Supporting Information

Electron donor-acceptor complex-catalyzed photoredox reactions mediated by DIPEA and inorganic carbonates

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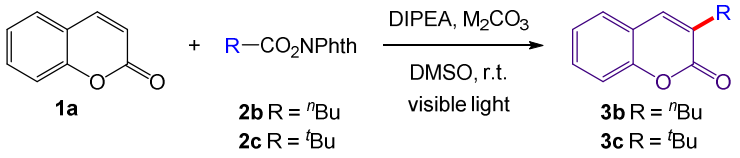
1. Optimization of Reactions

Table S1. Optimization of Reactions between coumarin (1a) and NHPI Esters 2b-c[a]



Entry	R	Base (equiv)	Visible light	Yield (%)[b]
1	^{n}Bu	Li_2CO_3 (1.2)	violet	80
2	^{n}Bu	Na_2CO_3 (1.2)	violet	79
3	^{n}Bu	K_2CO_3 (1.2)	violet	80
4	^{n}Bu	Cs_2CO_3 (1.2)	violet	71
5	^{n}Bu	Li_2CO_3 (1.2)	*blue*	*86*
6	^{n}Bu	Na_2CO_3 (1.2)	blue	66
7	^{n}Bu	K_2CO_3 (1.2)	blue	n.r.[c]
8	^{n}Bu	Cs_2CO_3 (1.2)	blue	n.r.[c]
9	^{t}Bu	Li_2CO_3 (1.2)	violet	57
10	^{t}Bu	Na_2CO_3 (1.2)	violet	73
11	^{t}Bu	K_2CO_3 (1.2)	violet	76
12	^{t}Bu	Cs_2CO_3 (1.2)	*violet*	*86*
13	^{t}Bu	Li_2CO_3 (1.2)	blue	60
14	^{t}Bu	Na_2CO_3 (1.2)	blue	80
15	^{t}Bu	K_2CO_3 (1.2)	blue	68
16	^{t}Bu	Cs_2CO_3 (1.2)	blue	82

[a] Condition: **1a** (0.2 mmol), **2** (2.0 equiv), base (1.2 equiv), DIPEA (0.2 equiv), DMSO (1 mL), light irradiation (36 W) at r.t. under argon. [b] Isolated yield. [c] No reaction.

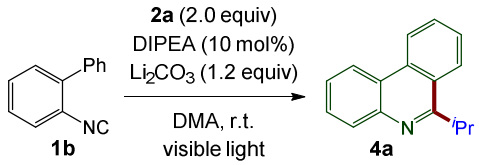
Table S2. Optimization of Reactions between 2-isocyanobiphenyl (1b) and NHPI Esters 2a-c[a]

Entry	R	DIPEA (mol %)	Base (equiv)	Visible light	Yield (%)[b]
1	^{i}Pr	60	Li_2CO_3 (1.2)	blue	84
2	^{i}Pr	100	Li_2CO_3 (1.2)	blue	84
3	^{i}Pr	40	Li_2CO_3 (1.2)	blue	84
4	^{i}Pr	5	Li_2CO_3 (1.2)	blue	66
5	^{i}Pr	60	Na_2CO_3 (1.2)	blue	78
6	^{i}Pr	60	K_2CO_3 (1.2)	blue	60
7	^{i}Pr	60	Cs_2CO_3 (1.2)	blue	trace
8	^{i}Pr	60	Li_2CO_3 (1.2)	violet	82
9	^{i}Pr	60	Li_2CO_3 (1.2)	violet	85
10	^{i}Pr	10	Li_2CO_3 (1.2)	***violet***	***85***
11	^{i}Pr	60	Cs_2CO_3 (1.2)	violet	83
12	^{i}Pr	10	Cs_2CO_3 (1.2)	violet	79
13	^{n}Bu	60	Li_2CO_3 (1.2)	violet	83
14	^{n}Bu	10	Li_2CO_3 (1.2)	***violet***	***83***
15	^{n}Bu	60	Cs_2CO_3 (1.2)	violet	83
16	^{n}Bu	10	Cs_2CO_3 (1.2)	violet	80
17	^{n}Bu	60	Li_2CO_3 (1.2)	blue	78
18	^{n}Bu	60	Na_2CO_3 (1.2)	blue	76
19	^{n}Bu	60	K_2CO_3 (1.2)	blue	70
20	^{n}Bu	60	Cs_2CO_3 (1.2)	blue	52
21	^{t}Bu	60	Li_2CO_3 (1.2)	violet	78
22	^{t}Bu	10	Li_2CO_3 (1.2)	violet	75
23	^{t}Bu	60	Cs_2CO_3 (1.2)	violet	82
24	^{t}Bu	10	Cs_2CO_3 (1.2)	***violet***	***82***
25	^{t}Bu	60	Li_2CO_3 (1.2)	blue	76
26	^{t}Bu	60	Na_2CO_3 (1.2)	blue	73
27	^{t}Bu	60	K_2CO_3 (1.2)	blue	74
28	^{t}Bu	60	Cs_2CO_3 (1.2)	blue	82

[a] Reaction condition: **1b** (0.2 mmol), **2** (2.0 equiv), base (1.2 equiv), DIPEA, DMA (1 mL), light irradiation (36 W) at r.t. under argon. [b] Isolated yield.

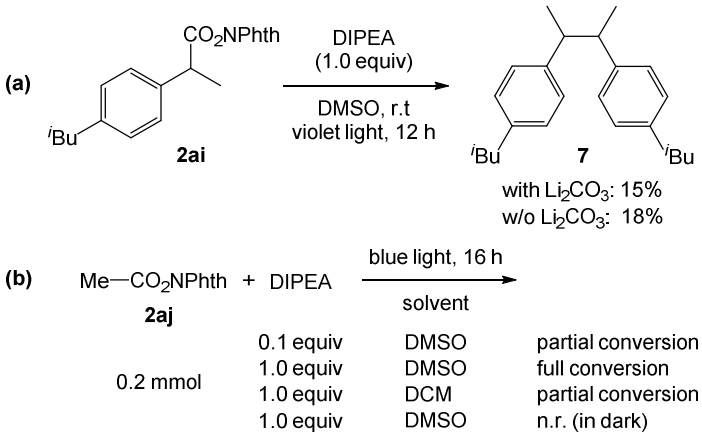
2. Control experiments

Table S3. Control Reactions of 2-Isocyanobiphenyl (1b) Alkylation-Cyclization [a]



entry	DIPEA	Li_2CO_3	light	yield	time
1	+	-	violet	65% [b]	17 h
2	-	+	violet	76% [b]	17 h
3	+	-	blue	n.r.	--
4	-	+	blue	n.r.	--
5	-	-	blue	n.r.	--
6	+	+	off	n.r.	--
7 [c]	+	+	blue	n.r.	--

[a] Standard condition: **1b** (0.2 mmol), **2** (2.0 equiv), base (1.2 equiv), DIPEA (0.1 equiv), DMA (1 mL), light irradiation (36 W) at r.t. under argon. [b] Incomplete conversion of **1b**. [c] with TEMPO (2.0 equiv).



Scheme S1. Photoreactions without radical acceptor

3. UV-vis Spectroscopic Analysis

3.1. Interaction between NHPI ester 2a and DIPEA

UV/vis absorption spectra of the following sample solutions were recorded in 1 cm path quartz cuvettes: (1) NHPI ester **2a** (0.4 M) in 1.0 mL DCM; (2) DIPEA (0.4 M) in 1.0 mL DCM; (3) NHPI ester **2a** (0.4 M) and DIPEA (0.4 M) in 1.0 mL DCM. A new absorption band was observed on the mixed sample (Figure 2).

3.2. Job's plot between NHPI ester 2a and DIPEA

The binding stoichiometry between NHPI ester **2a** and DIPEA was evaluated using Job's plot analysis. The absorption of DCM solutions at 390 nm with different **2a**/DIPEA ratios (0:1, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 1:0) with constant concentration (0.4 M) of the two components. The absorbance values were plotted against the molar fraction (%) of NHPI ester **2a**. The maximal absorbance at 50% molar fraction of **2a** indicated the 1:1 stoichiometry of the EDA complex in solution (Figure 2).

3.3. Time course UV-vis spectra of EDA complexes

Sample solutions of NHPI ester **2a**, **2a**-DIPEA (1:1), **2a**-metal carbonate (1:1) and **2a**-metal carbonate-DIPEA (1:1:1) in DMA (0.001 M, 3.0 mL), freshly prepared or stood in dark for 15 hours, were submitted to UV-vis spectroscopic analysis. As solid metal carbonates could not completely dissolve, the corresponding sample solutions were filtered prior to the measurement. Samples containing Cs_2CO_3 showed new absorption bands after overnight standing, but there was no visible change with Li_2CO_3.

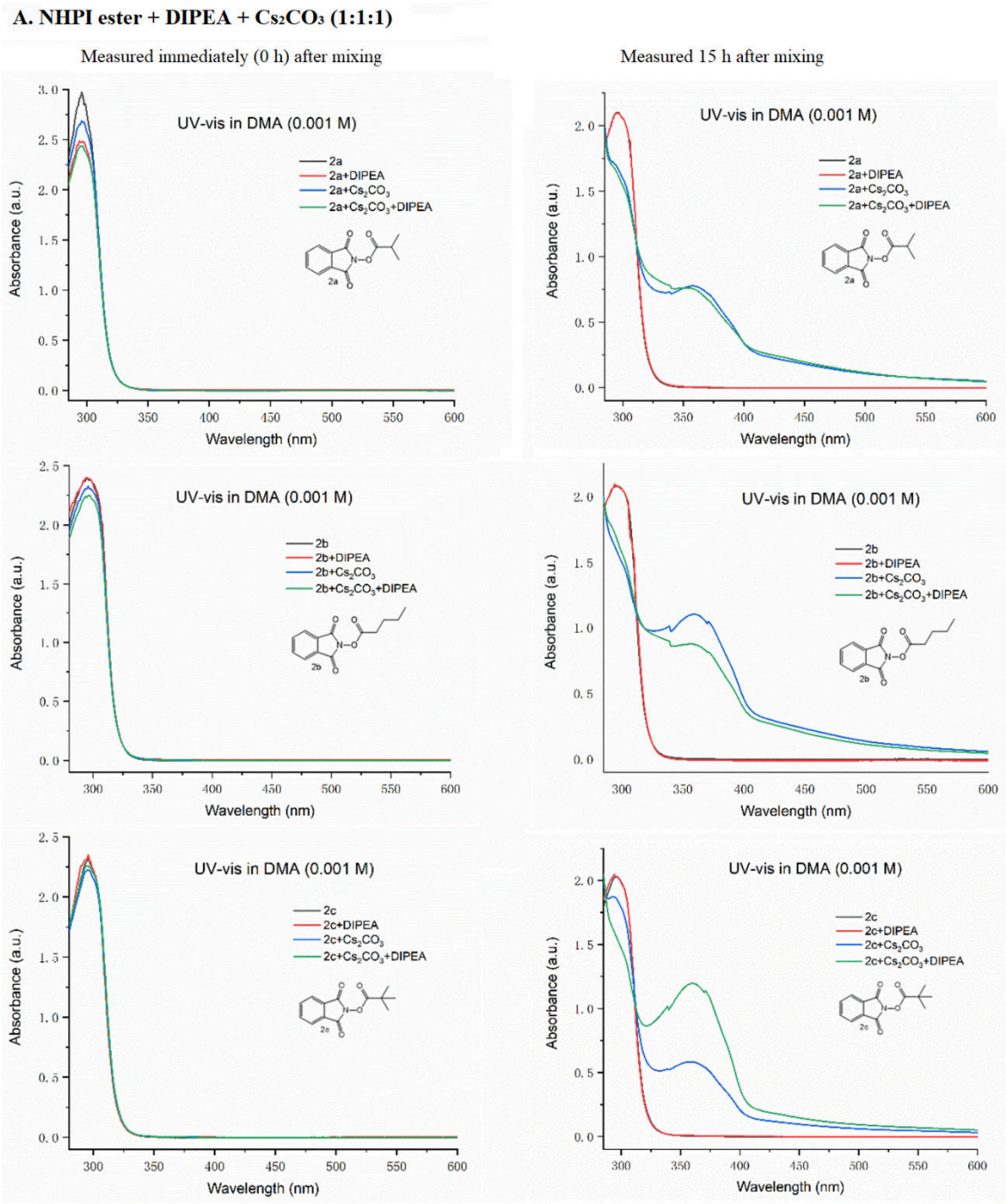


Fig. S1. UV-vis Spectroscopic Analysis on Metal Carbonate Effects

B. NHPI ester + DIPEA + Li_2CO_3 (1:1:1)

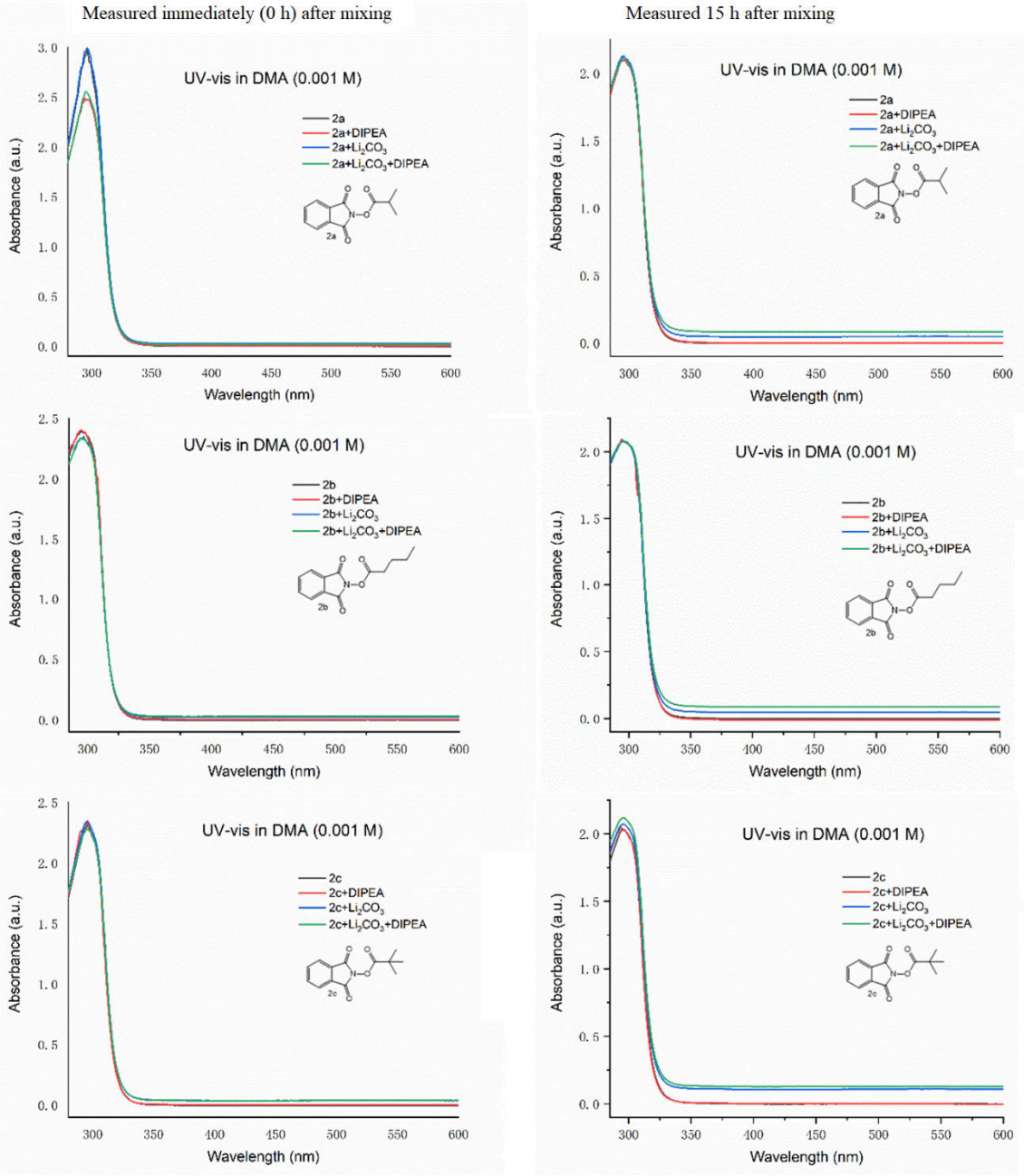


Fig. S1 (continued).

4. Computation Study

All DFT calculations were performed using Gaussian 16 code[1]. Geometry optimizations were carried out by the B3LYP functional with the D3 dispersion correction[2-5]. A mixed basis set, in which Lanl2dz was used for Cs and 6-311+G (d, p) for other atoms, was employed[6-7]. Vibrational frequency analyses were conducted at the same level of theory to obtain the thermal correction and verify the stationary points to be minimal. Solvation effects were introduced to all calculations, by using the SMD model with DSMO as the solvent[8]. Time- dependent density functional theory (TDDFT) with the CAM-B3LYP exchange-correlation functional[9] is applied to the study of UV-vis spectra.

References

[1] Gaussian 16, Revision A.03 (Gaussian Inc., Wallingford, CT, 2016).

[2] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.

[3] Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.

[4] Becke, D. A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

[5] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

[6] Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298.

[7] Frisch, M.; Pople, J.; Binkley, J. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets *J. Chem. Phys.* **1984**, *80*, 3265–3269.

[8] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[9] Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J. Excitation energies in density functional theory: an evaluation and a diagnostic test. *J. Chem. Phys.* **2008**, *128*, 044118.

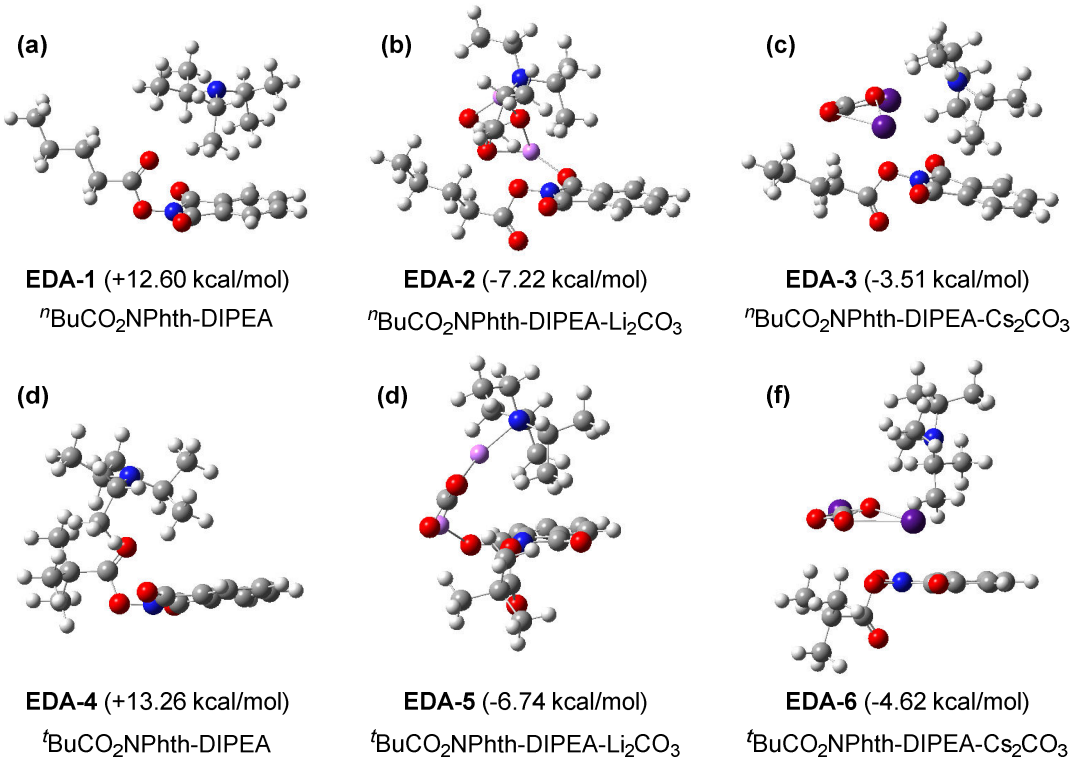


Fig. S2. Free energies of EDA complexes

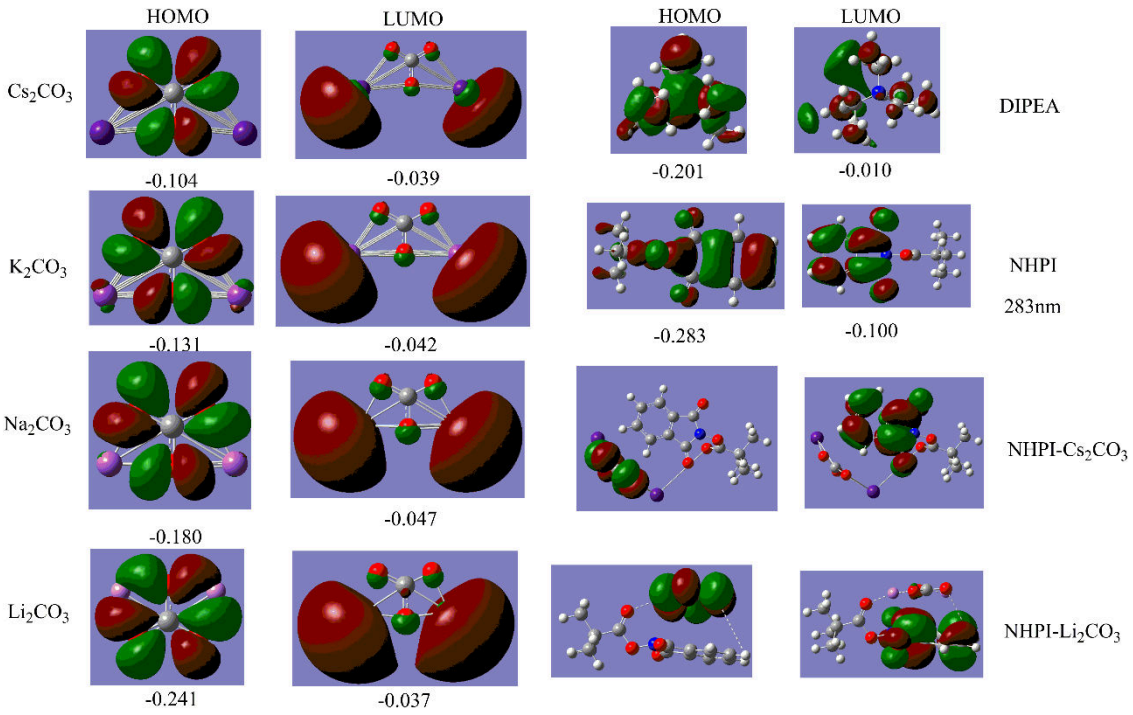


Fig. S3. HOMO and LUMO of components of EDA complexes

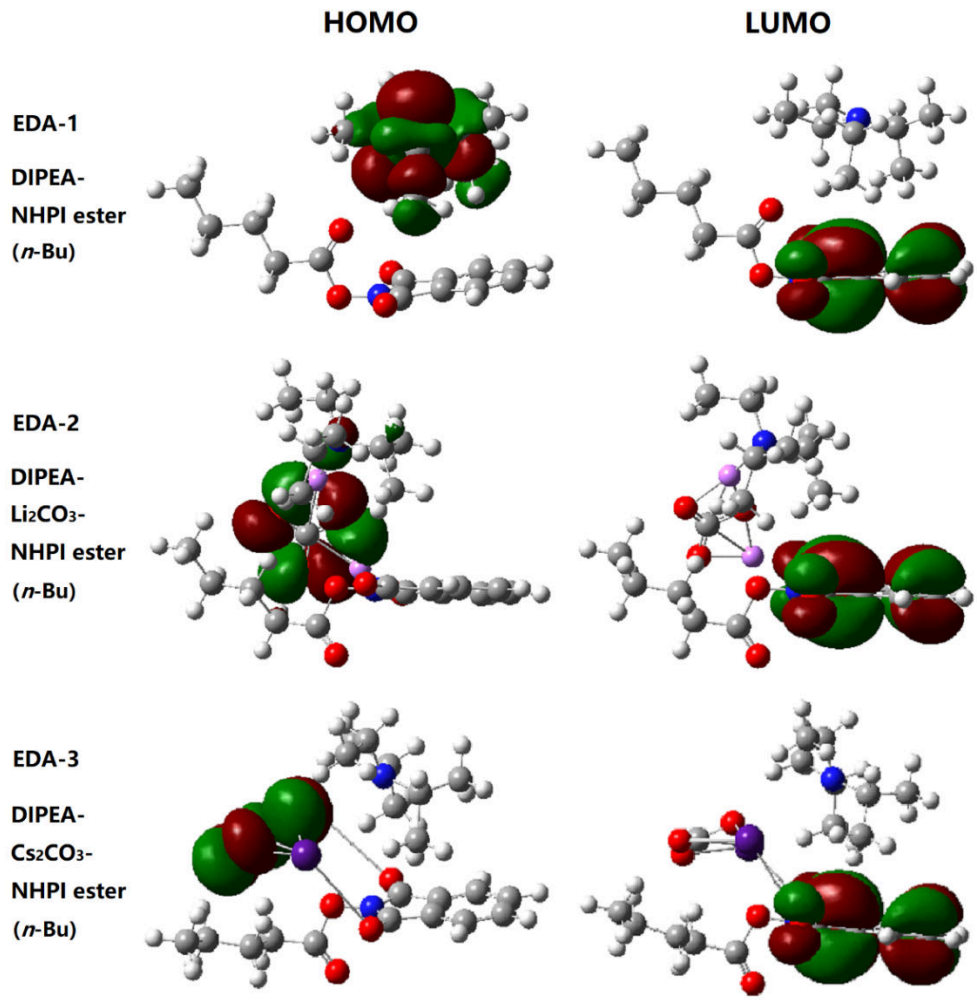


Fig. S4. Calculation of HOMO and LUMO of EDA complexes

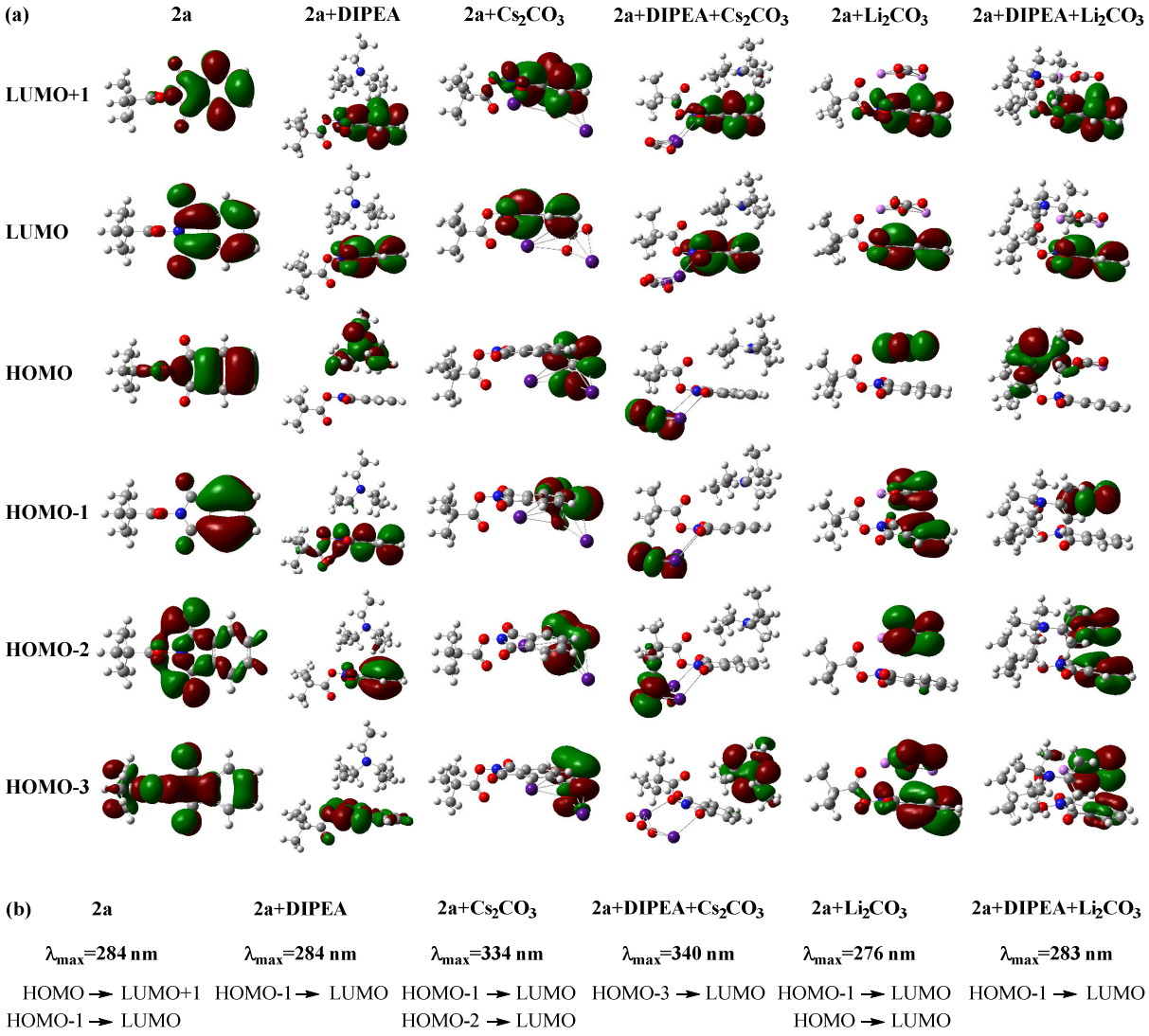
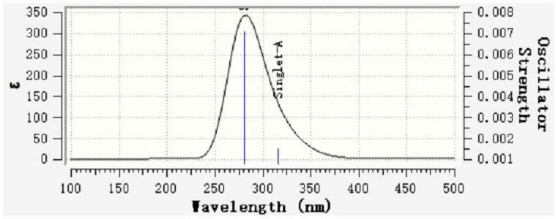
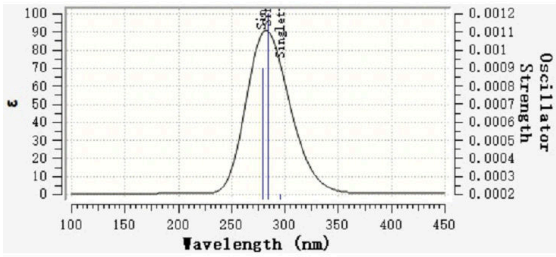


Fig. S5. Calculated molecular orbitals and maximum absorption wavelength (λ_{max}) of NHPI ester 2a and its EDA complexes in the ground S0 state (TDDFT method at the CAM-B3LYP/6-311+G(d,p) level)

A. EDA-1
DIPEA-
^{n}BuCO$_2$NPhth



B. EDA-2
DIPEA-Li_2CO_3-
^{n}BuCO$_2$NPhth



C. EDA-3
DIPEA-Cs_2CO_3
^{n}BuCO$_2$NPhth

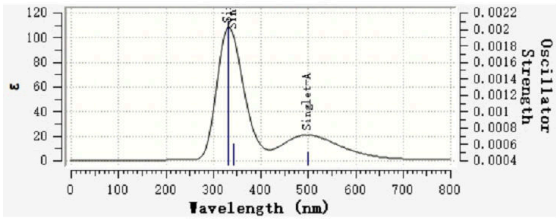


Fig. S6. Predicted UV-vis spectra of EDA complexes

5. Experimental

5.1. General

Chemicals were purchased from Energy Chemical, Titan, J&K Scientific and Innochem, and were used as received. Anhydrous solvents were prepared by standard methods. Column chromatography was performed using silica gel (300–400 mesh) with petroleum ether (PE) and ethyl acetate (EA) distilled prior to use. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance III HD 600 (600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR) spectrometer. Tetramethylsilane (TMS) was used as the internal reference. $CDCl_3$ was used as the NMR solvent unless otherwise indicated. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. HRMS were performed on an Agilent LC/MS TOF instrument. UV-vis absorption spectra were recorded in 1 cm path quartz cuvettes using a Shanghai Metash 8000 spectrometer. Prior to the reaction setup, the magnetic stirrers and reaction tubes were soaked in dilute hydrochloric acid and sodium carbonate solution successively, washed, dried in oven, and cooled to room temperature under argon. Unless otherwise stated, NHPI esters[1], 2-isocyanobiphenyl (**1b**)[2] and *N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide (**1c**)[3] and *N*-methyl-*N*-phenylmethacrylamide (**1d**)[4] were prepared following reported methods.

5.2. Setup of photoreaction

The light sources used in the photoreaction are two violet (18 W, 396 nm) or blue (18 W, 452 nm) LED lamps purchased from https://m.tb.cn/h.fHZ4N65?tk=fAR82kG9Kye. Photochemical experiments were performed in 10-mL reaction tubes positioned about 6 cm away from two 18 W violet or blue LED lamps in a fume hood. The temperature of the reaction mixtures maintained at about 35 °C.

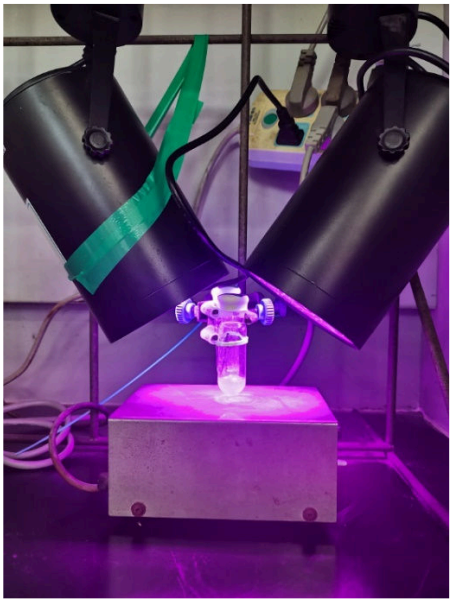


Fig. S7. Photoreaction setup

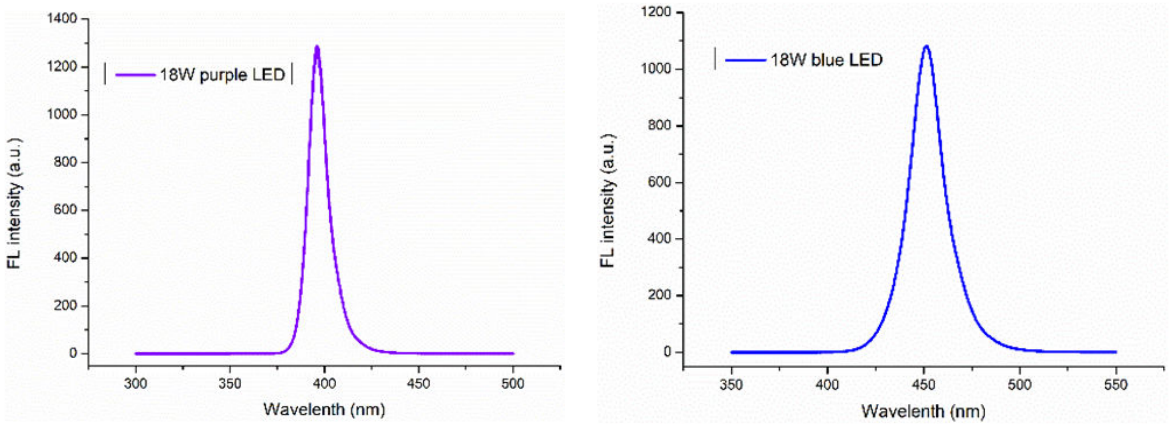
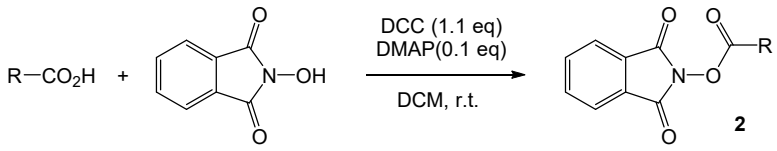


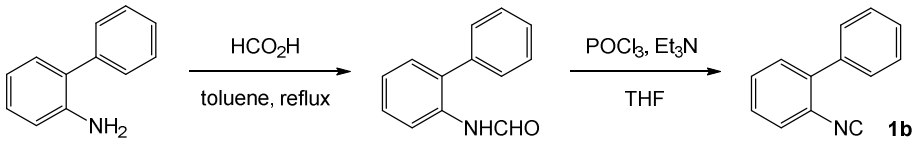
Fig. S8. Emission spectra of violet and blue LEDs used in this study

5.3. General procedure for the preparation of NHPI esters 2



The corresponding carboxylic acid (5 mmol), *N*-hydroxyphthalimide (5.5 mmol) and DMAP (4-dimethylaminopyridine, 0.5 mmol) were mixed in an oven-dried flask with a magnetic stirring bar. DCM (20 mL) was added. *N*,*N*'-dicyclohexylcarbodiimide (DCC, 5.5 mmol) was added at 0 °C with stirring, and the mixture was then stirred at room temperature for half an hour. The reaction was monitored by TLC. After the reaction was completed, the resulted slurry was diluted with dichloromethane and filtered. The filtrate was concentrated, and the residue was separated by silica gel flash chromatography to obtain the corresponding carboxylic acid-derived NHP ester.

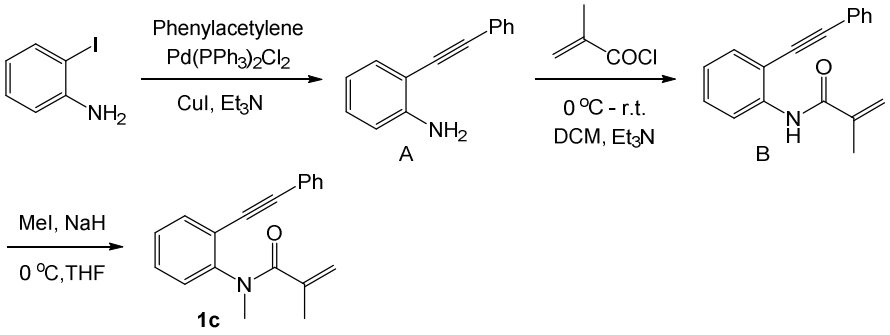
5.4. Preparation of 2-isocyanobiphenyl 1b



2-Aminodiphenyl (169 mg, 1 mmol) and formic acid (0.31 mL, 8 mmol) were dissolved in toluene (15 mL) in a 50-mL flask. The mixture was heated to reflux under argon. The reaction was monitored by TLC (petroleum ether/ethyl acetate 3:1). After the reaction was completed, volatile materials were evaporated under reduced pressure. The resulting residue (crude formamide) was used in the next step without purification. Dry tetrahydrofuran (THF, 15 mL) and triethylamine (TEA, 0.7 mL, 5 mmol) were added into the flask with syringe. The solution was cooled to 0 °C. $POCl_3$ (0.19 mL, 2 mmol) was added dropwise with a syringe. The reaction was stirred at 0 °C for 2 h, and then at room temperature overnight. After the reaction

was complete (monitored by TLC), the reaction was quenched by adding saturated aqueous solution of $NaHCO_3$, and the mixture was extracted with EtOAc for 3 times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to afford compound **1b** (167 mg, 93%).

5.5. Preparation of *N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide 1c

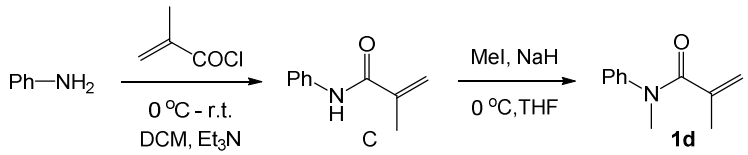


To a 50-mL flask was charged with 2-iodoaniline (219 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) and CuI (7.6 mg, 0.04 mmol) in Et_3N (15 mL) at room temperature under argon. After stirring for 5 minutes, phenylacetylene (0.16 mL, 1.5 mmol) was added dropwise to the reaction mixture. After the reaction was complete (monitored by TLC), the reaction mixture was filtered through a pad of celite, eluting with EtOAc (3 x 10 mL). The combined organics were sequentially washed with H_2O (2 x 10 mL) and brine (1 x 10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue (compound A) was used in the next step without purification.

The above-obtained compound A was dissolved in CH_2Cl_2 (20 mL). TEA (0.27 mL, 2 mmol) was added. Methacryloyl chloride (1.45 mL, 1.5 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature for 6 h. Then the reaction was quenched by adding saturated $NaHCO_3$ solution, and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate 20:1) to afford compound B (188 mg, 72%).

To a suspension of NaH (60%, 80 mg, 2 mmol) in THF (15 mL) at 0 °C was added a solution of compound B (262 mg, 1 mmol) in THF (2 mL) dropwise and the mixture was stirred for 5 min. Iodomethane (0.18 mL, 3 mmol) was added at 0 °C. The reaction was stirred at room temperature and was monitored by TLC. The reaction was quenched by adding water. The mixture was extracted with CH_2Cl_2 for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to afford compound **1c** (154 mg, 56%).

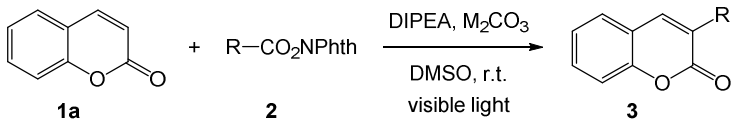
5.6. Preparation of *N*-methyl-*N*-phenylmethacrylamide 1d



Aniline (0.91 mL, 1.0 mmol) was dissolved in CH_2Cl_2 (20 mL). TEA (0.27 mL, 2 mmol) was added. Methacryloyl chloride (1.45 mL, 1.5 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature for 6 h. Then the reaction was quenched by adding saturated $NaHCO_3$ solution, and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate 15:1) to afford compound C (127 mg, 79%).

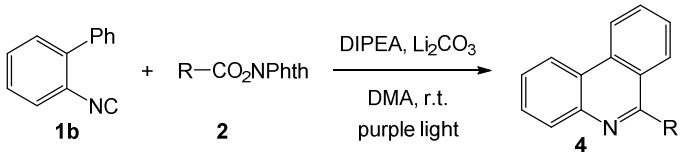
To a suspension of NaH (60%, 80 mg, 2.0 mmol) in THF (15 mL) at 0 °C was added a solution of compound C (161 mg, 1.0 mmol) in THF (2.0 mL) dropwise and the mixture was stirred for 5 min. Iodomethane (0.18 mL, 3 mmol) was added at 0 °C. The reaction was stirred at room temperature and was monitored by TLC. The reaction was quenched by adding water. The mixture was extracted with CH_2Cl_2 for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to afford compound **1d** (113 mg, 65%).

5.7. General procedure for photoredox alkylation of coumarin 1a



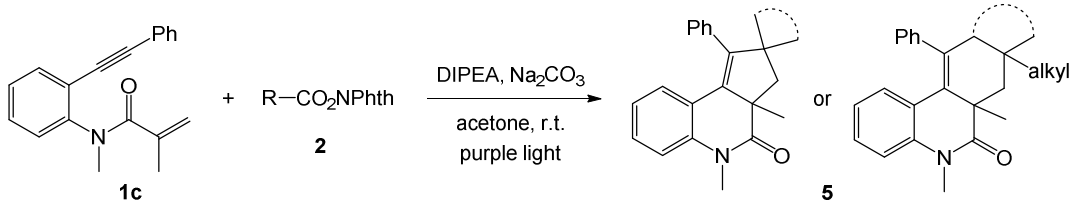
An oven-dried reaction tube was charged with coumarin **1a** (30 mg, 0.2 mmol), a corresponding NHPI ester **2** (2 equiv), Li_2CO_3 or Cs_2CO_3 (1.2 equiv), DIPEA (0.2 equiv) and DMSO (1 mL) under argon. The reaction was stirred under blue or violet light irradiation (18 W x 2) in a fume hood, and monitored by TLC. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography (petroleum ether/ethyl acetate) to give the corresponding product **3**.

5.8. General procedure for photoredox alkylation-cyclization of 2-isocyanobiphenyl 1b



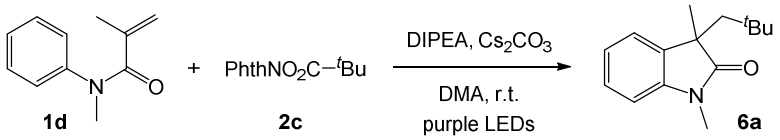
An oven-dried reaction tube was charged with 2-isocyanobiphenyl **1b** (35.6 mg, 0.2 mmol), a corresponding NHPI ester **2** (2 equiv), Li_2CO_3 or Cs_2CO_3 (1.2 equiv), DIPEA (0.1 equiv) and DMA (1 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood, and monitored by TLC. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography (petroleum ether/ethyl acetate) to give the corresponding product **4**.

5.9. General procedure for photoredox alkylation-cyclization of *N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide 1c



An oven-dried reaction tube was charged with *N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide **1d** (28 mg, 0.1 mmol), a corresponding NHPI ester **2** (4 equiv), Na_2CO_3 (1.0 equiv), DIPEA (0.5 equiv) and acetone (1 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood for about 12 hours, and monitored by TLC. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography (petroleum ether/ethyl acetate) to give the corresponding product **5**.

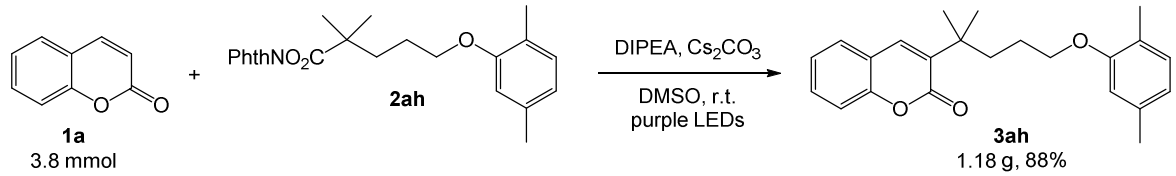
5.10. Photoredox alkylation-cyclization of *N*-methyl-*N*-phenylmethacrylamide 1d



An oven-dried reaction tube was charged with *N*-methyl-*N*-phenylmethacrylamide **1d** (35 mg, 0.2 mmol), NHPI ester **2c** (99 mg, 4 equiv), Cs_2CO_3 (78 mg, 1.2 equiv), DIPEA (14 μL, 0.4 equiv) and DMA (1 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood for about 12 hours, and monitored by TLC. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography (petroleum ether/ethyl acetate 15:1) to give the product **6a** (31 mg, 68%).

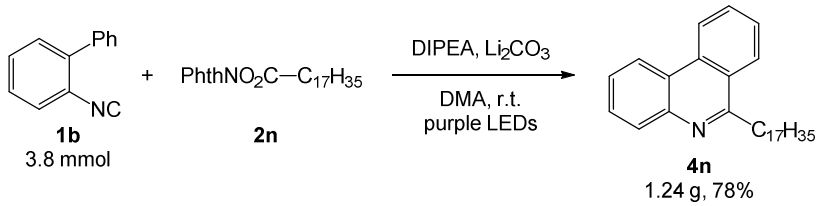
5.11. Gram-scale reactions

Gram-scale synthesis of **3ah**



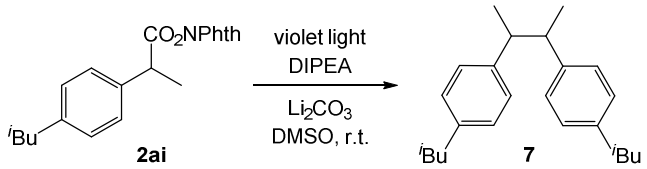
An oven-dried reaction tube was charged with coumarin **1a** (555 mg, 3.8 mmol), NHPI ester **2ah** (3.05 g, 2 equiv), Cs_2CO_3 (1.49 g, 1.2 equiv), DIPEA (0.13 mL, 0.2 equiv) and DMSO (19 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood for about 12 hours. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography (petroleum ether/ethyl acetate 18:1) to give the compound **3ah** (1.18 g, 88%).

Gram-scale synthesis of **4n**



An oven-dried reaction tube was charged with 2-isocyanobiphenyl **1b** (681 mg, 3.8 mmol), NHPI ester **2n** (3.27 g, 2 equiv), Li_2CO_3 (337 mg, 1.2 equiv), DIPEA (66 μL, 0.1 equiv) and DMA (19 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood for about 12 hours. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography (petroleum ether/ethyl acetate 40:1) to give the compound **4n** (1.24 g, 78%).

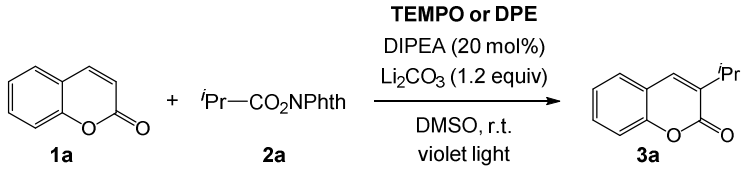
5.12. Control reaction: Synthesis of 4,4'-(butane-2,3-diyl)bis(isobutylbenzene) (7)



An oven-dried reaction tube was charged with NHPI ester **2ai** (70.3 mg, 0.20 mmol), Li_2CO_3 (17.8 mg, 0.24 mmol, 1.2 equiv), DIPEA (35 μL, 25.9 mg, 0.20 mmol, 1.0 equiv) and DMSO (1.0 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood for 12 hours. The reaction mixture was partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was separated by silica gel flash chromatography

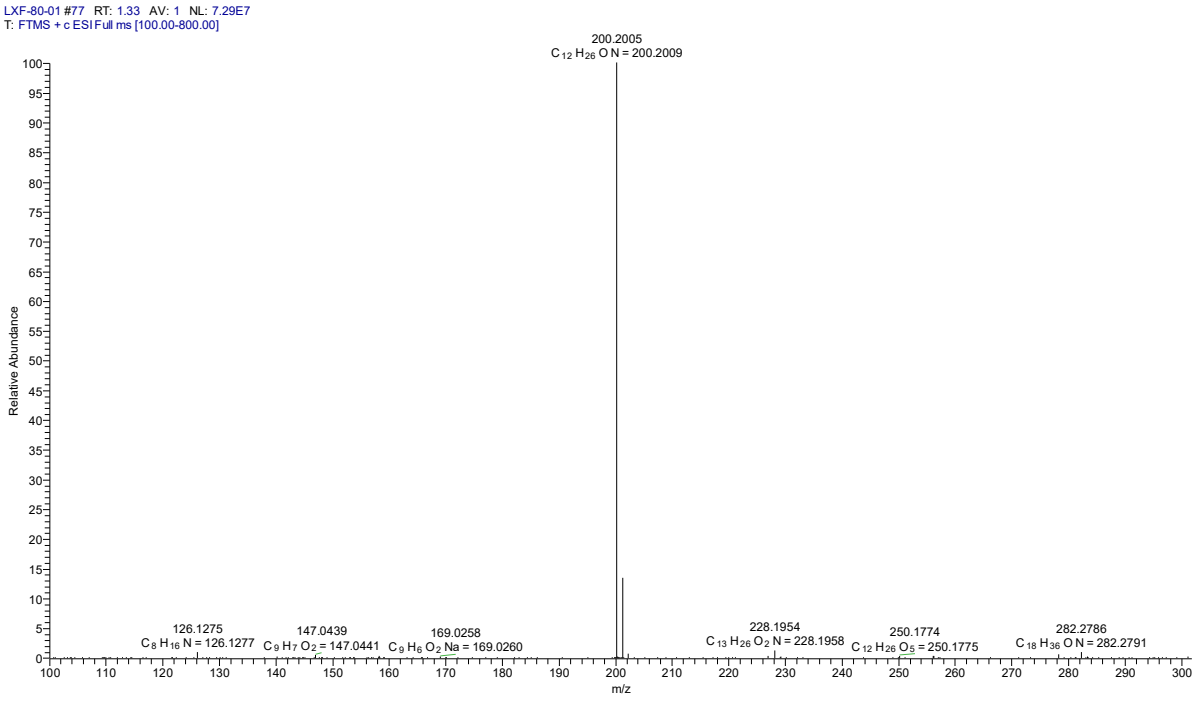
(petroleum ether to petroleum ether/ethyl acetate 15:1) to give compound **7** (11.5 mg, 18%).

5.13. Mechanistic study: Radical trapping experiments



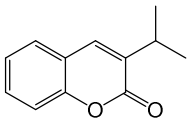
An oven-dried reaction tube was charged with coumarin **1a** (15 mg, 0.1 mmol), NHPI ester **2a** (47 mg, 0.20 mmol), Li_2CO_3 (8.9 mg, 0.12 mmol, 1.2 equiv), DIPEA (3.5 μL, 2.6 mg, 0.02 mmol, 0.2 equiv), TEMPO (31 mg, 0.2 mmol, 2.0 equiv) and DMSO (0.5 mL) under argon. The reaction was stirred under violet light irradiation (18 W x 2) in a fume hood for 12 hours. No reaction was detected. The reaction mixture was subjected to HRMS (ESI) analysis. The results revealed the formation of TEMPO-^{i}Pr.

TEMPO-^{i}Pr. HRMS: *m/z* calculated for $C_{12}H_{26}ON$: 200.2009 [M+H$^+$]; found: 200.2005.



5.14. Characterization of Compounds

3-Isopropyl-2H-chromen-2-one (3a)

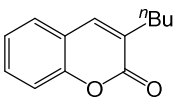


It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (32 mg, 84% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.37 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.21–7.16 (m, 1H), 3.73–2.85

(septet, J = 6.6 Hz, 1H), 1.20 (d, J = 6.6 Hz, 6H).

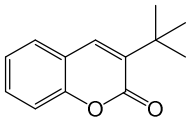
3-Butyl-2H-chromen-2-one (3b)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (35 mg, 86% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.48–7.43 (m, 2H), 7.32 (d, J = 7.8 Hz, 1H), 7.28–7.23 (m, 1H), 2.57 (t, J = 7.2 Hz, 2H), 1.67–1.60 (m, 2H), 1.46–1.38 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H).

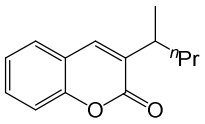
3-(Tert-butyl)-2H-chromen-2-one (3c)



It is obtained according to general procedure (**5.6**, with Cs_2CO_3 under violet light) as a white solid (35 mg, 86% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.40–7.35 (m, 2H), 7.21 (d, J = 7.8 Hz, 1H), 7.17 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 1.32 (s, 9H).

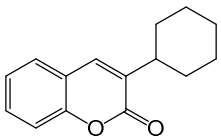
3-(Pentan-2-yl)-2H-chromen-2-one (3d)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (35 mg, 80% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.33 (m, 3H), 7.23 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 2.93 (qt, J = 7.0, 7.0 Hz, 1H), 1.64–1.57 (m, 1H), 1.45–1.38 (m, 1H), 1.34–1.20 (m, 2H), 1.16 (d, J = 7.0 Hz, 3H), 0.84 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.5, 151.7, 135.8, 133.8, 129.5, 126.2, 123.1, 118.6, 115.3, 36.7, 32.6, 19.5, 18.5, 13.1. **HRMS**: *m/z* calculated for $C_{14}H_{16}O_2$: 239.1043 [M+Na^+]; found: 239.1045.

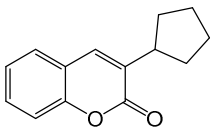
3-Cyclohexyl-2H-chromen-2-one (3e)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (42 mg, 91% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.35 (m, 3H), 7.22 (d, J = 7.8 Hz, 1H), 7.17 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 2.70 (tt, J = 11.9, 2.8 Hz, 1H), 1.91 (bd, J = 12.0 Hz, 2H), 1.80–1.74 (m, 2H), 1.69 (bd, J = 12.8 Hz, 1H), 1.41–1.32 (m, 2H), 1.26–1.12 (m, 3H).

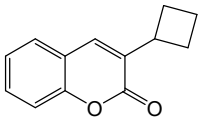
3-Cyclopentyl-2H-chromen-2-one (3f)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (36 mg, 84% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.40–7.35 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.07 (tt, *J* = 8.4 Hz, 1H), 2.06–1.99 (m, 2H), 1.77–1.68 (m, 2H), 1.68–1.60 (m, 2H), 1.54–1.47 (m, 2H).

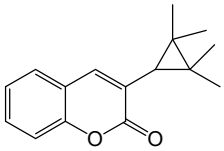
3-Cyclobutyl-2H-chromen-2-one (3g)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (24 mg, 61% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50–7.45 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.29–7.25 (m, 2H), 3.63–3.56 (m, 1H), 2.43–2.35 (m, 2H), 2.15–2.05 (m, 3H), 1.91–1.83 (m, 1H).

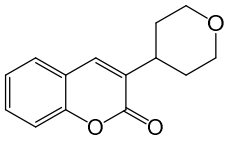
3-(2,2,3,3-Tetramethylcyclopropyl)-2H-chromen-2-one (3h)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (25 mg, 51% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.17 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 1.24 (d, *J* = 1.7 Hz, 1H), 1.21 (s, 6H), 0.97 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.2, 152.9, 140.7, 130.4, 127.9, 127.2, 124.1, 119.5, 116.2, 33.7, 24.2, 23.3, 18.4. **HRMS**: *m/z* calculated for $C_{16}H_{18}O_2$: 265.1199 [M+Na^+]; found: 265.1197.

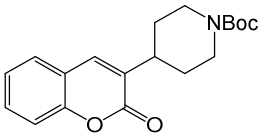
3-(Tetrahydro-2H-pyran-4-yl)-2H-chromen-2-one (3i)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (42 mg, 91% yield; petroleum ether/ethyl acetate 5:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44–7.39 (m, 3H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.05–4.00 (m, 2H), 3.55–3.48 (m, 2H), 3.01–2.93 (m, 1H), 1.87–1.81 (m, 2H), 1.66–1.58 (m, 2H).

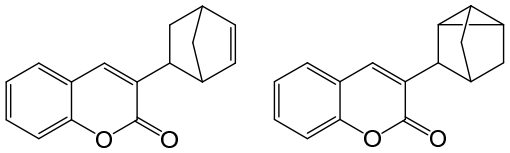
***tert*-Butyl 4-(2-oxo-2H-chromen-3-yl) piperidine-1-carboxylate (3j)**



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (57 mg, 86% yield; petroleum ether/ethyl acetate 10:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.37 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.22–7.18 (m, 1H), 4.35–4.03 (m, 2H), 2.86 (t, *J* = 12.0 Hz, 1H), 2.77 (bs, 2H), 1.88 (bd, *J* = 12.0 Hz, 2H), 1.40 (s, 9H).

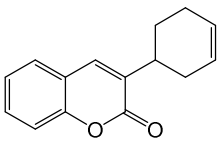
3-(Bicyclo[2.2.1]hept-5-en-2-yl)-2H-chromen-2-one and 3-(tricyclo[2.2.1.0^{2,6}]heptan-3-yl)-2H-chromen-2-one (3k/3k1, 1:1 inseparable mixture)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (33 mg, 70% yield; petroleum ether/ethyl acetate 10:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ Compound **3k**: 7.43 (s, 1H), 7.42-7.37 (m, 2H), 7.27-7.23 (m, 1H), 7.21–7.17 (m, 1H), 6.20 (dd, *J* = 5.5, 3.2 Hz, 1H), 6.13 (dd, *J* = 5.5, 2.9 Hz, 1H), 2.93 (s, 1H), 2.89 (s, 1H), 2.69 (dd, *J* = 8.7, 4.8 Hz, 1H), 1.68–1.63 (m, 1H), 1.52–1.48 (m, 1H), 1.44–1.38 (m, 2H). Compound **3k1**: δ 7.50 (s, 1H), 7.42-7.37 (m, 2H), 7.27-7.23 (m, 1H), 7.21–7.17 (m, 1H), 2.79 (s, 1H), 2.14 (s, 1H), 1.57–1.53 (m, 1H), 1.38-1.35 (m, 1H), 1.26–1.20 (m, 2H), 1.14-1.11 (m, 1H), 1.10–1.05 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ [161.1, 160.7], [152.0, 151.6], 137.0, 136.7, 135.5, 134.5, 133.1, 129.5, 129.4, 129.0, 126.3, 126.2, [123.2, 123.1], [118.5, 118.4], [115.3, 115.2], 44.7, 44.6, 44.1, 41.3, 37.6, 33.8, 31.9, 31.4, 28.0, 12.0, 10.3, 9.1. **HRMS**: *m/z* calculated for $C_{16}H_{14}O_2$: 261.0886 [M+Na$^+$]; found: 261.0886.

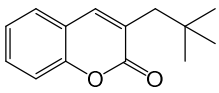
3-Cyclohex-3-en-1-yl-2H-chromen-2-one (3l)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (40 mg, 89% yield; petroleum ether/ethyl acetate 25:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44–7.35 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.20–7.16 (m, 1H), 5.72–5.63 (m, 2H), 3.05–2.98 (m, 1H), 2.41–2.31 (m, 1H), 2.20–2.10 (m, 1H), 2.09–1.96 (m, 2H), 1.92–1.86 (m, 1H), 1.70–1.61 (m, 1H).

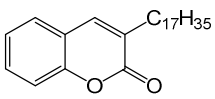
3-Neopentyl-2H-chromen-2-one (3m)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (38 mg, 88% yield; petroleum ether/ethyl acetate 10:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.36 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.20–7.17 (m, 1H), 2.46 (s, 2H), 0.91 (s, 9H).

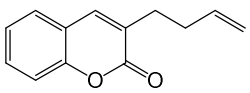
3-Heptadecyl-2H-chromen-2-one (3n)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (62 mg, 80% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50–7.42 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28–7.24 (m, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.64 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.41–1.21 (m, 28H), 0.88 (t, *J* = 7.2 Hz, 3H).

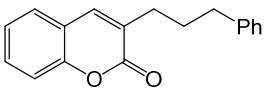
3-(3-Buten-1-yl)-2H-chromen-2-one (3o)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (21 mg, 52% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (bs, 1H), 7.43–7.38 (m, 1H), 7.45 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.21–7.17 (m, 1H), 5.82–5.74 (m, 1H), 5.03–4.98 (m, 1H), 4.97–4.93 (m, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.39–2.33 (m, 2H).

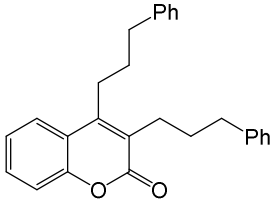
3-(3-Phenylpropyl)-2H-chromen-2-one (3p)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (32 mg, 60% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.42 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.33–7.27 (m, 3H), 7.25 (ddd, J = 7.8, 7.8, 1.2 Hz, 2H), 7.23–7.17 (m, 3H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.03–1.96 (m, 2H).

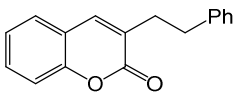
3,4-Bis(3-phenylpropyl)-2H-chromen-2-one (3p1)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (10 mg, 13% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45–7.41 (m, 1H), 7.36–7.32 (m, 3H), 7.32–7.28 (m, 3H), 7.27–7.24 (m, 2H), 7.23–7.18 (m, 6H), 2.71–2.65 (m, 4H), 2.65–2.61 (m, 2H), 2.57–2.52 (m, 2H), 1.87–1.79 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.9, 152.6, 150.0, 142.0, 141.1, 130.4, 128.6, 128.5, 128.4, 128.4, 126.3, 126.2, 126.0, 124.3, 124.1, 119.6, 117.0, 36.0, 35.9, 30.9, 30.6, 27.7, 27.1. **HRMS**: *m/z* calculated for $C_{27}H_{26}O_2$: 405.1825 [M+Na^+]; found: 405.1826.

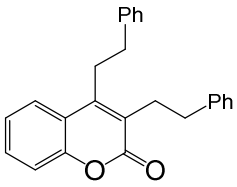
3-Phenethyl-2H-chromen-2-one (3q)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (35 mg, 70% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography). Spectral data is in agreement with the literature.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.40–7.36 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.31–7.27 (m, 2H), 7.26–7.19 (m, 4H), 3.00–2.96 (m, 2H), 2.91–2.86 (m, 2H).

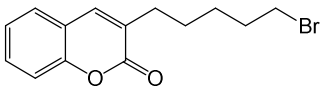
3,4-Biphenethyl-2H-chromen-2-one (3q1)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (6 mg, 8.5% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.52–7.48 (m, 1H), 7.37 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35–7.17 (m, 12H), 2.97–2.93 (m, 2H), 2.85 (s, 4H), 2.81–2.76 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.6, 151.7, 148.4, 140.3, 139.3, 129.6, 127.7, 127.5, 127.5, 127.1, 125.6, 125.1, 124.8, 123.4, 123.2, 118.3, 116.2, 34.0, 33.6, 29.3, 29.1. **HRMS**: *m/z* calculated for $C_{25}H_{22}O_2$: 377.1512 [M+Na^+]; found: 377.1512.

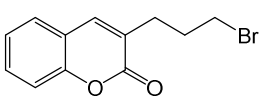
3-(5-Bromopentyl)-2H-chromen-2-one (3r)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (35 mg, 59% yield; petroleum ether/ethyl acetate 5:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.50–7.44 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.29–7.25 (m, 1H), 3.44 (t, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 1.93 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.69 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.55 (tt, *J* = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, CDCl3) δ 161.8, 153.1, 138.7, 130.6, 130.0, 127.2, 124.3, 119.5, 116.5, 33.8, 32.4, 30.8, 27.7, 27.1. **HRMS**: *m/z* calculated for $C_{14}H_{15}BrO_2$: 317.0148 [M+Na^+]; found: 317.0148.

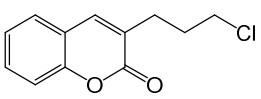
3-(3-Bromopropyl)-2H-chromen-2-one (3s)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (11 mg, 20% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.45–7.38 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.23–7.19 (m, 1H), 3.40 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.19–2.13 (tt, *J* = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, CDCl3) δ 160.9, 152.2, 138.8, 129.4, 126.6, 126.2, 123.4, 118.3, 115.5, 31.1, 29.4, 28.3. **HRMS**: *m/z* calculated for $C_{12}H_{11}BrO_2$: 288.9835 [M+Na^+]; found: 288.9833.

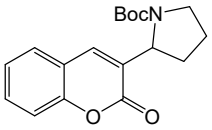
3-(3-chloropropyl)-2H-chromen-2-one (3t)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under blue light) as a white solid (28 mg, 62% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.44–7.38 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.21 (bdd, *J* = 7.8, 7.8 Hz, 1H), 3.54 (t, *J* = 7.2 Hz, 1H), 2.69 (t, *J* = 7.2 Hz, 1H), 2.08 (tt, *J* = 7.2, 7.2 Hz, 1H). **^{13}C NMR** (150 MHz, CDCl3) δ 160.6, 152.2, 138.1, 129.8, 126.9, 126.3, 123.4, 118.3, 114.4, 43.7, 29.4, 27.0. **HRMS**: *m/z* calculated for $C_{12}H_{11}ClO_2$: 245.0340 [M+Na^+]; found: 245.0340.

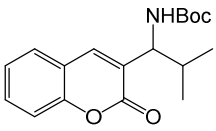
***tert*-Butyl 2-(2-oxo-2H-chromen-3-yl) pyrrolidine-1-carboxylate (3u)**



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (52 mg, 83% yield; petroleum ether/ethyl acetate 8:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47–7.35 (m, 3H), 7.32–7.27 (m, 1H), 7.26–7.15 (m, 1H), 4.96–4.86 (m, 1H), 3.63–3.39 (m, 2H), 2.35–2.18 (m, 1H), 1.90–1.80 (m, 2H), 1.78–1.70 (m, 1H), 1.41 (s, 3H), 1.24 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.7, 160.6, 154.4, 153.2, 153.0, 136.6, 136.3, 131.1, 130.9, 130.7, 129.9, 127.7, 127.6, 124.6, 124.3, 119.3, 119.0, 116.5, 116.4, 79.9, 79.8, 57.1, 56.8, 47.4, 46.9, 32.2, 31.1, 28.5, 28.3, 23.5, 22.8. **HRMS**: *m/z* calculated for $C_{18}H_{21}NO_4$: 338.1363 [M+Na^+]; found: 338.1361.

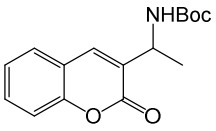
***tert*-Butyl (2-methyl-1-(2-oxo-2H-chromen-3-yl)propyl) carbamate (3v)**



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (55 mg, 87% yield; petroleum ether/ethyl acetate 10:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.46–7.40 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 7.8 7.8 Hz, 1H), 5.55 (d, *J* = 9.6 Hz, 1H), 4.13 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.25–2.15 (m, 1H), 1.34 (s, 9H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.7, 154.6, 152.2, 139.4, 130.3, 127.0, 126.9, 123.5, 117.9, 115.4, 78.4, 59.1, 29.6, 27.4, 19.5, 18.3. **HRMS**: *m/z* calculated for $C_{18}H_{23}NO_4$: 340.1519 [M+Na^+]; found: 340.1517.

***tert*-Butyl (1-(2-oxo-2H-chromen-3-yl)ethyl) carbamate (3w)**

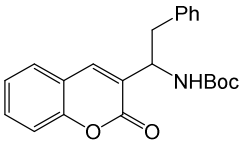


It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (49 mg, 84% yield; petroleum ether/ethyl acetate 12:1 for flash chromatography). Spectral data is in agreement with the literature.[8]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.53–7.47 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz,

1H), 5.50 (bd, *J* = 6.6 Hz, 1H), 4.76 (dq, *J* = 6.6 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H), 1.42 (s, 9H).

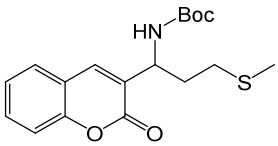
***tert*-Butyl (1-(2-oxo-2H-chromen-3-yl)-2-phenylethyl) carbamate (3x)**



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (61 mg, 83% yield; petroleum ether/ethyl acetate 12:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.8 Hz, 1H), 7.30–7.23 (m, 3H), 7.18–7.13 (m, 3H), 7.11–7.06 (m, 3H), 5.61 (d, *J* = 9.0 Hz, 1H), 4.78 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.17–3.06 (m, 2H), 1.31 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.8, 155.1, 153.2, 140.4, 137.5, 131.4, 129.3, 128.5, 128.0, 127.3, 126.6, 124.5, 123.4, 118.8, 116.4, 79.7, 54.9, 39.8, 29.7, 28.3. **HRMS**: *m/z* calculated for $C_{22}H_{23}NO_4$: 388.1519 [M+Na$^+$]; found: 388.1518.

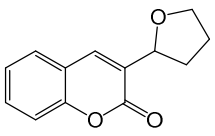
***tert*-Butyl (3-(methylthio)-1-(2-oxo-2H-chromen-3-yl)propyl) carbamate (3y)**



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (62 mg, 89% yield; petroleum ether/ethyl acetate 12:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.48–7.41 (m, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.22 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.59 (d, *J* = 9.6 Hz, 1H), 4.73–4.68 (m, 1H), 2.49–2.38 (m, 2H), 2.15–2.04 (m, 2H), 2.03 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.7, 154.2, 152.3, 139.5, 130.7, 126.8, 126.6, 123.6, 117.9, 115.5, 78.7, 51.4, 31.5, 29.8, 26.3, 14.6. **HRMS**: *m/z* calculated for $C_{18}H_{23}NO_4S$: 372.1240 [M+Na$^+$]; found: 372.1243.

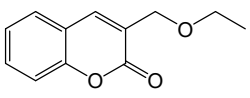
3-(Tetrahydrofuran-2-yl)-2H-chromen-2-one (3z)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (17 mg, 39% yield; petroleum ether/ethyl acetate 5:1 for flash chromatography). Spectral data is in agreement with the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.2 Hz, 1H), 7.53–7.47 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.28 (ddd, *J* = 8.4, 8.4, 1.2 Hz, 1H), 4.97 (ddd, *J* = 7.8, 6.6, 1.2 Hz, 1H), 4.15–4.09 (m, 1H), 3.96 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.57–2.49 (m, 1H), 2.06–1.99 (m, 1H), 1.98–1.91 (m, 1H), 1.81–1.74 (m, 1H).

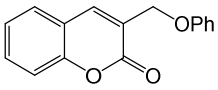
3-(Ethoxymethyl)-2H-chromen-2-one (3aa)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (19 mg, 46% yield; petroleum ether/ethyl acetate 5:1 for flash chromatography). Spectral data is in agreement with the literature.[9]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (bs, 1H), 7.54–7.49 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.29 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 4.47 (d, *J* = 1.2 Hz, 2H), 3.69 (q, *J* = 6.6 Hz, 2H), 1.33 (t, *J* = 6.6 Hz, 3H).

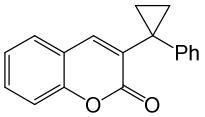
3-(Phenoxymethyl)-2H-chromen-2-one (3ab)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a colorless oil (16 mg, 31% yield; petroleum ether/ethyl acetate 5:1 for flash chromatography). Spectral data is in agreement with the literature.[10]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 7.56–7.51 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.36–7.28 (m, 3H), 7.05–6.99 (m, 3H), 5.05 (d, *J* = 1.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.3, 156.9, 152.1, 137.7, 130.4, 128.7, 126.9, 123.7, 123.6, 120.5, 118.0, 115.6, 115.0, 113.6, 63.3.

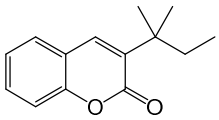
3-(1-Phenylcyclopropyl)-2H-chromen-2-one (3ac)



It is obtained according to general procedure (**5.6**, with Li_2CO_3 under violet light) as a white solid (47 mg, 90% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.48–7.44 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.30–7.23 (m, 4H), 7.18 (dd, *J* = 7.8, 7.8 Hz, 1H), 1.34 (t, *J* = 5.6 Hz, 2H), 1.28 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.6, 152.4, 141.7, 139.8, 131.4, 129.9, 127.3, 127.1, 126.5, 125.4, 123.1, 118.3, 115.2, 26.4, 13.3. **HRMS**: *m/z* calculated for $C_{18}H_{14}O_2$: 285.0886 [M+Na$^+$]; found: 285.0886.

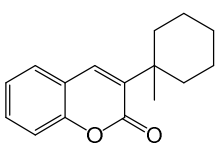
3-(*tert*-Pentyl)-2H-chromen-2-one (3ad)



It is obtained according to general procedure (**5.6**, with Cs_2CO_3 under violet light) as a white solid (33 mg, 76% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.41–7.36 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 8.4 Hz, 1H), 1.82 (q, *J* = 7.5 Hz, 2H), 1.27 (s, 6H), 0.65 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.8, 152.2, 137.2, 134.6, 129.5, 126.5, 123.0, 118.4, 115.0, 37.6, 31.0, 25.6. **HRMS**: *m/z* calculated for $C_{14}H_{16}O_2$: 239.1043 [M+Na$^+$]; found: 239.1044.

3-(1-Methylcyclohexyl)-2H-chromen-2-one (3ae)

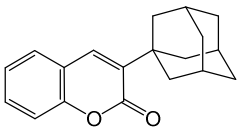


It is obtained according to general procedure (**5.6**, with Cs_2CO_3 under violet light) as a white solid (30 mg, 62% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.41–7.36 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.17 (td, *J* = 7.5,

1.0 Hz, 1H), 1.99–1.90 (m, 2H), 1.71–1.65 (m, 2H), 1.57–1.49 (m, 2H), 1.48–1.39 (m, 3H), 1.35–1.28 (m, 1H), 1.35 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.0, 152.0, 137.1 135.5, 129.5, 126.6, 123.0, 118.5, 114.9, 37.2, 34.8, 25.4, 23.3, 21.3. **HRMS**: m/z calculated for $C_{16}H_{18}O_2$: 265.1199 [M+Na$^+$]; found: 265.1198.

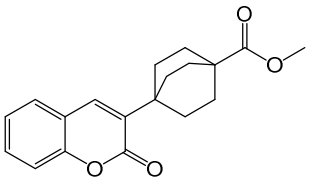
3-(Adamantan-1-yl)-2H-chromen-2-one (3af)



It is obtained according to general procedure (**5.6**, with Cs_2CO_3 under violet light) as a white solid (35 mg, 64% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[11]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.35 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.16 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 2.05–2.02 (m, 3H), 1.99 (d, *J* = 3.0 Hz, 6H), 1.72 (t, *J* = 3.0 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.6, 151.9, 136.1, 136.0, 129.4, 126.6, 122.9, 118.5, 114.9, 38.7, 36.1, 35.7, 27.5. **HRMS**: *m/z* calculated for $C_{19}H_{20}O_2$: 303.1356 [M+Na$^+$]; found: 303.1357.

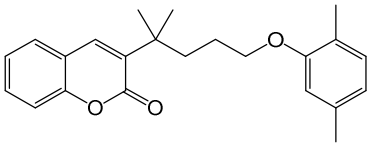
Methyl 4-(2-oxo-2H-chromen-3-yl) bicyclo[2.2.2]octane-1-carboxylate (3ag)



It is obtained according to general procedure (**5.6**, with Cs_2CO_3 under violet light) as a white solid (39 mg, 63% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.36 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 (td, *J* = 7.8, 1.0 Hz, 1H), 3.61 (s, 3H), 1.94–1.82 (m, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.3, 158.9, 152.0, 136.7, 134.3, 129.7, 126.6, 123.1, 118.3, 115.0, 50.8, 37.5, 34.3, 27.4, 27.1. **HRMS**: m/z calculated for $C_{19}H_{20}O_4$: 335.1254 [M+Na$^+$]; found: 335.1254.

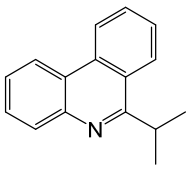
3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-2H-chromen-2-one (3ah)



It is obtained according to general procedure (**5.6**, with Cs_2CO_3 under violet light) as a white solid (58 mg, 82% yield; petroleum ether/ethyl acetate 18:1 for flash chromatography). Spectral data is in agreement with the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.40–7.36 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.49 (s, 1H), 3.80 (t, *J* = 6.6 Hz, 2H), 2.20 (s, 3H), 2.08 (s, 3H), 1.99–1.94 (m, 2H), 1.55–1.48 (m, 2H), 1.33 (s, 6H).

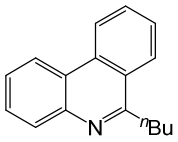
6-Isopropylphenanthridine (4a)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (37mg, 83% yield; petroleum ether/dichloromethane 10:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.16 (bs, 1H), 7.82 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.73–7.67 (m, 2H), 7.61 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.01 (septet, *J* = 6.6 Hz, 1H), 1.52 (d, *J* = 6.6 Hz, 6H).

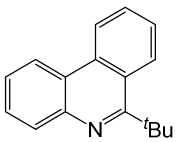
6-Butylphenanthridine (4b)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (42 mg, 89% yield; petroleum ether/ethyl acetate 25:1 for flash chromatography). Spectral data is in agreement with the literature.[17]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.82 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.73–7.66 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 3.40–3.35 (m, 2H), 1.94–1.87 (m, 2H), 1.60–1.52 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).

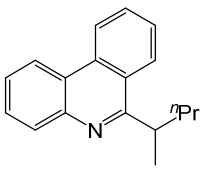
6-(*tert*-Butyl)phenanthridine (4c)



It is obtained according to general procedure (**5.7**, with Cs_2CO_3 under violet light) as a colorless oil (39 mg, 83% yield; petroleum ether/dichloromethane 20:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 6.6 Hz, 1H), 7.76 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.69 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.65 – 7.57 (m, 2H), 1.73 (s, 9H).

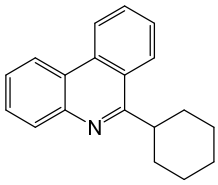
6-(Pentan-2-yl)phenanthridine (4d)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (45 mg, 90% yield; petroleum ether/ethyl acetate 50:1 for flash chromatography). Spectral data is in agreement with the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.15 (bs, 1H), 7.82 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.73–7.67 (m, 2H), 7.61 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.91–3.82 (m, 1H), 2.14–2.07 (m, 1H), 1.81–1.72 (m, 1H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.47–1.41 (m, 1H), 1.40–1.32 (m, 1H), 0.93 (t, *J* = 7.2 Hz, 3H).

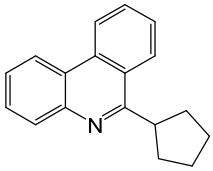
6-Cyclohexylphenanthridine (4e)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (42 mg, 80% yield; petroleum ether/dichloromethane 10:1 for flash chromatography). Spectral data is in agreement with the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.71–7.64 (m, 2H), 7.58 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.63–3.56 (m, 1H), 2.10–2.04 (m, 2H), 1.99–1.88 (m, 4H), 1.86–1.80 (m, 1H), 1.61–1.51 (m, 2H), 1.48–1.37 (m, 1H).

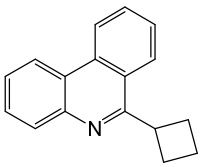
6-Cyclopentylphenanthridine (4f)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a yellowish oil (39 mg, 79% yield; petroleum ether/dichloromethane 10:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 6.6 Hz, 1H), 7.80 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.71–7.65 (m, 2H), 7.61–7.57 (m, 1H), 4.09–4.02 (m, 1H), 2.29–2.21 (m, 2H), 2.21–2.14 (m, 2H), 1.97–1.89 (m, 2H), 1.83–1.74 (m, 2H).

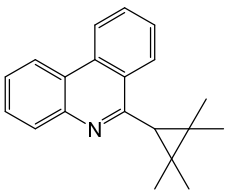
6-Cyclobutylphenanthridine (4g)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (34 mg, 73% yield; petroleum ether/dichloromethane 10:1 for flash chromatography). Spectral data is in agreement with the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.84–7.77 (m, 1H), 7.74–7.69 (m, 1H), 7.67–7.63 (m, 1H), 7.63–7.59 (m, 1H), 4.48–4.34 (m, 1H), 2.83–2.70 (m, 2H), 2.60–2.49 (m, 2H), 2.28– 2.16 (m, 1H), 2.05–1.93 (m, 1H).

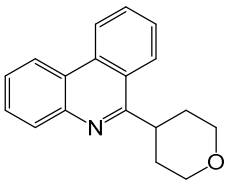
6-(2,2,3,3-Tetramethylcyclopropyl)phenanthridine (4h)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (15 mg, 27% yield; petroleum ether/ethyl acetate 25:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.8 Hz, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.05 (bd, *J* = 6.6 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.65–7.59 (m, 2H), 7.53 (bt, *J* = 7.8 Hz, 1H), 1.98 (s, 1H), 1.40 (s, 6H), 1.03 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.7, 131.5, 129.1, 128.8, 127.3, 126.5, 126.1, 125.9, 125.3, 120.9, 36.7, 24.0, 22.6, 17.8. **HRMS**: *m/z* calculated for $C_{20}H_{21}N$: 276.1747 [$M+H^+$]; found: 276.1745.

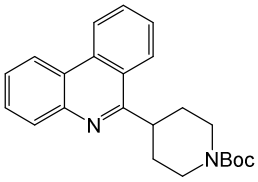
6-(Tetrahydro-2H-pyran-4-yl)phenanthridine (4i)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (40 mg, 76% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 6.6 Hz, 1H), 7.82 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.73–7.67 (m, 2H), 7.64–7.59 (m, 1H), 4.20 (dd, *J* = 11.2, 2.8 Hz, 2H), 3.86 (bt, *J* = 10.8 Hz, 1H), 3.73 (td, *J* = 12.2, 1.7 Hz, 2H), 2.40–2.29 (m, 2H), 1.95 (dd, *J* = 13.5, 1.4 Hz, 2H).

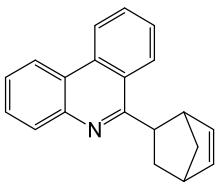
***tert*-Butyl 4-(phenanthridin-6-yl) piperidine-1-carboxylate (4j)**



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (56 mg, 77% yield; petroleum ether/ethyl acetate 10:1 for flash chromatography). Spectral data is in agreement with the literature.[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.81 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.72–7.65 (m, 2H), 7.63–7.58 (m, 1H), 4.47–4.28 (m, 2H), 3.74 (t, *J* = 10.2 Hz, 1H), 3.01 (bs, 2H), 2.26–1.90 (m, 4H), 1.51 (s, 9H).

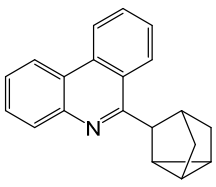
6-(Bicyclo[2.2.1]hept-5-en-2-yl)phenanthridine (4k)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (16 mg, 30% yield; petroleum ether/dichloromethane 20:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.05 (bd, *J* = 6.6 Hz, 1H), 7.75 (dd, *J* = 6.6, 6.6 Hz, 1H), 7.66–7.59 (m, 2H), 7.54 (dd, *J* = 6.6, 6.6 Hz, 1H), 6.37–6.32 (m, 1H), 6.29–6.25 (m, 1H), 3.49 (s, 1H), 3.23 (s, 1H), 2.99 (s, 1H), 2.41 (bd, *J* = 8.4 Hz, 1H), 1.84 (d, *J* = 8.4 Hz, 1H), 1.64 (t, *J* = 9.6 Hz, 1H), 1.40 (d, *J* = 6.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.42, 142.6, 137.8, 135.8, 131.7, 129.0, 128.8, 127.3, 126.0, 125.1, 125.0, 124.8, 122.3, 121.3, 120.7, 46.6, 45.3, 41.9, 41.3, 30.8. **HRMS**: *m/z* calculated for $C_{20}H_{17}N$: 272.1434 [$M+H^+$]; found: 272.1432.

6-(Tricyclo[2.2.1.0^{2,6}]heptan-3-yl)phenanthridine (4k1)

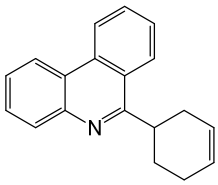


It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (15 mg, 28% yield; petroleum ether/dichloromethane 20:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.30

(d, *J* = 7.8 Hz, 1H), 8.09 (bs, 1H), 7.74 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.65–7.58 (m, 2H), 7.54 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.63 (s, 1H), 2.34 (s, 1H), 1.70 (d, *J* = 9.6 Hz, 1H), 1.64 (bs, 1H), 1.47 (d, *J* = 9.6 Hz, 1H), 1.37 (d, *J* = 9.6 Hz, 2H), 1.26 (bs, 1H), 1.08 (d, *J* = 9.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.2, 142.6, 131.5, 129.1, 128.8, 127.3, 125.9, 125.2, 125.1, 124.6, 122.5, 121.3, 120.7, 48.6, 34.8, 34.3, 29.0, 13.3, 10.2, 9.9. **HRMS**: *m/z* calculated for $C_{20}H_{17}N$: 272.1434 [M+H$^+$]; found: 272.1435.

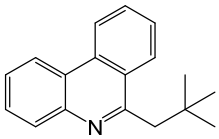
6-(Cyclohex-3-en-1-yl)phenanthridine (4l)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (35 mg, 68% yield; petroleum ether/dichloromethane 8:1 for flash chromatography). Spectral data is in agreement with the literature.[23]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.85–7.79 (m, 1H), 7.73–7.66 (m, 2H), 7.64–7.58 (m, 1H), 5.93–5.88 (m, 1H), 5.88–5.82 (m, 1H), 3.94–3.85 (m, 1H), 2.86–2.78 (m, 1H), 2.46–2.34 (m, 2H), 2.33–2.25 (m, 1H), 2.19–2.10 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.4, 142.8, 132.0, 129.0, 128.9, 127.4, 126.1, 126.0, 125.6, 125.2, 124.5 123.8, 122.3, 121.6, 120.8, 36.7, 29.8, 27.6, 25.1. **HRMS**: *m/z* calculated for $C_{19}H_{17}N$: 260.1434 [M+H$^+$]; found: 260.1433.

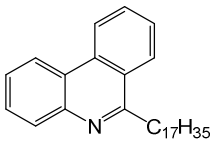
6-Neopentylphenanthridine (4m)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (39 mg, 78% yield; petroleum ether/dichloromethane 5:1 for flash chromatography). Spectral data is in agreement with the literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.84–7.78 (m, 1H), 7.74–7.70 (m, 1H), 7.69–7.65 (m, 1H), 7.64–7.60 (m, 1H), 3.34 (s, 2H), 1.08 (s, 9H).

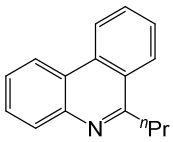
6-Heptadecylphenanthridine (4n)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (67 mg, 80% yield; petroleum ether/ethyl acetate 40:1 for flash chromatography). Spectral data is in agreement with the literature.[16]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.83–7.78 (m, 1H), 7.72–7.65 (m, 2H), 7.60 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.38–3.33 (m, 2H), 1.94–1.87 (m, 2H), 1.56–1.49 (m, 2H), 1.41-1.34 (m, 2H), 1.32–1.20 (m, 24H), 0.87 (t, *J* = 7.2 Hz, 3H).

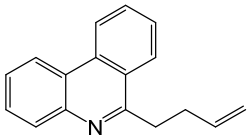
6-Propylphenanthridine (4o)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (35 mg, 79% yield; petroleum ether/ethyl acetate 25:1 for flash chromatography). Spectral data is in agreement with the literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.85–7.80 (m, 1H), 7.74–7.66 (m, 2H), 7.64–7.59 (m, 1H), 3.38–3.33 (m, 2H), 2.00–1.92 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).

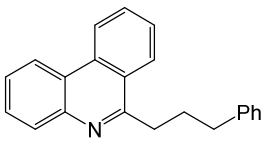
6-(But-3-en-1-yl)phenanthridine (4p)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (28 mg, 60% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.86–7.79 (m, 1H), 7.74–7.66 (m, 2H), 7.65–7.58 (m, 1H), 6.09–6.00 (m, 1H), 5.21–5.13 (m, 1H), 5.07–5.01 (m, 1H), 3.50–3.43 (m, 2H), 2.74–2.67 (m, 2H).

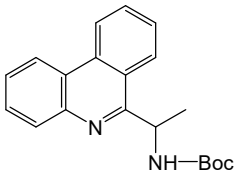
6-(3-Phenylpropyl)phenanthridine (4q)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a yellow solid (41 mg, 68% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 7.8 Hz, 1H), 8.51 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.79 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.70 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.64–7.58 (m, 2H), 7.32–7.27 (m, 2H), 7.27–7.23 (m, 2H), 7.21–7.17 (m, 1H), 3.39 (t, *J* = 7.8 Hz, 2H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.30–2.23 (m, 2H).

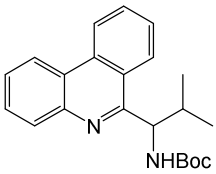
***tert*-Butyl (1-(phenanthridin-6-yl)ethyl) carbamate (4r)**



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (56 mg, 87% yield; petroleum ether/ethyl acetate 12:1 for flash chromatography). Spectral data is in agreement with the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.26 (bd, *J* = 7.8 Hz, 1H), 8.16 (bd, *J* = 7.8 Hz, 1H), 7.87 (t, *J* = 7.2 Hz, 1H), 7.76–7.70 (m, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 6.76 (bs, 1H), 5.76 (bt, *J* = 6.0 Hz, 1H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.51 (s, 9H).

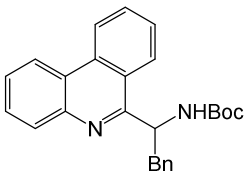
***tert*-Butyl (2-methyl-1-(phenanthridin-6-yl)propyl) carbamate (4s)**



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (56 mg, 80% yield; petroleum ether/ethyl acetate 12:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.67–7.60 (m, 2H), 7.56 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.29 (d, *J* = 9.0 Hz, 1H), 5.57 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.27–2.18 (m, 1H), 1.40 (s, 9H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.9, 155.2, 141.8, 131.9, 129.4, 128.7, 127.4, 126.4, 125.7, 124.70, 122.9, 122.5, 121.4, 120.9, 78.1, 54.2, 33.4, 27.4, 19.8, 15.7. **HRMS**: *m/z* calculated for $C_{22}H_{26}N_2O_2$: 351.2067 [M+H$^+$]; found: 351.2064.

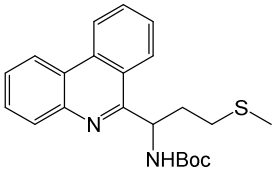
***tert*-Butyl (1-(phenanthridin-6-yl)-2-phenylethyl) carbamate (4t)**



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (75 mg, 94% yield; petroleum ether/ethyl acetate 8:1 for flash chromatography). Spectral data is in agreement with the literature.[20]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.80 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.71 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.60 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.11–7.06 (m, 3H), 6.96 (bs, 2H), 6.36 (d, *J* = 7.8 Hz, 1H), 5.97 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.40 (dd, *J* = 13.2, 6.6 Hz, 1H), 3.24 (dd, *J* = 13.2, 6.0 Hz, 1H), 1.43 (s, 9H).

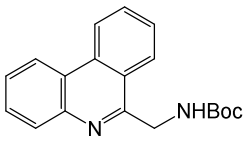
***tert*-Butyl (3-(methylthio)-1-(phenanthridin-6-yl)propyl) carbamate (4u)**



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (68 mg, 89% yield; petroleum ether/ethyl acetate 8:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.78 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.58 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.46 (d, *J* = 4.2 Hz, 1H), 5.82 (db, *J* = 4.2 Hz, 1H), 2.68–2.60 (m, 1H), 2.47–2.39 (m, 1H), 2.32–2.23 (m, 1H), 1.99 (s, 3H), 1.41 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.1, 154.8, 141.8, 132.5, 129.7, 128.7, 127.7, 126.7, 125.9, 124.3, 122.8, 122.5, 121.6, 121.0, 78.4, 48.8, 35.6, 29.3, 27.2, 14.6. **HRMS**: *m/z* calculated for $C_{22}H_{26}N_2O_2S$: 383.1788 [M+H$^+$]; found: 383.1785.

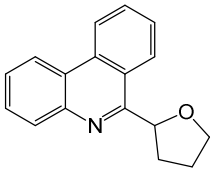
***tert*-Butyl (phenanthridin-6-yl)methyl carbamate (4v)**



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a colorless oil (13 mg, 21% yield; petroleum ether/ethyl acetate 12:1 for flash chromatography). Spectral data is in agreement with the literature.[19]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.2 Hz, 1H), 8.56 (d, *J* = 7.2 Hz, 1H), 8.19 (bs, 2H), 7.89 (dd, *J* = 7.2 Hz, 1H), 7.77–7.71 (m, 2H), 7.68 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.68 (bs, 1H), 5.06 (bd, *J* = 3.6 Hz, 2H), 1.55 (s, 9H).

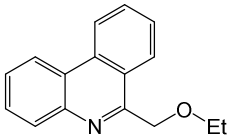
6-(Tetrahydrofuran-2-yl)phenanthridine (4w)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a brown solid (34 mg, 68% yield; petroleum ether/ ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.56 (dd, *J* = 8.4, 0.5 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.87–7.81 (m, 1H), 7.74–7.68 (m, 2H), 7.67–7.63 (m, 1H), 5.79 (t, *J* = 7.0 Hz, 1H), 4.26–4.20 (m, 1H), 4.11–4.05 (m, 1H), 2.75–2.67 (m, 1H), 2.48–2.40 (m, 1H), 2.25–2.09 (m, 1H).

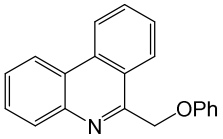
6-(Ethoxymethyl)phenanthridine (4x)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a yellowish oil (34 mg, 72% yield; petroleum ether/ ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[21]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.8 Hz, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 8.50 (d, *J* = 7.8 Hz, 1H), 8.21 (bd, *J* = 7.8 Hz, 1H), 7.87 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.77–7.71 (m, 2H), 7.69 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.19 (s, 2H), 3.70 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

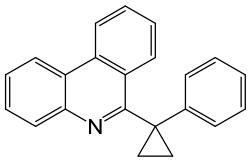
6-(Phenoxymethyl)phenanthridine (4y)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (39 mg, 68% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[21]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.8 Hz, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.21 (bd, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8, 7.8 Hz, 1H), 7.77 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.74–7.69 (m, 2H), 7.31 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.8 Hz, 1H), 5.72 (s, 2H).

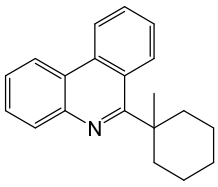
6-(1-Phenylcyclopropyl)phenanthridine (4z)



It is obtained according to general procedure (**5.7**, with Li_2CO_3 under violet light) as a white solid (47 mg, 79% yield; petroleum ether/ethyl acetate 30:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.20 (bd, *J* = 7.2 Hz, 1H), 7.72–7.66 (m, 2H), 7.61 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.47 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.13–7.08 (m, 2H), 7.05–7.00 (m, 3H), 1.69–1.65 (m, 2H), 1.60–1.56 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.1, 143.2, 142.6, 132.3, 129.2, 129.0, 127.6, 127.3, 127.1, 126.0, 125.9, 124.7, 124.5, 124.4, 123.0, 121.2, 120.8, 29.3, 16.2. **HRMS**: *m/z* calculated for $C_{22}H_{17}N$: 296.1434 [M+H$^+$]; found: 296.1433.

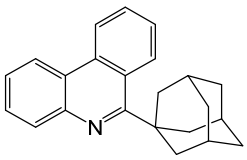
6-(1-Methylcyclohexyl)phenanthridine (4aa)



It is obtained according to general procedure (**5.7**, with Cs_2CO_3 under violet light) as a colorless oil (50 mg, 90% yield; petroleum ether/dichloromethane 30:1 for flash chromatography). Spectral data is in agreement with the literature.[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.8 Hz, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 8.52 (d, *J* = 7.8 Hz, 1H), 8.12 (bd, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.70 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.61 (dd, *J* = 7.8, 7.8 Hz, 2H), 2.61–2.54 (m, 2H), 1.96–1.88 (m, 2H), 1.70 (s, 3H), 1.66–1.60 (m, 4H), 1.57–1.49 (m, 1H), 1.48–1.40 (m, 1H).

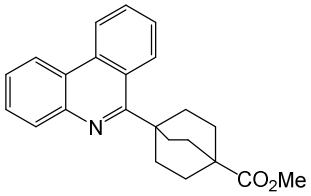
6-((3r,5r,7r)-Adamantan-1-yl)phenanthridine (4ab)



It is obtained according to general procedure (**5.7**, with Cs_2CO_3 under violet light) as a white solid (50 mg, 80% yield; petroleum ether/dichloromethane 15:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 7.8 Hz, 1H), 8.68 (d, *J* = 7.8 Hz, 1H), 8.51 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.69 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.59 (dd, *J* = 7.8, 7.8 Hz, 1H), 2.48 (bs, 6H), 2.23 (bs, 3H), 1.96–1.85 (m, 6H).

Methyl 4-(phenanthridin-6-yl)bicyclo[2.2.2]octane-1-carboxylate (4ac)

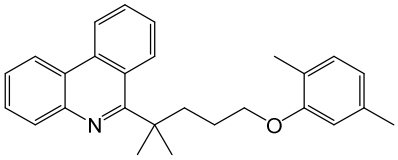


It is obtained according to general procedure (**5.7**, with Cs_2CO_3 under violet light) as a white solid (49 mg, 71% yield; petroleum ether/dichloromethane 8:1 for flash chromatography).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.03 (bs, 1H), 7.72 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.63 (d, *J* = 7.8, 7.8 Hz, 1H), 7.60–7.52 (m, 2H), 3.64 (s, 3H), 2.38–2.26 (m, 6H), 2.02–1.93 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ

178.6, 164.7, 133.8, 130.0, 129.4, 128.5, 127.9, 126.6, 126.0, 124.4, 123.2, 123.1, 121.7, 51.8, 40.4, 39.2, 30.5, 28.1. **HRMS**: *m/z* calculated for $C_{23}H_{23}NO_2$: 346.1802 [M+H$^+$]; found: 346.1802.

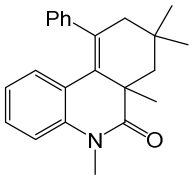
6-(5-(2,5-Dimethylphenyl)-2-methylpentan-2-yl)phenanthridine (4ad)



It is obtained according to general procedure (**5.7**, with Cs_2CO_3 under violet light) as a white solid (49 mg, 71% yield; petroleum ether/ dichloromethane 15:1 for flash chromatography). Spectral data is in agreement with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.51 (d, *J* = 7.8 Hz, 1H), 8.13 (bs, 1H), 7.76 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.69 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.64–7.57 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 7.2 Hz, 1H), 6.47 (s, 1H), 3.81 (t, *J* = 6.6 Hz, 2H), 2.39–2.34 (m, 2H), 2.23 (s, 3H), 2.09 (s, 3H), 1.75 (s, 6H), 1.66–1.59 (m, 2H).

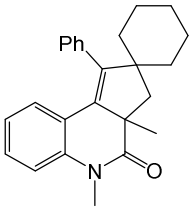
5,6A,8,8-Tetramethyl-10-phenyl-6a,7,8,9-tetrahydrophenanthridin-6(5H)-one (5a)



It is obtained according to general procedure (**5.8**, with Na_2CO_3 under violet light) as a yellow oil (21 mg, 64% yield; petroleum ether/ethyl acetate 15:1 for flash chromatography). Spectral data is in agreement with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22–7.14 (m, 3H), 7.11 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.01–6.93 (m, 3H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.59 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.41 (s, 3H), 2.69 (dd, *J* = 13.8, 1.8 Hz, 1H), 2.49 (d, *J* = 16.8 Hz, 1H), 2.00 (dd, *J* = 16.8, 1.8 Hz, 1H), 1.45 (d, *J* = 13.8 Hz, 1H), 1.11 (s, 3H), 1.07 (s, 3H), 0.95 (s, 3H).

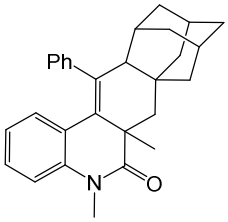
3A',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (5b)



It is obtained according to general procedure (**5.8**, with Na_2CO_3 under violet light) as a yellow oil (17 mg, 47% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.30 (m, 3H), 7.17–7.12 (m, 1H), 7.12–7.07 (bs, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.70–6.67 (m, 2H), 3.40 (s, 3H), 2.45 (d, *J* = 13.8 Hz, 1H), 2.29 (d, *J* = 13.8 Hz, 1H), 1.73–1.55 (m, 3H), 1.65–1.58 (m, 2H), 1.57–1.48 (m, 2H), 1.46–1.36 (m, 1H), 1.32 (s, 3H), 1.12 (td, *J* = 13.2, 3.6 Hz, 1H), 1.01–0.92 (m, 1H).

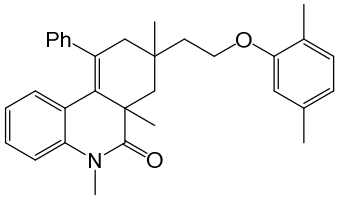
5,6A-Dimethyl-14-phenyl-5,6a,7,8,9,10,11,12,13,13a-decahydro-6H-7a,11:9,13-dimethanocycloocta[*j*] phenanthridin-6-one (5c)



It is obtained according to general procedure (**5.8**, with Na_2CO_3 under violet light) as a white solid (13 mg, 31% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.19–7.16 (m, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.50 (t, *J* = 7.8 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 3.32 (s, 3H), 2.66 (d, *J* = 13.8 Hz, 1H), 2.52 (s, 1H), 1.89 (bs, 1H), 1.73–1.67 (m, 3H), 1.66–1.50 (m, 5H), 1.47–1.42 (m, 1H), 1.34–1.29 (m, 1H), 1.24–1.19 (m, 1H), 1.14 (d, *J* = 13.8 Hz, 1H), 0.98 (d, *J* = 12.0 Hz, 1H), 0.89 (s, 3H).

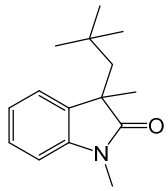
9-(2-(2,5-Dimethylphenoxy)ethyl)-5,6a,8,8-tetramethyl-10-phenyl-6a,7,8,9-tetrahydrophenanthridin-6(5H)-one (5d)



It is obtained according to general procedure (**5.8**, with Na_2CO_3 under violet light) as a white solid (14 mg, 30% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22–7.14 (m, 3H), 7.12–7.06 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.63 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 6.58 (s, 1H), 4.01–3.95 (m, 2H), 3.40 (s, 3H), 2.85 (dd, *J* = 14.4, 1.8 Hz, 1H), 2.38–2.31 (m, 1H), 2.30 (s, 3H), 2.27–2.22 (m, 1H), 2.09 (s, 3H), 1.98–1.95 (m, 1H), 1.58 (d, *J* = 14.4 Hz, 1H), 1.09 (s, 3H), 1.06 (s, 3H), 1.02 (s, 3H).

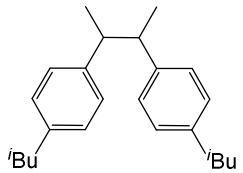
1,3-Dimethyl-3-neopentylindolin-2-one (6a)



It is obtained according to general procedure (with Li_2CO_3 under violet light) as a white solid (32 mg, 68% yield; petroleum ether/ethyl acetate 20:1 for flash chromatography). Spectral data is in agreement with the literature.[22]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.25 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.07–7.02 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 2.16 (d, *J* = 14.4 Hz, 1H), 1.87 (d, 1H), 1.30 (s, 3H), 0.61 (s, 9H).

4,4'-(Butane-2,3-diyl)bis(isobutylbenzene) (7)



Spectral data is in agreement with the literature.[24]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 2.90–2.83 (m, 1H), 2.77–2.70 (m, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.38 (d, *J* = 7.2 Hz, 2H), 1.90-1.81 (m, 1H), 1.81-1.73 (m, 1H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H), 0.84 (d, *J* = 6.6 Hz, 6H).

References

[1] (a) Shao, Z. Y.; Zhou, Q. L.; Wang, J. C.; Tang, R.; Shen, Y. H. Sodium Iodide-Triphenylphosphine-Mediated Photoredox Alkylation of Aldimines. *Chin. J. Org.Chem.* **2021**, *41*, 2676–2683. (b) Wang, J. C.; Shao Z. Y.; Tan, K.; Tang, R.; Zhou, Q. L.; Xu, M.; Li, Y. M.; Shen, Y. H. Synthesis of amino acids by base-enhanced photoredox decarboxylative alkylation of aldimines. *J. Org. Chem.* **2020**, *85*, 9944–9954. (c) Tang, R.; Shao Z. Y.; Wang, J. C.; Liu, Z. X.; Li, Y. M.; Shen, Y. H. Iron (II)-Catalyzed Radical Addition to Aldimines with Hantzsch Ester as Two-Hydrogen-Atom Donor. *J. Org. Chem*. **2019**, *84*, 8177–8184.

[2] Wadekar, K.; Aswale, S.; Yatham, V. R. PPh_3/NaI driven photocatalytic decarboxylative radical cascade alkylarylation reaction of 2-isocyanobiaryls. *RSC Adv*. **2020**, *10,* 16510–16514.

[3] Liu, H. Y.; Lu, Y.; Li, Y.; Li, J. H. Photocatalytic Decarboxylative [2 + 2 + *m*] Cyclization of 1,7-Enynes Mediated by Tricyclohexylphosphine and Potassium Iodide. *Org. Lett.* **2020**, *22*, 8819–8823.

[4] Li, Y. M.; Wei, X. H.; Li, X. A.; Yang, S. D. Metal-free carbonitration of alkenes using $K_2S_2O_8$. *Chem. Commun.* **2013**, *49*, 11701–11703.

[5] Jin, C.; Yan, Z. Y.; Sun, B.; Yang, J. Visible-Light-Induced Regioselective Alkylation of Coumarins via Decarboxylative Coupling with N-Hydroxyphthalimide Esters. *Org. Lett.* **2019**, *21*, 2064–2068.

[6] Liu, L. X.; Pan, N.; Sheng, W.; Su, L. B.; Liu, L.; Dong, J. Y.; Zhou, Y. B.; Yin, S. F. Visible Light-Induced Regioselective Decarboxylative Alkylation of the C(sp^2)–H Bonds of Non-Aromatic Heterocycles. *Adv. Synth. Catal*. **2019**, *361*, 4126–4132.

[7] Cao, H.; Jiang, H. M.; Feng, H. Y.; Kwan, J. M. C.; Liu, X. G.; Wu, J. Photo-induced Decarboxylative Heck-Type Coupling of Unactivated Aliphatic Acids and Terminal Alkenes in the Absence of Sacrificial Hydrogen Acceptors. *J. Am. Chem. Soc*. **2018**, *140*, 16360–16367.

[8] Li, Y. Y.; Dai, C. H.; Xie, S. T.; Liu, P.; Sun, P. P. Visible-Light-Induced C−H Bond Aminoalkylation of Heterocycles by the Decarboxylation Coupling of Amino Acids. *Org. Lett.* **2021**, *23*, 5906–5910.

[9] Tsai, J.-C.; Li, S.-R.; Chiang, M. Y.; Chen, L.-Y.; Chen, P.-Y.; Lo, Y.-F.; Wang, C.-H.; Lin, C.-N.; Wang, E.-C. Synthesis of 3-alkoxymethylcoumarin from 3-cyanochromene via a novel intermediate 2-phenylimino-3-alkoxymethylchromene. *J. Org. Chem*. **2009**, *74*, 8798–8801.

[10] Saha, S.; De, R. N.; Ghosh, S. K.; Majumdar, K. C. Sigmatropic Rearrangement of 3-(Aryloxymethyl) coumarins: A Simple Synthesis of Hydroxylated 3-Benzylcoumarins. *J. Chem. Soc., Perkin Trans. 1* **1993**, 715–718.

[11] Sun, J.; Yang, H.; Zhang, B. Metal-free visible-light-initiated direct C3 alkylation of quinoxalin-2(1H)-ones and coumarins with unactivated alkyl iodides. *Green Chem.* **2022**, *24*, 858–863.

[12] Lu, S. C.; Gong, Y. L.; Zhou, D. M. Transition Metal-Free Oxidative Radical Decarboxylation/Cyclization for the Construction of 6-Alkyl/Aryl Phenanthridines. *J. Org. Chem*. **2015**, *80,* 9336–9341.

[13] Zhang, Y. Q.; Jin, Y. H.; Wang, L. F.; Zhang, Q. Q.; Meng, C. G.; Duan, C. Y. Selective C(sp^3)–H activation of simple alkanes: visible light-induced metal-free synthesis of phenanthridines with H_2O_2 as a sustainable oxidant. *Green Chem.*

2021, *23*, 6926–6930.

[14] Yang, J. C.; Zhang, J. Y.; Zhang, J. J.; Duan, X. H.; Guo, L. N. Metal-Free, Visible-Light-Promoted Decarboxylative Radical Cyclization of Vinyl Azides with N-Acyloxyphthalimides. *J. Org. Chem.* **2018**, *83*, 1598–1605.

[15] Jaiswal, Y.; Kumar, Y.; Pal, J.; Subramanian, R.; Kumar, A. Rapid synthesis of polysubstituted phenanthridines from simple aliphatic/aromatic nitriles and iodo arenes via Pd(II) catalyzed domino C–C/C–C/C–N bond formation. *Chem. Commun.* **2018**, *54*, 7207–7210.

[16] Pan, C. D.; Zhang, H. L.; Han, J.; Cheng, Y. X.; Zhu, C. J. Metal-free radical oxidative decarboxylation/cyclization of acyl peroxides and 2-isocyanobiphenyls. *Chem. Commun*. **2015**, *51*, 3786–3788.

[17] Xu, Y. S.; Yu, C. Y.; Zhang, X. Y.; Fan, X. Y. Selective Synthesis of Dihydrophenanthridine and Phenanthridine Derivatives from the Cascade Reactions of o-Arylanilines with Alkynoates through C−H/N−H/C−C Bond Cleavage. *J. Org. Chem.* **2021**, *86*, 5805–5819.

[18] Cheng, W. M.; Shang, R.; Fu, Y. Photoredox/Brønsted Acid Co-Catalysis Enabling Decarboxylative Coupling of Amino Acid and Peptide Redox-Active Esters with N-Heteroarenes. *ACS Catal.* **2017**, *7*, 907–911.

[19] Zhu, Y. G.; Cao, S. Q.; Guo, K.; Chen, P.; Shi, Y. Method for preparation of phenanthridine heterocyclic compound by white light-induced photochemical reaction of isonitrile and N-(acyloxy)phthalimide. CN 108299296 A 20180720, 2018.

[20] Li, X. J.; Zhang, Q.; Zhang, W. G.; Wang, Y.; Pan, Y. Decarboxylative Alkylation of Heteroarenes Using N-Hydroxybenzimidoyl Chloride Esters. *J. Org. Chem*. **2019**, *84*, 14360–14368.

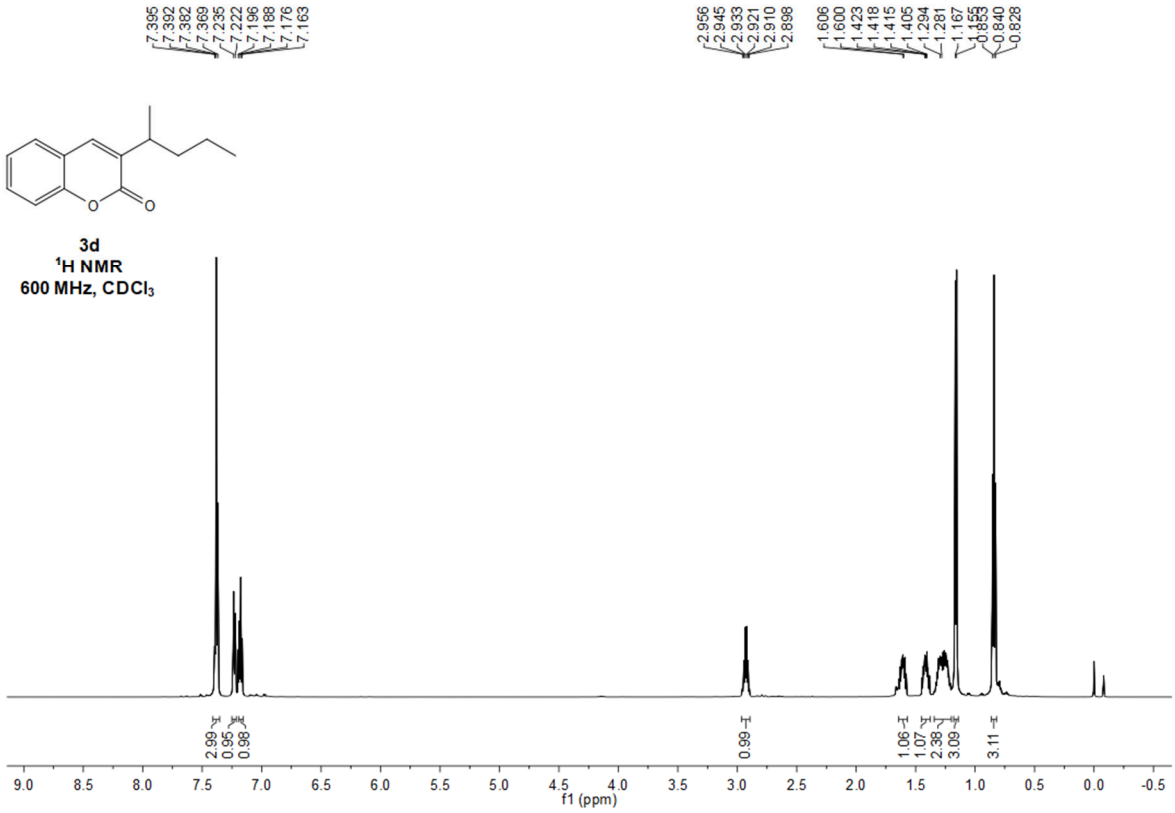
[21] Antonova, V. N.; Zakhs, É. R. Synthesis and properties of 6-alkoxymethylphenanthridines. *Chem. Heterocycl. Compd.* **1973**, *9*, 76–78.

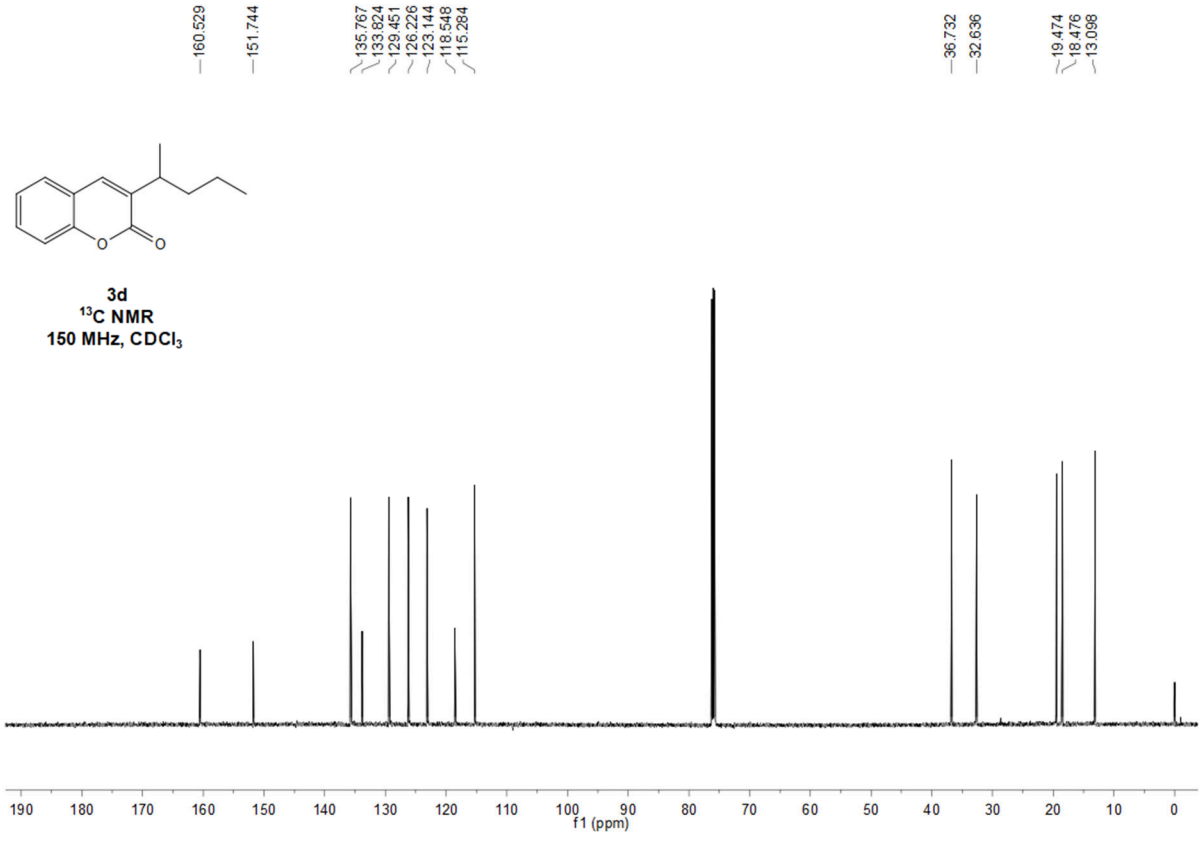
[22] Du, J.; Wang, X.; Wang, H. L.; Wei, J. H.; Huang, X.; Song, J.; Zhang, J. M. Photoinduced Palladium-Catalyzed Intermolecular Radical Cascade Cyclization of N-Arylacrylamides with Unactivated Alkyl Bromides. *Org. Lett.* **2021**, *23*, 5631–5635.

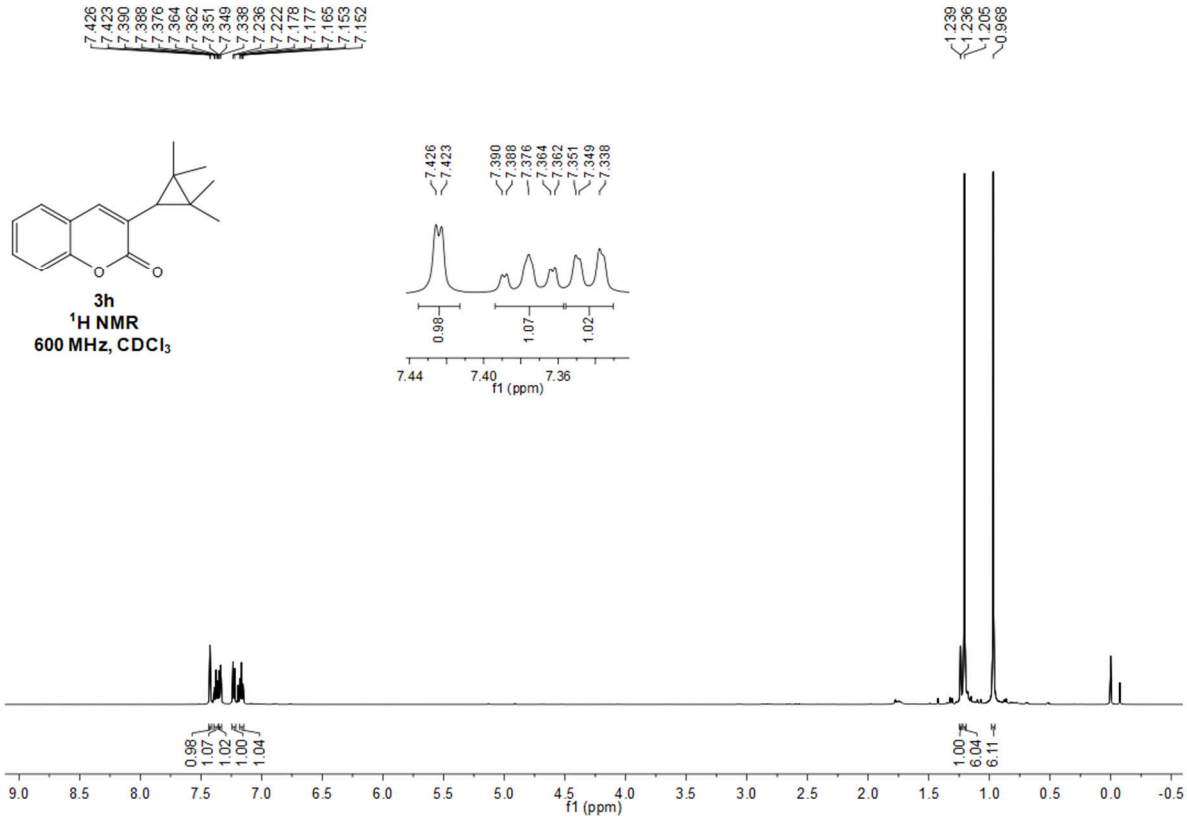
[23] Liu, M. T.; Liu, D. G.; Qin, Z. W.; Wang, G. Z. Visible light-induced sulphide anion-catalysed decarboxylative alkylations in batch and continuous flow. *ChemRxiv.* **2021**, 2573–2293.

[24] Yu, D. H.; To, W. P.; Tong, G. S. M.; Wu, L. L.; Chan, K. T.; Du, L. L.; Phillips, D. L.; Liu, Y. G.; Che, C. M. Luminescent tungsten(VI) complexes as photocatalysts for light-driven C–C and C–B bond formation reactions. *Chem. Sci.* **2020**, *11*, 6370–6382.

6. NMR Spectra of New Compounds



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7.178
7.177
7.165
7.153
7.152
1.239
1.236
1.205
0.968
3h
1H NMR
600 MHz, CDCl3
0.98
1.07
1.02
7.44
7.40
7.36
f1 (ppm)
1.00
6.04
6.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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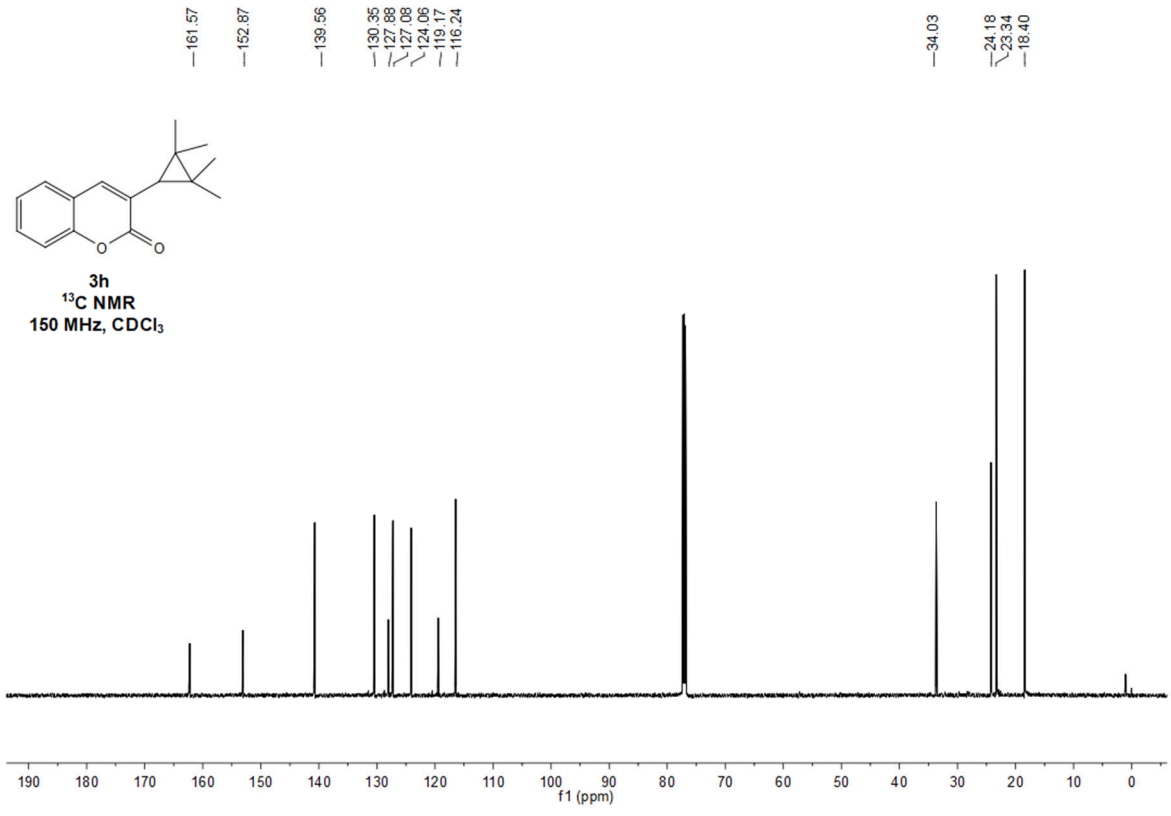
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18.40
3h
13C NMR
150 MHz, CDCl3
190
180
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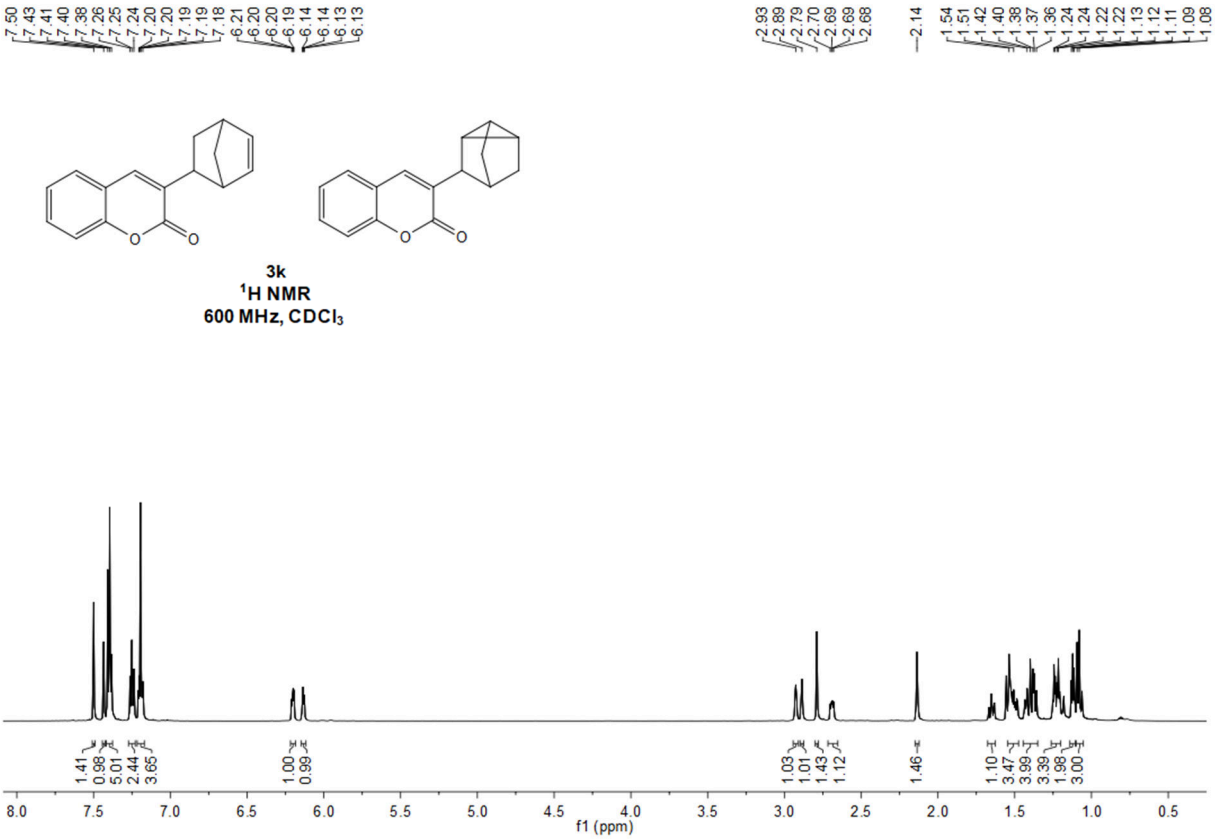
f1 (ppm)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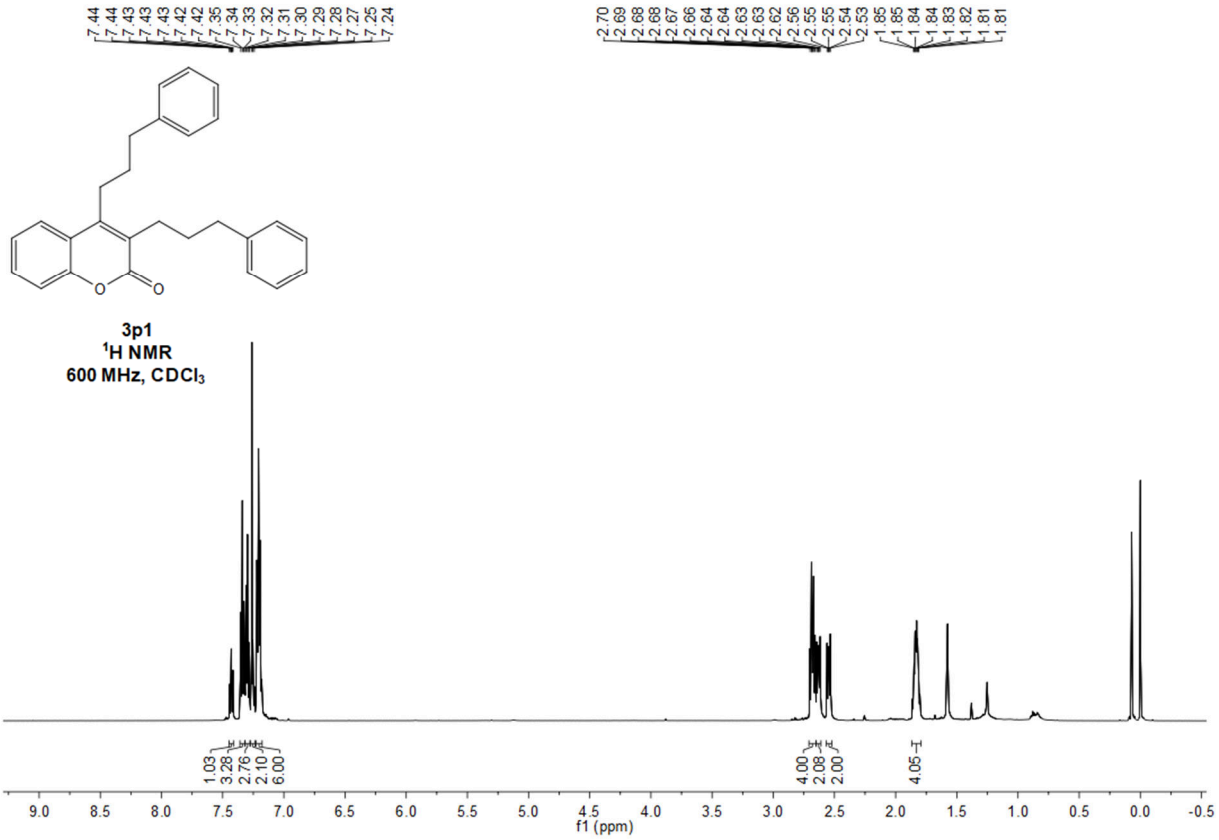
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7.0
6.5
6.0
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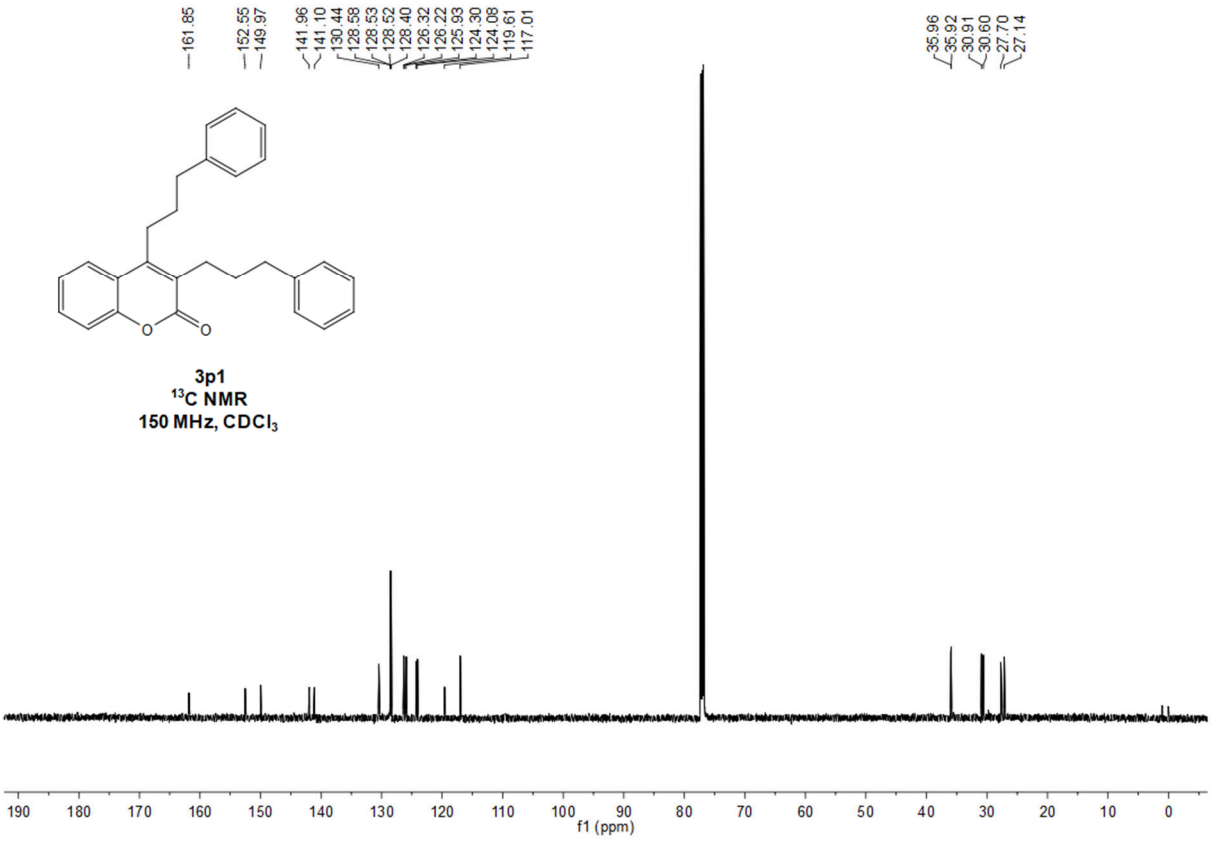
f1 (ppm)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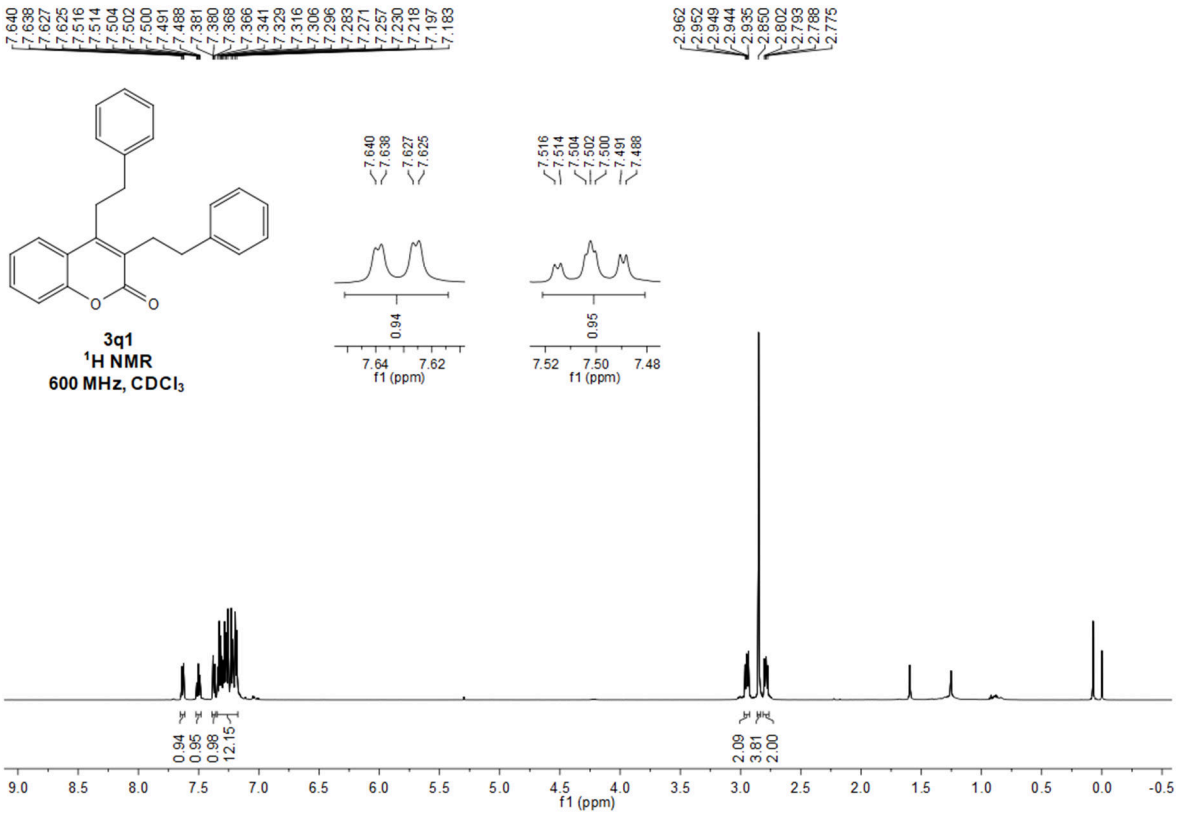
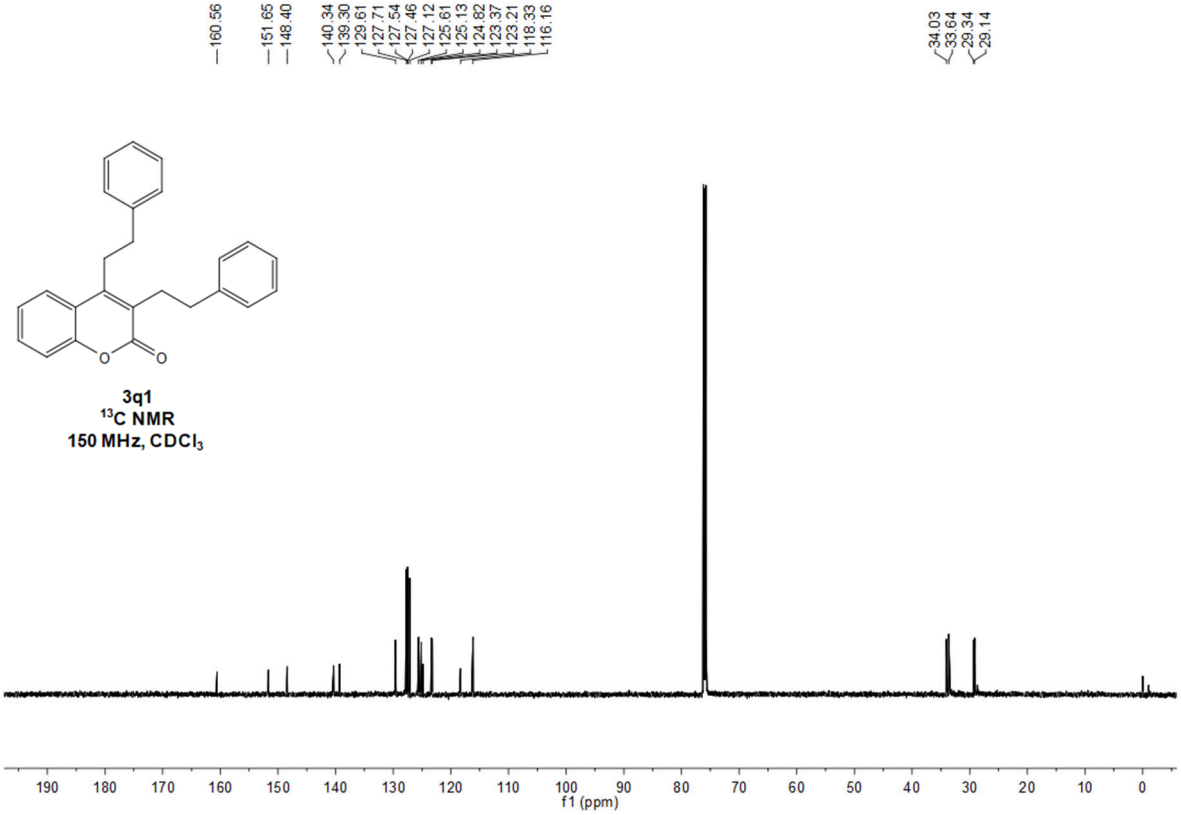
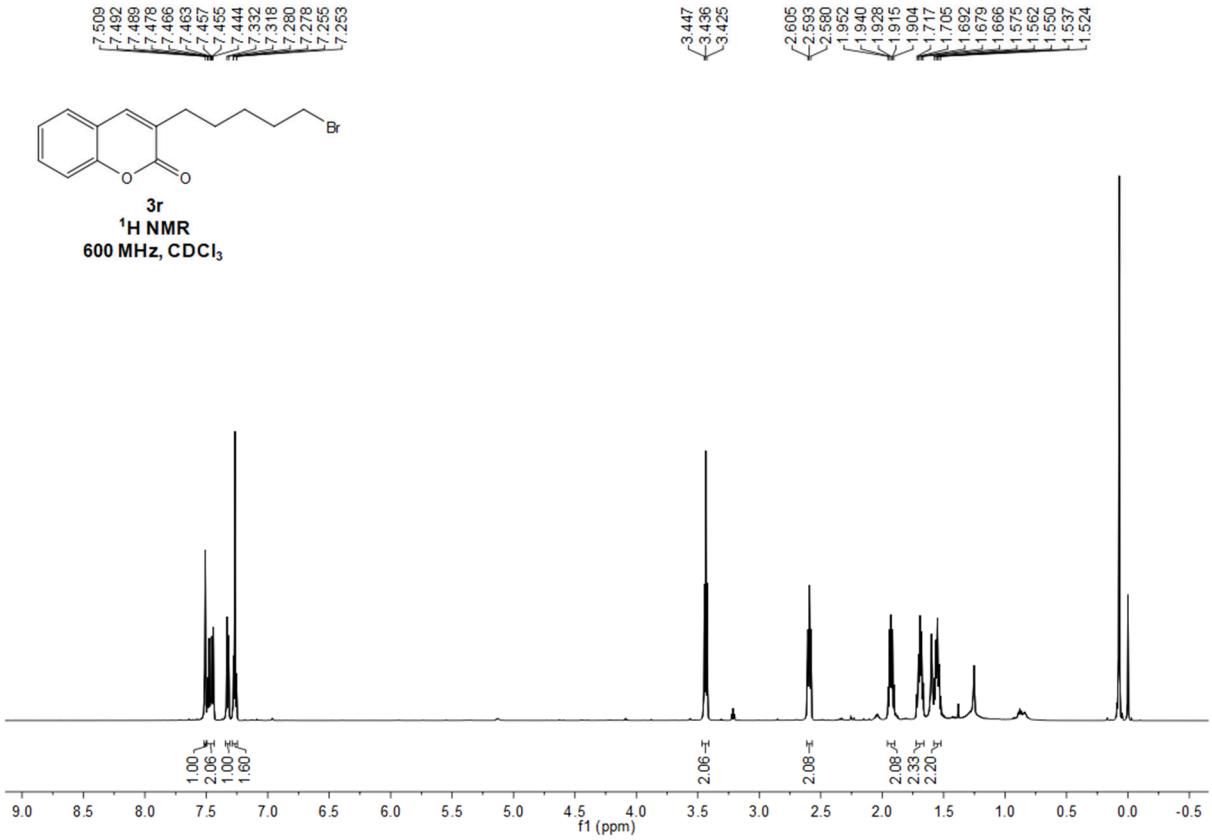
126.22
125.93
124.30
124.08
119.61
117.01
35.96
35.92
30.91
30.60
27.70
27.14
O
O
3p1
13C NMR
150 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



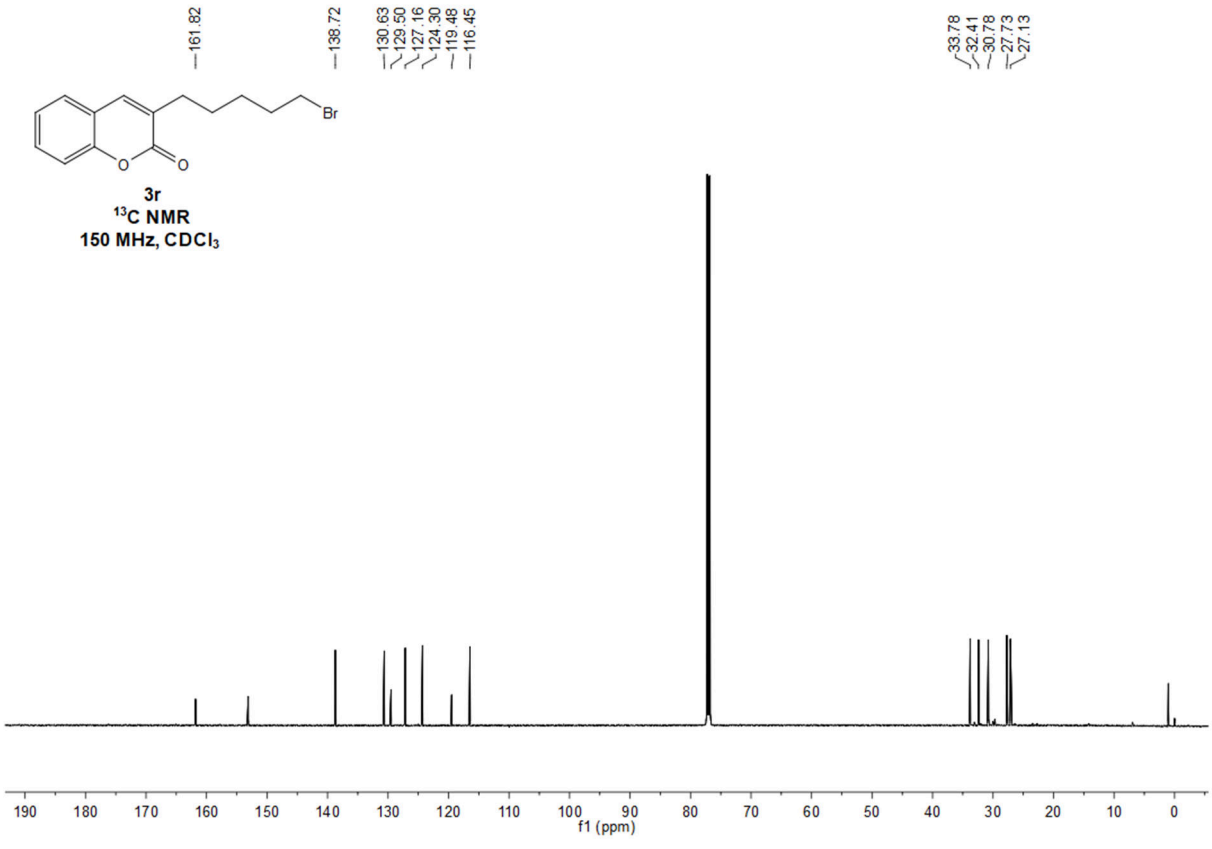
3q1
^{1}H NMR
600 MHz, $CDCl_3$



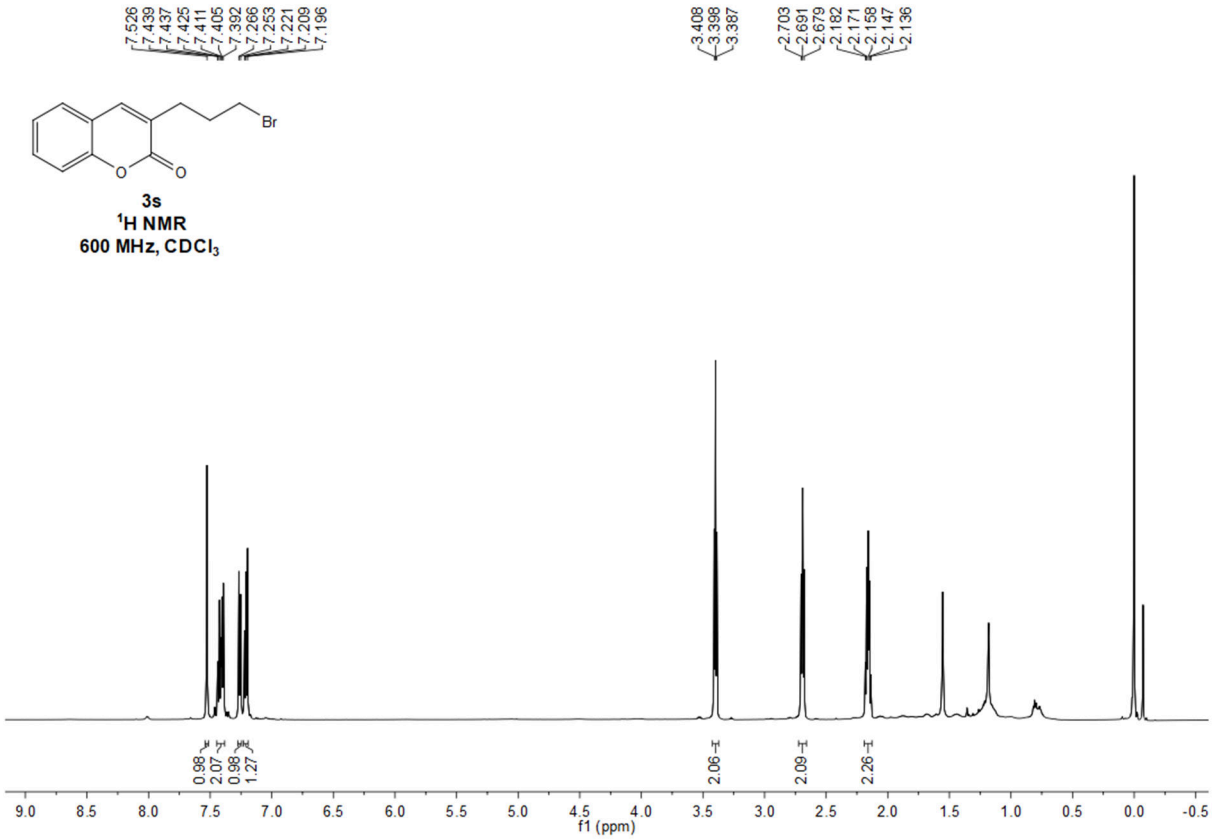
3q1
^{13}C NMR
150 MHz, $CDCl_3$



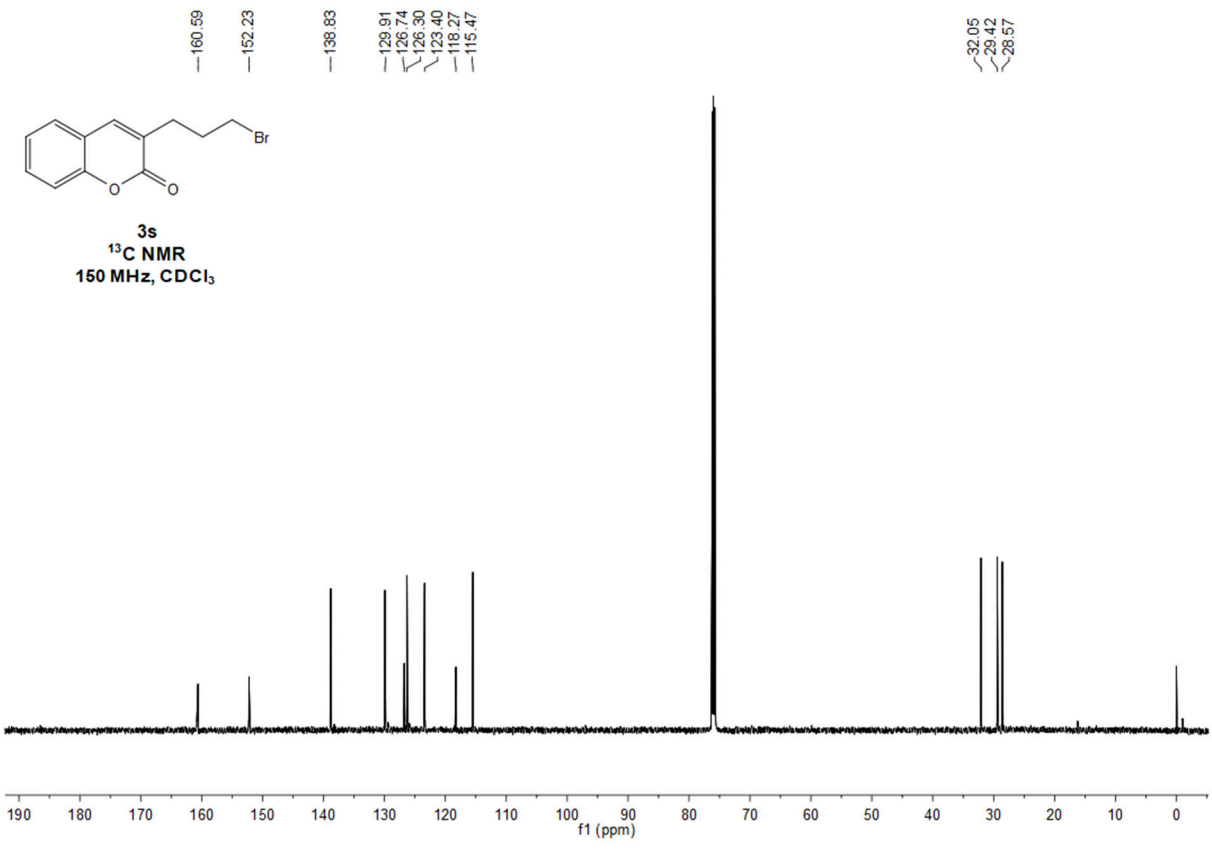
3r
^{1}H NMR
600 MHz, $CDCl_3$



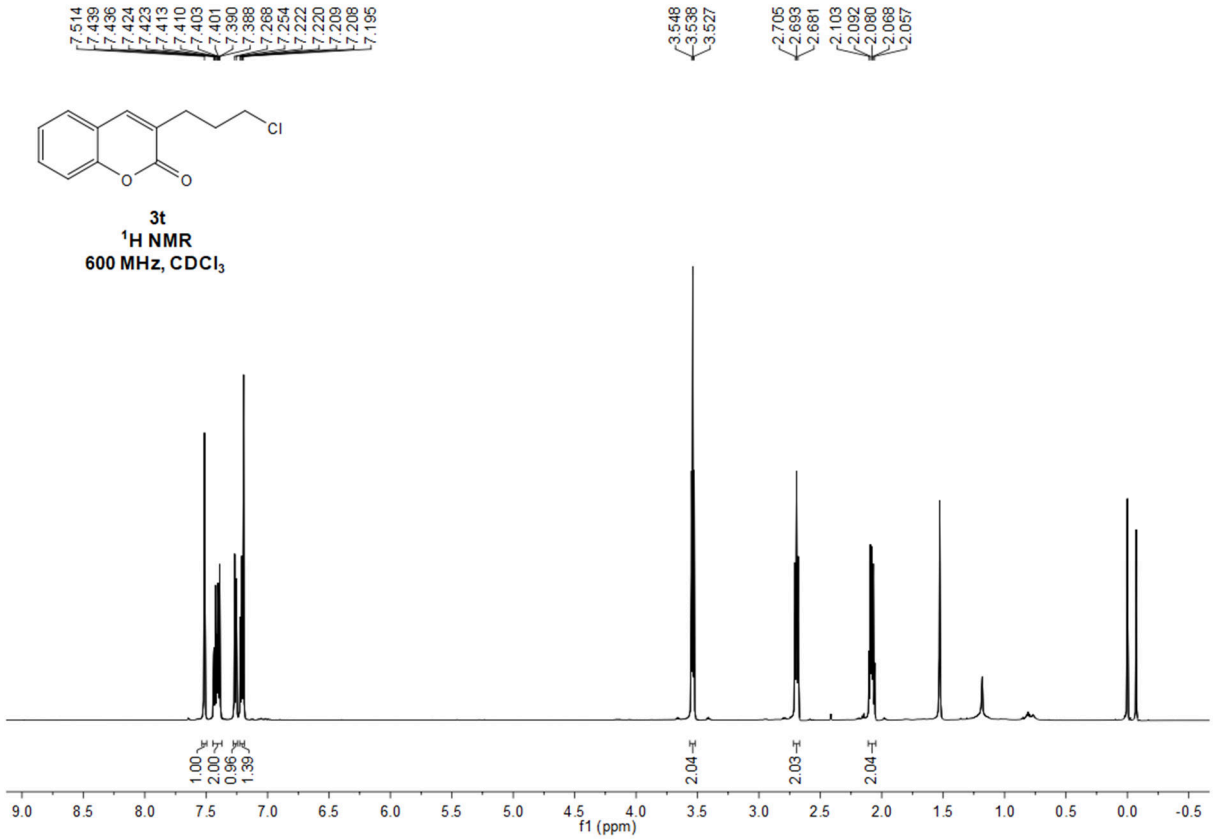
3r
^{13}C NMR
150 MHz, $CDCl_3$



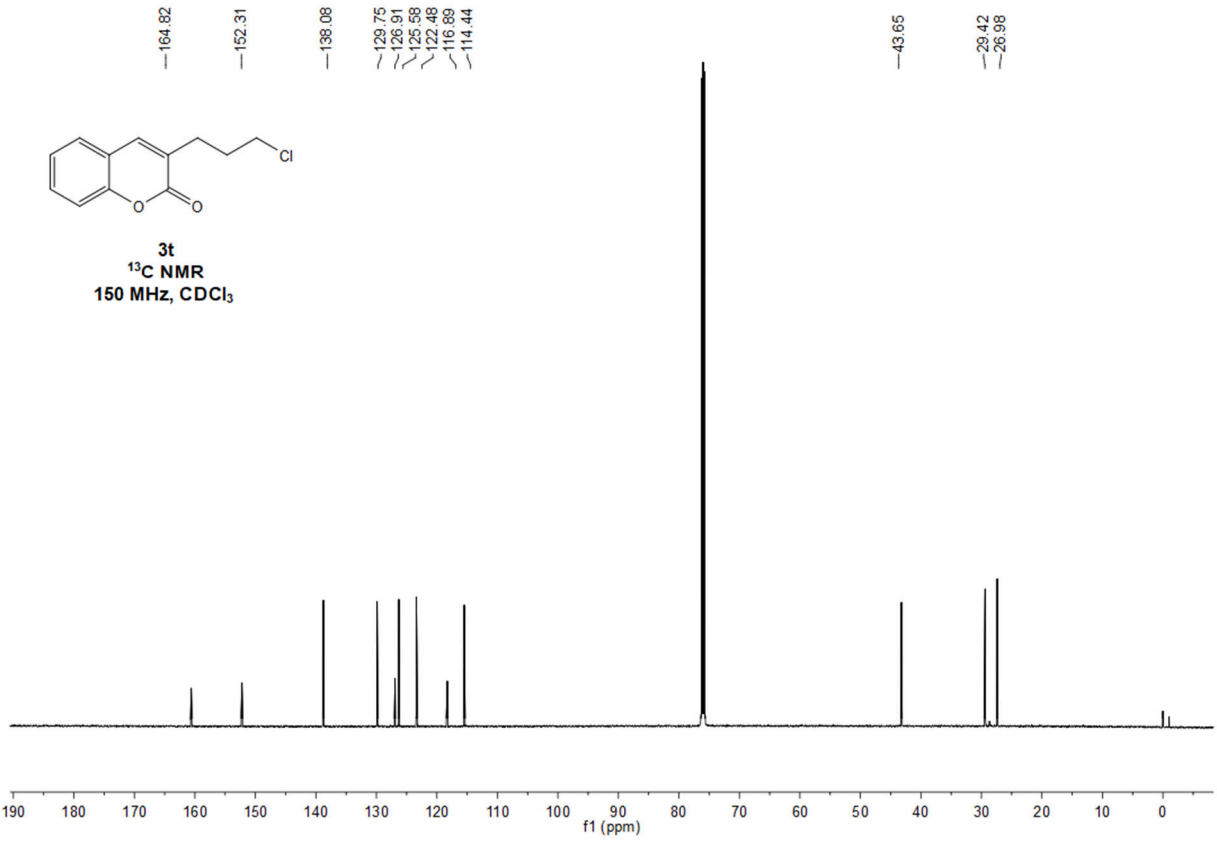
3s
^{1}H NMR
600 MHz, $CDCl_3$



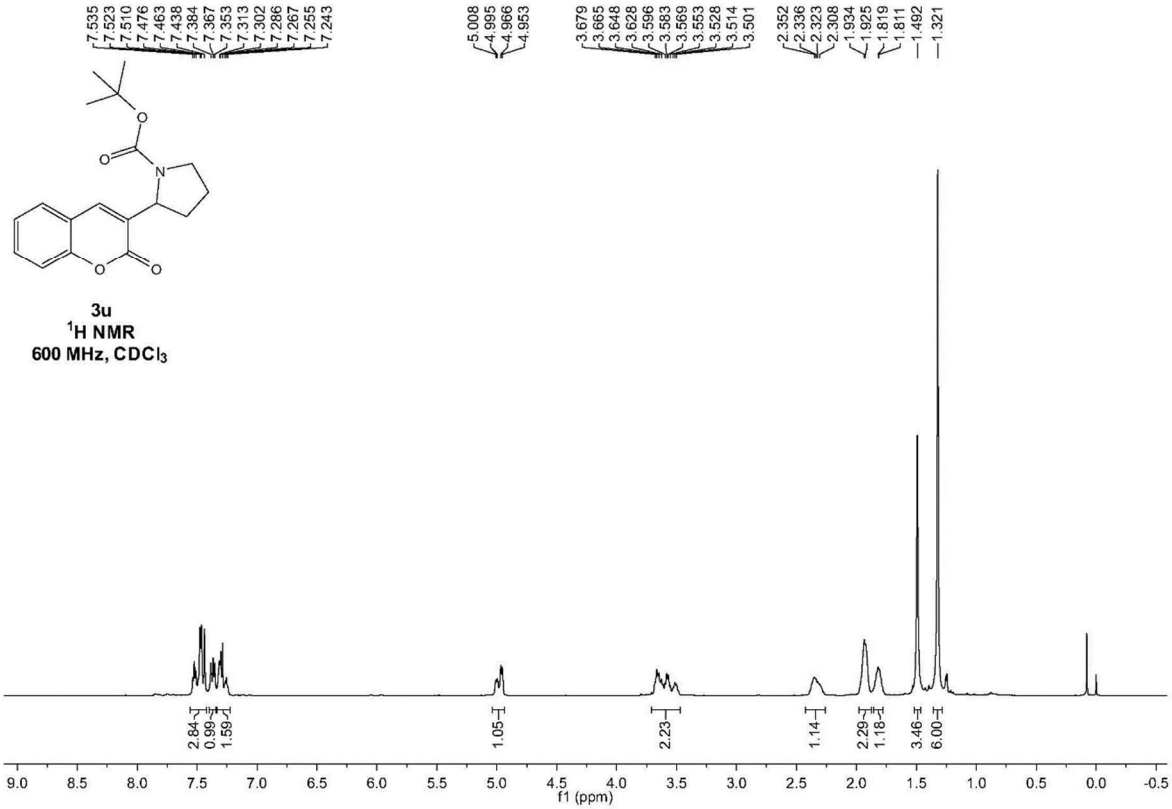
3s
^{13}C NMR
150 MHz, $CDCl_3$



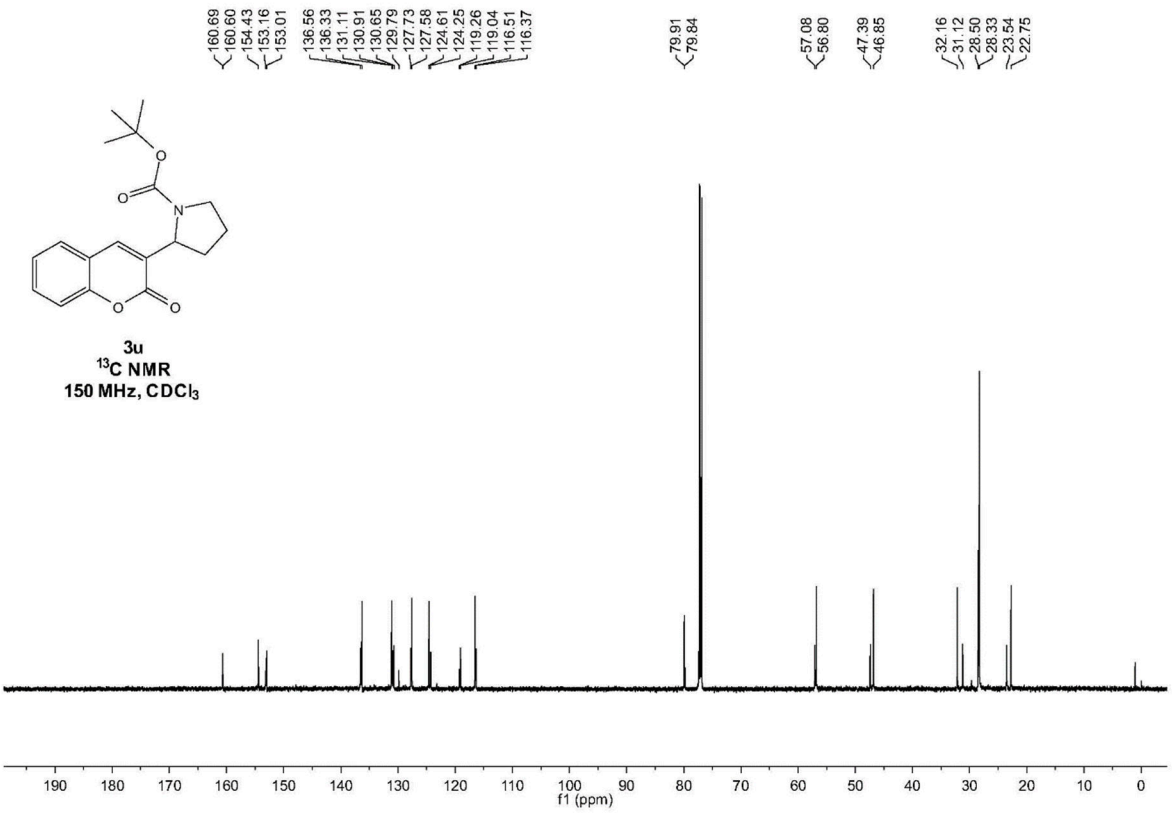
3t
^{1}H NMR
600 MHz, $CDCl_3$



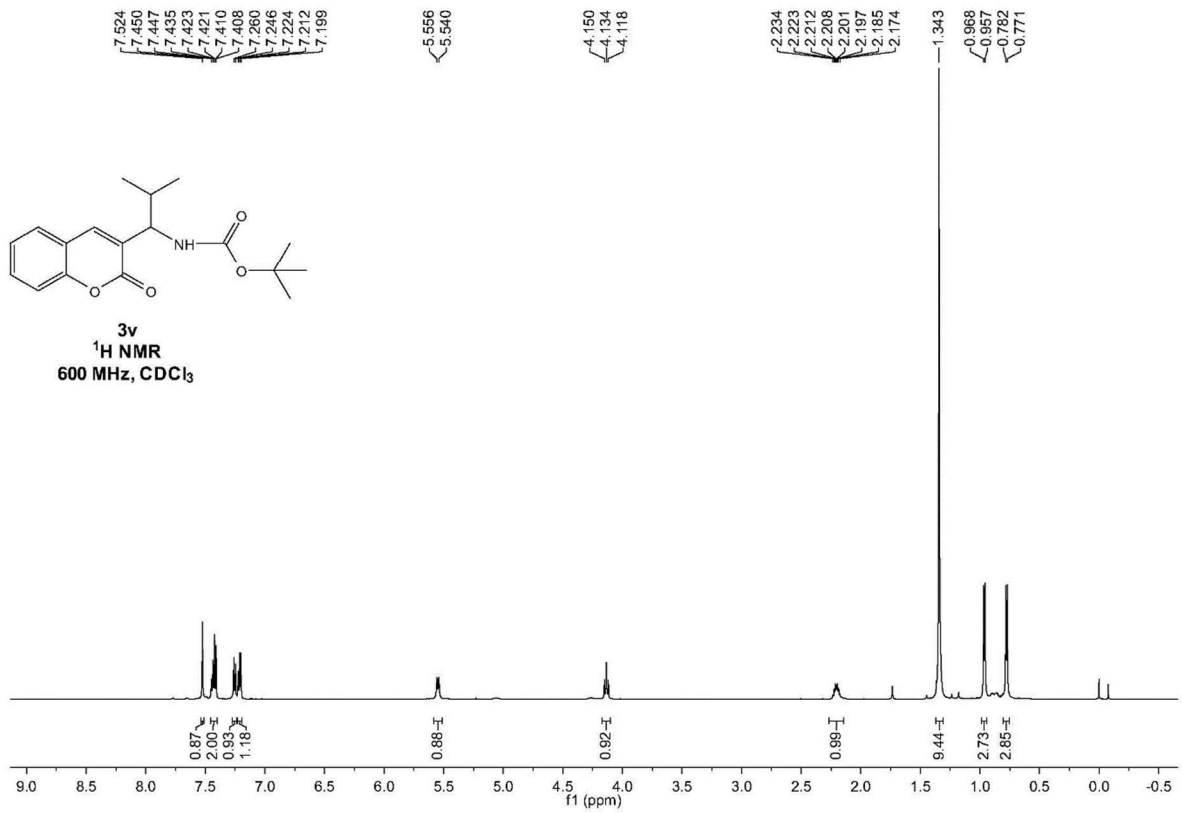
3t
^{13}C NMR
150 MHz, $CDCl_3$

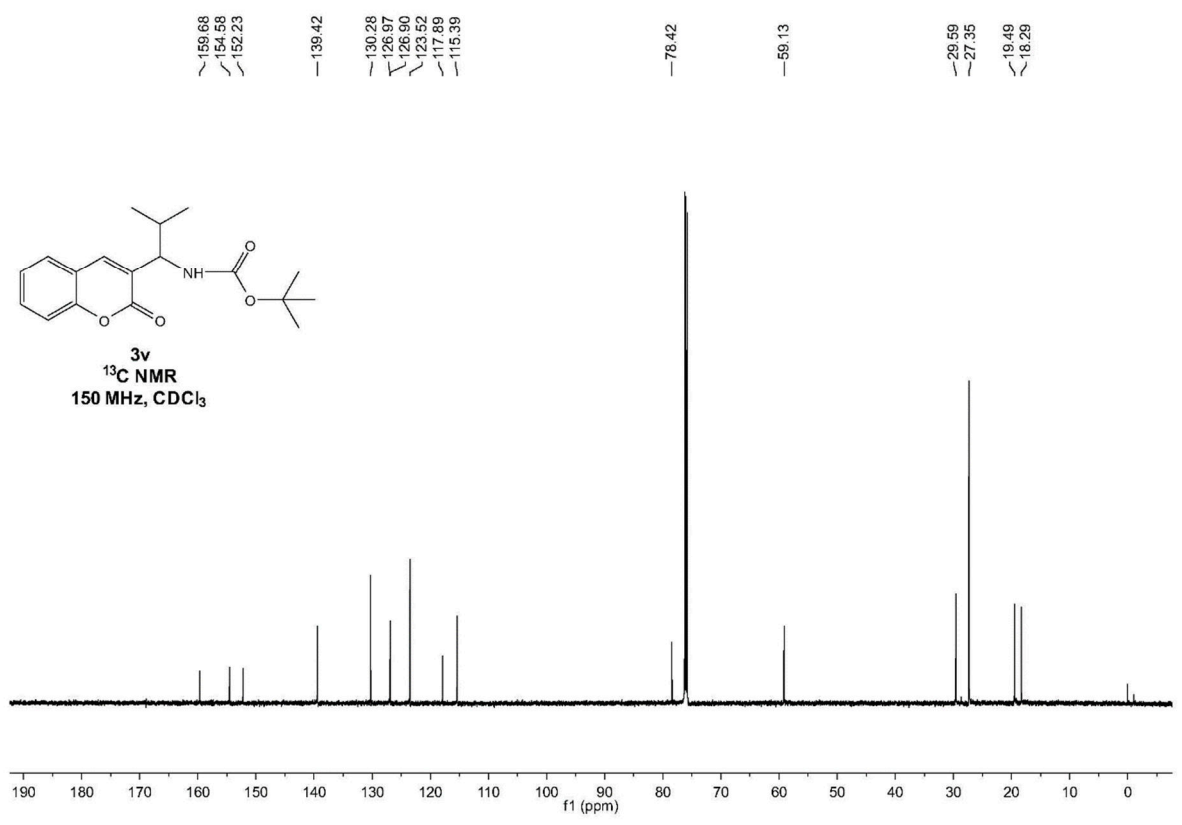


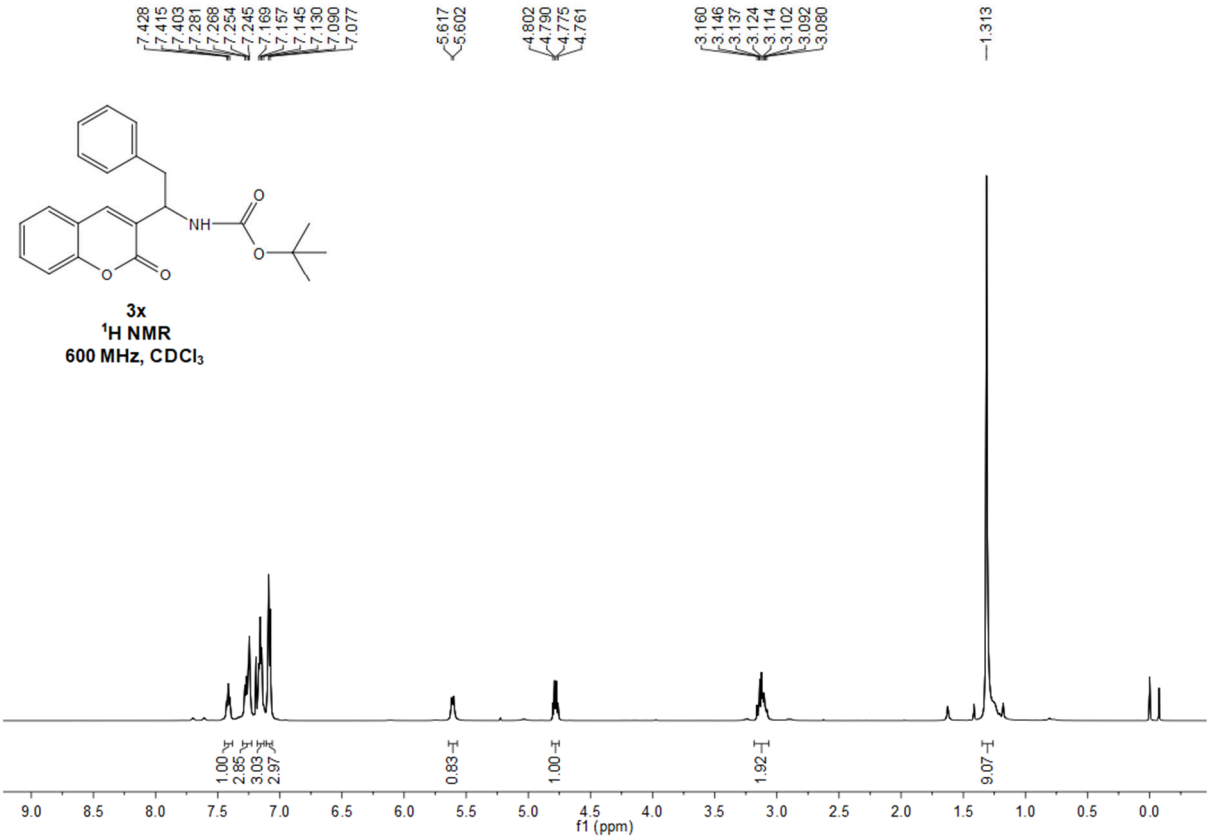
3u
^{1}H NMR
600 MHz, $CDCl_3$



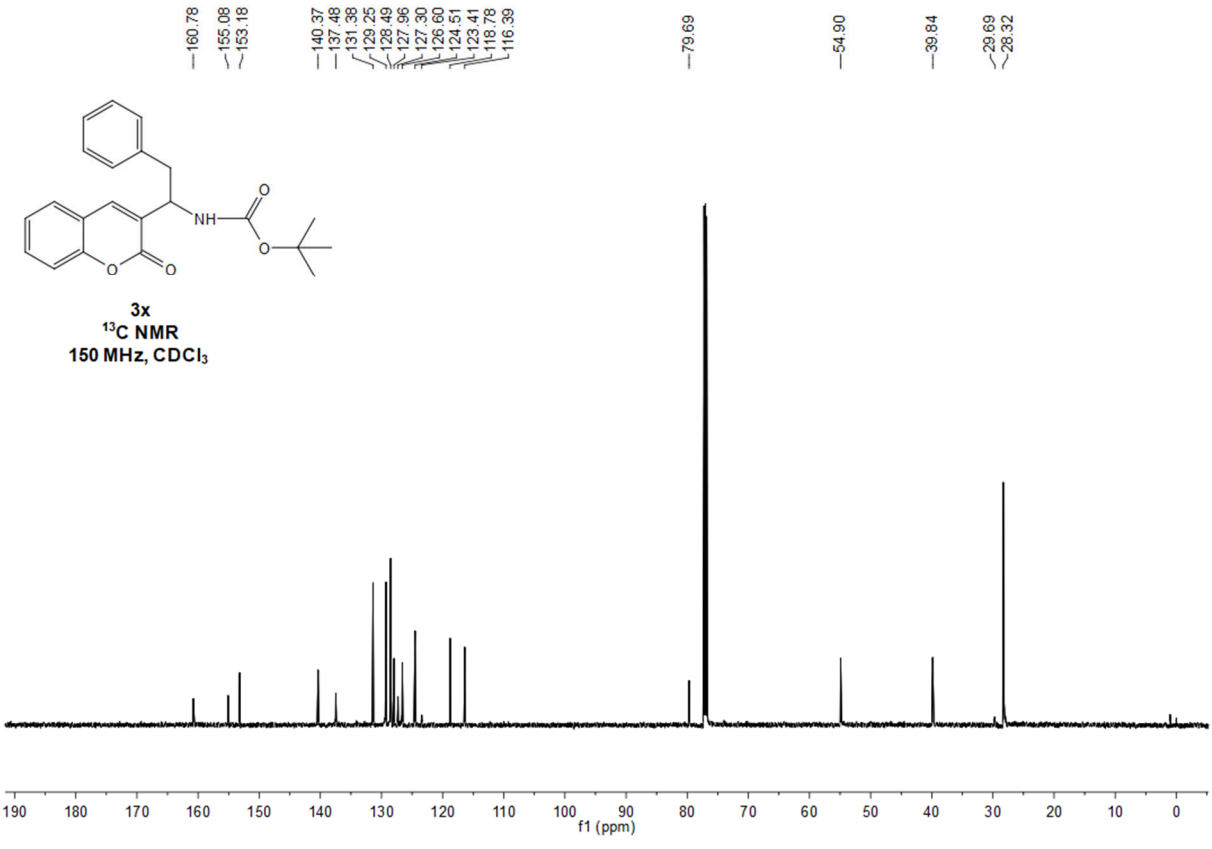
3u
^{13}C NMR
150 MHz, $CDCl_3$


7.524
7.450
7.447
7.435
7.423
7.421
7.410
7.408
7.260
7.246
7.224
7.212
7.199
5.556
5.540
4.150
4.134
4.118
2.234
2.223
2.212
2.208
2.201
2.197
2.185
2.174
1.343
0.968
0.957
0.782
0.771
NH
O
O
O
O
3v
1H NMR
600 MHz, CDCl3
0.87
2.00
0.93
1.18
0.88
0.92
0.99
9.44
2.73
2.85
f1 (ppm)

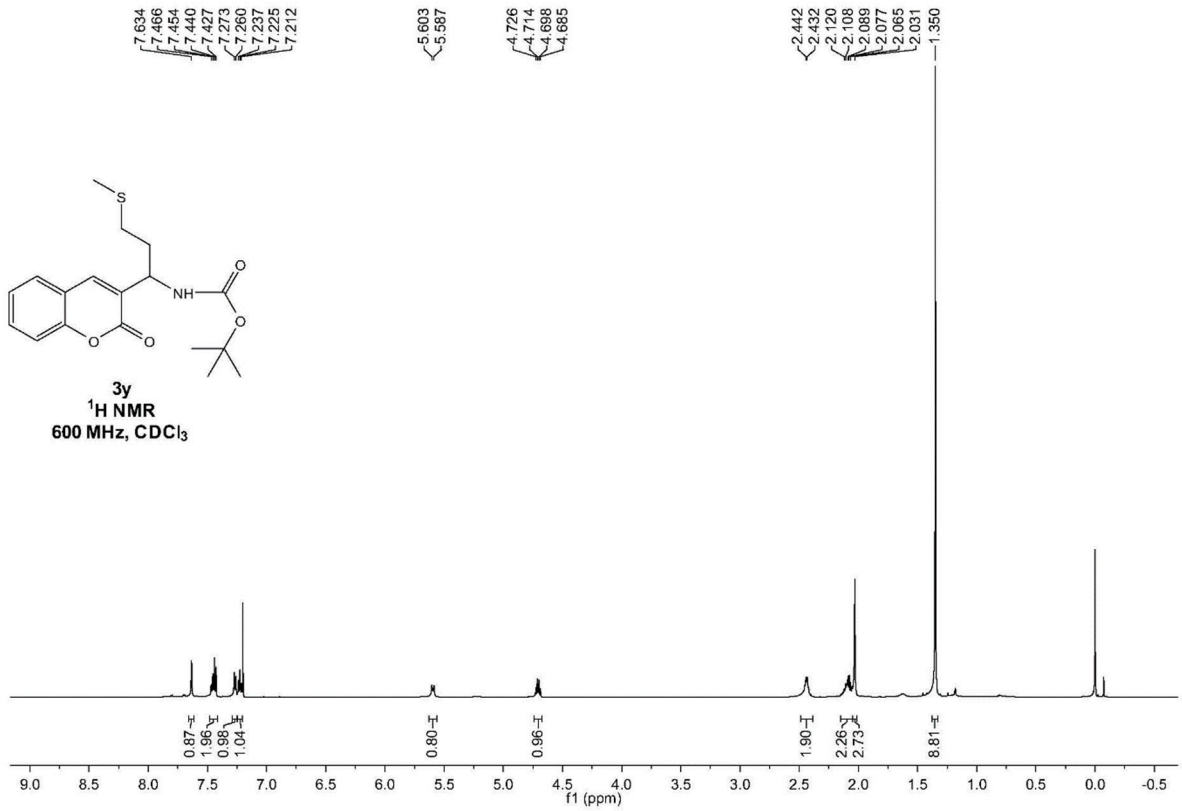

159.68
154.58
152.23
139.42
130.28
126.97
126.90
123.52
117.89
115.39
78.42
59.13
29.59
27.35
19.49
18.29
NH
O
O
O
O
3v
13C NMR
150 MHz, CDCl3
f1 (ppm)



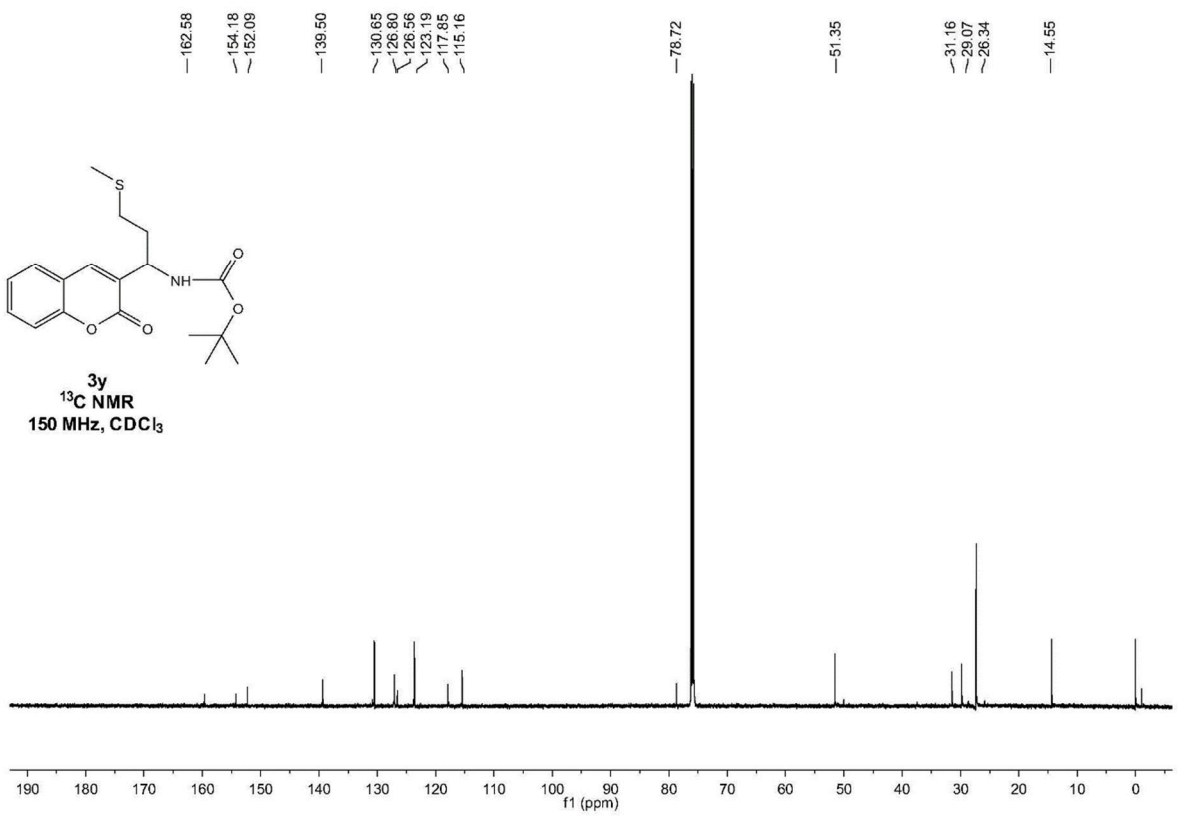
3x
^{1}H NMR
600 MHz, $CDCl_3$



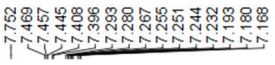
3x
^{13}C NMR
150 MHz, $CDCl_3$

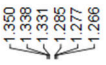


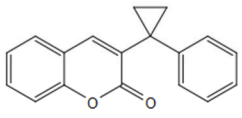
3y
^{1}H NMR
600 MHz, $CDCl_3$



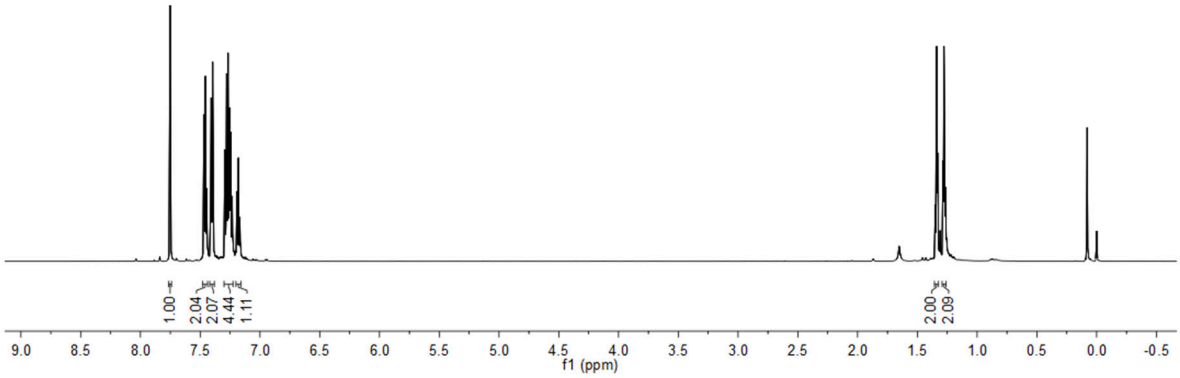
3y
^{13}C NMR
150 MHz, $CDCl_3$

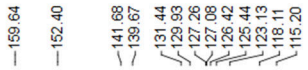


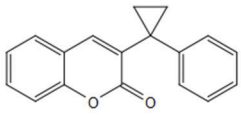




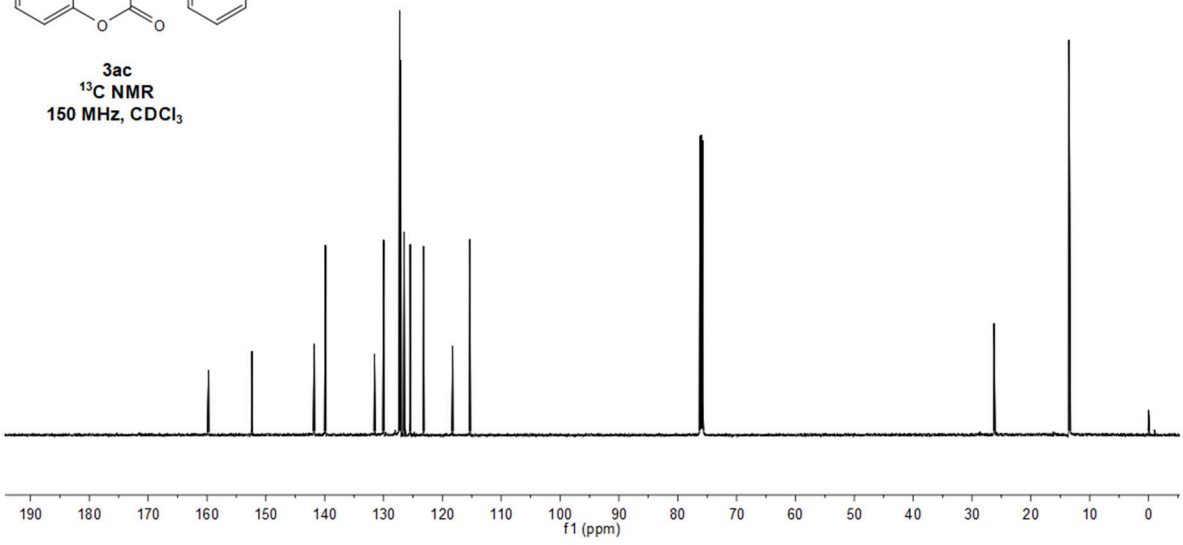
3ac
^{1}H NMR
600 MHz, $CDCl_3$

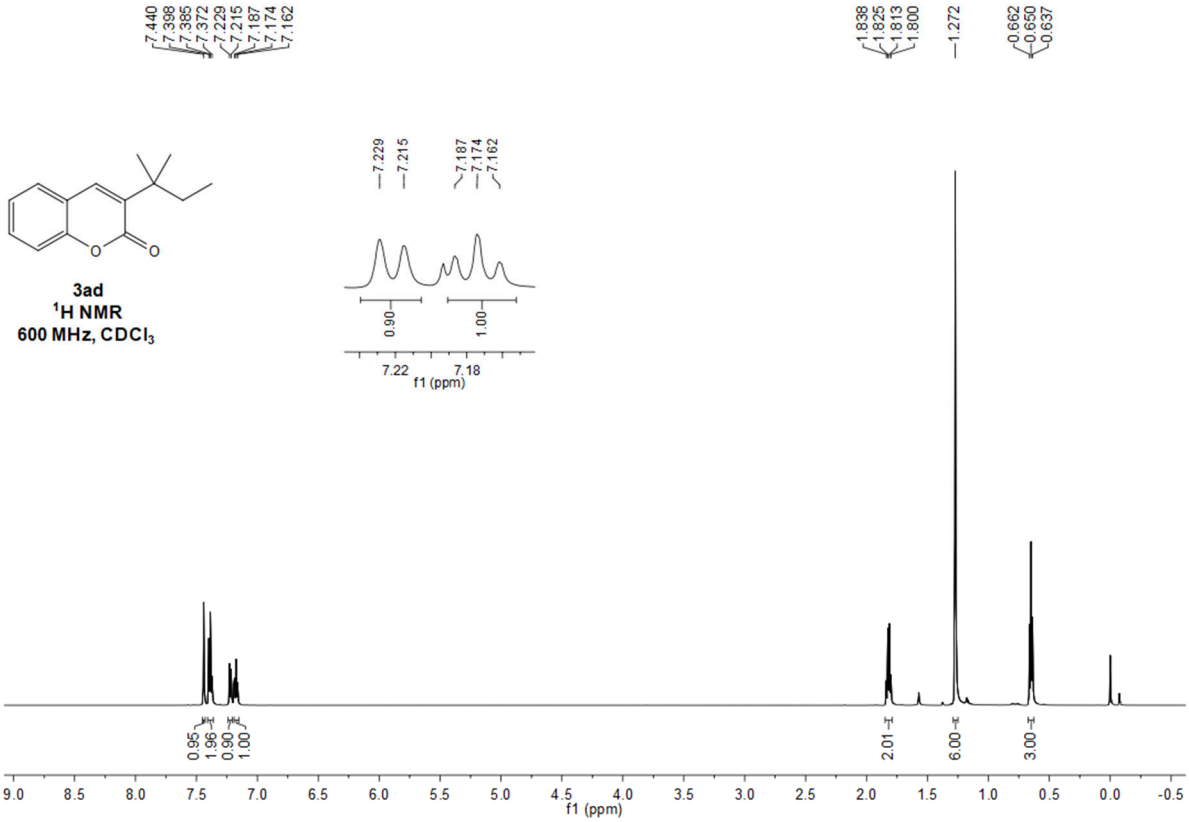


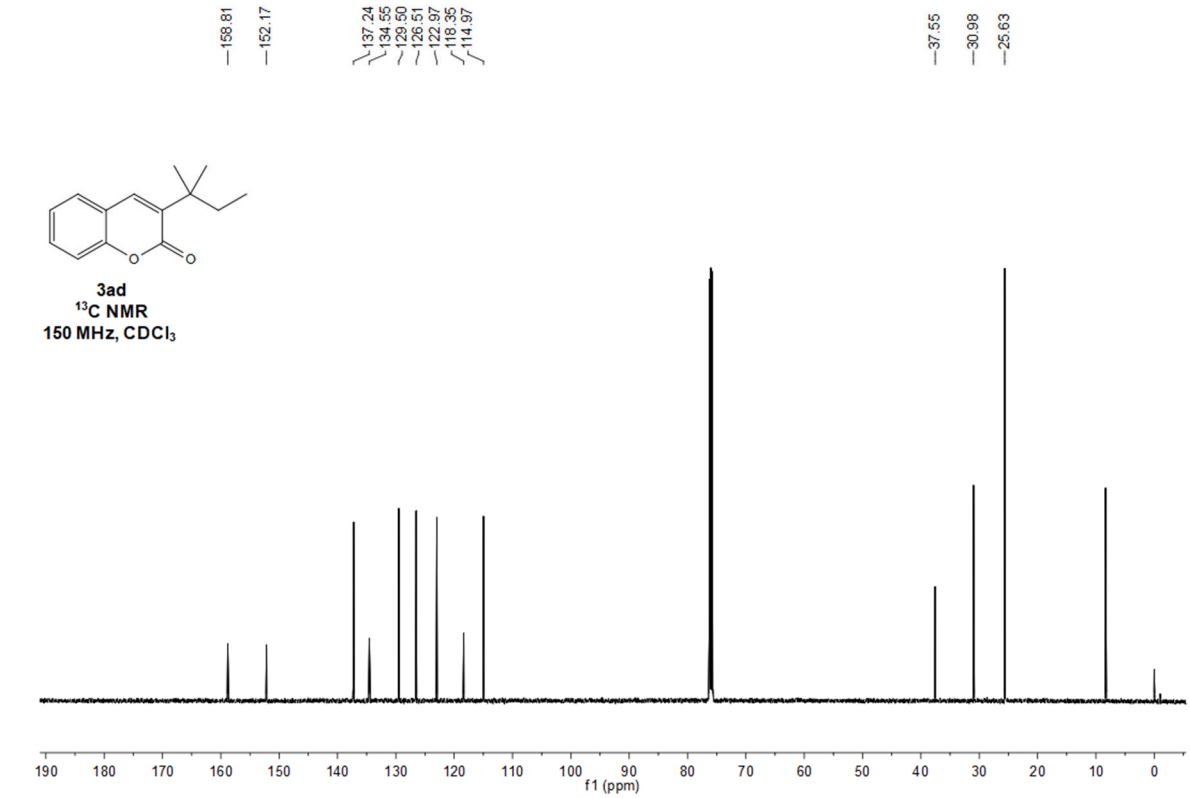


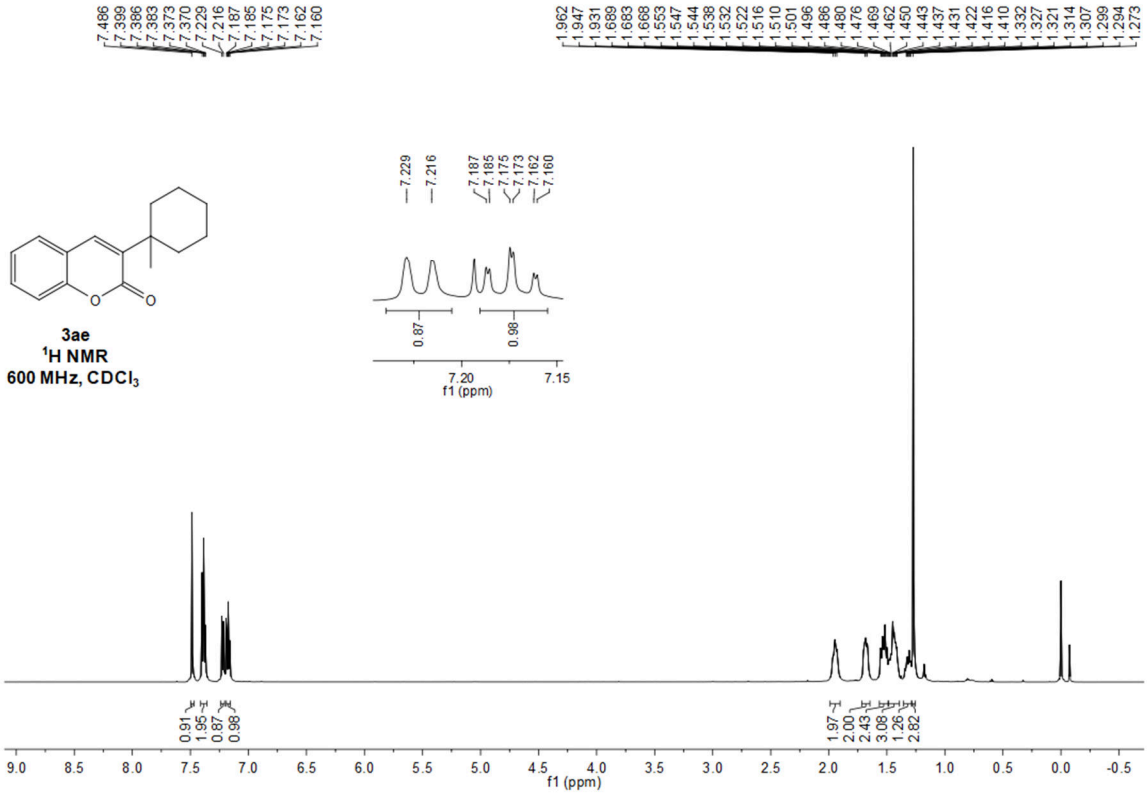


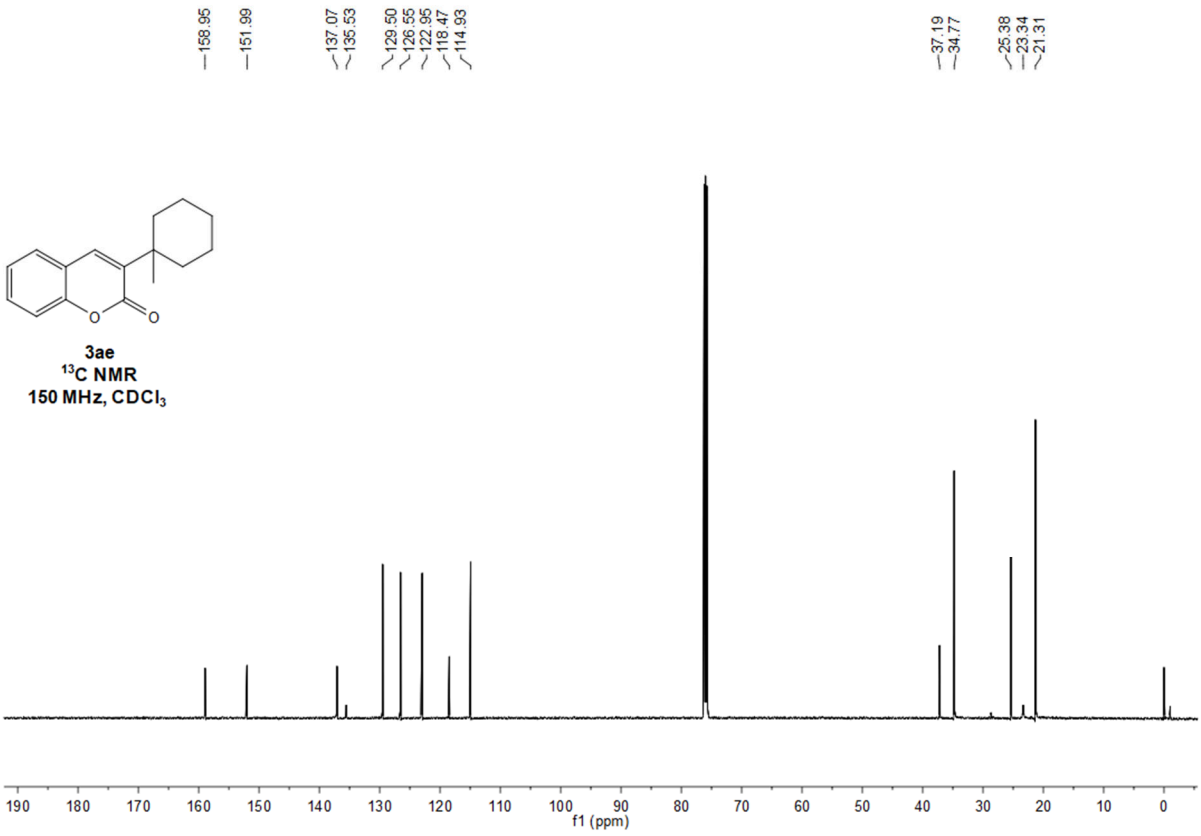
3ac
^{13}C NMR
150 MHz, $CDCl_3$

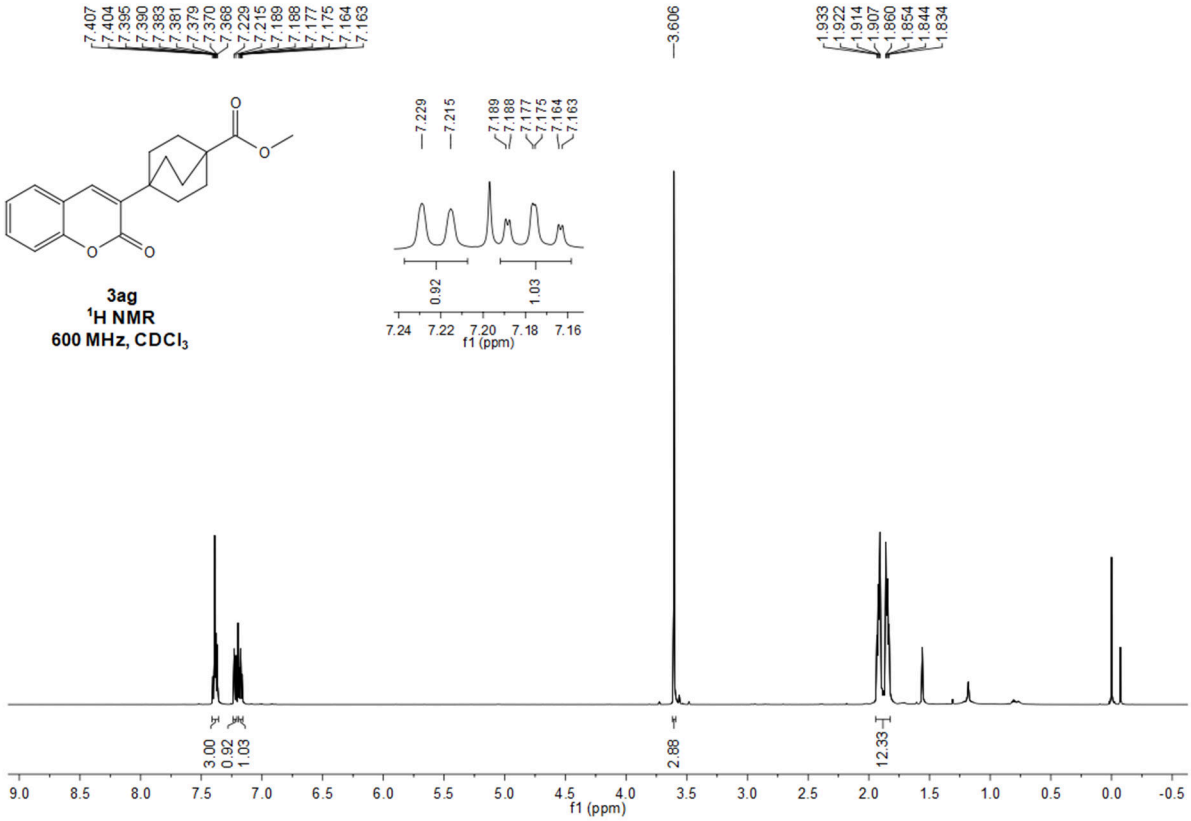


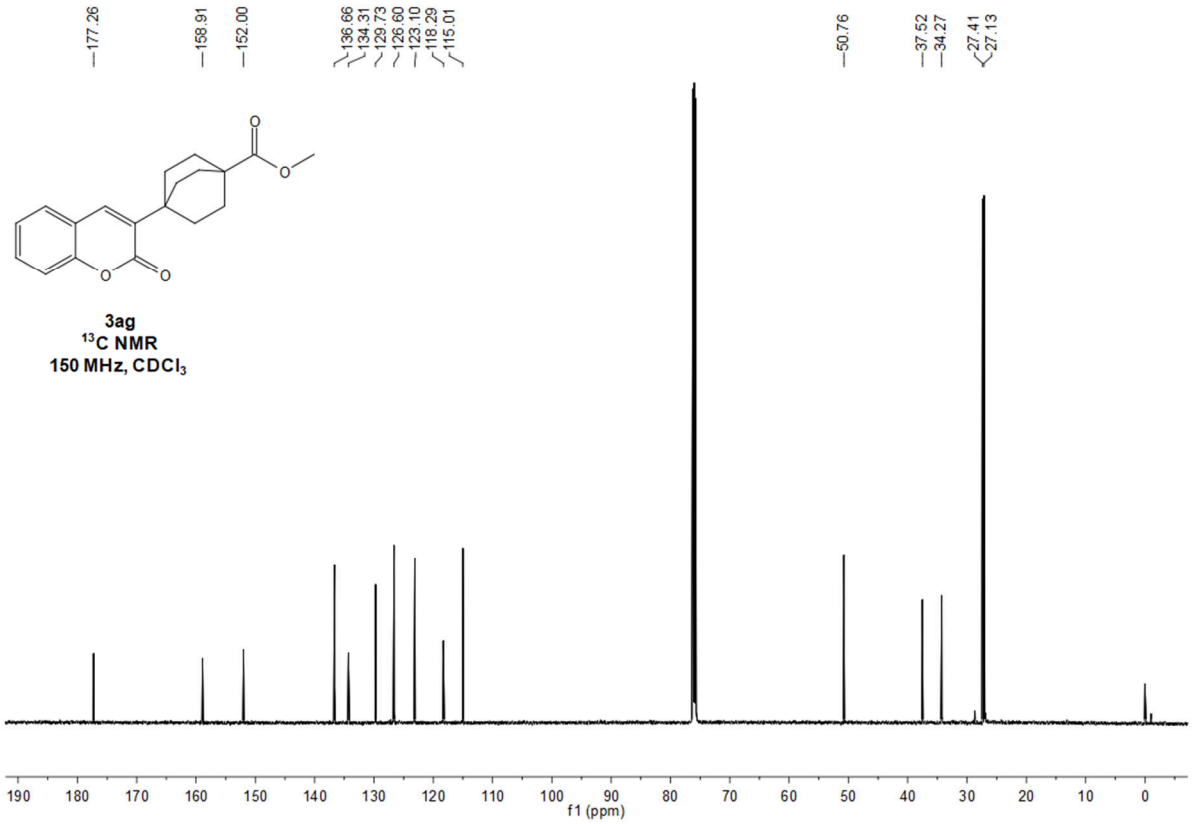

7.440
7.398
7.385
7.372
7.229
7.215
7.187
7.174
7.162
1.838
1.825
1.813
1.800
1.272
0.662
0.650
0.637
3ad
1H NMR
600 MHz, CDCl3
0.90
1.00
7.22
7.18
f1 (ppm)
0.95
1.96
0.90
1.00
2.01
6.00
3.00
f1 (ppm)

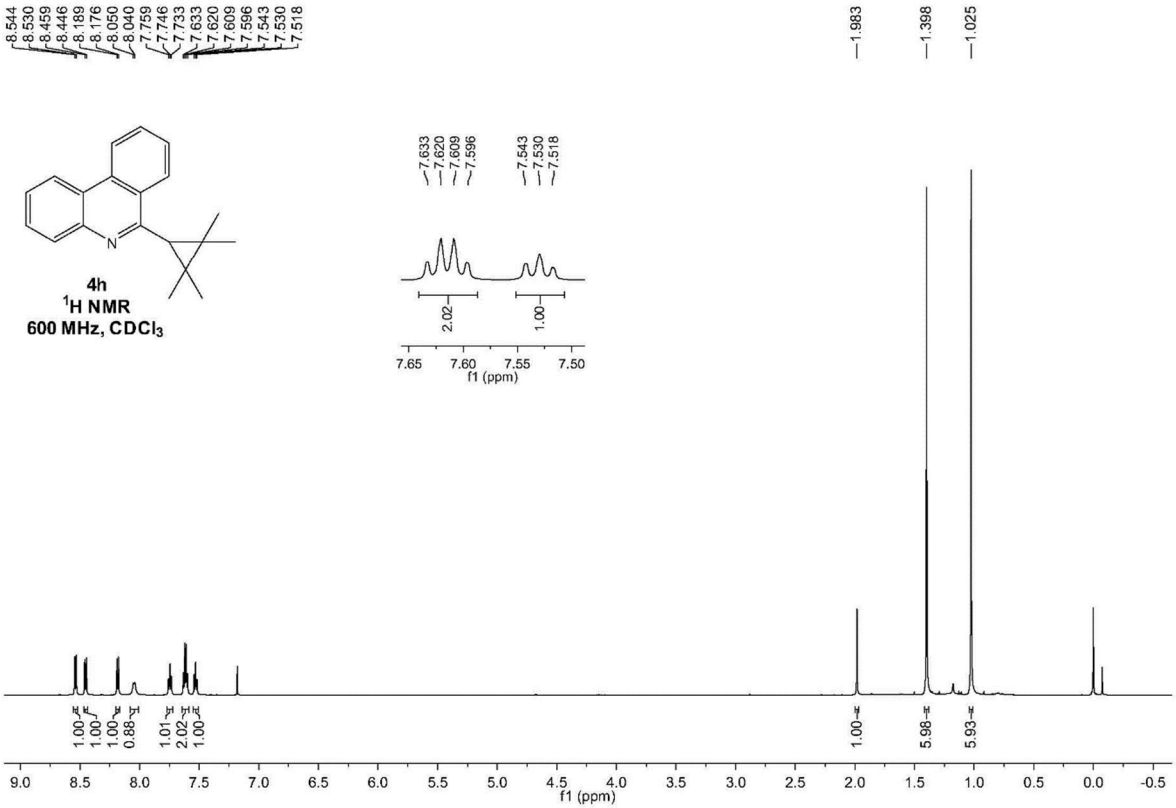

158.81
152.17
137.24
134.55
129.50
126.51
122.97
118.35
114.97
37.55
30.98
25.63
3ad
13C NMR
150 MHz, CDCl3
f1 (ppm)


7.486
7.399
7.386
7.383
7.373
7.370
7.229
7.216
7.187
7.185
7.175
7.173
7.162
7.160
1.962
1.947
1.931
1.689
1.683
1.668
1.553
1.547
1.544
1.538
1.532
1.522
1.516
1.510
1.501
1.496
1.486
1.480
1.476
1.469
1.462
1.450
1.443
1.437
1.431
1.422
1.416
1.410
1.332
1.327
1.321
1.314
1.307
1.299
1.294
1.273
3ae
1H NMR
600 MHz, CDCl3
0.87
0.98
7.20
7.15
f1 (ppm)
0.91
1.95
0.87
0.98
1.97
2.00
2.43
3.08
1.26
2.82
f1 (ppm)


158.95
151.99
137.07
135.53
129.50
126.55
122.95
118.47
114.93
37.19
34.77
25.38
23.34
21.31
3ae
13C NMR
150 MHz, CDCl3
f1 (ppm)


7.407
7.404
7.395
7.390
7.383
7.381
7.379
7.370
7.368
7.229
7.215
7.189
7.188
7.177
7.175
7.164
7.163
3.606
1.933
1.922
1.914
1.907
1.860
1.854
1.844
1.834
3ag
1H NMR
600 MHz, CDCl3
0.92
1.03
f1 (ppm)
3.00
0.92
1.03
2.88
12.33
f1 (ppm)


177.26
158.91
152.00
136.66
134.31
129.73
126.60
123.10
118.29
115.01
50.76
37.52
34.27
27.41
27.13
3ag
13C NMR
150 MHz, CDCl3
f1 (ppm)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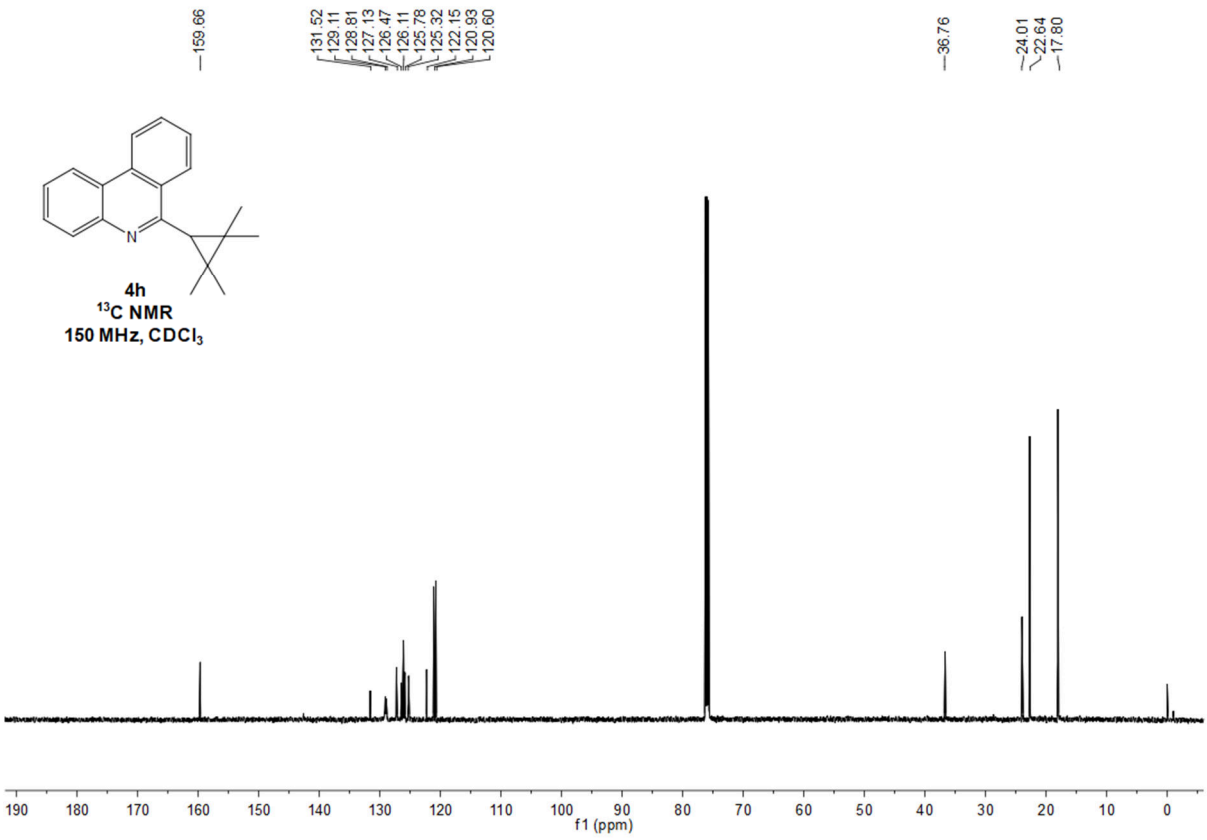
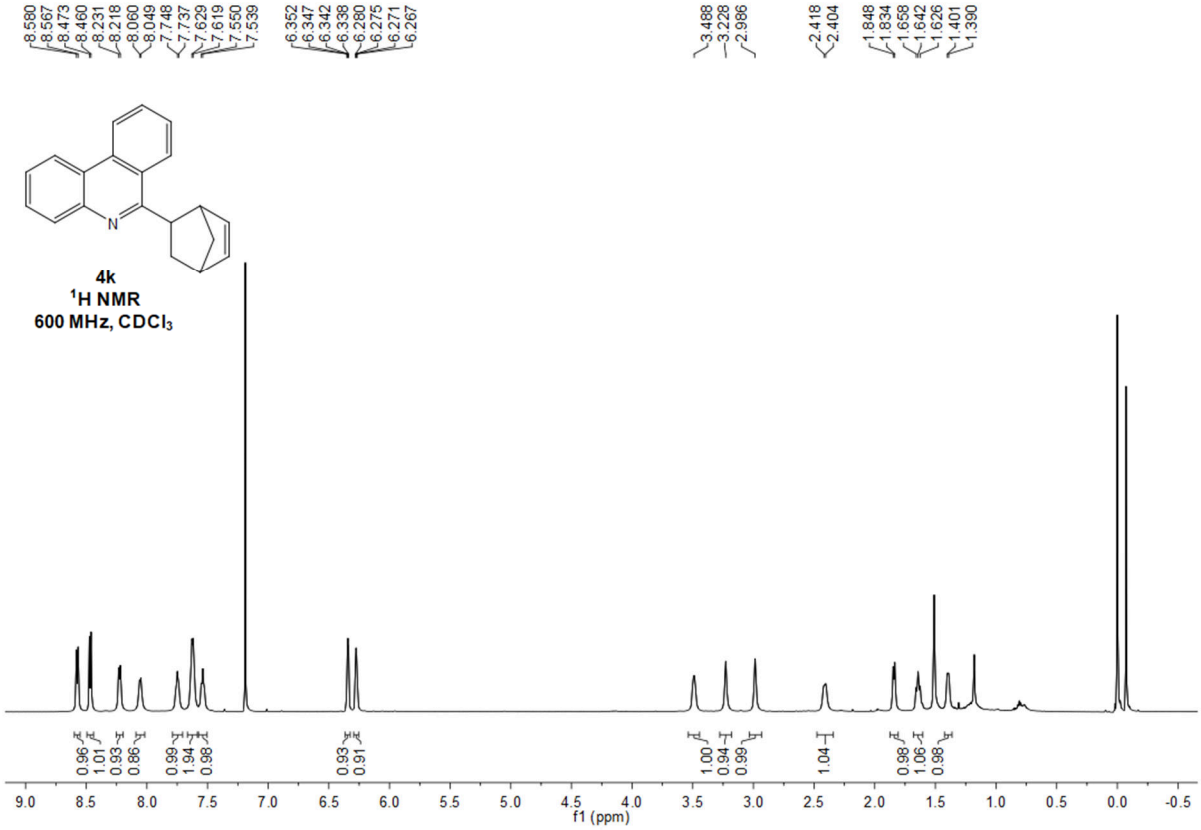
8.530
8.459
8.446
8.189
8.176
8.050
8.040
7.759
7.746
7.733
7.633
7.620
7.609
7.596
7.543
7.530
7.518
1.983
1.398
1.025
4h
1H NMR
600 MHz, CDCl3
7.633
7.620
7.609
7.596
7.543
7.530
7.518
2.02
1.00
7.65
7.60
7.55
7.50
f1 (ppm)
1.00
1.00
1.00
0.88
1.01
2.02
1.00
1.00
5.98
5.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


159.66
131.52
129.11
128.81
127.13
126.47
126.11
125.78
125.32
122.15
120.93
120.60
36.76
24.01
22.64
17.80
4h
13C NMR
150 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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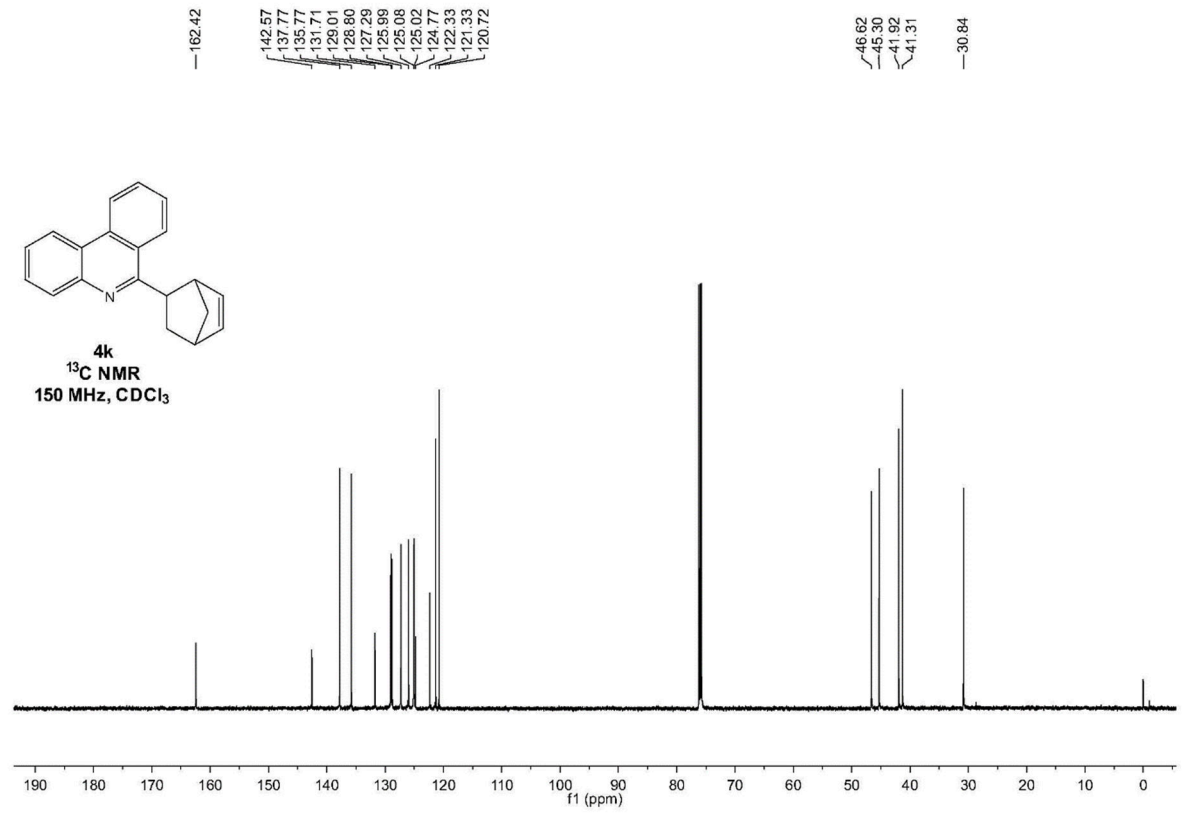
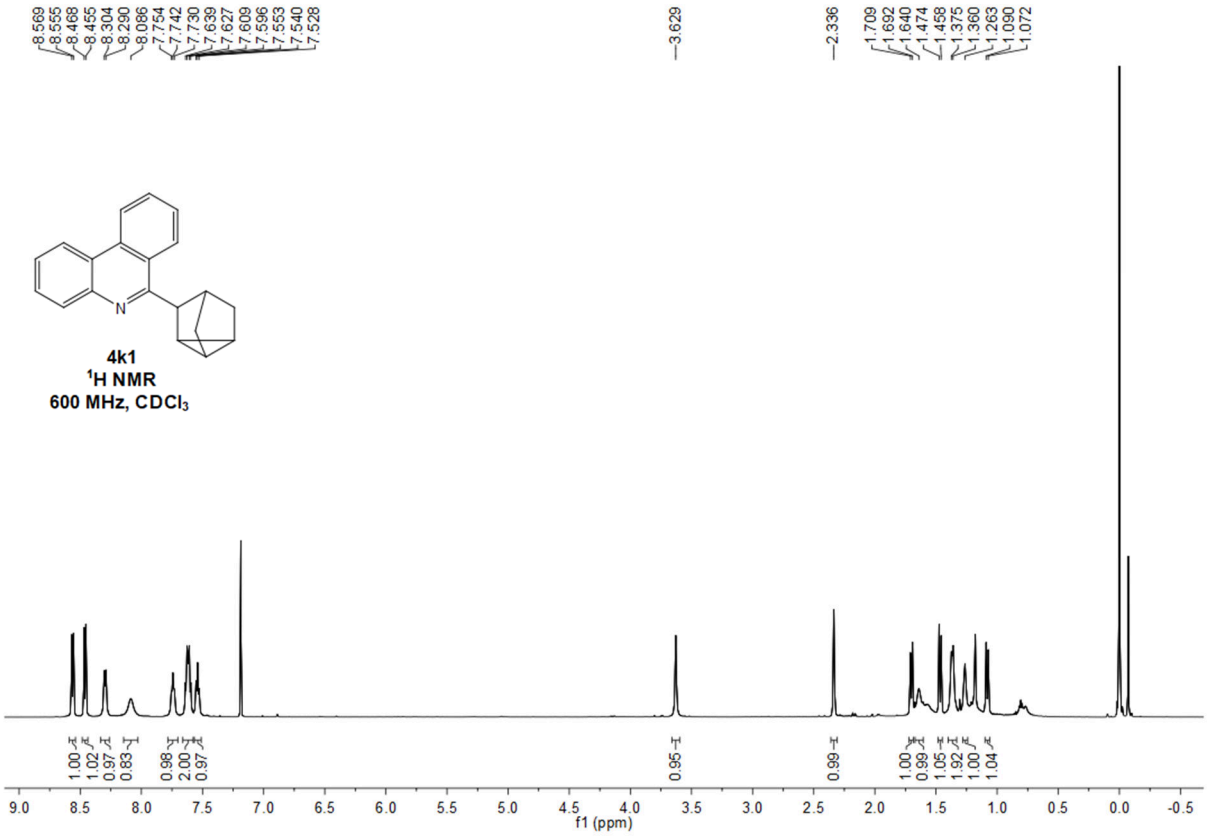
8.473
8.460
8.231
8.218
8.060
8.049
7.748
7.737
7.629
7.619
7.550
7.539
6.352
6.347
6.342
6.338
6.280
6.275
6.271
6.267
3.488
3.228
2.986
2.418
2.404
1.848
1.834
1.658
1.642
1.626
1.401
1.390
N
4k
1H NMR
600 MHz, CDCl3
0.96
1.01
0.93
0.86
0.99
1.94
0.98
0.93
0.91
1.00
0.94
0.99
1.04
0.98
1.06
0.98
f1 (ppm)


162.42
142.57
137.77
135.77
131.71
129.01
128.80
127.29
125.99
125.08
125.02
124.77
122.33
121.33
120.72
46.62
45.30
41.92
41.31
30.84
N
4k
13C NMR
150 MHz, CDCl3
f1 (ppm)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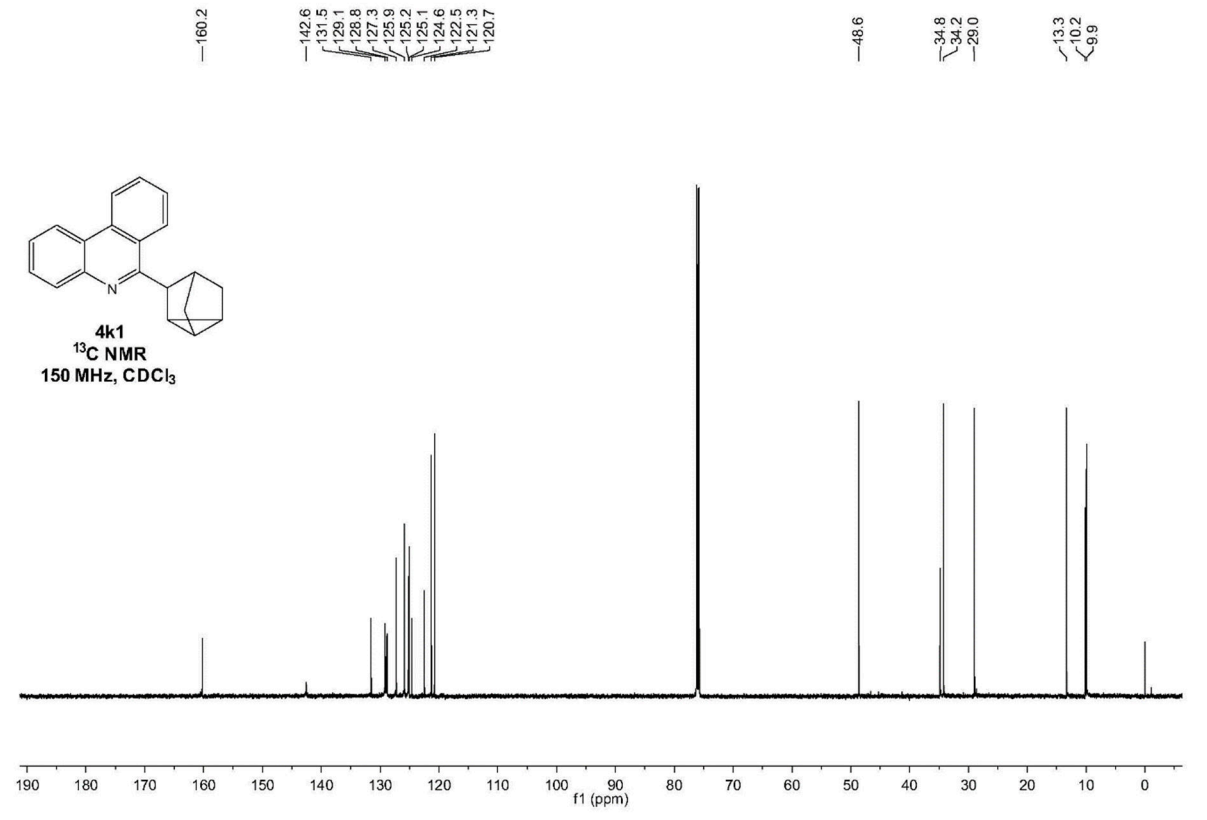
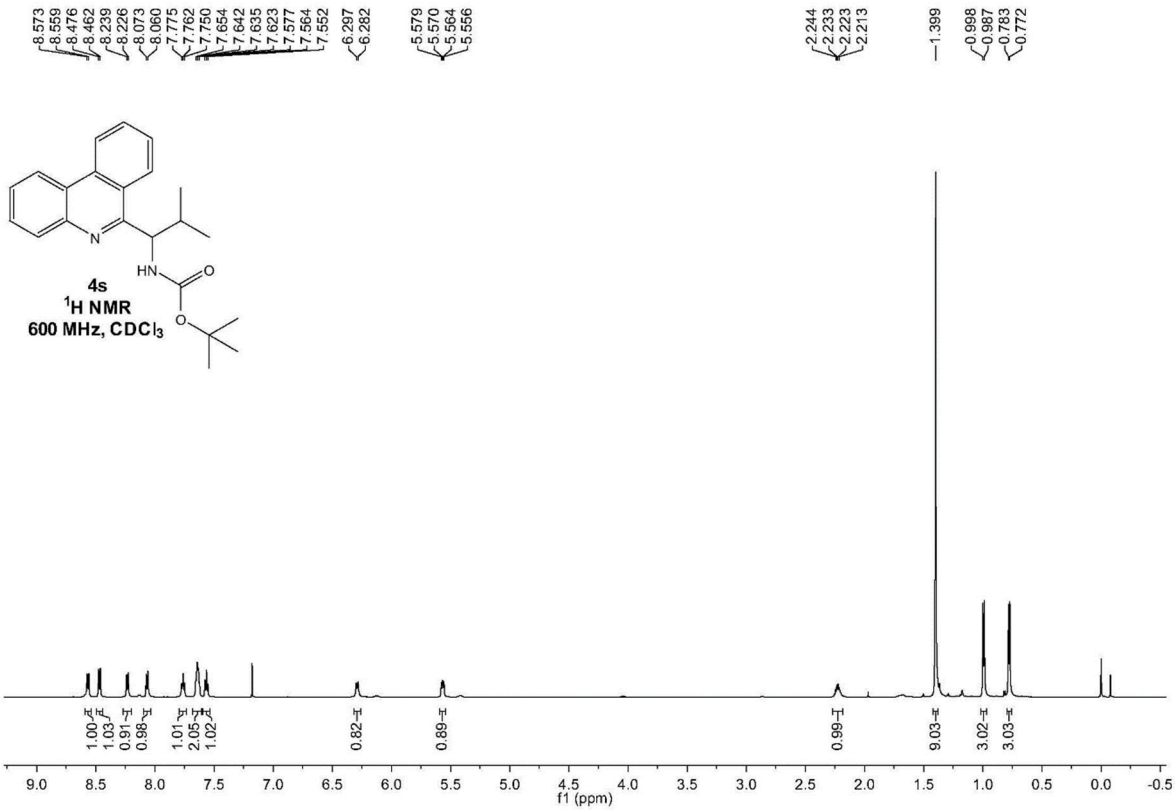
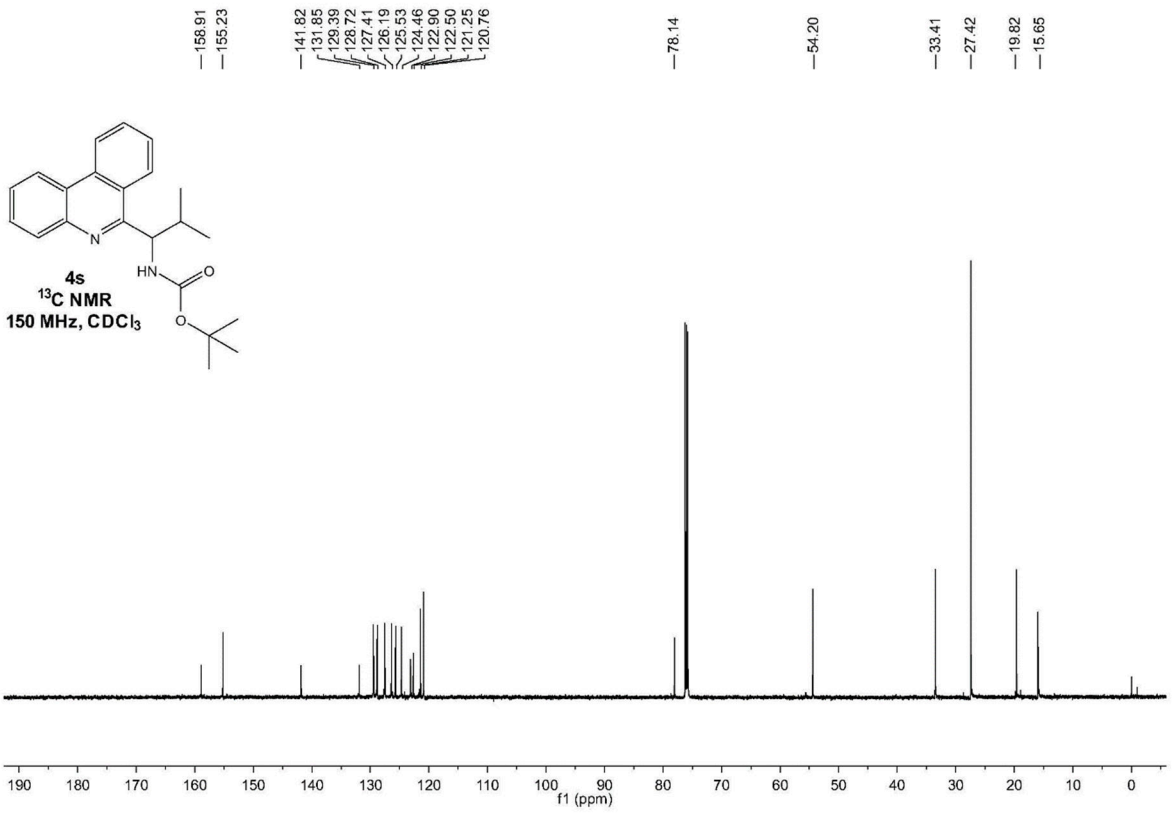
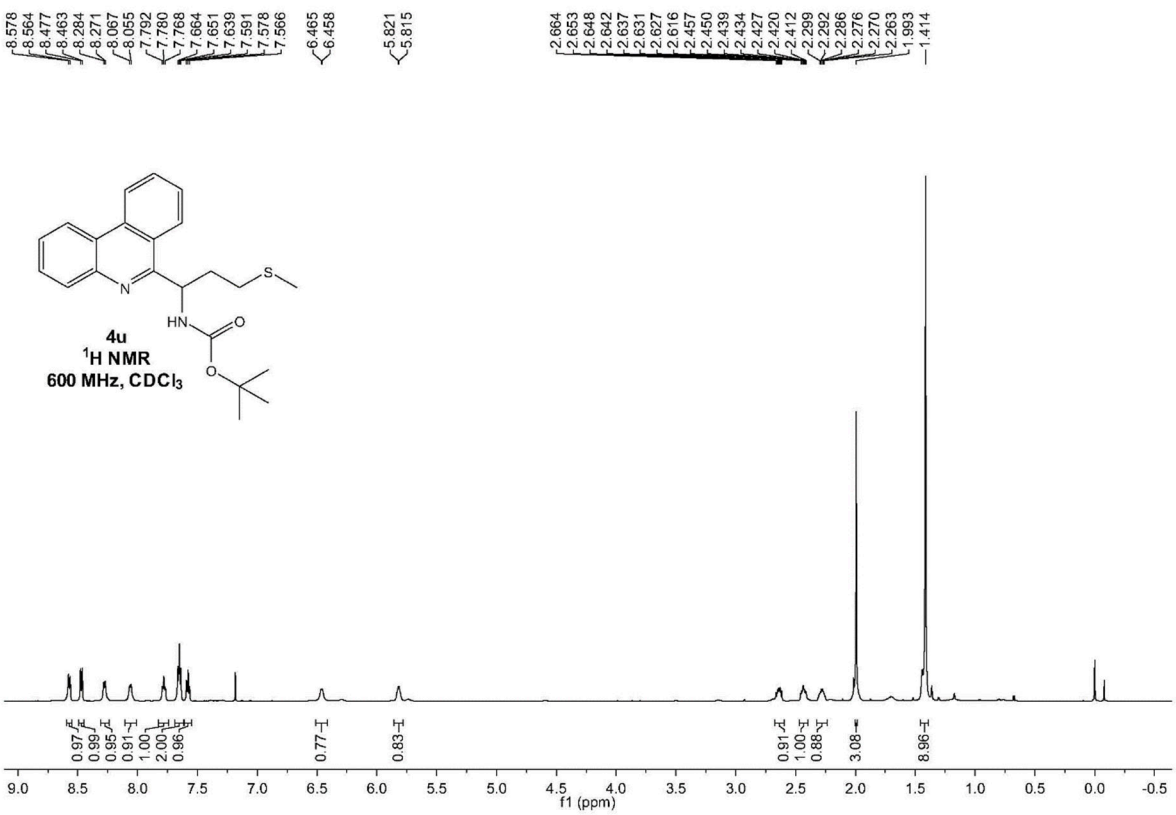
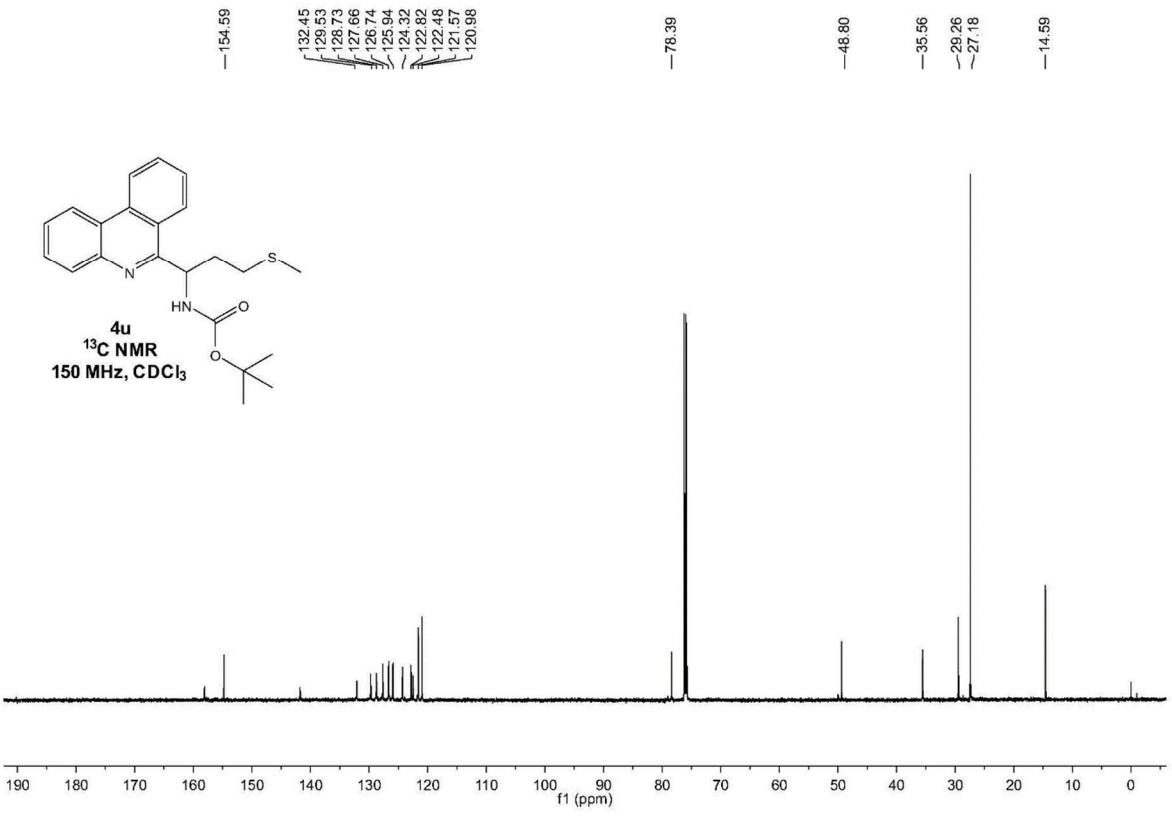
8.555
8.468
8.455
8.304
8.290
8.086
7.754
7.742
7.730
7.639
7.627
7.609
7.596
7.553
7.540
7.528
3.629
2.336
1.709
1.692
1.640
1.474
1.458
1.375
1.360
1.263
1.090
1.072
N
4k1
1H NMR
600 MHz, CDCl3
1.00
1.02
0.97
0.83
0.98
2.00
0.97
0.95
0.99
1.00
0.99
1.05
1.92
1.00
1.04
f1 (ppm)

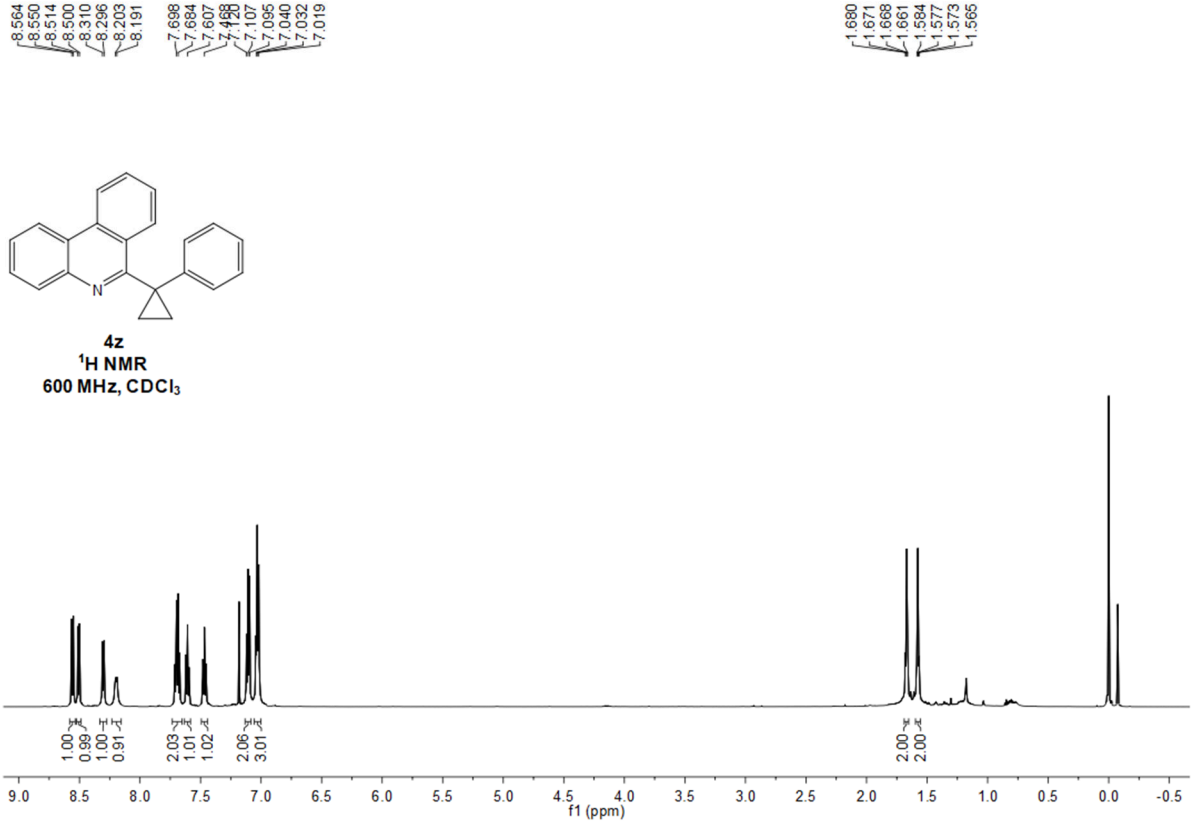

160.2
142.6
131.5
129.1
128.8
127.3
125.9
125.2
125.1
124.6
122.5
121.3
120.7
48.6
34.8
34.2
29.0
13.3
10.2
9.9
N
4k1
13C NMR
150 MHz, CDCl3
f1 (ppm)

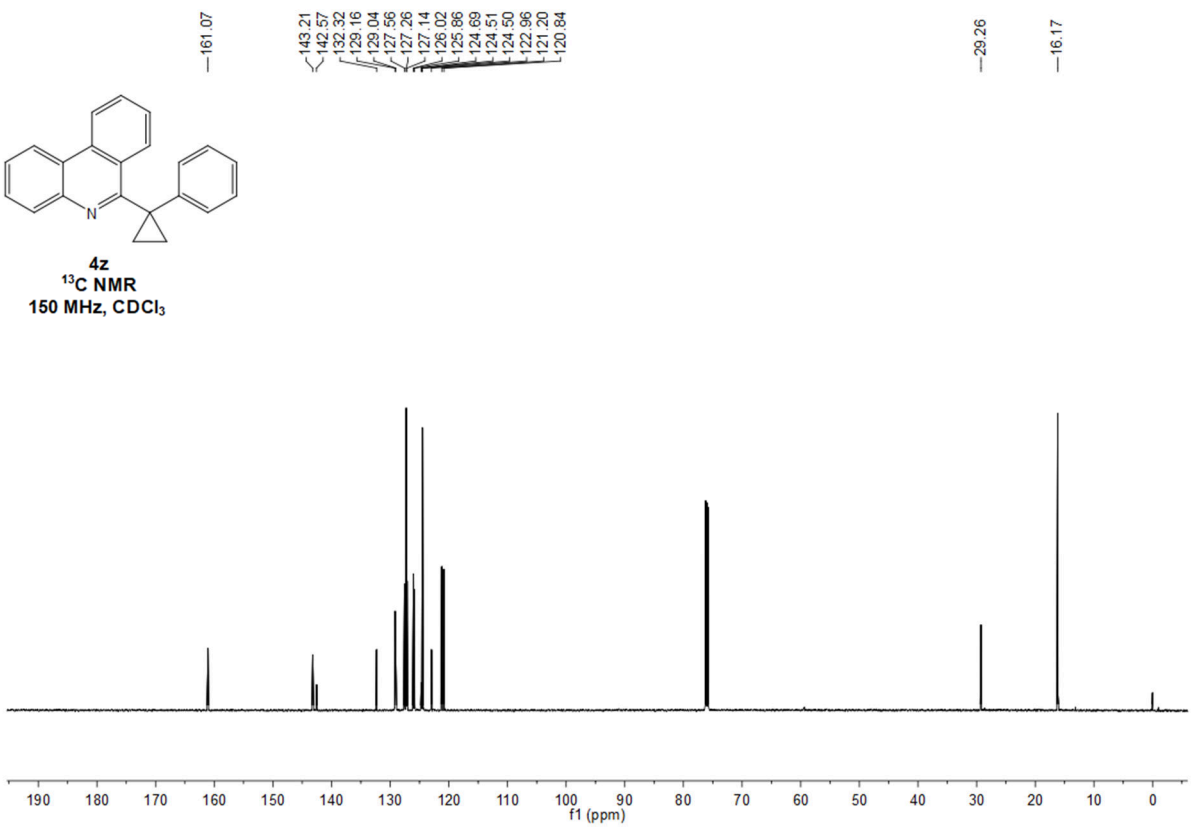

8.573
8.559
8.476
8.462
8.239
8.226
8.073
8.060
7.775
7.762
7.750
7.654
7.642
7.635
7.623
7.577
7.564
7.552
6.297
6.282
5.579
5.570
5.564
5.556
2.244
2.233
2.223
2.213
1.399
0.998
0.987
0.783
0.772
4s
1H NMR
600 MHz, CDCl3
1.00
1.03
0.91
0.98
1.01
2.05
1.02
0.82
0.89
0.99
9.03
3.02
3.03
f1 (ppm)

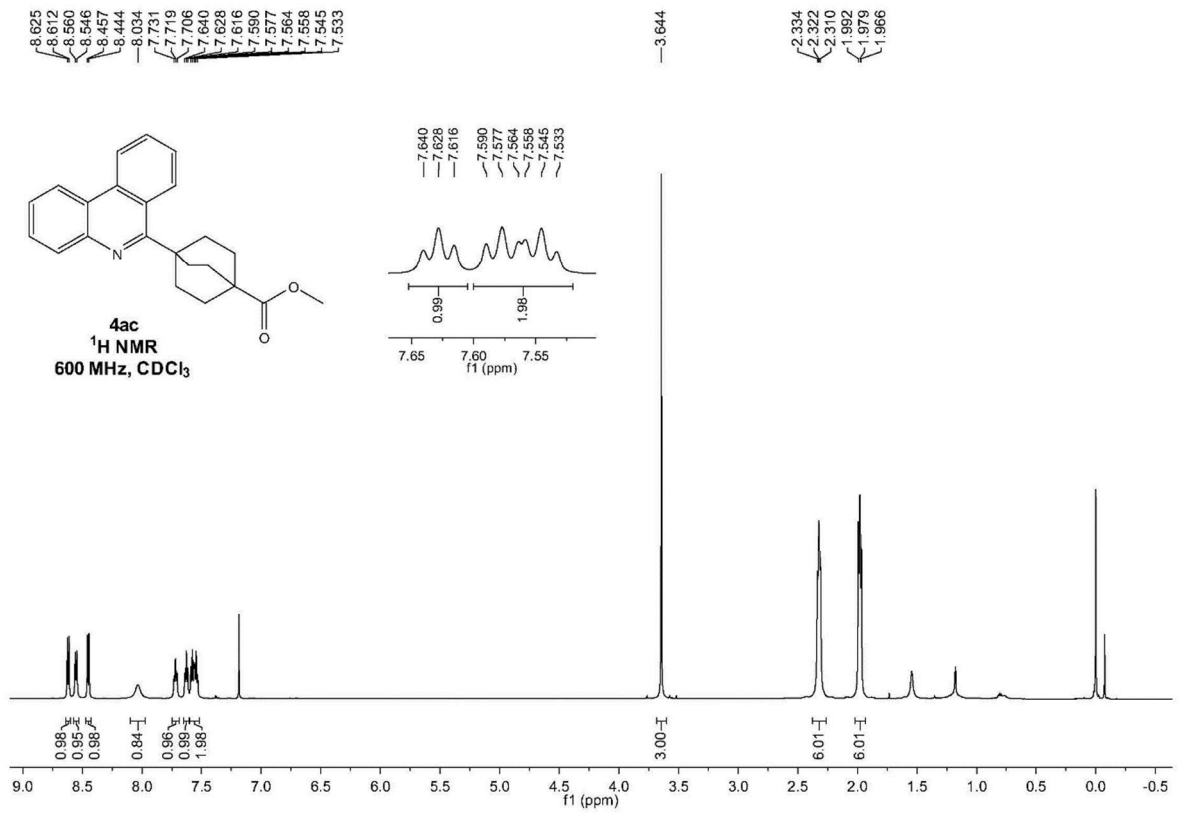

158.91
155.23
141.82
131.85
129.39
128.72
127.41
126.19
125.53
124.46
122.90
122.50
121.25
120.76
78.14
54.20
33.41
27.42
19.82
15.65
4s
13C NMR
150 MHz, CDCl3
f1 (ppm)

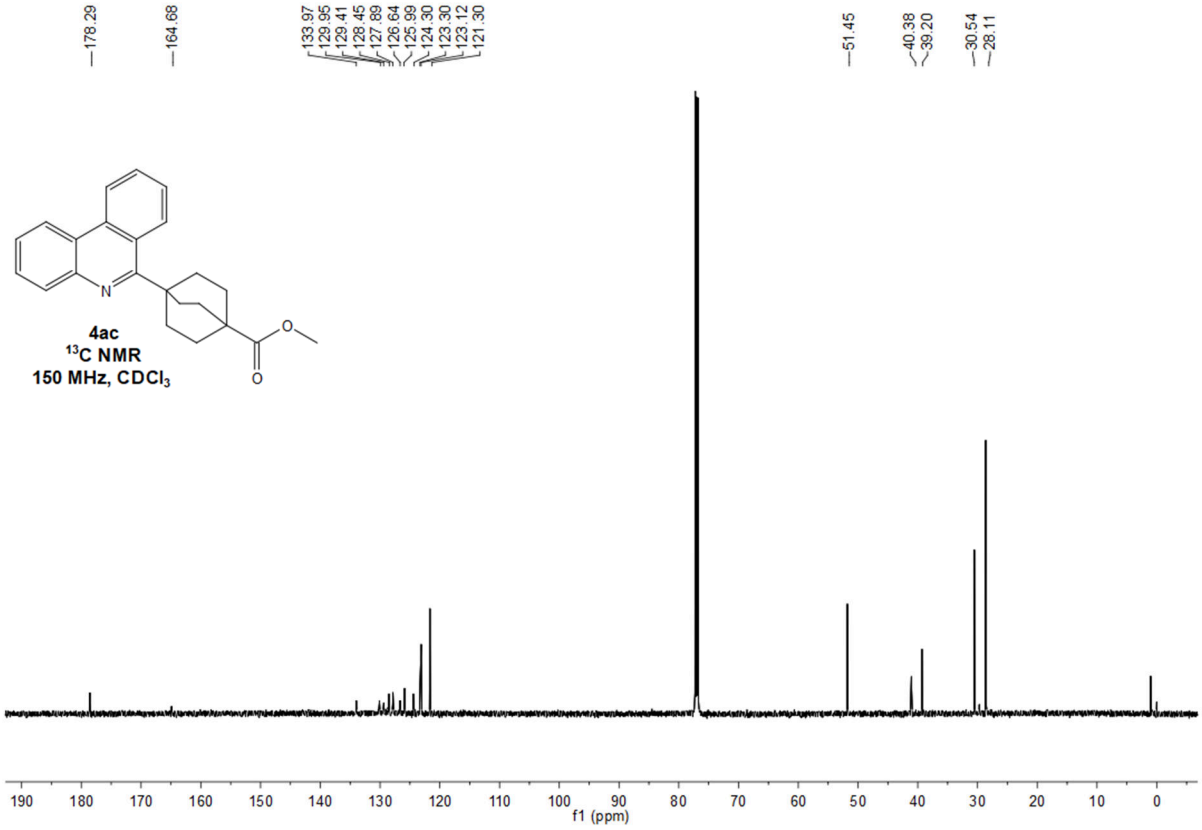

8.578
8.564
8.477
8.463
8.284
8.271
8.067
8.055
7.792
7.780
7.768
7.664
7.651
7.639
7.591
7.578
7.566
6.465
6.458
5.821
5.815
2.664
2.653
2.648
2.642
2.637
2.631
2.627
2.616
2.457
2.450
2.439
2.434
2.427
2.420
2.412
2.299
2.292
2.286
2.276
2.270
2.263
1.993
1.414
4u
1H NMR
600 MHz, CDCl3
0.97
0.99
0.95
0.91
1.00
2.00
0.96
0.77
0.83
0.91
1.00
0.88
3.08
8.96
f1 (ppm)


154.59
132.45
129.53
128.73
127.66
126.74
125.94
124.32
122.82
122.48
121.57
120.98
78.39
48.80
35.56
29.26
27.18
14.59
4u
13C NMR
150 MHz, CDCl3
f1 (ppm)

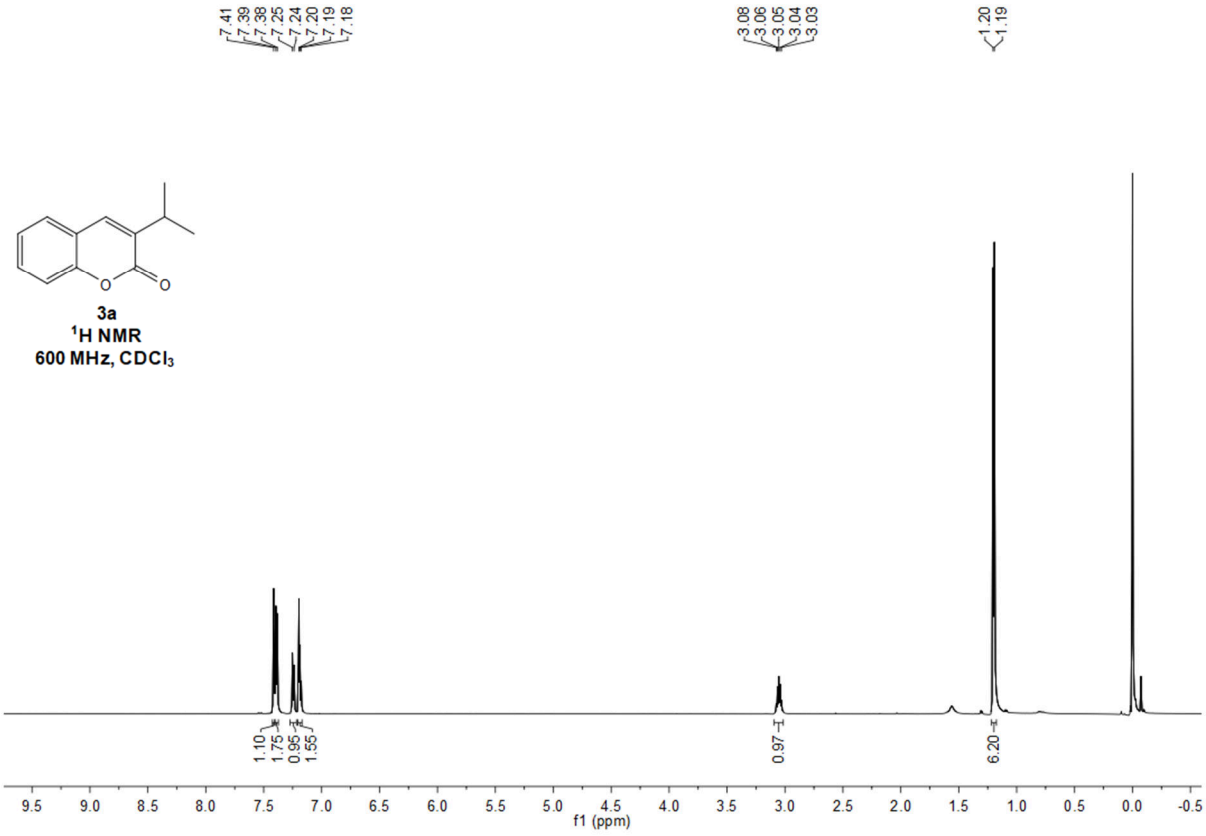

8.564
8.550
8.514
8.500
8.310
8.296
8.203
8.191
7.698
7.684
7.607
7.468
7.107
7.095
7.040
7.032
7.019
1.680
1.671
1.668
1.661
1.584
1.577
1.573
1.565
N
4z
1H NMR
600 MHz, CDCl3
1.00
0.99
1.00
0.91
2.03
1.01
1.02
2.06
3.01
2.00
2.00
f1 (ppm)


161.07
143.21
142.57
132.32
129.16
129.04
127.56
127.26
127.14
126.02
125.86
124.69
124.51
124.50
122.96
121.20
120.84
29.26
16.17
N
4z
13C NMR
150 MHz, CDCl3
f1 (ppm)

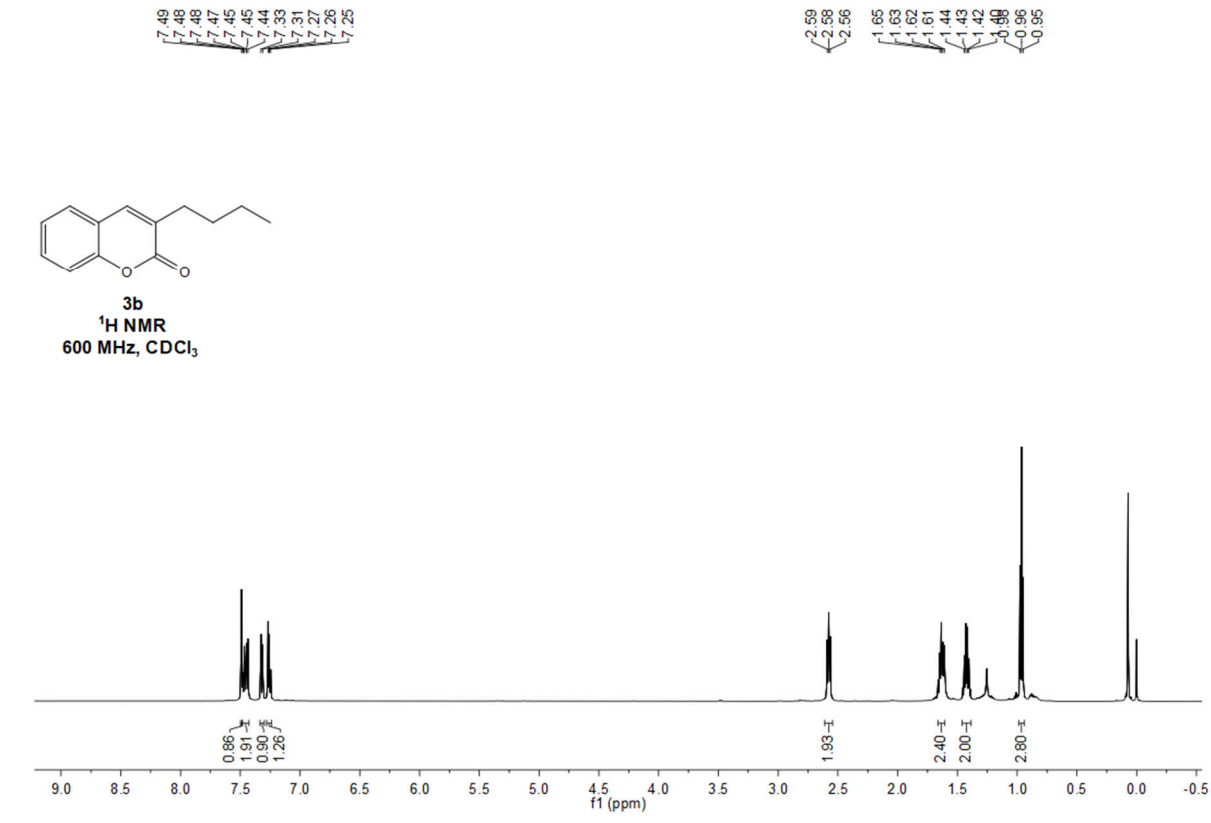

8.625
8.612
8.560
8.546
8.457
8.444
8.034
7.731
7.719
7.706
7.640
7.628
7.616
7.590
7.577
7.564
7.558
7.545
7.533
3.644
2.334
2.322
2.310
1.992
1.979
1.966
4ac
1H NMR
600 MHz, CDCl3
0.98
0.95
0.98
0.84
0.96
0.99
1.98
3.00
6.01
6.01
f1 (ppm)


178.29
164.68
133.97
129.95
129.41
128.45
127.89
126.64
125.99
124.30
123.30
123.12
121.30
51.45
40.38
39.20
30.54
28.11
4ac
13C NMR
150 MHz, CDCl3
f1 (ppm)

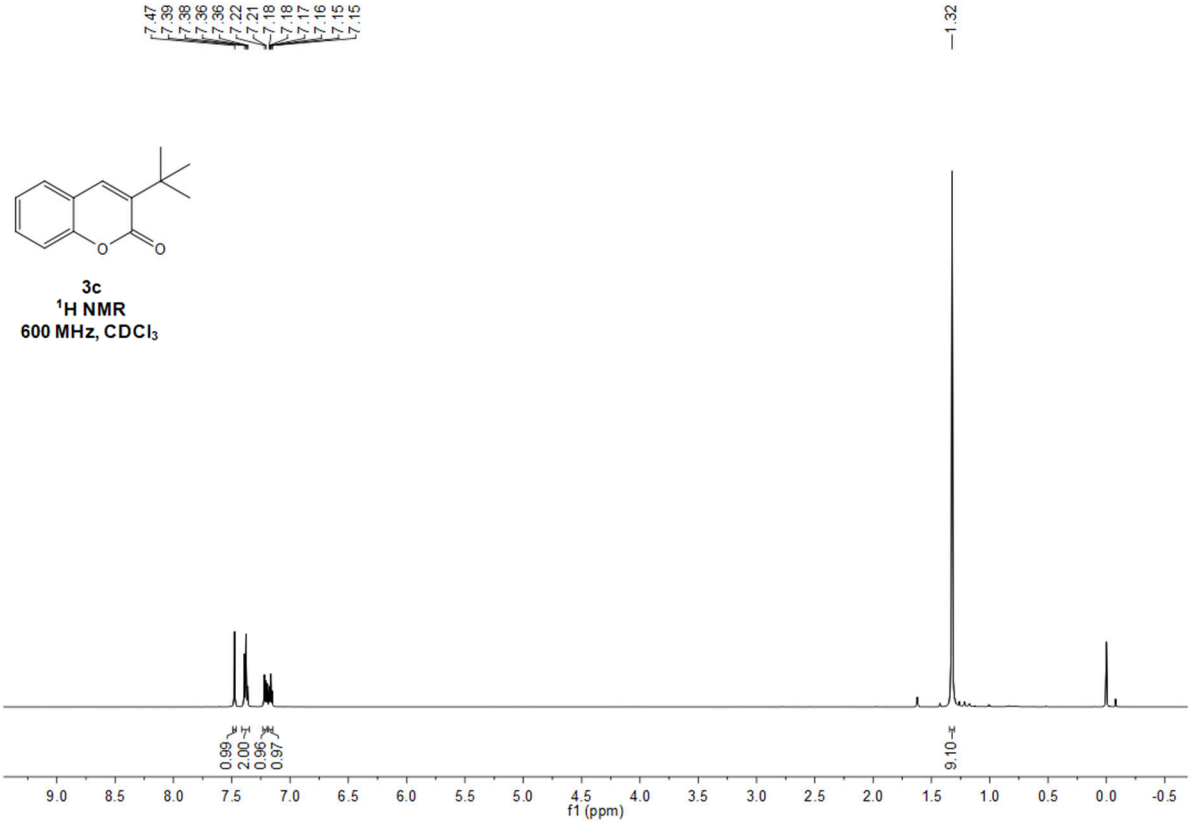
7. NMR Spectra of Known Compounds



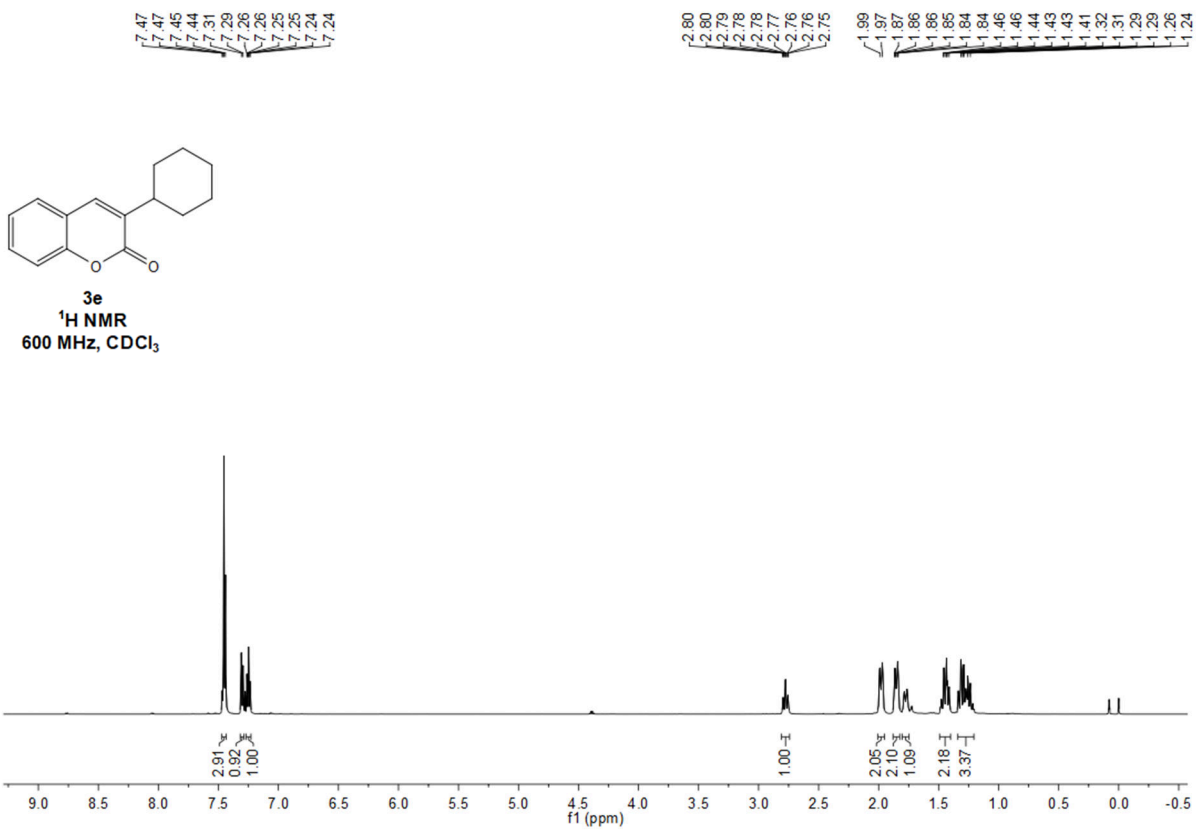
3a
^{1}H NMR
600 MHz, $CDCl_3$



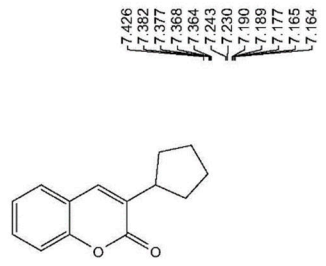
3b
^{1}H NMR
600 MHz, $CDCl_3$



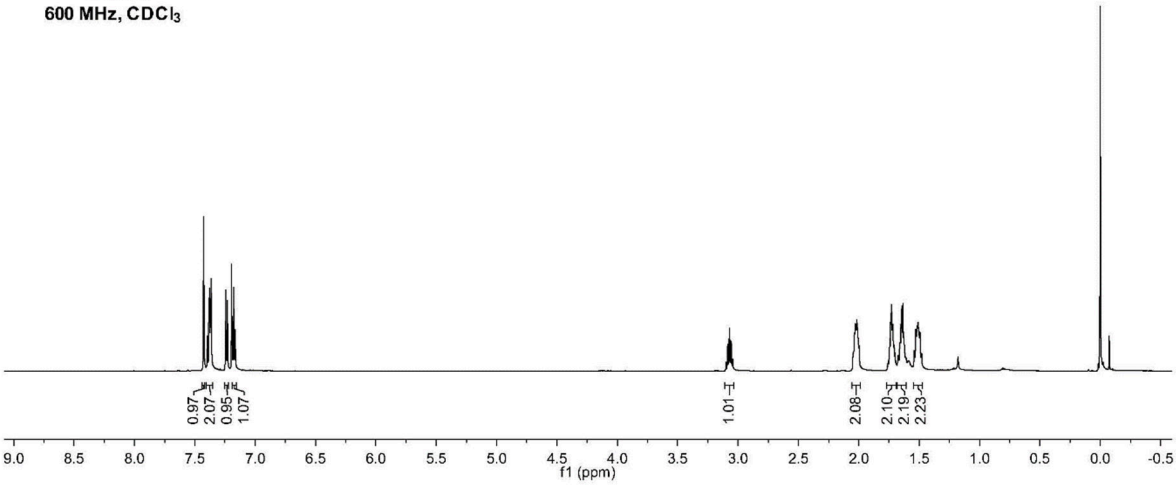
3c
^{1}H NMR
600 MHz, $CDCl_3$

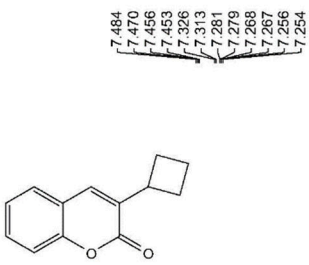


3e
^{1}H NMR
600 MHz, $CDCl_3$

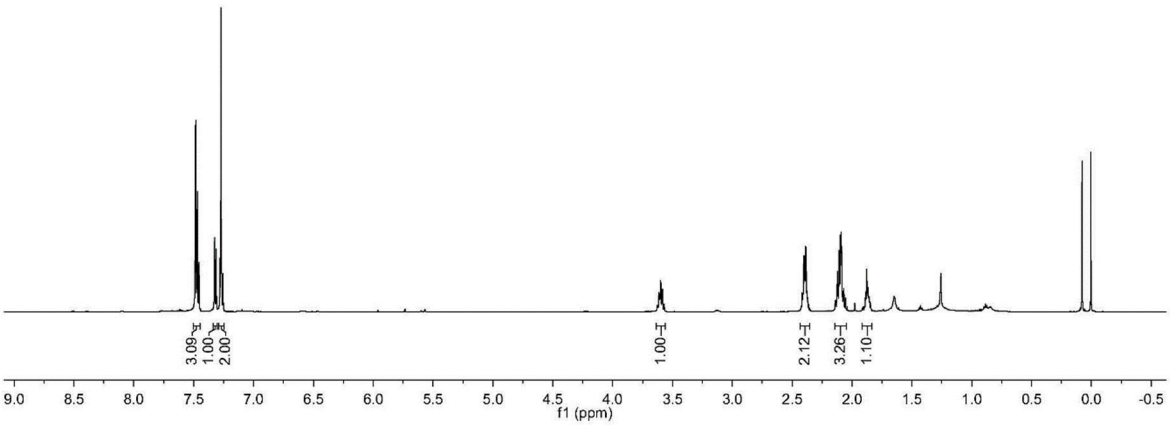


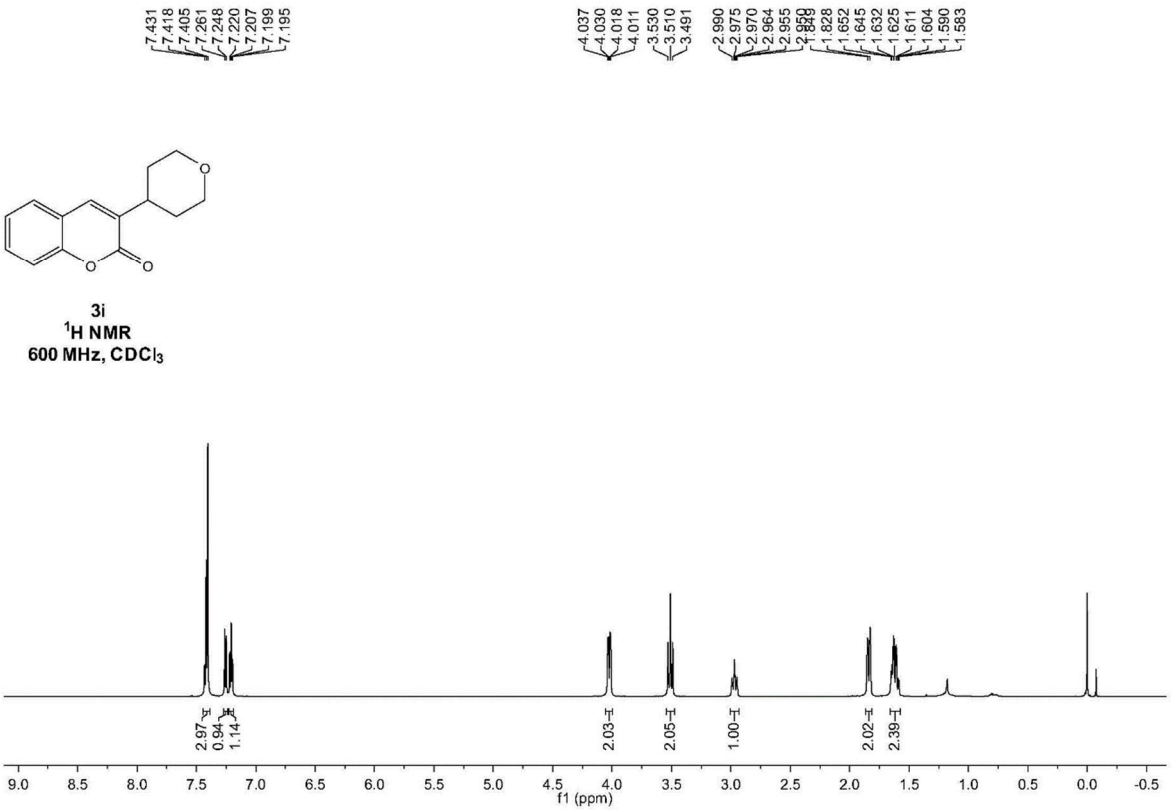
3f
^{1}H NMR
600 MHz, $CDCl_3$



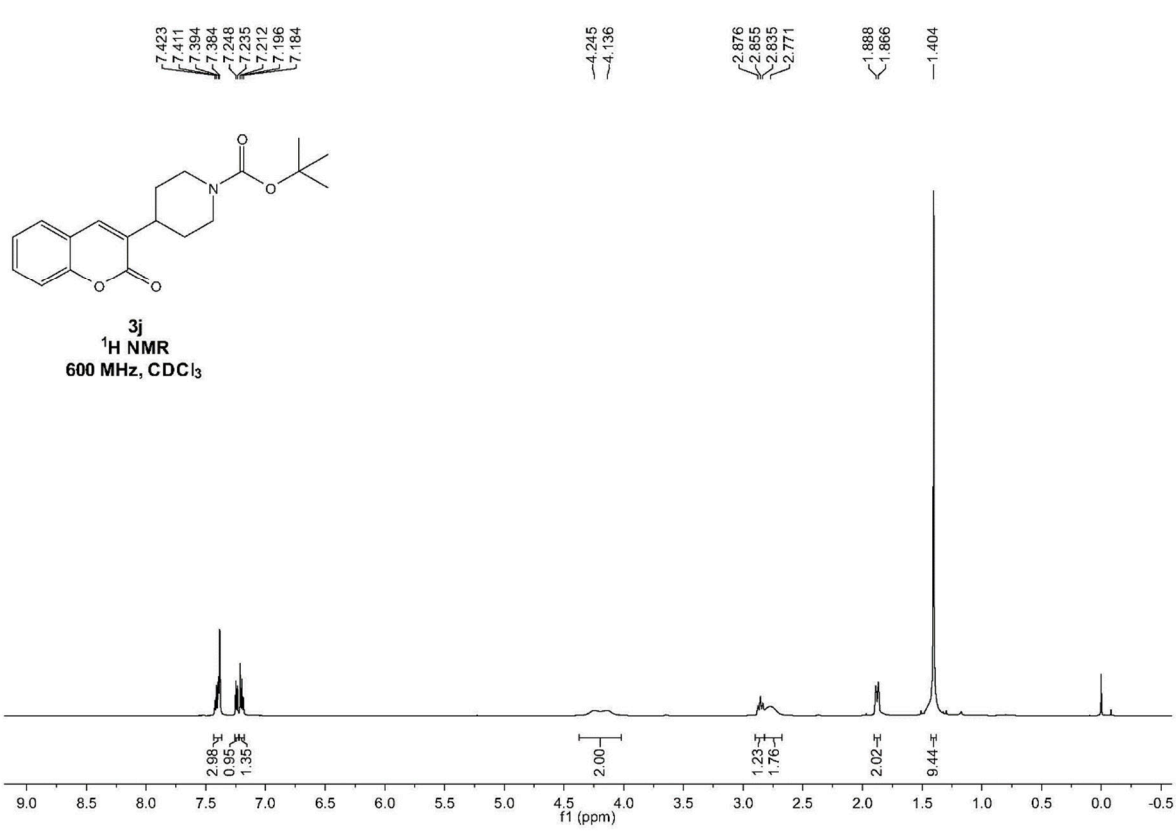


3g
^{1}H NMR
600 MHz, $CDCl_3$

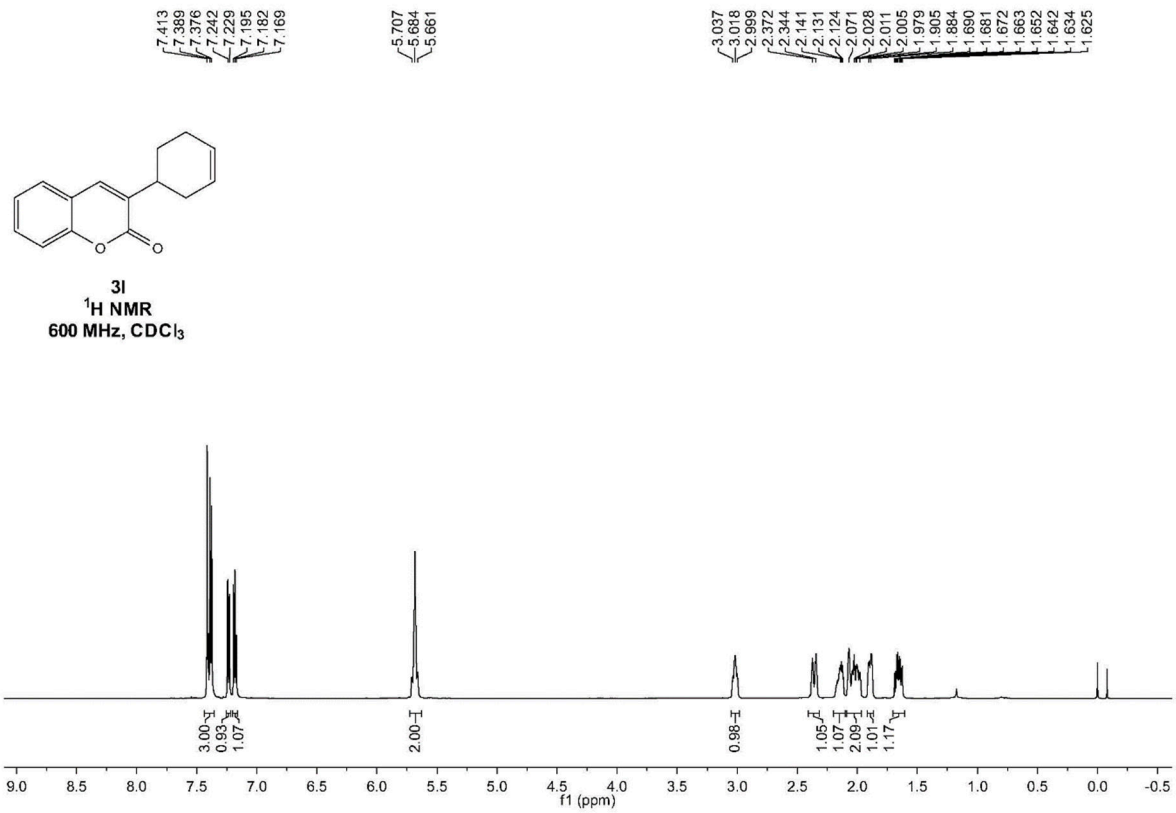




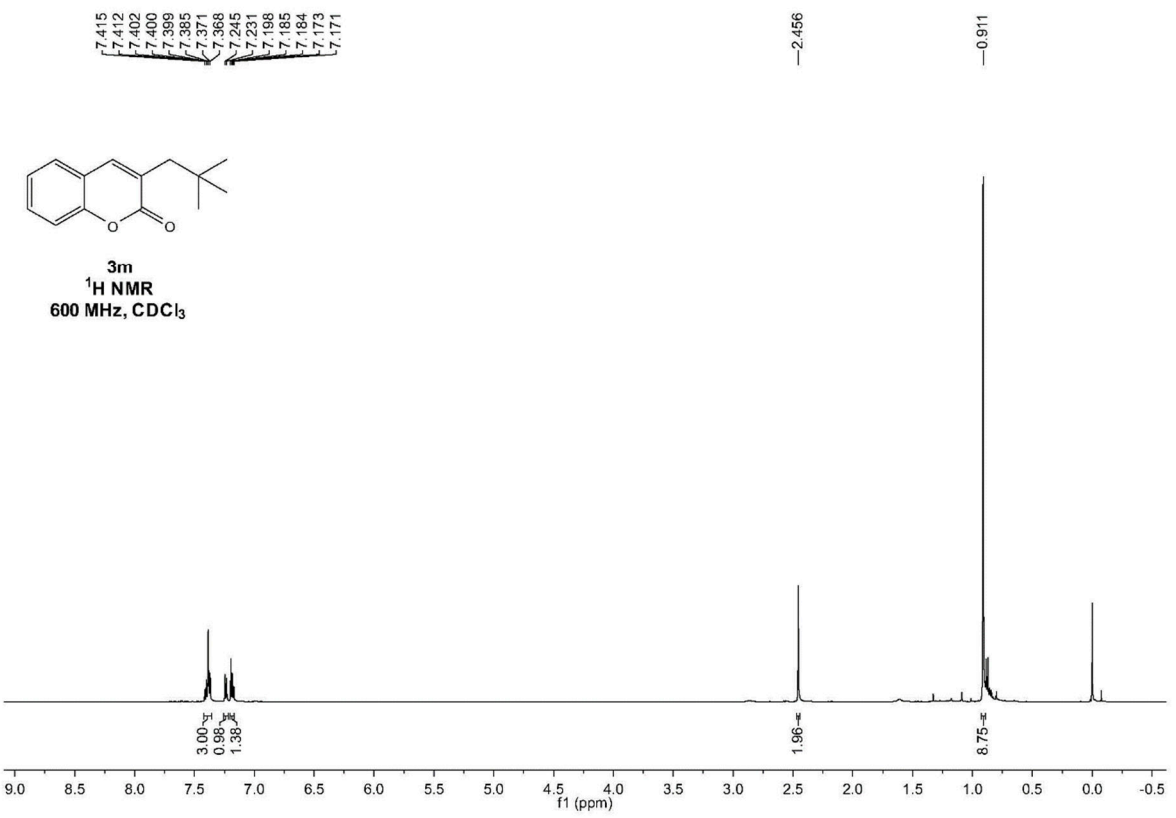
3i
^{1}H NMR
600 MHz, $CDCl_3$



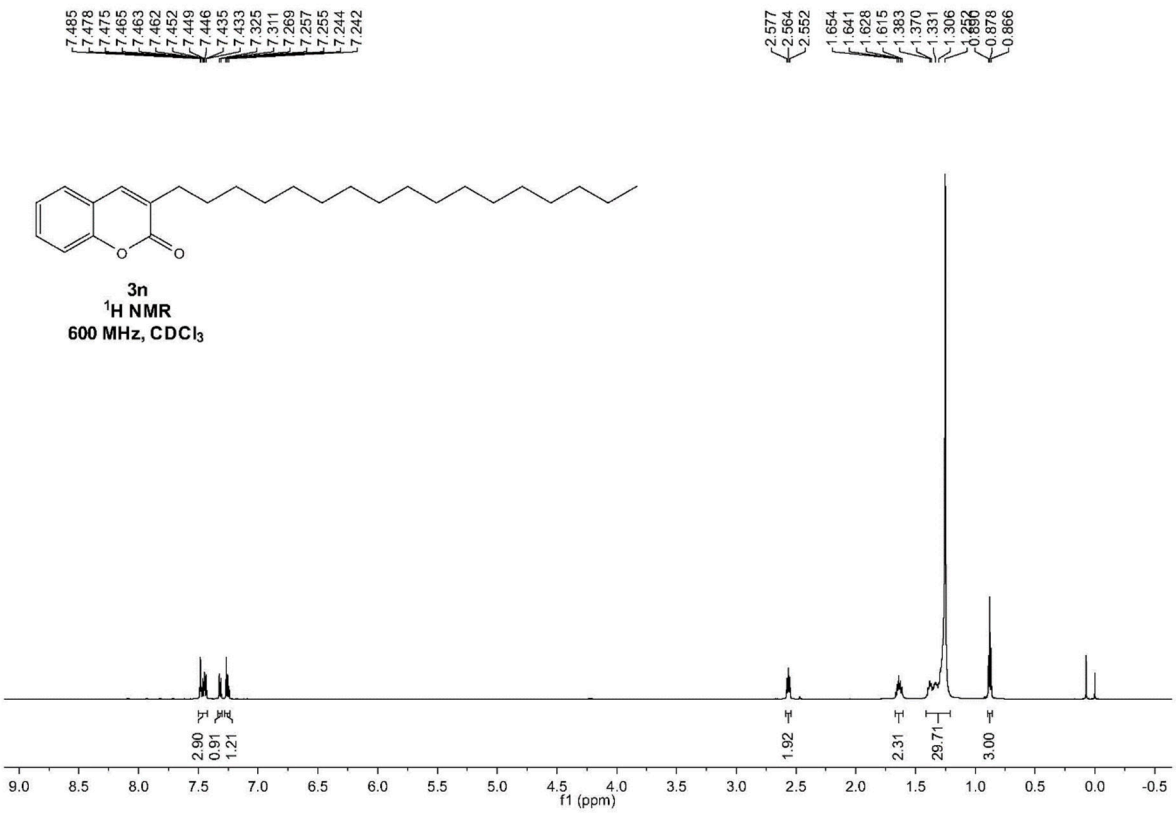
3j
^{1}H NMR
600 MHz, $CDCl_3$



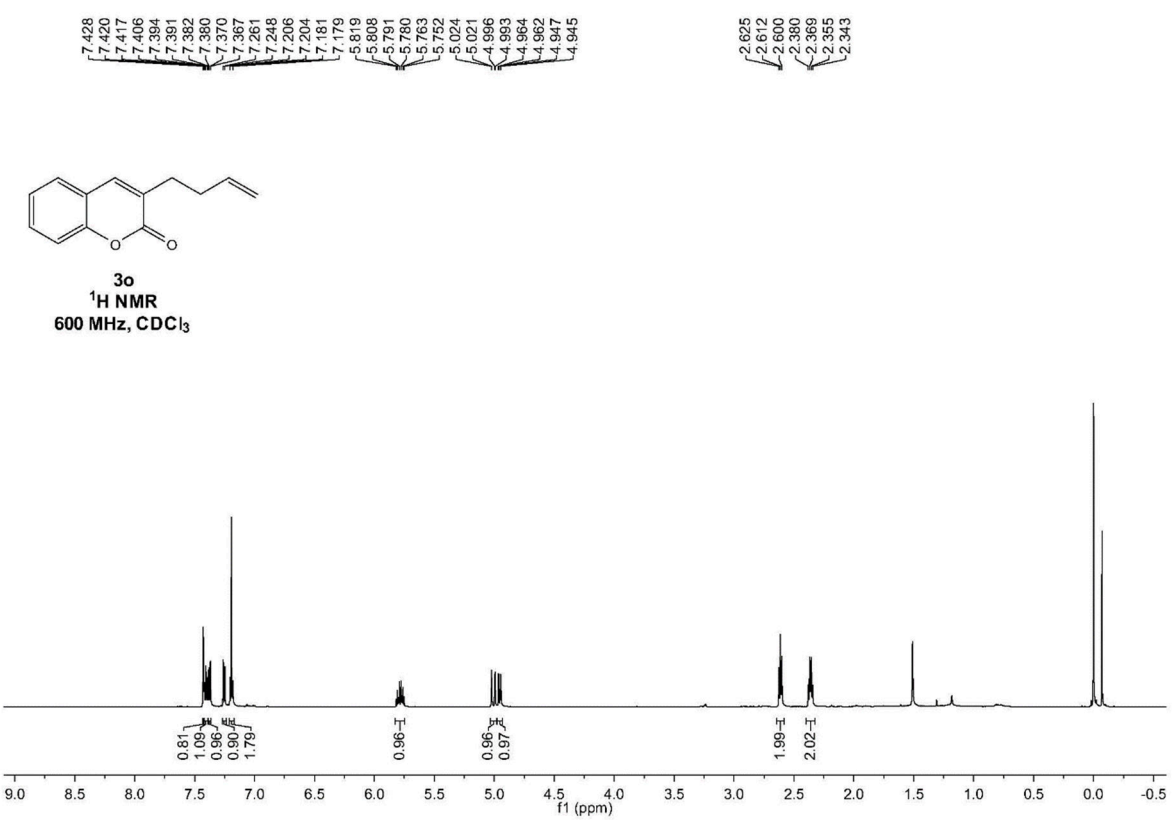
3l
^{1}H NMR
600 MHz, $CDCl_3$



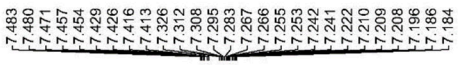
3m
^{1}H NMR
600 MHz, $CDCl_3$

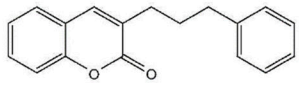


3n
^{1}H NMR
600 MHz, $CDCl_3$

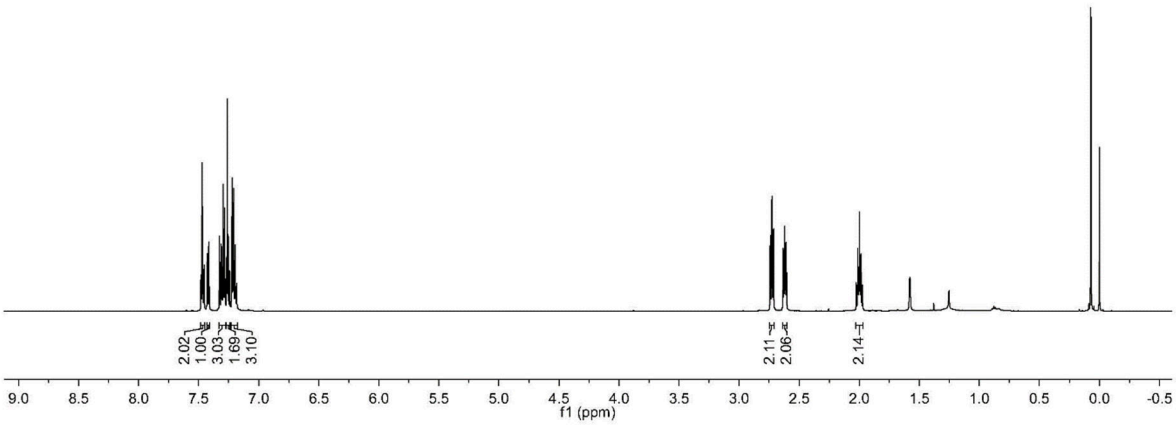


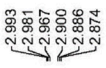
3o
^{1}H NMR
600 MHz, $CDCl_3$

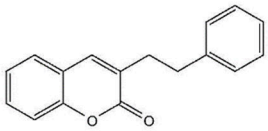




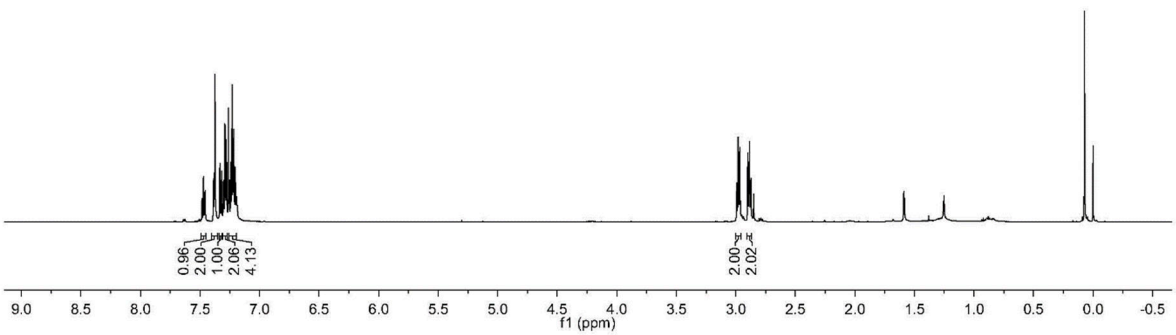
3p
^{1}H NMR
600 MHz, $CDCl_3$

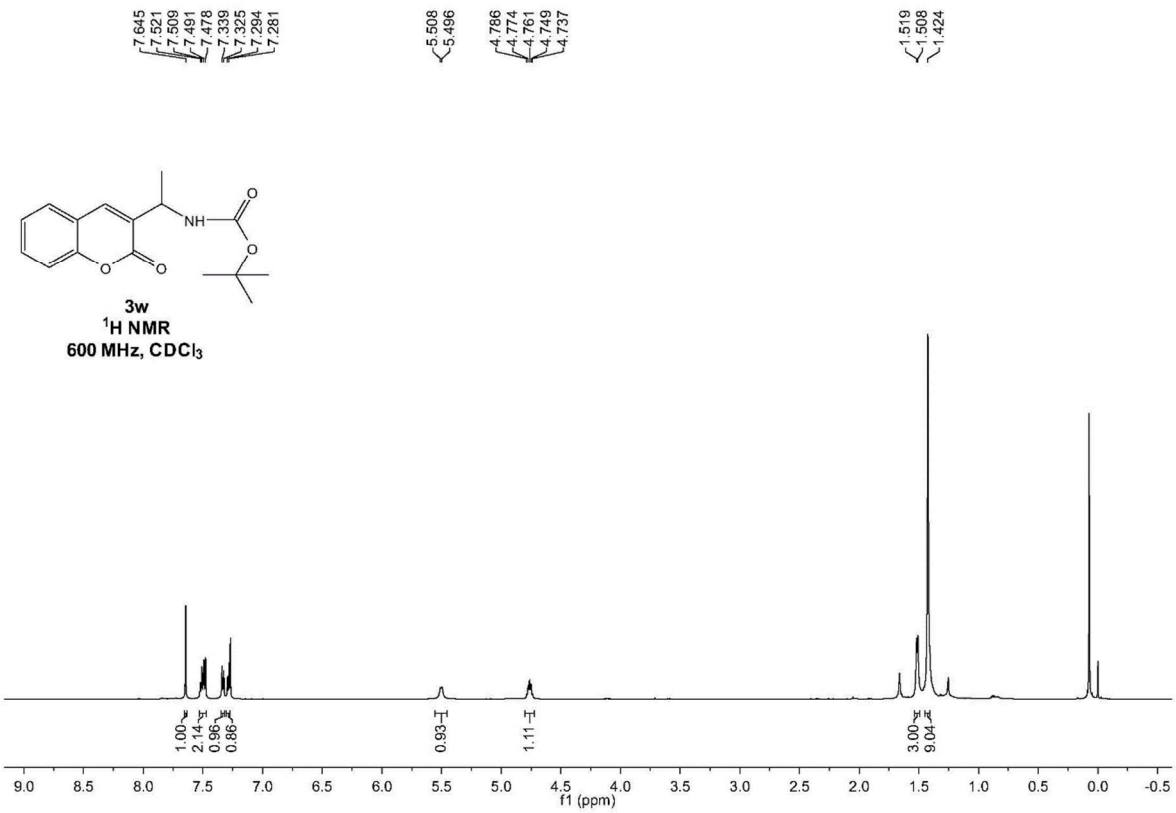




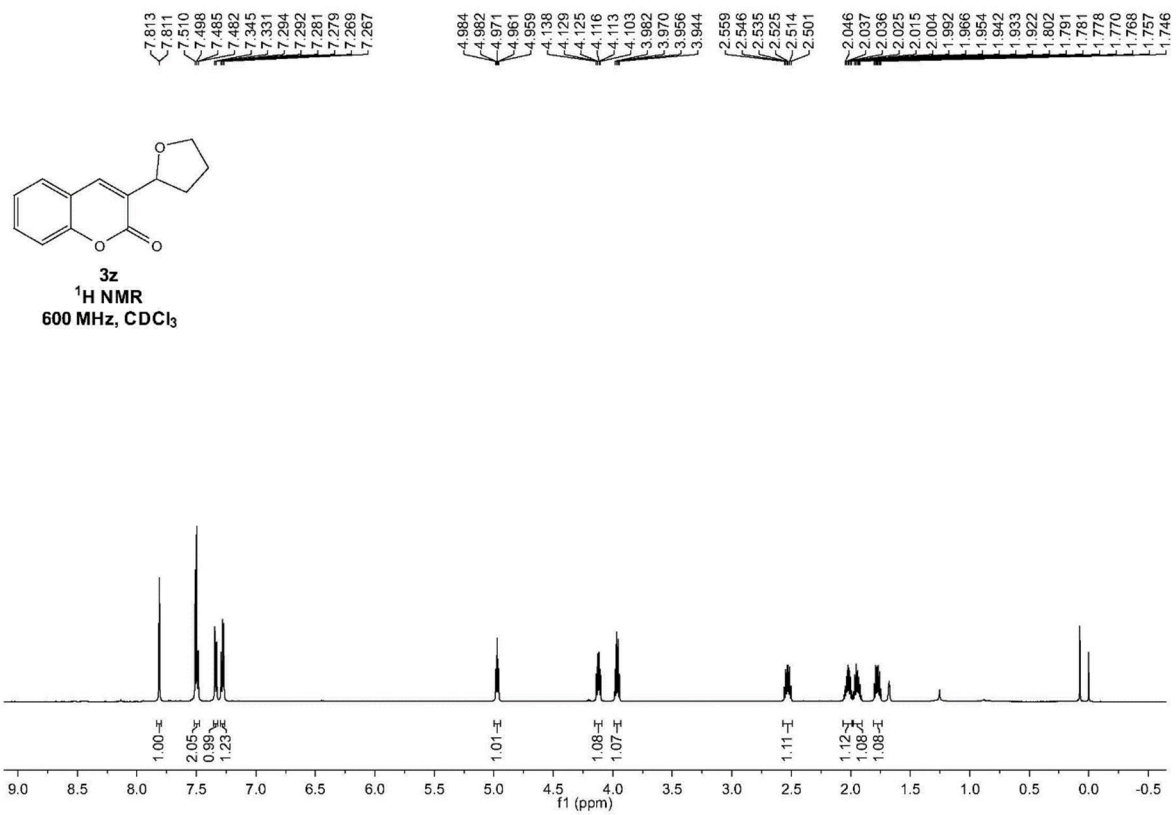


3q
^{1}H NMR
600 MHz, $CDCl_3$

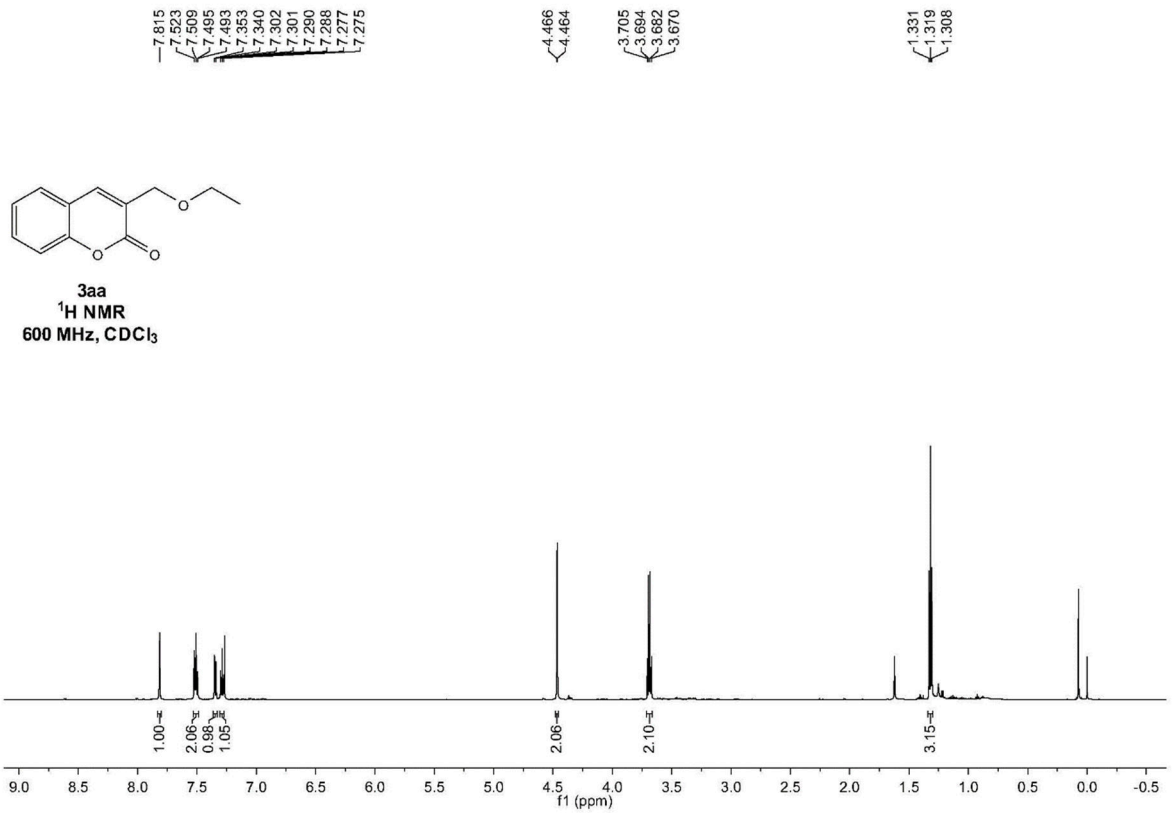




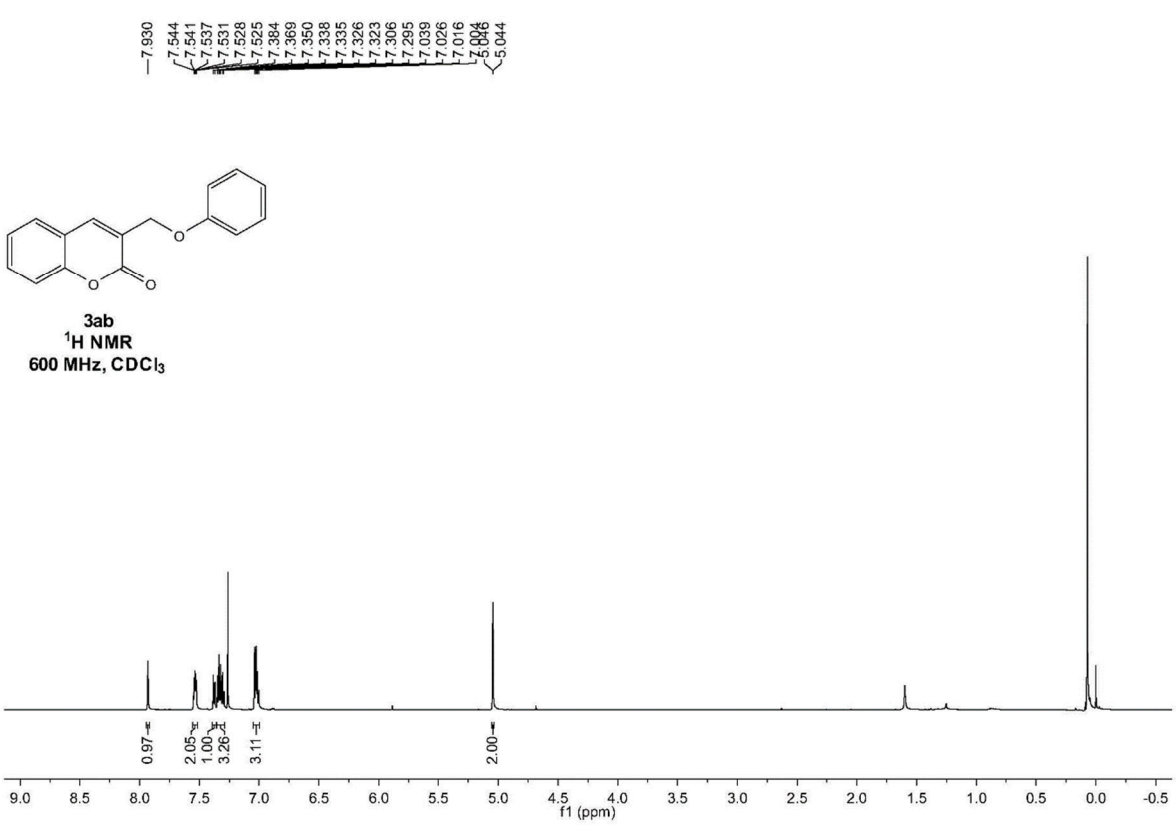
3w
^{1}H NMR
600 MHz, $CDCl_3$



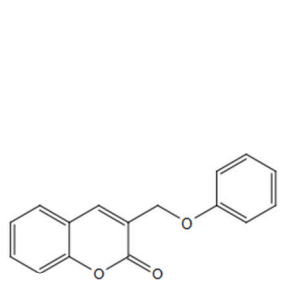
3z
^{1}H NMR
600 MHz, $CDCl_3$



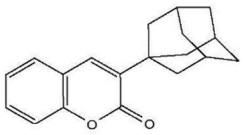
3aa
^{1}H NMR
600 MHz, $CDCl_3$



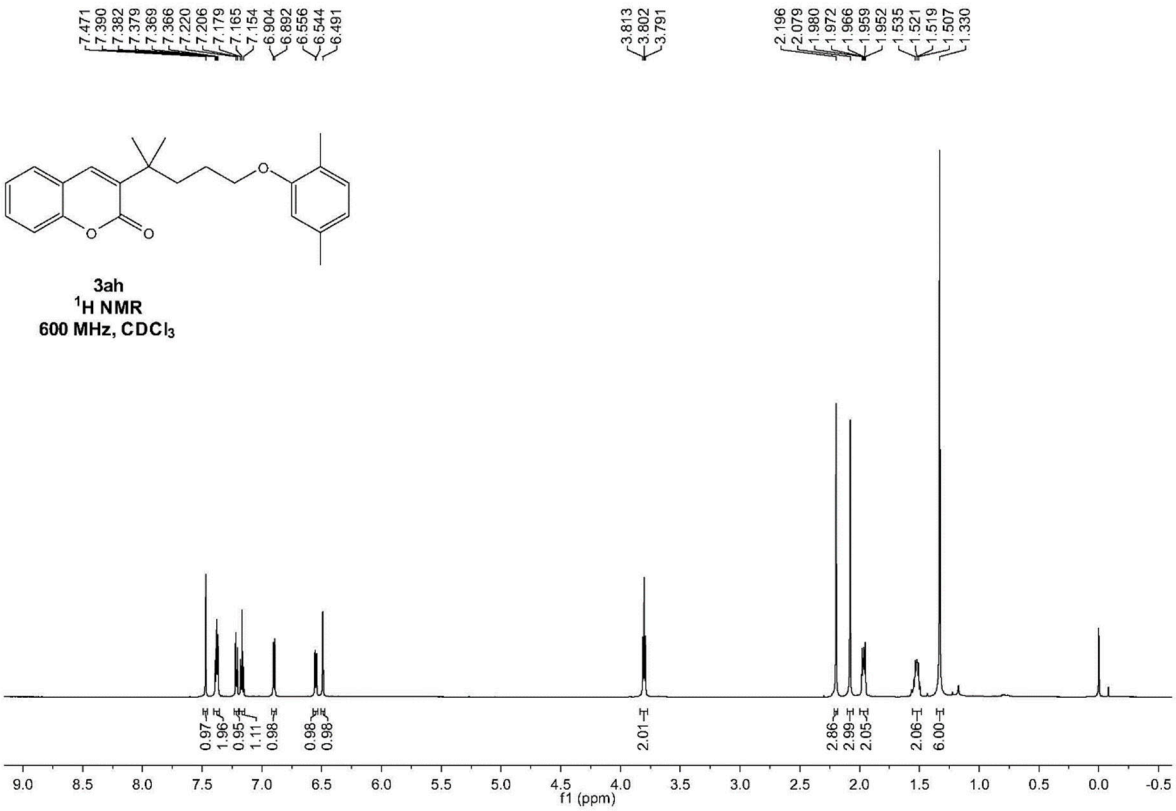
3ab
^{1}H NMR
600 MHz, $CDCl_3$

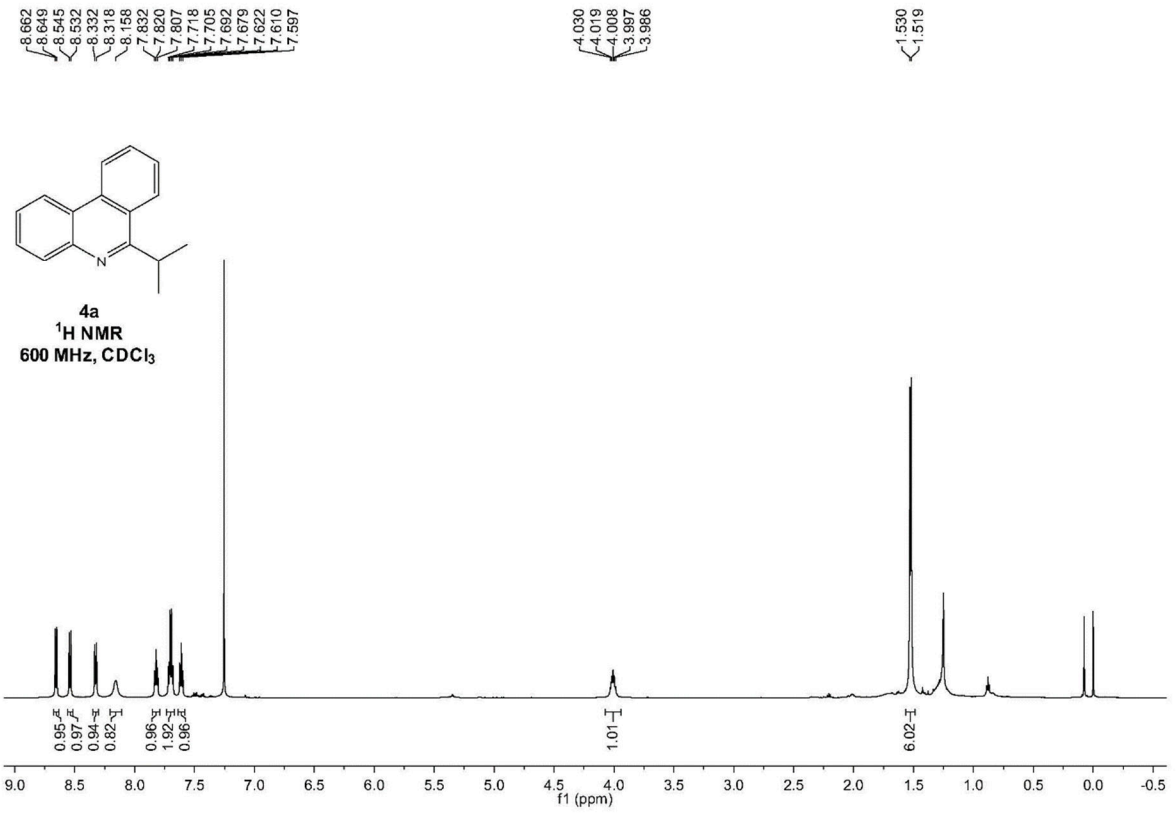


3ab
^{13}C NMR
150 MHz, $CDCl_3$

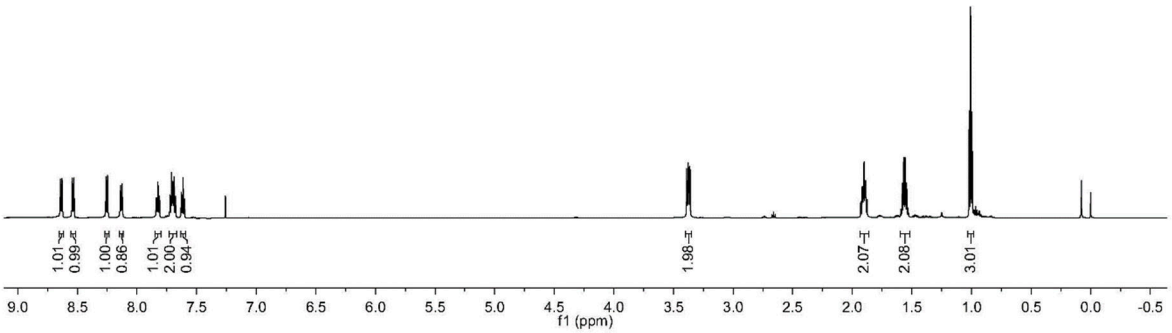


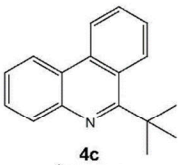
3af
^{1}H NMR
600 MHz, $CDCl_3$


7.471
7.390
7.382
7.379
7.369
7.366
7.220
7.206
7.179
7.165
7.154
6.904
6.892
6.556
6.544
6.491
3.813
3.802
3.791
2.196
2.079
1.980
1.972
1.966
1.959
1.952
1.535
1.521
1.519
1.507
1.330
O
O
O
3ah
1H NMR
600 MHz, CDCl3
0.97
1.96
0.95
1.11
0.98
0.98
0.98
2.01
2.86
2.99
2.05
2.06
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

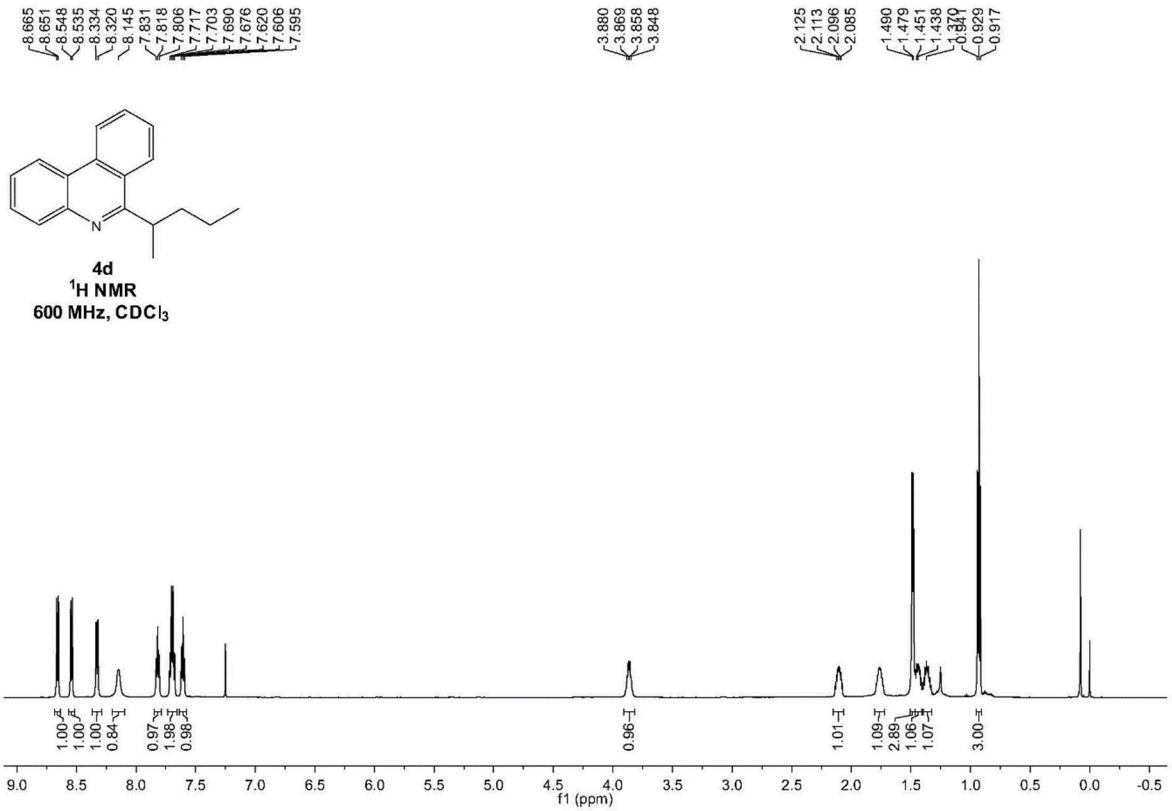

8.662
8.649
8.545
8.532
8.332
8.318
8.158
7.832
7.820
7.807
7.718
7.705
7.692
7.679
7.622
7.610
7.597
4.030
4.019
4.008
3.997
3.986
1.530
1.519
N
4a
1H NMR
600 MHz, CDCl3
0.95
0.97
0.94
0.82
0.96
1.92
0.96
1.01
6.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

4b
^{1}H NMR
600 MHz, $CDCl_3$

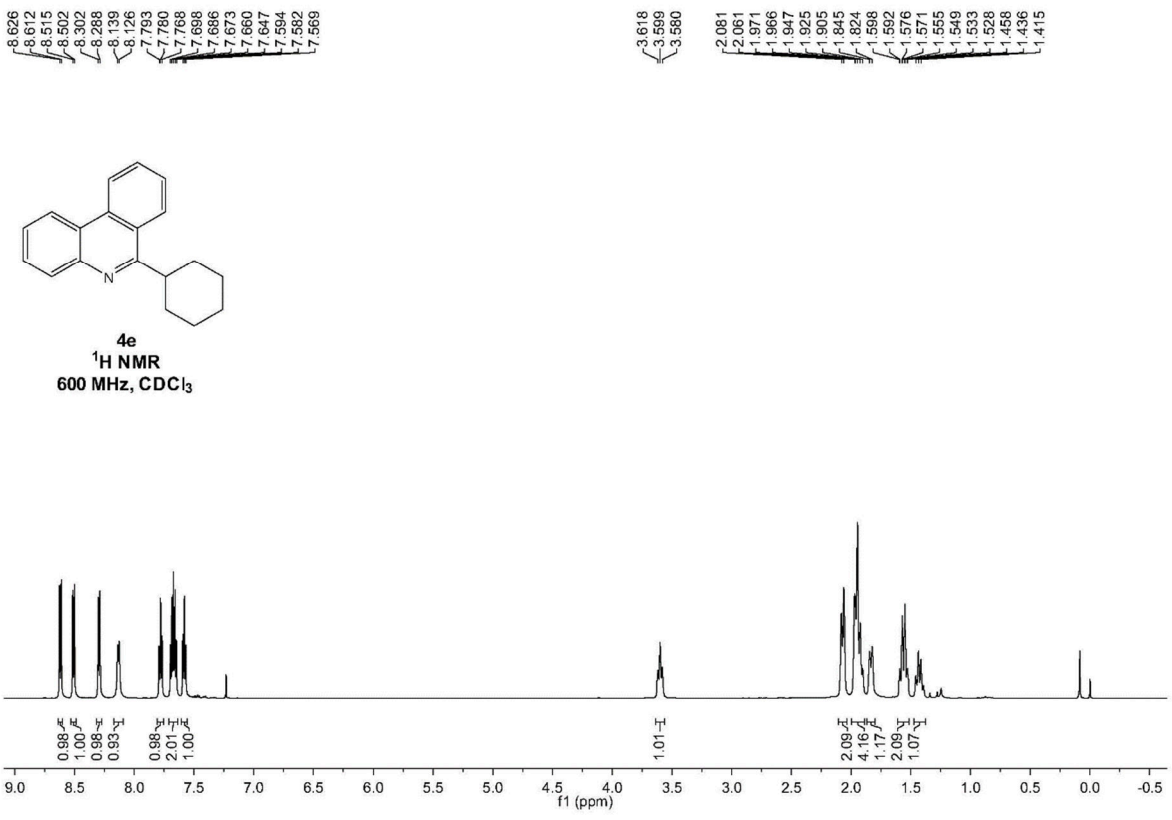




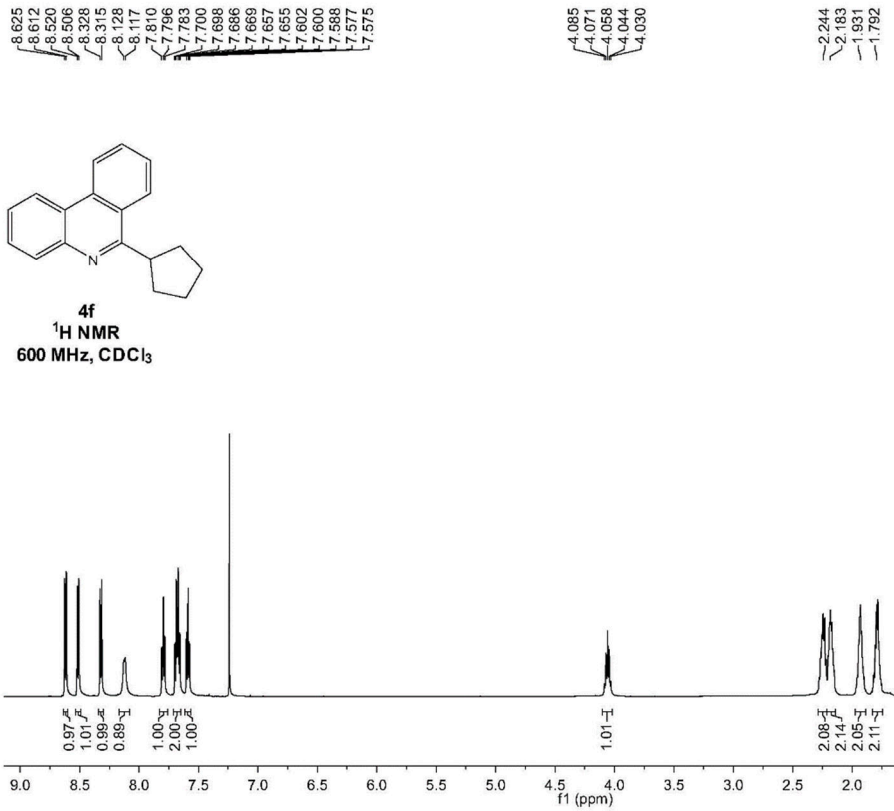
4c
^{1}H NMR
600 MHz, $CDCl_3$



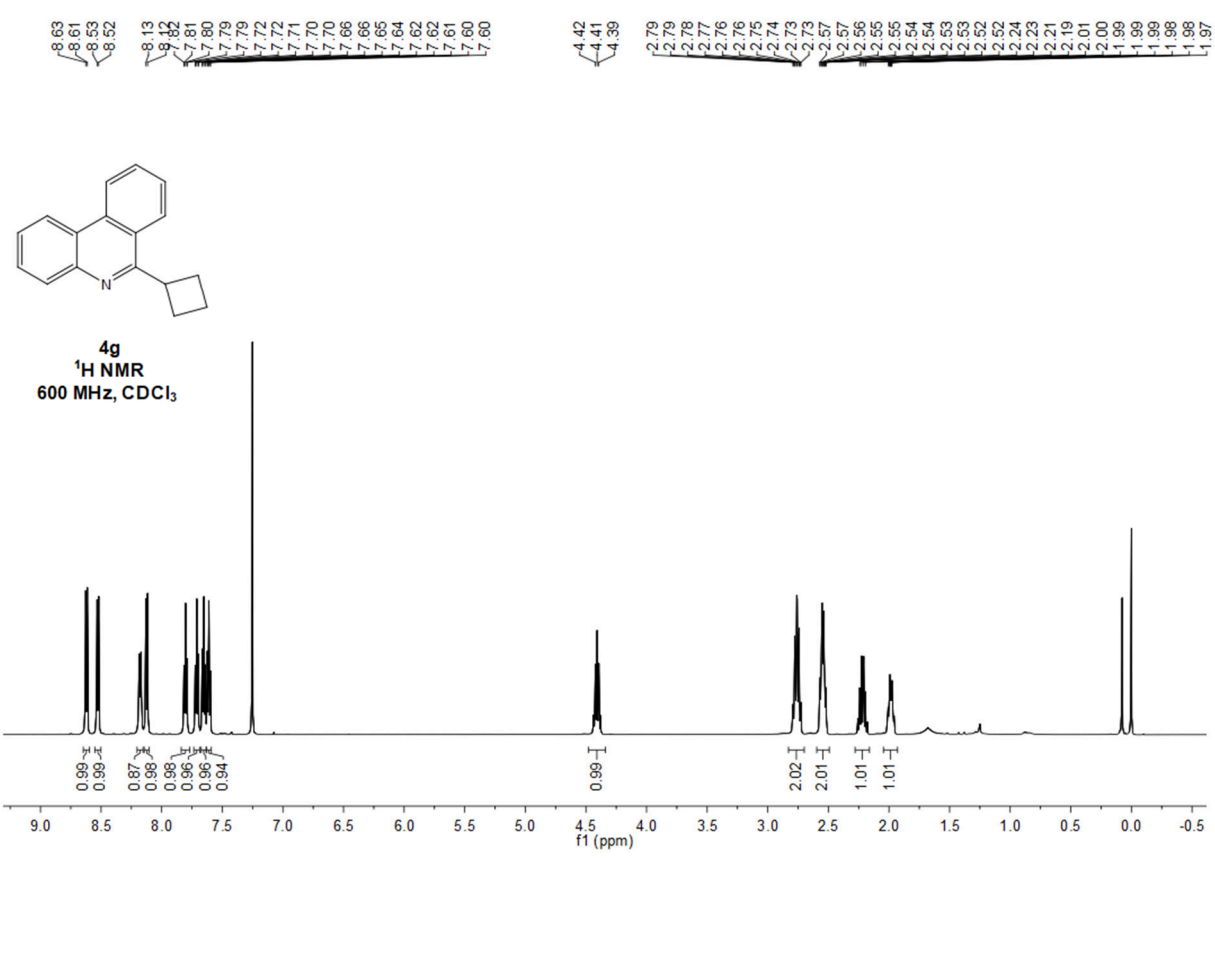
4d
^{1}H NMR
600 MHz, $CDCl_3$



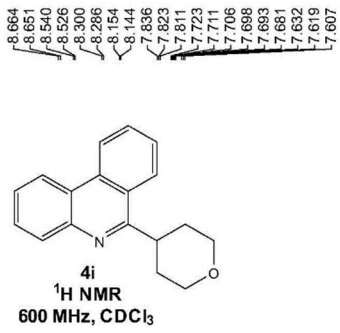
4e
^{1}H NMR
600 MHz, $CDCl_3$



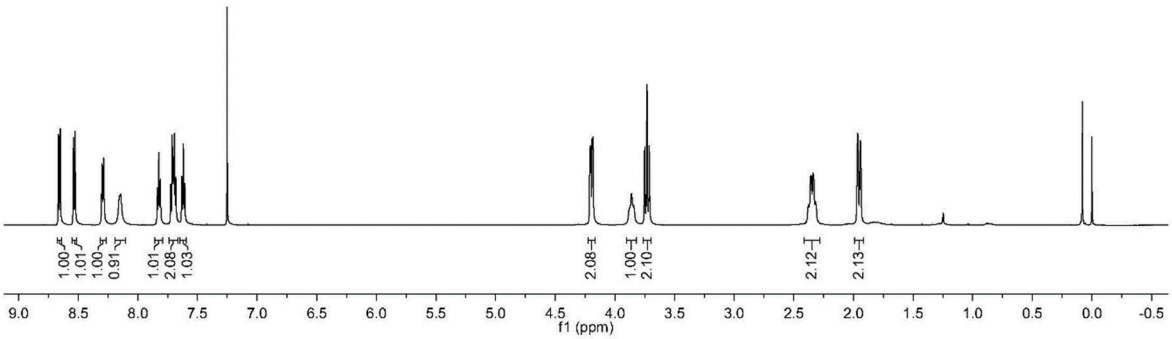
4f
^{1}H NMR
600 MHz, $CDCl_3$

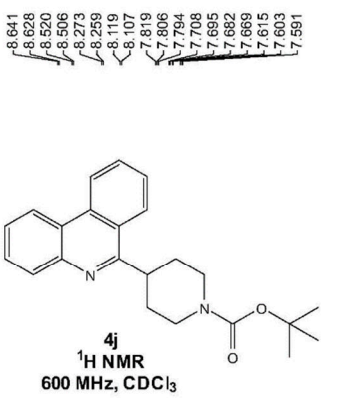


4g
^{1}H NMR
600 MHz, $CDCl_3$

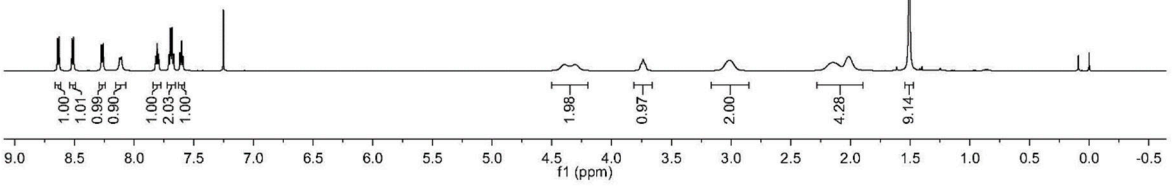


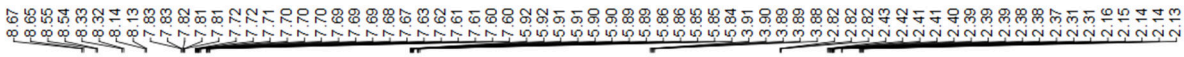
4i
^{1}H NMR
600 MHz, $CDCl_3$

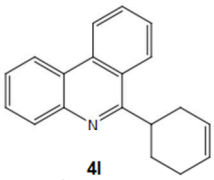




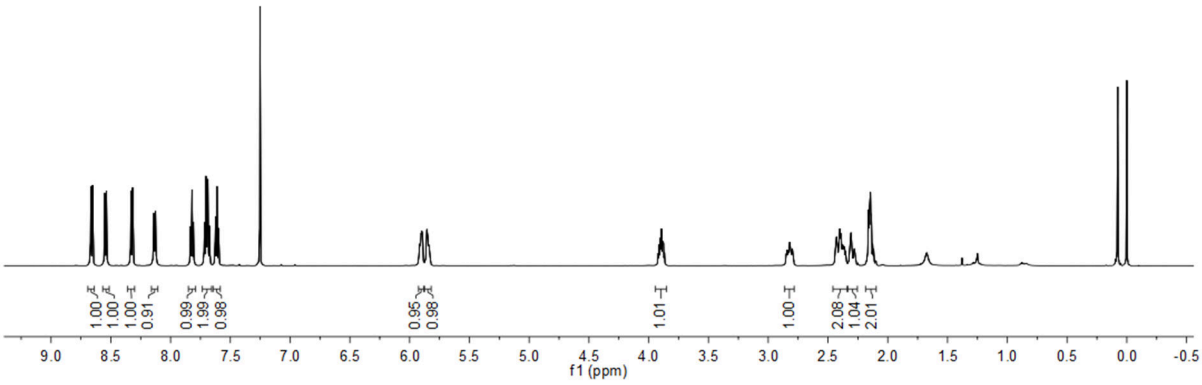
4j
^{1}H NMR
600 MHz, $CDCl_3$

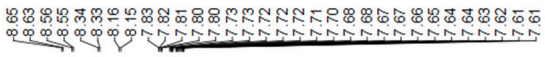


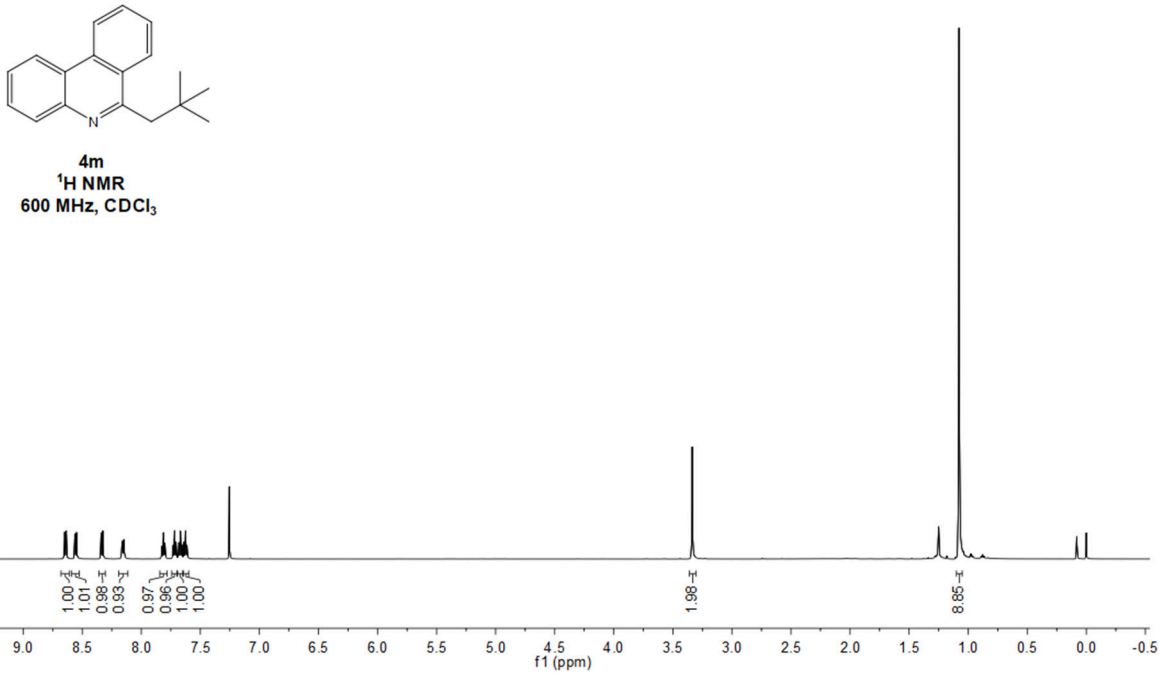




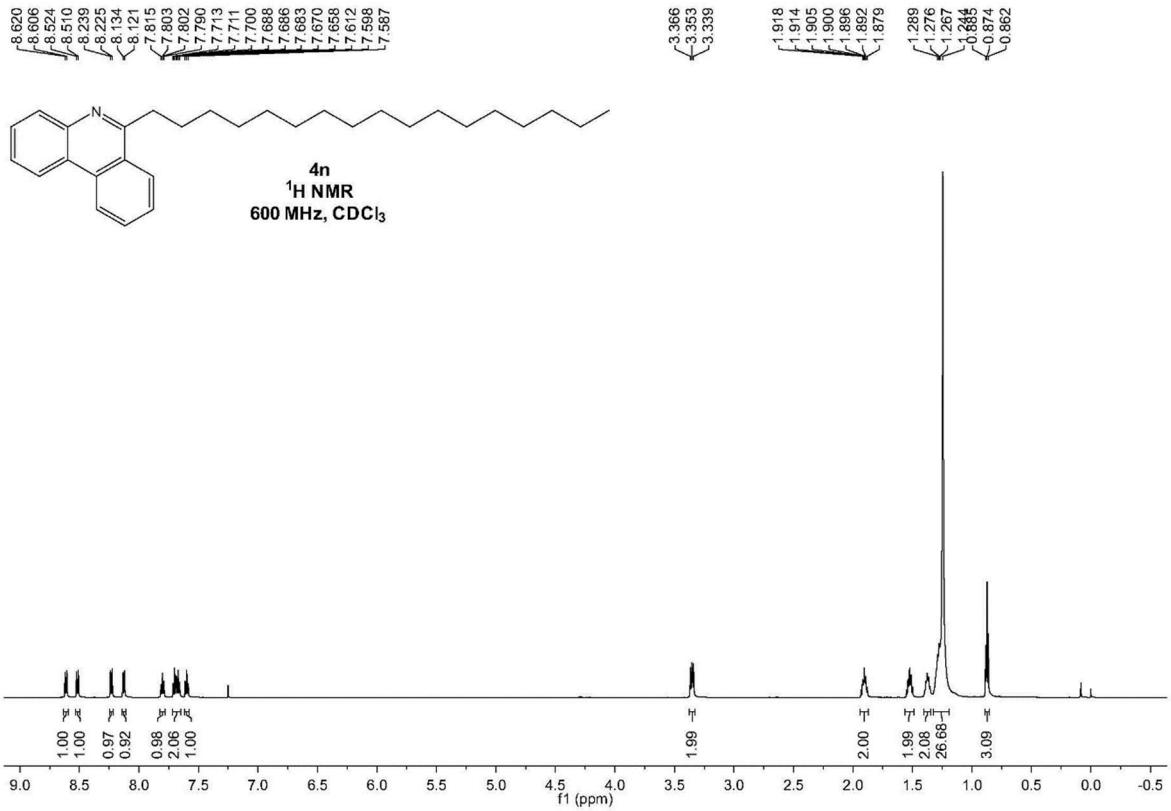
4l
^{1}H NMR
600 MHz, $CDCl_3$

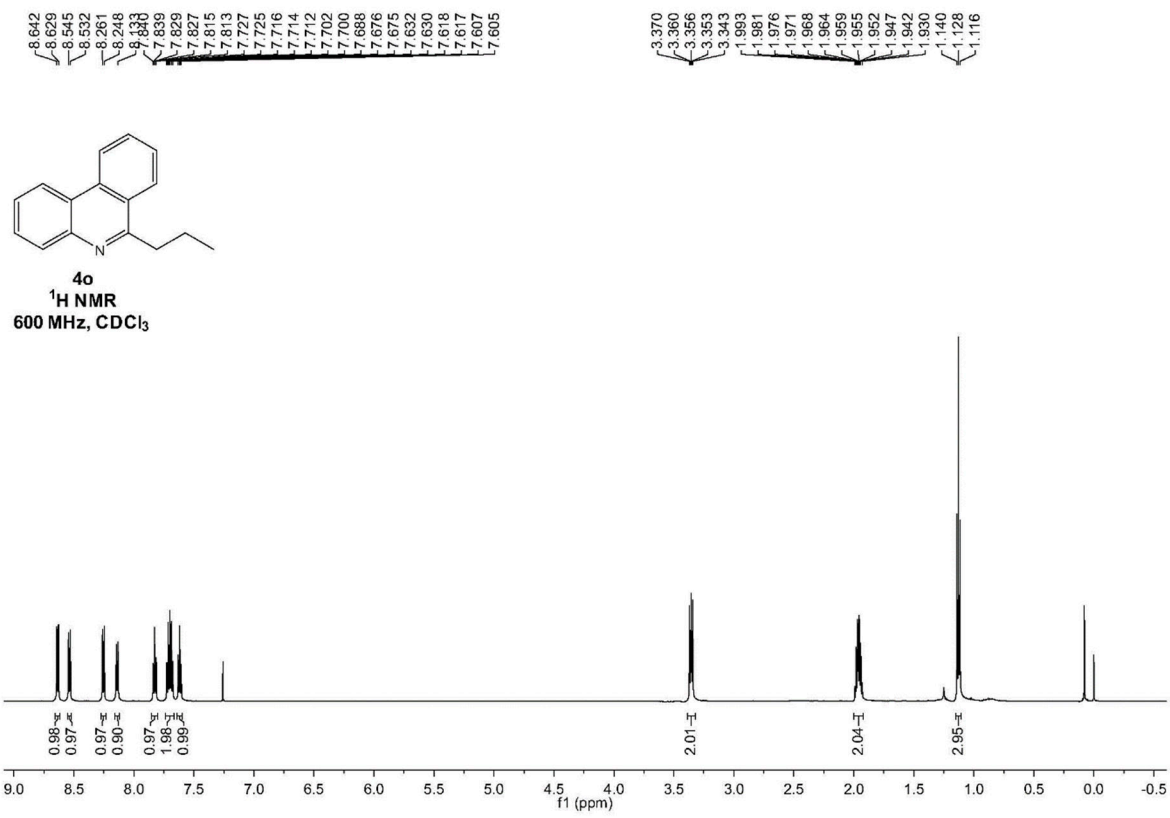


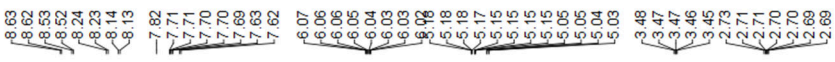


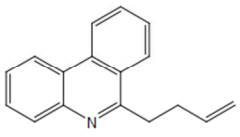


4m
^{1}H NMR
600 MHz, $CDCl_3$

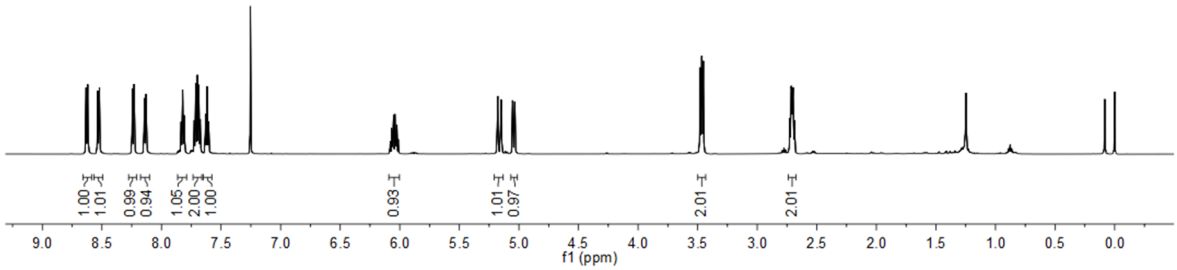

8.620
8.606
8.524
8.510
8.239
8.225
8.134
8.121
7.815
7.803
7.802
7.790
7.713
7.711
7.700
7.688
7.686
7.683
7.670
7.658
7.612
7.598
7.587
3.366
3.353
3.339
1.918
1.914
1.905
1.900
1.896
1.892
1.879
1.289
1.276
1.267
1.244
0.885
0.874
0.862
N
4n
1H NMR
600 MHz, CDCl3
1.00
1.00
0.97
0.92
0.98
2.06
1.00
1.99
2.00
1.99
2.08
26.68
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

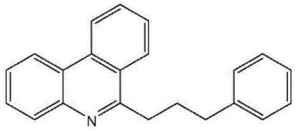

8.642
8.629
8.545
8.532
8.261
8.248
8.133
8.120
7.839
7.829
7.827
7.815
7.813
7.727
7.725
7.716
7.714
7.712
7.702
7.700
7.688
7.676
7.675
7.632
7.630
7.618
7.617
7.607
7.605
3.370
3.360
3.356
3.353
3.343
1.993
1.981
1.976
1.971
1.968
1.964
1.959
1.955
1.952
1.947
1.942
1.930
1.140
1.128
1.116
N
4o
1H NMR
600 MHz, CDCl3
0.98
0.97
0.97
0.90
0.97
1.98
0.99
2.01
2.04
2.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



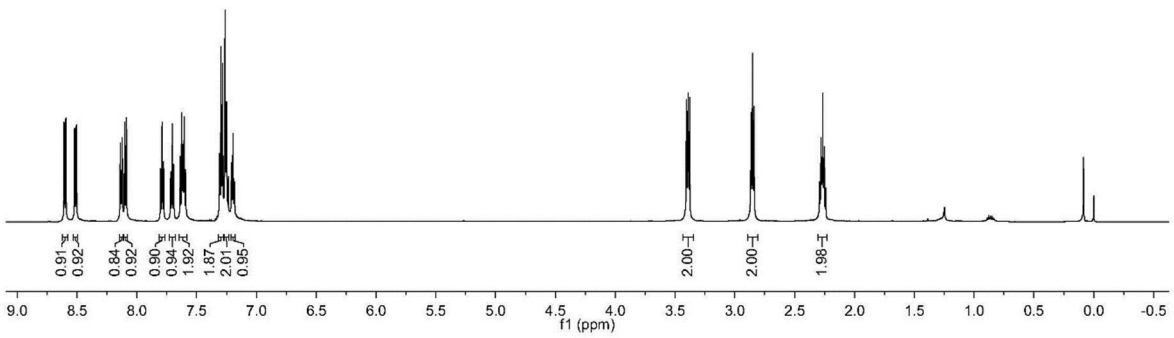


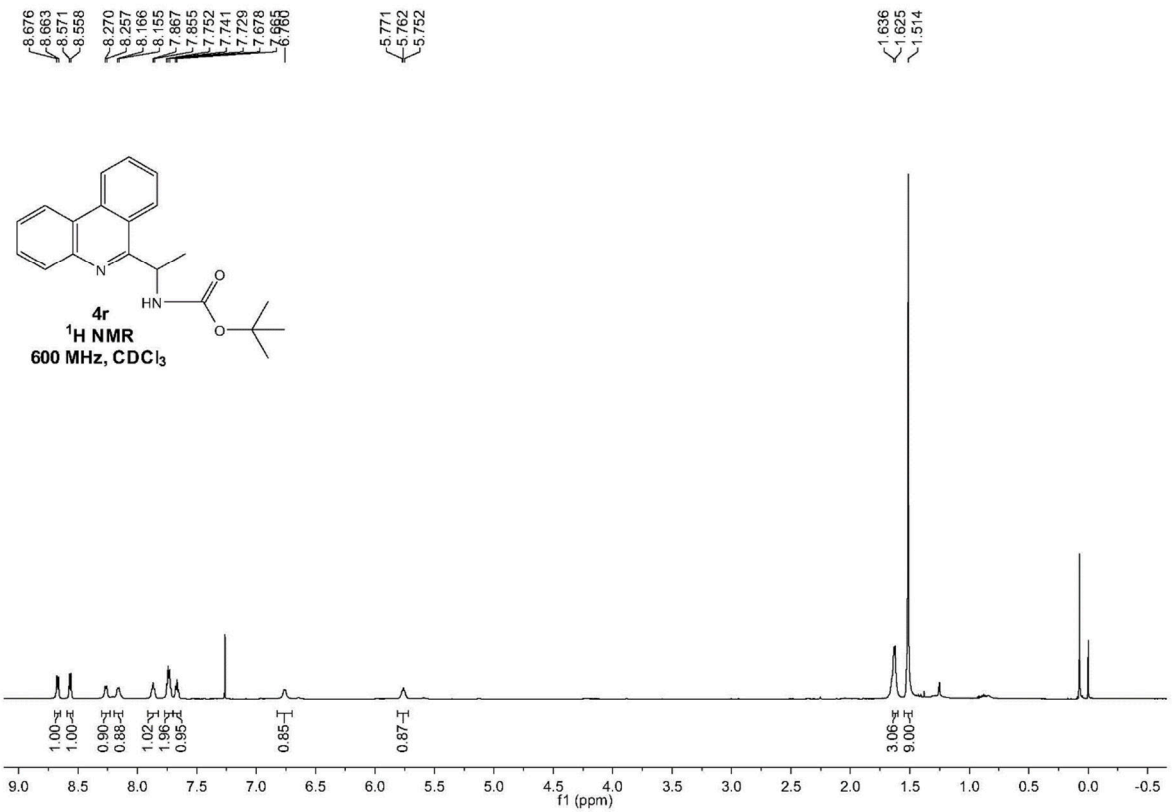
4p
^{1}H NMR
600 MHz, $CDCl_3$



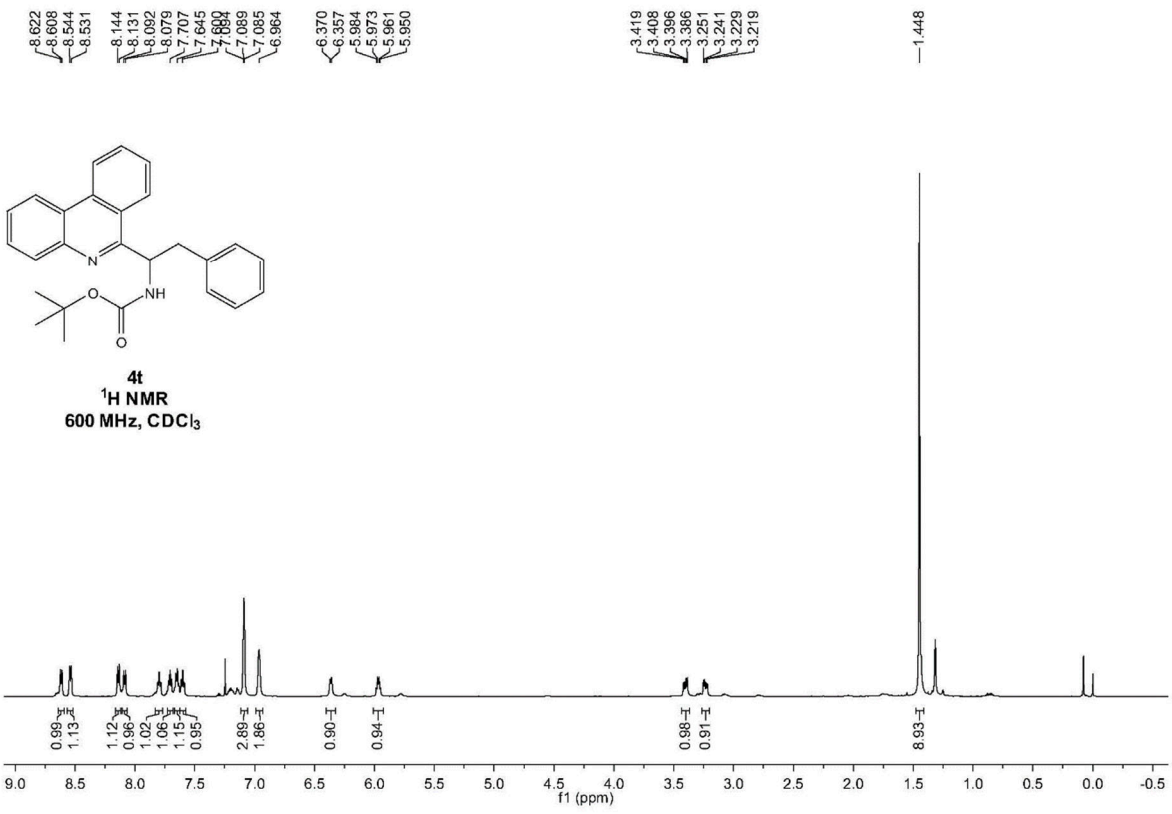


4q
^{1}H NMR
600 MHz, $CDCl_3$

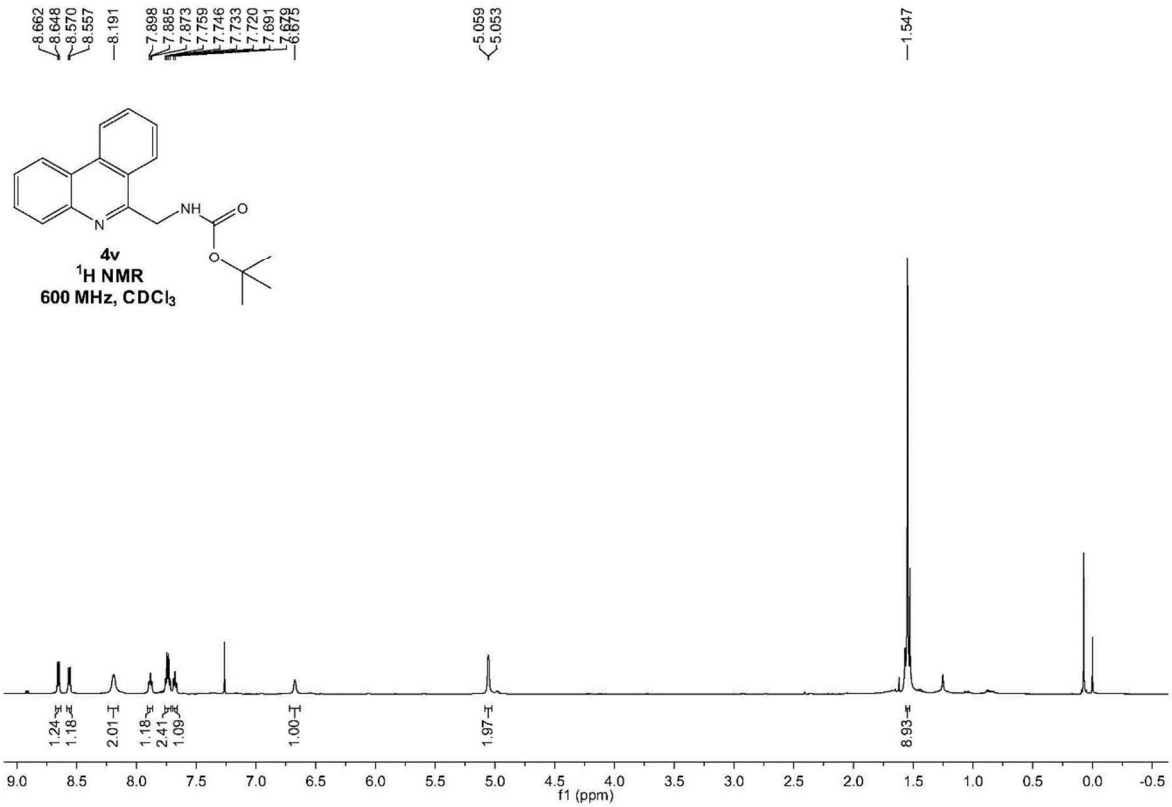


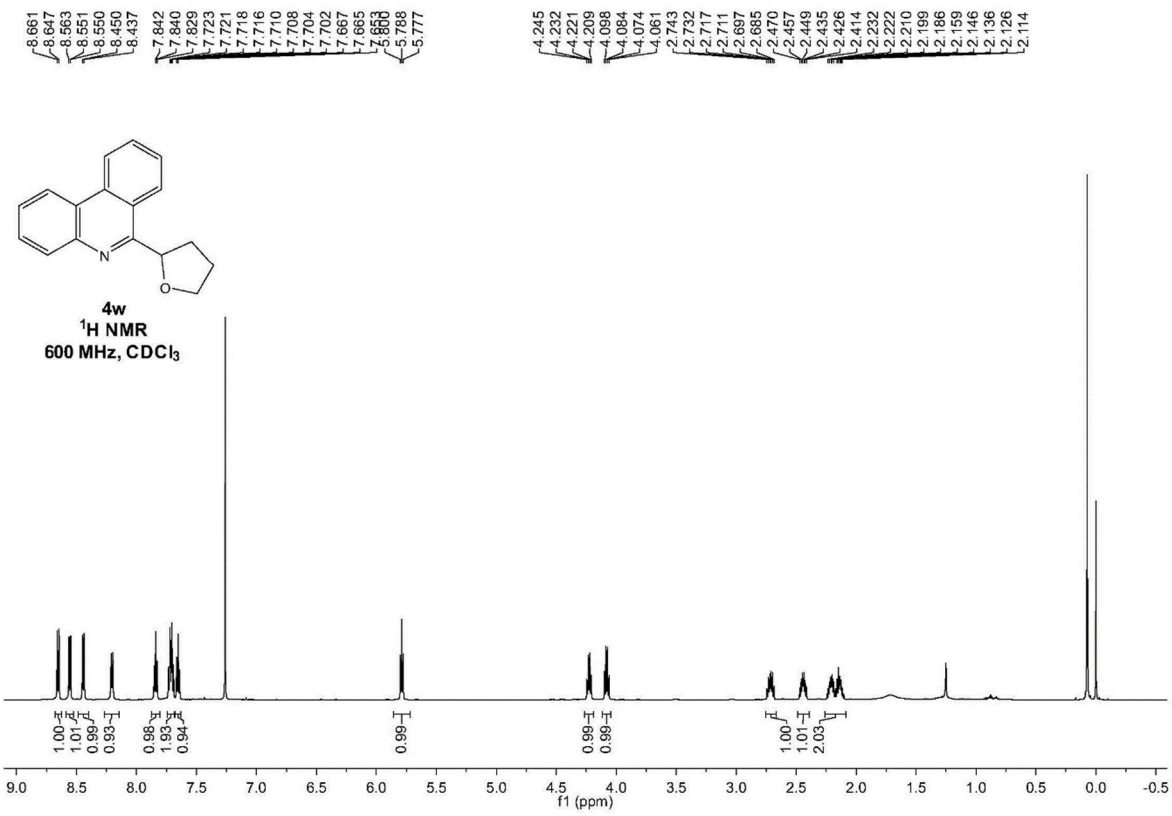


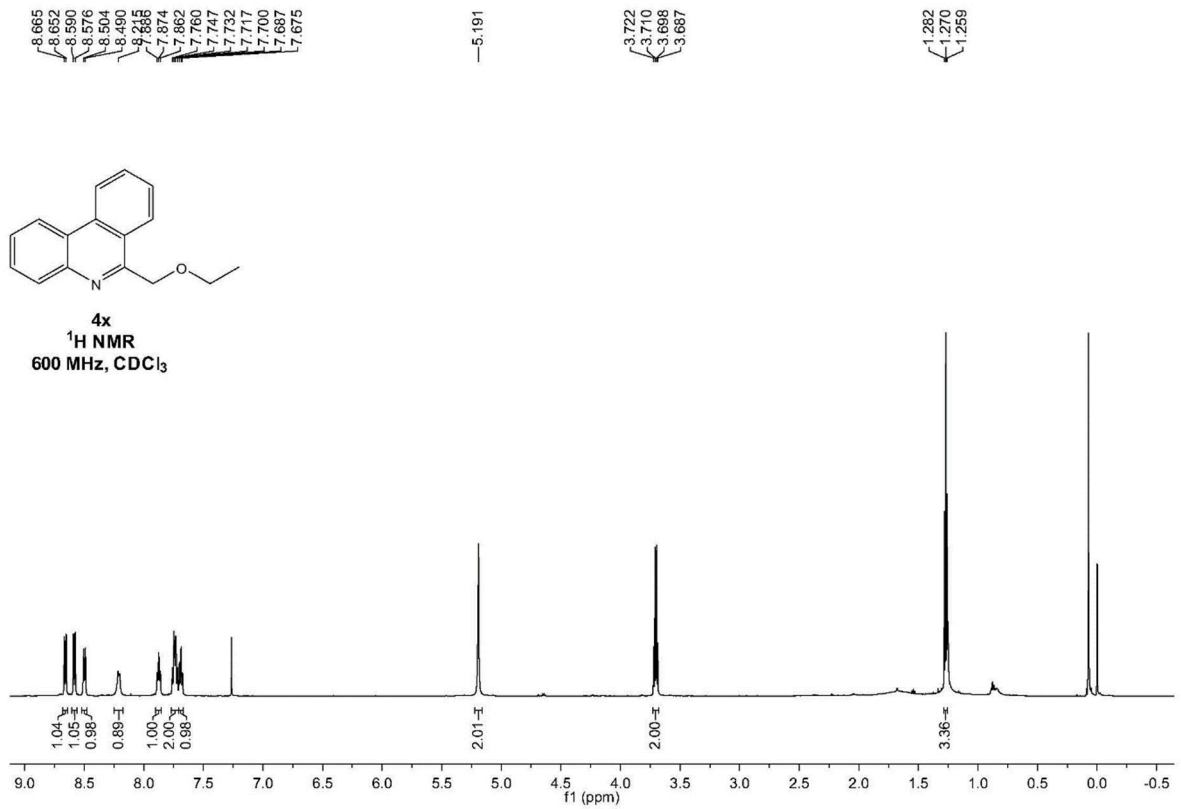
4r
^{1}H NMR
600 MHz, $CDCl_3$



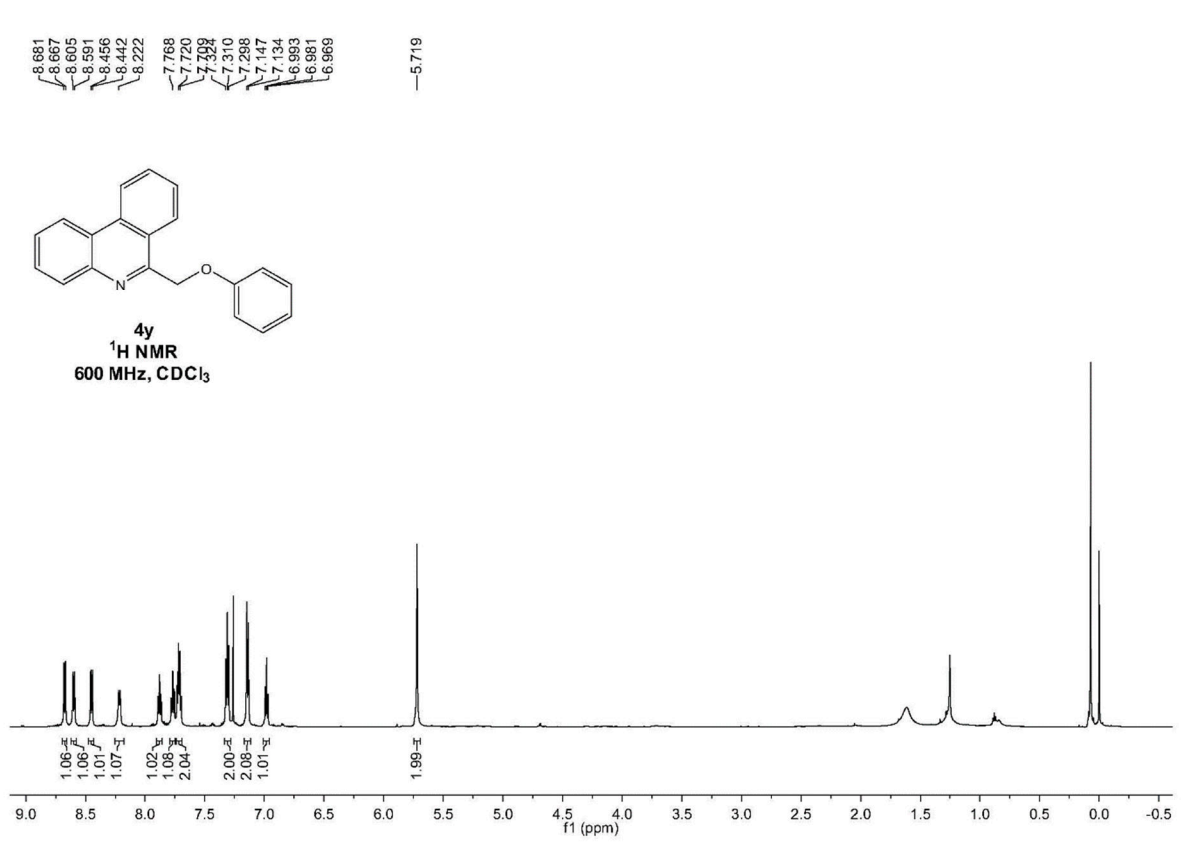
4t
^{1}H NMR
600 MHz, $CDCl_3$


8.662
8.648
8.570
8.557
8.191
7.898
7.885
7.873
7.759
7.746
7.733
7.720
7.691
5.059
5.053
1.547
NH
O
N
O
4v
1H NMR
600 MHz, CDCl3
1.24
1.18
2.01
1.18
2.41
1.09
1.00
1.97
8.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

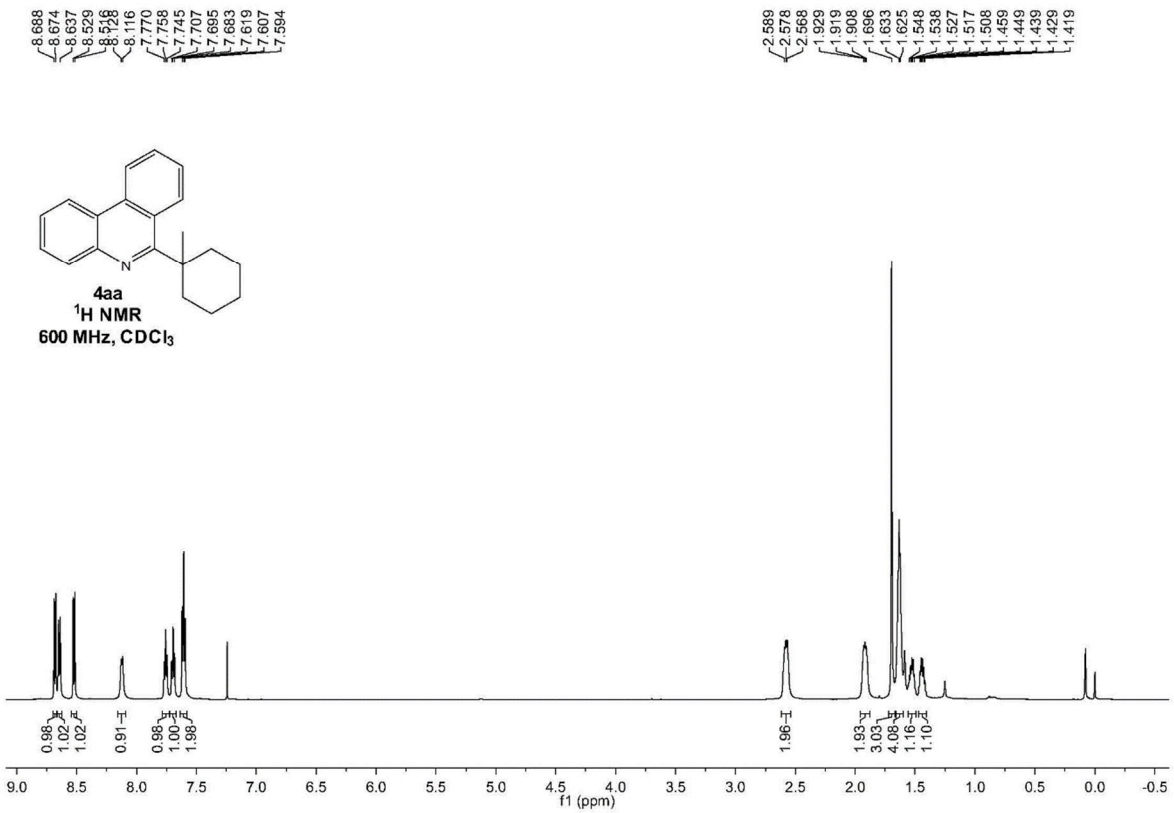

8.661
8.647
8.563
8.551
8.550
8.450
8.437
7.842
7.840
7.829
7.723
7.721
7.718
7.716
7.710
7.708
7.704
7.702
7.667
7.665
5.788
5.777
4.245
4.232
4.221
4.209
4.098
4.084
4.074
4.061
2.743
2.732
2.717
2.711
2.697
2.685
2.470
2.457
2.449
2.435
2.426
2.414
2.232
2.222
2.210
2.199
2.186
2.159
2.146
2.136
2.126
2.114
O
N
O
4w
1H NMR
600 MHz, CDCl3
1.00
1.01
0.99
0.93
0.98
1.93
0.94
0.99
0.99
0.99
1.00
1.01
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

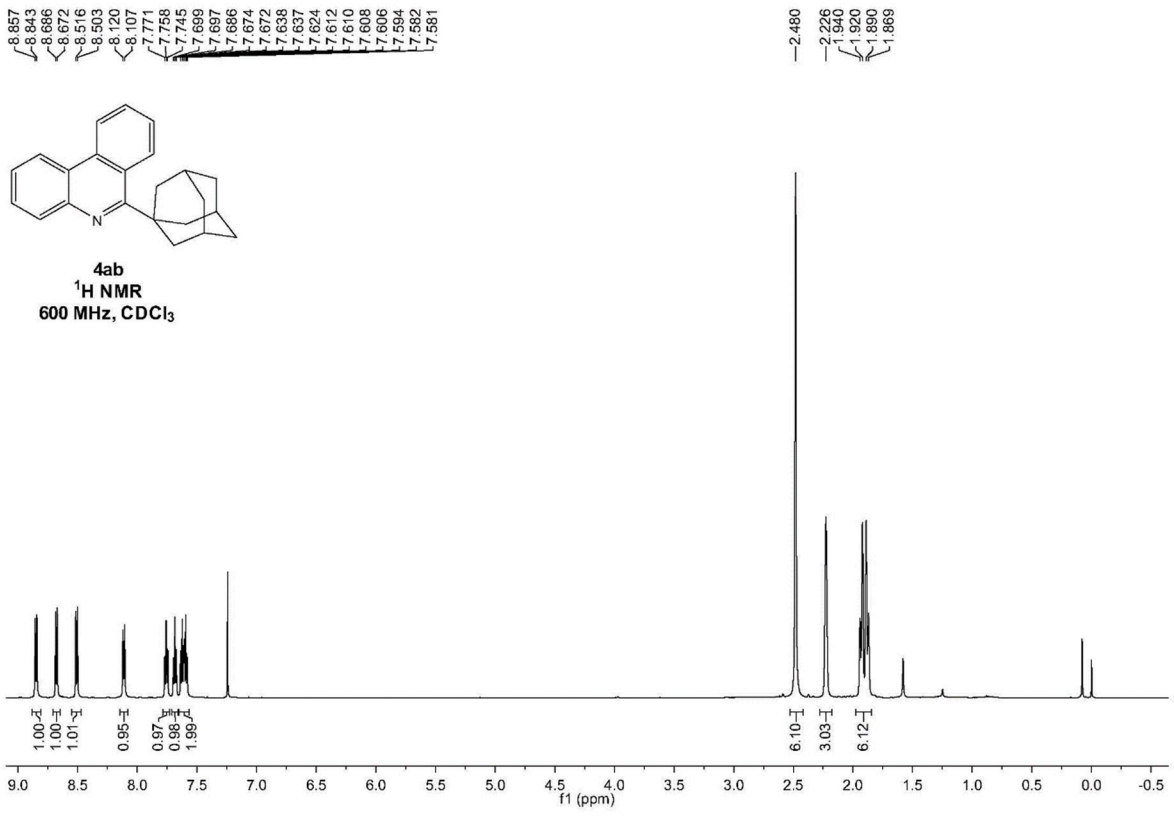


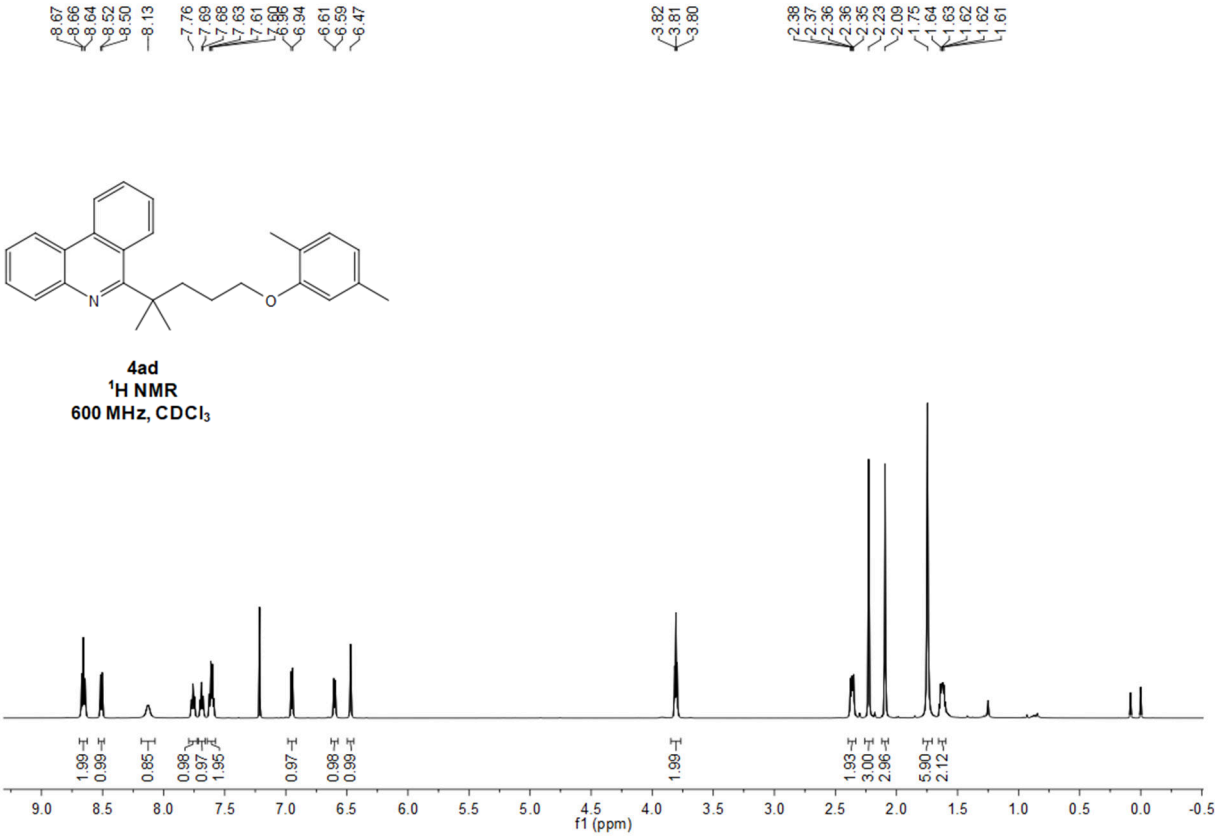
4x
^{1}H NMR
600 MHz, $CDCl_3$

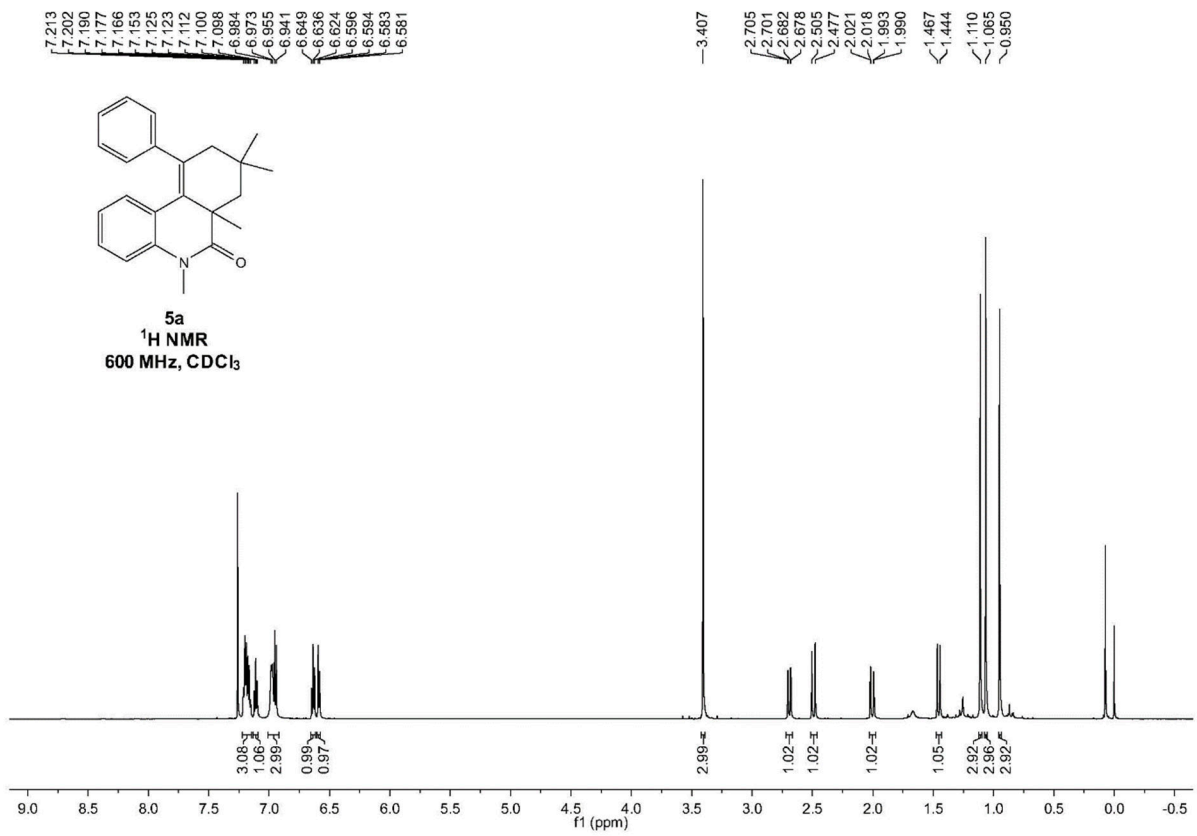


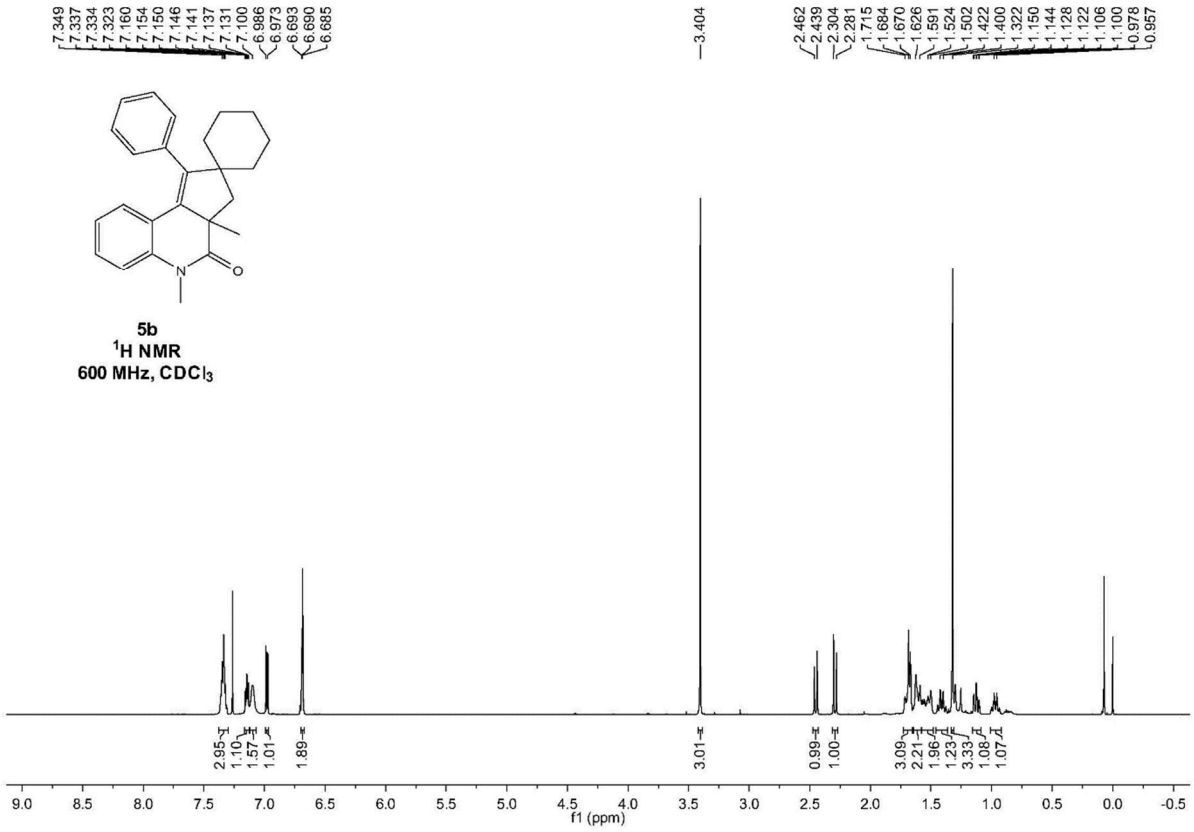
4y
^{1}H NMR
600 MHz, $CDCl_3$


8.688
8.674
8.637
8.529
8.116
7.770
7.758
7.745
7.707
7.695
7.683
7.619
7.607
7.594
2.589
2.578
2.568
1.929
1.919
1.908
1.696
1.633
1.625
1.548
1.538
1.527
1.517
1.508
1.459
1.449
1.439
1.429
1.419
4aa
1H NMR
600 MHz, CDCl3
0.98
1.02
1.02
0.91
0.98
1.00
1.98
1.96
1.93
3.03
4.08
1.16
1.10
f1 (ppm)

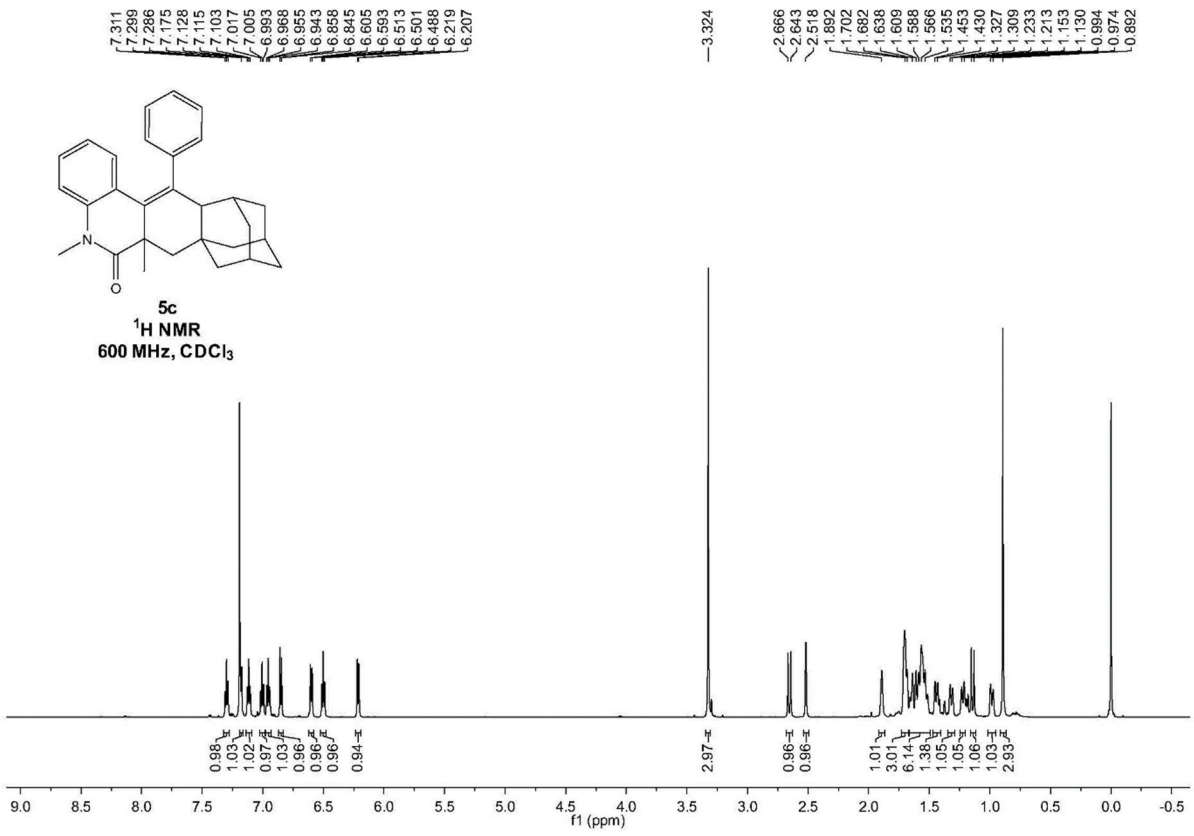

8.857
8.843
8.686
8.672
8.516
8.503
8.120
8.107
7.771
7.758
7.745
7.699
7.697
7.686
7.674
7.672
7.638
7.637
7.624
7.612
7.610
7.608
7.606
7.594
7.582
7.581
2.480
2.226
1.940
1.920
1.890
1.869
4ab
1H NMR
600 MHz, CDCl3
1.00
1.00
1.01
0.95
0.97
0.98
1.99
6.10
3.03
6.12
f1 (ppm)


8.67
8.66
8.64
8.52
8.50
8.13
7.76
7.69
7.68
7.63
7.61
7.60
6.96
6.94
6.61
6.59
6.47
3.82
3.81
3.80
2.38
2.37
2.36
2.36
2.35
2.23
2.09
1.75
1.64
1.63
1.62
1.62
1.61
N
O
4ad
1H NMR
600 MHz, CDCl3
1.99
0.99
0.85
0.98
0.97
1.95
0.97
0.98
0.99
1.99
1.93
3.00
2.96
5.90
2.12
f1 (ppm)

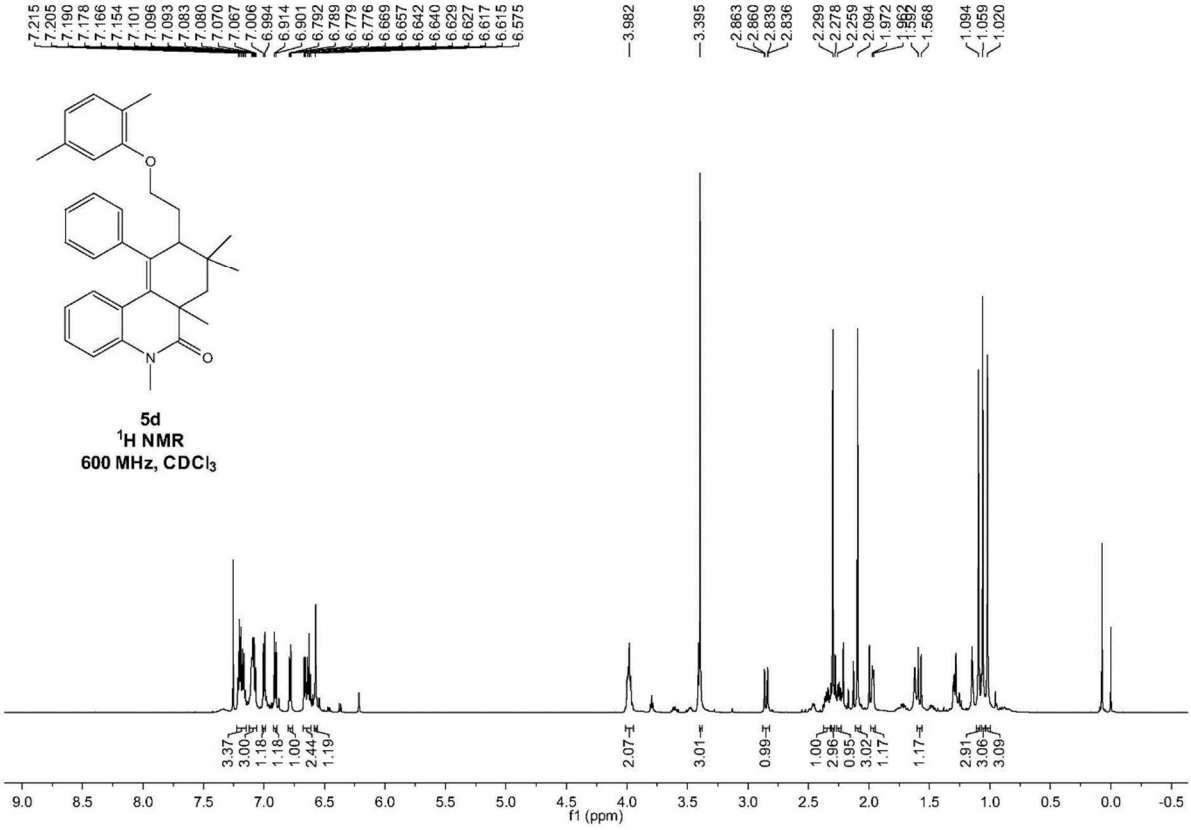

7.213
7.202
7.190
7.177
7.166
7.153
7.125
7.123
7.112
7.100
7.098
6.984
6.973
6.955
6.941
6.649
6.636
6.624
6.596
6.594
6.583
6.581
3.407
2.705
2.701
2.682
2.678
2.505
2.477
2.021
2.018
1.993
1.990
1.467
1.444
1.110
1.065
0.950
N
O
5a
1H NMR
600 MHz, CDCl3
3.08
1.06
2.99
0.99
0.97
2.99
1.02
1.02
1.02
1.05
2.92
2.96
2.92
f1 (ppm)



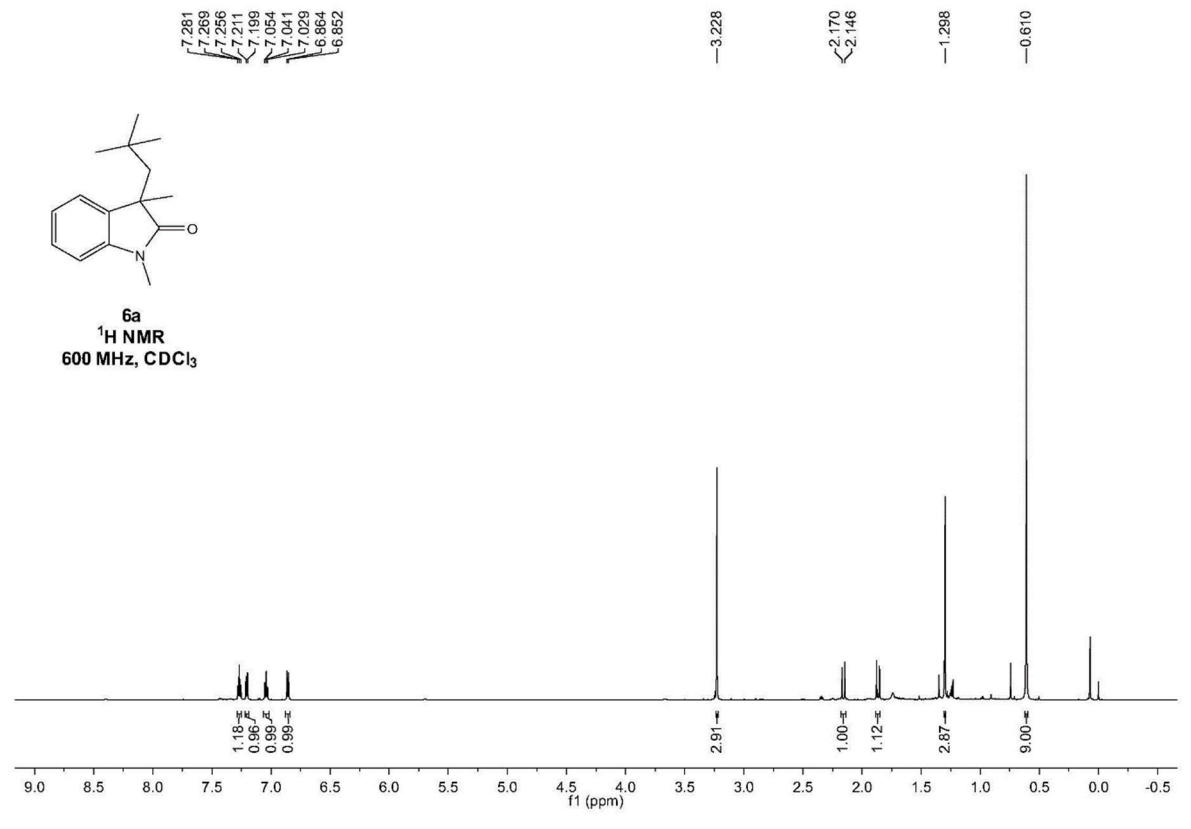
5b
^{1}H NMR
600 MHz, $CDCl_3$



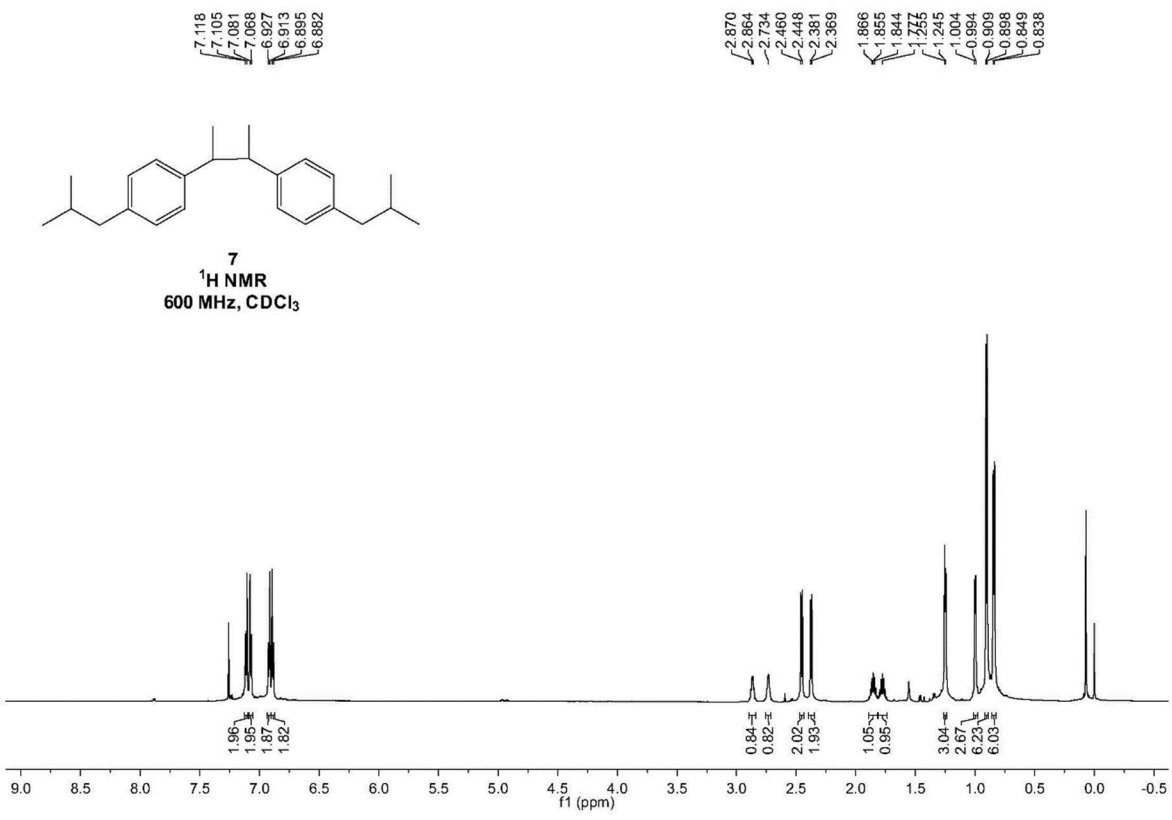
5c
^{1}H NMR
600 MHz, $CDCl_3$



5d
^{1}H NMR
600 MHz, $CDCl_3$



6a
^{1}H NMR
600 MHz, $CDCl_3$


7.118
7.105
7.081
7.068
6.927
6.913
6.895
6.882
2.870
2.864
2.734
2.460
2.448
2.381
2.369
1.866
1.855
1.844
1.245
1.004
0.994
0.909
0.898
0.849
0.838
7
1H NMR
600 MHz, CDCl3
1.96
1.95
1.87
1.82
0.84
0.82
2.02
1.93
1.05
0.95
3.04
2.67
6.23
6.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)