Catalyst-Controlled 5-*exo* and 6-*endo* Cyclization: Regiodivergent Access to Indolinones and Dihydroquinolinones

Xianzhou Zheng[a], Youzhi Xu[b], Genping Huang[b]*, and Weiming Yuan[a]*

[a] Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Bioinorganic Chemistry and Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), 1037 Luoyu Road, Wuhan 430074, P. R. China.

[b] Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, P. R. China.

Email: gphuang@tju.edu.cn; yuanwm@hust.edu.cn

Electronic Supplementary Information

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1 General Information

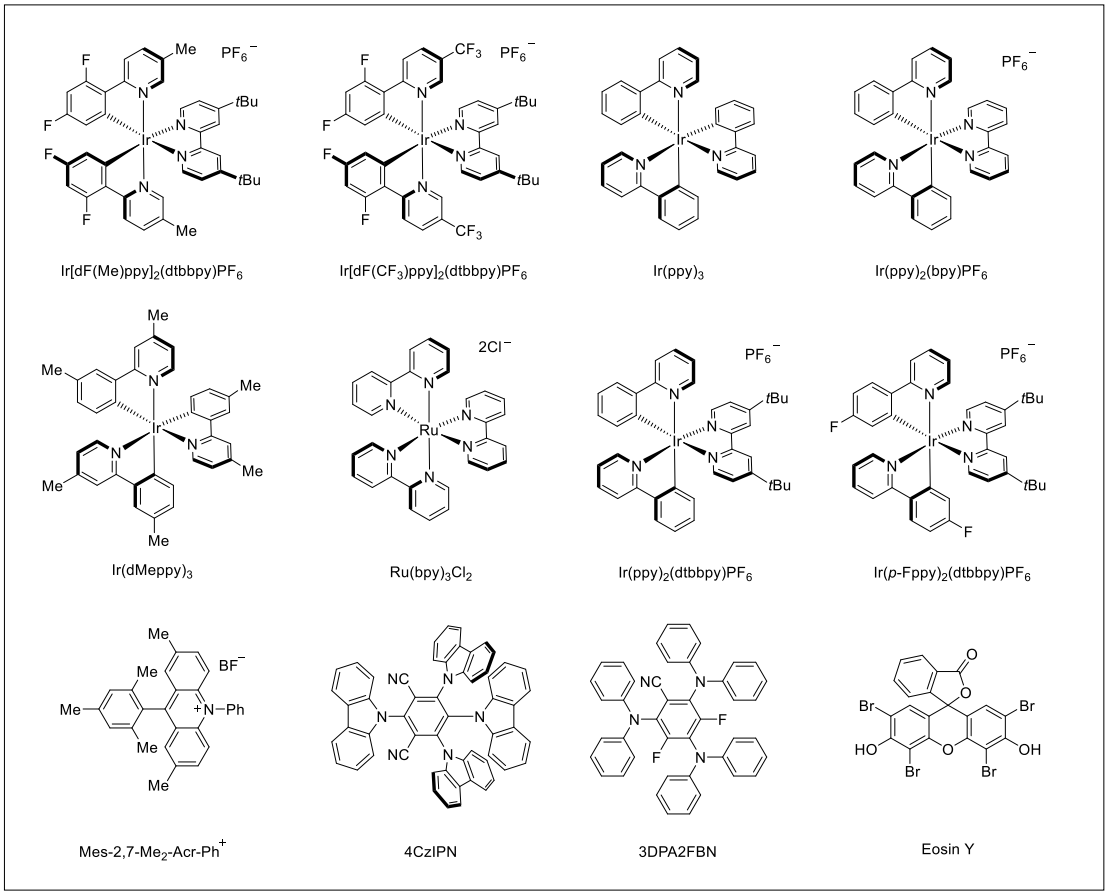
Reactions were performed in flame-dried glassware or conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. All the materials were purchased from Bidepharm, Energy Chemical, Adamas-beta® *etc*. and used as received unless otherwise noted; Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gels using the indicated solvents. The High Resolution MS analyses were performed on BRUKER FT-ICR-MS SolariX 7T with ESI mode. The IR analyses were performed on BRUKER Vertex 80/80v instrument. GC analyses were performed on SHIMADZU GC 2010pro instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a *Bruker* AV600 and *Bruker* AV400 instrument, respectively. Chemical shifts were reported in parts per million (ppm) and the residual solvent signals were used as references for ^{1}H (TMS: δ_H = 0.00 ppm) and ^{13}C NMR spectra ($CDCl_3$: δ_C = 77.16 ppm, middle line). Tridecane was used as an internal standard to calculate GC yields. Data were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration.

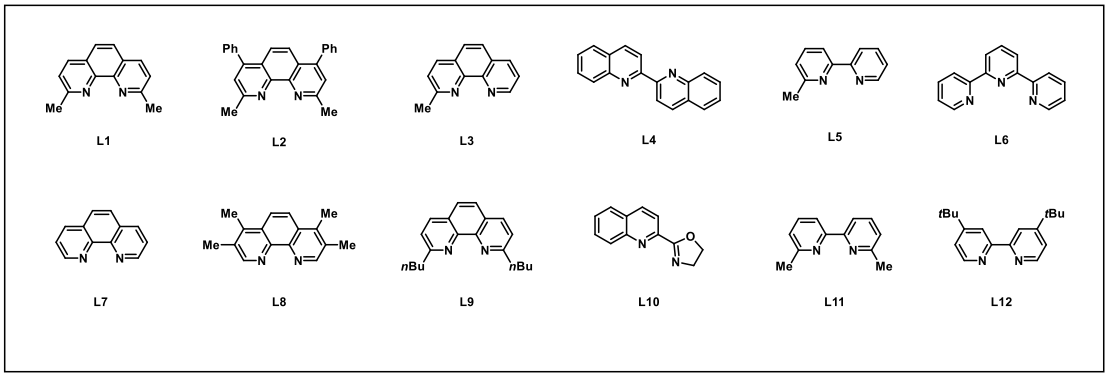
The photoreactor is homemade and each vial was illuminated by one lamp bead (parameters: 1.5 W blue LED, λ_{max} = 455 nm, Cree xpe2 royal blue). Unless otherwise photoredox reactions were set-up in 10 mL vial and stirred (1000 rpm) at a distance of 1.5 cm from the irradiating plate. In addition, fan (rear part) was used to maintain a temperature of 25−30 °C.

Figure S1. General set-up for photoredox reactions

2. Catalysts and Starting Materials

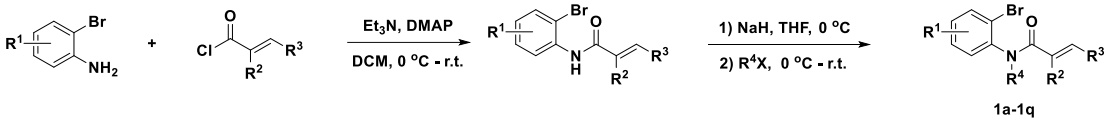
The photocatalysts and ligands used in this study are commercially available.



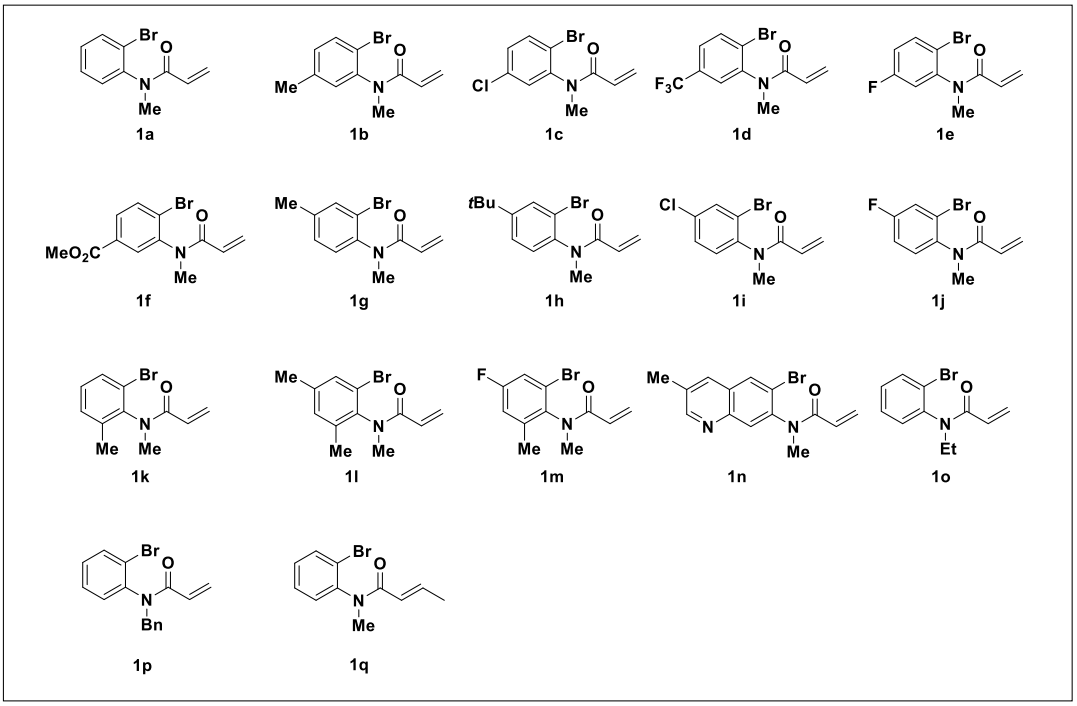


General procedure A for substituted 2-bromophenyl acrylamides synthesis

The following 2-bromophenyl acrylamides **1a-1q** were prepared according to literature procedures and data are consistent with literatures[1-4].



1a-1q



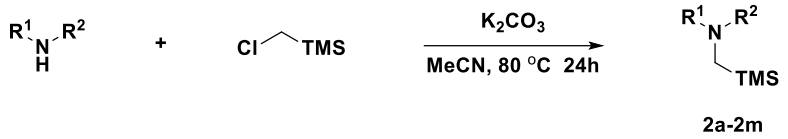
To a mixture of 2-bromoaniline (5.0 mmol, 1.0 equiv.), 4-dimethylaminopyridine（DMAP）(30.5 mg, 0.25 mmol, 5 mol%), and Et_3N (2.1 mL, 15.0 mmol, 3.0 equiv.) in DCM (20 mL) was added acryloyl chloride (6.0 mmol, 1.2 equiv.) at 0 °C dropwise. After stirring at 0 °C for 30 min then at room temperature overnight, the mixture was quenched with saturated $NaHCO_3$. The resulting mixture was then extracted with DCM, washed with brine three times, and dried over anhydrous Na_2SO_4 successively. After filtration and concentration, the crude amide was purified by flash column chromatography (FCC) on silica gel (eluent: petroleum ester (PE): ethyl acetate (EA) = 100:1 – 50: 1).

NaH (80 mg, 60% in mineral oil, 2.0 mmol, 2.0 equiv.) was added to a solution of the above purified amide (1.0 mmol, 1.0 equiv.) in THF (8.0 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, the alkyl halide R^4X (2.5 mmol, 2.5 equiv.) was added slowly, and the reaction mixture was stirred at room temperature for another 2 h. The reaction was quenched with water cautiously and the resulting mixture was extracted with EA three times. The combined organic

phase was washed with brine, dried over anhydrous Na_2SO_4, followed by filtration and concentration of organic phase. The residue was refined by flash column chromatography on silica gel with eluent (PE: EA = 30: 1: 10: 1) to afford the corresponding products **1a**-**1q**. For the synthesis of **1a**-**1n**, and **1q** the alkyl halide R^4X was MeI; For the synthesis of **1o** and **1p**, the alkyl halides R^4X were EtI and benzyl bromide respectively.

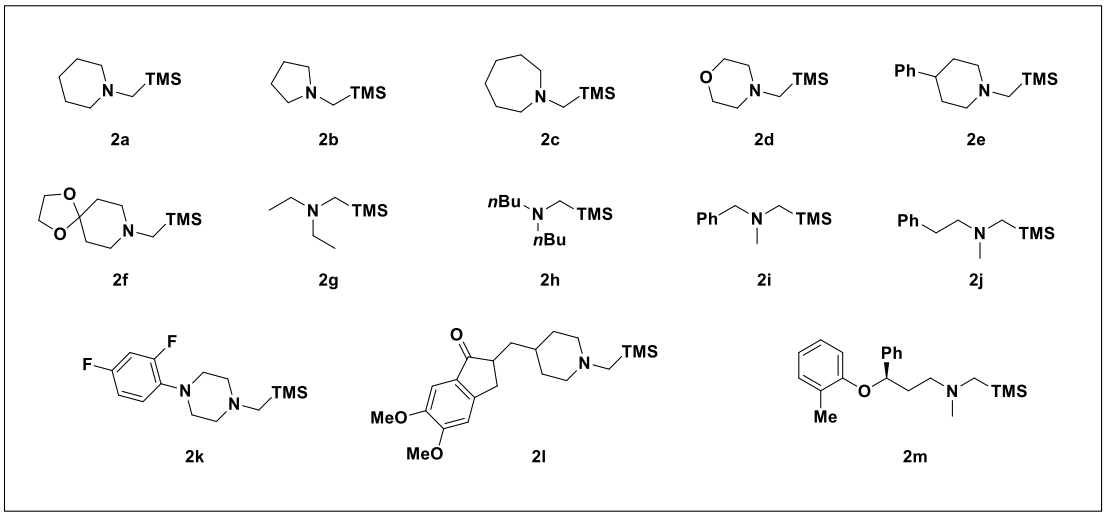
General Procedure B for the Synthesis of *α*-Silyl Amines

The following *α*-silyl amines **2a**-**2m** were prepared according to literature procedures, data are consistent with literature[S5-S9].



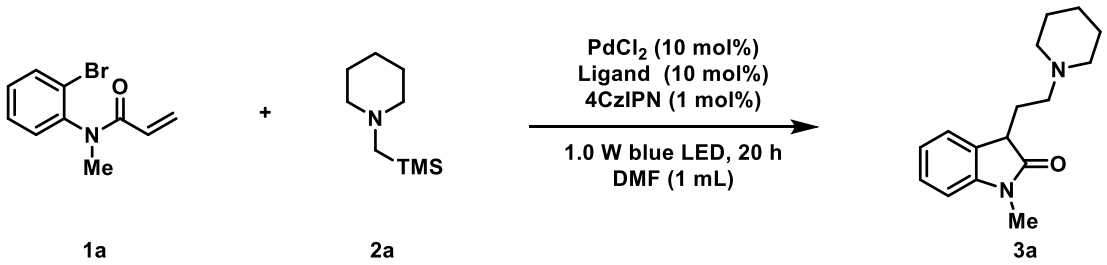
2a-2m

To an oven-dried 50 mL flask were added MeCN, chloromethyltrimethylsilane (1.67 mL, 12 mmol, 1.2 equiv.), the respective amine or amine hydrochloride (10 mmol, 1.0 equiv.) and K_2CO_3 (2.76 g, 20 mmol, 2.0 equiv.). The reaction mixture was reflux at 80 °C for 24 h. The mixture was cooled to room temperature and filtered, washed with EA three times, the combined organic layer was dried over anhydrous Na_2SO_4, filtrated and evaporated to remove the solvent. The crude residue was then purified by distillation or FCC to obtain the pure title compounds.



3. Optimization of the Reaction Conditions

Table S1. Screening of the ligands for 3a.

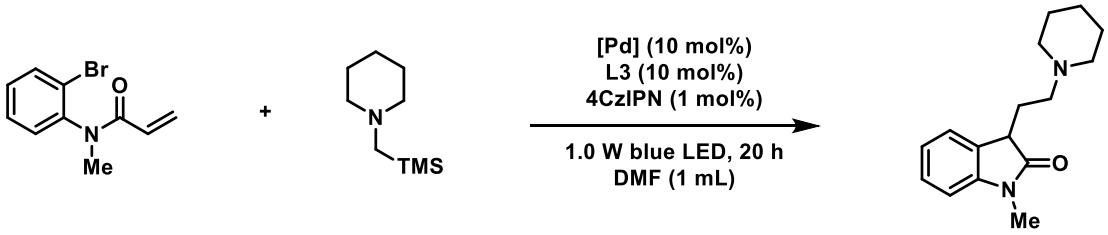


1a 2a 3a

entry[a]	Ligand	yield (%)[b]
1	L1	9
2	L2	8
3	L3	18
4	L4	16
5	L5	-
6	L6	-
7	L10	4
8	L12	3

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $PdCl_2$ (10 mol%), Ligand (10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S2. Screening of the Pd sources for 3a.

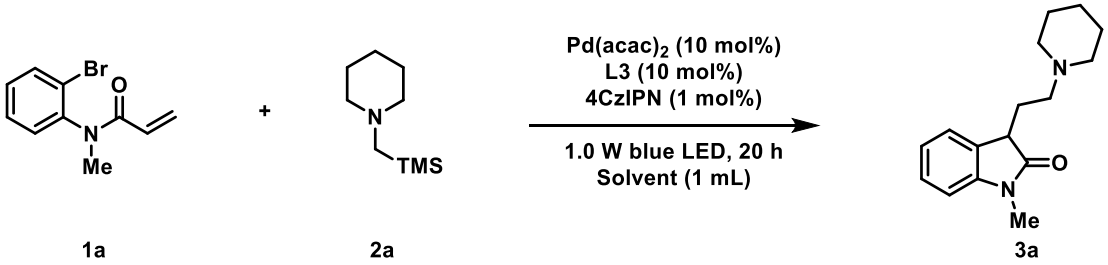


1a 2a 3a

entry[a]	[Pd]	yield (%)[b]
1	$PdCl_2$	18
2	$Pd(PPh_3)_2Cl_2$	18
3	$Pd(OAc)_2$	23
4	$Pd(acac)_2$	36
5	$Pd(PPh_3)_4$	-
6	$Pd_2(dba)_3$	7

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Pd source (10 mol%), **L3** (10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S3. Screening of the solvents for 3a.

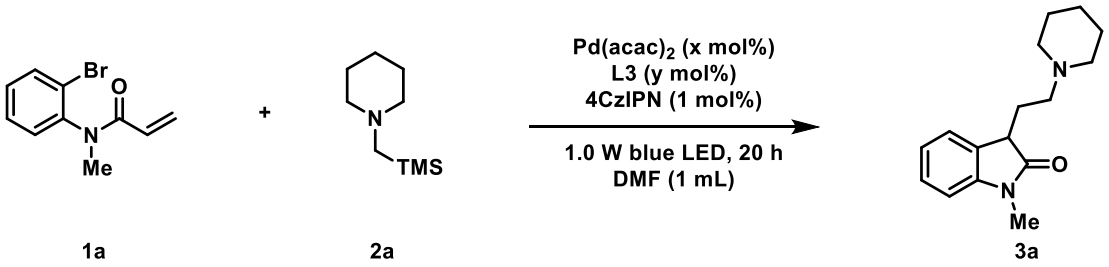


1a 2a 3a

entry[a]	solvent	yield (%)[b]
1	DMF	36
2	DMAc	36
3	NMP	32
4	DMSO	23
5	CH_3CN	30
6	THF	34
7	EA	34
8	DCE	34
9	Toluene	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(acac)_2$ (10 mol%), **L3** (10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S4. Screening of the ratio of metal to ligand for 3a.

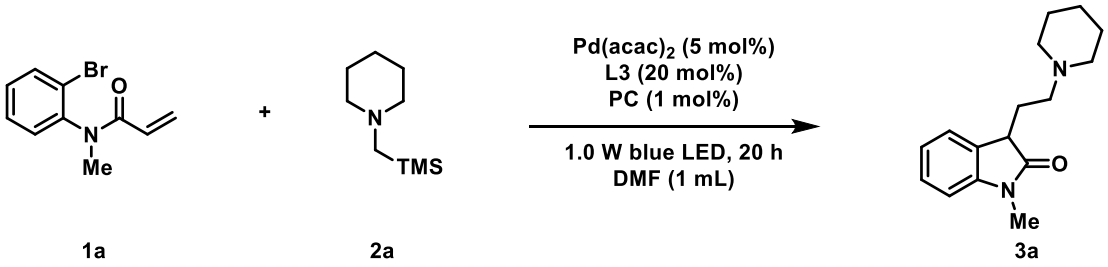


1a 2a 3a

entry[a]	x	y	x: y	yield (%)[b]
1	2.5	5	1: 2	trace
2	2.5	10	1: 4	34
3	5	5	1: 1	29
4	5	10	1：2	35
5	5	15	1: 3	38
6	5	20	1: 4	44
7	10	10	1: 1	36
8	10	20	1: 2	39

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(acac)_2$ (x mol%), **L3** (y mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S5. Screening of the photocatalysts for 3a.

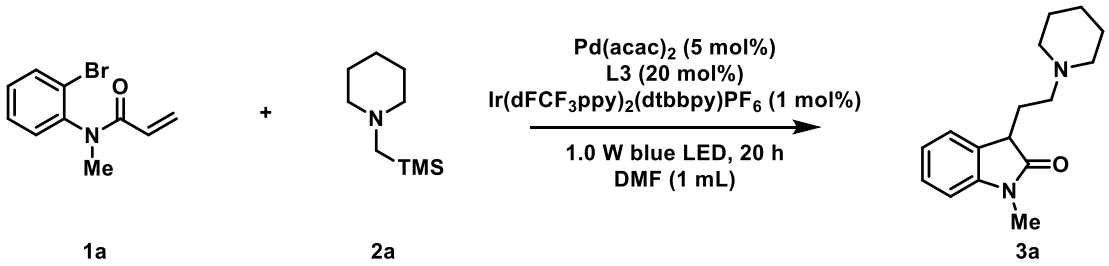


1a 2a 3a

entry[a]	PC	yield (%)[b]
1	4CzIPN	44
2	3DPA2FBN	trace
3	[Mes-Acr]ClO_4	-
4	Eosin Y	trace
5	Ir(ppy)$_3$	9
6	Ir(ppy)$_2$(bpy)PF_6	25
7	Ir(p-Fppy)$_2$(dtbbpy)PF_6	14
8	Ir(ppy)$_2$(dtbbpy)PF_6	33
9	Ir(dFppy)$_2$(dbtbpy)PF_6	42
10	Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF_6	51
11	Ru(bpy)$_3$Cl$_2$	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Pd(acac)$_2$ (5 mol%), **L3** (20 mol%), PC (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S6. Screening of the molecular ratio of 1a to 2a.

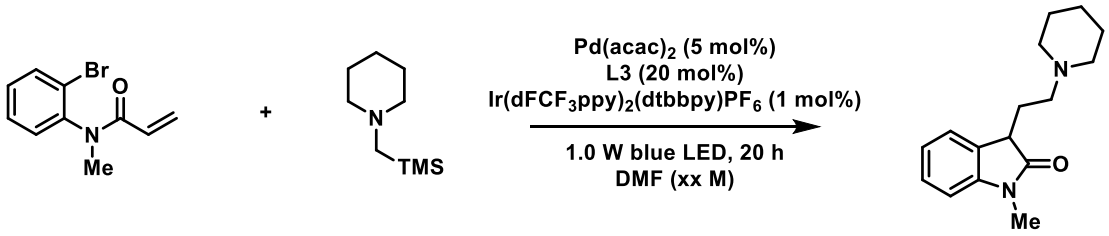


1a 2a 3a

entry[a]	x	y	x: y	yield (%)[b]
1	0.1	0.1	1: 1	31
2	0.1	0.15	1: 1.5	35
3	0.1	0.2	1: 2	51
4	0.1	0.25	1: 2.5	59
5	0.1	0.3	1: 3	57
6	0.1	0.4	1: 4	45
7	0.15	0.1	1.5: 1	25
8	0.2	0.1	2: 1	18

[a] Reaction conditions: **1a** (**x** mmol), **2a** (**y** mmol), $Pd(acac)_2$ (5 mol%), **L3** (20 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h. [b] GC yield without correction.

Table S7. Screening of the concentration for 3a.

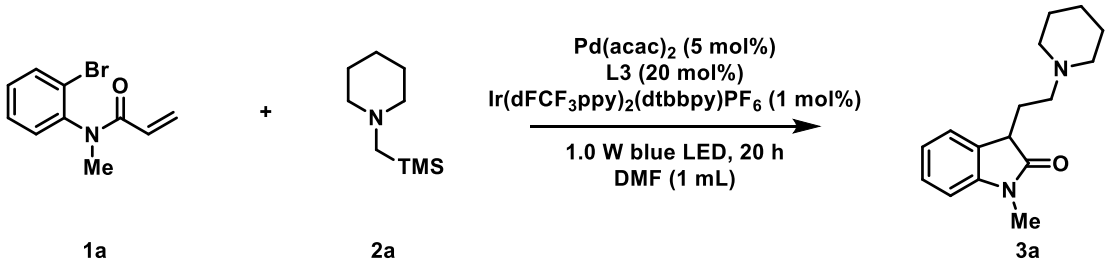


1a 2a 3a

entry[a]	concentration	yield (%)[b]
1	0.25 M	52
2	0.16 M	58
3	0.12 M	55
4	0.10 M	59
5	0.06 M	36
6	0.05 M	48

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), $Pd(acac)_2$ (5 mol%), **L3** (20 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1 mol%), Solvent (x mL), 1.0 W blue LED and the reaction time is 20 h. [b] GC yield without correction.

Table S8. Control experiments for 3a.

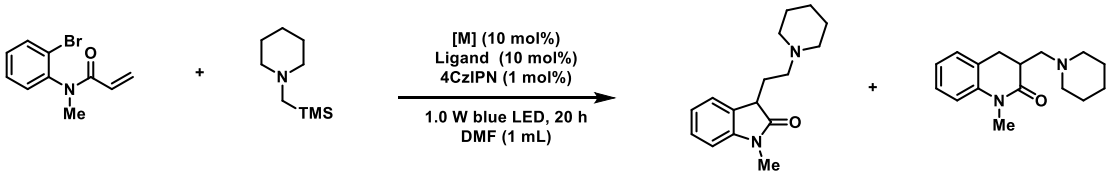


1a 2a 3a

entry[a]	deviation	yield (%)[b]
1	none	59 (46[c])
2	without Palladium	-
3	without Ligand	-
4	without PC	-
5	without Light	-
6	add 2.0 eq H_2O	24

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), $Pd(acac)_2$ (5 mol%), **L3** (20 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1 mol%), DMF (1 mL), 1.0 W blue LED and the reaction time is 20 h. [b] GC yield without correction. [c] isolated yield.

Table S9. Screening metal catalysts for 4a.

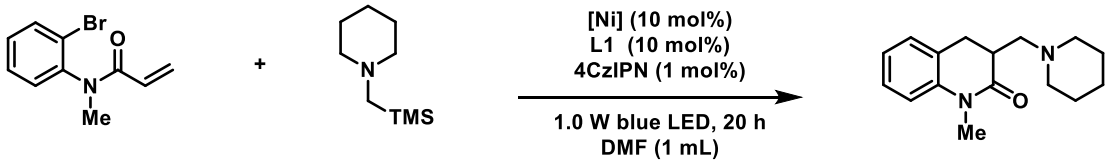


1a 2a 3a 4a

entry[a]	Metal catalyst	Ligand	3a (%)[b]	4a (%)[b]
1	$NiCl_2$	L1	-	19
2	$CoCl_2$	L1	-	trace
3	$PdCl_2$	L1	9	-
4	$CrCl_2$	L1	-	-
5	CuCl	L1	-	-
6	CuI	L1	-	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), metal catalyst (10 mol%), Ligand (10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S10. Screening nickel catalysts for 4a.

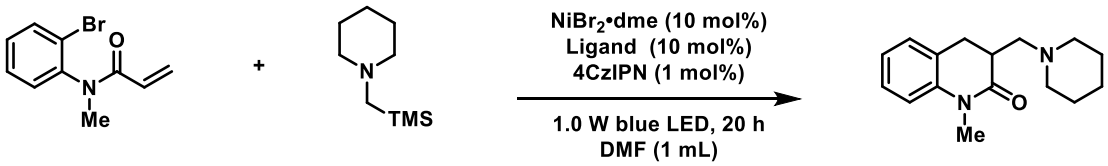


1a 2a 4a

entry[a]	Ni source	yield (%)[b]
1	$NiCl_2$	19
2	$NiCl_2$•dme	13
3	$NiBr_2$	62
4	$NiBr_2$•DME	63
5	NiI_2	57
6	$Ni(acac)_2$	14
7	$Ni(COD)_2$	53
8	$Ni(PPh_3)Cl_2$	52
9	$Ni(PPh_3)_2Br_2$	56
10	$Ni(PCy_3)_2Cl_2$	-
11	$Ni(P^nBu_3)_2Cl_2$	55
12	$Ni(dppf)Cl_2$	9
13	$Ni(dppe)Cl_2$	N.D.
14	$Ni(CF_3SO_3)_2$	45

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), nickel catalyst (10 mol%), L1(10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S11. Screening ligands for 4a.

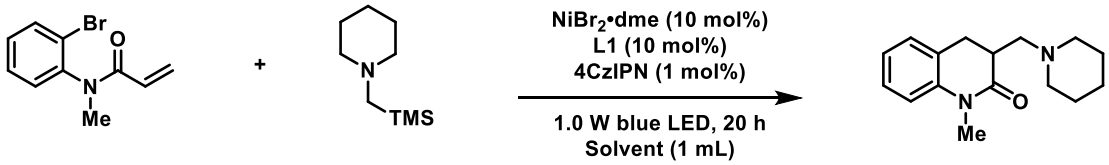


1a 2a 4a

entry[a]	Ligand	yield (%)[b]
1	L1	63
2	L2	63
3	L3	20
4	L4	42
5	L5	10
6	L6	0
7	L7	trace
8	L8	trace
9	L9	19
10	L11	43
11	L12	13

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$•dme (10 mol%), Ligand (10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S12. Screening solvents for 4a.

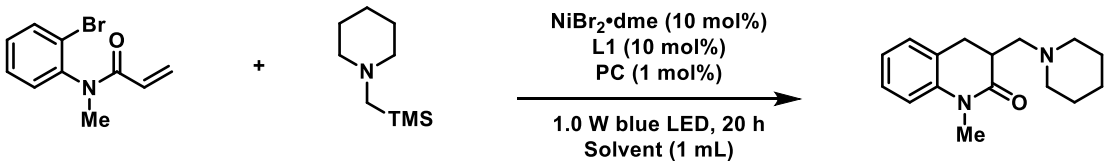


1a 2a 4a

entry[a]	solvent	yield (%)[b]
1	DMF	63
2	DMAc	18
3	DMSO	17
4	MeCN	27
5	EA	15
6	THF	32
7	DCE	trace
8	NMP	61

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$•dme (10 mol%), L1 (10 mol%), 4CzIPN (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S13. Screening photocatalysts for 4a.

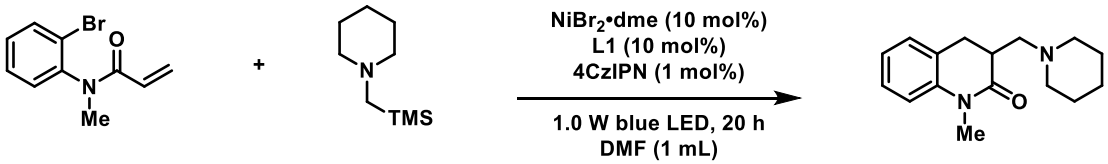


1a 2a 4a

entry[a]	PC	yield (%)[b]
1	4CzIPN	63
2	4DPAIPN	60
3	3DPA2FBN	-
4	$[(tBu)_2Mes\text{-}PhAcr]BF_4$	-
5	$[Mes\text{-}Acr]ClO_4$	-
6	Eosin Y	-
7	$Ir(p\text{-}Fppy)_2(bpy)PF_6$	34
8	$Ir(ppy)_2(dtbbpy)PF_6$	62
9	$Ir(dFppy)_2(dtbbpy)PF_6$	60
10	$Ir(dFCF_3ppy)_2(bpy)PF_6$	64
11	$Ir(ppy)_2(bpy)PF_6$	64
12	$Ir(bpy)_3$	44
13	$Ru(bpy)_3Cl_2$	19

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$•dme (10 mol%), L1 (10 mol%), PC (1 mol%), Solvent (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S14. Screening of the molecular ratio of 1a to 2a.

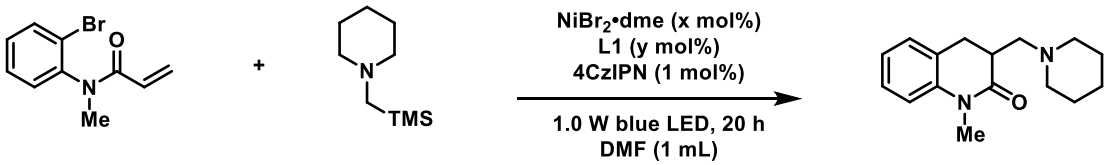


1a 2a 4a

entry[a]	x	y	x: y	yield (%)[b]
1	0.1	0.1	1: 1	57
2	0.1	0.15	1: 1.5	58
3	0.1	0.2	1: 2	63
4	0.1	0.25	1: 2.5	75
5	0.1	0.3	1: 3	76
6	0.15	0.1	1.5: 1	54
7	0.2	0.1	2: 1	59
8	0.3	0.1	3: 1	54

[a] Reaction conditions: **1a** (**x** mmol), **2a** (**y** mmol), $NiBr_2$•dme (10 mol%), L1 (10 mol%), 4CzIPN (1 mol%), DMF (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S15. Screening of the ratio of metal to ligand for 4a.

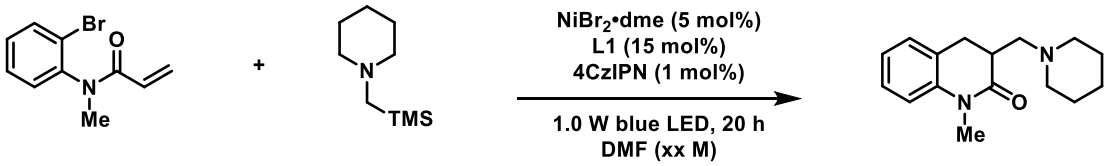


1a 2a 4a

entry[a]	x	y	x: y	yield (%)[b]
1	5	5	1: 1	39
2	5	10	1: 2	70
3	5	15	1: 3	76
4	10	5	2: 1	34
5	10	10	1: 1	75
6	10	15	1: 1.5	43
7	10	20	1: 2	44

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), $NiBr_2$•dme (**x** mol%), L1 (**y** mol%), 4CzIPN (1 mol%), DMF (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction.

Table S16. Screening of the ratio of metal to ligand for 4a.

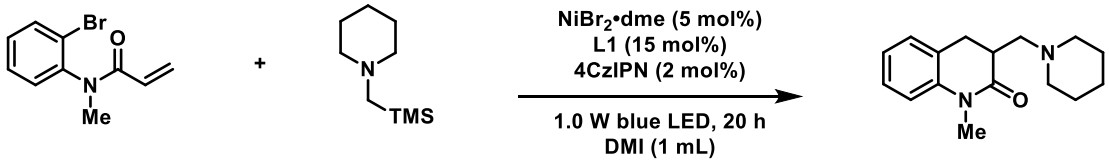


1a 2a 4a

entry[a]	concentration	yield (%)[b]
1	0.25 M	62
2	0.16 M	53
3	0.12 M	63
4	0.10 M	76
5	0.08 M	76
6	0.06 M	70
7	0.05 M	66
8[c]	0.10 M	78
9[d]	0.10 M	81

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), $NiBr_2$•dme (5 mol%), L1 (15 mol%), 4CzIPN (1 mol%), DMF (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction. [c] 4CzIPN (2 mol%). [d] 4CzIPN (2 mol%), DMI used as the solvent.

Table S17. Control experiments for 4a.



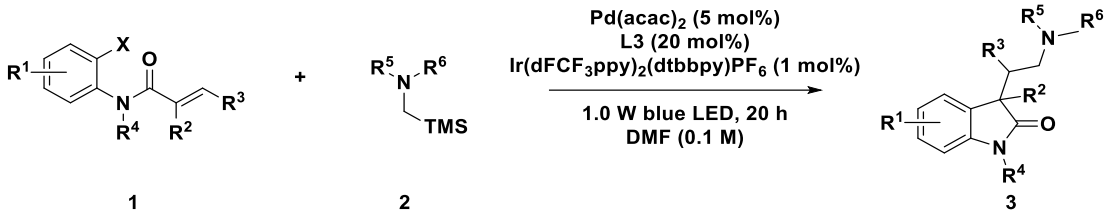
1a 2a 4a

entry[a]	deviation	yield (%)[b]
1	none	81 (74[c])
2	without Nickel	-
3	without Ligand	16
4	without PC	-
5	without Light	-
6	add 2.0 eq H_2O	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), $NiBr_2$•dme (5 mol%), L1 (15 mol%), 4CzIPN (2 mol%), DMI (1 mL), 1.0 W blue LED and the reaction time is 20 h.
[b] GC yield without correction. [c] isolated yield.

4. General Procedure for the Regiodivergent Cyclization

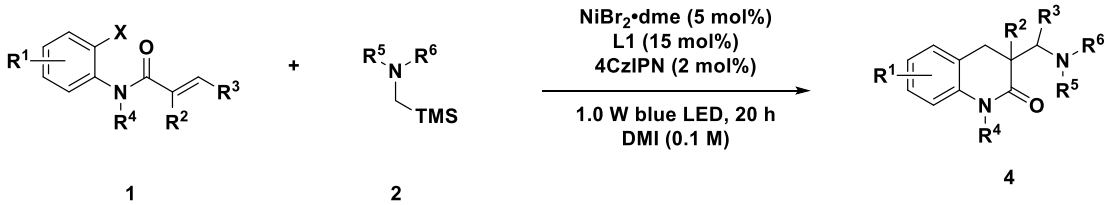
General procedure C for the synthesis of five-membered benzo-fused lactams (3)



1 2 3

In a glovebox, to a 10 mL reaction vial equipped with a stir bar were added $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%), DMF (2.0 mL). Then, α-silylamine **2** (0.5 mmol, 2.5 equiv.), **1** (0.2 mmol, 1.0 equiv.) was added. The vial was sealed and then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 20 h. The reaction was quenched by saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with H_2O (10 mL x 2) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography to give the corresponding product **3**.

General procedure D for the synthesis of six-membered benzo-fused lactams (4)

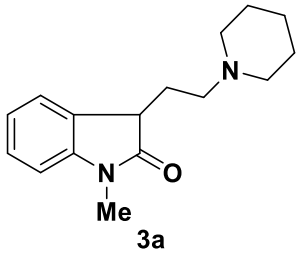


1 2 4

In a glovebox, to a 10 mL reaction vial equipped with a stir bar were added $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). Then, α-silylamine **2** (0.5 mmol, 2.5 equiv.), **1** (0.2 mmol, 1.0 equiv.) was added. The vial was sealed and then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 20 h. The reaction was quenched by saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with H_2O (10 mL x 2) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography to give the corresponding product **4**.

5. Spectroscopic Data of the Products

1-Methyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3a)



3a

Chemical Formula: $C_{16}H_{22}N_2O$
Molecular Weight: 258.3650

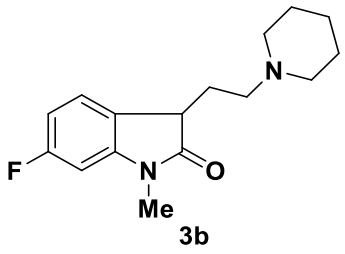
Prepared according to the **General Procedure C** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **3a** (24 mg, 46% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, CDCl3) δ 7.33 – 7.19 (m, 2H), 7.09 – 6.98 (m, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 3.51 (t, *J* = 6.1 Hz, 1H), 3.20 (s, 3H), 2.59 – 2.10 (m, 8H), 1.63 – 1.47(m, 4H), 1.45 – 1.35 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 144.5, 128.5, 127.8, 124.0, 122.2, 107.8, 55.0, 54.3, 43.7, 26.9, 26.2, 25.4, 24.0. ppm.

HRMS (ESI) for $C_{16}H_{23}N_2O^+$ [$(M+H)^+$]: calculated 259.1805, found 259.1805.

6-Fluoro-1-methyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3b)



3b

Chemical Formula: $C_{16}H_{21}FN_2O$
Molecular Weight: 276.3554

Prepared according to the **General Procedure C** using *N*-(2-bromophenyl-5-fluorophenyl)-*N*-methylacrylamide (**1e**) (52 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**)

(86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **3b** (32 mg, 58% yield) as a pale yellow oil.

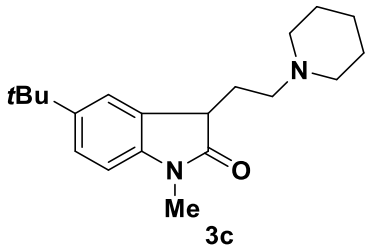
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.10 (m, 1H), 6.81 – 6.65 (m, 1H), 6.55 (d, J = 8.9 Hz, 1H), 3.46 (t, J = 6.0 Hz, 1H), 3.18 (s, 3H), 2.48 – 2.12 (m, 8H), 1.63 – 1.47 (m, 4H), 1.45 – 1.34 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 163.0 (d, J_{C-F} = 244.4 Hz), 146.0 (d, J_{C-F} = 121.2 Hz), 124.8 (d, J_{C-F} = 9.1 Hz), 123.64, 108.0 (d, J_{C-F} = 22.2 Hz), 96.6 (d, J_{C-F} = 27.3 Hz), 54.80, 54.26, 43.24, 26.82, 26.33, 25.42, 23.98 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -112.9 ppm.

HRMS (ESI) for $C_{16}H_{22}FN_2O^+$ [$(M+H)^+$]: calculated 277.1711, found 277.1710.

5-(Tert-butyl)-1-methyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3c)



3c

Chemical Formula: $C_{20}H_{30}N_2O$
Molecular Weight: 314.4730

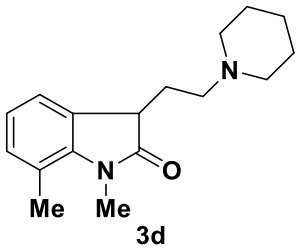
Prepared according to the **General Procedure C** using *N*-(2-bromophenyl-4-(*tert*-butyl)phenyl)-*N*-methylacrylamide (**1h**) (59 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **3c** (30 mg, 48% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 6.74 (d, J = 8.1 Hz, 1H), 3.49 (t, J = 6.2 Hz, 1H), 3.18 (s, 3H), 2.83 – 2.29 (m, 6H), 2.28 – 2.14 (m, 2H), 1.56 (s, 1H), 1.66 – 1.48 (m, 4H), 1.47 – 1.37 (m, 2H), 1.32 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 145.5, 142.1, 128.3, 124.3, 121.3, 107.2, 55.1, 54.3, 43.9, 34.5, 31.6, 27.0, 26.2, 25.5, 24.1 ppm.

HRMS (ESI) for $C_{20}H_{31}N_2O^+$ [$(M+H)^+$]: calculated 315.2431, found 315.2430.

1,7-Dimethyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3d)



3d

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

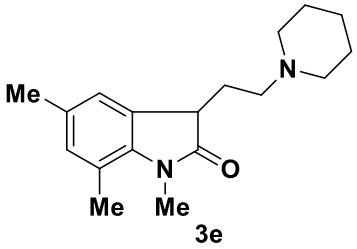
Prepared according to the **General Procedure C** using *N*-(2-bromophenyl-6-methylphenyl)-*N*-methylacrylamide (**1k**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **3d** (30 mg, 55% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 7.2 Hz, 1H), 6.99 (d, J = 7.7 Hz, 1H), 6.95 – 6.88 (m, 1H), 3.48 (s, 3H), 3.45 (t, J = 5.8 Hz, 1H), 2.57 (s, 3H), 2.53 – 208 (m, 8H), 1.66 – 1.52 (m, 4H), 1.49 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 142.1, 131.6, 128.9, 122.2, 121.9, 119.5, 54.8, 54.2, 43.2, 29.5, 26.9, 25.2, 23.9, 19.0 ppm.

HRMS (ESI) for $C_{17}H_{25}N_2O^+$ [$(M+H)^+$]: calculated 273.1961, found 273.1961.

1,5,7-Trimethyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3e)



3e

Chemical Formula: $C_{18}H_{26}N_2O$
Molecular Weight: 286.4190

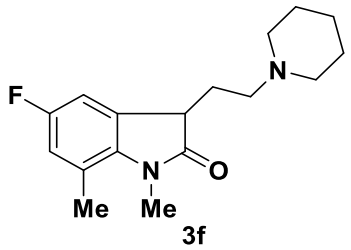
Prepared according to the **General Procedure C** using *N*-(2-bromophenyl-4,6-dimethylphenyl)-*N*-methylacrylamide (**1l**) (54 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 30:1) to give **3e** (29 mg, 51% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.80 (s, 1H), 3.45 (s, 3H), 3.42 (t, *J* = 6.0 Hz, 1H), 2.68 – 2.39 (m, 8H), 2.37 – 2.03 (m, 6H), 1.70 – 1.59 (m, 4H), 1.50 – 1.41 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 139.6, 132.1, 131.7, 129.0, 122.6, 119.1, 54.9, 54.2, 43.3, 29.5, 26.9, 25.0, 23.8, 20.8, 18.8 ppm.

HRMS (ESI) for $C_{18}H_{27}N_2O^+$ [$(M+H)^+$]: calculated 287.2118, found 287.2116.

5-Fluoro-1,7-dimethyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3f)



3f

Chemical Formula: $C_{17}H_{23}FN_2O$
Molecular Weight: 290.3824

Prepared according to the **General Procedure C** using *N*-(2-bromophenyl-4-fluoro-6-methylphenyl)-*N*-methylacrylamide (**1m**) (55 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10

μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 30:1) to give **3f** (29 mg, 50% yield) as a pale yellow oil.

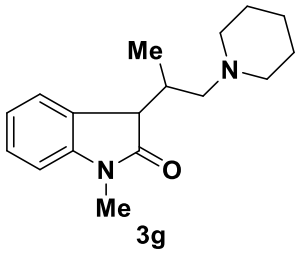
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.81 (m, 1H), 6.75 – 6.68 (m, 1H), 3.46 (s, 4H), 2.55 (s, 3H), 2.51 – 2.24 (m, 7H), 2.17-2.10 (m, 1H), 1.63 – 1.54 (m, 4H), 1.51 – 1.39 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 159.7, 157.3, 138.1, 120.7, 117.4 (d, $J_{C\text{-}F}$ = 23.0 Hz), 109.6 (d, $J_{C\text{-}F}$ = 23.9 Hz), 54.7, 54.2, 43.6, 29.6, 27.0, 25.3, 23.9, 18.8 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -122.0 ppm.

HRMS (ESI) for $C_{17}H_{24}FN_2O^+$ [$(M+H)^+$]: calculated 291.1867, found 291.1868.

1-Methyl-3-(1-(piperidin-1-yl)propan-2-yl)indolin-2-one (3g)



3g

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

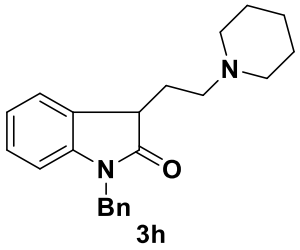
Prepared according to the **General Procedure C** using (*E*)-*N*-(2-bromophenyl)-*N*-methylbut-2-enamide (**1q**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), Pd(acac)$_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **3g** (33 mg, 61% yield, d.r. = 1.4:1) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: **Major** 7.32 – 7.12 (m, 2H), 7.01 (dd, *J* = 15.6, 7.8 Hz, 1H), 6.84 – 6.75 (m, 1H), 3.46 (s, 1H), 3.19 (s, 3H), 2.78 – 2.64 (m, 1H), 2.56 – 2.22 (m, 4H), 1.94 – 1.78 (m, 2H), 1.56 – 1.26 (m, 6H), 1.09 (d, *J* = 7.1 Hz, 3H) ppm; **Minor** 7.32 – 7.12 (m, 2H), 7.01 (dd, *J* = 15.6, 7.8 Hz, 1H), 6.84 – 6.75 (m, 1H), 3.78 (d, *J* = 3.3 Hz, 1H), 3.21 (s, 3H), 2.78 – 2.64 (m, 1H), 2.56 – 2.22 (m, 4H), 2.17 – 2.02 (m, 2H), 1.56 – 1.26 (m, 6H), 0.61 (d, *J* = 6.7 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 177.5, 145.2, 145.0, 128.0, 127.5, 127.5, 124.8, 123.9, 122.0, 121.5, 107.7, 107.5, 62.5, 61.9, 54.8, 54.7, 49.5, 47.7, 32.8, 32.7, 26.2, 26.1, 25.9, 24.6, 24.2, 17.1, 13.8 ppm.

HRMS (ESI) for $C_{17}H_{25}N_2O^+$ [$(M+H)^+$]: calculated 273.1961, found 273.1960.

1-Benzyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3h)



3h

Chemical Formula: $C_{22}H_{26}N_2O$
Molecular Weight: 334.4630

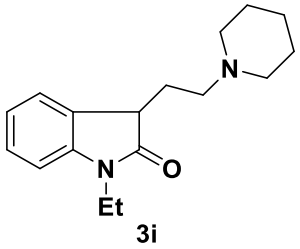
Prepared according to the **General Procedure C** using *N*-benzyl-*N*-(2-bromophenyl)acrylamide (**1p**) (63 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 40:1) to give **3h** (29 mg, 43% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 6H), 7.19 – 7.09 (m, 1H), 7.05 – 6.95 (m, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.6 Hz, 1H), 3.62 (t, *J* = 6.1 Hz, 1H), 2.60 – 2.40 (m, 6H), 2.33 – 2.16 (m, 2H), 1.66 – 1.51 (m, 4H), 1.48 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 143.5, 136.1, 128.7, 128.6, 127.8, 127.6, 127.3, 124.1, 122.3, 108.9, 55.1, 54.3, 43.8, 43.7, 27.2, 25.4, 24.0 ppm.

HRMS (ESI) for $C_{22}H_{27}N_2O^+$ [$(M+H)^+$]: calculated 335.2118, found 335.2117.

1-Ethyl-3-(2-(piperidin-1-yl)ethyl)indolin-2-one (3i)



3i

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

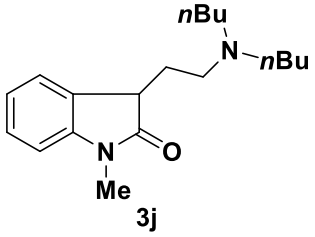
Prepared according to the **General Procedure C** using *N*-(2-bromophenyl)-*N*-ethylacrylamide (**1o**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **3i** (25 mg, 46% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.09 – 6.99 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.86 – 3.65 (m, 2H), 3.50 (t, *J* = 6.2 Hz, 1H), 2.63 – 2.26 (m, 6H), 2.27 – 2.13 (m, 2H), 1.65 – 1.50 (m, 4H), 1.47 – 1.38 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 143.5, 128.9, 127.8, 124.2, 122.1, 108.0, 55.0, 54.3, 43.7, 34.3, 27.0, 25.4, 24.0, 12.7 ppm.

HRMS (ESI) for $C_{17}H_{25}N_2O$ $[(M+H)^+]^+$: calculated 273.1961, found 273.1960.

Benzyl 2-(2-methoxypyridin-4-yl)-4-(piperidin-1-yl)butanoate (3j)



3j

Chemical Formula: $C_{19}H_{30}N_2O$
Molecular Weight: 302.4620

Prepared according to the **General Procedure C** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), *N*-butyl-*N*-((trimethylsilyl)methyl)butan-1-amine (**2h**) (108 mg, 0.5 mmol, 2.5 equiv.), $Pd(acac)_2$ (3.1 mg,

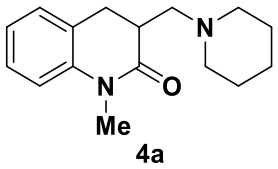
10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%) and DMF (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 30:1) to give **3j** (27 mg, 45% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.10 – 7.02 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.53 (t, *J* = 6.2 Hz, 1H), 3.20 (s, 3H), 2.73 – 2.63 (m, 2H), 2.55 – 2.43 (m, 4H), 2.26 – 2.09 (m, 2H), 1.49 – 1.35 (m, 4H), 1.35 – 1.25 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 144.4, 129.2, 127.7, 123.7, 122.2, 107.9, 53.6, 50.5, 43.5, 29.0, 28.0, 26.1, 20.7, 14.1 ppm.

HRMS (ESI) for $C_{19}H_{31}N_2O^+$ [$(M+H)^+$]: calculated 303.2431, found 303.2431.

1-Methyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (4a)



4a

Chemical Formula: $C_{16}H_{22}N_2O$
Molecular Weight: 258.3650

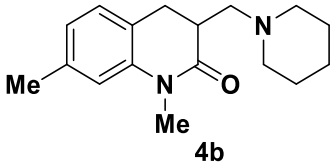
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4a** (38 mg, 74% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 2H), 7.06 – 6.99 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 3.35 (s, 3H), 3.13 – 3.02 (m, 1H), 2.88 – 2.71 (m, 3H), 2.62 – 2.20 (m, 5H), 1.68 – 1.49 (m, 4H),1.48 – 1.38 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 140.2, 128.3, 127.3, 125.7, 122.8, 114.4, 58.3, 54.8, 38.6, 29.8, 29.5, 25.9, 24.3 ppm.

HRMS (ESI) for $C_{16}H_{23}N_2O^+$ [$(M+H)^+$]: calculated 259.1805, found 259.1804.

1,7-Dimethyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4b)



4b

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

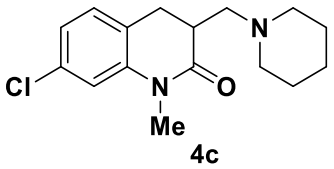
Prepared according to the **General Procedure D** using *N*-(2-bromo-5-methylphenyl)-*N*-methylacrylamide (**1b**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4b** (42 mg, 77% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 3.34 (s, 3H), 3.09 – 2.98 (m, 1H), 2.83 – 2.69 (m, 3H), 2.55 – 2.23 (m, 8H), 1.68 – 1.49 (m, 4H), 1.48 – 1.38 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 139.0, 136.0, 127.0, 122.4, 121.5, 114.3, 57.3, 53.8, 37.8, 28.7, 28.1, 24.8, 23.2, 20.5 ppm.

HRMS (ESI) for $C_{17}H_{25}N_2O^+$ [$(M+H)^+$]: calculated 273.1961, found 273.1961.

7-Chloro-1-methyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4c)



4c

Chemical Formula: $C_{16}H_{21}ClN_2O$
Molecular Weight: 292.8070

Prepared according to the **General Procedure D** using *N*-(2-bromo-5-chlorophenyl)-*N*-methylacrylamide (**1c**) (55 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and

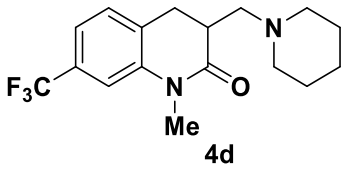
concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4c** (35 mg, 60% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.9 Hz, 1H), 6.94 – 6.85 (m, 2H), 3.25 (s, 3H), 3.02 – 2.90 (m, 1H), 2.82 – 2.59 (m, 3H), 2.44 – 2.26 (m, 3H), 2.21 (brs, 2H), 1.59 – 1.40 (m, 4H), 1.40 – 1.30 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 141.3, 132.9, 129.2, 124.0, 122.5, 114.8, 58.1, 54.8, 38.6, 29.8, 28.8, 25.9, 24.3 ppm.

HRMS (ESI) for $C_{16}H_{22}ClN_2O^+$ [$(M+H)^+$]: calculated 293.1415, found 293.1416.

1-Methyl-3-(piperidin-1-ylmethyl)-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4d)



4d

Chemical Formula: $C_{17}H_{21}F_3N_2O$
Molecular Weight: 326.3632

Prepared according to the **General Procedure D** using *N*-(2-bromo-5-(trifluoromethyl)phenyl)-*N*-methylacrylamide (**1d**) (62 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4d** (40 mg, 61% yield) as a pale yellow oil.

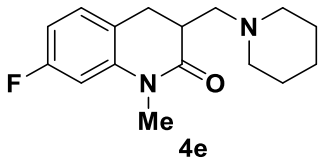
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 2H), 7.16 (s, 1H), 3.38 (s, 3H), 3.18 – 3.08 (m, 1H), 2.99 – 2.84 (m, 1H), 2.84 – 2.65 (m, 2H), 2.52 – 2.34 (m, 3H), 2.35 – 2.19 (m, 2H), 1.66 – 1.48 (m, 4H), 1.48 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 140.7, 129.8 (d, J_{C-F} = 32.5 Hz), 129.5, 128.7, 124.0 (d, J_{C-F} = 272.1 Hz), 119.5 (d, J_{C-F} = 4.0 Hz), 111.0 (d, J_{C-F} = 4.0 Hz), 58.1, 54.8, 38.3, 29.8, 29.2, 26.0, 24.3 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -62.4 ppm.

HRMS (ESI) for $C_{17}H_{22}F_3N_2O^+$ [$(M+H)^+$]: calculated 327.1679, found 327.1679.

7-Fluoro-1-methyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4e)



4e

Chemical Formula: $C_{16}H_{21}FN_2O$
Molecular Weight: 276.3554

Prepared according to the **General Procedure D** using *N*-(2-bromo-5-fluorophenyl)-*N*-methylacrylamide (**1e**) (52 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4e** (34 mg, 62% yield) as a pale yellow oil.

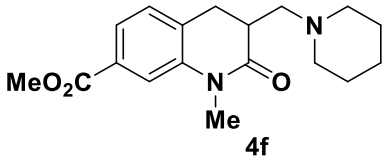
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 1H), 6.75 – 6.65 (m, 2H), 3.32 (s, 3H), 3.10 – 2.98 (m, 1H), 2.84 – 2.68 (m, 3H), 2.52 – 2.34 (m, 3H), 2.29 (brs, 2H), 1.66 – 1.48 (m, 4H), 1.48 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 162.2 (d, J_{C-F} = 243.1 Hz), 141.5 (d, J_{C-F} = 10.0 Hz), 129.1 (d, J_{C-F} = 9.2 Hz), 121.0 (d, J_{C-F} = 3.0 Hz), 108.9 (d, J_{C-F} = 21.2 Hz), 102.4 (d, J_{C-F} = 26.7 Hz), 58.2, 54.8, 38.7, 29.8, 28.7, 26.0, 24.3 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -114.3 ppm.

HRMS (ESI) for $C_{16}H_{21}FN_2NaO^+$ [$(M+Na)^+$]: calculated 299.1530, found 299.1530

Methyl 1-methyl-2-oxo-3-(piperidin-1-ylmethyl)-1,2,3,4-tetrahydroquinoline-7-carboxylate (4f)



4f

Chemical Formula: $C_{18}H_{24}N_2O_3$
Molecular Weight: 316.4010

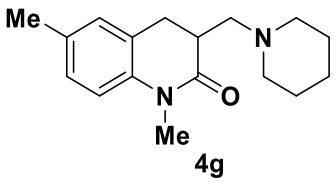
Prepared according to the **General Procedure D** using methyl 4-bromo-3-(N-methylacrylamido)benzoate (**1f**) (60 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4f** (36 mg, 57% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 1H), 7.63 (s, 1H), 7.30 – 7.24 (m, 1H), 3.93 (s, 3H), 3.40 (s, 3H), 3.17 – 3.07 (m, 1H), 2.96 – 2.83 (m, 1H), 2.83 – 2.66 (m, 2H), 2.55 – 2.37 (m, 3H), 2.29 (brs, 2H), 1.64 – 1.47 (m, 4H), 1.47 – 1.39 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 166.8, 140.4, 131.0, 129.4, 128.3, 124.2, 115.2, 58.2, 54.8, 52.3, 38.4, 29.9, 29.5, 25.9, 24.3 ppm.

HRMS (ESI) for $C_{18}H_{24}N_2NaO_3^+$ [$(M+Na)^+$]: calculated 339.1679, found 339.1681.

1,6-Dimethyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4g)



4g

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

Prepared according to the **General Procedure D** using *N*-(2-bromo-4-methylphenyl)-*N*-methylacrylamide (**1g**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol,

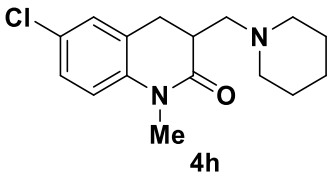
15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4g** (43 mg, 79% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 1H), 7.63 (s, 1H), 7.30 – 7.24 (m, 1H), 3.93 (s, 3H), 3.40 (s, 3H), 3.17 – 3.07 (m, 1H), 2.96 – 2.83 (m, 1H), 2.83 – 2.66 (m, 2H), 2.55 – 2.37 (m, 3H), 2.29 (brs, 2H), 1.64 – 1.47 (m, 4H), 1.47 – 1.39 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 137.8, 132.3, 129.0, 127.7, 125.5, 114.3, 58.3, 54.8, 38.7, 29.8, 29.5, 25.9, 24.3, 20.6 ppm.

HRMS (ESI) for $C_{17}H_{25}N_2O^+$ [$(M+H)^+$]: calculated 273.1961, found 273.1961.

6-Chloro-1-methyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4h)



4h

Chemical Formula: $C_{16}H_{21}ClN_2O$
Molecular Weight: 292.8070

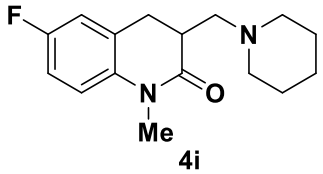
Prepared according to the **General Procedure D** using *N*-(2-bromo-4-chlorophenyl)-*N*-methylacrylamide (**1i**) (55 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4h** (36 mg, 61% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 3.33 (s, 3H), 3.09 – 2.98 (m, 1H), 2.89 – 2.68 (m, 3H), 2.54 – 2.35 (m, 3H), 2.29 (brs, 2H), 1.66 – 1.48 (m, 4H), 1.48 – 1.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 138.9, 128.2, 127.9, 127.4, 127.1, 115.5, 58.1, 54.8, 38.4, 29.9, 29.1, 26.0, 24.3.

HRMS (ESI) for $C_{16}H_{22}ClN_2O^+$ [$(M+H)^+$]: calculated 293.1415, found 293.1415.

6-Fluoro-1-methyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4i)



4i

Chemical Formula: $C_{16}H_{21}FN_2O$
Molecular Weight: 276.3554

Prepared according to the **General Procedure D** using *N*-(2-bromo-4-chlorophenyl)-*N*-methylacrylamide (**1j**) (52 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4i** (42 mg, 76% yield) as a pale yellow oil.

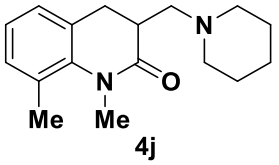
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.82 (m, 3H), 3.33 (s, 3H), 3.09 – 2.98 (m, 1H), 2.85 – 2.68 (m, 3H), 2.58 – 2.35 (m, 3H), 2.34 – 2.20 (m, 2H), 1.63 – 1.50 (m, 4H), 1.47 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 158.6 (d, $J_{C\text{-}F}$ = 242.6 Hz), 136.5 (d, $J_{C\text{-}F}$ = 2.6 Hz), 127.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 115.3 (d, $J_{C\text{-}F}$ = 22.9 Hz), 113.5 (d, $J_{C\text{-}F}$ = 22.5 Hz), 58.1, 54.8, 38.4, 30.0, 29.3, 26.0, 24.3 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -120.9 ppm.

HRMS (ESI) for $C_{16}H_{22}FN_2O^+$ [$(M+H)^+$]: calculated 277.1711, found 277.1710.

1,8-Dimethyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4j)



4j

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

Prepared according to the **General Procedure D** using *N*-(2-bromo-6-methylphenyl)-*N*-methylacrylamide (**1k**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol,

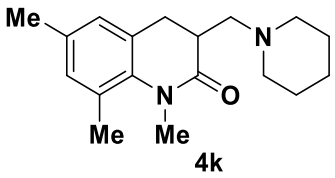
15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4j** (32 mg, 59% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.02 (m, 2H), 7.01 – 6.93 (m, 1H), 3.33 (s, 3H), 3.06 – 2.94 (m, 1H), 2.89 – 2.75 (m, 1H), 2.75 – 2.61 (m, 2H), 2.57 – 2.25 (m, 8H), 1.66 – 1.49 (m, 4H), 1.48 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 141.0, 131.0, 130.2, 127.3, 125.4, 124.0, 58.0, 54.8, 39.2, 36.0, 30.8, 25.8, 24.2, 20.8 ppm.

HRMS (ESI) for $C_{17}H_{25}N_2O^+$ [$(M+H)^+$]: calculated 273.1961, found 273.1960.

1,6,8-Trimethyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4k)



4k

Chemical Formula: $C_{18}H_{26}N_2O$
Molecular Weight: 286.4190

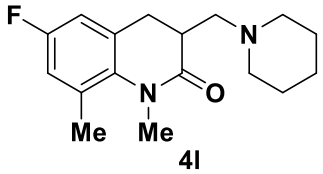
Prepared according to the **General Procedure D** using *N*-(2-bromo-4,6-dimethylphenyl)-*N*-methylacrylamide (**1l**) (54 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4k** (37 mg, 65% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 4.1 Hz, 2H), 3.31 (s, 3H), 3.00 – 2.89 (m, 1H), 2.88 – 2.77 (m, 1H), 2.71 – 2.57 (m, 2H), 2.51 – 2.38 (m, 3H), 2.39 – 2.32 (m, 2H), 2.31 (s, 3H), 2.27 (s, 3H), 1.64 – 1.52 (m, 4H), 1.48 – 1.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 138.6, 133.5, 131.5, 130.1, 127.1, 126.1, 58.1, 54.8, 39.2, 36.0, 30.8, 25.8, 24.2, 20.6, 20.5.

HRMS (ESI) for $C_{18}H_{27}N_2O^+$ [$(M+H)^+$]: calculated 287.2118, found 287.2118.

6-Fluoro-1,8-dimethyl-3-(piperidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4l)



4l

Chemical Formula: $C_{17}H_{23}FN_2O$
Molecular Weight: 290.3824

Prepared according to the **General Procedure D** using *N*-(2-bromo-4-fluoro-6-methylphenyl)-*N*-methylacrylamide (**1m**) (54 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4l** (39 mg, 67% yield) as a pale yellow oil.

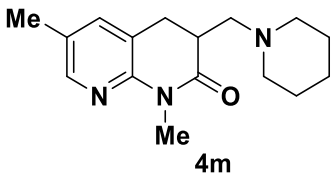
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.76 (s, 1H), 3.31 (s, 3H), 3.03 – 2.90 (m, 1H), 2.84 – 2.71 (m, 1H), 2.71 – 2.59 (m, 2H), 2.55 – 2.22 (m, 8H), 1.66 – 1.48 (m, 4H), 1.47 – 1.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 158.9 (d, $J_{C\text{-}F}$ = 243.7 Hz), 137.2 (d, $J_{C\text{-}F}$ = 2.6 Hz), 132.2 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.4 (d, $J_{C\text{-}F}$ = 7.8 Hz), 116.8 (d, $J_{C\text{-}F}$ = 21.8 Hz), 112.3 (d, $J_{C\text{-}F}$ = 22.4 Hz), 57.8, 54.8, 39.1, 36.1, 30.8, 25.9, 24.3, 20.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.9.

HRMS (ESI) for $C_{17}H_{24}FN_2O^+$ [$(M+H)^+$]: calculated 291.1867, found 291.1867.

1,6-Dimethyl-3-(piperidin-1-ylmethyl)-3,4-dihydro-1,8-naphthyridin-2(1H)-one (4m)



4m

Chemical Formula: $C_{16}H_{23}N_3O$
Molecular Weight: 273.3800

Prepared according to the **General Procedure D** using *N*-(3-bromo-5-methylpyridin-2-yl)-*N*-methylacrylamide (**1n**) (51 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)piperidine (**2a**) (86 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol,

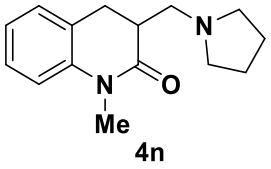
15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH/Et_3N = 100:1:0.2 to 20:1:0.2) to give **4m** (32 mg, 59% yield) as a brownish-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.31 (s, 1H), 3.44 (s, 3H), 3.08 – 2.96 (m, 1H), 2.89 – 2.70 (m, 3H), 2.54 – 2.37 (m, 3H), 2.30 – 2.26 (m, 5H), 1.66 – 1.48 (m, 4H), 1.48 – 1.38 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 150.2, 145.7, 137.0, 127.6, 119.7, 58.4, 54.8, 38.6, 28.2, 27.8, 25.9, 24.4, 17.6 ppm.

HRMS (ESI) for $C_{16}H_{24}N_3O^+$ [$(M+H)^+$]: calculated 274.1914, found 274.1915.

1-Methyl-3-(pyrrolidin-1-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4n)



4n

Chemical Formula: $C_{15}H_{20}N_2O$
Molecular Weight: 244.3380

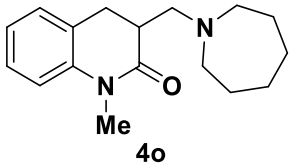
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)pyrrolidine (**2b**) (79 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4n** (24 mg, 49% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.10 – 6.99 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.36 (s, 3H), 3.13 (dd, *J* = 15.0, 4.3 Hz, 1H), 2.90 – 2.68 (m, 4H), 2.65 – 2.47 (m, 4H), 1.87 – 1.73 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 140.1, 128.3, 127.4, 125.6, 122.9, 114.5, 55.8, 54.4, 40.1, 29.8, 29.5, 23.6 ppm.

HRMS (ESI) for $C_{15}H_{21}N_2O^+$ [$(M+H)^+$]: calculated 245.1648, found 245.1647.

3-(Azepan-1-ylmethyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (4o)



4o

Chemical Formula: $C_{17}H_{24}N_2O$
Molecular Weight: 272.3920

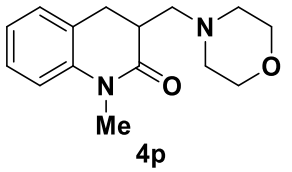
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 1-((trimethylsilyl)methyl)azepane (**2c**) (93 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4o** (23 mg, 42% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.08 – 6.99 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 3.35 (s, 3H), 3.11 (dd, *J* = 15.4, 5.6 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.87 (dd, *J* = 15.4, 8.7 Hz, 1H), 2.80 – 2.62 (m, 5H), 2.54 – 2.44 (m, 1H), 1.73 – 1.52 (m, 8H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 140.1, 128.4, 127.4, 125.4, 123.0, 114.4, 56.9, 55.4, 39.6, 29.8, 29.3, 27.2, 26.9.

HRMS (ESI) for $C_{17}H_{25}N_2O^+$ [$(M+H)^+$]: calculated 273.1961, found 273.1961.

1-Methyl-3-(morpholinomethyl)-3,4-dihydroquinolin-2(1H)-one (4p)



4p

Chemical Formula: $C_{15}H_{20}N_2O_2$
Molecular Weight: 260.3370

Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 4-((trimethylsilyl)methyl)morpholine (**2d**) (87 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and

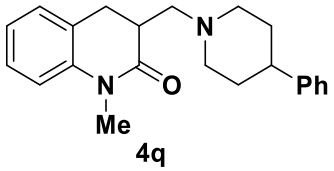
concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 50:1) to give **4p** (43 mg, 83% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.77 – 3.61 (m, 4H), 3.36 (s, 3H), 3.07 (dd, *J* = 14.8, 4.7 Hz, 1H), 2.87 – 2.76 (m, 3H), 2.56 – 2.32 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 140.1, 128.2, 127.4, 125.4, 122.9, 114.5, 67.0, 58.0, 53.9, 45.1, 38.4, 31.5, 29.8, 29.2 ppm.

HRMS (ESI) for $C_{15}H_{21}N_2O_2^+$ [$(M+H)^+$]: calculated 261.1598, found 261.1597.

1-Methyl-3-((4-phenylpiperidin-1-yl)methyl)-3,4-dihydroquinolin-2(1H)-one (4q)



4q

Chemical Formula: $C_{22}H_{26}N_2O$
Molecular Weight: 334.4630

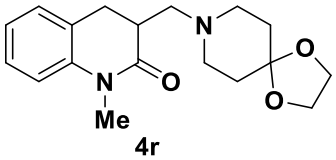
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 4-phenyl-1-((trimethylsilyl)methyl)piperidine (**2e**) (124 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4q** (38 mg, 57% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 7H), 7.07 – 6.99 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.36 (s, 3H), 3.09 (dd, *J* = 14.8, 4.3 Hz, 1H), 3.05 – 2.97 (m, 1H), 2.94 – 2.73 (m, 4H), 2.55 – 2.42 (m, 2H), 2.31 – 2.17 (m, 1H), 2.07 – 1.96 (m, 1H), 1.88 – 1.69 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 146.5, 140.3, 128.4, 128.3, 127.4, 126.9, 126.1, 125.7, 122.9, 114.5, 58.0, 56.1, 53.3, 42.7, 38.9, 33.6, 33.5, 29.8, 29.5 ppm.

HRMS (ESI) for $C_{22}H_{27}N_2O^+$ [$(M+H)^+$]: calculated 335.2118, found 335.2119.

3-((1,4-Dioxa-8-azaspiro[4.5]decan-8-yl)methyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (4r)



4r

Chemical Formula: $C_{18}H_{24}N_2O_3$
Molecular Weight: 316.4010

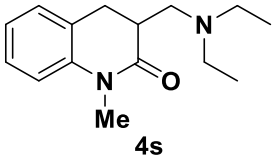
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 8-((trimethylsilyl)methyl)-1,4-dioxa-8-azaspiro[4.5]decane (**2f**) (115 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4r** (41 mg, 65% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.08 – 6.99 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.94 (s, 4H), 3.35 (s, 3H), 3.07 (dd, *J* = 15.1, 5.1 Hz, 1H), 2.89 – 2.66 (m, 3H), 2.66 – 2.56 (m, 2H), 2.50 – 2.39 (m, 3H), 1.81 – 1.63 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 140.2, 128.3, 127.3, 125.6, 122.8, 114.4, 107.2, 64.2, 57.1, 51.6, 39.1, 34.9, 29.8, 29.3 ppm.

HRMS (ESI) for $C_{18}H_{25}N_2O_3^+$ [$(M+H)^+$]: calculated 317.1860, found 317.1861.

3-((Diethylamino)methyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (4s)



4s

Chemical Formula: $C_{15}H_{22}N_2O$
Molecular Weight: 246.3540

Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), *N*-ethyl-*N*-((trimethylsilyl)methyl)ethanamine (**2g**) (80 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI

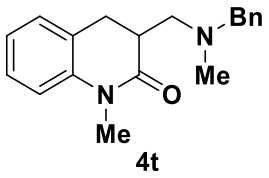
(2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4s** (32mg, 65% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 1H), 7.19 (d, *J* = 6.7 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 3.35 (s, 3H), 3.08 (dd, *J* = 15.3, 5.5 Hz, 1H), 2.91 – 2.76 (m, 2H), 2.77 – 2.68 (m, 1H), 2.66 – 2.54 (m, 2H), 2.51 – 2.38 (m, 3H), 0.97 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 140.2, 128.5, 127.3, 125.5, 122.8, 114.3, 52.4, 47.4, 39.8, 29.7, 29.0, 11.9 ppm.

HRMS (ESI) for $C_{15}H_{23}N_2O^+$ [$(M+H)^+$]: calculated 247.1805, found 247.1805.

3-((Benzyl(methyl)amino)methyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (4t)



4t

Chemical Formula: $C_{19}H_{22}N_2O$
Molecular Weight: 294.3980

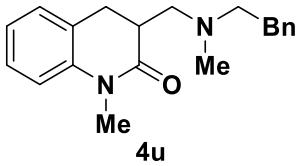
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), *N*-benzyl-*N*-methyl-1-(trimethylsilyl)methanamine (**2i**) (104 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 50:1) to give **4t** (50 mg, 85% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 6H), 7.15 (d, *J* = 6.6 Hz, 1H), 7.04 – 6.94 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 3.45 (m, 2H), 3.32 (s, 3H), 3.17 – 3.04 (m, 1H), 2.87 – 2.74 (m, 2H), 2.70 (dd, *J* = 12.4, 4.5 Hz, 1H), 2.57 – 2.46 (m, 1H), 2.21 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 140.1, 139.2, 128.9, 128.4, 128.2, 127.3, 126.9, 125.4, 122.8, 114.4, 62.7, 56.5, 42.4, 39.3, 29.7, 28.9 ppm.

HRMS (ESI) for $C_{19}H_{23}N_2O^+$ [$(M+H)^+$]: calculated 295.1805, found 295.1805.

1-Methyl-3-((methyl(phenethyl)amino)methyl)-3,4-dihydroquinolin-2(1H)-one (4u)



4u

Chemical Formula: $C_{20}H_{24}N_2O$
Molecular Weight: 308.4250

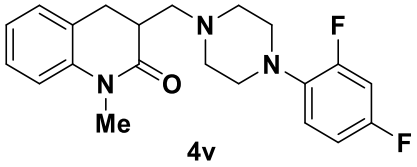
Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), *N*-methyl-2-phenyl-*N*-((trimethylsilyl)methyl)ethan-1-amine (**2j**) (111 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 30:1) to give **4u** (53 mg, 87% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 6H), 7.10 (d, *J* = 5.9 Hz, 1H), 7.06 – 6.97 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.34 (s, 3H), 3.02 – 2.87 (m, 1H), 2.87 – 2.63 (m, 6H), 2.63 – 2.45 (m, 2H), 2.32 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 140.5, 140.2, 128.8, 128.4, 128.3, 127.3, 125.9, 125.4, 122.9, 114.4, 59.7, 56.6, 42.4, 39.3, 33.6, 29.7, 28.9 ppm.

HRMS (ESI) for $C_{20}H_{25}N_2O^+$ $[(M+H)^+]$: calculated 309.1961, found 309.1961.

3-((4-(2,4-Difluorophenyl)piperazin-1-yl)methyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (4v)



4v

Chemical Formula: $C_{21}H_{23}F_2N_3O$
Molecular Weight: 371.4318

Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 1-(2,4-difluorophenyl)-4-((trimethylsilyl)methyl)piperazine (**2k**) (142 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI

(2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4v** (66 mg, 89% yield) as a yellow oil.

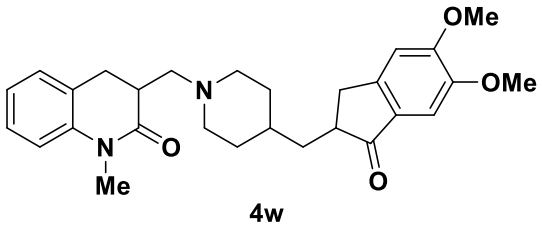
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.08 – 7.00 (m, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.94 – 6.85 (m, 1H), 6.85 – 6.70 (m, 2H), 3.37 (s, 3H), 3.15 – 2.96 (m, 5H), 2.92 – 2.76 (m, 3H), 2.75 – 2.63 (m, 2H), 2.63 – 2.44 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 160.1 – 152.9 (m), 156.7 (dd, J_{C-F} = 22.7, 11.5 Hz), 140.2, 136.9 – 136.7 (m), 128.2, 127.4, 125.4, 122.9, 119.4 (dd, J_{C-F} = 9.4, 4.2 Hz), 114.5, 110.6 (dd, J_{C-F} = 21.3, 3.8 Hz), 57.6, 53.5, 50.9 (d, J_{C-F} = 2.9 Hz), 38.7, 29.8, 29.4 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -118.5, -119.1 ppm.

HRMS (ESI) for $C_{21}H_{24}F_2N_3O^+$ $[(M+H)^+]$: calculated 372.1882, found 372.1882.

3-((4-((5,6-Dimethoxy-1-oxo-2,3-dihydro-1H-inden-2-yl)methyl)piperidin-1-yl)methyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (4w)



4w

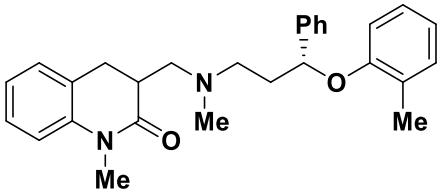
Chemical Formula: $C_{28}H_{34}N_2O_4$
Molecular Weight: 462.5900

Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), 5,6-dimethoxy-2-((1-((trimethylsilyl)methyl)piperidin-4-yl)methyl)-2,3-dihydro-1H-inden-1-one (**2l**) (188 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4w** (45 mg, 49% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.12 (m, 3H), 7.07 – 6.99 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.87 (s, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.36 (s, 3H), 3.30 – 3.18 (m, 1H), 3.12 – 3.02 (m, 1H), 2.98 – 2.88 (m, 1H), 2.88 – 2.66 (m, 6H), 2.51 – 2.40 (m, 1H), 2.20 – 2.08 (m, 1H), 1.96 – 1.83 (m, 2H), 1.74 (brs, 1H), 1.69 – 1.61 (m, 1H), 1.52 – 1.30 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 136.5, 135.0, 134.8, 131.3, 131.0, 130.1, 129.5, 129.0, 128.9, 128.6, 128.2, 124.0, 115.8, 73.6, 56.3, 50.8, 37.2, 32.9, 32.2, 30.7, 26.5, 24.4, 20.2.
HRMS (ESI) for $C_{28}H_{35}N_2O_4^+$ [$(M+H)^+$]$^+$ calculated 463.2591, found 463.2596.

1-Methyl-3-((methyl((R)-3-phenyl-3-(o-tolyloxy)propyl)amino)methyl)-3,4-dihydroquinolin-2(1H)-one (4x)



4x

Chemical Formula: $C_{28}H_{32}N_2O_2$
Molecular Weight: 428.5760

Prepared according to the **General Procedure D** using *N*-(2-bromophenyl)-*N*-methylacrylamide (**1a**) (48 mg, 0.2 mmol, 1.0 equiv.), (*R*)-*N*-methyl-3-phenyl-3-(o-tolyloxy)-*N*-((trimethylsilyl)methyl)propan-1-amine (**2m**) (171 mg, 0.5 mmol, 2.5 equiv.), $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). After extraction and concentration, the residue was purified by flash column chromatography (DCM/MeOH = 100:1 to 20:1) to give **4x** (35 mg, 41% yield, d.r. = 1.6:1) as a yellow oil.

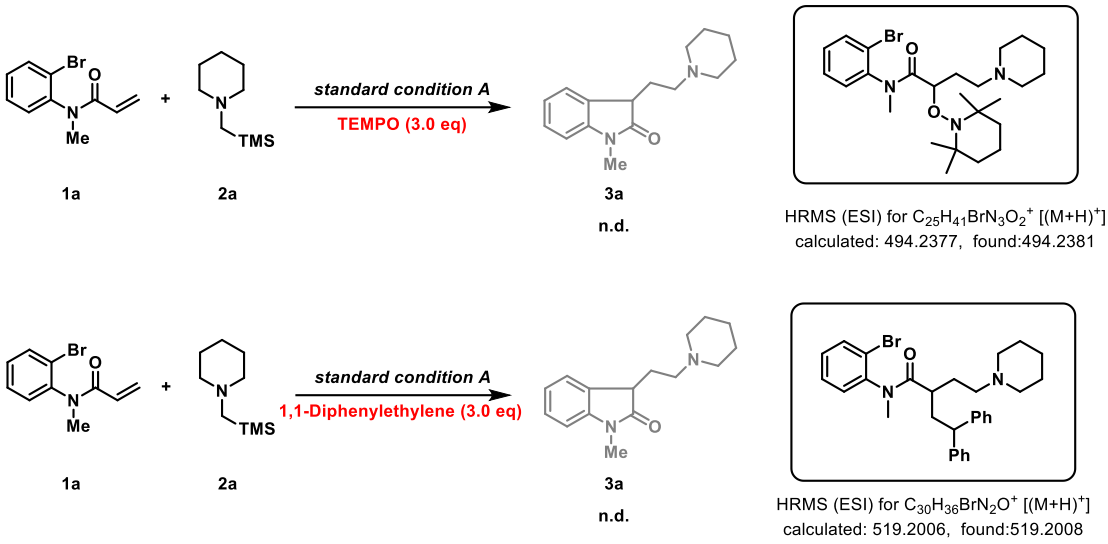
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 4H), 7.14 – 7.06 (m, 2H), 6.97 (d, *J* = 6.2 Hz, 1H), 6.90 – 6.73 (m, 4H), 6.68 – 6.60 (m, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 5.17 – 5.09 (m, 1H), 3.20 (d, *J* = 4.1 Hz, 3H), 2.91 – 2.76 (m, 1H), 2.69 – 2.49 (m, 3H), 2.46 – 2.39 (m, 1H), 2.36 – 2.28 (m, 1H), 2.26 – 2.19 (m, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 2.04 – 1.90 (m, 1H), 1.88 – 1.74 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) **Major**: δ 172.8, 157.2, 143.4, 141.1, 131.6, 129.6, 129.4, 128.4, 128.3, 128.0, 127.6, 126.8, 126.4, 123.9, 121.1, 115.4, 113.7, 78.5, 58.2, 55.6, 43.1, 40.4, 37.7, 30.7, 30.0, 17.6 ppm. **Minor**: δ172.8, 157.2, 143.4, 141.1, 131.6, 129.6, 129.5, 128.4, 128.3, 128.0, 127.5, 126.8, 126.3, 123.9, 121.1, 115.4, 113.8, 78.3, 57.8, 54.8, 43.6, 40.3, 37.7, 30.7, 29.8, 17.6 ppm.

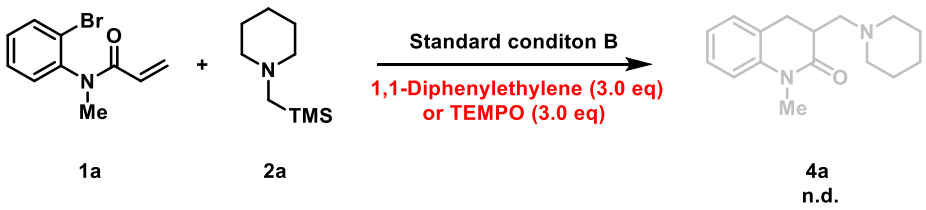
HRMS (ESI) for $C_{28}H_{33}N_2O_2^+$ [$(M+H)^+$]$^+$ calculated 429.2537, found 429.2538.

6. Mechanistic studies

6.1 Radical trapping experiments

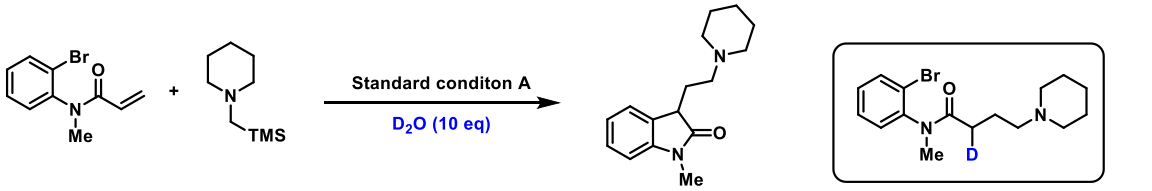


In a glovebox, to a 10 mL reaction vial equipped with a stir bar were added $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%), DMF (2.0 mL). Then, α-silylamine **2a** (86 mg, 0.5 mmol, 2.5 equiv.), **1a** (48mg, 0.2 mmol, 1.0 equiv.) and **TEMPO** (94 mg, 0.6 mmol, 3.0 equiv.) or **1,1-Diphenylethylene** (108 mg, 0.6 mmol, 3.0 equiv.) was added. The vial was sealed and then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 20 h. The reaction was quenched by saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with H_2O (10 mL x 2) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The desired product **3a** was not detected by GC, while the probable radical-adducts were discerned based on the analysis of HRMS. **HRMS** (ESI) for $C_{25}H_{41}BrN_3O_2^+$ [(M+H)$^+$], calculated: 494.2377, found: 494.2381. **HRMS** (ESI) for $C_{30}H_{36}BrN_2O^+$ [(M+H)$^+$], calculated: 519.2006, found: 519.2008.



In a glovebox, to a 10 mL reaction vial equipped with a stir bar were added $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). Then, α-silylamine **2a** (86 mg, 0.5 mmol, 2.5 equiv.), **1a** (48mg, 0.2 mmol, 1.0 equiv.) and **TEMPO** (94 mg, 0.6 mmol, 3.0 equiv.) or **1,1-Diphenylethylene** (108 mg, 0.6 mmol, 3.0 equiv.) was added. The vial was sealed and then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 20 h. The reaction was quenched by saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with H_2O (10 mL x 2) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The desired product **4a** was not detected by GC.

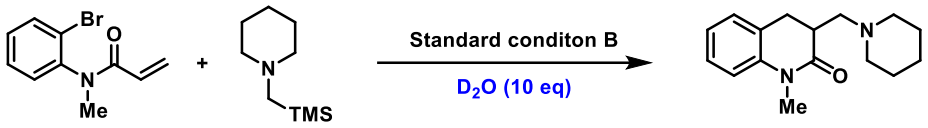
6.2 Deuterium-labelling experiments



1a **2a** **3a, 22%**

HRMS (ESI) for $C_{16}H_{23}DBrN_2O^+$ $[(M+H)]^+$ calculated: 340.1129, found: 340.1127.

In a glovebox, to a 10 mL reaction vial equipped with a stir bar were added $Pd(acac)_2$ (3.1 mg, 10 μmol, 5 mol%), **L3** (7.8 mg, 40 μmol, 20 mol%), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 2 μmol, 1 mol%), DMF (2.0 mL). Then, α-silylamine **2a** (86 mg, 0.5 mmol, 2.5 equiv.), **1a** (48mg, 0.2 mmol, 1.0 equiv.) and **D_2O** (40 mg, 1.0 mmol, 10 equiv.) was added. The vial was sealed and then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 20 h. The reaction was quenched by saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with H_2O (10 mL x 2) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The product **3a** was determined in 22% GC yield, meanwhile, the corresponding quenched intermediate by D_2O was detected through HRMS analysis. **HRMS** (ESI) for $C_{16}H_{23}DBrN_2O^+$ $[(M+H)^+]$: calculated: 340.1129, found: 340.1127.



1a 2a 4a, 5%

In a glovebox, to a 10 mL reaction vial equipped with a stir bar were added $NiBr_2$•dme (3.1 mg, 10 μmol, 5 mol%), **L1** (6.2 mg, 30 μmol, 15 mol%), 4-CzIPN (3.1 mg, 4 μmol, 2 mol%) and DMI (2 mL). Then, α-silylamine **2a** (86 mg, 0.5 mmol, 2.5 equiv.), **1a** (48mg, 0.2 mmol, 1.0 equiv.) and **D_2O** (40 mg, 1.0 mmol, 10 equiv.) was added. The vial was sealed and then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 20 h. The reaction was quenched by saturated $NaHCO_3$ (20 mL), extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with H_2O (10 mL x 2) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The product **4a** was provided in 5% GC yield. Unfortunately, we did not detect any deuterium-labelled products.

7. DFT Calculations

7.1 Computational details

The geometry optimizations were carried out using the Gaussian 09 package[10] at the (u)B3LYP-D3(BJ) level of theory with a mixed basis set of SDD for Ni, Pd and Br and 6-31G(*d*) for all other atoms.[11-13] Frequencies were computed analytically at the same level of theory to confirm whether the structures are minima (no imaginary frequencies) or transition states (only one imaginary frequency). Selected transition-state structures were confirmed to connect the correct reactants and products by intrinsic reaction coordinate (IRC) calculations.[14,15] Thorough conformation search of transition states was performed with the Conformer-Rotamer Ensemble Sampling Tool (CREST) that developed by Grimme and co-workers.[16] To obtain better accuracy, single-point energies of the optimized geometries were calculated at the TPSS0-D4[17,18]/def2-QZVP[19] level of theory using ORCA 5.0.3.[20-23] (with an auxiliary basis set def2/J[24]). The RIJCOSX approximation was used to accelerate the calculations. Solvation effects (DMF) were taken into account by performing single-point calculations using the SMD model[25]. Because the harmonic-oscillator approximation may lead to spurious results for the computed entropies in molecules with low-frequency vibrational modes, the quasiharmonic approximation from Grimme[26] was applied to compute the thermal corrections with a cutoff frequency of 100 cm^{-1} using GoodVibes.[27] The Gibbs free energies reported in the article are the large basis set solution-phase single-point energies corrected by gas-phase Gibbs free energy correction (at 298.15 K). The 3D diagrams of molecules were generated using CYLView.[28]

7.2 Marcus theory calculations for the free energy of activation of single electron transfer

We used the modified Marcus theory to estimate the barriers for the stepwise outer-sphere single electron transfer (OSET) processes, which were well established by Coote, Gennaro, Matyjaszewski and Liu[29,30], in the reduction of Ar-Br by Pd(I) complex **IM3**^{doublet} and Ni(I) complex **IM7**^{doublet}. The DFT calculations were performed at the (u)TPSS0-D4(SMD)/def2-QZVP//(u)B3LYP-D3(BJ)/SDD&6-31G* level of theory in DMF at 25 ℃.

(1) OSET process for reduction of Ar-Br 1a by IM3^{doublet}

$$[Pd^{I}\text{-}CH_2NR_2] + Ar\text{-}Br \longrightarrow [Pd^{II}\text{-}CH_2NR_2]^{+} + [Ar\text{-}Br]^{\bullet -} \quad (1)$$

$$[Ar\text{-}Br]^{\bullet -} \longrightarrow Ar\cdot + Br^{-} \quad (2)$$

According to the Marcus-Hush theory of electron transfer, the free energy barrier of a singlet electron transfer process can be estimated from the outer-sphere electron transfer model:

$$\Delta G^{\ddagger}_{OSET} = \Delta G_0^{\ddagger}\left(1+\frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

Here, $\Delta G_0^{\ddagger}$= 9.7 kcal/mol is the reaction (1) Gibbs energy of reaction given by DFT calculations. $\Delta G_0^{\ddagger}$ is the intrinsic barrier which can be calculated by solvent reorganization energy λ:

$$\Delta G_0^{\ddagger} = \frac{1}{4}\lambda$$

The reorganization energy λ is the total reorganization energy which can be estimated as the sum of the inner-sphere reorganization energy λ_i and outer-sphere reorganization energy λ_o. The outer-sphere reorganization energy can be calculated as the following equation:

$$\lambda_o = \frac{N_A e^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_s}\right)\left(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{r_1+r_2}\right)$$

Here, ε_{op}, ε_s is the optical and static dielectric constants, respectively; r_1 = 4.83 Å and r_2 = 3.86 Å are the hard sphere radii of donor [Pd^{I}-CH_2NR_2] and acceptor ArBr respectively, and distances from the center of molecules to Van der Waals surfaces when the isosurface of electron density 0.001 a.u. is taken according to Bader's AIM theory are used as the radii.[31] Due to the overestimated λ_o calculated by Marcus theory, the semi-empirical equation is morecommonly utilized:

$$\lambda_o = A\left(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{r_1+r_2}\right)$$

Here we adopt the value, A is an empirical constant. Here we use A = 99 kcal·mol^{-1}·Å as suggested in the Coote and Matyjaszewski's study.[32] Therefore, solvent reorganization energy can be calculated by:

$$\lambda_o = 99\times\left(\frac{1}{2\times4.83}+\frac{1}{2\times3.86}-\frac{1}{4.83+3.86}\right) = 11.7 \text{ kcal/mol}$$

In addition, the inner-sphere nuclear reorganization energy can be calculated from the equations:

$$\lambda_{i1} = \left|E^{D}(Q_P)-E^{D}(Q_R)\right| + \left|E^{D^+}(Q_P)-E^{D^+}(Q_R)\right|$$

$$\lambda_{i2} = \left|E^{A}(Q_P)-E^{A}(Q_R)\right| + \left|E^{A^-}(Q_P)-E^{A^-}(Q_R)\right|$$

$$\lambda_i = \frac{\lambda_{i1} + \lambda_{i2}}{2} = 45.3 \text{ kcal/mol}$$

Thus,

$$\lambda=\lambda_i+\lambda_o=57.0 \text{ kcal/mol}$$

Then the intrinsic barrier of reaction $\Delta G_0^{\ddagger}$ is given by:

$$\Delta G_0^{\ddagger}=\frac{1}{4}\times 57.0=14.25 \text{ kcal/mol}$$

Finally, we obtain the activation free energy of reaction:

$$\Delta G_{OSET}^{\ddagger}=14.25\times\left(1+\frac{9.7}{4\times 14.25}\right)^2=19.5 \text{ kcal/mol}$$

(2) OSET process for reduction of Ar-Br 1a by IM7^{doublet}

$$[Ni^{I}\text{-}CH_2NR_2] + Ar\text{-}Br \longrightarrow [Ni^{II}\text{-}CH_2NR_2]^{+} + [Ar\text{-}Br]^{\bullet -} \quad (3)$$

$$[Ar\text{-}Br]^{\bullet -} \longrightarrow Ar\cdot + Br^{-} \quad (4)$$

Thermodynamic and molecular parameters, $\Delta_r G^{\ominus}$= 8.8 kcal/mol, r_1 = 4.64 Å and r_2 = 3.86 Å are given by DFT calculations. According to the aforementioned calculation method, λ_o, $\Delta G_0^{\ddagger}$ and $\Delta G^{\ddagger}_{OSET}$ can be obtained by:

$$\lambda_o=99\times\left(\frac{1}{2\times 4.64}+\frac{1}{2\times 3.86}-\frac{1}{4.64+3.86}\right)=11.8 \text{ kcal/mol}$$

$$\lambda = \lambda_i + \lambda_o = 56.9 \text{ kcal/mol}$$

$$\Delta G_0^{\ddagger} = \frac{1}{4}\times 56.9=14.2 \text{ kcal/mol}$$

$$\Delta G^{\ddagger}_{OSET}=14.2\times\left(1+\frac{8.8}{4\times 14.2}\right)^2=19.0 \text{ kcal/mol}$$

7.3 Other possible initial steps

The other possible initial steps were thoroughly examined (Figure S2). The computations indicate that the C-Br bond cleavage via oxidative addition and halogen atom transfer pathways is higher in energy compared to the OSET process. Additionally, the formation of a metal-alkyl intermediate followed by the migratory insertion of the C-C double bond into the metal-carbon bond was found to be kinetically infeasible. The radical addition to the metal-bound alkene was also considered, but its energies were significantly higher than those of the Giese addition and OSET process.

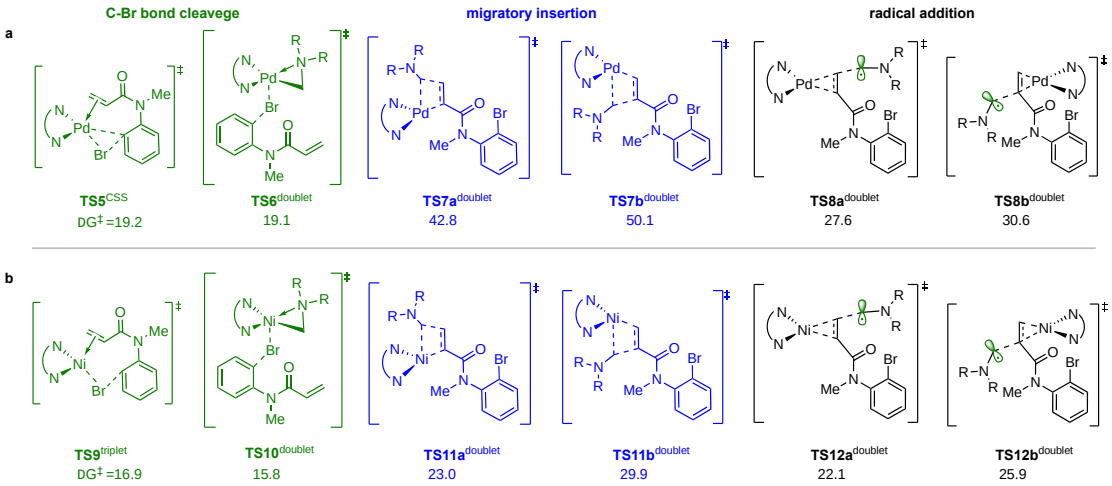


Figure S2. a) Other possible initial steps for Pd-catalyzed reaction. b) Other possible initial steps for Ni-catalyzed reaction. Gibbs free energies are given in kcal/mol.

7.4 Calculated energy profile of Pd-catalyzed reaction

The calculated energy profile of the palladium-catalyzed reaction is given in Figure S3. The computations show that the reaction is initiated by the Giese addition via transition state **TS1**, giving rise to *α*-carbonyl radical **IM1**. The radical addition to the internal carbon atom was found to proceed through transition state **TS1'**, which was calculated to be 7.3 kcal/mol higher in energy than **TS1**. This finding aligns with the experimentally observed regioselectivity and is likely due to the steric repulsion between the internal carbon and the radical.

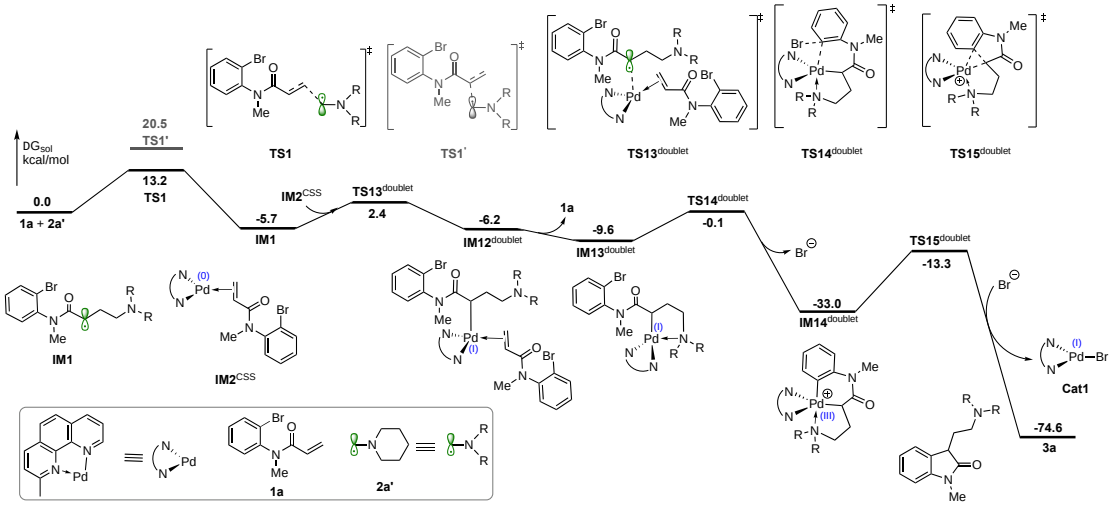


Figure S3. Calculated energy profile of Pd-catalyzed reaction.

Then, the addition of *α*-carbonyl radical **IM1** to the Pd center of **IM2**^{CSS} via transition state **TS13**^{doublet} leads to Pd(I) intermediate **IM12**^{doublet}, from which the dissociation of **1a** gives

intermediate **IM13**^{doublet}. The ensuing C-Br bond cleavage was found to take place via S_N2-type transition state **TS14**^{doublet} to afford cationic Pd(III) intermediate **IM14**^{doublet}, from which the C-C reductive elimination via transition state **TS15**^{doublet} yields the final 5-exo cyclization product **3a**.

7.5 Calculated energy profile of Ni-catalyzed reaction

The calculated energy profile of the nickel-catalyzed reaction is given in Figure S4. Unlike the palladium-catalyzed reaction, the nickel-catalyzed reaction begins with the addition of the *α*-amino radical **2a'** to the Ni center of **IM6**^{CSS} via transition state **TS16**^{doublet} to generate Ni(I) intermediate **IM15**^{doublet}, from which the dissociation of **1a** gives intermediate **IM7**^{doublet}. The subsequent C-Br bond cleavage occur via the OSET pathway, giving rise to **IM17** and **IM16**^{CSS}, from which intermediates **IM5** and **IM8**^{triplet} can be formed. The aryl radical **IM5** then undergoes the intramolecular 5-exo-trig cyclization via transition state **TS2** to generate 5-membered ring radical intermediate **IM9**. The intramolecular 6-endo-trig cyclization was also considered, which was found to take place via transition state **TS2'**. **TS2'** is higher in energy than **TS2** by 3.4 kcal/mol, showing that the 5-membered ring radical intermediate **IM9** should be formed exclusively at this stage.

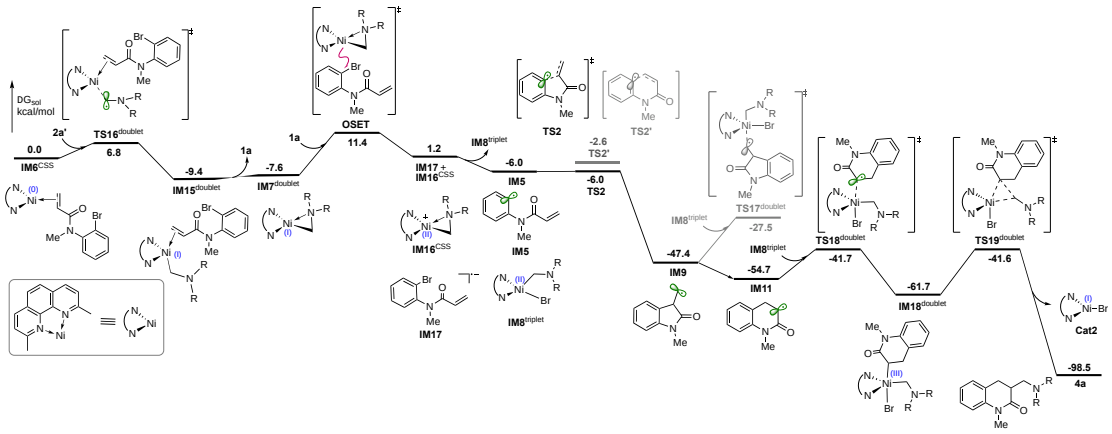


Figure S4. Calculated energy profile of Ni-catalyzed reaction.

Intermediate **IM9** can isomerize to more stable 6-membered ring radical intermediate **IM11** through 1,2-aryl migration (see Figure 4b for details). On the other hand, the addition of **IM9** to the Ni center of **IM8**^{triplet} occurs via transition state **TS17**^{doublet}, which is much higher in energy than the 1,2-aryl migration, in line with the experiments that the 6-endo cyclization

product **4a** was observed. The addition of **IM11** to the Ni center of **IM8**^{triplet} was found to take place via transition state **TS18**^{doublet}, leading to Ni(III) intermediate **IM18**^{doublet}, from which 6-endo cyclization product **4a** can be formed via the C-C reductive elimination through transition state **TS19**^{doublet}.

Table S18. Calculated Energies and Energy Corrections

Stationary point	Single-point energy-TPSS0-D4/def2-QZVP (a.u.)	Thermal correction to Gibbs free energy at 298.15 K (a.u.)
1a	-3091.38444807718	0.139222
2a'	-290.69437958414	0.143778
Br^{-}	-2574.29726132885	-0.016175
TS1	-3382.08070486979	0.305934
TS1'	-3382.06992776635	0.306819
IM1	-3382.11630088241	0.311320
IM2^{CSS}	-3830.52493201032	0.327068
IM3^{doublet}	-1029.83789033273	0.331136
IM4^{CSS}	-3604.03952756485	0.330348
IM5	-517.170691953486	0.139522
IM6^{CSS}	-5250.34074032185	0.356567
IM7^{doublet}	-2449.66122899585	0.35955
IM8^{triplet}	-5023.86763141791	0.354505
TS2	-517.171034040808	0.139856
TS2'	-517.165724529849	0.139972
IM9	-517.237135704632	0.139994
TS3	-517.214488367824	0.140967
IM10	-517.225661483479	0.142881
TS4	-517.215551179086	0.142184
IM11	-517.252018282351	0.143237
TS5^{CSS}	-3830.49379168052	0.326579
TS6^{doublet}	-4121.21465571390	0.496648
TS7a^{doublet}	-4121.17804471657	0.497717
TS7b^{doublet}	-4121.16324151213	0.494645
TS8a^{doublet}	-4121.19999992366	0.495582
TS8b^{doublet}	-4121.19462248541	0.494842
TS9^{triplet}	-5250.30834797571	0.351113
TS10^{doublet}	-5541.03281390115	0.523247
TS11a^{doublet}	-5541.02222004845	0.524136
TS11b^{doublet}	-5541.01084142140	0.523781
TS12a^{doublet}	-5541.02298822052	0.523404

TS12b^{doublet}	-5541.01536842324	0.521909
TS13^{doublet}	-7212.65621239251	0.666400
IM12^{doublet}	-7212.67112585195	0.667507
IM13^{doublet}	-4121.26431645390	0.500570
TS14a^{doublet}	-4121.24995160573	0.501310
TS14b^{doublet}	-4121.23000902217	0.501369
IM14^{doublet}	-1546.99718684172	0.509530
TS15^{doublet}	-1546.96440609518	0.508257
CAT1	-3313.28489661921	0.158481
3a	-808.058257552498	0.317309
TS16^{doublet}	-5541.04700806412	0.523049
IM15^{doublet}	-5541.07487453806	0.525127
IM16^{CSS}	-2449.56062297309	0.363922
IM17	-3091.47108209339	0.134922
TS17^{doublet}	-5541.10051941576	0.521903
TS18^{doublet}	-5541.12973368759	0.528512
IM18^{doublet}	-5541.16448525845	0.531411
TS19^{doublet}	-5541.13055476165	0.529536
CAT2	-4733.13612951020	0.184836
4a	-808.060287138885	0.319823

Cartesian coordinates

1a

C	1.20079700	2.28973800	-0.33268400
C	2.56589500	2.42166400	-0.59688700
C	3.25634500	3.59939600	-0.32779000
C	2.56157900	4.68020900	0.21585200
C	1.19506600	4.57625900	0.48075600
C	0.52379000	3.38708800	0.20839200
H	4.31598300	3.67032800	-0.54473400
H	3.09269500	5.60370300	0.42604300
H	0.65288800	5.42050100	0.89512600
N	0.51248100	1.06455800	-0.57899100
Br	3.54301500	0.92624000	-1.39100500
H	-0.54017400	3.28959700	0.39743400
C	-0.23647100	0.98117100	-1.73955200
O	-0.43948700	1.95936100	-2.44845200
C	-0.75945900	-0.35356100	-2.16284100
H	-1.74358500	-0.31049000	-2.62225500
C	-0.03563200	-1.47532700	-2.19125600
H	0.97534000	-1.51438700	-1.79484400
H	-0.42022600	-2.38566400	-2.64248100
C	0.56753400	0.06501800	0.48589900
H	0.38789700	0.55655500	1.44801500

H	-0.20377400	-0.68644500	0.32418500
H	1.54502800	-0.42992100	0.52448500

2a'

C	-2.07334600	-1.00799400	0.01555900
C	-0.53881500	-0.93437300	-0.01829000
C	-0.53708400	1.21742400	1.10847300
C	-2.07185300	1.23319500	1.18974700
C	-2.62068800	-0.20156000	1.20287900
H	-0.12480600	-1.42223100	0.87556900
H	-0.13547700	-1.45331900	-0.89370200
H	-2.45955500	-0.59254300	-0.92387000
H	-2.39814400	-2.05450500	0.07383000
H	-0.12345300	0.76003200	2.01833800
H	-0.13284900	2.23219200	1.03621600
H	-2.39543800	1.78117400	2.08366300
H	-2.45932300	1.76928200	0.31409100
H	-2.32178900	-0.69321500	2.14103700
H	-3.71712100	-0.19337300	1.18840500
N	-0.05807100	0.44718000	-0.03917400
C	-0.04908400	1.09399500	-1.27346700
H	0.26640800	2.13335600	-1.25582300
H	0.26405300	0.48736700	-2.11849500

TS1

C	1.12450700	2.34435800	-0.20901700
C	2.51478300	2.37818300	-0.34192700
C	3.26056200	3.52101300	-0.06912900
C	2.59506400	4.67723800	0.33793000
C	1.20467200	4.67802100	0.46367000
C	0.48018000	3.52030400	0.19457600
H	4.33852100	3.50813900	-0.18284100
H	3.16699800	5.57598300	0.54869000
H	0.68494800	5.58068200	0.76993500
N	0.38451600	1.15362100	-0.45159700
Br	3.46131000	0.78155800	-0.96794700
H	-0.60069900	3.50587700	0.27617500
C	-0.45368000	1.12923800	-1.56875700
O	-0.68262900	2.15228700	-2.20920200
C	-0.99891100	-0.17390100	-2.00662700
H	-1.91783600	-0.08371900	-2.57898600
C	-0.31068500	-1.33798100	-1.99422800
H	0.61730400	-1.45341400	-1.44699200
H	-0.73202200	-2.24304300	-2.41890000

C	0.34680600	0.18117500	0.63975700
H	0.24191500	0.71209900	1.59263600
H	-0.51271800	-0.47514100	0.50757000
H	1.25768500	-0.42756500	0.68079900
C	4.35561000	-3.36281200	-3.62285300
C	3.23670900	-2.44213400	-3.13334600
C	1.59283000	-3.62214100	-4.52441700
C	2.67328300	-4.57014100	-5.04908600
C	3.79779600	-4.73462400	-4.01995600
H	2.83261000	-2.82267100	-2.17653000
H	3.61693700	-1.43415100	-2.94632500
H	4.84352200	-2.89885200	-4.48954900
H	5.11184400	-3.46198200	-2.83495400
H	1.07280100	-4.08912700	-3.66713700
H	0.83917600	-3.42785400	-5.29418100
H	2.21883200	-5.53869900	-5.28934700
H	3.08391400	-4.15955100	-5.98042900
H	3.40175700	-5.23883700	-3.12630800
H	4.59399100	-5.37389100	-4.41862200
N	2.16794100	-2.34046000	-4.12408500
C	1.31173400	-1.26348600	-4.02213000
H	1.74231800	-0.33248900	-3.67195900
H	0.51371800	-1.21027800	-4.75457200

TS1’

C	0.91364600	2.17339500	-0.37290000
C	2.08251900	2.57343500	-1.02443600
C	2.55995200	3.87826200	-0.95151300
C	1.85251200	4.81473100	-0.19694300
C	0.68249600	4.44146600	0.46649200
C	0.22030900	3.13115600	0.37413500
H	3.46923500	4.15534500	-1.47254600
H	2.21911900	5.83489900	-0.13269200
H	0.12712400	5.17161500	1.04724100
N	0.45762400	0.82373600	-0.42936000
Br	3.08351000	1.26842500	-2.08316800
H	-0.69699600	2.82651300	0.86814100
C	-0.38602700	0.50633100	-1.49089300
O	-0.86813200	1.42685500	-2.15580800
C	-0.66578700	-0.91666800	-1.82913600
H	-1.67004100	-1.02439900	-2.23130200
C	-0.04167200	-2.04572900	-1.33374900
H	0.95263900	-2.02377800	-0.90363600
H	-0.44675900	-3.02765700	-1.55972000

C	0.79408400	-0.00736200	0.72357700
H	0.70963500	0.59811300	1.63217000
H	0.10115100	-0.84462100	0.79007400
H	1.81932700	-0.39518500	0.66308900
C	-2.49393800	-1.33351600	-6.56227500
C	-1.87902500	-1.48038300	-5.16832000
C	-1.43481500	0.93763900	-5.05230500
C	-2.02288800	1.13478200	-6.45075600
C	-3.08382900	0.06912800	-6.75210400
H	-2.67751700	-1.45005700	-4.40508600
H	-1.36876000	-2.44341700	-5.06567500
H	-1.71323400	-1.50956000	-7.31355600
H	-3.26201800	-2.10391100	-6.70099500
H	-2.19392000	1.12558400	-4.27980900
H	-0.62031100	1.63759700	-4.85524300
H	-2.45374900	2.14079600	-6.51871800
H	-1.21758900	1.07256200	-7.19458600
H	-3.93360100	0.20065100	-6.06664800
H	-3.47442200	0.18625300	-7.76975400
N	-0.90859700	-0.42178200	-4.90688000
C	0.08196100	-0.67179000	-3.99810600
H	0.48622200	-1.67945400	-4.01695600
H	0.78171200	0.13690800	-3.82307500

IM1

C	1.17571800	2.30929600	-0.23879500
C	2.56758100	2.42148800	-0.29528200
C	3.23397400	3.57727800	0.09967600
C	2.48613500	4.66434500	0.55267100
C	1.09335200	4.58580200	0.60319100
C	0.44709300	3.41582200	0.21321600
H	4.31532900	3.62830400	0.04351000
H	2.99670600	5.57271700	0.85822800
H	0.51073100	5.43552500	0.94539100
N	0.51849300	1.10439500	-0.61182400
Br	3.62359100	0.92618300	-0.98699900
H	-0.63425100	3.34082400	0.23634100
C	-0.26249300	1.10691600	-1.76692900
O	-0.55096400	2.15629200	-2.34732300
C	-0.66506200	-0.18345900	-2.32812500
H	-1.52573300	-0.11686600	-2.98877700
C	0.24638900	-1.34759300	-2.48154400
H	0.95956200	-1.41652400	-1.65669700
H	-0.32906200	-2.28185600	-2.50612600

C	0.46594400	0.04387200	0.39097200
H	0.23667500	0.47981000	1.37003900
H	-0.33126900	-0.65499300	0.13245200
H	1.41344100	-0.50190000	0.46573400
C	4.24602900	-3.25593900	-3.68324700
C	3.15320100	-2.32434800	-3.15272000
C	1.41889100	-3.61777000	-4.25308600
C	2.44854300	-4.59654200	-4.82505400
C	3.68664600	-4.66351700	-3.92267900
H	2.86136800	-2.65812800	-2.13614900
H	3.53396100	-1.30205800	-3.05599000
H	4.62859000	-2.84624900	-4.62657100
H	5.08072500	-3.28472000	-2.97209200
H	1.02283900	-4.03115600	-3.30317100
H	0.56805600	-3.51435700	-4.93702600
H	1.99225200	-5.58799100	-4.93436400
H	2.73980900	-4.25340800	-5.82571400
H	3.40632400	-5.11014700	-2.95723300
H	4.45135200	-5.31455800	-4.36282400
N	2.01557600	-2.29984500	-4.06686600
C	1.06420000	-1.23424100	-3.81778300
H	1.60855400	-0.28385500	-3.80407700
H	0.35911600	-1.19601800	-4.65655000

IM2^{CSS}

C	1.31590100	0.59412200	-1.41752900
C	2.58099200	0.24727700	-0.93271600
C	2.87844300	-1.04312200	-0.49858600
C	1.90276400	-2.03598700	-0.58533400
C	0.64853500	-1.73558500	-1.11873600
C	0.36333700	-0.43453400	-1.52102100
H	3.86527700	-1.26754500	-0.10961300
H	2.13098300	-3.04244100	-0.24736900
H	-0.10982900	-2.50737300	-1.20599200
N	1.00516300	1.89372400	-1.90698600
Br	3.99397400	1.59149100	-0.85603900
H	-0.60665700	-0.18435100	-1.93694300
C	-0.04195500	2.68239000	-1.38297900
O	-0.73373900	3.34225400	-2.15889000
C	-0.24194000	2.77512300	0.08364100
H	-1.04571000	3.47552500	0.30058200
C	0.75753600	2.54143100	1.07618300
H	1.77343000	2.28981800	0.78566100
H	0.69368900	3.10783300	2.00518900

C	1.26563900	2.05785700	-3.33946800
H	1.19692400	3.11565500	-3.59164500
H	2.27213000	1.68964100	-3.55355200
H	0.54046900	1.50760600	-3.95541500
C	-4.13548900	-1.24374400	-0.70672600
C	-3.91017800	-2.54294400	-0.30480900
C	-2.81746900	-2.83073400	0.54126500
C	-2.00559700	-1.74025100	0.93737400
C	-3.26994500	-0.20905200	-0.28035800
C	-2.49087600	-4.15585000	0.98190000
C	-0.86432000	-1.98047100	1.79024500
C	-0.55661700	-3.30543100	2.18957000
C	-1.40200000	-4.38515700	1.76817800
C	0.59460900	-3.49726200	2.98428500
H	0.86204400	-4.50021900	3.30554100
C	1.36412300	-2.40671100	3.33696500
C	0.97523000	-1.12654000	2.90243400
H	-3.12692700	-4.97759200	0.66464500
H	-4.96832100	-1.00068400	-1.35811800
H	-4.56077000	-3.34877500	-0.63396600
H	-1.15285900	-5.39271900	2.08902900
H	2.25715100	-2.51847800	3.94278500
N	-0.10372100	-0.91479800	2.15621100
N	-2.23195500	-0.46960400	0.51775700
Pd	-0.56081200	0.93272500	1.04556400
C	-3.47145000	1.21330500	-0.71535000
H	-3.46918500	1.87465000	0.15656400
H	-2.64843100	1.55146000	-1.35453500
H	-4.41219500	1.33270500	-1.26010800
H	1.55291600	-0.24516300	3.15918000

IM3doublet

C	5.04498300	0.20488000	-0.91458100
C	4.12907200	-1.94816300	-0.78707600
C	5.24188500	-2.51687600	-1.39461400
C	6.30877200	-1.67993800	-1.77820900
C	6.22441200	-0.30925800	-1.54338000
C	4.89794500	1.57495700	-0.65498700
C	3.56713800	3.32957300	0.20916300
C	4.54744300	4.25856100	-0.12308500
C	5.74364400	3.84338000	-0.73964700
C	5.93295600	2.49236200	-1.01425400
H	5.27615200	-3.58747800	-1.56434200
H	7.19427700	-2.09172700	-2.25479200

H	4.37622800	5.30606000	0.09979100
H	6.51287300	4.56462100	-1.00117800
N	3.72176200	2.00688700	-0.04308600
N	4.00557800	-0.63546400	-0.54106900
C	2.28927900	3.76703700	0.86620400
H	2.17075000	3.28145700	1.84134100
H	2.27478900	4.85139700	1.00719500
H	1.42510000	3.47602000	0.25879900
C	7.25488500	0.63040600	-1.89578100
C	7.11435100	1.96050800	-1.64308100
H	8.15558100	0.25182500	-2.37268900
H	7.90269600	2.65779400	-1.91613300
H	3.28808900	-2.56451600	-0.47745800
Pd	2.41475700	0.44096500	0.36781400
C	-1.57491200	-1.42272000	0.60779900
C	-0.18792100	-1.13257400	0.02637900
C	0.85658600	-1.42533700	2.23233700
C	-0.50309900	-1.72229500	2.87142000
C	-1.47132500	-2.32492600	1.84474700
H	0.28012000	-2.05656300	-0.33298600
H	-0.23222100	-0.43575400	-0.81304400
H	-2.05312500	-0.47233300	0.87987600
H	-2.19877600	-1.88725800	-0.16485100
H	1.33720700	-2.35223900	1.89783300
H	1.53823100	-0.93205000	2.92815000
H	-0.36083900	-2.40138700	3.72029300
H	-0.91932900	-0.78838100	3.27209000
H	-1.10518700	-3.31605600	1.54022100
H	-2.45973200	-2.47728600	2.29267500
N	0.71868400	-0.55170400	1.04375100
C	0.65437800	0.86765300	1.26357800
H	0.66474700	1.16025200	2.31334400
H	-0.11224000	1.37806100	0.68086100

IM4[CSS]

Br	1.27369400	2.06801300	-0.55037800
C	-1.61434500	-0.35920300	-3.65595700
C	-2.40533900	-1.07741000	-2.79106200
C	-1.84443300	-1.59694400	-1.60800400
C	-0.46378400	-1.36548800	-1.36317400
C	-0.25400500	-0.14996600	-3.35201500
C	-2.64121900	-2.32707600	-0.66726900
C	0.11648300	-1.89227800	-0.13730000
C	-0.71970100	-2.59023200	0.78157000

C	-2.10418700	-2.80184100	0.48714600
C	-0.13578500	-3.05508600	1.97980400
H	-0.75456400	-3.58394400	2.69996200
C	1.20221000	-2.82714200	2.22191500
C	1.94561600	-2.14287200	1.24161800
H	-3.69199800	-2.47981900	-0.89721900
H	-2.02159500	0.06360600	-4.56779300
H	-3.45882100	-1.24217300	-2.99992500
H	-2.71306700	-3.34331900	1.20582900
H	1.67923100	-3.16227500	3.13728900
N	1.42951400	-1.69913700	0.10929600
N	0.30043200	-0.65352500	-2.24061300
C	0.60173500	0.68418800	-4.25954300
H	0.88485700	1.60883100	-3.74320900
H	1.52816200	0.15519500	-4.50606400
H	0.06779100	0.93489500	-5.18136700
C	5.04369400	0.99881200	0.28008600
C	5.07465300	-0.25022900	-0.59765500
C	4.98441100	1.11468800	-2.64077700
C	4.96135500	2.40108200	-1.81816800
C	5.64847700	2.19927800	-0.46093200
H	6.11223500	-0.53954300	-0.82943000
H	4.58015700	-1.09516600	-0.11407300
H	4.00207600	1.21501800	0.54325300
H	5.59484500	0.79466000	1.20604400
H	6.01873800	0.82682300	-2.88918600
H	4.42025300	1.22550400	-3.56925000
H	5.45794800	3.19394700	-2.39015100
H	3.91773400	2.69597800	-1.66247900
H	6.72570500	2.03252500	-0.61249800
H	5.54640800	3.10424300	0.14727600
N	4.37119000	0.00381800	-1.87560800
C	3.81221300	-1.09150200	-2.57928100
H	3.94018000	-1.05478700	-3.66042800
H	3.99538500	-2.06794900	-2.13351300
H	3.00585500	-1.94847500	1.39431000
Pd	2.28874500	-0.01540400	-1.76674000

IM5

C	-4.63709700	-2.38837600	1.02063400
C	-4.91561900	-1.05655600	0.74639900
C	-6.16123200	-0.51037400	0.57092900
C	-7.26696900	-1.36523800	0.72074000
C	-7.05142100	-2.71057800	1.02041000

C	-5.76161500	-3.22565400	1.16702400
H	-6.29437900	0.54406700	0.34428900
H	-8.27520300	-0.97723400	0.60761800
H	-7.89904900	-3.37927800	1.13820900
N	-3.32552200	-2.86995800	1.19229500
H	-5.62759200	-4.27900100	1.38981600
C	-2.19330400	-2.18506900	0.74712100
O	-1.07529400	-2.46960900	1.16185000
C	-2.39573800	-1.13890100	-0.29721400
H	-3.25069300	-1.22053800	-0.96009500
C	-1.49418100	-0.16420600	-0.45291400
H	-0.63247900	-0.10044800	0.20469900
H	-1.59397700	0.58334800	-1.23381100
C	-3.11933600	-4.05420300	2.02200400
H	-3.69643800	-3.97104600	2.94813800
H	-3.42468400	-4.96388400	1.49182100
H	-2.05699200	-4.11032900	2.25140100

IM6^{CSS}

C	1.24476200	0.38539900	-1.24799400
C	2.48889000	0.03108500	-0.71090900
C	2.77868400	-1.27056100	-0.30838700
C	1.81788600	-2.26823900	-0.47332300
C	0.58607100	-1.95885800	-1.05064500
C	0.30860100	-0.64802200	-1.42704300
H	3.74720800	-1.49969800	0.12183000
H	2.03808300	-3.28239700	-0.15462000
H	-0.16119000	-2.73300800	-1.19442200
N	0.94906100	1.69439100	-1.71635500
Br	3.88173400	1.38353800	-0.51157700
H	-0.64452400	-0.39256800	-1.87742400
C	-0.18419400	2.41076500	-1.25580000
O	-0.86003300	3.03884900	-2.07341000
C	-0.47626800	2.43753200	0.18912600
H	-1.32268100	3.09419300	0.38480400
C	0.51255600	2.24506100	1.22143100
H	1.55942000	2.13946600	0.94703200
H	0.37436900	2.80408500	2.15038800
C	1.30686200	1.90947500	-3.12048900
H	1.20919200	2.97036300	-3.34935100
H	2.34217100	1.59225100	-3.26981700
H	0.65433100	1.34724600	-3.80327000
C	-4.17647900	-1.19326100	-0.58108000
C	-3.97276700	-2.49871900	-0.18871900

C	-2.85883000	-2.81098500	0.61922900
C	-2.00609000	-1.74054100	0.97443300
C	-3.27060000	-0.17566400	-0.19967400
C	-2.54831000	-4.13665700	1.06790400
C	-0.85114300	-1.98852800	1.79267500
C	-0.56313000	-3.30845900	2.20857300
C	-1.44175700	-4.37566900	1.82767600
C	0.60535100	-3.49885200	2.97523800
H	0.87081700	-4.49522700	3.31787900
C	1.39424800	-2.41017700	3.27609600
C	1.03922700	-1.11555300	2.83196800
H	-3.21115100	-4.94883800	0.78287500
H	-5.02960400	-0.92740100	-1.19611300
H	-4.65811500	-3.28609100	-0.49056200
H	-1.20455600	-5.38296400	2.15846500
H	2.29888300	-2.52825700	3.86317600
N	-0.06786500	-0.91284600	2.10384600
N	-2.19782800	-0.45918400	0.55124200
C	1.90789800	0.06111100	3.15857300
H	2.66251900	-0.20609600	3.90390800
H	2.41360600	0.41733000	2.25582800
H	1.30465700	0.89374900	3.52799100
C	-3.49116600	1.24430700	-0.62925300
H	-3.44736000	1.91071600	0.23709100
H	-2.71408500	1.58746300	-1.31993600
H	-4.46429000	1.35419200	-1.11599600
Ni	-0.62114500	0.71387200	1.08467700

IM7[doublet]

C	4.99307600	0.14869700	-0.87422400
C	4.03944400	-1.99586100	-0.98008200
C	5.22552600	-2.51927500	-1.48773200
C	6.34260300	-1.68859200	-1.68356900
C	6.23630100	-0.33259000	-1.38659200
C	4.81500700	1.50876800	-0.58895900
C	3.36010200	3.22068300	0.12963600
C	4.36123500	4.16743400	-0.07228100
C	5.63317600	3.78420900	-0.52972400
C	5.87475900	2.44110400	-0.80200400
H	5.27258700	-3.57452900	-1.73448000
H	7.27342400	-2.08980800	-2.07476400
H	4.14128900	5.21001000	0.12992300
H	6.41612500	4.52180000	-0.68221200
N	3.56445900	1.89805900	-0.10388300

N	3.90619600	-0.69031200	-0.64693400
C	2.01026000	3.66887400	0.61422200
H	1.79339800	3.26611400	1.60888300
H	1.96707000	4.76023100	0.66779000
H	1.21981900	3.31843900	-0.05671300
C	7.30038700	0.61612200	-1.57582100
C	7.12754900	1.93701000	-1.29722100
H	8.25127200	0.25151000	-1.95648600
H	7.93830600	2.64468900	-1.45169900
C	-1.50651500	-1.28048900	0.79693000
C	-0.16636900	-1.16698600	0.06366600
C	1.06864700	-1.39356000	2.17041500
C	-0.23660400	-1.52037000	2.96179000
C	-1.35206200	-2.10231400	2.08378400
H	0.17103300	-2.15712900	-0.25769200
H	-0.24158000	-0.53646600	-0.82581800
H	-1.86981300	-0.27378100	1.04129500
H	-2.24594400	-1.73673500	0.12805600
H	1.42742400	-2.38532600	1.87491600
H	1.85749900	-0.91971000	2.75948400
H	-0.06357900	-2.14976900	3.84275700
H	-0.53239200	-0.52859300	3.32785300
H	-1.10214600	-3.14075700	1.82181900
H	-2.29842600	-2.13441400	2.63562500
N	0.88684100	-0.59440900	0.93462400
C	0.85818400	0.84224700	1.11165200
H	0.91893900	1.16002600	2.15390800
H	0.04488400	1.33323600	0.57528500
C	2.84125200	-2.88397800	-0.80518700
H	2.52342100	-2.91452900	0.24181300
H	1.99783500	-2.50634400	-1.39404400
H	3.05893200	-3.90561000	-1.12781600
Ni	2.42175400	0.37013000	0.20242300

IM8[triplet]

Br	0.72487000	3.17442000	-1.31961500
C	-1.62959000	-1.18477000	-4.05622500
C	-2.12962500	-2.14667800	-3.20129400
C	-1.66266100	-2.21148400	-1.87066600
C	-0.68888000	-1.25858000	-1.49456000
C	-0.65057100	-0.27040800	-3.60634700
C	-2.11320200	-3.16907700	-0.90170800
C	-0.17073700	-1.25581200	-0.15414300
C	-0.62980000	-2.21259000	0.77891800

C	-1.61620100	-3.17024500	0.36919400
C	-0.06973800	-2.15005400	2.07370200
H	-0.38844300	-2.86072800	2.83148600
C	0.87604100	-1.18805000	2.36444300
C	1.28738700	-0.26544300	1.37398400
H	-2.86139100	-3.89697300	-1.20211800
H	-1.98001700	-1.11744100	-5.08056100
H	-2.88075500	-2.85399100	-3.54209300
H	-1.96247000	-3.89963200	1.09586500
H	1.31604000	-1.12445400	3.35382500
N	0.75820600	-0.31673700	0.15008700
N	-0.20345800	-0.32472800	-2.35055500
C	2.32684100	0.78297900	1.62015600
H	3.15771400	0.62740800	0.91617800
H	1.91435600	1.77758500	1.41203300
H	2.69504600	0.75078000	2.64887100
C	-0.06804900	0.79012400	-4.49333100
H	-0.18937800	1.77666700	-4.03155500
H	1.00931000	0.62796300	-4.61572300
H	-0.53887900	0.78978700	-5.47958600
Ni	1.26813900	0.82069900	-1.48380400
C	6.25344200	-0.38401800	-0.28512000
C	5.13657200	-0.76468600	-1.26032700
C	4.52884200	1.54752300	-1.59153100
C	5.62587300	2.02405500	-0.63723200
C	6.78411500	1.02117100	-0.59057700
H	5.55604400	-0.85534200	-2.28478500
H	4.72060300	-1.74396100	-0.99762500
H	5.85348000	-0.41217300	0.73755500
H	7.05955600	-1.12641500	-0.34060200
H	4.92044600	1.54810400	-2.63158700
H	3.68046300	2.23845200	-1.57025700
H	5.97939500	3.01279200	-0.95393500
H	5.19706500	2.14140300	0.36710000
H	7.28908800	1.00918500	-1.56748700
H	7.53373800	1.32381400	0.15095700
N	4.04689000	0.21324500	-1.23433100
C	2.89543400	-0.17974900	-2.04386600
H	3.10317500	-0.04141500	-3.12782500
H	2.70829800	-1.24950700	-1.88177500

TS2

C	-4.59930100	-2.45855500	0.99329900
C	-4.77745400	-1.17240200	0.50346400

C	-5.99000600	-0.56433100	0.29957800
C	-7.14451900	-1.28603100	0.65309000
C	-7.01486200	-2.57578200	1.16841600
C	-5.76115800	-3.17068700	1.33894900
H	-6.06224500	0.44310900	-0.10208200
H	-8.12625700	-0.83811400	0.52777800
H	-7.90302100	-3.13817800	1.44149800
N	-3.30427400	-2.98037000	1.14603300
H	-5.69186600	-4.17886500	1.73388400
C	-2.19813300	-2.26517400	0.69900800
O	-1.05956700	-2.53973900	1.05535900
C	-2.48038700	-1.16401000	-0.27919500
H	-3.09556800	-1.40521200	-1.14225400
C	-1.80029400	-0.00388700	-0.22145400
H	-1.12347600	0.20316600	0.60169800
H	-1.92227600	0.76366800	-0.97909700
C	-3.08901900	-4.16899600	1.95890300
H	-3.54152000	-4.04456200	2.94888300
H	-3.52508000	-5.05139200	1.47716500
H	-2.01353200	-4.30172200	2.06344000

TS2’

C	-4.57283500	-2.48511600	0.81753200
C	-4.84264100	-1.39544200	-0.00010200
C	-6.07668700	-0.82225300	-0.18771900
C	-7.17370000	-1.38687800	0.48208400
C	-6.96289100	-2.48905000	1.30908700
C	-5.68822600	-3.03309300	1.48469600
H	-6.20569600	0.03536800	-0.84351200
H	-8.16912400	-0.97091500	0.35397000
H	-7.79921900	-2.93700200	1.83789900
N	-3.27622100	-3.04235600	0.99292400
H	-5.56751100	-3.87778800	2.15299000
C	-2.08507800	-2.31988900	0.90157200
O	-1.05662700	-2.71390600	1.44032500
C	-2.06628800	-1.07388700	0.09266600
H	-1.52283800	-0.24631000	0.53893200
C	-2.58339800	-0.99103900	-1.14196400
H	-3.03087900	-1.84750300	-1.63502000
H	-2.49839500	-0.08201800	-1.73086300
C	-3.17294700	-4.33821400	1.66156500
H	-3.39007000	-4.26369700	2.73434600
H	-3.87333900	-5.03888400	1.20010000
H	-2.15215800	-4.69595100	1.54579200

IM9

C	-4.54395300	-2.57801900	1.02445600
C	-4.49642000	-1.43129000	0.21472800
C	-5.65636400	-0.72177800	-0.04689500
C	-6.86951500	-1.17173400	0.49750100
C	-6.90173500	-2.31666700	1.29416700
C	-5.73420400	-3.04082400	1.57288800
H	-5.62460300	0.17159700	-0.66452000
H	-7.78634900	-0.62563600	0.29774300
H	-7.84590100	-2.65613900	1.71043100
N	-3.25747000	-3.11633400	1.16476700
H	-5.76306900	-3.92779100	2.19744200
C	-2.31097300	-2.37476000	0.47365400
O	-1.12156500	-2.61790100	0.42090200
C	-3.06767200	-1.19211000	-0.21162100
H	-2.93651200	-1.34996000	-1.29355000
C	-2.50009300	0.13086100	0.17528500
H	-2.92646500	0.67880300	1.00822900
H	-1.52603500	0.42365000	-0.20018500
C	-2.92819200	-4.29280600	1.93876400
H	-3.19623600	-4.15262900	2.99261500
H	-3.45562500	-5.17305400	1.55306700
H	-1.85136400	-4.44624300	1.85319300

TS3

C	0.29521000	0.60467600	0.07634600
C	0.54771400	-0.80146100	-0.11418800
C	1.88212200	-1.21451100	-0.38802600
C	2.90533900	-0.28272100	-0.28336400
C	2.64251300	1.06388300	0.02429700
C	1.31901700	1.52260200	0.18082100
H	2.09000300	-2.25128000	-0.63522700
H	3.93025000	-0.59794800	-0.45719600
H	3.46333500	1.76914100	0.10510200
N	-1.08329400	0.82155200	0.05422100
H	1.11292600	2.57649600	0.34023900
C	-1.79358300	-0.34054600	-0.24555300
O	-2.99302400	-0.40361800	-0.43905000
C	-0.78357100	-1.47997100	-0.23675700
H	-0.96540000	-2.27567400	-0.95691300
C	-0.35844300	-1.84212000	1.14498100
H	-0.71065200	-1.27970200	2.00025100
H	0.17341300	-2.76986600	1.31215400

C	-1.71861000	2.11576700	0.17322500
H	-1.50925300	2.56079800	1.15229800
H	-1.36188300	2.79558300	-0.60947500
H	-2.79288200	1.96238500	0.06037300

IM10

C	-4.49945800	-2.41089600	1.18397600
C	-4.44951500	-1.20479700	0.32482700
C	-5.73730600	-0.76318300	-0.22177400
C	-6.89822400	-1.27155000	0.30508800
C	-6.89061500	-2.28270400	1.30011000
C	-5.67594600	-2.88700800	1.70421000
H	-5.74937500	0.02000200	-0.97390900
H	-7.85328300	-0.89586600	-0.05239700
H	-7.82870200	-2.64649500	1.70553200
N	-3.23474700	-2.98258700	1.22650500
H	-5.68532600	-3.75126700	2.36139200
C	-2.37457700	-2.44783200	0.25628200
O	-1.28758400	-2.91191000	-0.03667000
C	-3.05102500	-1.23456600	-0.31736700
H	-2.84213700	-0.96882800	-1.34772100
C	-3.36665800	-0.17675000	0.70264200
H	-2.91265900	-0.23568800	1.68828600
H	-3.53446300	0.82918100	0.32979700
C	-2.90445500	-4.18403000	1.96401000
H	-3.02747100	-4.02116600	3.03980900
H	-3.54712600	-5.01699100	1.65437900
H	-1.86479500	-4.42717900	1.74086400

TS4

C	-4.48113400	-2.32599800	1.23779900
C	-4.49704000	-1.08791000	0.47474900
C	-5.76290200	-0.64530500	-0.03648400
C	-6.92332100	-1.30286000	0.32361900
C	-6.88752200	-2.41323400	1.18957700
C	-5.65922300	-2.93692900	1.62855600
H	-5.79719000	0.25449700	-0.64376900
H	-7.87990500	-0.93692400	-0.03819900
H	-7.81139400	-2.89919600	1.48633200
N	-3.20342000	-2.87444300	1.32646200
H	-5.63402500	-3.84780800	2.21758200
C	-2.38559500	-2.49657400	0.23864400
O	-1.40840400	-3.13837500	-0.12231400
C	-2.89902700	-1.25768800	-0.36901400

H	-2.75253500	-1.07316100	-1.42594800
C	-3.29928100	-0.18573100	0.57490800
H	-2.79373800	-0.14311400	1.54113200
H	-3.45073700	0.79834000	0.13508700
C	-2.92764700	-4.10632300	2.04183000
H	-3.14918000	-3.98149200	3.10578800
H	-3.52268800	-4.93993800	1.64683900
H	-1.87110400	-4.33659200	1.90438900

IM11

C	-4.49315300	-2.51823100	0.84893400
C	-4.60638000	-1.39522900	0.00341500
C	-5.87059500	-0.87924900	-0.28287500
C	-7.02969100	-1.44355500	0.24453600
C	-6.91563600	-2.55353100	1.08011000
C	-5.66527200	-3.08658400	1.38057100
H	-5.93914400	-0.01257300	-0.93685000
H	-8.00243700	-1.02438400	0.00726900
H	-7.80292100	-3.01377100	1.50521500
N	-3.23550500	-3.06824700	1.16131400
H	-5.60551700	-3.94867300	2.03185500
C	-2.02554400	-2.55770300	0.66394400
O	-0.94027500	-3.06979900	0.95854400
C	-2.11378500	-1.41007200	-0.20411600
H	-1.16596000	-1.03622900	-0.57398600
C	-3.38104800	-0.74794600	-0.59204800
H	-3.46369700	-0.72536800	-1.69323700
H	-3.34188500	0.31873100	-0.30725400
C	-3.15161900	-4.22731000	2.03932200
H	-3.57305800	-3.99962900	3.02502400
H	-3.69108000	-5.07983500	1.61117400
H	-2.09756500	-4.47663600	2.14144000

TS5^{CSS}

C	-2.83874500	1.16993800	0.39101100
C	-1.47670300	1.20150300	0.76692900
C	-0.91496800	2.39074000	1.25955000
C	-1.65952200	3.56836900	1.25412000
C	-2.98740400	3.56386100	0.81810100
C	-3.56227800	2.36419200	0.39503000
H	0.09472600	2.37579500	1.65059600
H	-1.20589600	4.48489200	1.62277000
H	-3.57446300	4.47673900	0.82381700
N	-3.46630200	-0.03654100	-0.01744200

Br	-0.82691700	-0.55612300	1.94250900
H	-4.59132300	2.33704600	0.04664700
C	-2.93921100	-0.88434600	-0.97714700
O	-3.33381100	-2.04534200	-1.08268100
C	-1.88714600	-0.38023900	-1.91056900
H	-1.55973000	-1.18928700	-2.55884300
C	-1.62884500	0.94037800	-2.32144300
H	-2.20463400	1.78195900	-1.95283000
H	-1.14117500	1.09737200	-3.28107300
C	-4.49486600	-0.58582500	0.86813300
H	-4.03926200	-1.06193000	1.74501100
H	-5.15147900	0.22114700	1.20070700
H	-5.06473900	-1.33254700	0.31673600
C	2.56574500	-3.40606700	-0.01203000
C	3.78470400	-2.82375000	0.25866100
C	3.91773500	-1.42037700	0.19477900
C	2.75756000	-0.67740500	-0.14425100
C	1.45924500	-2.59510500	-0.35941100
C	5.15516900	-0.74396400	0.44913800
C	2.84175300	0.76832400	-0.20043900
C	4.09062500	1.40296300	0.04184900
C	5.24122600	0.61223800	0.36886300
C	4.14065600	2.80971500	-0.04777000
H	5.08273500	3.32175800	0.12839800
C	2.99364100	3.51486000	-0.35469800
C	1.79806300	2.80600600	-0.55533600
H	6.02732000	-1.34007500	0.70331100
H	2.44106600	-4.48287900	0.03289700
H	4.64709700	-3.43117600	0.52035500
H	6.18227800	1.12182300	0.55523200
H	2.99813100	4.59680700	-0.43385600
N	1.71983400	1.48137100	-0.47923700
N	1.57340900	-1.26883200	-0.42006300
Pd	-0.20674200	0.32754400	-0.80146500
C	0.12054400	-3.19510800	-0.67791600
H	-0.17842900	-2.93851500	-1.69931100
H	0.13761500	-4.28392400	-0.58104300
H	-0.64875000	-2.78827300	-0.01588300
H	0.86623900	3.32282200	-0.76193900

TS6[doublet]

C	-2.30052400	2.35718800	1.41411600
C	-2.23456900	2.57088100	0.04285500
C	-3.29408300	3.12938500	-0.65406200

C	-4.44568500	3.51196600	0.04552100
C	-4.52544800	3.31377600	1.42683900
C	-3.45439600	2.73833000	2.11183300
H	-3.23277600	3.26679400	-1.73121000
H	-5.28089200	3.96114200	-0.48763600
H	-5.42136200	3.60255600	1.96915100
N	-1.19416800	1.79192700	2.13581000
Br	-0.50789200	1.40152300	-1.10440700
H	-3.50119800	2.57363000	3.18568900
C	-1.00888400	0.44310200	2.28630900
O	-0.00868300	-0.02704300	2.84373600
C	-2.11027100	-0.42865500	1.77766600
H	-2.73939700	-0.04624900	0.98228000
C	-2.30977900	-1.63871200	2.30147100
H	-1.67660200	-2.00216600	3.10357500
H	-3.09978200	-2.29208600	1.94365600
C	-0.12488900	2.70890400	2.50320100
H	0.55645800	2.18738100	3.17457500
H	0.41700100	3.04159800	1.60885700
H	-0.55034800	3.58429900	3.00330100
C	-1.06410300	-1.96601000	-4.49884800
C	-1.77595200	-2.99405700	-3.89822200
C	-1.46743600	-3.35995600	-2.57718400
C	-0.42342800	-2.65445800	-1.92551100
C	-0.03320400	-1.31202500	-3.80649400
C	-2.14959500	-4.40673100	-1.87078600
C	-0.11161100	-2.95944000	-0.56677000
C	-0.79480300	-4.00713700	0.10785100
C	-1.81963400	-4.72731000	-0.58845700
C	-0.43861800	-4.26807400	1.44308900
H	-0.93546300	-5.06971500	1.98281200
C	0.51794200	-3.47812700	2.06021100
C	1.11340000	-2.43732300	1.33481200
H	-2.94074900	-4.94271800	-2.38800000
H	-1.28727500	-1.65820600	-5.51460300
H	-2.56729100	-3.51219100	-4.43215400
H	-2.33954900	-5.52487300	-0.06481000
H	0.79172800	-3.62610800	3.09875600
N	0.83712600	-2.19476900	0.05613200
N	0.29485100	-1.66454600	-2.54927500
C	0.71941000	-0.18248000	-4.43776900
H	0.51897100	0.73988400	-3.87825900
H	1.79767100	-0.36438100	-4.39518500
H	0.41847800	-0.04339300	-5.47958300

C	4.61642700	-0.74271900	0.95437800
C	4.61156500	-0.17263900	-0.46115200
C	3.05716500	1.61953900	0.19765200
C	3.03104900	1.11466600	1.63704600
C	4.31574100	0.35235500	1.98769000
H	5.41982800	0.56657900	-0.57801300
H	4.74660400	-0.95705200	-1.20876600
H	3.86316200	-1.53696800	1.00828600
H	5.59127200	-1.20496400	1.14957900
H	3.85243400	2.36907000	0.06034300
H	2.09907100	2.05918900	-0.08279000
H	2.90897400	1.97525900	2.30392300
H	2.14494000	0.48725200	1.78183800
H	5.16095900	1.05532400	2.01433200
H	4.23602700	-0.08331700	2.99011800
N	3.32565000	0.50267400	-0.74109100
C	2.92635000	0.65193500	-2.09355800
H	2.46957600	1.60940400	-2.33298500
H	3.64901700	0.28994000	-2.82451900
H	1.82330500	-1.77309400	1.80854700
Pd	1.69454800	-0.71963800	-1.26936300

TS7a$^{\text{doublet}}$

C	7.57971000	6.70452300	-0.67200600
C	6.24805400	6.65124400	-0.23108200
C	5.83815300	5.81943700	0.80769700
C	6.77345400	4.98152100	1.41778600
C	8.10103100	4.99430000	0.98840400
C	8.49644700	5.85373100	-0.03359600
H	4.79950300	5.81224100	1.11789000
H	6.45905200	4.32374800	2.22249100
H	8.83487300	4.34246600	1.45283900
N	8.00425300	7.62874400	-1.65569700
Br	4.89003300	7.72672700	-1.13245000
H	9.52966200	5.87945200	-0.35703300
C	8.71331500	7.29569600	-2.82493100
O	9.44662500	8.15688500	-3.32221400
C	8.53495900	5.98846200	-3.46941100
H	9.04995800	5.99085900	-4.42881200
C	7.33903800	5.17636600	-3.37540700
H	6.48677500	5.65058000	-2.89955400
H	7.06695100	4.63386000	-4.27766200
C	8.17376300	9.00939600	-1.18948800
H	9.16772100	9.16182900	-0.74889700

H	8.06624300	9.68956800	-2.03420300
H	7.40983100	9.22612000	-0.44094100
C	3.81983000	3.54619900	-1.99570100
C	4.83401600	3.19069200	-3.09585600
C	5.84608000	1.47471700	-1.73248200
C	4.88588000	1.75601800	-0.56681300
C	3.56310100	2.33519500	-1.08809700
H	4.40715500	2.41472800	-3.74590100
H	5.04000600	4.05653200	-3.72600900
H	4.20392600	4.38380700	-1.39999700
H	2.88608700	3.89179200	-2.45630500
H	5.41624100	0.69971600	-2.38401000
H	6.80420500	1.09799900	-1.36175800
H	4.70934600	0.83281000	-0.00017200
H	5.35980400	2.47080700	0.11925800
H	3.03637500	1.56009500	-1.66470800
H	2.90488500	2.60830500	-0.25433500
N	6.10460700	2.66684700	-2.56688800
C	11.08368700	1.67578900	-2.47986600
C	8.94269900	1.01547700	-3.09784300
C	9.30057600	-0.33900000	-3.06958300
C	10.60295600	-0.68555900	-2.74046900
C	11.53523000	0.32741600	-2.44580700
C	12.00159800	2.75243100	-2.23236300
C	12.39241700	5.04829600	-2.09277800
C	13.76470400	4.81507600	-1.87226600
C	14.25289600	3.52348200	-1.80849200
C	13.36879200	2.44671400	-1.99713400
H	8.56421000	-1.09378600	-3.32535100
H	10.91947000	-1.72485700	-2.72385700
H	14.42467700	5.66522600	-1.73633100
H	15.30605200	3.33078300	-1.62300200
N	11.52471200	4.03510600	-2.24690900
N	9.79934800	1.99473700	-2.80363800
C	11.86555700	6.44947800	-2.15479100
H	11.28628200	6.61814200	-3.06518300
H	11.18626300	6.65337700	-1.32096200
H	12.67963200	7.17800800	-2.11108500
C	12.91363000	0.05810200	-2.15550600
C	13.79354600	1.07708500	-1.95396500
H	13.24419200	-0.97642200	-2.12332000
H	14.84210700	0.87172900	-1.75581700
C	6.93941200	3.62866000	-1.92485500
H	6.44027000	4.36637700	-1.30605500

H	7.70284400	3.12419200	-1.33341100
H	7.94132100	1.33839900	-3.36996300
Pd	9.30647100	4.14818800	-2.70648400

TS7b[doublet]

C	7.15177200	8.10746600	-1.18545800
C	7.84987300	9.31721700	-1.11990900
C	7.41634400	10.38821600	-0.34359200
C	6.23345200	10.25994400	0.38329900
C	5.50483900	9.07043500	0.32533700
C	5.96391800	8.00738800	-0.44645500
H	7.98882700	11.30849700	-0.31960600
H	5.88281600	11.09265500	0.98589800
H	4.57797300	8.97056300	0.88223500
N	7.65233100	7.00853800	-1.93552600
Br	9.48296800	9.55808900	-2.17688900
H	5.39889400	7.08566600	-0.51395800
C	6.82098800	6.46513400	-2.93594400
O	5.66586500	6.87191800	-3.07319700
C	7.38714600	5.45677100	-3.84576400
H	6.62519100	5.03720500	-4.49194400
C	8.72233600	5.50382500	-4.34279600
H	9.33510800	6.33526000	-3.99297400
H	8.80101500	5.33521300	-5.42835400
C	8.70078900	6.24453900	-1.26091700
H	8.99856300	5.39514100	-1.87242100
H	9.57706200	6.87266000	-1.07989100
H	8.34364300	5.87664100	-0.28764000
C	11.20516700	1.60894300	-2.36803300
C	10.15243000	0.53536600	-4.12725500
C	10.51156800	-0.73120900	-3.63435800
C	11.17194200	-0.81298400	-2.42302100
C	11.52434600	0.37320000	-1.74480500
C	11.66670900	2.84401900	-1.77551600
C	12.01045100	5.13122000	-1.99729300
C	12.54716000	5.19670900	-0.69027600
C	12.68150800	4.04398800	0.05648000
C	12.27160300	2.80963100	-0.49408000
H	10.22998800	-1.62194300	-4.18587700
H	11.41572300	-1.77496400	-1.98073300
H	12.88974200	6.15185600	-0.30389200
H	13.12688900	4.06892500	1.04737800
N	11.54795300	3.98566600	-2.50294800
N	10.46597800	1.67337100	-3.51111400

C	11.97404500	6.34553100	-2.88220300
H	12.87405600	6.95440600	-2.74443200
H	11.89536000	6.03844400	-3.92694900
H	11.11109100	6.98067900	-2.65399800
C	12.15636800	0.37749100	-0.45678800
C	12.48206100	1.54951700	0.15772500
H	12.35553300	-0.57583600	0.02466500
H	12.94111100	1.54696700	1.14274300
C	6.63078600	0.40478300	-2.22480300
C	6.68820300	1.80142800	-2.84822000
C	7.89614800	2.67742200	-0.89224600
C	7.87622700	1.30551400	-0.21689200
C	7.80055300	0.18358800	-1.25847400
H	7.56288400	1.90320700	-3.51420100
H	5.79436100	1.99895000	-3.44756300
H	5.67948800	0.29499100	-1.68784200
H	6.64459100	-0.34777000	-3.02276700
H	8.83424900	2.81892800	-1.45348200
H	7.83387500	3.47726000	-0.14912100
H	8.77801400	1.19682100	0.39826400
H	7.00883200	1.25057200	0.45391900
H	8.73346100	0.16256700	-1.82744600
H	7.70916900	-0.79119200	-0.76433000
N	6.76670900	2.82133000	-1.80732200
C	6.29714800	4.07266300	-2.08126400
H	6.33892900	4.76778100	-1.25016600
H	5.41795600	4.13330800	-2.71247300
H	9.57192500	0.63528000	-5.03876400
Pd	9.62021700	3.68554100	-3.92596000

TS8a$^{\text{doublet}}$

C	-1.34396700	0.68219000	0.43757700
C	-1.56047700	0.01754700	1.64861300
C	-0.79054800	0.27010200	2.78317500
C	0.19962400	1.24953900	2.73081300
C	0.40518400	1.97178900	1.55320000
C	-0.34982000	1.67903900	0.42226500
H	-0.97381800	-0.28625200	3.69551600
H	0.80334300	1.44853000	3.61086900
H	1.16638400	2.74395000	1.50977900
N	-2.17627800	0.50008200	-0.70556900
Br	-2.98290600	-1.31804500	1.79129300
H	-0.19874200	2.22645500	-0.50221800
C	-1.65338700	0.13815600	-1.97135200

O	-2.12640500	0.67773300	-2.97826500
C	-0.64877500	-0.93717000	-2.05667100
H	-0.35157000	-1.08405200	-3.09420300
C	-0.71262700	-2.10933900	-1.21813000
H	-1.24621400	-2.10351900	-0.27871100
H	-0.05467700	-2.95098400	-1.40772200
C	-3.31661800	1.42168900	-0.73328200
H	-3.00433300	2.45535000	-0.93577500
H	-4.00445800	1.11419400	-1.52056100
H	-3.82036500	1.38100600	0.23577900
C	3.13421900	3.04843200	-2.26063000
C	3.86130500	3.41563900	-1.13902500
C	3.90163700	2.54778500	-0.02822000
C	3.18372400	1.32561600	-0.11870600
C	2.46140600	1.81797200	-2.26400400
C	4.62103000	2.85345600	1.17567700
C	3.15791500	0.42901600	1.00930500
C	3.87963300	0.76558700	2.18361100
C	4.61740300	1.99370000	2.23267900
C	3.79456500	-0.12441000	3.27243900
H	4.33347100	0.09693200	4.19001300
C	3.01738900	-1.25980500	3.16297100
C	2.31115900	-1.51717800	1.96695900
H	5.16776200	3.79109800	1.22681600
H	3.08662200	3.68910900	-3.13516600
H	4.39812600	4.35949100	-1.10220500
H	5.16136900	2.23353400	3.14241000
H	2.92639700	-1.95389600	3.99194500
N	2.38624400	-0.68911000	0.92339500
N	2.48090800	0.97492400	-1.23091000
C	1.41664200	-2.71543000	1.83305600
H	1.62013500	-3.23746600	0.89328200
H	1.54535400	-3.40697400	2.67115800
H	0.37047400	-2.39276300	1.79407200
C	-5.66706900	-2.00401000	-2.35038800
C	-4.29639700	-2.21513500	-1.70591900
C	-3.23481400	-2.28071700	-3.95464500
C	-4.60311200	-2.10824900	-4.61603000
C	-5.53237100	-1.29922200	-3.70468000
H	-3.88012100	-1.25327100	-1.37937400
H	-4.38289000	-2.83965800	-0.81038500
H	-6.15554200	-2.97718500	-2.49297300
H	-6.29336400	-1.42128200	-1.66391500
H	-2.74197900	-1.30169900	-3.88862400

H	-2.59654400	-2.94319900	-4.54927400
H	-4.46783200	-1.60486500	-5.58049700
H	-5.04657100	-3.09323900	-4.81536300
H	-5.10465300	-0.29744100	-3.55827500
H	-6.51680900	-1.16871400	-4.16960000
N	-3.36898600	-2.88128300	-2.62183200
C	-2.27360400	-3.49691000	-2.07482500
H	-1.63160200	-4.00262300	-2.79081800
H	-2.45565200	-4.02245300	-1.14045100
H	1.88497400	1.49432900	-3.12557100
Pd	1.02475400	-0.68874800	-0.82857700

TS8b[doublet]

C	0.47689200	-0.17402900	-1.78542000
C	1.25971000	-1.30730900	-2.01969100
C	0.74154100	-2.59790600	-1.94721300
C	-0.61285600	-2.76480900	-1.65114200
C	-1.43093300	-1.65321100	-1.45407600
C	-0.88735700	-0.37143500	-1.52268000
H	1.38497800	-3.45300600	-2.11952200
H	-1.02531300	-3.76736700	-1.58545200
H	-2.48404500	-1.78066500	-1.22773600
N	1.00622200	1.14383800	-1.85288300
Br	3.15587200	-1.09897700	-2.45701200
H	-1.51042600	0.50269600	-1.37294400
C	1.18589900	1.98699700	-0.75014500
O	1.26104700	3.20778800	-0.94863500
C	1.46008500	1.44974500	0.60475200
H	1.53064300	2.26967000	1.31565200
C	1.19215900	0.13612400	1.16275800
H	1.29584000	-0.74154600	0.53071700
H	1.60816600	-0.02517400	2.15969200
C	0.87329800	1.79031000	-3.15938700
H	-0.15628300	2.12829900	-3.34304100
H	1.53235900	2.65677600	-3.19021100
H	1.15640300	1.07315200	-3.93409700
C	-3.96382700	3.74126100	-0.06875500
C	-5.01783900	2.86561800	-0.25607600
C	-4.87704000	1.51497900	0.11335700
C	-3.63400100	1.12046200	0.67738700
C	-2.74285700	3.27209700	0.46520400
C	-5.89611500	0.52841500	-0.08770000
C	-3.42981700	-0.24096300	1.07849500
C	-4.44141600	-1.20691500	0.82346900

C	-5.67952300	-0.77852300	0.23411500
C	-4.17639000	-2.54731000	1.16673600
H	-4.92717500	-3.30994100	0.98144200
C	-2.94976200	-2.86679800	1.74427300
C	-2.02340300	-1.85215700	1.99086300
H	-6.83983400	0.84074400	-0.52695100
H	-4.05126800	4.78556200	-0.34893000
H	-5.95377900	3.20721100	-0.69067500
H	-6.44730000	-1.52587900	0.05238900
H	-2.71571700	-3.88626400	2.03398500
N	-2.24283900	-0.56484000	1.68574000
N	-2.58715400	1.99040900	0.80679500
C	5.56712600	1.50386200	3.38782400
C	4.29789400	1.78595900	2.58007000
C	4.63065500	-0.26740800	1.25780300
C	5.91621800	-0.58311100	2.02487500
C	5.85695800	-0.00136700	3.44241100
H	3.41585200	1.39888000	3.12005300
H	4.15068900	2.86217400	2.44636700
H	6.41062900	2.02385700	2.91575900
H	5.45090800	1.91613300	4.39709100
H	3.78282900	-0.80061700	1.71643200
H	4.69700200	-0.59973000	0.21890800
H	6.05894600	-1.66983700	2.05536900
H	6.77035100	-0.15429700	1.48491400
H	5.05871700	-0.50471600	4.00721200
H	6.79420200	-0.19186600	3.97801900
N	4.37224400	1.17286700	1.25675200
C	3.61649100	1.70868700	0.25222500
H	3.68098600	1.20000000	-0.70299000
H	3.54636900	2.79143700	0.22247700
Pd	-0.70624800	0.91822000	1.23172100
C	-1.56364800	4.18309300	0.64818400
H	-1.14708500	4.05609500	1.65289900
H	-0.76028900	3.93957100	-0.05834500
H	-1.84848900	5.23027700	0.50886200
H	-1.06923900	-2.06447000	2.46251700

TS9^{triplet}

C	-0.40516700	0.26740900	1.82023400
C	0.72854700	0.32979300	1.00974800
C	1.45873800	1.49480900	0.84040400
C	1.07037500	2.64333700	1.53970700
C	-0.05333600	2.60980100	2.36817300

C	-0.78490000	1.43005700	2.50523000
H	2.31798500	1.51308900	0.17608000
H	1.64427600	3.56013400	1.43248200
H	-0.36394400	3.50224500	2.90310000
N	-1.14564300	-0.93759500	2.01894600
Br	1.13761100	-1.34133500	-0.34107700
H	-1.66556500	1.39011400	3.14093100
C	-1.98429900	-1.46700700	1.05616600
O	-2.43492100	-2.61251900	1.15493300
C	-2.29438200	-0.59593300	-0.10820200
H	-2.06745000	0.46084400	-0.03601300
C	-3.07988500	-1.10035300	-1.14830600
H	-3.55281200	-2.07208700	-1.03369000
H	-3.50507900	-0.43346900	-1.89253600
C	-0.69778400	-1.79934800	3.10982000
H	0.30172400	-2.20196000	2.90006100
H	-0.66160000	-1.22486300	4.04018500
H	-1.40455700	-2.62311900	3.20094600
C	-0.39360300	1.54754000	-4.70573400
C	-0.19464700	0.72562700	-5.81455200
C	-0.25772600	-0.66576400	-5.65865500
C	-0.53226200	-1.16617900	-4.35730800
C	-0.66722900	0.98834300	-3.45003400
C	-0.05128900	-1.60585400	-6.72554000
C	-0.57336400	-2.56461000	-4.12690600
C	-0.35490000	-3.47826500	-5.19203300
C	-0.09962600	-2.94990500	-6.50311600
C	-0.40244000	-4.84615400	-4.88763200
H	-0.24822000	-5.58042700	-5.67340400
C	-0.64286600	-5.24916300	-3.57417000
C	-0.83340000	-4.29654500	-2.56398200
H	0.15085300	-1.21859300	-7.72060100
H	-0.34034300	2.62680000	-4.80116800
H	0.01489400	1.15237100	-6.79145400
H	0.06197500	-3.64966000	-7.31874800
H	-0.67597300	-6.30224400	-3.31634300
N	-0.80490300	-2.98001500	-2.83901400
N	-0.74215200	-0.34244400	-3.27643500
C	-1.02589700	-4.68607900	-1.12773000
H	-0.12175300	-4.44197500	-0.55324700
H	-1.84593200	-4.13181000	-0.65889500
H	-1.21779900	-5.75787800	-1.02820500
C	-0.89688300	1.85824900	-2.24563700
H	-1.94287600	1.80148800	-1.92080700

H	-0.27583300	1.53326400	-1.40521500
H	-0.66872200	2.90422600	-2.46709300
Ni	-1.13579100	-1.44455100	-1.60658000

TS10$^{\text{doublet}}$

C	-2.69338300	2.32093800	1.54556800
C	-2.01712600	2.77112800	0.41683300
C	-2.57877800	3.69783100	-0.44738800
C	-3.84695200	4.21729800	-0.16246400
C	-4.54122400	3.78465800	0.97029300
C	-3.96624900	2.84062600	1.82115900
H	-2.03924300	4.01600000	-1.33611600
H	-4.29305100	4.95445200	-0.82619500
H	-5.53026100	4.17729200	1.18831300
N	-2.10514300	1.39594700	2.46917700
Br	-0.16811400	1.59983700	-0.26888700
H	-4.49439600	2.49104600	2.70496700
C	-2.07409600	0.03343500	2.28517700
O	-1.49830800	-0.71303500	3.08283900
C	-2.78721500	-0.49616600	1.08648700
H	-3.22289200	0.20890400	0.38841700
C	-2.85241900	-1.81244100	0.87790800
H	-2.39848400	-2.49805300	1.58514000
H	-3.33967100	-2.23068400	0.00258400
C	-1.30221600	1.98344200	3.53469900
H	-1.04814300	1.19637000	4.24377900
H	-0.38347800	2.42024800	3.12204800
H	-1.87322800	2.77160300	4.03503800
C	-1.14726200	-1.92854100	-4.08821900
C	-1.53343400	-3.16086000	-3.57034300
C	-1.09798200	-3.52082000	-2.28462400
C	-0.24791200	-2.61218800	-1.60580200
C	-0.28785600	-1.07960900	-3.37803200
C	-1.48547000	-4.72918300	-1.61385200
C	0.12523600	-2.85617900	-0.26101000
C	-0.30989000	-4.03212100	0.39970100
C	-1.09830900	-4.98005600	-0.32981300
C	0.00231800	-4.15587300	1.76481300
H	-0.30410700	-5.04271600	2.31276400
C	0.62651200	-3.10228700	2.40736100
C	1.00854400	-1.94874800	1.69310300
H	-2.11400800	-5.43558800	-2.14933300
H	-1.50148500	-1.60695900	-5.06187100
H	-2.18570100	-3.82432000	-4.13065400

H	-1.41329200	-5.88910200	0.17536400
H	0.79359100	-3.12519700	3.47842400
N	0.83775100	-1.85865100	0.36725500
N	0.20045400	-1.43724300	-2.16769700
C	1.56278800	-0.76992300	2.43300800
H	2.60247200	-0.93066400	2.74119300
H	1.50114000	0.11880500	1.80522300
H	0.95586600	-0.60051600	3.32581100
C	0.09935500	0.25265600	-3.94706900
H	-0.00957500	1.03057900	-3.18526500
H	1.14308500	0.25699700	-4.27894200
H	-0.53017200	0.49701100	-4.80737000
Ni	1.46113700	-0.55426500	-1.02240400
C	4.84510200	-0.94120900	0.59887400
C	4.38699300	-0.67577200	-0.83044500
C	3.59310400	1.56963200	-0.21586300
C	4.11784800	1.39952400	1.20773400
C	5.25193600	0.36934000	1.28384200
H	5.21811100	-0.25006400	-1.41653300
H	4.06021200	-1.59554900	-1.32171300
H	4.02951500	-1.42563500	1.14661200
H	5.68551200	-1.64487400	0.57796800
H	4.35977400	2.05766000	-0.83834000
H	2.69277600	2.18678000	-0.22879500
H	4.46261800	2.37771600	1.56320100
H	3.29774100	1.09764300	1.86071400
H	6.14497000	0.76980500	0.78266400
H	5.53054000	0.18802000	2.32834500
N	3.25458500	0.27809800	-0.86654700
C	2.60414700	0.39539500	-2.14038100
H	2.34604800	1.41907600	-2.40706800
H	3.09296000	-0.15809600	-2.94532300

TS11a$^{\text{doublet}}$

C	7.39089900	7.30407700	-1.56167600
C	6.22098600	7.70134300	-2.22700700
C	4.96439200	7.59110000	-1.63648600
C	4.85898400	7.11227300	-0.32955200
C	6.01011100	6.75912500	0.37656800
C	7.25592900	6.85674500	-0.23826400
H	4.08030700	7.88411300	-2.19162700
H	3.88027200	7.02571900	0.13257300
H	5.93649700	6.39625500	1.39727400
N	8.67848400	7.34778300	-2.15119900

Br	6.32880500	8.39460700	-4.04317300
H	8.15715700	6.56088400	0.28794900
C	9.05115000	6.58933000	-3.30142400
O	9.98422300	7.01471100	-3.98891500
C	8.40646500	5.31548500	-3.59612300
H	8.65828800	4.98943200	-4.60218100
C	7.30815900	4.63224000	-2.93099200
H	6.68112900	5.22600600	-2.28543000
H	6.71751200	3.97825600	-3.56413100
C	9.42921200	8.57956100	-1.90652400
H	9.41872300	8.79845400	-0.83387100
H	10.45015100	8.42945000	-2.25497100
H	9.00031600	9.43302300	-2.44853900
C	4.60997900	3.18201900	0.16098200
C	4.91667600	3.19358200	-1.34610200
C	6.17694700	1.13620600	-1.18438600
C	5.93786400	1.03930100	0.32961600
C	4.62759900	1.74659400	0.70566300
H	4.10947600	2.67637300	-1.88337900
H	4.94607500	4.21837000	-1.72202200
H	5.36002200	3.78747600	0.68683100
H	3.63769200	3.65758600	0.34283300
H	5.38042600	0.59268200	-1.71312000
H	7.12742100	0.67008500	-1.46735500
H	5.91522700	-0.01258100	0.64162000
H	6.77904100	1.51267900	0.85492600
H	3.78360400	1.18880100	0.27291800
H	4.48298700	1.74199000	1.79288700
N	6.17747600	2.51865300	-1.68173100
C	11.09864600	1.82792300	-3.32841600
C	9.11053600	1.38915900	-4.47113000
C	9.73974200	0.35270800	-5.18025800
C	11.07783200	0.05509300	-4.96024600
C	11.79848400	0.80269800	-4.01740100
C	11.77267500	2.61970300	-2.36008300
C	11.63172700	4.35687200	-0.79784300
C	12.97556700	4.17362700	-0.45913900
C	13.74174100	3.19837600	-1.09292700
C	13.14074900	2.38740000	-2.06835000
H	9.16139000	-0.20986800	-5.90549300
H	11.56810500	-0.74481900	-5.50826000
H	13.41368700	4.80760800	0.30483100
H	14.78857500	3.05929800	-0.83956900
N	11.03495400	3.60254700	-1.74832100

N	9.77470600	2.11397700	-3.55168500
C	10.77012300	5.38156200	-0.12166100
H	10.24372700	5.99244300	-0.86341000
H	10.00641600	4.88887900	0.49550200
H	11.35911200	6.03802700	0.52481500
C	7.67483700	1.73770900	-4.73594400
H	7.61278200	2.70595500	-5.24860700
H	7.20301900	0.98655200	-5.37542200
H	7.10379200	1.82749500	-3.80668000
Ni	9.24437100	3.79015000	-2.51238900
C	13.18442600	0.58695800	-3.71269500
C	13.82658500	1.34504200	-2.77965100
H	13.71316300	-0.19847600	-4.24585700
H	14.87617200	1.17376700	-2.55658500
C	7.37239600	3.26537400	-1.37784400
H	7.27004600	3.98739400	-0.56147300
H	8.15927900	2.55349200	-1.11070600

TS11b[doublet]

C	6.58622000	8.16890800	-2.00019400
C	6.97664500	9.37821000	-2.58162000
C	6.16812900	10.50907200	-2.52925700
C	4.93802600	10.43411100	-1.87417200
C	4.52779000	9.23822500	-1.28382200
C	5.35101300	8.11633900	-1.34905200
H	6.49456000	11.43201300	-2.99472500
H	4.30274900	11.31371000	-1.83059100
H	3.56861800	9.17811600	-0.77886300
N	7.42919200	7.01812300	-2.02236700
Br	8.69089800	9.48872700	-3.50481500
H	5.04633000	7.17321600	-0.90542500
C	7.33873300	6.19274600	-3.12869800
O	6.49212900	6.39624000	-3.99052700
C	8.28813900	5.02427000	-3.28133300
H	7.94845800	4.47717100	-4.15316300
C	9.74198000	5.27093500	-3.28741900
H	10.09592600	6.22108100	-2.89116800
H	10.24798400	4.97387100	-4.20475000
C	8.39255100	6.90576700	-0.93522300
H	8.89375300	5.93928400	-0.98327000
H	9.15481100	7.69218300	-0.99552000
H	7.87290200	6.99653000	0.02591900
C	11.35006800	1.54883900	-3.22338100
C	9.52252500	1.40280700	-4.66639900

C	10.14585900	0.39716900	-5.42762700
C	11.41262500	-0.03527800	-5.06603500
C	12.05413100	0.54263900	-3.96407200
C	11.99246000	2.18882300	-2.11791400
C	11.98756700	3.82328900	-0.41290700
C	13.28939000	3.49822900	-0.05672500
C	13.97361900	2.48264100	-0.72945400
C	13.33142800	1.82163600	-1.78386500
H	9.63372000	-0.02234100	-6.28739300
H	11.92227300	-0.80844300	-5.63564800
H	13.76165600	4.03812000	0.75782200
H	14.98973900	2.21227600	-0.45870500
N	11.31555400	3.17097100	-1.40678200
N	10.08584000	1.94593400	-3.58331800
C	11.26959200	4.93779300	0.29016400
H	10.32740700	4.59692300	0.73120500
H	11.88927400	5.35919100	1.08752800
H	11.02523300	5.73427400	-0.42256500
C	8.17396000	1.92222100	-5.09888800
H	8.27881200	2.89546500	-5.59304700
H	7.69544200	1.23947600	-5.80676400
H	7.50376400	2.06124400	-4.24749800
Ni	9.61135100	3.76064500	-2.08720800
C	13.37966800	0.17148800	-3.57717800
C	13.99191000	0.79134900	-2.53377800
H	13.88983600	-0.60130100	-4.14658400
H	15.00671600	0.52650000	-2.24817500
C	6.50750000	1.01056000	-0.75244900
C	7.87474000	1.49308400	-1.24400300
C	7.91022600	3.28876800	0.40522100
C	6.54608700	2.85936200	0.95961100
C	6.30938600	1.36082800	0.72782900
H	8.67878300	0.97897100	-0.70355700
H	8.03189900	1.28900300	-2.30160700
H	5.71722800	1.48132800	-1.35387500
H	6.42580400	-0.07137800	-0.91178600
H	8.71821200	2.78701900	0.95144300
H	8.06044900	4.36474000	0.51525900
H	6.49389000	3.10427500	2.02745900
H	5.75737700	3.43928200	0.46004200
H	7.02536000	0.78546100	1.33247600
H	5.30678000	1.07343100	1.06464600
N	8.07034900	2.94179300	-1.02023100
C	7.42657600	3.83801100	-1.96092800

H	6.85277500	4.59655300	-1.43202600
H	6.78787100	3.30559200	-2.66350300

TS12a$^{\text{doublet}}$

C	-1.31990200	0.74709500	0.48037200
C	-1.50382800	0.07491600	1.69316200
C	-0.73598700	0.35484300	2.82196500
C	0.22329000	1.36398000	2.76111500
C	0.40225100	2.08589200	1.57945900
C	-0.35582800	1.77107300	0.45621700
H	-0.89416800	-0.20554100	3.73645700
H	0.82814000	1.58103400	3.63585000
H	1.14256000	2.87769800	1.52841800
N	-2.14577000	0.53041200	-0.65989600
Br	-2.88850400	-1.29780600	1.84931000
H	-0.22598100	2.31951600	-0.47068700
C	-1.57036200	0.21325000	-1.92220900
O	-2.01755900	0.78530700	-2.92928200
C	-0.54410400	-0.81724700	-1.99390500
H	-0.24491700	-0.97907000	-3.02826500
C	-0.48238500	-1.96285800	-1.11019300
H	-1.07918200	-2.03617100	-0.21282200
H	0.13094900	-2.81920300	-1.37082500
C	-3.30148700	1.43160800	-0.70179600
H	-3.00724700	2.47386700	-0.88739700
H	-3.96758000	1.11890300	-1.50564100
H	-3.82435000	1.37005200	0.25636700
C	3.01270400	2.96047900	-2.33138300
C	3.76618100	3.31524500	-1.22514800
C	3.78400600	2.46195200	-0.10594900
C	3.00652300	1.28062500	-0.18247700
C	2.26303100	1.76751500	-2.33911400
C	4.53160700	2.72805500	1.08964500
C	2.96147200	0.38189500	0.92975200
C	3.71742700	0.66354300	2.09385300
C	4.50534100	1.86141500	2.14179500
C	3.62190700	-0.25029000	3.15964100
H	4.18619300	-0.07851400	4.07228200
C	2.80337500	-1.35653100	3.02621600
C	2.05915000	-1.56055300	1.84600300
H	5.12357600	3.63806500	1.13728500
H	2.99546300	3.59318600	-3.21265300
H	4.34524600	4.23453800	-1.21478500
H	5.07590900	2.06842900	3.04316400

H	2.70996300	-2.07562700	3.83324700
N	2.13396700	-0.70330000	0.81627700
N	2.25231000	0.94787000	-1.27326300
C	1.13529800	-2.73623500	1.72508900
H	1.27310200	-3.23890400	0.76426000
H	1.30294800	-3.45030000	2.53674900
H	0.09308800	-2.40400000	1.76265200
C	1.45835800	1.37529200	-3.54369900
H	0.38217600	1.44690600	-3.35179400
H	1.70358600	2.01516300	-4.39647900
H	1.66080000	0.33344300	-3.80963700
Ni	1.01688600	-0.56947000	-0.82335600
C	-5.51194200	-2.03435400	-2.27239200
C	-4.13675000	-2.23620400	-1.63365200
C	-3.07791500	-2.23130300	-3.88578400
C	-4.45140700	-2.08134500	-4.54220500
C	-5.39393000	-1.30560200	-3.61559400
H	-3.73441300	-1.27786000	-1.28055700
H	-4.21308300	-2.88633000	-0.75571400
H	-5.98661400	-3.01206200	-2.43017600
H	-6.14504400	-1.47277500	-1.57456200
H	-2.61421100	-1.23942200	-3.80302400
H	-2.42183400	-2.86418000	-4.49281300
H	-4.33018200	-1.56020800	-5.49916200
H	-4.87371200	-3.07284200	-4.75492700
H	-4.98480800	-0.29811300	-3.45533700
H	-6.38213500	-1.18644400	-4.07559300
N	-3.19692300	-2.86105600	-2.56551100
C	-2.11648000	-3.50997600	-2.04057100
H	-1.44378300	-3.96609800	-2.75897600
H	-2.28167400	-4.03514500	-1.10526900

TS12b$^{\text{doublet}}$

C	0.39401300	-0.30124200	-1.82396600
C	1.20096800	-1.42472300	-2.02802300
C	0.70742800	-2.72250200	-1.93684000
C	-0.64766000	-2.90977000	-1.65369000
C	-1.48746700	-1.81021900	-1.48535900
C	-0.96733100	-0.52015100	-1.57194500
H	1.36942100	-3.56845100	-2.08245300
H	-1.04240000	-3.91833000	-1.57340800
H	-2.54024100	-1.95390700	-1.26941900
N	0.90247700	1.02114100	-1.90479100
Br	3.10334100	-1.18422900	-2.41986300

H	-1.60788300	0.34510600	-1.44358300
C	1.01506700	1.89315900	-0.81204000
O	1.08203800	3.11237100	-1.04795700
C	1.18120800	1.39049400	0.55680700
H	1.26418800	2.21881000	1.25599700
C	1.04681400	0.04961000	1.11222300
H	1.27127300	-0.80144800	0.47500000
H	1.49671100	-0.06411300	2.10306100
C	0.83746200	1.62546000	-3.23545300
H	-0.18748300	1.92488700	-3.49626700
H	1.46993600	2.51183600	-3.24744400
H	1.19276100	0.89801000	-3.97023800
C	-3.60695400	3.78274100	0.15158700
C	-4.70344600	2.98285900	-0.13142300
C	-4.63733300	1.60369600	0.13090900
C	-3.41861800	1.10579700	0.65938500
C	-2.41478900	3.21587700	0.64781300
C	-5.70961700	0.68212600	-0.10772700
C	-3.28709000	-0.27010900	0.99916000
C	-4.35828200	-1.16471500	0.74602100
C	-5.57036300	-0.64495800	0.17557500
C	-4.16359800	-2.51595900	1.08052300
H	-4.95660800	-3.23882500	0.91170200
C	-2.94804000	-2.90100000	1.63893900
C	-1.93305000	-1.96237500	1.87402100
H	-6.63688300	1.06321400	-0.52726000
H	-3.64328200	4.85295500	-0.02130300
H	-5.61487700	3.41210800	-0.53910800
H	-6.38481700	-1.33792300	-0.01837000
H	-2.77751500	-3.93428200	1.92364100
N	-2.09165200	-0.65815200	1.56365400
N	-2.31210000	1.89413000	0.85207100
C	-0.62646100	-2.38351200	2.47758600
H	-0.70920500	-3.37262800	2.93820400
H	0.14976900	-2.41872200	1.70532500
H	-0.29764100	-1.65927300	3.22742100
C	-1.22020300	4.06876100	0.95610800
H	-1.48991600	5.12904500	0.95285100
H	-0.82102600	3.80894100	1.94255500
H	-0.41847100	3.90579500	0.22427900
Ni	-0.73614700	0.71984200	1.19230300
C	5.35512000	1.66985300	3.38474100
C	4.08303100	1.88774800	2.56144900
C	4.54950100	-0.14141000	1.23157300

C	5.84120900	-0.38465600	2.01454200
C	5.72676900	0.18250300	3.43461000
H	3.21510900	1.45359300	3.08641900
H	3.88192000	2.95481000	2.42683100
H	6.17561300	2.23801600	2.92772900
H	5.20262000	2.06875400	4.39454800
H	3.72820300	-0.72431700	1.67419000
H	4.64752800	-0.45985500	0.19106700
H	6.04748200	-1.46124800	2.04044300
H	6.67657900	0.09752700	1.49029400
H	4.94900800	-0.36863900	3.98312200
H	6.66454900	0.04072300	3.98404400
N	4.20352000	1.28157000	1.23843400
C	3.48057300	1.79986600	0.21350800
H	3.54777200	1.28568200	-0.73678500
H	3.30684900	2.86898100	0.20352600

TS13doublet

C	4.54754800	1.20672300	0.17498900
C	5.50002100	1.81351200	-0.65096200
C	6.70437800	1.19280700	-0.97456200
C	6.98663900	-0.06389900	-0.44124400
C	6.06683400	-0.67815000	0.41090800
C	4.86478700	-0.04809000	0.71188600
H	7.41327500	1.69476900	-1.62313600
H	7.92641600	-0.55043000	-0.68503400
H	6.28079700	-1.65208600	0.84121600
N	3.28384200	1.80915500	0.42425000
Br	5.18293800	3.61221400	-1.35457100
H	4.15500500	-0.50821800	1.38135800
C	2.91410200	2.03072400	1.75328900
O	3.61730400	1.59899400	2.68023100
C	1.73424200	2.81493400	2.09765300
H	1.61060800	2.84196900	3.17533900
C	0.80763300	3.63876000	1.26930600
H	0.36416000	3.03037200	0.47678800
H	-0.02619000	3.97328700	1.89443600
C	2.36981800	1.90220400	-0.72116100
H	2.27625700	2.91897200	-1.10630700
H	2.76670900	1.27105000	-1.51837700
H	1.38338100	1.50973100	-0.45558300
C	-0.10502800	7.84213600	-1.09891700
C	0.96743500	7.02482800	-0.37564500
C	0.23875800	4.98702900	-1.43635900

C	-0.86347700	5.72036400	-2.20285200
C	-0.48239000	7.18661100	-2.43188100
H	1.91092000	7.05505400	-0.96150400
H	1.18381100	7.47045600	0.60189500
H	-0.99129800	7.90154700	-0.45447000
H	0.25878200	8.86504700	-1.25549000
H	1.15402900	4.93520300	-2.06499500
H	-0.07618900	3.95730600	-1.24519000
H	-1.04452800	5.20939400	-3.15640500
H	-1.79070300	5.66396400	-1.61881400
H	0.37828200	7.23414800	-3.11507300
H	-1.30255700	7.73140900	-2.91461500
N	0.52332200	5.64732100	-0.16133900
C	1.46521400	4.89958800	0.66299600
H	2.38223100	4.62672300	0.10918400
H	1.78505200	5.54860100	1.48569600
C	-3.32462900	-1.29891700	0.28691900
C	-3.56217200	-1.95285800	-0.92595400
C	-2.83870800	-3.07925500	-1.31309800
C	-1.86744300	-3.59557500	-0.45445200
C	-1.64084300	-2.99512700	0.78427900
C	-2.36246700	-1.85989100	1.14446500
H	-3.04108300	-3.54906300	-2.26902500
H	-1.30198800	-4.47367800	-0.75250700
H	-0.89341700	-3.39621900	1.46207900
N	-4.07006700	-0.16293200	0.70434800
Br	-4.94263900	-1.27977400	-2.12954500
H	-2.20270200	-1.38795200	2.10705200
C	-3.50692400	1.10382900	0.93745500
O	-4.00414700	1.82359800	1.80354600
C	-2.36936700	1.59329300	0.11560000
H	-2.12033500	2.60682400	0.42369600
C	-2.02723300	1.18422000	-1.20870000
H	-2.62640900	0.44995500	-1.73885300
H	-1.56994400	1.92620100	-1.86381300
C	-5.27869900	-0.47940600	1.46827200
H	-5.81201400	-1.28710800	0.96116100
H	-5.04253500	-0.79268400	2.49506500
H	-5.90787600	0.40868100	1.51691200
C	0.98933300	-0.23768600	4.35012400
C	1.97780000	-1.17478800	4.15501100
C	2.20101600	-1.69007300	2.86005100
C	1.40226100	-1.17132800	1.81270700
C	0.20691500	0.20690500	3.25864800

C	3.18090700	-2.69747900	2.57635600
C	1.61256900	-1.64708700	0.46473700
C	2.58515100	-2.65008300	0.21889300
C	3.35930100	-3.16727900	1.30920500
C	2.74725200	-3.08946000	-1.11298800
H	3.48816200	-3.85181500	-1.33716900
C	1.96512800	-2.54174100	-2.10982800
C	1.02713400	-1.54912500	-1.77231900
H	3.77977400	-3.07998100	3.39789500
H	0.79914600	0.17153500	5.33652000
H	2.58792000	-1.52321600	4.98335200
H	4.09982400	-3.93402400	1.10042000
H	2.06441200	-2.85768300	-3.14287500
N	0.85756800	-1.11226500	-0.53000400
N	0.42982700	-0.24716300	2.02328900
Pd	-0.68624200	0.33201600	0.14191200
C	-0.91918900	1.17831000	3.45908900
H	-1.01762900	1.83710700	2.59598300
H	-1.87636300	0.64991000	3.55135900
H	-0.77566500	1.76993100	4.36792100
H	0.39366800	-1.09140100	-2.52472400

IM12[doublet]

C	3.41968700	0.56781700	-1.12941700
C	4.26829000	1.32395400	-1.94720700
C	5.55964400	0.91041500	-2.26738000
C	6.04391500	-0.28335800	-1.73615900
C	5.23233000	-1.04272000	-0.89123100
C	3.94034800	-0.62209800	-0.59818700
H	6.17909600	1.52596900	-2.90977700
H	7.05248800	-0.60737400	-1.97537400
H	5.60294700	-1.96931100	-0.46205300
N	2.07717000	0.95306100	-0.87618100
Br	3.68182600	3.05971600	-2.63914200
H	3.31231100	-1.19808800	0.06253800
C	1.64199000	1.06262200	0.45777300
O	2.39825600	0.70991100	1.37418900
C	0.29841000	1.60090000	0.73773800
H	0.24890900	1.75253100	1.81498400
C	-0.24281800	2.81150200	0.00018600
H	-0.42848700	2.60874200	-1.05600300
H	-1.21047700	3.09167800	0.43017300
C	1.15855000	0.92384300	-2.01476300
H	1.04107000	1.89964600	-2.49505300

H	1.54929200	0.22482200	-2.76005200
H	0.18452900	0.56376300	-1.67826900
C	0.09385100	7.69524600	-0.53935600
C	0.77171800	6.44501500	0.02622700
C	0.28015400	5.18390000	-1.96133900
C	-0.42126800	6.37763400	-2.61224200
C	0.14445900	7.69513800	-2.07137500
H	1.85764700	6.48080300	-0.20468500
H	0.67759700	6.42821500	1.11801700
H	-0.95199500	7.70568300	-0.20653800
H	0.57887200	8.59151300	-0.13307500
H	1.34817600	5.17438100	-2.26538100
H	-0.16058200	4.25145200	-2.32628900
H	-0.30548000	6.32118200	-3.70179500
H	-1.49440400	6.31740400	-2.39042100
H	1.18922000	7.80041500	-2.39853600
H	-0.40473500	8.55254500	-2.47921500
N	0.15624800	5.22848100	-0.50405700
C	0.69448300	4.02542800	0.13204400
H	1.69338800	3.76831400	-0.26298700
H	0.82497600	4.24017600	1.19912400
C	-3.40695500	-2.31311200	0.76893100
C	-3.33615300	-3.07689900	-0.40232100
C	-2.43461600	-4.13002000	-0.54175200
C	-1.59591100	-4.45938100	0.52306900
C	-1.66483900	-3.73807200	1.71467800
C	-2.55658400	-2.67490200	1.82815500
H	-2.39958100	-4.69099400	-1.46883400
H	-0.89187500	-5.27883700	0.41567500
H	-1.02008700	-3.99240600	2.54950100
N	-4.38606000	-1.29933800	0.96753500
Br	-4.53793000	-2.68786300	-1.88795800
H	-2.62953800	-2.11152600	2.75163700
C	-4.06529500	0.03314200	1.27474300
O	-4.77454700	0.66003300	2.05935700
C	-2.94510500	0.71363500	0.57326900
H	-2.87283700	1.74336900	0.90847600
C	-2.45588500	0.37136600	-0.71252900
H	-2.88023200	-0.46785200	-1.25567700
H	-2.07256700	1.16703100	-1.34607200
C	-5.64647200	-1.79500000	1.53059700
H	-5.95234900	-2.68182000	0.97075600
H	-5.54428100	-2.05381200	2.59322200
H	-6.40424000	-1.01785400	1.43615100

C	0.50707000	-0.67883700	4.96725800
C	1.51634300	-1.60858500	4.83104900
C	1.76694300	-2.18184900	3.56860700
C	0.96250700	-1.74580900	2.48775300
C	-0.27244800	-0.31433300	3.84786800
C	2.77092600	-3.18261900	3.35235800
C	1.19587200	-2.29465400	1.17342400
C	2.17233000	-3.31228800	1.00052400
C	2.95652100	-3.73818800	2.12343300
C	2.33952900	-3.84549800	-0.29424500
H	3.07633600	-4.62683900	-0.45895400
C	1.57764700	-3.35411600	-1.33776500
C	0.65512300	-2.32892600	-1.07756200
H	3.37638200	-3.49635200	4.19809100
H	0.29268200	-0.22832100	5.93053700
H	2.11655900	-1.90900400	5.68549300
H	3.71012600	-4.50491400	1.96767600
H	1.68690700	-3.73716500	-2.34666000
N	0.46666300	-1.81664200	0.13352600
N	-0.04175000	-0.84769100	2.64547800
Pd	-1.03682300	-0.24460800	0.71116000
C	-1.38515500	0.68682500	3.97622500
H	-1.07857500	1.65078500	3.55386300
H	-2.27057300	0.37143400	3.41875200
H	-1.65461400	0.84549000	5.02401000
H	0.04550000	-1.91090900	-1.87133900

IM13[doublet]

C	-0.57051600	2.48016200	-1.03205600
C	-1.35042600	2.82832700	0.07458500
C	-2.52522600	2.14974300	0.39882200
C	-2.96052100	1.10893700	-0.42020400
C	-2.21422600	0.74319200	-1.54078200
C	-1.02273200	1.40783900	-1.82522800
H	-3.09674000	2.44396400	1.27189800
H	-3.87580600	0.58034700	-0.17228800
H	-2.54418300	-0.07239300	-2.17678700
N	0.60535700	3.17945400	-1.40313200
Br	-0.79599700	4.31111000	1.21718200
H	-0.43255500	1.13843300	-2.69542800
C	1.88930400	2.70307700	-1.04210500
O	2.86863400	3.06954000	-1.69648600
C	1.94423600	1.80769700	0.12851400
H	1.23705300	2.13678700	0.89737600

C	3.34222600	1.63986700	0.70951900
H	3.65247500	2.52314300	1.29092900
H	4.06722600	1.55157800	-0.10460200
C	0.49910300	4.01550900	-2.59223600
H	0.34289800	3.42559900	-3.50846900
H	-0.33746900	4.71153600	-2.47505900
H	1.43446800	4.56446200	-2.69548600
C	0.02468500	-3.10784700	-3.45076800
C	-1.17257300	-3.64168500	-3.01633900
C	-1.69446200	-3.24571000	-1.76789500
C	-0.95184200	-2.31154500	-0.99102300
C	0.68358800	-2.18022000	-2.63188800
C	-2.95278300	-3.73962600	-1.28961800
C	-1.48379200	-1.87930200	0.28827400
C	-2.75432200	-2.36618400	0.70214400
C	-3.46708000	-3.30873300	-0.10619400
C	-3.27314800	-1.86856500	1.91656600
H	-4.24491700	-2.21198700	2.26208900
C	-2.54995700	-0.94498000	2.63771200
C	-1.28016500	-0.53554600	2.16472500
H	-3.49273100	-4.45421700	-1.90449400
H	0.45590100	-3.38212700	-4.40768200
H	-1.72378000	-4.35497300	-3.62280300
H	-4.43019000	-3.66971900	0.24478800
H	-2.93552600	-0.53365400	3.56543300
N	-0.77025400	-1.00606900	1.03234900
N	0.22258400	-1.78515300	-1.44284800
C	-0.44891800	0.44678900	2.94205000
H	-1.07580100	1.12069500	3.53367700
H	0.22381400	-0.07779400	3.63332400
H	0.16424500	1.03236700	2.25650700
C	3.88210600	-2.55936900	-0.67436700
C	4.20896900	-1.28639600	0.10256500
C	2.65375600	-1.87733500	1.86070100
C	2.26934000	-3.17366200	1.15133900
C	3.41310000	-3.67629900	0.26411000
H	5.07551200	-1.47150800	0.76726700
H	4.48444700	-0.48280600	-0.58315400
H	3.09375900	-2.33001600	-1.39807600
H	4.76843400	-2.87095400	-1.24047800
H	3.47536200	-2.07423900	2.57706100
H	1.80085900	-1.49398400	2.42638400
H	2.00068100	-3.92607200	1.90327800
H	1.38078100	-2.98213300	0.54266700

H	4.25424000	-3.99243700	0.89789800
H	3.09897000	-4.55693100	-0.30937200
N	3.06387700	-0.82962300	0.91063800
C	3.39513100	0.42225700	1.62720100
H	4.37979500	0.32366100	2.11802000
H	2.64848900	0.54179000	2.41984100
Pd	1.21559800	-0.06607600	-0.47868300
H	1.61572300	-1.72439400	-2.94842900

TS14a$^{\text{doublet}}$

C	-0.04136100	2.30210100	-1.68216600
C	-1.09216400	1.76361000	-0.88711500
C	-2.03278900	0.86937100	-1.43968800
C	-1.90690300	0.44032200	-2.75316200
C	-0.86063100	0.92931600	-3.54299400
C	0.04805900	1.84078200	-3.01045300
H	-2.84906900	0.52058700	-0.81774200
H	-2.62335100	-0.26779400	-3.15822100
H	-0.75650900	0.60765400	-4.57515600
N	0.86544100	3.28688000	-1.21642700
Br	-1.77005600	2.75276600	0.69473900
H	0.86169500	2.21074300	-3.62453400
C	1.91284600	2.93509800	-0.29738800
O	3.03081300	3.41243800	-0.49902900
C	1.56750200	2.04477600	0.82212700
H	0.75980000	2.47909600	1.41238300
C	2.77165500	1.66766800	1.67957500
H	2.42469200	1.30471800	2.65554700
H	3.41891700	2.53443400	1.87376600
C	1.24800700	4.31939200	-2.18053300
H	2.01824300	3.98779900	-2.88926300
H	0.35621300	4.63433600	-2.72741600
H	1.65830200	5.16774200	-1.63127200
C	-0.14662000	-2.69836600	-3.19663500
C	-1.31183100	-3.32573300	-2.81260300
C	-1.85011300	-3.06786500	-1.53160700
C	-1.14287500	-2.17575900	-0.68099000
C	0.47743400	-1.81967500	-2.29317500
C	-3.08420600	-3.64872700	-1.09233300
C	-1.68435700	-1.87290000	0.62995400
C	-2.93040100	-2.43906300	1.00878500
C	-3.60970400	-3.33816500	0.12566500
C	-3.45120500	-2.06103900	2.26722600
H	-4.40919900	-2.46056500	2.58980400

C	-2.74492900	-1.18647800	3.06223100
C	-1.49194100	-0.69654600	2.61729500
H	-3.60208500	-4.32843400	-1.76342300
H	0.29000600	-2.86193800	-4.17629600
H	-1.83165600	-4.00585800	-3.48206000
H	-4.55698800	-3.76393200	0.44560000
H	-3.13113600	-0.87392600	4.02744400
N	-0.99245700	-1.03929500	1.43605300
N	0.00716600	-1.56744200	-1.07555000
C	-0.65907800	0.21455400	3.47541600
H	-0.04013900	0.84801400	2.83736600
H	-1.28336900	0.84124900	4.11968000
H	0.00628000	-0.37235400	4.12275200
C	3.76300600	-2.21722700	2.40893200
C	2.54441500	-1.46026200	1.86016700
C	3.47089300	-1.43858100	-0.37188400
C	4.73963300	-2.17216200	0.08587900
C	4.43086400	-3.04995800	1.30622800
H	1.77131000	-2.17361300	1.55164100
H	2.09781900	-0.82560700	2.62798900
H	4.48883600	-1.50786100	2.82705800
H	3.44021000	-2.85919400	3.23844900
H	2.72451300	-2.17747600	-0.68774900
H	3.67571000	-0.78508200	-1.22583600
H	5.12698600	-2.77926500	-0.74217900
H	5.52056800	-1.44296200	0.33688000
H	3.74709100	-3.85647000	1.00156600
H	5.34171700	-3.53198900	1.68096000
N	2.84356200	-0.61897600	0.68057900
C	3.63023700	0.59848700	1.00352500
H	3.99139300	1.00500200	0.05515000
H	4.51136500	0.35995900	1.61742200
Pd	0.76035600	0.28717600	-0.02258300
H	1.38909300	-1.29946800	-2.56554700

TS14b$^{\text{doublet}}$

C	2.53350600	1.27283000	-1.46196900
C	1.67646700	0.02252400	-3.20018200
C	2.64586900	0.49582200	-4.10608700
C	3.58913200	1.39132500	-3.64373500
C	3.55565200	1.81110500	-2.29655200
C	2.45471700	1.69072300	-0.07468500
C	1.37932900	1.61091000	2.00071000
C	2.30027500	2.53212000	2.53988500

C	3.31271800	3.03397500	1.75164300
C	3.40761400	2.62941400	0.40507800
H	2.64210500	0.15873100	-5.13766000
H	4.35853600	1.78513100	-4.30273000
H	2.19259600	2.84119100	3.57420300
H	4.03375200	3.74274800	2.14964800
N	1.47752700	1.18524300	0.73226200
N	1.62524400	0.38926500	-1.93139400
C	0.22443800	1.13136100	2.83375900
H	-0.03554100	0.09348100	2.60727300
H	0.43810500	1.23782700	3.90175800
H	-0.66472000	1.72802400	2.59256800
C	4.50190900	2.74476100	-1.76500000
C	4.42831900	3.13588600	-0.46432400
H	5.27384100	3.13622000	-2.42192800
H	5.14130300	3.84760200	-0.05713500
H	0.91276100	-0.68291600	-3.52270000
Pd	0.12340200	-0.52263200	0.12564400
C	-1.38224100	-1.96058500	-0.26007600
C	-0.74236100	-3.34192700	-0.44556600
H	-1.88765600	-1.61574500	-1.16258500
C	0.76008600	-3.25239100	-0.68134400
H	-0.94366600	-3.95685600	0.43573600
H	-1.18710700	-3.86320600	-1.30483900
H	1.22979700	-4.25225900	-0.67103400
H	0.96161100	-2.79835400	-1.65699900
C	1.30487400	-3.00386500	1.68260000
C	2.84597400	-2.23675700	-0.05125100
C	2.09225400	-2.23704700	2.74040700
H	1.68573700	-4.04026200	1.62142800
H	0.24757900	-3.03058400	1.94968300
C	3.67975000	-1.47169500	0.97395100
H	3.27676400	-3.24622100	-0.18026200
H	2.87245900	-1.73596900	-1.02181600
C	3.56890200	-2.10799100	2.36146900
H	1.97334700	-2.75440600	3.69965500
H	1.65319300	-1.24134700	2.85778000
H	4.72052800	-1.45523200	0.62748400
H	3.33986400	-0.43523900	1.02135500
H	4.11287300	-1.51078500	3.10305100
H	4.03313400	-3.10472500	2.34900800
N	1.42148600	-2.38792700	0.33210400
C	-2.22340000	-1.85783000	0.96090100
O	-1.88420000	-2.37937100	2.03953600

N	-3.39389900	-1.11730800	0.89231700
C	-4.10299700	-0.77870700	2.11905900
H	-5.11051300	-1.21289300	2.12448900
H	-3.53220500	-1.18061700	2.95530600
H	-4.19213200	0.31129100	2.20815900
C	-4.01022600	-0.67159800	-0.31767100
C	-5.04061200	-1.44134600	-0.87755100
C	-3.69198300	0.53475800	-0.93931000
C	-5.70046800	-1.02082200	-2.03290600
H	-5.30895400	-2.37812100	-0.39512400
C	-4.31582300	0.96393400	-2.09976300
C	-5.34214800	0.18275300	-2.64432600
H	-6.48802200	-1.63599400	-2.45868600
H	-4.01484200	1.89205800	-2.57797800
H	-5.85382000	0.51196500	-3.54561800
Br	-1.68543500	1.35646500	-0.30499200

IM14doublet

C	-0.04260400	2.39333300	-1.82337700
C	-0.60005900	1.27548800	-1.17491700
C	-1.98084700	1.09428400	-1.18434500
C	-2.81561000	1.99825800	-1.85205700
C	-2.26093200	3.10058800	-2.50018400
C	-0.88172100	3.30209000	-2.48469000
H	-2.41841800	0.23617800	-0.68426400
H	-3.88938000	1.83649200	-1.86408000
H	-2.89882300	3.81081800	-3.01670800
N	1.36507000	2.57146700	-1.86023300
H	-0.45715200	4.16690800	-2.98323100
C	2.20473300	2.20520200	-0.81759400
O	3.42936100	2.25443500	-0.93694400
C	1.53332000	1.74484700	0.45676900
H	0.74138500	2.43861600	0.73555000
C	2.50913200	1.43840600	1.59940400
H	2.28671200	2.06798300	2.46797100
H	3.51566300	1.70604600	1.26836800
C	1.97731700	3.19575800	-3.03393300
H	1.45148000	2.86713700	-3.93286500
H	1.93616500	4.28932900	-2.97131200
H	3.02212500	2.89055700	-3.06901200
C	-0.36775300	-3.41760100	-2.93486700
C	-1.16014600	-4.21275900	-2.13114400
C	-1.51850500	-3.76792300	-0.83883700
C	-1.01788800	-2.50965700	-0.41766800

C	0.08968500	-2.18784000	-2.43140800
C	-2.35683200	-4.52788200	0.04039600
C	-1.38743800	-1.98832400	0.87549300
C	-2.25022100	-2.75157600	1.69996100
C	-2.70567600	-4.03868800	1.26275100
C	-2.64611100	-2.17494000	2.92646600
H	-3.29793300	-2.73015300	3.59461400
C	-2.23128200	-0.90165800	3.24505300
C	-1.38000400	-0.18937000	2.36707600
H	-2.71696500	-5.49610500	-0.29303400
H	-0.09063500	-3.72484600	-3.93700300
H	-1.52208300	-5.17420600	-2.48329100
H	-3.35137900	-4.60904500	1.92340500
H	-2.55649000	-0.42409200	4.16261600
N	-0.94319200	-0.75469600	1.24028500
N	-0.20839400	-1.76240000	-1.20973500
C	-0.99319100	1.22982300	2.66780400
H	-1.55878700	1.61078000	3.52075900
H	0.07116100	1.31581200	2.90115200
H	-1.19594000	1.86109500	1.79792500
C	3.66110800	-1.91105900	-1.03508200
C	3.65052000	-0.89801900	0.10380900
C	2.20485200	-2.34397800	1.43699600
C	2.25803000	-3.43902100	0.37117100
C	3.51705200	-3.33547000	-0.49460300
H	4.49317200	-1.10159100	0.78492300
H	3.77132000	0.11701600	-0.27595800
H	2.84370800	-1.68298100	-1.73220700
H	4.59540000	-1.79410700	-1.59439100
H	2.99887800	-2.52531300	2.17916600
H	1.24932400	-2.36633500	1.96884300
H	2.21367500	-4.40756500	0.88220900
H	1.37515000	-3.37948000	-0.26782500
H	4.40230700	-3.58139700	0.10697000
H	3.47645700	-4.06427100	-1.31129700
N	2.38775000	-0.96670200	0.90003500
C	2.46996500	-0.02459600	2.05101600
H	3.35373000	-0.26460400	2.66087300
H	1.58715900	-0.21692200	2.66730800
Pd	0.66533500	0.01344800	-0.23563100
H	0.72044200	-1.53653500	-3.02775000

TS15[doublet]

C	0.52543200	-2.09085700	-1.51159500

C	-0.73814800	-1.77368200	-0.95597300
C	-1.67459400	-2.79064200	-0.76887900
C	-1.30855300	-4.12717200	-0.96625400
C	-0.01995900	-4.44132800	-1.40270700
C	0.89436900	-3.42720100	-1.69397100
H	-2.66265300	-2.56656900	-0.38755000
H	-2.02376500	-4.91620600	-0.75549100
H	0.26643000	-5.47726800	-1.55393800
N	1.33411200	-1.02101500	-1.91619000
H	1.86685000	-3.67134800	-2.10801800
C	0.70003500	0.18907900	-2.16880100
O	1.29561800	1.23049900	-2.41711500
C	-0.78508900	0.07023400	-2.08847400
H	-1.16678300	-0.66861800	-2.79203500
C	-1.62725700	1.32865200	-2.16373700
H	-1.67815600	1.64025500	-3.21722000
H	-1.16031000	2.15049900	-1.61693400
C	2.76627900	-1.15508500	-2.13284100
H	2.97928400	-1.69636500	-3.06173000
H	3.17953300	-0.14908900	-2.20377400
H	3.22013400	-1.68550700	-1.29240000
C	1.11069000	4.29435000	0.15038800
C	2.43374300	3.91182800	0.13042200
C	2.77330900	2.57584000	0.43229100
C	1.71625900	1.66732200	0.70943200
C	0.13722700	3.32648300	0.45378200
C	4.13471400	2.13616500	0.48699300
C	2.04291600	0.29916500	1.04185800
C	3.40341000	-0.07689900	1.16205200
C	4.43946200	0.86154900	0.85380000
C	3.68036000	-1.39252300	1.59652300
H	4.71283200	-1.71304700	1.70334900
C	2.64317800	-2.23996300	1.90587700
C	1.30688100	-1.81349700	1.72667600
H	4.91887000	2.84981000	0.25366300
H	0.81022800	5.31530000	-0.05763300
H	3.22073300	4.62403000	-0.09911500
H	5.47241300	0.53501500	0.92703400
H	2.83022100	-3.24109700	2.27921800
N	1.03259400	-0.58916200	1.26842300
N	0.41170600	2.05390100	0.70952600
C	0.18027800	-2.74359000	2.06674300
H	0.05479100	-3.50709900	1.29235900
H	0.39273600	-3.25700700	3.01036000

H	-0.76081600	-2.19935400	2.16323000
C	-3.09902800	1.63288400	2.09943900
C	-3.24019200	1.93350200	0.60881400
C	-4.08715700	-0.27212800	0.13681300
C	-3.98618900	-0.67934800	1.60478000
C	-4.08989600	0.54261200	2.52635800
H	-4.24754300	2.32717800	0.39788200
H	-2.52401100	2.68490300	0.27840900
H	-2.06765900	1.31469200	2.30784600
H	-3.26706900	2.55506100	2.66671400
H	-5.07353600	0.17463400	-0.06744200
H	-3.97768400	-1.13246900	-0.52536900
H	-4.77469200	-1.40550100	1.83100500
H	-3.02395300	-1.18742200	1.76208500
H	-5.11065200	0.94437600	2.47536600
H	-3.91579700	0.25249000	3.56760900
N	-3.03160300	0.71171100	-0.21111000
C	-3.04134000	1.04241700	-1.66199400
H	-3.71324600	1.88945000	-1.84946500
H	-3.44666500	0.17934200	-2.19909500
Pd	-0.89422000	-0.05439000	0.26076900
H	-0.90751400	3.61512100	0.49454300

CAT1

Br	1.98896500	-2.59592700	0.48433800
C	-4.21234200	-0.99380800	-2.01059300
C	-4.89644600	-0.27870700	-1.04992300
C	-4.27749800	-0.01110700	0.18974600
C	-2.96468800	-0.50384000	0.37373100
C	-2.90187800	-1.45460800	-1.75615300
C	-4.90894300	0.72285500	1.24889100
C	-2.28763100	-0.25917300	1.62081000
C	-2.93464600	0.46758700	2.64902300
C	-4.26627000	0.95333300	2.42888300
C	-2.21388100	0.67173900	3.84702500
H	-2.67534600	1.22475900	4.66042000
C	-0.93371700	0.16668200	3.96914800
C	-0.36827600	-0.54463600	2.89355700
H	-5.91741400	1.09315800	1.08842800
H	-4.66869600	-1.21153400	-2.97017400
H	-5.90482200	0.07997800	-1.23639400
H	-4.75344400	1.51025900	3.22401800
H	-0.35771400	0.30855100	4.87722400
N	-1.02987800	-0.74640800	1.76123300

N	-2.30238700	-1.20845200	-0.58647400
C	-2.12382300	-2.23379300	-2.77624700
H	-2.71253200	-2.40806500	-3.68071100
H	-1.20876300	-1.69509400	-3.04862000
H	-1.81483400	-3.20008700	-2.36155300
Pd	-0.32678800	-1.81296800	-0.01617200
H	0.63341500	-0.96210500	2.93475500

3a

C	-1.59866600	-2.62962000	-2.06508600
C	-2.46213800	-1.73895900	-2.70357900
C	-2.17747100	-0.36741000	-2.76070900
C	-1.00471000	0.07074500	-2.15760400
C	-0.12558800	-0.81206000	-1.50852700
C	-0.41902000	-2.16464100	-1.46249100
H	-1.83932100	-3.68784900	-2.03384000
H	0.25518100	-2.85866000	-0.96750100
H	-3.37197600	-2.10990200	-3.16675700
N	-0.49955400	1.37596600	-2.08316200
C	-1.12661800	2.54578100	-2.65519200
H	-2.11678300	2.71195200	-2.21487900
H	-0.48175100	3.39825700	-2.43615300
H	-1.23565900	2.43773900	-3.74086700
C	0.71059500	1.41647900	-1.40413400
O	1.36454500	2.42774500	-1.21042300
C	1.04846400	-0.02534100	-0.97761300
C	2.41496300	-0.49586400	-1.51571100
H	2.43721200	-0.33113600	-2.59904800
H	2.50080900	-1.57778900	-1.36265000
H	-2.85003900	0.32293700	-3.25948000
H	1.07571800	-0.04548000	0.12124200
C	7.25622400	-0.75842100	-0.72655900
C	5.94868100	-0.08019600	-0.31157600
C	5.25070000	0.15075400	-2.60419000
C	6.52877500	-0.51792500	-3.11472300
C	7.68132000	-0.30657100	-2.12758500
H	5.62607600	-0.45502300	0.66675700
H	6.12177900	1.01086500	-0.19886700
H	8.03638500	-0.53169500	0.01050700
H	7.10326500	-1.84534500	-0.72139600
H	4.42837700	-0.04827900	-3.29802700
H	5.39284800	1.25170500	-2.58215400
H	6.33853100	-1.59217500	-3.23505100
H	6.78200700	-0.11549900	-4.10322700

H	8.57914600	-0.84488300	-2.45464600
H	7.94167700	0.76146600	-2.09949800
N	4.88371500	-0.35247400	-1.27840800
C	3.60022700	0.18628000	-0.82608300
H	3.53624000	1.27917500	-0.95542200
H	3.52067600	-0.00668700	0.25144900

TS16[doublet]

C	1.38734800	0.42071400	-1.20867100
C	2.60013300	0.08358400	-0.59669600
C	2.82852600	-1.17736800	-0.04925700
C	1.83597800	-2.15273200	-0.14062000
C	0.63378400	-1.86368800	-0.78794100
C	0.41718200	-0.59106600	-1.30731800
H	3.77476200	-1.39262800	0.43445400
H	2.00825100	-3.13484000	0.28885600
H	-0.13687900	-2.62299700	-0.87638100
N	1.15564600	1.68215700	-1.82191800
Br	4.03667900	1.40119900	-0.49338900
H	-0.51367500	-0.34898600	-1.80896200
C	0.05635000	2.50132200	-1.46853700
O	-0.56200900	3.07903000	-2.36656500
C	-0.27387200	2.70209400	-0.04645500
H	-1.06627300	3.44288900	0.04508200
C	0.64425000	2.52696900	1.05110200
H	1.68422900	2.28630000	0.84530300
H	0.52948600	3.19882400	1.90563100
C	1.55156100	1.72845700	-3.23158100
H	1.51796400	2.76271300	-3.57301600
H	2.57032000	1.34226200	-3.32052900
H	0.88217600	1.13270700	-3.86819800
C	-4.22820700	-0.68483900	-0.68865100
C	-4.10607500	-1.98766600	-0.24963100
C	-3.03528500	-2.32922800	0.60310900
C	-2.13127500	-1.29491000	0.94076100
C	-3.26982900	0.29058900	-0.32882400
C	-2.82804200	-3.64298700	1.13862200
C	-1.04489800	-1.55963400	1.83991900
C	-0.86457600	-2.86513000	2.35249300
C	-1.78166800	-3.90091700	1.97439100
C	0.23247200	-3.07113500	3.21319500
H	0.41528700	-4.05734300	3.63097400
C	1.05847800	-2.00730100	3.51251700
C	0.81107200	-0.72641000	2.97187600

H	-3.52452500	-4.43025200	0.86384200
H	-5.05255800	-0.39283300	-1.33068000
H	-4.82902300	-2.74529100	-0.53939500
H	-1.62686800	-4.89900500	2.37473100
H	1.91042600	-2.13779800	4.17149000
N	-0.22552300	-0.50812500	2.14864700
N	-2.22487100	-0.02897400	0.44581800
C	-3.38905100	1.70395800	-0.81024900
H	-3.30777600	2.38601900	0.04022500
H	-2.57824200	1.96649500	-1.49807300
H	-4.34582500	1.86408900	-1.31545400
C	-4.75224800	-0.50354000	3.35718600
C	-3.69657900	0.52909000	3.75505000
C	-5.00389800	2.32807500	2.69825200
C	-6.07716700	1.32883100	2.26227900
C	-6.13595000	0.14325800	3.23205300
H	-3.87426000	0.86271200	4.79489800
H	-2.69551300	0.08924500	3.71780000
H	-4.47251000	-0.94782600	2.39693800
H	-4.76279300	-1.31067800	4.09981700
H	-5.30602400	2.80554600	3.64922700
H	-4.89309400	3.12569200	1.95659500
H	-7.04628000	1.83937300	2.20942200
H	-5.83884600	0.96627200	1.25441300
H	-6.46615400	0.49791800	4.21927900
H	-6.87502200	-0.59350300	2.89543200
N	-3.70821400	1.67432800	2.84992600
C	-2.58115900	2.47150300	2.83457500
H	-1.63306400	2.01479400	3.08847300
H	-2.60212600	3.36164100	2.21816300
C	1.71858600	0.42276100	3.29173100
H	2.32146800	0.67831000	2.41416400
H	1.13864900	1.31441800	3.54184800
H	2.38821000	0.17442800	4.12020000
Ni	-0.63773400	1.10395800	1.01930200

IM15doublet

C	3.63332800	-0.74616600	-0.34211600
C	3.98058200	0.53894100	0.08990600
C	5.19930300	0.81192500	0.70695100
C	6.09859600	-0.22890100	0.92920900
C	5.76878900	-1.52672000	0.53241600
C	4.55612500	-1.77585500	-0.09961300
H	5.42941000	1.82338000	1.02242800

H	7.04719400	-0.02379800	1.41635700
H	6.46116500	-2.34458100	0.70783800
N	2.41741300	-1.02123400	-1.01941200
Br	2.71496200	2.01795400	-0.10474800
H	4.28977200	-2.77955400	-0.40961100
C	1.57825600	-2.01886100	-0.50329800
O	1.81322000	-2.49545000	0.61381800
C	0.44909200	-2.42639800	-1.34103400
C	-0.52492700	-3.34709000	-0.88206600
H	-0.37368900	-3.85035400	0.06699600
C	2.21751900	-0.44263900	-2.34648200
H	1.21269300	-0.02357000	-2.43595700
H	2.93669100	0.36244500	-2.49299600
H	2.37278200	-1.18726000	-3.13957200
C	-5.31538400	-0.25114100	2.15121600
C	-4.06862700	-0.94445300	1.59489800
C	-4.54158100	-0.16931300	-0.63946000
C	-5.80940300	0.55224200	-0.17574200
C	-5.67761000	0.96673800	1.29407700
H	-3.19540700	-0.27483700	1.71721000
H	-3.85183900	-1.85393900	2.16734500
H	-6.15025200	-0.96370000	2.14784100
H	-5.13759000	0.04535400	3.19284700
H	-3.69882800	0.54897200	-0.64045000
H	-4.66194400	-0.52177600	-1.67131700
H	-5.98843600	1.42830200	-0.81232400
H	-6.66690200	-0.12286300	-0.29256400
H	-4.88042600	1.71996300	1.38472800
H	-6.60201100	1.43620100	1.65251300
N	-4.25449000	-1.31983300	0.20152600
C	-0.63406600	0.79605100	0.90656600
C	-0.46930200	-1.04457400	2.32205100
C	-0.09805200	-0.19393000	3.38482900
C	-0.01770000	1.17208700	3.20044600
C	-0.30004800	1.71175600	1.93150700
C	-0.92624500	1.28362300	-0.40517400
C	-1.54632900	0.75914600	-2.59106200
C	-1.49806800	2.11852700	-2.94430700
C	-1.17220100	3.07489600	-1.99601400
C	-0.87430200	2.67145400	-0.68042000
H	0.11196600	-0.63444400	4.35359100
H	0.25830100	1.83099100	4.01910300
H	-1.72739900	2.40675000	-3.96493700
H	-1.14299900	4.12904000	-2.25703400

N	-1.27200800	0.35843800	-1.34109100
N	-0.72710200	-0.54844000	1.10417800
C	-1.90716600	-0.31287000	-3.57785200
H	-1.04473200	-0.96275400	-3.77071400
H	-2.70214300	-0.94709100	-3.17070400
H	-2.24026500	0.11047900	-4.52899000
C	-0.60464900	-2.52113300	2.53117900
H	0.24774300	-3.02056200	2.05980900
H	-0.62719600	-2.76564700	3.59690100
H	-1.51833700	-2.88469200	2.05348500
Ni	-1.32890400	-1.53756600	-0.60979100
C	-0.25448600	3.11327900	1.63124000
C	-0.52767100	3.57656900	0.37780300
H	0.00978700	3.80269900	2.42817100
H	-0.48944500	4.64004700	0.15931500
C	-3.21808900	-2.20374500	-0.31821000
H	-3.18913300	-3.09386100	0.32211700
H	-3.54530800	-2.55092900	-1.31192000
H	0.49028800	-2.19896300	-2.40091200
H	-1.11414800	-3.90030900	-1.61166500

IM16^{CSS}

C	4.97055900	0.12512700	-0.86468600
C	3.99089500	-1.97764300	-1.04900600
C	5.21586800	-2.51356200	-1.50766600
C	6.32685900	-1.70957100	-1.63183000
C	6.22660600	-0.33724400	-1.31810100
C	4.79134200	1.51717500	-0.56890000
C	3.32331500	3.21835700	0.06257600
C	4.36385100	4.16502400	-0.08550100
C	5.62613200	3.77229600	-0.46684500
C	5.87356500	2.40903100	-0.73449000
H	5.26324600	-3.56628500	-1.76244900
H	7.27174200	-2.11579800	-1.98056800
H	4.14539400	5.20904200	0.10782800
H	6.42622300	4.49842300	-0.57619400
N	3.54686200	1.91413700	-0.15969200
N	3.88338800	-0.68641300	-0.71516400
C	1.95553400	3.68314300	0.46723500
H	1.71991100	3.35941000	1.48600500
H	1.89724000	4.77333400	0.43512800
H	1.19361600	3.27043100	-0.19805900
C	7.31466200	0.58573600	-1.45095400
C	7.14396200	1.90833300	-1.17017400

H	8.27529300	0.20998900	-1.78914300
H	7.96579200	2.60894700	-1.28008600
C	-1.49960800	-1.28403800	0.87411100
C	-0.19309100	-1.14980200	0.08849200
C	1.12948200	-1.38983800	2.15593500
C	-0.14607600	-1.53989200	2.98860200
C	-1.28864200	-2.11879300	2.14433600
H	0.14688200	-2.13243100	-0.24950500
H	-0.30697600	-0.51112900	-0.79113300
H	-1.86598900	-0.28397700	1.13941100
H	-2.25599400	-1.74085600	0.22658500
H	1.48596500	-2.37107900	1.82652900
H	1.93435600	-0.91541400	2.72275400
H	0.06812000	-2.18053000	3.85106500
H	-0.43368700	-0.55699000	3.38356700
H	-1.04644600	-3.15356200	1.86382400
H	-2.21188600	-2.15971600	2.73105000
N	0.88683000	-0.57066300	0.93528100
C	0.85309800	0.84861300	1.12238900
H	0.98305700	1.17871500	2.15330600
H	0.03785800	1.35333200	0.60527300
C	2.77640700	-2.85162300	-0.94509900
H	2.45926100	-2.95256900	0.09678400
H	1.94661500	-2.41671700	-1.50960900
H	2.97728400	-3.85047600	-1.33809400
Ni	2.37590900	0.37516700	0.15749400

IM17

C	-0.37100800	0.31181700	1.69928600
C	0.99108800	0.53931200	1.53536600
C	1.50326400	1.82306600	1.46183200
C	0.63836300	2.92302800	1.55117400
C	-0.73102200	2.71434600	1.73644200
C	-1.23391200	1.41617900	1.83112600
H	2.57262200	1.96540900	1.32688900
H	1.03095600	3.93676300	1.48554300
H	-1.40876600	3.56034500	1.82635600
N	-0.90053400	-1.01334700	1.79136300
Br	3.20260800	-1.26248000	1.33093300
H	-2.29438500	1.24775000	2.00537600
C	-2.01640700	-1.43878200	1.11534000
O	-2.61532500	-2.47745800	1.41105500
C	-2.43975800	-0.61519800	-0.06359700
H	-1.76335300	0.14911600	-0.43020100

C	-3.60636200	-0.85537000	-0.66529400
H	-4.26458400	-1.63034500	-0.28286700
H	-3.92136600	-0.30130000	-1.54542300
C	-0.28216500	-1.91043100	2.76630400
H	0.80308600	-1.85031000	2.65598500
H	-0.56880600	-1.62472300	3.78778500
H	-0.63334100	-2.92251200	2.56865900

TS17[doublet]

C	0.19733800	-0.87810300	-3.62177900
C	-0.17659400	-1.82941100	-2.67288700
C	-1.38795300	-1.72193300	-1.97691200
C	-2.20851300	-0.63888600	-2.27189700
C	-1.85335300	0.31625800	-3.24028500
C	-0.64772500	0.20519100	-3.91027600
H	1.14835800	-0.97186600	-4.13611700
H	-0.36115000	0.94487100	-4.65311300
H	0.48843300	-2.65819000	-2.45026900
N	-3.45434000	-0.32250100	-1.72496800
C	-4.14913100	-1.10693100	-0.73105800
H	-3.50174700	-1.29384600	0.13071400
H	-5.02374400	-0.53384700	-0.41945200
H	-4.47235800	-2.07077200	-1.14470400
C	-3.99487200	0.82510800	-2.30030200
O	-5.07379200	1.30406200	-2.01863300
C	-2.99720600	1.31220700	-3.37891700
C	-2.64611600	2.75801500	-3.26211000
H	-2.71544000	3.26318200	-2.30650000
H	-2.35830200	3.31609200	-4.14662400
H	-1.66732500	-2.45499000	-1.22732200
Br	-2.69319500	3.32255100	0.47881400
C	2.55583500	1.59229500	-2.25961400
C	3.06278300	0.35457200	-1.88974700
C	2.35961200	-0.43212100	-0.96316800
C	1.16325300	0.11026400	-0.43675400
C	1.35296600	2.06033900	-1.70366800
C	2.77310100	-1.73904300	-0.53228700
C	0.39557800	-0.63298800	0.51398000
C	0.80786100	-1.93074500	0.89985500
C	2.02619900	-2.46077800	0.35092800
C	-0.01419800	-2.61480100	1.81139400
H	0.25250900	-3.61850400	2.13094100
C	-1.15672400	-1.99717300	2.30156300
C	-1.48663900	-0.69057300	1.89763500

H	3.69524400	-2.14803900	-0.93594000
H	3.07570900	2.20943000	-2.98453500
H	3.99102500	-0.01443800	-2.31736200
H	2.34399900	-3.45248300	0.66064600
H	-1.80054300	-2.50700200	3.01025800
N	-0.72810200	-0.04231300	1.00151600
N	0.68007700	1.32390700	-0.80764800
C	-2.66098200	0.04707100	2.47216900
H	-3.32231300	-0.62825300	3.02175100
H	-2.31218300	0.82693600	3.16028300
H	-3.22623600	0.56399400	1.69221800
C	0.75409500	3.38120300	-2.08086500
H	0.57425900	3.99320100	-1.18967800
H	1.40207700	3.93339500	-2.76655000
H	-0.22171800	3.22523700	-2.55758700
Ni	-0.78168400	1.90295700	0.45747400
H	-3.49394400	1.13713400	-4.34677700
C	4.04886200	1.16789900	1.88314500
C	2.94403800	2.22274300	1.80389300
C	1.57209600	0.97170100	3.40063200
C	2.64524600	-0.11177500	3.51774200
C	4.03632500	0.46976900	3.24675900
H	3.18745300	3.05891600	2.49122000
H	2.89392500	2.64136000	0.79350600
H	3.89432500	0.42523200	1.09266500
H	5.01763000	1.64807700	1.69791900
H	1.68400800	1.69067900	4.23831500
H	0.57542600	0.52791100	3.49097600
H	2.59586100	-0.55964400	4.51788700
H	2.43660700	-0.90573100	2.79210000
H	4.28714100	1.19793900	4.03192800
H	4.79918400	-0.31720600	3.28588700
N	1.63264900	1.66498700	2.11923900
C	0.52398800	2.53759300	1.86235600
H	0.85550100	3.51346300	1.48932500
H	-0.10103400	2.68595500	2.75091700

TS18doublet

C	2.73126900	-0.52063400	3.36362800
C	1.75159800	0.22025600	4.02237000
C	1.13089000	1.29650400	3.38653400
C	1.48656000	1.65826200	2.07129500
C	2.49412000	0.91671600	1.40811900
C	3.09239700	-0.15405000	2.06432000

H	3.21542700	-1.36073200	3.85263300
H	3.85817400	-0.71799400	1.53758400
H	1.45894700	-0.03628600	5.03726700
N	0.83796100	2.69480200	1.40527900
C	-0.08463500	3.55613100	2.12157000
H	-0.42324500	4.31390700	1.41754500
H	-0.96867700	3.01521400	2.49154800
H	0.41873100	4.02355200	2.97552800
C	0.83707600	2.76518900	-0.03664500
O	-0.09295700	3.43396200	-0.57450000
C	1.79686200	2.01042500	-0.69535100
C	2.91321900	1.32101400	0.01546200
H	3.23396300	0.42778500	-0.54182900
H	3.82398000	1.95142300	0.07633200
H	0.36659400	1.85514800	3.91358000
Ni	-0.82837500	-0.42490300	-0.83713000
Br	-2.86922300	-1.64076500	-1.17927300
C	1.82169000	-3.21434900	1.21380800
C	2.85893200	-3.31150000	0.30751200
C	2.82819800	-2.53386700	-0.86658100
C	1.69848800	-1.70347500	-1.05833900
C	0.74176500	-2.34142700	0.97079700
C	3.86832800	-2.53633500	-1.85491600
C	1.59896400	-0.90427900	-2.24367000
C	2.64174600	-0.91675000	-3.19907500
C	3.78204900	-1.75663600	-2.97093900
C	2.48396700	-0.08381700	-4.32512900
H	3.25441400	-0.06226500	-5.09072000
C	1.34983500	0.70324000	-4.44008300
C	0.36175300	0.67762100	-3.43825100
H	4.73320100	-3.17308700	-1.69181200
H	1.82708600	-3.79579500	2.12895900
H	3.70038400	-3.97331100	0.49336800
H	4.57861700	-1.76010800	-3.70955900
H	1.21438900	1.35685100	-5.29514400
N	0.49783600	-0.11946200	-2.37089500
N	0.68619900	-1.61116800	-0.14846700
C	-0.82803900	1.59035700	-3.44834500
H	-1.74290100	1.03338500	-3.21309100
H	-0.68735200	2.36372700	-2.67821900
H	-0.95260700	2.07705100	-4.41947100
C	-0.35939300	-2.17484200	1.97317400
H	-1.32669200	-2.09534500	1.46962100
H	-0.38420900	-3.01568500	2.67150900

H	-0.18268500	-1.26097700	2.55361400
H	1.83626500	2.10903000	-1.77156800
C	-4.31859800	0.95117100	2.86662600
C	-3.25796400	0.21283900	2.04538200
C	-3.71950300	1.66715100	0.08922500
C	-4.77812100	2.43143100	0.88635300
C	-5.40801300	1.53435300	1.95851300
H	-2.41877000	-0.09886200	2.67202100
H	-3.68469200	-0.68753400	1.57786200
H	-4.74721700	0.25539600	3.59704600
H	-3.83526800	1.76048800	3.42986800
H	-3.18270900	2.32785200	-0.59631400
H	-4.17914200	0.86136900	-0.50103300
H	-4.31019800	3.30401800	1.36043400
H	-5.53950300	2.80586300	0.19290300
H	-6.13614700	2.09887700	2.55186100
H	-5.95565400	0.71407400	1.47358100
N	-2.73087800	1.06293600	0.98231000
C	-1.44251800	0.97136400	0.58525900
H	-0.75224400	0.67073800	1.36883500
H	-1.13333100	1.79448200	-0.07079800

IM18[doublet]

C	2.52559200	2.78771900	3.69811700
C	1.51083000	2.10094100	4.35938200
C	1.27400900	0.75321100	4.08644400
C	2.05662000	0.07467100	3.14104200
C	3.08824600	0.76274800	2.47278800
C	3.30483100	2.10702900	2.76020800
H	2.70429900	3.83938600	3.89979600
H	4.09348900	2.63127900	2.22553700
H	0.88685200	2.61238300	5.08708500
N	1.83638100	-1.28519700	2.85489900
C	0.98403400	-2.06488800	3.73860800
H	1.30950100	-1.94520300	4.77707500
H	-0.06720600	-1.75517400	3.66336700
H	1.06861400	-3.10645300	3.43600500
C	2.31907100	-1.90092200	1.68475400
O	2.02904500	-3.09206700	1.48016500
C	3.08969600	-1.05882200	0.75651200
C	3.92284300	-0.00302000	1.48332900
H	4.75218000	-0.49011800	2.02877300
H	4.39549700	0.69244400	0.78358400
H	0.46677800	0.24245600	4.59658900

Ni	1.70449100	-0.32200800	-0.65290700
Br	0.52007600	0.43161800	-2.76442400
C	3.42628900	3.76474300	-0.93478900
C	2.54591000	4.49878800	-0.16663400
C	1.45966100	3.85411400	0.46067200
C	1.35090700	2.45714500	0.26762500
C	3.23842800	2.37259900	-1.08465200
C	0.49564700	4.53120600	1.27667300
C	0.25853000	1.73507300	0.86348600
C	-0.67022700	2.43174700	1.67150600
C	-0.52174700	3.84431700	1.86680200
C	-1.71511500	1.67535700	2.23877300
H	-2.44222100	2.16230000	2.88309400
C	-1.81250700	0.33040600	1.95387900
C	-0.86805800	-0.28430000	1.10133100
H	0.59799100	5.60318500	1.41979300
H	4.26109800	4.24374800	-1.43550500
H	2.67775700	5.57035200	-0.04262500
H	-1.24751400	4.35720900	2.49154500
H	-2.62141200	-0.26800000	2.35946900
N	0.15307600	0.40894400	0.59905400
N	2.23212400	1.75323100	-0.47427400
C	-0.99435100	-1.71727500	0.68970000
H	-0.16134200	-2.31549600	1.06974200
H	-1.93317600	-2.15041200	1.04574500
H	-0.95811000	-1.77602400	-0.40186900
C	4.11893800	1.54042000	-1.97129700
H	5.00854200	2.09087100	-2.28879800
H	4.43170900	0.62343700	-1.46064900
H	3.54678100	1.24127400	-2.85829900
H	3.73266500	-1.70930100	0.15774200
C	-1.09554600	-3.12640600	-3.73447000
C	0.40293900	-3.01360200	-3.45835700
C	0.14246600	-4.26586100	-1.34393500
C	-1.35755600	-4.43940700	-1.60246500
C	-1.67143400	-4.39928900	-3.10307700
H	0.93723000	-3.83818800	-3.96526700
H	0.79047700	-2.06448800	-3.82708000
H	-1.58988000	-2.23702100	-3.32495500
H	-1.26033100	-3.12062400	-4.81839200
H	0.67495800	-5.16059700	-1.71396300
H	0.36409200	-4.17427900	-0.27897800
H	-1.68341800	-5.38857400	-1.15983800
H	-1.91039600	-3.64022700	-1.09631500

H	-1.22828800	-5.27971000	-3.59156400
H	-2.75400900	-4.45783800	-3.26649700
N	0.68222200	-3.08763100	-2.02591000
C	1.77434800	-2.45155100	-1.49396600
H	2.49228600	-2.08913300	-2.23244100
H	2.17360400	-2.94100400	-0.61357200

TS19doublet

C	-2.88011300	-2.39346600	-1.77466800
C	-3.14327900	-1.30634100	-2.60530400
C	-2.12482200	-0.41995200	-2.94913100
C	-0.81466100	-0.60239500	-2.46862300
C	-0.54951700	-1.69236900	-1.61124300
C	-1.58417900	-2.56877200	-1.29003100
H	-3.66871500	-3.08646100	-1.49815900
H	-1.36280300	-3.40650500	-0.63250400
H	-4.14675000	-1.13375600	-2.98365000
N	0.20781500	0.27874600	-2.83742200
C	-0.04889700	1.28352900	-3.85319600
H	-0.41990200	0.81676500	-4.77389900
H	-0.79010300	2.02053100	-3.51613300
H	0.89597400	1.78614800	-4.04864100
C	1.50293000	0.22959800	-2.25452600
O	2.34669100	1.08913300	-2.65151400
C	1.73631800	-0.71840900	-1.23248300
C	0.85182800	-1.93823600	-1.11067800
H	1.28204800	-2.77946700	-1.69045800
H	0.81028600	-2.30431500	-0.07613400
H	-2.35602500	0.42585900	-3.58400600
Ni	0.09114700	0.25981100	1.13060000
Br	1.64184600	0.23600000	3.00230800
C	-3.09045100	-2.53968400	2.15175000
C	-4.17753300	-1.91953100	1.57237200
C	-3.98800700	-0.71452200	0.86712900
C	-2.66857400	-0.20992100	0.80378000
C	-1.80182800	-1.97028700	2.05214200
C	-5.04593700	-0.00396900	0.21318900
C	-2.40666100	1.00280100	0.08381000
C	-3.46892900	1.68047900	-0.55678000
C	-4.79567300	1.14596900	-0.47443400
C	-3.14697400	2.86217500	-1.25476100
H	-3.92722100	3.41277000	-1.77311900
C	-1.84200500	3.30882500	-1.25754800
C	-0.83643400	2.58913600	-0.57538300

H	-6.05310800	-0.40719500	0.27124300
H	-3.20865500	-3.47181500	2.69418700
H	-5.17210500	-2.35095300	1.64626700
H	-5.59966100	1.67958800	-0.97371600
H	-1.56821600	4.22250300	-1.77484400
N	-1.11871800	1.45074900	0.06933500
N	-1.60578100	-0.82196100	1.39331100
C	0.57858000	3.08233400	-0.55734600
H	1.05379500	2.82470900	0.39411100
H	1.15749900	2.62734200	-1.36974500
H	0.61247000	4.16879000	-0.68453200
C	-0.61448300	-2.63945500	2.67964900
H	0.13447700	-2.88606200	1.91968100
H	-0.12274500	-1.96544200	3.38742600
H	-0.90935600	-3.55912800	3.19237000
H	2.78216800	-0.93073000	-1.06847600
C	5.61409300	-1.15024100	-1.33481000
C	5.27098200	0.33407800	-1.15577500
C	5.07424900	-0.00067300	1.32018900
C	5.35447400	-1.49528500	1.14923300
C	6.24725700	-1.74761600	-0.07207400
H	6.19049800	0.92918900	-1.07755700
H	4.66291100	0.70320900	-1.98475500
H	4.69678800	-1.69572500	-1.58465700
H	6.28717200	-1.24517300	-2.19459300
H	6.00791500	0.54159600	1.52129900
H	4.36698500	0.18468500	2.13060200
H	5.82412000	-1.86919100	2.06582000
H	4.39732100	-2.01996200	1.03838700
H	7.23309500	-1.29070900	0.09768700
H	6.41547200	-2.82181600	-0.20739300
N	4.49947000	0.55368700	0.08310200
C	3.31960200	1.10613800	0.05184300
H	2.96969000	1.49441100	-0.90047600
H	2.80078800	1.24325300	0.99215400

CAT2

C	-2.61992800	1.22008600	-1.23309600
C	-0.81864200	2.22405100	-2.31588800
C	-1.71354400	2.89922500	-3.17648300
C	-3.07733200	2.72242300	-3.05112500
C	-3.57620100	1.85813100	-2.05250100
C	-3.04639100	0.32598900	-0.19617800
C	-2.40140800	-1.09483300	1.53312300

C	-3.75855200	-1.38670500	1.79822100
C	-4.76180000	-0.80669600	1.04715100
C	-4.42254400	0.08504100	0.00657000
H	-1.30993600	3.55908700	-3.93704200
H	-3.76772200	3.24033400	-3.71114000
H	-3.99802500	-2.07440400	2.60227700
H	-5.80604100	-1.02923900	1.24844000
N	-2.06602500	-0.25116400	0.54974400
N	-1.27819500	1.40160200	-1.36529300
C	-1.28418500	-1.70548400	2.32696100
H	-0.67259800	-0.92422700	2.79149400
H	-1.66649500	-2.37150500	3.10489600
H	-0.61140700	-2.26854000	1.67071500
C	0.66869600	2.39139600	-2.42134400
H	1.15073000	1.42525400	-2.60694400
H	0.93520100	3.08472600	-3.22330800
H	1.08061000	2.76008900	-1.47552200
Ni	-0.24184500	0.33220000	-0.02857700
C	-4.96916800	1.59641100	-1.82677200
C	-5.37508700	0.74626900	-0.83915900
H	-5.69837600	2.09164200	-2.46161900
H	-6.43202500	0.55528000	-0.67655800
Br	1.97906000	-0.04046200	0.55687900

4a

C	-0.42036100	1.49552400	-2.05703700
C	-0.27428800	2.67154400	-1.32509900
C	0.48468300	2.68653500	-0.15376500
C	1.10086700	1.51330200	0.30054400
C	0.94097900	0.31513400	-0.42431700
C	0.19417300	0.32767200	-1.59949800
H	-1.00325700	1.48435600	-2.97299300
H	0.09098500	-0.59874700	-2.15889000
H	-0.74283800	3.59070300	-1.66495900
N	1.87954600	1.50964100	1.48318700
C	1.79225200	2.63647600	2.40468900
H	2.25741600	3.53577000	1.98248800
H	0.74366400	2.85101700	2.63067700
H	2.32501600	2.35884500	3.31221800
C	2.83136200	0.53144700	1.75083100
O	3.55089200	0.58175300	2.73981700
C	2.95583000	-0.57617000	0.71711000
C	1.59520500	-0.92852800	0.11304000
H	1.73501200	-1.66544000	-0.68187000

H	0.95885900	-1.38123500	0.88745300
H	0.60277400	3.61494100	0.39197600
H	3.36726800	-1.43229600	1.25749600
C	4.50333900	-1.64919800	-3.78496800
C	4.52022900	-0.57698200	-2.69363700
C	5.03031000	-2.21973300	-0.99238000
C	5.03712700	-3.35380500	-2.01919900
C	5.41206100	-2.82424700	-3.40769800
H	5.53060100	-0.12030200	-2.64431800
H	3.81427700	0.22346600	-2.94102900
H	3.47219200	-2.00536100	-3.90694100
H	4.81423600	-1.20611400	-4.73883800
H	6.06274700	-1.83567100	-0.85667800
H	4.70331700	-2.59997800	-0.01920800
H	5.73596500	-4.13511400	-1.69687700
H	4.03561200	-3.80189200	-2.05367900
H	6.45741500	-2.48314100	-3.39397600
H	5.34762800	-3.62136600	-4.15795400
N	4.12789600	-1.14441800	-1.40363900
C	3.96235800	-0.13056600	-0.37064400
H	4.91805200	0.13711600	0.11403200
H	3.57825600	0.77664800	-0.84818100

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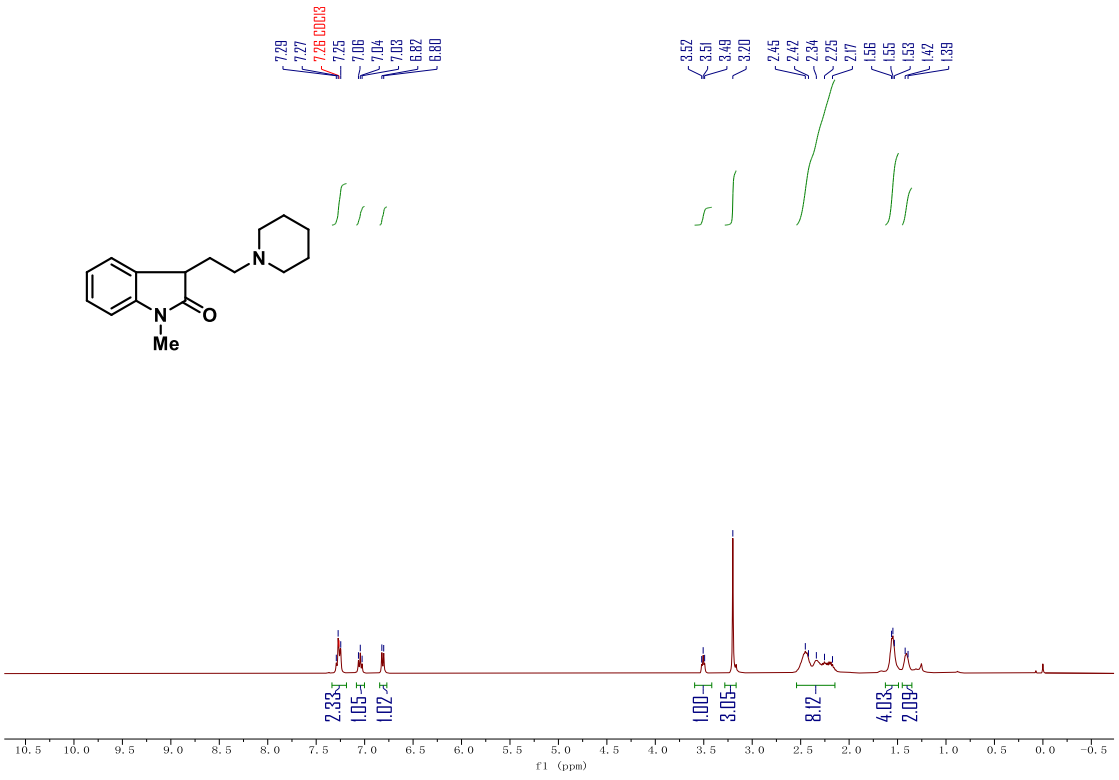
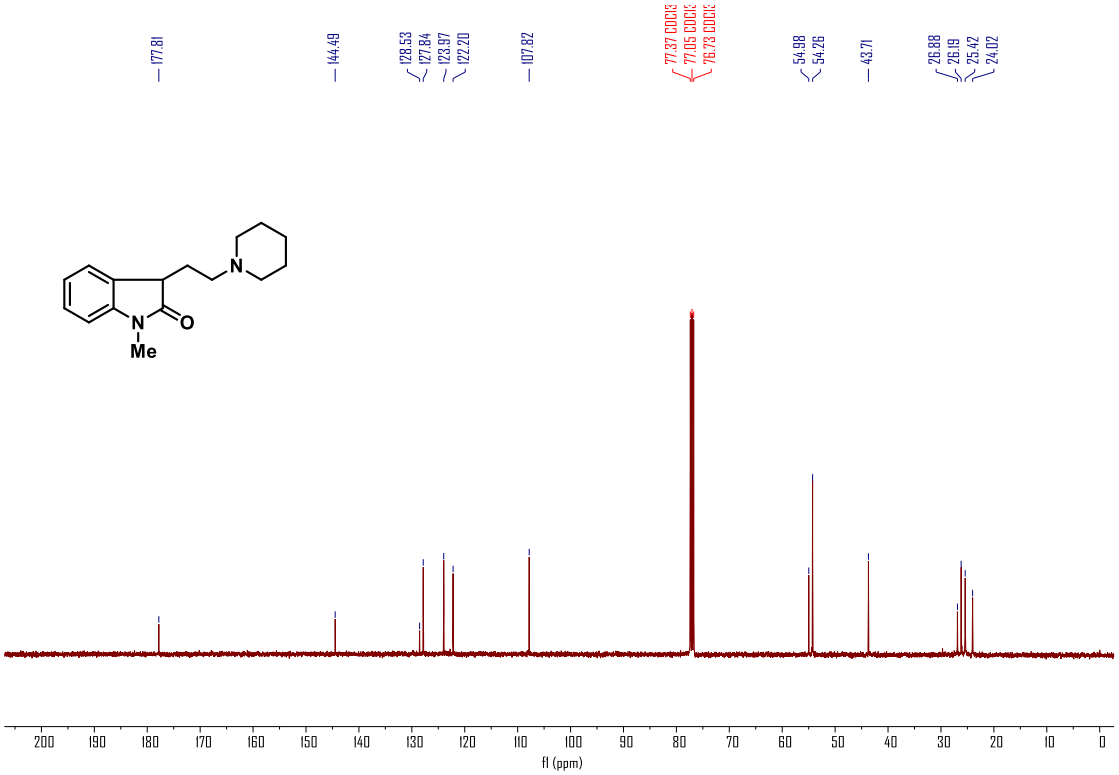
9. NMR Spectra

^{1}H NMR of 3a (400 MHz, $CDCl_3$)



^{13}C NMR of 3a (101 MHz, $CDCl_3$)



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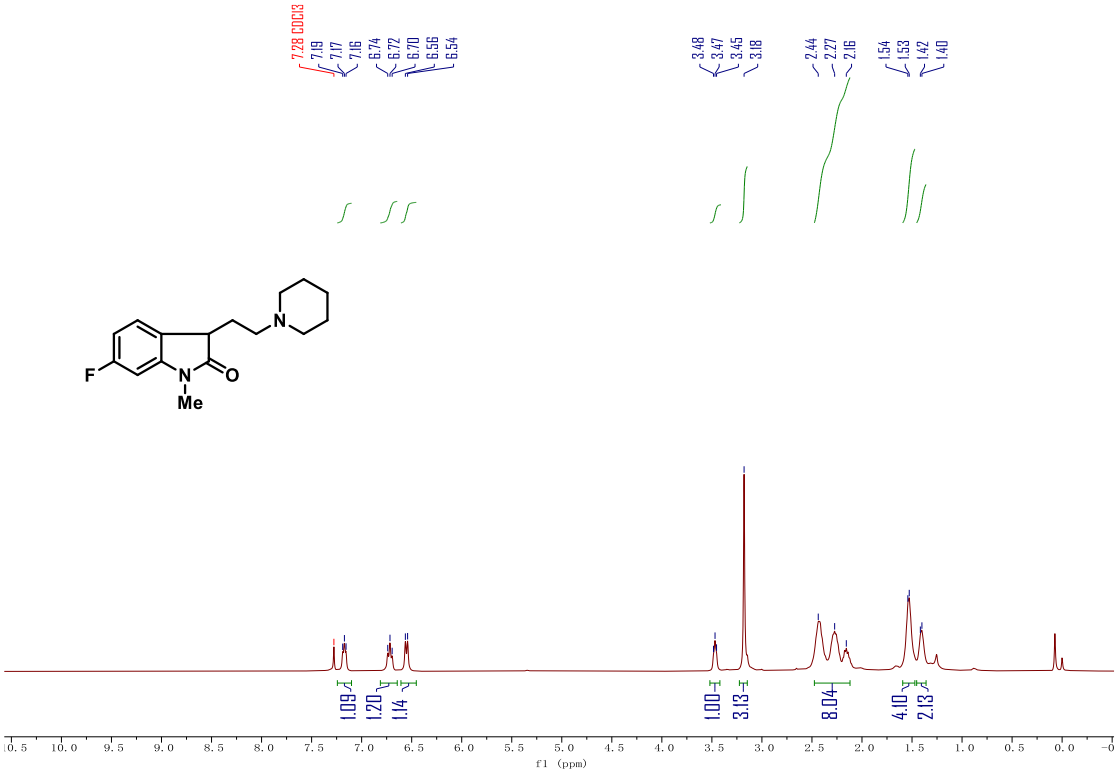

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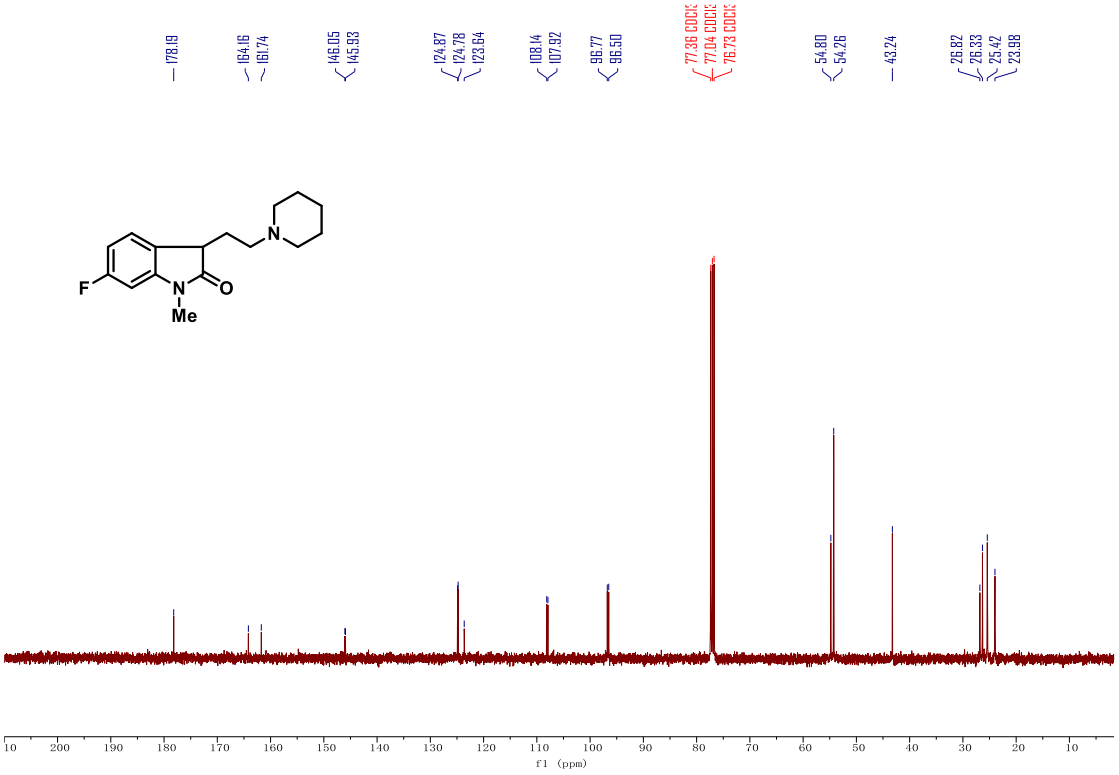

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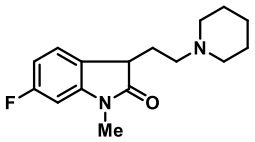

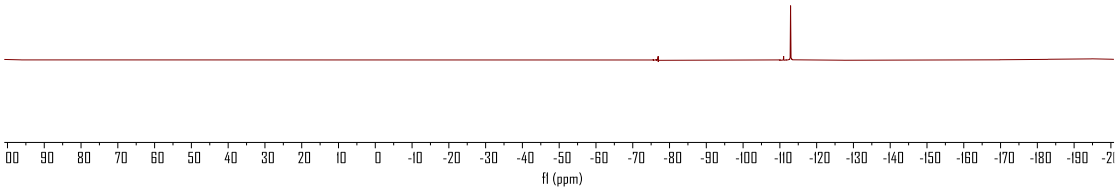

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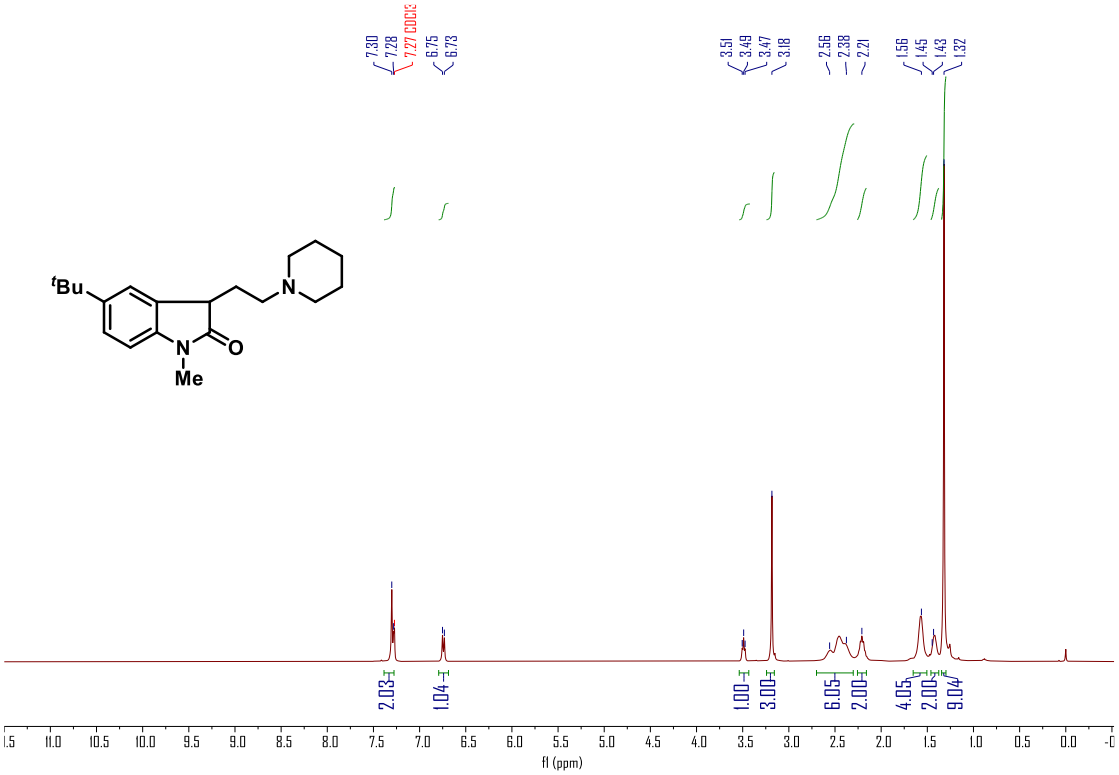

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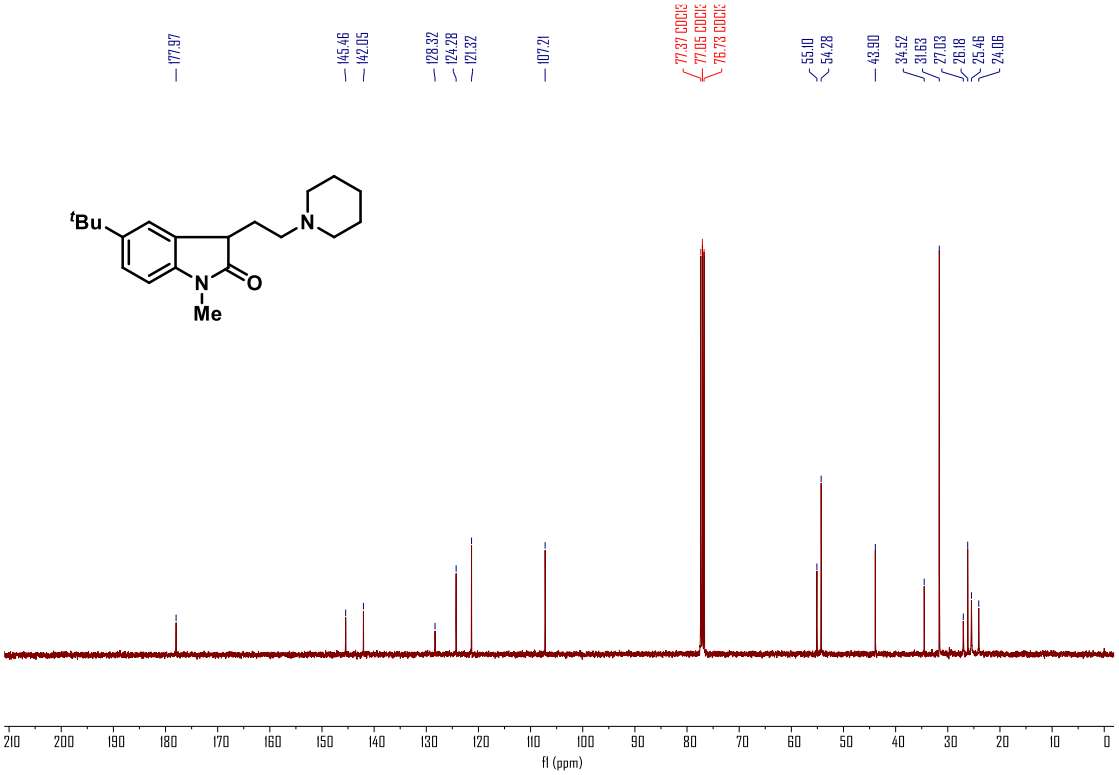

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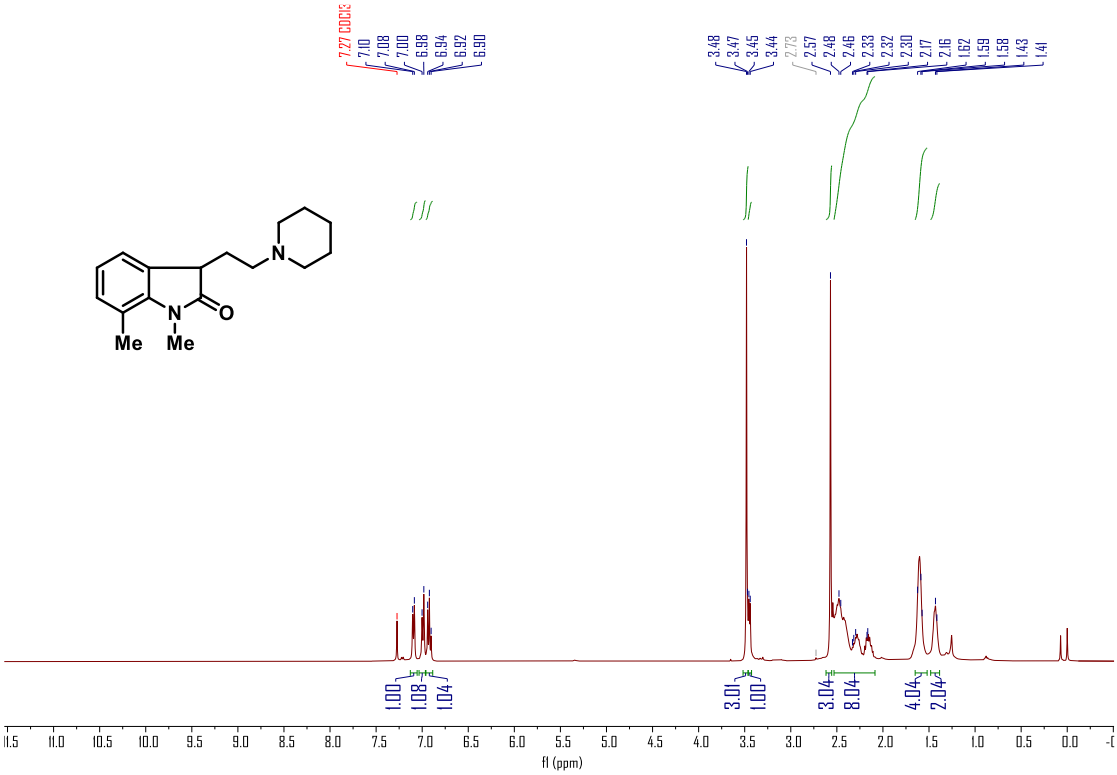

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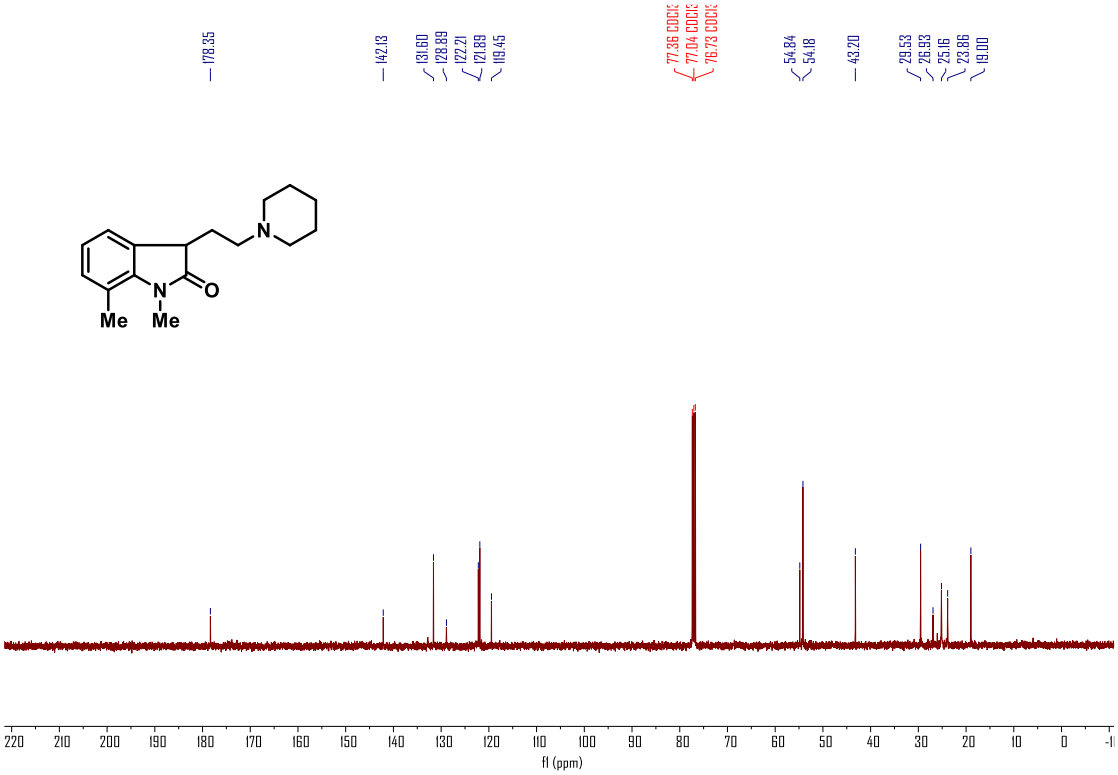

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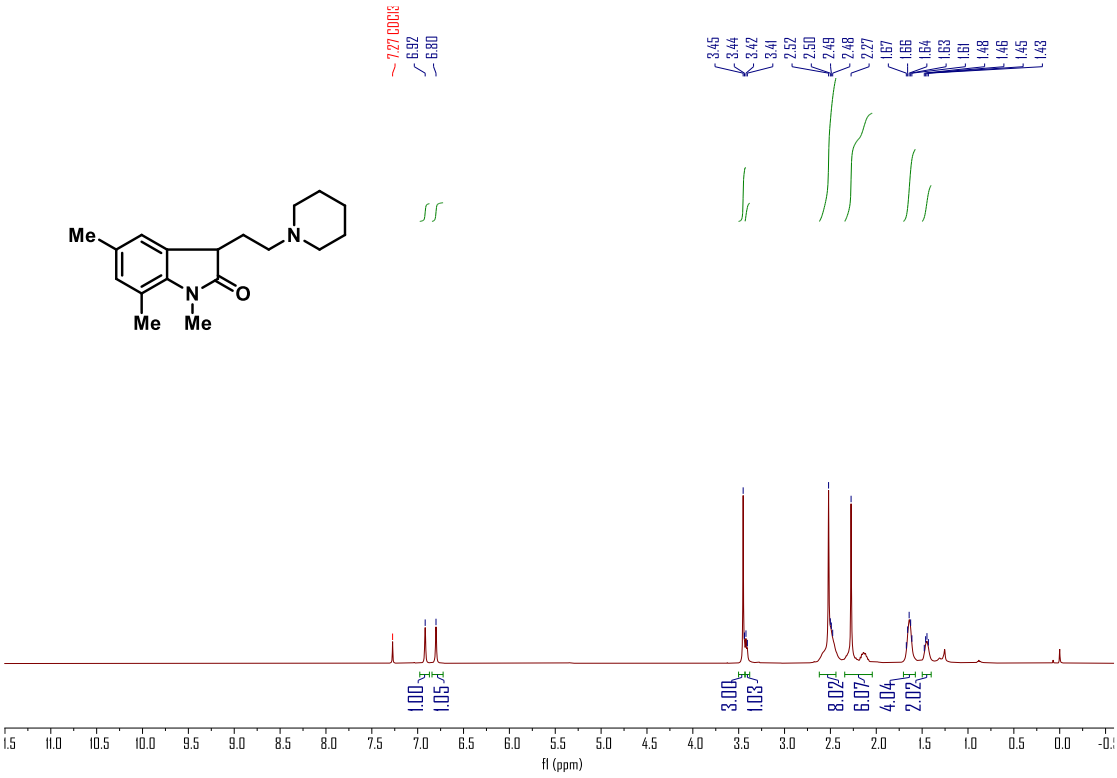
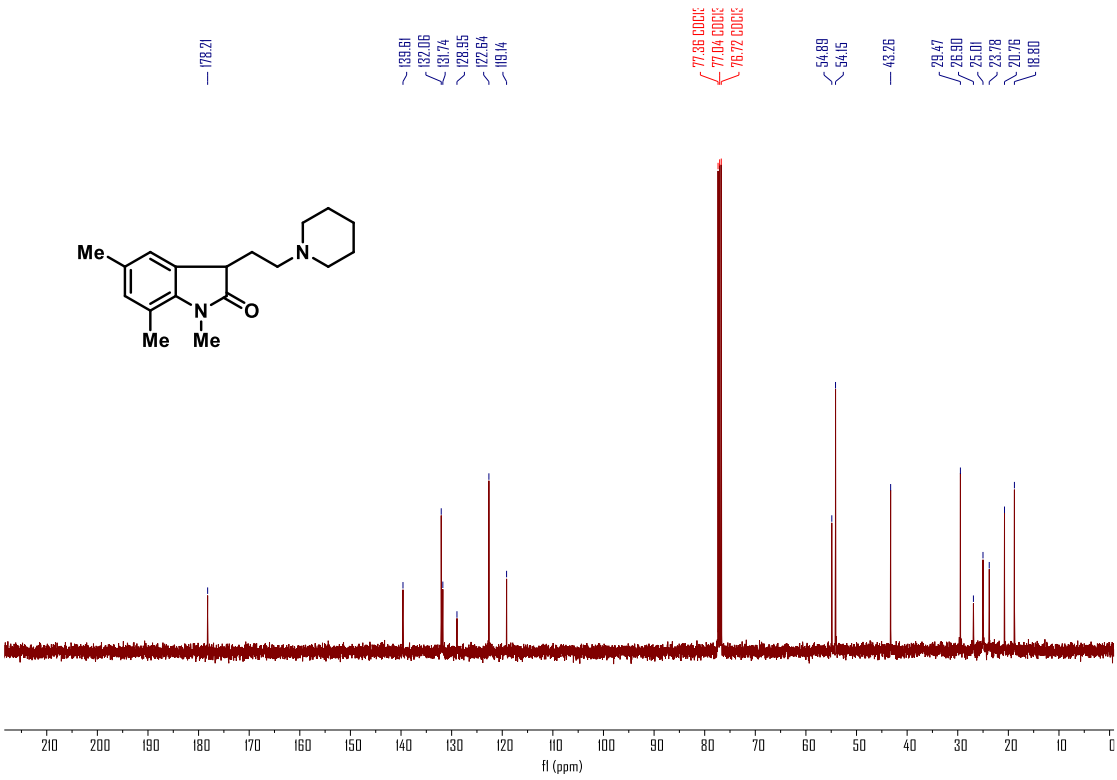
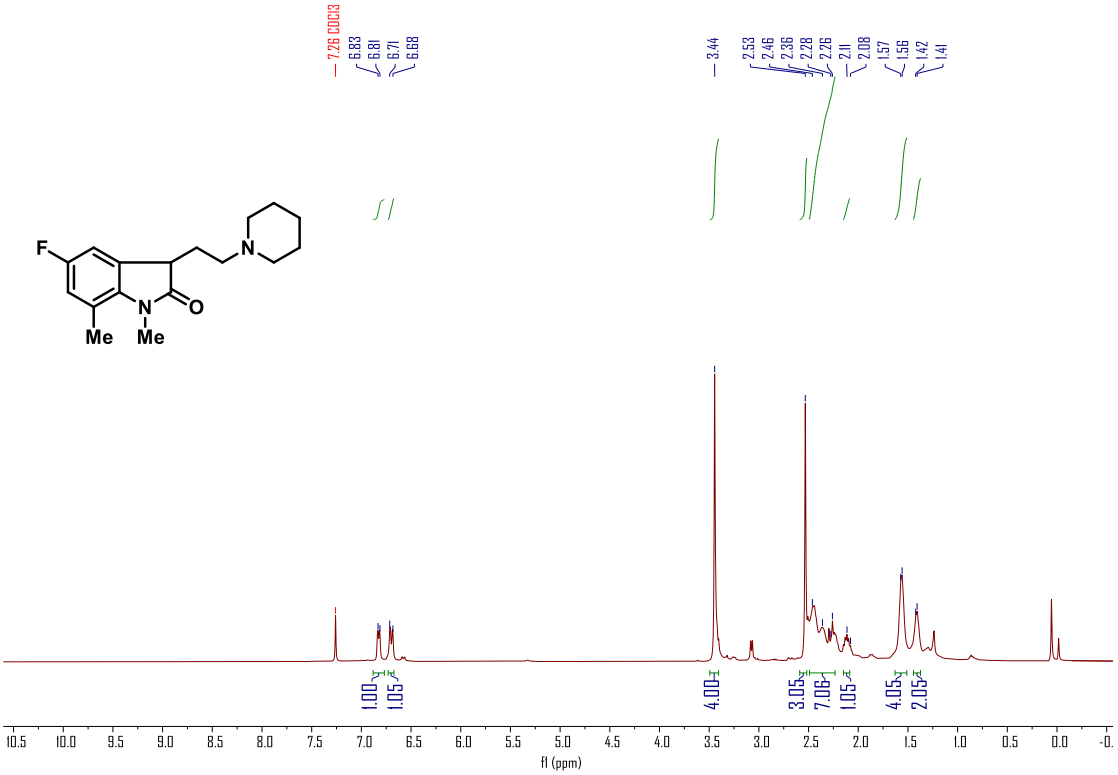


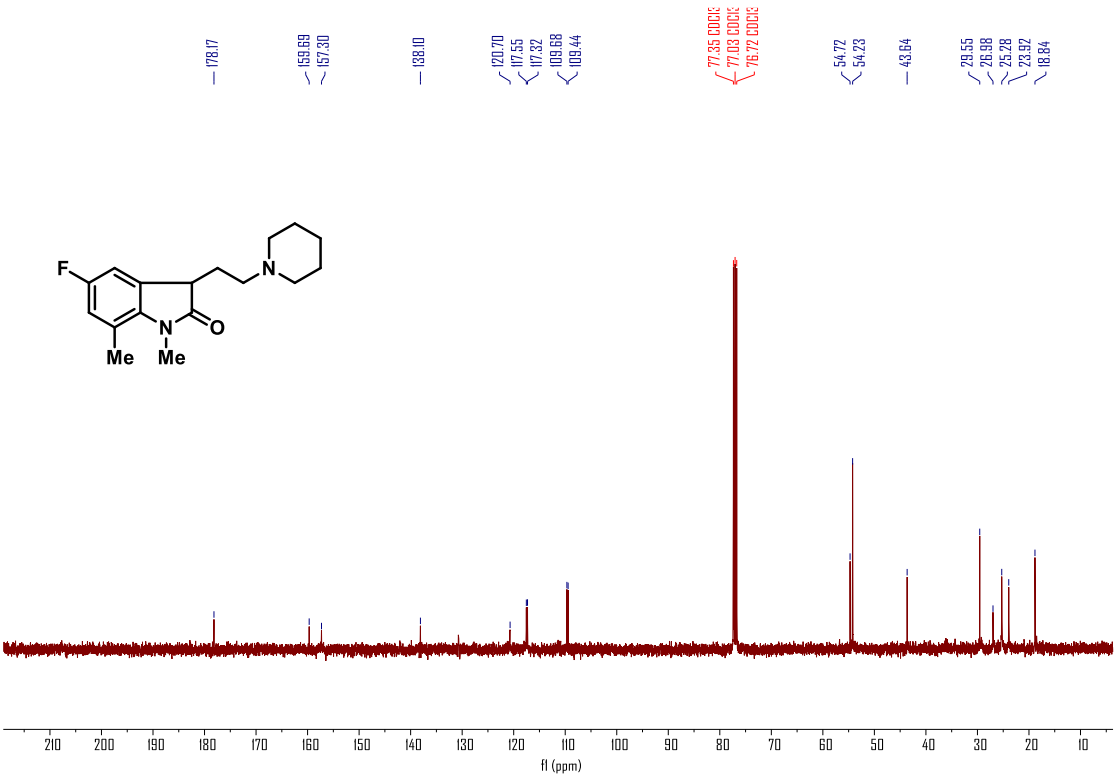
^{13}C NMR of 3e (101 MHz, $CDCl_3$)



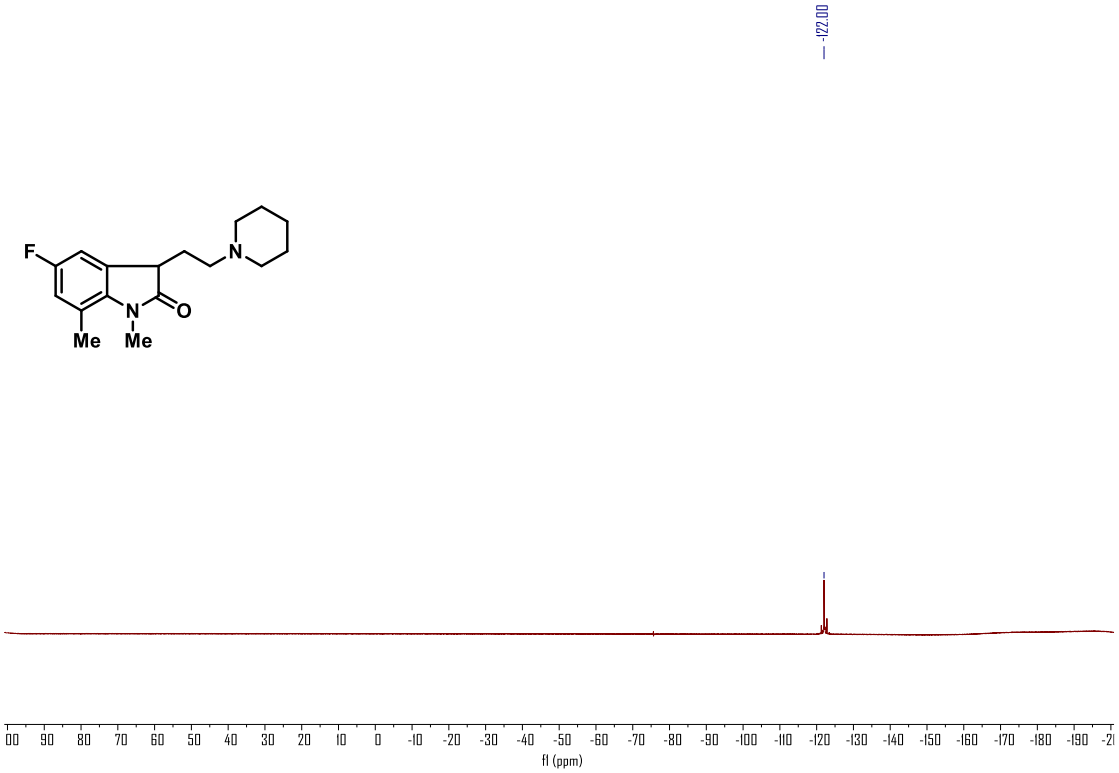
^{1}H NMR of 3f (400 MHz, $CDCl_3$)



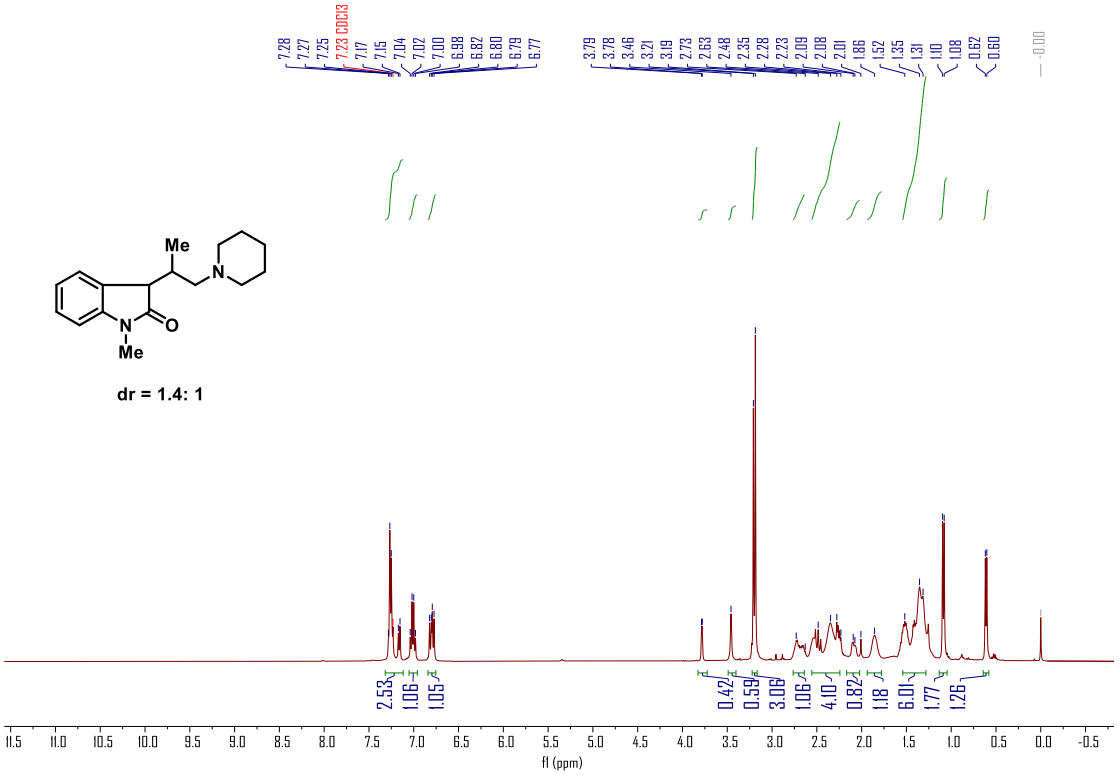
^{13}C NMR of 3f (101 MHz, $CDCl_3$)



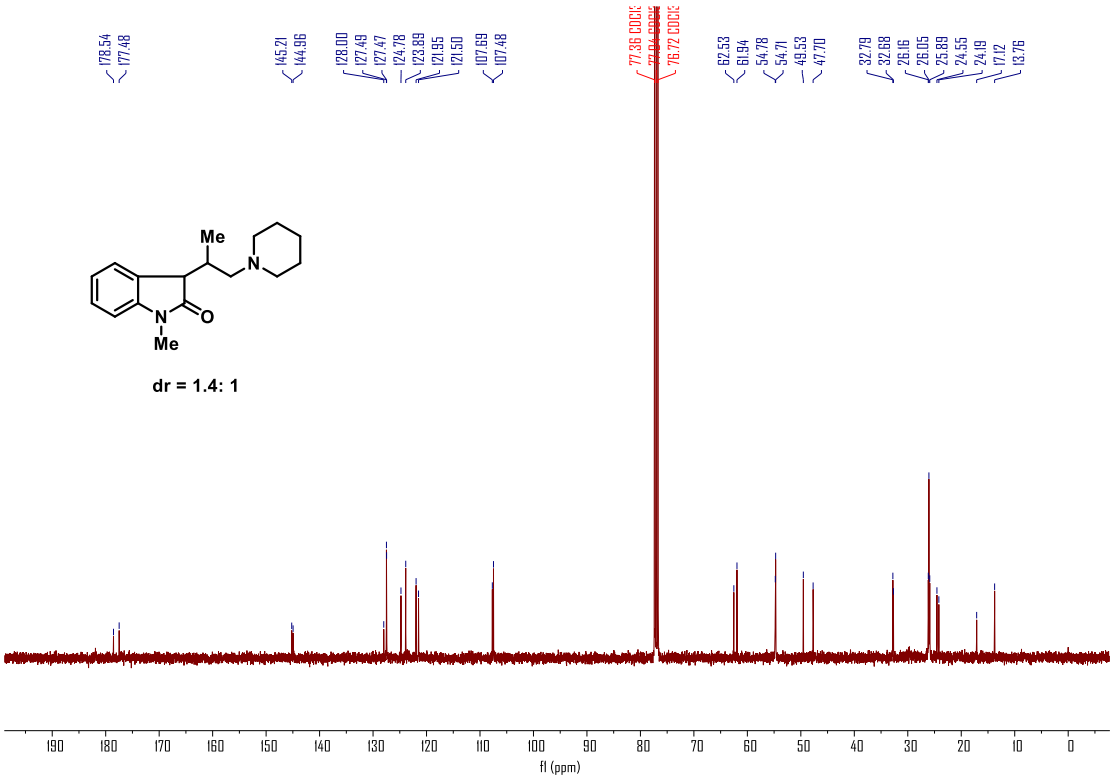
^{19}F NMR of 3f (375 MHz, $CDCl_3$)



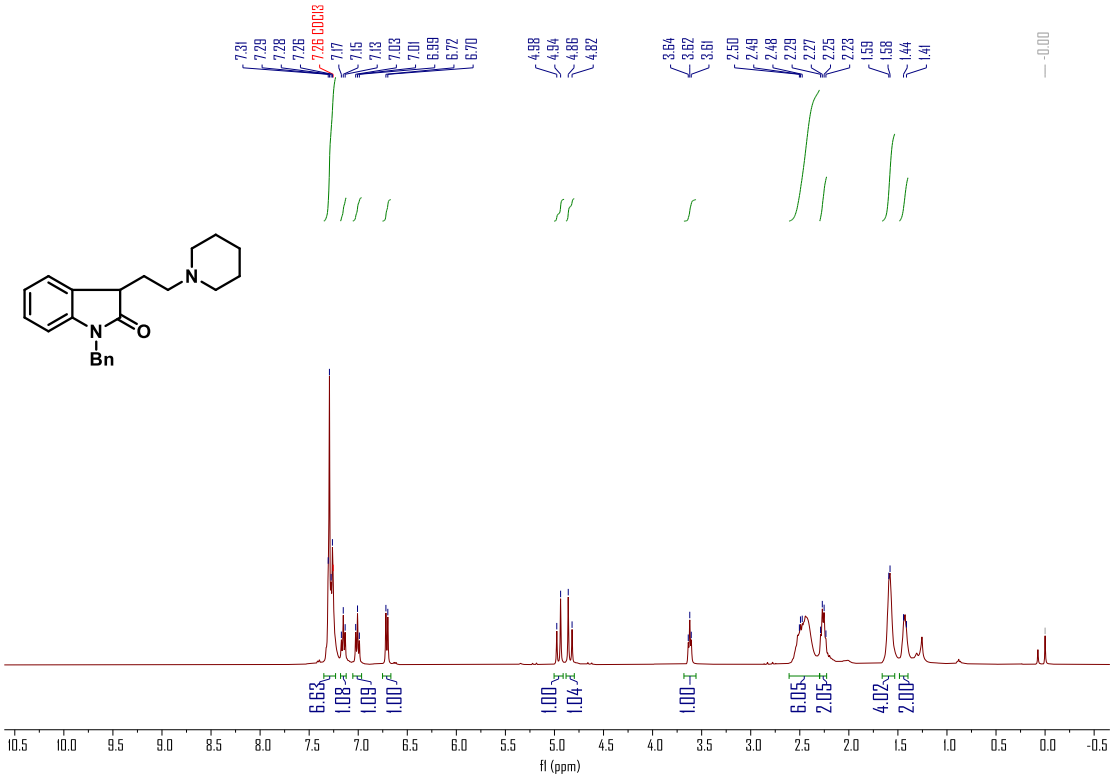
^{1}H NMR of 3g (400 MHz, $CDCl_3$)



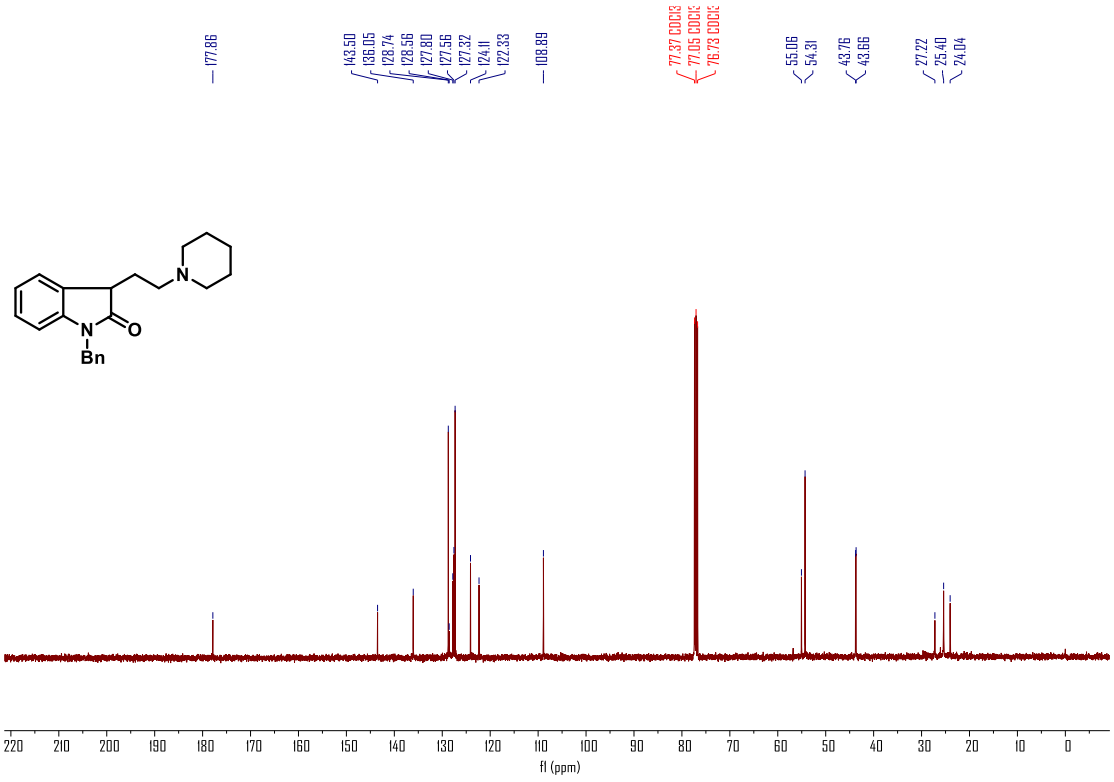
^{13}C NMR of 3g (101 MHz, $CDCl_3$)



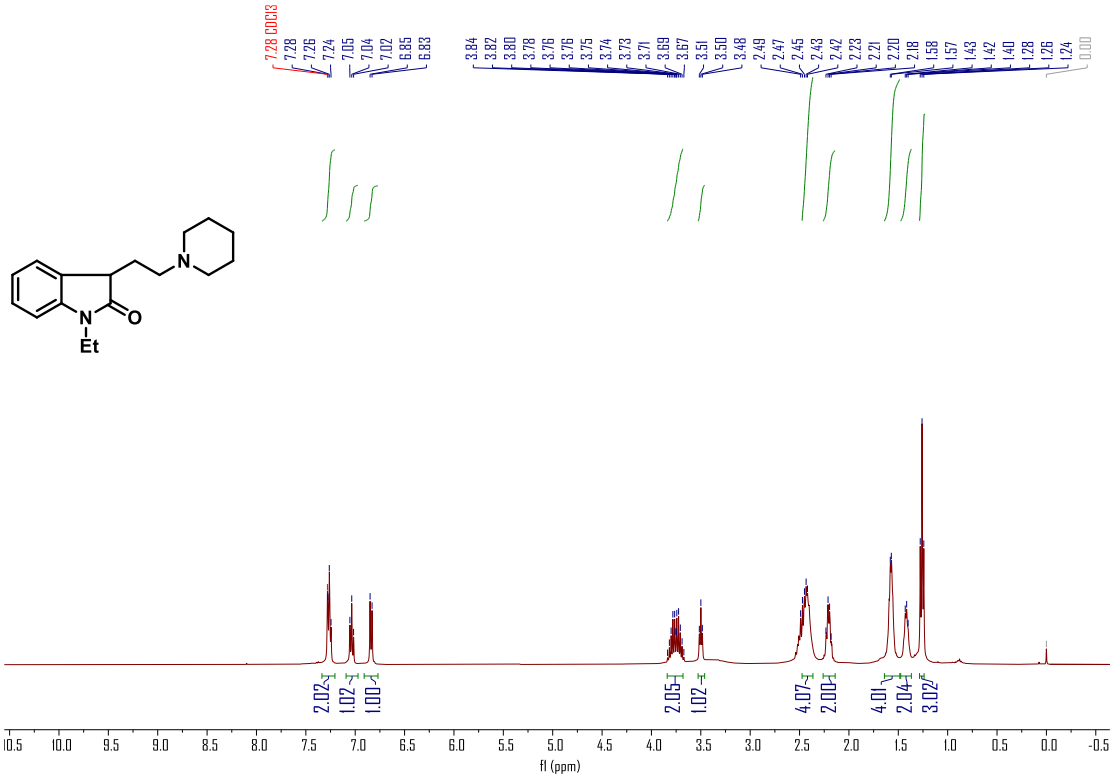
^{1}H NMR of 3h (400 MHz, $CDCl_3$)



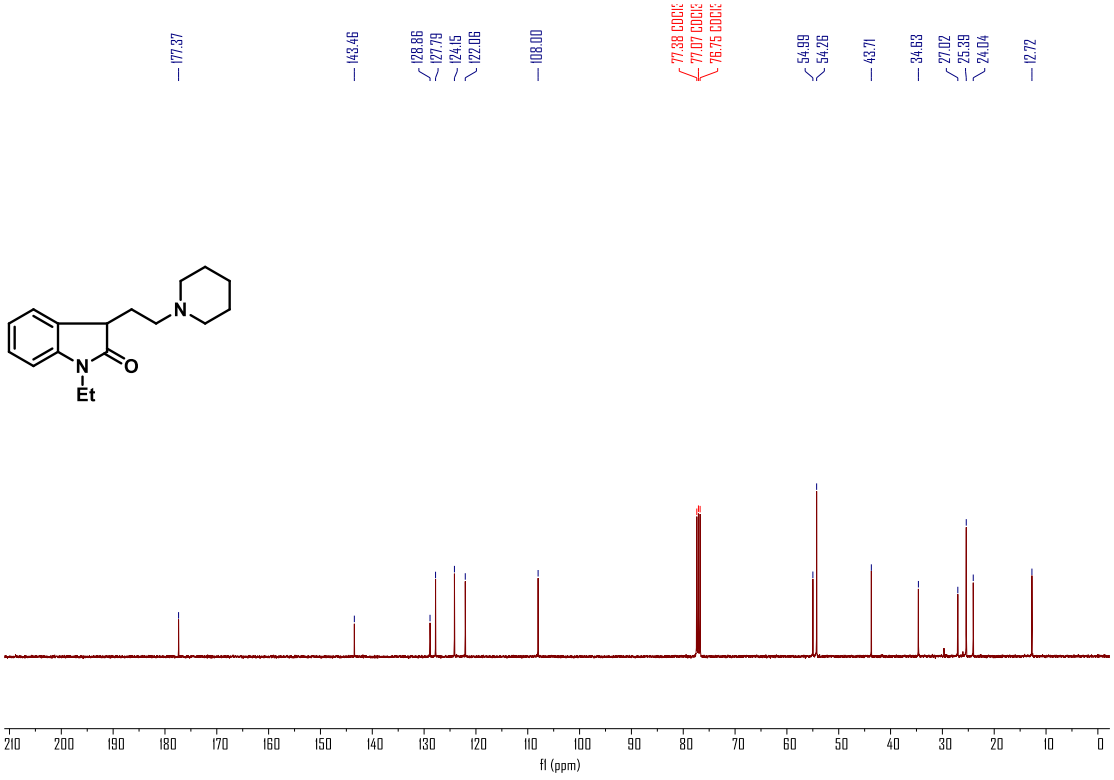
^{13}C NMR of 3h (101 MHz, $CDCl_3$)



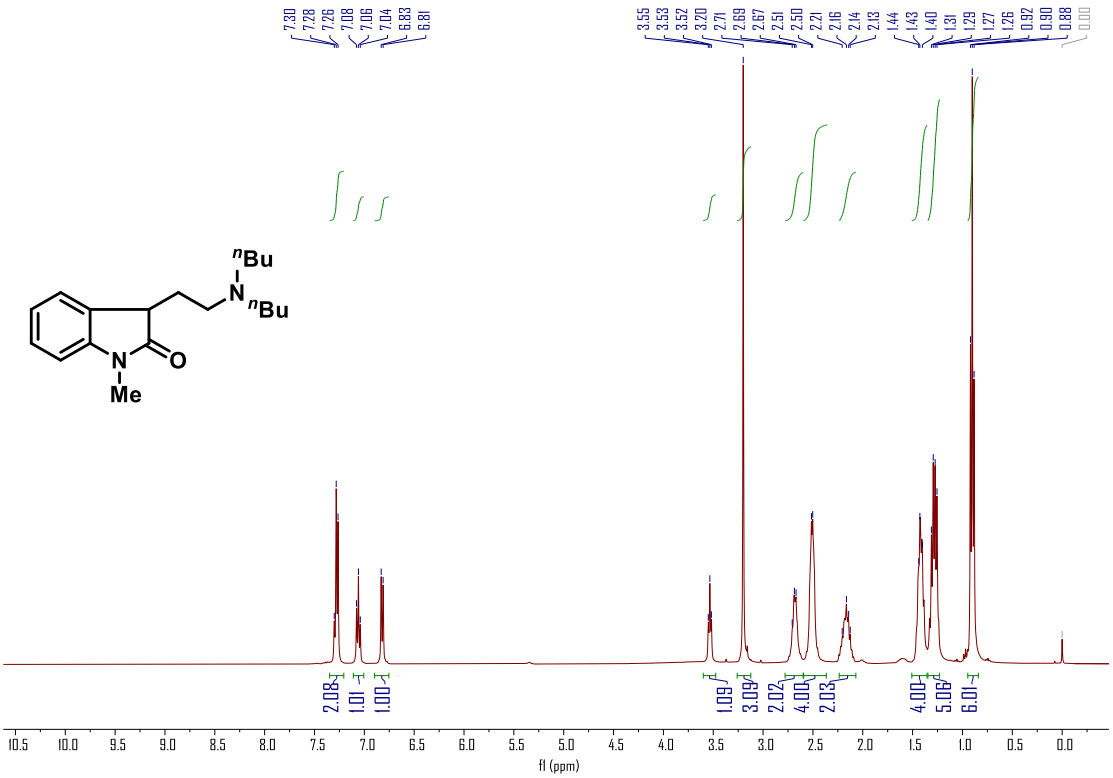
^{1}H NMR of 3i (400 MHz, $CDCl_3$)



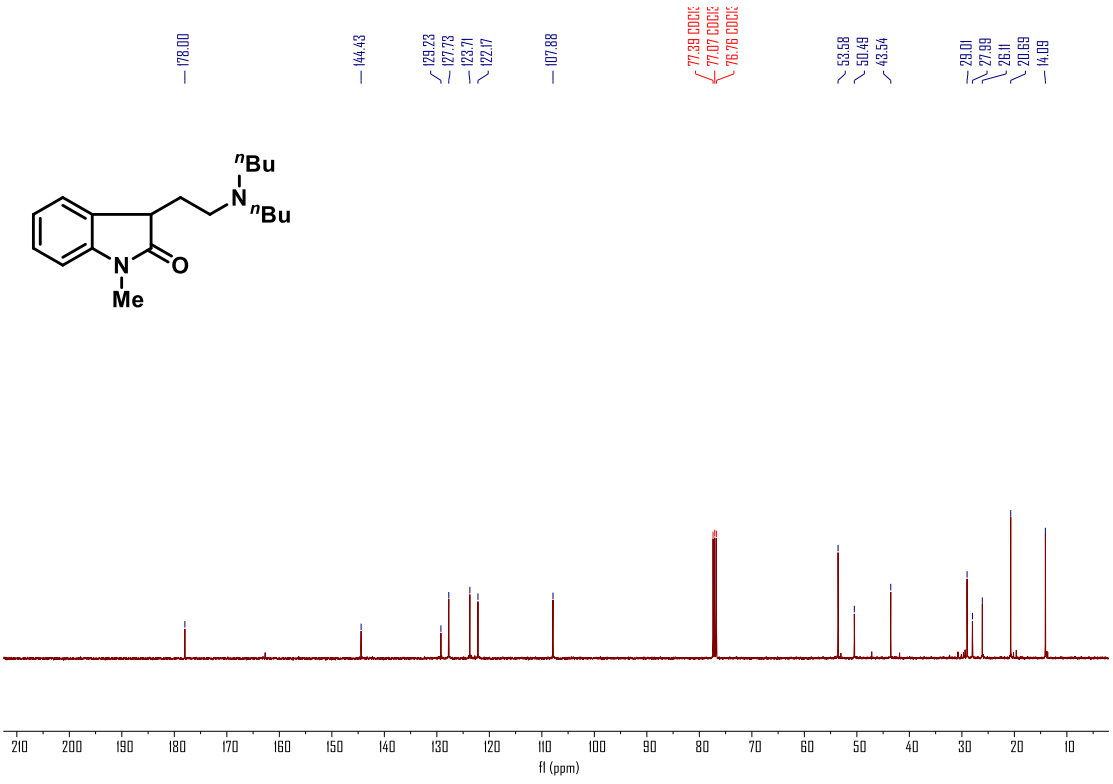
^{13}C NMR of 3i (101 MHz, $CDCl_3$)



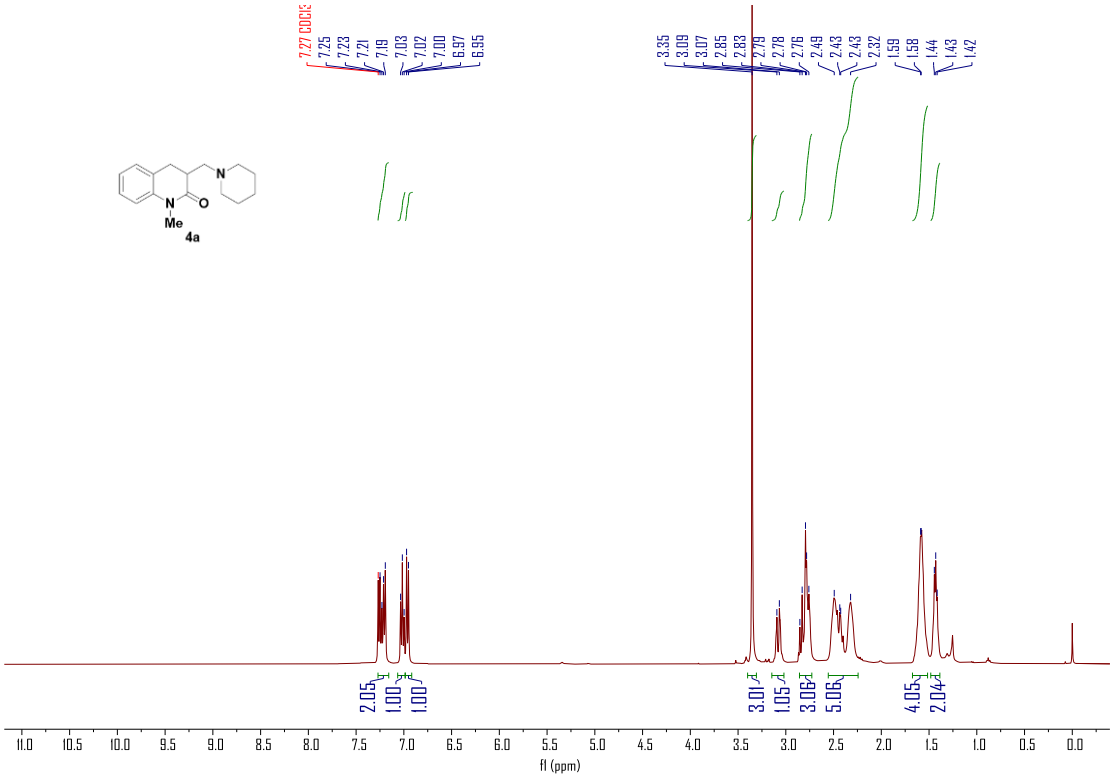
^{1}H NMR of 3j (400 MHz, $CDCl_3$)



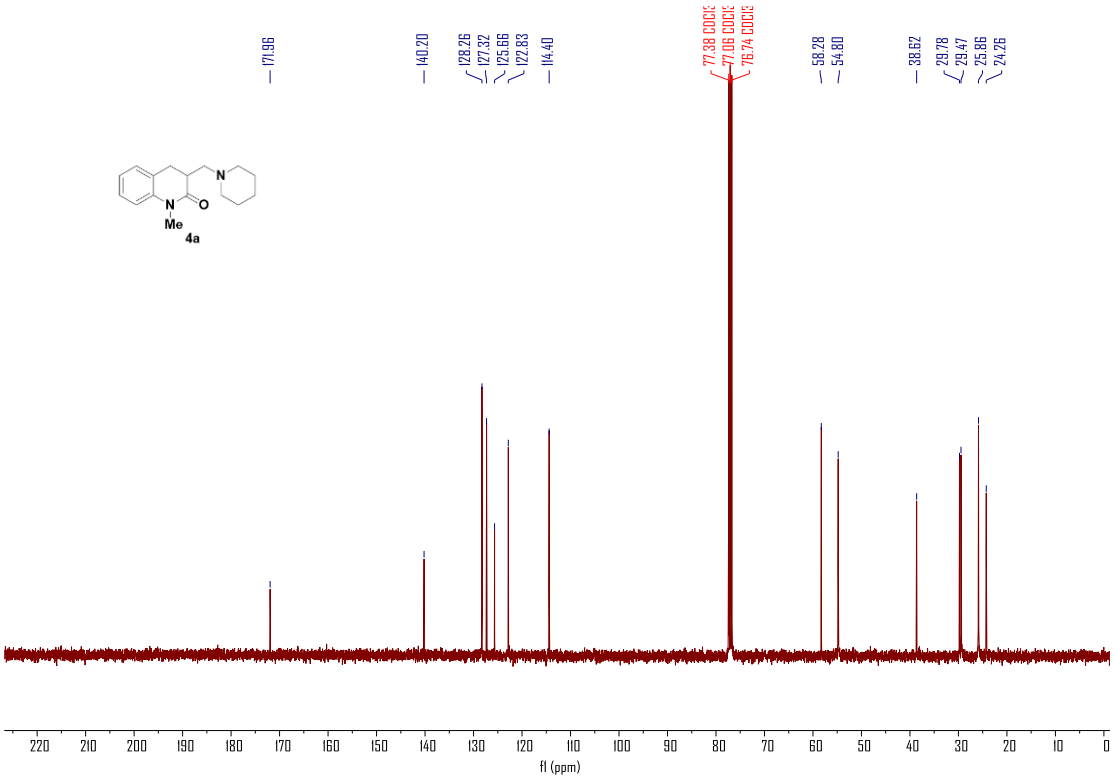
^{13}C NMR of 3j (101 MHz, $CDCl_3$)



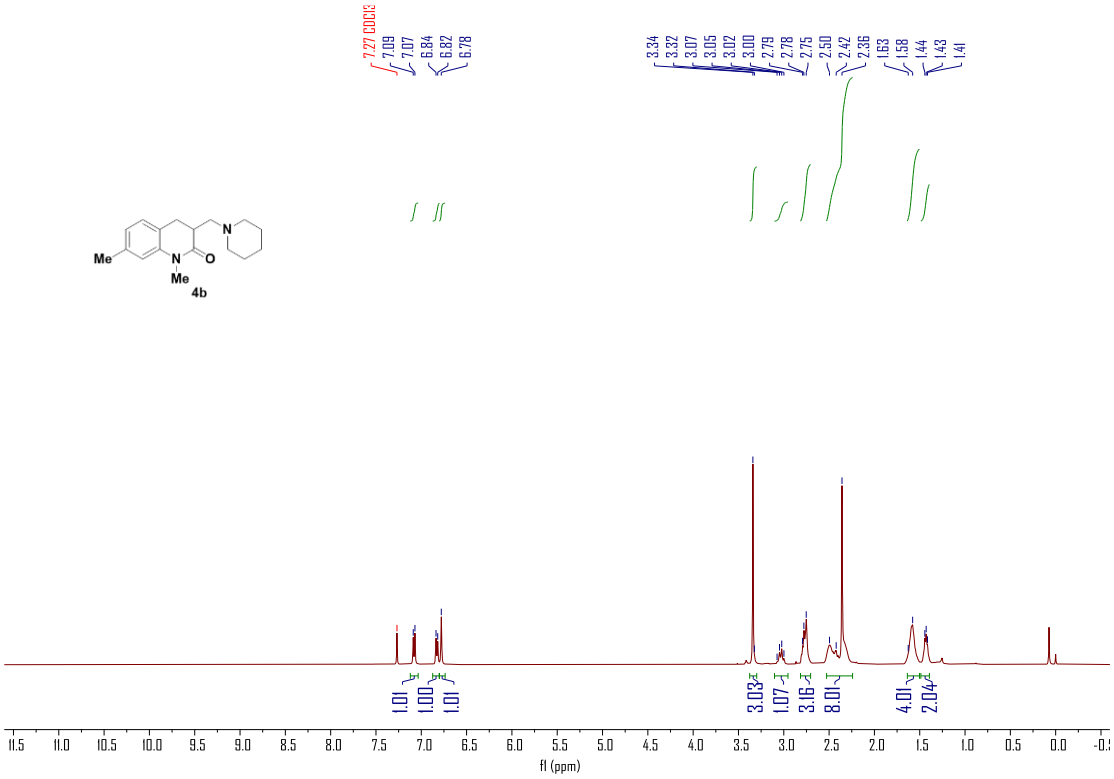
^{1}H NMR of 4a (400 MHz, $CDCl_3$)



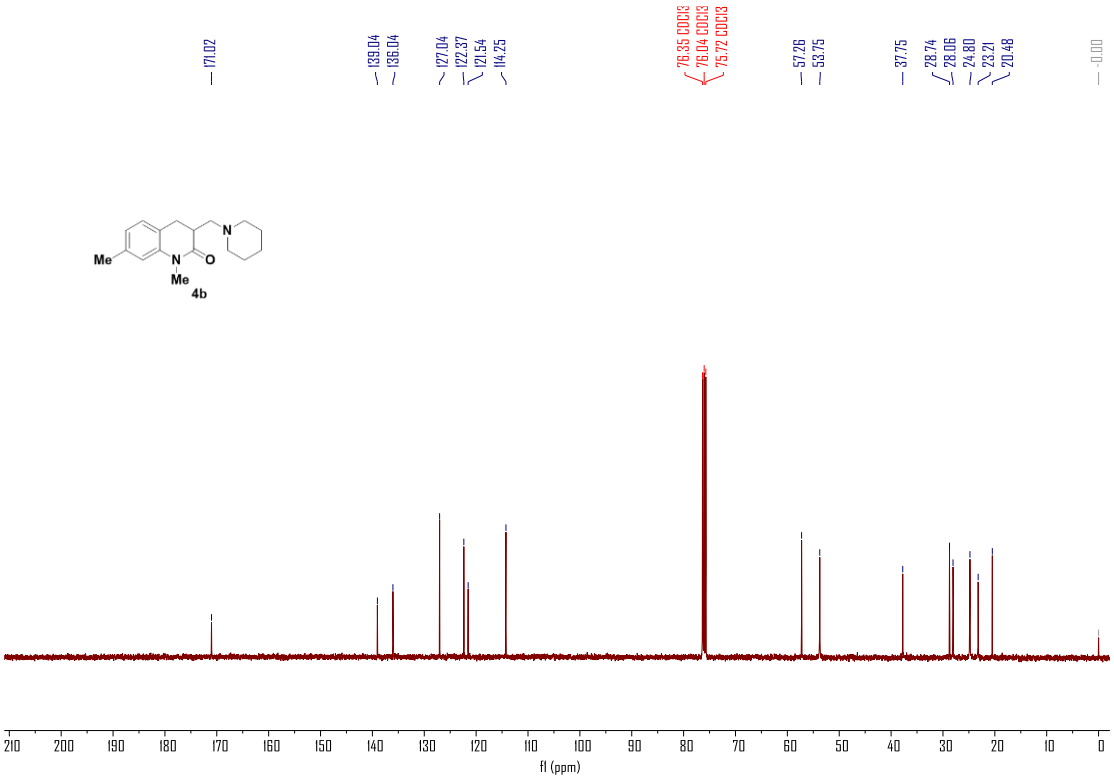
^{13}C NMR of 4a (101 MHz, $CDCl_3$)



^{1}H NMR of 4b (400 MHz, $CDCl_3$)



^{13}C NMR of 4b (101 MHz, $CDCl_3$)



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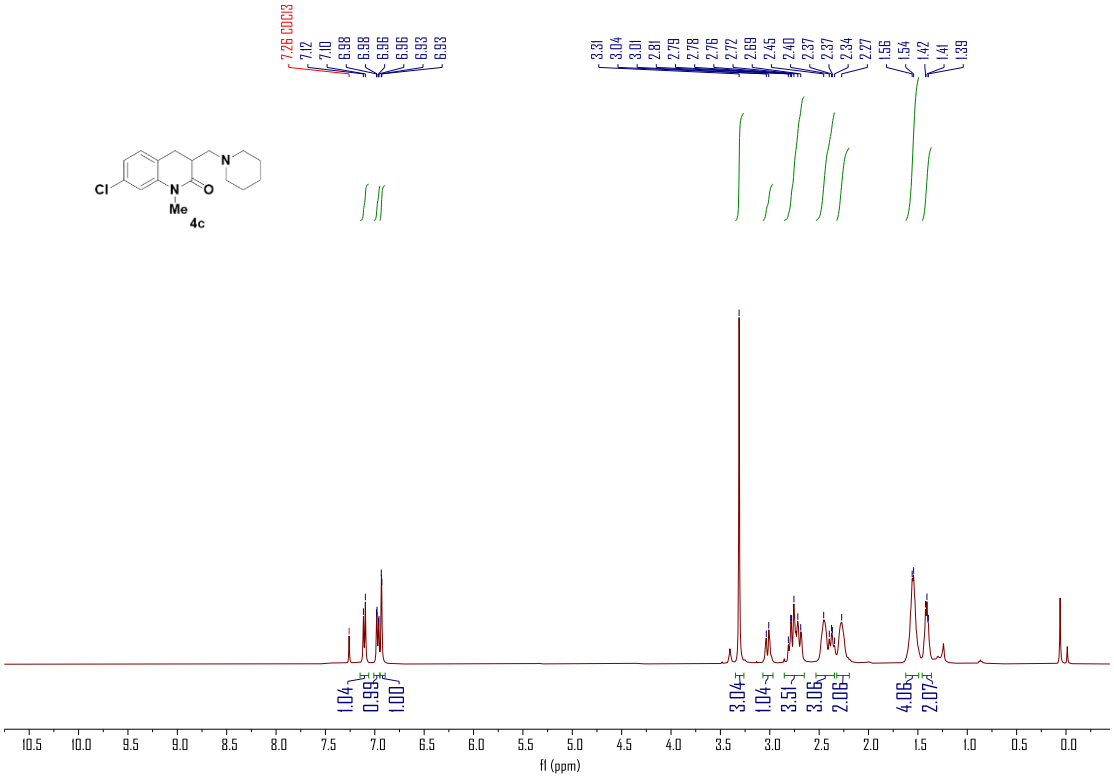
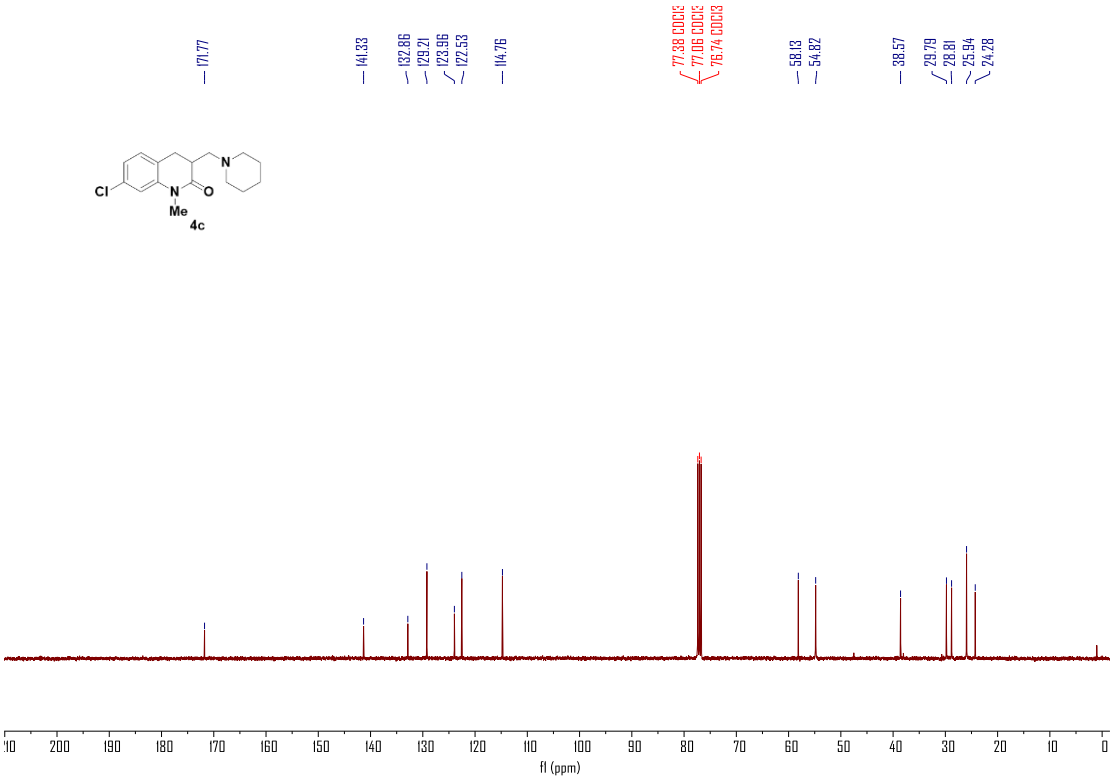
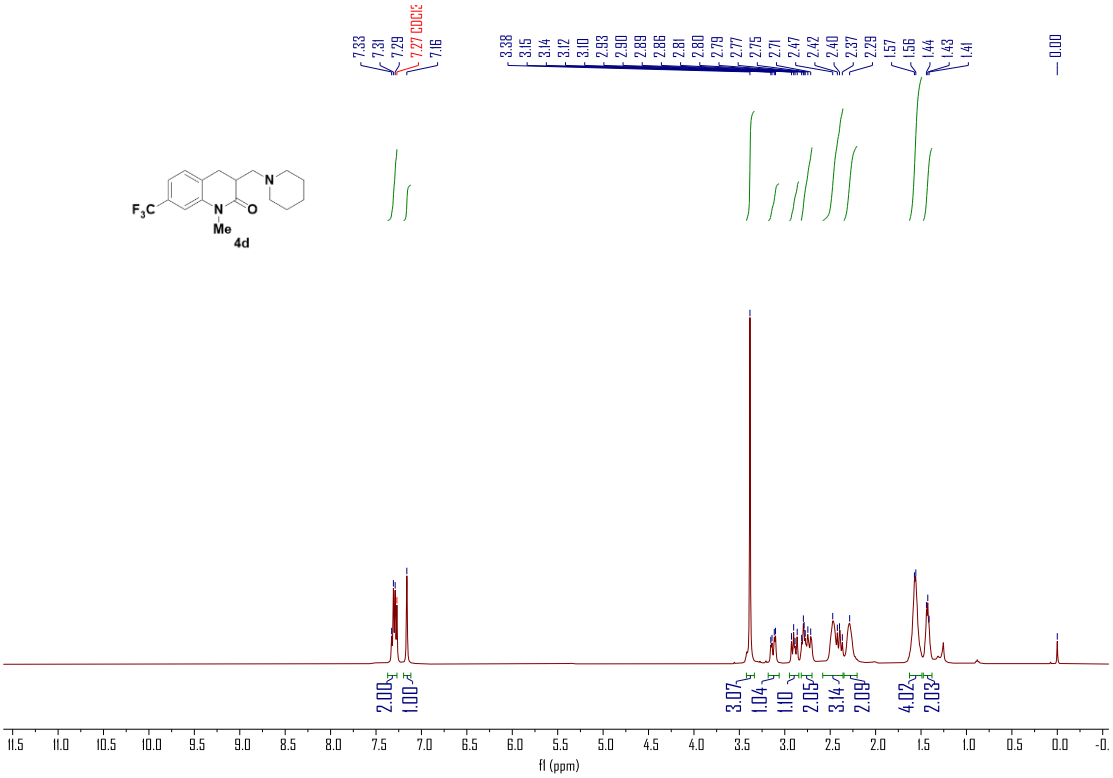


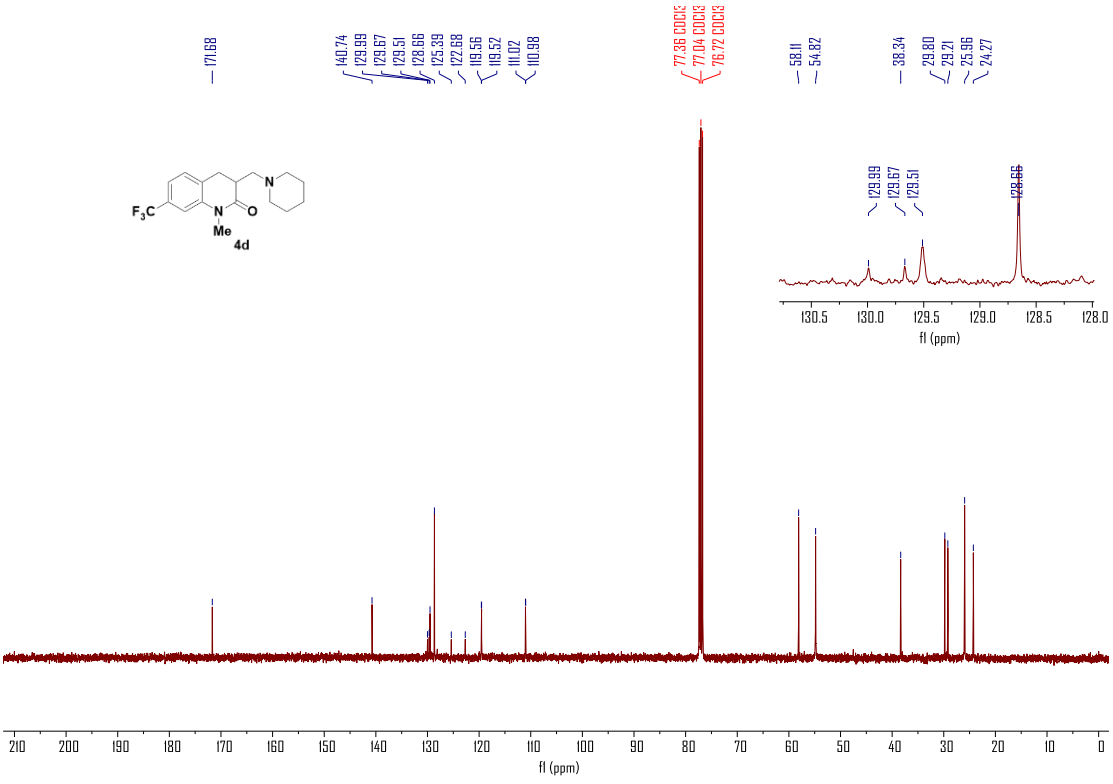
^{13}C NMR of 4c (101 MHz, $CDCl_3$)



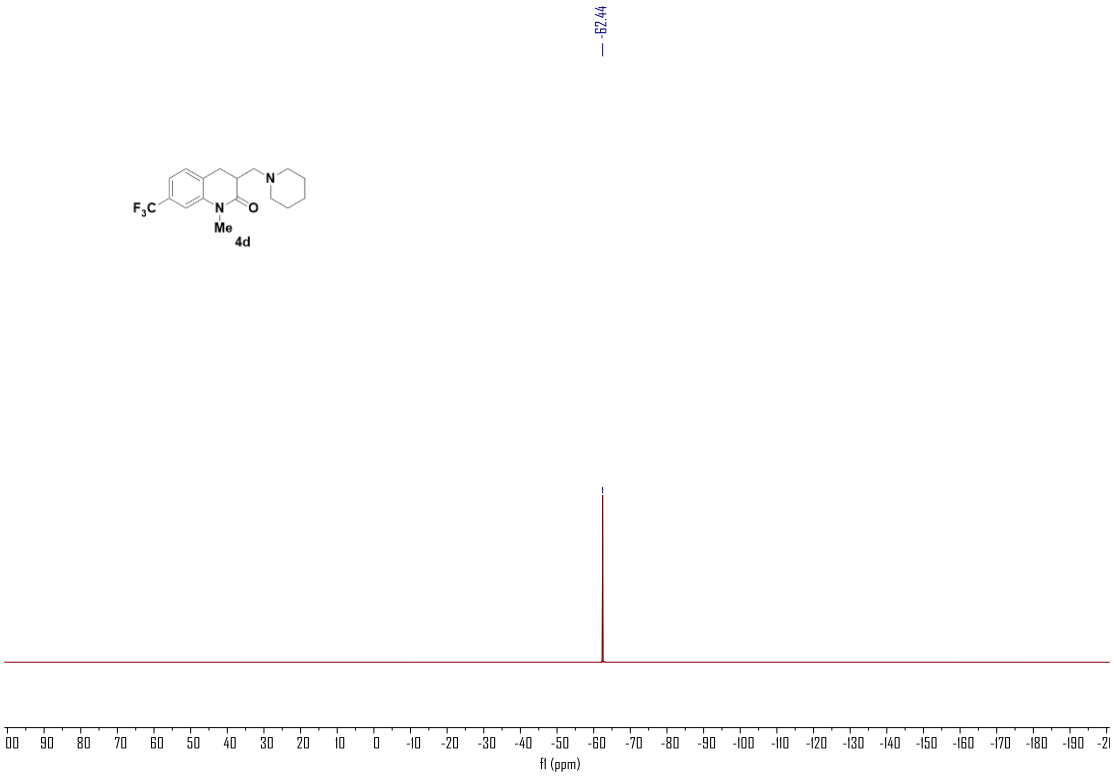
^{1}H NMR of 4d (400 MHz, $CDCl_3$)



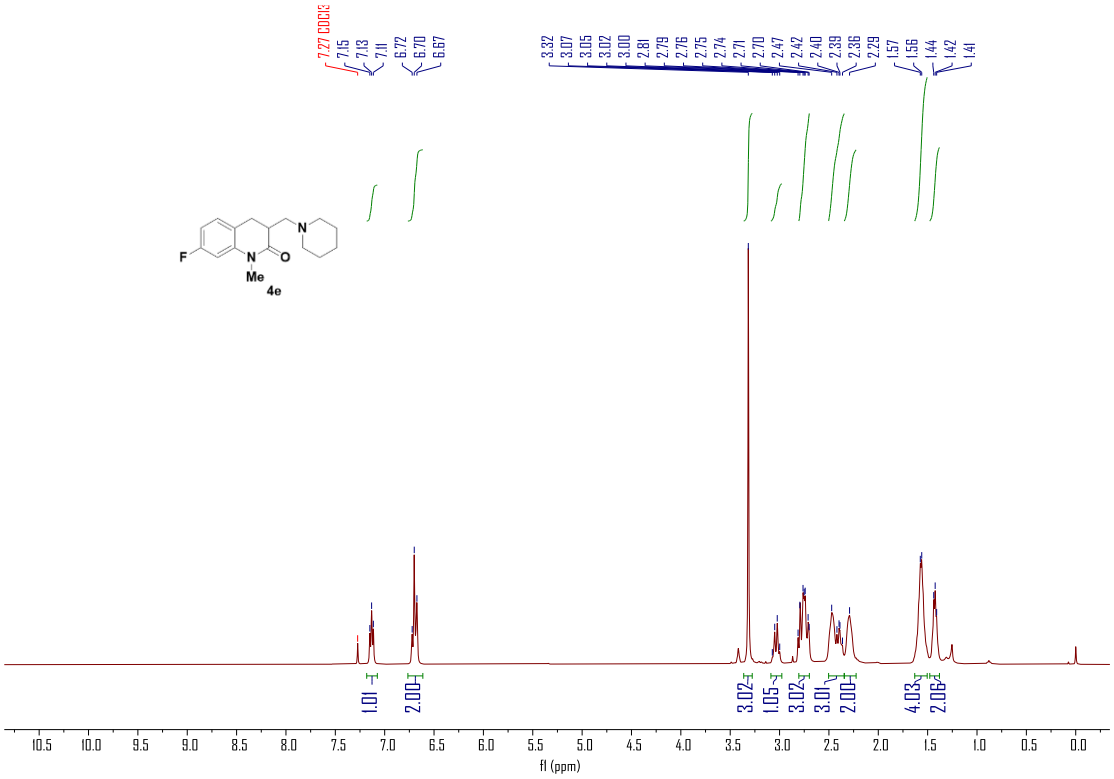
^{13}C NMR of 4d (101 MHz, $CDCl_3$)



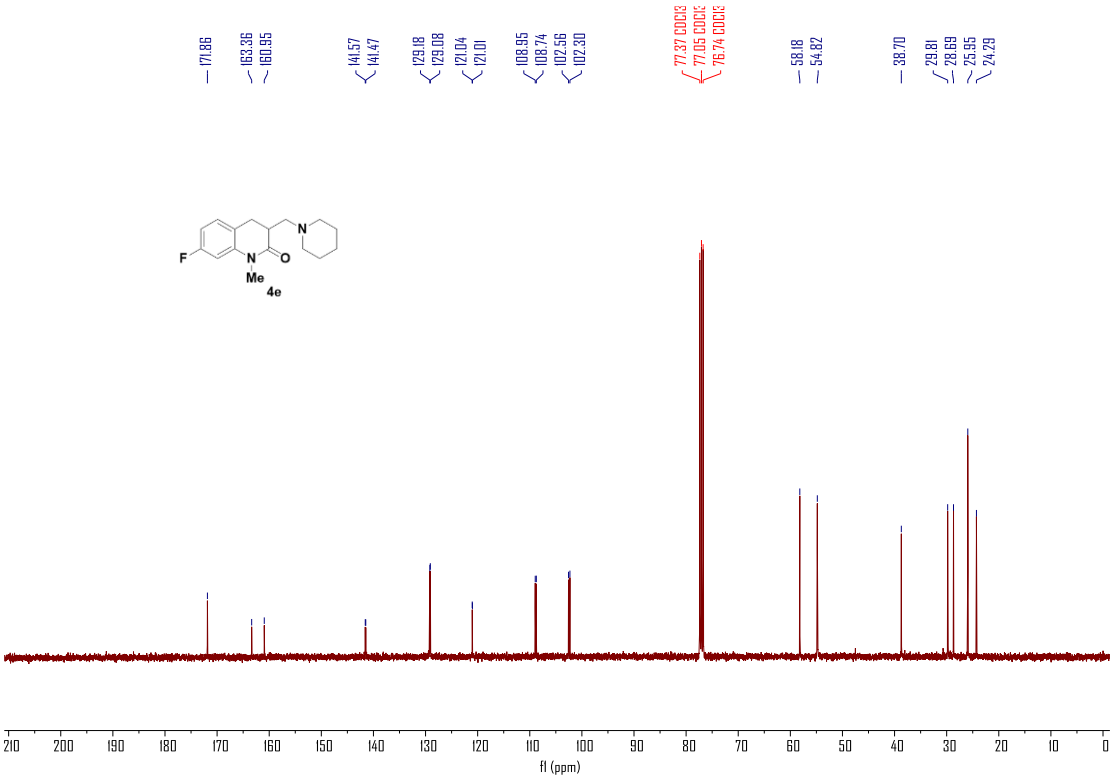
^{19}F NMR of 4d (375 MHz, $CDCl_3$)



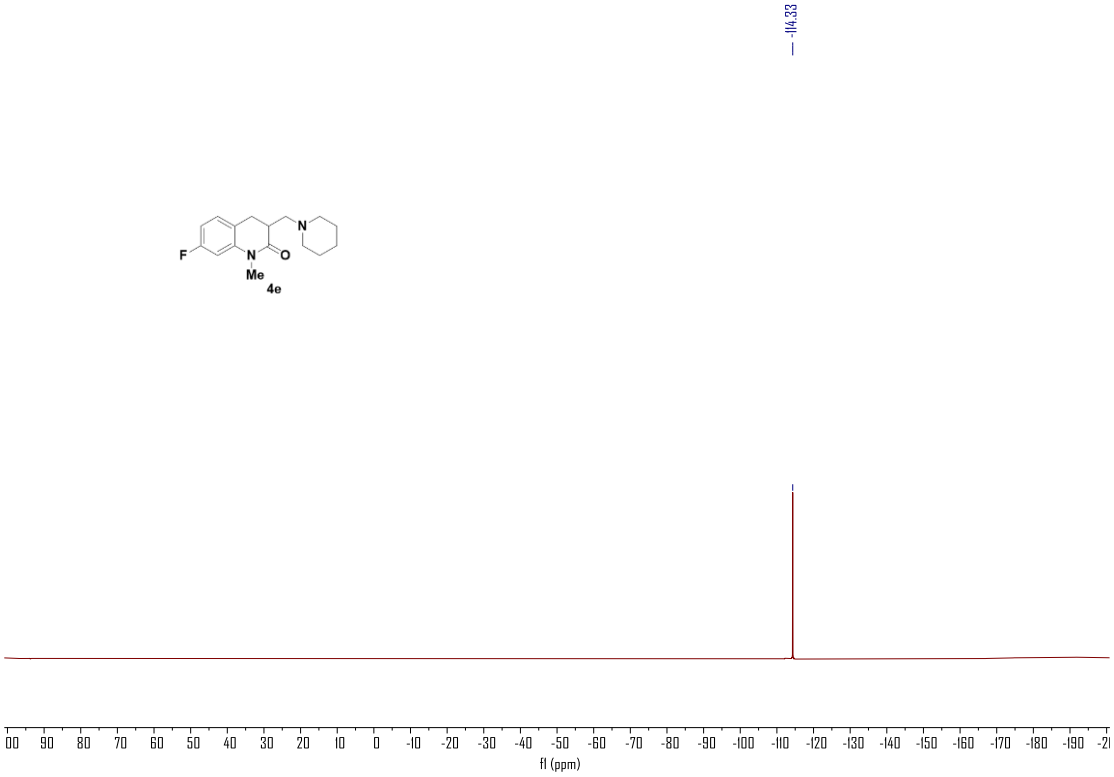
^{1}H NMR of 4e (400 MHz, $CDCl_3$)



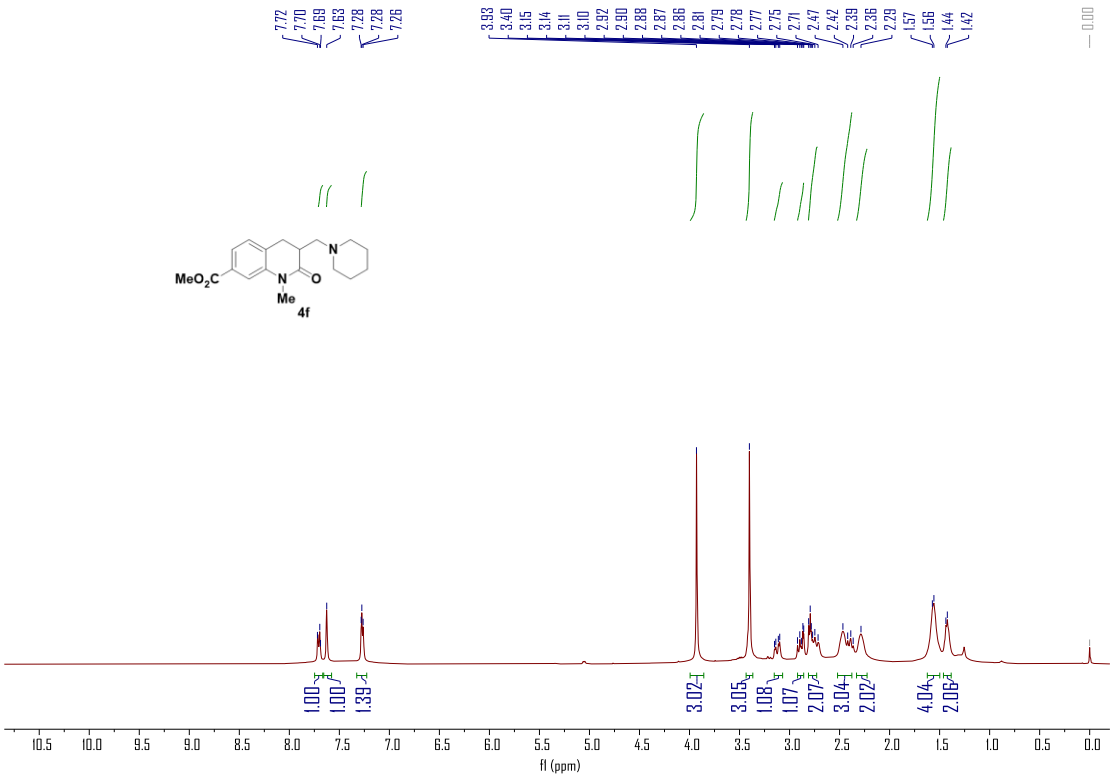
^{13}C NMR of 4e (101 MHz, $CDCl_3$)



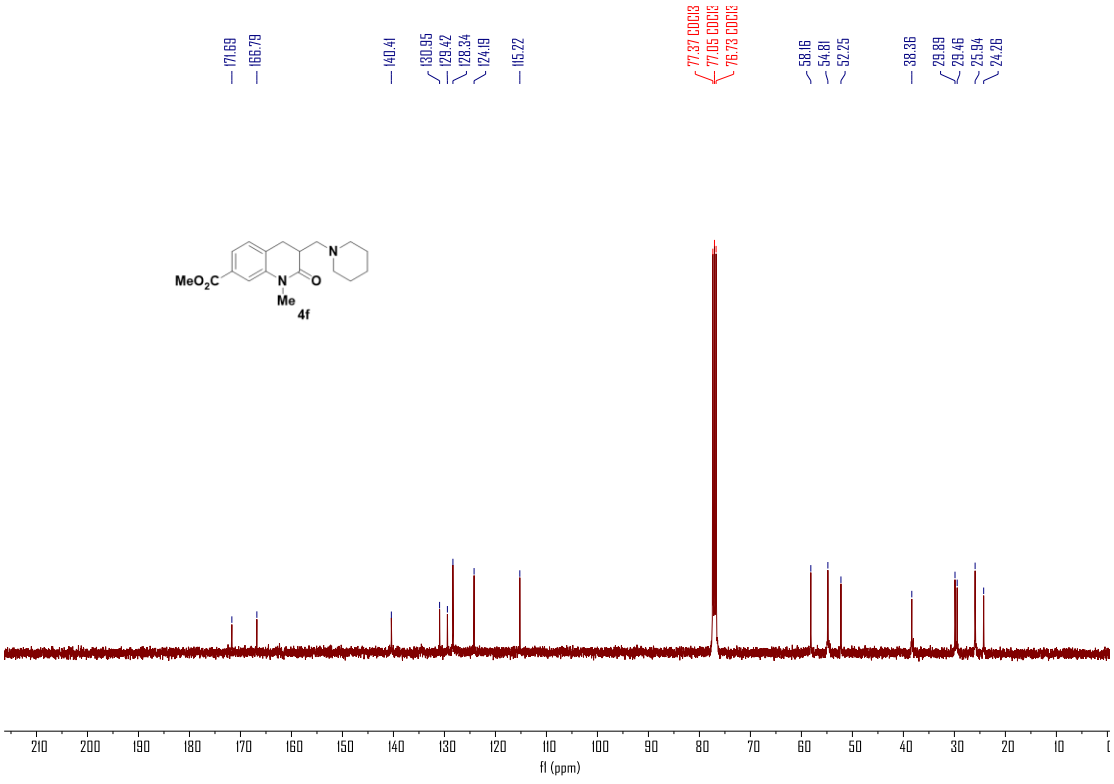
^{19}F NMR of 4e (375 MHz, $CDCl_3$)



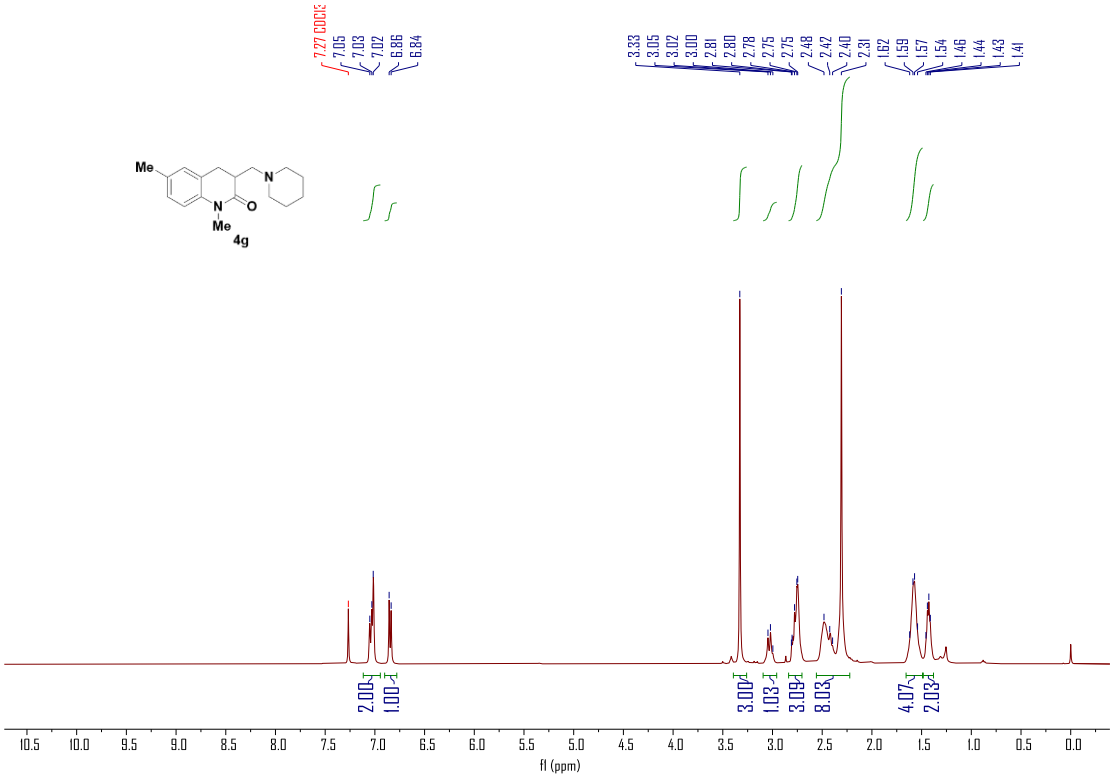
^{1}H NMR of 4f (400 MHz, $CDCl_3$)



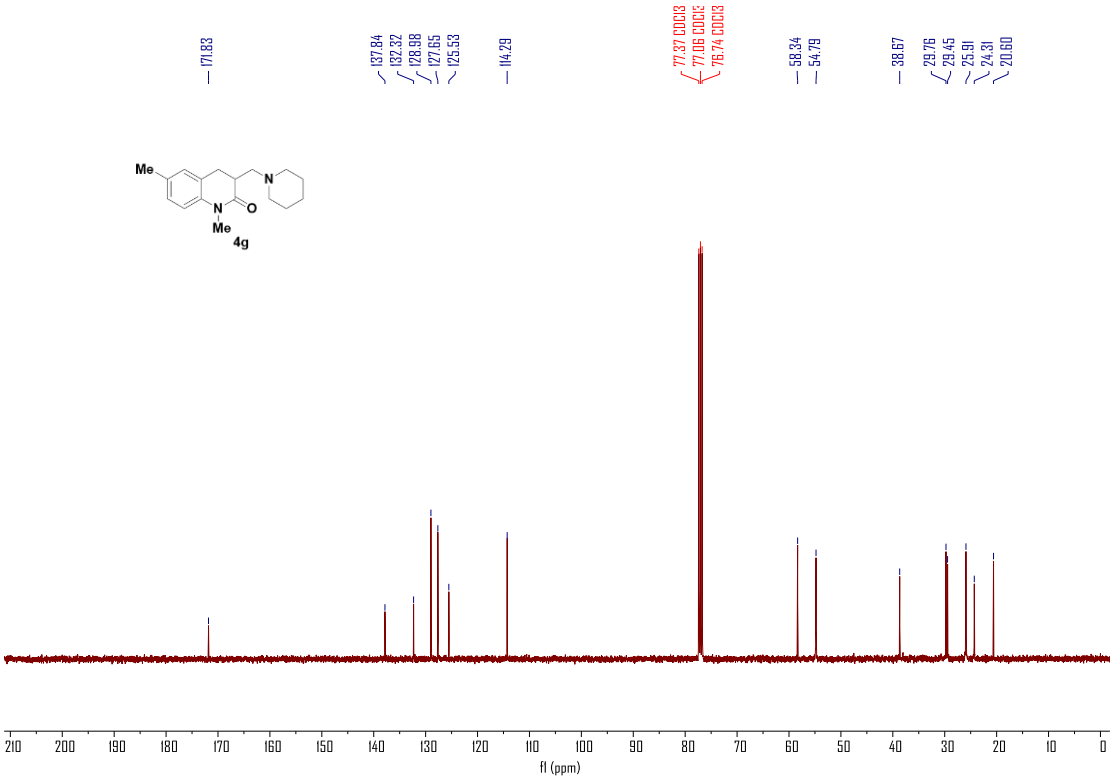
^{13}C NMR of 4f (101 MHz, $CDCl_3$)



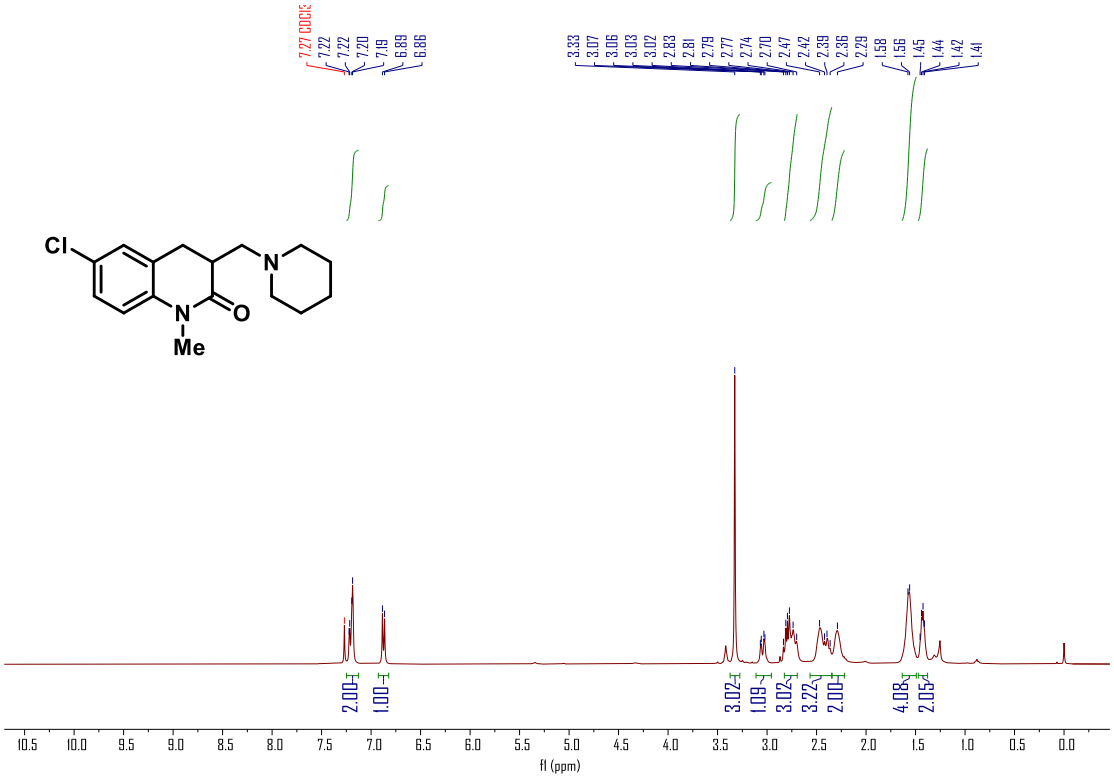
^{1}H NMR of 4g (400 MHz, $CDCl_3$)



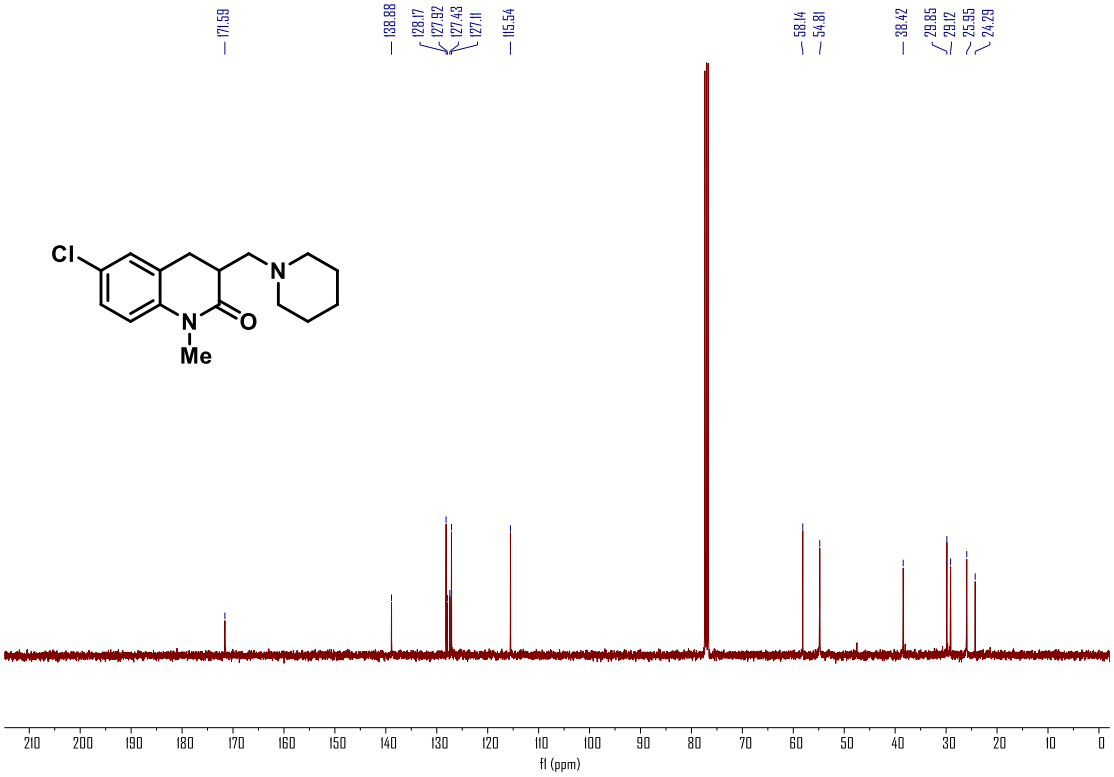
^{13}C NMR of 4g (101 MHz, $CDCl_3$)



^{1}H NMR of 4h (400 MHz, $CDCl_3$)



^{13}C NMR of 4h (101 MHz, $CDCl_3$)



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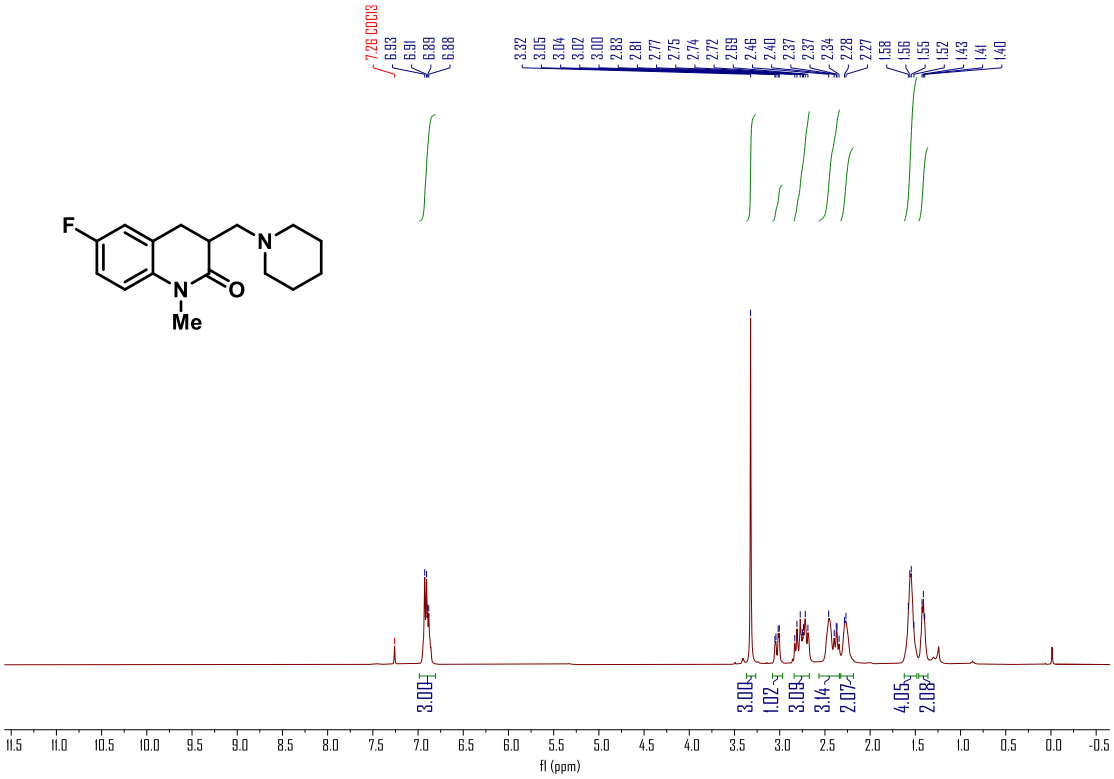
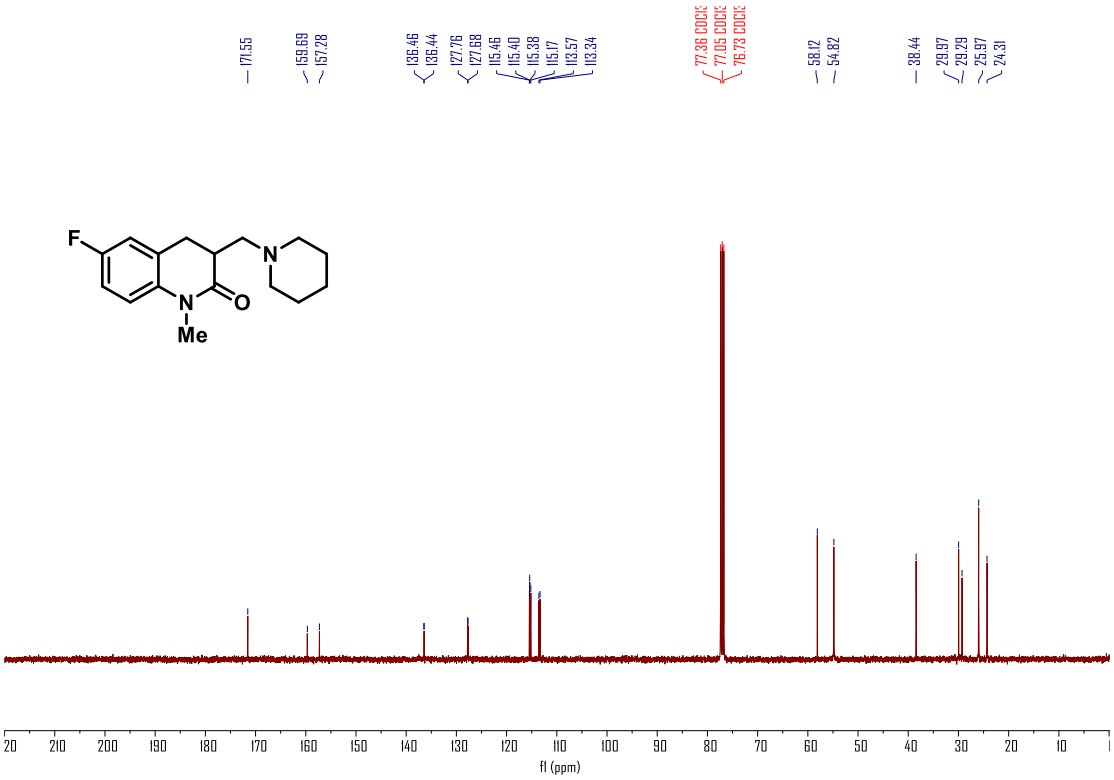
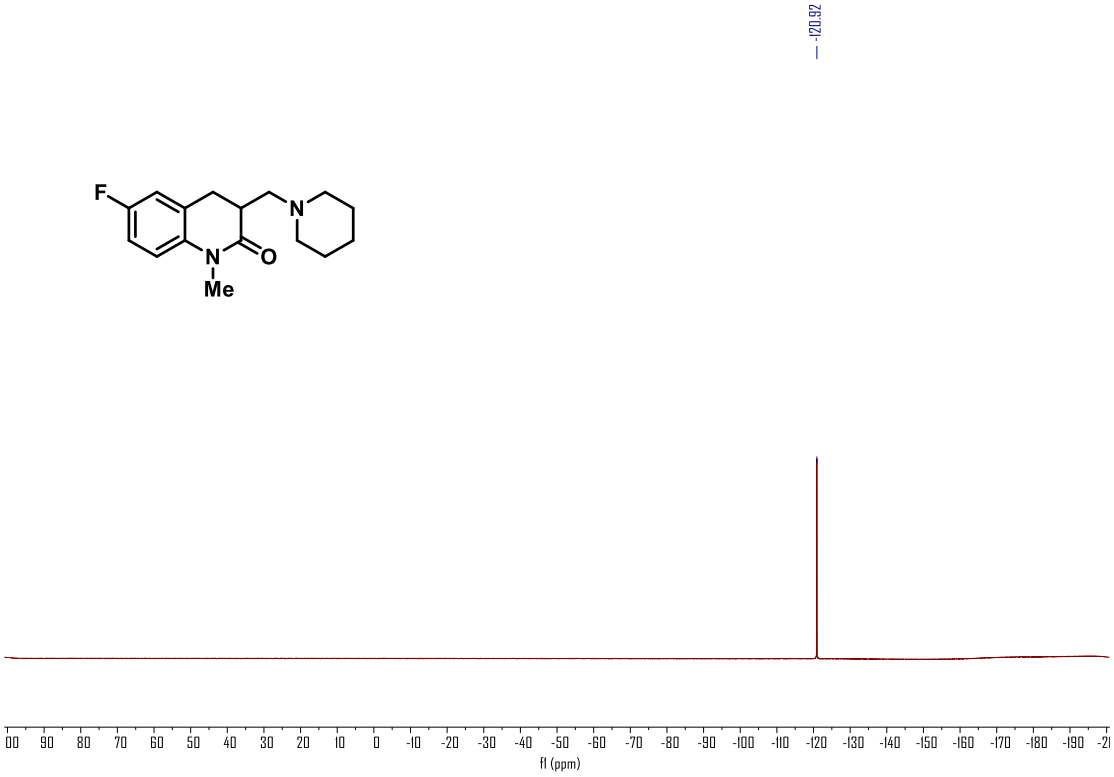


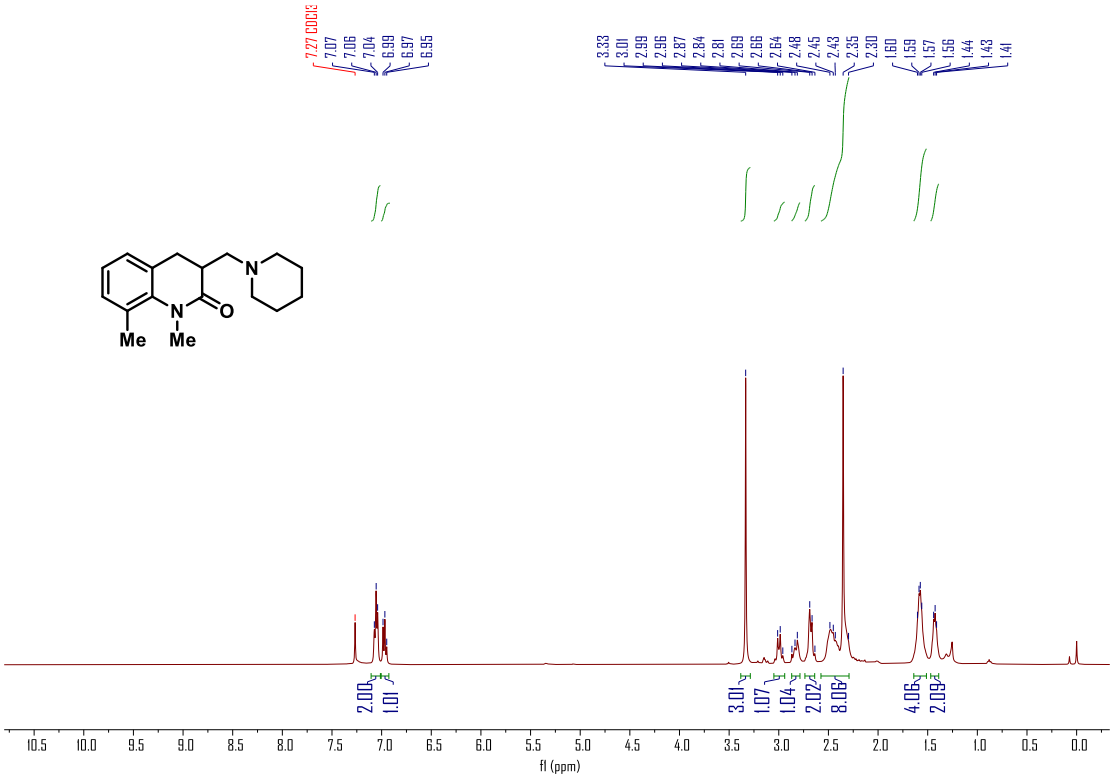
^{13}C NMR of 4i (101 MHz, $CDCl_3$)



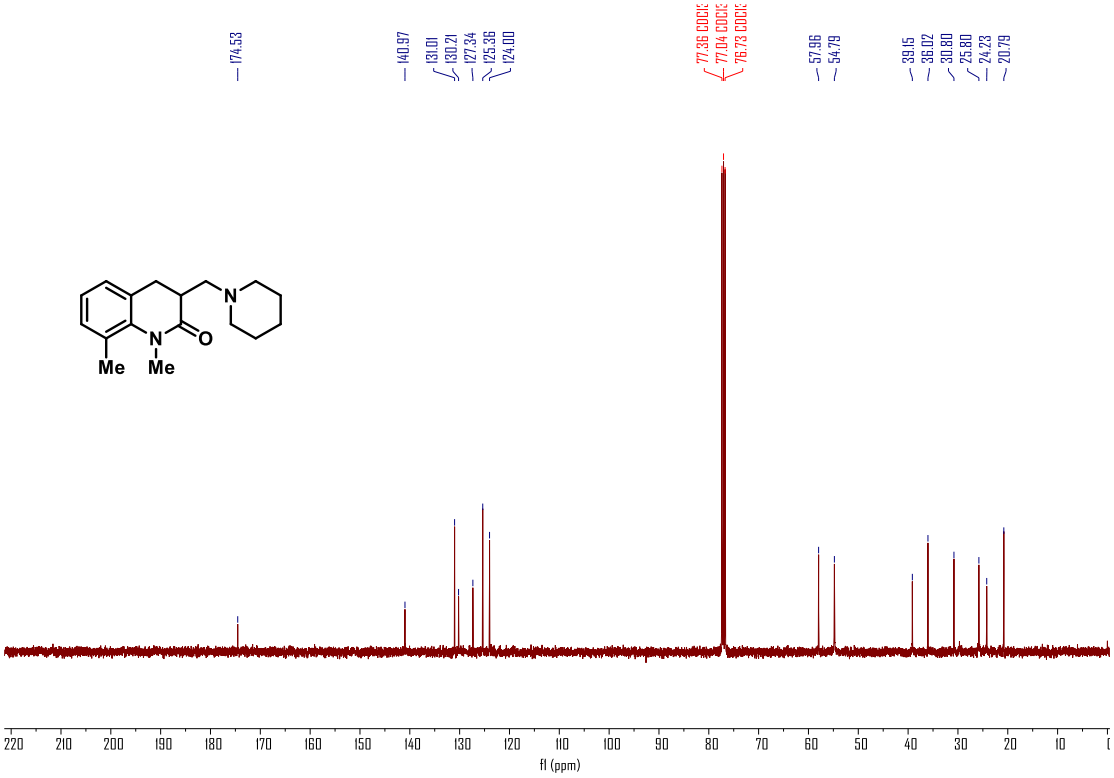
^{19}F NMR of 4i (375 MHz, $CDCl_3$)



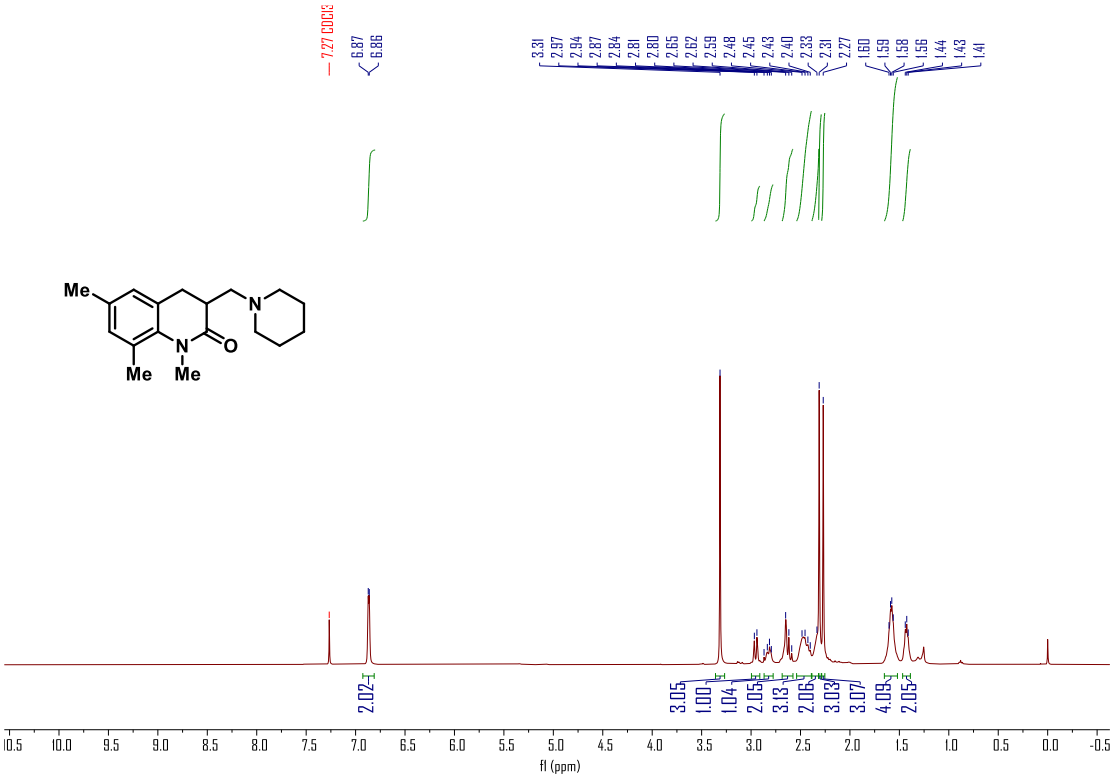
^{1}H NMR of 4j (400 MHz, $CDCl_3$)



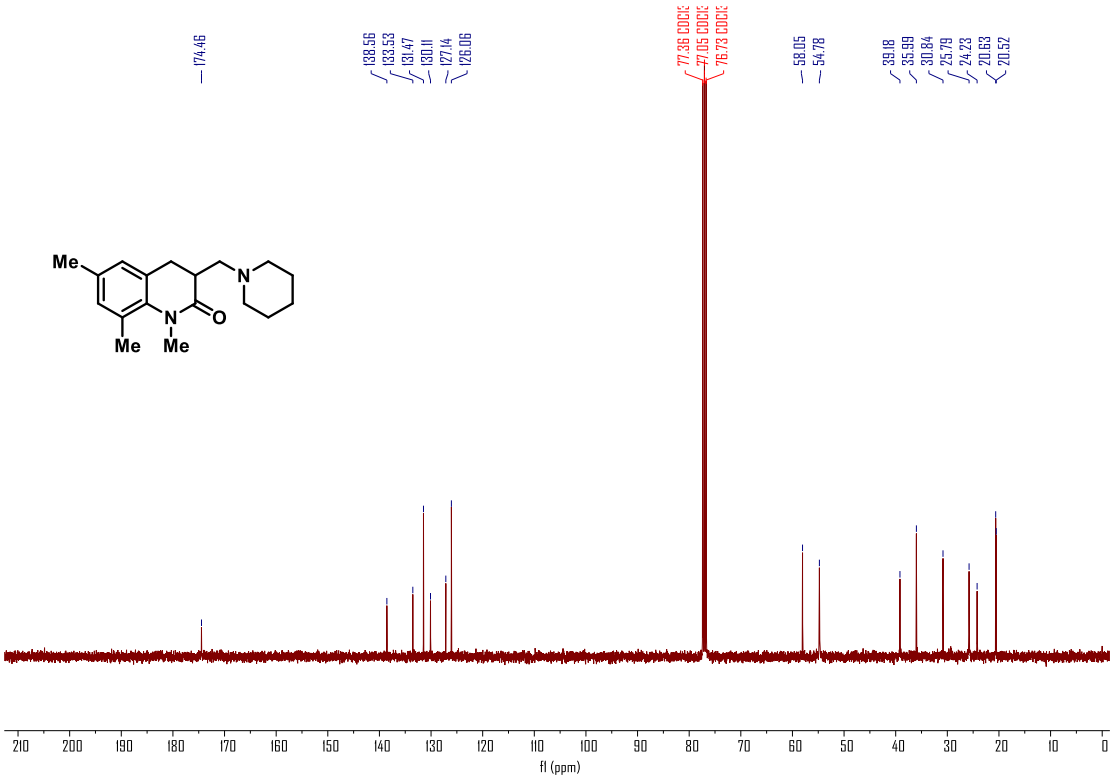
^{13}C NMR of 4j (101 MHz, $CDCl_3$)



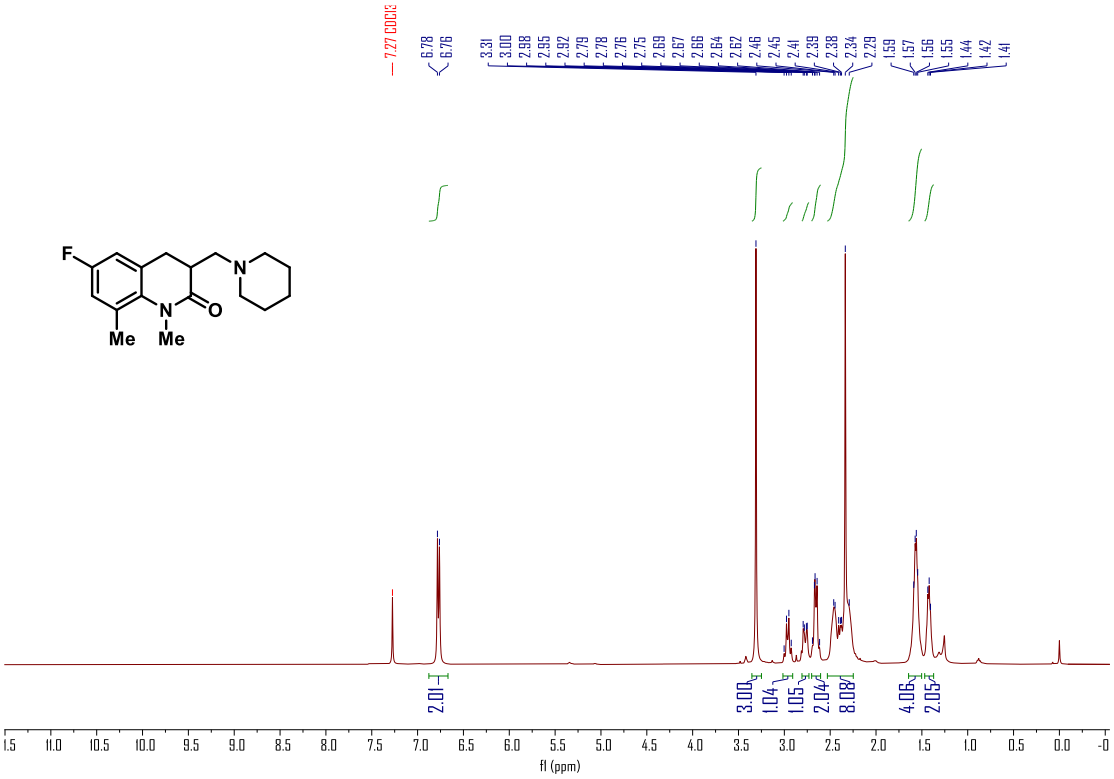
^{1}H NMR of 4k (400 MHz, $CDCl_3$)



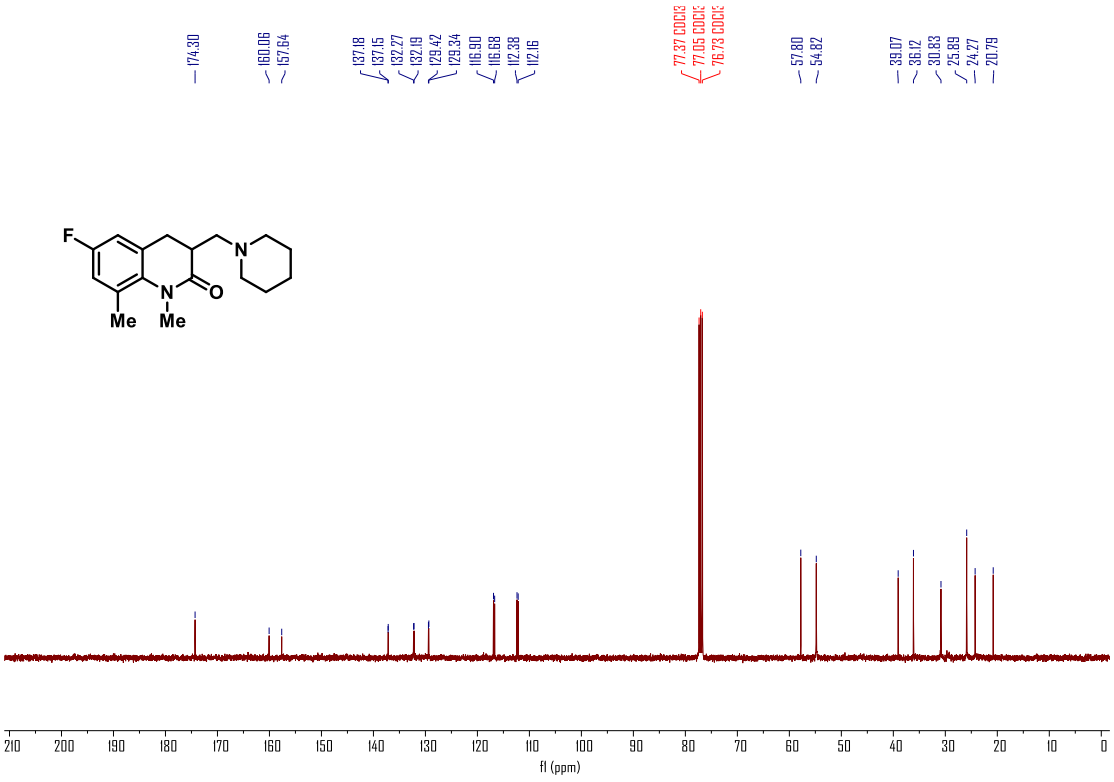
^{13}C NMR of 4k (101 MHz, $CDCl_3$)



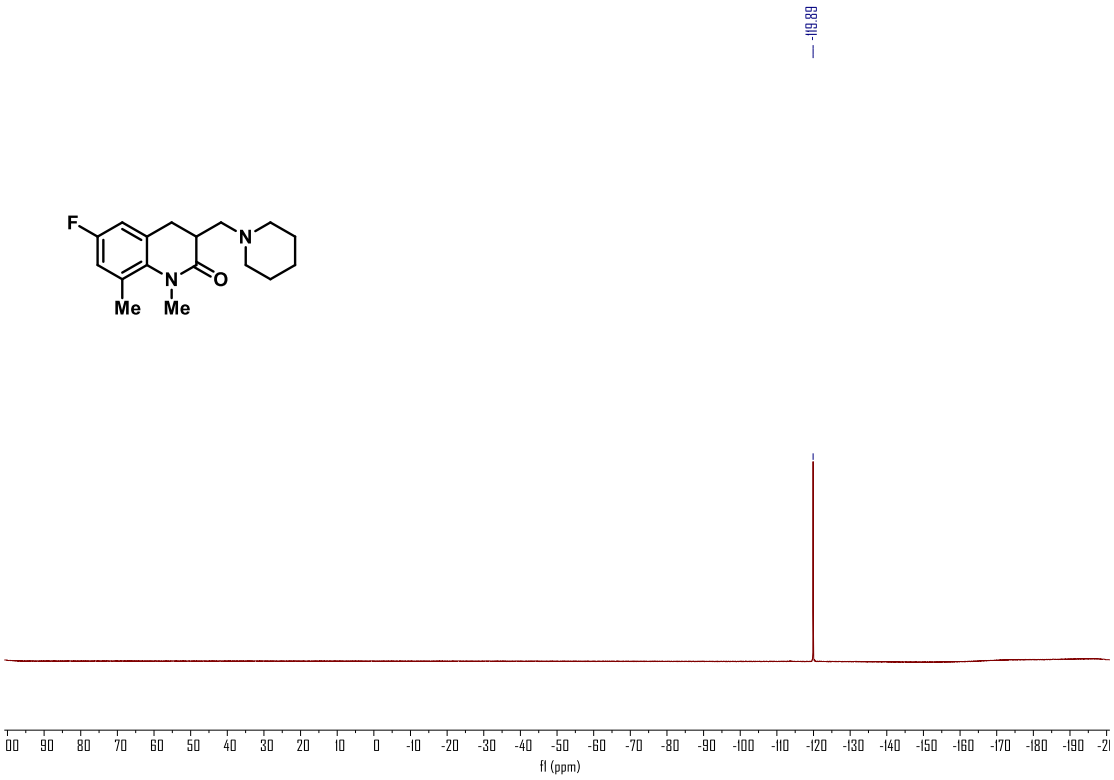
^{1}H NMR of 4l (400 MHz, $CDCl_3$)



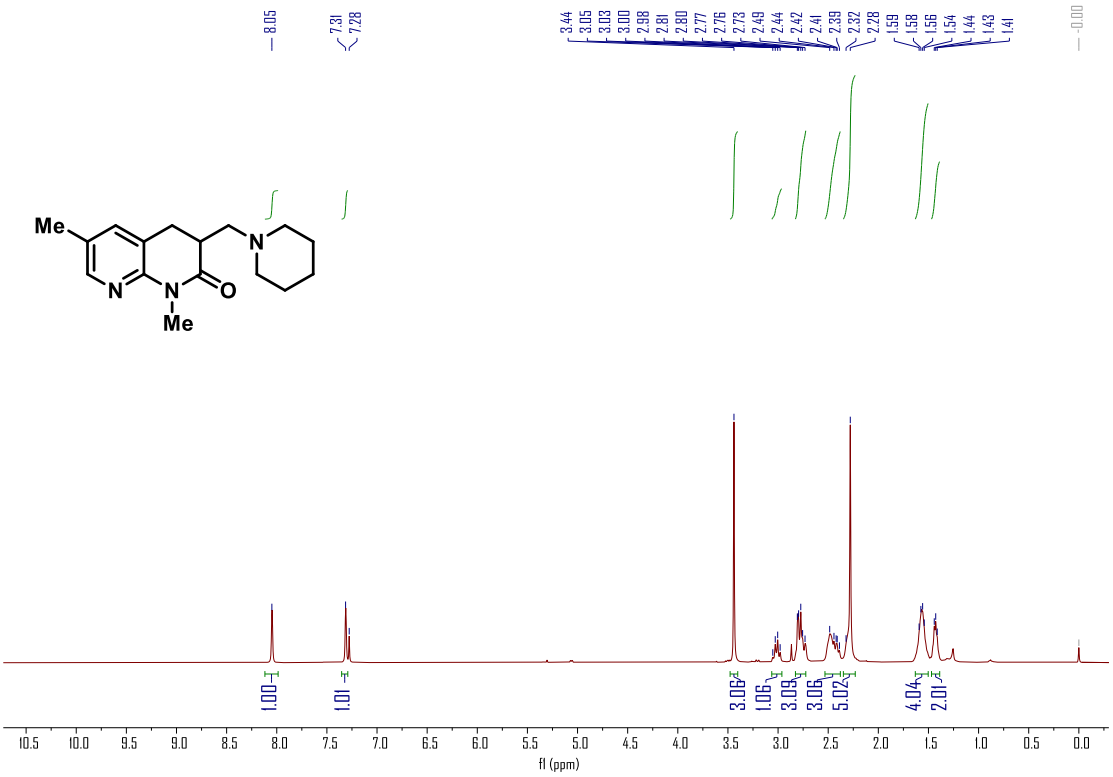
^{13}C NMR of 4l (101 MHz, $CDCl_3$)



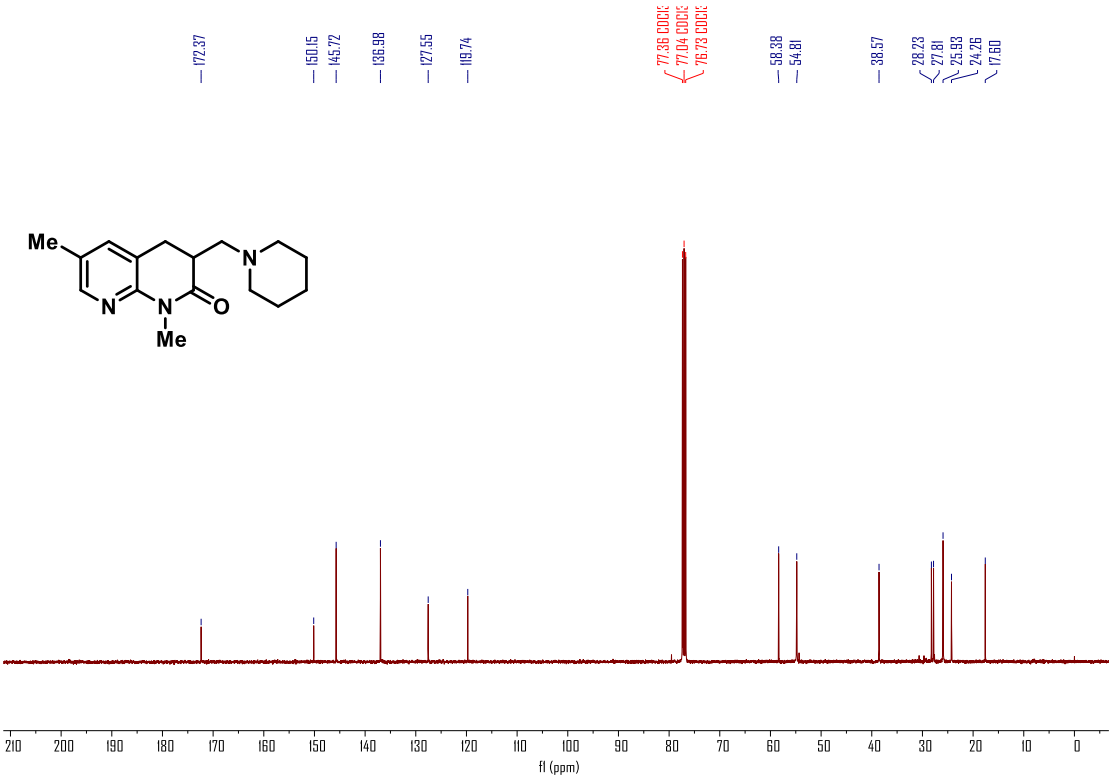
^{19}F NMR of 4l (375 MHz, $CDCl_3$)



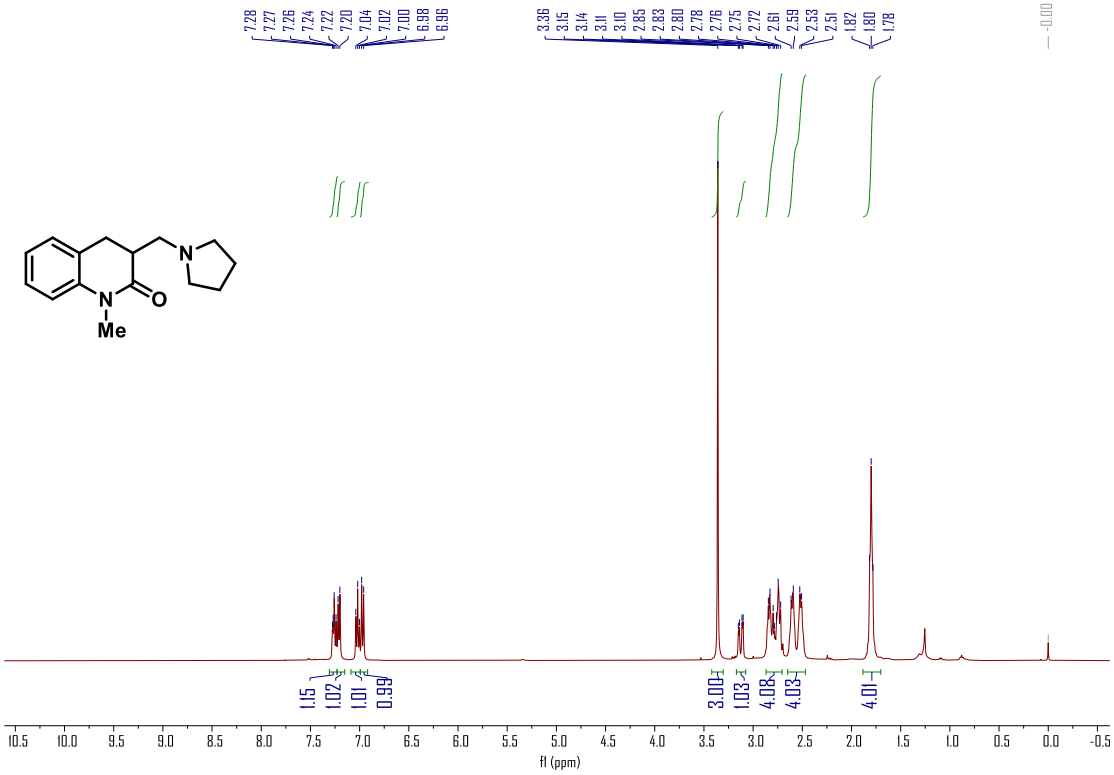
^{1}H NMR of 4m (400 MHz, $CDCl_3$)



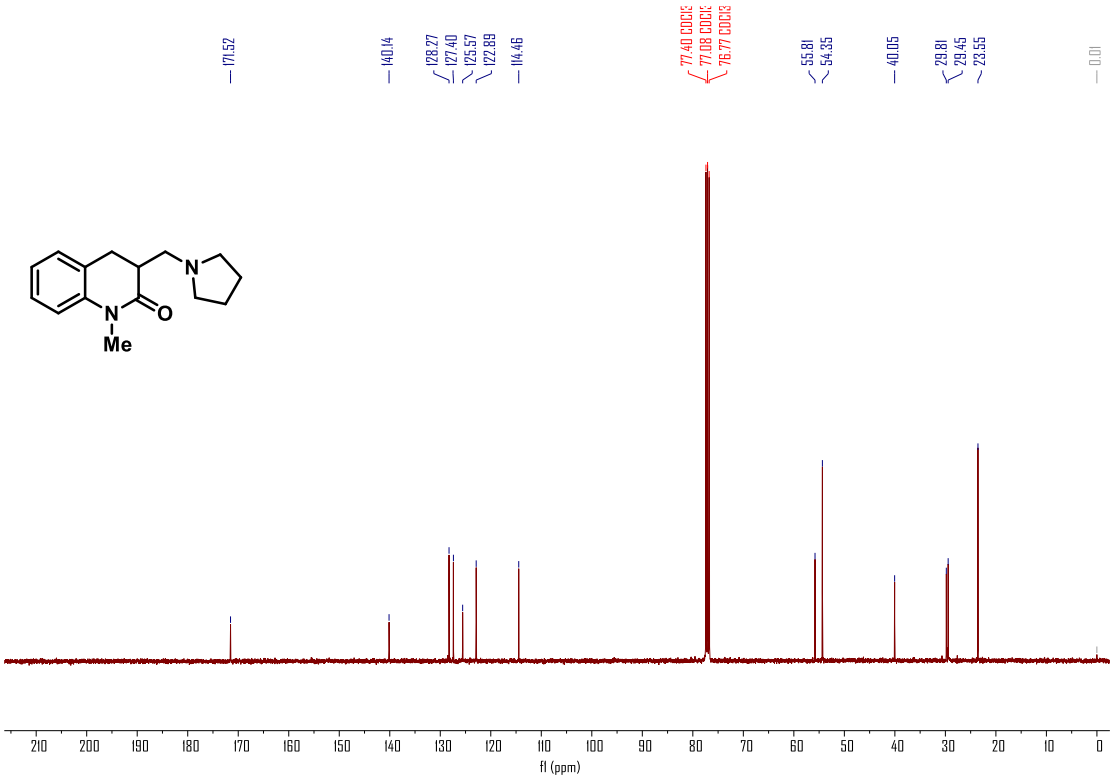
^{13}C NMR of 4m (101 MHz, $CDCl_3$)



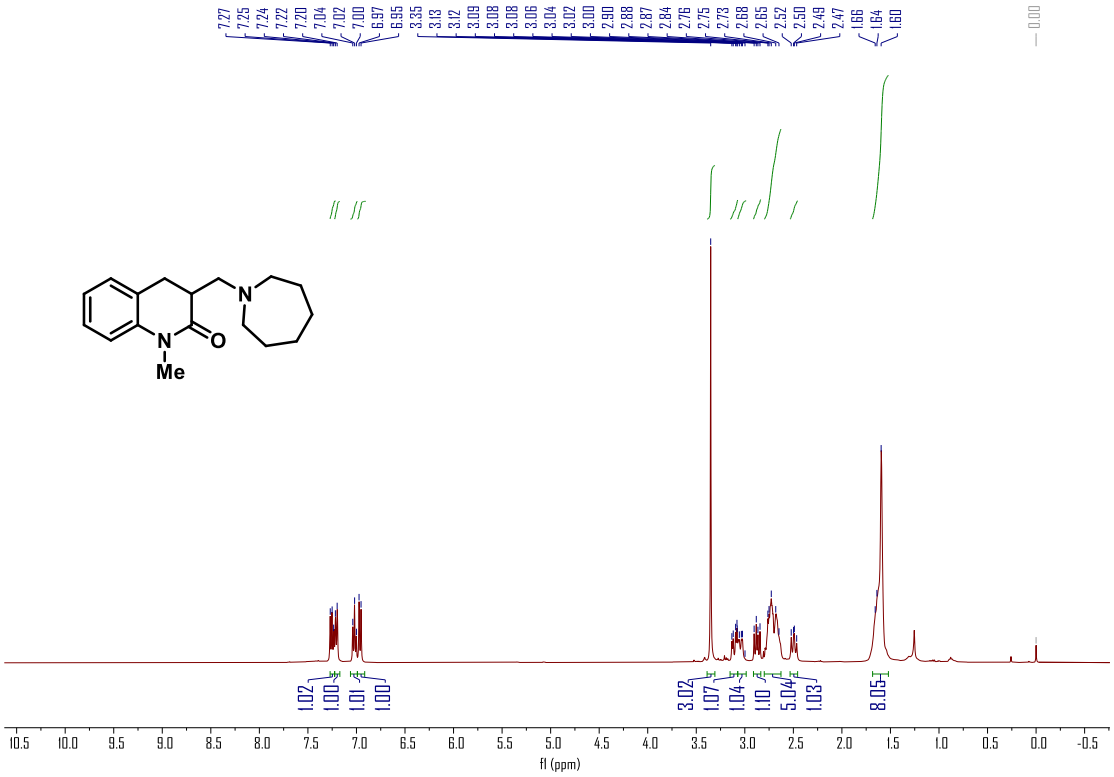
^{1}H NMR of 4n (400 MHz, $CDCl_3$)



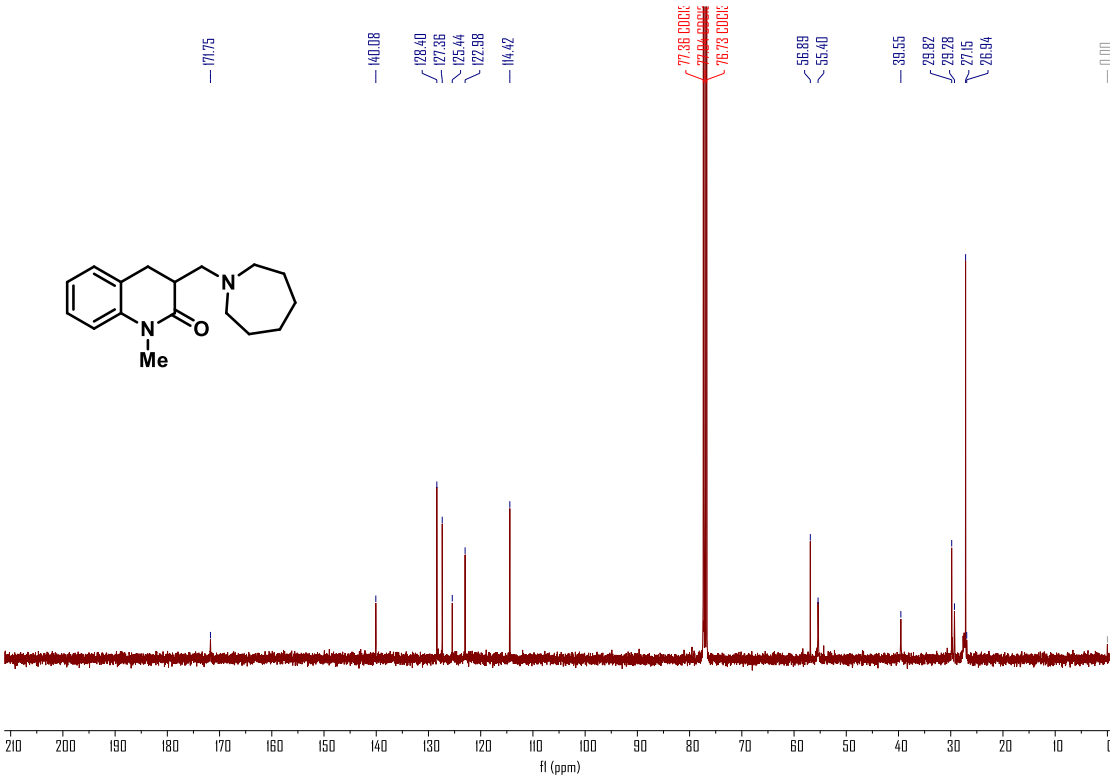
^{13}C NMR of 4n (101 MHz, $CDCl_3$)



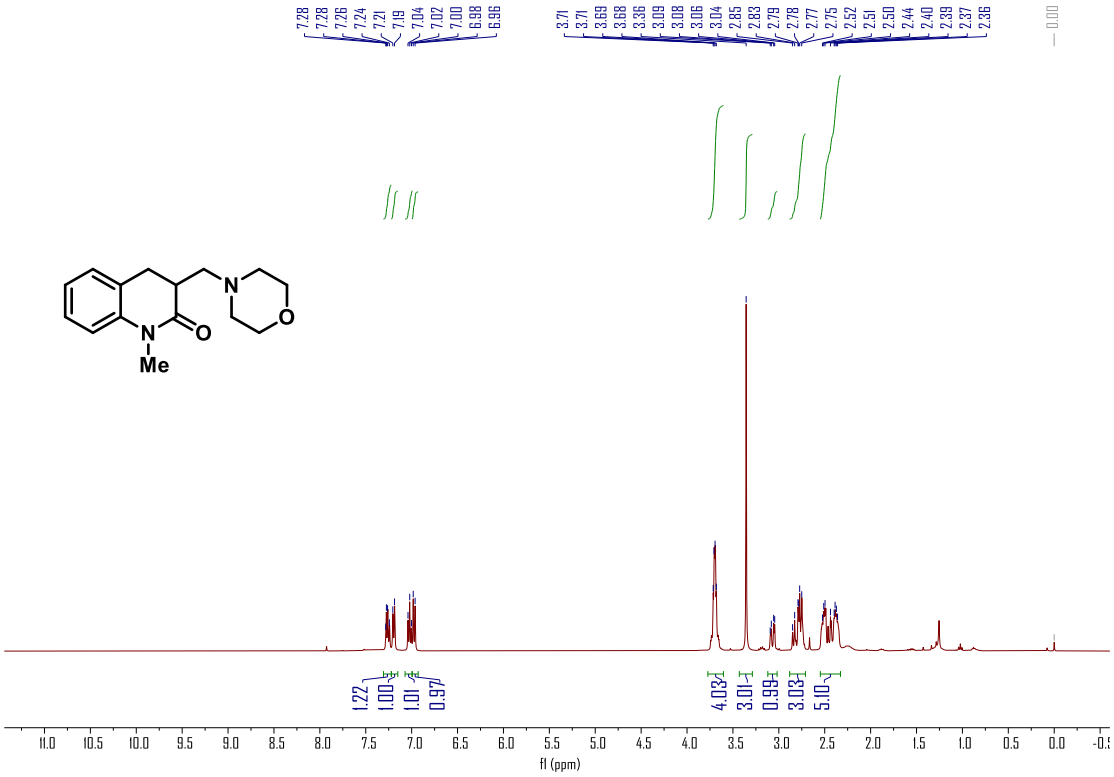
^{1}H NMR of 4o (400 MHz, $CDCl_3$)



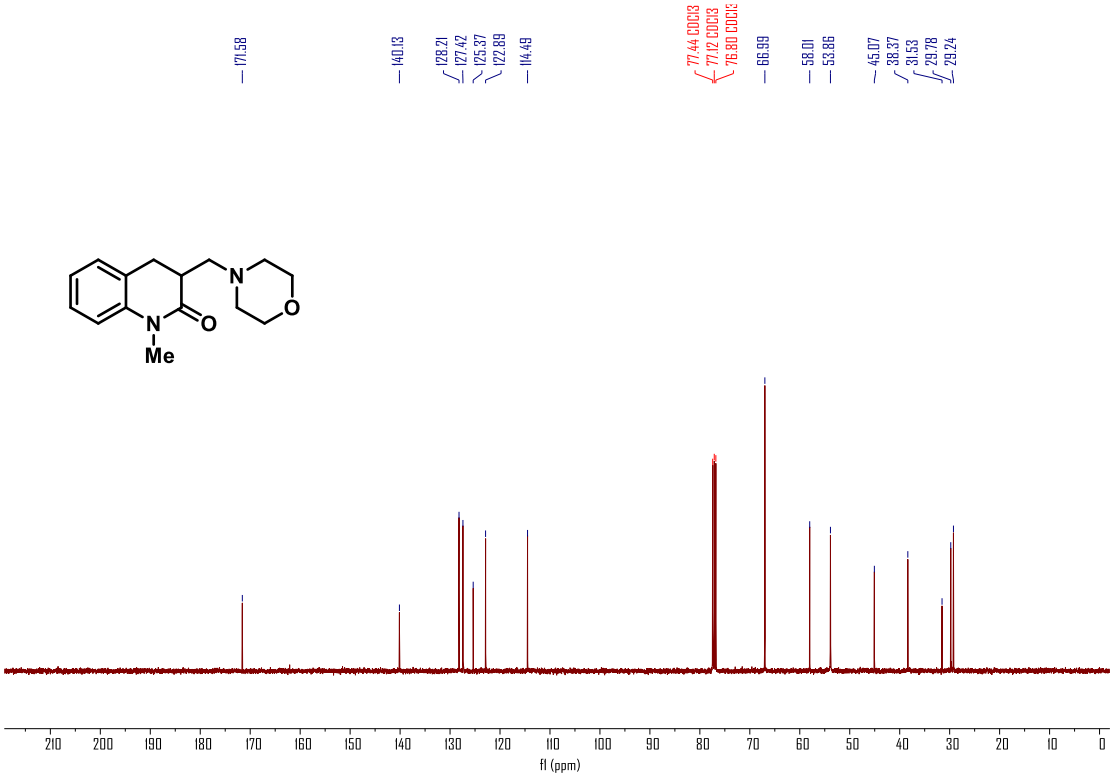
^{13}C NMR of 4o (101 MHz, $CDCl_3$)



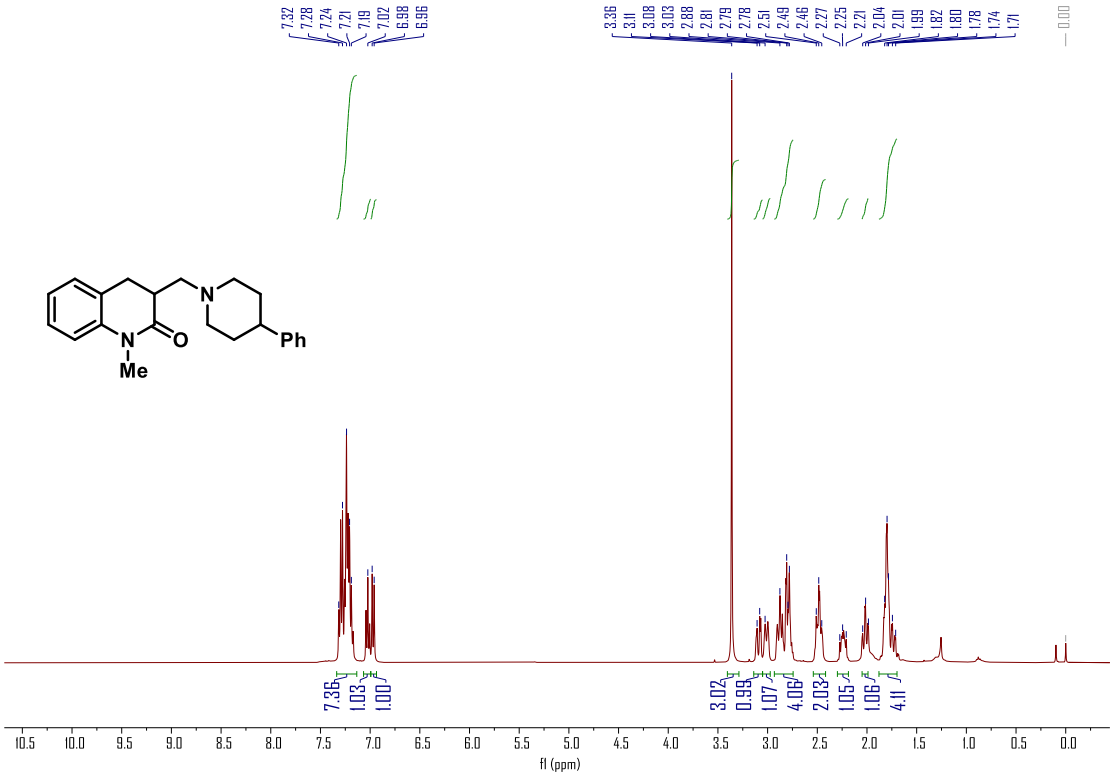
^{1}H NMR of 4p (400 MHz, $CDCl_3$)



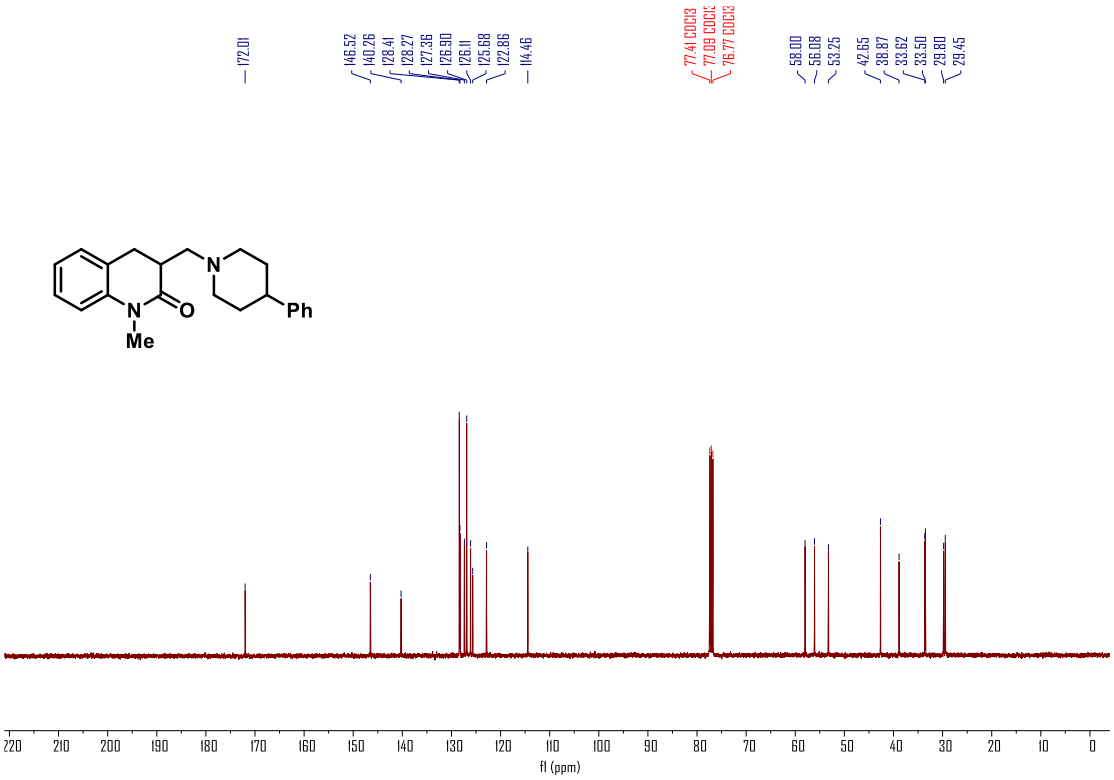
^{13}C NMR of 4p (101 MHz, $CDCl_3$)



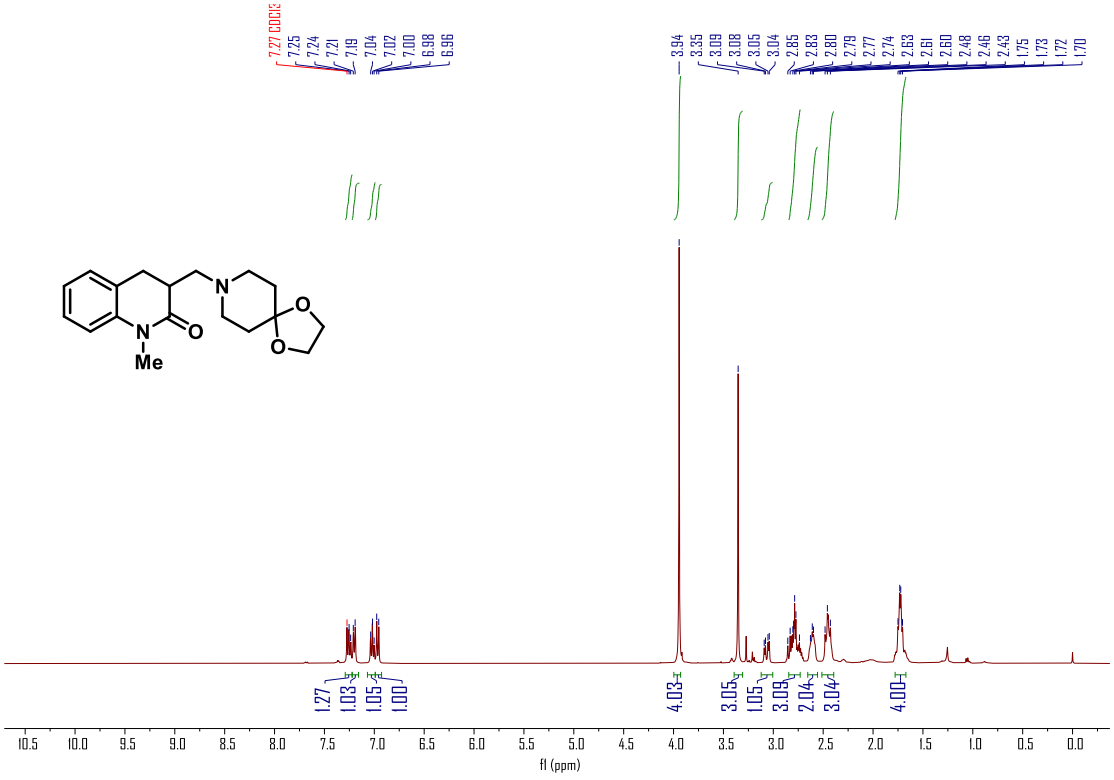
^{1}H NMR of 4q (400 MHz, $CDCl_3$)



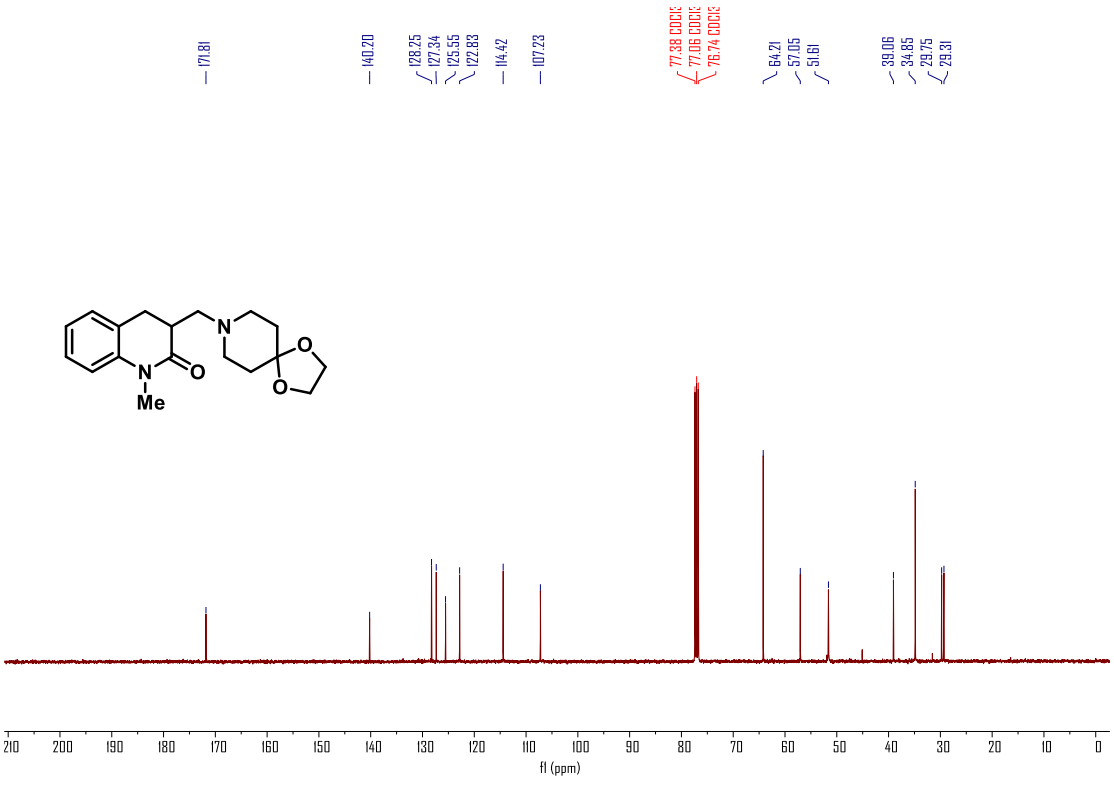
^{13}C NMR of 4q (101 MHz, $CDCl_3$)



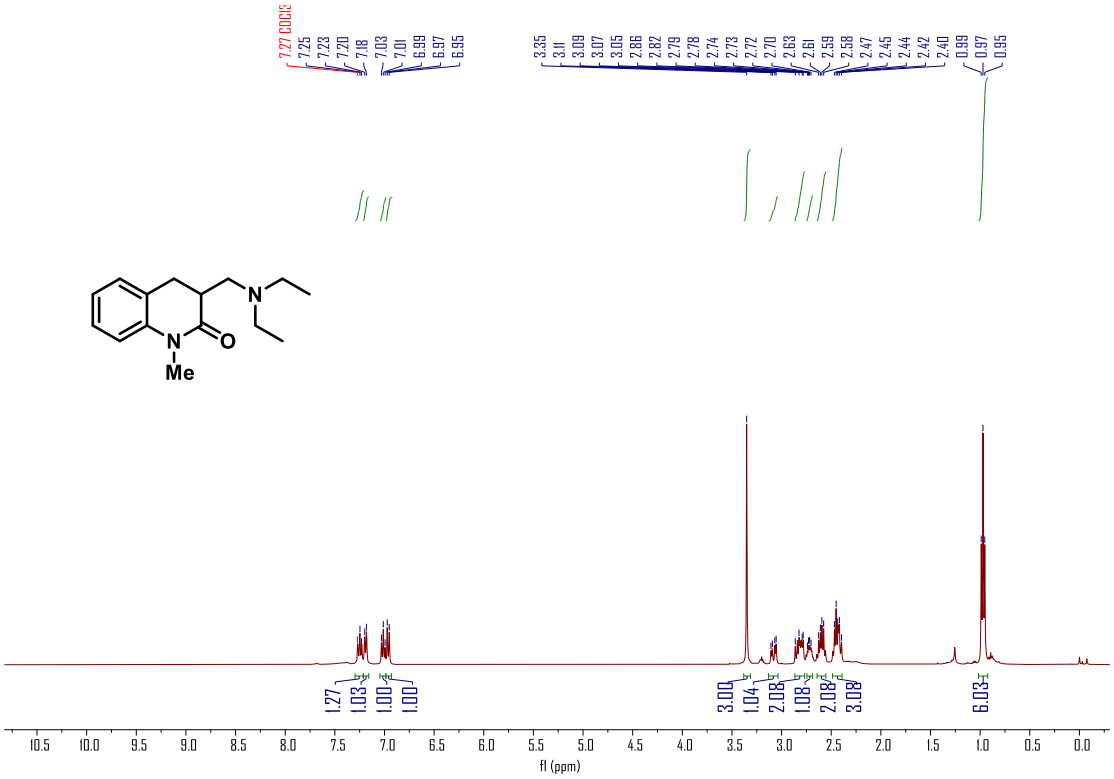
^{1}H NMR of 4r (400 MHz, $CDCl_3$)



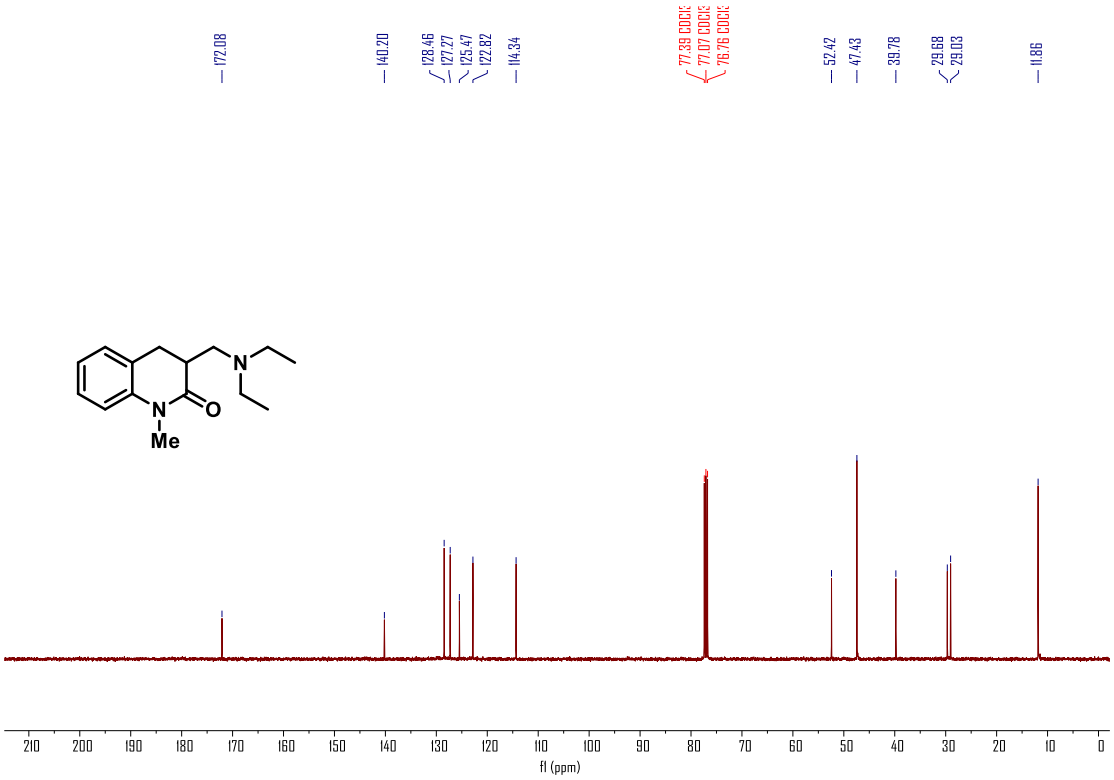
^{13}C NMR of 4r (101 MHz, $CDCl_3$)



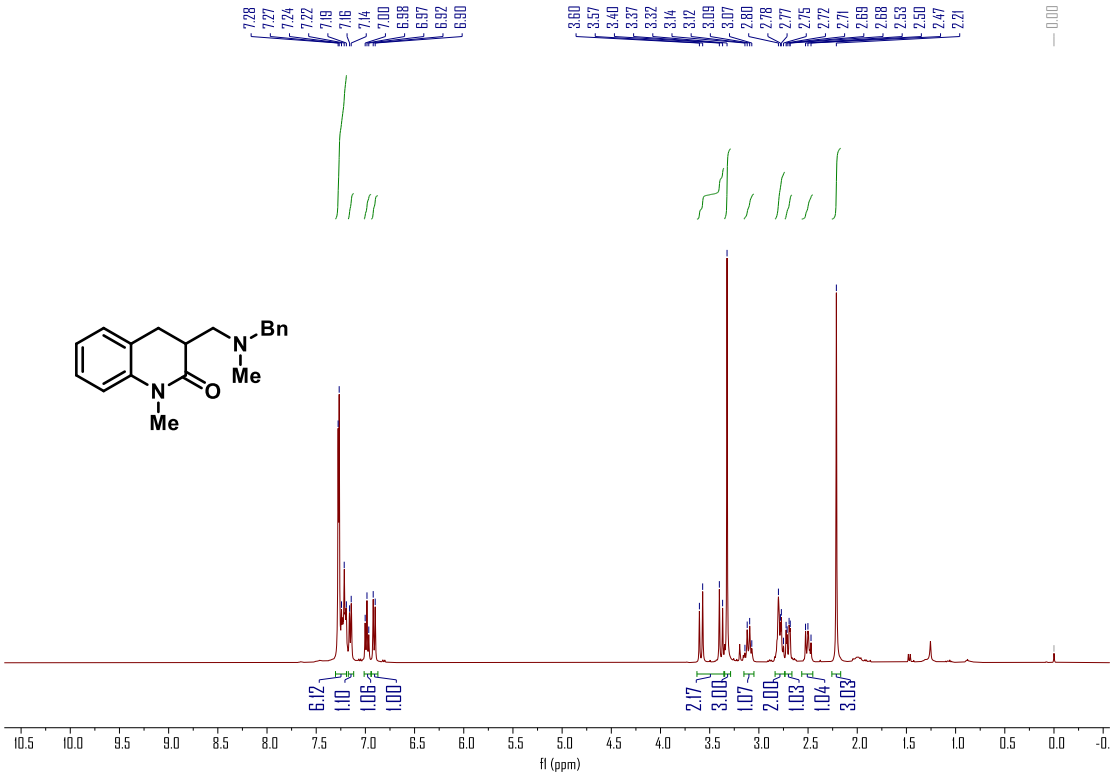
^{1}H NMR of 4s (400 MHz, $CDCl_3$)



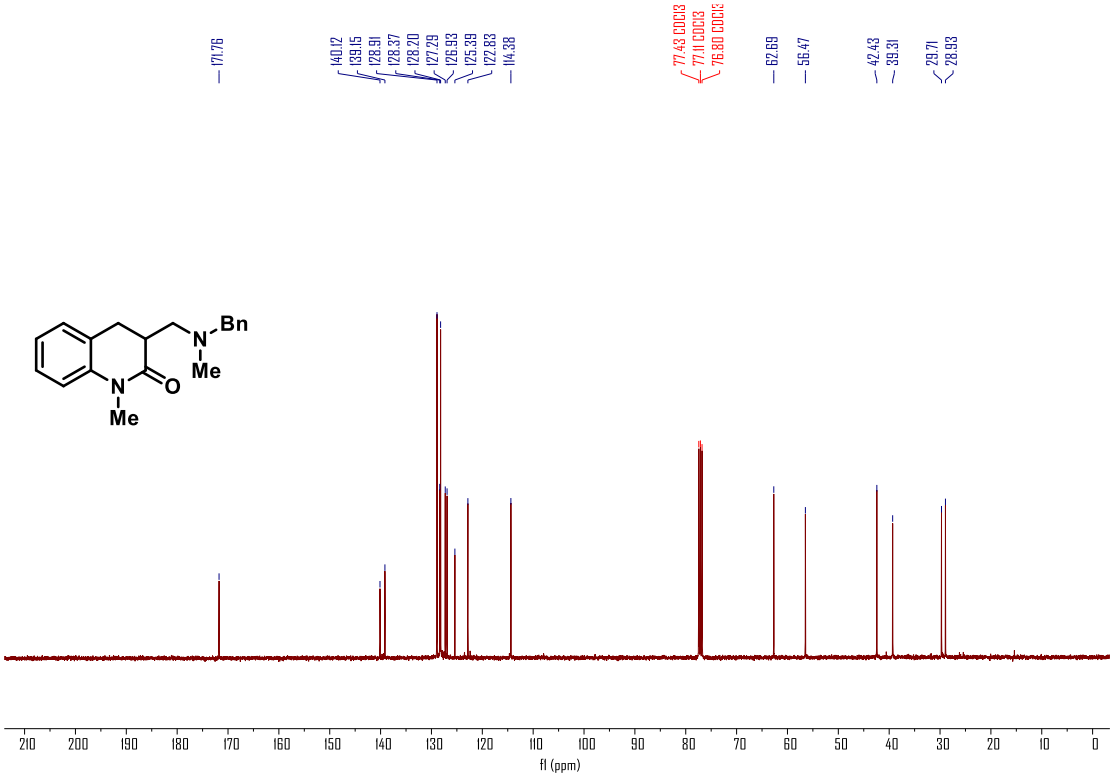
^{13}C NMR of 4s (101 MHz, $CDCl_3$)



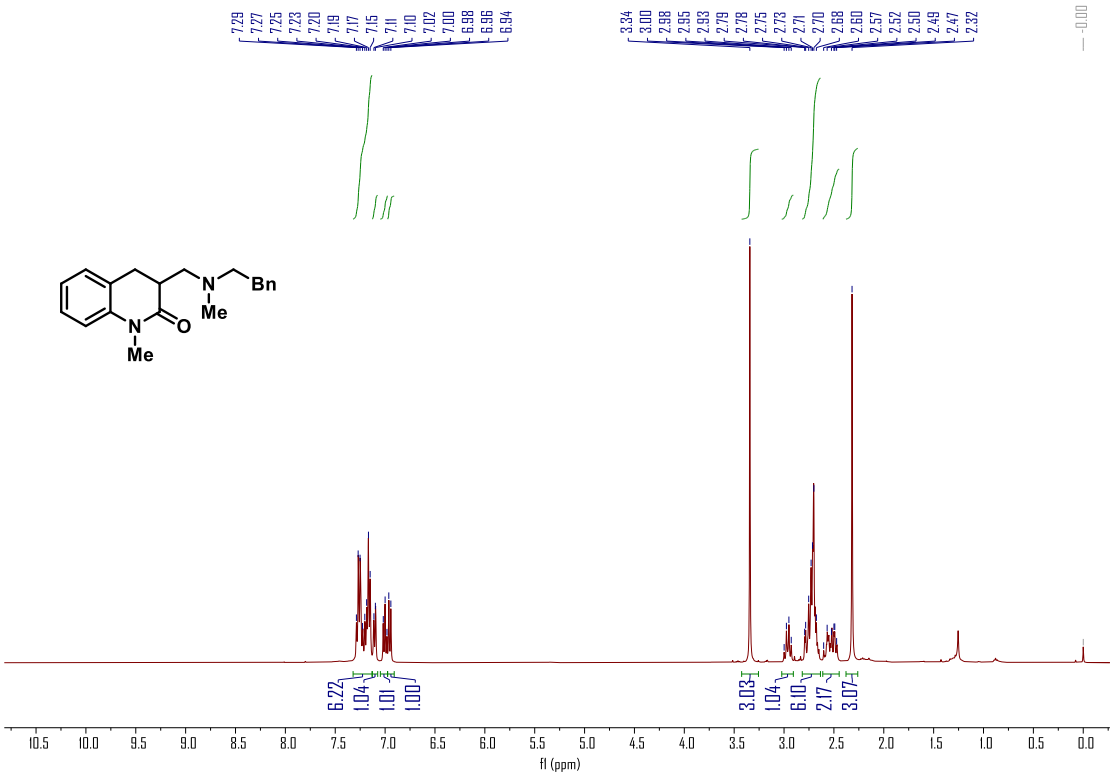
^{1}H NMR of 4t (400 MHz, $CDCl_3$)



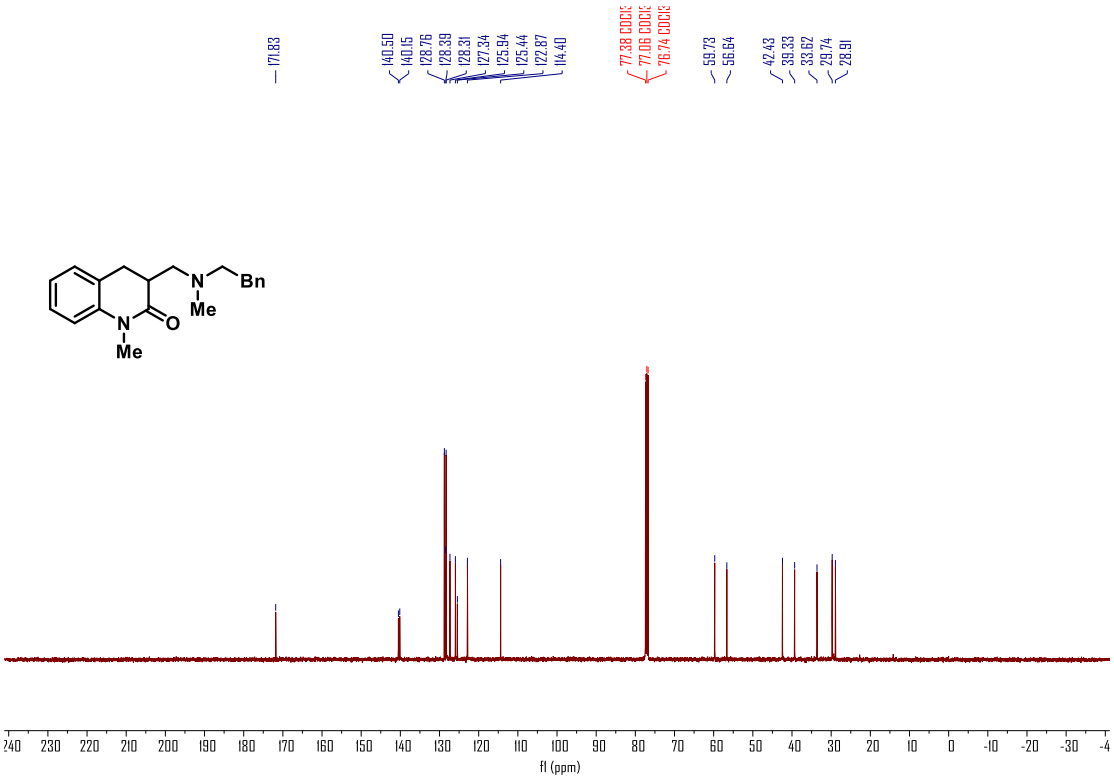
^{13}C NMR of 4t (101 MHz, $CDCl_3$)



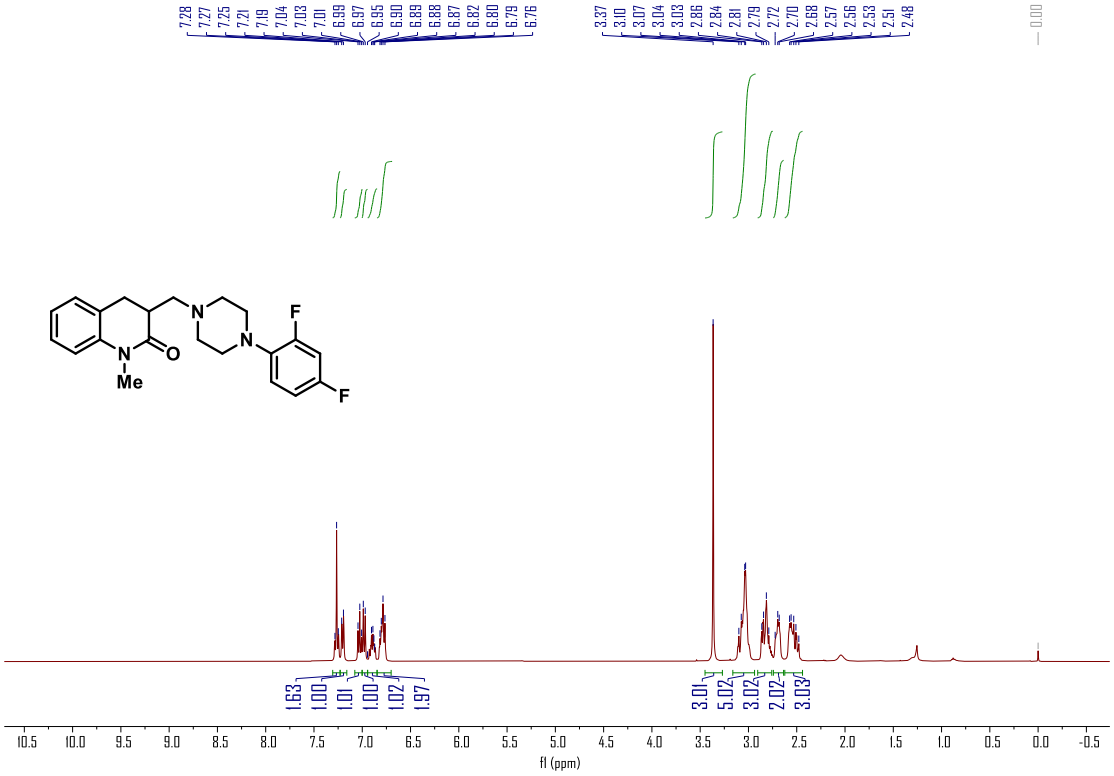
^{1}H NMR of 4u (400 MHz, $CDCl_3$)



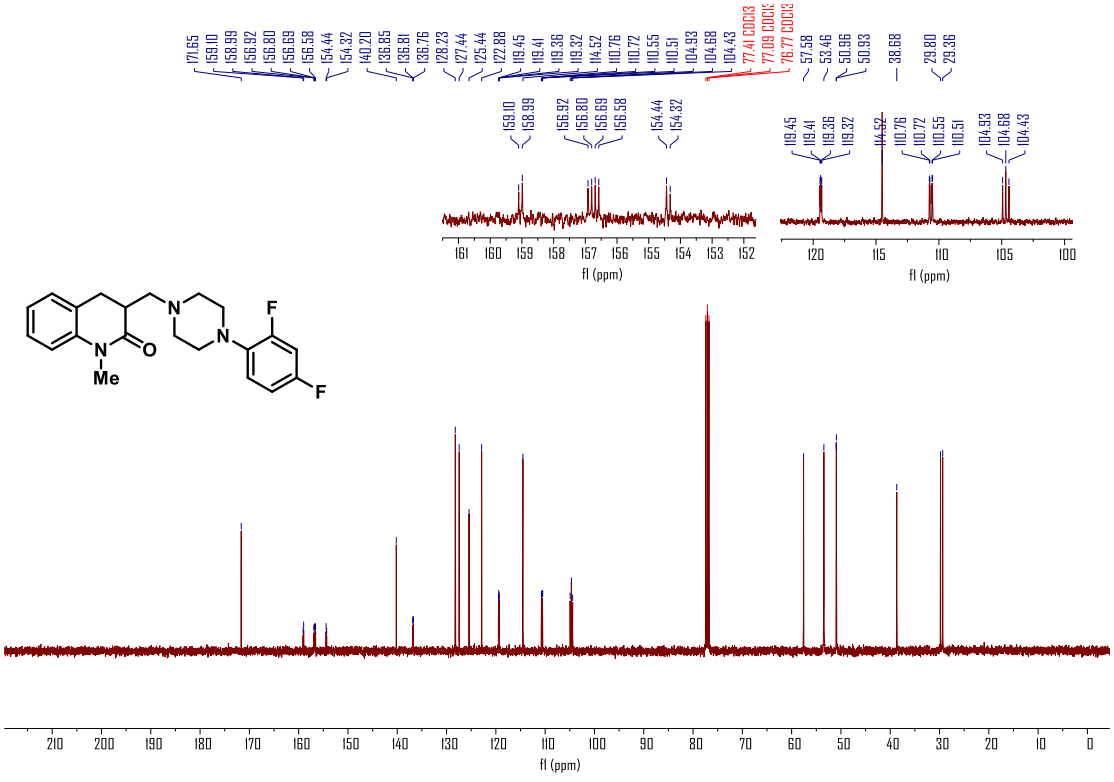
^{13}C NMR of 4u (101 MHz, $CDCl_3$)



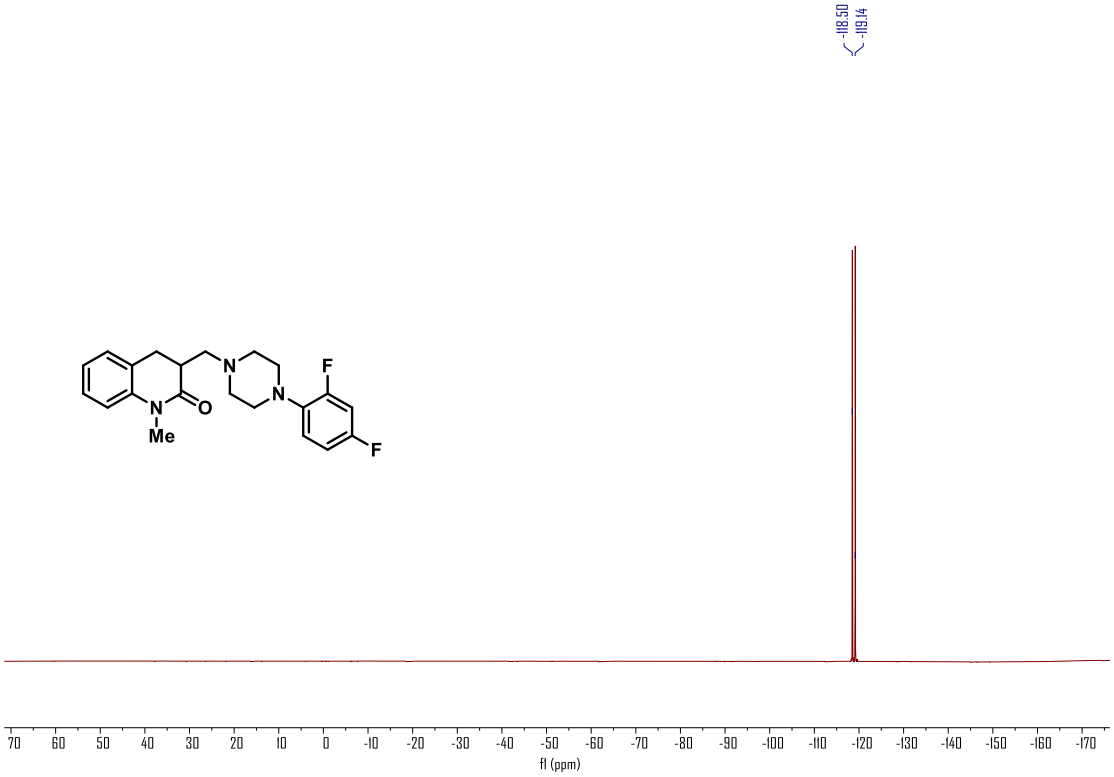
^{1}H NMR of 4v (400 MHz, $CDCl_3$)



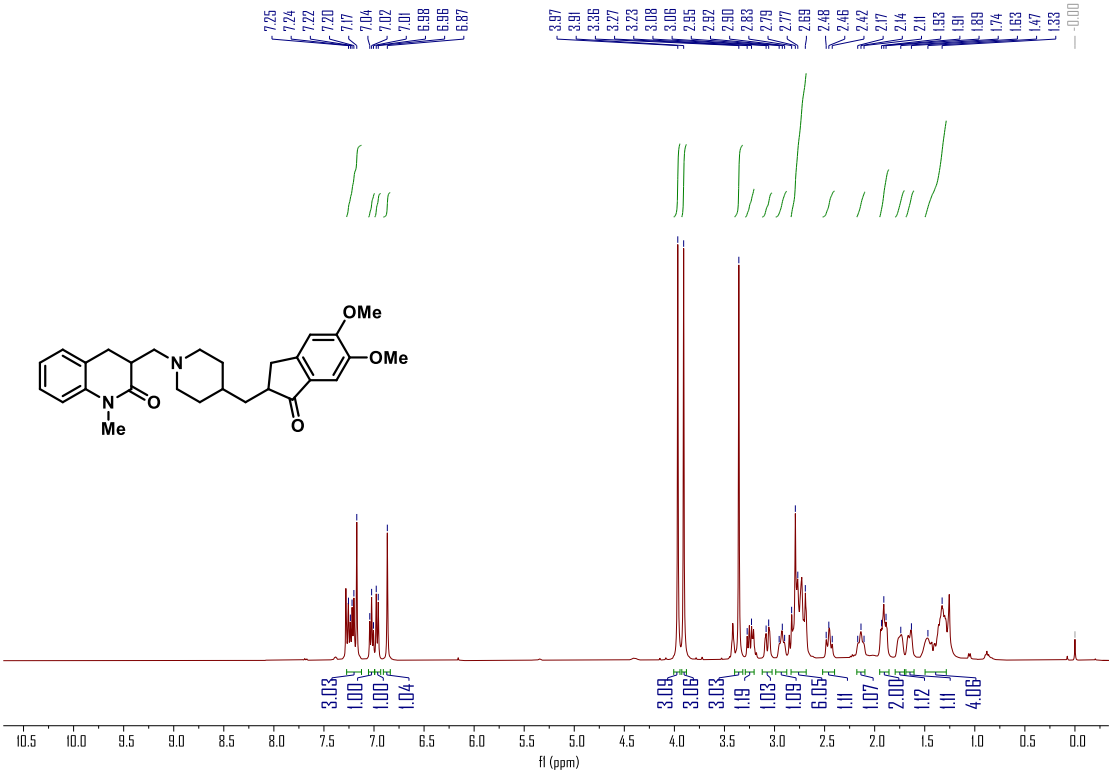
^{13}C NMR of 4v (101 MHz, $CDCl_3$)



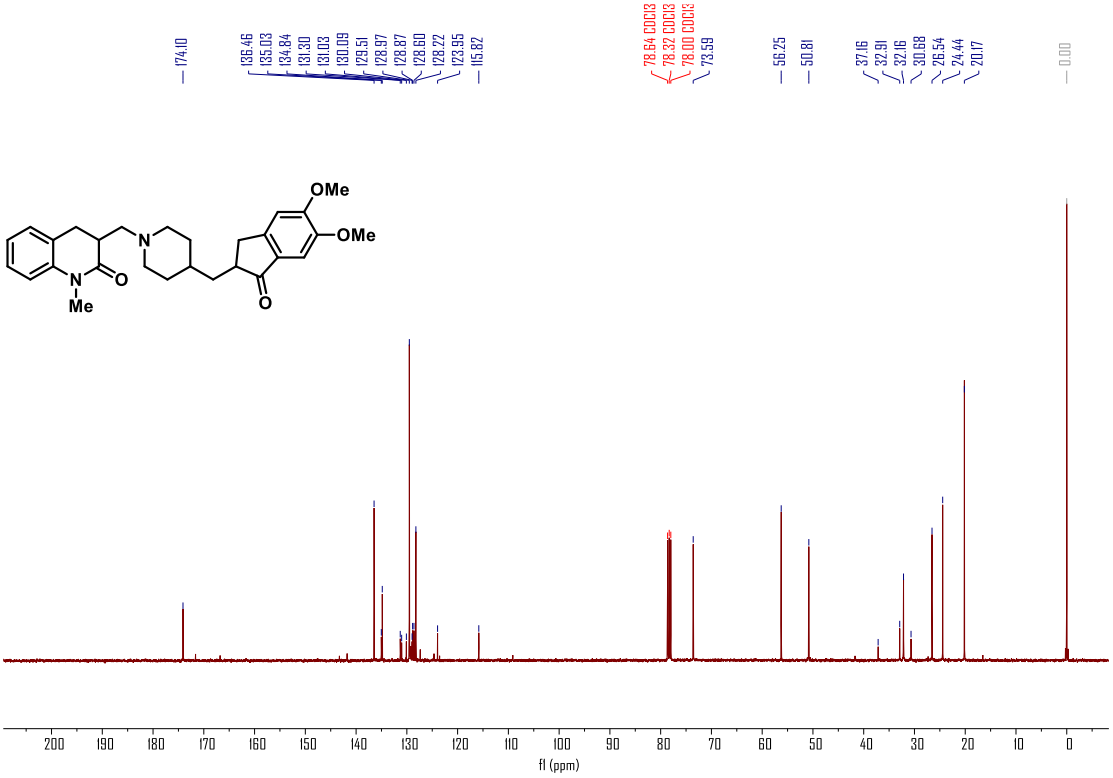
^{19}F NMR of 4v (375 MHz, $CDCl_3$)



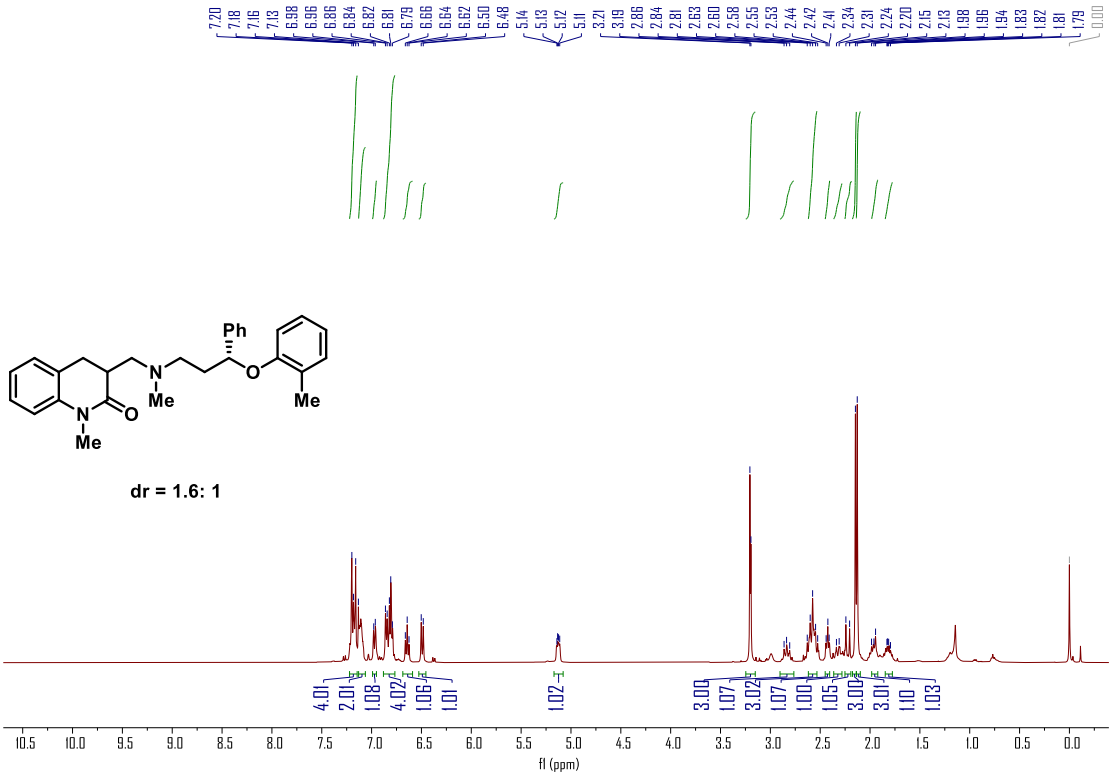
^{1}H NMR of 4w (400 MHz, $CDCl_3$)



^{13}C NMR of 4w (101 MHz, $CDCl_3$)



^{1}H NMR of 4x (400 MHz, $CDCl_3$)



^{13}C NMR of 4x (101 MHz, $CDCl_3$)