Supporting Information

Rh(III)-Catalyzed, Hydrazine-directed C−H Functionalization with 1-Alkynylcyclobutanols: A New Strategy for 1*H*-Indazoles

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1. General information

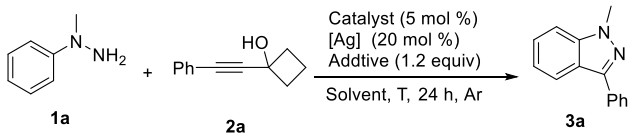
All chemicals were obtained from commercial sources and were used as received unless otherwise noted. 1-Alkynylcyclobutanols[1] were synthesized according to literature reports. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. ^{1}H NMR was recorded on Bruker Ascend^{TM} (400 MHz). Chemical shifts are reported downfield from TMS (= 0) for ^{1}H NMR. ^{13}C NMR was recorded on Bruker Ascend^{TM} (100 MHz) for ^{13}C NMR. chemical shifts are reported in the scale relative to $CDCl_3$ (= 77.0) or DMSO-d_6 (= 40.0). ^{19}F NMR were recorded on Bruker Ascend^{TM}. HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

2. Optimization of reaction conditions

Initially, the model substrates, 1-methyl-1-phenylhydrazine **1a** and 1-(phenylethynyl) cyclobutan-1-ol **2a** were used to optimize reaction parameters (Table S1). Among the transition- metal catalysts tested, $[Cp^*RhCl_2]_2$ gave 58% yield of ideal product **3a** (entries 1-3). A number of additives, such as $Zn(OTf)_2$, $Cu(OAc)_2$, and $Mn(OAc)_2$ were then screened along with different Ag-salts (entries 1 and 4-12). The combination of $Zn(OAc)_2$ and $AgSbF_6$ gave the best yield (entry 1). The reaction also proceeded in other solvents, such as dichloromethane (DCM), toluene, tetrahydrofuran (THF), and hexafluoroisopropanol (HFIP). Among them, toluene was found to be the most efficient one providing **3a** in 60% yield (entries 13−16). We were pleased to find that by increasing the amount of **1a** the conversion rate of **2a** was improved resulting in increase in yield of **3a** to 65% (entries 17 and 18). Further screening of the reaction temperature revealed that reaction temperature of 50 °C gave the best yields (entries 19 and 20). Then, $AgNO_3$ was used instead of $AgSbF_6$, which afforded the corresponding product **3a** in slightly lower yield (61%, entry 21). Finally, the optimal reaction conditions were determined as: **2a** (0.4 mmol), **1a** (1.2 equiv),

$[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), and $Zn(OAc)_2$ (1.2 equiv) in toluene (3.0 mL) at 50 °C for 24 h under Ar atmosphere.

Table S1 Optimization of reaction conditions[a]

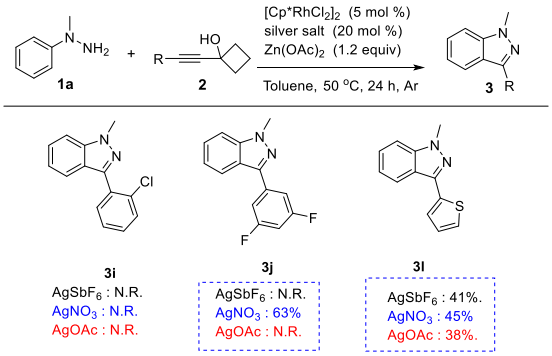


1a 2a 3a

Entry	[Cat]	Additive	[Ag]	Solvent	Yield[b](%) **3a**
1	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	DCE	58%
2	$[Cp^*IrCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	DCE	N.R.
3	$[RuCl_2(p\text{-cymene})]_2$	$Zn(OAc)_2$	$AgSbF_6$	DCE	N.R.
4	$[Cp^*RhCl_2]_2$	$Zn(OTf)_2$	$AgSbF_6$	DCE	30
5	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	$AgSbF_6$	DCE	N.R.
6	$[Cp^*RhCl_2]_2$	$Mn(OAc)_2$	$AgSbF_6$	DCE	N.R.
7	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgBF_4$	DCE	54
8	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgNTf_2$	DCE	55
9	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	AgOTf	DCE	53
10	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	AgOAc	DCE	57
11	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgPF_6$	DCE	47
12	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	CF_3CO_2Ag	DCE	56
13	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	DCM	49
14	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	60
15	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	THF	46
16	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	HFIP	43
17[c]	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	65
18[d]	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	65
19[c,e]	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	65
20[c,f]	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	53
21[c,g]	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgNO_3$	toluene	61

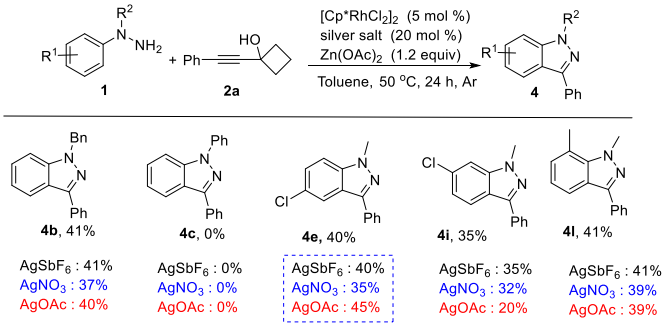
[a] Reaction conditions: **1a** (0.40 mmol), **2a** (0.48 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %) and $Zn(OAc)_2$ (1.2 equiv) in DCE (3.0 mL) at 80 °C for 24 h under Ar atmosphere. [b] Isolated yield. [c] **2a** (0.4 mmol), **1a** (1.2 equiv) was used. [d] **2a** (0.4 mmol), **1a** (2.1 equiv) was used. [e] The reaction temperature was 50 °C. [f] The reaction temperature was 25 °C. [g] $AgNO_3$ instead of $AgSbF_6$. N.R. = No Reaction.

Scheme S1 Effect of silver salt on the yield of product **3**.[a,b]



[a] Reaction conditions: **1a** (0.48 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), silver salt (20 mol %) and $Zn(OAc)_2$ (1.2 equiv.) in toluene (3.0 mL) at 50 °C for 24 h under Ar atmosphere. [b] Isolated yield calculated based on **2**.

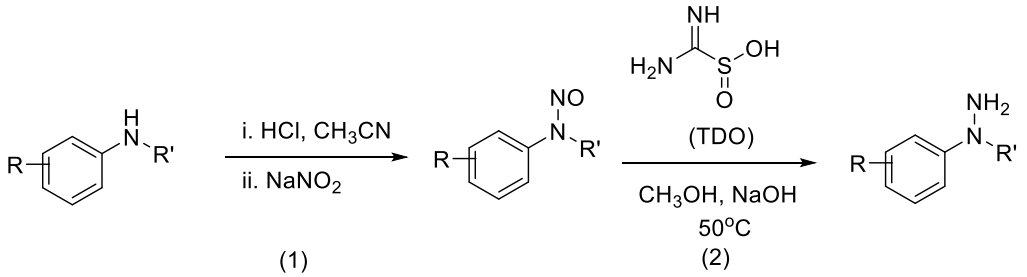
Scheme S2 Effect of silver salt on the yield of product **4**.[a,b]



[a]Reaction conditions: **1** (0.48 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), silver salt (20 mol %) and $Zn(OAc)_2$ (1.2 equiv) in toluene (3.0 mL) at 50 °C for 24 h under Ar atmosphere. [b] Isolated yield calculated based on **2a**.

Eight entries in Schemes S1 and S2 that gave relatively low yields under standard conditions were repeated using AgOAc and $AgNO_3$ as silver salt respectively. To our delight, $AgNO_3$ gave **3j** and **3l** in higher yields (63% and 45% respectively). Furthermore, the yield of **4e** could increase to 45% by using AgOAc as silver salt.

3. General procedure for the preparation of *N*-nitrosamines[2]

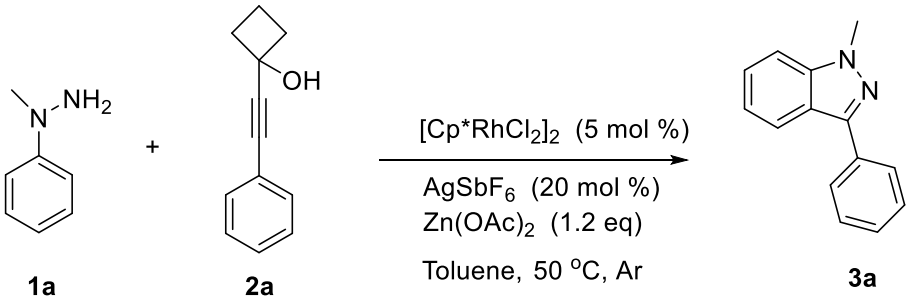


(1) (2)

(1) Aniline (15 mmol, 1.0 equiv) was dissolved in a 1:2 mixture of acetonitrile and water (6 mL) at 0 °C (ice bath). Concentrated aqueous HCl (6 mL, 4.8 equiv) was added dropwise, and the resulting mixture was stirred vigorously at 0 °C for half an hour. To this mixture was added an aqueous solution (4 mL) of $NaNO_2$ (1.04 g, 1.0 equiv) over the course of 10 min. The reaction was allowed to proceed for 1 h, then extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel to give the corresponding *N*-nitrosoaniline substrates.

(2) *N*-nitrosamine was allowed to stir in methanol (2 mmol/mL) approximately at 50 °C for 5 min and then aqueous solution of sodium hydroxide (1 M, 6 equiv) followed by thiourea dioxide (TDO) (3 equiv) was added. The reaction was stirred for 3-4 h and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulphate, concentrated and purified by for column chromatography (ethyl acetate/hexane) to obtain corresponding pure substituted *N*-aryl hydrazine.

4. General procedure for synthesis of 1*H*-Indazoles



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

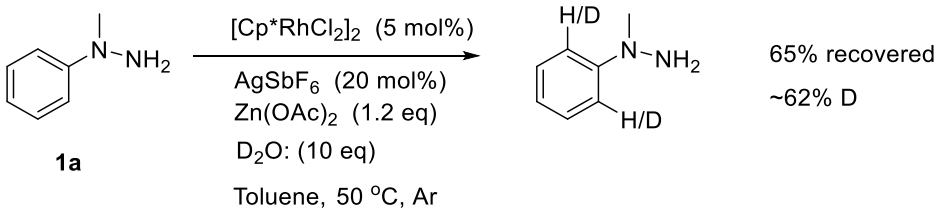
1-methyl-1-phenylhydrazine **1a** (0.48 mmol), 1-(phenylethynyl)cyclobutan-1-ol **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.02 mmol), $AgSbF_6$ (0.04 mmol) and $Zn(OAc)_2$ (0.48 mmol) were dissolved in toluene (3 mL). The mixture was stirred at 50 °C under argon atmosphere for 24 hours. The resulting mixture was cooled to room temperature and then purified by silica gel column chromatography (PE/EtOAc = 100:1 v/v) to afford the desired product **3a** as an off-white solid (54 mg, 65%).

5. Gram-scale synthesis of 3a

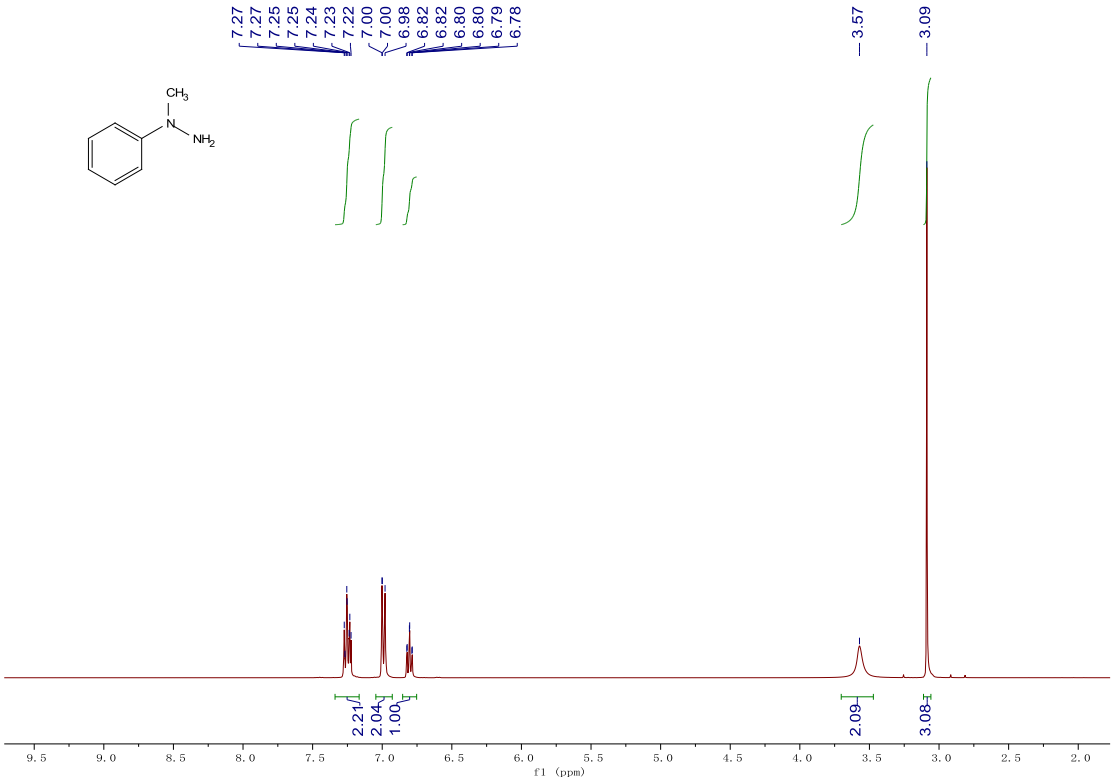
1-methyl-1-phenylhydrazine **1a** (2.128 g，17.442 mmol), **2a** (2.500 g，14.535 mmol), $[Cp^*RhCl_2]_2$ (450 mg，5 mol %), $AgSbF_6$ (999 mg，20 mol %) and $Zn(OAc)_2$ (3.20 g，1.2 eq) were dissolved in toluene (45 mL) in a three-neck flask. The mixture was stirred at 50 °C under argon atmosphere for 24 hours. The resulting mixture was cooled to room temperature and then diluted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ ethyl acetate =100:1 v/v) to give **3a** as an off-white solid (2.057 g，68% yield).

6. Mechanistic studies

6.1 Deuteration experiment



1-methyl-1-phenylhydrazine **1a** (0.48 mmol), $[Cp^*RhCl_2]_2$ (0.02 mmol), $AgSbF_6$ (0.04 mmol), and $Zn(OAc)_2$ (0.48 mmol) and D_2O (4.8 mmol) were dissolved in toluene (3 mL). The mixture was stirred at 50 °C under argon atmosphere for 24 hours. The resulting mixture was cooled to room temperature, and then purified on silica gel column chromatography (PE/EtOAc = 100:1 v/v) to afford the desired product **3a** as an off-white solid, 62% deuterium incorporation (determined by 1H NMR) was observed at the *ortho*-position.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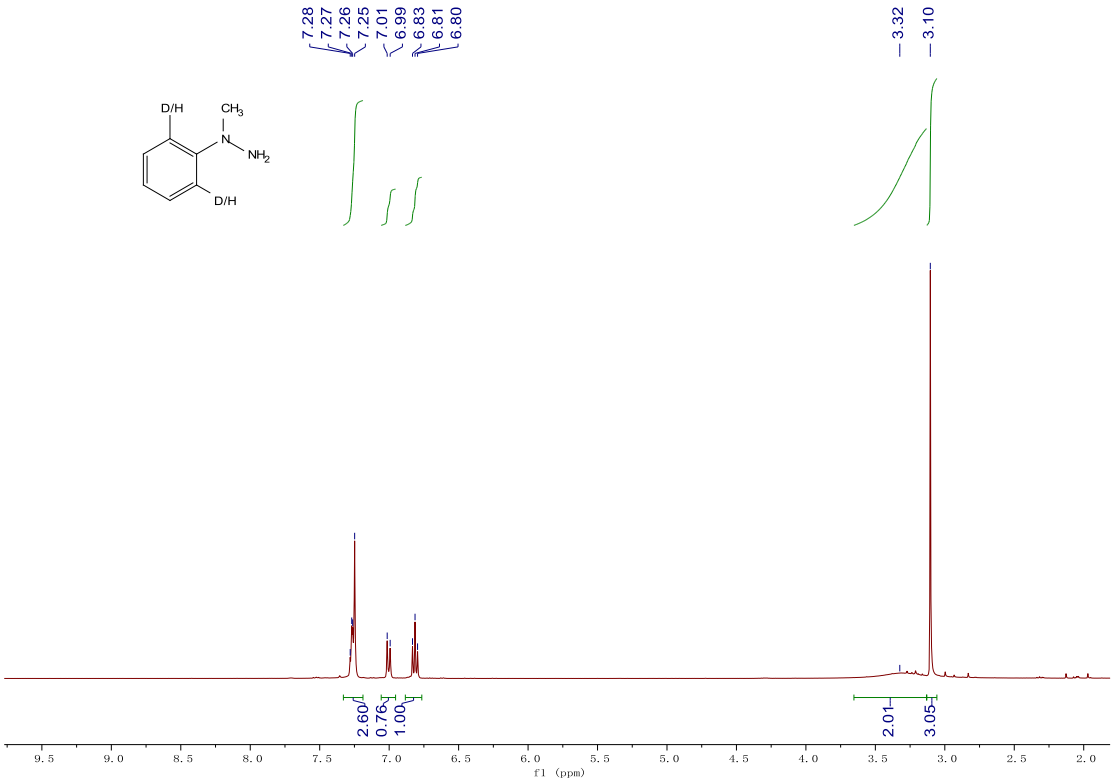
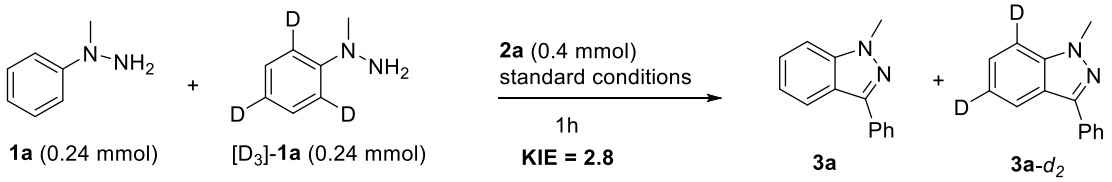
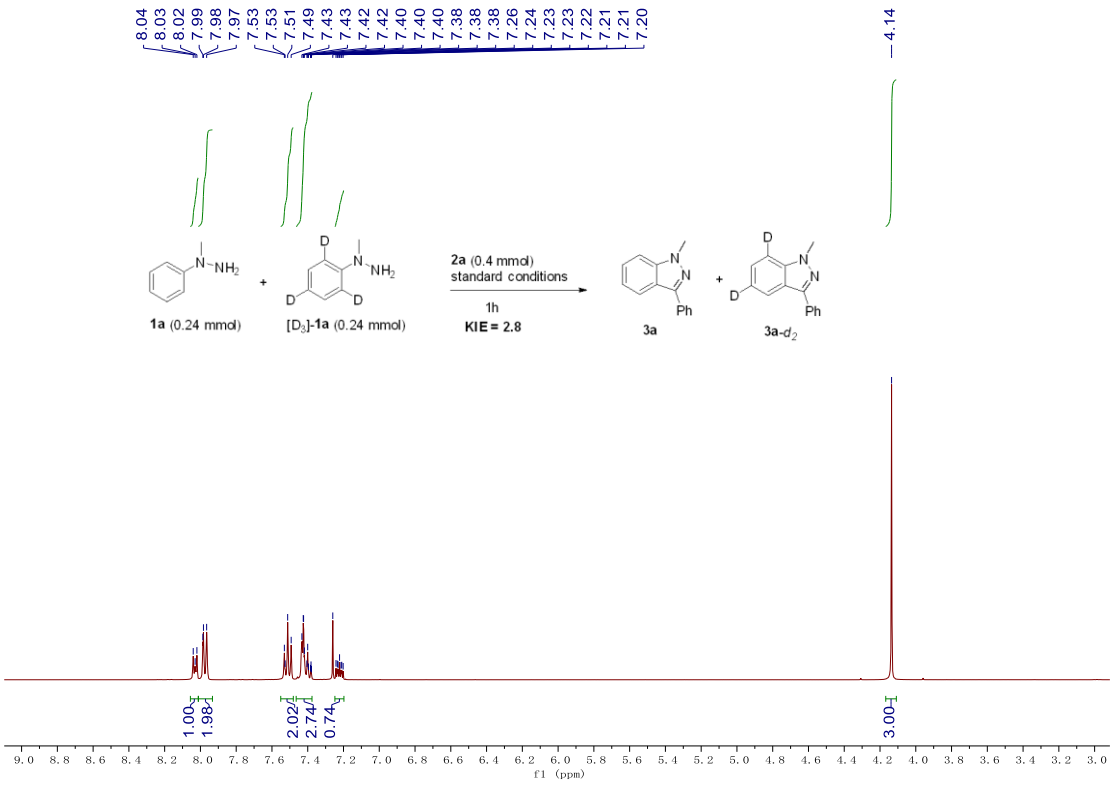
7.27
7.25
7.25
7.24
7.23
7.22
7.00
7.00
6.98
6.82
6.82
6.80
6.80
6.79
6.78
3.57
3.09
CH3
N
NH2
2.21
2.04
1.00
2.09
3.08
f1 (ppm)

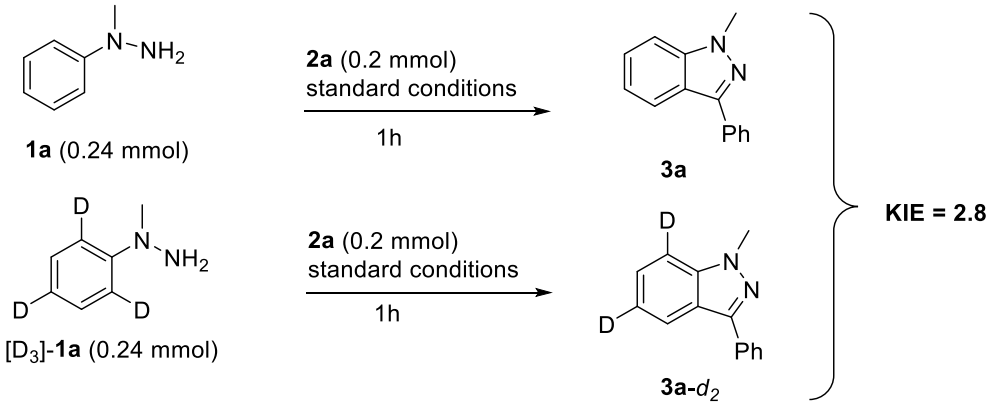

7.28
7.27
7.26
7.25
7.01
6.99
6.83
6.81
6.80
3.32
3.10
D/H
CH3
N
NH2
D/H
2.60
0.76
1.00
2.01
3.05
f1 (ppm)

6.2 KIE experiments

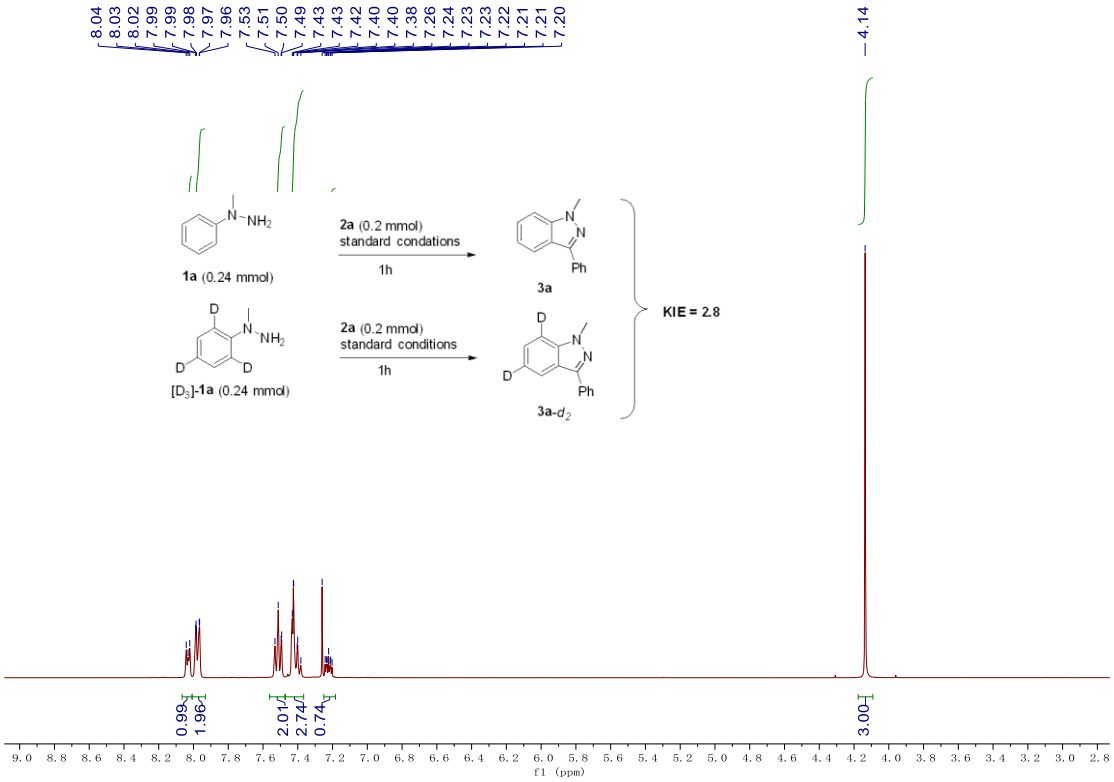


A mixture of 1-methyl-1-phenylhydrazine **1a** (29 mg, 0.24 mmol), 1-methyl-1-(phenyl-2,4,6-d_3) hydrazine [D_3]-**1a** (30 mg, 0.24 mmol), [Cp*$RhCl_2$]$_2$ (12 mg, 5 mol %), $AgSbF_6$ (0.04 mmol), $Zn(OAc)_2$ (0.48 mmol) and 1-(phenylethynyl) cyclobutan-1-ol **2a** (69 mg, 0.4 mmol) were dissolved in toluene (3 mL) under Ar. The reaction mixture was stirred at 50 ^oC for 1 hours. Purification was performed on flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired products. KIE value (k_H/k_D = 2.8) was determined on the basis of ^1H NMR analysis.

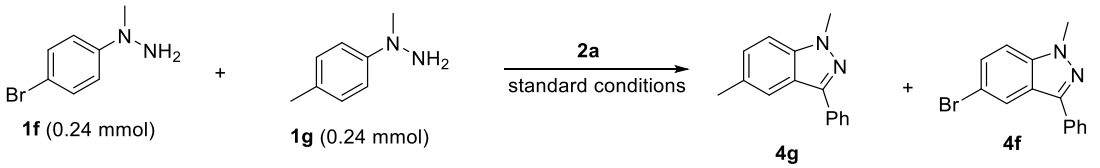




A mixture of 1-methyl-1-phenylhydrazine **1a** (29 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 5 mol %), $AgSbF_6$ (0.04 mmol), $Zn(OAc)_2$ (0.48 mmol) and 1-(phenylethynyl) cyclobutan-1-ol **2a** (35 mg, 0.2 mmol) were dissolved in toluene (3 mL) under Ar. To another tube were added 1-methyl-1-(phenyl-2,4,6-d3) hydrazine [D_3]-**1a** (30 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 5 mol %), $AgSbF_6$ (0.02 mmol), $Zn(OAc)_2$ (0.0.24 mmol) and 1-(phenylethynyl)cyclobutan-1-ol **2a** (35 mg, 0.2 mmol) were dissolved in toluene (3 mL) under Ar. These two reaction mixtures were stirred side-by-side in the same oil bath at 50 ^oC for 1 hours. The reactions tubes were quenched at 0 ^oC and these two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified on silica gel chromatography using PE/EA to afford the mixed product. KIE value (k_H/k_D = 2.8) was determined on the basis of ^1H NMR analysis.



6.3 Competition experiments



4g/**4f** = 1.7 by HPLC

To an oven-dried 10 mL pressure tube was added substrate **1f** (37 mg, 0.24 mmol), substrate **1g** (41 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 5 mol %), $AgSbF_6$ (0.04 mmol), $Zn(OAc)_2$ (0.48 mmol) and 1-(phenylethynyl) cyclobutan-1-ol **2a** (69 mg, 0.4 mmol) were dissolved in toluene (3 mL) under Ar. The reaction mixture was stirred at 50 °C for 24 hours. The resulting mixture was cooled to room temperature, and then concentrated in vacuum. the ratio of product **4g**/**4f** was analyzed by HPLC (Welchrom 4.5 x 250 mm, $CH_3CN:H_2O$ = 60:40, 1 mL/min, 210 nm, 25 °C. t_{4g} = 17.528 min, t_{4f} = 25.023 min).

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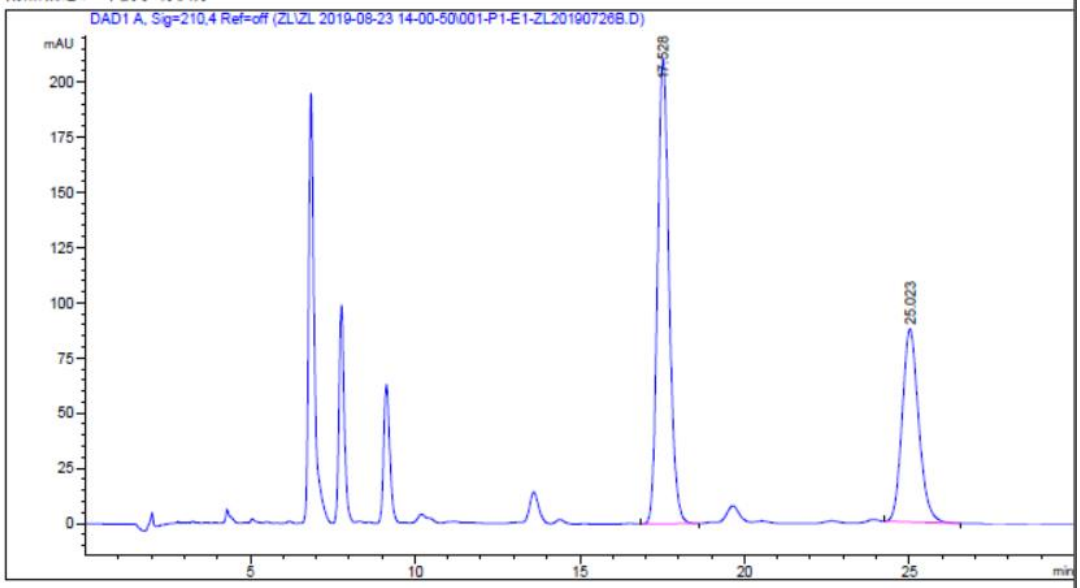
附加信息：峰被手动积分



面积百分比报告

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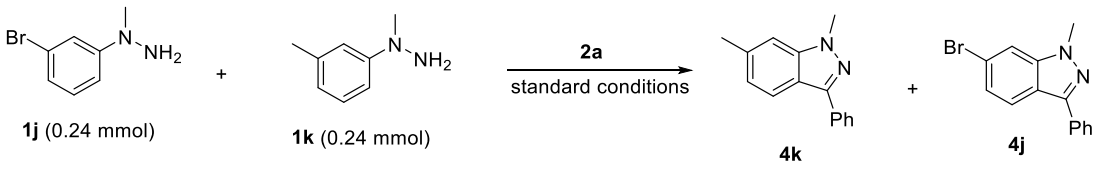
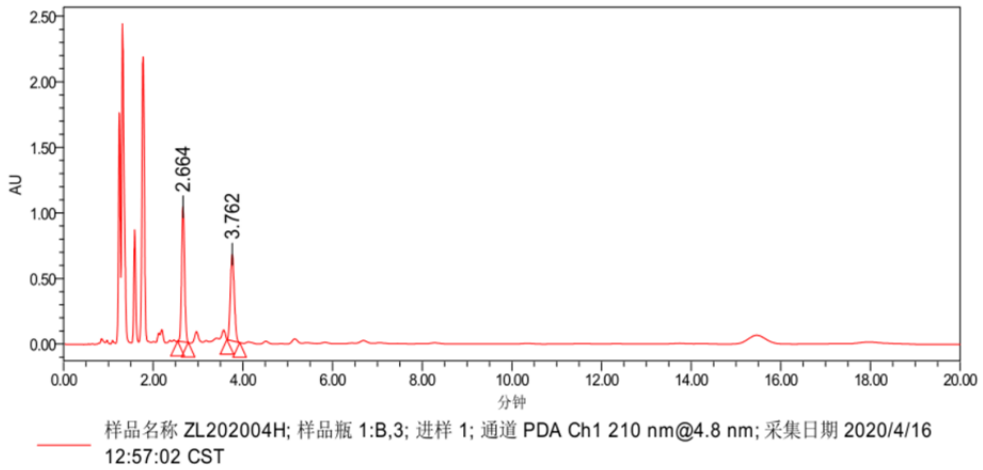


1j (0.24 mmol)　　**1k** (0.24 mmol)　　**4k**　　**4j**

4k/**4j** = 1.2 by HPLC

To an oven-dried 10 mL pressure tube was added substrate **1j** (48 mg, 0.24 mmol), substrate **1k** (33 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 5 mol %), $AgSbF_6$ (0.04 mmol), $Zn(OAc)_2$ (0.48 mmol) and 1-(phenylethynyl) cyclobutan-1-ol **2a** (69 mg, 0.4 mmol) were dissolved in toluene (3 mL) under Ar. The reaction mixture was stirred at 50 °C for 24 hours. The resulting mixture was cooled to room temperature, and then concentrated in vacuum. the ratio of product **4k**/**4j** was analyzed by HPLC (Waters UPLC BEH C18 2.1 x 50 mm,

$CH_3CN:H_2O$ = 60:40, 0.2 mL/min, 210 nm, 25 °C. t_{4k} = 2.664 min, t_{4j} = 3.762 min).



Time (min)	Area	Area (%)	Hight
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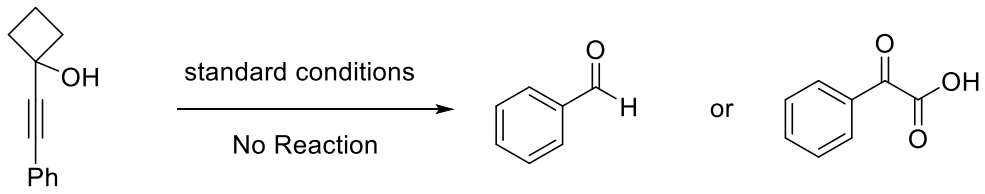
3.762	4030397	46.32	661179

6.4 Control experiment

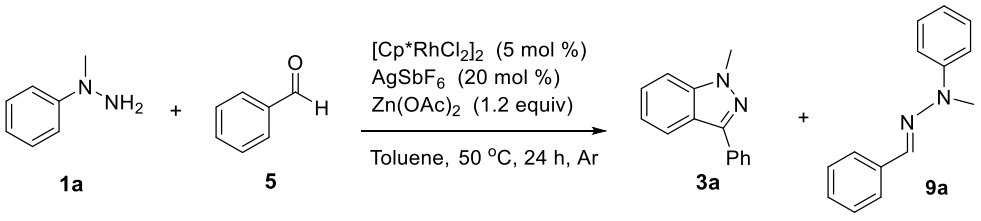


2a **5** **6**

To an oven-dried 10 mL pressure tube was added 1-(phenylethynyl)cyclobutan-1-ol **2a** (69 mg, 0.4 mmol) were dissolved in toluene (3 mL) under Ar. The reaction mixture was stirred at 50 °C for 24 hours. Then, monitoring by TLC analysis that was no reaction.

6.5 Optimization of reaction conditions

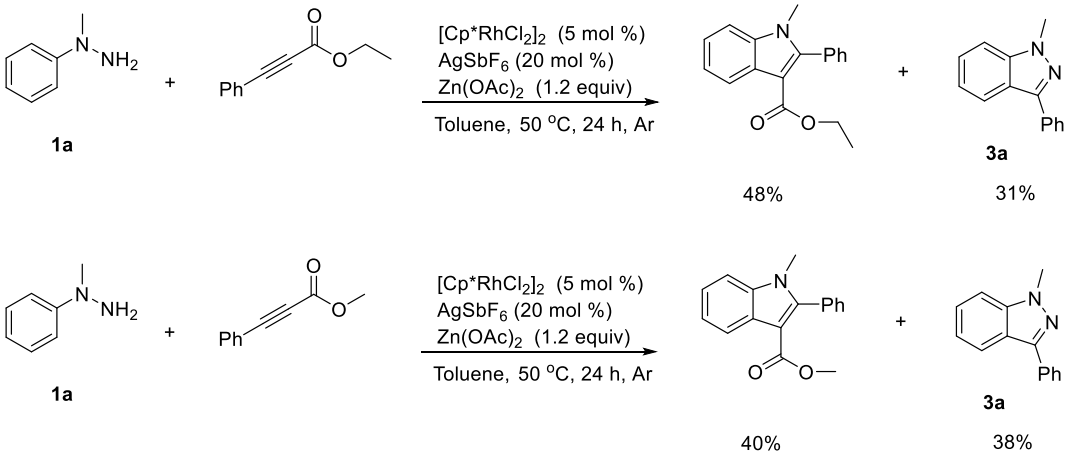
Table S2. Optimization of the reaction of **1a** and benzaldehyde **5**.



Entry	[Cat]	Additive	[Ag]	Solvent	Yield of **3a** (%)[b]	Yield of **9a** (%)[b]
1	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	N.D.	86
2	$[Cp^*IrCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	N.D.	93
3	$[RuCl_2(p\text{-cymene})]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	N.D.	90
4	-	$Zn(OAc)_2$	$AgSbF_6$	toluene	N.D.	91
5	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	AgOAc	toluene	N.D.	96
6	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgBF_4$	toluene	N.D.	93
7	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	AgOTf	toluene	N.D.	89
8	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgNTf_2$	toluene	N.D.	90
9	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	$AgSbF_6$	toluene	N.D.	85
10	$[Cp^*RhCl_2]_2$	$Mn(OAc)_2$	$AgSbF_6$	toluene	N.D.	87
11	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	DCE	N.D.	89
12	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	TFE	N.D.	92
13	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	CH_3CN	N.D.	86
14	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	THF	N.D.	83
15[c]	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	$AgSbF_6$	toluene	N.D.	88

[a] Reaction conditions: **1a** (0.48 mmol), **5** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %) and $Zn(OAc)_2$ (1.2 eq) in toluene (3.0 mL) at 50 °C for 24 h under Ar atmosphere. [b] Isolated yield. [c] The reaction temperature was 120 °C. N.D. = not detected. DCE = 1,2-dichloroethane, TFE = 2,2,2-trifluoroethanol, THF = tetrahydrofuran.

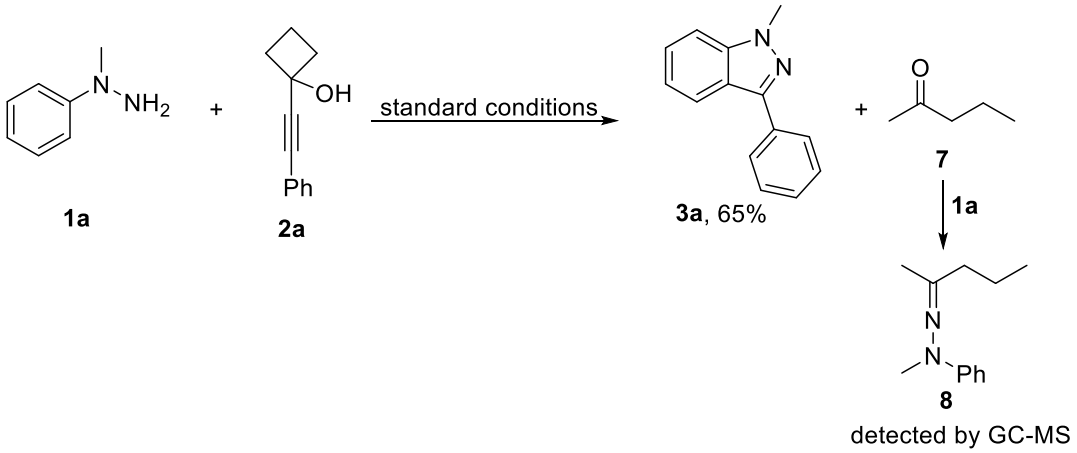
Reactions of **1a** with methyl/ethyl 3-phenylpropiolates



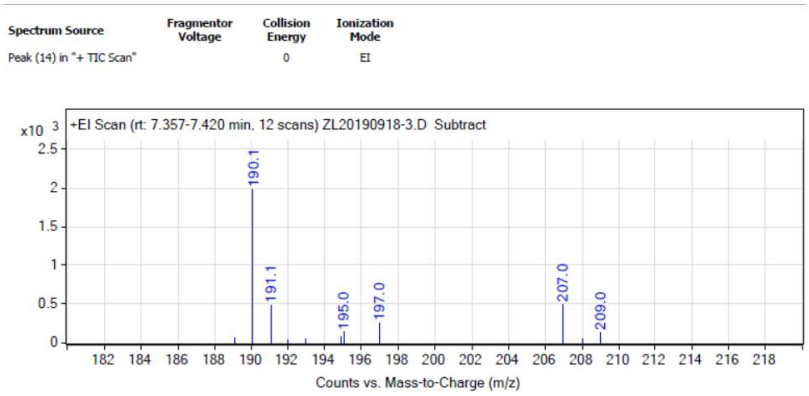
When the reaction of **1a** with methyl 3-phenylpropiolate and ethyl 3-phenylpropiolate

was conducted under standard conditions, we found these reactions not only produced corresponding product **3a,** but also gave indole products. It's worth noting that ethyl 3-phenylpropiolate gave higher yield of indole product.

6.6 Cleavage product trapping reaction



1-methyl-1-phenylhydrazine **1a** (0.48 mmol), 1-(phenylethynyl) cyclobutan-1-ol **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.02 mmol), $AgSbF_6$ (0.04 mmol), and $Zn(OAc)_2$ (0.48 mmol) were dissolved in toluene (3 mL). The mixture was stirred at 50 °C under argon atmosphere for 24 hours. The resulting mixture was then cooled to room temperature and submitted for GC-MS (**8**, $C_{12}H_{18}N_2$:190.1).

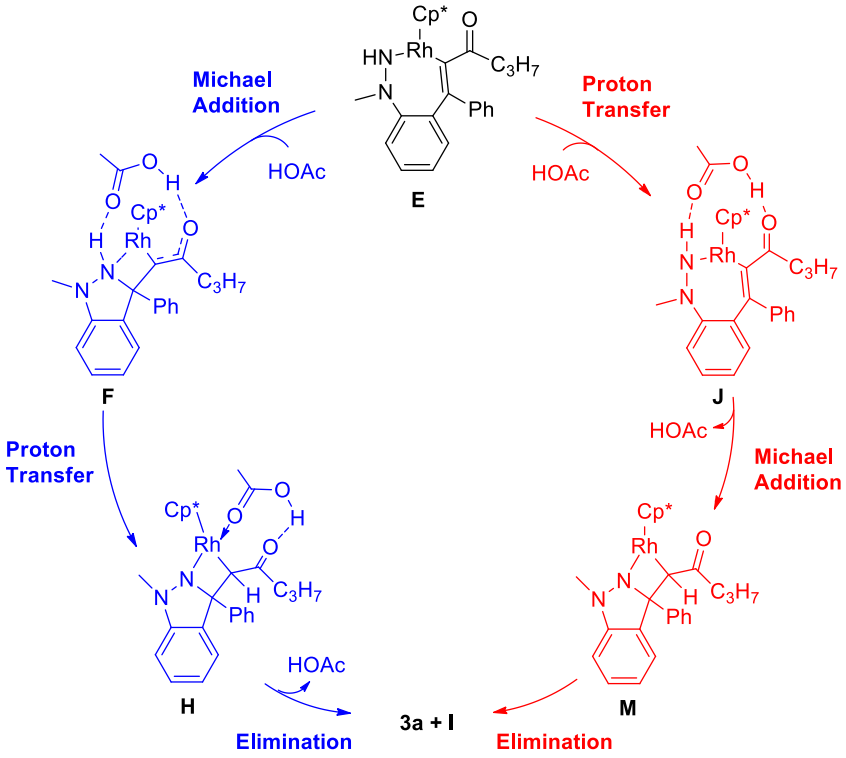


Peak List

m/z	z	Abund
77		983.23
79		602.41
91		646.83
106		1285.09
107.1	1	2277.41
147.1		724.6
190.1	1	1980.7
253	1	1820.02
327	1	650.34
331	1	649.91

7. Computational Study

All the calculations were carried out with the Gaussian 09 package.[3] Geometry optimization and energy calculations were performed with B3LYP.[4] The LANL2DZ basis set[5] with ECP was used for Rh, and the 6-31G(d) basis set[6] was used for other atoms. Frequency analysis was conducted at the same level of theory to verify that the stationary points are minima or saddle points. Single point energies were calculated at the M06[7]/6-311++G(d,p)[5]-SDD[8] level using SMD solvation model[9] (solvent = Toluene). Computed structures are illustrated using CYLView.[10] For clarity, all the unreacted hydrogen atoms are omitted in the 3D diagrams of molecules.



Scheme S3. The two possible pathways of Michael addition/elimination steps.

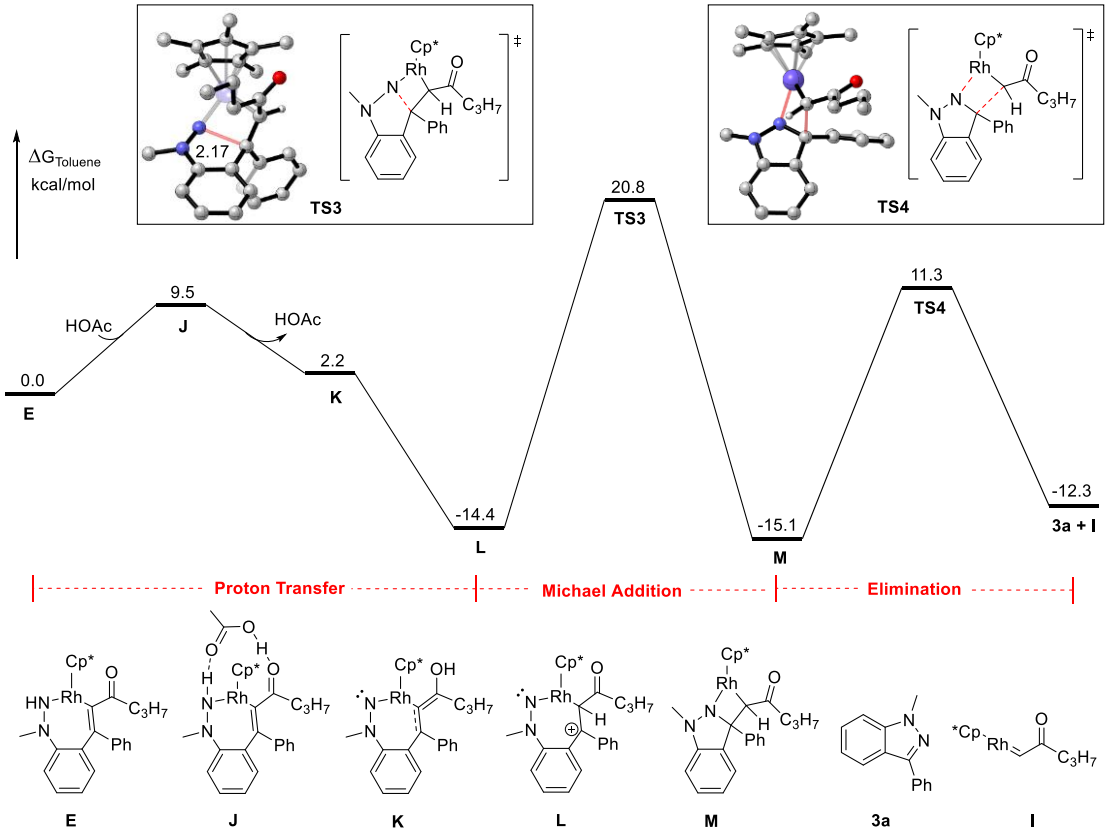


Figure S1. Free energy profiles for the proton transfer, Michael addition, and elimination steps. The distances are shown in Å. Calculations were done at the M06/6-311+G(d,p)-SDD(SMD$_{Toluene}$)//B3LYP/6-31G(d)-LANL2DZ level of theory.

Structures	ZPVE	TCE	TCH	TCG	E_{sol}	$G_{sol}(E_{sol}+TCG)$	Imaginary Frequency	ΔG_{sol} (kcal/mol)
E	0.572212	0.607576	0.608521	0.503388	-1420.782327	-1420.278939	—	—
HOAc	0.062012	0.066604	0.067548	0.034591	-229.0368917	-229.002301	—	—
F	0.637477	0.678456	0.679400	0.560334	-1649.826697	-1649.266363	—	9.3
G	0.637841	0.678494	0.679438	0.563563	-1649.827319	-1649.265827	—	9.7
H	0.636675	0.677085	0.678029	0.562848	-1649.865161	-1649.302313	—	-13.2
I	0.342286	0.364026	0.364970	0.291029	-770.884980	-770.593951	—	-12.3
J	0.636243	0.677692	0.678636	0.559554	-1649.825688	-1649.266134	—	9.5
K	0.573785	0.608619	0.609564	0.507835	-1420.783312	-1420.275477	—	2.2
L	0.573819	0.608432	0.609376	0.508308	-1420.810257	-1420.301949	—	-14.4
M	0.574162	0.60859	0.609534	0.508634	-1420.811635	-1420.303001	—	-15.1
3a	0.227590	0.240157	0.241101	0.187449	-649.892006	-649.704557	—	—
TS1	0.634772	0.675564	0.676508	0.559346	-1649.798014	-1649.238668	257.56*i*	26.7
TS2	0.635104	0.674973	0.675918	0.562855	-1649.828795	-1649.265940	342.98*i*	9.6
TS3	0.570833	0.605761	0.606705	0.503777	-1420.749593	-1420.245816	395.32*i*	20.8

TS4	0.566621	0.601620	0.602565	0.498511	-1420.739549	-1420.241038	542.37*i*	23.8

Table S4. Electronic Energies, Enthalpies, and Free Energies (in Hartree) of the Structures Calculated at the M06/6-311+G(d,p)-SDD($SMD_{Toluene}$)//B3LYP/6-31G(d)-LANL2DZ Level of Theory.

Cartesian coordinates of the structures

E

C	2.00720400	2.75478200	-1.08635400
C	1.46433200	1.89104700	-0.11968600
C	0.89074500	2.46985000	1.03495800
C	0.87457200	3.86267900	1.19292000
C	1.42058800	4.69677400	0.21774700
C	1.98129200	4.13945000	-0.93274100
H	2.47206900	2.31967600	-1.96669200
H	0.43798000	4.29898200	2.08648400
H	1.40636300	5.77463800	0.35809300
H	2.40845100	4.77889500	-1.70070900
C	1.59166100	0.41414300	-0.27665400
C	0.55696600	-0.44756100	-0.11636200
C	2.97527100	-0.06295900	-0.60780200
C	3.20719700	-1.00696300	-1.62437700
C	4.08881300	0.43302600	0.09799900
C	4.49985300	-1.45228700	-1.90917200
H	2.36724900	-1.38860900	-2.19424800
C	5.37785500	-0.01536500	-0.18320100
C	5.59004500	-0.96174900	-1.18992700
H	4.65262000	-2.17984600	-2.70246600
H	6.21946200	0.37483400	0.38400800
H	6.59593900	-1.30763400	-1.41364700
C	0.75884100	-1.91979900	-0.04652100
C	1.26416200	-2.43792400	1.30143800
H	0.61044400	-2.03356800	2.08670300
N	-0.91778100	1.08986600	1.67057400
C	-3.62414700	-0.74735400	0.13314800
C	-3.61132800	0.57233400	-0.37242300
C	-2.78922200	-1.58077000	-0.72879200
C	-2.74324300	0.58313200	-1.54350000
C	-2.30153700	-0.76379600	-1.79200300
C	-1.52149000	-1.23354800	-2.98514300
H	-2.19763900	-1.67387100	-3.73164300
H	-0.99292100	-0.40573900	-3.46650300
H	-0.78147700	-1.98188900	-2.69417500

C	-2.51175700	1.76611500	-2.43507600
H	-2.52664200	2.70330500	-1.87164100
H	-1.54753500	1.70043800	-2.94523700
H	-3.29539700	1.82746400	-3.20447100
C	-4.36861900	1.75714900	0.15492500
H	-4.63225500	1.63347200	1.20992800
H	-3.78687400	2.67999300	0.06300100
H	-5.30551300	1.90641600	-0.39945300
C	-2.64691800	-3.06926600	-0.61887800
H	-2.77668500	-3.40822600	0.41372400
H	-3.40958000	-3.57449300	-1.22945500
H	-1.66280300	-3.39917300	-0.95996300
H	3.93366900	1.17280300	0.87832300
C	-4.38928800	-1.25119500	1.32077100
H	-3.80003900	-1.96626400	1.90299100
H	-4.68581200	-0.43823900	1.98962600
H	-5.30548800	-1.76687600	1.00041800
Rh	-1.43750200	0.02859300	0.15781100
C	1.36114800	-3.96214900	1.39356200
C	1.89686200	-4.43463300	2.74922000
H	2.00451300	-4.33016000	0.58596900
H	0.37186800	-4.39939200	1.20892400
H	1.95888600	-5.52837700	2.79328600
H	2.90124500	-4.03666500	2.94086400
H	1.25009600	-4.10483700	3.57243900
H	2.24519400	-1.97276300	1.47696200
O	0.50494500	-2.70309000	-0.96187900
N	0.34787500	1.59456300	2.03417200
H	-1.64604300	1.61184600	2.17573600
C	0.36915300	2.04261800	3.41482800
H	1.35951400	2.43709300	3.65562600
H	-0.38412800	2.82469500	3.63773300
H	0.16458000	1.18443300	4.06233000

HOAc

C	-0.09243800	0.12560800	-0.00015200
O	-0.64546800	1.20209900	0.00003400
O	-0.77885900	-1.04658900	0.00000700
H	-1.72381600	-0.80257200	0.00017400
C	1.39746600	-0.10996900	0.00000600
H	1.68544900	-0.69064600	0.88258300
H	1.68543100	-0.69283600	-0.88111200
H	1.91738200	0.84813500	-0.00109900

F

C	-2.34883400	2.49643600	1.13416600
C	-1.62872000	1.93868200	0.08180200
C	-1.09146400	2.76877600	-0.91297700
C	-1.25644500	4.15279700	-0.87129400
C	-1.98049900	4.70278600	0.18983200
C	-2.51859200	3.88426500	1.18864500
H	-2.78441700	1.86248500	1.90060800
H	-0.82385200	4.78597900	-1.64073300
H	-2.11840500	5.77940400	0.24072600
H	-3.07294500	4.32715800	2.01123100
C	-1.34082900	0.47545100	-0.24939100
C	-0.39942800	-0.26215000	0.69670200
C	-2.60024400	-0.26125300	-0.74634400
C	-3.70873200	0.44215400	-1.24913100
C	-2.66536400	-1.66310400	-0.73408800
C	-4.83406500	-0.23004200	-1.72828900
H	-3.70054000	1.52688800	-1.25705800
C	-3.79227800	-2.33703900	-1.20689200
C	-4.88160000	-1.62453500	-1.70926800
H	-5.67769000	0.34041100	-2.10850100
H	-3.81617400	-3.42332100	-1.17854100
H	-5.75957800	-2.14944400	-2.07635600
C	-0.74383900	-1.18680800	1.75966400
C	-1.81173200	-0.81875000	2.78841200
H	-2.74619100	-0.61767300	2.24228300
N	-0.25744700	0.71610600	-1.32975300
C	3.43791800	-0.19083200	-0.72372100
C	3.42726100	1.20544400	-0.39081500
C	3.19208200	-0.94421400	0.48219500
C	3.12850800	1.33080700	0.99641400
C	2.95869500	-0.00765000	1.54362400
C	2.77392400	-0.35570900	2.99343800
H	3.73950900	-0.54575400	3.48386300
H	2.28362300	0.45711400	3.53813000
H	2.15653000	-1.25206400	3.10911400
C	3.06683700	2.60793800	1.78269900
H	2.75106400	3.45056700	1.16008400
H	2.36295600	2.53202400	2.61684100
H	4.05111100	2.85990400	2.20443400
C	3.67463400	2.33626600	-1.34914100
H	3.28158100	2.11304000	-2.34622400
H	3.19643900	3.26049600	-1.01124500
H	4.74909400	2.54128800	-1.45815900

C	3.31042700	-2.43174100	0.63537800
H	3.05621000	-2.95884000	-0.28759400
H	4.34265100	-2.70715600	0.89919300
H	2.65137200	-2.80793000	1.42129600
H	-1.83489800	-2.23877700	-0.34749200
C	3.76791400	-0.77824200	-2.06523300
H	3.18082900	-1.67986200	-2.26381700
H	3.56281900	-0.06939000	-2.87334700
H	4.83161000	-1.05074400	-2.13112100
Rh	1.32168900	0.26618000	0.08656800
C	-2.04234000	-1.88094600	3.86697800
C	-3.11323500	-1.46559400	4.88113400
H	-1.09470000	-2.08070100	4.38059200
H	-2.32397100	-2.82468400	3.38585700
H	-3.25937200	-2.24045800	5.64256100
H	-2.83565500	-0.53921100	5.40015300
H	-4.08128900	-1.29275700	4.39384800
O	-0.14884000	-2.27850100	1.85007200
N	-0.37026000	2.04651700	-1.89916400
C	-0.93293800	2.05300600	-3.25649400
H	-0.99788300	3.09056500	-3.59424100
H	-0.24962700	1.52283800	-3.92711700
H	-1.93064400	1.59334900	-3.31504900
H	-1.52743900	0.14013700	3.24611200
H	-0.27670900	-0.01343800	-2.04476900
C	0.36582200	-3.23024600	-1.89517100
O	0.19100400	-2.09874700	-2.31458600
O	0.42390000	-3.58551700	-0.60632500
H	0.34664000	-2.83069500	0.03515500
C	0.54803800	-4.43555000	-2.79349800
H	1.54429700	-4.86545100	-2.64202600
H	-0.17996500	-5.21106800	-2.53456600
H	0.42773300	-4.14097000	-3.83657000

G

C	-2.77386300	-0.84565600	1.92833100
C	-1.79353800	0.10380500	1.67523400
C	-1.18114300	0.77242900	2.75111600
C	-1.53752500	0.51994100	4.07508900
C	-2.52944800	-0.43893800	4.31082400
C	-3.13905800	-1.12063900	3.25539900
H	-3.25639000	-1.37528500	1.11287300
H	-1.05924200	1.03619700	4.90174400
H	-2.81887900	-0.66014900	5.33477500

H	-3.90072400	-1.86731800	3.46077200
C	-1.20476400	0.69709300	0.39397700
C	-0.44542300	-0.20859100	-0.58005200
C	-2.14176700	1.73512200	-0.27387600
C	-3.39609200	2.06982100	0.24977500
C	-1.71054100	2.39033400	-1.43926600
C	-4.20349300	3.02482700	-0.37754900
H	-3.75313800	1.58438200	1.15170100
C	-2.51237200	3.34335700	-2.06353700
C	-3.76691100	3.66453700	-1.53546000
H	-5.17529700	3.26523900	0.04655300
H	-2.15914800	3.83518300	-2.96659000
H	-4.39425100	4.40565300	-2.02401800
C	-0.98794800	-1.08342700	-1.44689400
C	-2.46245200	-1.32079900	-1.70406900
H	-3.06743200	-0.71384800	-1.02379400
N	0.01276200	1.36537200	0.93270800
C	3.37635700	1.26310500	-1.17318700
C	3.66624200	1.12396100	0.23626500
C	2.99772900	-0.01008100	-1.70253500
C	3.42822400	-0.23188300	0.59142200
C	2.97796000	-0.93589500	-0.60353000
C	2.80508400	-2.42171900	-0.71686500
H	3.75140900	-2.89198900	-1.02249500
H	2.50839200	-2.86371200	0.23799500
H	2.04354300	-2.67133600	-1.45800400
C	3.69082200	-0.88254400	1.91824600
H	3.72722900	-0.15025000	2.72989600
H	2.91859100	-1.61730400	2.16437000
H	4.65618700	-1.40970400	1.90752900
C	4.20942400	2.21107000	1.11995400
H	3.74786400	3.18032700	0.90207100
H	4.03932100	1.99518800	2.17886100
H	5.29341300	2.33209400	0.98252600
C	2.73987700	-0.34573800	-3.14358000
H	2.45511400	0.54267700	-3.71609900
H	3.64105000	-0.76407400	-3.61566000
H	1.92996100	-1.07221600	-3.23797700
H	-0.73930800	2.14156800	-1.85575200
C	3.51778600	2.53570300	-1.95529100
H	2.87974700	2.53554400	-2.84347300
H	3.25462900	3.41116700	-1.35330800
H	4.55519500	2.67049500	-2.29417100
Rh	1.42147700	0.56276300	-0.16326600

C	-2.87374200	-1.00595700	-3.15640200
C	-4.34844600	-1.31738500	-3.42941200
H	-2.23521800	-1.57818200	-3.83883900
H	-2.67475600	0.05460800	-3.35595300
H	-4.61723700	-1.08768200	-4.46716400
H	-4.57006400	-2.37820900	-3.25562200
H	-5.00700900	-0.72948200	-2.77794500
O	-0.16126600	-1.83875700	-2.27186200
N	-0.22011100	1.66994400	2.25636700
C	0.91105200	2.12177700	3.03252800
H	1.64013700	1.31309900	3.19726000
H	1.39962200	2.93685500	2.49432800
H	0.55960500	2.49787800	3.99649800
H	-2.69880200	-2.37646200	-1.49281600
H	-0.40731900	-2.77778600	-2.12828600
C	-0.39024000	-4.18093700	0.28265900
O	-0.66557000	-4.24014000	-0.90684800
O	-0.13190600	-3.05092200	0.94775100
H	-0.22038200	-2.25672100	0.35877000
C	-0.30038200	-5.39106100	1.18145200
H	0.71066100	-5.47257400	1.59481200
H	-0.98786900	-5.28012800	2.02621900
H	-0.54272400	-6.29050800	0.61491800

H

C	-2.76987700	1.51354900	2.15244100
C	-2.10827000	1.31377600	0.94912900
C	-1.93533900	2.37931800	0.05374600
C	-2.45963300	3.64666100	0.32600800
C	-3.13193700	3.83266300	1.53872800
C	-3.27641800	2.78621700	2.45425100
H	-2.91451000	0.69147900	2.84858900
H	-2.34306900	4.46989600	-0.37301200
H	-3.54161500	4.81223800	1.77169800
H	-3.79574700	2.95394400	3.39339500
C	-1.54784600	0.05597800	0.28173600
C	-0.43561400	-0.63250800	1.10286000
C	-2.73142700	-0.84091500	-0.13288600
C	-3.18842400	-0.88568800	-1.45241800
C	-3.41891800	-1.58190100	0.83861000
C	-4.30950000	-1.64661600	-1.79410300
H	-2.64175100	-0.34526900	-2.21750200
C	-4.53724000	-2.34215200	0.50165700
C	-4.99122500	-2.37479700	-0.81957700

H	-4.64493400	-1.67325500	-2.82807500
H	-5.05281200	-2.91316300	1.27004000
H	-5.86227000	-2.96817800	-1.08519300
C	-0.18100900	-2.06276200	0.99858000
C	0.42289400	-2.76218000	2.21723500
H	-0.42829400	-3.15777100	2.79518600
N	-0.77601500	0.61042900	-0.86869100
C	3.07186900	1.36645700	-0.83679000
C	2.25634000	2.31578600	-0.18711000
C	3.43698200	0.32762200	0.13004300
C	1.98503600	1.81687400	1.15185200
C	2.82353700	0.63257800	1.35877600
C	3.04294400	-0.04520000	2.67919900
H	3.82435000	0.47526400	3.25127500
H	2.13831300	-0.04031200	3.29460700
H	3.36256600	-1.08404600	2.55873200
C	1.30160000	2.60197100	2.23411800
H	0.46025400	3.17893100	1.84048600
H	0.91487600	1.95130800	3.02336400
H	2.00455600	3.30705400	2.70249600
C	1.70328800	3.59102000	-0.73857900
H	2.02914600	3.76235300	-1.76847900
H	0.60647100	3.57025700	-0.72712900
H	2.02894400	4.44970800	-0.13730900
C	4.34503300	-0.82431100	-0.18327900
H	4.04661800	-1.31041400	-1.11788100
H	5.38561900	-0.48927400	-0.29780200
H	4.32595200	-1.57971300	0.60737300
H	-3.07110400	-1.57338000	1.86921000
C	3.56118000	1.38993400	-2.25351900
H	3.30137300	0.45377600	-2.75889400
H	3.11926000	2.21400400	-2.82057900
H	4.65315600	1.50261300	-2.29382800
Rh	1.10515000	0.28917200	-0.10185200
C	1.37286600	-3.91290900	1.86632900
C	1.86508000	-4.67492000	3.10047000
H	2.23033800	-3.50995000	1.30964300
H	0.85732900	-4.59185000	1.17966800
H	2.54246800	-5.48969100	2.81969300
H	2.40635800	-4.01690600	3.79259700
H	1.02695800	-5.11604500	3.65471900
O	-0.44141800	-2.76561400	0.00316500
N	-1.15129200	1.96573600	-1.02479600
C	-1.37092900	2.41044200	-2.38785900

H	-1.47730500	3.49951600	-2.40156000
H	-0.49971500	2.14216500	-2.99089300
H	-2.26820300	1.96034100	-2.84084500
H	0.91551200	-2.03156900	2.86852200
H	-0.35847400	-0.26240500	2.12482300
C	0.70965900	-1.73060300	-2.85001400
O	1.47018700	-1.20126100	-2.03503900
O	-0.42251500	-2.32086100	-2.54575600
H	-0.54177600	-2.35136100	-1.53793700
C	0.99757300	-1.73729700	-4.33460800
H	0.78440200	-2.72054700	-4.76280600
H	0.33715600	-1.01354300	-4.82717600
H	2.03531100	-1.45673300	-4.52057700

I

C	1.32652100	0.00020300	-0.96743700
C	2.49296600	0.00014400	-0.08889700
C	3.87312800	0.00066200	-0.75630900
H	3.92905800	0.87519700	-1.42329900
C	-2.25638600	1.16296000	0.26121500
C	-2.88467200	-0.00001100	-0.28001800
C	-1.20624800	0.73022900	1.15837800
C	-2.25632900	-1.16318300	0.26063200
C	-1.20620500	-0.73082800	1.15799600
C	-0.40556200	-1.59026000	2.08951900
H	-0.84949200	-1.57975700	3.09587400
H	-0.37800300	-2.63004700	1.75059100
H	0.62265900	-1.22471200	2.16027900
C	-2.65835600	-2.58665800	0.00478600
H	-3.05161900	-2.72079300	-1.00776400
H	-1.81331400	-3.27026300	0.12557400
H	-3.44400700	-2.90633800	0.70481300
C	-4.01362600	0.00033500	-1.27147900
H	-3.98617400	0.88389200	-1.91723200
H	-3.98740600	-0.88379600	-1.91648100
H	-4.98750300	0.00124400	-0.76229000
C	-0.40570700	1.58919000	2.09042600
H	-0.37864500	2.62928000	1.75238000
H	-0.84938300	1.57764500	3.09687500
H	0.62267600	1.22397600	2.16063100
C	-2.65855800	2.58650000	0.00598900
H	-1.81375900	3.27021900	0.12780500
H	-3.05113700	2.72118000	-1.00675900
H	-3.44479100	2.90556500	0.70564700

Rh	-0.51490600	0.00020400	-0.74593000
C	5.04621500	-0.00076200	0.22518500
C	6.40706100	0.00030700	-0.47863800
H	4.96187300	-0.87524500	0.88133700
H	4.96178100	0.87173200	0.88394400
H	7.22878700	-0.00076300	0.24691800
H	6.52811100	-0.88337600	-1.11810700
H	6.52807100	0.88590700	-1.11545700
O	2.39961500	-0.00017000	1.14474900
H	3.92879300	-0.87204500	-1.42567400
H	1.53181700	0.00050500	-2.05884600

J

C	1.79484700	2.86633100	-1.76977400
C	1.38709600	2.13130700	-0.64637300
C	0.78643600	2.82882100	0.41531200
C	0.68329200	4.22472800	0.39014700
C	1.14525500	4.93954700	-0.71465600
C	1.67826200	4.25630400	-1.80873100
H	2.21099000	2.34020300	-2.62397100
H	0.22443400	4.75279500	1.22015300
H	1.06146200	6.02297300	-0.73042600
H	2.00979200	4.80324600	-2.68729900
C	1.65658300	0.66276400	-0.50504700
C	0.64533500	-0.24055100	-0.51025700
C	3.08120900	0.29256000	-0.20299900
C	4.17376400	0.75759600	-0.95918300
C	3.36027100	-0.53621100	0.90176100
C	5.47997300	0.38090300	-0.64884400
H	4.00484800	1.41506700	-1.80476500
C	4.66816500	-0.91185100	1.21325700
C	5.73550300	-0.45950700	0.43730700
H	6.30171800	0.74659000	-1.25972300
H	4.84982200	-1.55056000	2.07402500
H	6.75461200	-0.74900000	0.67979500
C	0.91833900	-1.69208200	-0.44751900
C	1.65950700	-2.32370000	-1.62305200
H	2.55836000	-1.72460400	-1.81328400
N	-0.93544800	1.39592200	1.11140000
C	-3.60040500	-0.30220000	0.05141400
C	-3.53195600	0.54659700	-1.09165800
C	-2.86455600	-1.50273900	-0.25048500
C	-2.78522500	-0.13642900	-2.13275600
C	-2.38587500	-1.40346800	-1.61288900

C	-1.79049700	-2.53285800	-2.40160600
H	-2.58886000	-3.15449100	-2.83137400
H	-1.17872900	-2.17139800	-3.23314300
H	-1.17249200	-3.18418000	-1.77861000
C	-2.59881200	0.35957300	-3.53718400
H	-2.46467800	1.44554400	-3.56515500
H	-1.72113700	-0.09202600	-4.00913400
H	-3.47066000	0.11955100	-4.16400600
C	-4.17257800	1.89449700	-1.25222200
H	-4.39561800	2.35691100	-0.28713800
H	-3.52458400	2.57992500	-1.80754000
H	-5.11756600	1.81149000	-1.80765800
C	-2.75808000	-2.70345800	0.63910600
H	-2.73620500	-2.40897700	1.69206000
H	-3.62138000	-3.36999000	0.49280500
H	-1.85004900	-3.27521300	0.43503500
H	2.54527000	-0.87019400	1.53477500
C	-4.30379400	-0.02260600	1.34821500
H	-3.70001200	-0.33898100	2.20487000
H	-4.52143900	1.04360600	1.46578000
H	-5.26270600	-0.55676300	1.40023300
Rh	-1.37866600	0.23302200	-0.37896700
C	2.01771800	-3.79944000	-1.43398100
C	2.74019600	-4.38623100	-2.65113800
H	1.10740400	-4.37364500	-1.22407600
H	2.64584200	-3.90086700	-0.54070600
H	2.99206700	-5.44108900	-2.49200600
H	2.11829800	-4.32578900	-3.55353000
H	3.67411200	-3.84908500	-2.85836000
O	0.50872900	-2.41658600	0.47183100
N	0.23119500	2.05326500	1.48092000
C	0.17745300	2.64536600	2.81206200
H	-0.60213300	3.42057900	2.90698000
H	-0.03550800	1.85389000	3.53586000
H	1.14927800	3.08502400	3.04688700
H	1.03319300	-2.18770200	-2.51614500
H	-1.49374400	1.23809000	1.95057100
C	-0.50352500	-1.24185700	3.83721400
O	-1.43700800	-0.59029600	3.39193800
O	0.34312400	-1.96293400	3.10691300
H	0.15805200	-1.92359500	2.12503600
C	-0.17029700	-1.32502500	5.31234600
H	-0.17807200	-2.37013500	5.63896800
H	0.83977500	-0.93988000	5.48929300

H	-0.89440400	-0.74917800	5.89001100

K

C	3.03309400	-0.78754300	-1.68038200
C	1.86497100	-1.07745000	-0.94325700
C	1.67492900	-2.43485700	-0.56062500
C	2.65483800	-3.39614800	-0.88354300
C	3.79959500	-3.06238400	-1.59461000
C	3.98732000	-1.74366900	-2.00457300
H	3.20691000	0.24126800	-1.97216900
H	2.52527300	-4.42813500	-0.58915800
H	4.53135600	-3.83090000	-1.82621700
H	4.87836600	-1.45373000	-2.55440400
C	1.01791700	0.07333500	-0.49817500
C	0.74051400	0.16040200	0.89059100
C	1.03366700	1.30069500	-1.36284300
C	1.20617800	2.57773300	-0.80351900
C	0.90089700	1.21151500	-2.76219000
C	1.24916400	3.71930100	-1.60728800
H	1.30902200	2.66627300	0.27366200
C	0.95254300	2.34843600	-3.56635900
C	1.12781200	3.61200800	-2.99404600
H	1.39154300	4.69393900	-1.14651400
H	0.85004500	2.24834800	-4.64421000
H	1.16933800	4.49875700	-3.62086000
C	1.25987200	0.28318100	2.10850100
C	2.67351200	0.68414500	2.43831400
H	3.24399800	0.77073100	1.50653100
N	-0.61908800	-2.26494000	0.26867000
C	-3.18209400	-0.25311900	-0.87812600
C	-3.31229000	-0.70253100	0.48587800
C	-2.65694000	1.07497700	-0.85400800
C	-2.87201500	0.35249400	1.34990300
C	-2.42873100	1.44033200	0.51457300
C	-1.99146200	2.79102000	1.00852300
H	-1.36058900	3.30023300	0.27507400
H	-2.85695900	3.43946300	1.20787100
H	-1.41781500	2.71283700	1.93769600
C	-2.99096700	0.39664200	2.84875000
H	-2.97177400	-0.60474600	3.29069700
H	-2.18443600	0.97969000	3.30435100
H	-3.93748600	0.86625400	3.15467900
C	-3.86327200	-2.03671300	0.89737900
H	-3.20437100	-2.84901200	0.56340900

H	-3.95623900	-2.11483000	1.98452000
H	-4.85793500	-2.20706300	0.46654600
C	-2.46116600	1.96574400	-2.04452500
H	-3.36652600	2.55926400	-2.23853800
H	-1.63366800	2.66433800	-1.89876600
H	-2.24652500	1.39027100	-2.94982900
H	0.75958900	0.23584900	-3.21916700
C	-3.64826200	-1.01179600	-2.08899800
H	-3.08367900	-0.73289300	-2.98419500
H	-3.53957900	-2.09196000	-1.95073800
H	-4.71015200	-0.81368000	-2.29852800
Rh	-1.04194100	-0.41757500	0.12414200
C	2.77612400	1.99322800	3.24444900
C	4.22040300	2.34405300	3.61494200
H	2.16888300	1.89907100	4.15221400
H	2.33463300	2.81150100	2.65906000
H	4.26937300	3.27707100	4.18824900
H	4.67539600	1.55396900	4.22533500
H	4.84277900	2.46971500	2.71993600
H	3.13436000	-0.12502700	3.02511000
O	0.51133400	0.04359300	3.24443000
N	0.47961500	-2.90261800	0.08234600
C	0.40640700	-4.33672000	0.45468700
H	0.45802000	-4.97607600	-0.43248700
H	1.21708100	-4.59519600	1.14204700
H	-0.55397700	-4.46637000	0.94714900
H	-0.34666700	-0.29203700	2.92619800

L

C	-2.41074800	2.51628300	0.05247800
C	-1.73412600	1.32643300	0.39595000
C	-2.33750400	0.51757500	1.39156700
C	-3.56373700	0.91188800	1.96851000
C	-4.20354600	2.08245100	1.58765800
C	-3.62171300	2.89657200	0.61572600
H	-1.96240200	3.14940500	-0.70570700
H	-4.03155600	0.29916400	2.72677000
H	-5.14834600	2.35266100	2.05042700
H	-4.10674100	3.81373300	0.29428700
C	-0.46594400	1.05218200	-0.36810800
C	-0.39651800	0.05166300	-1.41369700
C	0.39061100	2.28533500	-0.52436600
C	0.81520200	2.76357500	-1.77573200
C	0.75392700	3.03029400	0.61453800

C	1.59091800	3.92233700	-1.88213200
H	0.51937200	2.24178300	-2.68060600
C	1.51895800	4.18874200	0.51013500
C	1.94781100	4.64159500	-0.74193800
H	1.90028400	4.26905200	-2.86509000
H	1.78489100	4.73971300	1.40891900
H	2.54543600	5.54525900	-0.82555300
C	-1.36690000	-0.92132700	-1.97857500
C	-2.77618000	-1.10368100	-1.42381700
H	-3.25681100	-0.11838500	-1.35008300
N	-0.59990400	-1.18225900	1.51515600
C	2.70736700	-1.10058600	1.40307100
C	2.20922400	-2.33205000	0.82796000
C	3.07258900	-0.22377400	0.33240200
C	2.23808700	-2.20183700	-0.59244200
C	2.73975300	-0.87926200	-0.89542800
C	3.03560800	-0.37046700	-2.27788400
H	2.95179200	0.71941900	-2.33517300
H	4.05752300	-0.63692900	-2.58356600
H	2.35235600	-0.80162700	-3.01649700
C	1.86224100	-3.23370700	-1.61753700
H	1.41772100	-4.11660000	-1.14931000
H	1.13340200	-2.84268800	-2.33681500
H	2.74492500	-3.56740600	-2.18098200
C	1.76738900	-3.51875700	1.63148300
H	0.93282900	-3.24803200	2.29096600
H	1.42941100	-4.33657400	0.98900400
H	2.58294400	-3.90205000	2.25856100
C	3.75379800	1.10537300	0.46755100
H	4.84710500	0.98881000	0.43834600
H	3.47403600	1.78996800	-0.33789500
H	3.50165200	1.59446900	1.41289100
H	0.43088100	2.68300400	1.59211400
C	2.94886900	-0.87208800	2.86818000
H	2.92600000	0.19225900	3.12173700
H	2.19606300	-1.37798000	3.48029000
H	3.93261000	-1.26001300	3.17110800
Rh	0.71689900	-0.65153600	0.25434300
C	-3.63408800	-2.05993500	-2.25754900
C	-5.04533400	-2.22824100	-1.68547000
H	-3.13229600	-3.03219600	-2.31808800
H	-3.68859600	-1.69096700	-3.28852800
H	-5.64251900	-2.91366600	-2.29802400
H	-5.01854600	-2.63435900	-0.66577300

H	-5.57847300	-1.26990100	-1.64336900
H	-2.70472300	-1.46973300	-0.39168900
O	-1.00436000	-1.58440600	-2.95209500
N	-1.73954300	-0.69482300	1.85912200
C	-2.43612600	-1.45888500	2.92040800
H	-2.54779500	-0.85505000	3.82690100
H	-3.42151700	-1.78896800	2.57727300
H	-1.80731200	-2.32178700	3.12529500
H	0.37761500	0.21396300	-2.15843600

M

C	2.74490500	1.93598500	-1.81717000
C	2.04702200	1.55882900	-0.68067000
C	1.80604000	2.49334400	0.33911600
C	2.26253100	3.80707500	0.25250300
C	2.96900700	4.17464800	-0.89997500
C	3.20263300	3.25849500	-1.92782800
H	2.93044000	1.22497000	-2.61761100
H	2.07235300	4.52987900	1.04006600
H	3.32878200	5.19556600	-0.99636400
H	3.74186100	3.56939800	-2.81791100
C	1.48316400	0.21912700	-0.19474600
C	0.45098300	-0.44721100	-1.13243100
C	2.65952200	-0.63564500	0.30863700
C	3.55588200	-1.18780900	-0.61761600
C	2.88772600	-0.84626000	1.67240800
C	4.65114000	-1.93750600	-0.19119900
H	3.38987300	-1.04002500	-1.68183600
C	3.98693100	-1.59541400	2.10116700
C	4.87229100	-2.14373400	1.17347300
H	5.33188400	-2.36169800	-0.92490000
H	4.14792900	-1.75042400	3.16517300
H	5.72595000	-2.72741300	1.50756000
C	0.24237000	-1.88699600	-1.37075900
C	0.65358900	-2.94476200	-0.34067600
H	0.70990700	-2.50603100	0.66085600
N	0.57194400	0.67215500	0.87978000
C	-3.35868500	-0.43213800	0.79527000
C	-3.19172300	0.99255300	1.00853100
C	-3.17786600	-0.72539700	-0.58661800
C	-2.85462500	1.57772900	-0.24363500
C	-2.78434100	0.50239100	-1.22924900
C	-2.56932700	0.66035200	-2.70605800
H	-3.53351200	0.73053900	-3.22999200

H	-1.99960400	1.56542000	-2.93695700
H	-2.02454500	-0.19822100	-3.11067700
C	-2.70885300	3.03720100	-0.56139200
H	-2.55089300	3.63735200	0.33900400
H	-1.86875600	3.22094000	-1.23759700
H	-3.61603400	3.41563500	-1.05452500
C	-3.46745500	1.70756400	2.30059800
H	-3.09061700	1.14843000	3.16385200
H	-3.00608000	2.69891000	2.32208900
H	-4.54715400	1.84718100	2.45382800
C	-3.39965300	-2.03367500	-1.28623400
H	-3.56884700	-2.84540100	-0.57271000
H	-4.28737800	-1.97650000	-1.93192600
H	-2.54556700	-2.30972600	-1.91457700
H	2.19773500	-0.42862500	2.39746300
C	-3.73714100	-1.41406000	1.86474600
H	-3.41927700	-2.42881600	1.61063100
H	-3.28748300	-1.15335400	2.82804800
H	-4.82707900	-1.43339100	2.00778700
Rh	-1.17164100	0.11895000	0.17737700
C	-0.25402700	-4.17973700	-0.34387100
C	0.26207700	-5.29205600	0.57425900
H	-0.34766400	-4.54428500	-1.37195500
H	-1.26493200	-3.88468500	-0.03152400
H	-0.40467800	-6.16258100	0.55943800
H	1.25872800	-5.63115300	0.26473300
H	0.34098100	-4.95063100	1.61439700
O	-0.32218400	-2.24828700	-2.41358800
N	1.06786300	1.87654300	1.36472400
C	0.22802800	2.62107200	2.27367000
H	-0.61212200	3.10953900	1.75719200
H	-0.16835900	1.93265700	3.02330300
H	0.83081700	3.38157400	2.77771600
H	1.68083800	-3.25048400	-0.58783400
H	0.33229100	0.10430500	-2.06455200

TS1

C	-1.73385700	2.88307700	1.13375600
C	-1.14134600	2.15937200	0.08789800
C	-0.26692800	2.86422700	-0.77563400
C	0.00054500	4.22399300	-0.58808000
C	-0.61145300	4.91535100	0.45549300
C	-1.47321600	4.24205300	1.32473900
H	-2.40178700	2.36581200	1.81768300

H	0.69897600	4.72524500	-1.25265000
H	-0.40053700	5.97140500	0.60055700
H	-1.93282600	4.76813200	2.15693100
C	-1.44875300	0.69177800	-0.10394300
C	-0.61746300	-0.31927400	0.48259300
C	-2.83211000	0.36984400	-0.56372900
C	-3.86535400	1.32949400	-0.64705600
C	-3.12966200	-0.94305400	-0.99199000
C	-5.14392000	0.97733200	-1.07374900
H	-3.67111200	2.35805400	-0.36662500
C	-4.40939500	-1.29066600	-1.42033500
C	-5.42794500	-0.33654700	-1.45370000
H	-5.92188500	1.73578600	-1.11184100
H	-4.60355800	-2.30837500	-1.74884600
H	-6.42514500	-0.60736100	-1.79054000
C	-1.10769600	-1.49152000	1.19829100
C	-2.13433800	-1.29850200	2.31478600
H	-2.81882800	-0.48790400	2.03928300
N	0.27434200	0.78281900	-1.48771200
C	3.36247700	-0.87984000	-0.09603200
C	3.56079100	0.54121100	-0.06690800
C	2.77738100	-1.28656100	1.16947300
C	3.06526800	1.02702700	1.17714800
C	2.57226500	-0.10682600	1.94579100
C	2.09337700	-0.04976300	3.36797500
H	2.94140300	-0.05416600	4.06779800
H	1.51153300	0.85665300	3.56130400
H	1.46313400	-0.91006000	3.61067300
C	3.09236000	2.45027600	1.64769800
H	3.04158700	3.15154500	0.80965500
H	2.25273000	2.67048100	2.31356900
H	4.01833100	2.66280900	2.20235900
C	4.16435400	1.37913400	-1.15820700
H	4.12958700	0.86376700	-2.12244000
H	3.62973300	2.32726000	-1.27602100
H	5.21728400	1.61331000	-0.94859000
C	2.57796100	-2.70205600	1.62735700
H	2.38210800	-3.37319700	0.78812600
H	3.47631000	-3.06642100	2.14763400
H	1.73164000	-2.78949300	2.31261200
H	-2.33304500	-1.67414900	-1.04701900
C	3.81139300	-1.82186100	-1.17255700
H	3.13602500	-2.67780900	-1.25442900
H	3.85754400	-1.32915100	-2.14832800

H	4.81704000	-2.21022700	-0.95209300
Rh	1.28499100	0.02874000	0.12763400
C	-2.90785800	-2.56633200	2.69169500
C	-3.85980800	-2.34518200	3.87157000
H	-2.19376200	-3.36386600	2.92247900
H	-3.47468700	-2.90846800	1.81617800
H	-4.40488600	-3.26373400	4.11816100
H	-3.31485800	-2.03116800	4.77110300
H	-4.60196100	-1.56871400	3.64753600
O	-0.64229400	-2.63258000	1.00807200
N	0.34910500	2.12153100	-1.82522100
C	-0.07938900	2.43326700	-3.18993800
H	-0.04846700	3.51415800	-3.34277600
H	0.60547800	1.95680900	-3.89729600
H	-1.10479700	2.07574800	-3.38196200
H	-1.57484800	-0.92779300	3.18915400
H	-0.20481300	0.19830900	-2.17537400
C	0.28099200	-2.98285700	-2.40361200
O	-0.46238300	-2.02877300	-2.57323700
O	0.59604200	-3.50005100	-1.21664800
C	0.96677100	-3.71609700	-3.53792500
H	2.03932000	-3.48986700	-3.52536800
H	0.85969300	-4.79813200	-3.41646300
H	0.54436600	-3.39779900	-4.49204100
H	0.14566100	-3.01293000	-0.45778000

TS2

C	-3.58938700	1.73008900	-0.29821000
C	-2.24592100	1.61112100	-0.65936700
C	-1.49030800	2.75763100	-0.96085300
C	-2.06129100	4.03637700	-0.93289300
C	-3.40145800	4.13846300	-0.56552200
C	-4.16247000	3.00053800	-0.24884800
H	-4.18466900	0.84923200	-0.07956200
H	-1.48324900	4.92052700	-1.18379000
H	-3.86803300	5.11947400	-0.53061300
H	-5.20783700	3.11168400	0.02395600
C	-1.32873500	0.46030000	-0.82115900
C	-0.57084000	0.11074200	0.97272600
C	-1.87464200	-0.81641800	-1.39915300
C	-1.49748900	-1.19407200	-2.69700300
C	-2.85996600	-1.56613000	-0.74368500
C	-2.09042700	-2.29385600	-3.31701000
H	-0.73697000	-0.61354000	-3.20516700

C	-3.45689200	-2.66291700	-1.36547500
C	-3.07391500	-3.03274200	-2.65541900
H	-1.78715500	-2.56840300	-4.32435000
H	-4.21521300	-3.23289500	-0.83534100
H	-3.53679200	-3.88858700	-3.13973500
C	-1.08194700	-0.87519300	1.81455200
C	-1.93278900	-0.51204300	3.01969600
H	-2.23976400	0.53710700	2.94482900
N	-0.13291600	0.96212700	-1.35821200
C	3.67592500	0.21447600	-0.08858900
C	3.22808500	1.52642200	0.11761600
C	3.17332300	-0.61263900	1.01641500
C	2.37286400	1.53637900	1.29790500
C	2.45718800	0.22470400	1.90899100
C	1.93502600	-0.16519600	3.26001100
H	2.70506200	-0.00865300	4.02842000
H	1.06231700	0.42946600	3.54367000
H	1.64466100	-1.21933600	3.28879900
C	1.80090900	2.77110100	1.93325700
H	1.37029800	3.44114900	1.18262900
H	1.00668500	2.52241100	2.64341300
H	2.56944800	3.33290300	2.48343200
C	3.58044100	2.74530400	-0.68119700
H	3.87766100	2.49976700	-1.70501700
H	2.74690000	3.45151800	-0.72668000
H	4.42279700	3.27493300	-0.21350900
C	3.54613200	-2.04948700	1.23901500
H	3.72280700	-2.56315000	0.29025300
H	4.47029600	-2.12200100	1.83042600
H	2.75986100	-2.59799400	1.76280000
H	-3.15879800	-1.30144800	0.26415400
C	4.52325900	-0.30785800	-1.21011300
H	4.02446200	-1.14350500	-1.71484700
H	4.71971200	0.46312100	-1.96080600
H	5.49336000	-0.67105500	-0.84478500
Rh	1.27350000	0.08316700	-0.00286600
C	-3.15861500	-1.41221500	3.25552000
C	-3.88807800	-1.06621800	4.55751600
H	-2.83484100	-2.45777000	3.26853300
H	-3.85421900	-1.31221600	2.41127900
H	-4.76166700	-1.71138100	4.70417300
H	-3.23009100	-1.19450200	5.42602700
H	-4.23782300	-0.02625100	4.55789900
O	-0.89081000	-2.16616600	1.70332100

N	-0.19424800	2.37813800	-1.28407900
C	0.50050200	3.03176600	-2.38799400
H	0.64576500	4.09120000	-2.15729400
H	1.47394200	2.55736800	-2.50795400
H	-0.05883700	2.93947600	-3.33076900
H	-1.28127500	-0.58421800	3.90574600
H	-0.75306000	1.11079700	1.36439800
C	1.02757300	-2.81393800	-1.06806300
O	1.20764400	-1.58470900	-1.36020000
O	0.58572000	-3.26965900	0.01408400
H	-0.24098600	-2.46355000	0.94510400
C	1.35662600	-3.80857500	-2.17490400
H	1.70074300	-4.75268300	-1.74458300
H	0.43850500	-4.00896200	-2.73961900
H	2.10212900	-3.40561100	-2.86474900

TS3

C	3.73875100	-0.29322800	-0.88408800
C	2.60031800	-0.20722900	-0.08045900
C	2.72557900	0.32099000	1.21198000
C	3.95267600	0.79481300	1.69147900
C	5.06973900	0.73304100	0.85815900
C	4.96860600	0.18809200	-0.42512500
H	3.65808600	-0.72679300	-1.87725400
H	4.03343700	1.21993300	2.68664600
H	6.02336700	1.11206100	1.21513400
H	5.84307200	0.13657700	-1.06702000
C	1.25594200	-0.71025100	-0.52315800
C	0.36697000	0.09433000	-1.34155300
C	1.20531400	-2.20542700	-0.64883000
C	0.58302700	-2.87467400	-1.72060200
C	1.83946000	-2.99553400	0.33018400
C	0.57969800	-4.26651100	-1.79500400
H	0.11319200	-2.31163700	-2.51884500
C	1.82683600	-4.38641400	0.26134000
C	1.19459200	-5.03271500	-0.80277200
H	0.10202500	-4.75317500	-2.64149200
H	2.31676800	-4.96613100	1.03937300
H	1.18953500	-6.11756100	-0.86361000
C	0.49235200	1.50794400	-1.75289900
C	1.37246700	2.50431700	-0.99818000
H	2.42305900	2.23655800	-1.18117300
N	0.42575900	-0.05168400	1.37035400
C	-3.17148800	-0.38403700	1.31904100

C	-2.96171200	1.03107900	1.20852100
C	-3.26246500	-0.93339800	-0.00954100
C	-2.88338000	1.36527800	-0.18819600
C	-3.05532900	0.13462400	-0.93829700
C	-3.14045100	0.05924700	-2.43641400
H	-3.01088800	-0.96706000	-2.79504600
H	-4.12231900	0.40667200	-2.78805300
H	-2.37372200	0.68431600	-2.90553900
C	-2.81860400	2.73529400	-0.79438900
H	-2.47813000	3.48069900	-0.06879500
H	-2.13599100	2.76028800	-1.65013800
H	-3.81057300	3.05201900	-1.14973100
C	-2.89600700	2.00070600	2.35243300
H	-2.43575700	1.55030900	3.23777300
H	-2.31365300	2.88947900	2.09186000
H	-3.90097600	2.33848700	2.64381200
C	-3.55752600	-2.36558400	-0.35104100
H	-4.63786700	-2.53203400	-0.47355100
H	-3.07328900	-2.66659700	-1.28523500
H	-3.20955200	-3.04652000	0.43196100
H	2.33820800	-2.50983800	1.16263300
C	-3.35621300	-1.14854700	2.59818900
H	-2.97372200	-2.17091600	2.51483700
H	-2.83521400	-0.66824500	3.43224000
H	-4.41860600	-1.21714900	2.87305400
Rh	-1.14698800	0.00737100	0.20864100
C	1.13280400	3.96017800	-1.40915800
C	2.07174700	4.93293200	-0.68836700
H	0.08938500	4.22804500	-1.20226600
H	1.25300200	4.05131100	-2.49399400
H	1.88282900	5.96838900	-0.99535700
H	1.94468900	4.88151700	0.40079900
H	3.12371100	4.70839900	-0.90637700
H	1.22016200	2.37779900	0.07978500
O	-0.16489700	1.89609700	-2.72712800
N	1.53430600	0.24389500	1.96425400
C	1.58954500	0.30896600	3.43347700
H	2.41656300	-0.30120600	3.81550900
H	1.72402600	1.34386300	3.77132900
H	0.63944600	-0.07290300	3.80421500
H	-0.17063300	-0.45458200	-2.11195800

TS4

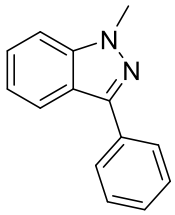
C	-2.73464200	-1.00580100	-2.09343600

C	-1.92189100	-1.21738100	-0.98276400
C	-1.35743800	-2.48067400	-0.75210300
C	-1.62979700	-3.56035200	-1.59854100
C	-2.46530600	-3.34352400	-2.69505900
C	-3.00730400	-2.07828100	-2.94868900
H	-3.13540300	-0.02240000	-2.30503700
H	-1.19891800	-4.53987500	-1.41274800
H	-2.68919000	-4.16997500	-3.36477500
H	-3.64358900	-1.92530700	-3.81560500
C	-1.49368600	-0.30001900	0.16623200
C	-0.48651700	0.72327200	-0.31626500
C	-2.65290200	0.25229700	1.01179900
C	-2.75924600	-0.09308900	2.36414900
C	-3.61274900	1.11530600	0.45899400
C	-3.80632100	0.40102600	3.14552800
H	-2.00748300	-0.74854400	2.79005800
C	-4.65691500	1.60931700	1.24173200
C	-4.76036800	1.25280100	2.58819600
H	-3.87309800	0.11927800	4.19365900
H	-5.39281000	2.27359700	0.79531800
H	-5.57571800	1.63752300	3.19545800
C	-0.79292600	1.96775600	-1.04633100
C	-0.13985400	3.26349500	-0.58700200
H	0.94319100	3.10073600	-0.51496700
N	-0.53003000	-1.15947600	0.95161700
C	3.24599800	-0.15610700	1.36409100
C	3.02459300	-1.40269400	0.72834000
C	3.31286000	0.87305100	0.32854300
C	2.85336800	-1.15971700	-0.67878600
C	3.09627700	0.25269800	-0.92457300
C	3.15236300	0.90274900	-2.27724700
H	4.14149700	0.76921200	-2.73745200
H	2.41261800	0.47551700	-2.96095000
H	2.96238500	1.97850900	-2.21701600
C	2.65072300	-2.21747500	-1.72445300
H	1.93827100	-2.97549000	-1.38540200
H	2.26131500	-1.79369100	-2.65436700
H	3.59630000	-2.72654200	-1.96233700
C	2.96183400	-2.75220500	1.37893900
H	2.76150300	-2.67677200	2.45170800
H	2.17619200	-3.36766700	0.93040100
H	3.91225600	-3.29013600	1.25672200
C	3.67838200	2.30805900	0.57859900
H	3.18641600	2.70149700	1.47392200

H	4.76200000	2.41522900	0.72898600
H	3.40360700	2.95108500	-0.26270500
H	-3.54420300	1.41159200	-0.58193500
C	3.51904700	0.07406900	2.82267200
H	3.13518300	1.04302000	3.15536900
H	3.05417200	-0.69563400	3.44536700
H	4.59900800	0.05967800	3.02891400
Rh	1.13721100	-0.04543100	0.32266100
C	-0.46594700	4.46351900	-1.47889400
C	0.17470800	5.75948700	-0.97146100
H	-1.55408200	4.58016600	-1.54039300
H	-0.13155300	4.25315700	-2.50202200
H	-0.07220600	6.60411300	-1.62456900
H	-0.17252300	6.00791600	0.03919100
H	1.26857500	5.67837200	-0.93342100
O	-1.54824500	1.93413300	-2.01652400
H	0.43609200	1.07227500	1.28450700
N	-0.53296100	-2.46320900	0.37962900
C	-0.70028200	-3.51252400	1.38504000
H	-0.55811500	-4.49104900	0.91634000
H	0.05819900	-3.38122300	2.15825900
H	-1.69584300	-3.47922900	1.85371100
H	-0.46801400	3.44681800	0.44804300

8. Experimental characterization data for products

1-methyl-3-phenyl-1*H*-indazole (3a)

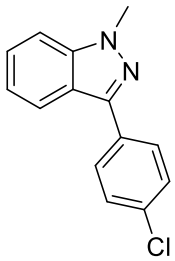


3a

Product **3a** was isolated as an off-white solid (54 mg, 65%); m.p. 72 – 74 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.90 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.23 – 7.19 (m, 1H), 4.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.69, 141.40, 133.65, 128.77, 127.77, 127.35, 126.23, 121.58, 121.32, 120.88, 109.16, 35.52. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_2$ $[M + H]^+$ 209.1073, found 209.1076.

3-(4-chlorophenyl)-1-methyl-1*H*-indazole (3b)

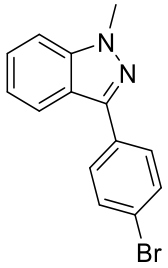


3b

Product **3b** was isolated as a brown solid (66 mg, 68%); m.p. 104 – 106 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.37 (m, 2H), 7.21 – 7.19 (m, 1H), 4.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.46, 141.43, 133.57, 132.20, 128.95, 128.46, 126.36, 121.41, 121.14, 121.01, 109.29, 35.54. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}ClN_2$ $[M + H]^+$ 243.0684, found 243.0685.

3-(4-bromophenyl)-1-methyl-1*H*-indazole (3c)

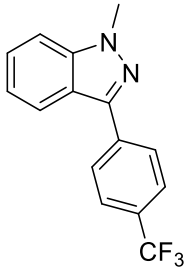


3c

Product **3c** was isolated as a brown solid (59 mg, 51%); m.p. 95 – 97 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.68 – 7.57 (m, 2H), 7.44 – 7.39 (m, 2H), 7.24– 7.20 (m, 1H), 4.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.47, 141.45, 132.66, 131.90, 128.76, 126.37, 121.76, 121.40, 121.17, 121.01, 109.31, 35.57. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M + H]^+$ 287.0178, found 287.0179.

1-methyl-3-(4-(trifluoromethyl)phenyl)-1*H*-indazole (3d)

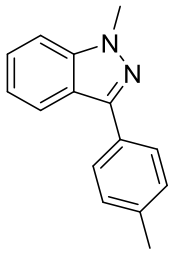


3d

Product **3d** was isolated as a brownish yellow solid (78 mg, 71%); m.p. 70 – 72 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 3.6 Hz, 2H), 7.29 – 7.21 (m, 1H), 4.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.06, 141.50, 137.49 – 136.85 (m), 129.51 (q, *J* = 32.5 Hz), 127.31, 126.48, 125.70 (q, *J* = 3.8 Hz), 124.28 (d, *J* = 271.9 Hz), 121.54, 121.49, 120.91, 109.45, 35.68. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}F_3N_2$ $[M + H]^+$ 277.0947, found 277.0952.

1-methyl-3-(p-tolyl)-1*H*-indazole (3e)

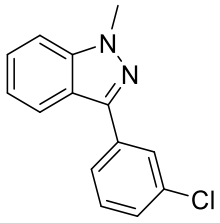


3e

Product **3e** was isolated as a brownish yellow solid (53 mg, 60%); m.p. 62 – 64 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.7 Hz, 1H), 7.95 – 7.80 (m, 2H), 7.45 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 – 7.15 (m, 1H), 4.11 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.79, 141.42, 137.56, 130.85, 129.48, 127.25, 126.17, 121.62, 121.41, 120.72, 109.10, 35.46, 21.30. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1235.

3-(3-chlorophenyl)-1-methyl-1*H*-indazole (3f)

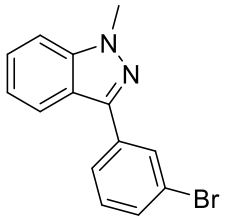


3f

Product **3f** was isolated as a brownish solid (71 mg, 73%); m.p. 69 – 71 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.84 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.34 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 4.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.19, 141.45, 135.51, 134.72, 129.99, 127.72, 127.23, 126.39, 125.31, 121.45, 121.26, 120.99, 109.32, 35.59. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}ClN_2$ $[M + H]^+$ 243.0684, found 243.069.

3-(3-bromophenyl)-1-methyl-1*H*-indazole (3g)

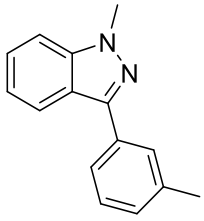


3g

Product **3g** was isolated as a brownish solid (70 mg, 61%); m.p. 71 – 73 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, *J* = 1.7 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.52 – 7.49 (m, 1H), 7.43 – 7.41 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.19 (m, 1H), 4.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.06, 141.45, 135.77, 130.64, 130.26, 130.12, 126.41, 125.77, 122.92, 121.44, 121.28, 120.98, 109.33, 35.61. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M + H]^+$ 287.0178, found 287.0183.

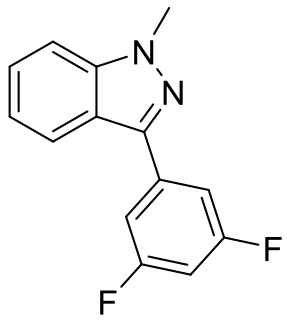
1-methyl-3-(m-tolyl)-1*H*-indazole (3h)



3h

Product **3h** was isolated as a yellow liquid (54 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.67 (m, 2H), 7.46 – 7.30 (m, 3H), 7.21 – 7.17(m, 2H), 4.10 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.83, 141.38, 138.42, 133.52, 128.63, 128.58, 127.95, 126.20, 124.50, 121.61, 121.39, 120.79, 109.11, 35.47, 21.52. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1230.

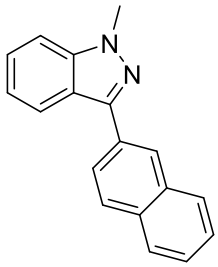
3-(3,5-difluorophenyl)-1-methyl-1*H*-indazole (3j)



3j

Product **3j** was isolated as light yellow solid (62 mg, 63%); m.p. 75 – 77 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.46 - 7.42 (m, 2H), 7.26 – 7.24 (m, 1H), 6.81 (t, *J* = 8.9 Hz, 1H), 4.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.32 (dd, *J* = 247.6, 13.2 Hz), 141.49, 141.27 (t, *J* = 3.0 Hz), 136.85 (t, *J* = 10.2 Hz), 126.52, 121.59, 121.27, 120.71, 109.84 (dd, *J* = 20.6, 5.6 Hz), 109.47, 102.88 (t, *J* = 25.4 Hz), 35.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.65. HRMS (ESI) *m/z* calcd for $C_{14}H_{11}F_2N_2$ $[M + H]^+$ 245.0885, found 245.0880.

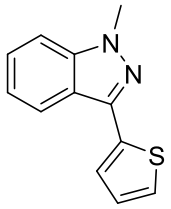
1-methyl-3-(naphthalen-2-yl)-1*H*-indazole (3k)



3k

Product **3k** was isolated as an off-white solid (76 mg, 74%); m.p. 79 – 81 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.19 – 8.08 (m, 2H), 7.95 (t, *J* = 7.6 Hz, 2H), 7.90 – 7.82 (m, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.39 (m, 2H), 7.28 – 7.22 (m, 1H), 4.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.58, 141.53, 133.65, 132.97, 131.20, 128.44, 128.23, 127.75, 126.32, 126.24, 126.01, 125.97, 125.49, 121.79, 121.42, 121.04, 109.26, 35.59. HRMS (ESI) *m/z* calcd for $C_{18}H_{15}N_2$ $[M + H]^+$ 259.1230, found 259.1241.

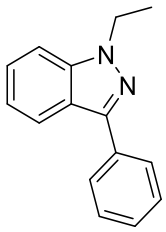
1-methyl-3-(thiophen-2-yl)-1*H*-indazole (3l)



3l

Product **3l** was isolated as an off-white solid (35 mg, 41%); m.p. 62 – 64 °C;
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, J = 8.2 Hz, 1H), 7.73 (dd, J = 3.6, 0.8 Hz, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.57 (dd, J = 5.2, 0.8 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.20 (dd, J = 5.2, 3.6 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.50, 138.07, 136.10, 128.51, 127.03, 125.75, 124.81, 121.85, 121.07, 120.43, 110.65, 35.89. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}N_2S$ $[M + H]^+$ 215.0637, found 215.0638.

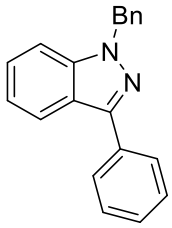
1-ethyl-3-phenyl-1*H*-indazole (4a)



4a

Product **4a** was isolated as a yellow liquid (52 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.20 (ddd, J = 7.8, 6.4, 1.3 Hz, 1H), 4.49 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65, 140.43, 133.80, 128.75, 127.70, 127.41, 126.05, 121.72, 121.38, 120.81, 109.16, 43.79, 15.04. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1239.

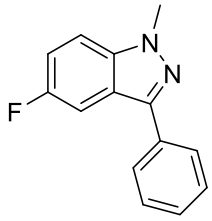
1-benzyl-3-phenyl-1*H*-indazole (4b)



4b

Product **4b** was isolated as a yellow liquid (47 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.93 (m, 3H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.23 (m, 7H), 7.21 – 7.17 (m, 1H), 5.65 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.14, 141.03, 136.84, 133.62, 128.76, 128.66, 127.86, 127.66, 127.50, 127.10, 126.35, 122.07, 121.39, 121.07, 109.61, 53.03. HRMS (ESI) *m/z* calcd for $C_{20}H_{17}N_2$ $[M + H]^+$ 285.1386, found 285.1391.

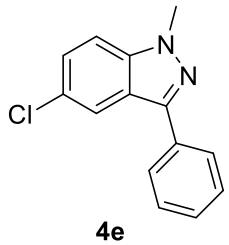
5-fluoro-1-methyl-3-phenyl-1*H*-indazole (4d)



4d

Product **4d** was isolated as a yellow liquid (51 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 2H), 7.62 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.51-7.47 (m, 2H), 7.43 – 7.30 (m, 2H), 7.19 (td, *J* = 8.8, 2.2 Hz, 1H), 4.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.23 (d, *J* = 238.1 Hz), 143.49 (d, *J* = 5.7 Hz), 138.45, 133.25, 128.85, 127.89, 127.08, 121.41 (d, *J* = 9.8 Hz), 115.86 (d, *J* = 27.6 Hz), 110.23 (d, *J* = 9.7 Hz), 105.39 (d, *J* = 24.1 Hz), 35.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.93. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}FN_2$ $[M + H]^+$ 227.0979, found 227.0989.

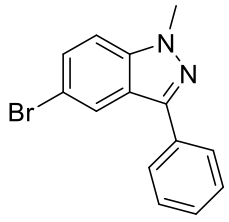
5-chloro-1-methyl-3-phenyl-1*H*-indazole (4e)



4e

Product **4e** was isolated as a yellow liquid (39 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 7.91 – 7.89 (m, 2H), 7.52 – 7.48 (m, 2H), 7.42 – 7.40 (m, 1H), 7.37 – 7.32 (m, 2H), 4.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.29, 139.90, 133.01, 128.89, 128.08, 127.26, 126.95, 126.71, 122.37, 120.56, 110.29, 35.75. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}ClN_2$ $[M + H]^+$ 243.0684, found 243.0695.

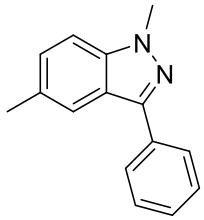
5-bromo-1-methyl-3-phenyl-1*H*-indazole (4f)



4f

Product **4f** was isolated as a yellow liquid (66 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 1.4 Hz, 1H), 7.90 – 7.88 (m, 2H), 7.52 – 7.47 (m, 3H), 7.44 – 7.36 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 4.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.18, 140.05, 132.94, 129.34, 128.88, 128.09, 127.27, 123.74, 123.04, 114.12, 110.62, 35.72. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M + H]^+$ 287.0178, found 287.0184.

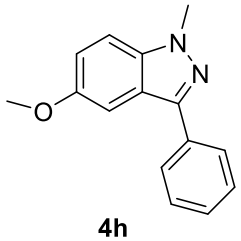
1,5-dimethyl-3-phenyl-1*H*-indazole (4g)



4g

Product **4g** was isolated as a yellow liquid (54 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.77 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 4.09 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.01, 140.16, 133.84, 130.33, 128.72, 128.30, 127.61, 127.30, 121.88, 120.32, 108.85, 35.55, 21.45. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1240.

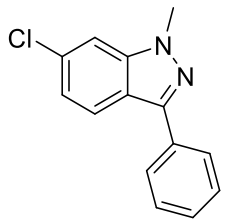
5-methoxy-1-methyl-3-phenyl-1*H*-indazole (4h)



4h

Product **4h** was isolated as a yellow liquid (48 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.38 (tt, *J* = 6.8, 1.2 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.10 (dd, *J* = 9.0, 2.2 Hz, 1H), 4.08 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.97, 142.87, 137.44, 133.87, 128.78, 127.55, 127.17, 121.68, 118.44, 110.18, 100.48, 55.79, 35.67. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2O$ $[M + H]^+$ 239.1179, found 239.1190.

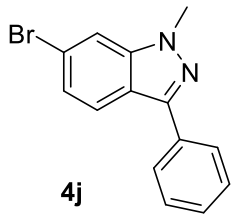
6-chloro-1-methyl-3-phenyl-1*H*-indazole (4i)



4i

Product **4i** was isolated as a yellow liquid (34 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 3H), 7.52-7.48 (m, 2H), 7.44 – 7.33 (m, 2H), 7.16 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.01, 141.81, 133.05, 132.72, 128.85, 128.11, 127.32, 122.32, 121.92, 120.21, 108.97, 35.61. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}ClN_2$ $[M + H]^+$ 243.0684, found 243.0695.

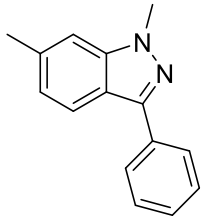
6-bromo-1-methyl-3-phenyl-1*H*-indazole (4j)



4j

Product **4j** was isolated as a yellow liquid (55 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.59 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.05, 142.18, 133.02, 128.85, 128.12, 127.32, 124.40, 122.52, 120.69, 120.47, 112.13, 35.62. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M + H]^+$ 287.0178, found 287.0177.

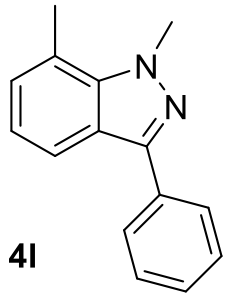
1,6-dimethyl-3-phenyl-1*H*-indazole (4k)



4k

Product **4k** was isolated as an off-white solid (68 mg, 77%); m.p. 59 – 61 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 4.08 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 142.03, 136.56, 133.79, 128.73, 127.68, 127.26, 123.16, 120.89, 119.79, 108.67, 35.39, 21.95. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1231.

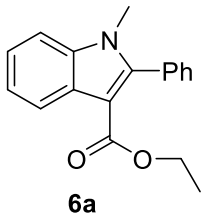
1,7-dimethyl-3-phenyl-1*H*-indazole (4l)



4l

Product **4l** was isolated as a yellow liquid (36 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.02 (m, 2H), 4.37 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.56, 140.93, 133.62, 128.72, 128.05, 127.73, 127.55, 122.52, 121.23, 120.55, 119.19, 39.19, 19.34. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1240.

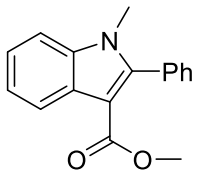
ethyl 1-methyl-2-phenyl-1*H*-indole-3-carboxylate (6a).



6a

Product **6a** was isolated as off-white solid (54 mg, 48%); m.p. 90 – 92 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.0 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.43 – 7.39 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.28 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.07, 146.74, 136.76, 131.61, 130.29, 128.84, 127.98, 126.66, 122.77, 122.04, 121.94, 109.68, 105.19, 59.26, 30.83, 14.15. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NNaO_2$ $[M + Na]^+$ 302.1151, found 302.1150.

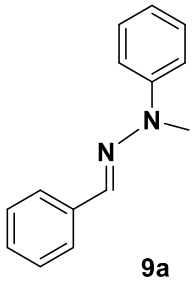
methyl 1-methyl-2-phenyl-1*H*-indole-3-carboxylate (8a).



8a

Product **8a** was isolated as off-white solid (42 mg, 40%); m.p. 111 – 113 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.42 – 7.37 (m, 3H), 7.34 – 7.30 (m, 2H), 3.75 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.54, 146.93, 136.77, 131.40, 130.26, 128.94, 128.06, 126.50, 122.82, 122.09, 121.96, 109.73, 104.94, 50.66, 30.85. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}NNaO_2$ $[M + Na]^+$ 288.0995, found 288.0986.

(*E*)-2-benzylidene-1-methyl-1-phenylhydrazine (9a)



9a

Product **9a** was isolated as a yellow solid (81 mg, 96%); m.p. 102 – 103 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.49 (s, 1H), 7.43 – 7.29 (m, 6H), 7.28 – 7.19 (m, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.84, 136.74, 131.82, 128.99, 128.53, 127.67, 126.03, 120.53, 115.21, 33.03. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}N_2$ $[M + H]^+$ 211.1230, found 211.1236.

9. References

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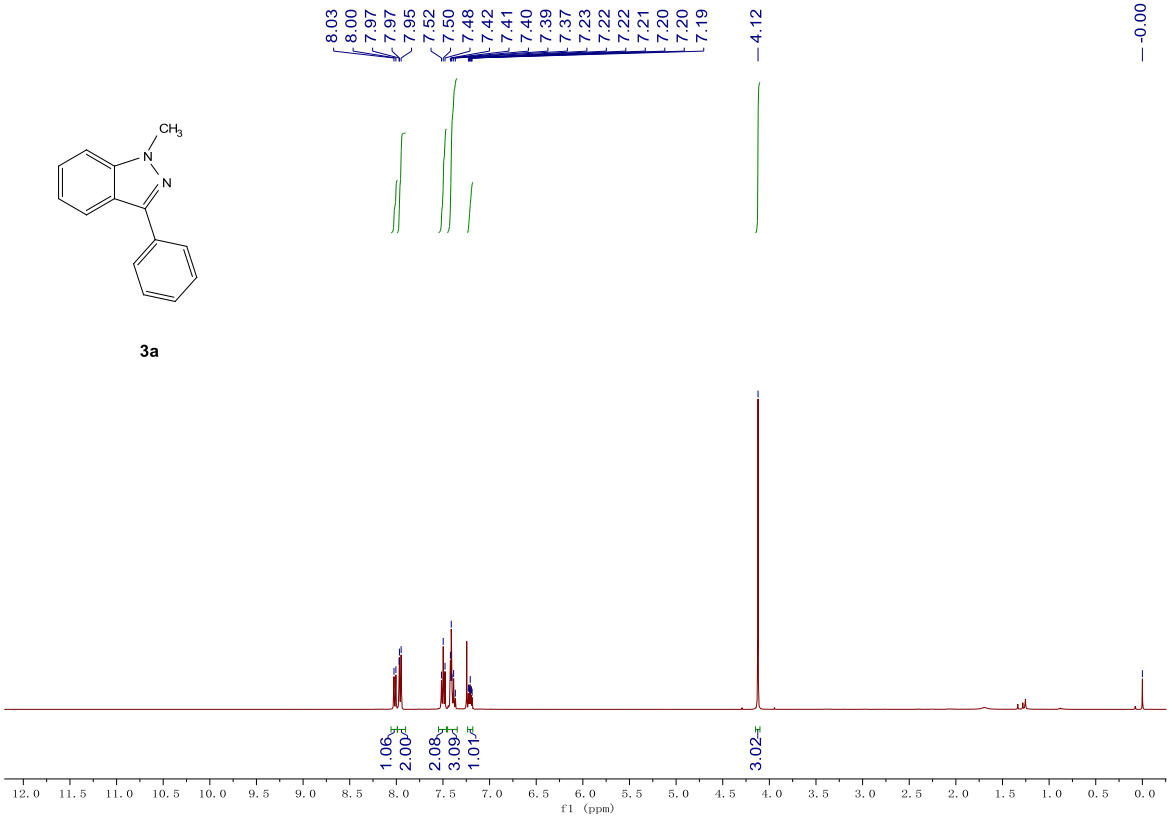
10. Copies of ^{1}H-NMR, ^{13}C-NMR, and ^{19}F--NMR spectra



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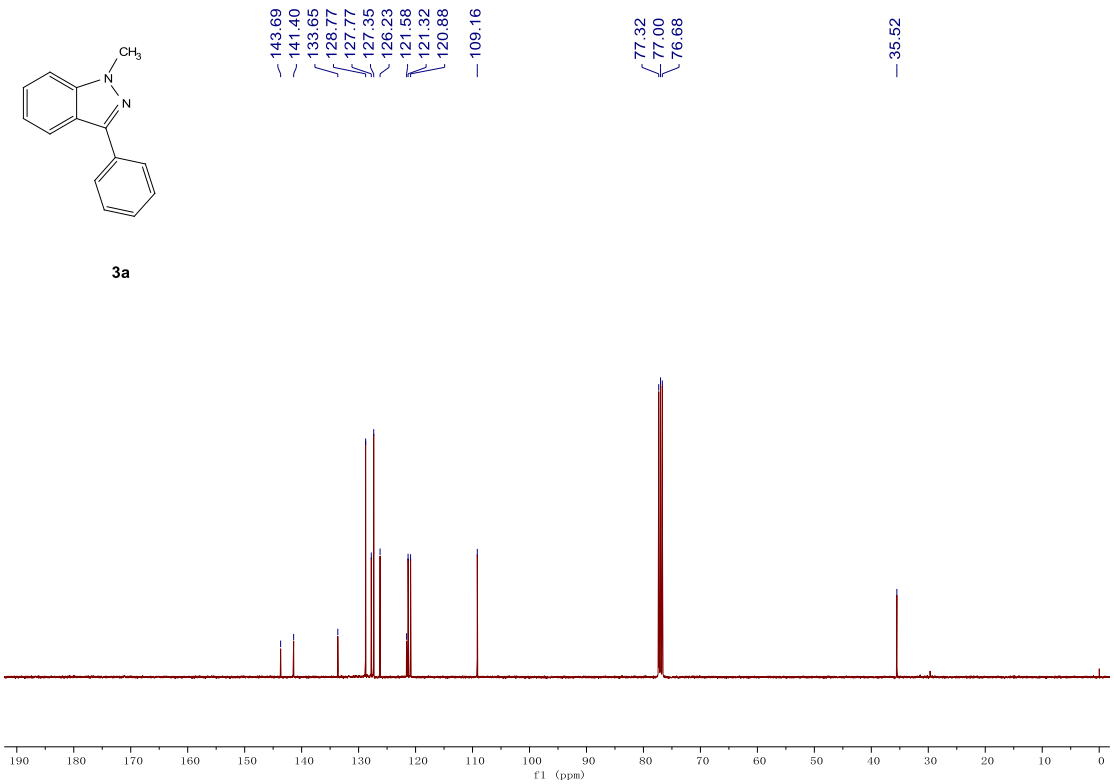

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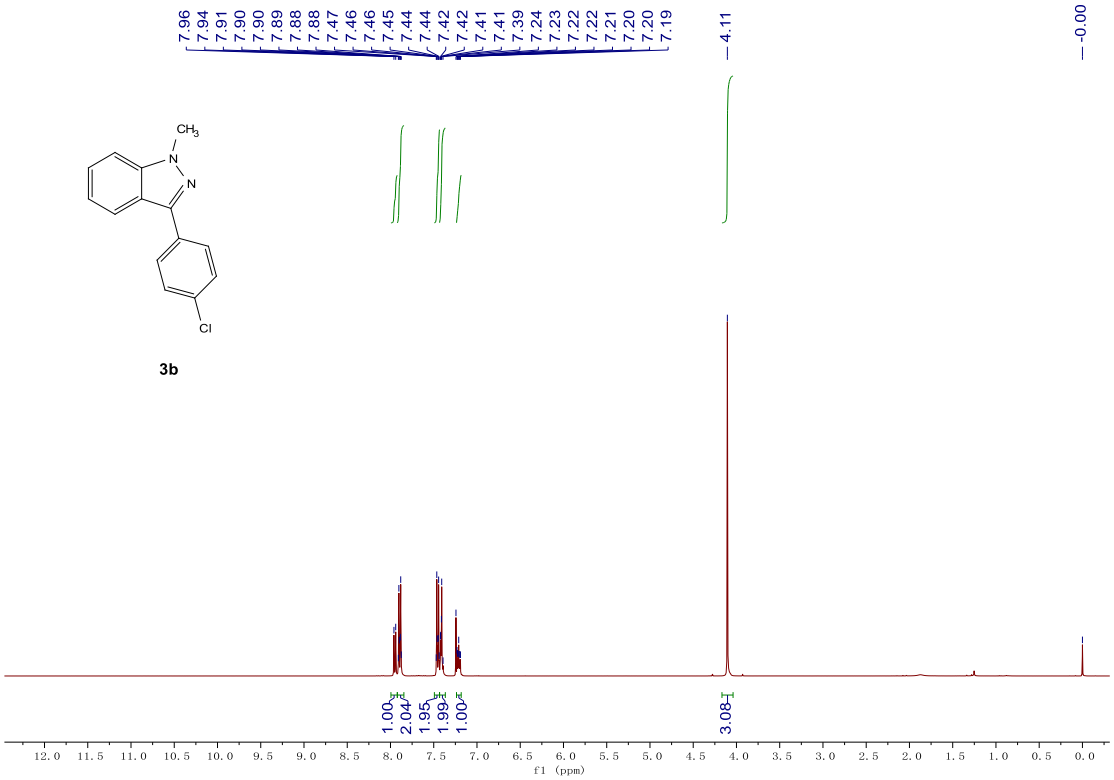
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7.44
7.44
7.42
7.42
7.41
7.41
7.39
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.19
4.11
0.00
CH3
N
N
Cl
1.00
2.04
1.95
1.99
1.00
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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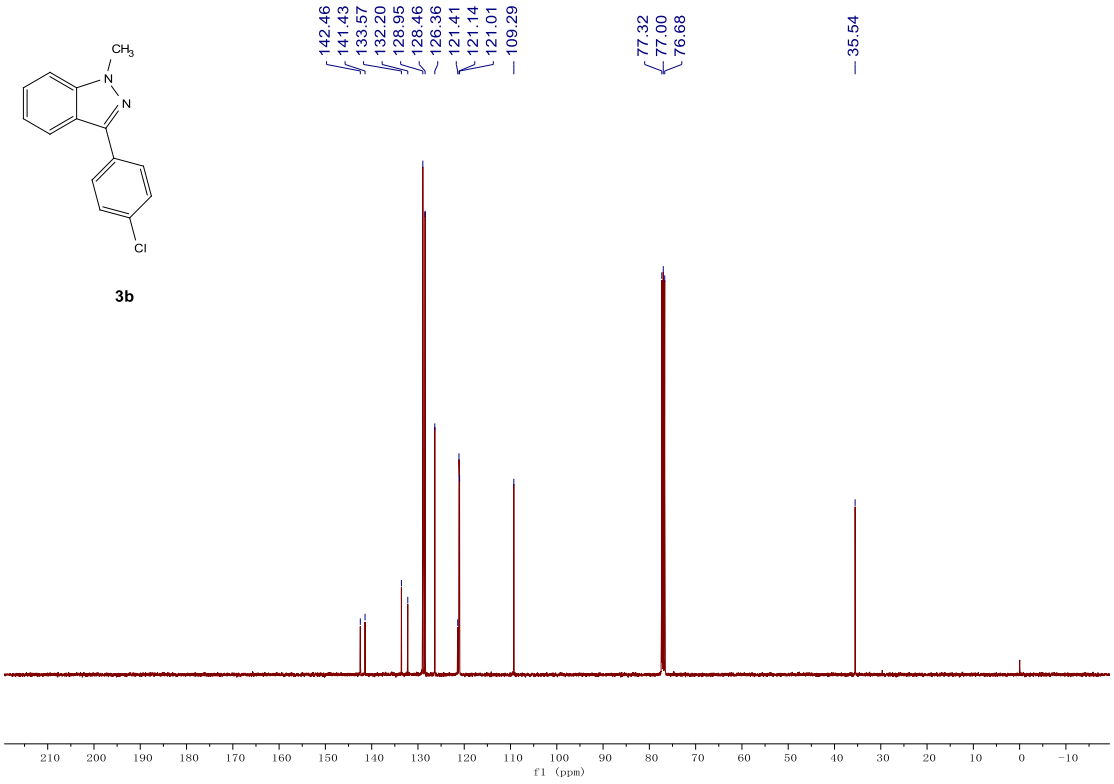
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Cl
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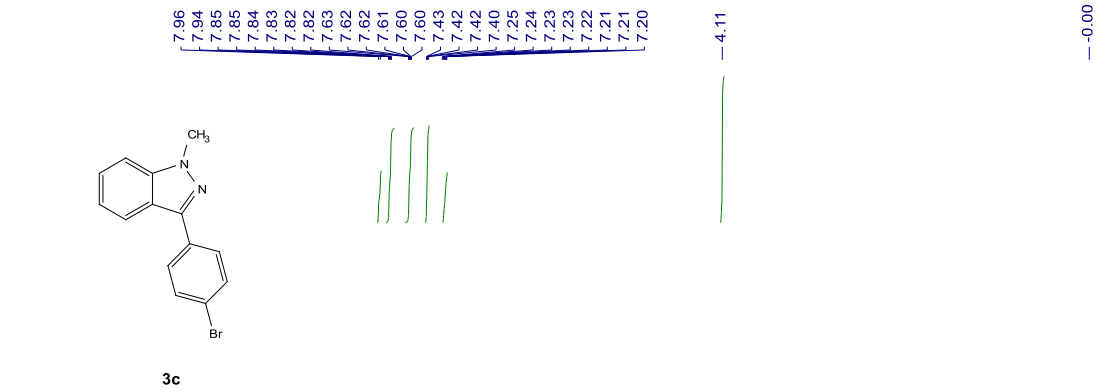
f1 (ppm)

3b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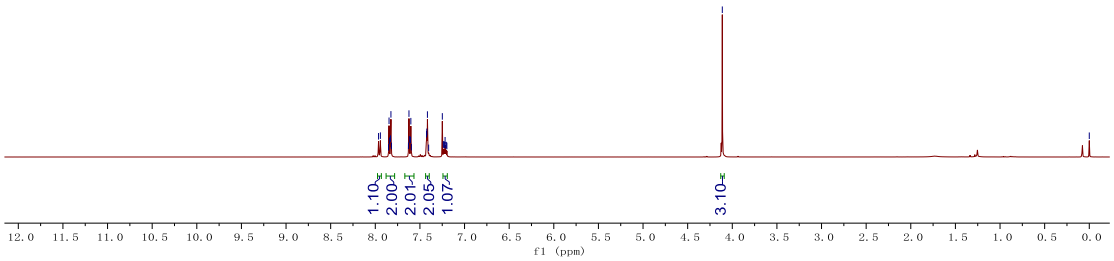
N
Br

3c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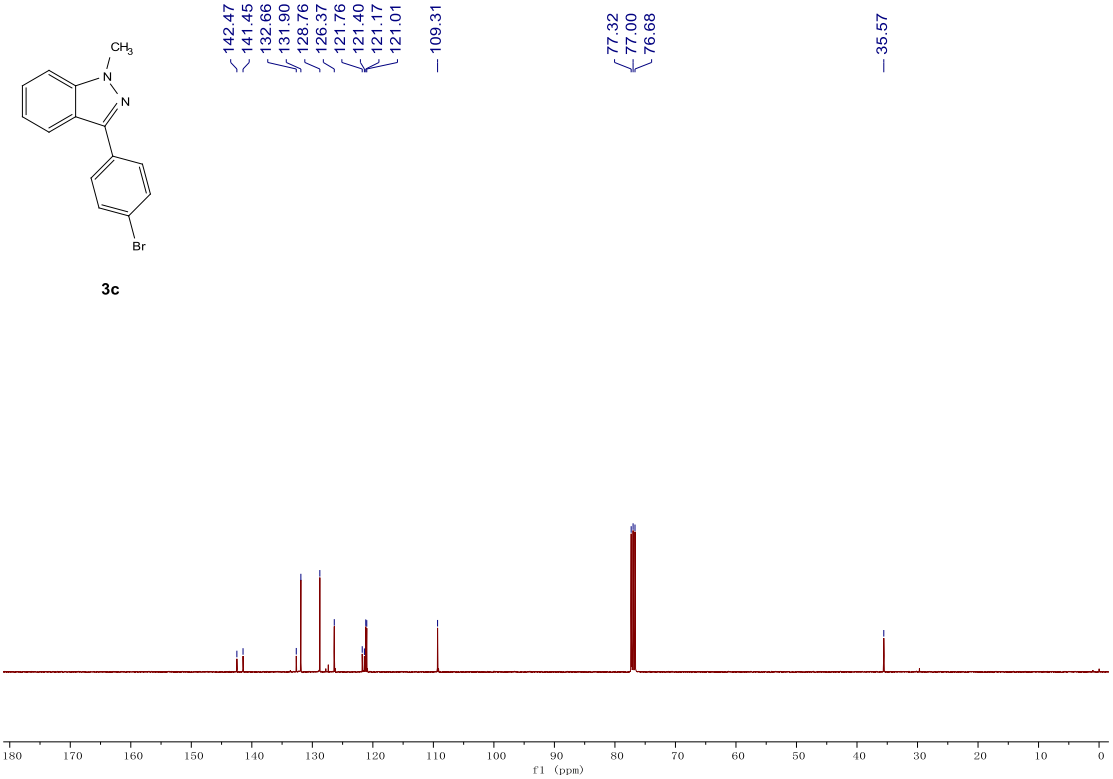
f1 (ppm)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35.57
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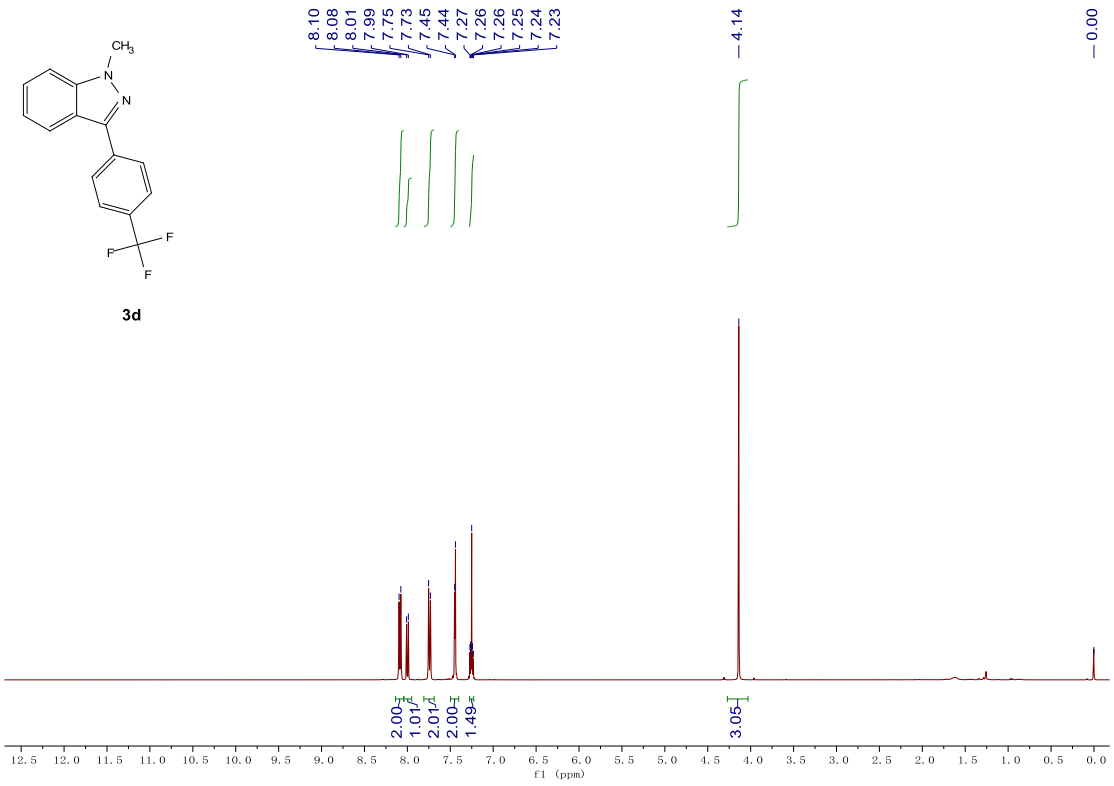
f1 (ppm)

CH3
N
N
Br

3c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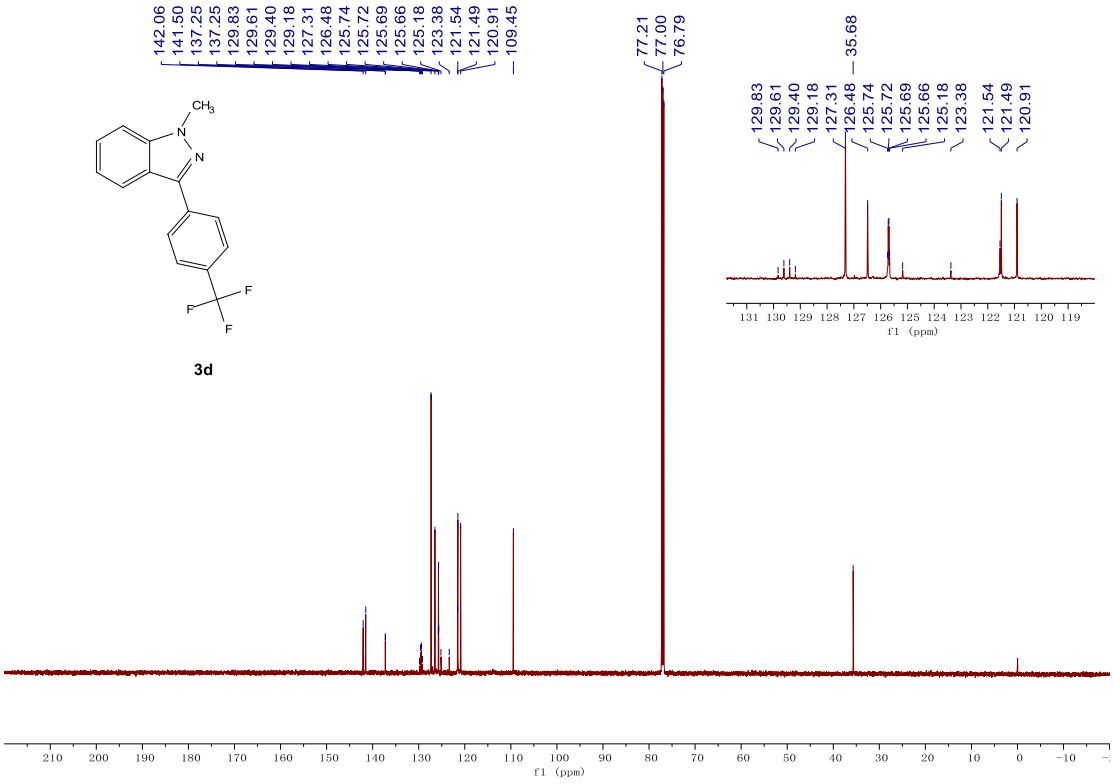
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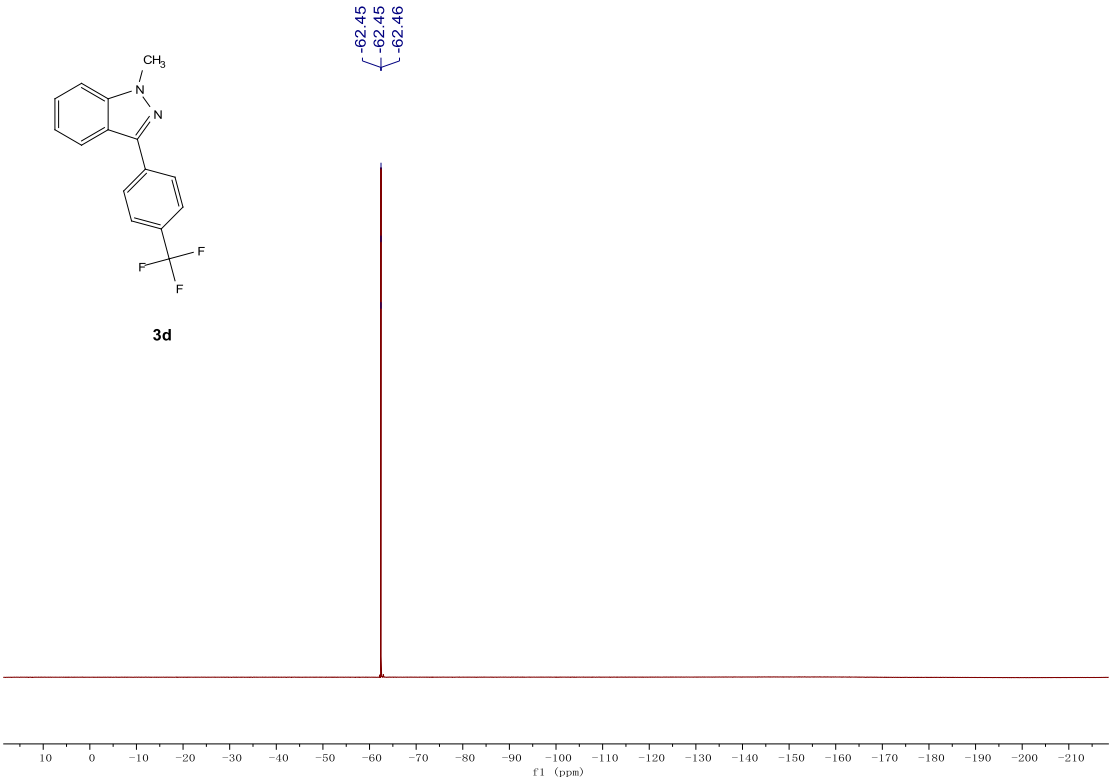
f1 (ppm)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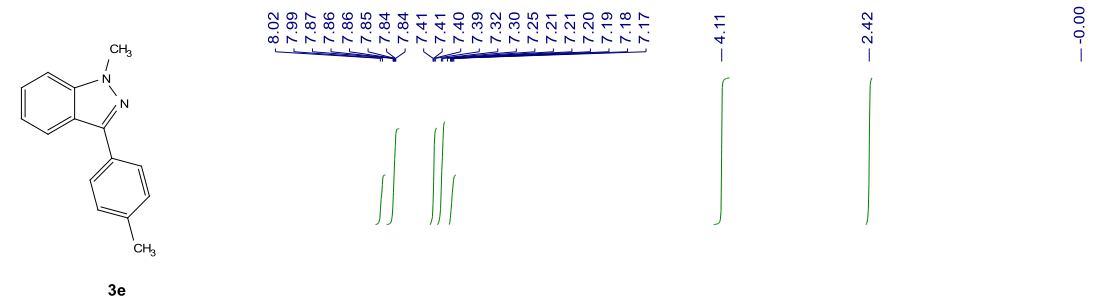
3d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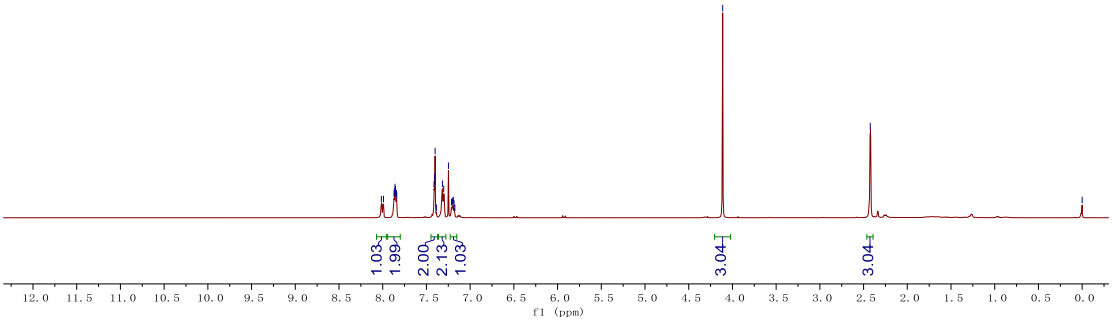
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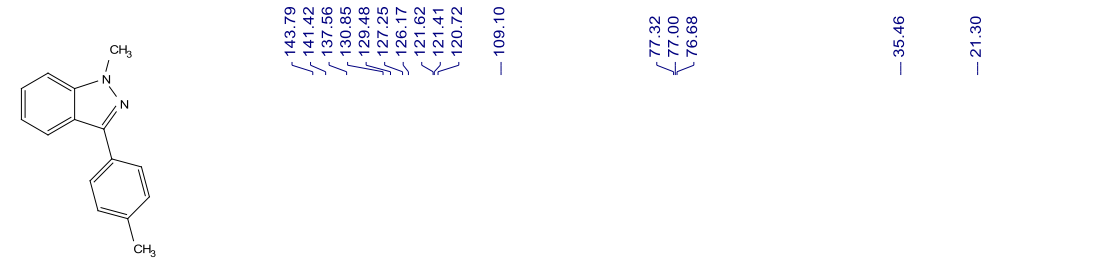
3e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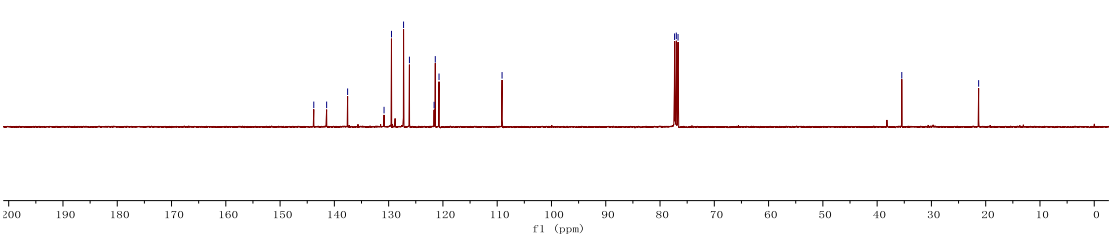
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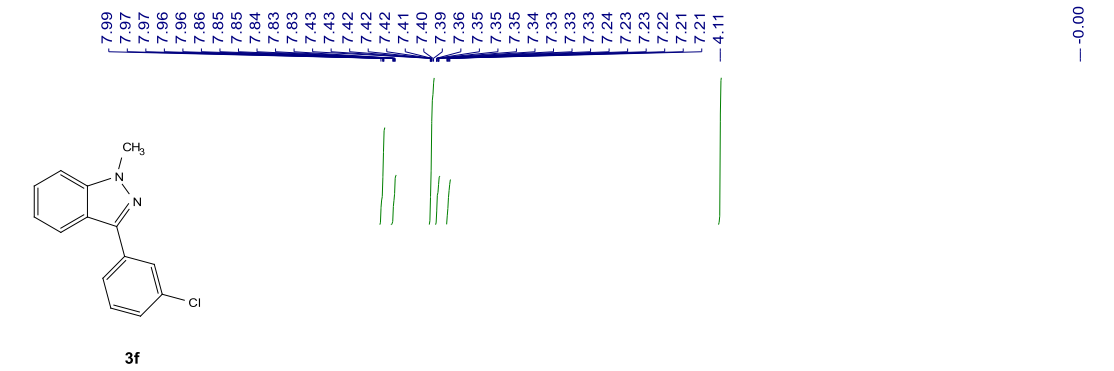
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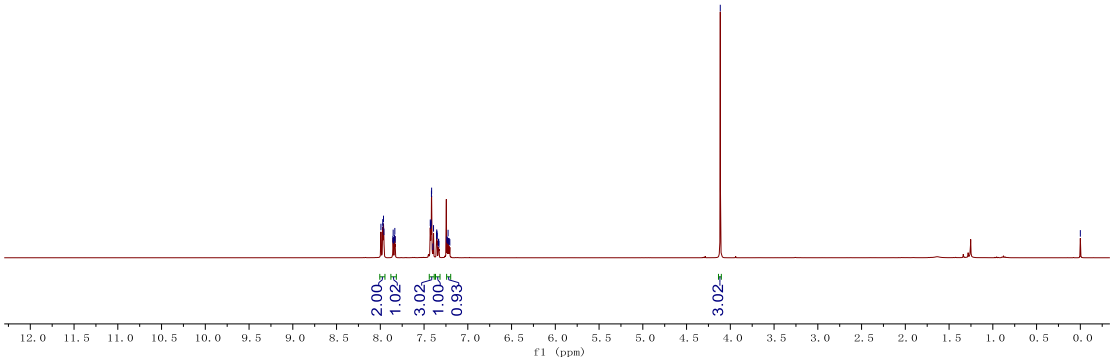
Cl

3f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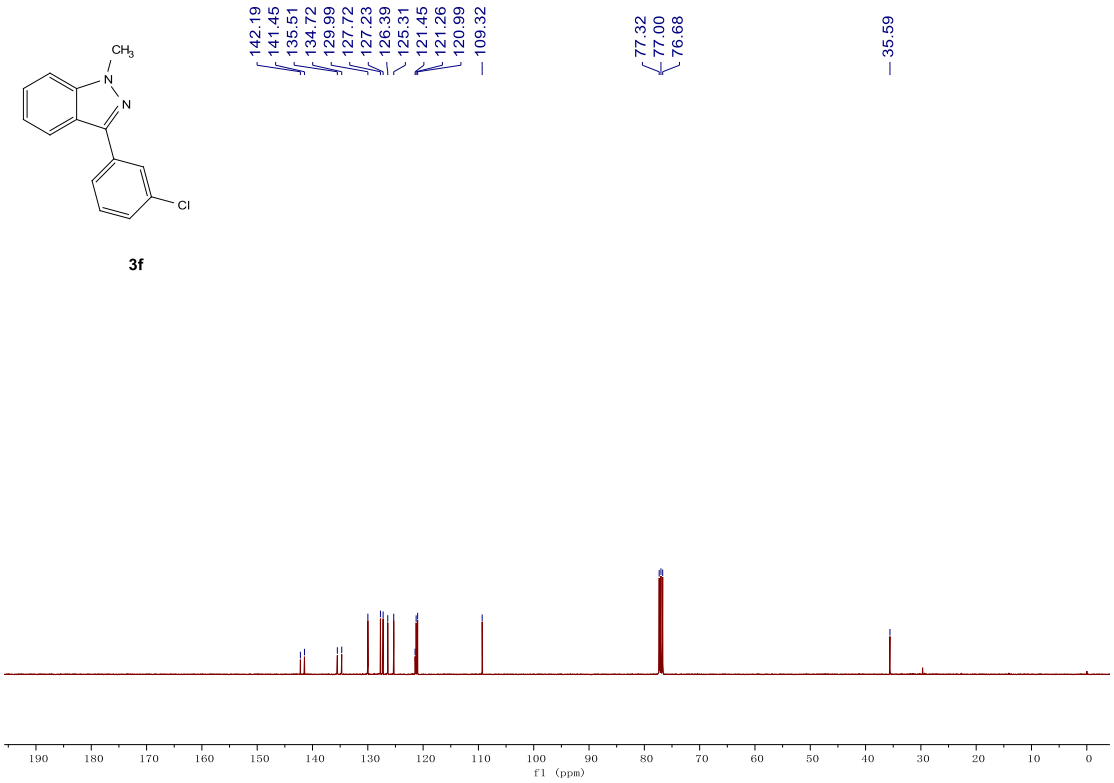
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CH3
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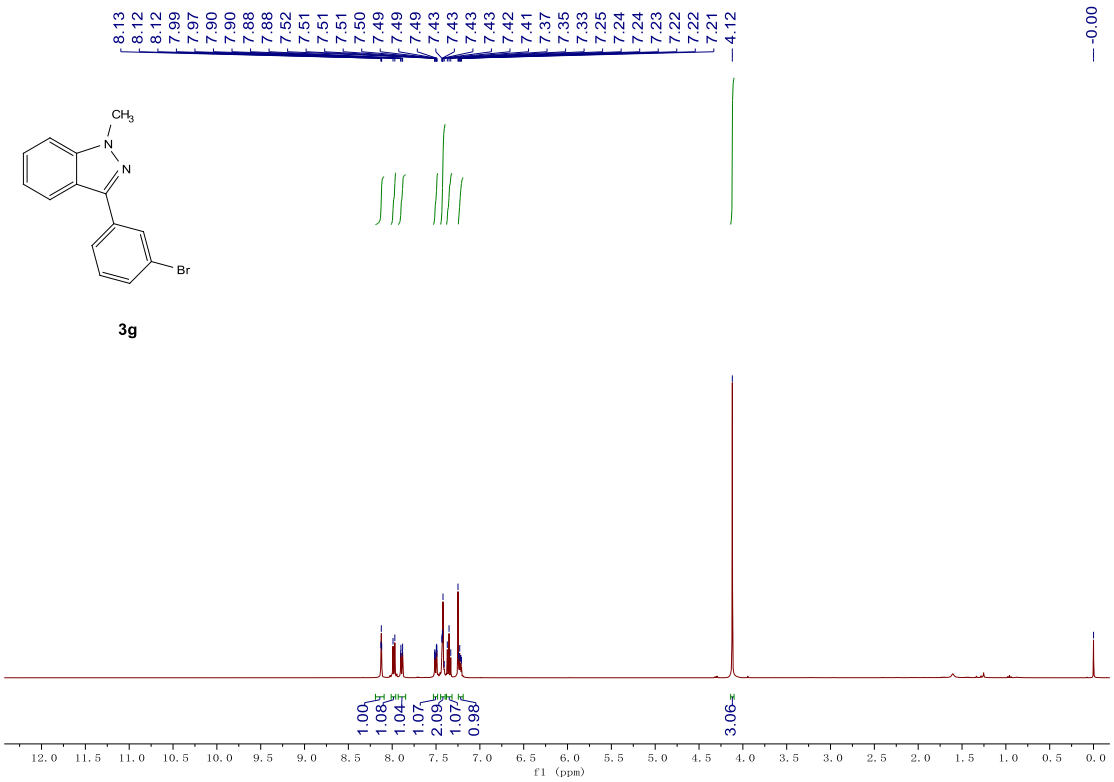
Cl
f1 (ppm)

3f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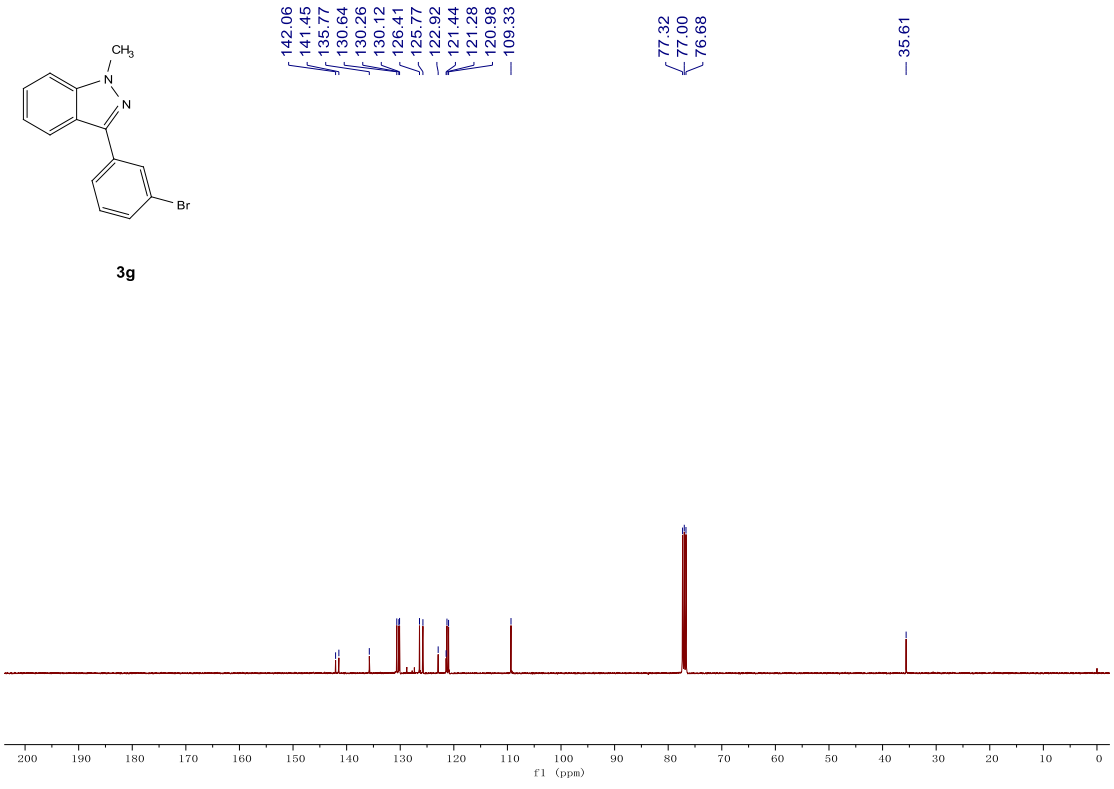
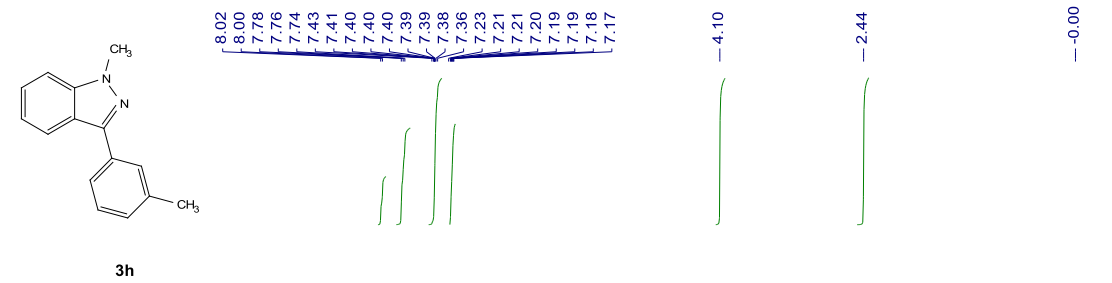
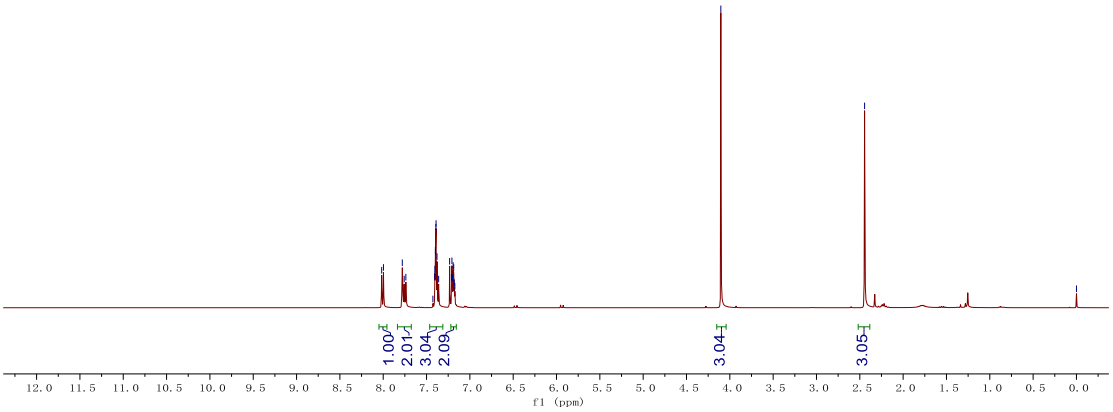
3g

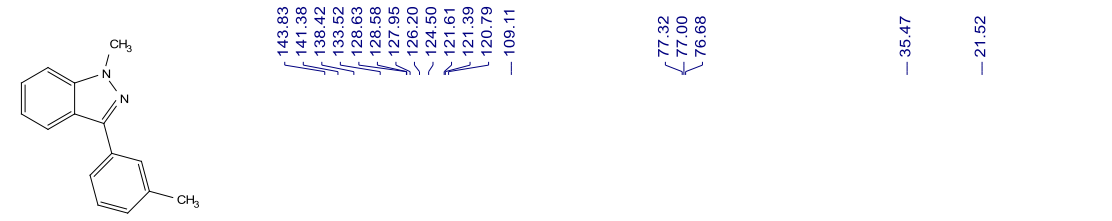

142.06
141.45
135.77
130.64
130.26
130.12
126.41
125.77
122.92
121.44
121.28
120.98
109.33
77.32
77.00
76.68
35.61
CH3
N
N
Br
f1 (ppm)

3g

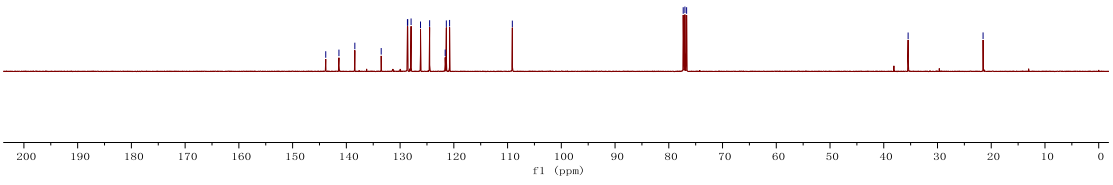

8.02
8.00
7.78
7.76
7.74
7.43
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.36
7.23
7.21
7.21
7.20
7.19
7.19
7.18
7.17
4.10
2.44
-0.00

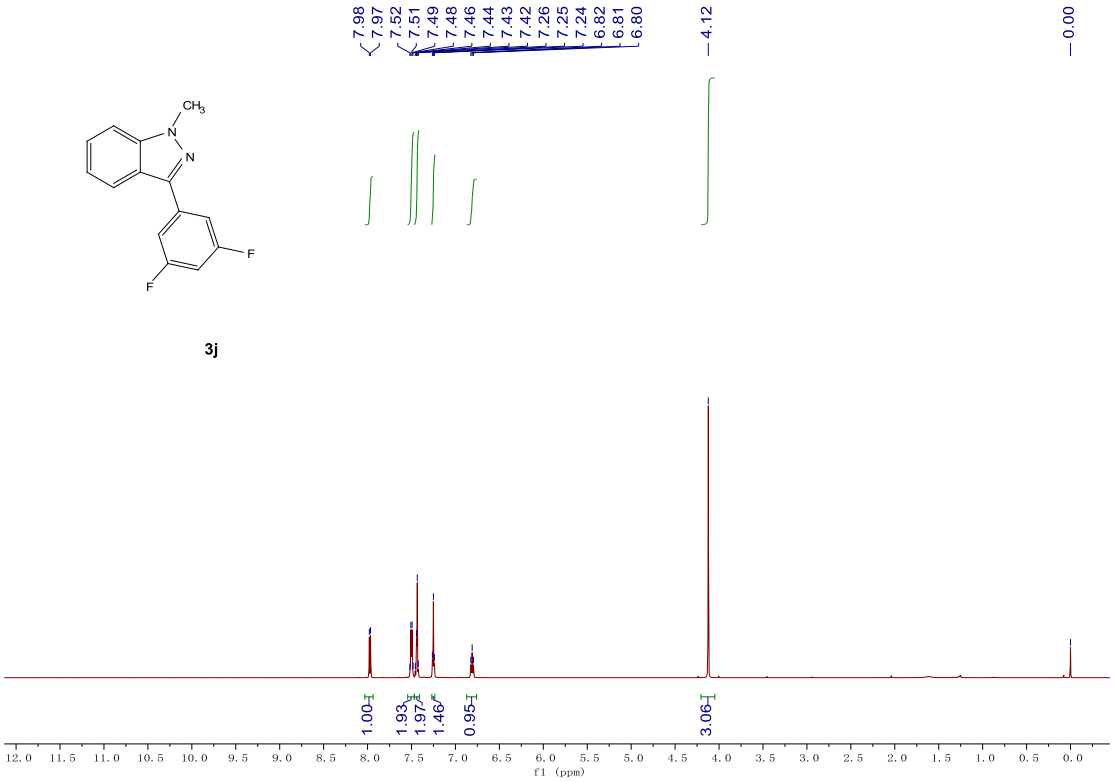
3h


1.00
2.01
3.04
2.09
3.04
3.05
f1 (ppm)

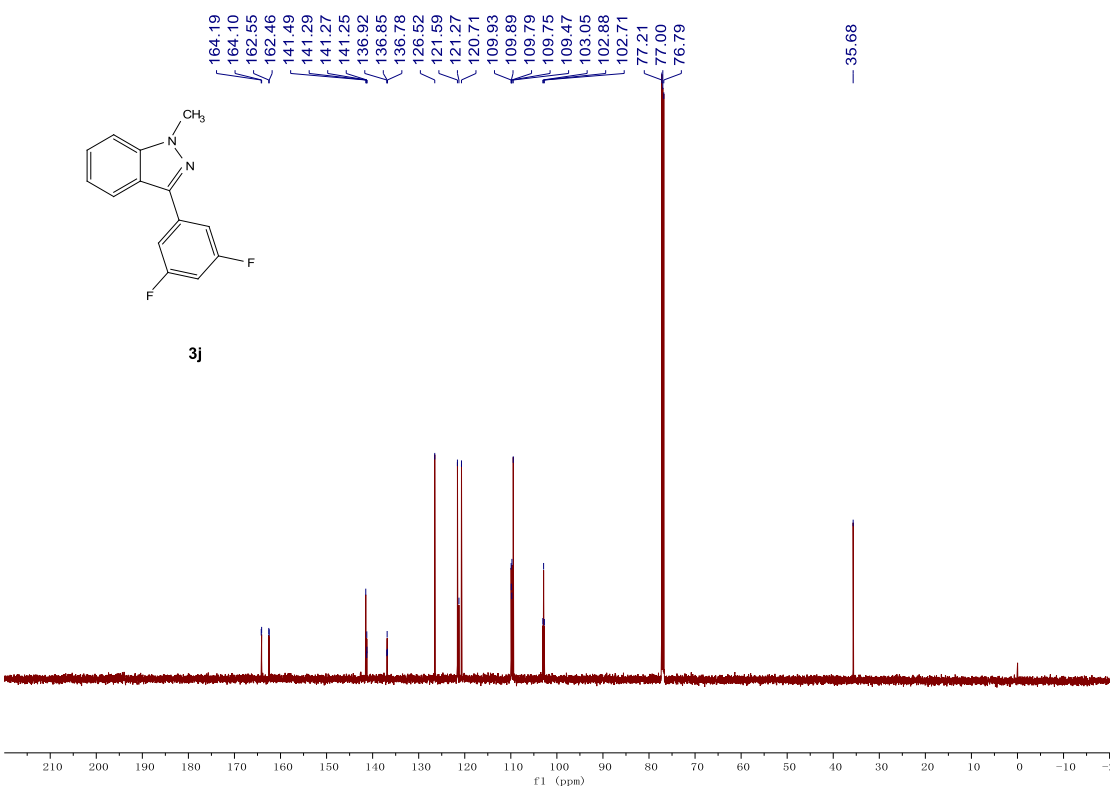

143.83
141.38
138.42
133.52
128.63
128.58
127.95
126.20
124.50
121.61
121.39
120.79
109.11
77.32
77.00
76.68
35.47
21.52

3h

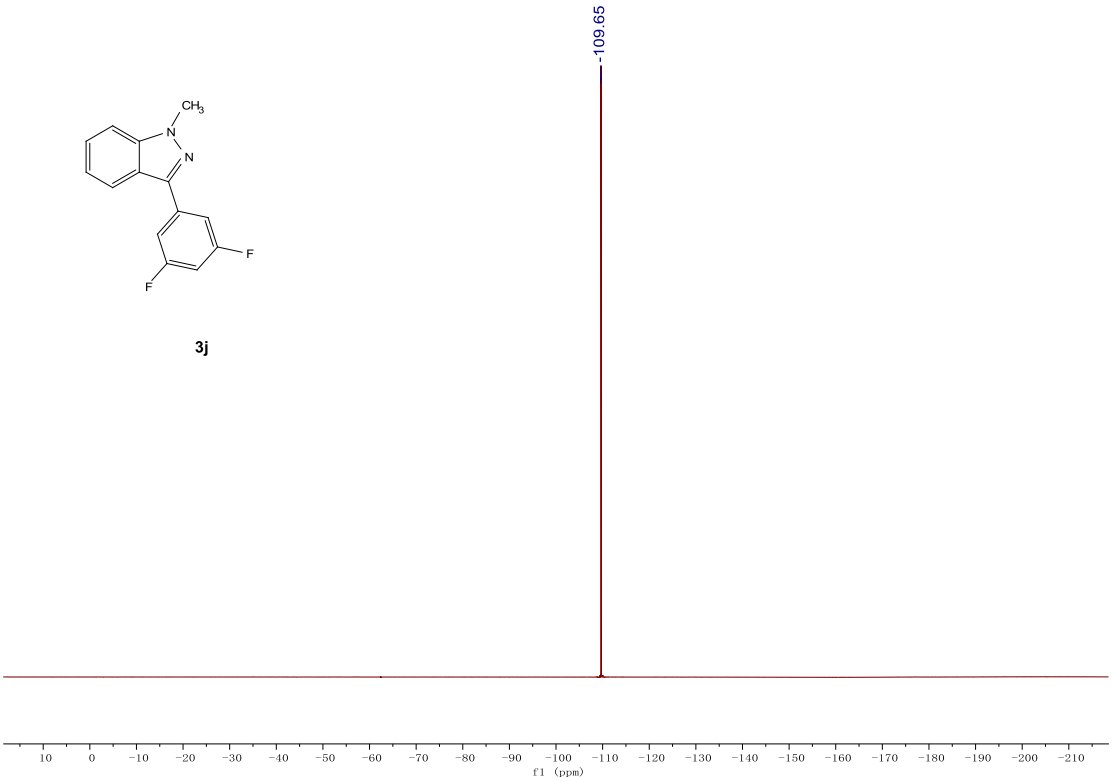

f1 (ppm)


7.98
7.97
7.52
7.51
7.49
7.48
7.46
7.44
7.43
7.42
7.26
7.25
7.24
6.82
6.81
6.80
4.12
0.00
CH3
N
N
F
F
1.00
1.93
1.97
1.46
0.95
3.06
f1 (ppm)

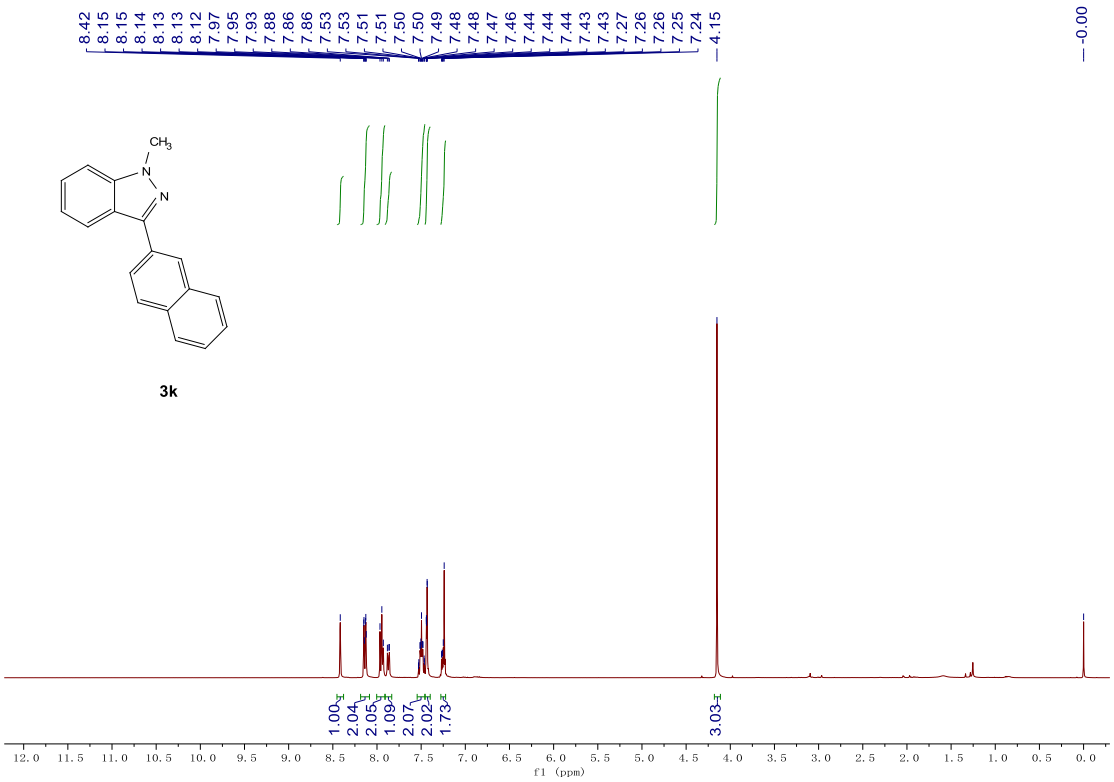
3j


164.19
164.10
162.55
162.46
141.49
141.29
141.27
141.25
136.92
136.85
136.78
126.52
121.59
121.27
120.71
109.93
109.89
109.79
109.75
109.47
103.05
102.88
102.71
77.21
77.00
76.79
35.68
CH3
N
N
F
F
f1 (ppm)

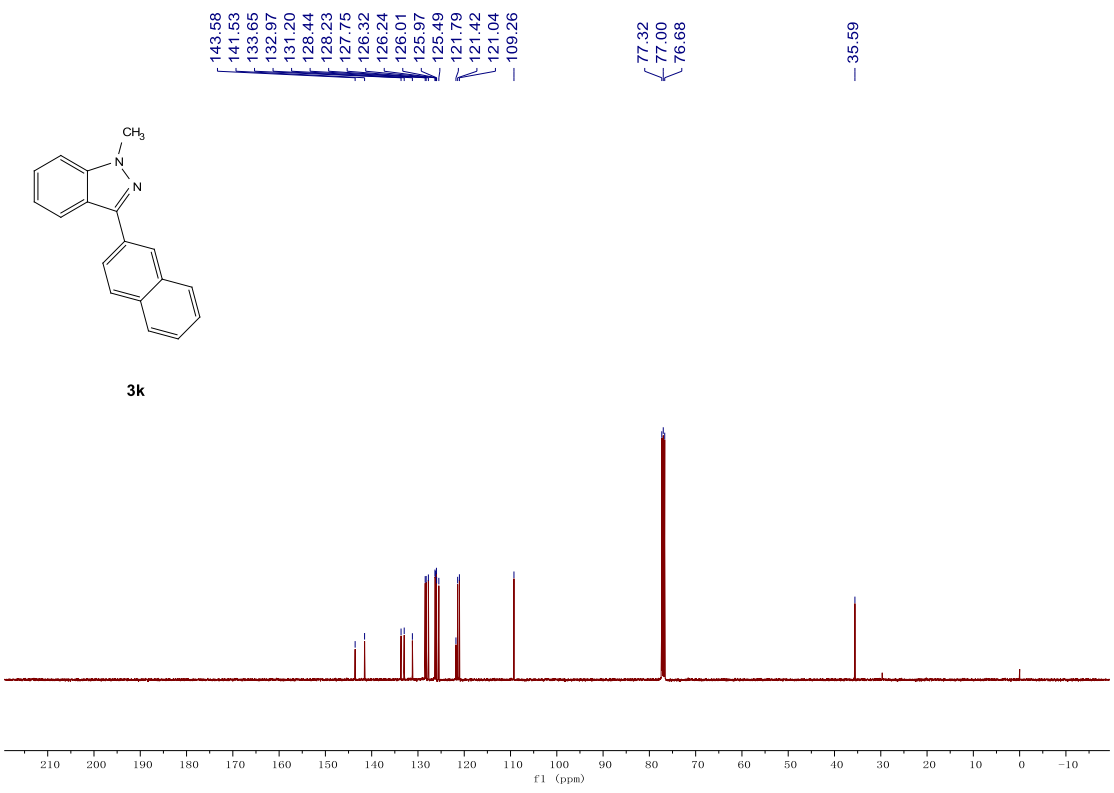
3j


-109.65
CH3
N
N
F
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

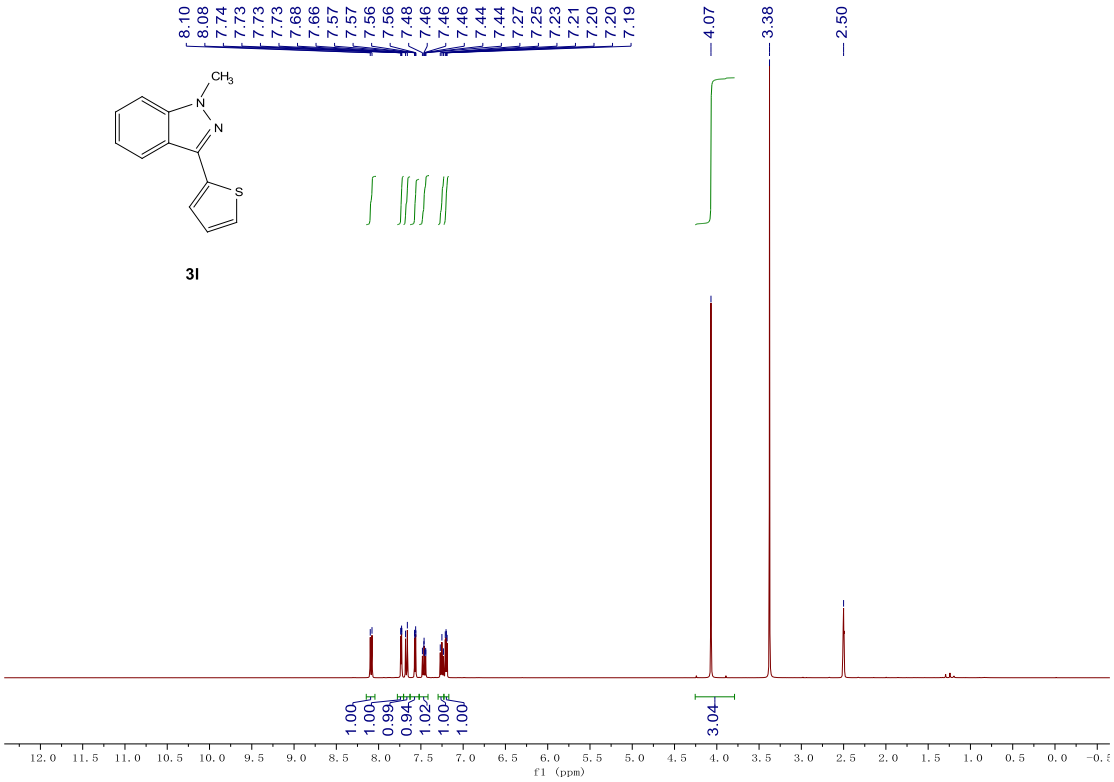
3j


8.42
8.15
8.15
8.14
8.13
8.13
8.12
7.97
7.95
7.93
7.88
7.86
7.86
7.53
7.53
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.44
7.44
7.43
7.43
7.27
7.26
7.26
7.25
7.24
4.15
-0.00
CH3
N
N
1.00
2.04
2.05
1.09
2.07
2.02
1.73
3.03
f1 (ppm)

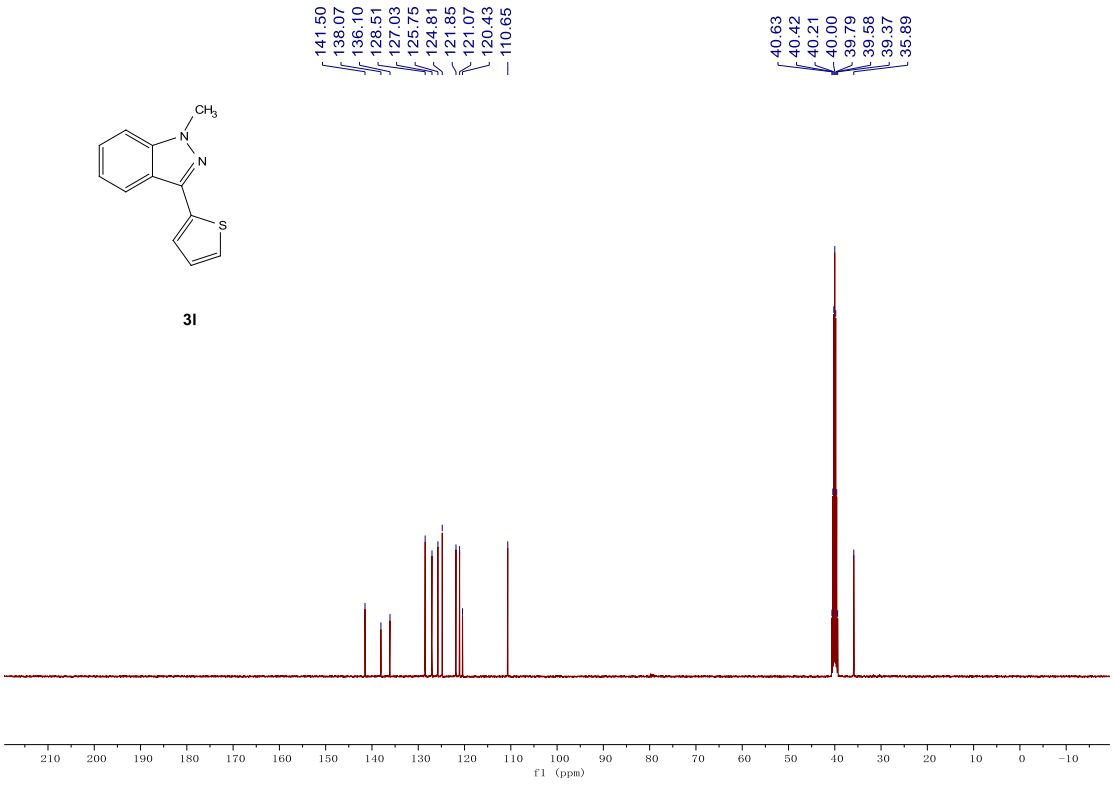
3k


143.58
141.53
133.65
132.97
131.20
128.44
128.23
127.75
126.32
126.24
126.01
125.97
125.49
121.79
121.42
121.04
109.26
77.32
77.00
76.68
35.59
CH3
N
N
f1 (ppm)

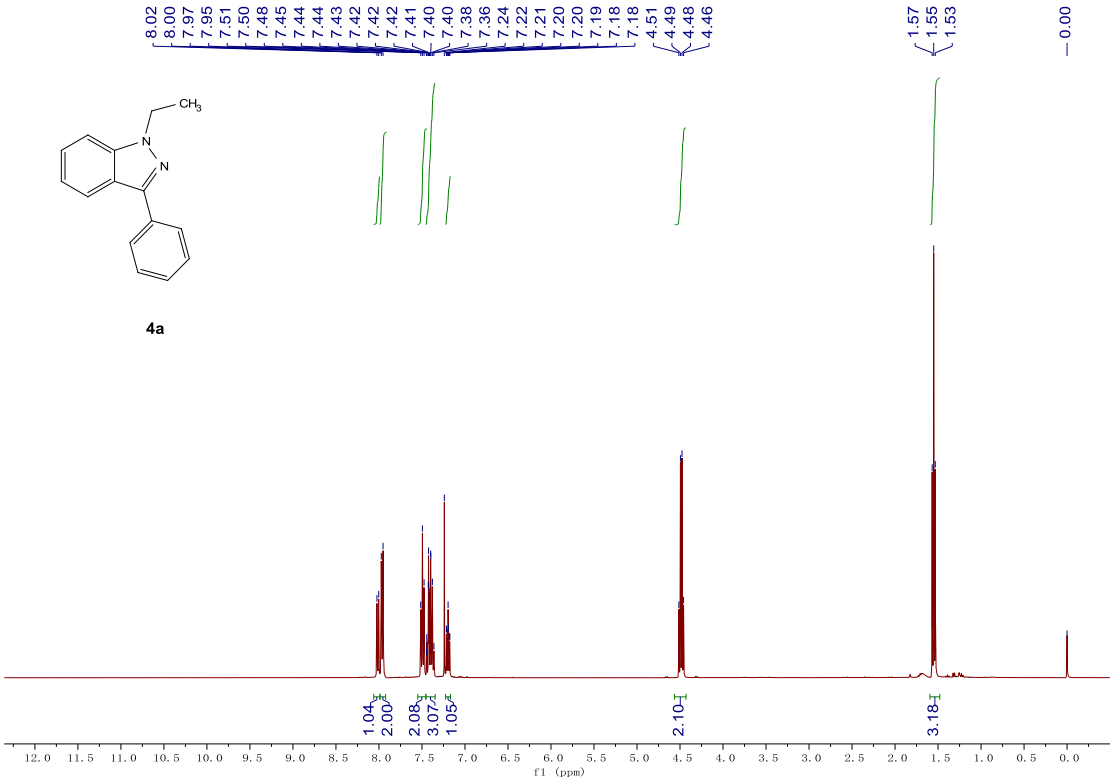
3k


8.10
8.08
7.74
7.73
7.73
7.73
7.68
7.66
7.57
7.57
7.56
7.56
7.48
7.46
7.46
7.46
7.44
7.44
7.27
7.25
7.23
7.21
7.20
7.20
7.19
4.07
3.38
2.50
CH3
N
N
S
1.00
1.00
0.99
0.94
1.02
1.00
1.00
3.04
f1 (ppm)

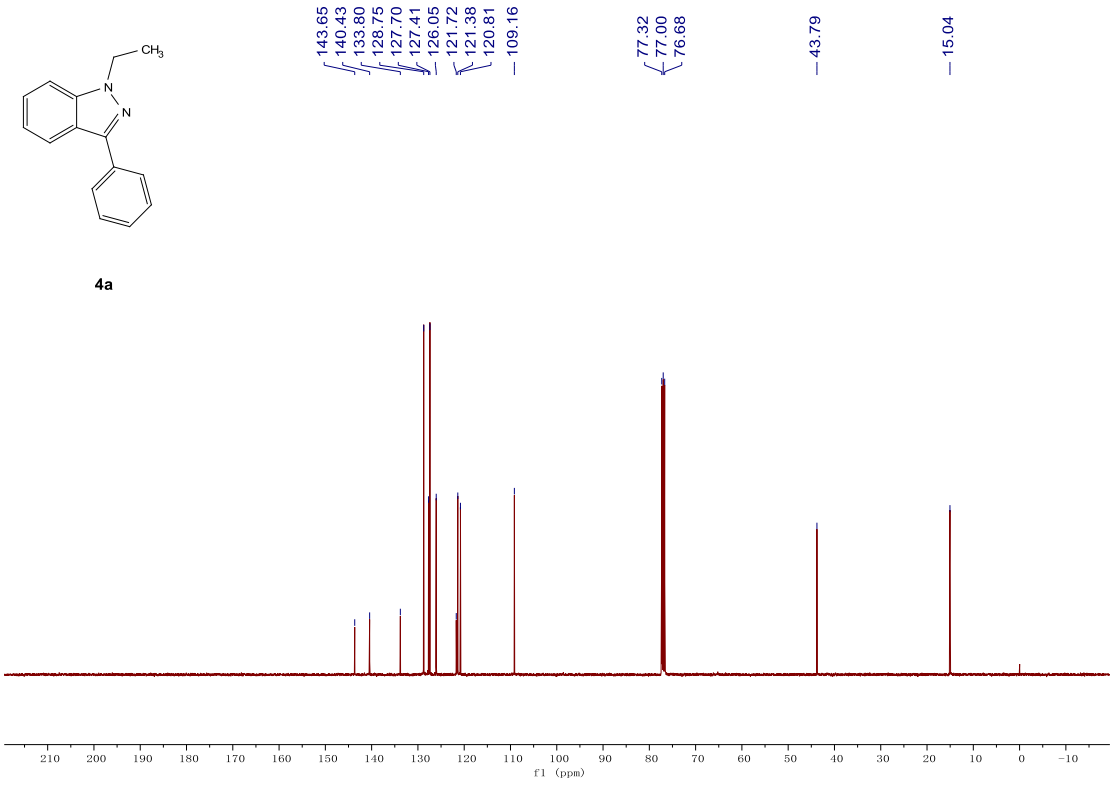
3l


141.50
138.07
136.10
128.51
127.03
125.75
124.81
121.85
121.07
120.43
110.65
40.63
40.42
40.21
40.00
39.79
39.58
39.37
35.89
CH3
N
N
S
f1 (ppm)

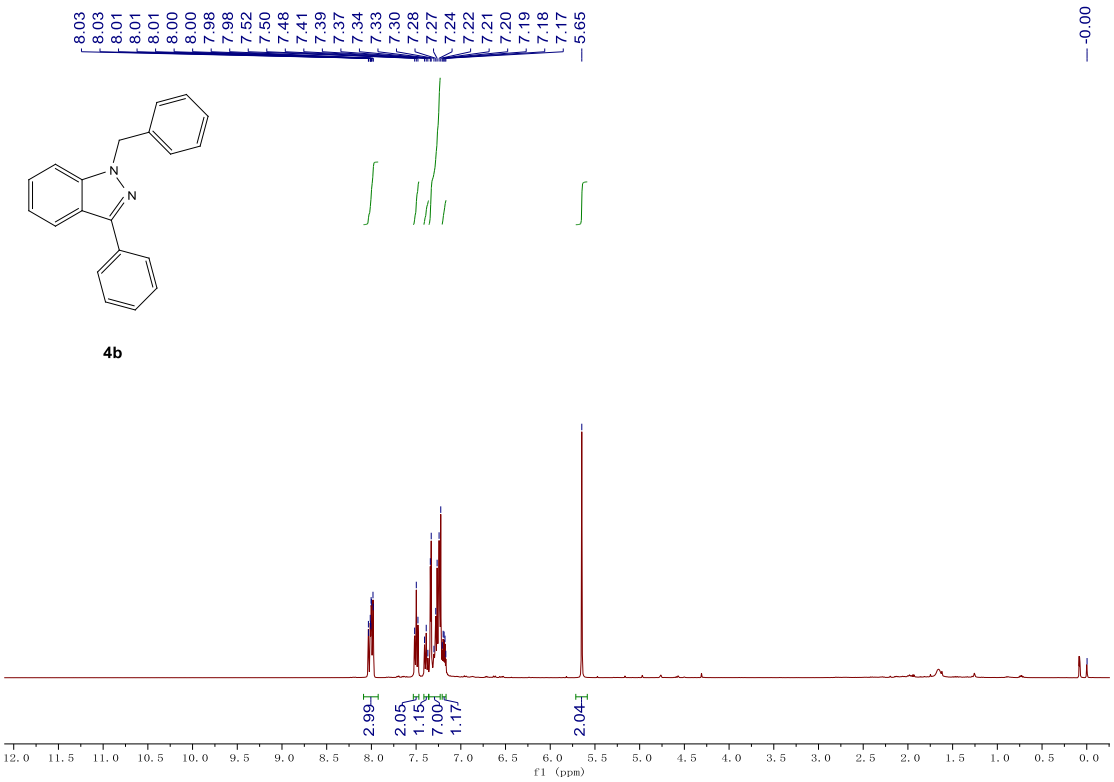
3l


8.02
8.00
7.97
7.95
7.51
7.50
7.48
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.38
7.36
7.24
7.22
7.21
7.20
7.20
7.19
7.18
7.18
4.51
4.49
4.48
4.46
1.57
1.55
1.53
0.00
CH3
N
N
1.04
2.00
2.08
3.07
1.05
2.10
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

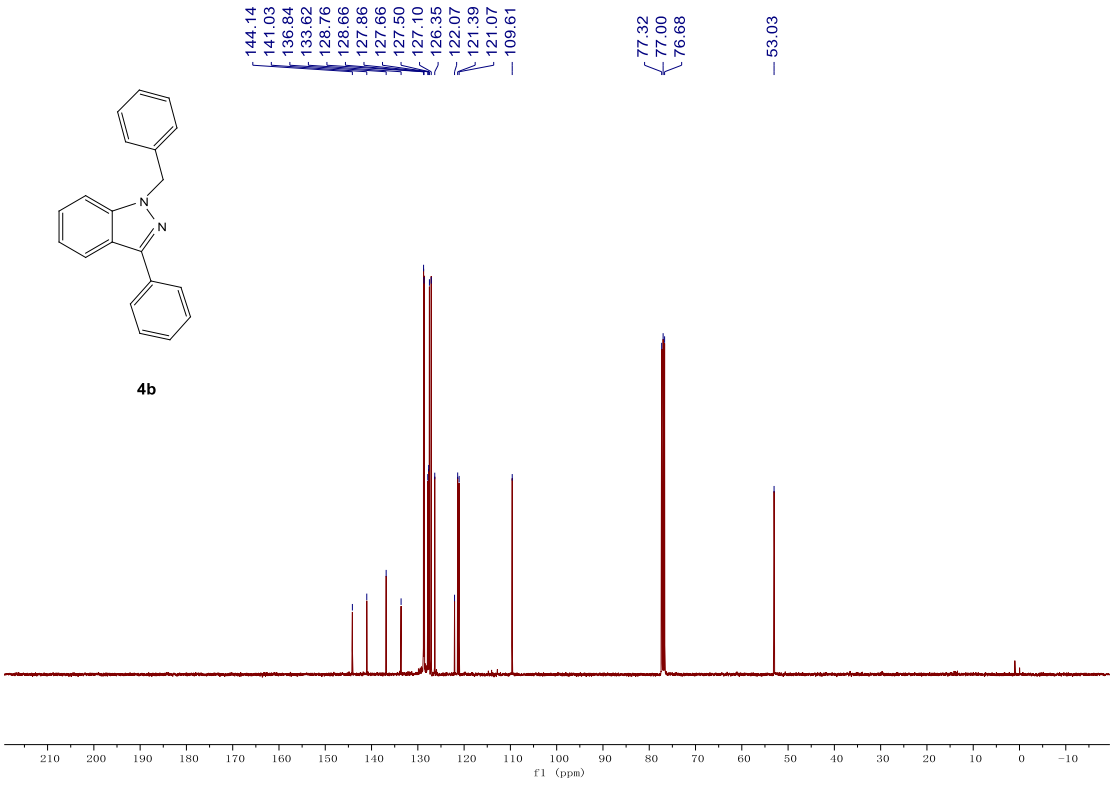
4a


143.65
140.43
133.80
128.75
127.70
127.41
126.05
121.72
121.38
120.81
109.16
77.32
77.00
76.68
43.79
15.04
CH3
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

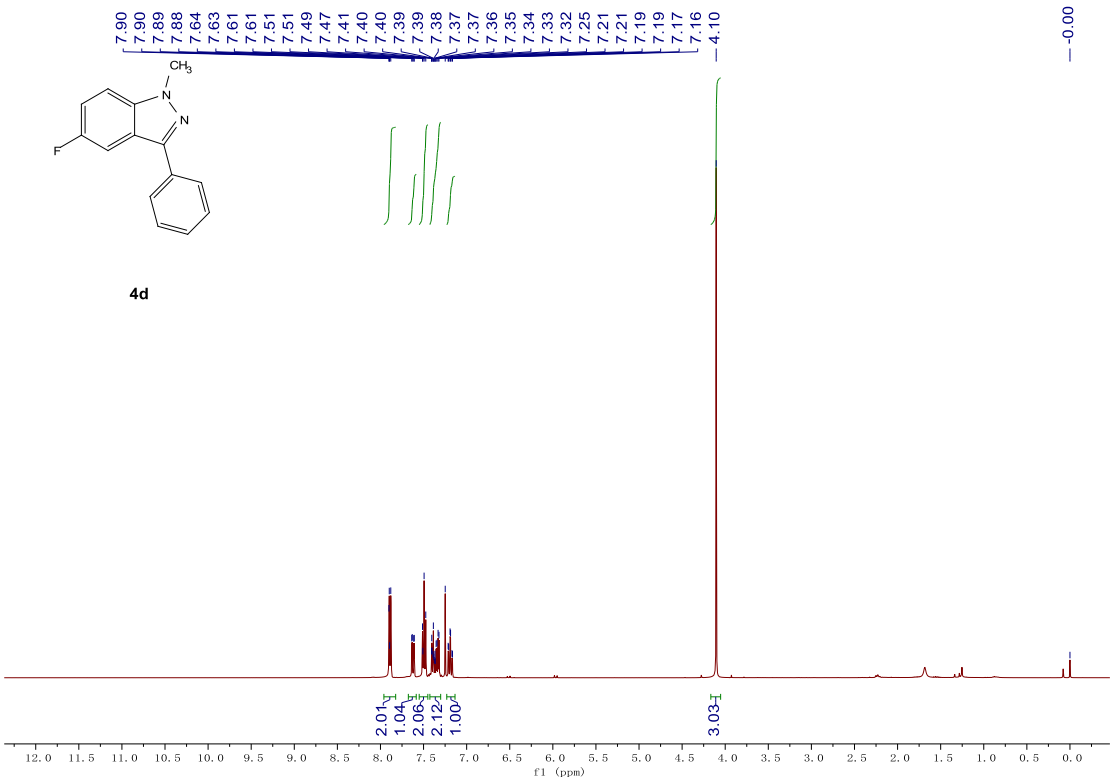
4a


8.03
8.03
8.01
8.01
8.01
8.00
8.00
7.98
7.98
7.52
7.50
7.48
7.41
7.39
7.37
7.34
7.33
7.30
7.28
7.27
7.24
7.22
7.21
7.20
7.19
7.18
7.17
5.65
0.00
2.99
2.05
1.15
7.00
1.17
2.04
f1 (ppm)

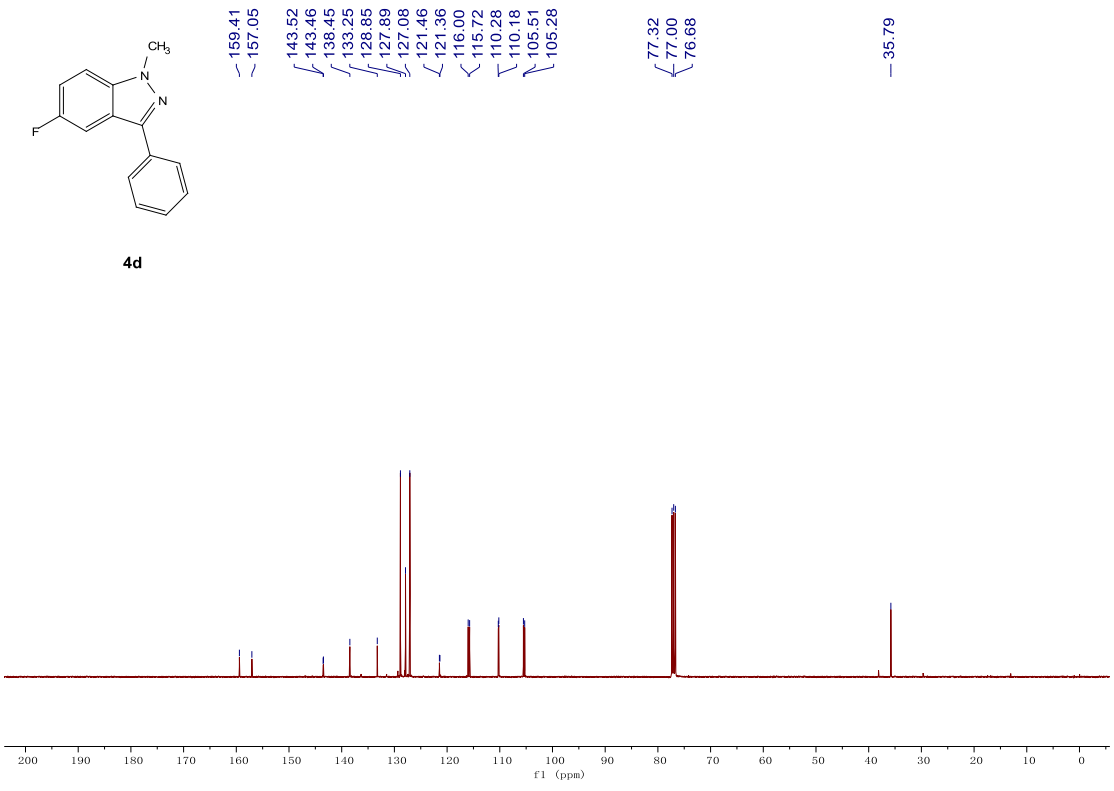
4b


144.14
141.03
136.84
133.62
128.76
128.66
127.86
127.66
127.50
127.10
126.35
122.07
121.39
121.07
109.61
77.32
77.00
76.68
53.03
f1 (ppm)

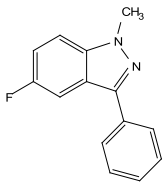
4b


7.90
7.90
7.89
7.88
7.64
7.63
7.61
7.61
7.51
7.51
7.49
7.47
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.25
7.21
7.21
7.19
7.19
7.17
7.16
4.10
-0.00
CH3
N
N
F
2.01
1.04
2.06
2.12
1.00
3.03
f1 (ppm)

4d

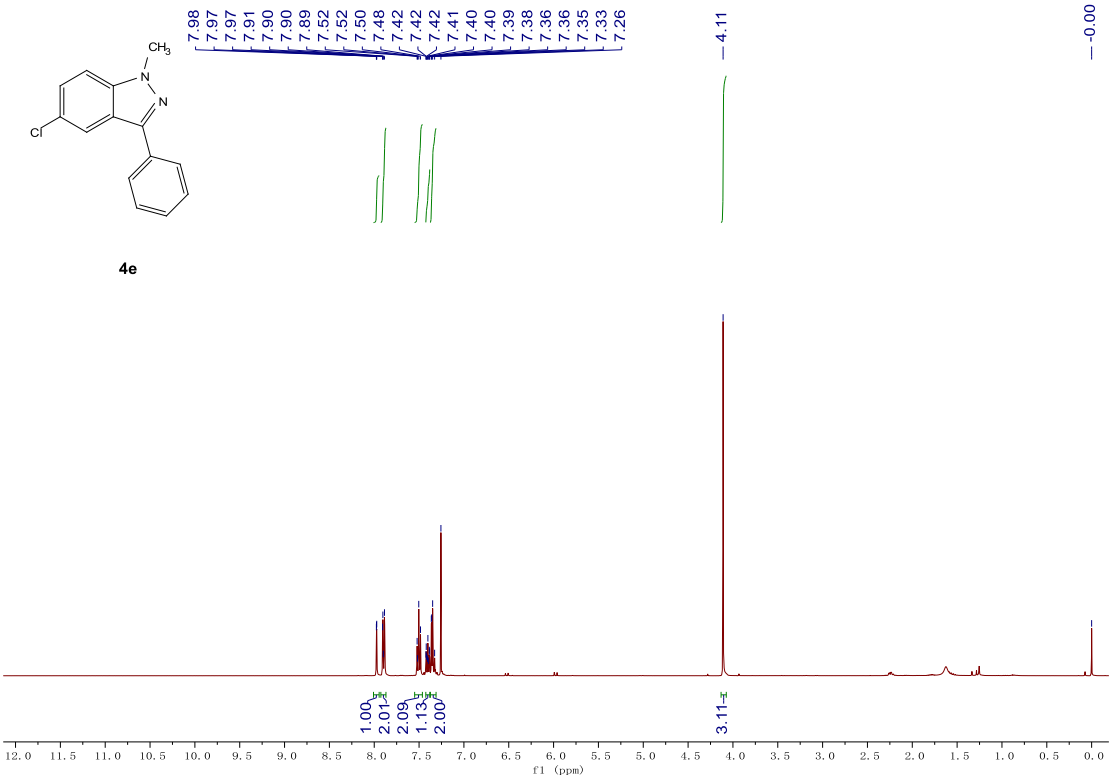

159.41
157.05
143.52
143.46
138.45
133.25
128.85
127.89
127.08
121.46
121.36
116.00
115.72
110.28
110.18
105.51
105.28
77.32
77.00
76.68
35.79
CH3
N
N
F
f1 (ppm)

4d

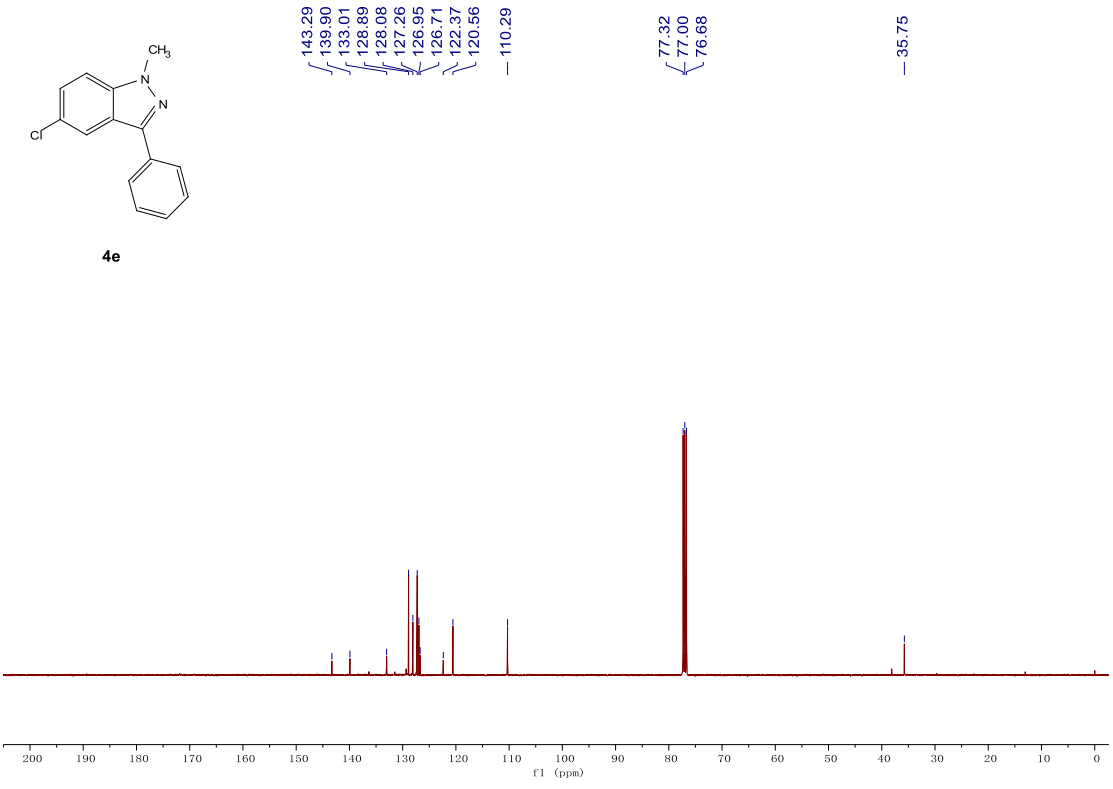

CH3
N
N
F

4d

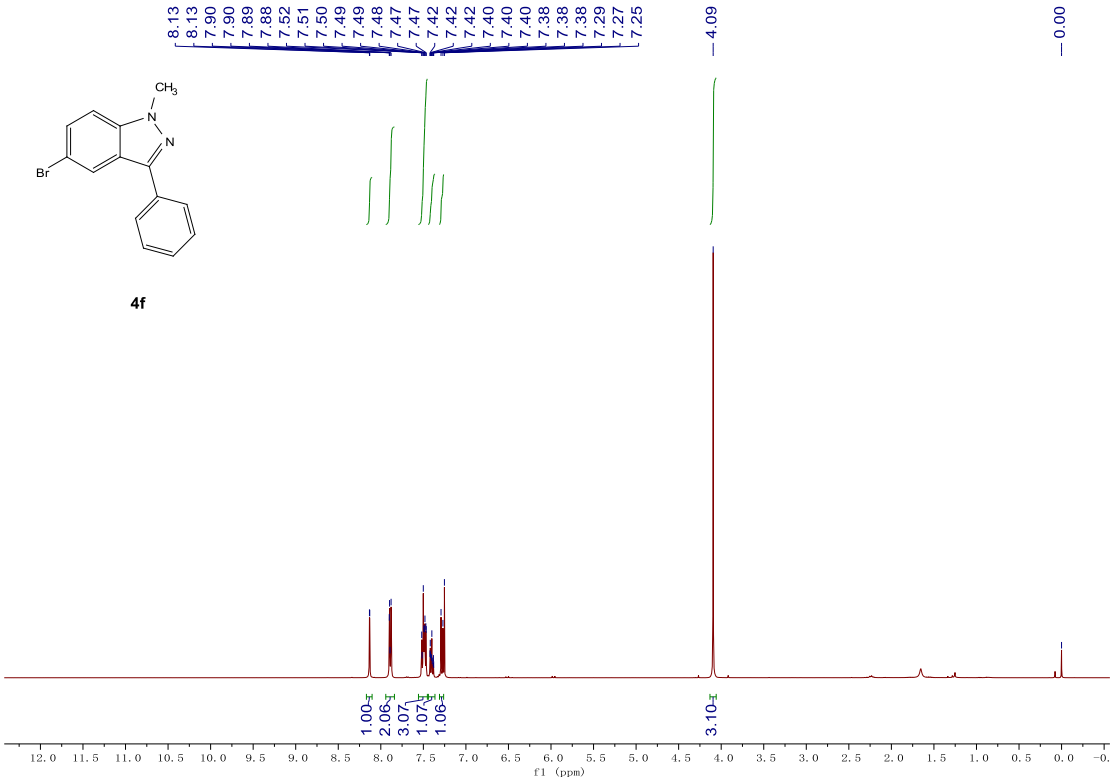
-122.93
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.98
7.97
7.97
7.91
7.90
7.90
7.89
7.52
7.52
7.50
7.48
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.36
7.36
7.35
7.33
7.26
4.11
-0.00
CH3
N
N
Cl
1.00
2.01
2.09
1.13
2.00
3.11
f1 (ppm)

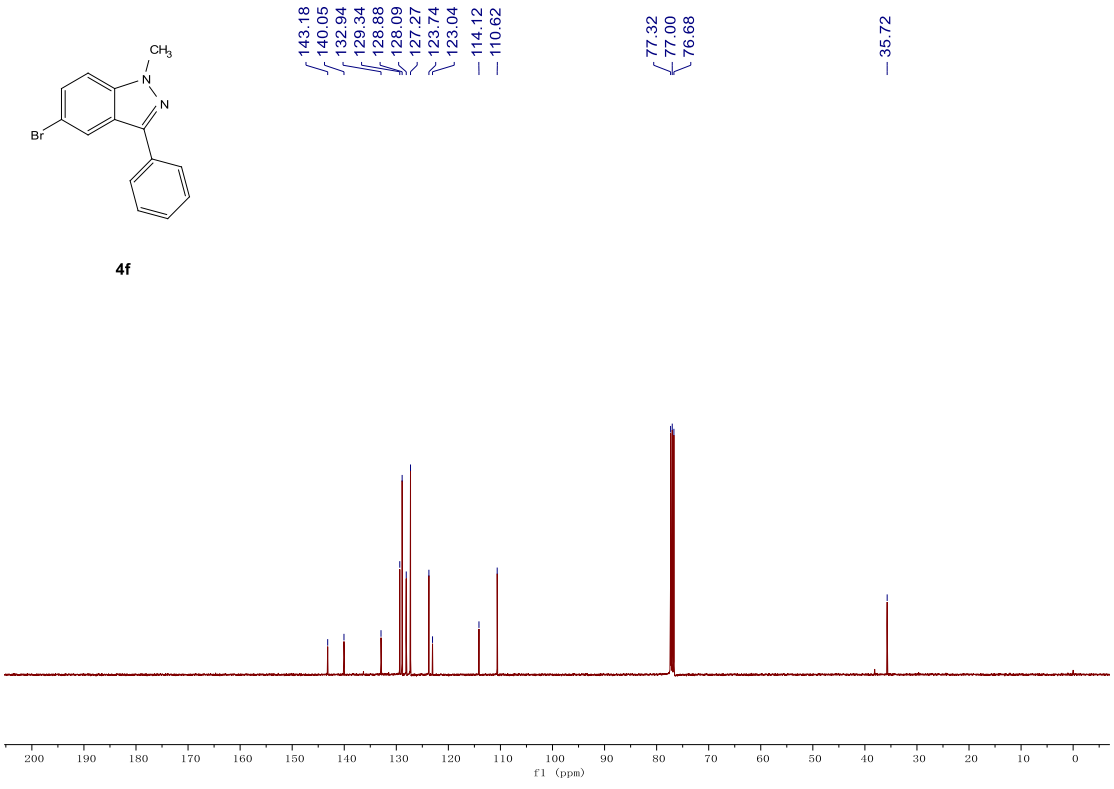
4e


143.29
139.90
133.01
128.89
128.08
127.26
126.95
126.71
122.37
120.56
110.29
77.32
77.00
76.68
35.75
CH3
N
N
Cl
f1 (ppm)

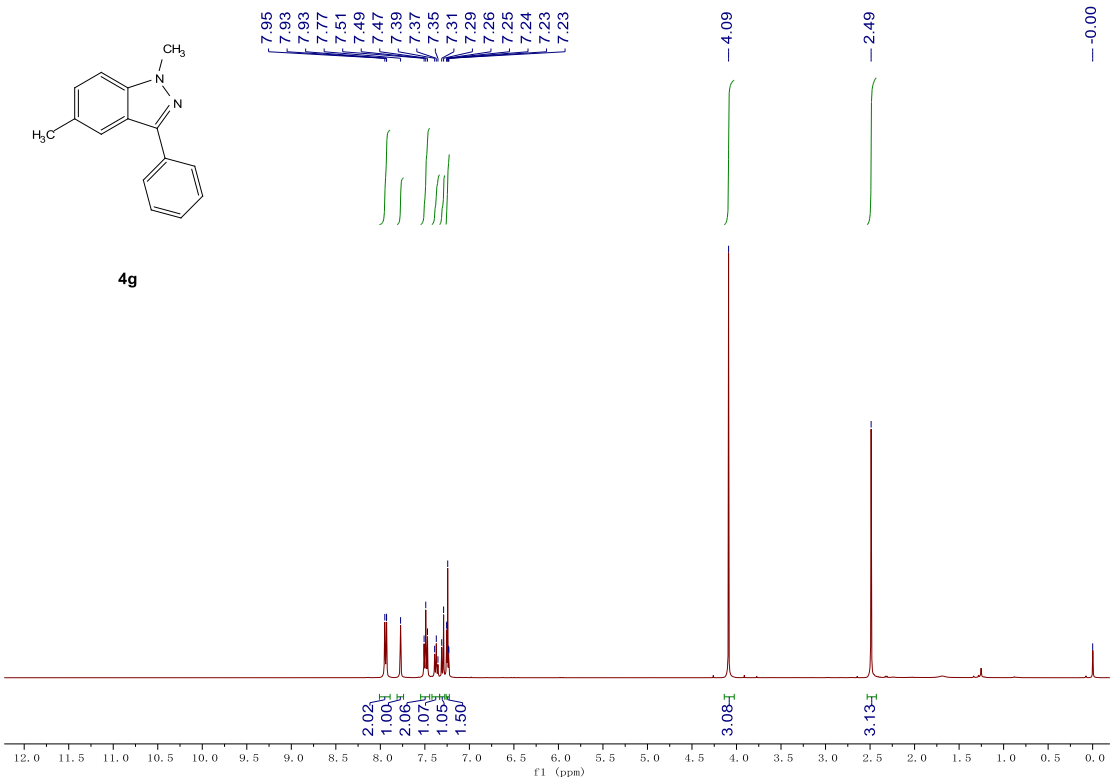
4e


8.13
8.13
7.90
7.90
7.89
7.88
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.42
7.42
7.42
7.40
7.40
7.40
7.38
7.38
7.29
7.27
7.25
4.09
0.00
CH3
N
N
Br
1.00
2.06
3.07
1.07
1.06
3.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

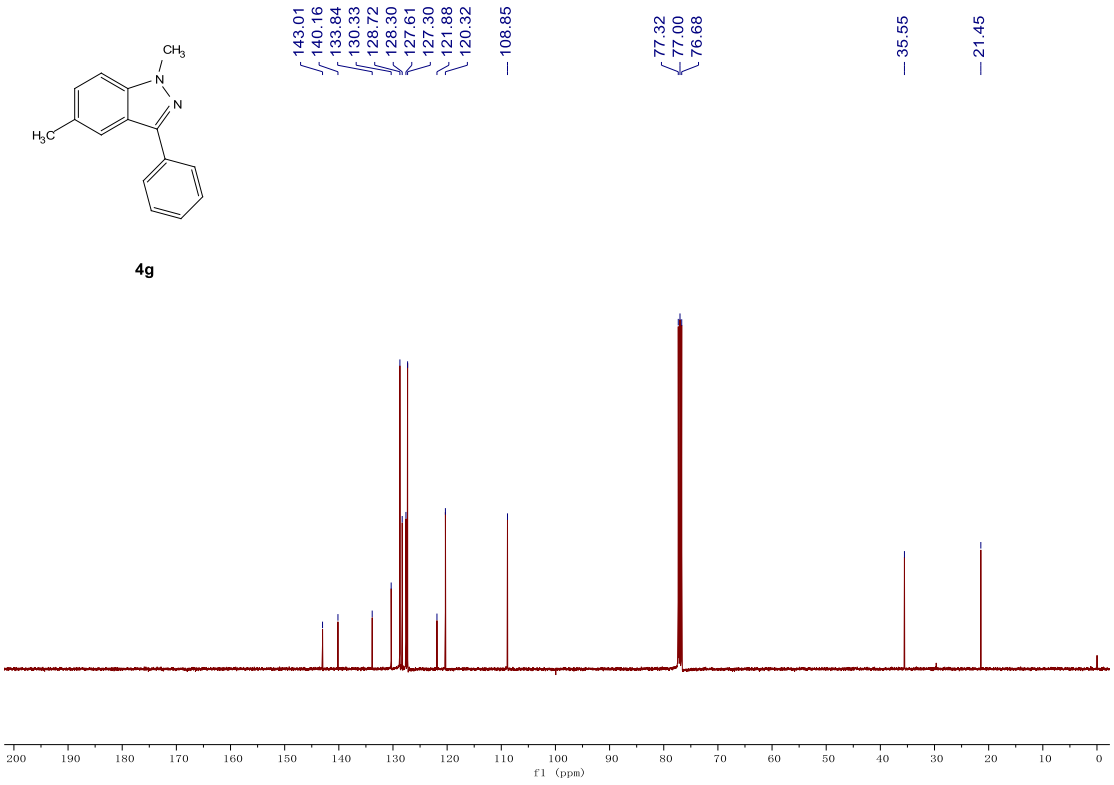
4f


143.18
140.05
132.94
129.34
128.88
128.09
127.27
123.74
123.04
114.12
110.62
77.32
77.00
76.68
35.72
CH3
N
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

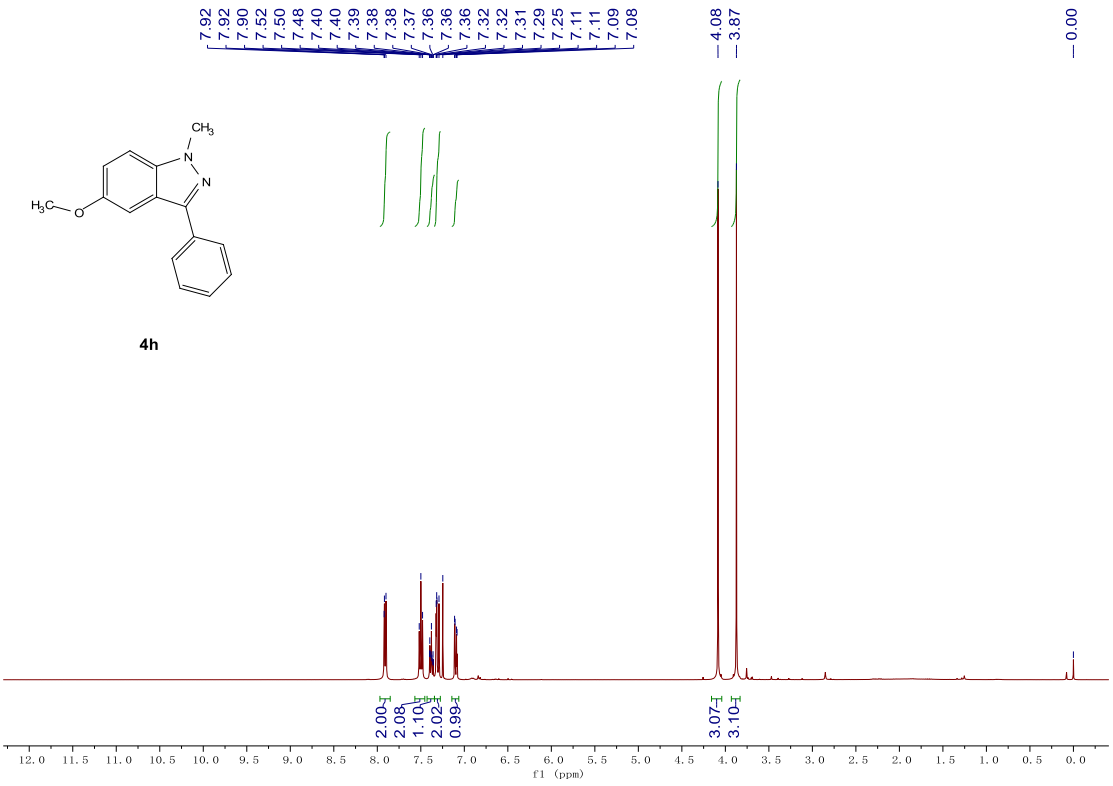
4f


7.95
7.93
7.93
7.77
7.51
7.49
7.47
7.39
7.37
7.35
7.31
7.29
7.26
7.25
7.24
7.23
7.23
4.09
2.49
-0.00
2.02
1.00
2.06
1.07
1.05
1.50
3.08
3.13
f1 (ppm)

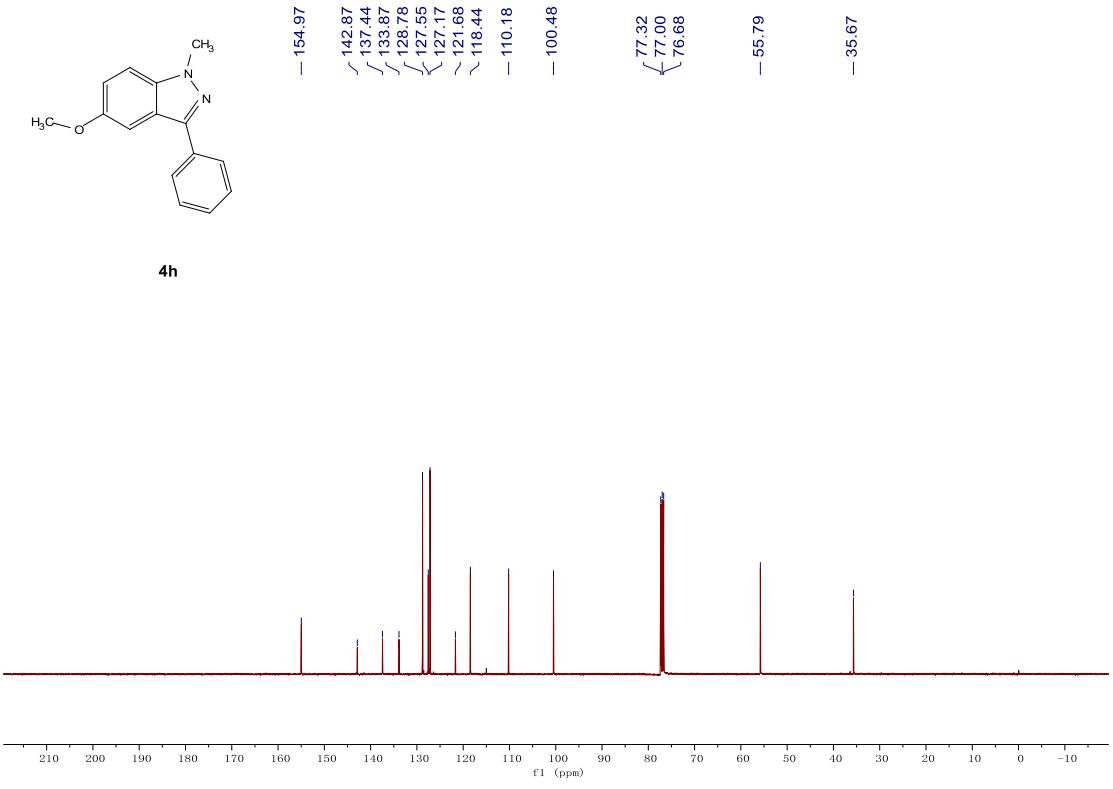
4g


143.01
140.16
133.84
130.33
128.72
128.30
127.61
127.30
121.88
120.32
108.85
77.32
77.00
76.68
35.55
21.45
f1 (ppm)

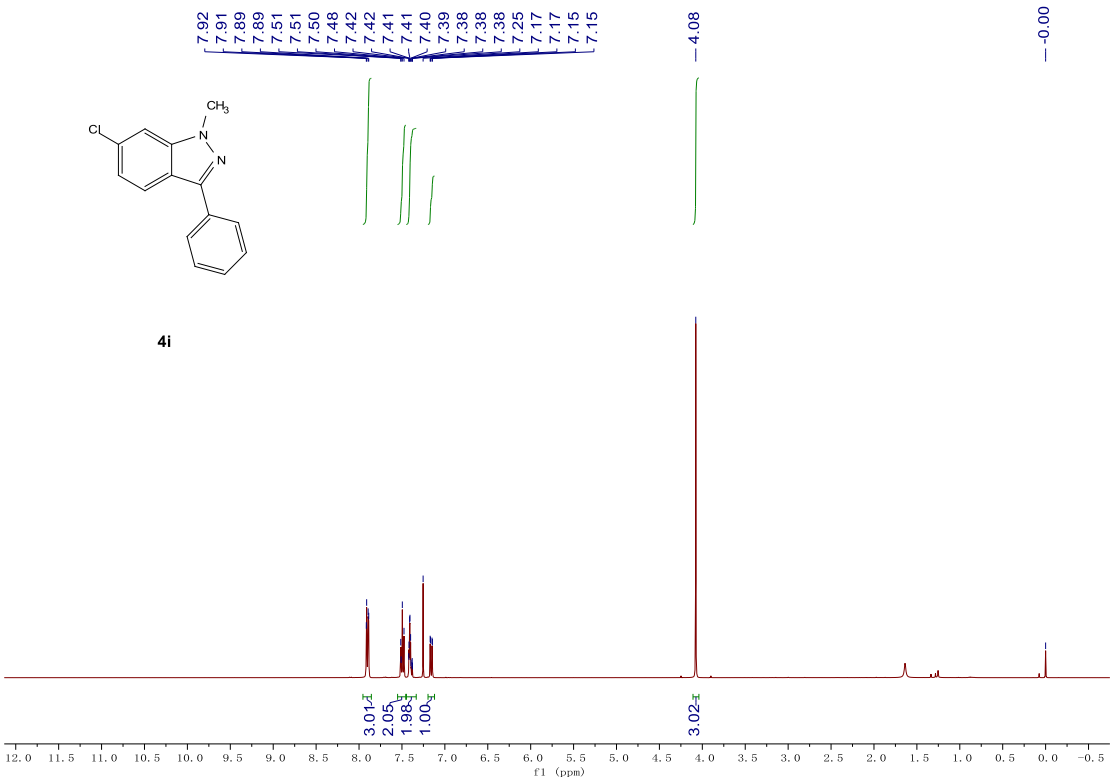
4g


7.92
7.92
7.90
7.52
7.50
7.48
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.32
7.32
7.31
7.29
7.25
7.11
7.11
7.09
7.08
4.08
3.87
0.00
2.00
2.08
1.10
2.02
0.99
3.07
3.10
f1 (ppm)

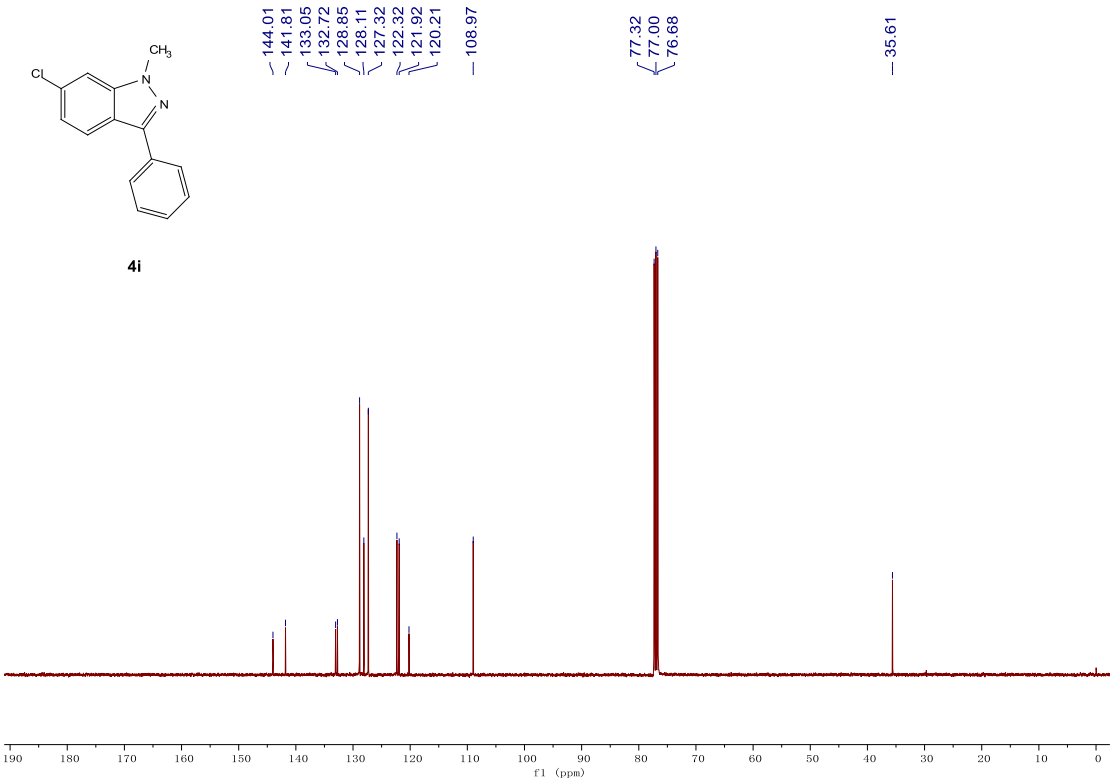
4h


154.97
142.87
137.44
133.87
128.78
127.55
127.17
121.68
118.44
110.18
100.48
77.32
77.00
76.68
55.79
35.67
f1 (ppm)

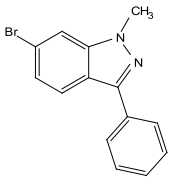
4h


7.92
7.91
7.89
7.89
7.51
7.51
7.50
7.48
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.25
7.17
7.17
7.15
7.15
4.08
-0.00
Cl
CH3
N
N
3.01
2.05
1.98
1.00
3.02
f1 (ppm)

4i

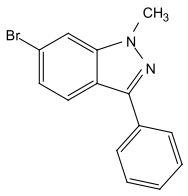

144.01
141.81
133.05
132.72
128.85
128.11
127.32
122.32
121.92
120.21
108.97
77.32
77.00
76.68
35.61
Cl
CH3
N
N
f1 (ppm)

4i


Br
CH3
N
N

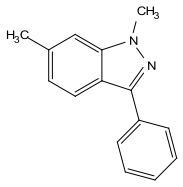
4j

7.91
7.89
7.85
7.83
7.59
7.51
7.49
7.48
7.42
7.40
7.38
7.30
7.28
7.25
4.07
0.00
1.96
0.99
0.96
2.01
1.00
1.00
3.01
f1 (ppm)


Br
CH3
N
N

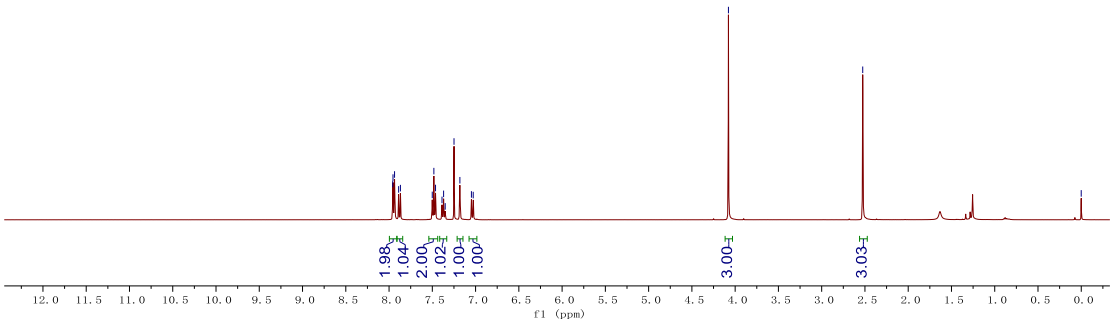
4j

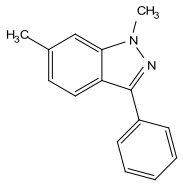
144.05
142.18
133.02
128.85
128.12
127.32
124.40
122.52
120.69
120.47
112.13
77.32
77.00
76.68
35.62
f1 (ppm)



4k

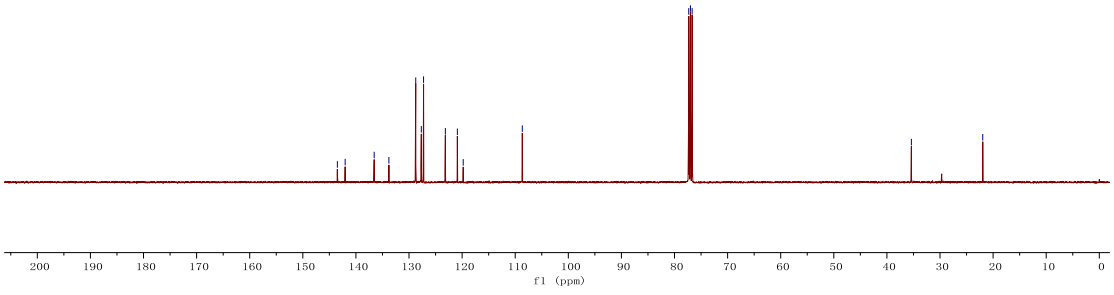
7.96
7.95
7.94
7.89
7.87
7.50
7.48
7.46
7.39
7.37
7.35
7.25
7.18
7.05
7.03
4.08
2.53
0.00

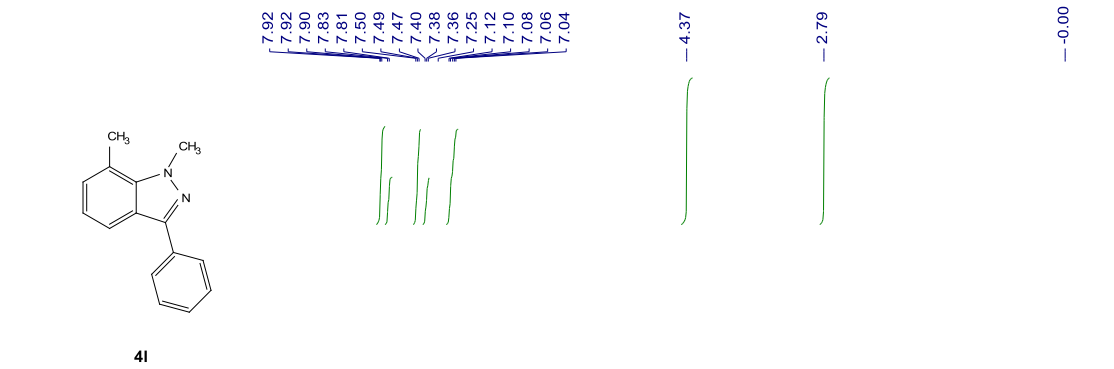

1.98
1.04
2.00
1.02
1.00
1.00
3.00
3.03
f1 (ppm)



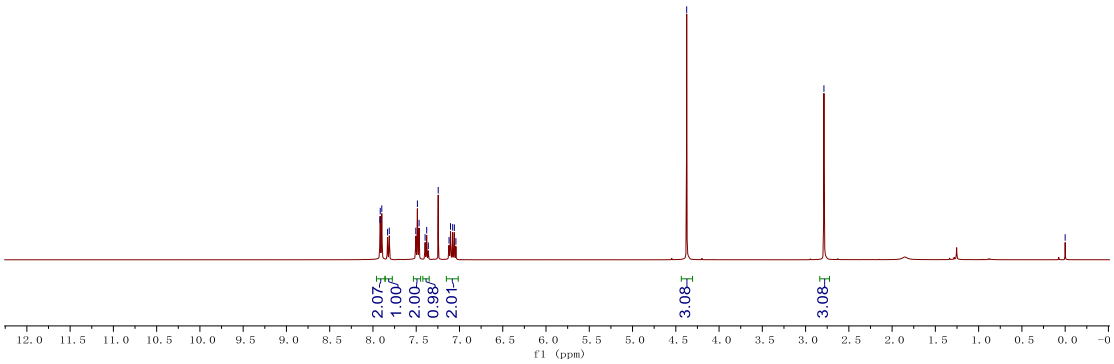
4k

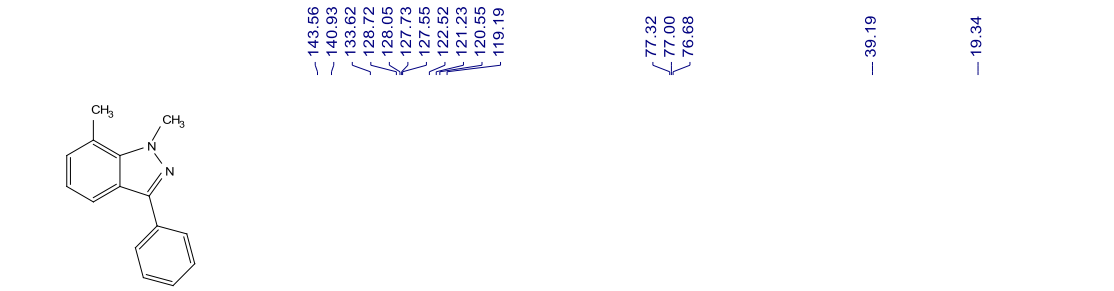

143.49
142.03
136.56
133.79
128.73
127.68
127.26
123.16
120.89
119.79
108.67
77.32
77.00
76.68
35.39
21.95


f1 (ppm)

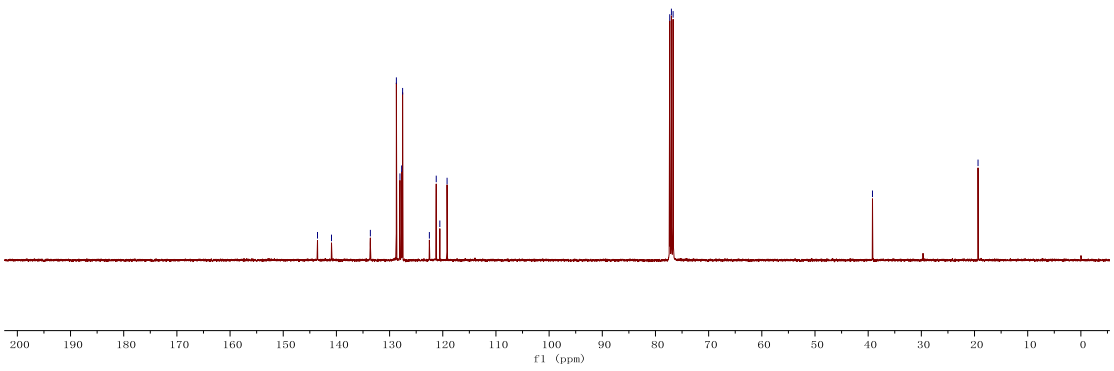

7.92
7.92
7.90
7.83
7.81
7.50
7.49
7.47
7.40
7.38
7.36
7.25
7.12
7.10
7.08
7.06
7.04
4.37
2.79
0.00
CH3
CH3
N
N

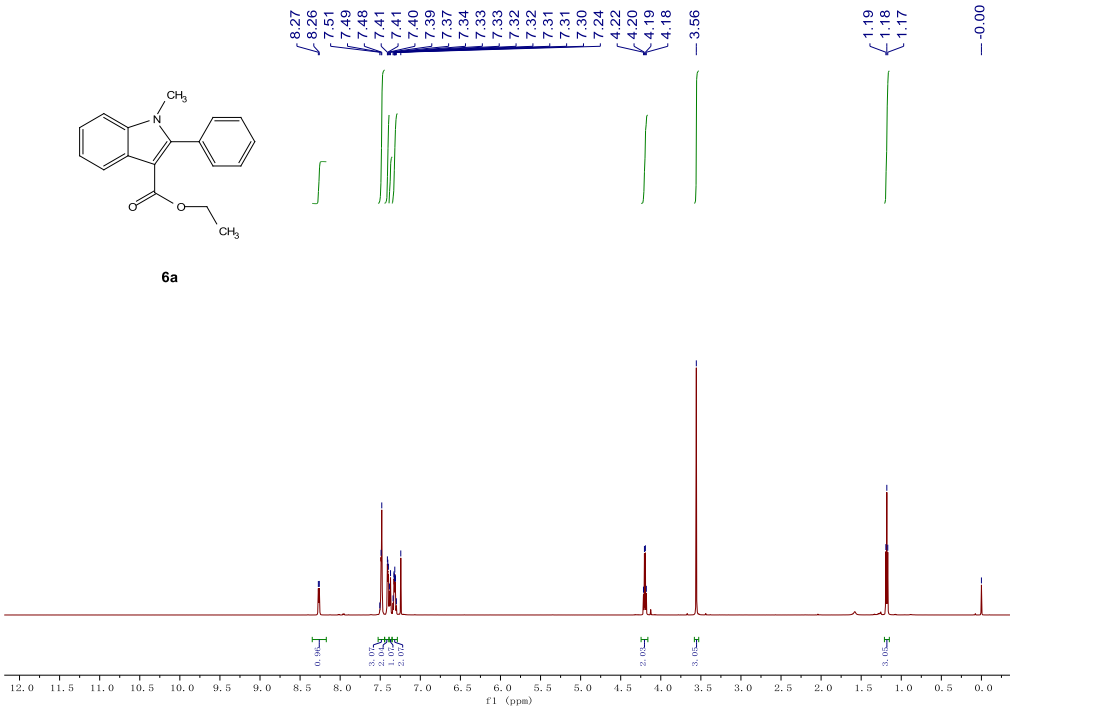
4l


2.07
1.00
2.00
0.98
2.01
3.08
3.08
f1 (ppm)

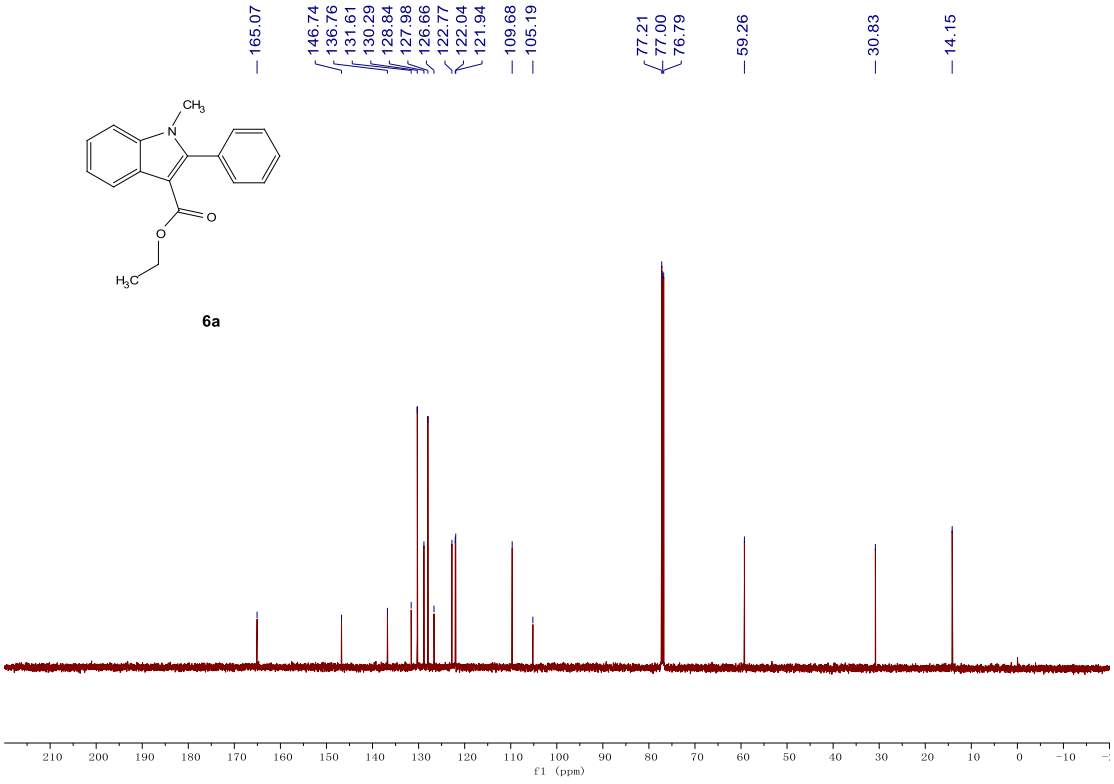

143.56
140.93
133.62
128.72
128.05
127.73
127.55
122.52
121.23
120.55
119.19
77.32
77.00
76.68
39.19
19.34
CH3
CH3
N
N

4l

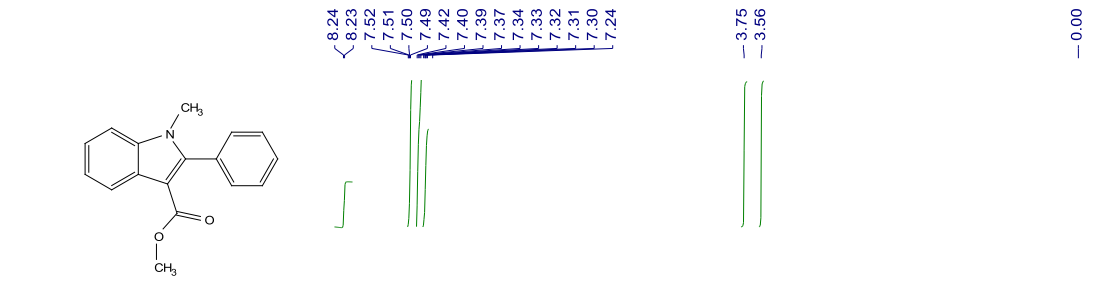

f1 (ppm)


8.27
8.26
7.51
7.49
7.48
7.41
7.41
7.40
7.39
7.37
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.24
4.22
4.20
4.19
4.18
3.56
1.19
1.18
1.17
-0.00
CH3
N
O
O
CH3
0.96
3.07
2.05
2.07
2.02
3.02
3.00
f1 (ppm)

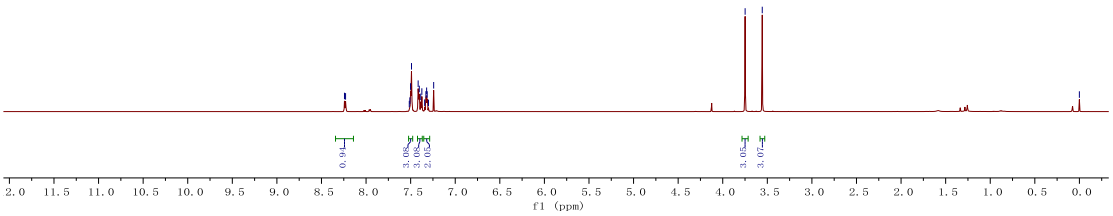
6a

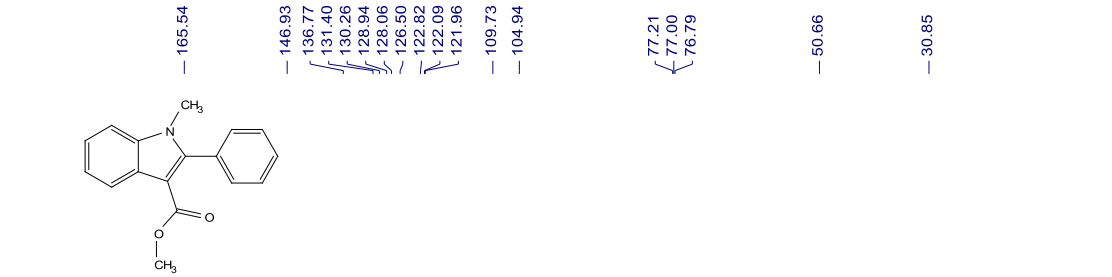

165.07
146.74
136.76
131.61
130.29
128.84
127.98
126.66
122.77
122.04
121.94
109.68
105.19
77.21
77.00
76.79
59.26
30.83
14.15
CH3
N
O
O
H3C
f1 (ppm)

6a

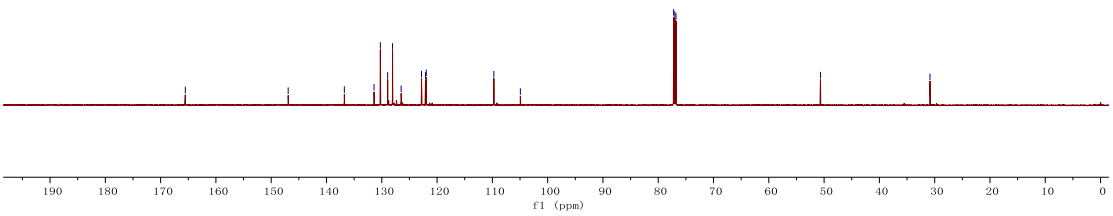

8.24
8.23
7.52
7.51
7.50
7.49
7.42
7.40
7.39
7.37
7.34
7.33
7.32
7.31
7.30
7.24
3.75
3.56
0.00
CH3
N
O
O
CH3

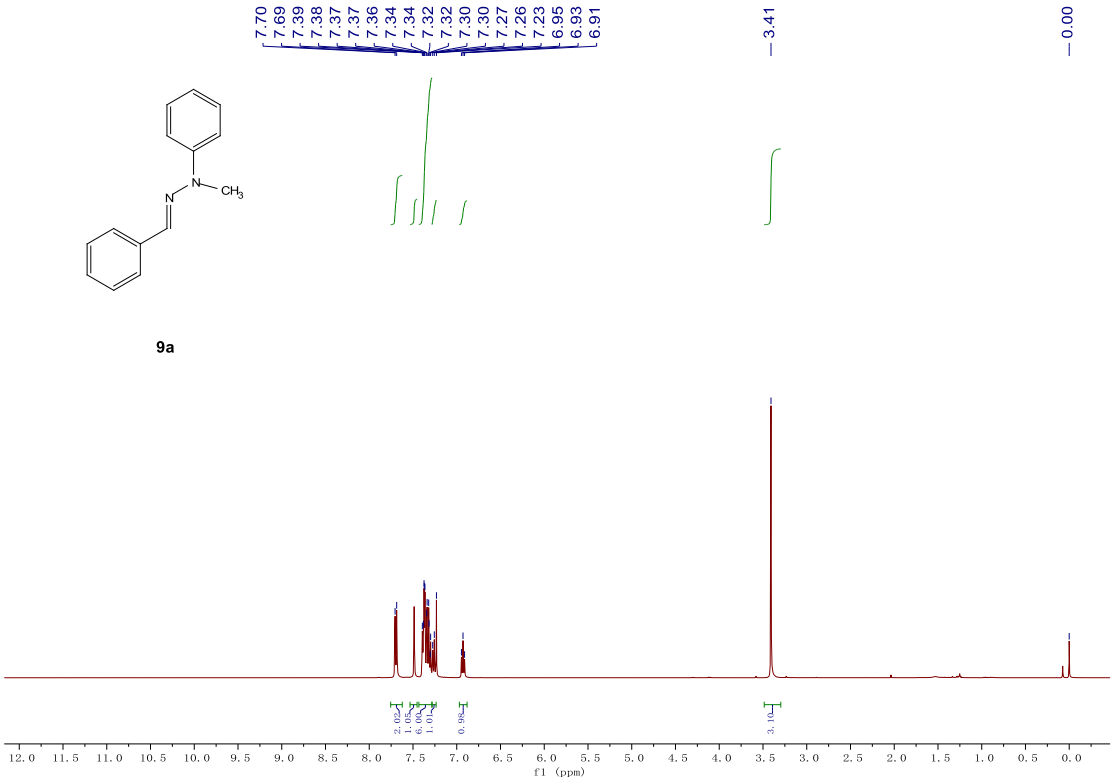
8a


0.94
3.08
3.08
2.02
3.05
3.07
f1 (ppm)

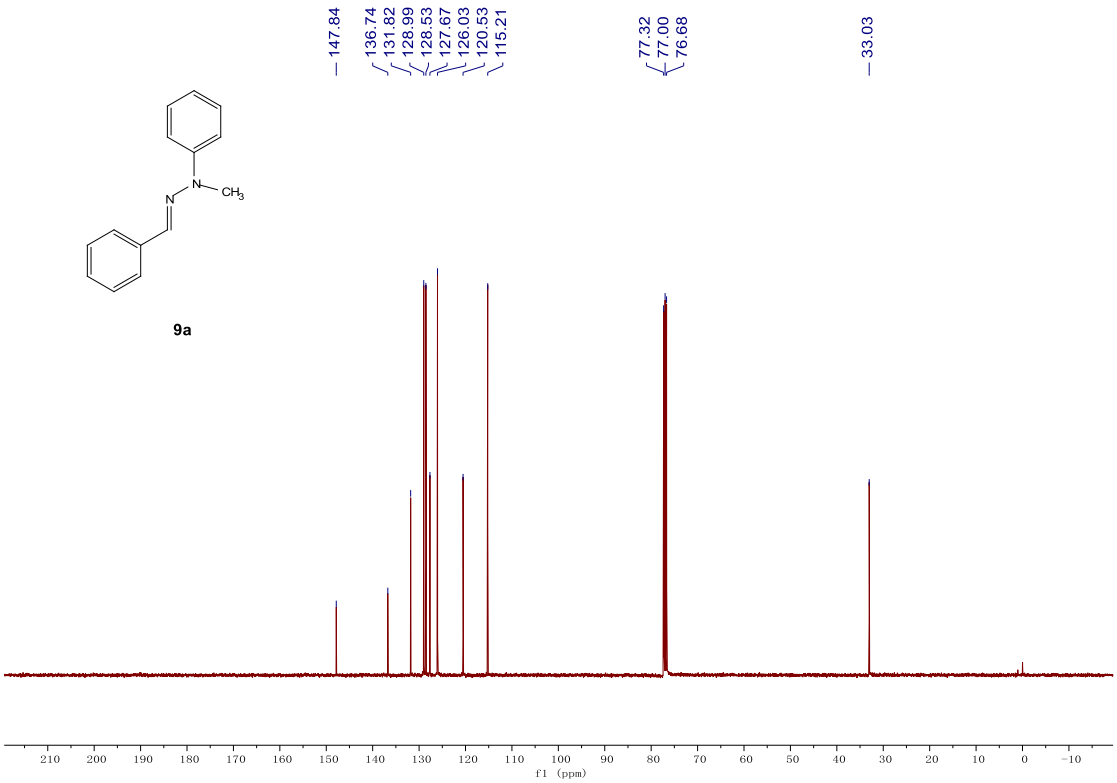

165.54
146.93
136.77
131.40
130.26
128.94
128.06
126.50
122.82
122.09
121.96
109.73
104.94
77.21
77.00
76.79
50.66
30.85
CH3
N
O
O
CH3

8a


f1 (ppm)


7.70
7.69
7.39
7.38
7.37
7.37
7.36
7.34
7.34
7.32
7.32
7.30
7.30
7.27
7.26
7.23
6.95
6.93
6.91
3.41
0.00
N
N
CH3
2.02
1.85
6.00
1.01
0.98
3.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9a


147.84
136.74
131.82
128.99
128.53
127.67
126.03
120.53
115.21
77.32
77.00
76.68
33.03
N
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

9a