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Supporting information

Merging dual photoredox/cobalt catalysis and boronic acid (derivatives) activation for the Minisci reaction

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Contents

1. General information

All components as well as reagents and solvents were used as received without further purification, unless stated otherwise. Reagents and solvents were bought from Sigma Aldrich and TCI and if applicable, kept under argon atmosphere. Technical solvents were bought from VWR International and Biosolve, and are used as received. Product isolation was performed using silica (60, F254, Merck™), and TLC analysis was performed using Silica on aluminum foils TLC plates (F254, Supelco Sigma-Aldrich™) with visualization under ultraviolet light (254 nm and 365 nm) or appropriate TLC staining. ^{1}H (400MHz) and ^{13}C (100MHz) NMR spectra were recorded at ambient temperature using a Bruker-Avance 400 or Mercury 400. ^{1}H NMR spectra are reported in parts per million (ppm) downfield relative to $CDCl_3$ (7.26 ppm), ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.2 ppm). NMR spectra uses the following abbreviations to describe the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, m = multiplet, dd = double doublet, td = triple doublet. Known products were characterized by comparing to the corresponding ^{1}H NMR and ^{13}C NMR from literature. GC analyses were performed on a GC-FID (Varian 430-GC) in combination with an auto sampler (Varian CP-8400) or GC-MS combination (Shimadzu GC-2010 Plus coupled to a Mass Spectrometer; Shimadzu GCMS-QP 2010 Ultra) with an auto sampler unit (AOC-20i, Shimadzu). Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and are uncorrected.

Chemicals: DMF (99.8%, extra dry), DMA (99.8%, extra dry) and DMSO (99.8%, extra dry) were purchased from Acros Organics and used as purchased. The transition metal photocatalysts $Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$, *fac*-Ir, Mes-Acr-$Me^+$ were purchased from commercial sources. The organic photocatalyst 4CzIPN was prepared in lab by the procedure outlined in previous publications.[1] The cobalt catalysts $(Co(dmgH)(dmgH_2)Cl_2$, $Co(dmgH)_2PyCl$,[2] $Co(dmgH)_2Py_2)$[3] were synthesized according to reported methodologies. Deuterated solvents were used as purchased (DMSO-d_6, DMF-d_7).

Photochemical experiments were performed magnetically stirred in 10 mL glass test-tubes with screw cap equipped with silicon septa. The tubes were irradiated with blue light (450 nm) using a coiled commercial LED strip fixed in 3D-printed reactor (1 m, from LEDXON, PN: 9009083) with a total power output of 14.0 W. To maintain a constant reaction temperature of 30°C, the setup was cooled by a constant air flow (Figure S1, A, B). Flow experiments were performed using a Vapourtec E-Series photoreactor (UV-150) (Figure S1,C).

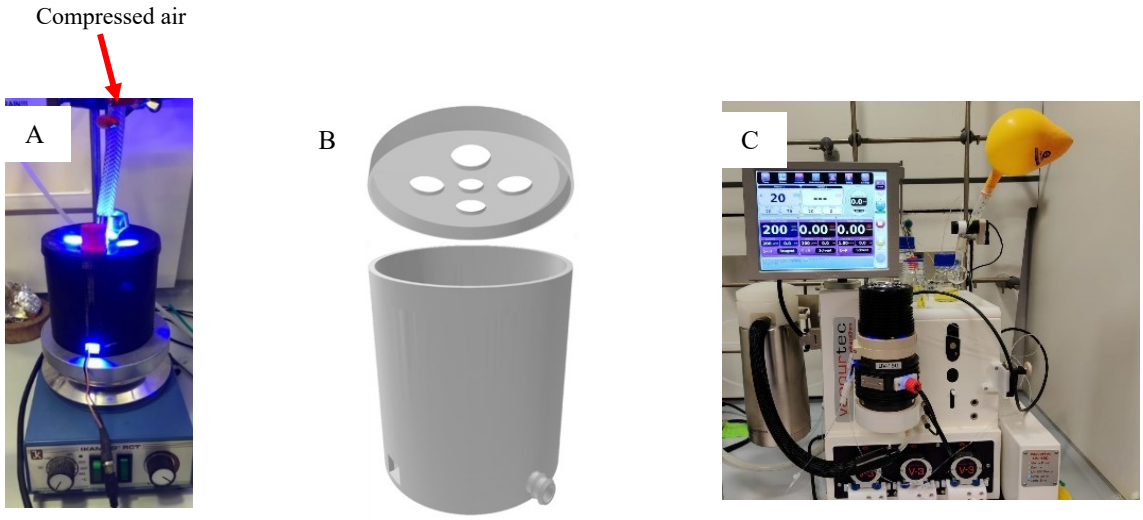
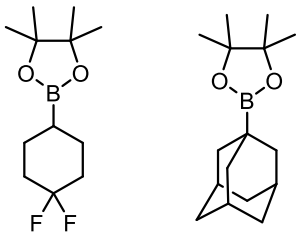


Figure S1: Reaction setup (in-house 3D printed reactor and flow reactor).

2. Synthesis and characterization of starting materials

Compound A1-A2[4]



A1

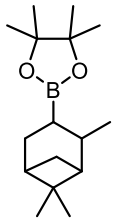
A2

The corresponding NHPI esters were dissolved *N*-Hydroxyphthalimide (1.0 equiv), DMAP (0.1 equiv) and carboxylic acid (1.0 equiv) in a round-bottomed flask using DCM (0.1 M) as solvent. DIC (1.0 equiv) was then added. The reaction mixture was allowed to stir at room temperature overnight, before

concentrating under reduced pressure. The crude residue was directly purified by flash-column chromatography (EtOAc:hep =1:9) to yield the pure NHPI ester.

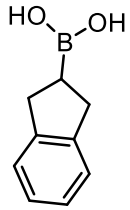
The NHPI ester (1.0 equiv, 0.6 mmol) and B_2cat_2 (40 mg, 1.25 equiv) were weighed into a 10 mL vial containing a stirring bar. DMA (6 mL, 0.1 M) was added and then the headspace of the vial was purged with a stream of argon for 10 seconds. The vial was sealed and stirred under blue LED irradiation overnight. Pinacol (4 equiv) was dissolved in Et_3N (1.25 mL), added to the reaction mixture and stirred for 1 h. The reaction mixture was transferred into a separatory funnel containing H_2O, NH_4Cl (saturated aqueous solution) and extracted with EtOAc. The organic layers were combined and concentrated under reduced pressure. The crude mixture was purified through a short silica gel column (EtOAc:hep 1:100).

Compound A3[5]



In a 2-neck round bottom flask, boron trichloride (1.1 equiv, 1 M in DCM) was added under inert atmosphere. A mixture of (±)-α-pinene (1.0 equiv) and triethylsilane (1.0 equiv) was dissolved in DCM (0.4 M). The mixture was then added dropwise to the boron trichloride at room temperature. After 2 hours, pinacol (2.0 equiv) was added portionwise at room temperature and stirred for another 12 hours. The volatiles were removed in vacuo and through a short silica gel column to get a colorless liquid.

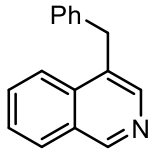
Compound A4[6]



A solution of 1-*H* indene (10.0 mmol) in THF (2 mL) was added dropwise to a solution of BH_3•THF (20 mL, 20 mmol, 1 M solution in THF) at 0 °C. The mixture was stirred for 2 h before adding 2 mL of H_2O (very slow addition!). After stirring for additional 3 h at room temperature, the reaction mixture was concentrated in vacuo, diluted with ethyl acetate (30 mL), and washed with saturated aqueous bicarbonate (20 mL) and brine (20 mL). The organic layer was dried over

sodium sulfate, filtered, and concentrated to approximately 5 mL. Et_2O was then added. The resultant precipitate was washed with Et_2O and dried under vacuum to afford the alkylboronic acid as a thick oil.

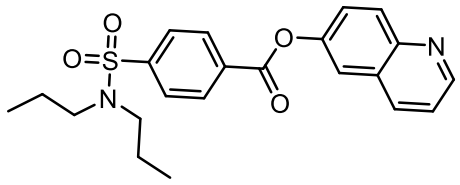
Compound A5[7]



Isoquinoline synthesis: $Pd(PPh_3)_4$ (5 mol%) and HCOONa (2.0 equiv) were loaded into a CEM-Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W. The reactions were carried out in 10 mL glass tubes, sealed with Teflon septum, and placed in the microwave cavity. The vial was evacuated and flushed with N_2. Oxazolidine* (0.15 mmol) dissolved in DMF (1.5 mL) was added, followed by distilled water (0.5 mL). The vial was sealed and microwave-irradiated with stirring at a ceiling temperature of 100 °C at 150 W maximum power level for 30 min. After completion of the reaction time, the vial was cooled with a stream of air. After dilution with DCM, the organic phase was washed several times with brine. The organic phase was then evaporated under reduced pressure to obtain a residue which was further purified by a silica gel column chromatography (heptane/ethyl acetate = 4:1) to give the desired product.

***Oxazolidine precursor:** in a 100 mL round bottom flask, to a solution of hydroxylamine (5.5 mmol, 1.1 equiv) and 37 wt% formaldehyde solution (5.0 mmol, 1.0 equiv) in 1,2-dichloroethane (15.0 mL) were added aldehyde (1.1 equiv), alkyne (0.8 equiv) and $CuCl_2$ (20% mmol). The reaction mixture was stirred at 80 ºC for 48 h in an oil bath. After completion, the solvent was evaporated under reduced pressure to obtain a residue which was purified by silica gel column chromatography (heptane/ethyl acetate) to afford the solid product.

Compound A6



6-Hydroxyquinoline (1 equiv, 1.5 mmol) and probenecid (1 equiv, 1mmol) were dissolved in DCM (0.1 M). The solution was cooled to 0 °C and EDC (1-ethyl-3-(-3-dimethylaminopropyl) carbodiimide hydrochloride, 1.2 equiv) was added dropwise, then followed by triethylamine (3 equiv) and DMAP (4-dimethylaminopyridine, 0.3 equiv). The reaction was allowed to stir at room temperature overnight. Upon completion, the solvent was removed in vacuo and the product was purified by column chromatography and isolated as a pale yellow solid.

Column Chromatography : Silica, gradient 50-60 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.39 – 8.36 (m, 2H), 8.22 – 8.19 (m, 2H), 7.99 – 7.95 (m, 3H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.39 (m, 2H), 3.16 – 3.11 (m, 4H), 1.64 – 1.52 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.88, 151.41, 151.28, 148.92, 145.26, 136.05, 132.67, 131.06, 129.32, 127.37, 126.67, 122.03, 121.30, 120.70, 50.09, 22.09, 11.30.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{22}H_{24}N2O_4S$: 413.1529, found: 413.1523

m.p.: 213 ºC.

3. Optimization studies

3.1 General procedure for optimization

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with cyclopentyl boronic acid (or cyclohexyl boronic acid pinacol ester/ potassium trifluoroborate), isoquinoline (or lepidine), photocatalyst and Co-catalyst. The solvent was then added, followed by trifluoroacetic acid. The vial was closed with a silicon septum and degassed with argon. The vial was then irradiated with a commercial blue LED strip (14.0 W, 450 nm) for 20-48 h in the aforementioned photoreactor. The progress of the reaction was monitored by TLC and GC/MS. After completion, the solution was diluted with EtOAc and transferred in a separatory funnel containing a saturated $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography (2-8% EtOAc/heptane).

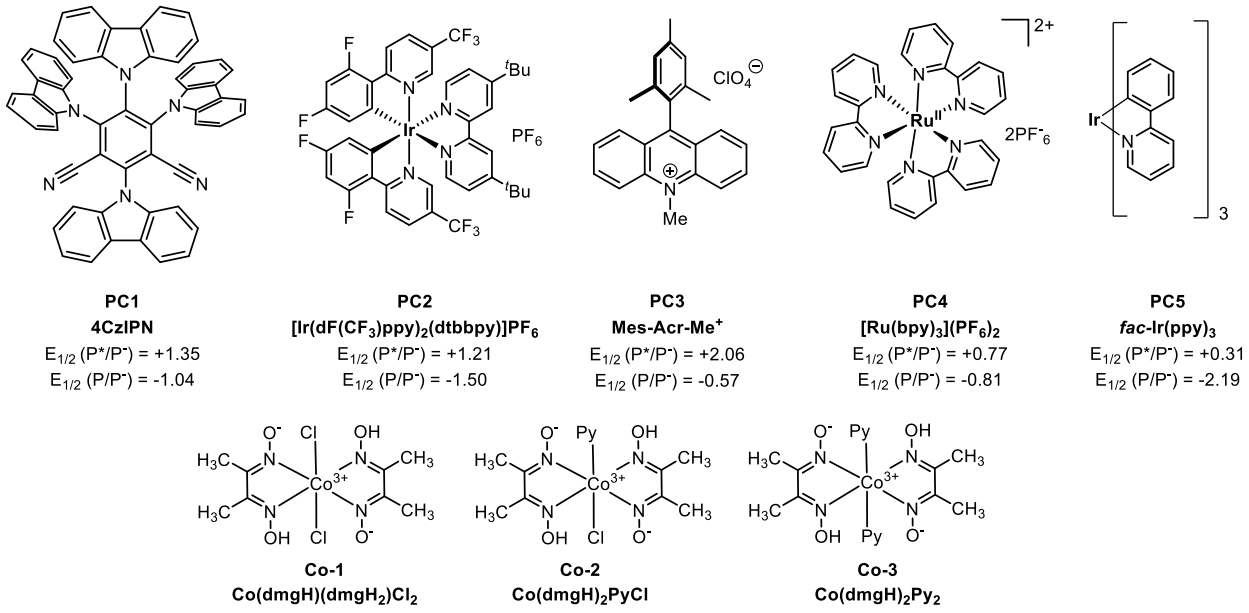
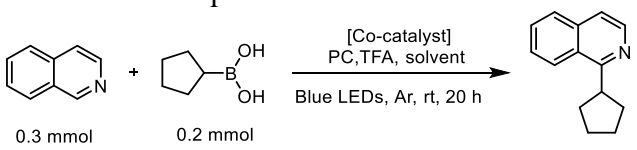


Figure S2: Photocatalysts and cobaloximes employed in the optimization studies.

Table S1. Optimization results with isoquinoline and boronic acid.

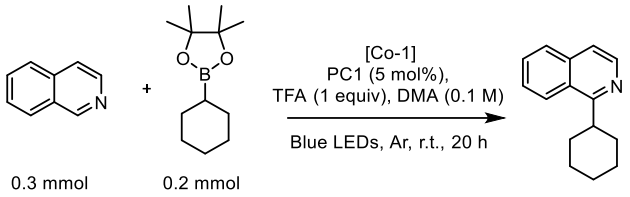


Entry	PC	[Co-1] (mol%)	TFA (equiv)	Solvent	Yield (%)[a]
1[b]	PC1 (5 mol%)	5	0.50	DMA	82%
2	PC1 (5 mol%)	5	-	DMA	40%
3	PC1 (5 mol%)	2	0.50	DMA	82%
4	PC1 (2 mol%)	2	0.50	DMA	65%
5	PC1 (5 mol%)	5	0.50	DMA	80%
6	PC1 (5 mol%)	2	0.20	ACN	59%
7	PC3 (5 mol%)	2	0.20	DMA	Traces
8	PC4 (2 mol%)	2	0.20	ACN	-
9[c]	PC1 (5 mol%)	5	0.20	DMA	72%
10	PC1 (5 mol%)	5	1.0	DMA	94%
11[d]	PC1 (5 mol%)	5	0.20	DMA	70%
12	PC1 (5 mol%)	5	2.0	DMA	97%
13[e]	PC1 (5 mol%)	5	2.0	DMA	82%

14[f]	PC1 (5 mol%)	5	0.20	DMA:ACN (1:1)	33%
15	PC1 (5 mol%)	5	1.0	toluene	29%

[a]Isolated yields. [b]48h reaction time. [c](Co(dmgH)$_2$ClPy. [d]1.5 equiv. of cyclopentyl boronic acid and 1 equiv of isoquinoline. [e][Co(dmgH)$_2$ClPy]. [f](CoBr$_2$+ dppp) and DMA:ACN (1:1).

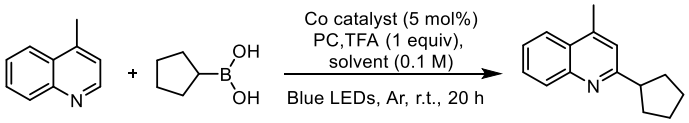
Table S2. Optimization results with isoquinoline and boronic acid pinacol ester.



Entry	Modified condition	Yield (%)[a]
1	Standard conditions	42%
2	No TFA, acetone	n.d
3	No TFA, DMA	n.d
4	1 equiv isoquinoline, 1.2 equiv CyBPin, 1 equiv TFA, acetone	80%
5	2 equiv isoquinoline, 1 equiv CyBPin, 1 equiv TFA, acetone	40%

[a]Isolated yields.

Table S3. Optimization results with quinoline and boronic acid.

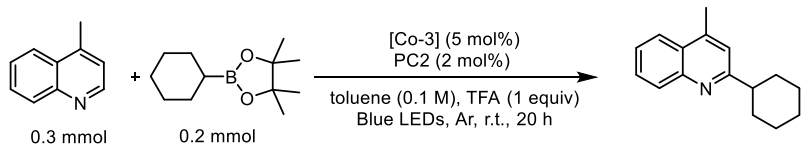


Entry	PC (mol%)	Co-catalyst (5 mol%)	Solvent	Yield(%)[a]
1	PC1 (5 mol%)	Co-1	DMA	27
2	PC1 (5 mol%)	Co-1	ACN	32
3	PC1 (5 mol%)	Co-1	DMA	40
4	PC2 (2 mol%)	Co-2	DMA	31
5	PC2 (2 mol%)	Co-3	DMA	13
6	PC5 (2 mol%)	Co-3	DMA	10
7[b]	PC1 (5 mol%)	Co-3	DMA	25

8[c]	PC1 (5 mol%)	Co-3	DMA	26
9	PC2 (2 mol%)	Co-3	DCE	56
10	PC2 (2 mol%)	Co-3	ACN	32
11	PC2 (2 mol%)	Co-3	DMA/DCE (1:1)	32
12	PC2 (2 mol%)	Co-1	DCE	46
13	PC2 (2 mol%)	Co-3	THF	52
14	PC2 (2 mol%)	Co-3	DCM	37
15	PC2 (2 mol%)	Co-3	1,4-dioxane	15
16	PC2 (2 mol%)	Co-3	Cl-benzene	64
17	PC2 (2 mol%)	Co-3	$CHCl_3$	51
18	PC2 (2 mol%)	Co-3	Toluene	80
19	PC2 (2 mol%)	Co-3	Xylene	48
20	PC2 (2 mol%)	Co-3	isopropylacetate	39

[a]Isolated yield. [b] Co-catalyst = 10 mol%. [c] Temperature = 65 ºC.

Table S4. Optimization results with quinoline and boronic acid pinacol ester.



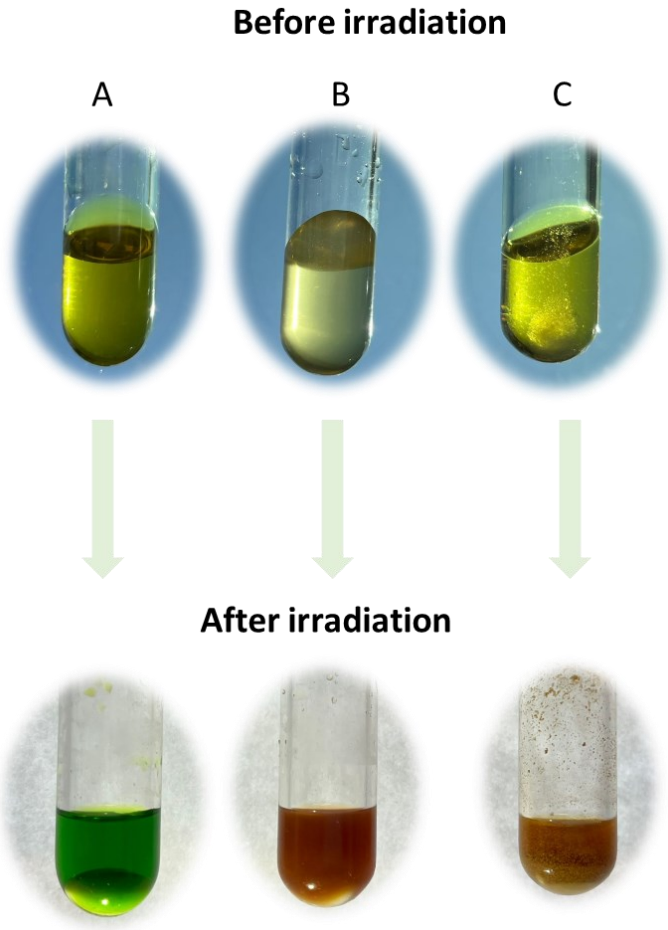
Entry	Modified condition	Yield (%)[a]
1	acetone	46
2	toluene	29
3	toluene, no inert atmosphere	54
4	toluene and quinuclidine 3-ol	71
5	1.2 equiv cyBPin, 1 equiv quinoline	<30

[a]Isolated yields were determined.

3.2 Optimization of the reaction conditions under continuous flow

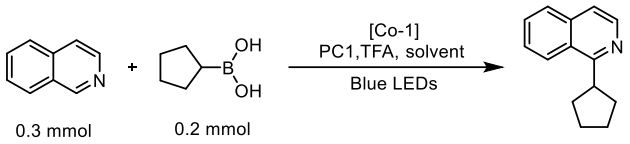
The reaction conditions here devised showed to be particularly suitable for an application under continuous-flow. The reaction mixture appears to be a clear homogenous solution before irradiation and throughout the irradiation time period, avoiding clogging and mixing issues. On

the contrary, upon the addition of inorganic oxidants, as in the case of mixtures B or C, a precipitate can be observed.

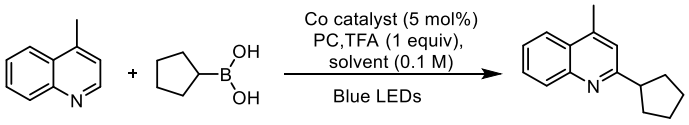


FigureS3: Reaction mixtures before and after irradiation. A) Our devised conditions in DMA. B) Cyclohexyl carboxylic acid in the presence of $(NH_4)_2S_2O_8$ in DMSO. C) Cyclohexyl potassium trifluoroborate in the presence of $K_2S_2O_8$ in ACN/H_2O (1:1).

Table S5. Optimization of the reaction conditions under continuous-flow.



Entry	TFA (mol%)	Solvent	T (°C)	Catalytic system (mol%)	Flow rate (mL/min)	Yield (%)[a]
1	100	DMA	30	PC1 (5), Co-1 (5)	0.2	64
2	-	DMA: ACN 1:4	27	PC1 (5), Co-1 (5)	0.2	19
3	20	DMA: ACN 1:4	27	PC1 (5), Co-1 (5)	0.4	50
4	20	DMA: ACN 1:4	27	PC1 (5), Co-1 (2)	0.2	70
5	20	DMA: ACN 1:1	27	PC1 (5), Co-1 (2)	0.2	74
6	20	NMP: ACN 1:1	27	PC1 (5), Co-1 (2)	0.2	51
7	20	DMA: ACN 1:1	35	PC1 (5), Co-1 (2)	0.2	60
8	20	DMSO: ACN 1:1	27	PC1 (5), Co-1 (2)	0.2	38%
9	200	DMA: ACN 1:1	27	PC1 (5), Co-1 (5)	0.2	74%
10	200	DMA: ACN 1:1	27	PC1 (5), Co-1 (5)	0.15	69%
11	100	DMA: ACN 1:1	25	PC1 (5), Co-1 (5)	0.2	77%
12	**100**	**DMA: ACN 1:1**	**30**	**PC1 (5), Co-1 (5)**	**0.2**	**80%**



Entry	**Catalytic system (mol%)**	**Temperature (°C)**	**Solvent**	**Yield(%)[a]**
1[a]	PC-2 (2), Co-3 (5)	30	Toluene (0.1 M)	-
2	PC-1 (5), Co-1 (5)	30	DMA (0.2 M)	23
3	PC-2 (2), Co-3 (5)	30	DMA/ACN (1:1)	-
4[b]	PC-1 (5), Co-1 (5)	30	DMA, toluene	18
	PC-2 (2), Co-3 (5)	30	DMA, toluene	traces
5[c]	PC-1 (5), Co-1 (5)	30	DMA, toluene	traces
6[d]	PC-2 (2), Co-3 (5)	30	DCE (ACN)	38
7[d]	PC-2 (2), Co-3 (5)	30	Toluene (ACN)	<20%

8	PC-2 (2), Co-3 (5)	30	Toluene, stop flow (2h)	40
9[d]	**PC-2 (2), Co-3 (5)**	**30**	**Toluene (ACN)**	**54%**
10[d]	PC-2 (5), Co-3 (10)	30	Toluene (ACN)	Increased side product formation

[a]Isolated yields were determined. Power = 40 W, Volume of reactor = 10 mL

[b]The solution was prepared in DMA, toluene was pumped through Pump B with a flow rate of 0.2 mL/min.
[c]The solution was prepared in DMA, toluene was pumped through Pump B with a flow rate of 0.4 mL/min.
[d]0.5 mL of ACN were added to solubilize totally the solids.

4. Mechanistic investigations

Control experiments: To explain the mechanism of the alkylation reaction, control experiments were performed. The results of the variation of the optimal reaction conditions are presented in Table S6. In the absence of light, photocatalyst and cobalt co-catalyst (**Entry 2-4**), the product was not detected; in the absence of inert atmosphere (**Entry 5**), the yield did not decrease. Therefore, no inert atmosphere was employed when studying the substrate scope of this reaction. These results confirm the photocatalyzed mechanism of the presented method. Despite not sensitive to water traces in not dry solvents, a mixture of 95:5 DMA/water led to a considerable decrease in product formation, with concomitant PC degradation (Figure S3).

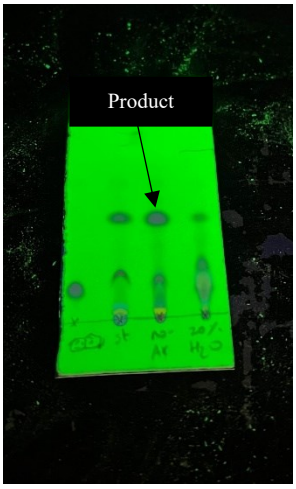
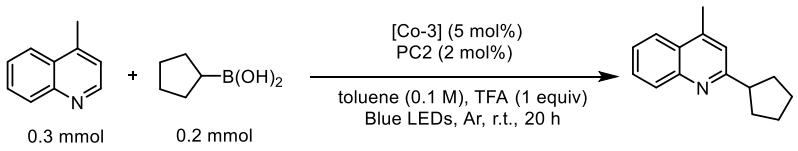


Figure S4: TLC of the control experiments.

Table S6: Control experiments.

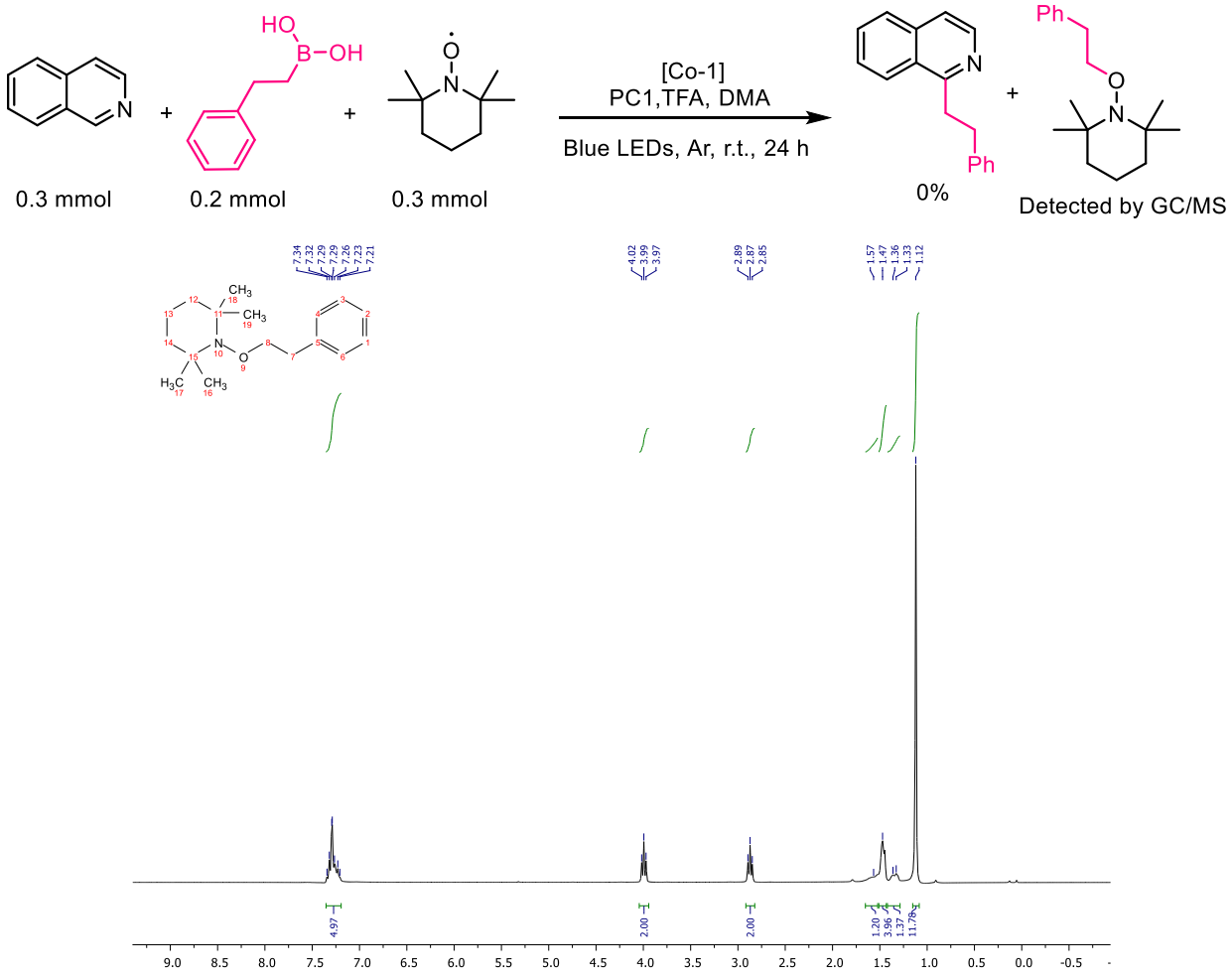


Entry	Deviation from standard conditions	Yield (%)[a]
1	none	80
2	No PC	-

3	No Co	traces
4	No light	-
5	Under air	83
6	Under air, no Co	55
7	Under air, no PC	traces
8	H_2O (20%)	10

[a]Isolated yields.

Radical inhibition experiment: Adding a radical quencher (TEMPO) to the reaction mixture, an adduct between the phenylethyl fragment (from phenylethyl boronic acid) and TEMPO itself was detected by GC-MS and isolated. These results support the radical based mechanism.



Scheme S1: Radical inhibition experiment.

Light-dark experiment: the experiment was performed to determine if a photoredox-catalyzed mechanism or a radical chain mechanism is ongoing. The reaction mixture was prepared according to the general procedure, adding hexamethylbenzene as internal standard. The yield was calculated through GC-MS.

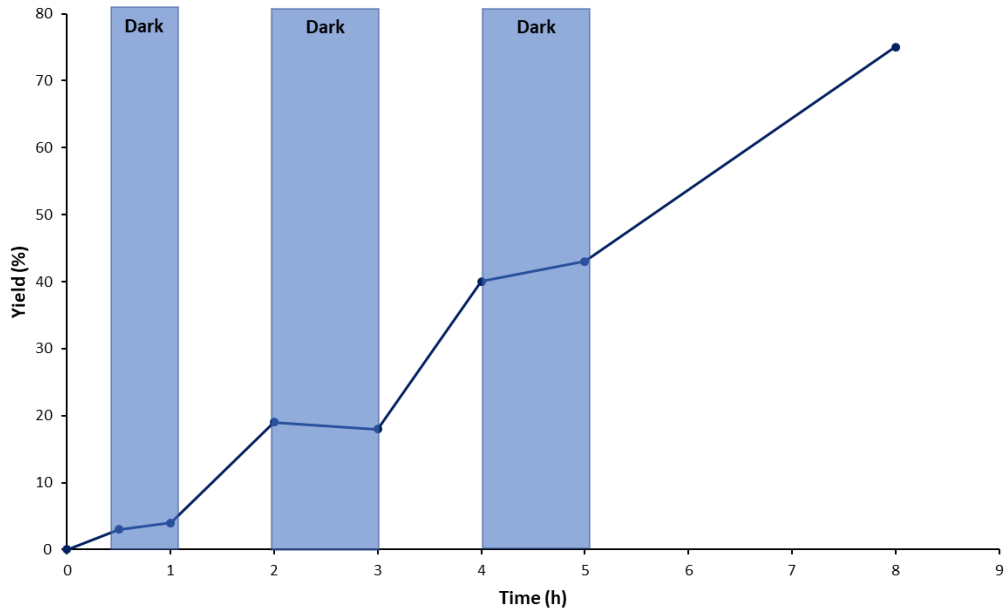


Figure S5: Light-dark experiment.

Quantum yield determination: the quantum yield of the reaction was determined according to a reported procedure.[8,9]

The photon flux of the blue LED system was determined through standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.750 mmol) in 5.0 mL of 0.20 M aqueous sulfuric acid. A 0.15 M buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (541 mg, 3.00 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 M aqueous sulfuric acid.

To a 10 mL borosilicate vial equipped with a stirring bar 0.50 mL of the ferrioxalate solution were added. The vial was sealed and placed 1 cm away from the walls of the irradiation system. After irradiation for 5 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution were added to the vial. The solution was then allowed to rest for 1 hour to allow the resultant

ferrous ions to react completely with 1,10-phenanthroline. 50 μL of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 M aqueous sulfuric acid.

The absorbance of the resulting solution in a cuvette (l = 1.0 cm) at 510 nm was measured by UV-Vis spectrometer. The procedure was repeated at different reaction times and the absorbance of a non-irradiated sample was measured as well.

As visible from Table S7, the photon flux value considered in the calculations was the medium value of the first 3 irradiation times. At higher irradiation times, due to ferrioxalate decomposition, the calculation of the photon flux is altered and not reliable.

Table S7: Photon flux calculation.

Time (s)	A (510 nm)	ΔA	mol Fe^{2+}	Photon flux (Einstein/s)
0	0,0523301			
5	0,1549489	0,102619	$3{,}23573*10^{-8}$	$3{,}28693*10^{-8}$
10	0,2505378	0,198208	$6{,}2498*10^{-8}$	$2{,}1132*10^{-8}$
17	0,3705754	0,318245377	$1{,}00348*10^{-7}$	$1{,}49584*10^{-8}$
30	0,6055324	0,553202357	$1{,}74433*10^{-7}$	$1{,}05699*10^{-8}$
45	0,7311608	0,678830709	$2{,}14046*10^{-7}$	$7{,}90601*10^{-9}$

To calculate the amount of Fe^{2+}, the following equation was used:

$$mol\ Fe^{2+} = \frac{V \text{ x } \Delta A}{l \text{ x } \varepsilon}$$

Where V is the total volume (0.0035 mL), ΔA is the difference in the absorbance at 510 nm between the irradiated and non-irradiated sample, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/mol x cm).

The photon flux was calculated as follows:

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \text{ x } t \text{ x } f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 M solution at λ = 457.9 nm), t is the irradiation time, and f is the fraction of light absorbed at 436 nm (0.996).

The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (2.5) of the 0.15 M solution of potassium ferrioxalate at 450 nm.

The photon flux is $7{,}42592*10^{-9}$ Einstein/s.

Quantum yield determination: An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with cyclopentyl boronic acid (1 equiv, 0.2 mmol), isoquinoline (1.5 equiv), 4CzIPN (5 mol%), $Co(dmgH)(dmgH_2)Cl_2$ (5 mol%) and an internal standard (hexamethylbenzene, 0.2 mmol). Then the solvent was added, followed by TFA (1 equiv). The vial was closed with a silicon septum and degassed with argon. The vial was then irradiated with blue LEDs (14.0 W, 450 nm) for 2 h in the aforementioned photoreactor. The vial was placed 1 cm far from the reactor wall. The reaction was cooled at 35 °C through compressed air. After 2 h, a 5 μL sample was taken, filtered an the conversion was evaluated through GC/MS. The calculated yield was 17%.

The quantum yield was calculated through the formula:

$$\Phi = \frac{mol\ product}{flux \text{ x } t \text{ x } f}$$

Where flux is the photon flux determined by ferrioxalate actinometry ($2.11 \text{ x } 10^{-8}$ Einstein/s), *t* is the time (7200 s), and *f* is the fraction of light absorbed by 4CzIPN at 450 nm.

A 1×10^{-3} M solution of 4CzIPN in DMA was prepared, and the absorbance of the solution at 450 nm was 0.9893. The fraction of light absorbed at 450 nm was calculated:

$f = 1.0000 - 10^{-A} = 1.0000 - 10^{-2.77} = 0.998$

The calculated quantum yield for the reaction therefore is: **0.64**

Fluorescence quenching experiment: The experiment was performed on a fluorescence spectrophotometer (FLS 920, Edinburgh Instruments, Photonic division). In a typical experiment, to a 0.1 mM solution of 4CzIPN (or $\{Ir[dF(CF_3)ppy]_2(dtbpy))PF_6\}$) in ACN, an appropriate amount of quencher (isoquinoline or lepidine respectively) was added in a 1.0 cm quartz cuvette. The solutions were irradiated at 400 nm and emission was measured at 540 nm. The relative intensity I0/I was calculated as a function of quencher concentration, where I0 is the luminescence intensity in the absence of quencher, while I is the intensity in the presence of the quencher. Before each measurement, the solutions were degassed and kept under nitrogen atmosphere.

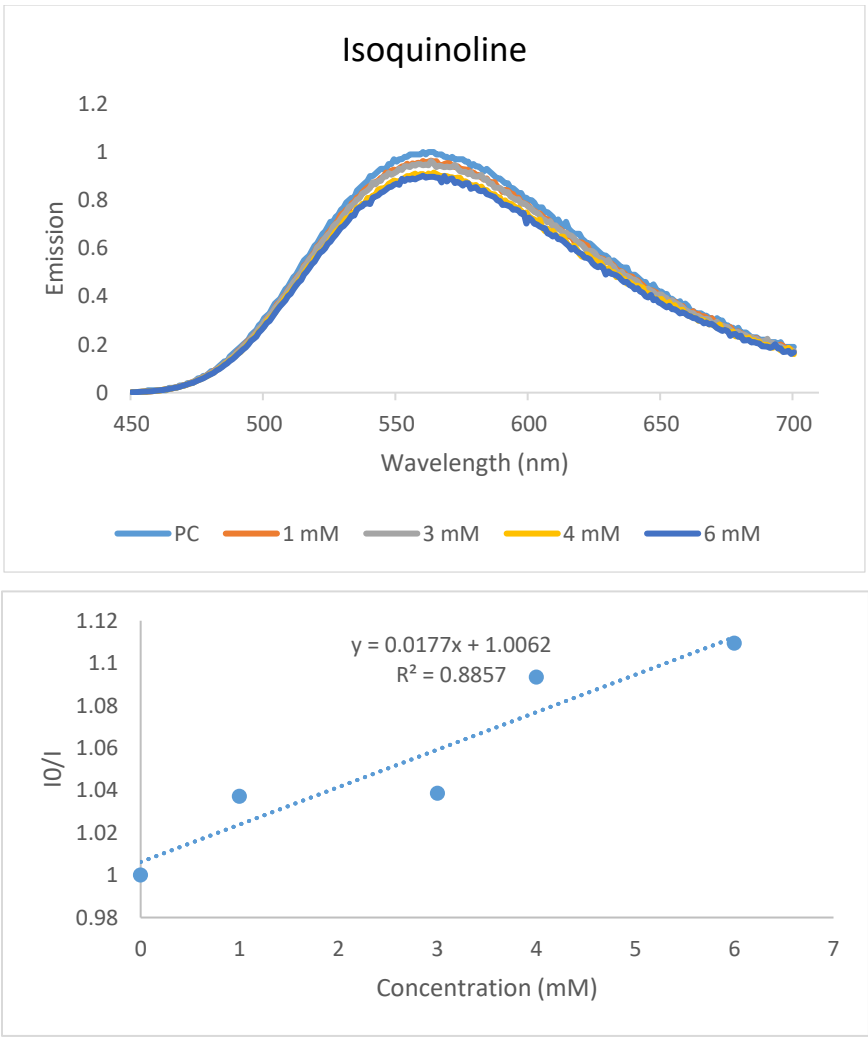
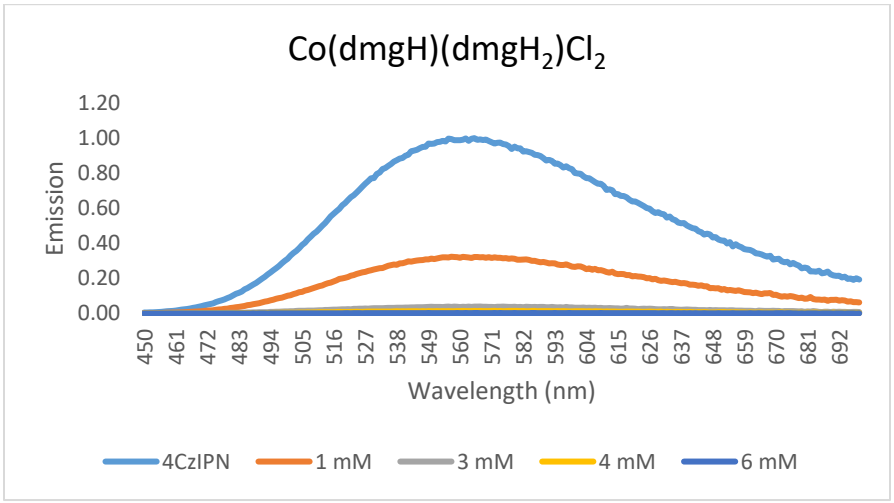


Figure S6: Fluorescence quenching and Stern-Volmer equation of 4CzIPN in the presence of isoquinoline.



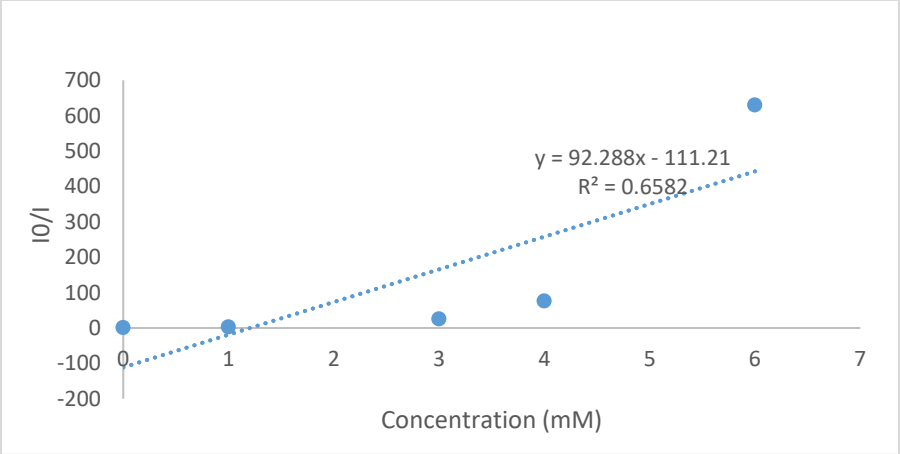


Figure S7: Fluorescence quenching and Stern-Volmer equation of 4CzIPN in the presence of $Co(dmgH)(dmgH_2)Cl_2$.

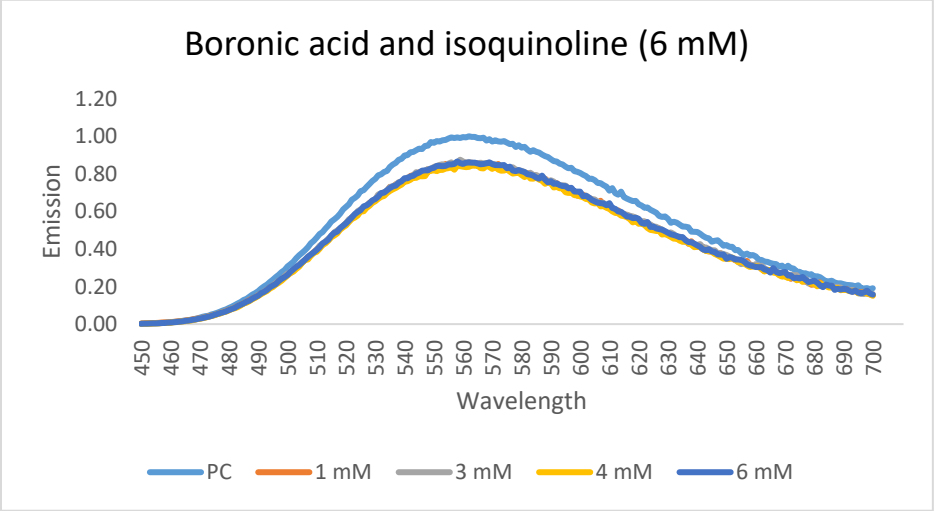


Figure S8: Fluorescence quenching of a mixture of cyclopentyl boronic acid and isoquinoline (6 mM).

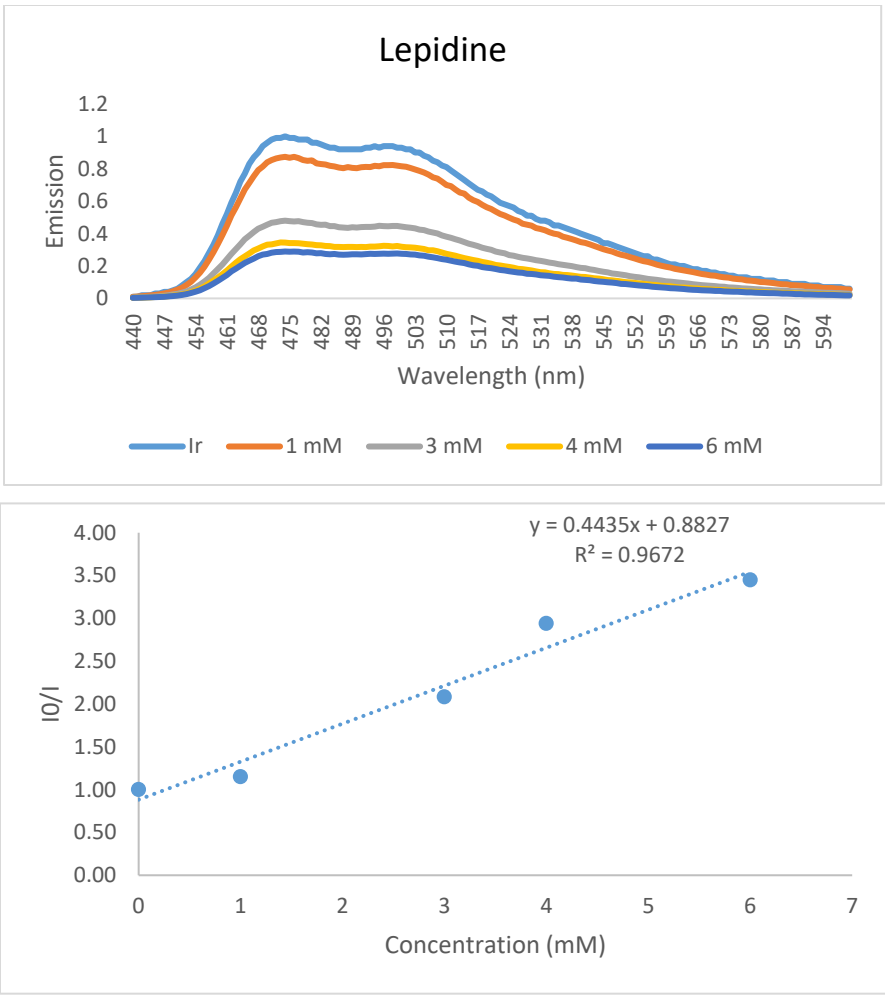


Figure S9: Fluorescence quenching and Stern-Volmer equation of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ in the presence of lepidine.

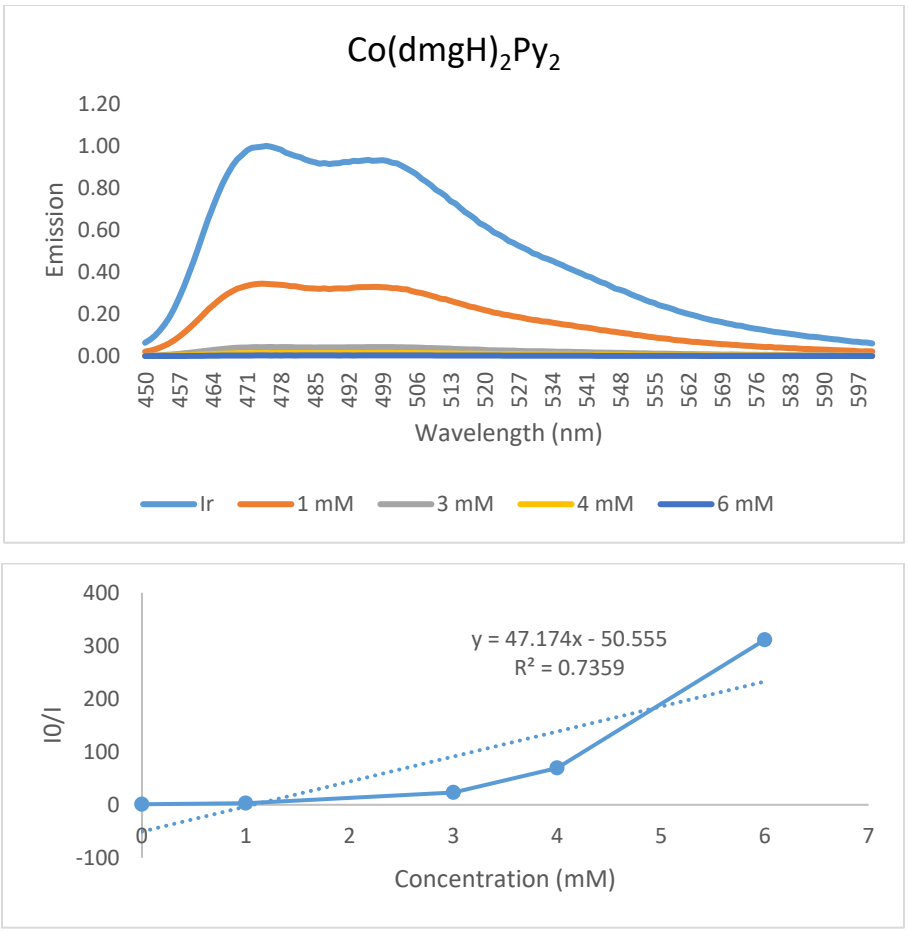


Figure S10: Fluorescence quenching and Stern-Volmer equation of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ in the presence of $Co(dmgH)_2Py_2$.

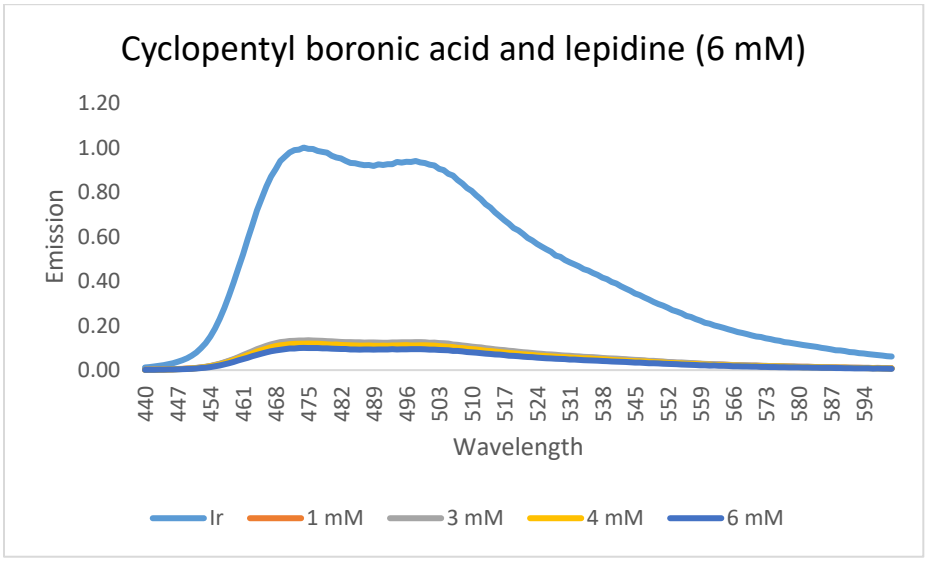


Figure S11: Fluorescence quenching of a mixture of cyclopentyl boronic acid and lepidine (6mM).

As a result of an energy transfer mechanism between isoquinoline/lepidine and the corresponding PC,[10] quenching can be observed for both the species. This result did not allow us to conclude the involvement of the basic heterocycles in the activation of boronic acids, as the quenching observed cannot be related to the complex between boron species and *N*-based heterocycles or to the heterocycle itself.

To gain further evidence, we performed different mechanistic studies.

Cyclic voltammetry measurements: The experiments were conducted using a cyclic potentiometer (Metrohm PGSTAT20 potentiostat/ galvanostat) with a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode. In the standard procedure, 0.02 mmol of substrate were dissolved in 10 mL of a 0.1 M $[N(Bu)_4]PF_6$ electrolyte solution in degassed MeCN. The reactor was sealed with a rubber septum and purged with nitrogen. Each measurement was conducted at 100 mV/s at room temperature under nitrogen atmosphere without stirring.[11]

Note: before each measurement, the solutions containing a mixture of BA and isoquinoline were stirred for 1h.

As evident from the graphs here reported, cyclohexyl boronic acid and isoquinoline have redox potentials that lie outside the redox window of 4CzIPN ($E_{1/2}$ (P^*/P^-) = +1.35, $E_{1/2}$ (P/P^-) = -1.04 *vs* SCE).

The solutions containing cyclohexyl boronic acid and isoquinoline all show a new local maximum at 1.01 V, as a result of the interaction between the two species.

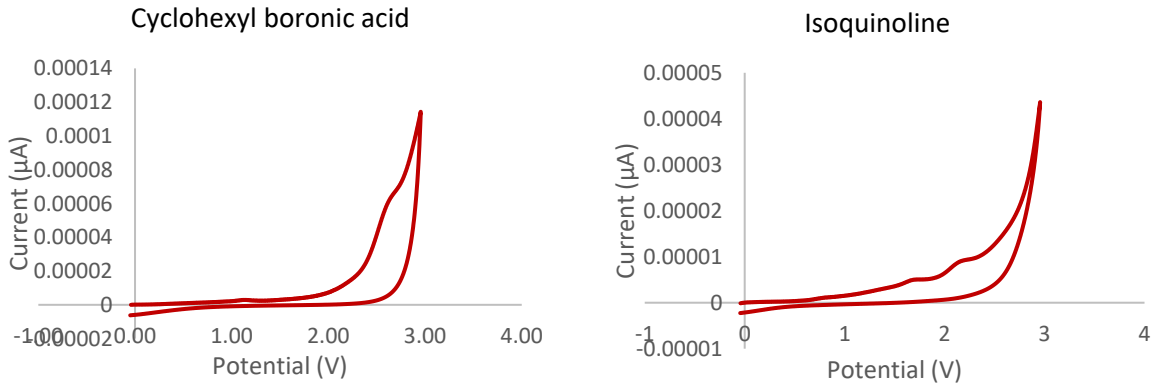


Figure S12: Cyclic voltammograms of boronic acid, isoquinoline and mixture of isoquinoline and boronic acid.

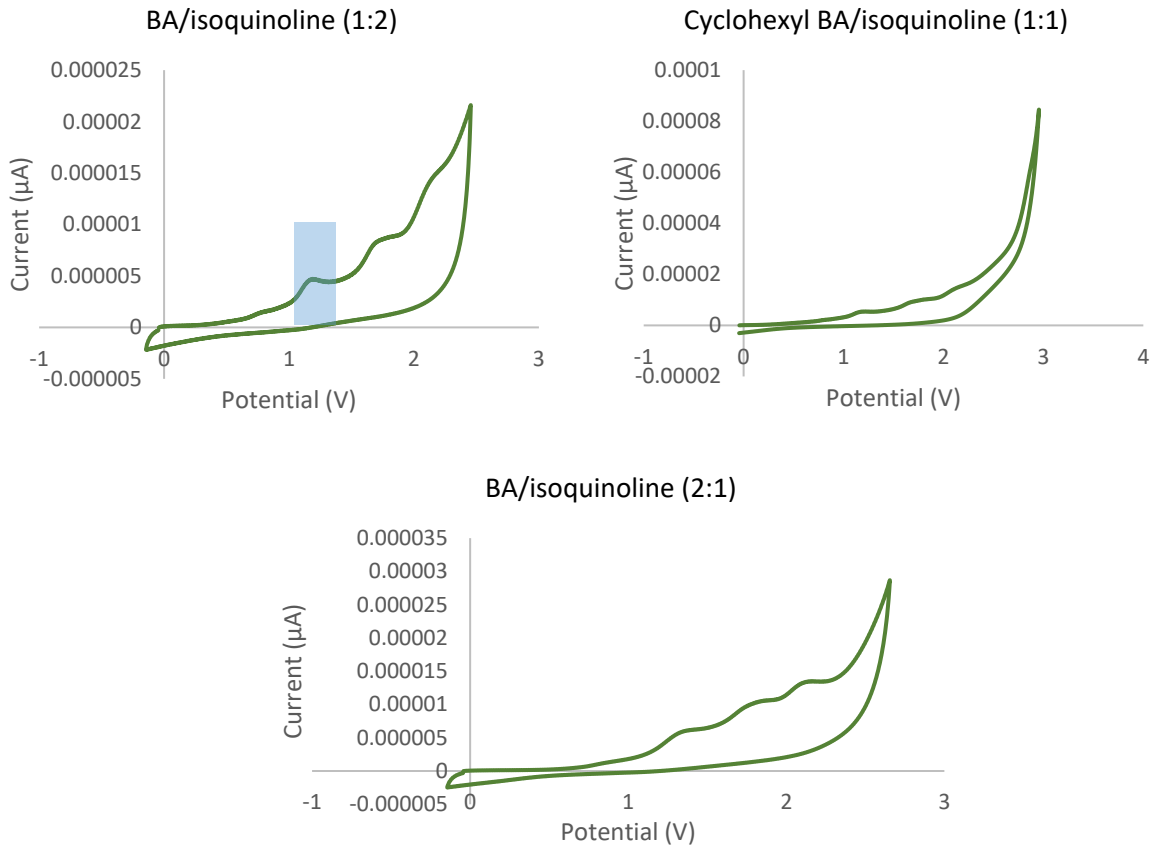


Figure S13: Cyclic voltammogram of boronic acid and isoquinoline mixtures.

To correctly define the oxidation potential of the new arising oxidizable species, in our case the Nernst equation could not be employed, since an irreversible cyclic voltammogram was obtained. This result can be accounted for the reactivity of the oxidized species, which undergoes degradation. To estimate the value of $E^0_{1/2}$, the half peak potential Ep/2 (which corresponds to the potential at half the maximum of the local maximum current in the cyclic voltammogram) was calculated with the following equation:[12]

$$f\left(\frac{Ep}{2}\right) = \frac{Cmax}{2}$$

For the mixture of boronic acid and isoquinoline, the half peak potential value was found to be 1.01 V *vs* SCE. This species can therefore quench the excited state of 4CzIPN, as the value found

lies in the redox window of the PC. The result obtained proves that isoquinoline can activate boronic acids towards oxidation.

Kinetic experiment: in order to evaluate the catalytic cycle responsible for the observed reactivity, the reaction rate in the presence of increasing concentrations of the Co-catalyst were performed.

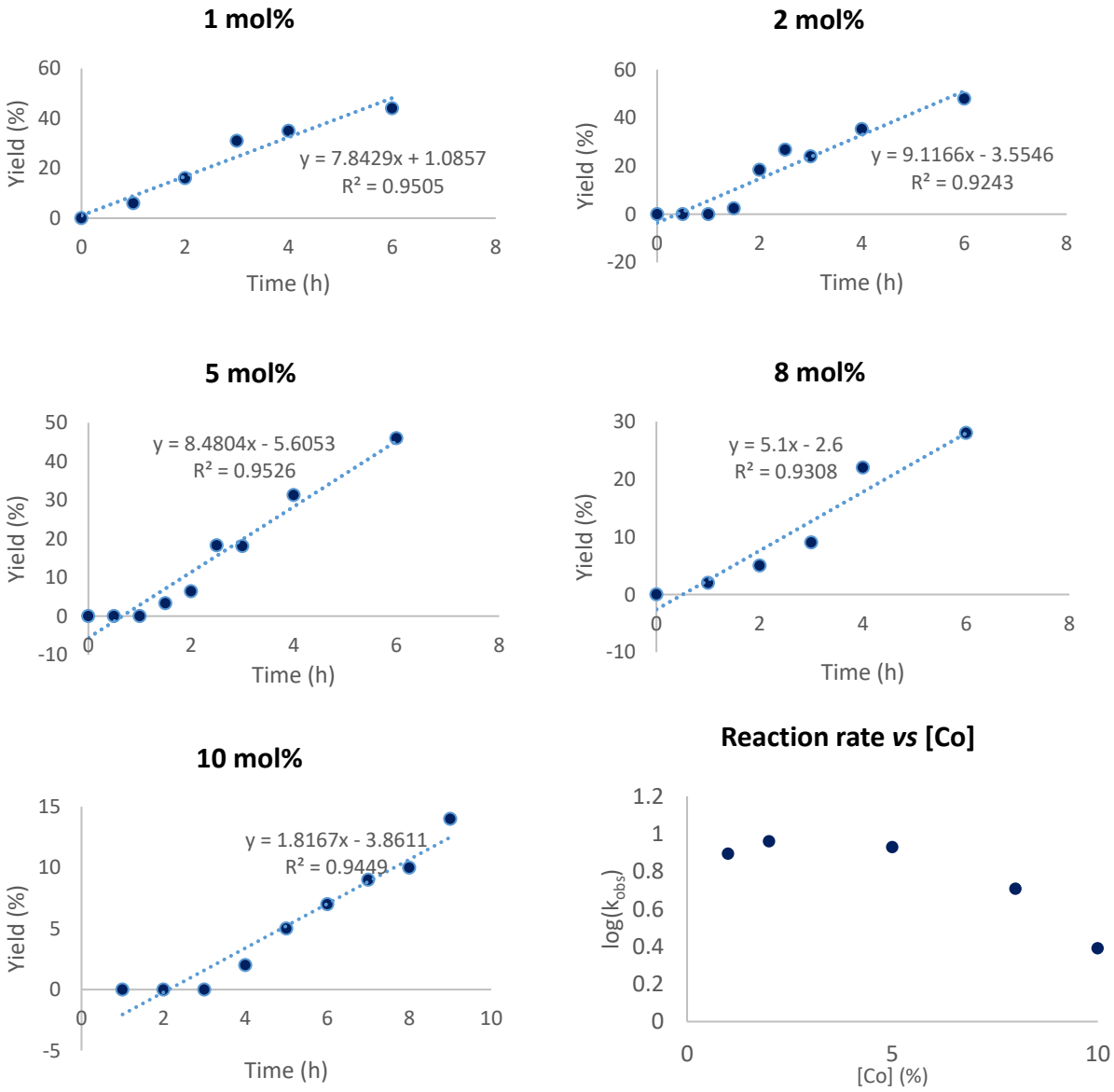


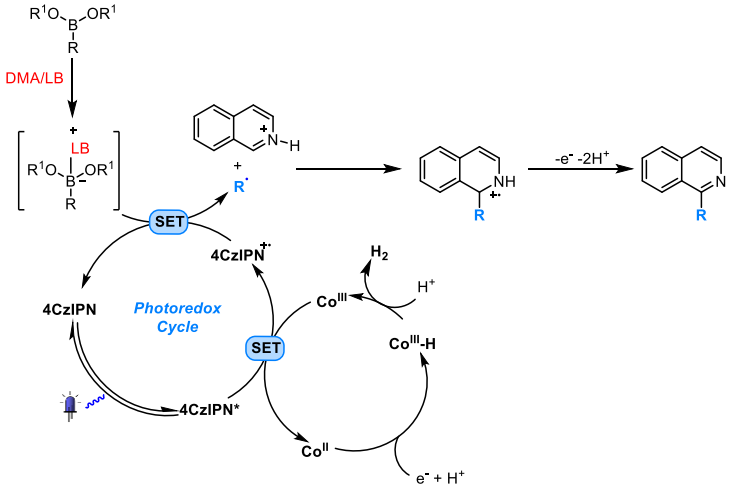
Figure S14: Kinetic profiles.

The reactions were prepared according to the general procedure: an oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with cyclopentyl boronic acid (1 equiv), isoquinoline (1.5 equiv), 4CzIPN (5 mol%), Co-catalyst and the internal standard of choice (hexamethyl benzene, 1 equiv). Then DMA was added, followed by TFA (1 equiv). The vial was closed with a silicon septum, and degassed with argon. The vial was then irradiated with a commercial blue LED strip (14.0 W, 450 nm), and samples were taken overtime and analysed by GC-MS.

The graphs above show how, at higher concentration of the Co-catalyst, product formation was substantially slowed down. After the same time frame, a considerable difference in the product amount (calculated from GC-MS, using hexamethylbenzene as internal standard) was observed between lower and higher concentrations of Co-catalyst. This suggests that the Co-catalyst can engage in detrimental secondary interaction with the PC, inhibiting radical formation.[13]

Proposed mechanism: the results obtained through the mechanistic investigations performed and previous reports[8,14] lead us to propose a reductive quenching cycle, where the first step is the oxidation of the boronic acid-DMA/heterocyclic complex, as shown in the manuscript.

Nevertheless, given the high quenching rate observed in the case of cobaloximes and aware of literature precedents[15,16], an oxidative quenching cycle cannot be completely ruled out. For the sake of clarity, this alternative cycle is here presented as well.



Scheme S2: Alternative mechanism for the presented transformation.

5. General procedure for the photoredox-cobalt catalyzed Minisci reaction

GP1: An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with boronic acid (1 equiv, 0.4 mmol) heterocyclic molecule (1.5 equiv), 4CzIPN (5 mol%) and $Co(dmgH)(dmgH_2)Cl_2$ (5 mol%). Then DMA was added (0.1 M, 4 mL), followed by TFA (1 equiv). The vial was closed with a silicon septum and irradiated with a commercial blue LED strip (14.0 W, 450 nm) for 20 h in the aforementioned photoreactor. After completion, the solution was diluted with EtOAc and transferred in a separatory funnel containing a saturated $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography.

Note: in the case of boronic acid pinacol esters, 1 equiv of heterocycle and 1.2 equiv of boronic acid pinacol ester were added. Acetone was employed as solvent.

In the case of trifluoroborates, 1 equiv of heterocycle and 1 equiv of trifluoroborate were added.

GP2: An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with boronic acid (1 equiv, 0.4 mmol) heterocyclic molecule (1.5 equiv), $\{Ir[dF(CF_3)ppy]_2(dtbpy))PF_6\}$ (2 mol%) and $Co(dmgH)_2Py_2$ (5 mol%). Then toluene was added (0.1 M, 4 mL), followed by TFA (1 equiv). The vial was closed with a silicon septum and irradiated with a commercial blue LED strip (14.0 W, 450 nm) for 20 h in the aforementioned photoreactor. After completion, the solvent was removed in vacuo. The residue was diluted with EtOAc and transferred in a separatory funnel containing a saturated $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography.

5.1 General procedure for continuous-flow experiments

An oven-dried 10 mL glass vial bar was charged with boronic acid (1 equiv, 0.4 mmol) heterocyclic molecule (1.5 equiv), 4CzIPN (5 mol%) and $Co(dmgH)(dmgH_2)Cl_2$ (5 mol%). Then DMA and ACN (1:1) were added (0.1 M, 4 mL), followed by TFA (1 equiv). The

resulting clear yellow solution was then pumped through a *10 mL volume reactor* at 0.2 mL/min (or 0.1 mL/min) flow rate, keeping the temperature set at 30 °C. Once the solution had been fully taken up by the pump, the input was changed to ACN solvent to push the reaction mixture through the reactor. The crude reaction mixture was collected in a round bottom flask. The solvent was evaporated and the residue diluted with EtOAc and transferred in a separatory funnel containing a saturated $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography.

6. DFT calculation

6.1 Computational details

Gaussview[17] were used to create initial structures of reactants, TS and products. Density Functional Theory (DFT) calculations were performed using Gaussian 09 program suit.[18] All geometry optimizations and frequency calculations were conducted using the unrestricted B3LYP hybrid functional[19,20] in combination with the def2-TZVP basis set[21] at 298.15 K and Grimme's D3 version (zero damping) for empirical dispersion correction[22]. Solvation effects were considered using the SMD implicit solvation model (toluene or dimethylacetamide).[23] Frequency calculations were performed on the optimized structures to verify that the geometries were true minima and to calculate thermodynamic data. An ultrafine grid was employed in all the calculations to minimize the integration grid errors[24,25]. Local minima were confirmed by the absence of imaginary frequencies. Transition states were confirmed by the presence of only one imaginary frequency. The correspondence of imaginary frequencies with the formation of the desired bond was checked by visual inspection. Intrinsic Reaction Coordinates (IRC) were determined all the transition states[26] All energies are reported in kcal/mol. Activation and reaction energies were computed taking the separated (non-interacting) reactants as reference. The contribution of the low frequency vibration modes to the partition functions were recalculated under the Quasic-Harmonic Approximation using the open-source Python toolkit GoodVibes, with a frequency cut-off value of 100.0 cm^{-1}.[27] The effect of the experimental concentration of 0.1

mol·L^{-1} on the thermodynamic properties was taken into account using GoodVibes. Equilibrium constants were calculated according to:

$$K_e^{\circ} = exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right)$$

Transition states were analyzed using the distortion/interaction model[28,29] also known as the activation strain model.[30,31] For each reaction, the transition structure was separated into two fragments, each containing a different reactant, followed by separate single-point energy calculations. The distortion energy (ΔE_{strain}) was calculated the difference between the electronic energies of the distorted fragments in the transition state and the electronic energies of the optimized ground-state geometries. The interaction energy (ΔE_{int}) was regarded as the difference between the activation energy ($\Delta E^{\ddagger}$) and the total distortion energy ($\Delta E_{strain}^{total}$), i.e. the sum of the distortion energies of the two reactants:

$$\Delta E^{\ddagger} = \Delta E_{strain}^{total}(r^{TS}) + \Delta E_{int}(r^{TS}) \qquad \Delta E_{strain}(r^{TS}) = E(r^{TS}) - E(r^{0})$$

Electronic wavefunction analysis used for conceptual-DFT was performed using Multiwfn program version 3.8.[32] For the prediction of the reactive sites we employed the Fukui function for a radical attack $f^0(r)$ [33] and the dual descriptor $\Delta f(r)$ [34], defined as:

$$f^0(r) = \frac{\rho(r)^{N+1} - \rho(r)^{N-1}}{2} \qquad \Delta f(r) = \rho(r)^{N+1} - 2 \cdot \rho(r)^{N} + \rho(r)^{N-1}$$

Where ρ(r) stands for the electron density of a given chemical species (with N electrons) and its ionized forms (with N+1 or N-1 electrons). Sites with large values of $f^0(r)$ and large and positive values of $\Delta f(r)$ were regard as the most reactive toward the attack of nucleophilic radicals.

The solution phase half-cell redox potentials (in standard conditions, i.e., c = 1 mol·L^{-1}) were calculated according to

$$\Delta E^{\circ}{}_{calc}^{SCE} = -\frac{\Delta_r G^{\circ}{}_{calc}^{298\,K}}{n_e F} - E^{\circ}{}_{calc}^{absolute}(SHE)$$

Where n_e is the number of electron transferred (one electron in all the calculations) and F is the Faraday constant (23.061 kcal·mol^{-1}·V^{-1}). The Gibbs free energy of reduction ($\Delta_r G_{calc}^{298\,K}$) for half-cell reactions were computed by the so-called direct approach, in which the solution phase reaction energy is computed as the difference between the Gibbs free energy of the product (reduced form) and the reactant (oxidized), each obtained from an optimization-frequency calculation in a continuum solvation model.[35,36] Solution-phase energies were referenced to the standard hydrogen electrode $E^{\circ}{}_{calc}^{absolute}(SHE)$ by subtraction of 5.67 V, which is the computational

estimated absolute potential in toluene.[37] Relevant Data from the original Gaussian 9 output files was organized in the supporting information using ESIgen tool.[38]

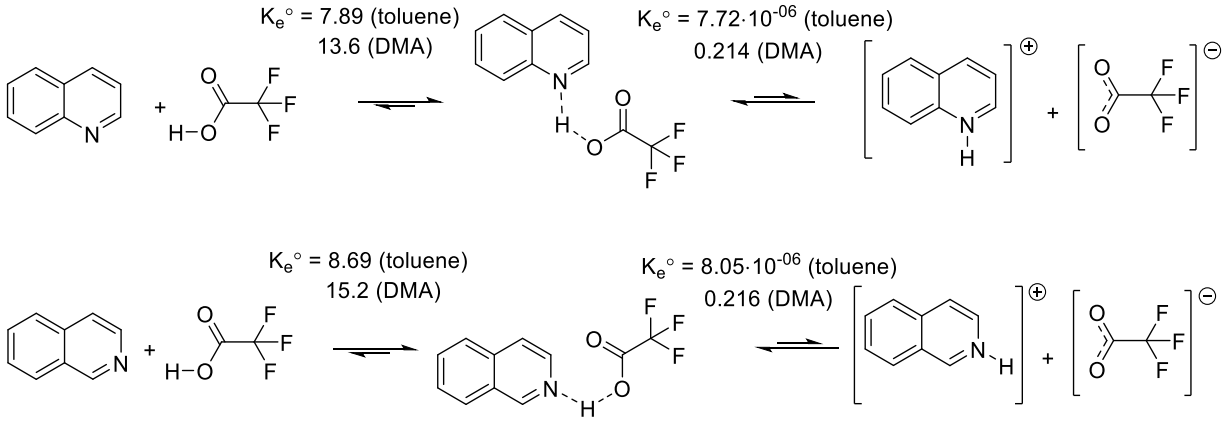
Non-covalent interactions analysis was performed using NCIplot with the default parameters[39] and starting from the optimized geometries. NCI detects covalent and non-covalent interactions in real space according to the reduced density gradient (s):

$$s = \frac{1}{2\,(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}}$$

Optimized structures were represented using CYLview software version 1.0.[40] Fukui functions and NCI were represented with using VMD 1.9.3.[41]

6.2 Acid-base equilibrium in solution

The nitrogen containing heterocycles are slightly basic and react with trifluoroacetic acid to establish an equilibrium between the free (non-interacting) molecules, hydrogen-bond aggregates (which can be regarded as ion pairs) and the free (solvated) ions. Thermodynamic equilibrium constants were calculated from energy values obtain from DFT calculations at the theoretical level UB3LYP-D3/def2-TZVP/SMD (toluene or dimethylacetamide). The values found for both systems differ only very little, reflecting the similar acid-base properties of the heterocycles.



Scheme S3: The acid-base equilibrium between trifluoracetic acid and the heterocycles.

Neglecting the effect of ionic activity, one can assume that the equilibrium constant is a function of the concentration ratio ($K_c \approx K_e°$). Likewise, disregarding the occurrence of collateral equilibriums, the concentration of each species in solution (before the reaction starts) can be estimated according to:

$c_{total}(B) = [B] + [HA \cdot B] + [HB^+] =$
$0.150\ molL^{-1}$ (1) Mass balance for the base

$c_{total}(HA) = [HA] + [HA \cdot B] + [A^-] =$
$0.100\ molL^{-1}$ (2) Mass balance for the acid

$[A^-] = [HB^+]$ (3) Charge balance

$K_1 = \frac{[HA \cdot B]}{[HA][B]}$ $K_2 = \frac{[A^-][HB^+]}{[HA \cdot B]}$ Equilibrium constants

Where HA represents the trifluoracetic acid and B the nitrogen base, $c_{total}(X)$ represents total concentration of the electrolyte X, [X] is the equilibrium concentration of the chemical species X, K_1 is the equilibrium constant in function of the concentrations for the formation of the hydrogen-bonded aggregate and K_2 is the equilibrium constant in function of the concentrations for the dissociation in iones. It turns out that, from equations 1-3:

$c_{total}(B) - c_{total}(HA) = [B] - [HA]$ (4)

Making $[A^-] = [HB^+] = x$, from the first and second equations:

$$[B] = \frac{x^2}{K_1 K_2 \left(c_{total}(B) - x - \frac{x^2}{K_2}\right)} \quad (5)$$

$$[HA] = \frac{x^2}{K_1 K_2 \left(c_{total}(HA) - x - \frac{x^2}{K_2}\right)} \quad (6)$$

Substituting equations 5 and 6 in equation 4 and after some algebraic work:

$$\left(c_{total}(HA) - x - \frac{x^2}{K_2}\right)\left(c_{total}(B) - x - \frac{x^2}{K_2}\right) = \frac{x^2}{K_1 K_2} \quad (7)$$

After finding the numerical solutions of equations (7) and rejecting those without physical sense, the following results are obtained.

Table S8: Calculated concentrations of free, hydrogen-bonded and protonated heterocylces.

Heterocycle	Solvent	Free base [B] ($mol \cdot L^{-1}$)	Hydrogen bonded species [HA·B] ($mol \cdot L^{-1}$)	Protonated base [HB^+] ($mol \cdot L^{-1}$)	Free acid [HA] ($mol \cdot L^{-1}$)	Deprotonated acid [A^-] ($mol \cdot L^{-1}$)
quinoline	toluene	0.105 (69.6%)	0.0449 (30.0%)	0.000589 (0.4%)	0.0545	0.000589
	DMA	0.0694 (46.3%)	0.0182 (12.1%)	0.0624 (41.6%)	0.0178	0.0624
isoquinoline	toluene	0.102 (68.4%)	0.0468 (31.2%)	0.000614 (0.4%)	0.0526	0.000614
	DMA	0.0680 (45.3%)	0.0186 (12.4%)	0.0634 (42.3%)	0.0180	0.0634

As showed in the table above, quinoline exists mostly in its free form and hydrogen-bonded to trifluoroacetic acid in toluene, while isoquinoline exists mostly in in its free form and protonated in dimethylacetamide.

6.3 Conceptual Density Functional Theory (c-DFT)

The Fukui function for a radical attack f^0 and the dual descriptor Δf were calculated for the nitrogen containing heterocycles in their free form, protonated, hydrogen-bonded to trifluoroacetic acid and forming a Lewis adduct with $[B(OH)_2]^+$ and $[BPin]^+$. Interaction of (iso)quinoline with acid diminishes the reactivity of the benzene fused ring and increases the reactivity on the pyridino ring. Positions highlighted with arrows (C1 of isoquinoline and C2 and C4 of quinoline) become more prone to undergo a nucleophilic attack after the interaction of the basic heterocycles with acid.

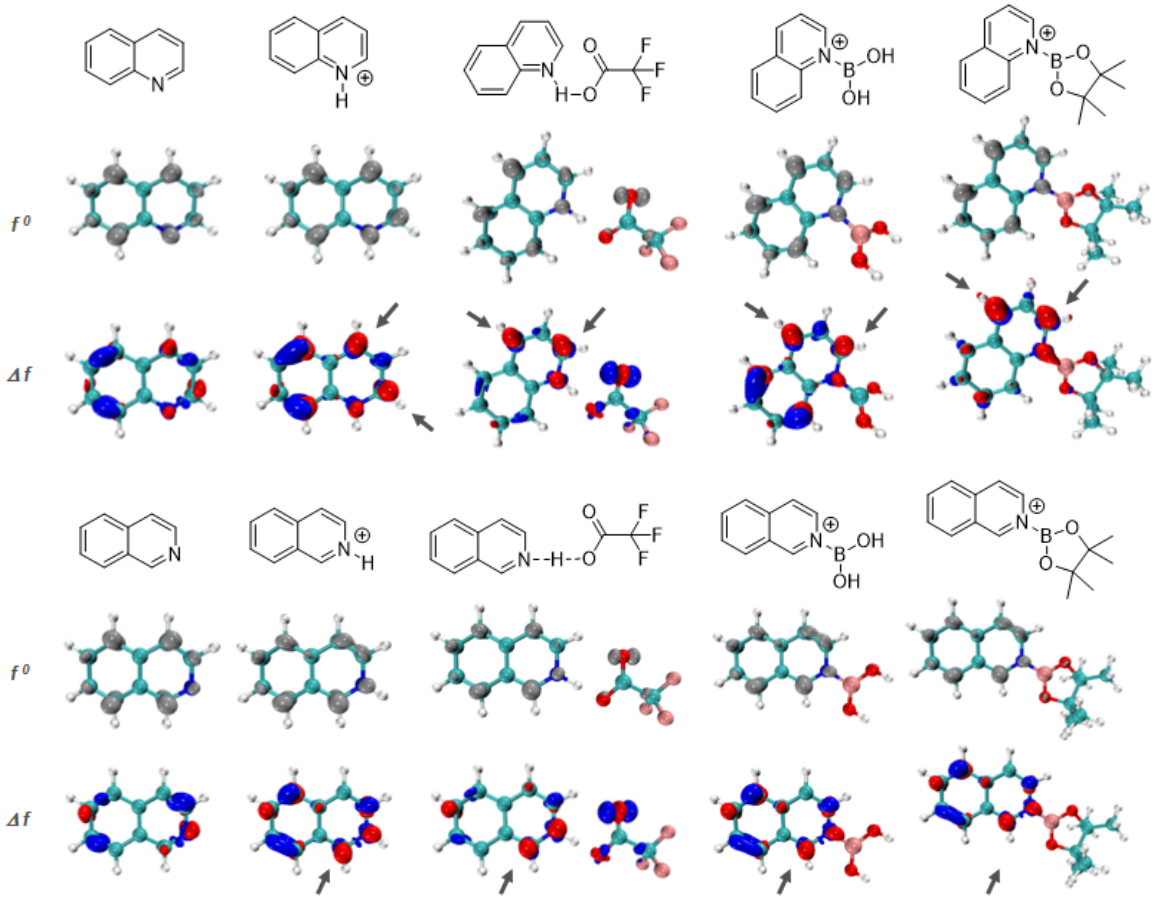
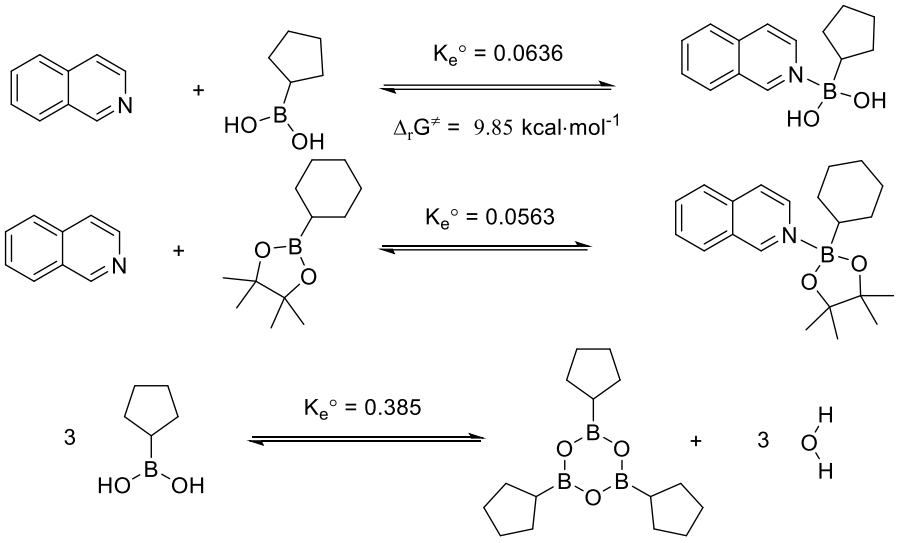


Figure S15: Fukui function for the radical attack and Dual descriptor for the reactant species in solution. The reactivity towards the addition of nucleophiles and radical is more localized on the C1 and C4 atoms of isoquinoline and C2 and C4 atoms of quinoline. This localization is higher for the protonated, complexed and hydrogen-bonded forms.

6.4 Formation of adducts between boronic acid derivatives and isoquinoline

The Gibbs free energies changes of reaction for the formation of Lewis acid-base adducts between isoquinoline and cyclohexyl BPin ester / cyclopentyl boronic acid / cyclopentyl boroxine were examined at the theoretical level UB3LYP-D3/def2-TZVP/SMD(toluene). The transition states for the formation of adduct between isoquinoline and cyclopentyl boronic acid was found using the same calculation method.

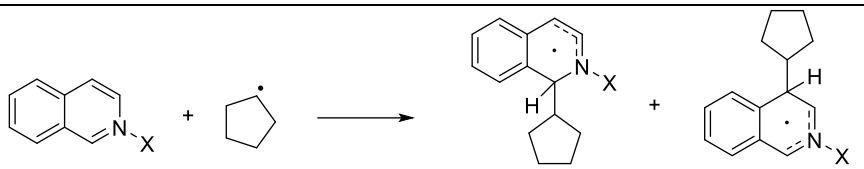


Scheme S4: Boronic acid (derivatives) can form Lewis adduct with isoquinoline or dehydrate to boroxine.

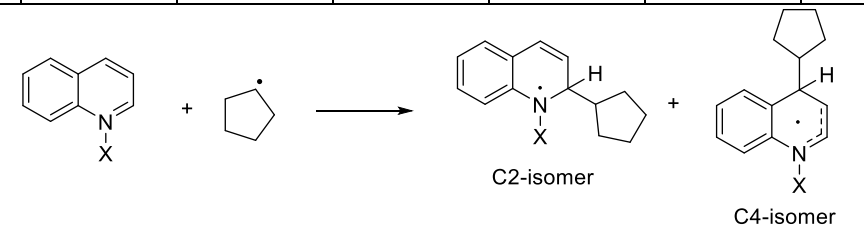
6.5 Study of the regioselectivity for the addition of cyclopentyl radical to (iso)quinoline

The Gibbs free energies change and of activations for the addition of cyclopentyl radical to (iso)quinoline (free, hydrogen-bonded, protonated and complexed to $[B(OH)_2]^+$) where calculated at the theoretical level UB3LYP-D3/def2-TZVP/SMD(toluene). When the heterocycles interact with acid species in the reaction media become more reactive, i.e., the activation Gibbs energies of the reaction diminishes. The activation energy was further decomposed in strain and interaction contributions. The preference for the radical attack to occur at C1 of isoquinoline and C2 of quinoline when hydrogen-bonded to trifluoroacetic acid is due mainly due to an increase in the interaction energy.

Table S9: Energetics of the reaction. Activation and reaction Gibbs energy variations. Decomposition of activation energies in interaction and strain energies.



Acid X	Reaction center	Δ_rG (kcalmol^{-1})	$\Delta_rG^{‡}$ (kcalmol^{-1})	$\Delta E^{‡}$ (kcalmol^{-1})	E_{int} (kcalmol^{-1})	E_{strain}^{total} (kcalmol^{-1})	$E_{strain}^{radical}$ (kcalmol^{-1})	$E_{strain}^{heterocycle}$ (kcalmol^{-1})
no X	C1	2.36	17.92	4.81	-3.36	8.16	2.28	5.88
	C4	2.45	19.82	6.86	-1.11	7.97	2.33	5.64
CF_3CO_2H	C1	1.29	13.04	-2.21	-11.93	9.72	2.46	7.26
	C4	2.84	18.80	5.94	-2.24	8.18	2.32	5.86
H^+	C1	-4.55	9.92	-3.59	-10.76	7.17	1.89	5.28
	C4	5.53	15.75	2.63	-6.51	9.14	2.35	6.79
$[B(OH)_2]^+$	C1	-4.73	10.37	-4.79	-11.72	6.94	1.76	5.17
	C4	5.62	16.33	2.62	-6.06	8.68	2.39	6.29

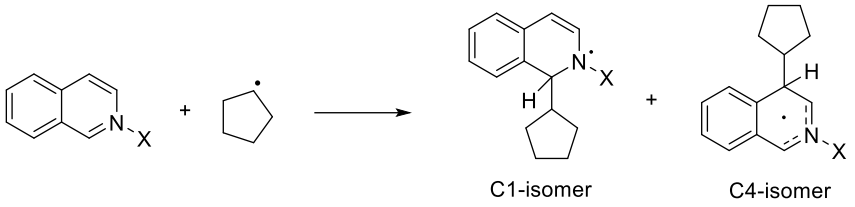


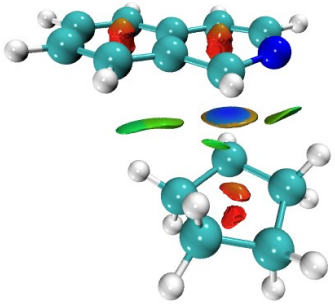
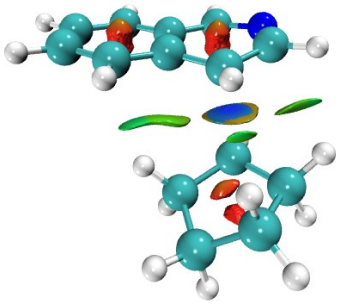
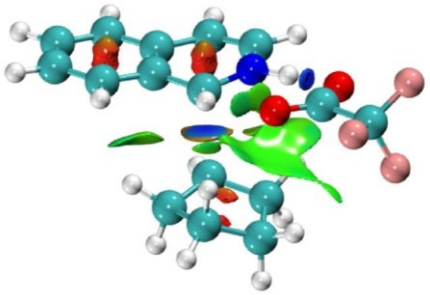
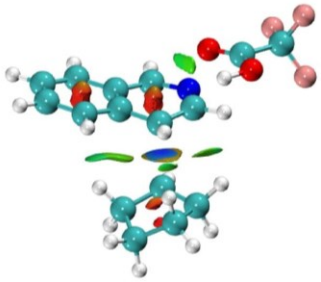
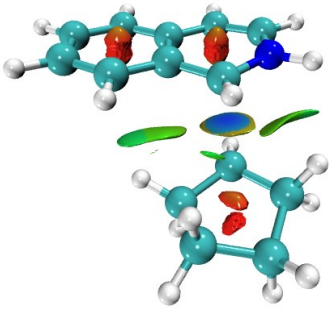
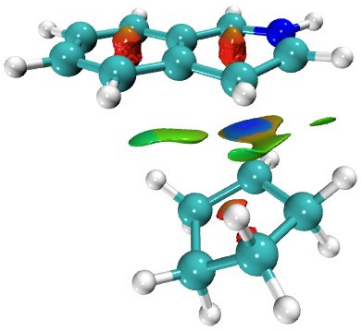
Acid X	Reaction center	$\Delta_rG°$ (kcalmol^{-1})	$\Delta_rG^{‡}$ (kcalmol^{-1})	$\Delta E^{‡}$ (kcalmol^{-1})	E_{int} (kcalmol^{-1})	E_{strain}^{total} (kcalmol^{-1})	$E_{strain}^{radical}$ (kcalmol^{-1})	$E_{strain}^{heterocyclel}$ (kcalmol^{-1})
no X	C2	7.17	20.07	6.86	-1.85	8.71	2.54	6.17
	C4	4.90	19.80	6.53	-2.10	8.63	2.55	6.07
CF_3CO_2H	C2	3.50	14.11	-1.02	-10.11	9.09	2.34	6.75
	C4	3.70	16.15	2.09	-6.25	8.34	2.33	6.01
H^+	C2	-1.01	10.99	-3.11	-10.47	7.36	1.99	5.37
	C4	3.60	10.48	-3.14	-10.98	7.83	2.27	5.57

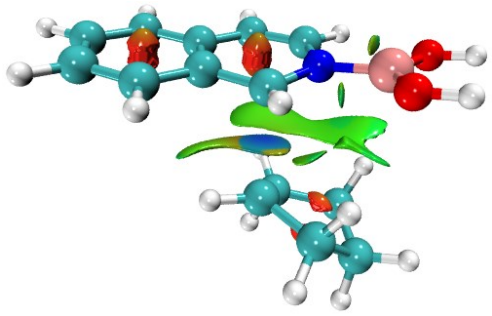
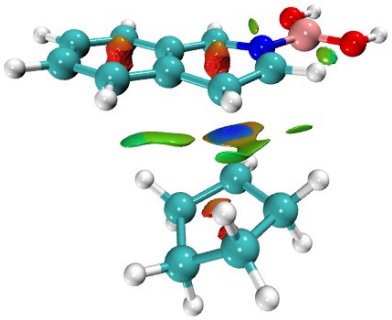
6.6 NCI analysis for the transition states

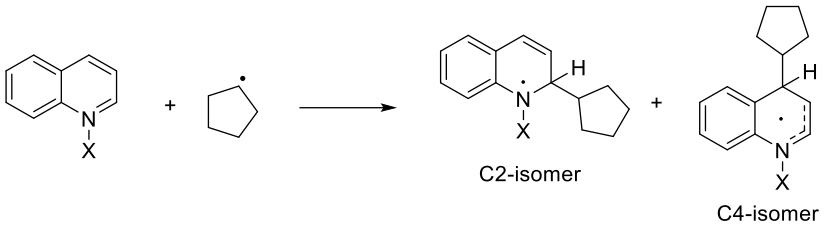
Non-covalent interactions analysis for all the transition states found for the addition of cyclopentyl radical to (iso)quinoline. Non-classical hydrogen bond NCI analyses were performed on the transition states (isosurfaces $s = 0.3$). An RGB-scale is used to differentiate between repulsive (red) and attractive (weak:green, strong:blue) interactions. For the TFA-mediated reaction of (iso)quinoline at the (C1) C2 position non-classical C-H/O hydrogen bond are observed (depicted as an attractive green surface) between the trifluoroacetate O and the cyclopentyl radical.

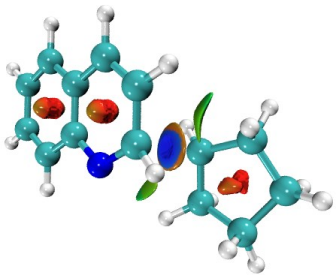
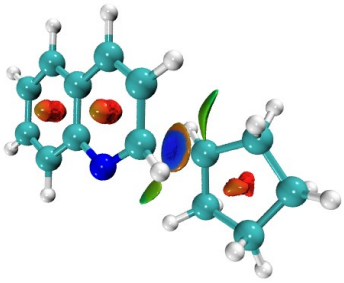
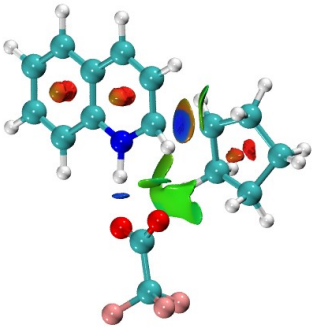
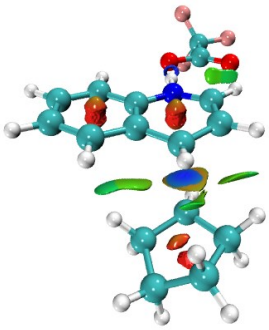
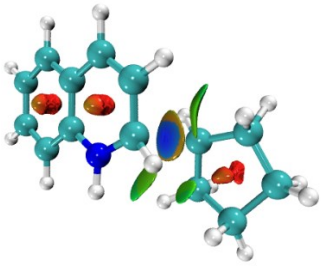
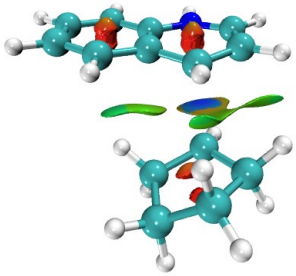
Table S10: Figures showing the non-covalent interaction for all the calculated transition states. The trifluoracetate counterion stabilizes the transition states for the addition of cyclopentyl radical to C1 of isoquinoline and C2 of quinoline through week non-classical hydrogen bonds.



Acid (X)	TS-C1	TS-C4
no X		
CF_3CO_2H		
H^+		

$[B(OH)_2]^+$		

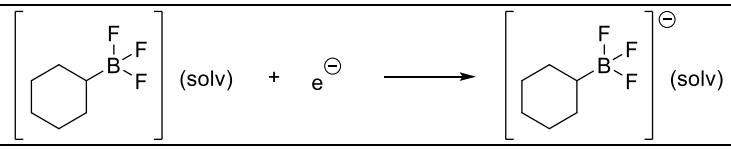
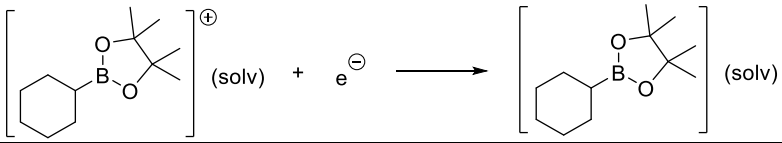
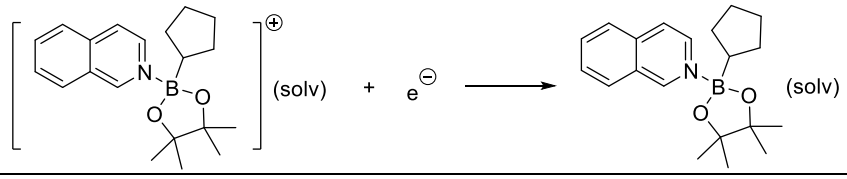
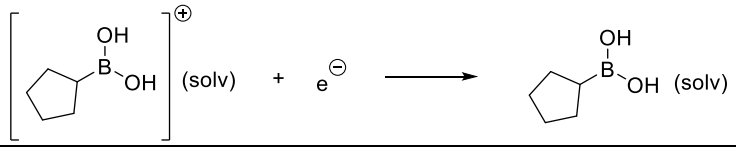
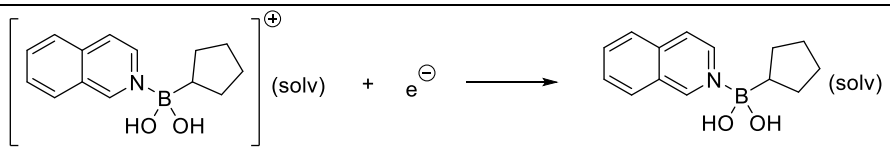
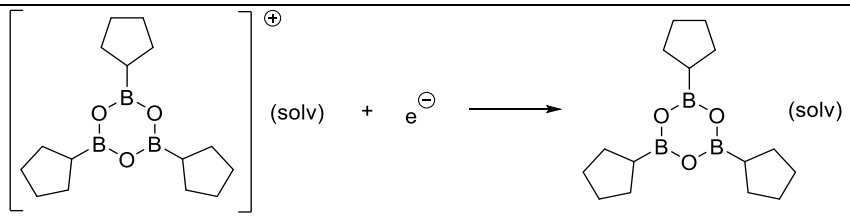


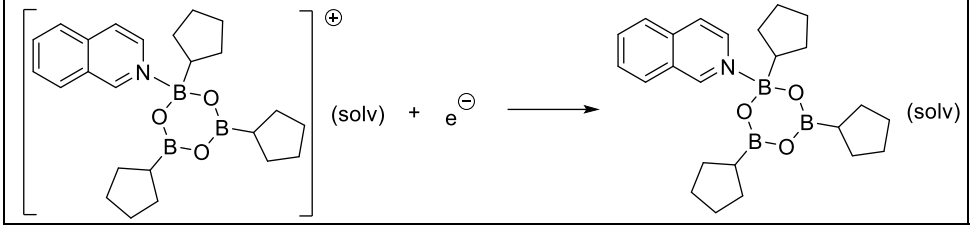
Acid (X)	TS-C2	TS-C4
no X		
CF_3CO_2H		
H^+		

6.7 Reduction potentials for some relevant species

Redox potentials were calculated from energy values obtain from DFT calculations at the theoretical level UB3LYP-D3/def2-TZVP/SMD(toluene). The potential has been calculated relative at the standard concentration of 1.0 mol·L^{-1}. The effect of concentration on the thermodynamic properties was considered using GoodVibes 3.0.1 program. The values are referenced to the theoretically estimated reduction potential of the Standard Hydrogen Electrode in toluene (5.67 V). The formation of Lewis acid-base adducts substantially reduces the oxidation potentials of boronic acids.

Table S11: Calculated electrode potential (relative to toluene) for boronic acid (derivatives) present in solution.

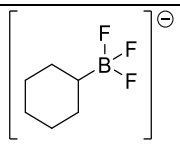
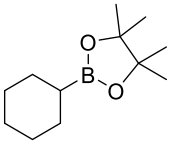
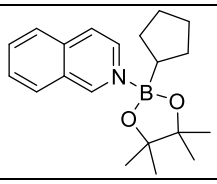
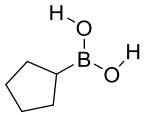
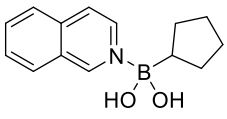
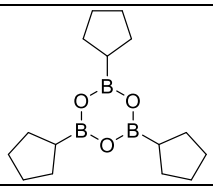
Reduction semi-equation	$\Delta_r G°$ (kcalmol^{-1})	$\Delta E°_{calc}^{SCE}$ (V)
	102.9	-1.21
	171.8	1.78
	126.5	-0.18
	181.1	2.18
	127.5	-0.14
	180.8	2.17

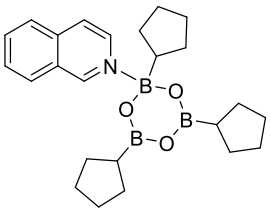
	134.0	0.14

6.8 Partial charges and spin densities of relevant atoms in boron species

Partial charges and spin densities for boron species in its reduced and oxidized (SET) form were calculated using the Natural Bond Orbitals formalism. Complexation with Lewis bases facilitates the oxidation of boronic acid (derivatives) by increasing the electron density on the boron atom.

Table S12: Partial charges and spin densities for relevant atoms in reduced and oxidized boron species

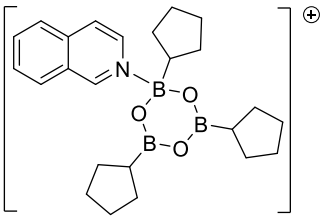
Structure	Atom	Reduced form		Oxidized form	
		Partial charge	Spin density	Partial charge	Spin density
	C (C-B)	-0.532	0	-0.082	0.754
	B	1.151	0	1.371	0.082
	F	-0.579	0	-0.502	0.022
	C (C-B)	0.565	0	-0.364	0.287
	B	1.132	0	1.196	0.123
	O1	-0.707	0	-0.7	0.018
	O2	-0.705	0	-0.71	0.013
	C (C-B)	-0.521	0	-0.082	0.906
	B	1.034	0	1.214	0.005
	O1	-0.749	0	-0.699	0.002
	O2	-0.753	0	-0.702	0.03
	N	-0.405	0	-0.515	-0.002
	C (C-B)	-0.57	0	-0.211	0.465
	B	1.10	0	1.202	0.157
	O1	-0.89	0	-0.862	0.068
	O2	-0.88	0	-0.835	0.013
	C (C-B)	-0.496	0	-0.086	0.871
	B	0.927	0	1.212	0.017
	O1	-0.938	0	-0.878	0.009
	O2	-0.927	0	-0.877	0.009
	N	-0.388	0	-0.514	-0.004
	C (C-B)	-0.572	0	-0.236	0.421
	B1	1.181	0	1.244	0.151
	B2	1.181	0	1.209	0.004
	B3	1.181	0	1.209	0.004
	O	-0.884	0	-0.869	0.039
	C1 (C-B)	-0.495	0	-0.067	0.825
	C2 (C-B)	-0.555	0	-0.592	0
	C3 (C-B)	-0.554	0	-0.598	0

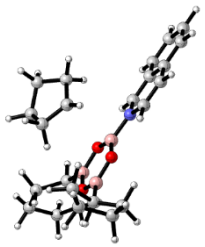
	B1	0.974	0	1.252	0.031
	B2	1.157	0	1.207	0.001
	B3	1.156	0	1.127	0.002
	O1	-0.897	0	-0.888	0.010
	O2	-0.903	0	-0.886	0.004
	O3	-0.893	0	-0.890	0.009
	N	-0.402	0	-0.525	-0.005

6.9 Atomic coordinates, structures and energetic data for all calculated compounds

Structures were represented using CYLview 1.0. Molecular formulae, charges, multiplicities, Cartesian coordinates and thermochemical data are indicated. Only the results of calculations using toluene as solvent (SMD model) are shown.

134L_o





Charge	1
Multiplicity	2
Stoichiometry	C24H34B3NO3
Electronic Energy (Eh)	-1290.7308904
Sum of electronic and zero-point Energies (Eh)	-1290.174146
Sum of electronic and thermal Energies (Eh)	-1290.144358
Sum of electronic and enthalpy Energies (Eh)	-1290.143414
Sum of electronic and thermal Free Energies (Eh)	-1290.241744
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
O           0.717412        3.220163       -0.400090
O           2.293917        2.619605        1.264591
O           0.099299        1.673764        1.287875
B          -0.245439        2.387551        0.132033
B           1.991232        3.353539        0.108454
B           1.353846        1.798426        1.791133
C           3.086821        4.214739       -0.577758
C           3.990508        5.041576        0.359479
C           4.124753        3.337735       -1.326318
H           2.617066        4.878637       -1.310665
C           5.268151        5.337761       -0.462607
H           4.241817        4.444469        1.240055
H           3.499484        5.948424        0.715733
C           5.275403        4.313123       -1.625420
H           3.718563        2.870547       -2.224863
H           4.471239        2.536358       -0.665337
H           5.250370        6.357099       -0.850420
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H           6.161084        5.253894        0.158478
H           5.083767        4.818428       -2.574092
H           6.231757        3.797896       -1.725907
C           2.398571       -0.496352        0.530613
C           1.753705       -1.687730        1.157796
C           1.874017       -0.270497       -0.848121
H           3.328073       -0.068635        0.883670
C           0.903581       -2.300961        0.023498
H           1.105910       -1.394545        1.998765
H           2.480541       -2.385964        1.583393
C           0.584912       -1.109697       -0.891794
H           2.600433       -0.650226       -1.583177
H           1.727963        0.780908       -1.110039
H           1.501925       -3.034797       -0.522115
H           0.011941       -2.810433        0.389103
H           0.307780       -1.409057       -1.902097
H          -0.245497       -0.532447       -0.477486
C          -1.654871        2.258525       -0.508228
C          -2.487443        3.560804       -0.407640
C          -1.647301        2.005727       -2.034180
H          -2.213887        1.458027       -0.011721
C          -3.639513        3.329133       -1.397281
H          -1.876532        4.409246       -0.730228
H          -2.833043        3.769020        0.606749
C          -3.037603        2.469979       -2.536242
H          -1.438200        0.963595       -2.278645
H          -0.861373        2.608899       -2.494420
H          -4.442566        2.783012       -0.897070
H          -4.066046        4.266291       -1.757446
H          -3.679136        1.615658       -2.756725
H          -2.942604        3.039083       -3.461878
C           0.179549       -1.539054        6.809980
C          -0.099055       -0.903321        5.630194
C           0.929875       -0.202331        4.953824
C           2.247949       -0.159424        5.504184
C           2.499309       -0.824661        6.718494
C           1.483375       -1.498842        7.352957
H          -0.285096        0.452701        3.283063
H          -0.599038       -2.076657        7.334357
H          -1.094553       -0.927119        5.205926
C           0.691599        0.453876        3.744988
C           3.237835        0.561241        4.789812
H           3.494691       -0.798149        7.142161
H           1.681062       -2.009595        8.286687
C           2.931160        1.182953        3.624345
H           4.246909        0.623257        5.173380
H           3.646663        1.744292        3.045682
N           1.655907        1.122450        3.101961
```

__Frequencies__ (First of 189)

```
  1.      14.4221 cm-1 (Symmetry: A)
```

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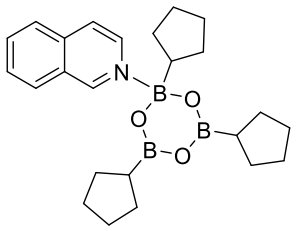
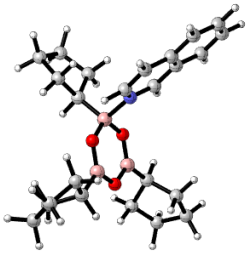
134L





Charge	0
Multiplicity	1
Stoichiometry	C24H34B3NO3
Electronic Energy (Eh)	-1290.94636859
Sum of electronic and zero-point Energies (Eh)	-1290.388539
Sum of electronic and thermal Energies (Eh)	-1290.359401
Sum of electronic and enthalpy Energies (Eh)	-1290.358457
Sum of electronic and thermal Free Energies (Eh)	-1290.456627
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
O           0.713585        3.263411       -0.285369
O           2.426699        1.828494        0.527641
O           0.118737        1.054187        0.372915
B          -0.242953        2.269369       -0.103347
B           2.046643        3.030532        0.035241
B           1.496533        0.722888        0.727941
C           3.107636        4.165555       -0.235608
C           4.345813        4.174576        0.676024
C           3.753368        4.046384       -1.636567
H           2.612595        5.143371       -0.183542
C           5.418159        4.988029       -0.087089
H           4.685134        3.145269        0.818951
H           4.135546        4.583281        1.666996
C           4.969425        4.987748       -1.573204
H           3.064444        4.295547       -2.445806
H           4.085261        3.014771       -1.795461
H           5.473886        6.009686        0.294298
H           6.411664        4.552703        0.037701
H           4.668774        5.993838       -1.875288
H           5.767385        4.677620       -2.250778
C           1.999201       -0.637614        0.021651
C           3.402818       -1.153473        0.369291
C           1.143078       -1.898245        0.214113
H           1.996922       -0.396996       -1.053035
C           3.475248       -2.547310       -0.283515
H           3.500901       -1.255549        1.456333
H           4.198556       -0.485032        0.036319
C           2.010161       -3.065113       -0.314673
H           0.173676       -1.831404       -0.281821
H           0.945026       -2.049513        1.281650
H           3.863201       -2.457204       -1.300886
H           4.145301       -3.224094        0.250989
H           1.719463       -3.324376       -1.334819
H           1.882770       -3.968248        0.285931
C          -1.744583        2.606040       -0.449124
C          -2.347552        3.729394        0.421769
C          -1.974452        3.165124       -1.867427
H          -2.356121        1.704177       -0.323608
C          -3.621682        4.170015       -0.328399
H          -1.636970        4.559481        0.475330
```

```
H          -2.551690        3.410429        1.446529
C          -3.374336        3.813791       -1.819341
H          -1.891737        2.400037       -2.642278
H          -1.214584        3.922832       -2.077721
H          -4.488364        3.624593        0.051987
H          -3.829472        5.232157       -0.185044
H          -4.130120        3.107598       -2.170086
H          -3.436161        4.689402       -2.468383
C          -0.848058       -1.008440        6.305651
C          -0.845604       -0.743340        4.961767
C           0.328131       -0.251042        4.343050
C           1.501208       -0.030805        5.119785
C           1.465757       -0.313079        6.503863
C           0.315400       -0.791208        7.078330
H          -0.486429       -0.103588        2.332979
H          -1.742275       -1.386164        6.784116
H          -1.731270       -0.906310        4.360228
C           0.378550        0.034239        2.966605
C           2.642529        0.467268        4.449960
H           2.354542       -0.146765        7.099659
H           0.293069       -1.006445        8.139266
C           2.595705        0.713290        3.110311
H           3.555638        0.658632        4.997729
H           3.433272        1.105103        2.555955
N           1.465927        0.492415        2.376767
```

__Frequencies__ (First of 189)

```
  1.       9.4567 cm-1 (Symmetry: A)
```

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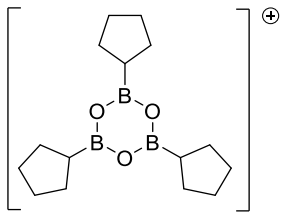
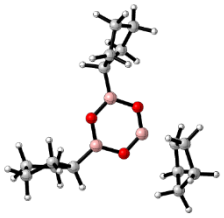
13_o





Charge	1
Multiplicity	2
Stoichiometry	C15H27B3O3
Electronic Energy (Eh)	-888.536913385
Sum of electronic and zero-point Energies (Eh)	-888.120533
Sum of electronic and thermal Energies (Eh)	-888.099383
Sum of electronic and enthalpy Energies (Eh)	-888.098439
Sum of electronic and thermal Free Energies (Eh)	-888.1749
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
O           0.658230        2.883370       -0.075613
O           2.667678        1.685689       -0.438754
O           0.567663        0.535069       -0.388004
B          -0.128346        1.758779       -0.152857
B           2.023384        2.938352       -0.208072
B           1.893512        0.605545       -0.514183
C           2.869803        4.223534       -0.056230
```

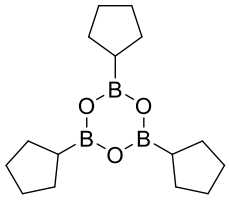
```
C            3.461562        4.316208        1.387410
C            4.104625        4.345112       -1.002999
H            2.212803        5.084909       -0.197421
C            4.707587        5.186340        1.202752
H            3.764343        3.327463        1.749002
H            2.740705        4.720930        2.098271
C            5.316632        4.651379       -0.094992
H            3.934325        5.152883       -1.715640
H            4.271981        3.439800       -1.589016
H            4.409471        6.231815        1.080433
H            5.390212        5.132471        2.052370
H            6.016969        5.347577       -0.557631
H            5.867589        3.730686        0.116100
C            2.730143       -0.904508       -0.825502
C            3.009305       -1.279419        0.623276
C            1.848724       -1.941034       -1.442671
H            3.532215       -0.479507       -1.433603
C            2.311087       -2.646324        0.803247
H            2.624163       -0.571805        1.374885
H            4.093623       -1.248799        0.785441
C            1.206680       -2.673140       -0.263053
H            2.533858       -2.616422       -1.989096
H            1.164171       -1.560078       -2.203902
H            3.046530       -3.429531        0.599915
H            1.938885       -2.783183        1.816250
H            0.894078       -3.684272       -0.517074
H            0.324948       -2.125025        0.075287
C           -1.669416        1.790088       -0.030752
C           -2.195975        2.590609        1.188650
C           -2.319255        2.497255       -1.281440
H           -2.052420        0.769472        0.026532
C           -3.572529        3.080019        0.731699
H           -1.551389        3.451298        1.388182
H           -2.227369        1.982955        2.094241
C           -3.318471        3.528358       -0.709258
H           -2.821489        1.749190       -1.894972
H           -1.581462        2.985523       -1.921691
H           -4.286630        2.251149        0.752411
H           -3.970296        3.876300        1.362739
H           -4.229227        3.589538       -1.306208
H           -2.864536        4.522317       -0.705645
```

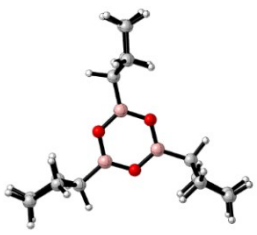
__Frequencies__ (First of 138)

```
  1.      18.2579 cm-1 (Symmetry: A)
```

***

13





Charge	0
Multiplicity	1
Stoichiometry	C15H27B3O3
Electronic Energy (Eh)	-888.825936145
Sum of electronic and zero-point Energies (Eh)	-888.40596

Sum of electronic and thermal Energies (Eh)	-888.384375
Sum of electronic and enthalpy Energies (Eh)	-888.38343
Sum of electronic and thermal Free Energies (Eh)	-888.465423
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
O           0.711158        3.058832        0.003417
O           2.594527        1.612803       -0.000600
O           0.400516        0.704729        0.004107
B          -0.147598        1.972357        0.005373
B           2.083020        2.899815        0.000218
B           1.770891        0.504211        0.001033
C           3.052990        4.127477       -0.005729
C           4.049124        4.152787        1.175278
C           4.011345        4.166741       -1.216609
H           2.467958        5.053827        0.006172
C           5.161356        5.131974        0.737737
H           4.464232        3.150965        1.315036
H           3.578505        4.443230        2.116456
C           5.097352        5.181807       -0.811858
H           3.508324        4.435175       -2.147722
H           4.453490        3.176112       -1.357115
H           4.982212        6.123382        1.158182
H           6.139233        4.808472        1.098386
H           4.812226        6.181885       -1.145469
H           6.058531        4.954589       -1.276155
C           2.349911       -0.949186       -0.000659
C           1.892086       -1.812972        1.195523
C           1.887669       -1.811678       -1.196087
H           3.444719       -0.904693       -0.002698
C           2.209832       -3.262803        0.774294
H           0.814590       -1.688869        1.335709
H           2.377040       -1.530004        2.131801
C           2.207476       -3.261831       -0.777705
H           2.368895       -1.527511       -2.133926
H           0.809592       -1.687730       -1.331918
H           3.191682       -3.556274        1.151200
H           1.488088       -3.968549        1.189027
H           3.188393       -3.554149       -1.157932
H           1.484954       -3.967515       -1.191191
C          -1.695565        2.198697        0.008708
C          -2.209224        3.030309        1.205020
C          -2.214427        3.028678       -1.186503
H          -2.205623        1.228968        0.010400
C          -3.624361        3.481799        0.787914
H          -1.560895        3.900443        1.341361
H          -2.204394        2.470606        2.142349
C          -3.628078        3.479550       -0.764055
H          -2.213022        2.468000       -2.123264
H          -1.567241        3.899126       -1.326313
H          -4.369429        2.780665        1.169360
H          -3.871171        4.461239        1.201158
H          -4.373849        2.776089       -1.139828
H          -3.878368        4.457360       -1.179067
```

__Frequencies__ (First of 138)

```
  1.       9.3506 cm-1 (Symmetry: A)
```

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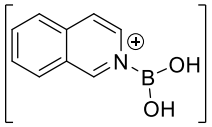
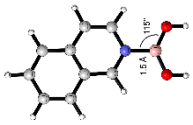
***
# 14L_od
```





Charge	1
Multiplicity	1
Stoichiometry	C9H9BNO2
Electronic Energy (Eh)	-578.656104163
Sum of electronic and zero-point Energies (Eh)	-578.483068
Sum of electronic and thermal Energies (Eh)	-578.472836
Sum of electronic and enthalpy Energies (Eh)	-578.471891
Sum of electronic and thermal Free Energies (Eh)	-578.518883
Number of Imaginary Frequencies	0

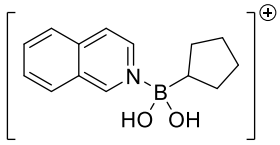
__Molecular Geometry in Cartesian Coordinates__

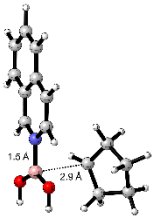
```xyz
C          -1.841907        0.689097       -0.731024
C          -1.305547        1.992114       -0.973011
C          -0.184885        2.393268       -0.207529
C           0.348343        1.562462        0.723774
H          -3.363696       -0.753344       -1.275028
C          -2.965831        0.235112       -1.466365
C          -1.910984        2.806239       -1.948703
H           0.256167        3.369150       -0.357108
H           1.199139        1.828191        1.329394
C          -2.999093        2.340799       -2.646563
C          -3.530288        1.052570       -2.406884
H          -1.511755        3.793868       -2.138595
H          -3.462894        2.969318       -3.395943
H          -4.388607        0.717972       -2.973900
O           1.448979       -0.045034        2.690715
H           1.869504       -0.585628        3.369846
O          -0.134764       -1.808958        2.113838
H           0.222054       -2.406327        2.781633
C          -1.239490       -0.110204        0.238637
H          -1.610100       -1.101324        0.456506
N          -0.183195        0.308598        0.946453
B           0.427980       -0.590088        2.003449
```

__Frequencies__ (First of 60)

```
  1.      77.2722 cm-1 (Symmetry: A)
```

```
***
# 14L_o
```





Charge	1
Multiplicity	2

Stoichiometry	C14H18BNO2
Electronic Energy (Eh)	-774.647863904
Sum of electronic and zero-point Energies (Eh)	-774.347846
Sum of electronic and thermal Energies (Eh)	-774.33071
Sum of electronic and enthalpy Energies (Eh)	-774.329766
Sum of electronic and thermal Free Energies (Eh)	-774.395025
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           2.820846       -2.730504        0.677235
C           4.233017       -2.159932        0.418853
C           3.986060       -0.698848        0.012395
C           2.683281       -0.765841       -0.805424
C           1.923446       -1.877249       -0.161818
H           2.738053       -3.794405        0.433950
H           2.565775       -2.659602        1.746209
H           4.693704       -2.699100       -0.412589
H           4.895955       -2.258184        1.278793
H           3.825505       -0.084845        0.902557
H           4.817569       -0.266827       -0.544442
H           2.137956        0.182683       -0.836936
H           2.904635       -1.015523       -1.854962
H           0.936083       -2.188059       -0.478292
C          -1.838407        0.686714       -0.735645
C          -1.314808        1.997287       -0.963301
C          -0.206270        2.404535       -0.184573
C           0.332901        1.568347        0.739553
H          -3.340097       -0.767181       -1.303622
C          -2.951011        0.226781       -1.484385
C          -1.920662        2.812103       -1.939118
H           0.221658        3.388546       -0.318178
H           1.176828        1.836739        1.353089
C          -2.996640        2.340330       -2.650755
C          -3.515664        1.044520       -2.424533
H          -1.530652        3.805604       -2.117545
H          -3.460327        2.968944       -3.400108
H          -4.365148        0.704366       -3.001537
O           1.545530       -0.103922        2.583523
H           1.955802       -0.643554        3.268380
O          -0.238829       -1.739035        2.238943
H           0.143392       -2.347179        2.881290
C          -1.233233       -0.114073        0.231575
H          -1.592421       -1.111267        0.439351
N          -0.182013        0.306042        0.943428
B           0.449201       -0.606796        1.977759
```

__Frequencies__ (First of 102)

```
  1.      18.3471 cm-1 (Symmetry: A)
```

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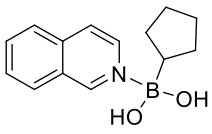
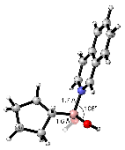
14L





Charge	0

Multiplicity	1
Stoichiometry	C14H18BNO2
Electronic Energy (Eh)	-774.8539500679999
Sum of electronic and zero-point Energies (Eh)	-774.552753
Sum of electronic and thermal Energies (Eh)	-774.536208
Sum of electronic and enthalpy Energies (Eh)	-774.535264
Sum of electronic and thermal Free Energies (Eh)	-774.59823
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

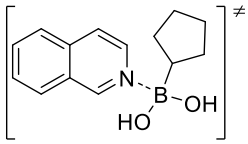
```xyz
C           2.952733       -2.406540        1.249914
C           4.093345       -2.526753        0.227892
C           4.168104       -1.137289       -0.456271
C           2.875276       -0.390223       -0.033992
C           1.947308       -1.451399        0.586157
H           2.511660       -3.367113        1.519287
H           3.339629       -1.960741        2.176502
H           3.836034       -3.293168       -0.508150
H           5.042615       -2.824565        0.678939
H           5.059038       -0.587726       -0.144447
H           4.230909       -1.240873       -1.541484
H           3.114199        0.365541        0.721449
H           2.410911        0.138916       -0.869012
H           1.467464       -2.008547       -0.232097
C          -1.804701        0.616620       -0.983978
C          -1.484911        2.004447       -0.977077
C          -0.456361        2.431534       -0.106019
C           0.190291        1.525722        0.682705
H          -3.061493       -0.924035       -1.830131
C          -2.827511        0.133446       -1.834518
C          -2.203700        2.874117       -1.828977
H          -0.181049        3.477021       -0.060791
H           0.975195        1.796010        1.370982
C          -3.189378        2.379101       -2.644356
C          -3.505358        1.001274       -2.649291
H          -1.965486        3.930543       -1.827934
H          -3.736493        3.049426       -3.295434
H          -4.287759        0.636410       -3.302087
O           1.192342       -0.127230        2.715386
H           2.038652       -0.424357        3.057685
O          -0.136564       -1.997774        1.899385
H          -0.592296       -1.791382        2.721990
C          -1.080039       -0.235761       -0.129965
H          -1.285896       -1.297047       -0.083892
N          -0.124083        0.199954        0.664553
B           0.778389       -0.925944        1.576198
```

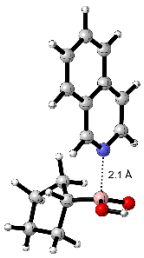
__Frequencies__ (First of 102)

```
  1.      26.0502 cm-1 (Symmetry: A)
```

***

14L_ts





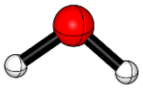
Charge	0
Multiplicity	1
Stoichiometry	C14H18BNO2
Electronic Energy (Eh)	-774.852636813
Sum of electronic and zero-point Energies (Eh)	-774.552027
Sum of electronic and thermal Energies (Eh)	-774.535907
Sum of electronic and enthalpy Energies (Eh)	-774.534963
Sum of electronic and thermal Free Energies (Eh)	-774.598035
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C            3.005920       -2.552592        1.241484
C            4.061278       -2.643322        0.129746
C            4.127839       -1.219771       -0.479696
C            2.888886       -0.465257        0.071132
C            1.979918       -1.535965        0.702975
H            2.558639       -3.516970        1.487510
H            3.460957       -2.164524        2.160572
H            3.726995       -3.358611       -0.626470
H            5.031551       -2.991132        0.490709
H            5.052544       -0.710497       -0.200467
H            4.112699       -1.260840       -1.570522
H            3.212439        0.253103        0.834039
H            2.376220        0.115706       -0.696850
H            1.424139       -2.031439       -0.104017
C           -1.775829        0.661400       -1.057820
C           -1.581058        2.069045       -0.958337
C           -0.648310        2.533709       -0.001730
C            0.027123        1.633220        0.774625
H           -2.840851       -0.926978       -2.062274
C           -2.699953        0.145078       -1.995915
C           -2.323091        2.922098       -1.808755
H           -0.473358        3.595720        0.115261
H            0.740889        1.944030        1.525670
C           -3.211672        2.394176       -2.710292
C           -3.403491        0.997161       -2.806618
H           -2.178990        3.993270       -1.737431
H           -3.776551        3.052161       -3.358911
H           -4.110852        0.604623       -3.525897
O            1.338582       -0.216633        2.864979
H            2.198948        0.183824        2.714160
O           -0.082624       -1.967293        2.119694
H           -0.535215       -1.716974        2.932500
C           -1.020753       -0.169867       -0.199884
H           -1.140549       -1.247623       -0.230886
N           -0.156066        0.294412        0.668908
B            0.934657       -1.054831        1.807932
```

__Frequencies__ (First of 102)

```
  1.     -79.8866 cm-1 (Symmetry: A)  *
```
***
14



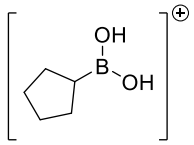
Charge	0
Multiplicity	1
Stoichiometry	H2O
Electronic Energy (Eh)	-76.4672546565
Sum of electronic and zero-point Energies (Eh)	-76.446205
Sum of electronic and thermal Energies (Eh)	-76.443369
Sum of electronic and enthalpy Energies (Eh)	-76.442425
Sum of electronic and thermal Free Energies (Eh)	-76.464508
Number of Imaginary Frequencies	0

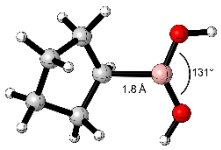
__Molecular Geometry in Cartesian Coordinates__

```xyz
O           0.765630        0.101631        0.000000
H           1.728922        0.140082        0.000000
H           0.480322        1.022505        0.000000
```

__Frequencies__ (First of 3)

```
  1.    1610.6453 cm-1 (Symmetry: A)
```
***
1_o





Charge	1
Multiplicity	2
Stoichiometry	C5H11BO2
Electronic Energy (Eh)	-372.4577189319999
Sum of electronic and zero-point Energies (Eh)	-372.298107
Sum of electronic and thermal Energies (Eh)	-372.289211
Sum of electronic and enthalpy Energies (Eh)	-372.288267
Sum of electronic and thermal Free Energies (Eh)	-372.332005
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           2.336873       -1.704699        0.096951
C           3.854861       -1.744693        0.282369
C           4.308752       -0.383275       -0.257369
C           3.203024        0.576363        0.235729
C           1.962584       -0.260468        0.217157
H           2.066987       -1.967003       -0.947299
H           1.755653       -2.400842        0.703471
H           4.311117       -2.587494       -0.233646
H           4.097383       -1.836950        1.344750
```

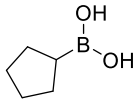
```
H           5.294637       -0.080221        0.088691
H           4.316054       -0.389321       -1.350366
H           3.448815        0.841352        1.277991
H           3.103418        1.515541       -0.310828
H           1.102910        0.106670       -0.384811
B           0.767105        0.043953        1.520509
O           0.809314        1.235948        2.102536
H           1.448709        1.910748        1.842813
O          -0.053507       -0.976242        1.708435
H          -0.728606       -0.873252        2.397528
```

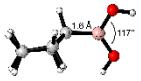
__Frequencies__ (First of 51)

```
  1.      77.7776 cm-1 (Symmetry: A)
```

***

1t





Charge	0
Multiplicity	1
Stoichiometry	C5H11BO2
Electronic Energy (Eh)	-372.750754858
Sum of electronic and zero-point Energies (Eh)	-372.5863
Sum of electronic and thermal Energies (Eh)	-372.577724
Sum of electronic and enthalpy Energies (Eh)	-372.57678
Sum of electronic and thermal Free Energies (Eh)	-372.621489
Number of Imaginary Frequencies	0

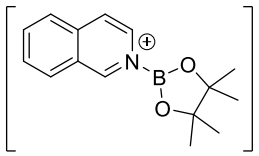
__Molecular Geometry in Cartesian Coordinates__

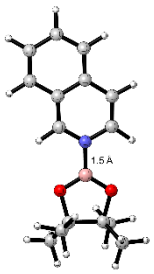
```xyz
C           2.540545       -1.693785        0.737870
C           3.924770       -1.724094        0.047007
C           4.231730       -0.257987       -0.358593
C           3.106624        0.584597        0.267433
C           1.893533       -0.360155        0.287441
H           1.924354       -2.559513        0.491763
H           2.667162       -1.690430        1.825358
H           3.900262       -2.368187       -0.833664
H           4.688587       -2.129973        0.712489
H           5.222234        0.067627       -0.036253
H           4.201424       -0.154369       -1.445466
H           3.387776        0.862260        1.291410
H           2.918524        1.513342       -0.274572
H           1.542782       -0.489781       -0.743106
B           0.664728        0.057241        1.182385
O           0.779496        0.722684        2.380399
H           1.684840        0.956411        2.609484
O          -0.597421       -0.288315        0.779942
H          -1.275868       -0.021459        1.413285
```

__Frequencies__ (First of 51)

```
  1.      20.7116 cm-1 (Symmetry: A)
```

***
24L_od





Charge	1
Multiplicity	1
Stoichiometry	C15H19BNO2
Electronic Energy (Eh)	-813.427468006
Sum of electronic and zero-point Energies (Eh)	-813.106755
Sum of electronic and thermal Energies (Eh)	-813.089992
Sum of electronic and enthalpy Energies (Eh)	-813.089048
Sum of electronic and thermal Free Energies (Eh)	-813.150935
Number of Imaginary Frequencies	0

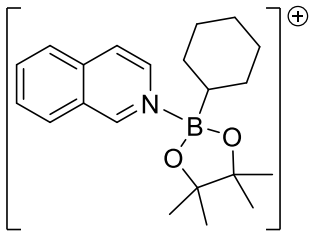
__Molecular Geometry in Cartesian Coordinates__

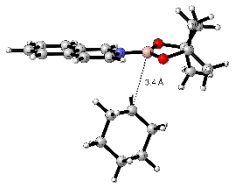
```xyz
B            1.964492        0.401355       -0.389284
O            2.523150       -0.559916       -1.147532
O            2.187951        0.353814        0.936181
C            3.055612       -1.557618       -0.185776
C            3.227687       -0.691654        1.120094
C            4.341209       -2.124627       -0.751738
H            4.804028       -2.797986       -0.028831
H            4.123808       -2.696348       -1.654396
H            5.053729       -1.343098       -1.006265
C            1.987503       -2.635949       -0.064983
H            1.785551       -3.049732       -1.053072
H            2.323340       -3.445847        0.582200
H            1.054787       -2.237229        0.336289
C            2.944227       -1.424236        2.415147
H            3.644264       -2.252287        2.536393
H            3.075551       -0.744688        3.257423
H            1.930198       -1.816603        2.448000
C            4.557220        0.046608        1.187465
H            4.524928        0.767323        2.004573
H            5.376882       -0.646740        1.374981
H            4.765690        0.585938        0.262078
C            0.870367        1.461258       -2.312732
C            0.597194        2.467826       -0.194936
C            0.078153        2.433926       -2.920694
H            1.315894        0.653047       -2.876400
C           -0.187350        3.444716       -0.717124
H            0.854275        2.403104        0.850516
C           -0.183042        2.410910       -4.313947
C           -0.480209        3.466367       -2.102531
H           -0.587164        4.208522       -0.064503
C           -0.971899        3.381570       -4.868001
H            0.245453        1.623919       -4.921155
C           -1.288089        4.448372       -2.707301
C           -1.525102        4.401130       -4.059653
H           -1.178304        3.374685       -5.929839
H           -1.716717        5.232970       -2.097721
H           -2.146907        5.157998       -4.520370
```

```
N           1.118662        1.478241       -0.998986
```

__Frequencies__ (First of 108)

```
  1.      23.4248 cm-1 (Symmetry: A)
```
***
24L_o





Charge	1
Multiplicity	2
Stoichiometry	C21H30BNO2
Electronic Energy (Eh)	-1048.7558773
Sum of electronic and zero-point Energies (Eh)	-1048.278077
Sum of electronic and thermal Energies (Eh)	-1048.253446
Sum of electronic and enthalpy Energies (Eh)	-1048.252501
Sum of electronic and thermal Free Energies (Eh)	-1048.333503
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -3.100376       -2.180160        0.792824
C          -1.581797       -1.965418        0.598851
C          -1.312064       -0.842665       -0.341858
C          -2.033511        0.440429       -0.115731
C          -3.548190        0.205421        0.082123
C          -3.805701       -0.868199        1.141155
H          -1.153147       -1.730932        1.585957
H          -1.110644       -2.890069        0.261881
H          -3.522951       -2.583959       -0.132862
H          -3.268187       -2.926271        1.573509
H          -1.654042        0.921890        0.799453
H          -1.865928        1.144989       -0.931932
H          -4.032880        1.144979        0.360552
H          -3.986097       -0.111960       -0.869768
H          -3.446267       -0.510849        2.113397
H          -4.880113       -1.037856        1.247547
H          -0.758187       -1.013411       -1.256348
B           1.872673        0.337474       -0.381765
O           2.476270       -0.593298       -1.144383
O           2.086209        0.284739        0.945683
C           3.076185       -1.562366       -0.195888
C           3.166069       -0.713650        1.134158
C           4.410770       -2.008622       -0.758977
H           4.918175       -2.661761       -0.047540
H           4.250209       -2.571670       -1.678579
H           5.061615       -1.166736       -0.984841
C           2.104005       -2.729525       -0.109869
H           1.944892       -3.135405       -1.109283
H           2.503558       -3.523046        0.521479
H           1.140995       -2.418030        0.290141
```

```
C            2.880810       -1.488273        2.404822
H            3.617480       -2.282712        2.533259
H            2.949790       -0.820764        3.264098
H            1.887746       -1.931882        2.396474
C            4.454996        0.087397        1.261933
H            4.364702        0.775112        2.102915
H            5.305658       -0.568396        1.446178
H            4.656626        0.672157        0.363248
C            0.741399        1.382873       -2.293351
C            0.688050        2.513877       -0.223847
C            0.005603        2.393854       -2.909536
H            1.076974        0.510504       -2.836593
C           -0.023348        3.539460       -0.757935
H            0.994542        2.473589        0.809077
C           -0.347407        2.322765       -4.280676
C           -0.396154        3.519059       -2.122847
H           -0.306503        4.372434       -0.129357
C           -1.072997        3.336462       -4.843887
H           -0.038452        1.464648       -4.863715
C           -1.141006        4.544758       -2.736975
C           -1.469134        4.449832       -4.067254
H           -1.348672        3.292783       -5.888985
H           -1.448620        5.401094       -2.151069
H           -2.042036        5.240291       -4.534826
N            1.065351        1.440016       -0.997916
```

__Frequencies__ (First of 159)

```
  1.      26.6363 cm-1 (Symmetry: A)
```

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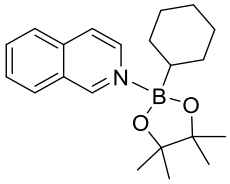
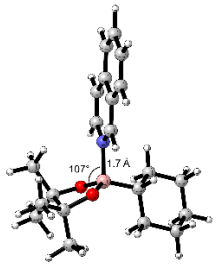
24L





Charge	0
Multiplicity	1
Stoichiometry	C21H30BNO2
Electronic Energy (Eh)	-1048.96233398
Sum of electronic and zero-point Energies (Eh)	-1048.483431
Sum of electronic and thermal Energies (Eh)	-1048.460313
Sum of electronic and enthalpy Energies (Eh)	-1048.459368
Sum of electronic and thermal Free Energies (Eh)	-1048.534816
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           -2.749997       -2.635982        0.686933
C           -1.292661       -2.182523        0.558608
C           -1.156722       -0.755185        0.001277
C           -2.003835        0.212595        0.844760
C           -3.463355       -0.235213        0.981973
```

```
C          -3.567393       -1.658395        1.533777
H          -0.821657       -2.219349        1.548291
H          -0.738910       -2.877657       -0.075592
H          -3.195079       -2.701951       -0.313568
H          -2.798551       -3.641476        1.117406
H          -1.557152        0.291210        1.843346
H          -1.981010        1.218744        0.416189
H          -4.015804        0.460376        1.622065
H          -3.941168       -0.199712       -0.004927
H          -3.187567       -1.672148        2.562591
H          -4.614246       -1.973696        1.581730
H          -1.580927       -0.765032       -1.015699
B           0.402074       -0.340874       -0.131503
O           1.223313       -1.189537       -0.963450
O           1.114035       -0.121758        1.097389
C           2.414132       -1.547806       -0.251637
C           2.491506       -0.464762        0.893955
C           3.591342       -1.532011       -1.221401
H           4.534047       -1.726573       -0.704660
H           3.452938       -2.311560       -1.973323
H           3.669693       -0.578504       -1.741412
C           2.233661       -2.968367        0.292098
H           1.980498       -3.630577       -0.537543
H           3.144634       -3.342732        0.763416
H           1.422817       -3.013342        1.016401
C           3.056107       -0.973152        2.215274
H           4.075846       -1.345291        2.093364
H           3.078993       -0.157082        2.940473
H           2.440034       -1.768910        2.629528
C           3.272153        0.788596        0.475100
H           3.113032        1.568486        1.221731
H           4.343932        0.591017        0.415030
H           2.944907        1.172356       -0.489570
C           0.334772        1.206327       -2.283872
C           0.323354        2.352899       -0.270086
C           0.247916        2.402483       -3.022615
H           0.394228        0.244390       -2.776926
C           0.240147        3.564611       -0.891277
H           0.374736        2.242391        0.802222
C           0.213670        2.412486       -4.437205
C           0.197686        3.631240       -2.303407
H           0.210292        4.472276       -0.302867
C           0.130256        3.602526       -5.110770
H           0.253263        1.471784       -4.972496
C           0.112652        4.842159       -3.028338
C           0.079448        4.822942       -4.399470
H           0.102631        3.614821       -6.192708
H           0.074249        5.779466       -2.487245
H           0.013847        5.753350       -4.949515
N           0.370136        1.186630       -0.969524
```

__Frequencies__ (First of 159)

```
  1.      24.3391 cm-1 (Symmetry: A)
```

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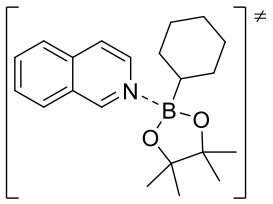
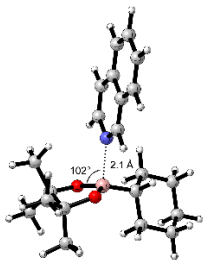
24L_TS





Charge	0
Multiplicity	1
Stoichiometry	C21H30BNO2
Electronic Energy (Eh)	-1048.89353546
Sum of electronic and zero-point Energies (Eh)	-1048.416446
Sum of electronic and thermal Energies (Eh)	-1048.393225
Sum of electronic and enthalpy Energies (Eh)	-1048.392281
Sum of electronic and thermal Free Energies (Eh)	-1048.469166
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -3.400325        2.980676       -1.164974
C          -2.992416        1.532584       -0.879849
C          -1.553846        1.420785       -0.327650
C          -1.396191        2.326539        0.903200
C          -1.807896        3.775814        0.624425
C          -3.233164        3.862966        0.074139
H          -3.688185        1.106565       -0.146328
H          -3.088281        0.929177       -1.785890
H          -2.774166        3.375883       -1.974040
H          -4.434567        3.019955       -1.521288
H          -2.011731        1.926752        1.717535
H          -0.363393        2.306341        1.258049
H          -1.716653        4.377334        1.534360
H          -1.115447        4.208919       -0.107867
H          -3.936551        3.530807        0.847298
H          -3.489938        4.900922       -0.158176
H          -0.878672        1.791640       -1.111617
B          -1.220018       -0.111867       -0.074820
O          -1.165135       -1.007038       -1.154852
O          -1.664277       -0.763962        1.079546
C          -1.733290       -2.265984       -0.739279
C          -1.661814       -2.187336        0.836254
C          -0.928016       -3.399599       -1.359226
H          -1.289584       -4.371584       -1.016691
H          -1.029301       -3.365884       -2.445554
H           0.130713       -3.317918       -1.119368
C          -3.167722       -2.302856       -1.270621
H          -3.143646       -2.169029       -2.353148
H          -3.660070       -3.252126       -1.052655
H          -3.763161       -1.494246       -0.847525
C          -2.857757       -2.792545        1.559825
H          -2.956276       -3.856505        1.334126
H          -2.721803       -2.687264        2.637783
H          -3.784778       -2.290216        1.290226
C          -0.374945       -2.781148        1.414022
H          -0.305733       -2.512044        2.469108
H          -0.373356       -3.870005        1.340546
H           0.510176       -2.401199        0.909779
C           1.696913        0.037543       -0.717541
```

```
C           1.380327        0.252825        1.552009
C           3.099272        0.171242       -0.591804
H           1.244110       -0.121395       -1.690946
C           2.718281        0.393597        1.795683
H           0.647001        0.261390        2.347222
C           3.970377        0.123165       -1.704798
C           3.632157        0.358652        0.715734
H           3.078549        0.528599        2.807703
C           5.322565        0.258271       -1.524995
H           3.553679       -0.020338       -2.694445
C           5.032023        0.494736        0.868246
C           5.853869        0.445391       -0.228922
H           5.991461        0.222633       -2.375422
H           5.442970        0.637845        1.860184
H           6.924625        0.550291       -0.105513
N           0.878139        0.078591        0.303689
```

__Frequencies__ (First of 159)

```
  1.     -90.2671 cm-1 (Symmetry: A)  *
```

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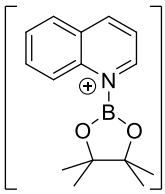
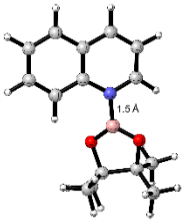
25L_od





Charge	1
Multiplicity	1
Stoichiometry	C15H19BNO2
Electronic Energy (Eh)	-813.422719472
Sum of electronic and zero-point Energies (Eh)	-813.101825
Sum of electronic and thermal Energies (Eh)	-813.085127
Sum of electronic and enthalpy Energies (Eh)	-813.084183
Sum of electronic and thermal Free Energies (Eh)	-813.146081
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
B           1.701071        0.356056       -0.629679
O           2.496782       -0.521464       -1.267574
O           1.843417        0.438860        0.708507
C           3.166030       -1.311843       -0.204169
C           3.053938       -0.349126        1.038583
C           4.580051       -1.612315       -0.658148
H           5.128835       -2.118777        0.137255
H           4.555341       -2.273577       -1.524700
H           5.120262       -0.709297       -0.934290
C           2.354550       -2.592380       -0.060732
H           2.334392       -3.112294       -1.018685
H           2.803513       -3.257649        0.676340
H           1.326453       -2.387399        0.240610
C           2.821330       -1.042172        2.365810
H           3.658917       -1.701987        2.596882
H           2.748171       -0.299027        3.160297
```

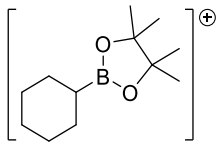
```
H           1.905165       -1.628846        2.363248
C           4.195530        0.653703        1.138545
H           3.950591        1.397818        1.896547
H           5.122166        0.160919        1.431975
H           4.364217        1.169760        0.192196
C           0.101612        0.969053       -2.537051
C           0.485391        2.436533       -0.707705
C           0.289430       -0.258992       -3.194032
C          -0.771542        1.942283       -3.108388
C          -0.356266        3.403249       -1.232227
H           0.997984        2.582710        0.231443
C          -0.361418       -0.498514       -4.381414
H           0.944094       -1.006357       -2.777784
C          -1.418600        1.657069       -4.334010
C          -0.978805        3.158453       -2.433768
H          -0.502161        4.325487       -0.689746
C          -1.216192        0.458080       -4.961283
H          -0.210671       -1.447443       -4.879418
H          -2.077302        2.404526       -4.756837
H          -1.640099        3.895989       -2.871667
H          -1.712310        0.238838       -5.897155
N           0.722682        1.267950       -1.327831
```

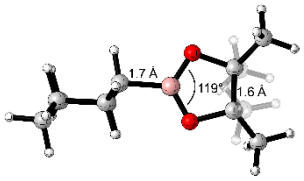
__Frequencies__ (First of 108)

```
  1.      12.1749 cm-1 (Symmetry: A)
```

***

2_o





Charge	1
Multiplicity	2
Stoichiometry	C12H23BO2
Electronic Energy (Eh)	-646.580191174
Sum of electronic and zero-point Energies (Eh)	-646.242432
Sum of electronic and thermal Energies (Eh)	-646.226349
Sum of electronic and enthalpy Energies (Eh)	-646.225404
Sum of electronic and thermal Free Energies (Eh)	-646.285621
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -3.209540       -2.323957        0.830127
C          -1.609566       -2.216002        0.916777
C          -1.253825       -1.081160        0.005891
C          -1.780935        0.259401        0.399563
C          -3.371205        0.137153        0.324264
C          -3.821027       -0.999217        1.216253
H          -1.337351       -2.022062        1.953659
H          -1.205069       -3.176777        0.598529
H          -3.484809       -2.615738       -0.183586
H          -3.466828       -3.136670        1.513359
H          -1.497926        0.528731        1.416086
```

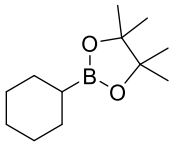
```
H          -1.488940        1.056220       -0.285491
H          -3.754687        1.109160        0.640949
H          -3.663919       -0.030565       -0.712996
H          -3.618341       -0.771202        2.265173
H          -4.914316       -1.093124        1.112823
H          -1.415995       -1.315697       -1.047837
B           0.426349       -1.000264        0.139520
O           1.175711       -1.340800       -0.914941
O           1.036521       -0.607240        1.264369
C           2.579063       -1.369617       -0.389867
C           2.470161       -0.436101        0.878315
C           3.491839       -0.860565       -1.484064
H           4.513668       -0.781081       -1.108631
H           3.492525       -1.561555       -2.318936
H           3.180073        0.113385       -1.854924
C           2.870721       -2.823925       -0.055933
H           2.727293       -3.431231       -0.949425
H           3.901604       -2.944450        0.277101
H           2.209767       -3.199994        0.726110
C           3.324158       -0.854443        2.056142
H           4.379598       -0.826006        1.780027
H           3.173384       -0.160955        2.883647
H           3.081474       -1.857236        2.400615
C           2.647887        1.042400        0.567260
H           2.365511        1.626816        1.442897
H           3.687795        1.265726        0.329664
H           2.026450        1.358882       -0.271522
```

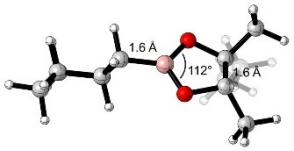
__Frequencies__ (First of 108)

```
  1.      22.2860 cm-1 (Symmetry: A)
```

***

2





Charge	0
Multiplicity	1
Stoichiometry	C12H23BO2
Electronic Energy (Eh)	-646.858233138
Sum of electronic and zero-point Energies (Eh)	-646.516918
Sum of electronic and thermal Energies (Eh)	-646.501377
Sum of electronic and enthalpy Energies (Eh)	-646.500432
Sum of electronic and thermal Free Energies (Eh)	-646.559856
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -3.201356       -2.374070        0.459186
C          -1.675475       -2.266253        0.527018
C          -1.170828       -0.896368        0.011366
C          -1.868720        0.248110        0.766245
C          -3.394163        0.135840        0.699037
C          -3.879901       -1.223999        1.207820
H          -1.354548       -2.396856        1.567751
H          -1.215024       -3.075127       -0.046981
```

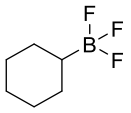
```
H          -3.513272       -2.353550       -0.591624
H          -3.528258       -3.335869        0.865537
H          -1.549798        0.229172        1.814097
H          -1.545227        1.213587        0.366396
H          -3.857737        0.942090        1.275158
H          -3.718544        0.266350       -0.340347
H          -3.651747       -1.308686        2.277065
H          -4.966926       -1.299377        1.112743
H          -1.448567       -0.832571       -1.049565
B           0.394351       -0.841709        0.094320
O           1.220813       -1.381461       -0.861749
O           1.091802       -0.299809        1.145268
C           2.570269       -1.413964       -0.313189
C           2.504641       -0.294761        0.788812
C           3.561779       -1.156041       -1.434835
H           4.578854       -1.091798       -1.042929
H           3.526705       -1.978201       -2.151224
H           3.335197       -0.235316       -1.969092
C           2.773674       -2.813947        0.262863
H           2.609919       -3.547806       -0.527144
H           3.784649       -2.945907        0.650437
H           2.063106       -3.018470        1.064777
C           3.324955       -0.571395        2.037277
H           4.384897       -0.658577        1.790238
H           3.208780        0.253183        2.742248
H           3.006372       -1.485499        2.534668
C           2.813578        1.100659        0.250680
H           2.550773        1.837689        1.010401
H           3.872148        1.213998        0.013295
H           2.230100        1.316946       -0.645056
```

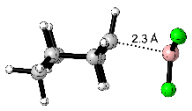
__Frequencies__ (First of 108)

```
  1.      10.8581 cm-1 (Symmetry: A)
```

***

3_o





Charge	0
Multiplicity	2
Stoichiometry	C6H11BF3
Electronic Energy (Eh)	-560.044515213
Sum of electronic and zero-point Energies (Eh)	-559.874733
Sum of electronic and thermal Energies (Eh)	-559.863971
Sum of electronic and enthalpy Energies (Eh)	-559.863026
Sum of electronic and thermal Free Energies (Eh)	-559.912855
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -2.945756       -0.173861        0.015220
C          -1.395577       -0.138170       -0.055776
C          -0.944232        1.283691       -0.040885
C          -1.395172        2.106581        1.118975
C          -2.945452        2.069029        1.189706
```

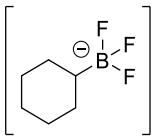
```
C          -3.459563        0.628652        1.211729
H          -1.003181       -0.662384        0.822070
H          -1.041378       -0.662797       -0.943522
H          -3.355992        0.242643       -0.910253
H          -3.276161       -1.213985        0.072642
H          -1.002470        1.683862        2.049792
H          -1.040800        3.134972        1.044049
H          -3.274903        2.614261        2.077695
H          -3.356084        2.592777        0.320606
H          -3.134232        0.143228        2.138545
H          -4.553000        0.624120        1.220723
H          -0.853972        1.786278       -1.001564
F           1.569071        2.502613        0.097878
F           1.568708        0.459887       -0.952247
F           1.399159        0.575390        1.334533
B           1.345043        1.186093        0.146973
```

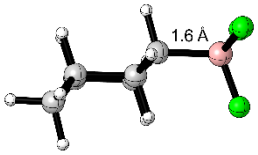
__Frequencies__ (First of 57)

```
  1.      35.5215 cm-1 (Symmetry: A)
```

***

3





Charge	-1
Multiplicity	1
Stoichiometry	C6H11BF3(1-)
Electronic Energy (Eh)	-560.212107134
Sum of electronic and zero-point Energies (Eh)	-560.041489
Sum of electronic and thermal Energies (Eh)	-560.031819
Sum of electronic and enthalpy Energies (Eh)	-560.030875
Sum of electronic and thermal Free Energies (Eh)	-560.076758
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -2.875139       -0.164008        0.002058
C          -1.341804       -0.172147        0.019646
C          -0.735195        1.239709        0.030739
C          -1.336347        2.059812        1.182774
C          -2.869088        2.078281        1.169556
C          -3.444372        0.658750        1.161929
H          -1.002442       -0.710832        0.913308
H          -0.961890       -0.733659       -0.838724
H          -3.220192        0.270616       -0.944764
H          -3.267966       -1.186676        0.038494
H          -0.995446        1.633283        2.134936
H          -0.947417        3.081333        1.148438
H          -3.257385        2.636969        2.028997
H          -3.213392        2.606310        0.271135
H          -3.186784        0.165727        2.107777
H          -4.538402        0.687636        1.111442
H          -1.027145        1.731351       -0.911388
F           1.415099        2.557037        0.054716
```

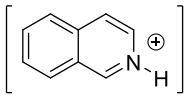
```
F           1.436573        0.530352       -1.051212
F           1.383575        0.586771        1.254242
B           0.889215        1.226265        0.072791
```

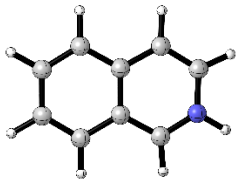
__Frequencies__ (First of 57)

```
  1.      52.7875 cm-1 (Symmetry: A)
```

***

4H





Charge	1
Multiplicity	1
Stoichiometry	C9H8N
Electronic Energy (Eh)	-402.526339944
Sum of electronic and zero-point Energies (Eh)	-402.376755
Sum of electronic and thermal Energies (Eh)	-402.369924
Sum of electronic and enthalpy Energies (Eh)	-402.36898
Sum of electronic and thermal Free Energies (Eh)	-402.408076
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

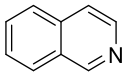
```xyz
C          -5.482120       -0.785832        0.000310
C          -4.113720       -0.786915        0.000130
C          -3.415442        0.445700        0.000238
C          -4.138739        1.682192        0.000537
C          -5.547163        1.641942        0.000717
C          -6.198139        0.433038        0.000597
H          -6.025771       -1.720963        0.000228
H          -3.556550       -1.714746       -0.000091
C          -3.402901        2.892511        0.000629
H          -6.103350        2.570211        0.000929
H          -7.280203        0.407514        0.000725
C          -2.043701        2.869883        0.000410
H          -3.919042        3.842314        0.000855
H          -1.419741        3.750103        0.000451
H          -0.379534        1.672638       -0.000054
H          -1.404664       -0.391566       -0.000191
C          -2.019921        0.497717        0.000033
N          -1.393272        1.667609        0.000118
```

__Frequencies__ (First of 48)

```
  1.     154.3087 cm-1 (Symmetry: A)
```

***

4



Charge	0
Multiplicity	1
Stoichiometry	C9H7N
Electronic Energy (Eh)	-402.097157373
Sum of electronic and zero-point Energies (Eh)	-401.961522
Sum of electronic and thermal Energies (Eh)	-401.954851
Sum of electronic and enthalpy Energies (Eh)	-401.953907
Sum of electronic and thermal Free Energies (Eh)	-401.992686
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

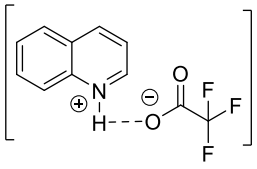
```xyz
C          -5.495587       -0.785788        0.000310
C          -4.124663       -0.770270        0.000130
C          -3.427747        0.460372        0.000234
C          -4.157203        1.682432        0.000526
C          -5.571701        1.634439        0.000706
C          -6.221755        0.426737        0.000600
H          -6.030183       -1.727244        0.000232
H          -3.560413       -1.695462       -0.000092
C          -3.409737        2.882953        0.000619
H          -6.130753        2.562454        0.000927
H          -7.304361        0.396423        0.000739
C          -2.041430        2.824919        0.000427
H          -3.918806        3.839003        0.000841
H          -1.449487        3.733021        0.000493
H          -1.435795       -0.382934       -0.000162
C          -2.012143        0.539068        0.000059
N          -1.336922        1.663118        0.000148
```

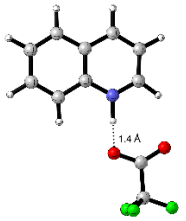
__Frequencies__ (First of 45)

```
  1.     170.6353 cm-1 (Symmetry: A)
```

***

57HB





Charge	0
Multiplicity	1
Stoichiometry	C11H8F3NO2
Electronic Energy (Eh)	-929.16626923
Sum of electronic and zero-point Energies (Eh)	-928.991938
Sum of electronic and thermal Energies (Eh)	-928.977501
Sum of electronic and enthalpy Energies (Eh)	-928.976557
Sum of electronic and thermal Free Energies (Eh)	-929.037213
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

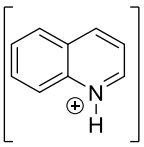
```xyz
C          -5.832821       -0.588867       -0.101128
C          -4.467508       -0.724134       -0.101039
C          -3.667208        0.432657       -0.039274
C          -4.259058        1.723213        0.022364
C          -5.670311        1.819542        0.020345
C          -6.437950        0.685789       -0.040230
H          -6.457105       -1.471709       -0.148093
H          -3.993462       -1.695729       -0.147098
C          -3.401040        2.843269        0.081772
H          -6.128575        2.799354        0.067218
H          -7.517436        0.761731       -0.041773
C          -2.038220        2.676974        0.079895
H          -3.833840        3.835210        0.128962
H          -1.363920        3.519850        0.124496
H          -0.453288        1.158433        0.013477
H          -1.833577       -0.685426       -0.082502
C           0.043023       -1.867944       -0.130275
O          -1.218331       -1.981365       -0.135684
O           0.732018       -0.853700       -0.089400
C           0.769129       -3.249299       -0.182150
F           2.105895       -3.137463       -0.190969
F           0.439822       -4.010649        0.885481
F           0.419884       -3.942592       -1.288749
C          -1.513456        1.380649        0.018623
N          -2.307074        0.328119       -0.037323
```

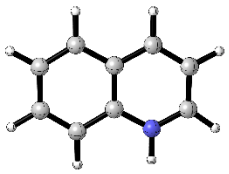
__Frequencies__ (First of 69)

```
  1.      20.3658 cm-1 (Symmetry: A)
```

***

5H





Charge	1
Multiplicity	1
Stoichiometry	C9H8N
Electronic Energy (Eh)	-402.5272905979999
Sum of electronic and zero-point Energies (Eh)	-402.377686
Sum of electronic and thermal Energies (Eh)	-402.370866
Sum of electronic and enthalpy Energies (Eh)	-402.369922
Sum of electronic and thermal Free Energies (Eh)	-402.40897
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -5.464733       -0.778006        0.000316
C          -4.091390       -0.774733        0.000116
C          -3.421316        0.457709        0.000221
C          -4.137981        1.685816        0.000522
C          -5.551946        1.636067        0.000710
```

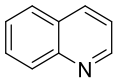
```
C          -6.198167        0.428395        0.000605
H          -5.994821       -1.721125        0.000245
H          -3.530315       -1.700418       -0.000110
C          -3.405115        2.889086        0.000618
H          -6.106533        2.565287        0.000923
H          -7.279138        0.391064        0.000746
C          -2.026858        2.878424        0.000415
C          -1.362254        1.657927        0.000120
H          -3.941894        3.829522        0.000842
H          -1.452274        3.792463        0.000479
H          -0.285547        1.570889       -0.000051
N          -2.052373        0.521062        0.000029
H          -1.541318       -0.356081       -0.000174
```

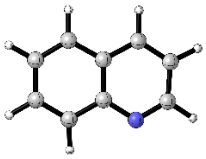
__Frequencies__ (First of 48)

```
  1.     164.1877 cm-1 (Symmetry: A)
```

***

5





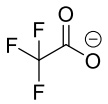
Charge	0
Multiplicity	1
Stoichiometry	C9H7N
Electronic Energy (Eh)	-402.09876158899993
Sum of electronic and zero-point Energies (Eh)	-401.963251
Sum of electronic and thermal Energies (Eh)	-401.956597
Sum of electronic and enthalpy Energies (Eh)	-401.955653
Sum of electronic and thermal Free Energies (Eh)	-401.994381
Number of Imaginary Frequencies	0

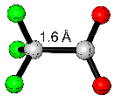
__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -5.462928       -0.773111        0.000311
C          -4.091866       -0.751214        0.000121
C          -3.395222        0.480457        0.000220
C          -4.141599        1.697193        0.000522
C          -5.555769        1.639877        0.000710
C          -6.202054        0.430870        0.000607
H          -5.988668       -1.719858        0.000234
H          -3.509922       -1.663978       -0.000106
C          -3.415282        2.909694        0.000616
H          -6.117634        2.566748        0.000936
H          -7.284195        0.393242        0.000752
C          -2.047210        2.872000        0.000417
C          -1.401590        1.614954        0.000121
H          -3.950676        3.852136        0.000843
H          -1.456898        3.778958        0.000481
H          -0.316277        1.571648       -0.000041
N          -2.033414        0.465002        0.000024
```

__Frequencies__ (First of 45)

```
  1.     173.7357 cm-1 (Symmetry: A)
```
***
7





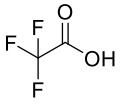
Charge	-1
Multiplicity	1
Stoichiometry	C2F3O2(1-)
Electronic Energy (Eh)	-526.556650103
Sum of electronic and zero-point Energies (Eh)	-526.531134
Sum of electronic and thermal Energies (Eh)	-526.525097
Sum of electronic and enthalpy Energies (Eh)	-526.524153
Sum of electronic and thermal Free Energies (Eh)	-526.562308
Number of Imaginary Frequencies	0

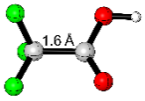
__Molecular Geometry in Cartesian Coordinates__

```xyz
C           0.282115       -0.810180        0.003078
O           0.757921        0.313277       -0.218067
O           0.801955       -1.919768        0.184110
C          -1.300828       -0.809363        0.017830
F          -1.826670        0.219787        0.732769
F          -1.861807       -1.933055        0.526088
F          -1.800791       -0.683189       -1.245807
```

__Frequencies__ (First of 15)

```
  1.      33.4327 cm-1 (Symmetry: A)
```
***
8





Charge	0
Multiplicity	1
Stoichiometry	C2HF3O2
Electronic Energy (Eh)	-527.040121737
Sum of electronic and zero-point Energies (Eh)	-527.001637
Sum of electronic and thermal Energies (Eh)	-526.995377
Sum of electronic and enthalpy Energies (Eh)	-526.994432
Sum of electronic and thermal Free Energies (Eh)	-527.033286
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           0.231091       -0.867220        0.083624
O           0.739847        0.314439       -0.256007
O           0.836608       -1.847787        0.397055
C          -1.318693       -0.807306        0.014308
F          -1.791272        0.145562        0.832758
F          -1.847021       -1.974104        0.374060
```

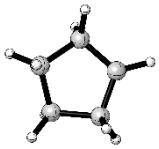
```
F          -1.720592       -0.523995       -1.235034
H           1.711064        0.264853       -0.212955
```

__Frequencies__ (First of 18)

```
  1.      22.1592 cm-1 (Symmetry: A)
```

***

9



Charge	0
Multiplicity	2
Stoichiometry	C5H9
Electronic Energy (Eh)	-195.982383829
Sum of electronic and zero-point Energies (Eh)	-195.857064
Sum of electronic and thermal Energies (Eh)	-195.851862
Sum of electronic and enthalpy Energies (Eh)	-195.850918
Sum of electronic and thermal Free Energies (Eh)	-195.885491
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

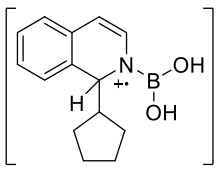
```xyz
C          -0.735039       -1.743075        0.285886
C           0.752971       -1.726886       -0.096952
C           1.230596       -0.322356        0.326747
C           0.007030        0.522799        0.183735
C          -1.214831       -0.310544       -0.026786
H          -1.303504       -2.510048       -0.242389
H          -0.837084       -1.936167        1.357873
H           0.855222       -1.835390       -1.180754
H           1.322803       -2.531814        0.369771
H           1.582250       -0.338335        1.370713
H           2.078054        0.037555       -0.266504
H           0.006022        1.603605        0.226646
H          -2.063655        0.000127        0.591782
H          -1.565210       -0.245241       -1.069279
```

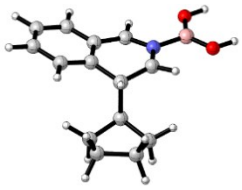
__Frequencies__ (First of 36)

```
  1.     170.4892 cm-1 (Symmetry: A)
```

***

14Lod9_C1





Datum	Value

Charge	1
Multiplicity	2
Stoichiometry	C14H18BNO2(1+,2)
Electronic Energy (Eh)	-774.671845011
Sum of electronic and zero-point Energies (Eh)	-774.367101
Sum of electronic and thermal Energies (Eh)	-774.35133
Sum of electronic and enthalpy Energies (Eh)	-774.350386
Sum of electronic and thermal Free Energies (Eh)	-774.411139
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

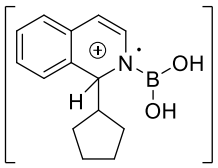
```xyz
C          -0.169569       -2.531142       -2.732538
C           0.505148       -1.219105       -3.204515
C           0.386848       -0.227579       -2.018795
C          -0.569277       -0.909003       -1.027796
C          -0.262588       -2.399828       -1.208166
H          -1.175385       -2.611189       -3.151139
H           0.377819       -3.421565       -3.041674
H           0.020752       -0.828125       -4.099161
H           1.551943       -1.385025       -3.460082
H           1.365601       -0.086294       -1.554125
H           0.032816        0.757258       -2.322360
H          -1.598089       -0.740454       -1.359995
H           0.709085       -2.645740       -0.767558
H          -1.009436       -3.051701       -0.755713
C           1.678753        0.342189        1.131523
C           1.419931        1.666741        0.800029
C           0.105460        2.090516        0.512221
C          -0.912806        1.105011        0.423754
H           0.561589        4.198647        0.434033
H           2.652033        0.053043        1.504012
H           2.229902        2.380837        0.855439
C          -0.224562        3.457252        0.367868
C          -2.223782        1.503462        0.225207
C          -2.534399        2.854414        0.097833
C          -1.531751        3.831560        0.159267
H          -3.011609        0.762754        0.167800
H          -3.564312        3.152585       -0.049930
H          -1.790019        4.876361        0.050458
H          -1.295660       -0.913393        0.998259
N           0.753157       -0.613767        1.079413
C          -0.549638       -0.353712        0.436169
B           1.022491       -1.947212        1.696745
O          -0.071930       -2.691526        1.973512
H           0.076433       -3.564296        2.354947
O           2.323849       -2.234969        1.934421
H           2.515075       -3.062007        2.391084
```

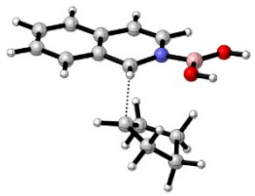
__Frequencies__ (First of 102)

```
  1.      44.6901 cm-1 (Symmetry: A)
```

***

14Lod9_C1_TS





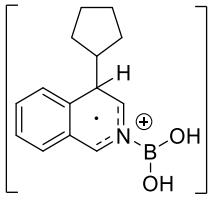
Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H18BNO2(1+,2)
Electronic Energy (Eh)	-774.6461139120001
Sum of electronic and zero-point Energies (Eh)	-774.344023
Sum of electronic and thermal Energies (Eh)	-774.328608
Sum of electronic and enthalpy Energies (Eh)	-774.327664
Sum of electronic and thermal Free Energies (Eh)	-774.386789
Number of Imaginary Frequencies	1

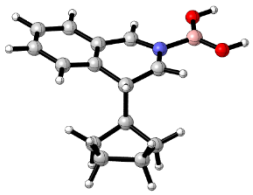
__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -2.169782       -2.027932       -0.979143
C          -1.112628       -0.919332       -0.866624
C          -1.949987        0.365707       -0.783500
C          -3.185120       -0.040864       -0.046729
C          -3.353140       -1.531849       -0.115033
H          -2.491947       -2.122425       -2.018283
H          -1.800587       -3.003297       -0.662613
H          -0.415307       -0.912233       -1.703824
H          -0.518337       -1.043724        0.041611
H          -1.433956        1.223785       -0.351034
H          -2.255606        0.679555       -1.792962
H          -4.051552        0.606315       -0.038664
H          -3.328405       -1.984287        0.879794
H          -4.329044       -1.793058       -0.533597
C          -0.491966        1.196923        2.307460
C          -0.804649        2.501613        2.124299
C          -2.166277        2.915841        2.038619
C          -3.169127        1.911307        2.091863
H          -1.789412        5.030977        1.893941
H           0.523397        0.853945        2.422742
H          -0.010296        3.233635        2.077977
C          -2.551992        4.263745        1.935365
C          -4.528284        2.278077        2.058021
C          -4.879533        3.604354        1.965109
C          -3.886999        4.599437        1.896803
H          -5.289359        1.509346        2.108490
H          -5.923521        3.887714        1.945275
H          -4.179310        5.638575        1.818903
H          -3.499374       -0.211142        2.417782
N          -1.465258        0.220197        2.386979
C          -2.775399        0.543191        2.153251
B          -1.079459       -1.171642        2.769979
O          -2.101647       -2.027593        3.007781
H          -1.868057       -2.928298        3.259460
O           0.248921       -1.412236        2.844238
H           0.522888       -2.292944        3.123962
```

__Frequencies__ (First of 102)

```
  1.    -191.3104 cm-1 (Symmetry: A)  *
```
***
14Lod9_C4





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H18BNO2(1+,2)
Electronic Energy (Eh)	-774.654142384
Sum of electronic and zero-point Energies (Eh)	-774.350282
Sum of electronic and thermal Energies (Eh)	-774.334544
Sum of electronic and enthalpy Energies (Eh)	-774.3336
Sum of electronic and thermal Free Energies (Eh)	-774.394746
Number of Imaginary Frequencies	0

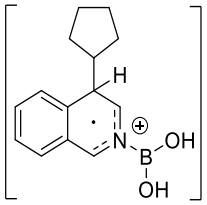
__Molecular Geometry in Cartesian Coordinates__

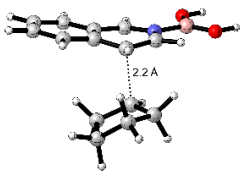
```xyz
C          -1.756817       -2.928107       -1.859285
C          -0.393485       -3.595312       -1.534072
C           0.660003       -2.475532       -1.670040
C          -0.118838       -1.165672       -1.450524
C          -1.428553       -1.461716       -2.194632
H          -2.270519       -3.418252       -2.685848
H          -2.427066       -2.985433       -0.999263
H          -0.171112       -4.427175       -2.201733
H          -0.396164       -4.002527       -0.521369
H           1.512040       -2.611266       -1.003928
H           1.057968       -2.457707       -2.686995
H           0.396900       -0.300273       -1.871412
H          -2.238362       -0.770931       -1.969009
H          -1.219154       -1.359479       -3.262590
C           1.000173       -0.639897        0.689373
C          -0.337874       -0.852928        0.099706
C          -1.220452        0.346698        0.319297
C          -0.608155        1.619045        0.423523
H          -3.083714       -0.705502        0.322829
H           1.632539       -1.469188        0.960853
H          -0.784227       -1.743727        0.545721
C          -2.602478        0.262814        0.366674
C          -1.402730        2.784310        0.482714
C          -2.777448        2.678808        0.488775
C          -3.377240        1.417337        0.450668
H          -0.921623        3.751781        0.551985
H          -3.390528        3.568574        0.540253
H          -4.455946        1.334258        0.478227
H           1.307793        2.644684        0.644240
C           0.790027        1.701734        0.578970
N           1.537473        0.580369        0.793999
B           2.997939        0.727875        1.197740
O           3.671785       -0.429248        1.334966
H           4.593929       -0.377487        1.613099
O           3.418538        1.996043        1.358162
```

```
H           4.344063        2.132828        1.593015
```

__Frequencies__ (First of 102)

```
  1.      38.9401 cm-1 (Symmetry: A)
```
14Lod9_C4_TS





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H18BNO2(1+,2)
Electronic Energy (Eh)	-774.634312025
Sum of electronic and zero-point Energies (Eh)	-774.333276
Sum of electronic and thermal Energies (Eh)	-774.317489
Sum of electronic and enthalpy Energies (Eh)	-774.316545
Sum of electronic and thermal Free Energies (Eh)	-774.377749
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -1.055595       -1.182263       -0.765707
C          -0.320719       -2.064335        0.255539
C           1.059069       -1.400980        0.368843
C           0.760635        0.065805        0.250672
C          -0.516753        0.247915       -0.518271
H          -0.797603       -1.500574       -1.777929
H          -2.139778       -1.241192       -0.673359
H          -0.263844       -3.109275       -0.047524
H          -0.832020       -2.033018        1.221967
H           1.622664       -1.674909        1.262890
H           1.682346       -1.690512       -0.489231
H           1.569613        0.768814        0.094734
H          -1.238162        0.863054        0.027702
H          -0.324115        0.793849       -1.446649
C           1.723420        0.906687        2.681379
C           0.391985        0.663956        2.347850
C          -0.513564        1.786169        2.329900
C           0.051498        3.093291        2.302632
H          -2.337579        0.651989        2.347983
H           2.416117        0.108013        2.889388
H          -0.006520       -0.314957        2.572746
C          -1.904524        1.643445        2.308894
C          -0.799542        4.219243        2.208902
C          -2.163200        4.048177        2.177676
C          -2.719113        2.759468        2.240928
H          -0.366010        5.210902        2.181557
H          -2.814879        4.909683        2.115131
H          -3.794438        2.639558        2.228618
H           1.921015        4.200250        2.416730
C           1.440798        3.235194        2.429548
N           2.238346        2.158492        2.659343
```

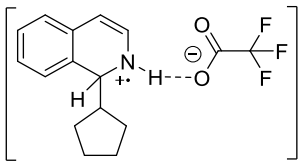
```
B           3.715573        2.362545        2.911923
O           4.436179        1.234140        3.077345
H           5.377752        1.333726        3.259629
O           4.125106        3.646682        2.935232
H           5.063527        3.810048        3.084838
```

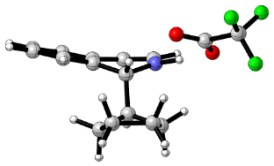
__Frequencies__ (First of 102)

```
  1.    -328.2396 cm-1 (Symmetry: A)  *
```

***

47HB9_C1_otro





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2
Electronic Energy (Eh)	-1125.17302914
Sum of electronic and zero-point Energies (Eh)	-1124.866004
Sum of electronic and thermal Energies (Eh)	-1124.846238
Sum of electronic and enthalpy Energies (Eh)	-1124.845294
Sum of electronic and thermal Free Energies (Eh)	-1124.918772
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -2.022950       -0.473663       -2.476782
C          -0.628008       -1.152774       -2.510961
C           0.398635       -0.008876       -2.351480
C          -0.382809        1.154390       -1.712215
C          -1.737744        1.036669       -2.422925
H          -2.639041       -0.735742       -3.337498
H          -2.575071       -0.788953       -1.588668
H          -0.462129       -1.698813       -3.439967
H          -0.530031       -1.867899       -1.695609
H           1.281801       -0.315889       -1.795014
H           0.742212        0.328534       -3.332568
H           0.093396        2.119437       -1.900831
H          -2.537940        1.617783       -1.968167
H          -1.604878        1.426566       -3.436001
C           1.451991        2.114988        0.829498
C           0.739926        3.306040        1.018018
C          -0.674316        3.293862        0.921328
C          -1.312062        2.108868        0.467451
H          -0.963487        5.282308        1.703856
H           2.499371        2.037405        1.095976
H           1.263022        4.188554        1.358587
C          -1.458385        4.379733        1.367110
C          -2.692826        2.012505        0.549787
C          -3.450656        3.084070        1.013103
C          -2.832681        4.276263        1.403073
H          -3.183810        1.094530        0.254012
H          -4.527441        2.990898        1.072488
```

```
H          -3.432021        5.107140        1.751785
H           1.427015        0.095719        0.367293
H          -0.883792        0.031063        0.097631
N           0.880543        1.032098        0.376381
C          -0.480113        1.016635       -0.140466
C           1.274983       -2.146249        0.634848
O           0.062190       -2.043929        0.809277
O           2.135430       -1.248870        0.418282
C           1.891410       -3.582783        0.648068
F           2.916617       -3.678436        1.522680
F           1.003455       -4.535055        0.976446
F           2.380338       -3.902385       -0.574025
```

__Frequencies__ (First of 111)

```
  1.      15.4646 cm-1 (Symmetry: A)
```

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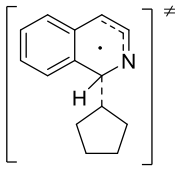
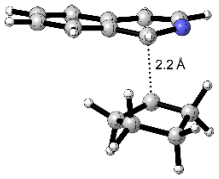
49_C1_TS





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.071878379
Sum of electronic and zero-point Energies (Eh)	-597.808607
Sum of electronic and thermal Energies (Eh)	-597.796328
Sum of electronic and enthalpy Energies (Eh)	-597.795384
Sum of electronic and thermal Free Energies (Eh)	-597.849103
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -3.666208       -1.330818       -1.077426
C          -2.280198       -1.897791       -1.423386
C          -1.275342       -0.904920       -0.789508
C          -2.065318        0.361019       -0.550239
C          -3.443597        0.187018       -1.114433
H          -4.447335       -1.666550       -1.760829
H          -3.960330       -1.636316       -0.068887
H          -2.155243       -1.909419       -2.509366
H          -2.139430       -2.920110       -1.070350
H          -0.854875       -1.287228        0.144231
H          -0.417103       -0.716540       -1.441629
H          -1.573650        1.322852       -0.633009
H          -4.207914        0.769245       -0.597564
H          -3.446229        0.538826       -2.157160
C          -0.340166        1.807903        2.063913
C          -1.055553        2.989792        2.043609
C          -2.470889        2.943794        1.956809
C          -3.074407        1.666279        1.803880
H          -2.841793        5.058780        2.172031
```

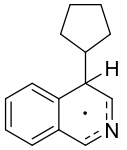
```
H           0.733117        1.829741        2.226153
H          -0.548453        3.939029        2.163475
C          -3.299964        4.082723        2.064043
C          -4.474929        1.557746        1.813203
C          -5.264052        2.682768        1.935996
C          -4.669953        3.952258        2.049278
H          -4.930043        0.577884        1.731383
H          -6.342835        2.591038        1.946444
H          -5.297551        4.830495        2.137796
H          -2.648225       -0.457020        1.685563
N          -0.882423        0.593232        1.912339
C          -2.202500        0.531421        1.627451
```

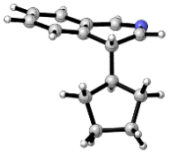
__Frequencies__ (First of 87)

```
  1.    -415.2391 cm-1 (Symmetry: A)  *
```

***

49_C4





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.099126705
Sum of electronic and zero-point Energies (Eh)	-597.8332
Sum of electronic and thermal Energies (Eh)	-597.820858
Sum of electronic and enthalpy Energies (Eh)	-597.819914
Sum of electronic and thermal Free Energies (Eh)	-597.873557
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -0.685025       -2.563651       -2.476884
C           0.573144       -3.355055       -2.042363
C           1.124869       -2.619993       -0.795363
C           0.339881       -1.296136       -0.711184
C          -1.033768       -1.679062       -1.274573
H          -0.451903       -1.929536       -3.335994
H          -1.510177       -3.212929       -2.773633
H           1.311165       -3.390906       -2.844862
H           0.323969       -4.389350       -1.799639
H           0.929839       -3.207929        0.106770
H           2.202098       -2.460980       -0.844117
H           0.798484       -0.566163       -1.387396
H          -1.584593       -2.257596       -0.524183
H          -1.645663       -0.818264       -1.542049
C           1.749728       -0.456845        1.162590
C           0.329454       -0.661679        0.716044
C          -0.430396        0.643197        0.746581
C           0.305017        1.845467        0.638919
H          -2.382928       -0.214408        0.932880
H           2.303303       -1.318135        1.523362
```

```
H          -0.153094       -1.393616        1.373834
C          -1.816040        0.702195        0.824831
C          -0.381336        3.070976        0.549570
C          -1.762648        3.106775        0.598521
C          -2.483980        1.921386        0.752596
H           0.187894        3.989131        0.461017
H          -2.283913        4.053584        0.531666
H          -3.564830        1.948187        0.811717
H           2.320012        2.683350        0.566260
C           1.732836        1.782704        0.705941
N           2.400852        0.670161        1.065394
```

__Frequencies__ (First of 87)

```
  1.      34.9016 cm-1 (Symmetry: A)
```

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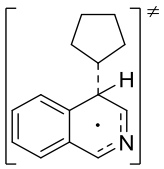
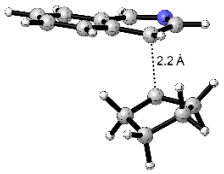
49_C4_TS





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.068603737
Sum of electronic and zero-point Energies (Eh)	-597.805575
Sum of electronic and thermal Energies (Eh)	-597.793249
Sum of electronic and enthalpy Energies (Eh)	-597.792304
Sum of electronic and thermal Free Energies (Eh)	-597.846012
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -1.070238       -1.352416       -0.789655
C          -0.181979       -2.144180        0.181484
C           1.091822       -1.291549        0.267128
C           0.578025        0.122351        0.217097
C          -0.755561        0.131813       -0.485692
H          -0.783603       -1.587846       -1.817961
H          -2.130343       -1.588408       -0.686373
H           0.007909       -3.166161       -0.149189
H          -0.656182       -2.201271        1.165916
H           1.710555       -1.505424        1.140863
H           1.723719       -1.481068       -0.612622
H           1.271587        0.934253        0.037962
H          -1.533256        0.583337        0.138285
H          -0.723486        0.744514       -1.391657
C           1.653277        0.871914        2.700142
C           0.303784        0.656383        2.355134
C          -0.552625        1.809771        2.322896
C           0.073917        3.085559        2.288864
H          -2.437657        0.769523        2.360394
H           2.296595        0.028906        2.925486
```

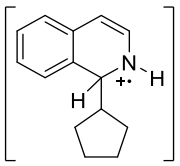
```
H          -0.140249       -0.309358        2.560925
C          -1.956348        1.738243        2.298267
C          -0.723885        4.246276        2.182276
C          -2.095521        4.147110        2.139834
C          -2.716495        2.887472        2.212426
H          -0.240628        5.215821        2.149073
H          -2.702594        5.040574        2.063378
H          -3.797184        2.820664        2.199427
H           1.990778        4.097086        2.386170
C           1.487224        3.135729        2.424325
N           2.239093        2.072259        2.672725
```

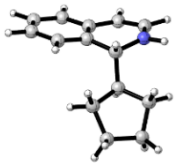
__Frequencies__ (First of 87)

```
  1.    -436.0703 cm-1 (Symmetry: A)  *
```

***

4H9_C1





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.541165986
Sum of electronic and zero-point Energies (Eh)	-598.259956
Sum of electronic and thermal Energies (Eh)	-598.247601
Sum of electronic and enthalpy Energies (Eh)	-598.246657
Sum of electronic and thermal Free Energies (Eh)	-598.300038
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -0.753123       -2.541114       -2.624310
C           0.776149       -2.769329       -2.635889
C           1.251197       -2.332923       -1.246423
C           0.342099       -1.136816       -0.930005
C          -1.039616       -1.601623       -1.424775
H          -1.093087       -2.104558       -3.563093
H          -1.289171       -3.482436       -2.501437
H           1.246878       -2.137186       -3.392112
H           1.048785       -3.799596       -2.863814
H           1.075041       -3.131290       -0.515837
H           2.314419       -2.087903       -1.227991
H           0.675359       -0.275113       -1.517243
H          -1.541626       -2.156017       -0.627643
H          -1.685841       -0.766379       -1.689235
C           2.364059        0.631309        1.099381
C           1.649257        1.823917        1.026166
C           0.238596        1.802357        0.938053
C          -0.427436        0.549878        0.822232
H          -0.002151        3.937497        1.126458
H           3.429501        0.618049        1.287490
H           2.183242        2.758785        1.117750
```

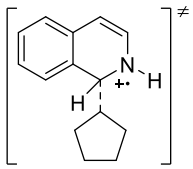
```
C          -0.519503        2.989878        1.047990
C          -1.810290        0.515284        0.887709
C          -2.539998        1.694325        1.015011
C          -1.894407        2.934140        1.078543
H          -2.331340       -0.430785        0.836885
H          -3.620058        1.648078        1.065232
H          -2.475475        3.842267        1.166492
H           2.321654       -1.376875        1.033331
H          -0.035570       -1.532108        1.157381
N           1.764814       -0.534138        0.970604
C           0.367435       -0.704196        0.567812
```

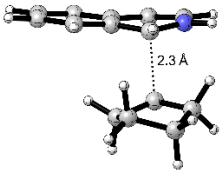
__Frequencies__ (First of 90)

```
  1.      37.8630 cm-1 (Symmetry: A)
```

***

4H9_C1_TS





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.514447784
Sum of electronic and zero-point Energies (Eh)	-598.236809
Sum of electronic and thermal Energies (Eh)	-598.224441
Sum of electronic and enthalpy Energies (Eh)	-598.223496
Sum of electronic and thermal Free Energies (Eh)	-598.277162
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -3.707912       -1.271959       -1.112530
C          -2.350321       -1.901176       -1.460240
C          -1.302915       -0.955873       -0.822781
C          -2.031337        0.343223       -0.600708
C          -3.413854        0.233254       -1.147944
H          -4.501806       -1.566943       -1.797441
H          -4.019678       -1.565608       -0.105405
H          -2.219457       -1.910757       -2.544102
H          -2.253556       -2.928577       -1.111291
H          -0.906451       -1.378492        0.106932
H          -0.428285       -0.801519       -1.461453
H          -1.501227        1.287761       -0.630814
H          -4.146559        0.864493       -0.643810
H          -3.383939        0.585377       -2.190676
C          -0.288232        1.910187        2.122597
C          -1.059413        3.030339        2.136276
C          -2.477028        2.925674        2.034537
C          -3.050205        1.635944        1.838330
H          -2.899300        5.019391        2.306733
H           0.782211        1.918456        2.261865
```

```
H          -0.593505        3.995307        2.277260
C          -3.330201        4.036790        2.162950
C          -4.448392        1.487907        1.812394
C          -5.258493        2.591423        1.957359
C          -4.696210        3.869820        2.121521
H          -4.878308        0.502208        1.690703
H          -6.334170        2.476636        1.946575
H          -5.346933        4.728131        2.226511
H          -0.264587       -0.126767        1.955893
H          -2.553539       -0.486649        1.700194
N          -0.862317        0.688310        1.950084
C          -2.177686        0.524698        1.651220
```

__Frequencies__ (First of 90)

```
  1.    -236.0159 cm-1 (Symmetry: A)  *
```

***

4H9_C4

Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.525612628
Sum of electronic and zero-point Energies (Eh)	-598.244633
Sum of electronic and thermal Energies (Eh)	-598.232591
Sum of electronic and enthalpy Energies (Eh)	-598.231647
Sum of electronic and thermal Free Energies (Eh)	-598.283519
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -1.089032       -2.560681       -1.644909
C           0.138252       -3.424545       -1.251196
C           1.351187       -2.465401       -1.263830
C           0.752317       -1.053156       -1.124319
C          -0.519895       -1.172040       -1.974818
H          -1.639248       -2.978716       -2.487357
H          -1.793694       -2.495146       -0.813165
H           0.292593       -4.253443       -1.941276
H           0.000145       -3.866242       -0.263070
H           2.090166       -2.716487       -0.502194
H           1.863763       -2.519533       -2.226292
H           1.416502       -0.278805       -1.512766
H          -1.231736       -0.361163       -1.834641
H          -0.204769       -1.135730       -3.020982
C           1.795386       -0.500012        1.036377
C           0.471264       -0.696615        0.407895
C          -0.405169        0.518587        0.586206
C           0.195577        1.790912        0.763899
H          -2.263672       -0.527777        0.427606
H           2.454890       -1.319986        1.274394
H          -0.007744       -1.572761        0.850066
C          -1.787596        0.438353        0.532013
C          -0.602027        2.953845        0.799495
C          -1.973600        2.849787        0.705705
C          -2.567668        1.590469        0.591115
```

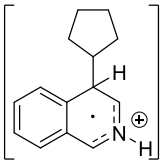
```
H          -0.127915        3.918712        0.928472
H          -2.589477        3.738477        0.738315
H          -3.645466        1.507104        0.540414
H           3.240262        0.807511        1.531596
H           2.112486        2.789668        1.175098
C           1.580876        1.863623        1.019203
N           2.281417        0.720152        1.208403
```

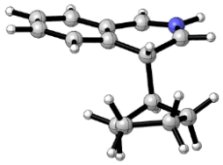
__Frequencies__ (First of 90)

```
  1.      67.0768 cm-1 (Symmetry: A)
```

***

4H9_C4_TS





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.505482466
Sum of electronic and zero-point Energies (Eh)	-598.227802
Sum of electronic and thermal Energies (Eh)	-598.215516
Sum of electronic and enthalpy Energies (Eh)	-598.214572
Sum of electronic and thermal Free Energies (Eh)	-598.267621
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -1.110296       -1.222659       -0.752681
C          -0.356949       -2.087502        0.270004
C           1.022735       -1.418915        0.351666
C           0.718771        0.044966        0.215630
C          -0.568984        0.211927       -0.538372
H          -0.869815       -1.557468       -1.763797
H          -2.192590       -1.281187       -0.640508
H          -0.301612       -3.136601       -0.018459
H          -0.853068       -2.043925        1.243956
H           1.600859       -1.678527        1.240917
H           1.633353       -1.720221       -0.511505
H           1.522488        0.750511        0.043790
H          -1.282760        0.837683        0.005433
H          -0.389258        0.740548       -1.479376
C           1.727959        0.913793        2.651487
C           0.392999        0.669181        2.321854
C          -0.507789        1.796745        2.300594
C           0.045822        3.111278        2.272068
H          -2.327199        0.654429        2.319107
H           2.444214        0.133823        2.855872
H          -0.010393       -0.305766        2.553103
C          -1.899570        1.648014        2.277297
C          -0.811167        4.230280        2.176350
C          -2.173642        4.050104        2.141663
C          -2.720540        2.757862        2.205616
```

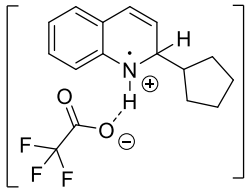
```
H          -0.384496        5.224869        2.149000
H          -2.830776        4.907183        2.076488
H          -3.794987        2.630664        2.192222
H           3.187863        2.312817        2.794835
H           1.935604        4.214950        2.406168
C           1.437145        3.257949        2.405630
N           2.198485        2.171916        2.624507
```

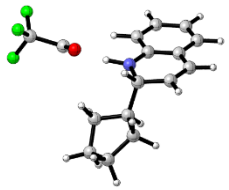
__Frequencies__ (First of 90)

```
  1.    -324.9488 cm-1 (Symmetry: A)  *
```

***

57HB9_C2





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2(2)
Electronic Energy (Eh)	-1125.16880715
Sum of electronic and zero-point Energies (Eh)	-1124.86266
Sum of electronic and thermal Energies (Eh)	-1124.842549
Sum of electronic and enthalpy Energies (Eh)	-1124.841604
Sum of electronic and thermal Free Energies (Eh)	-1124.916724
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           2.201851       -1.091107       -2.963480
C           3.581071       -0.594120       -2.488763
C           3.291386        0.565175       -1.498210
C           1.751267        0.661682       -1.404259
C           1.261684       -0.733640       -1.811178
H           1.896254       -0.555550       -3.867297
H           2.194399       -2.156085       -3.198648
H           4.211558       -0.276169       -3.319893
H           4.111447       -1.397687       -1.975185
H           3.712150        0.337182       -0.515897
H           3.731296        1.508897       -1.821860
H           1.383445        1.391547       -2.132268
H           1.398639       -1.427344       -0.977991
H           0.207800       -0.755266       -2.086600
C           1.791840        2.495813        0.310534
C           0.998929        3.572928        0.443709
C          -0.429216        3.451208        0.355268
C          -0.982127        2.133976        0.193213
H          -0.895995        5.527443        0.589565
H           2.866633        2.588349        0.386015
H           1.421128        4.551720        0.636321
C          -1.303917        4.531805        0.467164
C          -2.394084        1.951865        0.186980
C          -3.214520        3.041726        0.302120
```

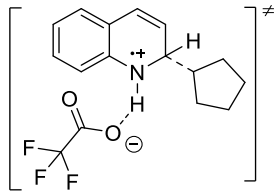
```
C          -2.674597        4.338377        0.435745
H          -2.787512        0.948689        0.089118
H          -4.288344        2.908726        0.291989
H          -3.340575        5.186658        0.524538
H           1.628461        0.397874        0.719332
C           1.260808        1.144105        0.001622
N          -0.180918        1.081382        0.066931
H          -0.626653        0.098440        0.097498
C          -0.535342       -1.976582        1.010128
O          -1.304978       -1.268408        0.305598
O           0.571402       -1.706911        1.474301
C          -1.109522       -3.404696        1.284332
F          -0.336975       -4.138462        2.101725
F          -2.337623       -3.347446        1.846545
F          -1.234428       -4.100082        0.128804
```

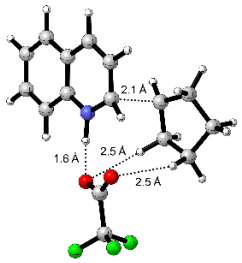
__Frequencies__ (First of 111)

```
  1.      14.8754 cm-1 (Symmetry: A)
```

***

57HB9_C2_TS





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2(2)
Electronic Energy (Eh)	-1125.15027351
Sum of electronic and zero-point Energies (Eh)	-1124.846312
Sum of electronic and thermal Energies (Eh)	-1124.826372
Sum of electronic and enthalpy Energies (Eh)	-1124.825428
Sum of electronic and thermal Free Energies (Eh)	-1124.89961
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           0.107720       -2.424575       -0.653867
C           1.412424       -1.703320       -1.016023
C           1.256170       -0.307819       -0.372187
C          -0.236973       -0.064406       -0.348331
C          -0.948152       -1.317717       -0.780200
H          -0.102512       -3.280153       -1.295610
H           0.141311       -2.782230        0.376687
H           1.492028       -1.600616       -2.101898
H           2.304226       -2.223964       -0.666228
H           1.664692       -0.328657        0.643904
H           1.791860        0.482420       -0.902335
H          -0.628018        0.890492       -0.678656
H          -1.873364       -1.519936       -0.240514
```

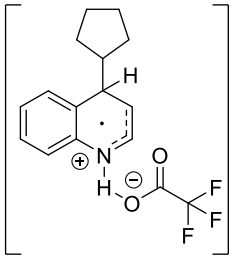
```
H          -1.232951       -1.183837       -1.833629
C          -0.138926        1.580168        1.862197
C          -0.896919        2.707547        1.884565
C          -2.318890        2.628764        1.784873
C          -2.912270        1.338032        1.731231
H          -2.713909        4.741796        1.813902
H           0.938652        1.625903        1.925344
H          -0.433866        3.681300        1.986587
C          -3.159905        3.755732        1.771372
C          -4.311223        1.197376        1.678490
C          -5.101132        2.323511        1.666147
C          -4.527885        3.607683        1.709567
H          -4.742274        0.205132        1.647556
H          -6.177611        2.219588        1.622598
H          -5.167823        4.480305        1.699422
H          -0.268231       -0.619054        1.986166
C          -0.758615        0.302832        1.698358
N          -2.109836        0.238201        1.760868
H          -2.550244       -0.734546        1.813654
C          -2.176069       -2.980324        2.226479
O          -3.099707       -2.212324        1.850033
O          -1.028389       -2.713479        2.585705
C          -2.568885       -4.491995        2.161269
F          -1.690984       -5.294830        2.785017
F          -3.780129       -4.732771        2.703082
F          -2.624581       -4.898132        0.867110
```

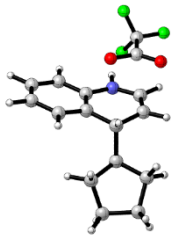
__Frequencies__ (First of 111)

```
  1.    -282.9619 cm-1 (Symmetry: A)  *
```

***

57HB9_C4





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2(2)
Electronic Energy (Eh)	-1125.16810526
Sum of electronic and zero-point Energies (Eh)	-1124.862429
Sum of electronic and thermal Energies (Eh)	-1124.842432
Sum of electronic and enthalpy Energies (Eh)	-1124.841488
Sum of electronic and thermal Free Energies (Eh)	-1124.916301
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -2.245462       -4.397585       -2.950368
C          -1.052984       -5.221168       -2.418255
```

```
C          -0.468503       -4.401514       -1.238971
C          -1.276493       -3.085763       -1.197888
C          -2.635954       -3.484591       -1.784737
H          -1.932620       -3.784461       -3.799572
H          -3.072806       -5.021598       -3.290937
H          -0.310444       -5.400213       -3.196258
H          -1.386491       -6.199757       -2.069251
H          -0.604126       -4.942257       -0.298113
H           0.600214       -4.218209       -1.348757
H          -0.811683       -2.357529       -1.869674
H          -3.208686       -4.047277       -1.039234
H          -3.238336       -2.632463       -2.096555
C           0.086224       -2.232499        0.685799
C          -1.317769       -2.426622        0.233608
C          -2.093154       -1.133568        0.237835
C          -1.400196        0.097108        0.267525
H          -4.040063       -2.018293        0.203258
H           0.686599       -3.100429        0.916497
H          -1.817387       -3.158461        0.878917
C          -3.481243       -1.092210        0.187934
C          -2.082344        1.323163        0.177977
C          -3.458834        1.326983        0.097110
C          -4.160800        0.118846        0.118960
H          -1.514454        2.244427        0.195832
H          -3.993506        2.265438        0.034399
H          -5.242582        0.123563        0.081984
H           1.713916       -0.824758        0.937404
C           0.669865       -0.998574        0.710147
N          -0.038492        0.112765        0.447243
H           0.492618        1.079554        0.461995
C           2.428317        2.181459        0.748808
O           3.028342        1.133086        0.968592
O           1.205269        2.367975        0.487615
C           3.244917        3.512955        0.782211
F           2.756648        4.361329        1.715348
F           4.544457        3.326099        1.060944
F           3.182187        4.152726       -0.407747
```

__Frequencies__ (First of 111)

```
  1.      13.8607 cm-1 (Symmetry: A)
```

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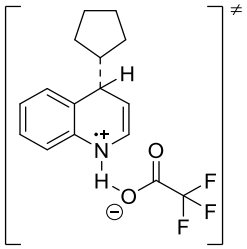
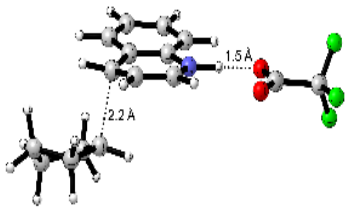
57HB9_C4_TS





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2(2)
Electronic Energy (Eh)	-1125.14532203
Sum of electronic and zero-point Energies (Eh)	-1124.842117

Sum of electronic and thermal Energies (Eh)	-1124.821987
Sum of electronic and enthalpy Energies (Eh)	-1124.821043
Sum of electronic and thermal Free Energies (Eh)	-1124.897046
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -1.041933       -1.337147       -0.788603
C          -0.191798       -2.143047        0.205582
C           1.096936       -1.317237        0.317935
C           0.621747        0.105028        0.239003
C          -0.681588        0.142091       -0.509421
H          -0.755500       -1.598692       -1.809845
H          -2.109804       -1.533522       -0.690753
H          -0.012231       -3.167860       -0.119458
H          -0.688106       -2.192019        1.179221
H           1.702164       -1.539937        1.197371
H           1.738676       -1.509445       -0.554148
H           1.336901        0.904516        0.096806
H          -1.463067        0.648618        0.063225
H          -0.576618        0.730643       -1.425691
C           1.638170        0.823748        2.750818
C           0.293206        0.645119        2.362447
C          -0.549528        1.808925        2.314585
C           0.064208        3.085797        2.356482
H          -2.434261        0.777996        2.215108
H           2.277144       -0.023894        2.949007
H          -0.182802       -0.313316        2.523832
C          -1.949913        1.746447        2.208165
C          -0.704272        4.257046        2.240197
C          -2.071312        4.156326        2.115783
C          -2.699826        2.899803        2.113851
H          -0.208638        5.218738        2.267368
H          -2.668641        5.055075        2.033697
H          -3.777718        2.839277        2.038644
H           3.211674        2.308968        3.003962
C           2.172709        2.094304        2.789291
N           1.416843        3.169574        2.553346
H           1.890538        4.145737        2.580404
C           3.805692        5.350791        2.806450
O           4.447486        4.316864        2.983540
O           2.570417        5.506972        2.604795
C           4.590393        6.703068        2.816877
F           4.104343        7.546833        3.755434
F           5.901611        6.552807        3.065891
F           4.485070        7.334735        1.624157
```

__Frequencies__ (First of 111)

```
  1.    -299.9251 cm-1 (Symmetry: A)  *
```

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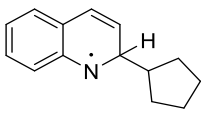
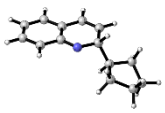
59_C2





Datum	Value

Charge	0
Multiplicity	2
Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.093186304
Sum of electronic and zero-point Energies (Eh)	-597.827414
Sum of electronic and thermal Energies (Eh)	-597.815176
Sum of electronic and enthalpy Energies (Eh)	-597.814232
Sum of electronic and thermal Free Energies (Eh)	-597.867929
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           2.082594       -3.451303       -1.399705
C           3.164317       -2.415028       -1.731428
C           2.881907       -1.287617       -0.736526
C           1.346789       -1.175279       -0.743371
C           0.838830       -2.619838       -1.005740
H           1.885822       -4.137514       -2.224935
H           2.411579       -4.057689       -0.551427
H           3.033413       -2.044766       -2.753274
H           4.178475       -2.811808       -1.654323
H           3.230041       -1.582090        0.260415
H           3.377036       -0.350494       -0.994125
H           1.050033       -0.531563       -1.576105
H           0.348361       -3.026647       -0.120883
H           0.088865       -2.619742       -1.796633
C           1.362146        0.800081        0.832199
C           0.625109        1.917311        0.890601
C          -0.802920        1.855013        0.708189
C          -1.391115        0.552228        0.504397
H          -1.170855        3.954821        0.894028
H           2.433533        0.836117        0.985924
H           1.081664        2.881275        1.086658
C          -1.622086        2.980703        0.741552
C          -2.810684        0.476647        0.357033
C          -3.587621        1.608342        0.395639
C          -2.997916        2.870694        0.586228
H          -3.245334       -0.503793        0.209518
H          -4.661505        1.531314        0.278109
H          -3.618137        3.757522        0.614361
H           1.028301       -1.227327        1.356853
C           0.749079       -0.534360        0.545048
N          -0.692202       -0.574743        0.448715
```

__Frequencies__ (First of 87)

```
  1.      25.7958 cm-1 (Symmetry: A)
```

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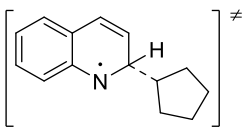
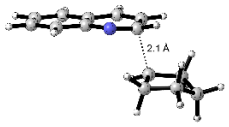
59_C2_TS





Datum	Value
Charge	0
Multiplicity	2

Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.070218032
Sum of electronic and zero-point Energies (Eh)	-597.806894
Sum of electronic and thermal Energies (Eh)	-597.794643
Sum of electronic and enthalpy Energies (Eh)	-597.793699
Sum of electronic and thermal Free Energies (Eh)	-597.847394
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

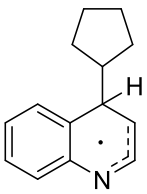
```xyz
C           0.170505       -2.397459        0.029981
C           1.475542       -1.681752       -0.343880
C           1.244648       -0.220794        0.103000
C          -0.261189       -0.036151        0.072184
C          -0.905505       -1.350533       -0.289325
H           0.027336       -3.335776       -0.507519
H           0.159232       -2.627648        1.099664
H           1.613760       -1.719458       -1.428076
H           2.359640       -2.127222        0.114831
H           1.641258       -0.073741        1.113181
H           1.759290        0.504185       -0.531931
H          -0.669095        0.870202       -0.359052
H          -1.853953       -1.509470        0.225205
H          -1.122342       -1.355541       -1.366421
C          -0.274034        1.682590        2.241428
C          -1.012725        2.816132        2.160961
C          -2.416547        2.725798        1.922882
C          -2.989088        1.414141        1.853115
H          -2.806890        4.839624        1.846781
H           0.792530        1.719922        2.420118
H          -0.558025        3.792381        2.284714
C          -3.249685        3.851318        1.793139
C          -4.391203        1.299737        1.671927
C          -5.177115        2.419248        1.546007
C          -4.606937        3.706311        1.603074
H          -4.815384        0.304443        1.630267
H          -6.245428        2.314736        1.400672
H          -5.238610        4.579848        1.502347
H          -0.388182       -0.483311        2.384681
C          -0.908841        0.403753        2.034711
N          -2.252914        0.286971        1.974718
```

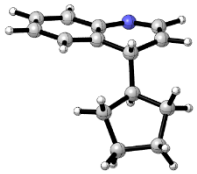
__Frequencies__ (First of 87)

```
  1.    -444.1848 cm-1 (Symmetry: A)  *
```

***

59_C4





Datum	Value
Charge	0
Multiplicity	2

Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.09774326
Sum of electronic and zero-point Energies (Eh)	-597.831329
Sum of electronic and thermal Energies (Eh)	-597.819183
Sum of electronic and enthalpy Energies (Eh)	-597.818238
Sum of electronic and thermal Free Energies (Eh)	-597.871171
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

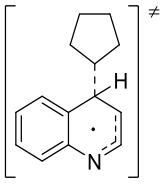
```xyz
C          -0.729742       -2.639961       -2.438359
C           0.470768       -3.475442       -1.942334
C           1.106778       -2.654042       -0.791166
C           0.330354       -1.319718       -0.739070
C          -1.056088       -1.702707       -1.272314
H          -0.441003       -2.044724       -3.308884
H          -1.579512       -3.255727       -2.737437
H           1.182537       -3.669927       -2.745647
H           0.137608       -4.447975       -1.575456
H           0.986296       -3.180076        0.160335
H           2.175996       -2.497338       -0.932691
H           0.784175       -0.615693       -1.444363
H          -1.611705       -2.243047       -0.497410
H          -1.654375       -0.843423       -1.572210
C           1.783467       -0.443995        1.077726
C           0.361735       -0.637672        0.672445
C          -0.380598        0.676588        0.689635
C           0.354909        1.889208        0.677625
H          -2.341247       -0.179362        0.747587
H           2.385777       -1.315204        1.298290
H          -0.128076       -1.344669        1.354259
C          -1.769874        0.738966        0.696216
C          -0.335368        3.114571        0.593414
C          -1.715695        3.148949        0.569562
C          -2.438872        1.956845        0.638377
H           0.251798        4.023947        0.573822
H          -2.235042        4.097475        0.514286
H          -3.521521        1.977236        0.645827
H           3.430475        0.891070        1.261550
C           2.367654        0.795784        1.059251
N           1.724189        1.944488        0.802268
```

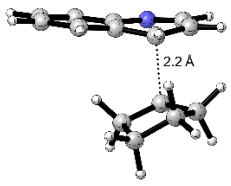
__Frequencies__ (First of 87)

```
  1.      42.2170 cm-1 (Symmetry: A)
```

***

59_C4_TS





Datum	Value
Charge	0
Multiplicity	2

Stoichiometry	C14H16N(2)
Electronic Energy (Eh)	-598.070740833
Sum of electronic and zero-point Energies (Eh)	-597.807389
Sum of electronic and thermal Energies (Eh)	-597.795151
Sum of electronic and enthalpy Energies (Eh)	-597.794206
Sum of electronic and thermal Free Energies (Eh)	-597.847791
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

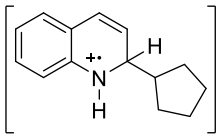
```xyz
C          -1.088321       -1.369844       -0.773198
C          -0.192772       -2.156845        0.195364
C           1.081381       -1.303980        0.268303
C           0.568930        0.111048        0.217981
C          -0.761771        0.116538       -0.491485
H          -0.817912       -1.619122       -1.802468
H          -2.148158       -1.597824       -0.652483
H          -0.004292       -3.179906       -0.132401
H          -0.659404       -2.210904        1.183437
H           1.709829       -1.516798        1.134814
H           1.702942       -1.491249       -0.619060
H           1.263444        0.918861        0.026664
H          -1.537672        0.590081        0.116112
H          -0.712925        0.712576       -1.407575
C           1.669808        0.854600        2.683589
C           0.322544        0.646900        2.329120
C          -0.522905        1.810861        2.309795
C           0.105965        3.089904        2.327851
H          -2.404429        0.767211        2.288557
H           2.331853        0.018546        2.864059
H          -0.140973       -0.312861        2.522176
C          -1.925971        1.739218        2.255808
C          -0.699069        4.246587        2.224797
C          -2.069190        4.145183        2.149908
C          -2.690912        2.885201        2.181209
H          -0.203792        5.209396        2.227271
H          -2.674724        5.040547        2.081695
H          -3.770874        2.815277        2.147112
H           3.234365        2.310340        2.885123
C           2.176857        2.152339        2.693040
N           1.454826        3.244260        2.483255
```

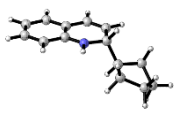
__Frequencies__ (First of 87)

```
  1.    -406.2298 cm-1 (Symmetry: A)  *
```

***

5H9_C2





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.535853163

Sum of electronic and zero-point Energies (Eh)	-598.255409
Sum of electronic and thermal Energies (Eh)	-598.243124
Sum of electronic and enthalpy Energies (Eh)	-598.24218
Sum of electronic and thermal Free Energies (Eh)	-598.295251
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C           2.117268       -3.441634       -1.432772
C           3.191196       -2.394692       -1.754098
C           2.910338       -1.279467       -0.745450
C           1.376654       -1.175808       -0.758045
C           0.870898       -2.623853       -1.015689
H           1.912512       -4.109811       -2.268838
H           2.450935       -4.062318       -0.598471
H           3.060736       -2.013408       -2.770899
H           4.205365       -2.787505       -1.678189
H           3.258365       -1.584137        0.247640
H           3.397817       -0.336881       -0.994397
H           1.071340       -0.528265       -1.583374
H           0.411901       -3.057125       -0.121907
H           0.110311       -2.628596       -1.797099
C           1.354443        0.796577        0.834029
C           0.603133        1.911517        0.902855
C          -0.816857        1.860990        0.724916
C          -1.430008        0.578573        0.501647
H          -1.185095        3.959070        0.937842
H           2.424649        0.841070        0.979301
H           1.062480        2.871674        1.101444
C          -1.637401        2.990096        0.770763
C          -2.835335        0.477357        0.340670
C          -3.599814        1.610003        0.392590
C          -3.004113        2.874593        0.607079
H          -3.281227       -0.495675        0.177378
H          -4.672170        1.540946        0.267834
H          -3.629430        3.756509        0.643600
H           1.052585       -1.228458        1.360247
C           0.790139       -0.542703        0.541063
N          -0.660396       -0.511901        0.454390
H          -1.115474       -1.403094        0.295807
```

__Frequencies__ (First of 90)

```
  1.      40.8971 cm-1 (Symmetry: A)
```

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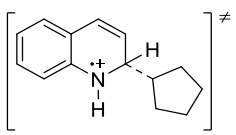
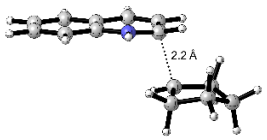
5H9_C2_TS





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.514634512
Sum of electronic and zero-point Energies (Eh)	-598.236373

Sum of electronic and thermal Energies (Eh)	-598.224185
Sum of electronic and enthalpy Energies (Eh)	-598.223241
Sum of electronic and thermal Free Energies (Eh)	-598.27611
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

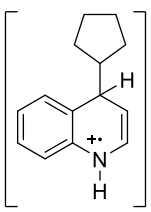
```xyz
C           0.085209       -2.370587        0.060516
C           1.470257       -1.774440       -0.231993
C           1.315773       -0.261820        0.056758
C          -0.163804        0.005556       -0.035521
C          -0.870178       -1.262573       -0.400778
H          -0.087414       -3.318457       -0.447687
H          -0.036460       -2.548570        1.133735
H           1.714763       -1.922876       -1.285827
H           2.264969       -2.232429        0.355455
H           1.711677       -0.011015        1.046052
H           1.868652        0.367346       -0.645595
H          -0.530642        0.954423       -0.407355
H          -1.891505       -1.337626       -0.022429
H          -0.960929       -1.279242       -1.496947
C          -0.262359        1.706886        2.193181
C          -1.041382        2.822373        2.138533
C          -2.448850        2.720979        1.940196
C          -3.027902        1.426618        1.870723
H          -2.864488        4.829272        1.889960
H           0.806530        1.772306        2.331952
H          -0.599780        3.804510        2.249686
C          -3.297384        3.838570        1.836450
C          -4.410695        1.265574        1.711755
C          -5.208974        2.383079        1.612232
C          -4.653695        3.673515        1.672182
H          -4.835721        0.270794        1.665020
H          -6.277105        2.265837        1.485231
H          -5.299595        4.537463        1.592129
H          -0.328738       -0.474439        2.333969
C          -0.842045        0.421794        2.015434
N          -2.198136        0.339665        1.986367
H          -2.621879       -0.578770        1.989036
```

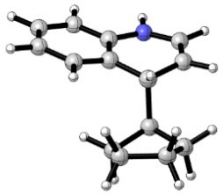
__Frequencies__ (First of 90)

```
  1.    -241.6488 cm-1 (Symmetry: A)  *
```

***

5H9_C4





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)
Electronic Energy (Eh)	-598.529820426

Sum of electronic and zero-point Energies (Eh)	-598.248726
Sum of electronic and thermal Energies (Eh)	-598.236755
Sum of electronic and enthalpy Energies (Eh)	-598.235811
Sum of electronic and thermal Free Energies (Eh)	-598.28767
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -1.105897       -2.587200       -1.654197
C           0.114537       -3.444798       -1.225696
C           1.333096       -2.497504       -1.280965
C           0.747253       -1.079557       -1.157052
C          -0.529187       -1.204667       -1.998444
H          -1.639870       -3.018394       -2.500545
H          -1.826919       -2.511056       -0.837529
H           0.259961       -4.305996       -1.877047
H          -0.024565       -3.839108       -0.217638
H           2.089611       -2.741733       -0.536337
H           1.820475       -2.568855       -2.255838
H           1.414813       -0.315687       -1.557425
H          -1.236830       -0.387610       -1.876032
H          -0.211995       -1.184194       -3.044728
C           1.831736       -0.506577        0.992254
C           0.491903       -0.698190        0.389196
C          -0.382462        0.509514        0.556933
C           0.196119        1.769155        0.836579
H          -2.244994       -0.496929        0.266573
H           2.481304       -1.358248        1.126788
H          -0.001071       -1.570597        0.827164
C          -1.765140        0.458362        0.429905
C          -0.574122        2.942775        0.893967
C          -1.936676        2.859665        0.721121
C          -2.535944        1.611936        0.509485
H          -0.091200        3.891113        1.097204
H          -2.544287        3.753033        0.768259
H          -3.610675        1.544297        0.404592
H           3.327264        0.904713        1.626224
C           2.320919        0.729705        1.275521
N           1.537651        1.826197        1.129877
H           1.938627        2.734993        1.333216
```

__Frequencies__ (First of 90)

```
  1.      54.4002 cm-1 (Symmetry: A)
```

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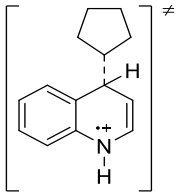
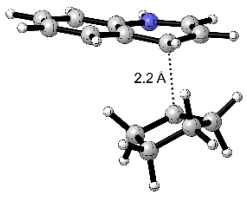
5H9_C4_TS





Datum	Value
Charge	1
Multiplicity	2
Stoichiometry	C14H17N(1+,2)

Electronic Energy (Eh)	-598.514682
Sum of electronic and zero-point Energies (Eh)	-598.236951
Sum of electronic and thermal Energies (Eh)	-598.224652
Sum of electronic and enthalpy Energies (Eh)	-598.223707
Sum of electronic and thermal Free Energies (Eh)	-598.277167
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

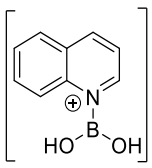
```xyz
C          -1.138214       -1.305688       -0.727684
C          -0.289799       -2.125183        0.258490
C           1.046384       -1.370434        0.293500
C           0.653008        0.068210        0.163485
C          -0.660406        0.156463       -0.551121
H          -0.936139       -1.635183       -1.748627
H          -2.208553       -1.417284       -0.557625
H          -0.177246       -3.166145       -0.041765
H          -0.745566       -2.122441        1.252838
H           1.676228       -1.592835        1.155756
H           1.642298       -1.625095       -0.595769
H           1.404754        0.829754        0.002923
H          -1.384653        0.765741       -0.003622
H          -0.524487        0.676299       -1.505039
C           1.741069        0.894239        2.625537
C           0.382581        0.678292        2.300033
C          -0.499157        1.810323        2.287186
C           0.057387        3.111963        2.340837
H          -2.338840        0.703095        2.199129
H           2.413832        0.063939        2.778364
H          -0.055692       -0.293615        2.479464
C          -1.898027        1.691500        2.208363
C          -0.757386        4.249121        2.274662
C          -2.122714        4.093646        2.178685
C          -2.697603        2.812848        2.157397
H          -0.311226        5.235133        2.314080
H          -2.758069        4.968207        2.132953
H          -3.772804        2.709035        2.101050
H           3.273586        2.393427        2.877269
C           2.234613        2.170870        2.682972
N           1.419752        3.229812        2.501820
H           1.813494        4.160701        2.555017
```

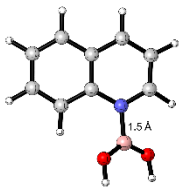
__Frequencies__ (First of 90)

```
  1.    -201.8122 cm-1 (Symmetry: A)  *
```

***

15oL_d





Datum	Value
Charge	1
Multiplicity	1

Stoichiometry	C9H9BNO2
Electronic Energy (Eh)	-578.649135477
Sum of electronic and zero-point Energies (Eh)	-578.476047
Sum of electronic and thermal Energies (Eh)	-578.465797
Sum of electronic and enthalpy Energies (Eh)	-578.464853
Sum of electronic and thermal Free Energies (Eh)	-578.512341
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
B          -3.621530       -2.197024        1.375109
O          -4.889446       -2.480000        1.024076
O          -2.543157       -1.981748        0.596412
H          -5.089693       -2.506728        0.079996
H          -2.659683       -2.067241       -0.357928
N          -3.321082       -2.171152        2.868586
C          -4.162278       -1.597863        3.815108
C          -3.823247       -1.732020        5.194101
C          -2.646699       -2.416990        5.546829
C          -1.827142       -2.938243        4.573794
C          -2.194240       -2.795723        3.244995
C          -4.666445       -1.154449        6.172666
C          -5.784429       -0.459023        5.800803
C          -6.093685       -0.310043        4.435247
C          -5.305962       -0.864504        3.454744
H          -1.584248       -3.196931        2.449238
H          -2.392155       -2.520349        6.594538
H          -0.912939       -3.460340        4.814497
H          -4.400598       -1.268858        7.215680
H          -6.427579       -0.015040        6.548564
H          -6.970326        0.255437        4.147360
H          -5.571499       -0.730777        2.418775
```

__Frequencies__ (First of 60)

```
  1.      37.4518 cm-1 (Symmetry: A)
```

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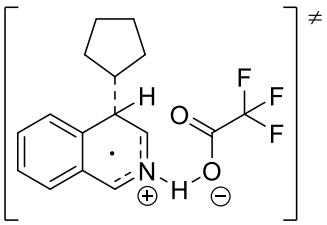
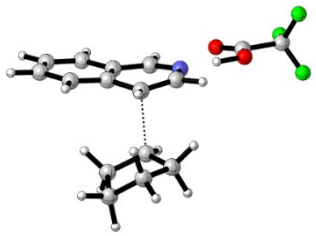
47HB9_C4_otro





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2
Electronic Energy (Eh)	-1125.16672495
Sum of electronic and zero-point Energies (Eh)	-1124.862011
Sum of electronic and thermal Energies (Eh)	-1124.841823
Sum of electronic and enthalpy Energies (Eh)	-1124.840879
Sum of electronic and thermal Free Energies (Eh)	-1124.916935
Number of Imaginary Frequencies	0

|:---|-------------------------:|

__Molecular Geometry in Cartesian Coordinates__

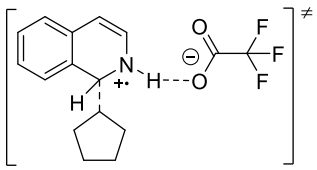
```xyz
C          -3.006077       -3.269831       -3.098397
C          -1.703831       -4.035985       -2.765621
C          -1.103052       -3.329154       -1.524052
C          -1.952735       -2.059201       -1.315133
C          -3.335210       -2.479180       -1.827731
H          -2.832734       -2.572622       -3.922049
H          -3.818496       -3.930784       -3.403708
H          -1.012084       -4.024732       -3.608663
H          -1.911887       -5.083966       -2.544408
H          -1.194086       -3.971111       -0.642713
H          -0.043531       -3.102319       -1.643757
H          -1.572103       -1.262676       -1.963521
H          -3.815111       -3.130676       -1.088716
H          -4.001751       -1.637014       -2.009655
C          -0.492543       -1.270824        0.526434
C          -1.919665       -1.515615        0.152361
C          -2.741005       -0.257208        0.307448
C          -2.081006        0.991825        0.247839
H          -4.632169       -1.235647        0.527969
H           0.145565       -2.112566        0.767874
H          -2.325771       -2.312803        0.784292
C          -4.121404       -0.283678        0.454949
C          -2.834818        2.180415        0.273726
C          -4.210886        2.131501        0.389740
C          -4.855848        0.897873        0.496688
H          -2.320090        3.132342        0.222141
H          -4.786532        3.048034        0.412795
H          -5.931950        0.857986        0.608874
H           1.560978        0.066772        0.685054
H          -0.103222        1.945927        0.182133
C          -0.655657        1.018208        0.253023
N           0.074923       -0.091865        0.478604
C           3.028392        1.369274        0.677264
O           2.616797        0.145700        0.829792
O           2.380628        2.351827        0.408599
C           4.566164        1.461863        0.890461
F           5.007714        2.712650        0.735593
F           4.904365        1.054234        2.128625
F           5.219744        0.680547        0.009207
```

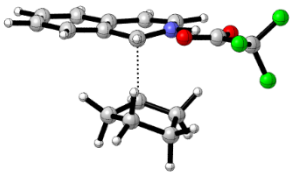
__Frequencies__ (First of 111)

```
  1.      12.0462 cm-1 (Symmetry: A)
```

***

47HB9_C1_TS_otro





Datum	Value
Charge	0

Multiplicity	2
Stoichiometry	C16H17F3NO2
Electronic Energy (Eh)	-1125.15099587
Sum of electronic and zero-point Energies (Eh)	-1124.846994
Sum of electronic and thermal Energies (Eh)	-1124.827053
Sum of electronic and enthalpy Energies (Eh)	-1124.826108
Sum of electronic and thermal Free Energies (Eh)	-1124.900109
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

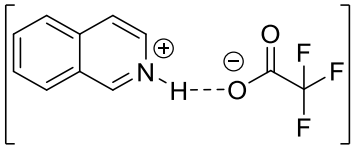
```xyz
C          -2.426000       -1.519696       -2.327077
C          -1.002166       -1.644085       -2.891570
C          -0.238186       -0.423220       -2.321791
C          -1.299685        0.529354       -1.840437
C          -2.641640       -0.002716       -2.236236
H          -3.173676       -2.015268       -2.946865
H          -2.465096       -1.963960       -1.330939
H          -1.027974       -1.586864       -3.982596
H          -0.528412       -2.587163       -2.622629
H           0.449716       -0.718678       -1.528692
H           0.385222        0.068212       -3.076025
H          -1.108807        1.595802       -1.867550
H          -3.457085        0.308016       -1.582977
H          -2.880051        0.404938       -3.230724
C           0.700283        1.747160        0.809057
C           0.024139        2.931901        0.880957
C          -1.400669        2.937188        0.845697
C          -2.074512        1.701056        0.638781
H          -1.652554        5.046252        1.207771
H           1.772969        1.672347        0.918375
H           0.568010        3.854035        1.031415
C          -2.163187        4.103394        1.055289
C          -3.477008        1.657178        0.696508
C          -4.198675        2.810712        0.916946
C          -3.538200        4.039682        1.083579
H          -3.982740        0.707013        0.585609
H          -5.278993        2.770412        0.968694
H          -4.116821        4.939304        1.250654
H           0.580595       -0.343539        0.613802
H          -1.706582       -0.461422        0.403051
N           0.043714        0.583907        0.620190
C          -1.286111        0.534841        0.357428
C           0.407649       -2.647345        0.474525
O          -0.820060       -2.561024        0.517247
O           1.280610       -1.741889        0.538722
C           1.019309       -4.071053        0.268406
F           1.999941       -4.335789        1.156179
F           0.113441       -5.056850        0.374984
F           1.566114       -4.170143       -0.969476
```

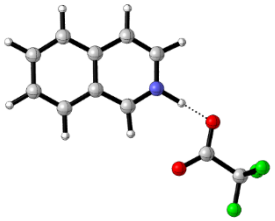
__Frequencies__ (First of 111)

```
  1.    -298.1644 cm-1 (Symmetry: A)  *
```

***

47HB_otro





Datum	Value
Charge	0
Multiplicity	1
Stoichiometry	C11H8F3NO2
Electronic Energy (Eh)	-929.16509537
Sum of electronic and zero-point Energies (Eh)	-928.990733
Sum of electronic and thermal Energies (Eh)	-928.976298
Sum of electronic and enthalpy Energies (Eh)	-928.975354
Sum of electronic and thermal Free Energies (Eh)	-929.036157
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

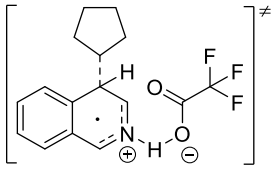
```xyz
C          -5.642109       -0.750613        0.068408
C          -4.277893       -0.871715        0.056299
C          -3.470319        0.288734        0.003466
C          -4.077311        1.580063       -0.037592
C          -5.486791        1.668085       -0.023997
C          -6.246002        0.526243        0.027957
H          -6.266012       -1.633858        0.108550
H          -3.802636       -1.843957        0.086328
C          -3.229997        2.713925       -0.089796
H          -5.956285        2.643086       -0.054627
H          -7.326119        0.599966        0.038419
C          -1.877717        2.550568       -0.100621
H          -3.653593        3.708538       -0.121426
H          -1.177935        3.372718       -0.139708
H          -0.214366        1.188277       -0.074574
H          -1.518296       -0.718950        0.014469
C          -2.067283        0.215246       -0.011694
N          -1.329954        1.306287       -0.061599
C           1.493063       -0.218080       -0.064956
O           0.746928       -1.191701       -0.020893
O           1.204947        1.014198       -0.094753
C           3.033371       -0.472799       -0.094281
F           3.648161        0.131517        0.946381
F           3.349152       -1.775572       -0.037780
F           3.584492        0.022189       -1.225290
```

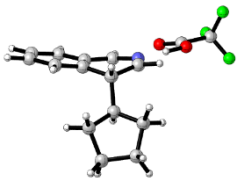
__Frequencies__ (First of 69)

```
  1.      14.8083 cm-1 (Symmetry: A)
```

***

47HB9_C4_TS_otro





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C16H17F3NO2
Electronic Energy (Eh)	-1125.13800817
Sum of electronic and zero-point Energies (Eh)	-1124.836756
Sum of electronic and thermal Energies (Eh)	-1124.816583
Sum of electronic and enthalpy Energies (Eh)	-1124.815639
Sum of electronic and thermal Free Energies (Eh)	-1124.891586
Number of Imaginary Frequencies	1

__Molecular Geometry in Cartesian Coordinates__

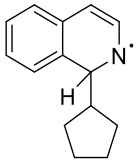
```xyz
C          -1.147381       -1.194633       -0.810433
C          -0.228397       -2.054213        0.070554
C           1.059548       -1.222765        0.152102
C           0.564184        0.196700        0.207360
C          -0.794778        0.265575       -0.438505
H          -0.913805       -1.373784       -1.862904
H          -2.205027       -1.420809       -0.669727
H          -0.065947       -3.055096       -0.330684
H          -0.660122       -2.168615        1.069390
H           1.714809       -1.497019        0.981224
H           1.649043       -1.361179       -0.765515
H           1.260454        1.011548        0.052566
H          -1.539214        0.696322        0.238250
H          -0.783010        0.927707       -1.309344
C           1.729550        0.811048        2.671921
C           0.372474        0.590315        2.383575
C          -0.509502        1.723342        2.473954
C           0.078474        3.018569        2.494549
H          -2.360214        0.625981        2.528036
H           2.418119       -0.013659        2.800338
H          -0.037948       -0.396968        2.548347
C          -1.908957        1.610581        2.511724
C          -0.752821        4.160338        2.505441
C          -2.121045        4.020528        2.524048
C          -2.702083        2.740504        2.541095
H          -0.297184        5.143087        2.514100
H          -2.755616        4.897555        2.538046
H          -3.779703        2.641902        2.574852
H           3.696879        2.228984        2.856175
H           1.993757        4.069185        2.571975
C           1.489406        3.110703        2.562477
N           2.262464        2.037419        2.693702
C           5.144226        3.581061        2.904728
O           4.777401        2.340111        2.974351
O           4.459229        4.562699        2.734602
C           6.685293        3.712496        3.073266
F           7.082191        4.986727        3.007231
F           7.083326        3.218394        4.261690
F           7.333561        3.029262        2.109284
```

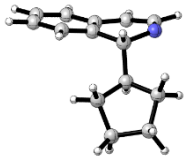
__Frequencies__ (First of 111)

```
  1.    -408.3395 cm-1 (Symmetry: A)  *
```

***

49_C1





Datum	Value
Charge	0
Multiplicity	2
Stoichiometry	C14H16N
Electronic Energy (Eh)	-598.099646814
Sum of electronic and zero-point Energies (Eh)	-597.833405
Sum of electronic and thermal Energies (Eh)	-597.821139
Sum of electronic and enthalpy Energies (Eh)	-597.820195
Sum of electronic and thermal Free Energies (Eh)	-597.873787
Number of Imaginary Frequencies	0

__Molecular Geometry in Cartesian Coordinates__

```xyz
C          -0.668048       -2.263759       -2.712146
C           0.596040       -3.087495       -2.387450
C           1.265617       -2.374646       -1.182992
C           0.401390       -1.128366       -0.891681
C          -0.986537       -1.525751       -1.409015
H          -0.451494       -1.532542       -3.496239
H          -1.497280       -2.878898       -3.065931
H           1.263713       -3.155748       -3.247605
H           0.324849       -4.110485       -2.118907
H           1.271537       -3.024486       -0.304972
H           2.303409       -2.106892       -1.373662
H           0.765483       -0.288765       -1.494112
H          -1.462812       -2.209590       -0.697225
H          -1.654646       -0.676510       -1.549521
C           2.377566        0.672959        0.966644
C           1.641766        1.871918        0.835478
C           0.221755        1.823765        0.848728
C          -0.394742        0.549081        0.838439
H          -0.100202        3.952166        0.959394
H           3.450842        0.743046        1.135272
H           2.156355        2.824389        0.837474
C          -0.577939        2.979506        0.960658
C          -1.770112        0.463485        1.011283
C          -2.547263        1.611125        1.137968
```

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C          -1.948457        2.872655        1.096004
H          -2.244676       -0.509577        1.039199
H          -3.618884        1.524711        1.267104
H          -2.556546        3.764138        1.185317
H           0.077574       -1.508362        1.189286
N           1.875932       -0.526122        0.930680
C           0.464665       -0.670359        0.598350
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__Frequencies__ (First of 87)

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  1.      27.6873 cm-1 (Symmetry: A)
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Corrected energy values

Effect of concentration on the thermodynamic properties was considered using GoodVibes 3.0.1 program (). For calculating the activation and reaction energy variations the concentration was set equal to the experimental value of 0.1 mol·L^{-1}. For calculating the equilibrium constant and reduction potentials the concentration was set to 1 mol·L^{-1} as reference state. [27] Under the column "Structure" the code used for the calculations is given.

Structure	E	ZPE	H	qh-H	T.S	T.qh-S	G(T)	qh-G(T)
10	-235.319825	0.152803	-235.159979	-235.160069	0.035943	0.035946	-235.195922	-235.196015
134L_od	-1094.733173	0.422961	-1094.285880	-1094.290817	0.081438	0.074523	-1094.367318	-1094.365339
134L_o	-1290.730890	0.548394	-1290.151401	-1290.158264	0.098260	0.088693	-1290.249660	-1290.246957
134L	-1290.946369	0.549462	-1290.366463	-1290.373255	0.098086	0.087310	-1290.464550	-1290.460565
13_o	-888.536913	0.410135	-888.104422	-888.108793	0.076157	0.070540	-888.180579	-888.179333
13	-888.825936	0.413677	-888.389489	-888.394870	0.081675	0.072651	-888.471163	-888.467521
14HB_od	-578.620731	0.167943	-578.439670	-578.441946	0.053333	0.050666	-578.493004	-578.492613
14HB_o	-774.596770	0.296403	-774.281751	-774.285534	0.068904	0.063381	-774.350655	-774.348915
14HB	-774.862740	0.297222	-774.547183	-774.550939	0.069818	0.063124	-774.617001	-774.614063
14Lod9_C1	-774.671845	0.300173	-774.354740	-774.357087	0.060323	0.058181	-774.415063	-774.415268
14Lod9_C1_TS	-774.646114	0.297559	-774.331974	-774.333863	0.058694	0.057291	-774.390668	-774.391154
14Lod9_C4	-774.654142	0.299302	-774.337938	-774.340400	0.060717	0.058271	-774.398656	-774.398670
14Lod9_C4_TS	-774.634312	0.296520	-774.320842	-774.323290	0.060775	0.058351	-774.381617	-774.381641
14L_od	-578.656104	0.170441	-578.474341	-578.475178	0.046405	0.045856	-578.520747	-578.521034
14L_o	-774.647864	0.295518	-774.334047	-774.336923	0.064851	0.061530	-774.398898	-774.398454
14L	-774.853950	0.296679	-774.539564	-774.542053	0.062548	0.059540	-774.602112	-774.601593
14L_ts	-774.852637	0.296100	-774.539260	-774.541845	0.062642	0.059039	-774.601902	-774.600884
14oL	-774.647892	0.295325	-774.334143	-774.337178	0.065512	0.061841	-774.399654	-774.399019
14oL_ts	-774.592873	0.293916	-774.281469	-774.283800	0.061760	0.059380	-774.343230	-774.343180
14	-76.467255	0.020734	-76.442741	-76.442741	0.021239	0.021239	-76.463979	-76.463979
15HB_od	-578.621747	0.167961	-578.440752	-578.442955	0.052847	0.050425	-578.493599	-578.493380
15HB_o	-774.595014	0.296370	-774.280275	-774.283695	0.066786	0.062385	-774.347061	-774.346080
15HB	-774.864863	0.297160	-774.549428	-774.553157	0.068756	0.062586	-774.618183	-774.615743
15oL_d	-578.649135	0.170492	-578.467305	-578.468230	0.046900	0.045943	-578.514206	-578.514174
15oL	-774.640827	0.295721	-774.326951	-774.329770	0.063827	0.060869	-774.390778	-774.390639
15oL_ts	-774.591446	0.293921	-774.280094	-774.282233	0.061740	0.059301	-774.341834	-774.341534
16HB_o	-660.499162	0.289049	-660.190891	-660.195082	0.070788	0.064598	-660.261680	-660.259680
16HB	-660.738319	0.291513	-660.427818	-660.431943	0.069678	0.063607	-660.497496	-660.495550
17HB_od	-703.136056	0.059454	-703.064992	-703.066744	0.048925	0.047127	-703.113917	-703.113871
17HB_o	-899.105031	0.187103	-898.899858	-898.904266	0.069697	0.062829	-898.969555	-898.967095
17HB	-899.342305	0.189380	-899.136011	-899.139646	0.064693	0.059598	-899.200704	-899.199244
18HB_od	-703.489729	0.071247	-703.406829	-703.408229	0.048222	0.047196	-703.455051	-703.455425
18HB_o	-899.513725	0.196910	-899.299222	-899.302513	0.064046	0.060544	-899.363268	-899.363056
18HB	-899.811748	0.201754	-899.592722	-899.596414	0.065153	0.060038	-899.657876	-899.656451
1_od	-176.422828	0.029042	-176.388717	-176.388730	0.028120	0.028123	-176.416837	-176.416853
1_o	-372.457719	0.157217	-372.290550	-372.291267	0.043097	0.042647	-372.333647	-372.333914
1t	-372.750755	0.161988	-372.579151	-372.580339	0.044048	0.042191	-372.623198	-372.622530
24L_od	-813.427468	0.315902	-813.093619	-813.095490	0.061494	0.059311	-813.155113	-813.154802
24L_o	-1048.755877	0.470633	-1048.259338	-1048.263629	0.080819	0.075872	-1048.340157	-1048.339501
24L	-1048.962334	0.471719	-1048.466216	-1048.469379	0.075249	0.071734	-1048.541464	-1048.541113
24L_TS	-1048.893535	0.469933	-1048.399108	-1048.402535	0.076681	0.072371	-1048.475788	-1048.474906

24oL	-1048.755877	0.470633	-1048.259338	-1048.263629	0.080816	0.075871	-1048.340155	-1048.339499
25L_od	-813.422719	0.316081	-813.088756	-813.090557	0.061505	0.059249	-813.150261	-813.149806
25L	-1048.967233	0.470674	-1048.470908	-1048.475438	0.081856	0.075313	-1048.552764	-1048.550750
26L	-934.834855	0.465516	-934.343035	-934.347781	0.082143	0.076412	-934.425178	-934.424193
2_od	-411.166896	0.175511	-410.980289	-410.980697	0.043811	0.043665	-411.024100	-411.024361
2_o	-646.580191	0.332693	-646.230245	-646.232037	0.059800	0.057877	-646.290045	-646.289914
2	-646.858233	0.336195	-646.505337	-646.507102	0.058988	0.056614	-646.564325	-646.563716
3_od	-324.715883	0.011940	-324.699446	-324.699451	0.029838	0.029839	-324.729284	-324.729290
3_o	-560.044515	0.167235	-559.865456	-559.867028	0.049221	0.047707	-559.914677	-559.914736
3	-560.212107	0.168059	-560.033313	-560.034270	0.045264	0.044465	-560.078577	-560.078735
47HB9_C1	-1125.173029	0.302420	-1124.849661	-1124.853570	0.073130	0.067992	-1124.922791	-1124.921563
47HB9_C1_TS	-1125.150996	0.299441	-1124.830431	-1124.834474	0.073653	0.068376	-1124.904084	-1124.902850
47HB9_C4	-1125.166725	0.300143	-1124.845214	-1124.849582	0.075710	0.069487	-1124.920924	-1124.919069
47HB9_C4_TS	-1125.138008	0.296734	-1124.819923	-1124.824235	0.075601	0.069431	-1124.895523	-1124.893666
47HB_o	-928.889495	0.173752	-928.700209	-928.702651	0.059265	0.056492	-928.759474	-928.759143
47HB_otro	-929.165095	0.171747	-928.977805	-928.980460	0.060299	0.056526	-929.038104	-929.036986
49_C1	-598.099647	0.262248	-597.824016	-597.825698	0.053064	0.051200	-597.877080	-597.876898
49_C1_TS	-598.071878	0.259323	-597.799161	-597.800853	0.053191	0.051273	-597.852352	-597.852126
49_C4	-598.099127	0.261938	-597.823730	-597.825458	0.053116	0.051305	-597.876846	-597.876763
49_C4_TS	-598.068604	0.259084	-597.796078	-597.797773	0.053179	0.051329	-597.849257	-597.849102
4H9_C1	-598.541166	0.276992	-598.250699	-598.252342	0.052858	0.051268	-598.303557	-598.303609
4H9_C1_TS	-598.514448	0.273474	-598.227485	-598.229162	0.053143	0.051345	-598.280628	-598.280507
4H9_C4	-598.525613	0.276765	-598.235681	-598.236995	0.051348	0.050440	-598.287030	-598.287435
4H9_C4_TS	-598.505482	0.273515	-598.218560	-598.220136	0.052526	0.051067	-598.271086	-598.271203
4H	-402.526340	0.147341	-402.371121	-402.371262	0.038416	0.038403	-402.409536	-402.409665
4o	-401.841539	0.132712	-401.700720	-401.700904	0.039554	0.039525	-401.740274	-401.740430
4	-402.097157	0.133601	-401.955842	-401.955956	0.038093	0.038090	-401.993935	-401.994046
57HB9_C2	-1125.168807	0.301555	-1124.845960	-1124.850183	0.074774	0.068963	-1124.920734	-1124.919145
57HB9_C2_TS	-1125.150274	0.299402	-1124.829749	-1124.833803	0.073835	0.068473	-1124.903584	-1124.902275
57HB9_C4	-1125.168105	0.301091	-1124.845837	-1124.850050	0.074465	0.068783	-1124.920302	-1124.918833
57HB9_C4_TS	-1125.145322	0.298657	-1124.825356	-1124.829684	0.075655	0.069328	-1124.901012	-1124.899012
57HB_o	-928.886558	0.173689	-928.697214	-928.699767	0.059577	0.056988	-928.756791	-928.756756
57HB	-929.166269	0.171716	-928.979008	-928.981678	0.060152	0.056439	-929.039160	-929.038117
59_C2	-598.093186	0.261786	-597.818044	-597.819716	0.053170	0.051161	-597.871214	-597.870876
59_C2_TS	-598.070218	0.259374	-597.797476	-597.799180	0.053168	0.051220	-597.850643	-597.850400
59_C4	-598.097743	0.262418	-597.822061	-597.823665	0.052404	0.050860	-597.874465	-597.874525
59_C4_TS	-598.070741	0.259401	-597.797985	-597.799658	0.053056	0.051166	-597.851041	-597.850824
5H9_C2	-598.535853	0.276238	-598.246208	-598.247776	0.052549	0.051041	-598.298757	-598.298817
5H9_C2_TS	-598.514635	0.274088	-598.227237	-598.228747	0.052345	0.050938	-598.279582	-598.279686
5H9_C4	-598.529820	0.276878	-598.239846	-598.241157	0.051335	0.050260	-598.291181	-598.291417
5H9_C4_TS	-598.514682	0.273565	-598.227696	-598.229263	0.052936	0.051234	-598.280632	-598.280497
5H	-402.527291	0.147361	-402.372063	-402.372192	0.038367	0.038360	-402.410430	-402.410552
5o	-401.838645	0.132223	-401.698297	-401.698485	0.039550	0.039519	-401.737847	-401.738004
5	-402.098762	0.133478	-401.957586	-401.957699	0.038042	0.038039	-401.995628	-401.995738
6	-287.965900	0.127836	-287.829322	-287.830286	0.040095	0.039230	-287.869418	-287.869516
7o	-526.353140	0.024327	-526.321668	-526.322190	0.038220	0.037491	-526.359888	-526.359682
7	-526.556650	0.025133	-526.524485	-526.524991	0.037410	0.036626	-526.561894	-526.561617
8o	-526.674775	0.035766	-526.631247	-526.631564	0.038633	0.038510	-526.669879	-526.670075
8	-527.040122	0.037908	-526.994953	-526.995467	0.038118	0.037134	-527.033071	-527.032601
9	-195.982384	0.123440	-195.852738	-195.852819	0.033825	0.033823	-195.886563	-195.886643

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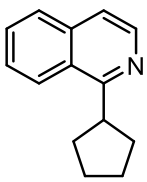
7. Product Characterization

1-cyclopentylisoquinoline[42]



Compound **1** was prepared according to the general procedure (GP1) and isolated as a yellow oil.

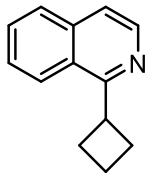
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 5.7 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.69-7.54 (m, 2H), 7.48 (d, *J* = 5.7 Hz, 1H), 4.07-3.09 (m, 1H), 2.22 – 2.01 (m, 4H), 1.97-1.85 (m, 2H), 1.83-1.73 (m, 2H).

^{13}C NMR (75 MHz, CDCl3) δ 164.87, 141.92, 136.40, 129.69, 127.50, 127.32, 126.90, 125.38, 119.05, 43.11, 32.91, 26.18.

Spectroscopic data were consistent with literature values.

1-cyclobutylisoquinoline[42]



Compound 2 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

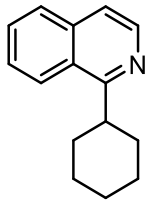
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-d) δ 8.48 (d, J = 5.8 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.53 (t, J = 6.84 Hz, 1H), 4.46 – 4.26 (m, 1H), 2.79 – 2.39 (m, 4H), 2.17 (q, J = 9.4 Hz, 1H), 2.00-1.90 (m, 1H).

^{13}C NMR (75 MHz, CDCl3) δ 163.52, 141.79, 136.18, 129.75, 127.35, 126.83, 126.40, 125.28, 119.11, 39.39, 27.81, 18.63.

Spectroscopic data were consistent with literature values.

1-cyclohexylisoquinoline[43]



Compound 3 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

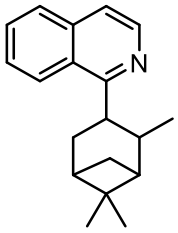
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-d) δ 8.48 (d, J = 5.7 Hz, 1H), 8.21 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.64-7.52 (m, 2H), 7.45 (d, J = 5.7 Hz, 1H), 3.65 – 3.46 (m, 1H), 2.08 – 1.89 (m, 4H), 1.90 – 1.72 (m, 3H), 1.66 – 1.32 (m, 3H).

^{13}C NMR (75 MHz, CDCl3) δ 165.72, 141.95, 136.41, 129.57, 127.58, 126.84, 126.31, 124.75, 118.93, 41.58, 32.64, 26.94, 26.31.

Spectroscopic data were consistent with literature values.

1-(2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)isoquinoline



Compound 4 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

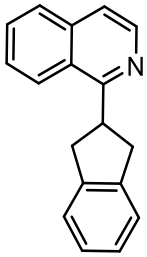
Column Chromatography: Silica, gradient 2% EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.7 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.54 (m, 2H), 7.48 (d, *J* = 5.6 Hz, 1H), 4.16 (dt, *J* = 10.6, 7.2 Hz, 1H), 2.99 (td, *J* = 7.3, 1.9 Hz, 1H), 2.60 – 2.37 (m, 2H), 2.10 – 1.91 (m, 4H), 1.32 (d, *J* = 5.1 Hz, 6H), 1.03 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.40, 142.53, 136.52, 129.65, 127.72, 127.55, 126.95, 125.27, 118.66, 48.19, 41.94, 41.40, 39.87, 39.35, 36.04, 33.36, 28.44, 23.40, 22.06.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{19}H_{23}N$: 266.1903, found: 266.1900

1-(2,3-dihydro-1H-inden-2-yl)isoquinoline



Compound 5 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

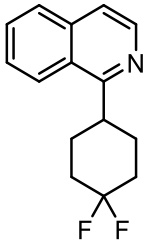
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.7 Hz, 1H), 8.29 – 8.23 (m, 1H), 7.88 – 7.81 (m, 1H), 7.69 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.61 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.53 (dd, *J* = 5.6, 0.9 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.21 – 7.17 (m, 2H), 4.70 (p, *J* = 8.8 Hz, 1H), 3.63 (dd, *J* = 15.6, 9.0 Hz, 2H), 3.48 – 3.37 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 163.09, 142.92, 141.93, 136.59, 129.87, 127.71, 127.21, 127.17, 126.55, 125.11, 124.48, 119.54, 43.47, 39.27.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{18}H_{15}N$: 246.1277, found: 246.1269

1-(4,4-difluorocyclohexyl)isoquinoline[44]



Compound 6 was prepared according to the general procedure (GP1) and isolated as a pale-yellow solid.

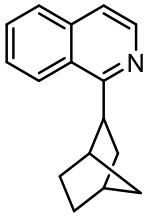
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.6 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.55 (m, 2H), 7.52 (d, *J* = 5.7 Hz, 1H), 3.64 (t, *J* = 11.4 Hz, 1H), 2.41 – 2.13 (m, 4H), 2.11 – 2.04 (m, 3H), 2.02-1.88 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.19, 141.99, 136.52, 129.85, 128.12, 127.26, 126.31, 124.32, 123.33 (d, *J* = 1.5 Hz), 119.57, 39.44 (d, *J* = 1.8 Hz), 34.06 (dd, *J* = 25.7, 22.7 Hz), 28.61 (d, *J* = 9.9 Hz).

Spectroscopic data were consistent with literature values.

1-((1R,4S)-bicyclo[2.2.1]heptan-2-yl)isoquinoline[45]



Compound 7 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

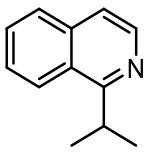
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.50 (m, 2H), 7.44 (d, *J* = 5.7 Hz, 1H), 3.60-3.56 (m, 1H), 2.63 – 2.56 (m, 1H), 2.45-2.37 (m, 2H), 1.80 – 1.62 (m, 4H), 1.62 – 1.52 (m, 1H), 1.46 – 1.35 (m, 1H), 1.24 – 1.14 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.30, 141.36, 136.39, 129.49, 127.47, 127.07, 126.79, 125.45, 118.88, 45.60, 43.08, 36.85, 36.18, 36.00, 30.32, 29.63.

Spectroscopic data were consistent with literature values.

1-isopropylisoquinoline[46]



Compound 8 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

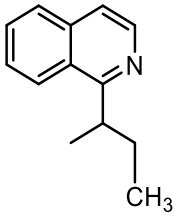
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 8.49 (d, J = 5.7 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.64 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.57 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 3.98-3.91 (m, 1H), 1.45 (d, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, CDCl3) δ 166.41, 141.99, 136.47, 129.66, 127.64, 126.97, 126.35, 124.87, 119.10, 31.08, 22.33.

Spectroscopic data were consistent with literature values.

1-(sec-butyl)isoquinoline[44]



Compound 9 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

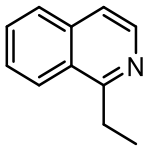
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.7 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.75 (m, 1H), 7.70 – 7.51 (m, 2H), 7.47 (d, *J* = 5.7 Hz, 1H), 3.71 (h, *J* = 6.9 Hz, 1H), 2.13 – 1.93 (m, 1H), 1.77 (dp, *J* = 14.4, 7.3 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.96, 142.06, 136.44, 129.63, 127.62, 126.91, 124.87, 118.92, 37.84, 29.71, 20.27, 12.49.

Spectroscopic data were consistent with literature values.

1-ethylisoquinoline[47]



Compound 10 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

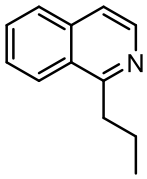
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-d) δ 8.43 (d, J = 5.8 Hz, 1H), 8.14 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.71 – 7.51 (m, 2H), 7.47 (d, J = 5.7 Hz, 1H), 3.32 (q, J = 7.6 Hz, 2H), 1.44 (t, J = 7.6 Hz, 3H).

^{13}C NMR (75 MHz, CDCl3) δ 163.22, 141.82, 136.31, 129.92, 127.47, 127.09, 126.76, 125.31, 119.33, 28.49, 13.73.

Spectroscopic data were consistent with literature values.

1-propylisoquinoline[47]



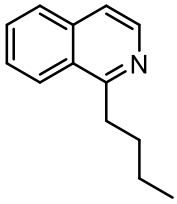
Compound 11 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 5.7 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.61 (m, 2H), 7.49 (d, *J* = 5.7 Hz, 1H), 3.31 – 3.24 (t, *J* = 7.78 Hz, 2H), 1.91 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

Spectroscopic data were consistent with literature values.

1-butylisoquinoline[48]



Compound 12 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

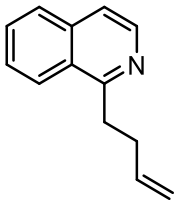
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.51 (m, 2H), 7.47 (d, *J* = 5.8 Hz, 1H), 3.35 – 3.22 (m, 2H), 1.84 (ddd, *J* = 13.2, 8.9, 6.6 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.51, 141.93, 136.34, 129.83, 127.45, 127.00, 125.46, 119.22, 35.35, 32.03, 23.09, 14.11.

Spectroscopic data were consistent with literature values.

1-(but-3-en-1-yl)isoquinoline[49]



Compound 13 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

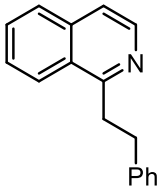
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.50 (d, *J* = 5.8 Hz, 1H), 5.98 (m, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 3.39 (m, 2H), 2.70 – 2.56 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.39, 141.85, 138.04, 136.37, 129.99, 127.52, 127.19, 127.05, 125.33, 119.49, 115.20, 34.70, 33.62.

Spectroscopic data were consistent with literature values.

1-phenethylisoquinoline[47]



Compound 14 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

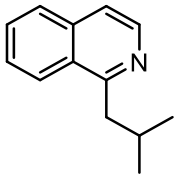
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.7 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.57 (m, 2H), 7.32 (m, 4H), 7.28 – 7.18 (m, 1H), 3.65 – 3.57 (m, 2H), 3.24 – 3.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.18, 142.01, 141.97, 136.42, 130.03, 128.63, 128.6, 127.59, 127.29, 127.08, 126.21, 125.24, 119.62, 37.36, 35.66.

Spectroscopic data were consistent with literature values.

1-isobutylisoquinoline[47]



Compound 15 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

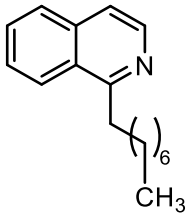
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.59 – 7.51 (m, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 3.16 (d, *J* = 7.3 Hz, 2H), 2.29 (hept, *J* = 6.8 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.74, 141.85, 136.39, 129.82, 127.49, 127.44, 126.94, 125.70, 119.24, 44.29, 29.66, 22.95.

Spectroscopic data were consistent with literature values.

1-octylisoquinoline[50]



Compound 16 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

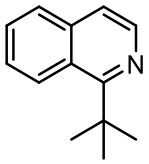
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.68-7.62 (m, 1H), 7.60 – 7.53 (m, 1H), 7.49 (d, *J* = 5.8 Hz, 1H), 3.34 – 3.21 (m, 2H), 1.85 (p, *J* = 7.6 Hz, 2H), 1.38 – 1.19 (m, 10H), 0.90 – 0.84 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.61, 142.01, 136.39, 129.87, 127.50, 127.04, 125.52, 119.25, 35.74, 32.01, 30.07, 29.99, 29.64, 29.39, 22.80, 14.24.

Spectroscopic data were consistent with literature values.

1-(tert-butyl)isoquinoline[51]



Compound 17 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

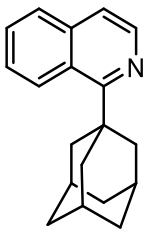
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.6 Hz, 1H), 8.44 (d, *J* = 5.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.64-7.54 (m, 2H), 7.49 (d, *J* = 5.7 Hz, 1H), 1.67 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.51, 140.73, 137.56, 128.94, 128.38, 127.46, 126.32, 125.84, 119.92, 40.03, 31.37.

Spectroscopic data were consistent with literature values.

1-((3r,5r,7r)-adamantan-1-yl)isoquinoline[42]



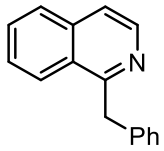
Compound 18 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

Column Chromatography: Silica, gradient 2 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 8.7 Hz, 1H), 8.45 (d, *J* = 5.5 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 2.39 (d, *J* = 3.0 Hz, 6H), 2.19 (s, 3H), 1.90 – 1.86 (m, 6H).

Spectroscopic data were consistent with literature values.

1-benzylisoquinoline[50]



Compound 19 was prepared according to the general procedure (GP1 and GP3, flow) and isolated as a yellow oil.

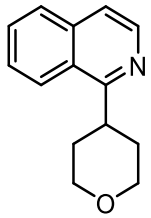
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 8.50 (d, J = 5.7 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.63 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.57 (d, J = 4.9 Hz, 1H), 7.54-7.50 (m, 1H), 7.31 – 7.22 (m, 4H), 7.20 – 7.12 (m, 1H), 4.68 (s, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 160.29, 142.14, 139.59, 136.74, 130.01, 128.75, 128.66, 127.50, 127.37, 126.40, 125.98, 119.97, 42.20.

Spectroscopic data were consistent with literature values.

1-(tetrahydro-2H-pyran-4-yl)isoquinoline[44]



Compound 20 was prepared according to the general procedure (GP1) and isolated as a yellow solid.

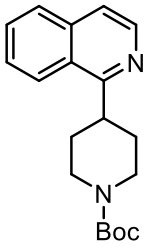
Column Chromatography: Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-d) δ 8.48 (d, J = 5.7 Hz, 1H), 8.20 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.68-7.56 (m, 2H), 7.50 (d, J = 5.7 Hz, 1H), 4.16 (dd, J = 11.4, 4.3 Hz, 2H), 3.86 – 3.75 (m, 1H), 3.74 – 3.63 (m, 2H), 2.23 (qd, J = 12.4, 4.3 Hz, 2H), 1.92 – 1.80 (m, 2H).

^{13}C NMR (75 MHz, CDCl3) δ 163.46, 142.08, 136.52, 129.77, 127.83, 127.15, 126.25, 124.38, 119.41, 68.38, 39.03, 32.28.

Spectroscopic data were consistent with literature values.

tert-butyl 4-(isoquinolin-1-yl)piperidine-1-carboxylate[44]



Compound 21 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

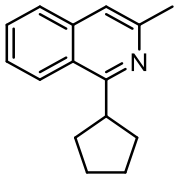
Column Chromatography: Silica, gradient 2-15 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.7 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.54 (m, 2H), 7.50 (d, *J* = 5.7 Hz, 1H), 4.33 (br, 2H), 3.70 (m, 1H), 2.97 (m, 2H), 2.11 – 1.85 (m, 4H), 1.49 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.53, 154.80, 141.96, 136.46, 129.77, 127.77, 127.15, 126.22, 124.30, 119.39, 79.40, 44.29 (br), 39.77, 31. 51 (br), 28.56.

Spectroscopic data were consistent with literature values.

1-cyclopentyl-3-methylisoquinoline



Compound 22 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

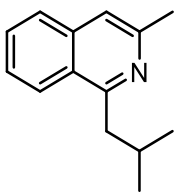
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.61-7.57 (m, 1H), 7.51-7.47 (m, 1H), 7.30 (s, 1H), 4.00 (p, *J* = 8.3 Hz, 1H), 2.68 (s, 3H), 2.19-2.13 (m, 4H), 1.99-1.90 (m, 2H), 1.85 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.94, 150.43, 137.16, 129.37, 126.85, 125.69, 125.30, 125.21, 116.73, 43.27, 32.81, 26.09, 24.61.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{15}H_{17}N$: 212.1434, found: 212.1433

1-isobutyl-3-methylisoquinoline



Compound 23 was prepared according to the general procedure (GP3) and isolated as a yellow oil.

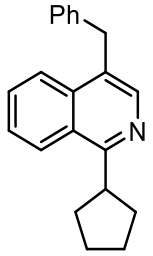
Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.50-7.46 (m, 1H), 7.33 (s, 1H), 3.14 (d, *J* = 7.3 Hz, 2H), 2.66 (s, 3H), 2.26 (dt, *J* = 13.6, 6.8 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.33, 150.44, 137.20, 129.73, 126.86, 125.91, 125.74, 125.64, 117.20, 44.22, 29.91, 29.84, 24.54, 22.92.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{14}H_{17}N$: 200.1433, found: 200.2

4-benzyl-1-cyclopentylisoquinoline



Compound 24 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

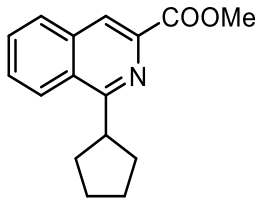
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 8.42 (s, 1H), 8.35 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.69-7.60 (m, 2H), 7.39 – 7.22 (m, 5H), 4.43 (s, 2H), 4.17 – 3.99 (m, 1H), 2.29 – 2.14 (m, 4H), 2.06 – 1.93 (m, 2H), 1.93 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 163.94, 142.67, 140.15, 135.32, 129.65, 128.71, 128.63, 127.54, 127.18, 126.47, 126.33, 125.91, 124.27, 43.04, 36.46, 32.87, 26.17.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{21}H_{21}N$: 288.1747, found: 288.1743

methyl 1-cyclopentylisoquinoline-3-carboxylate[52]



Compound 25 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

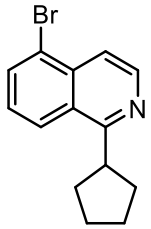
Column Chromatography: Silica, gradient 5-15 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.33 – 8.23 (m, 1H), 7.98 – 7.89 (m, 1H), 7.76 – 7.65 (m, 2H), 4.05-3.94 (s, 4H), 2.27 – 2.09 (m, 4H), 2.00-1.87 (m, 2H), 1.85 – 1.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99, 165.16, 140.55, 136.06, 130.26, 129.12, 129.02, 128.71, 125.58, 122.63, 52.75, 43.87, 32.58, 26.03.

Spectroscopic data were consistent with literature values.

5-bromo-1-cyclopentylisoquinoline



Compound 26 was prepared according to the general procedure (GP1) and isolated as a yellow oil.

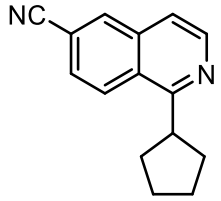
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 8.56 (d, *J* = 6.0 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 7.93 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.85 (d, *J* = 6.5 Hz, 1H), 7.42 (dd, *J* = 8.4, 7.6 Hz, 1H), 4.05 – 3.95 (m, 1H), 2.20 – 2.02 (m, 4H), 1.97 – 1.84 (m, 2H), 1.83 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 165.31, 143.31, 135.52, 133.47, 128.43, 127.11, 125.10, 122.56, 117.83, 43.25, 33.03, 26.17.

HRMS (ESI^{+}): $[M+H]^{+}$cal'd for $C_{14}H_{14}BrN$: 276.0310, found: 276.0377

1-cyclopentylisoquinoline-6-carbonitrile



Compound 27 was prepared according to the general procedure (GP1) and isolated as a dark yellow oil.

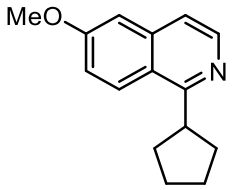
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.7 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 1.6 Hz, 1H), 7.72 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.52 (dd, *J* = 5.8, 0.9 Hz, 1H), 4.00 (p, *J* = 8.2 Hz, 1H), 2.19 – 2.03 (m, 4H), 1.96 – 1.86 (m, 2H), 1.82-1.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.60, 143.78, 135.43, 133.52, 127.86, 127.54, 126.83, 118.65, 118.44, 113.42, 43.20, 32.97, 26.18.

HRMS (ESI^{+}): $[M+H]^{+}$cal'd for $C_{15}H_{14}N_2$: 223.1229, found: 223.1227

1-cyclopentyl-6-methoxyisoquinoline



Compound 28 was prepared according to the general procedure (GP1 and GP3) and isolated as a yellow oil.

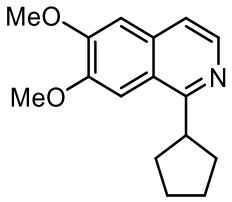
Column Chromatography: Silica, gradient 5-15% % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 8.38 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 9.3 Hz, 1H), 7.37 (d, J = 5.7 Hz, 1H), 7.19 (dd, J = 9.3, 2.6 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 3.94 (s, 3H), 2.14-2.03 (m, 4H), 1.97 – 1.84 (m, 1H), 1.80-1.71 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 164.27, 160.32, 142.65, 138.43, 127.23, 122.97, 119.52, 118.47, 105.03, 55.54, 43.12, 32.93, 26.18.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{15}H_{17}NO$: 228.1383, found: 228.1381

1-cyclopentyl-6,7-dimethoxyisoquinoline



Compound 29 was prepared according to the general procedure (GP1 and GP3) and isolated as a yellow solid.

Column Chromatography: Silica, gradient 5-15% EtOAc/Heptane

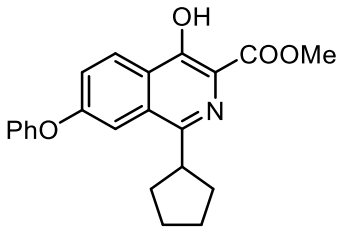
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 5.6 Hz, 1H), 7.43 (s, 1H), 7.33 (d, *J* = 5.6 Hz, 1H), 7.04 (s, 1H), 4.03 (s, 3H), 4.01 (s, 3H), 3.87 (p, *J* = 8.4 Hz, 1H), 2.19 – 2.03 (m, 4H), 1.97 – 1.86 (m, 2H), 1.84 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.30, 152.35, 149.77, 141.03, 133.13, 122.96, 117.92, 105.51, 103.83, 56.09, 43.22, 32.66, 26.21.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{16}H_{19}NO_2$: 258.1488, found: 258.1486

m.p.: 76 ºC.

methyl 1-cyclopentyl-4-hydroxy-7-phenoxyisoquinoline-3-carboxylate



Compound 30 was prepared according to the general procedure (GP1) and isolated as a yellow solid.

Column Chromatography: Silica, gradient 5-20% EtOAc/Heptane

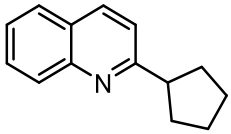
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.24 – 7.19 (m, 1H), 7.13 – 7.09 (m, 2H), 4.05 (s, 3H), 3.62 (p, *J* = 8.4 Hz, 1H), 2.06-1.99 (m, , 4H), 1.81-1.78 (m, 2H), 1.71 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 159.01, 156.04, 155.52, 154.18, 132.11, 130.27, 126.13, 124.64, 124.19, 122.00, 119.89, 118.65, 111.68, 52.91, 43.73, 31.97, 25.92.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{22}H_{21}NO_4$: 364.1543, found: 364.1533

m.p.: 94 ºC.

2-cyclopentylquinoline[53]



Compound 31 was prepared according to the general procedure (GP2) and isolated as a dark yellow oil.

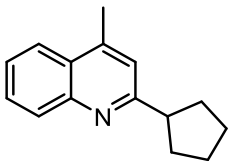
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 12.5, 8.5 Hz, 2H), 7.77 (d, *J* = 6.7 Hz, 1H), 7.67 (t, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.28 – 2.11 (m, 2H), 1.96 – 1.83 (m, 4H), 1.83 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 147.86, 136.31, 129.34, 129.13, 127.55, 127.02, 125.72, 120.19, 49.04, 33.75, 26.17. Ratio (2:4) = 4:1

Spectroscopic data were consistent with literature values.

2-cyclopentyl-4-methylquinoline[46]



Compound 32 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

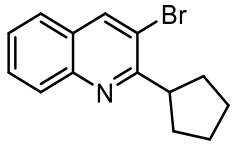
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 1H), 7.93 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.17 (d, *J* = 1.2 Hz, 1H), 3.39 – 3.28 (m, 1H), 2.68 (d, *J* = 1.0 Hz, 3H), 2.22 – 2.14 (m, 2H), 1.91 – 1.85 (m, 4H), 1.78 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.06, 147.67, 144.22, 129.62, 129.04, 127.10, 125.48, 123.67, 120.77, 48.95, 33.71, 26.18, 18.95.

Spectroscopic data were consistent with literature values.

3-bromo-2-cyclopentylquinoline[54]



Compound 33 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

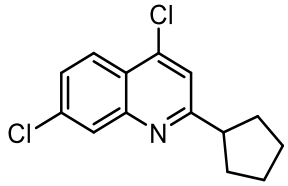
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 3.84 - 3.77 (m, *J* = 1H), 2.17 – 2.00 (m, 4H), 1.96 – 1.86 (m, 2H), 1.80 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.10, 146.56, 138.59, 129.46, 129.30, 128.05, 126.55, 126.46, 119.60, 46.19, 32.24, 26.09. Ratio (2:4) = 6:1

Spectroscopic data were consistent with literature values.

4,7-dichloro-2-cyclopentylquinoline[55]



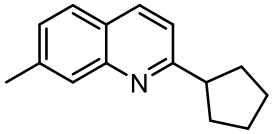
Compound 34 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.40 (s, 1H), 3.39 – 3.27 (m, 1H), 2.21 – 2.10 (m, 2H), 1.95 – 1.80 (m, 4H), 1.80 – 1.70 (m, 2H).

Spectroscopic data were consistent with literature values.

2-cyclopentyl-7-methylquinoline



Compound 35 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

Ratio (2:4) = 4:1

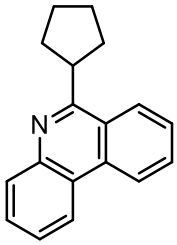
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.92 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.50 – 3.40 (m, 1H), 2.28 – 2.24 (m, 2H), 2.01 – 1.92 (m, 4H), 1.87 – 1.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.26, 148.04, 139.47, 135.91, 128.21, 127.83, 127.13, 124.98, 119.34, 48.95, 33.67, 26.11, 21.93.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{15}H_{17}N$: 212.1433, found: 212.1431

6-cyclopentylphenanthridine[56]



Compound 36 was prepared according to the general procedure (GP2) and isolated as a dark yellow oil.

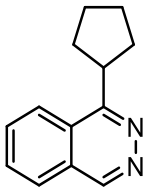
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.2 Hz, 1H), 8.53 (d, *J* = 7.2 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 8.17 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.80 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.70 (dddd, *J* = 16.3, 8.2, 7.0, 1.3 Hz, 2H), 7.61 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 4.12 - 4.04 (m, 1H), 2.38 – 2.11 (m, 4H), 2.04 – 1.91 (m, 2H), 1.91 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 164.24, 143.86, 133.02, 130.08, 129.98, 128.46, 127.10, 126.28, 126.18, 125.72, 123.58, 122.48, 121.90, 43.65, 32.31, 26.14.

Spectroscopic data were consistent with literature values.

1-cyclopentylphthalazine



Compound 37 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

Column Chromatography: Silica, gradient 10-40% % EtOAc/Heptane

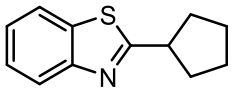
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.83 (m, 3H), 3.96 (p, *J* = 8.1 Hz, 1H), 2.28 – 2.12 (m, 4H), 1.99 – 1.86 (m, 2H), 1.84 – 1.70 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.76, 150.38, 132.30, 131.75, 127.08, 126.61, 125.88, 124.13, 42.04, 32.46, 26.08.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{13}H_{14}N_2$: 199.1229, found: 199.1220

Note: the dialkylated product was also observed in a ratio 1:2.

2-cyclopentylbenzo[d]thiazole[56]



Compound 38 was prepared according to the general procedure (GP2) and isolated as a dark yellow oil.

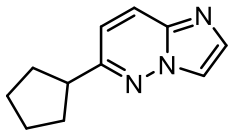
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.44 (ddd, J = 8.2, 7.2, 1.3 Hz, 1H), 7.33 (ddd, J = 8.2, 7.3, 1.2 Hz, 1H), 3.55 (p, J = 8.2 Hz, 1H), 2.34 – 2.20 (m, 2H), 2.08 – 1.82 (m, 4H), 1.85 – 1.59 (m, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 177.24, 153.38, 134.96, 125.93, 124.64, 122.64, 121.61, 44.95, 34.19, 25.73.

Spectroscopic data were consistent with literature values.

3-cyclopentylimidazo[1,2-b]pyridazine



Compound 39 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

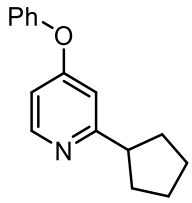
Column Chromatography: Silica, gradient 10-20% EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 4.7 Hz, 1H), 7.92 (d, *J* = 1.3 Hz, 1H), 7.70 (d, *J* = 1.2 Hz, 1H), 6.83 (dd, *J* = 4.7, 0.9 Hz, 1H), 3.79 – 3.63 (m, 1H), 2.32 – 2.16 (m, 2H), 1.94 – 1.68 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.54, 143.42, 139.94, 132.64, 116.83, 112.39, 40.46, 32.71, 25.52.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{12}H_{15}N_2$: 188.1307, found: 188.1183

2-cyclopentyl-4-phenoxypyridine



Compound 40 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

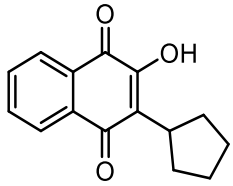
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 5.7 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.32 – 7.26 (m, 1H), 7.17 – 7.12 (m, 2H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.67 (dd, *J* = 5.6, 2.4 Hz, 1H), 3.16 (p, *J* = 8.3 Hz, 1H), 2.19 – 2.05 (m, 2H), 1.94 – 1.63 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.11, 165.21, 154.42, 150.72, 130.24, 125.30, 120.86, 110.20, 109.69, 48.12, 33.51, 25.88.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{16}H_{17}NO$: 240.1383, found: 240.1377

2-cyclopentyl-3-hydroxynaphthalene-1,4-dione



Compound 41 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

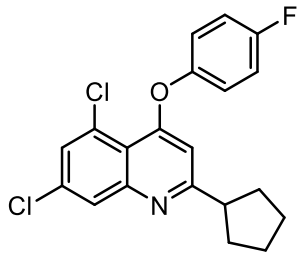
Column Chromatography: Silica, gradient 10-20% EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.08 (m, 1H), 8.04 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.73 (td, *J* = 7.6, 1.4 Hz, 1H), 7.65 (td, *J* = 7.5, 1.3 Hz, 1H), 7.49 (s, 1H), 3.48 – 3.38 (m, 1H), 1.96 – 1.81 (m, 6H), 1.67 – 1.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 184.77, 181.68, 152.97, 134.97, 133.39, 132.87, 129.40, 127.67, 127.01, 126.09, 35.02, 30.90, 26.93.

MS: [M]cal'd for $C_{15}H_{14}O_3$: 242.09438, found: 242.3

5,7-dichloro-2-cyclopentyl-4-(4-fluorophenoxy)quinolone[52]



Compound 42 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

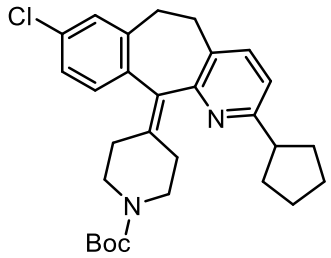
Column Chromatography: Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.18 – 7.08 (m, 4H), 6.53 (s, 1H), 3.21 – 3.09 (m, 1H), 2.07 – 1.99 (m, 2H), 1.80 – 1.73 (m, 4H), 1.69 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.15, 162.27, 159.98 (d, *J* = 243.9 Hz), 151.52, 150.50 (d, *J* = 2.7 Hz), 134.86, 130.00, 128.71, 127.69, 122.08 (d, *J* = 8.5 Hz), 117.12 (d, *J* = 23.5 Hz), 117.12, 106.41, 48.67, 33.28, 25.94.

Spectroscopic data were consistent with literature values.

tert-butyl 4-(8-chloro-2-cyclopentyl-5H-benzo[5,6]cyclohepta[1,2-b]pyridin-11(6H)-ylidene)piperidine-1-carboxylate



Compound 43 was prepared according to the general procedure (GP2) and isolated as a yellow oil.

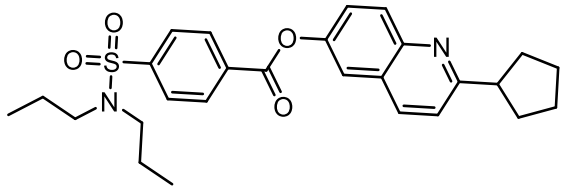
Column Chromatography: Silica, gradient 15% EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.9 Hz, 1H), 7.17 – 7.10 (m, 3H), 6.97 (d, *J* = 7.9 Hz, 1H), 3.78-3.70 (m, 2H), 3.43 – 3.31 (m, 1H), 3.33 – 3.21 (m, 1H), 3.18 – 3.05 (m, 3H), 2.86 – 2.71 (m, 2H), 2.52-2.46 (s, 1H), 2.37 – 2.23 (m, 3H), 2.10 – 1.97 (m, 2H), 1.85 – 1.75 (m, 2H), 1.73 – 1.63 (m, 4H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.74, 154.97, 140.12, 138.46, 137.93, 137.64, 134.49, 132.77, 130.68, 130.13, 128.83, 126.09, 119.43, 79.63, 47.89, 45.24, 34.11, 33.38, 32.01, 31.91, 31.56, 31.14, 30.80, 28.58, 25.77, 25.70.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{29}H_{35}ClN_2O_2$: 479.2459, found: 479.2452

2-cyclopentylquinolin-6-yl 4-(N,N-dipropylsulfamoyl)benzoate



Compound 44 was prepared according to the general procedure (GP2) and isolated as a green oil.

Column Chromatography: Silica, gradient 50-60% EtOAc/Heptane

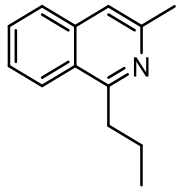
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.5 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.39 – 7.33 (m, 2H), 3.39 (p, *J* = 8.3 Hz, 1H), 3.19 – 3.10 (m, 4H), 2.22 – 2.13 (m, 2H), 1.96 – 1.84 (m, 4H), 1.80 – 1.74 (m, 2H), 1.58 (dt, *J* = 9.6, 7.5 Hz, 4H), 0.90 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.10, 167.46, 163.93, 151.18, 148.43, 145.15, 136.04, 132.86, 131.03, 128.85, 127.36, 125.25, 120.78, 120.50, 120.35, 50.12, 48.87, 33.64, 31.06, 26.15, 22.11, 11.31.

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{27}H_{32}N_2O_4S$: 481.2155, found: 481.2166

Note: the dialkylated product was also observed in a ratio 1:2.

3-methyl-1-propylisoquinoline



Compound 45 was prepared according to the general procedure (GP3) and isolated as a yellow oil.

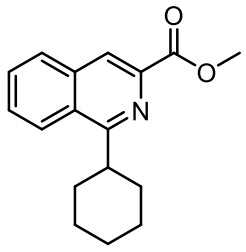
Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.33 (s, 1H), 3.29 – 3.21 (m, 2H), 2.66 (s, 3H), 1.92 – 1.81 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 150.53, 137.23, 129.79, 126.91, 126.02, 125.55, 125.14, 117.24, 37.87, 24.50, 23.81, 14.54.

MS (ESI^+): $[M+H]^+$cal'd for $C_{13}H_{15}N$: 186.1277, found: 186.1

methyl 1-cyclohexylisoquinoline-3-carboxylate[57]



Compound 46 was prepared according to the general procedure (GP3) and isolated as a yellow oil.

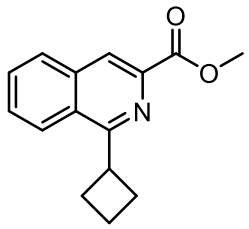
Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 8.29 – 8.25 (m, 1H), 7.96 – 7.92 (m, 1H), 7.74 – 7.68 (m, 1H), 4.02 (s, 3H), 3.63 – 3.52 (m, 1H), 2.06 – 1.90 (m, 6H), 1.85 – 1.78 (m, 1H), 1.62 – 1.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 166.24, 140.82, 136.15, 130.22, 129.18, 129.14, 127.88, 125.08, 122.54, 52.80, 42.19, 32.36, 26.91, 26.19.

Spectroscopic data were consistent with literature values.

methyl 1-cyclobutylisoquinoline-3-carboxylate[58]



Compound 47 was prepared according to the general procedure (GP3) and isolated as a yellow solid.

Column Chromatography: Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.75 – 7.66 (m, 2H), 4.43-4.36 (m, *J* = 8.8 Hz, 1H), 4.04 (s, 3H), 2.77-2.67 (m, 2H), 2.60 – 2.49 (m, 2H), 2.26-2.14 (m 1H), 2.05 – 1.91 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.97, 164.14, 140.54, 135.94, 130.47, 129.22, 129.00, 127.92, 125.54, 122.81, 52.84, 39.68, 27.52, 18.56.

Spectroscopic data were consistent with literature values.

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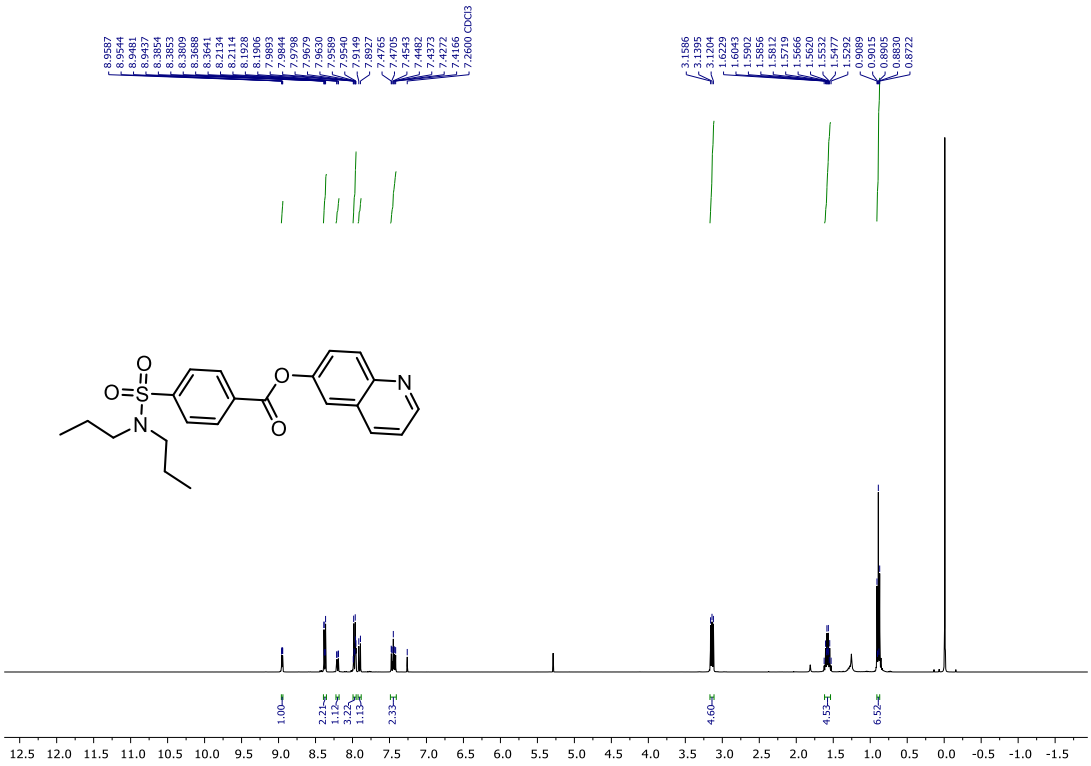
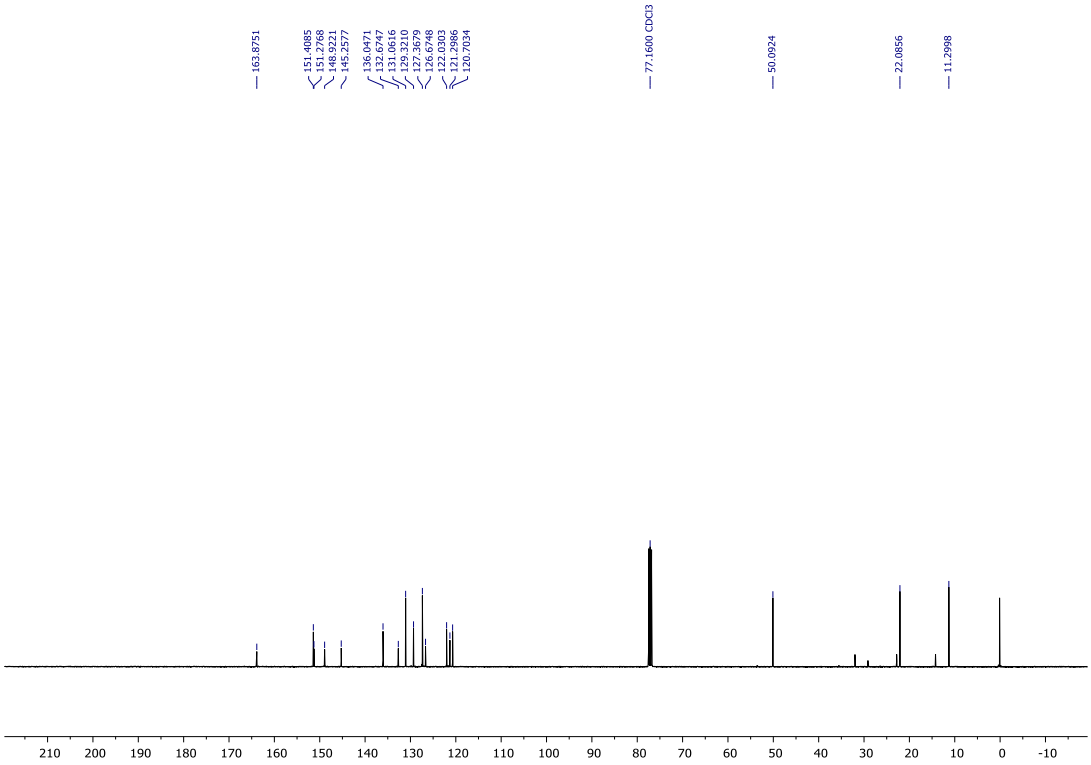
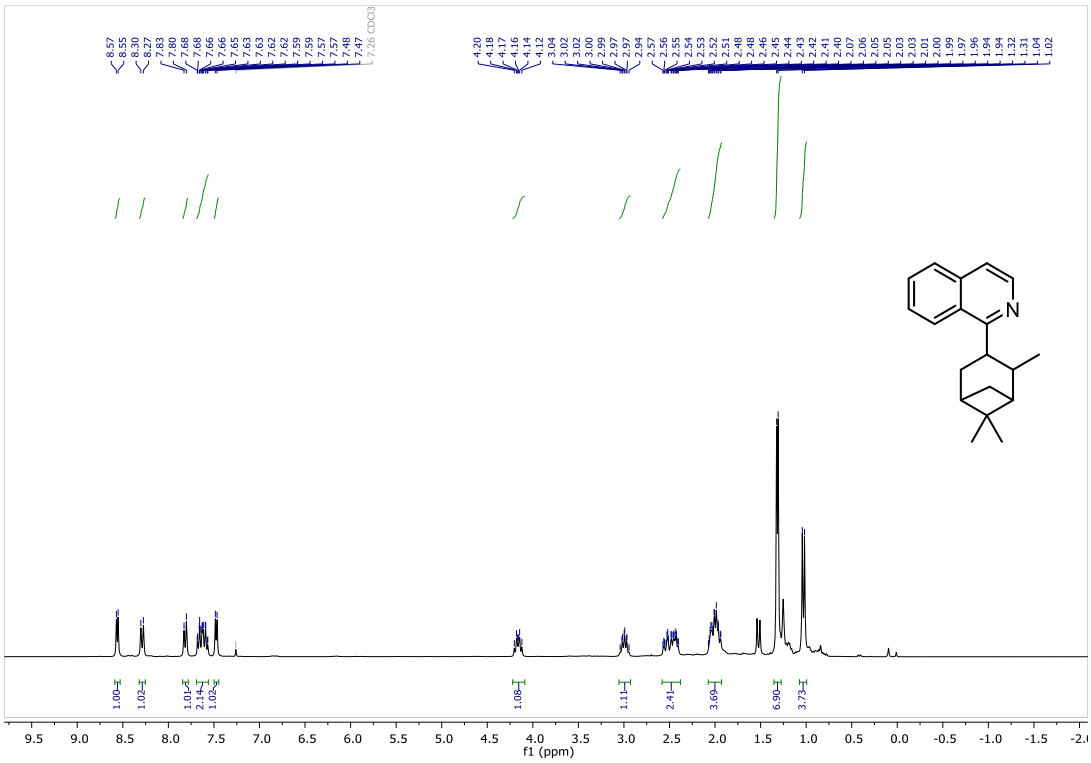


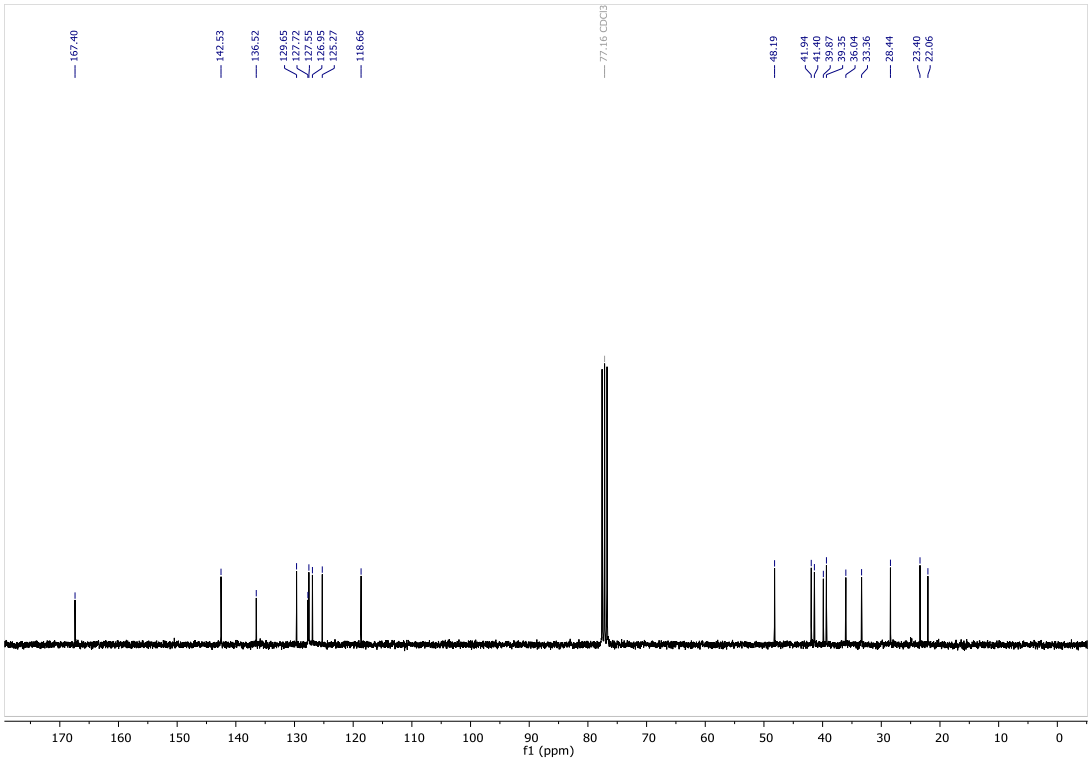
^{1}H NMR of compound **A6**



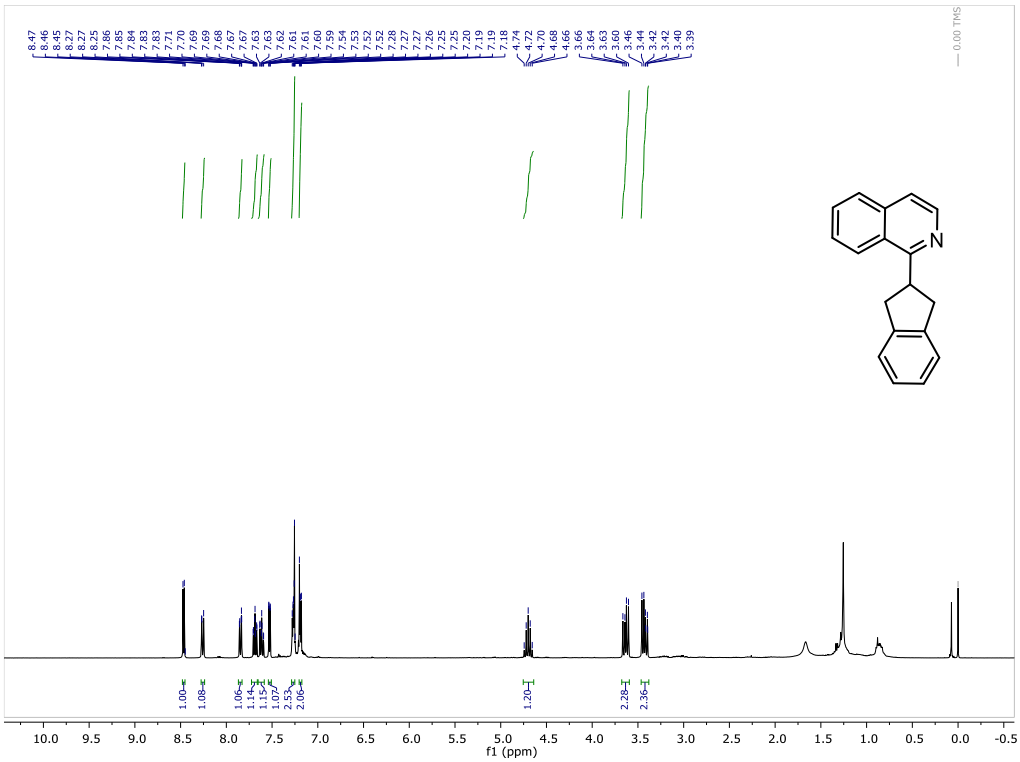
^{13}C of compound **A6**



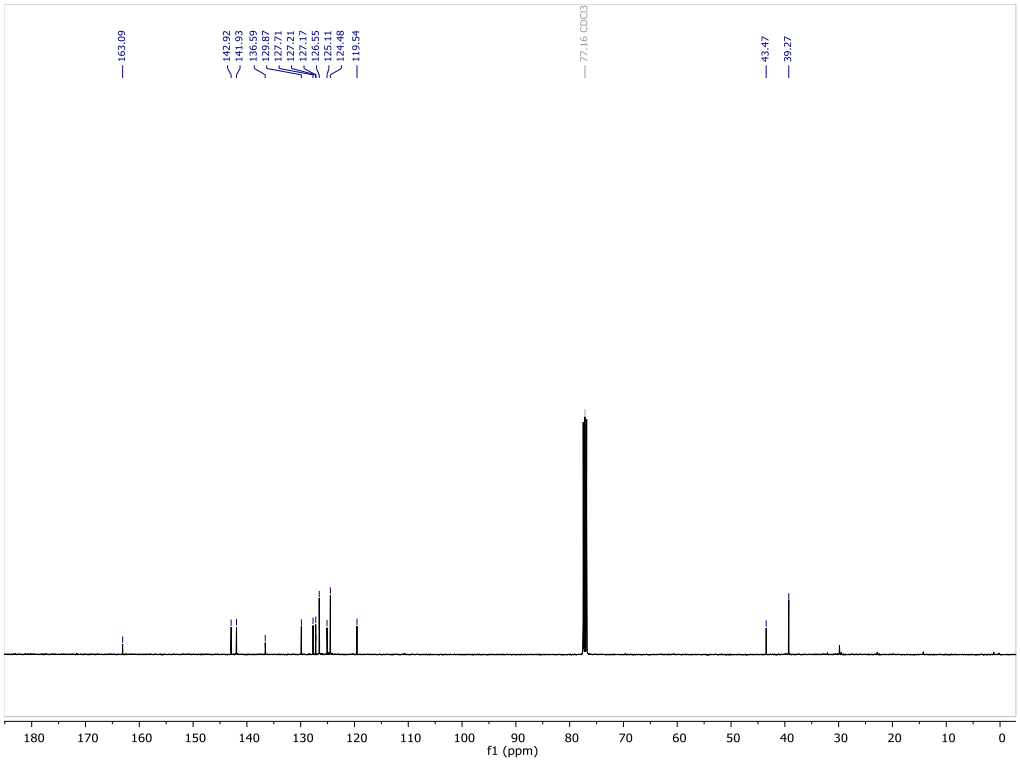
^{1}H NMR of compound **4**



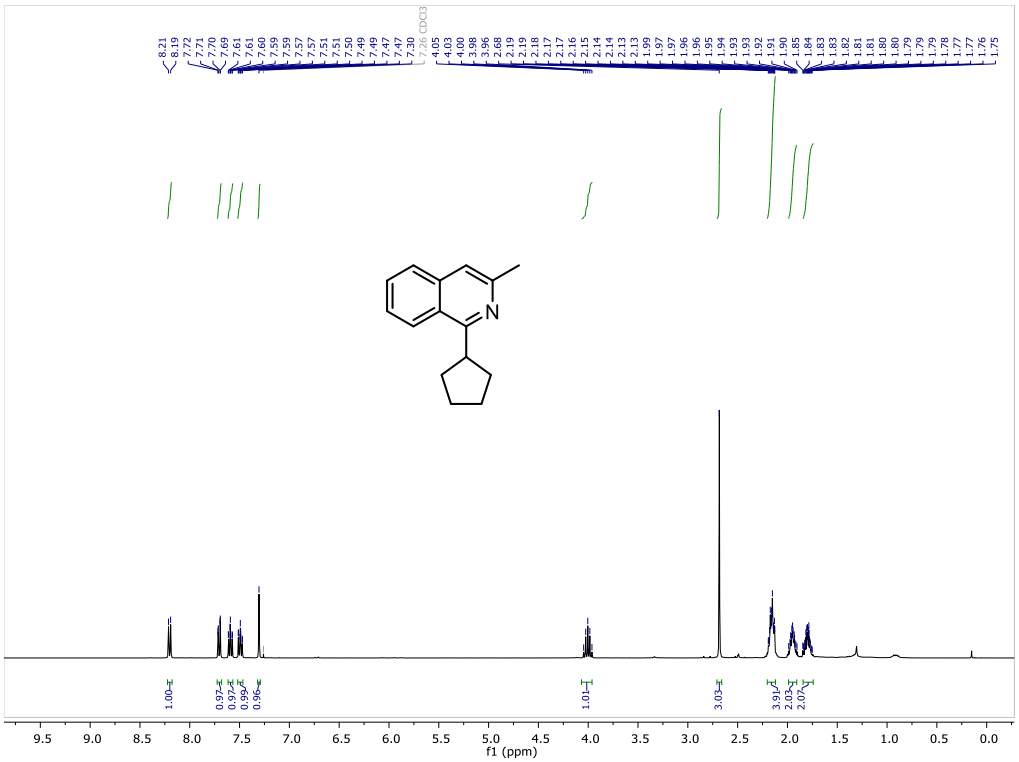
^{13}C of compound **4**



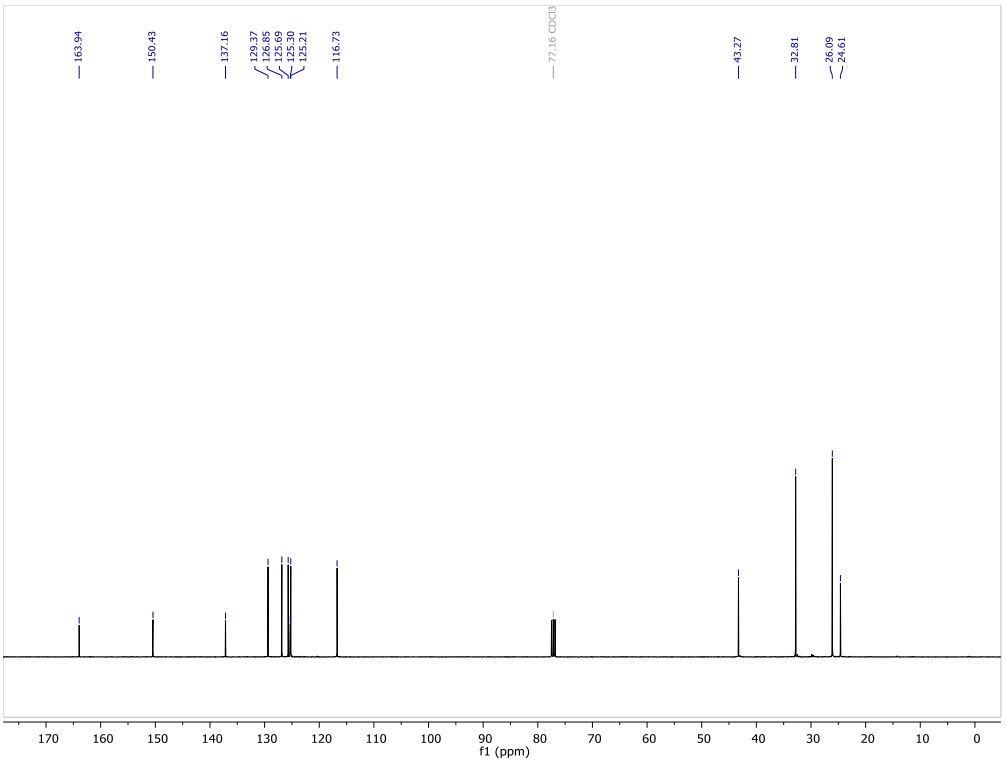
^{1}H NMR of compound **5**



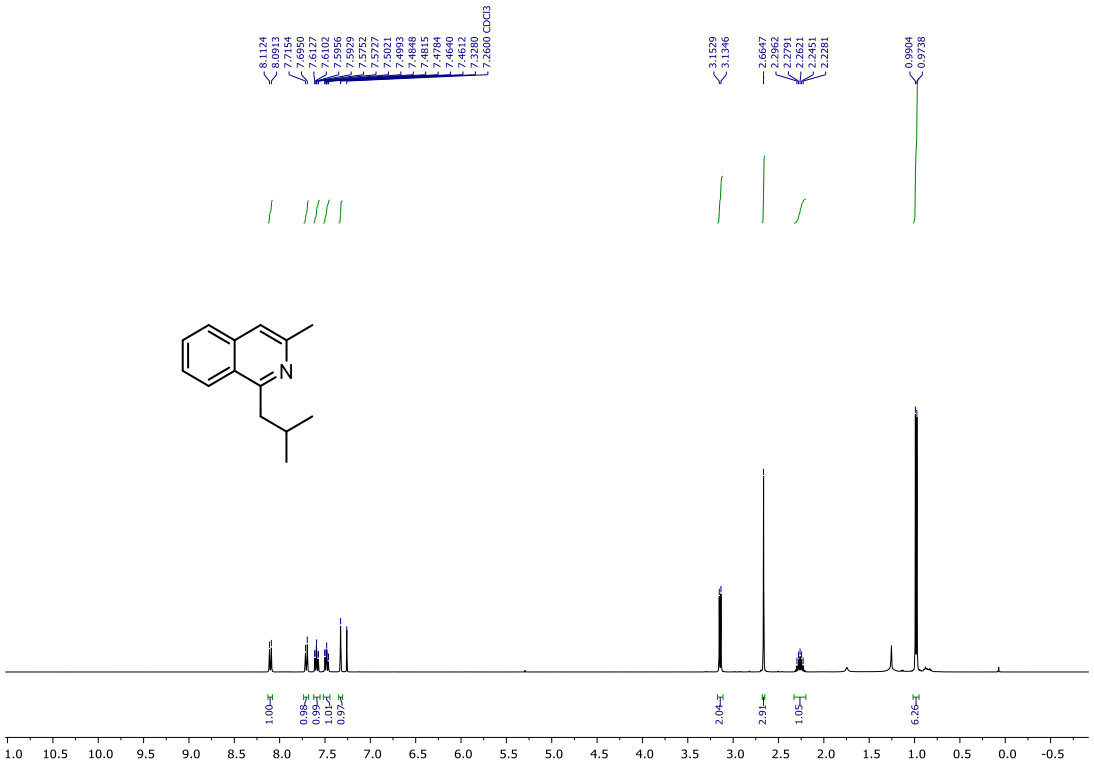
^{13}C of compound **5**



^{1}H NMR of compound **22**



^{13}C NMR of compound **22**



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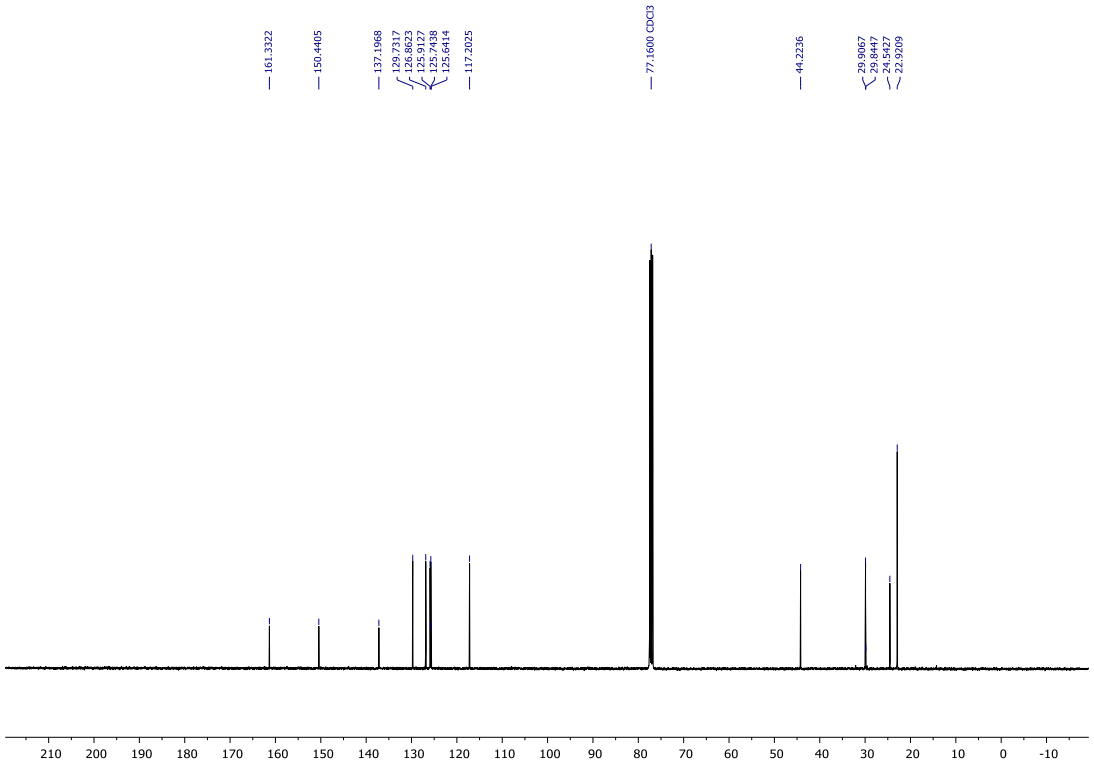

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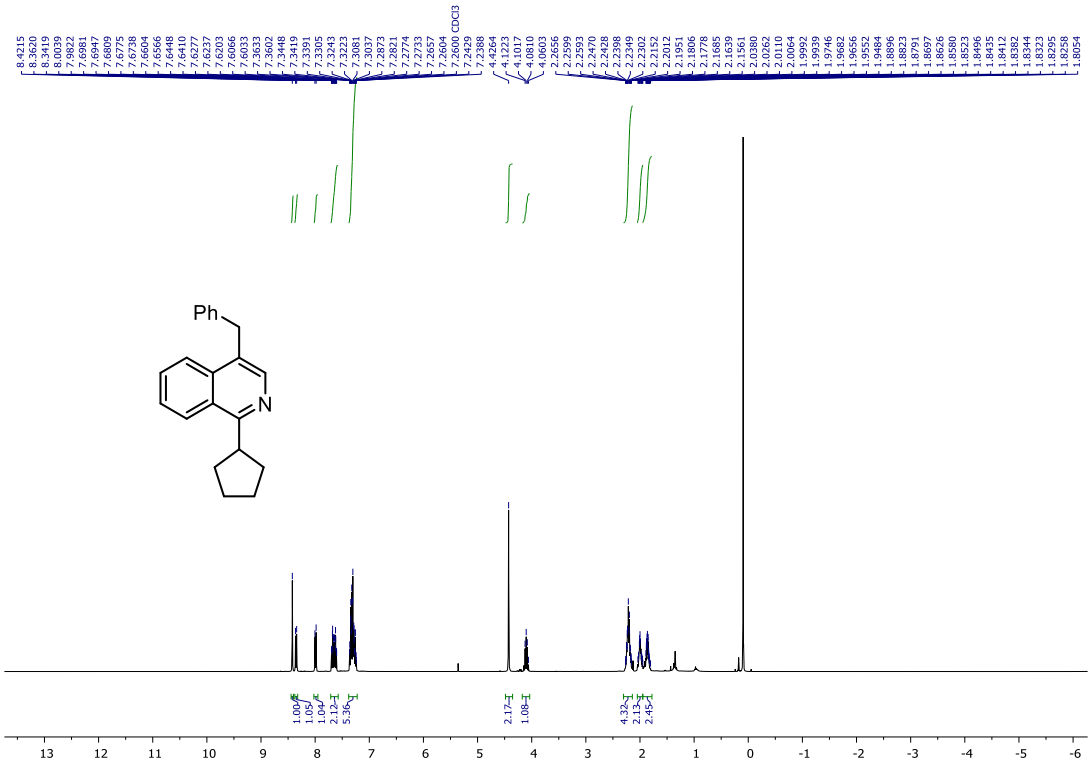
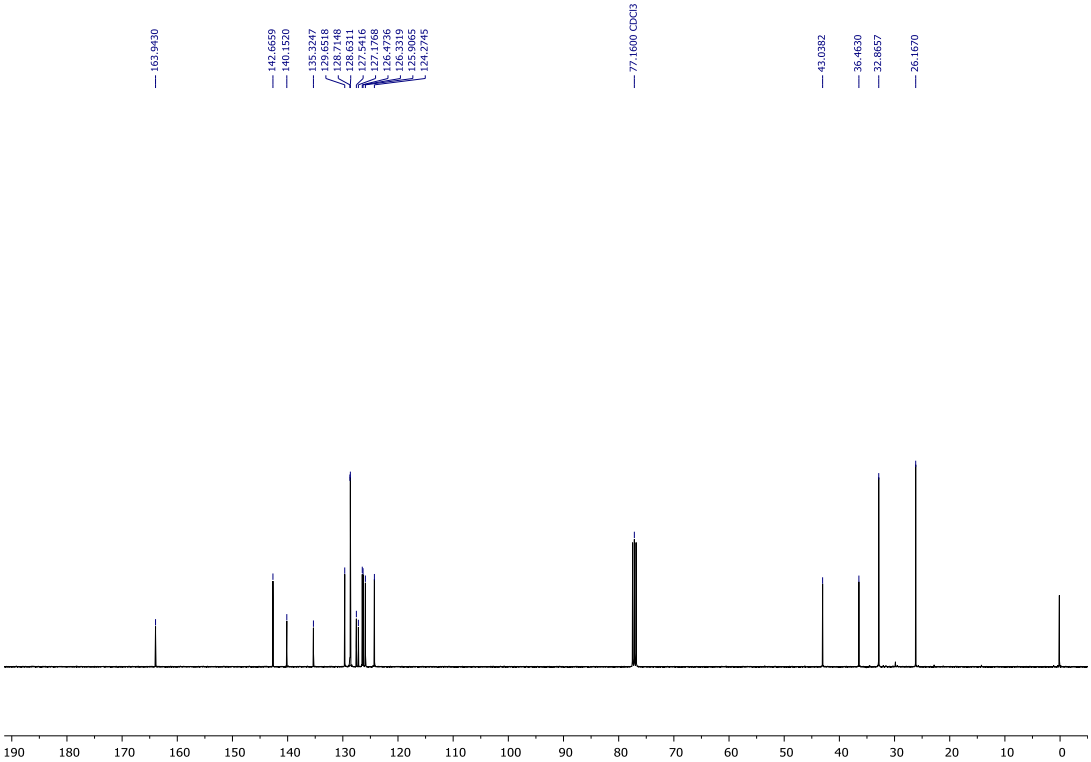
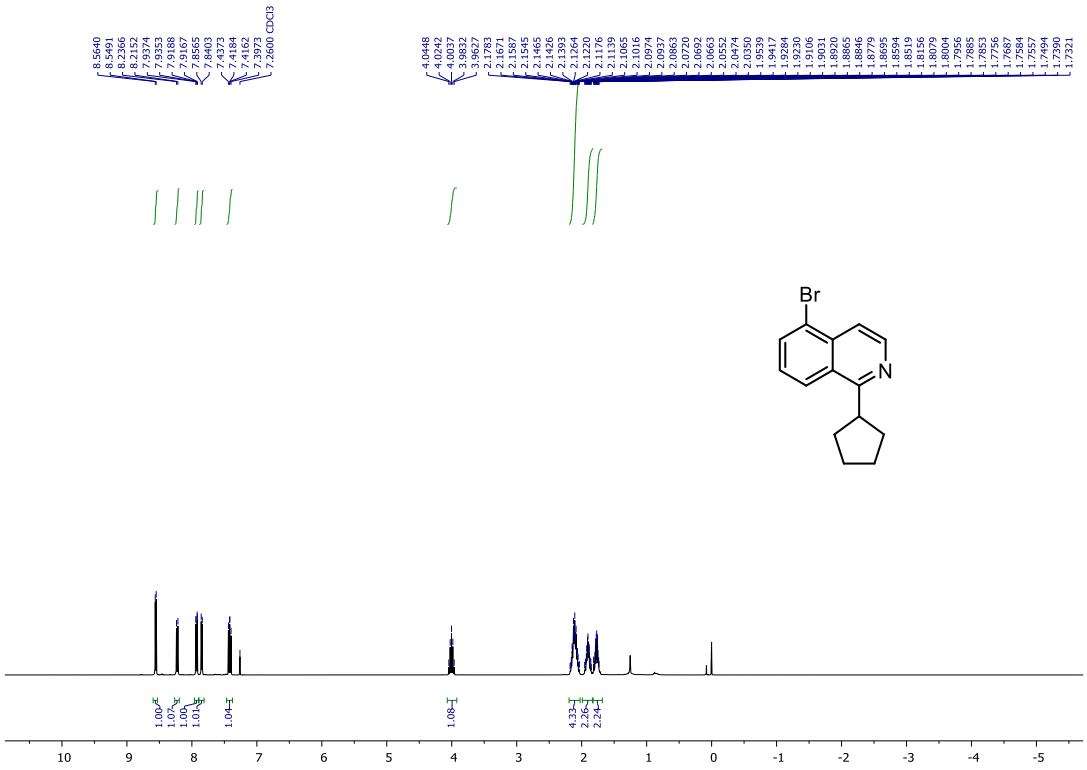


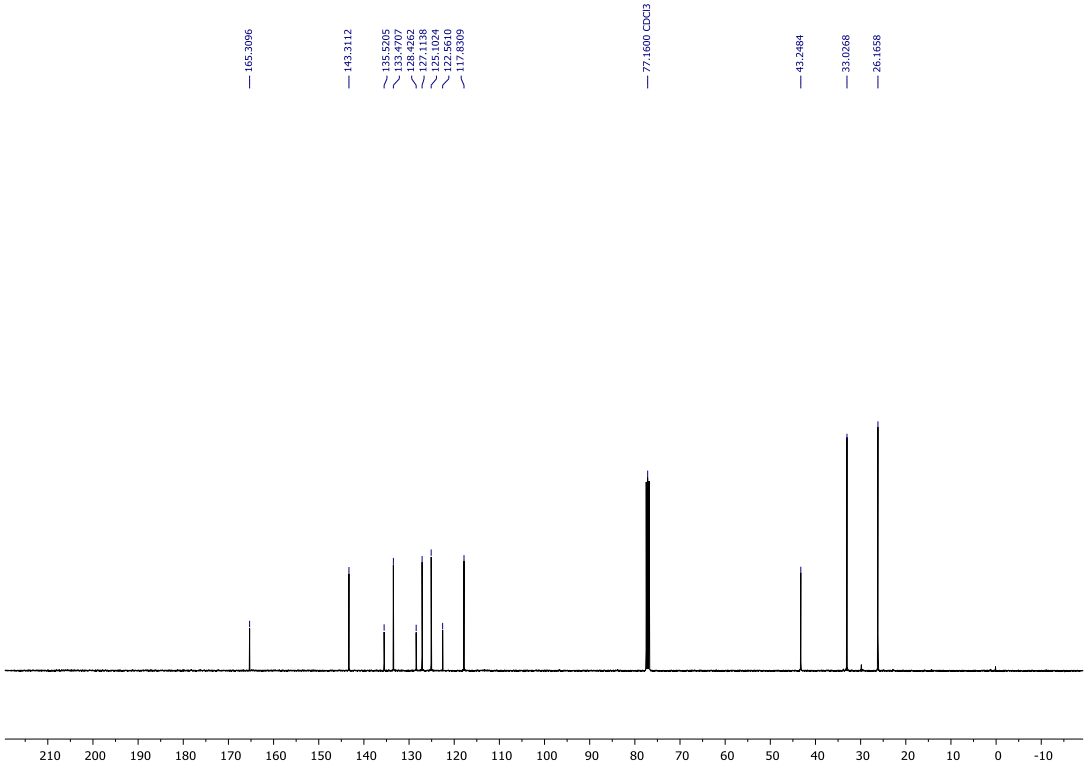
^{1}H NMR of compound **24**



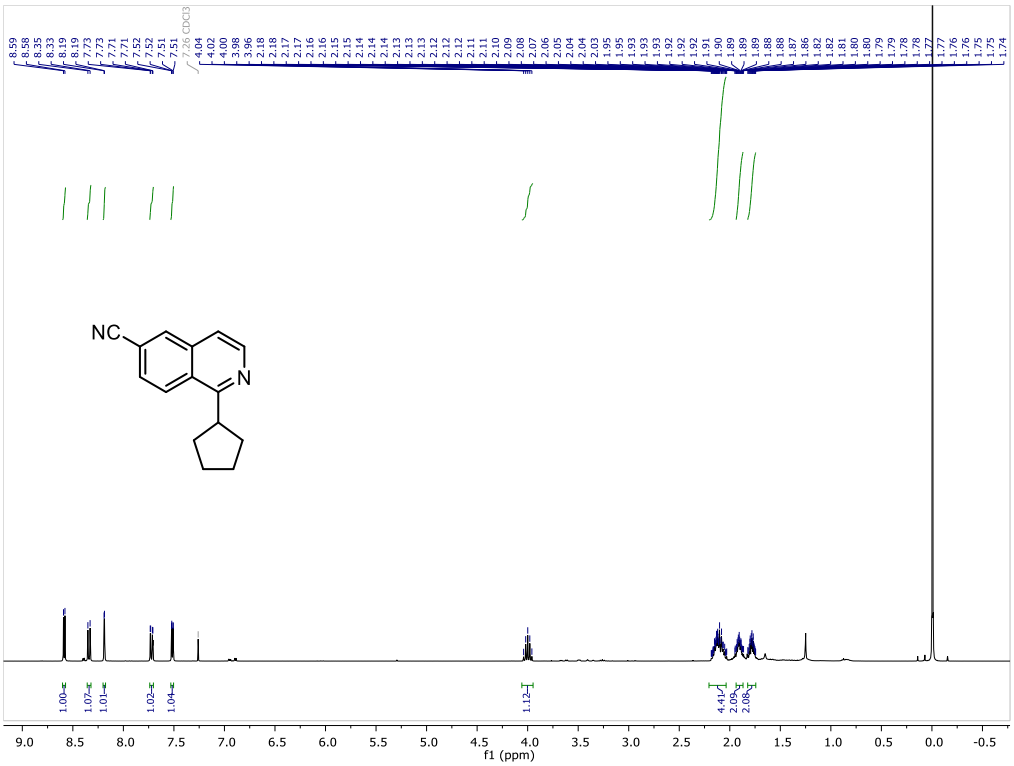
^{13}C NMR of compound **24**



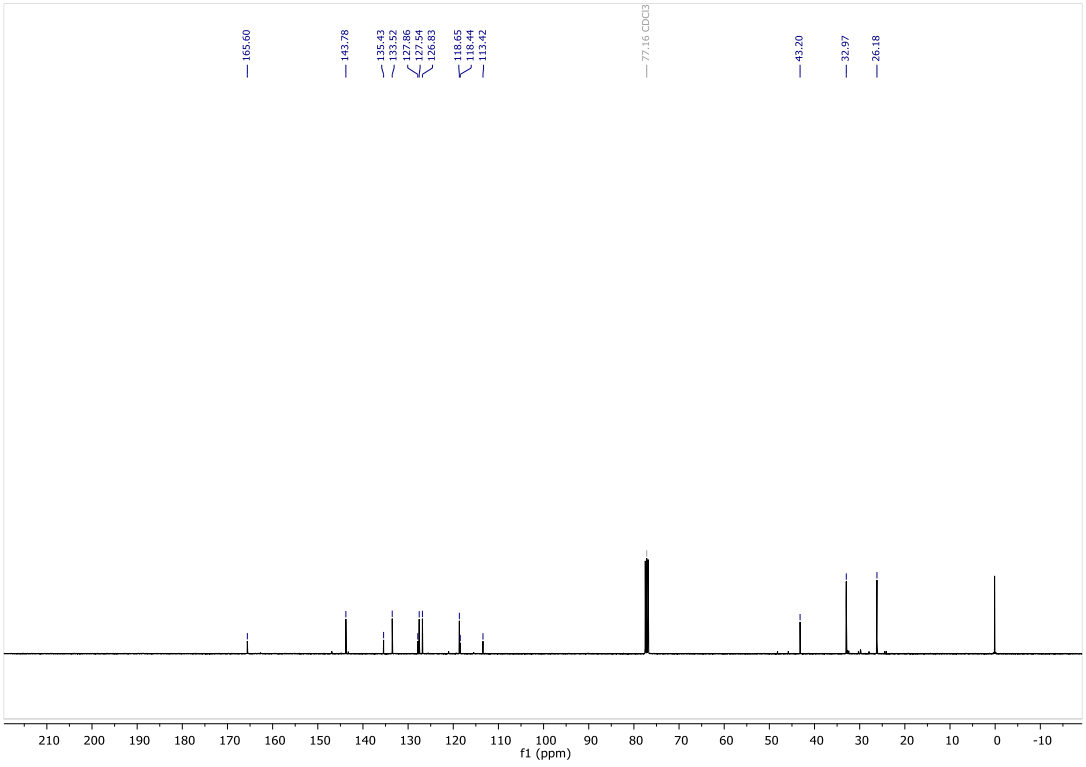
^{1}H NMR of compound **26**



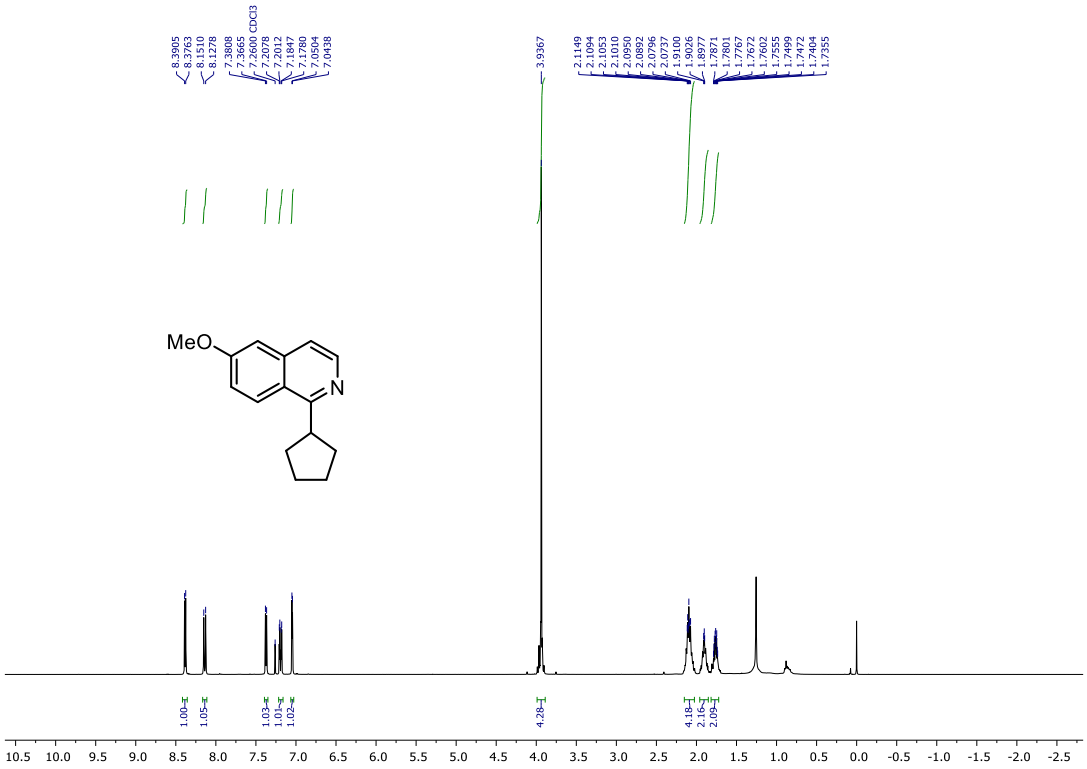
^{13}C NMR of compound **26**



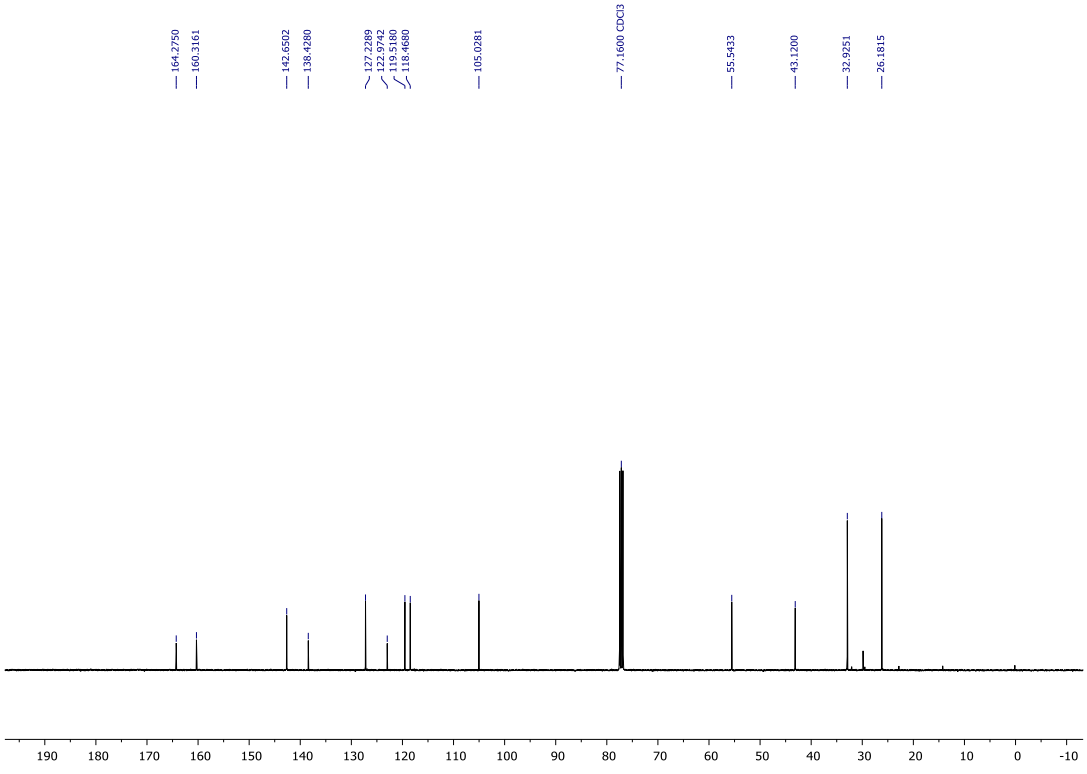
^{1}H NMR of compound **27**



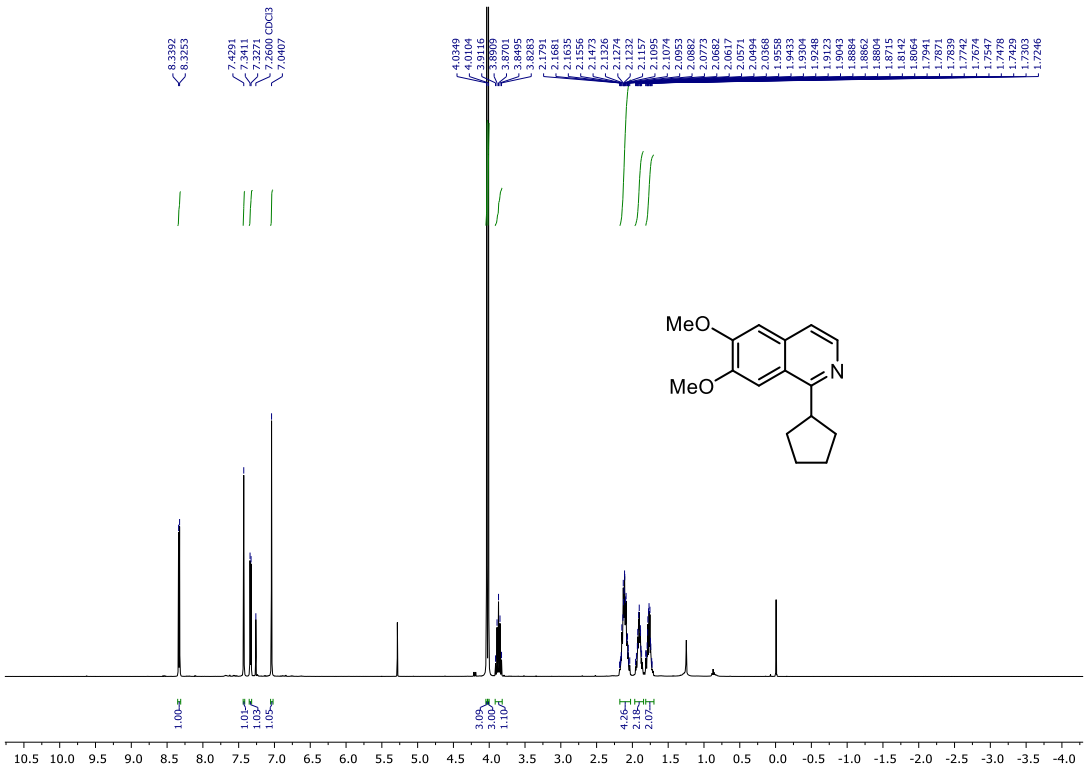
^{13}C NMR of compound **27**



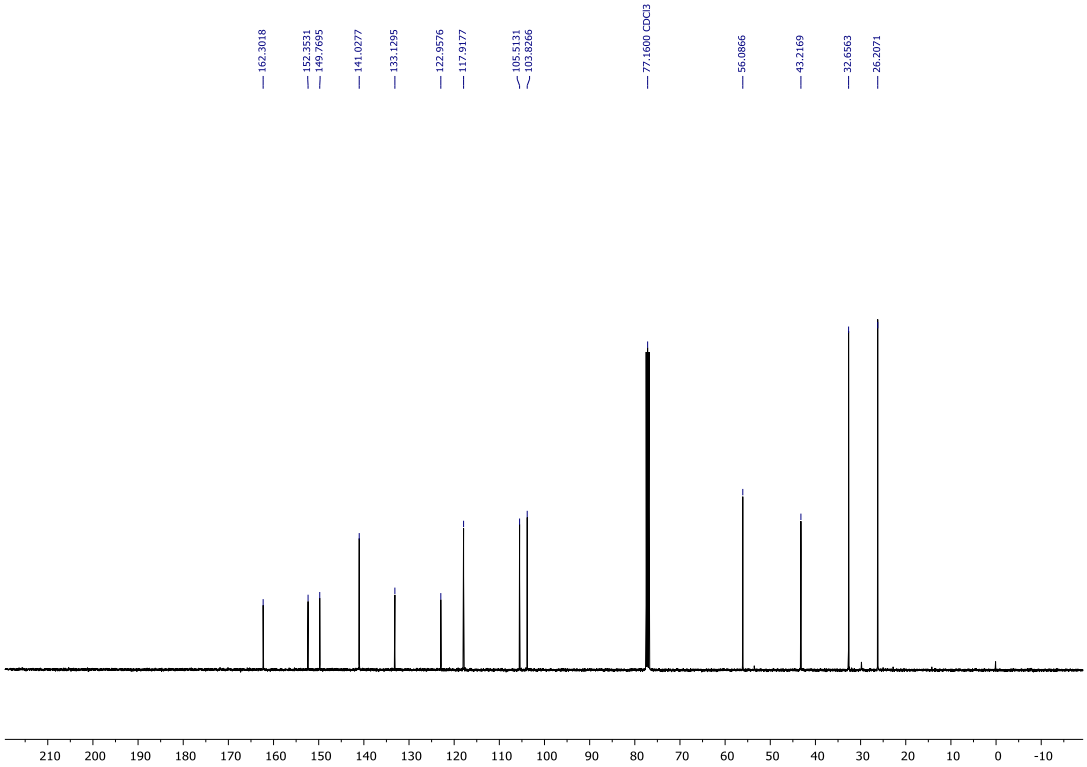
^{1}H NMR of compound **28**



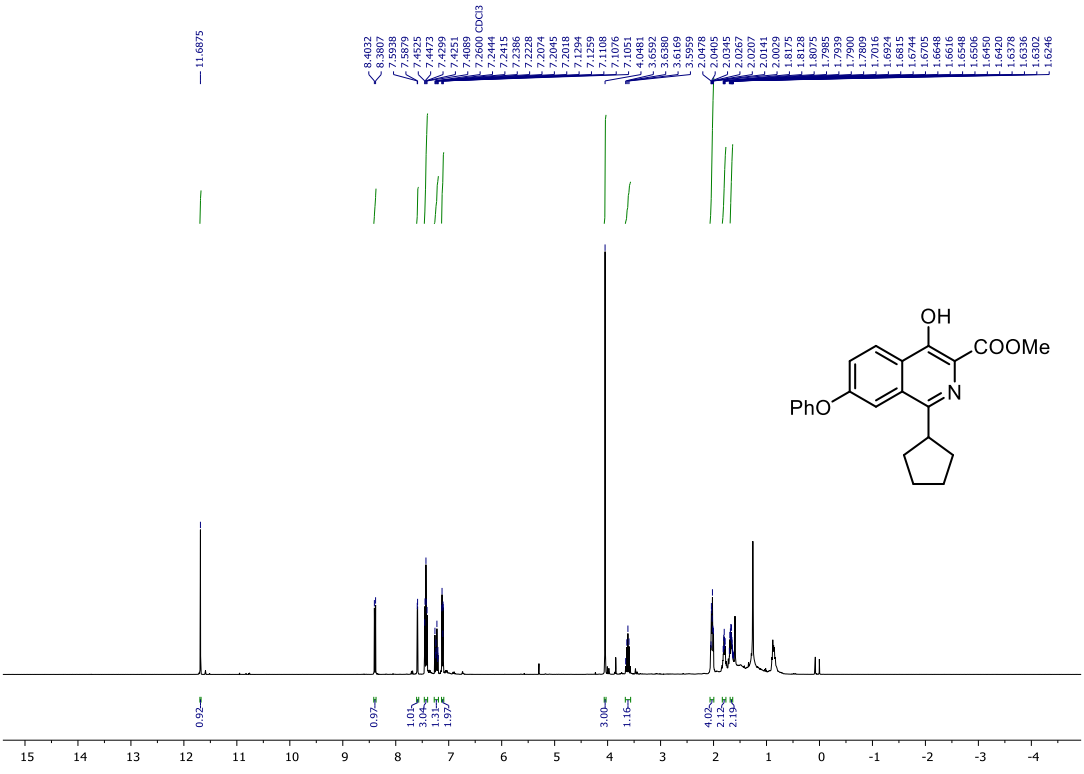
^{13}C NMR of compound **28**



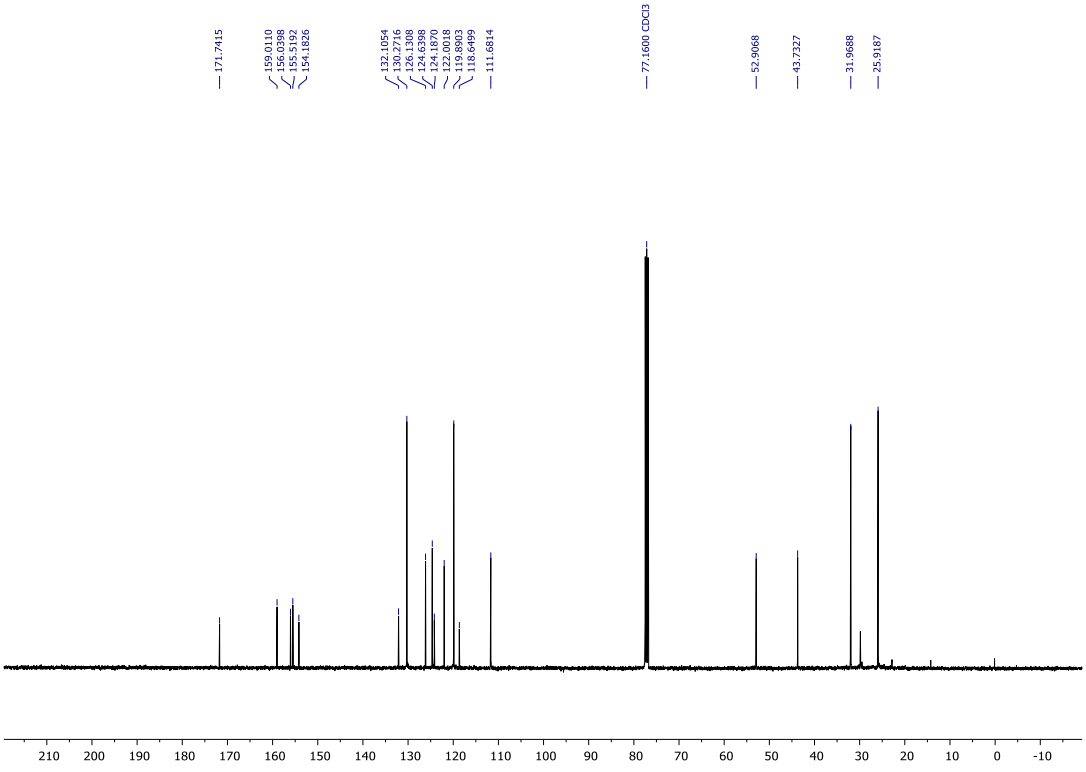
^{1}H NMR of compound 29



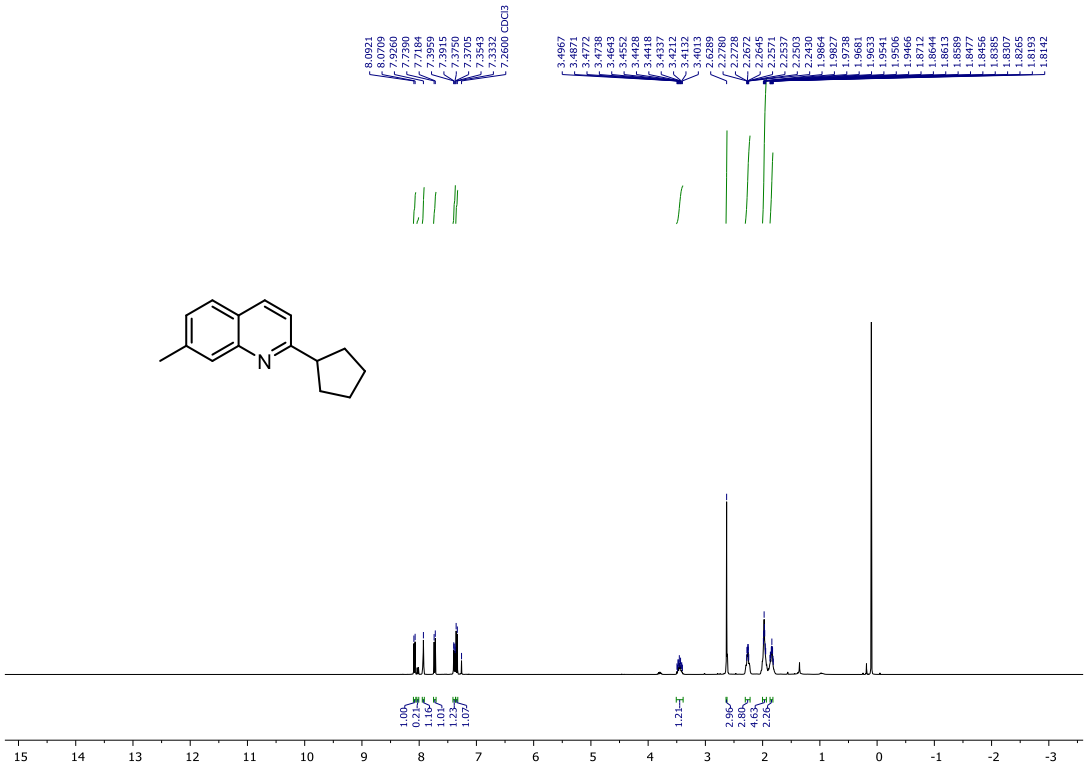
^{13}C NMR of compound **29**



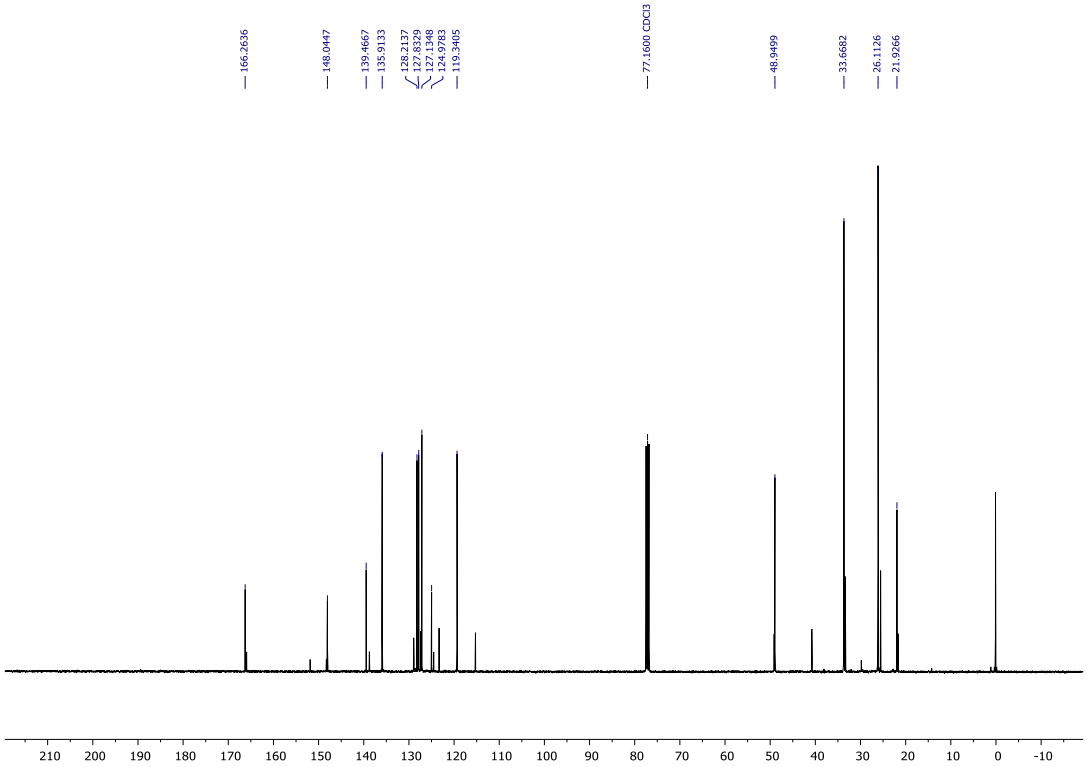
^{1}H NMR of compound **30**



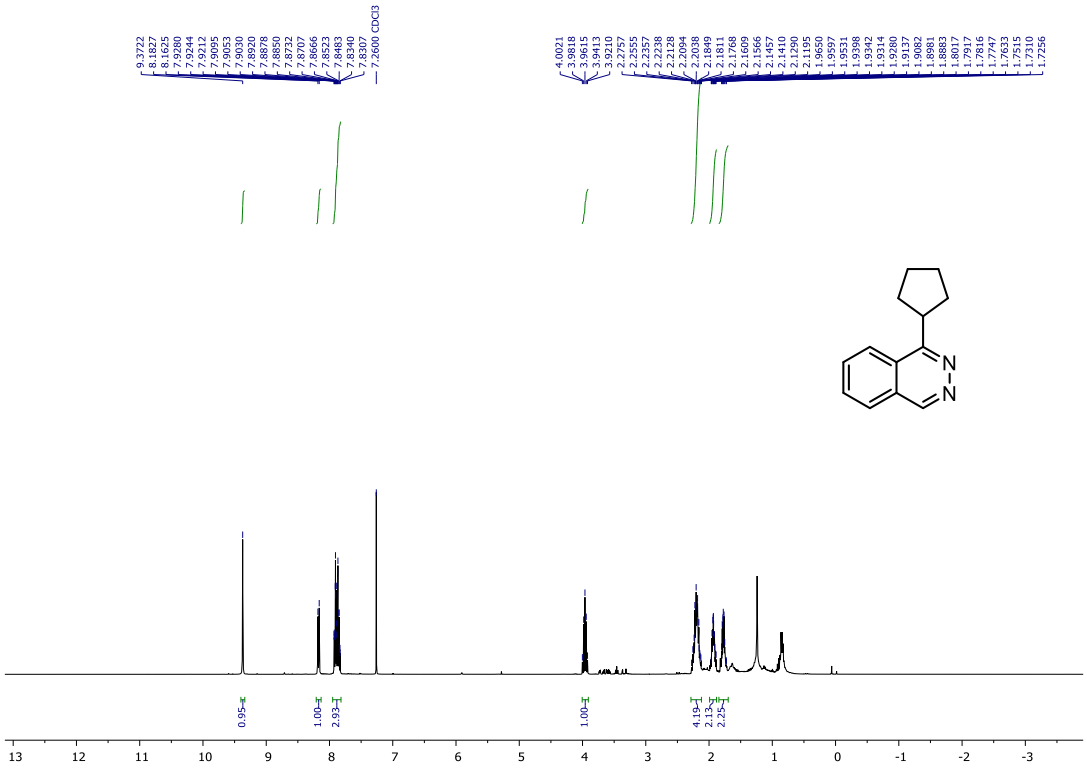
^{13}C NMR of compound **30**



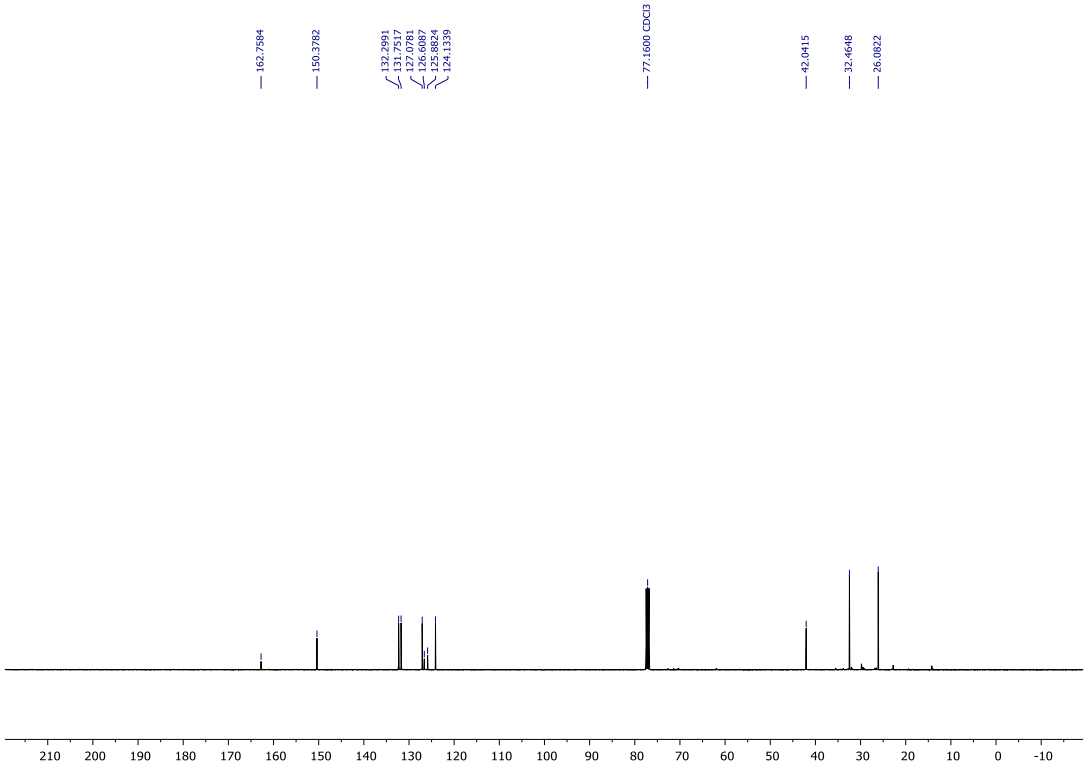
^{1}H NMR of compound **35**



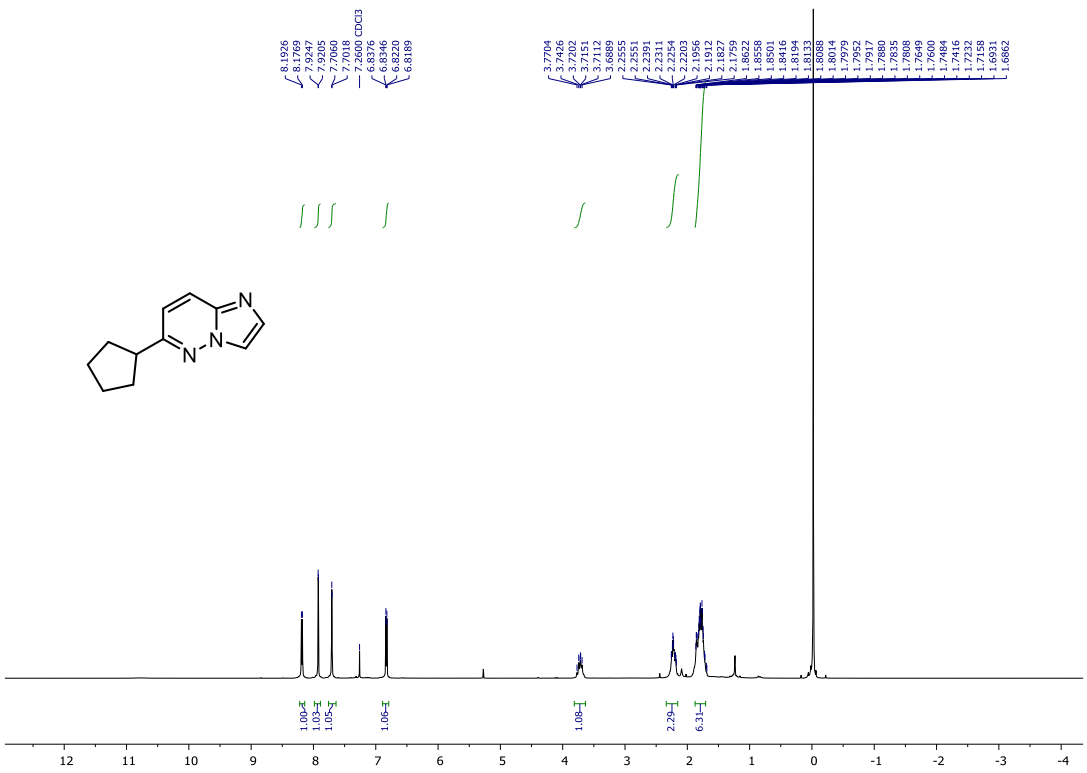
^{13}C NMR of compound **35**



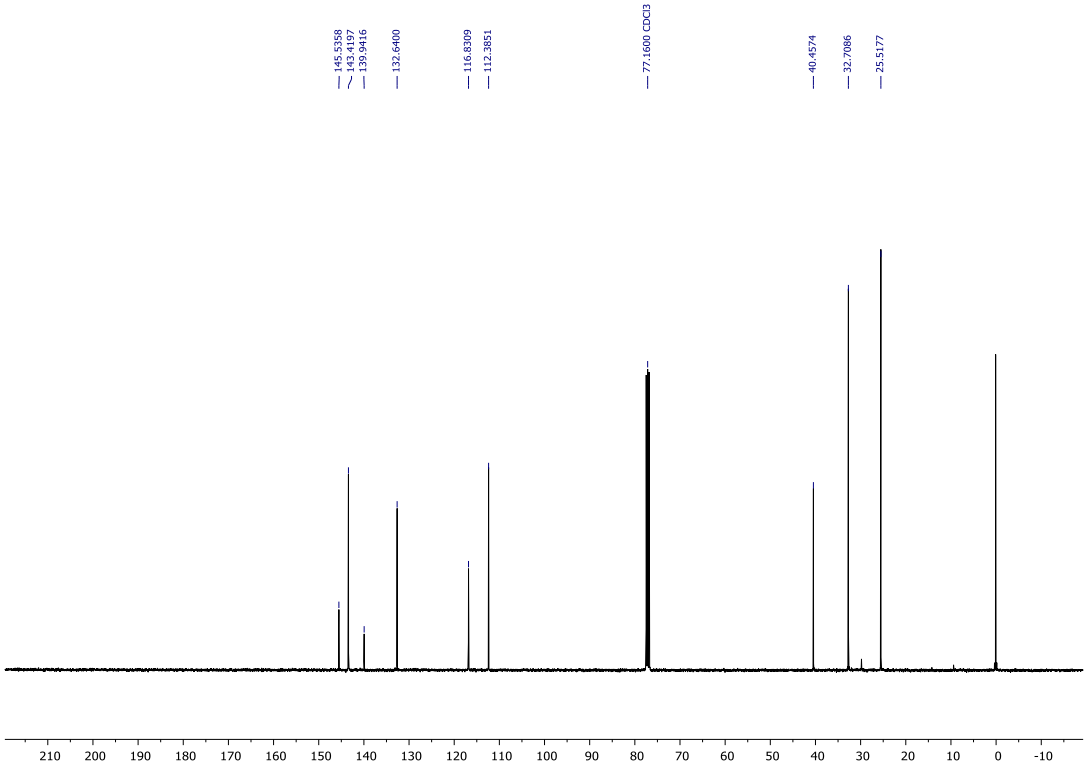
^{1}H NMR of compound **37**



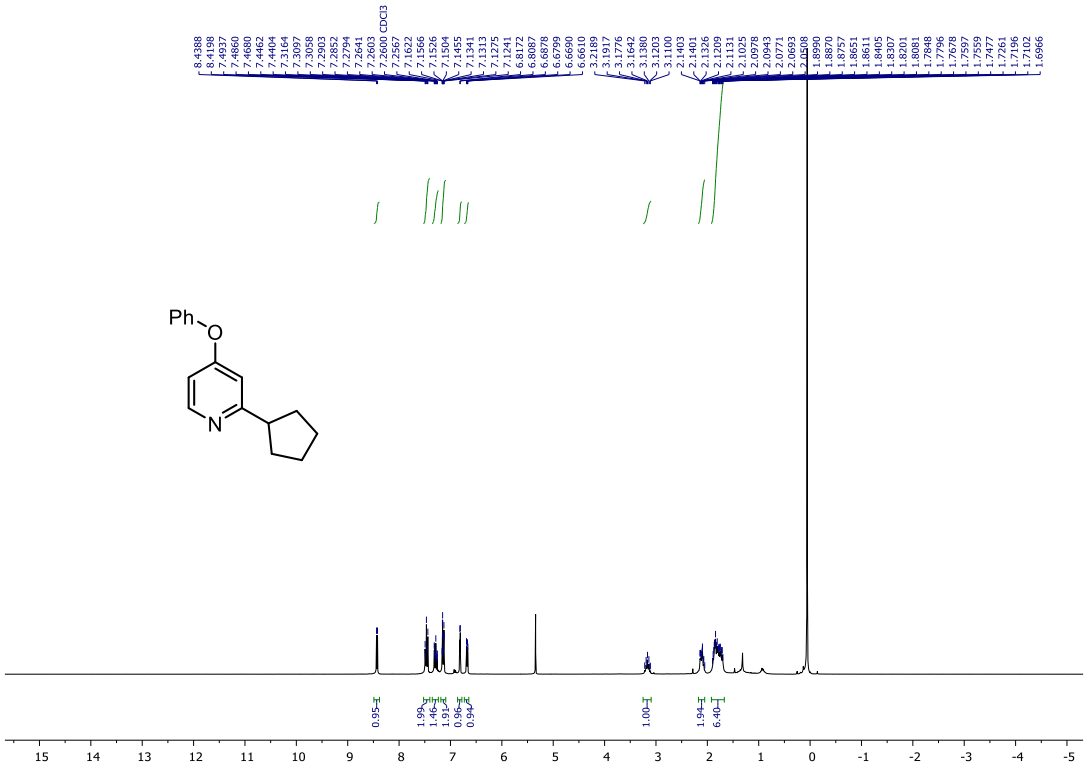
^{13}C NMR of compound **37**



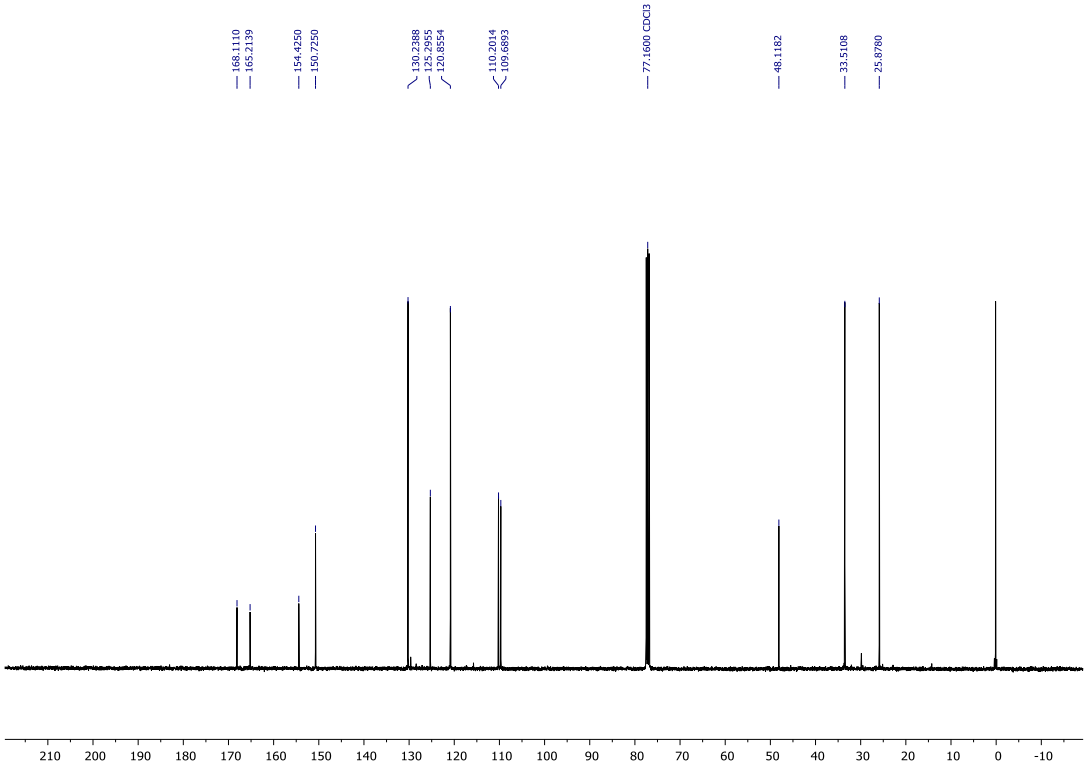
^{1}H NMR of compound **39**



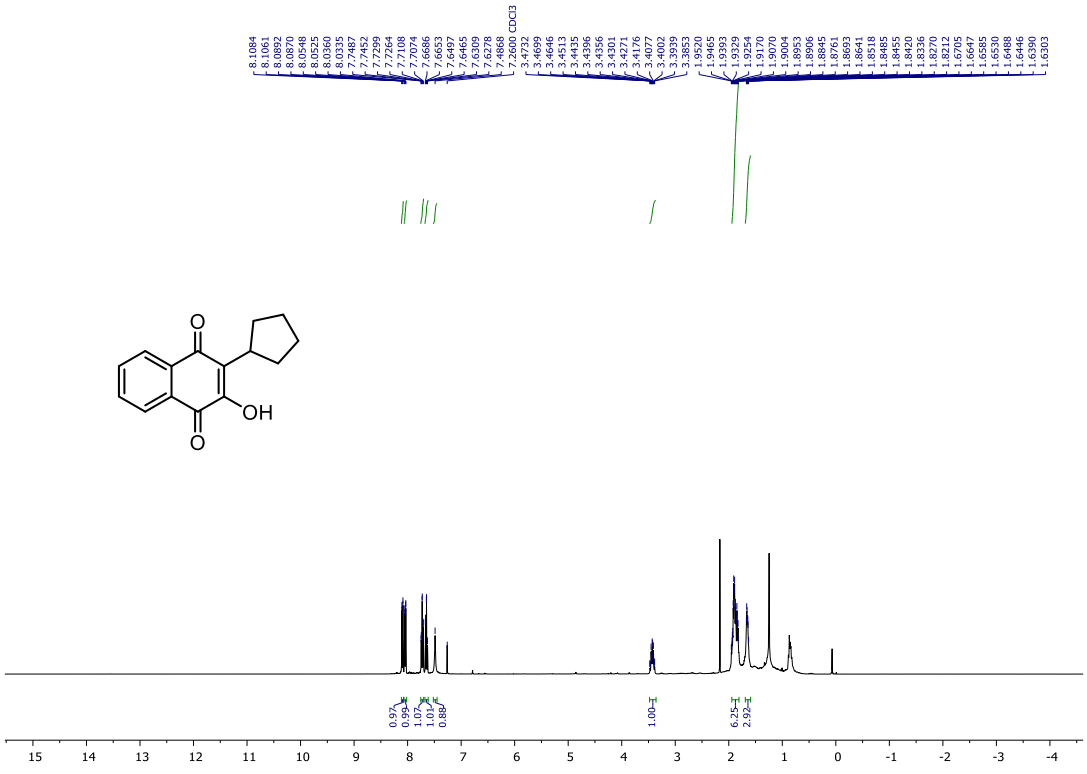
^{13}C NMR of compound **39**



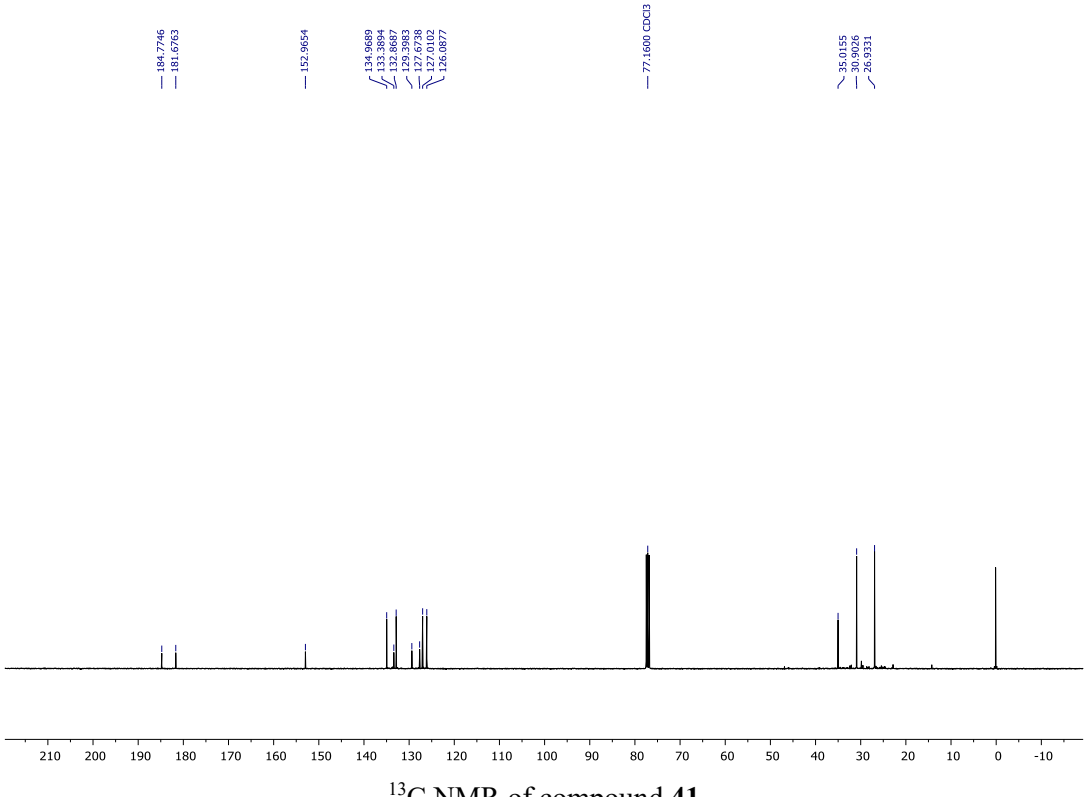
^{1}H NMR of compound **40**



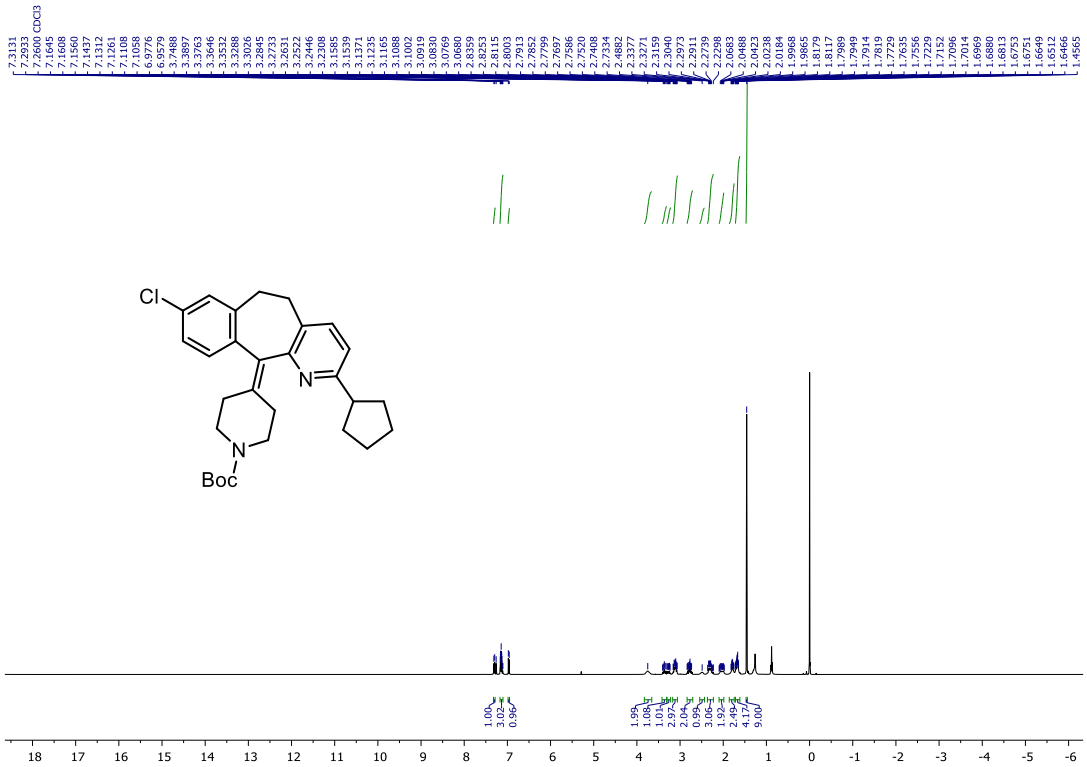
^{13}C NMR of compound **40**



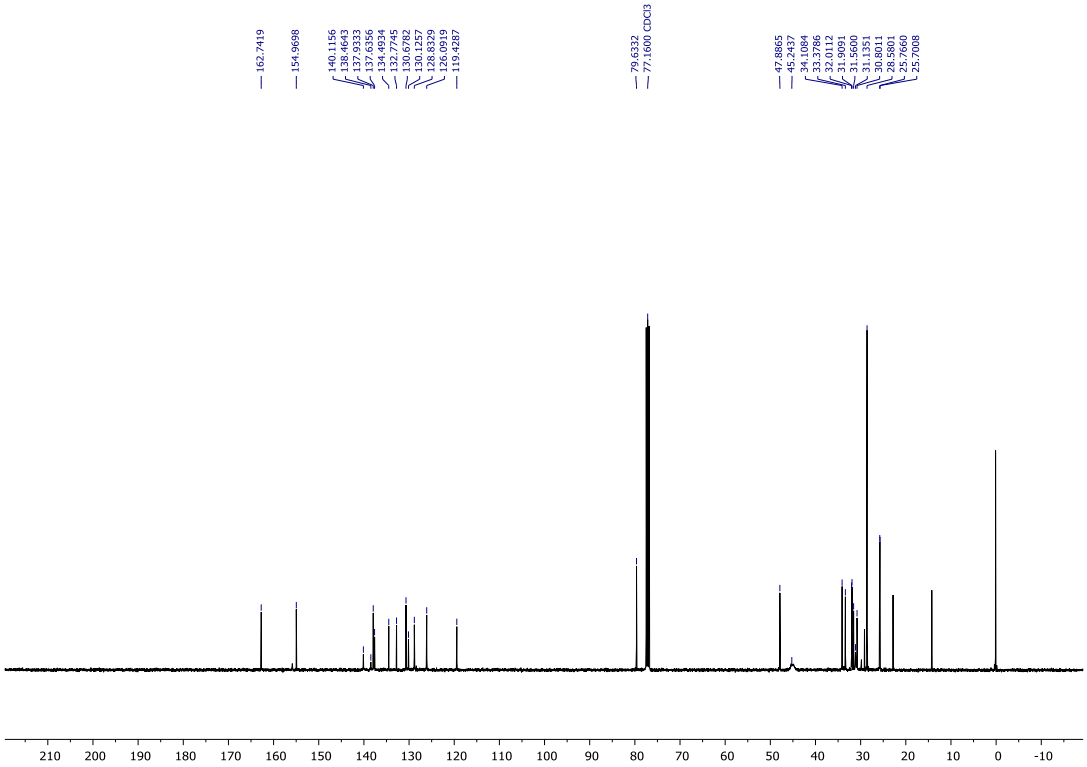
^{1}H NMR of compound **41**



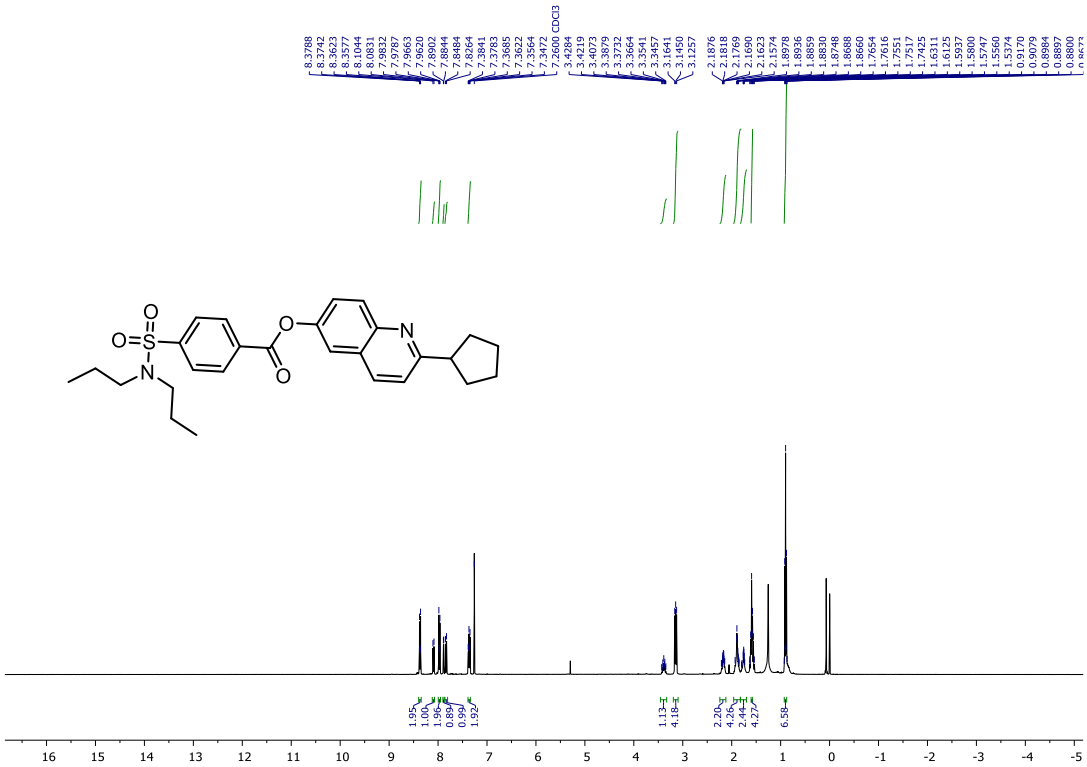
^{13}C NMR of compound **41**



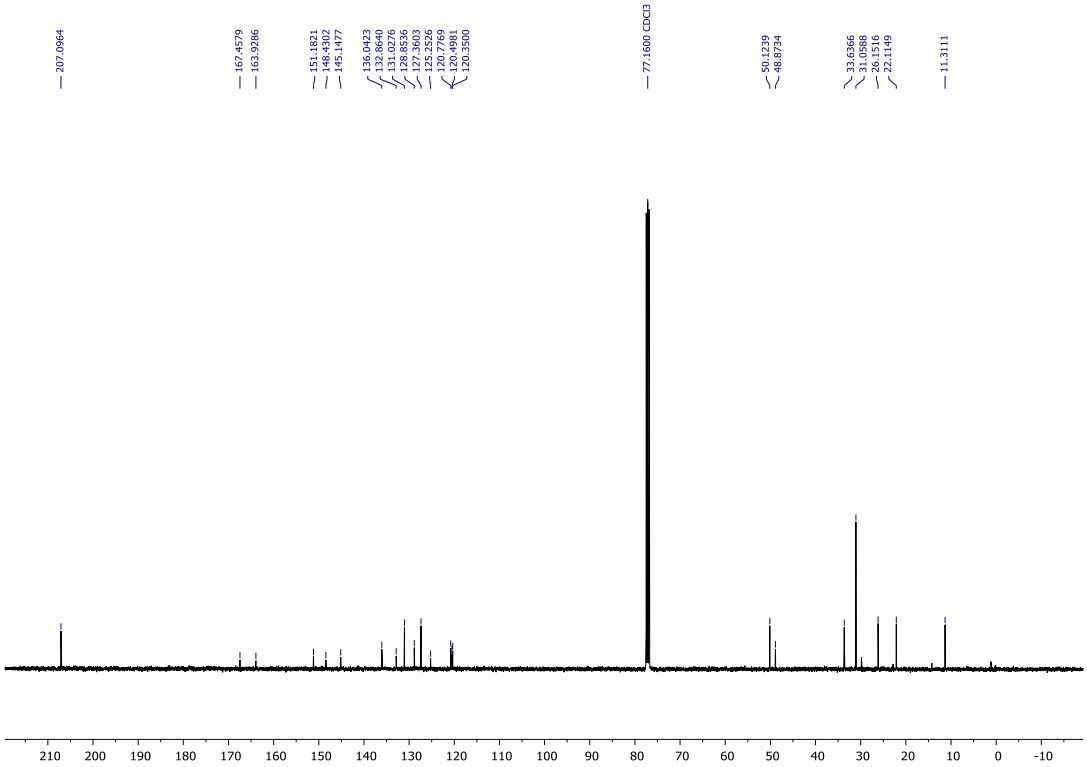
^{1}H NMR of compound **43**



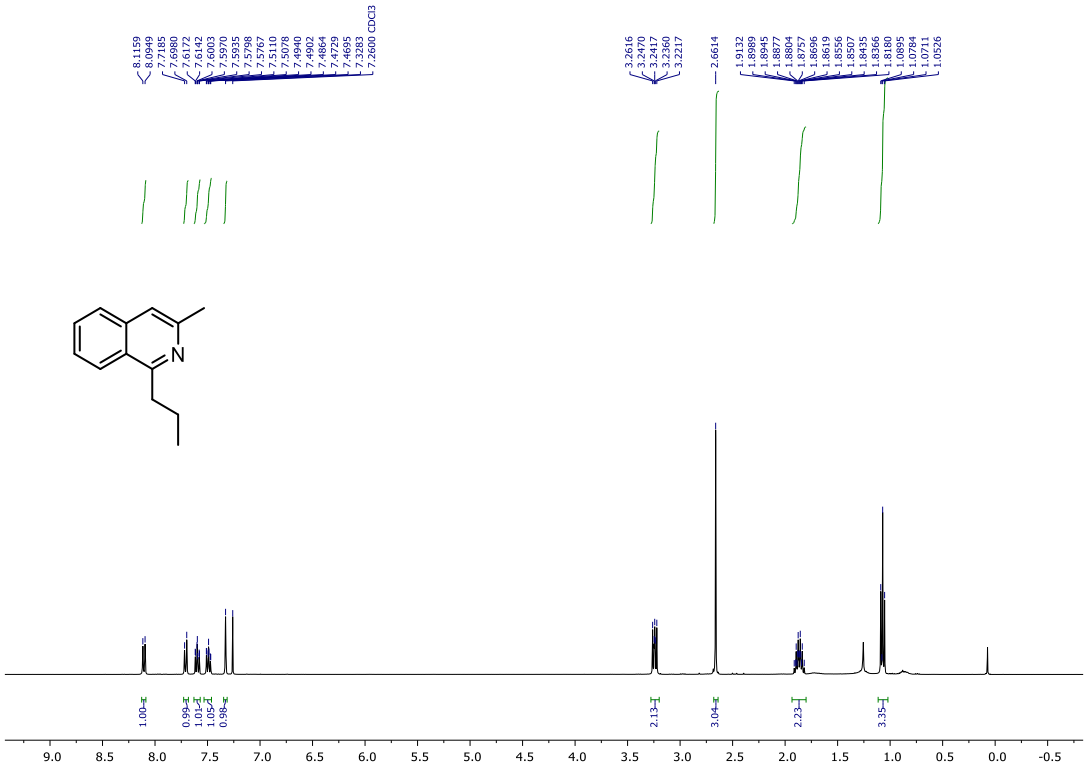
^{13}C NMR of compound **43**



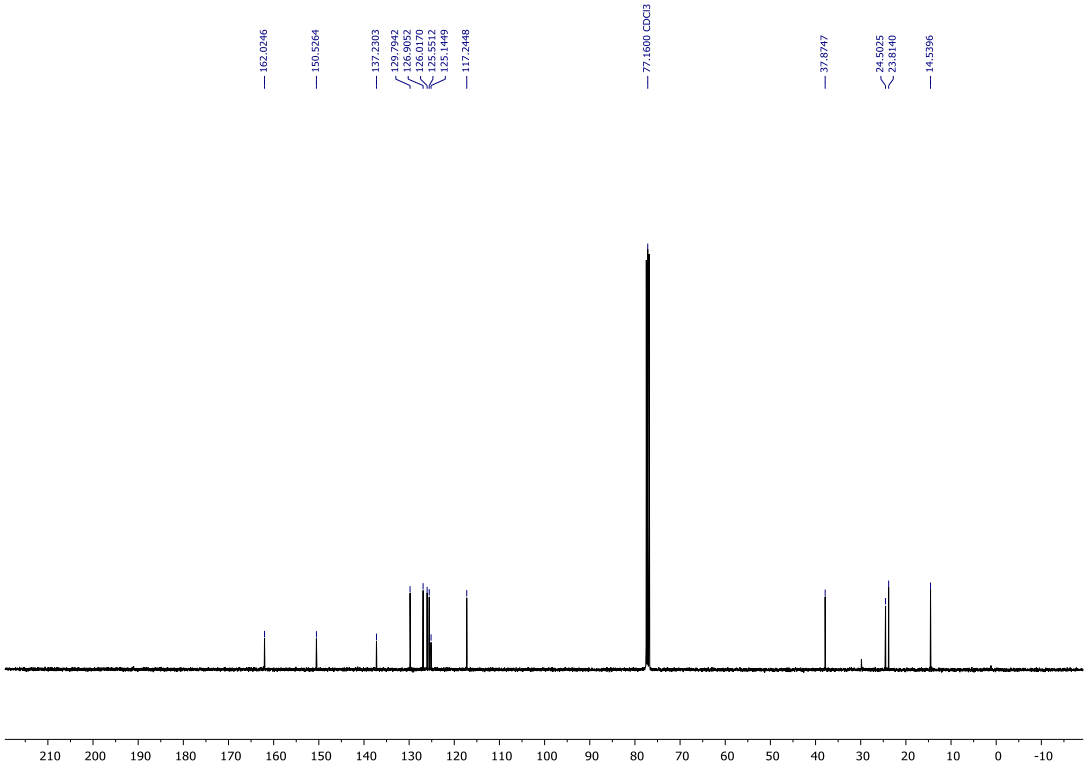
^{1}H NMR of compound **44**



^{13}C NMR of compound **44**



^{1}H NMR of compound **45**



^{13}C NMR of compound **45**