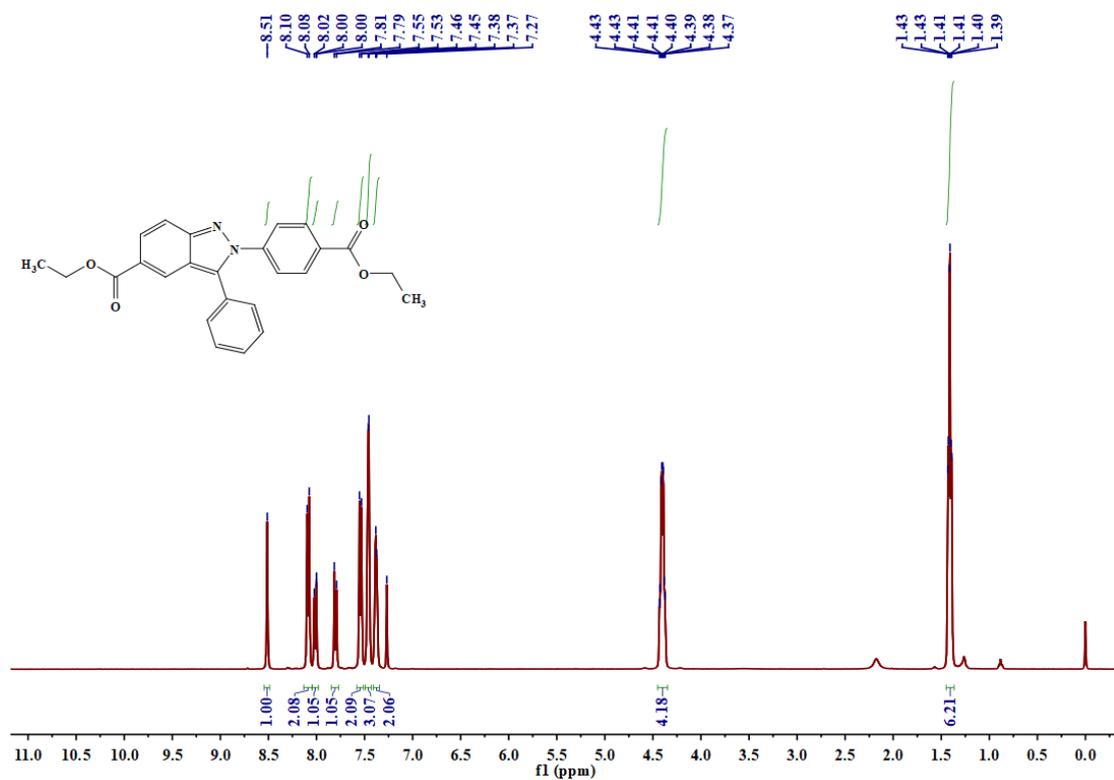


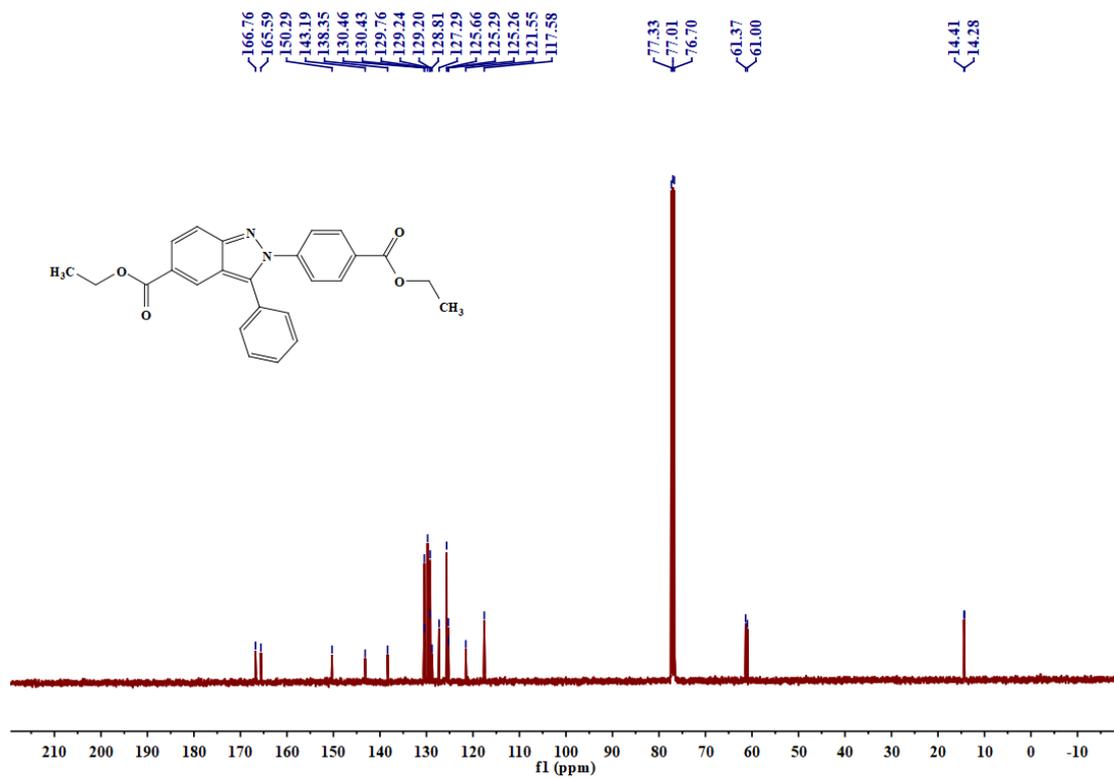
2H-Indazole 4f



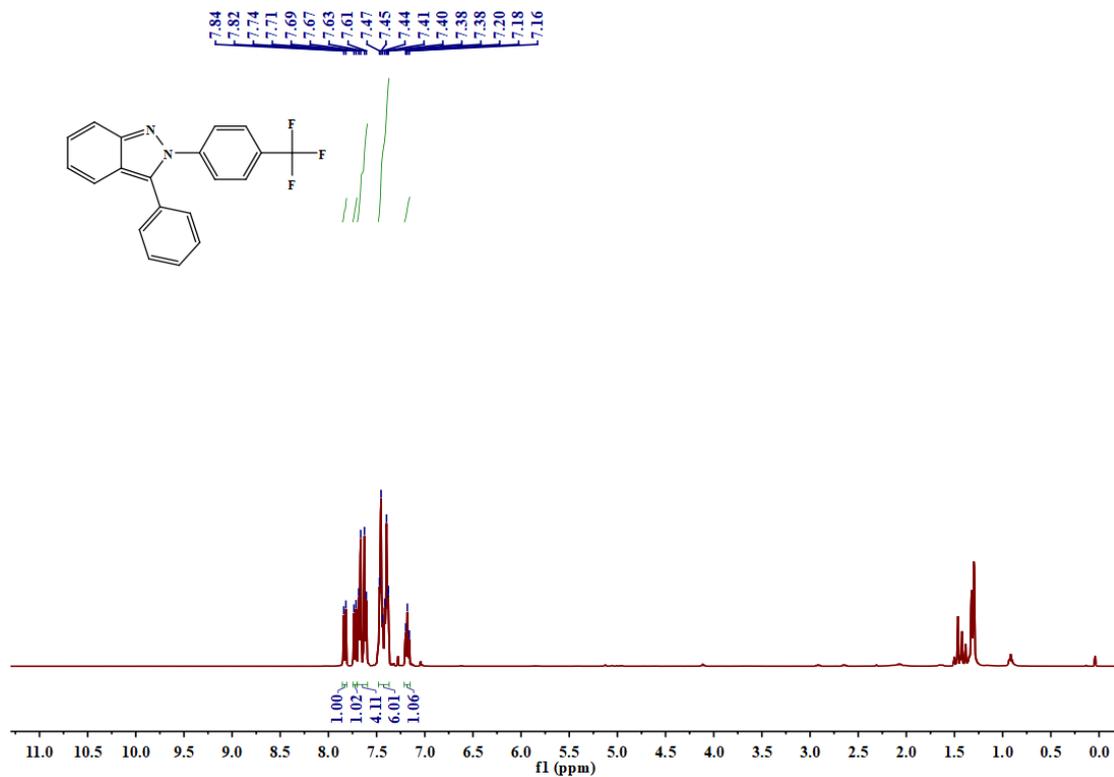


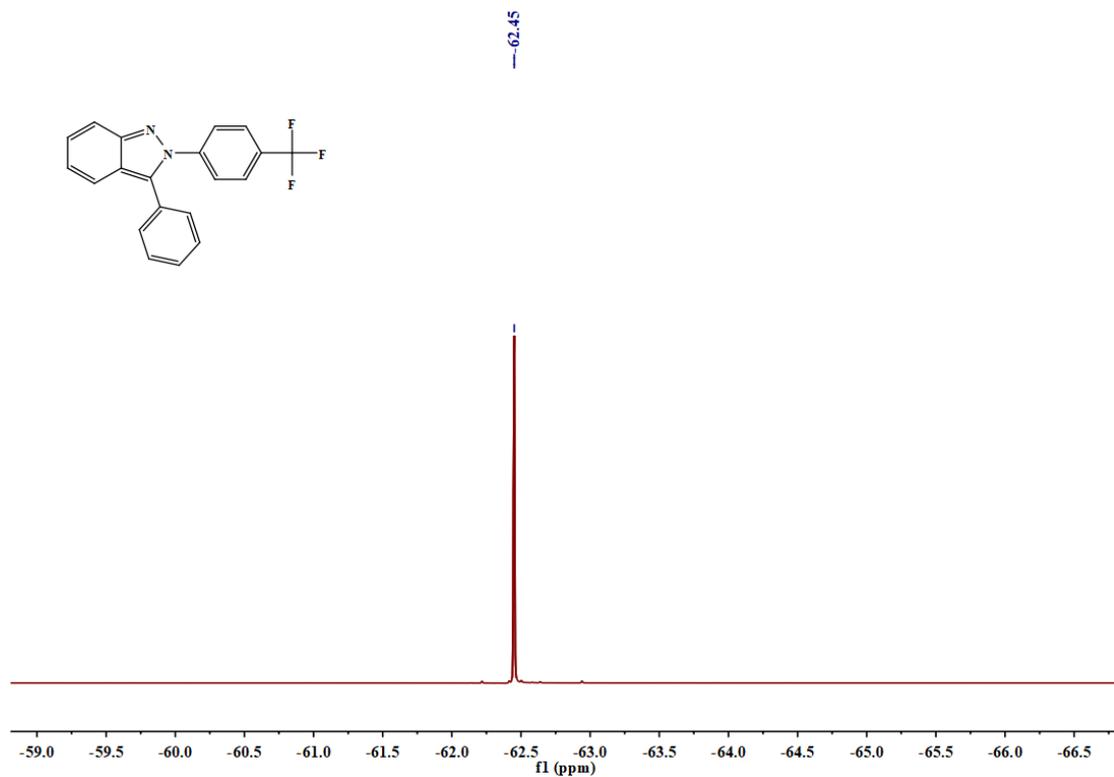
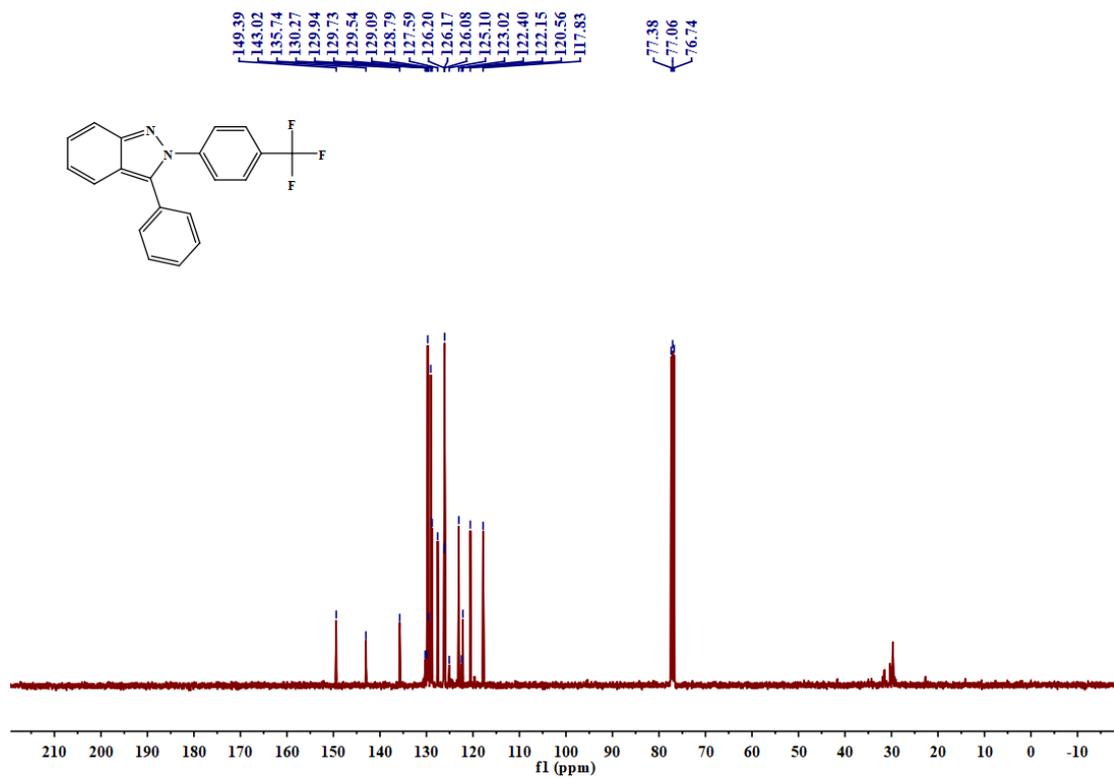
2H-Indazole 4g



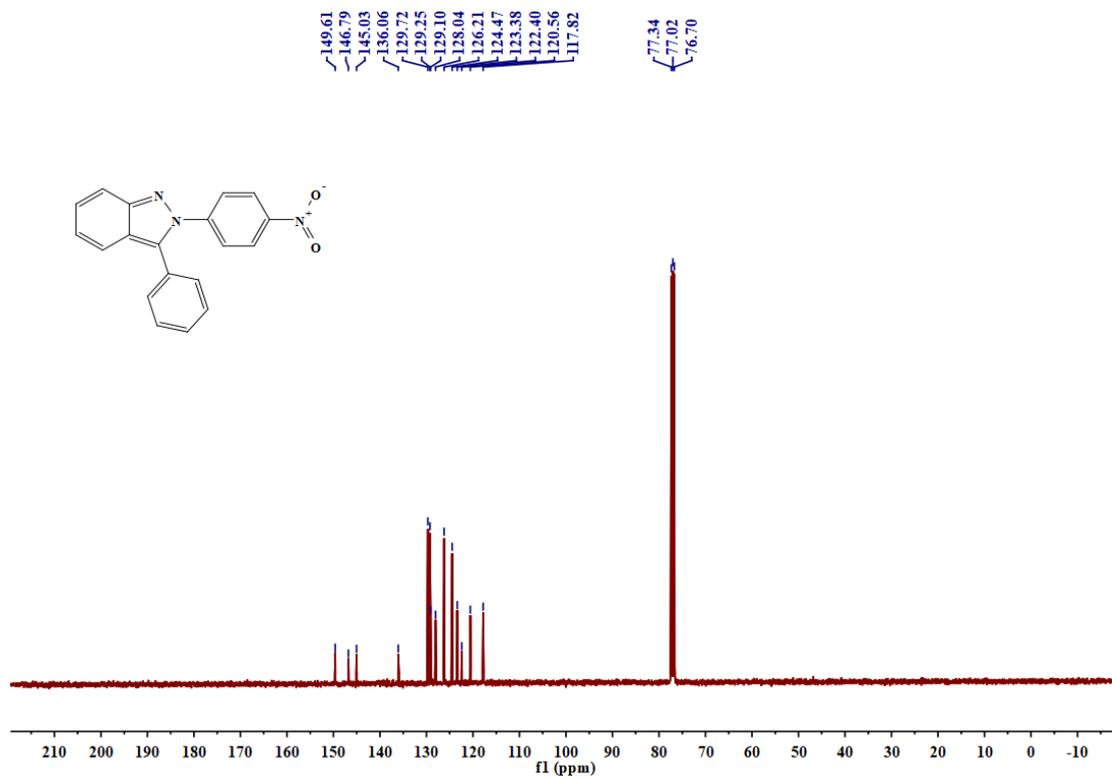
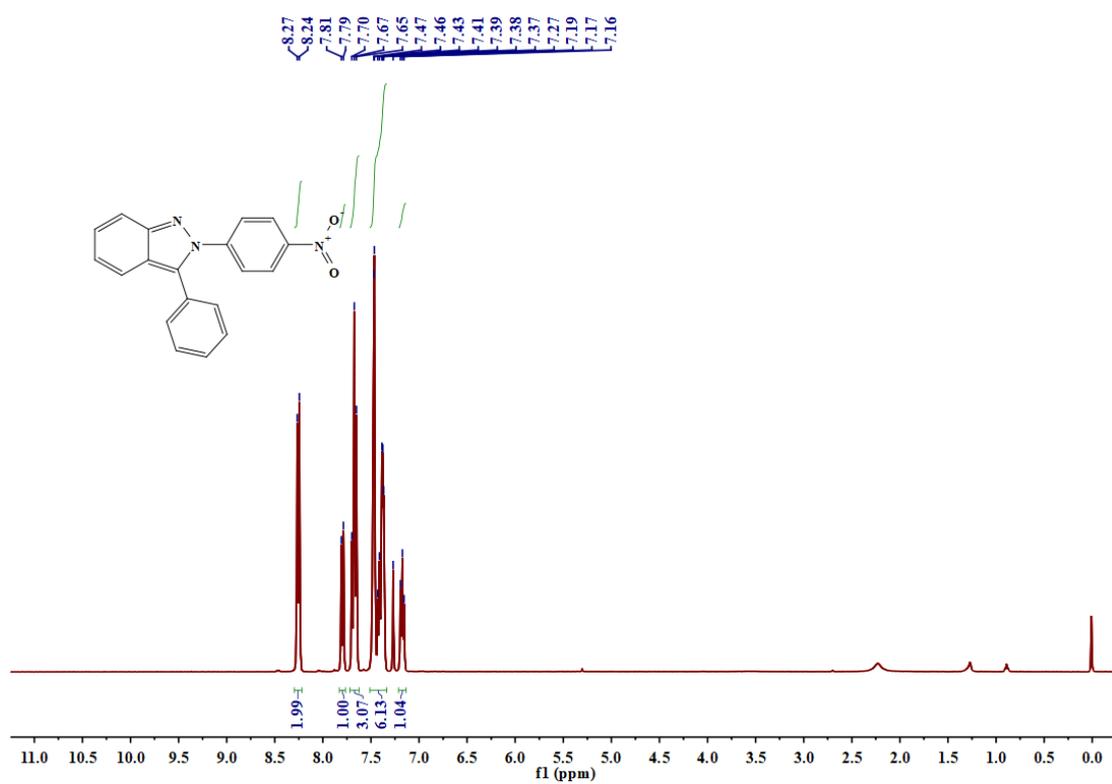


2H-Indazole 4h

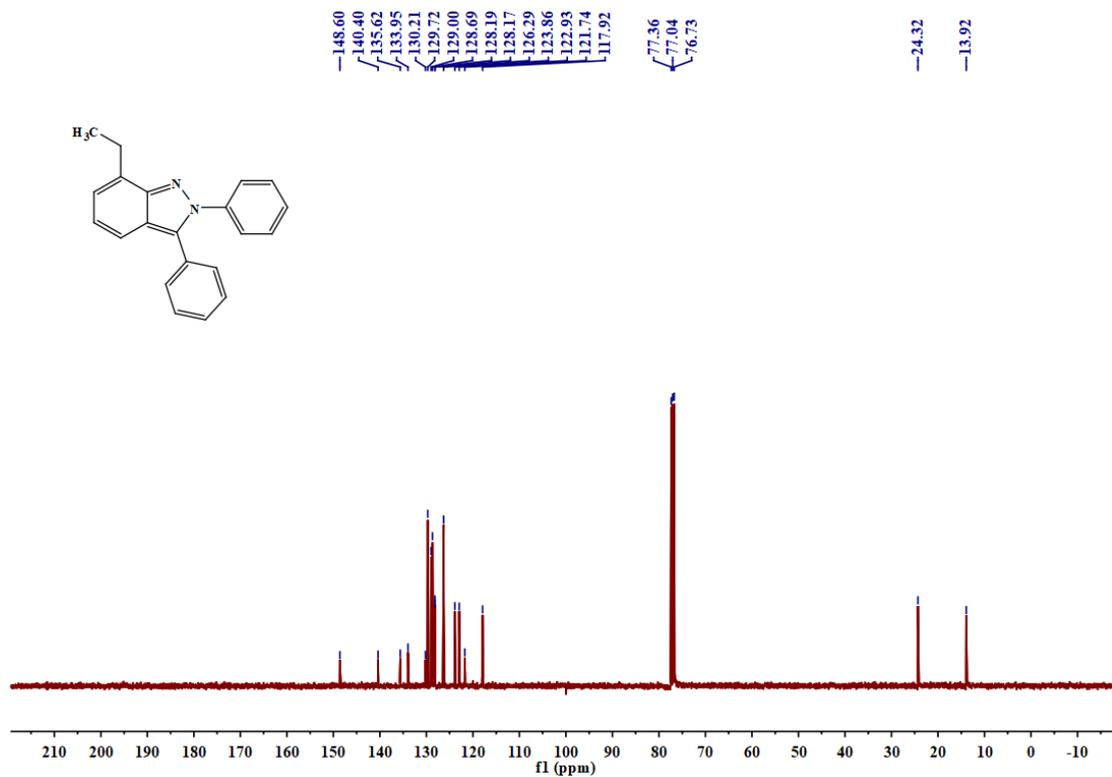
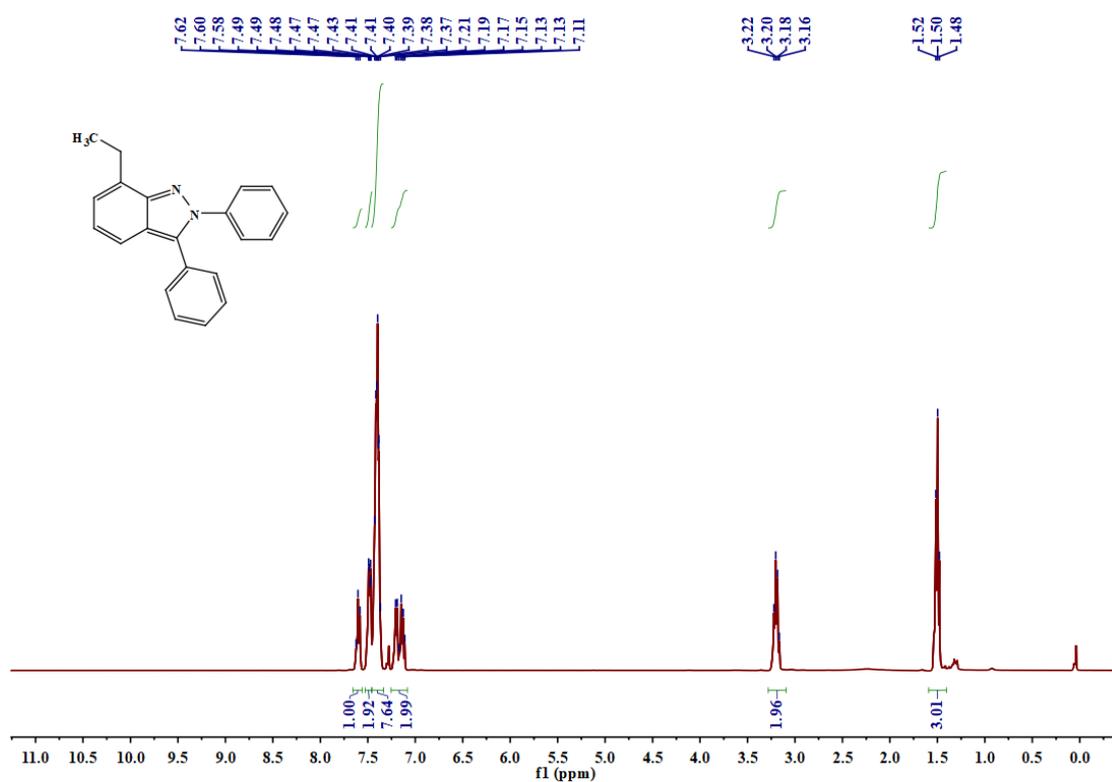




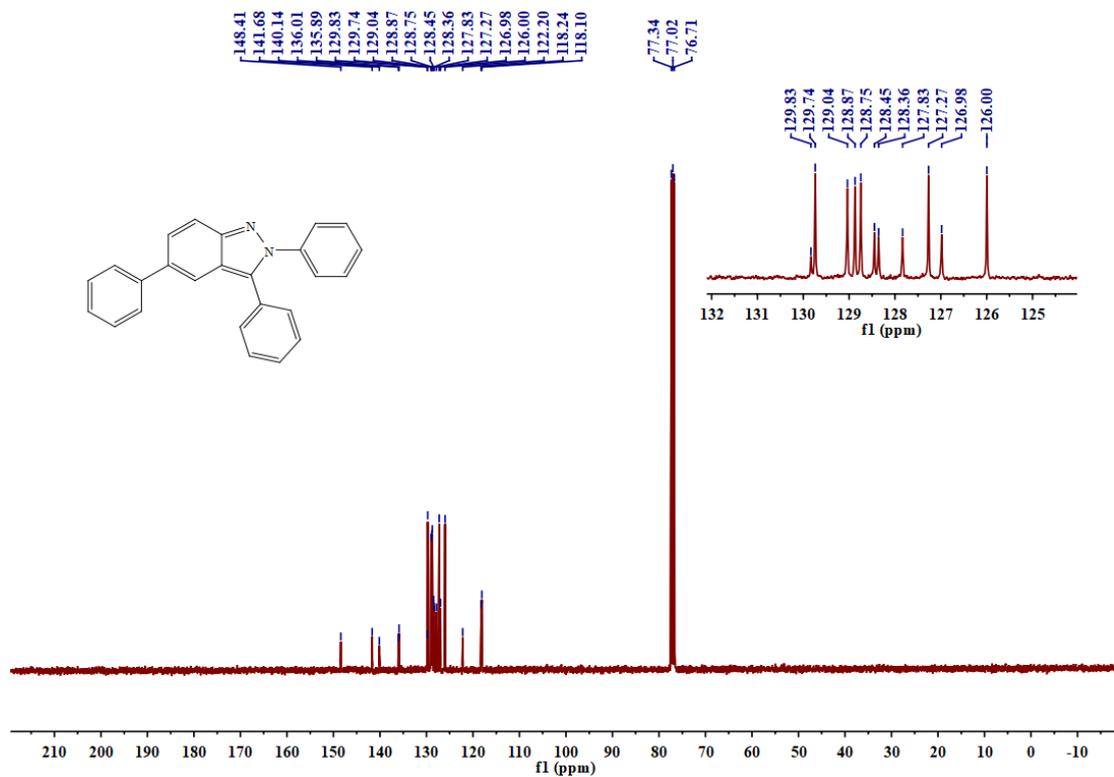
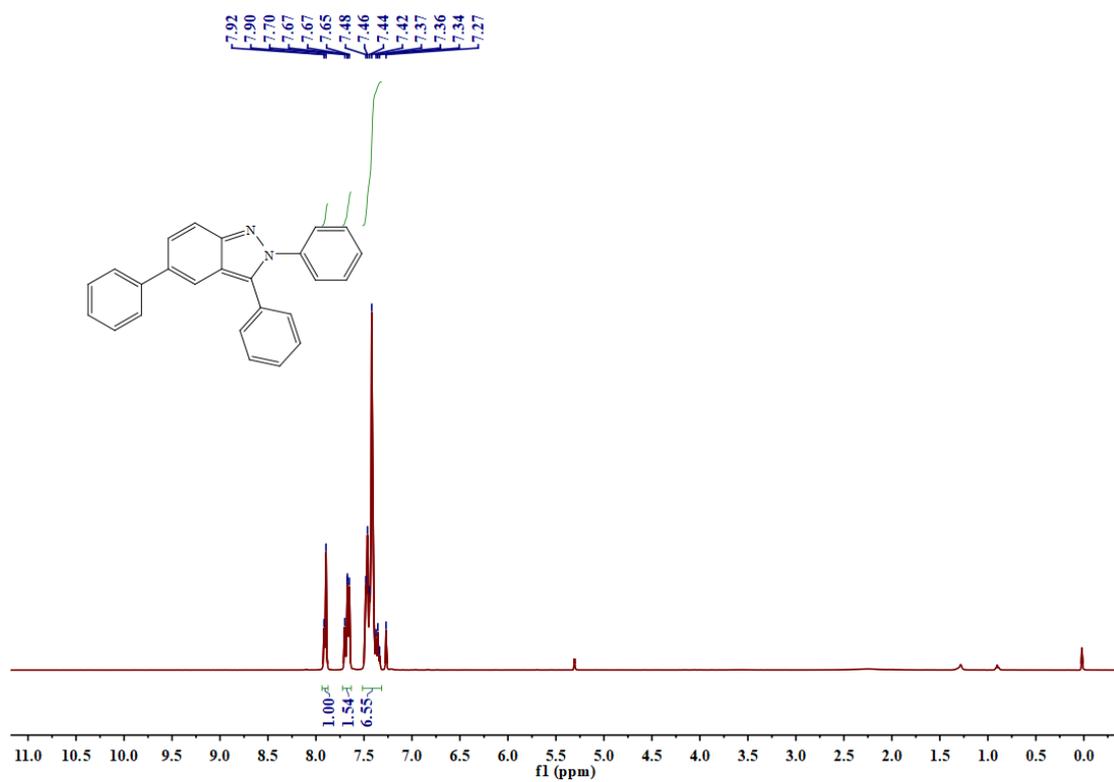
2H-Indazole 4i



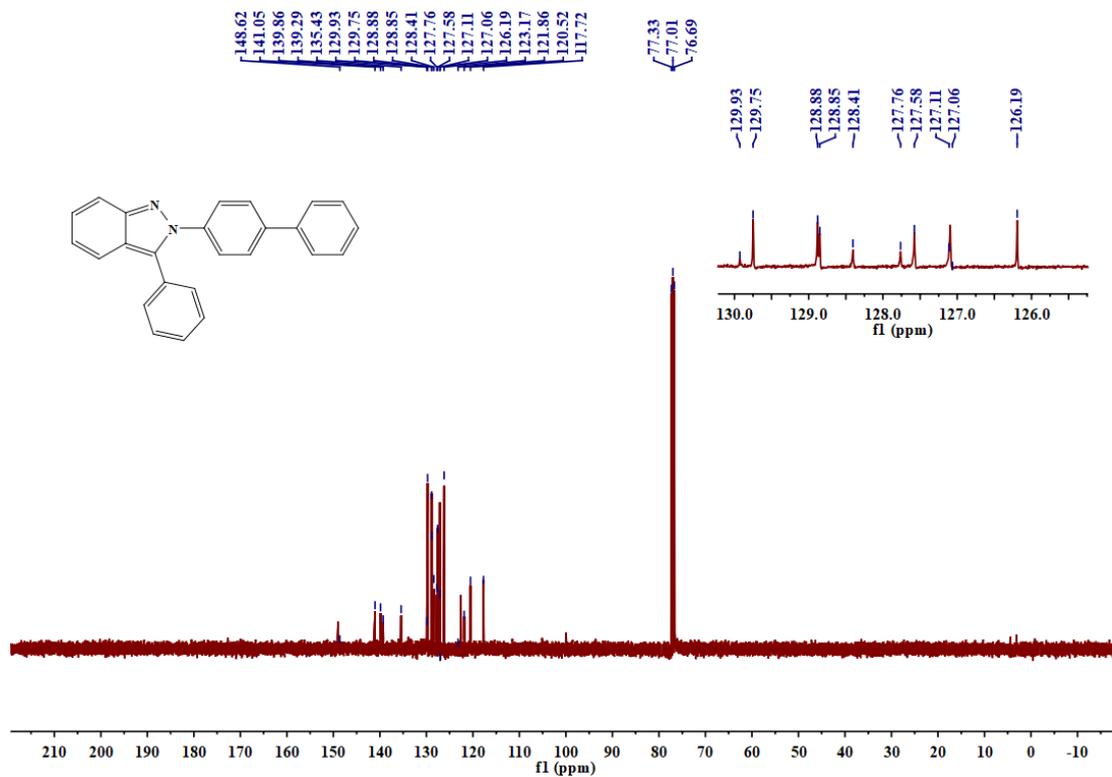
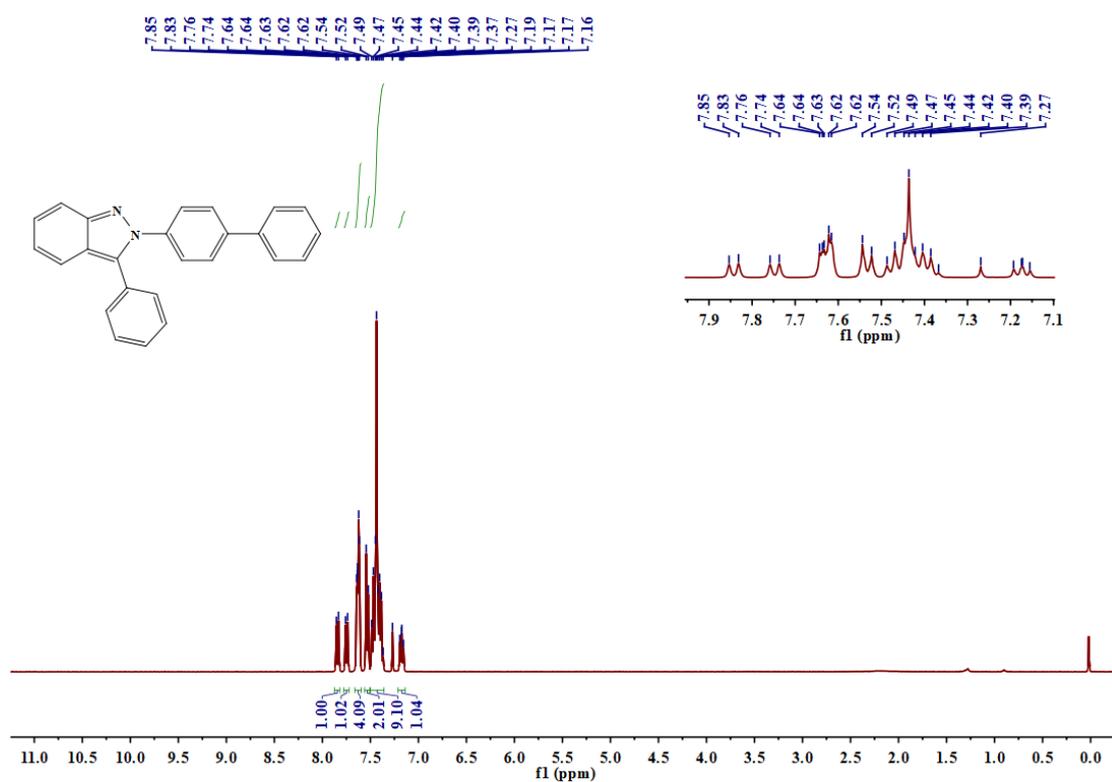
2H-Indazole 4j



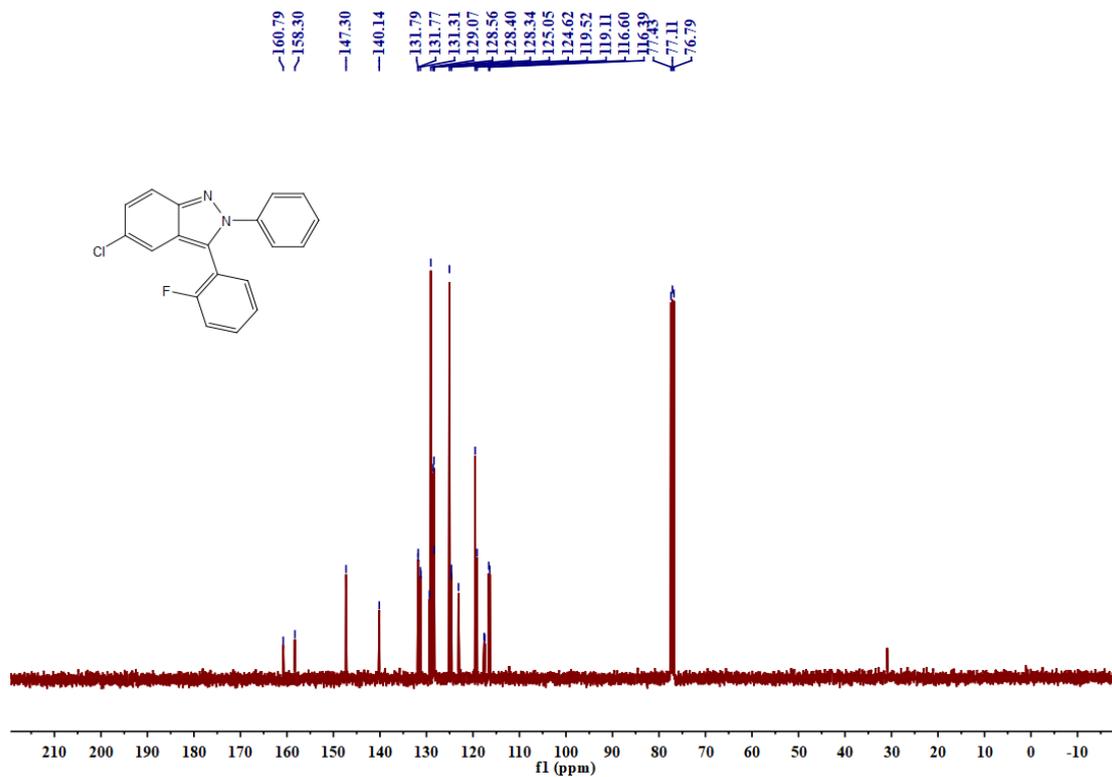
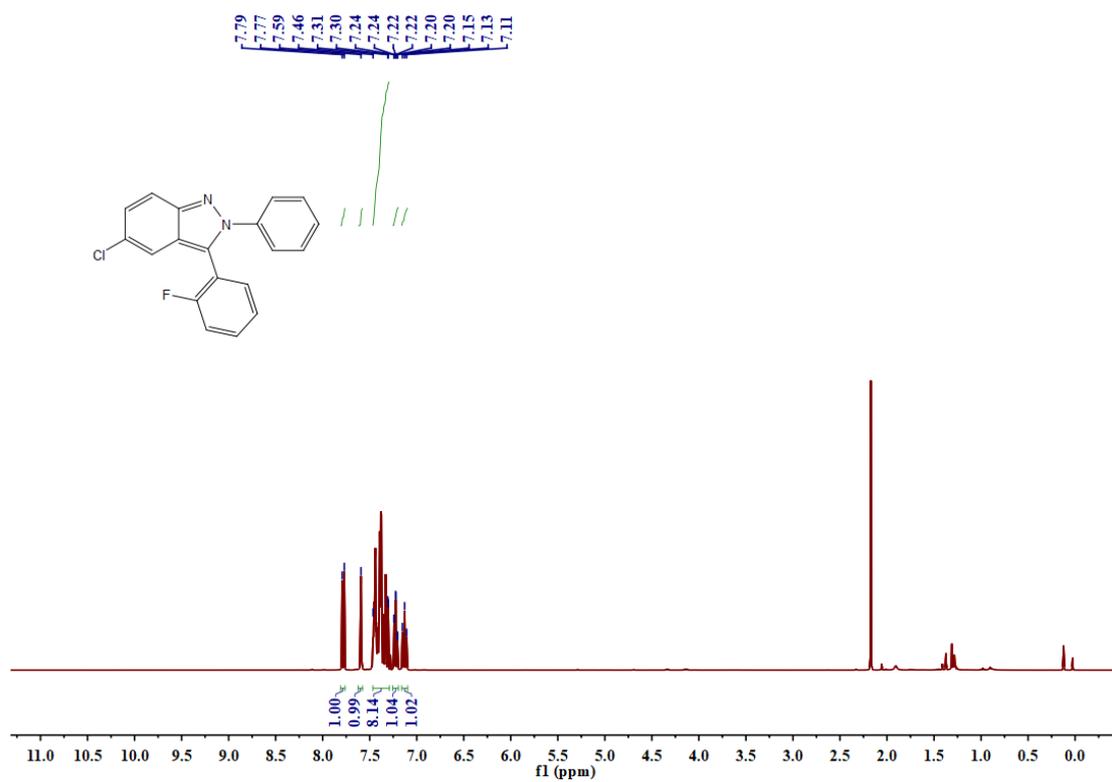
2H-Indazole 4k

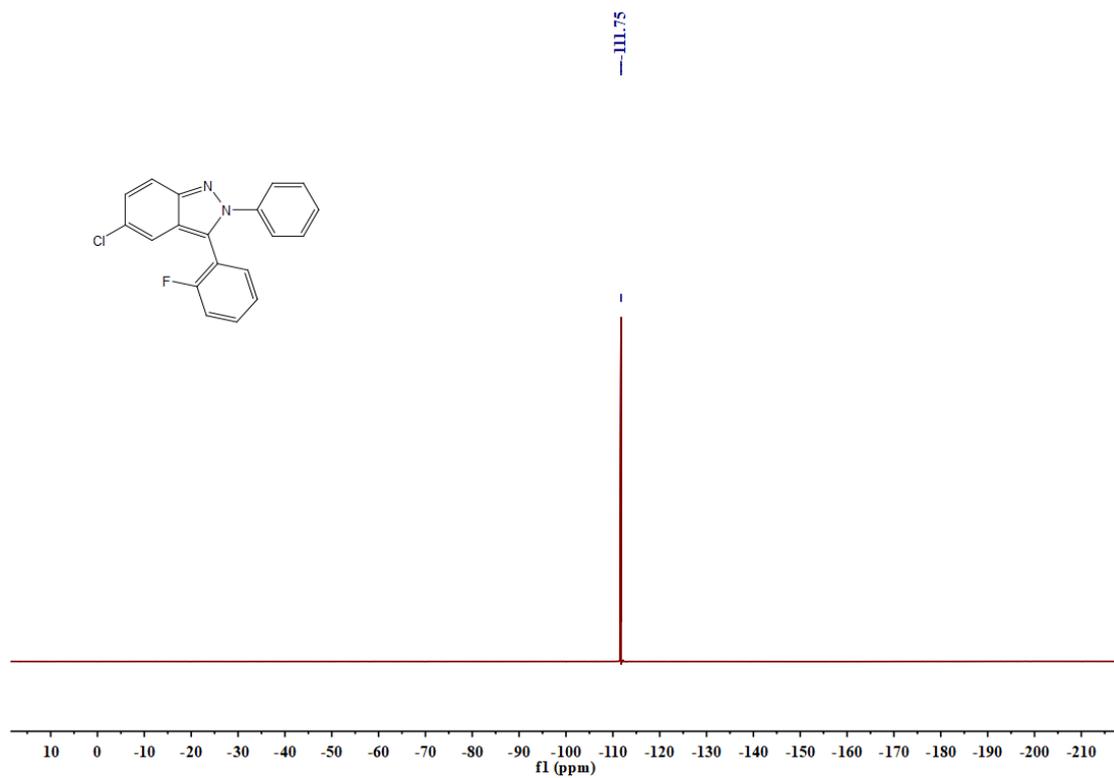


2H-Indazole 4l

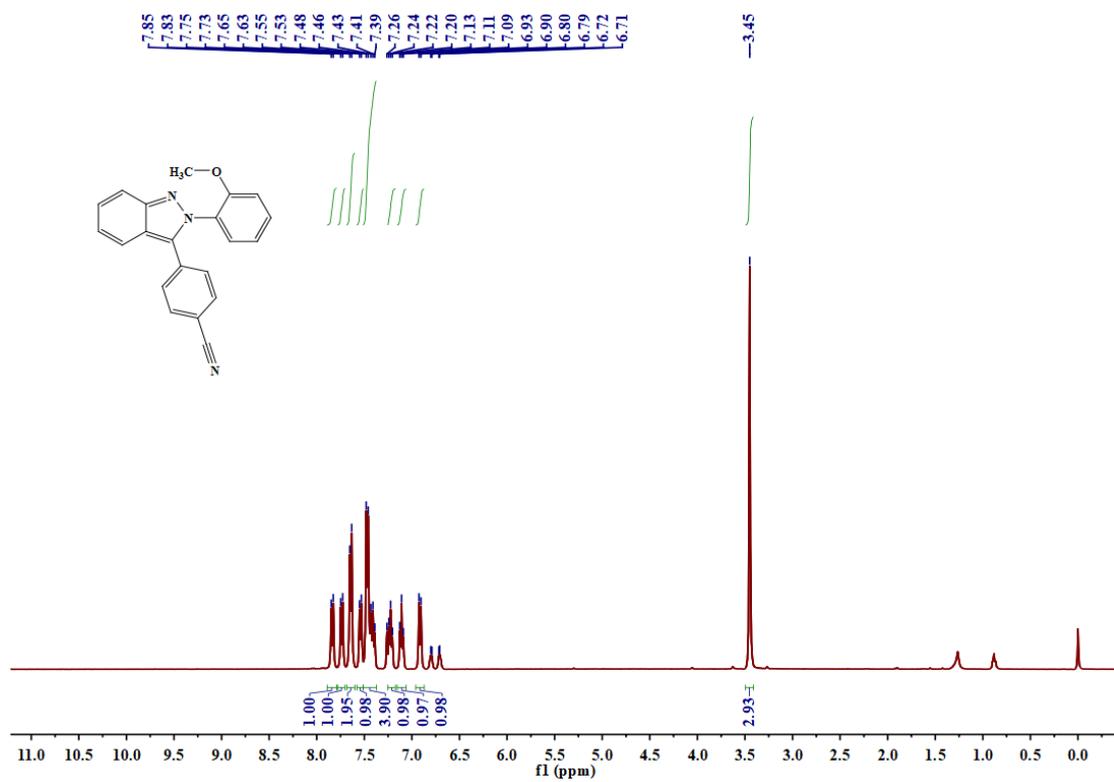


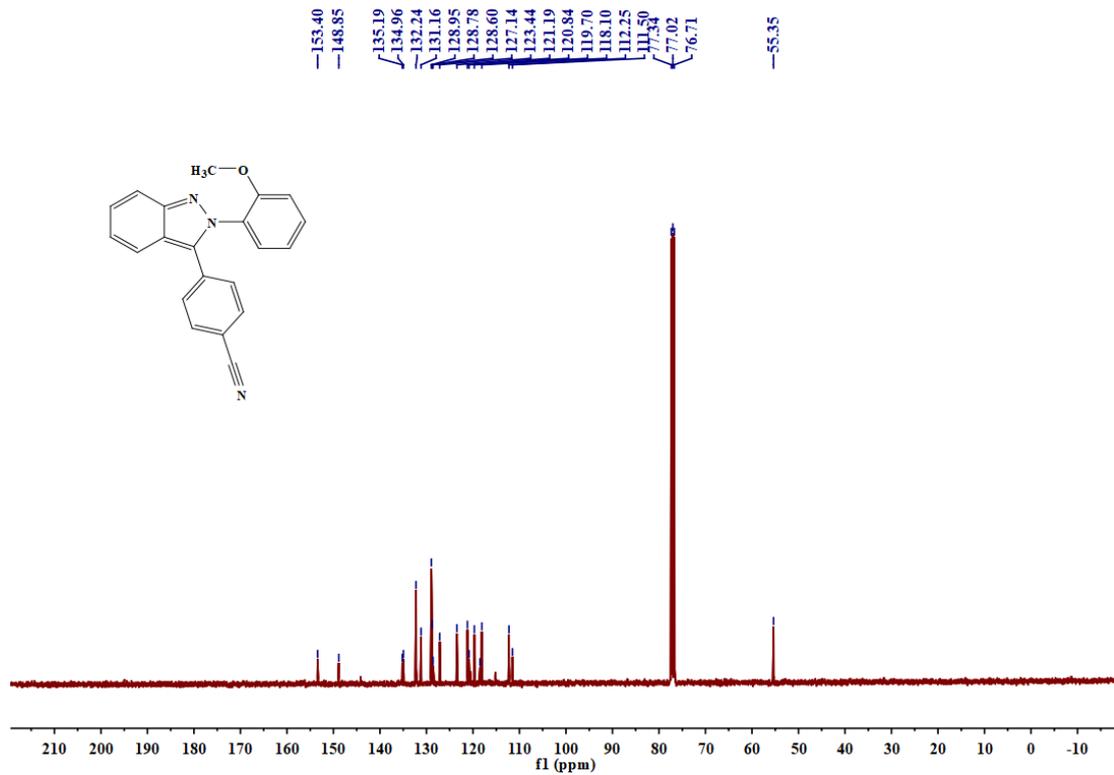
2H-Indazole 6a



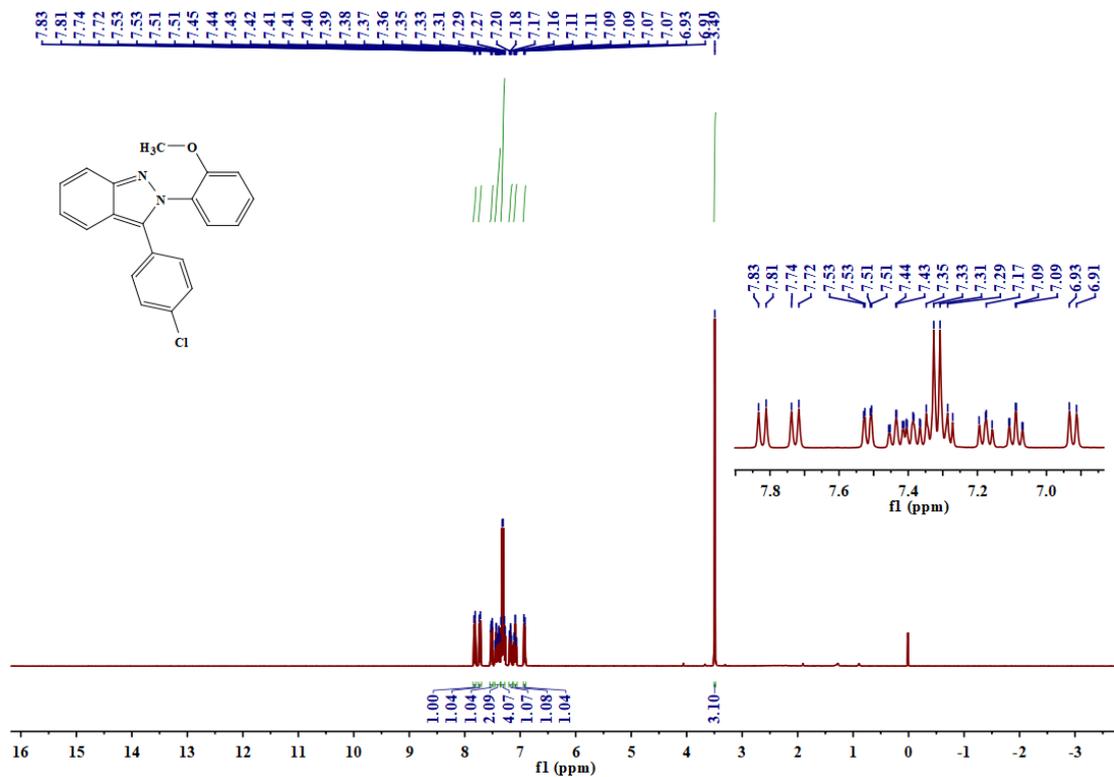


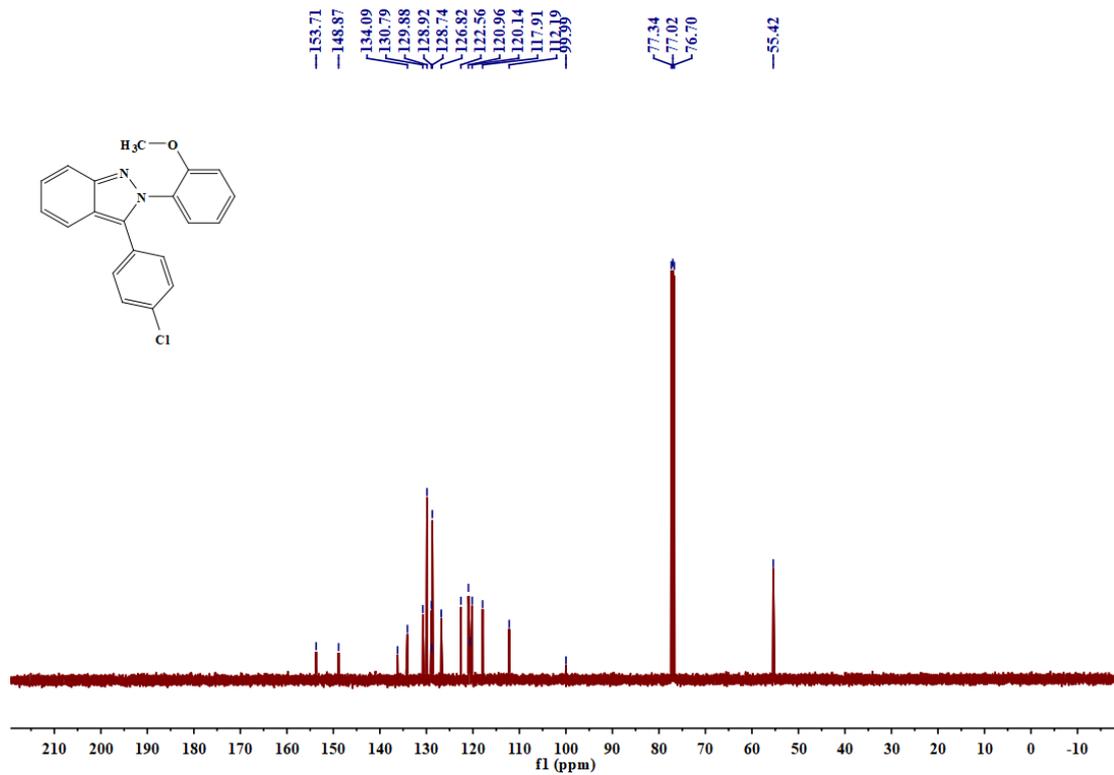
2H-Indazole 6b



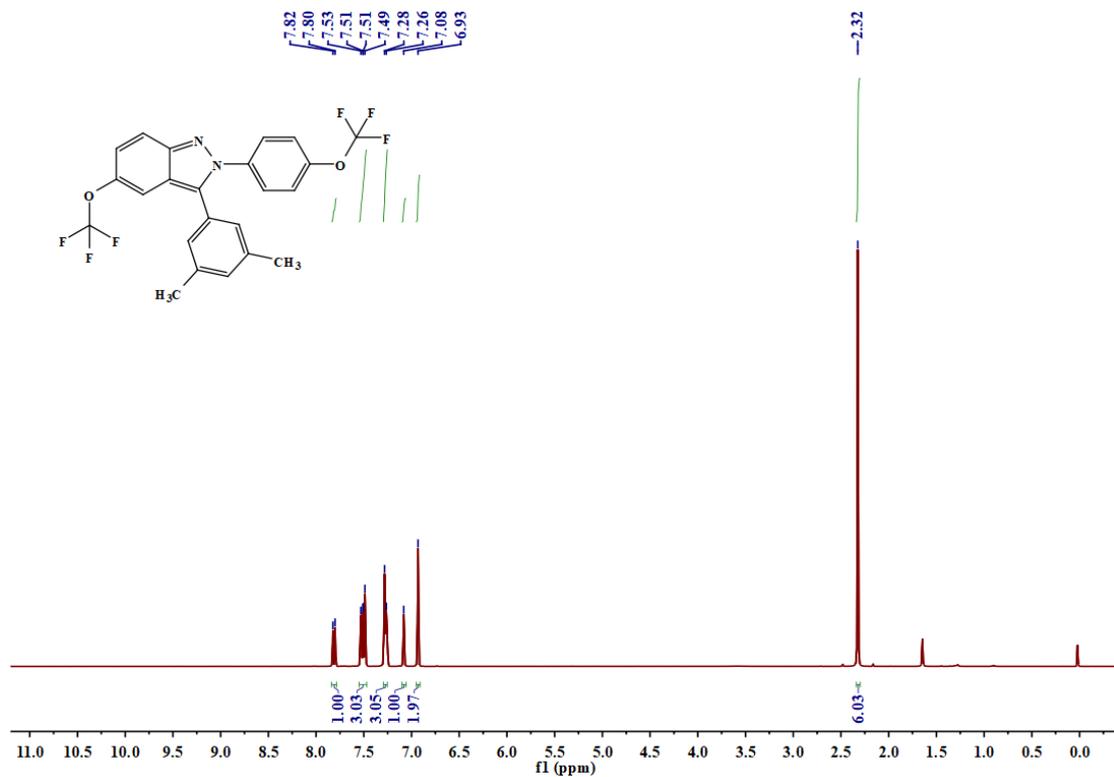


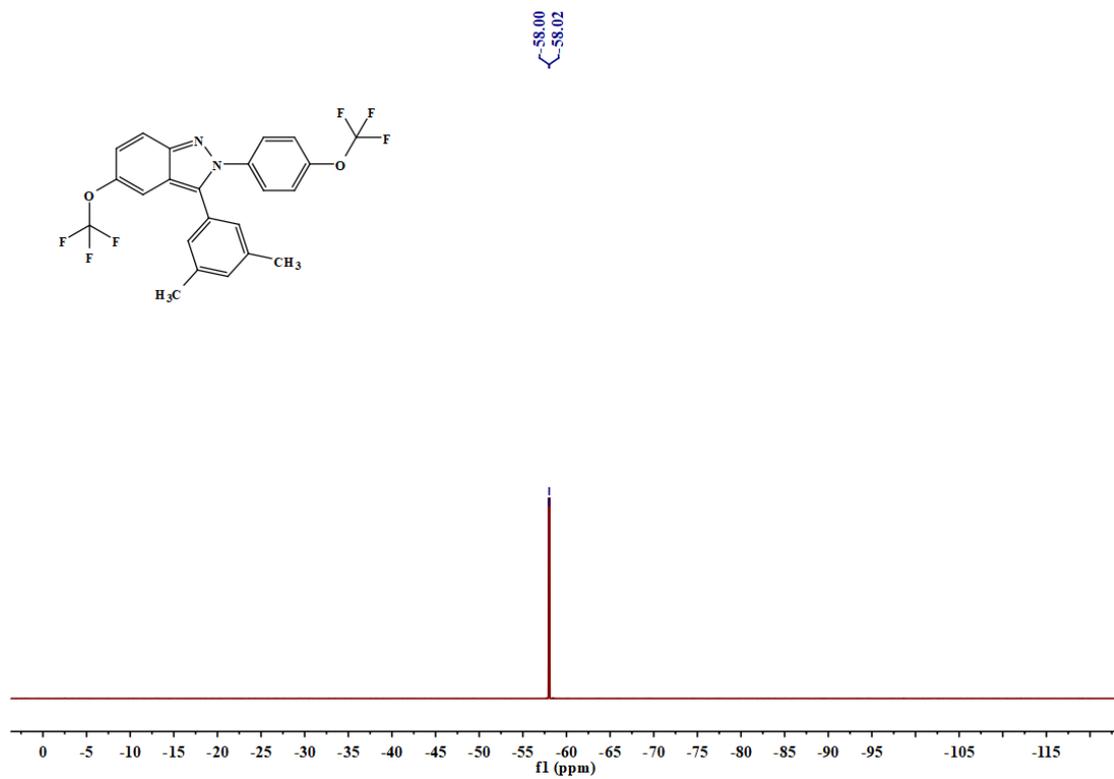
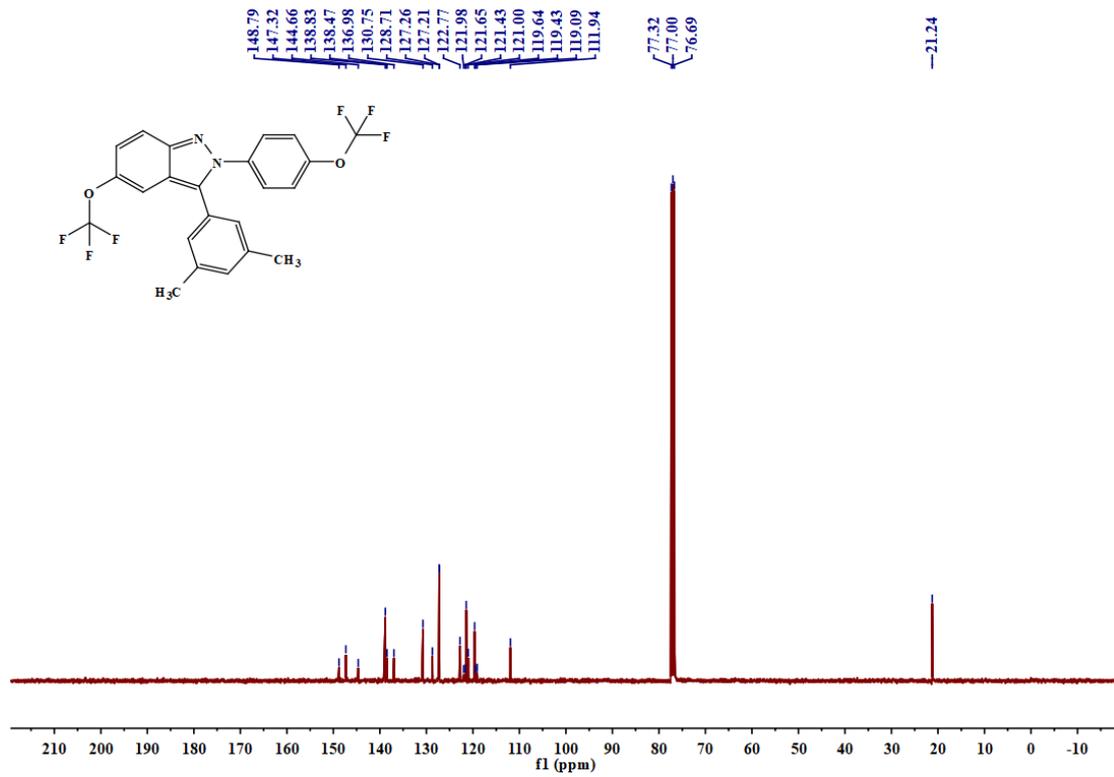
2H-Indazole 6c



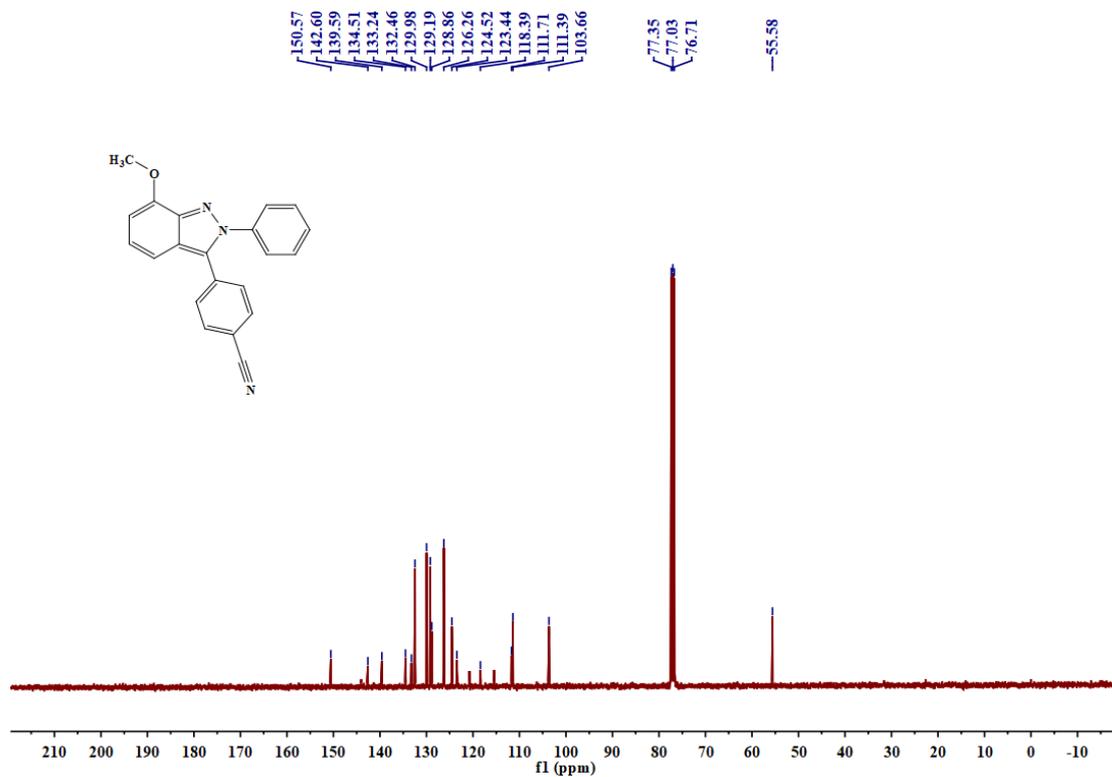
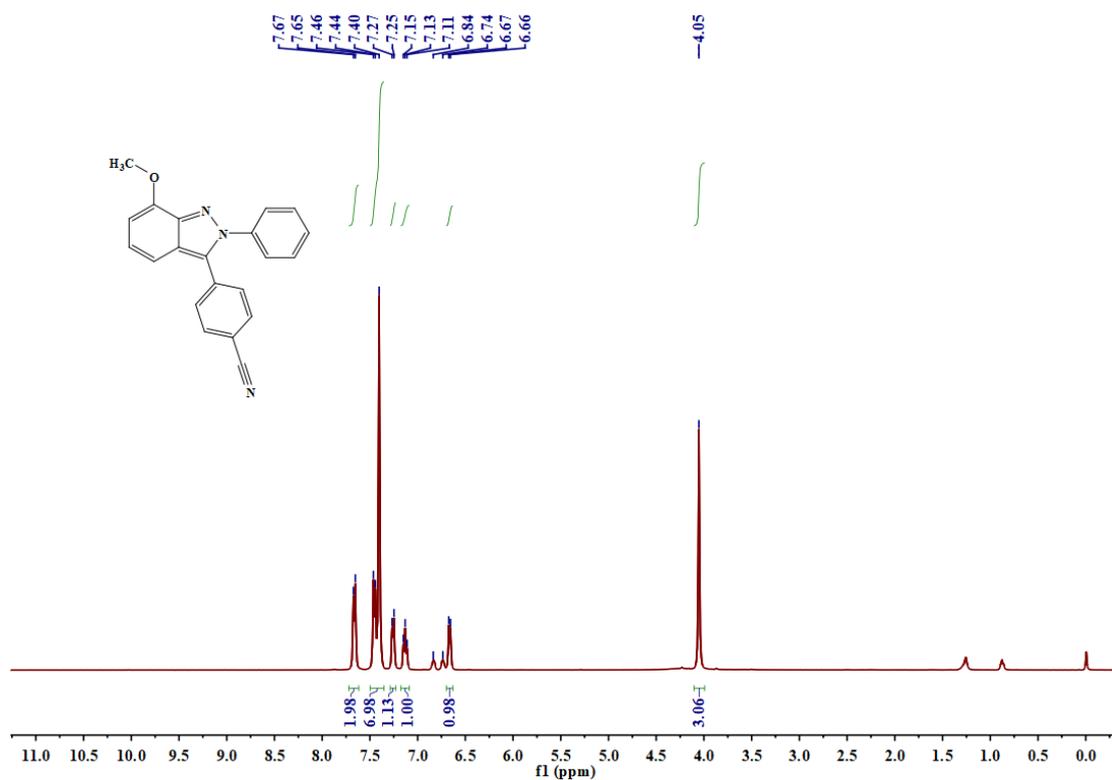


2H-Indazole 6d

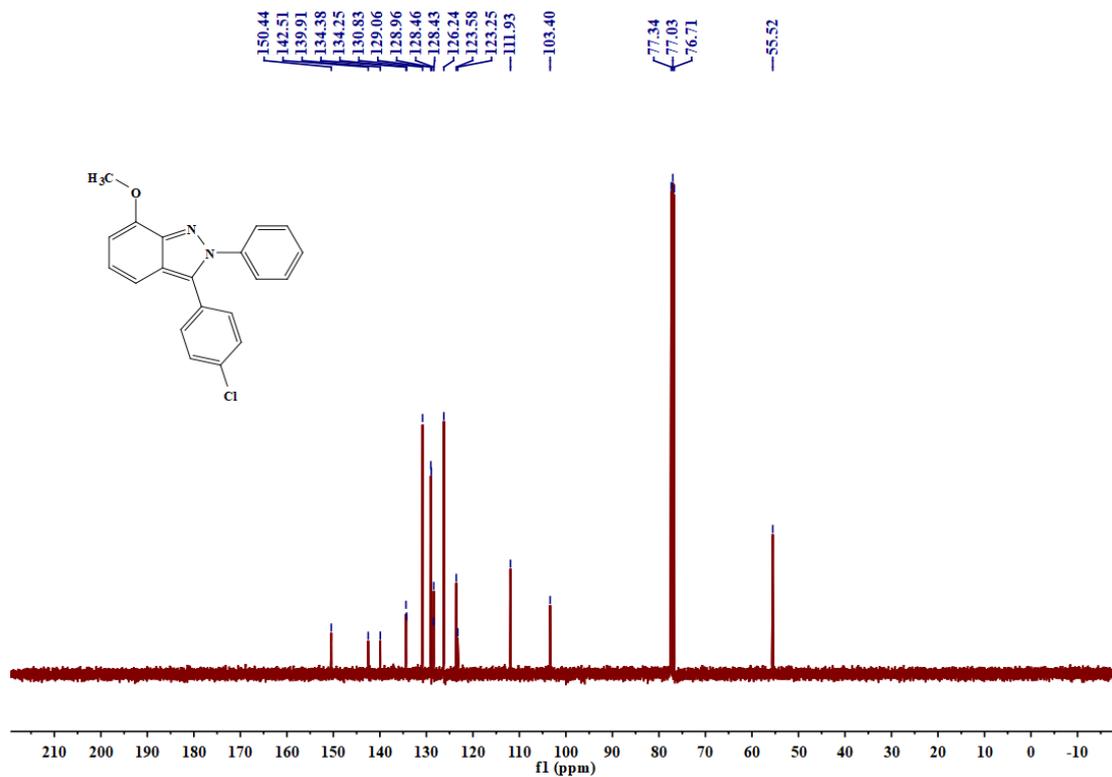
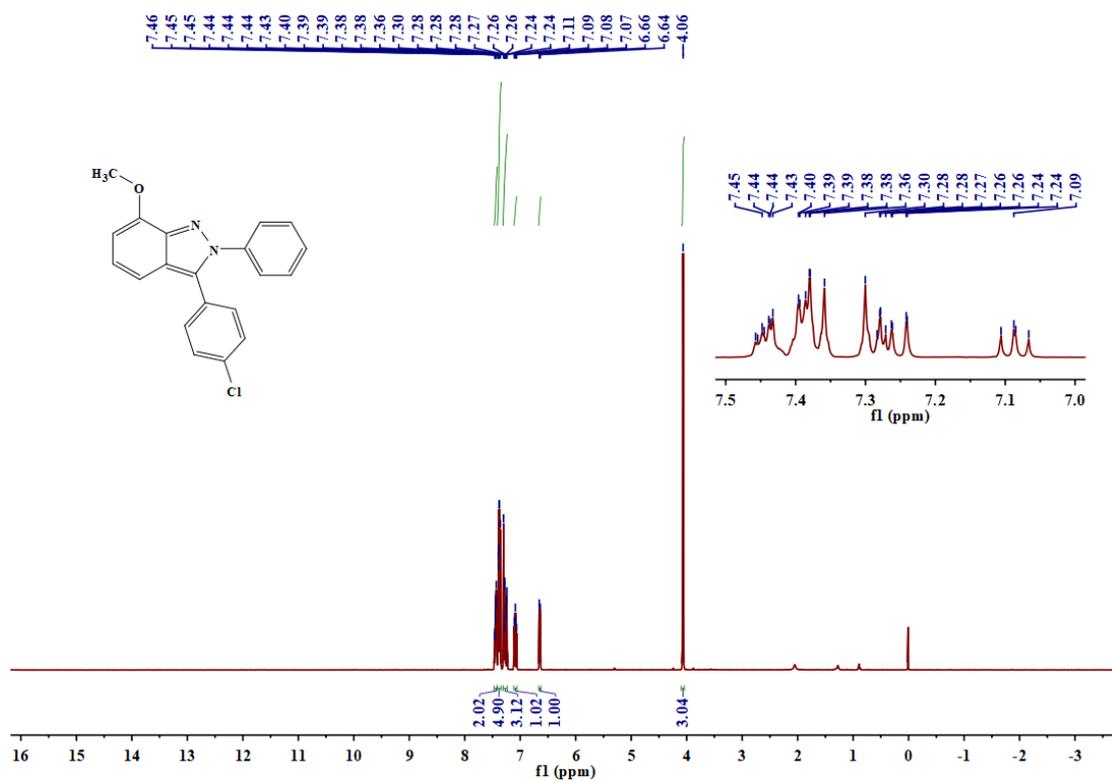




2H-Indazole 6e



2H-Indazole 6f



6. Reference

- [1] C. Zhang, N. Jiao, Copper-Catalyzed Aerobic Oxidative Dehydrogenative Coupling of Anilines Leading to Aromatic Azo Compounds Using Dioxygen as an Oxidant, *Angew. Chem. Int. Ed.* 2010, **49**, 6174-6177.
- [2] E. V. Brown, W. H. Kipp, Mechanism of the Base-Catalyzed Synthesis of Azobenzenes, *J. Org. Chem.* 1971, **36**, 170-173.
- [3] H. Li, P. Li, L. Wang, Direct Access to Acylated Azobenzenes via Pd-Catalyzed C-H Functionalization and Further Transformation into an Indazole Backbone, *Org. Lett.* 2013, **15**, 620-623.
- [4] P. Jessop, Editorial: Evidence of a significant advance in green chemistry. *Green Chem.* 2020, **22**, 13-15.
- [5] J. Martínez, J. F. Cortés, R. Miranda, Green Chemistry Metrics. A Review. *Processes* 2022, **10**, 1274.
- [6] R. A. Sheldon, The E Factor 25 Years on: the Rise of Green Chemistry and Sustainability. *Green Chem.* 2017, **19**, 18-43.
- [7] K. V. Aken, L. Streckowski, L. Patiny, EcoScale, A Semi-Quantitative Tool to Select an Organic Preparation Based on Economical and Ecological Parameters. *Beilstein J. Org. Chem.* 2006, **2**, 3.
- [8] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [9] Y. Zhao, D. G. Truhlar, The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Account.* 2008, **120**, 215-241.
- [10] A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* 2009, **113**, 6378-6396.