Supporting information

For

Homogenization Offers Access to Quinoxalines in Minutes: A Solvent-free, Catalyst-free Protocol with Near-zero E-factor

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Table of contents, spectral data, and copies of spectra

General experimental details: The chemicals were obtained from Sigma-Aldrich, Alfa Aesar, or TCI India and used directly without further purification. Common reagents and solvents of AR grade were obtained from local suppliers. The mechanochemical reactions were carried out in 2 mL homogenizing tubes made of polypropylene with 1 g of 2 mm SS ball in iRupt Jr, an indigenous mini-cell homogenizer (Neuation). The reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel aluminum plates (60F-254) using UV light (254 or 365 nm) to monitor the progress of the reactions. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (500 MHz) NMR instrument with $CDCl_3$ as the solvent. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H and ^{13}C NMR spectroscopy. Chemical shifts are reported in parts per million (δ) units. Coupling constants are reported in hertz (Hz). Standard abbreviations are used for representing the multiplicity of NMR peaks, such as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet). The melting point was measured in the EZ-Melt, Automatic Melting Point Apparatus (Stanford Research System). Mass spectra were recorded on a single quad LC-MS, Agilent using electrospray ionization (ESI) as an ion source.

General procedure for the synthesis of quinoxalines: *o*-Diaminoarene (**1**, 0.5 mmol) and 1,2-dicarbonyl compound (**2**, 0.5 mmol) was taken in a 2 mL polypropylene tube containing 1 g of 2 mm SS balls. The reaction was set to a speed of 4000 RPM in iRupt Jr instrument and was homogenized for 1 x 3 min with intermittent mixing (if required). The progress of the reaction was monitored by TLC. The product was taken out from the tube, the balls were separated using a magnetic retriever whenever possible, and the solid mass was air-dried to afford the corresponding quinoxaline derivative (**3**).

In selective cases, as mentioned in Table 2, the crude product was subjected to flash chromatography (silica gel, 230-400 mesh) and eluted by 10% EtOAc in petroleum ether to afford the pure product (**3**).

Procedure for scale-up: *o*-Diaminoarene (2.5 mmol) and 1,2-dicarbonyl (2.5 mmol) were taken in a 2 mL homogenizing tube containing 1 g of 2 mm SS balls. The reaction was set to a speed of 4000 RPM in the iRupt Jr instrument and was homogenized for 3 min. The product was isolated, as mentioned before.

Reaction monitoring by solid-state infrared spectroscopy

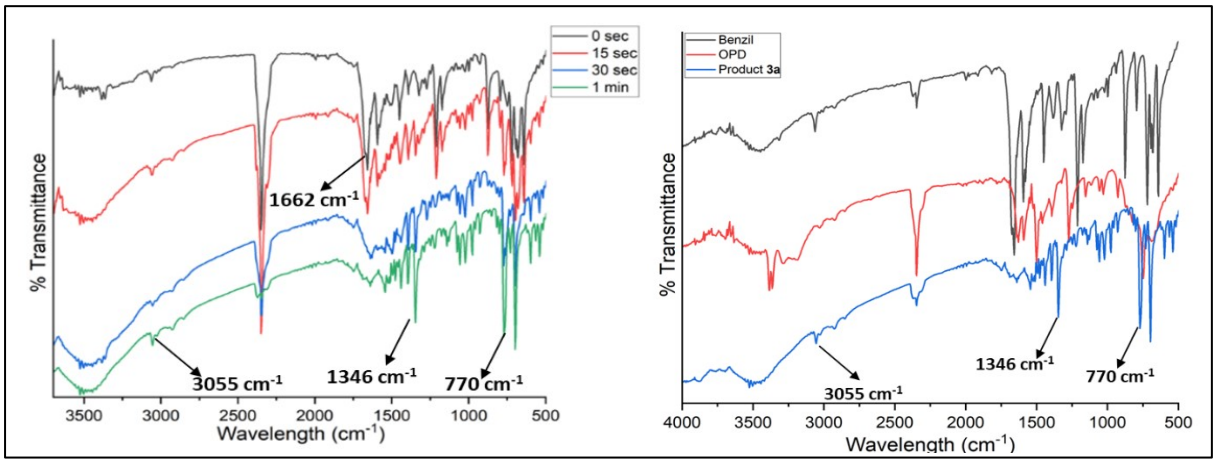


Figure S1. Monitoring of the reaction mixture in solid state by time-scale infrared spectroscopy. The disappearance of the carbonyl peak at 1662 cm^{-1} and the gradual increase of the signature peaks at 1346, and 770 cm^{-1} just after 30 sec indicates the formation of **3a.**

Schematic representation of high-throughput synthesis of quinoxalines

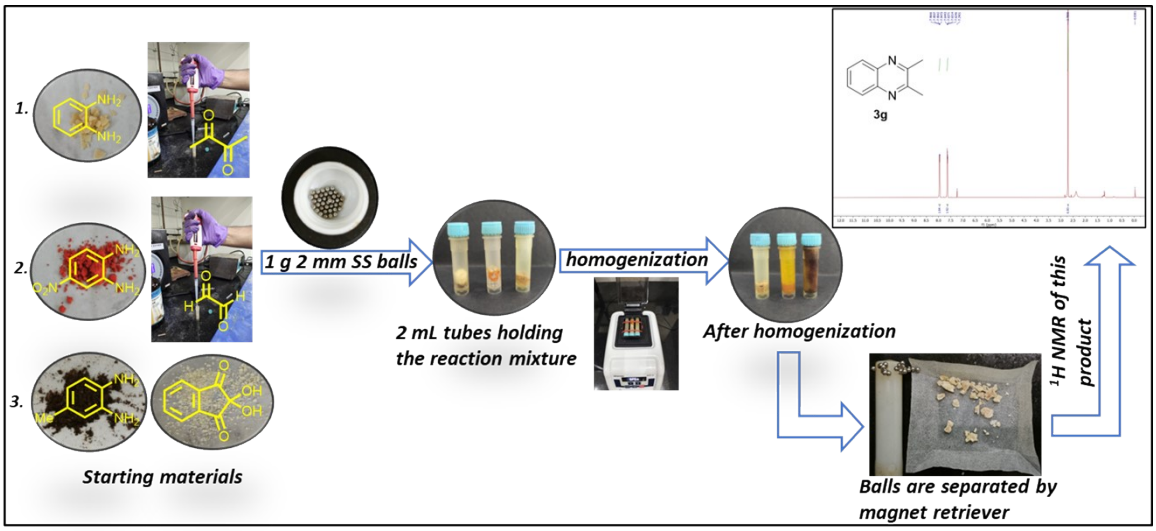
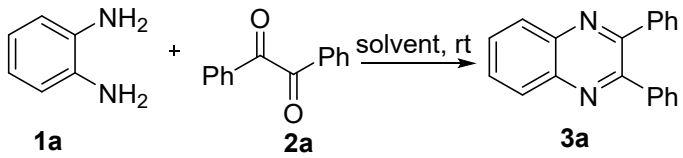


Figure S2. Schematic representation of reaction set-up for semi high-throughput synthesis of quinoxalines using homogenizer.

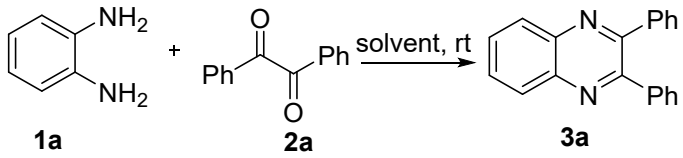
Table S1: Comparison with solution phase:



Entry	Solvent	Time (min)	Yield (%)[b]	% recovery of 2
1	Neat	120	11	69
2	Acetonitrile	120	82	12
3	Ethanol	60	91	--
4	Chloroform	120	68	18
5	Tetrahydrofuran	120	62	24

[a]In each case, 0.5 mmol each of **1a** and **2a** are taken in 2 mL of solvent (other than entry 1) and the mixture was stirred at room temperature. [b]All are isolated yields.

Table S2: Comparative study of quinoxaline synthesis (selected methods)[a]



1a **2a** **3a**

Entry	Media	Condition	Catalyst	Time (min)	Yield (%)	E-factor[b]	Eco-scale	Reference
Conventional solution phase								
1	CH_3CN	rt	Iodine	3	98	1.6	89	1
2	Ethanol	rt	$CuSO_4.5H_2O$	8	96	8.8	97	2
3	DMSO	rt	Iodine	35	95	4.2	97	3
4	Ethanol	rt	$MnCl_2$	17	94	9	96	4
Green-protocols								
5	Water	rt	Itaconic acid	60	96	0.2	97	5
6	Solid phase	heating (100 °C)	CuO@g-C_3N_4	3	87	0.3	89	6
7	Water	ultrasonication	-	0.8	98	0.1[c]	96	7
8	Glycerol	microwave	-	3	93	9.7	82	8
9	Neat	**homogenizer**	**-**	**3**	**99**	**0.01**	**97.5**	**Our work**

[a] Unless otherwise noted the comparisons are done taking **3a** as the model product. [b]Water formed as the side product of the reaction was not considered as waste during the E-factor calculation. [c] Ninhydrin was used instead of benzil to calculate the E-factor and eco-scale scores.

Table S3: Mechanochemical methods using diamine and dicarbonyl[a]

Entry	Mechanical technique	Catalyst	Milling auxiliary	Milling condition /time	Isolation/ Purification	Yield (%)	E-factor	Reference
1	Hand grinding	-	EtOH (LAG)	10 min	Recrystallization (EtOH)	95	0.16	9
2	Hand grinding	-	SiO_2	15 min	Recrystallization (EtOH)	94	4	10
3	Hand grinding	nano-kaolin/ BF_3/ Fe_3O_4	-	20 min	Recrystallization (EtOH)	98	0.26	11
4	Hand grinding	Acetic acid	-	10 min	Recrystallization (acetone)	92[c]	0.34	12
5	Hand grinding	-	Al_2O_3	10 min	Chromatography	98	1.96	13

6	Planetary ball mill	$La(DS)_3$	NaCl	600 RPM, 30 min	Chromato-graphy	99	2.1	14
7	Mixer mill	TCCA, *p*-TSA, K_2CO_3	-	20 Hz, 10 h	Chromato-graphy	78	1.8	15
8	**Homoge-nizer**	**-**	**-**	**4000 RPM, 3 min**	**no work-up, no purification**	**99**	**0.01**	**Our work**

[a] Unless otherwise noted the comparisons are done taking **3a** as the model product. [b]Water formed as the side product of the reaction was not considered as waste during the E-factor calculation. [c] Ninhydrin was used instead of benzil to calculate the E-factor. [d]The calculations are done using 4-bromoacetophenone and OPD as the reactants.

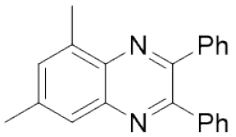
For a typical E-factor calculation:

Parameters	Values	Remarks
%Yield	99	Calculated for **3a**
Wt. of generated waste (mg)	3	
Wt. of end product (mg)	279	
E-factor = Wt. of generated waste/Wt. of end product	0.01	

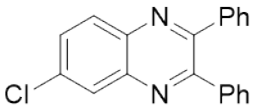
For a typical Ecoscale score calculation:

Parameters	Penalty points	Remarks
%Yield = (100-%Yield)/2	0.5	Calculated for **3a**
Price of the reaction component	0	Inexpensive (<10US$)
Technical setup	2	Unconventional activation technique (Homogenizer)
Temperature/Time	0	Room temperature reaction/<1 h
Workup and purification	0	None
Sum of penalty points	**2.5**	
Eco-scale score (100-Sum of penalty)	**97.5**	

Spectral characterization



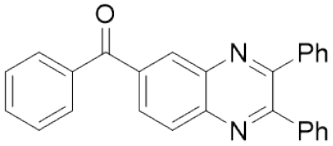
3c



3d

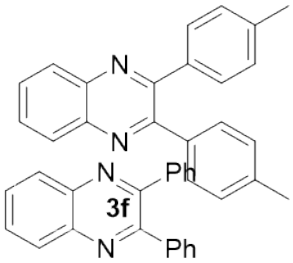
2,3-Diphenylquinoxaline (3a):[9] White solid, 140 mg (99%) m.p.: 124-125 °C (Lit. m.p.: 126-127 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.30-7.34 (m, 6H), 7.49-7.51 (m, 4H), 7.74-7.76 (m, 2H), 8.15-8.17 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 128.3, 128.8, 129.2, 129.8, 130.0, 139.1, 141.2, 153.5. ESI-MS: *m/z* 283 $[M + H]^+$.

6-Methyl-2,3-diphenylquinoxaline (3b):[9] Light brown solid; 147 mg (99%), m.p.: 114-116 °C (Lit. m.p.: 118-119 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.59 (s, 3H), 7.28-7.34 (m, 6H), 7.49 (d, J = 6.8 Hz, 4H), 7.58 (dd, J_1 = 1.9 Hz, J_2 = 8.5 Hz, 1H), 7.93 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 21.9, 128.0, 128.2, 128.6, 128.7, 129.8, 129.9, 132.3, 139.2, 139.7, 140.5, 141.3, 152.6, 153.3; ESI-MS: *m/z* 297 $[M + H]^+$.



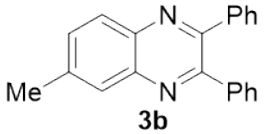
3e

5,7-Dimethyl-2,3-diphenylquinoxaline (3c):[9] Off-white solid, 153 mg (99%), m.p.: 94-96 °C (Lit. m.p.: 94-96 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.54 (s, 3H), 2.79 (s, 3H), 7.29-7.32 (m, 6H), 7.42 (s, 1H), 7.48-7.54 (m, 4H), 7.75 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 17.0, 21.9, 125.7, 128.0, 128.2, 128.5, 128.6, 129.8, 130.1, 132.2, 137.0, 138.9, 139.5, 139.6, 140.1, 141.3, 150.9, 152.7; ESI-MS: *m/z* 311 $[M + H]^+$.



3a

6-Chloro-2,3-diphenylquinoxaline (3d):[9] White solid, 157 mg (99%), m.p.: 119-121 °C (Lit. m.p.: 124-125 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.30-7.36 (m, 6H), 7.48 (d, J =7.4 Hz, 4H), 7.69 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.9 Hz, 1H), 8.15 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 128.1, 128.3, 129.0, 129.1, 129.81, 129.85, 130.4, 130.9, 135.6, 138.6, 138.7, 139.7, 141.5, 153.6, 154.3; ESI-MS: *m/z* 317 $[M + H]^+$.



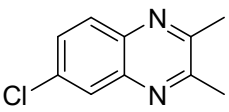
3b

6-Benzoyl-2,3-diphenylquinoxaline (3e):[10] White solid, 183 mg (95%), m.p.: 149-151 °C (Lit. m.p.: 147-148 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.30-7.39 (m, 6H), 7.49-7.54 (m, 6H), 7.61 (t, J = 7.5 Hz, 1H), 7.89 (d, J = 7.3 Hz, 2H), 8.23-8.28 (m, 2H), 8.52 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 128.4, 128.5, 129.1, 129.3, 129.7, 129.8, 129.9, 129.92, 130.1, 132.4, 132.8, 137.2, 138.3, 138.61, 138.64, 140.2, 143.0, 154.6, 155.1, 195.8; ESI-MS: *m/z* 387 $[M + H]^+$.

2,3-Di-*p*-tolylquinoxaline (3f):[9] White solid, 153 mg (99%), m.p.: 146-147 °C (Lit. m.p.: 146-147 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.35 (s, 6H), 7.13 (d, J = 7.8 Hz, 4H), 7.41 (d, J =

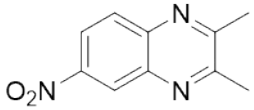
8.1 Hz, 4H), 7.72 (dd, J_1 = 3.5 Hz, J_2 = 6.5 Hz, 2H), 8.13 (dd, J_1 = 3.5 Hz, J_2 = 6.5 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 21.3, 129.0, 129.1, 129.6, 129.7, 136.3, 138.7, 141.1, 153.5; ESI-MS: *m/z* 311 $[M + H]^+$.

2,3-Dimethylquinoxaline (3g):[9] Light brown solid, 78 mg (99%), m.p.: 92-94 °C (Lit. m.p.: 105-106 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.70 (s, 6H), 7.63 (dd, J_1 = 3.4 Hz, J_2 = 6.4 Hz, 2H), 7.95 (dd, J_1 = 3.6 Hz, J_2 = 6.4 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 23.1, 128.2, 128.9, 140.9, 153.4; ESI-MS: *m/z* 159 $[M + H]^+$.

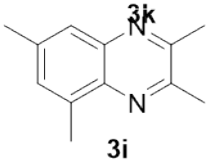


3j

2,3,5-Trimethylquinoxaline (3h):[9] Brown solid, 85 mg (99%), m.p.: 90-92 °C (Lit. m.p.: 90-91 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.51 (s, 3H), 2.66 (s, 6H), 7.44 (dd, J_1 = 2.0 Hz, J_2 = 8.6 Hz, 1H), 7.70 (s, 1H), 7.82 (d, J = 8.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, CDCl3): δ (ppm) 21.7, 23.0, 23.1, 127.2, 127.8, 131.0, 139.1, 139.4, 141.1, 152.4, 153.3; ESI-MS: *m/z* 173 $[M + H]^+$.

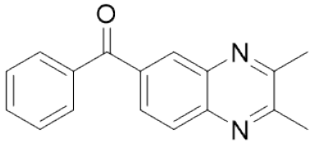


3k



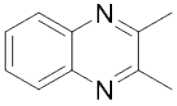
3i

2,3,5,7-Tetramethylquinoxaline (3i):[9] White solid, 92 mg (99%), m.p.: 68-69 °C (Lit. m.p.: 68-69 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.48 (s, 3H), 2.69 (s, 5H), 2.71 (s, 3H), 7.32 (s, 1H), 7.64 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 17.0, 21.7, 22.4, 23.1, 124.2, 131.5, 136.2, 139.0, 139.4, 151.4, 151.9; ESI-MS: *m/z* 187 $[M + H]^+$.



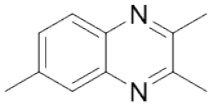
3l

6-Chloro-2,3-dimethylquinoxaline (3j):[9] Brown solid, 95 mg (99%), m.p.: 84-86 °C (Lit. m.p. : 84–86 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.69 (s, 6H), 7.57 (dd, J_1 = 2.3 Hz, J_2 = 8.9 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 2.4 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 23.1, 23.2, 127.3, 129.5, 129.8, 134.4, 139.5, 141.4, 153.7, 154.5; ESI-MS: *m/z* 193 $[M + H]^+$.



3g

2,3-Dimethyl-6-nitroquinoxaline (3k):[9] Brown solid, 100 mg (99%), m.p.: 134-135 °C (Lit. m.p: 135–136 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.76 (s, 6H), 8.06 (dd, J_1 = 2.8 Hz, J_2 = 9.1 Hz, 1H), 8.38 (dt, J_1 = 3.0 Hz, J_2 = 9.1 Hz, 1H), 8.84 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 23.3, 23.5, 122.3, 124.8, 129.9, 139.9, 143.7, 147.1, 156.3, 157.2; ESI-MS: *m/z* 204 $[M + H]^+$.

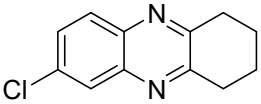


3h

6-Benzoyl-2,3-Dimethyl-quinoxaline (3l):[16] Yellow solid, 126 mg (96%) m.p.: 122-124 °C (Lit. m.p.: 107-110 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.70 (s, 3H), 2.73 (s, 3H), 7.46 (t, J = 7.6 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.82 (d, J = 7.9 Hz, 2H), 8.04 (d, J = 8.7 Hz, 1H), 8.11 (dd, J_1 = 1.8 Hz, J_2 = 8.7 Hz, 1H), 8.31 (s, 1H); ^{13}C {^{1}H} NMR

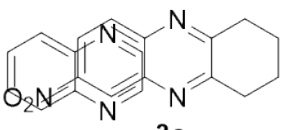
(125 MHz, $CDCl_3$): δ (ppm) 23.2, 23.4, 128.4, 128.8, 128.9, 130.0, 131.7, 132.7, 137.2, 137.3, 140.0, 142.9, 154.8, 155.7, 195.9. ESI-MS: *m/z* 263 $[M + H]^+$.

1,2,3,4-Tetrahydrophenazine (3m):[5] Brown solid, 98 mg (98%), m.p.: 87-88 °C (Lit. m.p.: 90 °C) ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.95 (s, 4H), 3.07 (s, 4H), 7.55-7.58 (m, 2H), 7.86-7.90 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 22.6, 33.02, 33.04, 118.2, 128.1, 128.2, 128.7, 128.8, 141.02, 141.03, 153.9, 154.0. ESI-MS: *m/z* 185 $[M + H]^+$.



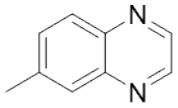
3p

7-Methyl-1,2,3,4-tetrahydrophenazine (3n):[5] Yellow solid, 95 mg (96%), m.p.: 88-90 °C (Lit. m.p.: 92 °C); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.97 (s, 4H), 2.50 (s, 3H), 3.08 (s, 4H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.68 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 21.7, 22.81, 22.83, 33.0, 33.1, 127.1, 127.7, 131.2, 139.2, 139.6, 141.2, 153.0, 153.9. ESI-MS: *m/z* 199 $[M + H]^+$.



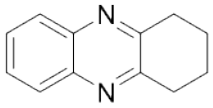
3q **3o**

7-Nitro-1,2,3,4-tetrahydrophenazine (3o):[5] Light brown solid, 106 mg (93%), m.p.: 103-105 °C (Lit. m.p.: 101 °C)**;** ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.04 (t, *J* = 3.6 Hz, 4H), 3.17 (t, *J* = 3.0 Hz, 4H), 8.04 (d, *J* = 9.1 Hz, 1H), 8.38 (dd, J_1 = 2.7 Hz, J_2 = 9.1 Hz, 1H), 8.82 (d, *J* = 2.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 22.4, 33.2, 33.5, 122.3, 124.9, 129.9, 139.9, 143.7, 147.1, 157.0, 158.0; ESI-MS: *m/z* 230 $[M + H]^+$.



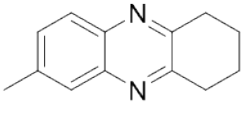
3r

7-Chloro-1,2,3,4-tetrahydrophenazine (3p):[5] Yellow solid, 102 mg (94%), m.p.: 91-93 °C (Lit. m.p.: 94 °C); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.00 (t, *J* = 3.6 Hz, 4H), 3.10-3.12 (m, 4H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.92 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 22.6, 22.7, 33.1, 33.2, 127.3, 129.6, 129.9, 134.5, 139.7, 141.4, 154.4, 155.2; ESI-MS: *m/z* 219 $[M + H]^+$.



3m

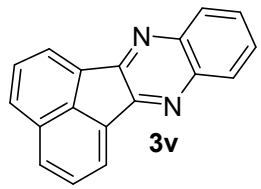
Quinoxaline (3q):[9] Light yellow liquid, 60 mg (92%); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.69 (dd, J_1 = 3.5 Hz, J_2 = 6.5 Hz, 2H), 8.03 (dd, J_1 = 3.6 Hz, J_2 = 6.5 Hz, 2H), 8.76 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 129.3, 129.9, 142.8, 144.8; ESI-MS: *m/z* 131 $[M + H]^+$.



3n

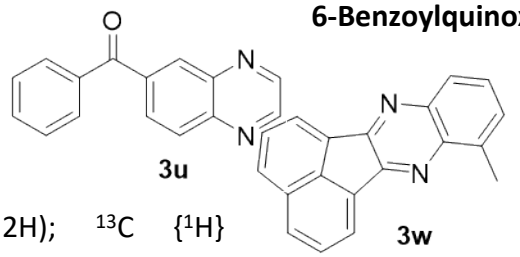
6-Methylquinoxaline (3r):[9] Colourless liquid, 68 mg (95%); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.55 (s, 3H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.82 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 8.74 (d, *J* = 11.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 21.8, 128.2, 128.9, 132.4, 140.6, 141.5, 143.0, 144.0, 144.8; ESI-MS: *m/z* 145 $[M + H]^+$.

6-Chloroquinoxaline (3s):[9] Off-white solid, 77 mg (94%), m.p.: 63-65 °C (Lit. m.p.: 62-64 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.68 (dd, J_1 = 2.4 Hz, J_2 = 11.3 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 8.07 (d, J = 2.4 Hz, 1H), 8.81 (dd, J_1 = 1.9 Hz, J_2 = 6.8 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 128.4, 130.7, 131.1, 135.9, 141.5, 143.2, 145.0, 145.7; ESI-MS: *m/z* 165 [M + H]$^+$.



3v

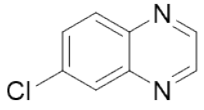
6-Nitroquinoxaline (3t):[9] Light yellow solid, 86 mg (98%), m.p.: 158-160 °C (Lit. m.p.: 158-160 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.25 (d, J = 9.2 Hz, 1H), 8.52 (dd, J_1 = 2.5 Hz, J_2 = 9.2 Hz, 1H), 8.91-9.07 (m, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 123.5, 126.0, 131.4, 141.9, 145.3, 147.0, 147.7; ESI-MS: *m/z* 176 [M + H]$^+$.



3u 3w

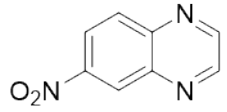
6-Benzoylquinoxaline (3u):[17] Light Brown solid, 106 mg (91%), m.p: 116-118 °C (Lit. m.p. 117 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.49 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.84 (d, J = 7.9 Hz, 2H), 8.20 (t, J = 10.8 Hz, 2H), 8.44 (s, 1H), 8.90 (dd, J_1 = 2.0 Hz, J_2 = 6.2 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 128.5, 129.9, 130.0, 130.1, 132.5, 133.0, 136.9, 138.5, 142.1, 144.6, 146.0, 146.6, 195.5; ESI-MS: *m/z* 235 [M + H]$^+$.

Acenaphtho[1,2-*b*]quinoxaline (3v):[9] Light yellow solid, 125 mg (99%), m.p.: 244-246 °C (Lit. m.p.: 243–245 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.70-7.72 (m, 2H), 7.76-7.80 (m, 2H), 8.04 (dd, J_1 = 2.4 Hz, J_2 = 8.2 Hz, 2H), 8.15-8.18 (m, 2H), 8.37 (d, J = 7.1 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 121.8, 128.6, 129.2, 129.4, 129.5, 130.0, 131.7, 136.4, 141.2, 154.0; ESI-MS: *m/z* 255 [M + H]$^+$.



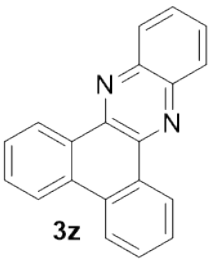
3s

5-Methylacenaphtho[1,2-*b*]quinoxaline (3w):[9] Light yellow solid, 132 mg (99%), m.p.: 282-284 °C (Lit. m.p.: 282-284 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.93 (s, 3H), 7.57-7.64 (m, 2H), 7.82 (t, J = 8.4 Hz, 2H), 8.03 (d, J = 8.2 Hz, 1H), 8.08 (dd, J_1 = 3.1 Hz, J_2 = 8.4 Hz, 2H), 8.42 (t, J = 6.1 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 17.5, 121.7, 127.4, 128.60, 128.63, 128.8, 129.2, 129,3, 129.5, 130.0, 132.1, 132.4, 136.4, 138.0, 140.4, 141.3, 153.0, 153.6. ; ESI-MS: *m/z* 269 [M + H]$^+$.

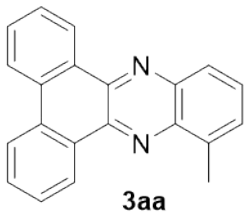


3t

6-Methylacenaphtho[1,2-*b*]quinoxaline (3x):[9] Light yellow solid, 132 mg (99%), m.p.: 233-235 °C (Lit. m.p.: 233-235 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.57 (s, 3H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.91 (s, 1H), 7.99-8.03 (m, 3H), 8.31 (t, *J* = 6.5 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 21.7, 121.5, 121.7, 128.5, 128.6, 128.7, 129.0, 129.1, 129.3, 129.9, 131.3, 131.9, 132.0, 136.2, 139.5, 139.6, 141.2, 153.3, 154.0; ESI-MS: *m/z* 269 [M + H]$^{+}$.

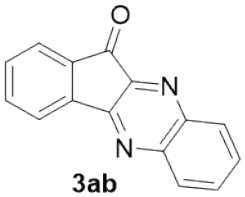


3z



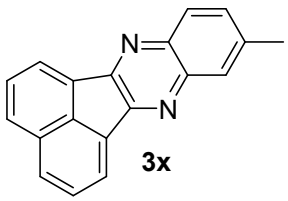
3aa

6-Chloroacenaphtho[1,2-*b*]quinoxaline (3y):[9] Dark brown solid, 142mg (99%) m.p.: 240-242 °C (Lit. m.p.: 240-242 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.61 (d, *J* = 8.8 Hz, 1H), 7.75-7.78 (m, 2H), 8.02-8.04 (m, 3H), 8.09 (s, 1H), 8.29-8.32 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 122.0, 122.2, 128.5, 128.6, 129.6, 129.81, 129.88, 129.9, 130.5, 131.3, 131.3, 134.7, 136.5, 139.6, 141.5, 154.0, 154.6; ESI-MS: *m/z* 289 [M + H]$^{+}$.



3ab

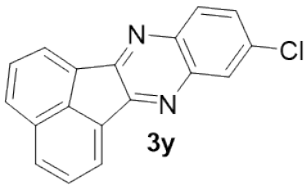
Phenanthro[9,10-*b*]quinoxaline (3z):[9] Yellow solid, 138 mg (99%), m.p.: 226-227 °C (Lit. m.p.: 225–226 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.68-7.76 (m, 4H), 7.80-7.82 (m, 2H), 8.27 (dd, J_1 = 3.5 Hz, J_2 = 6.4 Hz, 2H), 8.49 (d, *J* = 7.9 Hz, 2H), 9.34 (d, *J* = 6.3 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 122.8, 126.2, 127.9, 129.4, 129.7, 130.2, 130.3, 132.0, 142.1, 142.4; ESI-MS: *m/z* 281 [M + H]$^{+}$.



3x

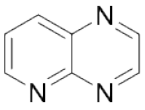
5-Methylphenanthro[9,10-*b*]quinoxaline (3aa):[9] Brown solid, 145 mg (99%), m.p.: 222-224 °C (Lit. mp.: 222-224 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.98 (s, 3H), 7.61-7.75 (m, 6H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.48-8.50 (m, 2H), 9.32-9.36 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 17.4, 122.83, 122.85, 126.1, 127.2, 127.7, 127.8, 129.3, 129.6, 130.0, 130.1, 130.3, 130.6, 131.9, 137.7, 141.0, 141.3, 141.8, 142.2; ESI-MS: *m/z* 295 [M + H]$^{+}$.

11*H*-Indeno[1,2-*b*]quinoxalin-11-one (3ab):[7] Yellow solid, 115 mg (99%), m.p.: 216-218 °C (Lit. m.p.: 217–218 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55 (t, *J* = 7.4 Hz, 1H), 7.71 (q, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 8.05,(t, *J* = 7.6 Hz, 2H), 8.18 (d, *J* = 8.2 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 122.5, 124.7, 129.6, 130.2, 131.5, 132.4, 132.5, 136.6, 136.8, 141.5, 142.6, 143.0, 149.2, 156.5, 189.8; ESI-MS: *m/z* 233 [M + H]$^{+}$.



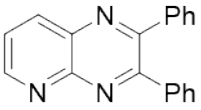
3y

6-Methyl-11*H*-indeno[1,2-*b*]quinoxalin-11-one (3ac):[18] Yellow solid, 122 mg (99%), m.p.: 224-225 °C (Lit. m.p: 227-229 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.77 (s, 3H), 7.50-7.59 (m, 3H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.99-8.03 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 17.3, 122.3, 124.5, 129.3, 129.8, 132.1, 132.7, 136.5, 136.6, 138.3, 141.8, 142.1, 142.7, 148.7, 155.4, 190.3; ESI-MS: *m/z* 247 $[M + H]^+$.



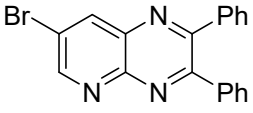
3af

2,3-di(pyridin-2-yl)quinoxaline (3ad):[19] Brown solid, 141 mg (99%), m.p.: 185-187 °C (Lit. m.p.: 188-191 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.18-7.20 (m, 2H), 7.75-7.78 (m, 4H), 7.92 (d, *J* = 7.8 Hz, 2H), 8.18-8.20 (m, 2H), 8.34 (d, *J* = 4.5 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 122.9, 124.1, 129.2, 130.4, 136.5, 141.0, 148.4, 152.2, 157.2; ESI-MS: *m/z* 285 $[M + H]^+$.



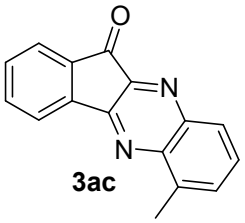
3ag

2,3-Dimethylpyrido[2,3-*b*]pyrazine (3ae):[9] Light brown solid, 79 mg (99%), m.p.: 133-135 °C (Lit. m.p.: 133-135 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.70 (s, 3H), 2.74 (s, 3H), 7.54-7.56 (m, 1H), 8.26 (dd, J_1 = 1.9 Hz, J_2 = 8.4 Hz, 1H), 8.97 (d, *J* = 2.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 23.0, 23.4, 124.3, 135.8, 137.3, 150.1, 152.5, 155.0, 157.3; ESI-MS: *m/z* 160 $[M + H]^+$.



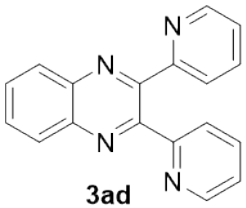
3ah

Pyrido[2,3-*b*]pyrazine (3af):[9] Light brown solid, 60 mg (91%), m.p.: 135-137 °C (Lit. m.p.: 133-135 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.71-7.74 (m, 1H), 8.46 (dd, J_1 = 1.9 Hz, J_2 = 8.3 Hz, 1H), 8.93 (s, 1H), 9.06 (s, 1H), 9.17 (dd, J_1 = 1.9 Hz, J_2 = 4.2 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 125.5, 138.4, 138.6, 146.1, 147.8, 151.4, 154.3; ESI-MS: *m/z* 132 $[M + H]^+$.



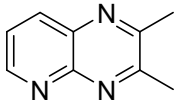
3ac

2,3-diphenylpyrido[2,3-b]pyrazine (3ag):[10] Yellow solid, 140 mg (99%), m.p.: 141–143 °C (Lit. m.p.: 144-145 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.18-7.29 (m, 6H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.57-7.58 (m, 1H), 8.39 (d, *J* = 8.7 Hz, 1H), 9.04-9.05 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 125.0, 127.9, 128.2, 129.1, 129.2, 129.6, 130.0, 135.9, 137.8, 137.9, 138.3, 149.6, 153.9, 154.5, 156.0; ESI-MS: *m/z* 284 $[M + H]^+$.

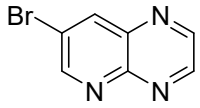


3ad

Bromo-2,3-diphenylpyrido[2,3-*b*]pyrazine (3ah):[9] White solid, 179 mg (99%), m.p.: 148-150 °C (Lit. m.p.: 148-150 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.28-7.39 (m, 6H), 7.50 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 7.0 Hz, 2H), 8.63 (d, *J* = 2.4 Hz, 1H), 9.11 (d, *J* = 2.4 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 120.9, 128.2, 128.4, 129.6, 129.7, 129.8, 130.2, 136.4, 137.7, 138.0, 139.4, 148.2, 155.1, 155.4, 156.5; ESI-MS: *m/z* 364 $[M + H]^+$ (for ^{79}Br), 366 $[M + H]^+$ (for ^{81}Br).

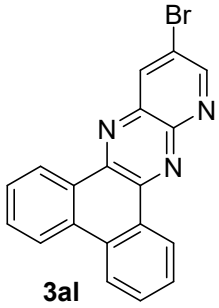


3ae



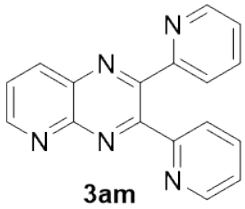
3ak

Bromo-2,3-dimethylpyrido[2,3-*b*]pyrazine (3ai):[9] Brown solid, 117 mg (99%), m.p.: 120-122 °C (Lit. m.p.: 120-122 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.72 (s, 3H), 2.74 (s, 3H), 8.44 (d, *J* = 2.6 Hz, 1H), 8.99 (d, *J* = 2.6 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 23.0, 23.5, 119.8, 136.2, 138.8, 148.6, 153.6, 156.1, 157.6; ESI-MS: *m/z* 238 $[M + H]^+$ (for ^{79}Br), 240 $[M + H]^+$ (for ^{81}Br).



3al

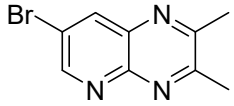
3-Bromo-6,7,8,9-tetrahydropyrido[2,3-*b*]quinoxaline (3aj): Yellow solid, 126 mg (96%), m.p.: 126-128 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.01-2.04 (m, 4H), 3.13-3.21 (m, 4H), 8.44 (s, 1H), 9.01 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 22.3, 22.5, 33.1, 33.5, 119.9, 136.4, 138.7, 148.5, 153.9, 156.8, 158.3; ESI-MS: *m/z* 264 $[M + H]^+$ (for ^{79}Br), 266 $[M + H]^+$ (for ^{81}Br).



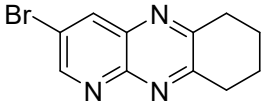
3am

7-Bromopyrido[2,3-*b*]pyrazine (3ak):[9] Off-white solid, 101 mg (97%), m.p.: 158-160 °C (Lit. m.p.: 158-160 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.62 (d, *J* = 2.5 Hz, 1H), 8.91 (s, 1H), 9.05 (s, 1H), 9.15 (d, *J* = 2.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 121.4, 138.6, 139.9, 146.8, 147.9, 149.7, 155.5; ESI-MS: *m/z* 210 $[M + H]^+$ (for ^{79}Br), 212 $[M + H]^+$ (for ^{81}Br).

12-Bromodibenzo[*f,h*]pyrido[2,3-*b*]quinoxaline (3al):[20] Yellow solid, 178 mg (94%), m.p.: 216-216 °C ; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.60-7.77 (m, 4H), 8.42 (d, *J* = 8.1 Hz, 2H), 8.67 (s, 1H), 9.08 (d, *J* = 7.9 Hz, 1H), 9.18 (s, 1H), 9.33 (d, *J* = 8.0 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 120.5, 122.8, 122.9, 126.5, 127.3, 128.1, 128.2, 129.1, 129.3, 131.2, 131.3, 132.4, 132.5, 137.3, 139.4, 143.9, 144.6, 148.0, 155.3; ESI-MS: *m/z* 347 $[M + H]^+$ (for ^{79}Br), 349 $[M + H]^+$ (for ^{81}Br).



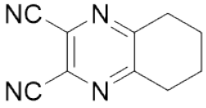
3ai



3aj

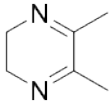
2,3-Di(pyridin-2-yl)pyrido[2,3-*b*]pyrazine (3am):[19] Brown solid, 134 mg (94%), m.p.: 267-269 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.25-7.29 (m, 2H), 7.77-7.80 (m, 1H), 7.84-7.92 (m, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 8.28 (d, *J* = 4.5 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.40 (d, *J* = 4.8 Hz, 1H), 8.59 (dd, J_1 = 1.9 Hz, J_2 = 8.3 Hz, 1H), 9.23-9.24 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 123.2, 123.5, 124.1, 124.7, 125.7, 136.2, 136.7, 136.9, 138.3, 148.1, 148.6, 149.6, 153.9, 154.6, 155.2, 156.4, 157.0; ESI-MS: *m/z* 286 $[M + H]^+$.

5,6-Dimethylpyrazine-2,3-dicarbonitrile (3an):[21] Gray solid, 78 mg (99%), m.p.: 168-170 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.68 (s, 6H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 22.6, 113.1, 130.3, 157.8; ESI-MS: *m/z* 159 $[M + H]^+$.



3aq

Pyrazine-2,3-dicarbonitrile (3ao):[22] White solid, 62 mg (95%), m.p.: 132–134 °C (Lit. m.p.: 133–134 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.92 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 112.6, 134.0, 147.1; ESI-MS: *m/z* 131 $[M + H]^+$.

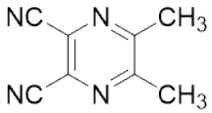


3ar

5,6-Diphenylpyrazine-2,3-dicarbonitrile (3ap):[10] Brown solid, 134 mg (95%), m.p.: 210-212 °C (Lit. m.p.: 209-210 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.35 (t, *J* = 7.6 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 4H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 113.1, 128.8, 129.8, 131.1, 135.2, 155.4; ESI-MS: *m/z* 283 $[M + H]^+$.

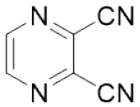
5,6,7,8-Tetrahydroquinoxaline-2,3-dicarbonitrile (3aq):[23] White solid, 91 mg (99%), m.p.: 140-142 °C (Lit. m.p.: 138-139 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.96-1.99 (m, 4H), 3.05-3.08 (m, 4H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 21.5, 32.2, 113.1, 130.1, 158.6. ESI-MS: *m/z* 185 $[M + H]^+$.

5,6-Dimethyl-2,3-dihydropyrazine (3ar):[24] Liquid, 100 mg (91%); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.09 (s, 6H), 3.30 (s, 4H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 23.1, 44.7, 159.3. ESI-MS: *m/z* 111 $[M + H]^+$.



3an

References:



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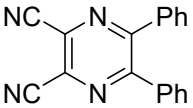

3ap

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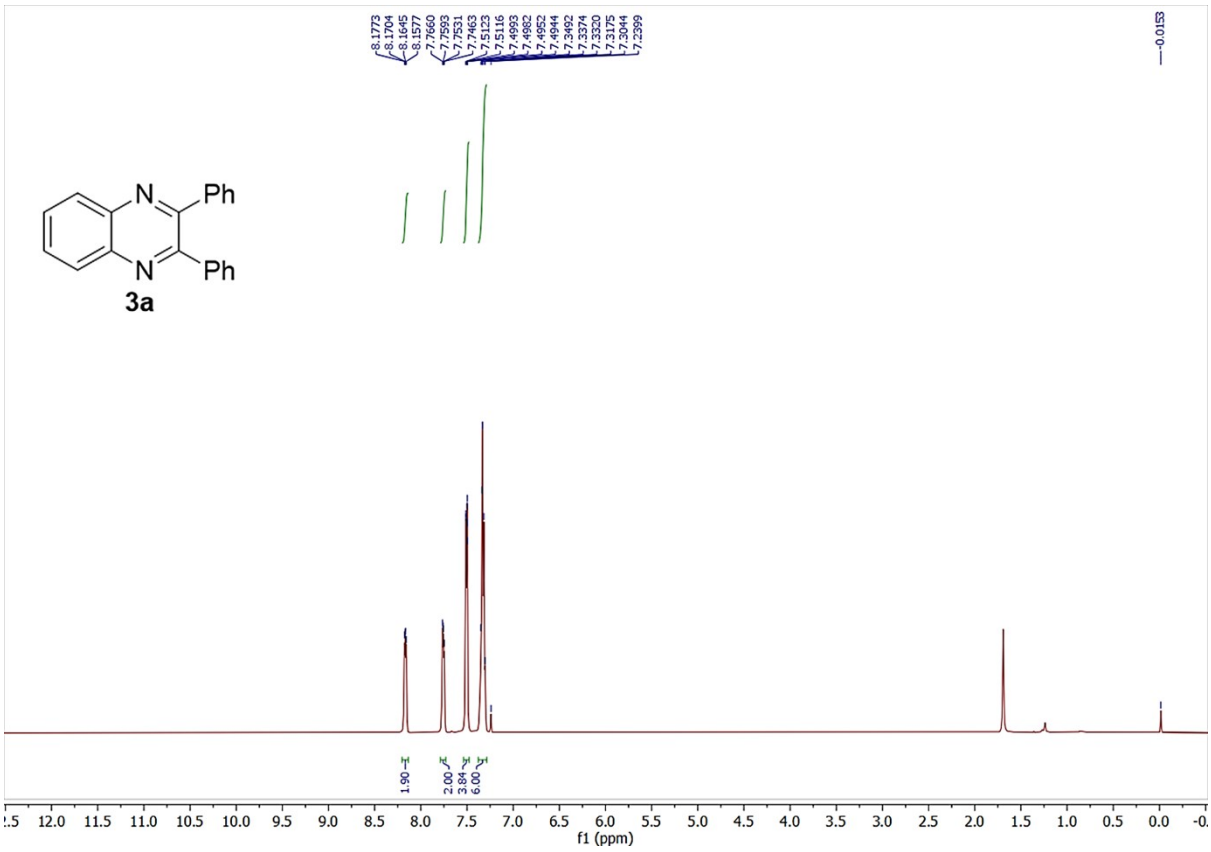
^{1}H NMR and ^{13}C NMR of quinoxalines



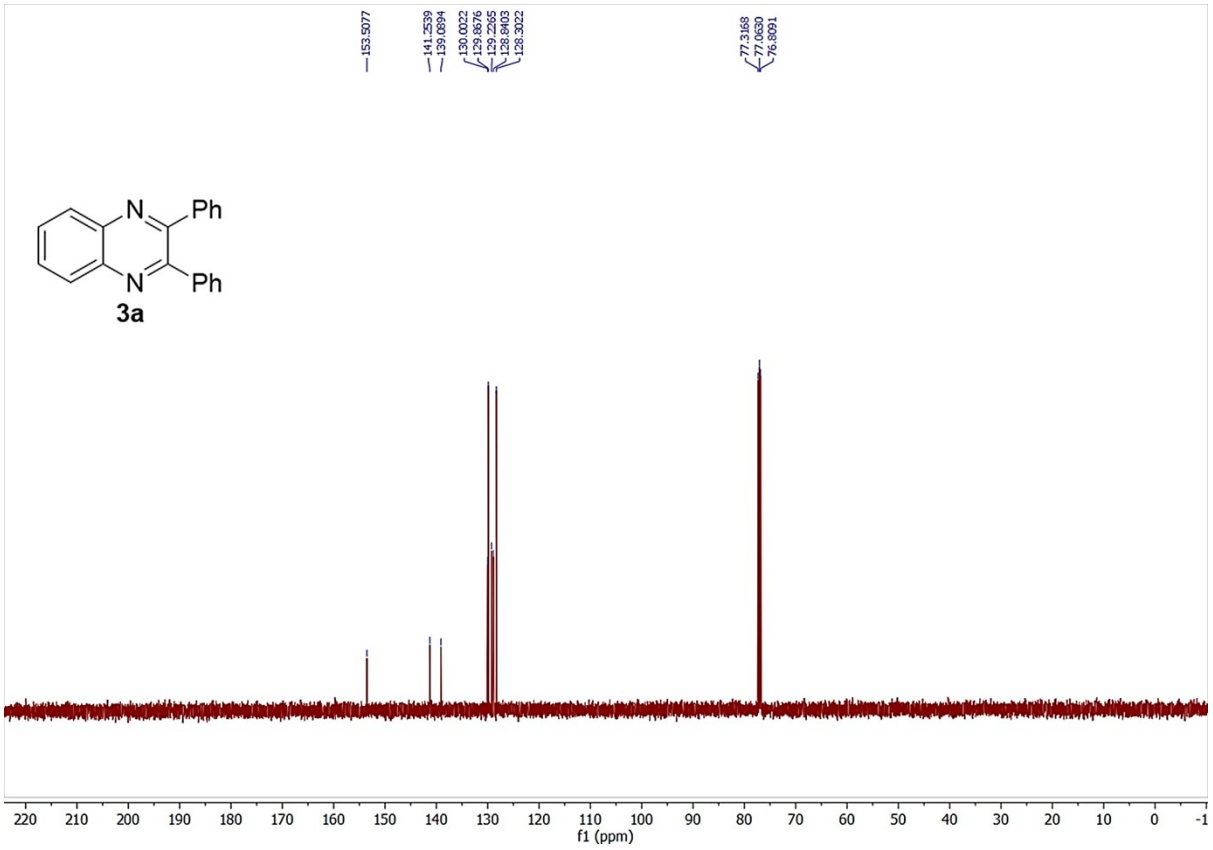
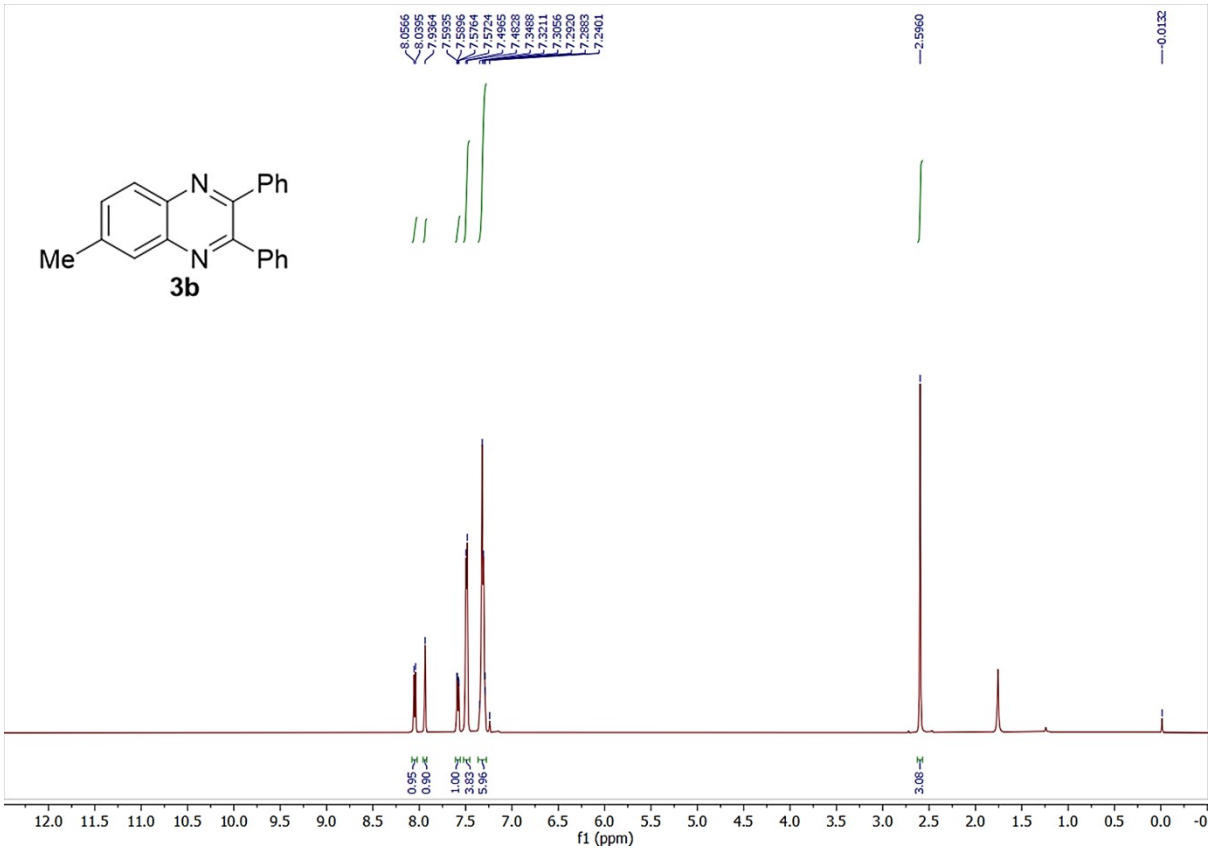


Figure S3: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3a**.



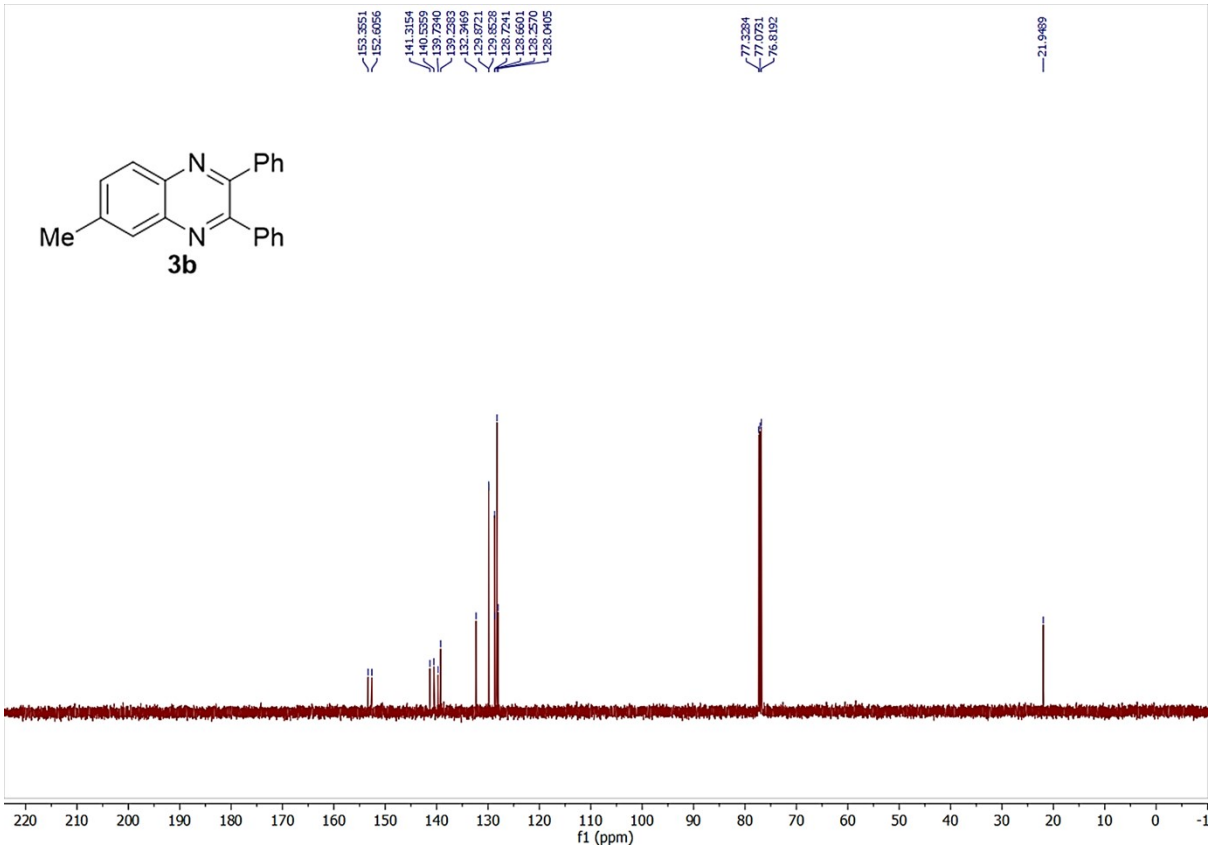
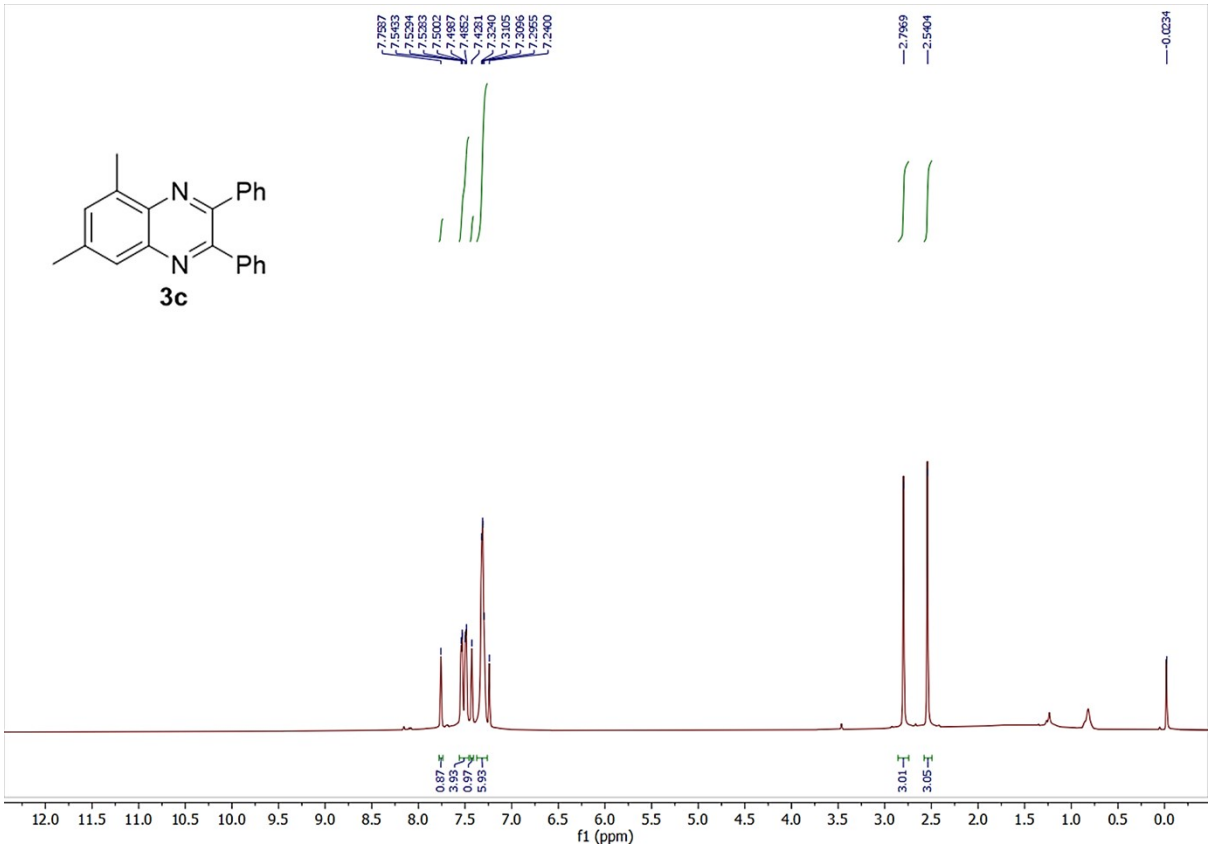


Figure S4: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3b**.



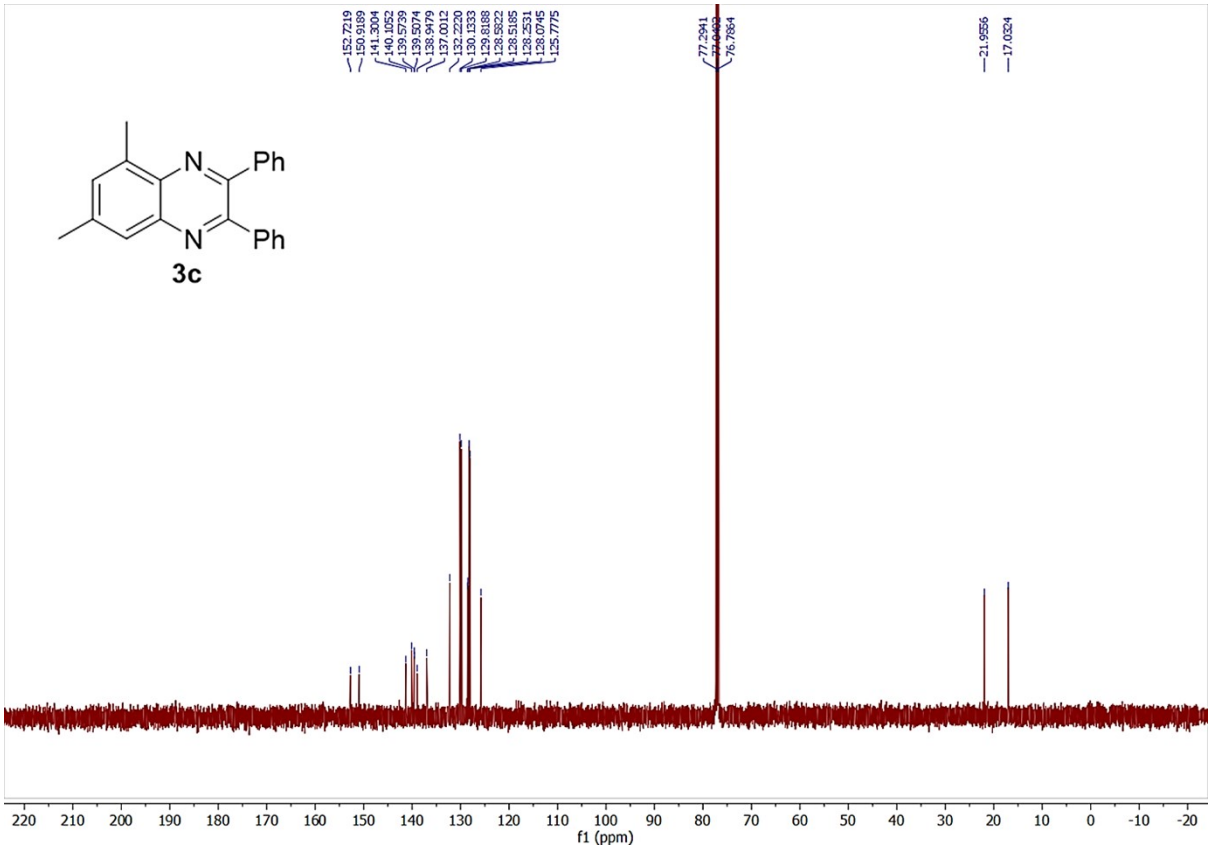
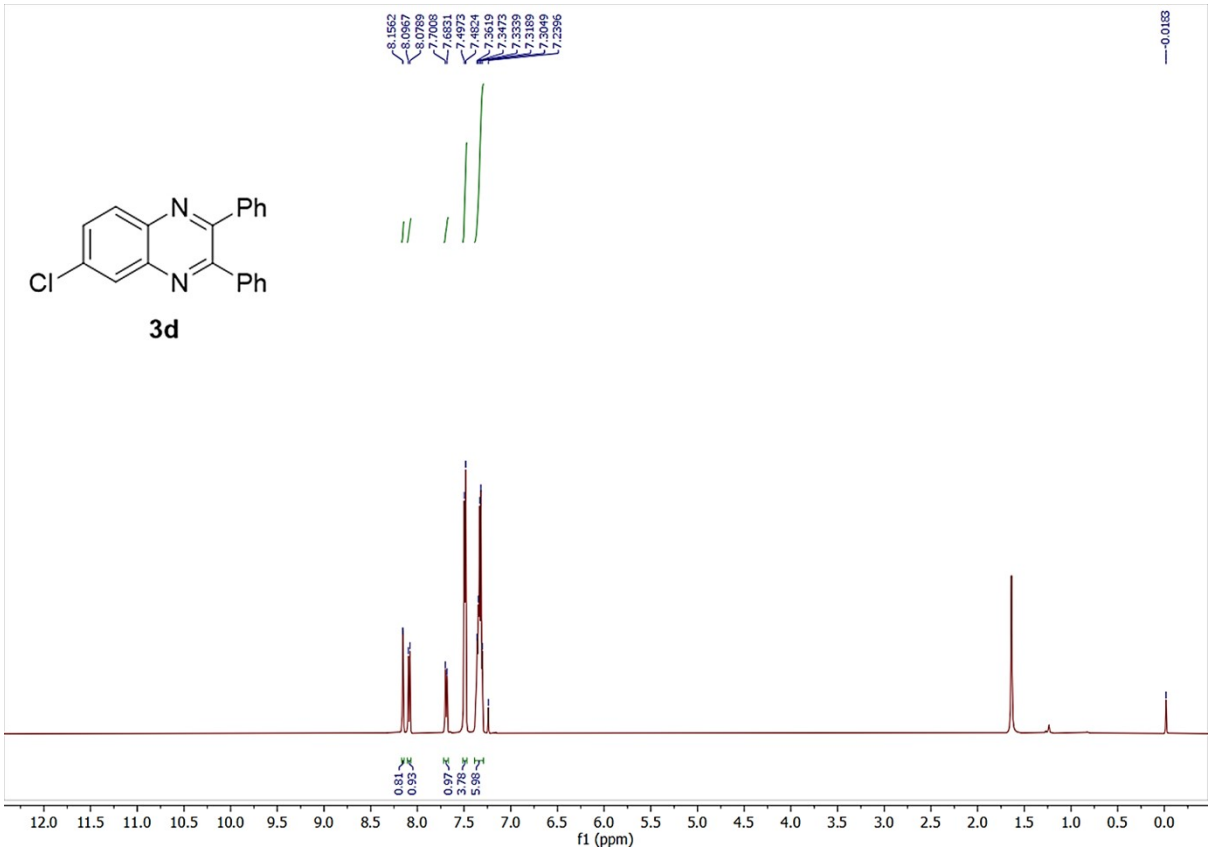


Figure S5: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3c**.



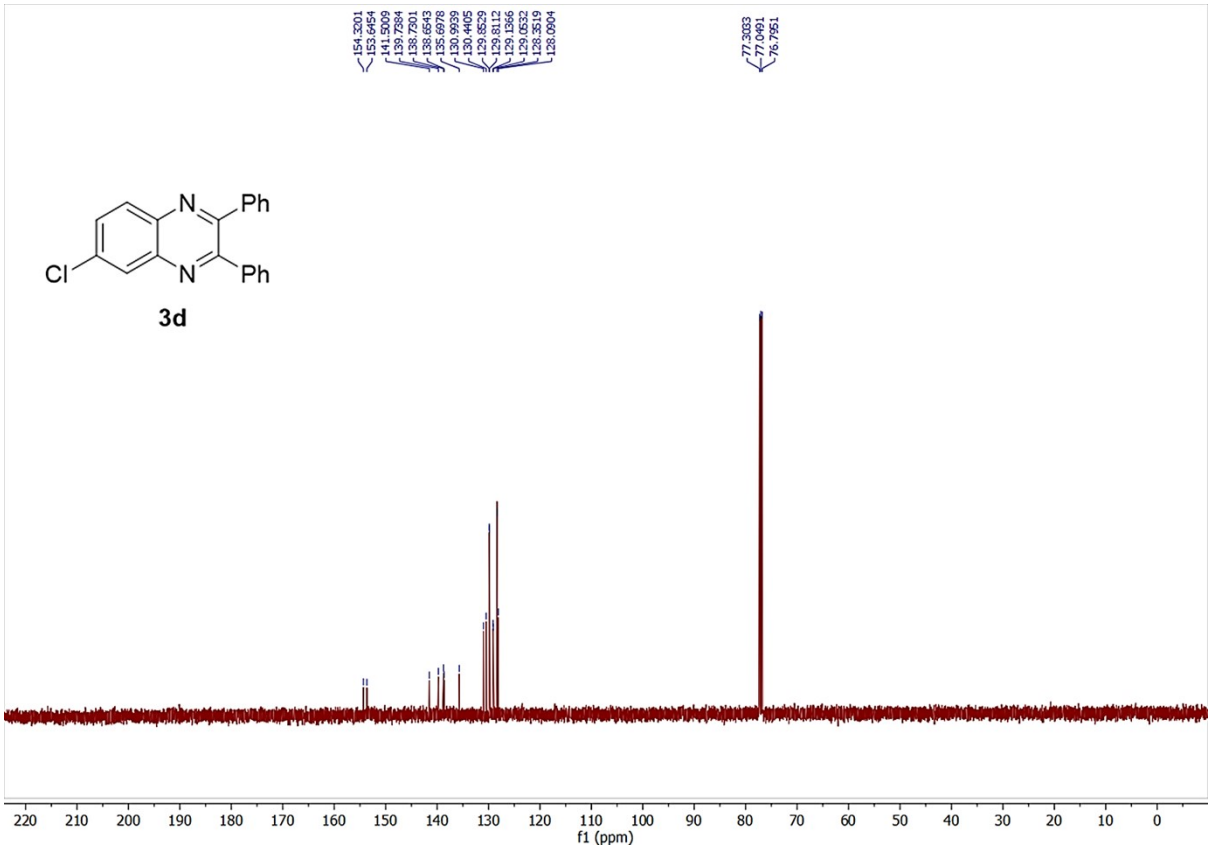
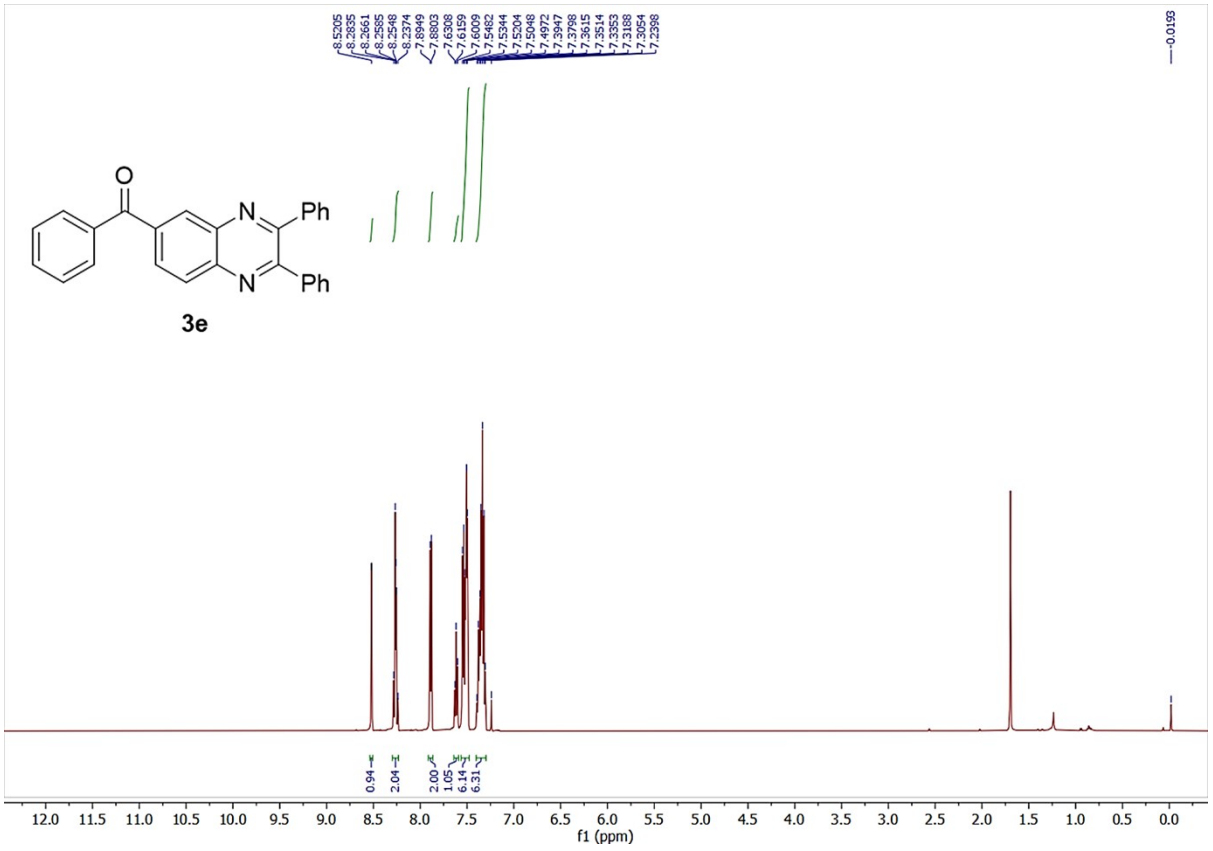


Figure S6: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3d**.



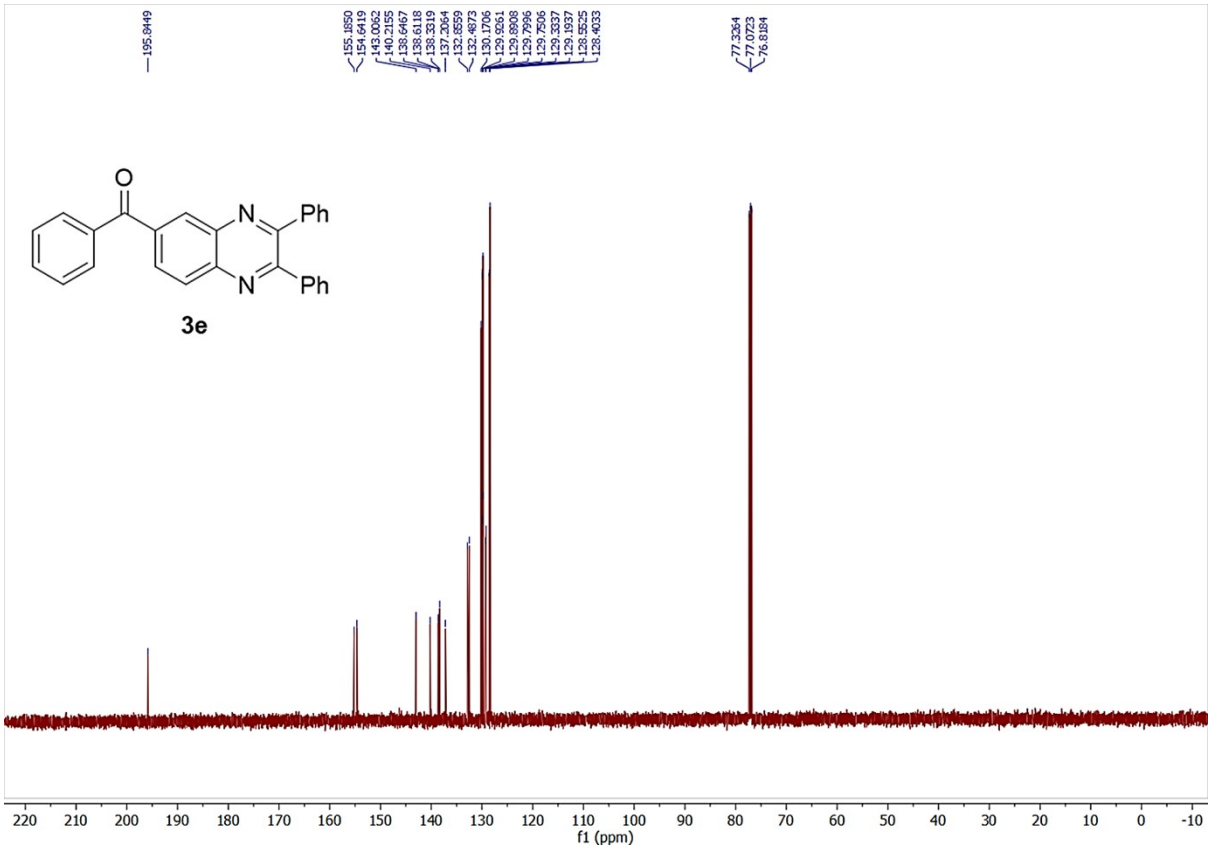
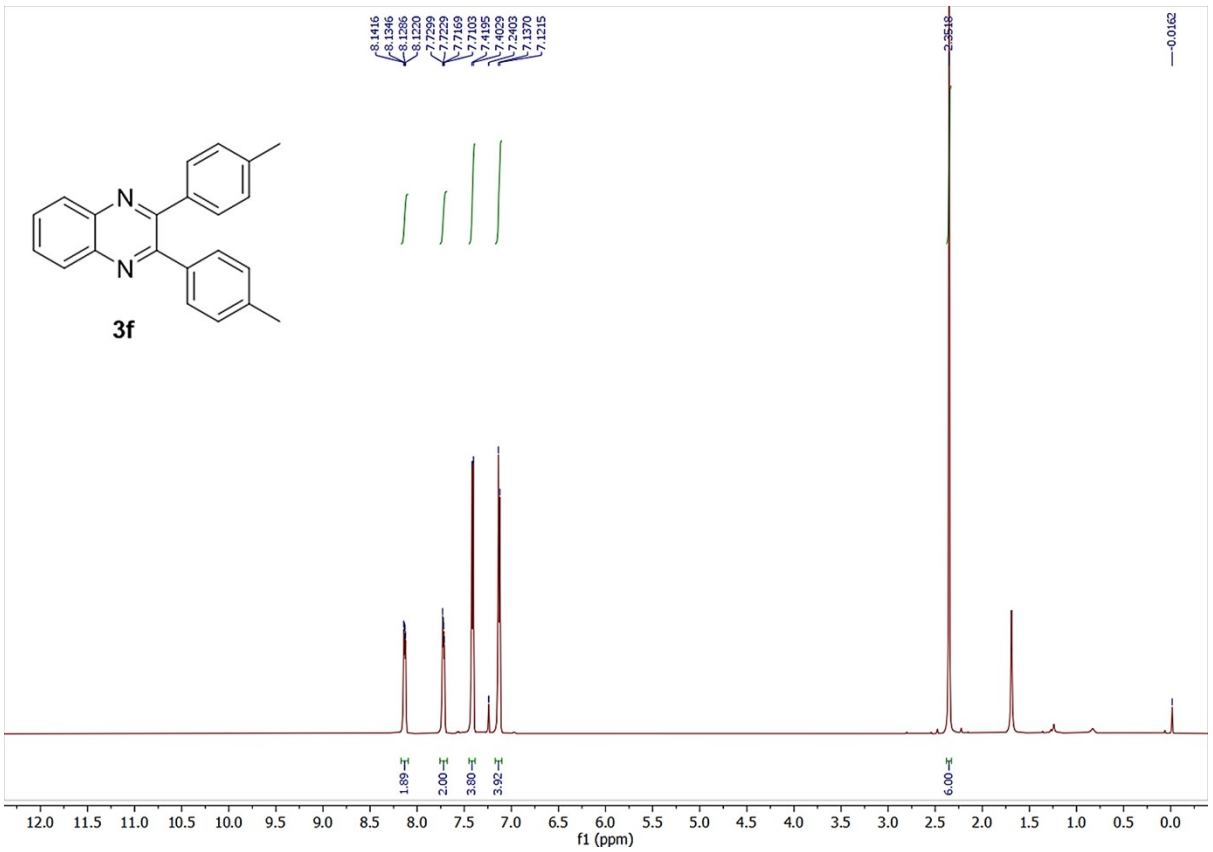


Figure S7: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3e**.



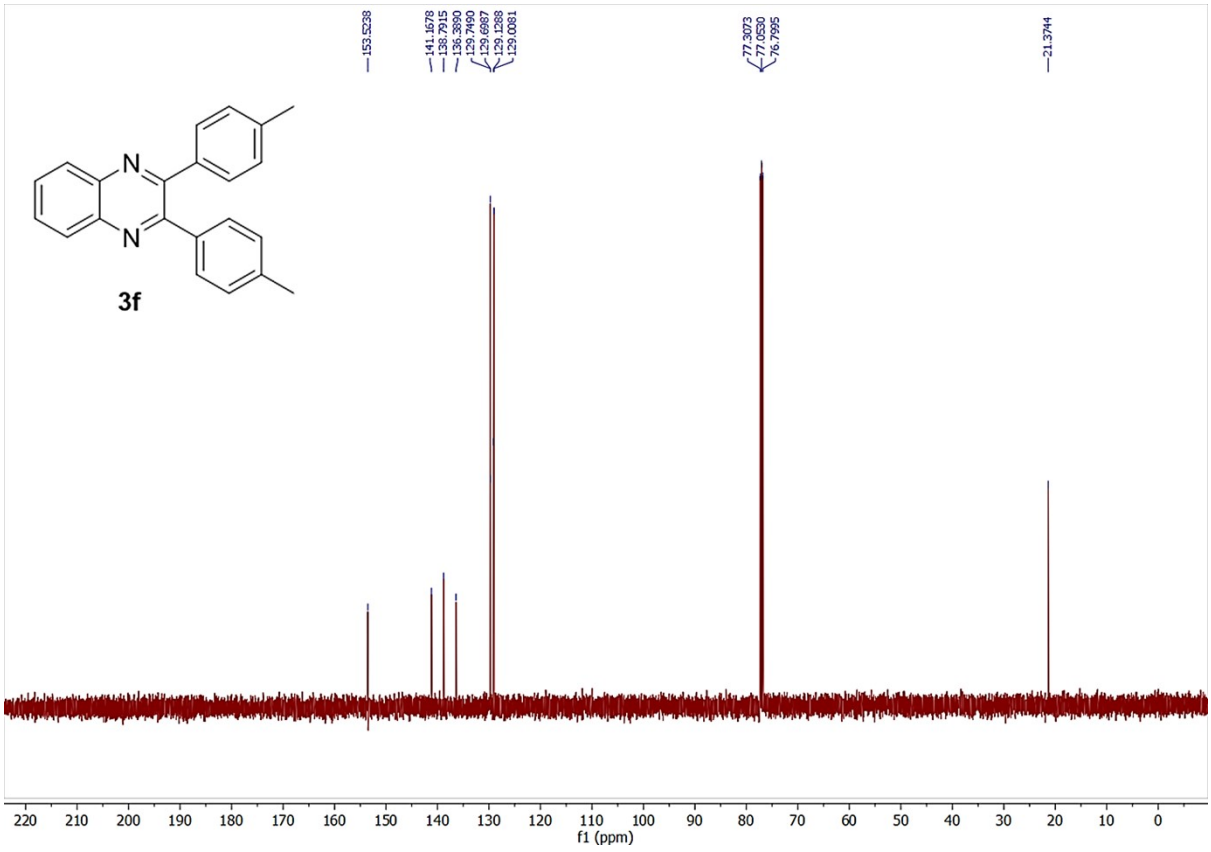
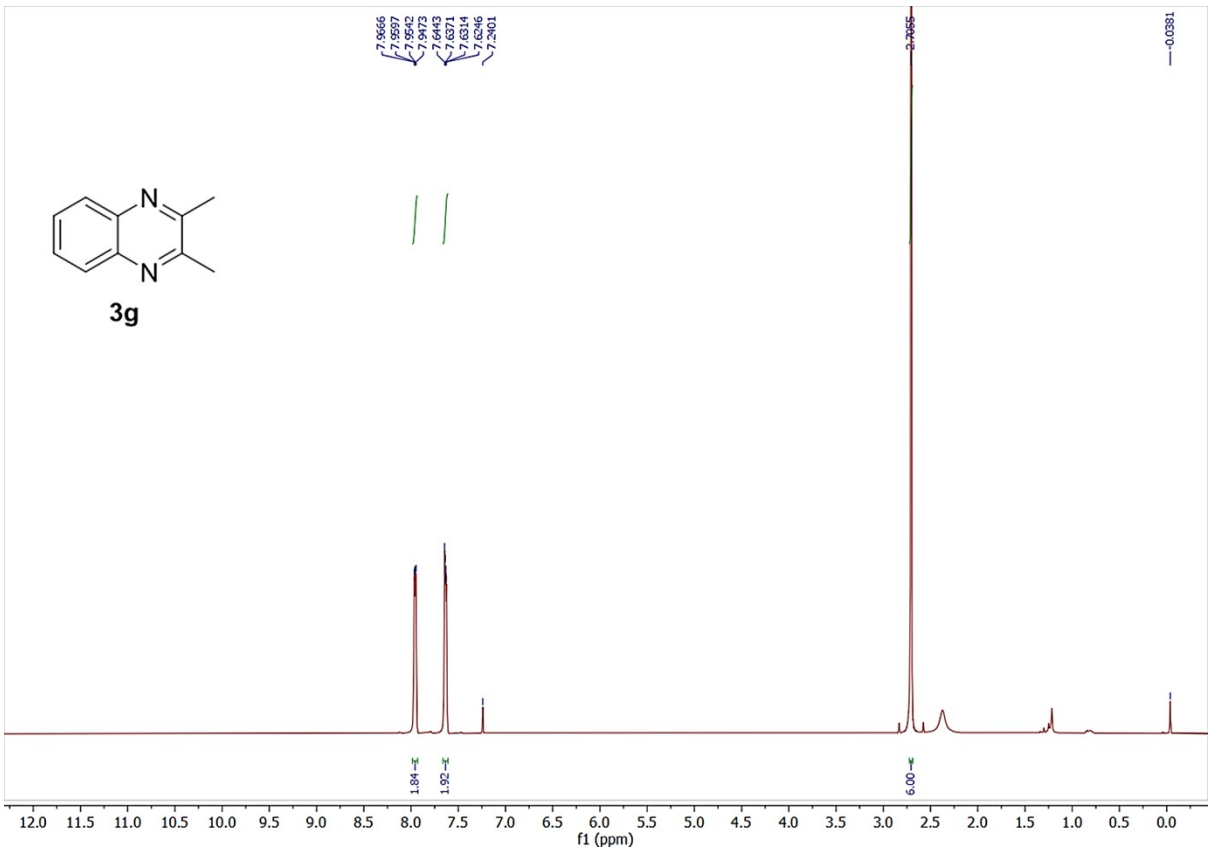


Figure S8: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3f**.



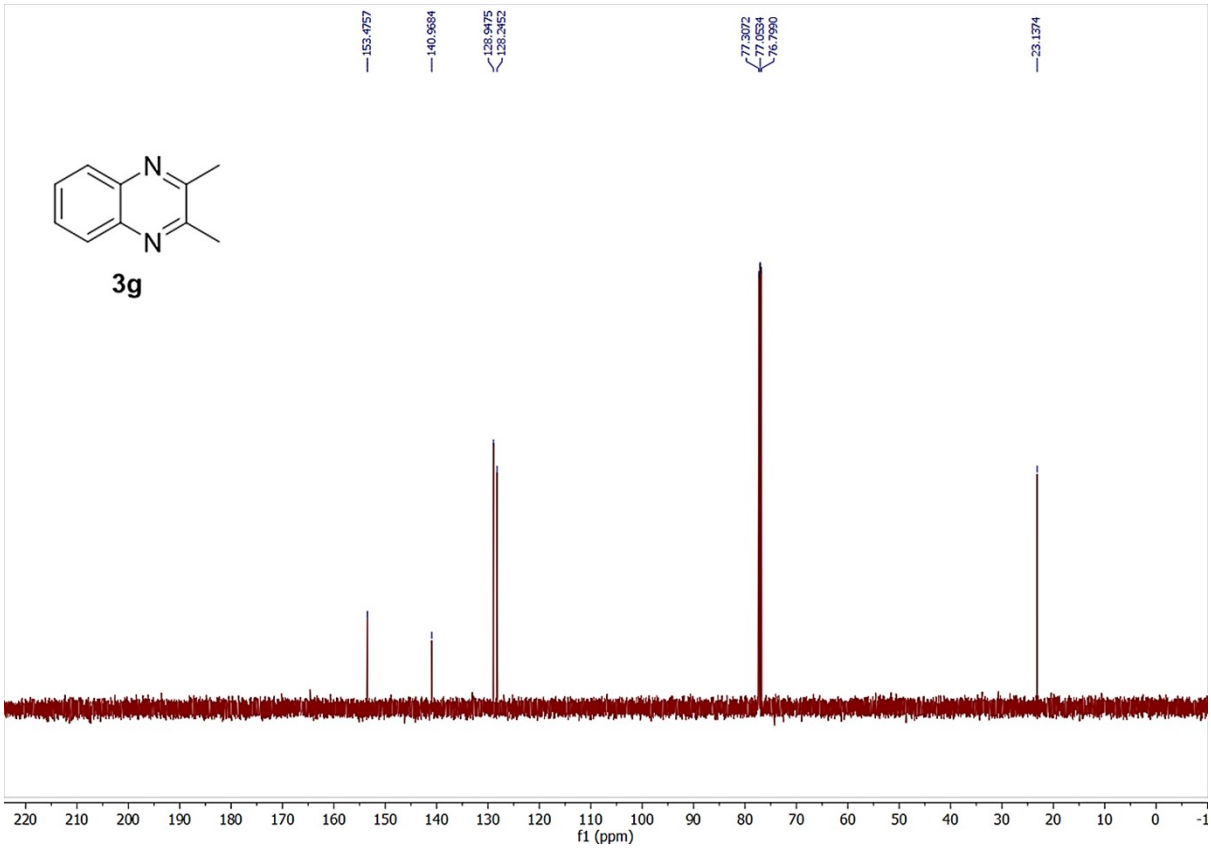
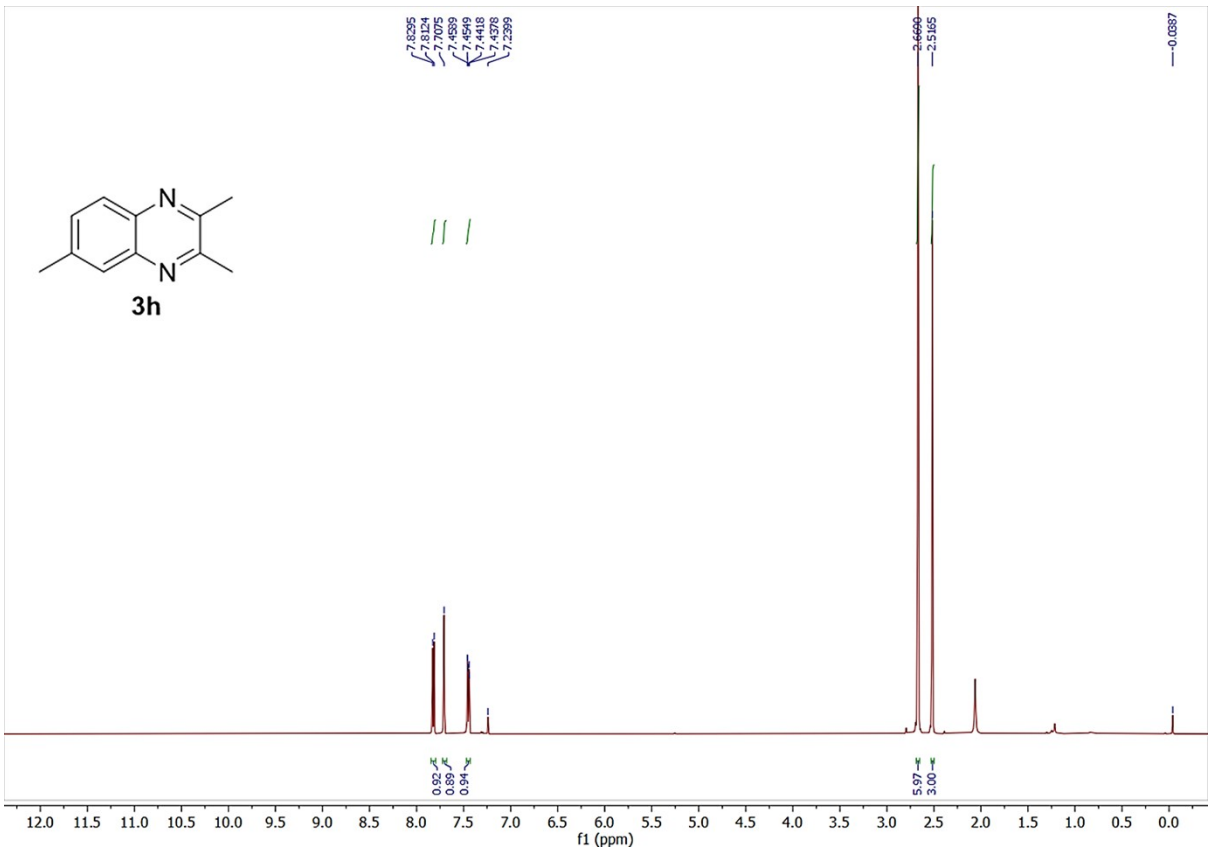


Figure S9: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3g**.



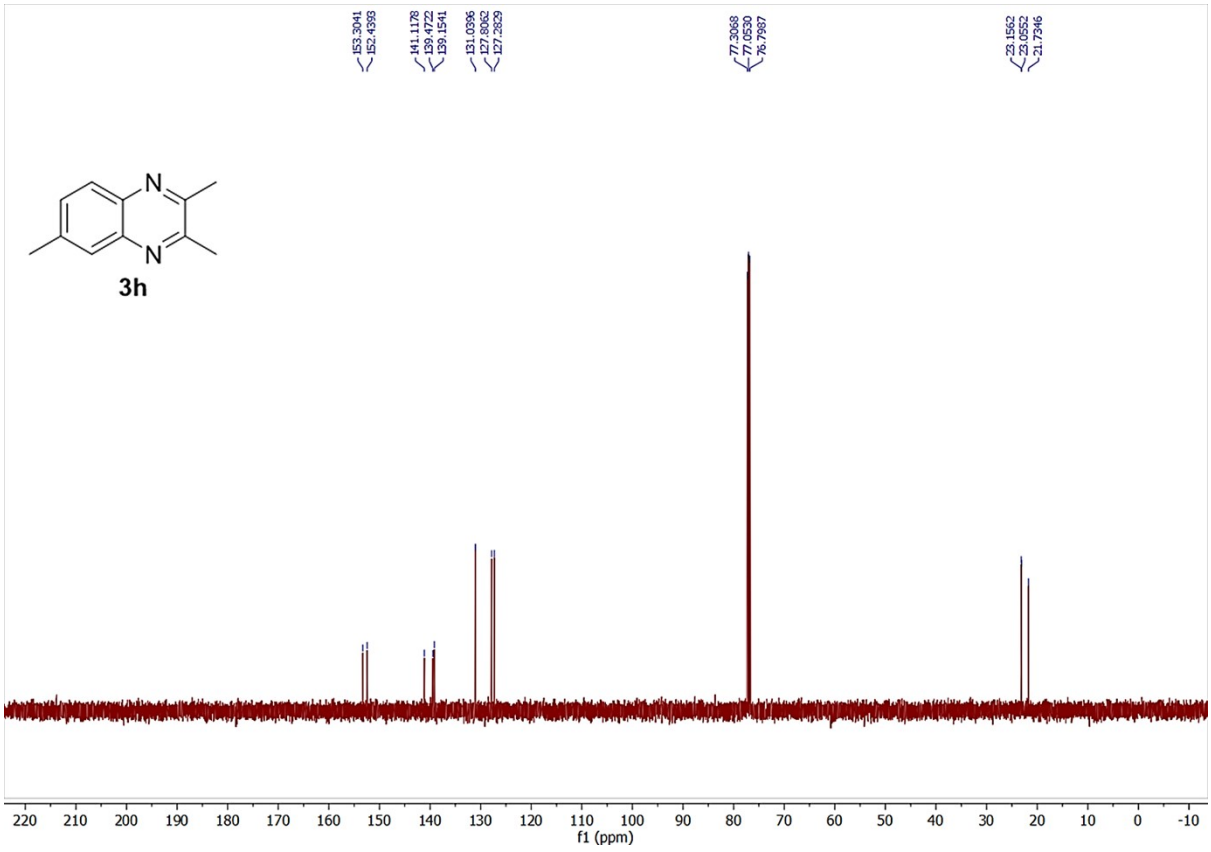
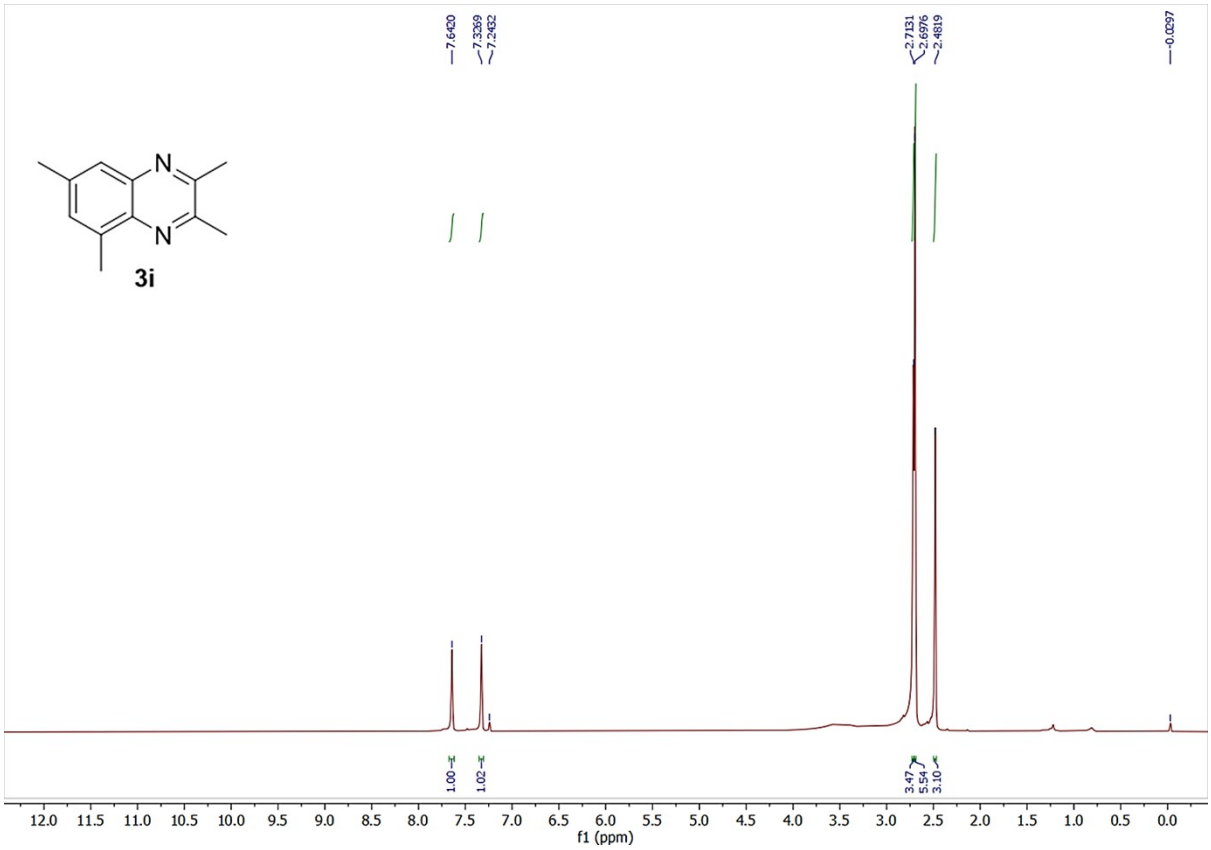


Figure S10: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3h**.



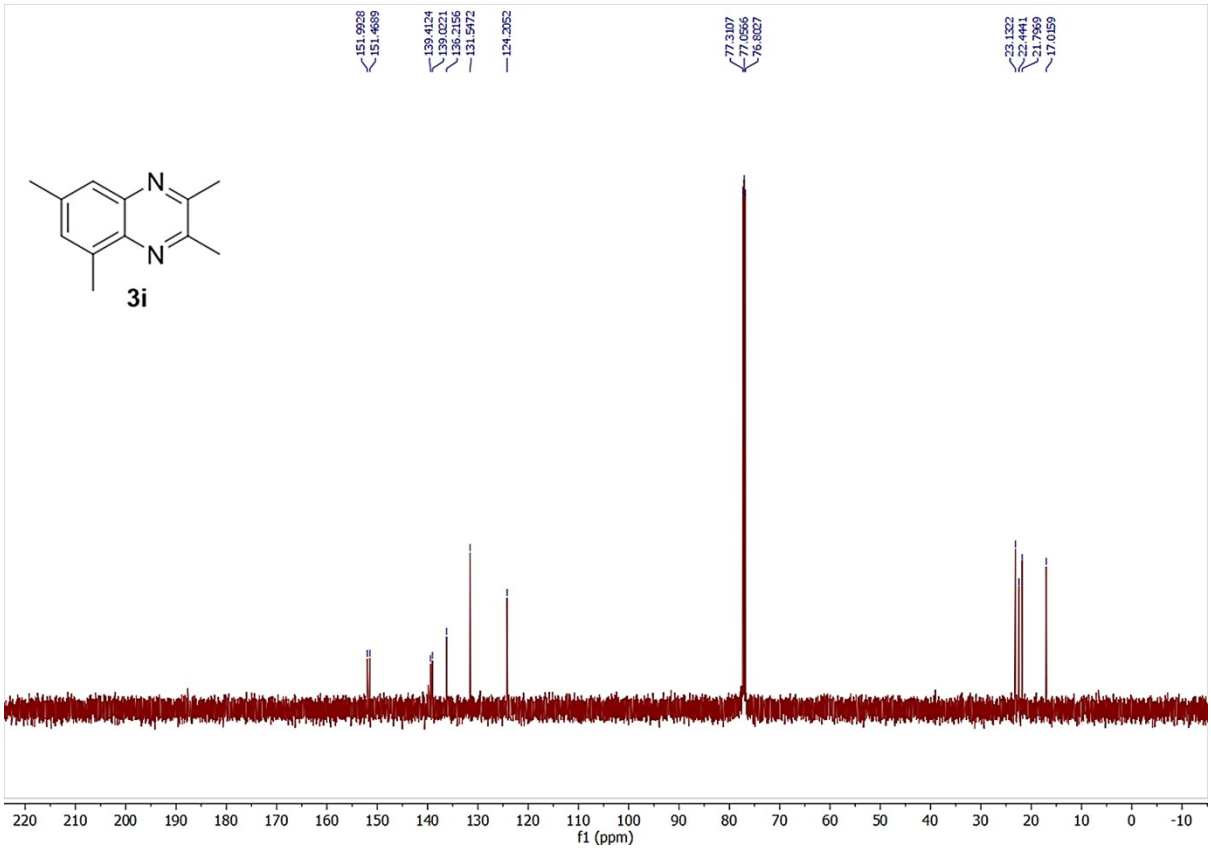
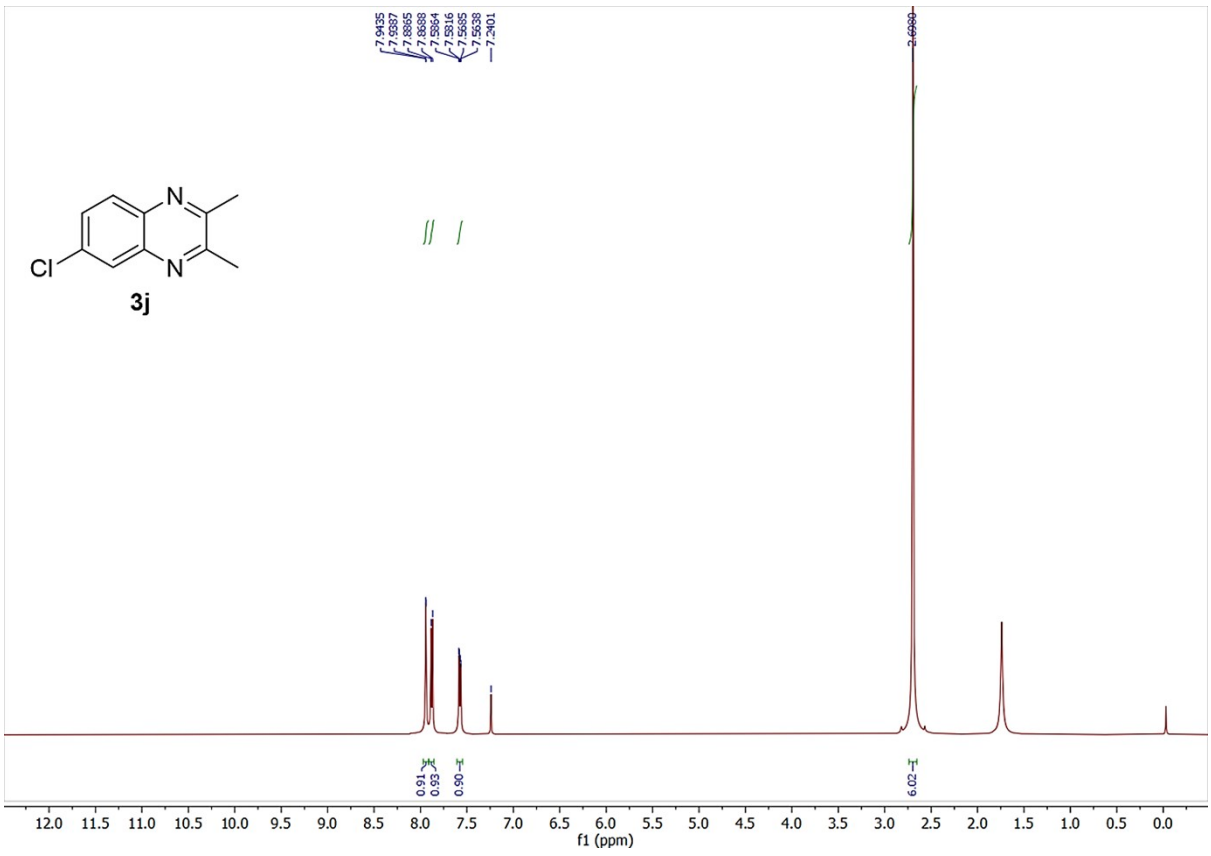


Figure S11: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3i**.



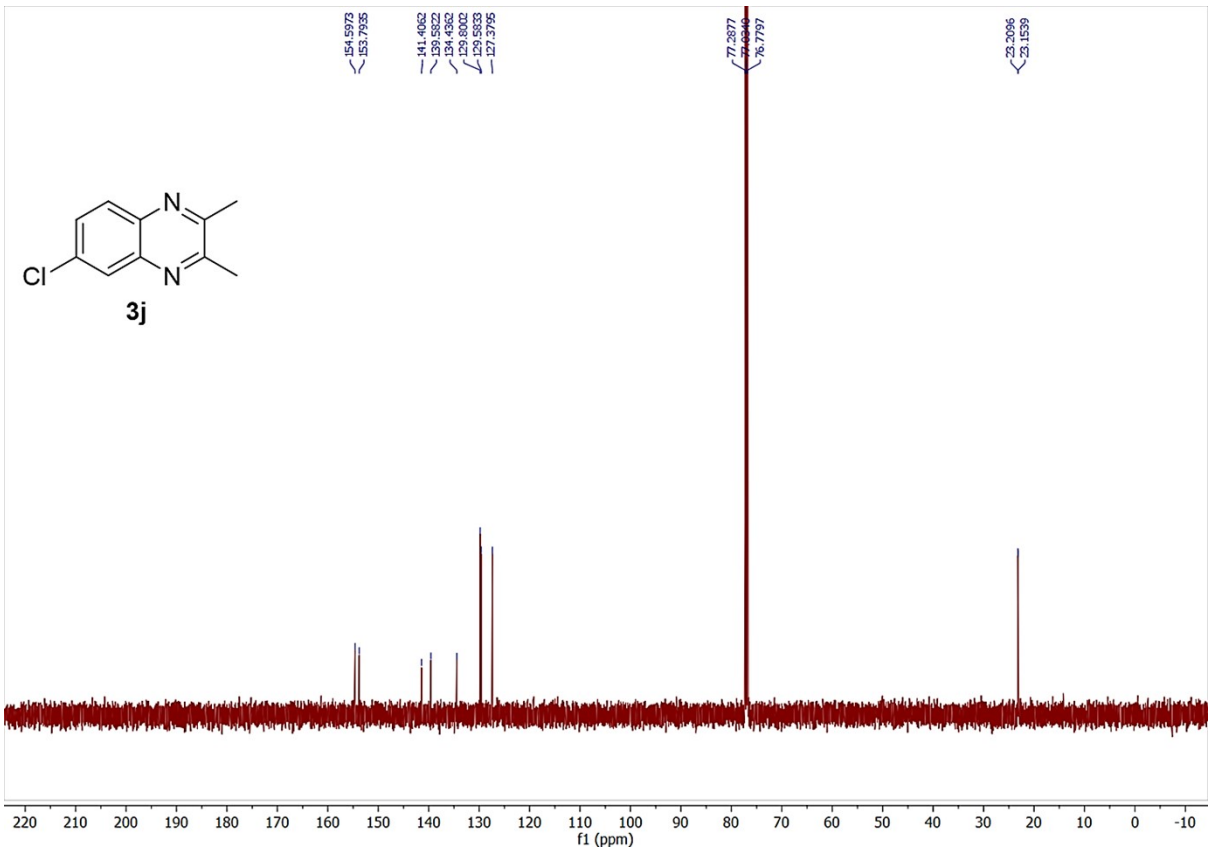
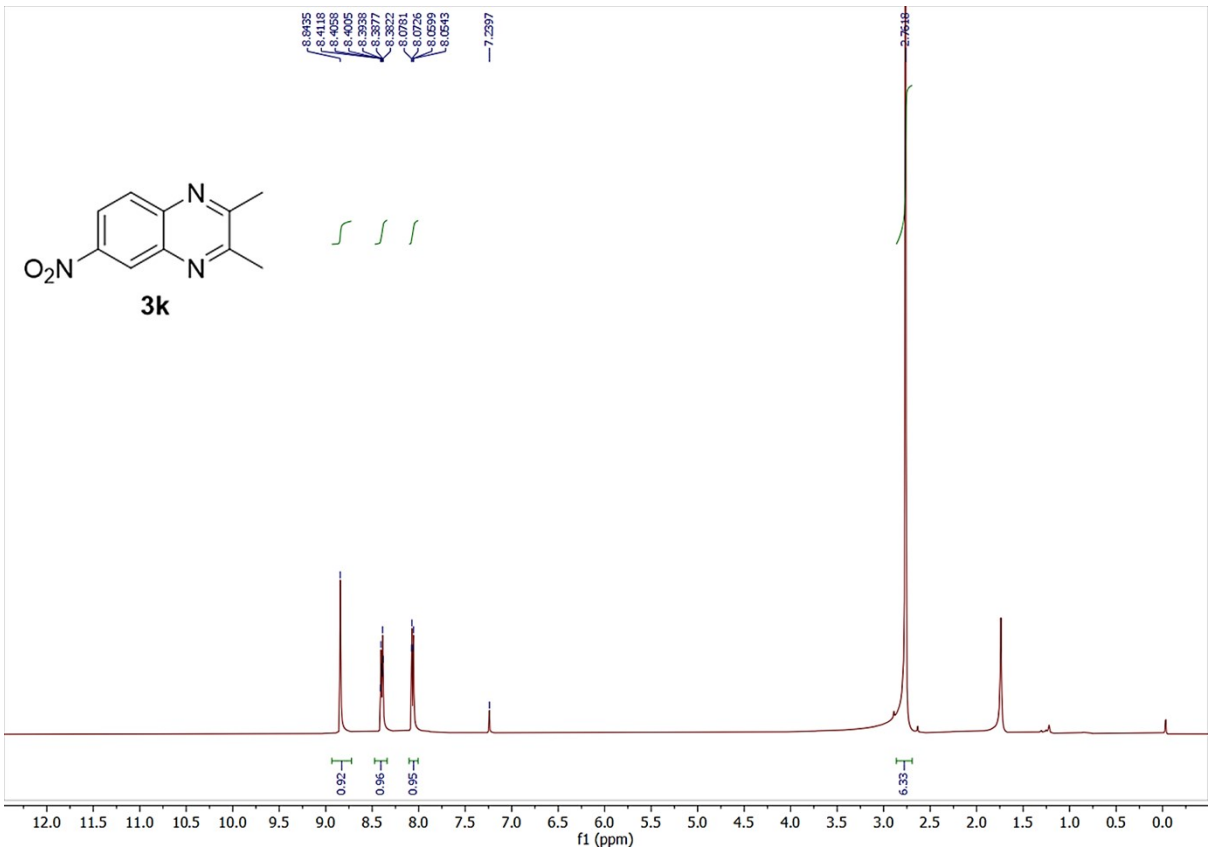


Figure S12: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3j**.



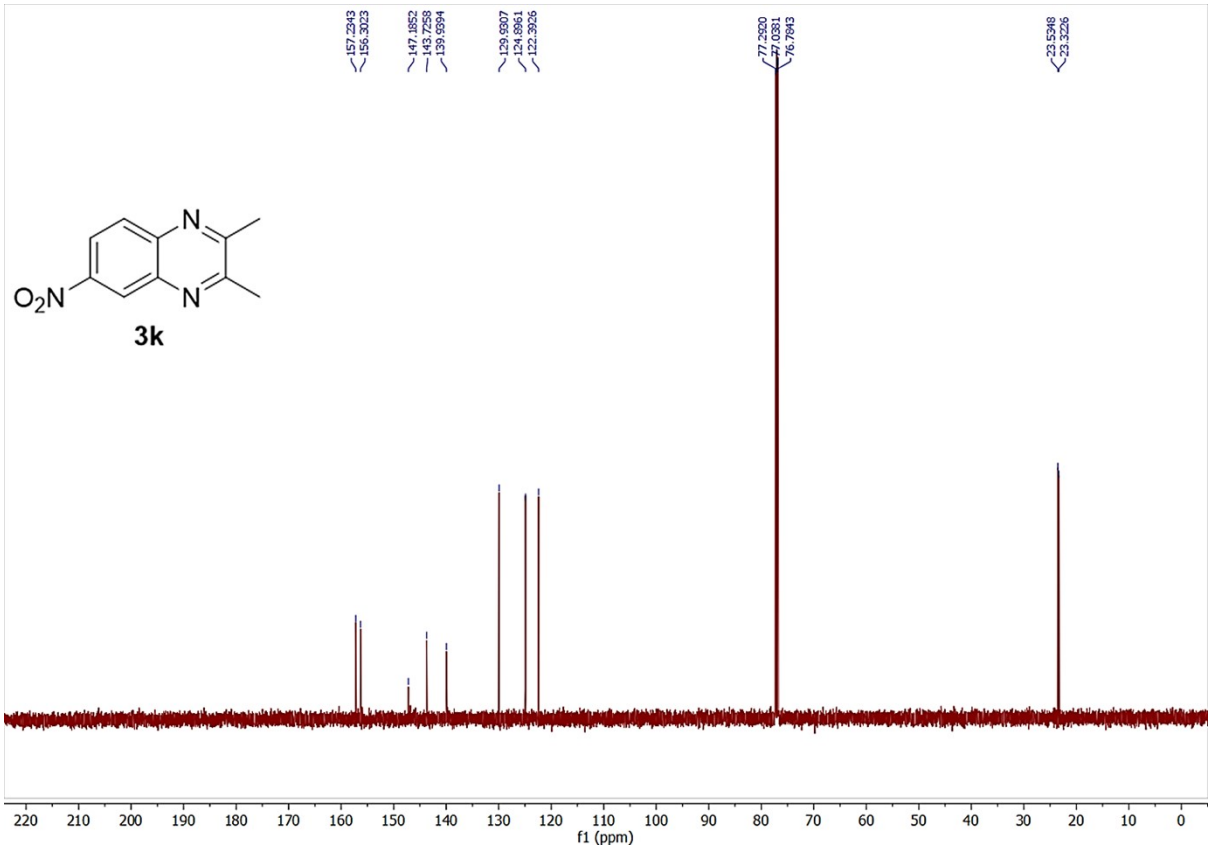
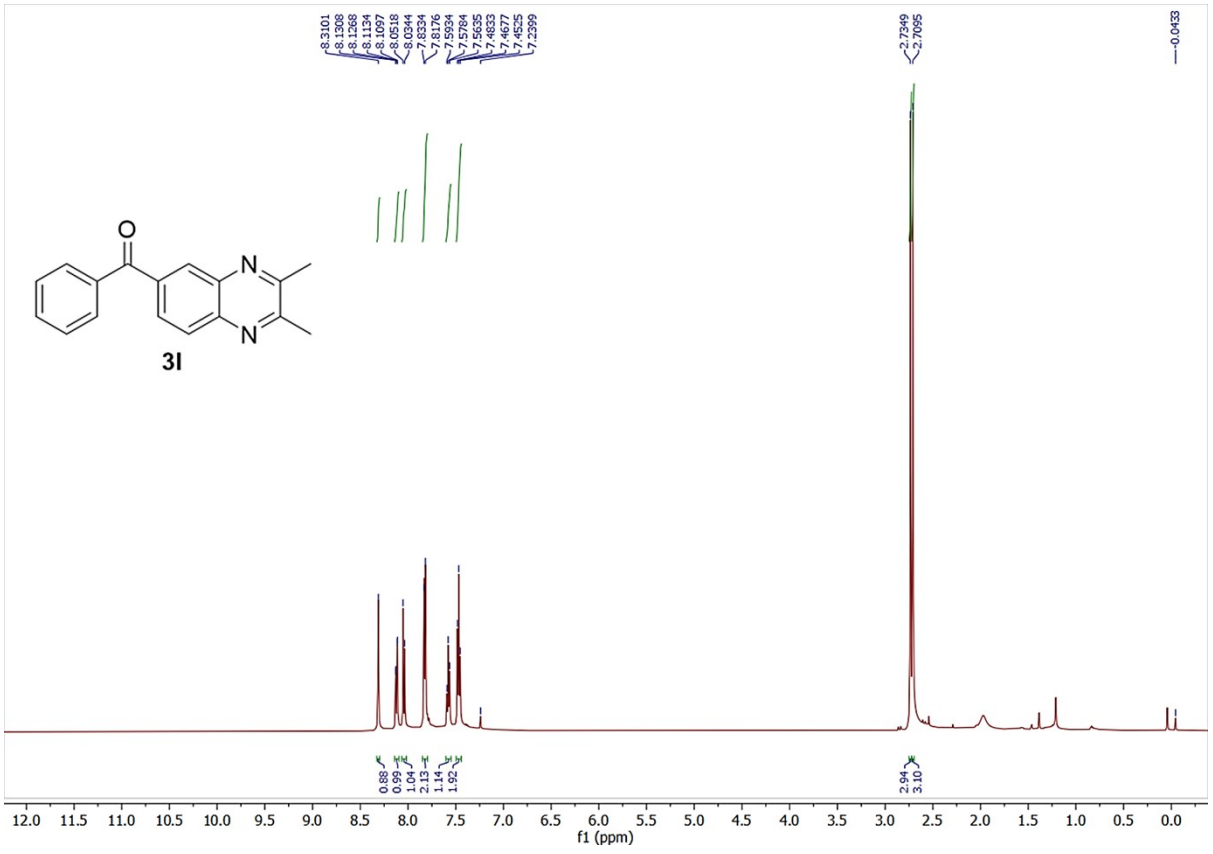


Figure S13: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3k**.



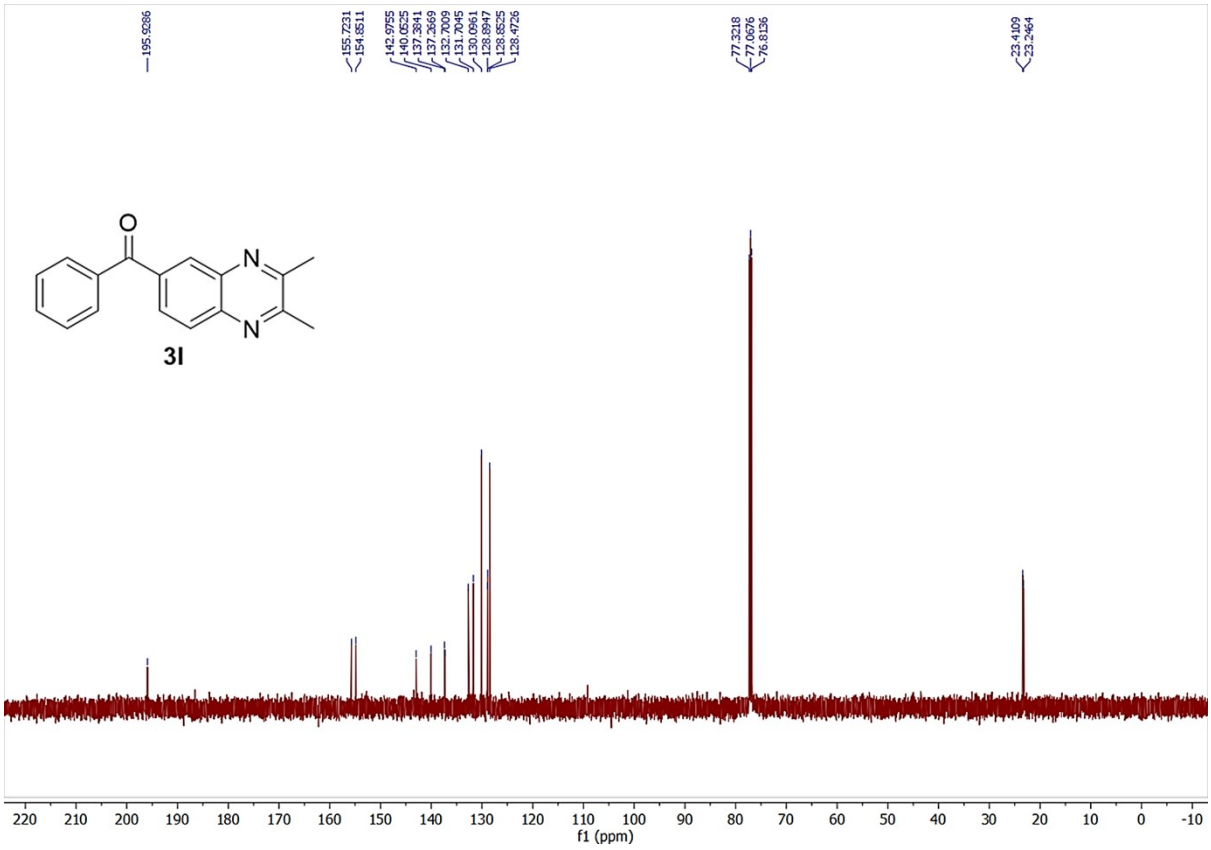
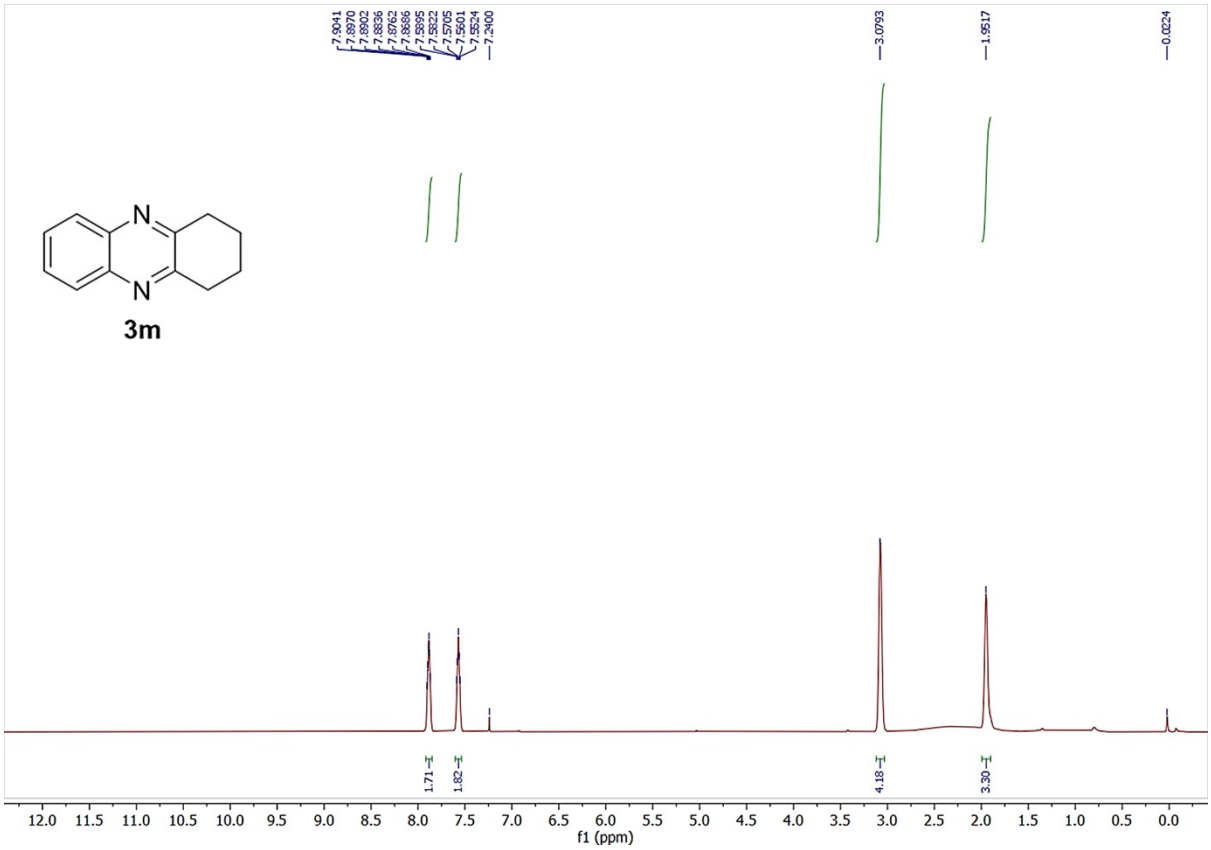


Figure S14: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3l**.



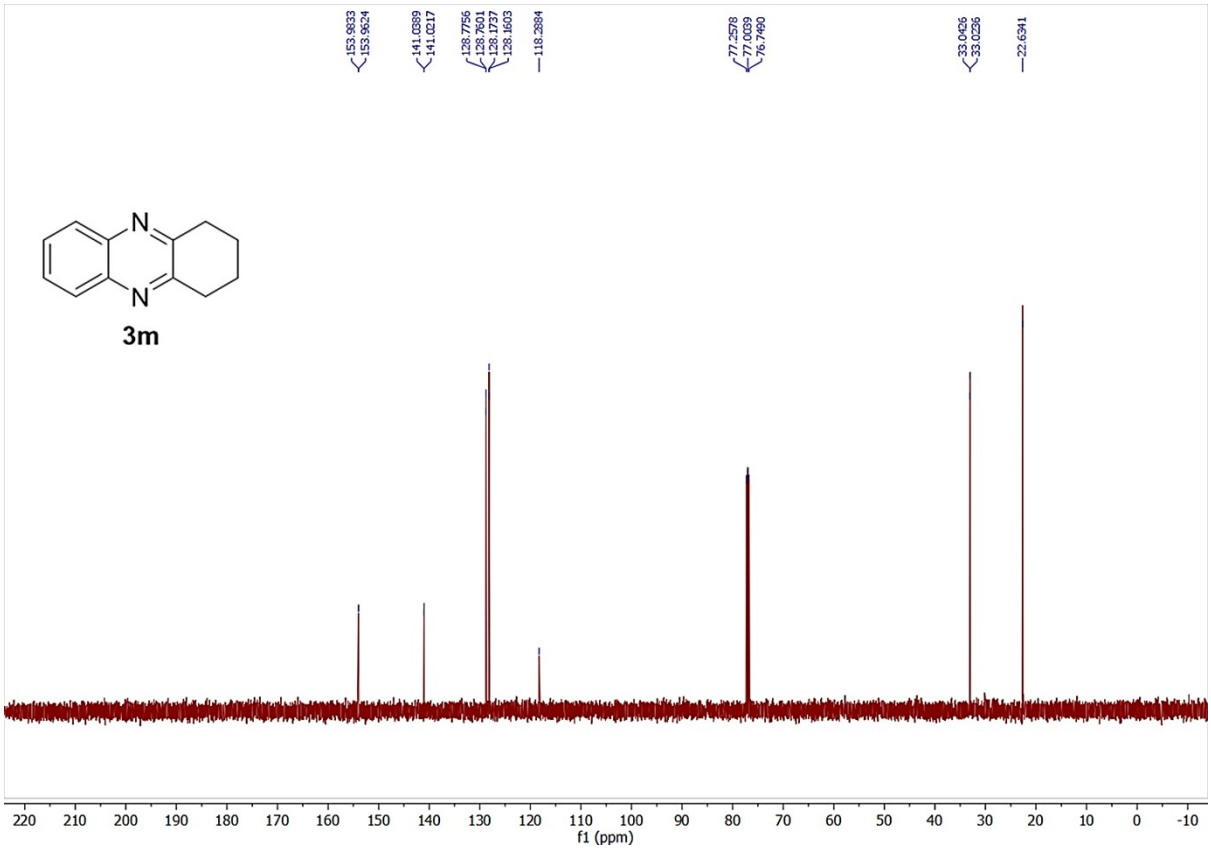
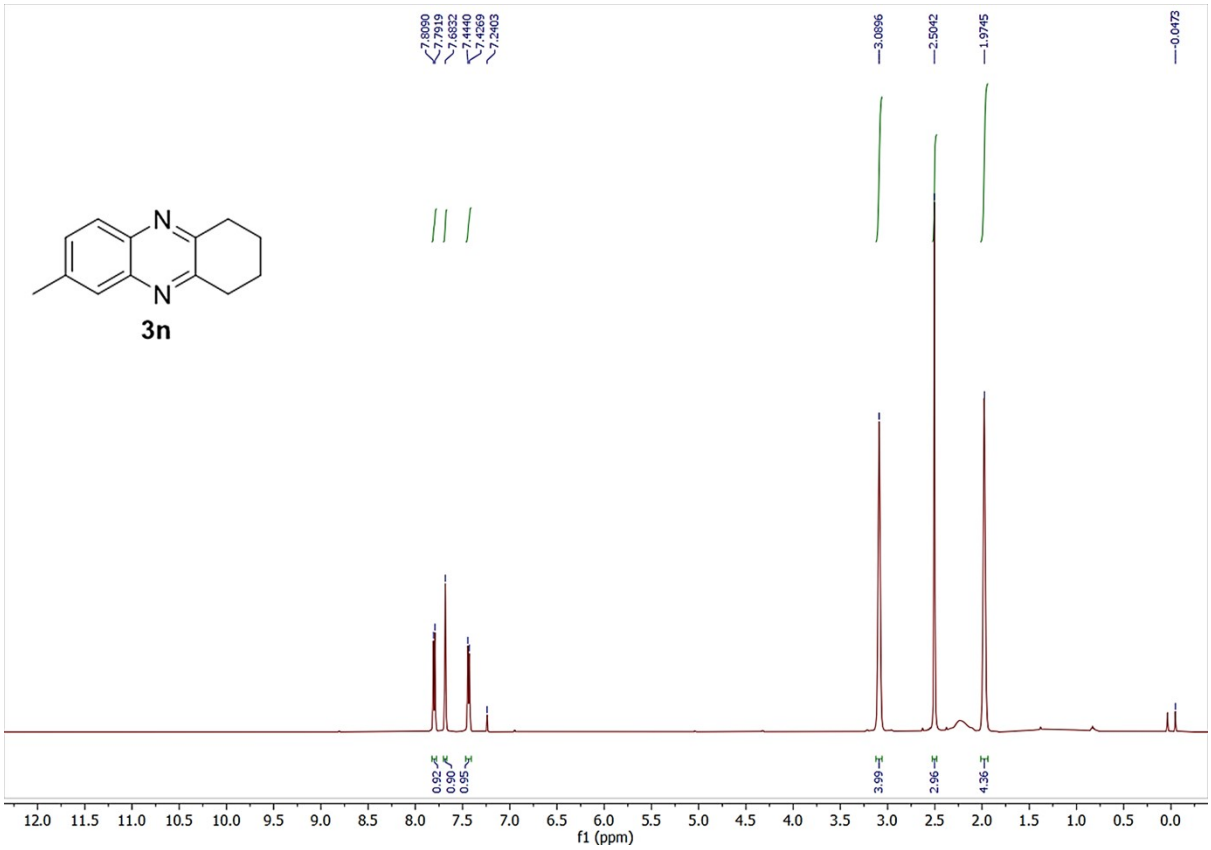


Figure S15: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3m**.



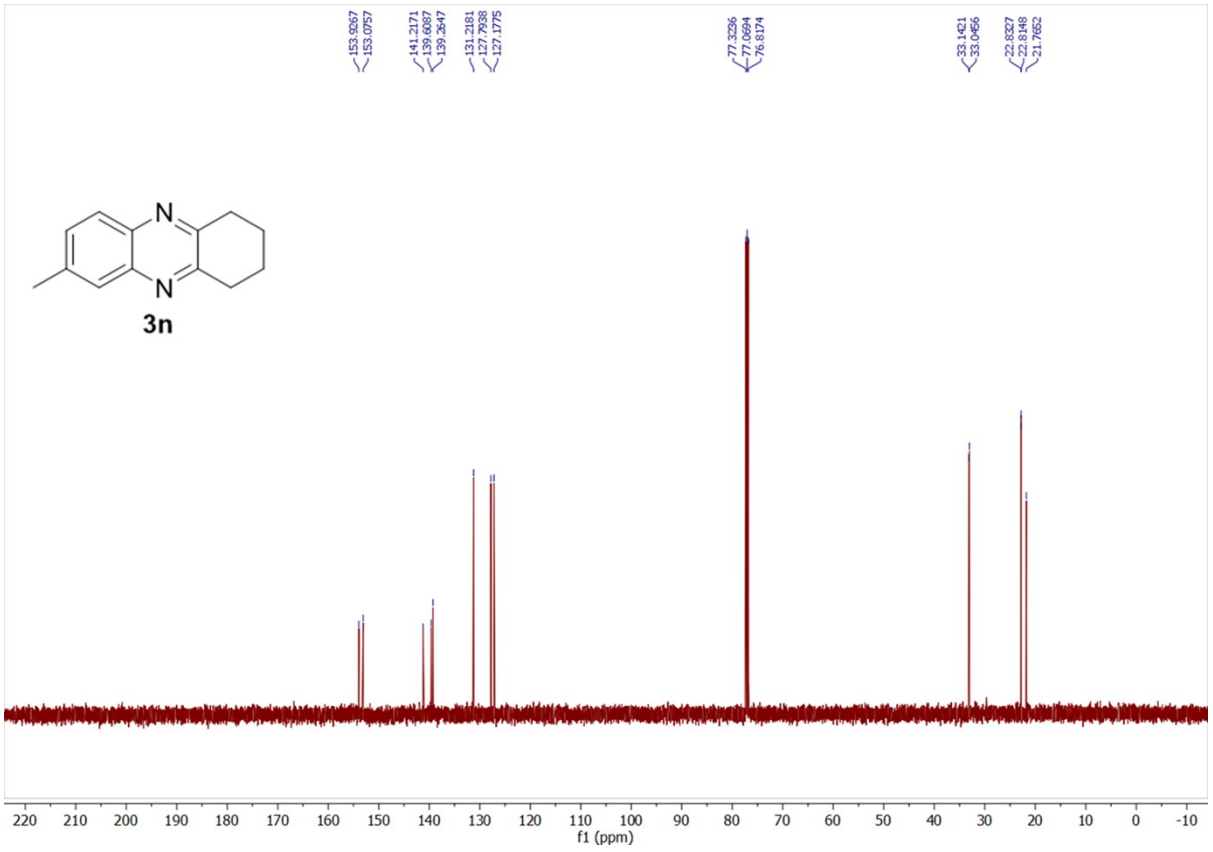
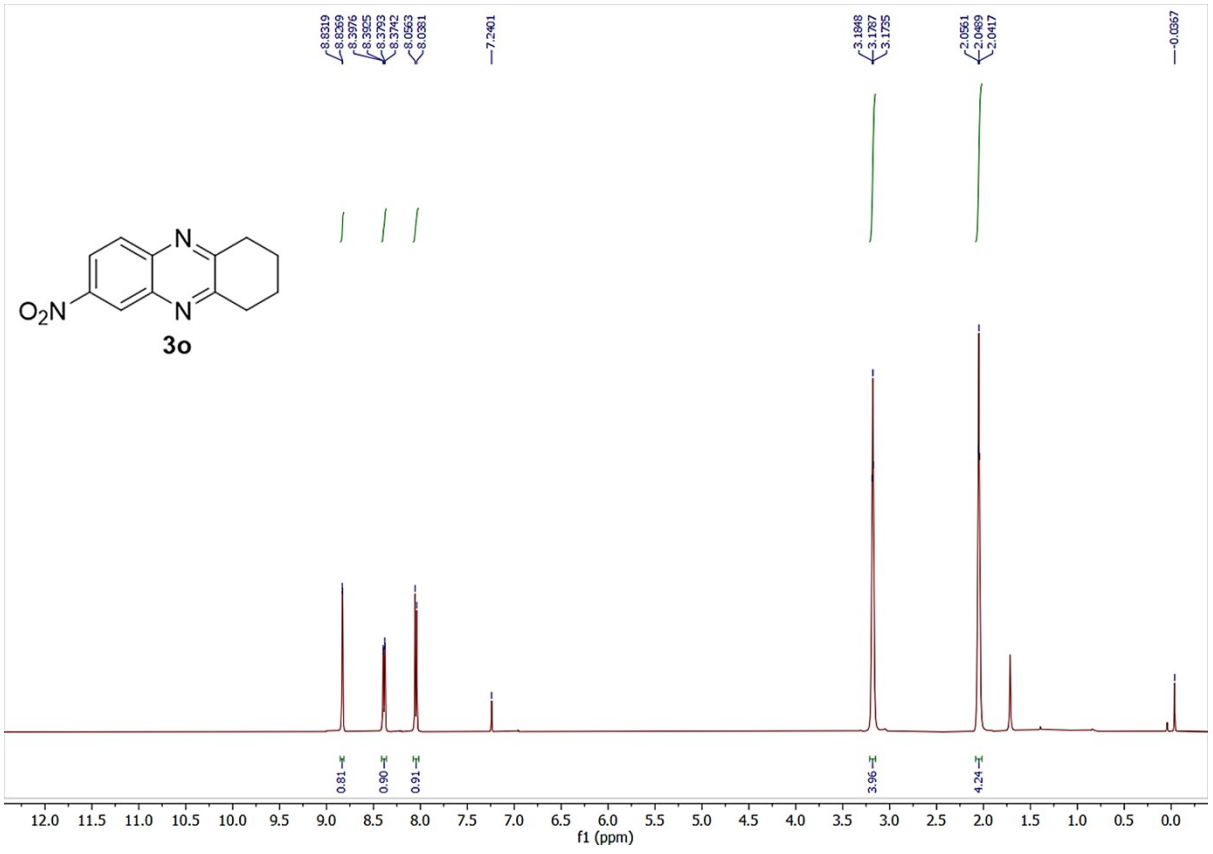


Figure S16: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3n**.



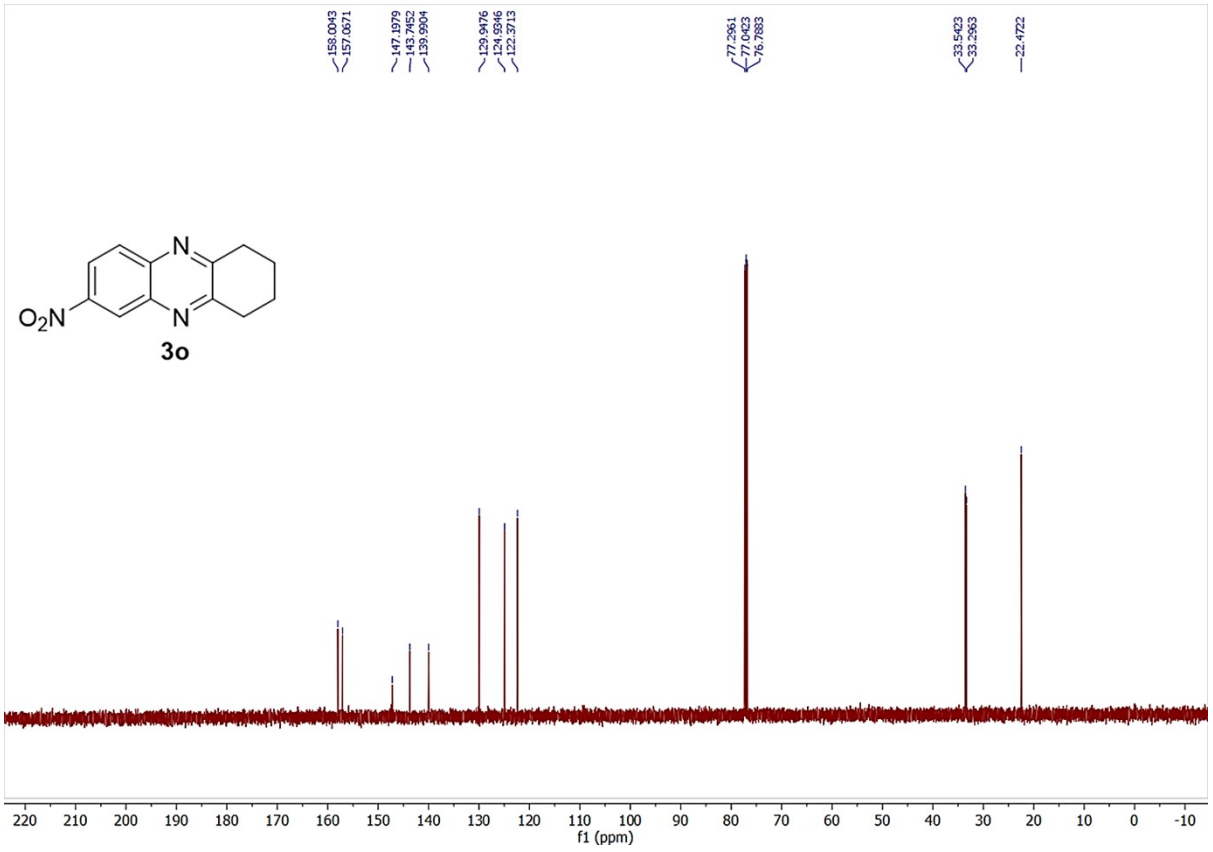
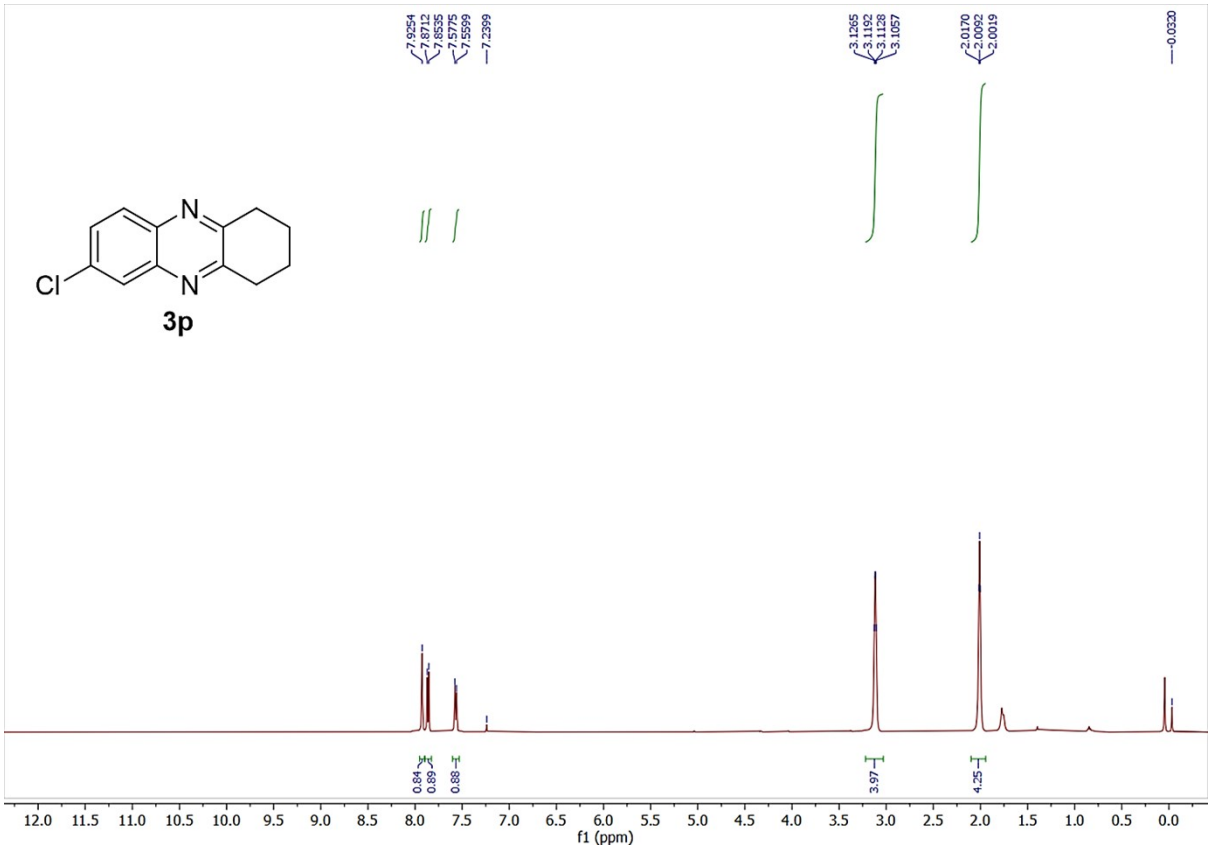


Figure S17: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3o**.



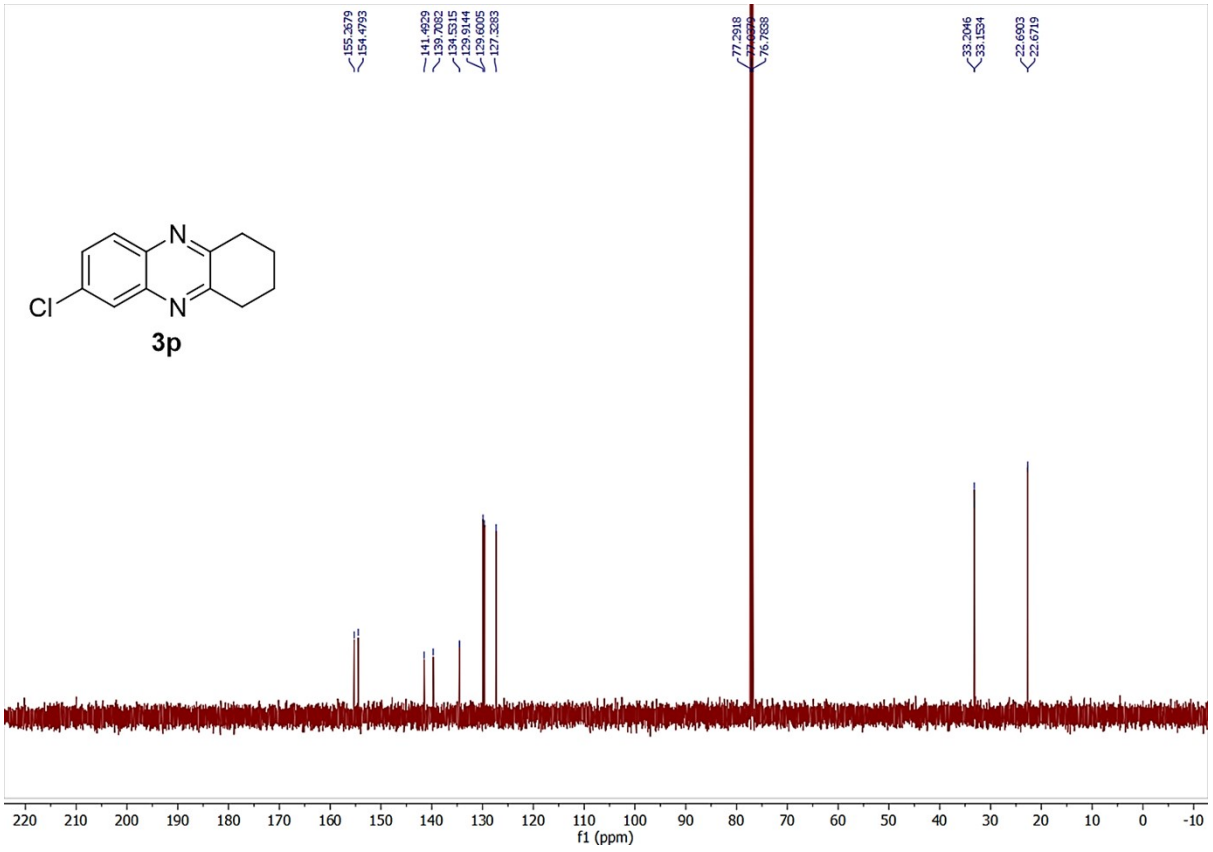
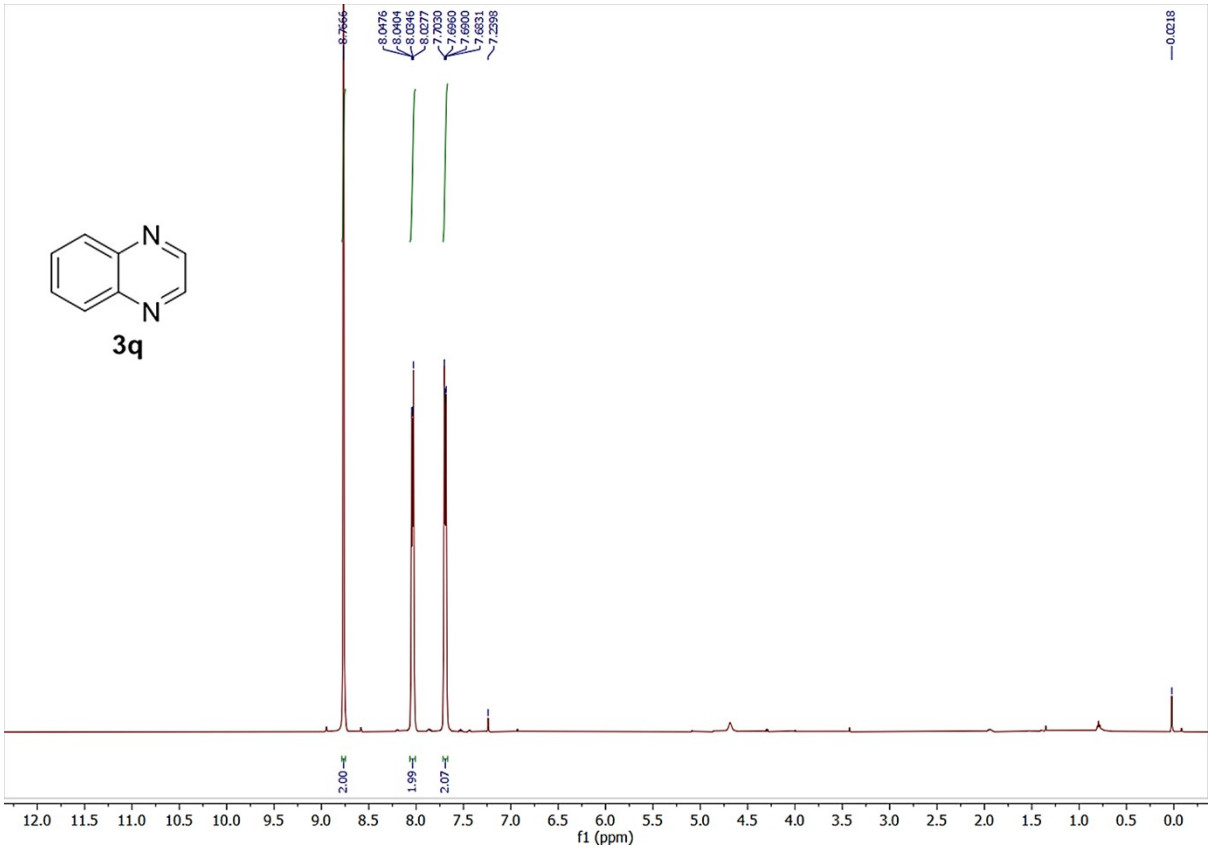


Figure S18: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3p**.



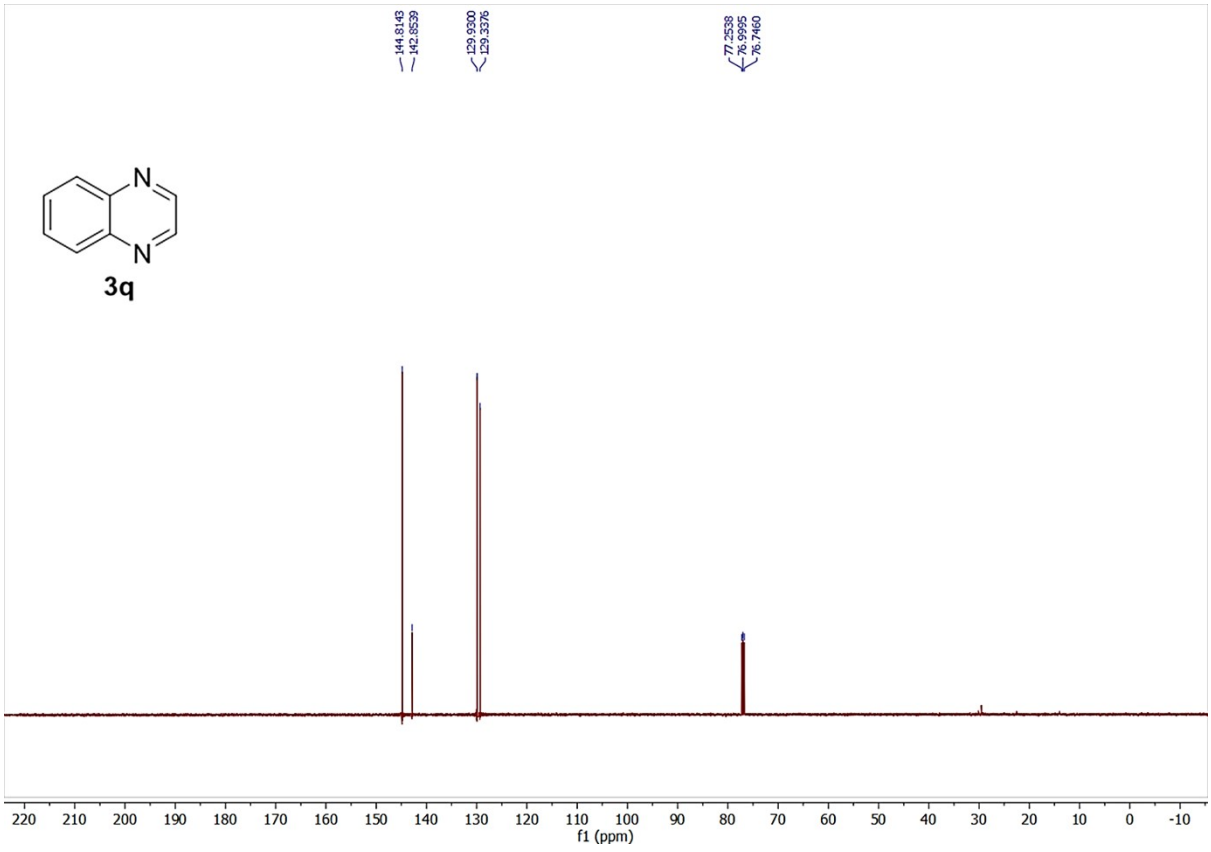
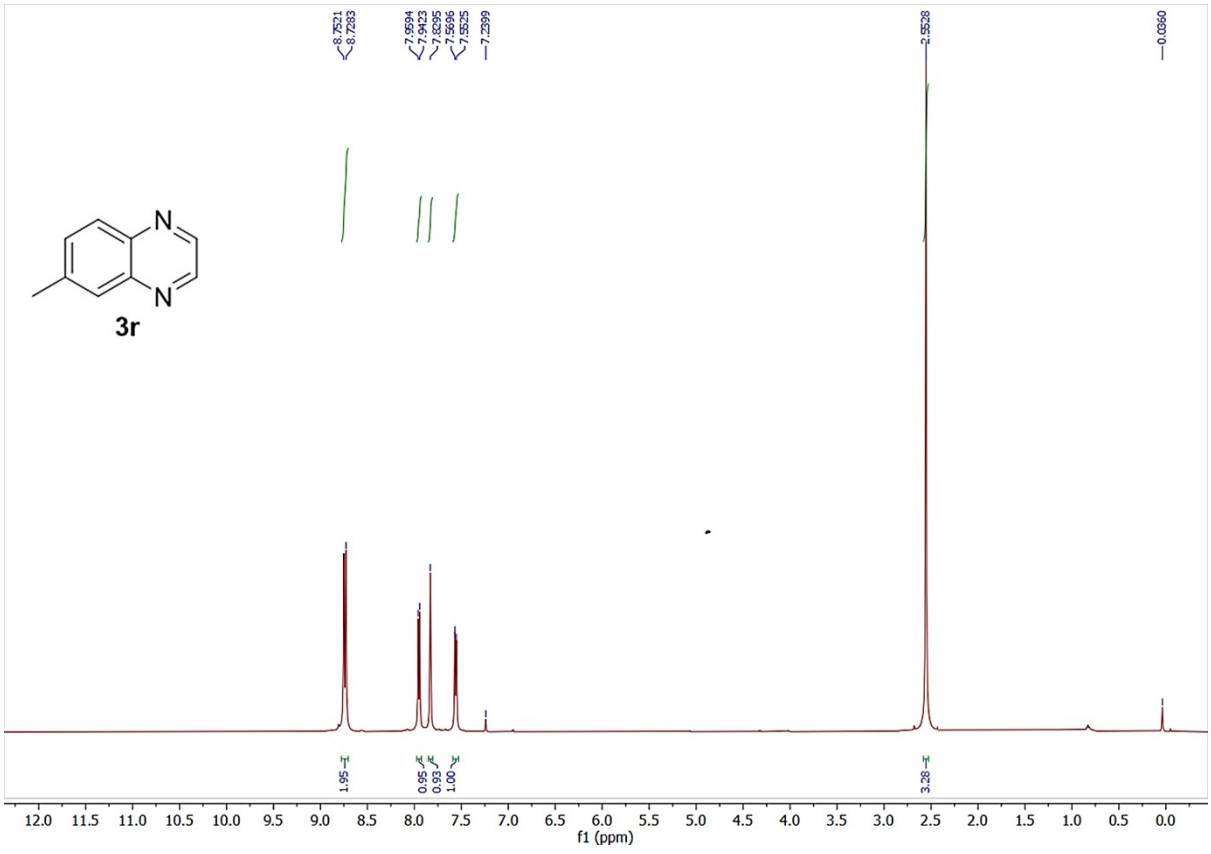


Figure S19: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3q.**



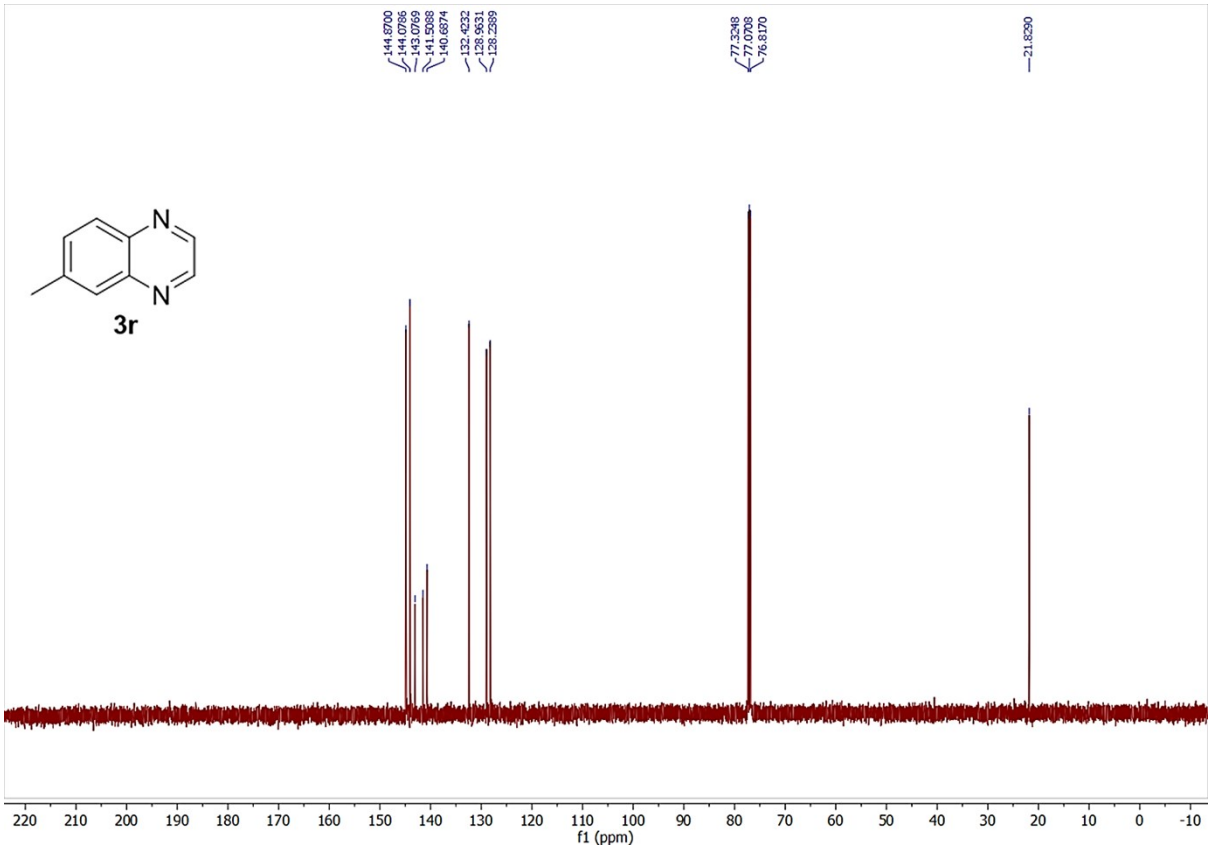
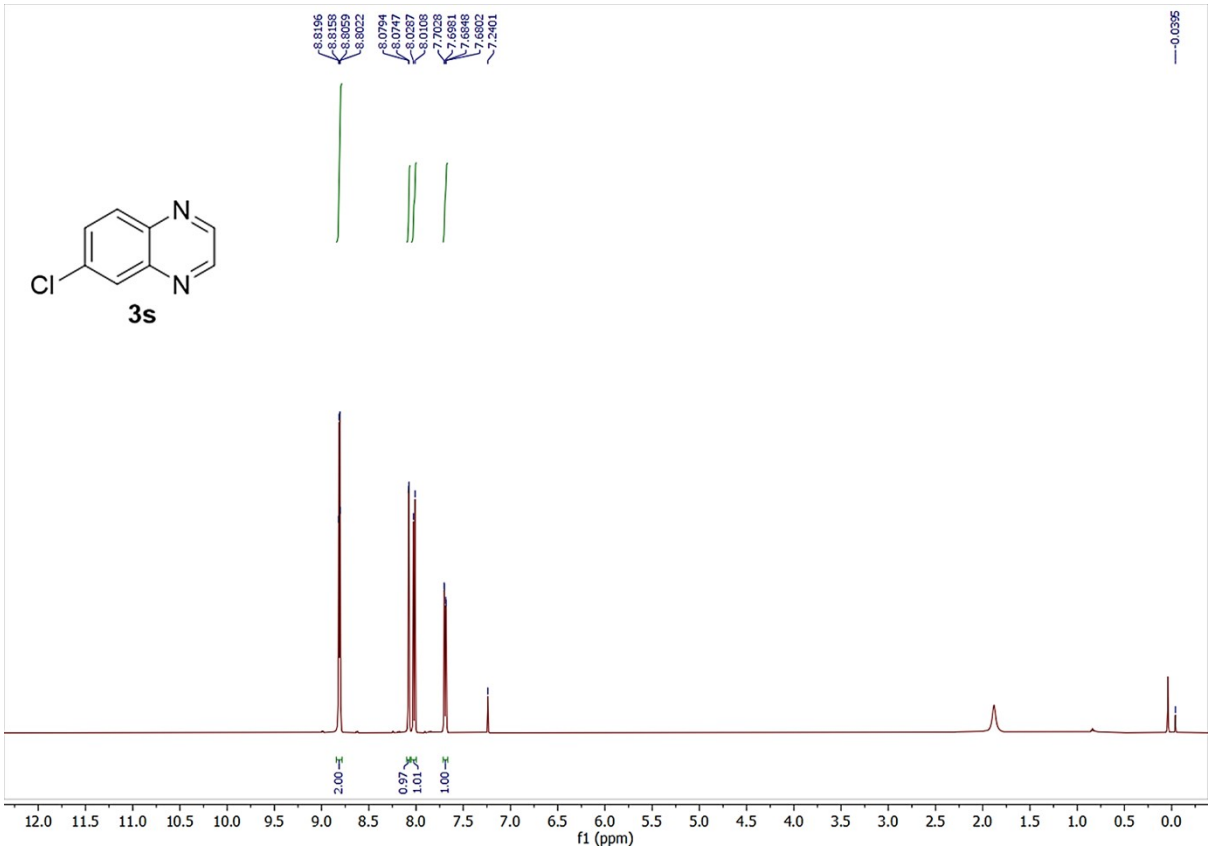


Figure S20: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3r**.



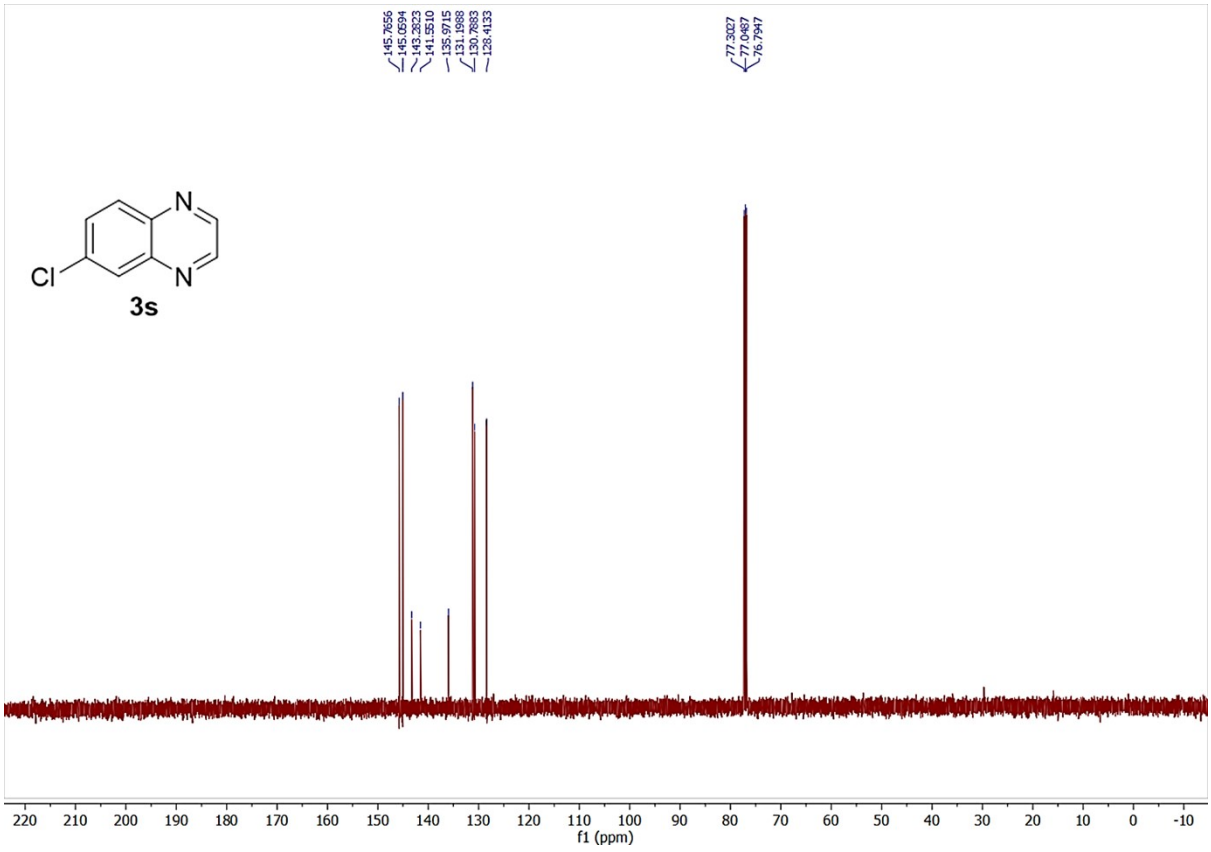
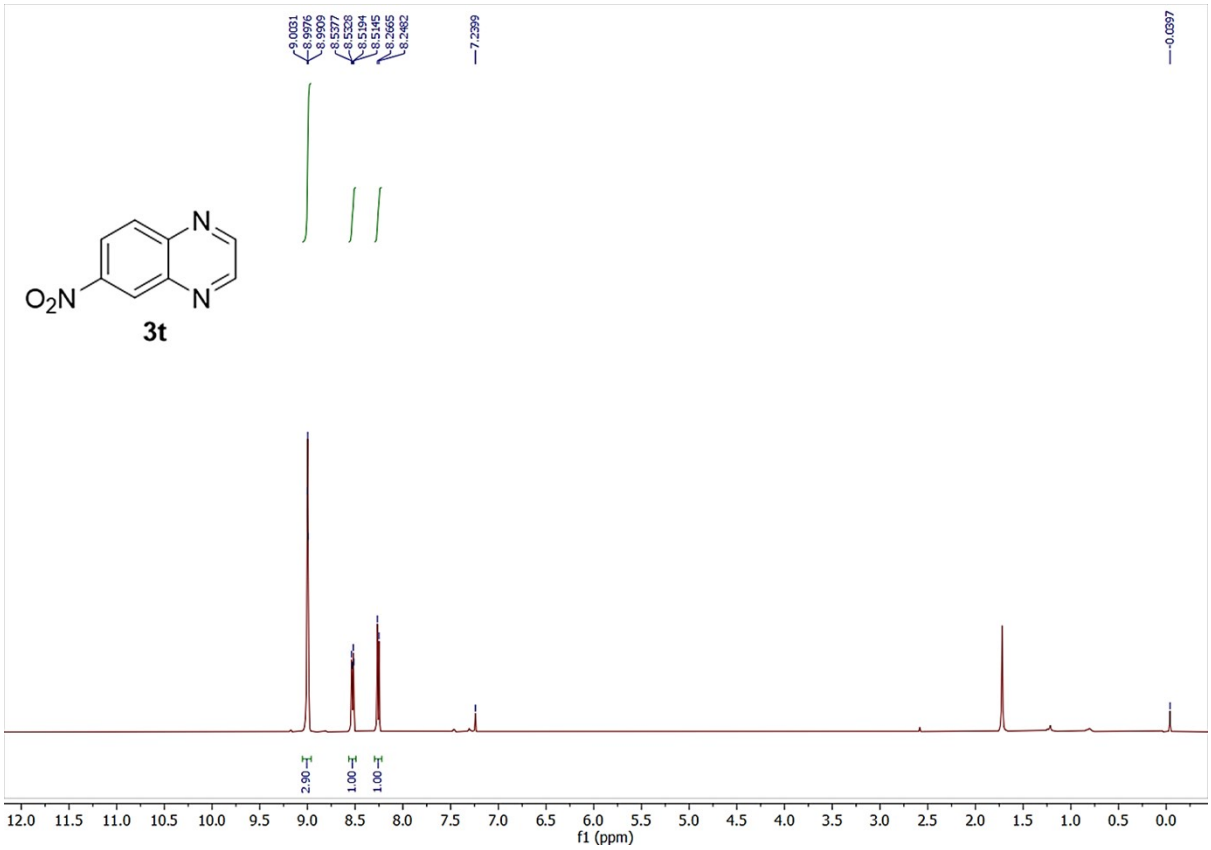


Figure S21: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3s**.



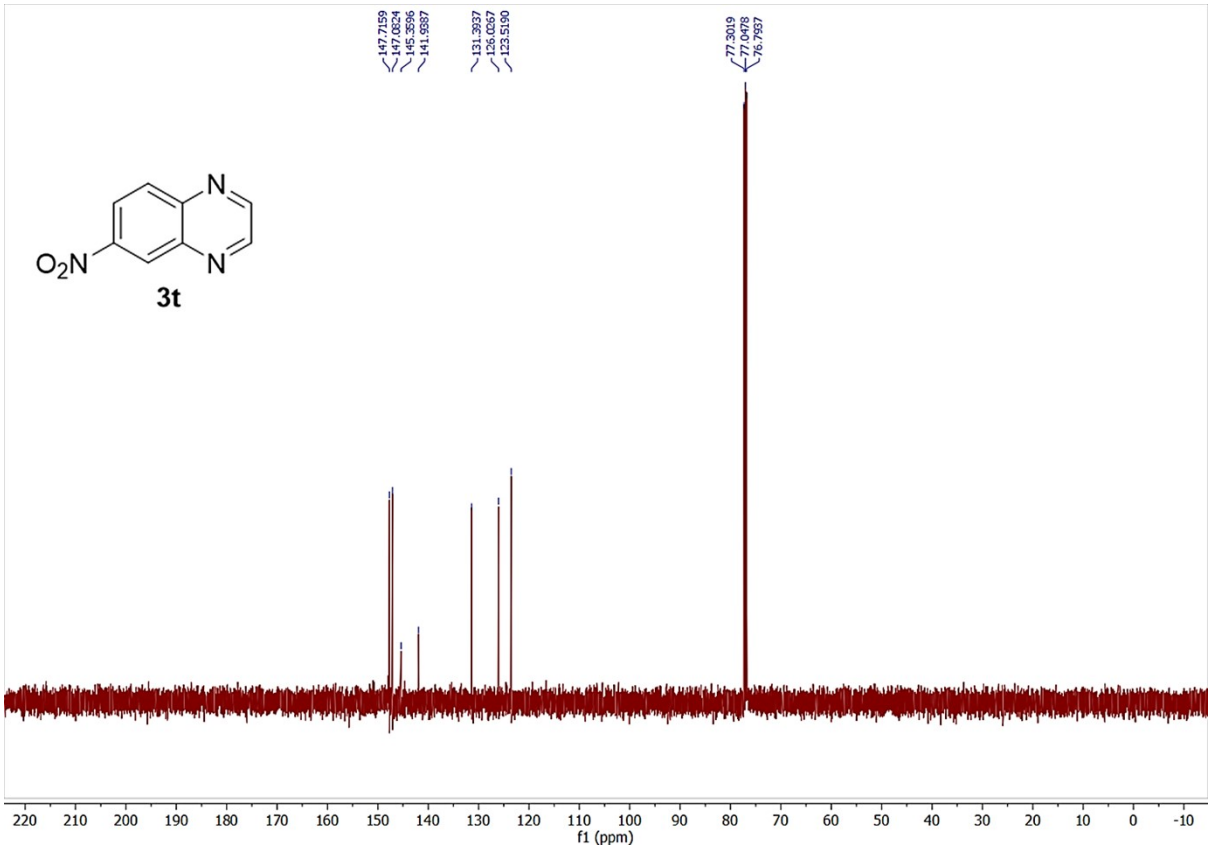
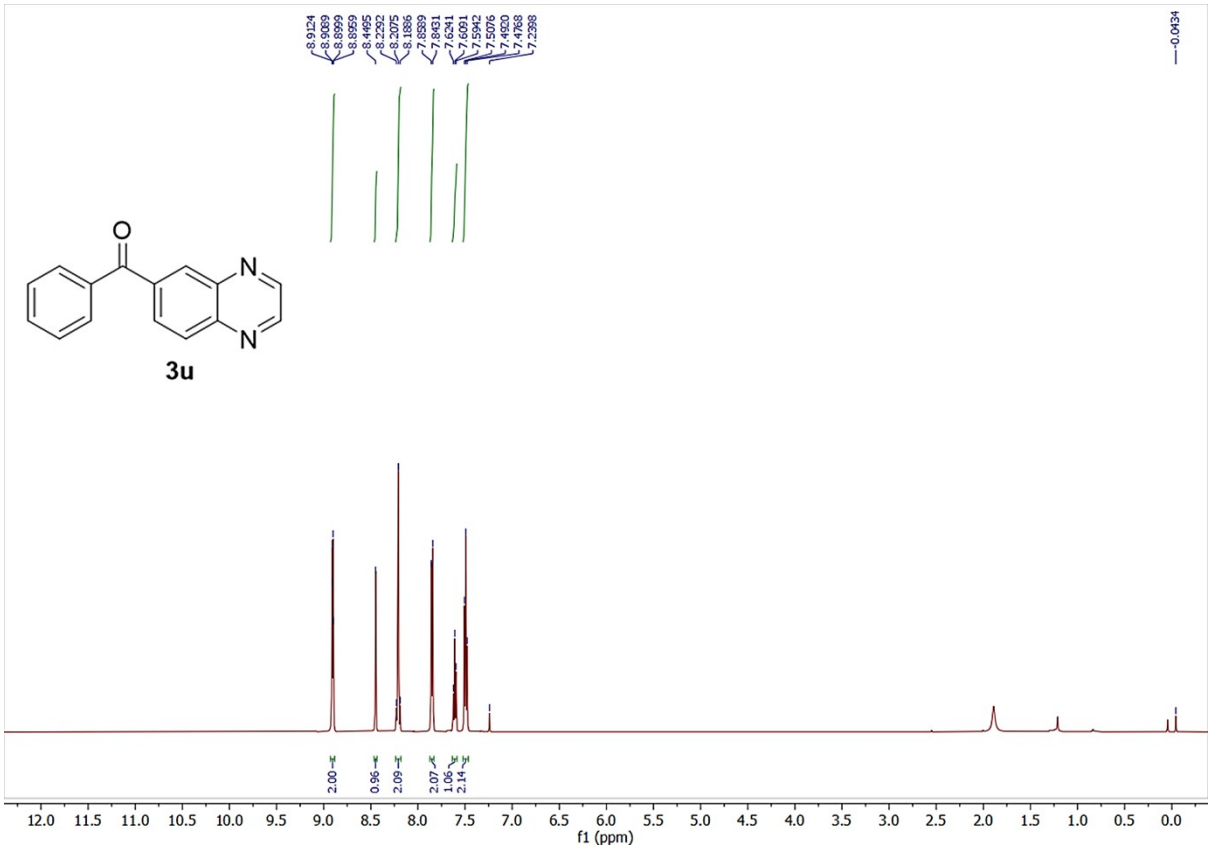


Figure S22: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3t**.



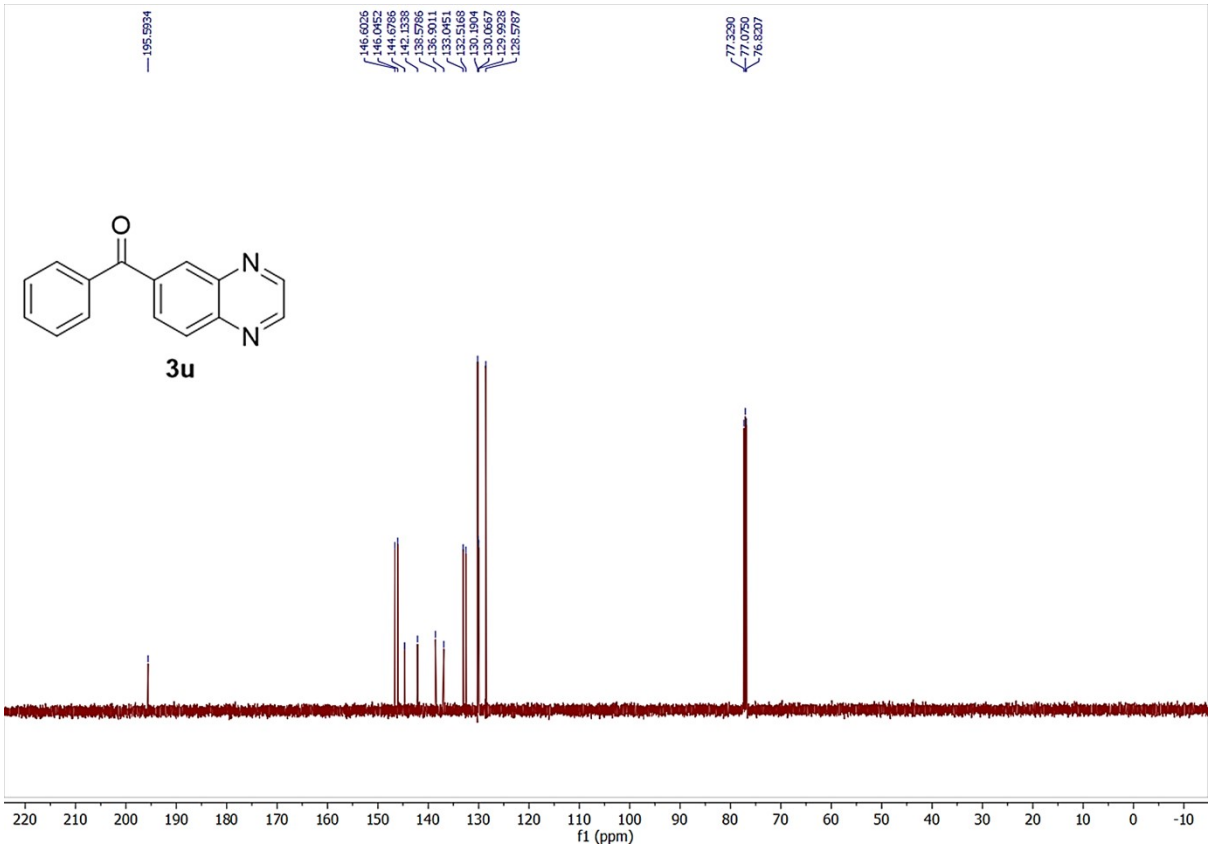
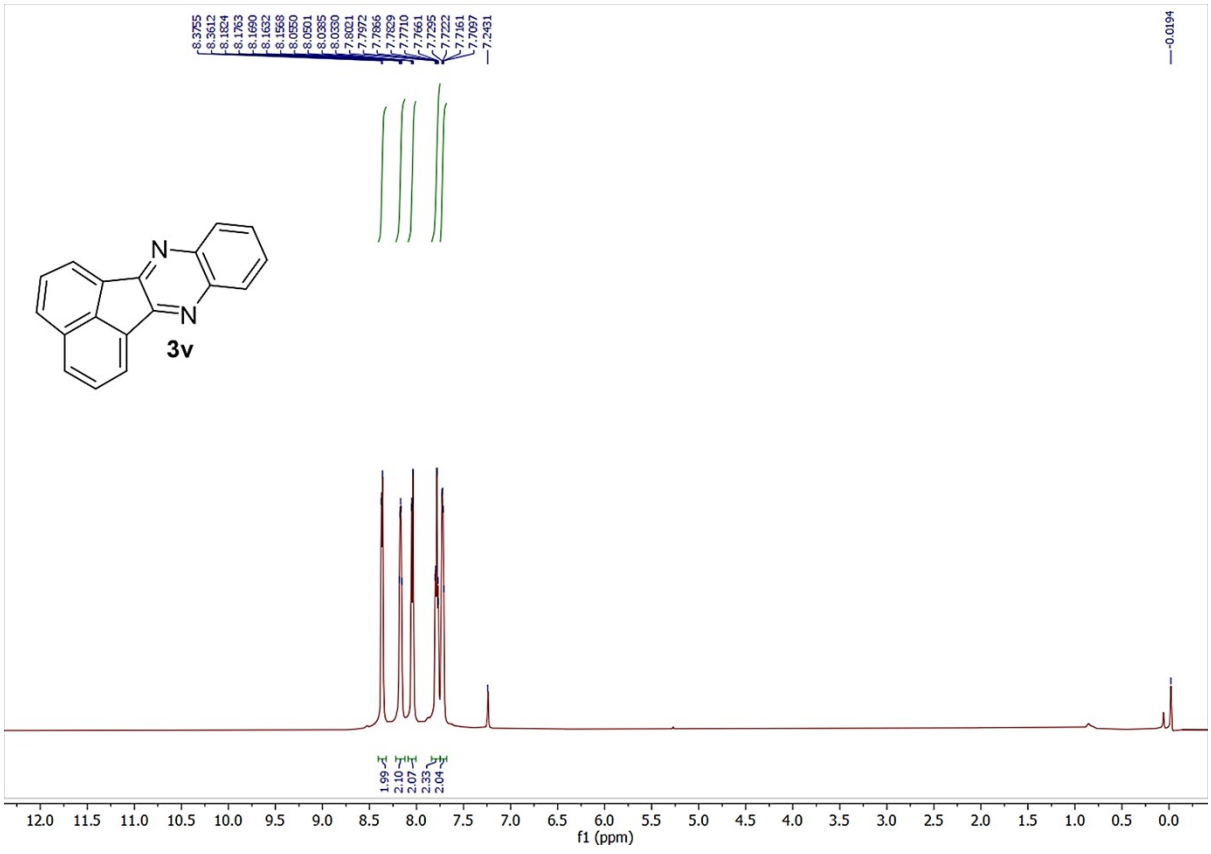


Figure S23: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3u**.



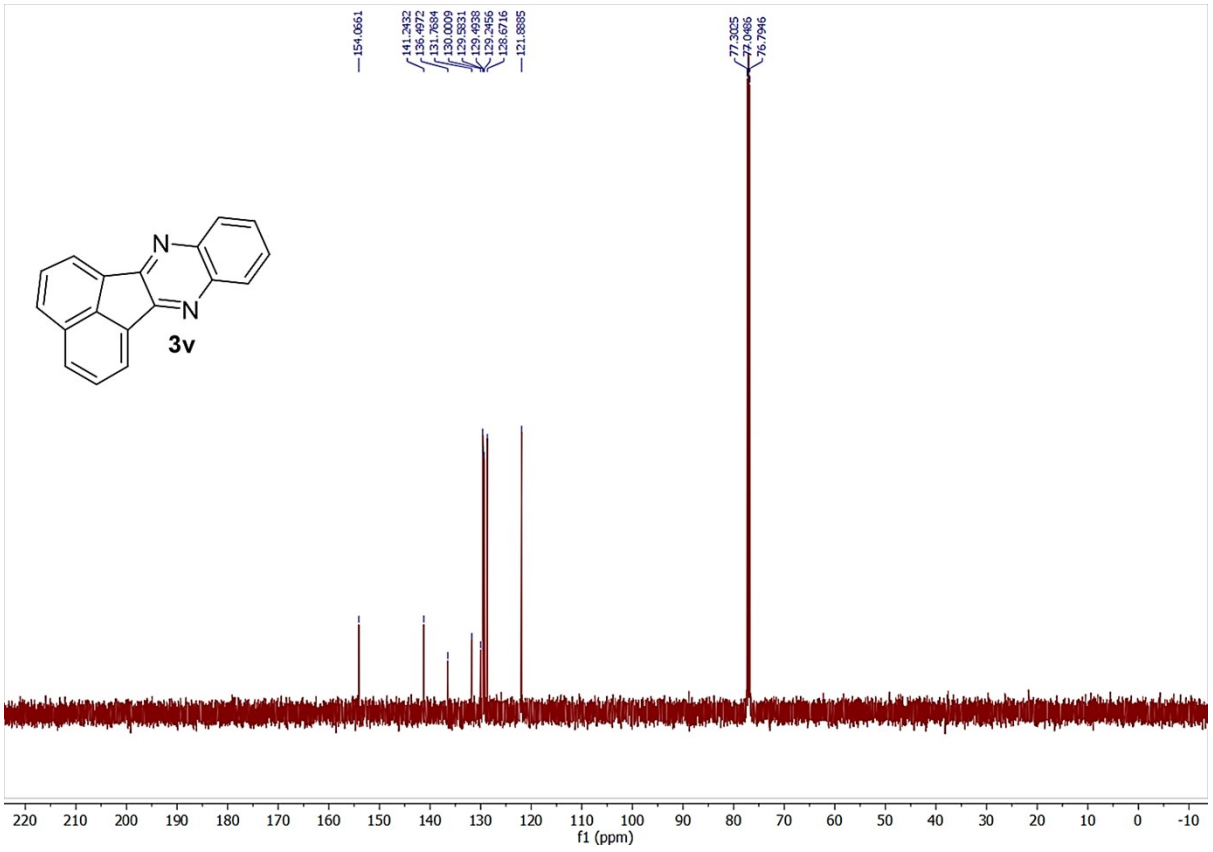
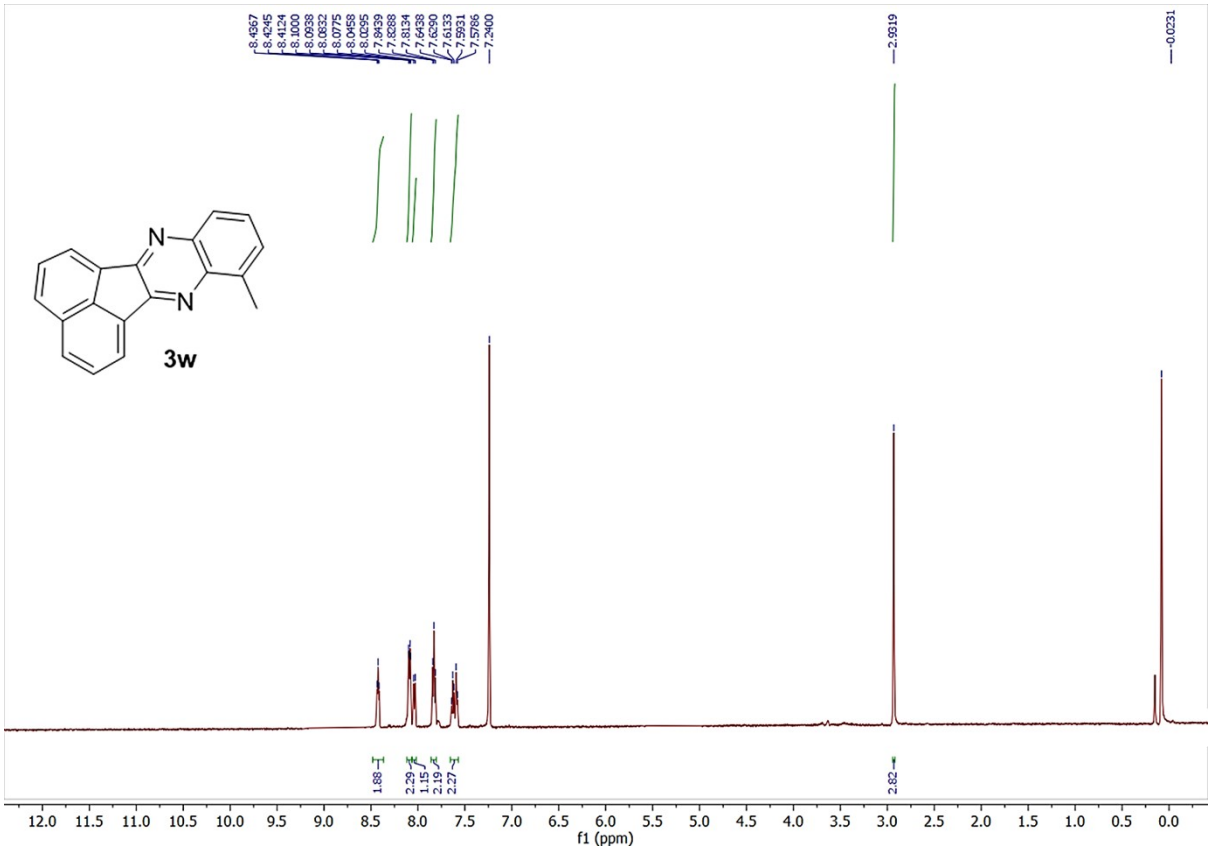


Figure S24: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3v**.



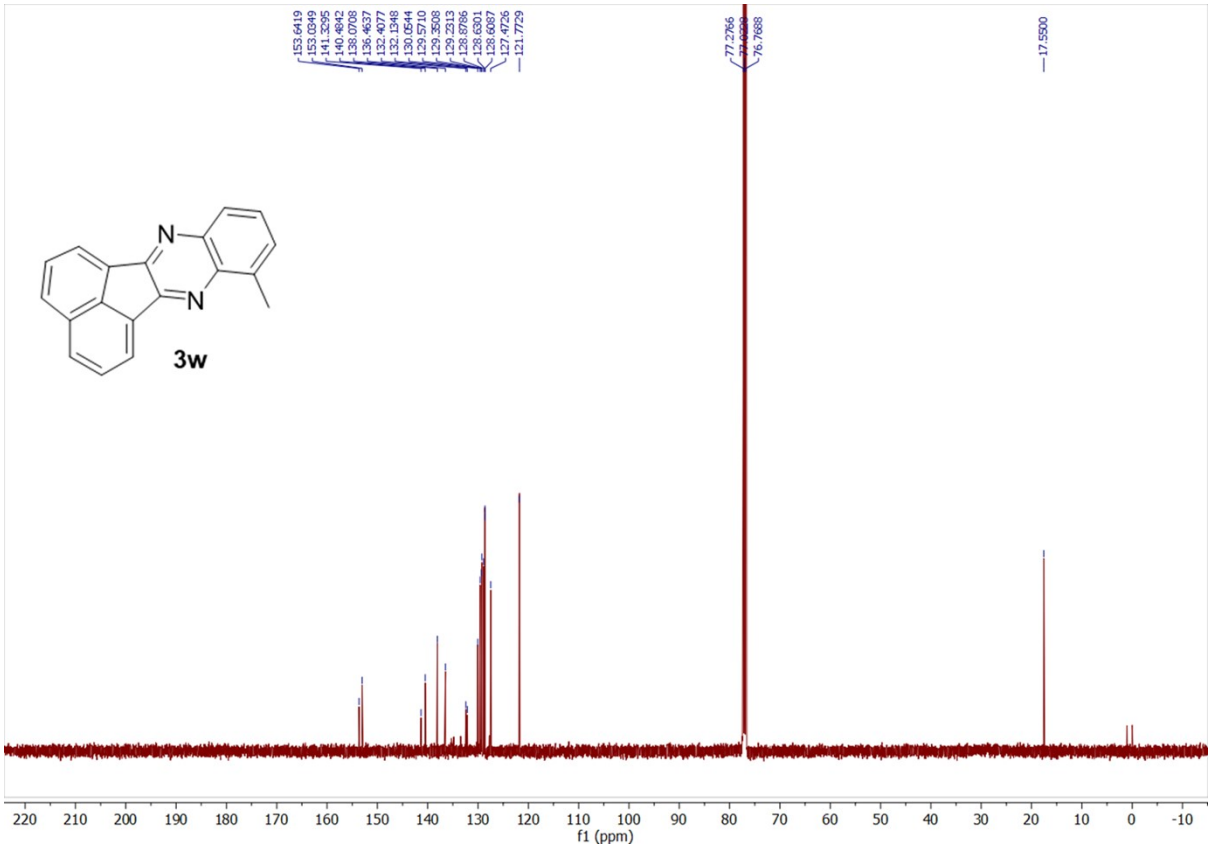
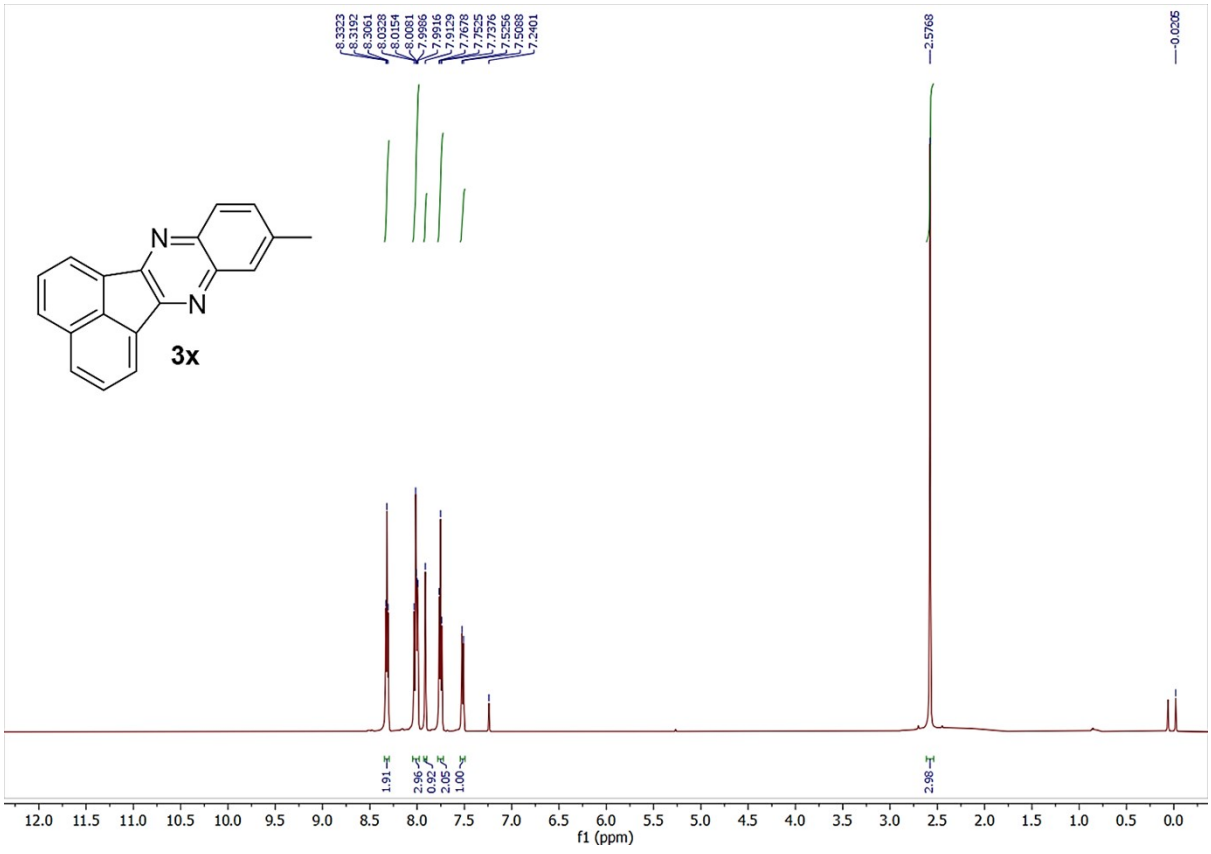


Figure S25: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3w**.



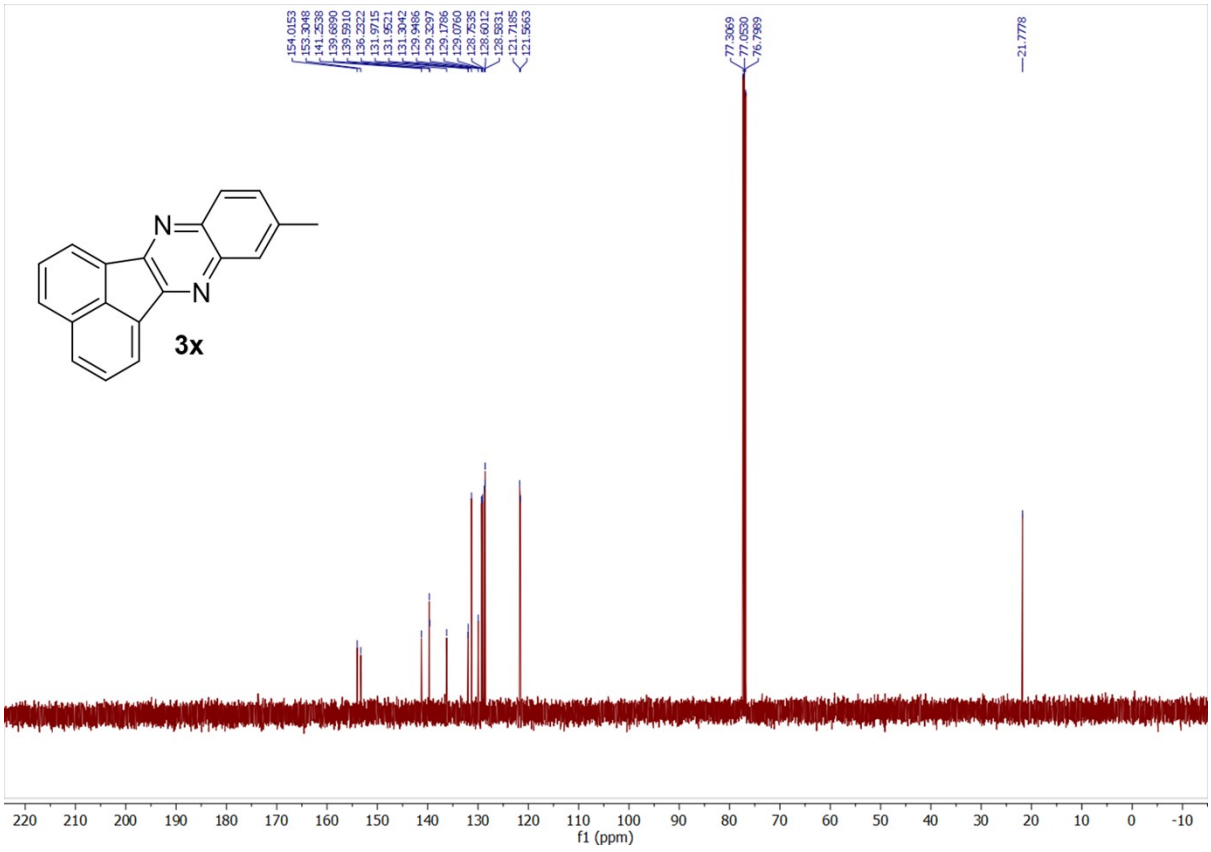
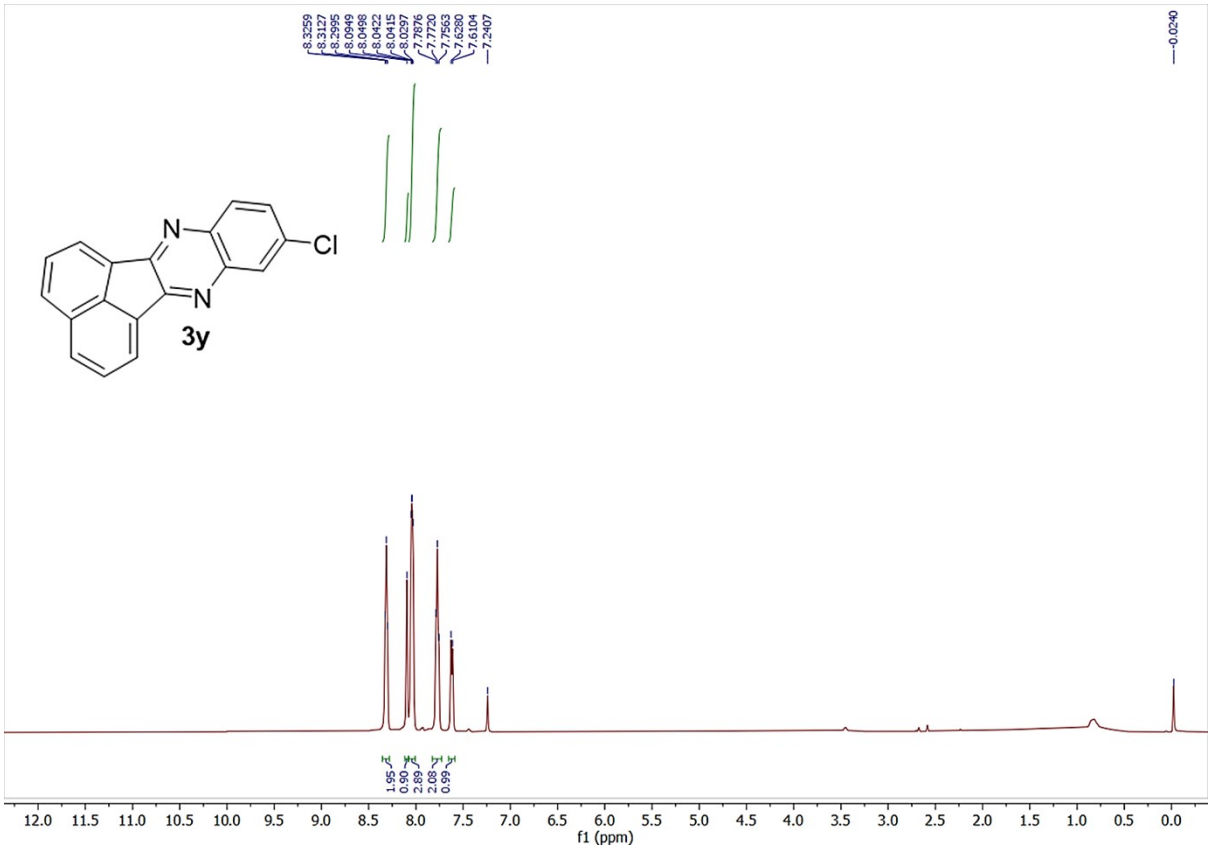


Figure S26: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3x**.



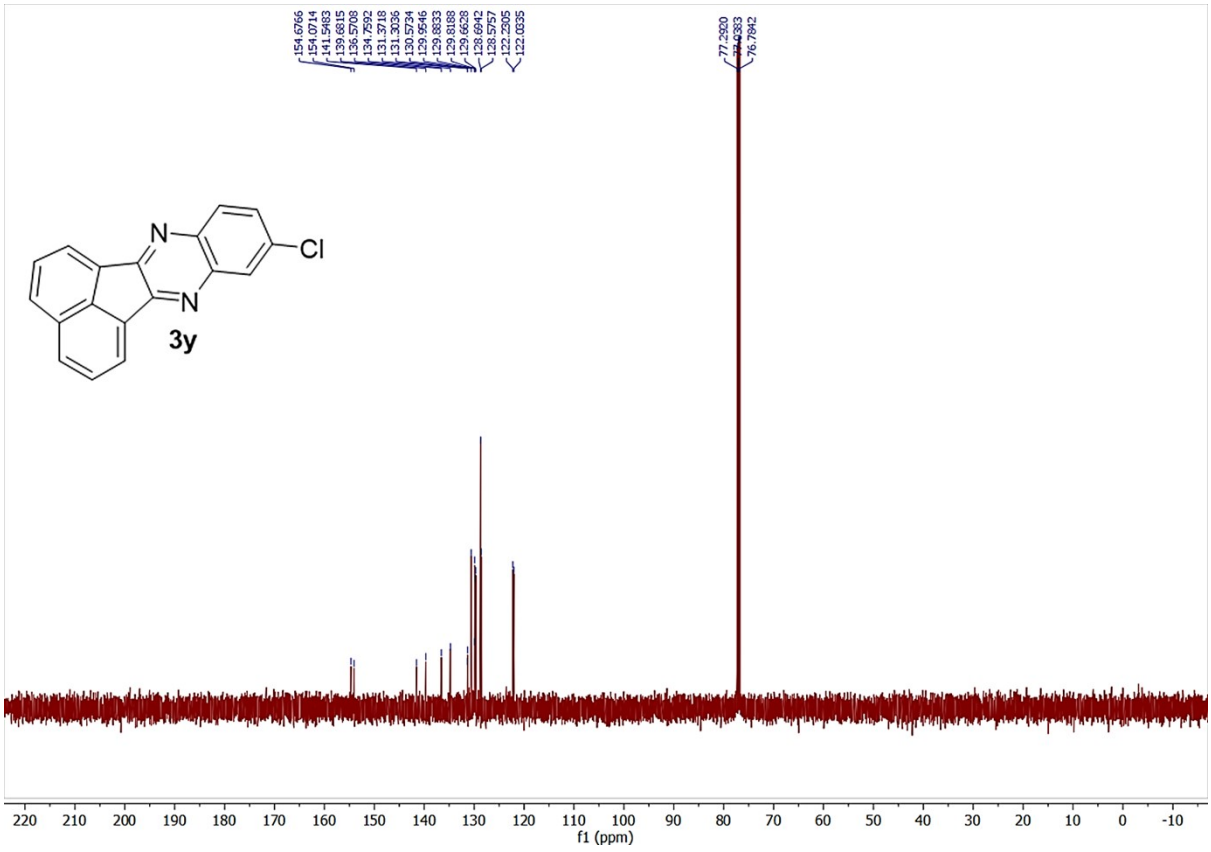
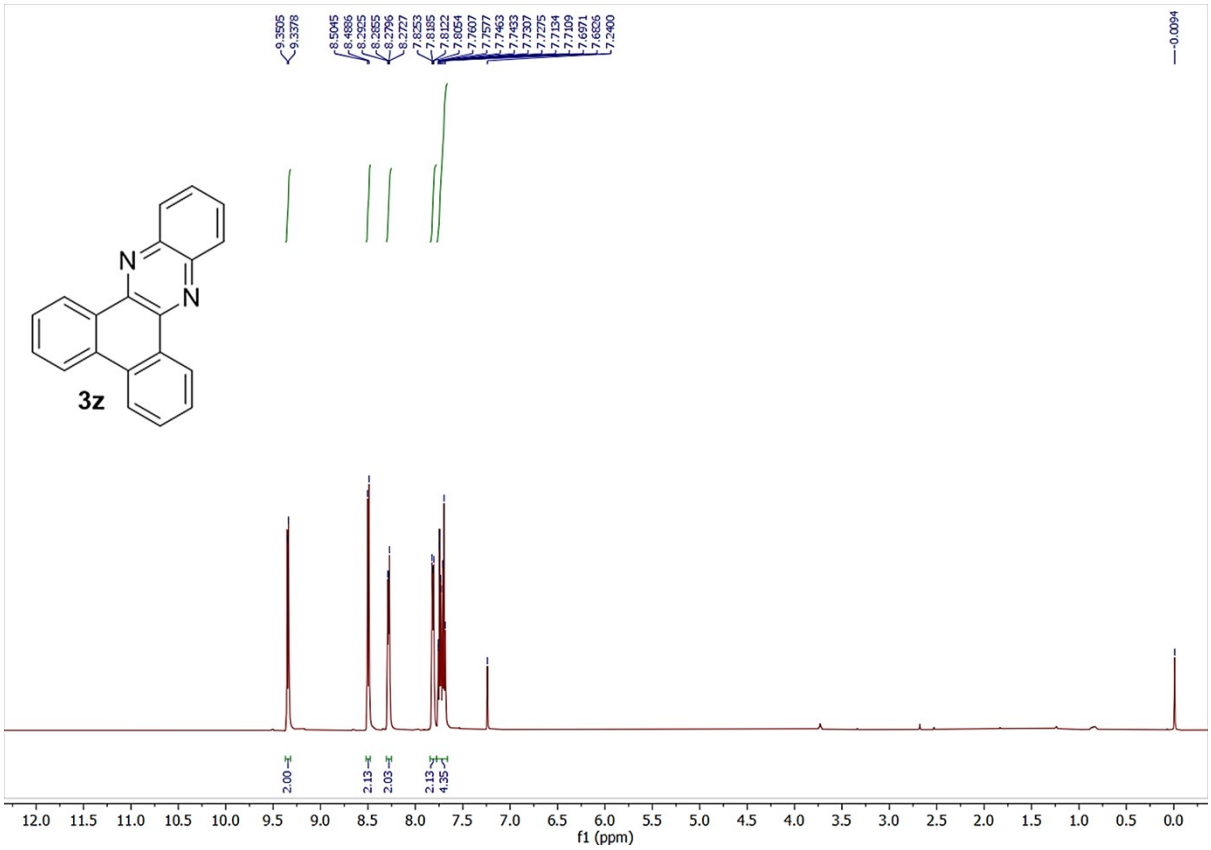


Figure S27: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3y**.



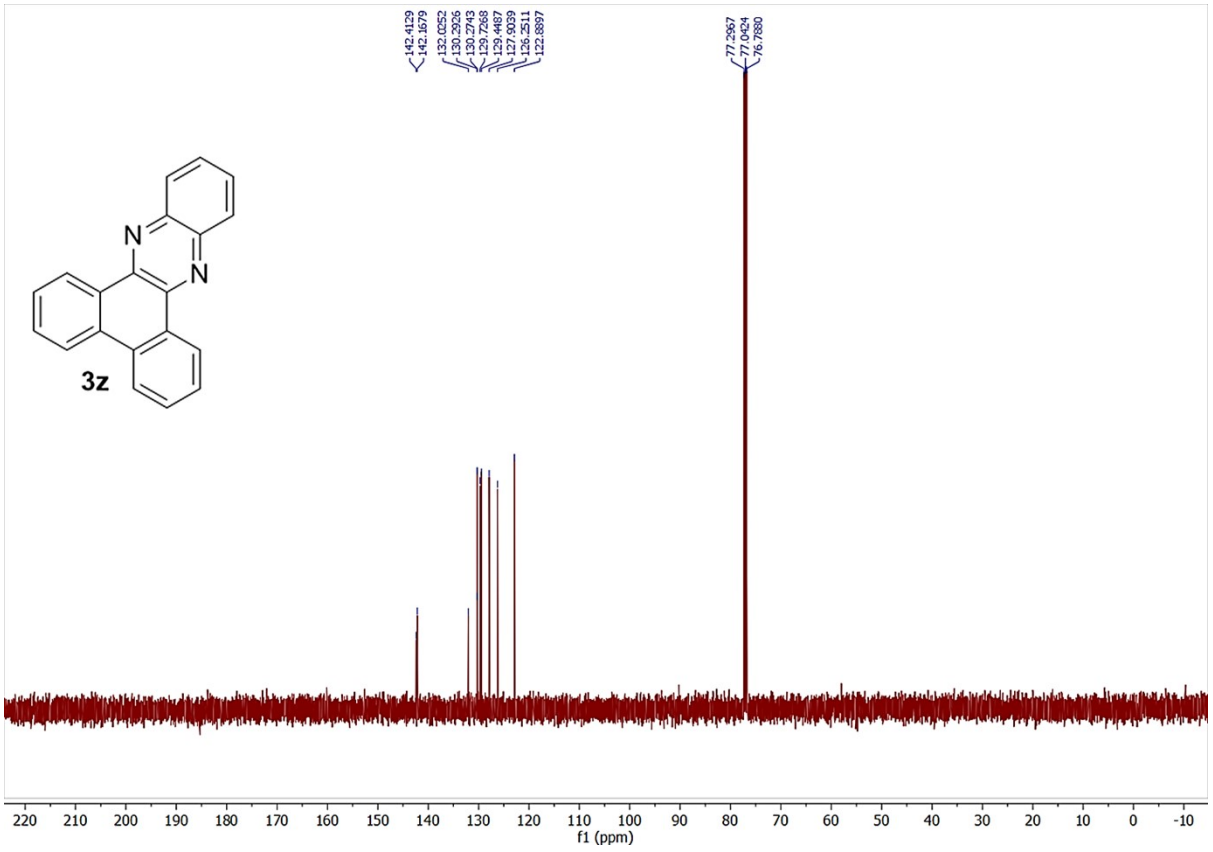
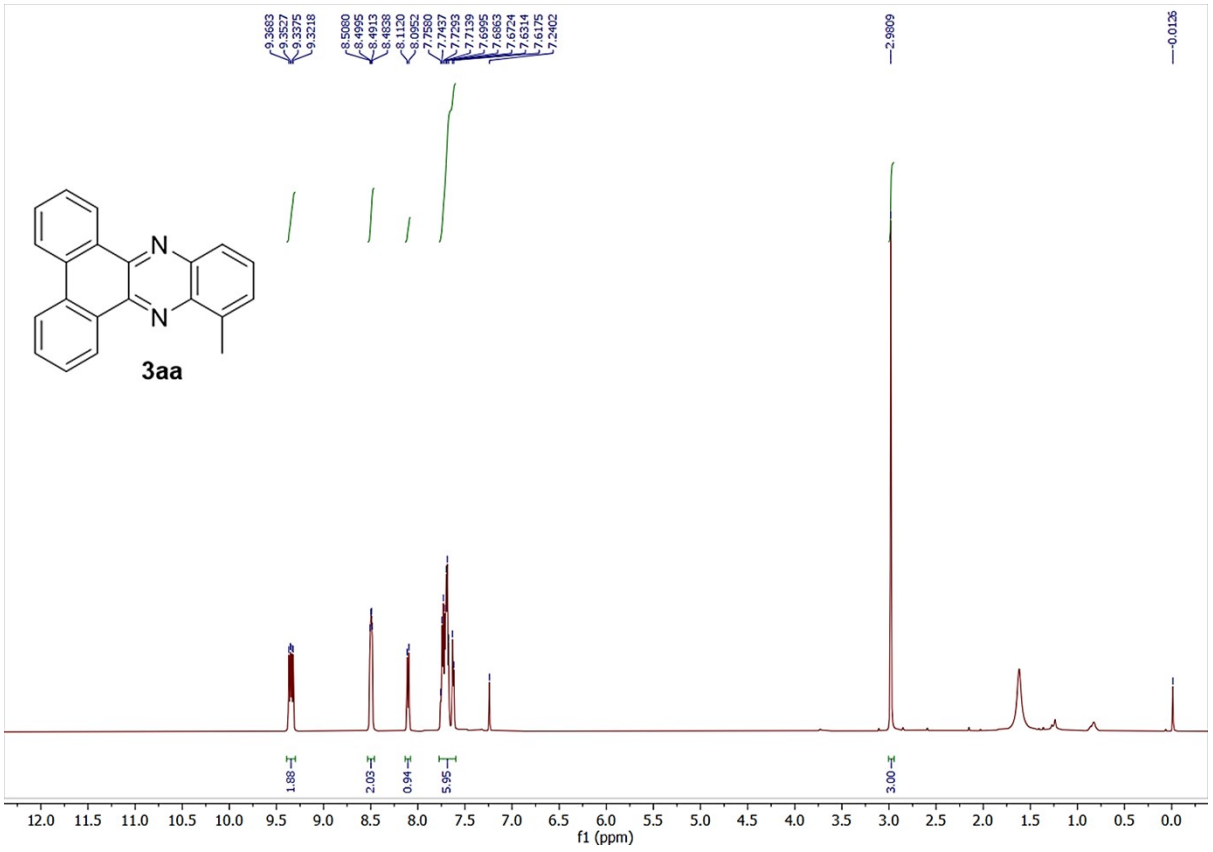


Figure S28: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3z**.



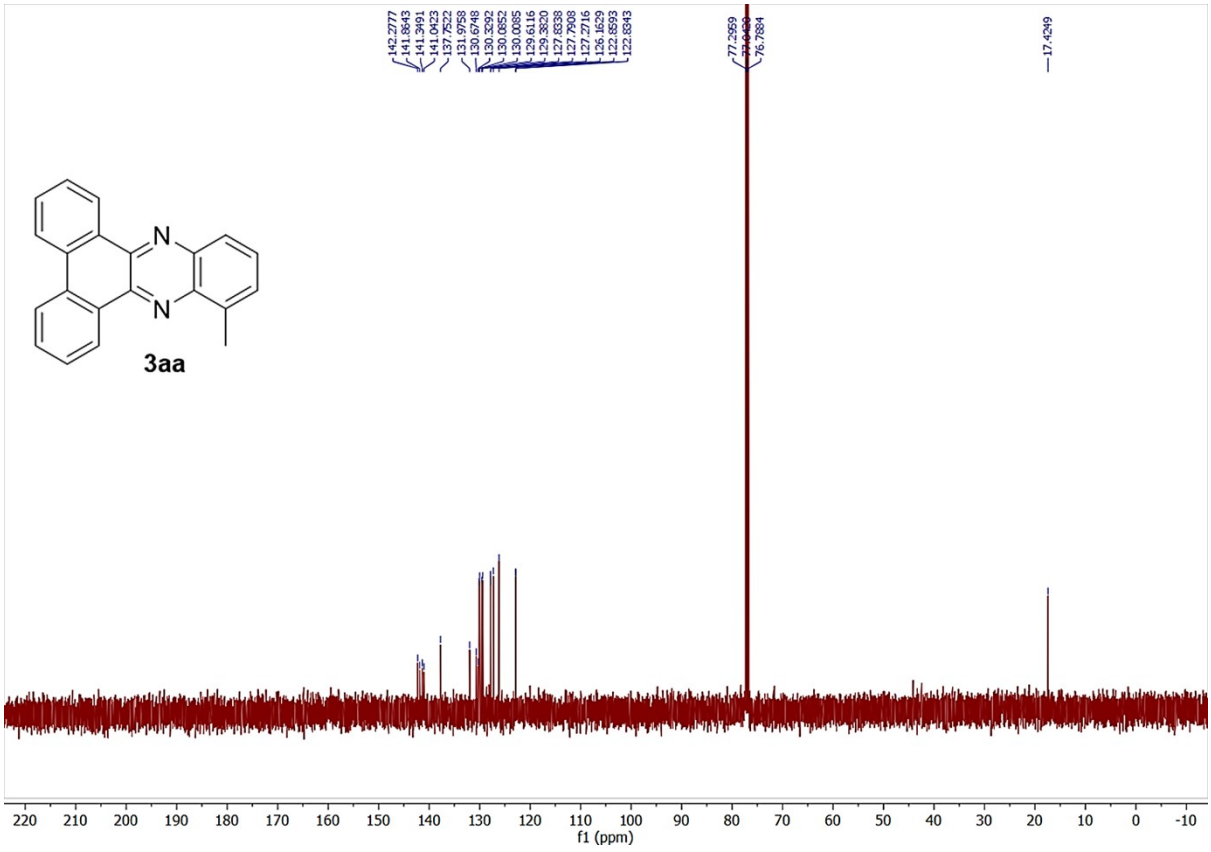
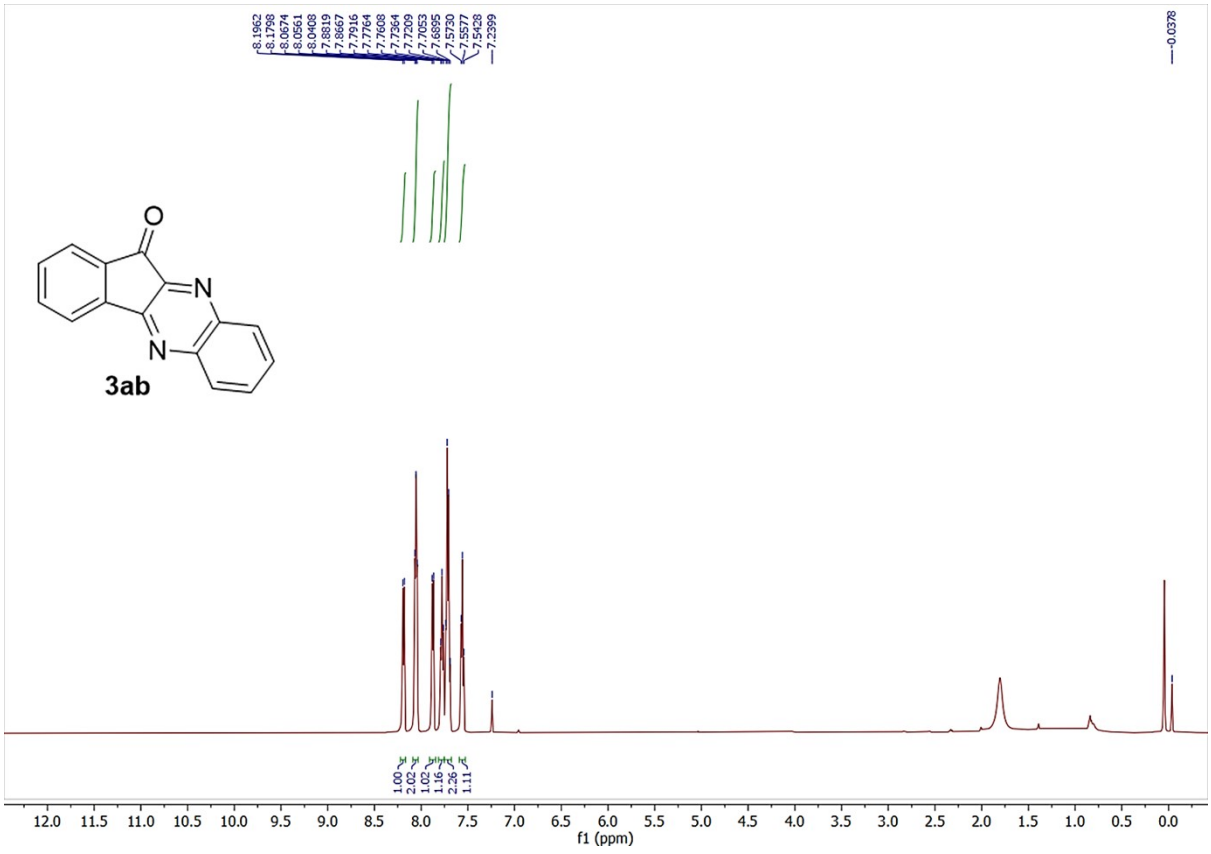


Figure S29: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3aa**.



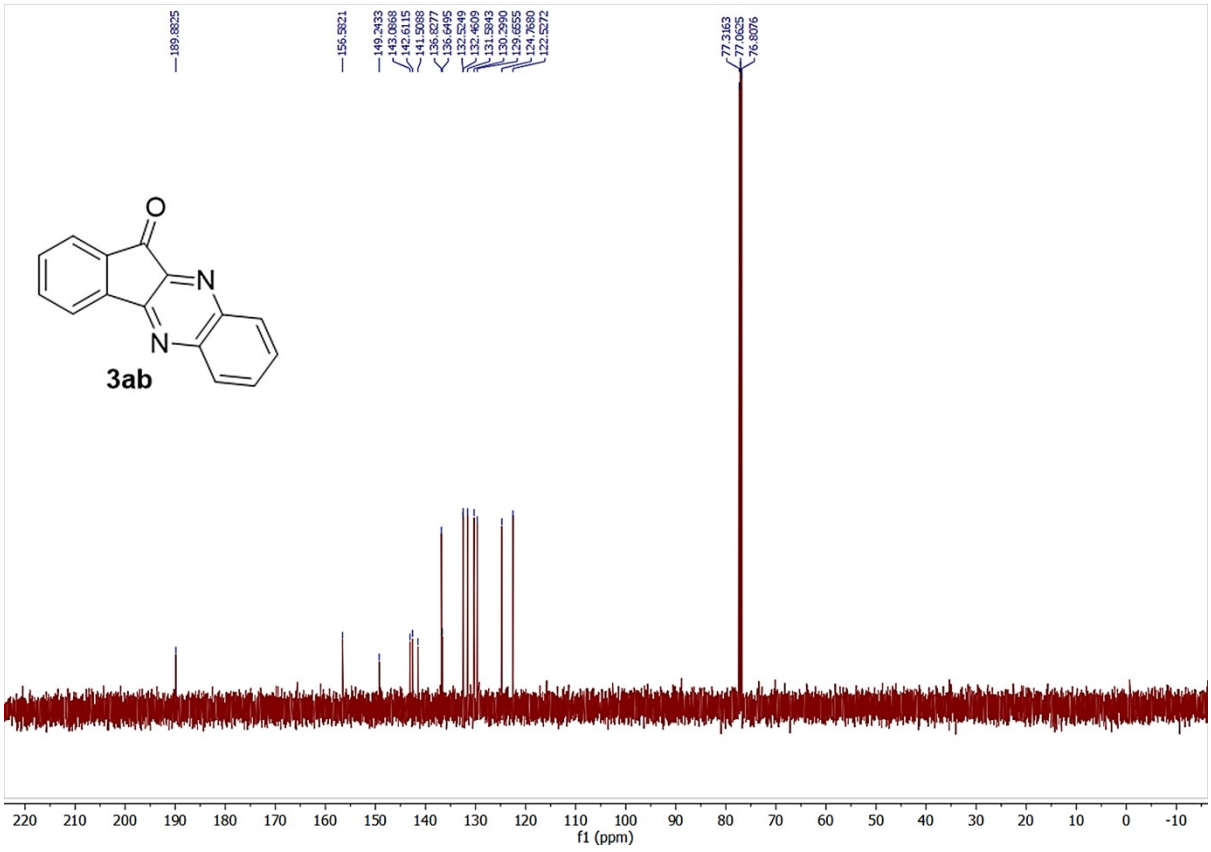
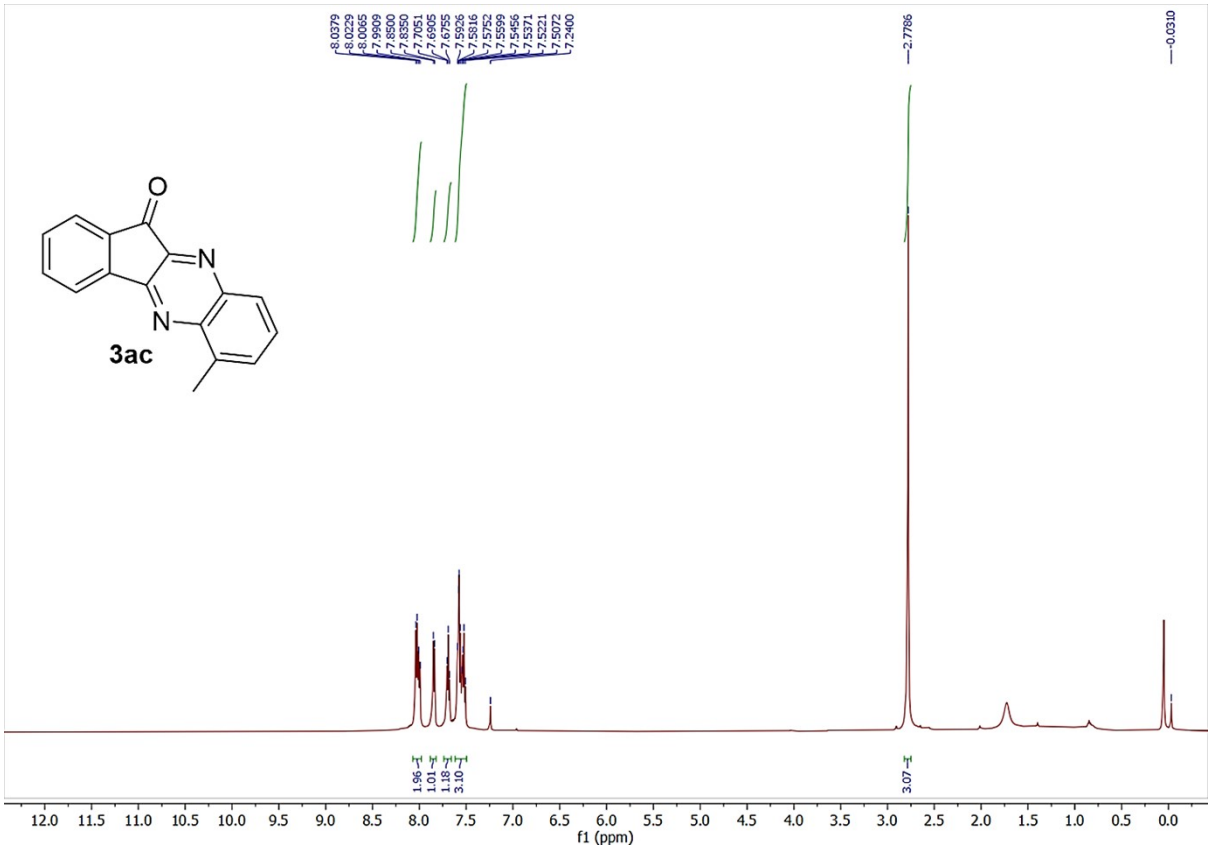


Figure S30: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ab**.



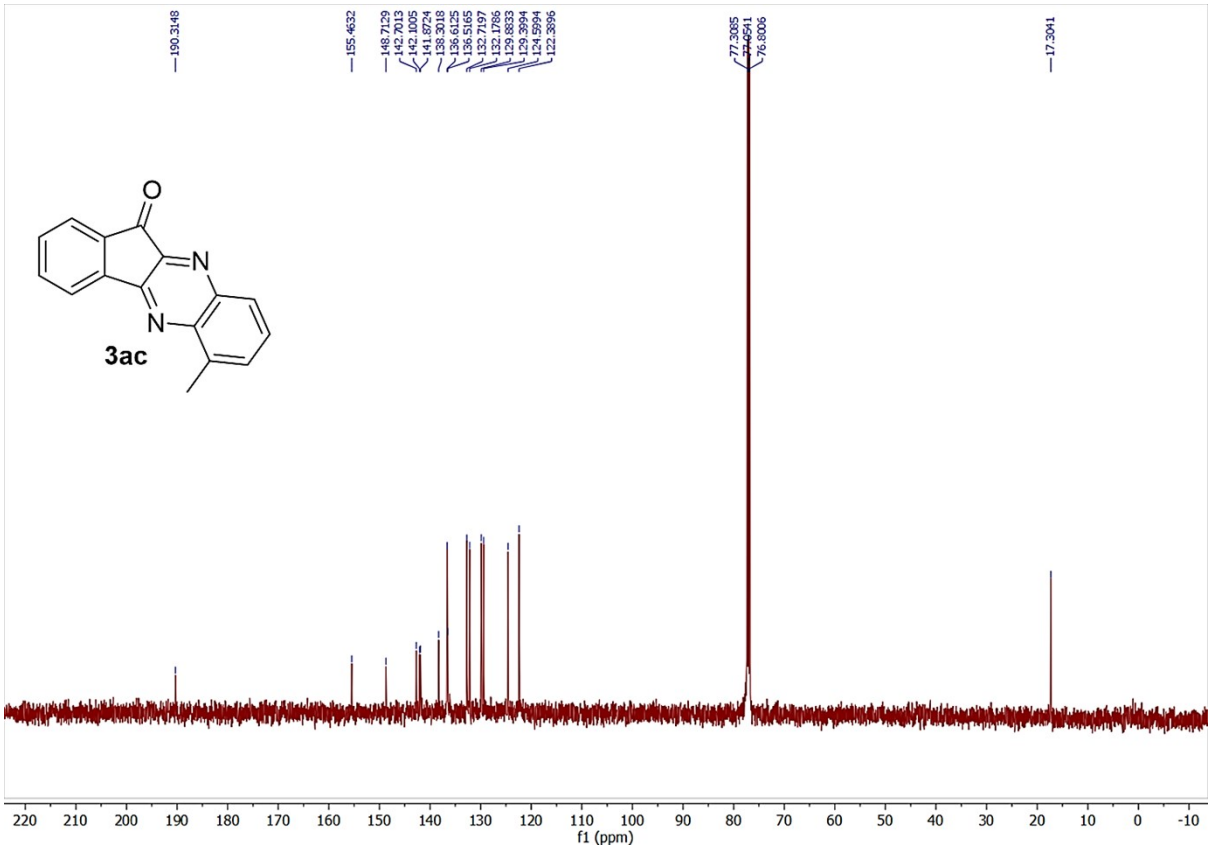
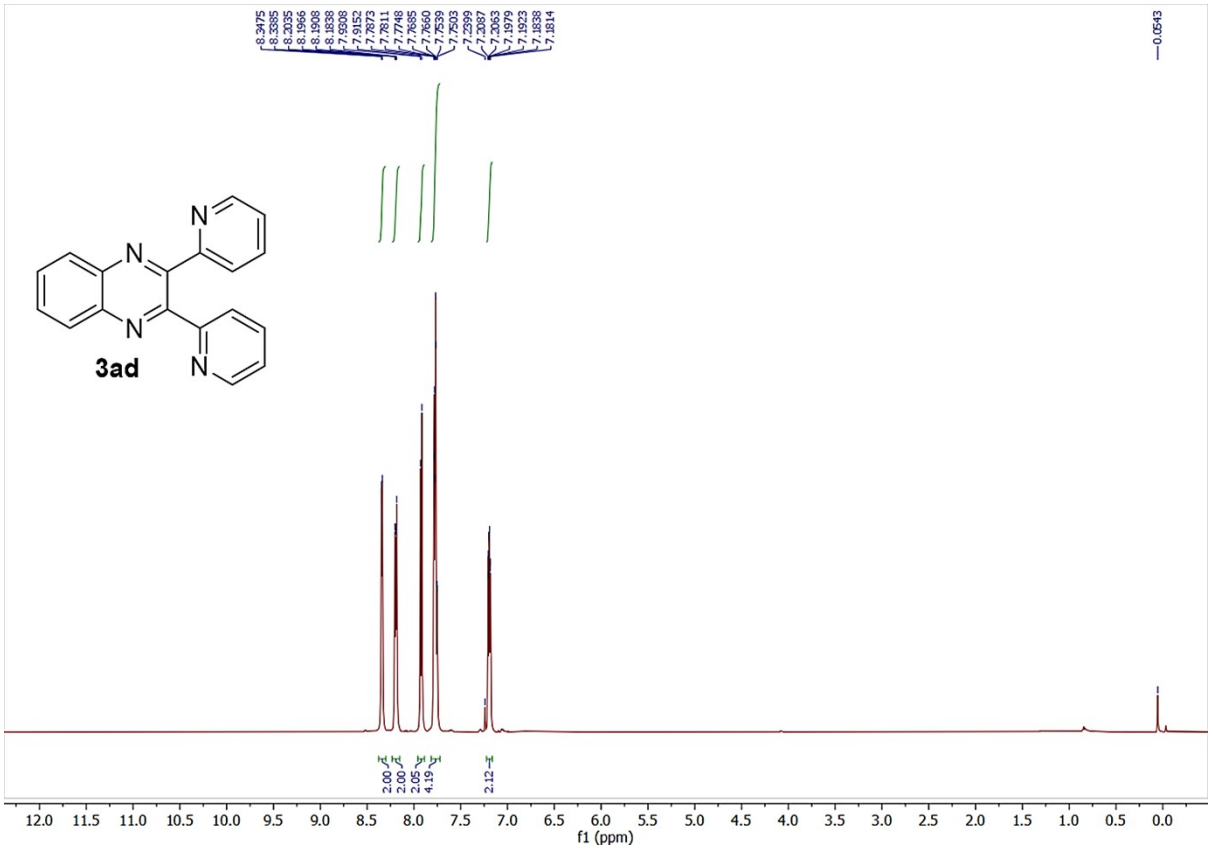


Figure S31: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ac**.



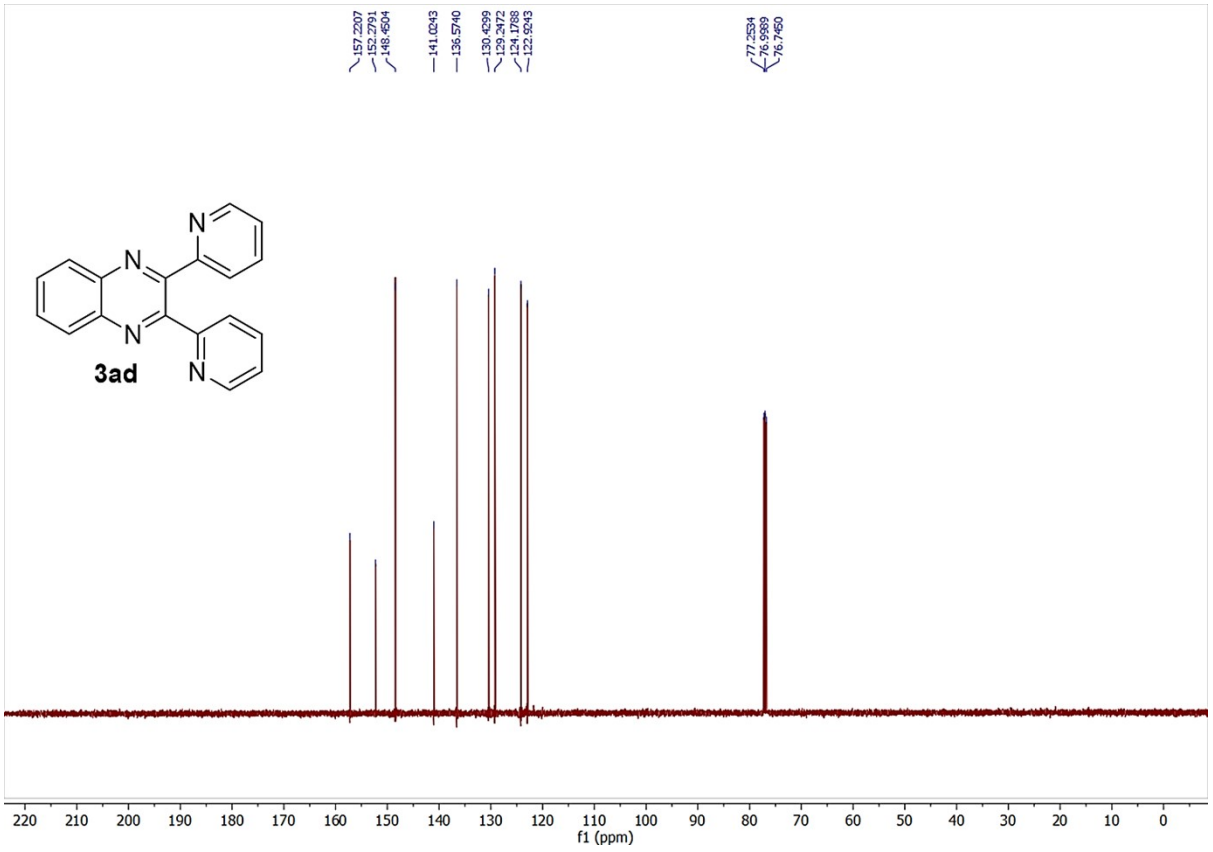
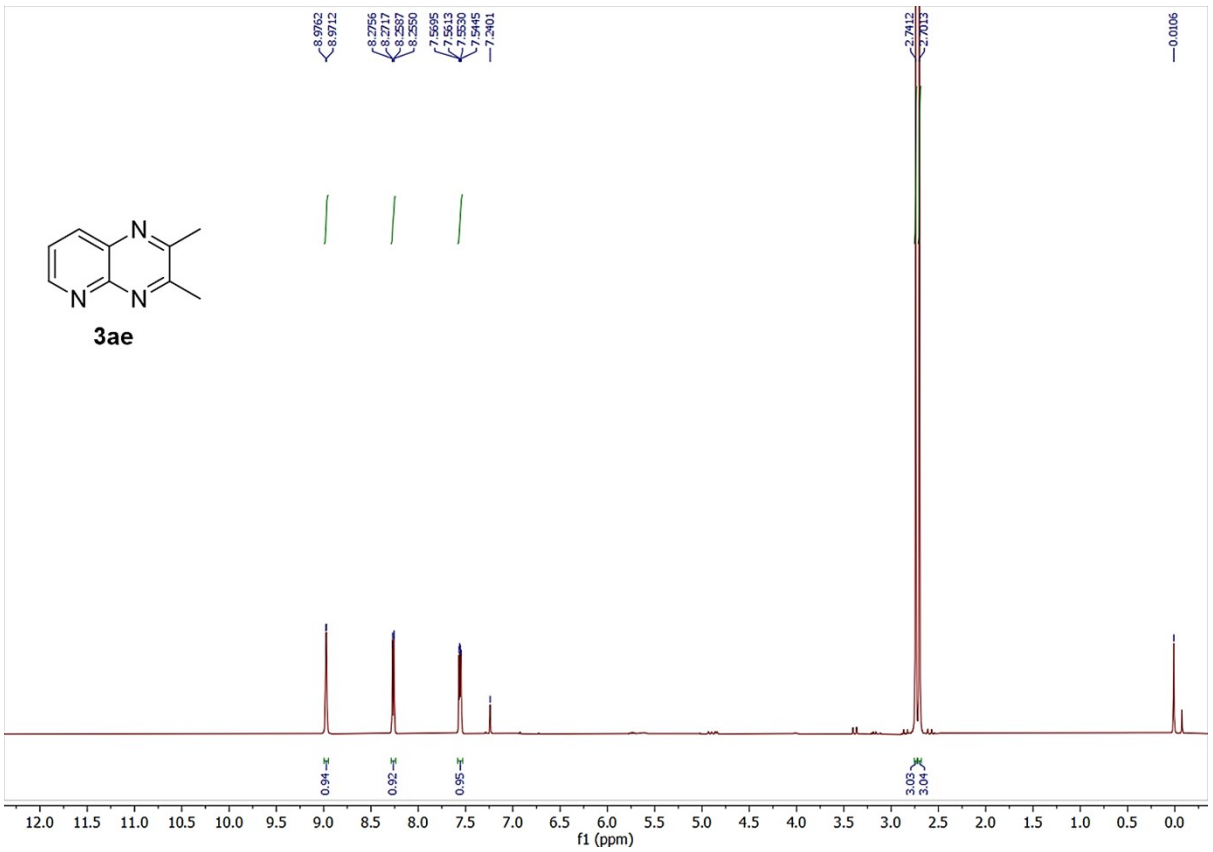


Figure S32: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ad**.



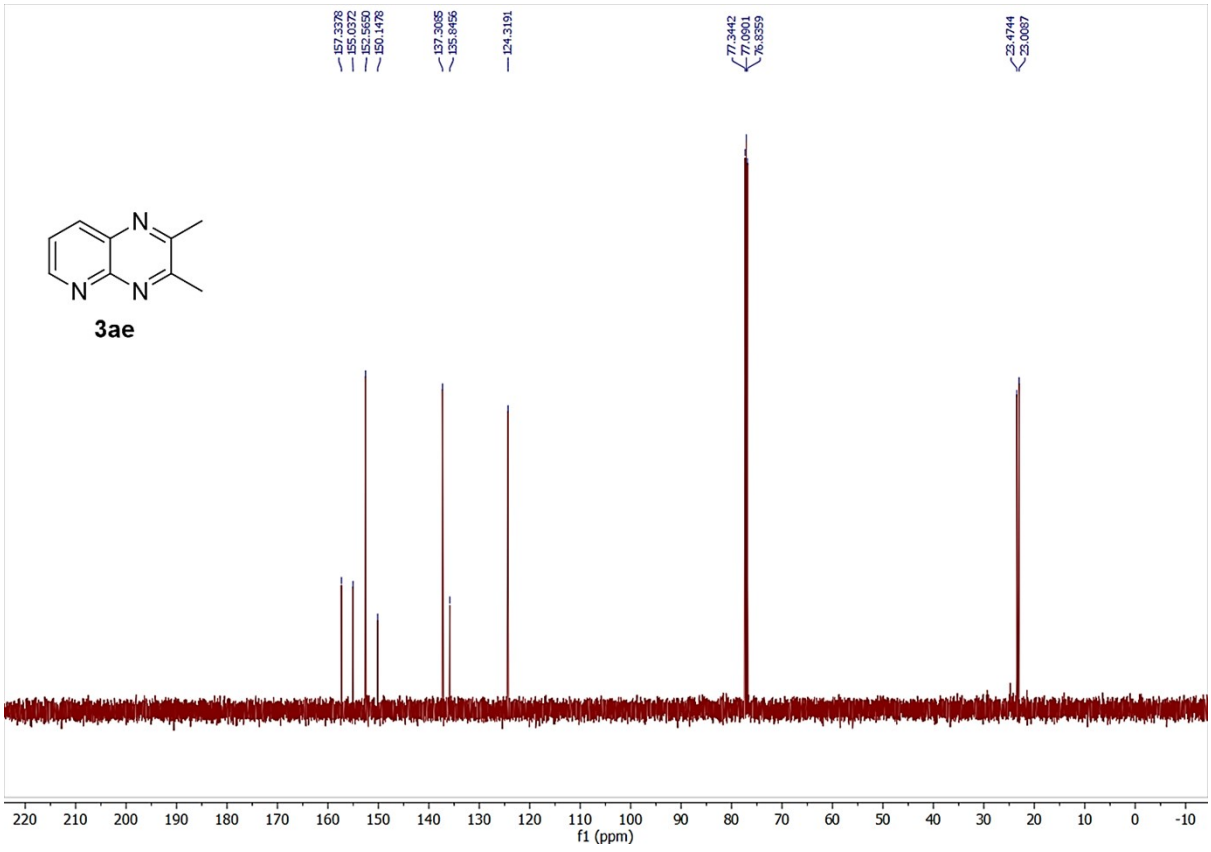
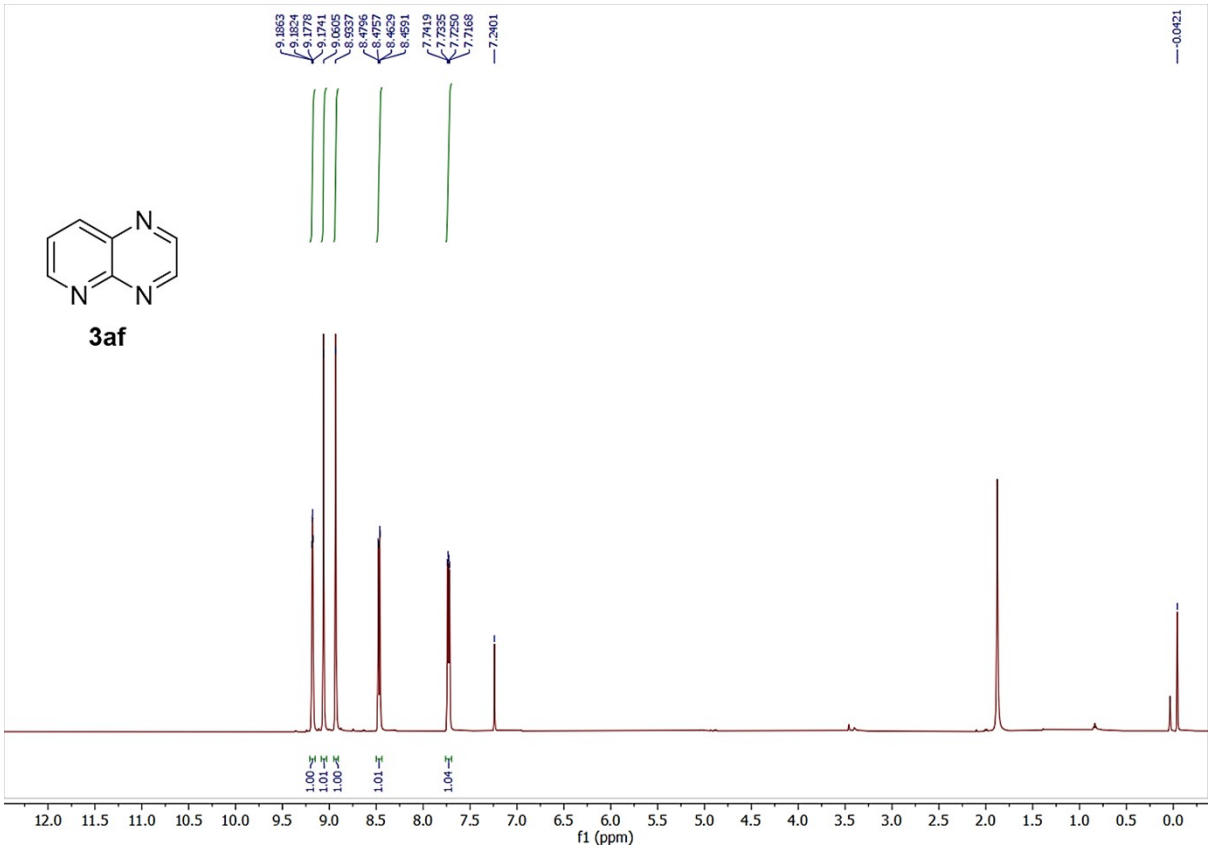


Figure S33: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ae**.



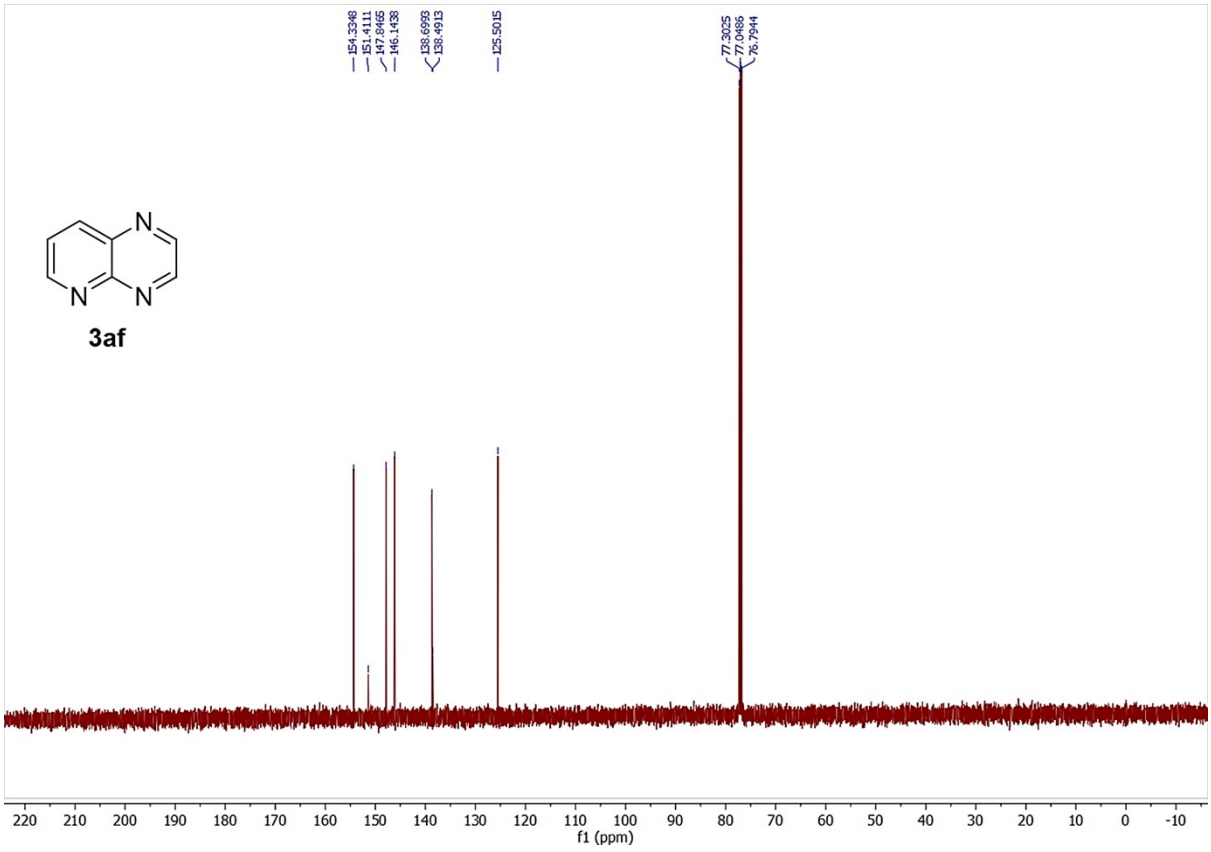
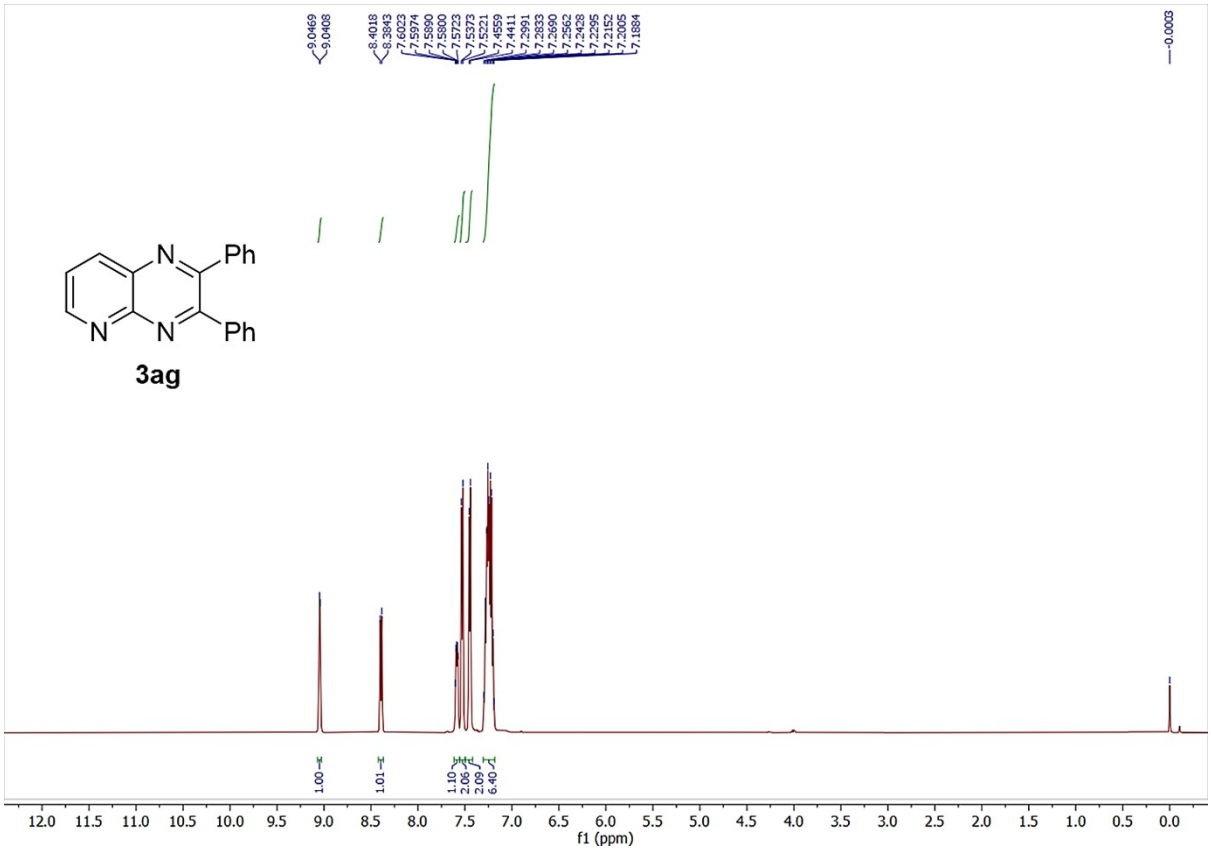


Figure S34: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3af**.



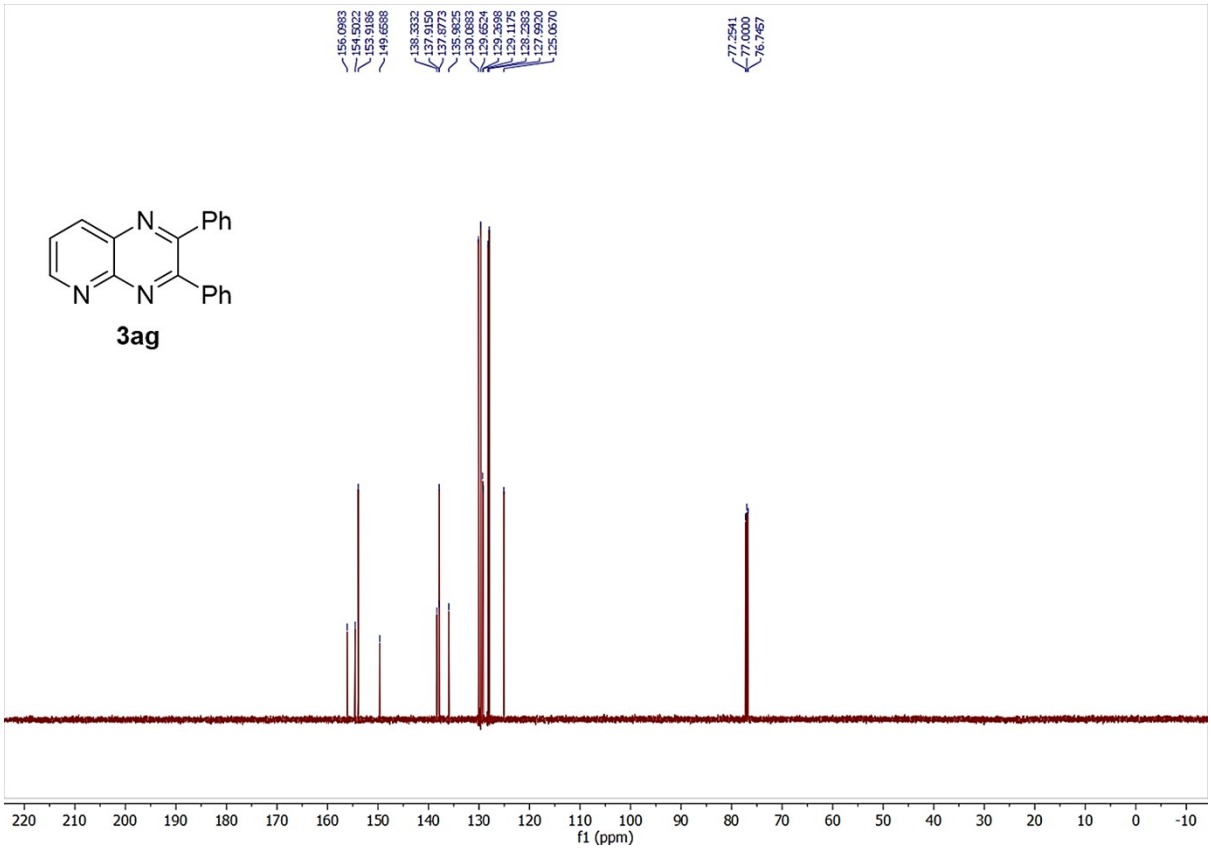
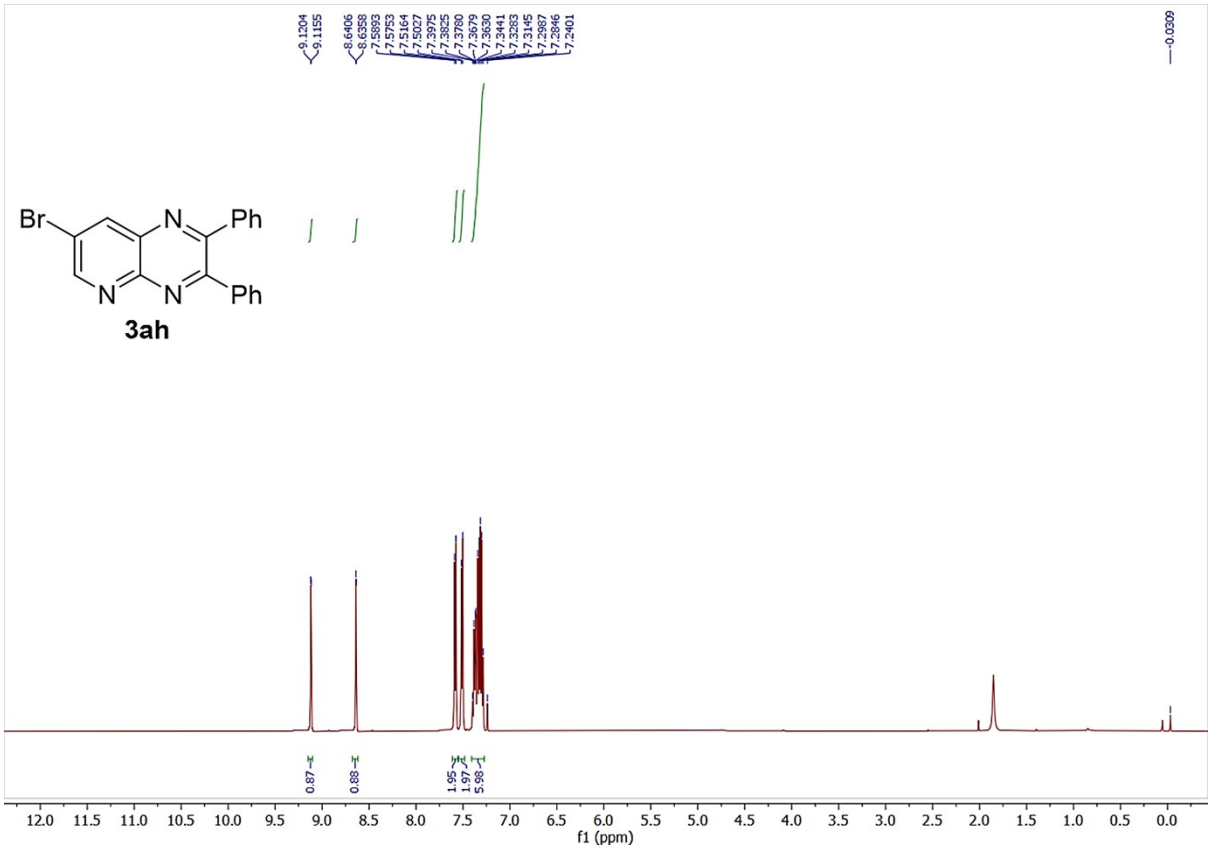


Figure S35: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ag**.



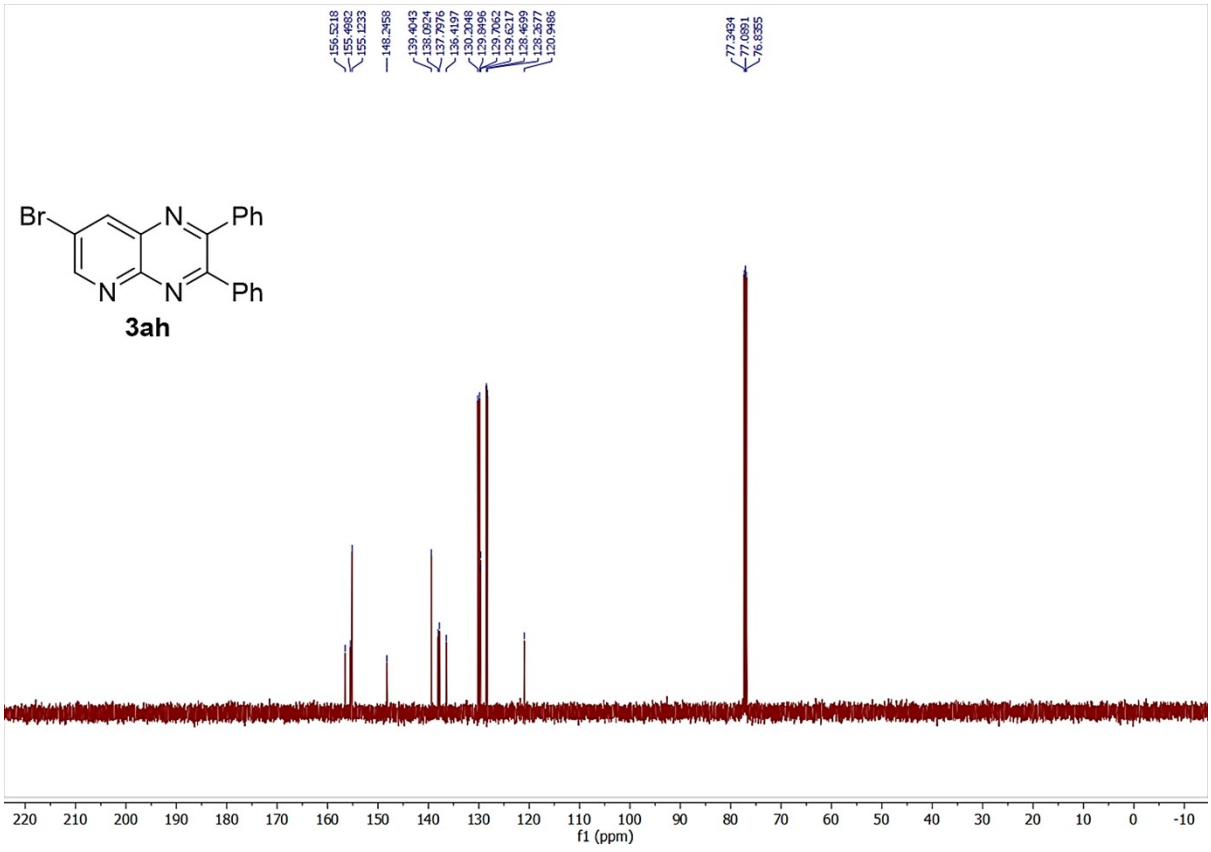
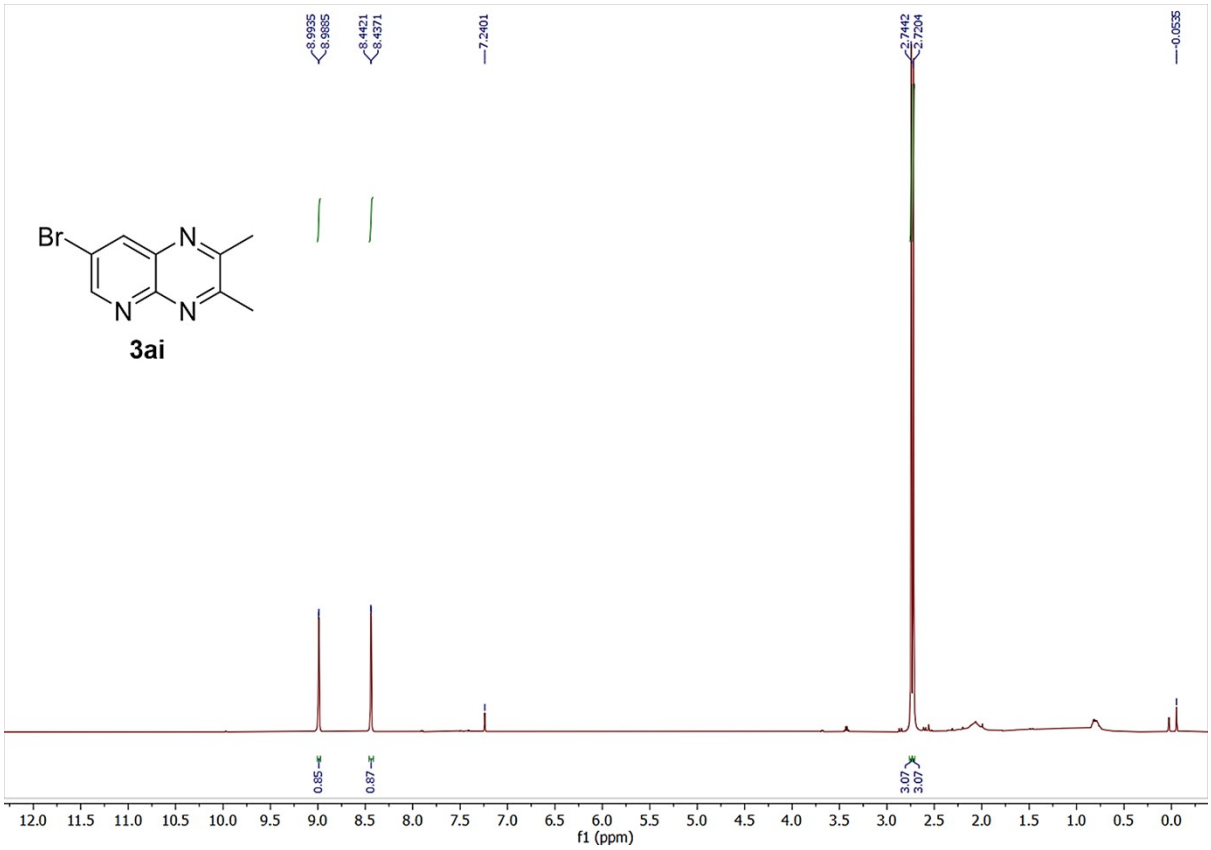


Figure S36: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ah**.



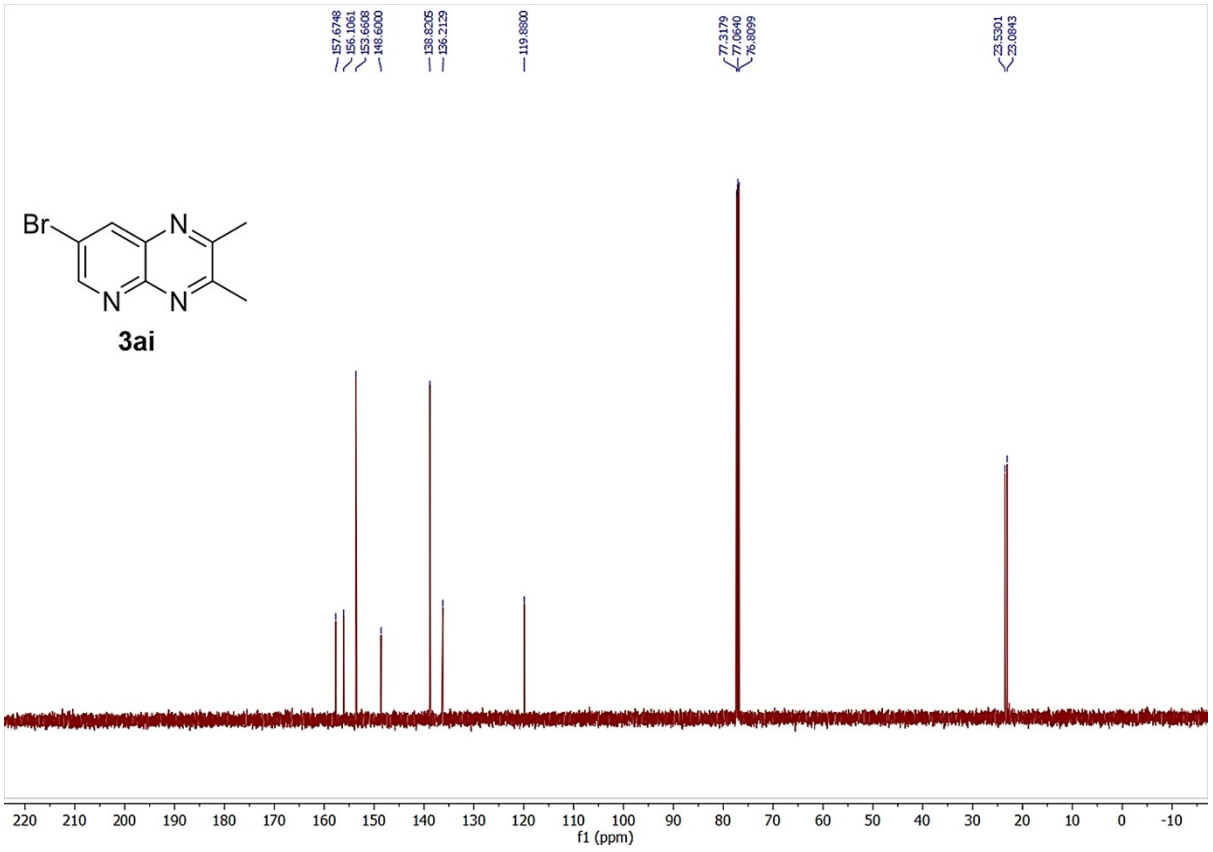
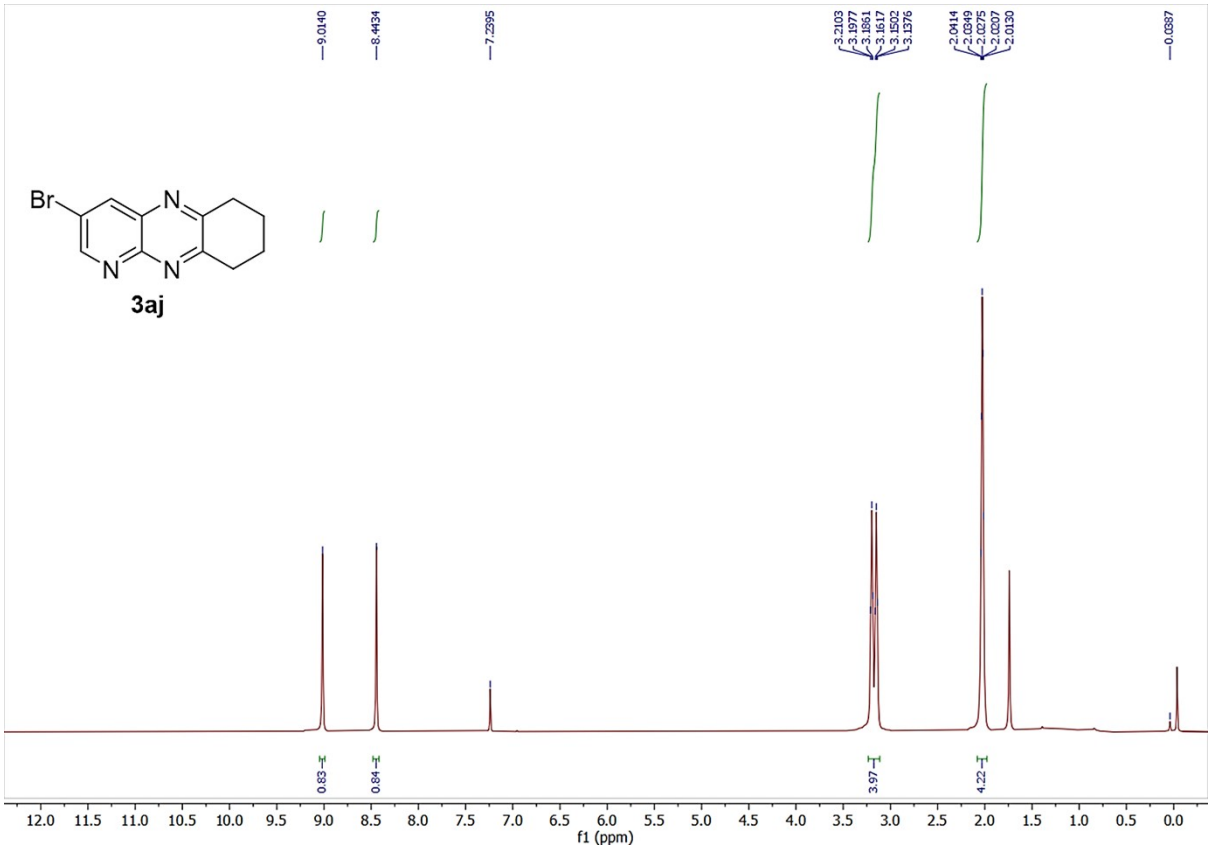


Figure S37: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ai.**



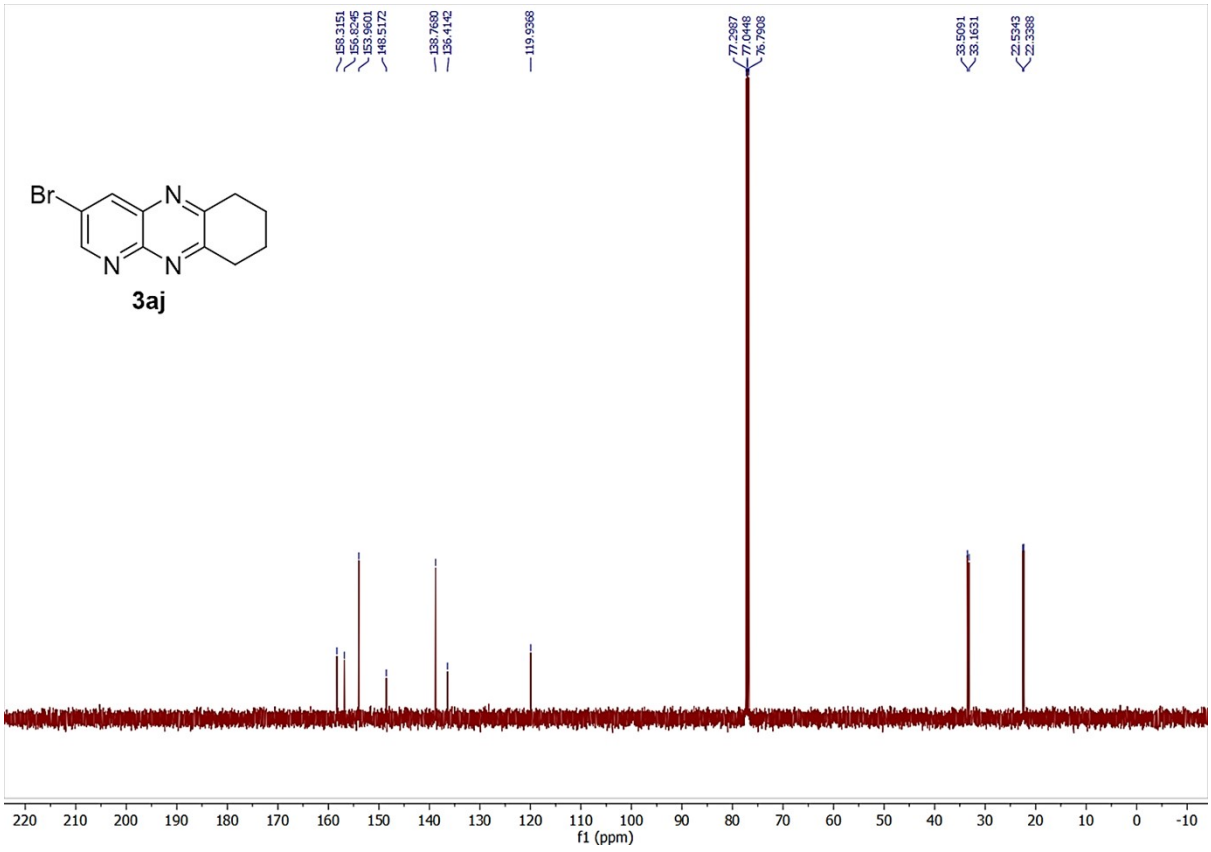
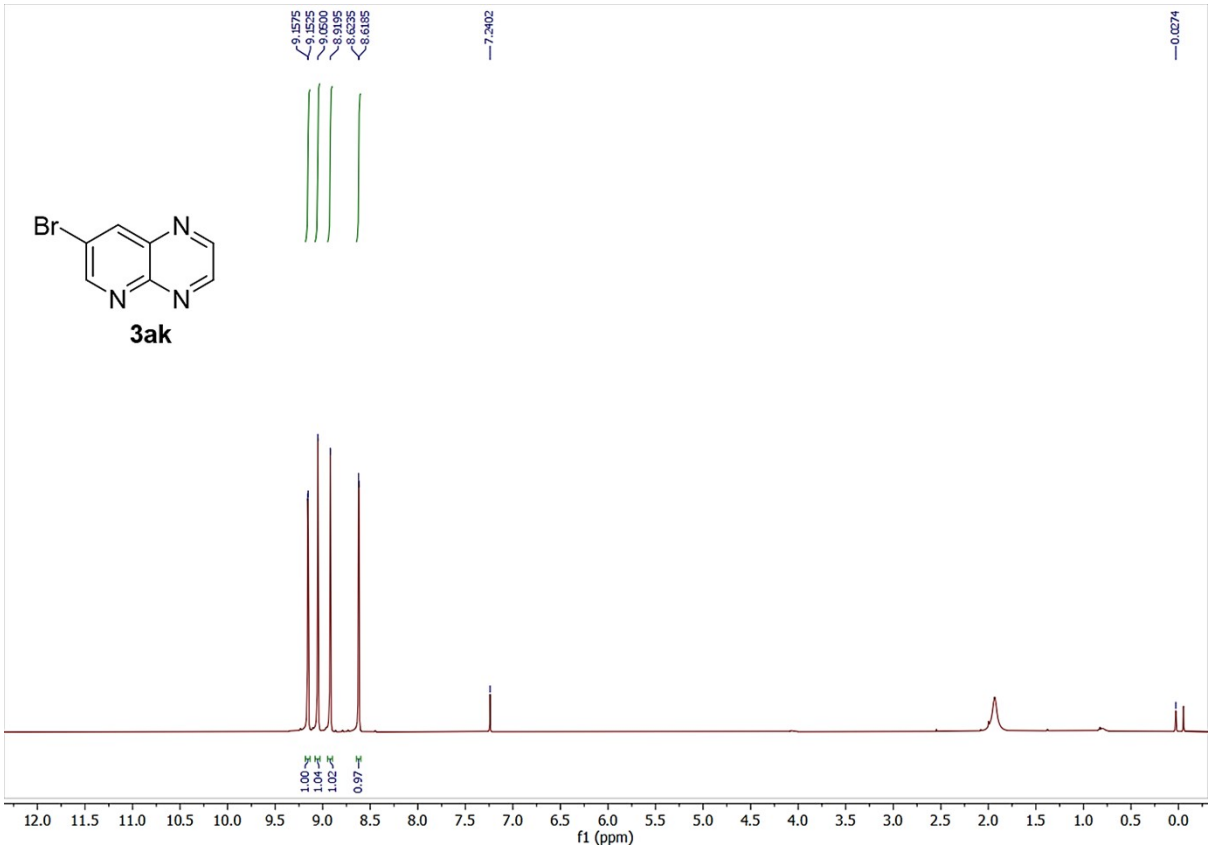


Figure S38: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3aj**.



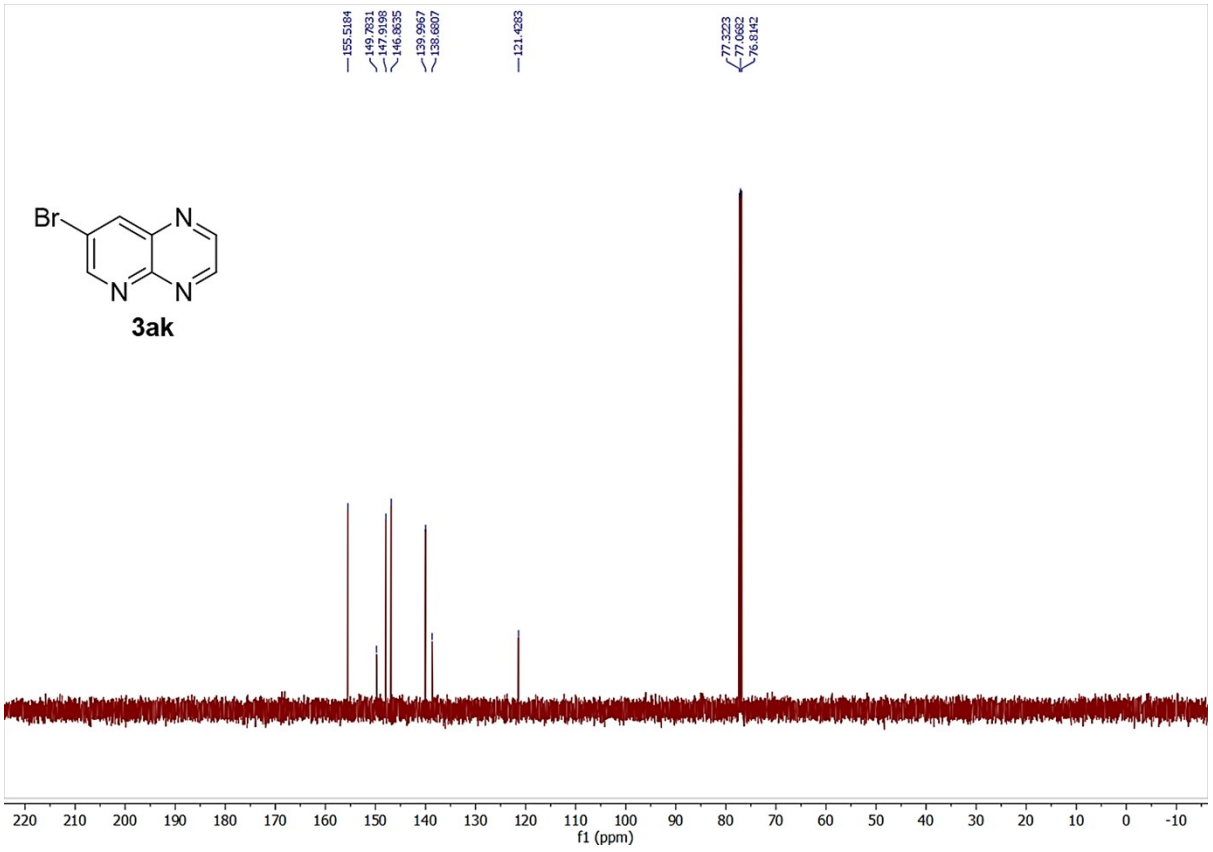
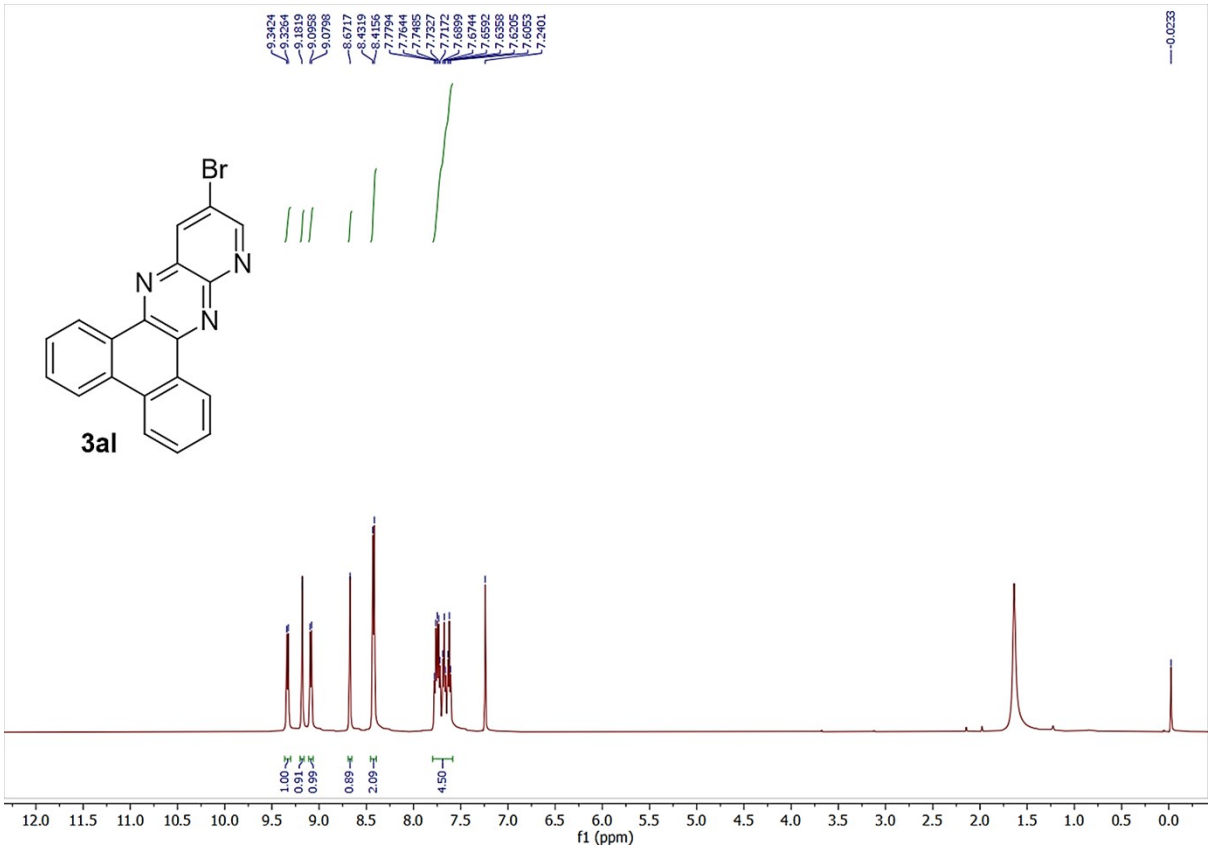


Figure S39: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ak**.



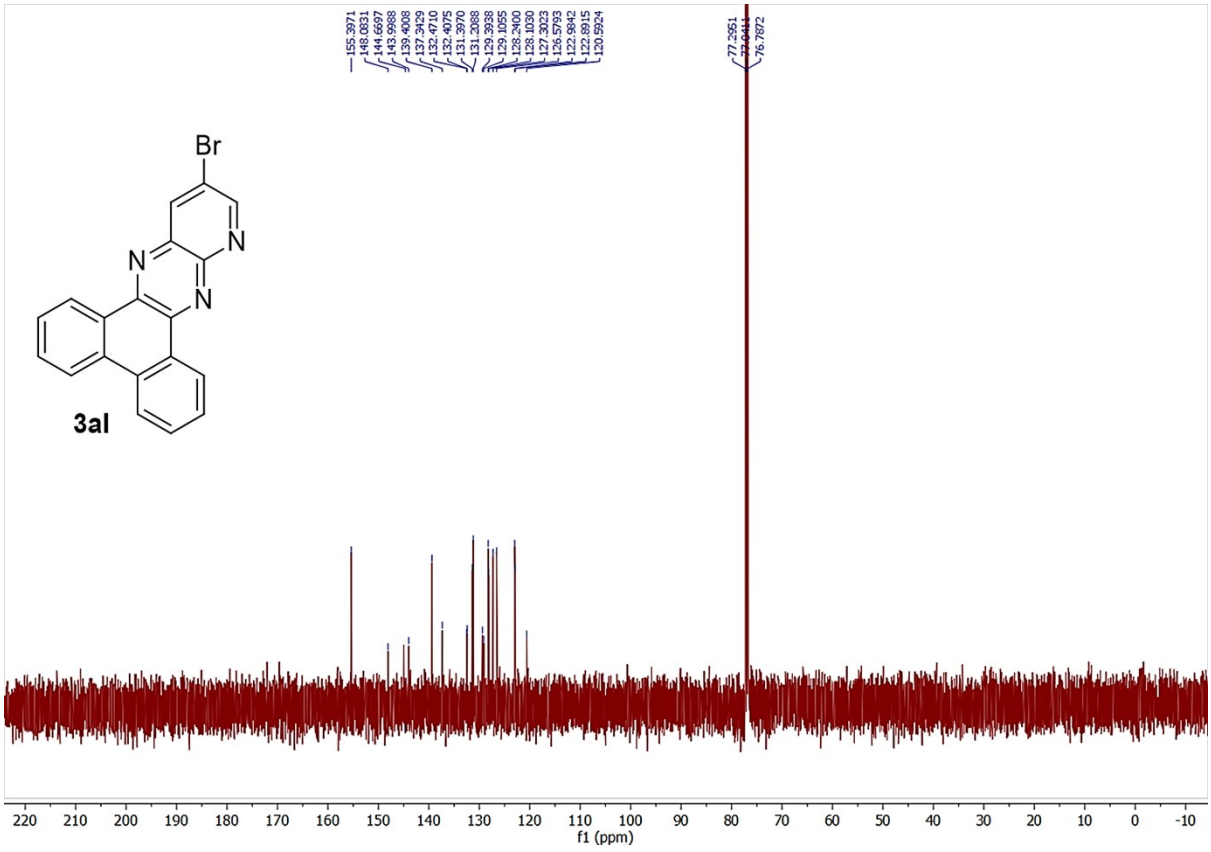
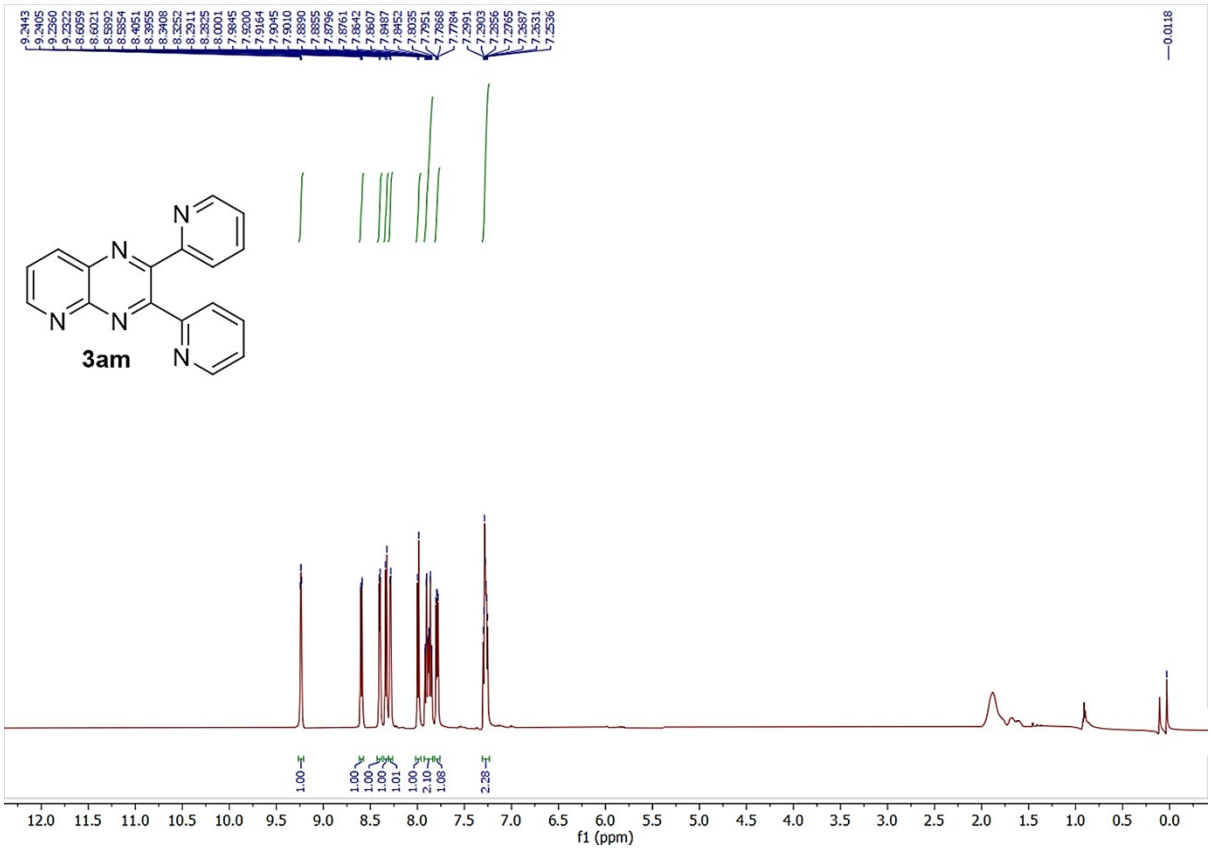


Figure S40: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3al**.



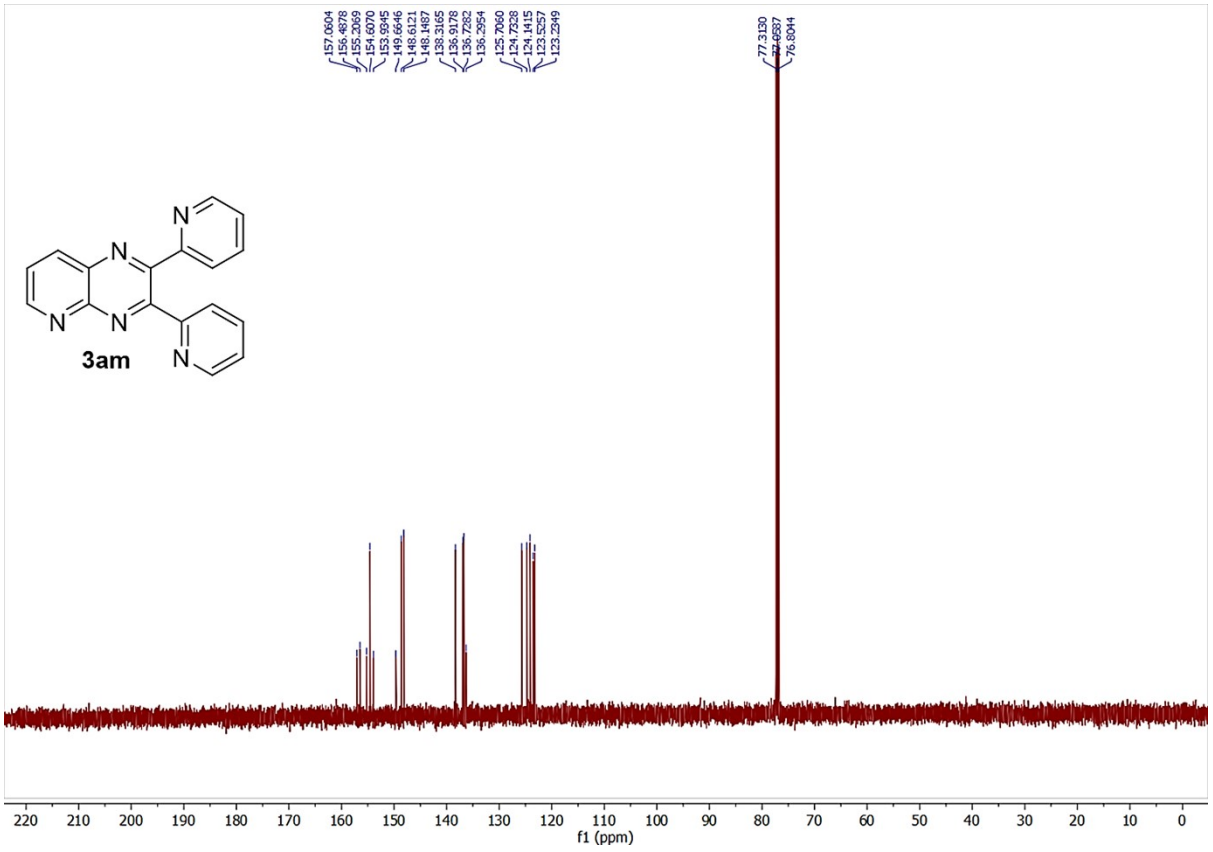
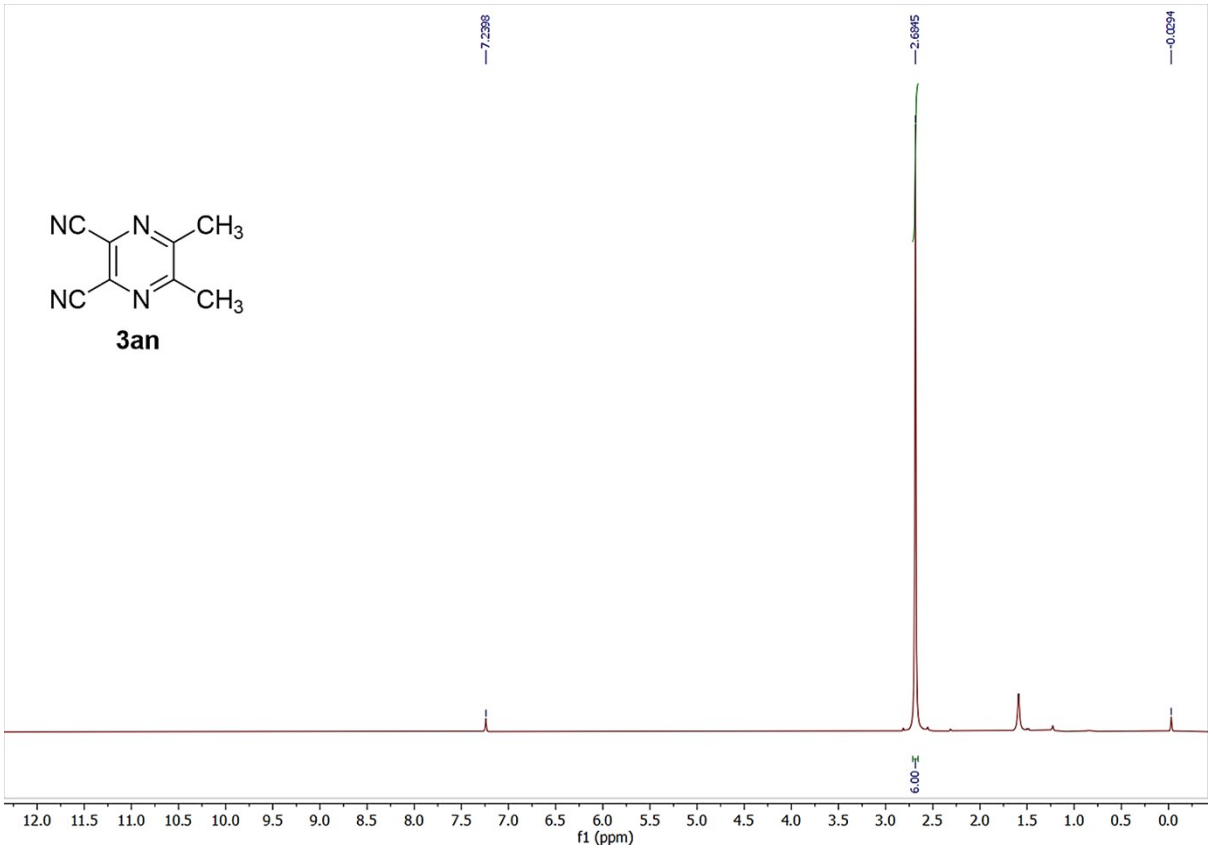


Figure S41: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3am**.



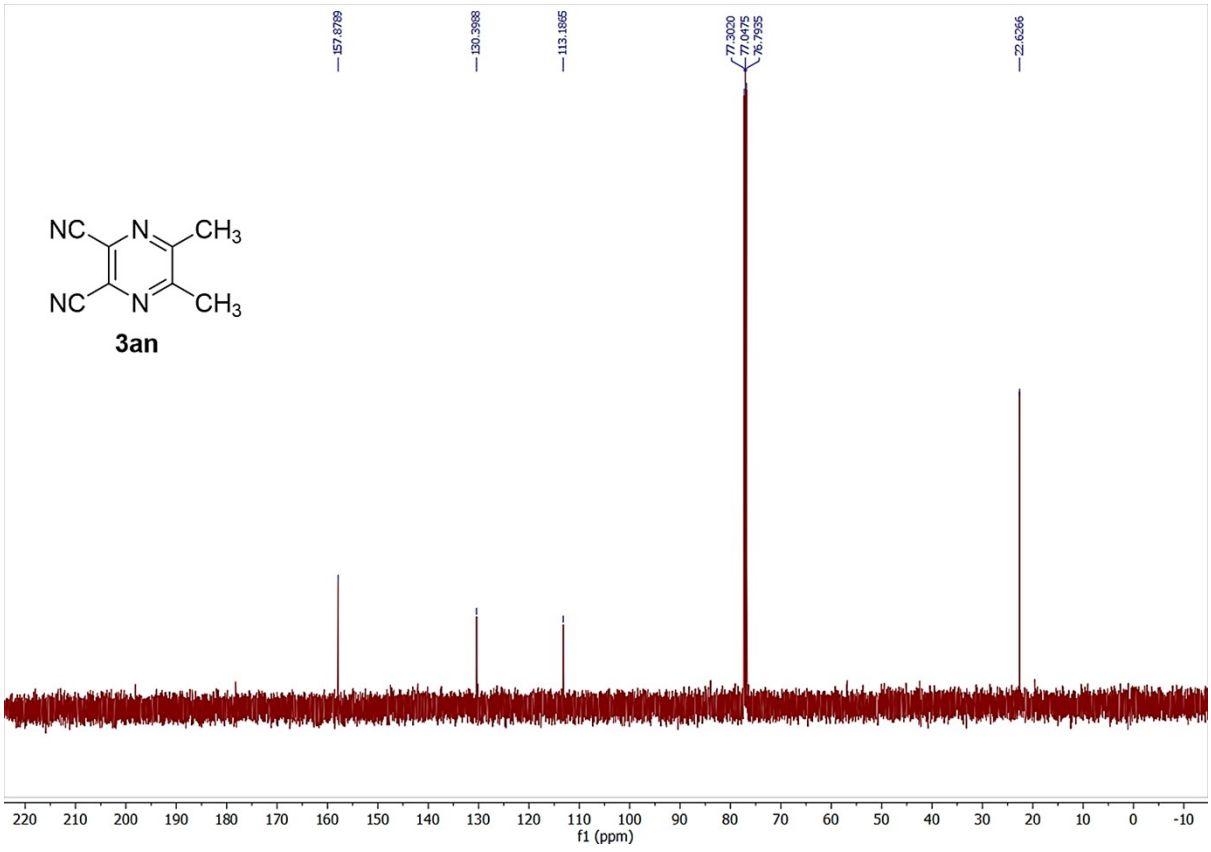
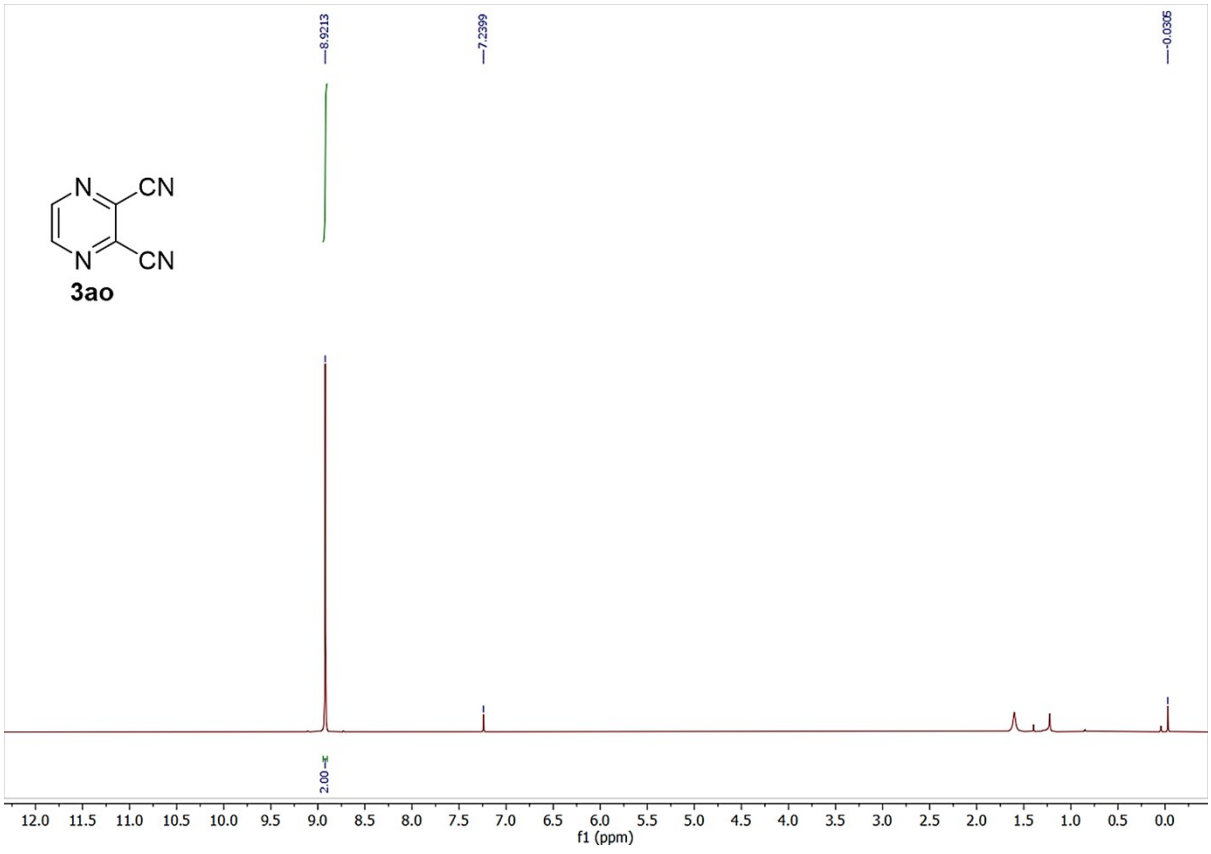


Figure S42: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3an**.



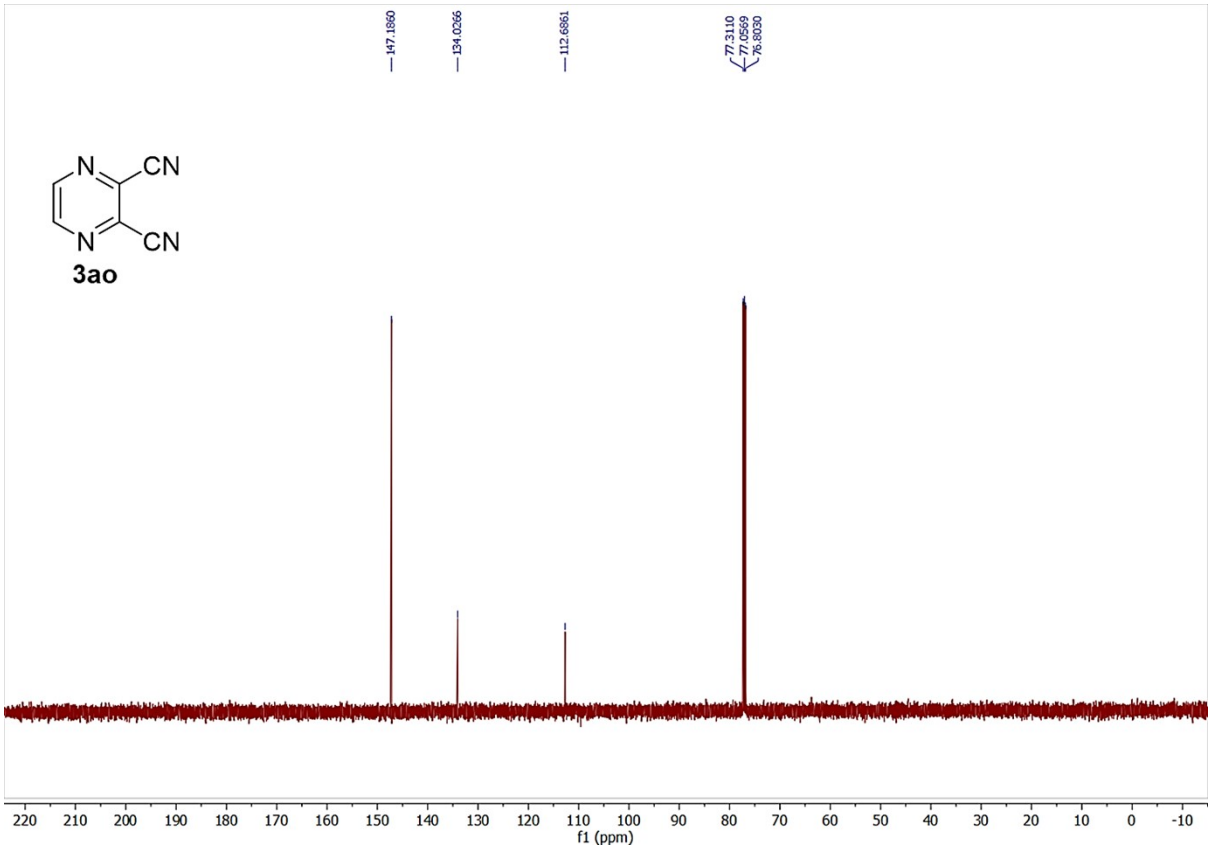
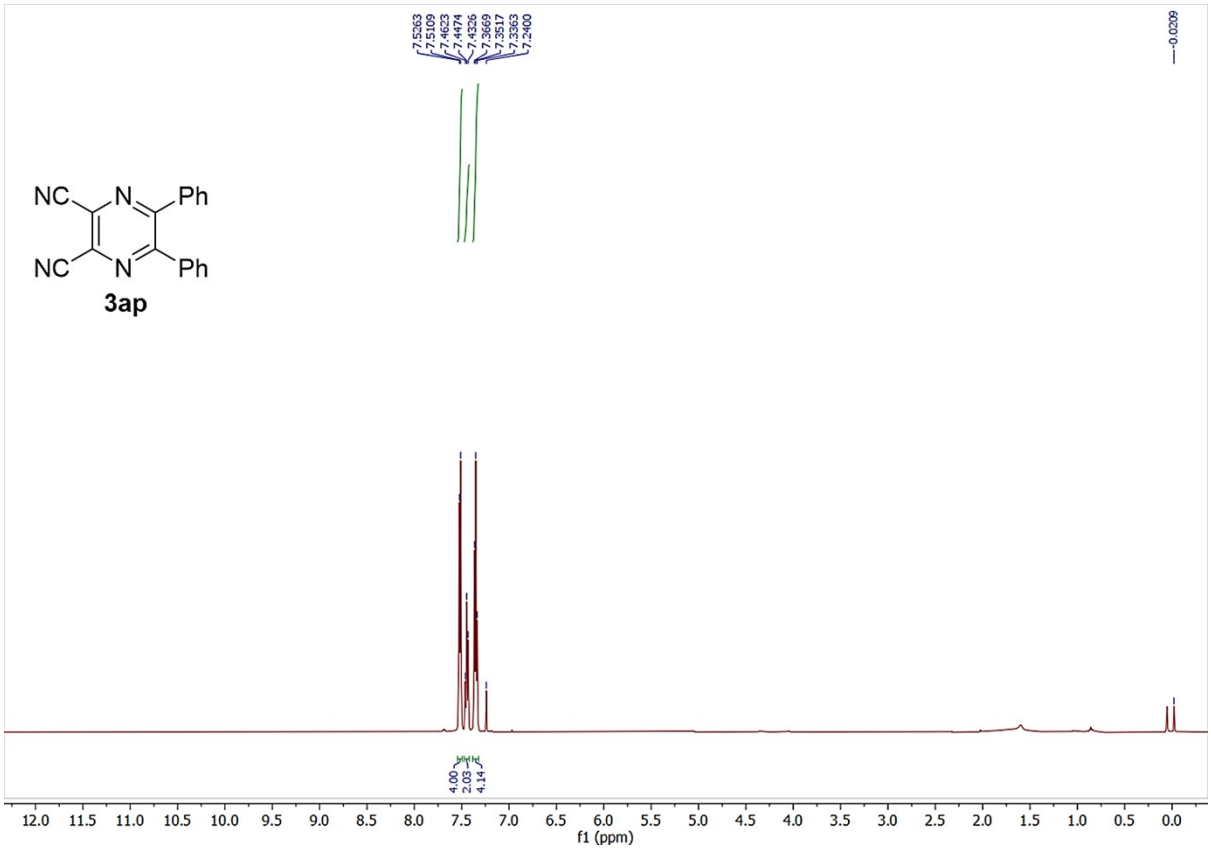


Figure S43: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ao**.



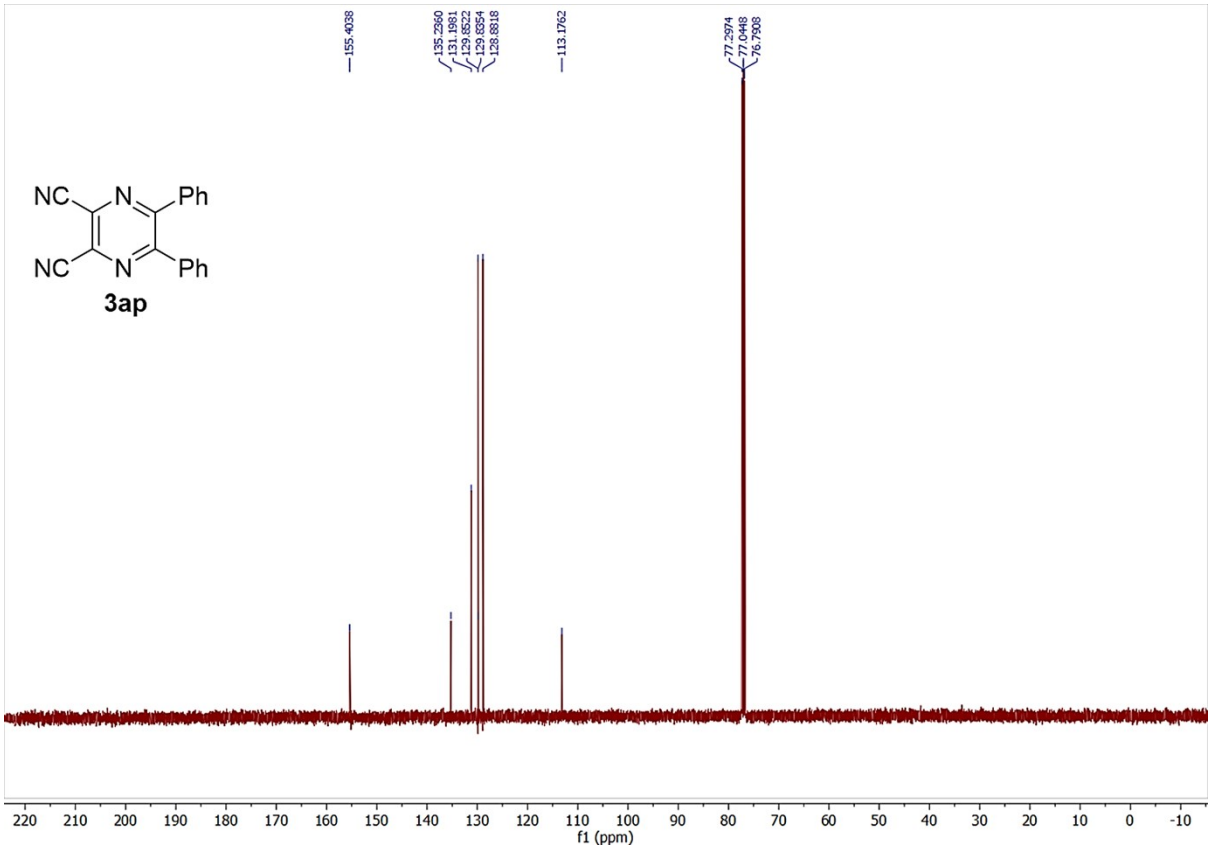
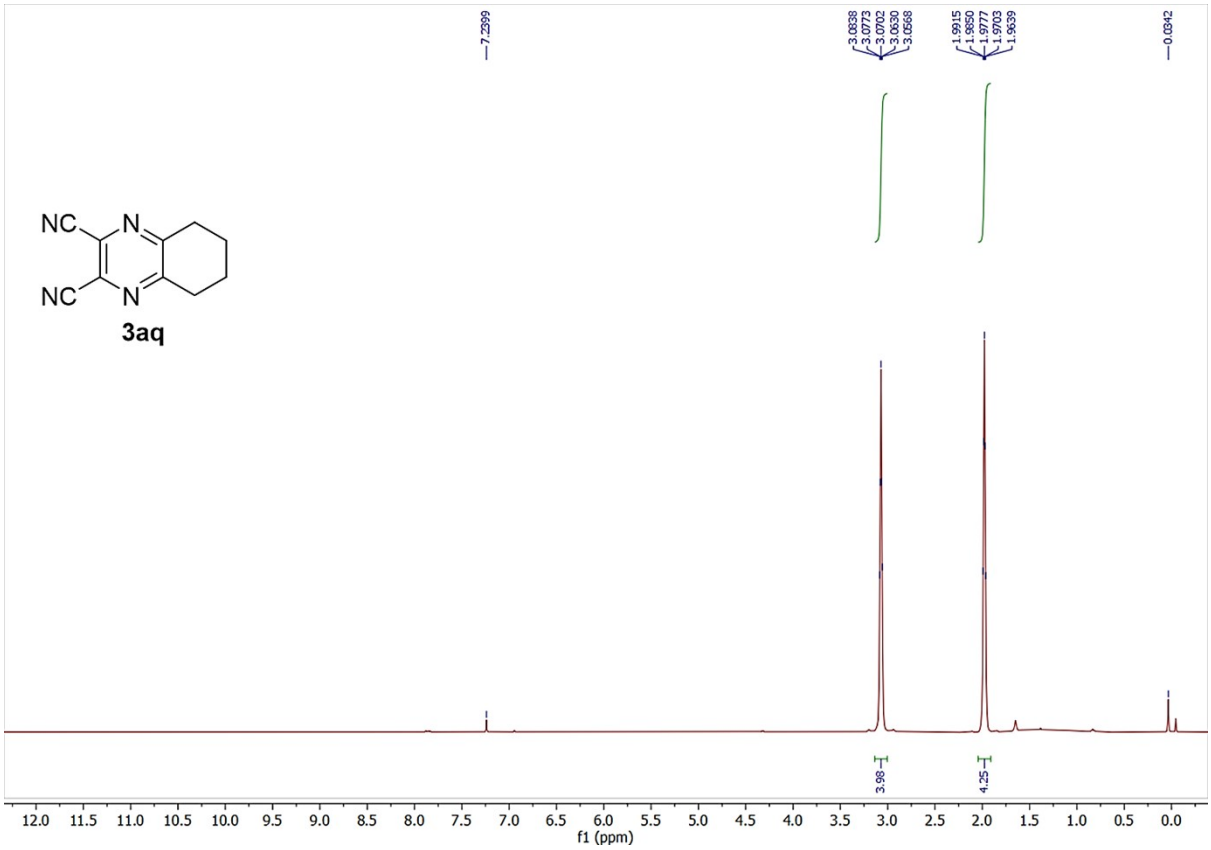


Figure S44: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ap**.



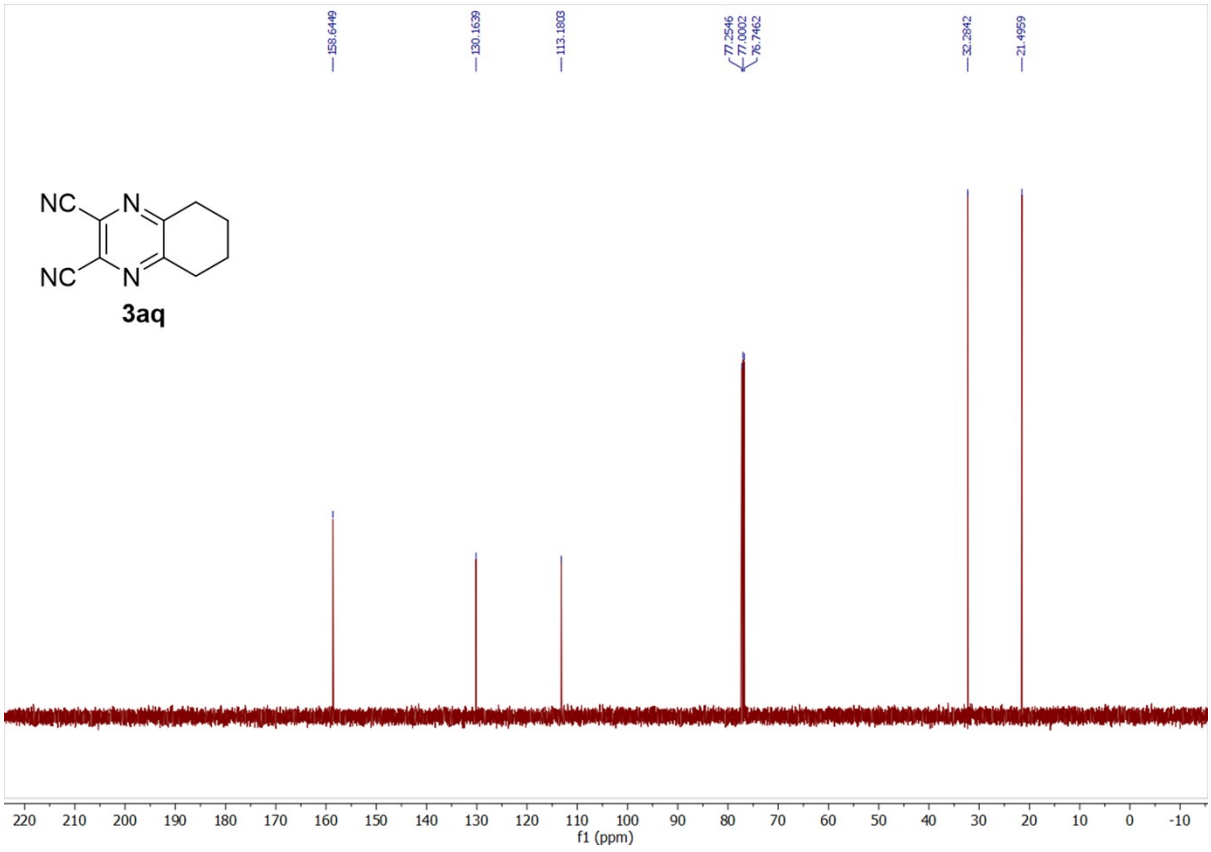
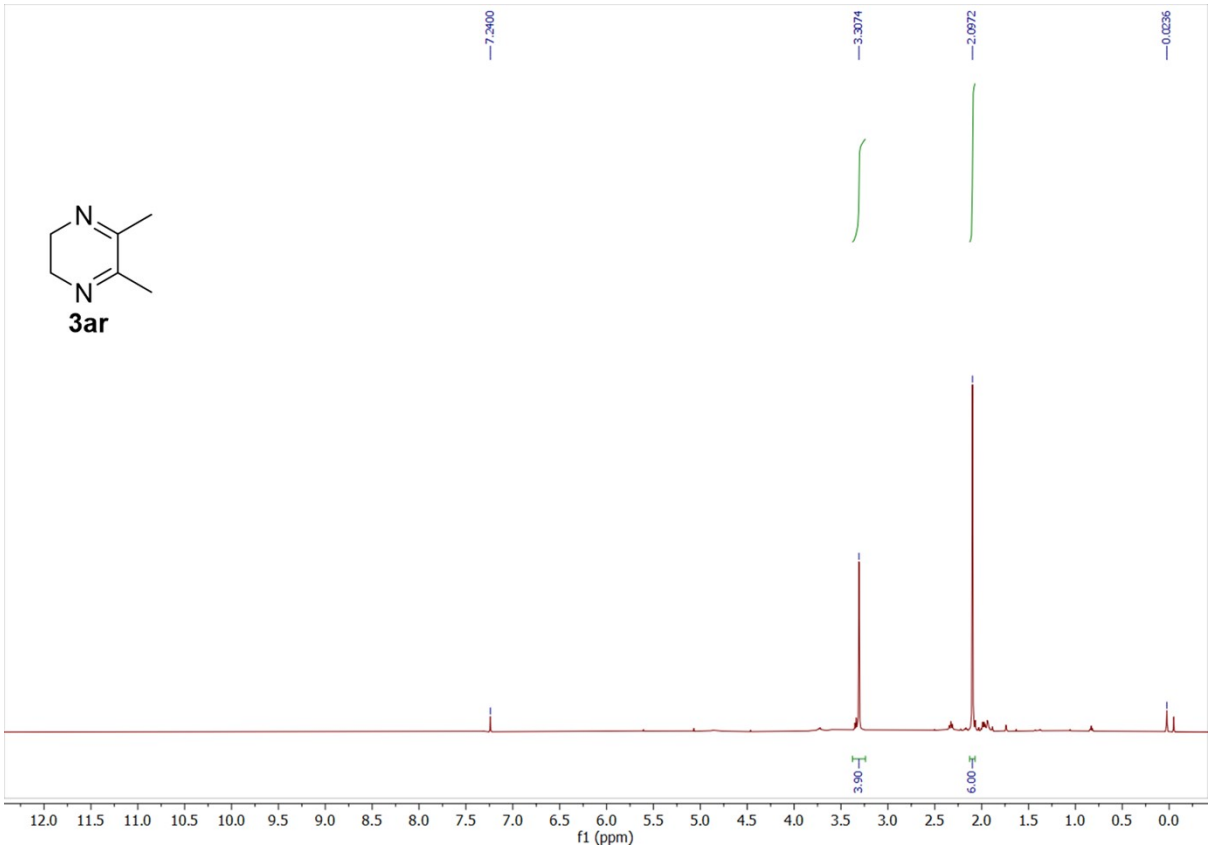


Figure S45: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3aq**.



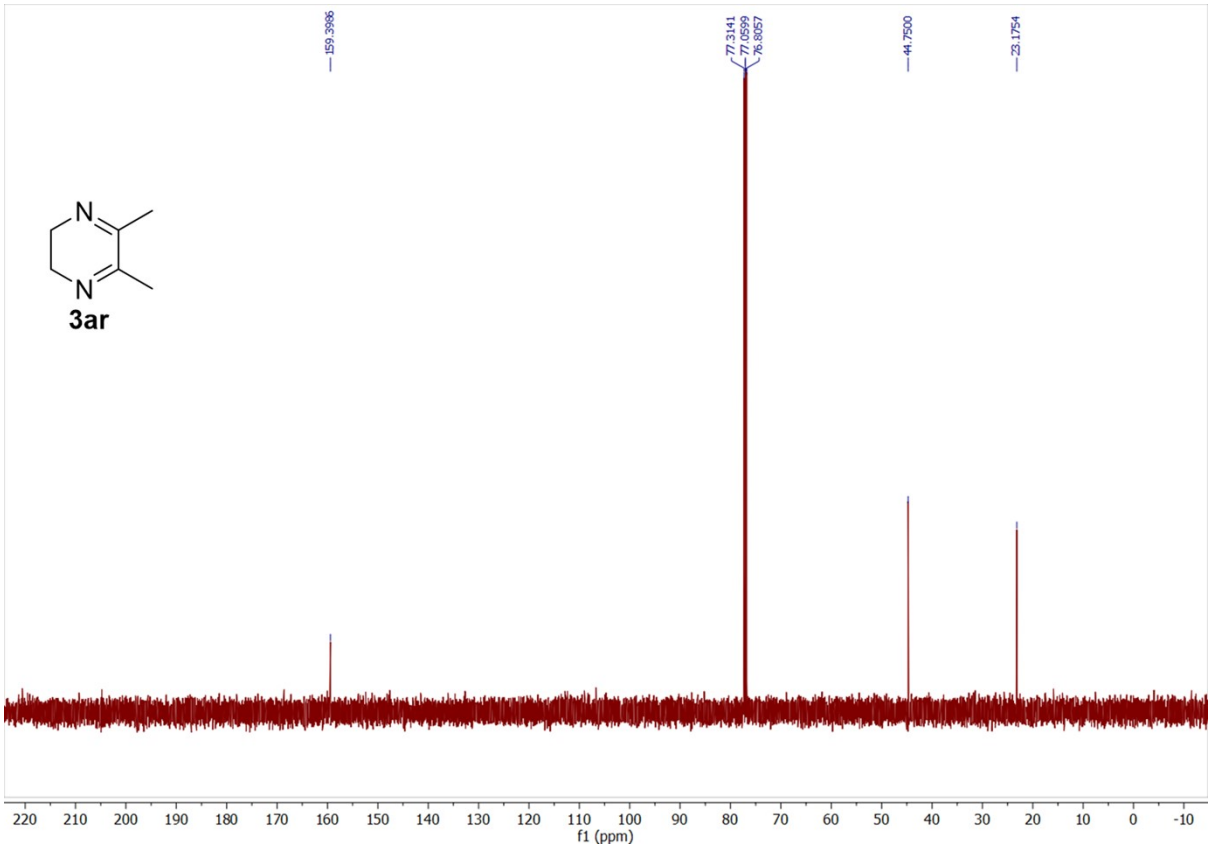


Figure S46: ^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR spectra of compound **3ar**.