Electronic Supporting Information

Rh(III)-catalyzed oxidative [4+2] annulation of 2-arylquinoxalines and 2-aryl-2*H*-indazoles with allyl alcohols

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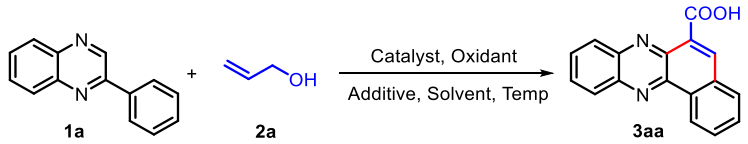
1. General information:

All chemicals and solvents purchased from commercial suppliers and used without purification unless otherwise noted. 2-Arylquinoxalines and 2-aryl-2*H*-indazoles were synthesized by following the reported procedure.[1, 2] All reactions were monitored by thin layer chromatography (TLC) on pre-coated silica gel 60 F254 aluminium foils and visualized under a UV lamp (366 or 254 nm). Desired products were purified by column chromatography (silica gel 100-200 mesh size) using a gradient of ethyl acetate and hexanes as mobile phase. The ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were recorded on a Bruker Avance III spectrometer. Chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometer. X-ray analysis was performed on a Rigaku Oxford XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer.

2. Optimization of reaction conditions

Table S1. Selected experiments for optimization of reaction conditions for **3aa**.[a]



Entry	Catalyst	Oxidant	Solvent	Additive	% Yield[b]
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	DCE	-	41
2	$[Ru(p\text{-cymene})Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	DCE	-	NR
3	$Pd(OAc)_2$	$Cu(OAc)_2{\cdot}H_2O$	DCE	-	NR
4	$[CoCp^*(CO)I_2]$	$Cu(OAc)_2{\cdot}H_2O$	DCE	-	18
5	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	DCE	-	54
6	$[RhCp^*Cl_2]_2$	$Cu(OTf)_2$	DCE	-	44
7	$[RhCp^*Cl_2]_2$	$CuSO_4{\cdot}5H_2O$	DCE	-	37
8	$[RhCp^*Cl_2]_2$	Ag_2CO_3	DCE	-	39
9	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	MeOH	-	NR
10	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	DMA	-	63
11	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	DMF	-	57
12	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	DMSO	-	54
13	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	HFIP	-	69
14[c,d,e]	**$[RhCp^*Cl_2]_2$**	**$Cu(OAc)_2{\cdot}H_2O$**	**HFIP**	**ADA**	**81**
15	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	HFIP	PiOH	78
16	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	HFIP	AcOH	74
17	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	HFIP	NaOAc	67
18	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$	HFIP	KOAc	65
19	-	$Cu(OAc)_2{\cdot}H_2O$	HFIP	ADA	NR
20	$[RhCp^*Cl_2]_2$	-	HFIP	ADA	32

[a]Reaction conditions: **1a** (0.24 mmol), **2a** (0.97 mmol, 4 equiv.), catalyst (5 mol %), oxidant (2 equiv), additive (1 equiv), solvent (2 mL) in a sealed tube at 100 °C for 24 h. [b]Isolated yield. [c]Using **2a** (3 equiv.), **3aa** obtained in 66% yield. [d]Using **2a** (1 equiv.), **3aa** obtained in 28% yield. [e]Under N_2, **3aa** obtained in 53% yield.

3. General procedure for the synthesis of 3.

A 10 mL oven-dried sealed tube was charged with compounds **1** (0.24 mmol) and **2** (0.97 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.48 mmol), Ad-COOH (0.24 mmol), $[RhCp^*Cl_2]_2$ (0.012 mmol, 5 mol %) and HFIP (2 mL) at room temperature. The reaction tube was capped tightly, and the reaction mixture was stirred at 100 °C in an oil bath for 24 h. The reaction mixture was cooled, diluted with water (5 mL), and then extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography (silica gel 100−200 mesh) using EtOAc-hexanes as an eluent to afford the desired product.

4. General procedure for the synthesis of 5.

A 10 mL oven-dried sealed tube was charged with compounds **4** (0.25 mmol) and **2** (0.77 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.51 mmol), Ad-COOH (0.25 mmol), $[RhCp^*Cl_2]_2$ (0.012 mmol, 5 mol %) and DCE (2 mL) at room temperature. The reaction tube was capped tightly, and the reaction mixture was stirred at 80 °C in an oil bath for 16 h. The reaction mixture was cooled, diluted with water (5 mL), and then extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography (silica gel 100−200 mesh) using EtOAc-hexanes as an eluent to afford the desired product.

5. Gram scale synthesis of 3aa.

An oven-dried sealed tube was charged with compound **1a** (1 g, 4.85 mmol) and **2a** (1.12 g, 19.41 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.931 g, 9.70 mmol), Ad-COOH (881 mg, 4.85 mmol), followed by $[RhCp^*Cl_2]_2$ (150 mg, 0.24 mmol, 5 mol %) in HFIP (8 mL) at room temperature, and the reaction mixture was stirred at 100 °C in an oil bath for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was allowed to attain room temperature. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The resulting crude was purified by column chromatography (silica gel 100-200 mesh) using EtOAc-hexanes as an eluent to afford **3aa**.

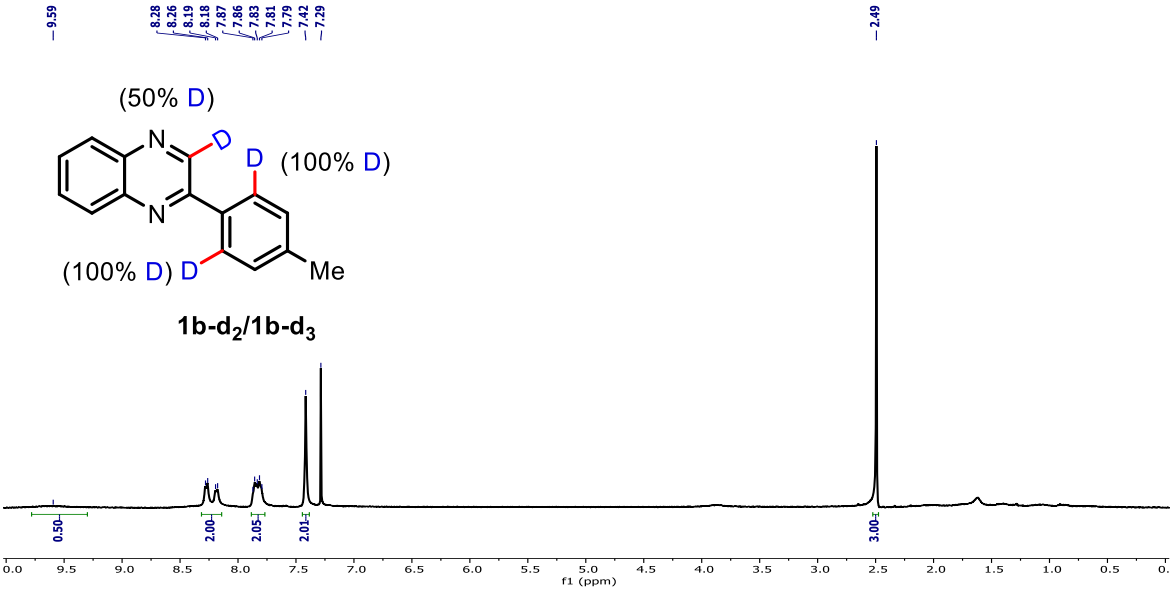
6. Gram scale synthesis of 5aa.

An oven-dried sealed tube was charged with compound **4a** (1 g, 5.15 mmol) and **2a** (897 mg, 15.46 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.05 g, 10.30 mmol), Ad-COOH (938 mg, 5.15 mmol),

followed by $[RhCp^*Cl_2]_2$ (159 mg, 0.25 mmol, 5 mol %) in DCE (8 mL) at room temperature, and the reaction mixture was stirred at 80 °C in an oil bath for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was allowed to attain room temperature. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The resulting crude was purified by column chromatography (silica gel 100-200 mesh) using EtOAc-hexanes as an eluent to afford **5aa**.

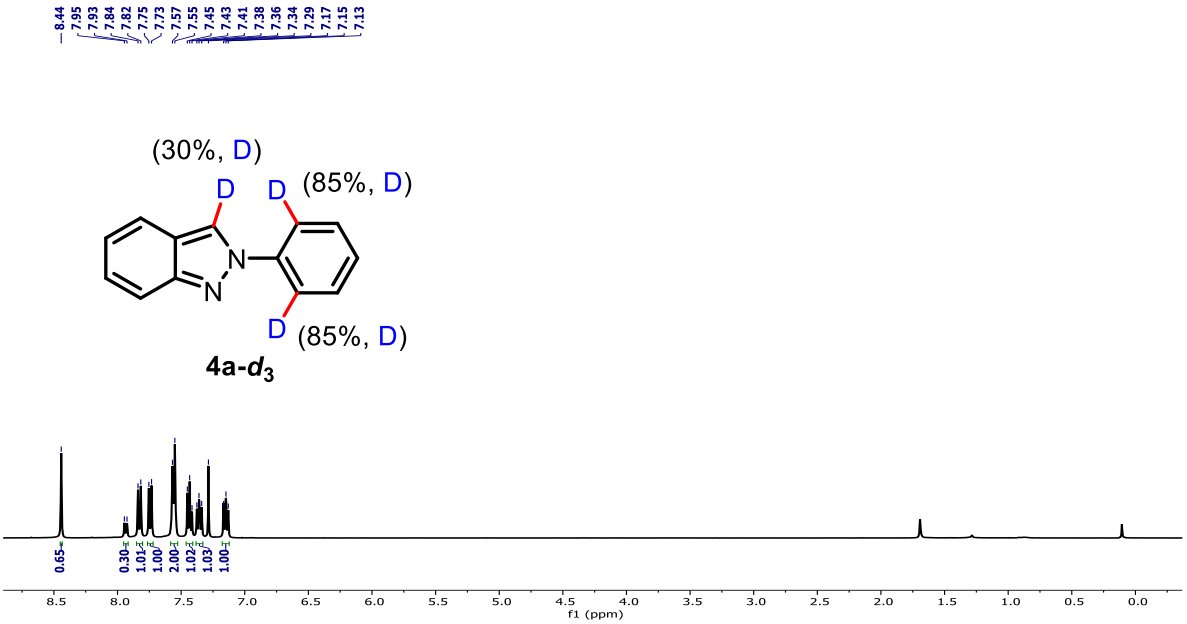
7. Deuterium Exchange Studies

7.1. Deuterium exchange of 1b: An oven-dried 10 mL pressure tube charged with **1b** (50 mg, 0.22 mmol), $Cu(OAc)_2 \cdot H_2O$ (90 mg, 0.45 mmol), Ad-COOH (41 mg, 0.22 mmol), $[RhCp^*Cl_2]_2$ (7 mg, 0.011 mmol, 5 mol %) followed by D_2O (92 µL, 5.68 mmol, 25 equiv.) in HFIP (2 mL) at room temperature. The reaction mixture was stirred at 100 °C in an oil bath for 24 h. After completion of the reaction, it was cooled to ambient temperature and extracted in ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography on (100-200 mm) size silica gel using hexanes-EtOAc as eleuent. From, ^1H NMR data of the product, 100% of deuterium incorporation was observed at both ortho C−H bonds of the 2-phenyl ring and 50% of deuterium incorporation was observed at the C3-position.



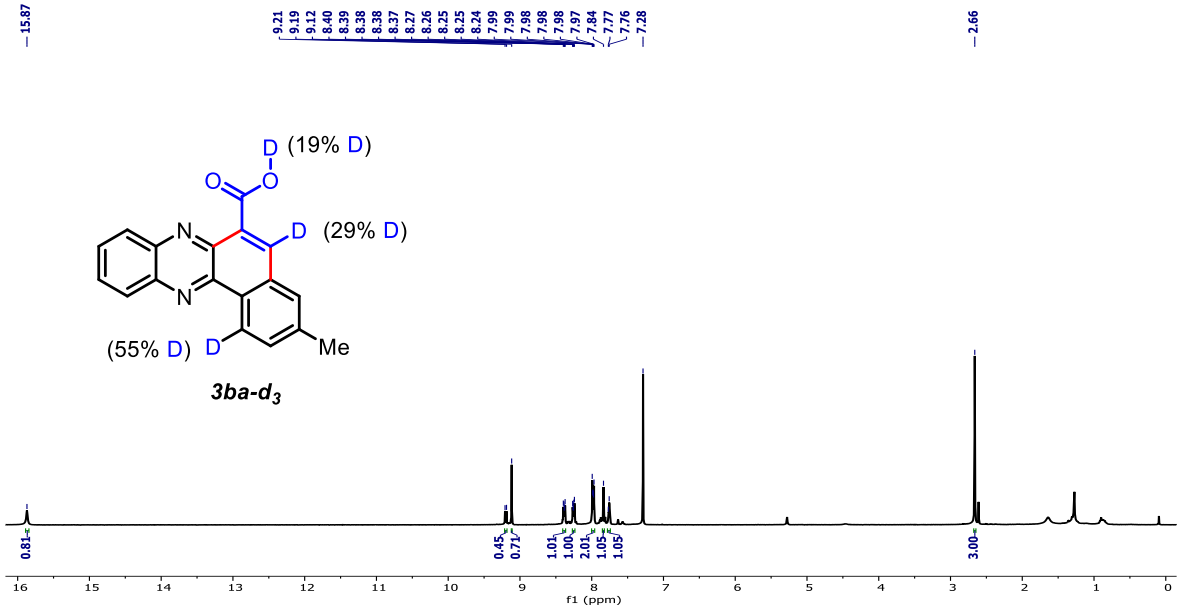
7.2 Deuterium exchange of 4a: An oven-dried 10 mL pressure tube charged with **4a** (50 mg, 0.25 mmol), $Cu(OAc)_2 \cdot H_2O$ (102 mg, 0.51 mmol), Ad-COOH (47 mg, 0.25 mmol), $[RhCp^*Cl_2]_2$ (7 mg, 0.012 mmol, 5 mol %) followed by D_2O (116 µL, 6.44 mmol, 25 equiv.) in DCE (2 mL) at room temperature. The reaction mixture was stirred at 80 °C in an oil bath

for 16 h. After completion of the reaction, it was cooled to ambient temperature, and extracted in ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography (100-200 mm) size silica gel using EtOAc-hexanes as eluent. ^{1}H NMR analysis of isolated product indicated 85% of deuterium incorporation at both ortho C−H bonds of the 2-phenyl ring, and 35% of deuterium incorporation at the C3-position.



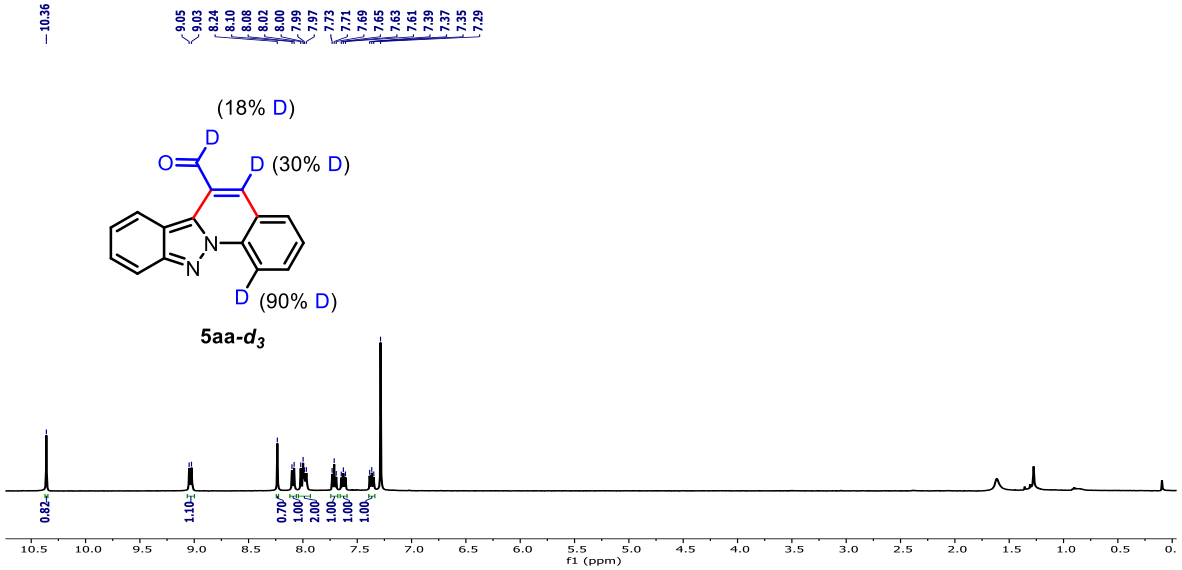
7.3. Deuterium exchange of 1b in the presence of 2a.

Procedure was similar as mentioned in section 7.1 except **2a** (58 mg, 0.90 mmol) also taken in the reaction mixture



7.4. Deuterium exchange of 4a in the presence of 2a.

Procedure was similar as mentioned in section 7.2 except **2a** (58 mg, 0.90 mmol) also taken in the reaction mixture



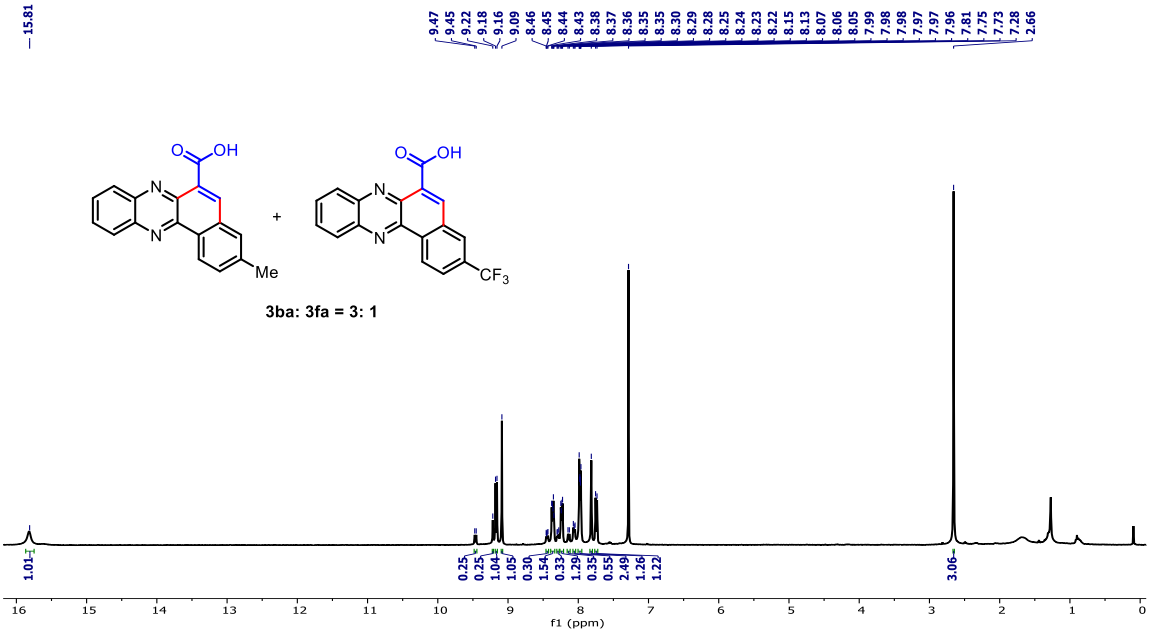
8. Intermediate isolation.

8.1 Experimental procedure for of 6ab: An oven-dried 10 mL pressure tube was charged with **1a** (50 mg, 0.24 mmol), **2b** (70 mg, 0.97 mmol), $Cu(OAc)_2 \cdot H_2O$ (96 mg, 0.48 mmol), Ad-COOH (44 mg, 0.24 mmol), $[RhCp^*Cl_2]_2$ (7 mg, 0.012 mmol, 5 mol %) in HFIP (2 mL) at room temperature. The reaction mixture was stirred at 60 °C in an oil bath for 4 h. After that the reaction mixture was cooled to ambient temperature, quenched with water, and extracted in ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography using hexanes/EtOAc as eluent on (100-200 mm) size silica gel to afford the product **6ab** with 68% yield.

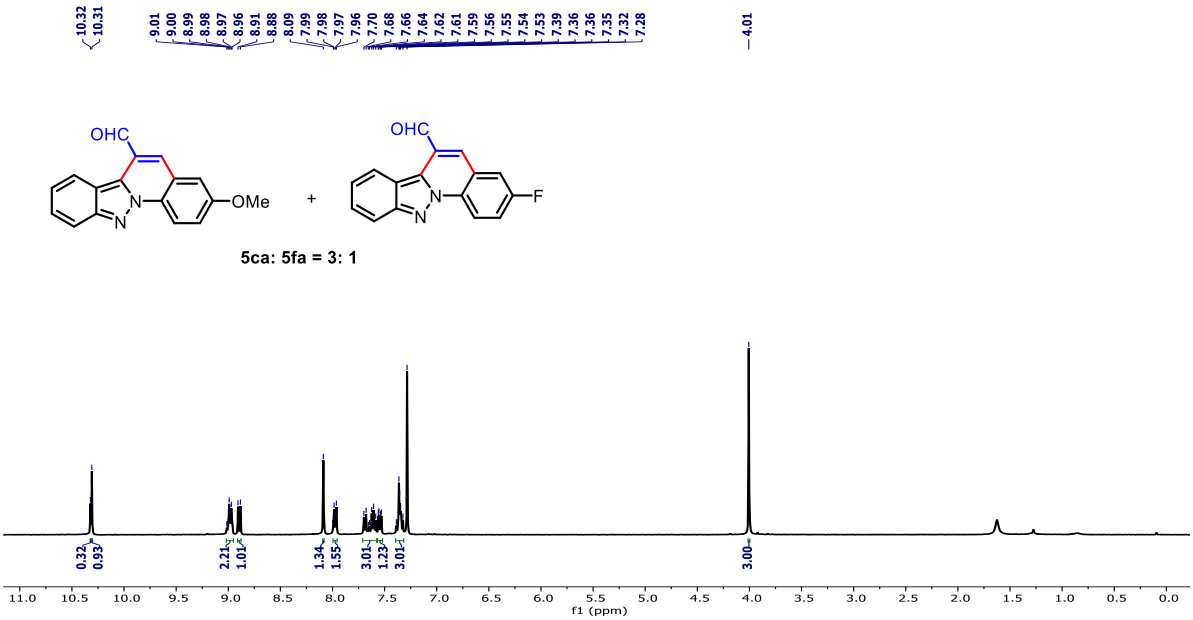
8.2 Experimental procedure for isolation of 7ac: An oven-dried 10 mL pressure tube charged with **4a** (50 mg, 0.25 mmol), **2c** (66 mg, 0.77 mmol) $Cu(OAc)_2 \cdot H_2O$ (102 mg, 0.51 mmol), Ad-COOH (47 mg, 0.25 mmol), $[RhCp^*Cl_2]_2$ (8 mg, 0.012 mmol, 5 mol %) in DCE (2 mL) at room temperature. The reaction mixture was stirred at 60 °C in an oil bath for 4 h. After that the reaction mixture was cooled to ambient temperature, quenched with water, and extracted in ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography using hexanes/EtOAc as eluent on (100-200 mm) size silica gel to afford the product **7ac** with 71% yield.

9. Competition experiment.

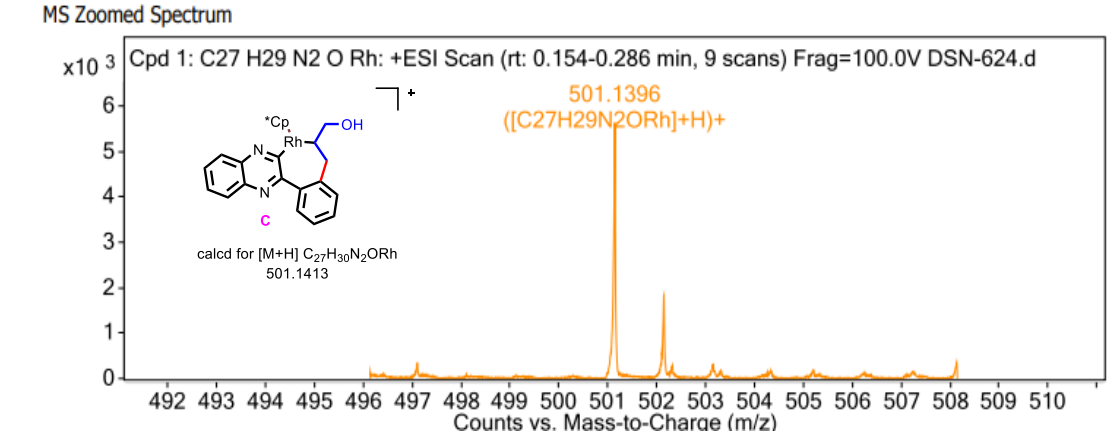
9.1 Experimental procedure for competition between 1b and 1f: A 10 mL oven-dried sealed tube was charged with **1b** (30 mg, 0.13 mmol), **1f** (30 mg, 0.13 mmol), **2a** (31 mg, 0.54 mmol), $Cu(OAc)_2 \cdot H_2O$ (54 mg, 0.27 mmol), Ad-COOH (25 mg, 0.13 mmol), $[RhCp^*Cl_2]_2$ (4 mg, 0.006 mmol, 5 mol %) in HFIP (2 mL) at room temperature. The reaction tube was caped tightly and stirred at 100 °C in an oil bath for 24 h. After completion of the reaction, it was cooled to ambient temperature, quenched with water, and extracted in ethyl acetate (5 mL × 3). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified through a filter column chromatography on silica gel (100-200) to afford the mixture of products **3ba** and **3fa**, which on ^1H NMR analysis indicated formation of **3ba** and **3fa** in 3: 1 ratio.

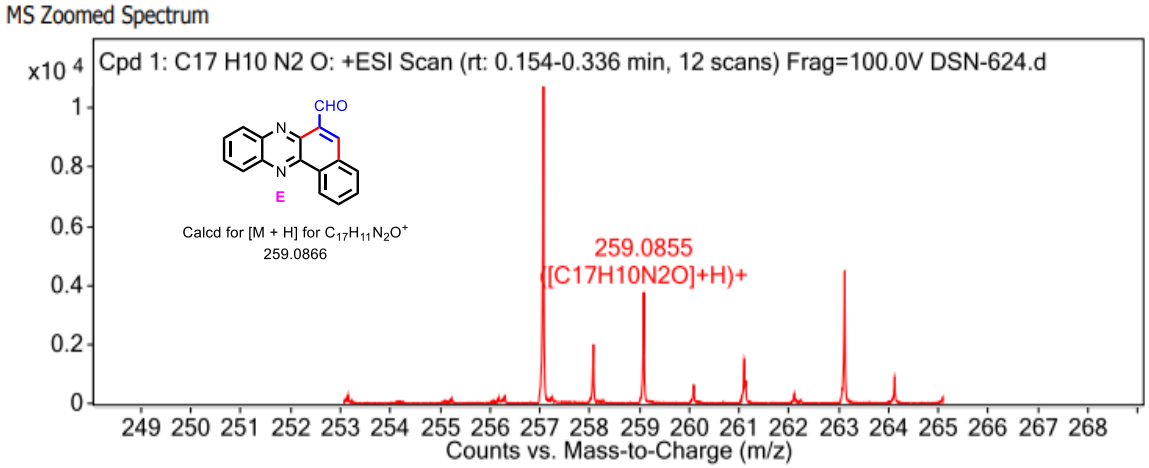


9.2 Experimental procedure for competition between 4c and 4f: A 10 mL oven-dried sealed tube was charged with compounds **4c** (30 mg, 0.13 mmol), **4f** (30 mg, 0.13 mmol), allyl alcohol **2a** (23 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (53 mg, 0.26 mmol), Ad-COOH (24 mg, 0.13 mmol), $[RhCp^*Cl_2]_2$ (4 mg, 0.006 mmol, 5 mol %) in DCE (2 mL) at room temperature, The reaction tube was caped tightly and stirred at 80 °C in an oil bath for 16 h. After completion of the reaction, it was cooled to ambient temperature, quenched with water, and extracted in ethyl acetate (5 mL × 3). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by through filter column chromatography using hexanes/EtOAc as eluent on silica gel (100-200 mesh size) to afford the mixture of products **5ca** and **5fa** in 3: 1 as predicted by ^1H NMR of the mixture.



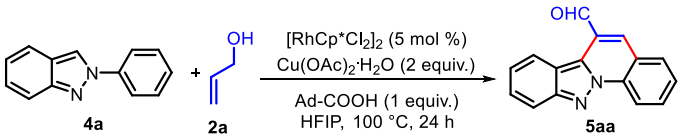
10. HRMS of rhodacycle intermediate C and intermediate E.





11. Optimization of reaction conditions for 5aa.

Table S2: Selected experiments for optimization of reaction conditions for **5aa**.[a]



Entry	Variation from standard conditions	% Yield **5aa**[b]
1	none	38
2	80 °C and 24 h	49
3	80 °C and 16 h	58
4	60 °C and 16 h	46
5	toluene as solvent	63
6	**DCE as solvent**	**72**
7	2 equivalent of **2a**	57
8	3 equivalent of **2a**	71
9	[Ru(*p*-cymene)Cl_2]$_2$ as a catalyst	Trace
10	$Pd(OAc)_2$ as a catalyst	NR
11	[CoCp*(CO)I_2]	21

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.77 mmol), catalyst (5 mol %), oxidant (2 equiv), additive (1 equiv), solvent (2 mL) in a sealed tube at 80 °C for 16 h, [b]Isolated yield.

12. Physical and spectral data of 3aa-5hb, 6ab, 7ac, 8, 9, 10, 11 and 12

Benzo[*a*]phenazine-6-carboxylic acid (3aa): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (54 mg, 81%); mp = 272-274 °C (Lit. mp 274-276 °C)[3]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.88 (s, 1H), 9.42 (d, *J* = 8.0 Hz, 1H), 9.25 (s, 1H), 8.45 (dd, *J* = 6.4, 3.6 Hz, 1H), 8.33 – 8.30 (m, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.04 – 7.97 (m, 3H), 7.94 – 7.91 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 142.8, 142.2, 141.8, 140.3, 138.4, 132.4, 132.1, 131.3, 131.2, 131.1, 130.9, 130.8, 129.1, 127.6, 125.5, 121.9; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{11}N_2O_2^+$ 275.0810; Found 275.0812.

3-Methylbenzo[*a*]phenazine-6-carboxylic acid (3ba): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (56 mg, 86%); mp = 276-278 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.94 (s, 1H), 9.28 (d, *J* = 8.2 Hz, 1H), 9.19 (s, 1H), 8.45 – 8.42 (m, 1H), 8.31 – 8.29 (m, 1H), 8.02 – 7.99 (m, 2H), 7.90 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 2.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 142.9, 142.2, 141.8, 141.6, 140.2, 138.2, 132.7, 131.8, 131.5, 131.1, 130.6, 130.1, 129.9, 127.6, 125.5, 121.8, 21.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O_2^+$ 289.0972; Found 289.0981.

3-Methoxybenzo[*a*]phenazine-6-carboxylic acid (3ca): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3, *v/v*) as an eluent; yellow solid (43 mg, 67%); mp = 268-270 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.98 (s, 1H), 9.31 (d, *J* = 8.8 Hz, 1H), 9.18 (s, 1H), 8.42 – 8.40 (m, 1H), 8.29 – 8.27 (m, 1H), 8.01 – 7.96 (m, 2H), 7.56 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 4.06 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 161.7, 142.8, 142.4, 141.5, 139.7, 137.9, 133.1, 131.5, 131.2, 129.8, 127.6, 127.4, 126.2, 122.4, 120.6, 111.6, 55.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O_3^+$ 305.0921; Found 305.0924.

3-Chlorobenzo[*a*]phenazine-6-carboxylic acid (3da): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (40 mg, 62%); mp = 282-284 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.81 (s, 1H), 9.39 (d, *J* = 8.8 Hz, 1H), 9.18 (s, 1H), 8.47 (dd, *J* = 6.6, 3.4 Hz, 1H), 8.34 (dd, *J* = 6.6, 3.4 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 8.06 (dd, *J* = 6.6, 3.4 Hz, 1H), 7.95 – 7.93 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 142.4, 142.3, 140.3, 140.0, 138.6, 137.2, 132.4, 131.6, 131.4, 130.7, 130.0, 129.7, 127.7, 127.2, 123.3; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{10}ClN_2O_2^+$ 309.0425; Found 309.0421.

3-Bromobenzo[*a*]phenazine-6-carboxylic acid (3ea): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (42 mg, 68%); mp = 272-274 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.80 (s, 1H), 9.31 (d, *J* = 8.6 Hz, 1H), 9.18 (s, 1H), 8.48 – 8.46 (m, 1H), 8.35 – 8.33 (m, 1H), 8.29 (d, *J* = 3.6 Hz, 1H), 8.10 – 8.04 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 140.2, 140.0, 138.6, 134.1, 132.8, 132.6, 132.4, 131.6, 131.2, 131.0, 130.9, 130.8, 130.0, 127.7, 127.2, 125.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{10}N_2BrN_2O_2^+$ 352.9920; Found 352.9923.

3-(Trifluoromethyl)benzo[*a*]phenazine-6-carboxylic acid (3fa): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3, *v/v*) as an eluent; Yellow solid (47 mg, 76%); mp = 244-246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.71 (s, 1H), 9.56 (d, *J* = 8.4 Hz, 1H), 9.29 (s, 1H), 8.52 – 8.49 (m, 1H), 8.41 (s, 1H), 8.38 – 8.34 (m, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.13 – 8.04 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 142.5, 141.8, 140.6, 140.4, 138.9, 134.6, 133.0, 132.7 (q, $^2J_{C\text{-}F}$ = 31.6 Hz), 131.8, 131.0, 130.1, 127.7, 127.6 (q, $^4J_{C\text{-}F}$ = 4.5 Hz), 126.9 (q, $^4J_{C\text{-}F}$ = 3.5 Hz), 126.5, 123.5, 123.7 (q, $^1J_{C\text{-}F}$ = 279.3 Hz); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{10}F_3N_2O_2^+$ 343.0689; Found 343.0693.

1-Methylbenzo[*a*]phenazine-6-carboxylic acid (3ga): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (45 mg, 69%); mp = 254-258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.07 (s, 1H), 9.15 (s, 1H), 8.41 – 8.38 (m, 1H), 8.26 – 8.23 (m, 1H), 8.01 – 7.95 (m, 3H), 7.78 – 7.73 (m, 2H), 3.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 145.2, 143.0, 141.1, 140.7, 140.6, 136.4,

135.4, 132.5, 131.9, 130.7, 130.0, 129.95, 129.94, 129.92, 127.2, 121.4, 26.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O_2^+$ 289.0972; Found 289.0983.

1-Methoxybenzo[*a*]phenazine-6-carboxylic acid (3ha): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3 *v/v*) as an eluent; yellow solid (50 mg, 78%); mp = 276-278 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.48 (dd, *J* = 6.6, 3.2 Hz, 1H), 8.28 (dd, *J* = 6.5, 3.3 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.87 (t, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 4.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 160.0, 144.0, 142.5, 141.8, 140.2, 136.4, 133.6, 132.0, 131.4, 130.8, 130.3, 127.1, 124.1, 122.2, 120.7, 114.6, 56.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O_3^+$ 305.0921; Found 305.0918.

2-(Trifluoromethyl)benzo[*a*]phenazine-6-carboxylic acid (3ia): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3 *v/v*) as an eluent; yellow solid (42 mg, 67%); mp = 264-266 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 15.80 (s, 1H), 9.72 (s, 1H), 9.29 (s, 1H), 8.53 (dd, *J* = 6.6, 3.4 Hz, 1H), 8.37 (dd, *J* = 6.4, 3.6 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.14 – 8.07 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$: DMSO) δ 166.3, 142.4, 142.0, 140.2, 139.9, 138.9, 133.1, 132.9, 132.6, 132.3, 131.9, 131.4, 129.9, 127.6, 126.8 (q, $^4J_{C\text{-}F}$ = 3.0 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 123.7, 122.7 (q, $^4J_{C\text{-}F}$ = 4.1 Hz); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{10}F_3N_2O_2^+$ 343.0689; Found 343.0687.

10-Chlorobenzo[*a*]phenazine-6-carboxylic acid (3ja): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (50 mg, 78%); mp = 276-278 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.50 (s, 1H), 9.37 (d, *J* = 7.6 Hz, 1H), 9.25 (s, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.02 – 7.98 (m, 1H), 7.96 – 7.92 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 166.1, 143.4, 142.3, 142.2, 140.3, 137.4, 136.9, 133.3, 132.1, 131.5, 131.3, 131.31, 130.9, 128.8, 128.5, 125.7, 121.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{10}ClN_2O_2^+$ 309.0425; Found 309.0431.

10-Bromobenzo[*a*]phenazine-6-carboxylic acid (3ka): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (52 mg, 84%); mp = 262-264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.50 (s, 1H), 9.36 (d, *J* = 8.0 Hz, 1H), 9.26 (s, 1H), 8.63 (d, *J* = 2.0 Hz, 1H), 8.16 (dd, *J* = 17.0, 8.6 Hz, 2H), 8.07 (dd, *J* = 9.2, 2.0 Hz, 1H), 8.02 – 7.98 (m, 1H), 7.96 – 7.92 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$ + MeOH) δ 166.3, 143.3, 142.4, 142.3, 140.3, 137.1, 135.7, 132.1, 131.9, 131.5, 131.3, 130.9, 128.7, 125.69, 125.67, 121.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{10}N_2BrN_2O_2^+$ 352.9920; Found 352.9904.

10-Fluorobenzo[*a*]phenazine-6-carboxylic acid (3la): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 2.3, *v/v*) as an eluent; yellow solid (48 mg, 74%); mp = 288-290 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.53 (s, 1H), 9.40 (d,

J = 7.6 Hz, 1H), 9.24 (s, 1H), 8.34 (dd, *J* = 9.0, 5.4 Hz, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 8.06 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.01 (t, *J* = 7.2 Hz, 1H), 7.95 (t, *J* = 7.0 Hz, 1H), 7.85 – 7.80 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$ + MeOH) δ 166.48, 163.45 (d, $^{1}J_{C\text{-}F}$ = 255.2 Hz), 143.27, 142.84 (d, $^{3}J_{C\text{-}F}$ = 13.6 Hz), 141.84 (d, $^{4}J_{C\text{-}F}$ = 1.4 Hz), 139.70 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 135.74, 131.98, 131.48, 131.30, 131.25, 130.83, 129.82 (d, $^{3}J_{C\text{-}F}$ = 10.3 Hz), 125.66, 123.49 (d, $^{2}J_{C\text{-}F}$ = 27.3 Hz), 121.58, 112.74 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{10}FN_2O_2^+$ 293.0721; Found 293.0727.

9,10-Dimethylbenzo[*a*]phenazine-6-carboxylic acid (3ma): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (53 mg, 82%); mp = 258-260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.02 (s, 1H), 9.29 (d, *J* = 8.0 Hz, 1H), 9.14 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.94 (t, *J* = 7.0 Hz, 2H), 7.87 (t, *J* = 7.2 Hz, 1H), 2.61 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.7, 143.8, 142.6, 141.8, 141.4, 140.6, 139.3, 137.4, 132.5, 131.1, 130.7, 130.5, 130.4, 128.4, 126.1, 125.2, 121.8, 20.8, 20.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O_2^+$ 303.1128; Found 303.1139.

9,10-Dichlorobenzo[*a*]phenazine-6-carboxylic acid (3na): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3, *v/v*) as an eluent; yellow solid (37 mg, 59%); mp = 282-284 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.26 (s, 1H), 9.37 (d, *J* = 7.2 Hz, 1H), 9.29 (s, 1H), 8.60 (s, 1H), 8.47 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.03 (t, *J* = 7.6 Hz, 1H), 7.97 (t, *J* = 7.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.8, 143.5, 143.0, 141.0, 140.6, 137.3, 137.1, 136.4, 132.1, 131.54, 131.50, 131.0, 130.2, 128.0, 125.8, 121.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_9Cl_2N_2O_2^+$ 343.0036; Found 343.0027.

Thieno[3,2-*a*]phenazine-5-carboxylic acid (3oa): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (56 mg, 84%); mp = 248-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.77 (s, 1H), 9.30 (s, 1H), 8.49 (d, *J* = 5.2 Hz, 1H), 8.37 – 8.34 (m, 1H), 8.27 – 8.23 (m, 1H), 8.03 – 7.97 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 142.5, 140.2, 140.1, 139.3, 139.1, 138.4, 133.5, 132.7, 132.1, 131.4, 129.8, 127.7, 124.8, 120.1; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_9N_2O_2S^+$ 281.0379; Found 281.0382.

Naphtho[2,3-*a*]phenazine-6-carboxylic acid (3pa): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3, *v/v*) as an eluent; yellow solid (56 mg, 89%); mp = 274-276 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.84 (s, 1H), 9.72 (s, 1H), 9.21 (s, 1H), 8.49 (s, 1H), 8.43 – 8.41 (m, 1H), 8.25 – 8.20 (m, 2H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.03 – 7.95 (m, 2H), 7.78 – 7.69 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 144.0, 143.3, 141.7, 141.4, 137.9, 133.8, 133.7, 131.6, 131.4, 131.1, 129.7, 129.3, 128.8, 128.6, 128.5, 128.4, 128.1, 127.5, 126.0, 121.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{13}N_2O_2^+$ 325.0972; Found 325.0969.

1-(Benzo[*a*]phenazin-6-yl)ethan-1-one (3ab): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (53 mg, 80%); mp = 188-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 7.6 Hz, 1H), 8.37 (s, 1H), 8.34 – 8.32 (m, 1H), 8.28 – 8.25 (m, 1H), 8.33, 7.98 (d, *J* = 7.2 Hz, 1H), 7.90 – 7.77 (m, 4H), 3.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.8, 142.0, 141.9, 141.5, 141.2, 137.0, 134.5, 132.4, 131.7, 130.4, 130.2, 130.1, 129.8, 129.6, 129.5, 125.4, 32.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O^+$ 273.1022; Found 273.1020.

1-(Benzo[*a*]phenazin-6-yl)propan-1-one (3ac): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (54 mg, 78%); mp = 184-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 8.0 Hz, 1H), 8.39 – 8.36 (m, 1H), 8.32 (s, 1H), 8.31 – 8.28 (m, 1H), 8.02 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.94 – 7.81 (m, 4H), 3.53 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 205.7, 142.1, 142.0, 141.6, 141.3, 137.6, 133.9, 132.2, 131.9, 130.4, 130.3, 130.2, 129.7, 129.64, 129.62, 129.4, 125.5, 38.1, 8.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O^+$ 287.1179; Found 287.1184.

1-(3-Methylbenzo[*a*]phenazin-6-yl)ethan-1-one (3bb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (55 mg, 84%); mp = 184-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 8.4 Hz, 1H), 8.33 – 8.31 (m, 2H), 8.27 – 8.25 (m, 1H), 7.91 – 7.84 (m, 2H), 7.75 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 3.10 (s, 3H), 2.62 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.9, 142.2, 141.7, 141.1, 140.6, 137.0, 134.6, 131.8, 131.2, 130.3, 130.1, 130.0, 129.7, 129.6, 129.5, 125.4, 32.8, 21.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O^+$ 287.1179; Found 287.1186.

1-(3-Methoxybenzo[*a*]phenazin-6-yl)ethan-1-one (3cb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (48 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 8.8 Hz, 1H), 8.33 – 8.30 (m, 2H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.37 (s, 1H), 4.01 (s, 3H), 3.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.0, 161.2, 142.2, 141.7, 141.5, 140.6, 137.6, 134.2, 133.3, 130.4, 129.7, 129.6, 129.3, 127.3, 126.2, 119.0, 110.9, 55.7, 32.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O_2^+$ 303.1128; Found 303.1136.

1-(3-Chlorobenzo[*a*]phenazin-6-yl)ethan-1-one (3db): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (43 mg, 67%); mp = 242-244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 7.6 Hz, 1H), 8.32 – 8.28 (m, 2H), 8.00 (s, 1H), 7.95 – 7.91 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 3.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.7, 142.1, 141.7, 141.6, 140.9, 138.5, 136.4, 132.9, 132.8, 130.8, 130.7, 130.6, 129.9, 129.7, 129.6, 128.8, 127.1, 32.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{12}ClN_2O^+$ 307.0633; Found 307.0641.

1-(3-Bromobenzo[*a*]phenazin-6-yl)ethan-1-one (3eb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (43 mg, 69%); mp = 234-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 8.4 Hz, 1H), 8.39 – 8.37 (m, 1H), 8.33 – 8.31 (m, 1H), 8.28 (s, 1H), 8.17 (d, *J* = 1.2 Hz, 1H), 7.99 – 7.92 (m, 3H), 3.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.6, 142.2, 141.75, 141.72, 140.9, 138.5, 133.1, 132.8, 132.6, 132.0, 131.0, 130.9, 130.6, 129.7, 129.6, 127.2, 124.7, 32.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}BrN_2O^+$ 351.0128; Found 351.0121.

1-(3-(Trifluoromethyl)benzo[*a*]phenazin-6-yl)ethan-1-one (3fb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1:19, *v/v*) as an eluent; Yellow solid (47 mg, 75%); mp = 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, *J* = 8.5 Hz, 1H), 8.38 – 8.36 (m, 2H), 8.33 – 8.28 (m, 1H), 8.27 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.98 – 7.93 (m, 2H), 3.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.3, 142.4, 141.7, 141.3, 141.1, 138.6, 134.5, 133.2, 131.8 (q, $^{2}J_{C\text{-}F}$ = 35.8 Hz), 131.4, 131.1, 131.0, 129.73, 129.68, 126.8 (q, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 126.4, 125.3 (q, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 122.6 (q, $^{1}J_{C\text{-}F}$ = 273.3 Hz), 32.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{12}F_3N_2O^+$ 341.0896; Found 341.0889.

1-(3-Fluorobenzo[*a*]phenazin-6-yl)ethan-1-one (3qb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (47 mg, 72%); mp = 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (dd, *J* = 9.0, 5.8 Hz, 1H), 8.35 (dd, *J* = 7.2, 2.4 Hz, 1H), 8.31 – 7.28 (m, 2H), 7.95 – 7.89 (m, 2H), 7.65 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.61 – 7.56 (m, 1H), 3.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.7, 163.6 (d, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 141.9, 141.7, 140.7, 138.5, 133.4, 133.4, 133.1 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 130.7, 130.3, 129.7, 129.5, 128.8 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 128.2, 128.1, 118.0 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 114.5 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 32.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{12}FN_2O^+$ 291.0928; Found 291.0934.

Indazolo[2,3-*a*]quinoline-6-carbaldehyde (5aa): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (46 mg, 72%); mp = 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.00 (t, *J* = 7.6 Hz, 2H), 8.18 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.8, 149.8, 135.8, 134.3, 132.9, 129.9, 128.6, 128.5, 128.4, 126.8, 124.3, 123.1, 121.8, 117.9, 117.2, 116.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{11}N_2O^+$ 247.0866; Found 247.0877.

3-Methylindazolo[2,3-*a*]quinoline-6-carbaldehyde (5ba): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (49 mg, 78%); mp = 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.02 – 8.99 (m, 1H), 8.87 (d, *J* = 8.4 Hz, 1H), 8.12 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.81 (s, 1H),

7.77 (dd, J = 8.4, 2.0 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.37 – 7.32 (m, 1H), 2.61 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.9, 149.7, 136.9, 134.6, 134.3, 134.0, 129.2, 128.5, 128.4, 128.2, 124.2, 123.2, 121.6, 117.6, 117.2, 116.5, 21.3; HRMS (ESI) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O^+$ 261.1022; Found 261.1025.

3-Methoxyindazolo[2,3-*a*]quinoline-6-carbaldehyde (5ca): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (46 mg, 75%); mp = 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.95 (d, J = 8.4 Hz, 1H), 8.85 (d, J = 9.2 Hz, 1H), 8.01 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.51 (dd, J = 9.2, 2.8 Hz, 1H), 7.35 – 7.29 (m, 2H), 3.98 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.8, 158.1, 149.5, 133.5, 130.6, 128.6, 128.2, 127.6, 124.2, 124.1, 122.9, 121.5, 119.3, 117.1, 116.3, 109.5, 55.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2^+$ 277.0972; Found 277.0979.

3-Chloroindazolo[2,3-*a*]quinoline-6-carbaldehyde (5da): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (43 mg, 70%); mp = 192-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.91 (d, J = 8.6 Hz, 1H), 8.85 (d, J = 9.0 Hz, 1H), 7.96 – 7.92 (m, 3H), 7.83 (dd, J = 9.2, 2.4 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.4, 149.8, 134.0, 132.9, 132.6, 132.4, 129.2, 128.8, 128.5, 128.2, 124.1, 123.9, 122.2, 119.4, 117.2, 116.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}ClN_2O^+$ 281.0476, Found 281.0485

3-Bromoindazolo[2,3-*a*]quinoline-6-carbaldehyde (5ea): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (44 mg, 74%); mp = 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.96 (d, J = 8.8 Hz, 2H), 8.85 (d, J = 9.2 Hz, 1H), 8.18 (d, J = 2.0 Hz, 2H), 8.05 (s, 1H), 8.01 (dd, J = 9.2, 2.0 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.38 – 7.34 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.4, 149.9, 135.6, 134.4, 132.4, 131.7, 129.3, 128.8, 128.3, 124.4, 124.1, 122.2, 120.3, 119.6, 117.2, 116.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}BrN_2O^+$ 324.9971; Found 324.9977.

3-Fluoroindazolo[2,3-*a*]quinoline-6-carbaldehyde (5fa): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (43 mg, 69%); mp = 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.01 – 8.94 (m, 2H), 8.08 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.38 – 7.34 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.5, 160.6 (d, $^{1}J_{C\text{-}F}$ = 247.2 Hz), 149.7, 132.7 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 132.4, 129.4, 128.6, 128.0, 124.2, 124.2, 124.1, 122.0, 121.3 (d, $^{2}J_{C\text{-}F}$ = 24.6 Hz), 120.2 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 117.2, 116.6, 114.0 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O^+$ 265.0772; Found 265.0771.

2-Methylindazolo[2,3-*a*]quinoline-6-carbaldehyde (5ga): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow

solid (51 mg, 81%); mp = 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 9.00 (d, *J* = 8.4 Hz, 1H), 8.76 (s, 1H), 8.09 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 2.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.6, 149.8, 144.6, 135.7, 134.5, 129.6, 128.6, 128.52, 128.48, 127.6, 124.4, 121.5, 120.9, 117.5, 117.1, 116.4, 22.4; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O^+$ 261.1022; Found 261.1014.

8-Chloroindazolo[2,3-*a*]quinoline-6-carbaldehyde (5ha): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (45 mg, 73%); mp = 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 9.07 (d, *J* = 1.6 Hz, 1H), 8.98 (d, *J* = 8.8 Hz, 1H), 8.22 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.01 – 7.96 (m, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.53 (dd, *J* = 9.2, 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.7, 148.1, 135.8, 135.2, 133.2, 129.9, 129.8, 128.4, 127.9, 127.2, 127.1, 123.25, 123.22, 118.0, 117.9, 117.6; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}ClN_2O^+$ 281.0476; Found 281.0482.

8-Fluoroindazolo[2,3-*a*]quinoline-6-carbaldehyde (5ia): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (47 mg, 75%); mp = 188-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.67 (dd, *J* = 10.4, 2.0 Hz, 1H), 8.12 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.71 – 7.67 (m, 1H), 7.42 – 7.37 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.8, 157.9 (d, $^{1}J_{C\text{-}F}$ = 247.2 Hz), 147.41, 135.8, 134.7, 132.9, 129.8, 128.5, 128.46, 128.41, 127.0, 123.1, 119.7 (d, $^{2}J_{C\text{-}F}$= 28.8 Hz), 118.3 (d, $^{3}J_{C\text{-}F}$= 9.5 Hz), 117.7, 116.7 (d, $^{3}J_{C\text{-}F}$ = 12.6 Hz), 107.6 (d, $^{2}J_{C\text{-}F}$= 26.8 Hz); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O^+$ 265.0772; Found 265.0777.

1-(Indazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5ab): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (46 mg, 68%); mp = 166-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.8 Hz, 1H), 8.09 (s, 1H), 7.96 (t, *J* = 9.0 Hz, 2H), 7.90 – 7.86 (m, 1H), 7.65 – 7.56 (m, 2H), 7.31 – 7.27 (m, 1H), 2.87 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.3, 149.9, 135.2, 131.9, 129.7, 129.4, 128.9, 128.3, 127.1, 126.6, 124.2, 123.1, 121.5, 117.7, 116.6, 116.5, 28.3; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O^+$ 261.1022; Found 261.1014.

1-(Indazolo[2,3-*a*]quinolin-6-yl)propan-1-one (5ac): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (46 mg, 65%); mp = 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H), 8.10 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.92 – 7.88 (m, 1H), 7.68 – 7.64 (m, 1H), 7.61 – 7.57 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 3.26 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.7, 149.9, 135.2, 131.6, 129.9,

129.3, 129.0, 128.2, 126.6, 125.6, 123.8, 123.3, 121.5, 117.7, 116.7, 116.6, 33.8, 8.5; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O^+$ 275.1179; Found 275.1187.

1-(3-Methylindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5bb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (47 mg, 71%); mp = 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.8 Hz, 1H), 8.64 (d, *J* = 8.8 Hz, 1H), 8.07 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.75 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.31 – 7.29 (m, 1H), 2.88 (s, 3H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.4, 149.8, 136.7, 133.6, 129.7, 128.8, 128.7, 128.1, 127.0, 124.1, 123.2, 121.3, 117.5, 116.8, 116.5, 28.4, 21.3; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O^+$ 275.1179; Found 275.1185.

1-(3-Methoxyindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5cb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow solid (45 mg, 69%); mp = 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 9.2 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.51 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.32 – 7.29 (m, 2H), 4.00 (s, 3H), 2.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.4, 158.1, 149.7, 130.2, 128.3, 127.9, 126.5, 124.3, 123.9, 121.9, 121.2, 119.2, 116.8, 116.3, 109.3, 55.8, 28.4; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O_2^+$ 291.1128; Found 291.1137.

1-(3-Chloroindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5db): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (43 mg, 67%); mp = 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 9.2 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 1H), 7.94 – 7.89 (m, 3H), 7.79 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.28 (m, 1H), 2.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 149.9, 133.5, 132.3, 132.0, 130.7, 128.7, 128.5, 128.2, 125.3, 124.02, 124.00, 121.8, 119.2, 116.8, 116.6, 28.4; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}ClN_2O^+$ 295.0633; Found 295.0630.

1-(3-Bromoindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5eb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (40 mg, 64%); mp = 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 9.2 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 8.00 – 7.95 (m, 3H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.29 (m, 1H), 2.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.1, 150.0, 134.7, 134.0, 131.4, 130.8, 128.8, 128.5, 125.2, 124.5, 124.0, 121.9, 120.1, 119.5, 116.9, 116.6, 28.4; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}BrN_2O^+$ 339.0128; Found 339.0136.

1-(3-Fluoroindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5fb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (42 mg, 65%); mp = 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 10.0, 4.8 Hz, 1H), 8.57 (d, *J* = 8.8 Hz, 1H), 8.01 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.63 – 7.57

(m, 3H), 7.33 – 7.29 (m, 1H), 2.88 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.2, 160.6 (d, $^{1}J_{C\text{-}F}$ = 246.4 Hz), 149.8, 131.9, 130.9, 128.5, 128.3, 125.5 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 124.3 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 123.9, 121.7, 120.3 (d, $^{2}J_{C\text{-}F}$ = 24.7 Hz), 120.0 (d, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 116.9, 116.6, 113.6 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 28.5; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}FN_2O^+$ 279.0928; Found 279.0934.

1-(2-Methylindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5gb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 9, *v/v*) as an eluent; yellow solid (46 mg, 70%); mp = 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.09 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.27 (m, 1H), 2.86 (s, 3H), 2.68 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.2, 149.9, 143.4, 135.2, 129.24, 129.18, 128.8, 128.4, 128.3, 127.4, 124.3, 121.3, 120.9, 117.4, 116.8, 116.4, 28.3, 22.3; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O^+$ 275.1179; Found 275.1185.

1-(8-Chloroindazolo[2,3-*a*]quinolin-6-yl)ethan-1-one (5hb): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1:9, *v/v*) as an eluent; yellow solid (41 mg, 64%); mp = 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 8.4 Hz, 1H), 8.70 (d, *J* = 1.6 Hz, 1H), 8.18 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 9.0, 2.2 Hz, 1H), 2.89 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.0, 148.2, 135.3, 132.2, 129.55, 129.47, 129. 4, 128.6, 127.9, 127.0, 126.8, 123.3, 123.2, 117.9, 117.7, 117.3, 28.2; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}ClN_2O^+$ 295.0633; Found 295.0628.

4-(2-(Quinoxalin-2-yl)phenyl)butan-2-one (6ab): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow oily liquid (46 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.19 – 8.17 (m, 1H), 8.12 – 8.10 (m, 1H), 7.85 – 7.80 (m, 2H), 7.56 – 7.53 (m, 1H), 7.48 – 7.39 (m, 3H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 207.8, 154.7, 145.8, 141.7, 141.1, 140.3, 136.9, 130.5, 130.4, 130.3, 129.9, 129.7, 129.5, 129.3, 126.7, 45.7, 29.9, 27.5; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O^+$ 277.1335; Found 277.1344.

1-(2-(2*H*-Indazol-2-yl)phenyl)pentan-3-one (7ac): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow oily liquid (51 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 0.8 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.47 – 7.35 (m, 5H), 7.19 – 7.15 (m, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 210.4, 149.3, 140.1, 137.5, 130.5, 129.5, 127.05, 127.00, 126.5, 124.6, 122.3, 122.0, 120.4, 117.9, 43.0, 35.9, 25.7, 7.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O^+$ 279.1492; Found 279.1484.

Methyl benzo[*a*]phenazine-6-carboxylate (8): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; off white solid (24 mg, 76%); mp = 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, *J* = 8.0 Hz, 1H), 8.51 (s, 1H), 8.40 – 8.37 (m, 2H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.94 – 7.89 (m, 3H), 7.87 – 7.83 (m, 1H), 4.16 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 142.6, 141.9, 141.7, 140.9, 135.6, 132.4, 131.4, 130.6, 130.2, 130.12, 130.10, 129.7, 129.5, 129.4, 129.2, 125.6, 52.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O_2^+$ 289.0972; Found 289.0978.

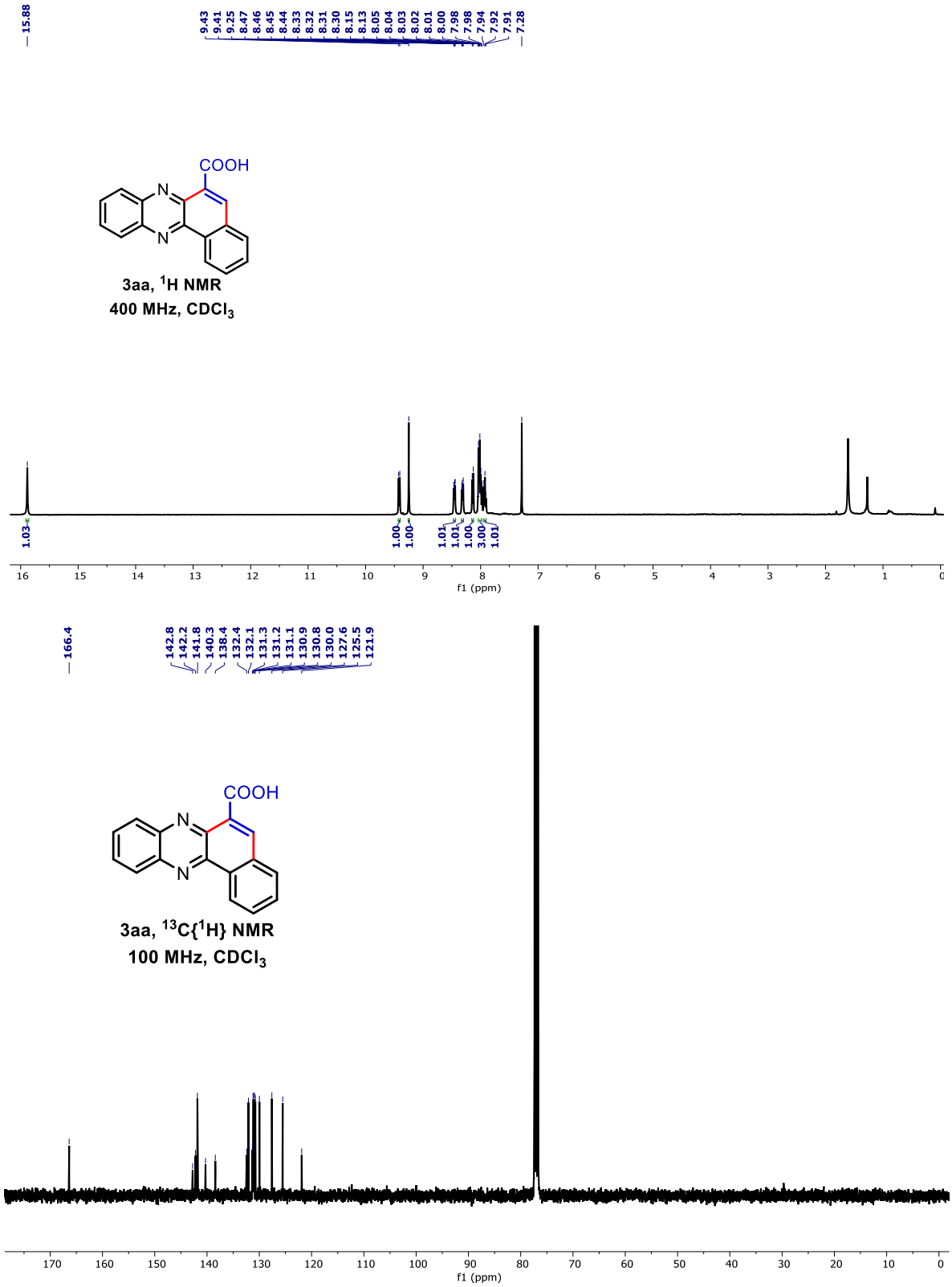
Benzo[*a*]phenazine (9): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 19, *v/v*) as an eluent; yellow solid (30 mg, 72%); mp = 232-234 °C (Lit. mp 236-237 °C)[4]; ^{1}H NMR (400 MHz, $CDCl_3$) 9.47 – 9.44 (m, 1H), 8.41 – 8.39 (m, 1H), 8.33 – 8.30 (m, 1H), 8.06 – 7.99 (m, 2H), 7.96 – 7.94 (m, 1H), 7.91 – 7.89 (m, 2H), 7.86 – 7.79 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.6, 142.7, 142.0, 133.4, 133.3, 131.2, 130.1, 129.90, 129.86, 129.7, 129.2, 128.3, 128.0, 127.2, 125.4; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{11}N_2^+$ 231.0917; Found 231.0917.

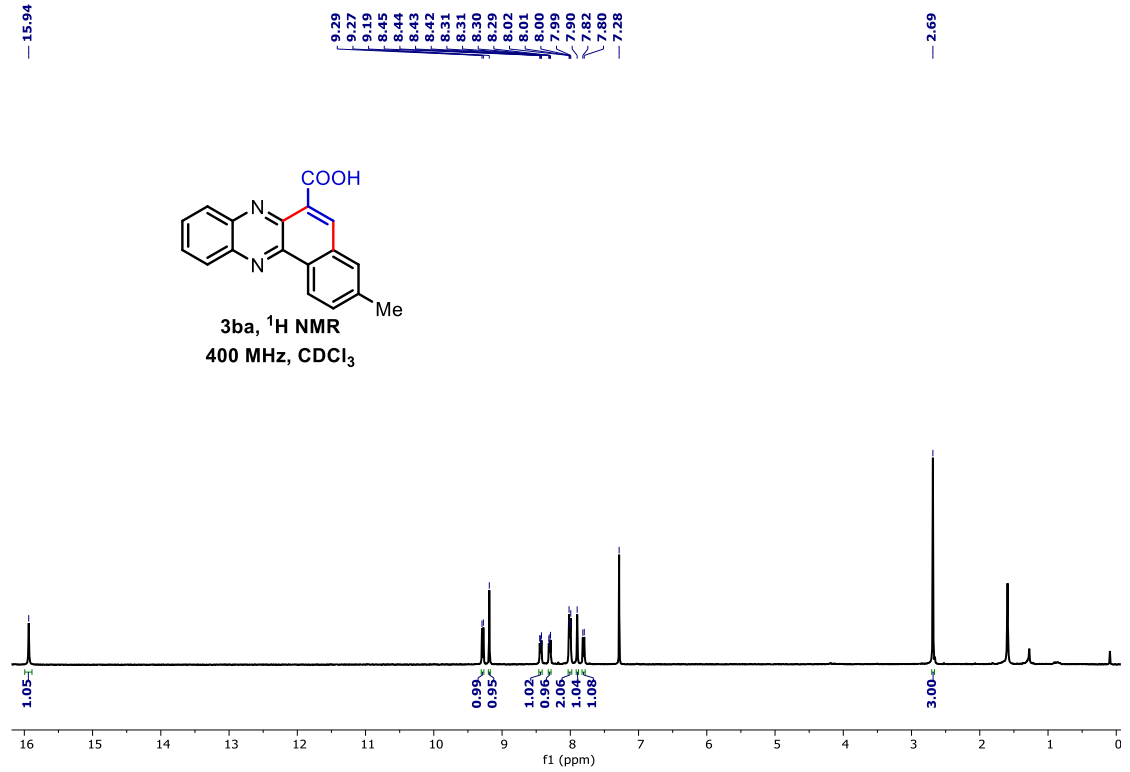
***N, N*-Dimethylbenzo[*a*]phenazine-6-carboxamide (10):** The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 3, *v/v*) as an eluent; off white solid (21 mg, 64%); mp = 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.41 – 8.38 (m, 1H), 8.34 – 8.31 (m, 1H), 8.06 (s, 1H), 7.97 – 7.81 (m, 5H), 3.38 (s, 3H), 2.92 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.4, 142.7, 142.0, 141.9, 140.8, 135.0, 132.3, 131.3, 131.0, 130.4, 130.1, 129.9, 129.6, 128.7, 128.6, 125.4, 38.8, 35.1; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{16}N_3O^+$ 302.1288; Found 302.1292.

1-(3-Methylbenzo[*a*]phenazin-6-yl)ethan-1-ol (11): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1:4, *v/v*) as an eluent; off white solid (28 mg, 90%); mp = 184-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 8.0 Hz, 1H), 8.36 – 8.34 (m, 1H), 8.25 – 8.23 (m, 1H), 7.91 – 7.83 (m, 3H), 7.67 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 5.63 (q, *J* = 6.8 Hz, 1H), 5.37 (s, 1H), 2.62 (s, 3H), 1.86 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.2, 142.5, 141.6, 140.7, 140.4, 139.0, 132.9, 130.0, 129.9, 129.5, 129.4, 129.08, 129.07, 128.4, 128.2, 125.2, 69.0, 22.9, 21.8; HRMS (ESI) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O^+$ 289.1335; Found 289.1341.

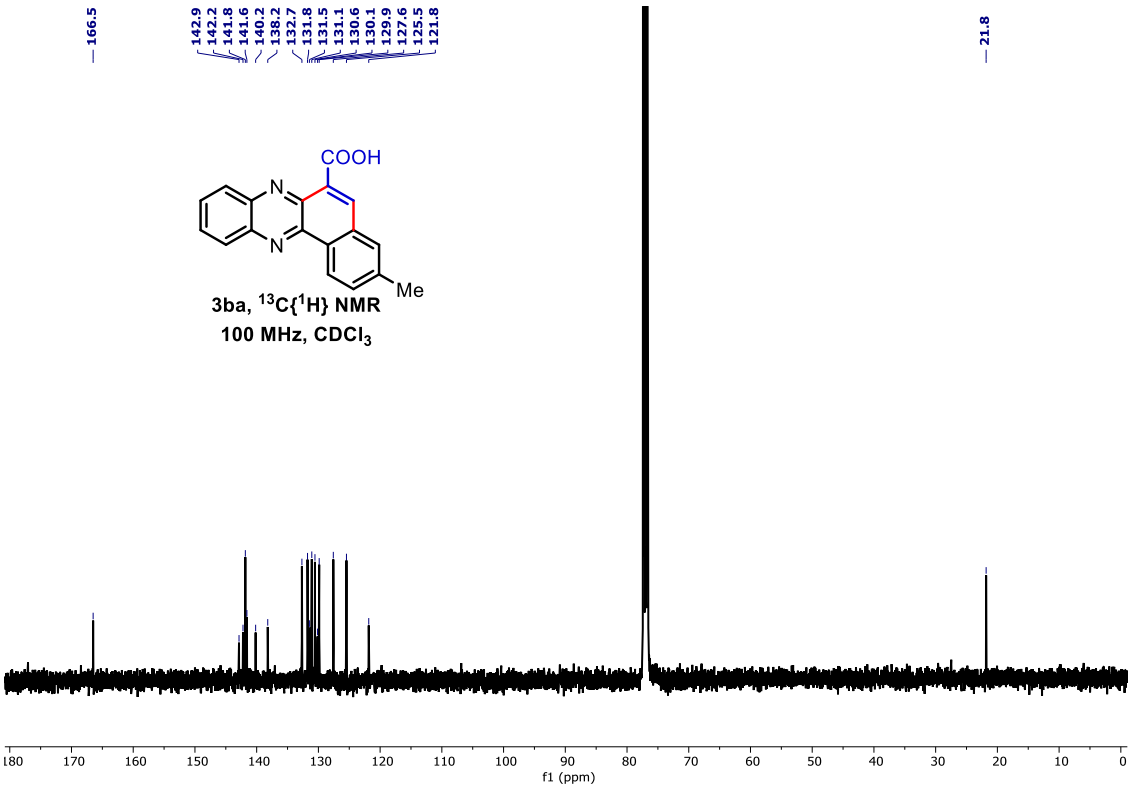
1-(3-Oxopropyl)indazolo[2,3-*a*]quinoline-6-carbaldehyde (12): The title compound was purified by column chromatography on silica gel using EtOAc/hexanes (1: 4, *v/v*) as an eluent; yellow oily liquid (17 mg, 22%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 10.02 (s, 1H), 9.02 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.37 (t, *J* = 6.6 Hz, 2H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 6.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.2, 189.6, 149.3, 136.7, 135.2, 133.0, 129.7, 129.3, 128.2, 128.1, 127.3, 126.4, 125.1, 123.9, 122.0, 116.8, 115.9, 46.1, 29.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O_2^+$ 303.1128; Found 303.1132.

13 Copies of ^{1}H NMR, $^{13}\{^{1}H\}$ NMR of 3aa-5hb, 6ab, 7ac, 8, 9, 10, 11 and 12

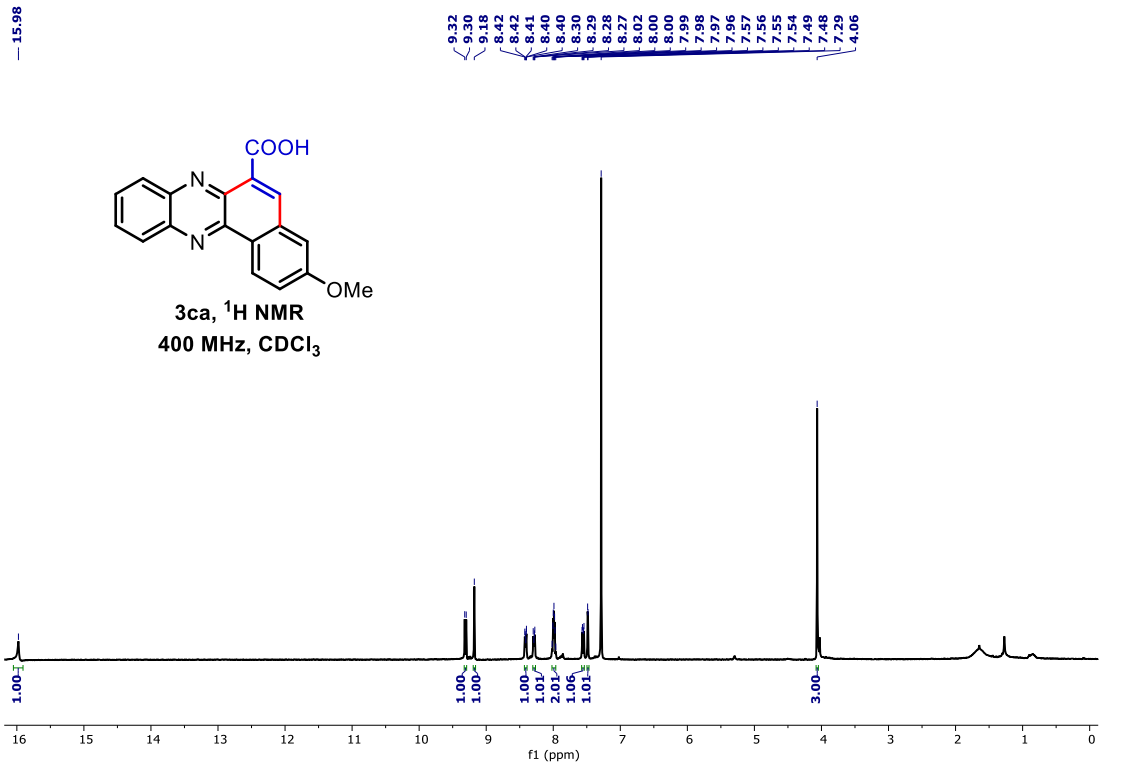




3ba, ^{1}H NMR
400 MHz, $CDCl_3$



3ba, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$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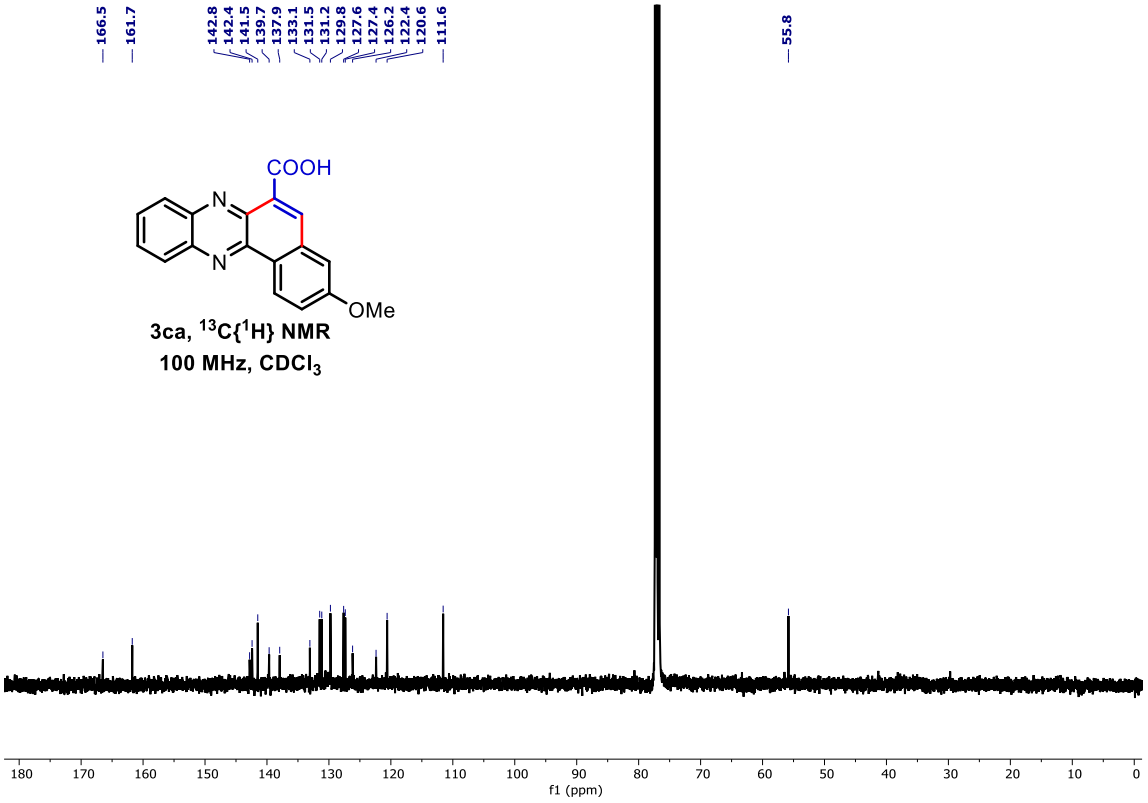
8.02
8.00
8.00
7.99
7.98
7.97
7.96
7.57
7.56
7.55
7.54
7.49
7.48
7.29
4.06
COOH
N
N
OMe
3ca, 1H NMR
400 MHz, CDCl3
1.00
1.00
1.00
1.00
1.01
2.01
1.06
1.01
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.5
161.7
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142.4
141.5
139.7
137.9
133.1
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131.2
129.8
127.6
127.4
126.2
122.4
120.6
111.6
55.8
COOH
N
N
OMe
3ca, 13C{1H} NMR
100 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
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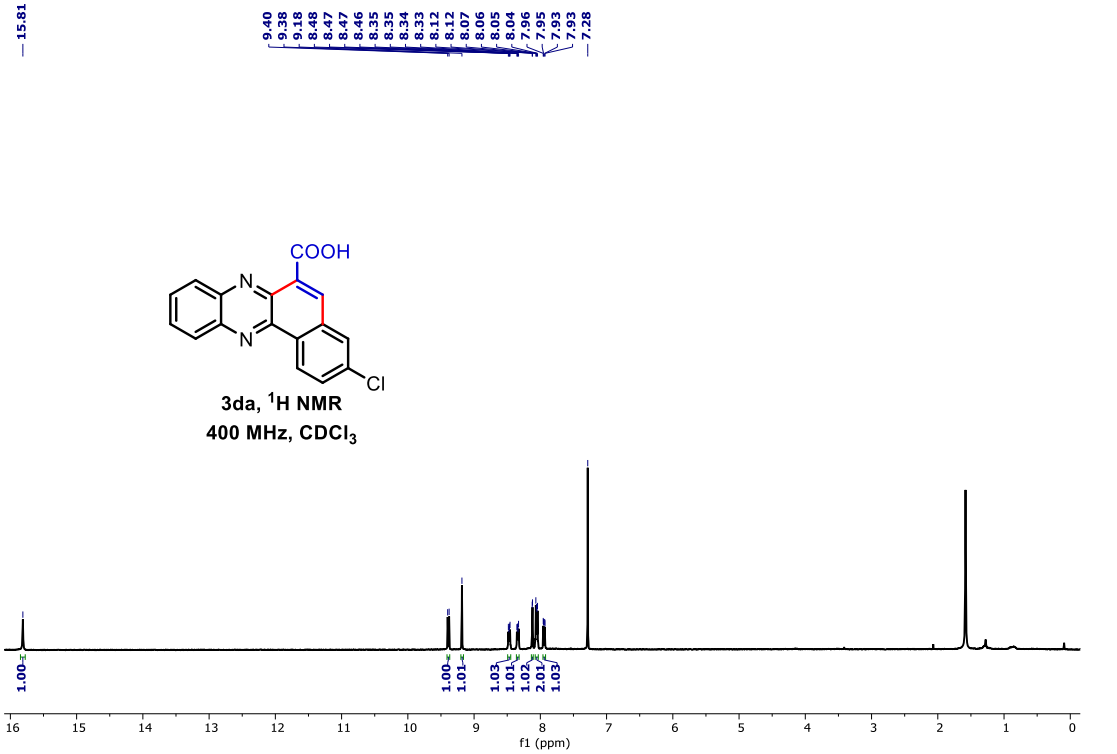
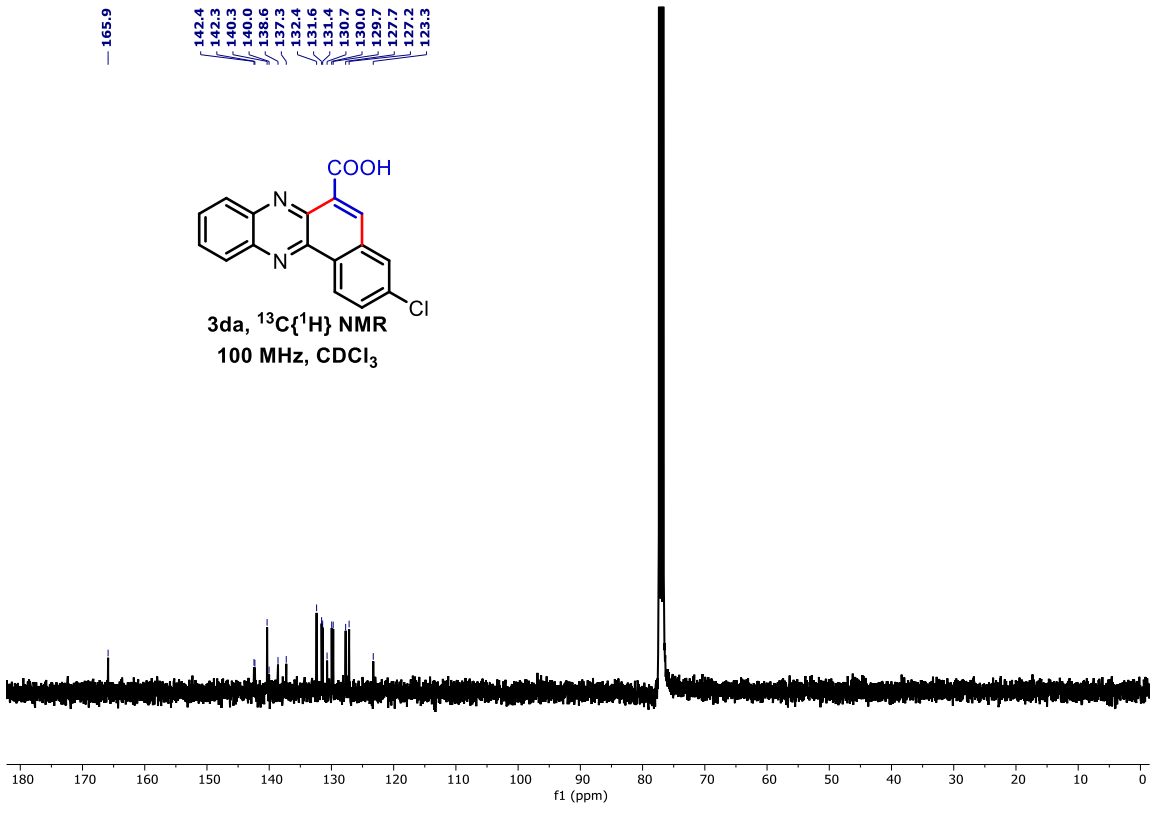
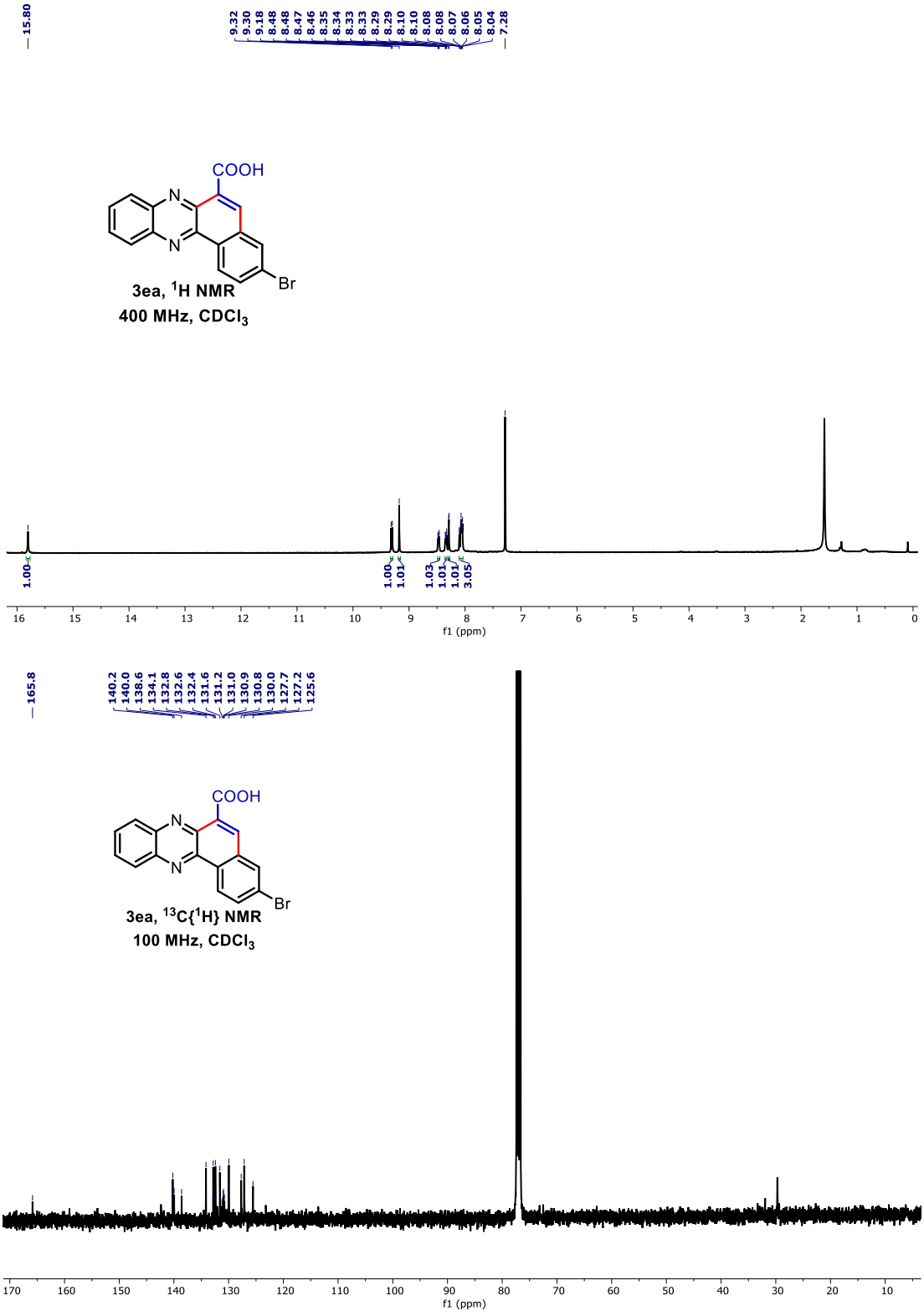
f1 (ppm)



3da, ^{1}H NMR
400 MHz, $CDCl_3$



3da, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$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8.48
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8.34
8.33
8.33
8.29
8.29
8.10
8.08
8.08
8.07
8.06
8.05
8.04
7.28
COOH
N
N
Br
3ea, 1H NMR
400 MHz, CDCl3
1.00
1.00
1.01
1.03
1.01
1.01
3.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
165.8
140.2
140.0
138.6
134.1
132.8
132.6
132.4
131.6
131.2
131.0
130.9
130.8
130.0
127.7
127.2
125.6
COOH
N
N
Br
3ea, 13C{1H} NMR
100 MHz, CDCl3
170
160
150
140
130
120
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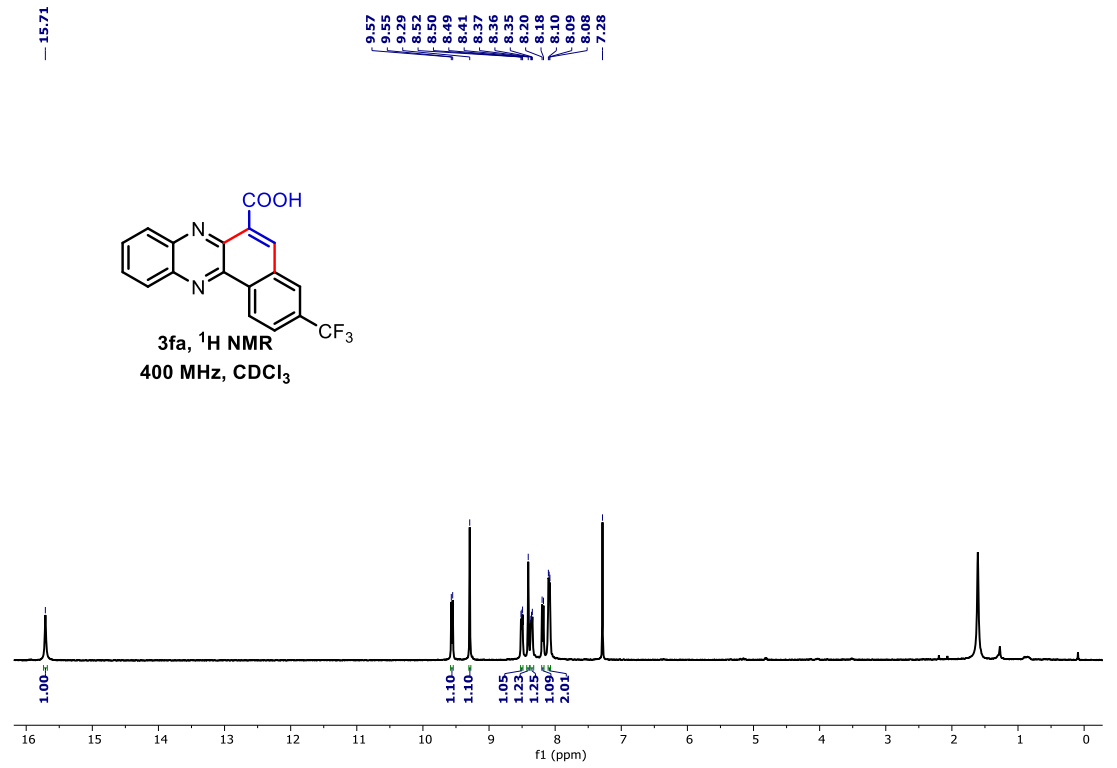
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.35
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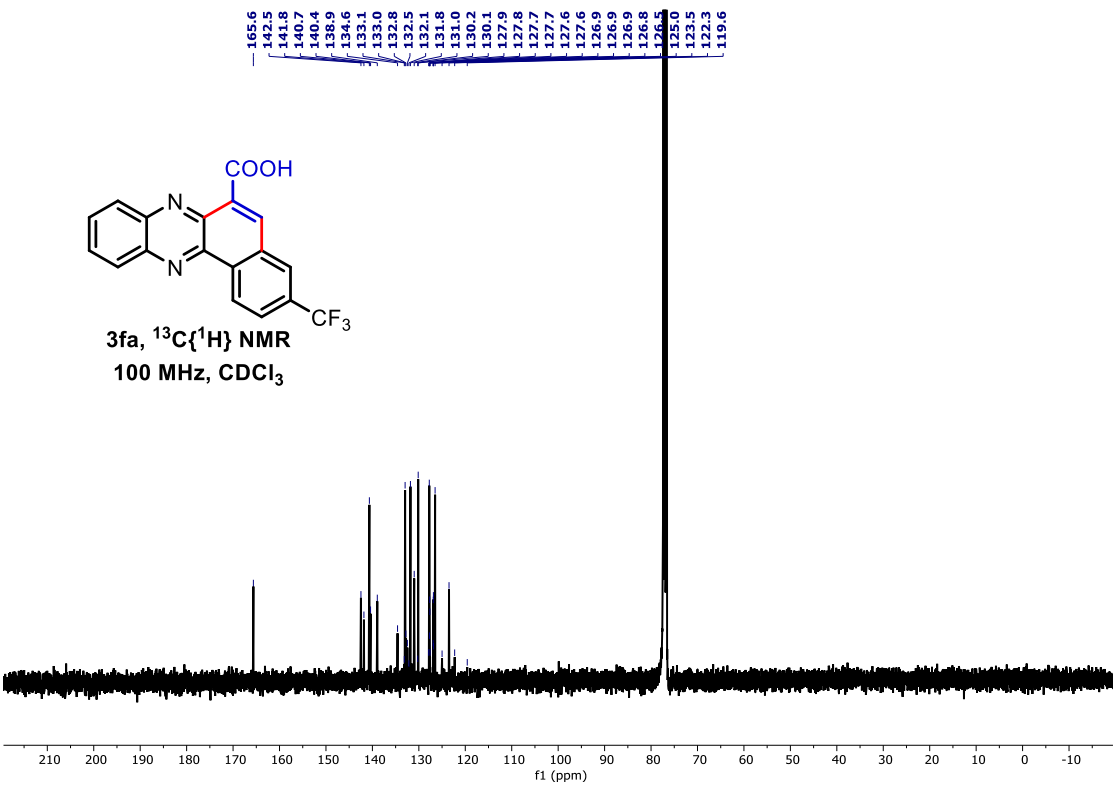
8.18
8.10
8.09
8.08
7.28
COOH
N
N
CF3
3fa, 1H NMR
400 MHz, CDCl3
1.00
1.10
1.10
1.05
1.23
1.25
1.09
2.01
f1 (ppm)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132.8
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131.8
131.0
130.2
130.1
127.9
127.8
127.7
127.7
127.6
127.6
126.9
126.9
126.9
126.8
126.5
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COOH
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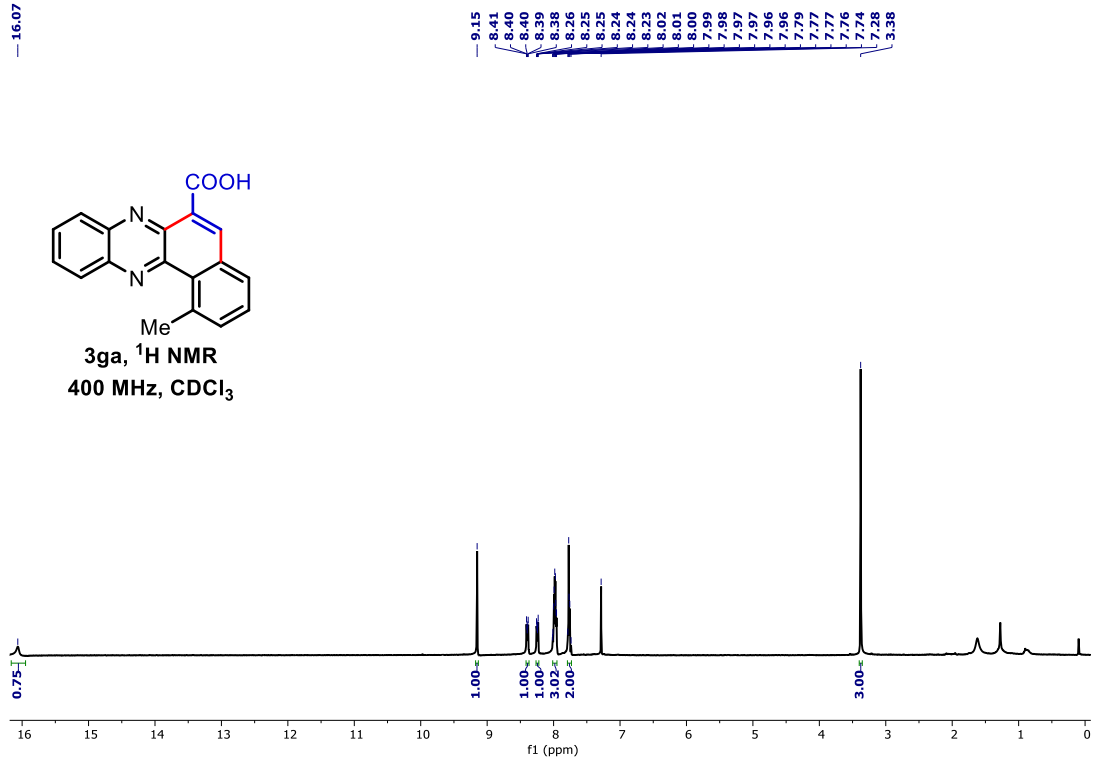
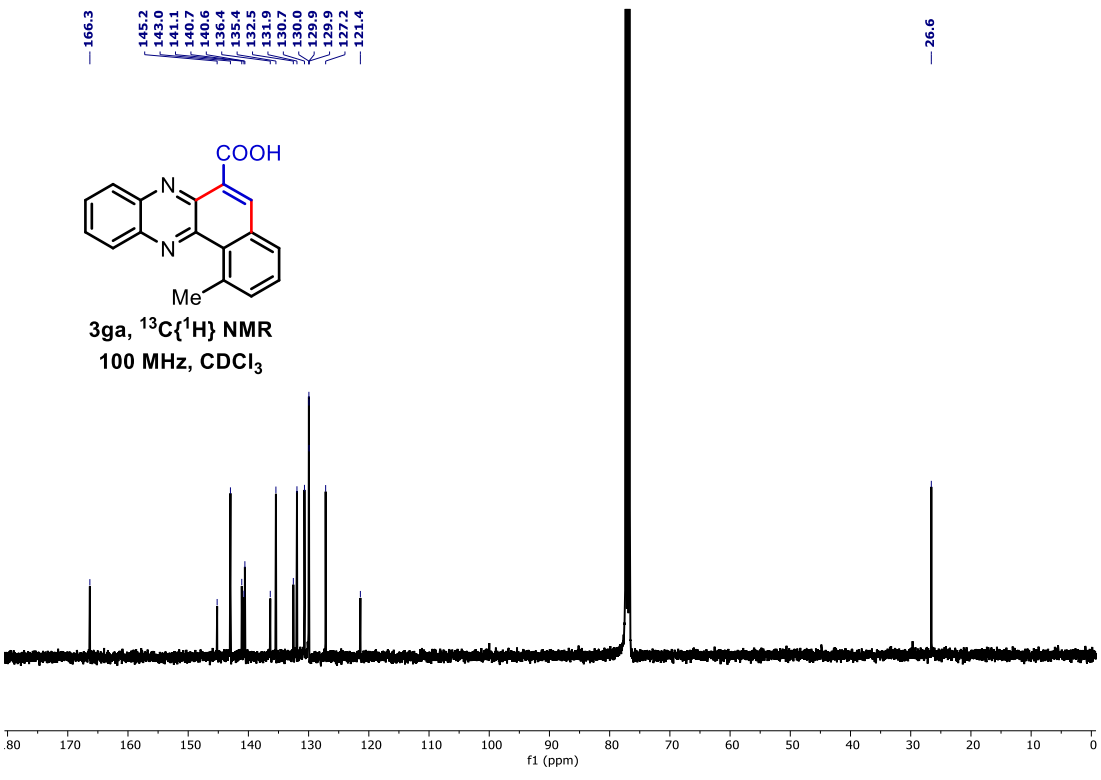
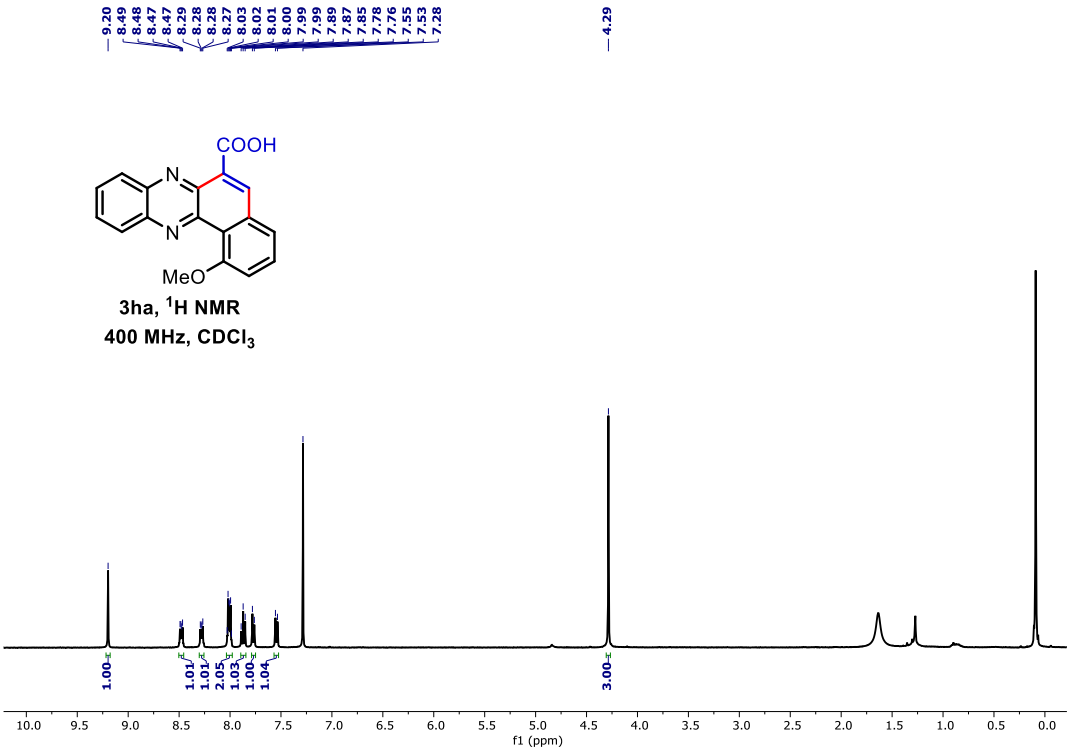
CF3
3fa, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)



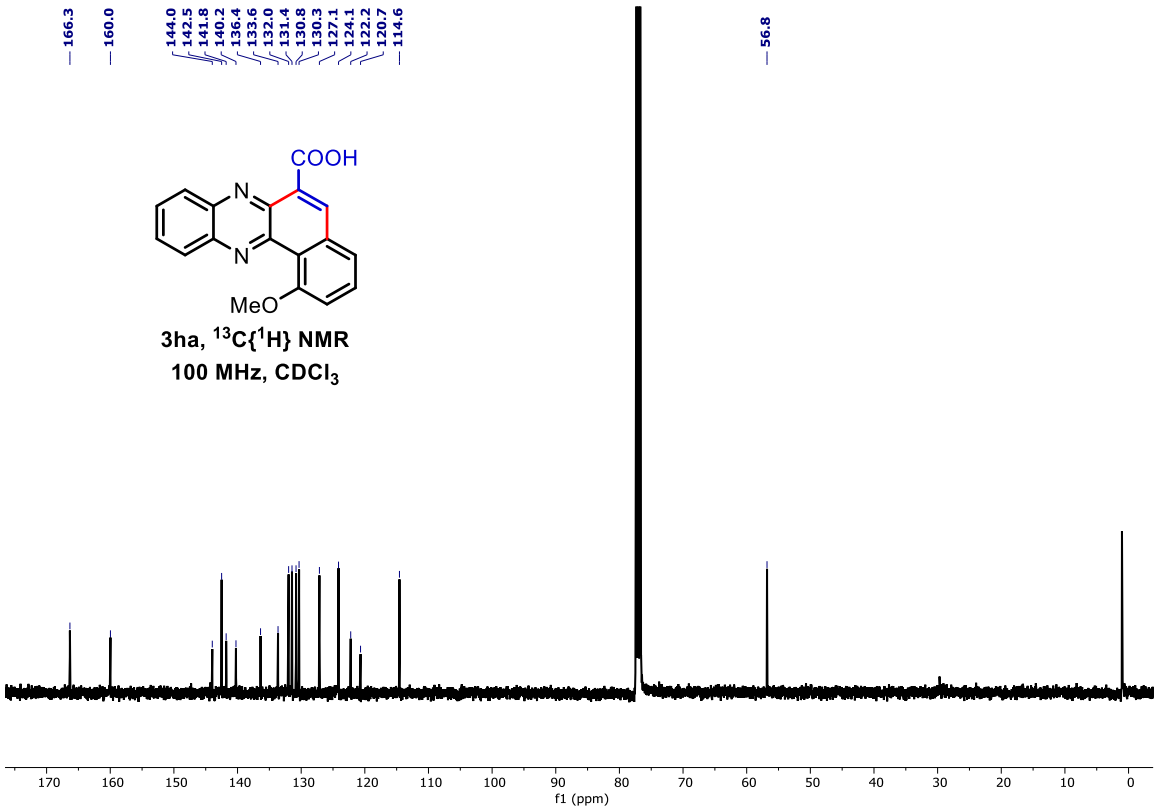
3ga, ^{1}H NMR
400 MHz, $CDCl_3$



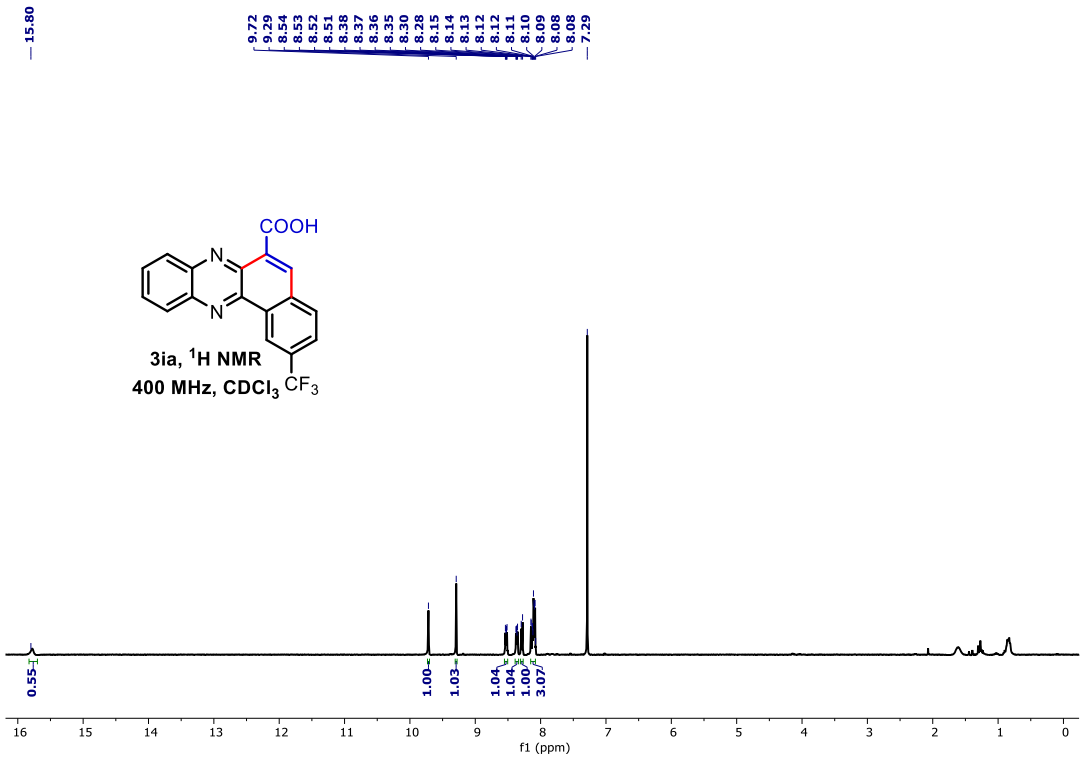
3ga, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



3ha, ^{1}H NMR
400 MHz, $CDCl_3$



3ha, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$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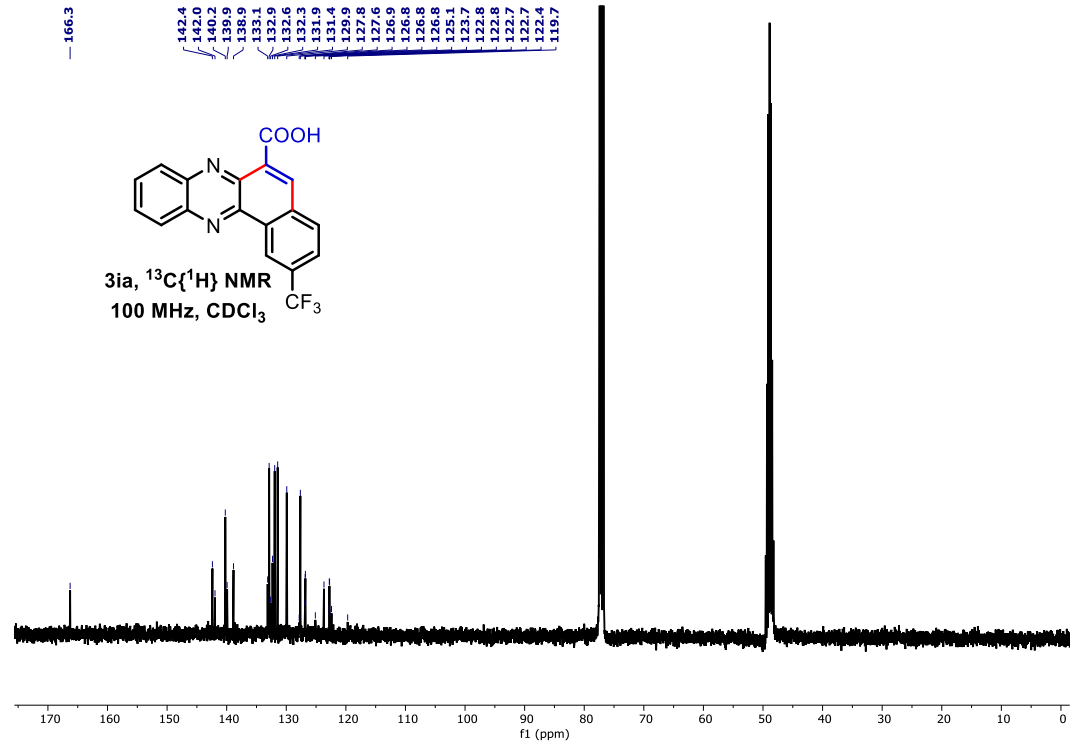
8.30
8.28
8.15
8.14
8.13
8.12
8.12
8.11
8.10
8.09
8.08
8.08
7.29
COOH
N
N
CF3
3ia, 1H NMR
400 MHz, CDCl3
0.55
1.00
1.03
1.04
1.04
1.00
3.07
f1 (ppm)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138.9
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132.9
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132.3
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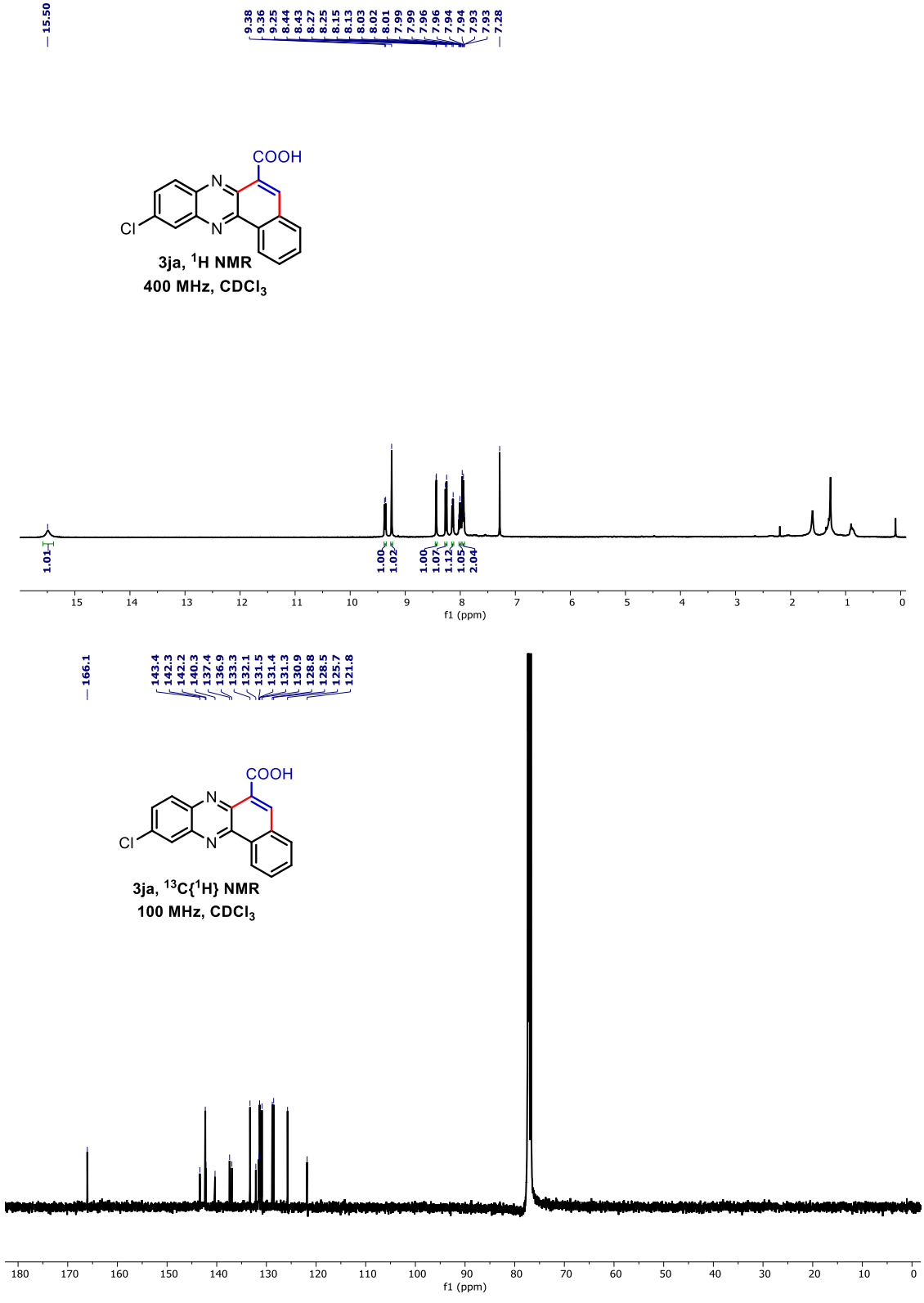
129.9
127.8
127.6
126.9
126.8
126.8
126.8
125.1
123.7
122.8
122.8
122.7
122.7
122.4
119.7
COOH
N
N
CF3
3ia, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)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8.25
8.15
8.13
8.03
8.02
8.01
7.99
7.99
7.96
7.96
7.94
7.94
7.93
7.93
7.28
COOH
N
N
Cl
3ja, 1H NMR
400 MHz, CDCl3
1.01
1.00
1.02
1.00
1.07
1.12
1.05
2.04
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
166.1
143.4
142.3
142.2
140.3
137.4
136.9
133.3
132.1
131.5
131.4
131.3
130.9
128.8
128.5
125.7
121.8
COOH
N
N
Cl
3ja, 13C{1H} NMR
100 MHz, CDCl3
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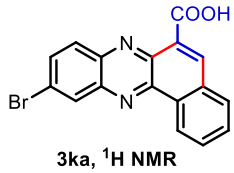
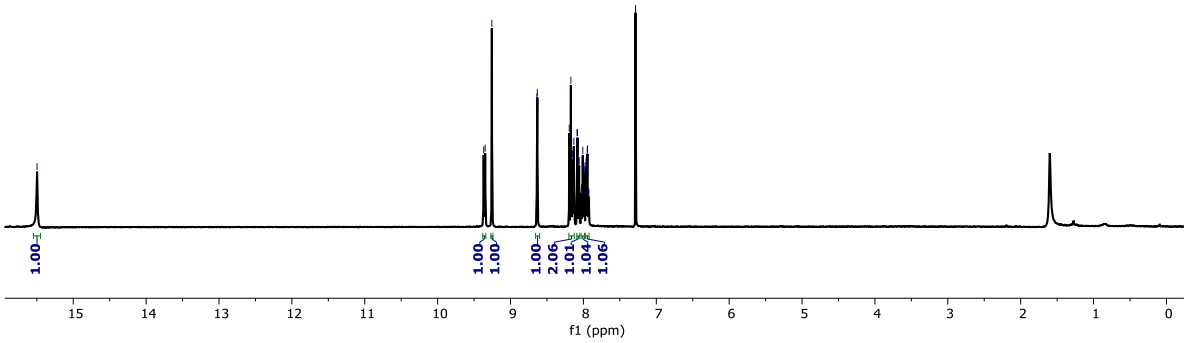
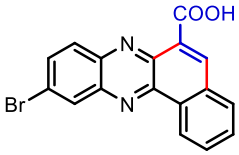
f1 (ppm)

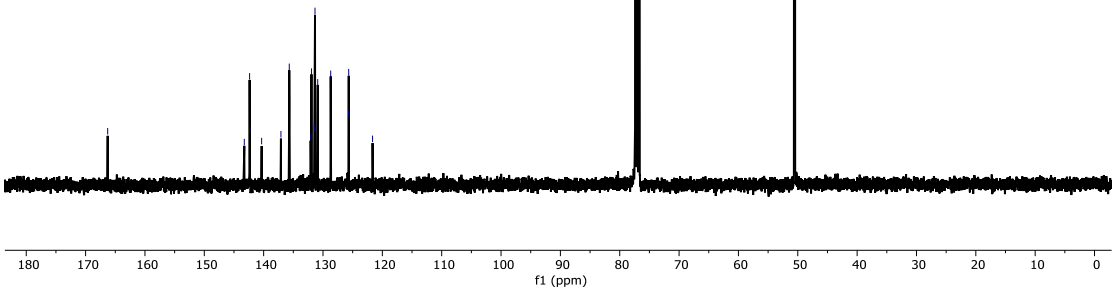


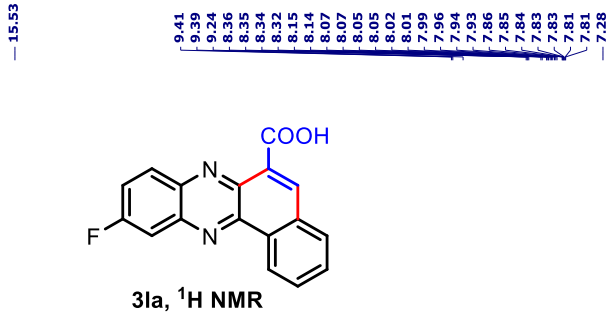
3ka, ^{1}H NMR
400 MHz, $CDCl_3$





3ka, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$





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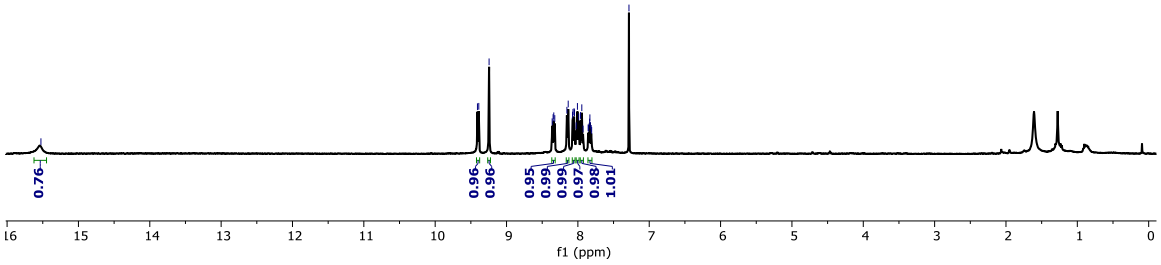
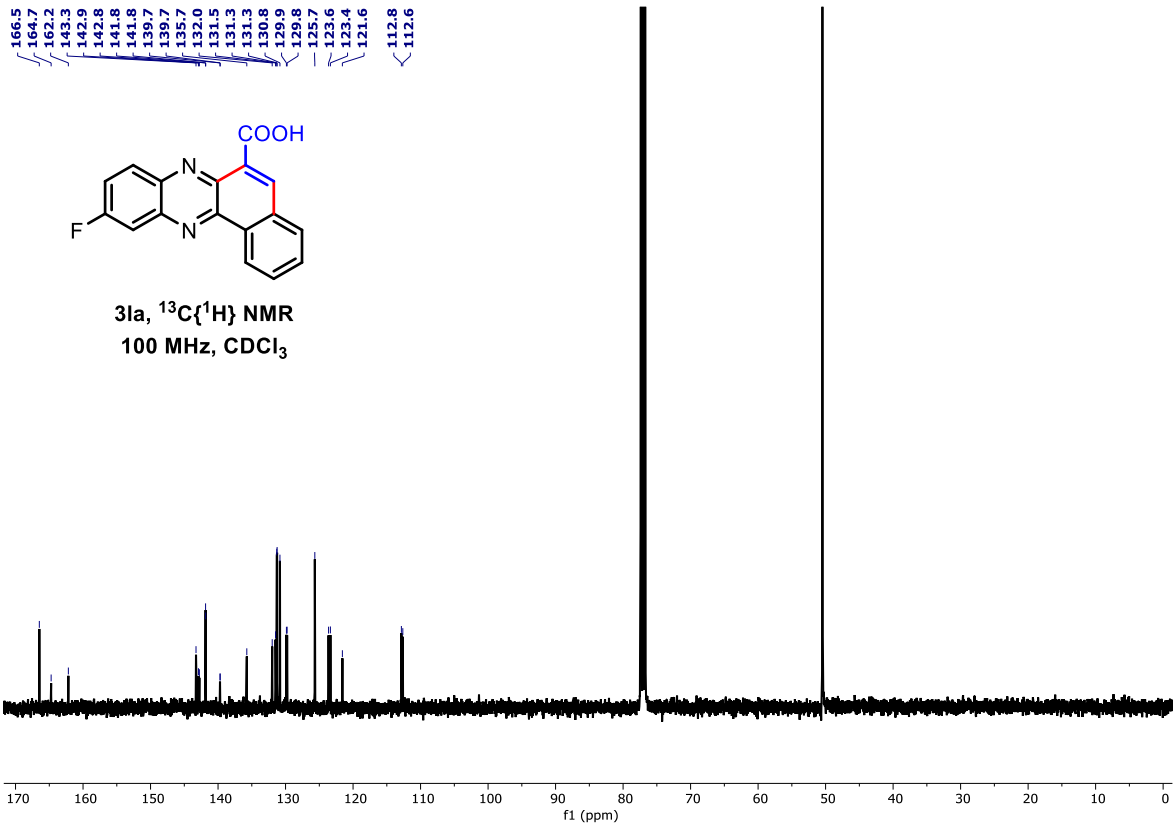
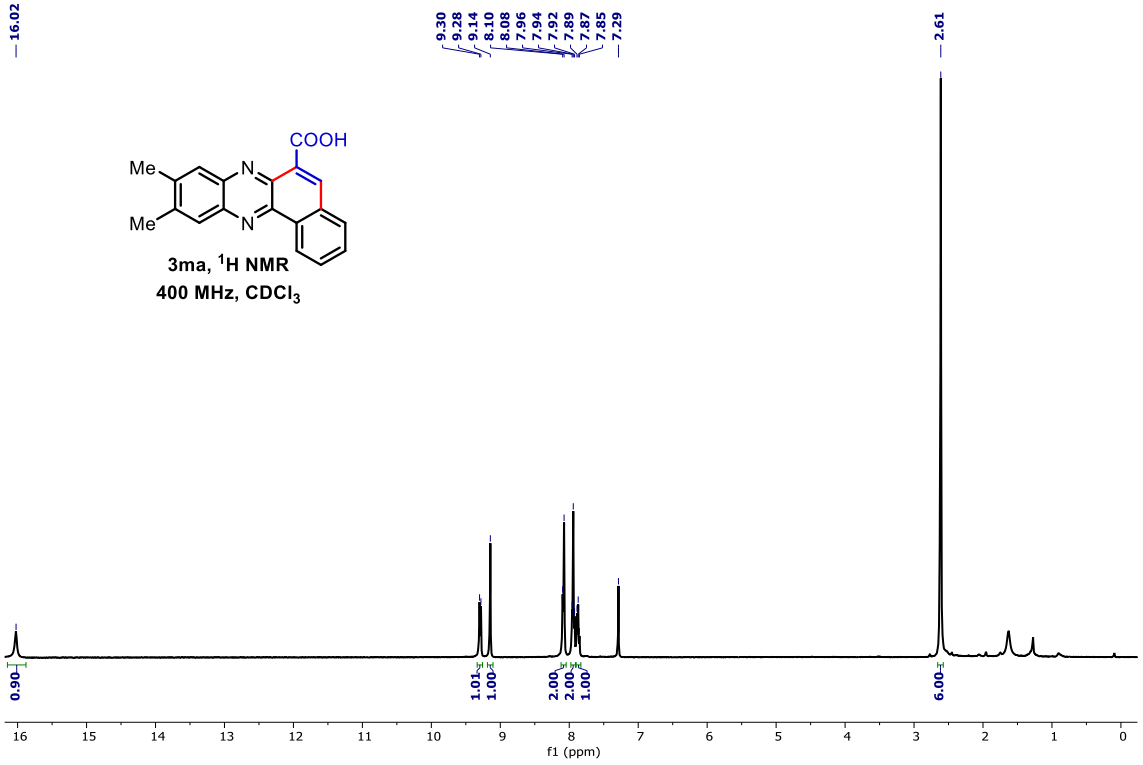
400 MHz, $CDCl_3$

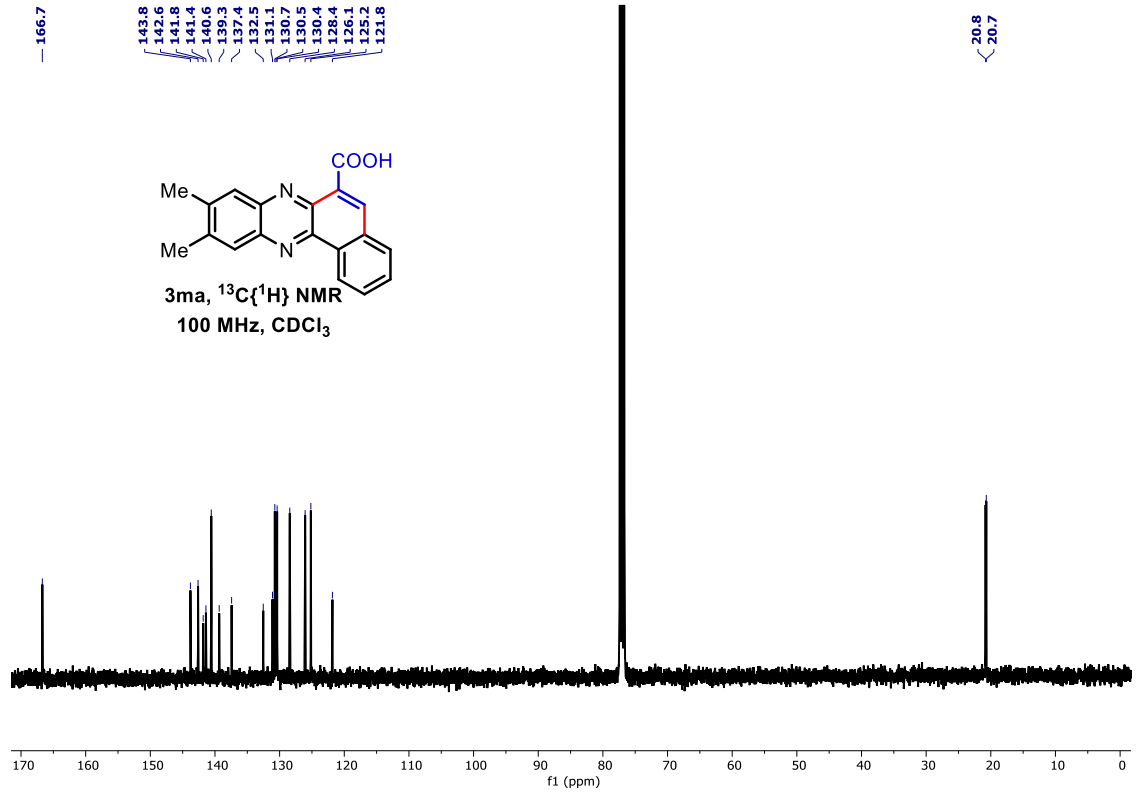




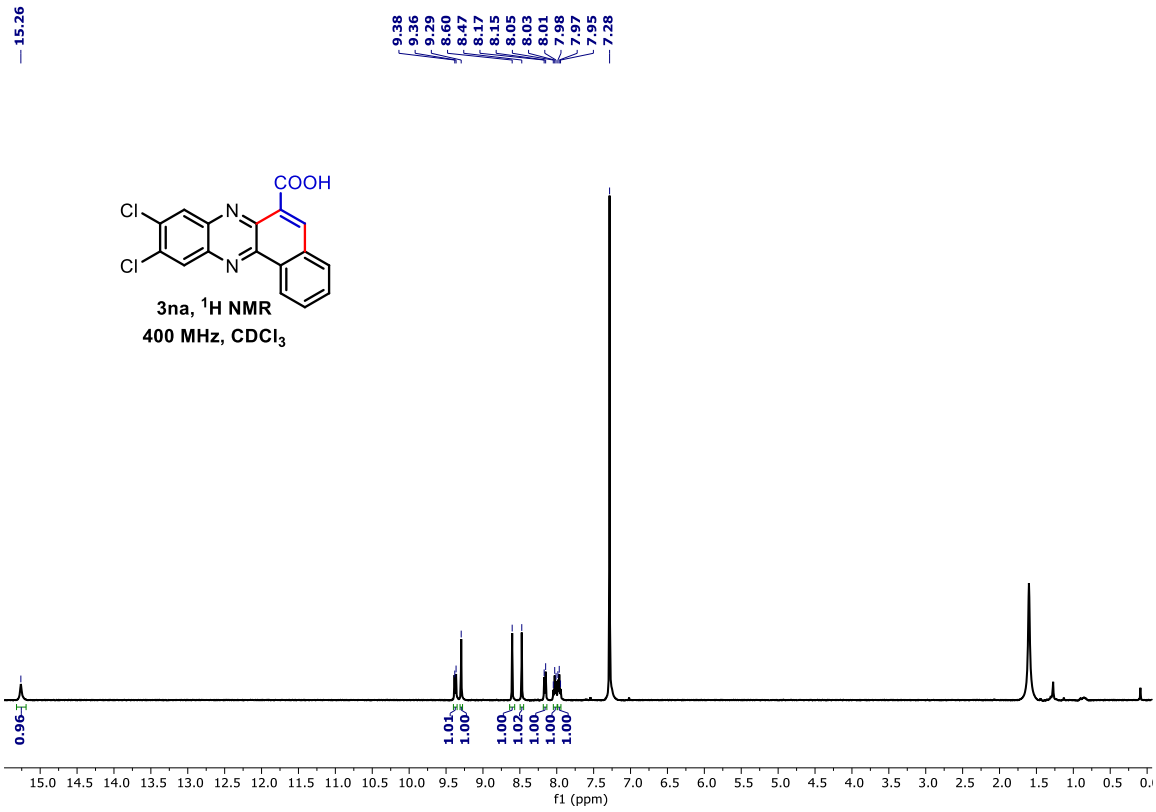
3la, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



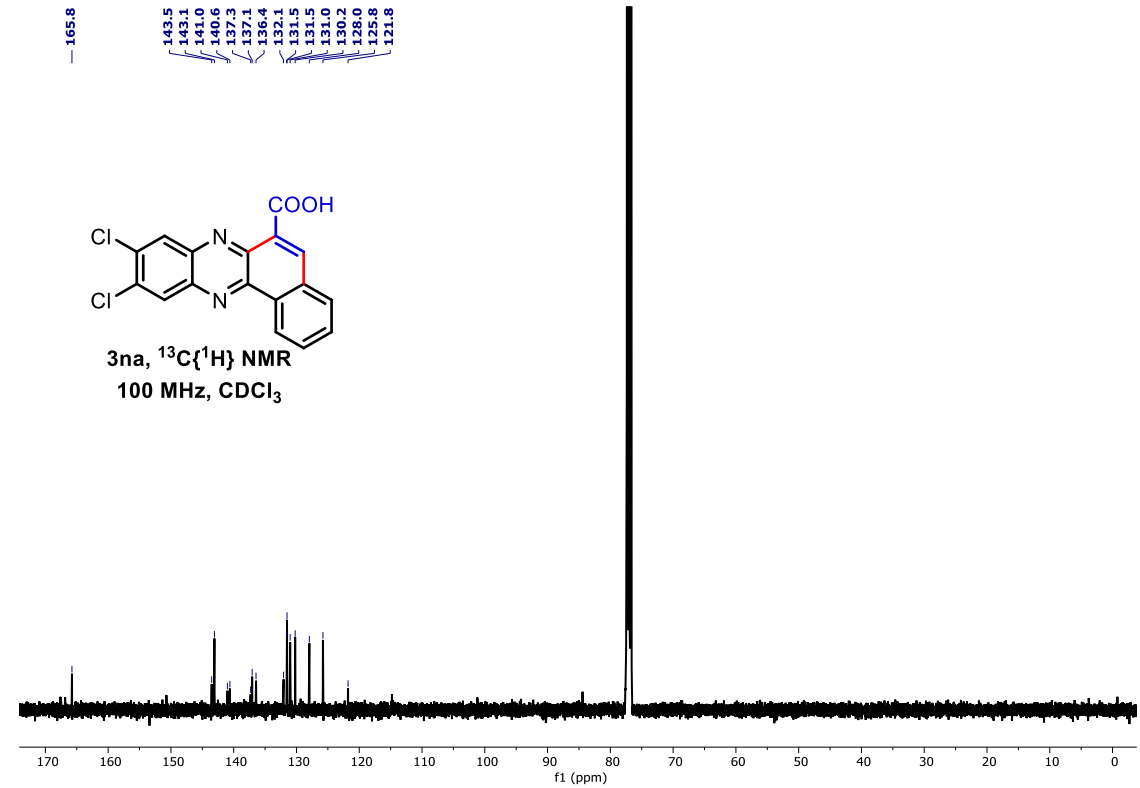
3ma, ^{1}H NMR
400 MHz, $CDCl_3$



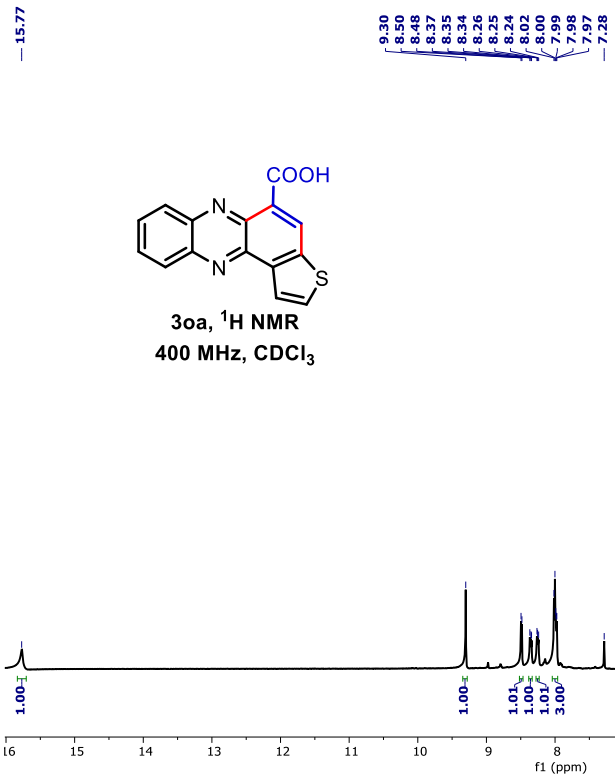
3ma, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



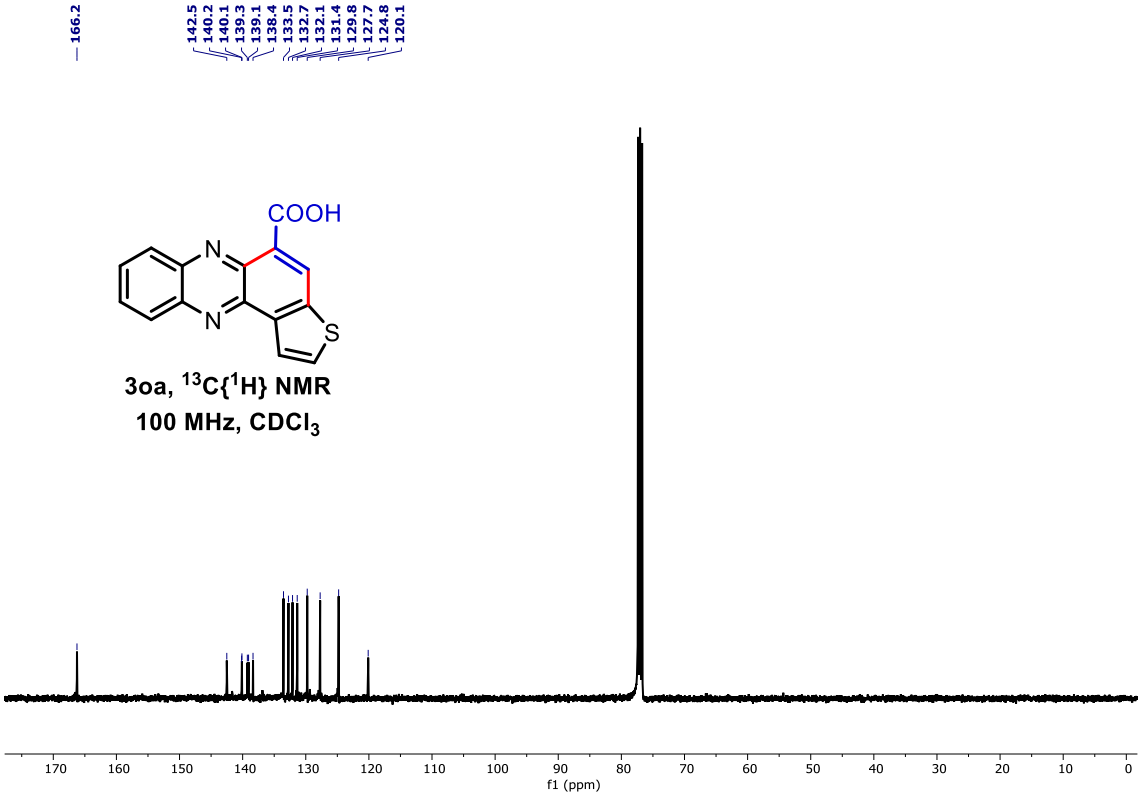
3na, ^{1}H NMR
400 MHz, $CDCl_3$



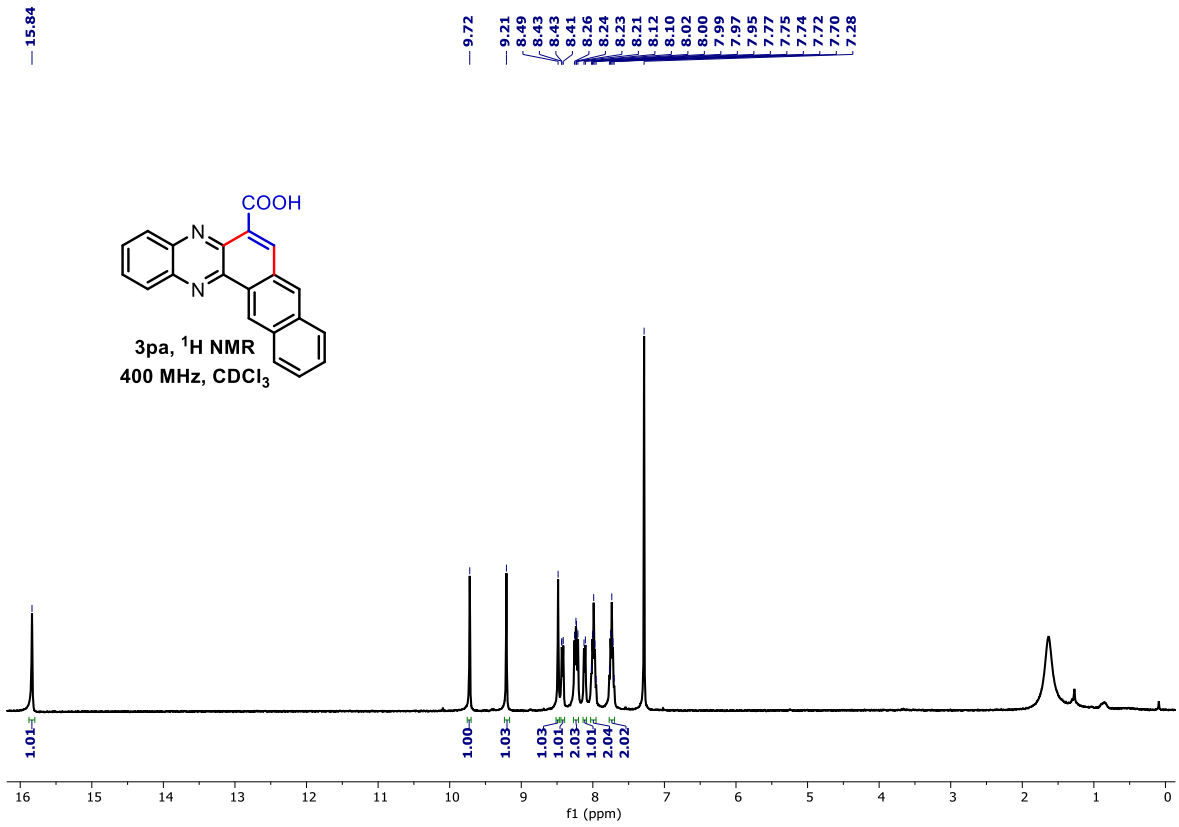
3na, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



3oa, ^{1}H NMR
400 MHz, $CDCl_3$



3oa, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$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8.23
8.21
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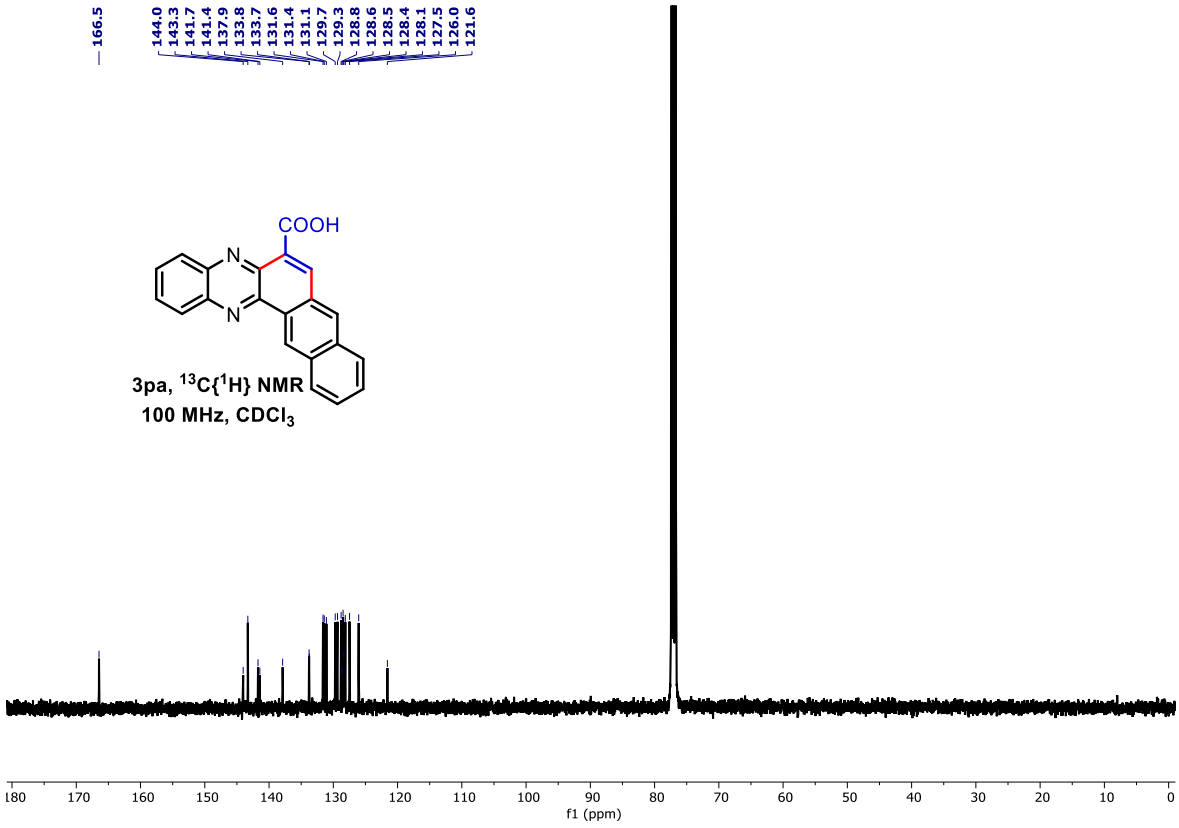
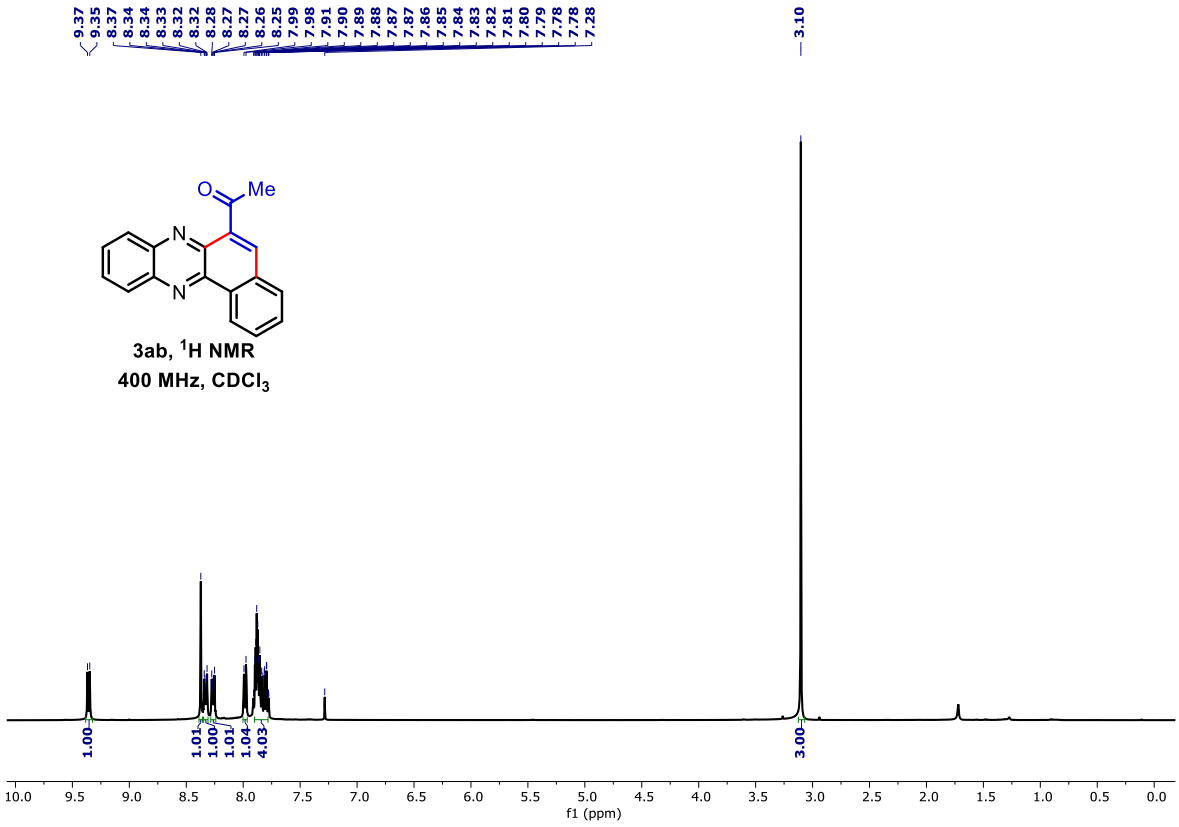
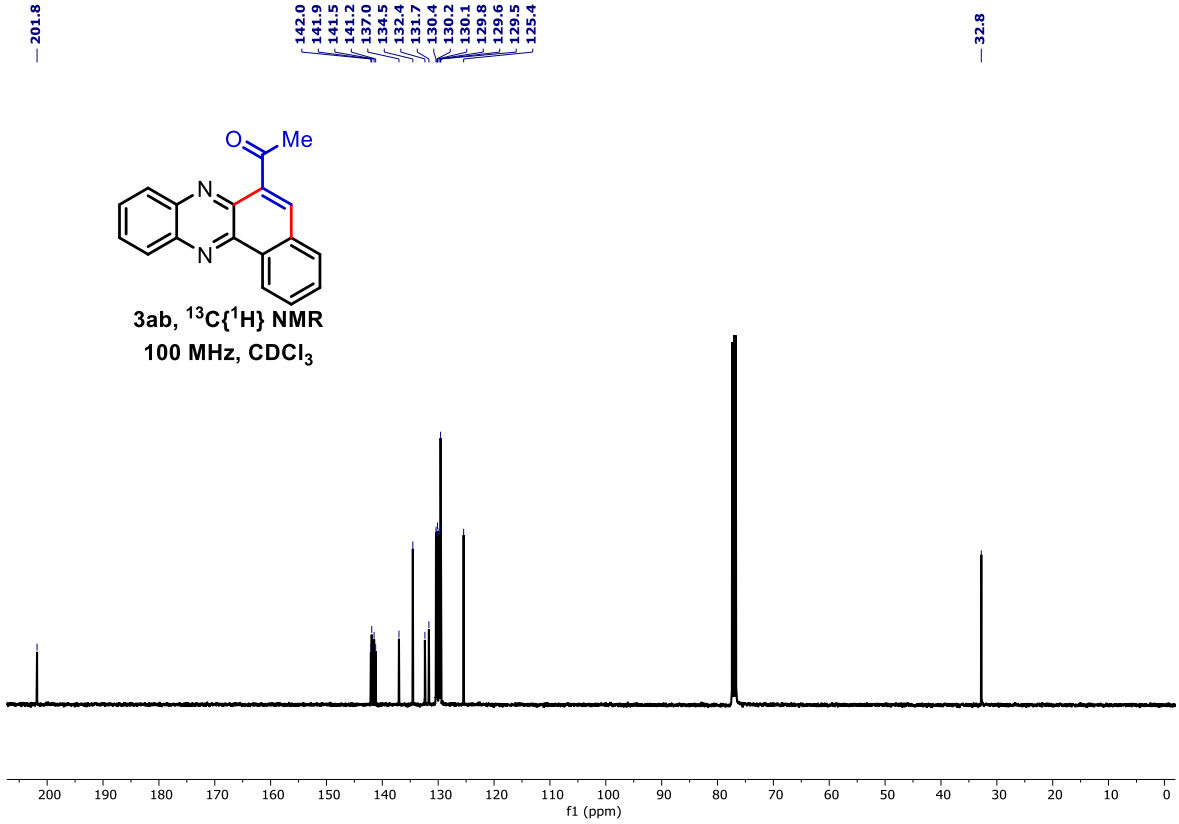
8.10
8.02
8.00
7.99
7.97
7.95
7.77
7.75
7.74
7.72
7.70
7.28
COOH
N
N
3pa, 1H NMR
400 MHz, CDCl3
1.01
1.00
1.03
1.03
1.01
2.03
1.01
2.04
2.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

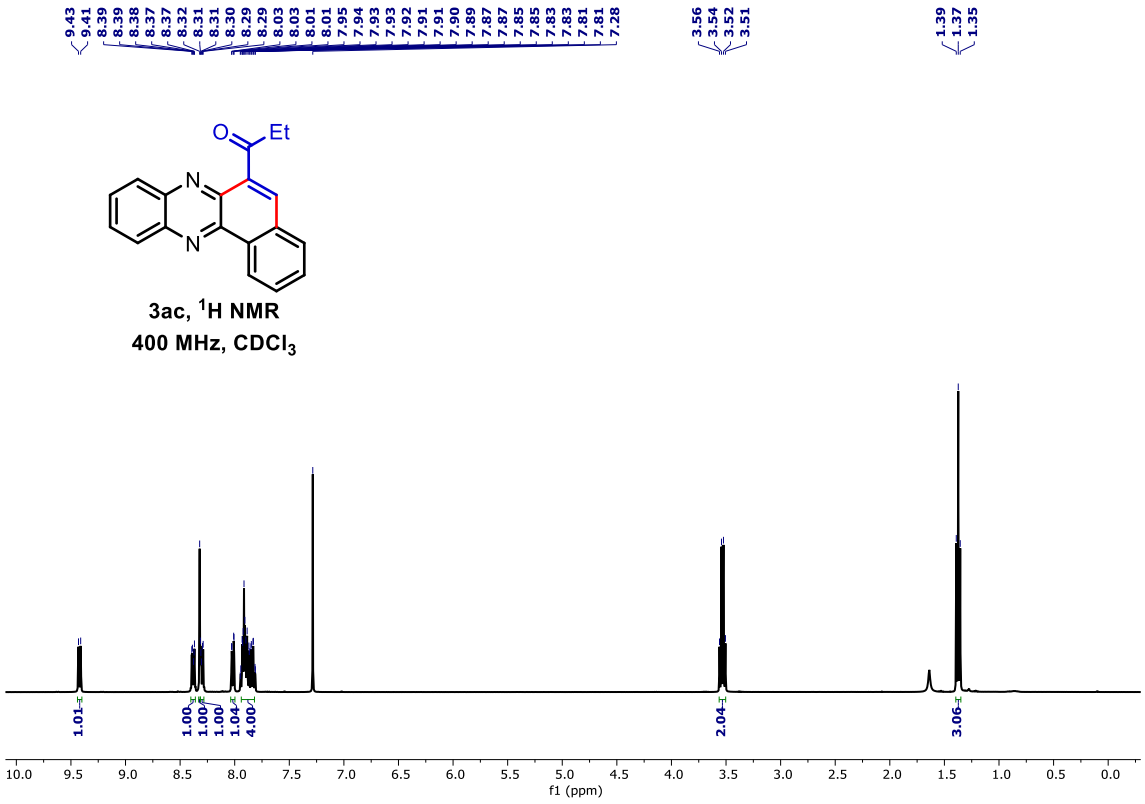

166.5
144.0
143.3
141.7
141.4
137.9
133.8
133.7
131.6
131.4
131.1
129.7
129.3
128.8
128.6
128.5
128.4
128.1
127.5
126.0
121.6
COOH
N
N
3pa, 13C{1H} NMR
100 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

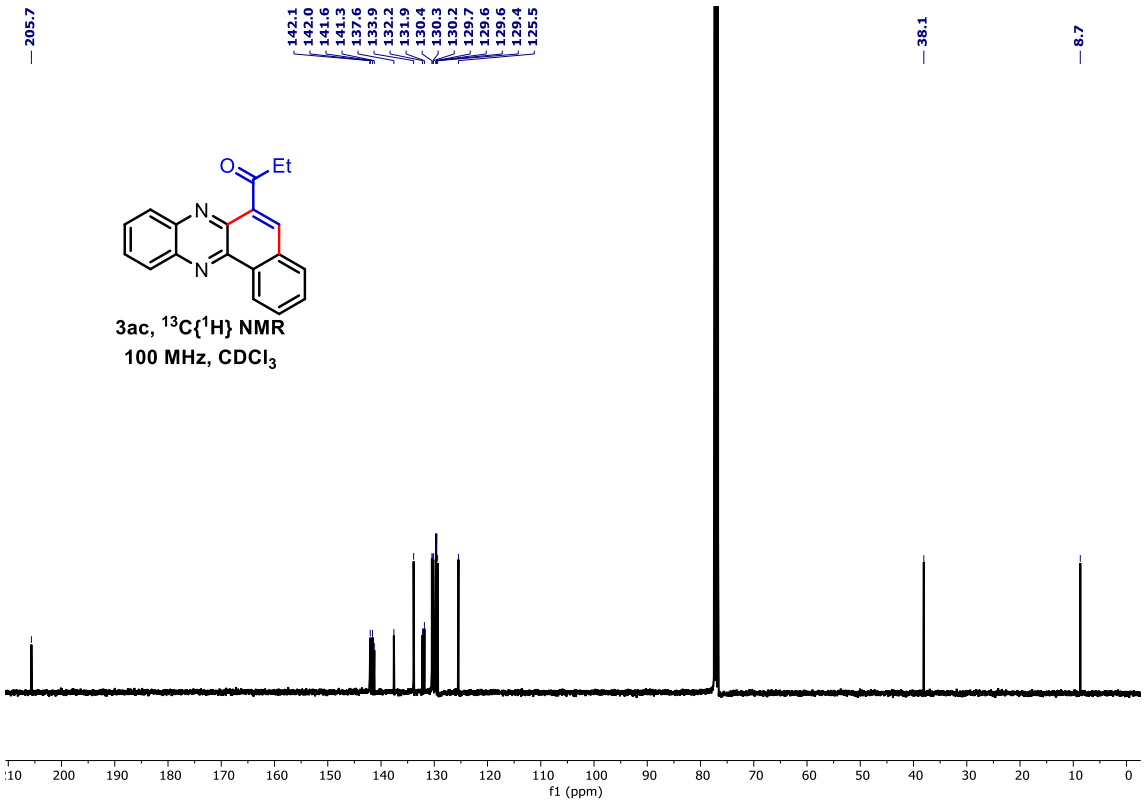


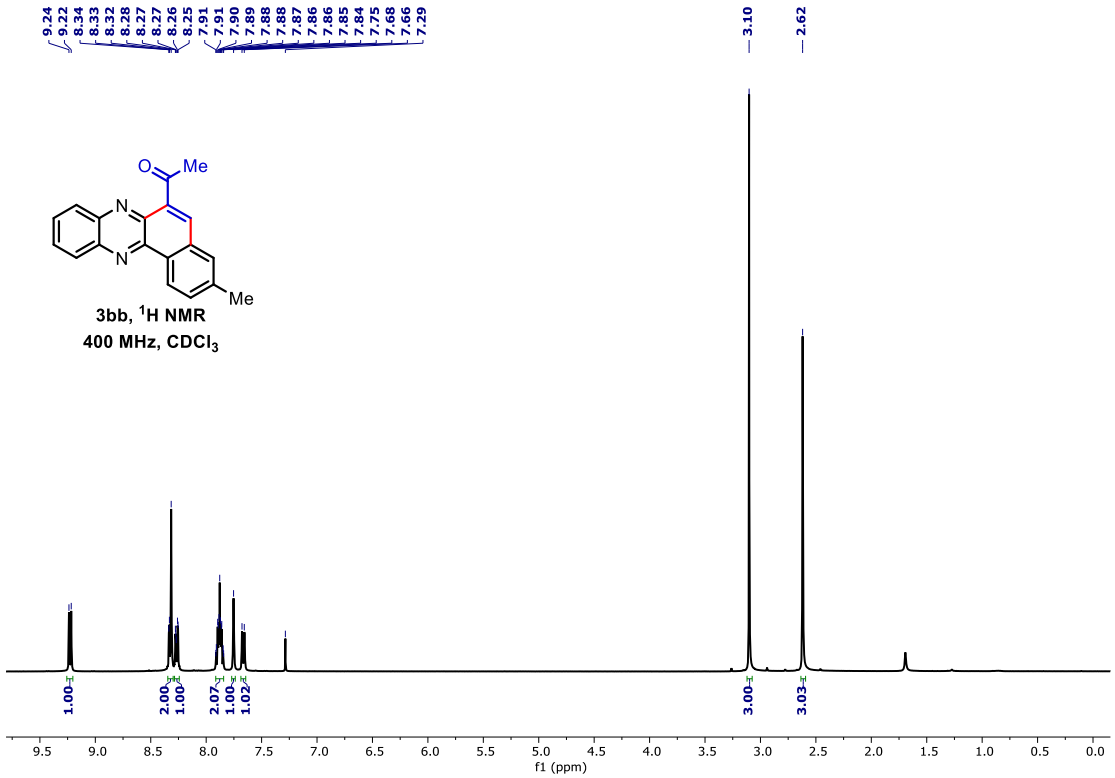
3ab, ^{1}H NMR
400 MHz, $CDCl_3$



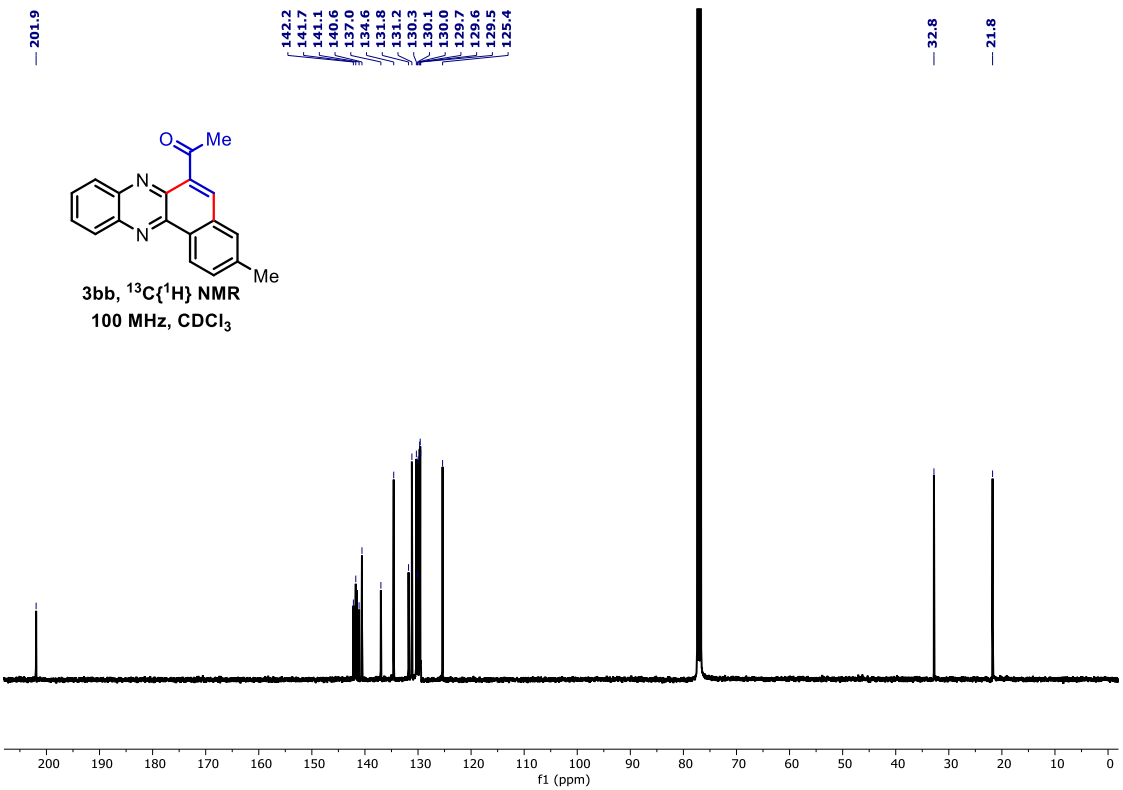
3ab, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$


9.43
9.41
8.39
8.39
8.38
8.37
8.37
8.32
8.31
8.31
8.30
8.29
8.29
8.03
8.03
8.01
8.01
7.95
7.94
7.93
7.93
7.92
7.91
7.91
7.90
7.89
7.87
7.87
7.85
7.85
7.83
7.83
7.81
7.81
7.28
3.56
3.54
3.52
3.51
1.39
1.37
1.35
O
Et
N
N
3ac, ^{1}H NMR
400 MHz, CDCl$_3$
1.01
1.00
1.00
1.00
1.04
4.00
2.04
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

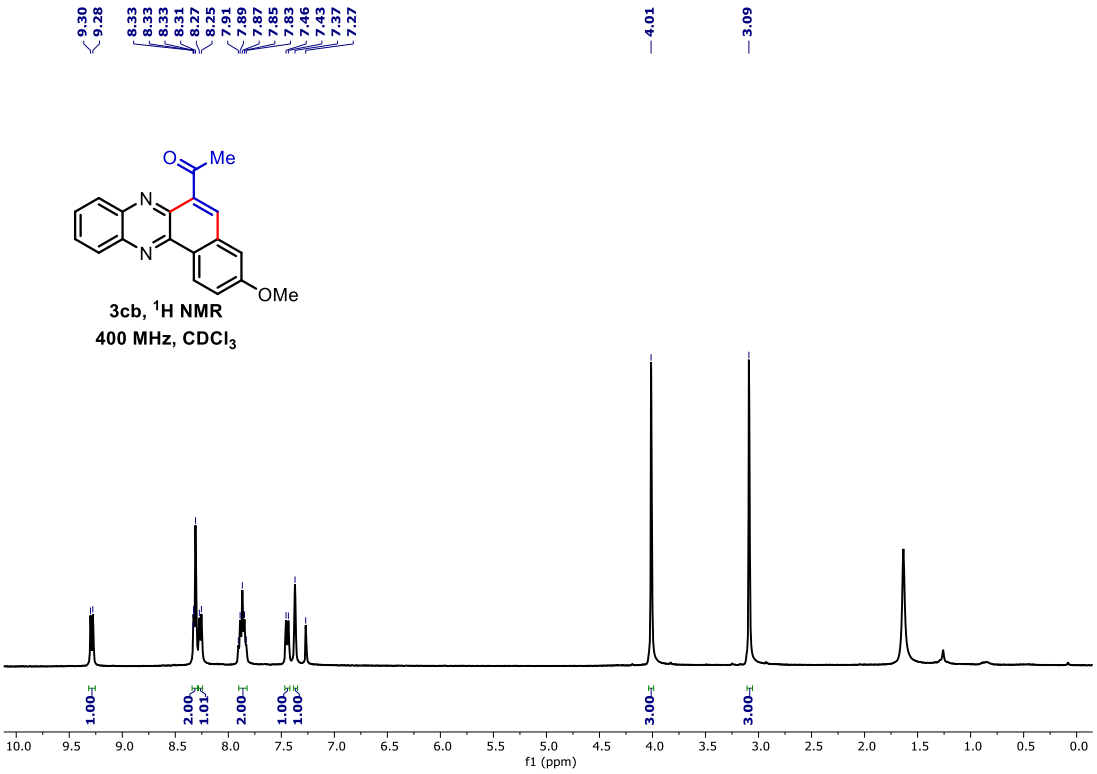

205.7
142.1
142.0
141.6
141.3
137.6
133.9
132.2
131.9
130.4
130.3
130.2
129.7
129.6
129.6
129.4
125.5
38.1
8.7
O
Et
N
N
3ac, ^{13}C{^{1}H} NMR
100 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



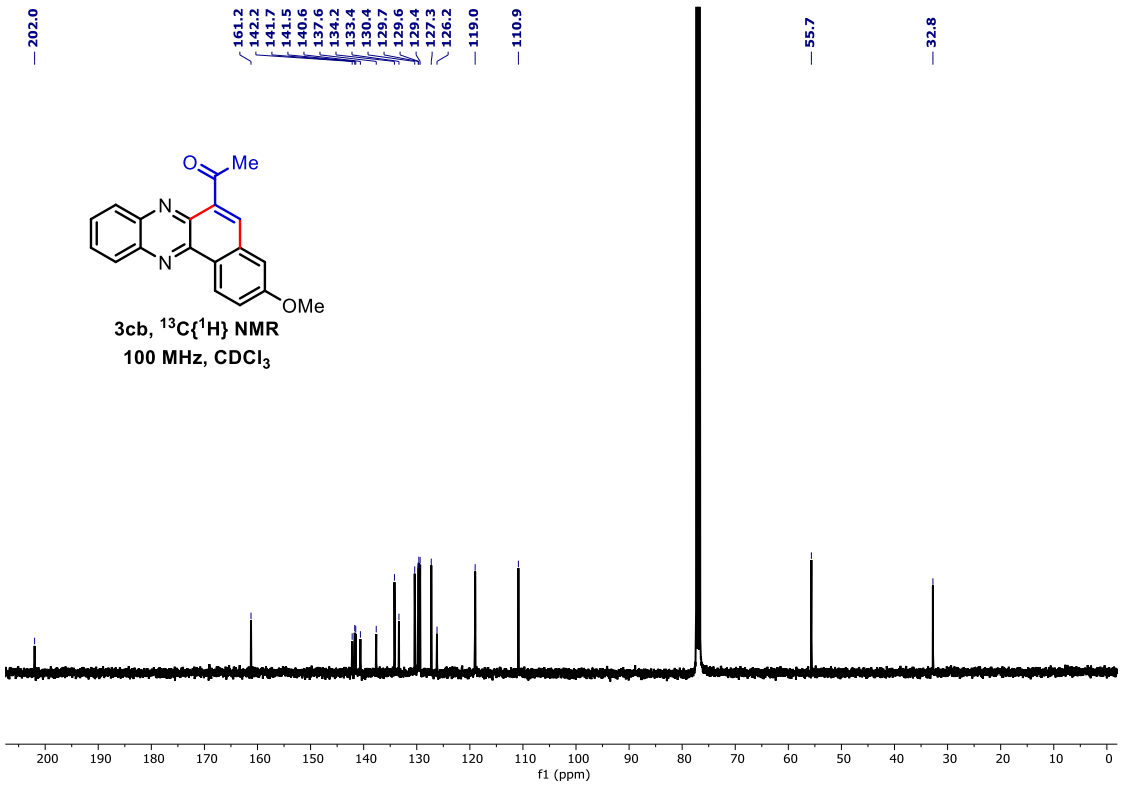
3bb, ^{1}H NMR
400 MHz, $CDCl_3$



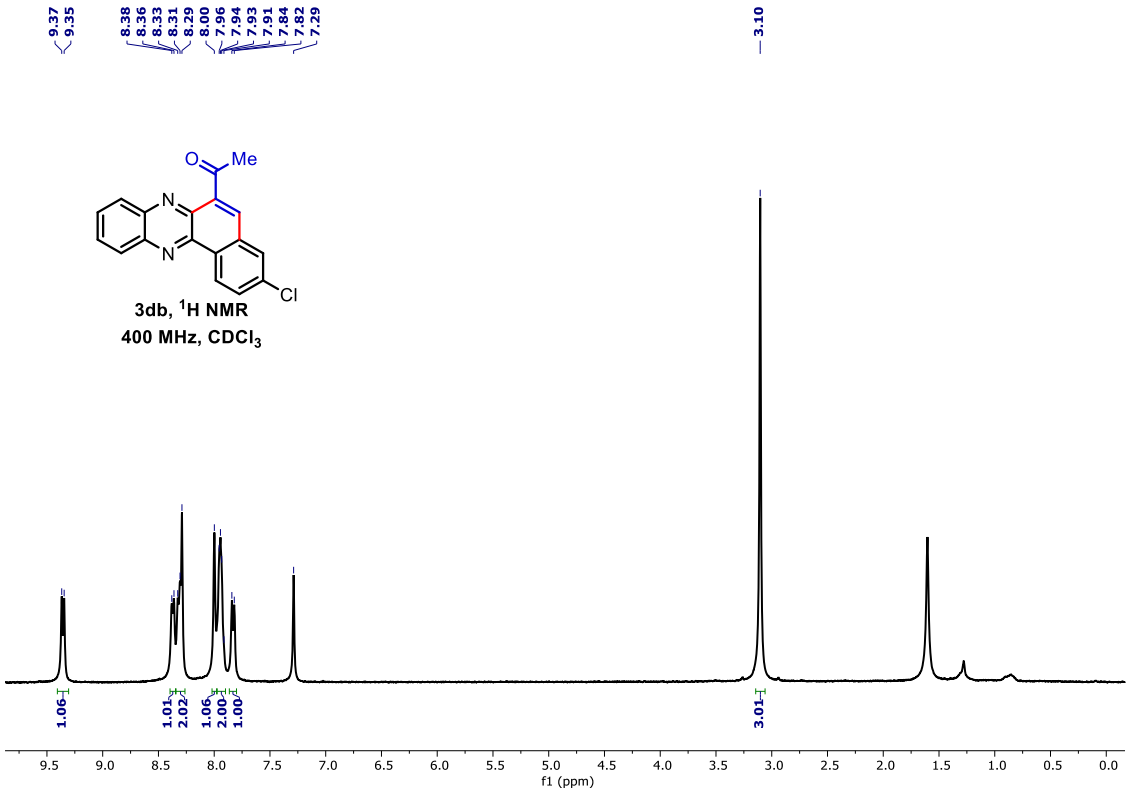
3bb, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



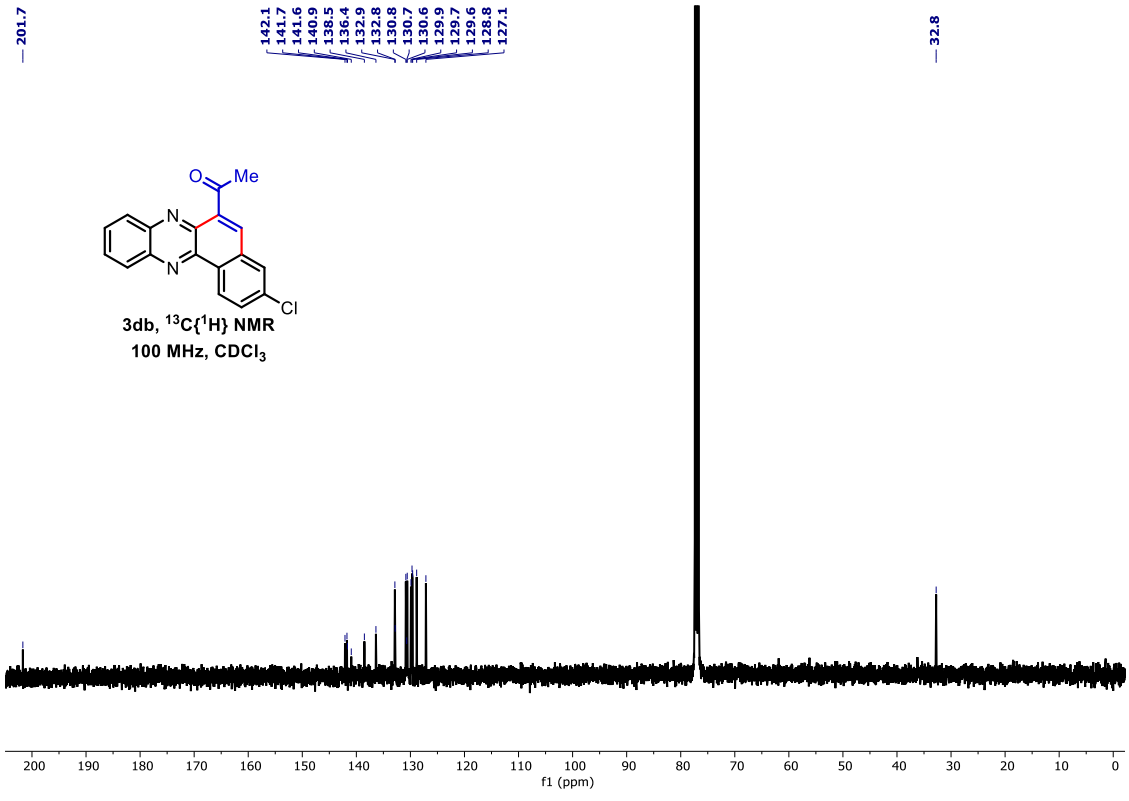
3cb, ^{1}H NMR
400 MHz, $CDCl_3$



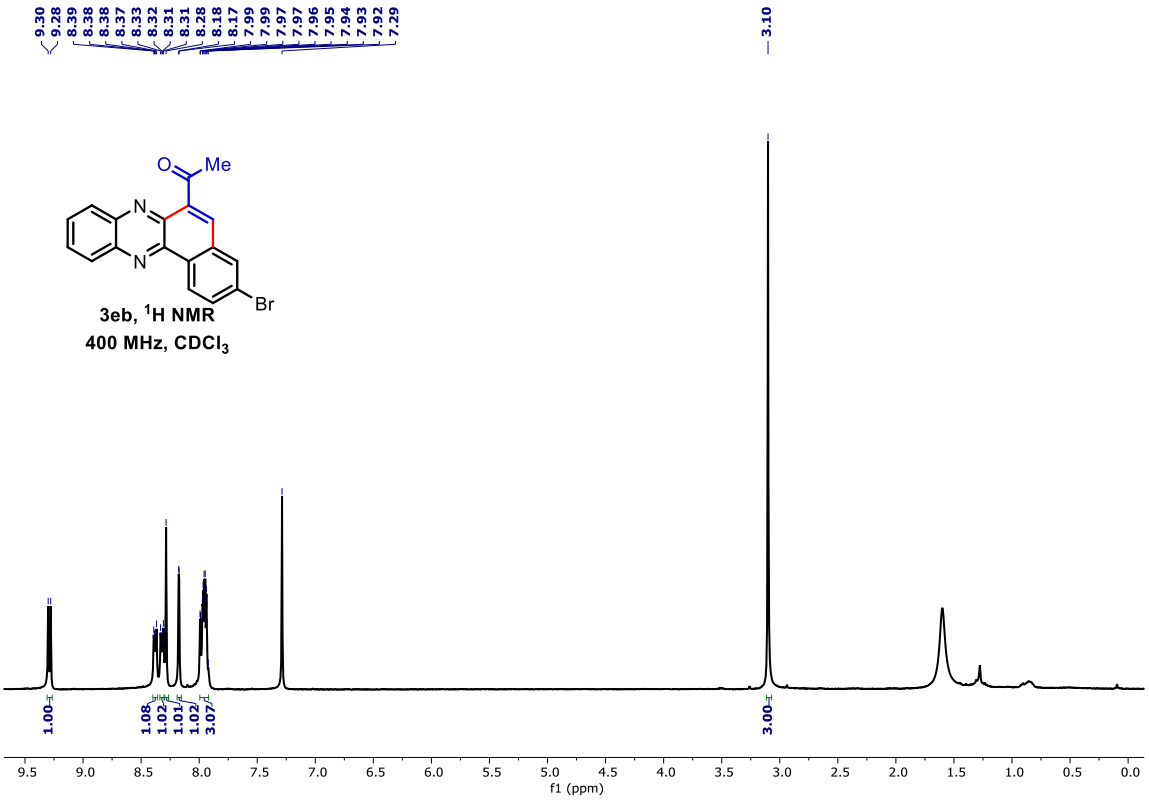
3cb, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

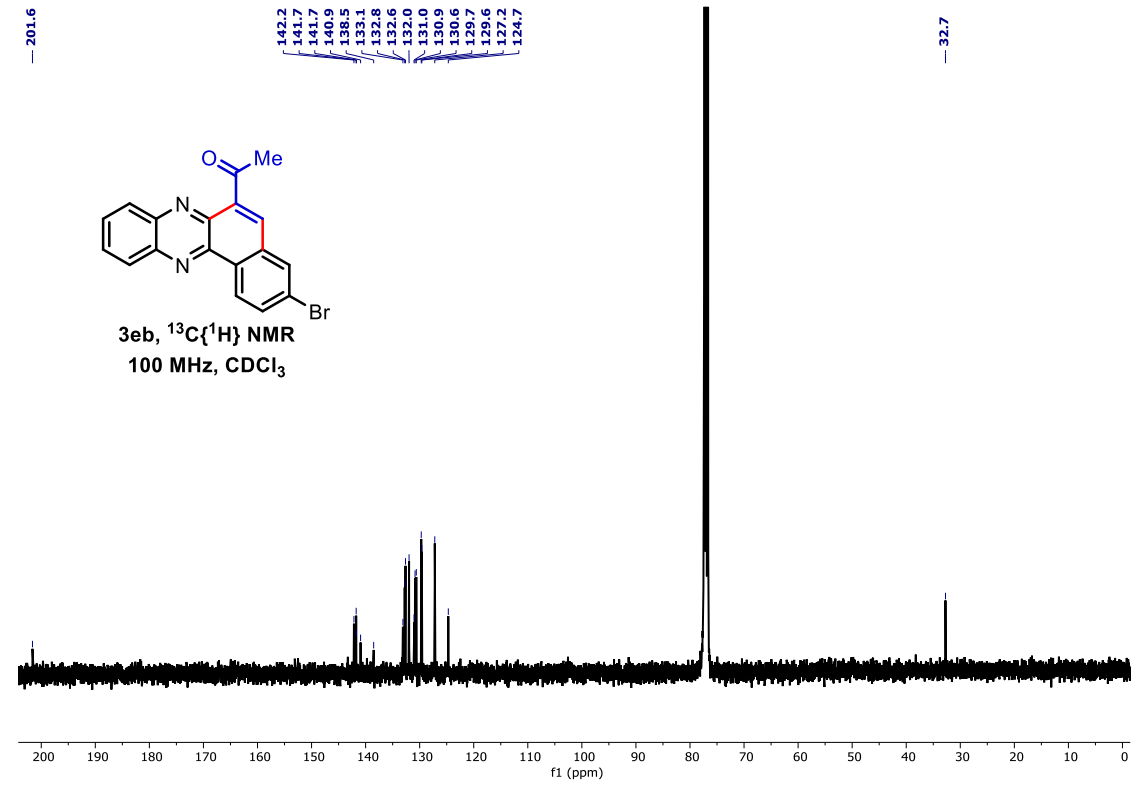


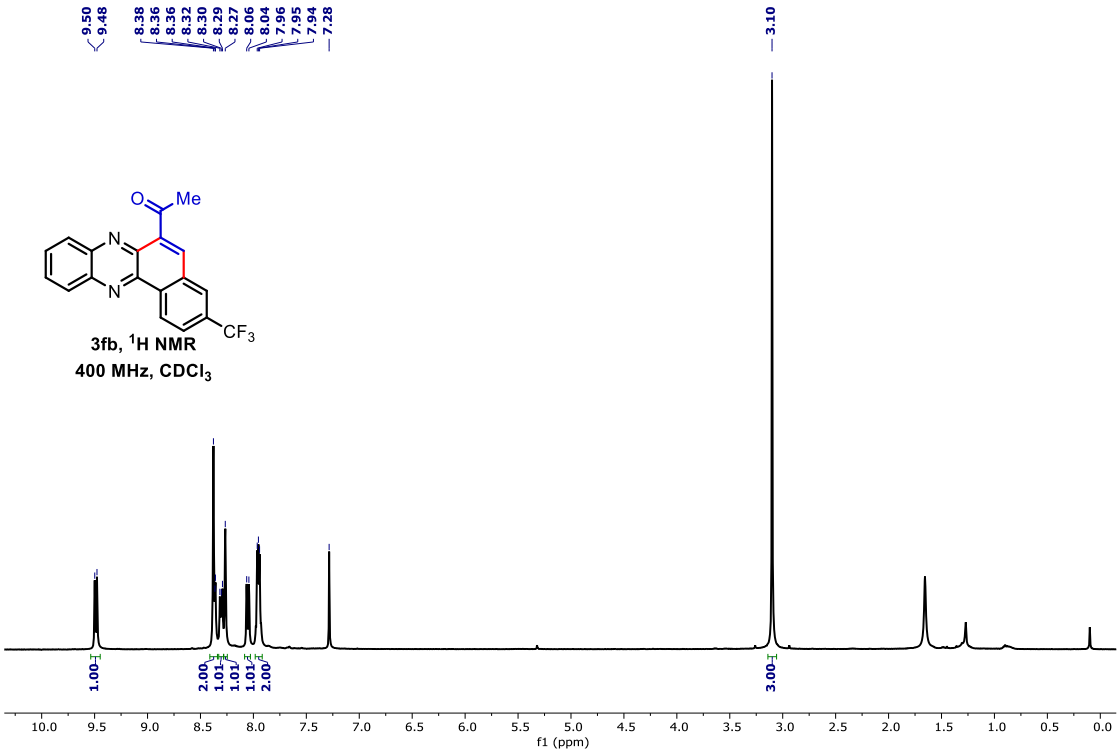
3db, ^{1}H NMR
400 MHz, $CDCl_3$

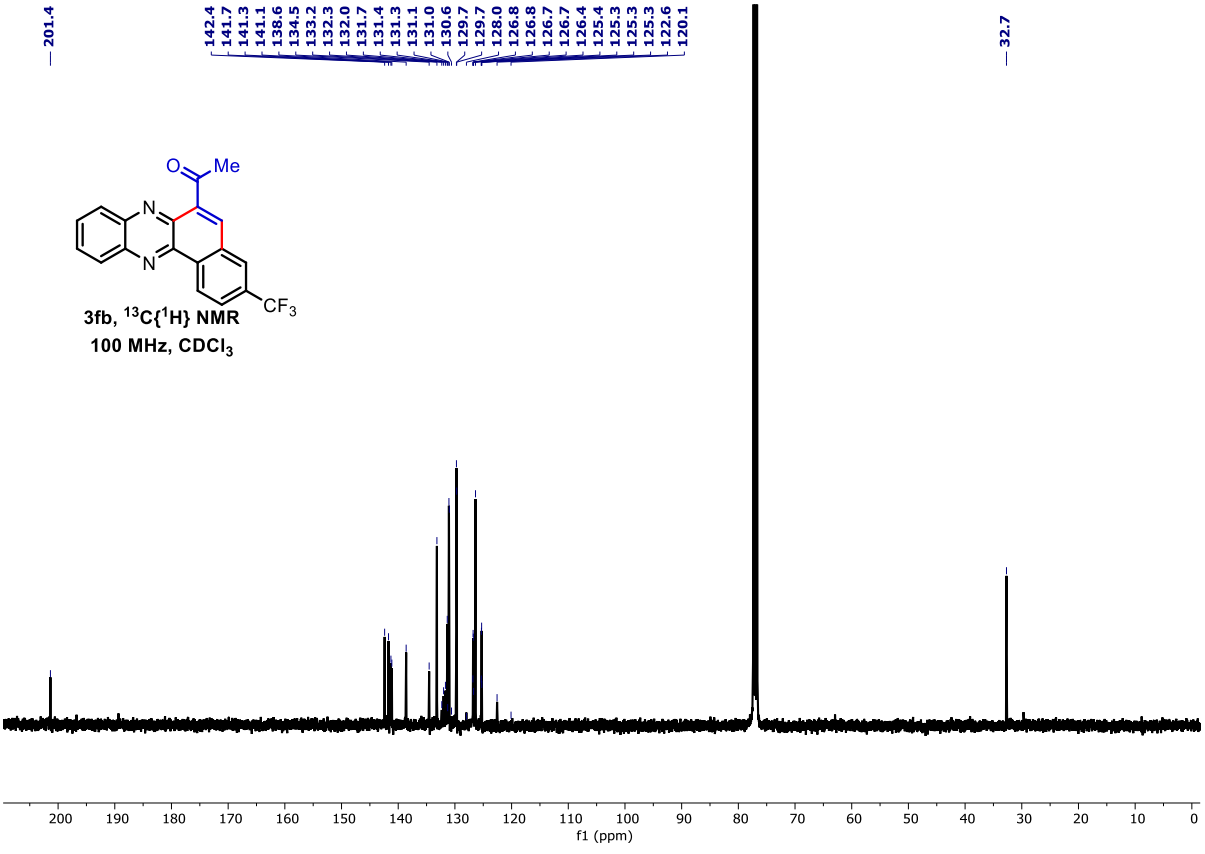


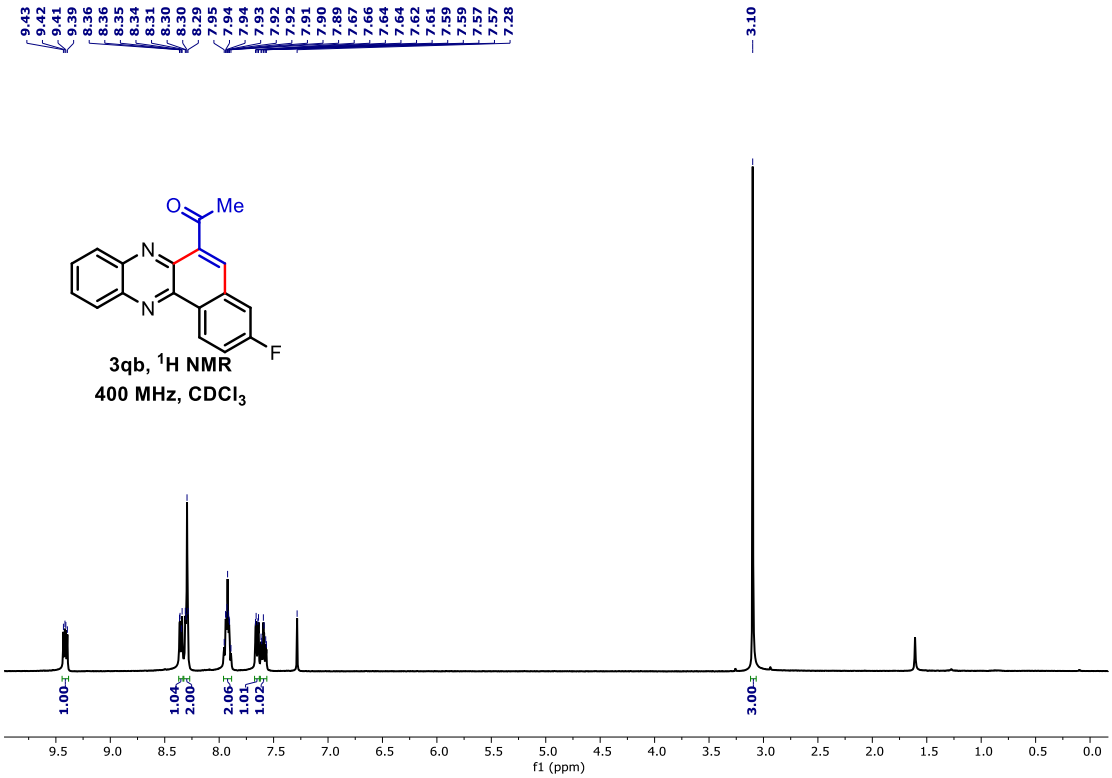
3db, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$


9.30
9.28
8.39
8.38
8.38
8.37
8.33
8.32
8.31
8.31
8.28
8.18
8.17
7.99
7.99
7.97
7.97
7.96
7.95
7.94
7.93
7.92
7.29
3.10
O
Me
N
N
Br
3eb, ^{1}H NMR
400 MHz, CDCl$_3$
1.00
1.08
1.02
1.01
1.02
3.07
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

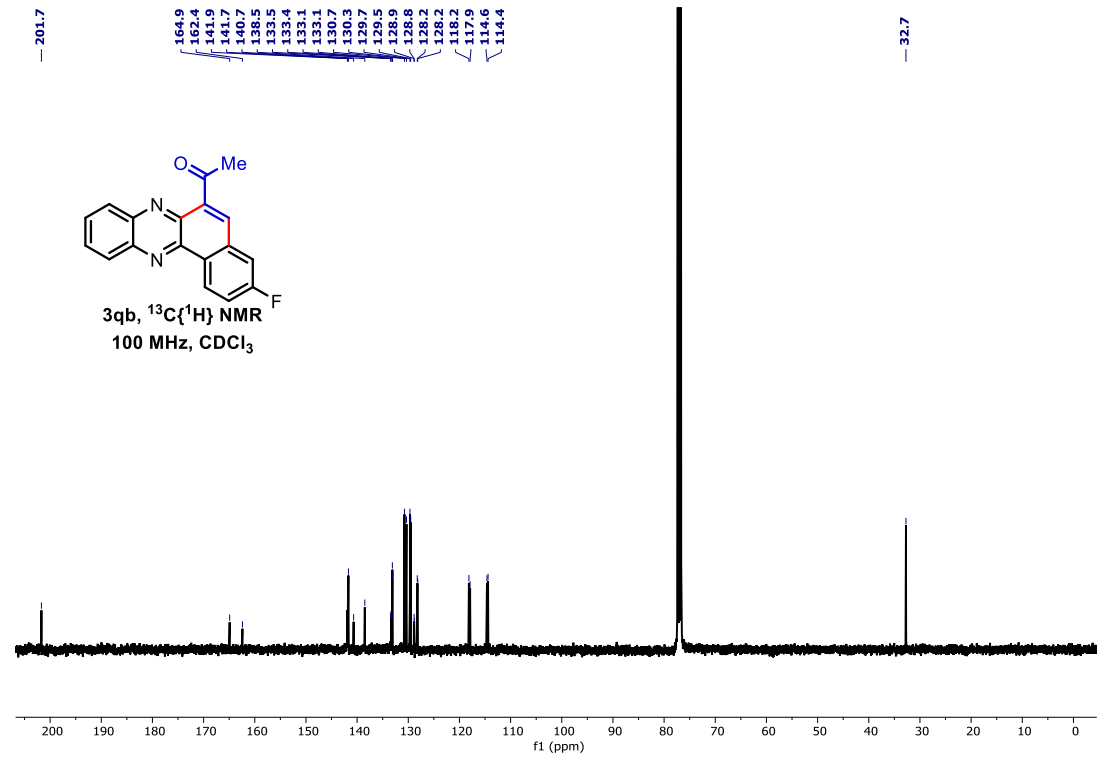

201.6
142.2
141.7
141.7
140.9
138.5
133.1
132.8
132.6
132.0
131.0
130.9
130.6
129.7
129.6
127.2
124.7
32.7
O
Me
N
N
Br
3eb, ^{13}C{^{1}H} NMR
100 MHz, CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.50
9.48
8.38
8.36
8.36
8.32
8.30
8.29
8.27
8.06
8.04
7.96
7.95
7.94
7.28
3.10
O
Me
N
N
CF3
3fb, 1H NMR
400 MHz, CDCl3
1.00
2.00
1.01
1.01
1.01
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

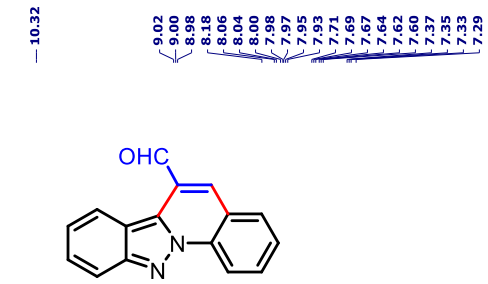

201.4
142.4
141.7
141.3
141.1
138.6
134.5
133.2
132.3
132.0
131.7
131.4
131.3
131.1
131.0
130.6
129.7
129.7
128.0
126.8
126.8
126.7
126.7
126.4
125.4
125.3
125.3
125.3
122.6
120.1
32.7
O
Me
N
N
CF3
3fb, 13C{1H} NMR
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



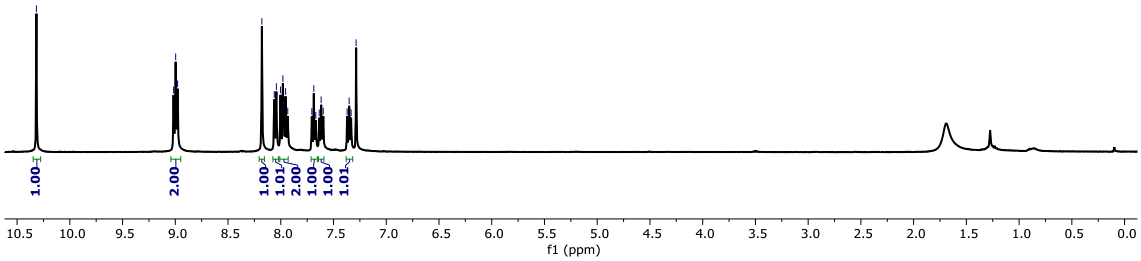
3qb, ^{1}H NMR
400 MHz, $CDCl_3$

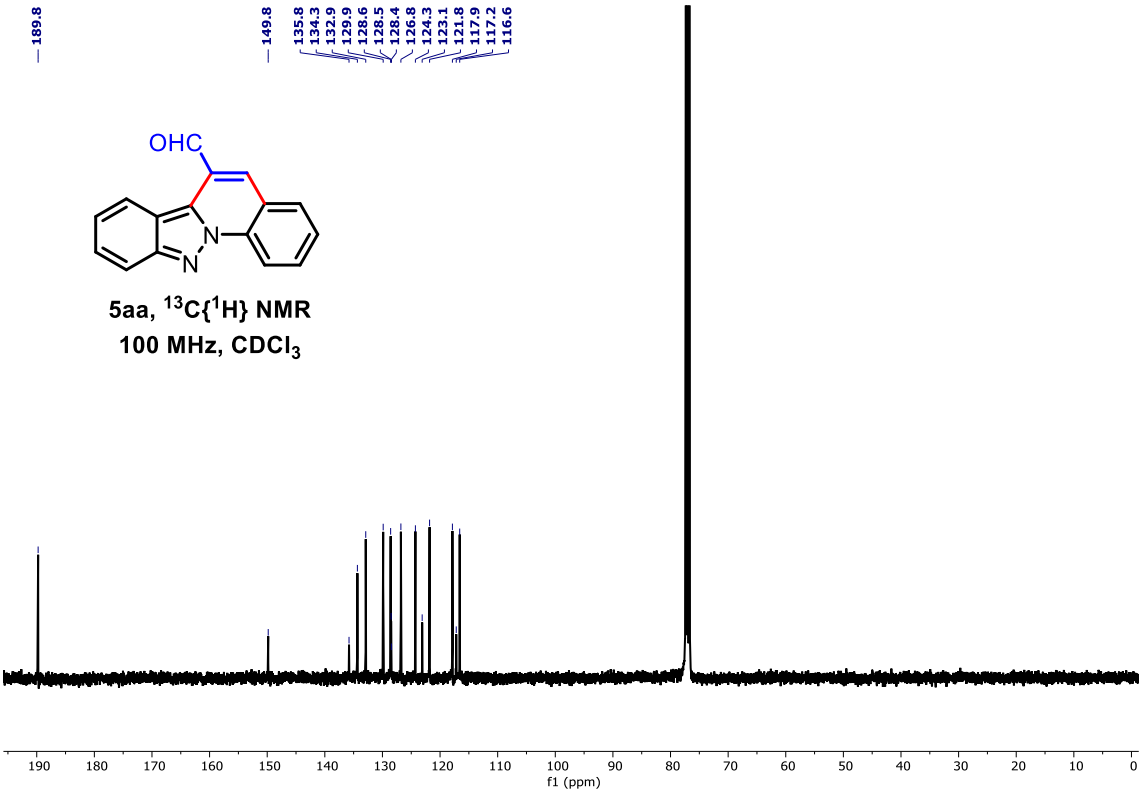


3qb, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

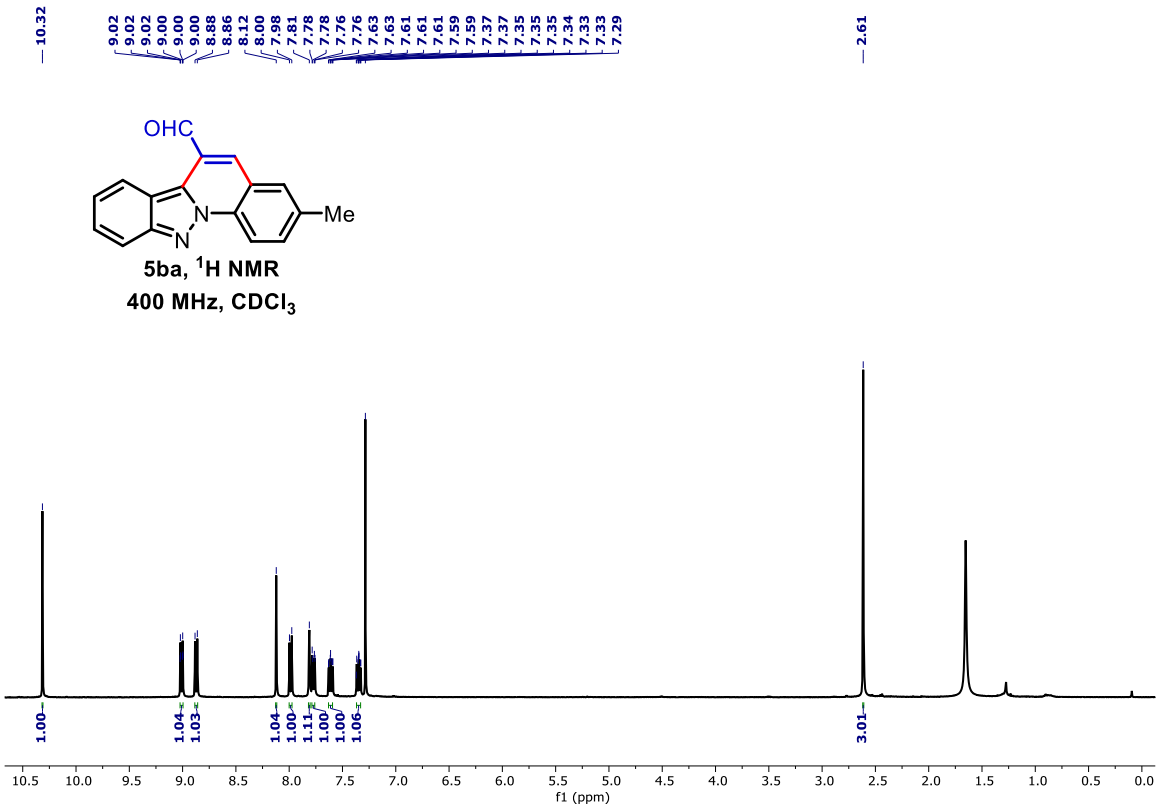


5aa, ^{1}H NMR
400 MHz, $CDCl_3$

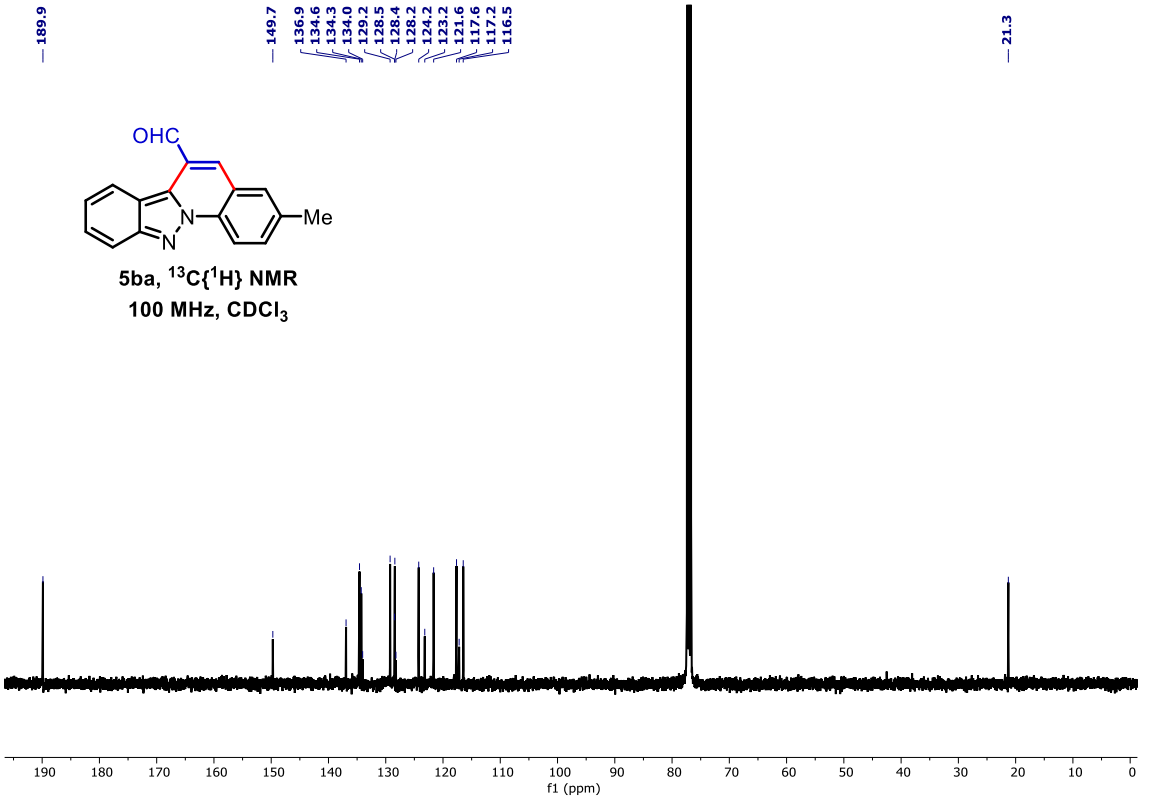




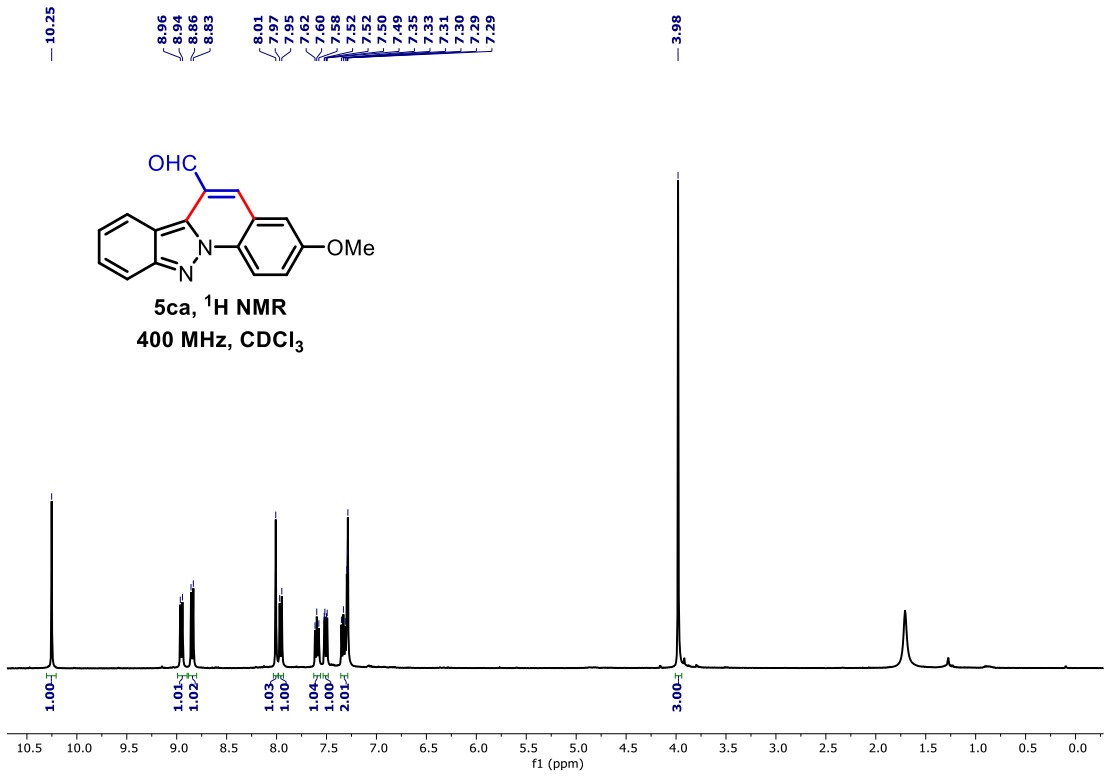
5aa, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



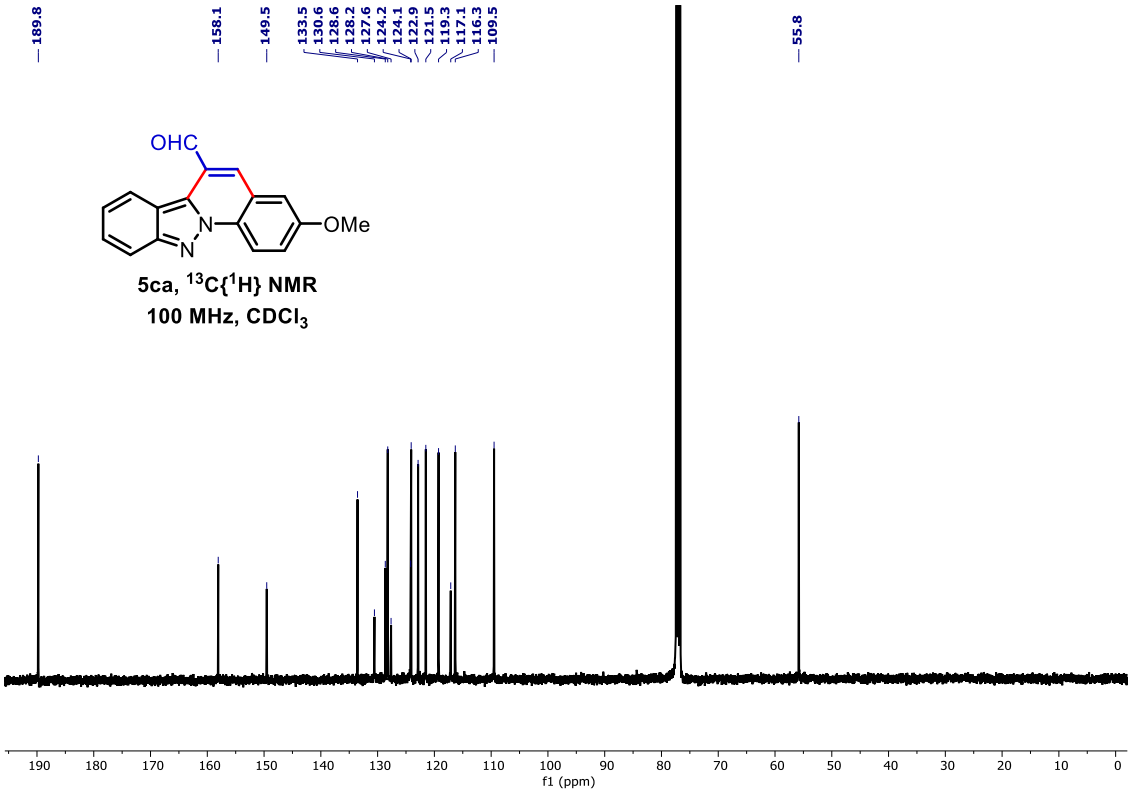
5ba, ^{1}H NMR
400 MHz, $CDCl_3$



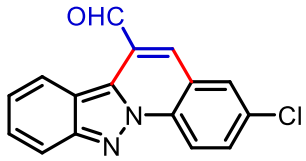
5ba, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



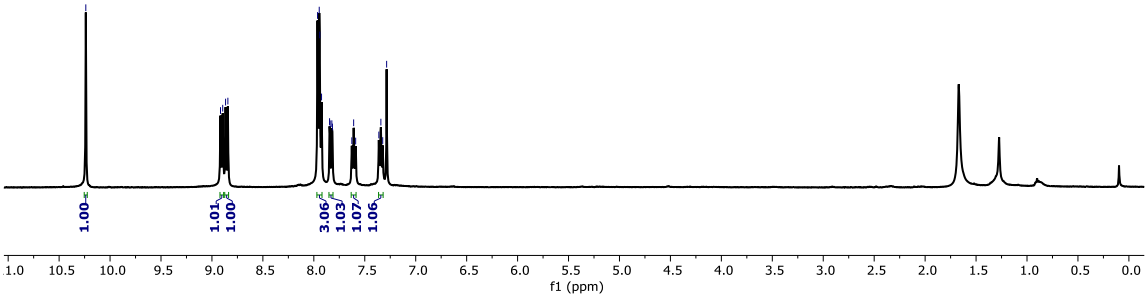
5ca, ^{1}H NMR
400 MHz, $CDCl_3$

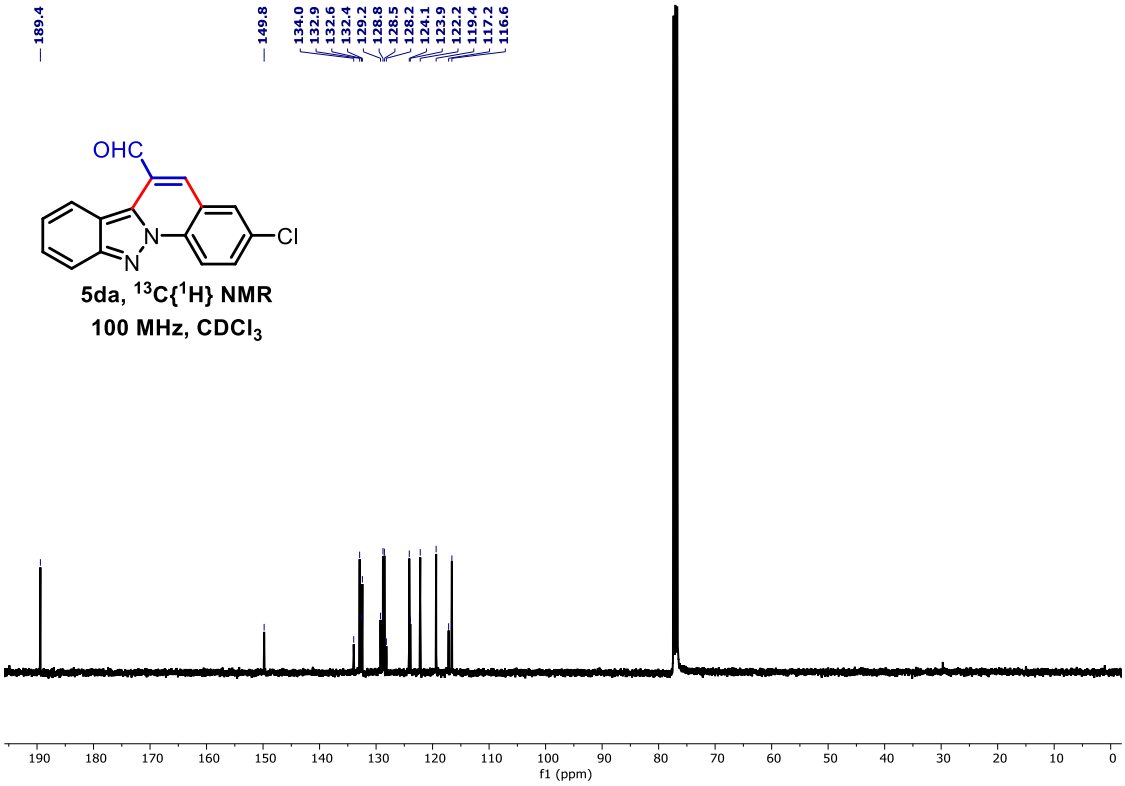


5ca, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$

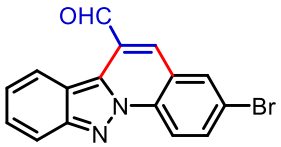


5da, ^{1}H NMR
400 MHz, $CDCl_3$

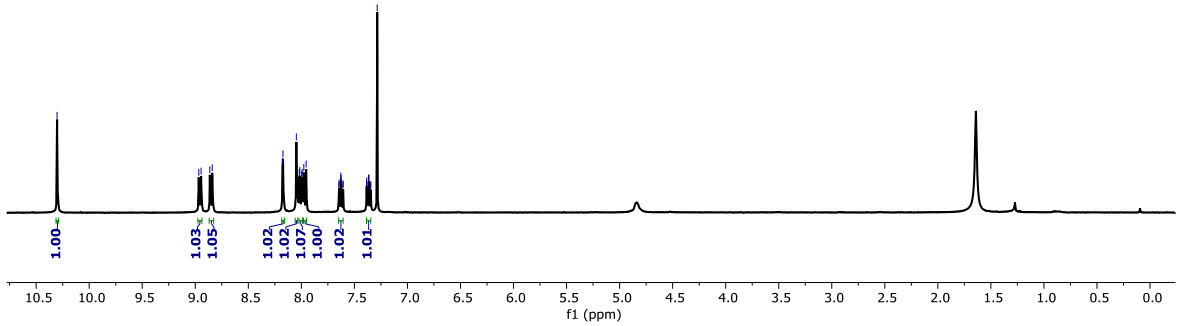


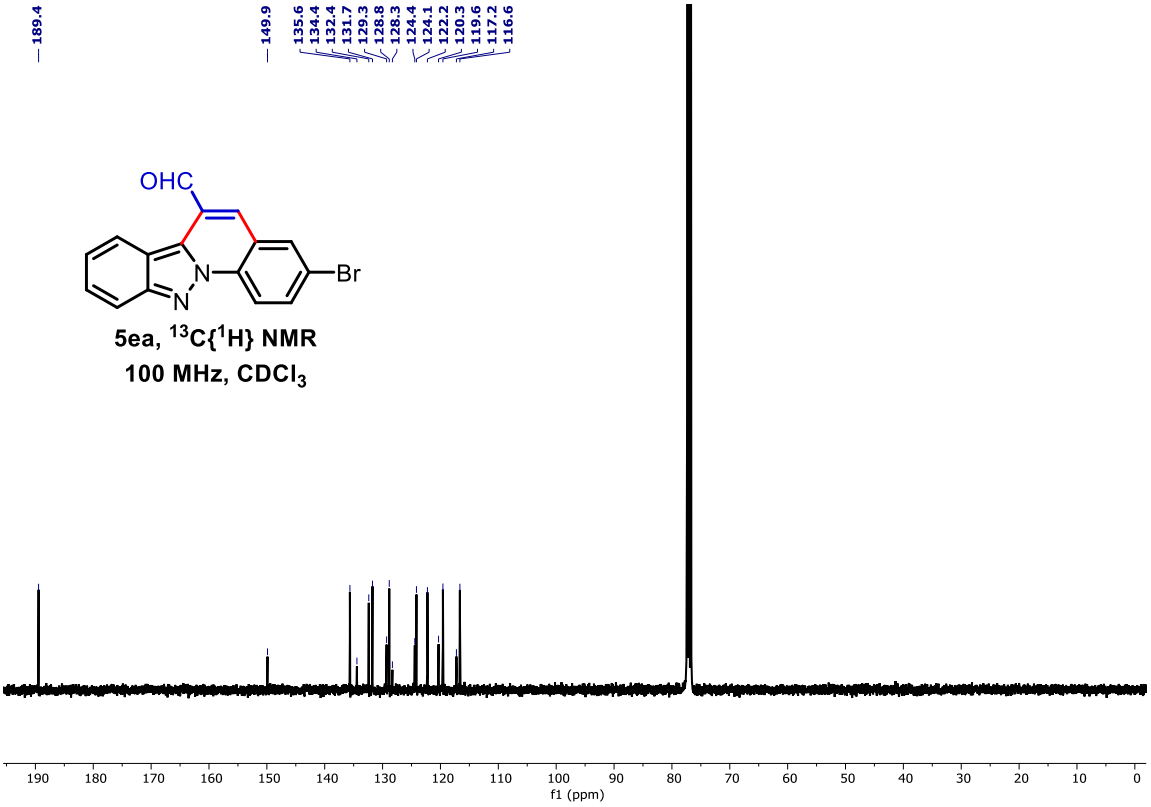


5da, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

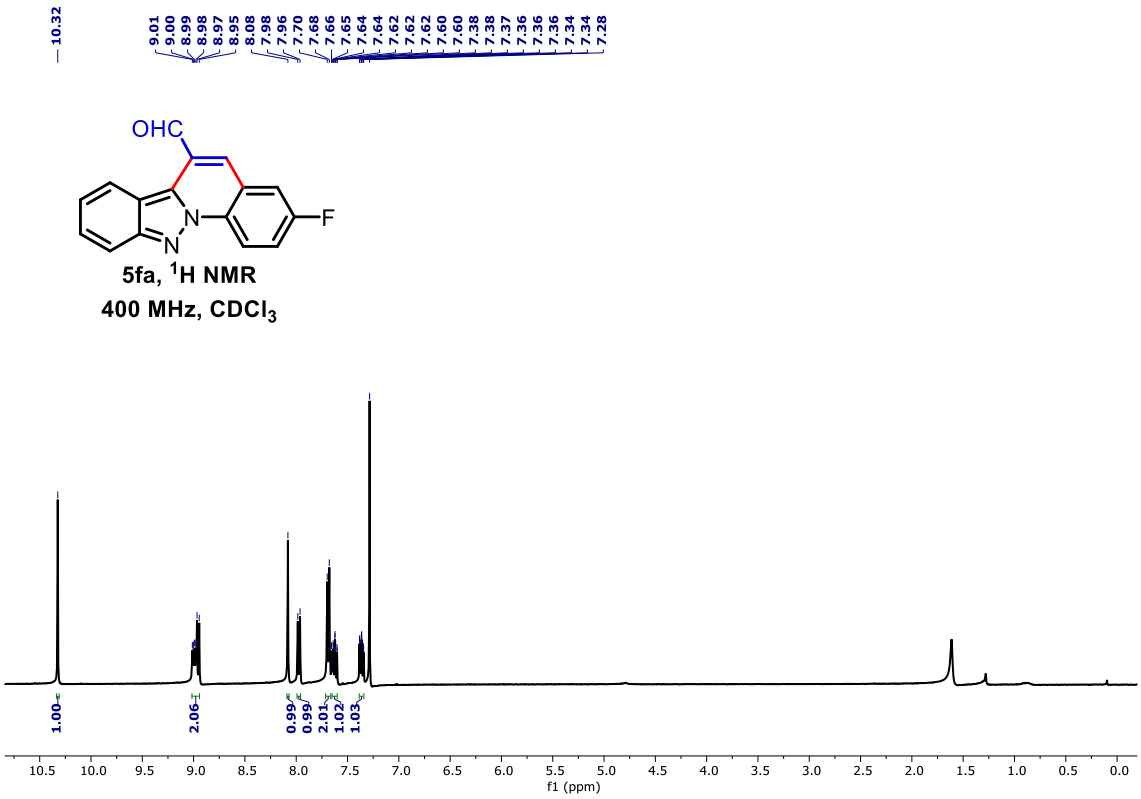


5ea, ^{1}H NMR
400 MHz, $CDCl_3$

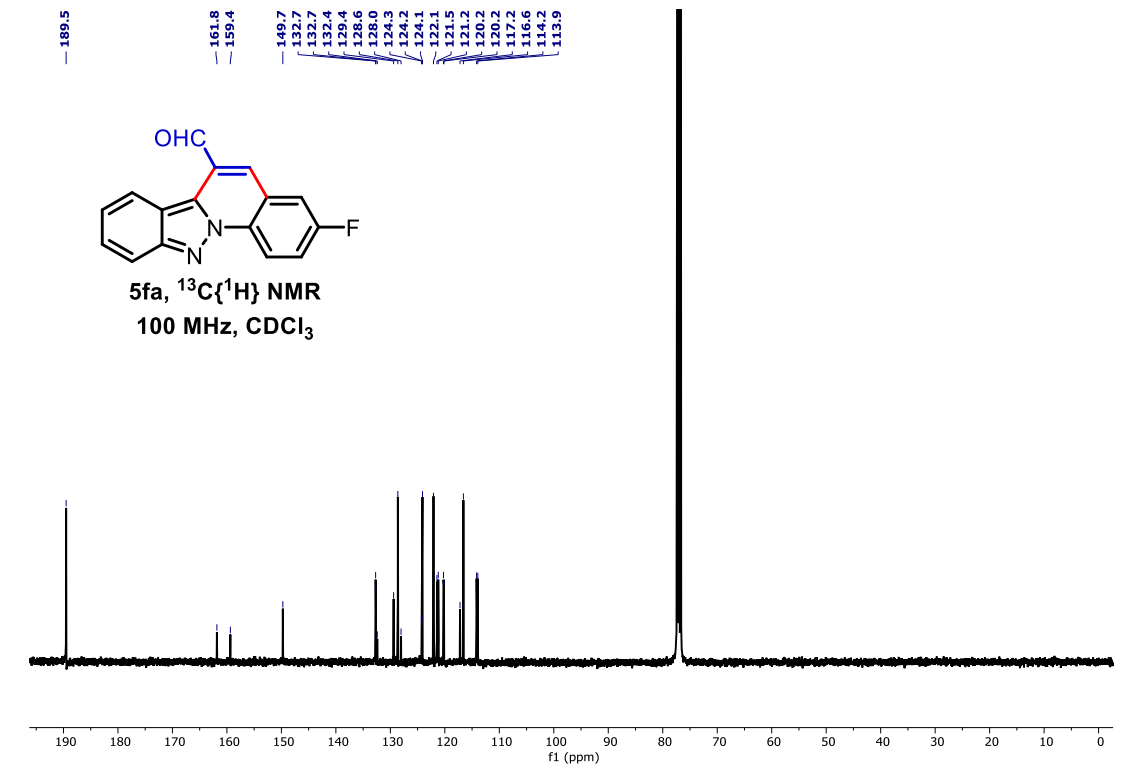




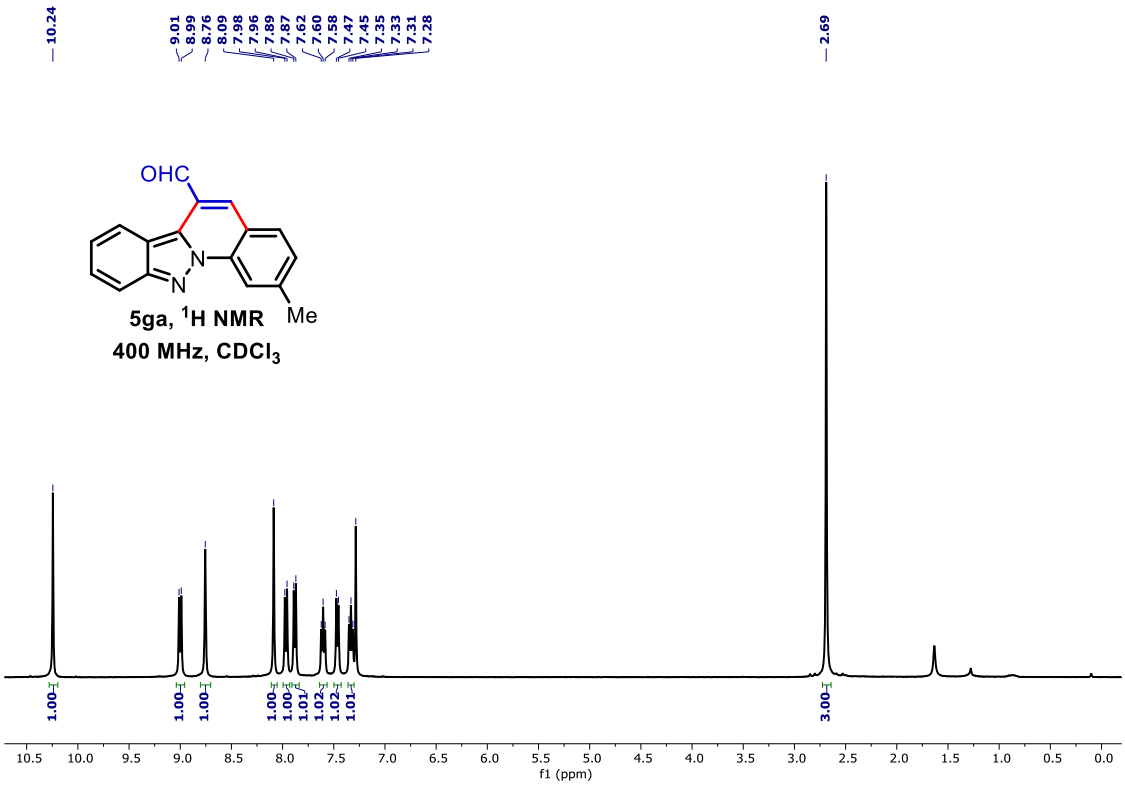
5ea, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



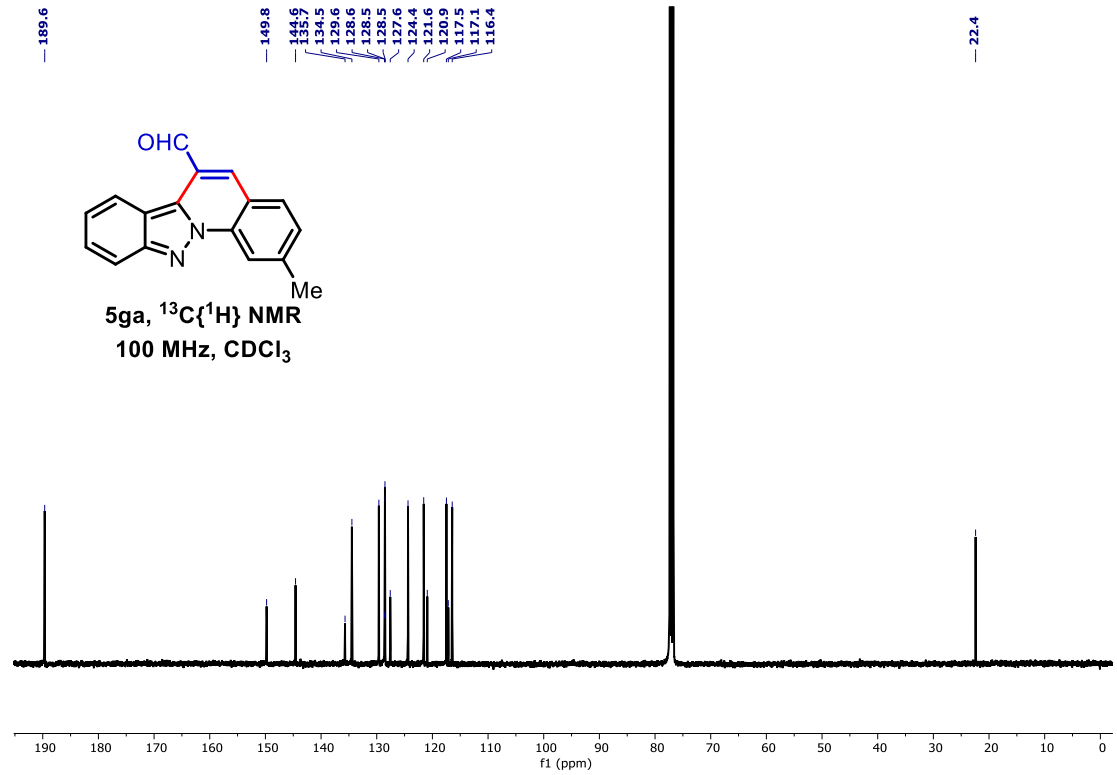
5fa, ^{1}H NMR
400 MHz, $CDCl_3$



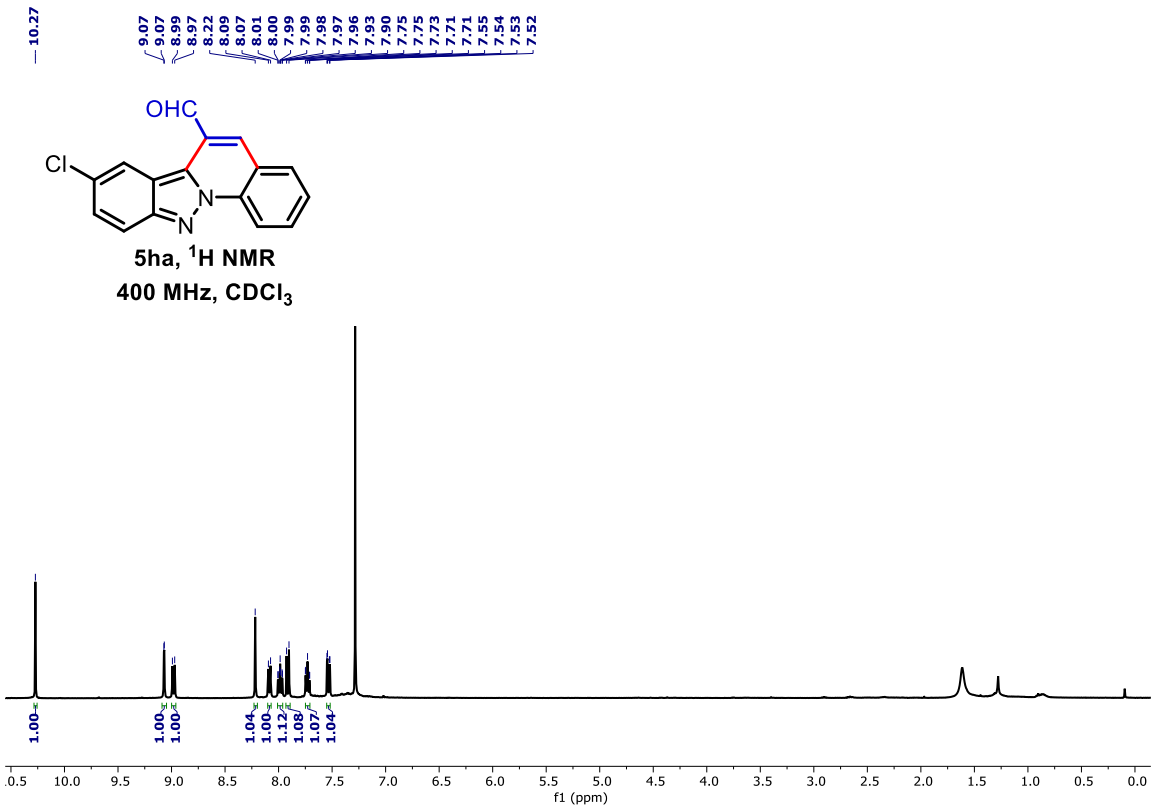
5fa, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



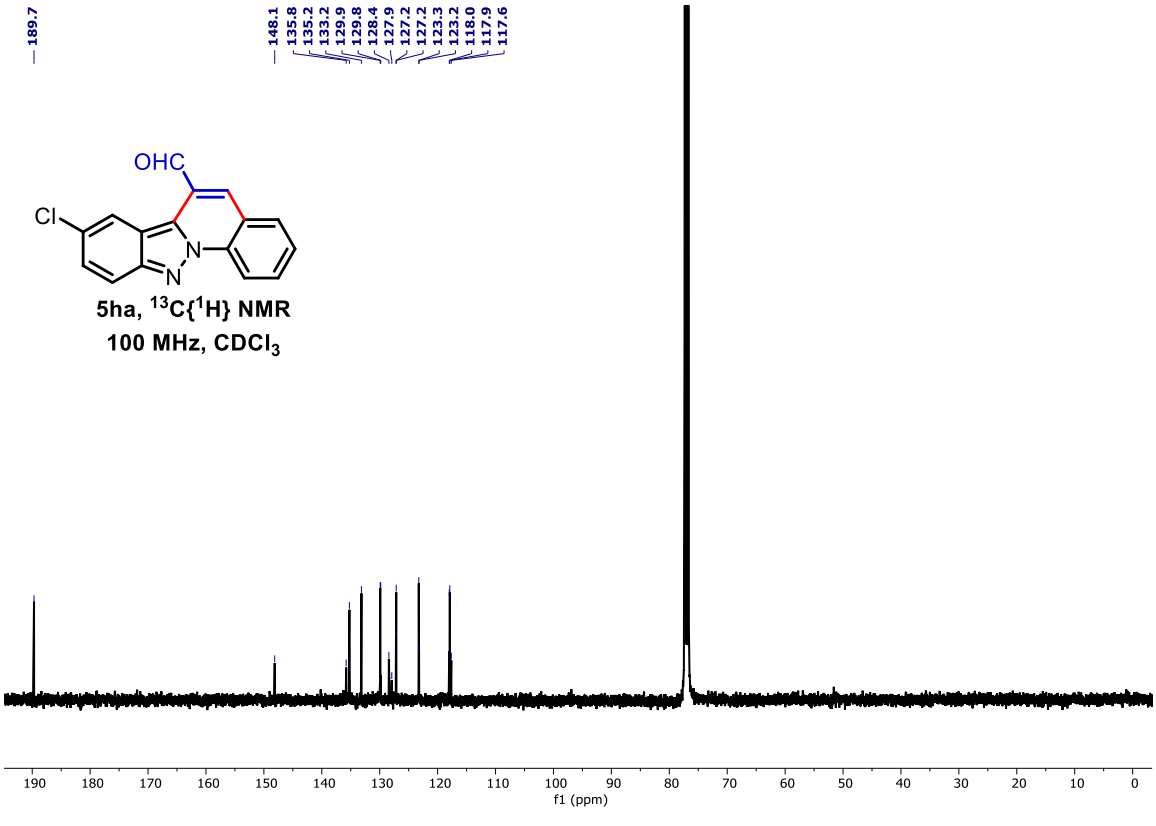
5ga, ^{1}H NMR
400 MHz, $CDCl_3$



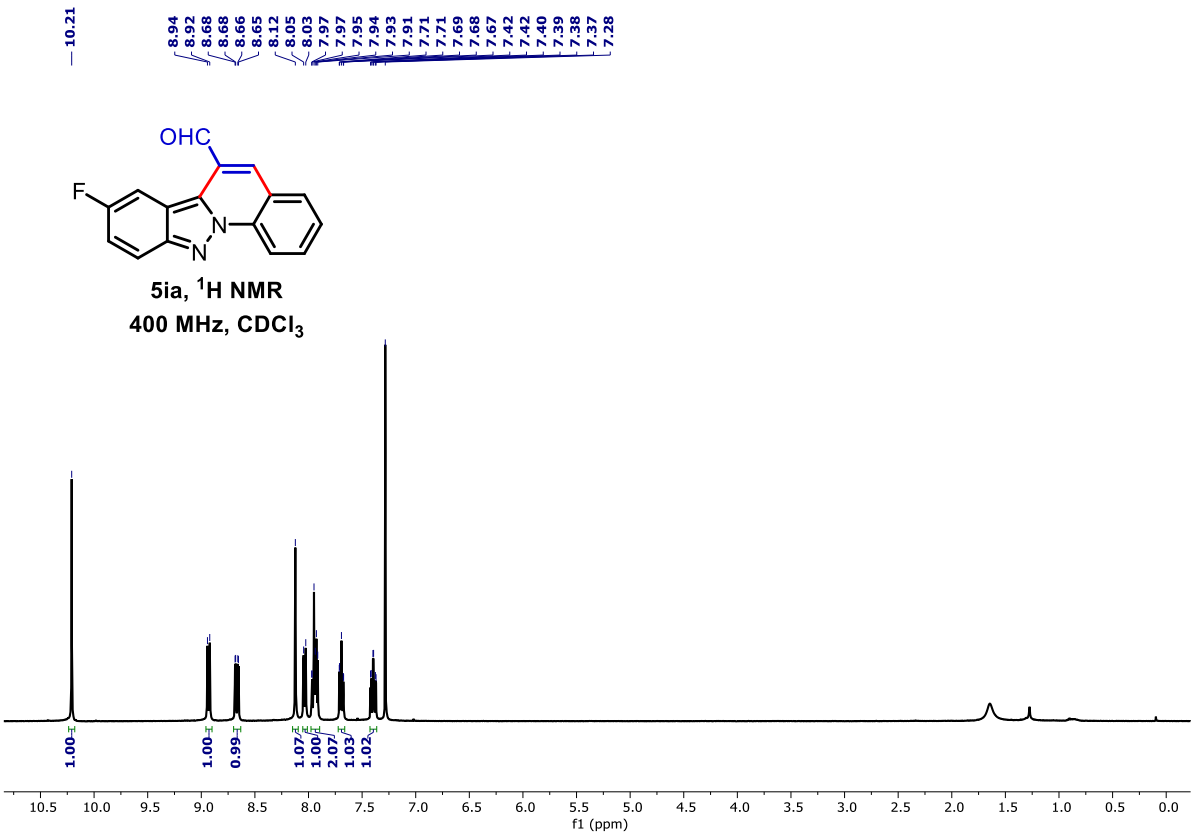
5ga, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



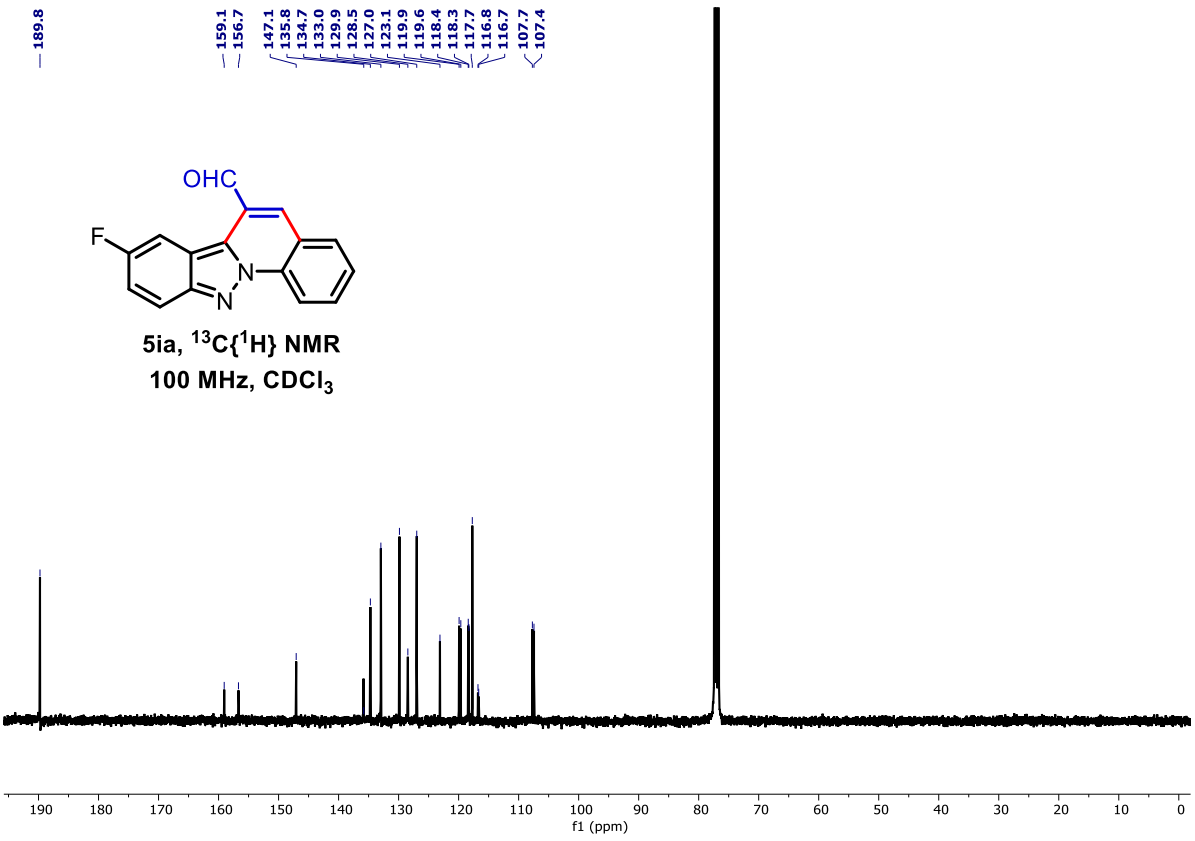
5ha, ^{1}H NMR
400 MHz, $CDCl_3$



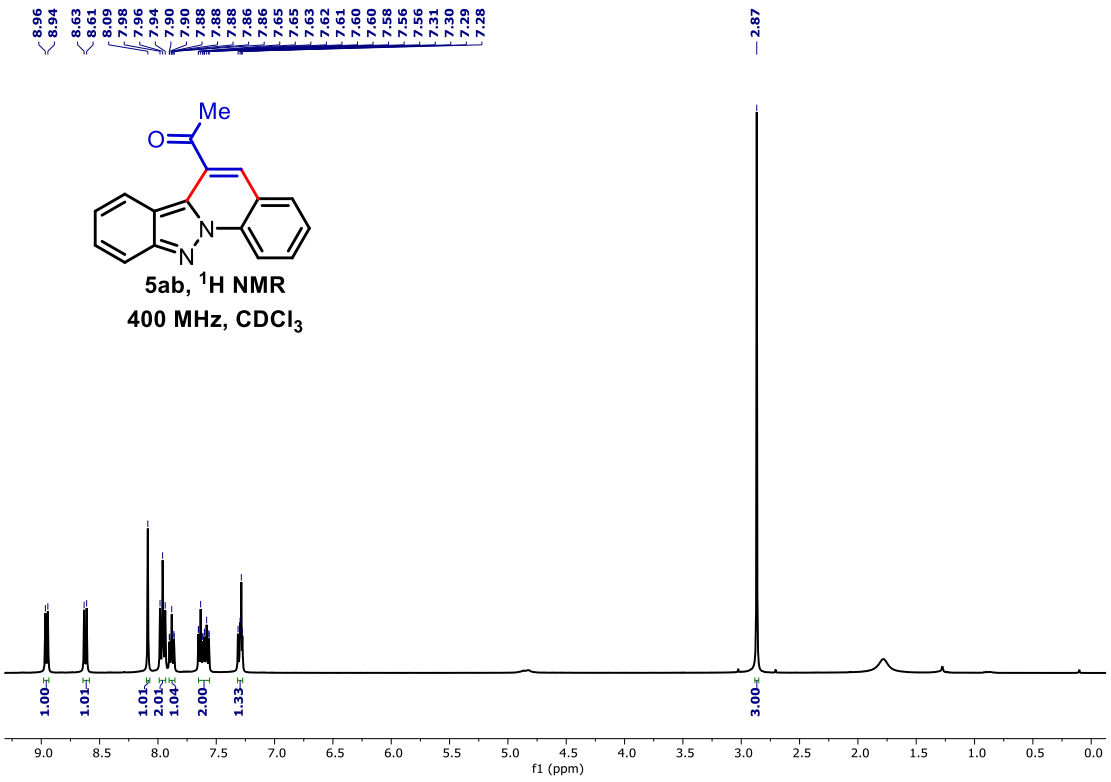
5ha, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



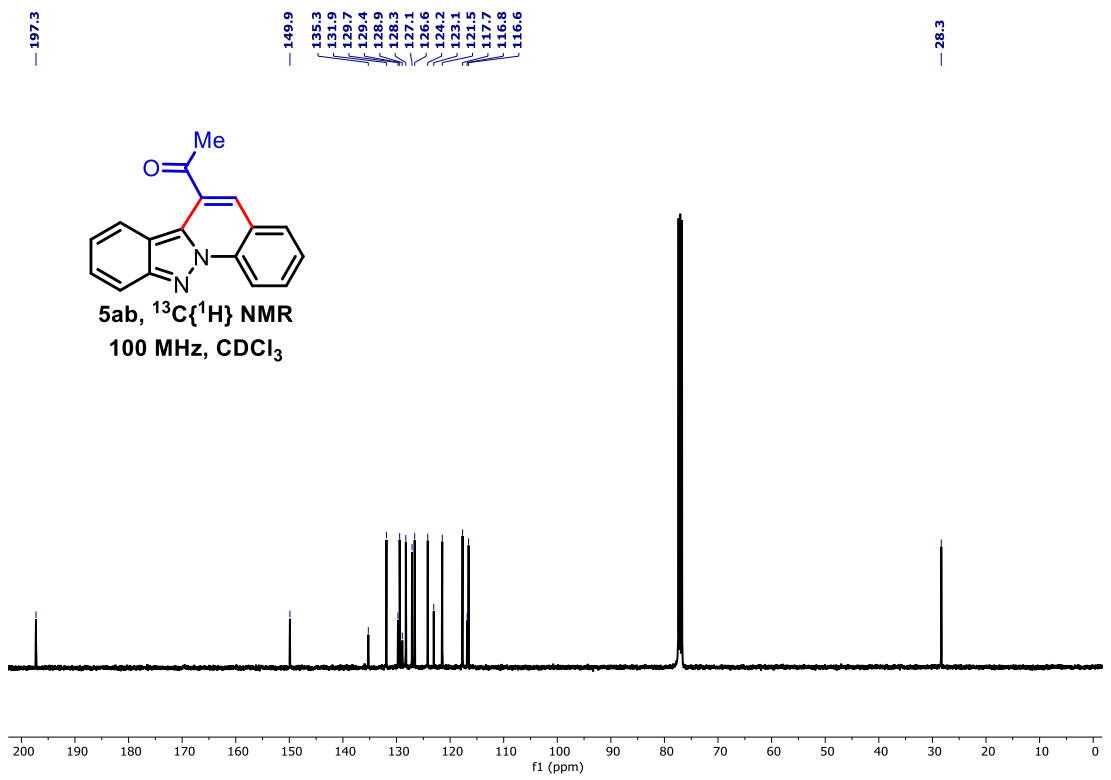
5ia, ^{1}H NMR
400 MHz, $CDCl_3$



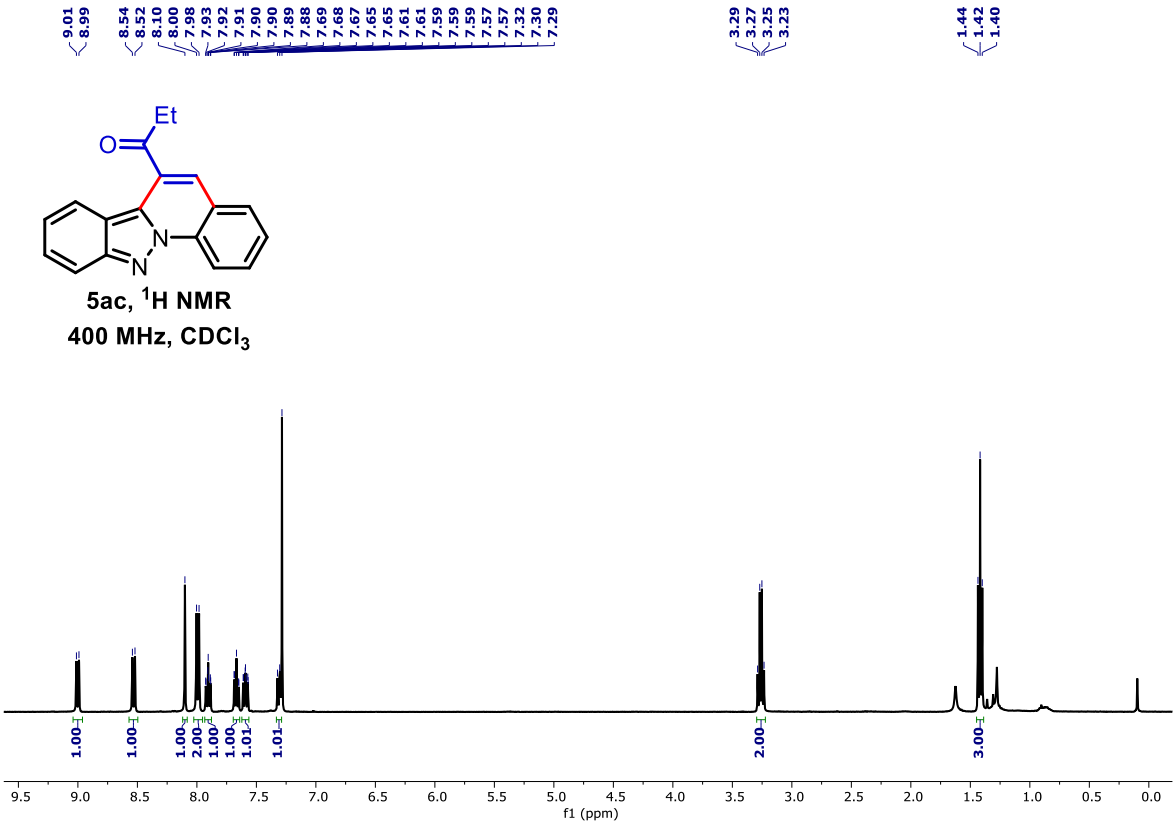
5ia, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



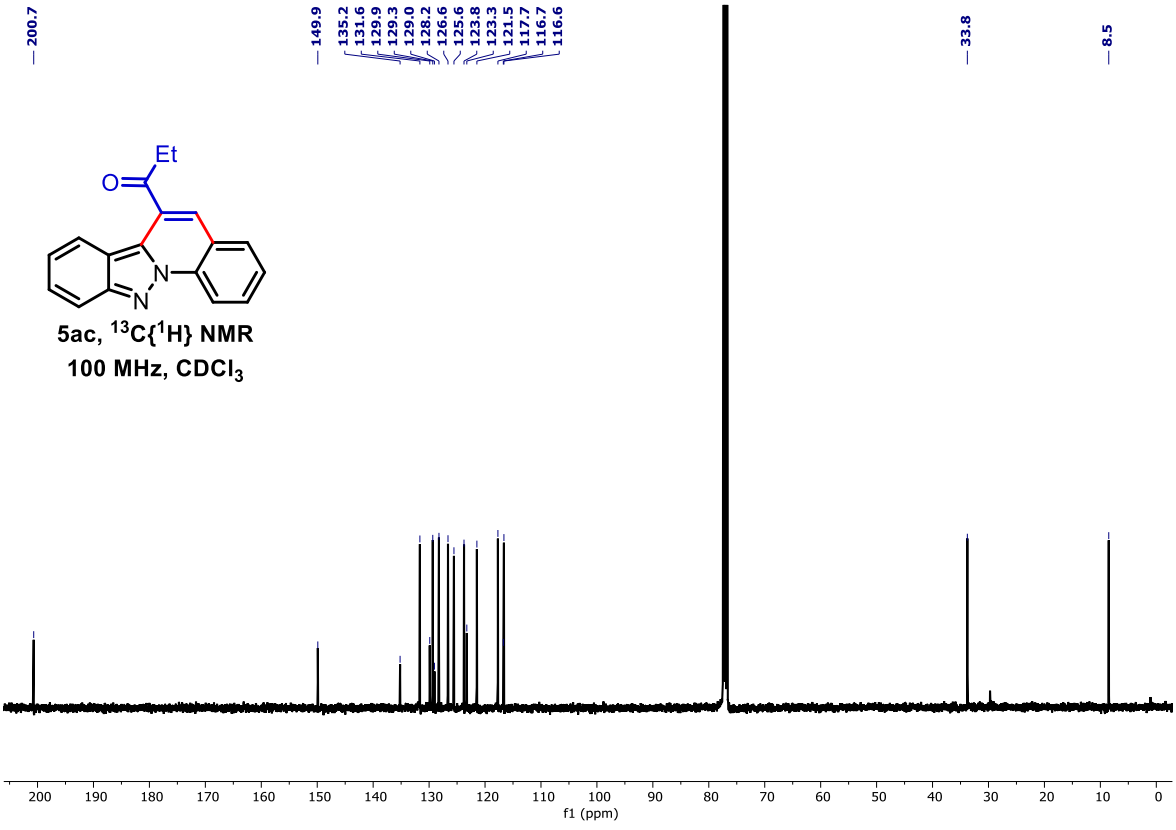
5ab, ^{1}H NMR
400 MHz, $CDCl_3$



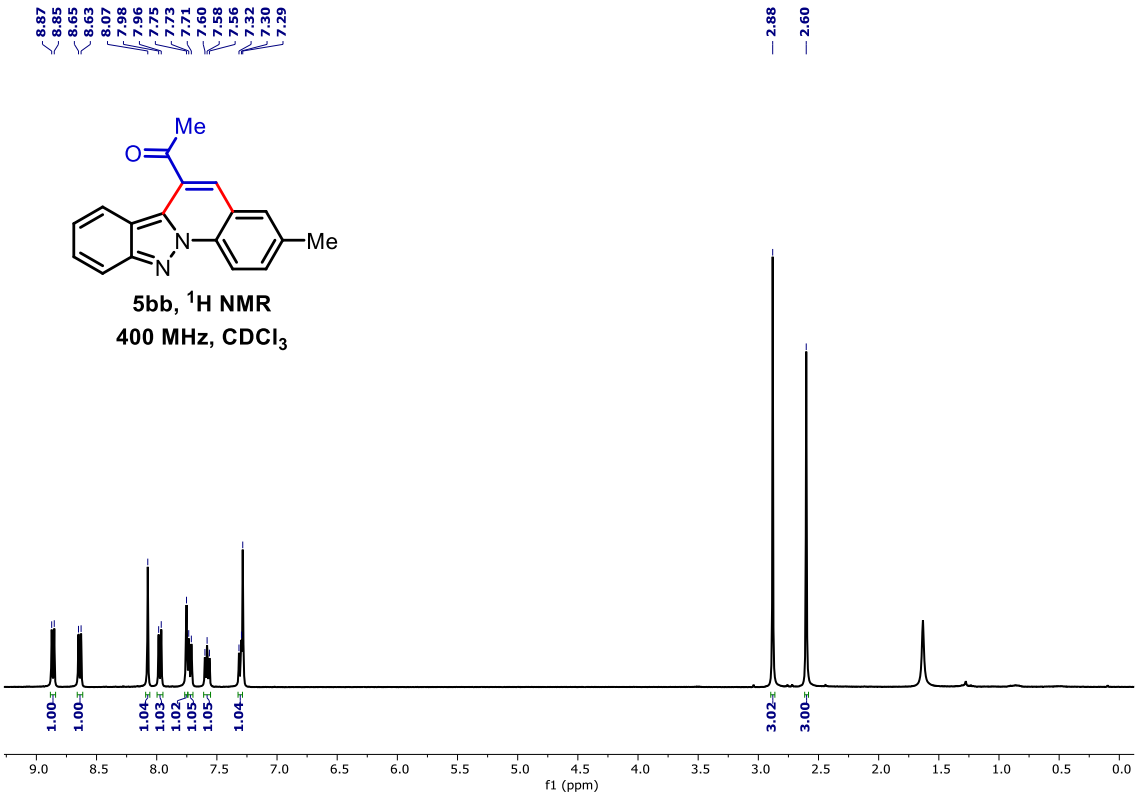
5ab, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



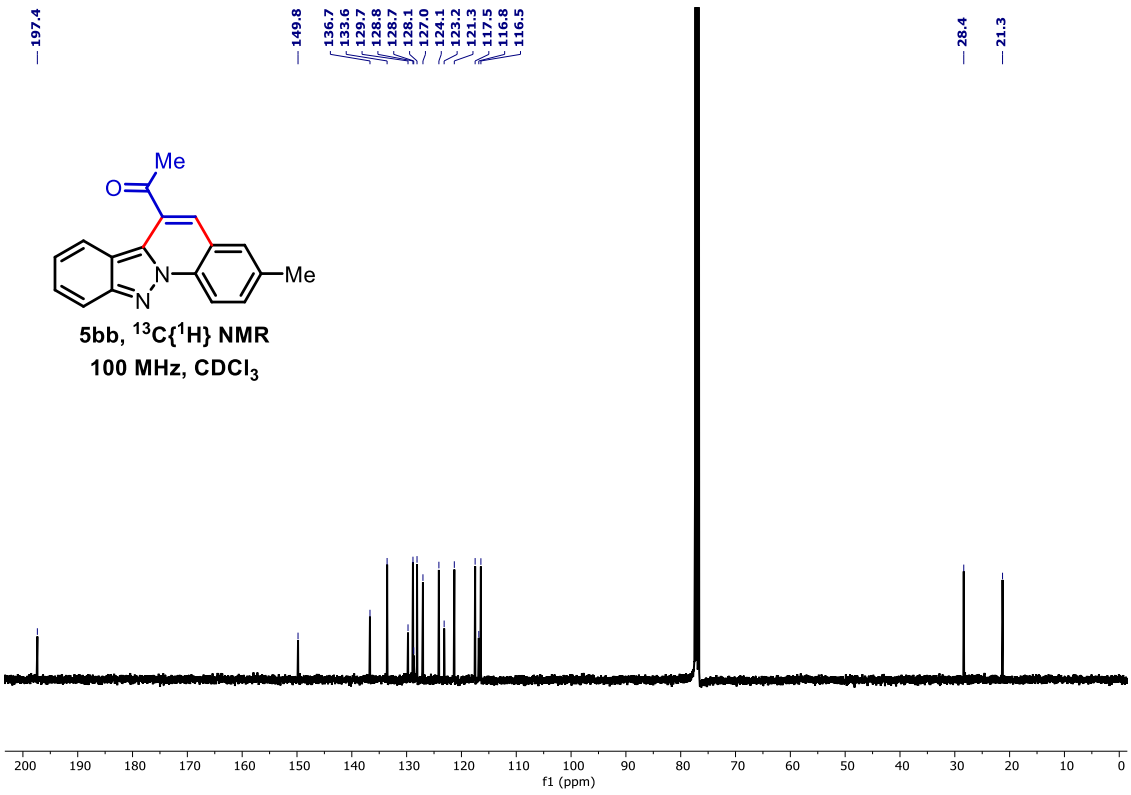
5ac, ^{1}H NMR
400 MHz, $CDCl_3$



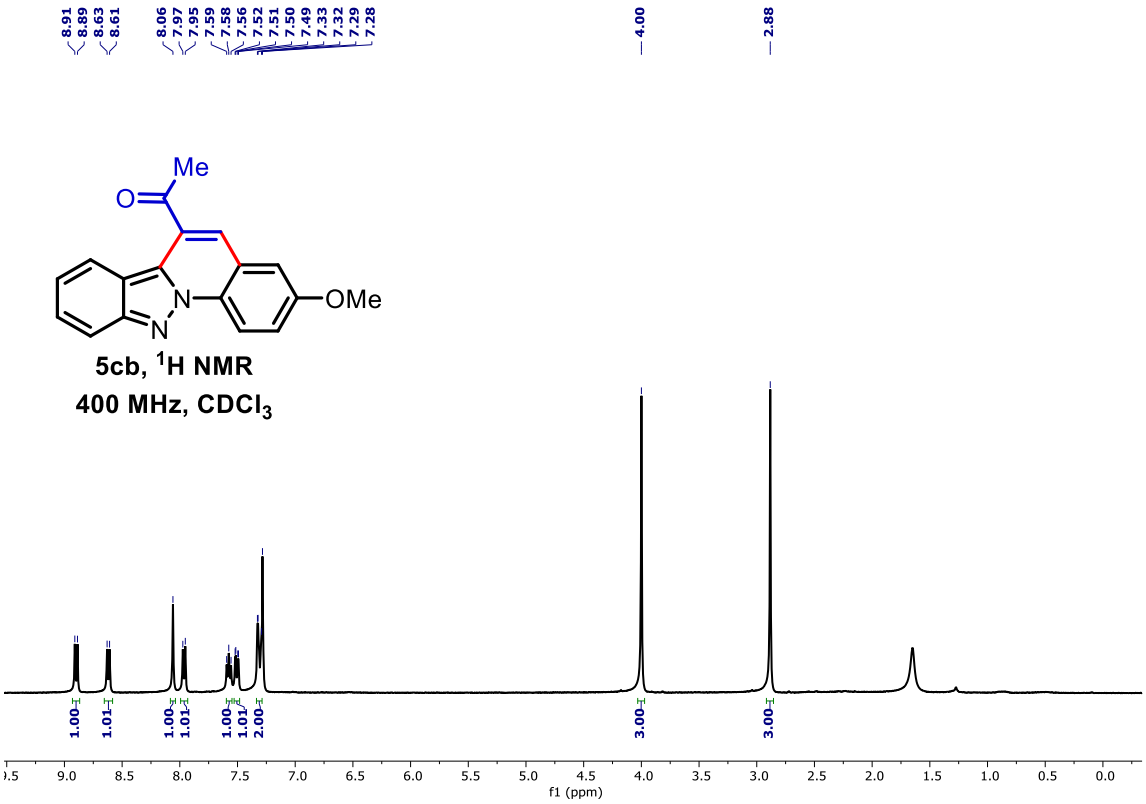
5ac, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



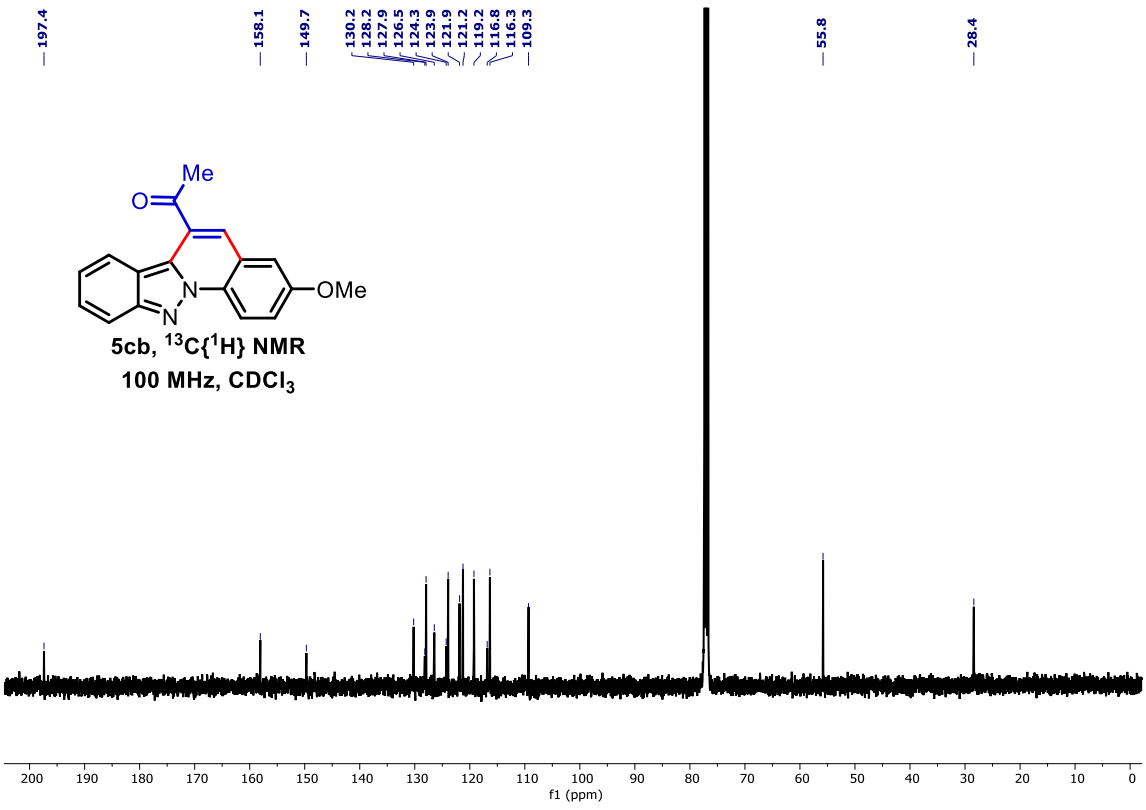
5bb, ^{1}H NMR
400 MHz, $CDCl_3$



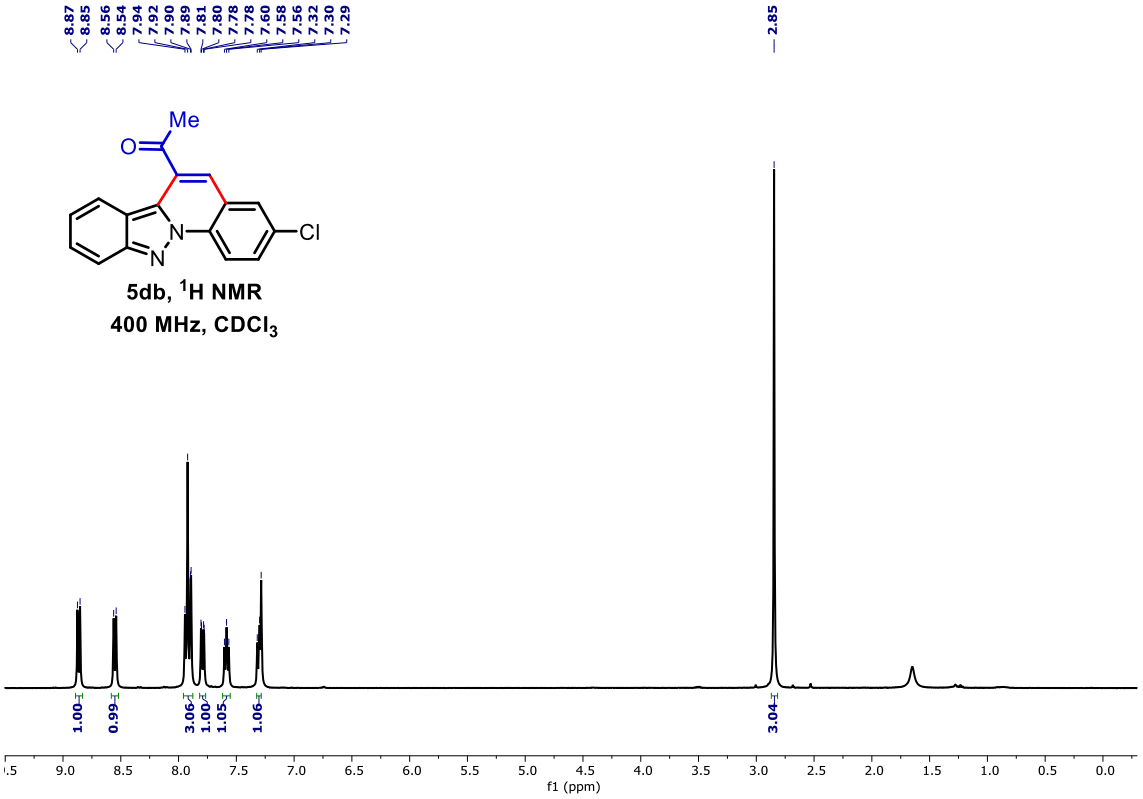
5bb, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



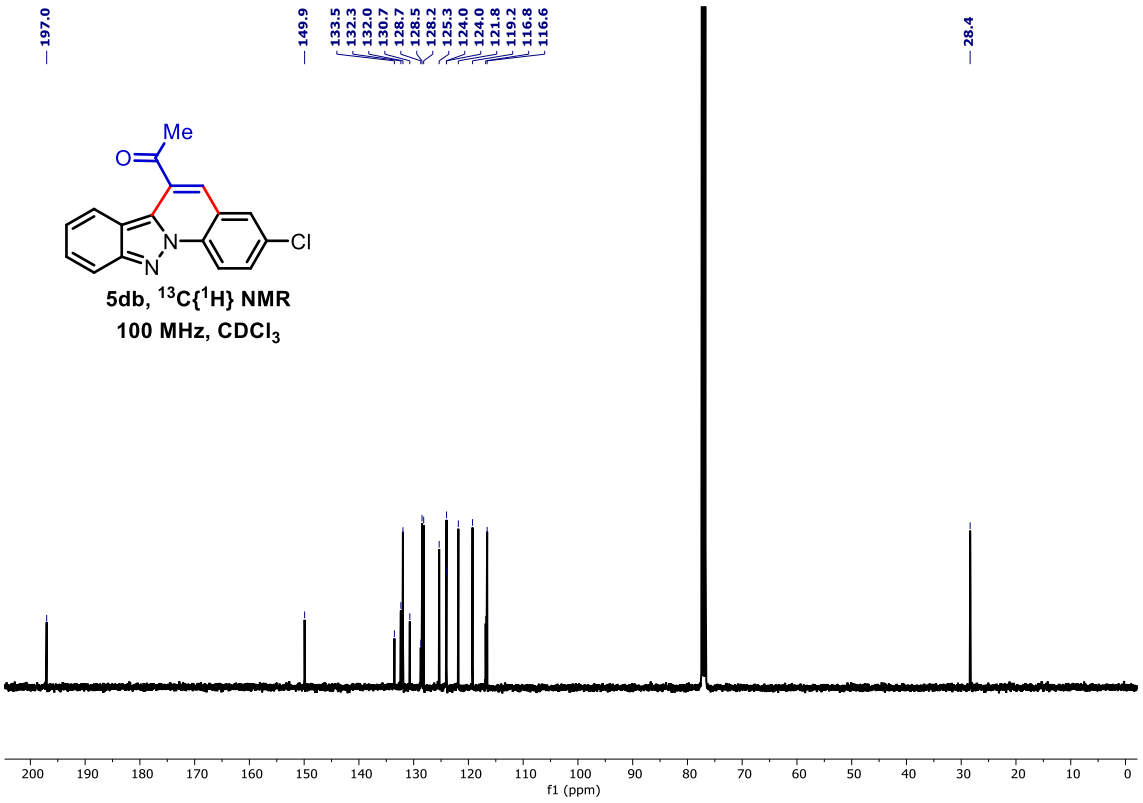
5cb, ^{1}H NMR
400 MHz, $CDCl_3$



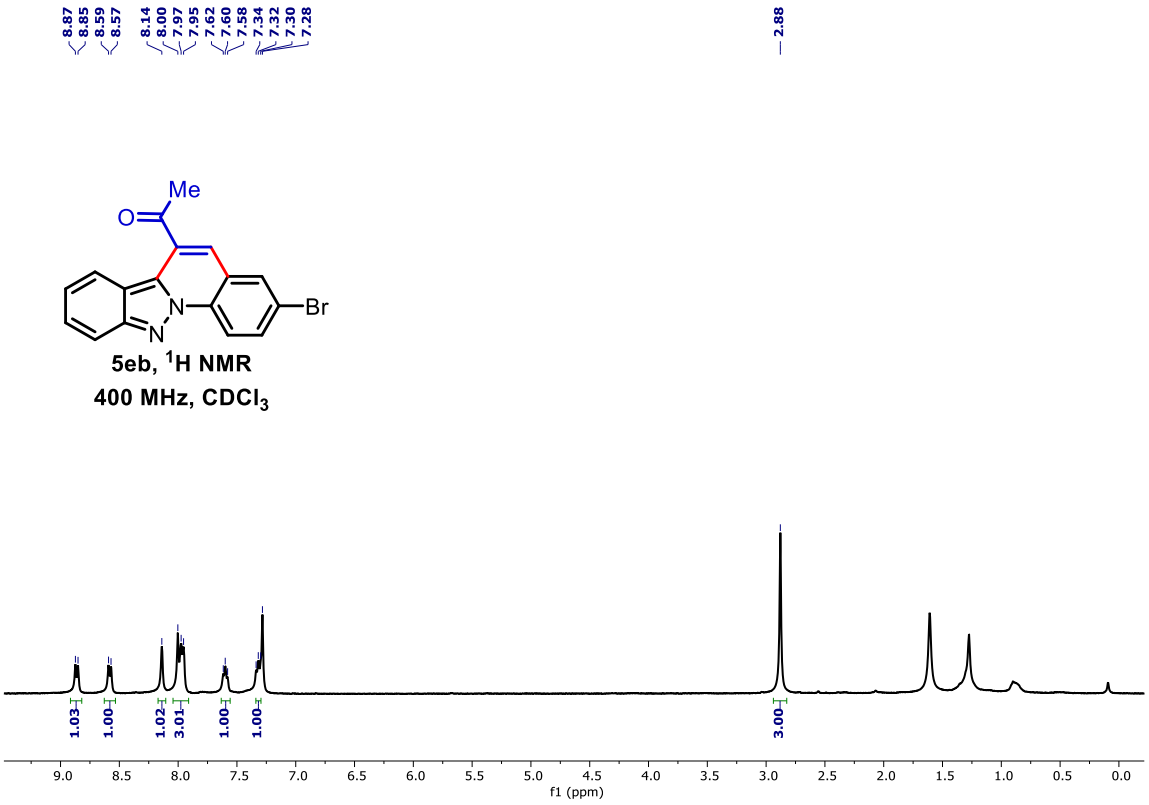
5cb, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



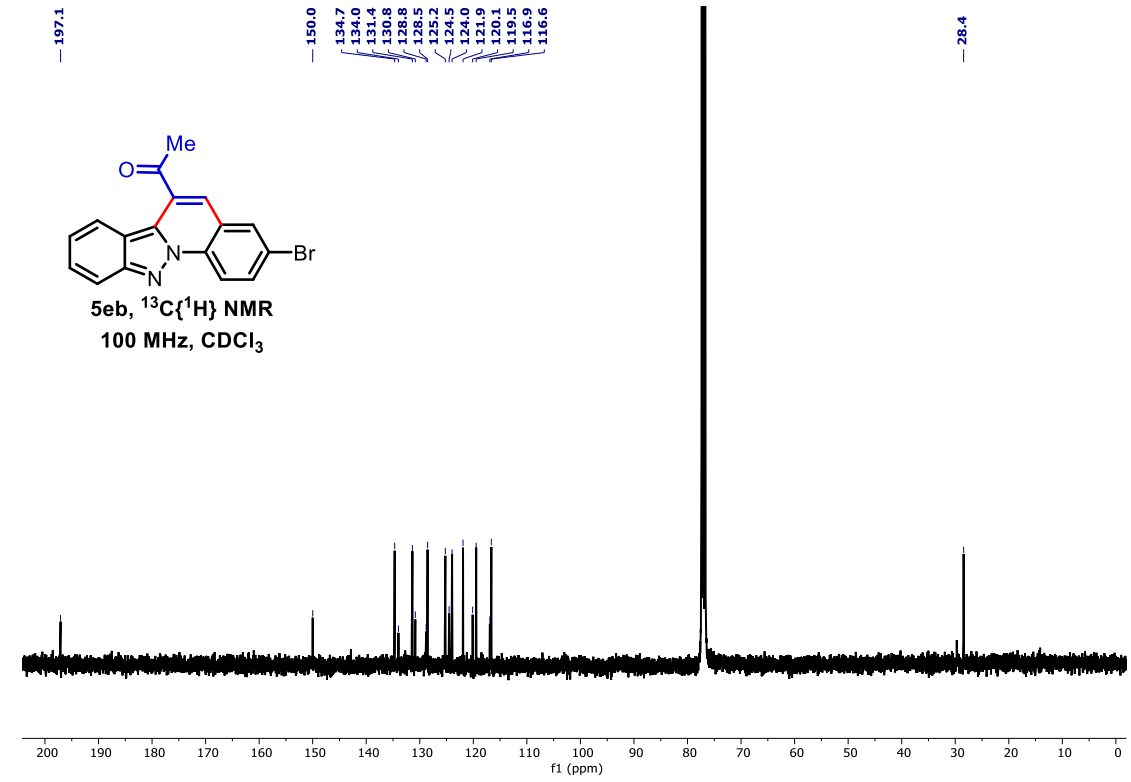
5db, ^{1}H NMR
400 MHz, $CDCl_3$



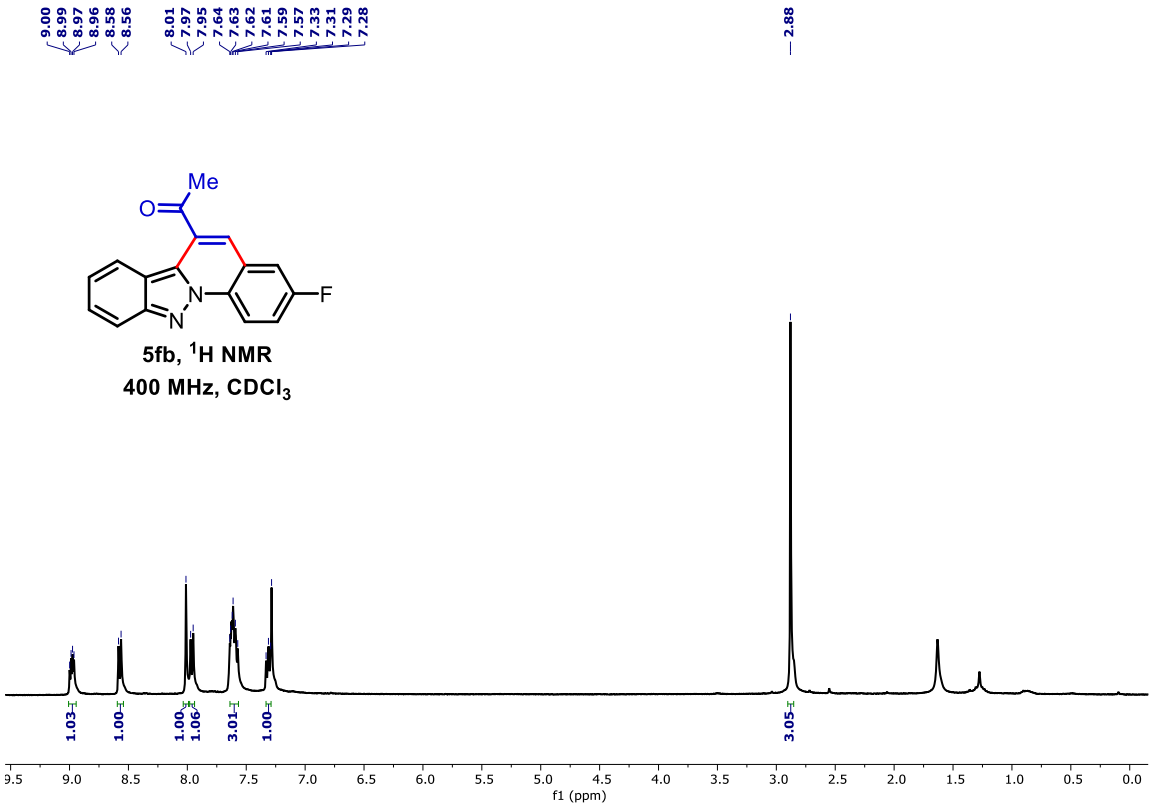
5db, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



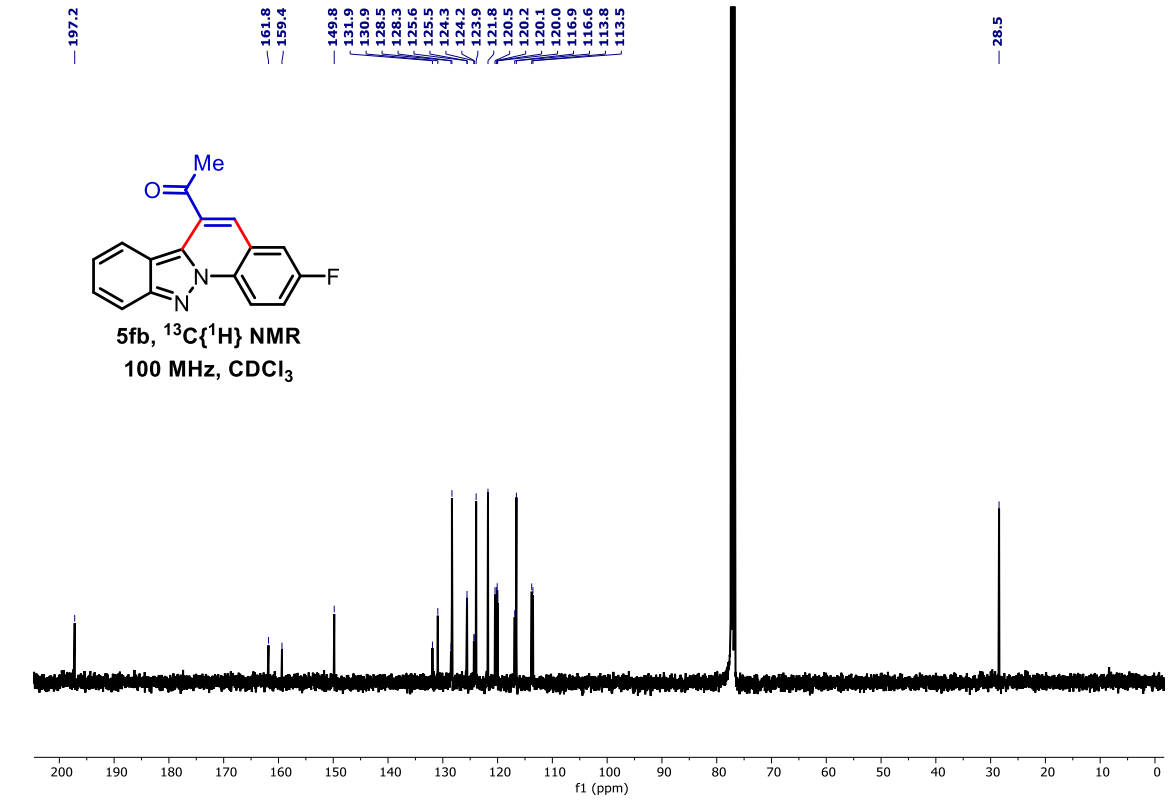
5eb, ^{1}H NMR
400 MHz, $CDCl_3$



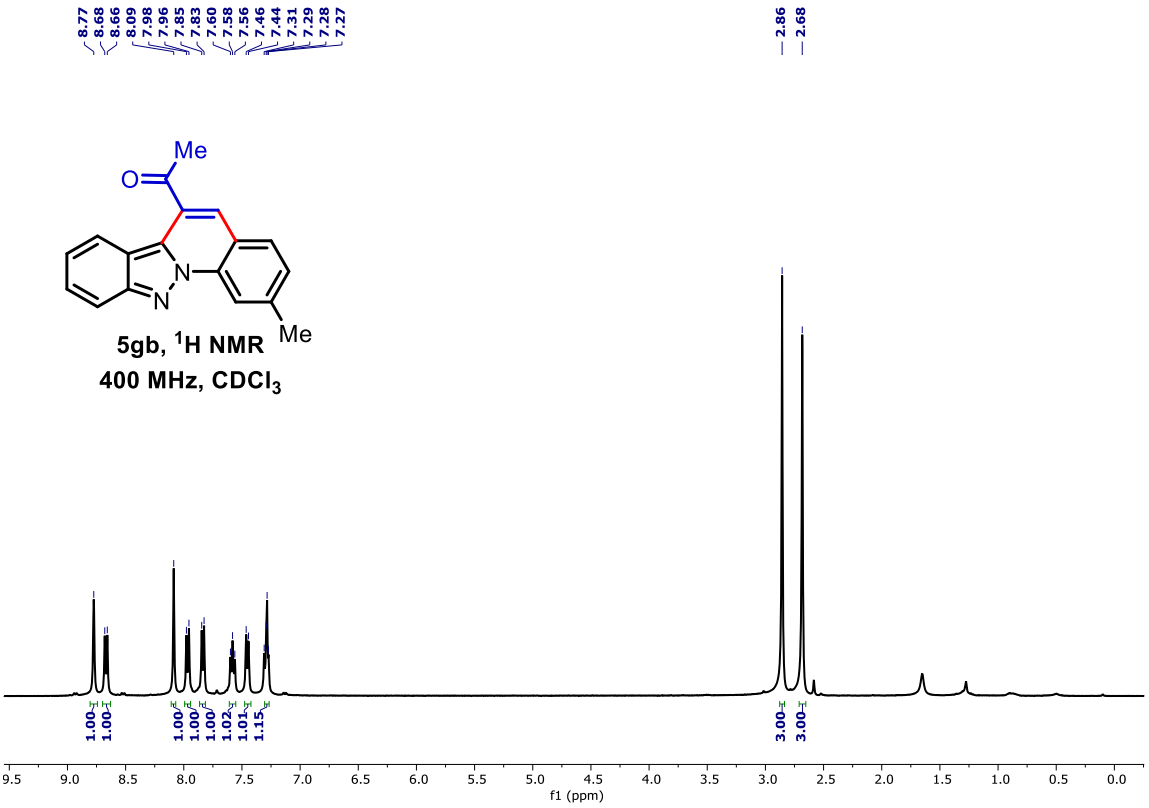
5eb, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



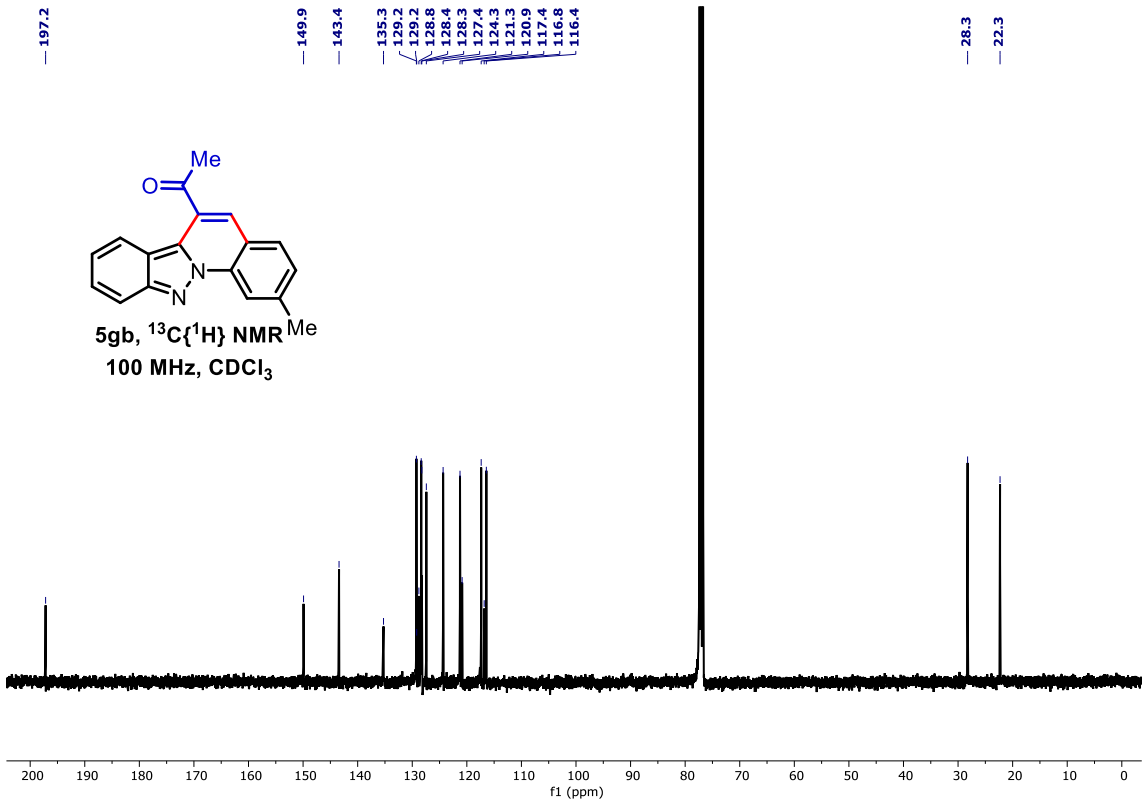
5fb, ^{1}H NMR
400 MHz, $CDCl_3$



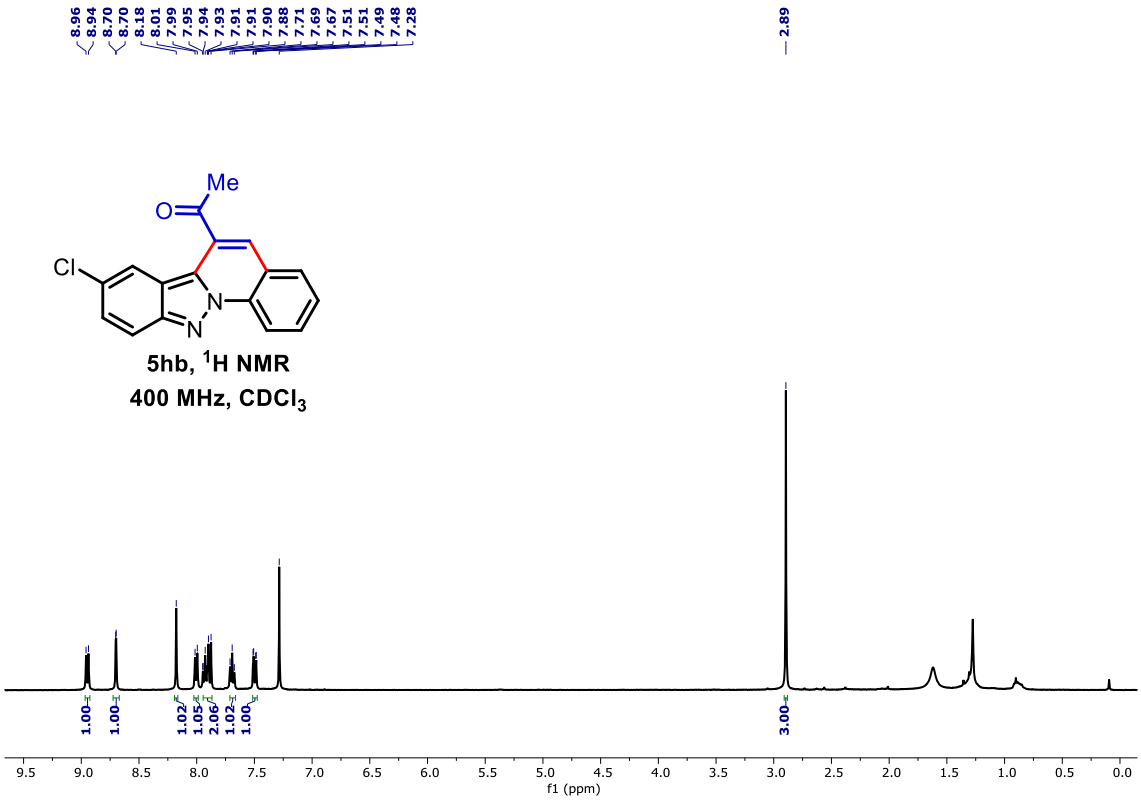
5fb, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



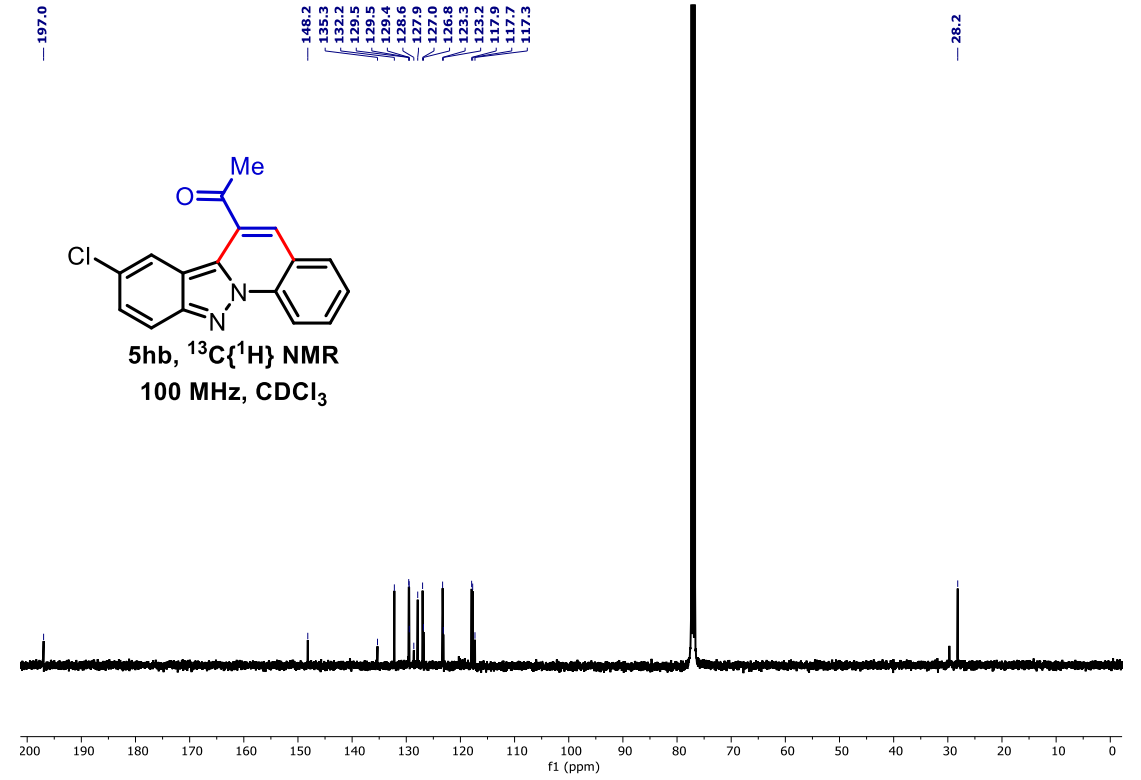
5gb, ^{1}H NMR
400 MHz, $CDCl_3$



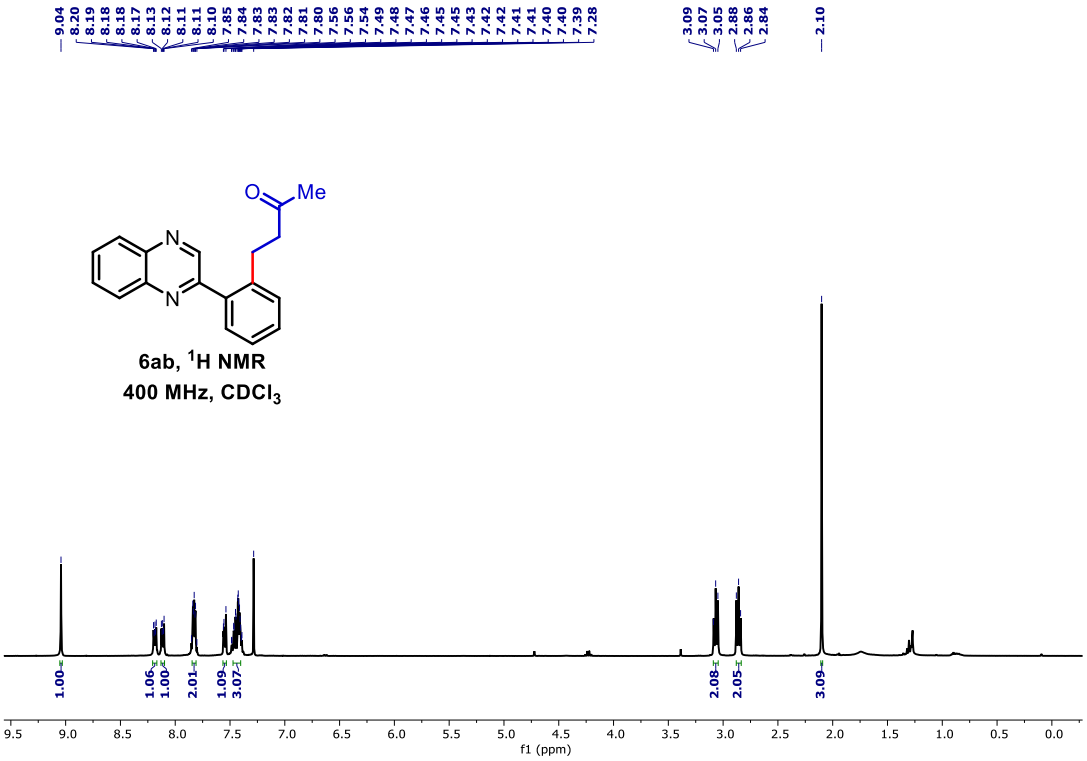
5gb, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

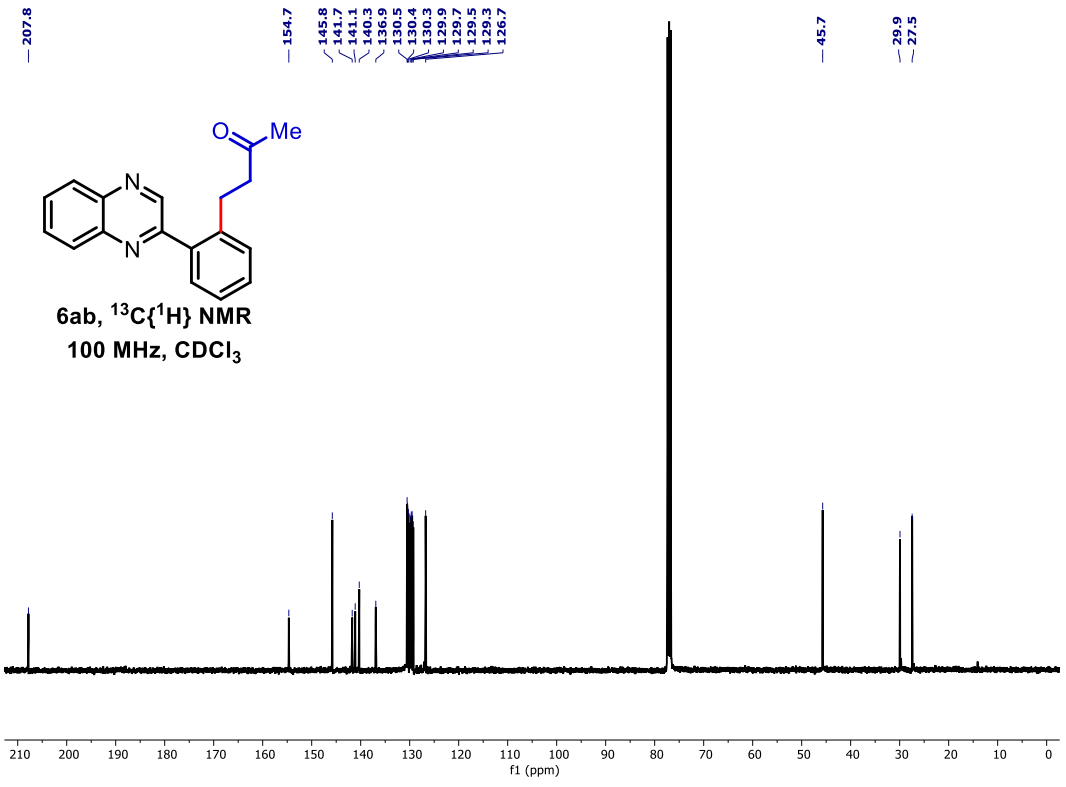


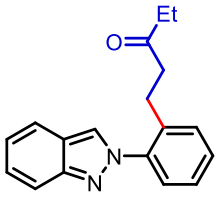
5hb, ^{1}H NMR
400 MHz, $CDCl_3$



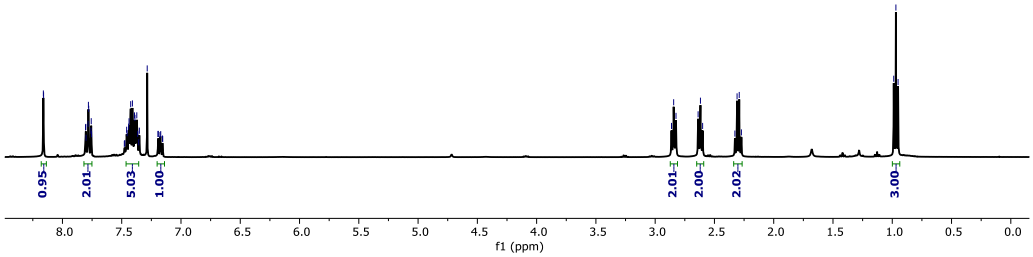
5hb, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$

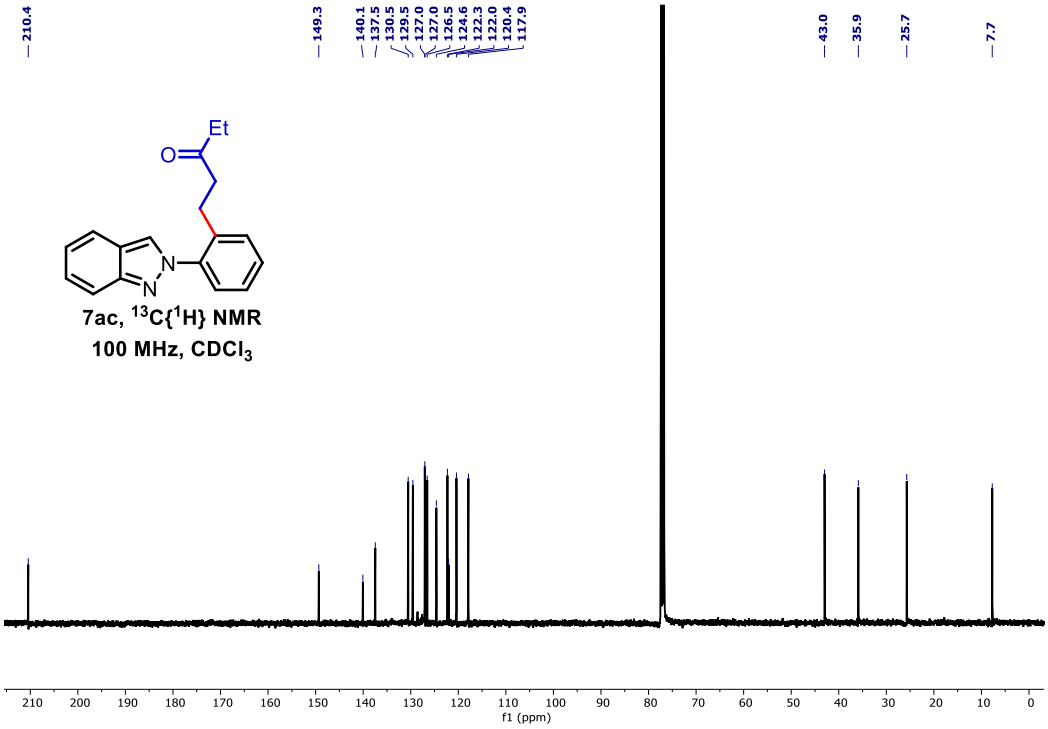

9.04
8.20
8.19
8.18
8.18
8.17
8.13
8.12
8.11
8.11
8.10
7.85
7.84
7.83
7.83
7.82
7.81
7.80
7.56
7.54
7.49
7.48
7.47
7.46
7.45
7.45
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.28
3.09
3.07
3.05
2.88
2.86
2.84
2.10
O
Me
N
N
6ab, 1H NMR
400 MHz, CDCl3
1.00
1.06
1.00
2.01
1.09
3.07
2.08
2.05
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.8
154.7
145.8
141.7
141.1
140.3
136.9
130.5
130.4
130.3
129.9
129.7
129.5
129.3
126.7
45.7
29.9
27.5
O
Me
N
N
6ab, 13C{1H} NMR
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

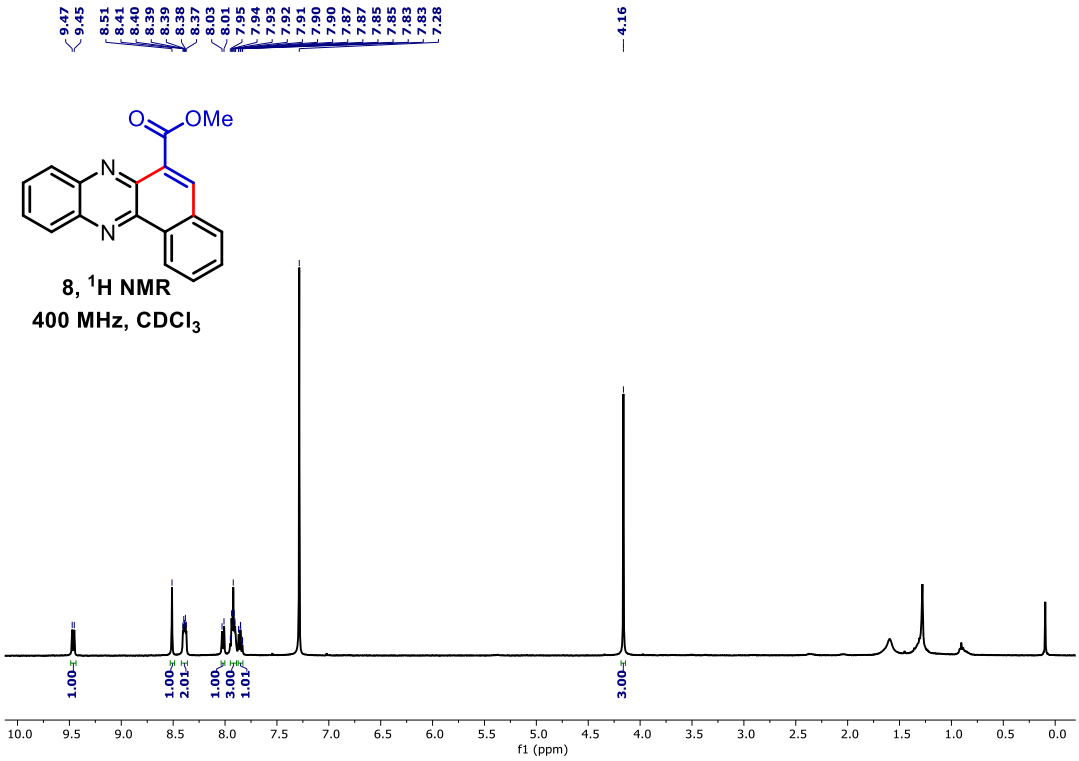


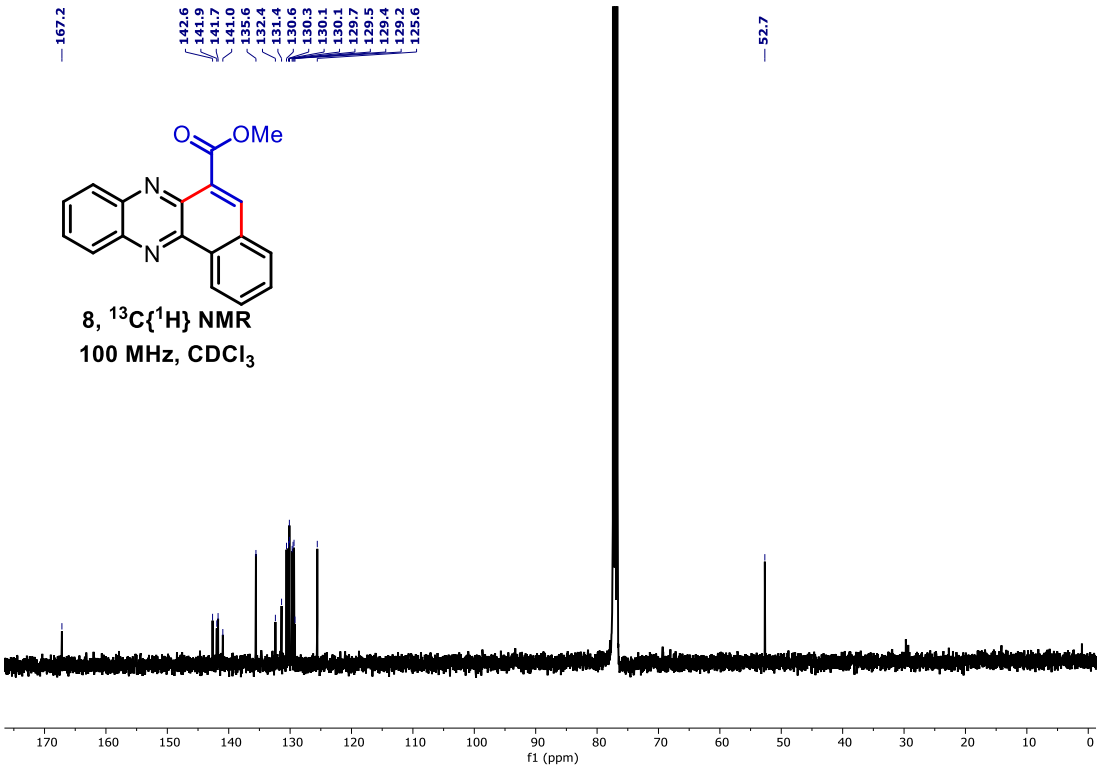
7ac, ^{1}H NMR
400 MHz, $CDCl_3$

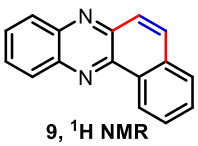




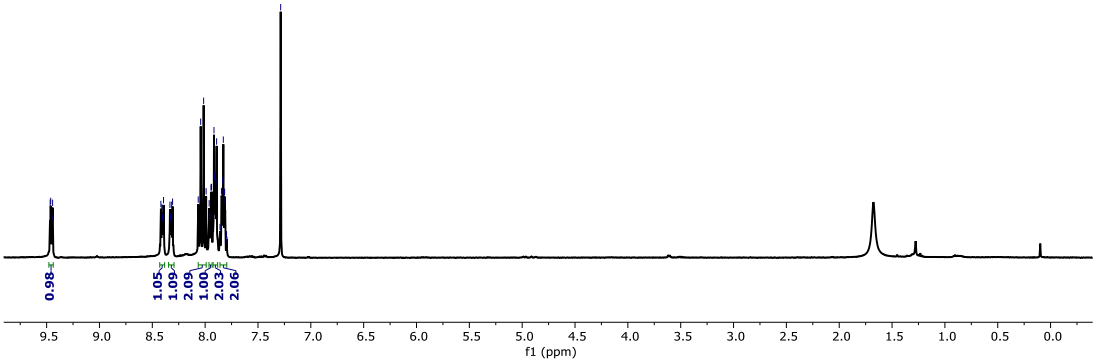
7ac, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

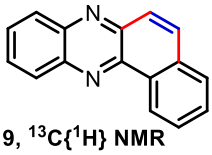

9.47
9.45
8.51
8.41
8.40
8.39
8.39
8.38
8.37
8.03
8.01
7.95
7.94
7.93
7.92
7.91
7.90
7.90
7.87
7.87
7.85
7.85
7.83
7.83
7.28
4.16
O
OMe
N
N
8, ^{1}H NMR
400 MHz, $CDCl_3$
1.00
1.00
2.01
1.00
3.00
1.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.2
142.6
141.9
141.7
141.0
135.6
132.4
131.4
130.6
130.3
130.1
130.1
129.7
129.5
129.4
129.2
125.6
52.7
O
OMe
N
N
8, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

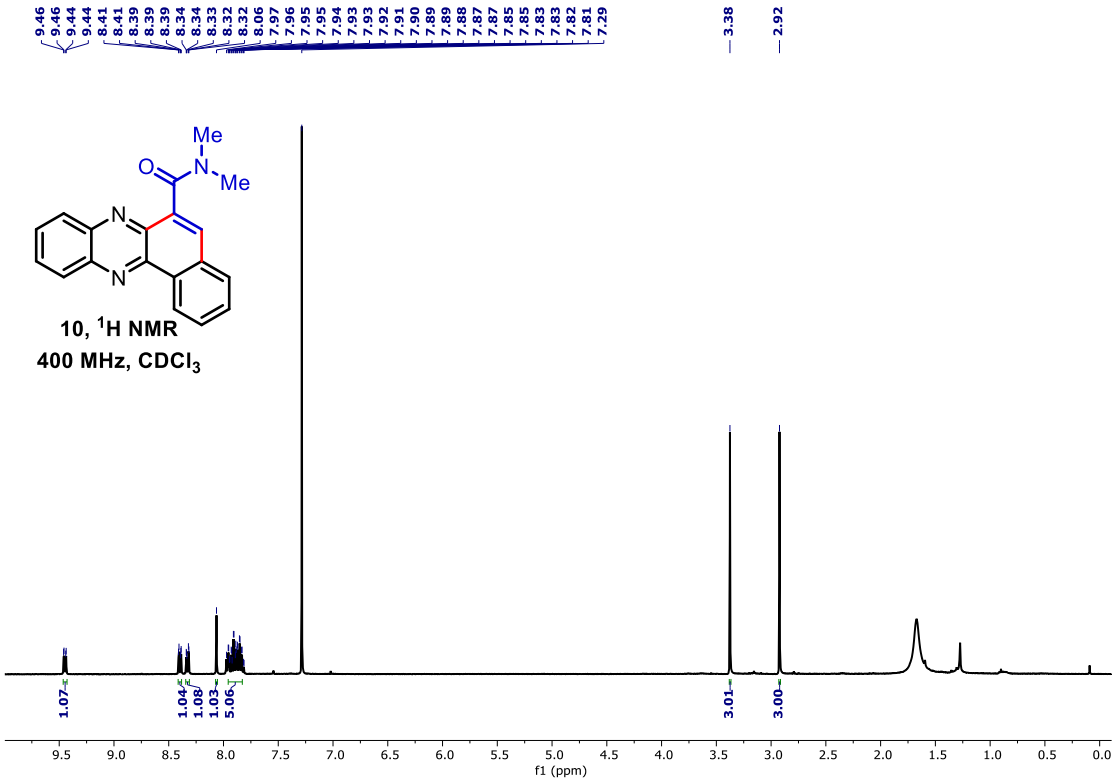


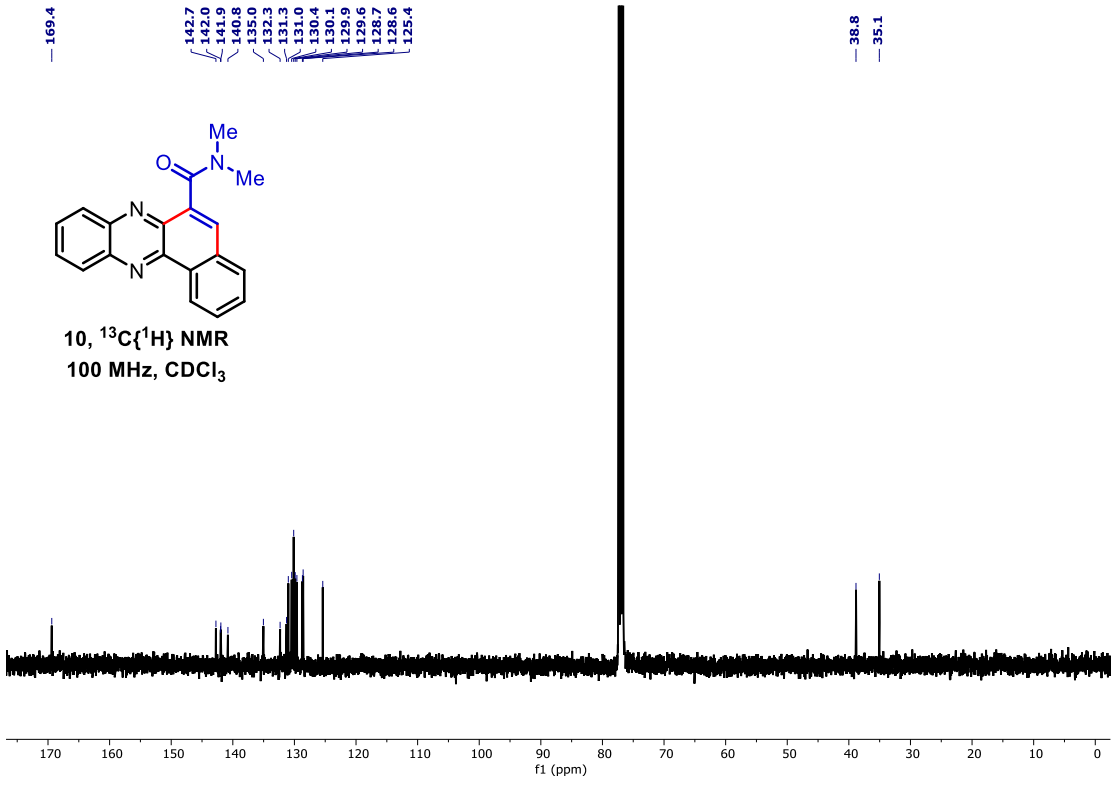
9, ^{1}H NMR
400 MHz, $CDCl_3$

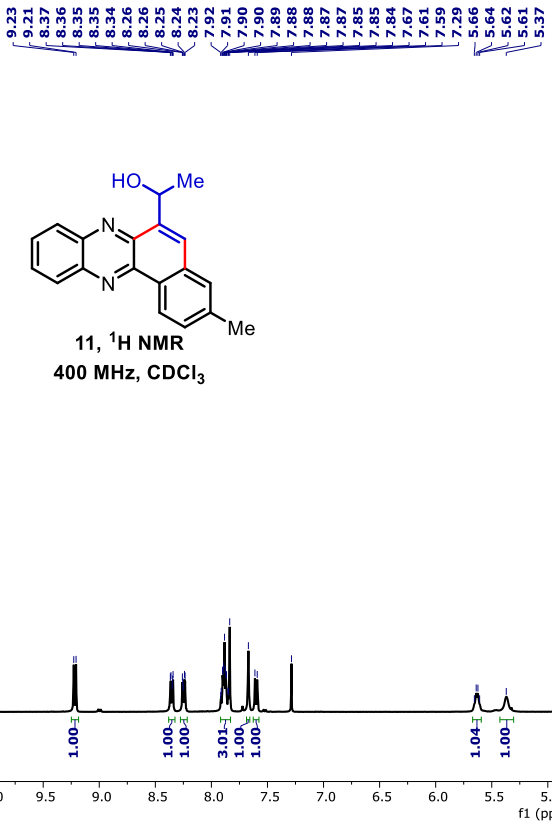


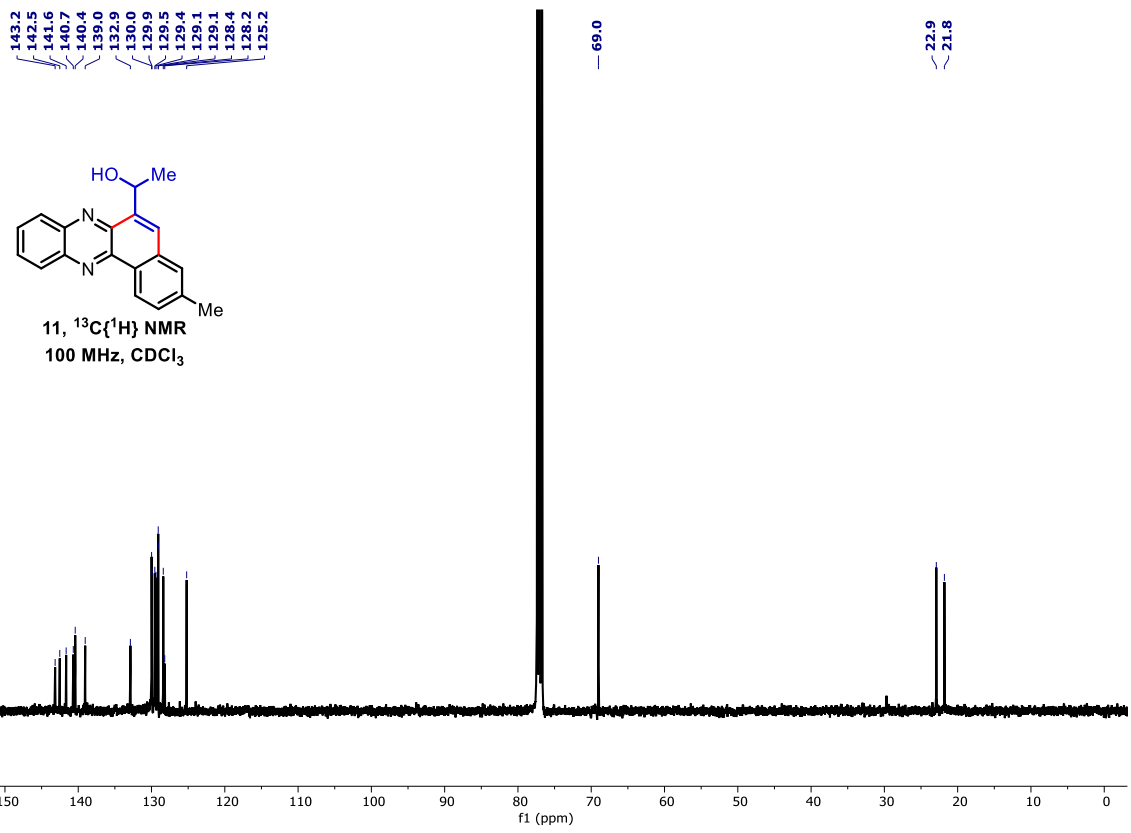


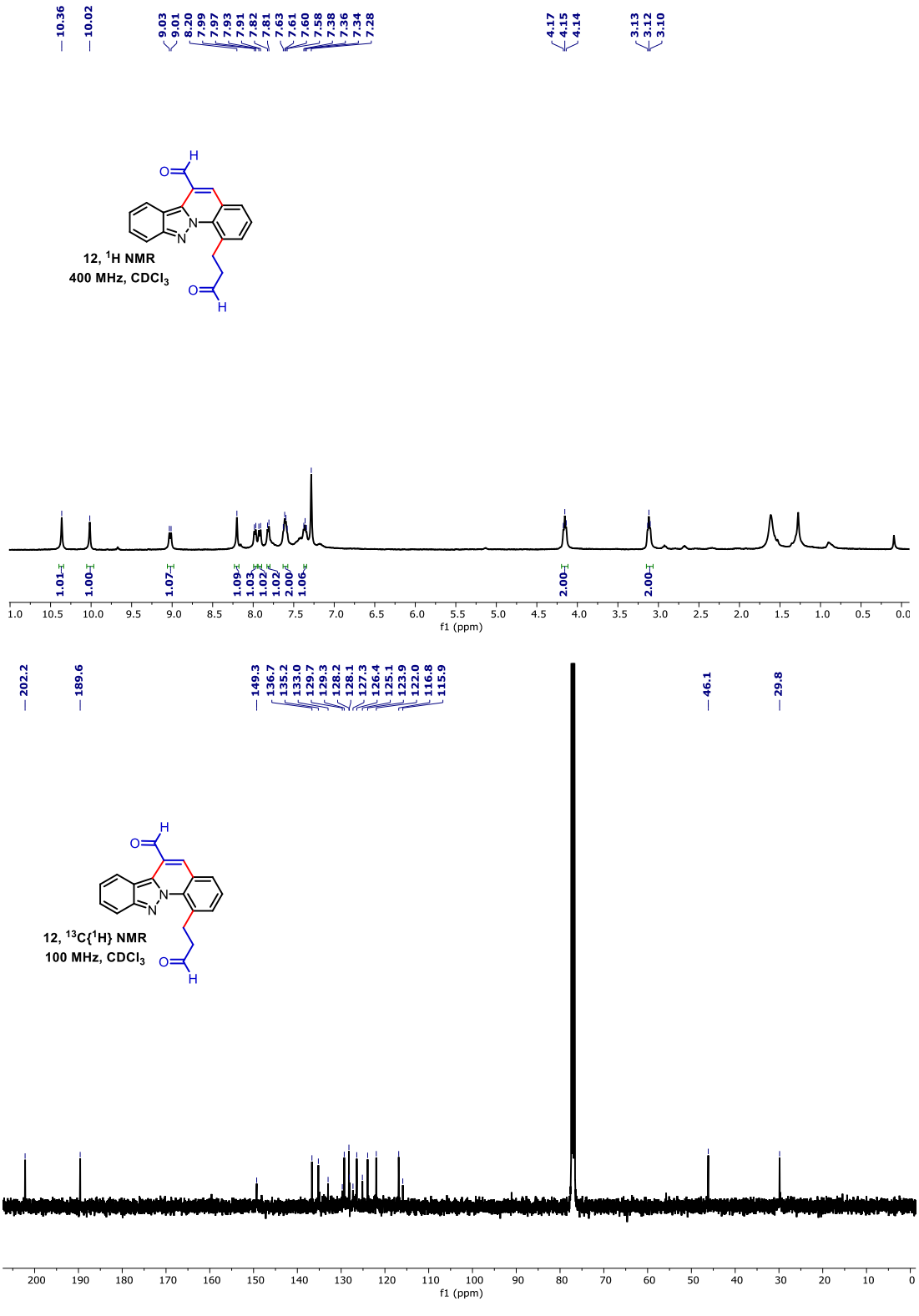
9, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$


9.46
9.46
9.44
9.44
8.41
8.41
8.39
8.39
8.39
8.34
8.34
8.33
8.32
8.32
8.06
7.97
7.96
7.95
7.95
7.94
7.93
7.93
7.92
7.91
7.90
7.89
7.89
7.88
7.87
7.87
7.85
7.85
7.83
7.83
7.82
7.81
7.29
3.38
2.92
Me
O
N
Me
N
N
10, ^{1}H NMR
400 MHz, CDCl$_3$
1.07
1.04
1.08
1.03
5.06
3.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.4
142.7
142.0
141.9
140.8
135.0
132.3
131.3
131.0
130.4
130.1
129.9
129.6
128.7
128.6
125.4
38.8
35.1
Me
O
N
Me
N
N
10, ^{13}C{^{1}H} NMR
100 MHz, CDCl$_3$
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.23
9.21
8.37
8.36
8.35
8.35
8.34
8.26
8.26
8.25
8.24
8.23
7.92
7.91
7.90
7.90
7.89
7.88
7.88
7.87
7.87
7.85
7.85
7.84
7.67
7.61
7.59
7.29
5.66
5.64
5.62
5.61
5.37
2.62
1.87
1.86
HO
Me
N
N
Me
11, ^{1}H NMR
400 MHz, CDCl$_3$
1.00
1.00
1.00
3.01
1.00
1.00
1.04
1.00
3.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.2
142.5
141.6
140.7
140.4
139.0
132.9
130.0
129.9
129.5
129.4
129.1
129.1
128.4
128.2
125.2
69.0
22.9
21.8
HO
Me
N
N
Me
11, ^{13}C{^{1}H} NMR
100 MHz, CDCl$_3$
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.36
10.02
9.03
9.01
8.20
7.99
7.97
7.93
7.91
7.82
7.81
7.63
7.61
7.60
7.58
7.38
7.36
7.34
7.28
4.17
4.15
4.14
3.13
3.12
3.10
12, 1H NMR
400 MHz, CDCl3
1.01
1.00
1.07
1.09
1.03
1.02
1.02
2.00
1.06
2.00
2.00
f1 (ppm)
202.2
189.6
149.3
136.7
135.2
133.0
129.7
129.3
128.2
128.1
127.3
126.4
125.1
123.9
122.0
116.8
115.9
46.1
29.8
12, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

14. Single crystal X-ray diffraction data of 5aa

Single crystals of [$C_{16}H_{10}N_2O$] **5aa** were grown from slow evaporation of chloroform: hexane solution. A suitable crystal was selected and mounted on a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The crystal was kept at 123(2) K during data collection. Using Olex2[5], the structure was solved with the SHELXT[6] structure solution program using Intrinsic Phasing and refined with the SHELXL[7] refinement package using Least Squares minimisation.

Table S3 Crystal data and structure refinement for 5aa

Empirical formula	$C_{16}H_{10}N_2O$
Formula weight	246.26
Temperature/K	123(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.0807(2)
b/Å	11.4488(3)
c/Å	13.0502(4)
α/°	75.453(2)
β/°	79.894(2)
γ/°	79.458(2)
Volume/Å^3	1138.21(6)
Z	4
ρ_{calc}g/cm^3	1.437
μ/mm^{-1}	0.736
F(000)	512.0
Crystal size/mm^3	0.19 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.064 to 159.736
Index ranges	$-9 \leq h \leq 6$, $-14 \leq k \leq 14$, $-16 \leq l \leq 15$
Reflections collected	12496
Independent reflections	4788 [R_{int} = 0.0315, R_{sigma} = 0.0394]
Data/restraints/parameters	4788/0/343
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1073
Final R indexes [all data]	R_1 = 0.0440, wR_2 = 0.1105
Largest diff. peak/hole / e Å^{-3}	0.21/-0.30

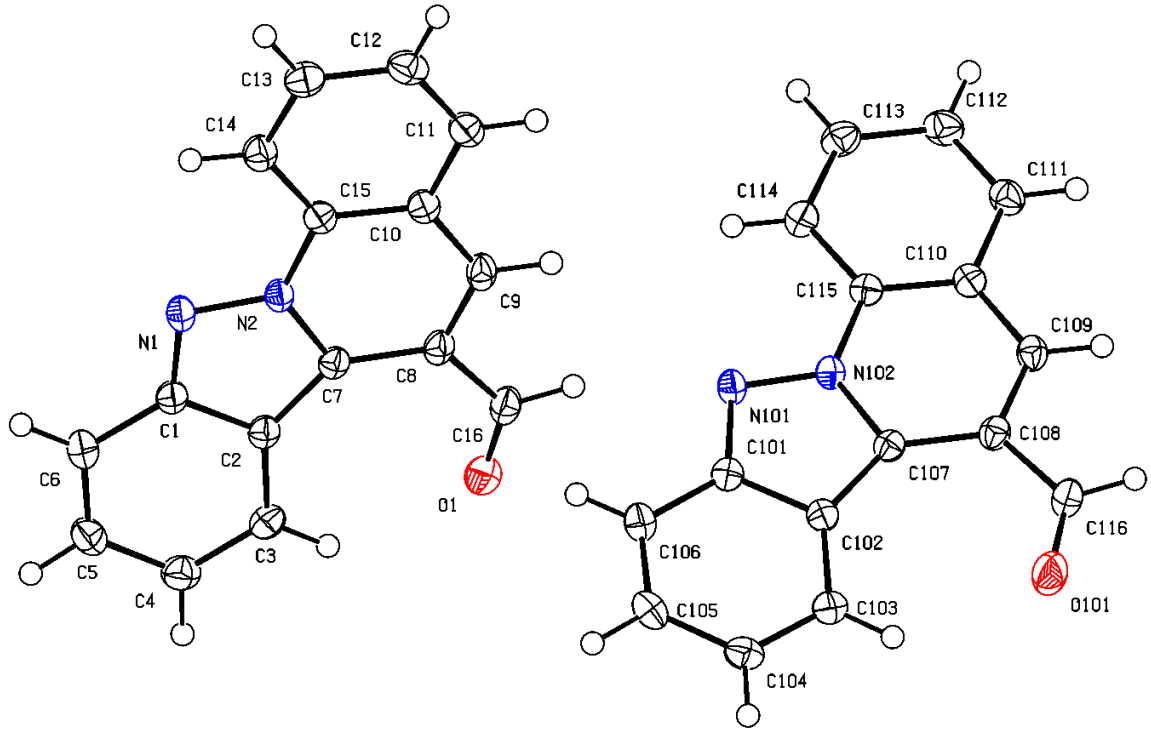


Figure S1. The ORTEP diagram of **5aa** [CCDC No 2294834].

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