Electronic Supplementary Information

Well-defined Cobalt(II) Catalyzed Synthesis of Perimidine Derivatives via Acceptorless Dehydrogenative Annulation

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1. General considerations:

Unless otherwise mentioned, all chemicals (**1a**, **2a** – **2y**, **2za**, **2zd** – **2zk**) were purchased from common commercially available sources such as Sigma-Aldrich, Alfa Aesar, TCI, Avra, Thermo Fisher Scientific, BLDpharm and used without further purification. Starting materials **2z**[2], **2zb**[2], **2zc**[3], **2a-d$_2$**[4] were synthesized according to the reported literature procedure. All solvents were dried by using standard procedure. The preparation of catalyst was carried out under open atmosphere with methanol. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques, JACOMAX glove box filled with argon. DRX-400 Varian spectrometer and Bruker Advance III 400 MHz, 500 MHz and 600 MHz spectrometers were used to record ^{1}H, ^{19}F and ^{13}C NMR spectra using $CDCl_3$, DMSO-d_6 as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (*J*) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet and brs = broad singlet. Q-TOF ESI-MS instrument (Agilent: 6546 LC/Q-TOF) was used for recording mass spectra. PerkinElmer clarus-590 GC instrument using Elite Plot-Q is used for GC analysis. SRL silica gel (100-200 mesh size) was used for column chromatography. The melting points were recorded in an open capillary tube on BÜCHI Melting Point B-510 automated melting point system with heating rate of 6 °C per min and were uncorrected.

2. Synthesis of NNO-ligands:

All three ligands were prepared according to previous reported literature methods.[1] To an oven dried 50 mL round bottomed flask, Pyridine-2-carboxaldehyde (0.535 g, 5.0 mmol, 1.0 equiv.) and 2-amino ethanol derivatives (5.0 mmol, 1.0 equiv.) were dissolved in 15 mL of dry CH_2Cl_2 and then Na_2SO_4 (2.131 g, 15.0 mmol, 3.0 equiv.) was added to the reaction mixture. The resulting suspension was stirred for 12 h at room temperature. Then, it was filtered, the residue was washed thoroughly with CH_2Cl_2 and the combined solvent was removed under reduced pressure. The residue obtained was directly used for the next step without further purification. The residue was dissolved in 30 mL of methanol and $NaBH_4$

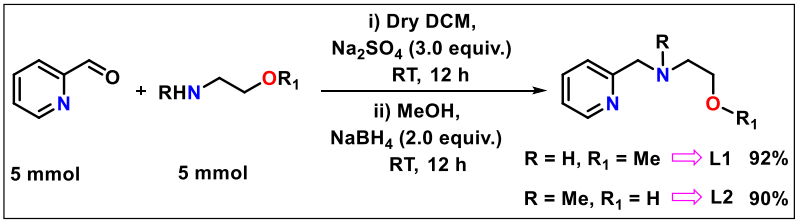


Figure S1. Synthesis of PyNNO-ligands.

(0.378 g, 10.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the crude product, which was further purified

by silica gel (100-200 mesh size) column chromatography using 60 –70% ethyl acetate in Petroleum ether (**Figure S1**).[1b]

To an oven dried 50 mL round bottomed flask, 2-Quinolinecarboxaldehyde (0.785 g, 5.0 mmol, 1.0 equiv.) and 2-Methoxyethylamine (0.375 g, 5.0 mmol, 1.0 equiv.) were dissolved in 15 mL of dry CH_2Cl_2 and then Na_2SO_4 (2.131 g, 15.0 mmol, 3.0 equiv.) was added to the reaction mixture. The resulting suspension was stirred for 12 h at room temperature. Then, it was filtered, the residue was washed thoroughly with CH_2Cl_2 and the combined solvent was removed under reduced pressure. The residue obtained was directly used for the next step without further purification. The residue was dissolved in 30 mL of methanol and $NaBH_4$ (0.378 g, 10.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4.

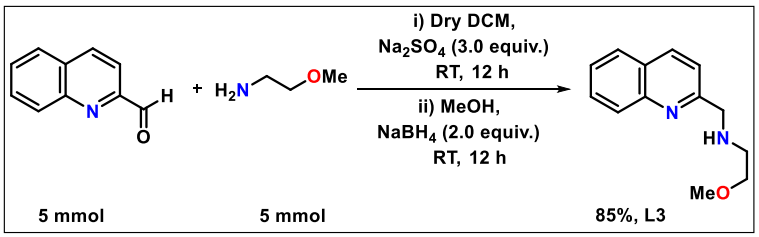


Figure S2. Synthesis of QuinNNO-ligand.

Then the solvent was evaporated to get the crude product, which was further purified by silica gel (100-200 mesh size) column chromatography using 60 –70% ethyl acetate in Petroleum ether (**Figure S2**).[1c]

3. Procedure for synthesis of Co (II) complexes (Co1-Co3):

Three complexes were prepared according to the previous reported literature methods.[1a] In an oven dried 25 mL round bottomed flask, $CoBr_2$ (0.219 g, 1.0 mmol, 1.0 equiv.) and methanolic solution of [$(PyCH_2)RN(CH_2CH_2OR_1)$, R = H, Me, R_1 = H, Me] (0.166 g, 1.0 mmol, 1.0 equiv.) was

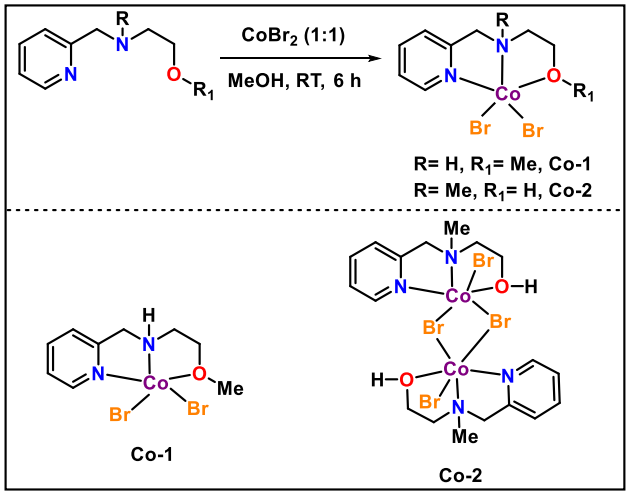


Figure S3. Synthesis of PyNNO Co(II) complexes.

added drop wise. Then, the suspension was stirred at room temperature under argon atmosphere for 6 h. After 6 h, the solvent was removed under reduced pressure and the residue was rinsed with diethyl ether and dried under vacuum to get deep violet crystalline solid.

In an oven dried 25 mL round bottomed flask, $CoBr_2$ (0.219 g, 1.0 mmol, 1.0 equiv.) and methanolic solution of 2-methoxy-N-(quinolin-2-ylmethyl)ethan-1-amine **(L3)** (0.217 g, 1.0 mmol, 1.0 equiv.) was added drop wise. Then, the suspension was stirred at room temperature under argon atmosphere for 6 h. After 6 h, the solvent was removed under reduced pressure and the residue was rinsed with diethyl ether and dried under vacuum to get deep violet crystalline solid.

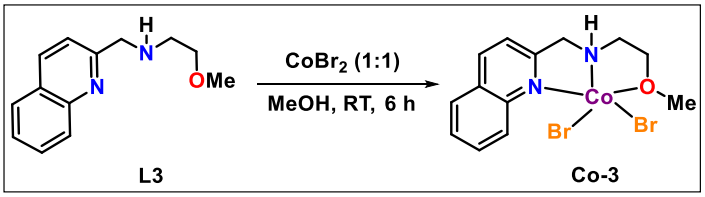
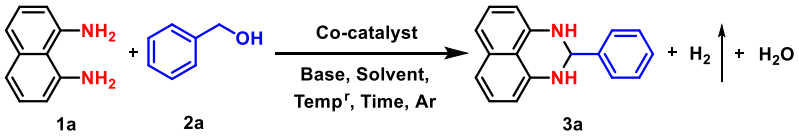


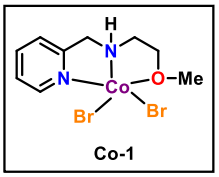
Figure S4. Synthesis of QuinNNO Co(II) complex.

4. Optimization of the reaction conditions for the synthesis of 2,3-Dihydro-1*H*-Perimidine [a]

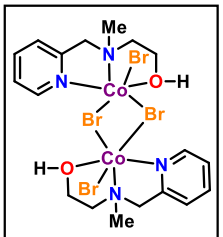


1a 2a 3a

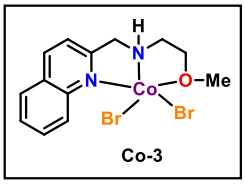
Entry	Cat. (mol%)	Solvent	Base (equiv)	1a:2a	Temp (°C)	Time (h)	Yield[b] (%)
1.	Co-1 (5)	Xylene	KO^{t}Bu(1.0)	1:1	140	36	64
2.	Co-1 (5)	Xylene	KO^{t}Bu(1.0)	1:1.2	140	36	78
3.	Co-1 (5)	Xylene	KO^{t}Bu(1.0)	1:1.5	140	36	78
4.	Co-1 (5)	Xylene	KO^{t}Bu(0.75)	1:1.2	140	36	78
5.	Co-1 (5)	Xylene	KO^{t}Bu(0.5)	1:1.2	140	36	62
6.	Co-1 (4)	Xylene	KO^{t}Bu(0.75)	1:1.2	140	36	67
7.	Co-1 (5)	Xylene	KO^{t}Bu(0.75)	1:1.2	140	24	60
8.	Co-1 (5)	Xylene	KO^{t}Bu(0.75)	1:1.2	120	36	64
9.	Co-1 (5)	Xylene	NaO^{t}Bu(0.75)	1:1.2	140	36	65
10.	Co-1 (5)	Xylene	KOH(0.75)	1:1.2	140	36	68
11.	Co-1 (5)	Xylene	NaOH(0.75)	1:1.2	140	36	55
12.	Co-1 (5)	Xylene	CsOH(0.75)	1:1.2	140	36	46
13.	Co-1 (5)	Xylene	K_2CO_3(0.75)	1:1.2	140	36	35
14.	Co-1 (5)	Xylene	Na_2CO_3(1.0)	1:1.2	140	36	28
15.	Co-1 (5)	Toluene	KO^{t}Bu(0.75)	1:1.2	140	36	56
16.	Co-1 (5)	^{t}AmOH	KO^{t}Bu(0.75)	1:1.2	140	36	N.D.
17.	Co-2 (2.5)	Xylene	KO^{t}Bu(0.75)	1:1.2	140	36	63
18.	Co-3 (5)	Xylene	KO^{t}Bu(0.75)	1:1.2	140	36	61
19.	-	Xylene	KO^{t}Bu(0.75)	1:1.2	140	36	18
20.	Co-1 (5)	Xylene	-	1:1.2	140	36	N.D.
21.	$CoBr_2$ (5)	Xylene	KO^{t}Bu(0.75)	1:1.2	140	36	15



Co-1



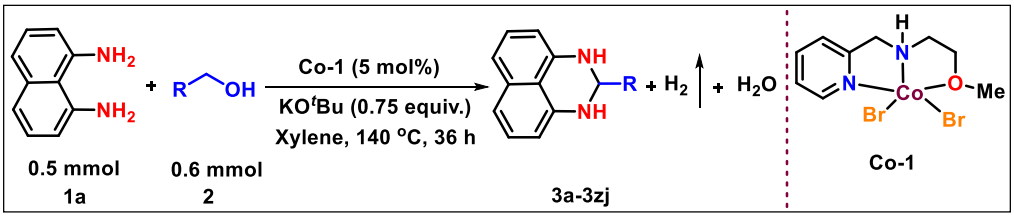
Co-2



Co-3

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5-0.75 mmol), base (0.25-0.5 mmol), Co-cat. (2.5-5 mol %), solvent = 2 mL, 120 –140 °C, preheated oil bath under argon. [b]Isolated yield. N.D. = Not detected.

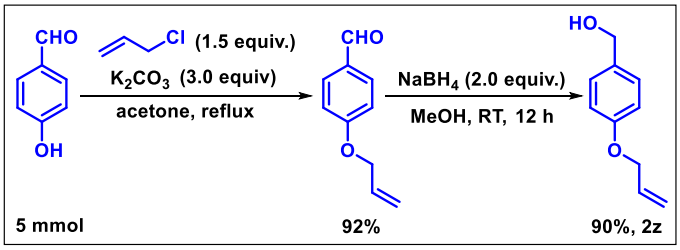
5. General experimental procedure for the synthesis of 2,3-Dihydro-1*H*-Perimidine derivatives:



To an oven dried 10 mL round bottomed flask, 1,8-diaminonapthalene **1a** (0.50 mmol, 1.0 equiv.), primary aryl or alkyl alcohols **2** (0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.) and Co-**1** (0.010 g, 0.025 mmol, 5 mol%) were taken under argon atmosphere, afterwards 2 mL of xylene was added to the reaction mixture. The reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography using 5-60% ethyl acetate in Petroleum ether as an eluent to get the desired products.

6. Preparation of various starting materials:

6a. Preparation procedure of (4-(allyloxy)phenyl)methanol (2z):[2]



To an oven dried 50 mL round-bottom flask equipped with a condenser and a magnetic stir bar, 4-hydroxybenzaldehyde (0.611 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.073 g, 15 mmol, 3.0 equiv.) were taken in 10 mL of anhydrous acetone. After that allyl chloride (0.574 g, 0.611 mL, 7.5 mmol, 1.5 equiv.) was added in a dropwise manner to the reaction mixture at room temperature. After being stirred for 30 min at room temperature, the reaction mixture was refluxed for overnight. The reaction was cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 40/1) to afford a colourless oil in 92% yield (0.746 g, 4.6 mmol). Afterwards, it was dissolved in 20 mL of methanol and $NaBH_4$ (0.348 g, 9.2 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2

and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired (4-(allyloxy)phenyl)methanol **(2z)** in 90% yield (0.680 g, 4.14 mmol) as a colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.05 (ddt, *J* = 16.2, 10.5, 5.3 Hz, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.59 (s, 2H), 4.53 (d, *J* = 5.0 Hz, 2H), 1.79 (s, 1H).

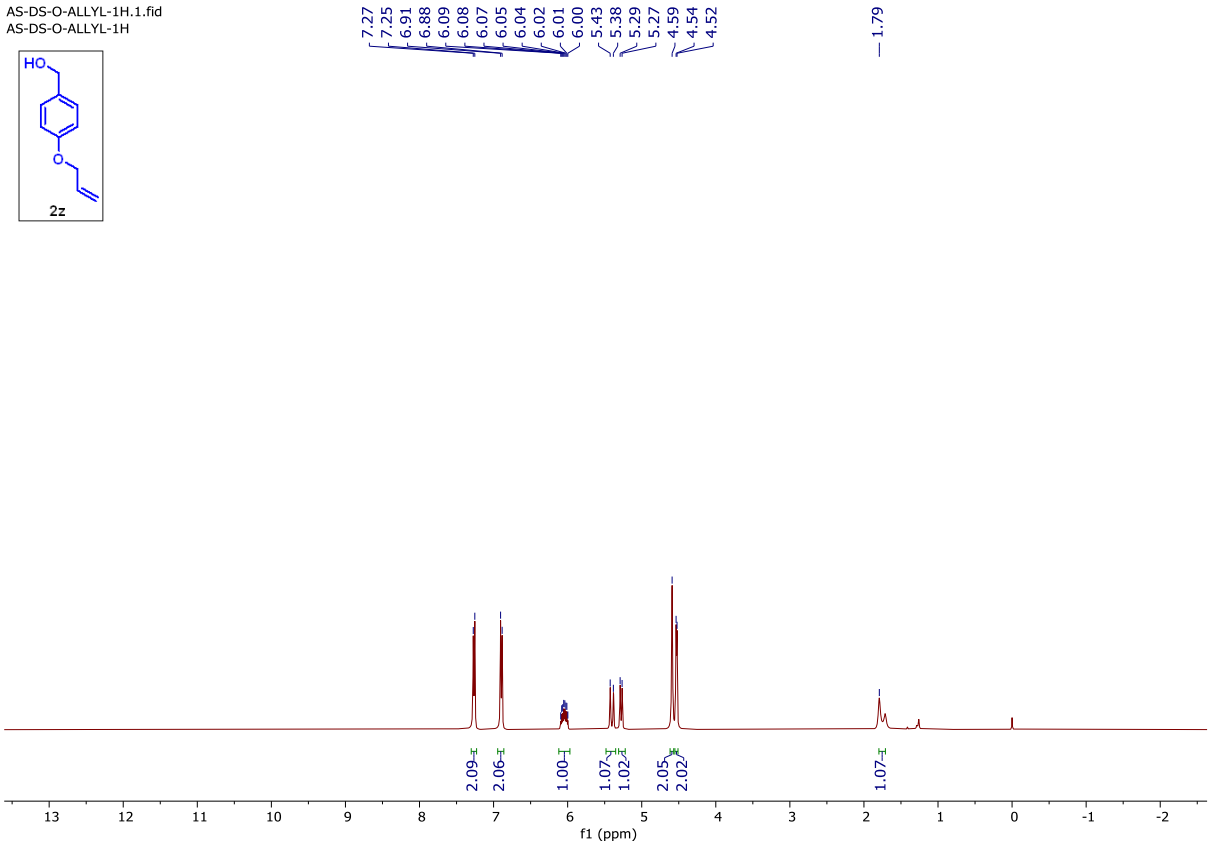
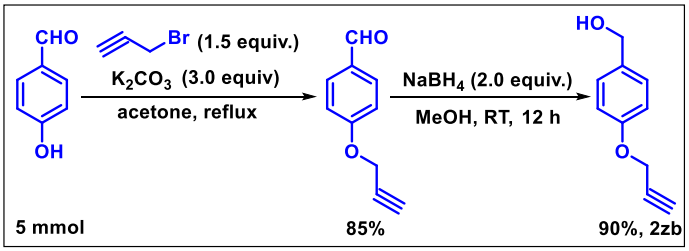


Figure S5. ^{1}H (400 MHz) NMR Spectrum of **(4-(allyloxy)phenyl)methanol (2z)** in $CDCl_3$.

6b. Preparation procedure of (4-(prop-2-yn-1-yloxy)phenyl)methanol (2zb):[2]



To an oven dried 50 mL round-bottom flask equipped with a condenser and a magnetic stir bar, 4-hydroxybenzaldehyde (0.611 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (2.073 g, 15 mmol, 3.0 equiv.) were taken in 10 mL of anhydrous acetone. After that propargyl bromide (0.892 g, 0.568 mL, 7.5 mmol, 1.5 equiv.) was added in a dropwise manner to the reaction mixture at room temperature. After being stirred for 30 min at room temperature, the reaction mixture was refluxed for overnight. The reaction was cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure and the

crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 40/1) to afford an off-white solid in 85% yield (0.681 g, 4.25 mmol). Afterwards, it was dissolved in 20 mL of methanol and $NaBH_4$ (0.321 g, 8.5 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired (4-(prop-2-yn-1-yloxy)phenyl)methanol **(2zb)** in 90% yield (0.621 g, 3.83 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.67 (s, 2H), 4.59 (s, 2H), 2.51 (s, 1H), 1.98 (s, 1H).

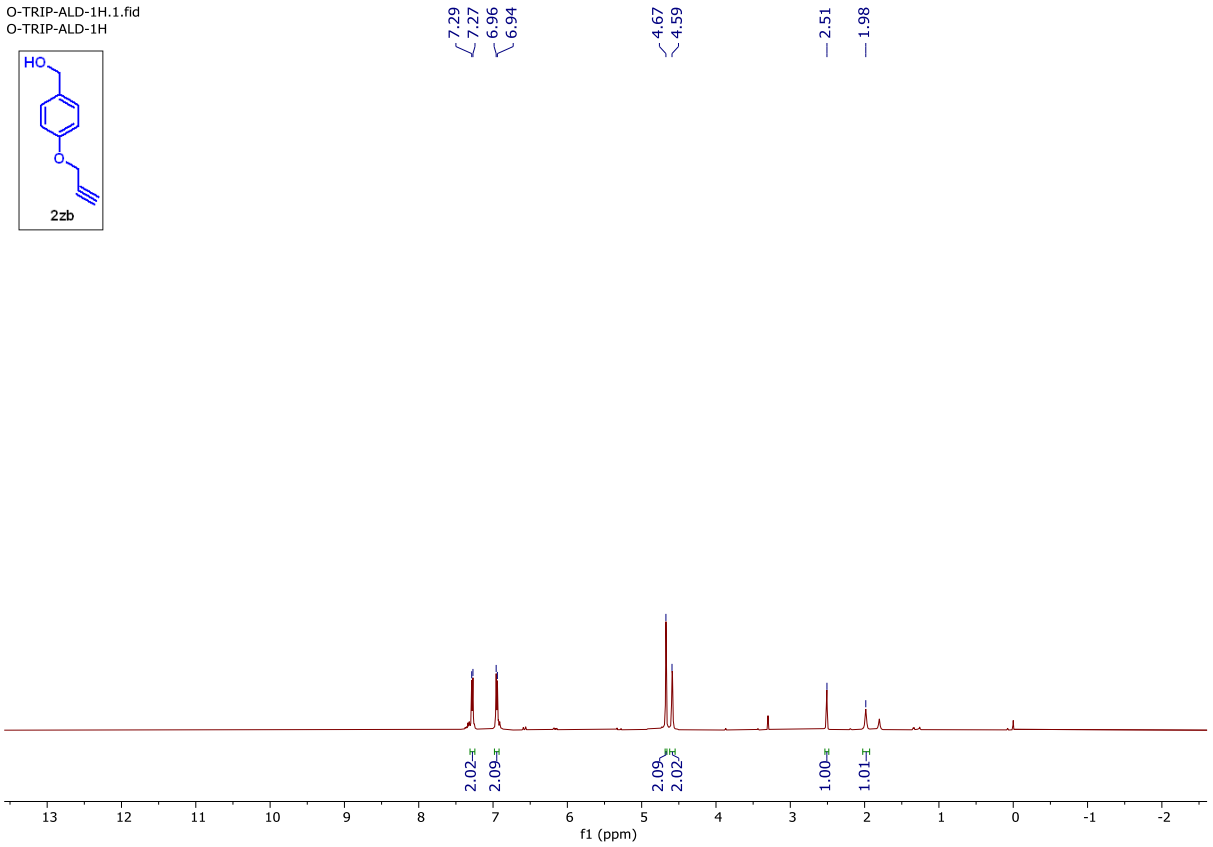
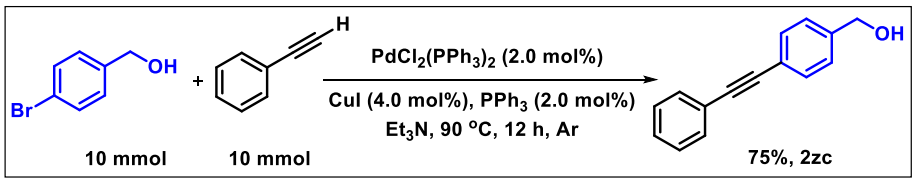


Figure S6. ^{1}H (500 MHz) NMR Spectrum of **(4-(prop-2-yn-1-yloxy)phenyl)methanol (2zb)** in $CDCl_3$.

6c. Preparation procedure of (4-(phenylethynyl)phenyl)methanol (2zc):[3]



To an oven dried 100 mL round bottomed flask, 4-Bromobenzyl alcohol (1.87 g, 10.0 mmol, 1.0 equiv.), ethynylbenzene (1.02 g, 10.0 mmol, 1.0 equiv.), bis(triphenylphosphine)palladium(II) dichloride (0.140 g, 0.2 mmol, 2 mol%) and anhydrous Et_3N (40 mL) were taken under argon atmosphere. The

reaction mixture was stirred magnetically for 10 min at room temperature and then copper iodide (0.076 g, 0.4 mmol, 4 mol%) and triphenylphosphine (0.052 g, 0.2 mmol, 2 mol%) were added into it and refluxed at 90 °C in a preheated oil bath for 12 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 90/10) to afford the desired (4-(phenylethynyl)phenyl)methanol **(2zc)** in 75% yield (1.56 g, 7.5 mmol) as a yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.45 (m, 4H), 7.34 (dd, *J* = 6.7, 3.9 Hz, 5H), 4.71 (d, *J* = 5.4 Hz, 2H), 1.70 (t, *J* = 5.8 Hz, 1H).

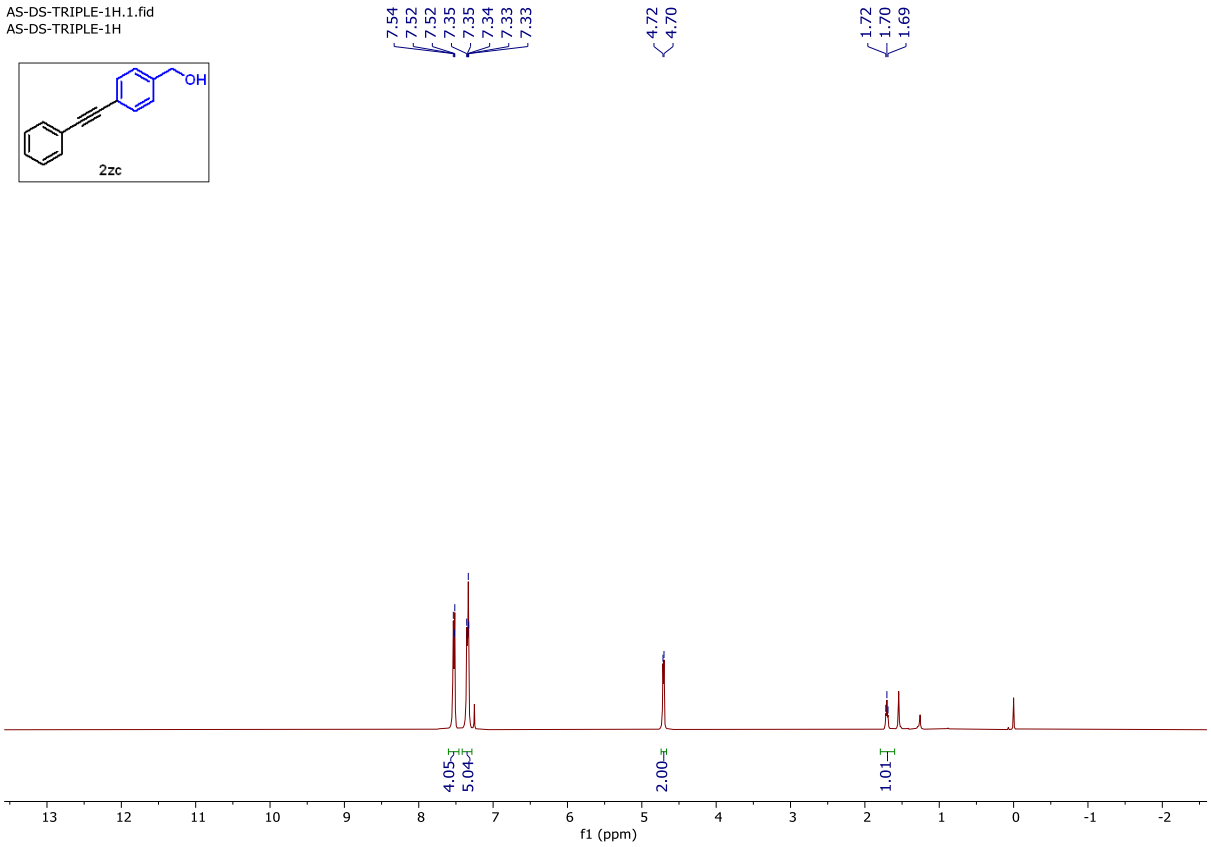
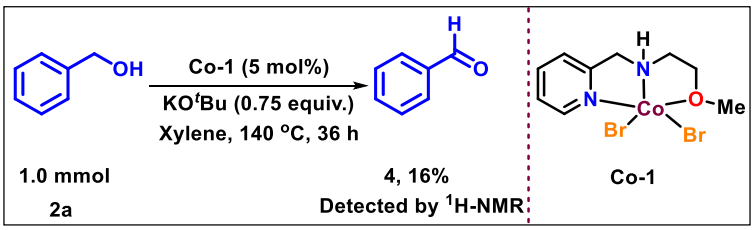


Figure S7. ^{1}H (400 MHz) NMR Spectrum of **(4-(phenylethynyl)phenyl)methanol (2zc)** in $CDCl_3$.

7. Mechanistic investigation:

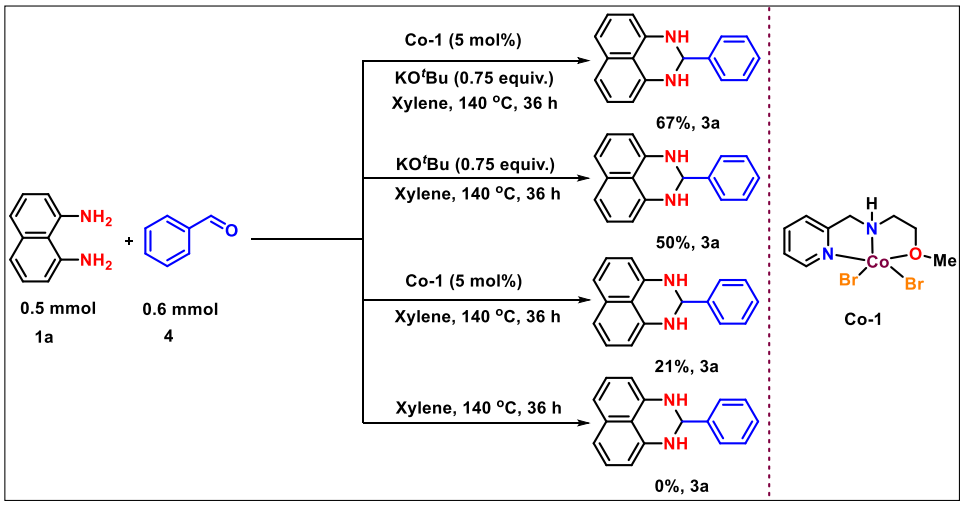
7.1. Cobalt catalysed dehydrogenation of alcohol:



To an oven dried 10 mL round bottomed flask, Benzyl alcohol **2a** (0.108 g, 1.0 mmol, 1.0 equiv.), KO^{t}Bu (0.084 g, 0.75 mmol, 0.75 equiv.) and **Co-1** (0.020 g, 0.05 mmol, 5 mol%) were taken under argon atmosphere, afterwards 2

of xylene was added to the reaction mixture. The reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude reaction mixture was submitted and analysed by ^{1}H-NMR confirming that 16% of Benzaldehyde **(4)** was detected.

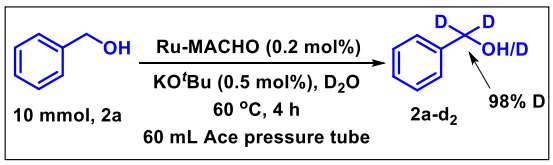
7.2. Cobalt catalysed synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine (3a) from 1,8-diaminonapthalene (1a) and benzaldehyde (4):



To an oven dried 10 mL round bottomed flask, 1,8-diaminonapthalene **1a** (0.079 g, 0.50 mmol, 1.0 equiv.), benzaldehyde **4** (0.064 g, 0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.) and **Co-1** (0.010 g, 0.025 mmol, 5 mol%) were taken under argon atmosphere, afterwards 2 mL of xylene was added to the reaction mixture. The reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford the desired 2-phenyl-2,3-dihydro-1*H*-perimidine **(3a)** in 67% yield (0.083 g, 0.335 mmol) as a white solid. When the reaction was conducted either in absence of **Co-1** or in absence of KO^{t}Bu, it only furnished 50% (0.062 g, 0.25 mmol) and 21% yield (0.026 g, 0.105 mmol) of our desired product **3a** respectively, however, in absence of both **Co-1** and KO^{t}Bu no detectable conversion of the desired product **3a** was observed.

7.3. Deuterium labelling experiment:

7.3.1. Preparation of phenylmethan-d_2-ol (2a-d_2):[4]



Phenylmethan-d_2-ol **(2a-d_2)** was prepared according to previously reported literature method.[4] Initially, benzyl alcohol **2a** (1.08 g, 10 mmol, 1.0 equiv.), Ru-MACHO (0.012 g, 0.02 mmol, 0.2 mol%), KO^{t}Bu (0.006 g, 0.05 mmol, 0.5 mol%) were charged successively to an oven dried Ace pressure tube (60 mL) containing a stirring bar. Then, the degassed D_2O (8 mL, 400 mmol, 40.0 equiv.) was added using syringe in the reaction mixture under gentle stream of argon and the tube was sealed with cap and heated at 60 °C in a preheated oil bath. The reaction was stopped after 4 h, subjected to cool at room temperature and reaction mixture was extracted by CH_2Cl_2 and the organic phase was dried over Na_2SO_4. Then the solvent was evaporated under reduced pressure provided pure products for further reaction. The ^{1}H-NMR data reveals that 98% deuterium incorporation occur in benzyl alcohol furnishing phenylmethan-d_2-ol **(2a-d_2)**.

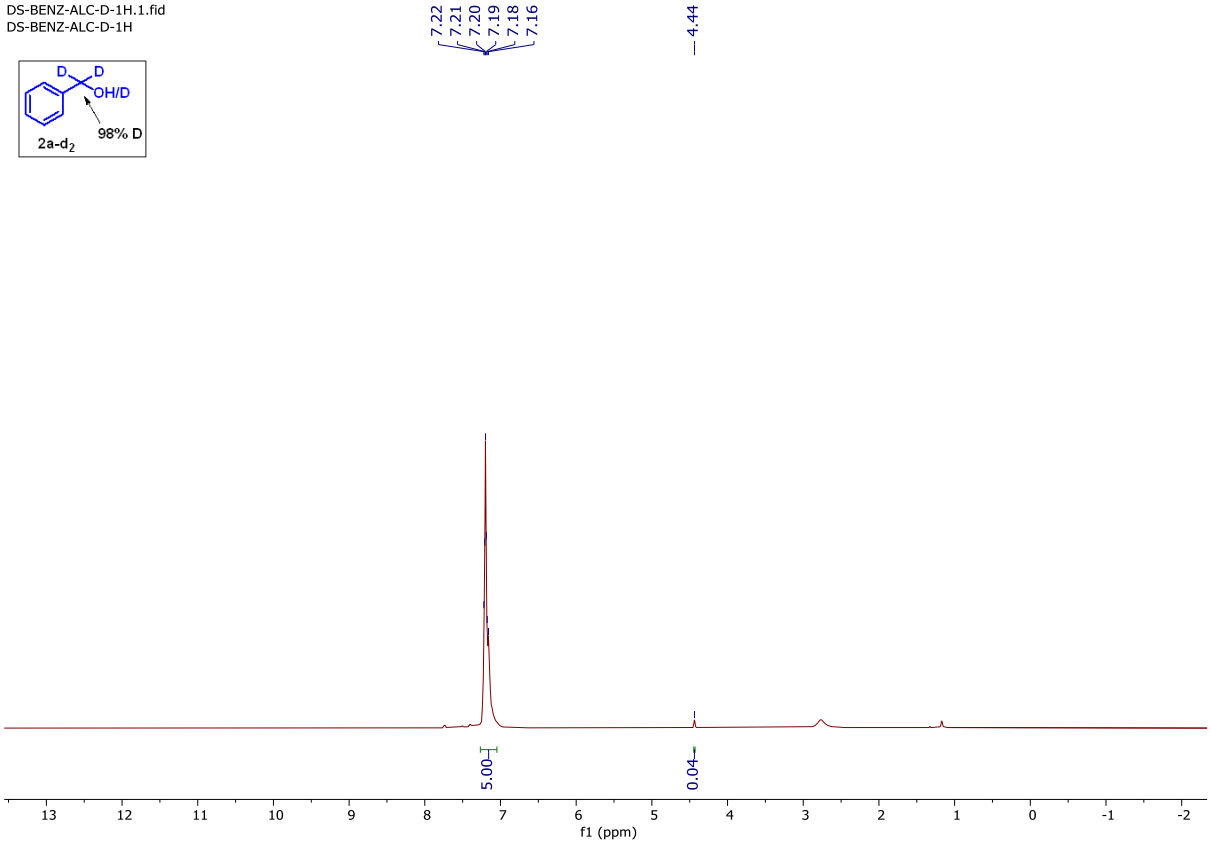
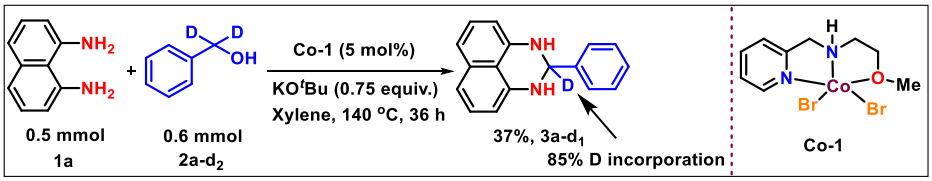
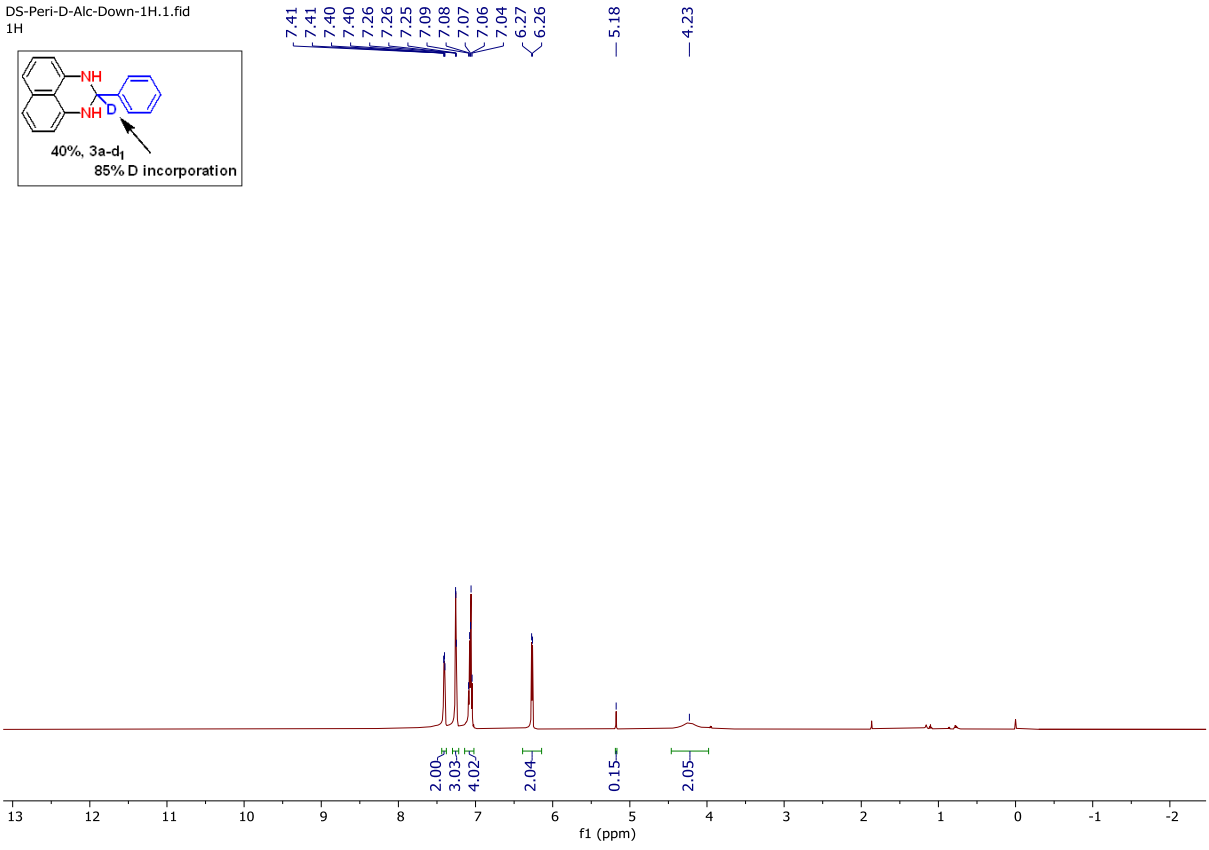


Figure S8. ^{1}H (500 MHz) NMR Spectrum of **phenylmethan-d_2-ol (2a-d_2)** in $CDCl_3$.

7.3.2. Cobalt catalysed synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine-2-*d* (3a-d_1) from 1,8-diaminonapthalene (1a) and phenylmethan-d_2-ol (2a-d_2):



To an oven dried 10 mL round bottomed flask, 1,8-diaminonapthalene **1a** (0.079 g, 0.50 mmol, 1.0 equiv.), phenylmethan-d_2-ol **2a-d_2** (0.066 g, 0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.) and **Co-1** (0.010 g, 0.025 mmol, 5 mol%) were taken under argon atmosphere, afterwards 2 mL of xylene was added to the reaction mixture. The reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford the 2-phenyl-2,3-dihydro-1*H*-perimidine-2-*d* **(3a-d_1)** in 37% yield (0.049 g, 0.20 mmol) as a white solid with 85% deuterium incorporation. The percentage of deuterium incorporation was analysed using ^{1}H NMR spectroscopy.



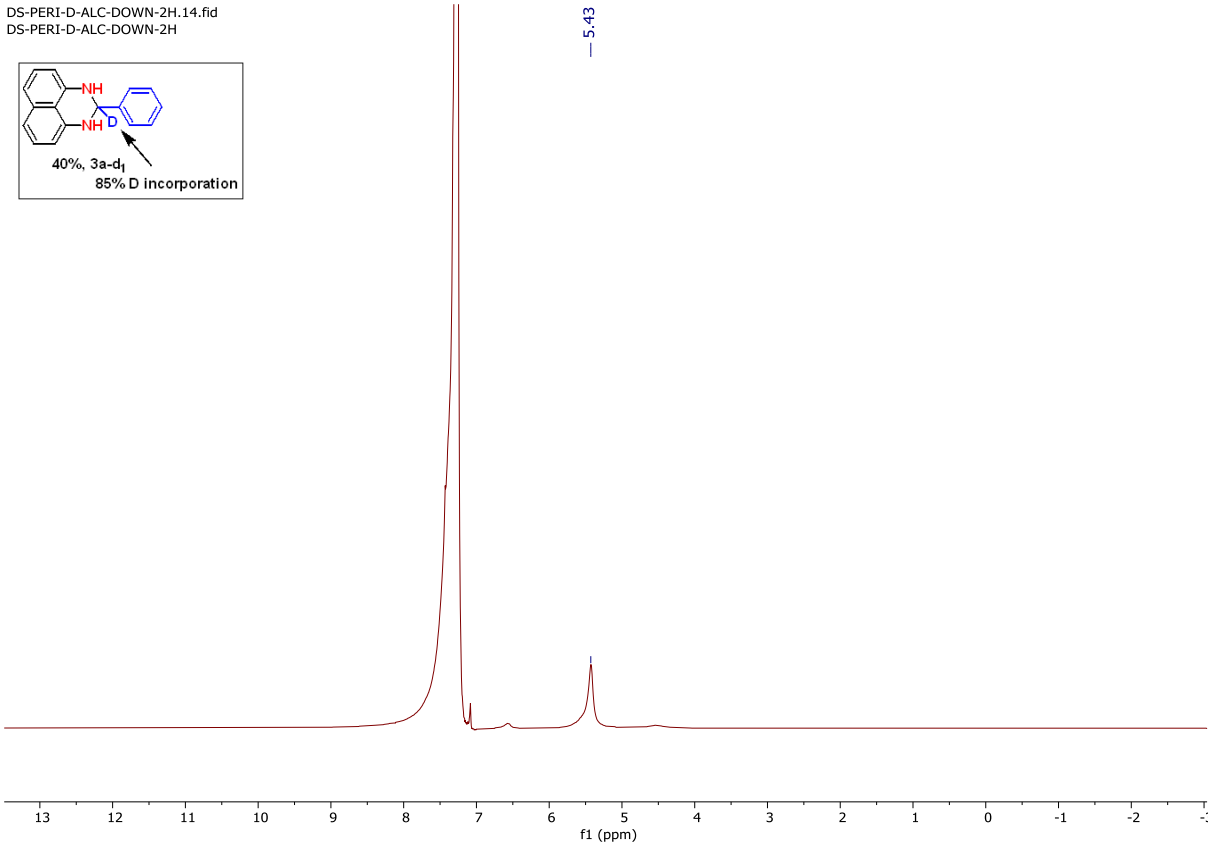
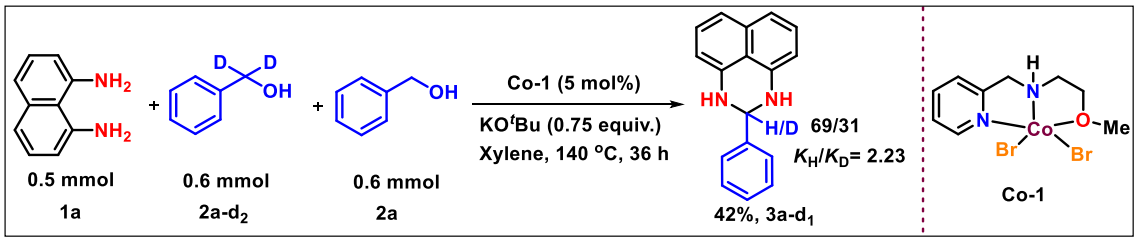


Figure S9. ^{1}H and ^{2}H (400 MHz) NMR Spectrum of **2-phenyl-2,3-dihydro-1*H*-perimidine-2-*d* (3a-d_1)** in $CDCl_3$.

7.4. Competitive Experiment:



To an oven dried 10 mL round bottomed flask, 1,8-diaminonapthalene **1a** (0.079 g, 0.50 mmol, 1.0 equiv.), phenylmethan-d_2-ol **2a-d_2** (0.066 g, 0.60 mmol, 1.2 equiv.), benzyl alcohol **2a** (0.065 g, 0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.) and **Co-1** (0.010 g, 0.025 mmol, 5 mol%) were taken under argon atmosphere, afterwards 2 mL of xylene was added to the reaction mixture. The reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford a mixture of 2-phenyl-2,3-dihydro-1*H*-perimidine **(3a)** and 2-phenyl-2,3-dihydro-1*H*-perimidine-2-*d* **(3a-d_1)** in 42% yield as a white solid. The experiment revealed that the value of KIE= k_H/k_D= 2.23.

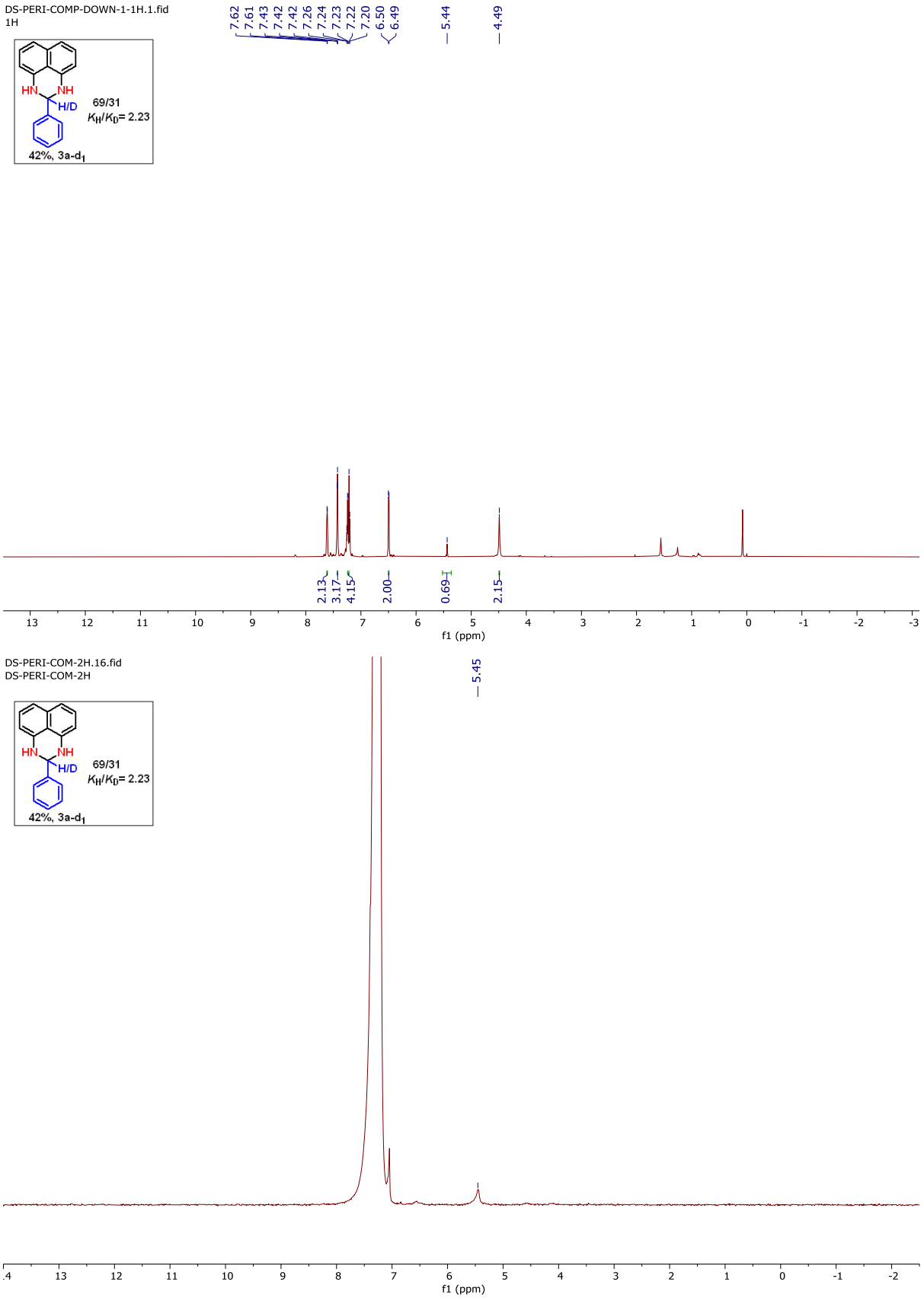
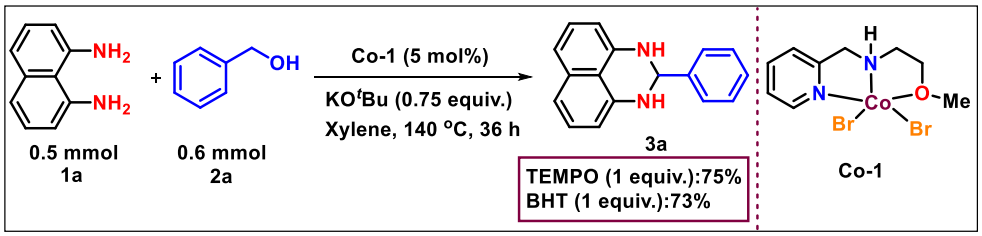


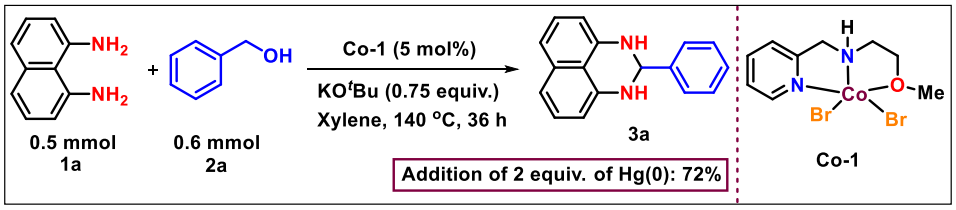
Figure S10. ^{1}H and ^{2}H (600 MHz) NMR Spectrum of **2-phenyl-2,3-dihydro-1*H*-perimidine-2-*d* (3a-d_1)** in $CDCl_3$.

7.5. Radical involvement test in the catalysis:



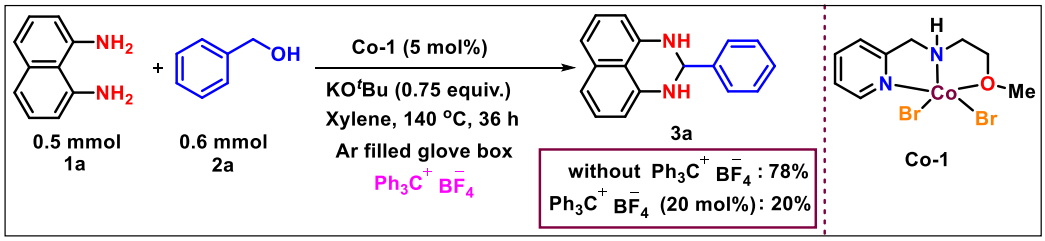
To an oven dried 10 mL round bottomed flask, 1,8-diaminonapthalene **1a** (0.079 g, 0.50 mmol, 1.0 equiv.), benzyl alcohol **2a** (0.065 g, 0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.), **Co-1** (0.010 g, 0.025 mmol, 5 mol%) and TEMPO or BHT (0.078 g or 0.110 g, 0.50 mmol, 1.0 equiv.) were taken under argon atmosphere, afterwards 2 mL of xylene was added to the reaction mixture. The reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford the desired 2-phenyl-2,3-dihydro-1*H*-perimidine **(3a)** as a white solid. (for TEMPO, 75% yield, 0.092 g, 0.375 mmol and for BHT, 73% yield, 0.090 g, 0.365 mmol).

7.6. Homogeneity test:



To an oven dried 10 mL round bottomed flask, 1,8-diaminonapthalene **1a** (0.079 g, 0.50 mmol, 1.0 equiv.), benzyl alcohol **2a** (0.065 g, 0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.) and 2.0 equiv. metallic Hg were taken together and connected with high vacuum for 10 minutes. Afterwards, **Co-1** (0.010 g, 0.025 mmol, 5 mol%) and 2 mL of xylene was added to the reaction mixture under gentle stream of argon. Then the resulting reaction mixture was heated at 140 °C in a preheated oil bath for 36 h. After completion of the reaction, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford the desired 2-phenyl-2,3-dihydro-1*H*-perimidine **(3a)** in 72% yield (0.089 g, 0.36 mmol) as a white solid.

7.7. Metal hydride trapping experiment:



To an oven dried 100 mL Ace pressure tube, 1,8-diaminonapthalene **1a** (0.079 g, 0.50 mmol, 1.0 equiv.), benzyl alcohol **2a** (0.065 g, 0.60 mmol, 1.2 equiv.), KO^{t}Bu (0.042 g, 0.375 mmol, 0.75 equiv.) and **Co-1** (0.010 g, 0.025 mmol, 5 mol%) were added sequentially inside the argon filled glove box. Afterwards 2 mL of xylene was added to the reaction mixture and the reaction mixture was allowed to stir at room temperature. After stirring for 0.5 h, tritylium tetrafluoroborate (Ph_3C^+ BF_4^-) (0.033 g, 0.10 mmol, 20 mol%) was added to the reaction mixture. Then, the tube was sealed and placed at 140 °C in a preheated oil bath. After stirring for 36 h, the reaction mixture was subjected to cool at room temperature and ethyl acetate (15 mL) was added to dilute the mixture and filtered through celite. The resultant volatiles were evaporated under reduced pressure and the crude product was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford the desired 2-phenyl-2,3-dihydro-1*H*-perimidine **(3a)** in 20% yield (0.025 g, 0.10 mmol) as a white solid. The drastic detriment in the yield manifested that the in situ formed cobalt hydride involved in the catalytic cycle.

7.8. Detection of evolved gas by GC-Thermal Detector (GC-TCD):

A mixture of 1,8-diaminonapthalene **1a** (0.316 g, 2.0 mmol, 1.0 equiv.), benzyl alcohol **2a** (0.260 g, 2.4 mmol, 1.2 equiv.), KO^{t}Bu (0.168 g, 1.5 mmol, 0.75 equiv.) were taken in an oven dried Ace pressure tube (100 mL) containing a stirring bar and connected with high vacuum for 10 mins, then **Co-1** (0.039 g, 0.1 mmol, 5 mol%) and 5 mL of xylene was added to the mixture under gentle flow of argon. Afterwards, the reaction mixture was kept for stirring into preheated oil bath at 140 °C for next 36 h. After completion of the reaction, the Ace pressure tube was cooled at 0 °C, the evolved gas was syringe out and detected from PerkinElmer clarus-590 GC instrument using Elite Plot-Q column (30 m length x 530 µm x 20 µm ID) employing the following method:

TCD starting temperature: 40 °C

Oven temperature: 60 °C

Time at starting temperature: 0 min

Hold time: 5 min

Ramp: 28 °C/ min up to 200 °C

Flow rate: 5 mL/ min (N_2)

Split ration: 20

Inlet temperature: 40 °C

Detector temperature TCD: 200 °C

The detected gas chromatogram was shown in figure **S11** (right).

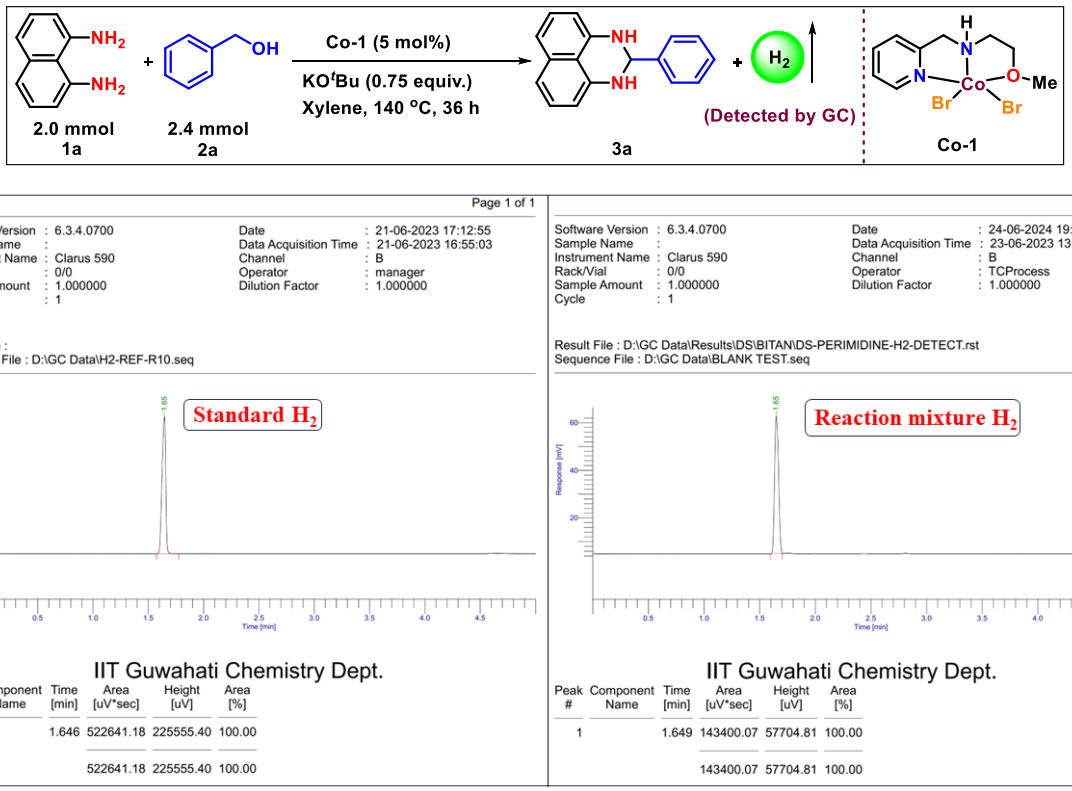
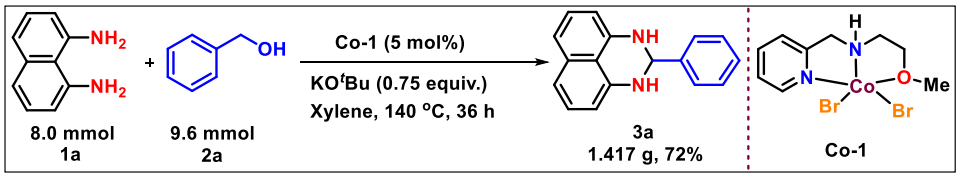


Figure S11. Chromatogram of standard hydrogen gas (left) and evolved hydrogen gas during catalysis (right).

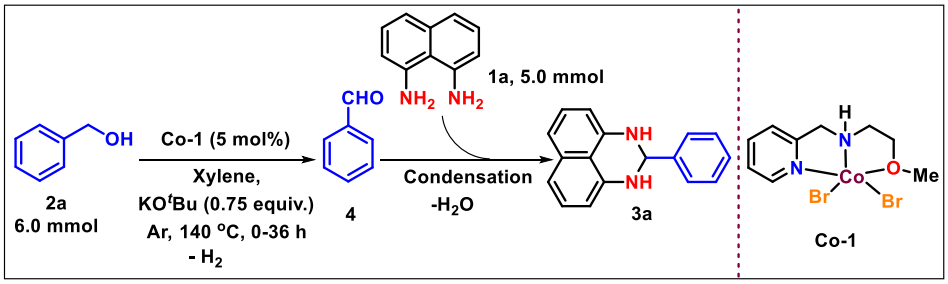
8. Gram scale synthesis:



To an oven dried 50 mL round bottomed flask, 1,8-diaminonapthalene **1a** (1.266 g, 8.0 mmol, 1.0 equiv.), benzyl alcohol **2a** (1.038 g, 9.6 mmol, 1.2 equiv.) and KO^{t}Bu (0.673 g, 6.0 mmol, 0.75 equiv.) were taken sequentially and connected with high vacuum for 15 minutes. Then **Co-1** (0.154 g, 0.40 mmol, 5 mol%) and 15 mL of xylene was added to the reaction mixture under gentle stream of argon. The resulting reaction mixture was heated at 140 °C in a preheated oil bath. After stirring for 36 h, the reaction mixture was subjected to cool at room temperature and ethyl acetate (30 mL) was added to dilute the mixture and filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel (100−200 mesh size) column chromatography (eluent: Pet. ether/EtOAc = 95/5) to afford the desired 2-phenyl-2,3-dihydro-1*H*-perimidine **(3a)** in 72% yield (1.417 g, 5.6 mmol) as a white solid.

9. Kinetic experiments:

9.1. Monitoring the kinetics of the reaction:



Experimental procedure: To an oven dried 10 mL 2-neck round bottomed flask equipped with a condenser and a magnetic stir bar, 1,8-diaminonapthalene **1a** (0.791 g, 5.0 mmol, 1.0 equiv.), benzyl alcohol **2a** (0.649 g, 6.0 mmol, 1.2 equiv.) and KO^{t}Bu (0.421 g, 3.75 mmol, 0.75 equiv.) were taken sequentially and connected with high vacuum for 15 minutes. Then, **Co-1** (0.096 g, 0.25 mmol, 5 mol%), mesitylene (0.601 g, 5.0 mmol, 1.0 equiv.) as an internal standard and dry xylene were added to the mixture under gentle flow of argon to make up the total volume of the reaction mixture 5 mL. Afterwards, the reaction mixture was kept in a preheated oil bath for stirring at 140 °C. At regular intervals (1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 9 h, 12 h, 15 h, 18 h, 21 h, 24 h, 27 h, 30 h, 33 h, 36 h) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of the product (mmolar) *vs* time (h) plot **(Figure S12)**.

Time (h)	Concentration of benzyl alcohol **2a** (mmolar)	Concentration of benzaldehyde **4** (mmolar)	Concentration of 1,8-diaminonapthalene **1a** (mmolar)	Concentration of 2-phenyl-2,3-dihydro-1*H*-perimidine **3a** (mmolar)
0	1.2	0	1	0
1	1.13	0.0316	0.942	0.007
2	1.04	0.0389	0.862	0.0125
3	0.973	0.0472	0.806	0.0245
4	0.885	0.0673	0.726	0.0624
5	0.791	0.0907	0.659	0.1076
6	0.675	0.121	0.563	0.1569
9	0.546	0.1473	0.446	0.2256
12	0.437	0.1864	0.352	0.2917
15	0.345	0.2142	0.2875	0.3819
18	0.291	0.184	0.24	0.4813

21	0.246	0.149	0.198	0.5739
24	0.184	0.116	0.153	0.6912
27	0.156	0.0654	0.128	0.7465
30	0.102	0.0416	0.085	0.792
33	0.061	0.0295	0.051	0.834
36	0.032	0.0168	0.0258	0.8621

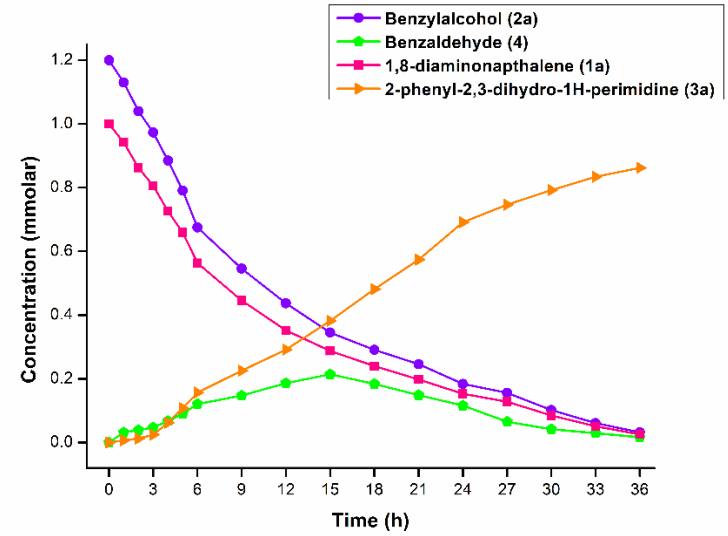
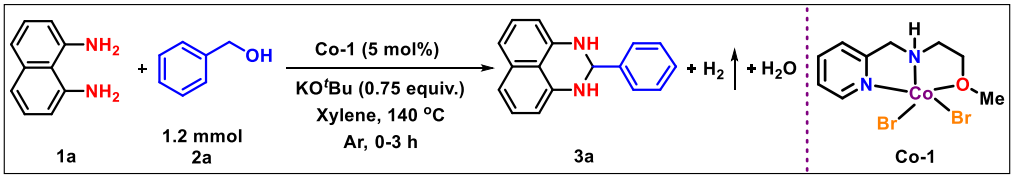


Figure S12. Kinetic monitoring of Cobalt (II)-catalysed acceptorless dehydrogenative coupling (ADC) of 1,8-diaminonapthalene **1a** with benzyl alcohol **2a** towards the synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine **3a**.

9.2. Rate order determination:

The initial rate method was used to determine the rate order for the synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine **3a** with respect to various components of the reaction. The data of the concentration (mM) *vs* time (h) plot was fitted to linear using origin pro 8.5. The slope of the linear fitted curve represents the initial rate of the reaction. The order of the reaction was determined by plotting initial rate (mM/h) *vs* concentration (mM) of that particular component.

9.2.1. Rate order determination with respect to 1,8-diaminonapthalene (1a):



To determine the order of the 2-phenyl-2,3-dihydro-1*H*-perimidine **3a** synthesis reaction, initial rates at different initial concentration of 1,8-diaminonapthalene **1a** were recorded.

Experimental procedure: To an oven dried 10 mL 2-neck round bottomed flask equipped with a condenser and a magnetic stir bar, benzyl alcohol **2a** (0.130 g, 1.2 mmol, 1.2 equiv.) and KO^{t}Bu (0.84 g, 0.75 mmol, 0.75 equiv.) were taken together and connected with high vacuum for 10 minutes. Then, **Co-1** (0.019 g, 0.05 mmol, 5 mol%), mesitylene (0.120 g, 1.0 mmol, 1.0 equiv.) as an internal standard, specific amount of 1,8-diaminonapthalene **1a** and dry xylene were added to the mixture under gentle flow of argon to make up the total volume of the reaction mixture 5 mL. Afterwards, the reaction mixture was kept in an oil bath of 140 °C for stirring. At regular intervals (0 min, 30 min, 60 min, 90 min, 120 min, 150 min, 180 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of 1,8-diaminonapthalene **1a** (mM) *vs* time (h) plot **(Figure S13)**. The rate of the reaction at different initial concentration of 1,8-diaminonapthalene **1a** was given below and used to plot the log(rate) *vs* log(concentration of 1,8-diaminonapthalene **1a**) to determine the order of the reaction with respect to 1,8-diaminonapthalene **1a** **(Figure S14)**.

Time (min)	Concentration of 1,8-diaminonapthalene **1a** (0.18 mM)	Concentration of 1,8-diaminonapthalene **1a (**0.20 mM)	Concentration of 1,8-diaminonapthalene **1a (**0.22 mM)	Concentration of 1,8-diaminonapthalene **1a (**0.24 mM)
0	0.18	0.20	0.22	0.24
30	0.1776	0.1954	0.2122	0.2282
60	0.1734	0.1907	0.2071	0.2226
90	0.169	0.1858	0.2018	0.2167
120	0.1646	0.1809	0.1964	0.2109
150	0.16	0.1758	0.1907	0.2047
180	0.1554	0.1706	0.1851	0.1985

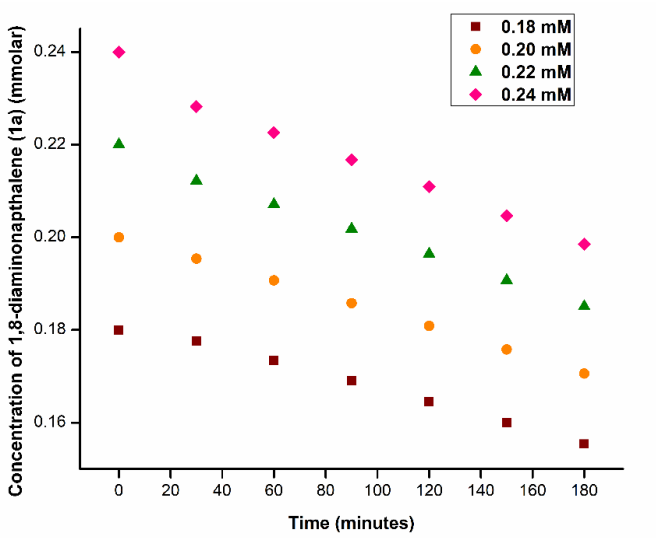


Figure S13: Concentration versus time plot at various concentration of 1,8-diaminonapthalene **(1a)**

log(concentration of 1,8-diaminonapthalene **1a**)	log(rate)
-0.7447	-3.8531
-0.6989	-3.7849
-0.6576	-3.7235
-0.6198	-3.6613

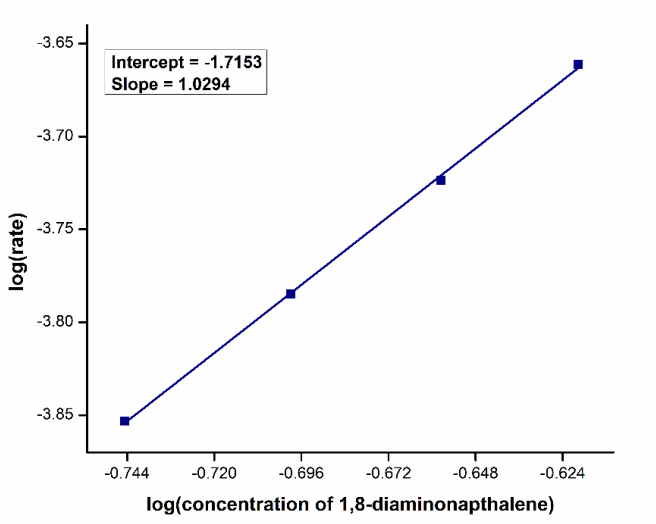
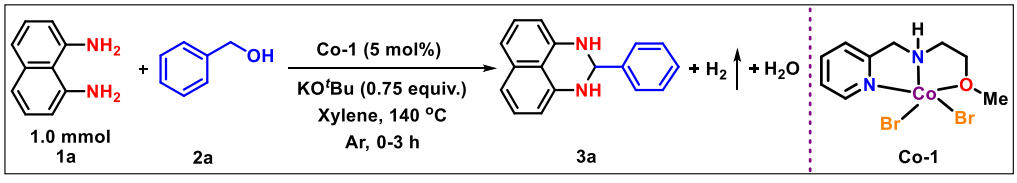


Figure S14: Plot for determining the order of the reaction with respect to 1,8-diaminonapthalene **(1a)**

9.2.2. Rate order determination with respect to benzyl alcohol (2a):



To determine the order of the 2-phenyl-2,3-dihydro-1*H*-perimidine **3a** synthesis reaction, initial rates at different initial concentration of benzyl alcohol **2a** were recorded.

Experimental procedure: To an oven dried 10 mL 2-neck round bottomed flask equipped with a condenser and a magnetic stir bar, 1,8-diaminonapthalene **1a** (0.158 g, 1.0 mmol, 1.0 equiv.) and KO^{t}Bu (0.84 g, 0.75 mmol, 0.75 equiv.) were taken together and connected with high vacuum for 10 minutes. Then, **Co-1** (0.019 g, 0.05 mmol, 5 mol%), mesitylene (0.120 g, 1.0 mmol, 1.0 equiv.) as an internal standard, specific amount of benzyl alcohol **2a** and dry xylene were added to the mixture under gentle flow of argon to make up the total volume of the reaction mixture 5 mL. Afterwards, the reaction mixture was kept in an oil bath of 140 °C for stirring. At regular intervals (0 min, 30 min, 60 min, 90 min, 120 min, 150 min, 180 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of benzyl alcohol **2a** (mM) *vs* time (h) plot **(Figure S15)**. The rate of the reaction at different initial concentration of benzyl alcohol **2a** was given below and used to plot the log(rate) *vs* log(concentration of benzyl alcohol **2a**) to determine the order of the reaction with respect to benzyl alcohol **2a (Figure S16)**.

Time (min)	Concentration of benzyl alcohol **2a** **(**0.16 mM)	Concentration of benzyl alcohol **2a** **(**0.20 mM)	Concentration of benzyl alcohol **2a** **(**0.24 mM)	Concentration of benzyl alcohol **2a** **(**0.28 mM)
0	0.16	0.20	0.24	0.28
30	0.1571	0.1944	0.2304	0.2649
60	0.1527	0.1888	0.2237	0.2571
90	0.1479	0.1829	0.2165	0.2488
120	0.1432	0.177	0.2096	0.2406
150	0.1382	0.1707	0.202	0.2317
180	0.1331	0.1644	0.1944	0.2229

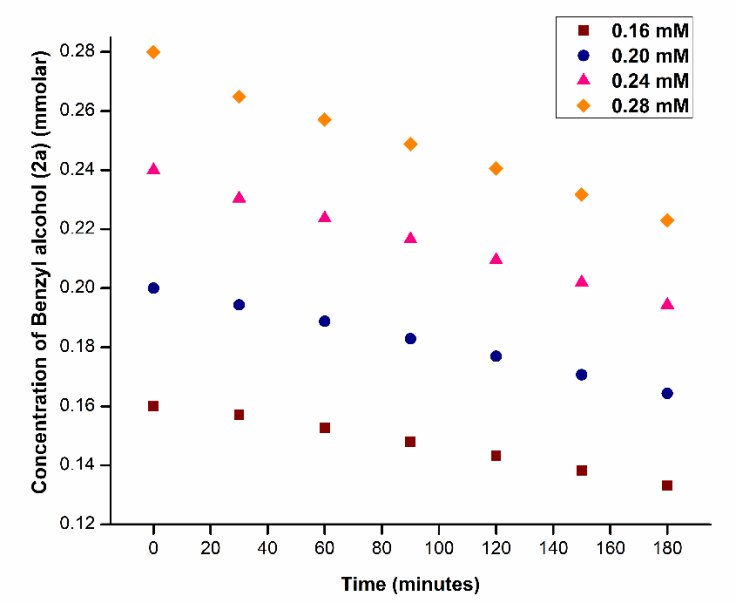


Figure S15: Concentration versus time plot at various concentration of Benzyl alcohol **(2a)**

log(concentration of benzyl alcohol **2a**)	log(rate)
-0.7958	-3.8171
-0.6989	-3.7042
-0.6197	-3.6068
-0.5528	-3.5191

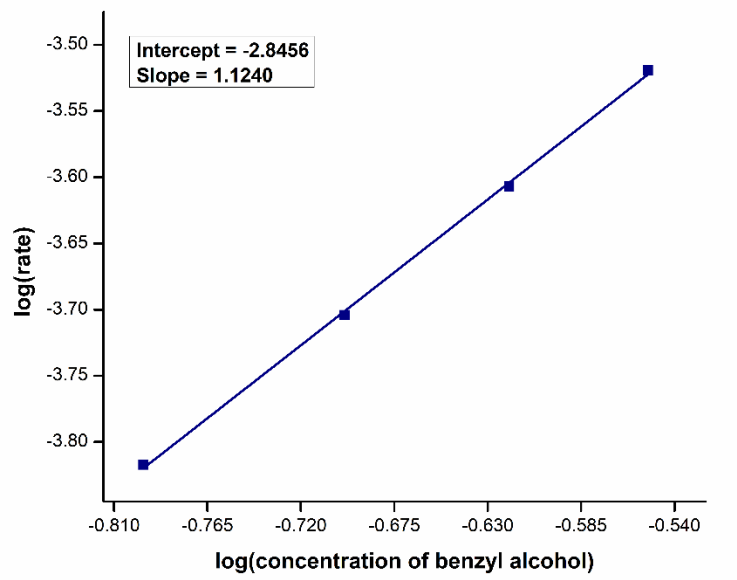
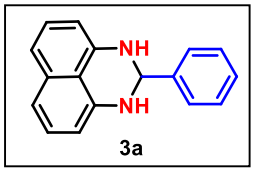


Figure S16: Plot for determining the order of the reaction with respect to Benzyl alcohol **(2a)**

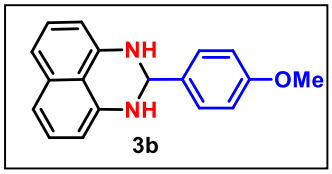
10. Analytical data for substrate scopes:

2-phenyl-2,3-dihydro-1*H*-perimidine (3a):[5]



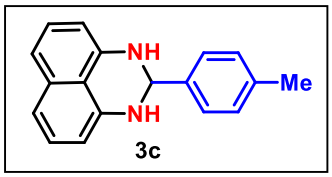
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 78% yield (0.192 g, 0.78 mmol) as a white solid. m. p. 104 – 105 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.56 (m, 2H), 7.40 – 7.39 (m, 3H), 7.23 – 7.17 (m, 4H), 6.44 (d, *J* = 6.8 Hz, 2H), 5.37 (s, 1H), 4.45 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.2, 140.2, 135.0, 129.7, 128.9, 128.0, 126.9, 117.9, 113.5, 105.9, 68.4.

2-(4-methoxyphenyl)-2,3-dihydro-1*H*-perimidine (3b):[5]



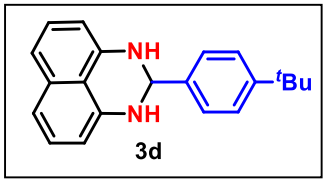
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 78% yield (0.215 g, 0.78 mmol) as a white solid. m. p. 161 – 163 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.09 (m, 4H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 7.1 Hz, 2H), 5.26 (s, 1H), 4.36 (brs, 2H), 3.72 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 160.6, 142.4, 135.0, 132.4, 129.2, 126.9, 117.8, 114.2, 113.5, 105.8, 68.0, 55.5.

2-(*p*-tolyl)-2,3-dihydro-1*H*-perimidine (3c):[5]



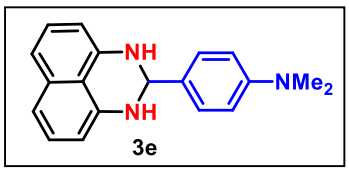
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 75% yield (0.195 g, 0.75 mmol) as a white solid. m. p. 165 – 167 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.09 (m, 6H), 6.35 (d, *J* = 6.7 Hz, 2H), 5.26 (s, 1H), 4.34 (brs, 2H), 2.29 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.3, 139.5, 137.3, 135.0, 129.5, 127.9, 127.0, 117.9, 113.5, 105.9, 68.2, 21.4.

2-(4-(*tert*-butyl)phenyl)-2,3-dihydro-1*H*-perimidine(3d):[6]



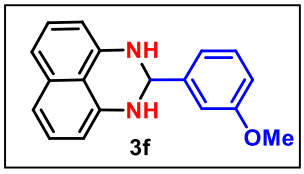
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 80% yield (0.242 g, 0.80 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.11 (m, 4H), 6.40 (d, *J* = 7.1 Hz, 2H), 5.35 (s, 1H), 4.41 (brs, 2H), 1.27 (s, 9H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 152.9, 142.3, 137.3, 135.1, 127.7, 127.0, 125.9, 117.9, 113.6, 105.9, 68.2, 34.9, 31.5.

4-(2,3-dihydro-1*H*-perimidin-2-yl)-N,N-dimethylaniline (3e):[7]



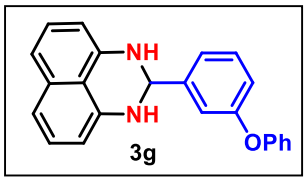
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 74% yield (0.214 g, 0.74 mmol) as a brown solid. m. p. 166 – 167 °C, **1H NMR (500 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.18 (m, 4H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 7.5 Hz, 2H), 5.31 (s, 1H), 4.43 (brs, 2H), 2.94 (s, 6H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 151.5, 142.7, 135.1, 128.8, 127.7, 126.9, 117.6, 113.5, 112.4, 105.7, 68.2, 40.6.

2-(3-methoxyphenyl)-2,3-dihydro-1*H*-perimidine (3f):[6]



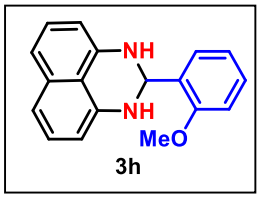
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 65% yield (0.180 g, 0.65 mmol) as a white solid. m. p. 152 – 153 °C, **^1H NMR (500 MHz, $CDCl_3$)** δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.16 – 7.10 (m, 5H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.88 – 6.85 (m, 1H), 6.39 (d, *J* = 7.0 Hz, 2H), 5.29 (s, 1H), 4.41 (brs, 2H), 3.71 (s, 3H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 160.1, 142.1, 141.7, 135.0, 129.9, 127.0, 120.2, 118.0, 115.7, 113.5, 112.8, 105.9, 68.4, 55.5.

2-(3-phenoxyphenyl)-2,3-dihydro-1*H*-perimidine (3g):



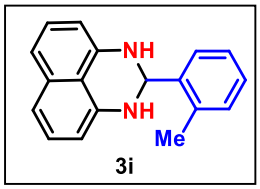
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 72% yield (0.244 g, 0.72 mmol) as a white solid. m. p. 160 – 161 °C, **^1H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.39 (m, 4H), 7.36 – 7.35 (m, 1H), 7.32 – 7.29 (m, 2H), 7.28 – 7.27 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.11 (m, 3H), 6.54 (d, *J* = 7.5 Hz, 2H), 5.41 (s, 1H), 4.56 (brs, 2H). **$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)** δ 157.8, 156.7, 142.1, 141.9, 134.8, 130.2, 130.0, 126.9, 123.7, 122.6, 119.7, 119.2, 118.0, 117.9, 113.4, 105.9, 68.0. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{23}H_{19}N_2O$ is 339.1497 Found 339.1480

2-(2-methoxyphenyl)-2,3-dihydro-1*H*-perimidine (3h):[5]



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 52% yield (0.144 g, 0.52 mmol) as a white solid. m. p. 148 – 150 °C, **^1H NMR (500 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.08 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 7.2 Hz, 2H), 5.80 (s, 1H), 4.55 (brs, 2H), 3.75 (s, 3H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 157.1, 142.2, 135.0, 129.8, 128.7, 127.5, 126.9, 121.1, 117.7, 113.5, 110.6, 106.0, 61.4, 55.6.

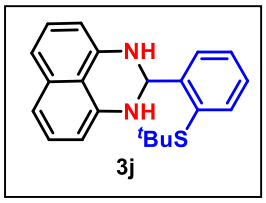
2-(*o*-tolyl)-2,3-dihydro-1*H*-perimidine (3i):[6]



3i

Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 50% yield (0.130 g, 0.50 mmol) as a yellow liquid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63 – 7.61 (m, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.07 (m, 5H), 6.36 (d, *J* = 7.2 Hz, 2H), 5.56 (s, 1H), 4.28 (brs, 2H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.5, 137.6, 136.6, 135.0, 131.0, 129.1, 128.2, 126.9, 126.7, 117.9, 113.6, 106.0, 65.2, 19.2.

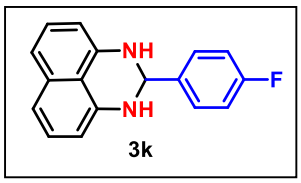
2-(2-(*tert*-butylthio)phenyl)-2,3-dihydro-1*H*-perimidine (3j):



3j

Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 48% yield (0.161 g, 0.48 mmol) as a white solid. m. p. 130 – 132 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 – 7.90 (m, 1H), 7.61 – 7.60 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 (td, *J* = 7.6 Hz, 1.7 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.20 – 7.18 (m, 2H), 6.49 (d, *J* = 7.0 Hz, 2H), 6.29 (s, 1H), 4.49 (brs, 2H), 1.28 (s, 9H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 145.0, 142.3, 138.9, 134.9, 131.9, 130.0, 128.9, 128.8, 127.0, 117.8, 113.4, 105.9, 64.9, 47.3, 31.1. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{21}H_{23}N_2S$ is 335.1582. Found 335.1604.

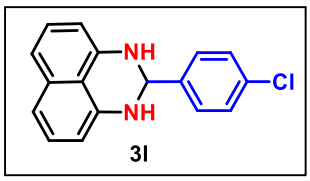
2-(4-fluorophenyl)-2,3-dihydro-1*H*-perimidine (3k):[5]



3k

Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 72% yield (0.190 g, 0.72 mmol) as a white solid. m. p. 178 – 179 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 – 7.47 (m, 2H), 7.17 – 7.12 (m, 4H), 7.01 (t, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 6.9 Hz, 2H), 5.31 (s, 1H), 4.36 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 163.5 (d, *J* = 246.6 Hz), 142.1, 136.1 (d, *J* = 3.0 Hz), 135.0, 129.9 (d, *J* = 8.5 Hz), 127.0, 118.1, 115.8 (d, *J* = 21.5 Hz), 113.5, 106.0, 67.8. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -111.74.

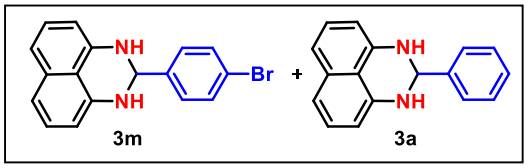
2-(4-chlorophenyl)-2,3-dihydro-1*H*-perimidine (3l):[5]



3l

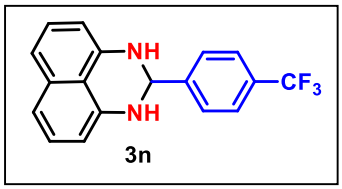
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 68% yield (0.191 g, 0.68 mmol) as a white solid. m. p. 158 – 160 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.14 (m, 4H), 6.43 (d, *J* = 6.8 Hz, 2H), 5.34 (s, 1H), 4.38 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 141.9, 138.8, 135.5, 135.0, 129.4, 129.2, 127.0, 118.2, 113.5, 106.1, 67.8.

2-(4-bromophenyl)-2,3-dihydro-1*H*-perimidine (3m):[7]



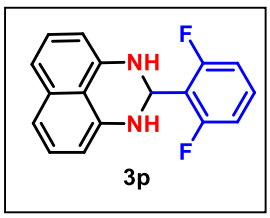
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 62% yield (0.202 g, 0.62 mmol) as a yellow solid. m. p. 138 – 139 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 – 7.51 (m, 1H), 7.46 – 7.44 (m, 2H), 7.37 – 7.35 (m, 2H), 7.34 – 7.33 (1H), 7.17 – 7.10 (m, 7H), 6.41 – 6.39 (m, 3H), 5.27 (s, 1H), 4.35 (brs, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.2, 141.8, 140.2, 139.2, 135.0, 134.9, 132.1, 129.7, 128.9, 128.0, 127.0, 123.7, 118.2, 118.0, 113.6, 113.5, 106.1, 105.9, 68.5, 67.8.

2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-perimidine (3n):[8]



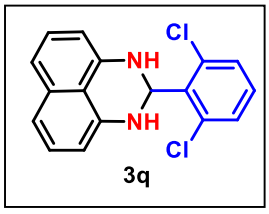
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 92/8) which afforded the title compound in 57% yield (0.179 g, 0.57 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 – 7.66 (m, 4H), 7.25 – 7.21 (m, 4H), 6.52 – 6.50 (m, 2H), 5.46 (s, 1H), 4.45 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 144.1, 141.6, 135.0, 131.9 (q, *J* = 32.3 Hz), 128.5, 127.0, 125.9 (q, *J* = 3.7 Hz), 124.1 (d, *J* = 270.7 Hz), 118.4, 113.6, 106.3, 67.8. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -62.63.

2-(2,6-difluorophenyl)-2,3-dihydro-1*H*-perimidine (3p):[9]



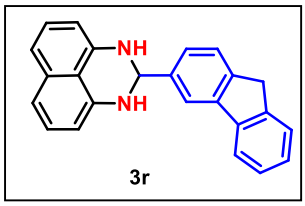
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 90/10) which afforded the title compound in 54% yield (0.152 g, 0.54 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 – 7.21 (m, 1H), 7.18 – 7.15 (m, 4H), 6.85 (t, *J* = 8.7 Hz, 2H), 6.52 – 6.49 (m, 2H), 5.87 (s, 1H), 4.53 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 161.8 (dd, *J* = 251.0, 7.0 Hz), 141.6, 135.0, 131.2 (t, *J* = 10.8 Hz), 126.8, 118.8, 115.4 (t, *J* = 14.5 Hz), 114.8, 112.4 (dd, *J* = 21.5, 4.5 Hz), 107.6, 60.3 (t, *J* = 3.1 Hz). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -112.27.

2-(2,6-dichlorophenyl)-2,3-dihydro-1*H*-perimidine (3q):[9]



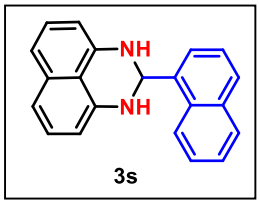
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 90/10) which afforded the title compound in 50% yield (0.158 g, 0.54 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.27 (m, 6H), 6.62 (dd, *J* = 5.9, 2.4 Hz, 2H), 6.36 (s, 1H), 4.56 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 141.6, 136.6, 135.0, 133.0, 130.7, 130.1, 126.9, 118.6, 114.2, 107.5, 65.0.

2-(9*H*-fluoren-3-yl)-2,3-dihydro-1*H*-perimidine (3r):[10]



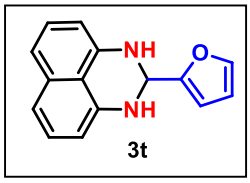
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 67% yield (0.224 g, 0.67 mmol) as a white solid. m. p. 168 – 169 °C **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.79 (m, 3H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.20 (m, 4H), 6.50 (d, *J* = 6.9 Hz, 2H), 5.49 (s, 1H), 4.52 (brs, 2H), 3.91 (s, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 144.0, 143.7, 143.3, 142.3, 141.2, 138.7, 135.1, 127.3, 127.0, 126.8, 125.3, 124.6, 120.3, 120.1, 118.0, 113.6, 106.0, 68.7, 37.0.

2-(naphthalen-1-yl)-2,3-dihydro-1*H*-perimidine (3s):[5]



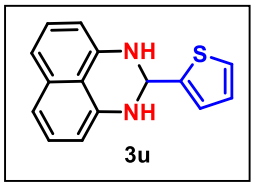
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 65% yield (0.193 g, 0.65 mmol) as a white solid. m. p. 164 – 165 °C **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.18 – 7.13 (m, 4H), 6.40 (d, *J* = 6.3 Hz, 2H), 6.01 (s, 1H), 4.42 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.4, 135.2, 134.9, 134.3, 131.3, 130.2, 129.0, 127.0, 126.6, 126.5, 126.2, 125.5, 124.6, 118.0, 113.7, 106.1.

2-(furan-2-yl)-2,3-dihydro-1*H*-perimidine (3t):[5]



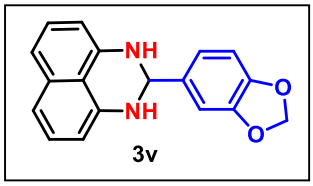
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 92/8) which afforded the title compound in 72% yield (0.170 g, 0.72 mmol) as a white solid. m. p. 100 – 102 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 (s, 1H), 7.08– 7.03 (m, 4H), 6.31 (dd, *J* = 6.3, 2.4 Hz, 2H), 6.12 (s, 2H), 5.32 (s, 1H), 4.49 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 153.4, 142.4, 140.7, 134.6, 126.8, 118.0, 113.7, 110.4, 107.6, 106.5, 61.3.

2-(thiophen-2-yl)-2,3-dihydro-1*H*-perimidine (3u):[5]



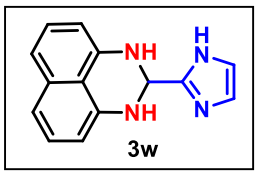
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 92/8) which afforded the title compound in 78% yield (0.197 g, 0.78 mmol) as a white solid. m. p. 112 – 115 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.25 – 7.24 (m, 1H), 7.14 – 7.07 (m, 5H), 6.89– 6.88 (m, 1H), 6.37 (d, *J* = 8.2 Hz, 2H), 5.61 (s, 1H), 4.50 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 144.1, 141.4, 134.9, 127.0, 126.9, 126.5, 126.4, 118.2, 113.7, 106.2, 63.8.

2-(benzo[*d*][1,3]dioxol-5-yl)-2,3-dihydro-1*H*-perimidine (3v):[6]



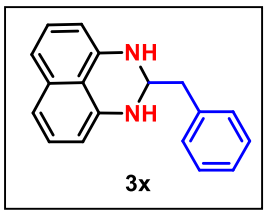
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 92/8) which afforded the title compound in 70% yield (0.203 g, 0.70 mmol) as a white solid. m. p. 159 – 160 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.26 – 7.20 (m, 4H), 7.17 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 7.0 Hz, 2H), 5.99 (s, 2H), 5.37 (s, 1H), 4.46 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 148.7, 148.3, 142.2, 135.0, 134.3, 127.0, 121.7, 118.0, 113.5, 108.3, 108.2, 105.9, 101.5, 68.2.

2-(1*H*-imidazol-2-yl)-2,3-dihydro-1*H*-perimidine (3w):[11]



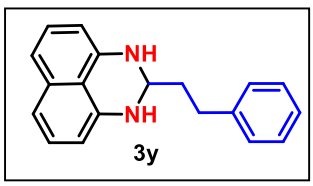
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 50/50) which afforded the title compound in 70% yield (0.184 g, 0.70 mmol) as a white solid. m. p. 185 – 186 °C, **^{1}H NMR (500 MHz, DMSO-d_6)** δ 12.33 (brs, 1H), 7.18 (t, *J* = 7.8 Hz, 2H), 7.04 – 7.02 (m, 4H), 6.87 (s, 2H), 6.56 (d, *J* = 7.5 Hz, 2H), 5.51 (s, 1H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 147.0, 142.6, 134.4, 127.1, 126.9 (2C), 115.7, 112.7, 104.8, 61.6.

2-benzyl-2,3-dihydro-1*H*-perimidine (3x):[12]



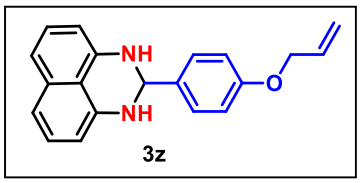
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 56% yield (0.146 g, 0.56 mmol) as a white solid. m. p. 109 – 110 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 – 7.44 (m, 3H), 7.42 – 7.37 (m, 4H), 7.31 (d, *J* = 6.9 Hz, 2H), 6.56 (d, *J* = 7.8 Hz, 2H), 4.64 (t, *J* = 6.6 Hz, 1H), 4.49 (brs, 2H), 2.98 (d, *J* = 6.7 Hz, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 141.2, 135.9, 134.8, 129.4, 128.8, 127.0, 126.9, 117.4, 113.7, 105.9, 65.1, 42.0.

2-phenethyl-2,3-dihydro-1*H*-perimidine (3y):[13]



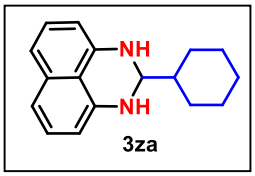
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 60% yield (0.165 g, 0.60 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 (t, *J* = 7.5 Hz, 2H), 7.13 – 7.07 (m, 7H), 6.31 (d, *J* = 7.2 Hz, 2H), 4.30 (t, *J* = 5.5 Hz, 1H), 4.10 (brs, 2H), 2.65 (t, *J* = 7.9 Hz, 2H), 1.88 – 1.82 (m, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 141.8, 141.0, 134.9, 128.7, 128.4, 126.9, 126.4, 117.7, 114.0, 106.1, 64.6, 37.2, 30.9.

2-(4-(allyloxy)phenyl)-2,3-dihydro-1*H*-perimidine (3z):



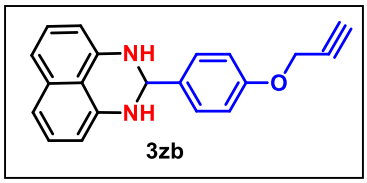
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 65% yield (0.196 g, 0.65 mmol) as a white solid. m. p. 153 – 154 °C,**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.10 (m, 4H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.38 (d, *J* = 7.1 Hz, 2H), 6.01 – 5.93 (m, 1H), 5.34 (d, *J* = 17.3 Hz, 1H), 5.28 (s, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 4.46 (d, *J* = 5.3 Hz, 2H), 4.37 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 159.7, 142.4, 135.1, 133.2, 132.6, 129.2, 127.0, 117.9 (2C), 115.1, 113.6, 105.8, 69.0, 68.0. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{20}H_{19}N_2O$ is 303.1497. Found 303.1481.

2-cyclohexyl-2,3-dihydro-1*H*-perimidine (3za):[14]



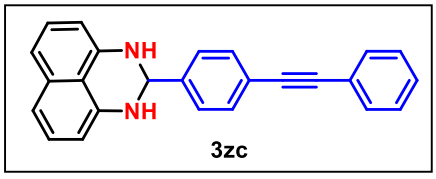
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 60% yield (0.151 g, 0.60 mmol) as a white solid. m. p. 75 – 76 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.39 (d, *J* = 7.3 Hz, 2H), 4.26 (brs, 2H), 4.14 (d, *J* = 5.4 Hz, 1H), 1.80 – 1.72 (m, 4H), 1.65 – 1.62 (m, 1H), 1.52 – 1.47 (m, 1H), 1.22 – 1.03 (m, 5H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.1, 135.0, 127.0, 117.4, 113.9, 105.8, 69.0, 42.3, 27.9, 26.5, 26.1.

2-(4-(prop-2-yn-1-yloxy)phenyl)-2,3-dihydro-1*H*-perimidine (3zb):



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 60% yield (0.180 g, 0.60 mmol) as a yellow liquid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.19 – 7.12 (m, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 7.0 Hz, 2H), 5.34 (s, 1H), 4.65 (s, 2H), 4.40 (brs, 2H), 2.46 (s, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 158.6, 142.3, 135.1, 133.4, 129.3, 127.0, 118.0, 115.3, 113.6, 105.9, 78.5, 75.9, 68.0, 56.0. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{20}H_{17}N_2O$ is 301.1341. Found 301.1339.

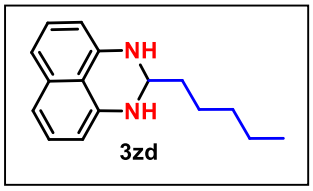
2-(4-(phenylethynyl)phenyl)-2,3-dihydro-1*H*-perimidine (3zc):



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 95/5) which afforded the title compound in 68% yield (0.235 g, 0.68 mmol) as a white solid. m. p. 168 – 169 °C **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (s, 4H), 7.55 – 7.53 (m, 2H), 7.35 – 7.33 (m, 3H), 7.24 – 7.20 (m, 4H), 6.49 (d, *J* = 6.9 Hz, 2H), 5.40 (s, 1H), 4.46 (brs, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.0, 140.2, 132.1, 131.8, 128.6, 128.5,

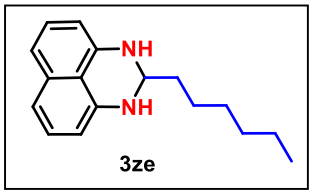
128.0, 127.0, 124.7, 123.1, 118.1, 113.6, 106.1, 90.5, 89.0, 68.1. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{25}H_{19}N_2$ is 347.1548. Found 347.1538.

2-pentyl-2,3-dihydro-1*H*-perimidine (3zd):[15]



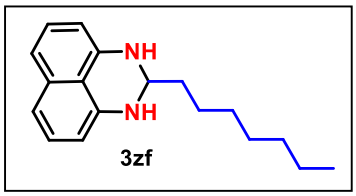
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 45% yield (0.108 g, 0.45 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.11 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 7.3 Hz, 2H), 4.27 (t, *J* = 5.8 Hz, 1H), 4.18 (brs, 2H), 1.55 – 1.51 (m, 2H), 1.35 – 1.29 (m, 2H), 1.26 – 1.17 (m, 4H), 0.82 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.1, 135.0, 126.9, 117.6, 114.1, 105.9, 64.9, 35.9, 31.8, 24.1, 22.6, 14.1.

2-hexyl-2,3-dihydro-1*H*-perimidine (3ze):[15]



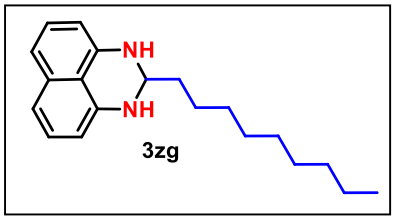
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 48% yield (0.122 g, 0.48 mmol) as a white solid. m. p. 58 – 59 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (t, *J* = 8.5 Hz, 2H), 7.10 – 7.08 (m, 2H), 6.43 (d, *J* = 7.1 Hz, 2H), 4.40 (t, *J* = 5.7 Hz, 1H), 4.27 (brs, 2H), 1.69 – 1.64 (m, 2H), 1.46 – 1.39 (m, 2H), 1.35 – 1.29, (m, 2H), 1.28 – 1.23 (m, 4H), 0.8 (t, J = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.1, 135.1, 127.0, 117.8, 114.2, 106.1, 65.0, 36.1, 31.8, 29.4, 24.5, 22.7, 14.2.

2-heptyl-2,3-dihydro-1*H*-perimidine (3zf):[5]



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 52% yield (0.140 g, 0.52 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.14 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.07 (m, 2H), 6.41 (d, *J* = 7.2 Hz, 2H), 4.36 (t, *J* = 5.8 Hz, 1H), 4.24 (brs, 2H), 1.65 – 1.60 (m, 2H), 1.42 – 1.36 (m, 2H), 1.28 – 1.18 (m, 8H), 0.82 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.1, 135.0, 126.9, 117.7, 114.1, 106.0, 65.0, 36.0, 31.9, 29.7, 29.3, 24.5, 22.7, 14.2.

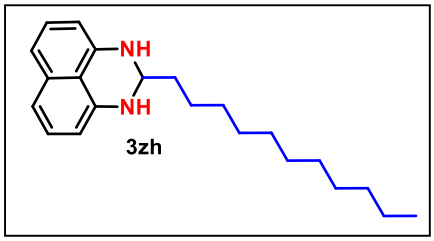
2-nonyl-2,3-dihydro-1*H*-perimidine (3zg):[16]



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 56% yield (0.166 g, 0.56 mmol) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.10 (t, *J* = 7.7 Hz, 2H), 7.06 – 7.04 (m, 2H), 6.35 (d, *J* = 7.2 Hz, 2H), 4.23 (t, *J* = 5.7 Hz, 1H), 4.15 (brs, 2H), 1.52 – 1.47 (m, 2H), 1.29 – 1.26 (m, 2H), 1.23 – 1.19 (s, 12H), 0.81 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H}**

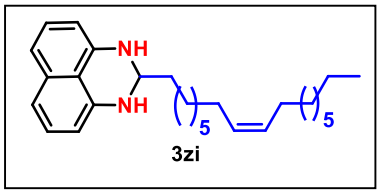
NMR (125 MHz, $CDCl_3$) δ 142.0, 135.0, 126.8, 117.5, 114.0, 105.9, 64.8, 35.9, 31.9, 29.6 (3C), 29.4, 24.4, 22.7, 14.2.

2-undecyl-2,3-dihydro-1*H*-perimidine (3zh):[16]



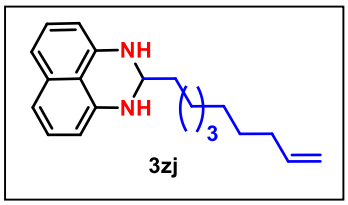
Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 60% yield (0.195 g, 0.60 mmol) as a white solid. m. p. 109 – 110 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09 (t, *J* = 7.7 Hz, 2H), 7.05 – 7.03 (m, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 4.20 (t, *J* = 5.7 Hz, 1H), 4.12 (brs, 2H), 1.48 – 1.44 (m, 2H), 1.27 – 1.22 (m, 4H), 1.21 – 1.18 (m, 14H), 0.80 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.0, 134.9, 126.8, 117.5, 114.0, 105.9, 64.8, 35.8, 32.0, 29.7 (2C), 29.6 (2C), 29.4, 24.4, 22.7, 14.2.

(*Z*)-2-(heptadec-8-en-1-yl)-2,3-dihydro-1*H*-perimidine (3zi):



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 54% yield (0.220 g, 0.54 mmol) as a yellow liquid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09 – 7.04 (m, 4H), 6.34 (d, *J* = 7.1 Hz, 2H), 5.28 – 5.25 (m, 2H), 4.26 – 4.23 (m, 1H), 4.15 (brs, 2H), 1.95 – 1.91 (m, 4H), 1.52 – 1.49 (m, 2H), 1.30 – 1.15 (m, 22H), 0.8 (t, *J* = 6.2 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.0, 134.9, 130.1, 129.8, 126.8, 117.5, 114.0, 105.9, 64.8, 35.9, 32.0, 29.8, 29.6, 29.5, 29.4, 29.2, 27.3, 24.4, 22.7, 14.2. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{28}H_{43}N_2$ is 407.3426. Found 407.3440.

2-(non-8-en-1-yl)-2,3-dihydro-1*H*-perimidine (3zj):



Purification was done by column chromatography (SiO_2, 100–200 mesh size, eluent: Pet. ether/EtOAc = 98/2) which afforded the title compound in 59% yield (0.174 g, 0.59 mmol) as a yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12 – 7.04 (m, 4H), 6.34 (d, *J* = 7.2 Hz, 2H), 5.77 – 5.67 (m, 1H), 4.94 – 4.84 (m, 2H), 4.21 (t, *J* = 5.5 Hz, 1H), 4.15 (brs, 2H), 1.98 – 1.92 (m, 2H), 1.49 – 1.44 (m, 2H), 1.30 – 1.18 (m, 10H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.0, 139.1, 134.9, 126.8, 117.5, 114.3, 114.0, 105.8, 64.8, 35.8, 33.8, 29.5, 29.4, 29.0, 28.9, 24.4. HRMS (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{20}H_{27}N_2$ is 295.2174. Found 295.2175.

11. NMR Spectra of the compounds:

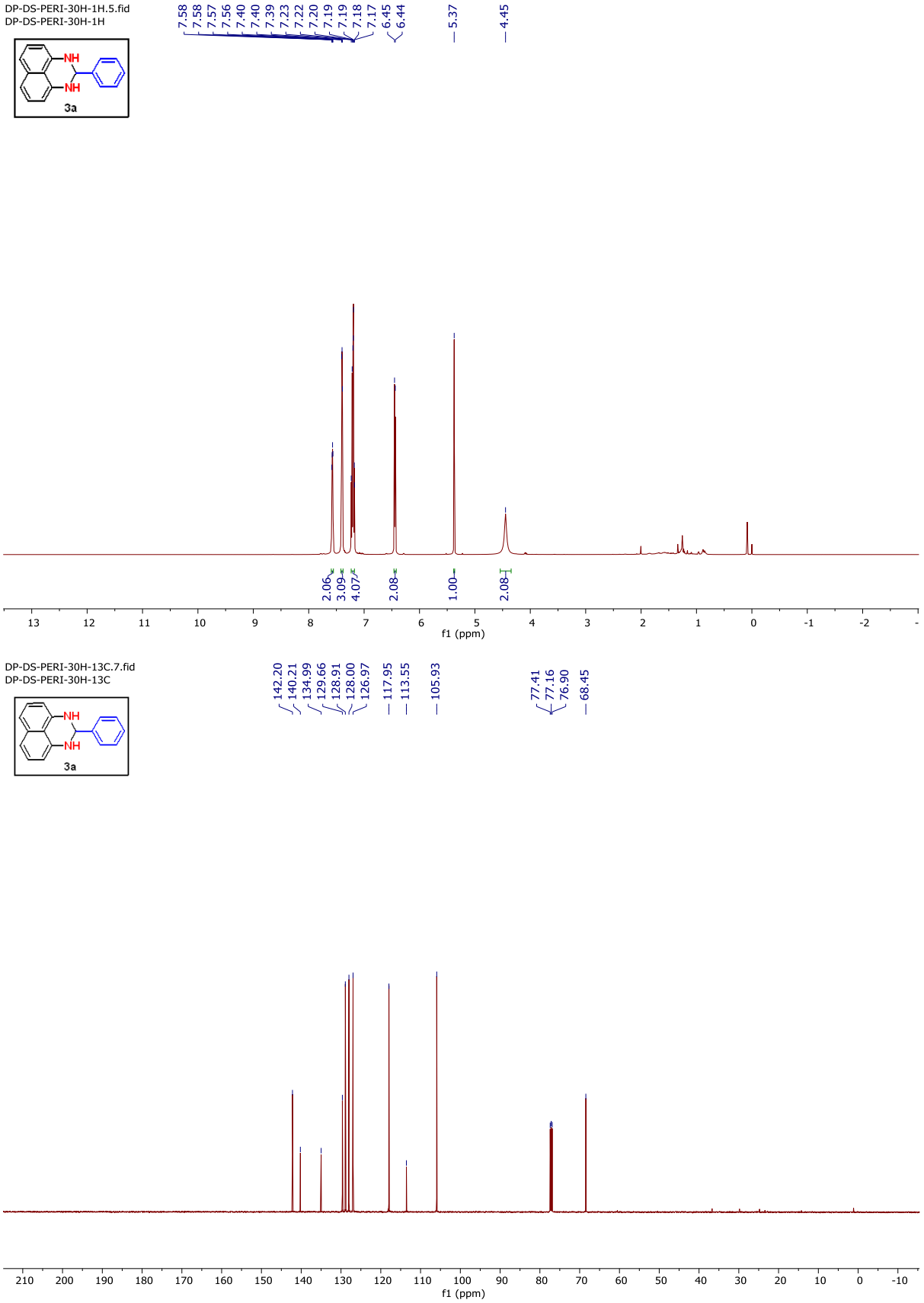


Figure S17. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-phenyl-2,3-dihydro-1*H*-perimidine (3a)** in $CDCl_3$.

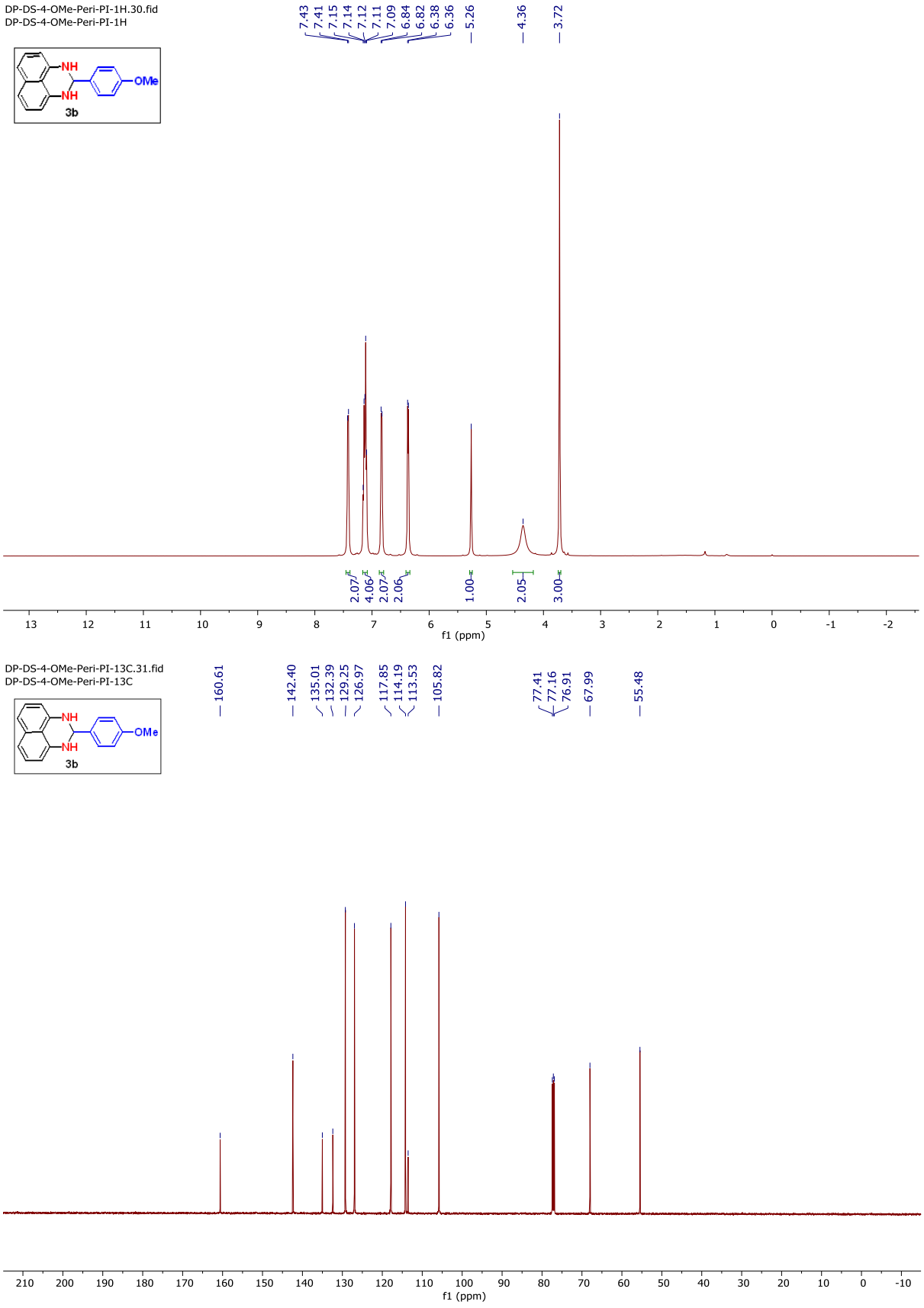


Figure S18. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-methoxyphenyl)-2,3-dihydro-1*H*-perimidine (3b)** in $CDCl_3$.

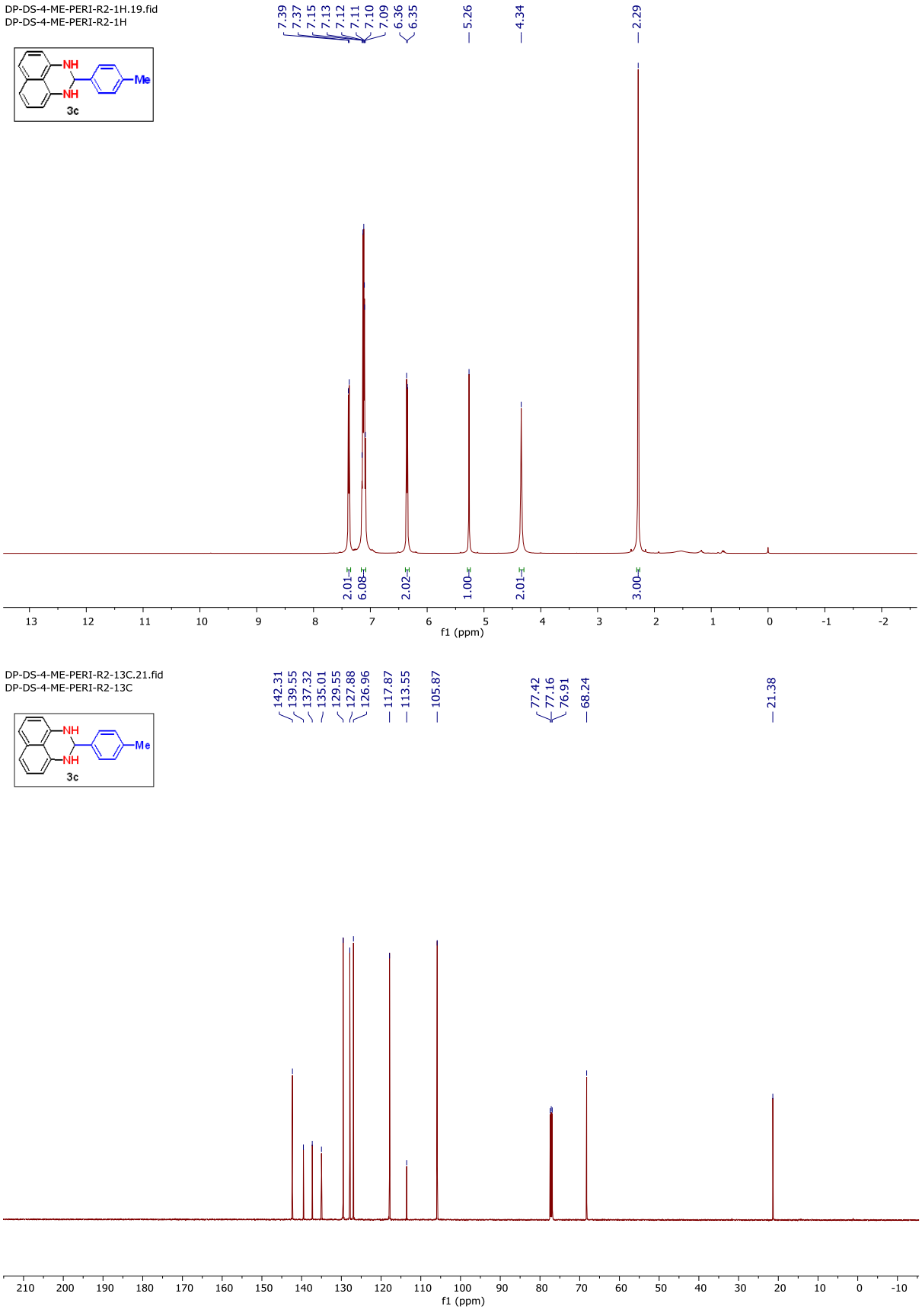


Figure S19. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(*p*-tolyl)-2,3-dihydro-1*H*-perimidine (3c)** in $CDCl_3$.

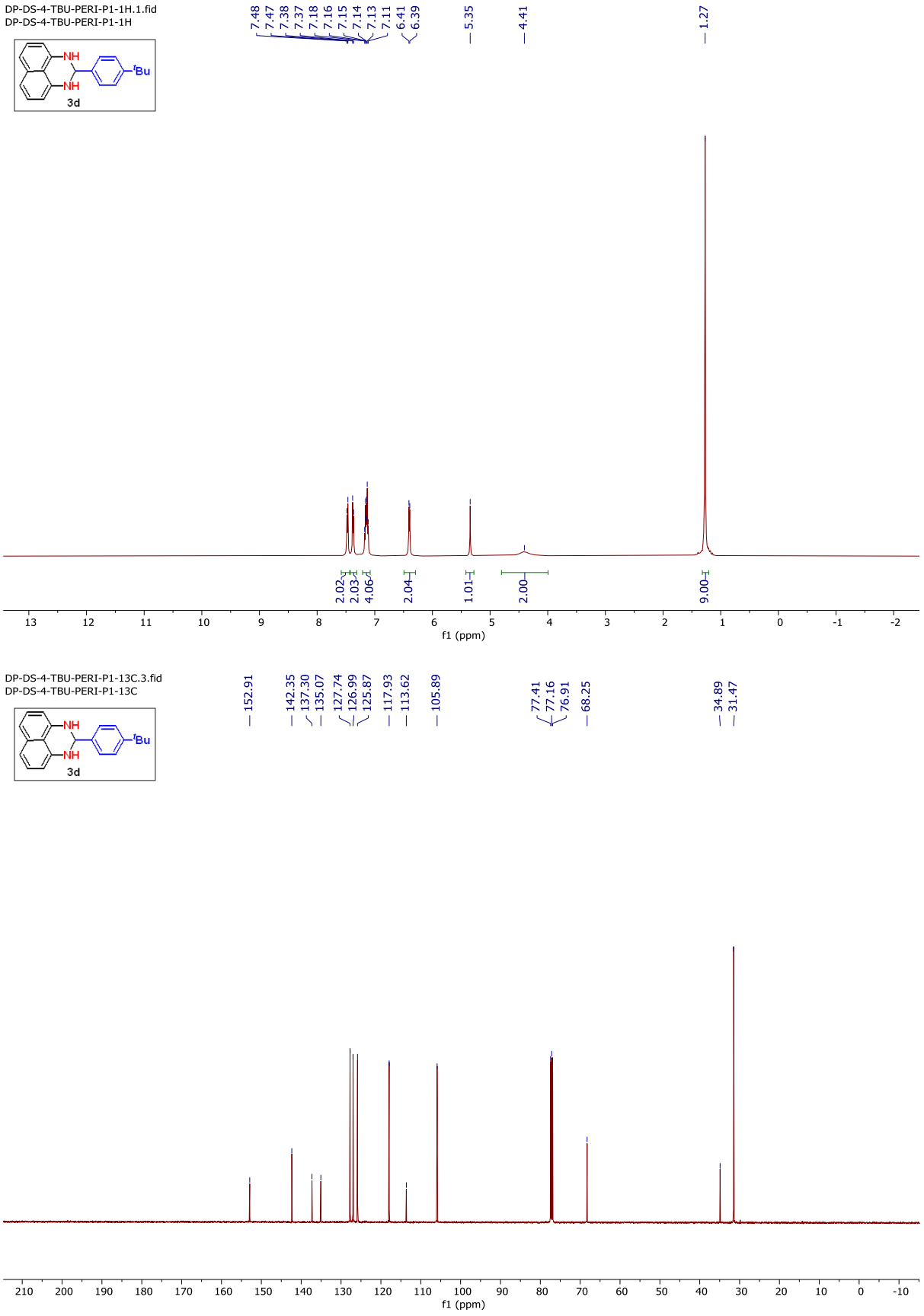


Figure S20. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-(*tert*-butyl)phenyl)-2,3-dihydro-1*H*-perimidine(3d)** in $CDCl_3$.

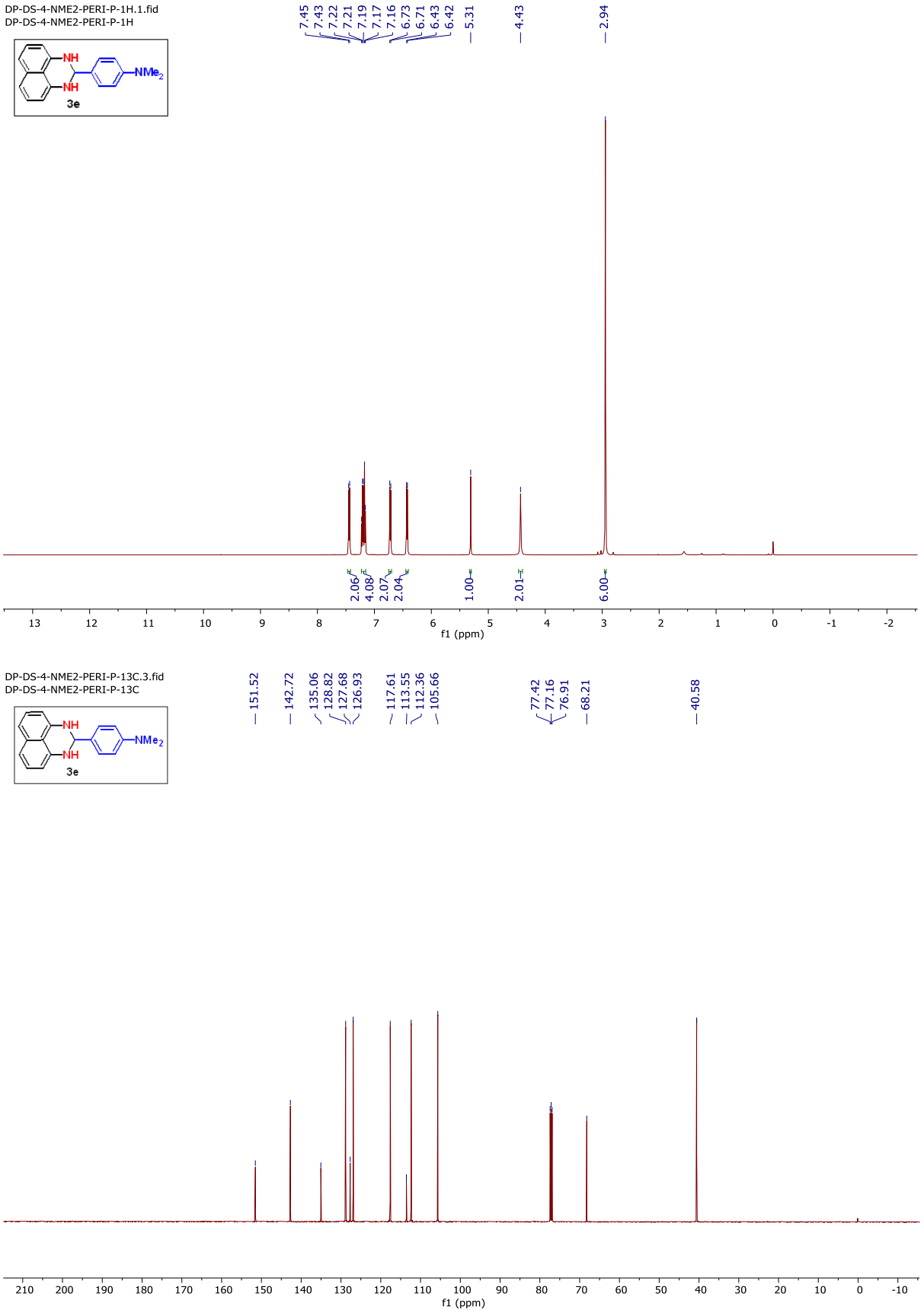


Figure S21. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **4-(2,3-dihydro-1*H*-perimidin-2-yl)-N, N-dimethylaniline (3e)** in $CDCl_3$.

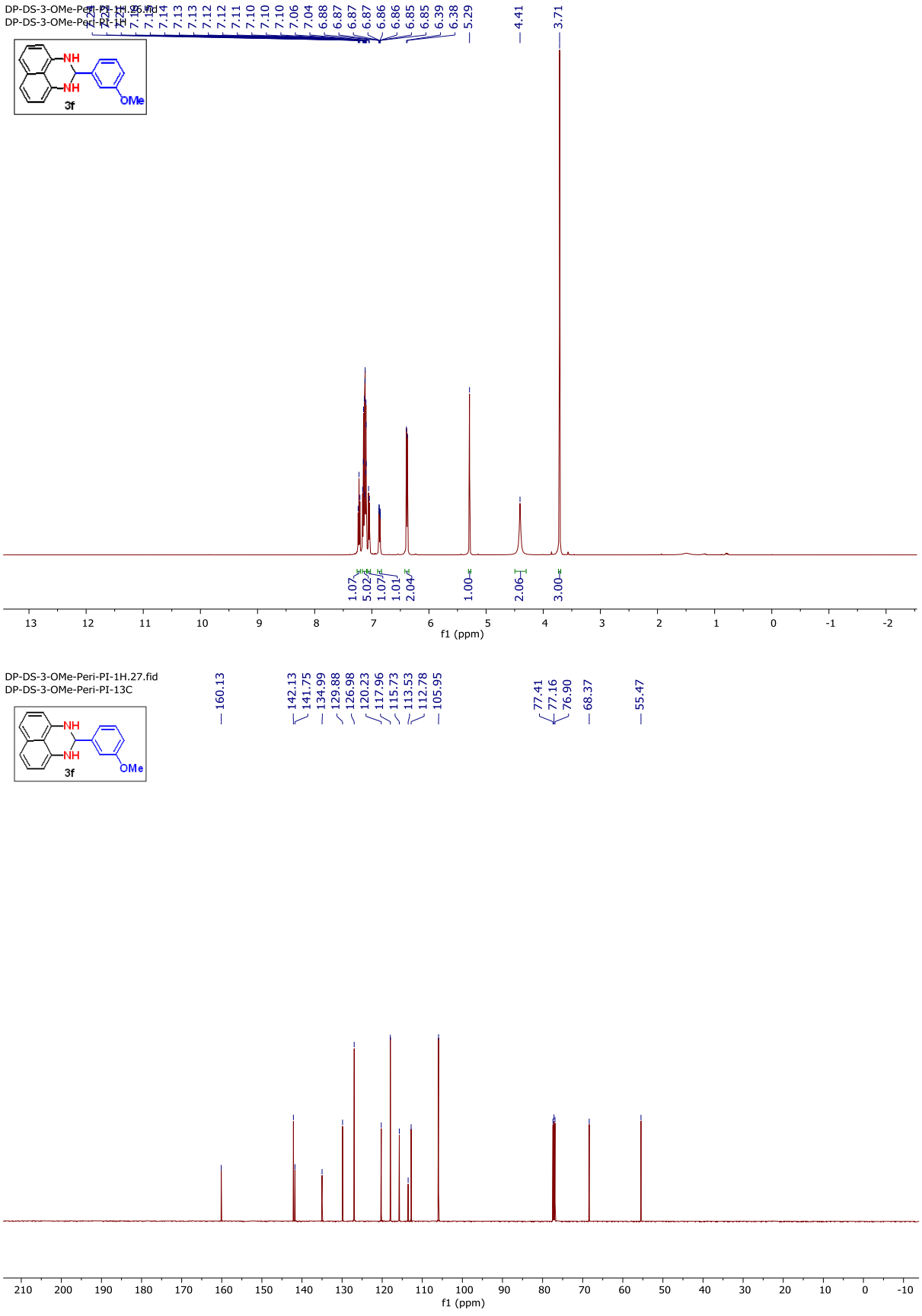


Figure S22. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(3-methoxyphenyl)-2,3-dihydro-1*H*-perimidine (3f)** in $CDCl_3$.

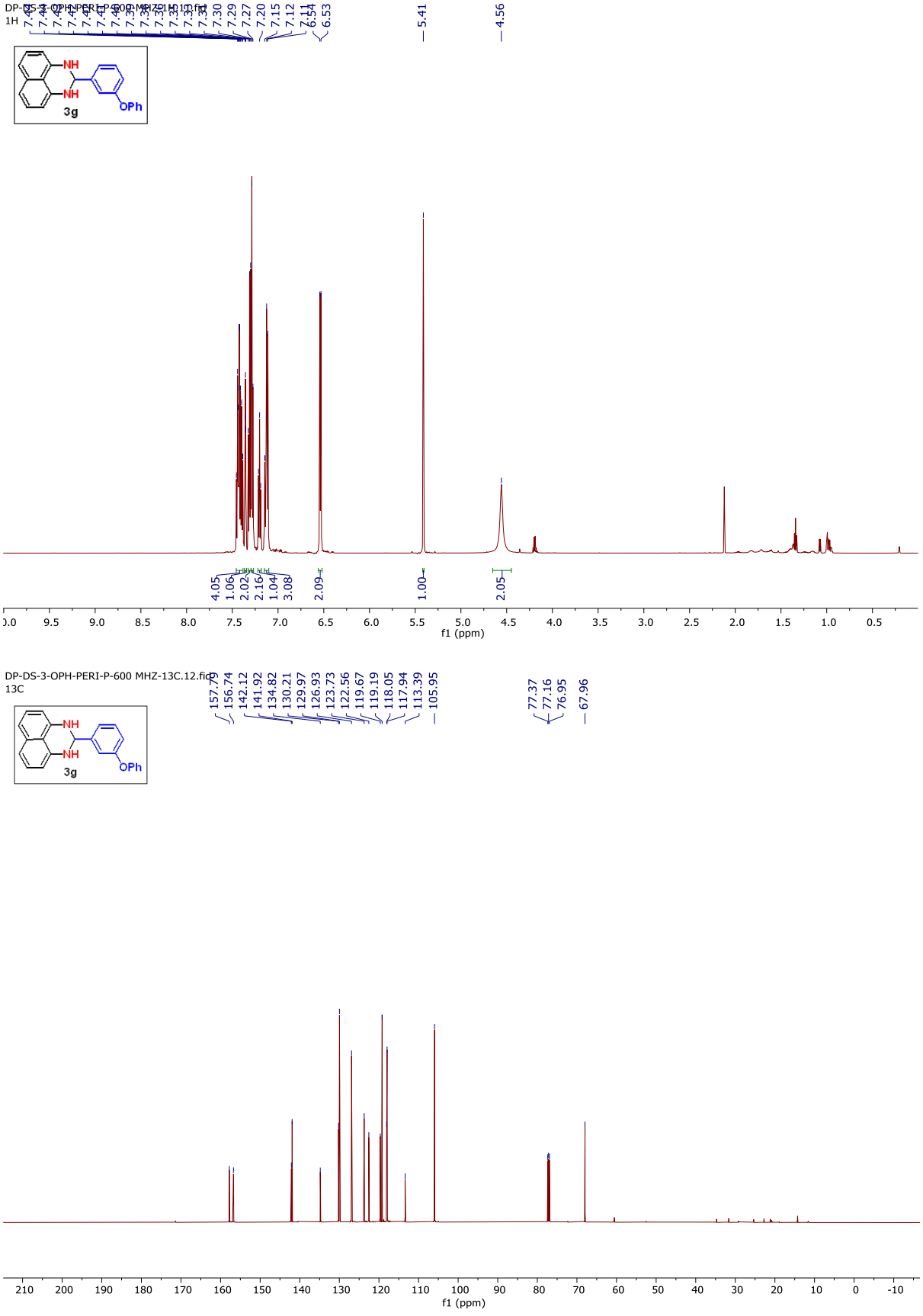


Figure S23. ^{1}H (600 MHz) and $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectrum of **2-(3-phenoxyphenyl)-2,3-dihydro-1*H*-perimidine (3g)** in $CDCl_3$.

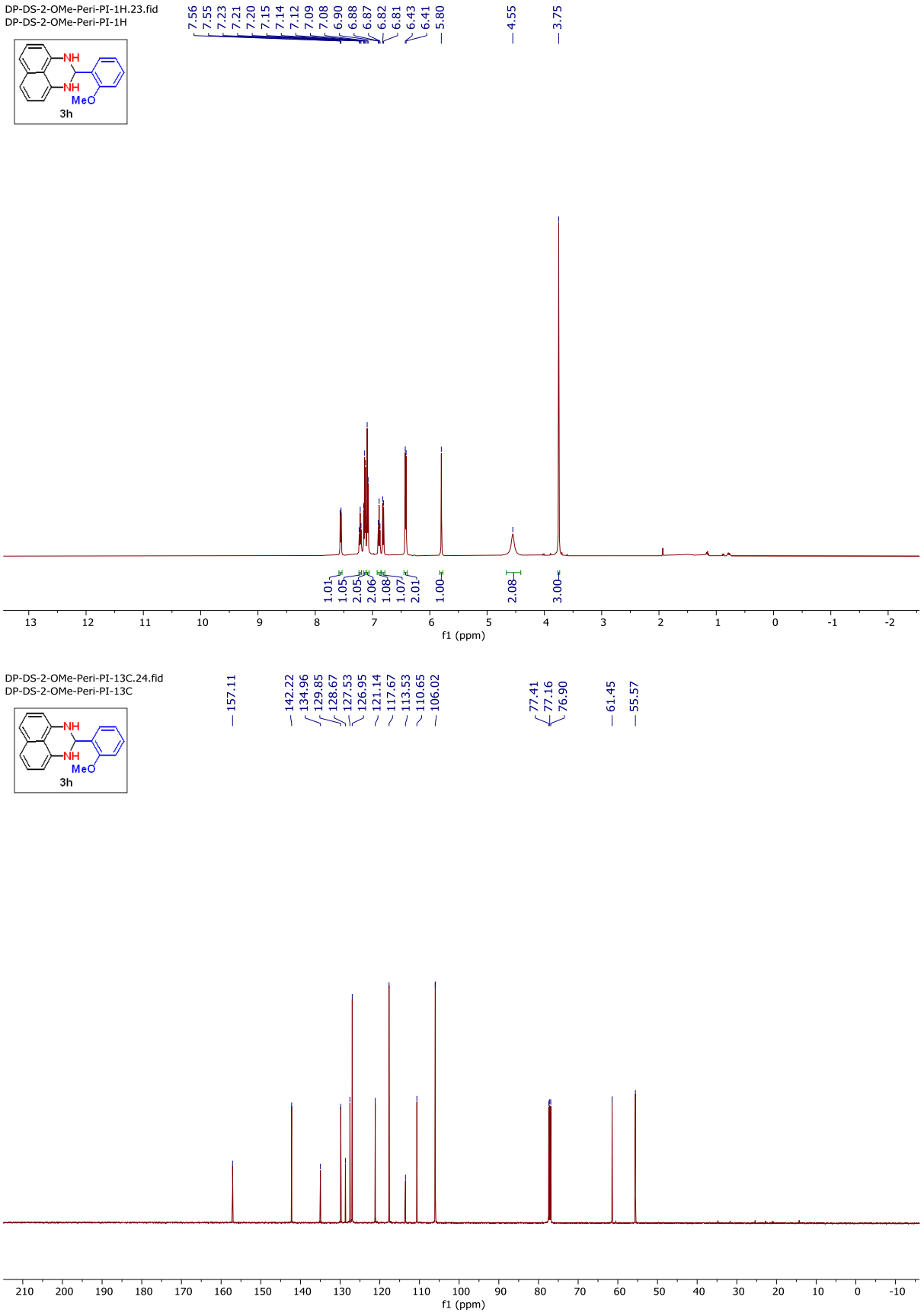


Figure S24. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(2-methoxyphenyl)-2,3-dihydro-1*H*-perimidine (3h)** in $CDCl_3$.

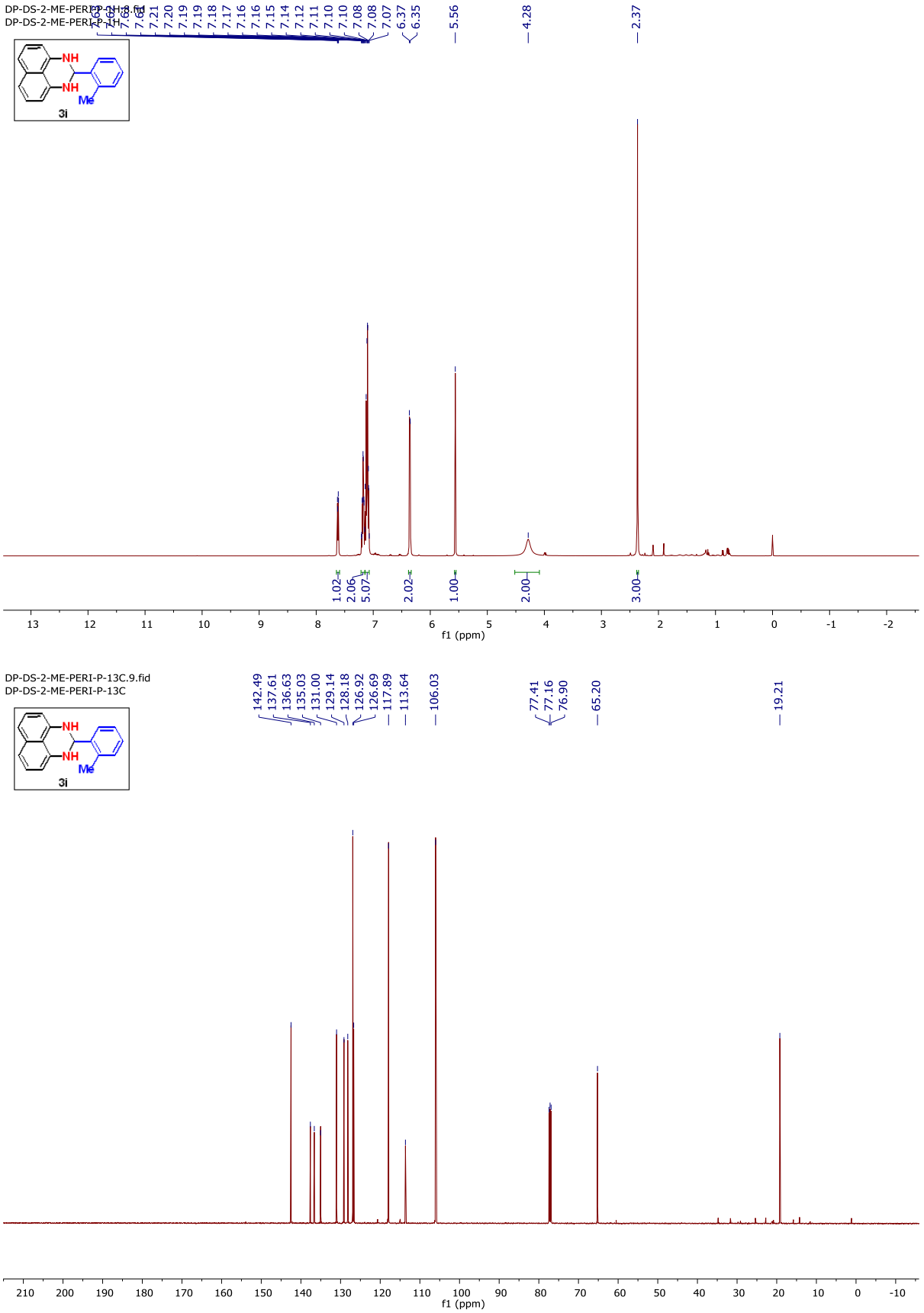


Figure S25. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(*o*-tolyl)-2,3-dihydro-1*H*-perimidine (3i)** in $CDCl_3$.

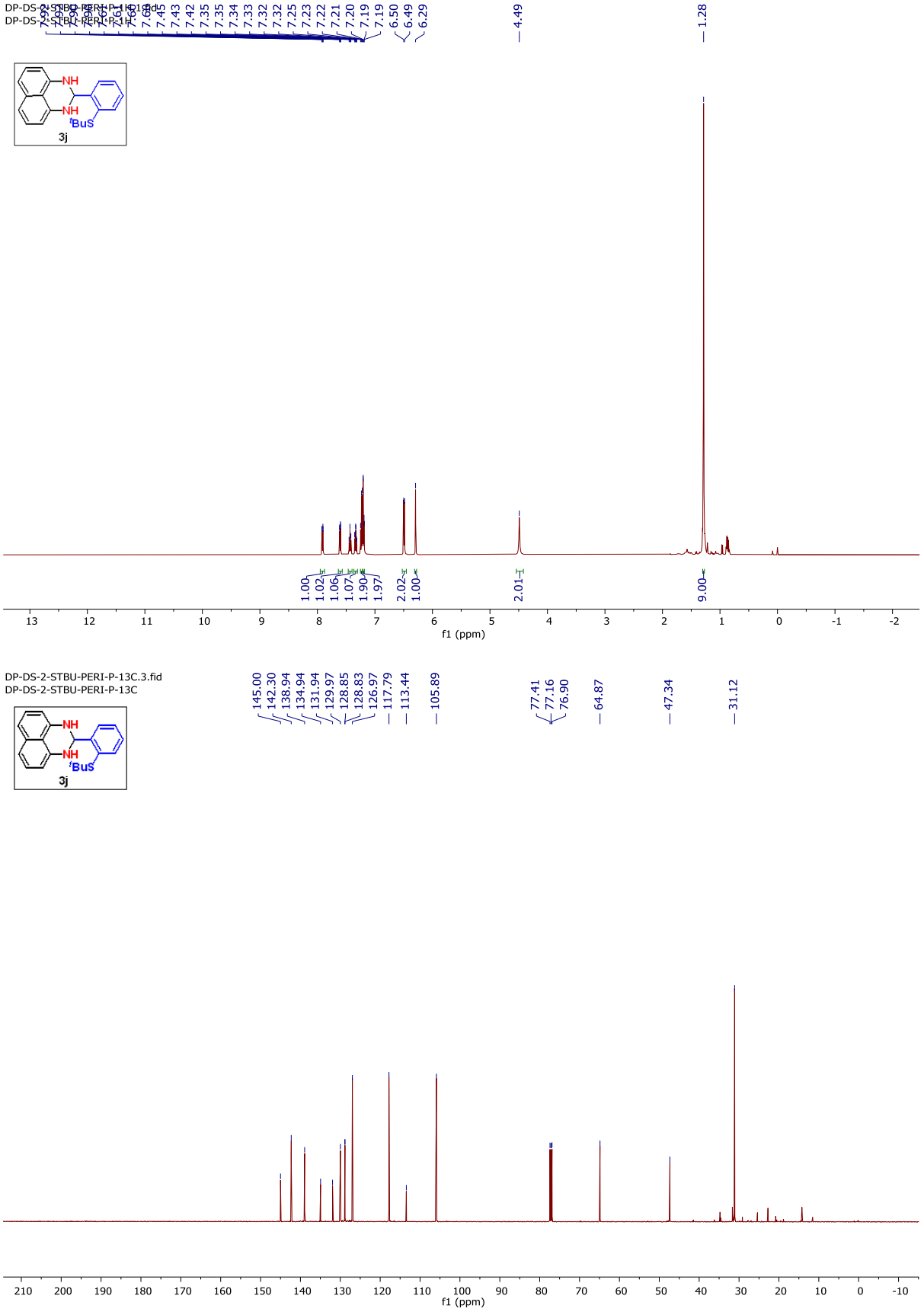
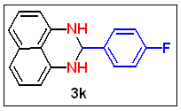
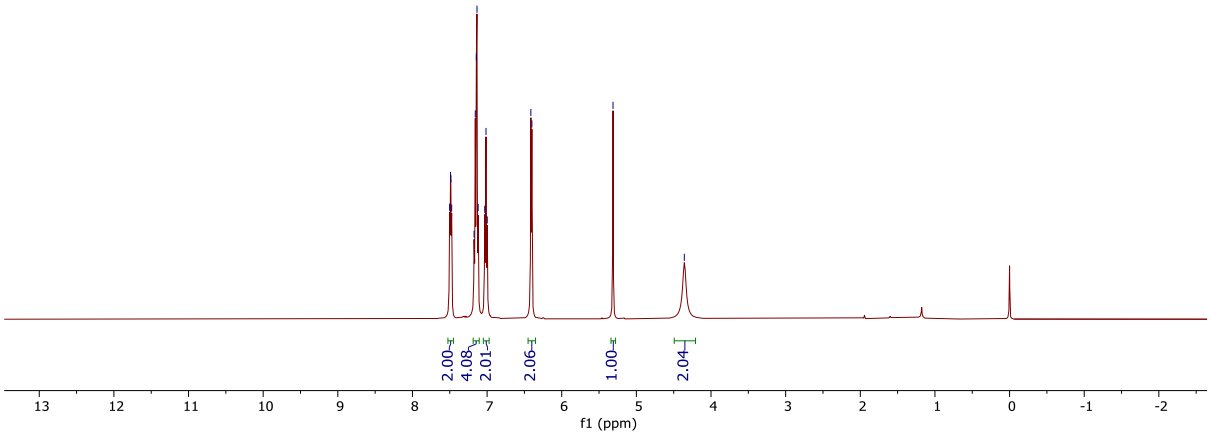


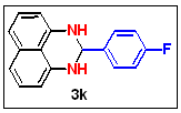
Figure S26. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(2-(*tert*-butylthio)phenyl)-2,3-dihydro-1*H*-perimidine (3j)** in $CDCl_3$.

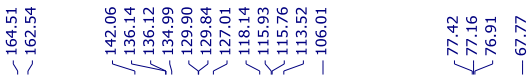
DP-DS-4-F-PERI-P-1H.1.fid
DP-DS-4-F-PERI-P-1H

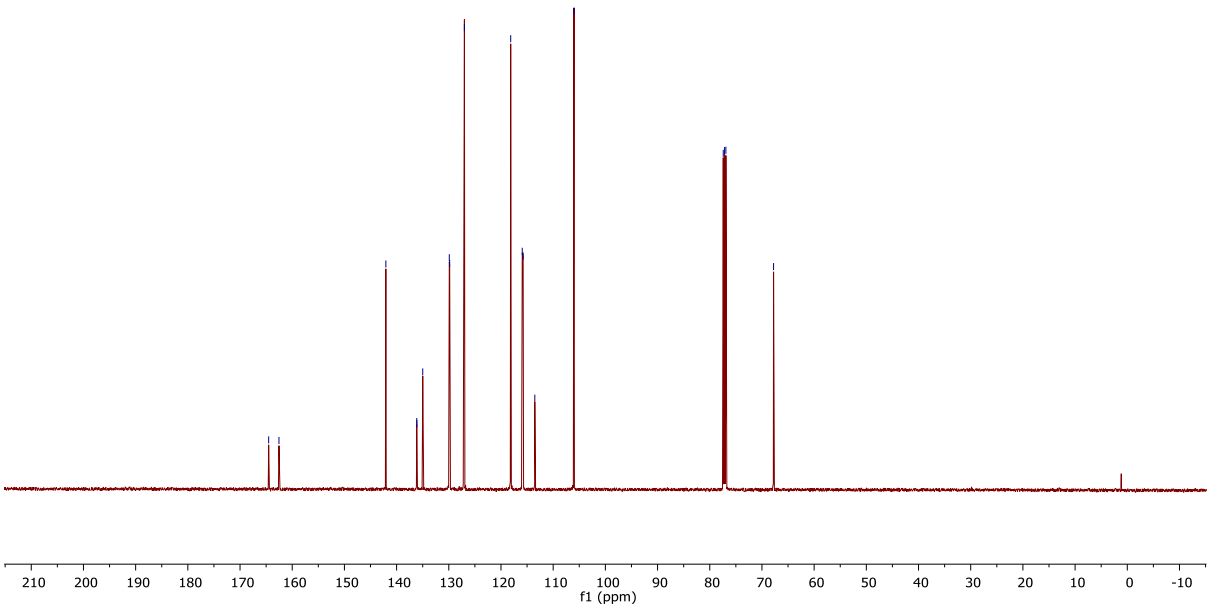




DP-DS-4-F-PERI-P-13C.5.fid
DP-DS-4-F-PERI-P-13C







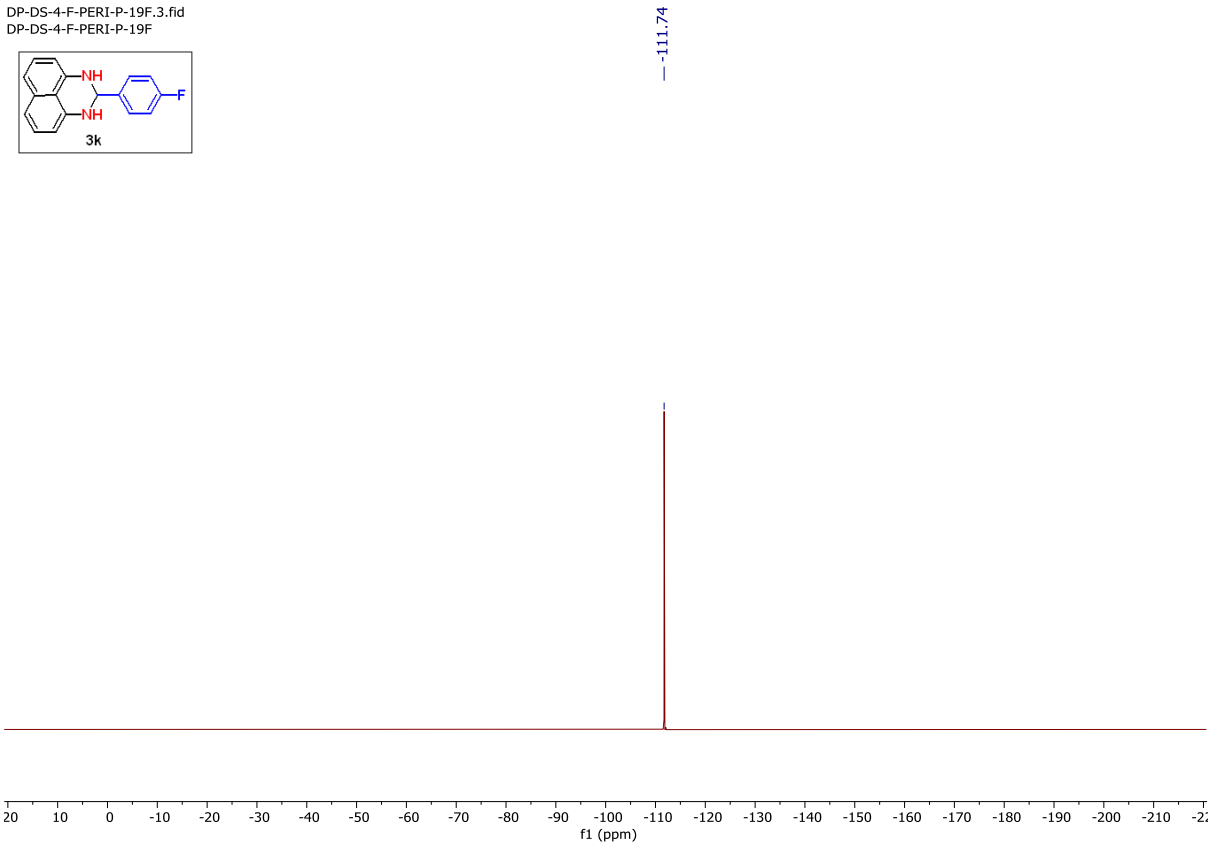


Figure S27. ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (125 MHz) and ^{19}F (470 MHz) NMR Spectrum of **2-(4-fluorophenyl)-2,3-dihydro-1*H*-perimidine (3k)** in $CDCl_3$.

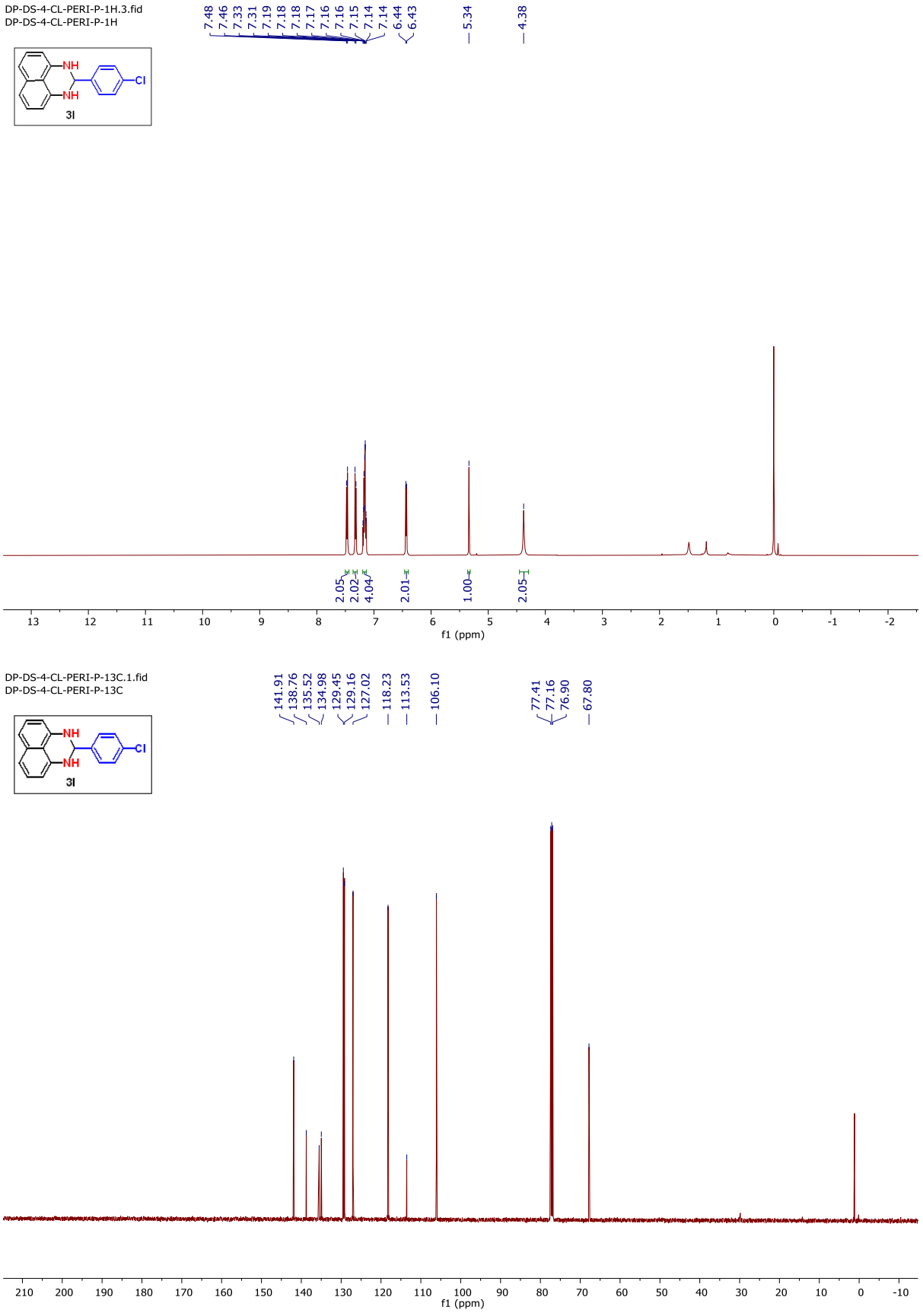


Figure S28. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-chlorophenyl)-2,3-dihydro-1*H*-perimidine (3l)** in $CDCl_3$.

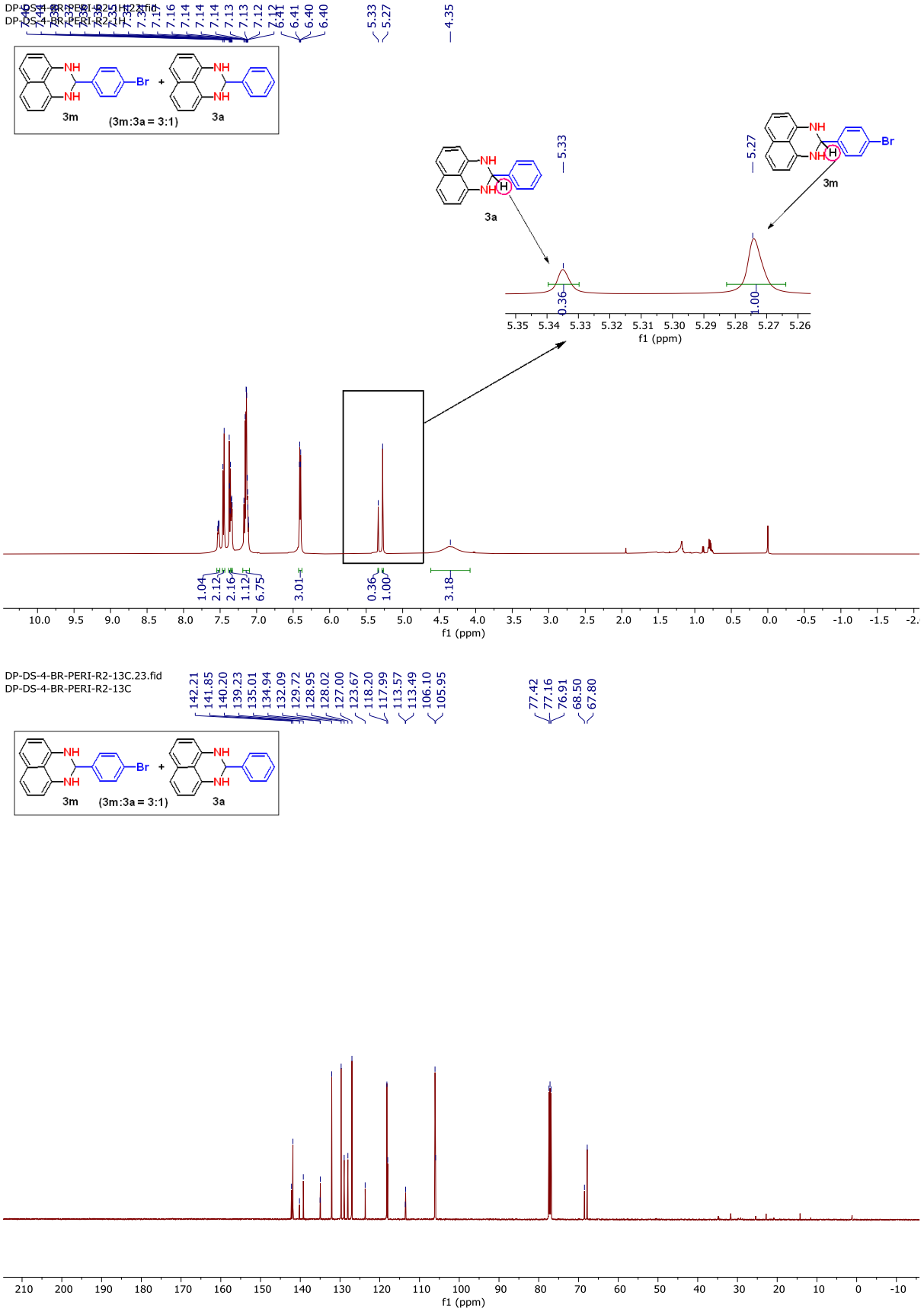
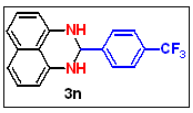
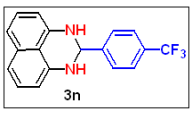


Figure S29. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-bromophenyl)-2,3-dihydro-1*H*-perimidine (3m)** in $CDCl_3$.

DP-DS-4-CF3-1-PERI-P-G-1H.1.fid
DP-DS-4-CF3-1-PERI-P-G-1H



DP-DS-4-CF3-PERI-P-13C.7.fid
DP-DS-4-CF3-PERI-P-13C



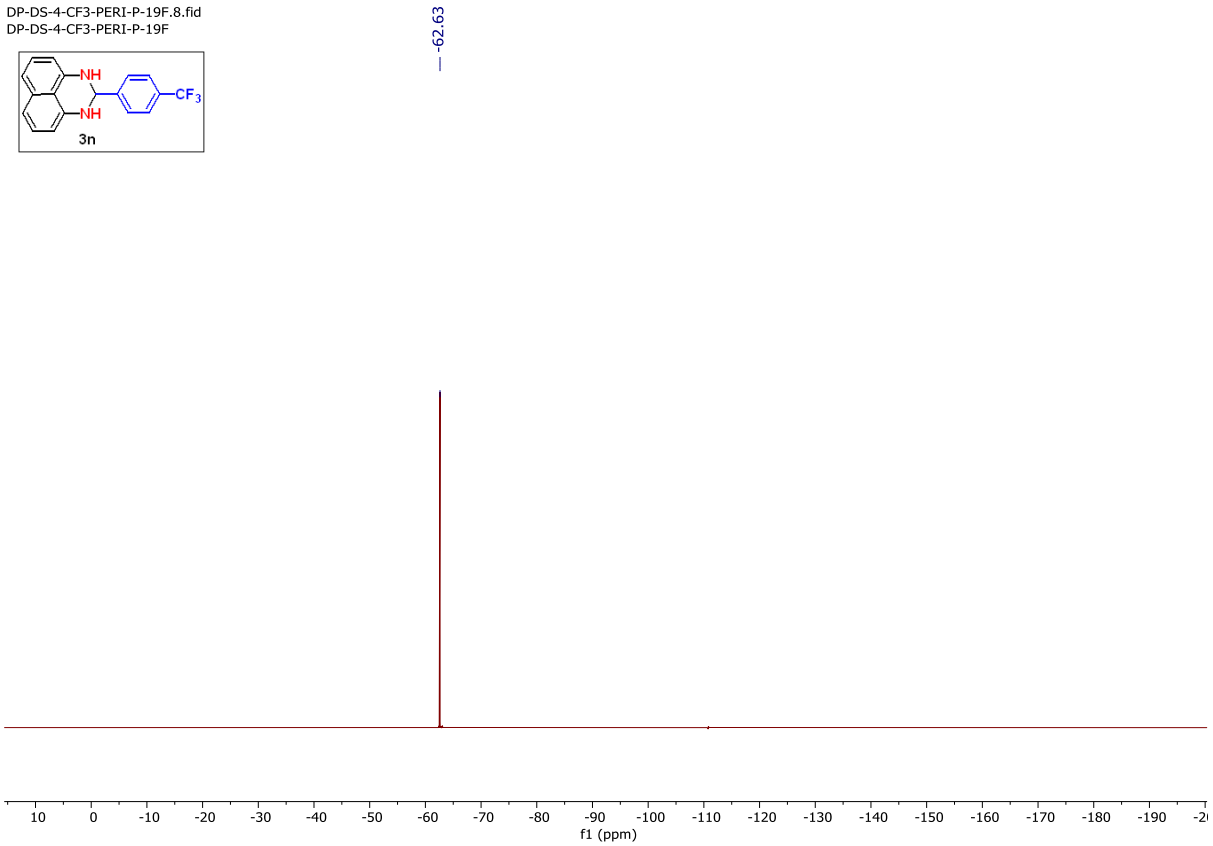
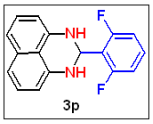
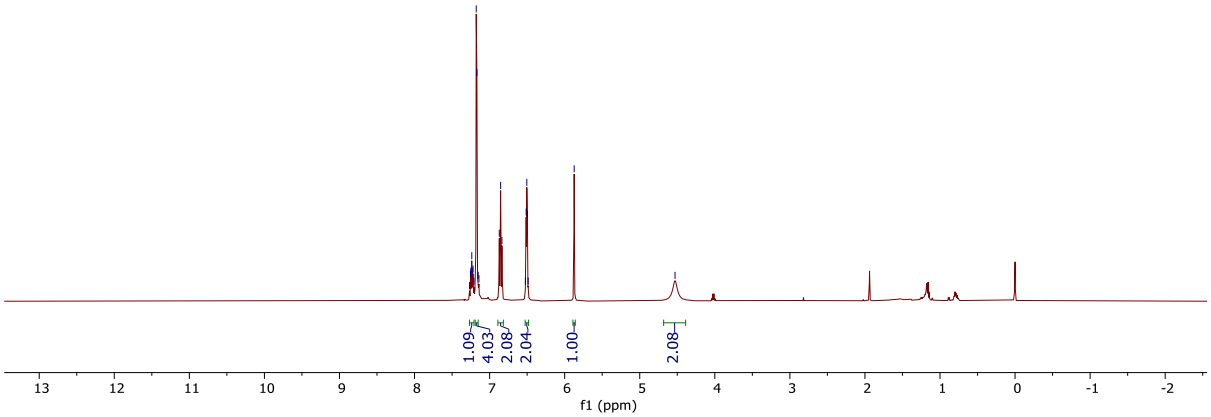


Figure S30. ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (125 MHz) and ^{19}F (470 MHz) NMR Spectrum of **2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-perimidine (3n)** in $CDCl_3$.

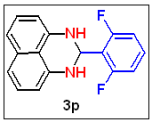
DP-DS-2,6-DI-FLUORO-PERI-1H-1.fid
DP-DS-2,6-DI-FLUORO-PERI-1H-1.fid



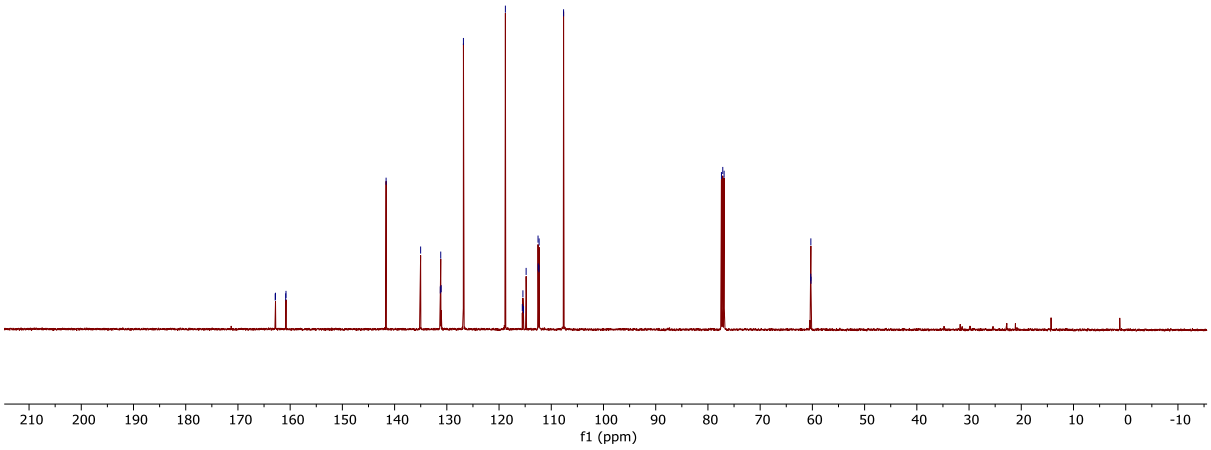
7.27 7.24 7.25 7.24 7.23 7.22 7.21 7.18 7.17 7.15 7.14 6.87 6.85 6.84 6.52 6.51 6.50 6.50 6.49 5.87 4.53



DP-DS-2,6-DI-FLUORO-PERI-500-13C-1.fid
DP-DS-2,6-DI-FLUORO-PERI-500-13C-1.fid



162.87 162.83 160.86 160.80 141.63 135.02 131.25 131.17 131.08 126.82 118.79 115.55 115.43 115.32 114.81 112.54 112.50 112.36 112.33 107.65 77.41 77.16 76.91 60.32 60.29 60.27



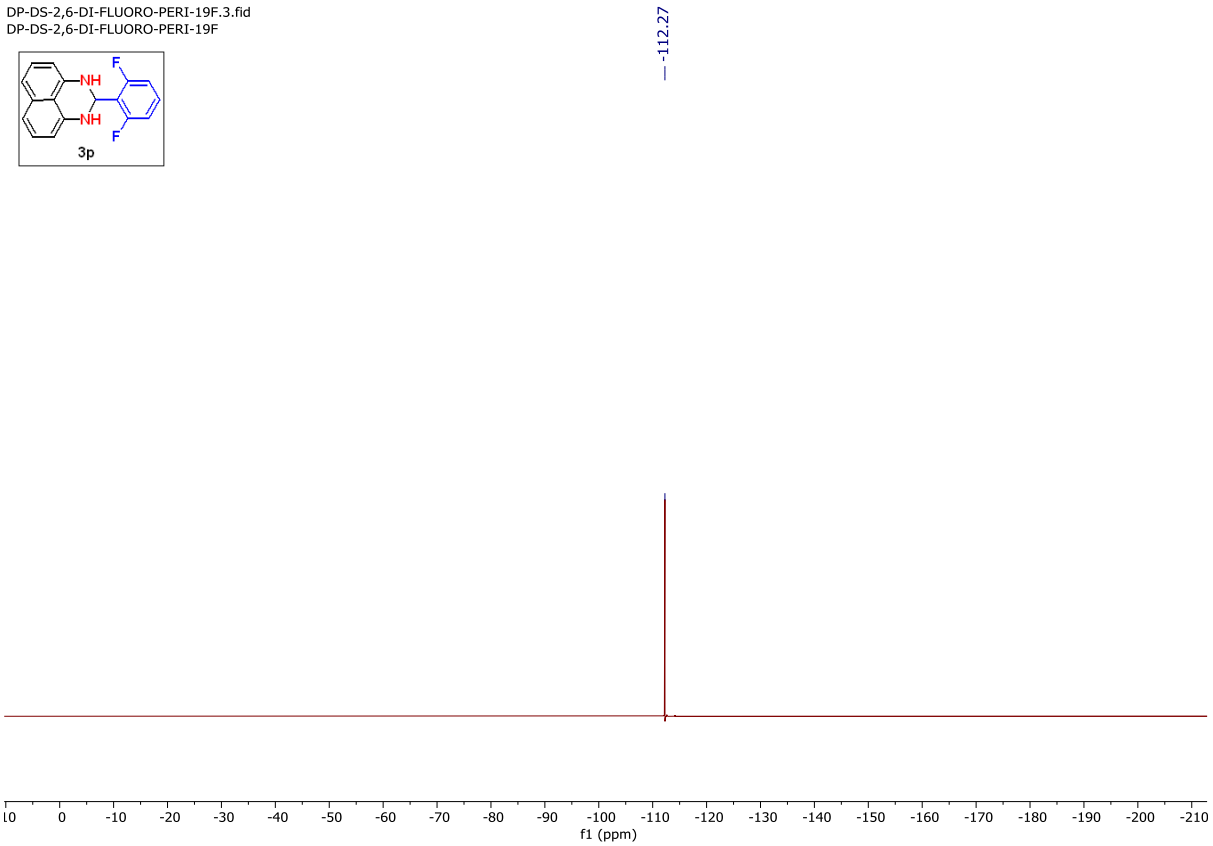


Figure S31. ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (125 MHz) and ^{19}F (470 MHz) NMR Spectrum of **2-(2,6-difluorophenyl)-2,3-dihydro-1*H*-perimidine (3p)** in $CDCl_3$.

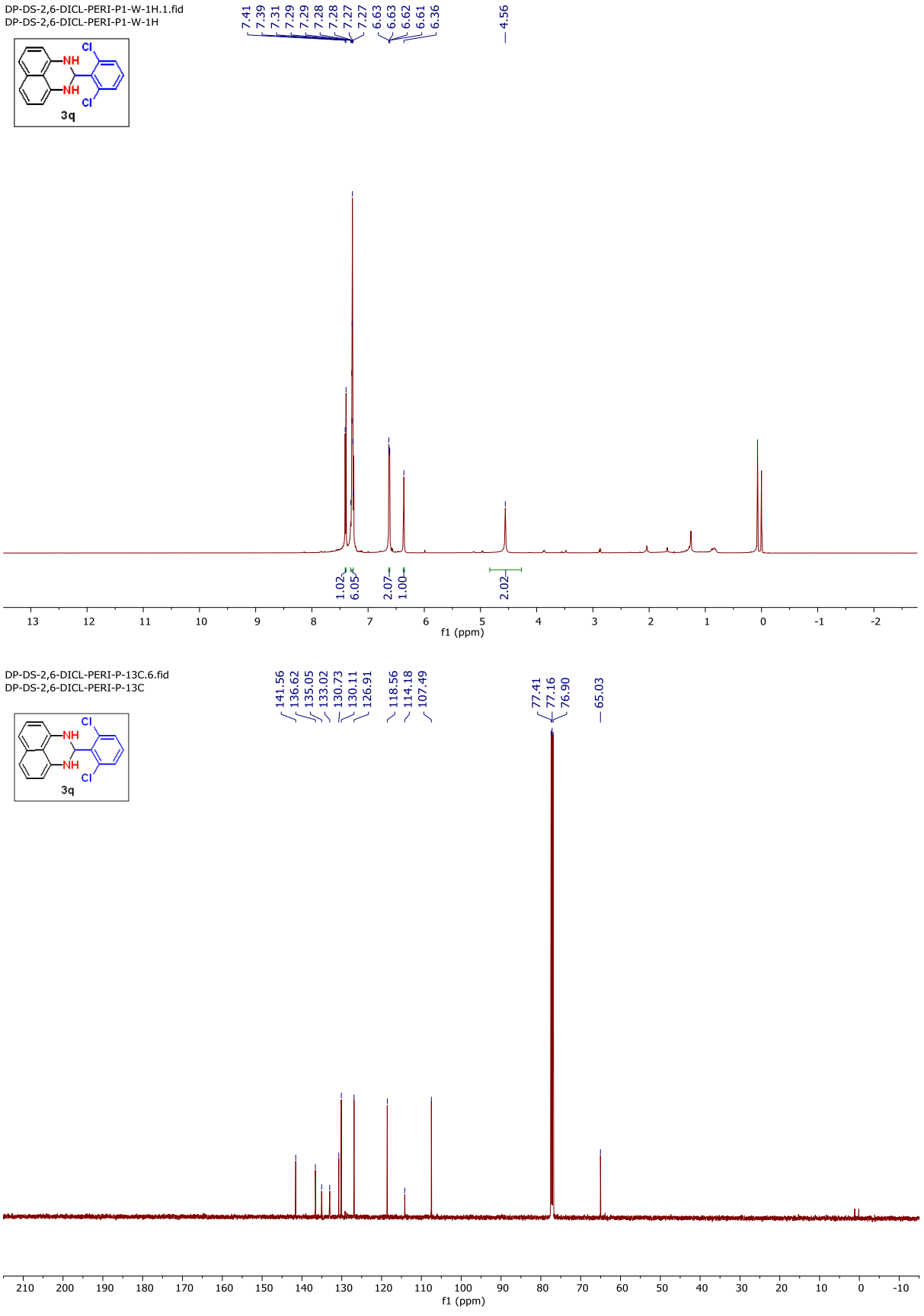


Figure S32. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(2,6-dichlorophenyl)-2,3-dihydro-1*H*-perimidine (3q)** in $CDCl_3$.

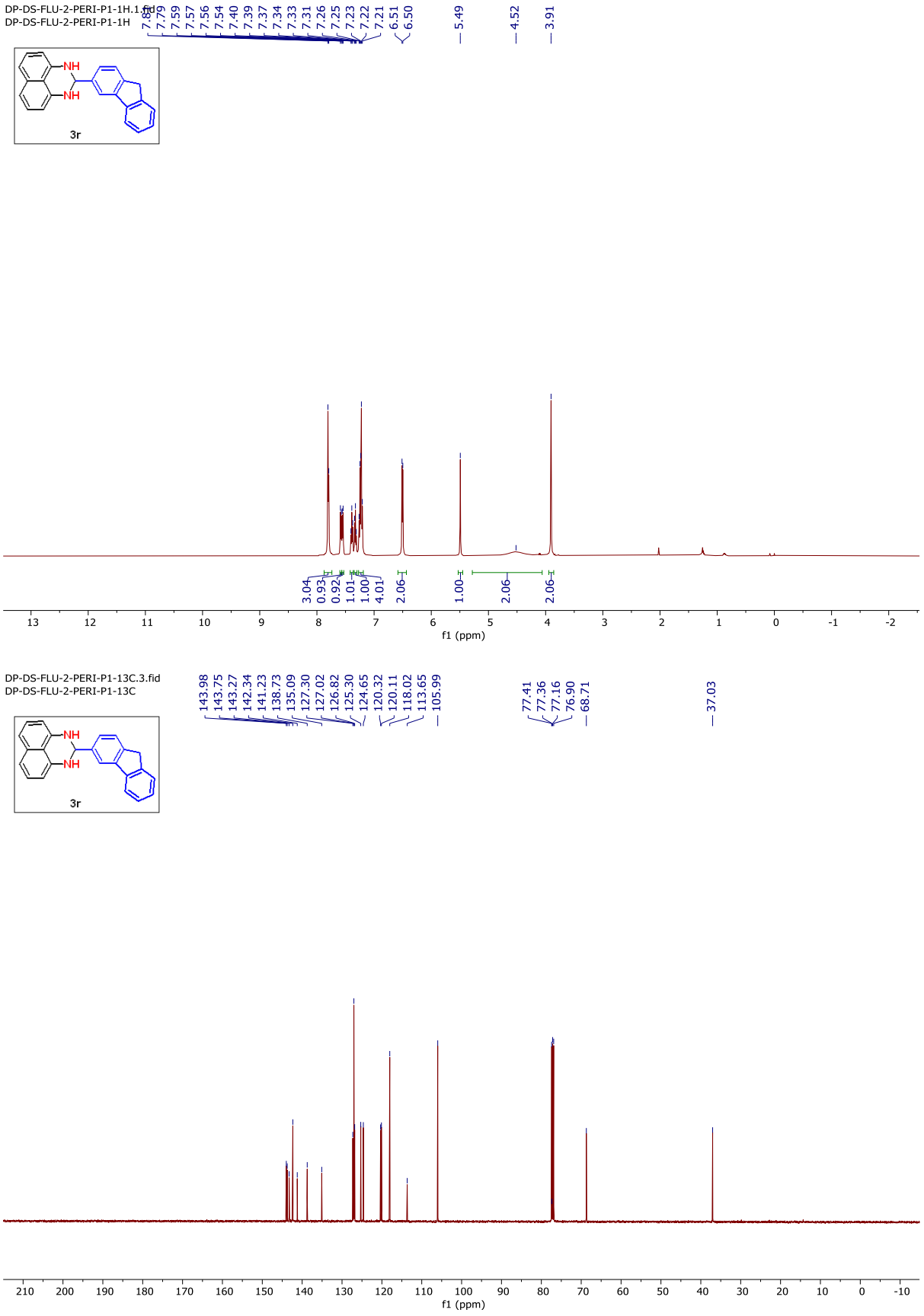


Figure S33. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(9*H*-fluoren-3-yl)-2,3-dihydro-1*H*-perimidine (3r)** in $CDCl_3$.

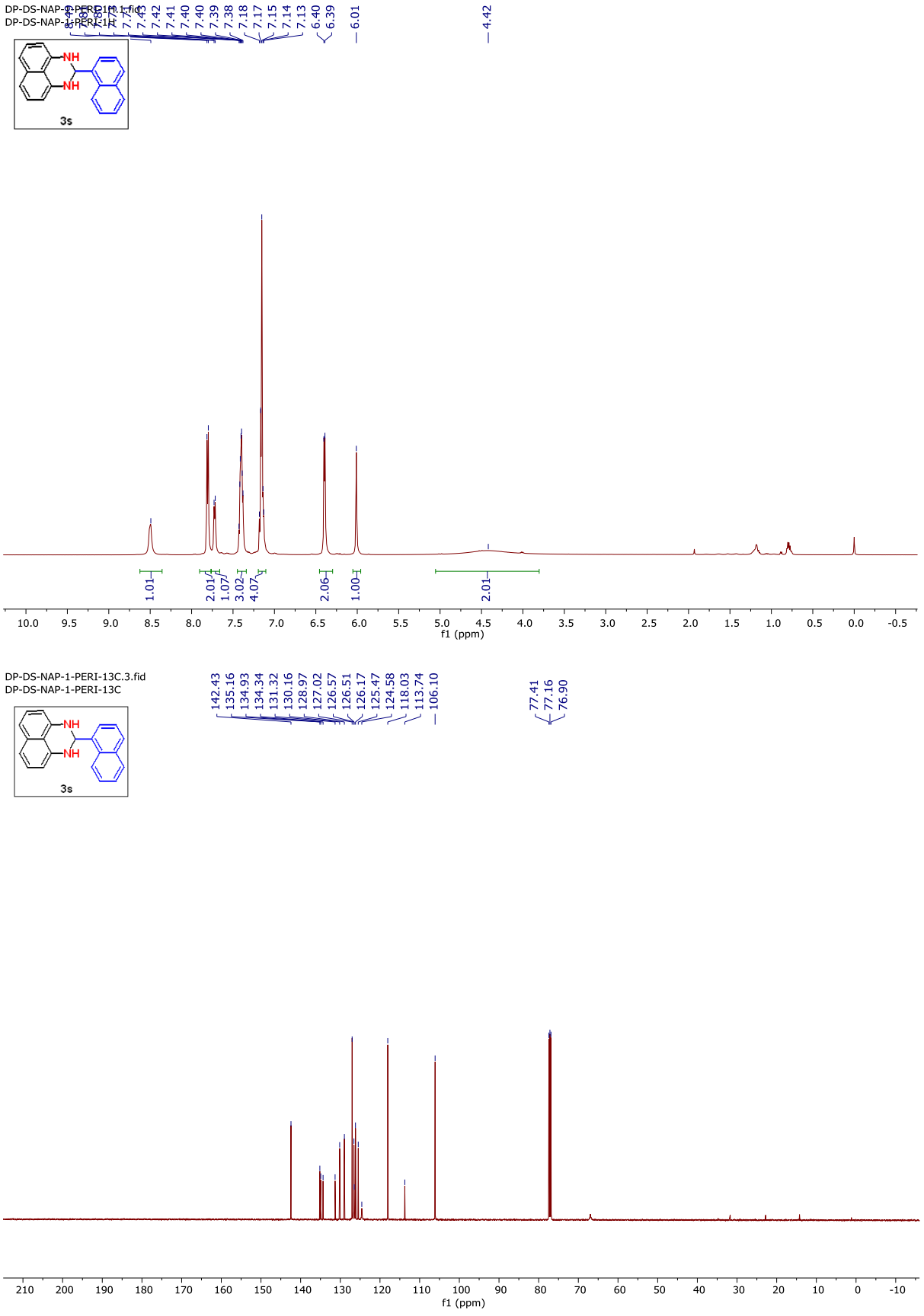


Figure S34. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(naphthalen-1-yl)-2,3-dihydro-1*H*-perimidine (3s)** in $CDCl_3$.

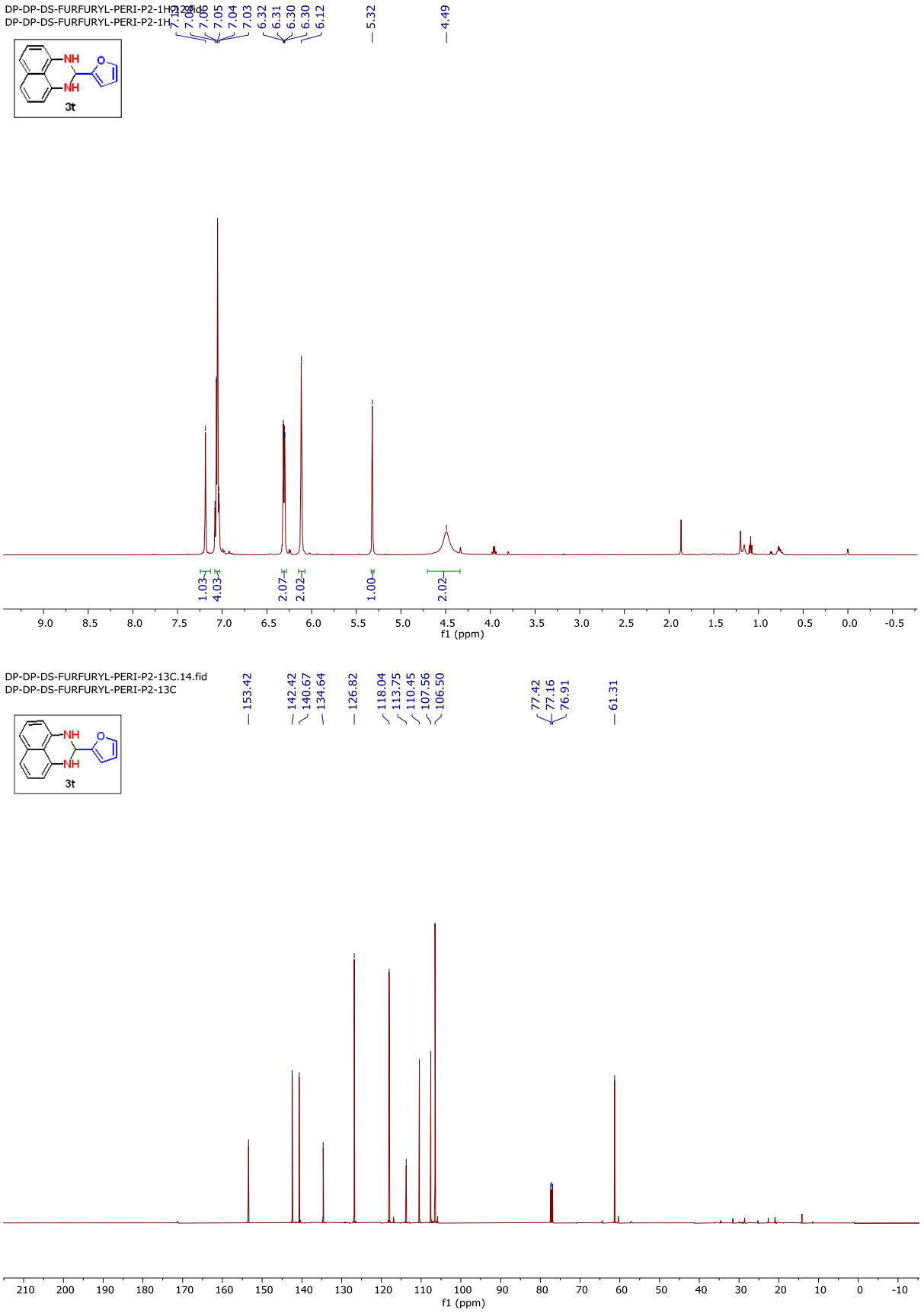


Figure S35. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(furan-2-yl)-2,3-dihydro-1*H*-perimidine (3t)** in $CDCl_3$.

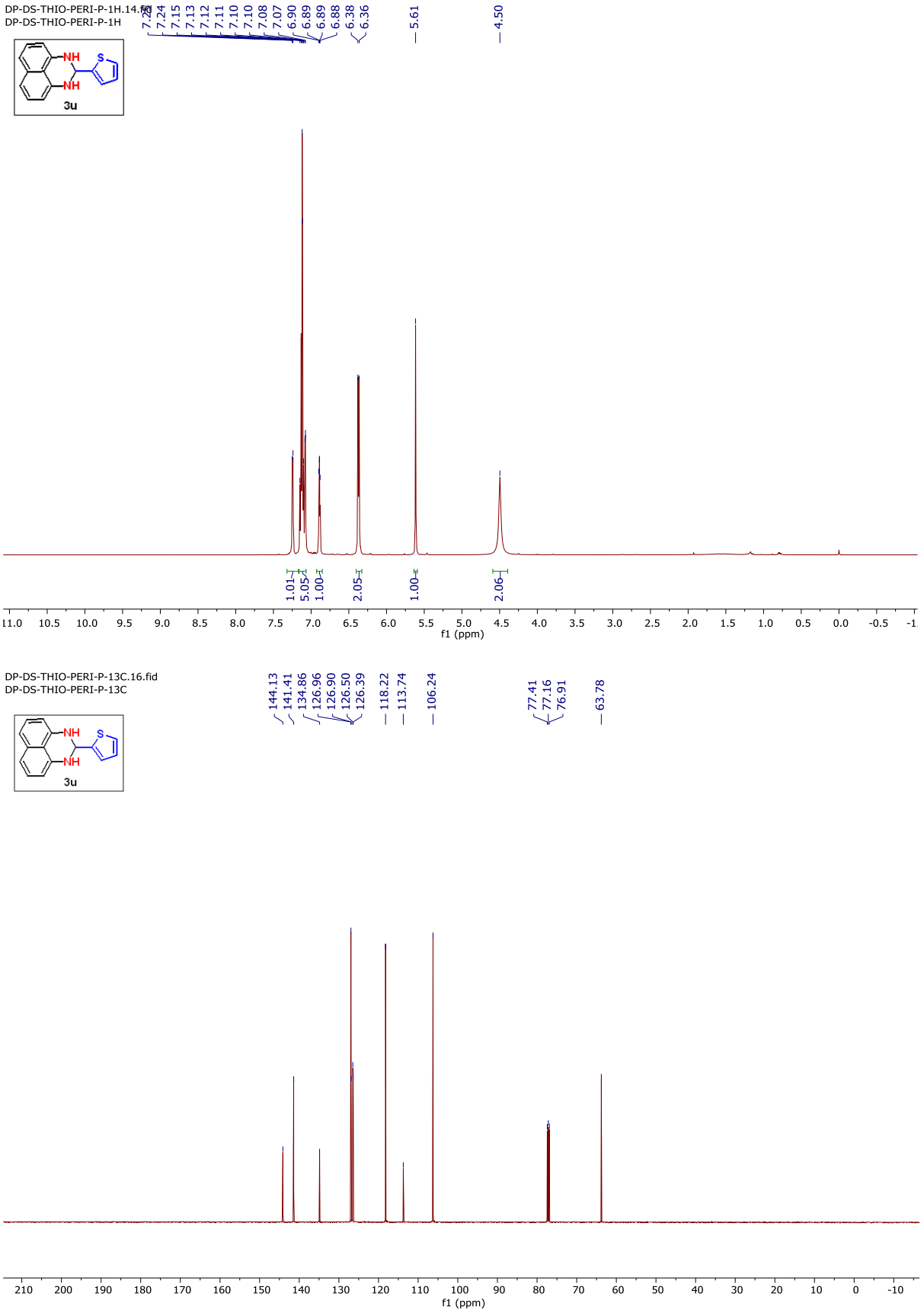


Figure S36. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(thiophen-2-yl)-2,3-dihydro-1*H*-perimidine (3u)** in $CDCl_3$.

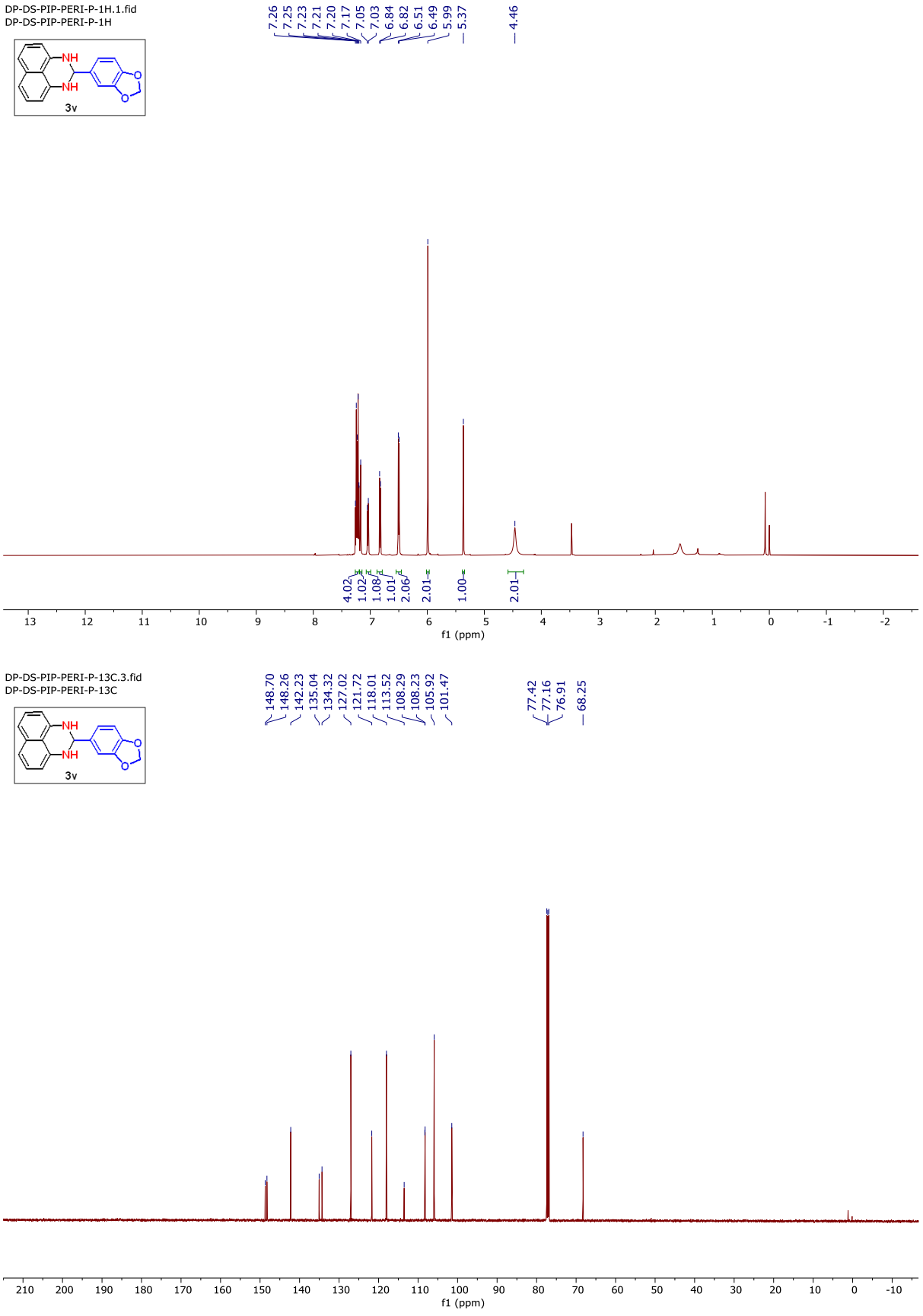


Figure S37. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(benzo[*d*][1,3]dioxol-5-yl)-2,3-dihydro-1*H*-perimidine (3v)** in $CDCl_3$.

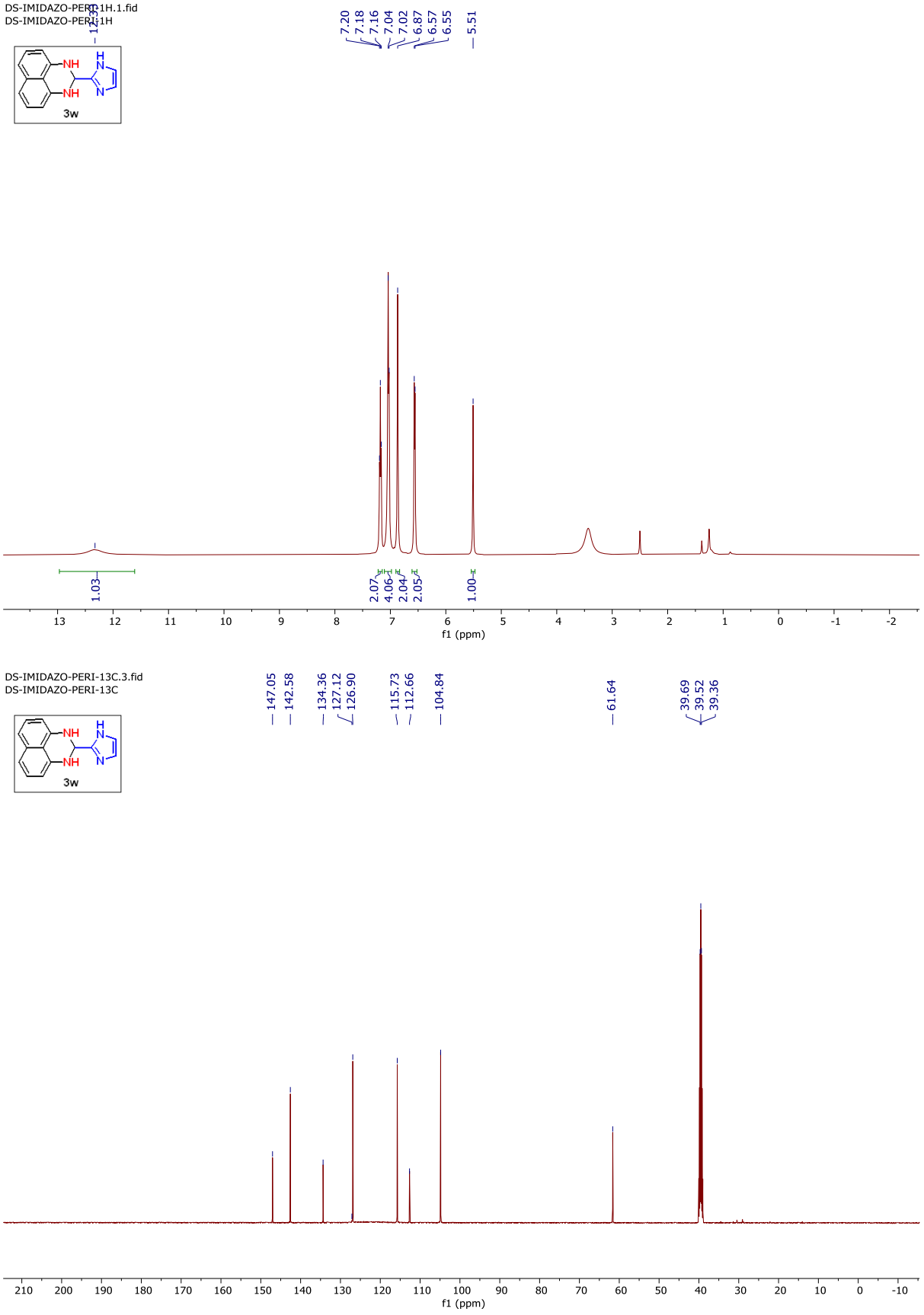


Figure S38. ^{1}H (400 MHz) and ^{13}C{^{1}H} (125 MHz) NMR Spectrum of **2-(1*H*-imidazol-2-yl)-2,3-dihydro-1*H*-perimidine (3w)** in DMSO-d_6.

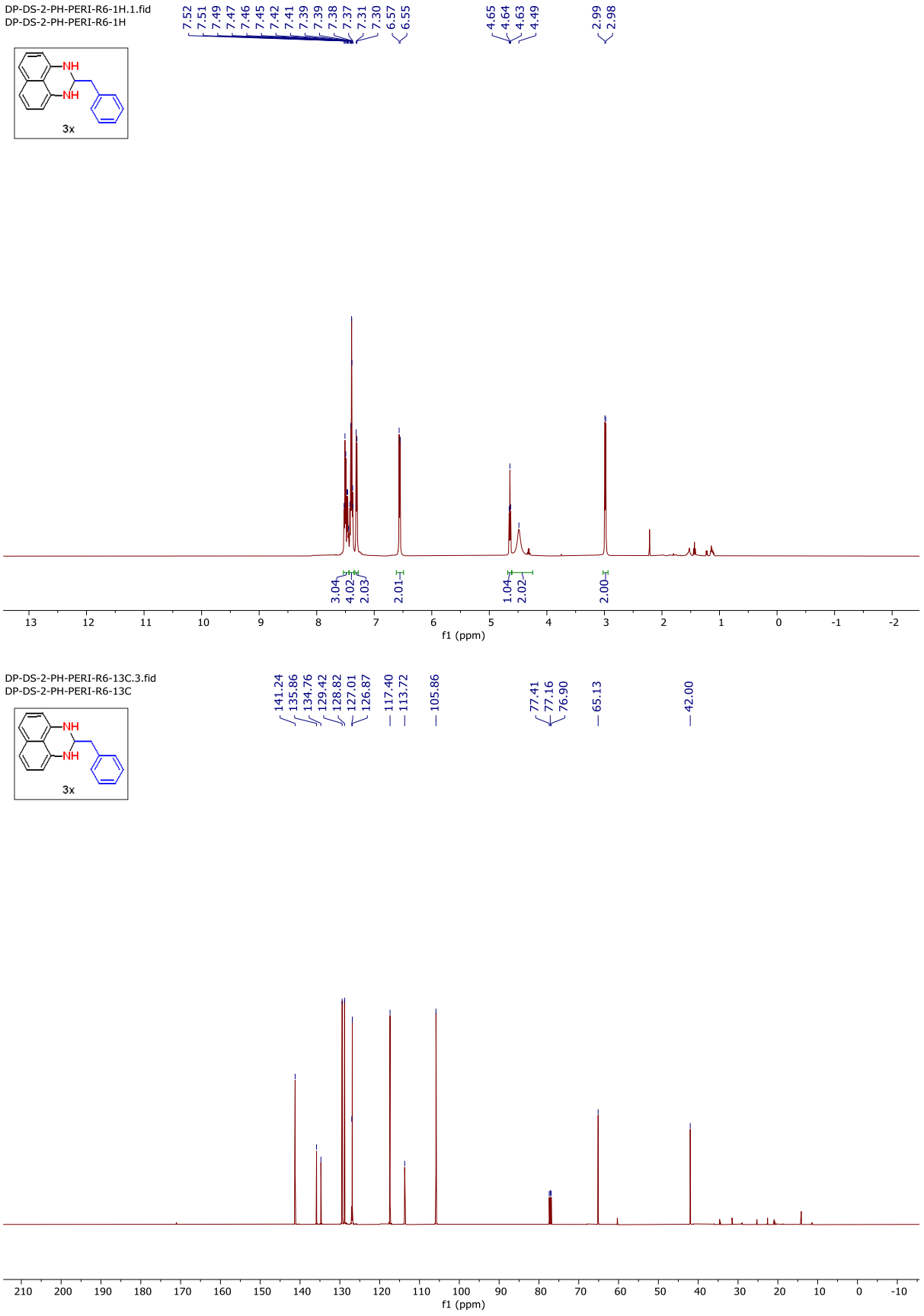


Figure S39. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-benzyl-2,3-dihydro-1*H*-perimidine (3x)** in $CDCl_3$.

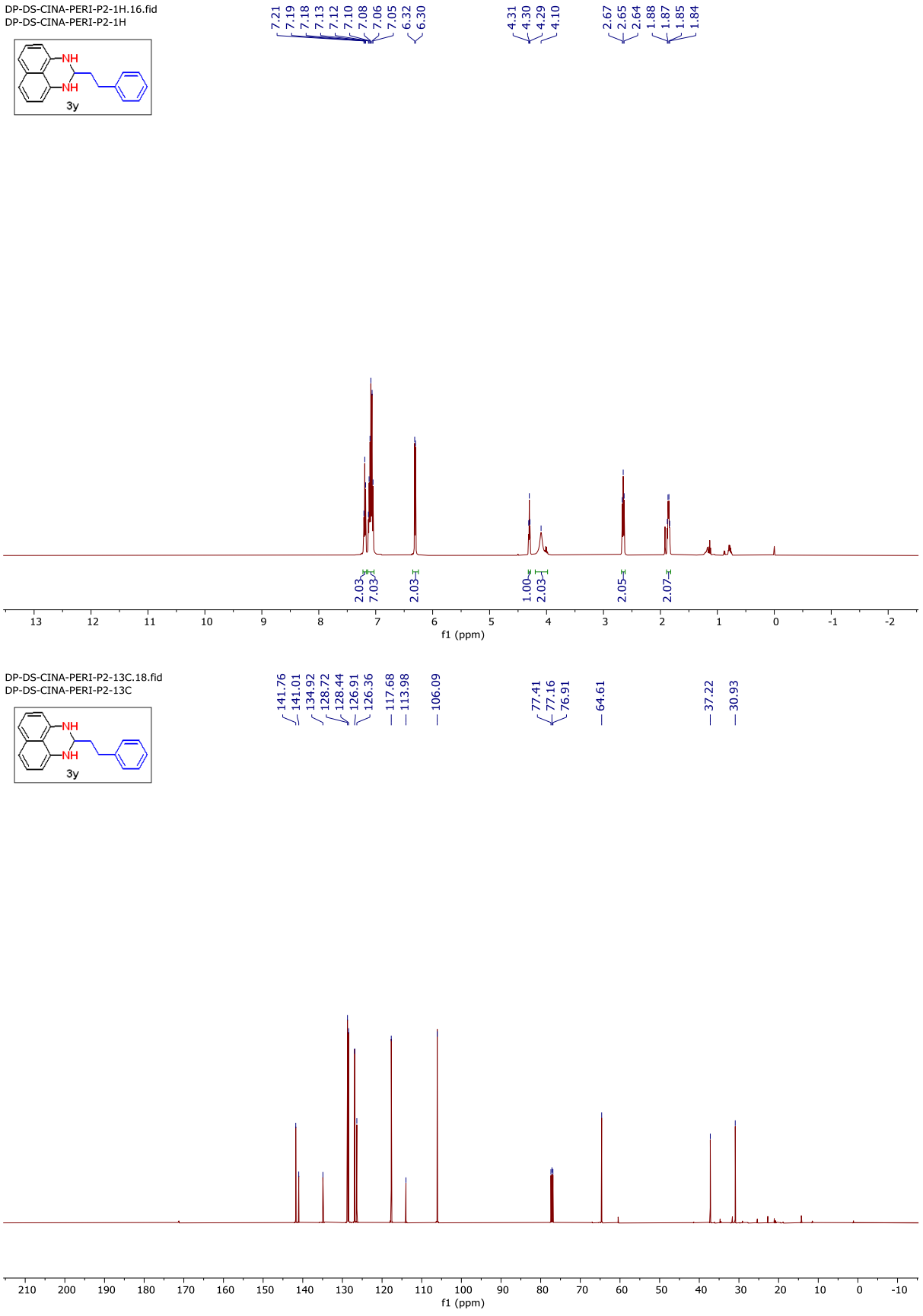


Figure S40. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-phenethyl-2,3-dihydro-1*H*-perimidine (3y)** in $CDCl_3$.

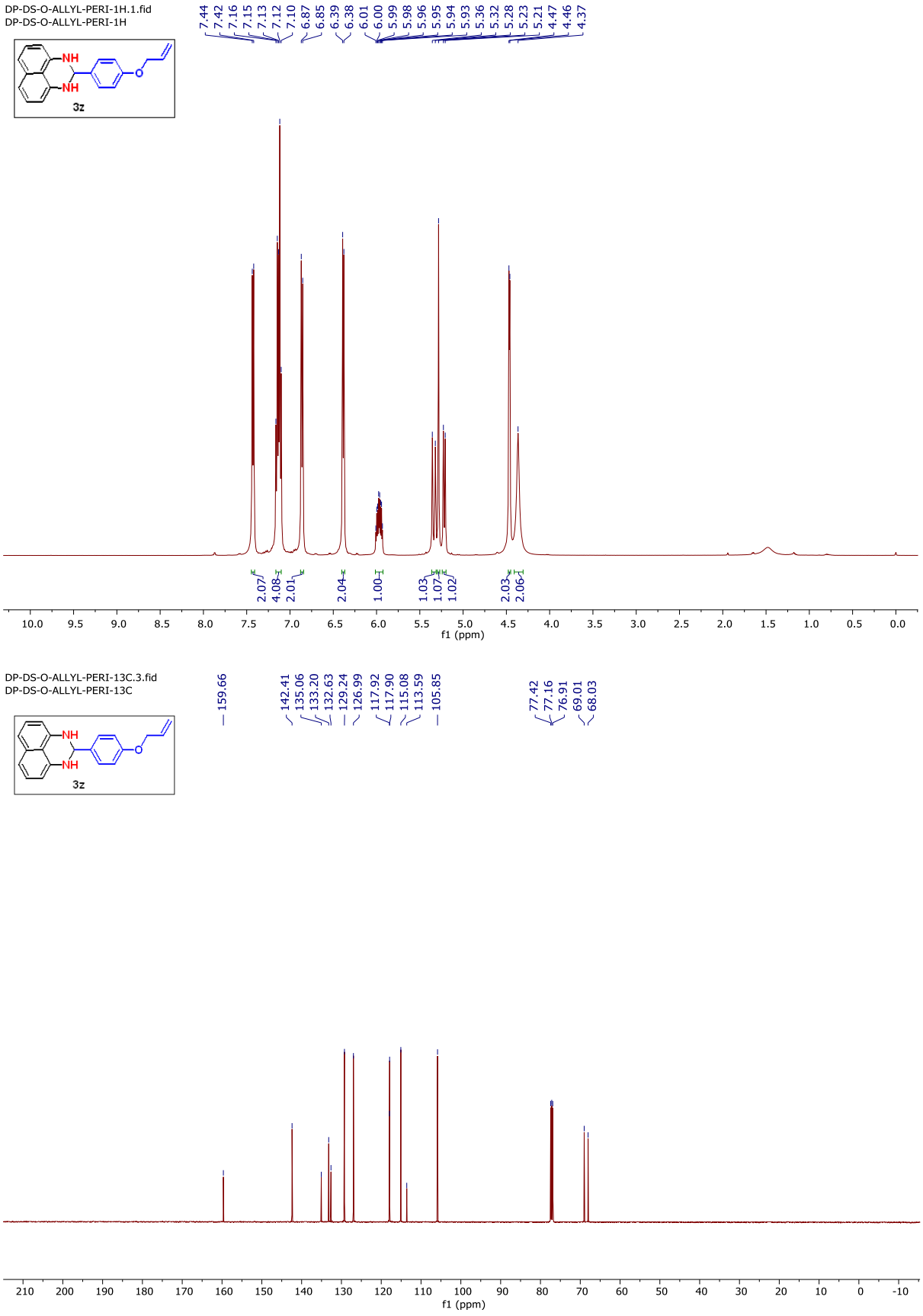


Figure S41. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-(allyloxy)phenyl)-2,3-dihydro-1*H*-perimidine (3z)** in $CDCl_3$.

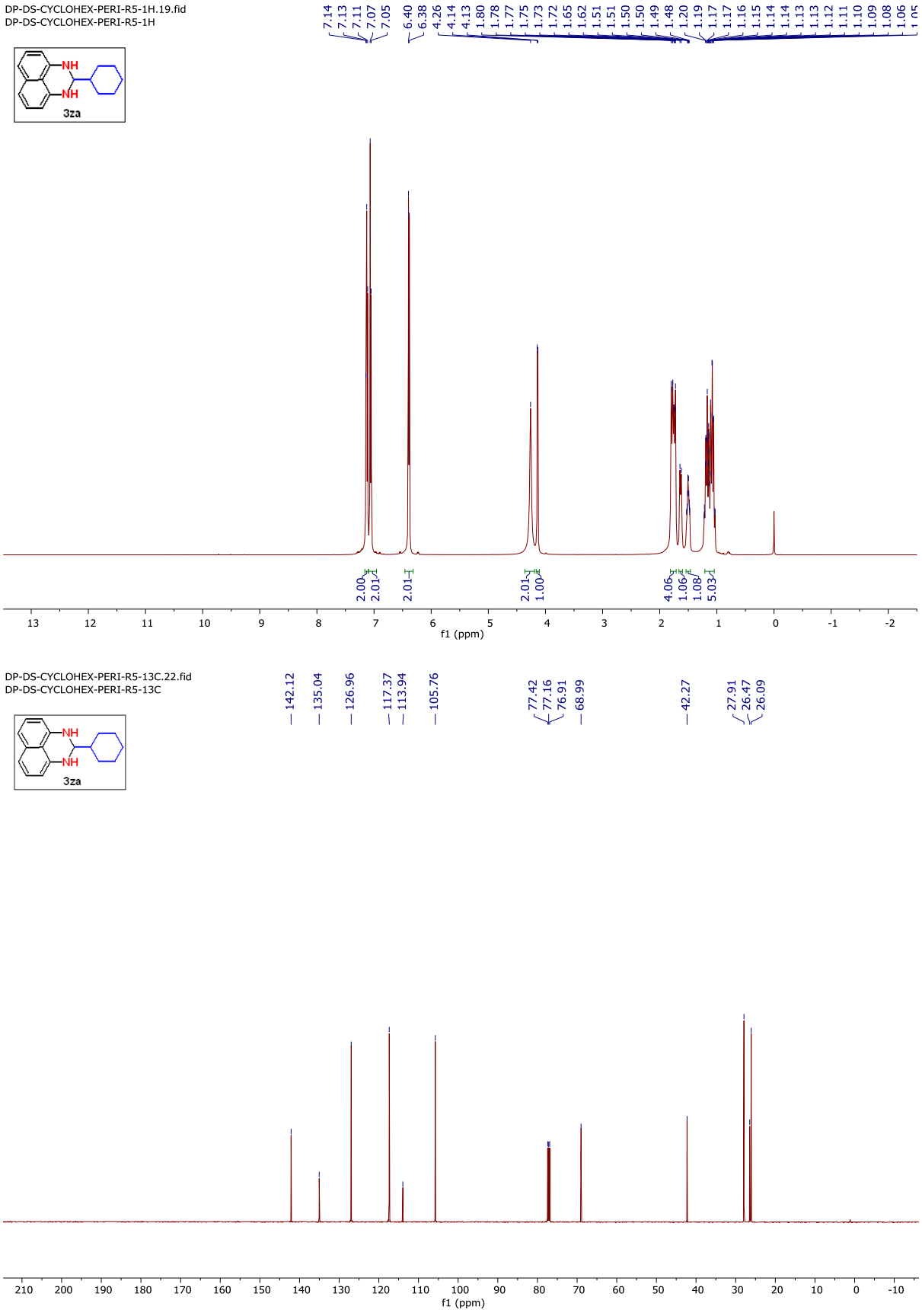


Figure S42. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-cyclohexyl-2,3-dihydro-1*H*-perimidine (3za)** in $CDCl_3$.

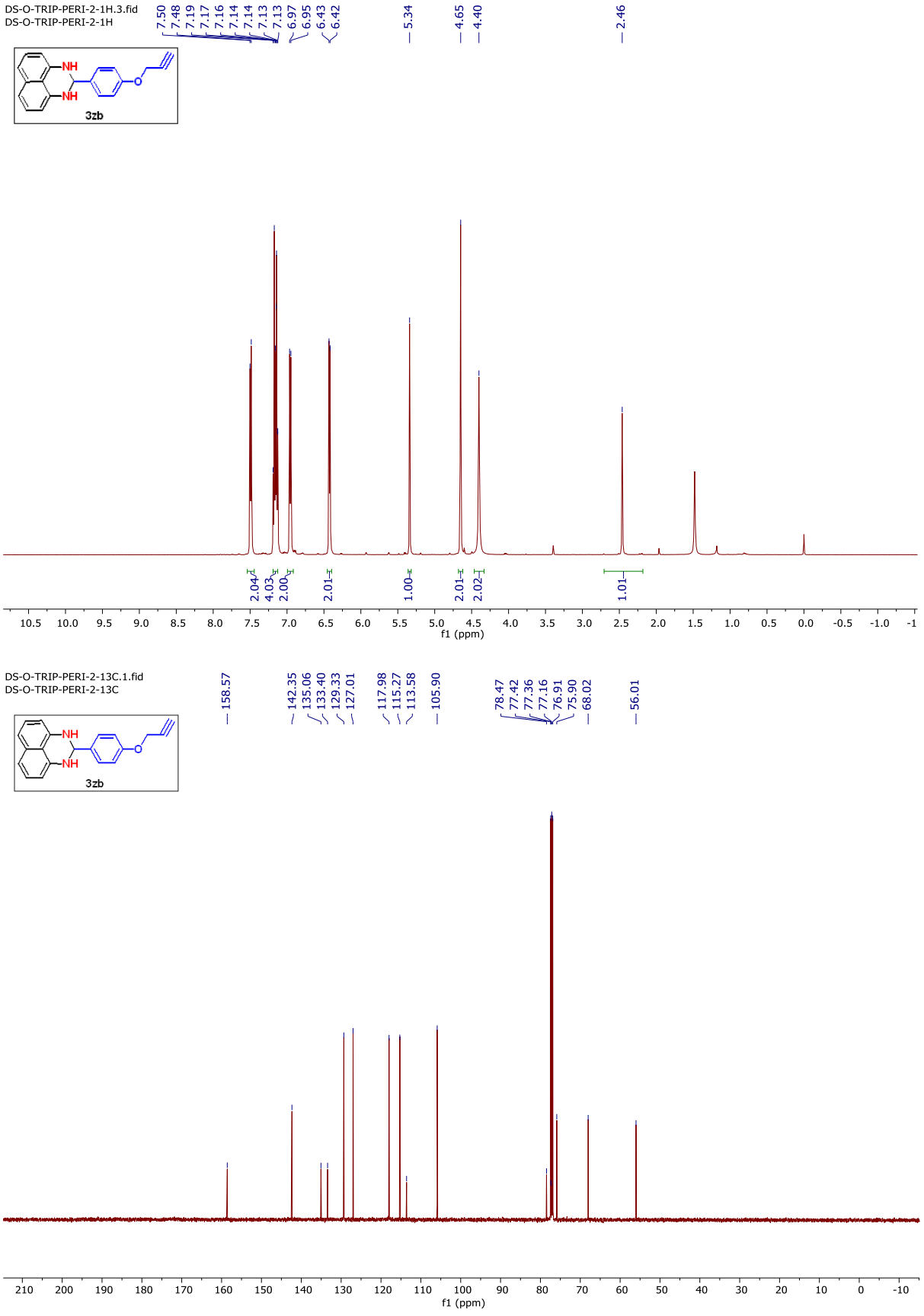


Figure S43. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-(prop-2-yn-1-yloxy)phenyl)-2,3-dihydro-1*H*-perimidine (3zb)** in $CDCl_3$.

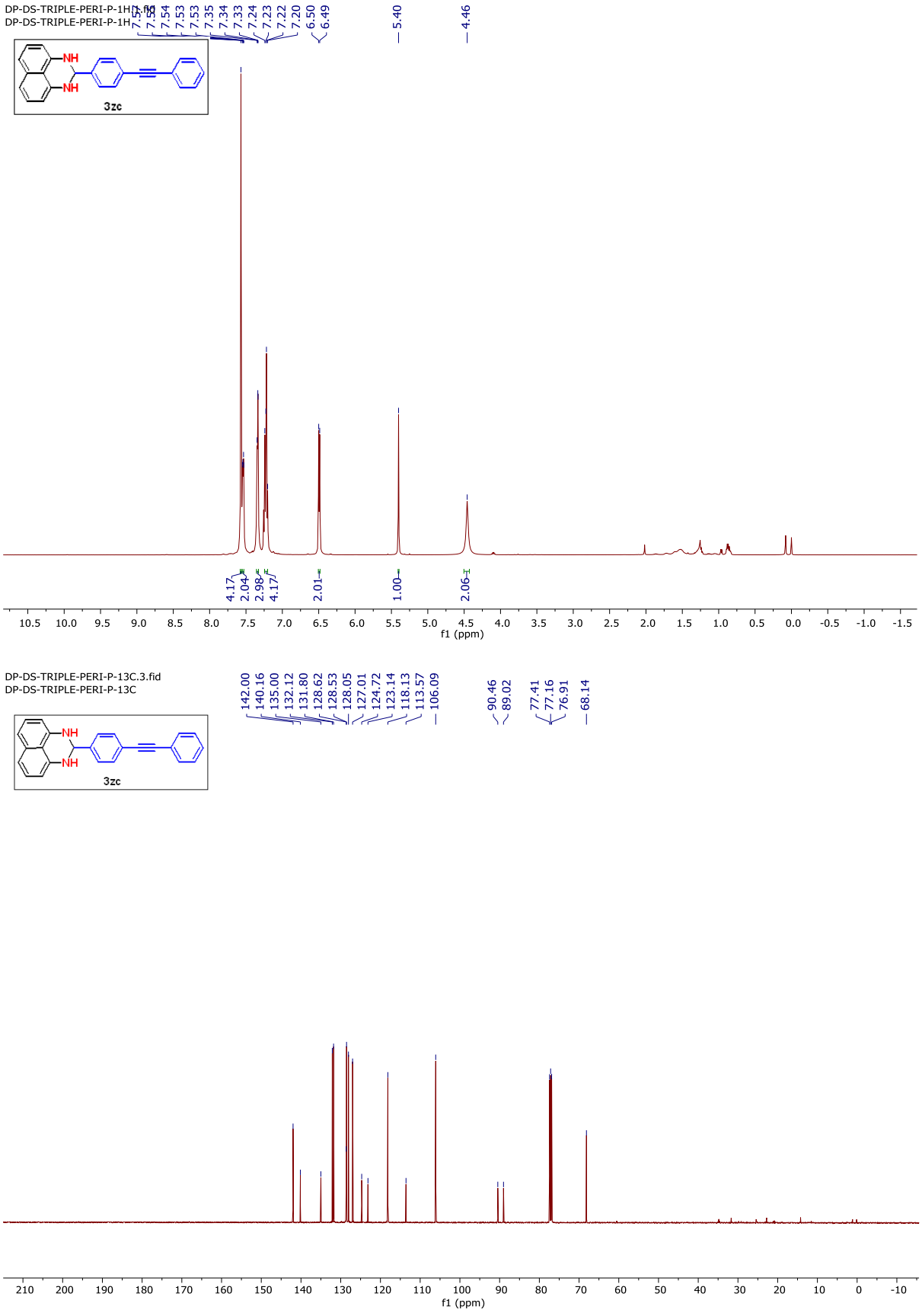


Figure S44. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(4-(phenylethynyl)phenyl)-2,3-dihydro-1*H*-perimidine (3zc)** in $CDCl_3$.

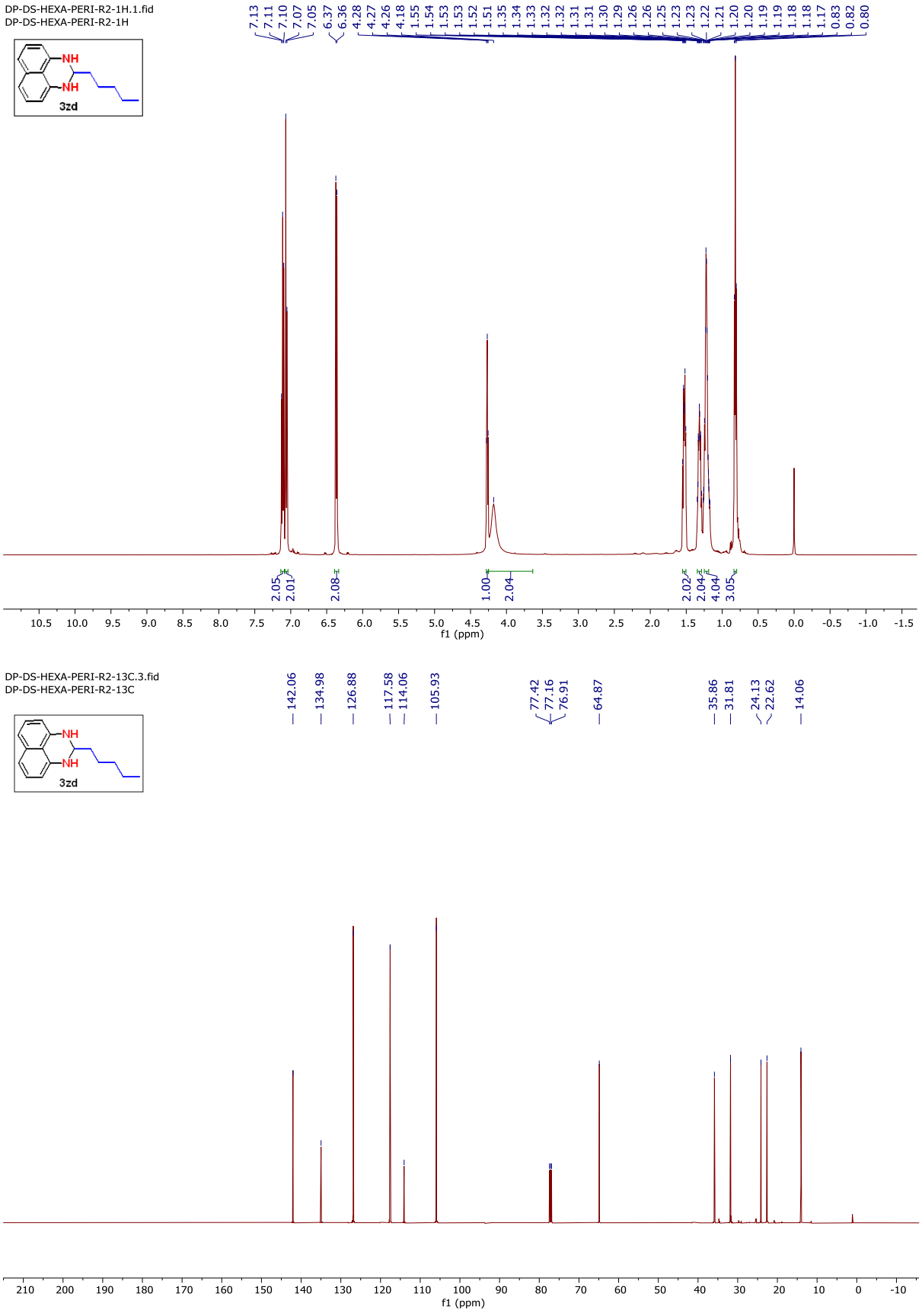


Figure S45. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-pentyl-2,3-dihydro-1*H*-perimidine (3zd)** in $CDCl_3$.

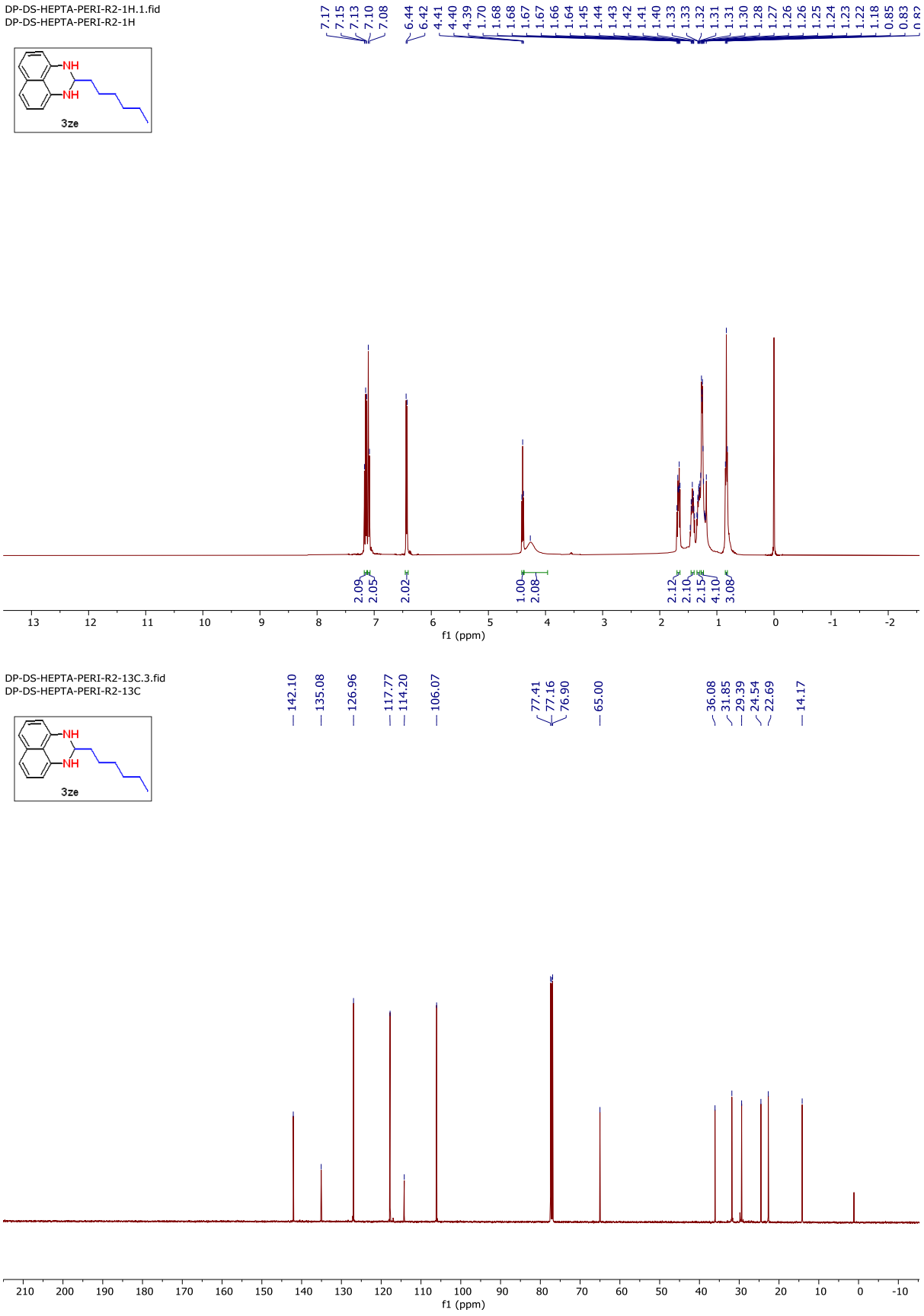


Figure S46. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-hexyl-2,3-dihydro-1*H*-perimidine (3ze)** in $CDCl_3$.

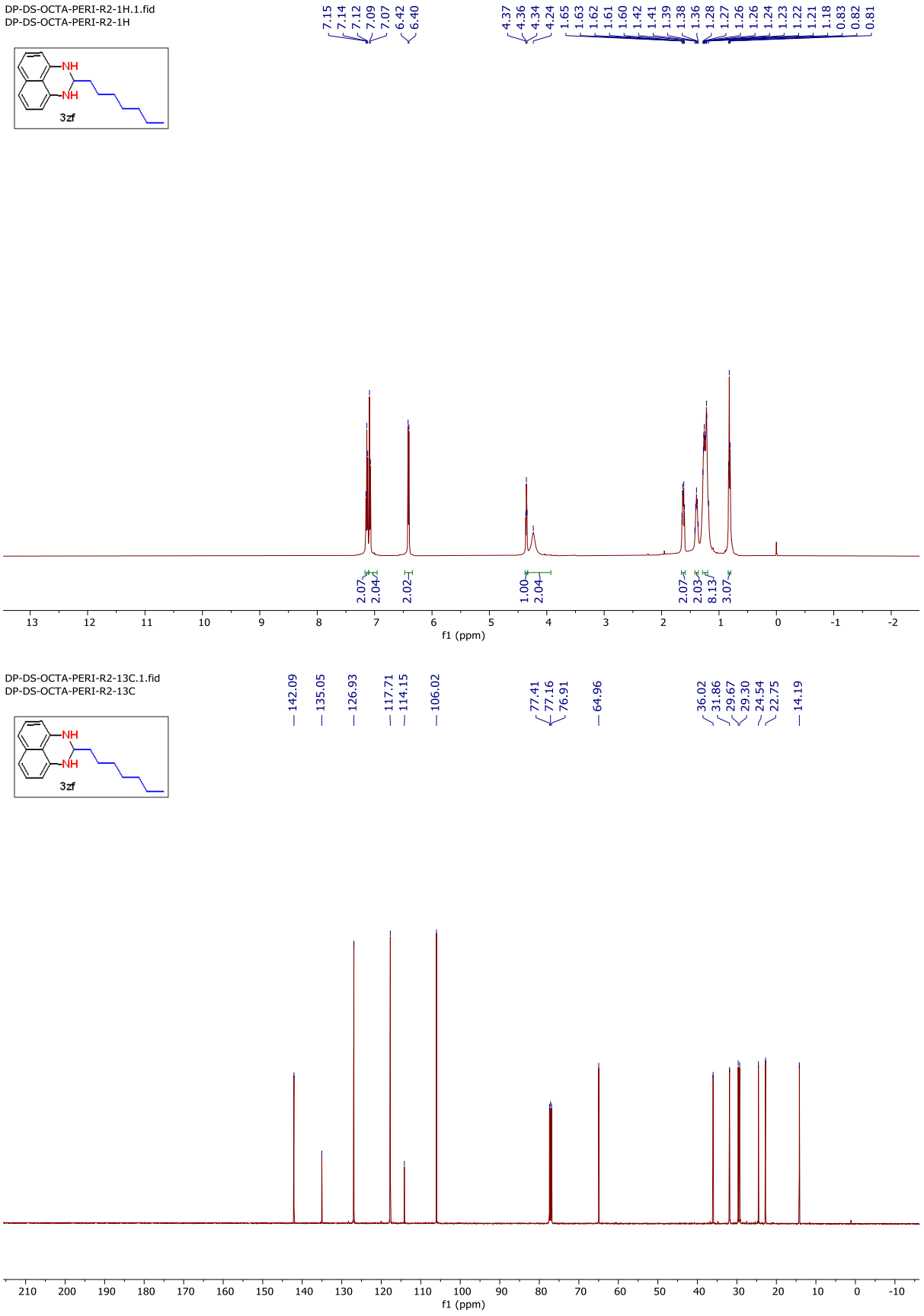


Figure S47. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-heptyl-2,3-dihydro-1*H*-perimidine (3zf)** in $CDCl_3$.

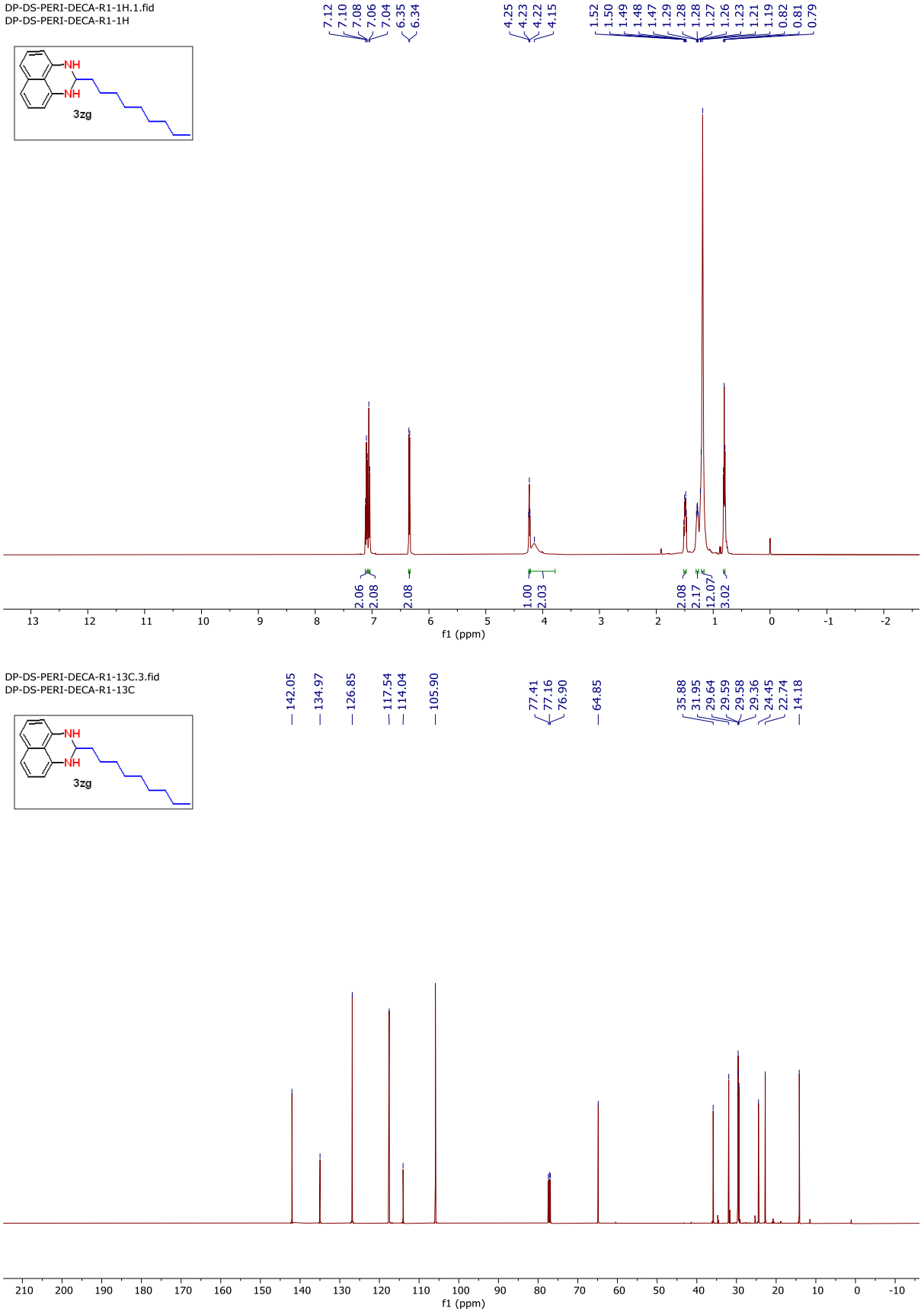


Figure S48. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-nonyl-2,3-dihydro-1*H*-perimidine (3zg)** in $CDCl_3$.

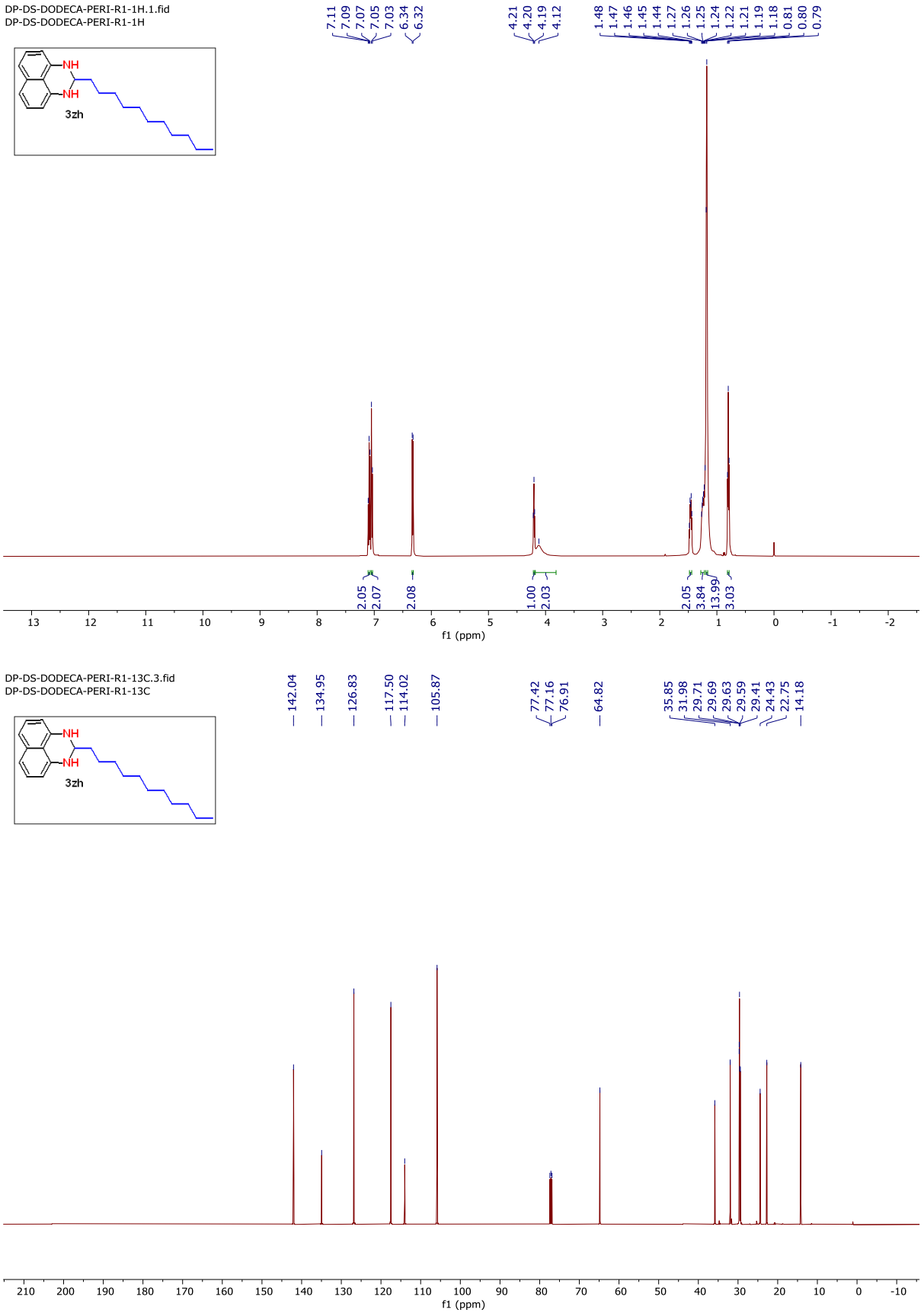


Figure S49. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-undecyl-2,3-dihydro-1*H*-perimidine (3zh)** in $CDCl_3$.

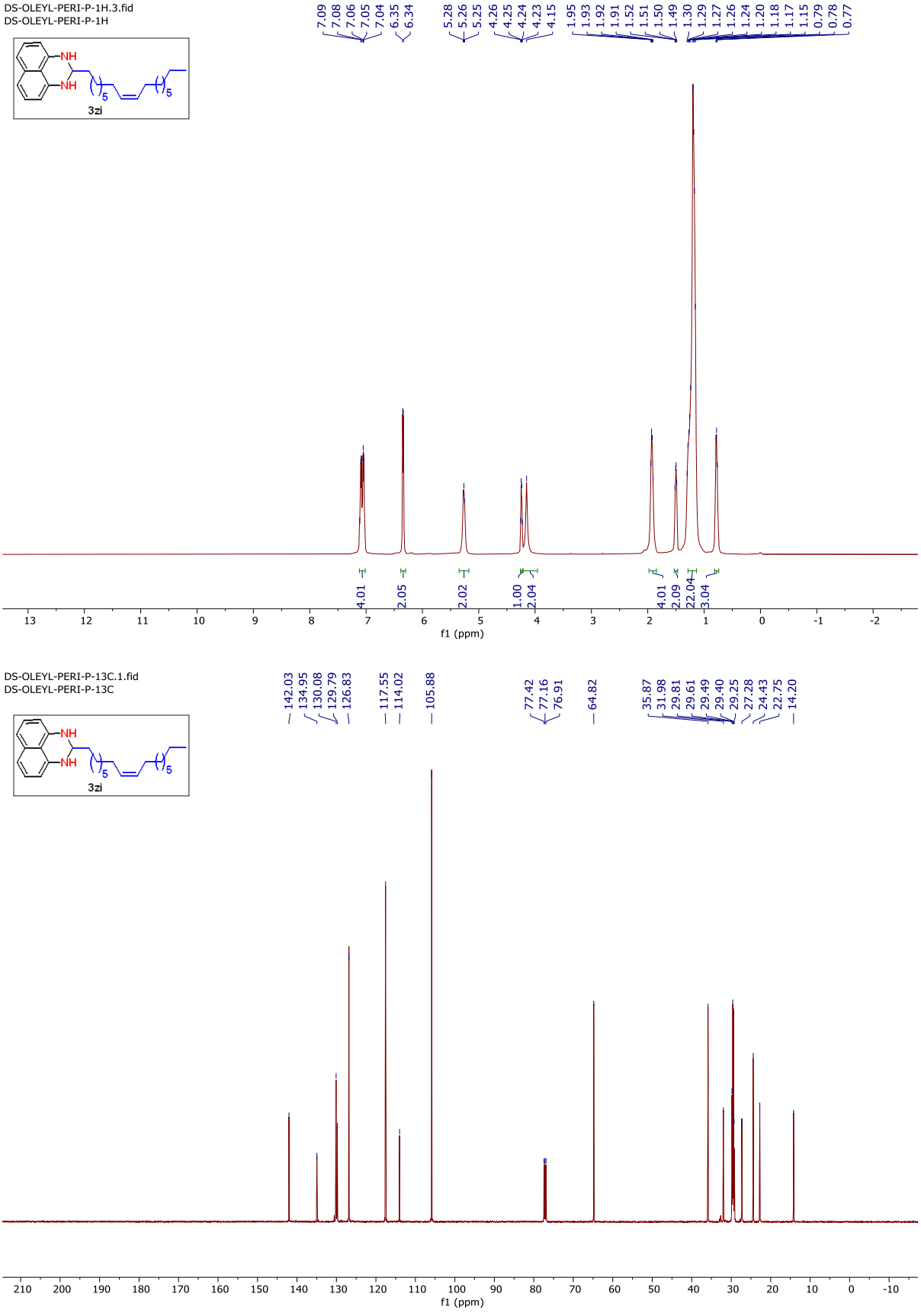


Figure S50. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **(*Z*)-2-(heptadec-8-en-1-yl)-2,3-dihydro-1*H*-perimidine (3zi)** in $CDCl_3$.

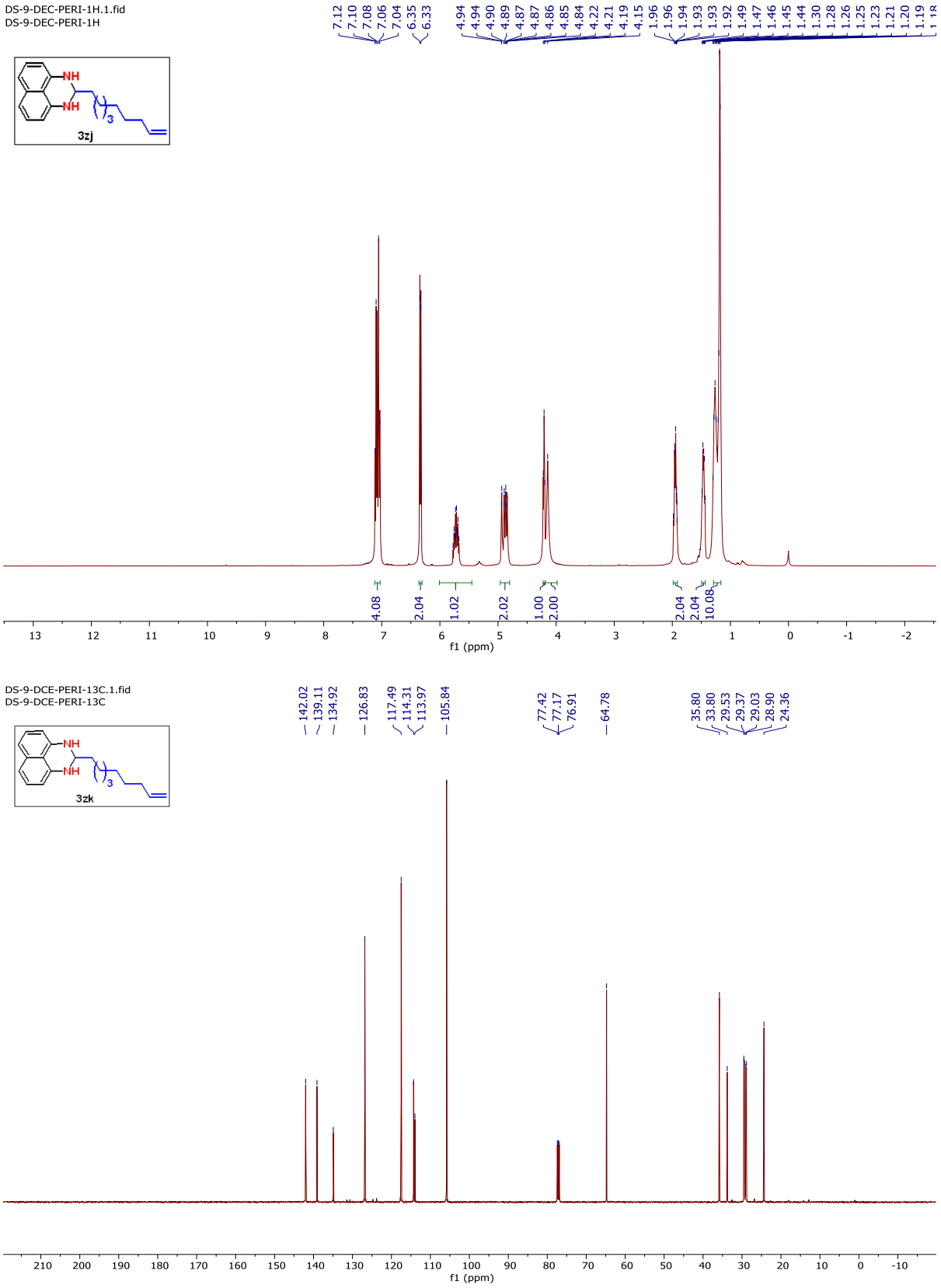


Figure S51. ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **2-(non-8-en-1-yl)-2,3-dihydro-1*H*-perimidine (3zj)** in $CDCl_3$.

12. References:

1. (a) D. Pal, A. Mondal, R. Sarmah, D. Srimani, *Org. Lett.* **2024**, *26*, 514−518; (b)S. A. Stoian, Y. -R. Peng, C. C. Beedle, Y.-J. Chung, G.-H. Lee, E.-C. Yang, S. Hil, *Inorg. Chem*. **2017**, *56*, 10861−10874; (c) V. A. Rao, P. C. Jain, N. Anand, R. C. Srimal, P. R. Dua, *J. Med. Chem.* **1970**, *13*, 516–522.

2. T. Lv, J. Wu, F. Kang, T. Wang, B. Wan, J.-J. Lu, Y. Zhang, Z. Huang, *Org. Lett.* **2018**, *20*, 2164−2167.

3. C.-R. Elie, A. Hébert, M. Charbonneau, A. Haiunb, A. R. Schmitzer, *Org. Biomol. Chem.* **2013**, *11*, 923–928.

4. B. Chatterjee, C. Gunanathan, *Org. Lett.* **2015**, *17*, 4794−4797.

5. K. Das, A. Mondal, D. Pal, H. K. Srivastava, D. Srimani, *Organometallics* **2019**, *38*, 1815−1825.

6. B. Zhang, J. Li, H. Zhu, X.-F. Xia, D. Wang, *Catal. Lett.* **2023**, *153*, 2388–2397.

7. M. Mannarsamy, M. Nandeshwar, G. Muduli, G. Prabusankar, *Chem.–Asian J.* **2022**, *17*, e202200594.

8. J. Soni, A. Sethiya, N. Sahiba, D. Joshi, S. Agarwal, *Polycyclic. Aromat. Compd.* **2023**, *43*, 674–685.

9. Z. Sadri, F. K. Behbahani, E. Keshmirizadeh, *Polycyclic Aromat. Compd.* **2023**, *43*, 1898−1913.

10. A. Mobinikhaledi, N. Forughifar, N. Bassaki, *Turk. J. Chem.* **2009**, *33*, 555-560.

11. Z. Petkova, R. Rusew, S. Bakalova, B. Shivachev, V. Kurteva, *Molbank* **2023**, *2023*, M1587.

12. C.-C. Chou, H.-J. Liu, L. H.-C. Chao, H.-B. Syu, T.-S. Kuo, *Polyhedron* **2012,** *37*, 60–65.

13. K. Bahrami, S. Saleh, *Synth. React. Inorg., Met.-Org., NanoMet. Chem.* **2016**, *46*, 852–856.

14. R. Parui, N. Zehraa, P. K. Iyer, *J. Mater. Chem. C* **2023**, *11*, 11243–11251.

15. S. Ernst, J. Mistol, B. Senns, L. Hennig, D. Keil, *Dyes Pigm.* **2018**, *154*, 216– 228.

16. R.F. Malherbe, US Patent 4389321 (1983).