Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Iron Promoted Regioselective C3-H Nitration of 2*H*-Indazole; Direct Access to 3-Nitro-2*H*-Indazole

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Contents

1. General Considerations:

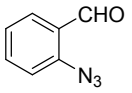
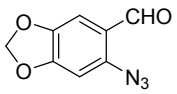
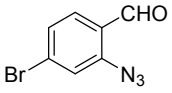
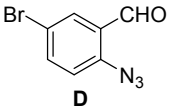
IR spectra were recorded on a FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the 1HNMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electro thermal melting point apparatus and are uncorrected. *o*-azidobenzaldehydes prepared by using literature known procedures, 2-aminophenols all were commercial available. Pd-catalysts and all bases were purchased from Sigma Aldrich. All dry solvents were used, toluene were dried over sodium metal and DMSO, CH_3CN and DMF were dried over calcium hydride and which are commercial available.

All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Reactions were generally run under argon, nitrogen and oxygen atmosphere wherever necessary. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 ˚C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20g per one gram of crude material). All 2-azidobenzaldehydes (**1a-1c and 1e**) except **1d** have been synthesized by using literature known procedures. [1—3]

2. Preparation of azidoaldehyde

The following 2-azido aldehydes are known in the literature.[1,2]

Table S1:

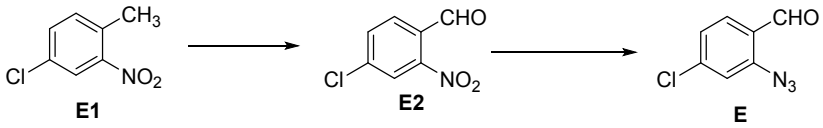
			
A	**B**	**C**	**D**

The following 2-Azido-4-chlorobenzaldehyde (E) was synthesized using the below strategy. [1-3]

Step 1: A solution of 4-chloro-2-nitrotoluene (1.0 equiv) in DMF.DMA (3.0 equiv) was refluxed at 140°C for two days. The reaction mixture was then cooled to rt. The imine was then added dropwise to a solution of NaIO4 (3.0 equiv) in DMF (13 mL) and H_2O (25 mL). The reaction mixture was then stirred at rt for 4 h. The solid formed was filtered off and washed with toluene (2 x 15 mL). The combined organic layer was washed with water (30 mL) and then with brine (10 mL). The solvent was completely removed and the resulting crude product was recrystallized from hexane to afford pure aldehyde as brown solid (90% yield).

Step 2: To a stirring solution of 2-Nitro-4-chlorobenzaldehyde (1.0 equiv) in HMPA was added sodium azide (2.0 equiv). The reaction mixture was stirred at ambient temperature and monitored by TLC. Once the starting material had disappeared, the mixture was diluted with ice-cold water and extracted with diethyl ether (3 × 25 mL). The ether layer was washed with water (3 × 25 mL), brine (1 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated to give the crude product, which was further purified by column chromatography to give the final analytically pure product (82% yield).

Table S2:



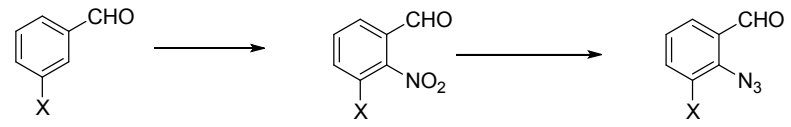
2-Azido-4-chlorobenzaldehyde (E). White solid (3.9 mg, 80%); mp 84−86 °C; IR (MIR-ATR, 4000−600 cm−1) υmax = 3340, 3261, 3034, 2864, 2768, 2408, 2342, 2216, 2120, 1679, 1591, 1568, 1492, 1426, 1396, 1330, 1289, 1265, 1203, 1077, 949, 841, 816; 1 H NMR(CDCl3, 400 MHz) δH = 10.22 (s, 1H), 7.88 (d, 1H, J = 8.3 Hz), 6.89 (dd, 1H, Ja = 8.3 and Jb = 1.5 Hz), 6.81 (d, 1H, J = 1.5 Hz); 13C NMR (CDCl3, 100 MHz) 187.1 (s, −CHO), 147.4 (s, Ar−C), 144.8 (s, Ar− C), 130.9 (d, Ar−CH), 123.9 (s, Ar−C), 115.5 (d, Ar−CH), 109.1 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_7H_4ClN_3O]+$ = [M]+ 181.0037, found 181.0030.

The following 2-Azido-3-halobenzaldehyde (f &g) was synthesized using the below strategy[3f]

Step 1: To a mixture of H_2SO_4 (16 mL) and conc. nitric acid (2 mL) was slowly added aldehyde such that the temperature of the reaction mixture was maintained below 10 °C. After the addition was complete (40 min), the reaction mixture was stirred for an additional 30 min at 5-10 °C, and then poured onto crushed ice (100 mL). On slow warming of this mixture with stirring (30 min) a yellow precipitate formed, which was filtered and washed with water until the filtrate was no longer acidic to litmus. The precipitate was air dried to give 83 g of a yellow amorphous solid.

Step 2: Step 2: To a stirring solution of 2-Nitro-3-halobenzaldehyde (1.0 equiv) in HMPA was added sodium azide (2.0 equiv). The reaction mixture was stirred at ambient temperature and monitored by TLC. Once the starting material had disappeared, the mixture was diluted with ice-cold water and extracted with diethyl ether (3 × 25 mL). The ether layer was washed with water (3 × 25 mL), brine (1 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated to give the crude product, which was further purified by column chromatography to give the final analytically pure product (85% yield).

Table S2:



X= Cl, Br

2-Azido-3-bromobenzaldehyde (f). Yellow solid (82%); mp 80−82 °C; IR (MIR-ATR, 4000−600 cm−1) υmax = 2886, 2118, 1680, 1611, 1483, 1298, 1248, 1192, 1001, 815, 690; 1H NMR (CDCl3, 400 MHz) δH = 10.32 (s, 1H), 7.56 (d, 1H, J = 2.4 Hz), 7.32 - 7.18 (m, 3H); 13C NMR (CDCl3, 100 MHz) 187.6, 139.4, 126.1, 120.7, 118.4; HR-MS (ESI+) m/z calculated for $[C_7H_5BrN_3O]+$ = [M]+ 225.96105, found 225.96108.

2-Azido-3-chlorobenzaldehyde (g). lemon Yellow solid (78%); mp 82−84 °C; IR (MIR-ATR, 4000−600 cm−1) υmax = 2922, 2886, 2130, 1680, 1572, 1485, 1304, 1192, 1000, 940, 815, 690, 563; 1 H NMR(CDCl3, 400 MHz) δH = 10.32 (s, 1H), 7.57 (d, 1H, J = 2.0 Hz), 7.33 - 7.17 (m, 2H); 13C NMR (CDCl3, 100 MHz) 187.6, 139.4, 137.5, 127.7, 126.1, 120.7, 118.4; HR-MS (ESI+) m/z calculated for $[C_7H_4ClN_3O]+$ = [M]+ 182.01157, found 182.01155.

General procedure (GP-I) for the synthesis of 2-phenyl-2*H*-indazole:[3-5]

Azidobenzaldehyde **1** (1 mmol), aniline **2** (1 mmol) were taken in a 10 mL oven dried schlenck tube and it was closed with stopcock with argon balloon and placed in external heating oil bath at 120 ˚C for 1-3 hrs (oil bath temperature). After completion of the starting material, the mixture was cooled to room temperature and was purified on a silica gel column chromatography (hexane/ethylacetate 90:10) which furnished the respective products **1a-x.**

3. General procedure (GP-II) for the synthesis of 3-nitro-2-phenyl-2*H*-indazole:

In an oven dried 10 ml schlenck tube, under oxygen atmosphere, 2-phenyl-2*H*-indazole **2a-v** (1 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (2 mmol), TEMPO (1mmol), were added and followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at 80 °C for 5-10h under oxygen atmosphere. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by addition of aq. NH_4Cl solution and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried (Na_2SO_4) and concentrated in

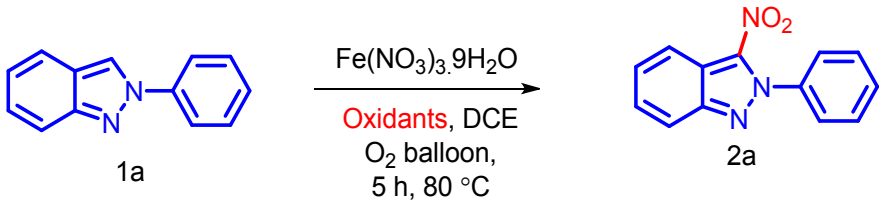
vacuum. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as (petroleum ether/ethylacetate 97:3 to 95:5) eluent furnished the product nitro indazole **2a-v**.

4. General procedure (GP-II) for the synthesis of Indazolo[2,3-a]quinazoline:

In an oven dried 10 ml schlenck tube, under argon atmosphere, C3-nitro indazole **2a, 2m, 2l and 2k** (1mmol) and $P(OEt_3)$ (1mL) were added. The resulting reaction mixture was stirred at 80 °C for 1h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by addition of aq. NH_4Cl solution and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuum. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as (petroleum ether/ethylacetate 97:3 to 95:5) eluent furnished the product benzimidazoindazole **3a-d.**

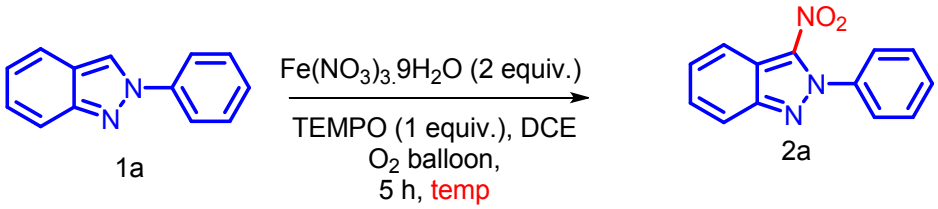
5. Optimization Details

Table S3. Optimization of Oxidants



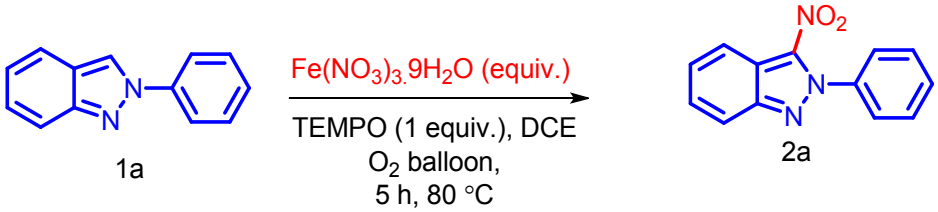
Entry	Oxidants (equiv.)	Yield (%)[b]
1	TBHP (1)	n.d.
2	DTP (1)	n.d.
3	DDQ (1)	10
4	TEMPO (0.5)	40
5	TEMPO (1)	85
6	TEMPO (1.5)	85
7	TEMPO (2)	85

Table S4. Optimization of Temperature



Entry	Temp (˚C)	Yield (%)[b]
1	40	Trace
2	60	62
3	80	85
4	100	80

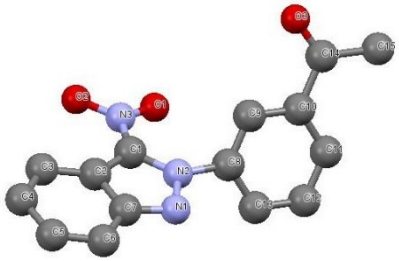
Table S5. Optimization of Nitro source

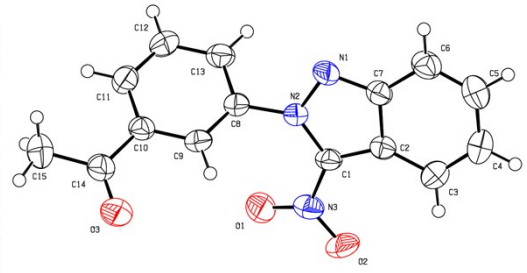


Entry	Nitro source (equiv.)	Yield (%)[b]
1	$Fe(NO_3)_3.9H_2O$ (0.5)	15
2	$Fe(NO_3)_3.9H_2O$ (1)	33
3	$Fe(NO_3)_3.9H_2O$ (2)	85
4	$Fe(NO_3)_3.9H_2O$ (3)	85

6. Single crystal X-ray data

Figure 1: X-ray crystal structure data for 1-(3-(3-nitro-2H-indazol-2-yl)phenyl)ethanone (2t) CCDC: 1825398





Identification code	exp_7218
Empirical formula	$C_{15}H_{11}N_3O_3$
Formula weight	281.27
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	7.8053(18)
b/Å	8.2606(17)
c/Å	11.869(2)
α/°	91.064(17)
β/°	108.89(2)
γ/°	113.92(2)
Volume/Å^3	651.9(3)
Z	2
ρ_{calc}g/cm^3	1.4329
μ/mm^{-1}	0.103
F(000)	292.1
Crystal size/mm^3	0.06 × 0.04 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.9 to 58.02

Index ranges	$-10 \leq h \leq 9$, $-10 \leq k \leq 11$, $-16 \leq l \leq 15$
Reflections collected	5672
Independent reflections	2992 [R_{int} = 0.0387, R_{sigma} = 0.0936]
Data/restraints/parameters	2992/0/190
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0643, wR_2 = 0.1059
Final R indexes [all data]	R_1 = 0.1431, wR_2 = 0.1401

7. Mass data for Intermediates

Figure 2: The HR-MS data for the intermediate 2,2,6,6-tetramethylpiperidin-1-ol

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Dept Of Chemistry
HRMS Report

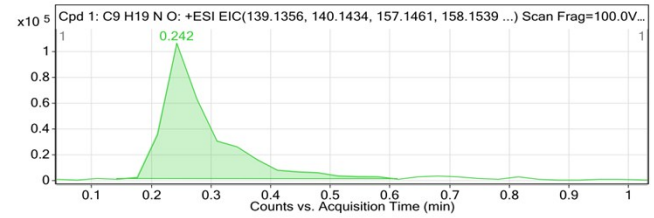
Data File	AVM-472-00.d	**Sample Name**	AVM-472
Position	P2-A7	**Acq Method**	HRMS_Dual ESI_POS_SD_Agilent.m
Acquired Time	29-Feb-16 2:39:22 PM	**DA Method**	SD_IITH.m

Sample Group **Info.**
Acquisition SW 6200 series TOF/6500 series
Version Q-TOF B.05.00 (B5042.2)

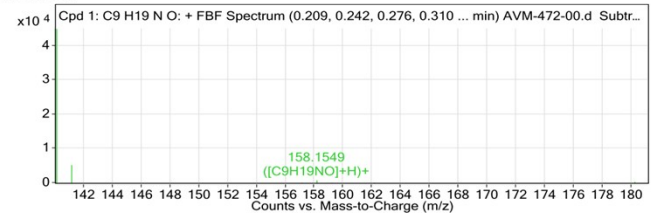
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C9 H19 N O	0.242	157.1458	44827	C9 H19 N O	157.1467	-5.81	C9 H19 N O	C9 H19 N O

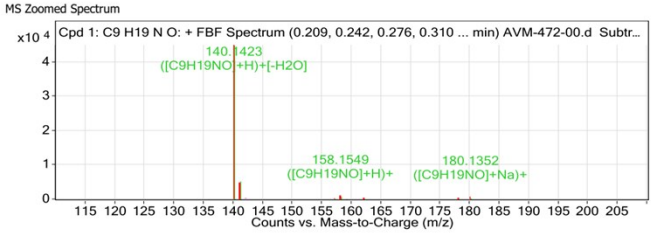
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C9 H19 N O	140.1423	0.242	Find By Formula	157.1458



MS Spectrum

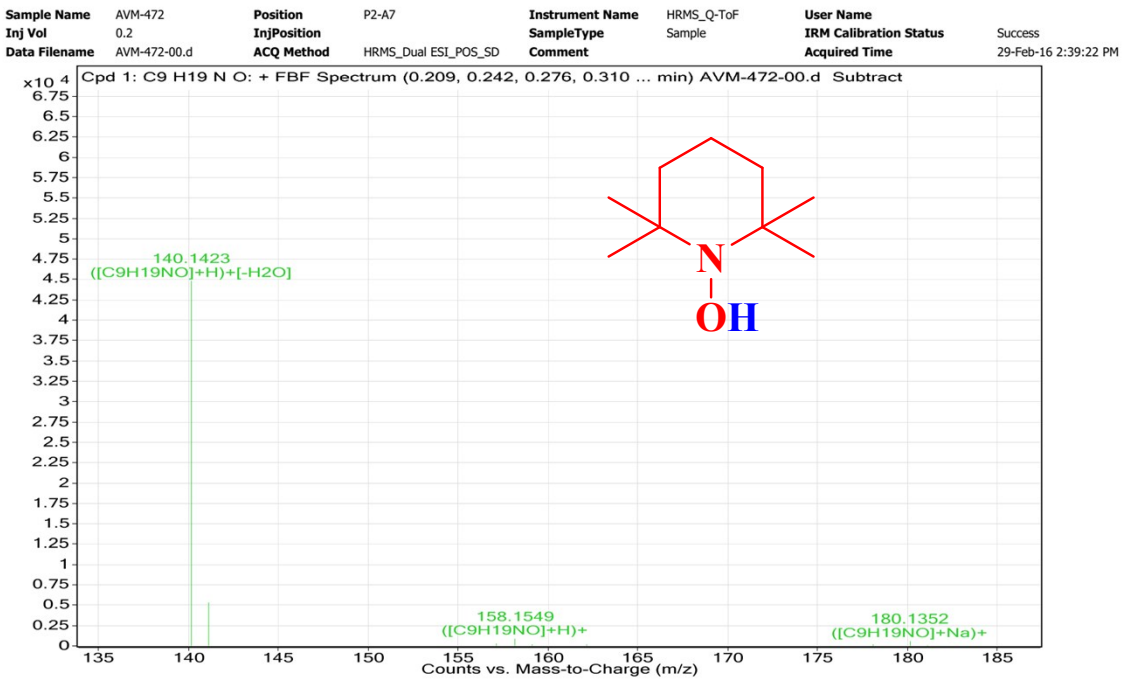


MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
140.1423	1	44826.87	C9H19NO	(M+H)+[-H2O]
141.146	1	5354.23	C9H19NO	(M+H)+[-H2O]
157.1497	1	267.72	C9H19NO	M+

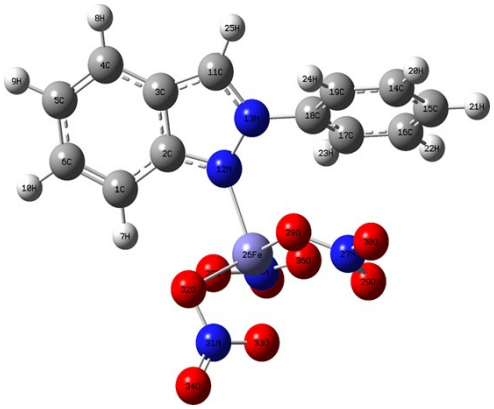


8. Quantum Chemical Calculation

Computational Methods

The quantum chemical calculations were carried out using Gaussian 09 program[6]. The structure was optimized at the M06L[7] meta–GGA level of theory with pseudopotential SDD[8] and 6-31G(d,p) basis set for Fe and other atoms, respectively. The optimized structure has no imaginary frequency. The Hirshfeld[9] charges of atoms were computed at the M06L/6-31G(d,p) level on the optimized structures. NBO[10] analysis for the optimized structure was performed at M06L/6-31G(d,p) level with NBO 3.1 implemented in Gaussian 09 program.

Structure of the optimized complex obtained from quantum chemical calculations



C	-3.25737059	-0.26317235	0.15537335
C	-2.12105211	-1.08645954	0.05472907
C	-2.24061046	-2.46082910	-0.30425429
C	-3.50795582	-3.03394241	-0.53477404
C	-4.61050878	-2.22066052	-0.41977990
C	-4.48042682	-0.85025907	-0.08353318
H	-3.17114055	0.78560819	0.41130060
H	-3.60290499	-4.08355760	-0.79518153
H	-5.60150845	-2.62910452	-0.59088678
H	-5.37725499	-0.24239073	-0.01160570
C	-0.92985015	-2.93884585	-0.32242889
N	-0.80879949	-0.76637995	0.24886865
N	-0.11683233	-1.91691481	-0.00483580
C	3.42711681	-2.73723174	-0.64078236
C	4.03195600	-2.20847111	0.49759050
C	3.25941205	-1.58455206	1.47336666
C	1.88007088	-1.49001345	1.32290760
C	1.29489768	-2.00798354	0.17167927
C	2.05270901	-2.63347214	-0.81508939
H	4.02944360	-3.20412671	-1.41350106
H	5.10870566	-2.27315372	0.61782539
H	3.72632282	-1.16665373	2.35949827
H	1.26633286	-1.01803317	2.08134699
H	1.57268925	-2.98315305	-1.72428217
H	-0.51865741	-3.92551742	-0.47662357
Fe	-0.07272603	1.06649261	0.03455566
N	2.41881777	0.87706622	-1.17642875
O	1.13349963	0.43596668	-1.24780993
O	2.72977842	1.55791098	-0.21092276
O	3.13050515	0.50765078	-2.08988154
N	-0.71459750	2.89309849	-1.37842420
O	-1.33476908	1.74705232	-1.30970204
O	0.28134957	2.93459279	-0.56363555
O	-1.04719097	3.78491264	-2.10458958
N	-0.29522157	1.65209272	2.37751609
O	0.81425144	1.32259318	1.79539708
O	-0.38942459	1.93178182	3.54056436
O	-1.28238024	1.64427547	1.54642546

9. Reference

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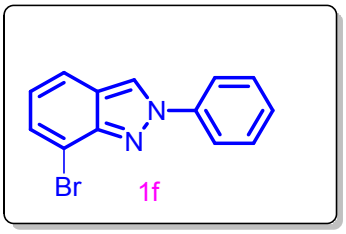
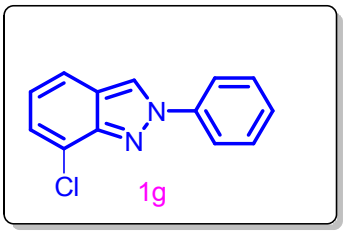
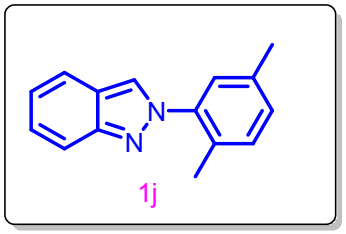
10. <u>Characterization Data of the Products</u>



7-bromo-2-phenyl-2*H*-indazole (1f): Brown Solid (86%); mp 90-92 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3127, 3073, 2924, 2373, 2113, 1635, 1540, 1501, 1291, 903, 806, 729, 645; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.34 (s, 1H), 7.93 - 7.84 (m, 2H), 7.79 (td, 1H, J = 1.0, 9.3 Hz), 7.59 - 7.49 (m, 2H), 7.45 - 7.37 (m, H), 7.32 (dd, 1H, J = 1.0, 2.0 Hz), 7.02 (dd, 1H, J = 2.2, 9.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.0, 140.3, 134.5, 129.6, 128.1, 122.8, 121.0, 120.9, 119.9, 119.8, 107.9; HR-MS (ESI+) m/z calculated for $[C_{13}H_{19}BrN_2]^+$ = $[M+H]^+$: 274.0053; found: 274.0053.

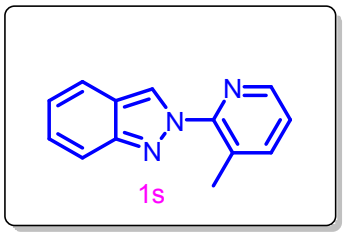


7-chloro-2-phenyl-2*H*-indazole (1g): Yellowish Brown Solid (76%); mp 88-90 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3051, 2925, 2372, 2115, 1522, 1279, 903, 806, 726, 649; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.02 (dd, 1H), 7.32 (dd, 1H), 7.39 - 7.45 (m, 1H), 7.47 - 7.59 (m, 2H), 7.73 - 7.83 (m, 1H), 7.83 - 7.95 (m, 2H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.0, 140.3, 134.5, 129.6, 128.1, 122.8, 121.0, 120.9, 120.0, 119.8, 107.9; HR-MS (ESI+) m/z calculated for $[C13H10ClN2]^+$ = $[M+H]^+$: 182.0115; found: 182.0121.



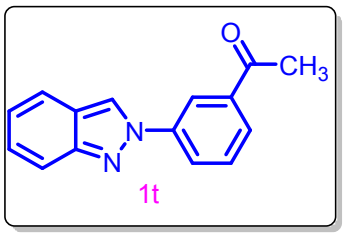
2-(2,5-dimethylphenyl)-2H-indazole (1j): Brown Solid (85%); mp 60-62 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3057, 2921, 2858, 1624, 1518, 1469, 1383, 1345, 1292, 1263, 1132,

814, 783, 755, 611; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.11 (s, 1H), 7.86 (d, 1H, *J* = 8.8 Hz), 7.77 (d, 1H, *J* = 8.3 Hz), 7.38 (t, 1H, *J* = 7.8 Hz), 7.34 - 7.11 (m, 4H), 2.41 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 149.3, 140.1, 136.5, 131.1, 130.4, 129.9, 127.2, 126.4, 124.3, 122.1, 122.0, 120.4, 117.9, 20.8, 17.5; HR-MS (ESI+) m/z calculated for $[C_{15}H_{15}N_2]^+$ = $[M+H]^+$: 223.1230; found: 223.1231.



1s

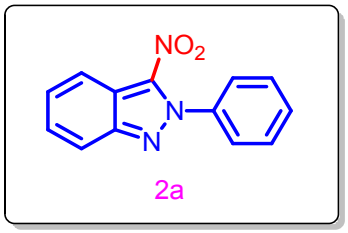
2-(3-methylpyridin-2-yl)-2*H*-indazole (1s): Brownish Yellow Solid (80%); mp 96-98 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3062, 2921, 2853, 1700, 1655, 1606, 1562, 1515, 1473, 1312, 1143, 1057, 947, 908, 789, 755, 735; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.95 (s, 1H), 8.31 - 8.10 (m, 1H), 7.97 (m, 1H), 7.73 - 7.49 (m, 2H), 7.28 - 7.15 (m, 1H), 7.05 - 6.77 (m, 2H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.9, 150.5, 150.2, 148.0, 127.5, 123.8, 122.6, 122.3, 121.2, 120.7, 118.0, 114.5, 21.2; HR-MS (ESI+) m/z calculated for $[C_{13}H_{12}N_3]^+$ = $[M+H]^+$: 210.1026; found: 210.1027.



1t

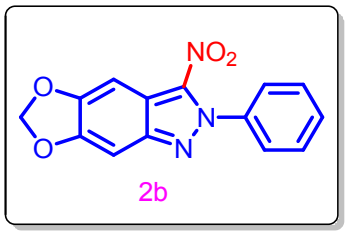
1-(3-(2*H*-indazol-2-yl)phenyl)ethan-1-one (1t): Yellow Solid (80%); mp 62-64 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3062, 2911, 1682, 1586, 1517, 1441, 1387, 1354, 1255, 1052, 782, 752, 733, 682, 589, 541; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.57 - 8.43 (m, 2H), 8.21 - 8.13 (m, 1H), 7.99 (dd, 1H, *J* = 1.0, 7.8 Hz), 7.81 (dd, 1H, *J* = 1.0, 8.8 Hz), 7.75 - 7.70 (m, 1H), 7.64 (t, 1H, *J* = 7.8 Hz), 7.40 - 7.31 (m, 1H), 7.19 - 7.09 (m, 1H), 2.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 197.0, 150.0, 140.9, 138.4, 130.0, 127.5, 127.2, 125.2, 123.0, 122.8, 120.5,

120.2, 118.0, 26.8; HR-MS (ESI+) m/z calculated for $[C_{15}H_{13}N_20]^+$ = $[M+H]^+$: 237.1022; found: 237.1016.



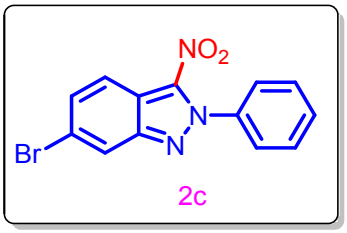
2a

3-nitro-2-phenyl-2*H*-indazole (2a): Lemon yellow Solid (52 mg, 85%); mp 110-112 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3076, 2922, 2851, 1594, 1557, 1490, 1460, 1440, 1382, 1321, 1301, 1266, 1206, 821, 754, 691; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.23 (dt, 1H, J_a=8.3 and J_b = 1.2 Hz), 7.90-7.88 (m, 1H), 7.59-7.51 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147, 139, 130, 129, 129, 128, 125, 120, 119, 118; HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}N_30_2]^+$ = $[M+H]^+$: 240.0768; found: 240.0774.

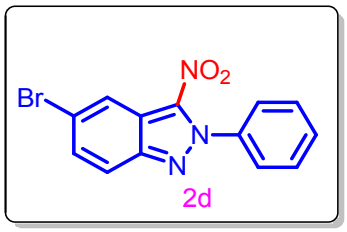


2b

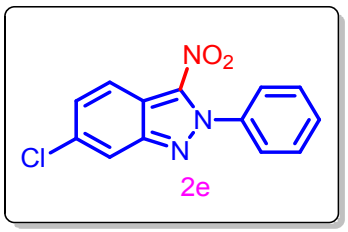
3-nitro-2-(m-tolyl)-2*H*-indazole (2b): Yellow Solid (44 mg, 74%); mp 86-88 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2990, 2882, 1992, 1504, 1476, 1340, 1202, 839, 724, 678; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.55-7.52 (m, 3H), 7.50-7.47 (m, 2H), 7.45 (s, 1H), 7.07 (s, 1H), 6.12 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.3, 150.6, 145, 139.6, 129.7, 129.1, 125.8, 115.8, 102.1, 95.7, 95.4; HR-MS (ESI+) m/z calculated for $[C_{14}H_{10}N_30_4]^+$ = $[M+H]^+$: 284.0666; found: 284.0670.



6-bromo-3-nitro-2-phenyl-2*H*-indazole (2c): Yellow Solid (22 mg, 38%); mp 86-88 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3106, 2991, 2881, 2314, 1989, 1548, 1504, 1392, 1325, 1207, 816, 725; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.12-8.02 (m, 2H), 7.62-7.58 (m, 4H), 7.52-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.7, 139.1, 132.5, 130.3, 129.3, 125.8, 122.4, 121.7, 121.6, 116.6; HR-MS (ESI+) m/z calculated for $[C_{13}H_9BrN_3O_2]^+$ = $[M+H]^+$: 317.9873; found: 317.9871.

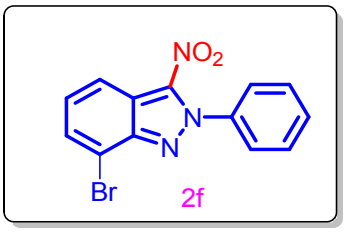


5-bromo-3-nitro-2-phenyl-2*H*-indazole (2d): Golden yellow Solid (26 mg, 45%); mp 102-104 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3108, 2873, 2683, 2308, 1989, 1972, 1633, 1539, 1509, 1372, 1341, 1263, 807, 730,701; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.35 (s, 1H), 7.94-7.80 (m, 2H), 7.70-7.65 (m, 1H), 7.56-7.50 (m, 2H), 7.45-7.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.1, 130.5, 129.7, 129.3, 128.3, 125.8, 123.9, 122.5, 121.0, 119.8, 119.7, 116.0; HR-MS (ESI+) m/z calculated for $[C_{13}H_9BrN_3O_2]^+$ = $[M+H]^+$: 317.9873; found: 317.9874.

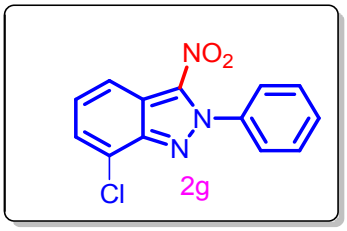


6-chloro-3-nitro-2-phenyl-2*H*-indazole (2e): Brownish orange Solid (21 mg, 35%); mp 98-100 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3055, 2931, 2119, 1687, 1593, 1540, 1492,

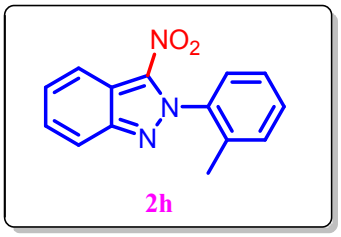
1395, 1326, 1263, 731, 702; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.20 (d, 1H, *J* = 8.3 Hz), 7.62 - 7.54 (m, 3H), 7.54 - 7.49 (m, 2H), 7.47 (d, 1H, *J* = 1.5 Hz), 7.20 (dd, 1H, *Ja* = 2.0 and *Ja* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.5, 140.9, 139.2, 130.2, 129.2, 125.8, 122.9, 122.1, 115.8, 106.6; HR-MS (ESI+) m/z calculated for $[C_{13}H_9BrN_3O_2]^+$ = $[M+H]^+$: 317.9873; found: 317.9871.



7-bromo-3-nitro-2-phenyl-2*H*-indazole (2f): Golden yellow Solid (28 mg, 38%); mp 102-104 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2921, 2851, 2113, 1648, 1492, 1386, 1345, 1304, 1249, 1182, 893, 808, 757, 645; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.93 - 7.75 (m, 2 H), 7.67 - 7.47 (m, 6 H), 7.15 (dd, J = 2.0, 9.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): 145.3, 141.7, 139.4, 130.2, 129.2, 125.8, 122.8, 121.5, 119.1, 107.8; HR-MS (ESI+) m/z calculated for $[C_{13}H_9BrN_3O_2]^+$ = $[M+H]^+$: 317.9873; found: 317.9876.

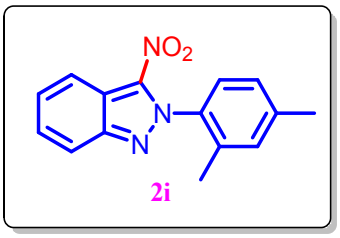


7-chloro-3-nitro-2-phenyl-2*H*-indazole (2g): Orange Solid (18 mg, 30%); mp 104-106 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2921, 2851, 2110, 1594, 1490, 1387, 1303, 1248, 1302, 1147, 907, 834, 738, 688, 600; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.93 - 7.78 (m, 2H), 7.64 - 7.49 (m, 5H), 7.19 - 7.13 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 145.3, 141.7, 139.4, 130.2, 129.2, 125.8, 122.8, 121.5, 119.1, 107.8; HR-MS (ESI+) m/z calculated for $[C_{13}H_9BrN_3O_2]^+$ = $[M+H]^+$: 317.9873; found: 317.9870.



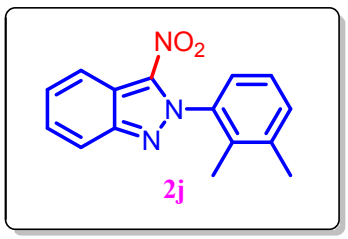
2h

3-nitro-2-(*o*-tolyl)-2*H*-indazole (2h): Brown Solid (27 mg, 45%); mp 60-62 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2923, 2854, 1498, 1459, 1385, 1318, 1202, 821, 755, 720, 635; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.27-8.25 (m, 1H), 7.91-7.89 (m, 1H), 7.59-7.47 (m, 3H), 7.42-7.37 (m, 2H), 7.32-7.30 (m, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.5, 139.0, 134.6, 131.0, 128.9, 128.3, 126.8, 126.3, 120.4, 119.4, 117.3, 17.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_30_2]^+$ = $[M+H]^+$: 254.0924; found: 254.0927.



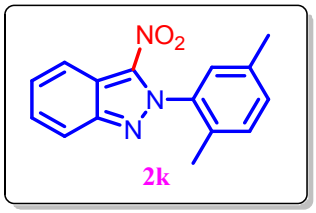
2i

2-(2,4-dimethylphenyl)-3-nitro-2*H*-indazole (2i): Brown Solid (45 mg, 75%); mp: 120-122 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3018, 2923, 2203, 1558, 1499, 1386, 1319, 1212, 1118, 1042, 826, 755, 612; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.25 - 8.23 (m, 1H) 7.90 - 7.87 (m, 1H) 7.46 - 7.61 (m, 2H) 7.15 - 7.23 (m, 3H) 2.44 (s, 3H) 2.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.39, 140.48, 136.60, 134.19, 131.65, 128.81, 128.25, 127.45, 126.11, 120.48, 119.44, 117.40, 21.32, 17.02; HR-MS (ESI+) m/z calculated for $[C_{15}H_{14}N_3O_2]^+$ = $[M+H]^+$: 268.1081; found: 268.1083.



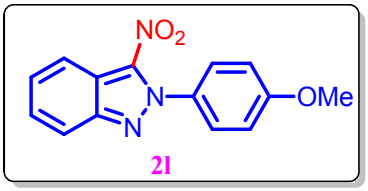
2j

2-(2,3-dimethylphenyl)-3-nitro-2*H*-indazole (2j): Brown Solid (42 mg, 70%); mp: 140-142 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3073, 2981, 2317, 1558, 1501, 1474, 1388, 1321, 1199, 822, 755; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.22 - 8.28 (m, 1H), 7.86 - 7.92 (m, 1H), 7.49 - 7.61 (m, 2H), 7.38 (d, 1H, *J* = 7.82 Hz), 7.27 - 7.30 (m, 1H), 7.16 (d, 1H, *J* = 7.82 Hz), 2.39 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.38, 139.14, 138.46, 133.22, 131.71, 128.85, 128.29, 126.18, 124.01, 120.48, 119.45, 117.33, 20.25, 13.96; HR-MS (ESI+) m/z calculated for $[C_{15}H_{14}N_3O_2]^+ = [M+H]^+$: 268.1081; found: 268.1083.



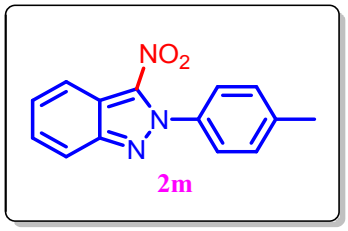
2k

2-(2,5-dimethylphenyl)-3-nitro-2*H*-indazole (2k): Orange Solid (30 mg, 50%); mp 68-70 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3032, 2916, 1938, 1610, 1489, 1385, 1306, 1196, 821, 784, 750; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.22 - 8.28 (m, 1H), 7.86 - 7.93 (m, 1H), 7.48 - 7.60 (m, 2H), 7.24 - 7.32 (m, 2H), 7.13 (s, 1H), 2.39 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.4, 138.9, 136.8, 131.3, 131.1, 130.8, 128.8, 128.3, 126.7, 120.5, 119.4, 117.3, 20.8, 16.6; HR-MS (ESI+) m/z calculated for $[C_{15}H_{14}N_3O_2]^+ = [M+H]^+$: 268.1081; found: 268.1074.



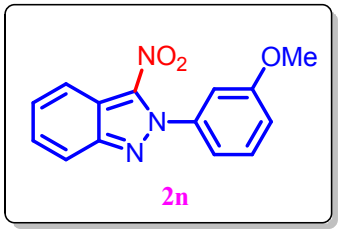
2l

2-(4-methoxyphenyl)-3-nitro-2*H*-indazole (2l): Yellow solid (57 mg, 95%); mp 130-132 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2993, 2944, 2839, 1800, 1602, 1509, 1387, 1324, 1301, 1255, 832, 749; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.17 - 8.22 (m, 1H), 7.84 - 7.89 (m, 1H), 7.48 - 7.55 (m, 2H), 7.42 - 7.48 (m, 2H), 7.03 - 7.07 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.7, 147.1, 132.3, 128.8, 128.3, 127.1, 120.4, 119.3, 118.2, 114.3, 55.7; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O_3]^+ = [M+H]^+$: 270.0873; found: 270.0877.



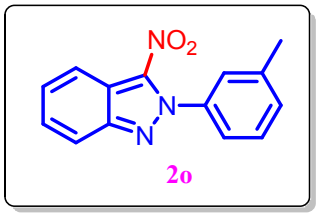
2m

3-nitro-2-(*p*-tolyl)-2*H*-indazole (2m): Light yellow solid (58 mg, 96%); mp 148-150 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3075, 2992, 2945, 2315, 1537, 1509, 1389, 1324, 1301, 1209, 1145, 820, 750, 663; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.21 (dt, 1H, J = 8.31, 1.22 Hz), 7.80 - 7.95 (1H, m), 7.45 - 7.63 (2H, m), 7.32 - 7.45 (4H, m), 2.48 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 147.2, 140.4, 137.0, 129.8, 128.9, 128.3, 125.6, 120.4, 119.4, 118.2, 21.4; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O_2]^+ = [M+H]^+$: 254.0924; found: 254.0925.



2n

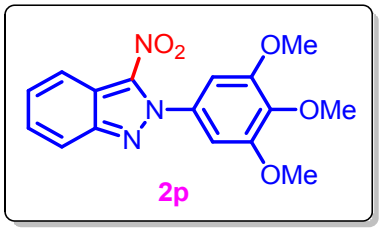
2-(3-methoxyphenyl)-3-nitro-2*H*-indazole (2n): Yellow solid (44 mg, 74%); mp 120-122 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3075, 2942, 2836, 2317, 1606, 1495, 1437, 1386, 1319, 1242, 1206, 1132, 1035, 821, 754; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.12 - 8.22 (m, 1H), 7.80 - 7.90 (m, 1H), 7.40 - 7.58 (m, 3H), 7.01 - 7.14 (m, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.1, 147.3, 140.4, 130.0, 129.0, 128.4, 120.4, 119.4, 118.1, 118.1, 116.2, 111.5, 55.7; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O_3]^+ = [M+H]^+$: 270.0873; found: 270.0873.



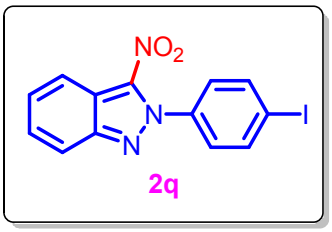
2o

3-nitro-2-(*m*-tolyl)-2*H*-indazole (2o): Lemon yellow solid (48 mg, 79%); mp 122-124 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2952, 2830, 1504, 1449, 1385, 1320, 1196, 1117, 822, 754,

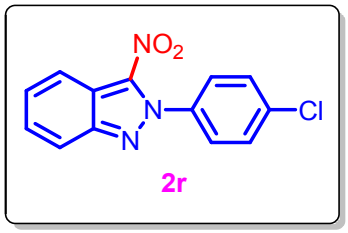
654; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.15 - 8.24 (m, 1H), 7.82 - 7.90 (m, 1H), 7.40 - 7.55 (m, 3H), 7.27 - 7.40 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 139.5, 139.5, 130.9, 129.0, 128.9, 128.4, 126.3, 122.9, 120.4, 119.3, 118.2, 21.3; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O_2]^+ = [M+H]^+$: 254.0924; found: 254.0925.



3-nitro-2-(3,4,5-trimethoxyphenyl)-2*H*-indazole (2p): Reddish yellow solid (50 mg, 88%); mp 142-144 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3002, 2943, 2832, 1600, 1503, 1461, 1334, 1309, 1126, 838, 752; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.21 (d, 1H, J = 7.34 Hz), 7.88 (d, 1H, J = 7.83 Hz), 7.49 - 7.59 (m, 2H), 6.74 (s, 2H), 3.94 (s, 3H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 153.5, 147.2, 139.4, 134.9, 129.1, 128.5, 120.4, 119.3, 118.1, 103.6, 61.1, 56.4; HR-MS (ESI+) m/z calculated for $[C_{16}H_{16}N_3O_5]^+ = [M+H]^+$: 330.1084; found: 330.1089.

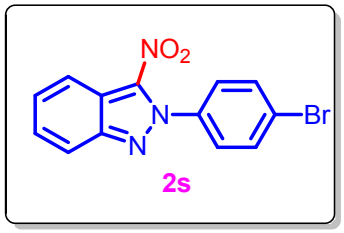


2-(4-iodophenyl)-3-nitro-2*H*-indazole (2q): Yellow solid (44 mg, 77%); mp 136-138 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3065, 2922, 2852, 2203, 1495, 1386, 1322, 1207, 779, 727; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.21 (d, 1H, J = 8.3 Hz), 7.97 - 7.82 (m, 3H), 7.60 - 7.47 (m, 2H), 7.28 (d, 2H, J = 8.3 Hz, 2H; ^{13}C NMR (100 MHz, $CDCl_3$): 147.6, 139.2, 138.4, 129.3, 128.7, 127.6, 120.4, 119.4, 118.3, 96; HR-MS (ESI+) m/z calculated for $[C_{13}H_9N_3O_2I]^+ = [M+H]^+$: 365.9734; found: 365.9739.



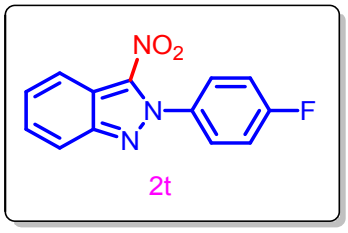
2r

2-(4-chlorophenyl)-3-nitro-2*H*-indazole (2r): Yellow solid (39 mg, 65%); mp 132-134 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3054, 2922, 2854, 1771, 1684, 1572, 1507, 1457, 1264, 730, 702, 518; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.21 (d, 1H, *J* = 8.31 Hz), 7.88 (d, 1H, *J* = 8.31 Hz), 7.45 - 7.58 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.5, 137.9, 136.3, 129.5, 129.3, 128.7, 127.2, 120.4, 119.4, 118.3; HR-MS (ESI+) m/z calculated for $[C_{13}H_9N_3O_2Cl]^+$ = $[M+H]^+$: 274.0378; found: 274.0387.



2s

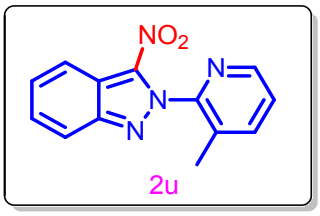
2-(4-bromophenyl)-3-nitro-2*H*-indazole (2s): Yellow solid (42 mg, 72%); mp 160-162 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3159, 3098, 2919, 1929, 1770, 1494, 1387, 1310, 1207, 832, 752, 604, 582; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.22 (d, 1H, *J* = 8.80 Hz), 7.88 (d, 1H, *J* = 8.31 Hz), 7.71 (d, 2H, *J* = 8.31 Hz), 7.47 - 7.59 (m, 2H), 7.42 (d, 2H, *J* = 8.31 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 147.5, 138.4, 132.4, 129.3, 128.7, 127.5, 124.3, 120.4, 119.4; HR-MS (ESI+) m/z calculated for $[C_{13}H_9N_3O_2Br]^+$ = $[M+H]^+$: 317.9873; found: 317.9869.



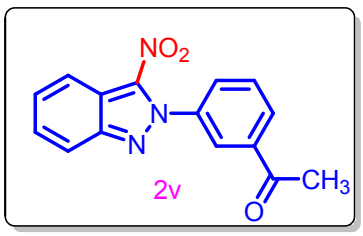
2t

2-(4-fluorophenyl)-3-nitro-2*H*-indazole (2t): Yellow solid; (21mg, 35%); mp 190-192 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3076, 2923, 2853, 1599, 1505, 1493, 1391, 1312, 1236,

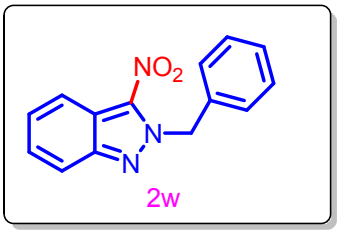
1312, 1264, 1209, 838, 753, 731; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.22 (dt, 1H, J_a = 8.31 and J_b = 1.22 Hz), 7.85 - 7.90 (m, 1H), 7.48 - 7.58 (m, 4H), 7.23 - 7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.5, 162.0, 147.4, 135.5, 129.2, 128.6, 128.0, 127.9, 120.4, 119.4, 118.2, 116.4, 116.2; HR-MS (ESI+) m/z calculated for $[C_{13}H_8N_3O_2F]$+= $[M+H]^+$: 258.0673; found: 258.0676.



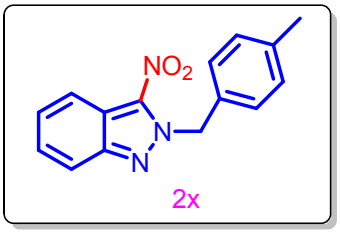
2-(3-methylpyridin-2-yl)-3-nitro-2*H*-indazole (2u): Brown solid (30 mg, 50%); mp 86-88 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3074, 2925, 1503, 1461, 1392, 1322, 1304, 1210, 1072, 821, 794, 750; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.13 - 8.19 (m, 1H), 7.84 - 7.92 (m, 2H), 7.46 - 7.54 (m, 3H), 7.37 (d, 1H, J = 7.34 Hz), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.0, 151.0, 147.5, 139.0, 128.9, 128.6, 124.8, 120.1, 119.5, 118.0, 117.0, 24.1; HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}N_4O_2]^+$ = $[M+H]^+$: 255.0877; found: 255.0884.



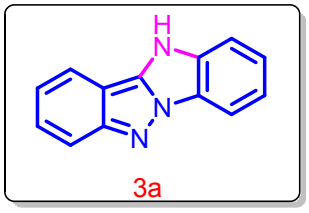
1-(3-(3-nitro-2*H*-indazol-2-yl)phenyl)ethanone (2v): Yellow Solid (18 mg, 30%); mp 168-170 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} =3073, 2930, 1980, 1686, 1536, 1499, 1388, 1305, 1250, 1142, 822, 754, 688, 588; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.25 - 8.09 (m, 3H), 7.91 - 7.84 (m, 1H), 7.76 - 7.66 (m, 2H), 7.60 - 7.48 (m, 2H), 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 196.3, 147.6, 140.0, 138.1, 130.3, 129.8, 129.6, 129.4, 128.8, 125.9, 120.4, 119.4, 118.2, 26.7; HR-MS (ESI+) m/z calculated for $[C_{15}H_{12}N_3O_2]^+$ = $[M+H]^+$: 282.0873; found: 282.0879.



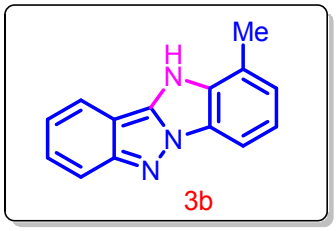
2-benzyl-3-nitro-2*H*-indazole (2w): Yellowish brown solid (36 mg, 60%); mp: 74-76 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3150, 3036, 1559, 1495, 1440, 1408, 1334, 1287, 1245, 1173, 821, 754, 707; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.12 - 8.18 (m, 1H), 7.84 - 7.89 (m, 1H), 7.43 - 7.51 (m, 2H), 7.28 - 7.38 (m, 5H), 6.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.5, 134.5, 128.9, 128.7, 128.6, 128.1, 127.9, 120.5, 119.2, 118.3, 58.2; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O_2]^+ = [M+H]^+$: 254.0924; found: 254.0917.



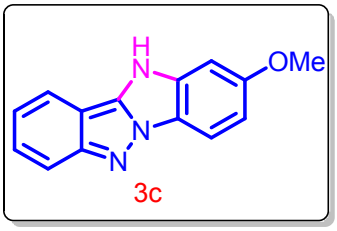
2-(4-methylbenzyl)-3-nitro-2*H*-indazole (2x): Dark yellow solid (26 mg, 43%); mp 82-84 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3029, 2924, 2854, 1950, 1561, 1495, 1441, 1400, 1335, 1291, 1245, 1170, 1099, 823, 752, 732; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.19 - 8.11 (m, 1H), 7.89 - 7.82 (m, 1H), 7.51 - 7.41 (m, 2H), 7.27 (d, 2H, J = 7.8 Hz), 7.12 (d, 2H, J = 7.8 Hz), 6.09 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.4, 138.5, 131.6, 129.5, 128.6, 128.1, 127.8, 120.4, 119.2, 118.4, 58.0, 21.2; HR-MS (ESI+) m/z calculated for $[C_{15}H_{14}N_3O_2]^+ = [M+H]^+$: 268.1081; found: 254.1094.



11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3a): Red solid (38 mg, 88%); mp 40-42 ℃; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3398, 3065, 2924, 2853, 1990, 1744, 1585, 1502, 1270, 1148, 1071, 774, 686; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.02 - 8.07 (m, 2 H), 7.90 (m, 1 H), 7.85 (m, 1 H), 7.70 (m, 1 H), 7.50 - 7.62 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): 153.2, 152.3, 133.6, 133.4, 132.5, 130.9, 129.3, 123.7, 117.1, 116.9, 113.2; HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}N_3]^+ = [M+H]^+$: 208.0869; found: 208.0865.

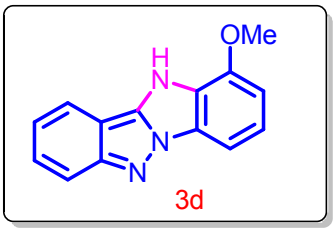


1-methyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3b): Red solid (28 mg, 68%); mp 42-44 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3053, 3922, 2854, 2230, 1593, 1477, 1433, 1264, 1095, 883, 764, 734, 686; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.82 - 7.91 (m, 4 H), 7.70 (m, 1 H), 7.55 (m, 1 H), 7.40 - 7.46 (m, 1 H), 7.34 - 7.38 (m, 1 H), 2.47 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 152.3, 139.2, 133.6, 133.3, 133.3, 130.7 129.1, 123.8, 121.3, 117.2, 116.9, 112.9, 21.3; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3]^+ = [M+H]^+$: 222.1026; found: 222.1030.



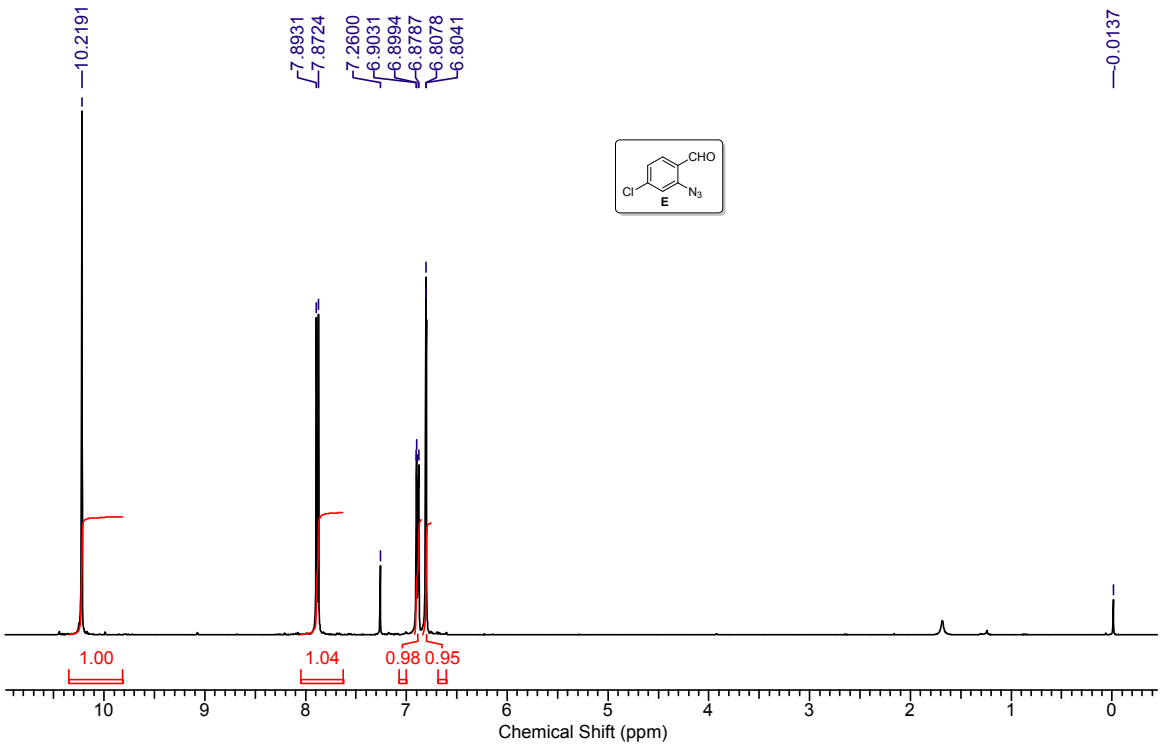
2-methoxy-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3c): Red solid (30 mg, 70%); mp 100–102 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3398, 3091, 2955, 2923, 2230, 2172, 1598, 1504, 1262, 1146, 1023, 838, 768, 743, 604; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.00 - 8.06 (m, 2 H), 7.80 - 7.90 (m, 2 H), 7.64 - 7.71 (m, 1 H), 7.47 - 7.53 (m, 1 H), 7.01 - 7.07 (m, 2 H), 3.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.3, 153.5, 146.8, 133.5, 133.3, 130.2, 125.9, 117.1,

117.0, 114.4, 112.6, 55.7; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O]^+$ = $[M+H]^+$: 238.0975; found: 238.0982.

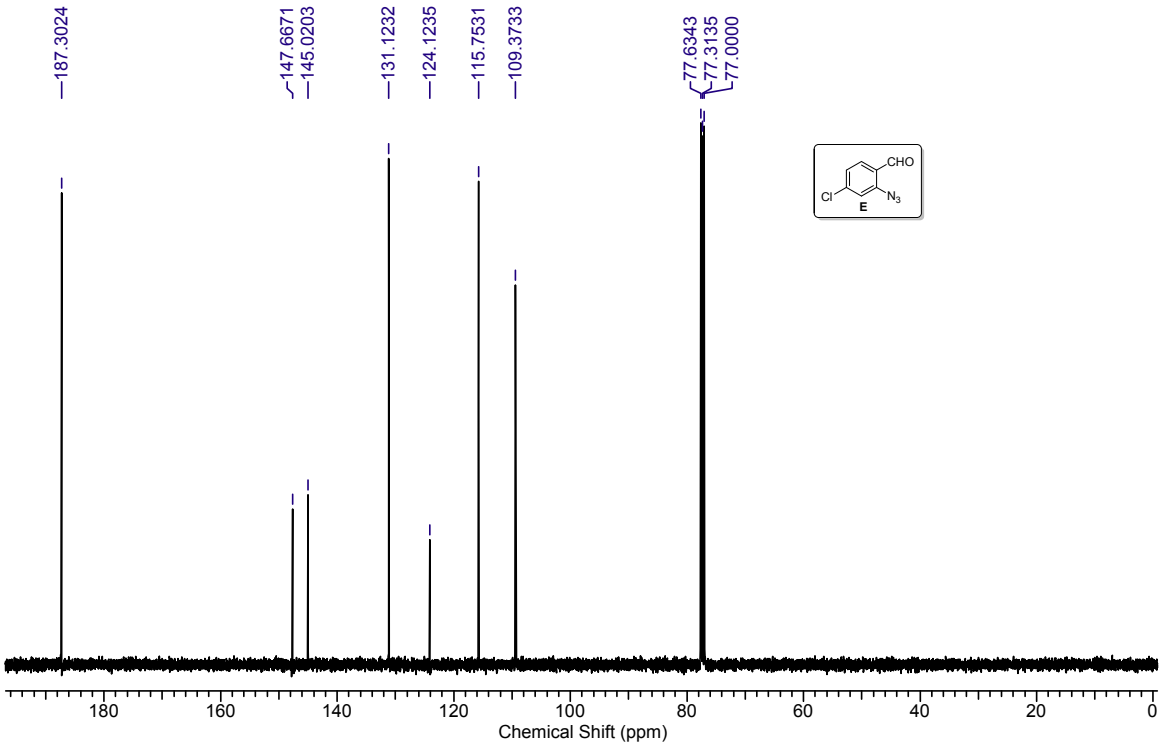


1-methoxy-11*H*-benzo[4,5]imidazo[1,2-b]indazole (3d): Red solid (37 mg, 85%); mp 64-66 °C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3398, 3077, 2934, 2229, 1989, 1955, 1601, 1487, 1478, 1284, 1257, 1132, 1040, 862, 766, 681; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.94 - 7.82 (m, 2 H), 7.74 - 7.64 (m, 2 H), 7.60 - 7.53 (m, 2 H), 7.46 (t, *J* = 8.1 Hz, 1 H), 7.11 (td, *J* = 1.7, 8.4 Hz, 1 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.4, 153.5, 153.1, 133.7, 133.4, 130.9, 130.0, 119.5, 118.3, 117.2, 116.9, 113.2, 106.1, 55.5; HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O]^+$ = $[M+H]^+$: 238.0975; found: 238.0980.

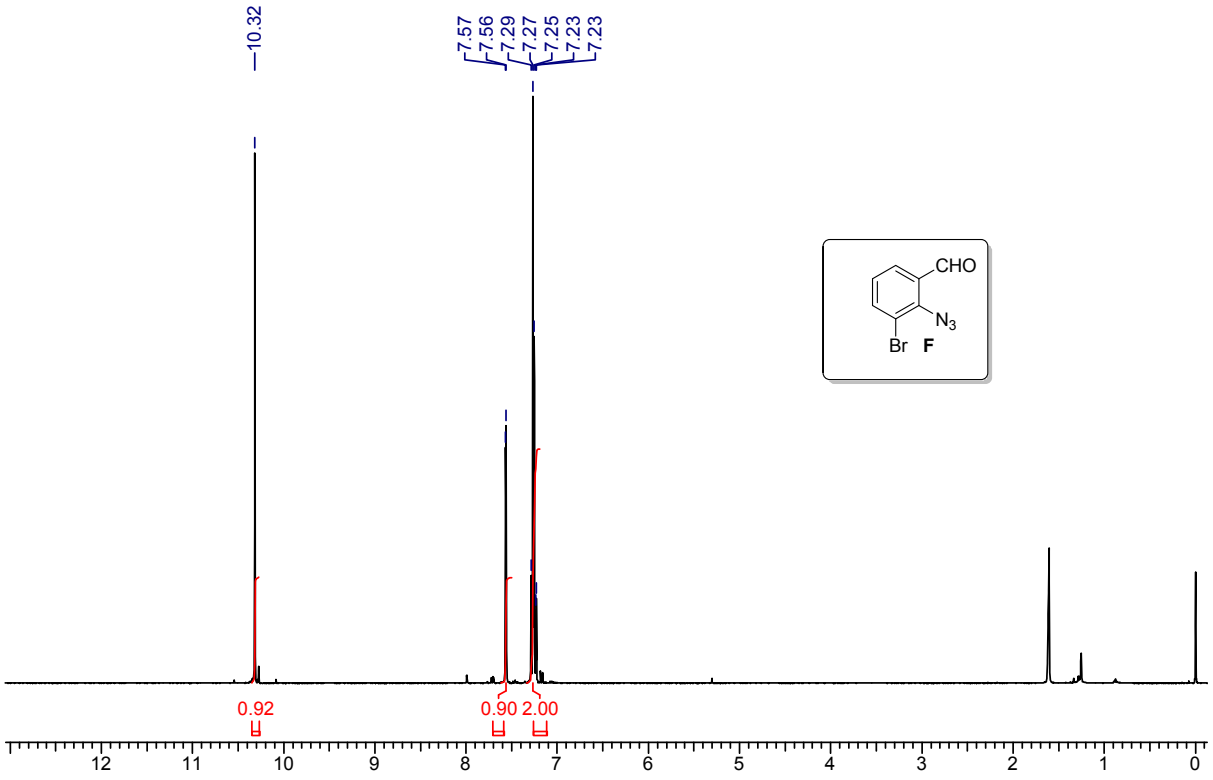
11. Copies of ^1H, ^{13}C NMR spectra for the all compounds



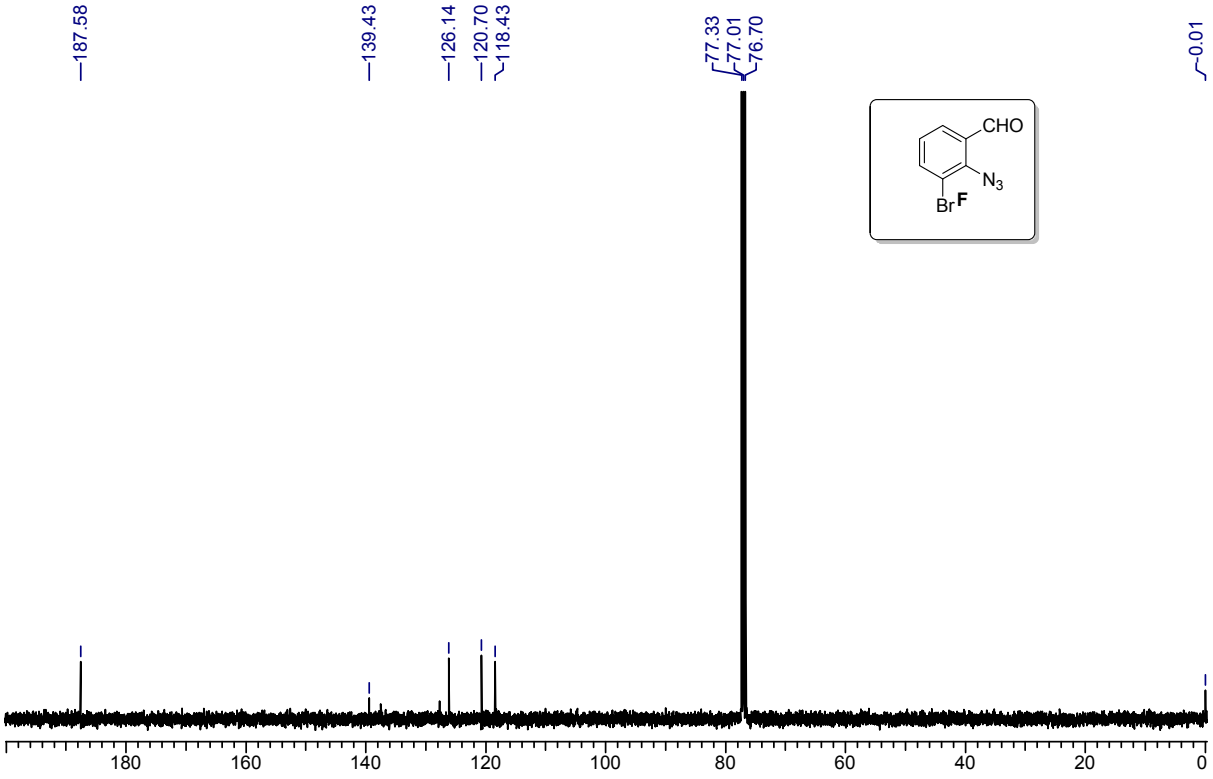
^{1}H NMR (400 MHz) spectrum of compound **E** in $CDCl_3$



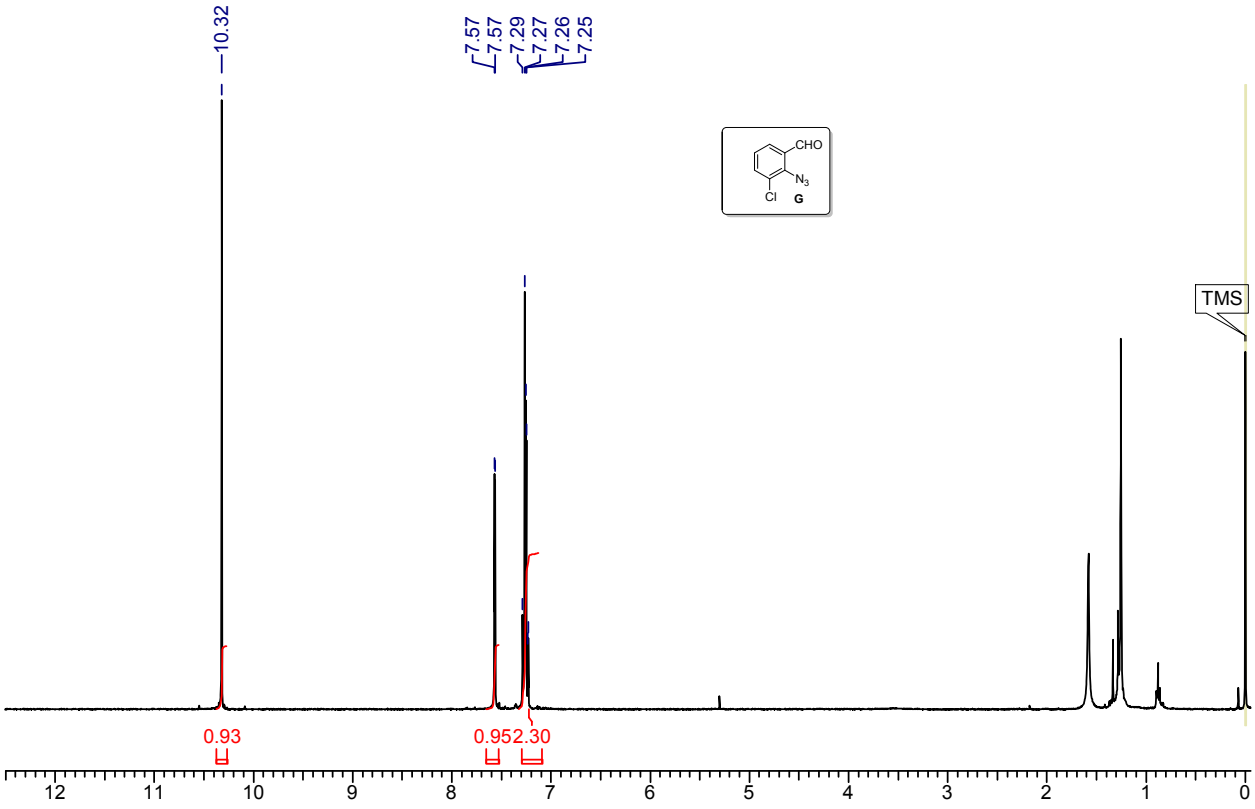
^{13}C NMR (100 MHz) spectrum of compound **E** in $CDCl_3$



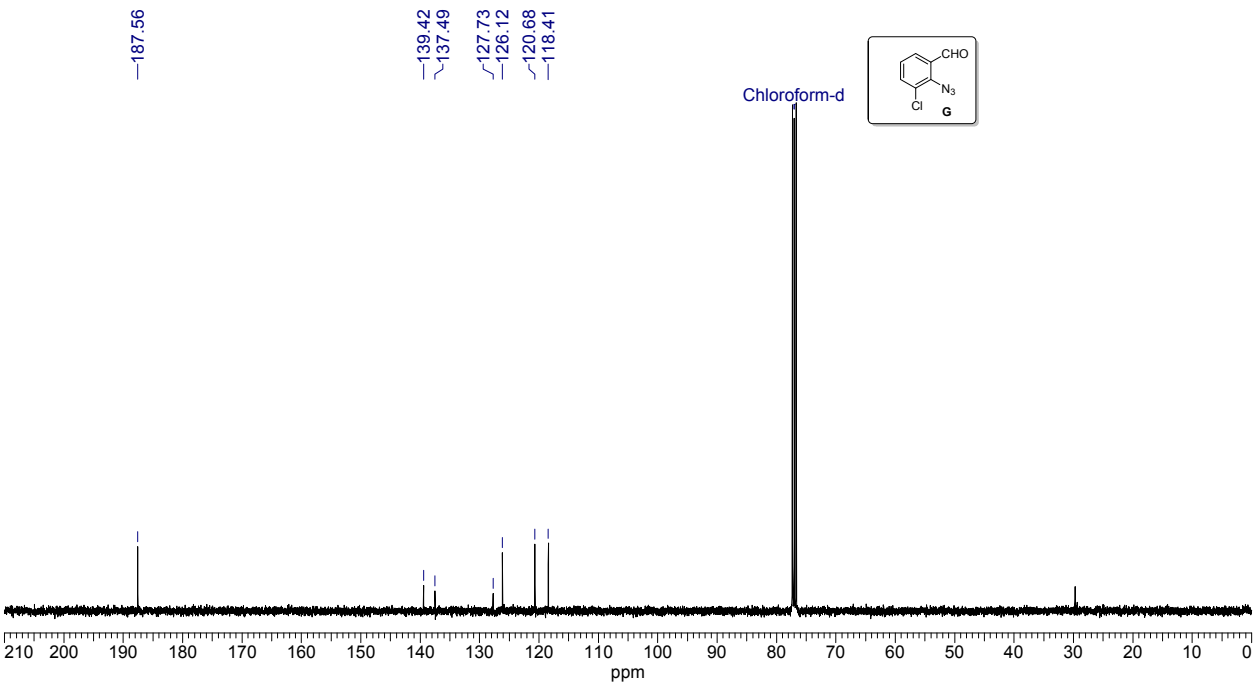
^{1}H NMR (400 MHz) spectrum of compound **F** in $CDCl_3$



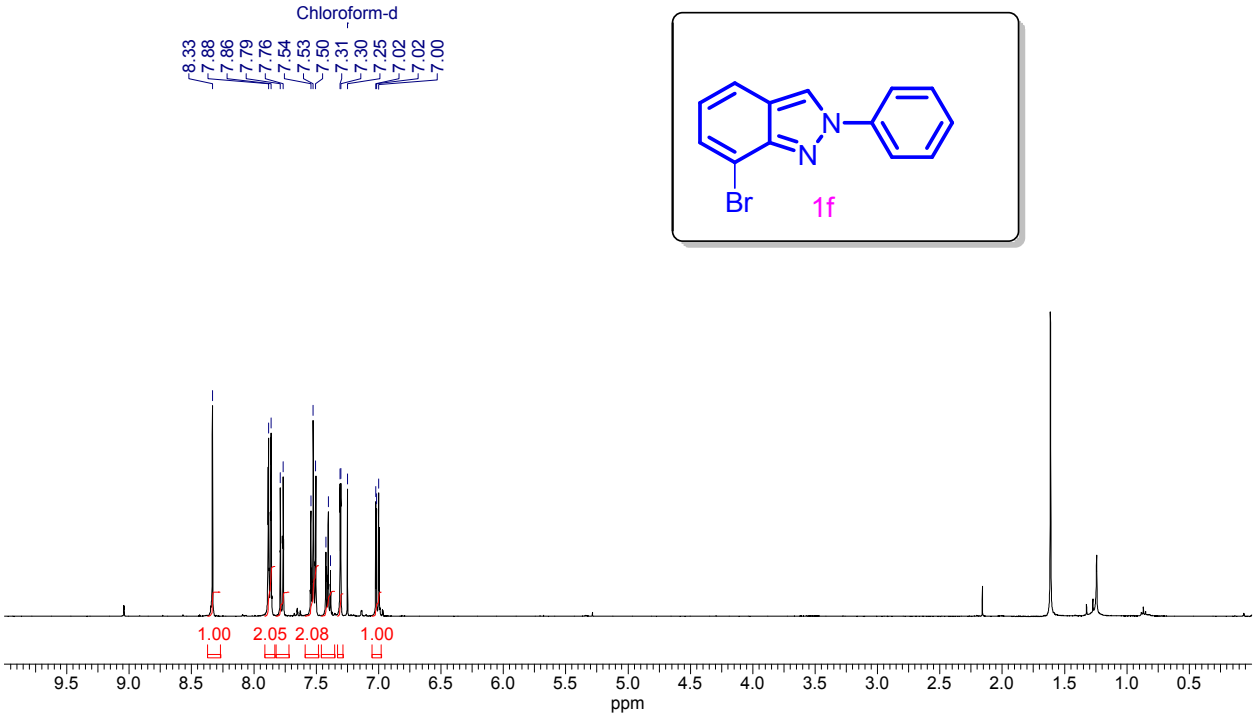
^{13}C NMR (100 MHz) spectrum of compound F in $CDCl_3$



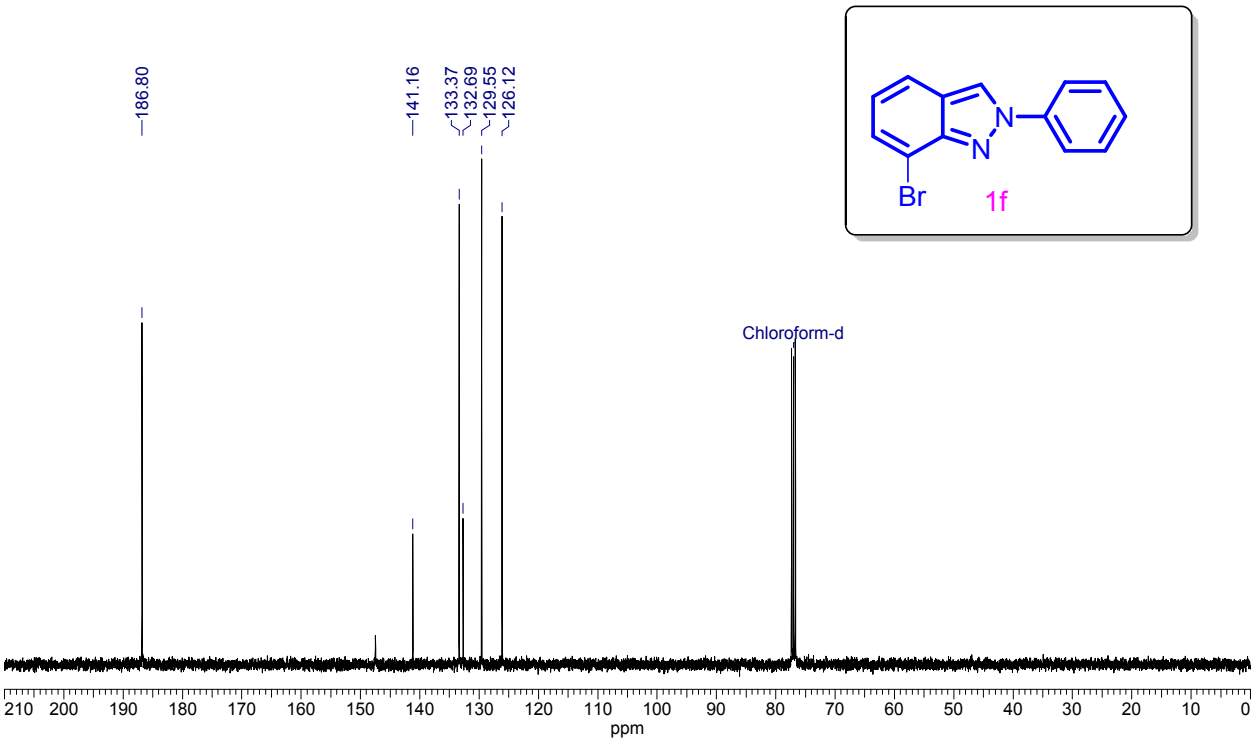
^{1}H NMR (400 MHz) spectrum of compound **G** in $CDCl_3$



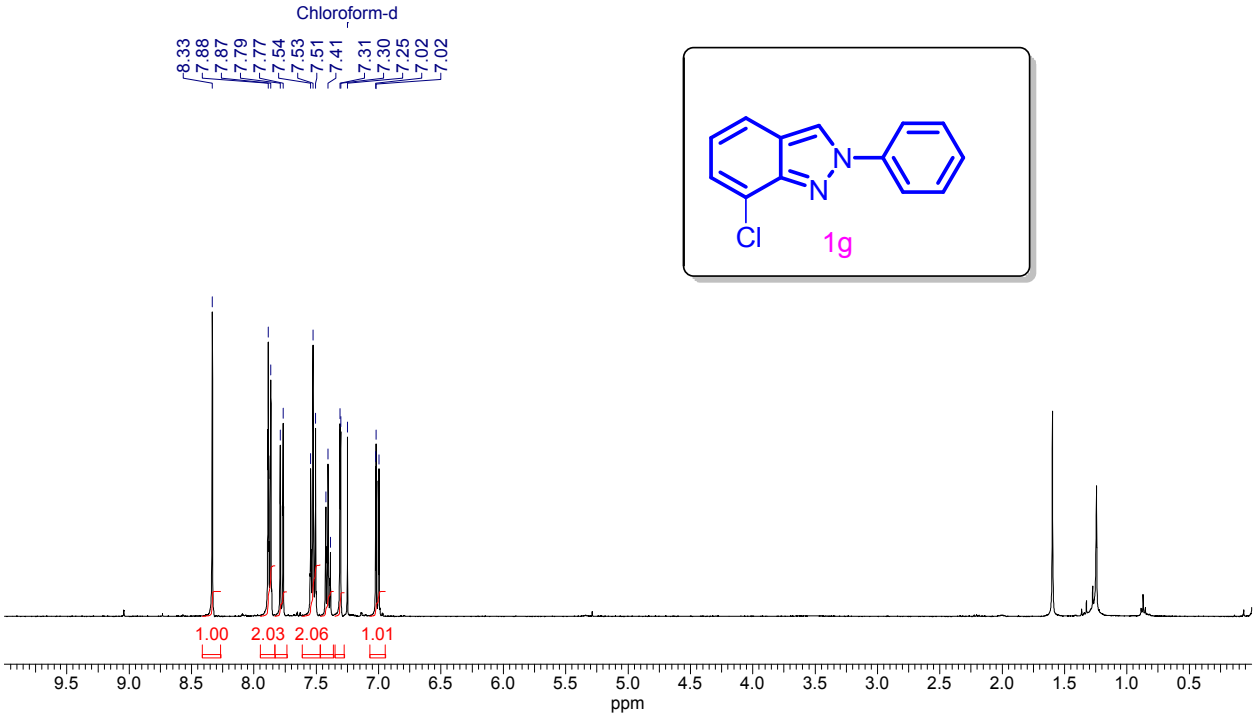
^{13}C NMR (100 MHz) spectrum of compound **G** in $CDCl_3$



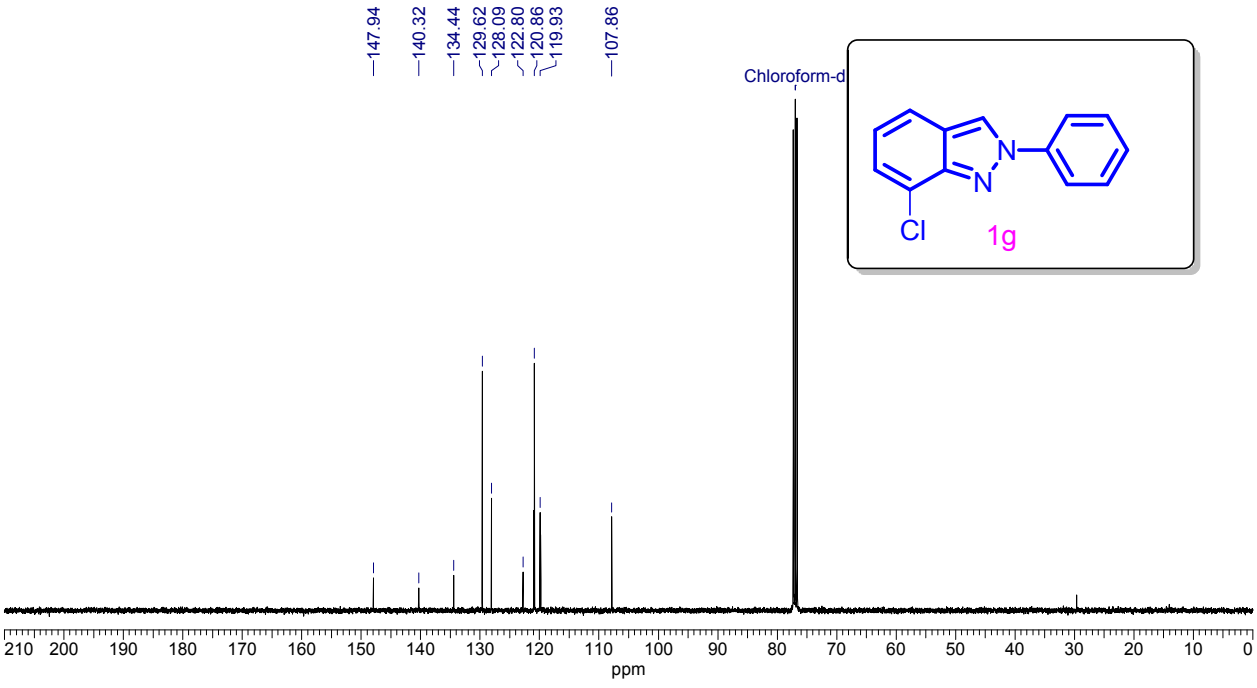
^{1}H NMR (400 MHz) spectrum of compound **1f** in $CDCl_3$



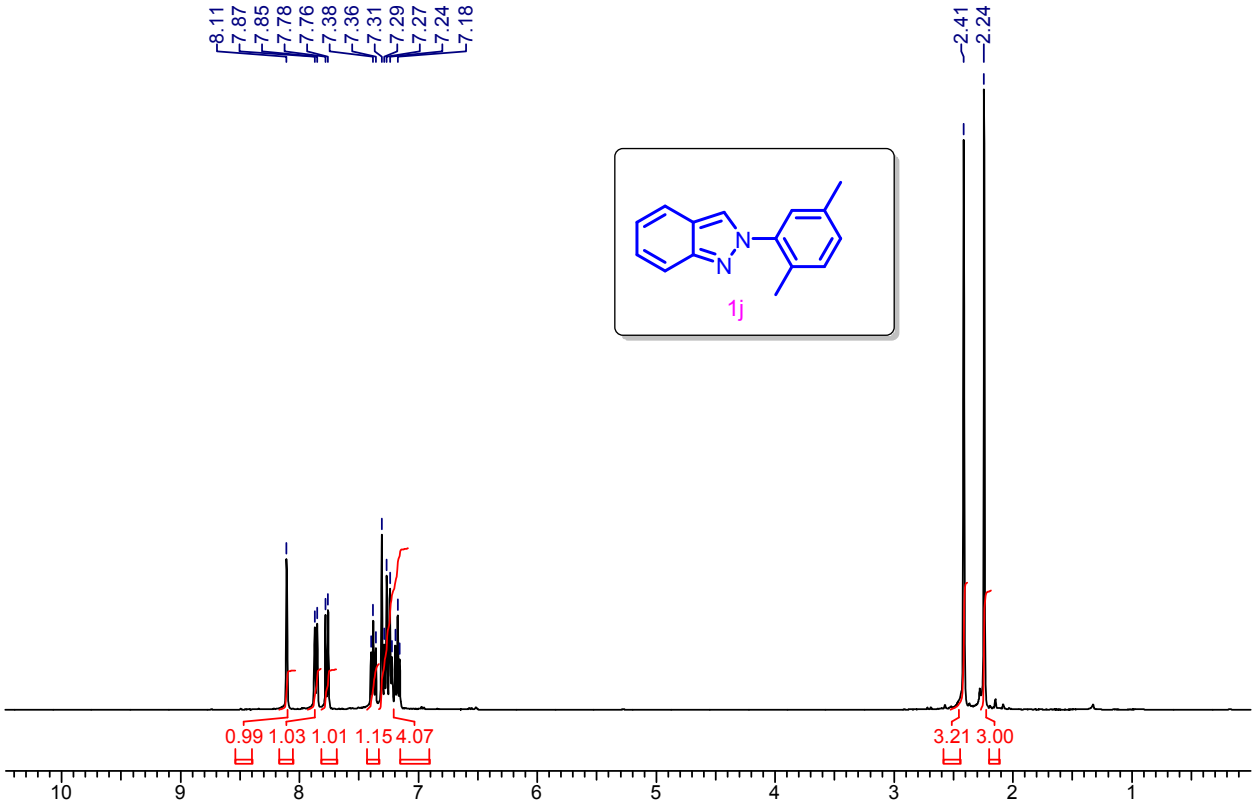
^{13}C NMR (400 MHz) spectrum of compound **1f** in $CDCl_3$



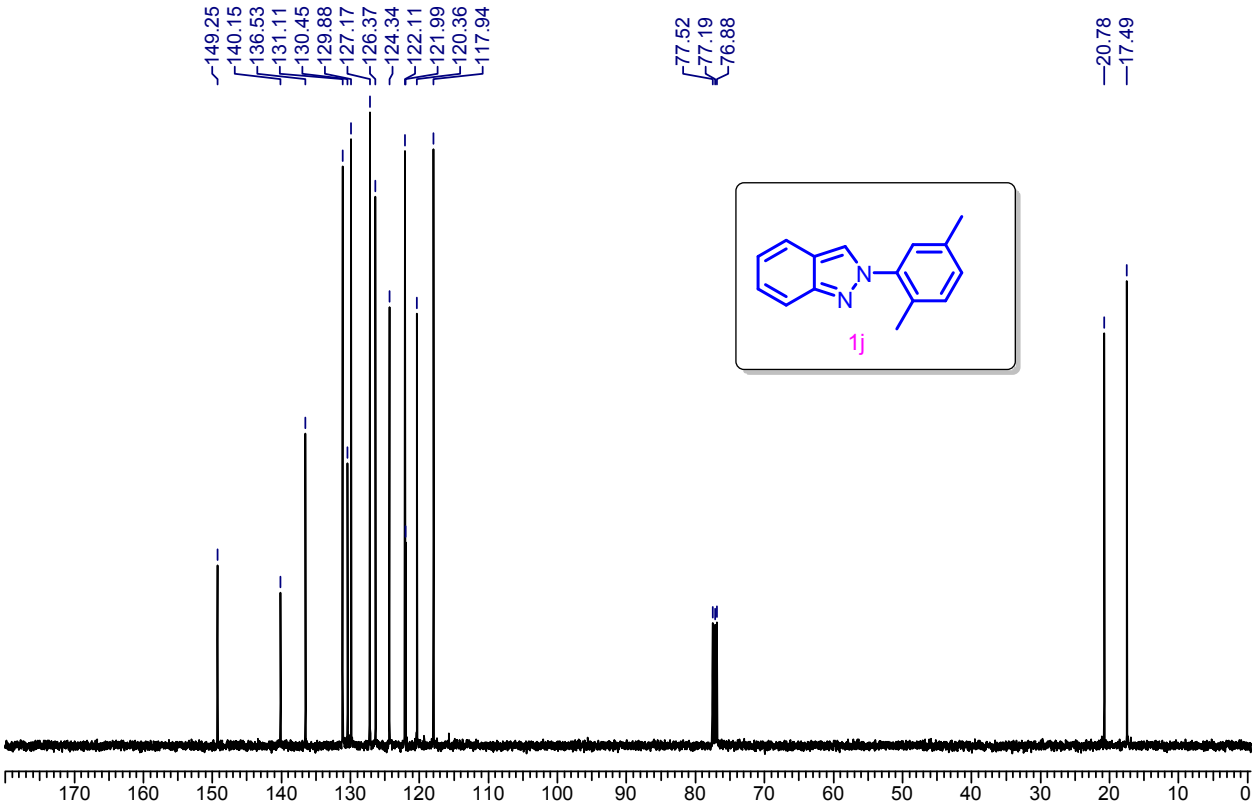
^{1}H NMR (400 MHz) spectrum of compound **1g** in $CDCl_3$



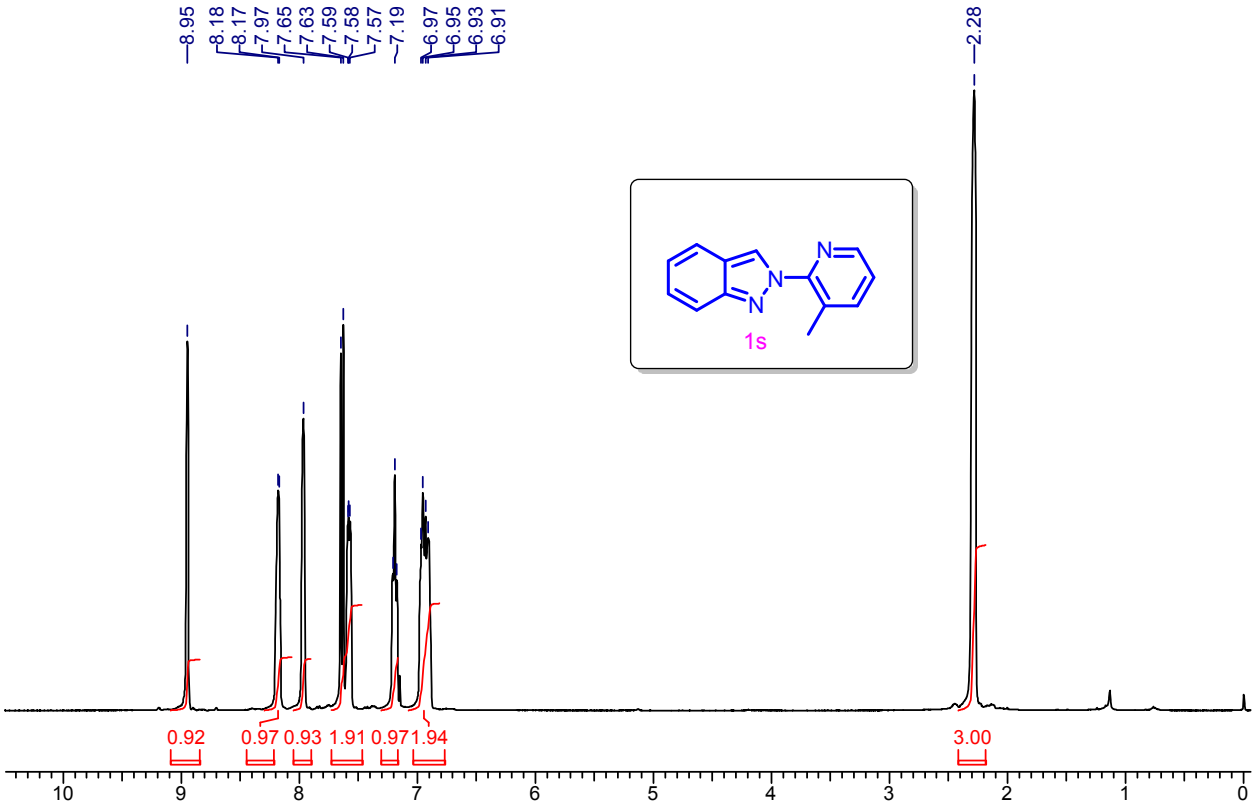
^{13}C NMR (400 MHz) spectrum of compound **1f** in $CDCl_3$



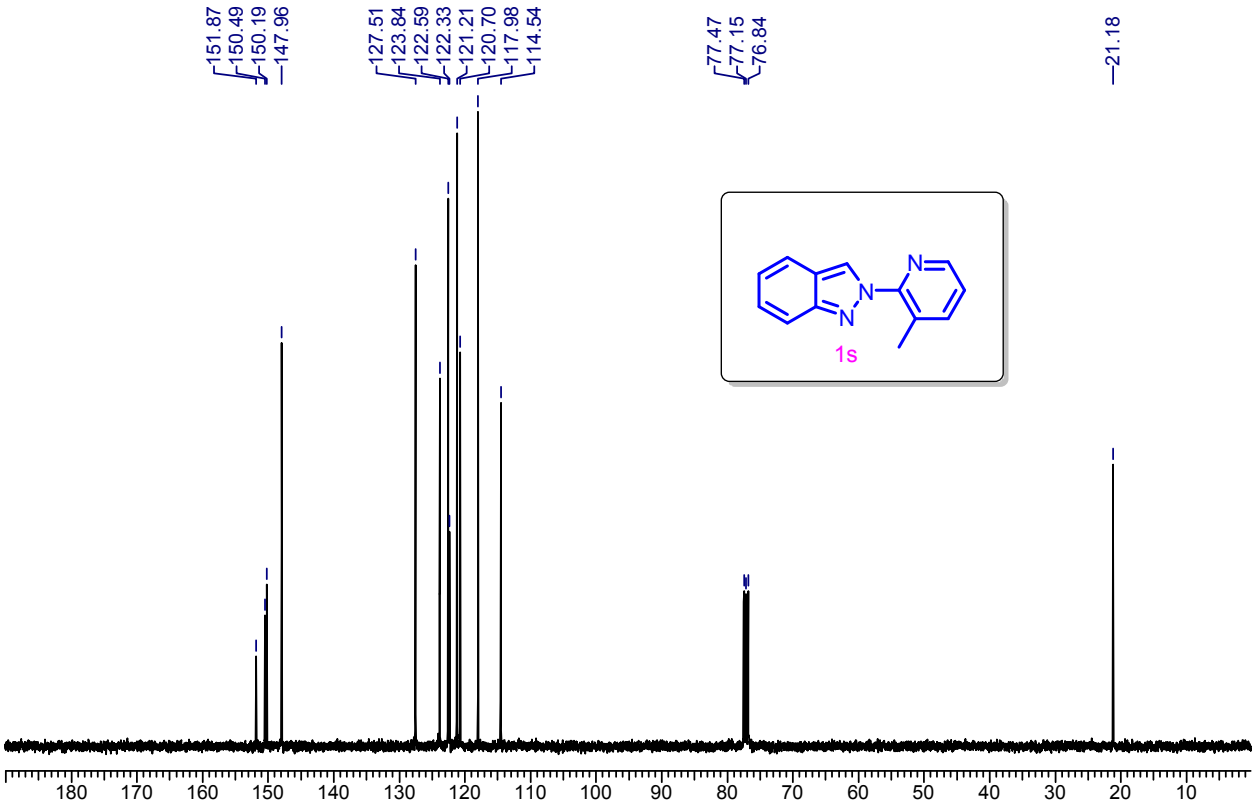
^{1}H NMR (400 MHz) spectrum of compound **1j** in $CDCl_3$



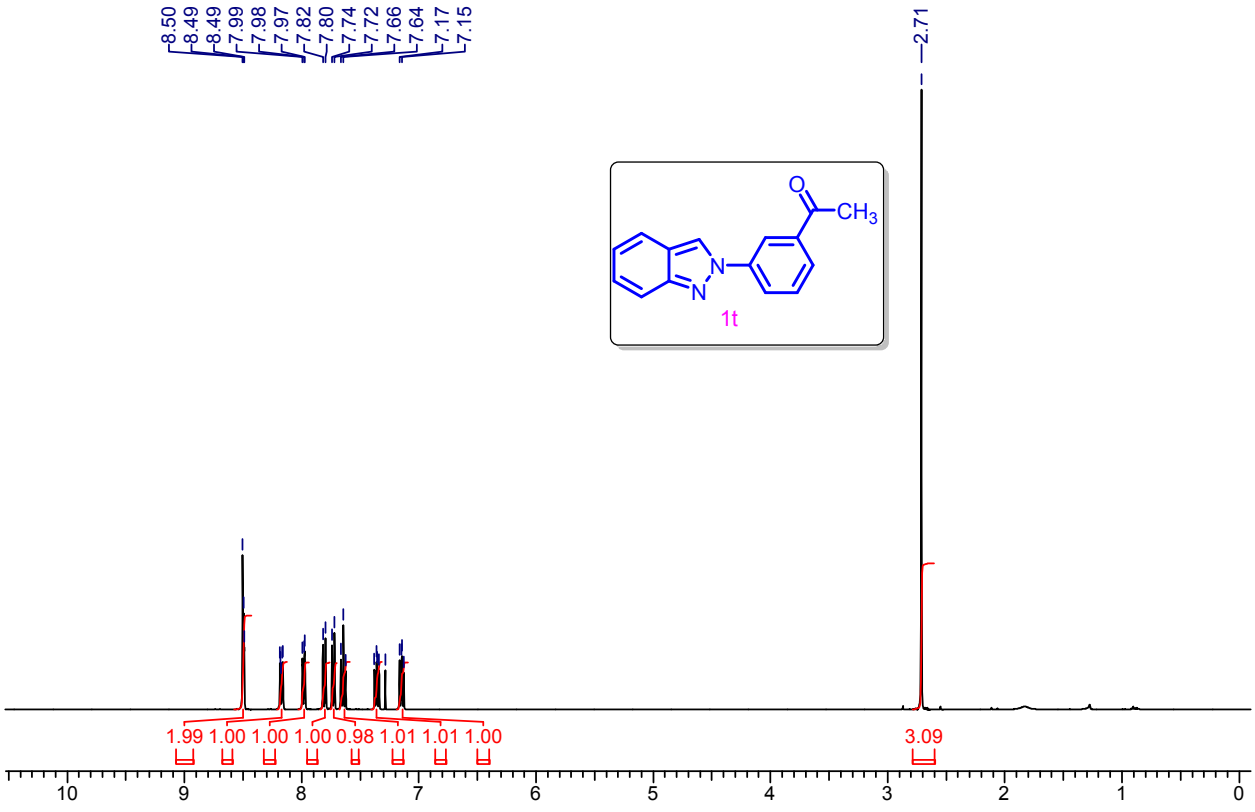
^{13}C NMR (400 MHz) spectrum of compound **1j** in $CDCl_3$



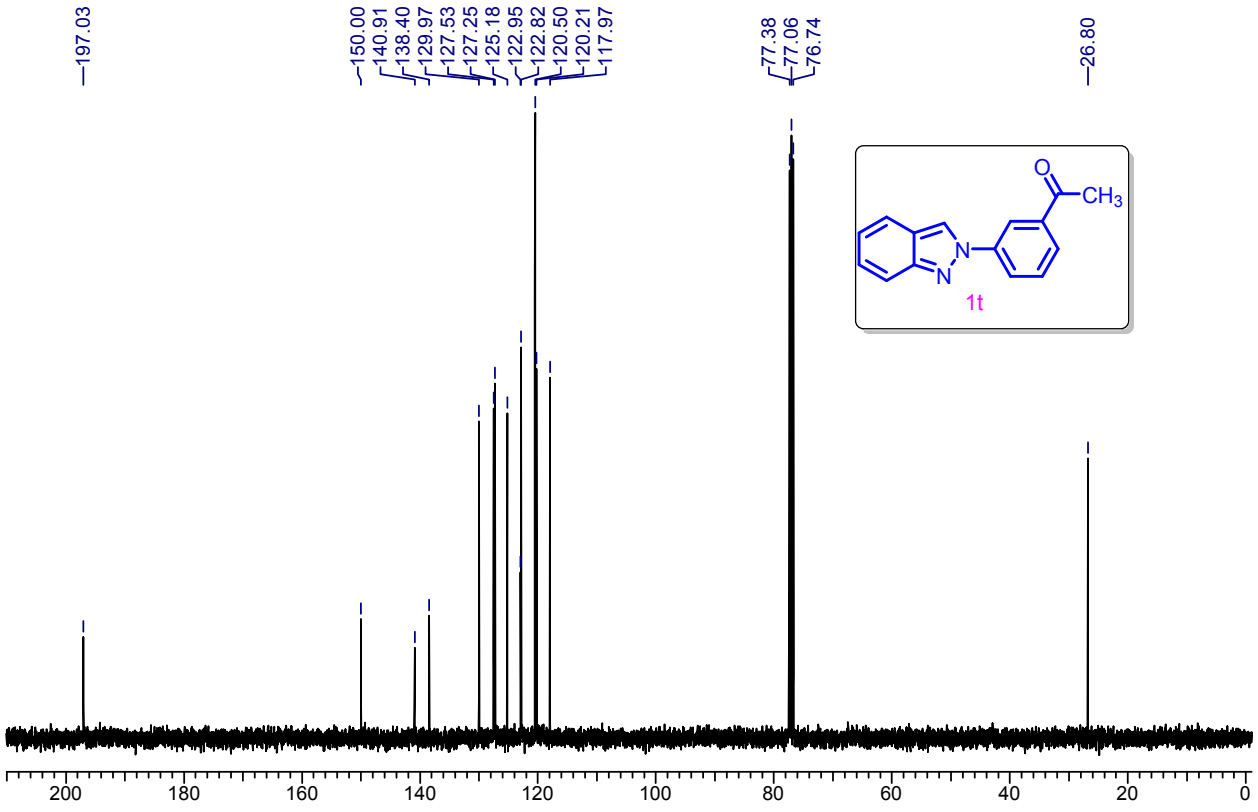
^{1}H NMR (400 MHz) spectrum of compound **1s** in $CDCl_3$



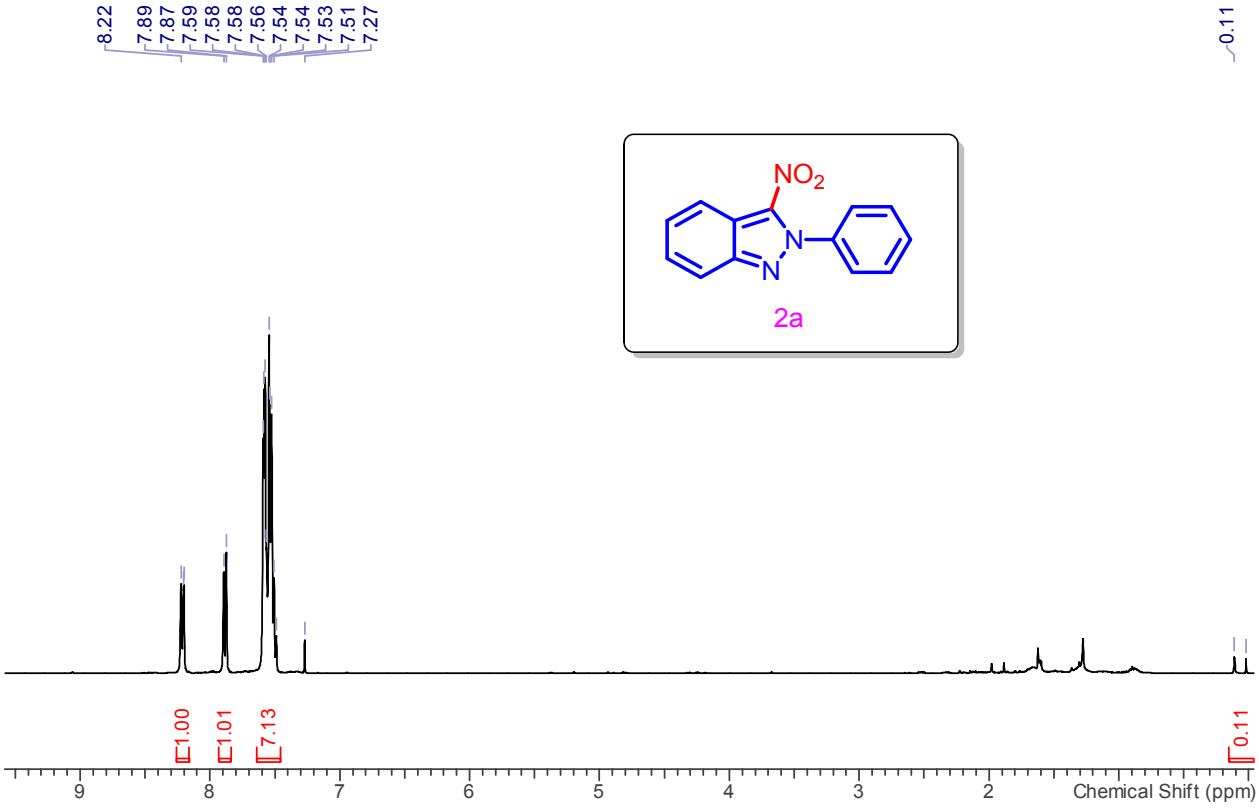
^{13}C NMR (400 MHz) spectrum of compound **1s** in $CDCl_3$



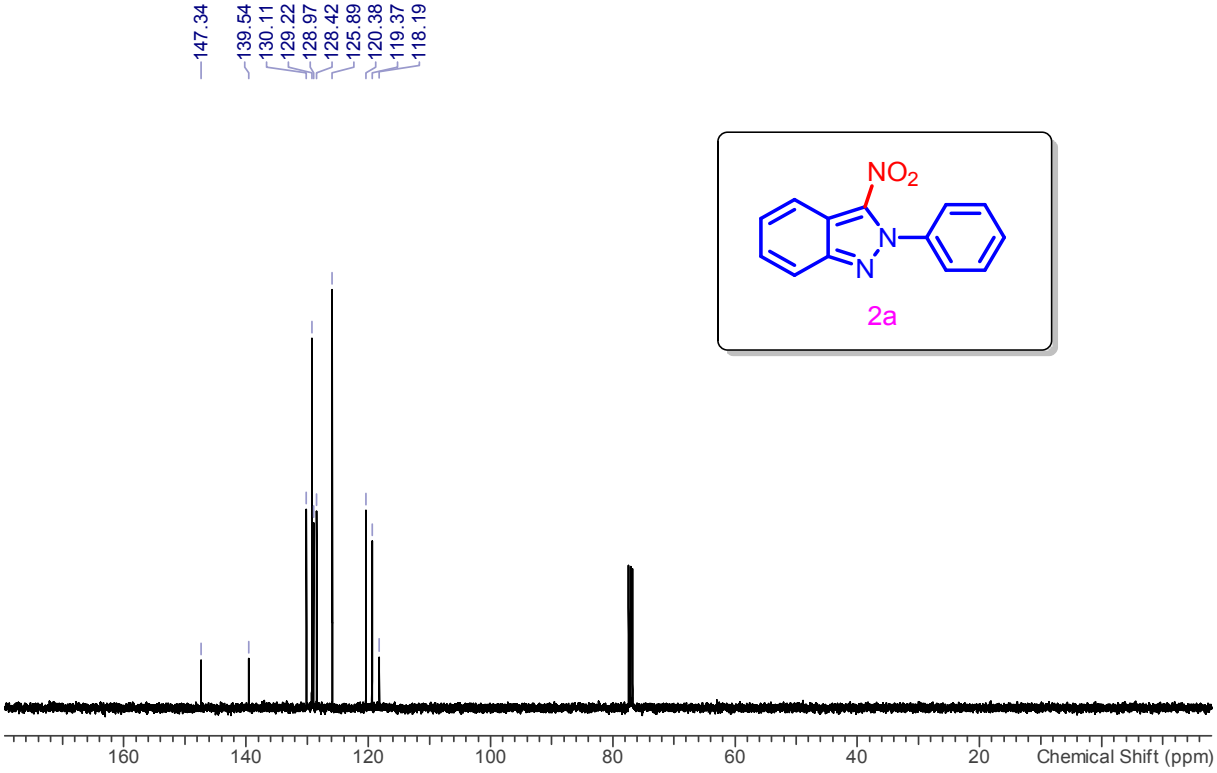
^{1}H NMR (400 MHz) spectrum of compound **1t** in $CDCl_3$



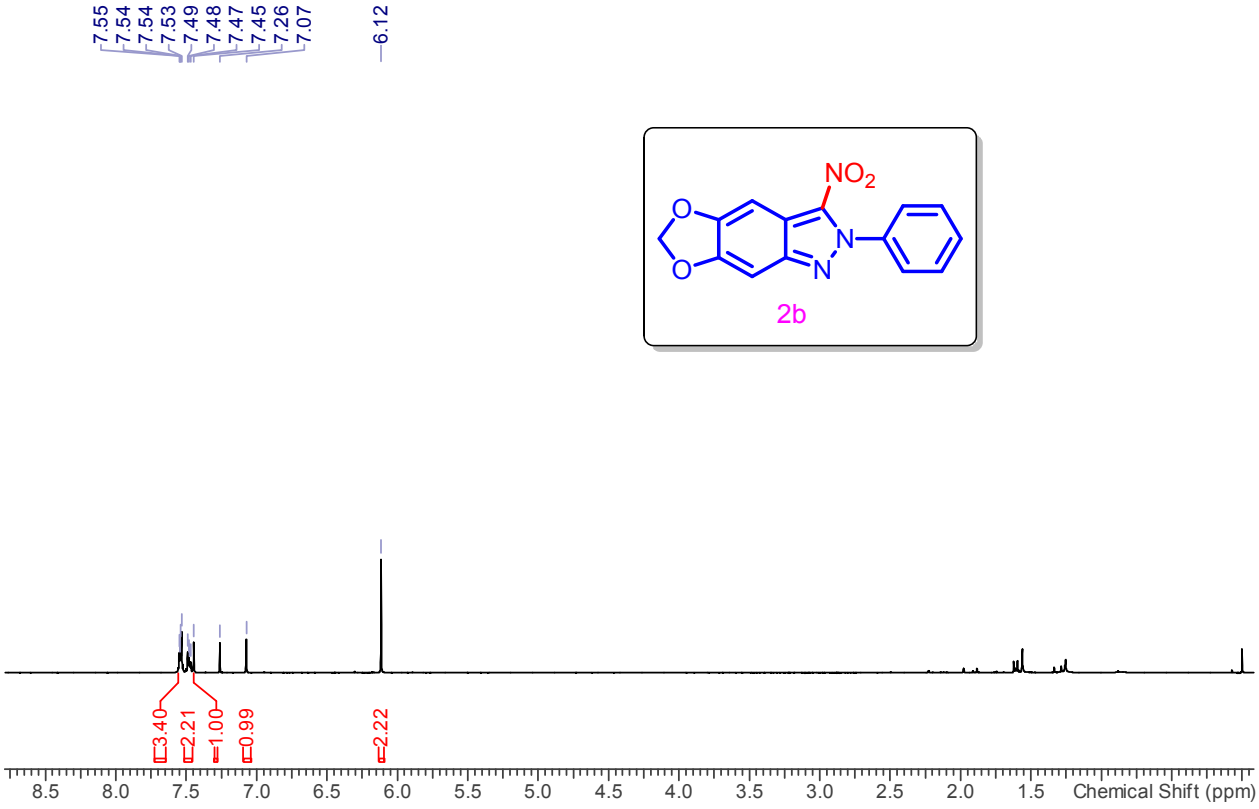
^{13}C NMR (400 MHz) spectrum of compound **1t** in $CDCl_3$



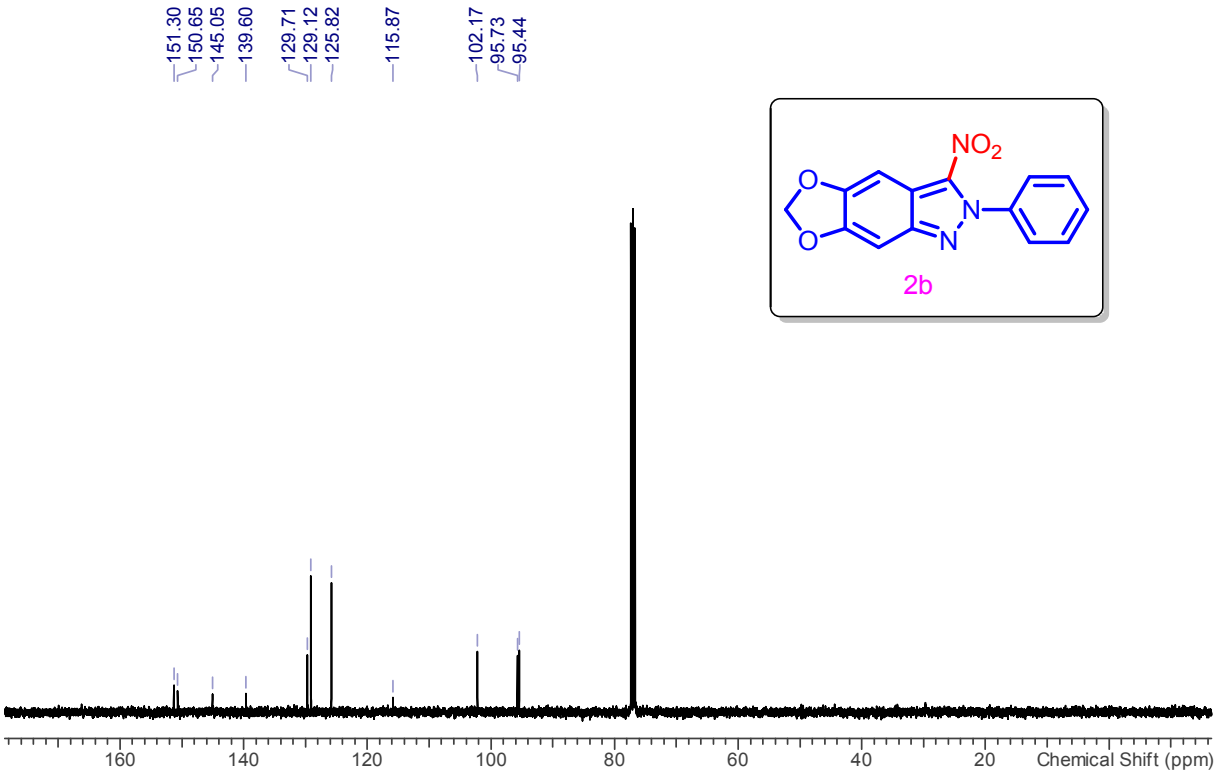
^{1}H NMR (400 MHz) spectrum of compound **2a** in $CDCl_3$



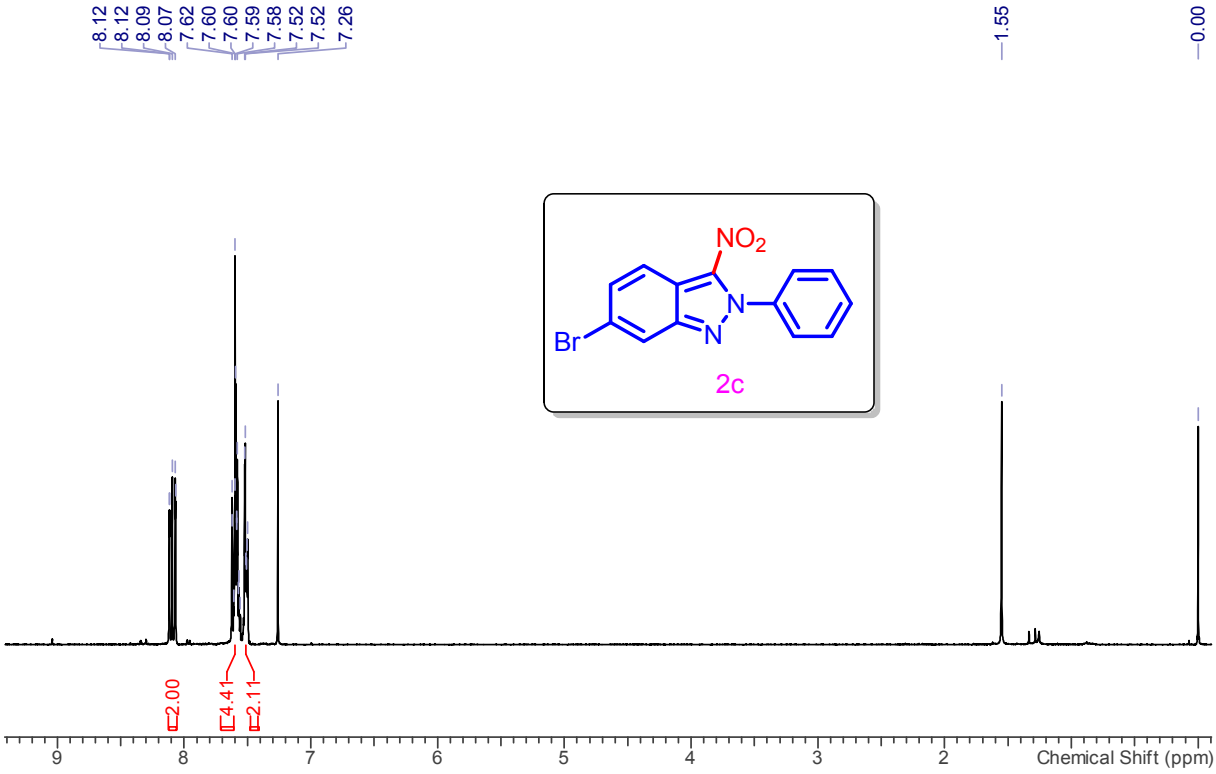
^{13}C NMR (100 MHz) spectrum of compound **2a** in $CDCl_3$



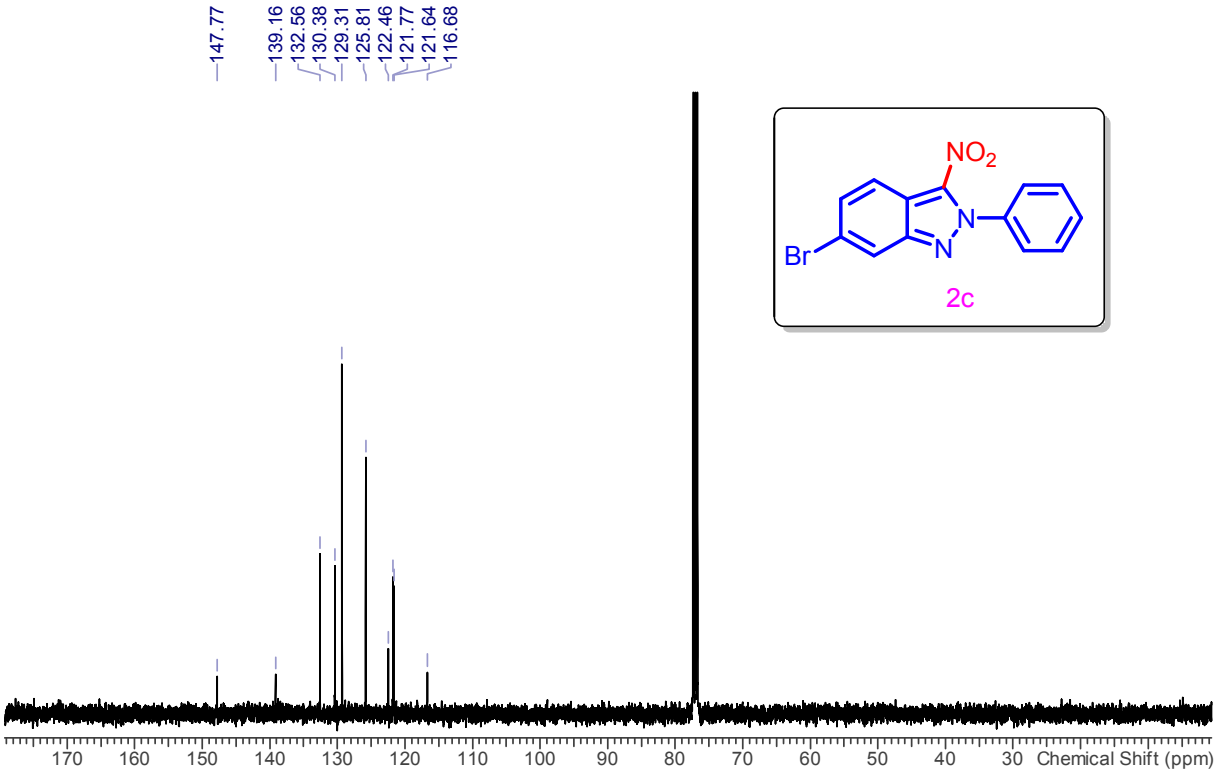
^{1}H NMR (400 MHz) spectrum of compound **2b** in $CDCl_3$



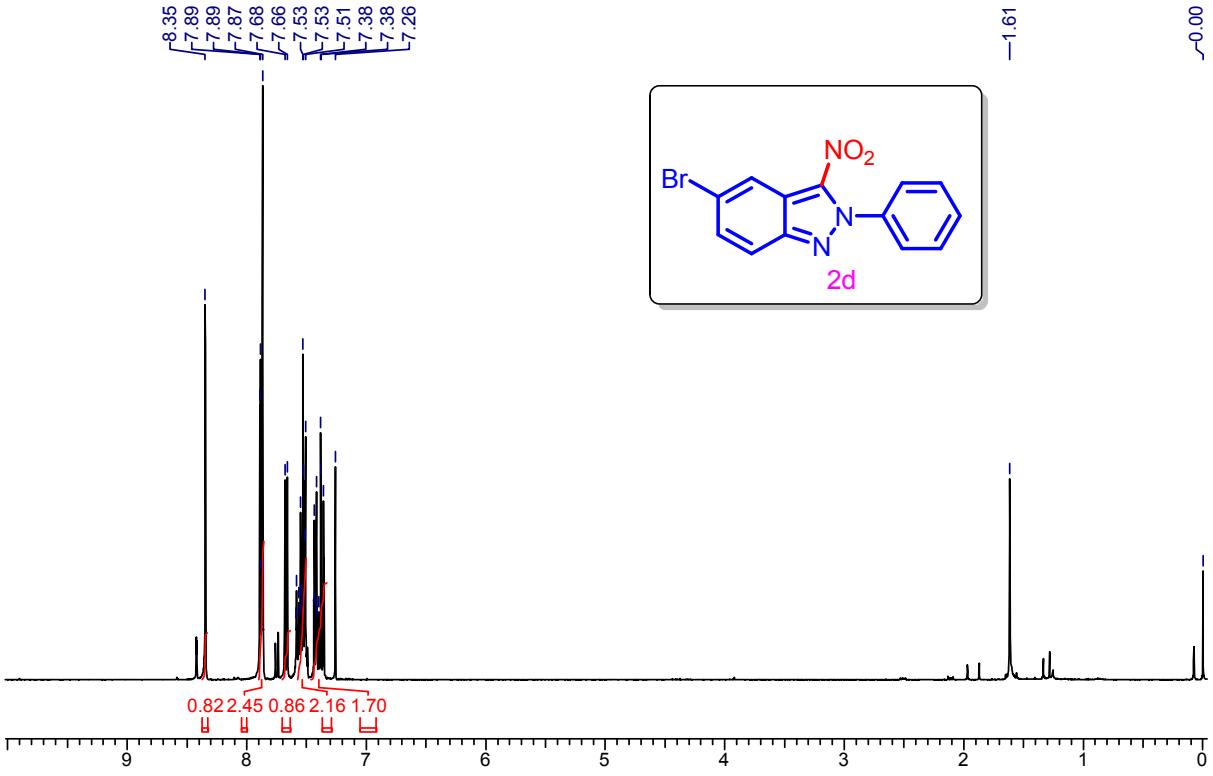
^{13}C NMR (100 MHz) spectrum of compound **2b** in $CDCl_3$



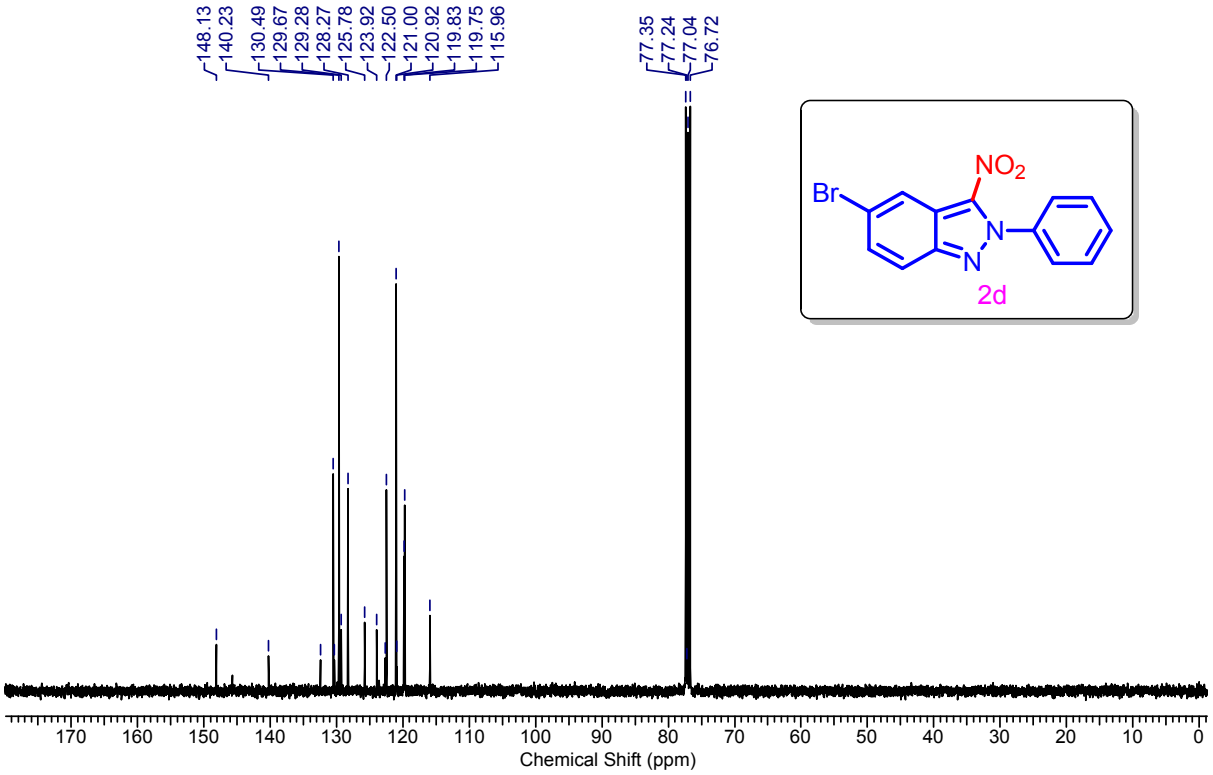
^{1}H NMR (400 MHz) spectrum of compound **2c** in $CDCl_3$



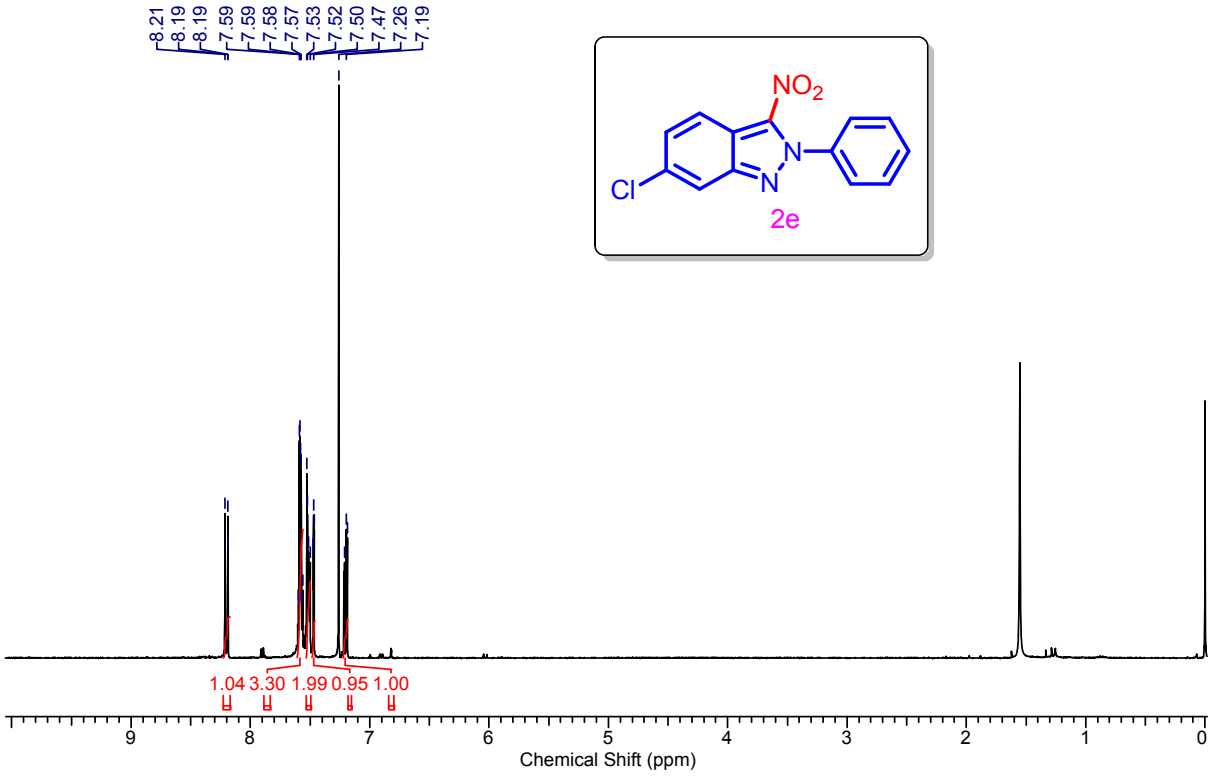
^{13}C NMR (100 MHz) spectrum of compound **2c** in $CDCl_3$



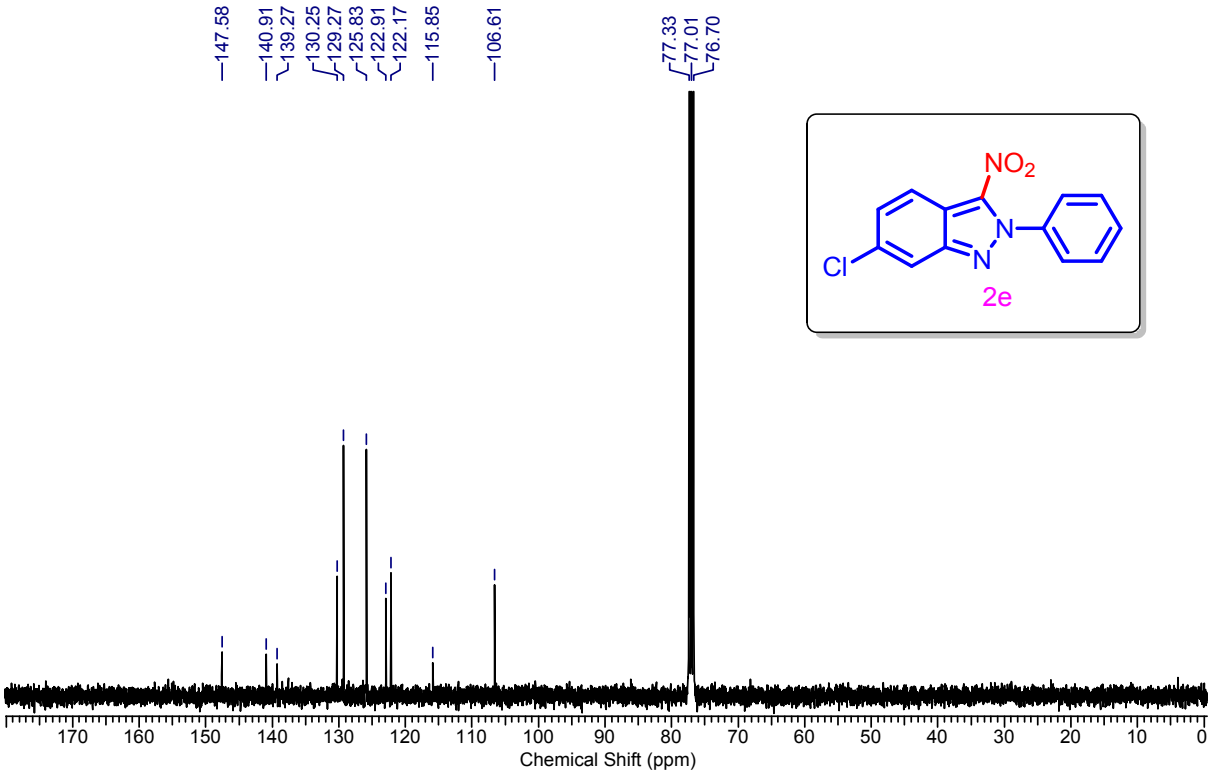
^{1}H NMR (400 MHz) spectrum of compound **2d**in $CDCl_3$



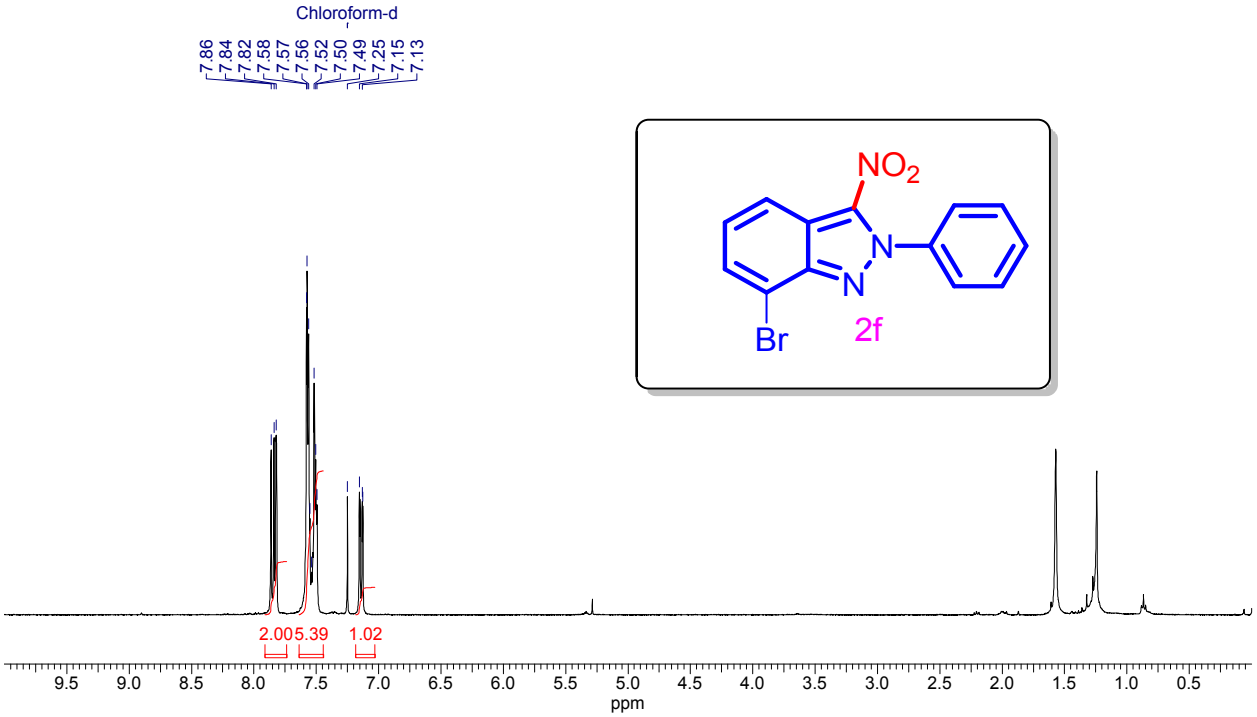
^{13}C NMR (100 MHz) spectrum of compound **2d** in $CDCl_3$



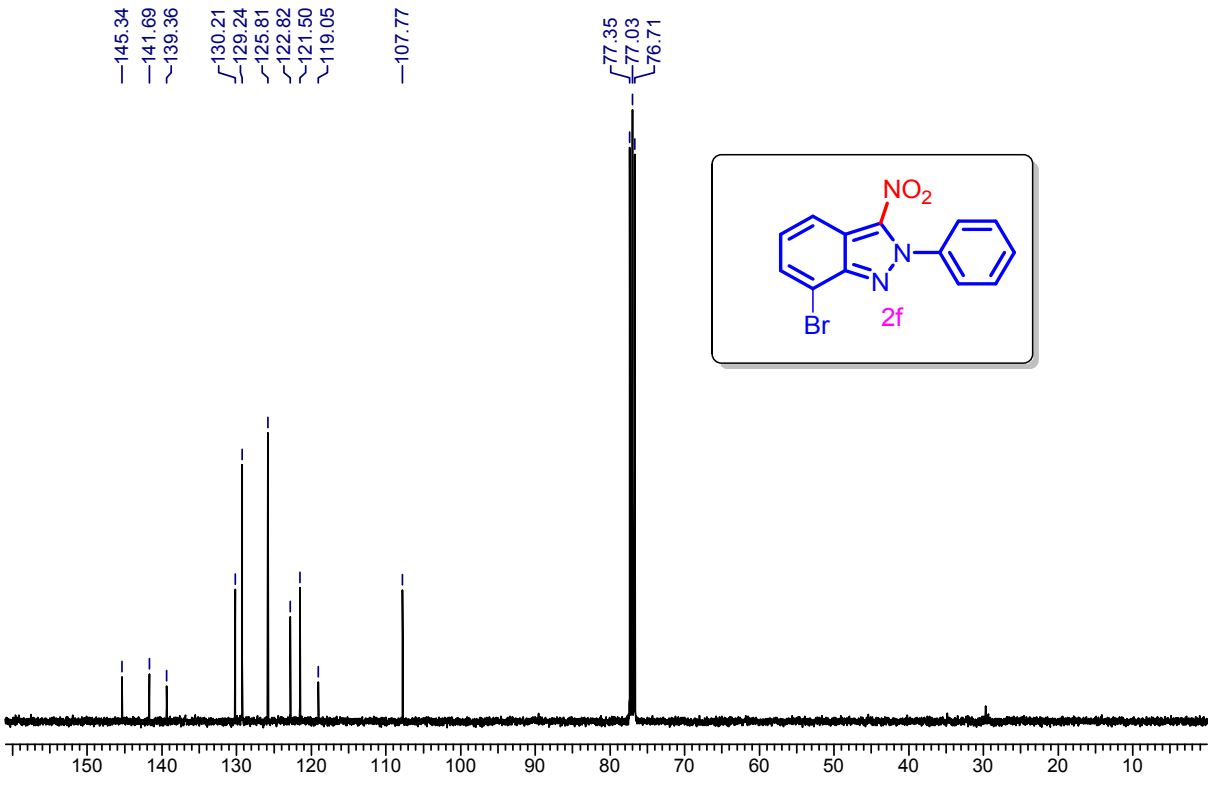
^{1}H NMR (400 MHz) spectrum of compound **2e** in $CDCl_3$



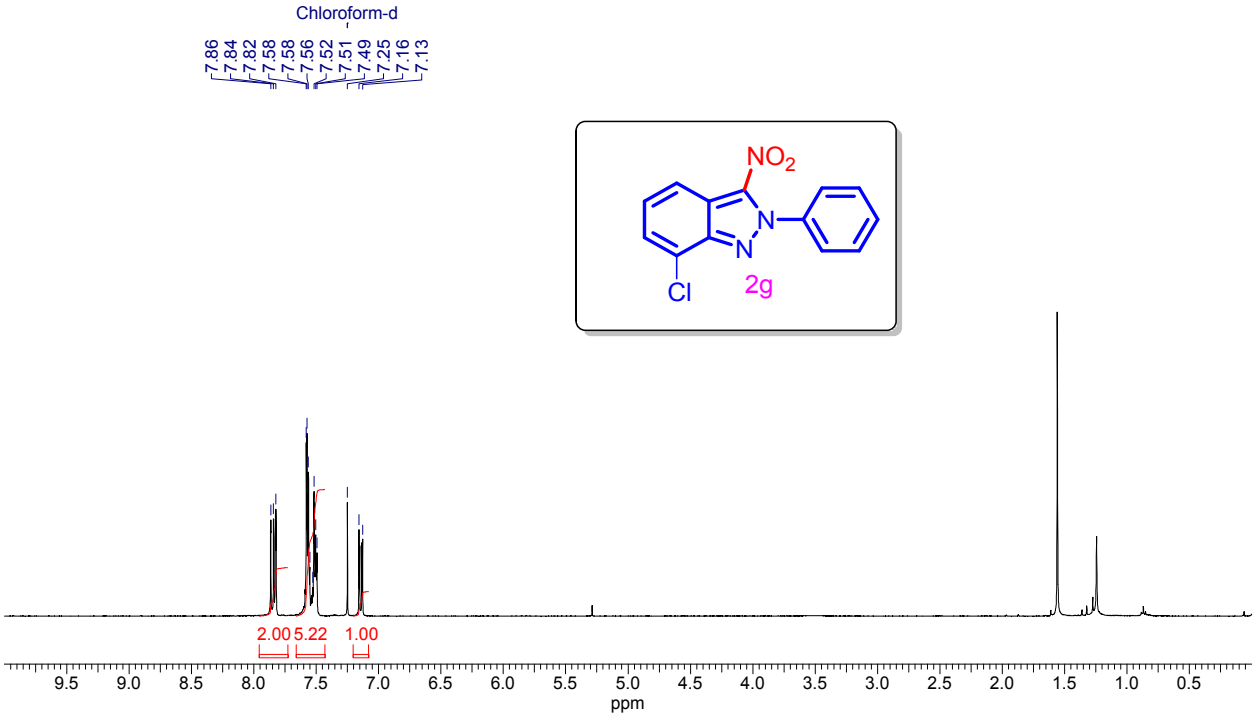
^{13}C NMR (100 MHz) spectrum of compound **2e** in $CDCl_3$



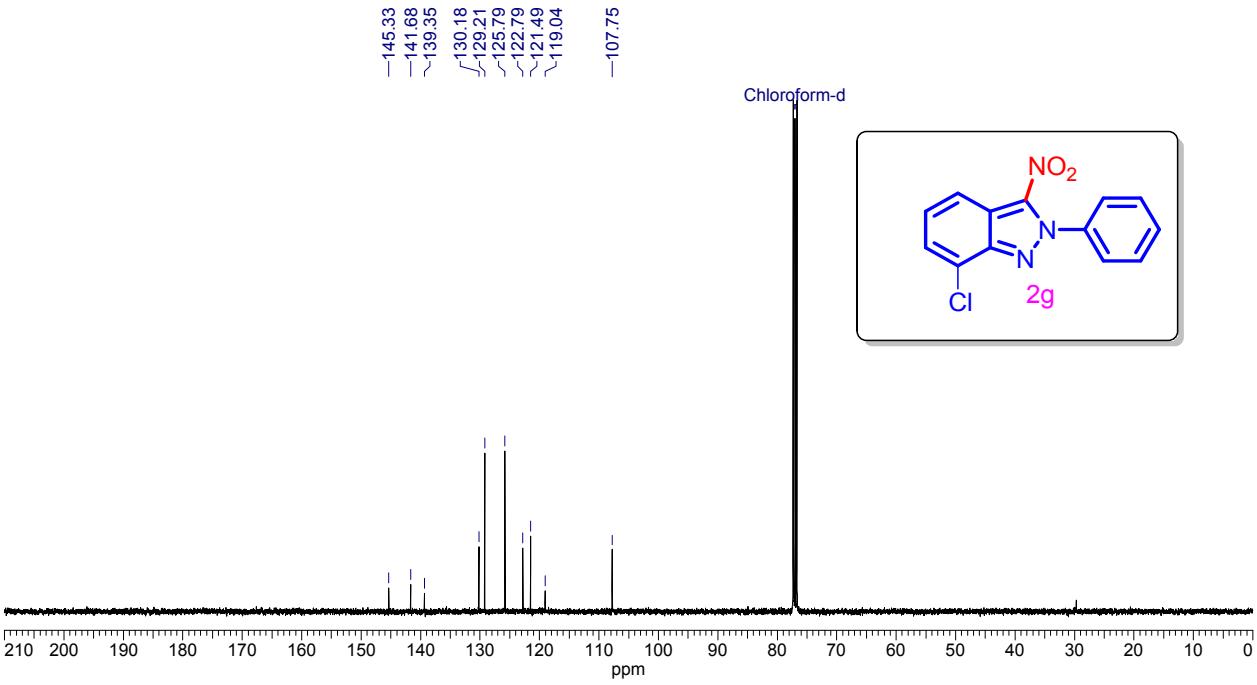
^{1}H NMR (400 MHz) spectrum of compound **2f** in $CDCl_3$



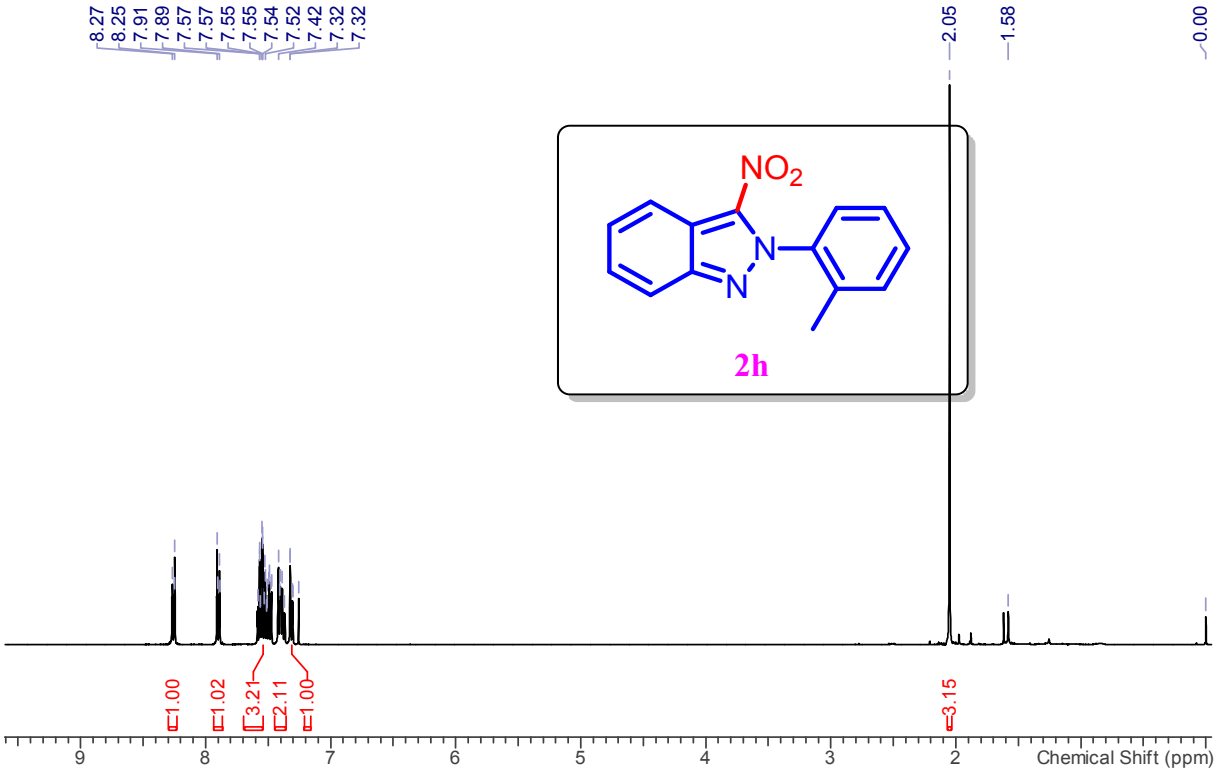
^{13}C NMR (100 MHz) spectrum of compound **2f** in $CDCl_3$



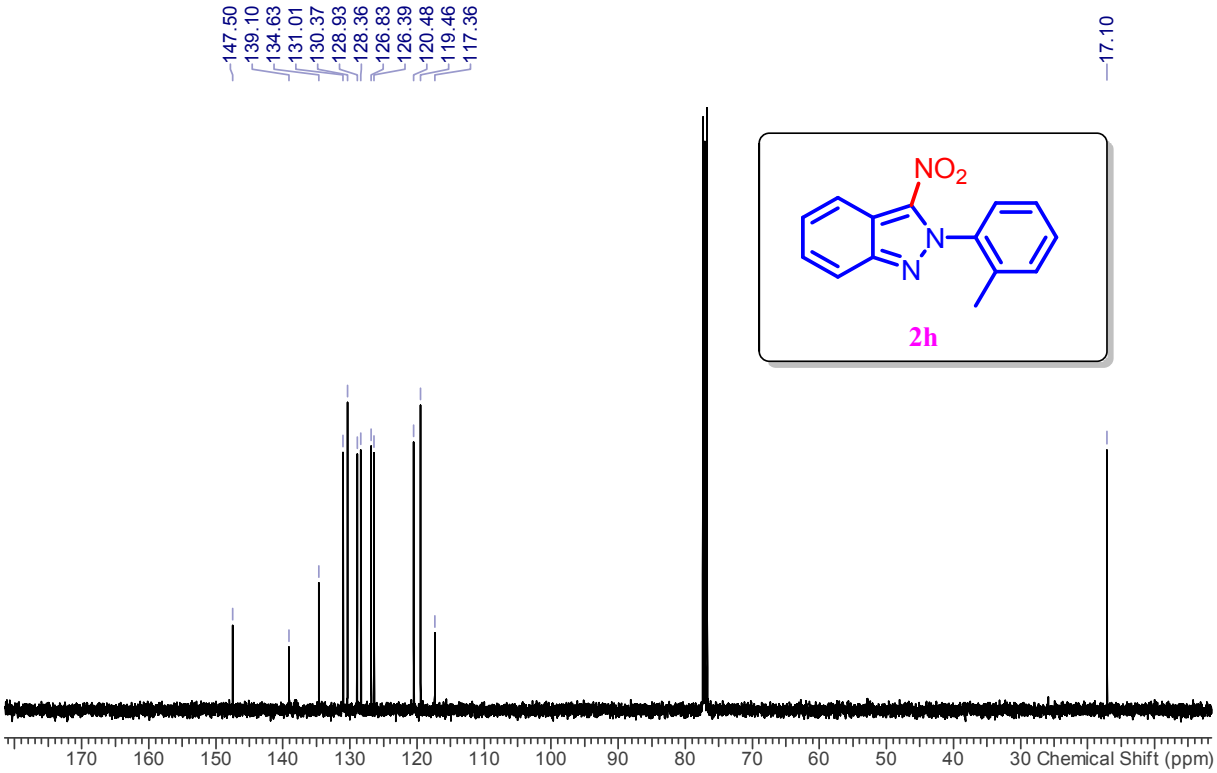
^{1}H NMR (400 MHz) spectrum of compound **2g** in $CDCl_3$



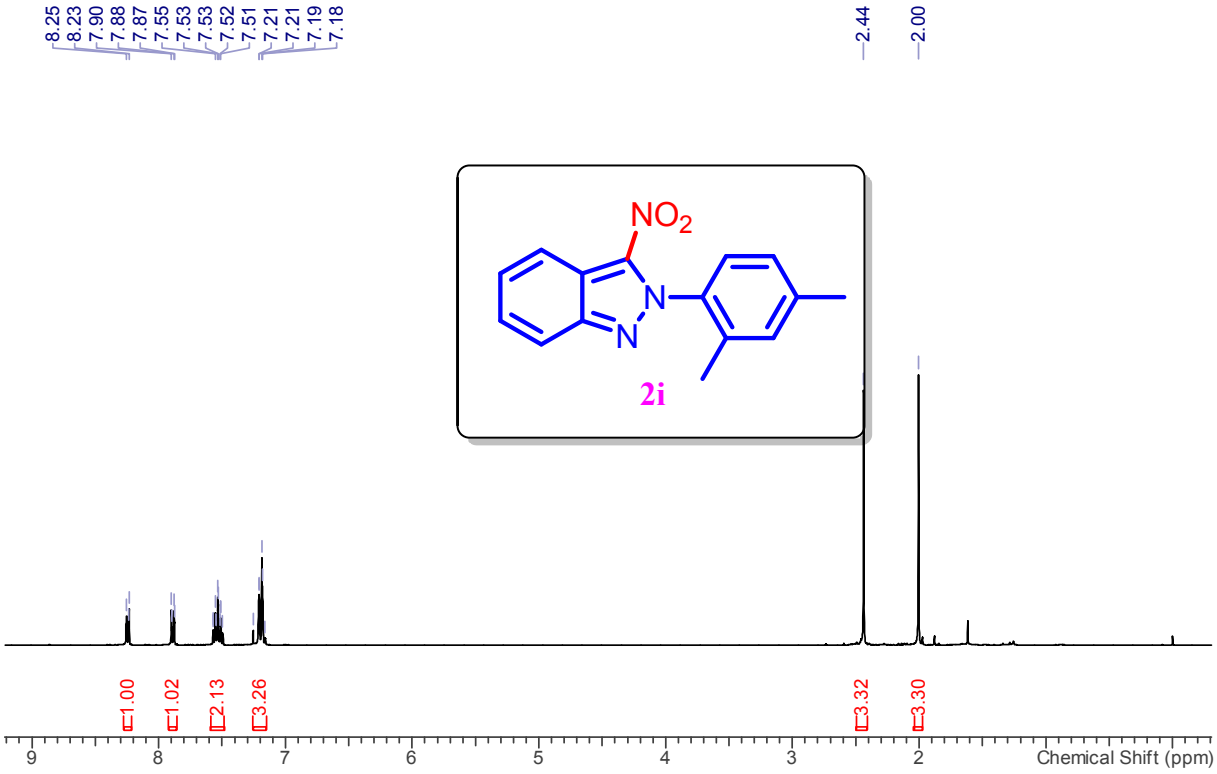
^{13}C NMR (100 MHz) spectrum of compound **2g** in $CDCl_3$



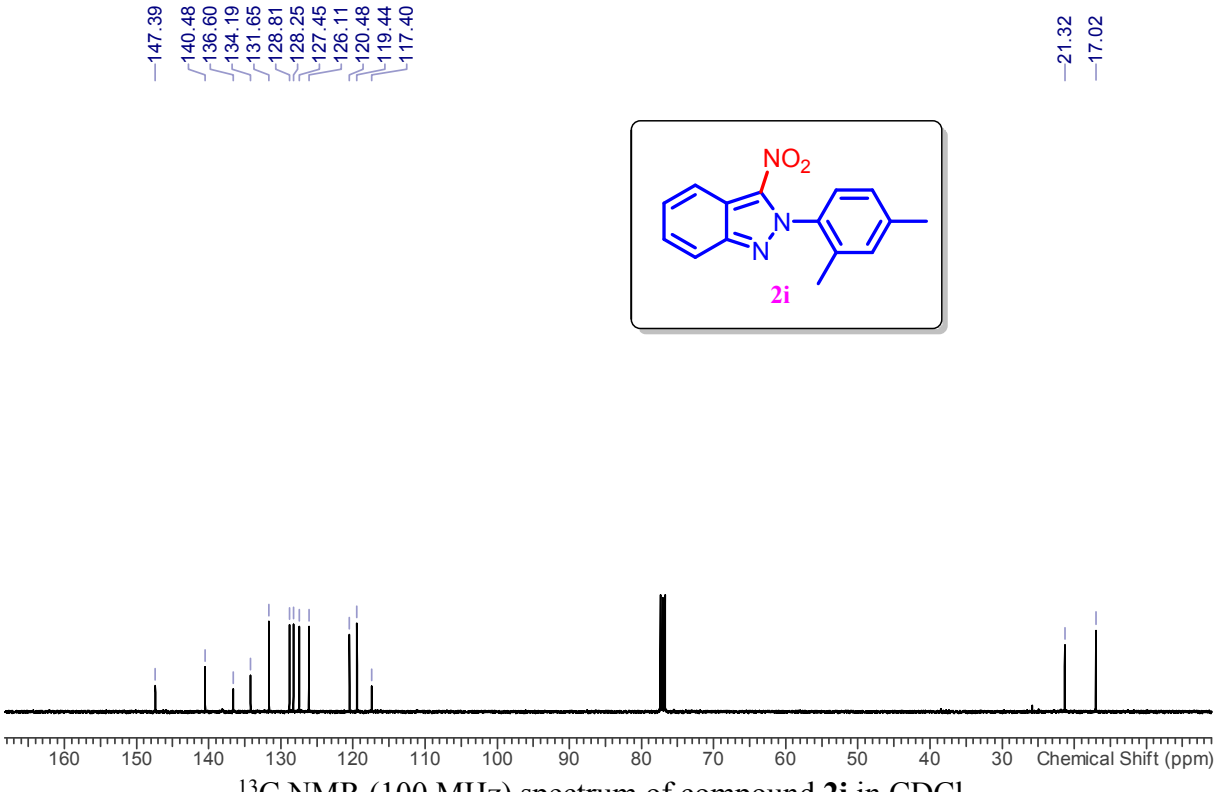
^{1}H NMR (400 MHz) spectrum of compound **2h** in $CDCl_3$



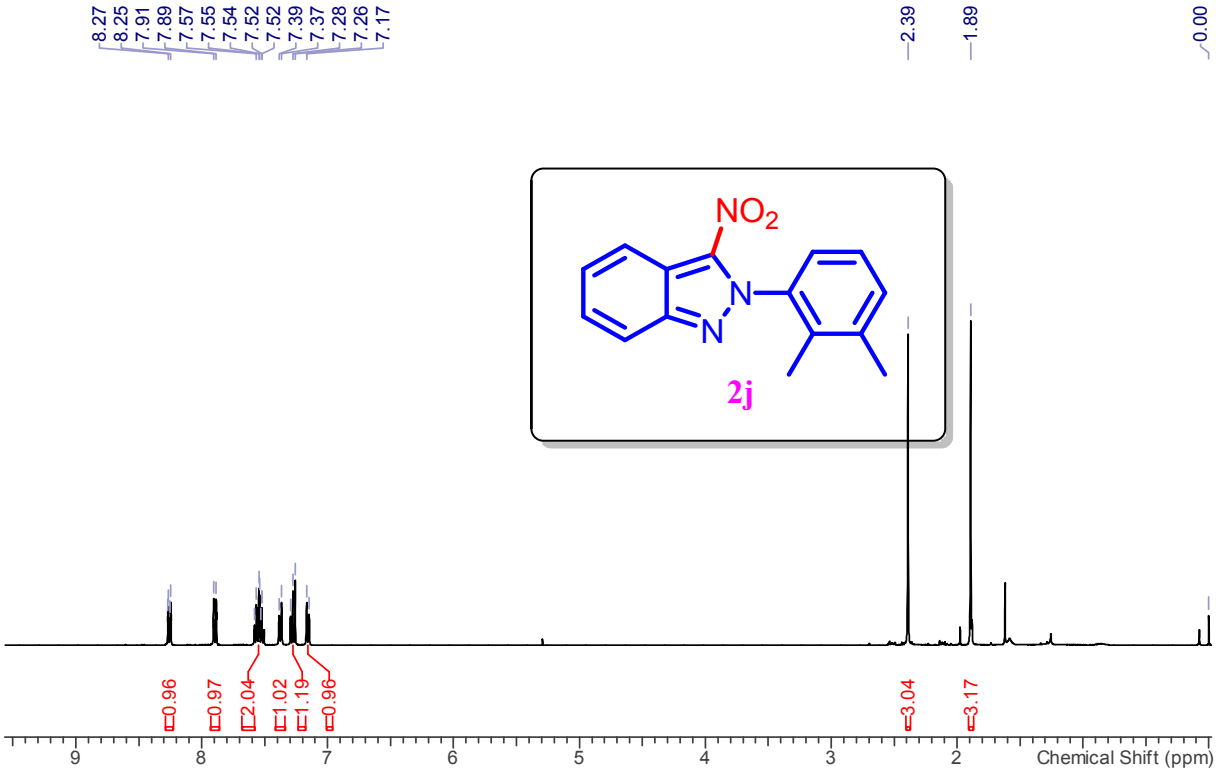
^{13}C NMR (100 MHz) spectrum of compound **2h** in $CDCl_3$



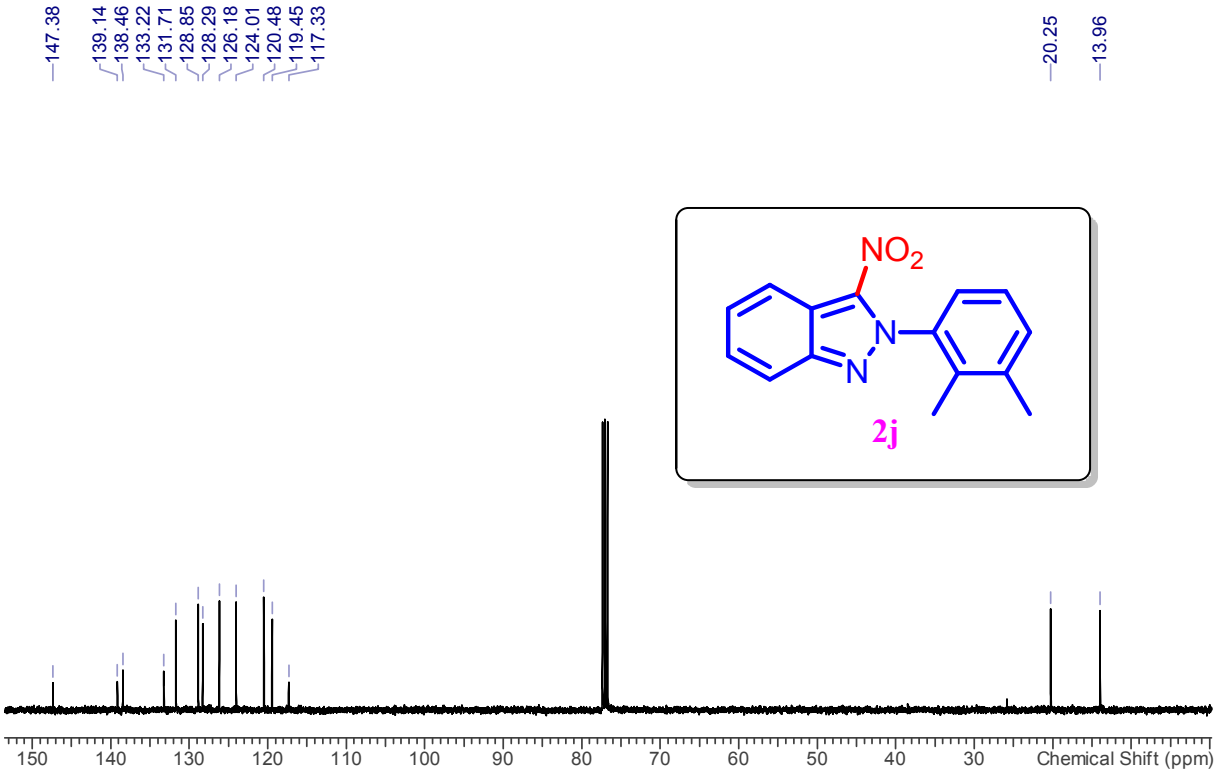
^{1}H NMR (400 MHz) spectrum of compound **2i** in $CDCl_3$



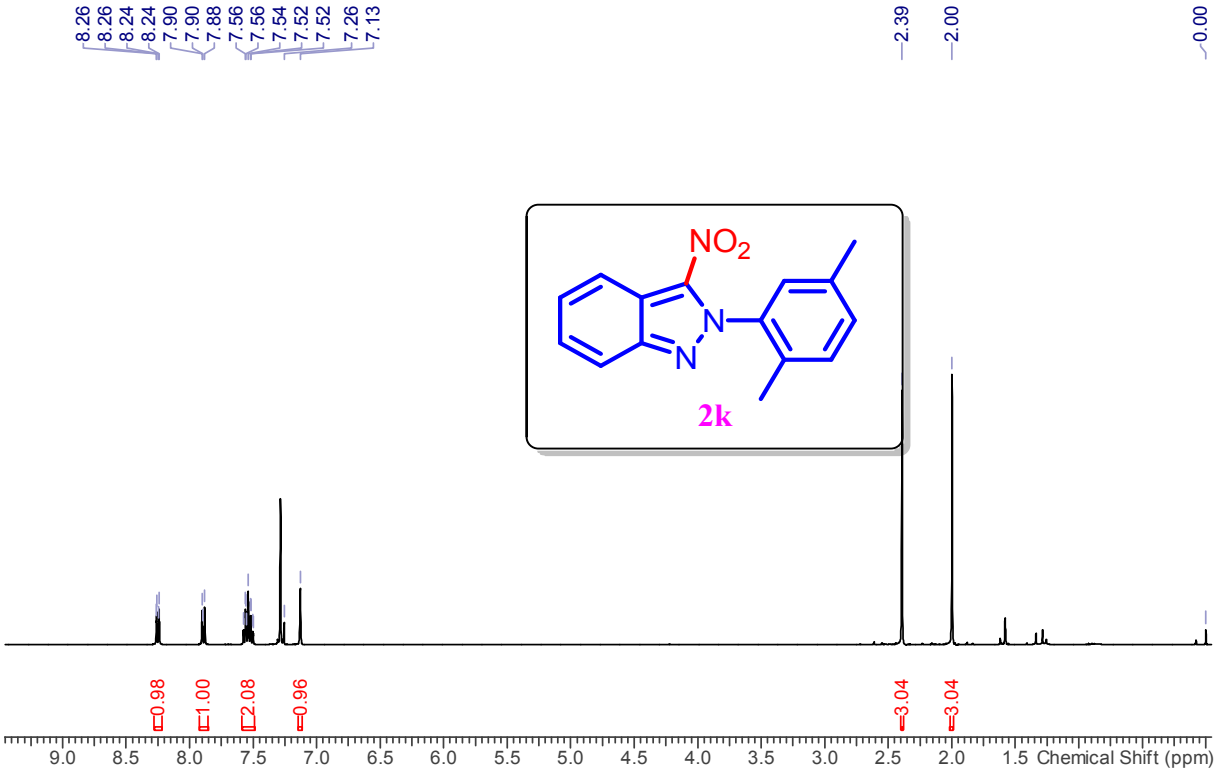
^{13}C NMR (100 MHz) spectrum of compound **2i** in $CDCl_3$



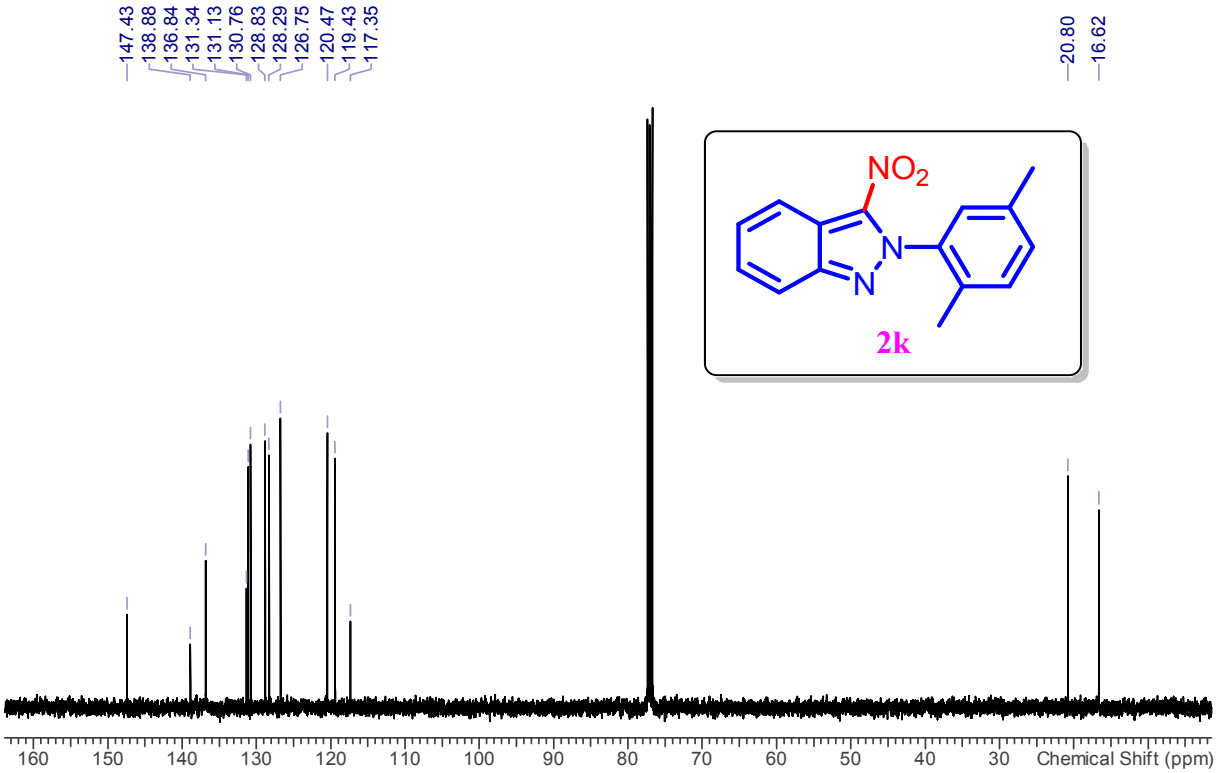
^{1}H NMR (400 MHz) spectrum of compound **2j** in $CDCl_3$



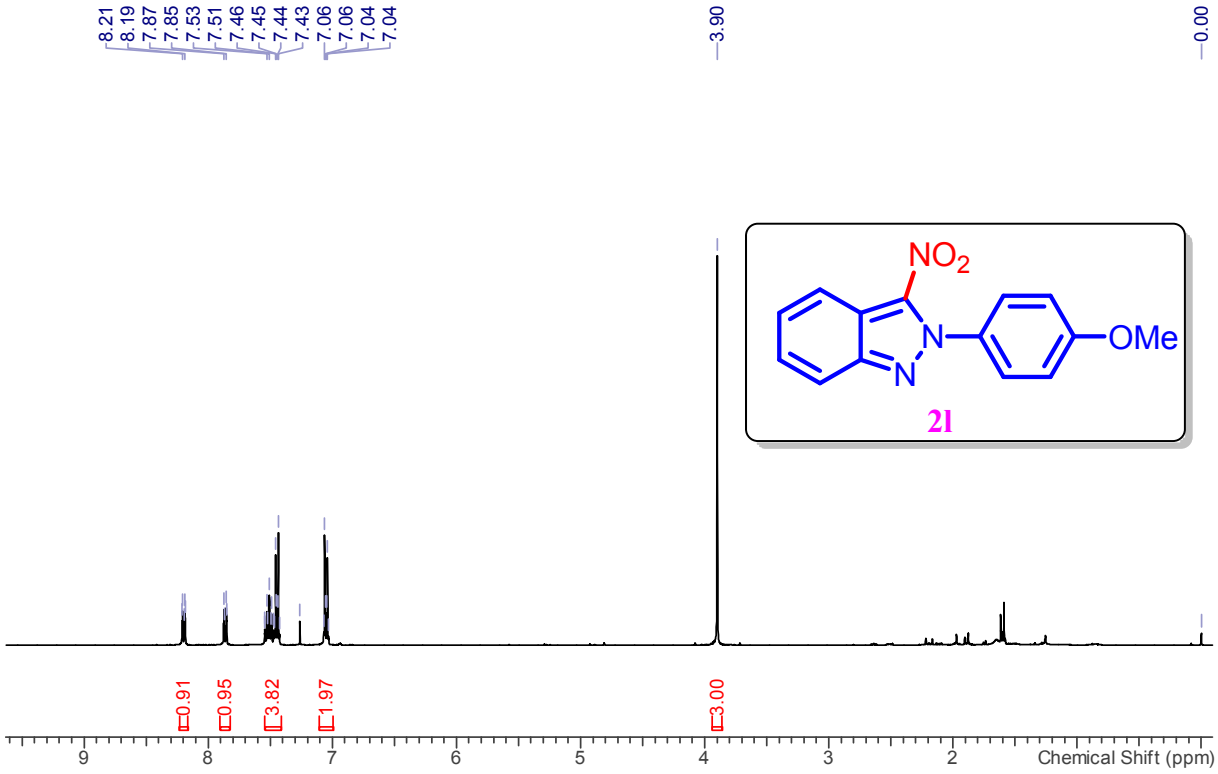
^{13}C NMR (100 MHz) spectrum of compound **2j** in $CDCl_3$



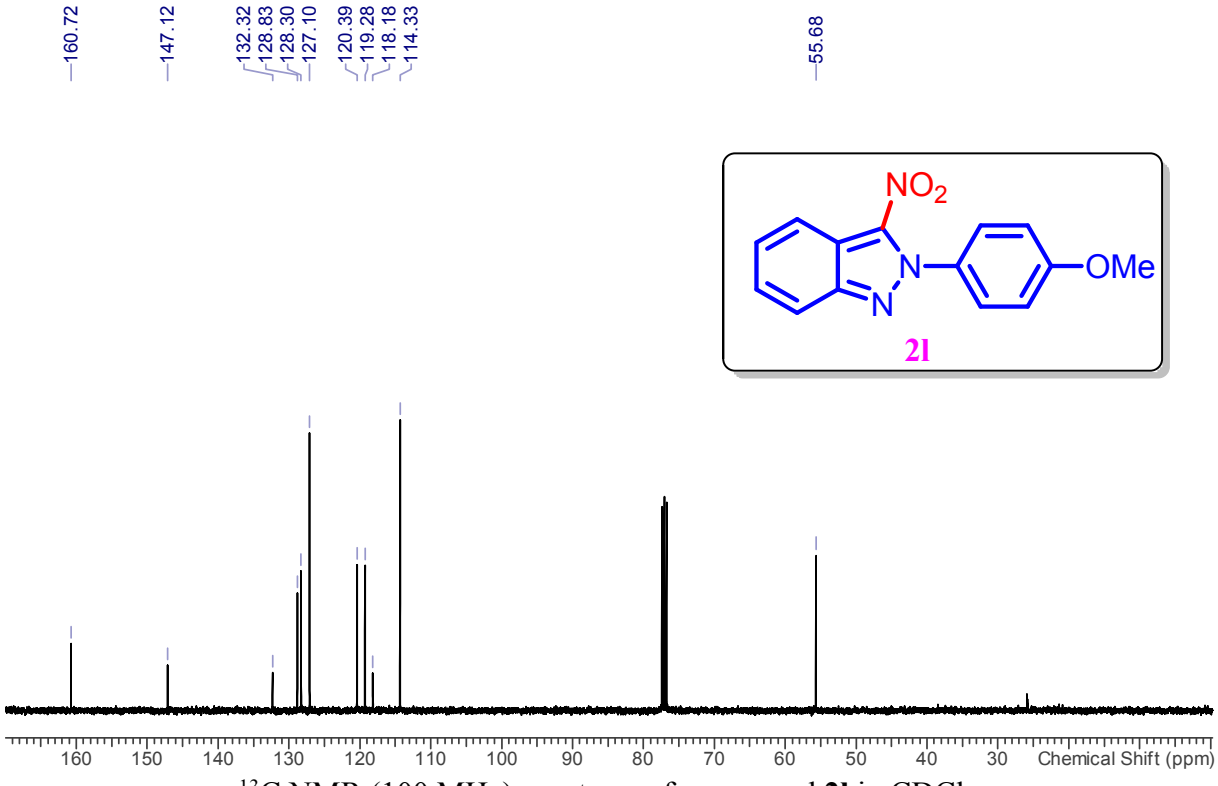
^{1}H NMR (400 MHz) spectrum of compound **2k** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **2k** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound **2l** in $CDCl_3$



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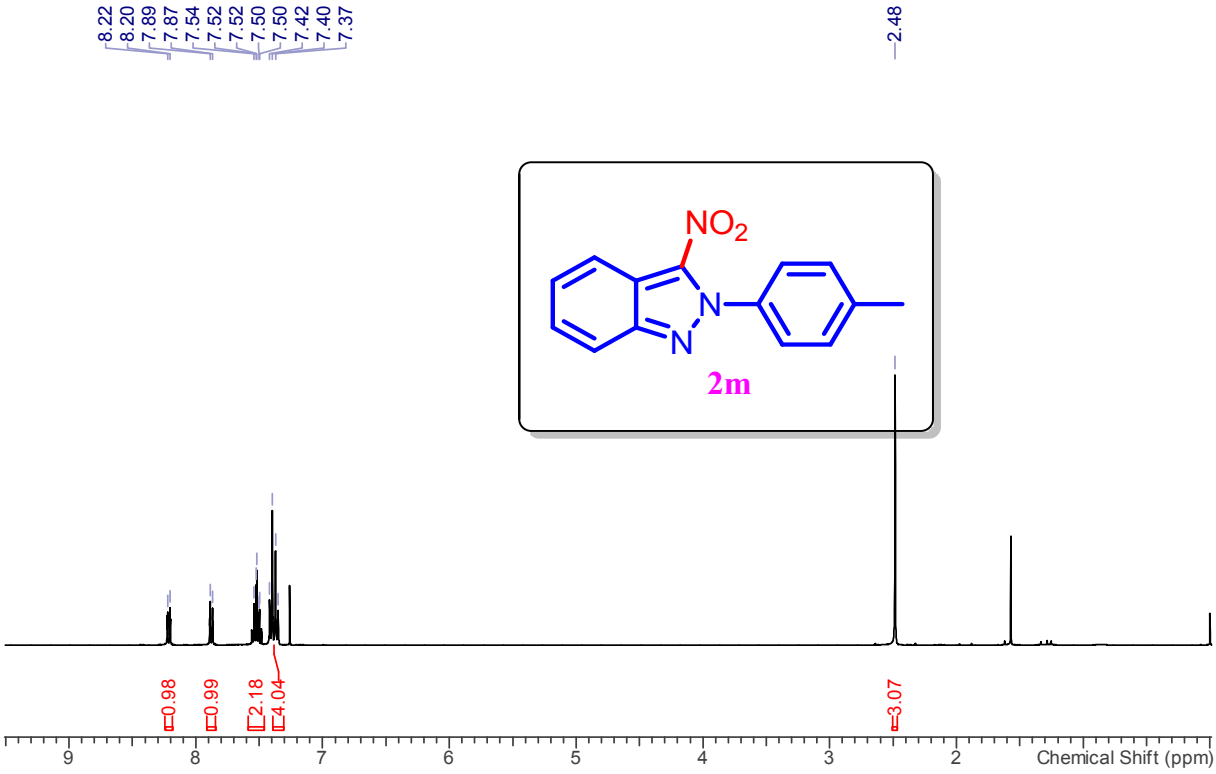
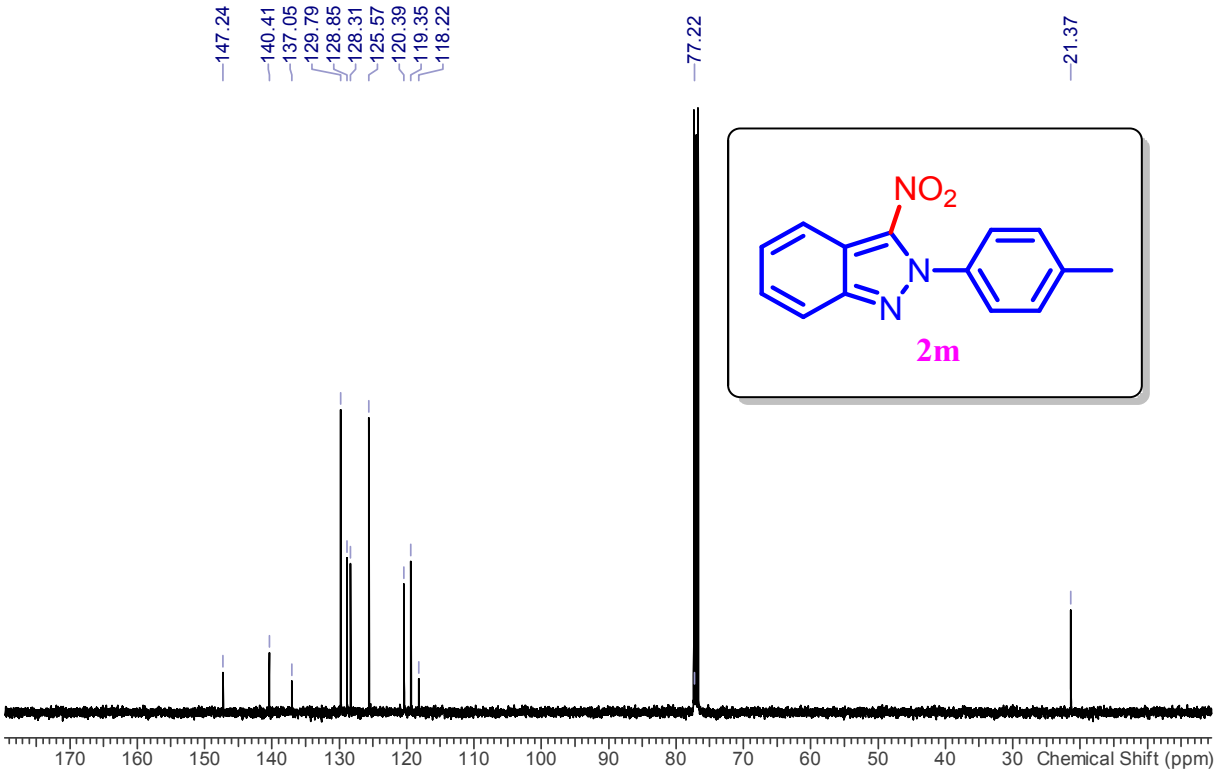
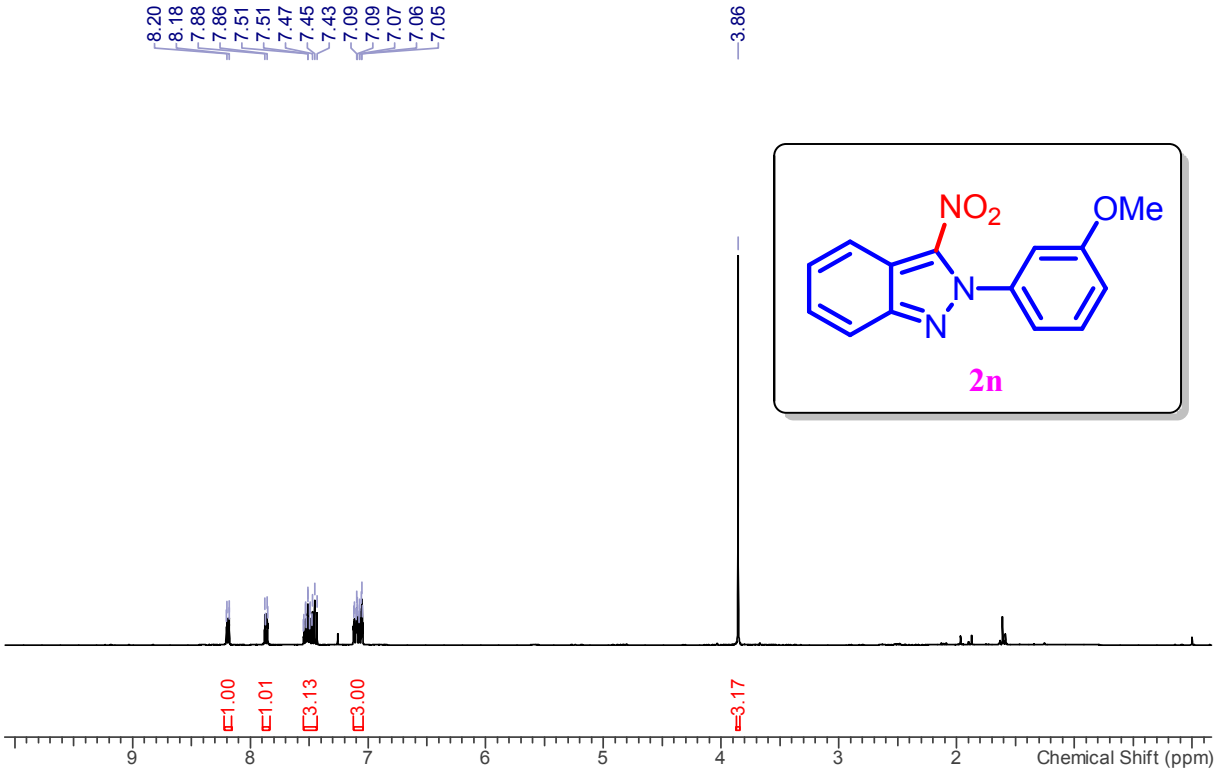


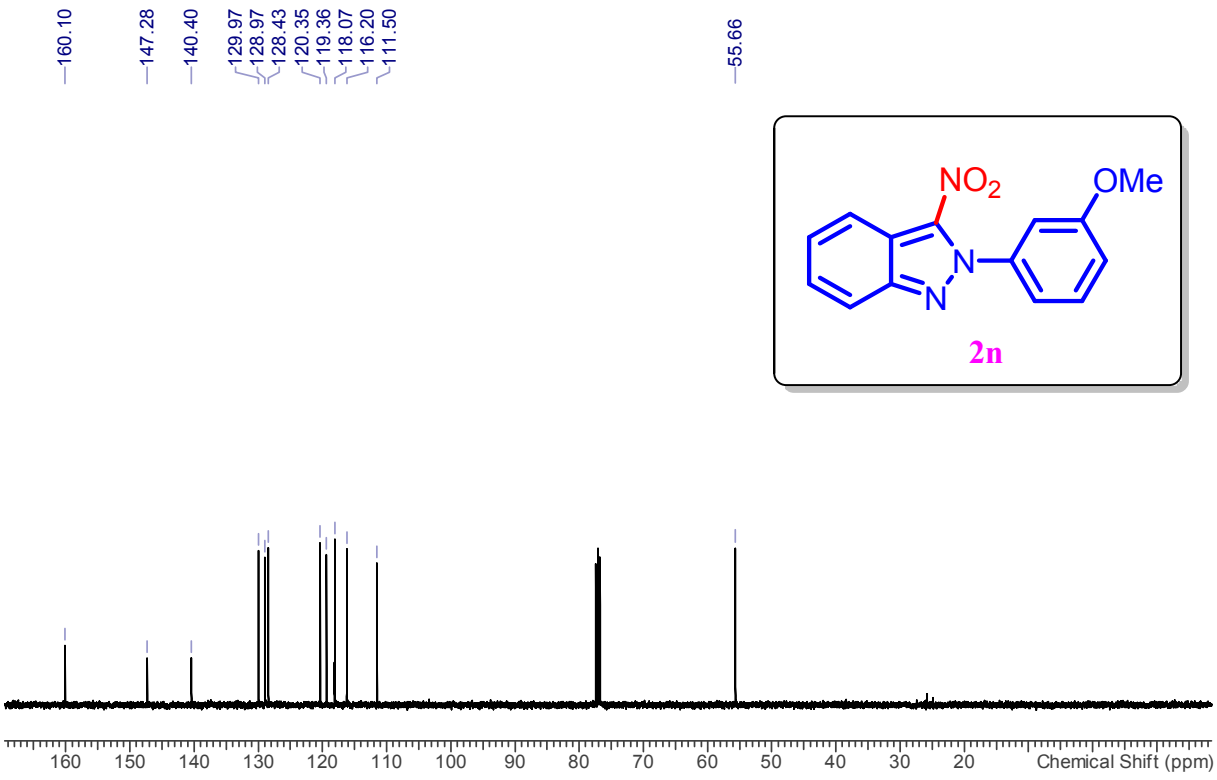
^{1}H NMR (400 MHz) spectrum of compound **2m** in $CDCl_3$



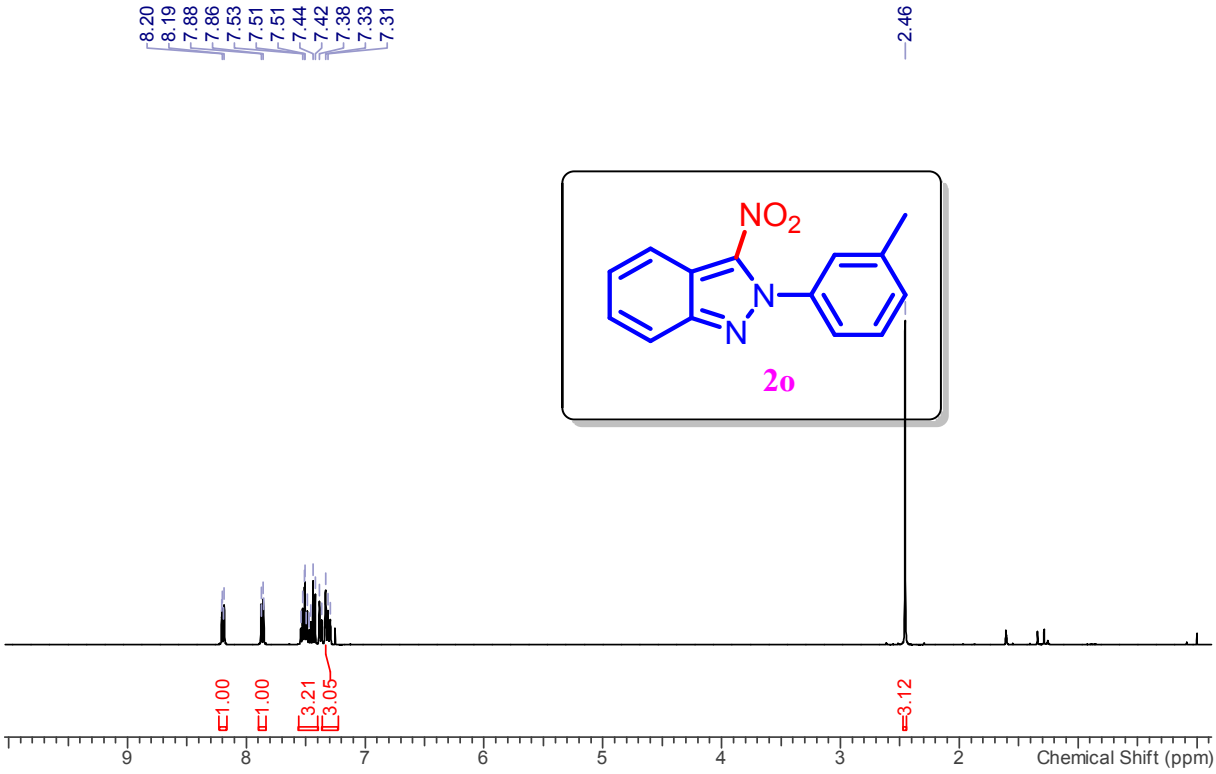
^{13}C NMR (100 MHz) spectrum of compound **2m** in $CDCl_3$



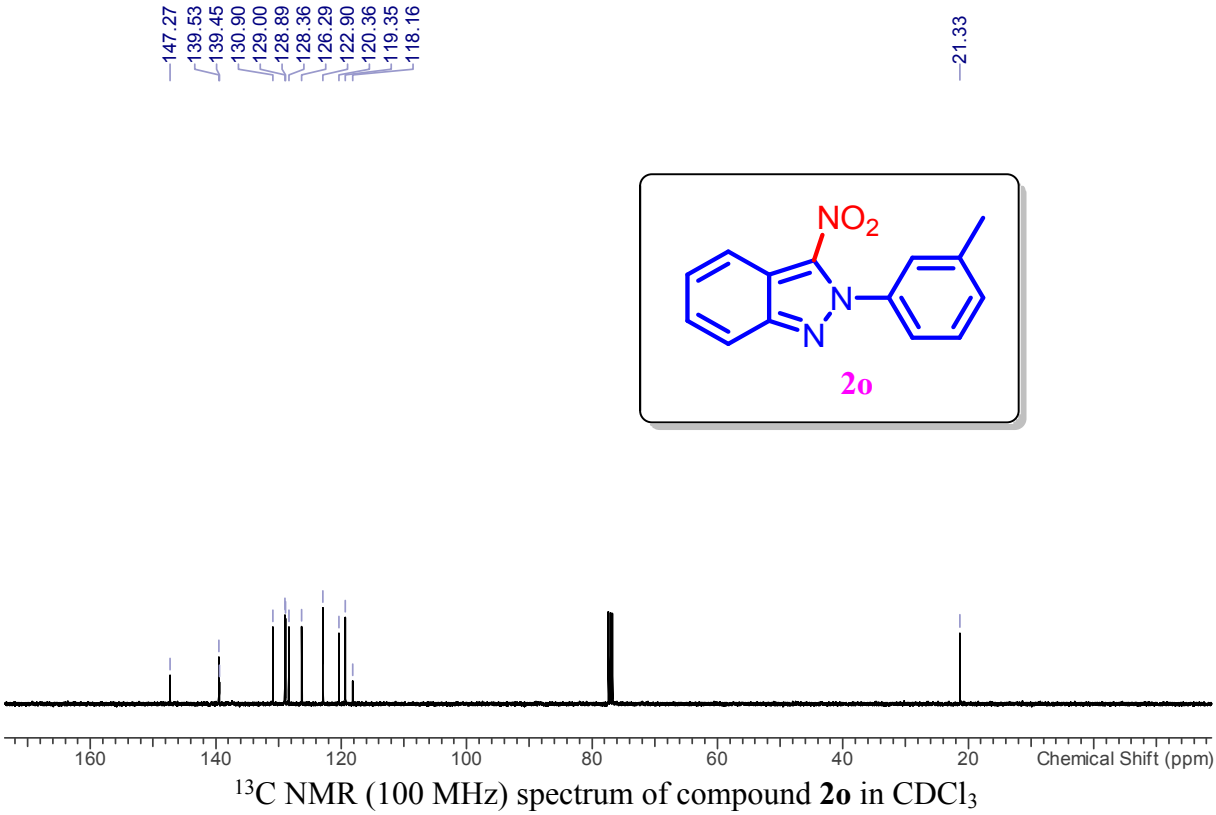
^{1}H NMR (400 MHz) spectrum of compound **2n** in $CDCl_3$



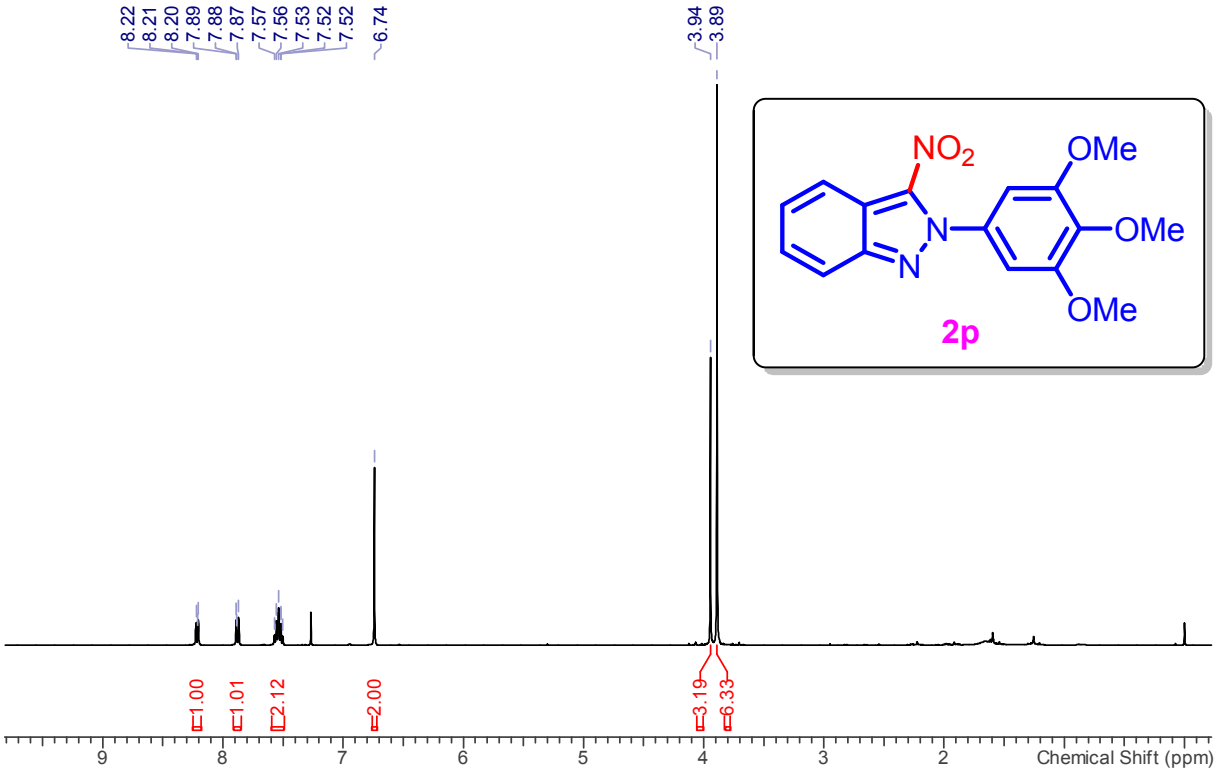
^{13}C NMR (100 MHz) spectrum of compound **2n** in $CDCl_3$



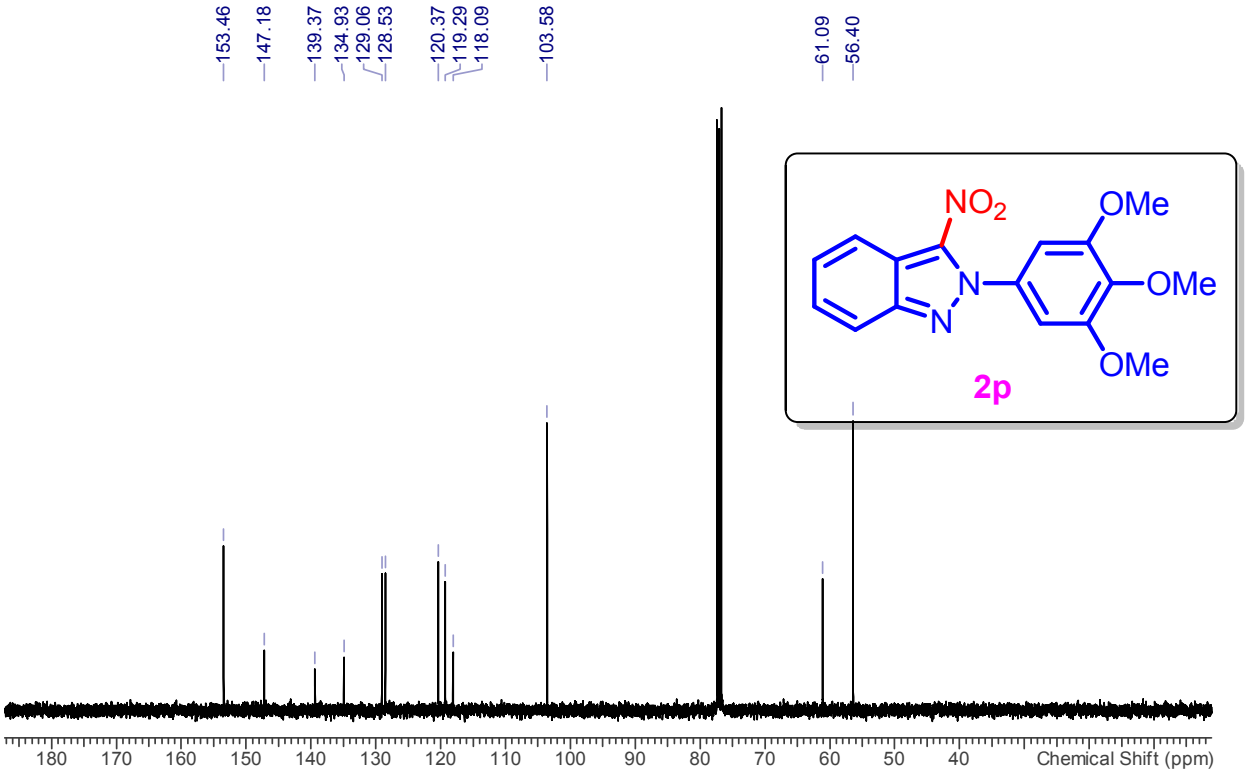
^{1}H NMR (400 MHz) spectrum of compound **2o** in $CDCl_3$



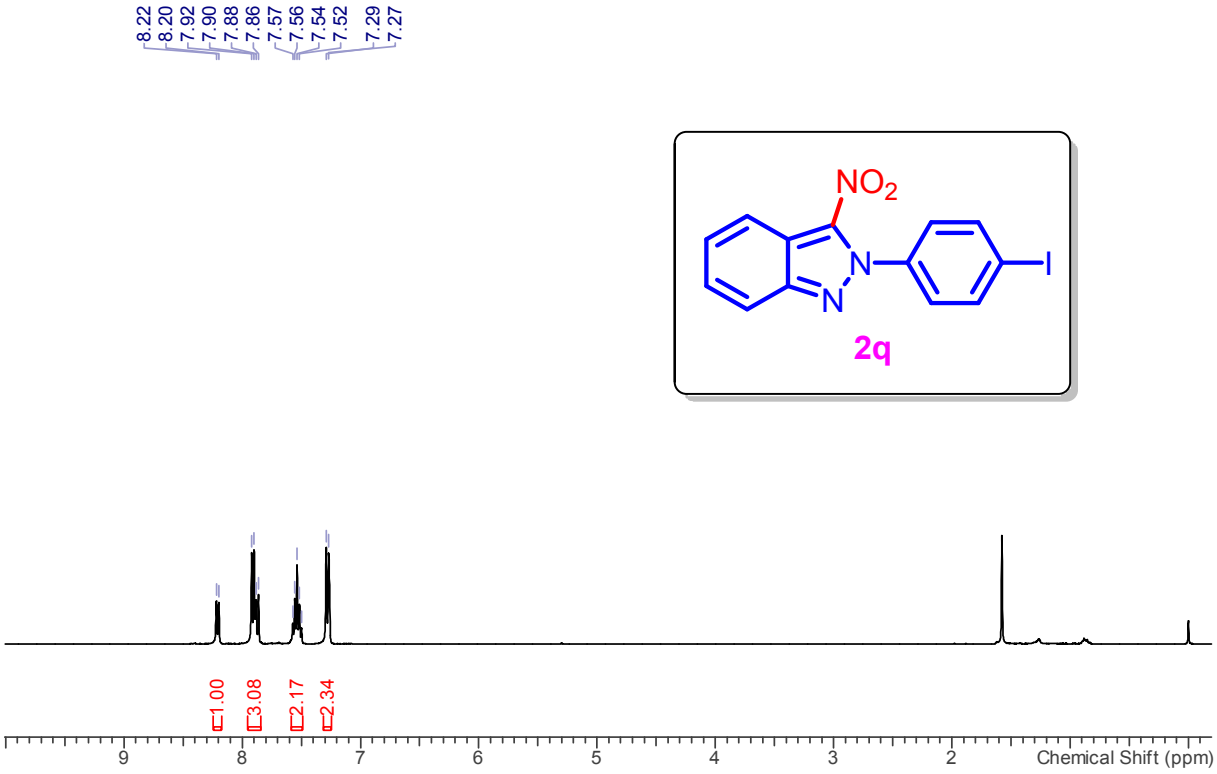
^{13}C NMR (100 MHz) spectrum of compound **2o** in $CDCl_3$



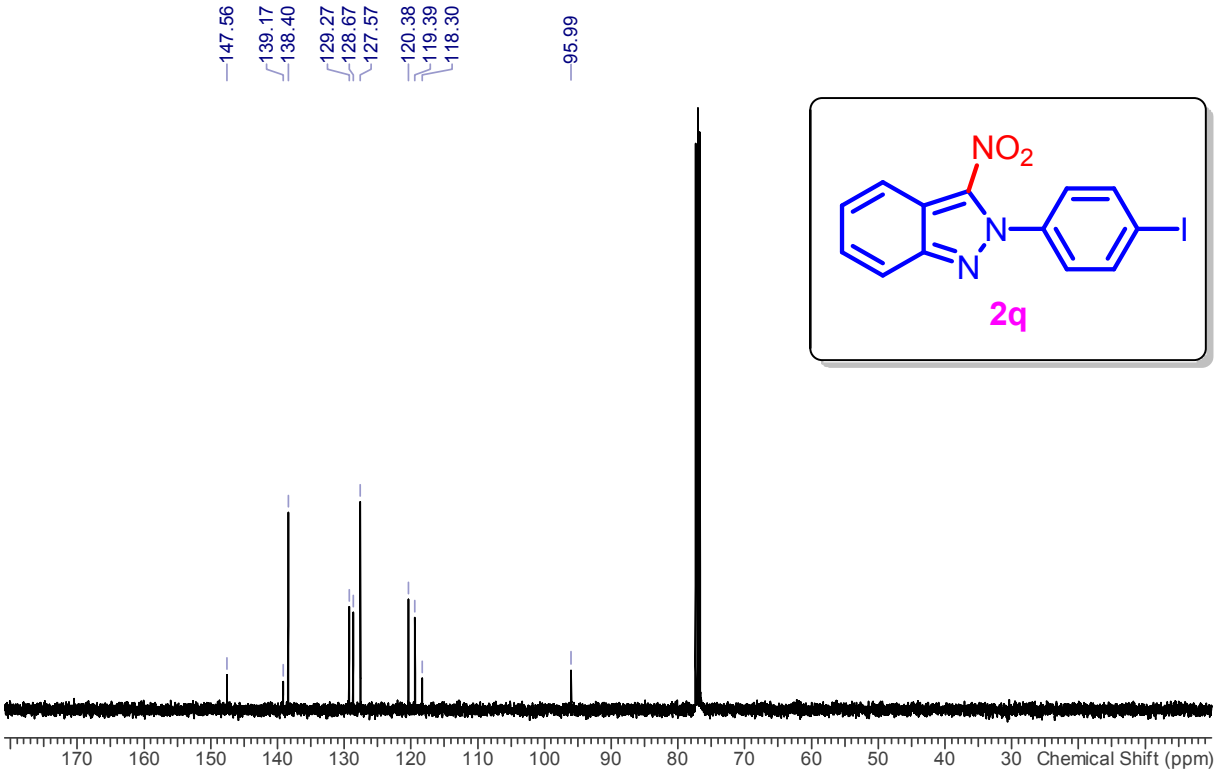
^{1}H NMR (400 MHz) spectrum of compound **2p** in $CDCl_3$



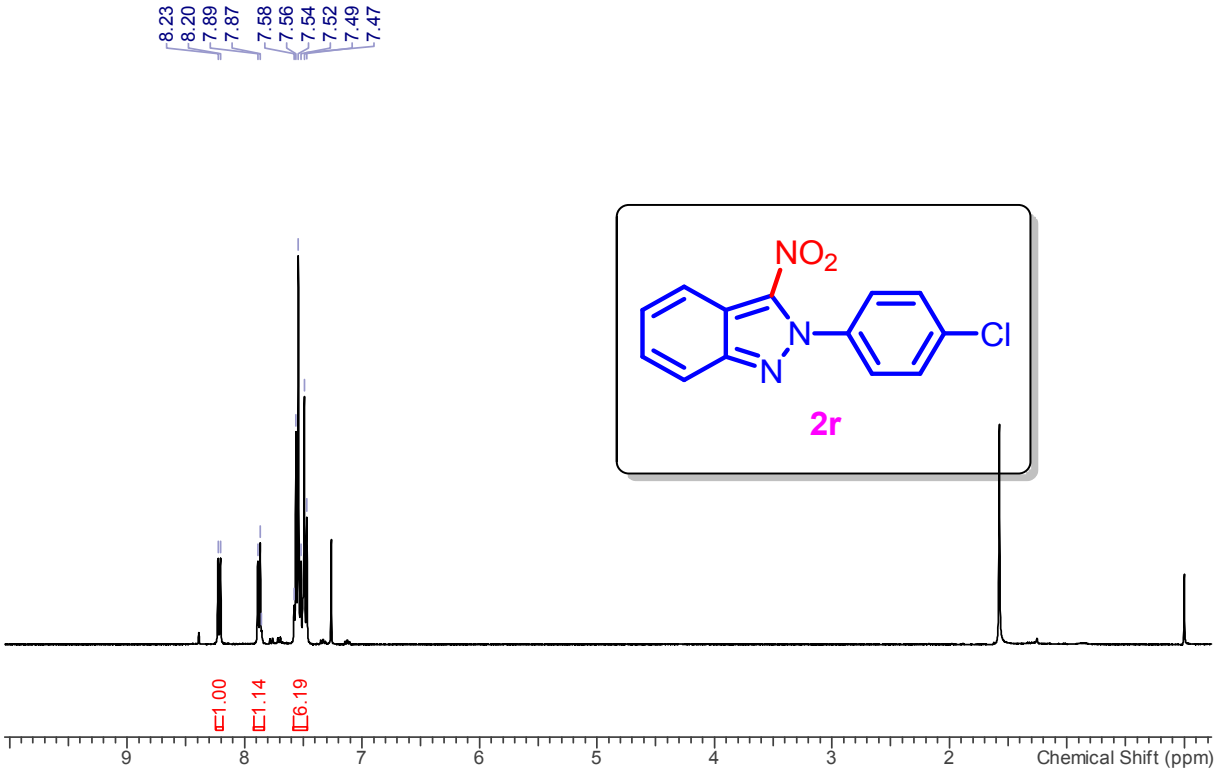
^{13}C NMR (100 MHz) spectrum of compound **2p** in $CDCl_3$



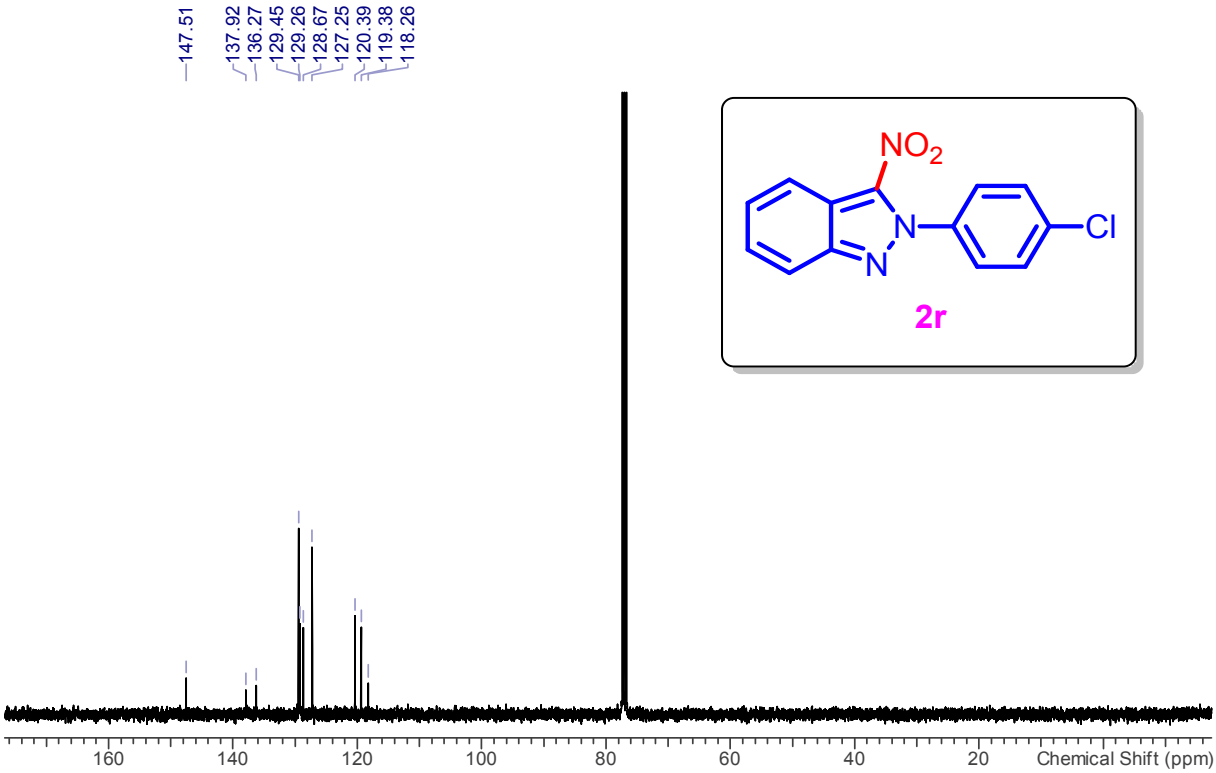
^{1}H NMR (400 MHz) spectrum of compound **2q** in $CDCl_3$



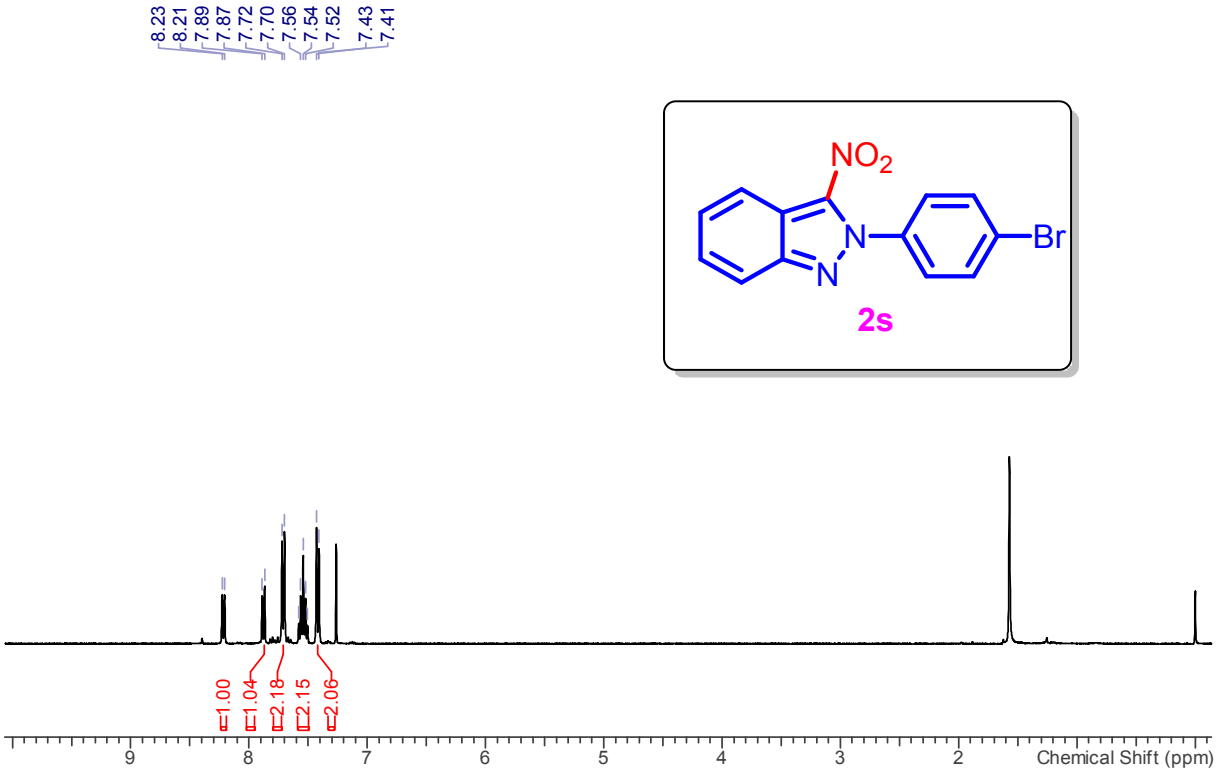
^{13}C NMR (100 MHz) spectrum of compound **2q** in $CDCl_3$



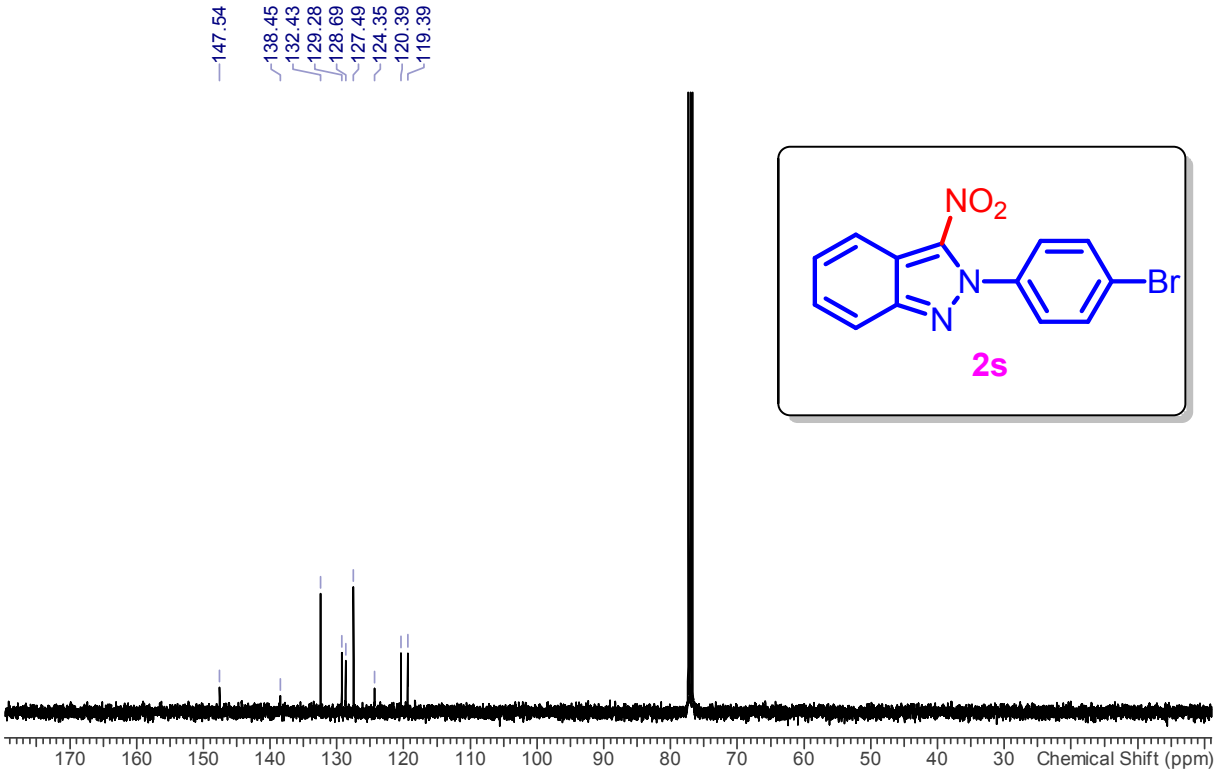
^{1}H NMR (400 MHz) spectrum of compound **2r** in $CDCl_3$



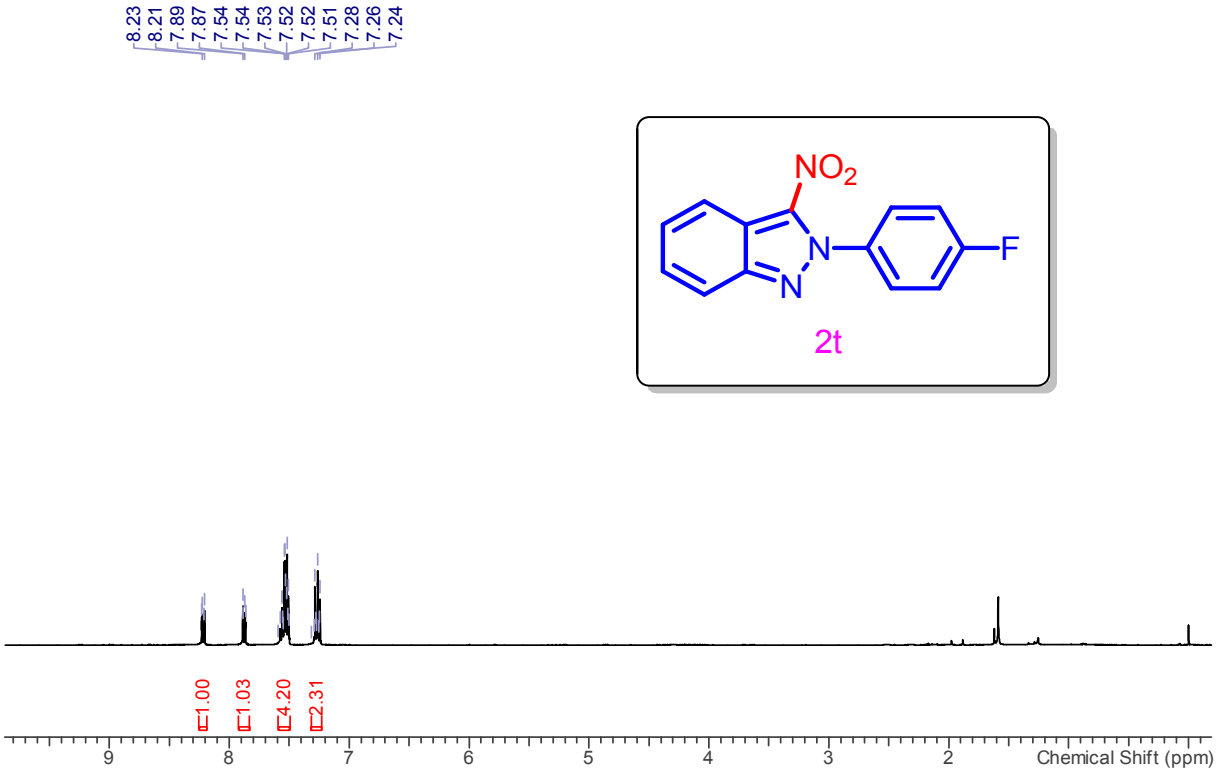
^{13}C NMR (100 MHz) spectrum of compound **2r** in $CDCl_3$



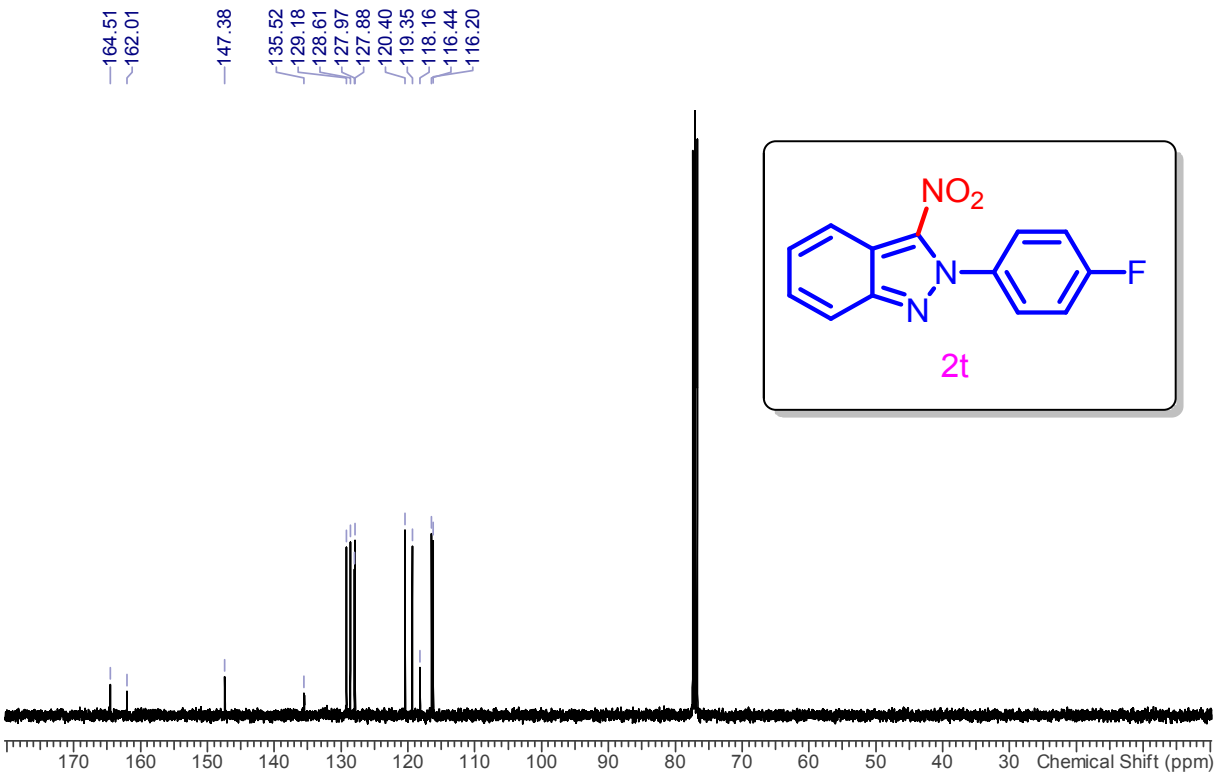
^{1}H NMR (400 MHz) spectrum of compound **2s** in $CDCl_3$



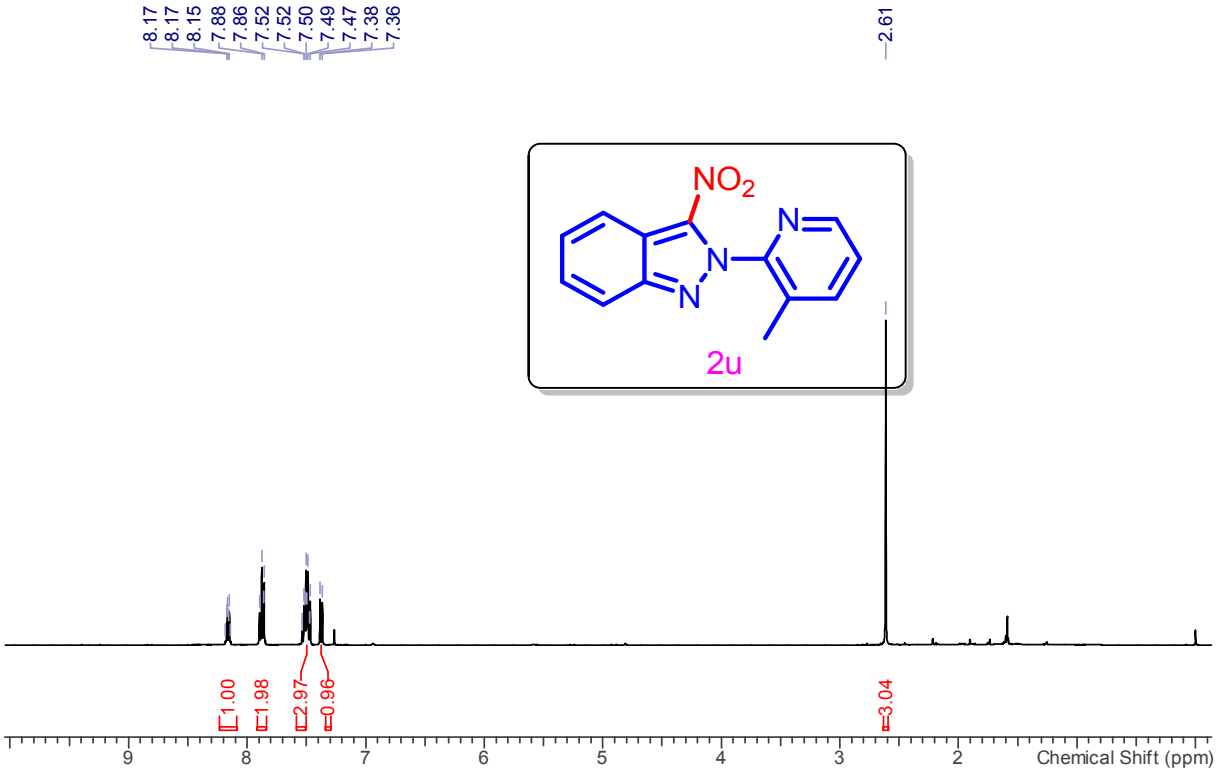
^{13}C NMR (100 MHz) spectrum of compound **2s** in $CDCl_3$



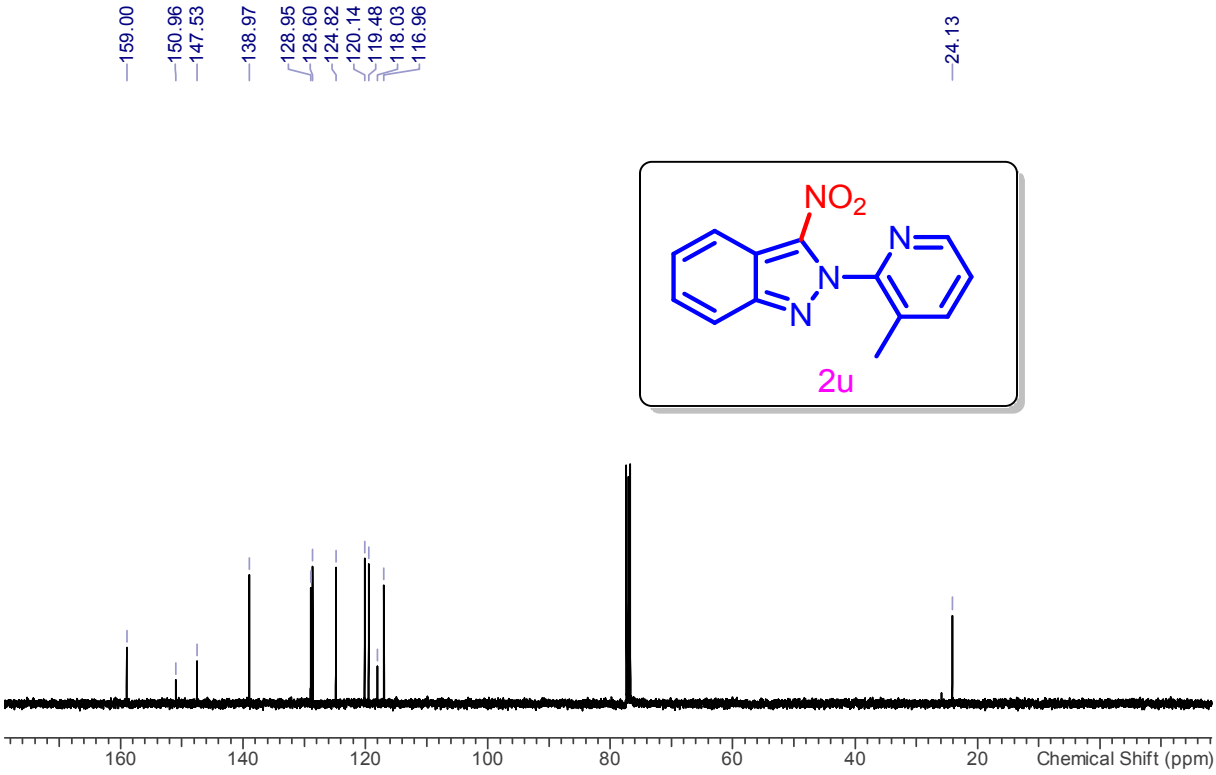
^{1}H NMR (400 MHz) spectrum of compound **2t** in $CDCl_3$



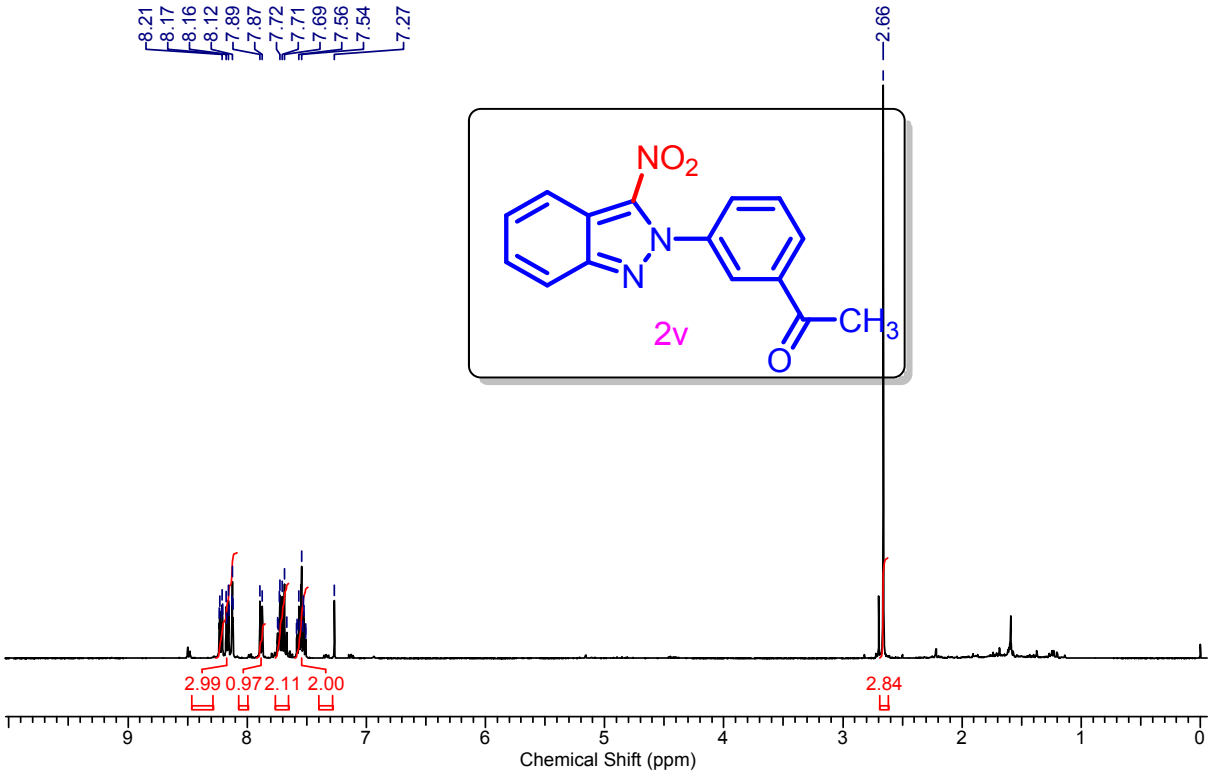
^{13}C NMR (100 MHz) spectrum of compound **2t** in $CDCl_3$



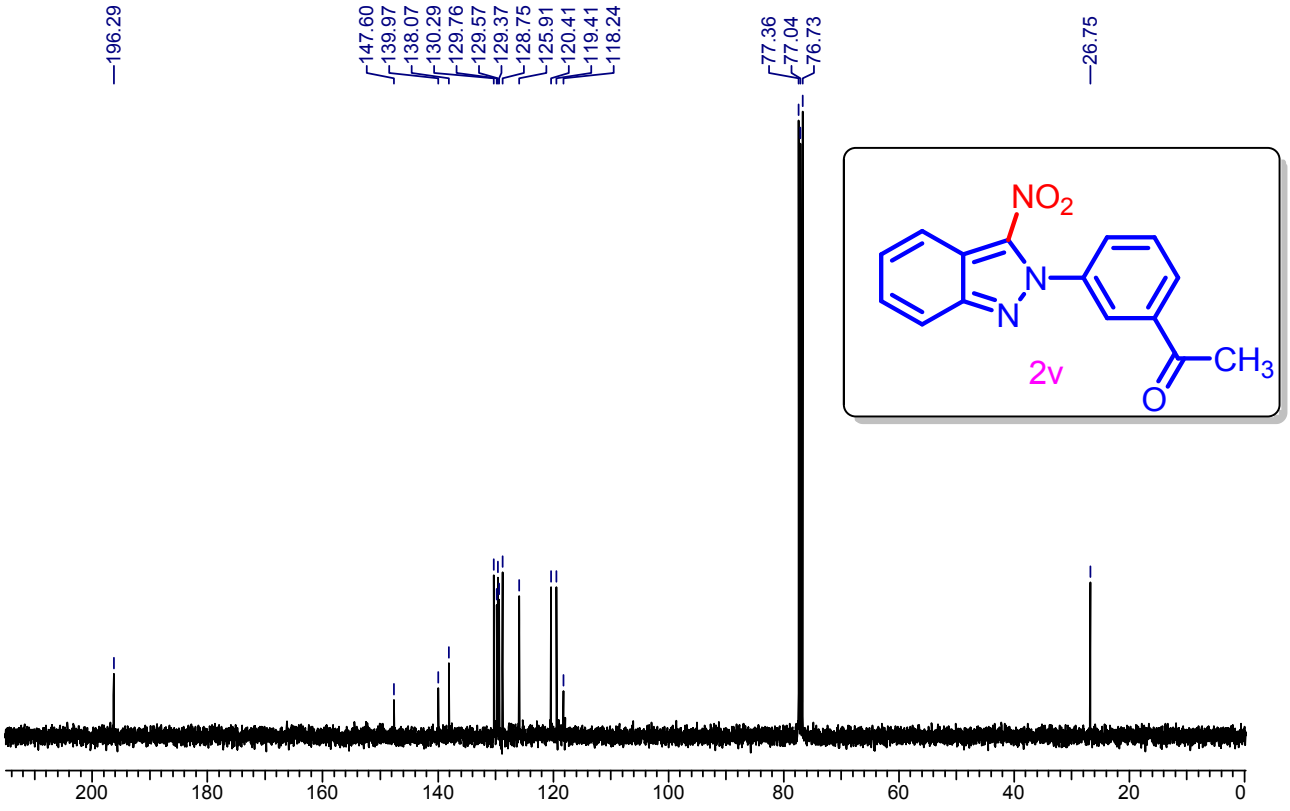
^{1}H NMR (400 MHz) spectrum of compound **2u** in $CDCl_3$



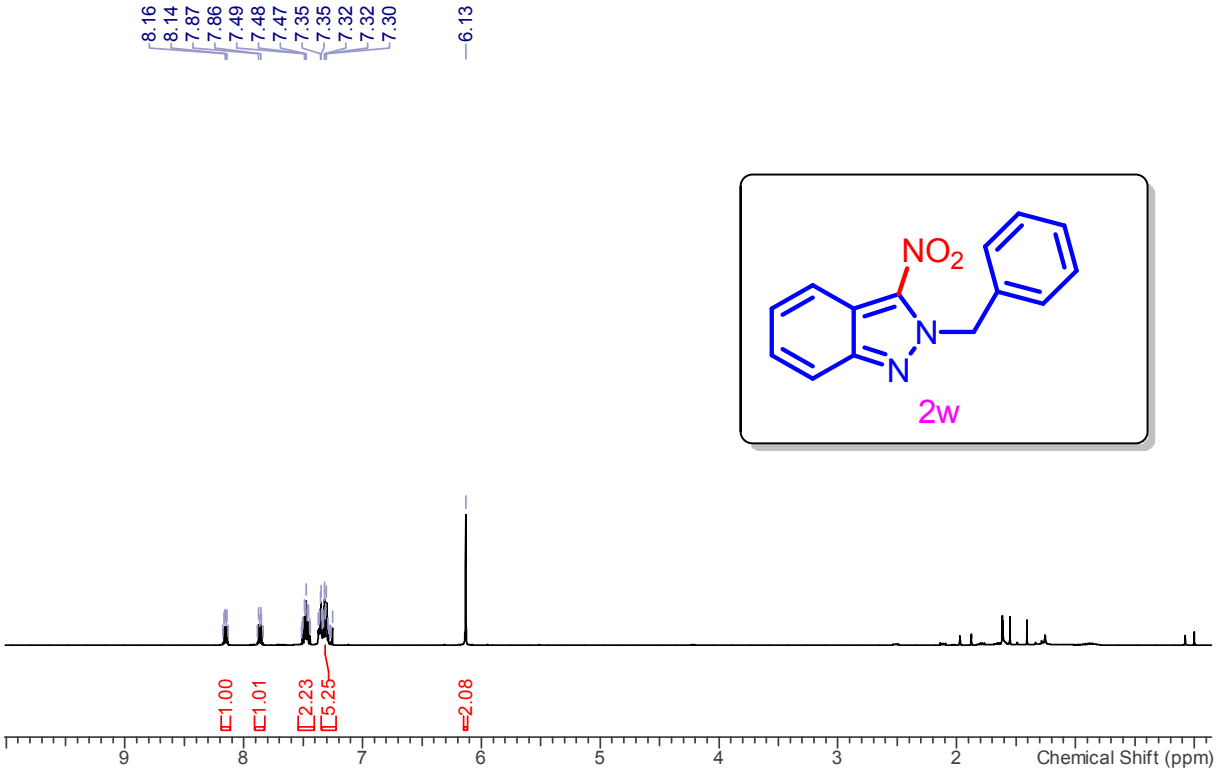
^{13}C NMR (100 MHz) spectrum of compound **2u** in $CDCl_3$



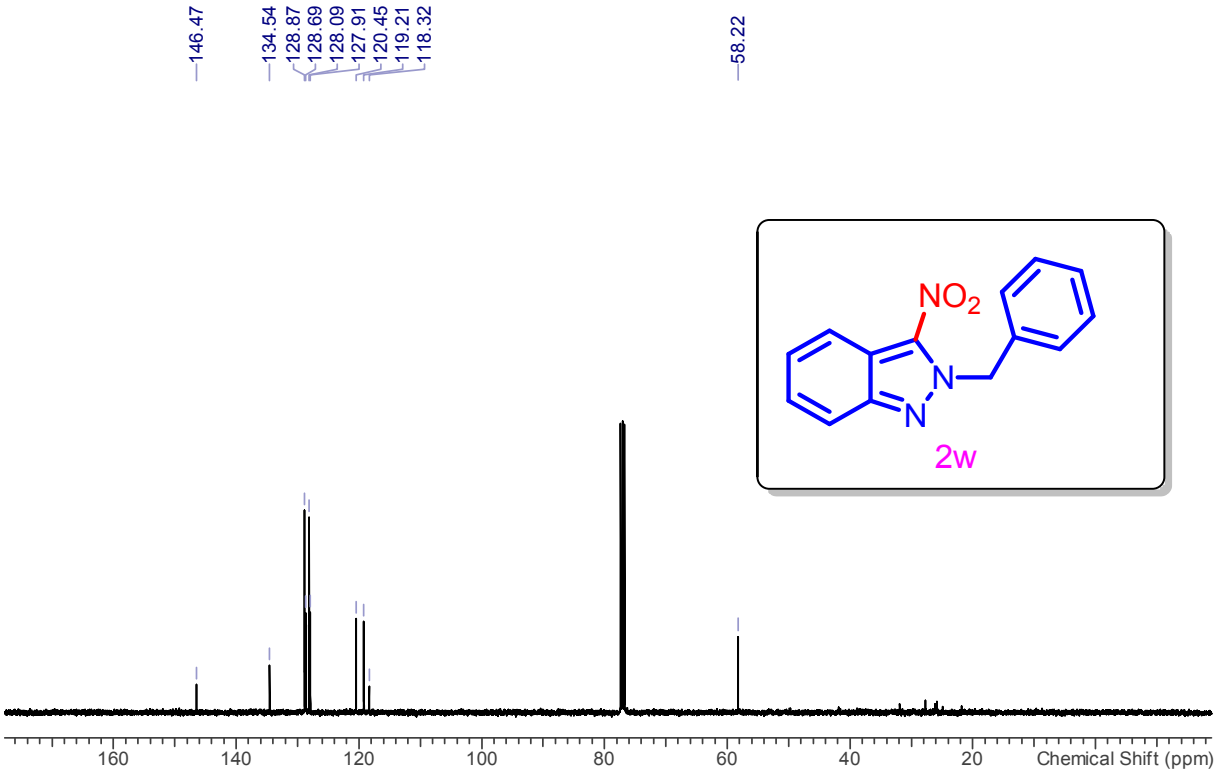
^{1}H NMR (400 MHz) spectrum of compound **2v** in $CDCl_3$



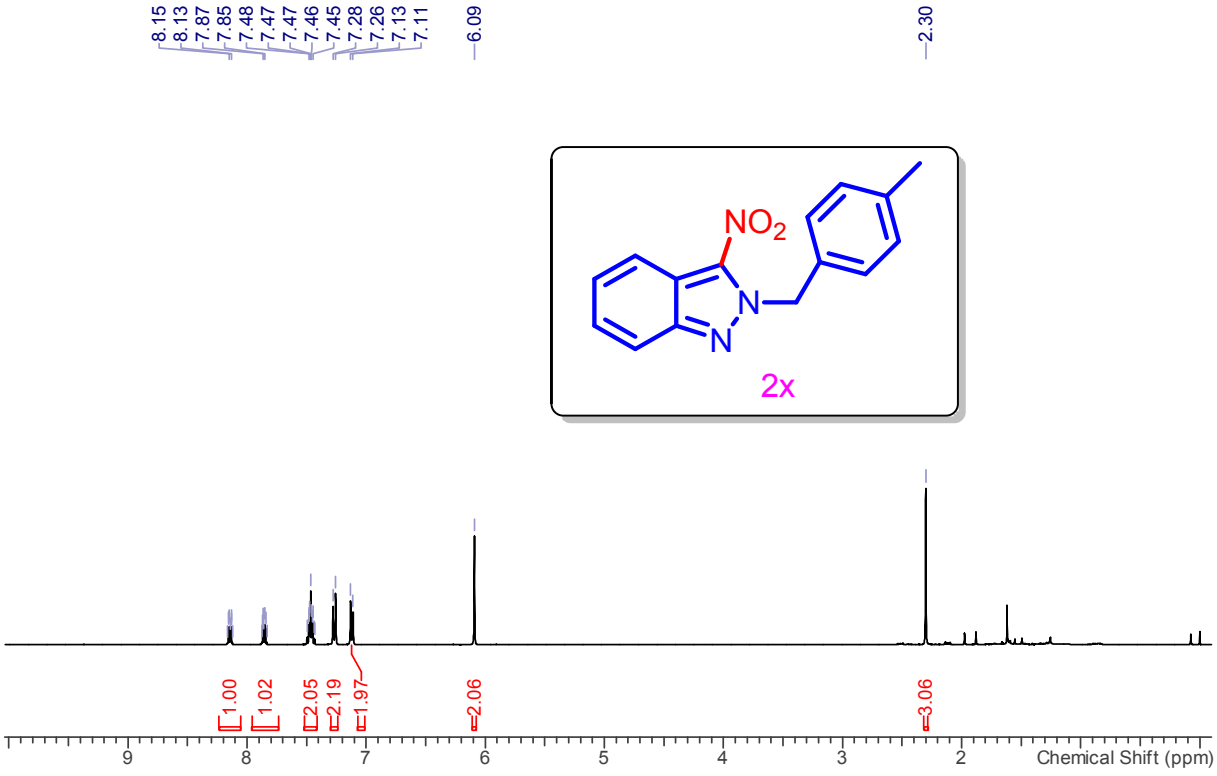
^{13}C NMR (100 MHz) spectrum of compound **2v** in $CDCl_3$



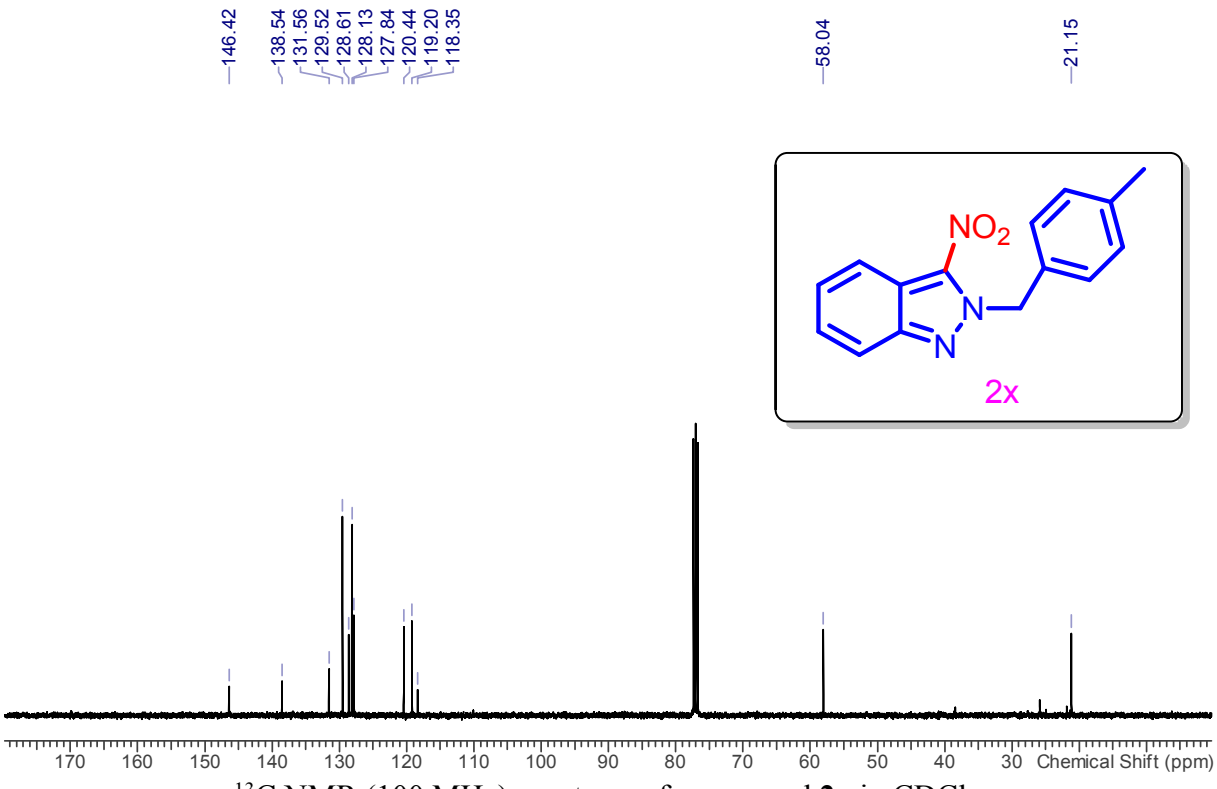
^{1}H NMR (400 MHz) spectrum of compound **2w** in $CDCl_3$



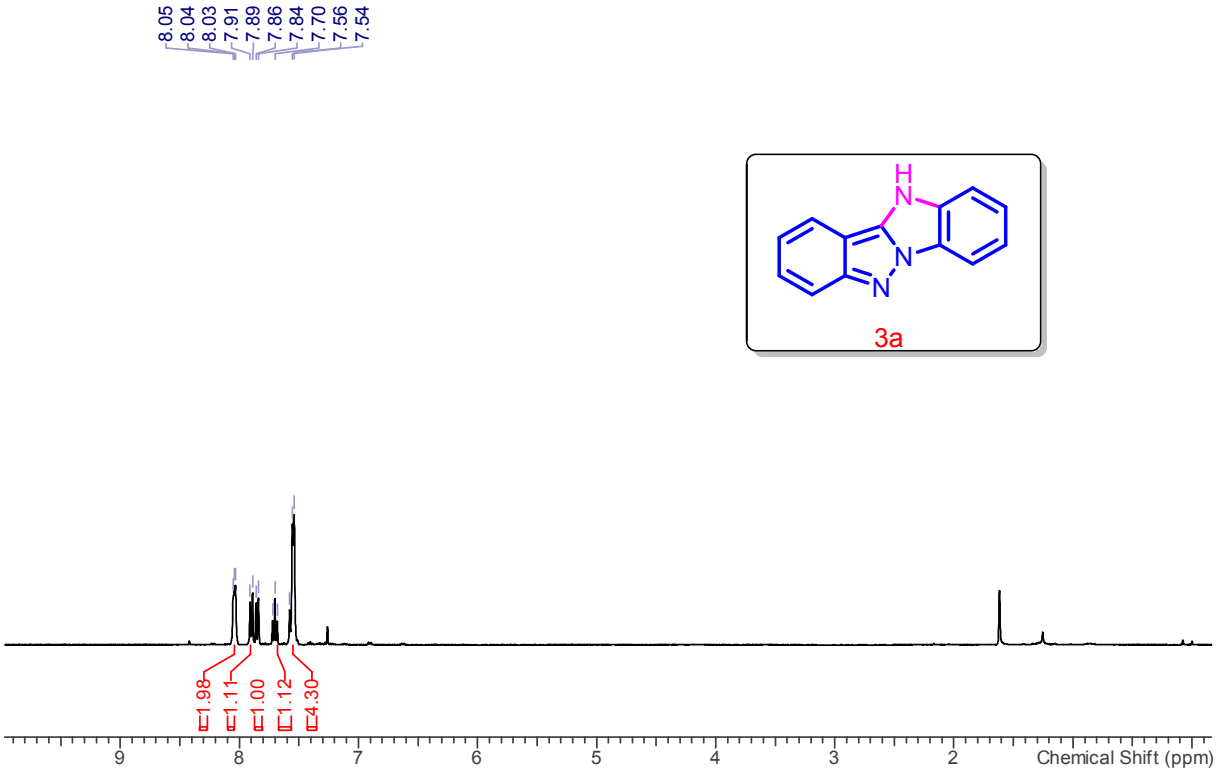
^{13}C NMR (100 MHz) spectrum of compound **2w** in $CDCl_3$



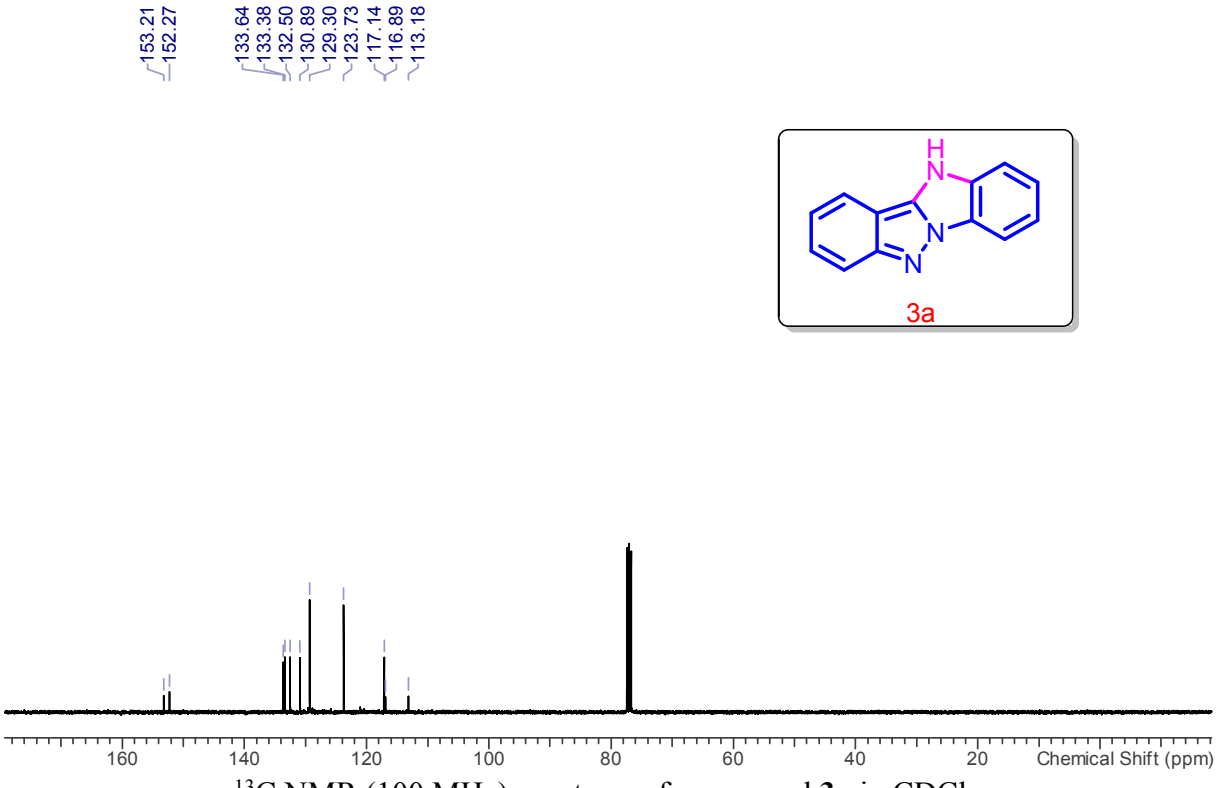
^{1}H NMR (400 MHz) spectrum of compound **2x** in $CDCl_3$



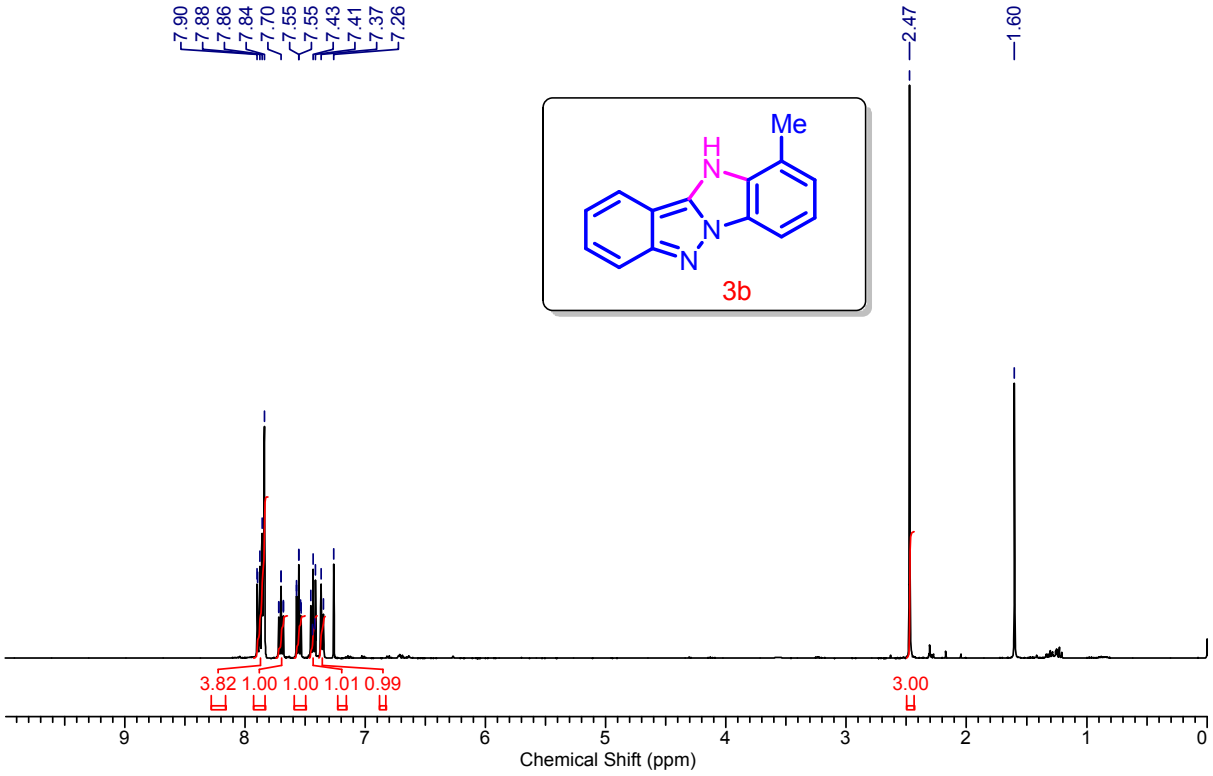
^{13}C NMR (100 MHz) spectrum of compound **2x** in $CDCl_3$



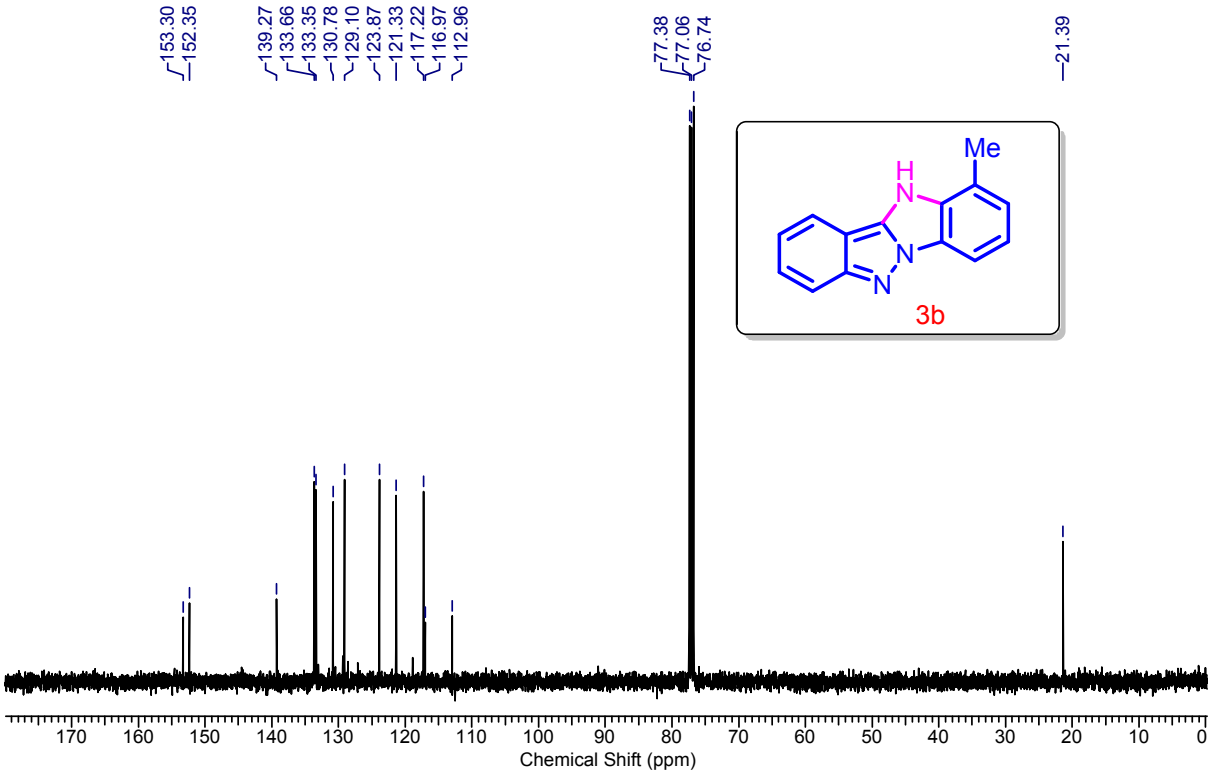
^{1}H NMR (400 MHz) spectrum of compound **3a** in $CDCl_3$



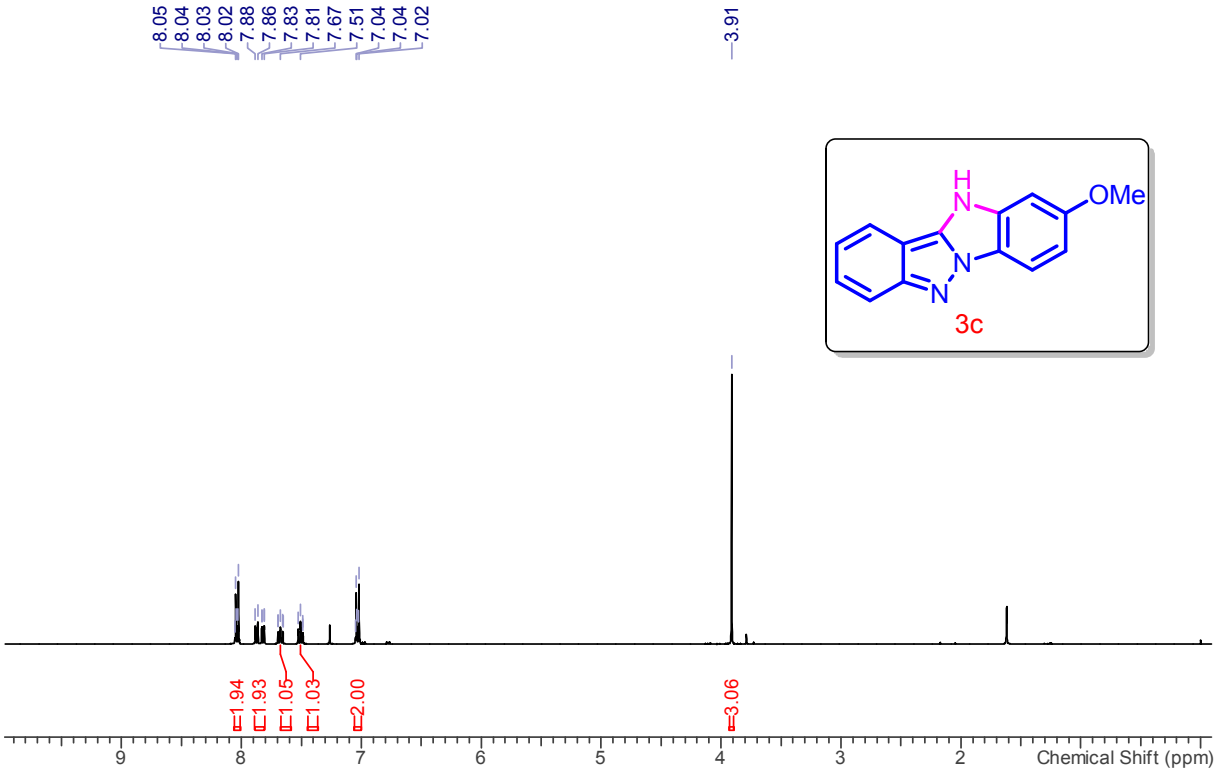
^{13}C NMR (100 MHz) spectrum of compound **3a** in $CDCl_3$



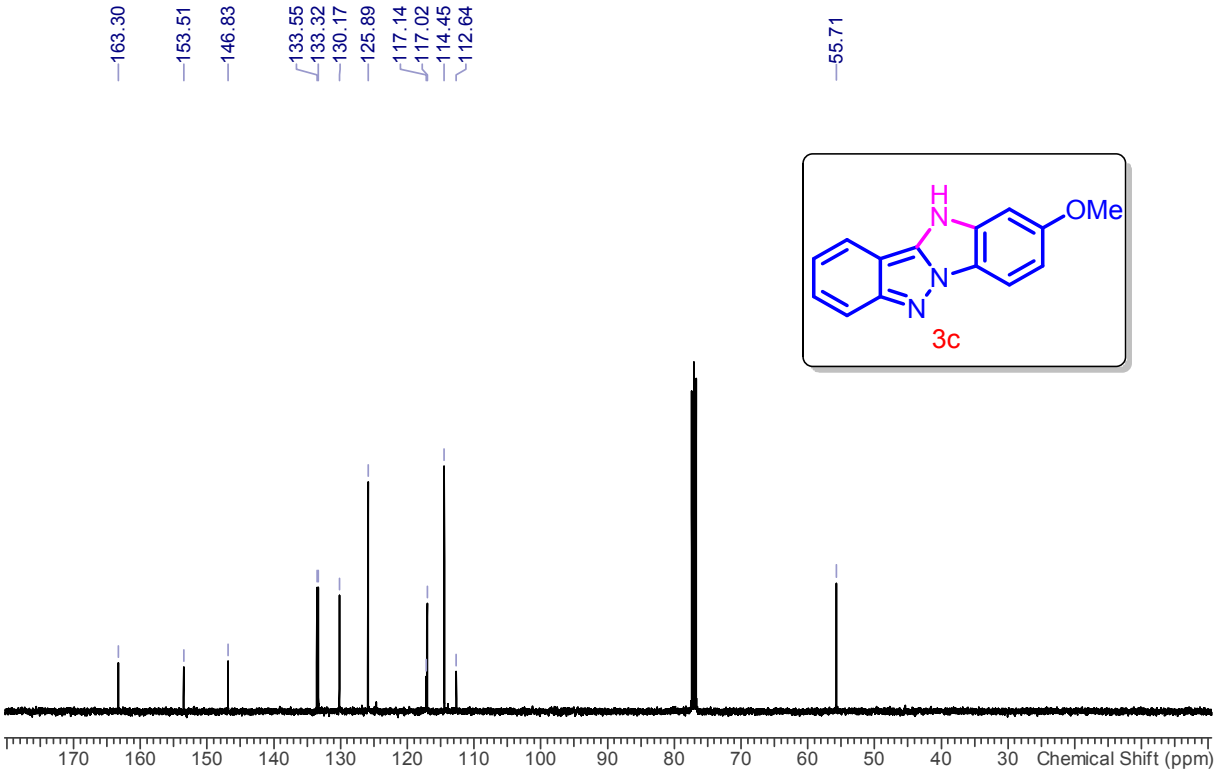
^{1}H NMR (400 MHz) spectrum of compound **3b** in $CDCl_3$



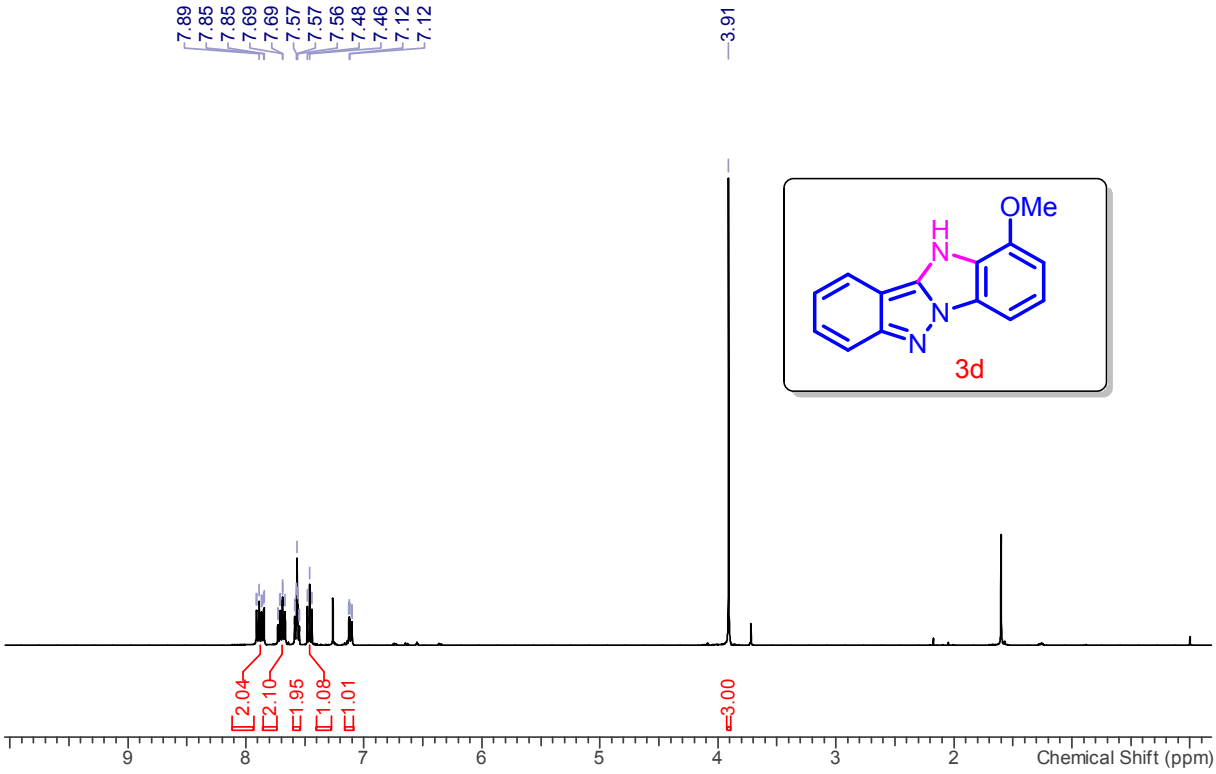
^{13}C NMR (100 MHz) spectrum of compound **3b** in $CDCl_3$



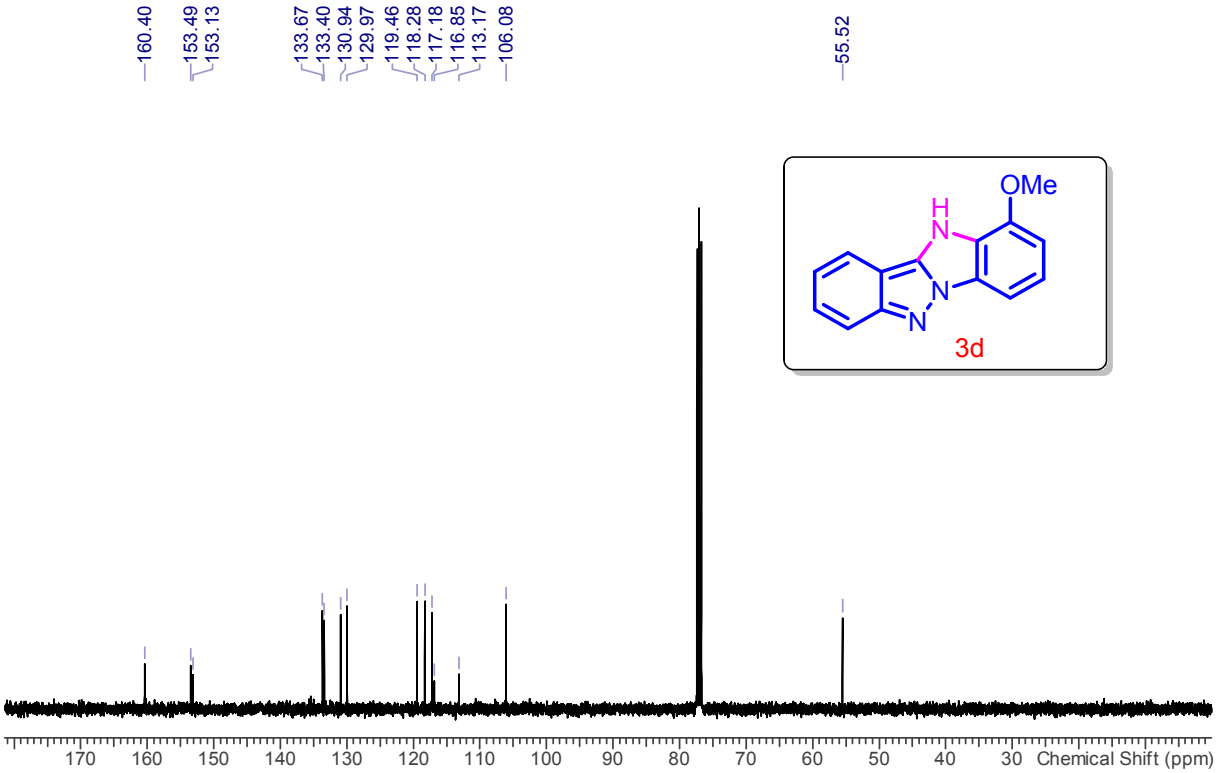
^{1}H NMR (400 MHz) spectrum of compound **3c** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **3c** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound **3d** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **3d** in $CDCl_3$