nature catalysis

Article

https://doi.org/10.1038/s41929-022-00886-0

Mild and metal-free Birch-type hydrogenation of (hetero)arenes with boron carbonitride in water

In the format provided by the authors and unedited

Table of Contents

Supplementary Methods……4

General considerations....4

Synthesis of starting materials....5

Characterization data of BCN photocatalysts....8

Photochemical reaction devices....12

Reaction condition optimization....13

The apparent quantum efficiency (AQE) analysis....17

The gram-scale reaction setup....18

Quadratic dependency of the product yield on irradiation density....19

Fluorescence quenching experiments....21

Elimination unimolecular conjugate base (E1cB) reaction....24

Deuterium-labeling experiment....25

Characterization data for products....28

Photocatalytic hydrodehalogenation of alkyl chloride....50

Photocatalytic reductive intramolecular cyclization of alkyl chloride....51

NMR spectra of substrate....54

NMR spectra of product....60

Supplementary References……52

Supplementary Notes

Supplementary Note 1. Solid-state NMR data analysis....10

Supplementary Note 2. Fourier transform infrared (FT-IR) spectroscopy of BCN for isoquinoline adsorption....16

Supplementary Note 3. DFT calculations....23

Supplementary Tables

Supplementary Table 1. The BET surface areas and pore structures of BCN-x....9

Supplementary Table 2. CP-MAS ^{11}B NMR deconvolution data of BCN-x....10

Supplementary Table 3. Optimization of BCN-x photocatalyst. 14
Supplementary Table 4. Optimization of reductant. 14
Supplementary Table 5. Optimization of solvent. 15
Supplementary Table 6. Wavelength dependence of AQE for hydrogenation of **1a**. 17
Supplementary Table 7. Time dependence of AQE for **1a** hydrogenation under 450 nm LEDs illumination. 18
Supplementary Table 8. Comparison of this work with Na-SG and other known methods. 27

Supplementary Figures

Supplementary Figure 1. Preparation procedure and structure diagram of BCN-x. 5
Supplementary Figure 2. The XRD patterns of BCN-x. 8
Supplementary Figure 3. N_2 physical adsorption and desorption analysis of BCN-x. 8
Supplementary Figure 4. XPS survey spectrum of BCN-3. 9
Supplementary Figure 5. Solid-state NMR spectra of BCN-x. 10
Supplementary Figure 6. FT-IR spectra of BCN-x. 12
Supplementary Figure 7. UV-Vis DRS spectra of BCN-x. 12
Supplementary Figure 8. Photograph of the photochemical reaction device. 13
Supplementary Figure 9. Photographs of the reaction mixtures. 16
Supplementary Figure 10. FT-IR spectra of BCN for isoquinoline adsorption 17
Supplementary Figure 11. Photochemical reactor used for larger-scale hydrogenation reaction. 19
Supplementary Figure 12. The XRD patterns of BCN before and after gram-scale production. 19
Supplementary Figure 13. The control and measurement of light intensity. 20
Supplementary Figure 14. Time-resolved fluorescence (FL) decay spectrum of BCN 21
Supplementary Figure 15. FL spectra of BCN upon successive addition of isoquinoline in suspension 21
Supplementary Figure 16. FL spectra of BCN upon successive addition of DIPEA in suspension 22
Supplementary Figure 17. Cyclic voltammograms of substrate and additive. 22
Supplementary Figure 18. DFT calculations of anthracene hydrogenation on BCN. 23
Supplementary Figure 19. E1cB reaction and possible reaction pathway. 24
Supplementary Figure 20. ^{1}H NMR spectrum of deuterated **2a'** in $CDCl_3$ 25
Supplementary Figure 21. Energy scheme for the triplet sensitization of anthracene on BCN. 26
Supplementary Figure 22. List of failed or inferior substrates for Birch reduction 26

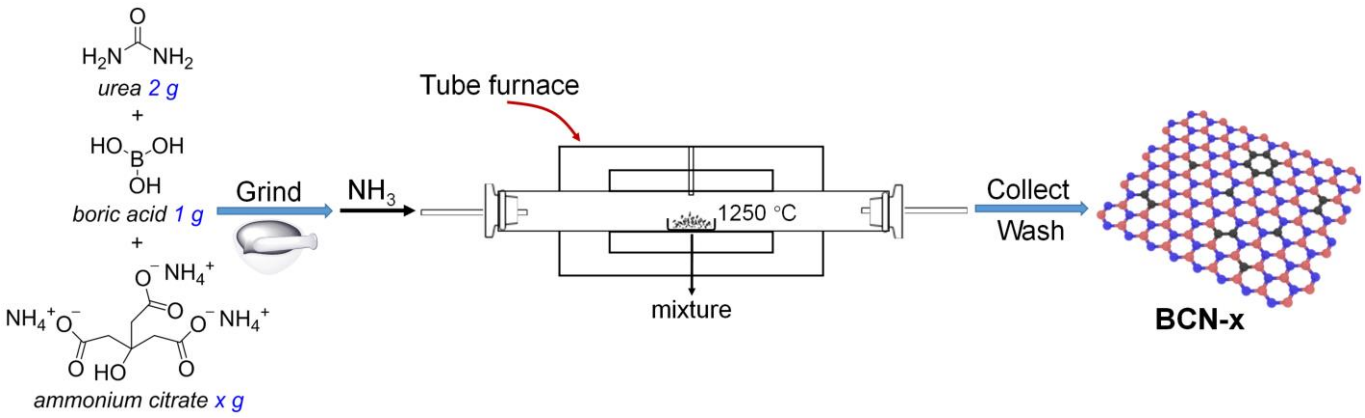
Supplementary Figure 23. ^{1}H NMR spectrum of the mixture of **2j** + **2j'** 41
Supplementary Figure 24. ^{1}H NMR spectrum of the mixture of **2k** + **2k'**.....42
Supplementary Figure 25. ^{1}H and ^{19}F NMR spectra of reaction mixture containing **2n**.....43
Supplementary Figure 26. ^{1}H NMR spectrum of the mixture of **2o** + **2o'**. 44
Supplementary Figure 27. ^{1}H NMR spectrum of the mixture of **2q** + **2q'**.....45
Supplementary Figure 28. GC-MS spectra of reaction mixture containing **2s**.....46
Supplementary Figure 29. ^{1}H NMR spectrum of the mixture of **1aj** + **2aj** + **2aj'**.....47
Supplementary Figure 30. ^{1}H NMR spectrum of reaction mixture containing **2ap**. 48
Supplementary Figure 31. ^{1}H NMR spectrum of reaction mixture containing **2aq**. 49
Supplementary Figure 32. ^{1}H NMR spectrum of reaction mixture containing **2ar** 50
Supplementary Figure 33. GC-MS spectra of reaction mixture containing **3b**. 51

Supplementary Methods

General considerations

Unless otherwise noted, reagents and solvents were used as commercially available without further treatment. Thin-layer chromatography (TLC) was performed using silica gel plates 60 F254: Visualization was accomplished with short wavelength UV light (254 nm) sources. Gas chromatography mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer and a TR-5MS column (0.25 mm × 30 m, Film: 0.25 μm). The reaction mixture of benzene hydrogenation was analyzed by GC (Shimadzu 2030) with a flame ionization detector (FID). Column chromatographic purification of products was accomplished using 300-400 mesh silica gel. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance spectrometers (600 MHz, 151 MHz) in $CDCl_3$ solutions with internal solvent signals (for ^{1}H and ^{13}C) as reference (7.26, 77.2 for $CDCl_3$). ^{1}H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz), and numbers of protons. Data for ^{13}C NMR are reported in terms of chemical shift, multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and no special nomenclature is used for equivalent carbons. ^{19}F data are reported as follows: chemical shift (ppm), multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and numbers of fluorines (wherever applicable).

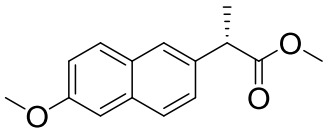
Solid-state nuclear magnetic resonance (SSNMR) experiments were performed on a Bruker Avance III 400 NMR spectrometer equipped with a 9.4 T magnet using a 4 mm magic angle spinning (MAS) probe with a spinning rate of 12 kHz. The resonance frequencies were 128.4 and 40.5 MHz for ^{11}B and ^{15}N, respectively. ^{11}B MAS NMR spectra were recorded using a one pulse sequence. 100 scans were accumulated with 4 s recycle delay. Chemical shifts were referenced to 1 M H_3BO_3 aqueous solution at 19.6 ppm. ^{15}N CP/MAS NMR spectra were also recorded using the cross-polarization sequence. 40960 scans were accumulated with 4 s recycle delay. Chemical shifts were referenced to glycine at 33.4 ppm.



Supplementary Figure 1. Preparation procedure and structure diagram of BCN-x.

Synthesis of starting materials

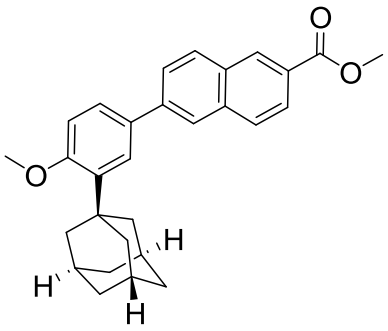
Synthesis of methyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**1aj**, methyl ester of naproxen):



To a methanol solution (15 mL) of (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (naproxen, 0.25 g, 1.1 mmol) was added 3 drops of conc. H_2SO_4 and the reaction mixture was stirred for 4 h at 60 ℃ before it was diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ aq. solution and dried over Na_2SO_4. Solvent was evaporated under reduced pressure to afford the esterification product **1aj** (0.23 g, 86% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.71 (s, 1H), 7.67 (d, J = 1.7 Hz, 1H), 7.41 (dd, J = 8.4, 1.7 Hz, 1H), 7.15 (dd, J = 8.9, 2.5 Hz, 1H), 7.12 (d, J = 2.5 Hz, 1H), 3.91 (s, 3H), 3.87 (q, J = 7.2 Hz, 1H), 3.68 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.26, 157.78, 135.80, 133.83, 129.39, 129.06, 127.29, 126.30, 126.05, 119.10, 105.74, 55.41, 52.13, 45.47, 18.70. MS (m/z, EI): 244, 185, 170, 154, 141, 115, 92.

Synthesis of methyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (**1ak**, methyl ester of adapalene):

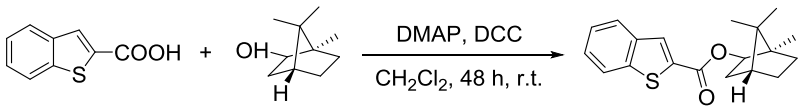


To a methanol solution (15 mL) of 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid (adapalene, 0.45 g, 1.1 mmol) was added 3 drops of conc. H_2SO_4 and the reaction mixture was stirred for 4 h at 60 ℃ before it was diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ aq. solution and dried over Na_2SO_4. Solvent was evaporated under reduced pressure to afford the esterification product **1ak** (0.37 g, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.01 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 2.19 (d, *J* = 2.6 Hz, 6H), 2.11 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.48, 159.04, 141.52, 139.11, 136.07, 132.67, 131.35, 130.97, 129.83, 128.35, 127.02, 126.62, 126.11, 125.86, 125.69, 124.86, 112.21, 55.29, 52.35, 40.72, 37.33, 37.25, 29.22. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{29}H_{31}O_3^+$, 427.2268; found, 427.2270.

Synthesis of esters **1al-1an**:

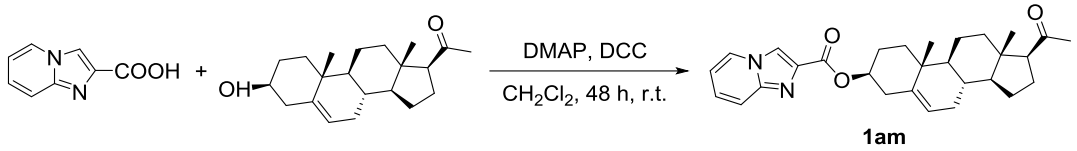
The series of the compounds was synthesized using slightly modified esterification conditions reported in the literature[1]. 4-Dimethylaminopyridine (DMAP, 61 mg, 0.5 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC, 1.0 g, 5.0 mmol), aromatic acid (5.0 mmol) and the corresponding bioactive alcohol or phenol (3.8 mmol) were weight into a 100 mL crimp vial. Then dichloromethane (30 mL) and magnetic stirring bar were added. The reaction vial was sealed, and the reaction mixture was stirred at room temperature for 48 h. After reaction, the reaction mixture was filtered and the organic phase was washed with water, 5% acetic acid, saturated sodium bicarbonate solution, water, and brine and then dried over anhydrous sodium sulfate. Silica gel was added to the combined organic phases which contained a crude product and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the product.



1al

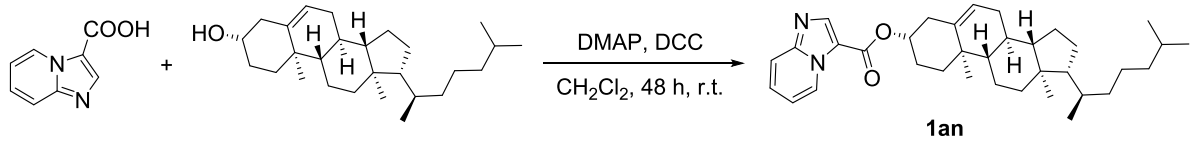
The compound **1al** was obtained following the procedure from benzo[*b*]thiophene-2-carboxylic acid (0.89 g, 5.0 mmol) and (1*R*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (isoborneol, 0.59 g, 3.8 mmol). The crude product was purified by flash chromatography (PE: EA = 30: 1, v: v) to give 0.81 g of pale yellow solid. Isolated yield = 68%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 0.8 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.38 (m, 1H), 4.93 (dd, *J* = 7.4, 4.2 Hz, 1H), 1.94 (dd, *J* = 7.3, 3.4 Hz, 2H),

1.82 (t, *J* = 4.0 Hz, 1H), 1.75 (tq, *J* = 10.9, 3.3 Hz, 1H), 1.65 – 1.60 (m, 1H), 1.27 – 1.20 (m, 1H), 1.17 – 1.12 (m, 4H), 0.96 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.38, 142.28, 138.89, 134.49, 130.17, 126.93, 125.59, 124.96, 122.84, 82.35, 49.25, 47.17, 45.21, 38.91, 33.73, 27.18, 20.27, 20.16, 11.69. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{19}H_{23}O_2S^+$, 315.1413; found, 315.1406.



1am

The compound **1am** was obtained following the procedure from imidazo[1,2-*a*]pyridine-2-carboxylic acid (0.81 g, 5.0 mmol) and 1-((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-17-yl)ethan-1-one (pregnenolone, 1.2 g, 3.8 mmol). The crude product was purified by flash chromatography (PE: EA = 1: 2, v: v) to give 1.2 g of white solid. Isolated yield = 70%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.12 (dt, *J* = 6.9, 1.0 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.85 (td, *J* = 6.8, 1.0 Hz, 1H), 5.41 – 5.37 (m, 1H), 4.94 (tt, *J* = 11.4, 4.8 Hz, 1H), 2.59 – 2.50 (m, 2H), 2.50 – 2.45 (m, 1H), 2.20 – 2.13 (m, 1H), 2.11 (s, 3H), 2.06 – 1.99 (m, 2H), 1.94 – 1.88 (m, 2H), 1.87 – 1.79 (m, 1H), 1.71 – 1.59 (m, 4H), 1.59 – 1.54 (m, 1H), 1.52 – 1.43 (m, 3H), 1.24 – 1.11 (m, 3H), 1.03 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 209.72, 162.87, 145.36, 139.78, 137.22, 126.21, 126.13, 122.53, 119.21, 117.10, 113.93, 74.68, 63.77, 56.91, 49.96, 44.08, 38.87, 38.15, 37.15, 36.74, 31.90, 31.86, 31.66, 27.81, 24.56, 22.87, 21.12, 19.42, 13.31. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{29}H_{37}N_2O_3^+$, 461.2799; found, 461.2797.

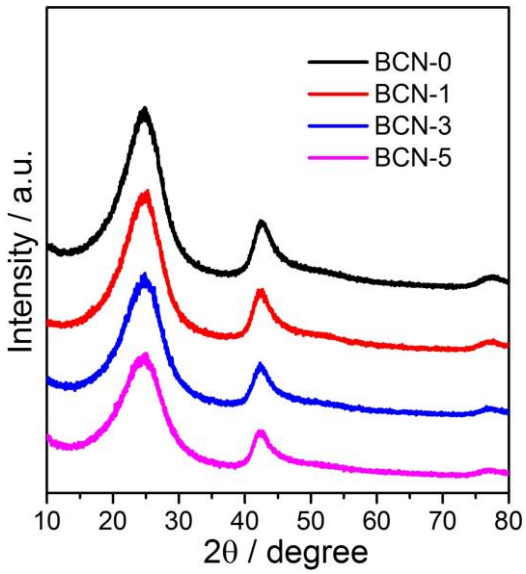


1an

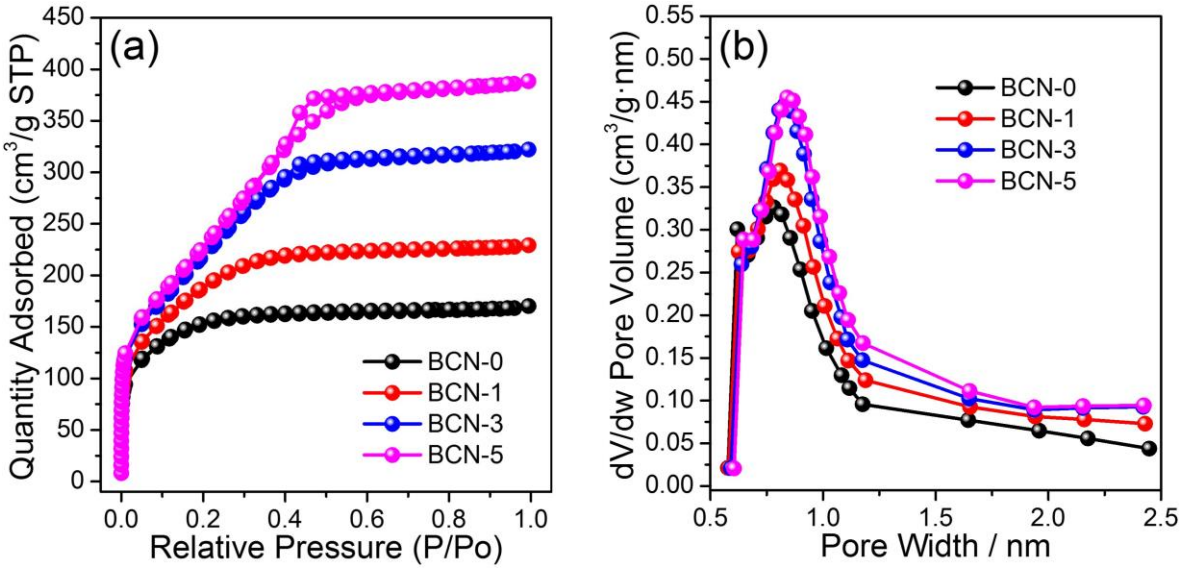
The compound **1an** was obtained following the procedure from imidazo[1,2-*a*]pyridine-3-carboxylic acid (0.81 g, 5.0 mmol) and (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-ol (*β*-cholesterol, 1.5 g, 3.8 mmol). The crude product was purified by flash chromatography (PE: EA = 3: 1, v: v) to give 1.3 g of white solid. Isolated yield = 65%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.32 – 9.27 (m, 1H), 8.29 (d, *J* = 1.7 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.43 – 7.37 (m, 1H), 7.06 – 7.00 (m, 1H), 5.42 (d, *J* = 3.4 Hz, 1H), 4.89 (tt, *J* = 10.6, 5.4 Hz, 1H), 2.54 – 2.43 (m, 2H), 2.06 – 1.96 (m, 3H), 1.95 – 1.87 (m, 2H), 1.87 – 1.72 (m, 2H), 1.61 – 1.55 (m, 2H), 1.54 – 1.44 (m, 4H), 1.38 – 1.31 (m, 3H), 1.28 – 1.16 (m, 3H), 1.15 – 1.08 (m, 4H), 1.07 (d, *J* = 1.4 Hz, 3H), 1.03 – 0.95 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88 – 0.83 (m, 6H), 0.68 (d, *J* =

1.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.31, 148.54, 141.56, 139.70, 127.84, 127.53, 123.01, 117.99, 116.24, 114.29, 74.42, 56.82, 56.26, 50.17, 42.44, 39.85, 39.63, 38.50, 37.17, 36.78, 36.30, 35.92, 32.06, 31.99, 28.36, 28.14, 25.74, 24.41, 23.96, 22.95, 22.69, 21.18, 19.51, 18.84, 11.99. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{35}H_{51}N_2O_2^+$, 531.3945; found, 531.3950.

Characterization data of BCN photocatalysts



Supplementary Figure 2. The XRD patterns of BCN-x.



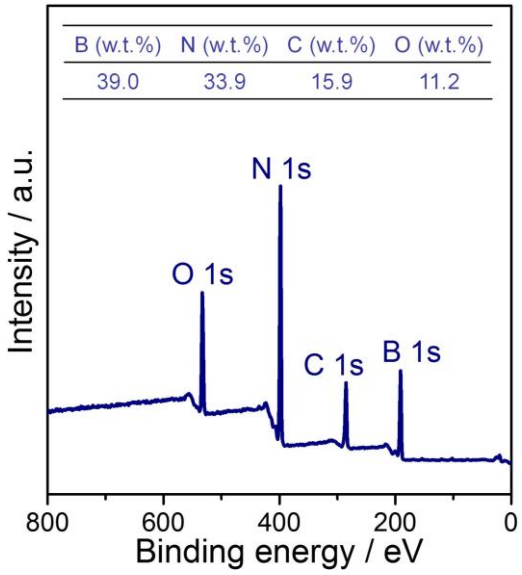
Supplementary Figure 3. N_2 physical adsorption and desorption analysis of BCN-x.

(a) N_2 physical adsorption and desorption isotherms and (b) the corresponding pore-size distribution curves.

Supplementary Table 1. The BET surface areas and pore structures of BCN-x.

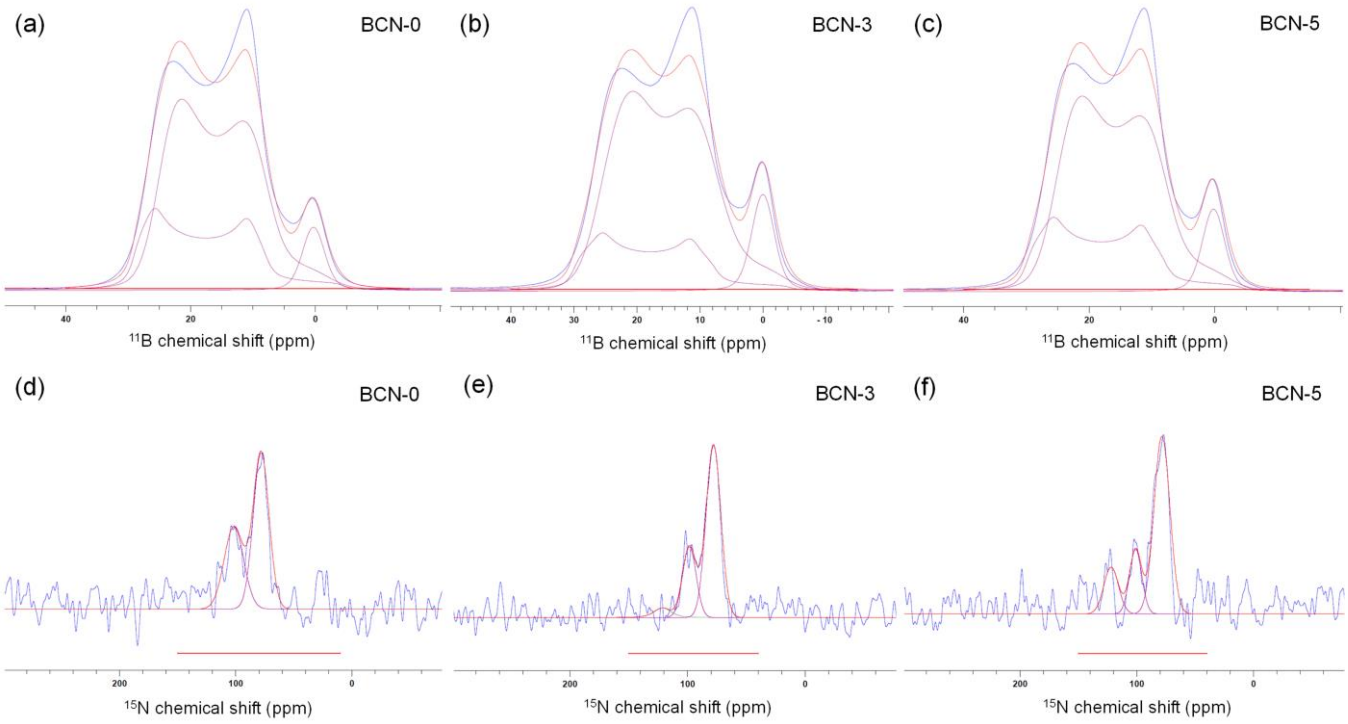
Sample	$S_{BET}(m^2/g)$	$V_p{}^a(cm^3/g)$	$V_{micro}{}^b(cm^3/g)$	*Pore Size*^{c}*(nm)*
BCN-0	499	0.26	0.23	2.1
BCN-1	665	0.35	0.31	2.1
BCN-3	830	0.49	0.44	2.4
BCN-5	870	0.60	0.54	2.7

[a] Total pore volume at $P/P_0 = 0.95$. [b]DFT total pore volume. [c]Average pore diameter calculated by BET.



Supplementary Figure 4. XPS survey spectrum of BCN-3.

Inset: the element contents of BCN-3 calculated from XPS survey spectrum.



Supplementary Figure 5. Solid-state NMR spectra of BCN-x.

(a-c) ^{11}B and (d-f) ^{15}N NMR spectra.

Supplementary Table 2. CP-MAS ^{11}B NMR deconvolution data of BCN-x.

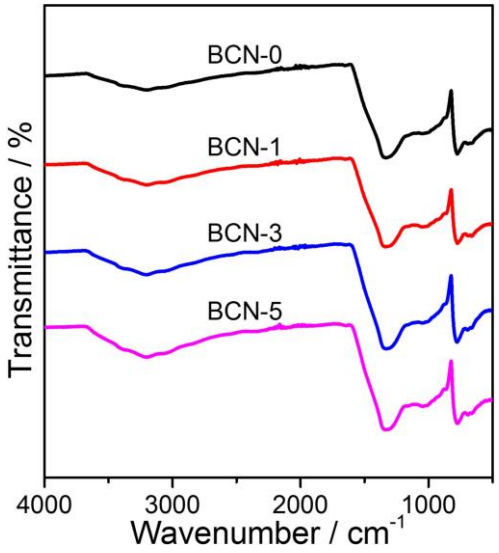
δ_{iso}	B-related species	BCN-0 boron composition	BCN-3 boron composition	BCN-5 boron composition
~28 ppm	$BN_2(OH)$	28.8%	20.7%	26.4%
~22 ppm	$BN(OH)_2$/ BNO(OH)	65.7%	71.2%	66.6%
~1 ppm	$BN_xO_y(OH)_{4-x-y}$/B–C	5.5%	8.1%	7.0%

Supplementary Note 1. Solid-state NMR data analysis

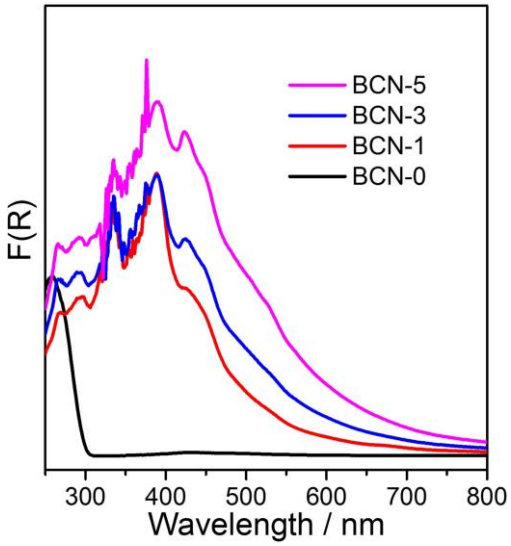
^{11}B solid-state NMR experiments were performed at 9.4 T on a 400 MHz Bruker Avance III system with HX probe. To identify the boron-related bonding of boron nanomaterials, the as obtained CP-MAS ^{11}B NMR spectra (Supplementary Figure 5a-c) were deconvoluted using topspin solid-line shaped analysis (SOLA)[2-5]. The solid-state ^{11}B NMR spectra of BCN-x exhibit three major peaks and δ_{iso} centered at ~28

ppm, ~22 ppm, and ~1 ppm, respectively. Based on previous literature studies on CP-MAS ^{11}B NMR of boron nitride and their related structures, the peak with a δ_{iso} of ~28 ppm likely arise from edge sites species with a single –OH group (trigonal-planar $BN_2(OH)$)[2,3]. Sites with lower δ_{iso} at ~22 ppm is attributed to another trigonal boron site with two hydroxyl groups or one hydroxyl group and one bridging oxygen atom ($BN(OH)_2$ or BNO(OH) sites). The sharp, well-resolved peak at δ_{iso} of ~1 ppm corresponds to a tetracoordinated B site, which coordinated with nitrogen and multiple hydroxyl groups or a bridging oxygen atom or C–B bonding[2,3,6]. The CP-MAS ^{11}B NMR analysis of BCN-x reveals the boron-related bonding composed of B–N, B–O, and B–C bonds, which is commensurate with the XPS analysis. Furthermore, solid-state ^{11}B NMR analysis also indicates that most boron (> 90%) is bonded with nitrogen and with one or more hydroxyl groups as the $BN_x(OH)_{3-x}$ species. These hydroxylated species are speculated to provide colloidal stability in the aqueous solution through hydrogen bonding[2]. Moreover, we observe the content of the trigonal-planar ($BN(OH)_2$ or BNO(OH) sites) and tetracoordinate B-species (Supplementary Table 2) is in consistent with the hydrogenation activity (Supplementary Table 3). BCN-3 with the highest content of the trigonal-planar ($BN(OH)_2$ or BNO(OH) sites) and tetracoordinate B-species, exhibits the prior hydrogenation activity among the BCN-x samples. The results imply that B–O/B–OH related chemical bonding in BCN-x samples may be responsible for the photocatalytic activity.

^{15}N solid-state NMR spectra (Supplementary Figure 5d-f) were deconvoluted using topspin solid-line shaped analysis (SOLA) as well. It has been established previously that ^{15}N solid-state NMR spectra of borazine-based compounds contain typical trigonal-planar δ_{iso} (^{15}N) signals at ~-266, ~-286, and ~-310 ppm, corresponding to the NB_2C, NB_3, and NB_2H environments (referenced to nitromethane)[3,5,7]. The signals at ~-266, ~-286, and ~-310 ppm (referenced to nitromethane) correspond to values at ~117.4, ~97.4, and ~73.4 ppm (referenced to glycine). Therefore, the signals at ~117.4, ~97.4, and ~73.4 ppm (referenced to glycine) are attributed to the NB_2C, NB_3, and NB_2H environments, respectively. Generally, ^{15}N is a spin 1/2 with a very low sensitivity in natural abundance, therefore, ^{15}N CP-MAS NMR experiments are not quantitative. It is difficult to estimate the relative proportion of NB_2C, NB_3, and NB_2H environments in BCN-x[7].



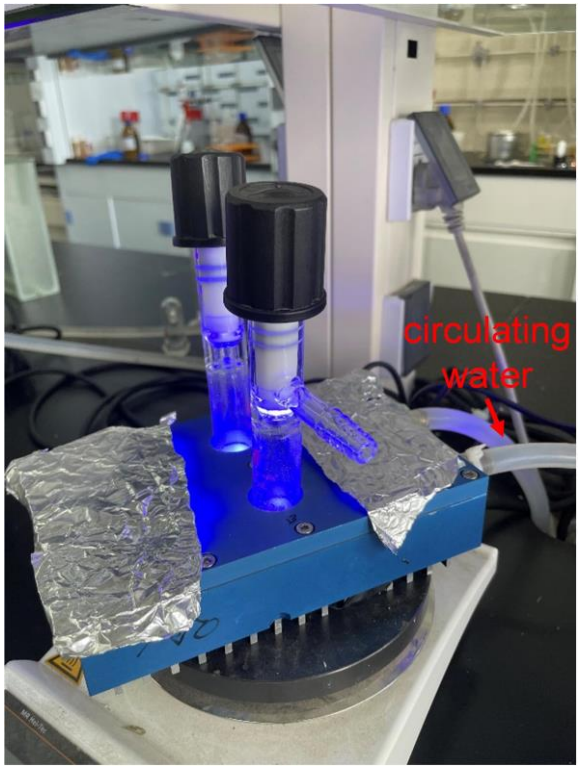
Supplementary Figure 6. FT-IR spectra of BCN-x.



Supplementary Figure 7. UV-Vis DRS spectra of BCN-x.

Photochemical reaction devices

Reactions were irradiated using a simple photoreactor consisting of Eaglerise ELP8X3LS 3W blue LEDs (λ = 450 nm), which was connected to HAAKE-FK cyclic water-cooling system. The reactor was illuminated from the bottom side. In order to ensure that the reactions are run near room temperature, a simple cooling fan was installed above the reactor to aid in dissipating the heat generated from both nonradioactive decay pathways of the excited state catalysts and the heat generated from the LEDs. An equilibrium temperature of 25 °C was measured with a standard alcohol thermometer[8].

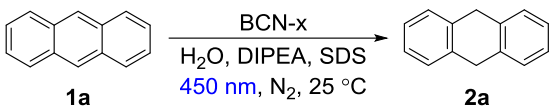


Supplementary Figure 8. Photograph of the photochemical reaction device.

Reaction condition optimization

A 10 mL Schlenk flask was equipped with the BCN-x (10 mg), anthracene (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), reductant (0.15 mmol, 1.5 equiv.) and a stirring bar. After adding solvent (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilled with N_2 (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LEDs for 7 h at 25 ℃. After reaction, the mixture was quenched by adding brine (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously. After phase separation, the organic layer was filtrated and analyzed by GC-MS. The yield of product was determined with mesitylene as internal standard.

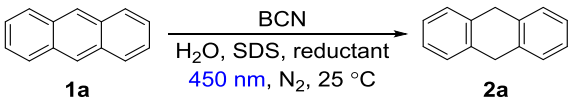
Supplementary Table 3. Optimization of BCN-x photocatalyst. [a]



Entry	Photocatalyst	Reductant	Solvent	Yield / %[b]
1	BCN-0	DIPEA	H_2O	Trace
2	BCN-1	DIPEA	H_2O	28
3	BCN-3 (BCN)	DIPEA	H_2O	93
4	BCN-5	DIPEA	H_2O	86

[a] The reactions were carried out with BCN-x (10 mg), **1a** (0.10 mmol), SDS (0.15 mmol), DIPEA (0.15 mmol), and H_2O (1 mL) under N_2 atmosphere with bule LEDs (3 W, 450 nm) irradiation for 7 h. [b] The yield was determined by GC-MS with mesitylene as an internal standard.

Supplementary Table 4. Optimization of reductant. [a]



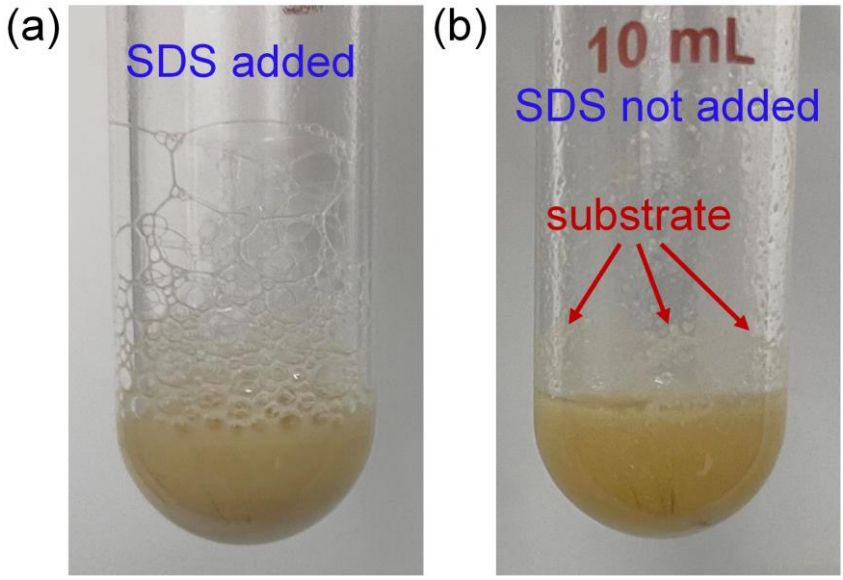
Entry	Photocatalyst	Reductant	Solvent	Yield / %[b]
1	BCN	DIPEA	H_2O	93
2	BCN	Et_3N	H_2O	78
3	BCN	TEOA	H_2O	17
4	BCN	Hantzsch ester	H_2O	14
5	BCN	L-Ascorbic acid	H_2O	Trace
6	BCN	Sodium ascorbate	H_2O	9
7	BCN	MeOH	H_2O	Trace
8	BCN	Na_2SO_3	H_2O	2
9	BCN	Ph_3N	H_2O	Trace
10	BCN	PhSSPh	H_2O	5

[a] The reactions were carried out with BCN (10 mg), **1a** (0.10 mmol), SDS (0.15 mmol), reductant (0.15 mmol), and H_2O (1 mL) under N_2 atmosphere with bule LEDs (3 W, 450 nm) irradiation for 7 h. [b] The yield was determined by GC-MS with mesitylene as an internal standard.

Supplementary Table 5. Optimization of solvent. [a]

Entry	Photocatalyst	Reductant	Solvent	Yield / %[b]
1[c]	BCN	DIPEA	H_2O	93
2	BCN	DIPEA	1,4-dioxane	50
3	BCN	DIPEA	DMF	56
4	BCN	DIPEA	THF	76
5	BCN	DIPEA	MeCN	91
6	BCN	DIPEA	MeOH	49
7	BCN	DIPEA	EtOH	67
8[d]	BCN	DIPEA	1,4-dioxane	78
9[e]	BCN	DIPEA	1,4-dioxane	84
10[f]	BCN	DIPEA	1,4-dioxane	93

[a] The reactions were carried out with BCN (10 mg), **1a** (0.10 mmol), DIPEA (0.15 mmol), and solvent (1 mL) under N_2 atmosphere with bule LEDs (3 W, 450 nm) irradiation for 7 h. [b] The yield was determined by GC-MS with mesitylene as an internal standard. [c] SDS (0.15 mmol) was added. [d] 50 μL of water was added. [e] 100 μL of water was added. [f] 200 μL of water was added. The yield was improved with adding water, which is attributed to the proton donation by water.

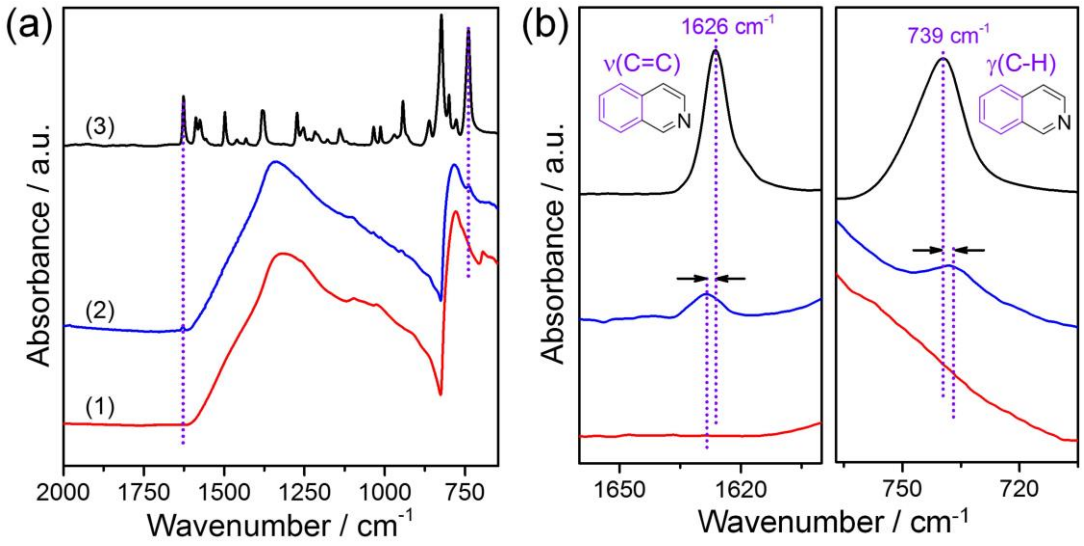


Supplementary Figure 9. Photographs of the reaction mixtures.

(a) With and (b) without the addition of SDS. Obviously, the addition of SDS facilitates the dispersion of **1a** in water, whereas the substrate adheres to the inner wall of the reaction tube in the absence of SDS.

Supplementary Note 2. Fourier transform infrared (FT-IR) spectroscopy of BCN for isoquinoline adsorption

The fascinating regioselectivity of isoquinoline hydrogenation could be explained by the molecular adsorption mode on the surface of BCN. The FT-IR spectrum for isoquinoline adsorption over BCN reveals the priority of carbocyclic ring adsorption, as the characteristic peak at approximately 1626 cm^{-1}, resulting from the characteristic stretching vibration of the C=C network in benzene ring, and characteristic peak at 739 cm^{-1} attributed to C–H bond vibration, have experienced slight shifts compared with those of pure isoquinoline. The experimental results suggest the interaction between BCN and carbocyclic ring of isoquinoline, leading to the unusual regioselectivity for isoquinoline hydrogenation.



Supplementary Figure 10. FT-IR spectra of BCN for isoquinoline adsorption.

(a) (1) BCN after degassing at 180 °C for 3 h; (2) evacuation of excess isoquinoline at 150 °C for 15 min under 6×10^{-2} hPa after adsorbing isoquinoline for 30 min (chemisorption); (3) FT-IR spectrum of pure isoquinoline. (b) Zoom-in of characteristic peaks for the FT-IR spectra.

The apparent quantum efficiency (AQE) analysis

The AQE for hydrogenation of anthracene was measured using monochromatic LED lamps with wavelengthes of 405, 420, 450, 470 and 520 nm. The irradiation area was controlled as 1×1 cm^2. The light intensities were determined by ILT 950 spectroradiometer. The AQE was calculated as $AQE=N_e/N_p*100\% = 2MN_Ahc/SPt\lambda*100\%$, where N_e is the amount of reaction electrons, N_p is the amount of incident photons, M is the amount of hydrogenation products, N_A is Avogadro constant, h is the Planck constant, c is the speed of light, S is the irradiation area, P is the intensity of the irradiation, t is the photo-irradiation time, and λ is the wavelength of the monochromatic light[9].

Supplementary Table 6. Wavelength dependence of AQE for hydrogenation of 1a.

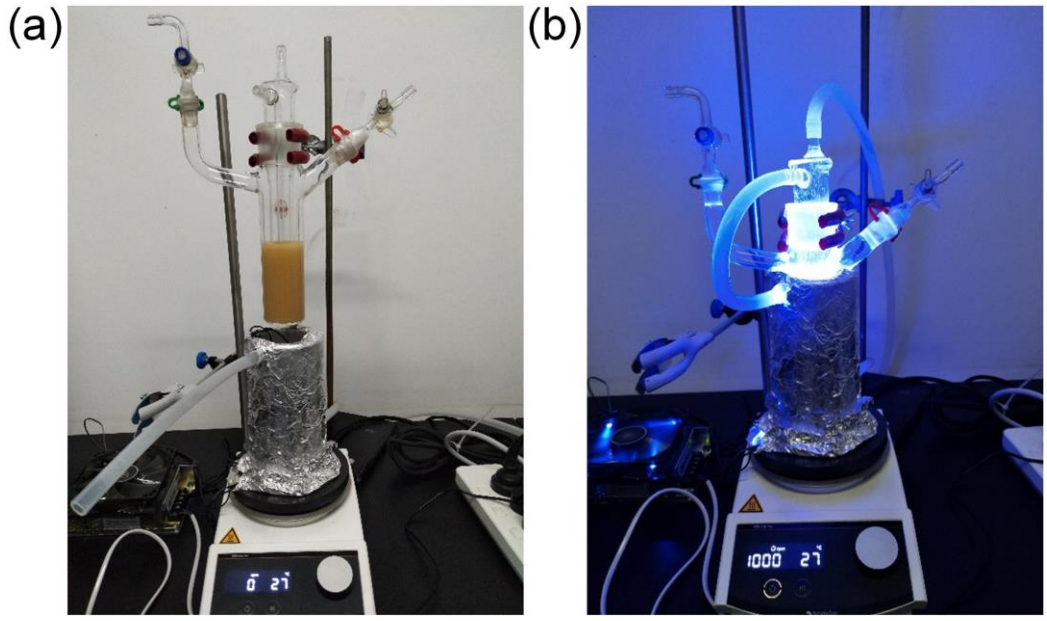
Entry	Wavelength / nm	Irradiation time t / h	AQE / %
1	405	1	6.2
2	420	1	5.1
3	450	1	4.1
4	470	1	2.8
5	520	1	0.5

Supplementary Table 7. Time dependence of AQE for 1a hydrogenation under 450 nm LEDs illumination.

Entry	Wavelength / nm	Irradiation time *t* / h	AQE / %
1	450	1	4.1
2	450	3	3.7
3	450	5	3.5
4	450	7	2.8

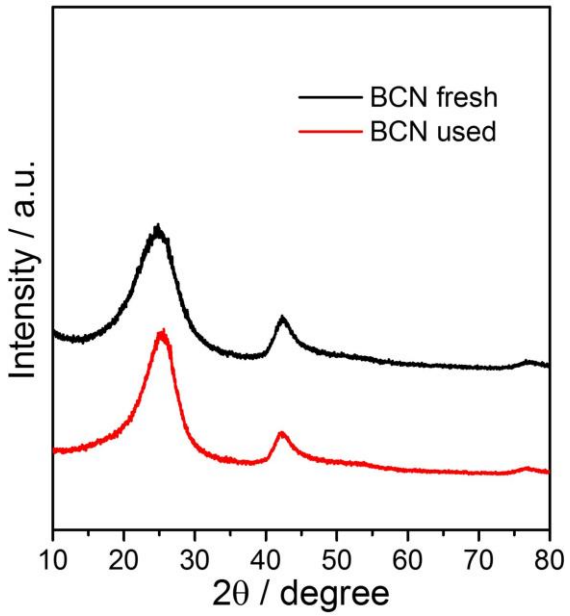
The gram-scale reaction setup

The reaction was scaled to 6.0 mmol using a customized reactor consisted of 6 cm diameter reaction vessel, with a central water-cooling system. The reaction vessel was surrounded with 20 blue LEDs light bar (20 × 3 W) attached to the inner wall of cylindrical glass. The reaction vessel was equipped with BCN (0.3-0.60 g), anthracene **1a** (6.0 mmol, 1.1 g, 1.0 equiv.), DIPEA (9.0 mmol, 1.8 mL, 1.5 equiv.), SDS (9.0 mmol, 2.4 g, 1.5 equiv.), and a stirring bar. After adding 60 mL of H_2O into the reaction vessel, the vessel was sealed and degassed with a vacuum pump and backfilled with N_2 (1 bar). The reaction mixture was stirred and irradiated using abovementioned 450 nm (± 10 nm) LEDs for 7 h at 25 ℃. Upon completion of the reaction, the reaction mixture was quenched by adding brine (100 mL), followed by ethyl acetate (AcOEt, 100 mL). The mixture was shaken vigorously. After phase separation, 2 mL of the solution from organic layer was sucked out, filtrated and analyzed by GC-MS. The yield of product was determined with mesitylene as internal standard.



Supplementary Figure 11. Photochemical reactor used for larger-scale hydrogenation reaction.

(a) Without and (b) with blue light irradiation.

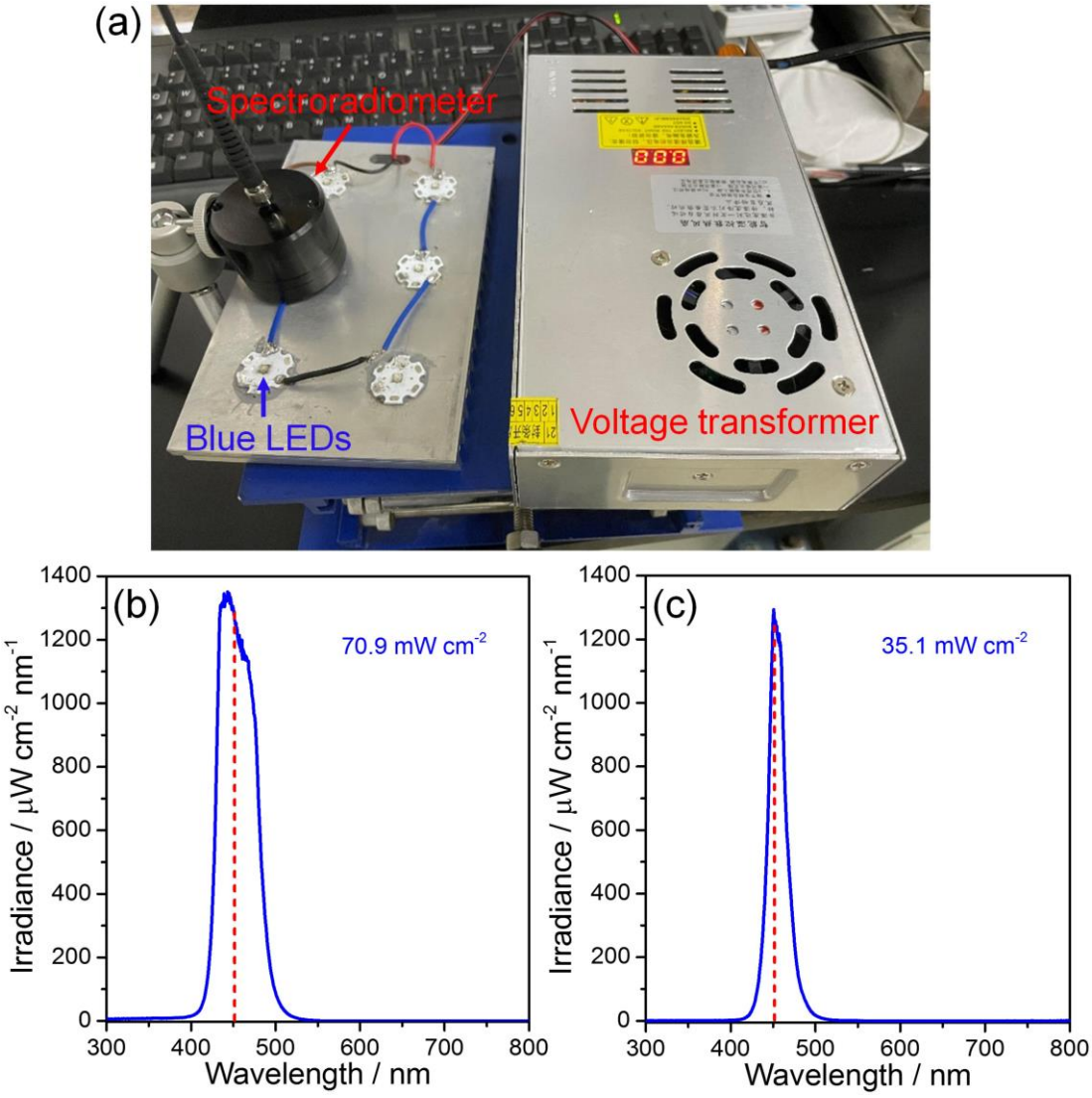


Supplementary Figure 12. The XRD patterns of BCN before and after gram-scale production.

Quadratic dependency of the product yield on irradiation density

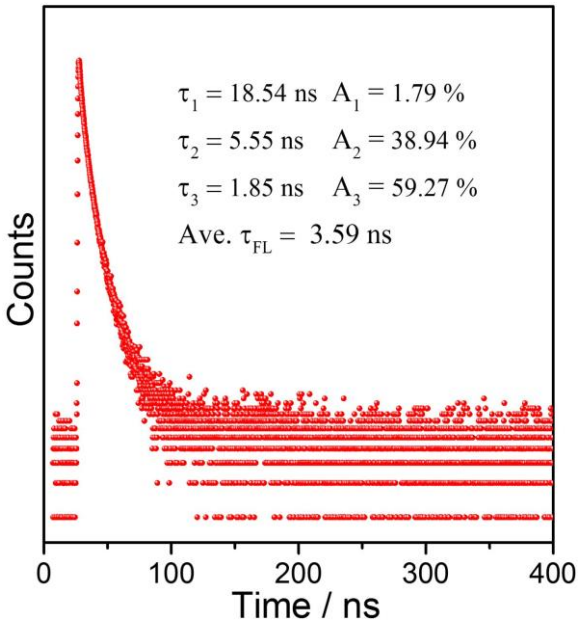
The irradiation power of light was adjusted in a simple photoreactor consisting of Eaglerise ELP8X3LS 3 W blue LEDs (λ = 450 nm) by turning the voltage. ILT 950 spectroradiometer was also used to verify the

emitted light power. Two reactions with the same amount of anthracene (0.10 mmol, 1.0 equiv.), BCN (10 mg), DIPEA (1.5 equiv.), SDS (1.5 equiv.), and 1 mL H_2O are irradiated with the same lamp bead of blue LEDs device. To exclude other influencing factors, such as, adverse effects of prolonged reaction time, the reactions were irradiated only for 2 hours. After 2 hours, the irradiation was stopped for both the reactions, and mesitylene (internal standard) was added to both mixtures. Yields were determined by GC-MS analysis. The slope showed an approximately 4:1 (full power: half power) relation, which supported a mechanism involving overall two photons[10].



Supplementary Figure 13. The control and measurement of light intensity.

(a) Photograph of the photochemical reaction setup, voltage transformer, and spectroradiometer. (b) The original light intensity of blue LEDs is determined to be 70.9 mW cm^{-2}. (c) The light intensity is halved by voltage transformer.

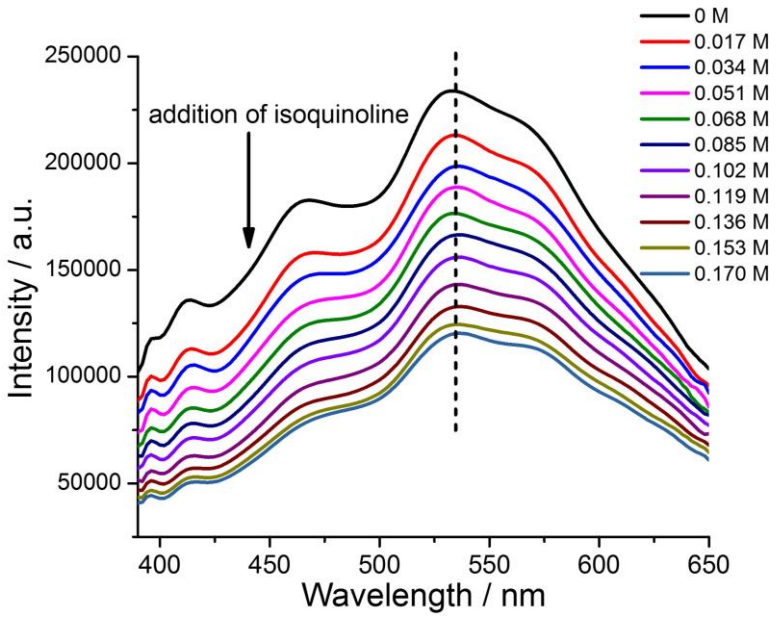


Supplementary Figure 14. Time-resolved fluorescence (FL) decay spectrum of BCN.

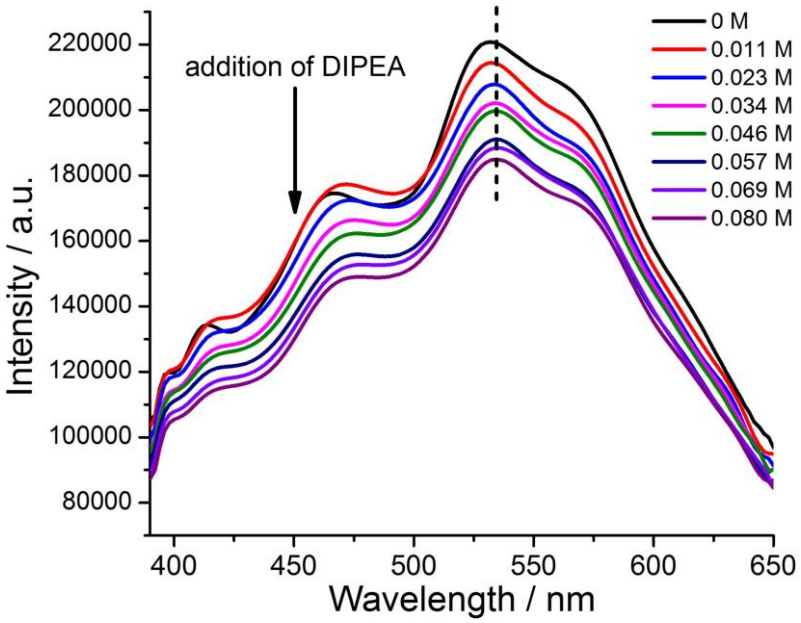
Recorded under emission at 530 nm and upon excitation at 375 nm.

Fluorescence quenching experiments

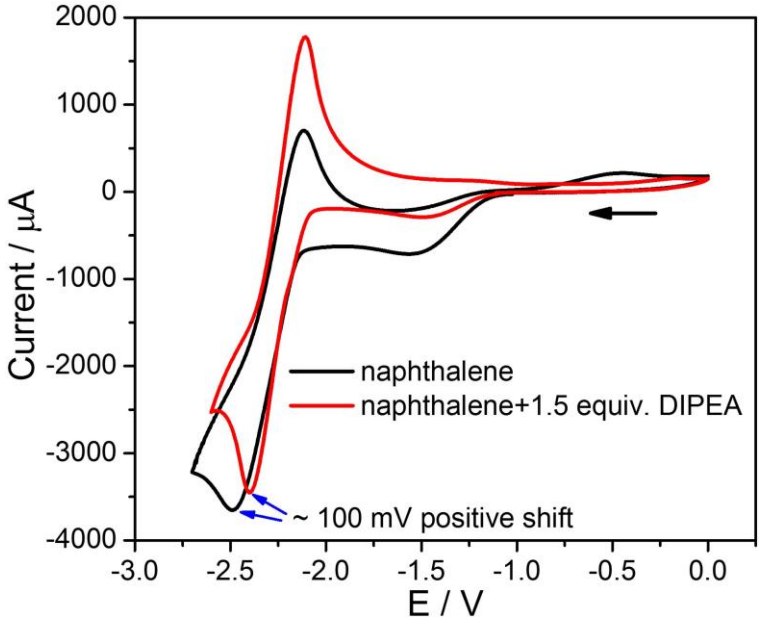
For fluorescence quenching experiments, a suspension of the BCN photocatalyst (5 mg) in H_2O (2.5 mL, containing 50 mg of SDS) was prepared under nitrogen atmosphere in a gas-tight 10 mm quartz cuvette. The BCN was excited with 375 nm and the change of the fluorescence emission upon addition of different potential quenchers was recorded.



Supplementary Figure 15. FL spectra of BCN upon successive addition of isoquinoline in suspension.



Supplementary Figure 16. FL spectra of BCN upon successive addition of DIPEA in suspension.

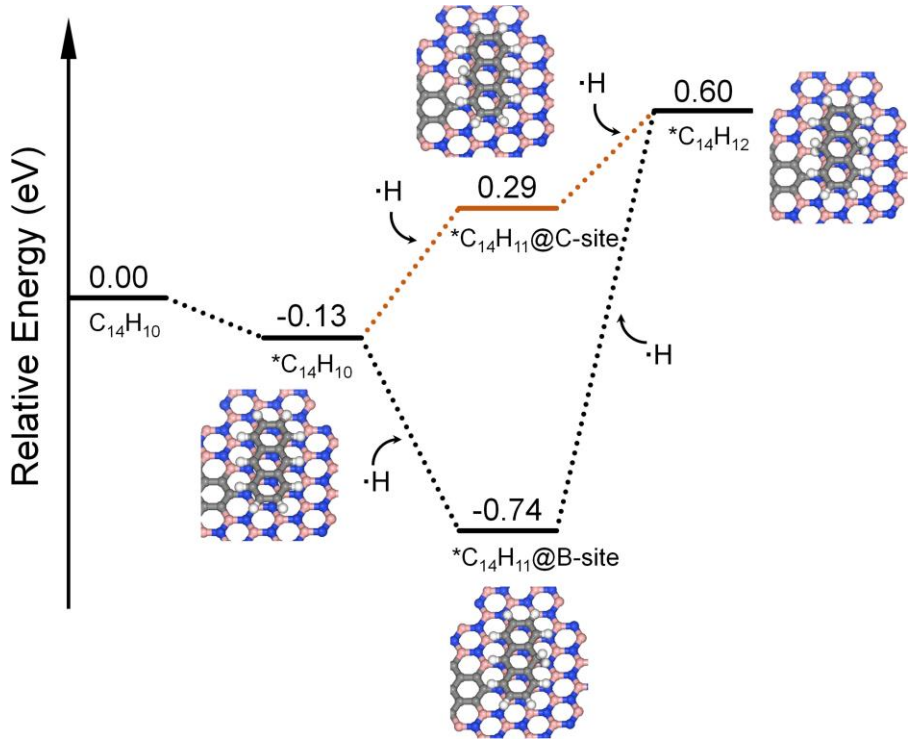


Supplementary Figure 17. Cyclic voltammograms of substrate and additive.

Naphthalene (1.0 equiv.) and DIPEA (1.5 equiv.) in CH_3CN under argon atmosphere (scan direction indicated by black arrow). The peak at -2.48 V shows the reduction of naphthalene. It shifted to lower potential (-2.38 V) upon addition of DIPEA, indicating the promotion of electron transfer. The measurement was performed with a scan rate of 100 mV/s and with tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte.

Supplementary Note 3. DFT calculations

The density functional theory (DFT) was carried out to get further insight into the catalytic transfer hydrogenation route of anthracene on BCN. The structural model of BCN we adopted is in agreement with that reported in the previous literature[11]. After screening by computer simulation, we obtain an optimized anthracene adsorption model. As shown in Supplementary Fig. 18, the anthracene adsorption on the B–N–B site near the carbon ring is most stable, which exhibits the energy of -0.13 eV (*$C_{14}H_{10}$). Based on the experimental results, the hydrogen atom could be regarded as the active hydrogen specie in the process. The calculations indicate a stepwise hydrogenation process. As illustrated, the energy levels of the first step hydrogenation intermediates at the C site and B site of BCN are different. The energy of hydrogenated intermediate at C site (*$C_{14}H_{11}$@C-site) increases to 0.29 eV while that at B site (*$C_{14}H_{11}$@B-site) declines to -0.74 eV, indicating the preference for the first step hydrogenation at B site. However, the energy barriers for the second hydrogenation on anthracene intermediates vary greatly. For *$C_{14}H_{11}$@C-site, the hydrogenation to final product *$C_{14}H_{12}$ experiences a slight energy elevation of 0.31 eV whereas the *$C_{14}H_{11}$@B-site needs to overcome a huge energy barrier (1.34 eV) to produce *$C_{14}H_{12}$.



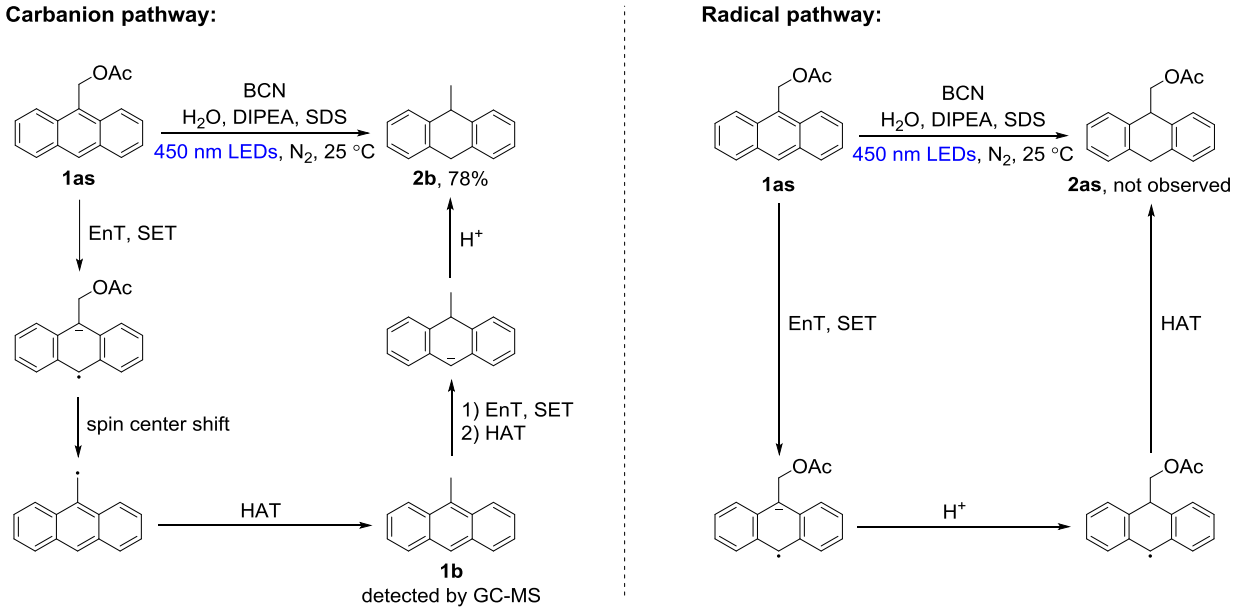
Supplementary Figure 18. DFT calculations of anthracene hydrogenation on BCN.

The insets are the optimized structures of the intermediates along the reaction path.

Elimination unimolecular conjugate base (E1cB) reaction

The synthesis of 9-anthracenemethyl acetate **1as**: A round bottom flask was charged with the corresponding 9-anthracenemethanol (4.8 mmol, 1.0 g, 1.0 equiv.) and dissolved in CH_2Cl_2 (15 mL). Triethylamine (1.1 equiv.) and acetyl chloride (5.8 mmol, 0.41 mL, 1.1 equiv.) were subsequently added dropwise to the reaction vessel at 0 ℃. The mixture was then allowed to warm to room temperature, and stirred for 8 hours. The mixture was quenched with 5% aq. HCl and extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (PE: EtOAc = 20: 1, v: v) to afford 1.0 g (85%) of the corresponding **1as** as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.35 (d, J = 8.9 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 6.16 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.40, 131.50, 131.16, 129.30, 129.22, 126.76, 126.32, 125.21, 124.03, 58.92, 21.10. MS (m/z, EI): 250, 191, 179, 94.

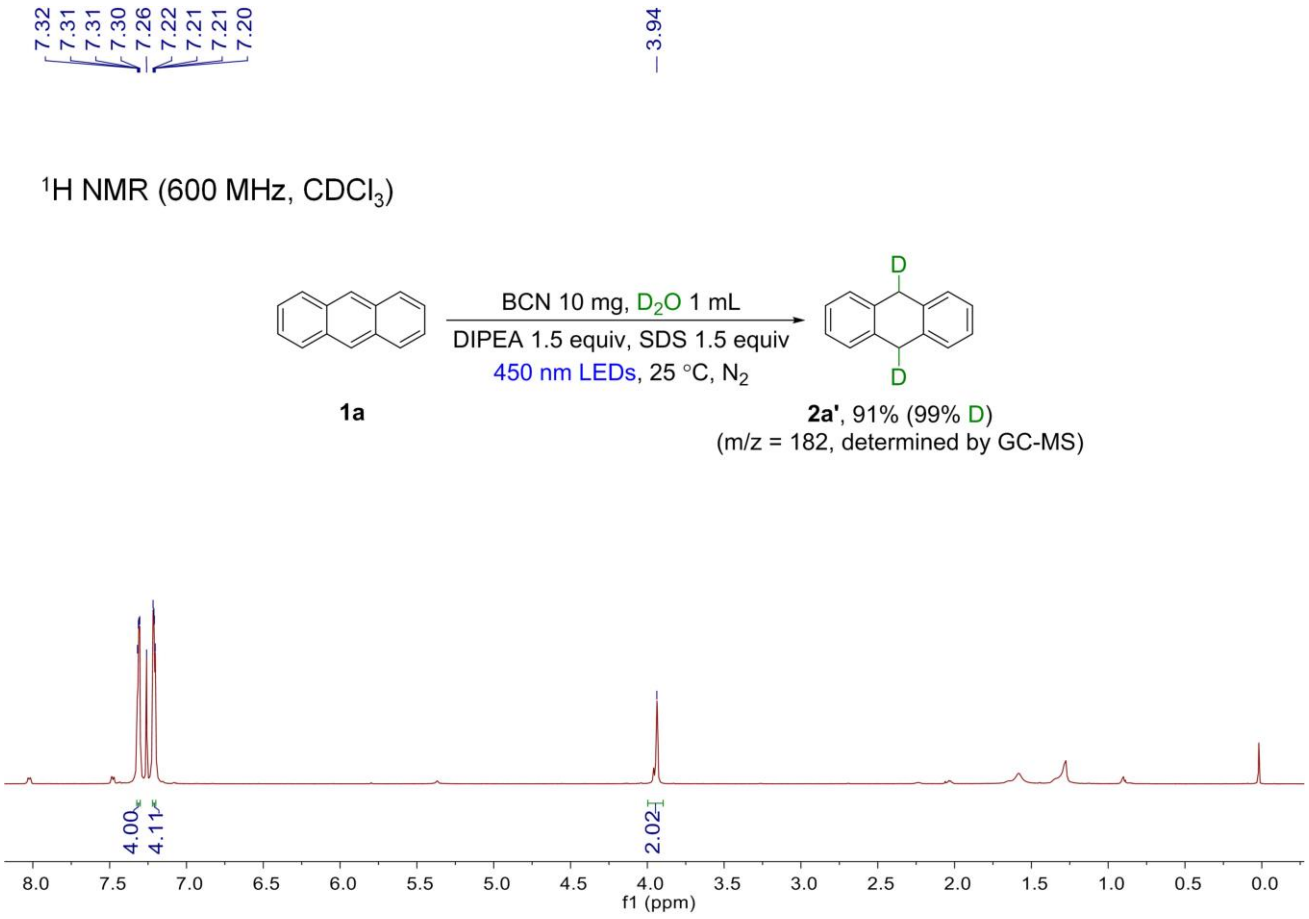


Supplementary Figure 19. E1cB reaction and possible reaction pathway.

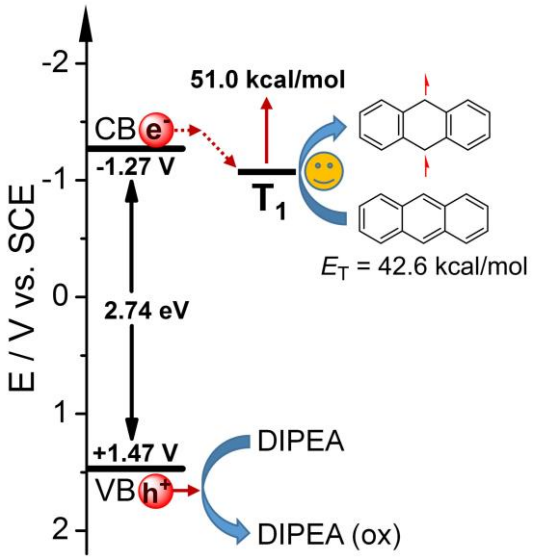
E1cB reaction indicates the carbanion intermediate[12]. The carbanion formed in benzylic position of **1as** and a spin-center shift followed by HAT could lead to the formation of **1b** detected by GC-MS, which undergoes EnT, SET followed by HAT and protonation to afford final product **2b** with a yield of 78% determined by GC-MS. Radical pathway can be excluded because no reduced product **2as** observed under standard reaction conditions.

Deuterium-labeling experiment

For deuteration experiment, a 10 mL Schlenk flask was equipped with the BCN (10 mg), anthracene (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.15 mmol, 1.5 equiv.) and a stirring bar. After adding D_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilled with N_2 (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LEDs for 7 h at 25 ℃. After reaction, the mixture was quenched by adding brine (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously. After phase separation, the organic layer was filtrated and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. The residue was purified by column chromatography on silica gel using pure petroleum ether as eluent to afford the final deuterated product with 99% deuterium incorporation. It implies the hydrogen source is from the proton in the solution.

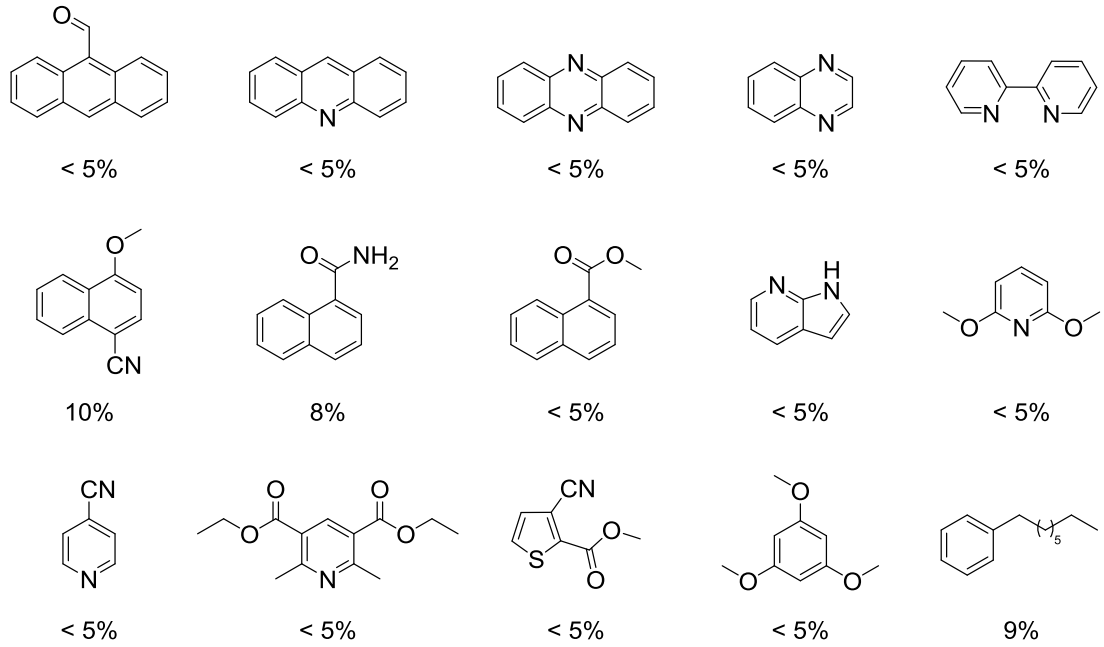


Supplementary Figure 20. ^{1}H NMR spectrum of deuterated 2a' in $CDCl_3$.



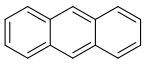
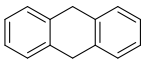
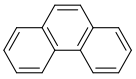
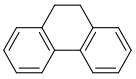
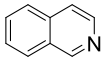
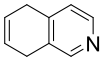
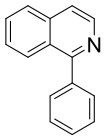
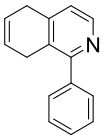
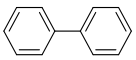
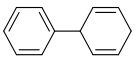
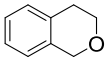
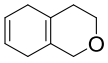
Supplementary Figure 21. Energy scheme for the triplet sensitization of anthracene on BCN.

The triplet energy of BCN (E_T = 51.0 kcal/mol, calculated from PH spectrum) is higher than that of anthracene (E_T = 42.6 kcal/mol), illustrating the feasibility of energy transfer from BCN to anthracene.



Supplementary Figure 22. List of failed or inferior substrates for Birch reduction.

Supplementary Table 8. Comparison of this work with Na-SG and other known methods.

Entry	Substrate (**a**)	Product (**b**)	BCN method[a]	Time (h)	Yield (%)[b]	Na-SG / other method Yield (%)[b]
1			A	7	91	94[c]/89[d]
2			B	24	76[e]	83[f]/50[g]
3			A	7	85	34[h]/88[g]
4			A	7	75	–[i]/39[j]
5			B	72	52	62[k]/72[j]
6			A	24	79	–/–[l]
7			B	48	65	–/–[l]
8			B	24	64[e]	–/63[m]
9			C	24	27[n]	–/–
10			C	24	56[e]	–/–

[a] *Method A*: substrate (0.1 mmol), BCN (10 mg), DIPEA (0.15 mmol), and SDS (0.15 mmol) in H_2O (1 mL) at 25 °C; *Method B*: substrate (0.1 mmol), BCN (10 mg), DIPEA (0.2 mmol), and H_2O (0.3 mL) in DMF (1 mL) at 25 °C; *Method C*: substrate (0.1 mmol), BCN (10 mg), DIPEA (0.2 mmol), SDS (0.15 mmol), and DBU (0.2 mL) in H_2O (1 mL) at 25 °C.

[b] Isolated yield after purification.

[c] Substrate (1.0 mmol), Na-SG (7.0 mmol), *t*-BuOH (7.6 mmol) in 1,4-dioxane at r.t. for 2.5 h (Ref. 13.)[13].

[d] Substrate (0.5 mmol), $[Ca_2N]^+ \bullet e^-$ (1.0~1.5 mmol), and *i*PrOH (2 mL) in THF (2 mL) at 65 °C for 24 h (Ref. 14.)[14].

[e] The yield was determined by ^{1}H NMR.

[f] Substrate (1.0 mmol), Na-SG (7.0 mmol), EDA (7.0 mmol), *t*-AmOH (8.4 mmol) in THF at 5 °C for 1 h (Ref 13)[13].

[g] Substrate (0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (1 mol%), DIPEA (0.2 mmol), and $MeNH_3Cl$ (10 mol%) in DMF (2 mL) at 25 °C with blue light irradiation for 18 h (Ref. 12.)[12].

[h] Substrate (1.0 mmol) and Na-SG (7.0 mmol) in THF at r.t. for 15 min, cool to -74 °C, add EDA (7.0 mmol), stir at -74 °C for 45 min, add 4.2 equiv of *t*-BuOH and stir at -74 °C for 4 h (Ref. 13.)[13].

[i] Substrate (1.0 mmol), Na-SG (11.2 mmol), EDA (11.2 mmol), *t*-AmOH (8.4 mmol) in THF at 5 °C for 24 h. 2-Ethylphenol as the major product (Ref 13)[13].

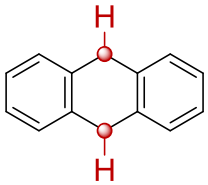
[j] Substrate (0.5 mmol) and Na/*i*PrOH/15-crown- (3.0-6.0 equiv) in THF (3 mL) at 0 °C (Ref. 15.)[15].

[l] No literature reported.

[m] Substrate (1.0 equiv), SmI_2 (2.5 equiv), and amine (5.0 equiv) were mixed, and finally H_2O (7.5 equiv) was added (Ref. 16.)[16].

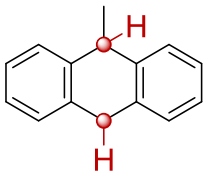
[n] The yield was determined by GC-FID.

Characterization data for products



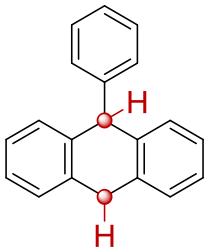
9,10-dihydroanthracene (**2a**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (16.4 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.24 – 7.19 (m, 4H), 3.96 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.82, 127.52, 126.22, 36.30. MS (m/z, EI): 180, 165, 152, 89, 76.



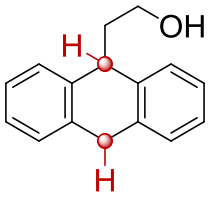
9-methyl-9,10-dihydroanthracene (**2b**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (16.5 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, J = 14.6, 7.4 Hz, 4H), 7.29 – 7.19 (m, 4H), 4.16 (d, J = 18.2 Hz, 1H), 4.08 (q, J = 7.3 Hz, 1H), 3.93 (d, J = 18.2 Hz, 1H), 1.47 (d, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.87, 135.90, 127.80, 127.00, 126.49, 126.07, 41.22, 35.24, 23.64. MS (m/z, EI): 194, 179, 152, 96, 89.



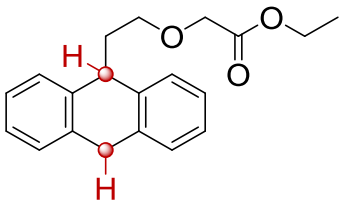
9-phenyl-9,10-dihydroanthracene (**2c**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (21.2 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.26 – 7.18 (m, 6H), 7.16 – 7.13 (m, 1H), 7.10 – 7.06 (m, 2H), 5.27 (s, 1H), 4.02 (d, J = 18.0 Hz, 1H), 3.92 (d, J = 18.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.69, 139.62, 136.57, 128.58, 128.57, 128.18, 127.90, 126.55, 126.51, 126.35, 51.57, 35.81. MS (m/z, EI): 256, 239, 178, 152.



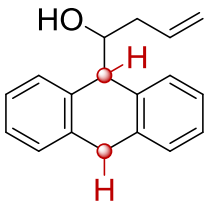
2-(9,10-dihydroanthracen-9-yl)ethan-1-ol (**2d**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10: 1, v: v) as an eluent to provide as white solid (20.2 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.28 – 7.22 (m, 4H), 4.19 (t, *J* = 7.7 Hz, 1H), 4.14 (d, *J* = 18.2 Hz, 1H), 3.91 (d, *J* = 18.2 Hz, 1H), 3.64 (t, *J* = 6.3 Hz, 2H), 1.89 (q, *J* = 6.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.16, 136.29, 127.96, 127.93, 126.35, 126.28, 60.61, 43.65, 39.48, 35.33. MS (m/z, EI): 224, 205, 191, 179, 152, 115, 89.



ethyl 2-(2-(9,10-dihydroanthracen-9-yl)ethoxy)acetate (**2e**)

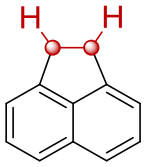
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (50: 1, v: v) as an eluent to provide as white solid (24.8 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 27.2, 7.0 Hz, 4H), 7.23 (h, *J* = 7.1, 6.3 Hz, 4H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.22 (t, *J* = 7.7 Hz, 1H), 4.10 (d, *J* = 11.4 Hz, 3H), 3.89 (d, *J* = 18.2 Hz, 1H), 3.49 (t, *J* = 6.2 Hz, 2H), 1.93 (q, *J* = 6.5 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.58, 140.11, 136.31, 128.13, 127.90, 126.29, 126.24, 69.40, 68.51, 60.92, 43.37, 36.39, 35.36, 14.32. MS (m/z, EI): 310, 236, 206, 179, 152, 115, 89.



1-(9,10-dihydroanthracen-9-yl)but-3-en-1-ol (**2f**)

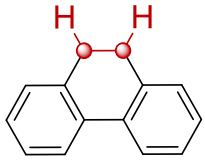
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20: 1, v: v) as an eluent to provide as colorless oil (15.7 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) **mixture of diastereomers and rotamers:** δ 7.42 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 4H), 5.92 – 5.82 (m, 1H), 5.16 (s, 1H), 5.15 – 5.12 (m, 1H), 4.23 (d, *J* = 18.4 Hz, 1H), 4.05 (d, *J* = 6.8 Hz, 1H), 3.91 (d, *J* = 18.4 Hz, 1H), 3.83 – 3.78 (m, 1H), 2.41 – 2.35 (m, 1H), 2.20 – 2.12 (m, 1H), 1.81 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) **mixture of diastereomers and rotamers:** δ 137.13, 137.01,

136.91, 136.61, 135.20, 129.42, 129.17, 128.10, 127.90, 126.82, 126.68, 126.22, 126.08, 117.80, 74.10, 53.31, 38.68, 35.93. MS (m/z, EI): 250, 209, 191, 180, 165, 152, 126, 89. Diastereoisomers were determined by ^{1}H NMR analysis as 1.15:1.



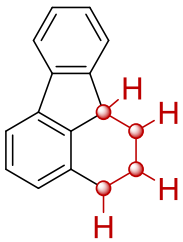
1,2-dihydroacenaphthylene (**2g**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (14.2 mg, 92% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 6.8 Hz, 2H), 3.42 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.13, 139.41, 131.74, 127.91, 122.35, 119.29, 30.48. MS (m/z, EI): 154, 126, 76, 63.



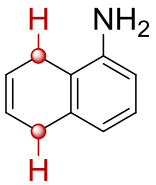
9,10-dihydrophenanthrene (**2h**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (15.3 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.21 (m, 4H), 2.90 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.53, 134.62, 128.26, 127.51, 127.09, 123.84, 29.19. MS (m/z, EI): 180, 165, 152, 89, 76.



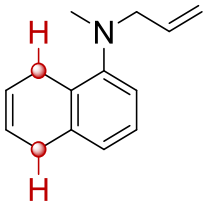
1,2,3,10b-tetrahydrofluoranthene (**2i**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (13.4 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.37 (tt, J = 7.5, 0.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.07 (dq, J = 7.6, 1.0 Hz, 1H), 3.66 (dd, J = 12.3, 5.1 Hz, 1H), 3.07 – 3.00 (m, 1H), 2.78 (dt, J = 17.2, 8.6 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.22 – 2.10 (m, 2H), 1.24 – 1.16 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.24, 146.10, 141.73, 139.45, 135.04, 127.54, 127.04, 126.58, 125.80, 124.21, 120.57, 117.19, 45.43, 26.06, 25.19, 23.48. MS (m/z, EI): 206, 178, 165, 152, 89, 76.



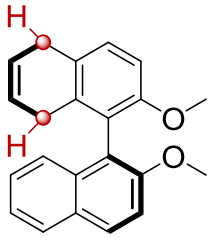
5,8-dihydronaphthalen-1-amine (**2l**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (15: 1, v: v) as an eluent to provide as colorless oil (7.7 mg, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (t, J = 7.7 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 5.93 – 5.87 (m, 2H), 3.58 (s, 2H), 3.40 (t, J = 5.5 Hz, 2H), 3.10 (t, J = 5.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.94, 134.79, 126.68, 124.94, 123.28, 119.39, 119.07, 112.55, 29.81, 25.24. MS (m/z, EI): 145, 130, 115, 103, 71.



N-allyl-N-methyl-5,8-dihydronaphthalen-1-amine (**2m**)

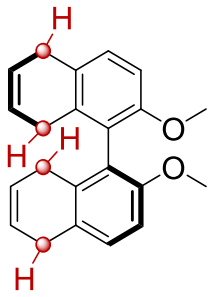
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (100: 1, v: v) as an eluent to provide as colorless oil (9.6 mg, 48% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 5.99 – 5.84 (m, 3H), 5.26 (d, J = 17.2 Hz, 1H), 5.16 (d, J = 10.2 Hz, 1H), 3.45 (d, J = 6.0 Hz, 2H), 3.40 – 3.35 (m, 4H), 2.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.75, 135.99, 135.93, 130.26, 126.18, 125.66, 124.66, 123.66, 117.81, 117.00, 60.04, 41.30, 30.73, 26.35. MS (m/z, EI): 199, 158, 143, 128, 115, 77.



(*S*)-2,2'-dimethoxy-5,8-dihydro-1,1'-binaphthalene (**2p**)

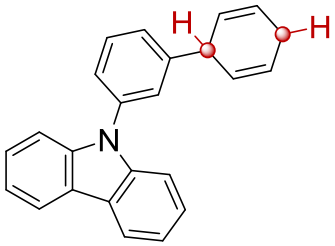
The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (13.0 mg, 41% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.9 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.68 – 7.63 (m, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 6.99 (td, J = 7.4, 1.2 Hz, 1H), 6.88 (td, J = 7.7, 1.1 Hz, 1H), 6.31 (dd, J = 7.7, 0.8 Hz, 1H), 3.85 (s, 3H), 3.45 (s, 3H), 3.16 (td, J = 8.1, 3.6 Hz, 2H), 2.77 – 2.70 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.33, 154.90, 136.90, 133.92, 132.48, 129.38, 129.03, 128.07, 126.87, 126.61, 126.42, 125.42, 124.90, 123.91, 123.59, 120.14, 114.18, 111.65, 56.96, 55.67, 29.25, 24.28. MS (m/z, EI): 316, 285, 273, 241, 195,

158, 115, 91. HPLC analysis: AD-H, 1% IPA in hexanes, 1 mL/min, 254 nm, t_R (minor) = 30.44 min, t_R (major) = 27.94 min, 91% ee.



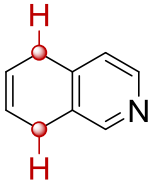
(*S*)-2,2'-dimethoxy-5,5',8,8'-tetrahydro-1,1'-binaphthalene (**2p'**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as colorless oil (10.8 mg, 34% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.10 (m, 2H), 7.01 – 6.98 (m, 4H), 6.91 – 6.88 (m, 2H), 3.58 (s, 6H), 3.04 (q, *J* = 7.5 Hz, 4H), 2.65 – 2.60 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.00, 136.47, 132.65, 126.83, 126.68, 124.82, 123.80, 111.67, 55.72, 29.14, 24.22. MS (m/z, EI): 318, 303, 253, 228, 202, 145, 117, 91. HPLC analysis: AD-H, 1% IPA in hexanes, 1 mL/min, 254 nm, t_R (minor) = 28.05 min, t_R (major) = 26.53 min, 77% ee.



9-(1',4'-dihydro-[1,1'-biphenyl]-3-yl)-9H-carbazole (**2r**)

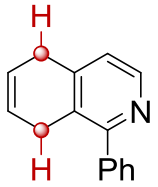
The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (19.3 mg, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 4.0 Hz, 6H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.29 (dt, *J* = 7.9, 3.8 Hz, 2H), 5.88 – 5.79 (m, 4H), 4.11 – 4.04 (m, 1H), 2.79 – 2.70 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.42, 140.99, 138.03, 130.01, 128.16, 127.11, 126.81, 126.02, 125.00, 124.46, 123.46, 120.41, 119.96, 109.98, 42.04, 25.96. MS (m/z, EI): 321, 291, 243, 166, 139, 77.



5,6-dihydroisoquinoline (**2t**)

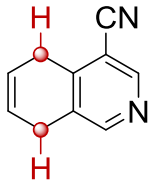
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5: 1, v: v) as an eluent to provide as colorless oil (10.3 mg, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$)

δ 8.36 (s, 1H), 8.32 (d, *J* = 5.1 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 6.00 – 5.92 (m, 1H), 5.92 – 5.84 (m, 1H), 3.41 – 3.28 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.94, 146.96, 143.35, 130.35, 124.75, 123.81, 123.26, 29.11, 26.72. MS (m/z, EI): 131, 103, 77, 51.



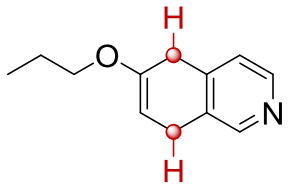
1-phenyl-5,6-dihydroisoquinoline (**2u**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5: 1, v: v) as an eluent to provide as yellow oil (13.5 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.0 Hz, 1H), 7.49 – 7.42 (m, 4H), 7.42 – 7.37 (m, 1H), 7.05 (d, *J* = 5.0 Hz, 1H), 5.94 – 5.84 (m, 2H), 3.44 (t, *J* = 5.4 Hz, 2H), 3.28 (t, *J* = 5.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.65, 146.45, 144.45, 140.66, 128.92, 128.32, 128.04, 125.55, 123.53, 122.49, 30.01, 28.10. MS (m/z, EI): 207, 128, 103, 77.



5,8-dihydroisoquinoline-4-carbonitrile (**2v**)

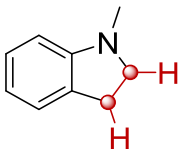
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10: 1, v: v) as an eluent to provide as yellow solid (7.2 mg, 46% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.54 (s, 1H), 6.00 – 5.95 (m, 1H), 5.94 – 5.89 (m, 1H), 3.56 – 3.53 (m, 2H), 3.45 – 3.42 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.05, 150.46, 131.11, 124.17, 122.47, 115.86, 109.63, 28.08, 26.55. MS (m/z, EI): 156, 128, 101, 77.



6-propoxy-5,8-dihydroisoquinoline (**2w**)

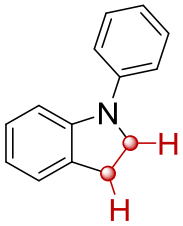
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10: 1, v: v) as an eluent to provide as yellow oil (10.0 mg, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.0 Hz, 1H), 8.21 (s, 1H), 6.80 (d, *J* = 5.0 Hz, 1H), 5.47 (s, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.45 (t, *J* = 8.2 Hz, 2H), 1.77 (q, *J* = 6.9 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.07, 148.31, 147.24, 143.81, 126.78, 119.14, 95.14, 69.51, 27.55, 25.12, 22.32,

10.68. MS (m/z, EI): 189, 147, 130, 118, 91.



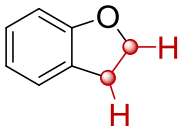
1-methylindoline (**2x**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20: 1, v: v) as an eluent to provide as colorless oil (6.9 mg, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.08 (m, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 3.31 (t, *J* = 8.2 Hz, 2H), 2.96 (t, *J* = 8.1 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.54, 130.45, 127.46, 124.40, 117.92, 107.38, 56.31, 36.43, 28.89. MS (m/z, EI): 133, 117, 103, 91, 77.



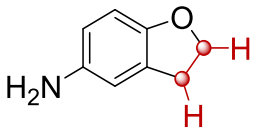
1-phenylindoline (**2y**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20: 1, v: v) as an eluent to provide as brown solid (12.1 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.17 (m, 2H), 7.14 – 7.08 (m, 1H), 7.04 – 6.97 (m, 1H), 6.84 – 6.76 (m, 1H), 3.99 (td, *J* = 8.4, 1.6 Hz, 2H), 3.16 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.14, 144.23, 131.36, 129.25, 127.16, 125.14, 121.00, 118.93, 117.73, 108.21, 52.17, 28.27. MS (m/z, EI): 195, 167, 116, 91, 77.



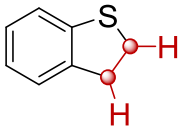
2,3-dihydrobenzofuran (**2z**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as colorless oil (9.0 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (dq, *J* = 7.3, 1.4 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.85 (td, *J* = 7.4, 1.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.22 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.12, 128.04, 126.99, 125.02, 120.44, 109.48, 71.13, 29.87. MS (m/z, EI): 120, 91, 77, 65, 51.



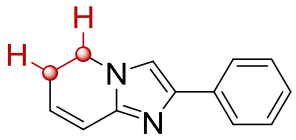
2,3-dihydrobenzofuran-5-amine (**2aa**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5: 1, v: v) as an eluent to provide as brown solid (8.8 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.60 (d, *J* = 7.7 Hz, 2H), 6.46 (d, *J* = 7.8 Hz, 1H), 4.49 (t, *J* = 8.5 Hz, 2H), 3.39 (br s, 2H), 3.13 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.31, 139.97, 127.94, 114.78, 112.85, 109.44, 71.04, 30.35. MS (m/z, EI): 135, 106, 79, 67, 53.



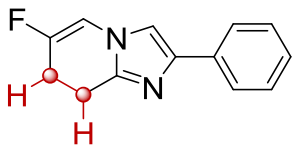
2,3-dihydrobenzo[*b*]thiophene (**2ab**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (50: 1, v: v) as an eluent to provide as colorless oil (10.9 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (td, *J* = 7.4, 1.1 Hz, 1H), 3.38 – 3.34 (m, 2H), 3.29 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.63, 140.13, 127.41, 124.49, 124.19, 122.23, 36.32, 33.40. MS (m/z, EI): 136, 102, 91, 77.



2-phenyl-5,6-dihydroimidazo[1,2-*a*]pyridine (**2ac**)

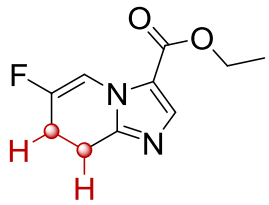
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (2: 1, v: v) as an eluent to provide as white solid (15.3 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 6.07 – 5.99 (m, 1H), 5.91 – 5.83 (m, 1H), 4.66 – 4.50 (m, 2H), 3.60 – 3.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.55, 141.08, 134.18, 128.64, 126.79, 124.89, 123.09, 119.76, 113.22, 45.07, 25.13. MS (m/z, EI): 196, 167, 130, 103, 78.



6-fluoro-2-phenyl-7,8-dihydroimidazo[1,2-*a*]pyridine (**2ad**)

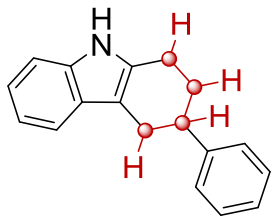
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (2: 1, v: v) as an eluent to provide as white solid (18.0 mg, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.13 (s, 1H), 5.68 – 5.58 (m, 1H), 4.64 (t, *J* = 4.8 Hz, 2H), 3.61 (p, *J* = 4.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.62 (d, *J* = 249.0 Hz),

142.56, 141.73 (d, J = 2.4 Hz), 133.99, 128.72, 127.06, 124.92, 113.16 (d, J = 2.8 Hz), 99.55 (d, J = 16.3 Hz), 43.80 (d, J = 41.6 Hz), 22.80 (d, J = 8.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.83 (dt, J = 15.9, 4.8 Hz). MS (m/z, EI): 214, 194, 116, 103, 91.



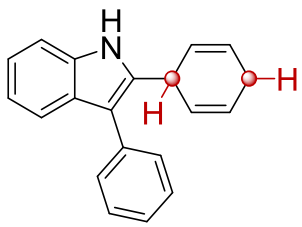
ethyl 6-fluoro-7,8-dihydroimidazo[1,2-*a*]pyridine-3-carboxylate (**2ae**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5: 1, v: v) as an eluent to provide as white solid (17.4 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 5.60 – 5.48 (m, 1H), 4.89 (t, J = 5.3 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.59 (p, J = 5.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.33, 152.41 (d, J = 249.2 Hz), 146.22, 137.46, 122.14, 97.81 (d, J = 16.8 Hz), 60.61, 44.60 (d, J = 43.6 Hz), 23.21 (d, J = 8.2 Hz), 14.43. ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.15 (dt, J = 15.5, 4.7 Hz). MS (m/z, EI): 210, 181, 163, 137, 96.



3-phenyl-2,3,4,9-tetrahydro-1H-carbazole (**2af**)

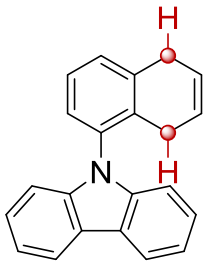
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10: 1, v: v) as an eluent to provide as colorless oil (20.3 mg, 82% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (br s, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.30 (d, J = 8.1 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 3.14 – 3.04 (m, 2H), 2.96 – 2.87 (m, 1H), 2.86 – 2.80 (m, 2H), 2.26 – 2.19 (m, 1H), 2.18 – 2.09 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.83, 136.13, 133.76, 128.61, 127.67, 127.19, 126.36, 121.32, 119.39, 117.88, 110.57, 110.28, 41.28, 30.46, 29.39, 23.49. MS (m/z, EI): 247, 143, 115, 102, 77.



2-(cyclohexa-2,5-dien-1-yl)-3-phenyl-1H-indole (**2ag**)

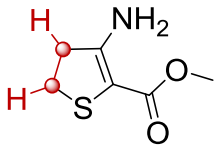
The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as yellow oil (18.5 mg, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (br s, 1H),

7.68 (d, J = 7.9 Hz, 1H), 7.54 (dt, J = 7.8, 1.4 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.37 – 7.33 (m, 2H), 7.23 – 7.18 (m, 1H), 7.15 – 7.11 (m, 1H), 5.98 – 5.91 (m, 2H), 5.84 – 5.78 (m, 2H), 4.52 – 4.45 (m, 1H), 2.92 – 2.76 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.26, 135.55, 135.13, 129.80, 128.71, 128.02, 126.80, 126.28, 125.24, 122.06, 120.07, 119.40, 114.12, 110.77, 33.28, 25.86. MS (m/z, EI): 271, 241, 193, 165, 127.



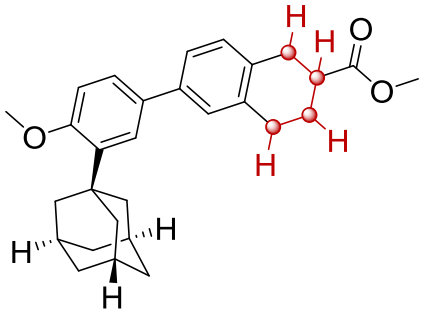
9-(5,8-dihydronaphthalen-1-yl)-9H-carbazole (**2ah**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (17.1 mg, 58% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 – 8.15 (m, 2H), 7.43 – 7.36 (m, 3H), 7.33 (d, J = 7.2 Hz, 1H), 7.28 (td, J = 7.7, 0.9 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.07 – 7.04 (m, 2H), 5.92 – 5.86 (m, 1H), 5.68 – 5.62 (m, 1H), 3.59 – 3.53 (m, 2H), 2.89 – 2.83 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.30, 136.69, 135.48, 133.98, 129.26, 127.20, 127.16, 126.04, 124.33, 124.20, 123.09, 120.45, 119.65, 109.90, 30.11, 25.46. MS (m/z, EI): 295, 254, 166, 139, 115.



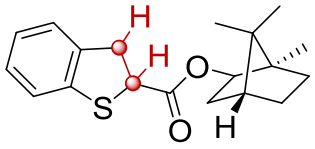
methyl 3-amino-4,5-dihydrothiophene-2-carboxylate (**2ai**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (1: 1, v: v) as an eluent to provide as yellow solid (8.6 mg, 54% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83 (br s, 1H), 3.72 (s, 3H), 3.06 (t, J = 8.0 Hz, 2H), 2.89 (t, J = 8.0 Hz, 2H), 1.70 (br s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.30, 90.43, 51.23, 39.34, 27.80. MS (m/z, EI): 159, 127, 100, 74, 54.



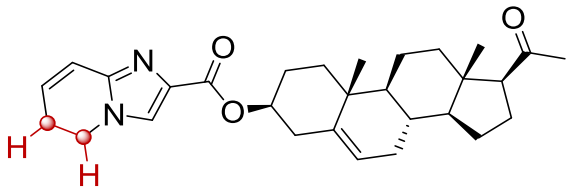
methyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2ak**)

The crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide as white solid (31.5 mg, 73% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.32 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.09 – 2.99 (m, 2H), 2.99 – 2.87 (m, 2H), 2.82 – 2.74 (m, 1H), 2.29 – 2.22 (m, 1H), 2.15 (d, *J* = 2.9 Hz, 6H), 2.08 (s, 3H), 1.95 – 1.85 (m, 1H), 1.79 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.07, 158.44, 139.64, 138.79, 136.03, 133.42, 133.32, 129.53, 127.35, 125.73, 125.28, 124.71, 112.08, 55.27, 51.95, 40.76, 40.21, 37.29, 31.52, 29.27, 28.88, 26.15. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{29}H_{35}O_3^+$, 431.2581; found, 431.2583.



(1*R*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2,3-dihydrobenzo[*b*]thiophene-2-carboxylate (**2al**)

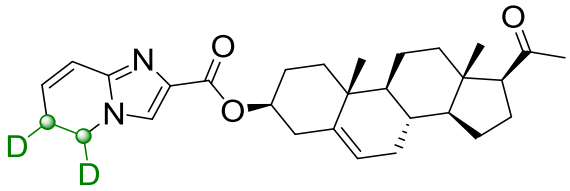
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (50: 1, v: v) as an eluent to provide as colorless oil (19.7 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) **mixture of diastereomers and rotamers:** δ 7.19 – 7.08 (m, 3H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.68 – 4.62 (m, 1H), 4.38 (td, *J* = 8.5, 5.1 Hz, 1H), 3.61 (dd, *J* = 15.9, 5.1 Hz, 1H), 3.49 – 3.42 (m, 1H), 1.82 – 1.76 (m, 1H), 1.75 – 1.69 (m, 2H), 1.68 – 1.64 (m, 1H), 1.52 (td, *J* = 12.0, 11.3, 4.2 Hz, 1H), 1.15 – 1.09 (m, 1H), 1.05 (td, *J* = 10.4, 9.4, 3.9 Hz, 1H), 0.83 (d, *J* = 25.9 Hz, 3H), 0.80 (d, *J* = 5.0 Hz, 3H), 0.76 (d, *J* = 21.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) **mixture of diastereomers and rotamers:** δ 171.34, 171.28, 139.51, 139.39, 138.75, 138.73, 128.59, 128.37, 127.65, 127.64, 124.77, 124.76, 124.66, 124.62, 121.76, 82.49, 82.39, 49.46, 49.17, 49.00, 48.84, 47.03, 46.98, 45.06, 38.77, 38.59, 38.43, 38.24, 33.79, 33.76, 27.10, 20.18, 20.16, 19.89, 19.69, 11.44, 11.30. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{19}H_{25}O_2S^+$, 317.1570; found, 317.1573. Diastereoisomers were determined by ^{1}H NMR analysis as 1.14:1.



(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 5,6-dihydroimidazo[1,2-*a*]pyridine-2-carboxylate (**2am**)

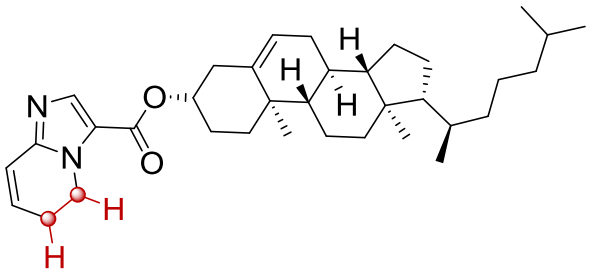
The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (1: 2, v: v) as an eluent to provide as white solid (27.8 mg, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 6.08 – 6.01 (m, 1H), 5.92 – 5.86 (m, 1H), 5.41 – 5.38 (m, 1H), 4.88 (tt, *J* = 11.5, 4.8 Hz,

1H), 4.62 (tt, *J* = 5.1, 2.7 Hz, 2H), 3.57 – 3.52 (m, 2H), 2.57 – 2.49 (m, 2H), 2.47 – 2.42 (m, 1H), 2.23 – 2.15 (m, 1H), 2.12 (s, 3H), 2.06 – 2.03 (m, 1H), 2.02 – 1.97 (m, 2H), 1.90 (dt, *J* = 13.3, 3.5 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.72 – 1.67 (m, 2H), 1.65 – 1.60 (m, 2H), 1.60 – 1.55 (m, 1H), 1.52 – 1.44 (m, 3H), 1.22 – 1.15 (m, 3H), 1.03 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.77, 162.83, 143.41, 140.02, 133.48, 123.86, 123.30, 122.40, 119.35, 74.04, 63.84, 56.99, 50.03, 45.41, 44.14, 38.95, 38.25, 37.24, 36.79, 31.97, 31.92, 31.71, 27.89, 25.25, 24.62, 22.94, 21.18, 19.48, 13.36. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{29}H_{39}N_2O_3^+$, 463.2955; found, 463.2953.



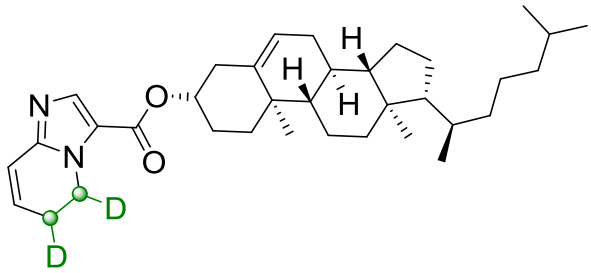
(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 5,6-dihydroimidazo[1,2-*a*]pyridine-2-carboxylate-5,6-*d*$_2$ (**2am'**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (1: 2, v: v) as an eluent to provide as white solid (19.0 mg, 41% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 6.07 – 6.02 (m, 1H), 5.89 (dt, *J* = 10.4, 2.6 Hz, 1H), 5.42 – 5.37 (m, 1H), 4.88 (tt, *J* = 11.5, 4.8 Hz, 1H), 4.64 – 4.58 (m, 1H), 3.56 – 3.49 (m, 1H), 2.57 – 2.48 (m, 2H), 2.48 – 2.42 (m, 1H), 2.23 – 2.16 (m, 1H), 2.13 (s, 3H), 2.07 – 2.03 (m, 1H), 2.02 – 1.97 (m, 2H), 1.90 (dt, *J* = 13.3, 3.5 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.72 – 1.66 (m, 2H), 1.62 – 1.60 (m, 2H), 1.59 – 1.55 (m, 1H), 1.51 – 1.45 (m, 3H), 1.23 – 1.15 (m, 3H), 1.03 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.77, 162.85, 143.41, 140.03, 133.50, 123.86, 123.33, 122.41, 119.36, 74.06, 63.86, 57.01, 50.06, 45.51 – 44.86 (m), 44.15, 38.96, 38.27, 37.25, 36.80, 31.99, 31.93, 31.71, 27.90, 25.39 – 24.77 (m), 24.63, 22.96, 21.19, 19.49, 13.37. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{29}H_{37}D_2N_2O_3^+$, 465.3081; found, 465.3077. The deuterium incorporation was determined by ^{1}H NMR analysis as 93%.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 5,6-dihydroimidazo[1,2-*a*]pyridine-3-carboxylate (**2an**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (3: 1, v: v) as an eluent to provide as white solid (33.6 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (s, 1H), 5.99 – 5.87 (m, 2H), 5.40 (d, *J* = 5.0 Hz, 1H), 4.86 (tt, *J* = 5.2, 2.3 Hz, 2H), 4.77 (tt, *J* = 10.9, 5.6 Hz, 1H), 3.58 – 3.51 (m, 2H), 2.45 – 2.38 (m, 2H), 2.05 – 1.98 (m, 2H), 1.98 – 1.88 (m, 3H), 1.84 – 1.80 (m, 1H), 1.74 – 1.67 (m, 1H), 1.58 – 1.44 (m, 6H), 1.38 – 1.31 (m, 4H), 1.18 – 1.08 (m, 6H), 1.05 (s, 3H), 1.02 – 0.96 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.8 Hz, 6H), 0.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.12, 147.06, 139.74, 136.80, 122.93, 122.24, 121.28, 120.64, 74.17, 56.83, 56.27, 50.17, 46.04, 42.45, 39.86, 39.65, 38.43, 37.16, 36.77, 36.31, 35.93, 32.06, 31.99, 28.37, 28.15, 28.09, 25.65, 24.42, 23.96, 22.96, 22.70, 21.18, 19.50, 18.85, 11.99. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{35}H_{53}N_2O_2^+$, 533.4102; found, 533.4101.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 5,6-dihydroimidazo[1,2-*a*]pyridine-3-carboxylate-5,6-d_2 (**2an'**)

The crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (3: 1, v: v) as an eluent to provide as white solid (24.6 mg, 46% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 6.00 – 5.89 (m, 2H), 5.41 (d, *J* = 4.7 Hz, 1H), 4.84 (s, 1H), 4.78 (tt, *J* = 10.9, 5.1 Hz, 1H), 3.57 – 3.44 (m, 1H), 2.48 – 2.37 (m, 2H), 2.06 – 1.99 (m, 2H), 1.98 – 1.91 (m, 3H), 1.87 – 1.80 (m, 1H), 1.72 – 1.67 (m, 1H), 1.57 – 1.45 (m, 6H), 1.37 – 1.31 (m, 4H), 1.16 – 1.09 (m, 6H), 1.06 (s, 3H), 1.02 – 0.96 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.5, 2.6 Hz, 6H), 0.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.15, 147.07, 139.77, 136.80, 122.95, 122.29, 121.31, 120.65, 74.21, 56.85, 56.29, 50.19, 46.39 – 45.39 (m), 42.47, 39.88, 39.66, 38.44, 37.17, 36.80, 36.33, 35.94, 32.08, 32.02, 28.38, 28.16, 28.10, 25.57 – 25.14 (m), 24.44, 23.98, 22.97, 22.71, 21.20, 19.52, 18.87, 12.01. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{35}H_{51}D_2N_2O_2^+$, 535.4227; found, 535.4228. The deuterium incorporation was determined by ^{1}H NMR analysis as 91%.

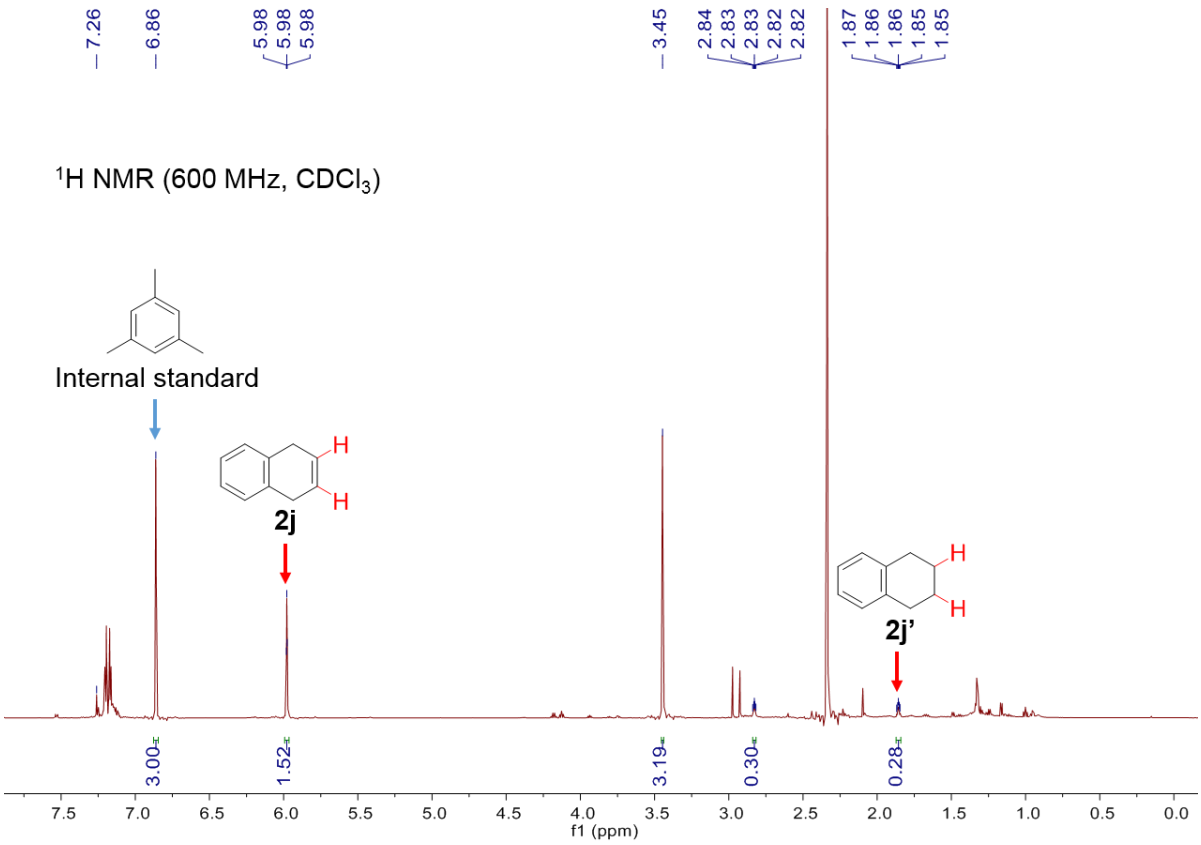
Reduction of **1j**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1j** (0.10 mmol, 1.0 equiv.), DIPEA (0.20

mmol, 2.0 equiv.) and a stirring bar. After adding DMF (1 mL) and H_2O (0.3 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilled with N_2 (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LEDs for 24 h at 25 ℃. After reaction, the mixture was filtrated and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Mesitylene (0.10 mmol, internal standard) was added to the crude mixture and ^{1}H NMR was measured for the mixture.

1,4-dihydronaphthalene, **2j:** 76%

1,2,3,4-tetrahydronaphthalene, **2j':** 7%



Supplementary Figure 23. **^{1}H NMR spectrum of the mixture of 2j + 2j'.**

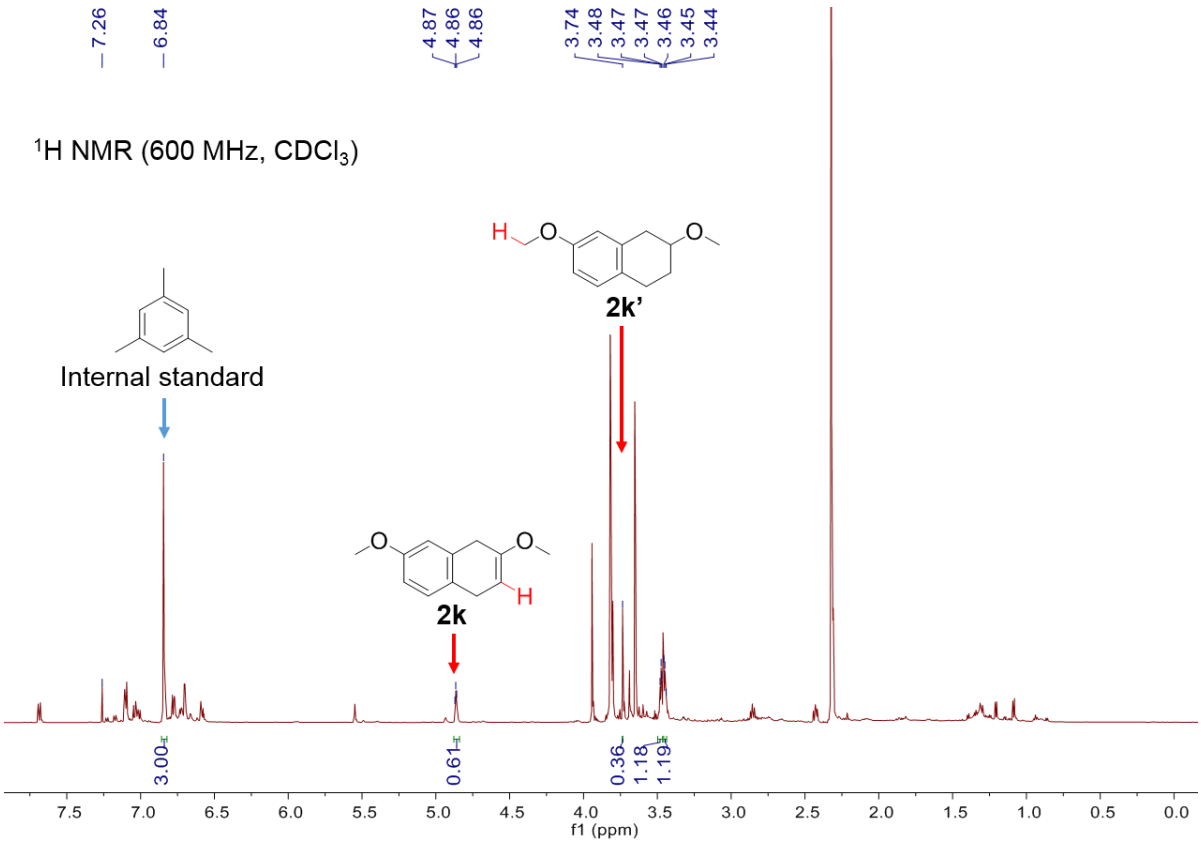
Reduction of **1k**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1k** (0.10 mmol, 1.0 equiv.), DIPEA (0.20 mmol, 2.0 equiv.) and a stirring bar. After adding DMF (1 mL) and H_2O (0.3 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilled with N_2 (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LEDs for 24 h at 25 ℃. After reaction, the mixture was filtrated and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture

was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Mesitylene (0.10 mmol, internal standard) was added to the crude mixture and ^1H NMR was measured for the mixture.

2,7-dimethoxy-1,4-dihydronaphthalene, **2k:** 61%

2,7-dimethoxy-1,2,3,4-tetrahydronaphthalene, **2k':** 12%

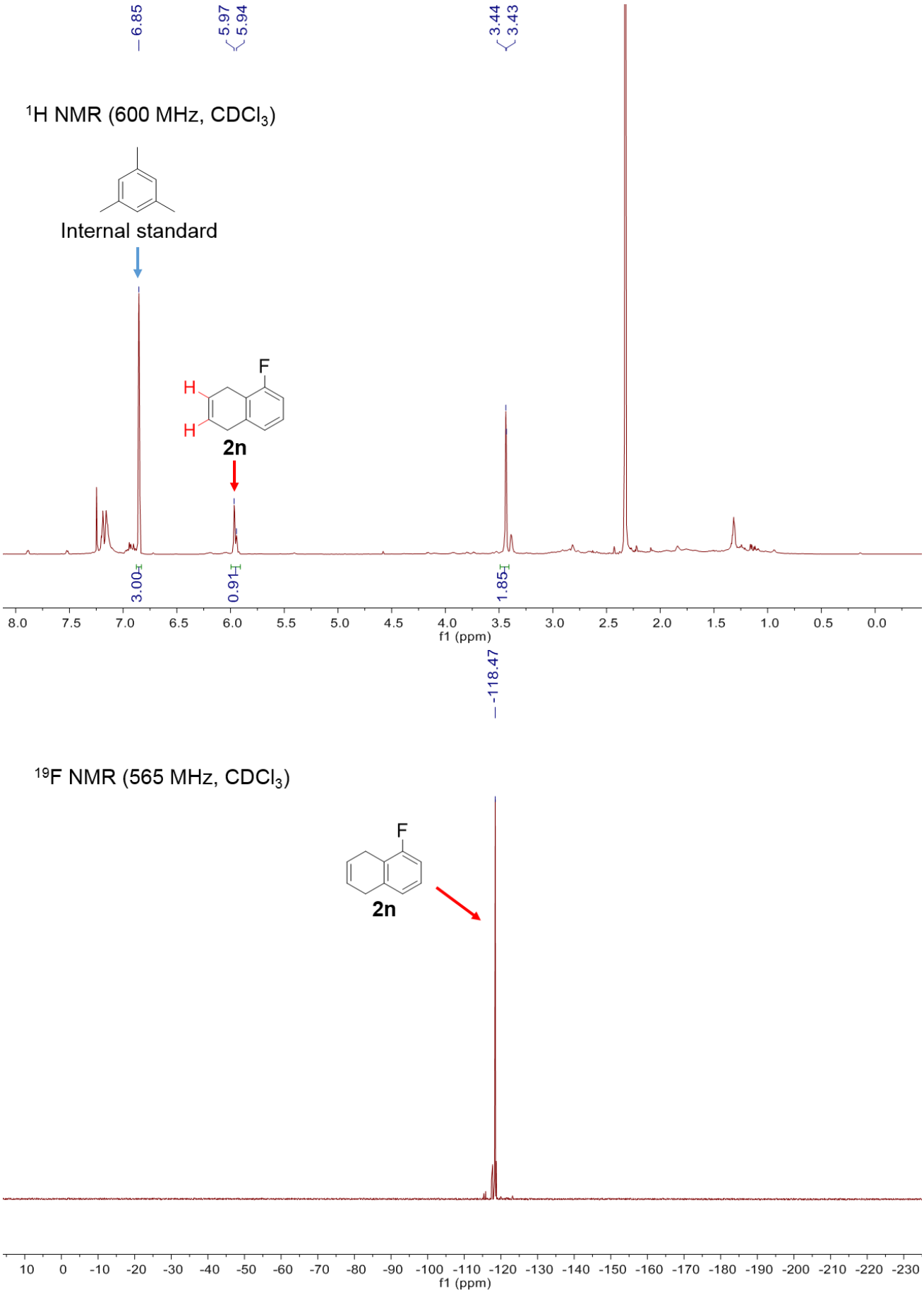


Supplementary Figure 24. **^1H NMR spectrum of the mixture of 2k + 2k'.**

Reduction of **1n**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1n** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.15 mmol, 1.5 equiv.) and a stirring bar. After adding H_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (±10 nm) LED for 7 h at 25 ℃. After reaction, the mixture was quenched by adding brine (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously, filtrated, and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Mesitylene (0.10 mmol, internal standard) was added to the crude mixture and ^1H NMR was measured for the mixture.

5-fluoro-1,4-dihydronaphthalene, **2n:** 45%



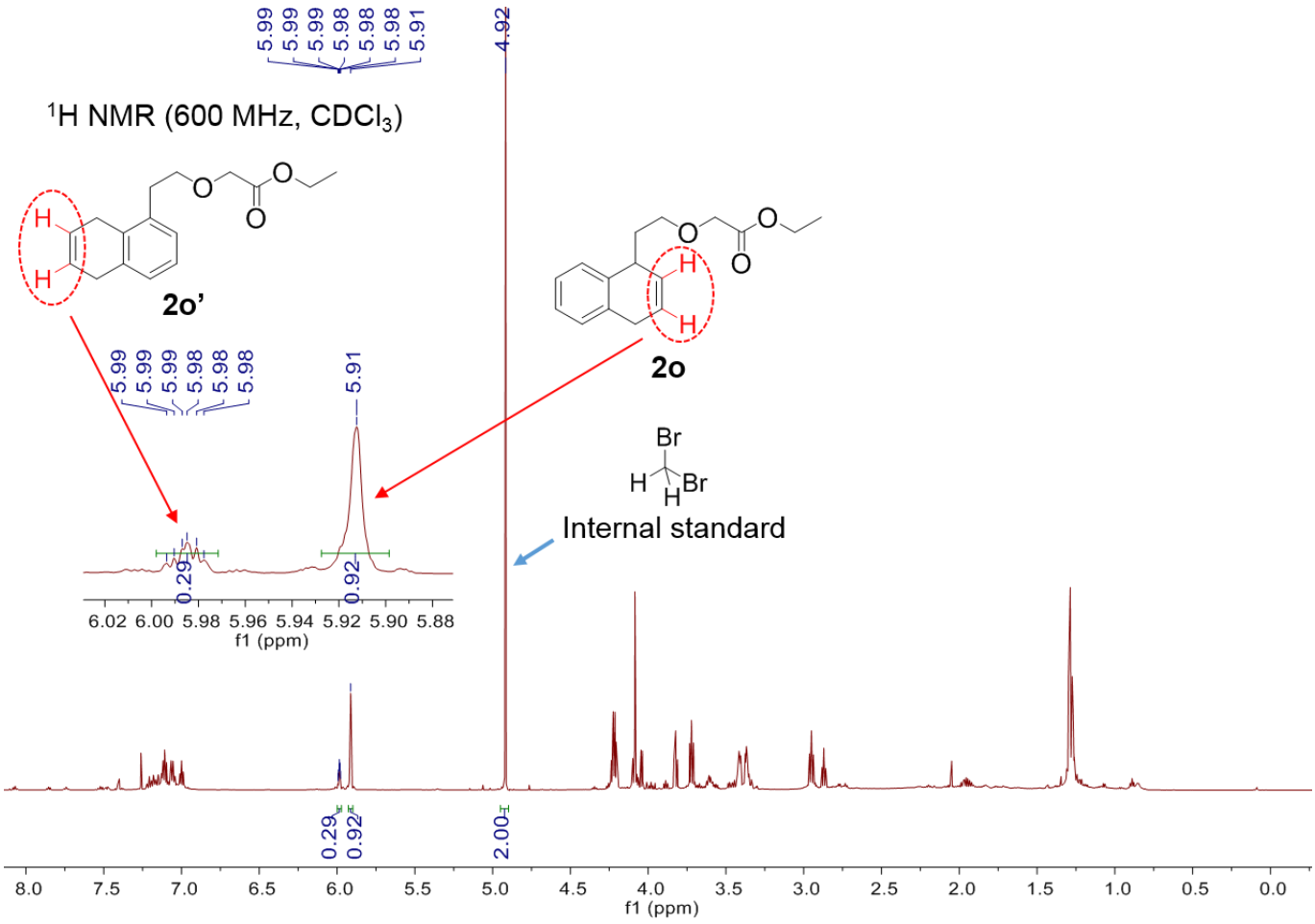
Supplementary Figure 25. ^{1}H and ^{19}F NMR spectra of reaction mixture containing 2n.

Reduction of **1o**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1o** (0.10 mmol, 1.0 equiv.), DIPEA (0.20 mmol, 2.0 equiv.) and a stirring bar. After adding DMF (1 mL) and H_2O (0.3 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was filtrated and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Dibromomethane (0.10 mmol, internal standard) was added to the crude mixture and ^{1}H NMR was measured for the mixture.

ethyl 2-(2-(1,4-dihydronaphthalen-1-yl)ethoxy)acetate, **2o:** 46%

ethyl 2-(2-(5,8-dihydronaphthalen-1-yl)ethoxy)acetate, **2o':** 15%



Supplementary Figure 26. ^{1}H NMR spectrum of the mixture of 2o + 2o'.

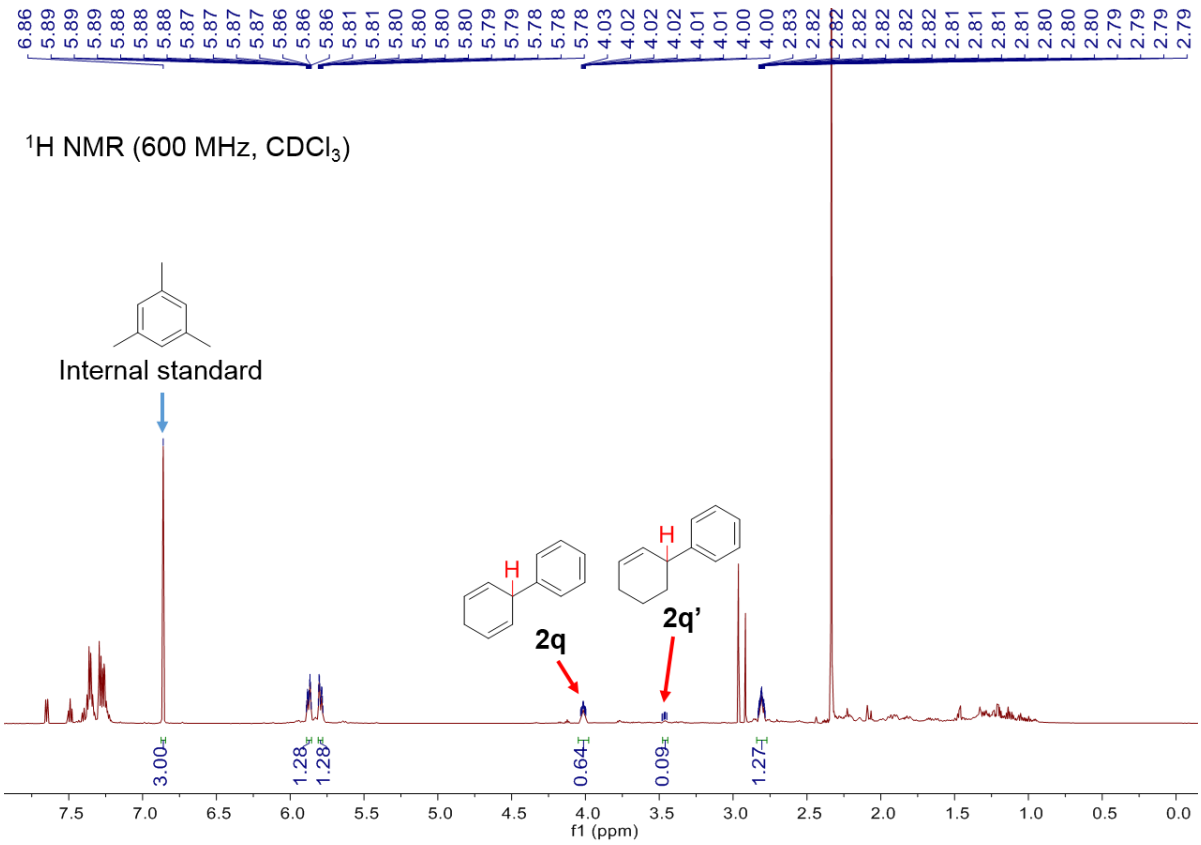
Reduction of **1q**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1q** (0.10 mmol, 1.0 equiv.), DIPEA (0.20

mmol, 2.0 equiv.) and a stirring bar. After adding DMF (1 mL) and H_2O (0.3 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was filtrated and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Mesitylene (0.10 mmol, internal standard) was added to the crude mixture and ^{1}H NMR was measured for the mixture.

1,4-dihydro-1,1'-biphenyl, **2q:** 64%

1,2,3,4-tetrahydro-1,1'-biphenyl, **2q':** 9%



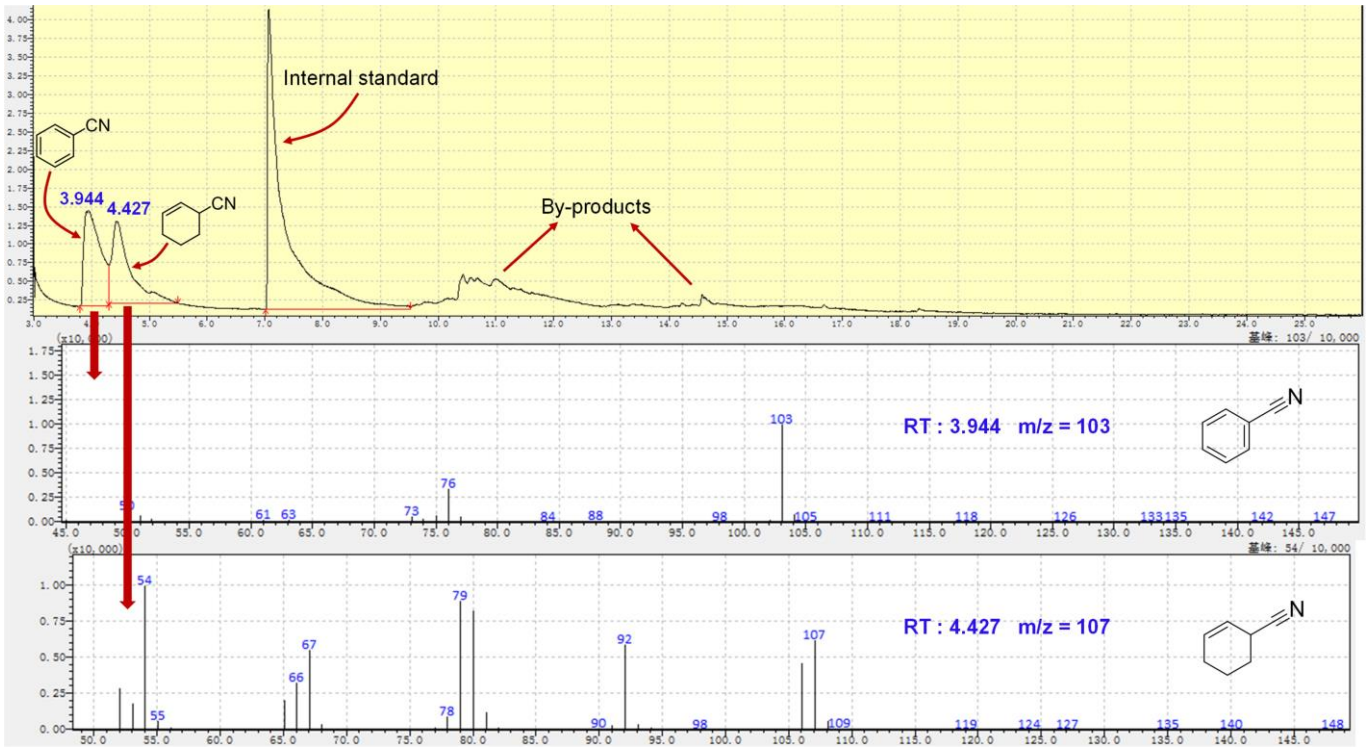
Supplementary Figure 27. ^{1}H NMR spectrum of the mixture of 2q + 2q'.

Reduction of **1s**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1s** (0.10 mmol, 1.0 equiv.), DIPEA (0.20 mmol, 2.0 equiv.) and a stirring bar. After adding DMF (1 mL) and H_2O (0.3 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was quenched by adding brine (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The

mixture was shaken vigorously. After phase separation, the organic layer was filtrated and analyzed by GC-MS. The yield of product was determined with 1,3-dimethoxybenzene as internal standard.

cyclohex-2-ene-1-carbonitrile, **2s:** 24%



Supplementary Figure 28. GC-MS spectra of reaction mixture containing 2s.

Reduction of **1aj**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1aj** (0.10 mmol, 1.0 equiv.), DIPEA (0.20 mmol, 2.0 equiv.) and a stirring bar. After adding DMF (1 mL) and H_2O (0.3 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was filtrated and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Purification was performed by column chromatography on silica gel using petroleum ether: ethyl acetate (50: 1, v: v) as eluent to afford a mixture of (**1aj**+**2aj** + **2aj'**).

methyl (*S*)-2-(6-methoxy-1,4-dihydronaphthalen-2-yl)propanoate, **2aj**: 35%

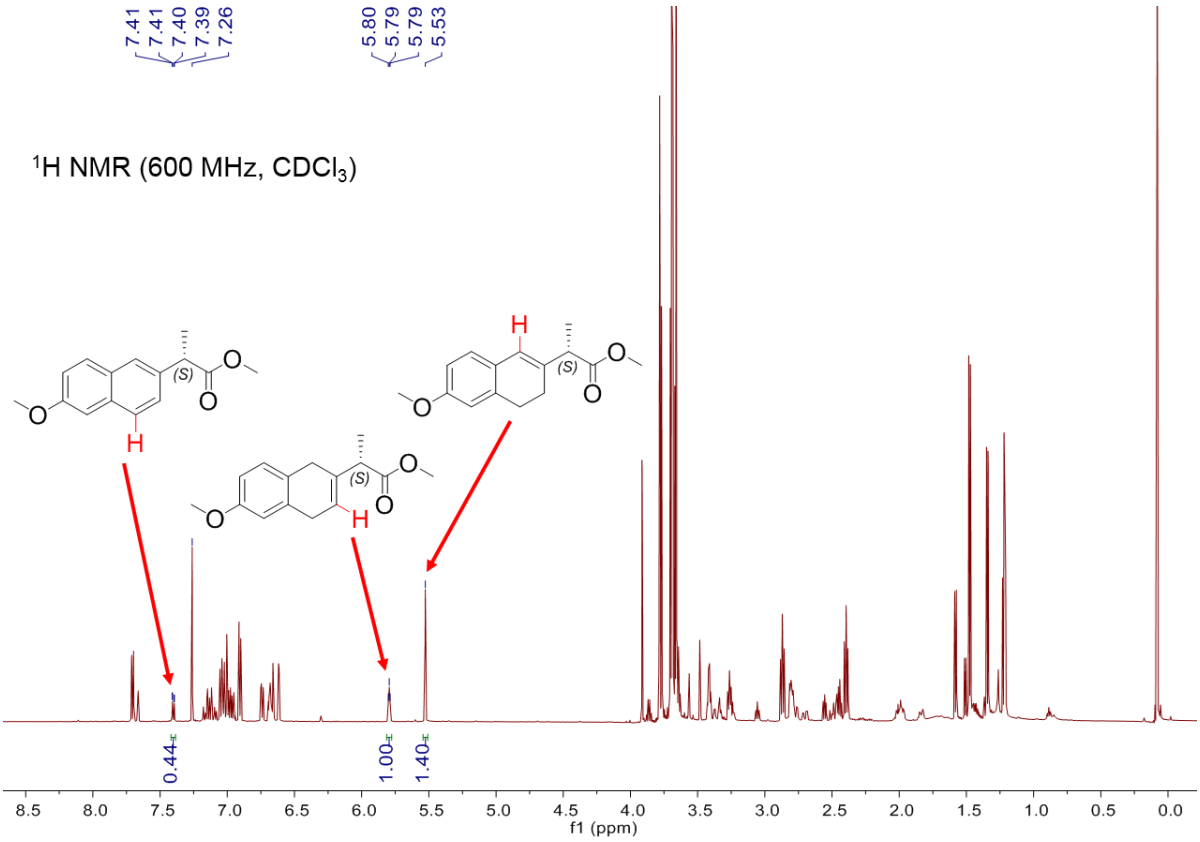
methyl (*S*)-2-(6-methoxy-3,4-dihydronaphthalen-2-yl)propanoate, **2aj'**: 49%

Starting material, **1aj**: 15%

Note: The isolated compounds contain starting material **1aj** and two reduced products **2aj** and **2aj'**. This

mixture could not be separated by column chromatography. Therefore, the NMR yield of the two reduced products **2aj** + **2aj'** is calculated from the overall isolated yield.

Spectroscopic data matched those reported in the literature[12].



Supplementary Figure 29. **^{1}H NMR spectrum of the mixture of 1aj + 2aj + 2aj'.**

Reduction of **1ao**:

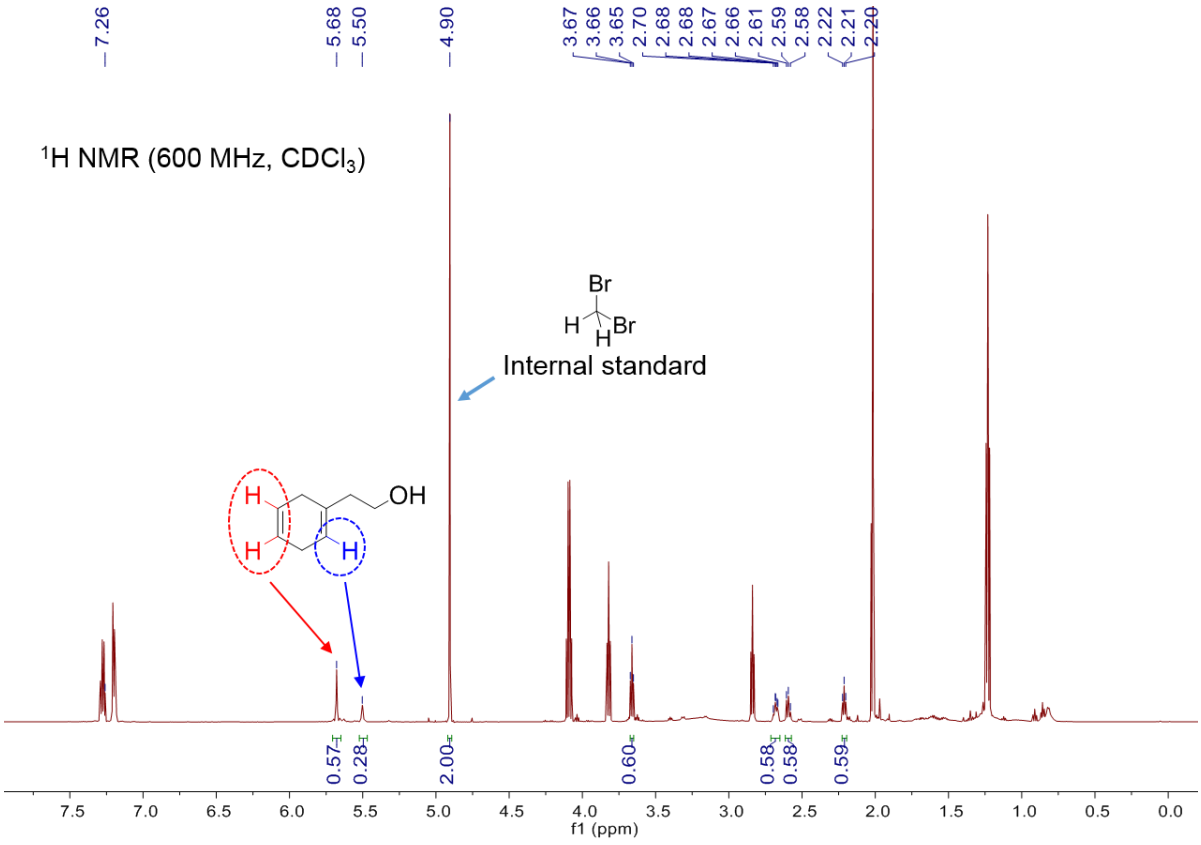
A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1ao** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.20 mmol, 2.0 equiv.), DBU (0.2 mL) and a stirring bar. After adding H_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was quenched by adding 2 M HCl (2 mL) and extracted with ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously. After phase separation, the organic layer was filtrated and analyzed by GC-FID. The yield of product was determined with toluene (0.1 mmol) as internal standard. Because of the volatility of 1,4-cyclohexadiene, the reaction solution was not concentrated in vacuo and isolated.

1,4-cyclohexadiene, **2ao:** 27%

Reduction of **1ap**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1ap** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.20 mmol, 2.0 equiv.), DBU (0.2 mL) and a stirring bar. After adding H_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was quenched by adding 2 M HCl (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously, filtrated, and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Dibromomethane (0.10 mmol, internal standard) was added to the crude mixture and ^{1}H NMR was measured for the mixture.

2-(cyclohexa-1,4-dien-1-yl)ethan-1-ol, **2ap:** 28%



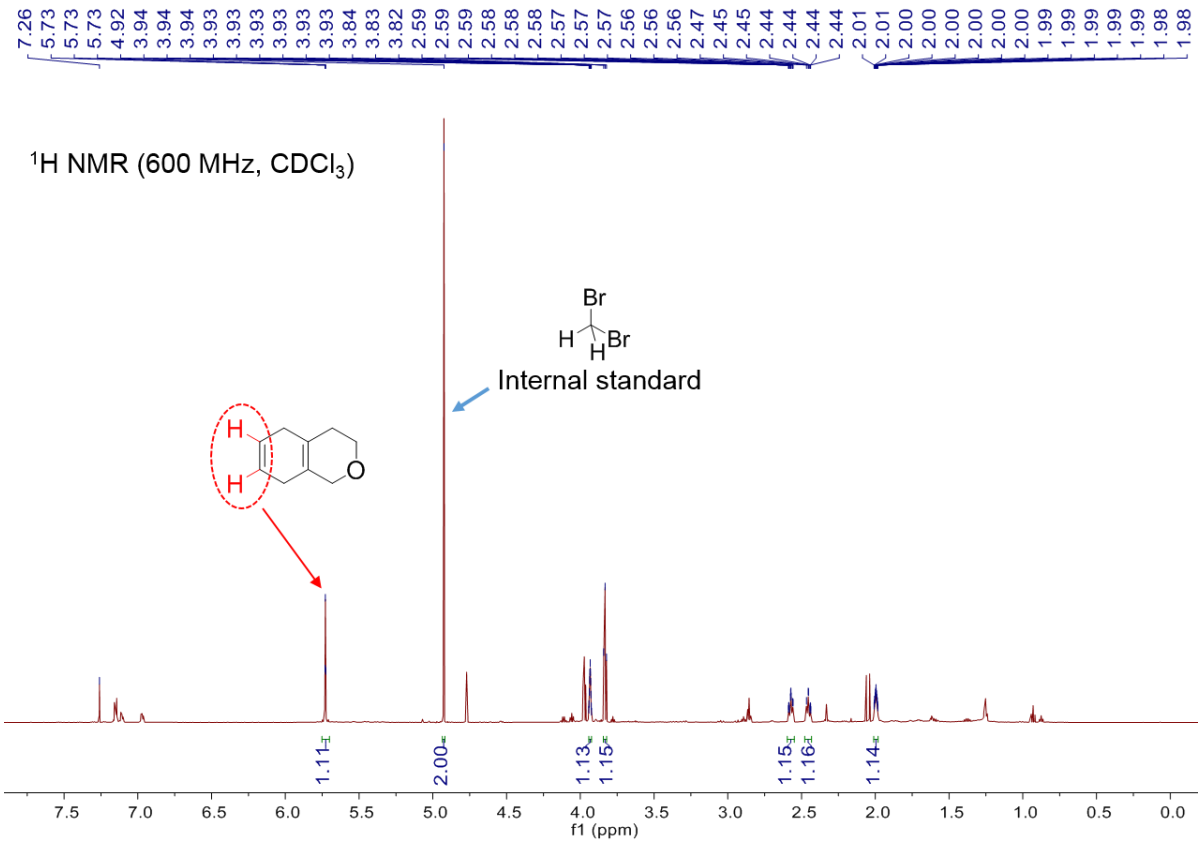
Supplementary Figure 30. ^{1}H NMR spectrum of reaction mixture containing 2ap.

Reduction of **1aq**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1aq** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.20 mmol, 2.0 equiv.), DBU (0.2 mL) and a stirring bar. After adding H_2O (1 mL)

into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was quenched by adding 2 M HCl (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously, filtrated, and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Dibromomethane (0.10 mmol, internal standard) was added to the crude mixture and ^{1}H NMR was measured for the mixture.

3,4,5,8-tetrahydro-1H-isochromene, **2aq:** 56%



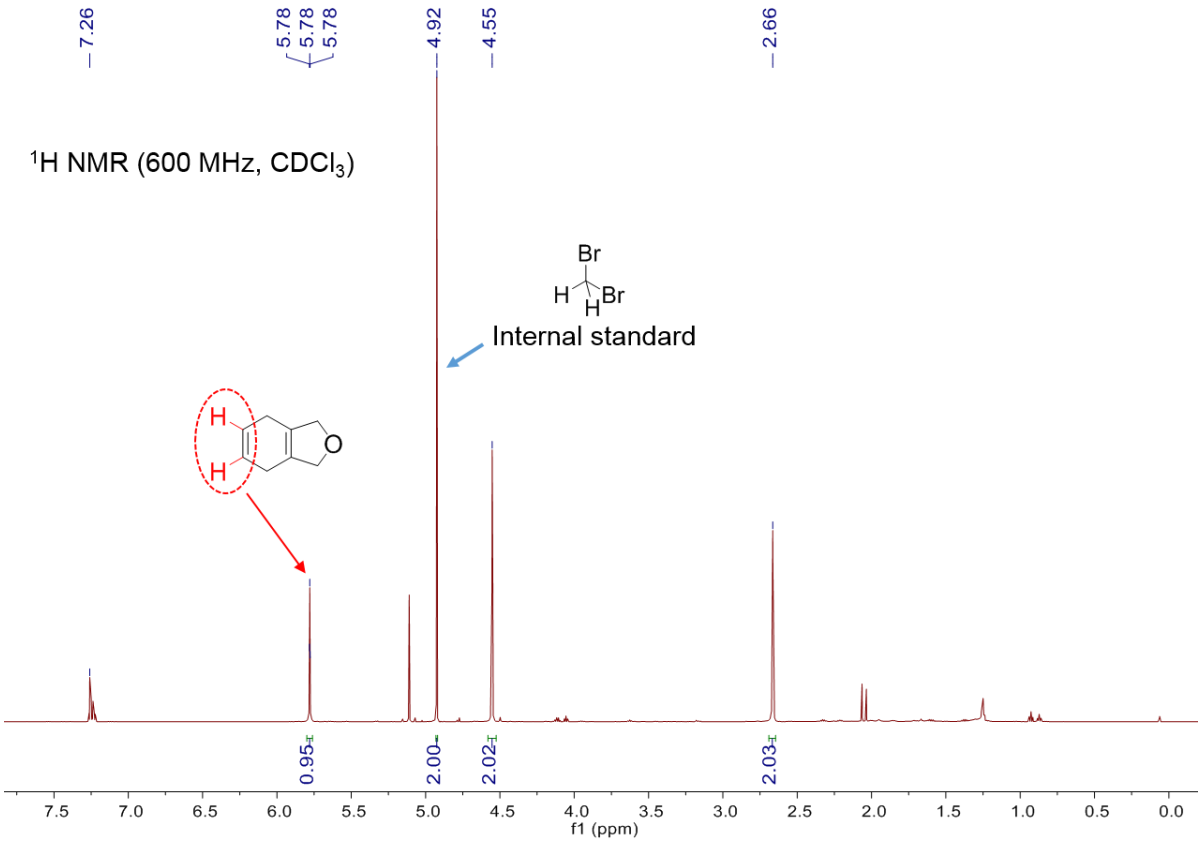
Supplementary Figure 31. ^{1}H NMR spectrum of reaction mixture containing 2aq.

Reduction of **1ar**:

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **1ar** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.20 mmol, 2.0 equiv.), DBU (0.2 mL) and a stirring bar. After adding H_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was quenched by adding 2 M HCl (2 mL), followed by ethyl

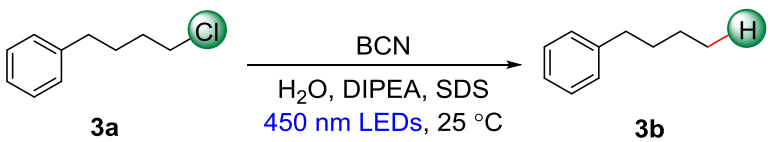
acetate (AcOEt, 2 mL). The mixture was shaken vigorously, filtrated, and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Dibromomethane (0.10 mmol, internal standard) was added to the crude mixture and ^1H NMR was measured for the mixture.

1,3,4,7-tetrahydroisobenzofuran, **2ar:** 48%



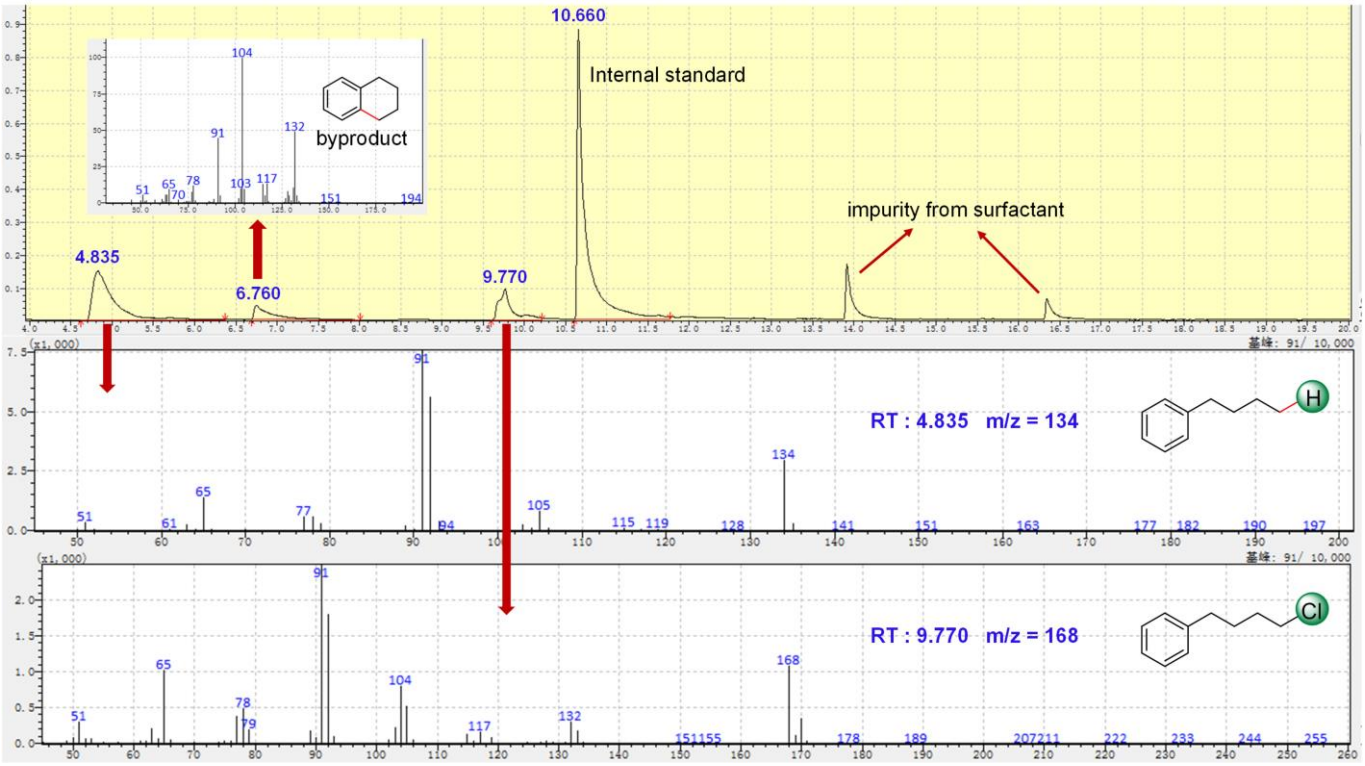
Supplementary Figure 32. **^1H NMR spectrum of reaction mixture containing 2ar.**

Photocatalytic hydrodehalogenation of alkyl chloride



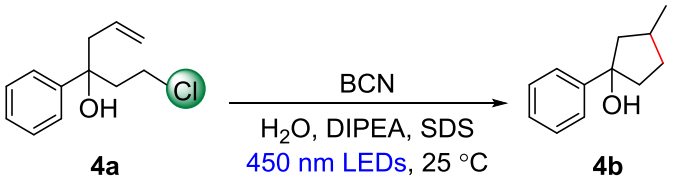
A 10 mL Schlenk flask was equipped with the BCN (10 mg), **3a** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.15 mmol, 1.5 equiv.) and a stirring bar. After adding H_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilling with pure nitrogen gas (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (±10 nm) LED for 24 h at 25 ℃. After reaction, the mixture was quenched by adding brine (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The

mixture was shaken vigorously. After phase separation, the organic layer was filtrated and analyzed by GC-MS. The yield of product was determined with 1,3,5-trimethoxybenzene as internal standard. butylbenzene, **3b:** 48%



Supplementary Figure 33. GC-MS spectra of reaction mixture containing 3b.

Photocatalytic reductive intramolecular cyclization of alkyl chloride



4a **4b**

A 10 mL Schlenk flask was equipped with the BCN (10 mg), **4a** (0.10 mmol, 1.0 equiv.), SDS (0.15 mmol, 1.5 equiv.), DIPEA (0.15 mmol, 1.5 equiv.) and a stirring bar. After adding H_2O (1 mL) into the reaction tube, the Schlenk flask was degassed with a vacuum pump and backfilled with N_2 (1 bar). Then the reaction mixture was stirred and irradiated using a 450 nm (± 10 nm) LEDs for 24 h at 25 ℃. After reaction, the mixture was quenched by adding brine (2 mL), followed by ethyl acetate (AcOEt, 2 mL). The mixture was shaken vigorously, filtrated, and then transferred to a separatory funnel. Brine (10 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). Combined organic fractions were washed with fresh brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. Purification was performed by column chromatography on silica gel using petroleum ether: ethyl acetate (40: 1, v: v) as eluent to afford product

4b as colorless oil (9.9 mg, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.25 – 2.17 (m, 2H), 2.17 – 2.12 (m, 1H), 2.05 – 1.98 (m, 1H), 1.69 – 1.63 (m, 2H), 1.48 – 1.39 (m, 1H), 1.12 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.43, 128.34, 126.91, 125.09, 84.12, 51.13, 41.68, 32.97, 32.73, 21.02. MS (m/z, EI): 176, 147, 133, 120, 105, 91, 77.

Supplementary References

1 Sellergren, B., Wieschemeyer, J., Boos, K. S. & Seidel, D. Imprinted polymers for selective adsorption of cholesterol from gastrointestinal fluids. *Chem. Mater.* **10**, 4037-4046, (1998).

2 Chien, L. C., Chiang, C. W., Lao, C. C. *et al.* Boron carbon oxynitride as a novel metal-free photocatalyst. *Nanoscale Res. Lett.* **16**, 176, (2021).

3 Dorn, R. W., Ryan, M. J., Kim, T. H. *et al.* Identifying the molecular edge termination of exfoliated hexagonal boron nitride nanosheets with solid-state NMR spectroscopy and plane-wave DFT calculations. *Chem. Mater.* **32**, 3109-3121, (2020).

4 Kroeker, S. & Stebbins, J. F. Three-coordinated boron-11 chemical shifts in borates. *Inorg. Chem.* **40**, 6239-6246, (2001).

5 Gervais, C., Framery, E., Duriez, C. *et al.* ^{11}B and ^{15}N solid state NMR investigation of a boron nitride preceramic polymer prepared by ammonolysis of borazine. *J. Eur. Ceram. Soc.* **25**, 129-135, (2005).

6 Chen, S. R., Li, P., Xu, S. T. *et al.* Carbon doping of hexagonal boron nitride porous materials toward CO_2 capture. *J. Mater. Chem. A.* **6**, 1832-1839, (2018).

7 Toury, B., Gervais, C., Dibandjo, P. *et al.* High-resolution ^{15}N solid-state NMR investigations on borazine-based precursors. *Appl. Organomet. Chem.* **18**, 227-232, (2004).

8 Ghosh, I., Khamrai, J., Savateev, A. *et al.* Organic semiconductor photocatalyst can bifunctionalize arenes and heteroarenes. *Science* **365**, 360-366, (2019).

9 Shi, J. L., Yuan, T., Zheng, M. F. & Wang, X. C. Metal-free heterogeneous semiconductor for visible-light photocatalytic decarboxylation of carboxylic acids. *ACS Catal.* **11**, 3040-3047, (2021).

10 Xu, J. H., Cao, J. L., Wu, X. Y. *et al.* Unveiling extreme photoreduction potentials of donor-acceptor cyanoarenes to access aryl radicals from aryl chlorides. *J. Am. Chem. Soc.* **143**, 13266-13273, (2021).

11 Huang, C. J., Chen, C., Zhang, M. W. *et al.* Carbon-doped BN nanosheets for metal-free photoredox catalysis. *Nat. Commun.* **6**, 7698, (2015).

12 Chatterjee, A. & König, B. Birch-type photoreduction of arenes and heteroarenes by sensitized electron transfer. *Angew. Chem. Int. Ed.* **58**, 14289-14294, (2019).

13 Costanzo, M. J., Patel, M. N., Petersen, K. A. & Vogt, P. F. Ammonia-free Birch reductions with sodium stabilized in silica gel, Na-SG(I). *Tetrahedron Lett.* **50**, 5463-5466, (2009).

14 Il Yoo, B., Kim, Y. J., You, Y., Yang, J. W. & Kim, S. W. Birch reduction of aromatic compounds by inorganic electride $[Ca_2N]^+ \bullet e^-$ in an alcoholic solvent: an analogue of solvated electrons. *J. Org. Chem.* **83**, 13847-13853, (2018).

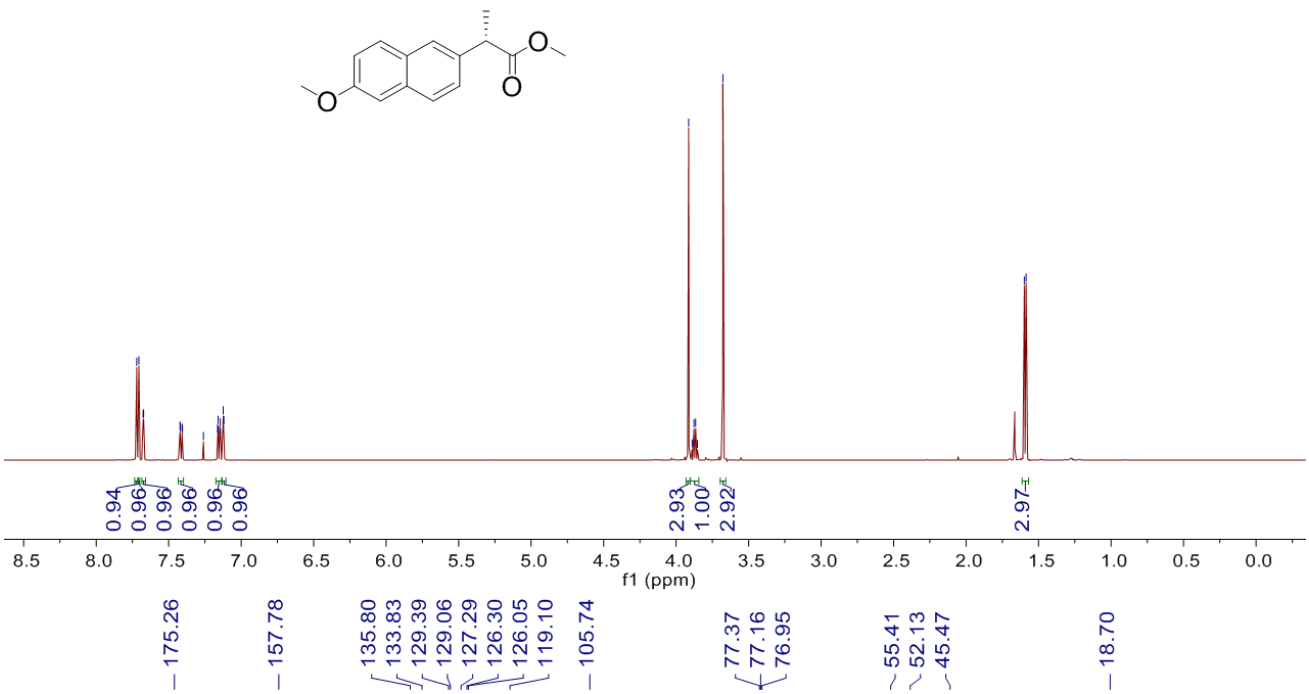
15 Lei, P., Ding, Y. X., Zhang, X. H. *et al.* A practical and chemoselective ammonia-free Birch reduction. *Org. Lett.* **20**, 3439-3442, (2018).

16 Dahlen, A., Nilsson, A. & Hilmersson, G. Estimating the limiting reducing power of SmI_2/H_2O/amine and YbI_2/H_2O/amine by efficient reduction of unsaturated hydrocarbons. *J. Org. Chem.* **71**, 1576-1580, (2006).

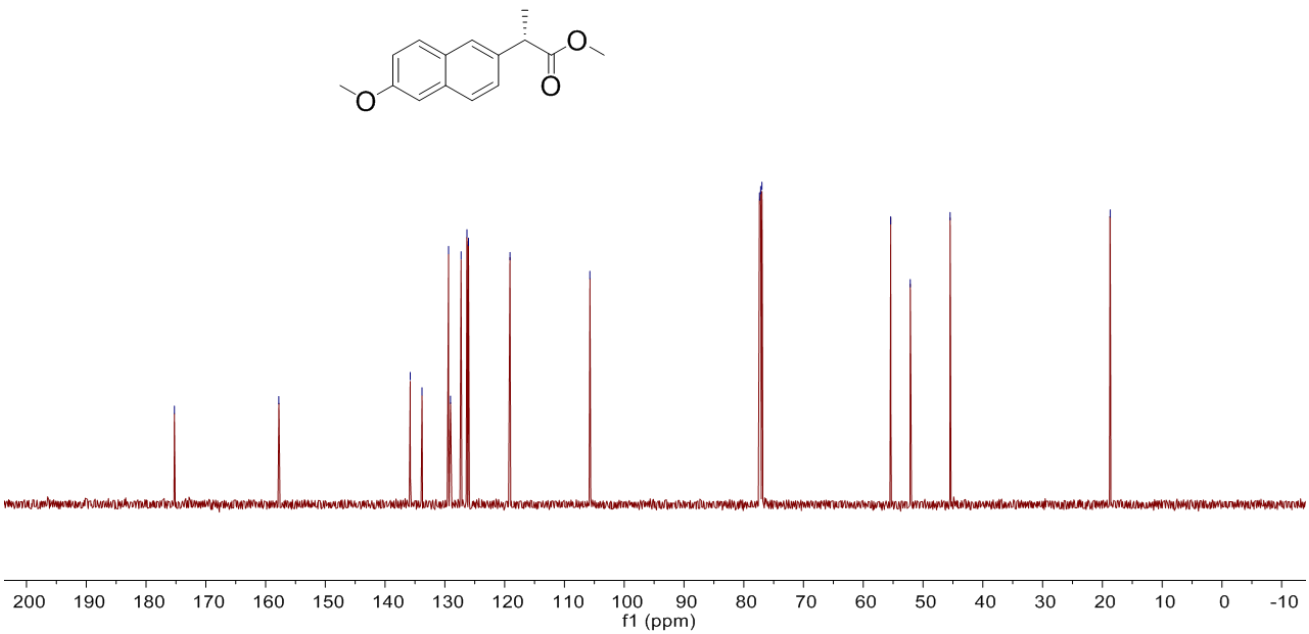
NMR spectra of substrate

1aj

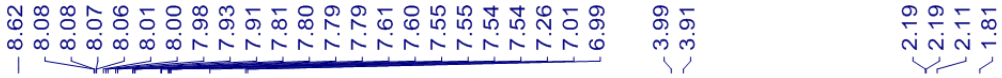
^{1}H NMR (600 MHz, $CDCl_3$)



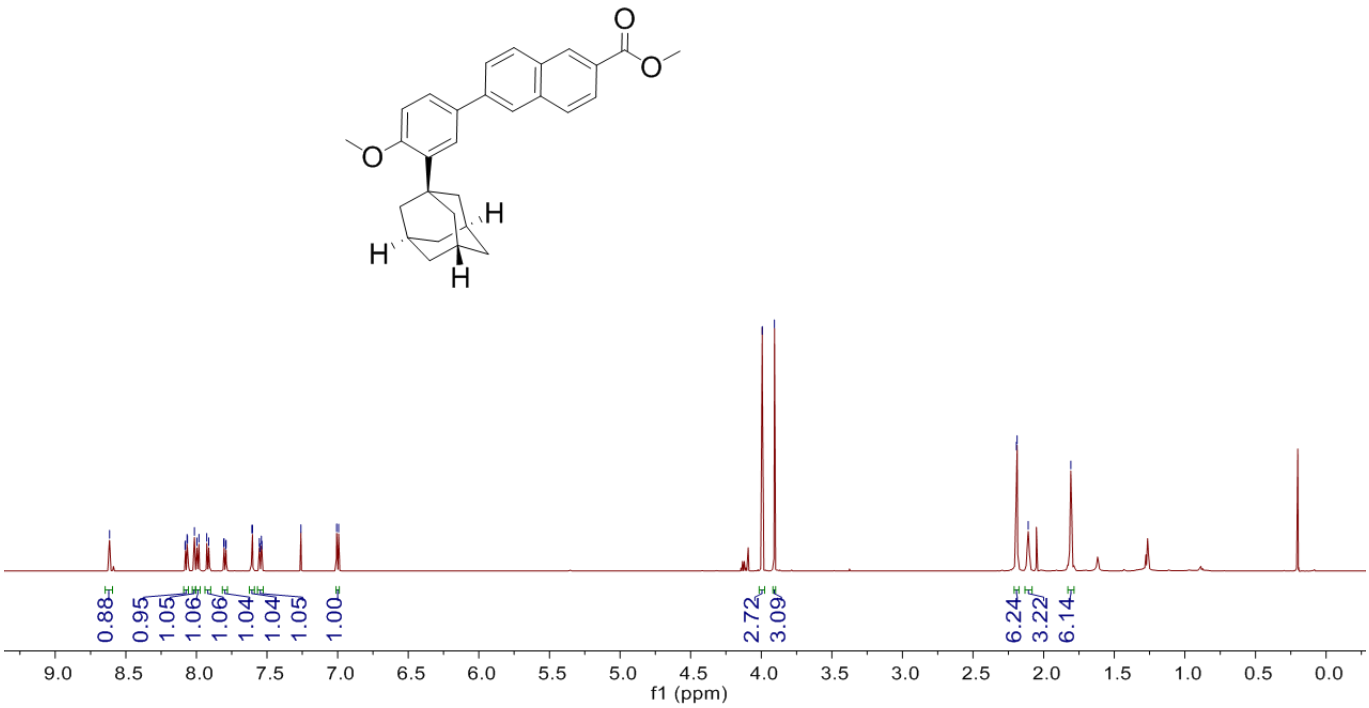
^{13}C NMR (151 MHz, $CDCl_3$)



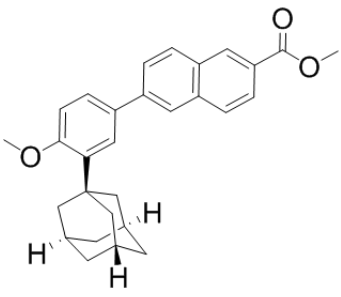
1ak



^{1}H NMR (600 MHz, $CDCl_3$)

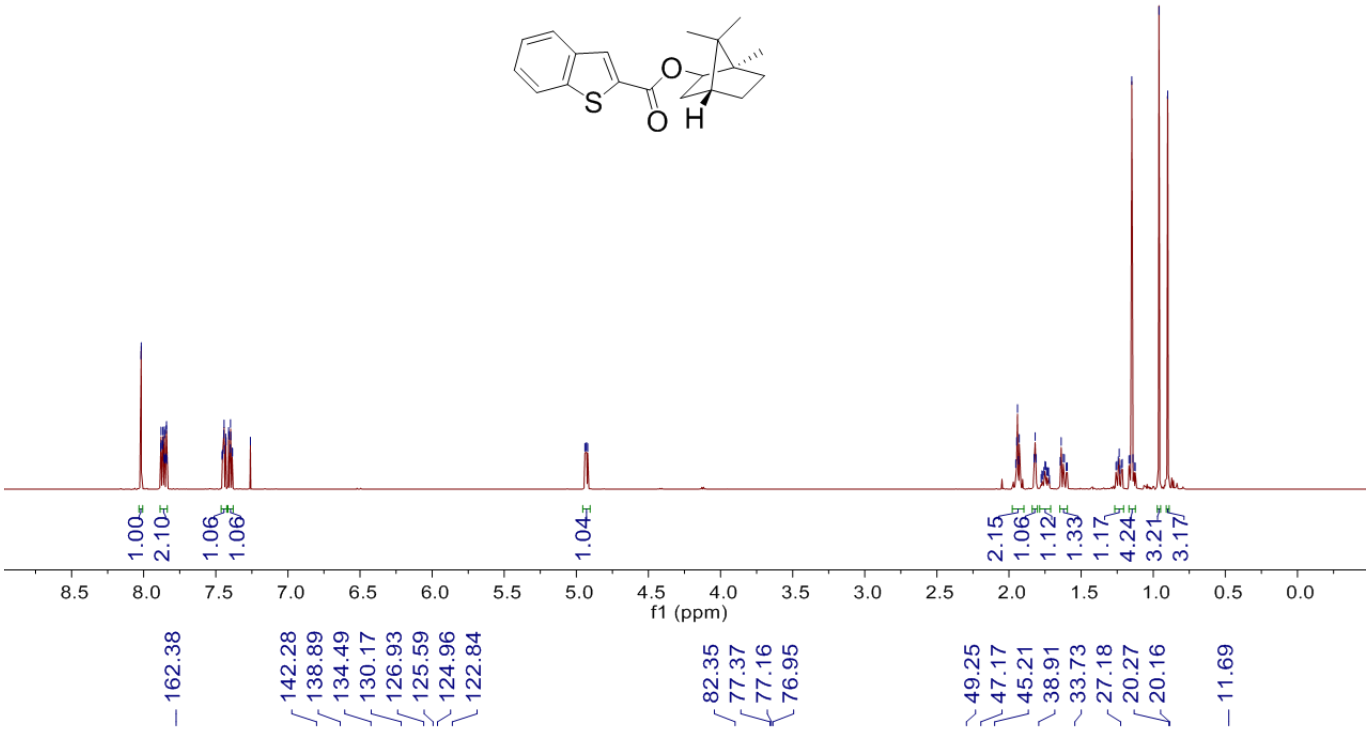


^{13}C NMR (151 MHz, $CDCl_3$)

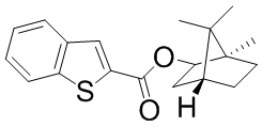


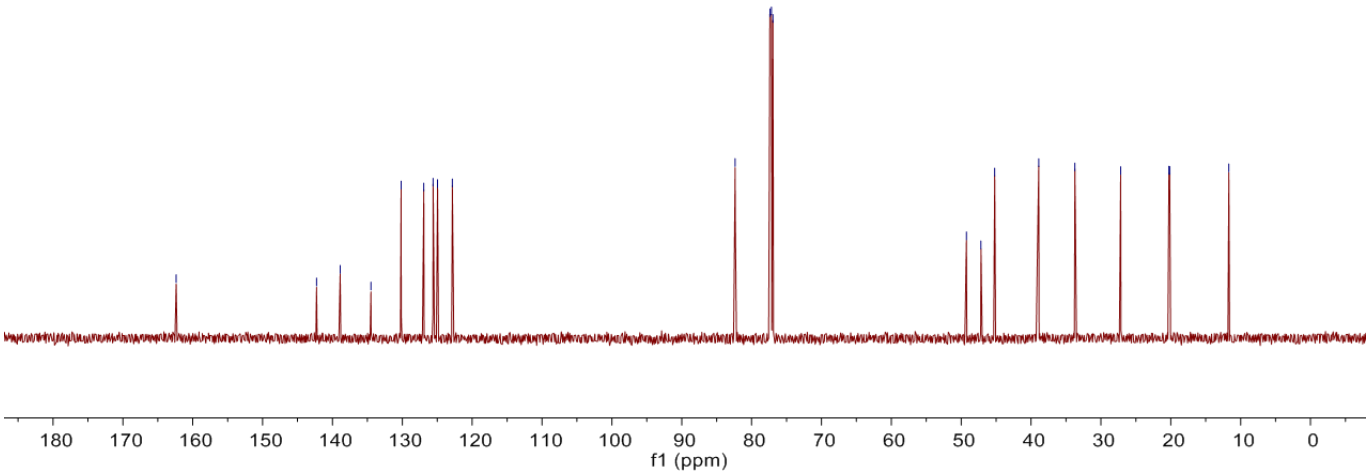
1al

^{1}H NMR (600 MHz, $CDCl_3$)



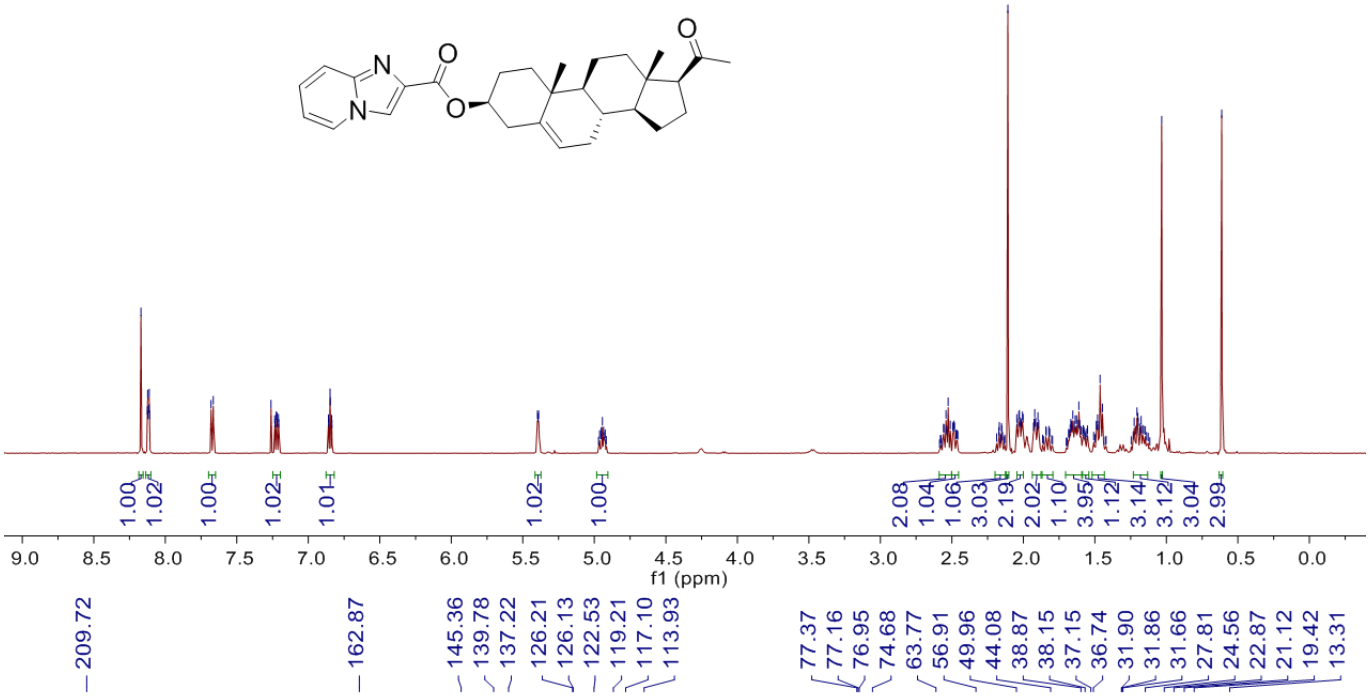
^{13}C NMR (151 MHz, $CDCl_3$)



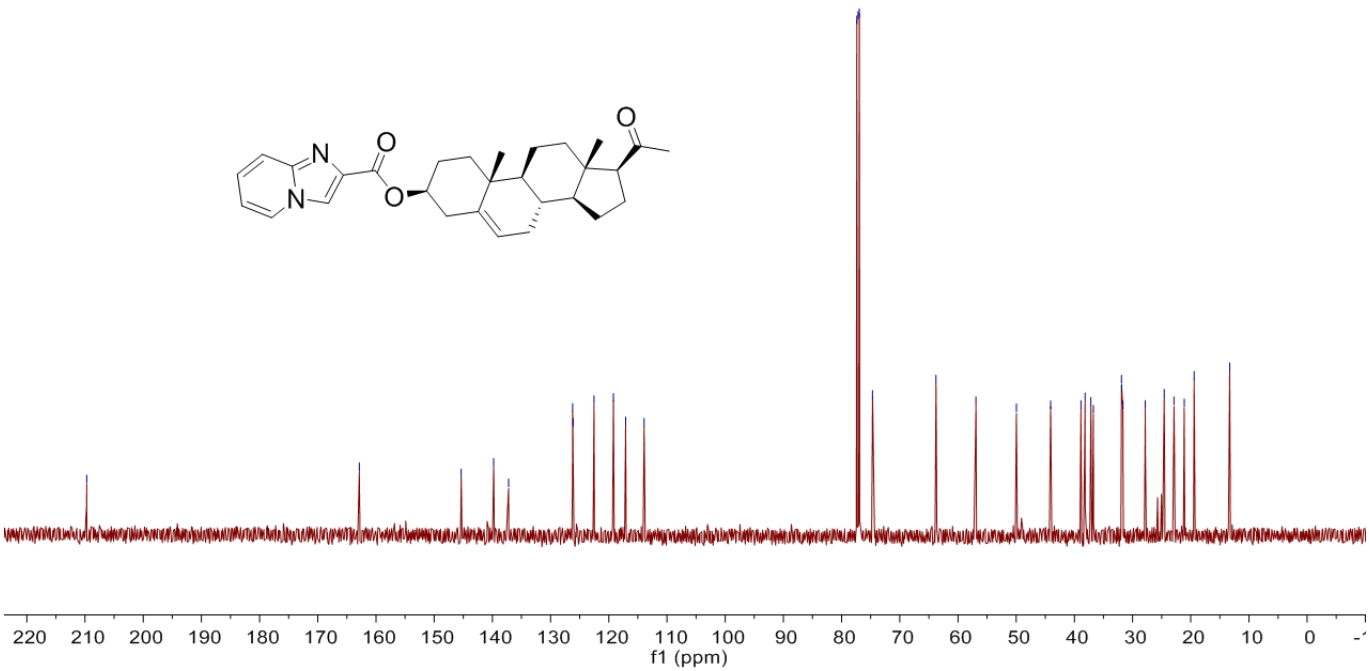


1am

^{1}H NMR (600 MHz, $CDCl_3$)

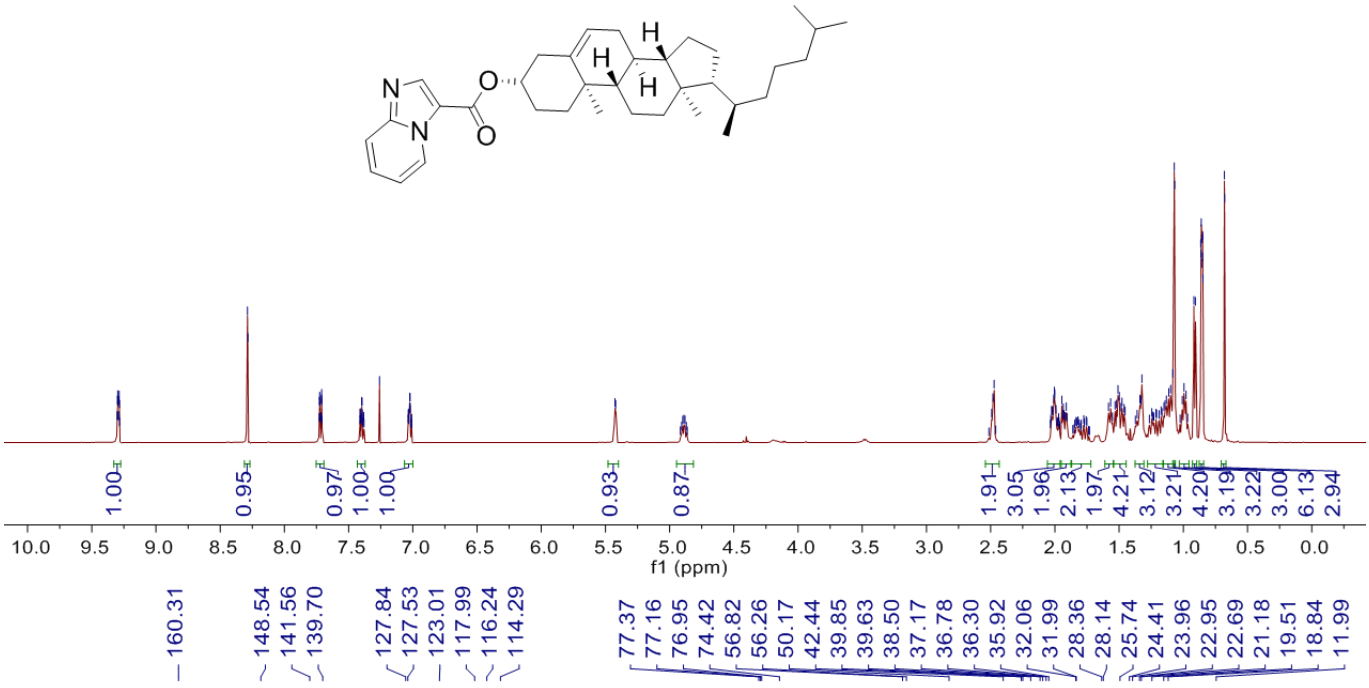


^{13}C NMR (151 MHz, $CDCl_3$)

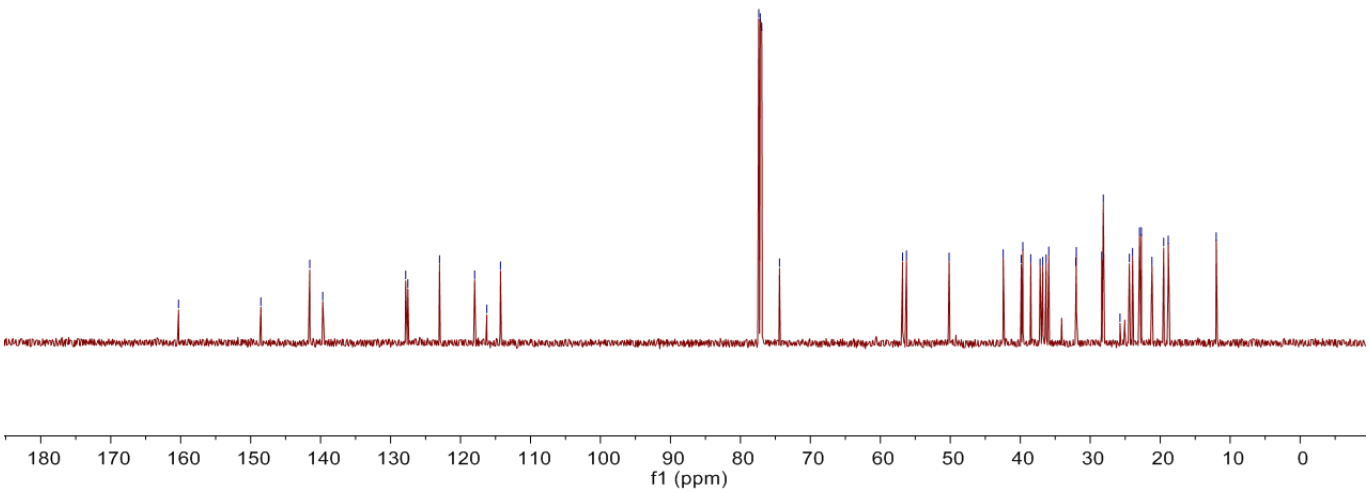


1an

^{1}H NMR (600 MHz, $CDCl_3$)

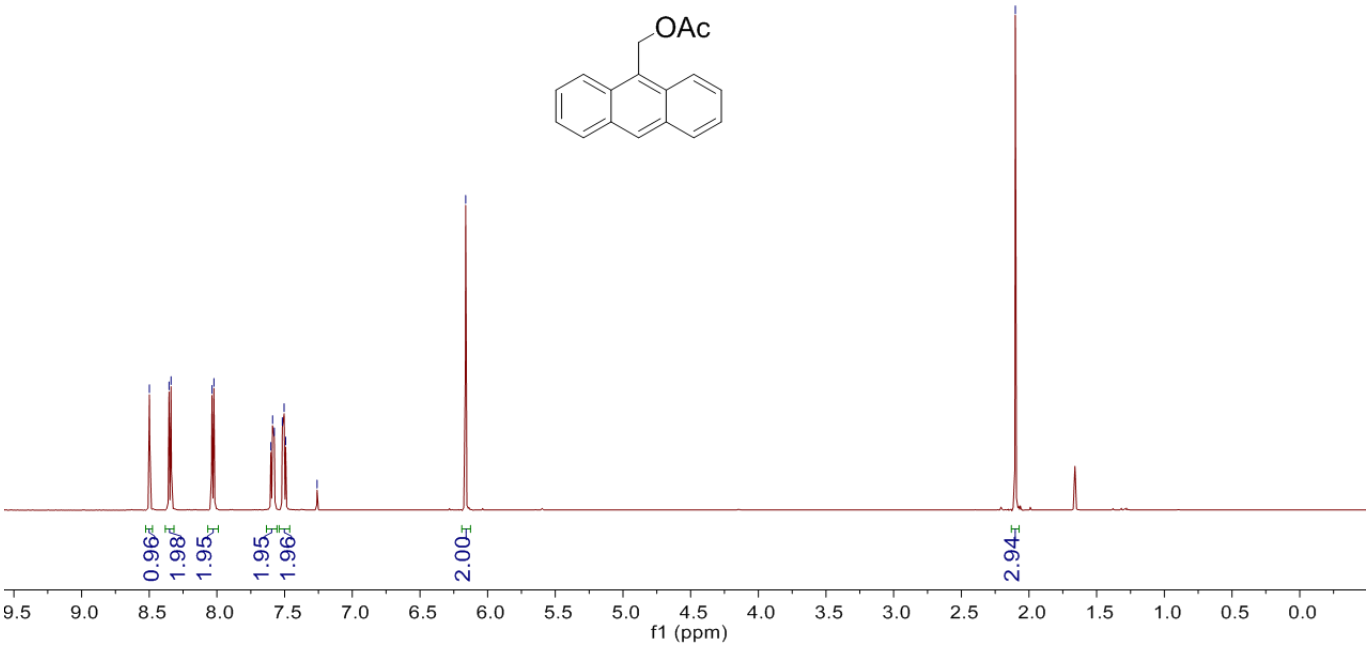


^{13}C NMR (151 MHz, $CDCl_3$)

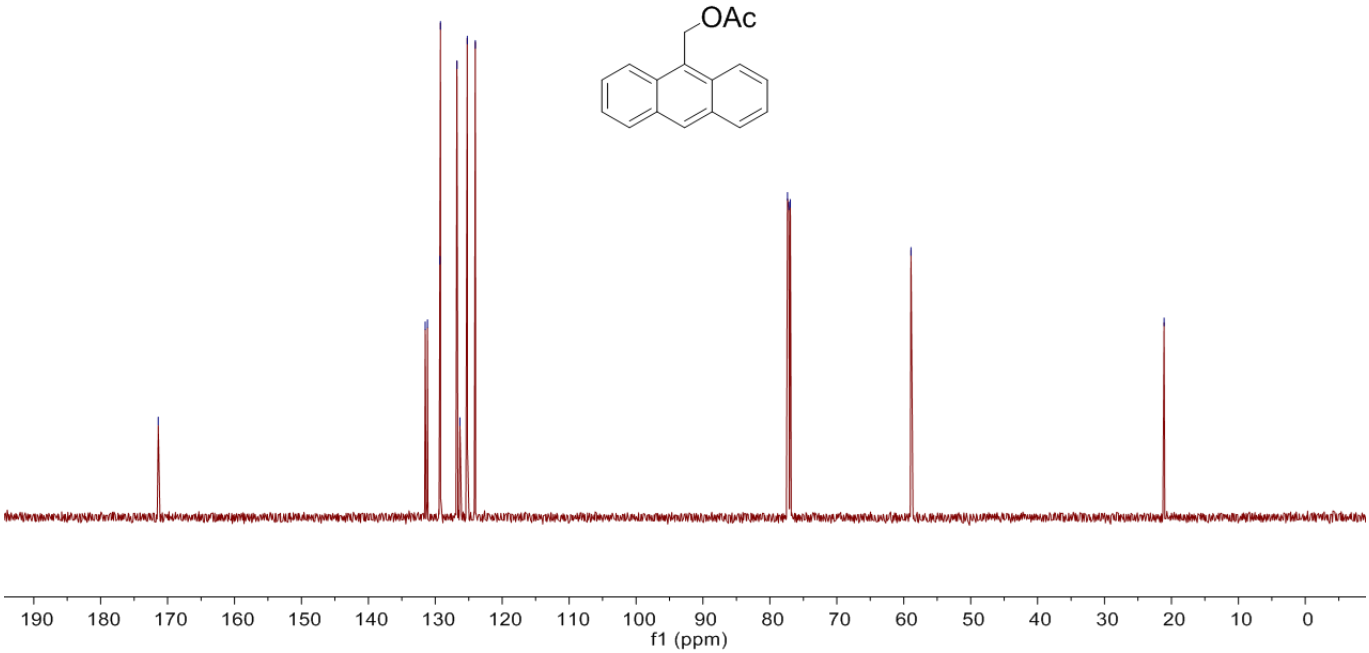


1as

^{1}H NMR (600 MHz, $CDCl_3$)



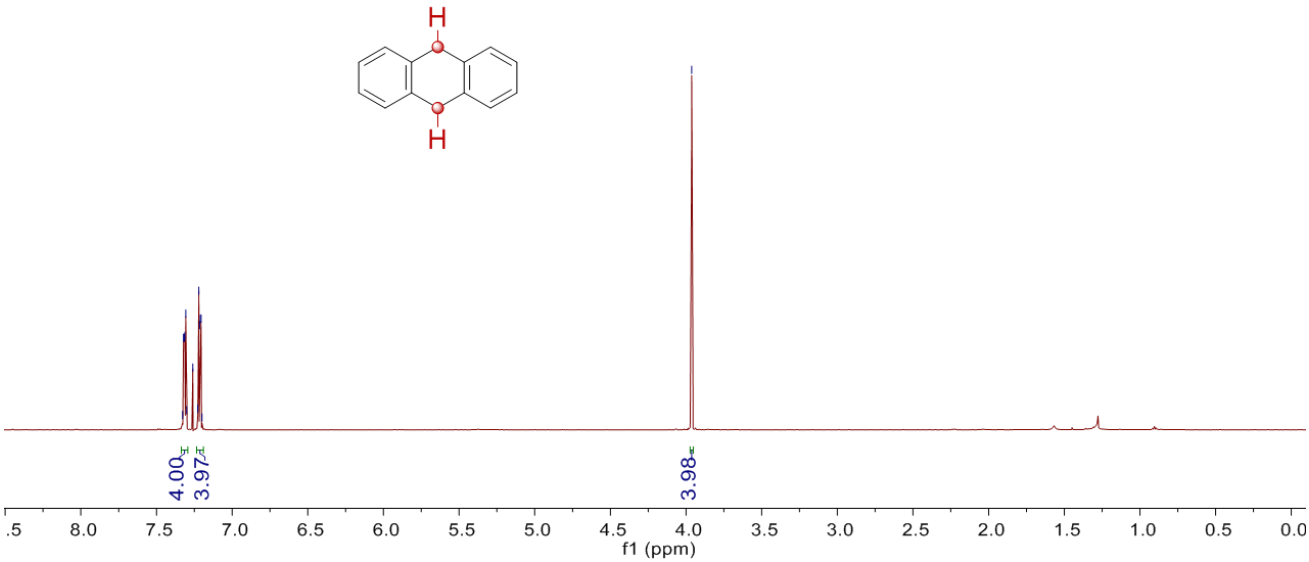
^{13}C NMR (151 MHz, $CDCl_3$)



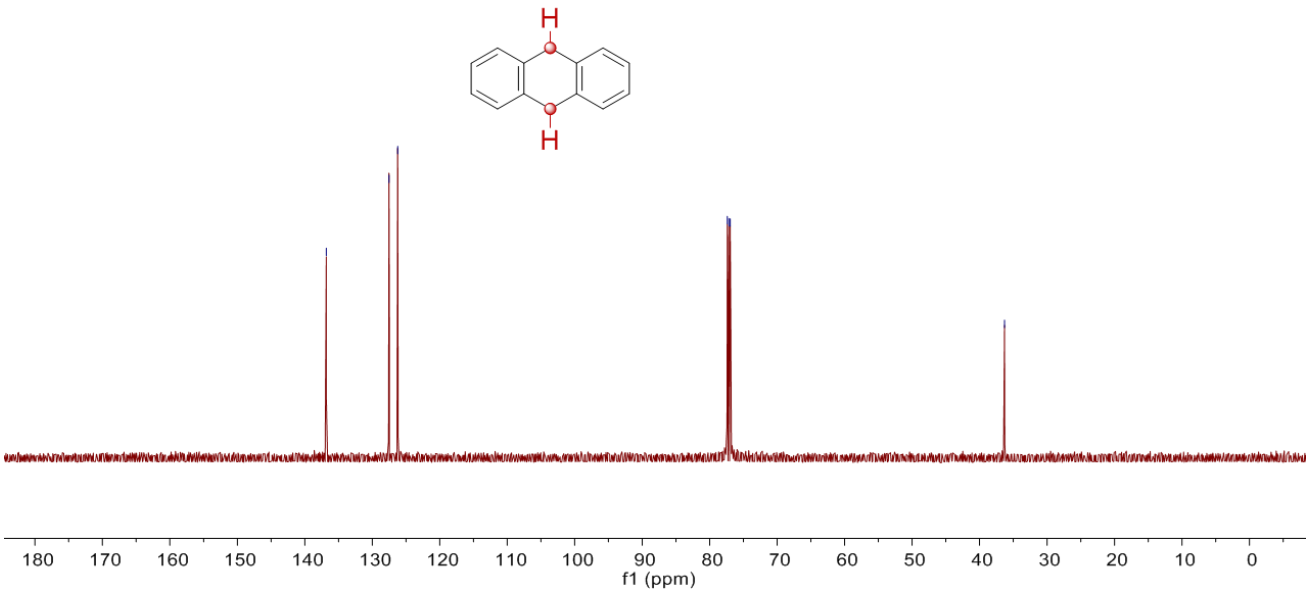
NMR spectra of product

2a

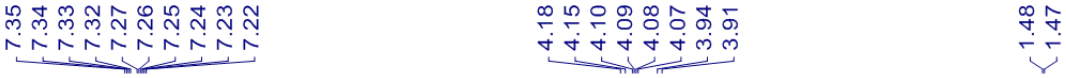
^{1}H NMR (600 MHz, $CDCl_3$)



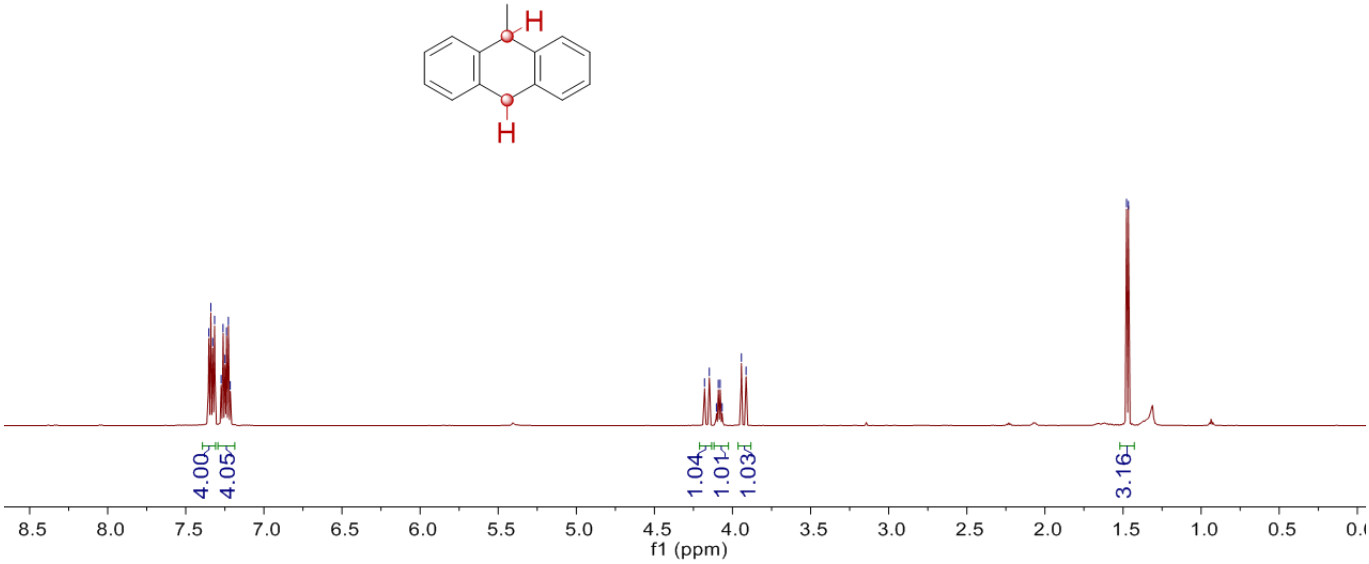
^{13}C NMR (151 MHz, $CDCl_3$)



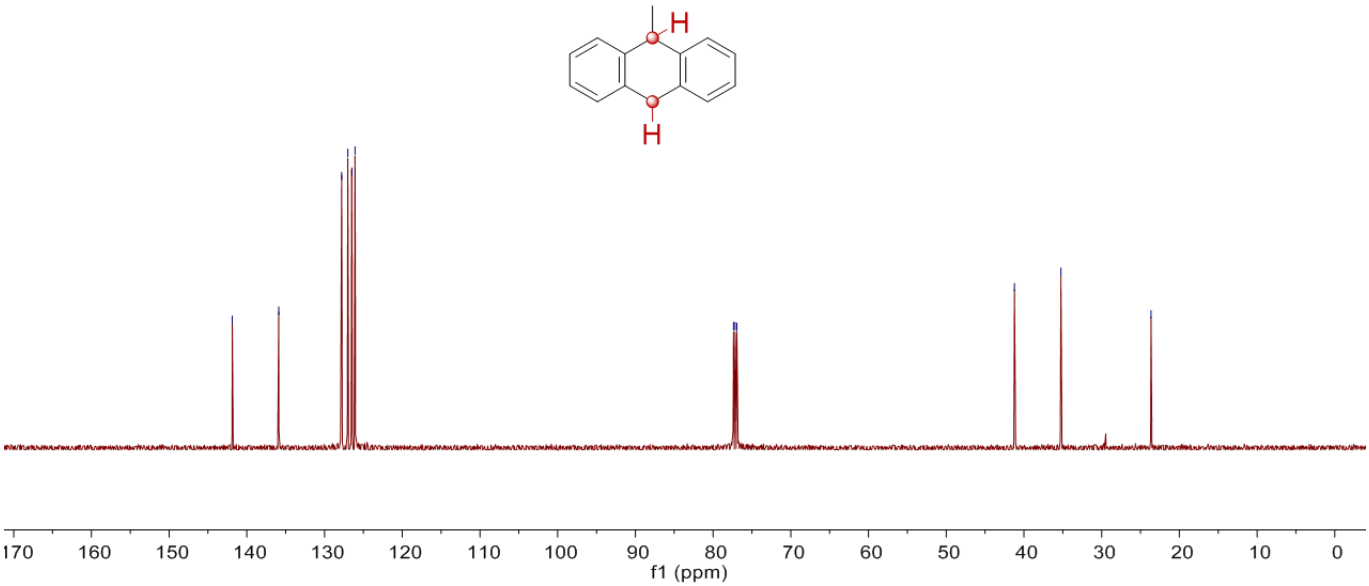
2b



^{1}H NMR (600 MHz, $CDCl_3$)

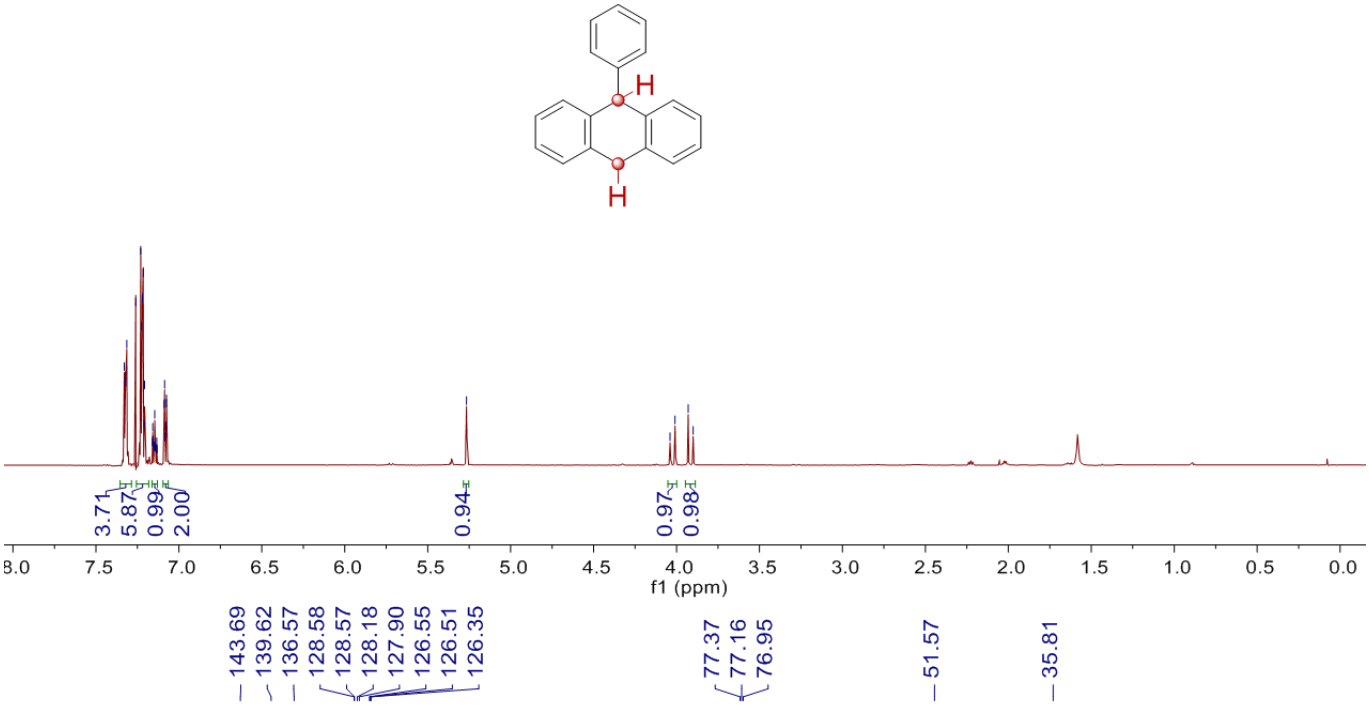


^{13}C NMR (151 MHz, $CDCl_3$)

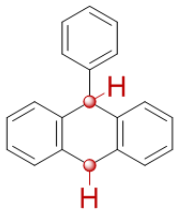


2c

^{1}H NMR (600 MHz, $CDCl_3$)

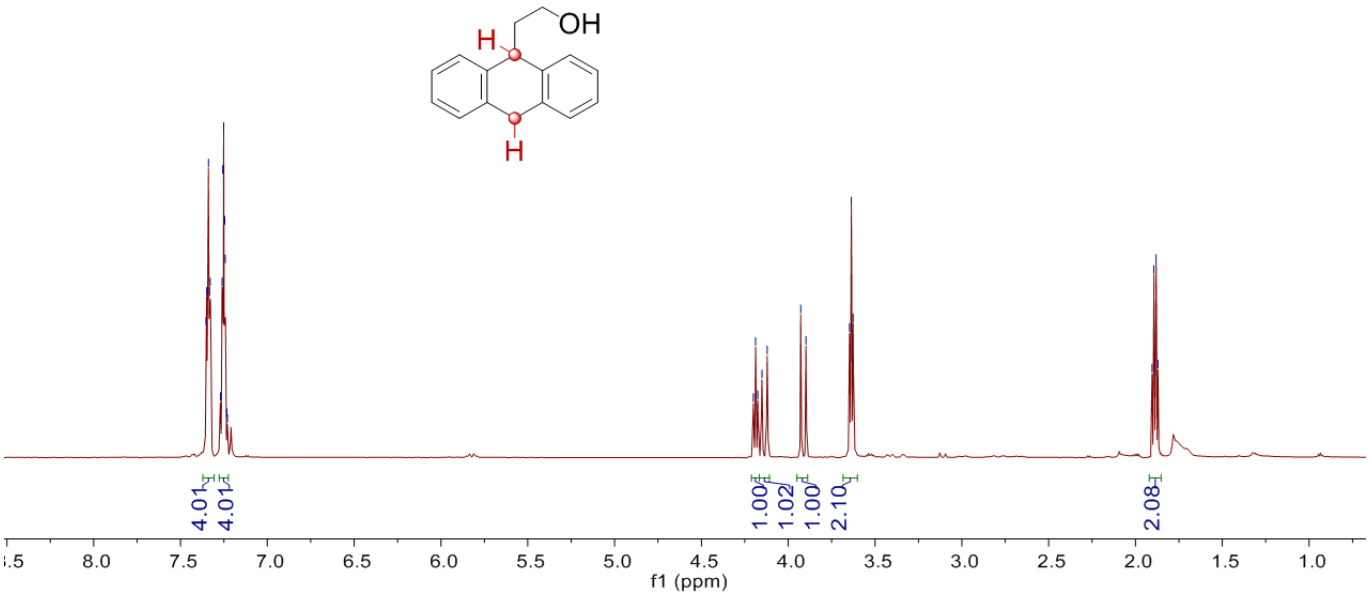


^{13}C NMR (151 MHz, $CDCl_3$)

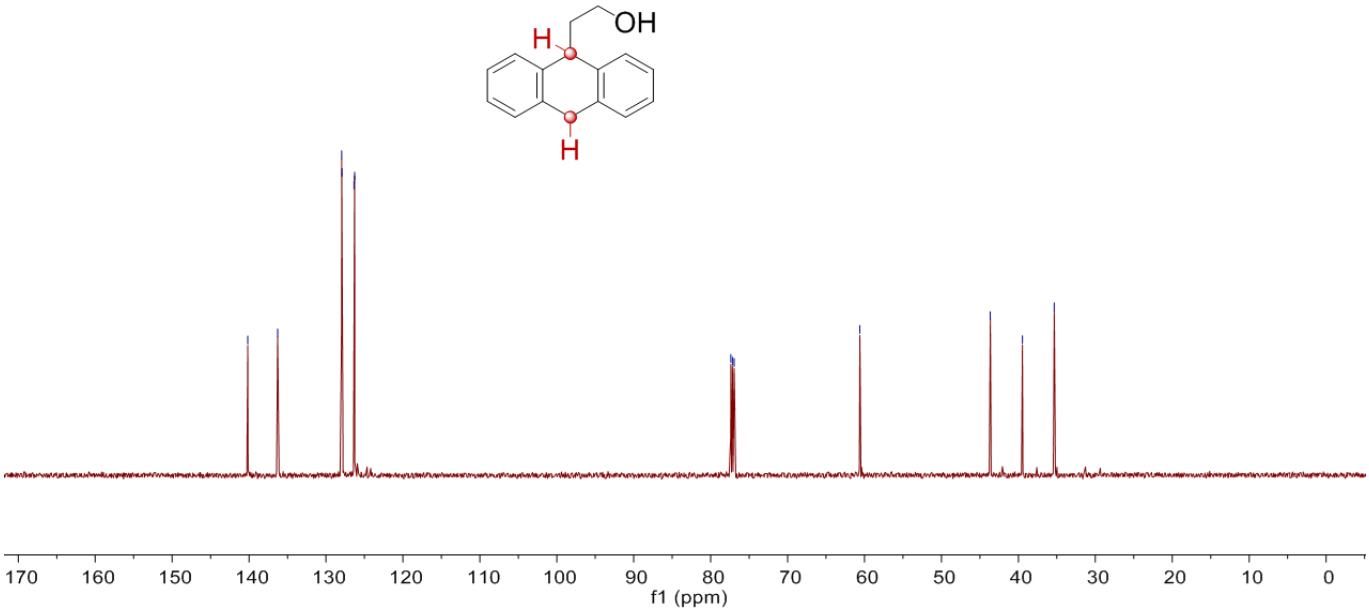


2d

^{1}H NMR (600 MHz, $CDCl_3$)

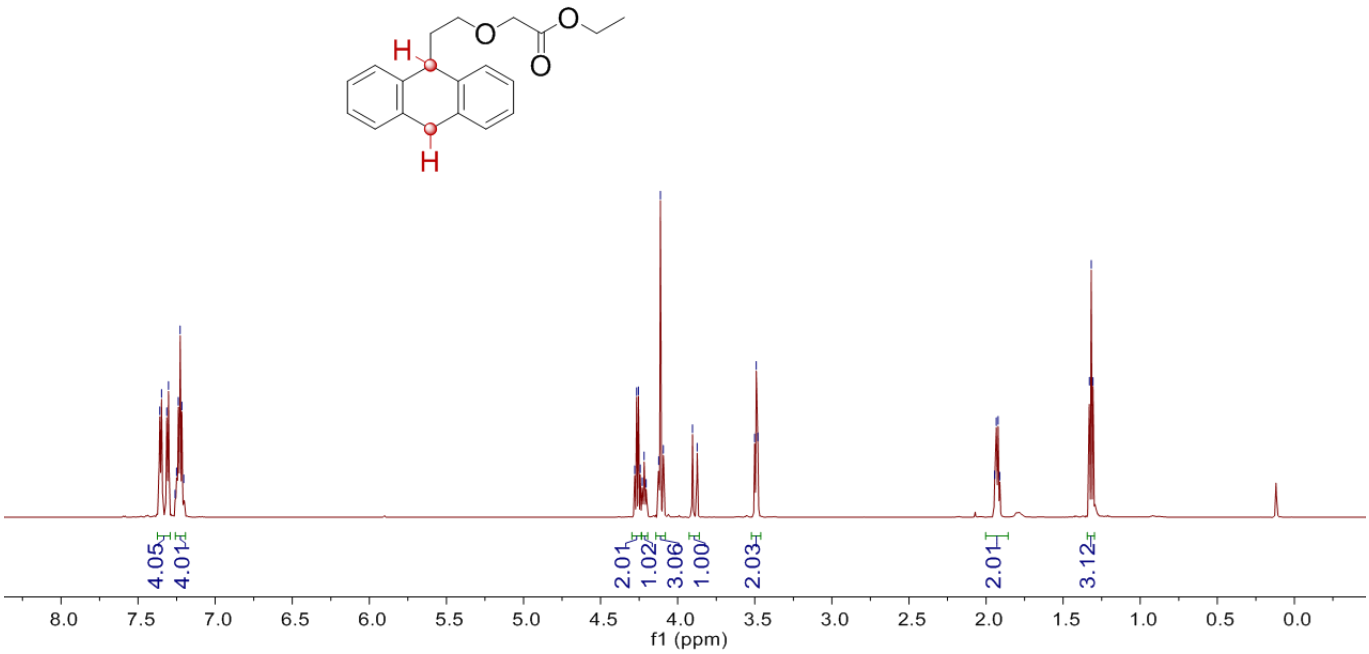


^{13}C NMR (151 MHz, $CDCl_3$)

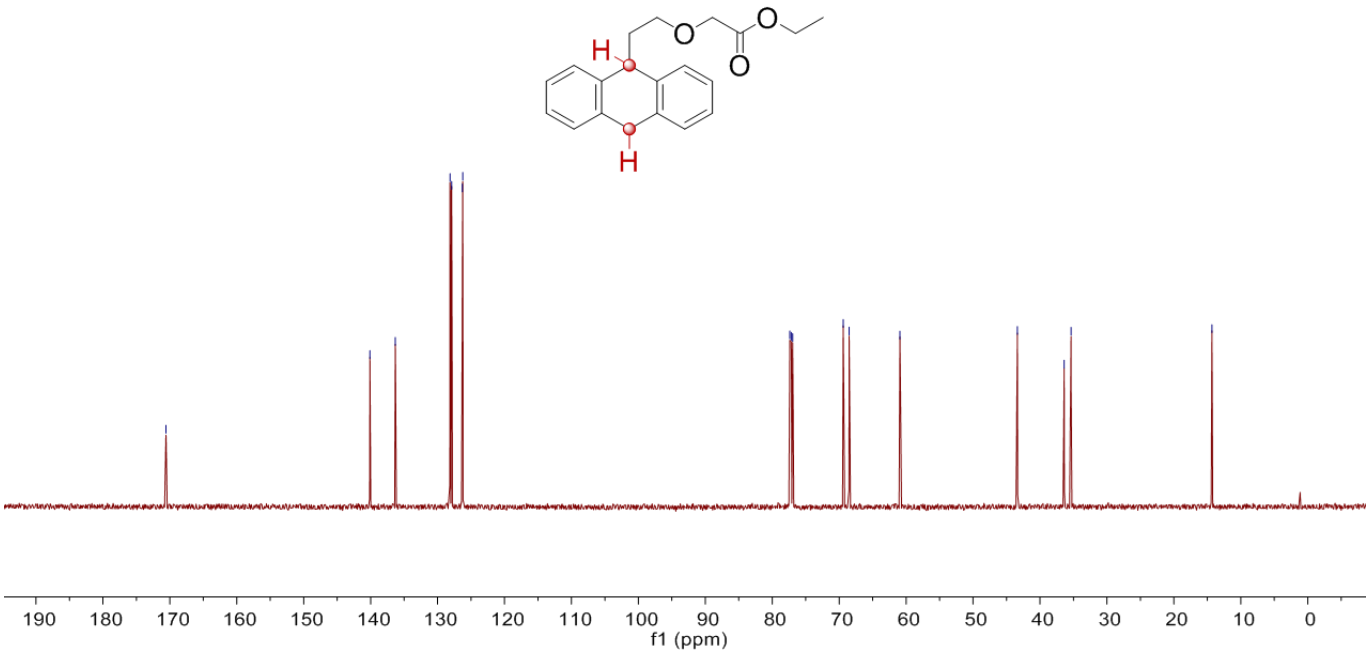


2e

^{1}H NMR (600 MHz, $CDCl_3$)

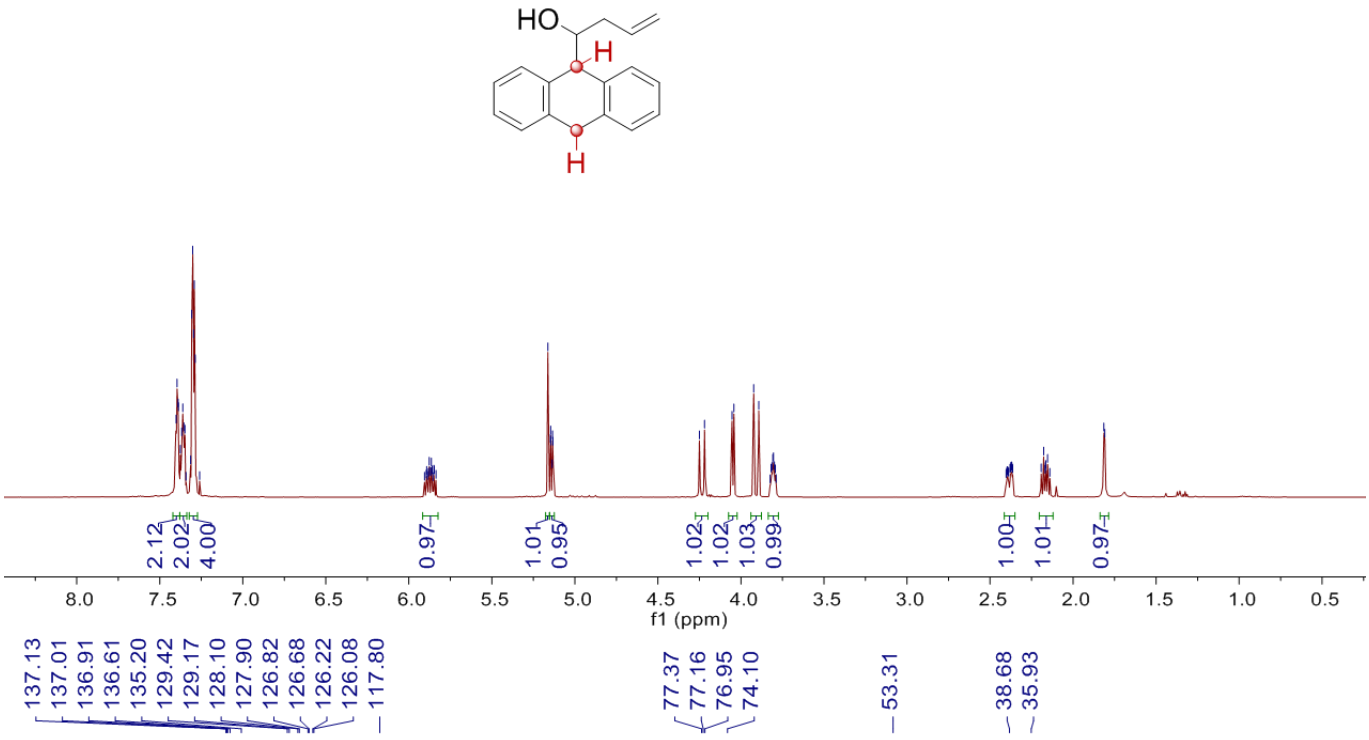


^{13}C NMR (151 MHz, $CDCl_3$)

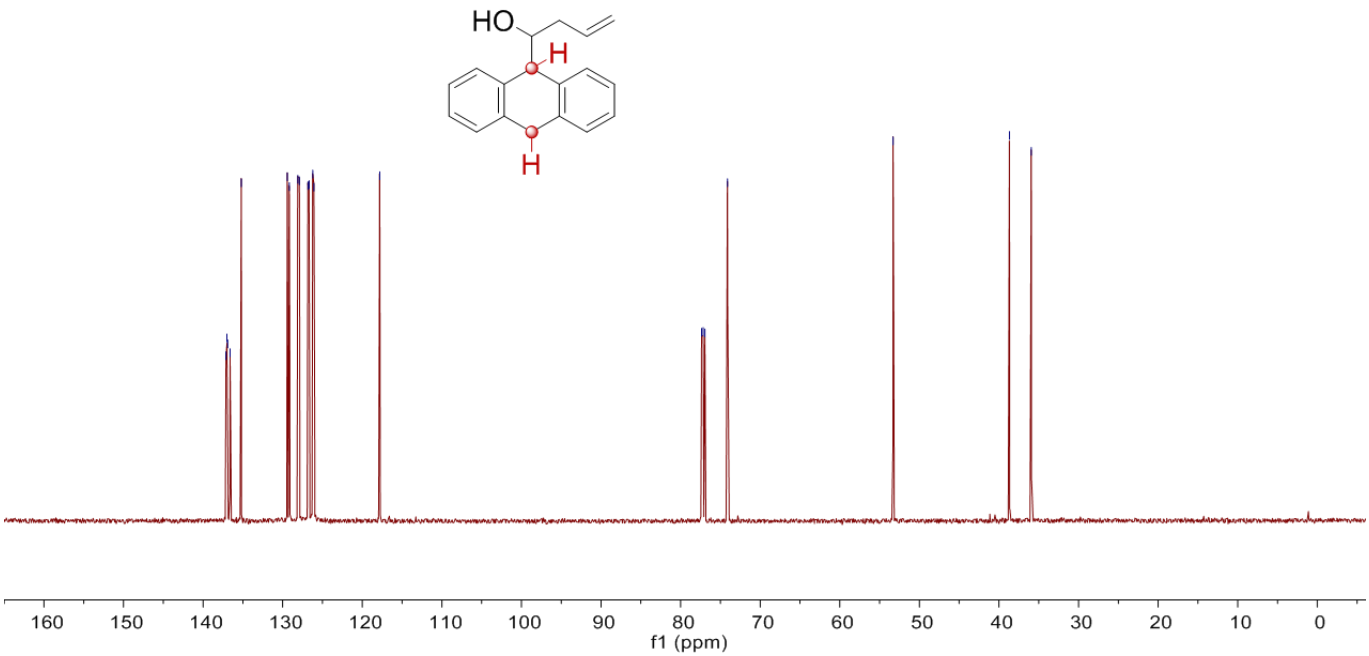


2f

^{1}H NMR (600 MHz, $CDCl_3$)

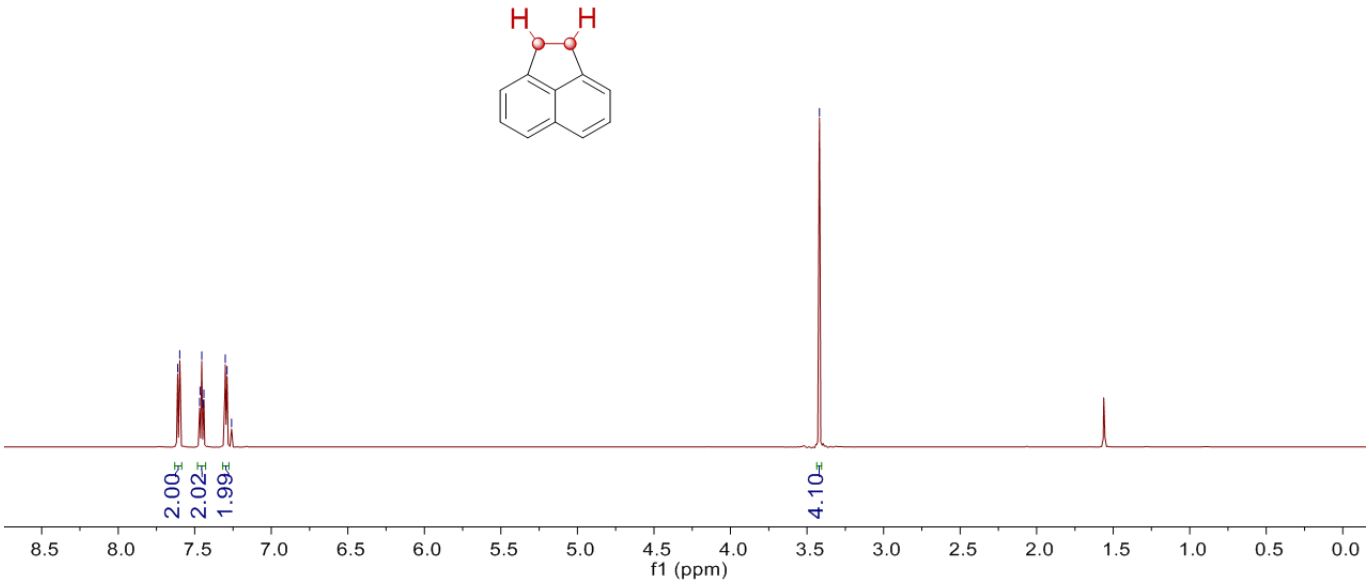


^{13}C NMR (151 MHz, $CDCl_3$)

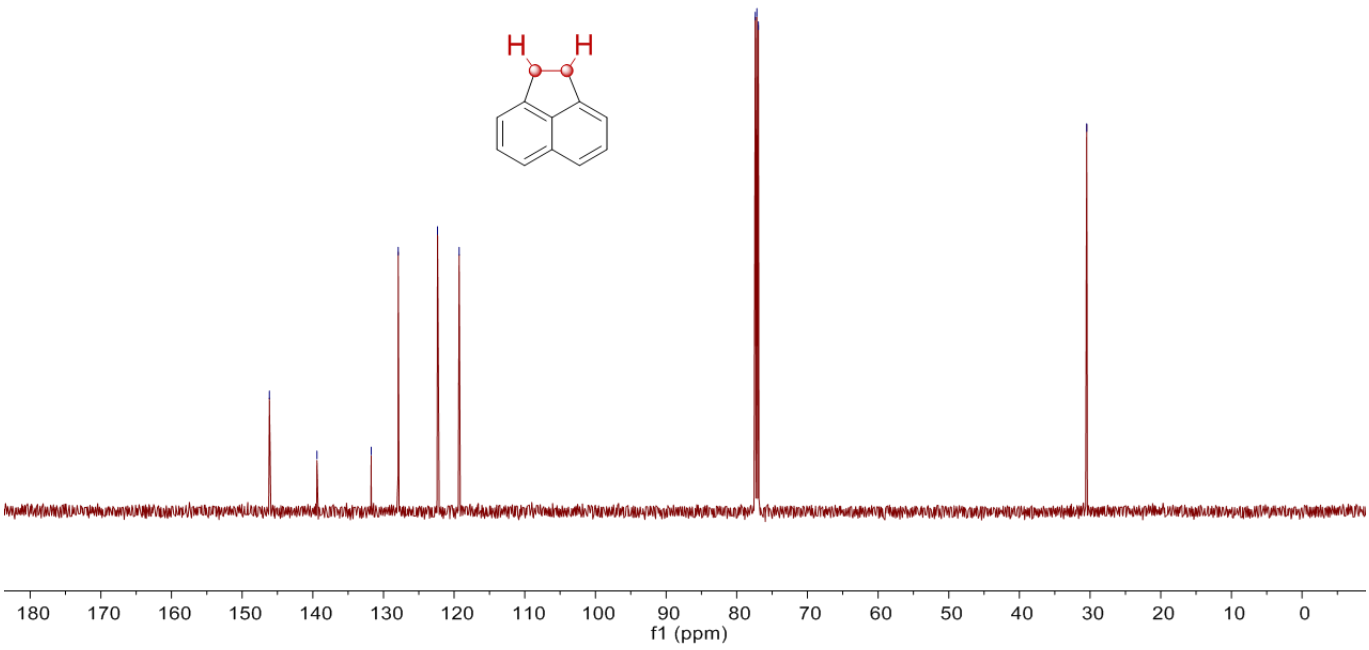


2g

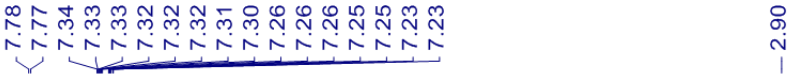
^{1}H NMR (600 MHz, $CDCl_3$)



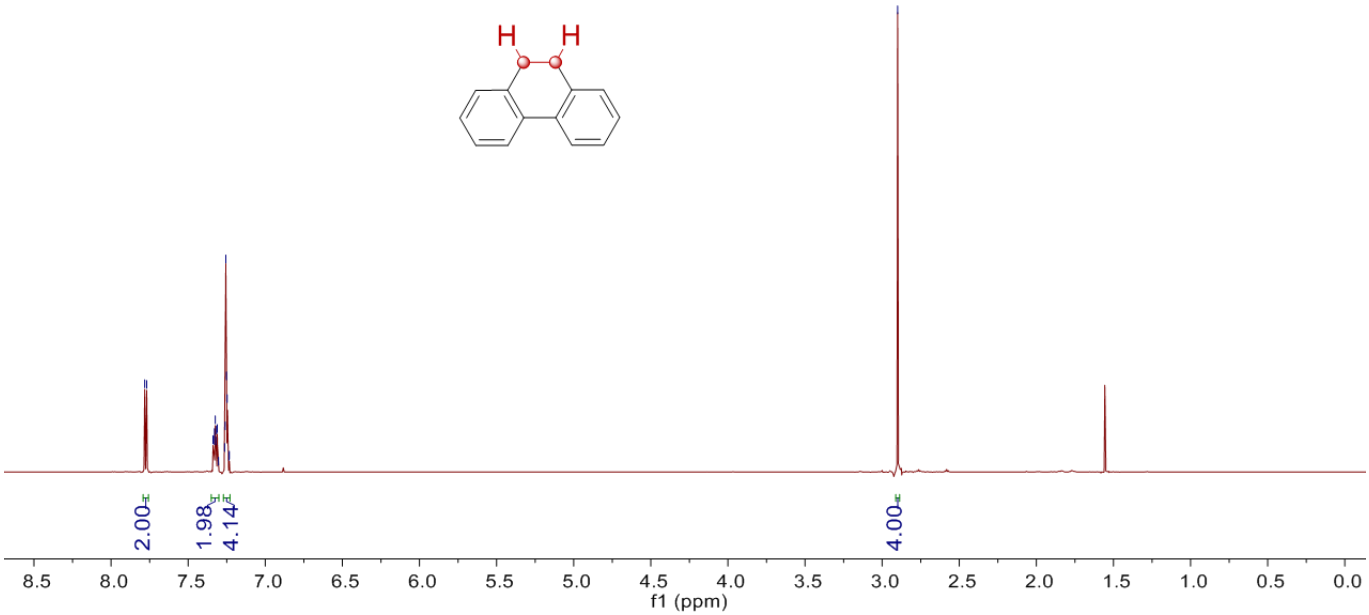
^{13}C NMR (151 MHz, $CDCl_3$)



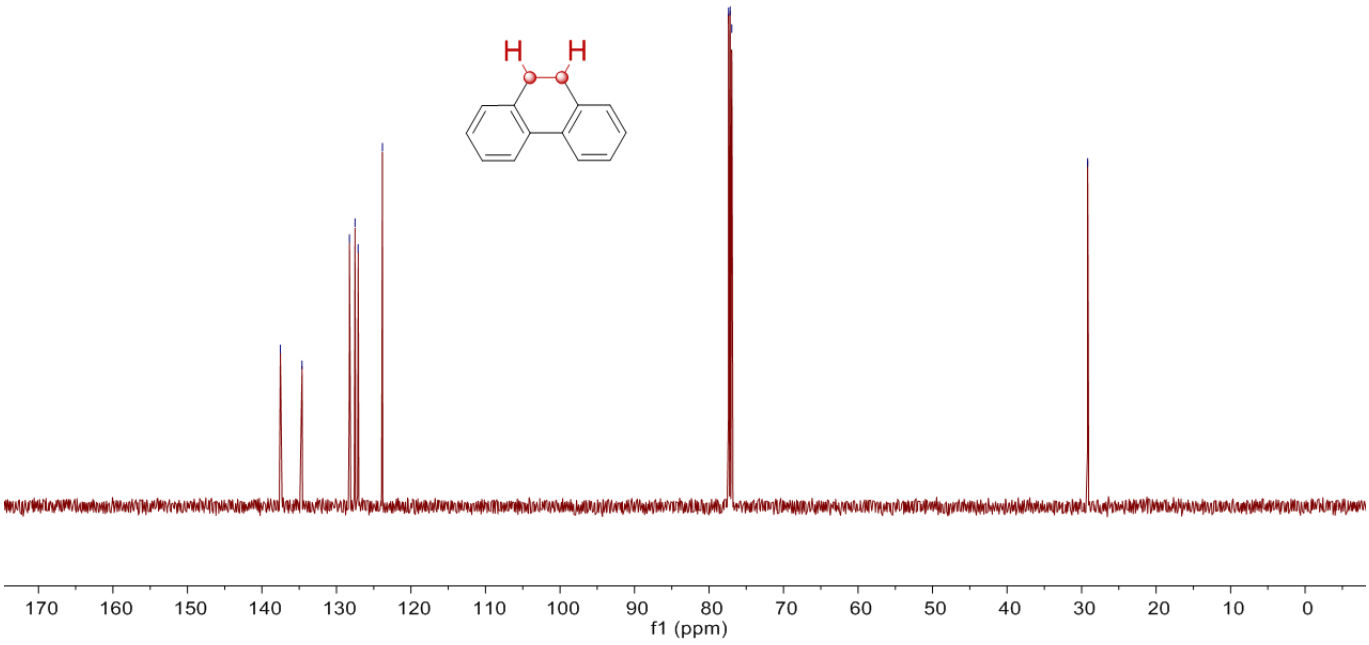
2h



^{1}H NMR (600 MHz, $CDCl_3$)

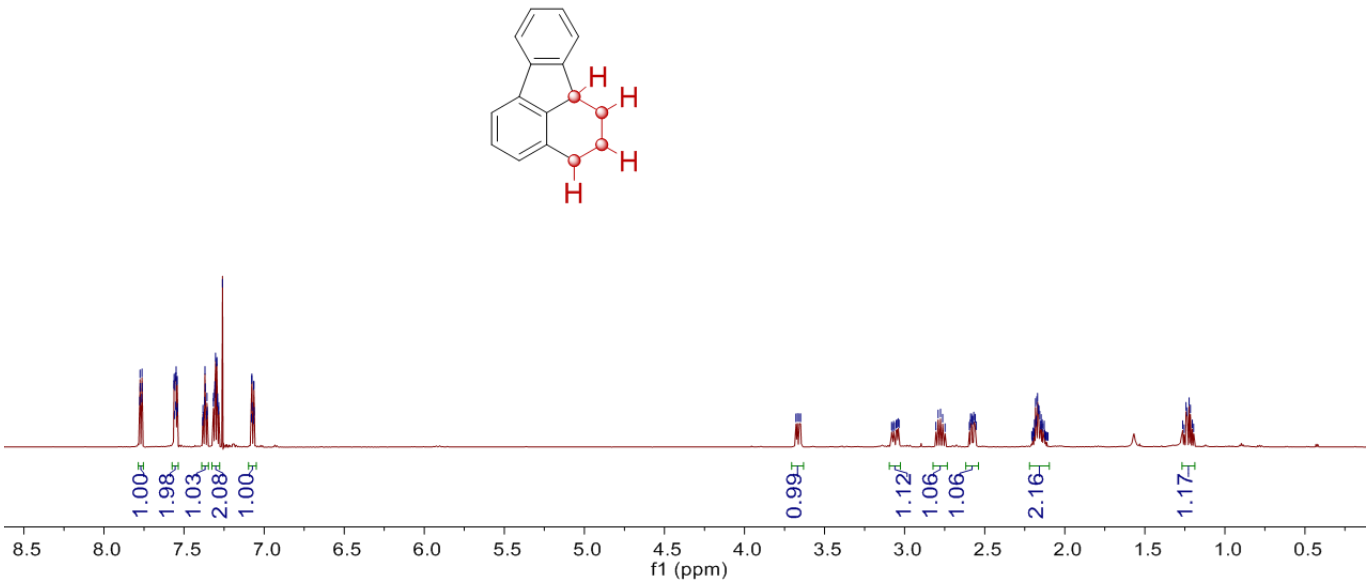


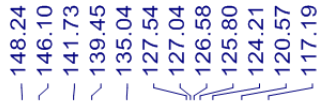
^{13}C NMR (151 MHz, $CDCl_3$)



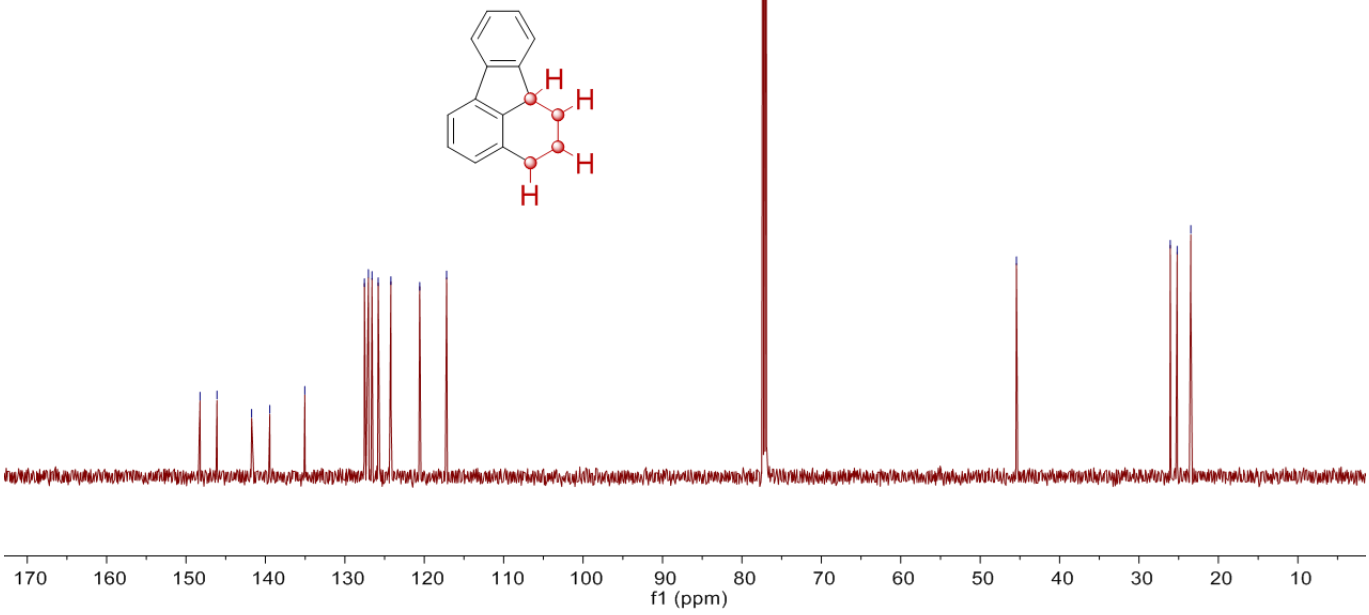
2i

^{1}H NMR (600 MHz, $CDCl_3$)



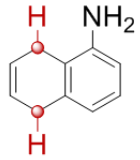


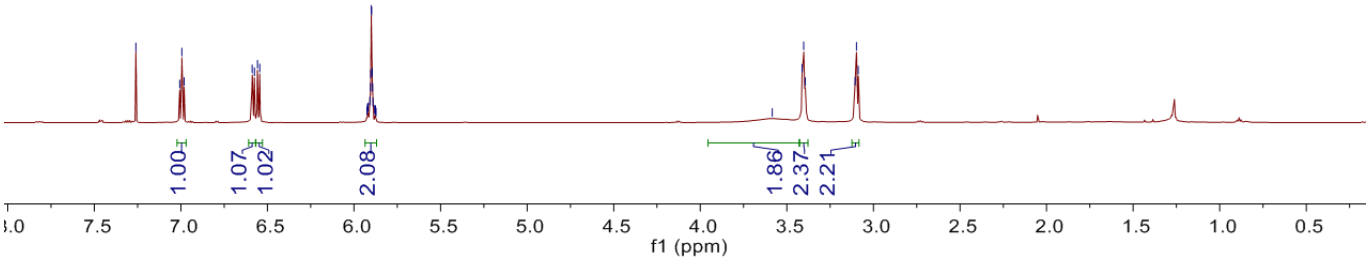
^{13}C NMR (151 MHz, $CDCl_3$)

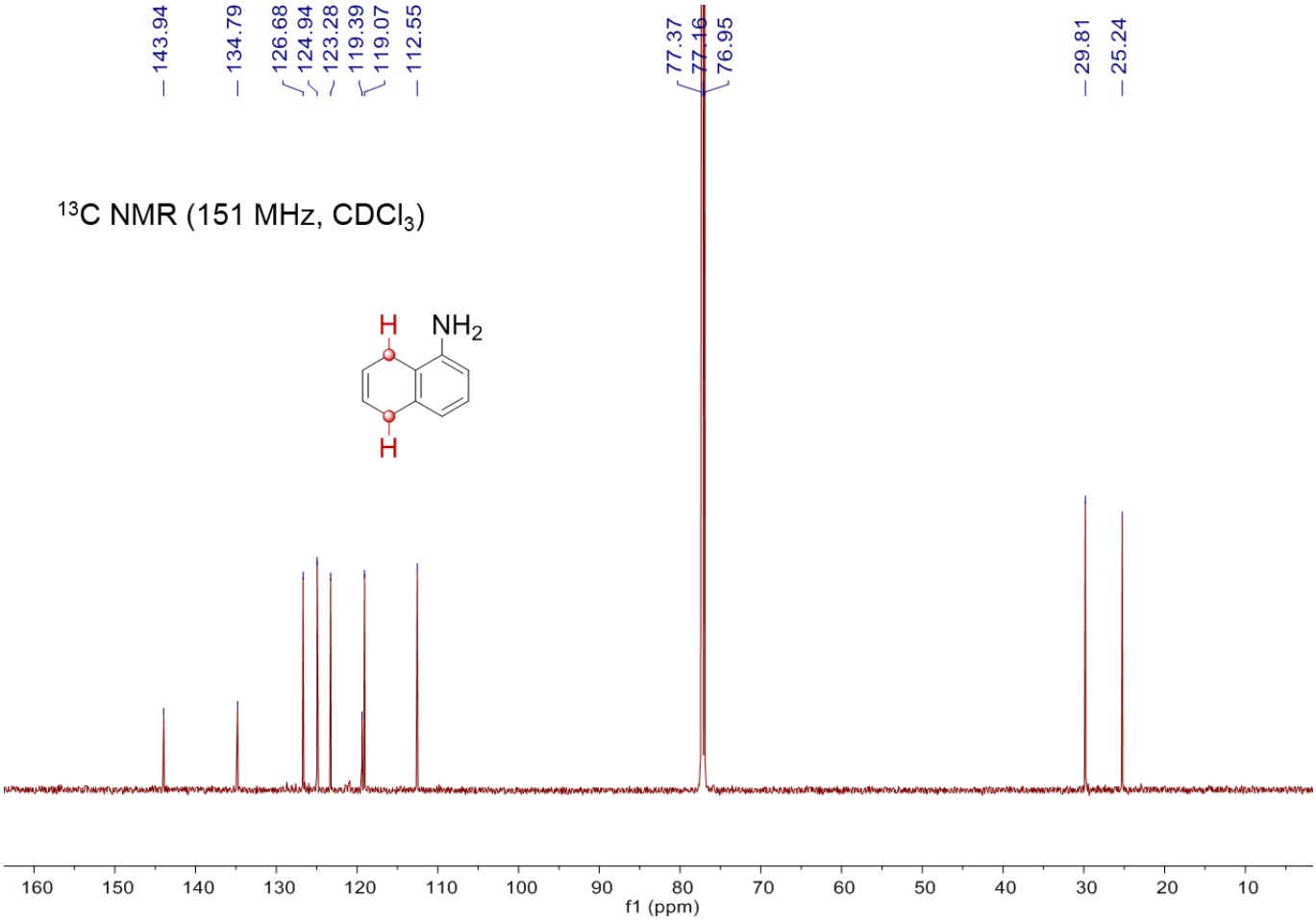


2l

^{1}H NMR (600 MHz, $CDCl_3$)



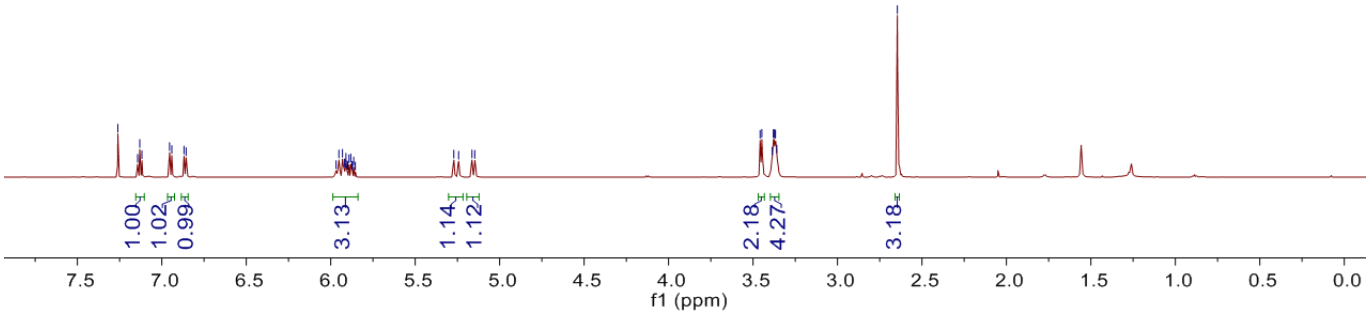


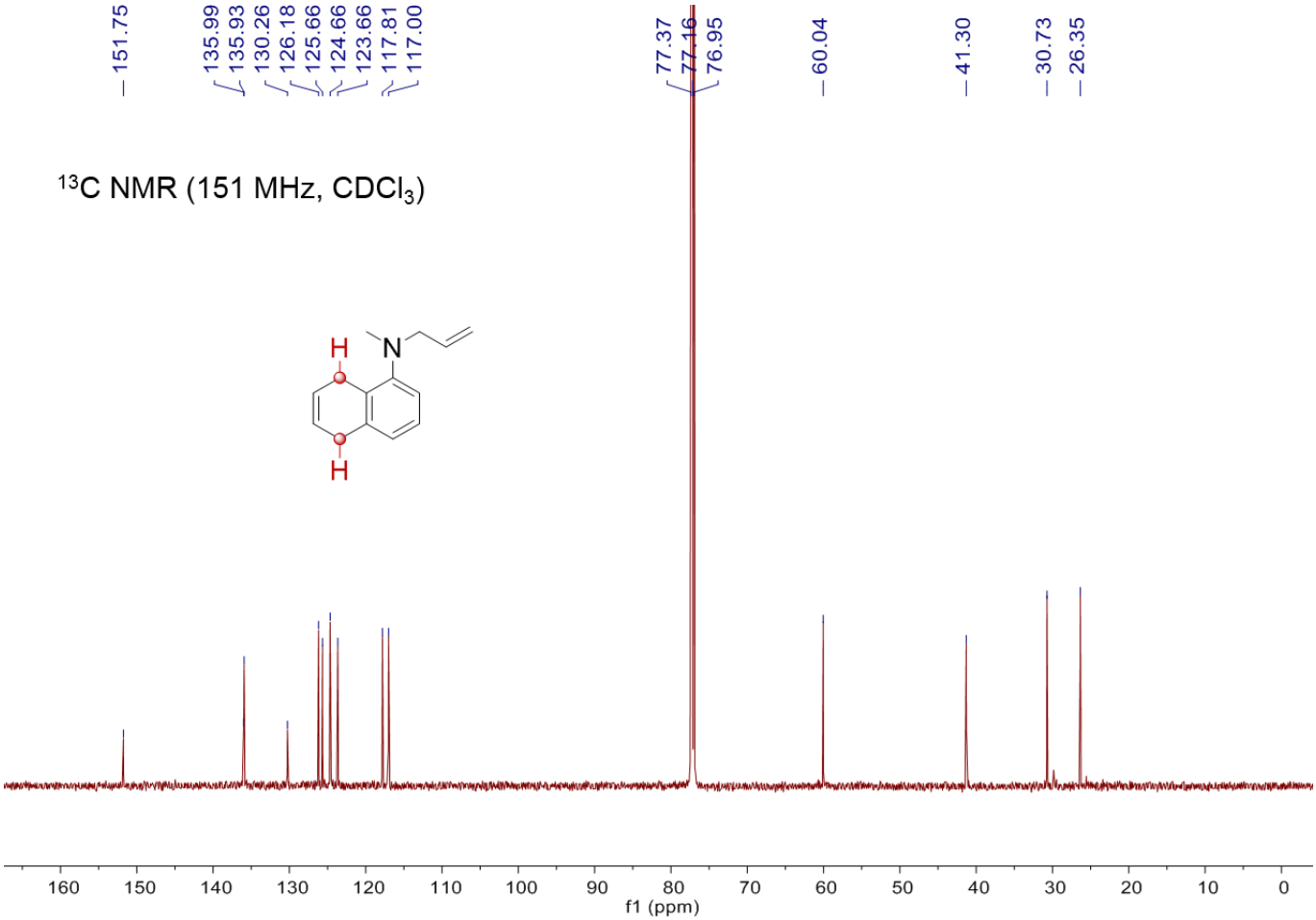


^{13}C NMR (151 MHz, $CDCl_3$)

2m

^{1}H NMR (600 MHz, $CDCl_3$)

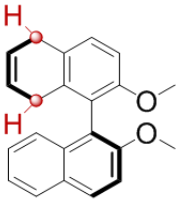


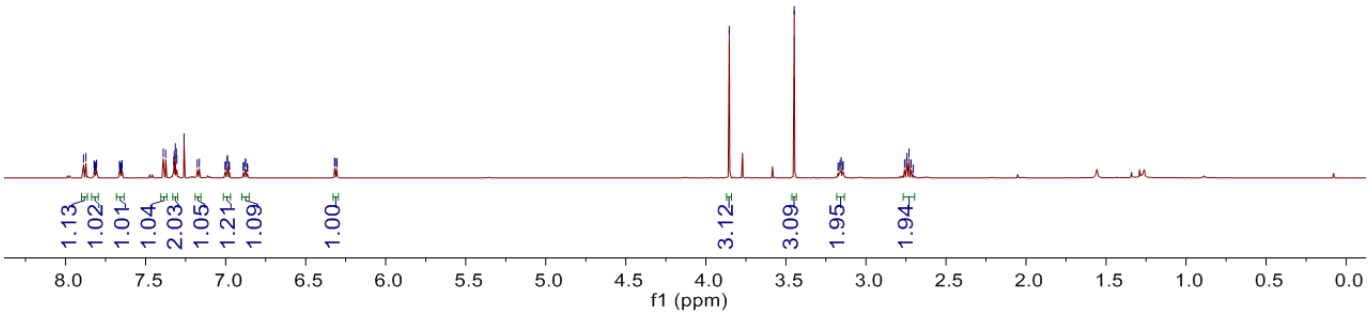


^{13}C NMR (151 MHz, $CDCl_3$)

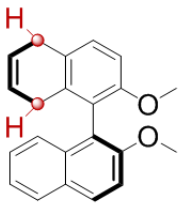
2p

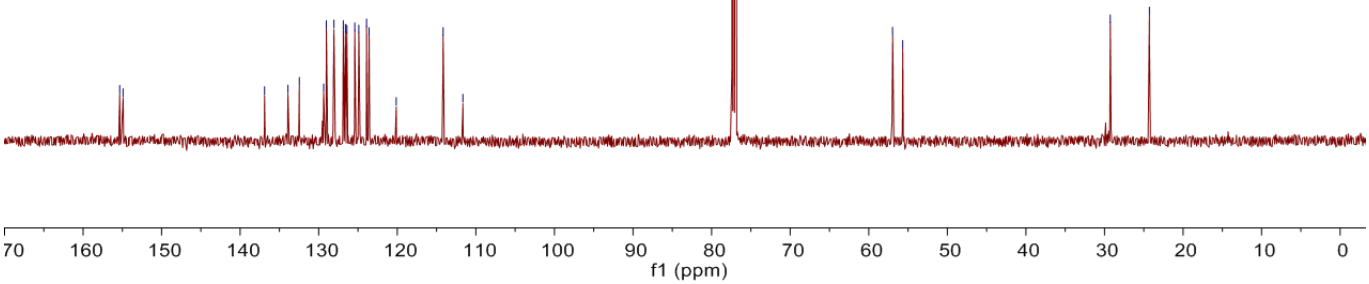
^{1}H NMR (600 MHz, $CDCl_3$)



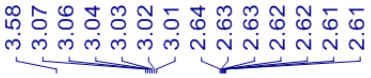


^{13}C NMR (151 MHz, $CDCl_3$)

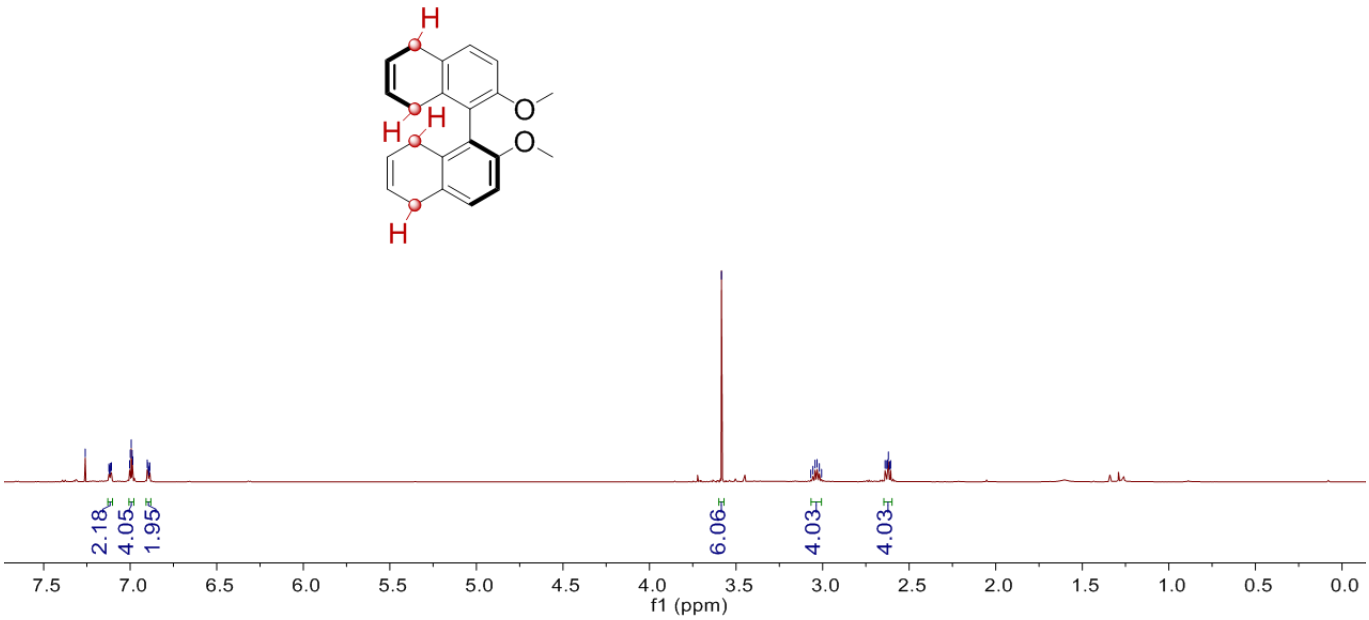


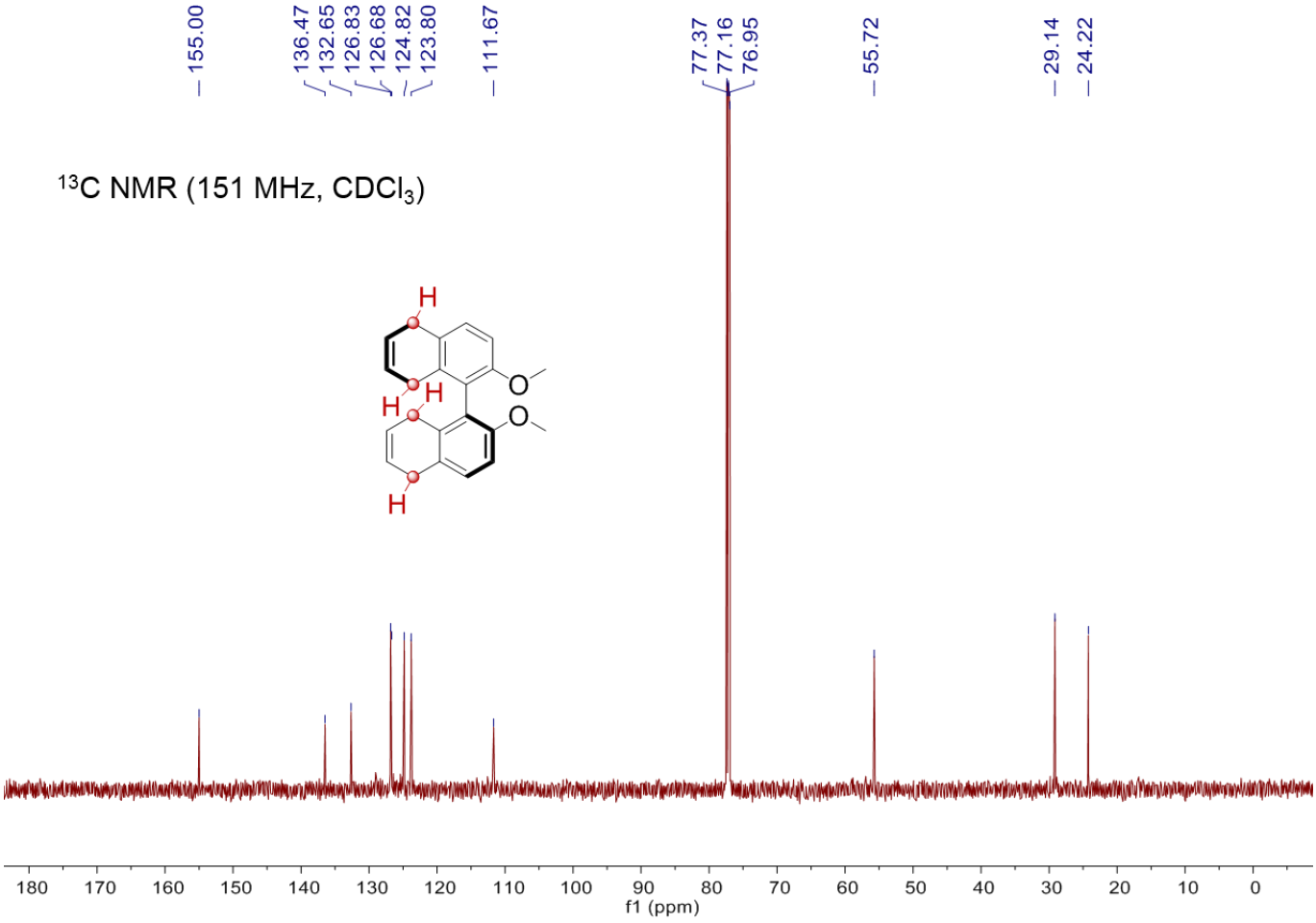


2p'



^{1}H NMR (600 MHz, $CDCl_3$)

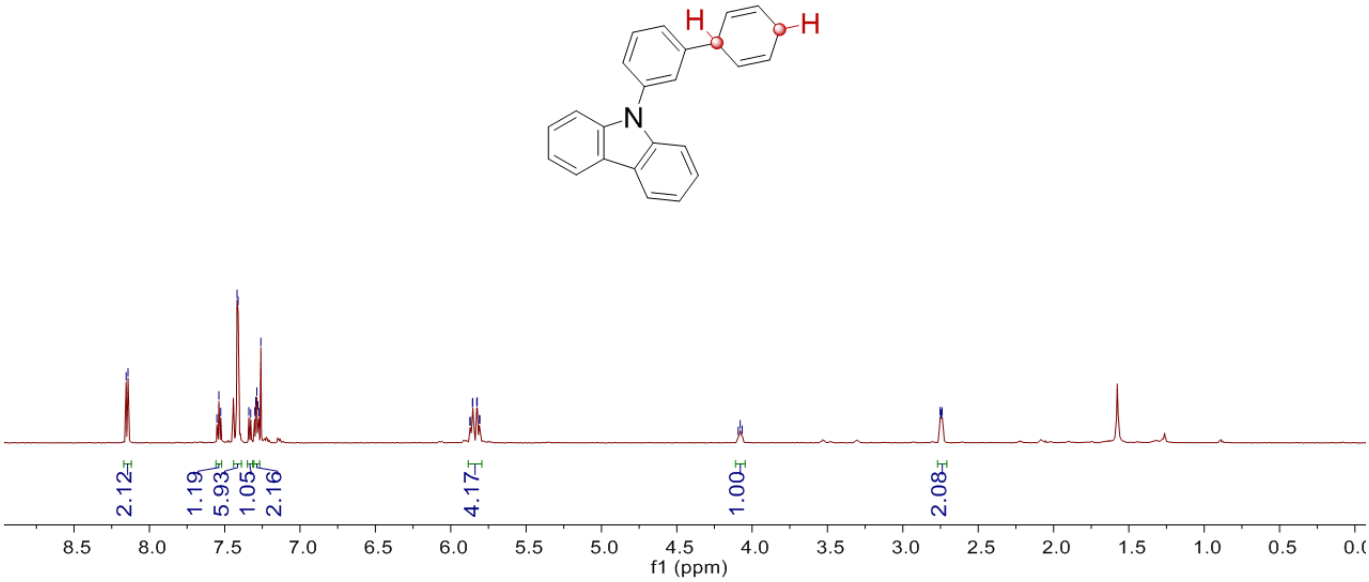


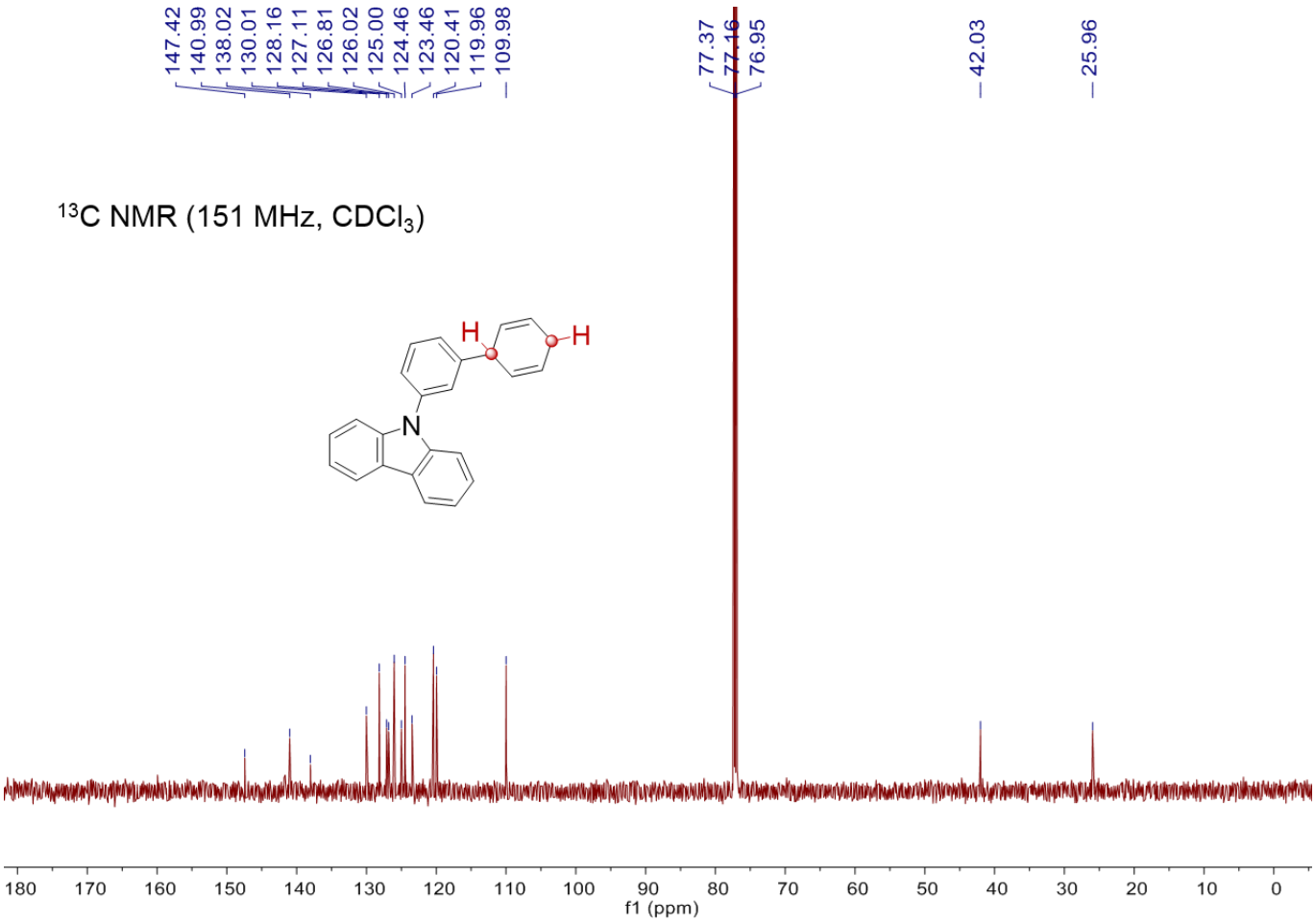


^{13}C NMR (151 MHz, $CDCl_3$)

2r

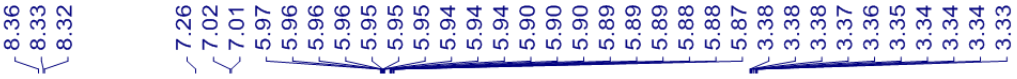
^{1}H NMR (600 MHz, $CDCl_3$)



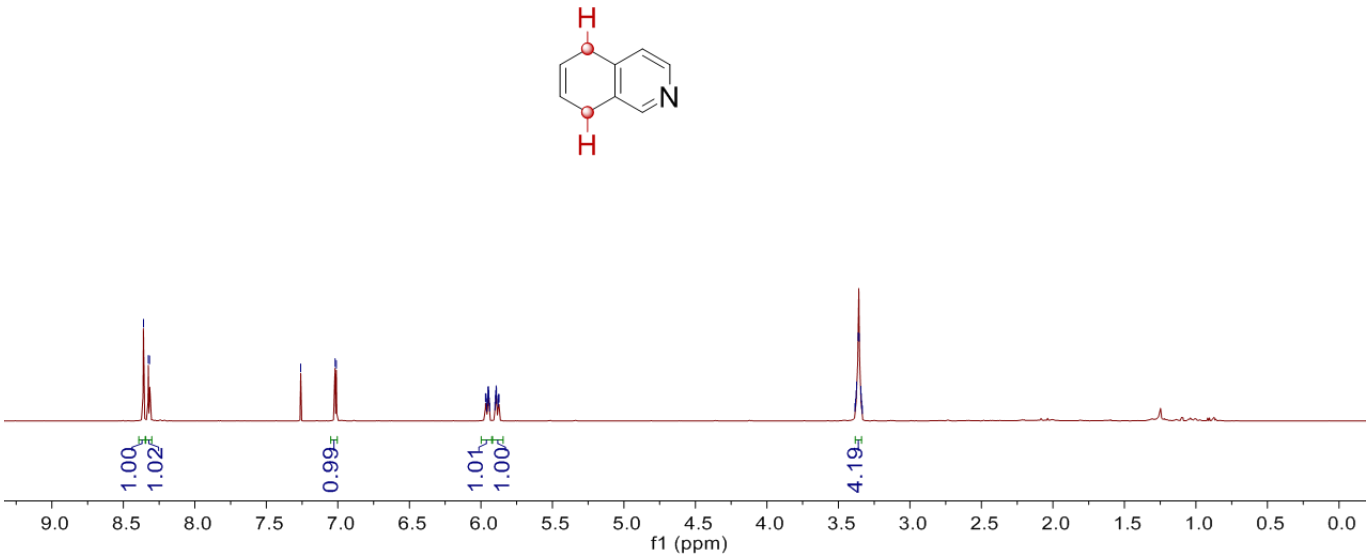


^{13}C NMR (151 MHz, $CDCl_3$)

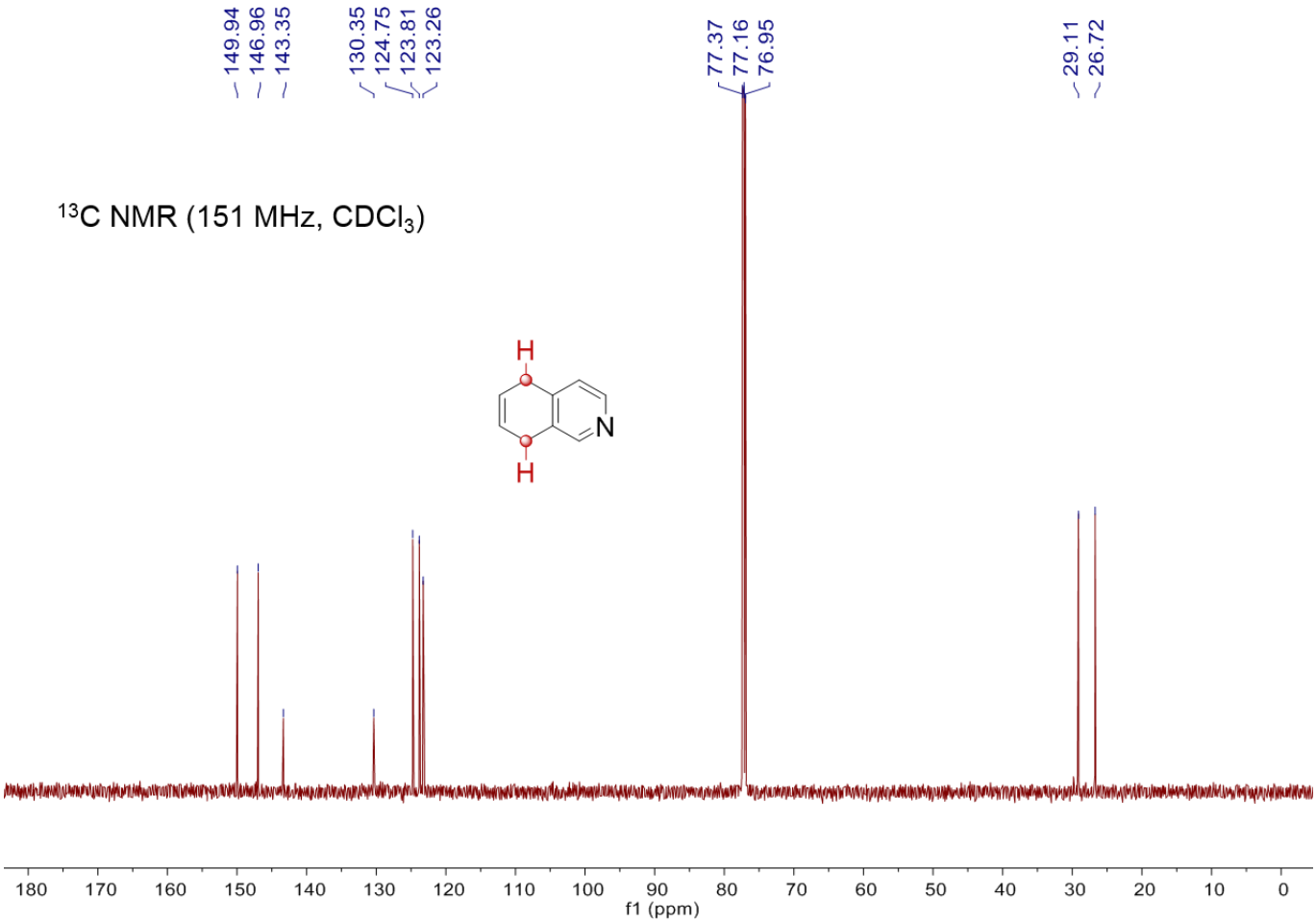
2t



^{1}H NMR (600 MHz, $CDCl_3$)

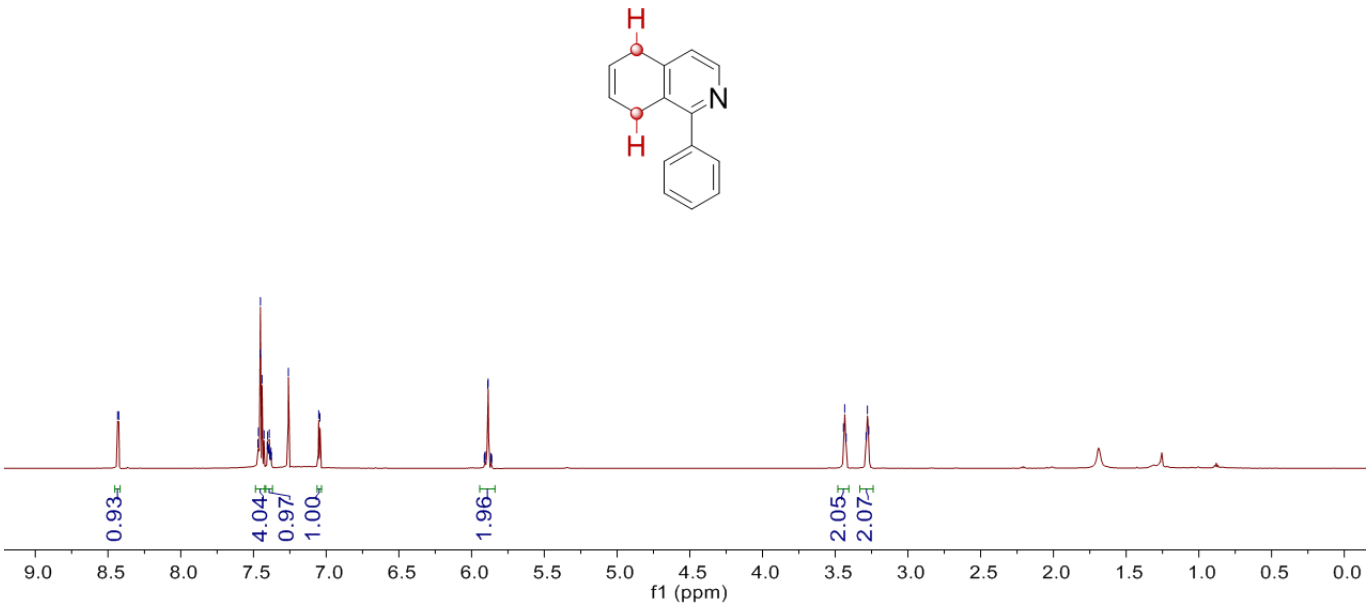


^{13}C NMR (151 MHz, $CDCl_3$)

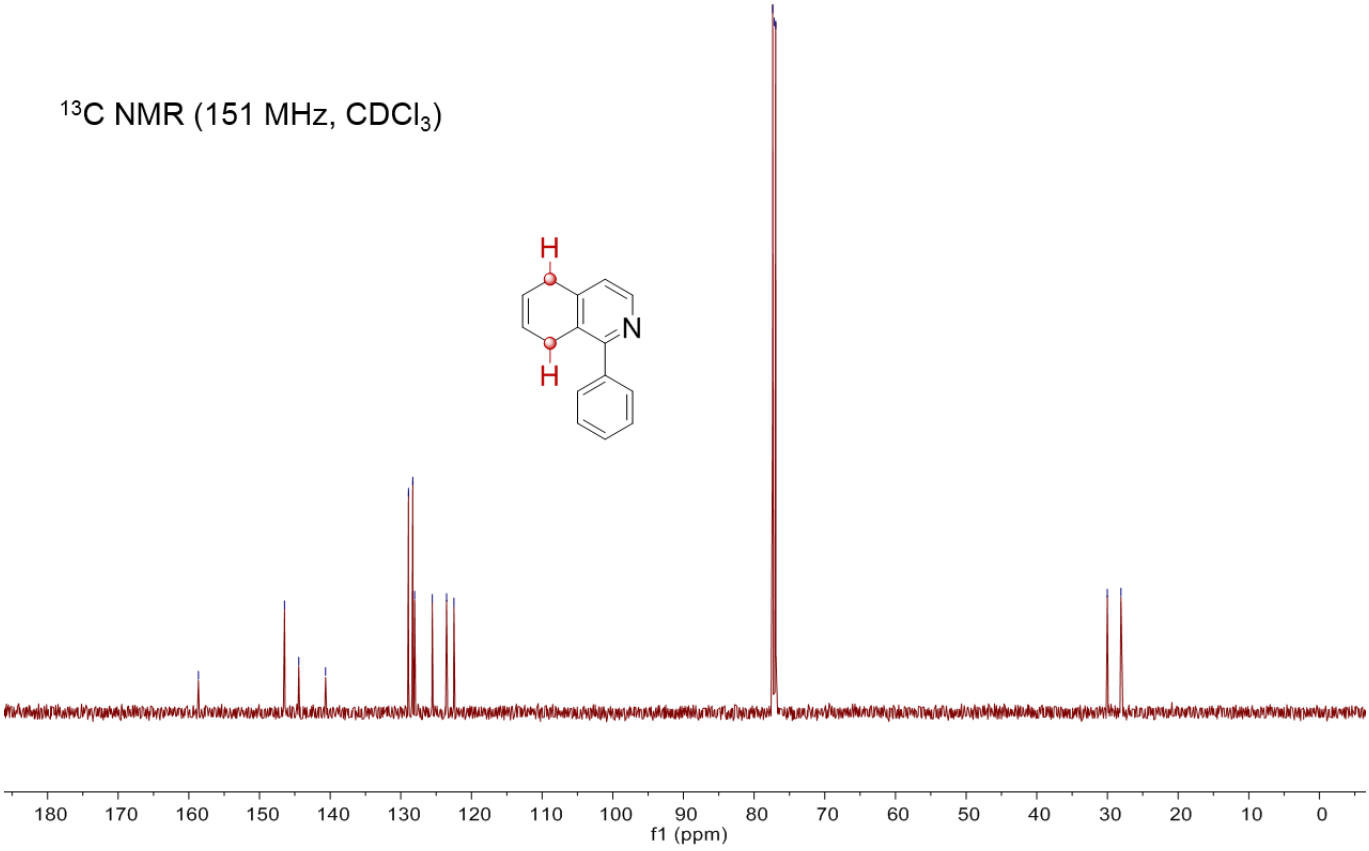


2u

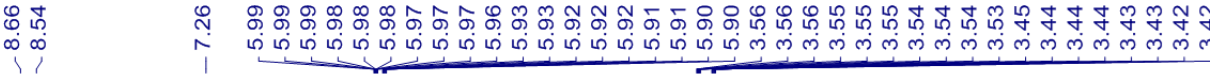
^{1}H NMR (600 MHz, $CDCl_3$)



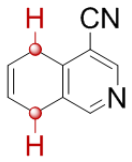
^{13}C NMR (151 MHz, $CDCl_3$)

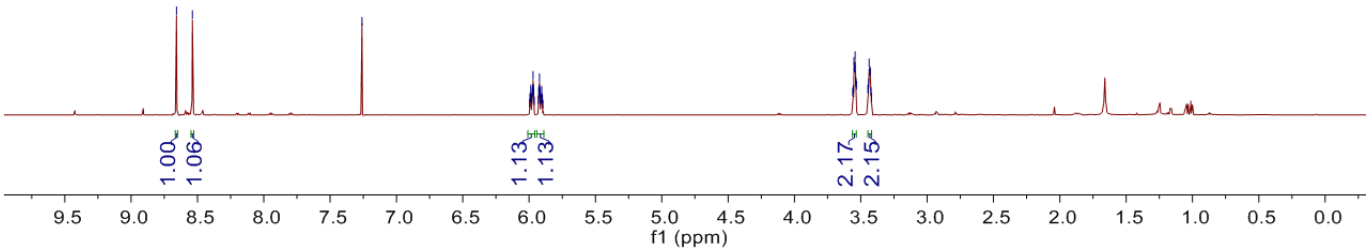


2v

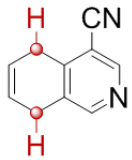


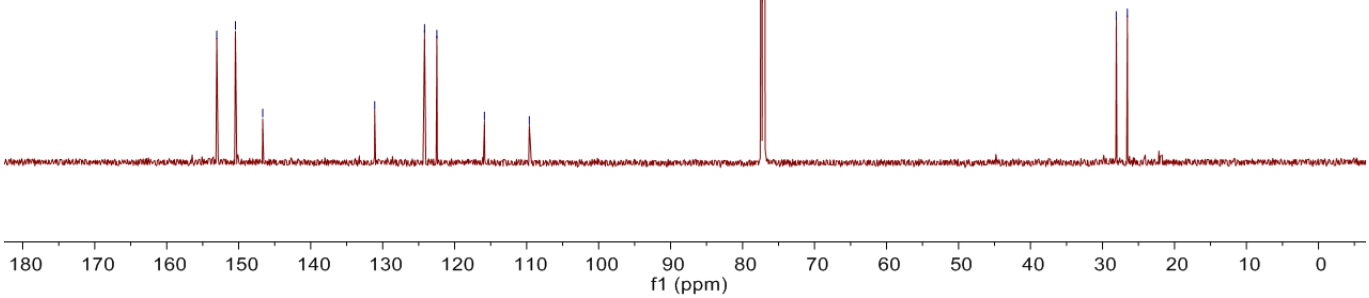
^{1}H NMR (600 MHz, $CDCl_3$)





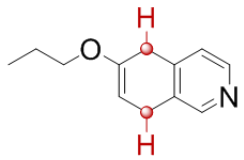
^{13}C NMR (151 MHz, $CDCl_3$)

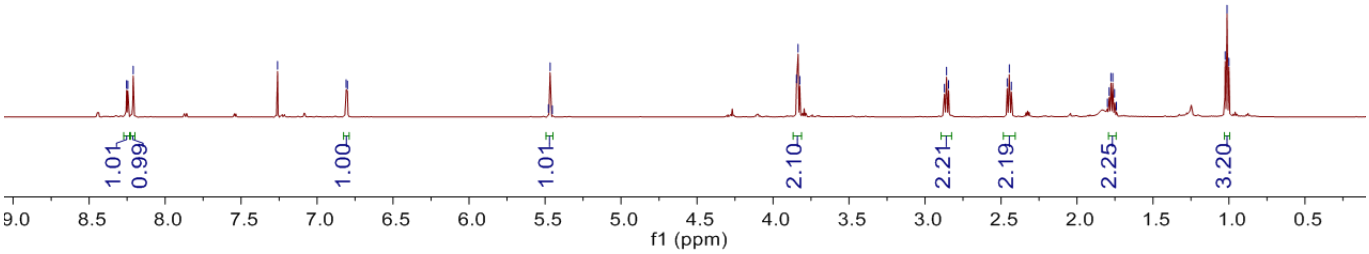




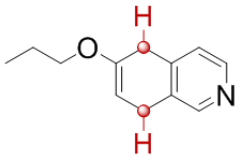
2w

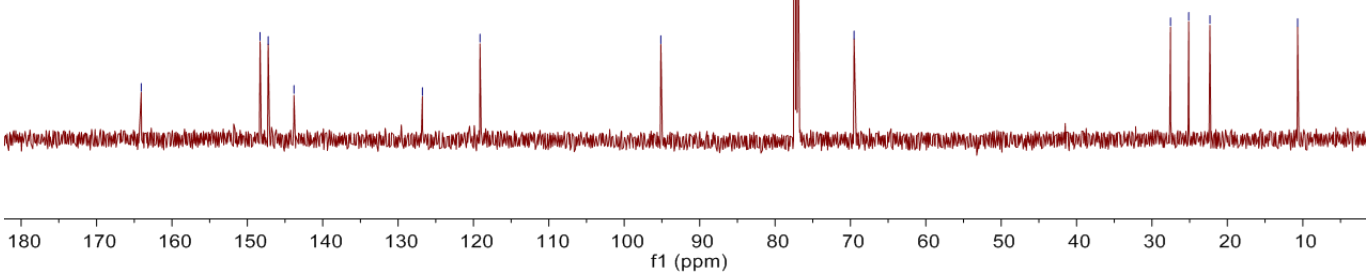
^{1}H NMR (600 MHz, $CDCl_3$)





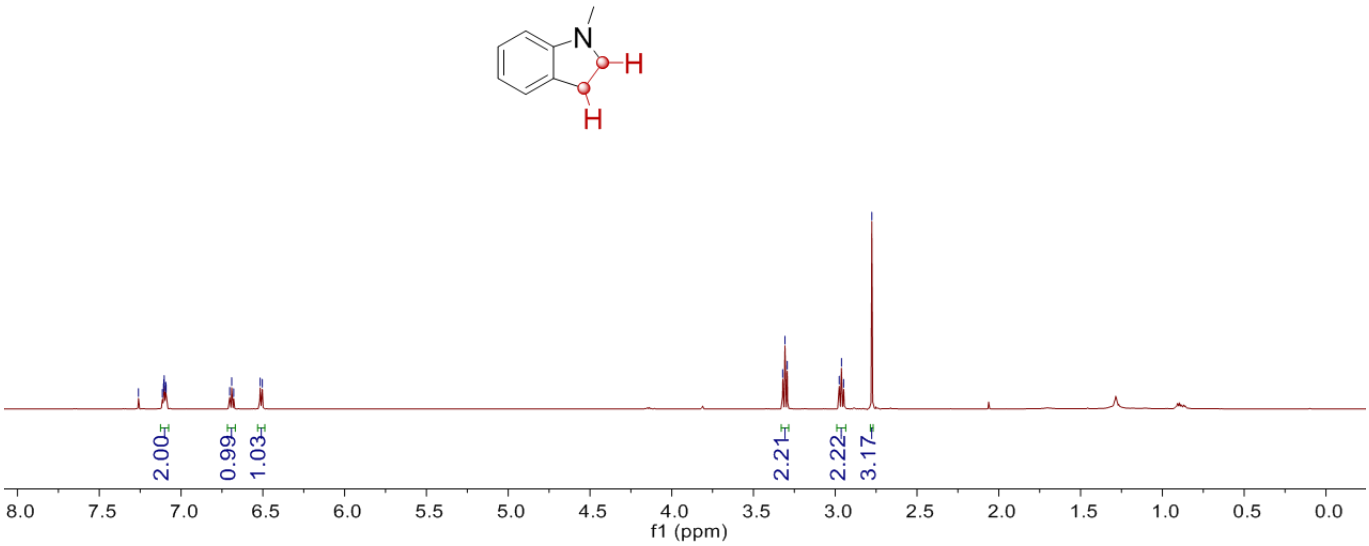
^{13}C NMR (151 MHz, $CDCl_3$)

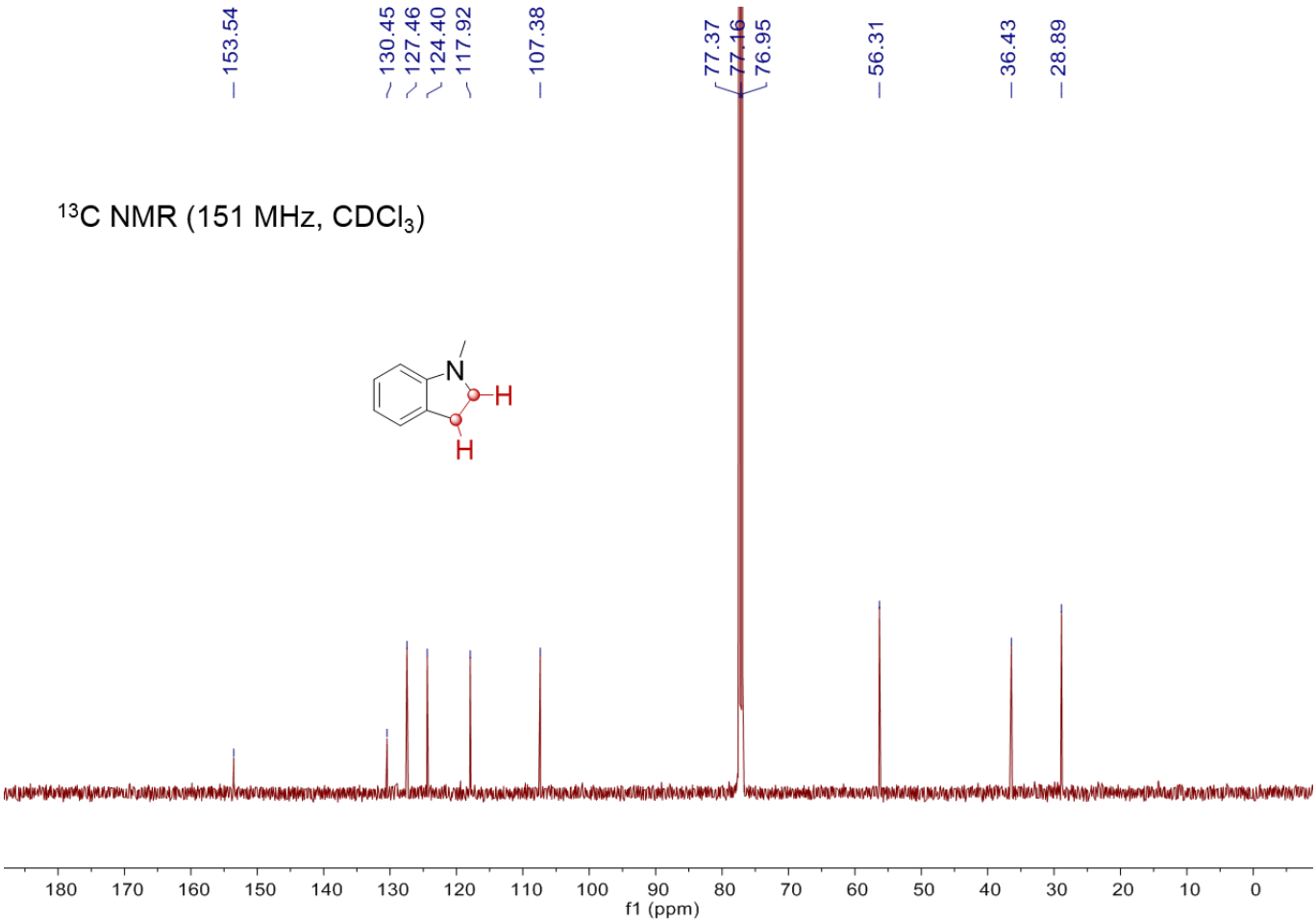




2x

^{1}H NMR (600 MHz, $CDCl_3$)

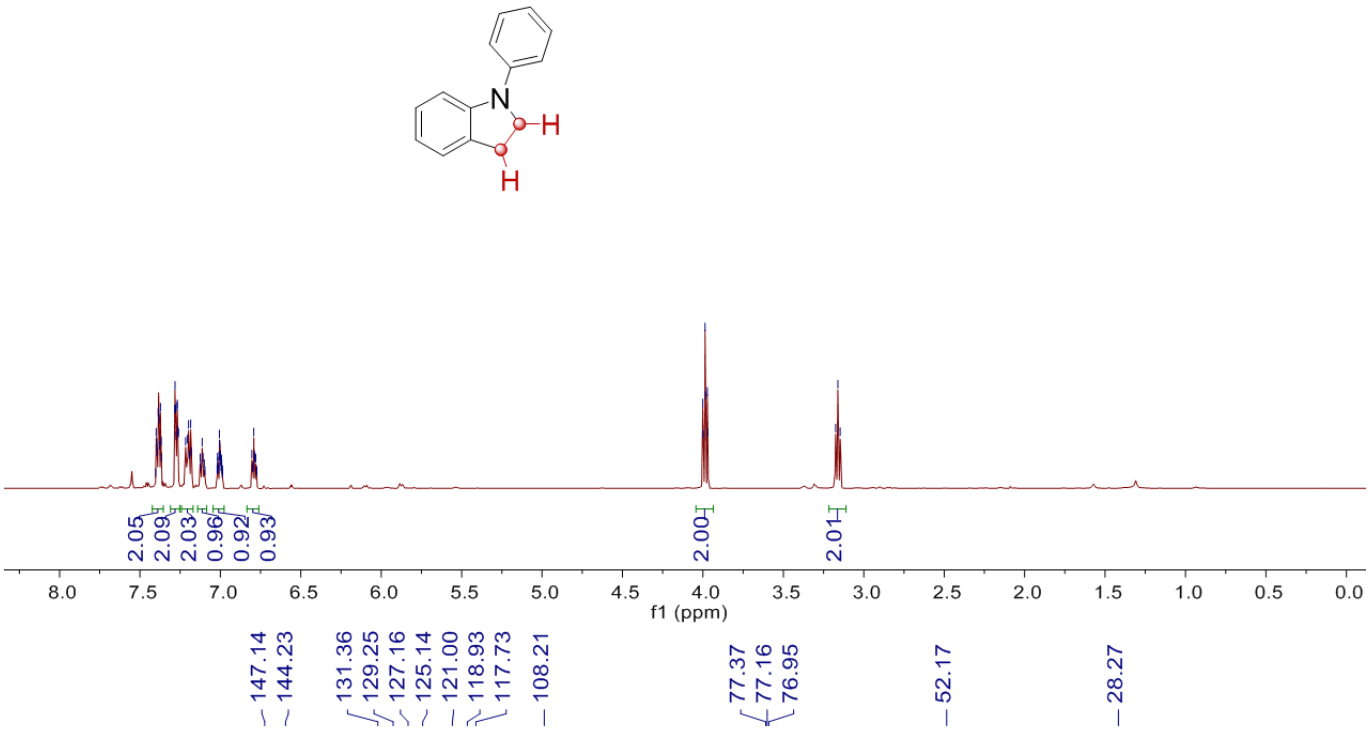




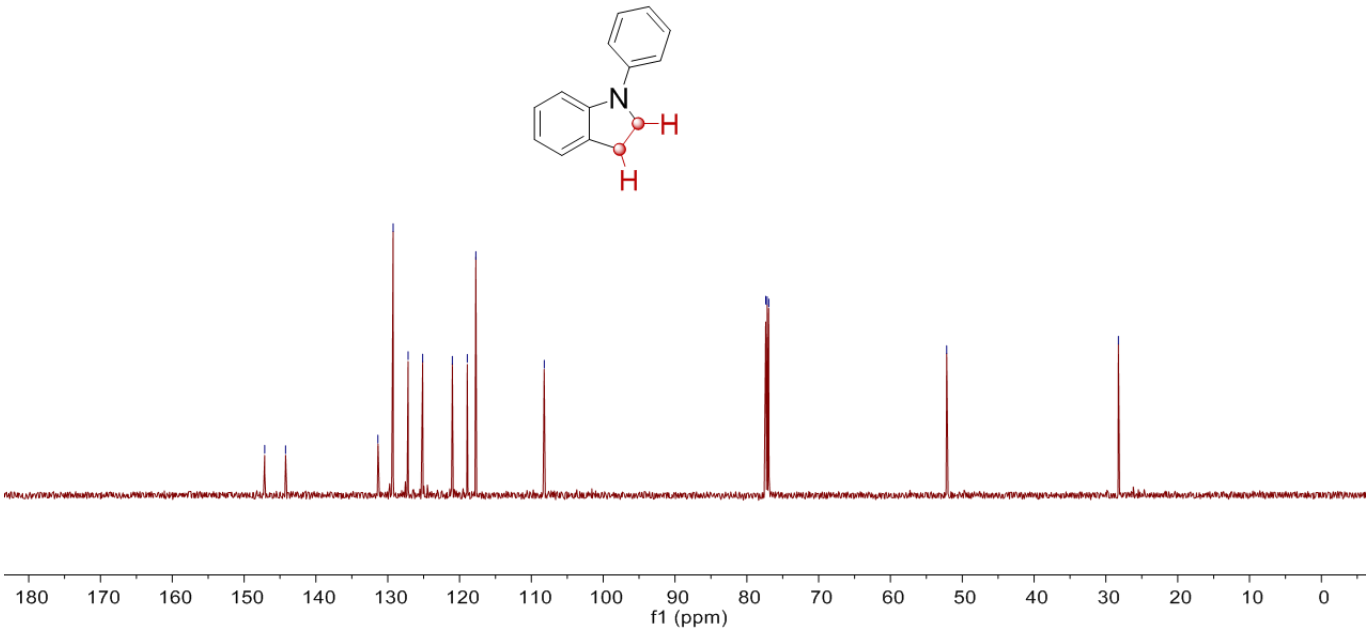
^{13}C NMR (151 MHz, $CDCl_3$)

2y

^{1}H NMR (600 MHz, $CDCl_3$)

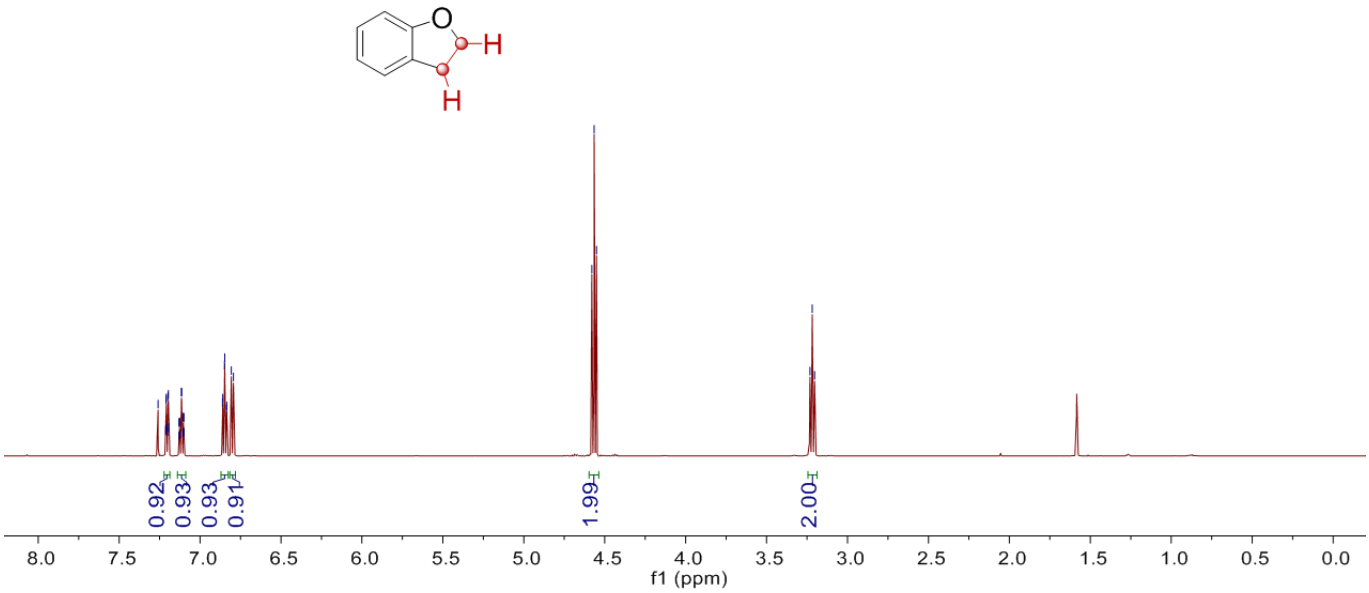


^{13}C NMR (151 MHz, $CDCl_3$)

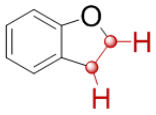


2z

^{1}H NMR (600 MHz, $CDCl_3$)

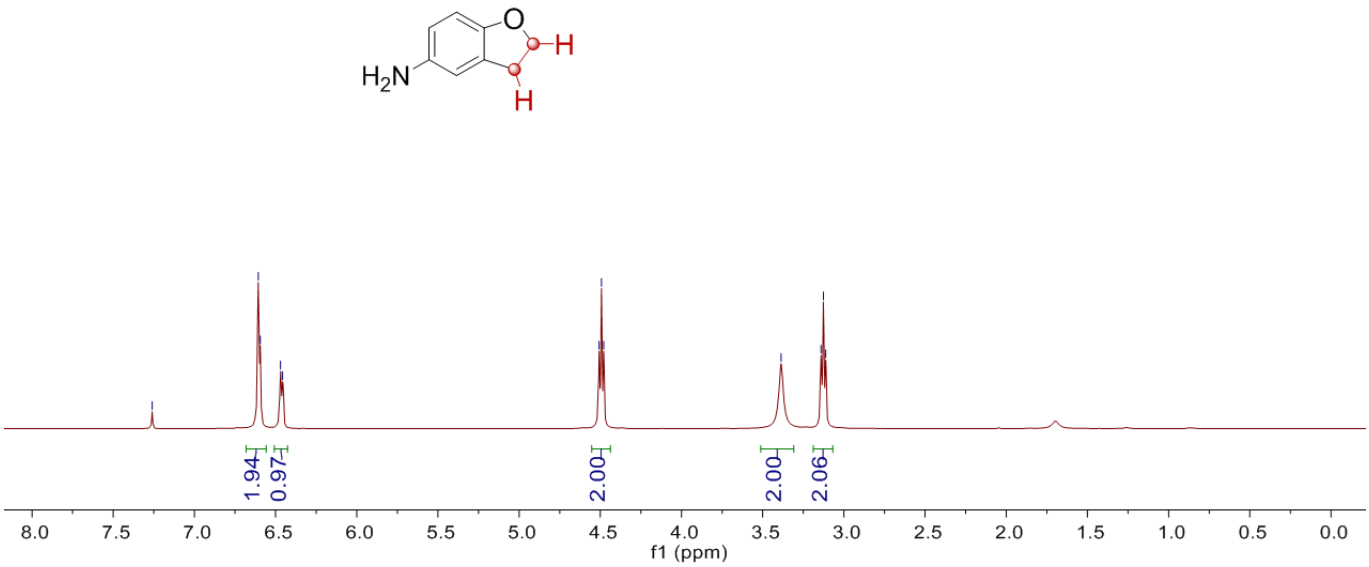


^{13}C NMR (151 MHz, $CDCl_3$)

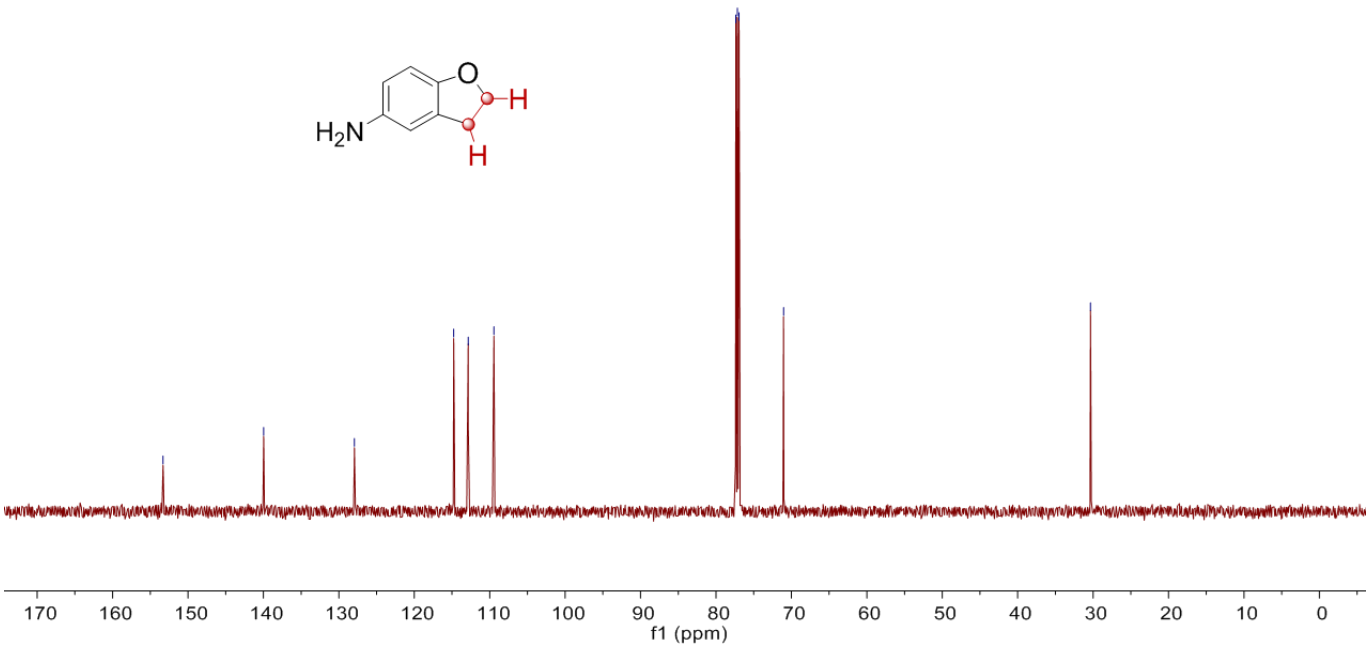


2aa

^{1}H NMR (600 MHz, $CDCl_3$)

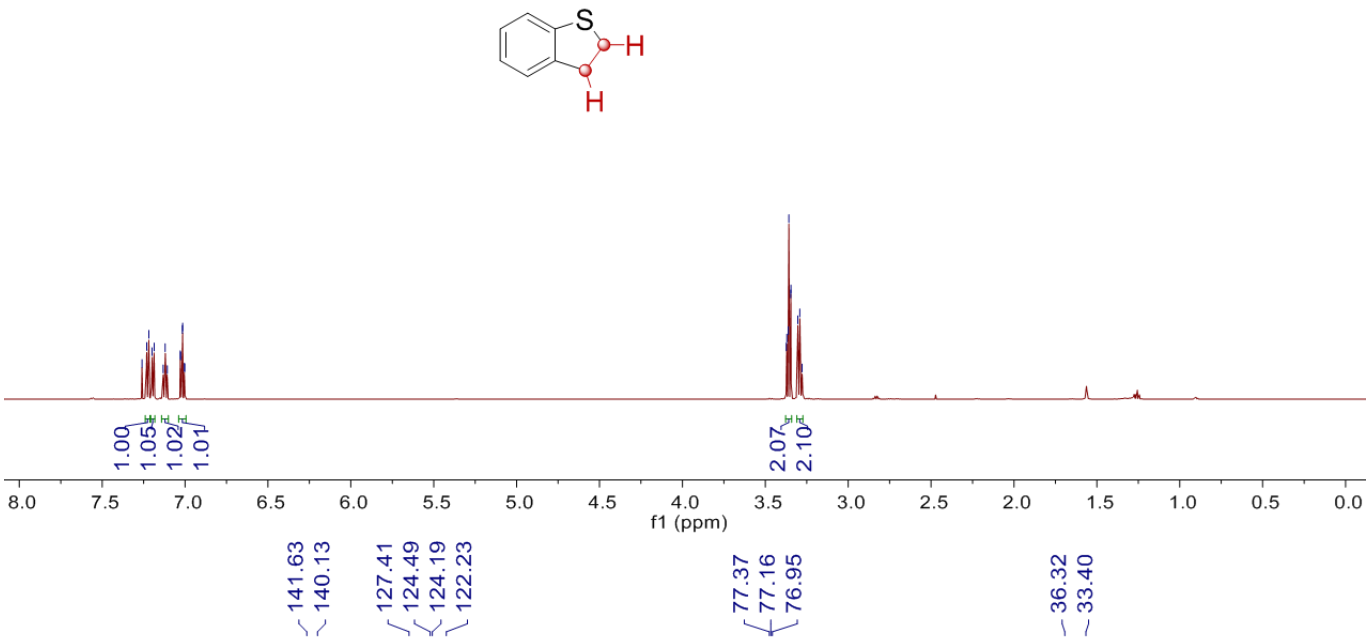


^{13}C NMR (151 MHz, $CDCl_3$)

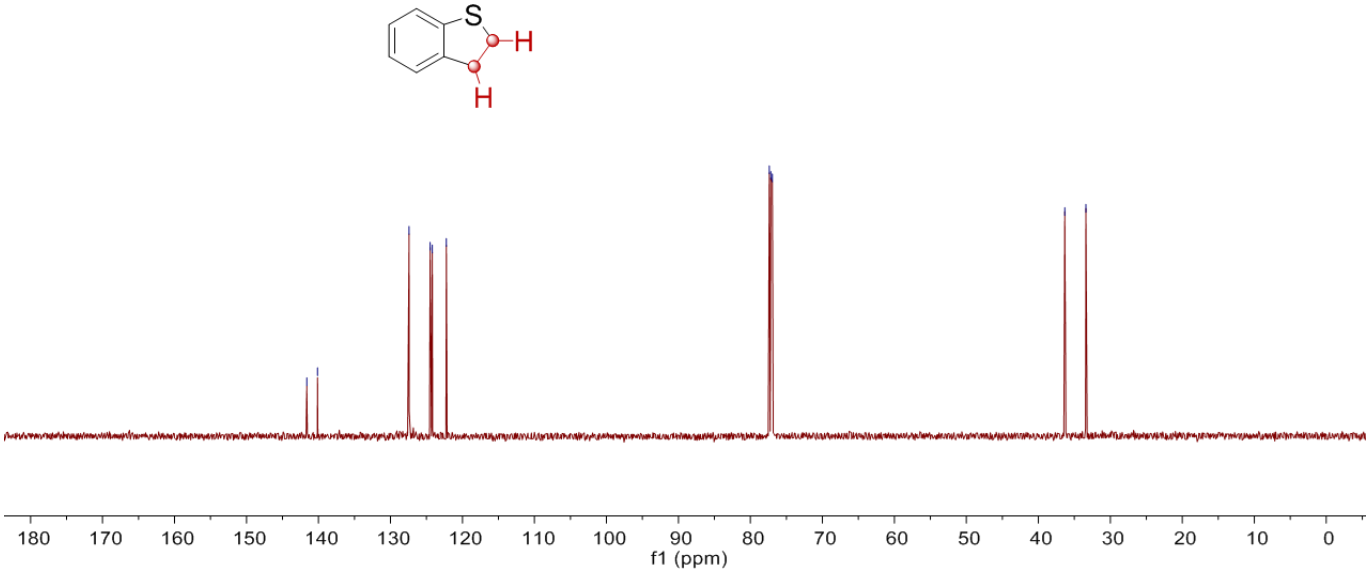


2ab

^{1}H NMR (600 MHz, $CDCl_3$)

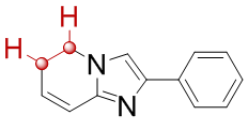


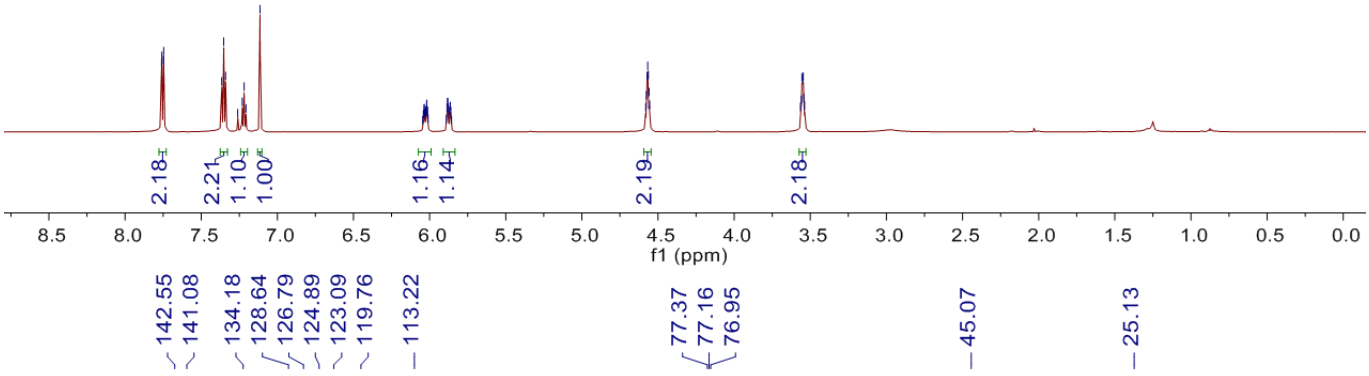
^{13}C NMR (151 MHz, $CDCl_3$)



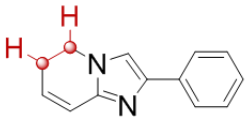
2ac

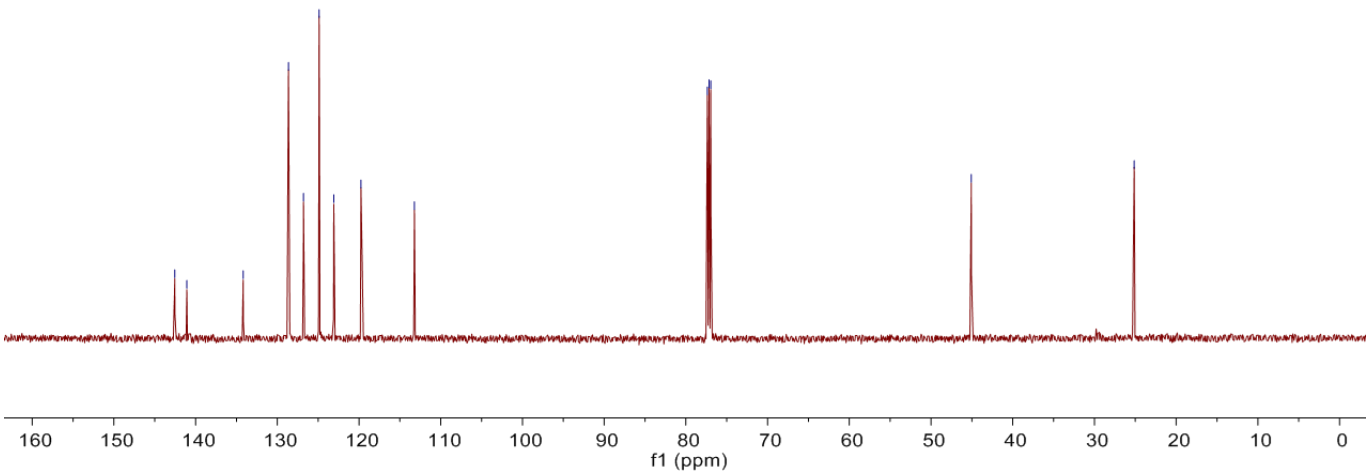
^{1}H NMR (600 MHz, $CDCl_3$)





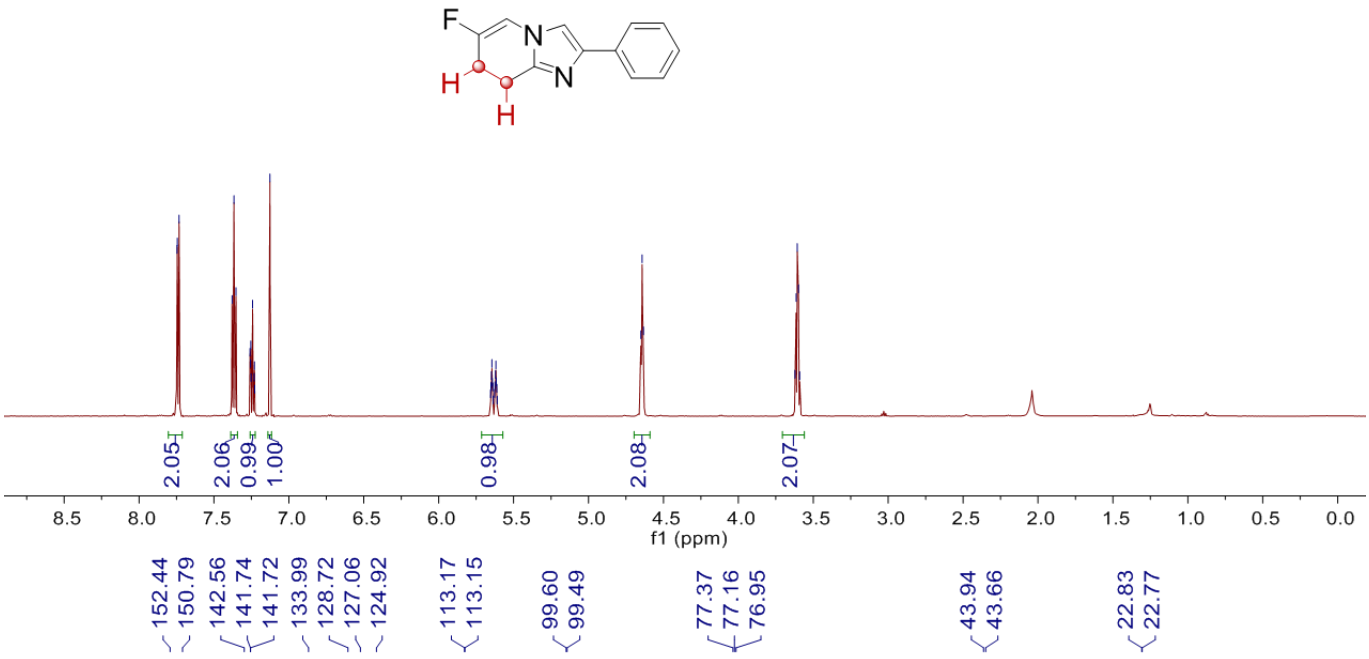
^{13}C NMR (151 MHz, $CDCl_3$)



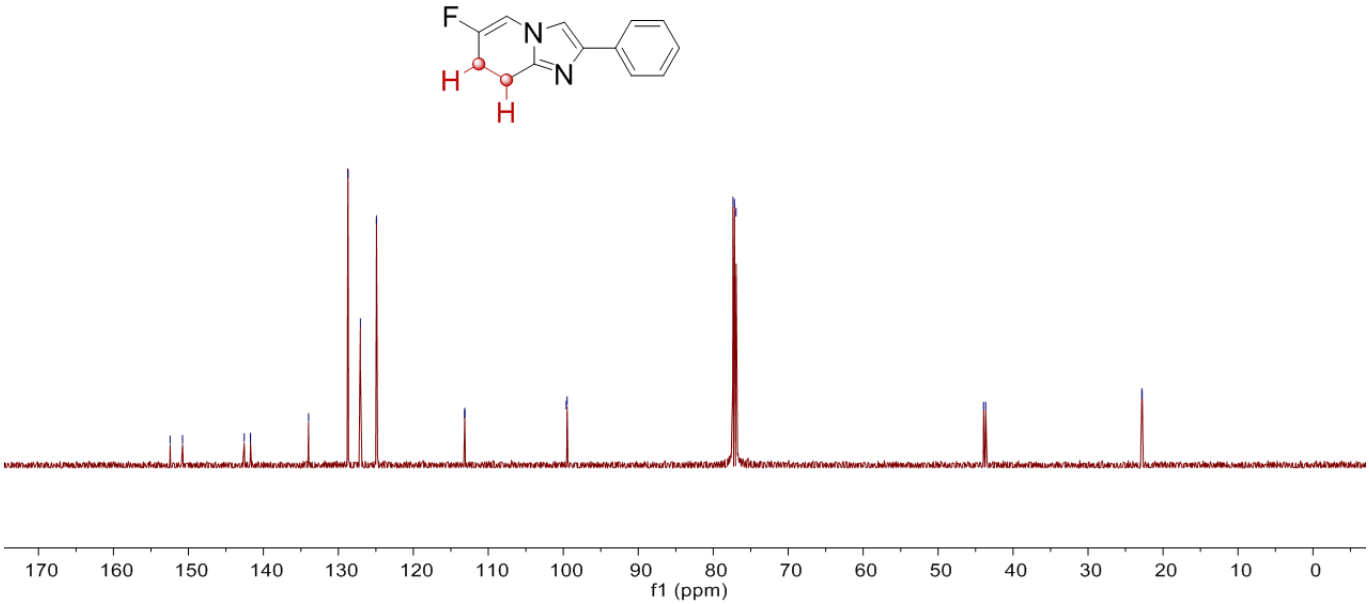


2ad

^{1}H NMR (600 MHz, $CDCl_3$)

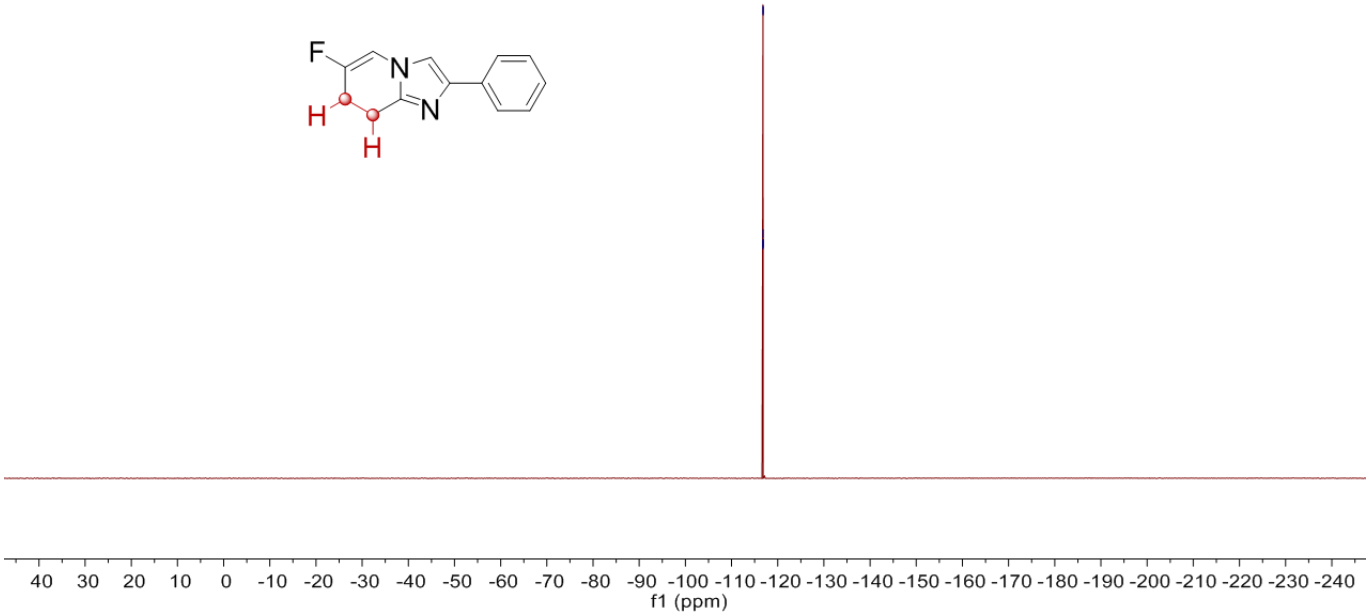


^{13}C NMR (151 MHz, $CDCl_3$)



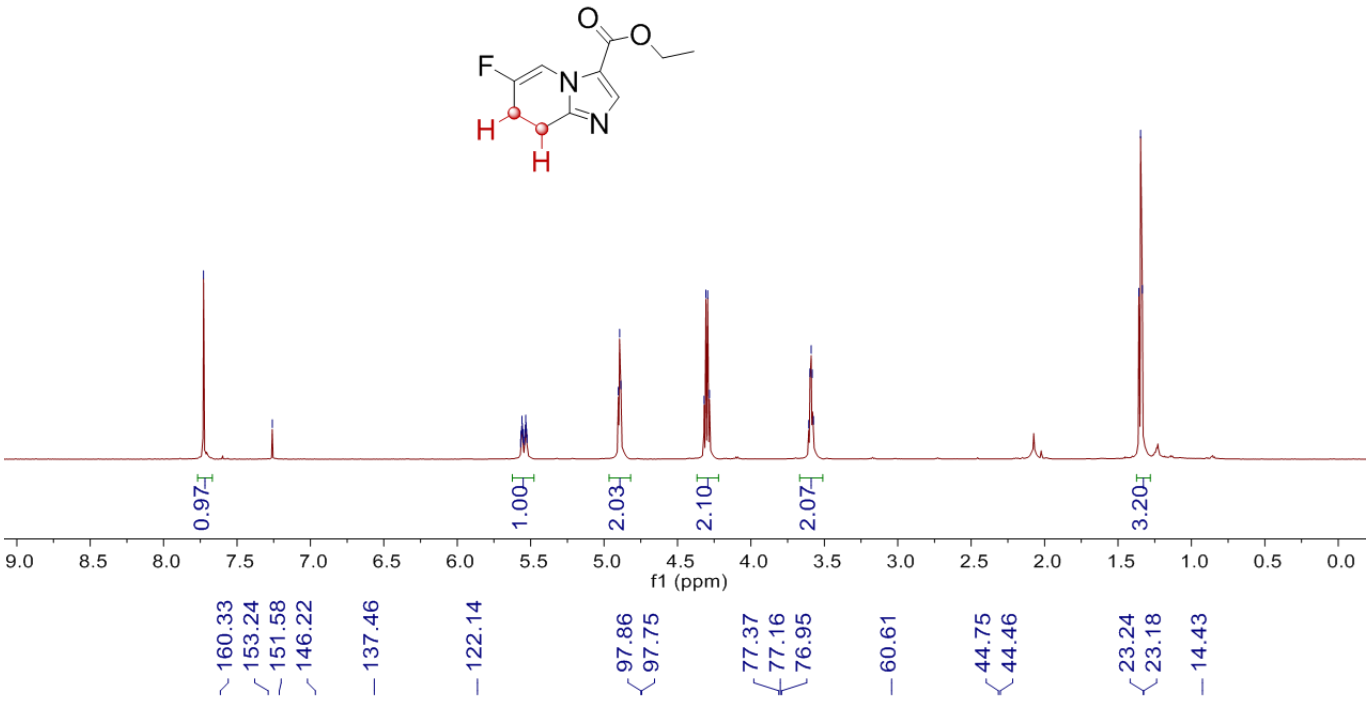
-116.81
-116.81
-116.82
-116.83
-116.84
-116.85

^{19}F NMR (565 MHz, $CDCl_3$)

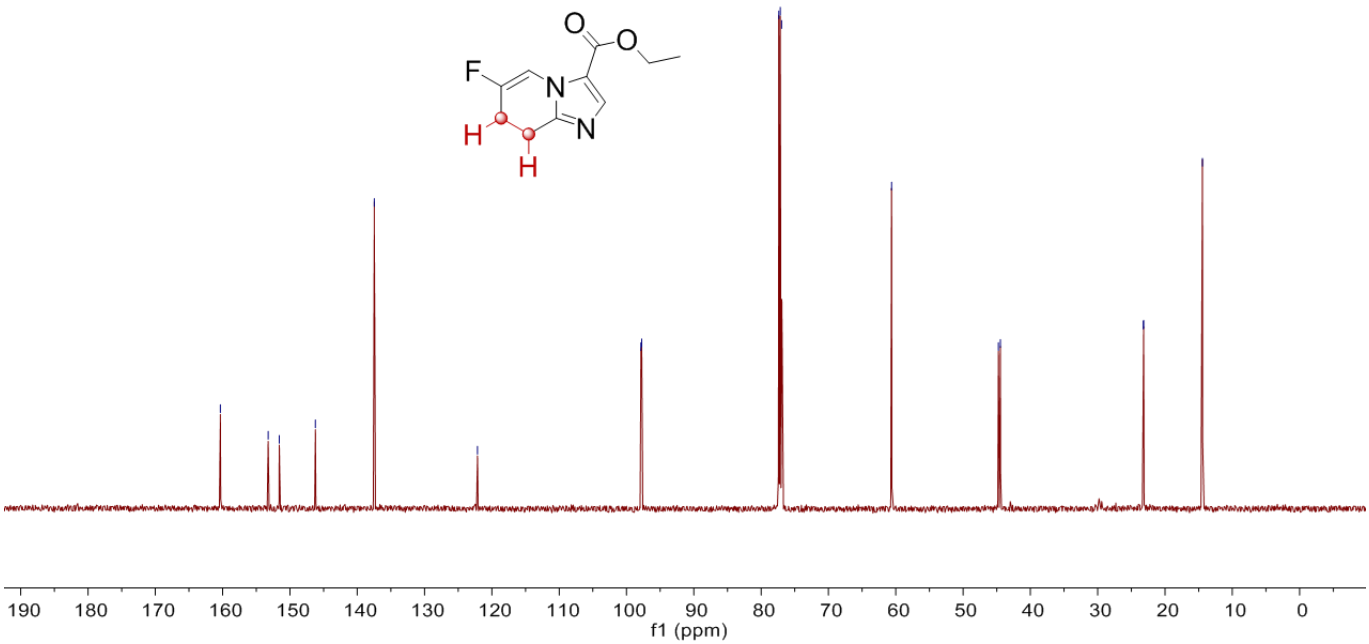


2ae

^{1}H NMR (600 MHz, $CDCl_3$)

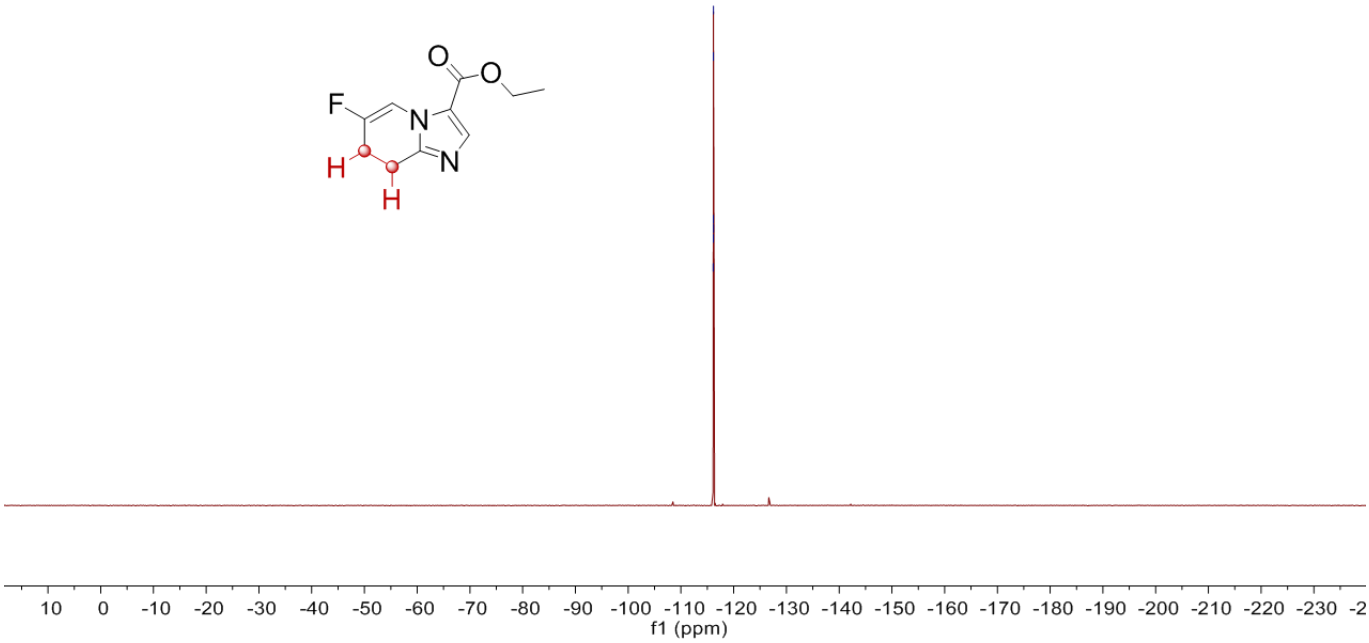


^{13}C NMR (151 MHz, $CDCl_3$)



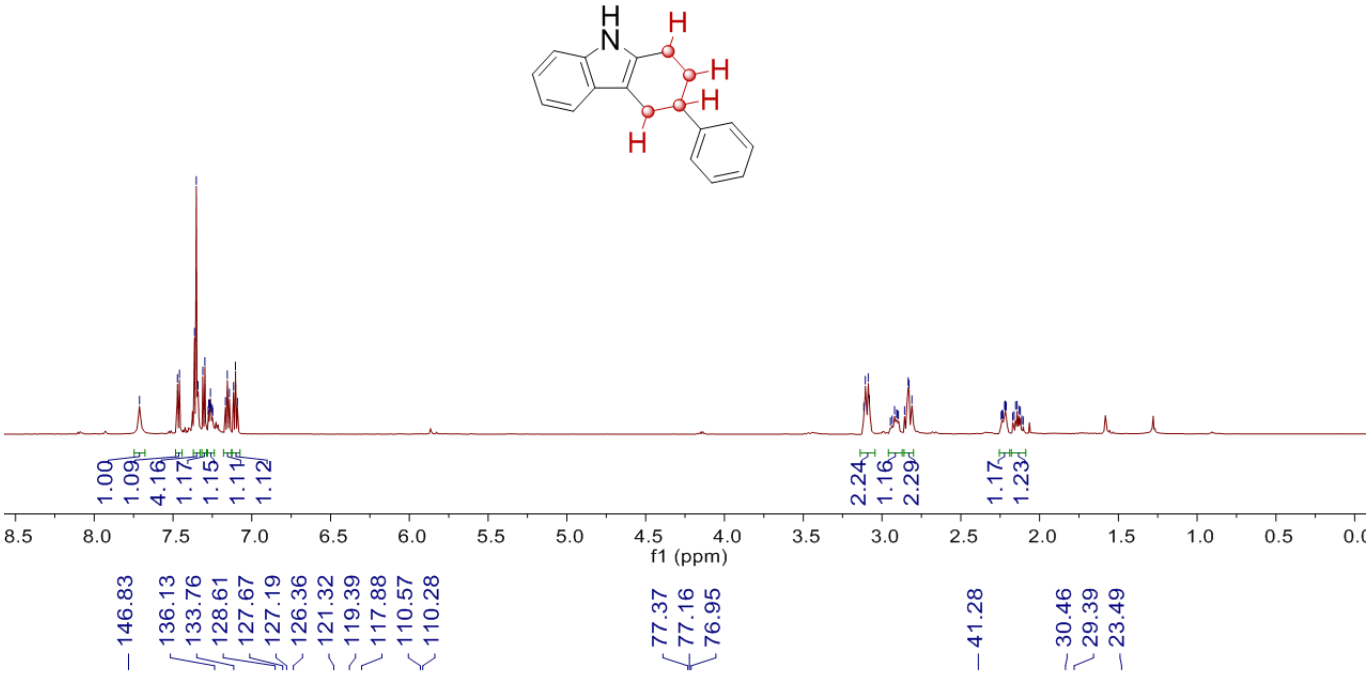
-116.13
-116.14
-116.15
-116.16
-116.17
-116.18

^{19}F NMR (565 MHz, $CDCl_3$)

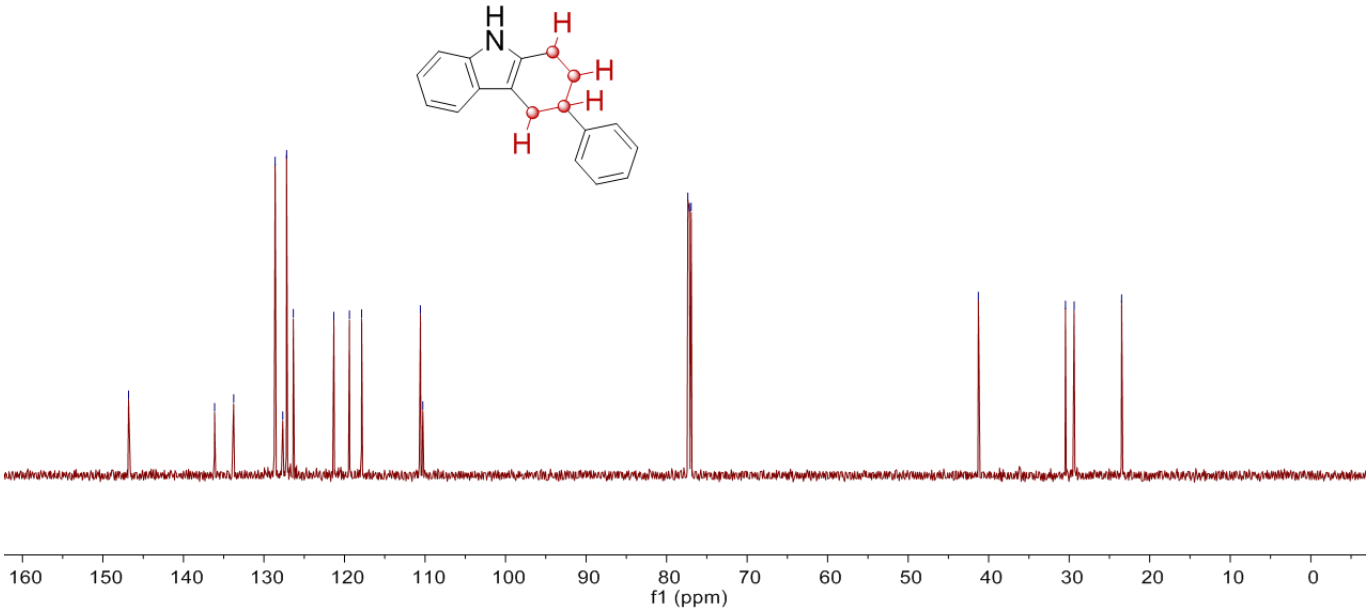


2af

^{1}H NMR (600 MHz, $CDCl_3$)

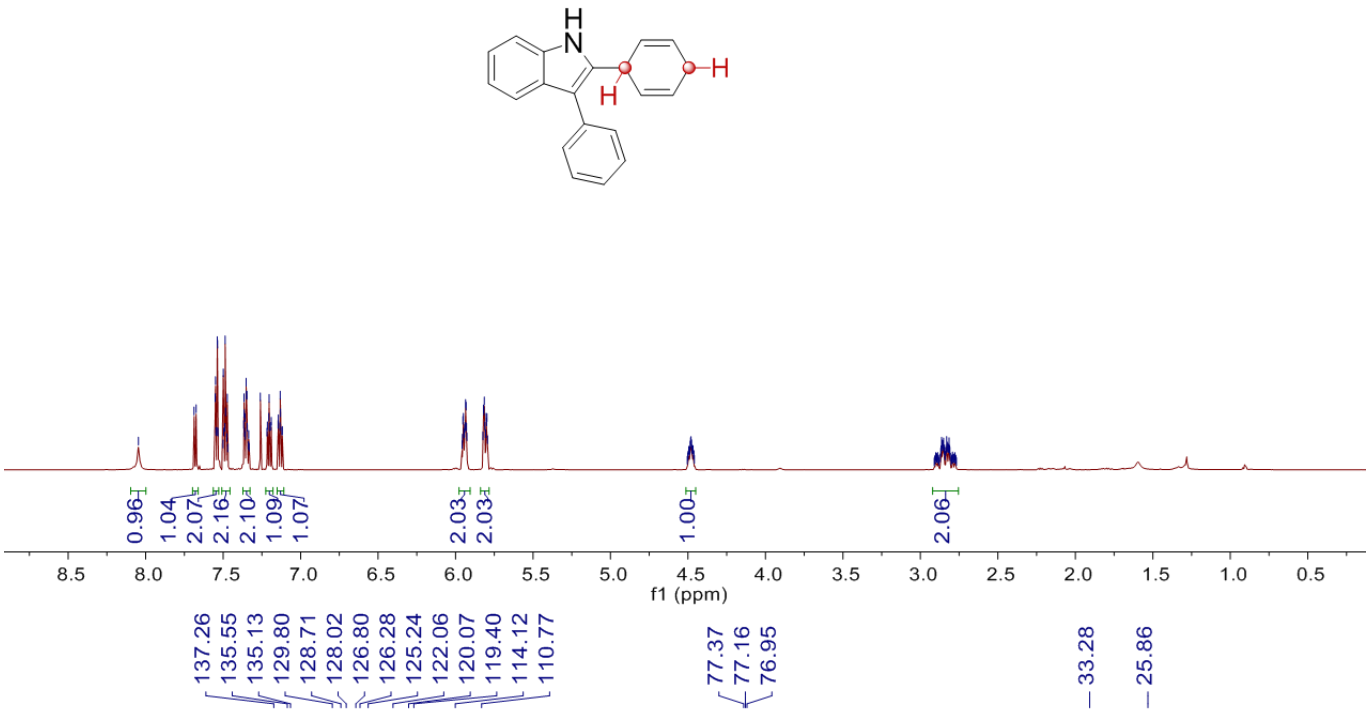


^{13}C NMR (151 MHz, $CDCl_3$)

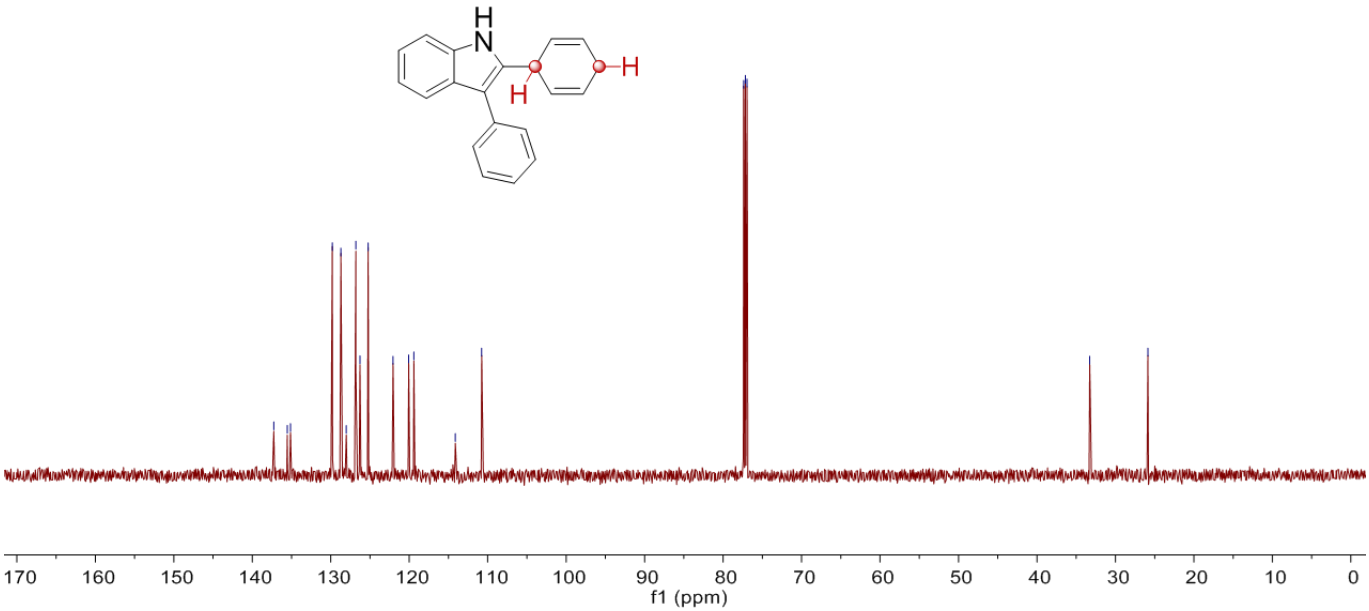


2ag

^{1}H NMR (600 MHz, $CDCl_3$)

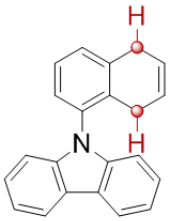


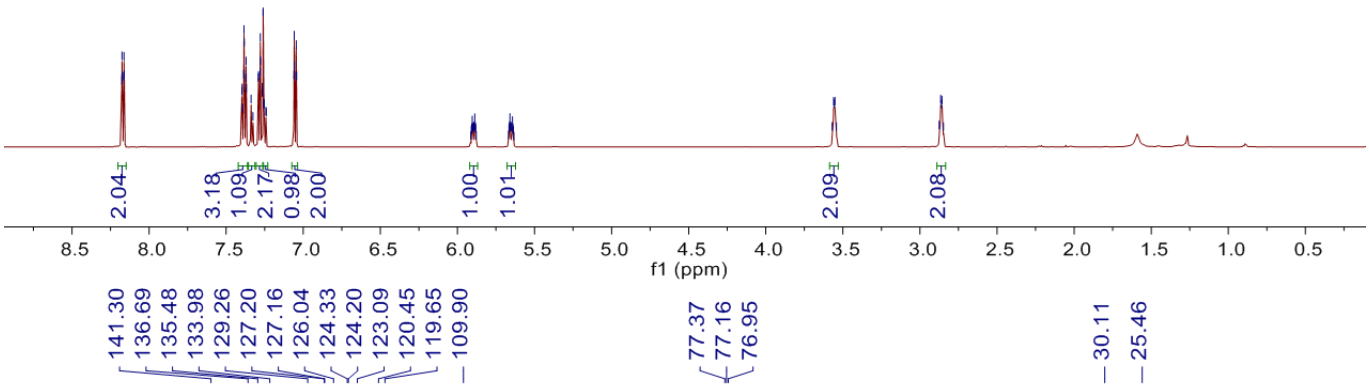
^{13}C NMR (151 MHz, $CDCl_3$)



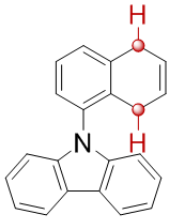
2ah

^{1}H NMR (600 MHz, $CDCl_3$)



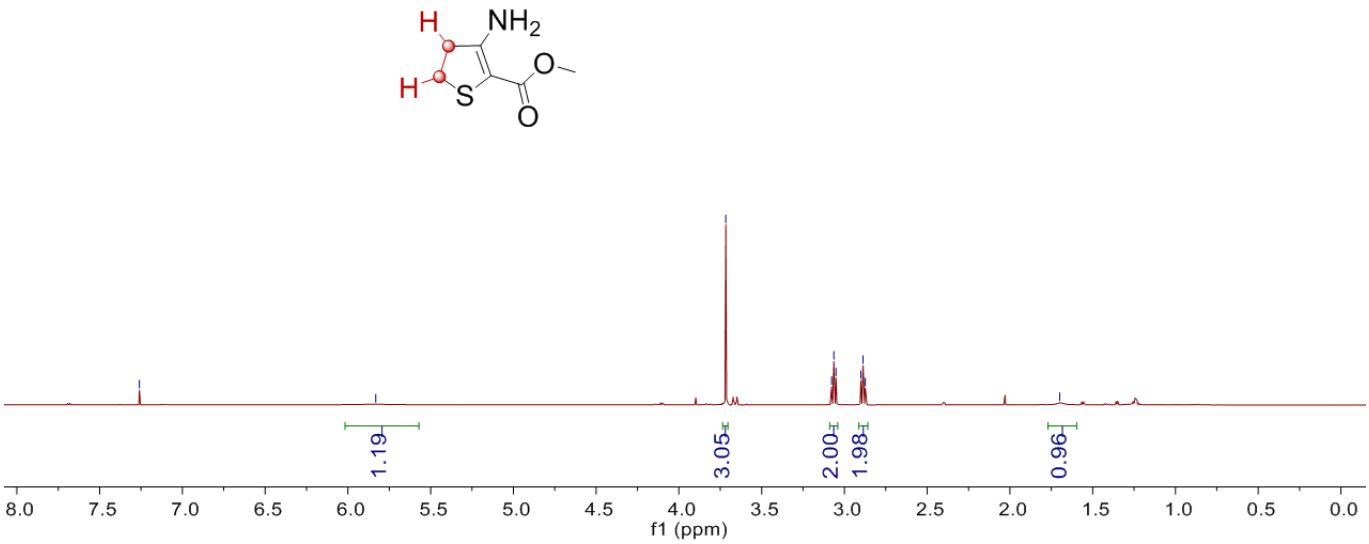


^{13}C NMR (151 MHz, $CDCl_3$)

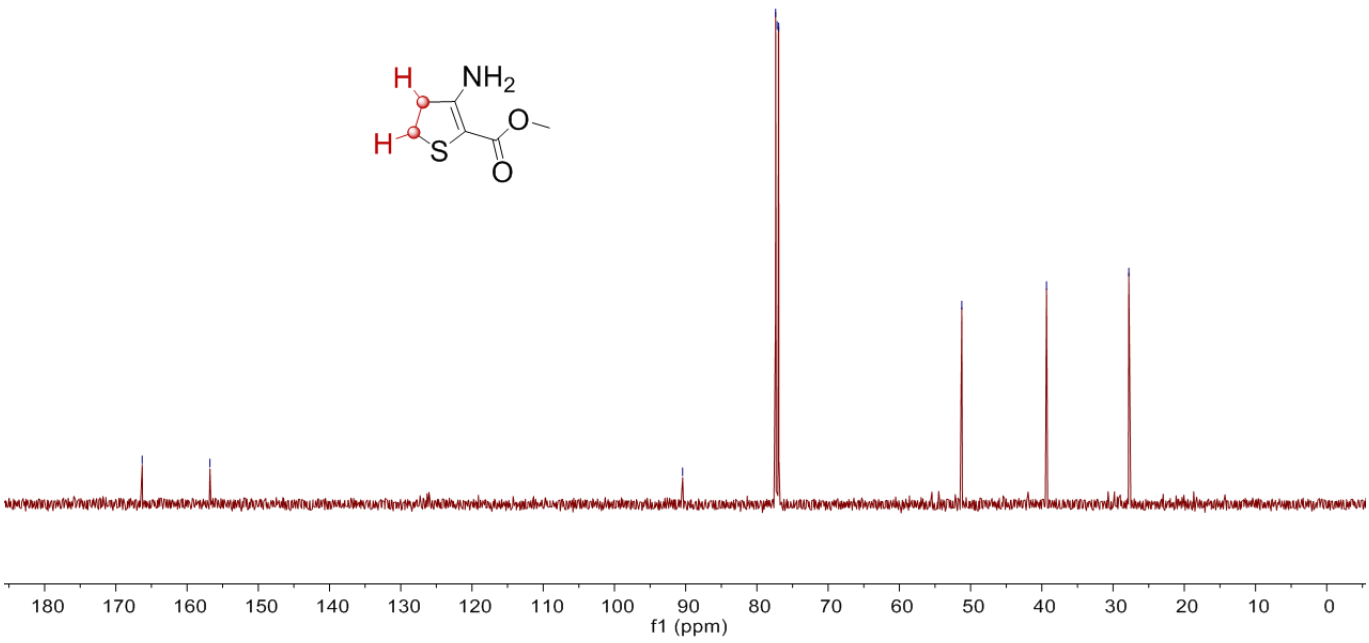


2ai

^{1}H NMR (600 MHz, $CDCl_3$)

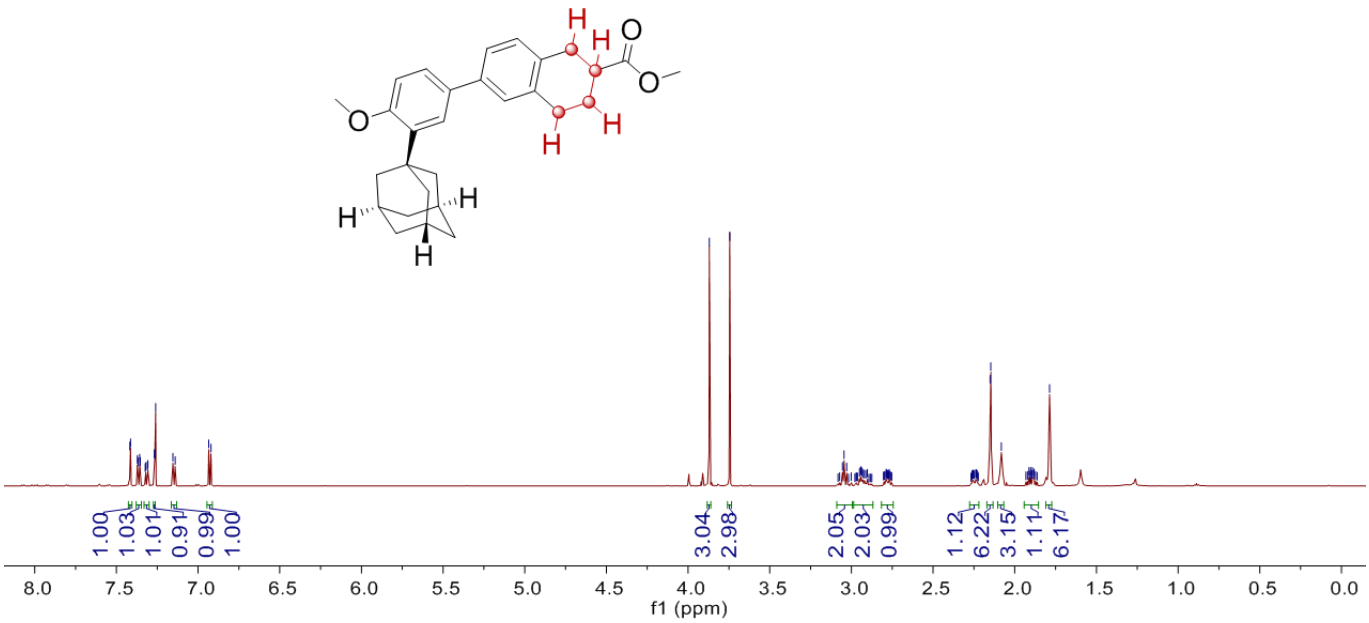


^{13}C NMR (151 MHz, $CDCl_3$)

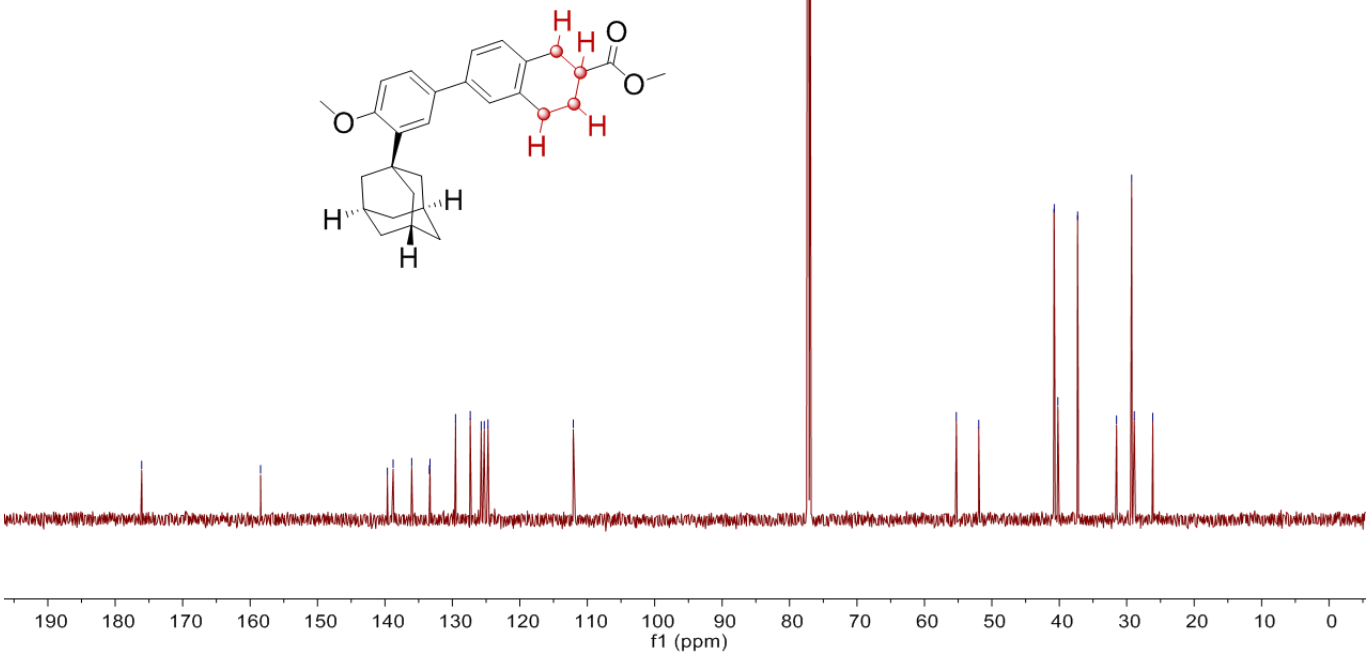


2ak

^{1}H NMR (600 MHz, $CDCl_3$)

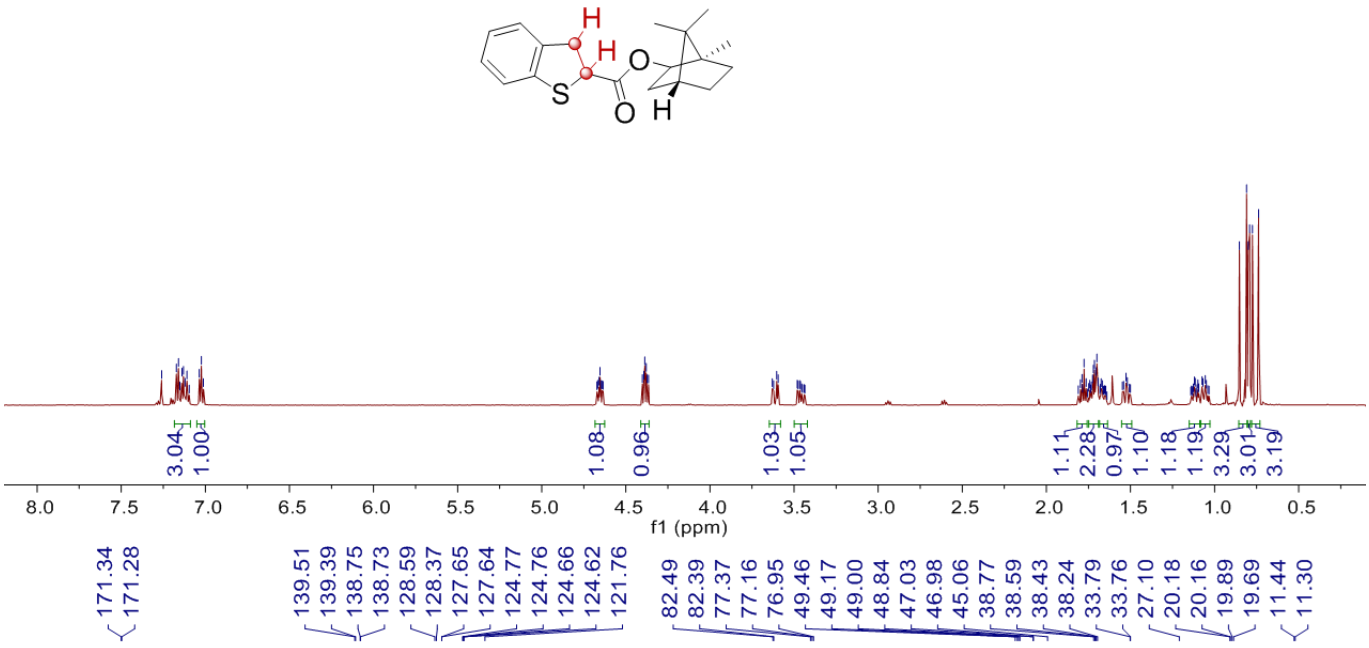


^{13}C NMR (151 MHz, $CDCl_3$)

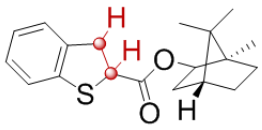


2al

^{1}H NMR (600 MHz, $CDCl_3$)

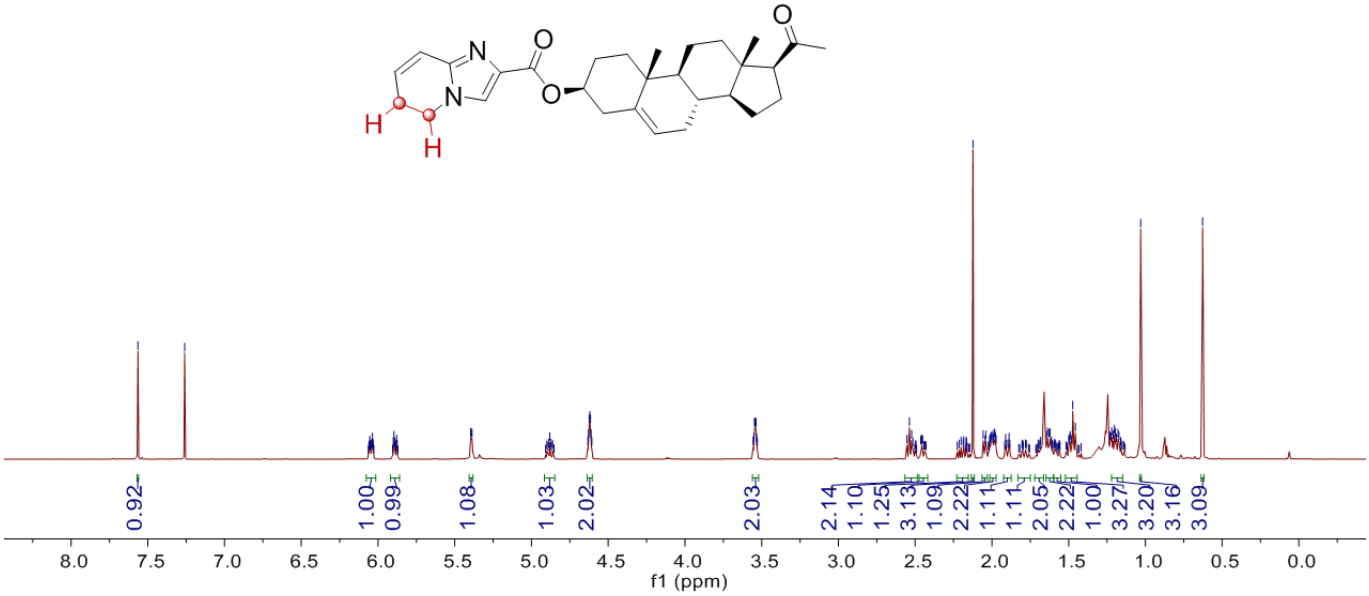


^{13}C NMR (151 MHz, $CDCl_3$)

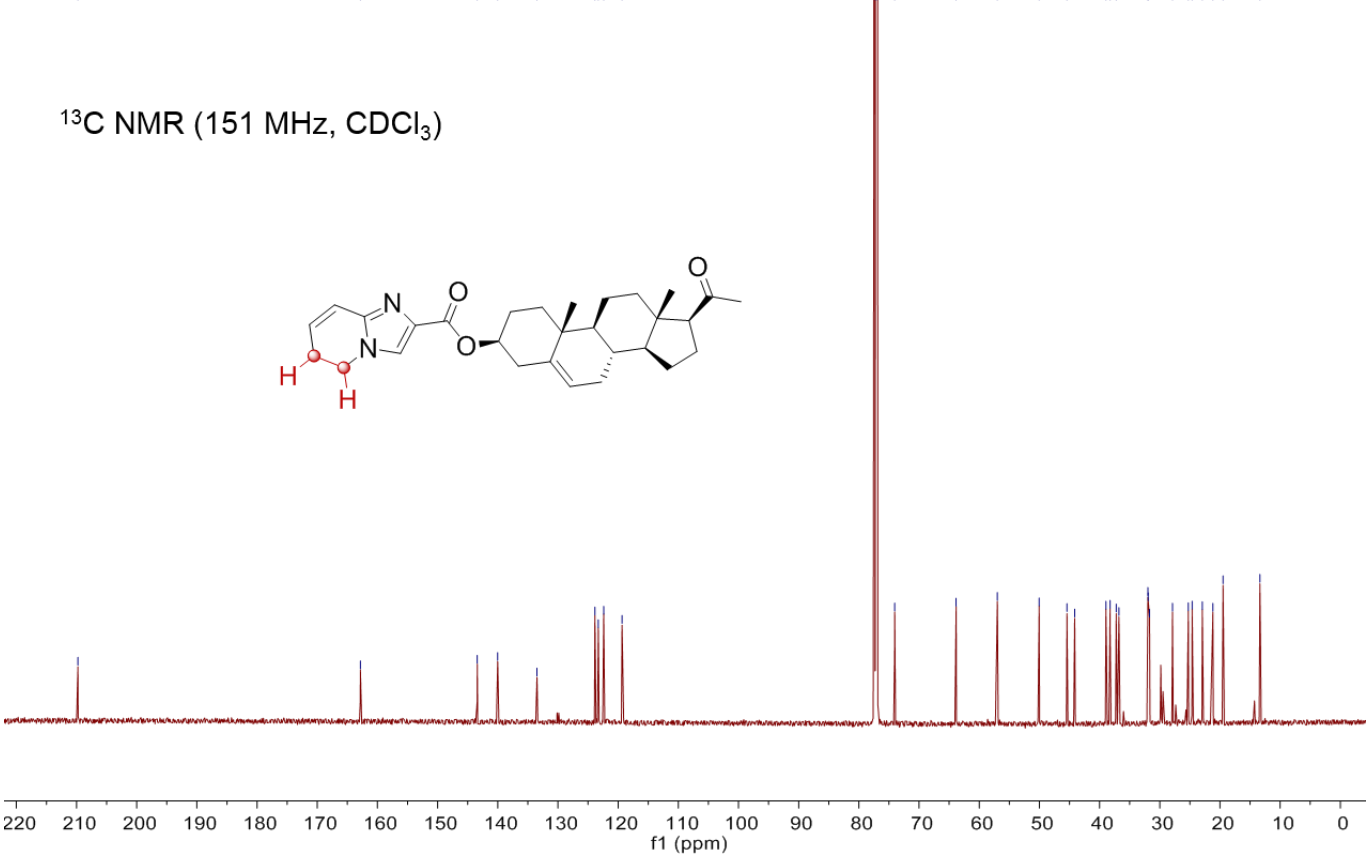


2am

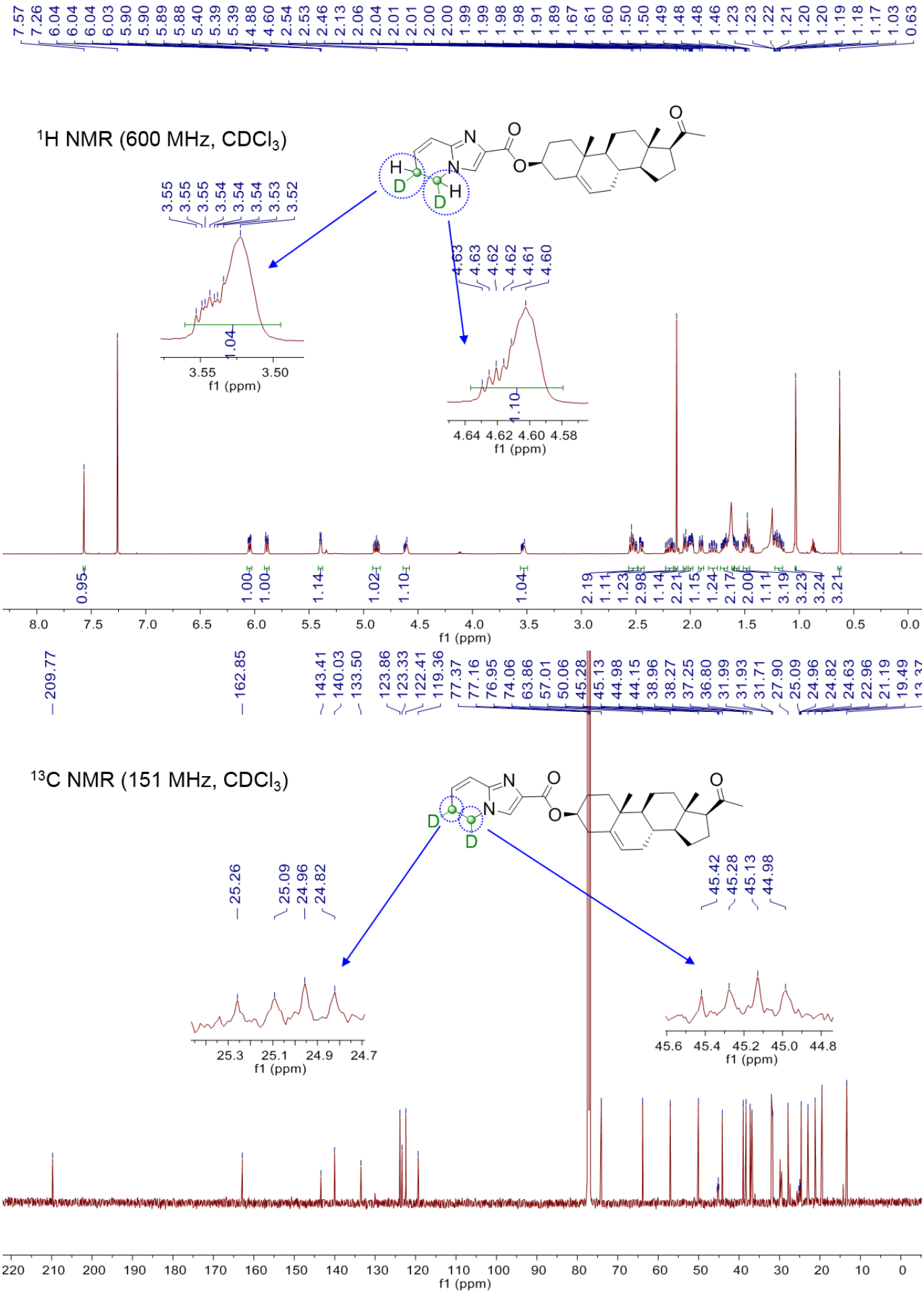
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

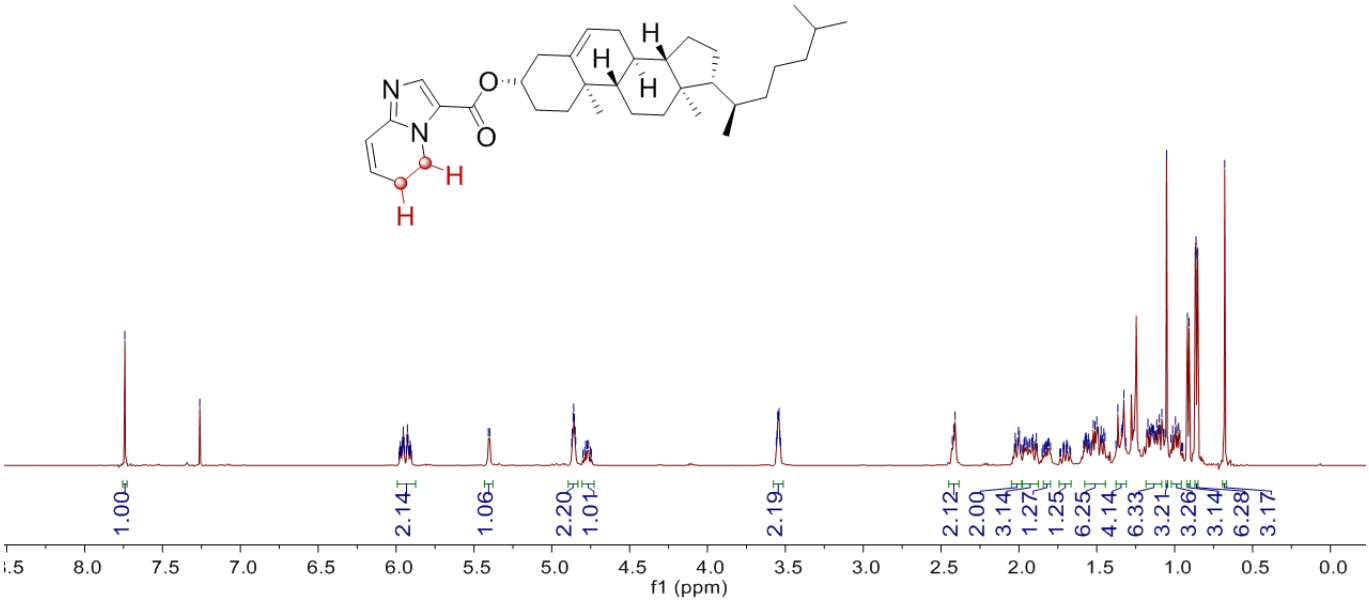


2am’

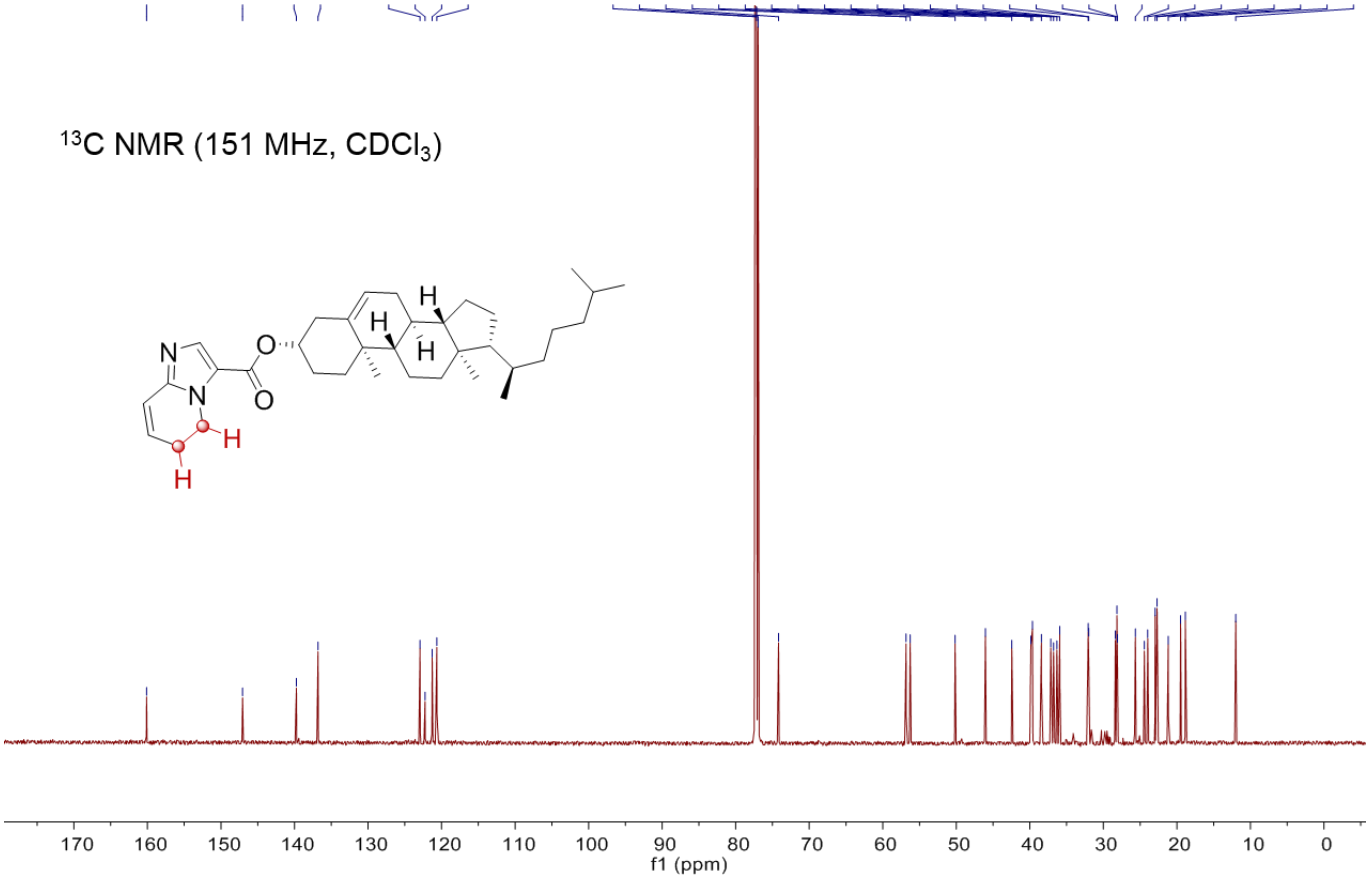

7.57 7.26 6.04 6.04 6.04 6.03 5.90 5.90 5.89 5.88 5.40 5.39 5.39 4.88 4.60 2.54 2.53 2.46 2.13 2.06 2.04 2.01 2.01 2.00 2.00 1.99 1.99 1.98 1.98 1.91 1.89 1.67 1.61 1.60 1.50 1.50 1.49 1.48 1.48 1.46 1.23 1.23 1.22 1.21 1.20 1.20 1.19 1.18 1.17 1.03 0.63
^{1}H NMR (600 MHz, $CDCl_3$)
3.55 3.55 3.55 3.54 3.54 3.54 3.53 3.52
1.04
3.55 3.50
f1 (ppm)
4.63 4.63 4.62 4.62 4.61 4.60
1.10
4.64 4.62 4.60 4.58
f1 (ppm)
0.95 1.00 1.00 1.14 1.02 1.10 1.04 2.19 1.11 1.23 2.98 1.14 2.21 1.15 1.24 2.17 2.00 1.11 3.19 3.23 3.24 3.21
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
209.77 162.85 143.41 140.03 133.50 123.86 123.33 122.41 119.36 77.37 77.16 76.95 74.06 63.86 57.01 50.06 45.28 45.13 44.98 44.15 38.96 38.27 37.25 36.80 31.99 31.93 31.71 27.90 25.09 24.96 24.82 24.63 22.96 21.19 19.49
^{13}C NMR (151 MHz, $CDCl_3$)
25.26 25.09 24.96 24.82
25.3 25.1 24.9 24.7
f1 (ppm)
45.42 45.28 45.13 44.98
45.6 45.4 45.2 45.0 44.8
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2an

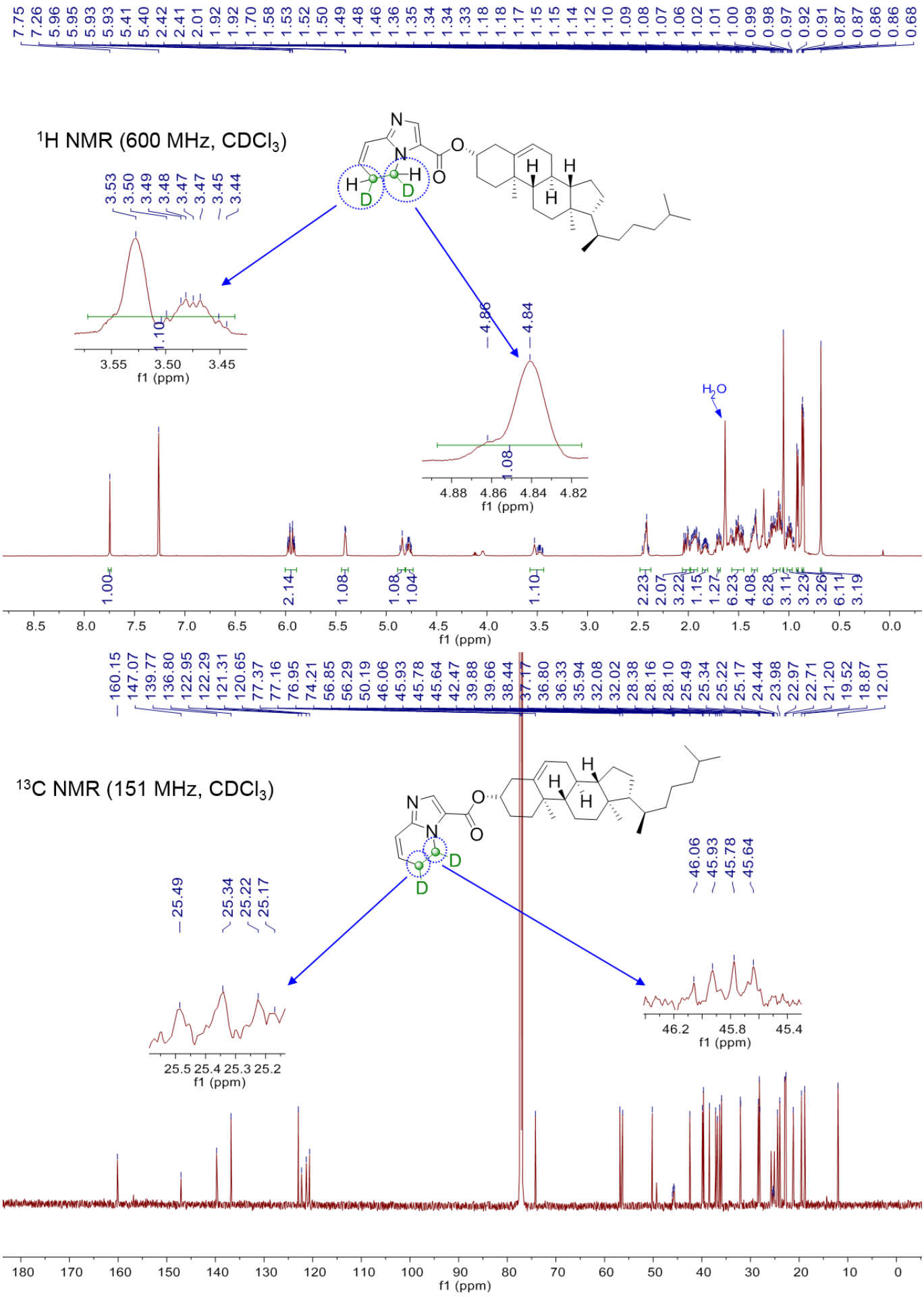
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

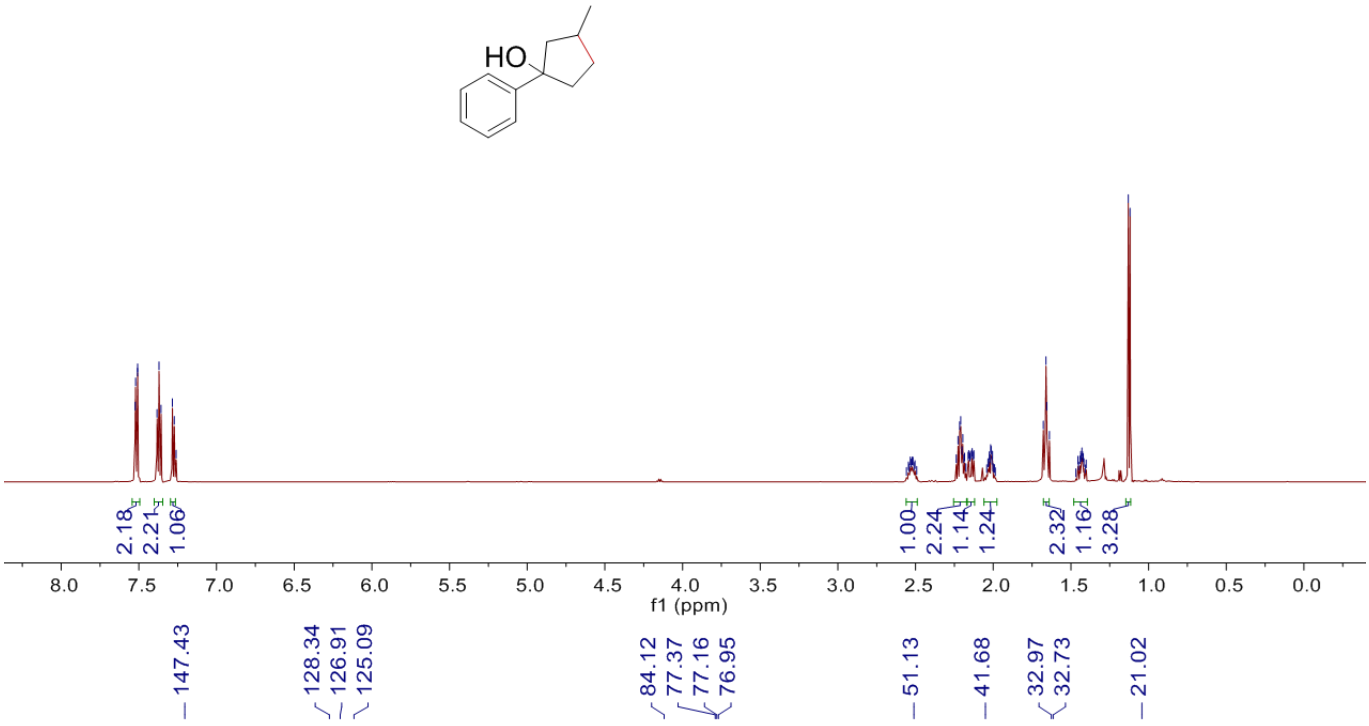


2an'



4b

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)