Supporting Information

I_2-mediated 2*H*-indazole synthesis *via* halogen-bond-assisted benzyl C-H functionalization

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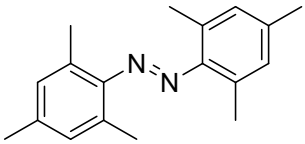
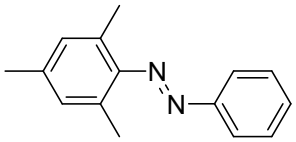
1. General Information

Chemicals used in this article were either purchased or synthesized according to reported procedures. Solvents such as toluene, CH_3CN, 1,2-dichloroethane (DCE) and $CHCl_3$ were dried over activated 4Å molecular sieves and used directly. Gas Chromatography-Mass Spectrometer (GC-MS) was used for reaction monitoring and product analysis. ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz NMR spectrometer to identify the structure of substrates and products. Chemical shifts (δ) were given in ppm, with solvent signal as reference. ^1H-NMR yields were obtained by adding trichloroethylene (9.00 μL, 0.080 mmol) to the crude product as the internal standard. All chemical yields are calculated based on azobenzenes **1**. Far infrared spectra was recorded on PerkinElmer FT-IR/ FIR spectrometer. Radical observation experiments were conducted on JEOL FA-200 EPR spectrometer.

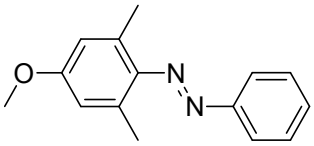
2. Specific synthetic procedures and characterization data of substrates



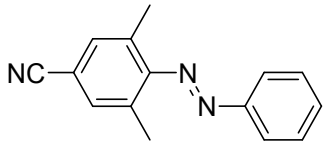
1,2-Dimesityldiazene **(1a):**[1, 2] Synthesized *via* homocoupling of 2,4,6-trimethylaniline: 5 mmol 2,4,6-trimethylaniline was dissolved in 20 mL toluene in a flask.[3] Then, 0.3 mmol CuBr (43.2 mg) and 0.9 mmol pyridine (75 μL) were added to the solution. The reaction mixture was vigoriously stirred and heated at 60 °C open in the air for 24 h. The product was separated by column chromatography (red crystal, 62% isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (s, 4H), 2.43 (s, 12H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 138.5, 131.8, 130.2, 21.2, 20.2.



1-Mesityl-2-phenyldiazene **(1b):** [1] Synthesized *via* GP1 (red oil, 57% isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.57 – 7.45 (m, 3H), 6.96 (d, J = 0.6 Hz, 2H), 2.39 (s, 6H), 2.34 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 149.0, 138.5, 131.5, 130.8, 130.1, 129.2, 122.6, 21.2, 19.3.

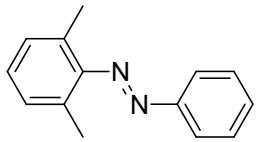


1-(4-Methoxy-2,6-dimethylphenyl)-2-phenyldiazene **(1c):** Synthesized *via* GP1 (red oil, 61% isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.55 – 7.48 (m, 2H), 7.48 – 7.41 (m, 1H), 6.68 (s, 2H), 3.85 (s, 3H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 153.3, 144.7, 134.9, 130.4, 129.1, 122.4, 114.6, 55.5, 20.4. GC-MS: 240; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 240.1263, found 240.1264.

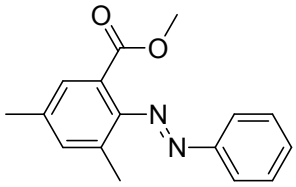


3,5-Dimethyl-4-(phenyldiazenyl)benzonitrile **(1d):** Synthesized *via* modified GP1 (100 °C, red crystal, 32%); M.p. 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.89 (m, 2H), 7.59 – 7.54 (m, 3H), 7.42 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):

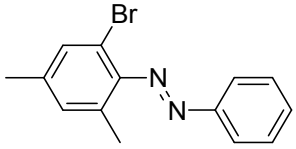
δ 155.0, 152.5, 132.7, 132.3, 131.2, 129.4, 122.9, 119.0, 111.1, 18.3. GC-MS: 235; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 235.1109, found 235.1111.



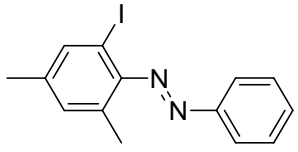
1-(2,6-Dimethylphenyl)-2-phenyldiazene **(1e):** [1] Synthesized via GP1 (orange oil, 48% isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.89 (m, 2H), 7.57 – 7.46 (m, 3H), 7.16 – 7.11 (m, 3H), 2.35 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 151.6, 131.2, 130.7, 129.2, 128.2, 122.6, 18.9.



Methyl 3,5-dimethyl-2-(phenyldiazenyl)benzoate **(1f):** Synthesized *via* modified GP1 (60 ^{o}C, red oil, 59 %);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.55 – 7.47 (m, 3H), 7.27 – 7.25 (m, 1H), 7.23 – 7.20 (m, 1H), 3.71 (s, 3H), 2.55 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 152.5, 148.3, 139.6, 136.2, 134.0, 131.4, 129.2, 127.8, 123.6, 123.0, 52.1, 21.2, 18.0. GC-MS: 268; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 268.1212, found 268.1215.

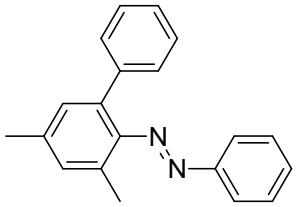


1-(2-Bromo-4,6-dimethylphenyl)-2-phenyldiazene **(1g):** Synthesized *via* modified GP1 (60 ^{o}C, red oil, 48%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.92 (m, 2H), 7.59 – 7.51 (m, 3H), 7.39 (s, 1H), 7.03 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 148.1, 139.3, 131.8, 131.6, 131.1, 130.8, 129.3, 122.9, 118.3, 20.9, 19.3. GC-MS: 288; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 288.0262, found 288.0261.

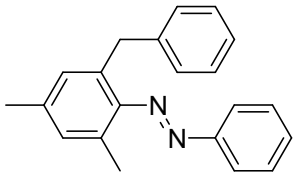


1-(2-Iodo-4,6-dimethylphenyl)-2-phenyldiazene **(1h):** Synthesized via modified GP1 (60 ^{o}C, red oil, 74 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.94 (m, 2H), 7.70 – 7.68

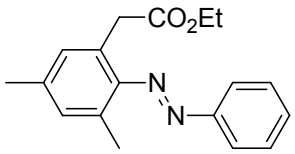
(m, 1H), 7.58 – 7.50 (m, 3H), 7.06 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 149.6, 139.8, 138.1, 133.1, 131.6, 129.9, 129.3, 123.1, 95.0, 20.7, 19.5. GC-MS: 336; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 336.0123, found 336.0125.



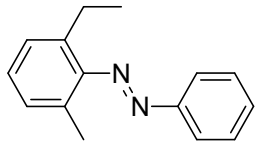
1-(3,5-Dimethyl-[1,1'-biphenyl]-2-yl)-2-phenyldiazene **(1i):** Synthesized *via* coupling of **1eq** with phenylboronic acid : A seal tube were charged with 0.6 mmol azobenzene, 0.7 mmol phenylboronic acid, 6 mmol Na_2CO_3, 0.03 mmol $Pd(PPh_3)_4$, 9 mL THF and 3 mL H_2O. The vessel was heated at 80 ^oC for 24 h. The product was separated by column chromatography (red oil, 80% isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.65 (m, 2H), 7.49 – 7.44 (m, 3H), 7.37 – 7.29 (m, 5H), 7.19 (s, 1H), 7.16 (s, 1H), 2.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 148.5, 140.1, 138.2, 136.8, 131.8, 130.8, 130.5, 129.6, 129.6, 129.1, 127.7, 126.7, 122.6, 21.3, 19.5. GC-MS: 286; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 286.1470, found 286.1473.



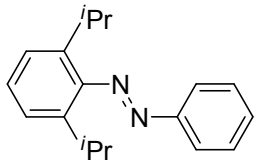
1-(2-Benzyl-4,6-dimethylphenyl)-2-phenyldiazene **(1j):** Synthesized *via* coupling of **1g** with benzylmagnesium chloride[3]: A seal tube were charged with 0.05 mmol $Pd(PPh_3)_2Cl_2$ and 1.5 mL THF under N_2 atmosphere. Then, 100 µL DIBAL solution ($(i\text{-}Bn)_2AlH$ in hexane, 1M) was added to the reaction which was latter stirred for 5 min at room temperature till the mixture turned deep brown. 0.5 mmol **1g** and 0.55 mL benzylmagnesium chloride (1.4 M in THF) were in turn added to the reaction solution which was subsequently stirred for 6 h at room temperature. The product was separated by column chromatography (yellow oil, 40% isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.78 (m, 2H), 7.54 – 7.44 (m, 3H), 7.24 – 7.12 (m, 5H), 6.99 (s, 1H), 6.96 (s, 1H), 4.19 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 148.7, 141.5, 138.7, 135.7, 131.0, 130.9, 130.2, 129.7, 129.1, 129.0, 128.4, 125.9, 122.6, 37.9, 21.3, 19.8. GC-MS: 300; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2$+H^+ 300.1626, found 300.1624.



Ethyl 2-(3,5-dimethyl-2-(phenyldiazenyl)phenyl)acetate **(1k):** Synthesized *via* coupling of **1g** with (2-ethoxy-2-oxoethyl)zinc(II) bromide[4]: 0.55 mmol ethyl bromoacetate (61μL) reacted with 0.75 mmol Zn (49 mg) in 1mL THF under N_2 atmosphere in schlenk tube A at room temperature for 10 min. A second schlenk tube (B) was charged with 5.8 mg $Pd(dba)_2$ and 26 μL $P(^tBu)_3$ solution (10% in hexane), 0.5 mmol **1g** (140 mg) and 2 mL THF under N_2 atmosphere, and the mixture was stirred for 5 min. The solution in tube B was transferred into tube A. The reaction was heated at 66 ^oC for 12 h. The product was separated by column chromatography. (orange solid, 21% isolated yield); M.p. 57-59 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.1, 1.1 Hz, 2H), 7.54 – 7.41 (m, 3H), 7.08 (s, 1H), 6.97 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.79 (s, 2H), 2.53 (s, 3H), 2.37 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 153.1, 147.5, 139.8, 134.4, 132.0, 131.0, 130.8, 129.1, 128.0, 122.6, 60.8, 40.1, 21.4, 19.7, 14.3. GC-MS: 296; HRMS (ESI positive mode) calcd for $C_{18}H_{18}N_2O_2+H^+$ 296.1525, found 296.1525.



1-(2-Ethyl-6-methylphenyl)-2-phenyldiazene **(1l):**[1] Synthesized *via* GP1 (orange oil, 65% isolated yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.90 (m, 2H), 7.58 – 7.49 (m, 3H), 7.23 – 7.12 (m, 3H), 2.75 (q, J = 7.5 Hz, 2H), 2.33 (s, 3H), 1.19 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 151.4, 137.6, 131.2, 129.5, 129.3, 129.3, 128.3, 127.6, 122.7, 25.2, 19.1, 15.8.



1-(2,6-Diisopropylphenyl)-2-phenyldiazene **(1o):**[1] Synthesized via GP1 (orange oil, 33% isolated yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.90 (m, 2H), 7.59 – 7.52 (m, 3H), 7.31 – 7.24 (m, 3H), 3.06 (hept, J = 6.9 Hz, 2H), 1.20 (d, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 151.3, 139.5, 131.4, 129.3, 127.9, 123.7, 122.8, 27.9, 23.7.

3. Mechanistic investigations

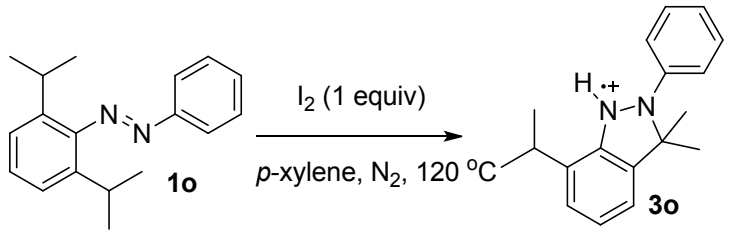
3.1. Characterization of halogen bond by far infrared spectroscopy[5]

Solution A (0.1 mol/L of **1c** in cyclohexane) and solution B (0.1 mol/L of **1c** and 0.1 mol/L of I_2 in cyclohexane) was respectively prepared. The sample solution was filled in a polyethylene cell (optic path: 4 mm) for measurement. The far infrared spectra (400 cm^{-1} ~ 100 cm^{-1}) were recorded on PerkinElmer FT-IR/ FIR spectrometer for both solution A and B.

3.2. ^{1}H-NMR characterization of halogen bond

Solution C (0.05 mol/L **1b** in $CDCl_3$) and solution D (0.05 mol/L **1b** and 0.05 mol/L I_2 in $CDCl_3$) was respectively prepared. ^{1}H-NMR spectra were recorded for both solution.

3.3. EPR monitoring of reaction and signal simulation



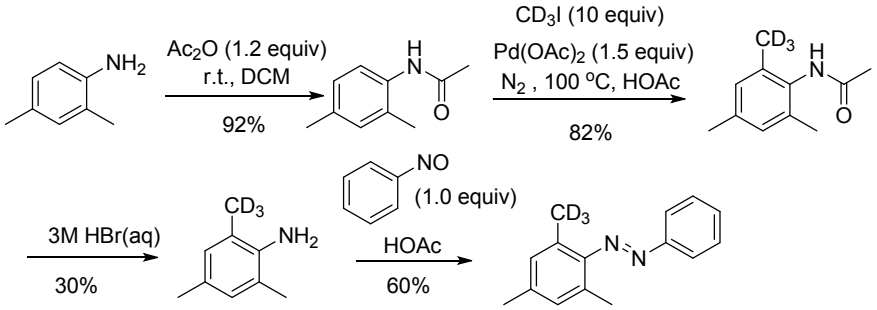
(S1)

0.05 mmol of **1o** (13.3 mg) and 0.05 mmol of I_2 (12.7 mg) were dissolved in 1 mL of *p*-xylene in a EPR tube under N_2 atmosphere. The sample tube was placed in the detecting chamber of JEOL FA-200 EPR spectrometer (9.45 GHz) and then heated to 120 °C. The EPR signal was collected every 2 minutes.

The obtained signal at 18 min was simulated using JEOL IsoSimu (Version 2.2.0) mainly considering the coupling of the two N (nuclear spin= 1) and one H (nuclear spin= 1/2) with the single electron. When the parameters were properly adjusted: signal center= 324.72 mT, A_{iso}(N1)= 0.63 mT, A_{iso}(N2)= 0.52 mT, A_{iso}(H)= 0.395 mT, line width= 0.46 mT, the experimental singnal could be well simulated.

3.4. Determination of KIE value

1b-d_3 was synthesized following the procedure in Scheme S1.[6]



Scheme S1 Synthetic procedure for **1b**-d_3.

1b-d_3 reacted with I_2 according to GP2, and the ^{1}H-NMR of the product is displayed in Figure S3.

S(δ=2.410): S(δ=2.671) = **2b**-d_1 : (**2b**-d_1+ **2b**-d_3)=0.10: 1.00;

Thus, **2b**-d_3 /**2b**-d_1 =(1.00-0.10)/0.10= 9.0;

KIE= k(**2b**-d_3)/k(**2b**-d_1)= **2b**-d_3 /**2b**-d_1= 9.0.

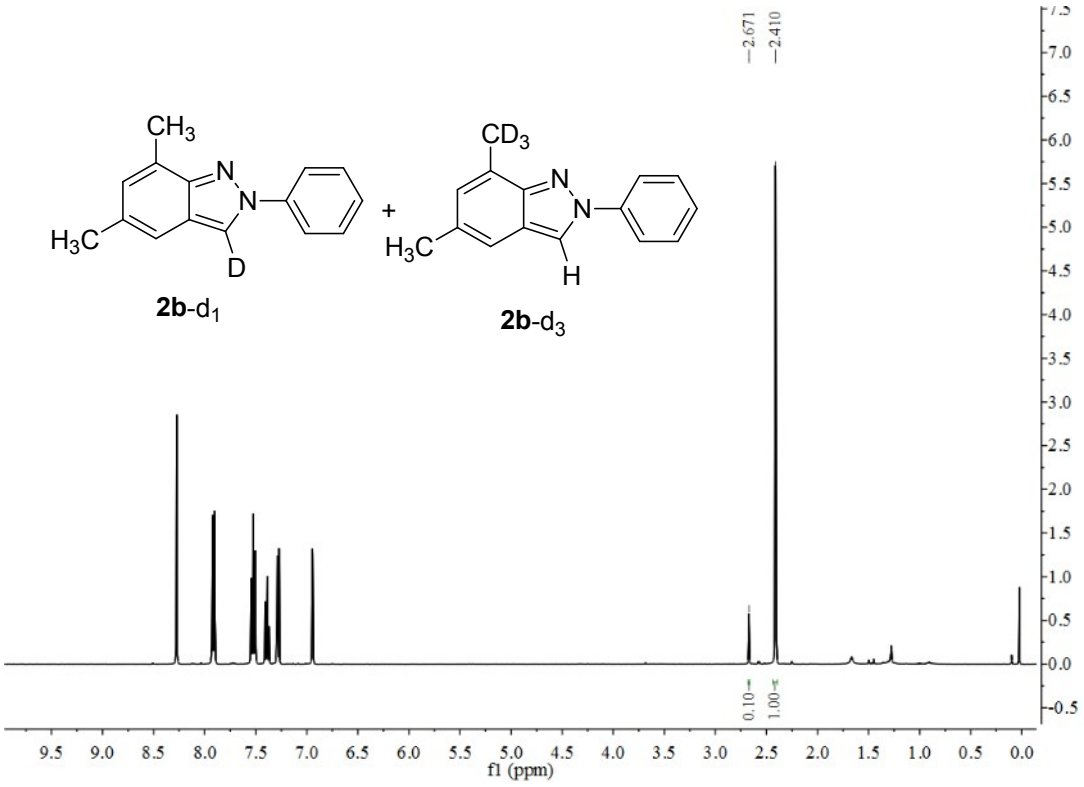


Figure S1 ^{1}H-NMR of the products from **1b**-d_3

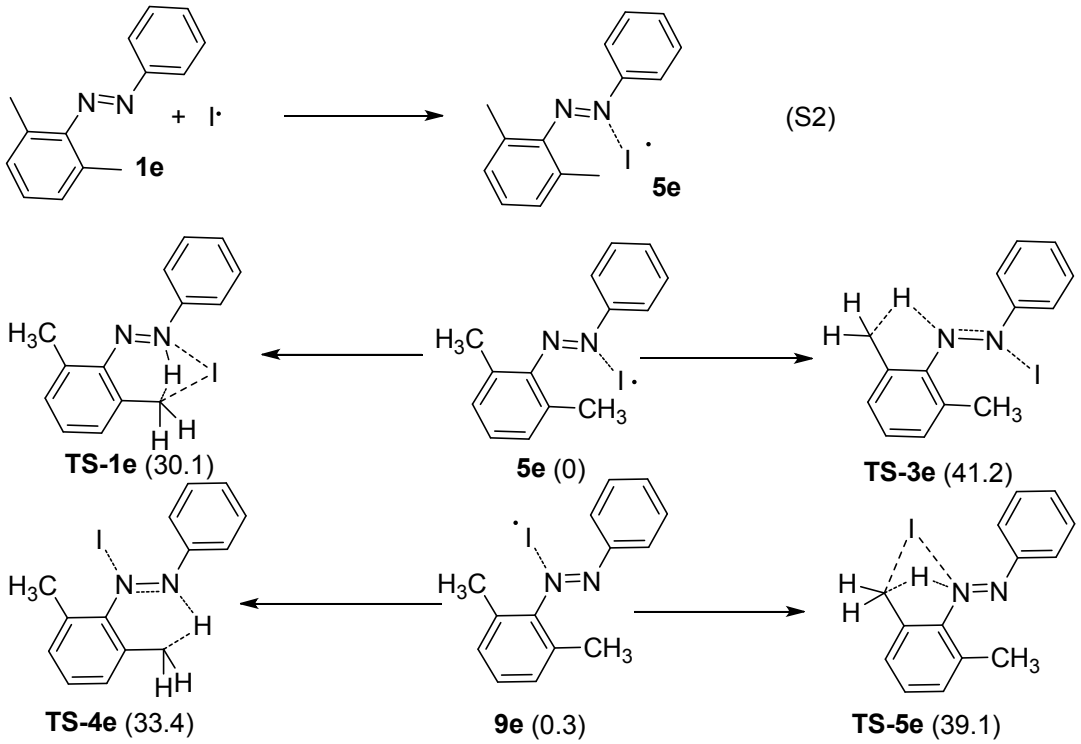
3.5. DFT calculation of mechanism

DFT calculations were performed with Gaussian 09 program using M06-2X functional.[7] The SDD basis set was used for iodine and the 6-31+g(d) basis set for the other atoms (keyword 5D was used in the calculations) during the geometry

optimization. The vibrational frequencies were calculated using the same basis set to obtain the thermal correction to Gibbs Free Energy. The single-point energies and solvent effects in DCE were calculated using 6-311+g(d,p)[SDD for I] based on the corresponding optimized structures. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the CPCM approach, where UFF radii were used to define the atomic radii.

The combination of iodine radical to azo group is thermodynamically favored with a $\Delta_r G_{sol}$= -4.7 kcal/mol (eq. S2). The N-I distance is 2.76 Å and the Mulliken spin density for I is 0.78 in the optimized structure. Both parameters are consistent with the chemical structure of **5e** shown in eq. S2.

The transition states of hydrogen abstraction for four possible cases (Scheme S2) were calculated. All these transition states involve the transfer of hydrogen to nitrogen. Among them, transformation from **5e** to **TS-1do** represents the lowest energy barrier, and thus well corroborate the mechanism in Scheme 2.



Scheme S2 Transition states calculation for four possible hydrogen abstraction process in the reaction of **1e**. The Gibbs free energies in solution ($\Delta G_{sol,}$ in kcal/mol) are given in parentheses.

4. Coordinates and Energies of Stationary Point

I_2

G_{sol} = -22.756315 Hartree

I 0.00000000 0.00000000 1.40937700 I 0.00000000 0.00000000 -1.40937700

I·

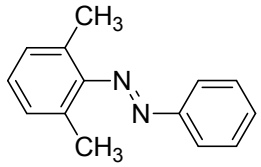
G_{sol} = -11.356971 Hartree

HI

G_{sol} = -11.975611 Hartree

I 0.00000000 0.00000000 0.03033900

H 0.00000000 0.00000000 -1.60795200



1e

G_{sol} = -651.067553 Hartree

C 3.72702300 1.05445200 -0.22861600

C 2.34789100 1.22473100 -0.13579500

C 1.53365300 0.08922100 0.05132300

C 2.08809900 -1.20120500 0.19294300

C 3.47890900 -1.31705800 0.11638500

C 4.29348900 -0.21138600 -0.10419400

H 4.36018700 1.92282400 -0.39126100

H 3.92673900 -2.30017500 0.23791000

H 5.37090900 -0.33515400 -0.16550300

C 1.27498700 -2.44154400 0.46854000

H 0.50066400 -2.25960900 1.21958300

H 0.76008800 -2.79078900 -0.43013600

H 1.93276900 -3.23770000 0.82926700

C 1.73662100 2.59800700 -0.25801900

H 1.08575800 2.66957800 -1.13505600

H 1.12035800 2.83304400 0.61484600

H 2.52046000 3.35465700 -0.34923500

N 0.14843400 0.38571900 0.15007400

N -0.62966100 -0.50955500 -0.22730000

C -2.01285200 -0.18028900 -0.09424000

C -2.90312700 -1.11663000 -0.62093800

C -2.48985700 0.98451700 0.51860600

C -4.27591500 -0.89015500 -0.54745000

H -2.49916300 -2.01143300 -1.08564300

C -3.86004400 1.20284000 0.59064900

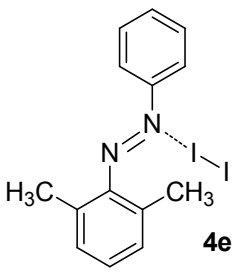
H -1.78091200 1.69661200 0.92718500

C -4.75518700 0.26935200 0.05817300

H -4.96898700 -1.61698200 -0.95993000

H -4.23785100 2.10417600 1.06456200

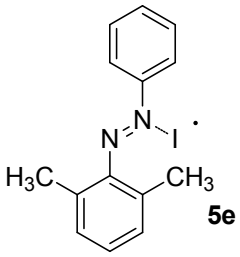
H -5.82456200 0.44869600 0.11979600



4e

G_{sol} = -673.828496 Hartree

C	-0.40688700	4.05174300	-0.92522700
C	-1.24079600	2.94776400	-1.09139000
C	-1.51380100	2.15648900	0.03372100
C	-1.03047100	2.46447100	1.31581000
C	-0.22332000	3.59681000	1.43765500
C	0.10092400	4.37561300	0.33040100
H	-0.15831400	4.66231600	-1.78921400
H	0.15765900	3.86551400	2.41951700
H	0.74241700	5.24386600	0.44832400
C	-1.38328300	1.64824600	2.53582400
H	-2.43177700	1.33461700	2.52519300
H	-0.77069300	0.74318300	2.60460700
H	-1.21248700	2.23880800	3.43973000
C	-1.79119600	2.56682700	-2.44060100
H	-1.33742500	1.63753600	-2.80369200
H	-2.87296500	2.40323700	-2.39183000
H	-1.58975100	3.35093800	-3.17461800
N	-2.38237700	1.04215300	-0.16711600
N	-1.91221200	-0.04935700	0.17823900
C	-2.77233500	-1.18245800	0.03933800
C	-2.37321300	-2.34188300	0.70237200
C	-3.95278700	-1.15111300	-0.71048900
C	-3.16925000	-3.48272000	0.62834900
H	-1.45082400	-2.33600300	1.27556700
C	-4.73158800	-2.29837600	-0.78985100
H	-4.23726200	-0.23676400	-1.22017300
C	-4.34490200	-3.46241600	-0.11875900
H	-2.86781700	-4.38563100	1.14976000
H	-5.64434600	-2.28909400	-1.37761000
H	-4.96126800	-4.35407100	-0.18302500
I	0.78524900	-0.47673600	0.09868400
I	3.58634400	-0.99801900	-0.22478500

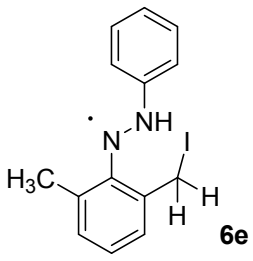


5e

G_{sol} = -662.431947 Hartree

C	3.66666600	1.40782500	-0.71696600
C	2.29297300	1.62129100	-0.79825900
C	1.48872500	1.14827100	0.25136300
C	2.01947300	0.52347600	1.39334000
C	3.40533000	0.35782200	1.44066500
C	4.22146400	0.77941900	0.39565200
H	4.30441300	1.74171300	-1.53100900
H	3.84603200	-0.11220600	2.31596100
H	5.29536600	0.62851400	0.45376500
C	1.16894600	0.07801000	2.55674500
H	0.35388200	0.77961300	2.75879000
H	0.71931600	-0.90122000	2.36442900

H	1.78462500	0.00060000	3.45695700
C	1.66817700	2.28864800	-1.99543300
H	1.03524600	1.58779700	-2.55092800
H	1.03483000	3.12873300	-1.69164700
H	2.44017400	2.66125900	-2.67333500
N	0.09758500	1.41026200	0.12227000
N	-0.66039800	0.45838300	0.32404900
C	-2.06432200	0.70723000	0.23548300
C	-2.90165300	-0.31184800	0.68532400
C	-2.58590800	1.90316900	-0.26858200
C	-4.28206000	-0.13149600	0.64093900
H	-2.46084200	-1.23106900	1.05915700
C	-3.96428200	2.06775700	-0.31760500
H	-1.90870300	2.67652300	-0.61495200
C	-4.81294100	1.05466800	0.13823400
H	-4.94052400	-0.91951600	0.99224200
H	-4.38174800	2.98818700	-0.71425200
H	-5.88929300	1.19196700	0.09571100
I	0.12798900	-2.04277100	-0.54133100

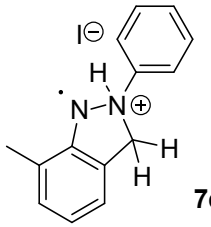


6e

G_{sol} = -662.435388 Hartree

C	2.98399400	2.93403000	-0.32942200
C	1.60046500	2.86999700	-0.25802800
C	0.97543000	1.65374600	0.13431300
C	1.78393400	0.55198200	0.52975600
C	3.17803300	0.66684700	0.43638900
C	3.78263700	1.83335200	-0.00109300
H	3.44987200	3.86165600	-0.65277800
H	3.78749600	-0.18416600	0.73348400
H	4.86393200	1.90018300	-0.06630500
C	1.24793200	-0.66584300	1.19437100
H	0.25517600	-0.54734200	1.62224300
H	1.93912100	-1.04506000	1.94421200
C	0.74894900	4.05719000	-0.62020800
H	0.10918100	3.83665800	-1.48063900
H	0.08258200	4.32576800	0.20564600
H	1.37650700	4.91892500	-0.86231700
N	-0.40819100	1.69996600	0.14967200
N	-1.02761600	0.56099800	-0.11310200
C	-2.41772400	0.45615500	-0.04445900
C	-3.01573300	-0.74816000	-0.43741700
C	-3.20088200	1.51983700	0.41744800
C	-4.39727100	-0.88269000	-0.37029800
H	-2.39529400	-1.57042300	-0.78681300
C	-4.58256500	1.36688200	0.47444300
H	-2.71771400	2.44200800	0.71845100

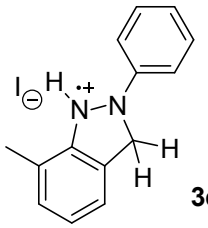
C	-5.18943600	0.17255100	0.08444800
H	-4.85650800	-1.81816200	-0.67570400
H	-5.19195300	2.19335800	0.82836200
H	-6.26816300	0.06414900	0.13479400
H	-0.52408200	-0.20801400	-0.55763000
I	1.04064000	-2.42852000	-0.16268800



7e

G_{sol} = -662.446408 Hartree

C	1.65160000	-1.16743600	0.14893600
C	1.60287600	-0.73307200	-1.20126600
C	2.75450000	-0.59715800	-1.94427000
C	3.97040400	-0.90756700	-1.31872400
C	4.02024900	-1.34823600	0.01392400
C	2.87645900	-1.49369500	0.78669000
H	2.73065800	-0.25867400	-2.97509500
H	4.89710400	-0.80252100	-1.87412500
H	4.98641400	-1.56808800	0.46029400
C	-1.82254900	-1.07298400	-0.08627800
C	-2.81829400	-0.22773300	-0.56722600
C	-2.10608100	-2.33555200	0.41908300
C	-4.13711700	-0.67529700	-0.55204400
H	-2.56593500	0.76881300	-0.92118200
C	-3.43163300	-2.76626700	0.42997600
H	-1.30557600	-2.95578100	0.80647900
C	-4.44485800	-1.94136000	-0.05557700
H	-4.92480200	-0.02431800	-0.91762900
H	-3.66992200	-3.74903700	0.82477000
H	-5.47542600	-2.28230400	-0.04143600
C	0.15696700	-0.55895900	-1.53737700
C	2.89115100	-1.92494500	2.22191200
H	2.25896000	-2.80649700	2.37177800
N	-0.44629200	-0.59388100	-0.15275500
N	0.44617800	-1.23420400	0.74673800
H	2.48907500	-1.13207500	2.86152200
H	3.90689400	-2.16036000	2.54807800
H	-0.09941800	0.39576100	-2.00506300
H	-0.43421400	0.52131900	0.15316000
H	-0.25511400	-1.39759900	-2.10912700
I	-0.17962100	2.58018000	0.30402200

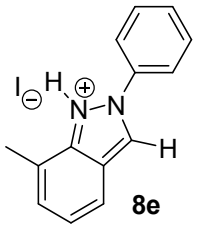


3e

G_{sol} = -662.466554 Hartree

C	1.81379600	-0.74327700	0.35532400
C	1.91036600	-1.91105000	-0.39953900
C	3.14912100	-2.39443400	-0.78773800
C	4.27710200	-1.66884200	-0.39623000
C	4.15716300	-0.49716200	0.35758600

C	2.91839200	0.00862800	0.75947000
H	3.24491700	-3.30083600	-1.37778500
H	5.26404100	-2.01913500	-0.68139600
H	5.05507600	0.04306200	0.64563900
H	0.10883900	0.56102400	0.44999100
C	-1.66401300	-1.43440300	0.21531700
C	-2.41955000	-2.34875000	-0.53506500
C	-2.29746100	-0.52898600	1.08033300
C	-3.80340000	-2.34636000	-0.42023300
H	-1.93487500	-3.04391100	-1.21262100
C	-3.68313800	-0.53848600	1.17237000
H	-1.71276100	0.16757600	1.67021900
C	-4.44214200	-1.44162300	0.42841600
H	-4.38626400	-3.05014300	-1.00606600
H	-4.17062800	0.17079200	1.83337300
H	-5.52430800	-1.44047600	0.50840700
C	0.51680500	-2.40486300	-0.66014800
C	2.76337600	1.27116400	1.55722200
H	1.99562500	1.15638700	2.32967300
N	-0.28068700	-1.42827900	0.08720200
N	0.47162700	-0.46331000	0.65286700
H	0.32048800	-3.41286000	-0.27553600
H	0.24737300	-2.37226100	-1.72515500
H	2.44539800	2.09823100	0.91210300
H	3.70663900	1.54281600	2.03804000
I	-0.47499400	2.41531200	-0.48399800

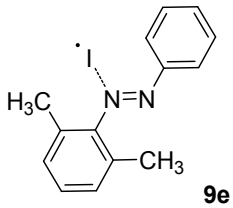


8e

G_{sol} = -661.905511 Hartree

C	2.08610000	-0.27107900	0.11519000
C	2.49444900	-1.61821800	-0.05884700
C	3.87130600	-1.93885200	-0.15664600
C	4.76055400	-0.89810900	-0.08833900
C	4.32453900	0.45017700	0.07625100
C	3.00024200	0.81203400	0.18120000
H	4.20032500	-2.96504700	-0.28124100
H	5.82578300	-1.09350200	-0.15951400
H	5.07722500	1.23303700	0.12375500
H	0.04152900	0.59511600	0.09361600
C	-1.11225200	-1.80847200	0.11898400
C	-1.62191200	-2.73236600	-0.79002300
C	-1.91499300	-1.17447700	1.06128400
C	-2.97674000	-3.04364200	-0.73615800
H	-0.97649400	-3.17184500	-1.54474700
C	-3.27148400	-1.48430100	1.08908700
H	-1.49498100	-0.44108800	1.74154500
C	-3.79996500	-2.41875200	0.20036800
H	-3.39115600	-3.75553400	-1.44241900

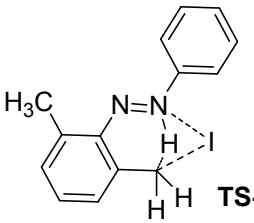
H	-3.91470400	-0.98004700	1.80231700
H	-4.86000100	-2.65053200	0.22699500
C	1.30358100	-2.35937900	-0.07642000
C	2.52279800	2.22438700	0.34861000
H	1.86559500	2.32120800	1.22000200
N	0.28684300	-1.50491100	0.06978900
N	0.73617500	-0.24541500	0.20918700
H	1.93085100	2.54714800	-0.51488100
H	3.37070300	2.90315400	0.46902800
I	-1.39525400	2.23958100	-0.21229100
H	1.11534000	-3.42128800	-0.14310700



9e

G_{sol} = -662.431454 Hartree

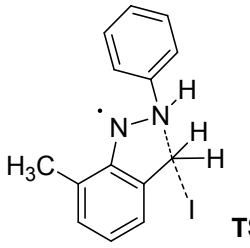
C	3.56867400	1.50032800	0.91633500
C	2.18075100	1.35207300	0.86663200
C	1.64516100	0.75121000	-0.28321400
C	2.43828400	0.27565100	-1.33720000
C	3.81625500	0.46509600	-1.25013400
C	4.37952600	1.07438200	-0.13159400
H	4.01562100	1.94959600	1.79933400
H	4.45043400	0.12166800	-2.06295800
H	5.45599600	1.20394000	-0.06928900
C	1.80796500	-0.39794000	-2.52794100
H	1.22778000	-1.27386000	-2.21622400
H	1.12469300	0.27729200	-3.05458000
H	2.57615800	-0.72417300	-3.23357200
C	1.32616900	1.77469300	2.03441100
H	0.81722900	2.72273200	1.83666000
H	0.55659000	1.02620000	2.25359800
H	1.94876200	1.89617900	2.92480600
N	0.24238300	0.51176400	-0.40597400
N	-0.51491000	1.45852600	-0.17052400
C	-1.90793900	1.21397000	-0.29098800
C	-2.73925300	2.08833200	0.41084300
C	-2.44142800	0.19966400	-1.09304600
C	-4.11885700	1.91786500	0.35251300
H	-2.28730900	2.88015500	1.00110200
C	-3.82144600	0.05048600	-1.16015700
H	-1.77867000	-0.44631000	-1.65954600
C	-4.65876400	0.89939800	-0.43268100
H	-4.77104200	2.58183900	0.91107800
H	-4.24725500	-0.72996700	-1.78307300
H	-5.73578500	0.77214100	-0.48810400
I	-0.19426600	-1.98190000	0.59308600



TS-1e

G_{sol} = -662.3840083 Hartree

C	4.04812500	1.48595200	-0.39891300
C	2.75248400	1.96927300	-0.33717100
C	1.76758900	1.16751000	0.29801700
C	2.09357900	-0.07801900	0.90551900
C	3.40625300	-0.55663600	0.73827600
C	4.36672200	0.21862800	0.11499000
H	4.81882000	2.08327000	-0.87777900
H	3.65942300	-1.53313700	1.14108200
H	5.38288700	-0.15469000	0.02564800
C	1.08701900	-0.87277500	1.60275000
H	0.66338900	-0.41725200	2.50706900
H	1.38125800	-1.90262200	1.78873100
C	2.38280700	3.29304900	-0.95160900
H	1.65197400	3.16005600	-1.75502800
H	1.93136100	3.96294400	-0.21370800
H	3.27031600	3.77879100	-1.36443000
N	0.46191300	1.60407100	0.12626700
N	-0.45031900	0.90432600	0.63551400
C	-1.79919800	1.24433800	0.36442800
C	-2.77476600	0.36951000	0.84616200
C	-2.15167100	2.41300000	-0.31785100
C	-4.11877900	0.66573700	0.64004900
H	-2.47513600	-0.53997900	1.35875000
C	-3.49706900	2.69953600	-0.51130000
H	-1.37447800	3.07624500	-0.68118700
C	-4.48178900	1.82924400	-0.03621300
H	-4.88024100	-0.01600100	1.00506800
H	-3.78170600	3.60502400	-1.03841900
H	-5.53074600	2.05912500	-0.19639400
I	-0.43883000	-2.44359100	-0.48600200
H	-0.02813200	-0.30029300	0.98340300

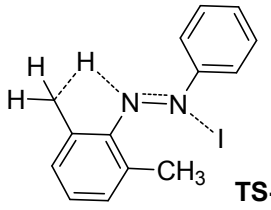


TS-2e

G_{sol} = -662.600291 Hartree

C	-1.85362000	3.68634400	-0.09439400
C	-0.48397700	3.48266600	-0.13328900
C	-0.01688700	2.15980800	0.11573100
C	-0.91996300	1.06404600	0.31875900
C	-2.27843800	1.31817600	0.34932300
C	-2.73676900	2.62921800	0.16025500
H	-2.24638600	4.68590500	-0.26064000
H	2.97748400	0.49974900	0.47808400
H	3.80507400	2.82022500	0.18385600
C	0.22448800	-0.25753400	0.39001900
H	0.21553900	-0.86854200	1.28183800
H	0.14089000	-0.71518400	-0.52280300
C	0.49982900	4.58805100	-0.38389900
H	1.13249100	4.75778400	0.49365300

1.16921000 4.33220600 -1.21149500 H -0.01999100 5.51840300 -0.62454600 N 1.30654200 1.90481400 0.14543400 N 1.45551600 0.63961300 0.73131800 C 2.61584700 -0.10437900 0.34221900 C 3.12345400 -1.05369900 1.22726100 C 3.15376200 0.05842500 -0.93160400 C 4.19732600 -1.84597500 0.83324100 H 2.68066900 -1.17777100 2.21320000 C 4.23259100 -0.73704800 -1.31077300 H 2.73630600 0.80248000 -1.60153600 C 4.75523900 -1.68778600 -0.43503300 H 4.59634400 -2.58648600 1.51887700 H 4.66325700 -0.61362800 -2.29944400 H 5.59312900 -2.30615100 -0.74033000 H 1.40414300 0.72876400 1.75054900 I -2.23716600 -2.14133200 -0.17893300

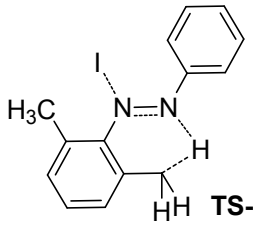


TS-3e

G_{sol} = -662.366228 Hartree

C -3.72235200 -1.40903700 -1.05416500 C -2.32999700 -1.22049200 -1.08786000 C -1.66645900 -0.89199600 0.11676200 C -2.33163200 -0.55462800 1.31118000 C -3.71349600 -0.68079700 1.27073600 C -4.39700800 -1.12021500 0.11887800 H -4.25661400 -1.70448600 -1.95206300 H -4.28295000 -0.45537600 2.16852100 H -5.47872600 -1.21121700 0.15335200 C -1.59871500 -0.15053600 2.55977300 H -0.80719100 -0.86784100 2.80253400 H -1.12014400 0.82518900 2.43224000 H -2.29204800 -0.09616500 3.40298400 C -1.41717400 -1.32305700 -2.20541200 H -0.28436000 -1.56074400 -1.16255900 H -1.65173700 -1.99580900 -3.02795600 H -0.90079800 -0.40776900 -2.49989000 N -0.30464800 -1.12958300 -0.03201900 N 0.58521600 -0.39097600 0.49653400 C 1.91842400 -0.83169600 0.31779900 C 2.93498800 0.02910600 0.74944400 C 2.23971900 -2.08169400 -0.22941300 C 4.26366500 -0.34894400 0.61224600 H 2.66387000 0.99367300 1.16768600 C 3.57632600 -2.44684300 -0.36540600 H 1.45525600 -2.77538600 -0.51363700 C 4.58990300 -1.58454200 0.04873500 H 5.04889100 0.32389800 0.94260900 H 3.82415100 -3.41635200 -0.78706400

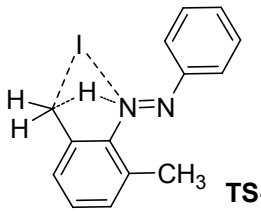
H	5.63001000	-1.87677700	-0.05851400
I	0.19643900	2.12379800	-0.36414400



TS-4e

G_{sol} = -662.378696 Hartree

C	-3.25243700	1.65106400	-0.97974600
C	-1.96182500	1.84977200	-0.41313500
C	-1.56548200	0.92934300	0.61589800
C	-2.50332900	0.03674700	1.22371600
C	-3.77997700	-0.00313700	0.71744400
C	-4.13994100	0.77164700	-0.41314900
H	-3.54823700	2.27478600	-1.81834900
H	-4.51167200	-0.67011700	1.16440400
H	-5.14211400	0.68044300	-0.82186900
C	-2.06500300	-0.84818900	2.35533700
H	-1.30684400	-1.56098900	2.01077100
H	-1.61880900	-0.26533900	3.16721000
H	-2.91440400	-1.41045400	2.75094700
C	-1.05733300	2.82155800	-0.93592100
H	0.14776300	2.12005800	-0.57346600
H	-1.29986200	3.23177400	-1.91484000
H	-0.64898000	3.55934300	-0.24168700
N	-0.24375000	0.66520000	0.84405700
N	0.62162400	1.48430500	0.38203700
C	1.97639900	1.07789100	0.35913100
C	2.83676800	1.74905100	-0.51249900
C	2.45443200	0.07433600	1.20651400
C	4.18327100	1.40430100	-0.54606100
H	2.44218000	2.51903800	-1.16995300
C	3.80550700	-0.25383200	1.16873500
H	1.76847300	-0.43227200	1.87688000
C	4.67119200	0.40313600	0.29450000
H	4.85148100	1.91541300	-1.23226300
H	4.18274700	-1.03257800	1.82437600
H	5.72294900	0.13552700	0.26742500
I	0.03050500	-1.81308100	-0.73050600



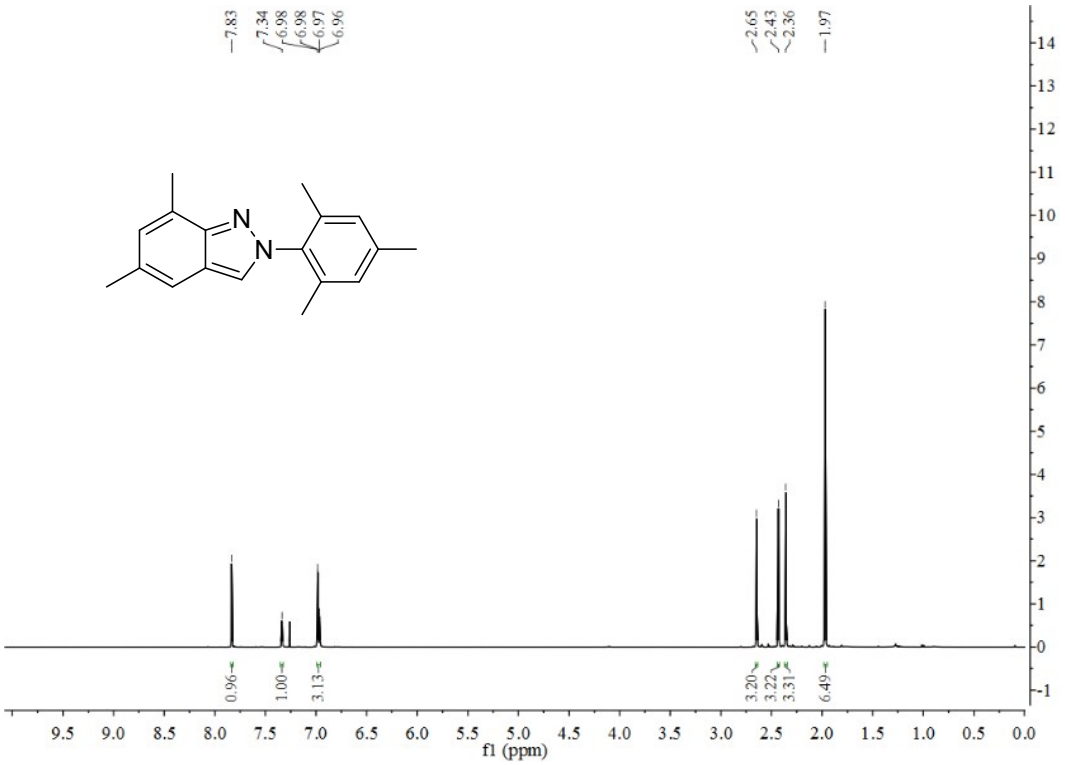
TS-5e

G_{sol} = -662.369697 Hartree

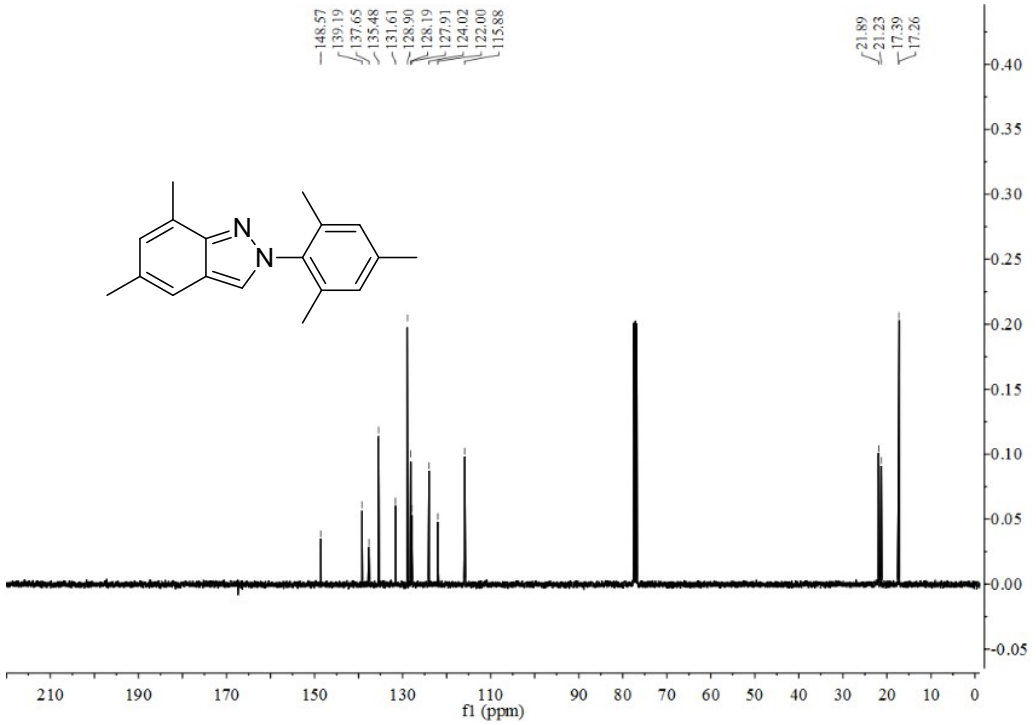
C	-3.24046800	2.62609500	-0.47561500
C	-1.85390500	2.50421500	-0.48632500
C	-1.33346500	1.40645100	0.22235000
C	-2.13106500	0.48704200	0.93712800
C	-3.52197800	0.62581000	0.87870100
C	-4.06146900	1.70021100	0.18473100
H	-3.69659900	3.45230500	-1.01445500
H	-4.16026300	-0.08558100	1.39384400
H	-5.13909600	1.83163400	0.15060600

C	-1.37187100	-0.56031200	1.62557100	C	3.28716300	2.13704100	0.17413400
H	-0.21841200	-0.23539300	0.73354400	C	2.54420100	-0.17899400	0.07550500
H	-0.76045200	-0.24117800	2.47508800	C	4.61105600	1.71565600	0.20067400
H	-1.92504500	-1.46494100	1.86040100	H	3.02512000	3.19040900	0.20002100
C	-0.99094700	3.46587500	-1.25601800	C	3.87180000	-0.58809200	0.10086000
H	-0.38400900	4.08223100	-0.58719800	H	1.74941200	-0.91379600	-0.00705500
H	-0.29443300	2.93311800	-1.91236000	C	4.90377100	0.35170400	0.16653200
H	-1.61569900	4.12025500	-1.86907500	H	5.41248000	2.44629000	0.24658300
N	-0.00791000	0.96160600	0.22188200	H	4.10165100	-1.64833200	0.06039400
N	0.95938800	1.74739000	0.12737500	H	5.93722000	0.01868900	0.18381900
C	2.25482500	1.19226900	0.12164000	I	-0.49996400	-2.59921700	-0.36185200

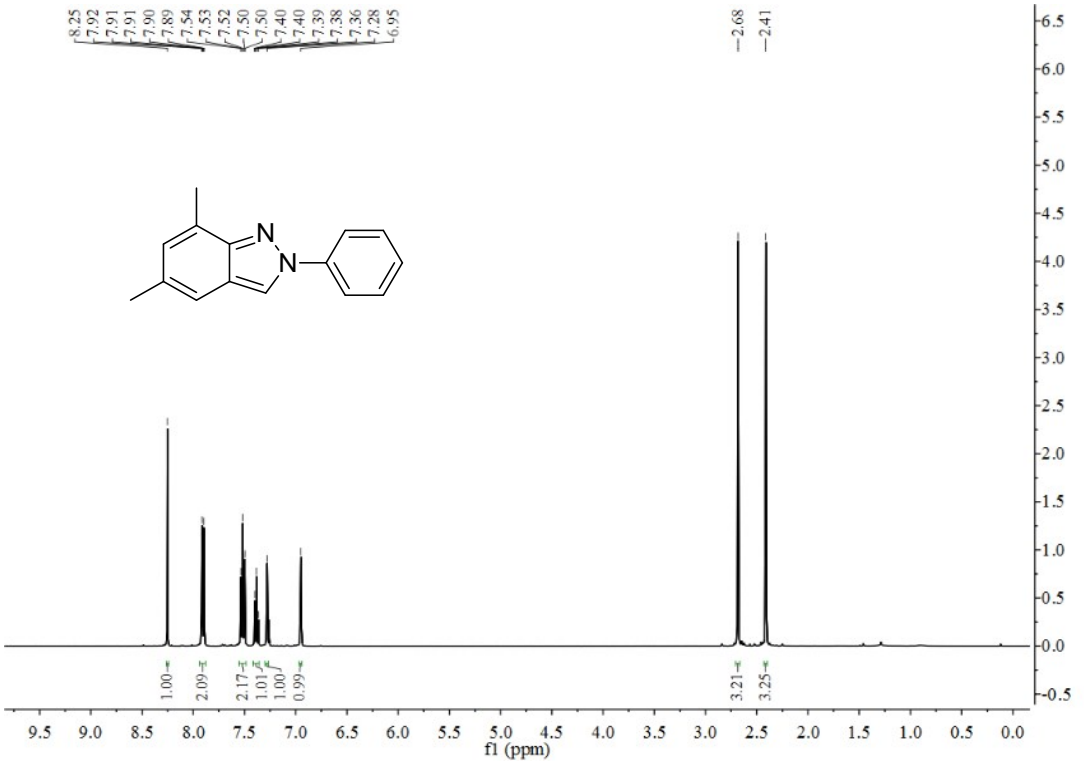
5. Copies of ^{1}H and ^{13}C NMR Spectra



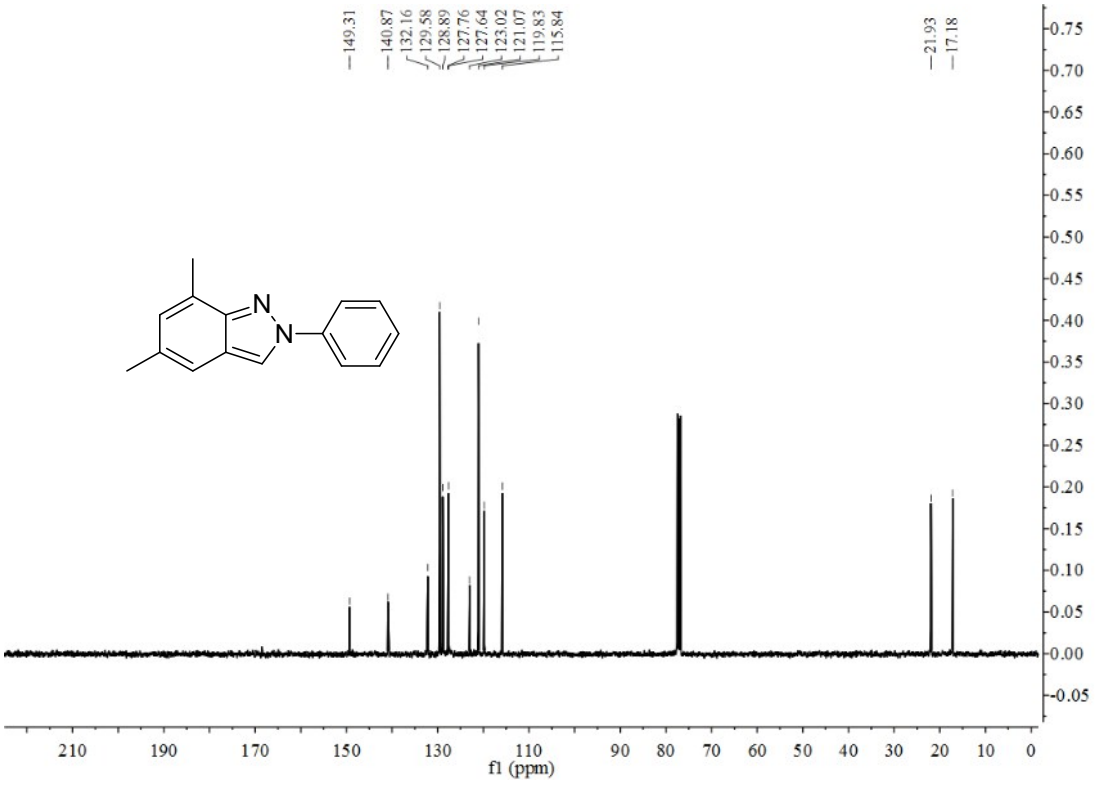
^{1}H NMR of Compound **2a**



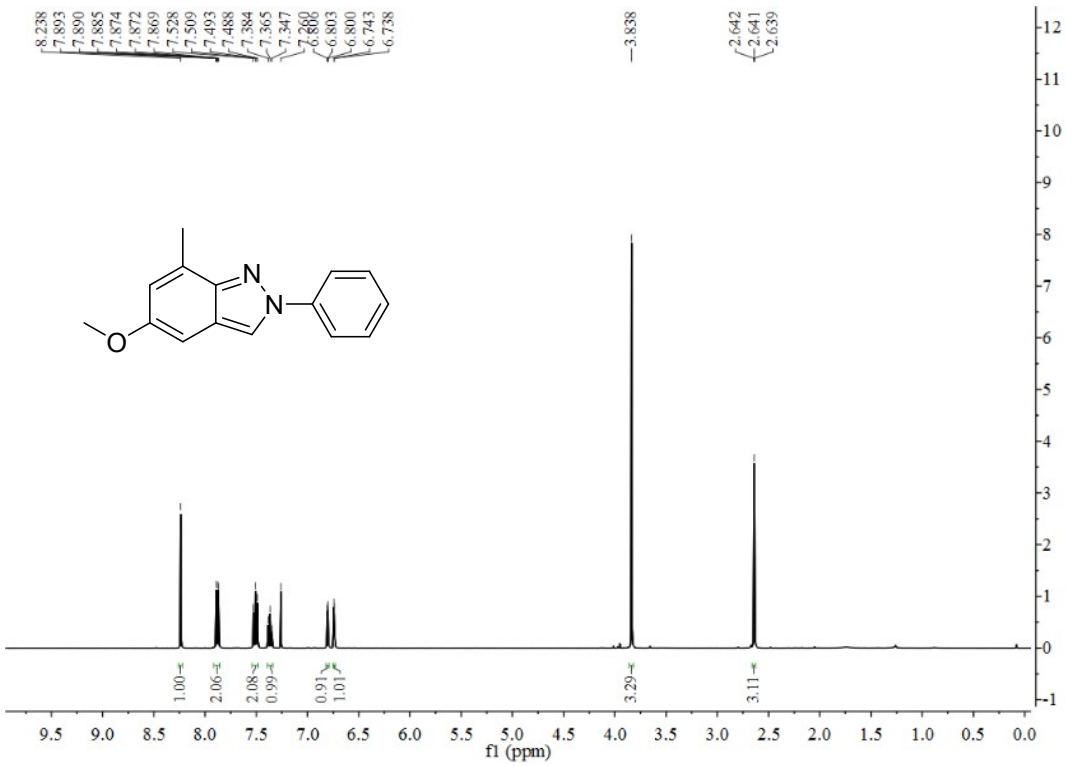
^{13}C NMR of Compound **2a**



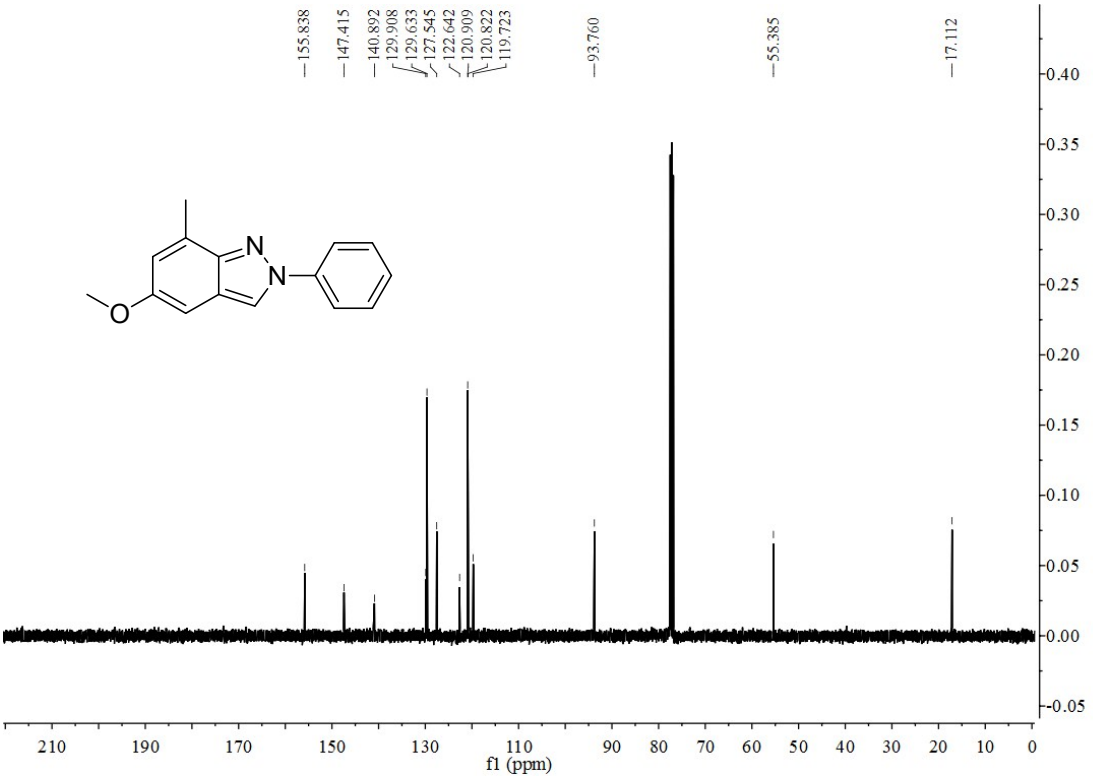
^{1}H NMR of Compound **2b**



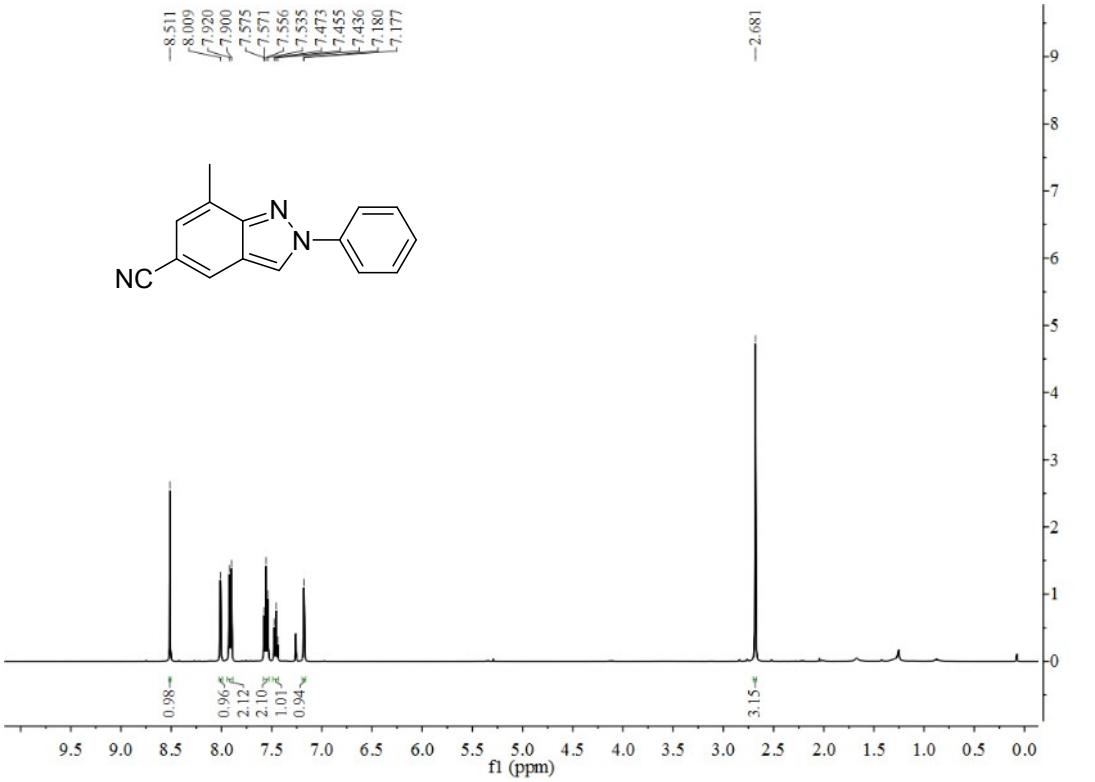
^{13}C NMR of Compound **2b**



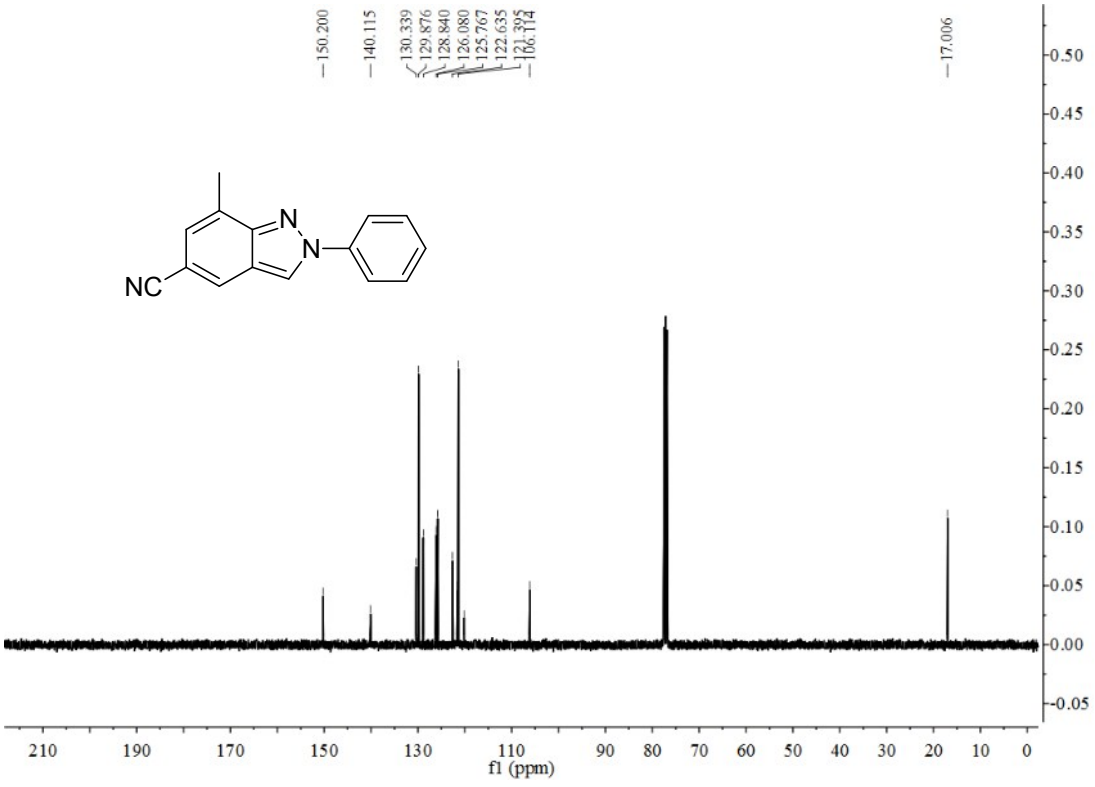
^{1}H NMR of Compound **2c**



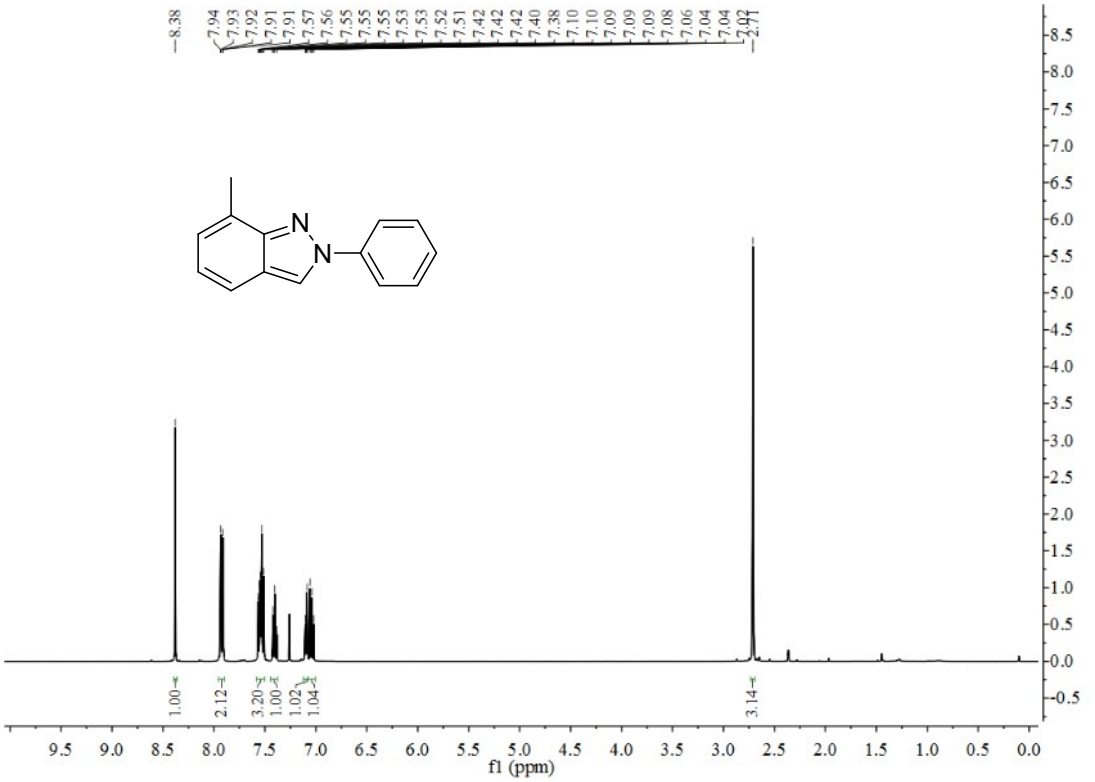
^{13}C NMR of Compound **2c**



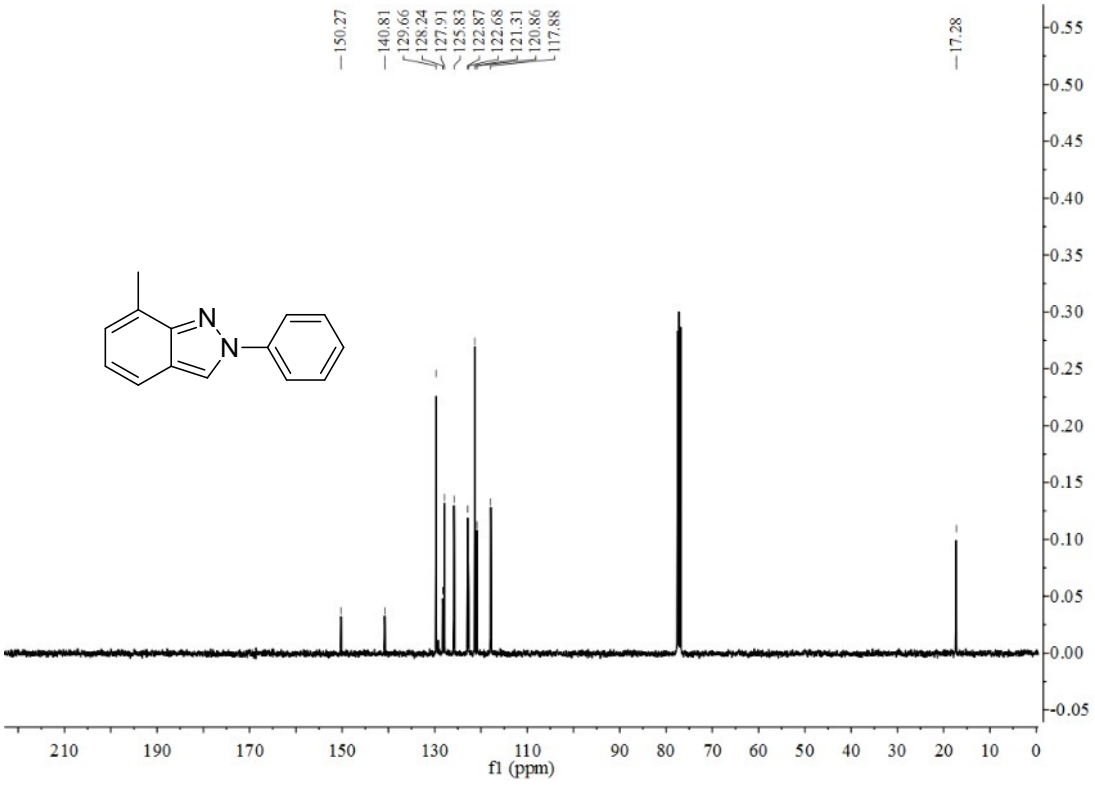
^{1}H NMR of Compound **2d**



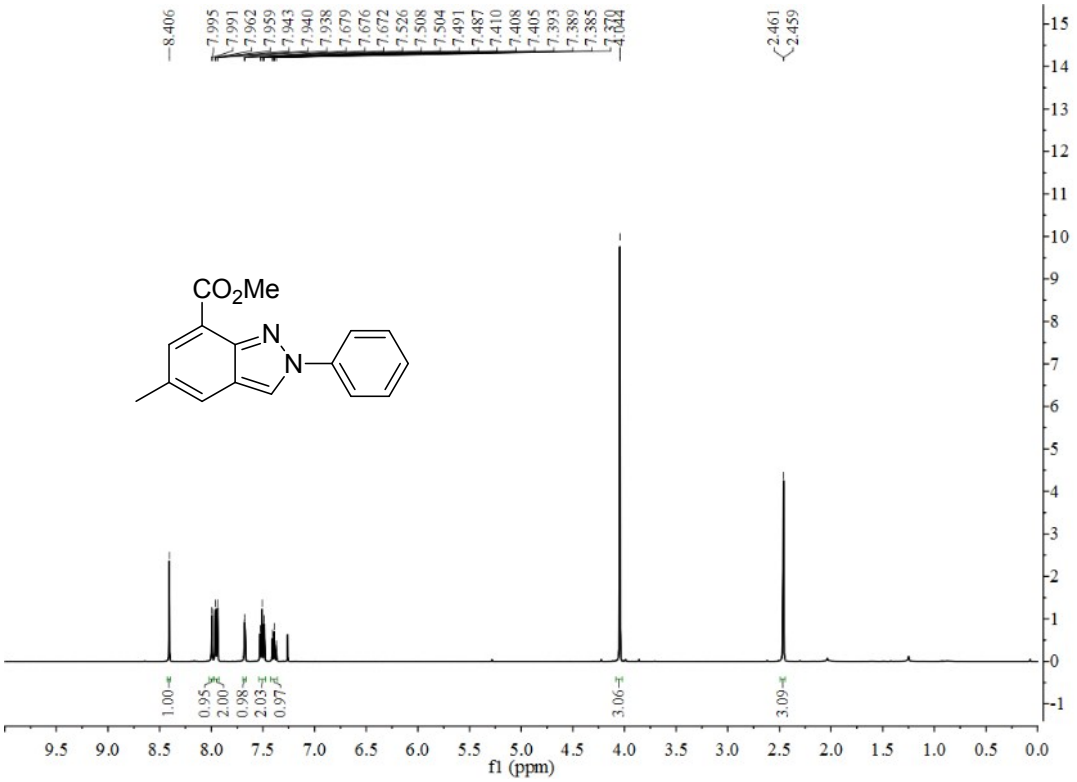
^{13}C NMR of Compound **d**



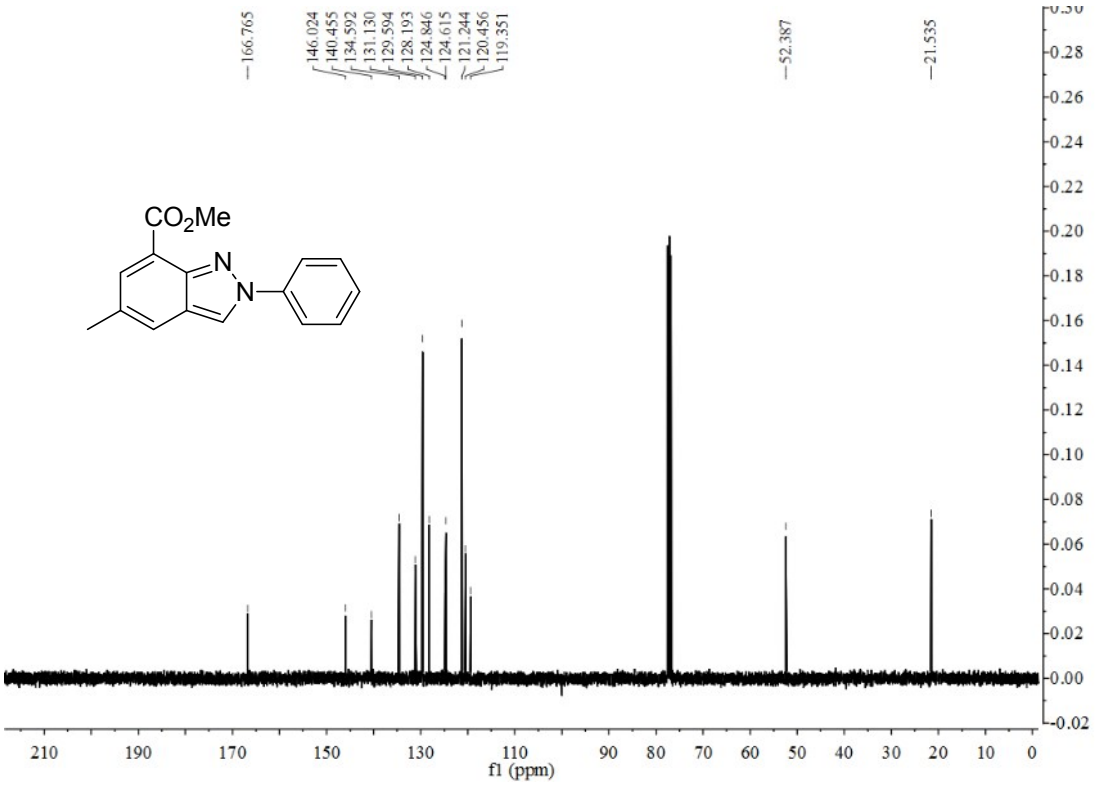
^{1}H NMR of Compound **2e**



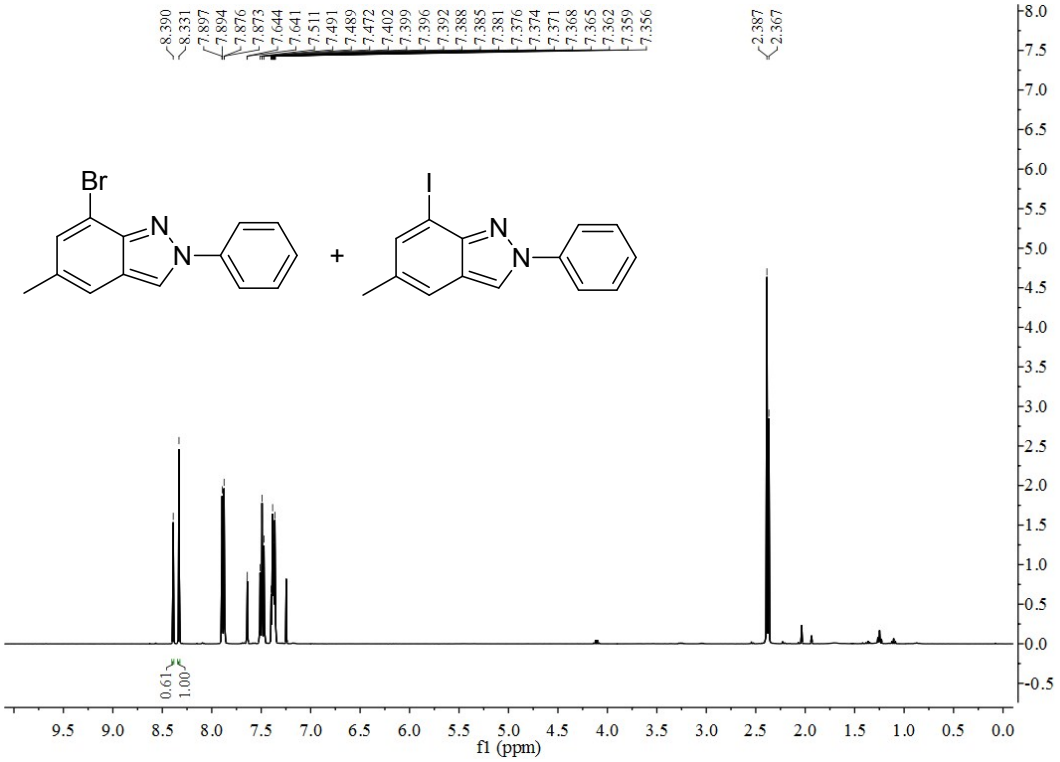
^{13}C NMR of Compound **2e**



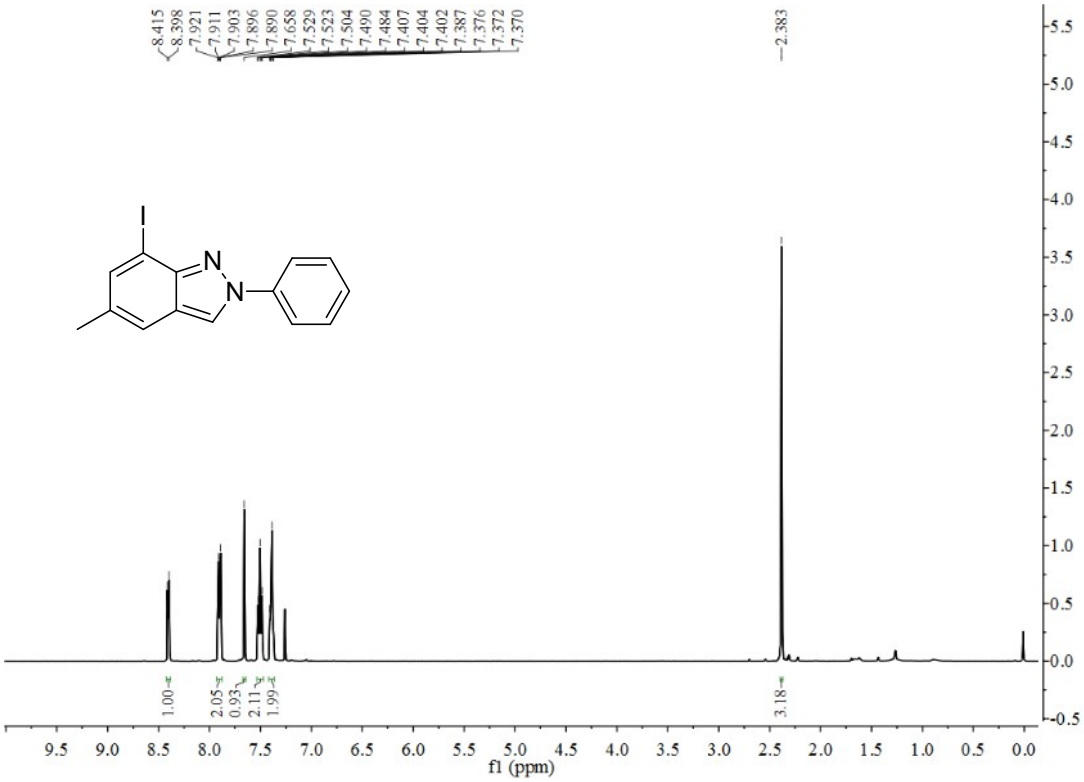
^{1}H NMR of Compound **2f**



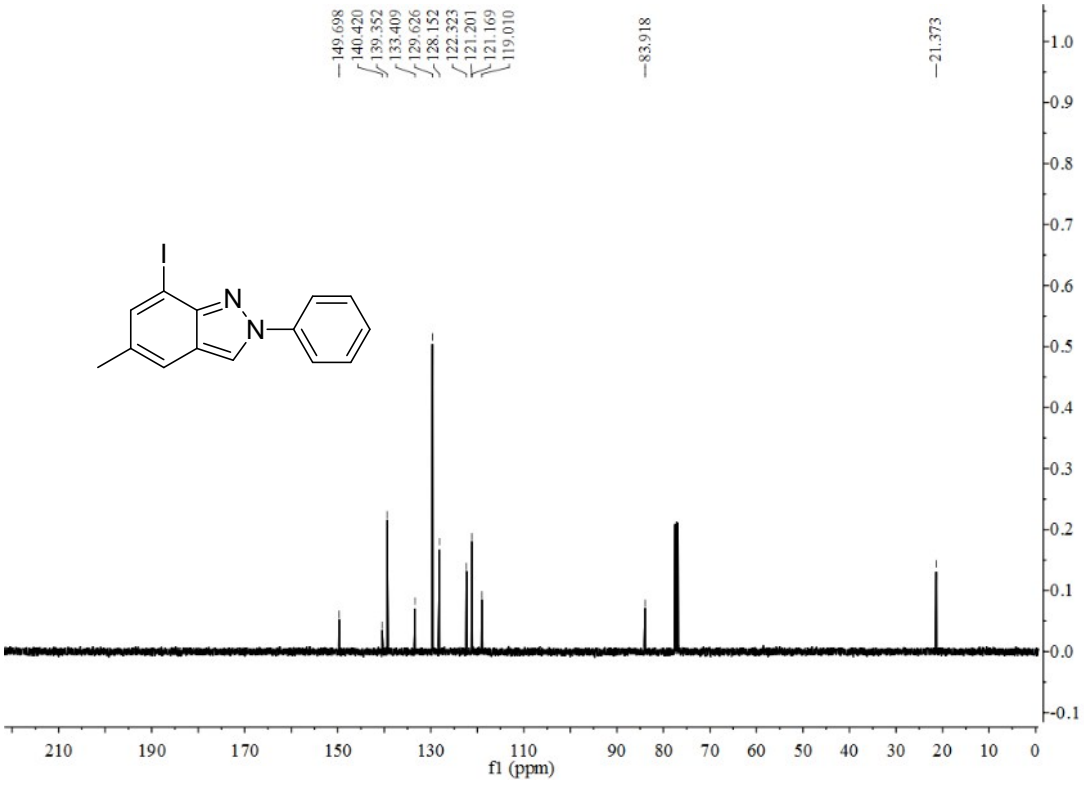
^{13}C NMR of Compound **2f**



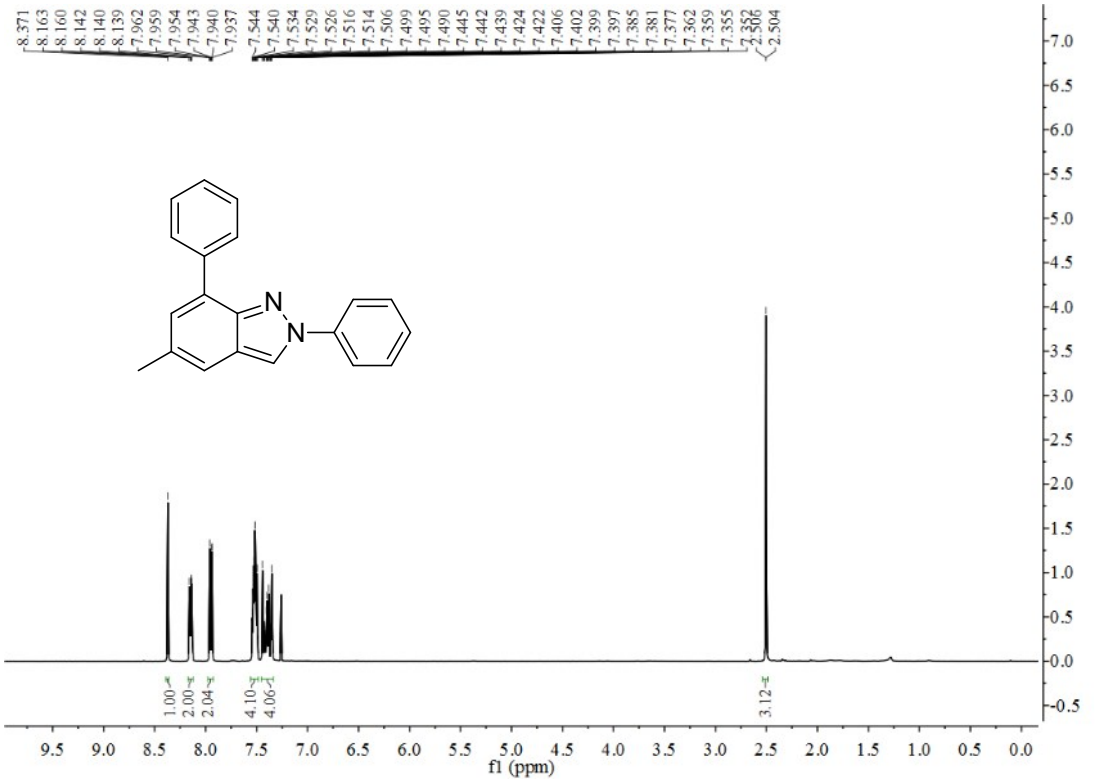
^{1}H NMR of Compound **2g+2h (1:0.60)**



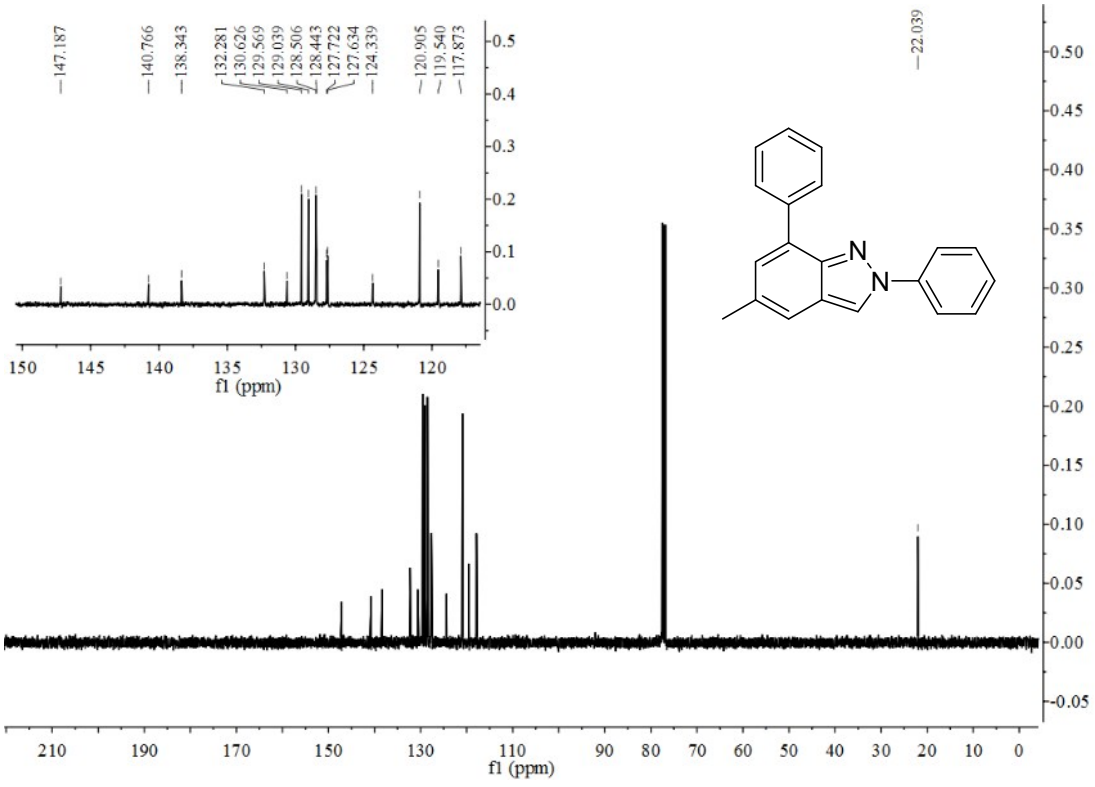
^{1}H NMR of Compound **2h**



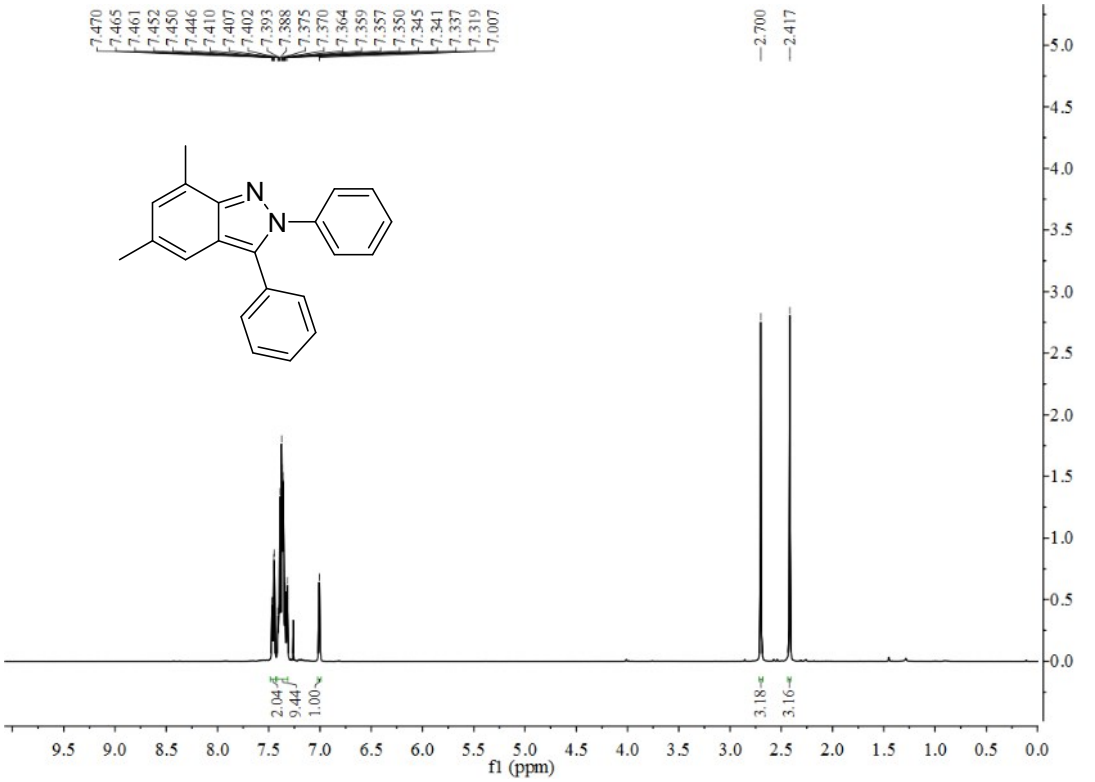
^{13}C NMR of Compound **2h**



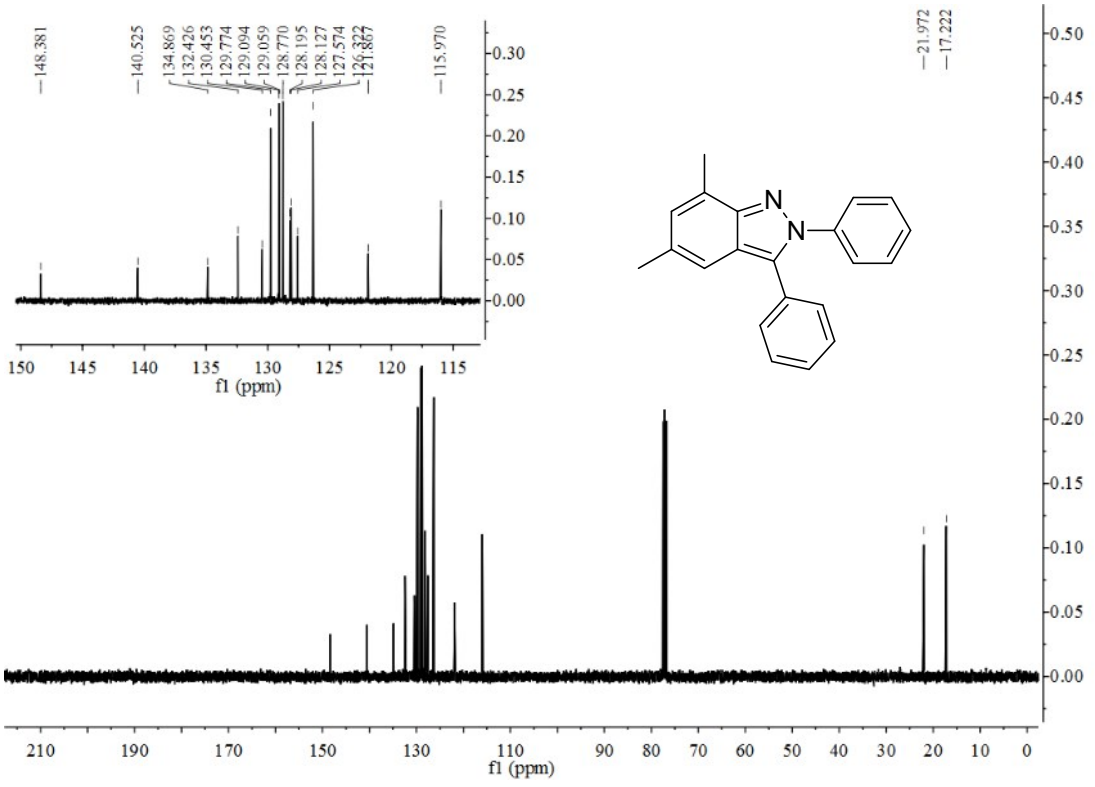
^{1}H NMR of Compound **2i**



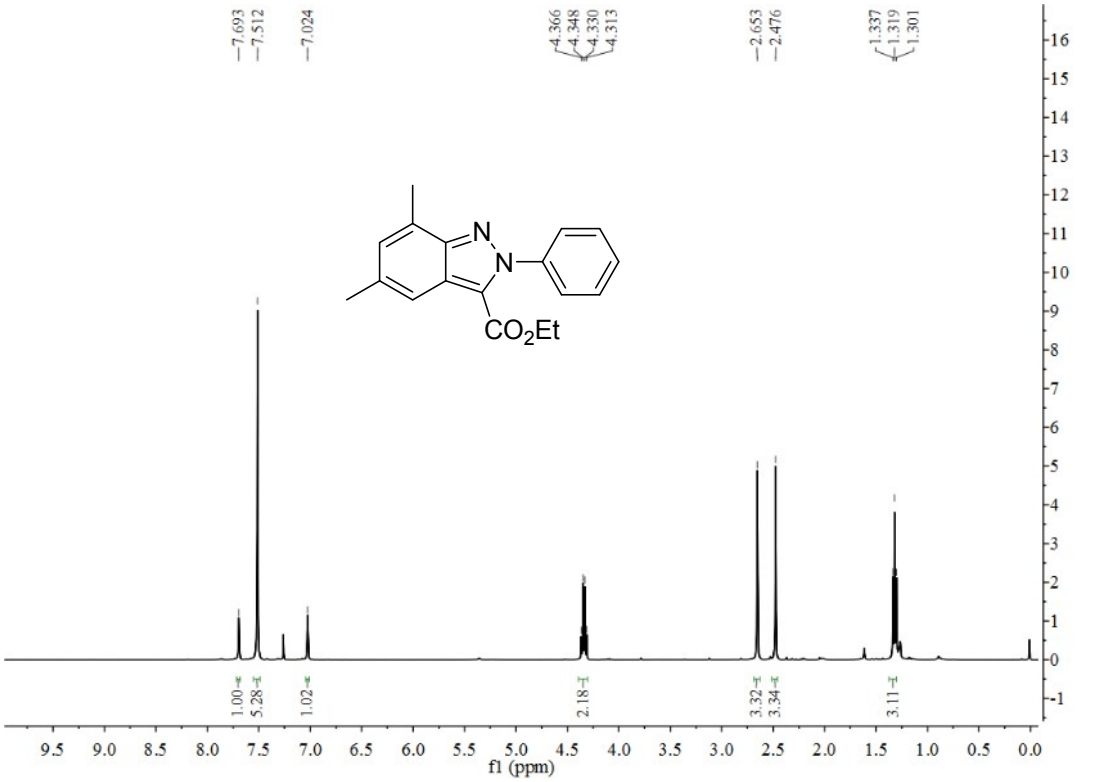
^{13}C NMR of Compound **2i**



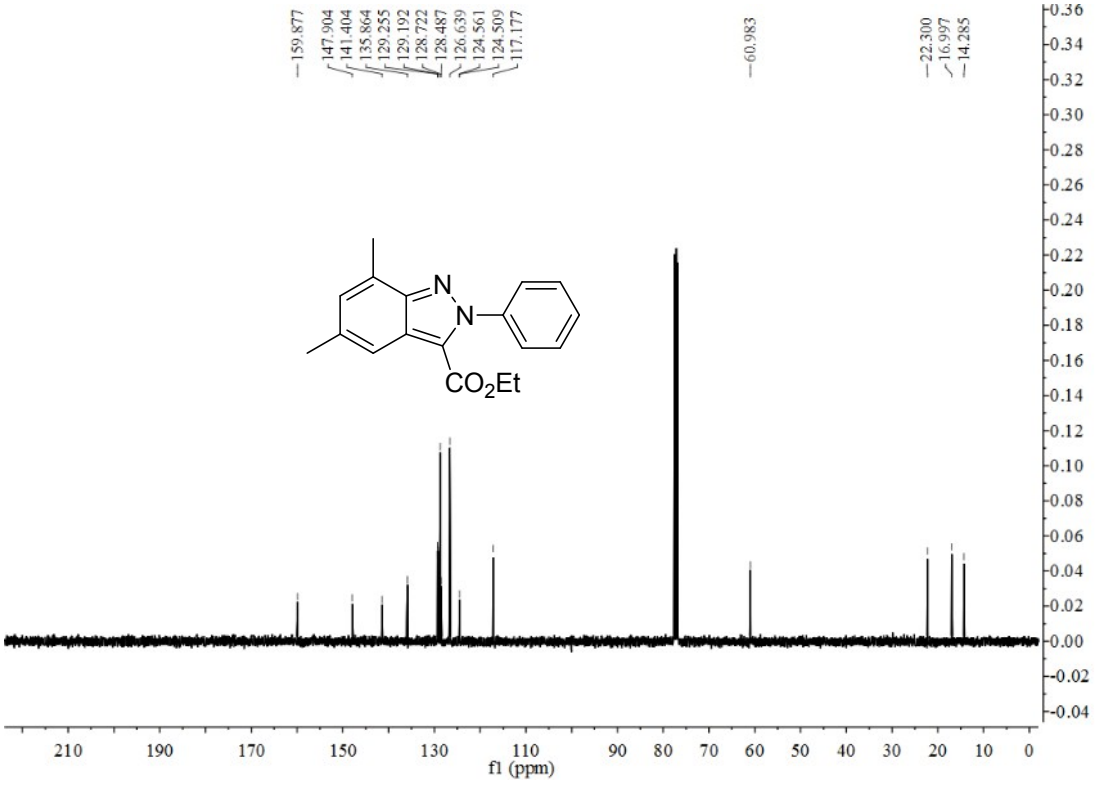
^{1}H NMR of Compound **2j**



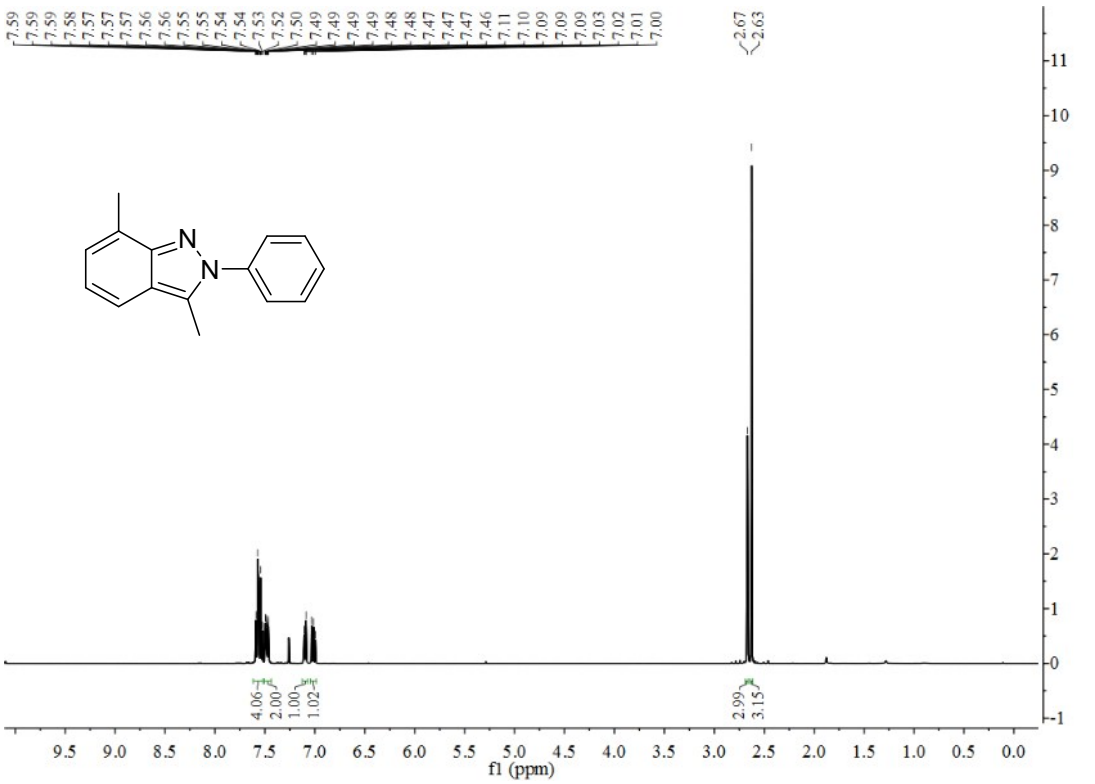
^{13}C NMR of Compound **2j**



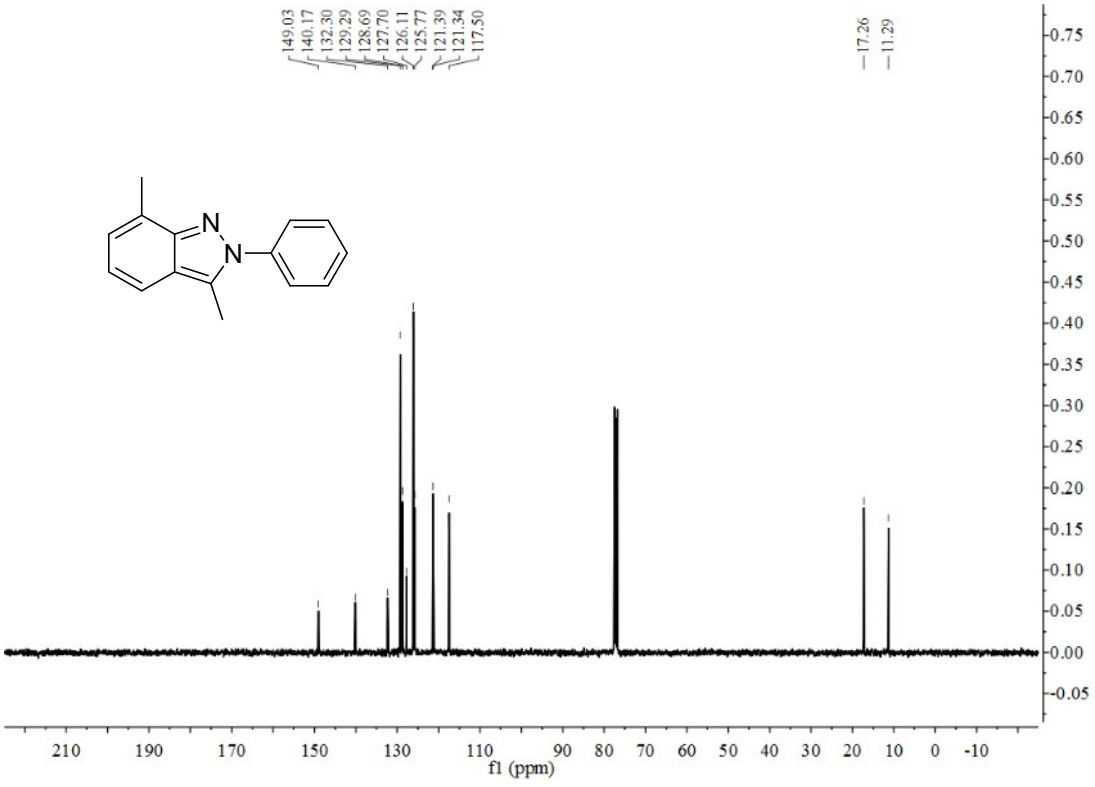
^{1}H NMR of Compound **2k**



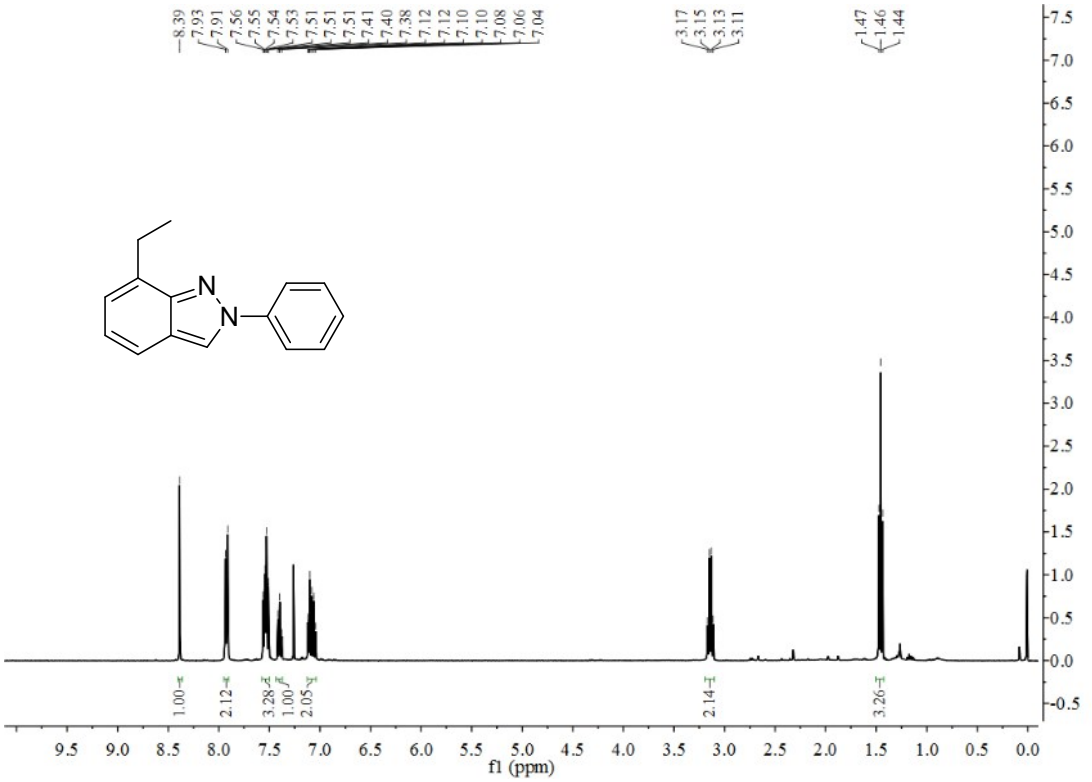
^{13}C NMR of Compound **2k**



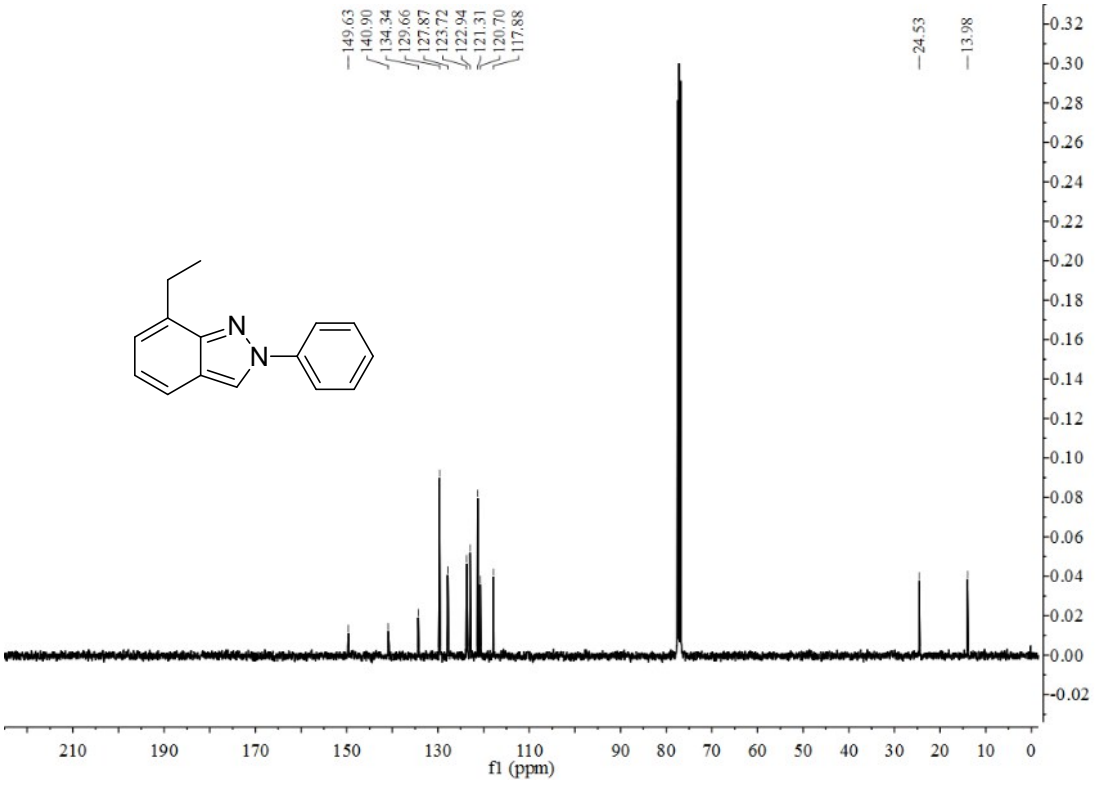
^{1}H NMR of Compound **2l**



^{13}C NMR of Compound **2l**



^{1}H NMR of Compound **2l'**



^{13}C NMR of Compound **2l'**

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