Supporting Information

Oxoammonium salt-promoted diverse functionalization of saturated cyclic amines with dinucleophiles

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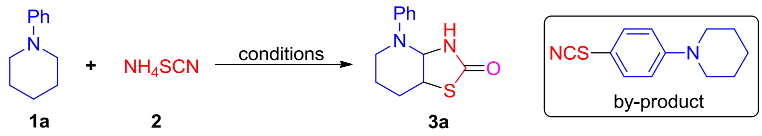
Contents

I. General experimental information

TEMPO salts were synthesized with a previously described procedure.[1] *N*-Aryl cyclic amines (**1**) were prepared based on a literature procedure.[2] Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz, and the ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz or 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High-resolution mass spectra (HRMS) were performed on a microTOF mass spectrometer. All the reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

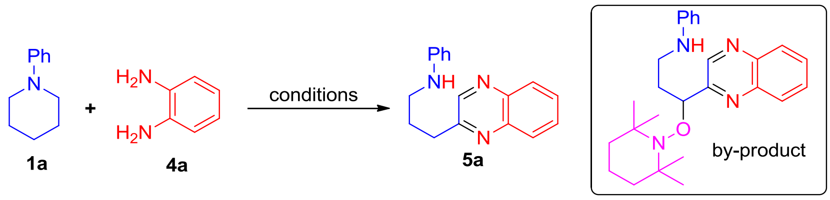
1. Optimization studies for the formation of 3a[a]



entry	oxoammonium salt (equiv)	additive (equiv)	solvent	yield (%)[b] **3a**
1	$T^+BF_4^-$ (2)	-	CH_3CN	20
2	$T^+BF_4^-$ (2)	-	THF	trace
3	$T^+BF_4^-$ (2)	-	DMF	trace
4	$T^+BF_4^-$ (2)	-	EtOAc	trace
5	$T^+BF_4^-$ (2)	-	acetone	34
6	$T^+BF_4^-$ (2)	-	acetone/H_2O = 49/1	30
7	$T^+ClO_4^-$(2)	-	acetone	21
8	$T^+PF_6^-$ (2)	-	acetone	24
9	T^+OTf^- (2)	-	acetone	40
10[c]	4-oxo-T^+OTf^- (2)	-	acetone	21
11[d]	4-OMe-T^+OTf^- (2)	-	acetone	42
12[e]	4-OH-T^+OTf^- (2)	-	acetone	48
13[f]	4-NHAc-T^+OTf^- (2)	-	acetone	trace
14[e]	4-OH-T^+OTf^- (3)	-	acetone	38
15[e]	4-OH-T^+OTf^- (2)	HOAc (0.2)	acetone	trace
16[e]	4-OH-T^+OTf^- (2)	TFA (0.2)	acetone	trace
17[e]	4-OH-T^+OTf^- (2)	H_3BO_3 (0.2)	acetone	40
18[e]	4-OH-T^+OTf^- (2)	K_2CO_3 (0.2)	acetone	24
19[e]	4-OH-T^+OTf^- (2)	Cs_2CO_3 (0.2)	acetone	20
20[e]	4-OH-T^+OTf^- (2)	DBU (0.2)	acetone	26
21[e,g]	4-OH-T^+OTf^- (2)	-	acetone	54
22[e,g,h]	4-OH-T^+OTf^- (2)	-	acetone	31
23[e,g,i]	4-OH-T^+OTf^- (2)	-	acetone	46
24[e,g,j]	4-OH-T^+OTf^- (2)	-	acetone	42
25[e,g,k]	**4-OH-T^+OTf^- (2)**	**-**	**acetone**	**62**

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), solvent (1 mL), rt, air, 6 h. [b] Isolated yield. [c] 4-oxo-T^+ (2,2,6,6-Tetramethyl-1,4-dioxopiperidin-1-ium). [d] 4-OMe-T^+ (4-Methoxy-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium). [e] 4-OH-T^+ (4-Hydroxy-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium). [f] 4-NHAc-T^+ (4-Acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium). [g] **2** (0.6 mmol). [h] 50 °C. [i] 0 °C. [j] Under O_2. [k] Under N_2, by-product 1-(4-thiocyanatophenyl)piperidine was obtained in a yield of 11%.

2. Optimization studies for the formation of 5a[a]



entry	oxoammonium salt (equiv)	additive (equiv)	solvent	yield (%)[b] **5a**
1	$T^+ClO_4^-$ (2)	KSCN (1)	EtOH	40
2	$T^+ClO_4^-$ (2)	KSCN (2)	EtOH	35
3	$T^+ClO_4^-$ (2)	-	EtOH	20
4	$T^+ClO_4^-$ (2)	KSCN (1)	DMF	50
5	$T^+ClO_4^-$ (2)	KSCN (1)	DMSO	30
6	$T^+ClO_4^-$ (2)	KSCN (1)	CH_3CN	21
7	$T^+ClO_4^-$ (2)	KSCN (1)	THF	18
8	$T^+ClO_4^-$ (2)	KSCN (1)	DCM	36
9[c]	**$T^+BF_4^-$ (2)**	**KSCN (1)**	**DMF**	**68**
10	$T^+PF_6^-$ (2)	KSCN (1)	DMF	54
11	T^+OTf^- (2)	KSCN (1)	DMF	40
12	$T^+BF_4^-$ (3)	KSCN (1)	DMF	67
13[d]	$T^+BF_4^-$ (2)	KSCN (1)	DMF	31
14[e]	$T^+BF_4^-$ (2)	KSCN (1)	DMF	60
15[f]	$T^+BF_4^-$ (2)	KSCN (1)	DMF	50
16[g]	$T^+BF_4^-$ (2)	KSCN (1)	DMF	62

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.4 mmol), solvent (1 mL), rt, air, 6 h. [b] Isolated yield. [c] By-product N-(3-(quinoxalin-2-yl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)aniline was obtained in a yield of 7%. [d] **4a** (0.6 mmol). [e] **4a** (0.3 mmol). [f] Under O_2. [g] Under N_2.

3. A typical procedure for the synthesis of 3a and the spectroscopic data of 3a-3q

To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), acetone (1 mL), NH_4SCN (**2**, 46 mg, 0.6 mmol), and 4-OH-T^+OTf^- (114 mg, 0.4 mmol). The resulting mixture was then stirred at room temperature under N_2 for 6 h. Upon completion, the mixture was diluted with ethyl acetate (10 mL × 3) and aqueous $NaHCO_3$ (10 mL, 1 M). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (3:1) as the eluent to afford **3a** as yellow solid in 29 mg (62%). **3b-3q** were obtained in an analogous manner.

4-Phenylhexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (3a)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (29 mg, 62%), mp 134-135 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32-7.30 (m, 2H), 6.99-6.96 (m, 3H), 5.68 (d, *J* = 5.4 Hz, 1H), 5.36 (br s, 1H), 3.72-3.68 (m, 1H), 3.38-3.35 (m, 1H), 3.19-3.15 (m, 1H), 2.21-2.18 (m, 1H), 1.98-1.90 (m, 2H), 1.74-1.56 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.4, 148.9, 129.8, 121.7, 117.4, 71.6, 44.1, 42.5, 29.5, 23.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}N_2OS$ 235.0900; Found 235.0892.

4-(*p*-Tolyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (3b)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (34 mg, 68%), mp 131-132 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 5.4 Hz, 1H), 5.35 (br s, 1H), 3.71-3.67 (m, 1H), 3.30-3.26 (m, 1H), 3.17-3.13 (m, 1H), 2.29 (s, 3H), 2.20-2.17 (m, 1H), 1.95-1.88 (m, 2H), 1.71-1.68 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.5, 146.6, 131.5, 130.2, 117.8, 72.1, 44.2, 42.8, 29.5, 23.8, 20.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2OS$ 249.1056; Found 249.1047.

4-(4-Ethylphenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (3c)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (34 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 5.62 (s, 1H), 5.36 (br s, 1H), 3.70-3.68 (m, 1H), 3.30-3.28 (m, 1H), 3.17-3.16 (m, 1H), 2.59 (q, *J* = 7.2 Hz, 2H), 2.19-2.17 (m, 1H), 1.94-1.89 (m, 2H), 1.71-1.69 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.5, 146.8, 138.0, 129.0, 117.8, 72.1, 44.2, 42.8, 29.5, 28.0, 23.8, 15.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}N_2OS$ 263.1213; Found 263.1211.

4-(4-(*Tert*-butyl)phenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (3d)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (36 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H), 6.94-6.90 (m, 2H), 5.63 (d, *J* = 5.6 Hz, 1H), 5.36 (br s, 1H), 3.71-3.66 (m, 1H), 3.34-3.29 (m, 1H), 3.18-3.12 (m, 1H), 2.20-2.16 (m, 1H), 1.98-1.87 (m, 2H), 1.74-1.67 (m, 1H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.4, 146.4, 144.7, 126.5, 117.2, 71.9, 44.2, 42.6, 34.1, 31.4, 29.5, 23.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}N_2OS$ 291.1526; Found 291.1524.

4-(4-Methoxyphenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3e**)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (38 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.96-6.94 (m, 2H), 6.87-6.85 (m, 2H), 5.45 (d, *J* = 4.8 Hz, 1H), 5.38 (br s, 1H), 3.78 (s, 3H), 3.73-3.69 (m, 1H), 3.18-3.13 (m, 2H), 2.18-2.15 (m, 1H), 1.96-1.88 (m, 2H), 1.72-1.68 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.7, 155.3, 142.8, 120.3, 114.9, 73.2, 55.6, 44.3, 43.6, 29.4, 23.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2O_2S$ 265.1005; Found 265.0999.

4-(4-Fluorophenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3f**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (23 mg, 45%), mp 120-121 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02-6.94 (m, 4H), 5.56 (br s, 1H), 5.51 (d, *J* = 5.4 Hz, 1H), 3.72-3.68 (m, 1H), 3.22-3.15 (m, 2H), 2.20-2.15 (m, 1H), 1.96-1.88 (m, 2H), 1.73-1.66 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.6, 158.2 (d, $^1J_{C-F}$ = 240.9 Hz), 145.4 (d, $^4J_{C-F}$ = 3.3 Hz), 119.9 (d, $^3J_{C-F}$ = 8.7 Hz), 116.2 (d, $^2J_{C-F}$ = 21.9 Hz), 72.6, 44.2, 43.3, 29.3, 23.7. ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz): δ -121.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}FN_2OS$ 253.0805; Found 253.0797.

4-(4-Chlorophenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3g**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (27 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.25 (m, 2H), 6.91-6.89 (m, 2H), 5.62 (d, *J* = 5.4 Hz, 1H), 5.39 (br s, 1H), 3.71-3.67 (m, 1H), 3.33-3.30 (m, 1H), 3.17-3.13 (m, 1H), 2.20-2.17 (m, 1H), 1.97-1.90 (m, 2H), 1.73-1.68 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.3, 147.5, 129.7, 126.7, 118.6, 71.4, 44.0, 42.7, 29.3, 23.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}ClN_2OS$ 269.0510; Found 269.0501.

4-(4-Bromophenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3h**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (36 mg, 58%), mp 136-137 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.62 (d, J = 5.4 Hz, 1H), 5.40 (br s, 1H), 3.71-3.67 (m, 1H), 3.34-3.32 (m, 1H), 3.17-3.13 (m, 1H), 2.19-2.17 (m, 1H), 1.97-1.90 (m, 2H), 1.71-1.68 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.3, 147.9, 132.6, 118.9, 114.0, 71.2, 44.0, 42.5, 29.3, 23.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}BrN_2OS$ 313.0005; Found 313.0000.

4-(4-Iodophenyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3i**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (40 mg, 55%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 6.75-6.72 (m, 2H), 5.63 (d, J = 5.4 Hz, 1H), 5.42 (br s, 1H), 3.70-3.66 (m, 1H), 3.36-3.33 (m, 1H), 3.16-3.12 (m, 1H), 2.20-2.17 (m, 1H), 1.96-1.90 (m, 2H), 1.72-1.67 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.2, 148.5, 138.5, 119.1, 83.7, 70.9, 44.0, 42.3, 29.3, 23.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}IN_2OS$ 360.9866; Found 360.9853.

4-(*m*-Tolyl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3j**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (29 mg, 58%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, J = 8.0 Hz, 1H), 6.79-6.77 (m, 3H), 5.67 (d, J = 4.8 Hz, 1H), 5.32 (br s, 1H), 3.71-3.66 (m, 1H), 3.38-3.33 (m, 1H), 3.19-3.12 (m, 1H), 2.33 (s, 3H), 2.21-2.17 (m, 1H), 1.98-1.88 (m, 2H), 1.72-1.67 (m, 1H).$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.3, 148.9, 139.6, 129.6, 122.6, 118.2, 114.5, 71.7, 44.1, 42.6, 29.6, 23.8, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2OS$ 249.1056; Found 249.1043.

4-([1,1'-Biphenyl]-4-yl)hexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3k**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (32 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.72 (d, *J* = 5.6 Hz, 1H), 5.48 (br s, 1H), 3.73-3.68 (m, 1H), 3.45-3.41 (m, 1H), 3.23-3.16 (m, 1H), 2.22-2.16 (m, 1H), 2.00-1.91 (m, 2H), 1.77-1.68 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.3, 148.1, 140.4, 134.4, 128.8, 128.3, 127.0, 126.7, 117.4, 71.3, 44.1, 42.5, 29.5, 23.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2OS$ 311.1213; Found 311.1200.

4-Mesitylhexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3l**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (26 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 2H), 5.20 (br s, 1H), 5.00 (d, *J* = 5.2 Hz, 1H), 3.92-3.88 (m, 1H), 3.34-3.28 (m, 1H), 2.96-2.90 (m, 1H), 2.27 (s, 6H), 2.24 (s, 3H), 2.15-2.04 (m, 2H), 1.96-1.91 (m, 1H), 1.67-1.64 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.1, 142.8, 137.4, 136.0, 135.9, 130.1, 130.0, 72.5, 46.5, 44.8, 28.6, 24.2, 20.7, 19.3, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}N_2OS$ 277.1369; Found 277.1364.

7-Methyl-4-phenylhexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3m**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (26 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 6.99-6.94 (m, 3H), 5.75 (d, *J* = 5.2 Hz, 1H), 5.34 (br s, 1H), 3.42-3.38 (m, 1H), 3.23-3.14 (m, 2H), 2.00-1.85 (m, 2H), 1.51-1.40 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.4, 148.7, 129.8, 121.6, 117.2, 72.1, 52.3, 42.9, 35.1, 32.5, 20.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2OS$ 249.1056; Found 249.1051.

4-(4-Methoxyphenyl)-7-methylhexahydrothiazolo[4,5-*b*]pyridin-2(3*H*)-one (**3n**)

Eluent: petroleum ether/ethyl acetate (3:1). Brown liquid (31 mg, 56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.94 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.58 (d, *J* = 4.8 Hz, 1H), 5.35 (br s, 1H), 3.80-3.77 (m, 3H), 3.21-3.15 (m, 3H), 1.95-1.91 (m, 1H), 1.87-1.85 (m, 1H), 1.47-1.44 (m, 1H), 1.10 (d, J = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 155.1, 142.6, 119.8, 115.0, 73.7, 55.6, 52.4, 43.5, 35.1, 32.6, 20.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}N_2O_2S$ 279.1162; Found 279.1150.

4-(4-Fluoro phenyl)hexahydro-2*H*-pyrrolo[2,3-*d*]thiazol-2-one (**3o**)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (16 mg, 33%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.02-6.97 (m, 2H), 6.60-6.57 (m, 2H), 6.34 (br s, 1H), 5.66 (d, J = 7.2 Hz, 1H), 4.48-4.43 (m, 1H), 3.63-3.57 (m, 1H), 3.44-3.39 (m, 1H), 2.55-2.50 (m, 1H), 2.30-2.25 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.7, 156.4 (d, $^1J_{C\text{-}F}$ = 236.3 Hz), 141.5 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 116.4 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 114.1 (d, $^3J_{C\text{-}F}$ = 6.5 Hz), 72.9, 46.9, 45.8, 33.1. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz): δ -128.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}FN_2OS$ 239.0649; Found 239.0657.

4-(4-Chlorophenyl)hexahydro-2*H*-pyrrolo[2,3-*d*]thiazol-2-one (**3p**)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (21 mg, 41%), mp 118-119 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H), 6.56 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 2H), 6.31 (br s, 1H), 5.65 (d, J = 7.2 Hz, 1H), 4.49-4.44 (m, 1H), 3.65-3.59 (m, 1H), 3.47-3.42 (m, 1H), 2.55-2.50 (m, 1H), 2.31-2.26 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.5, 143.5, 129.7, 123.7, 114.1, 72.4, 46.9, 45.7, 32.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}ClN_2OS$ 255.0353; Found 255.0347.

4-(2-Oxohexahydro-4*H*-pyrrolo[2,3-*d*]thiazol-4-yl)benzonitrile (**3q**)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (15 mg, 30%), mp 200-201 ℃. ^1H NMR (400 MHz, acetone-d_6): δ 8.08 (br s, 1H), 7.57-7.54 (m, 2H), 6.91-6.87 (m, 2H), 5.83 (dd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 4.74-4.69 (m, 1H), 3.81-3.75 (m, 1H), 3.67-3.61 (m, 1H), 2.62-2.55 (m, 1H), 2.33-2.28 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, acetone-d_6): δ 171.3, 148.5, 133.3, 119.6, 113.2, 99.3, 72.4, 47.4, 46.1, 31.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}N_3OS$ 246.0696; Found 246.0696.

4. A typical procedure for the synthesis of 5a and the spectroscopic data of 5a-5s

To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), DMF (1 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *o*-phenylenediamine (**4a**, 43 mg, 0.4 mmol), and KSCN (19 mg, 0.2 mmol). The resulting mixture was then stirred at room temperature under air for 6 h. Upon completion, the mixture was diluted with ethyl acetate and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **5a** as brown solid in 36 mg (68%). **5b-5s** were obtained in an analogous manner.

***N*-(3-(Quinoxalin-2-yl)propyl)aniline (5a)**

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (36 mg, 68%), mp 78-79 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.10-8.04 (m, 2H), 7.76-7.71 (m, 2H), 7.18-7.14 (m, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 3.88 (br s, 1H), 3.28 (t, *J* = 6.8 Hz, 2H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.24-2.20 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.7, 148.2, 145.8, 142.2, 141.3, 130.1, 129.3, 129.2, 129.1, 128.9, 117.4, 112.8, 43.4, 33.8, 28.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}N_3$ 264.1495; Found 264.1486.

4-Methyl-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5b)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (33 mg, 60%), mp 107-108 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.09-8.03 (m, 2H), 7.77-7.69 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 3.70 (br s, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.23-2.16 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.8, 145.9, 145.8, 142.2, 141.3, 130.1, 129.8, 129.3, 129.1, 128.9, 126.7, 113.1, 43.8, 33.8, 28.7, 20.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3$ 278.1652; Found 278.1641.

4-Fluoro-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5c)

Eluent: petroleum ether/ethyl acetate (2:1). Brown liquid (42 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 5.2 Hz, 1H), 8.10-8.03 (m, 2H), 7.78-7.70 (m, 2H), 6.90-6.84 (m, 2H), 6.56-6.51 (m, 2H), 3.78 (br s, 1H), 3.23 (t, *J* = 6.8 Hz, 2H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.24-2.17 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.6, 155.8 (d, $^1J_{C-F}$ = 233.3 Hz), 145.9, 144.5 (d, $^4J_{C-F}$ = 2.1 Hz), 142.2, 141.3, 130.1, 129.2 (d, $^3J_{C-F}$ = 9.4 Hz), 128.9, 115.7 (d, $^2J_{C-F}$ = 22.3 Hz), 113.6, 113.5, 44.1, 33.7, 28.5. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz): δ -128.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}FN_3$ 282.1401; Found 282.1392.

4-Chloro-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5d)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (39 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.10-8.03 (m, 2H), 7.77-7.72 (m, 2H), 7.10 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 6.52 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 3.99 (br s, 1H), 3.24 (t, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.23-2.19 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.5, 146.6, 145.8, 142.1, 141.3, 130.2, 129.3, 129.2, 129.1, 128.8, 122.0, 113.9, 43.6, 33.6, 28.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}ClN_3$ 298.1106; Found 298.1091.

4-Bromo-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5e)

Eluent: petroleum ether/ethyl acetate (2:1). Brown liquid (49 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.09-8.03 (m, 2H), 7.78-7.70 (m, 2H), 7.24-7.21 (m, 2H), 6.47 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H), 3.92 (br s, 1H), 3.23 (t, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.23-2.18 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.5, 147.2, 145.8, 142.1, 141.3, 132.0, 130.2, 129.3, 129.2, 128.9, 114.3, 108.9, 43.4, 33.7, 28.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_3$ 342.0600; Found 342.0576.

3-Methyl-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5f)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (31 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.10-8.04 (m, 2H), 7.76-7.71 (m, 2H), 7.07-7.03 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.44-6.42 (m, 2H), 3.76 (br s, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.26-2.19 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.7, 148.2, 145.8, 142.2, 141.3, 139.1, 130.1, 129.2, 129.15, 129.1, 128.9, 118.3, 113.6, 110.0, 43.4, 33.8, 28.7, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3$ 278.1652; Found 278.1637.

3-Bromo-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5g)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (42 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.03-7.98 (m, 2H), 7.72-7.64 (m, 2H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.75 (t, *J* = 0.8 Hz, 1H), 6.73-6.69 (m, 1H), 6.47 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 3.19 (t, *J* = 6.8 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.19-2.11 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.4, 149.2, 145.8, 142.1, 141.4, 130.5, 130.2, 129.3, 129.2, 128.8, 123.4, 120.3, 115.4, 111.8, 43.4, 33.6, 28.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_3$ 342.0600; Found 342.0580.

2-Fluoro-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5h)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (37 mg, 66%), mp 88-89 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.10-8.05 (m, 2H), 7.78-7.70 (m, 2H), 7.00-6.92 (m, 2H), 6.73-6.84 (m, 1H), 6.63-6.59 (m, 1H), 4.14 (br s, 1H), 3.32 (t, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.29-2.22 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.5, 151.6 (d, $^1J_{C\text{-}F}$ = 237.3 Hz), 145.8, 142.2, 141.3, 136.7 (d, $^2J_{C\text{-}F}$ = 12.0 Hz), 130.1, 129.2 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 128.9, 124.6 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 116.5 (d, $^3J_{C\text{-}F}$ = 6.6 Hz), 114.4 (d, $^2J_{C\text{-}F}$ = 18.6 Hz), 112.0, 111.9, 43.1, 33.6, 28.4.

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz):δ -136.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}FN_3$ 282.1401; Found 282.1395.

2-Chloro-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5i)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (36 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.09-8.03 (m, 2H), 7.75-7.67 (m, 2H), 7.23-7.20 (m, 1H), 7.11 (d, J = 7.2 Hz, 1H), 6.66 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 6.61-6.57 (m, 1H), 4.45 (br s, 1H), 3.31 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 2.28-2.21 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.4, 145.8, 143.9, 142.2, 141.4, 130.1, 129.3, 129.2, 129.1, 128.9, 127.8, 110.1, 117.2, 111.2, 43.1, 33.6, 28.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}ClN_3$ 298.1106; Found 298.1086.

2-Bromo-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5j)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (34 mg, 50%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.09-8.05 (m, 2H), 7.77-7.71 (m, 2H), 7.40 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.18-7.15 (m, 1H), 6.66 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 6.57-6.54 (m, 1H), 4.44 (br s, 1H), 3.35-3.32 (m, 2H), 3.17 (t, J = 7.2 Hz, 2H), 2.31-2.25 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.4, 145.8, 144.8, 142.2, 141.3, 132.4, 130.1, 129.2, 129.1, 128.9, 128.5, 117.7, 111.3, 109.7, 43.2, 33.6, 28.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_3$ 342.0600; Found 342.0576.

2-Methyl-*N*-(3-(quinoxalin-2-yl)propyl)aniline (5k)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (30 mg, 54%), mp 63-64 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.09-8.04 (m, 2H), 7.77-7.69 (m, 2H), 7.13-7.09 (m, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.66-6.62 (m, 2H), 3.65 (br s, 1H), 3.32 (t, J = 6.8 Hz, 2H), 3.17 (t, J = 6.8 Hz, 2H), 2.31-2.23 (m, 2H), 2.09 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.8, 146.1, 145.9, 142.2, 141.4, 130.2, 130.1, 129.3, 129.2, 128.9, 127.2, 122.0, 117.0, 109.7, 43.4, 33.9, 28.5, 17.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3$ 278.1652; Found 278.1644.

***N*-(3-(Quinoxalin-2-yl)propyl)naphthalen-1-amine (5l)**

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (30 mg, 48%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.79-7.72 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.37-7.32 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.64 (br s, 1H), 3.45 (t, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 7.2 Hz, 2H), 2.40-2.38 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.8, 145.9, 143.3, 142.2, 141.4, 134.3, 130.1, 129.3, 129.2, 128.9, 128.6, 126.6, 125.7, 124.6, 123.4, 119.9, 117.3, 104.2, 43.8, 34.0, 28.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}N_3$ 314.1652, Found 314.1647.

N-(3-(Quinoxalin-2-yl)propyl)-[1,1'-biphenyl]-4-amine (5m)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (38 mg, 56%), mp 97-98 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.10-8.04 (m, 2H), 7.78-7.69 (m, 2H), 7.54-7.51 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24-7.22 (m, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.92 (br s, 1H), 3.32 (t, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 7.6 Hz, 2H), 2.27-2.20 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.7, 147.6, 145.9, 142.2, 141.4, 141.3, 130.3, 130.2, 129.3, 129.2, 128.9, 128.7, 128.0, 126.3, 126.1, 113.1, 43.5, 33.8, 28.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}N_3$ 340.1808; Found 340.1796.

***N*-(3-(Quinoxalin-2-yl)butyl)aniline (5n)**

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (35 mg, 63%), mp 79-80 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.07 (t, *J* = 8.0 Hz, 2H), 7.77-7.70 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 2H), 3.66 (br s, 1H), 3.35-3.30 (m, 1H), 3.16-3.13 (m, 2H), 2.32-2.27 (m, 1H), 2.09-2.04 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 160.6, 148.2, 145.3, 142.3, 141.6, 130.2, 129.4, 129.34, 129.3, 129.2, 117.5, 113.0, 42.2, 38.3, 36.0, 21.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3$ 278.1652; Found 278.1643.

4-Fluoro-*N*-(3-(quinoxalin-2-yl)butyl)aniline (5o)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (38 mg, 64%), mp 67-68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.09-8.04 (m, 2H), 7.77-7.69 (m, 2H), 6.83 (t, J = 8.4 Hz, 2H), 6.47-6.44 (m, 2H), 3.57 (br s, 1H), 3.34-3.29 (m, 1H), 3.11-3.07 (m, 2H), 2.31-2.26 (m, 1H), 2.07-2.02 (m, 1H), 1.46 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 160.4, 155.8 (d, $^1J_{C\text{-}F}$ = 233.0 Hz), 145.1, 144.5, 142.1, 141.5, 130.0, 129.2 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 129.0, 115.6 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 113.6 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 42.7, 38.2, 35.7, 20.8. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ -128.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}FN_3$ 296.1558; Found 296.1547.

4-Methyl-*N*-(4-(quinoxalin-2-yl)butan-2-yl)aniline (5p)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (32 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.09-8.03 (m, 2H), 7.76-7.70 (m, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 8.4 Hz, 2H), 3.62-3.58 (m, 1H), 3.16-3.12 (m, 2H), 2.22 (s, 3H), 2.11-2.05 (m, 2H), 1.26 (d, J = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 157.2, 145.9, 145.1, 142.2, 141.2, 130.0, 129.8, 129.2, 129.1, 128.8, 126.4, 113.5, 48.7, 36.3, 33.1, 21.1, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}N_3Na$ 314.1628; Found 314.1628.

***N*-(3-(8-Methylquinoxalin-2-yl)propyl)aniline/*N*-(3-(5-methylquinoxalin-2-yl)propyl)aniline (5q/5q')**

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (34 mg, 61%, regio-isomers: 4/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 0.2H), 8.71 (s, 0.8H), 7.92-7.90 (m, 1H), 7.64-7.56 (m, 2H), 7.18-7.14 (m, 2H), 6.71-6.67 (m, 1H), 6.61 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 2H), 3.92 (br s, 1H), 3.30-3.25 (m, 2H), 3.17-3.12 (m, 2H), 2.79 (s, 3H), 2.27-2.18 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.3, 148.3, 145.3, 144.4, 141.3, 141.2, 137.2, 130.0, 129.9, 129.3, 129.2, 128.8, 127.0, 126.7, 117.4, 117.3, 112.8, 43.4, 43.3, 33.7, 33.5, 28.7, 28.2, 17.3, 17.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3$ 278.1652; Found 278.1637.

***N*-(3-(7-Fluoroquinoxalin-2-yl)propyl)aniline/*N*-(3-(6-Fluoroquinoxalin-2-yl)propyl)aniline (5r/5r')**

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (29 mg, 52%, regio-isomers: 3/1). ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.09-8.05 (m, 1H), 7.68-7.65 (m, 1H), 7.51-7.46 (m, 1H), 7.18-7.14 (m, 2H), 6.69 (t, J = 7.2 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 3.86 (br s, 1H), 3.27 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 2.24-2.17 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 162.9 (d, $^1J_{C\text{-}F}$ = 250.5 Hz), 157.6, 148.1, 146.6, 145.1 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 143.1, 143.0, 138.5, 131.3 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 130.9 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 120.4 (d, $^2J_{C\text{-}F}$ = 26.3 Hz), 119.5 (d, $^2J_{C\text{-}F}$ = 27.9 Hz), 117.5, 112.9, 112.8, 112.7, 112.6, 112.4, 43.4, 33.7, 33.6, 28.6, 28.5. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz):δ -108.0, -109.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}FN_3$ 282.1401; Found 282.1390.

***N*-(3-(7-Bromoquinoxalin-2-yl)propyl)aniline or *N*-(3-(6-Bromoquinoxalin-2-yl)propyl)aniline (5s or 5s')**

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (28 mg, 41%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.26 (d, J = 2.0 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.83 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.19-7.15 (m, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.62-6.60 (m, 2H), 3.82 (br s, 1H), 3.28 (t, J = 7.2 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 2.24-2.17 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 157.7, 148.1, 146.1, 142.8, 140.1, 132.7, 131.3, 130.6, 129.3, 124.1, 117.5, 112.8, 43.3, 33.7, 28.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_3$ 342.0600; Found 342.0585.

***N*-(3-(7-Bromoquinoxalin-2-yl)propyl)aniline or *N*-(3-(6-Bromoquinoxalin-2-yl)propyl)aniline (5s or 5s')**

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (12 mg, 18%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.23 (d, *J* = 1.8 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.79 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.18-7.16 (m, 2H), 6.70 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 3.82 (br s, 1H), 3.27 (t, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.21-2.18 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 157.1, 148.1, 146.6, 141.9, 141.0, 133.6, 131.6, 130.2, 129.3, 122.9, 117.5, 112.8, 43.3, 33.7, 28.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_3$ 342.0600; Found 342.0580.

5. A typical procedure for the synthesis of 6a and the spectroscopic data of 6a-6f

To a reaction tube equipped with a stir bar were added 1-phenyl-1,2,3,4,10,10a-hexahydropyrido[2,3-*b*]quinoxaline (**5a**, 53 mg, 0.2 mmol), THF (1 mL), ^{t}BuONO (80 μL, 0.6 mmol, 90%). The resulting mixture was then stirred at rt under air for 12 h. Upon completion, the mixture was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (3:1) as the eluent to afford **6a** as yellow liquid in 36 mg (58%). **6b-6f** were obtained in an analogous manner.

***N*-(3-Oxo-3-(quinoxalin-2-yl)propyl)-*N*-phenylnitrous amide (6a)**

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (36 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 8.18-8.13 (m, 2H), 7.92-7.83 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.50-7.47 (m, 2H), 7.40-7.36 (m, 1H), 4.52 (t, *J* = 7.2 Hz, 2H), 3.64 (t, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 198.7, 145.7, 144.1, 142.9, 141.4, 140.9, 132.5, 131.0, 130.4, 129.6, 129.5, 127.6, 119.8, 39.9, 34.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N_4O_2$ 307.1190; Found 307.1188.

***N*-(3-Oxo-3-(quinoxalin-2-yl)propyl)-*N*-(*p*-tolyl)nitrous amide (6b)**

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (27 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 8.19-8.13 (m, 2H), 7.93-7.86 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.50 (t, *J* = 7.2 Hz, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (150

MHz, $CDCl_3$): δ 198.7, 145.7, 142.9, 140.9, 139.0, 137.8, 132.5, 130.9, 130.5, 130.2, 129.5, 120.0, 40.2, 34.6, 21.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_4O_2$ 321.1346; Found 321.1347.

***N*-(4-Chlorophenyl)-*N*-(3-oxo-3-(quinoxalin-2-yl)propyl)nitrous amide (6c)**

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (46 mg, 67%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 8.18-8.12 (m, 2H), 7.91-7.85 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 4.48 (t, *J* = 7.2 Hz, 2H), 3.62 (t, *J* = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 198.6, 145.6, 144.2, 142.9, 140.9, 140.0, 133.3, 132.6, 131.1, 130.4, 129.8, 129.5, 120.8, 39.7, 34.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}ClN_4O_2$ 341.0800; Found 341.0798.

***N*-(4-Bromophenyl)-*N*-(3-oxo-3-(quinoxalin-2-yl)propyl)nitrous amide (6d)**

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (49 mg, 64%), mp 126-127 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 8.19-8.13 (m, 2H), 7.91-7.86 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 4.48 (t, *J* = 7.2 Hz, 2H), 3.62 (t, *J* = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 198.5, 145.6, 144.2, 142.9, 140.9, 140.5, 132.7, 132.6, 131.0, 130.4, 129.5, 121.1, 121.0, 39.6, 34.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}BrN_4O_2$ 385.0295; Found 385.0320.

***N*-(3-Oxo-3-(quinoxalin-2-yl)propyl)-*N*-(*m*-tolyl)nitrous amide (6e)**

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (35 mg, 54%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 8.19-8.13 (m, 2H), 7.93-7.84 (m, 2H), 7.41-7.37 (m, 3H), 7.20-7.19 (m, 1H), 4.51 (t, *J* = 7.2 Hz, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 198.8, 145.7, 144.1, 142.9, 141.4, 140.9, 139.7, 132.5, 131.0, 130.5, 129.5, 129.4, 128.4, 120.7, 117.0, 40.1, 34.6, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_4O_2$ 321.1346; Found 321.1352.

***N*-(3-Bromophenyl)-*N*-(3-oxo-3-(quinoxalin-2-yl)propyl)nitrous amide (6f)**

Eluent: petroleum ether/ethyl acetate (3:1). Yellow liquid (46 mg, 60%). ^1H NMR (400 MHz,

$CDCl_3$): δ 9.46 (s, 1H), 8.19-8.15 (m, 2H), 7.93-7.81 (m, 3H), 7.58-7.50 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 4.48 (t, *J* = 7.2 Hz, 2H), 3.61 (t, *J* = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 198.5, 145.6, 144.2, 142.9, 142.6, 140.9, 132.6, 131.0, 130.9, 130.5, 130.4, 129.5, 123.3, 122.6, 117.9, 39.6, 34.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}BrN_4O_2$ 385.0295; Found 385.0302.

6. Control Experiments

6.1. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), acetone (1 mL), NH_4SCN (**2**, 46 mg, 0.6 mmol), 4-OH-T^+OTf^- (114 mg, 0.4 mmol), and BHT (132 mg, 0.6 mmol). The resulting mixture was then stirred at room temperature under N_2 for 6 h. Upon completion, the mixture was diluted with ethyl acetate (10 mL × 3) and aqueous $NaHCO_3$ (10 mL, 1 M). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (3:1) as the eluent to afford **3a** as yellow solid in 25 mg (54%).

6.2. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), DMF (1 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *o*-phenylenediamine (**4a**, 43 mg, 0.4 mmol), KSCN (19 mg, 0.2 mmol), and BHT (132 mg, 0.6 mmol). The resulting mixture was then stirred at room temperature under air for 6 h. Upon completion, the mixture was diluted with ethyl acetate and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **5a** as brown solid in 32 mg (61%).

6.3. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), acetone (1 mL), NH_4SCN (**2**, 46 mg, 0.6 mmol), and 4-OH-T^+OTf^- (114 mg, 0.4 mmol).

The resulting mixture was then stirred at room temperature under N_2 for 1 h. Subsequent HRMS analysis of the resulting mixture showed that 5-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1-phenyl-2,3,4,5-tetrahydropyridin-1-ium **i** (calcd, 331.2380; found 331.2371) was formed (Fig. S1).

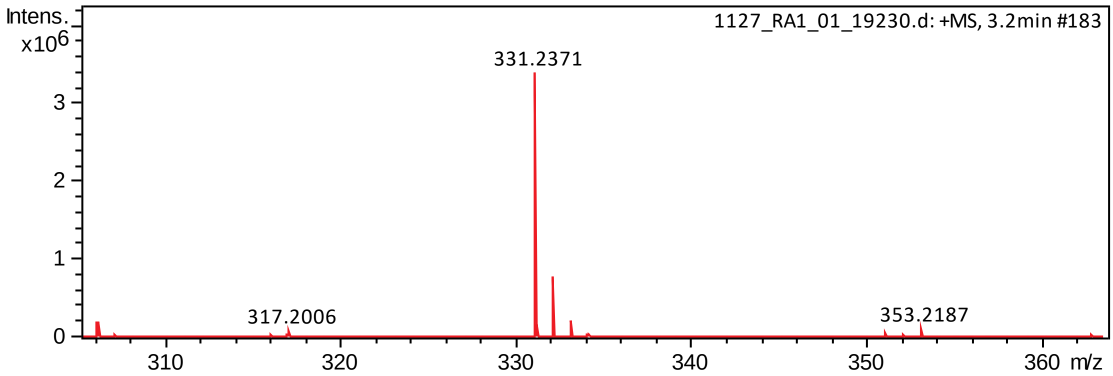


Fig. S1 Copy of HRMS Spectra of the Reaction Mixture for the Formation of 3a

6.4. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), DMF (1 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *o*-phenylenediamine (**4a**, 43 mg, 0.4 mmol), and KSCN (19 mg, 0.2 mmol). The resulting mixture was then stirred at room temperature under air for 1 h. Subsequent HRMS analysis of the resulting mixture showed that 5-oxo-1-phenyl-2,3,4,5-tetrahydropyridin-1-ium **ii** (calcd, 174.0913; found, 174.0916) was formed (Fig. S2).

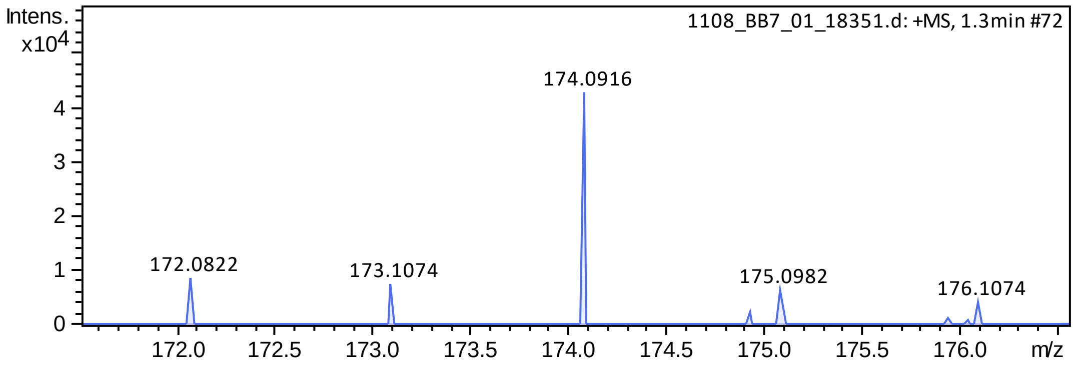


Fig. S2 Copy of HRMS Spectra of the Reaction Mixture for the Formation of 5a

6.5. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2

mmol), acetone (1 mL), NH_4SCN (**2**, 46 mg, 0.6 mmol), 4-OH-T^+OTf^- (114 mg, 0.4 mmol), and 4 Å MS (200 mg). The resulting mixture was then stirred at room temperature under N_2 for 6 h. Upon completion, the mixture was diluted with ethyl acetate (10 mL × 3) and aqueous $NaHCO_3$ (10 mL, 1 M). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (3:1) as the eluent to afford **3a** as yellow solid in 7 mg (15%).

6.6. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), DMF (1 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *o*-phenylenediamine (**4a**, 43 mg, 0.4 mmol), KSCN (19 mg, 0.2 mmol), and 4 Å MS (200 mg). The resulting mixture was then stirred at room temperature under air for 6 h. Upon completion, the mixture was diluted with ethyl acetate and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **5a** as brown solid in 22 mg (41%).

6.7. To a reaction tube equipped with a stir bar were added **1a** (32 mg, 0.2 mmol), **1a-*α*-*d*$_4$** (33 mg, 0.2 mmol) (Fig. S3), acetone (1 mL), NH_4SCN (**2**, 46 mg, 0.6 mmol), and 4-OH-T^+OTf^- (114 mg, 0.4 mmol). The resulting mixture was then stirred at room temperature under N_2 for 2 h. Upon completion, the mixture was diluted with ethyl acetate (10 mL × 3) and aqueous $NaHCO_3$ (10 mL, 1 M). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (3:1) as the eluent to afford **3a** and **3a-*d*$_3$**. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **3a** to **3a-*d*$_3$** was determined to be 2.6:1

(Fig. S4). Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be 2.6.

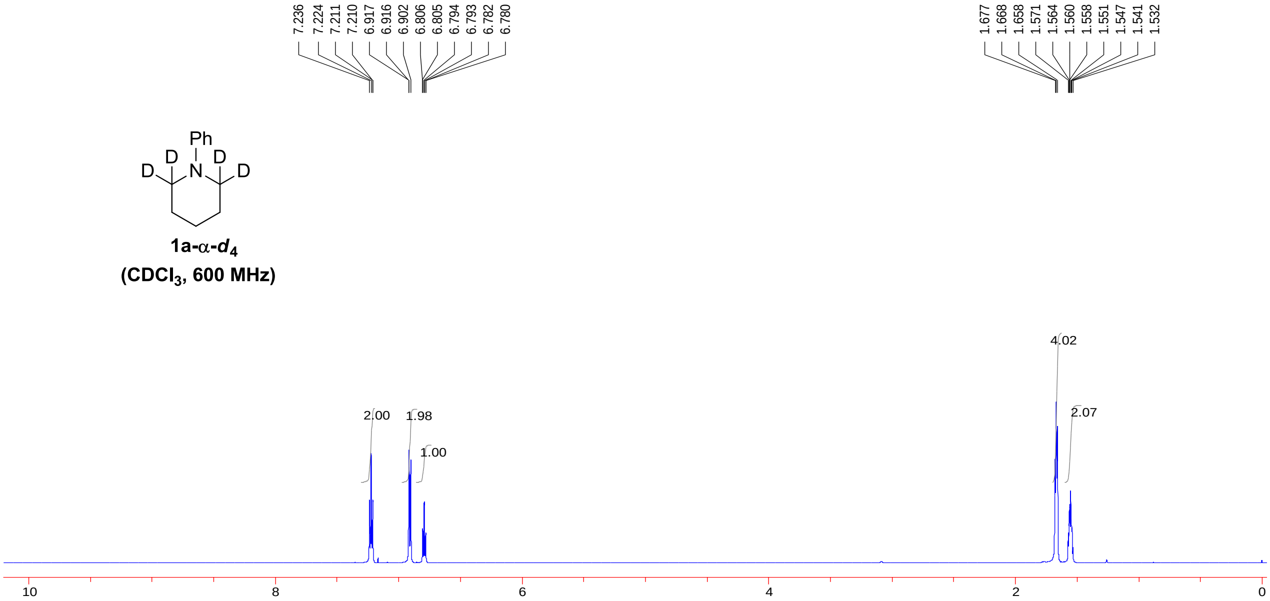


Fig. S3 Copy of ^{1}HNMR Spectrum of 1a-*α*-*d*$_4$

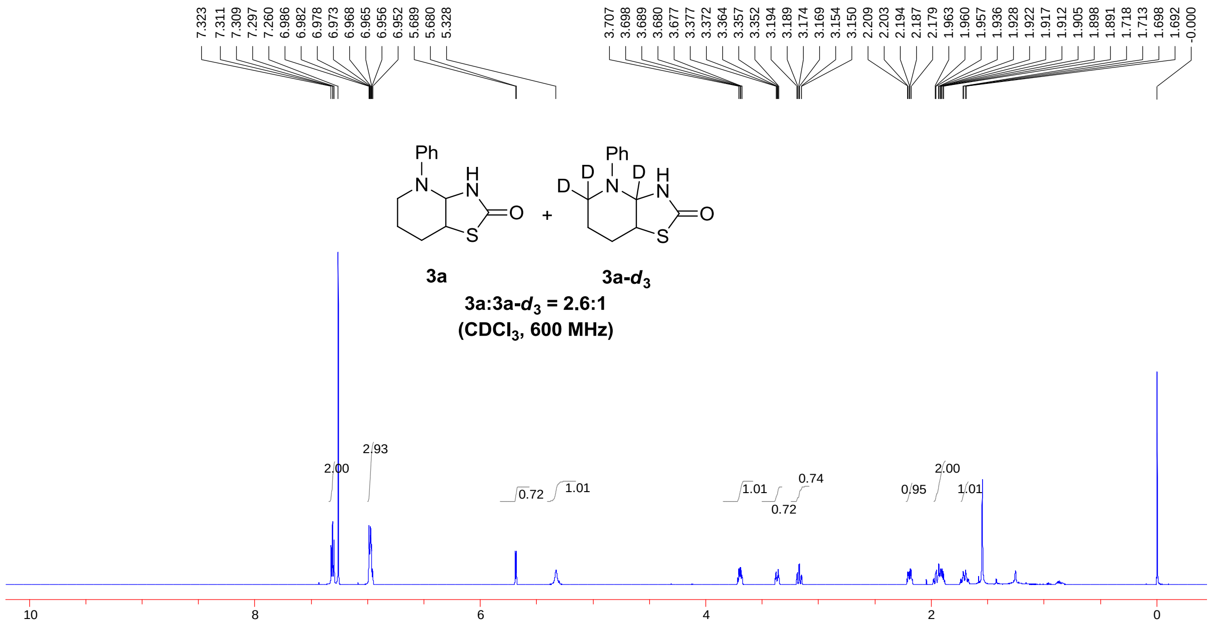


Fig. S4 Copy of ^{1}HNMR Spectrum of the Products 3a and 3a-*d*$_3$

6.8. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 32 mg, 0.2 mmol), **1a-α-*d*$_4$** (33 mg, 0.2 mmol), DMF (1 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *o*-phenylenediamine (**4a**, 43 mg, 0.4 mmol), and KSCN (19 mg, 0.2 mmol). The resulting mixture was then stirred at room temperature under air for 5 min. Upon completion, the mixture was diluted with ethyl acetate and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **5a** and **5a-*d*$_3$**. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **5a** to **5a-*d*$_3$** was determined to be 3:1 (Fig. S5). Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be 3.

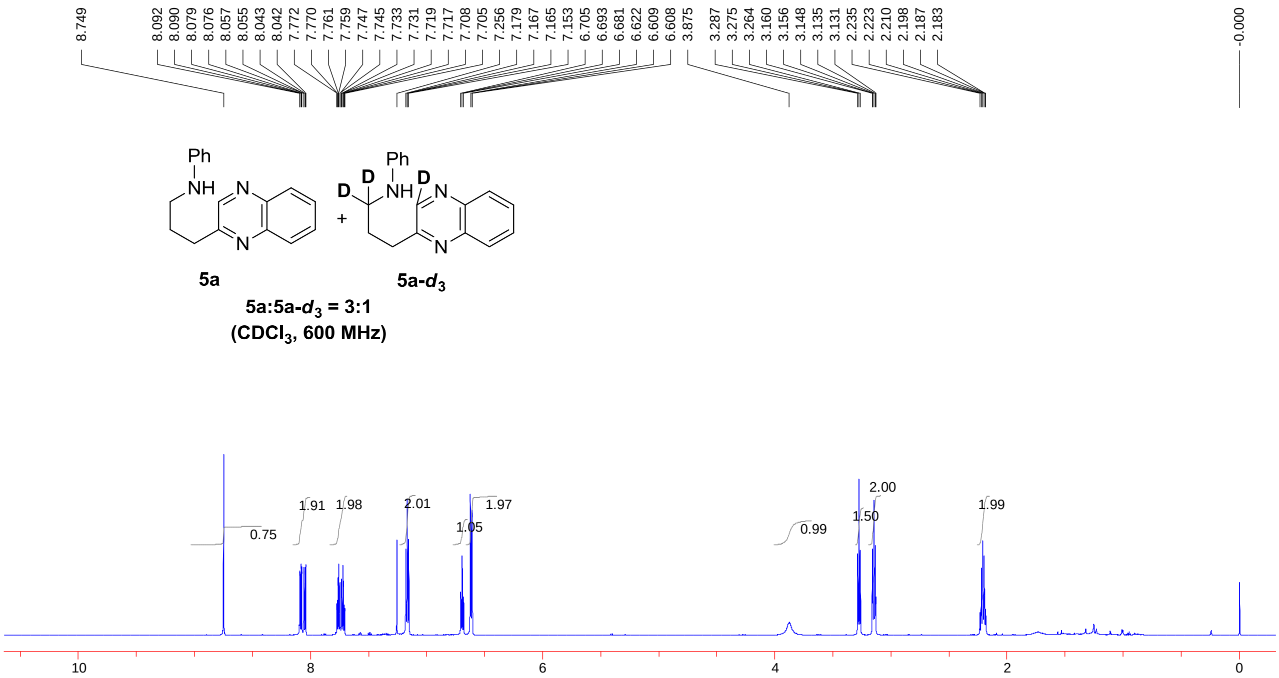


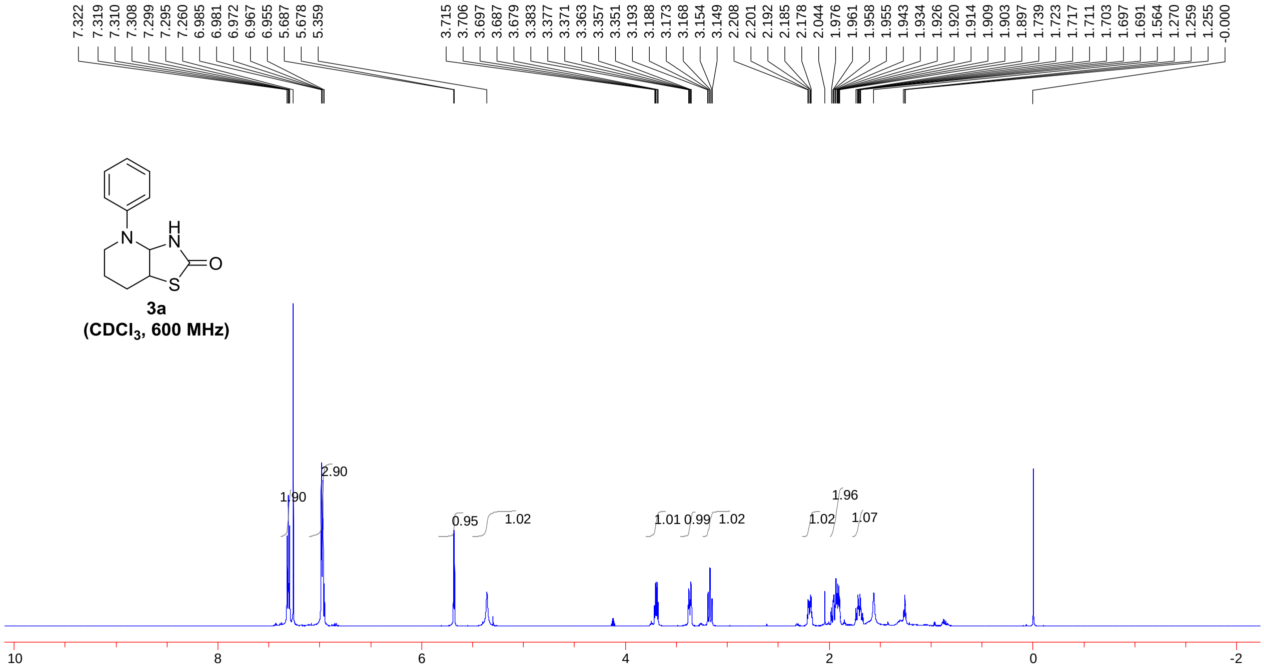
Fig. S5 Copy of ^{1}HNMR Spectrum of the Products 5a and 5a-*d*$_3$

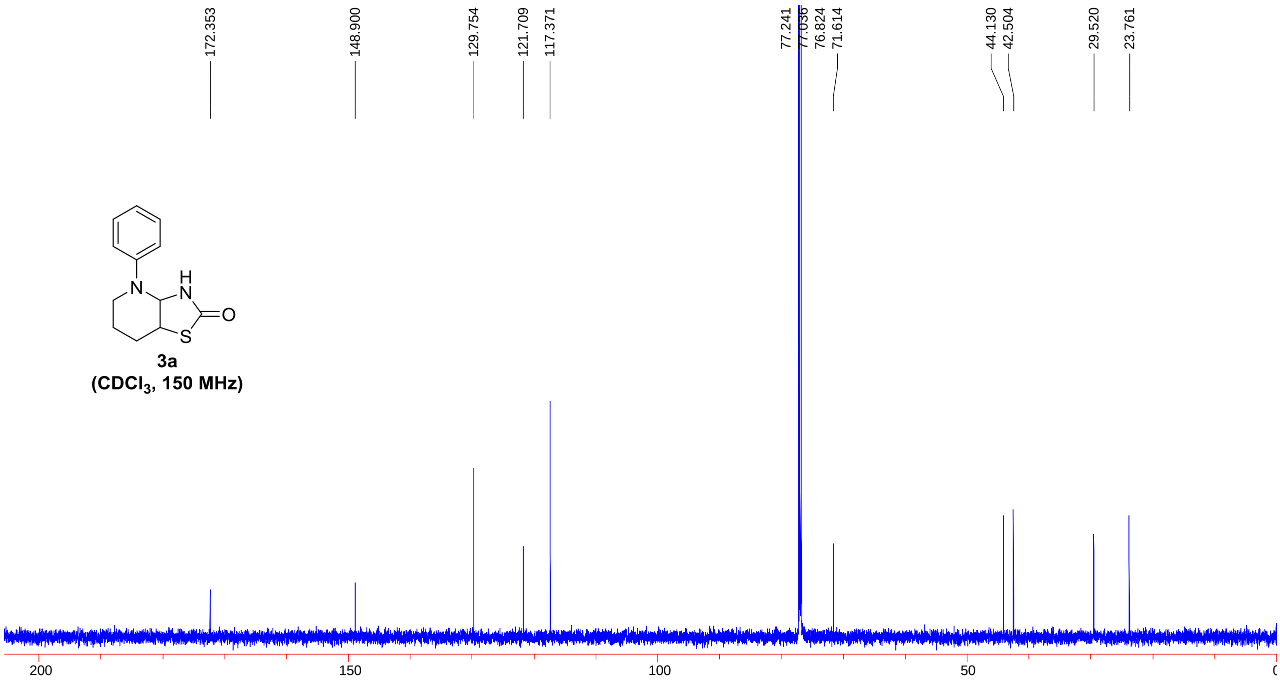
7. Gram-Scale Reaction

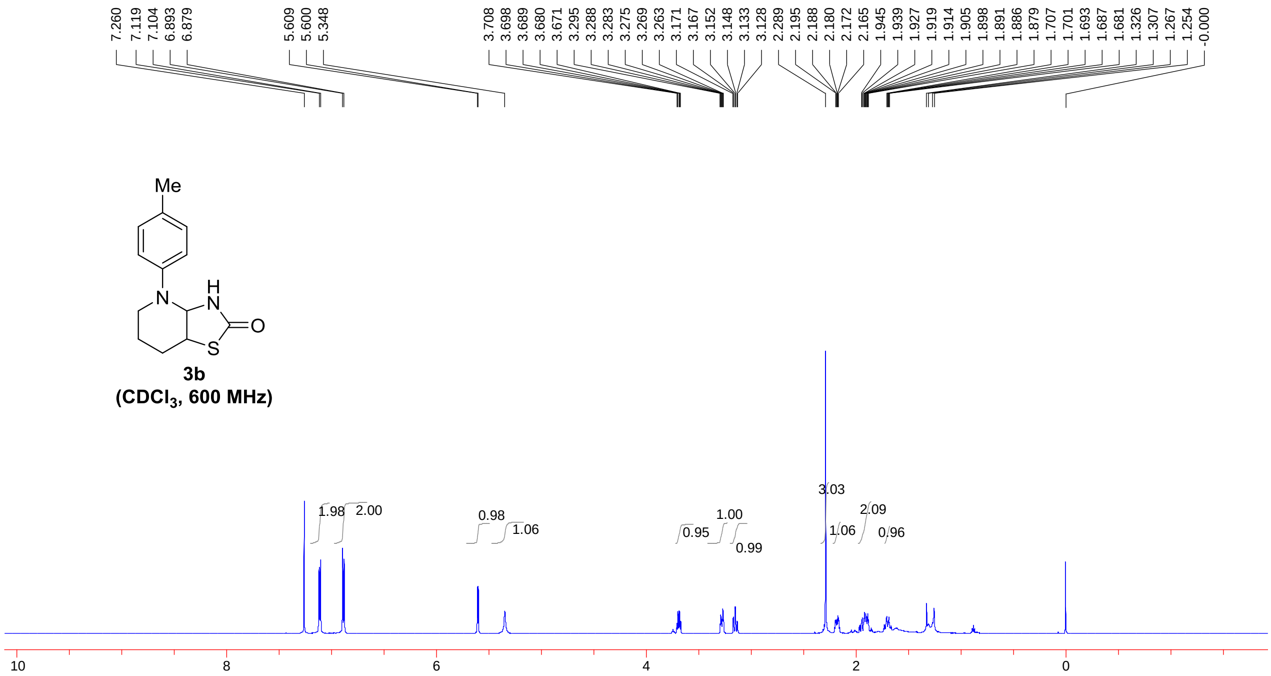
7.1. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 1.288 g, 8 mmol), acetone (40 mL), NH_4SCN (**2**, 1.827 g, 24 mmol), and 4-OH-T$^+$OTf$^-$ (5.136 g, 16 mmol). The resulting mixture was then stirred at room temperature under N_2 for 6 h. Upon completion, the mixture was diluted with ethyl acetate (100 mL × 3) and aqueous $NaHCO_3$ (100 mL, 1 M). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (3:1) as the eluent to afford **3a** as yellow solid in 1.086 g (58%).

7.2. To a reaction tube equipped with a stir bar were added 1-(phenyl)piperidine (**1a**, 1.288 g, 8 mmol), DMF (30 mL), $T^+BF_4^-$ (3.888 g, 16 mmol), *o*-phenylenediamine (**4a**, 1.730 g, 16 mmol), and KSCN (0.777 g, 8 mmol). The resulting mixture was then stirred at room temperature under air for 6 h. Upon completion, the mixture was diluted with ethyl acetate (100 mL × 3) and aqueous NaCl (100 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **5a** as brown solid in 1.304 g (62%).

III. Copies of the NMR spectra of 3a-3q



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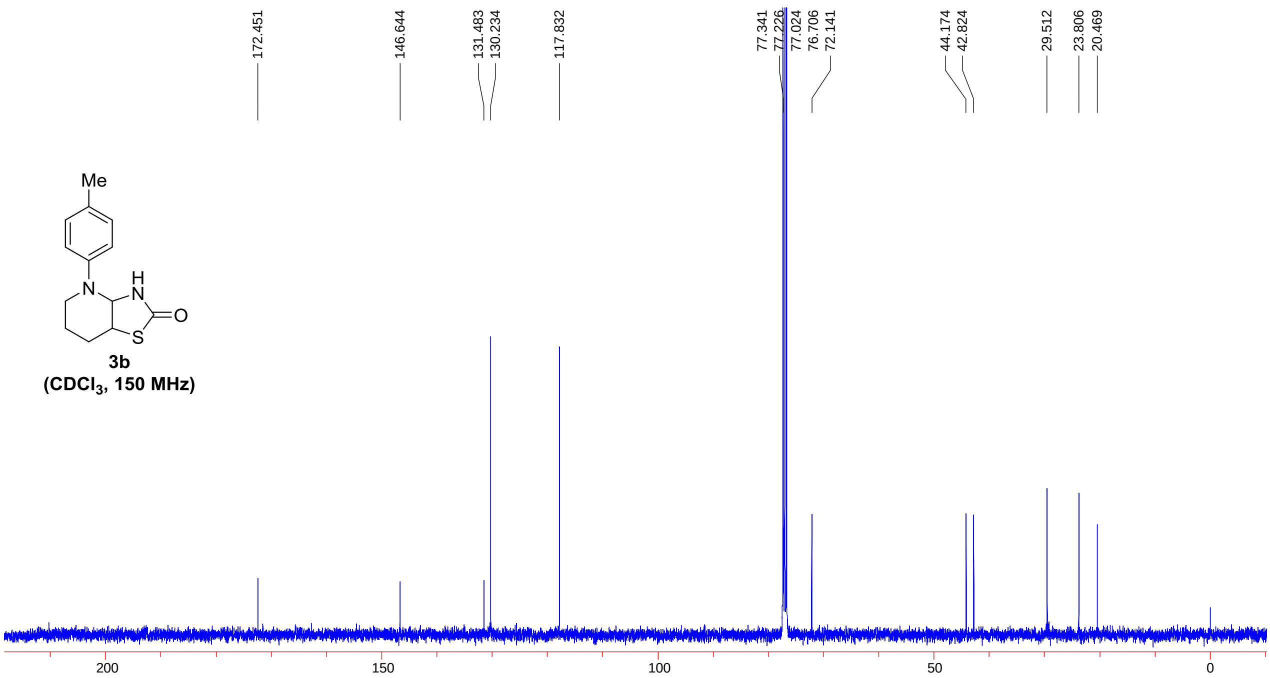
Me
N
H
N
O
S
3b
(CDCl3, 600 MHz)
1.98 2.00 0.98 1.06 0.95 1.00 0.99 3.03 1.06 2.09 0.96
10 8 6 4 2 0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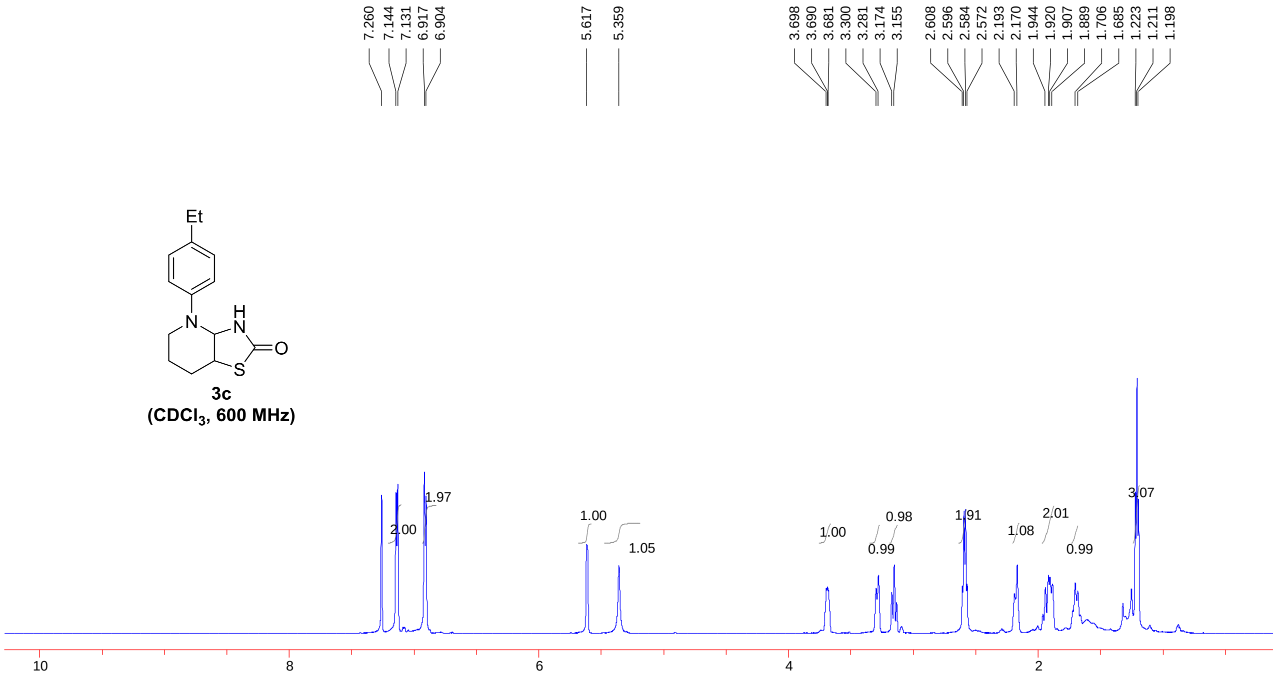
Me
N
H
N
O
S
3b
(CDCl3, 150 MHz)
200 150 100 50 0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7.144
7.131
6.917
6.904
5.617
5.359
3.698
3.690
3.681
3.300
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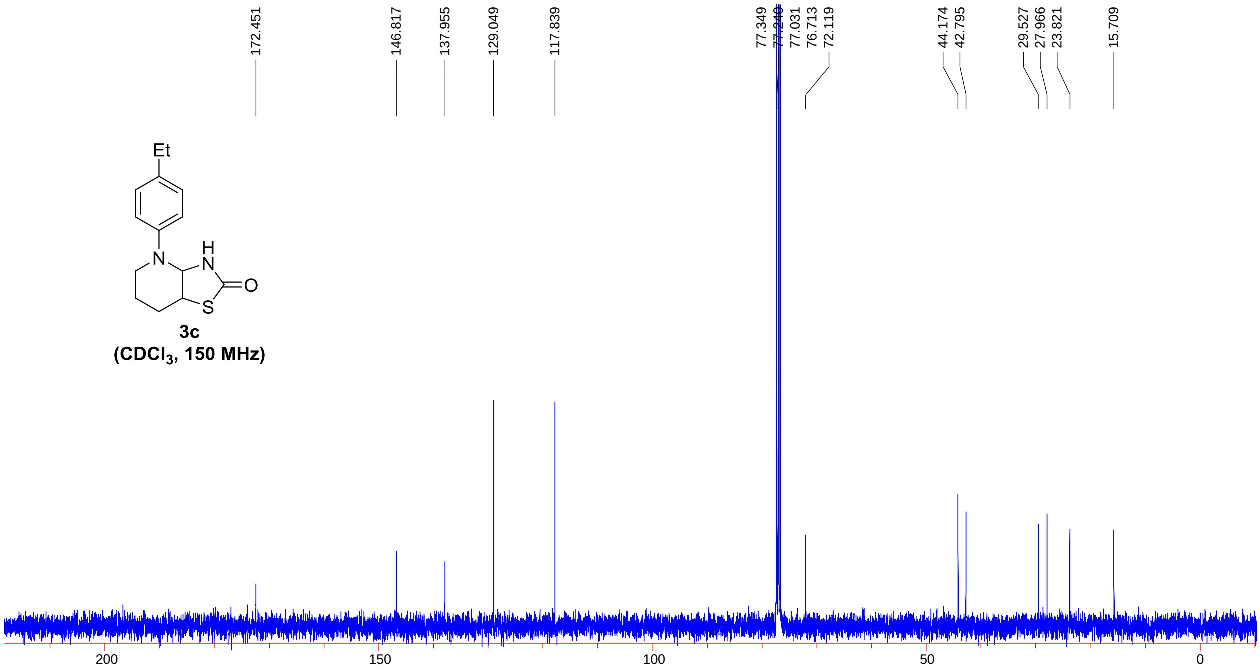
3.155
2.608
2.596
2.584
2.572
2.193
2.170
1.944
1.920
1.907
1.889
1.706
1.685
1.223
1.211
1.198
Et
N
H
N
O
S
3c
(CDCl3, 600 MHz)
2.00
1.97
1.00
1.05
1.00
0.99
0.98
1.91
1.08
2.01
0.99
3.07
10
8
6
4
2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117.839
77.349
77.240
77.031
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72.119
44.174
42.795
29.527
27.966
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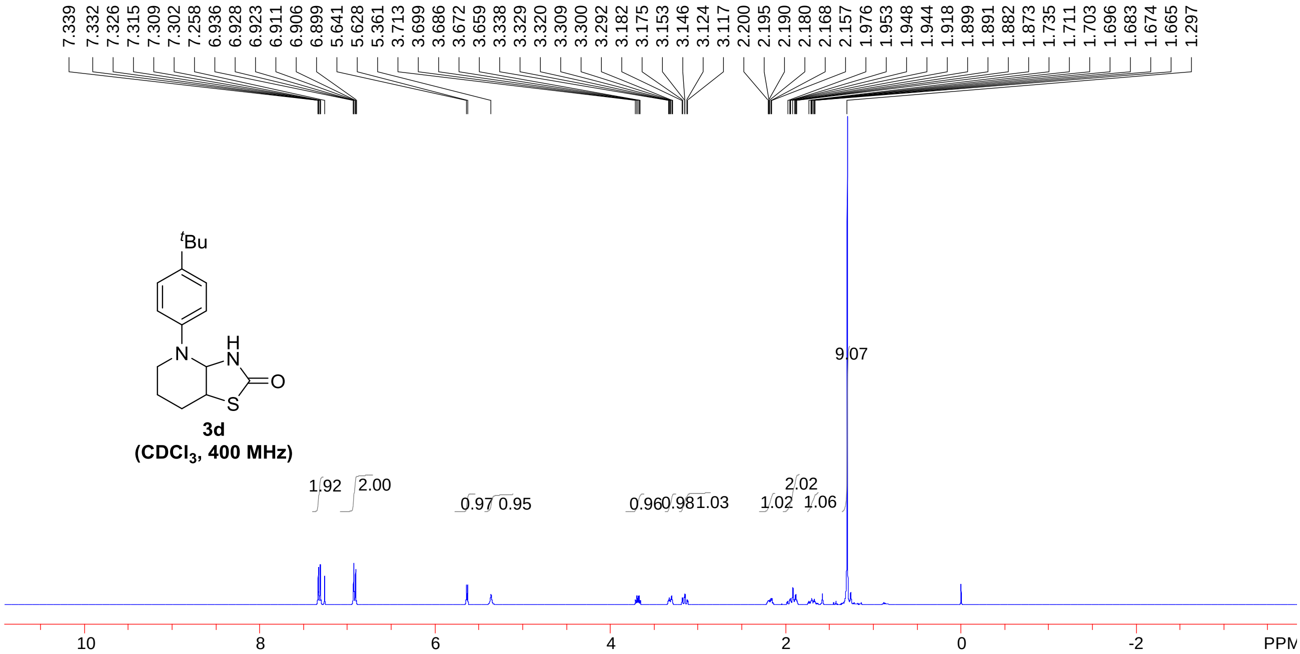
Et
N
H
N
O
S
3c
(CDCl3, 150 MHz)
200
150
100
50
0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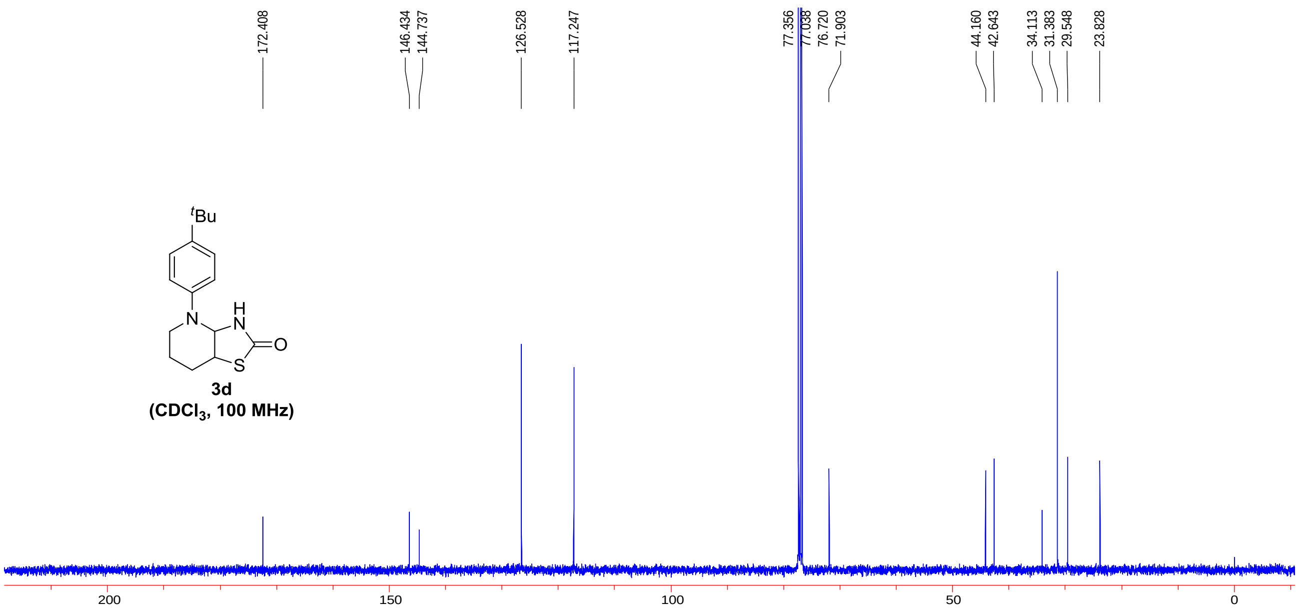
tBu
N
H
N
O
S
3d
(CDCl3, 400 MHz)
1.92 2.00 0.97 0.95 0.96 0.98 1.03 1.02 2.02 1.06 9.07
10 8 6 4 2 0 -2 PPM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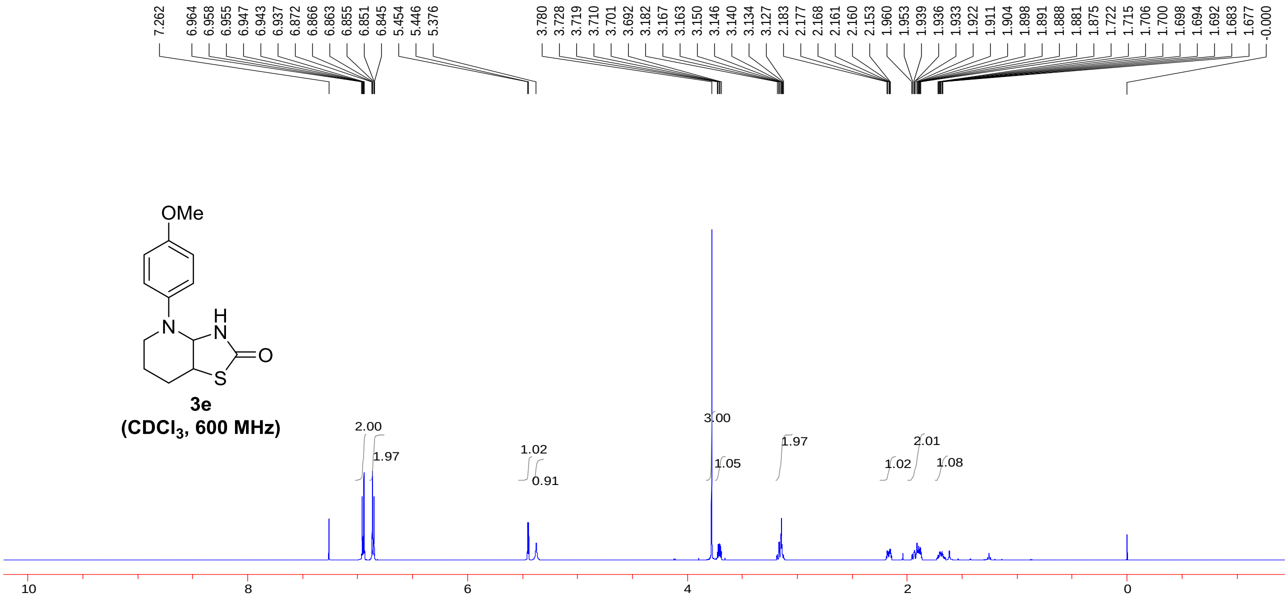
tBu
N
H
N
O
S
3d
(CDCl3, 100 MHz)
200 150 100 50 0


OMe
N
H
N
O
S
3e
(CDCl3, 600 MHz)
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6.958
6.955
6.947
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6.937
6.872
6.866
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6.855
6.851
6.845
5.454
5.446
5.376
3.780
3.728
3.719
3.710
3.701
3.692
3.182
3.167
3.163
3.150
3.146
3.140
3.134
3.127
2.183
2.177
2.168
2.161
2.160
2.153
1.960
1.953
1.939
1.936
1.933
1.922
1.911
1.904
1.898
1.891
1.888
1.881
1.875
1.722
1.715
1.706
1.700
1.698
1.694
1.692
1.683
1.677
-0.000
2.00
1.97
1.02
0.91
3.00
1.05
1.97
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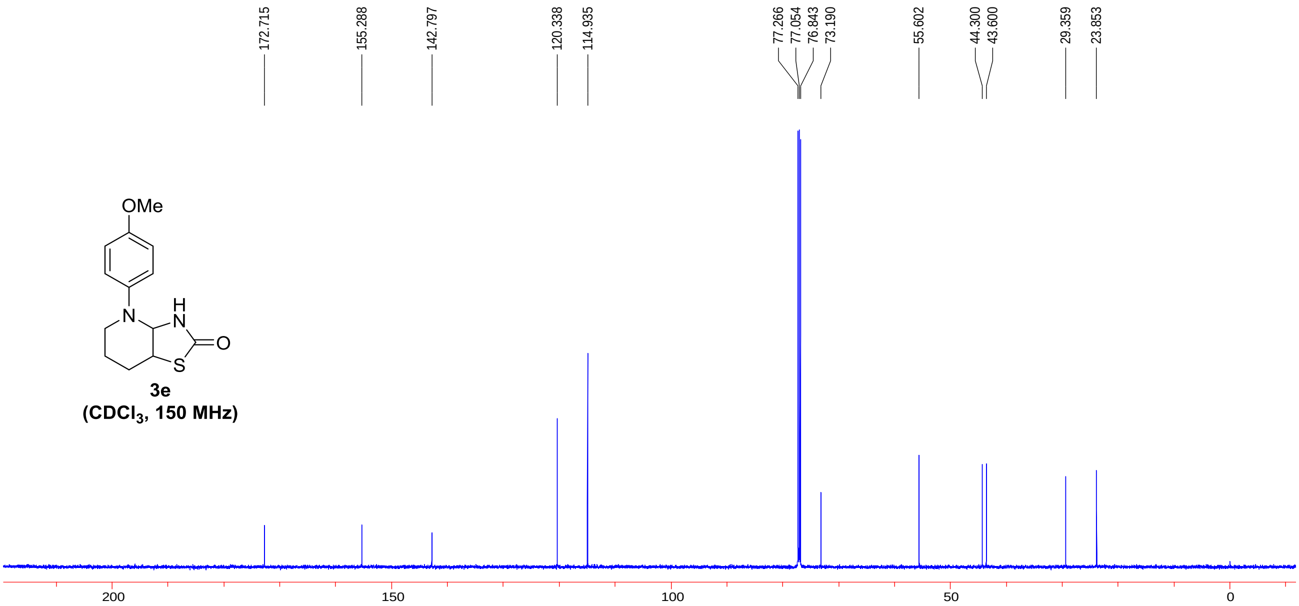
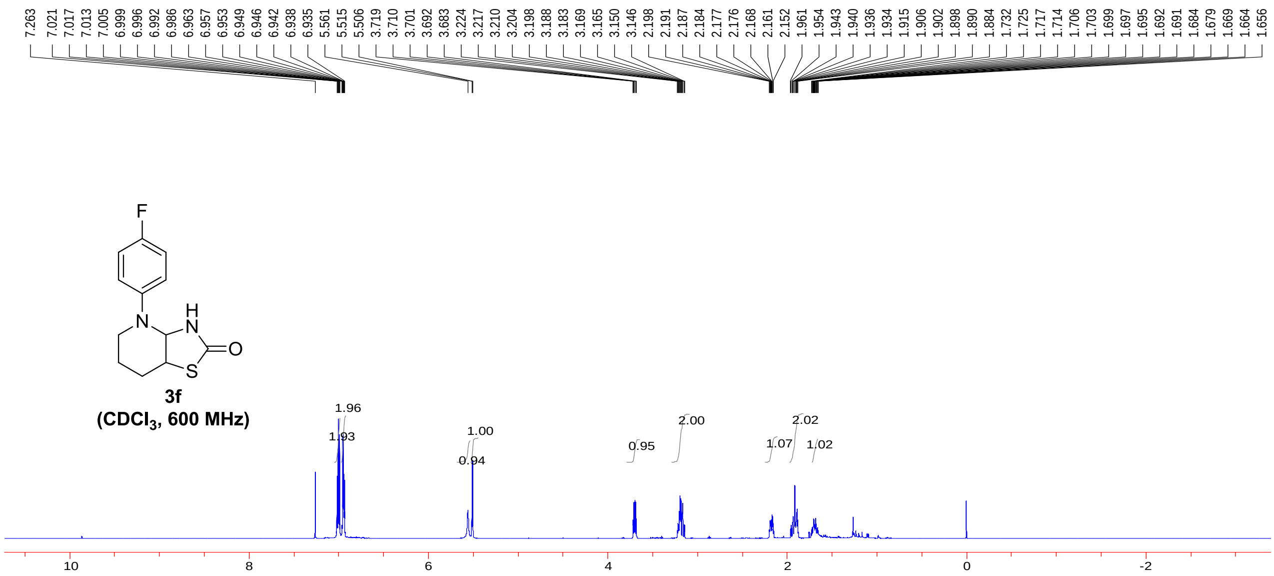
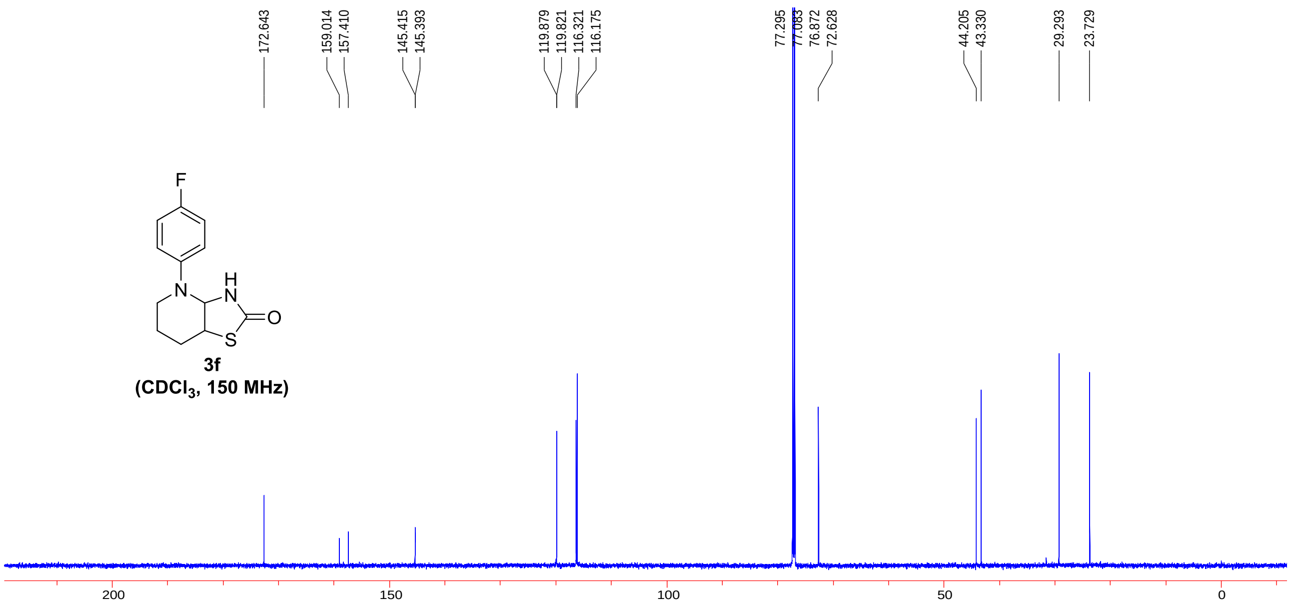
2.01
1.08
10
8
6
4
2
0

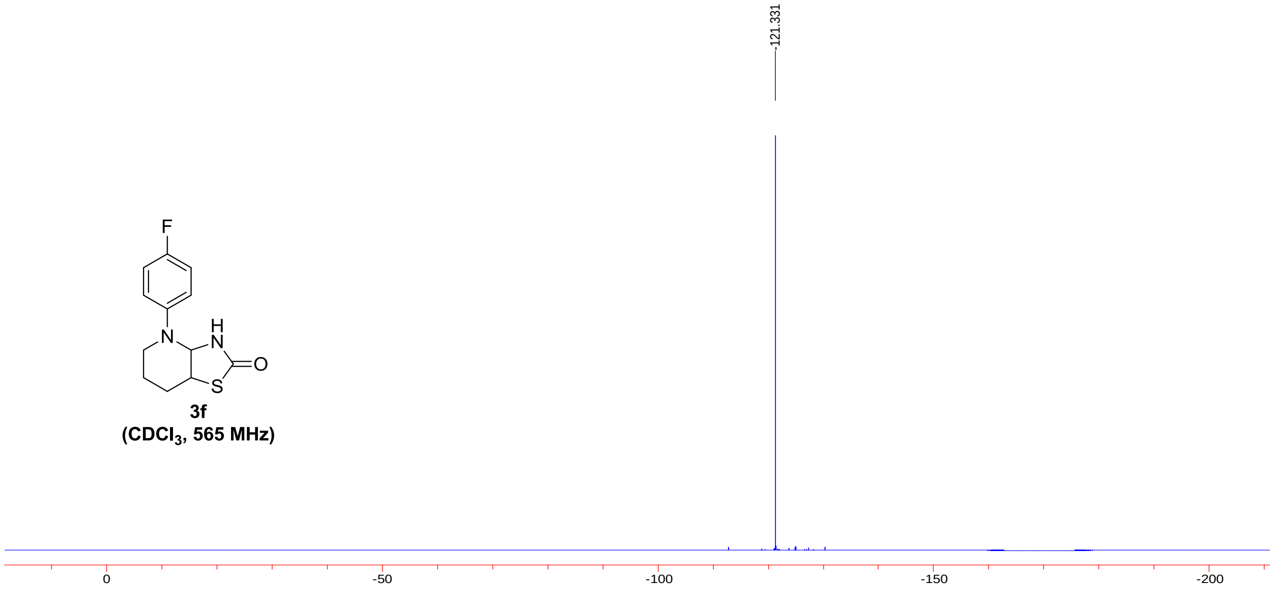

OMe
N
H
N
O
S
3e
(CDCl3, 150 MHz)
172.715
155.288
142.797
120.338
114.935
77.266
77.054
76.843
73.190
55.602
44.300
43.600
29.359
23.853
200
150
100
50
0



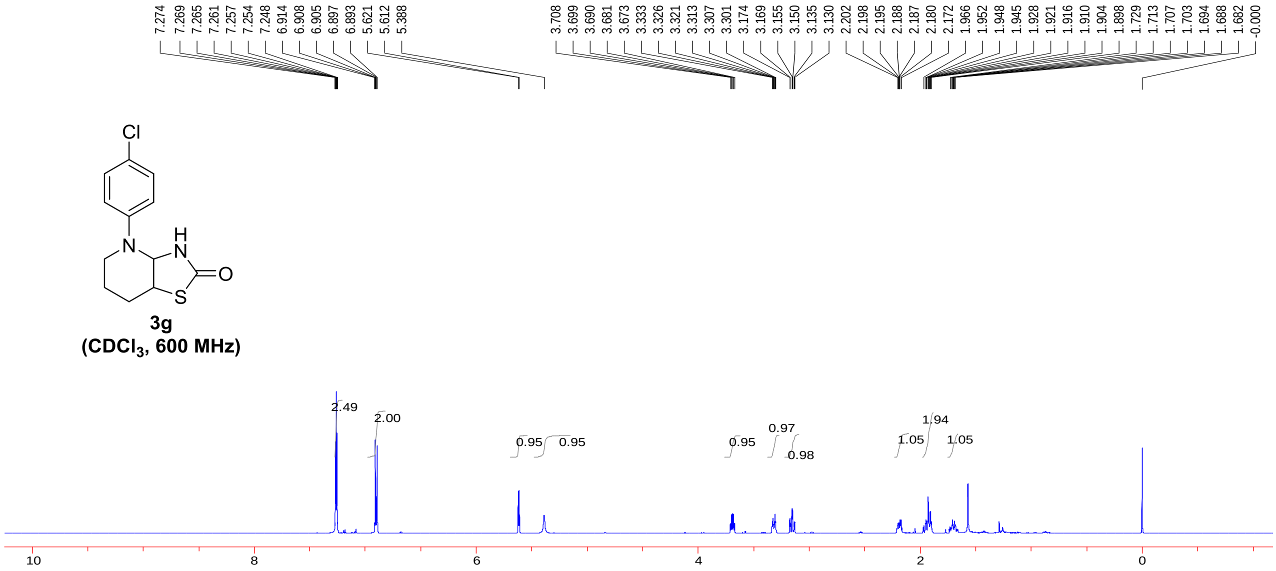
3f
(CDCl$_3$, 600 MHz)

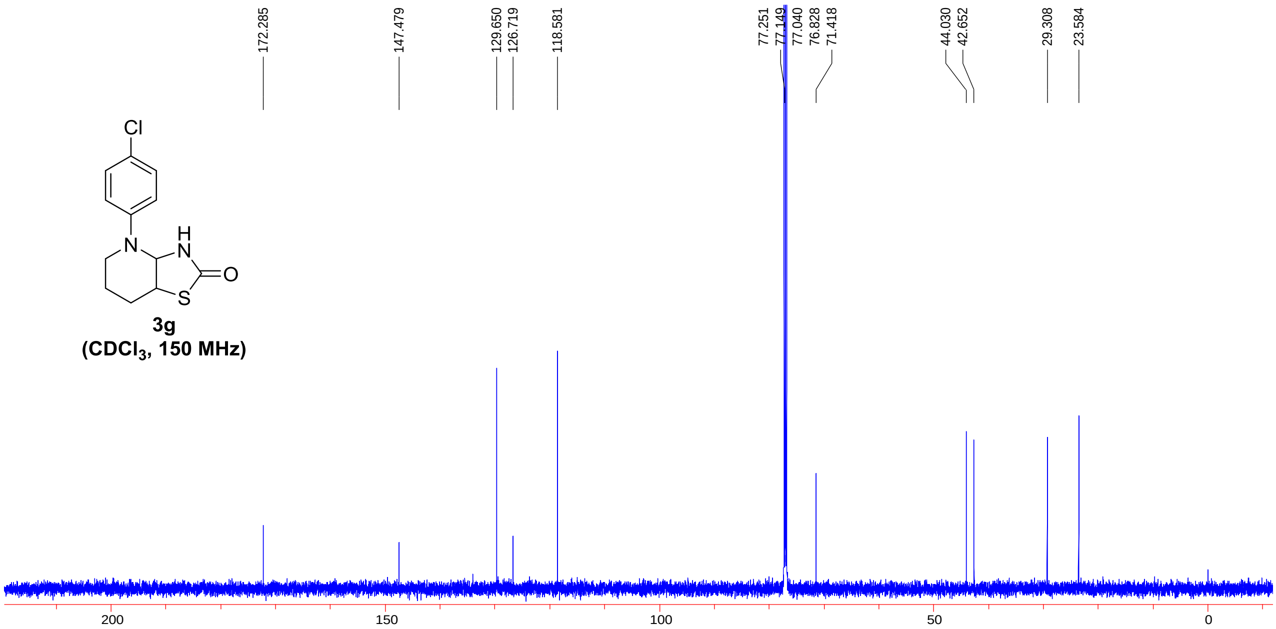


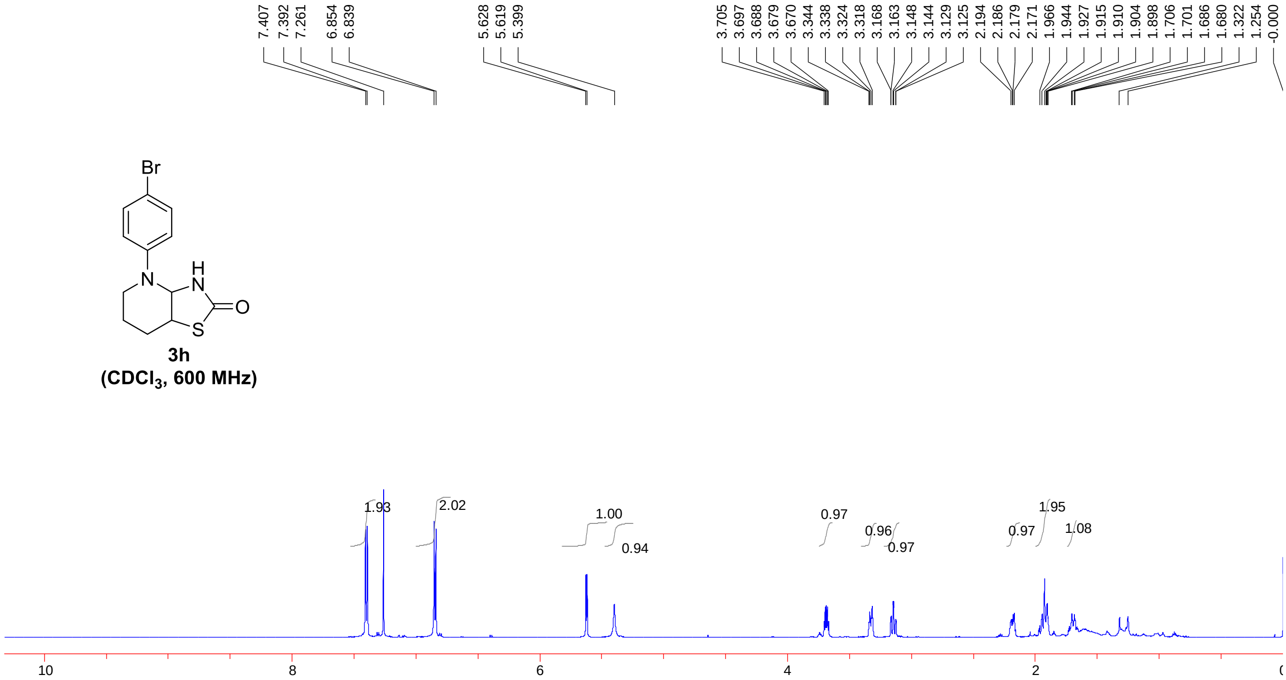
3f
(CDCl$_3$, 150 MHz)



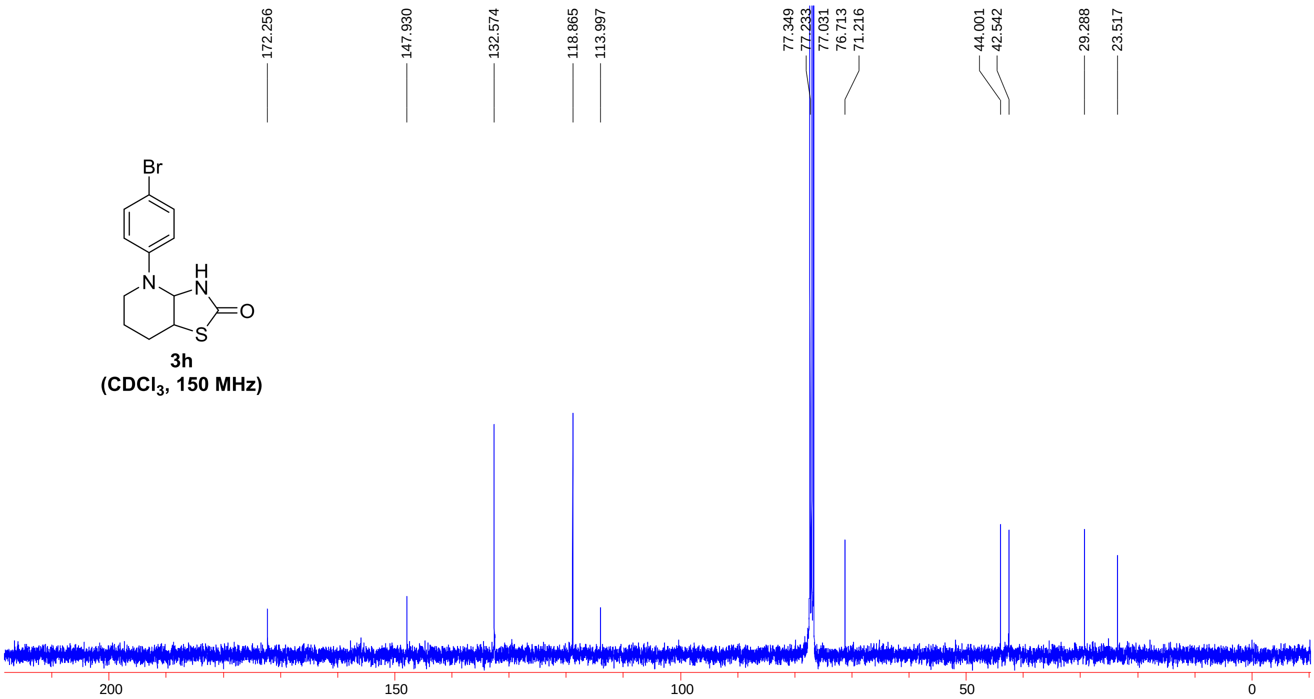
3f
($CDCl_3$, 565 MHz)


7.274
7.269
7.265
7.261
7.257
7.254
7.248
6.914
6.908
6.905
6.897
6.893
5.621
5.612
5.388
3.708
3.699
3.690
3.681
3.673
3.333
3.326
3.321
3.313
3.307
3.301
3.174
3.169
3.155
3.150
3.135
3.130
2.202
2.198
2.195
2.188
2.187
2.180
2.172
1.966
1.952
1.948
1.945
1.928
1.921
1.916
1.910
1.904
1.898
1.729
1.713
1.707
1.703
1.694
1.688
1.682
-0.000
Cl
N
H
N
O
S
3g
(CDCl3, 600 MHz)
2.49
2.00
0.95
0.95
0.95
0.97
0.98
1.05
1.94
1.05
10
8
6
4
2
0

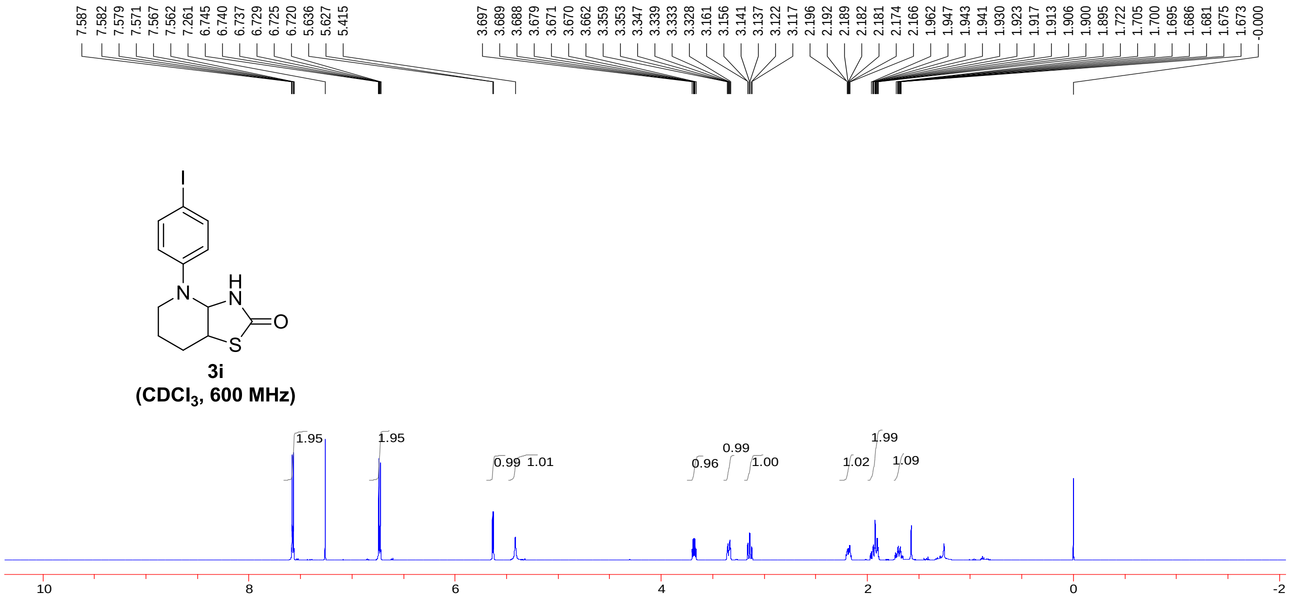

172.285
147.479
129.650
126.719
118.581
77.251
77.149
77.040
76.828
71.418
44.030
42.652
29.308
23.584
Cl
N
H
N
O
S
3g
(CDCl3, 150 MHz)
200
150
100
50
0

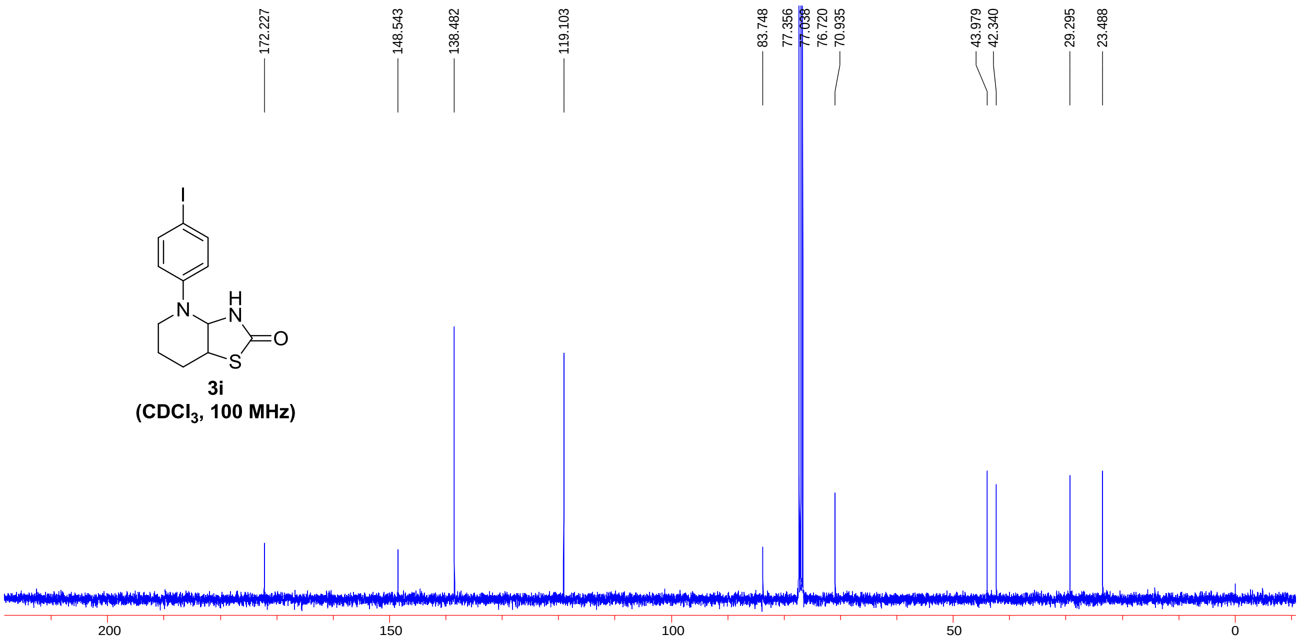


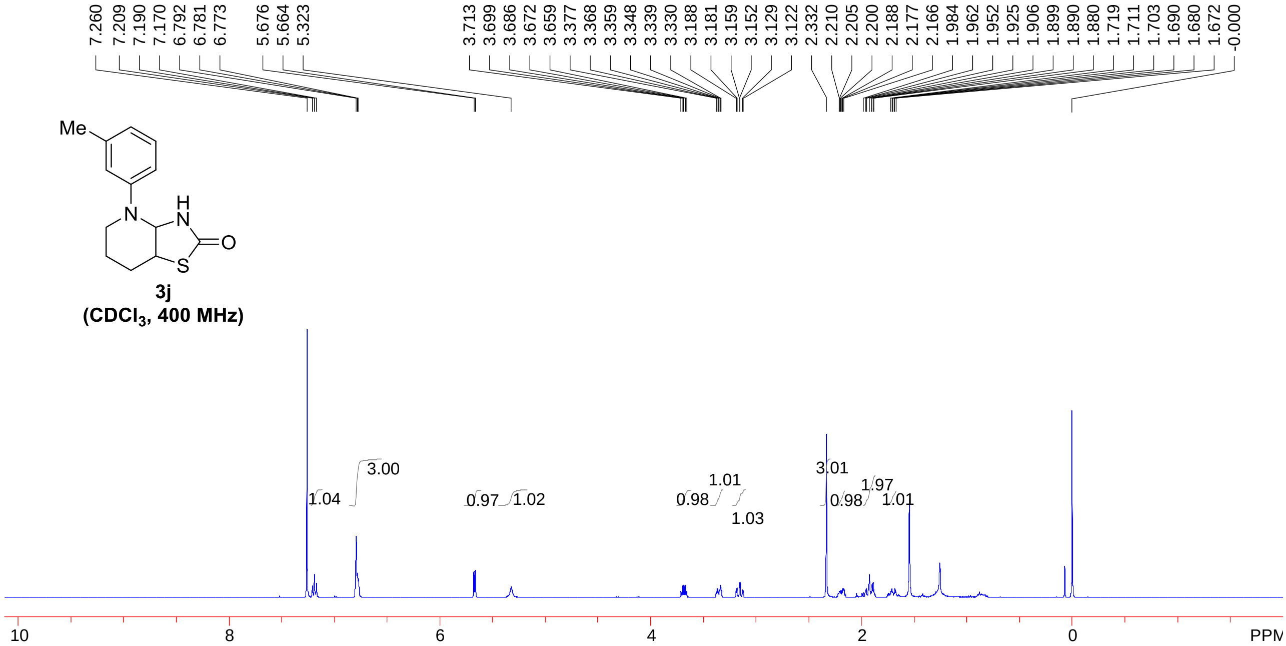
3h
($CDCl_3$, 600 MHz)



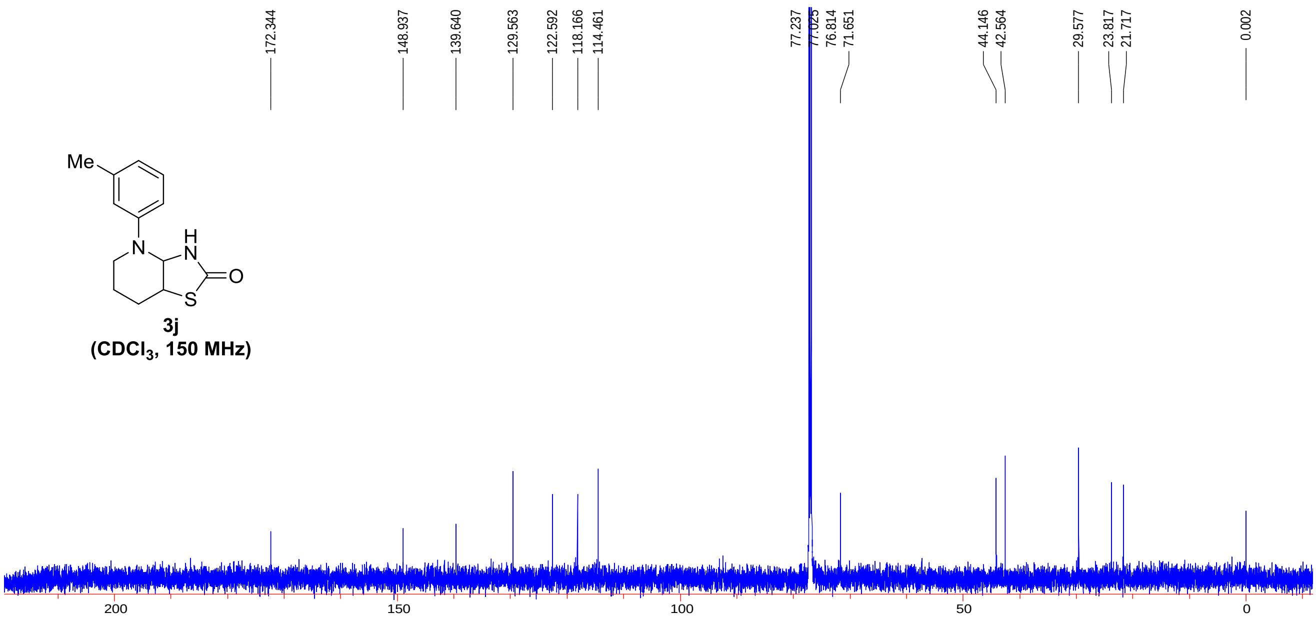
3h
($CDCl_3$, 150 MHz)


7.587 7.582 7.579 7.571 7.567 7.562 7.261 6.745 6.740 6.737 6.729 6.725 6.720 5.636 5.627 5.415
3.697 3.689 3.688 3.679 3.671 3.670 3.662 3.359 3.353 3.347 3.339 3.333 3.328 3.161 3.156 3.141 3.137 3.122 3.117 2.196 2.192 2.189 2.182 2.181 2.174 2.166 1.962 1.947 1.943 1.941 1.930 1.923 1.917 1.913 1.906 1.900 1.895 1.722 1.705 1.700 1.695 1.686 1.681 1.675 1.673 -0.000
3i
(CDCl3, 600 MHz)
1.95
1.95
0.99 1.01
0.96
0.99
1.00
1.02
1.99
1.09
10
8
6
4
2
0
-2

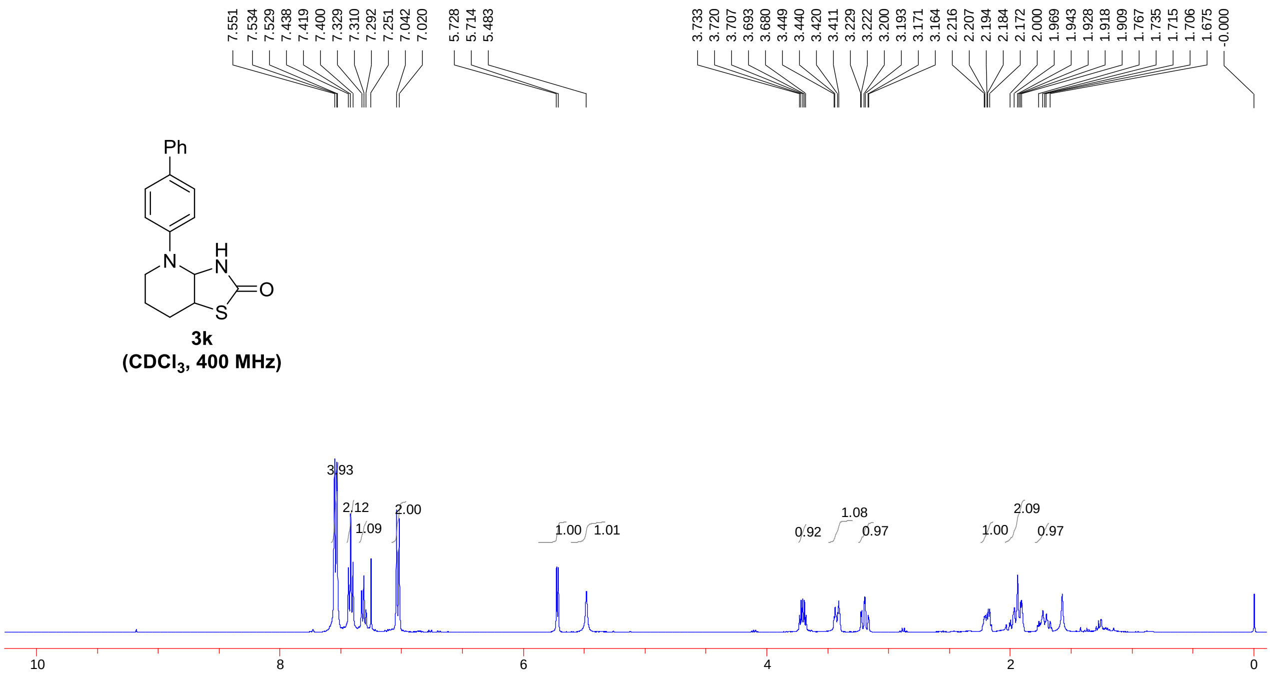

172.227
148.543
138.482
119.103
83.748
77.356
77.038
76.720
70.935
43.979
42.340
29.295
23.488
3i
(CDCl3, 100 MHz)
200
150
100
50
0

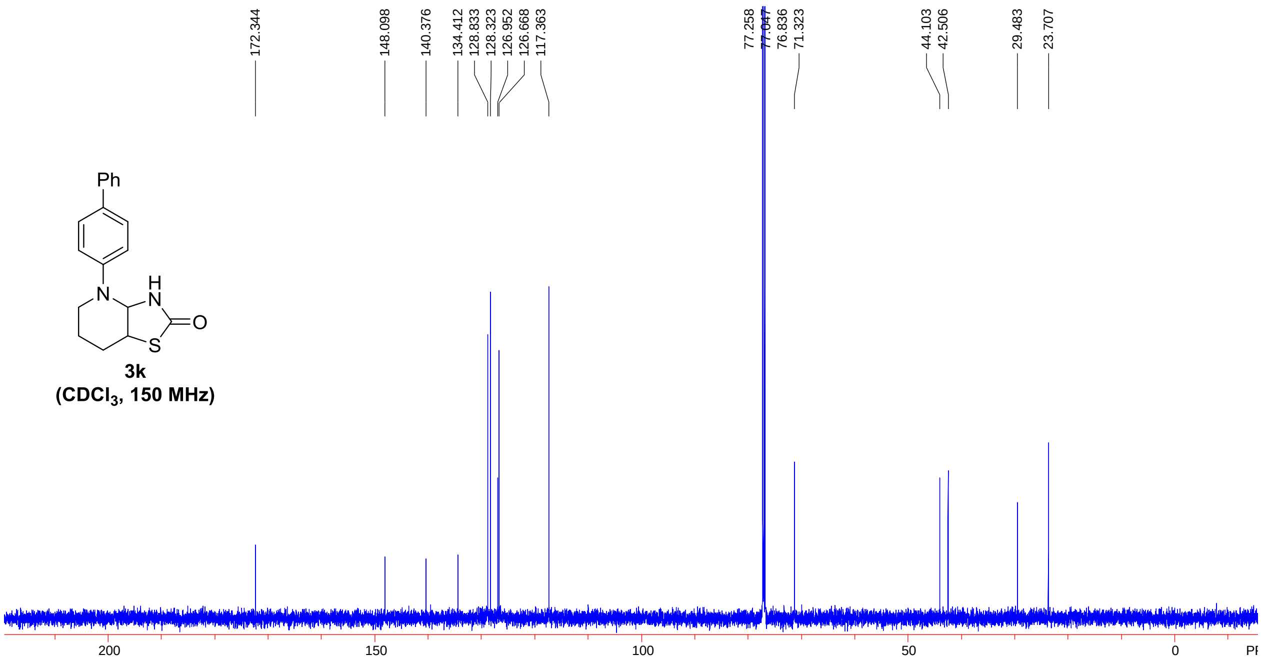


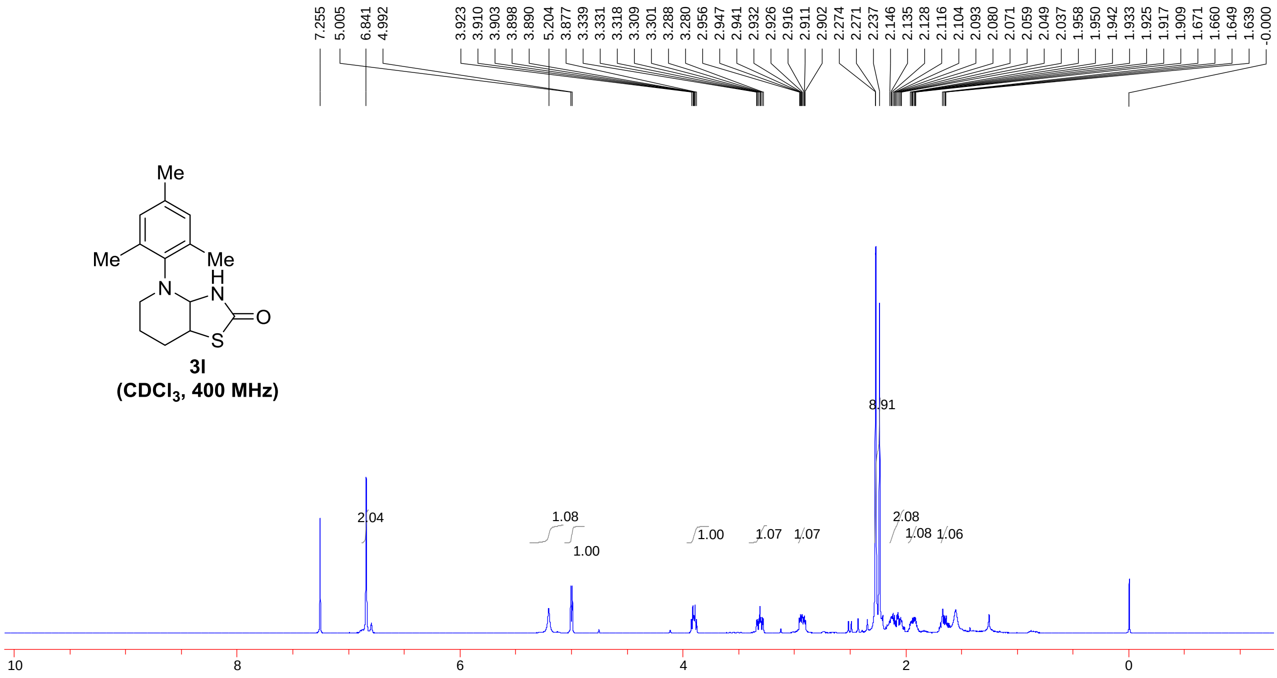
3j
($CDCl_3$, 400 MHz)



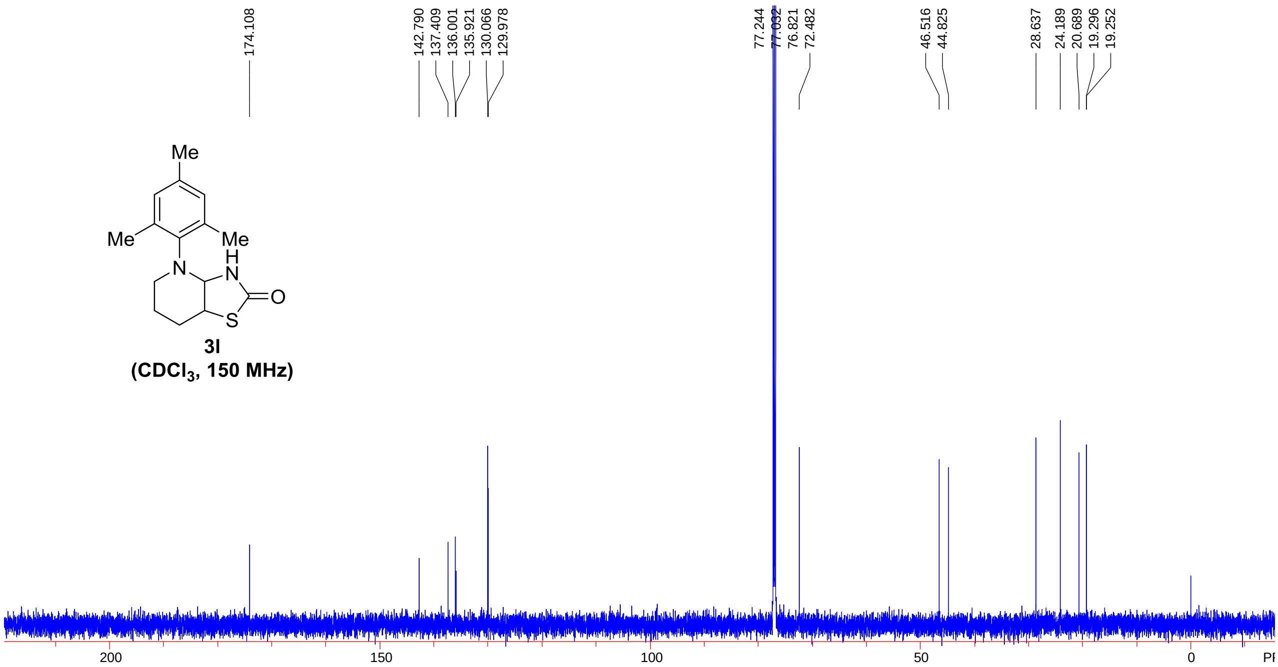
3j
($CDCl_3$, 150 MHz)


Ph
N
H
N
O
S
3k
(CDCl3, 400 MHz)
7.551 7.534 7.529 7.438 7.419 7.400 7.329 7.310 7.292 7.251 7.042 7.020 5.728 5.714 5.483 3.733 3.720 3.707 3.693 3.680 3.449 3.440 3.420 3.411 3.229 3.222 3.200 3.193 3.171 3.164 2.216 2.207 2.194 2.184 2.172 2.000 1.969 1.943 1.928 1.918 1.909 1.767 1.735 1.715 1.706 1.675 -0.000
3.93 2.12 1.09 2.00 1.00 1.01 0.92 1.08 0.97 1.00 2.09 0.97
10 8 6 4 2 0

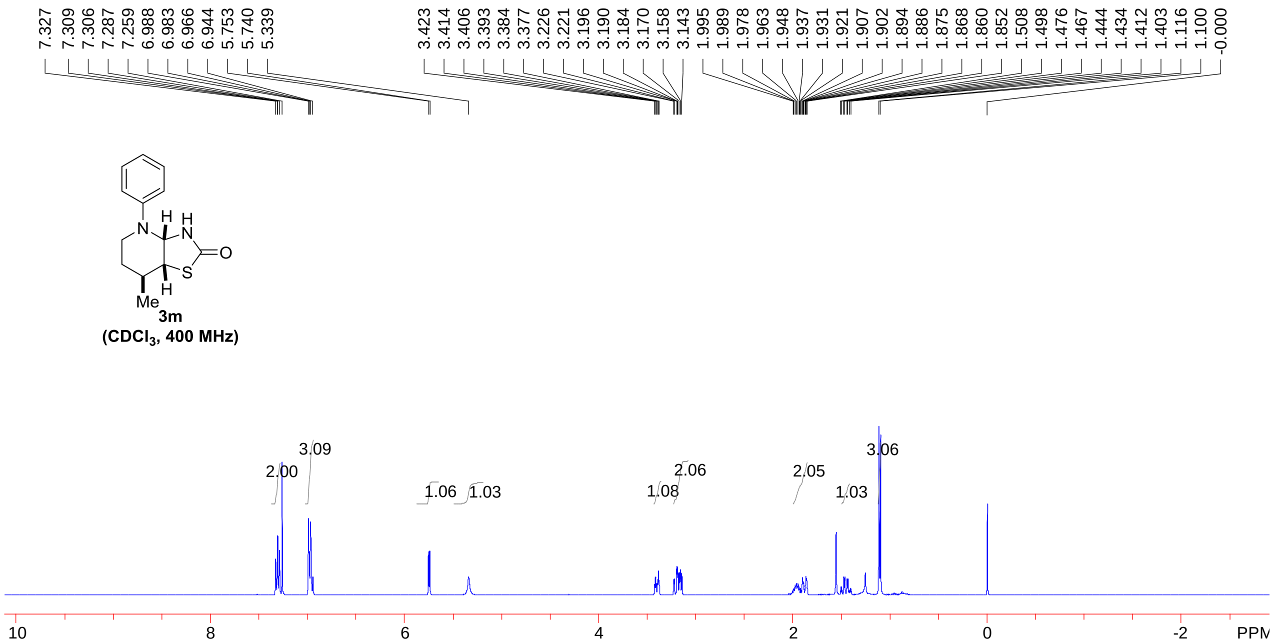

Ph
N
H
N
O
S
3k
(CDCl3, 150 MHz)
172.344 148.098 140.376 134.412 128.833 128.323 126.952 126.668 117.363 77.258 77.047 76.836 71.323 44.103 42.506 29.483 23.707
200 150 100 50 0 PI

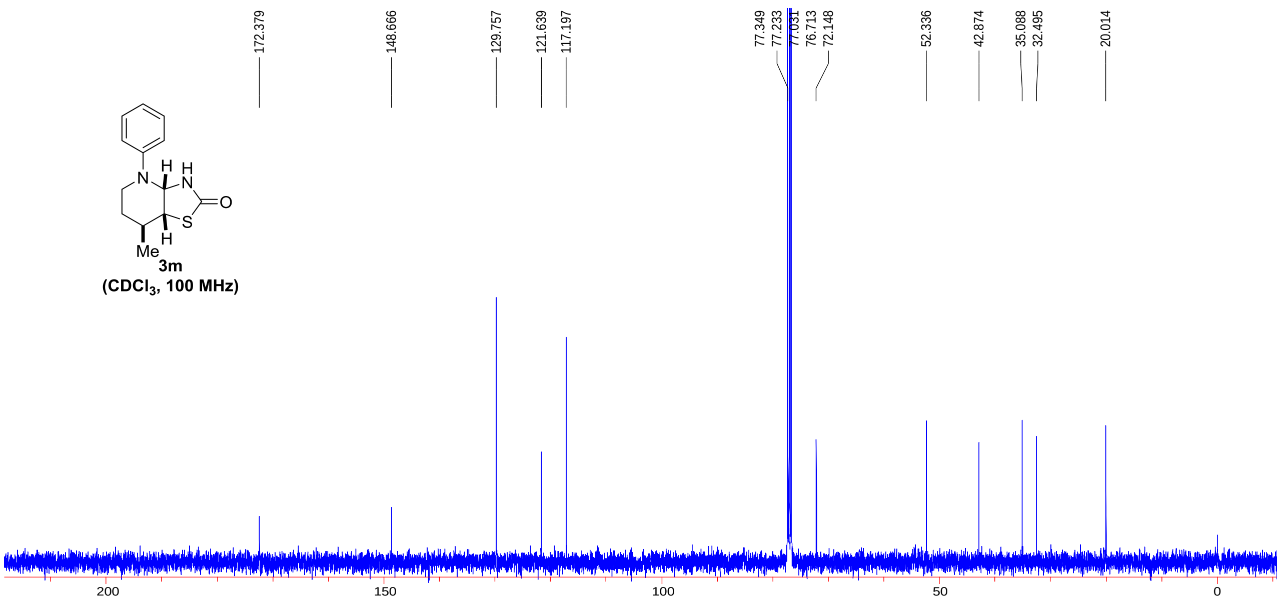


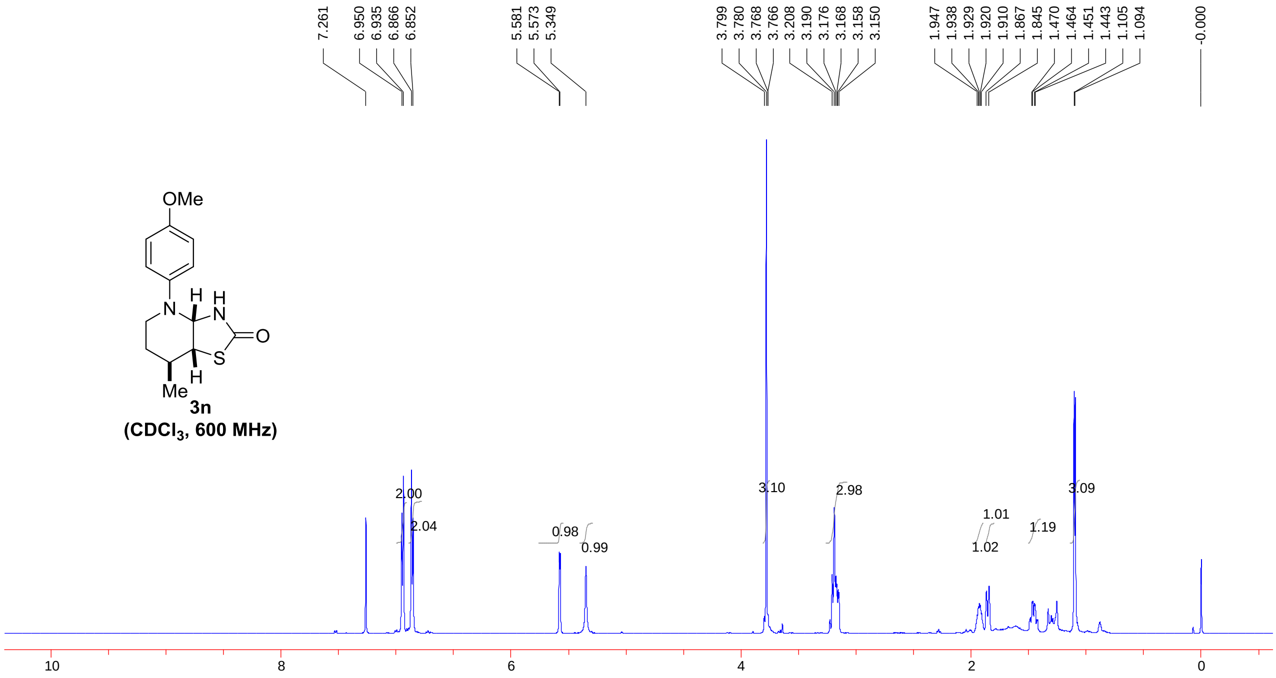
7.255
5.005
6.841
4.992
3.923
3.910
3.903
3.898
3.890
5.204
3.877
3.339
3.331
3.318
3.309
3.301
3.288
3.280
2.956
2.947
2.941
2.932
2.926
2.916
2.911
2.902
2.274
2.271
2.237
2.146
2.135
2.128
2.116
2.104
2.093
2.080
2.071
2.059
2.049
2.037
1.958
1.950
1.942
1.933
1.925
1.917
1.909
1.671
1.660
1.649
1.639
-0.000
Me
Me
Me
N
H
N
O
S
3l
(CDCl3, 400 MHz)
8.91
2.04
1.08
1.00
1.00
1.07
1.07
2.08
1.08
1.06
10
8
6
4
2
0

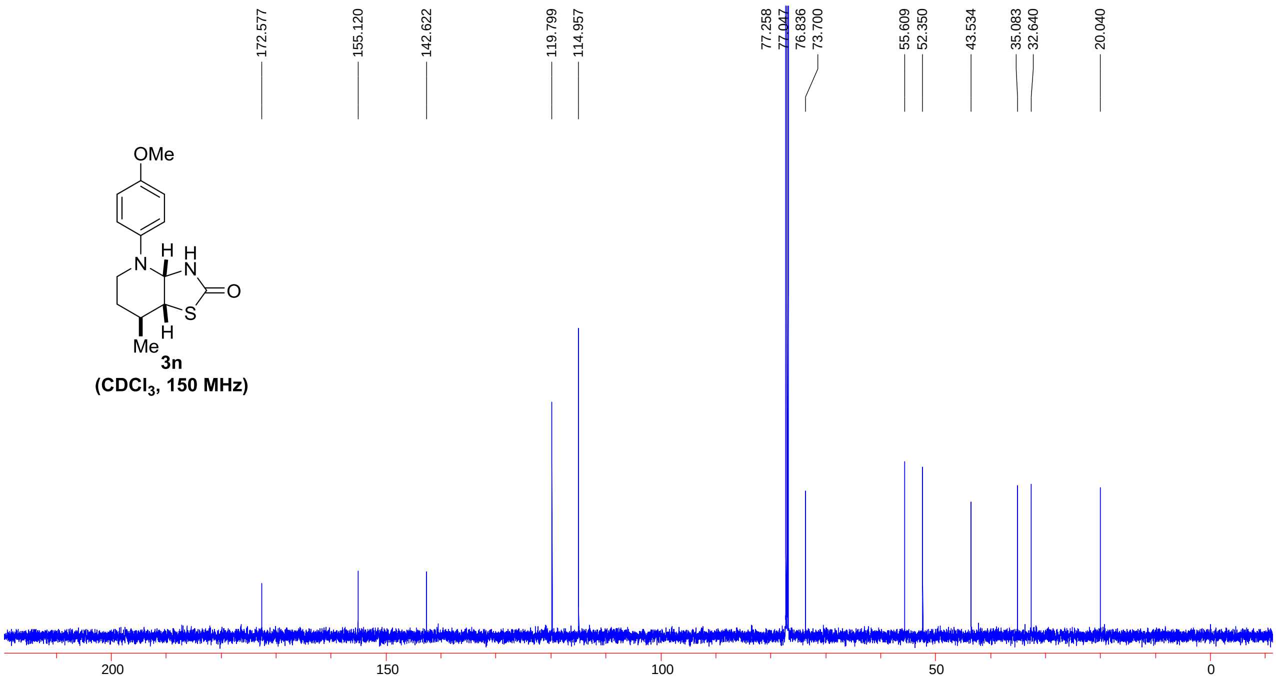


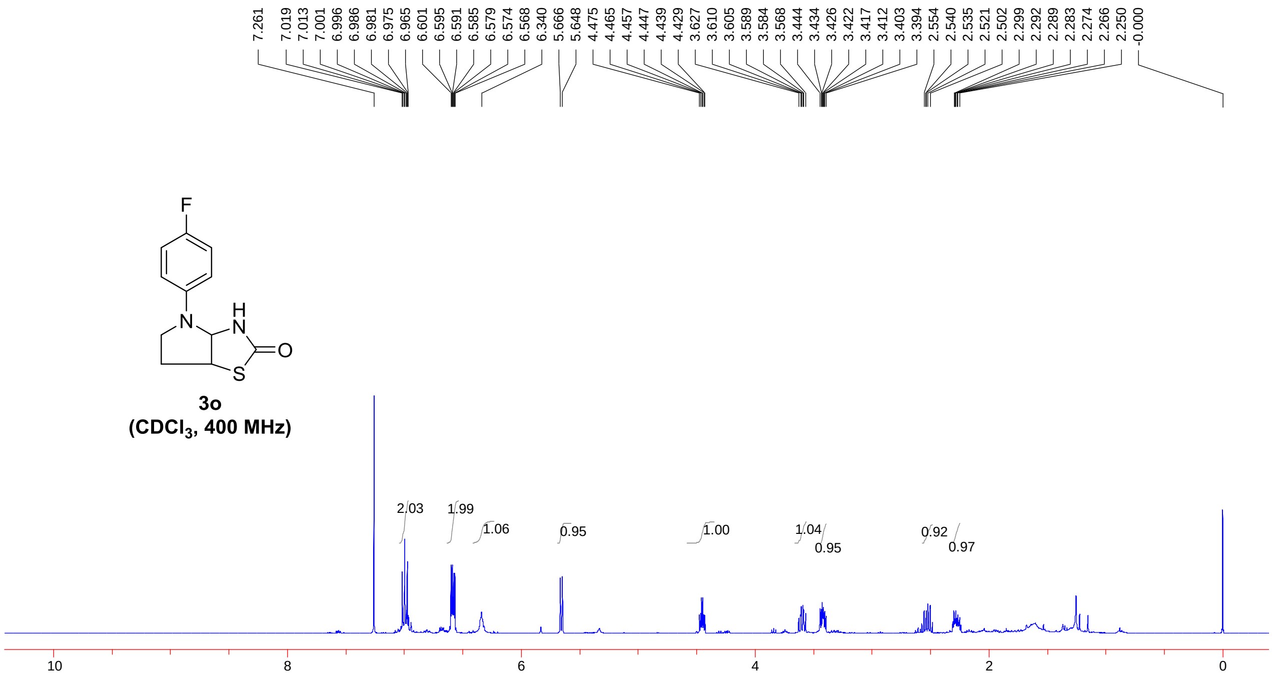
174.108
142.790
137.409
136.001
135.921
130.066
129.978
77.244
77.032
76.821
72.482
46.516
44.825
28.637
24.189
20.689
19.296
19.252
Me
Me
Me
N
H
N
O
S
3l
(CDCl3, 150 MHz)
200
150
100
50
0

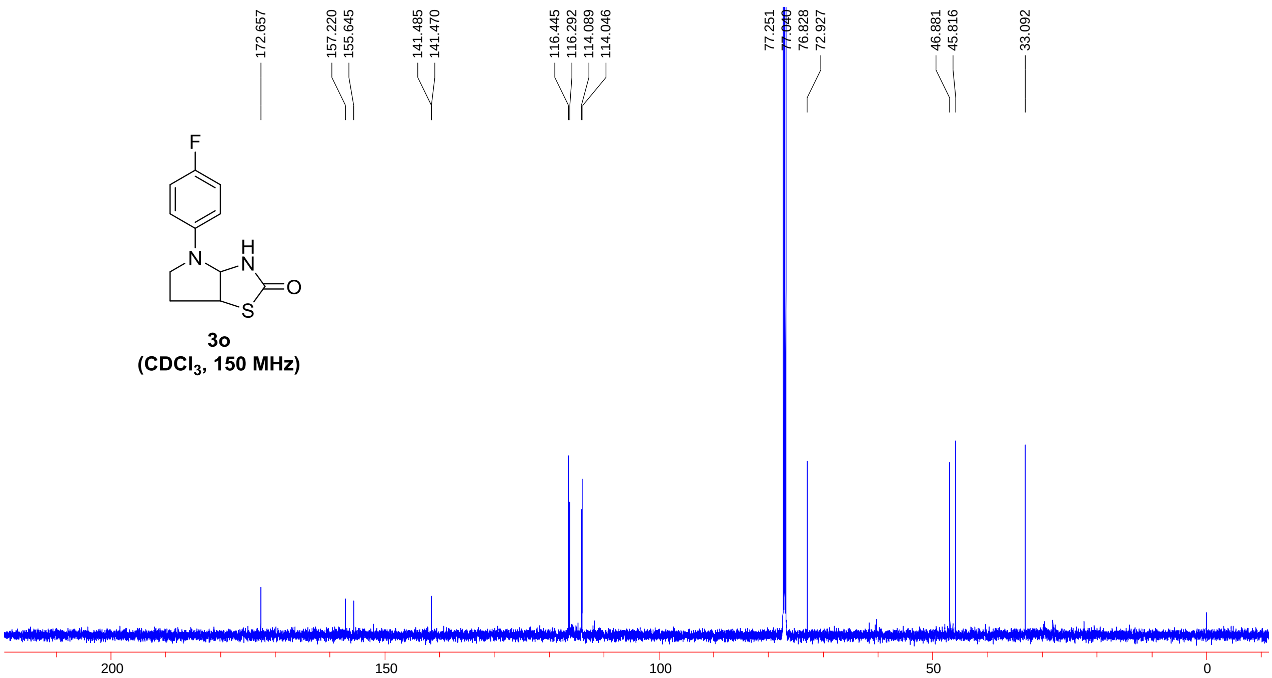

7.327 7.309 7.306 7.287 7.259 6.988 6.983 6.966 6.944 5.753 5.740 5.339
3.423 3.414 3.406 3.393 3.384 3.377 3.226 3.221 3.196 3.190 3.184 3.170 3.158 3.143 1.995 1.989 1.978 1.963 1.948 1.937 1.931 1.921 1.907 1.902 1.894 1.886 1.875 1.868 1.860 1.852 1.508 1.498 1.476 1.467 1.444 1.434 1.412 1.403 1.116 1.100 -0.000
3m
(CDCl3, 400 MHz)
2.00 3.09 1.06 1.03 1.08 2.06 2.05 1.03 3.06
10 8 6 4 2 0 -2 PPM

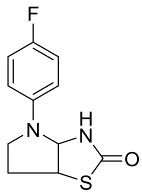

172.379 148.666 129.757 121.639 117.197 77.349 77.233 77.031 76.713 72.148 52.336 42.874 35.088 32.495 20.014
3m
(CDCl3, 100 MHz)
200 150 100 50 0


7.261
6.950
6.935
6.866
6.852
5.581
5.573
5.349
3.799
3.780
3.768
3.766
3.208
3.190
3.176
3.168
3.158
3.150
1.947
1.938
1.929
1.920
1.910
1.867
1.845
1.470
1.464
1.451
1.443
1.105
1.094
-0.000
OMe
H
H
N
N
O
S
H
Me
3n
(CDCl3, 600 MHz)
2.00
2.04
0.98
0.99
3.10
2.98
1.01
1.02
1.19
3.09
10
8
6
4
2
0

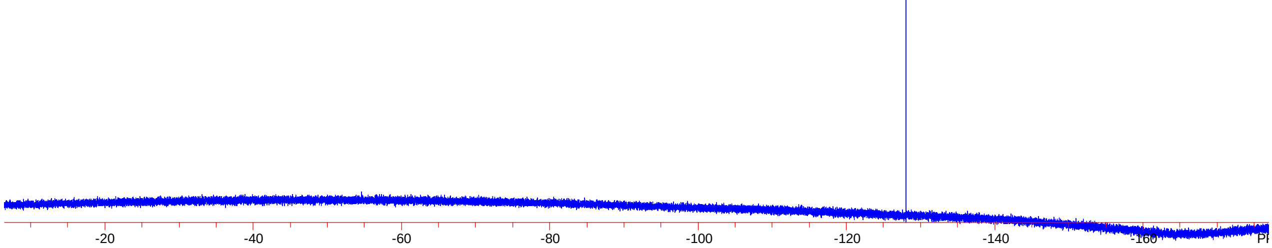

172.577
155.120
142.622
119.799
114.957
77.258
77.047
76.836
73.700
55.609
52.350
43.534
35.083
32.640
20.040
OMe
H
H
N
N
O
S
H
Me
3n
(CDCl3, 150 MHz)
200
150
100
50
0

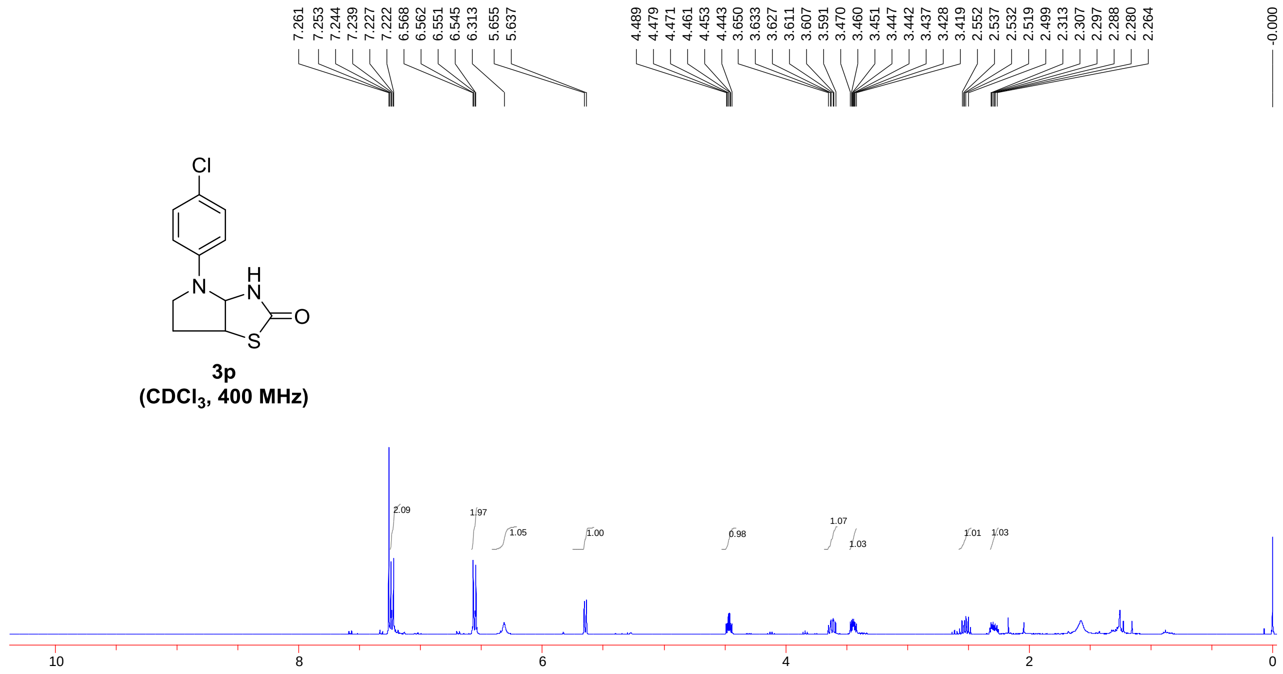

7.261 7.019 7.013 7.001 6.996 6.986 6.981 6.975 6.965 6.601 6.595 6.591 6.585 6.579 6.574 6.568 6.340 5.666 5.648 4.475 4.465 4.457 4.447 4.439 4.429 3.627 3.610 3.605 3.589 3.584 3.568 3.444 3.434 3.426 3.422 3.417 3.412 3.403 3.394 2.554 2.540 2.535 2.521 2.502 2.299 2.292 2.289 2.283 2.274 2.266 2.250 -0.000
F
N
H
N
O
S
3o
(CDCl3, 400 MHz)
2.03
1.99
1.06
0.95
1.00
1.04
0.95
0.92
0.97
10
8
6
4
2
0

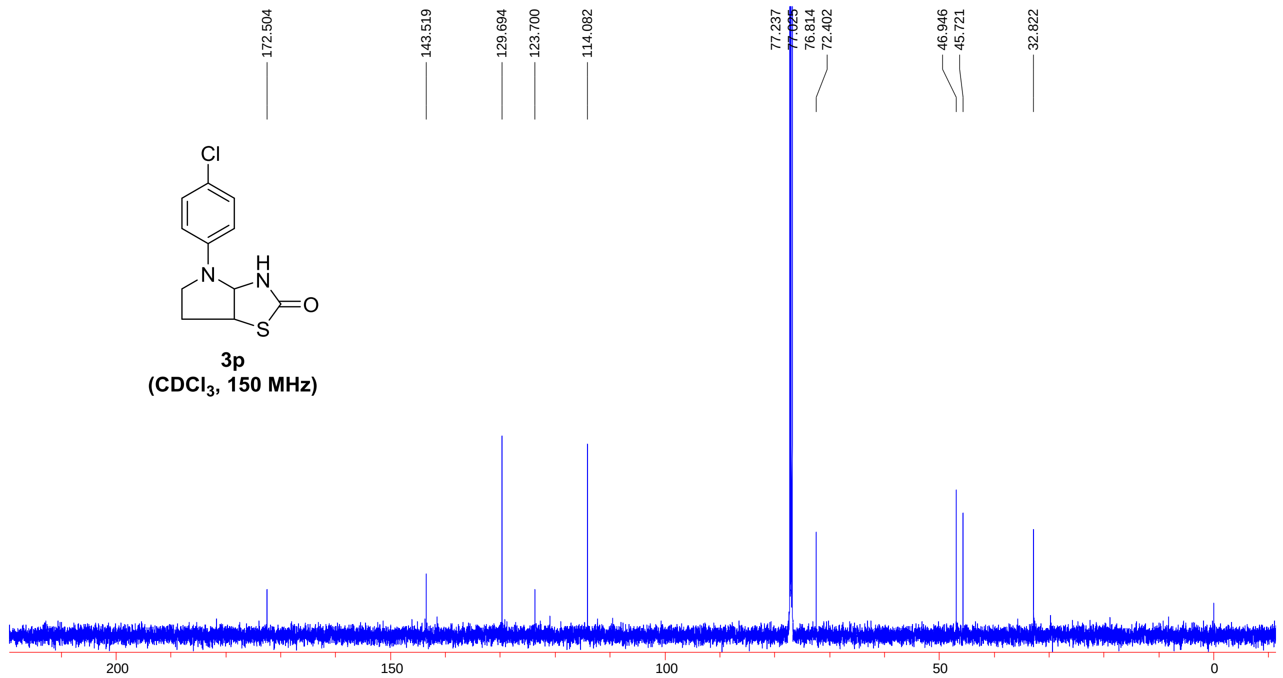

172.657
157.220 155.645
141.485 141.470
116.445 116.292 114.089 114.046
77.251 77.040 76.828 72.927
46.881 45.816
33.092
F
N
H
N
O
S
3o
(CDCl3, 150 MHz)
200
150
100
50
0

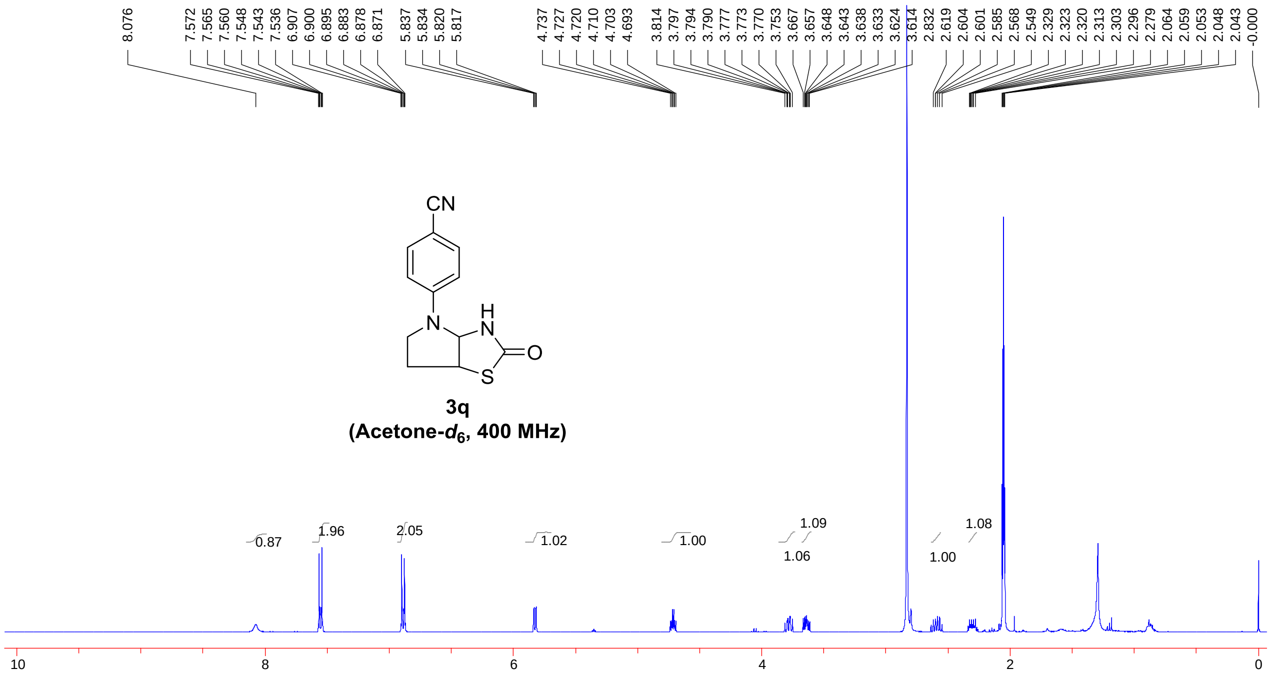


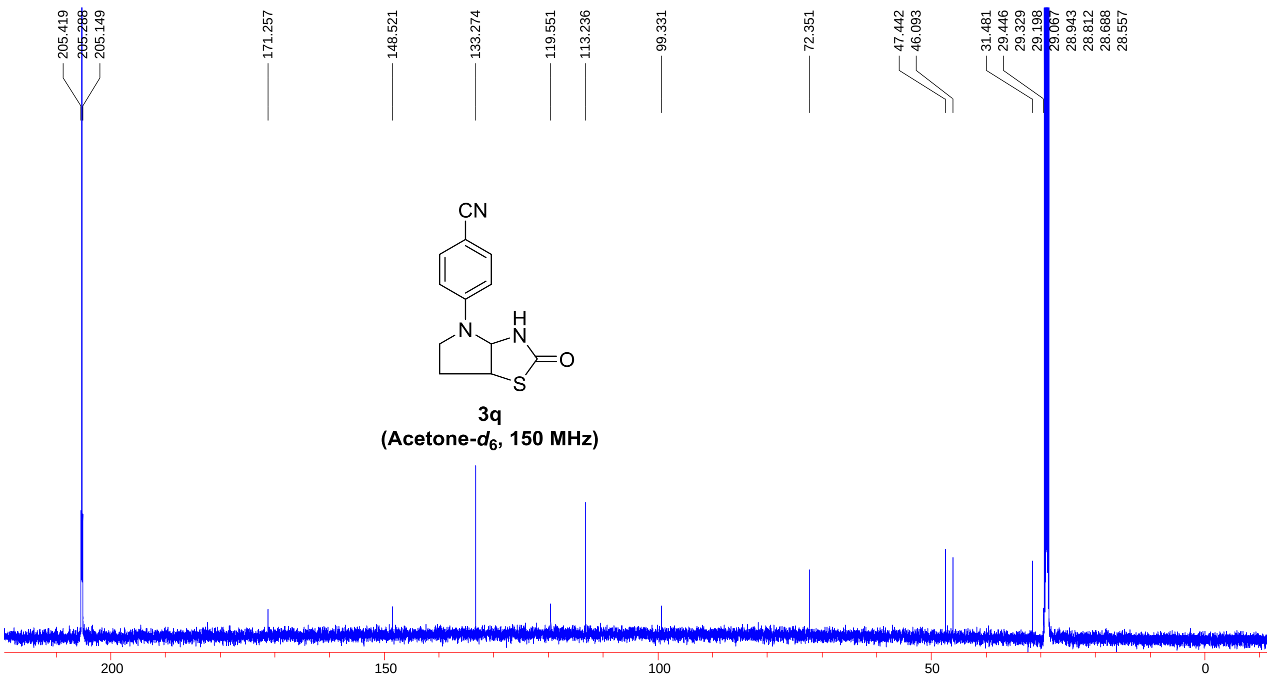
3o
($CDCl_3$, 376 MHz)



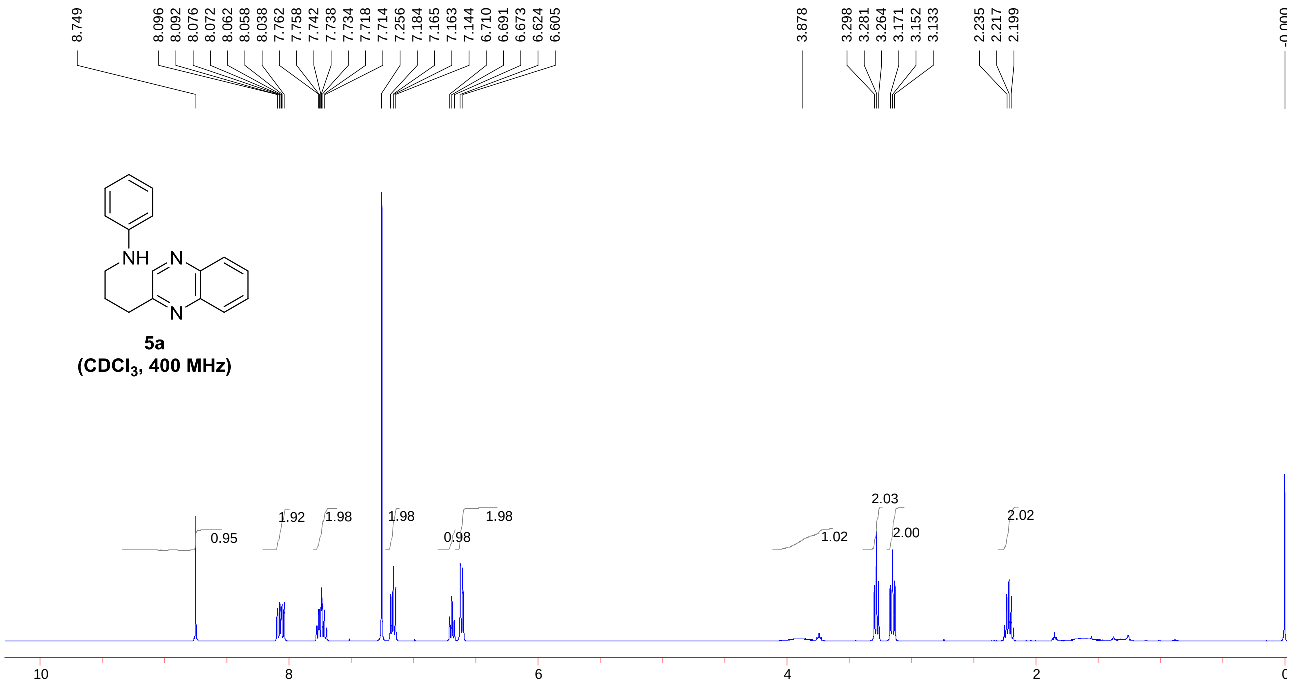

7.261 7.253 7.244 7.239 7.227 7.222 6.568 6.562 6.551 6.545 6.313 5.655 5.637
4.489 4.479 4.471 4.461 4.453 4.443 3.650 3.633 3.627 3.611 3.607 3.591 3.470 3.460 3.451 3.447 3.442 3.437 3.428 3.419 2.552 2.537 2.532 2.519 2.499 2.313 2.307 2.297 2.288 2.280 2.264
-0.000
Cl
N
H
N
O
S
3p
(CDCl3, 400 MHz)
2.09 1.97 1.05 1.00 0.98 1.07 1.03 1.01 1.03
10 8 6 4 2 0

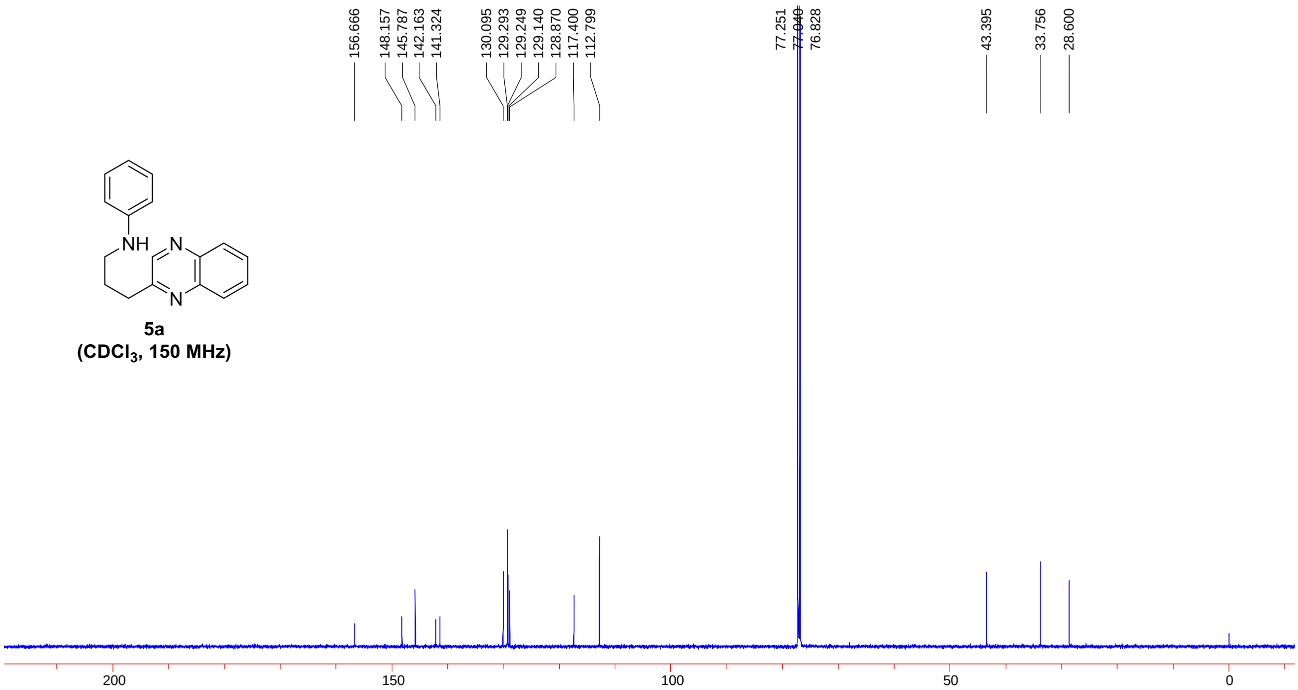

172.504 143.519 129.694 123.700 114.082 77.237 77.025 76.814 72.402 46.946 45.721 32.822
Cl
N
H
N
O
S
3p
(CDCl3, 150 MHz)
200 150 100 50 0

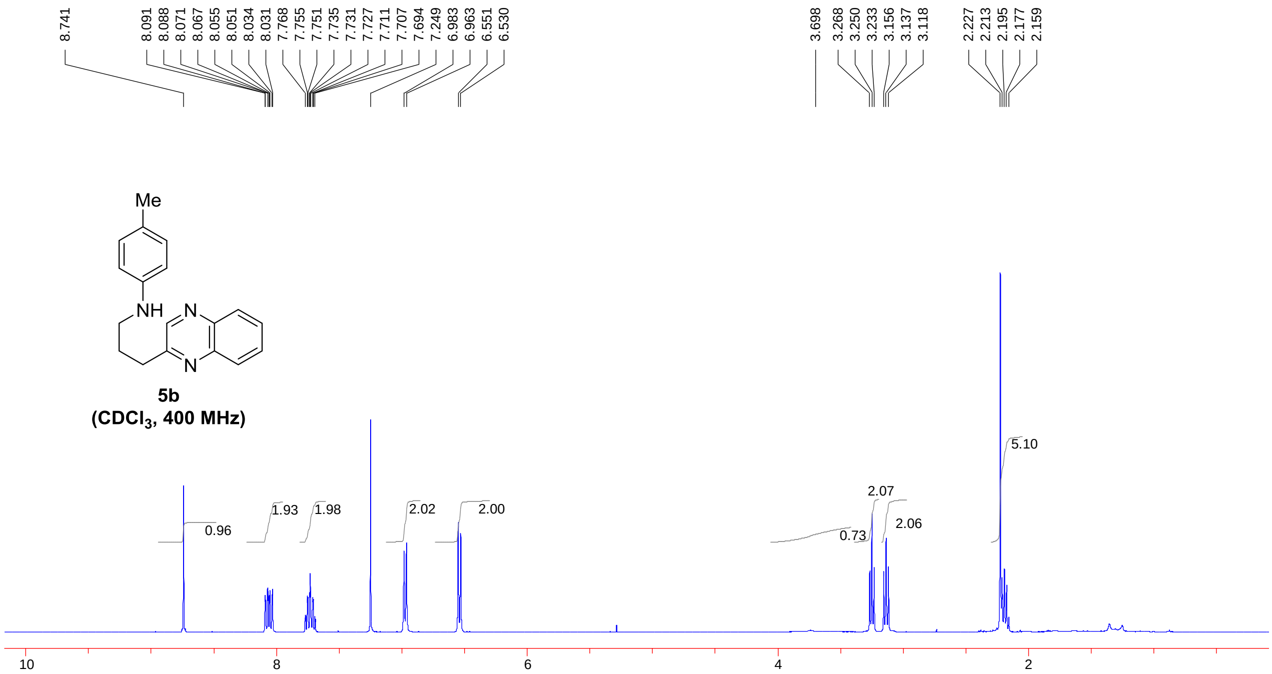

8.076
7.572
7.565
7.560
7.548
7.543
7.536
6.907
6.900
6.895
6.883
6.878
6.871
5.837
5.834
5.820
5.817
4.737
4.727
4.720
4.710
4.703
4.693
3.814
3.797
3.794
3.790
3.777
3.773
3.770
3.753
3.667
3.657
3.648
3.643
3.638
3.633
3.624
3.614
2.832
2.619
2.604
2.601
2.585
2.568
2.549
2.329
2.323
2.320
2.313
2.303
2.296
2.279
2.064
2.059
2.053
2.048
2.043
-0.000
CN
H
N
N
O
S
3q
(Acetone-d_6, 400 MHz)
0.87
1.96
2.05
1.02
1.00
1.09
1.06
1.00
1.08
10
8
6
4
2
0

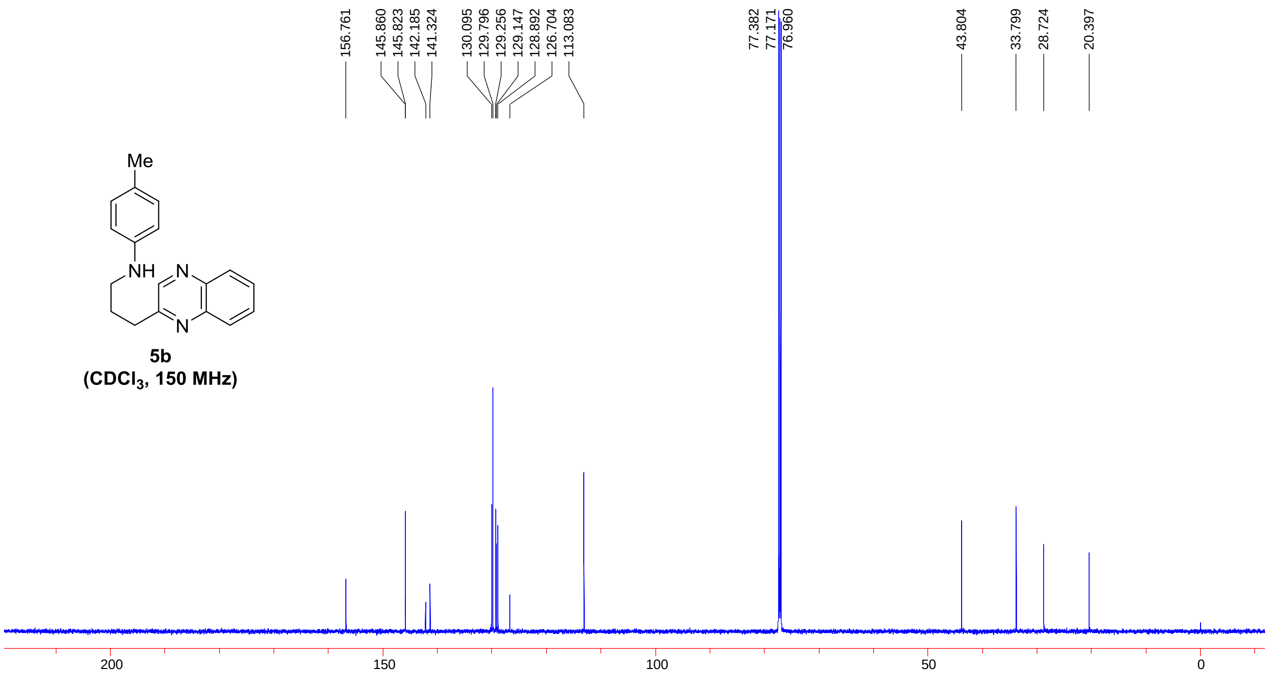

205.419
205.280
205.149
171.257
148.521
133.274
119.551
113.236
99.331
72.351
47.442
46.093
31.481
29.446
29.329
29.198
29.067
28.943
28.812
28.688
28.557
CN
H
N
N
O
S
3q
(Acetone-d_6, 150 MHz)
200
150
100
50
0

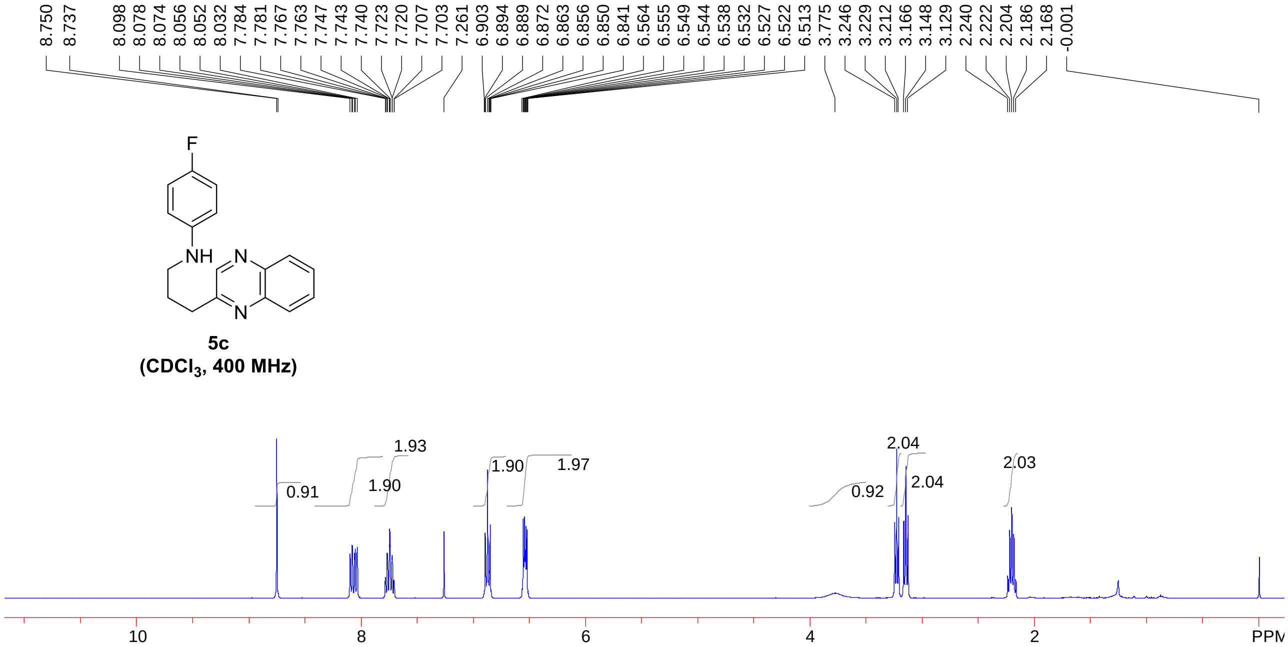
IV. Copies of the NMR spectra of 5a-5s

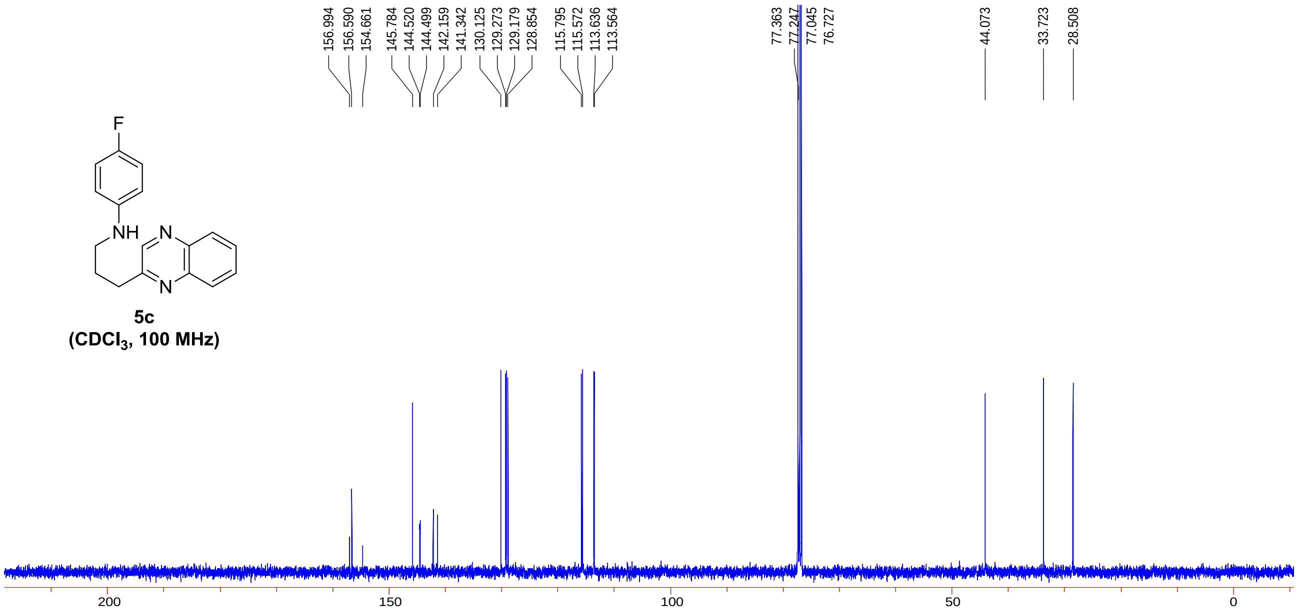


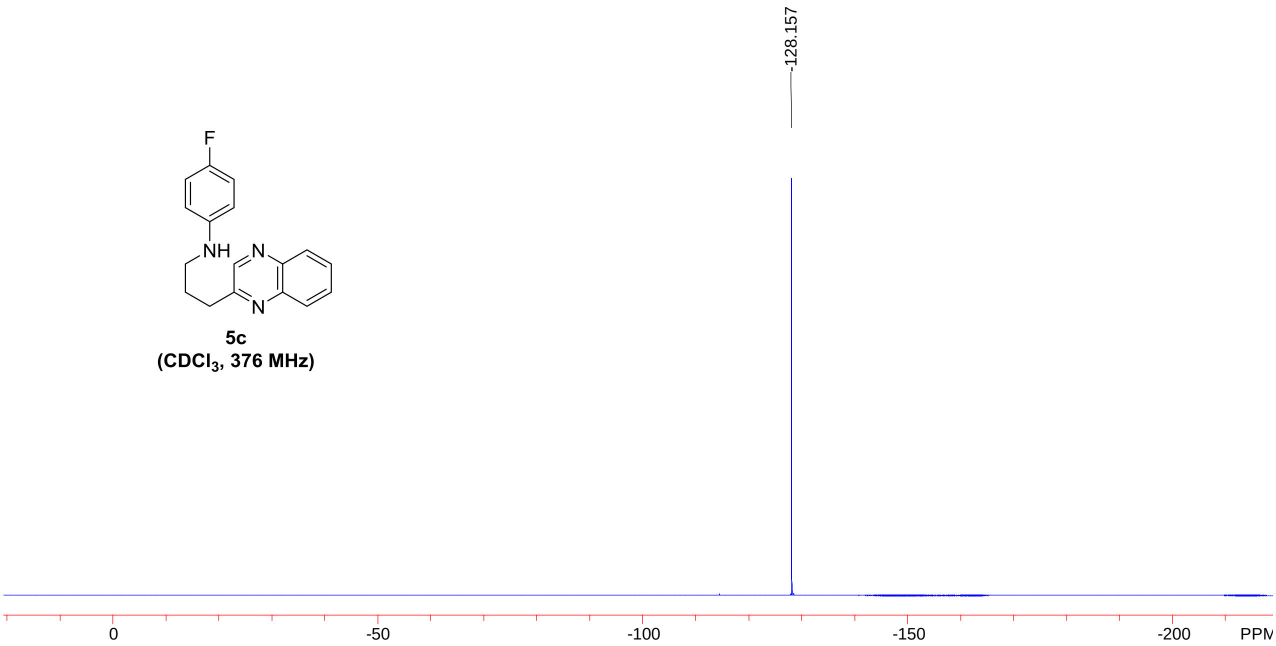



8.741
8.091
8.088
8.071
8.067
8.055
8.051
8.034
8.031
7.768
7.755
7.751
7.735
7.731
7.727
7.711
7.707
7.694
7.249
6.983
6.963
6.551
6.530
3.698
3.268
3.250
3.233
3.156
3.137
3.118
2.227
2.213
2.195
2.177
2.159
Me
NH
N
N
5b
(CDCl3, 400 MHz)
0.96
1.93
1.98
2.02
2.00
0.73
2.07
2.06
5.10
10
8
6
4
2

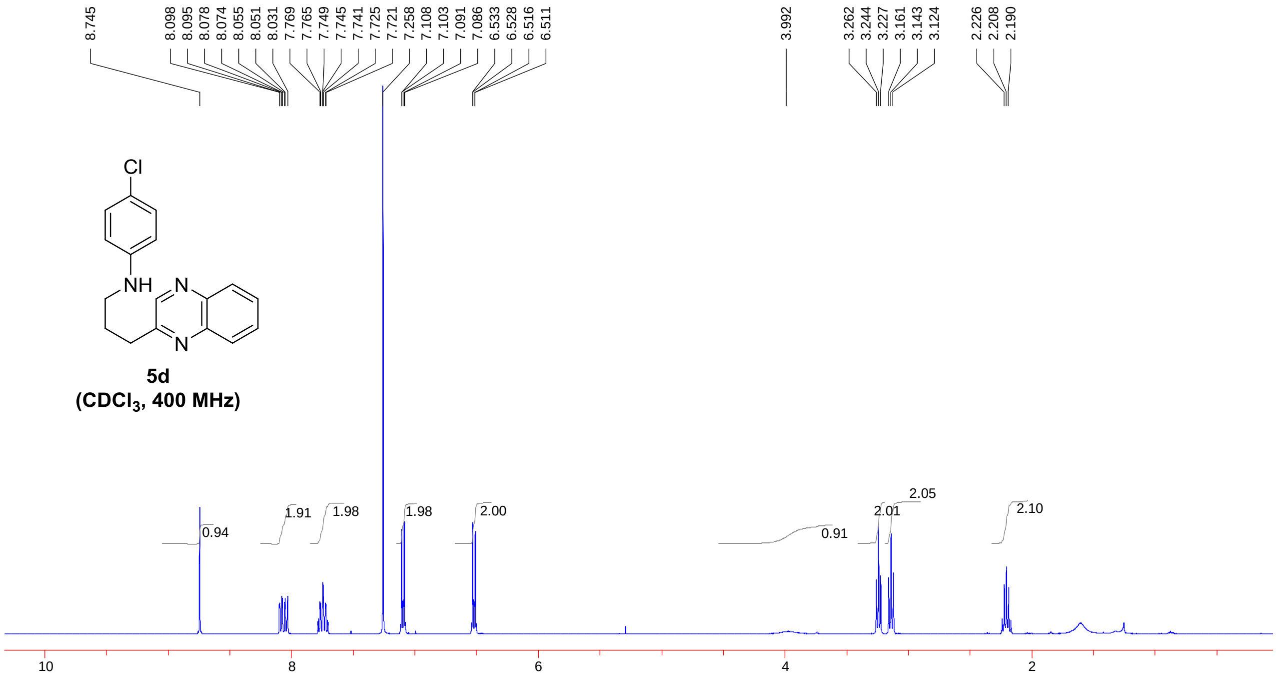

156.761
145.860
145.823
142.185
141.324
130.095
129.796
129.256
129.147
128.892
126.704
113.083
77.382
77.171
76.960
43.804
33.799
28.724
20.397
Me
NH
N
N
5b
(CDCl3, 150 MHz)
200
150
100
50
0

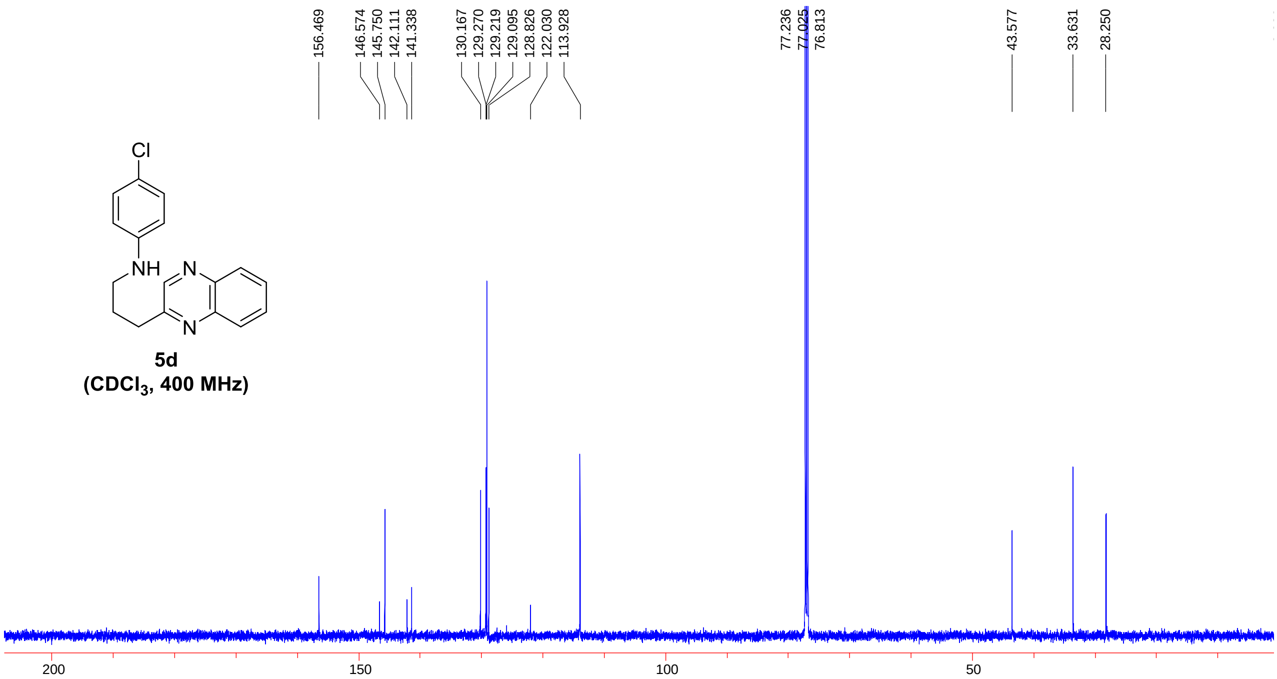

8.750 8.737 8.098 8.078 8.074 8.056 8.052 8.032 7.784 7.781 7.767 7.763 7.747 7.743 7.740 7.723 7.720 7.707 7.703 7.261 6.903 6.894 6.889 6.872 6.863 6.856 6.850 6.841 6.564 6.555 6.549 6.544 6.538 6.532 6.527 6.522 6.513 3.775 3.246 3.229 3.212 3.166 3.148 3.129 2.240 2.222 2.204 2.186 2.168 -0.001
F
NH
N
N
5c
(CDCl$_3$, 400 MHz)
0.91
1.90
1.93
1.90
1.97
0.92
2.04
2.04
2.03
10
8
6
4
2
PPM

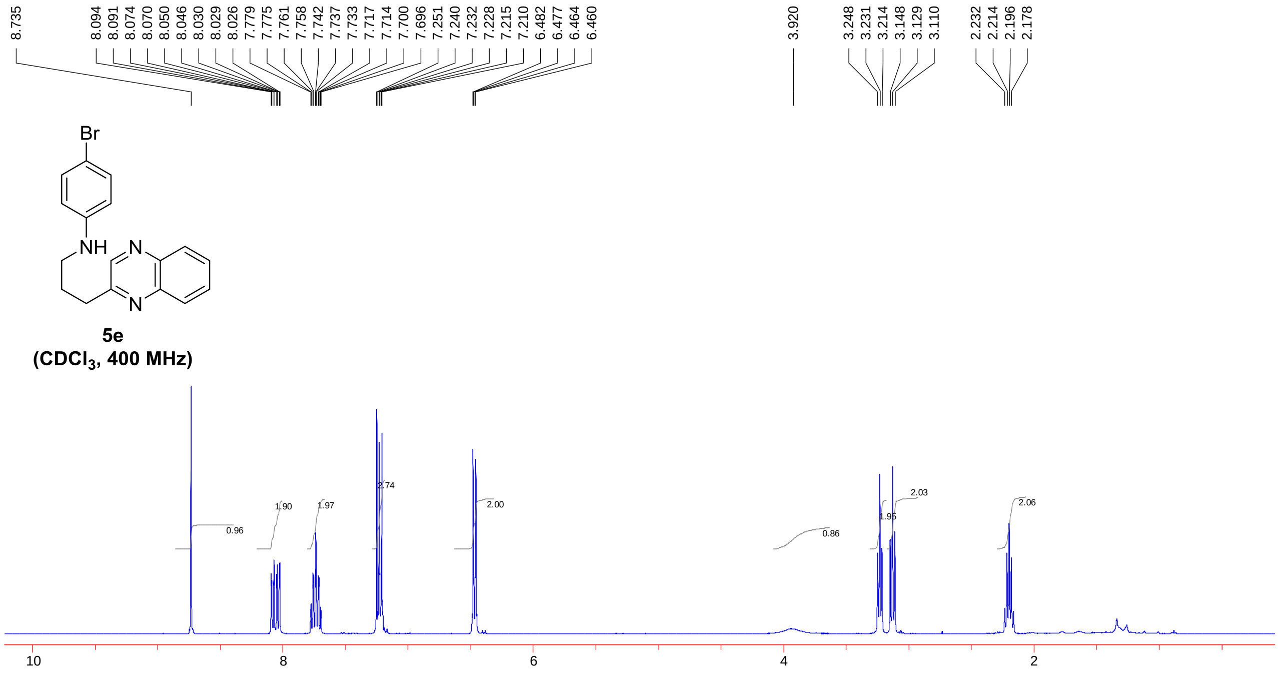

156.994 156.590 154.661 145.784 144.520 144.499 142.159 141.342 130.125 129.273 129.179 128.854 115.795 115.572 113.636 113.564
77.363 77.247 77.045 76.727
44.073 33.723 28.508
F
NH
N
N
5c
(CDCl$_3$, 100 MHz)
200
150
100
50
0

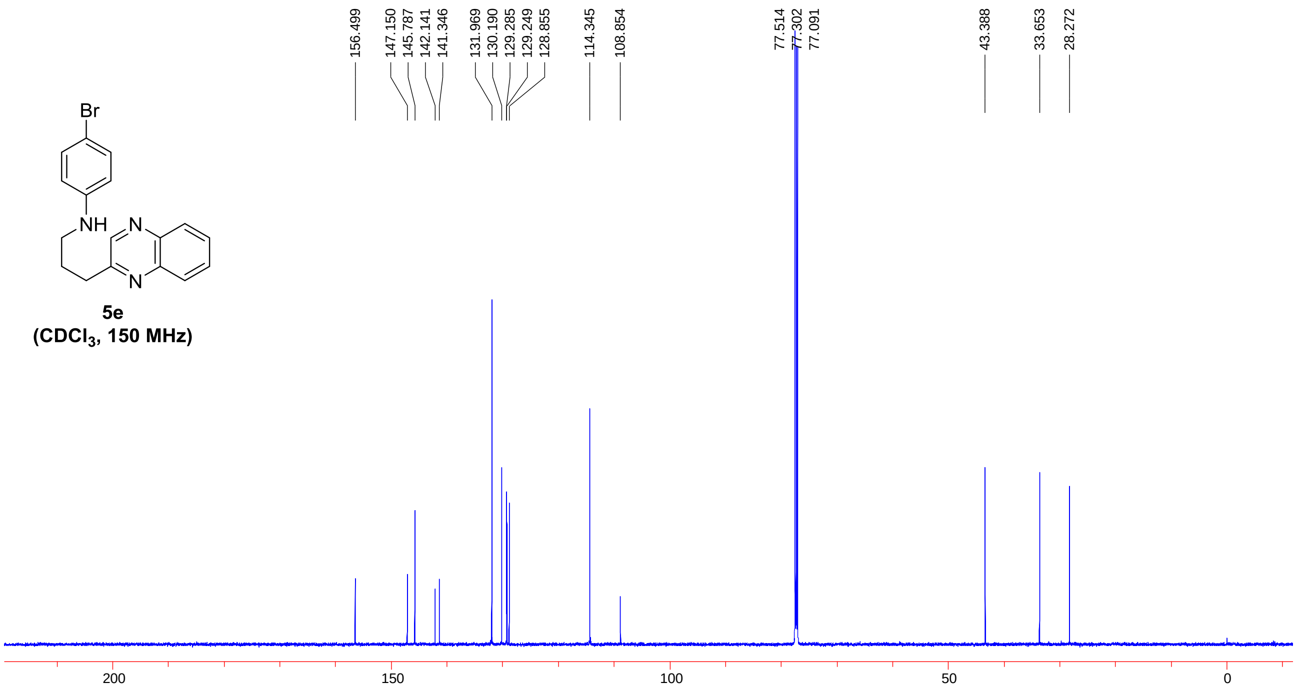


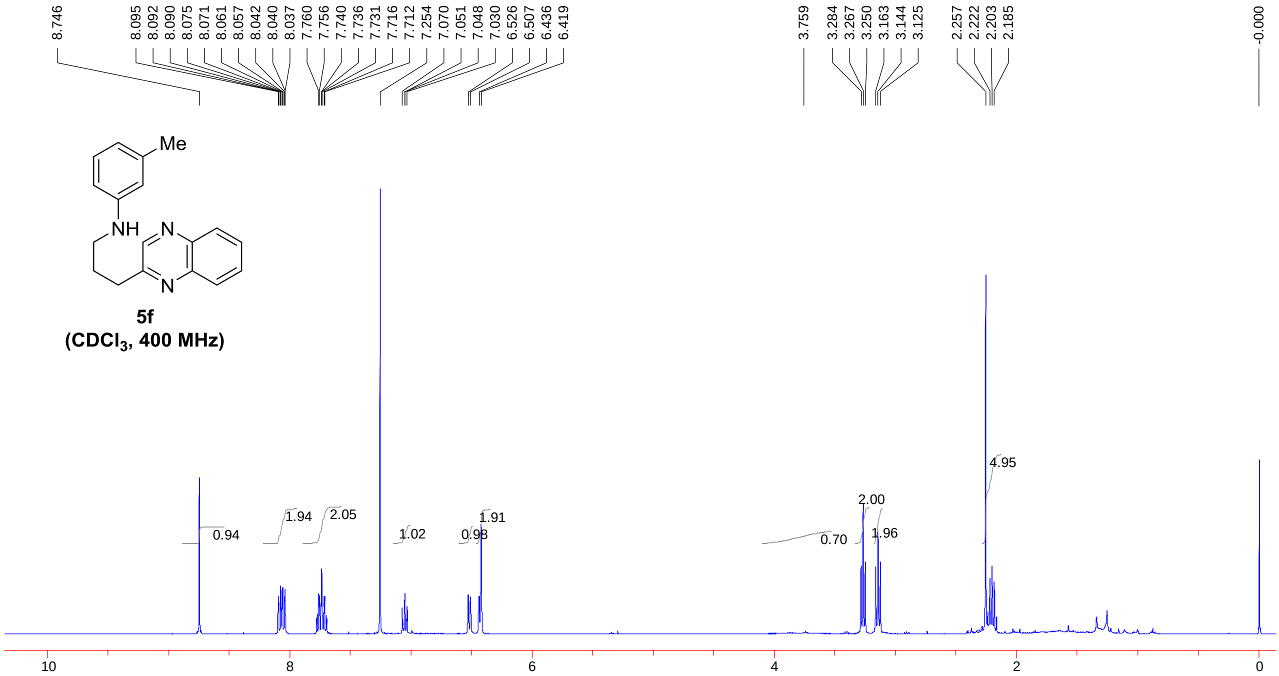
5c
($CDCl_3$, 376 MHz)

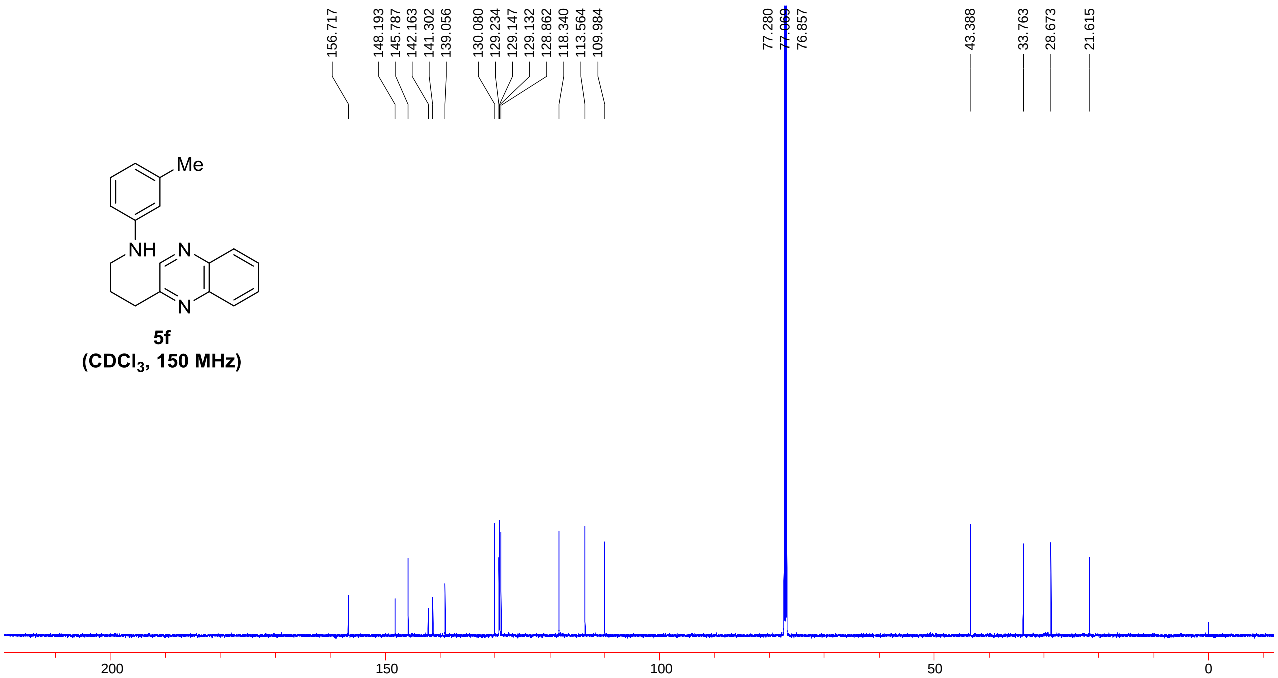

8.745
8.098 8.095 8.078 8.074 8.055 8.051 8.031 7.769 7.765 7.749 7.745 7.741 7.725 7.721 7.258 7.108 7.103 7.091 7.086 6.533 6.528 6.516 6.511
3.992
3.262 3.244 3.227 3.161 3.143 3.124
2.226 2.208 2.190
Cl
NH
N
N
5d
(CDCl3, 400 MHz)
0.94
1.91
1.98
1.98
2.00
0.91
2.01
2.05
2.10
10
8
6
4
2

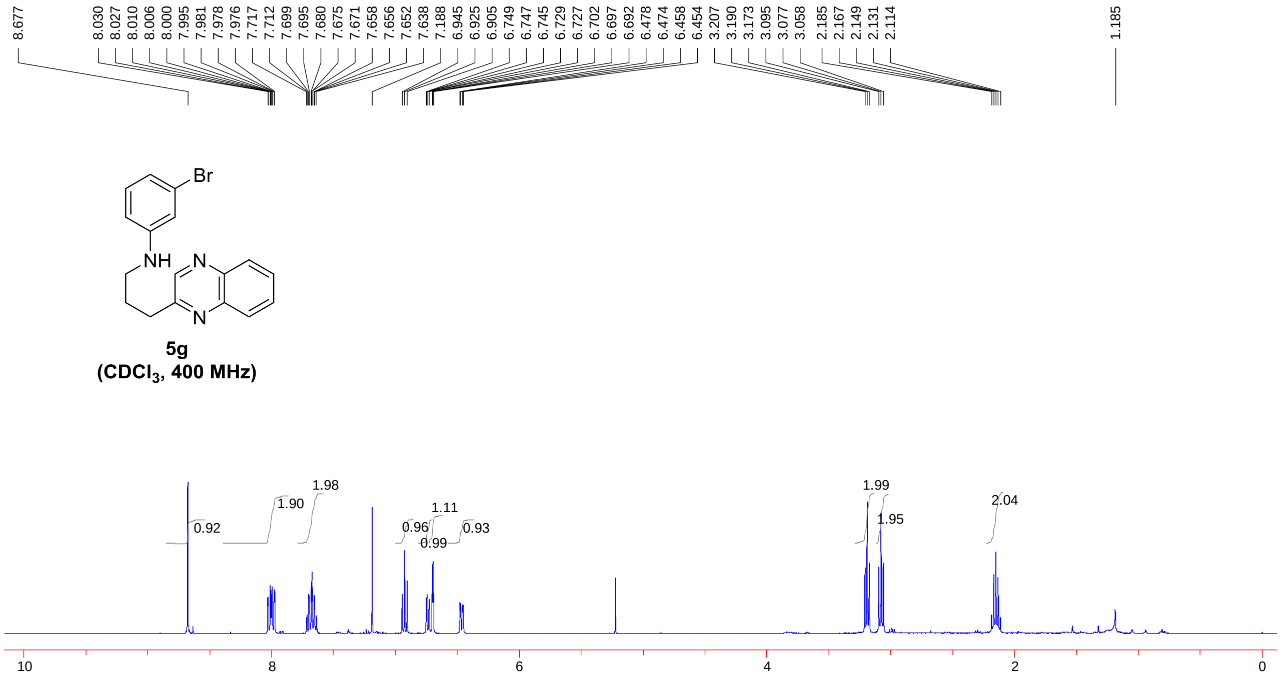

156.469
146.574 145.750 142.111 141.338
130.167 129.270 129.219 129.095 128.826 122.030 113.928
77.236 77.025 76.813
43.577
33.631
28.250
Cl
NH
N
N
5d
(CDCl3, 400 MHz)
200
150
100
50


8.735
8.094 8.091 8.074 8.070 8.050 8.046 8.030 8.029 8.026 7.779 7.775 7.761 7.758 7.742 7.737 7.733 7.717 7.714 7.700 7.696 7.251 7.240 7.232 7.228 7.215 7.210 6.482 6.477 6.464 6.460
3.920
3.248 3.231 3.214 3.148 3.129 3.110
2.232 2.214 2.196 2.178
Br
NH
N
N
5e
(CDCl3, 400 MHz)
0.96
1.90
1.97
2.74
2.00
0.86
1.95
2.03
2.06
10
8
6
4
2

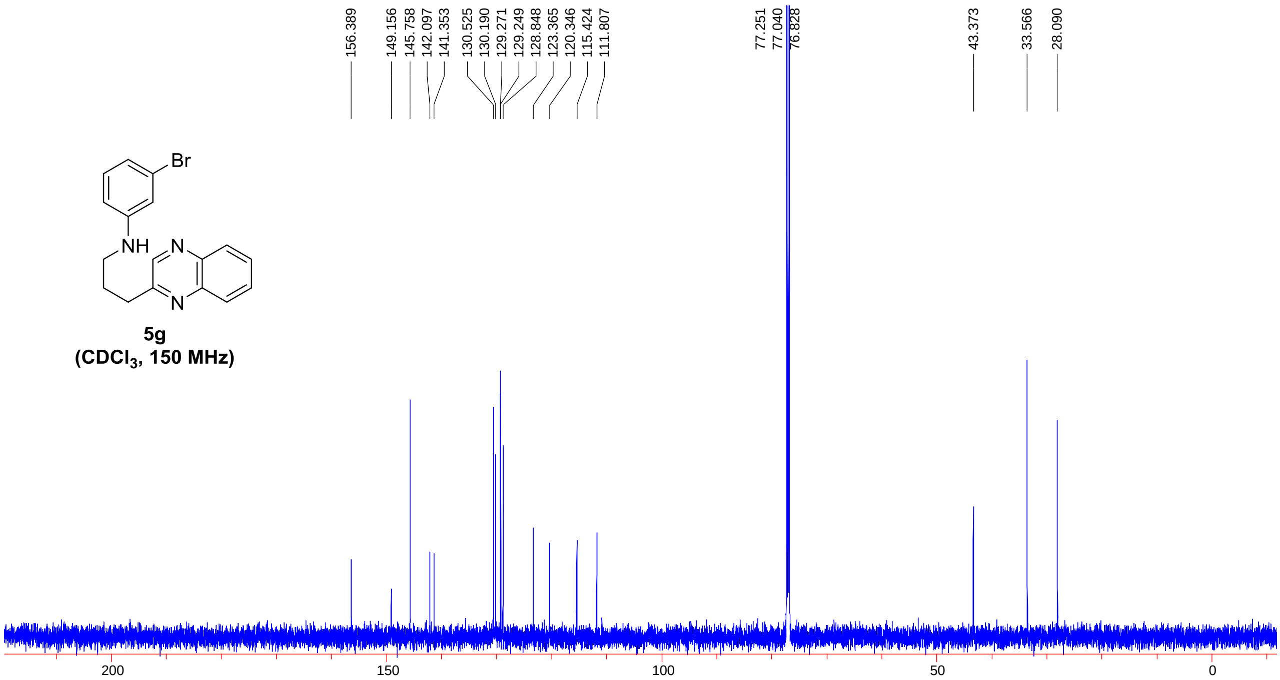

156.499
147.150 145.787 142.141 141.346
131.969 130.190 129.285 129.249 128.855
114.345 108.854
77.514 77.302 77.091
43.388
33.653
28.272
Br
NH
N
N
5e
(CDCl3, 150 MHz)
200
150
100
50
0


8.746
8.095 8.092 8.090 8.075 8.071 8.061 8.057 8.042 8.040 8.037 7.760 7.756 7.740 7.736 7.731 7.716 7.712 7.254 7.070 7.051 7.048 7.030 6.526 6.507 6.436 6.419
3.759 3.284 3.267 3.250 3.163 3.144 3.125
2.257 2.222 2.203 2.185
-0.000
Me
NH
N
N
5f
(CDCl3, 400 MHz)
0.94
1.94
2.05
1.02
0.98
1.91
0.70
2.00
1.96
4.95
10
8
6
4
2
0

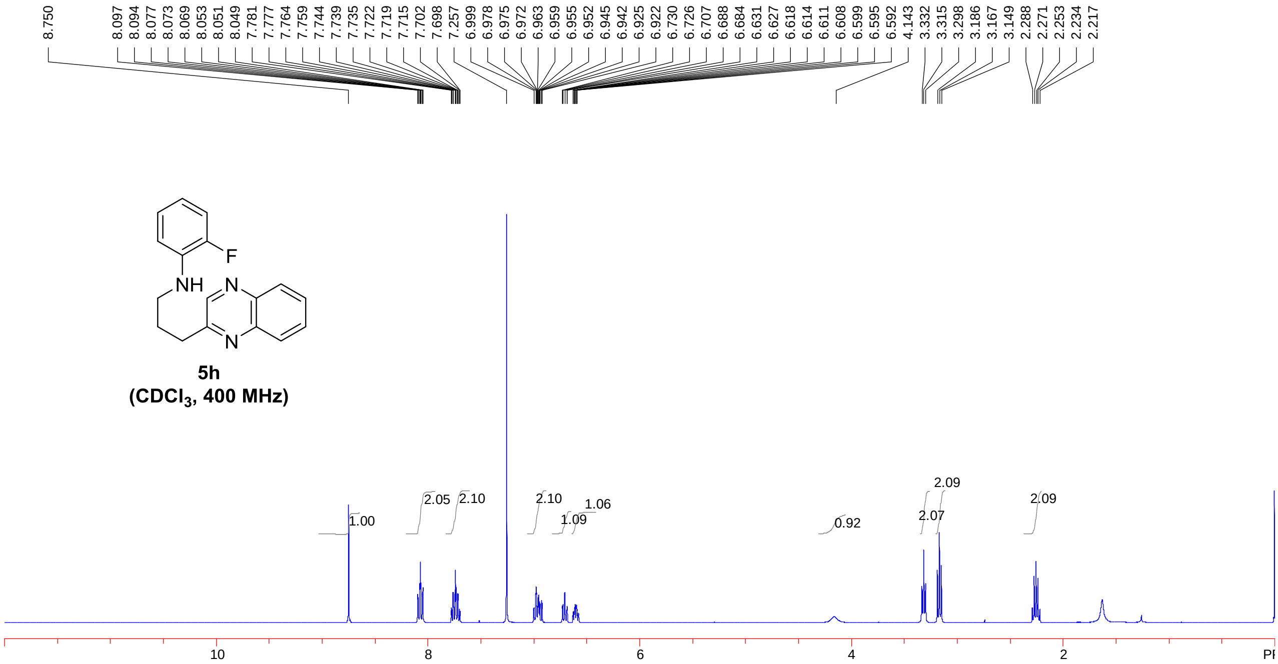

156.717
148.193 145.787 142.163 141.302 139.056
130.080 129.234 129.147 129.132 128.862 118.340 113.564 109.984
77.280 77.069 76.857
43.388
33.763 28.673 21.615
Me
NH
N
N
5f
(CDCl3, 150 MHz)
200
150
100
50
0

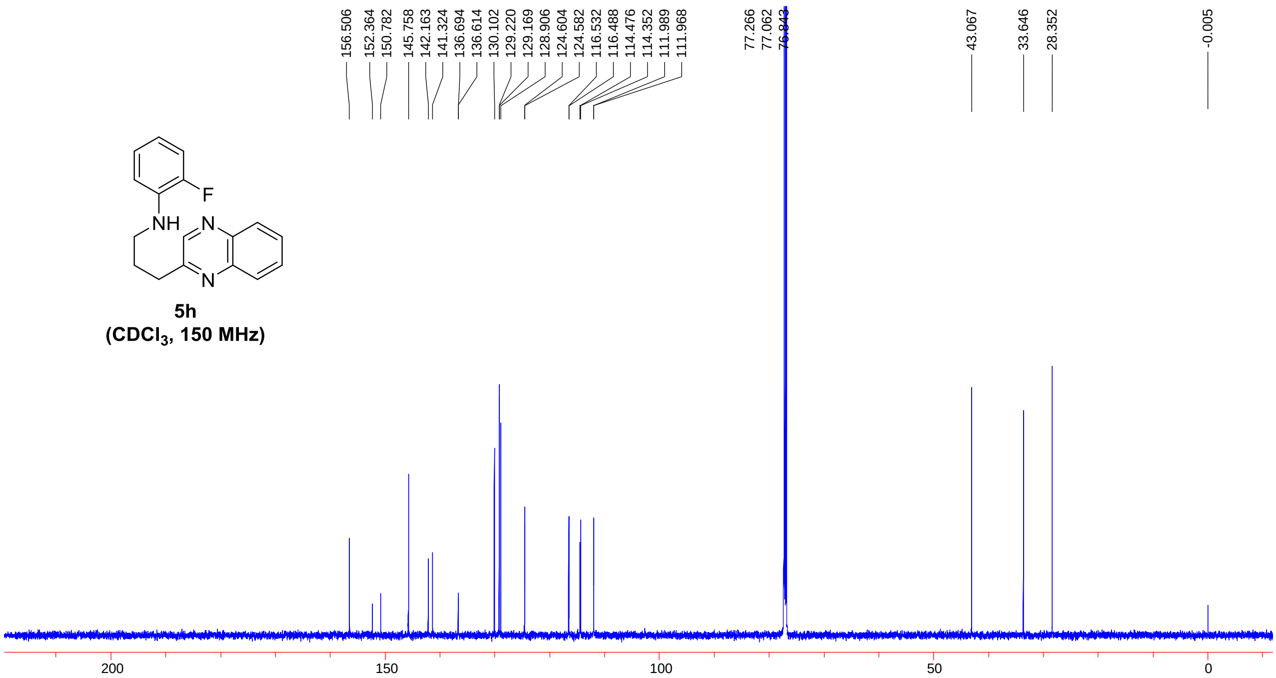


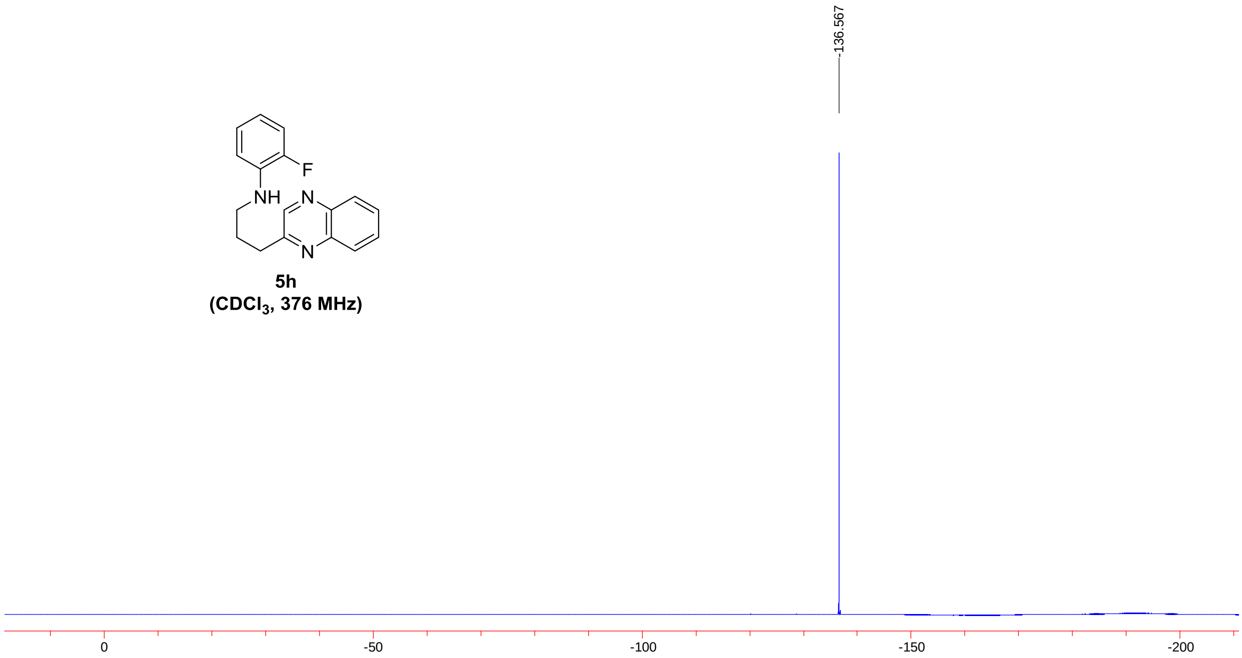
5g
($CDCl_3$, 400 MHz)



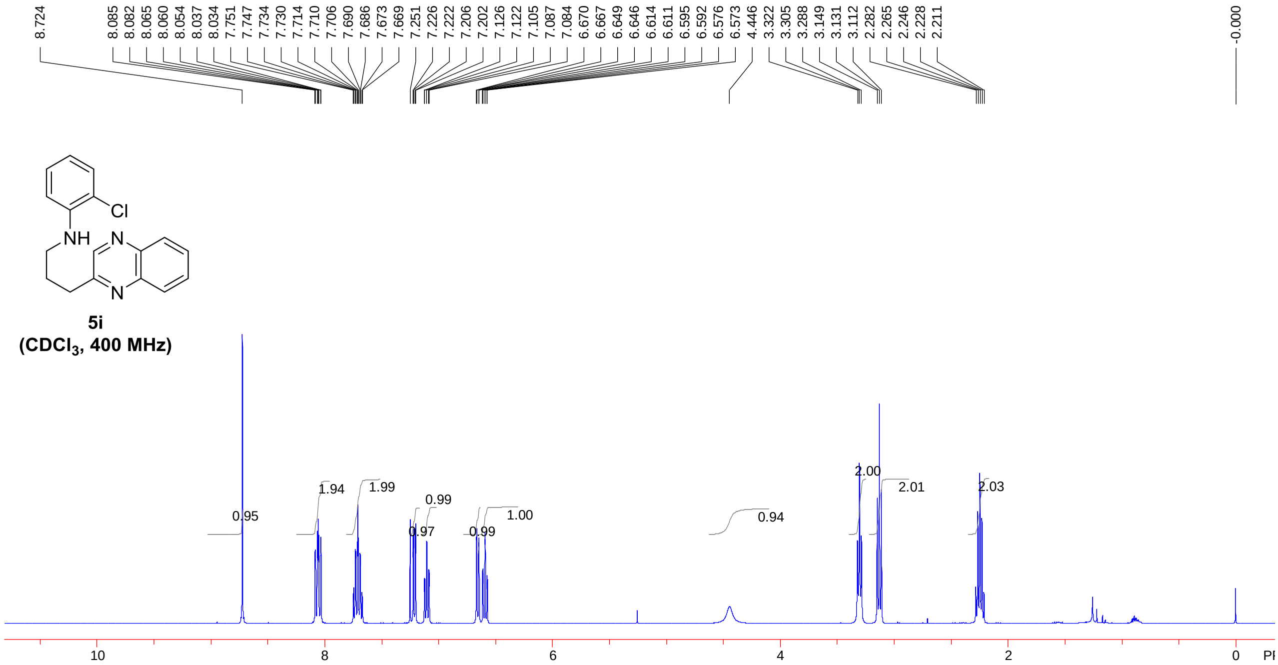
5g
($CDCl_3$, 150 MHz)


8.750
8.097 8.094 8.077 8.073 8.069 8.053 8.051 8.049 7.781 7.777 7.764 7.759 7.744 7.739 7.735 7.722 7.719 7.715 7.702 7.698 7.257 6.999 6.978 6.975 6.972 6.963 6.959 6.955 6.952 6.945 6.942 6.925 6.922 6.730 6.726 6.707 6.688 6.684 6.631 6.627 6.618 6.614 6.611 6.608 6.599 6.595 6.592 4.143 3.332 3.315 3.298 3.186 3.167 3.149 2.288 2.271 2.253 2.234 2.217
F
NH
N
N
5h
(CDCl3, 400 MHz)
1.00
2.05
2.10
2.10
1.09
1.06
0.92
2.07
2.09
2.09
10
8
6
4
2
PI

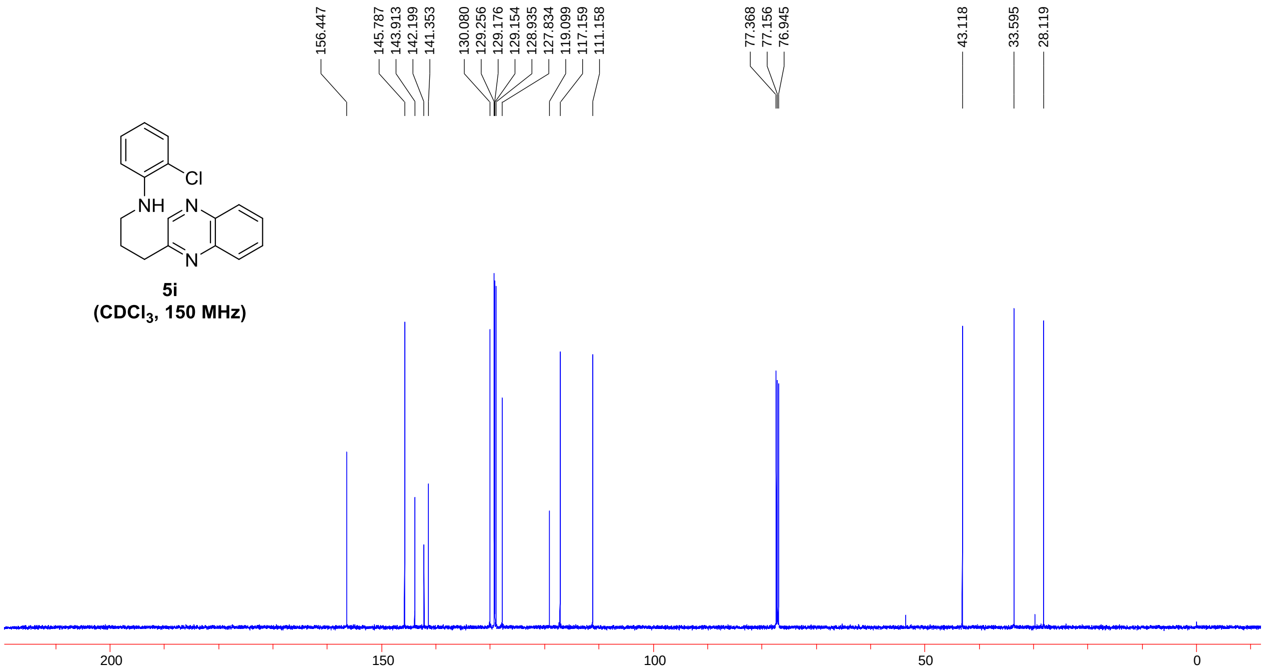

156.506 152.364 150.782 145.758 142.163 141.324 136.694 136.614 130.102 129.220 129.169 128.906 124.604 124.582 116.532 116.488 114.476 114.352 111.989 111.968
77.266 77.062 76.8
43.067
33.646
28.352
-0.005
F
NH
N
N
5h
(CDCl3, 150 MHz)
200
150
100
50
0



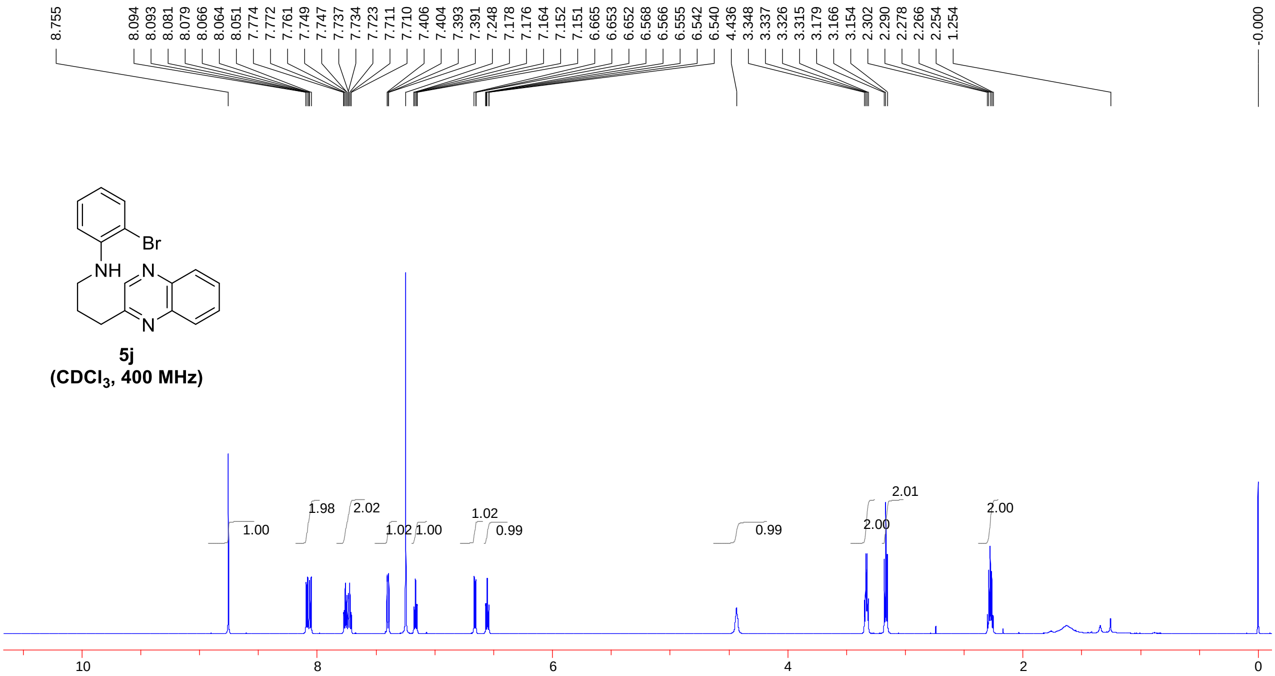
5h
($CDCl_3$, 376 MHz)



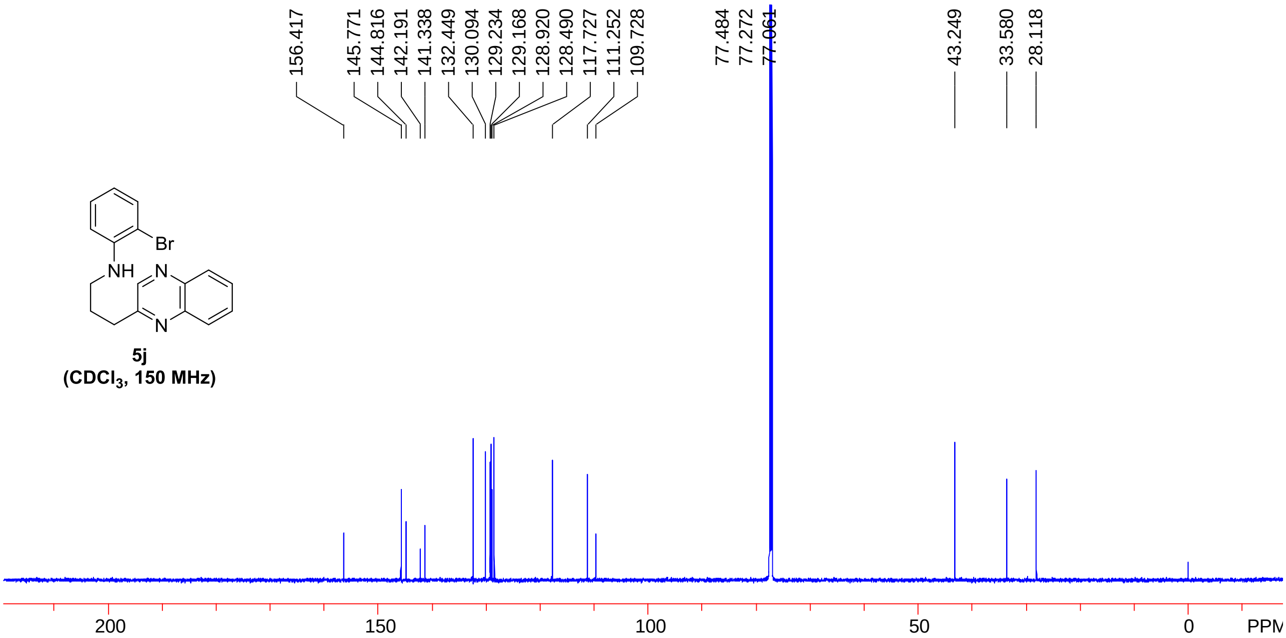
8.724
8.085
8.082
8.065
8.060
8.054
8.037
8.034
7.751
7.747
7.734
7.730
7.714
7.710
7.706
7.690
7.686
7.673
7.669
7.251
7.226
7.222
7.206
7.202
7.126
7.122
7.105
7.087
7.084
6.670
6.667
6.649
6.646
6.614
6.611
6.595
6.592
6.576
6.573
4.446
3.322
3.305
3.288
3.149
3.131
3.112
2.282
2.265
2.246
2.228
2.211
-0.000
Cl
NH
N
N
5i
(CDCl3, 400 MHz)
0.95
1.94
1.99
0.97
0.99
0.99
1.00
0.94
2.00
2.01
2.03
10
8
6
4
2
0



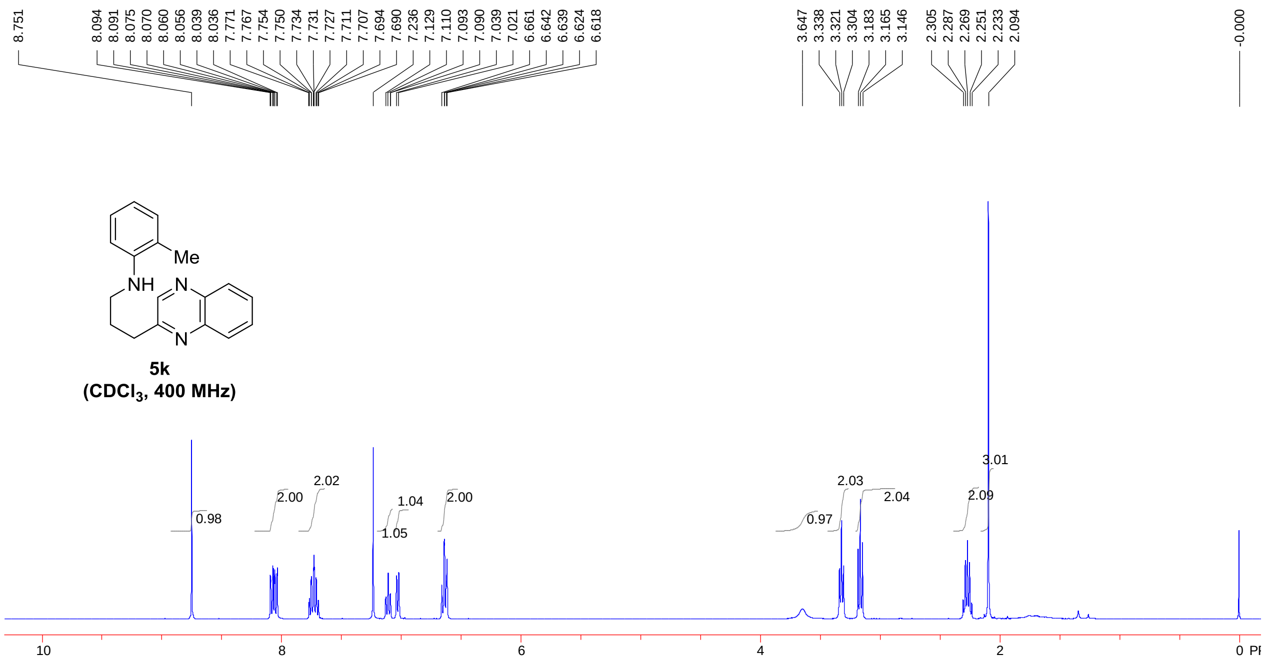
156.447
145.787
143.913
142.199
141.353
130.080
129.256
129.176
129.154
128.935
127.834
119.099
117.159
111.158
77.368
77.156
76.945
43.118
33.595
28.119
Cl
NH
N
N
5i
(CDCl3, 150 MHz)
200
150
100
50
0



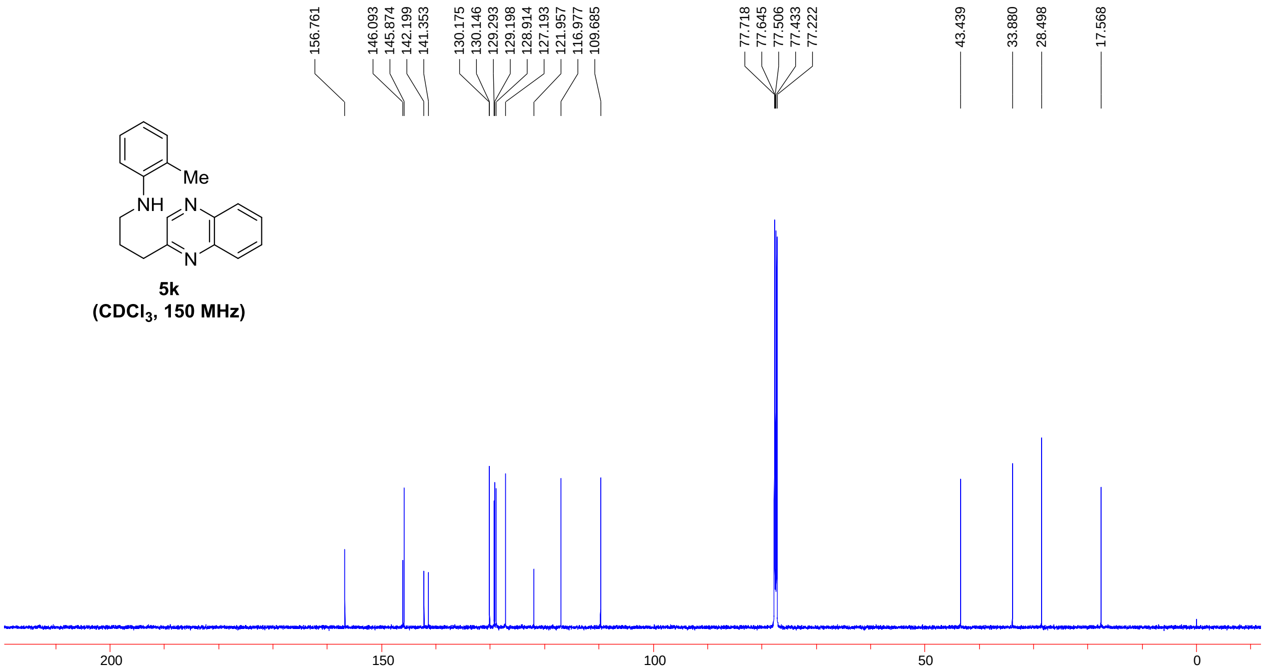
5j
($CDCl_3$, 400 MHz)



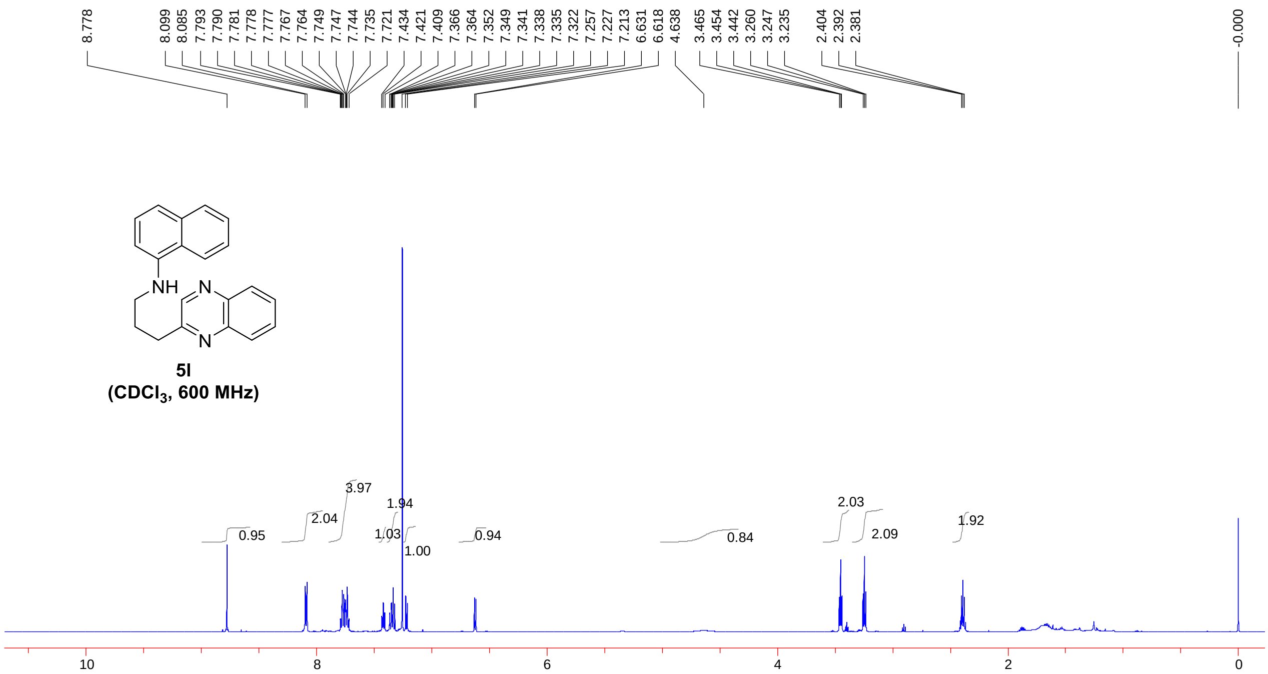
5j
($CDCl_3$, 150 MHz)



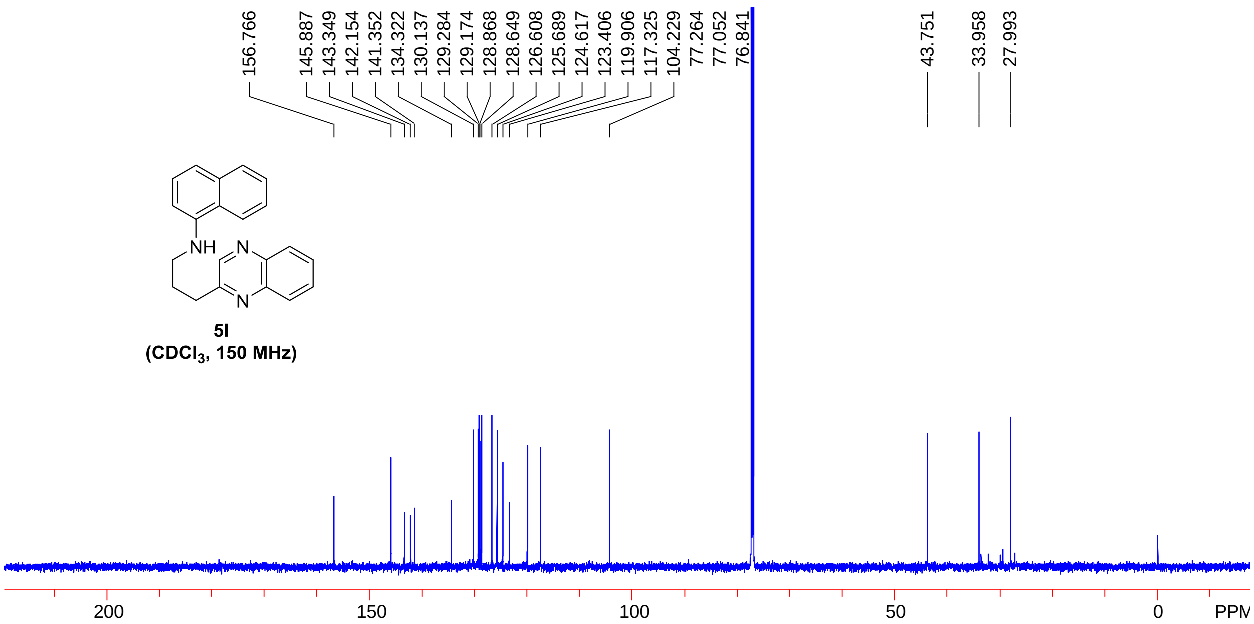
5k
(CDCl$_3$, 400 MHz)



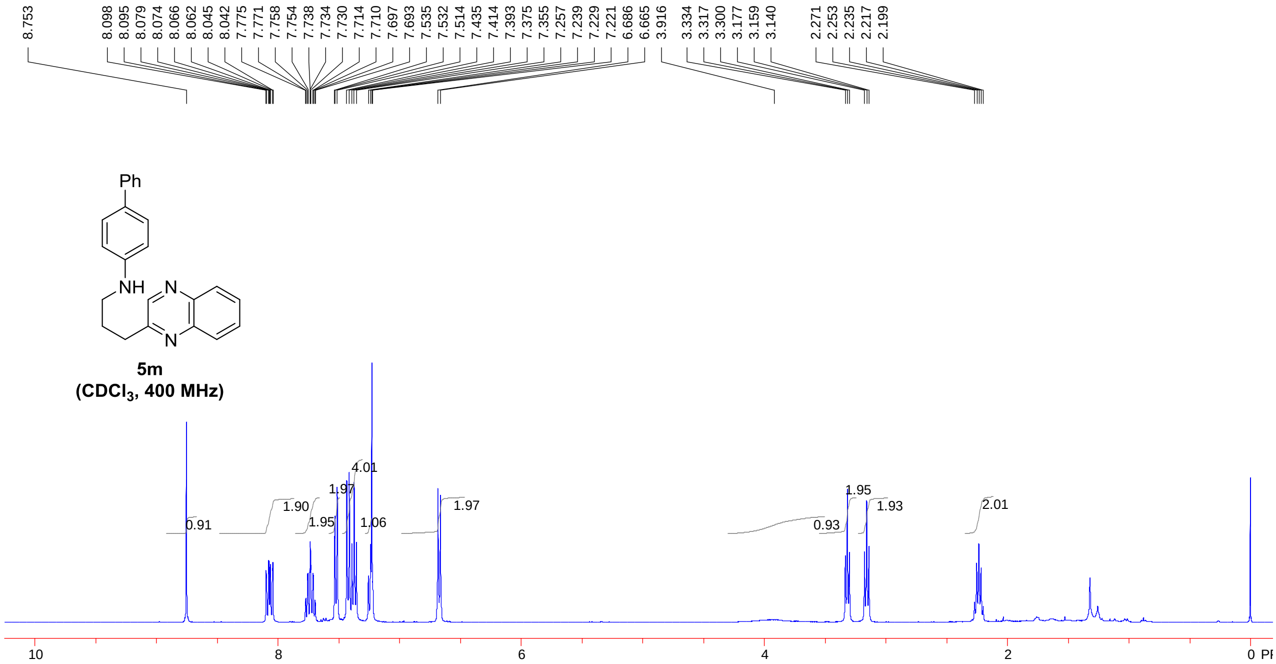
5k
(CDCl$_3$, 150 MHz)

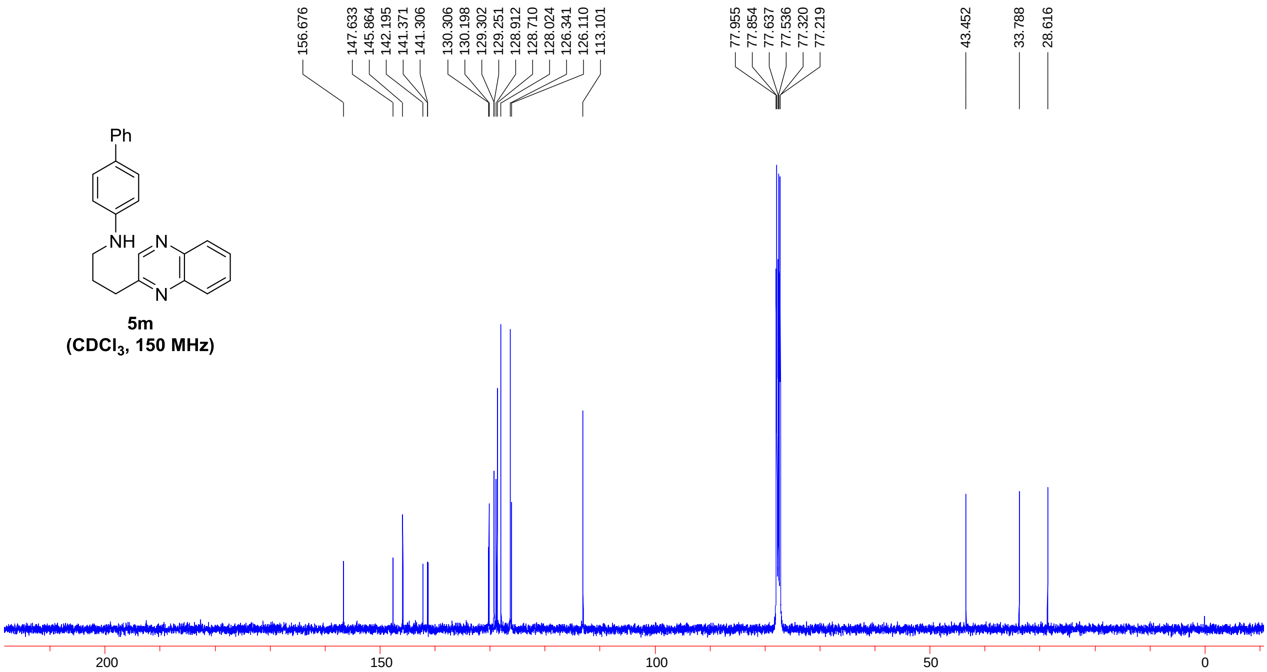


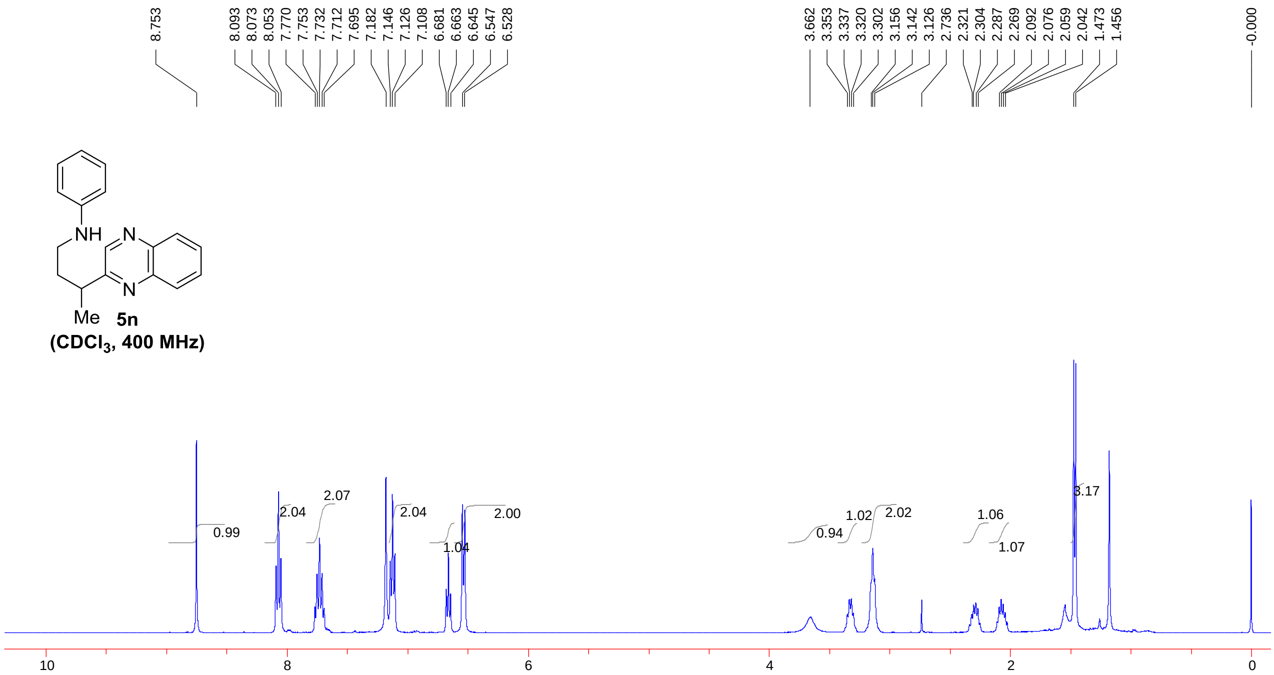
5l
($CDCl_3$, 600 MHz)

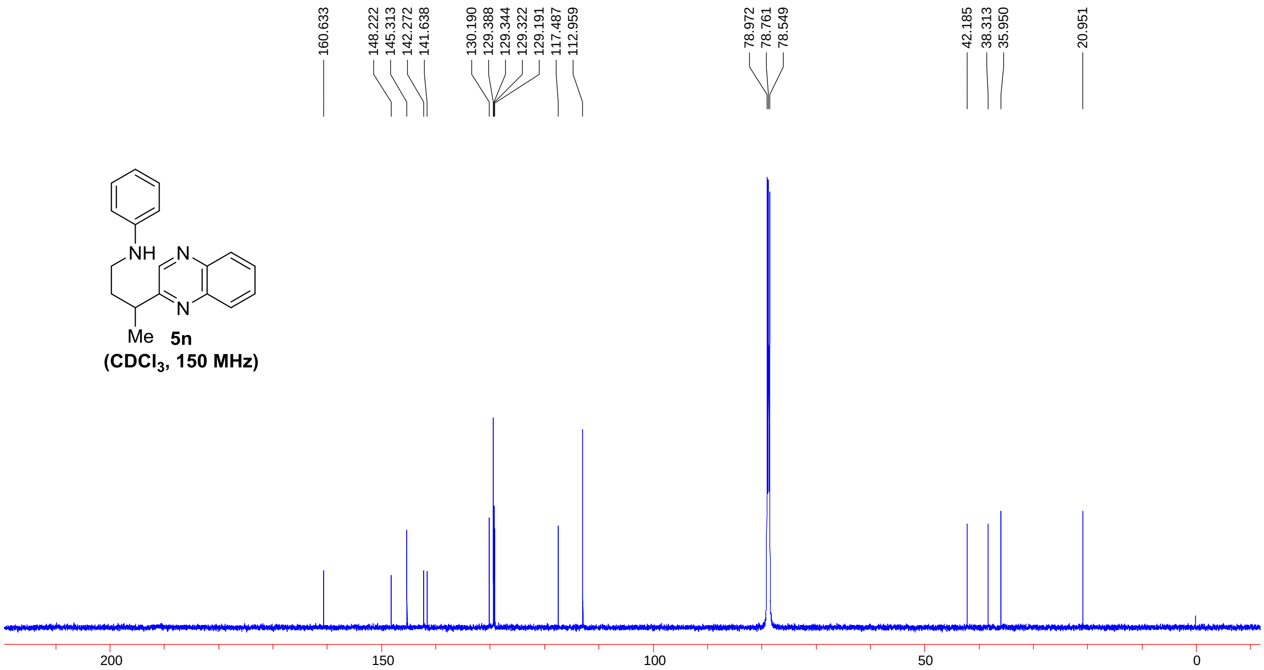


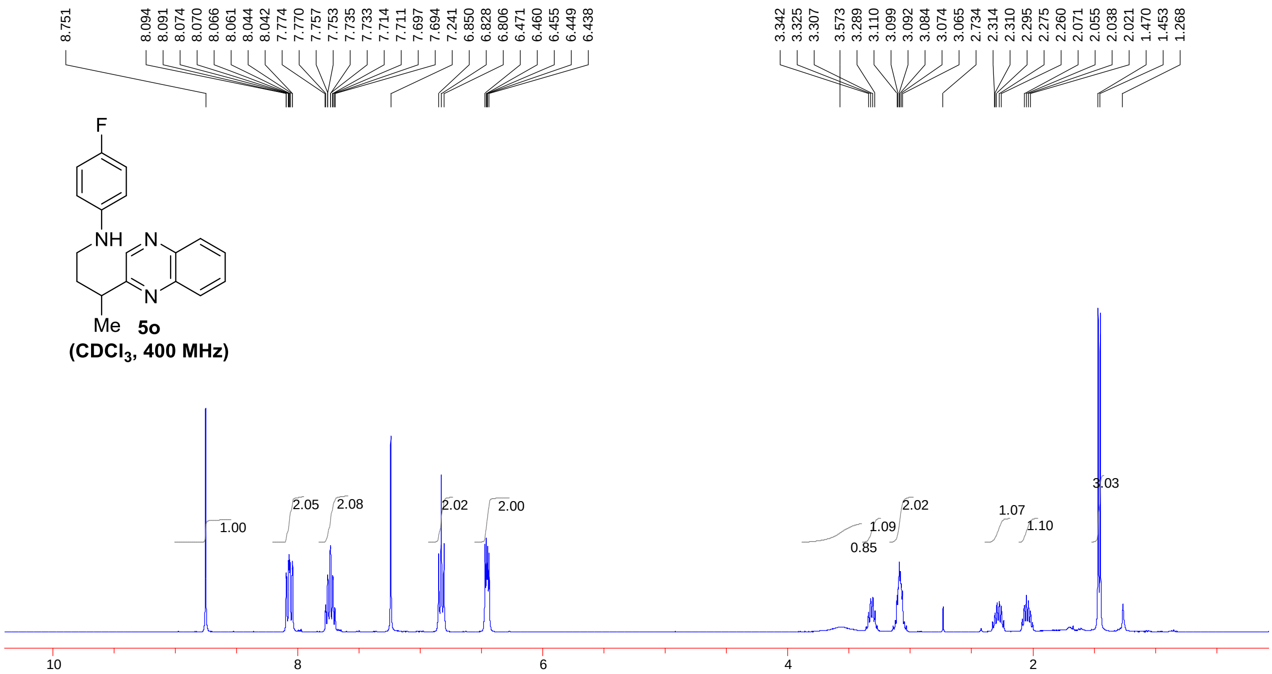
5l
($CDCl_3$, 150 MHz)

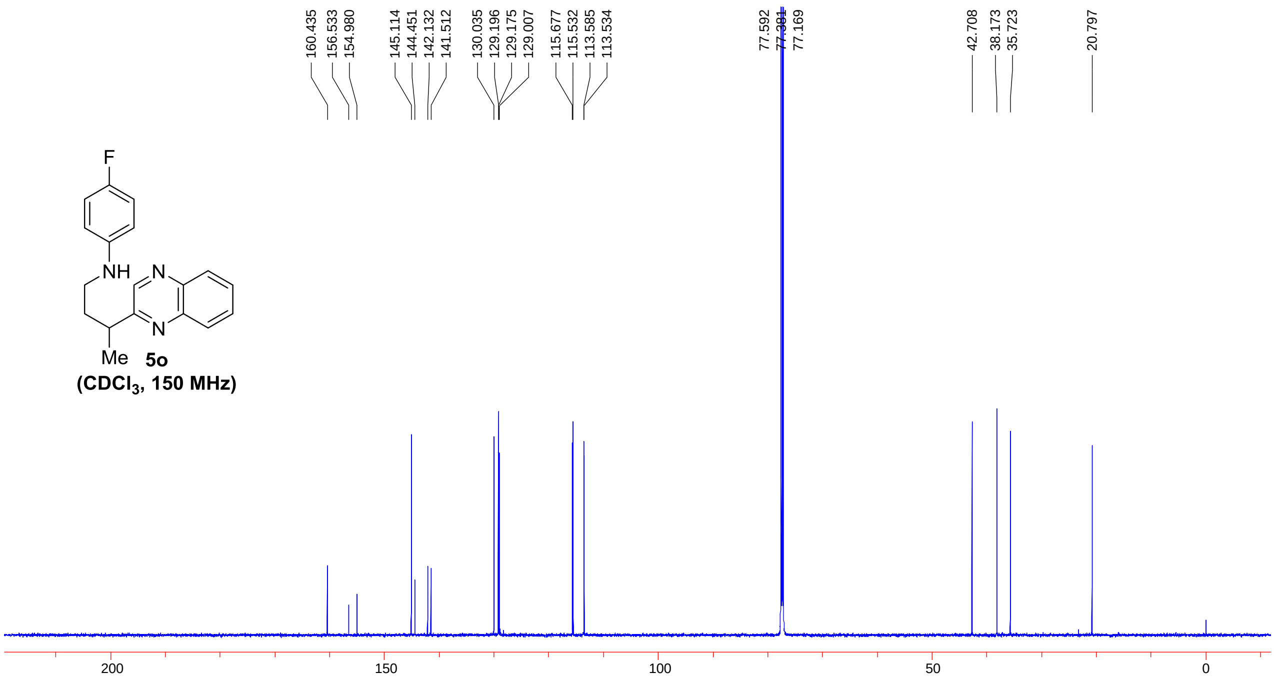

8.753
8.098 8.095 8.079 8.074 8.066 8.062 8.045 8.042 7.775 7.771 7.758 7.754 7.738 7.734 7.730 7.714 7.710 7.697 7.693 7.535 7.532 7.514 7.435 7.414 7.393 7.375 7.355 7.257 7.239 7.229 7.221 6.686 6.665
3.916
3.334 3.317 3.300 3.177 3.159 3.140
2.271 2.253 2.235 2.217 2.199
Ph
NH
N
N
5m
(CDCl3, 400 MHz)
0.91
1.90
1.95
1.97
4.01
1.06
1.97
0.93
1.95
1.93
2.01
10
8
6
4
2
0 PPM

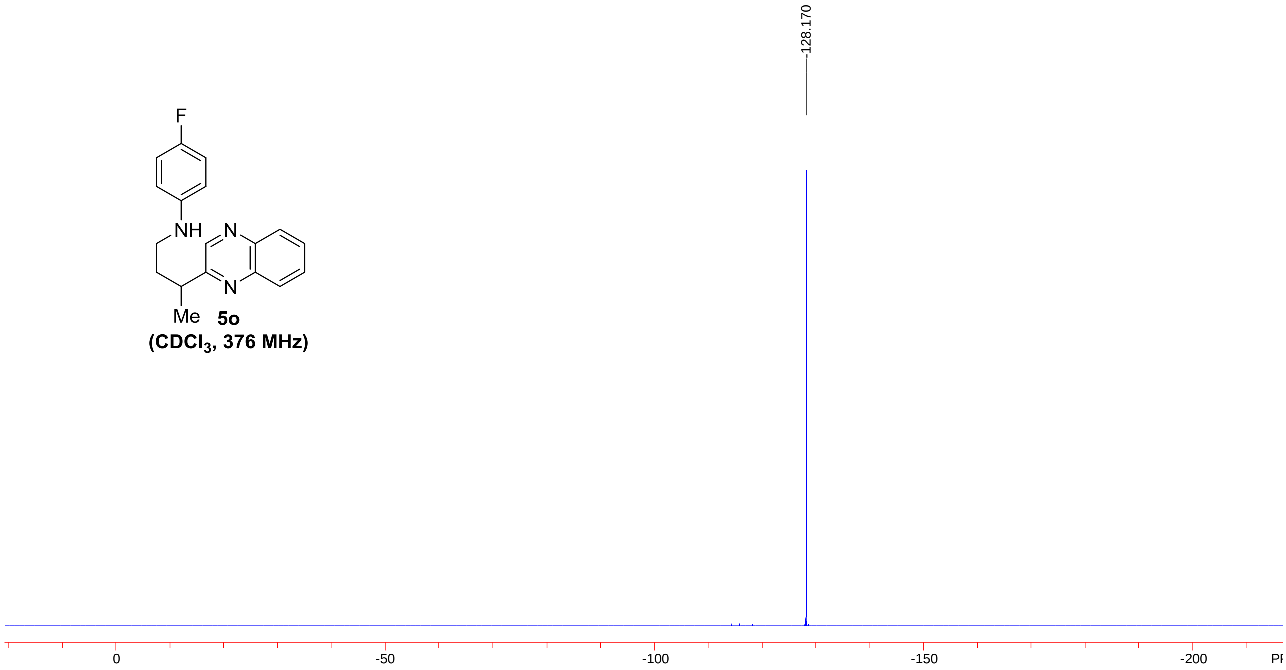

156.676
147.633 145.864 142.195 141.371 141.306
130.306 130.198 129.302 129.251 128.912 128.710 128.024 126.341 126.110 113.101
77.955 77.854 77.637 77.536 77.320 77.219
43.452
33.788
28.616
Ph
NH
N
N
5m
(CDCl3, 150 MHz)
200
150
100
50
0

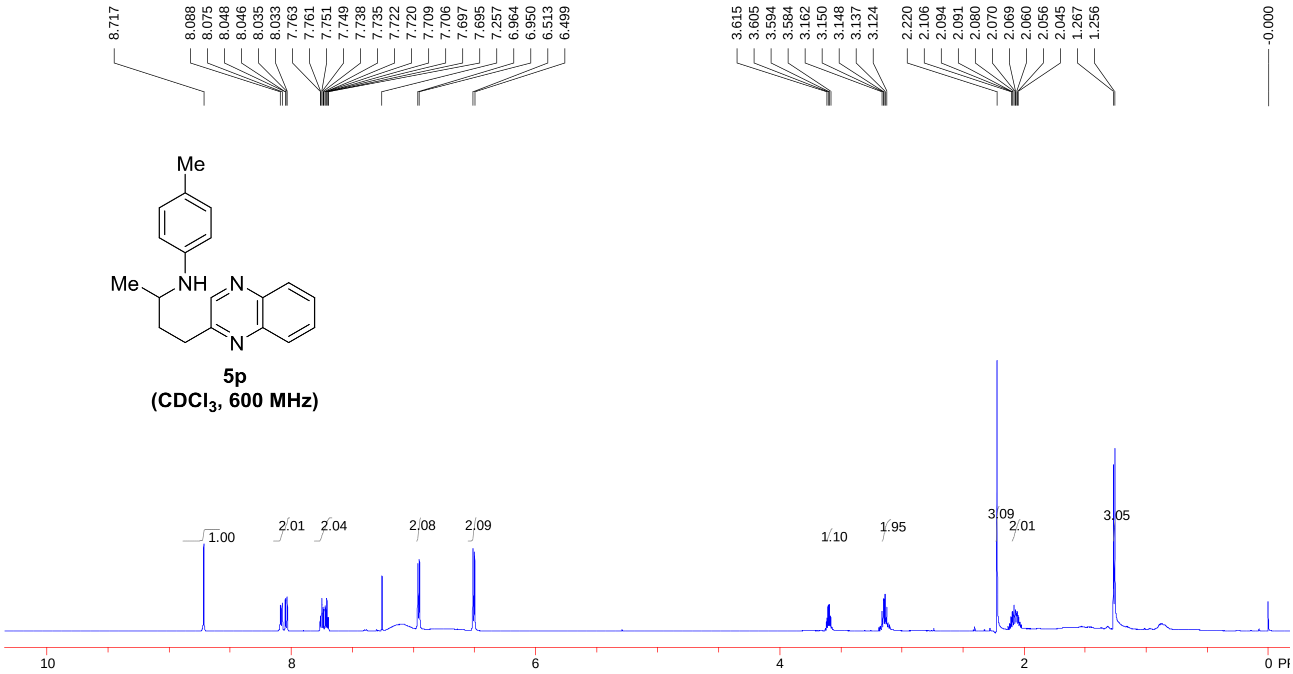

8.753
8.093 8.073 8.053 7.770 7.753 7.732 7.712 7.695 7.182 7.146 7.126 7.108 6.681 6.663 6.645 6.547 6.528
3.662 3.353 3.337 3.320 3.302 3.156 3.142 3.126 2.736 2.321 2.304 2.287 2.269 2.092 2.076 2.059 2.042 1.473 1.456
-0.000
NH
N
N
Me
5n
(CDCl$_3$, 400 MHz)
0.99
2.04
2.07
2.04
1.04
2.00
0.94
1.02
2.02
1.06
1.07
3.17
10
8
6
4
2
0

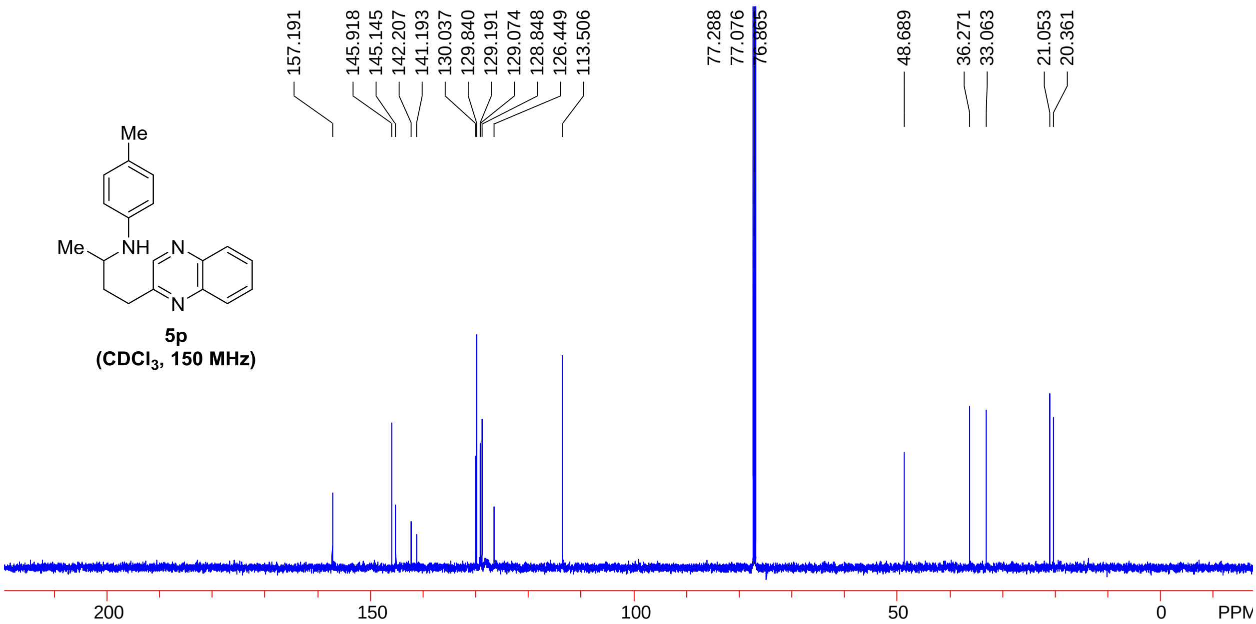

160.633
148.222 145.313 142.272 141.638
130.190 129.388 129.344 129.322 129.191 117.487 112.959
78.972 78.761 78.549
42.185 38.313 35.950
20.951
NH
N
N
Me
5n
(CDCl$_3$, 150 MHz)
200
150
100
50
0

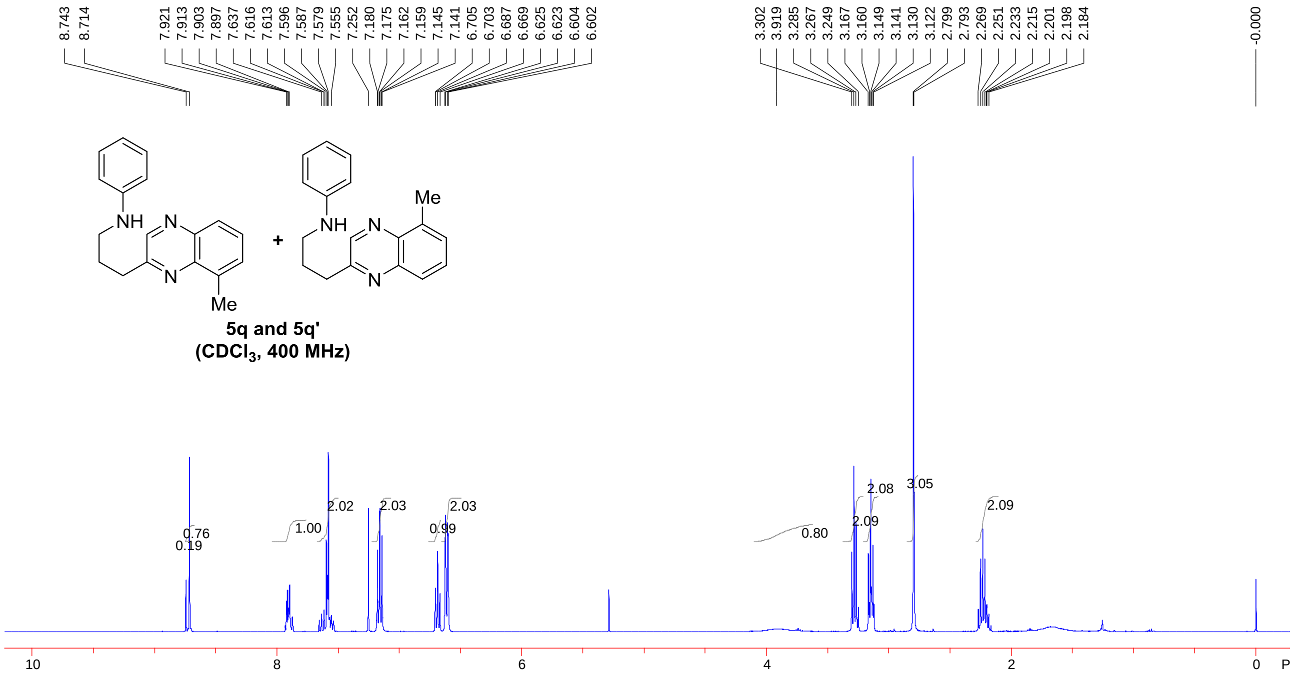

5o
(CDCl3, 400 MHz)

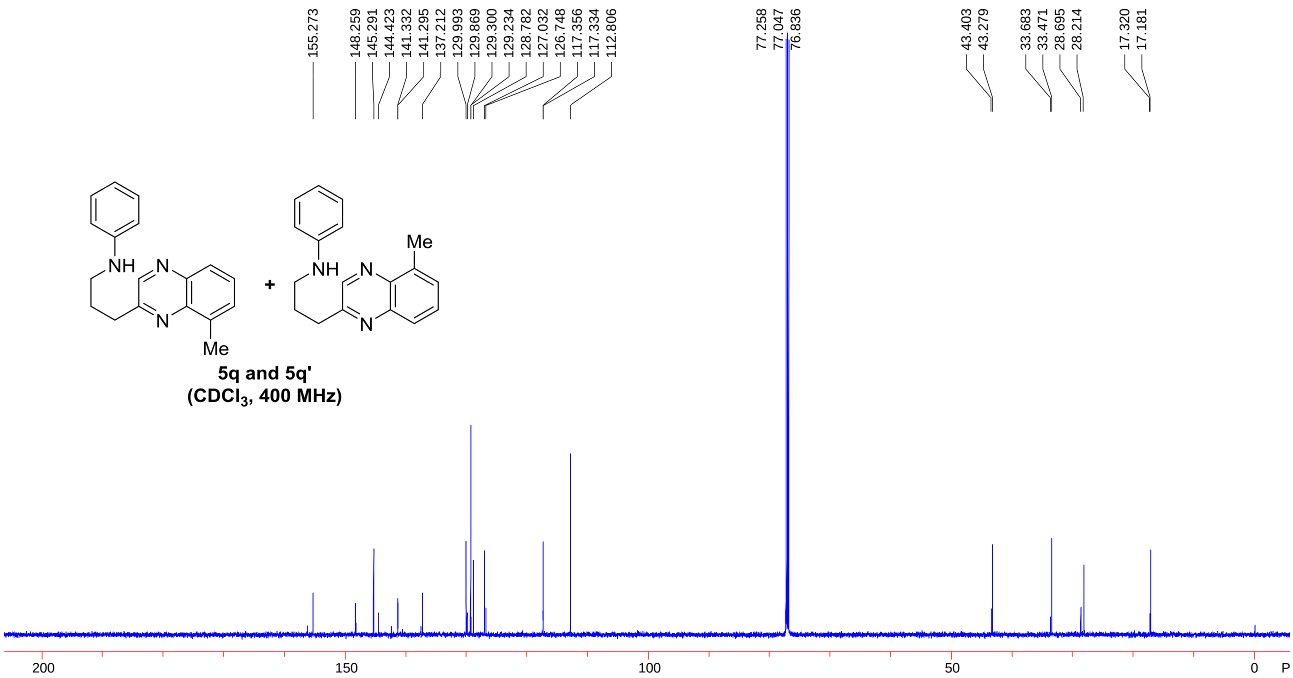

5o
(CDCl3, 150 MHz)

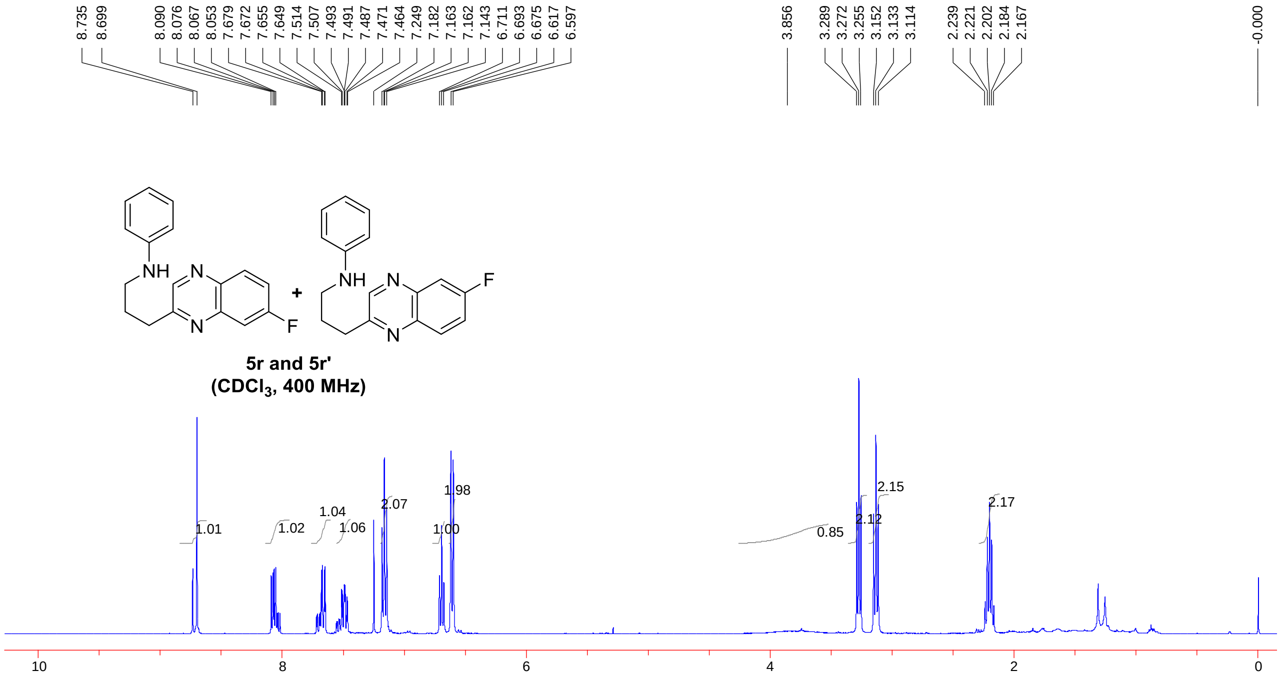

-128.170
F
NH
N
N
Me
5o
(CDCl$_3$, 376 MHz)
0
-50
-100
-150
-200
P

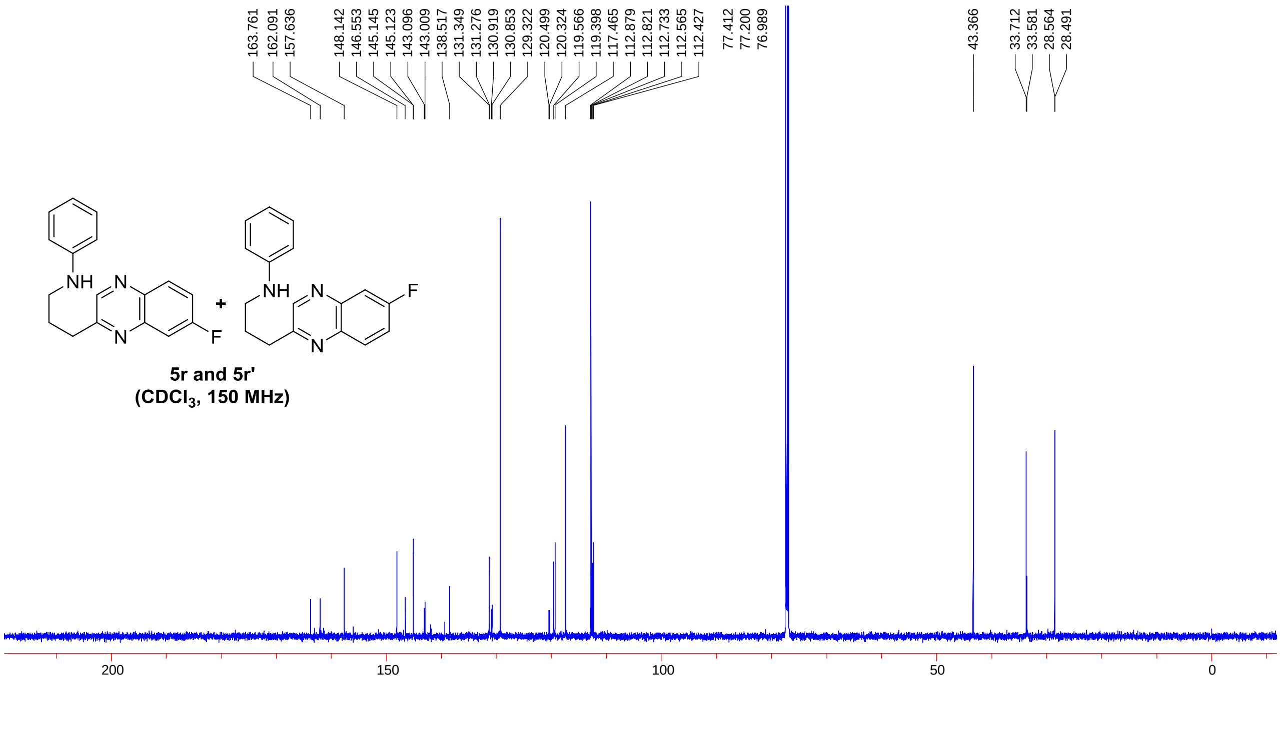

8.717
8.088
8.075
8.048
8.046
8.035
8.033
7.763
7.761
7.751
7.749
7.738
7.735
7.722
7.720
7.709
7.706
7.697
7.695
7.257
6.964
6.950
6.513
6.499
3.615
3.605
3.594
3.584
3.162
3.150
3.148
3.137
3.124
2.220
2.106
2.094
2.091
2.080
2.070
2.069
2.060
2.056
2.045
1.267
1.256
-0.000
Me
Me
NH
N
N
5p
(CDCl3, 600 MHz)
1.00
2.01
2.04
2.08
2.09
1.10
1.95
3.09
2.01
3.05
10
8
6
4
2
0 PPM

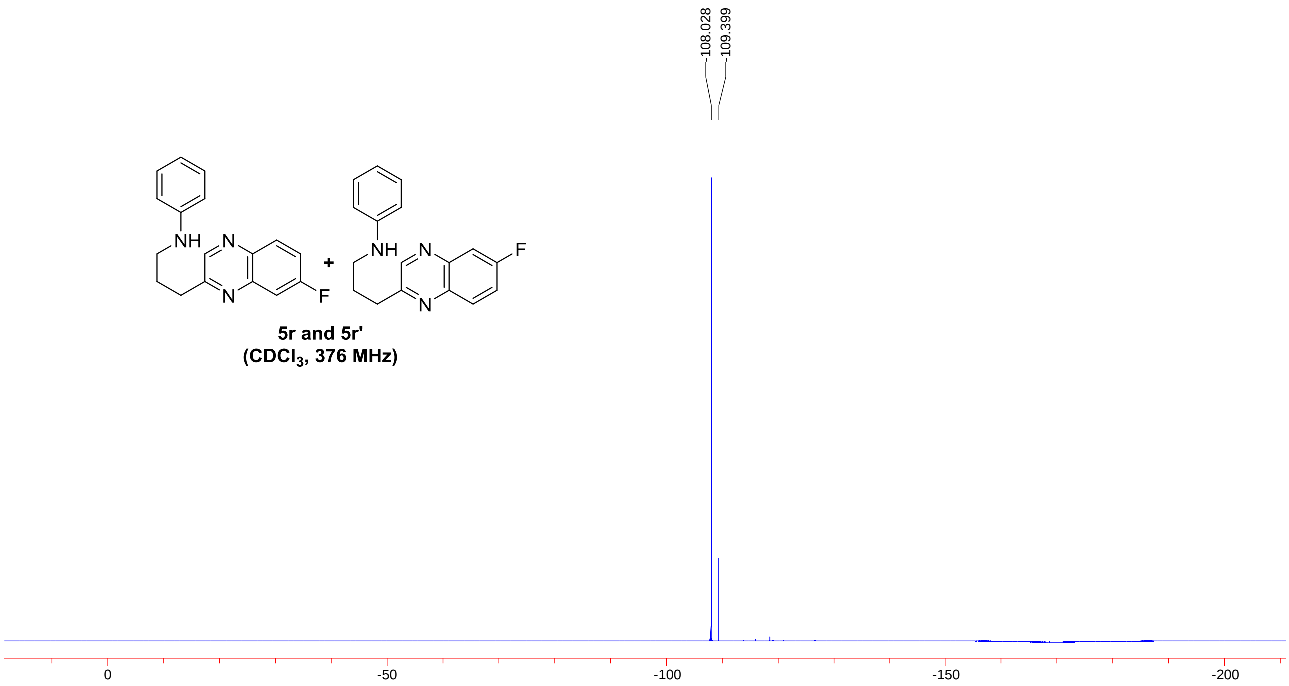

157.191
145.918
145.145
142.207
141.193
130.037
129.840
129.191
129.074
128.848
126.449
113.506
77.288
77.076
76.865
48.689
36.271
33.063
21.053
20.361
Me
Me
NH
N
N
5p
(CDCl3, 150 MHz)
200
150
100
50
0
PPM


5q and 5q'
(CDCl3, 400 MHz)

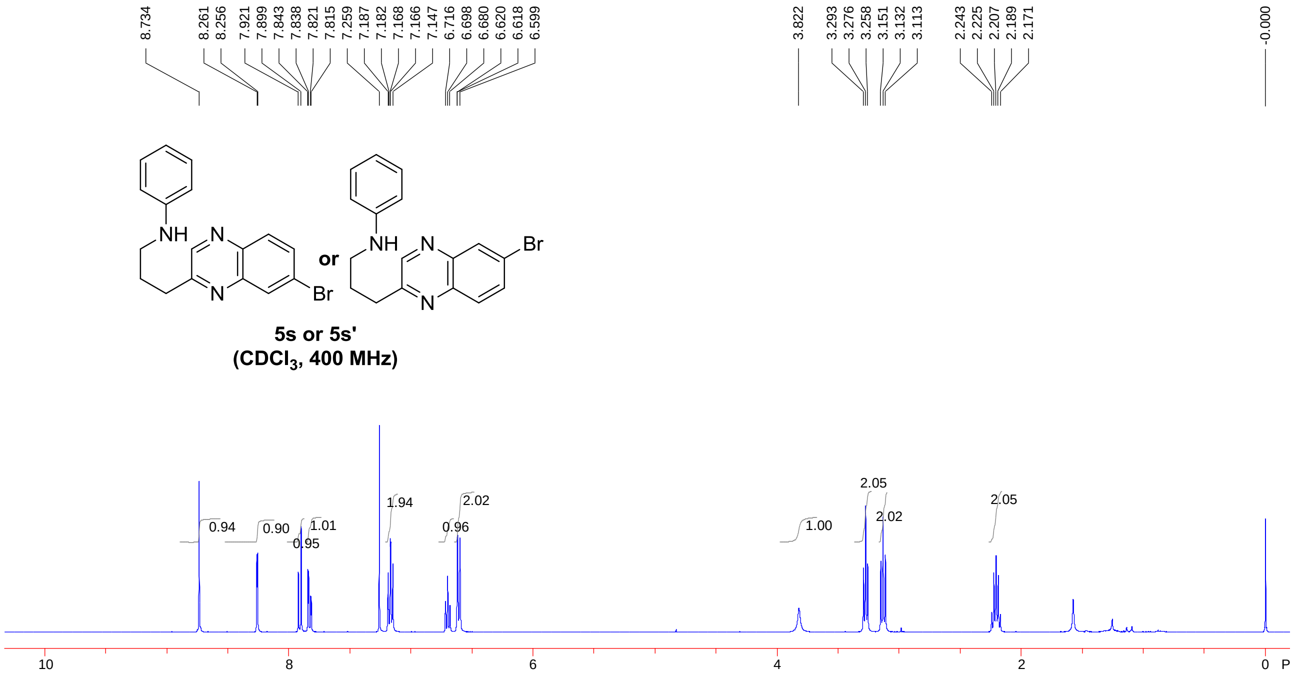

5q and 5q'
(CDCl3, 400 MHz)

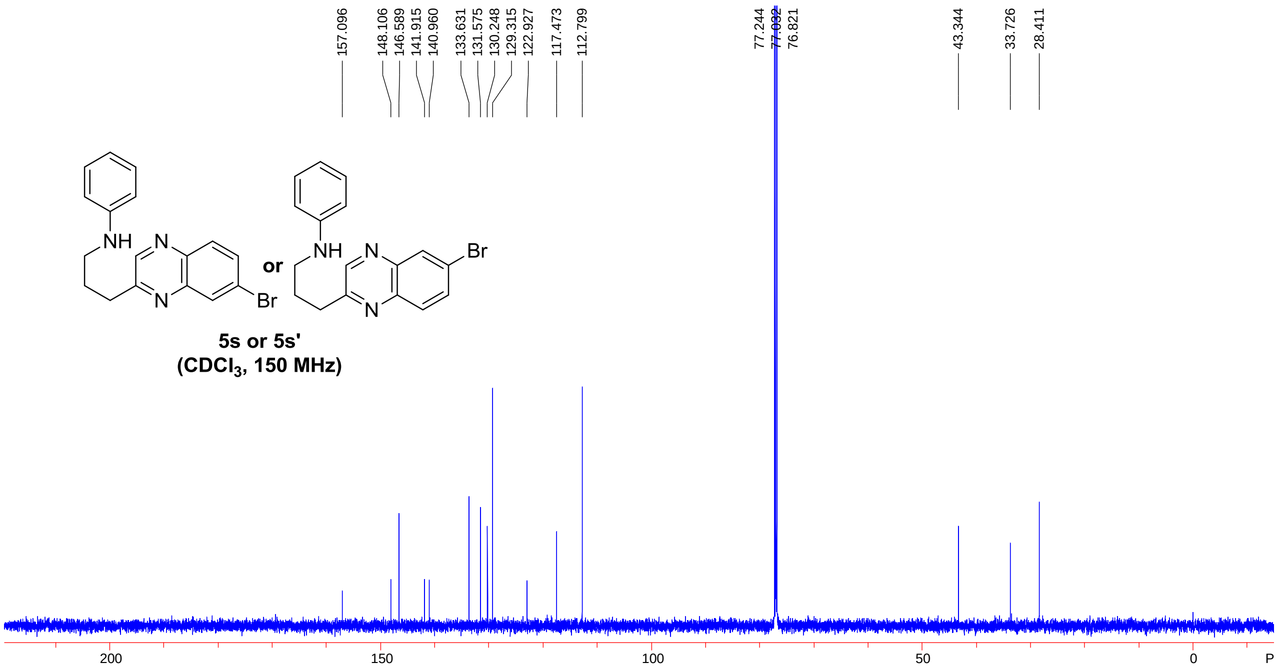

5r and 5r'
($CDCl_3$, 400 MHz)

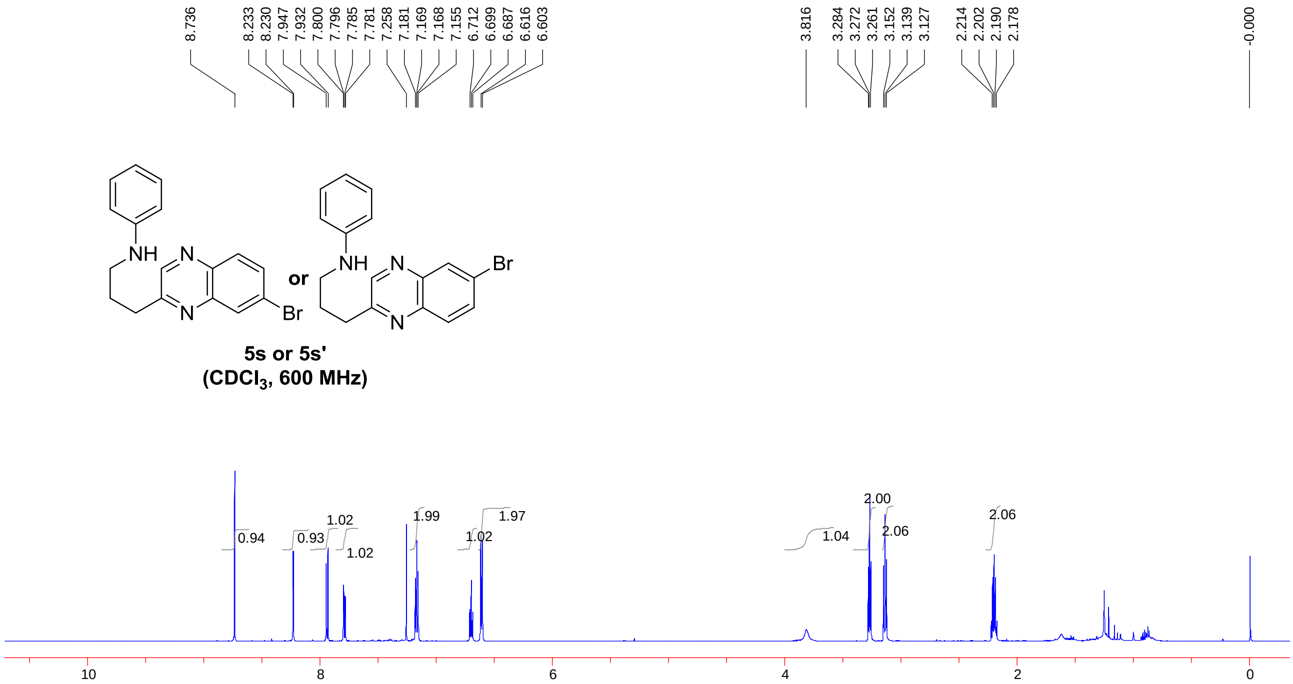

5r and 5r'
($CDCl_3$, 150 MHz)

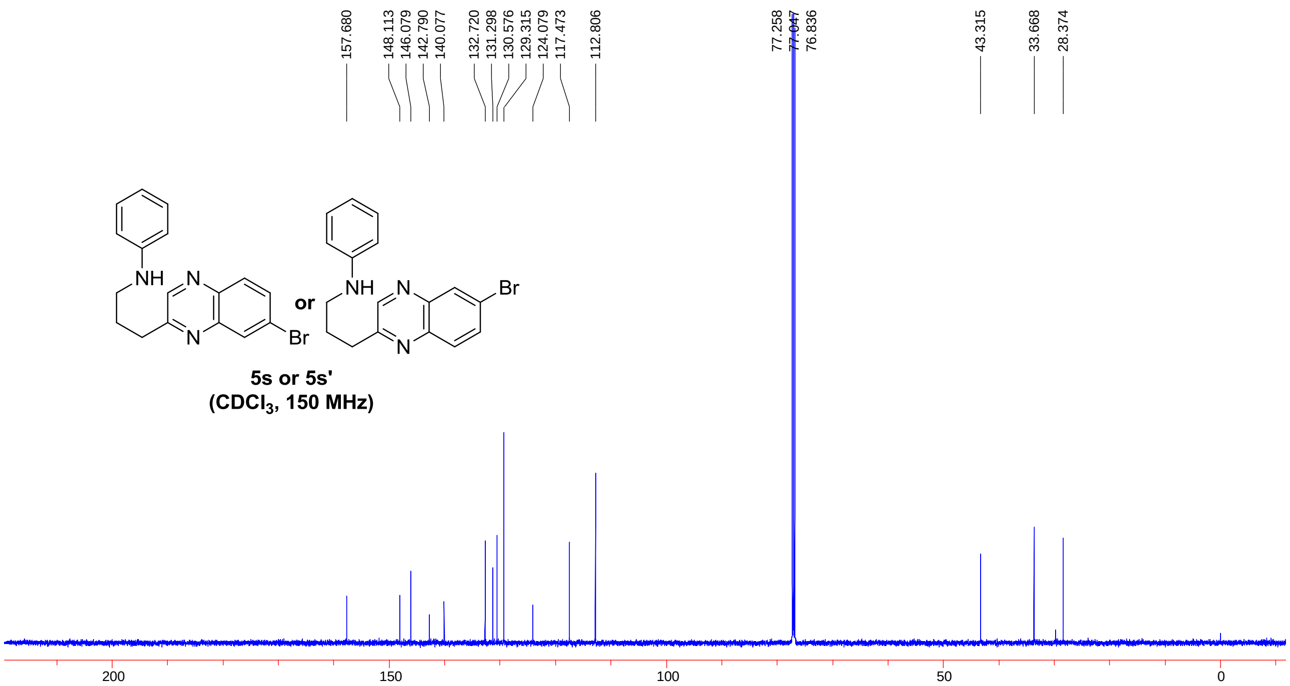


5r and 5r'
($CDCl_3$, 376 MHz)

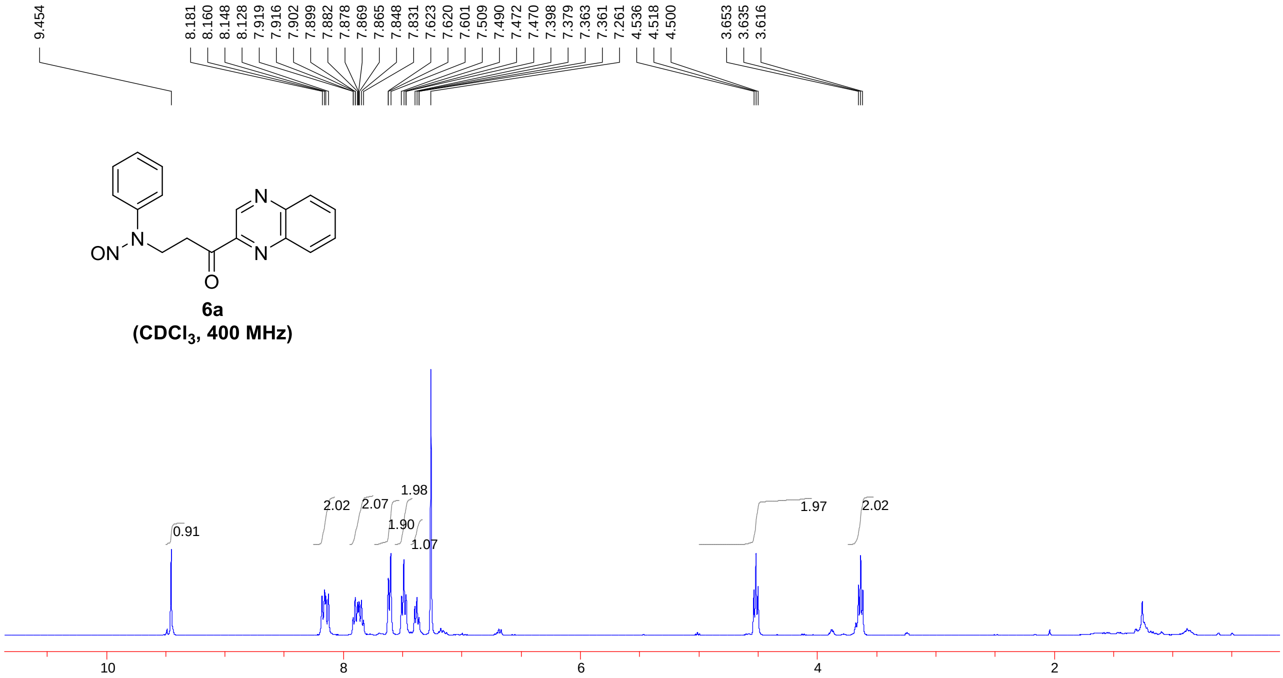

5s or 5s'
(CDCl3, 400 MHz)
8.734
8.261
8.256
7.921
7.899
7.843
7.838
7.821
7.815
7.259
7.187
7.182
7.168
7.166
7.147
6.716
6.698
6.680
6.620
6.618
6.599
3.822
3.293
3.276
3.258
3.151
3.132
3.113
2.243
2.225
2.207
2.189
2.171
-0.000

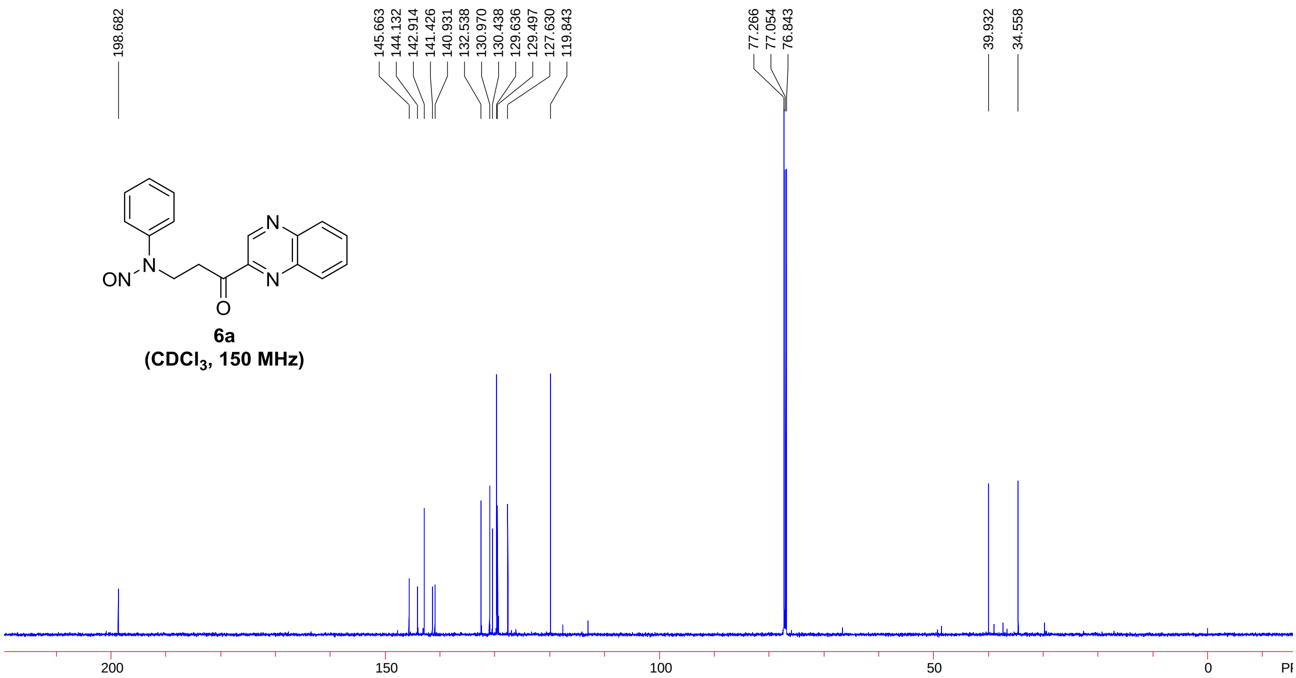

5s or 5s'
(CDCl3, 150 MHz)
157.096
148.106
146.589
141.915
140.960
133.631
131.575
130.248
129.315
122.927
117.473
112.799
77.244
77.032
76.821
43.344
33.726
28.411

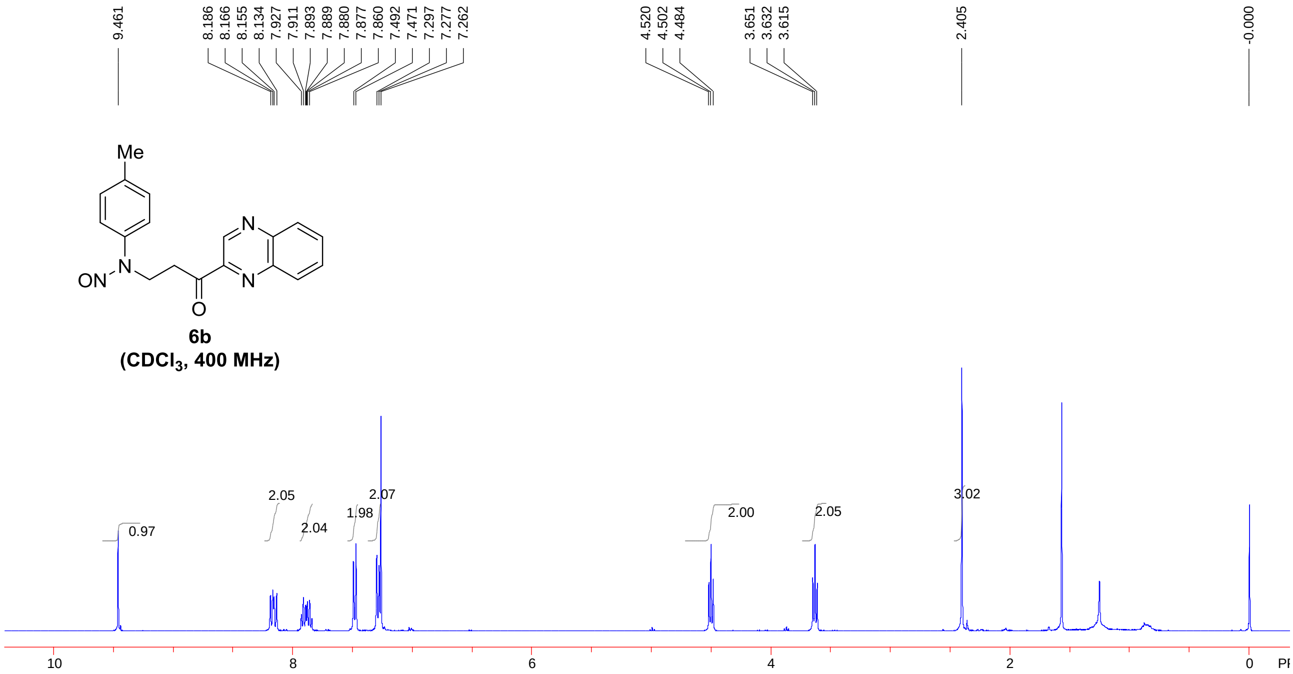

8.736
8.233
8.230
7.947
7.932
7.800
7.796
7.785
7.781
7.258
7.181
7.169
7.168
7.155
6.712
6.699
6.687
6.616
6.603
3.816
3.284
3.272
3.261
3.152
3.139
3.127
2.214
2.202
2.190
2.178
-0.000
NH
N
N
Br
or
NH
N
N
Br
5s or 5s'
(CDCl3, 600 MHz)
0.94
0.93
1.02
1.02
1.99
1.02
1.97
1.04
2.00
2.06
2.06
10
8
6
4
2
0

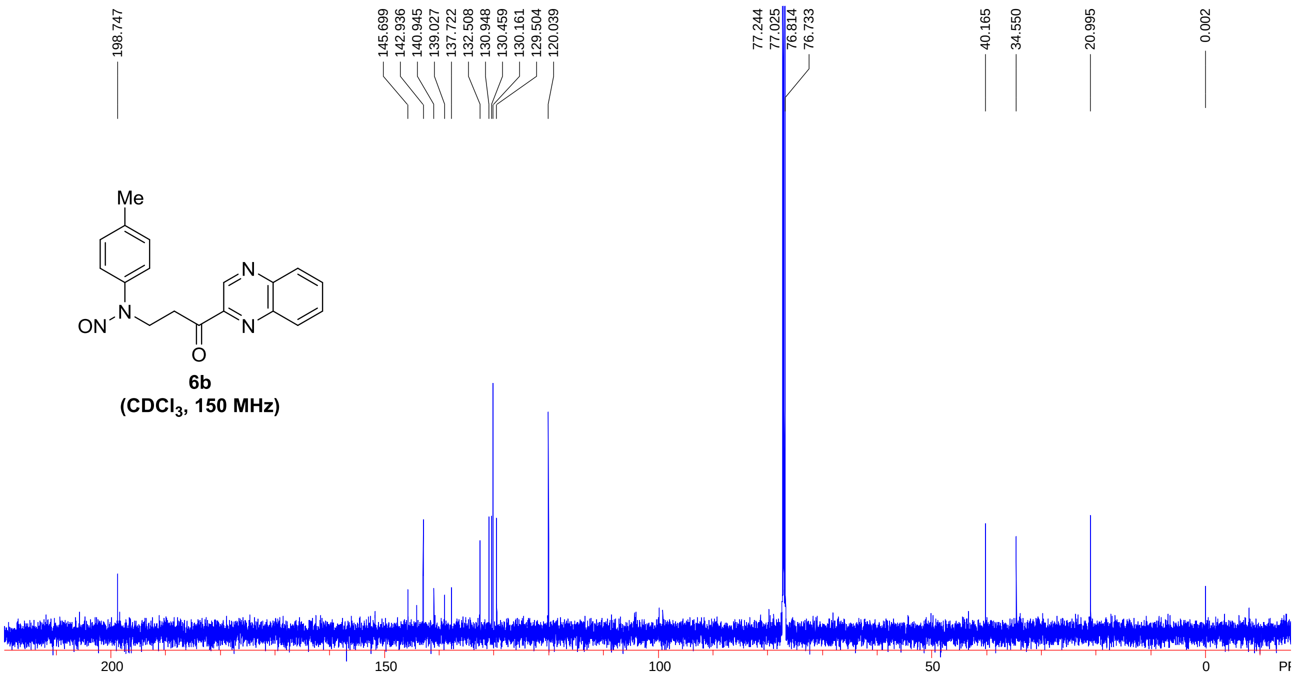

157.680
148.113
146.079
142.790
140.077
132.720
131.298
130.576
129.315
124.079
117.473
112.806
77.258
77.047
76.836
43.315
33.668
28.374
NH
N
N
Br
or
NH
N
N
Br
5s or 5s'
(CDCl3, 150 MHz)
200
150
100
50
0

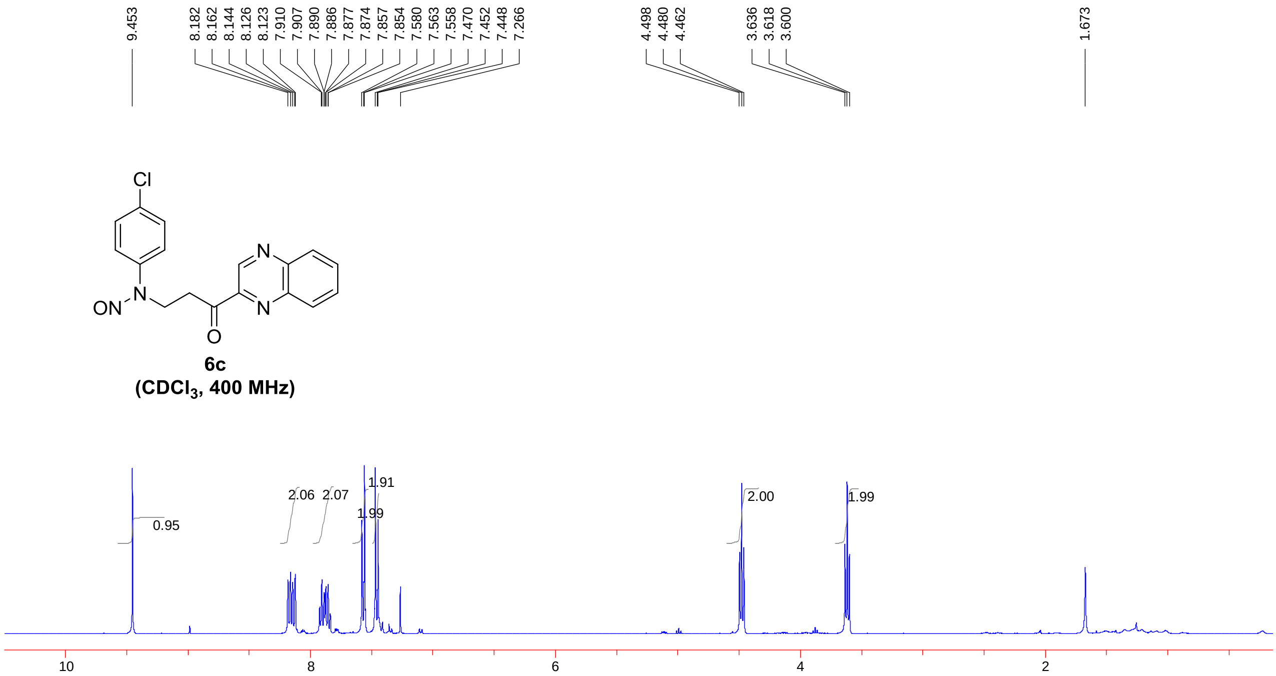
V. Copies of the NMR spectra of 6a-6f

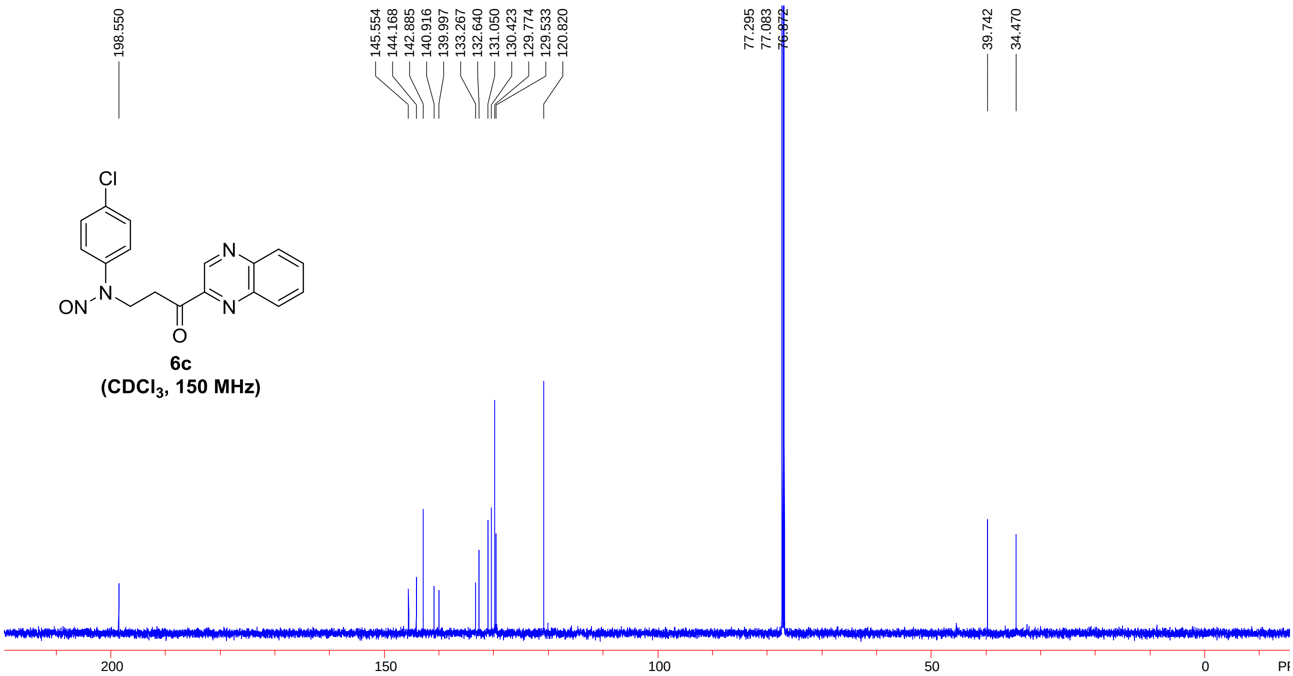


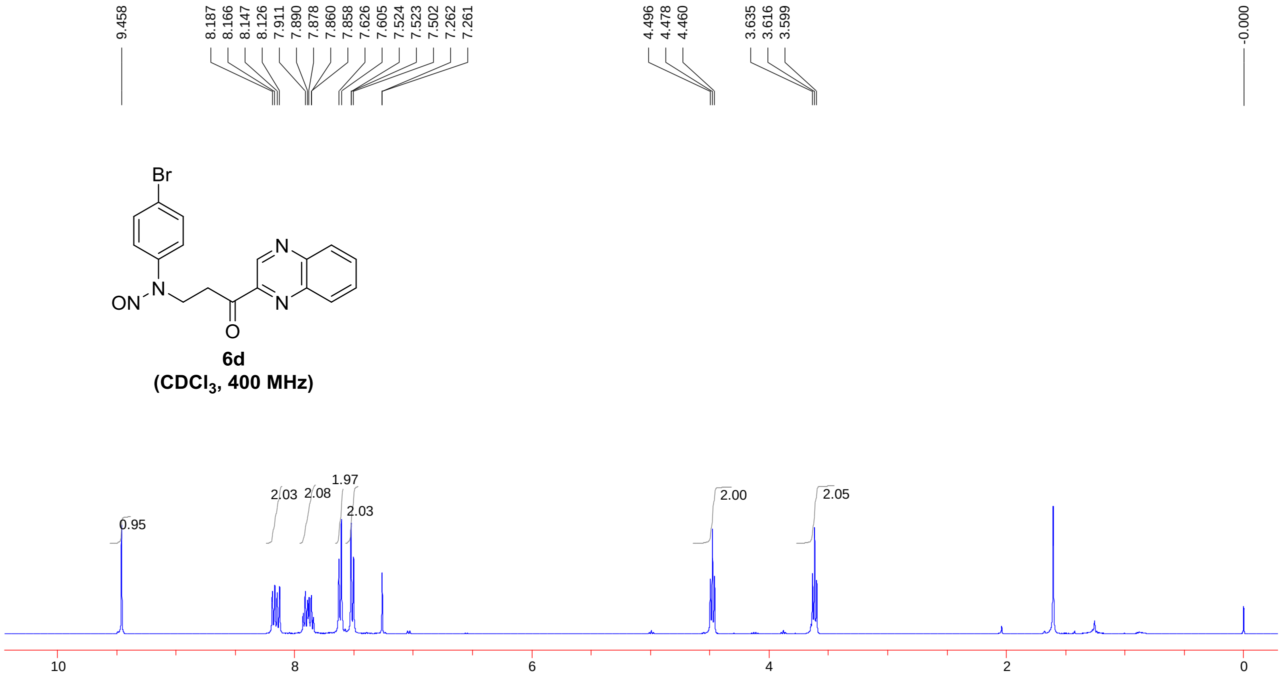



9.461
8.186
8.166
8.155
8.134
7.927
7.911
7.893
7.889
7.880
7.877
7.860
7.492
7.471
7.297
7.277
7.262
4.520
4.502
4.484
3.651
3.632
3.615
2.405
-0.000
Me
N
N
ON
N
O
6b
(CDCl3, 400 MHz)
0.97
2.05
2.04
1.98
2.07
2.00
2.05
3.02
10
8
6
4
2
0

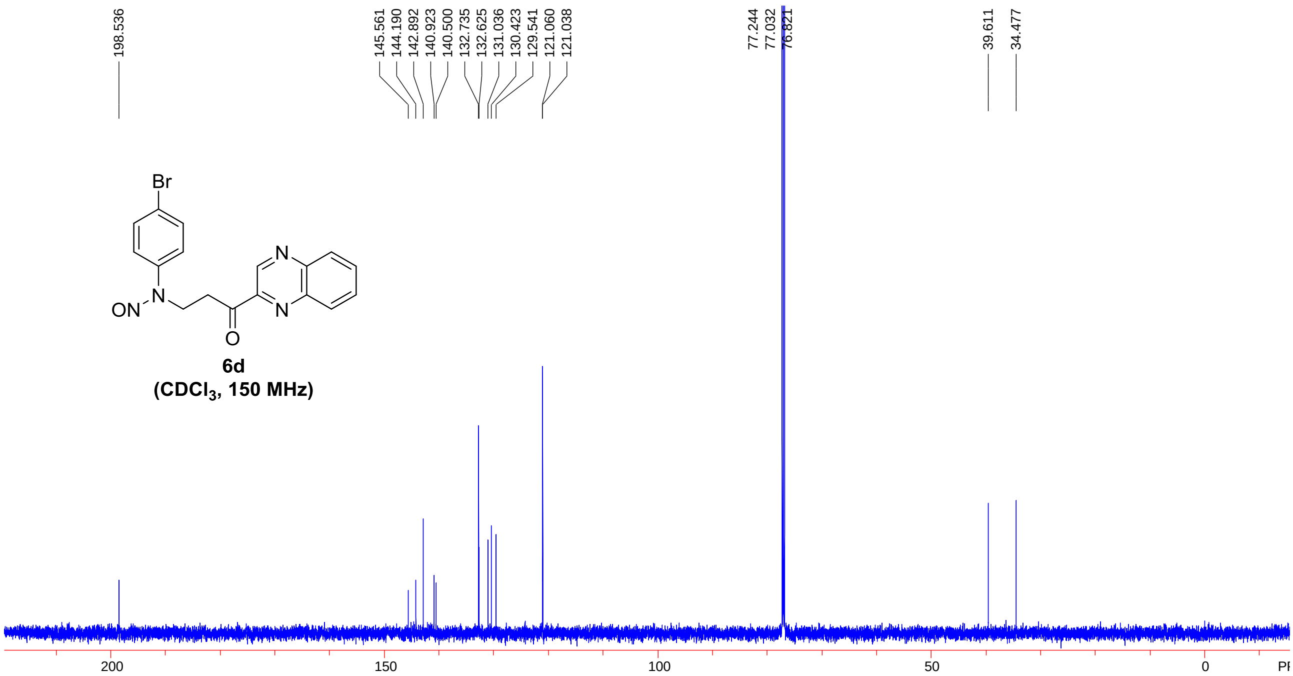

198.747
145.699
142.936
140.945
139.027
137.722
132.508
130.948
130.459
130.161
129.504
120.039
77.244
77.025
76.814
76.733
40.165
34.550
20.995
0.002
Me
N
N
ON
N
O
6b
(CDCl3, 150 MHz)
200
150
100
50
0


9.453
8.182
8.162
8.144
8.126
8.123
7.910
7.907
7.890
7.886
7.877
7.874
7.857
7.854
7.580
7.563
7.558
7.470
7.452
7.448
7.266
4.498
4.480
4.462
3.636
3.618
3.600
1.673
Cl
N
N
ON
N
O
6c
(CDCl3, 400 MHz)
0.95
2.06
2.07
1.91
1.99
2.00
1.99
10
8
6
4
2

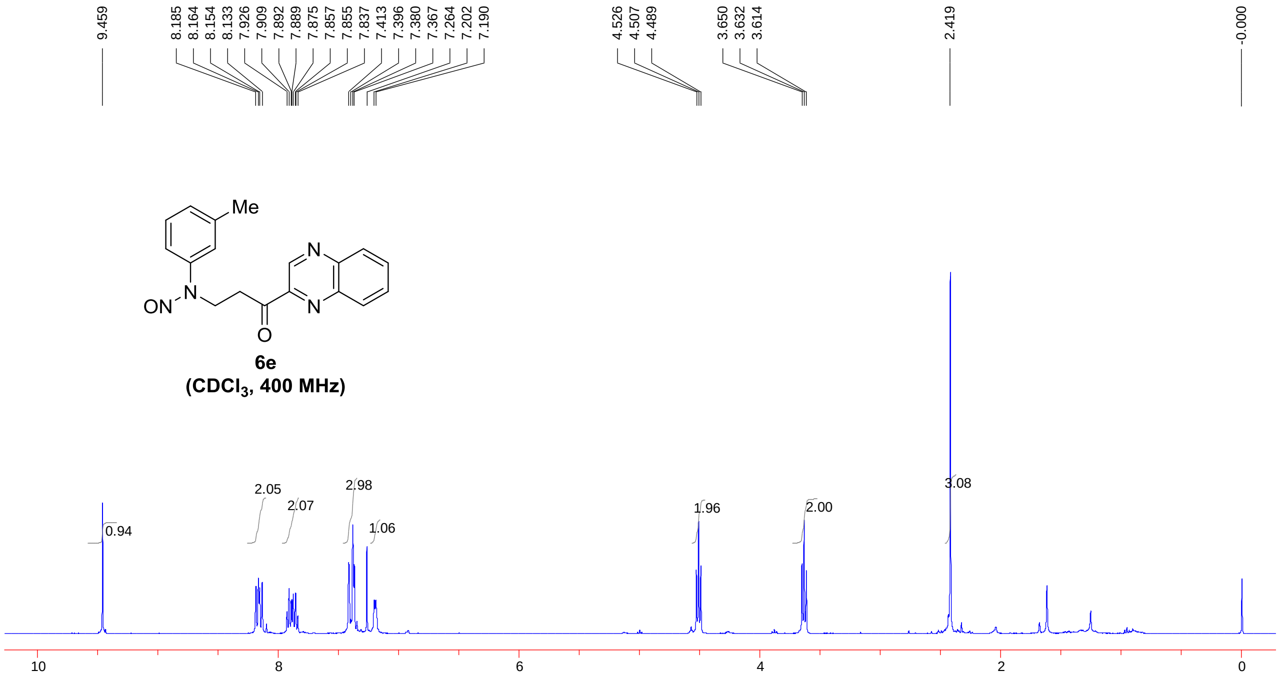

198.550
145.554
144.168
142.885
140.916
139.997
133.267
132.640
131.050
130.423
129.774
129.533
120.820
77.295
77.083
76.872
39.742
34.470
Cl
N
N
ON
N
O
6c
(CDCl3, 150 MHz)
200
150
100
50
0
PI



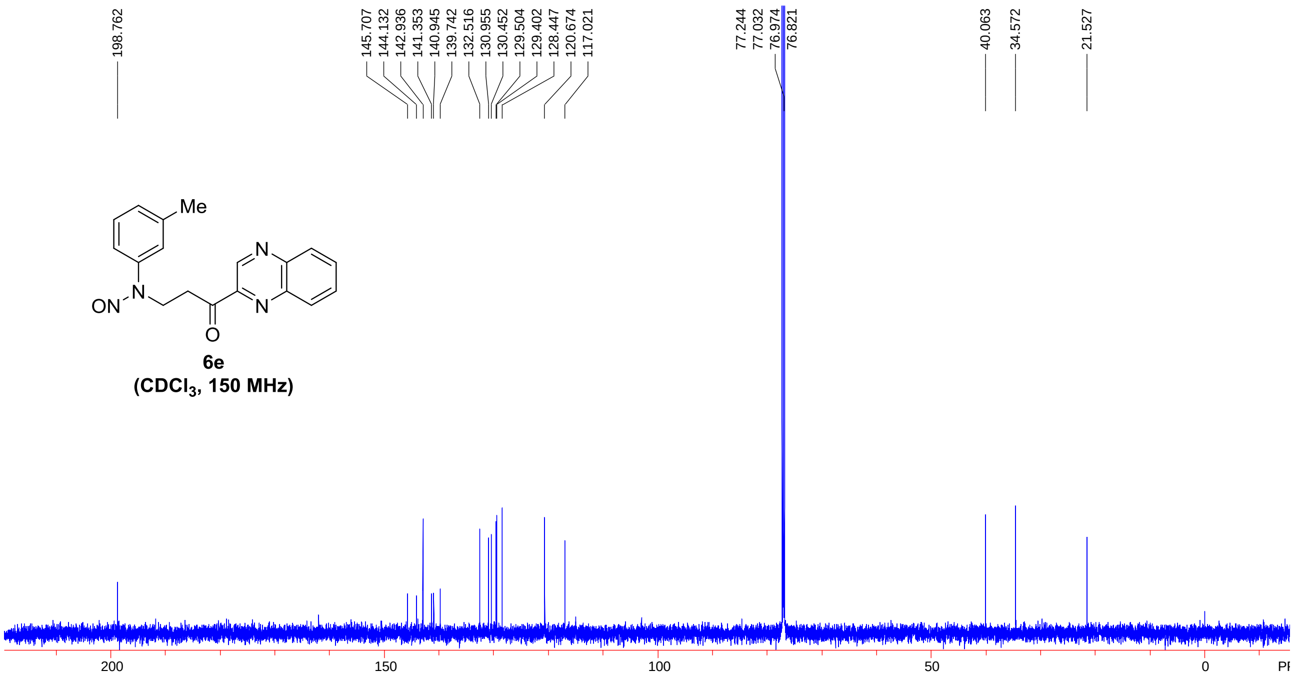
6d
($CDCl_3$, 400 MHz)



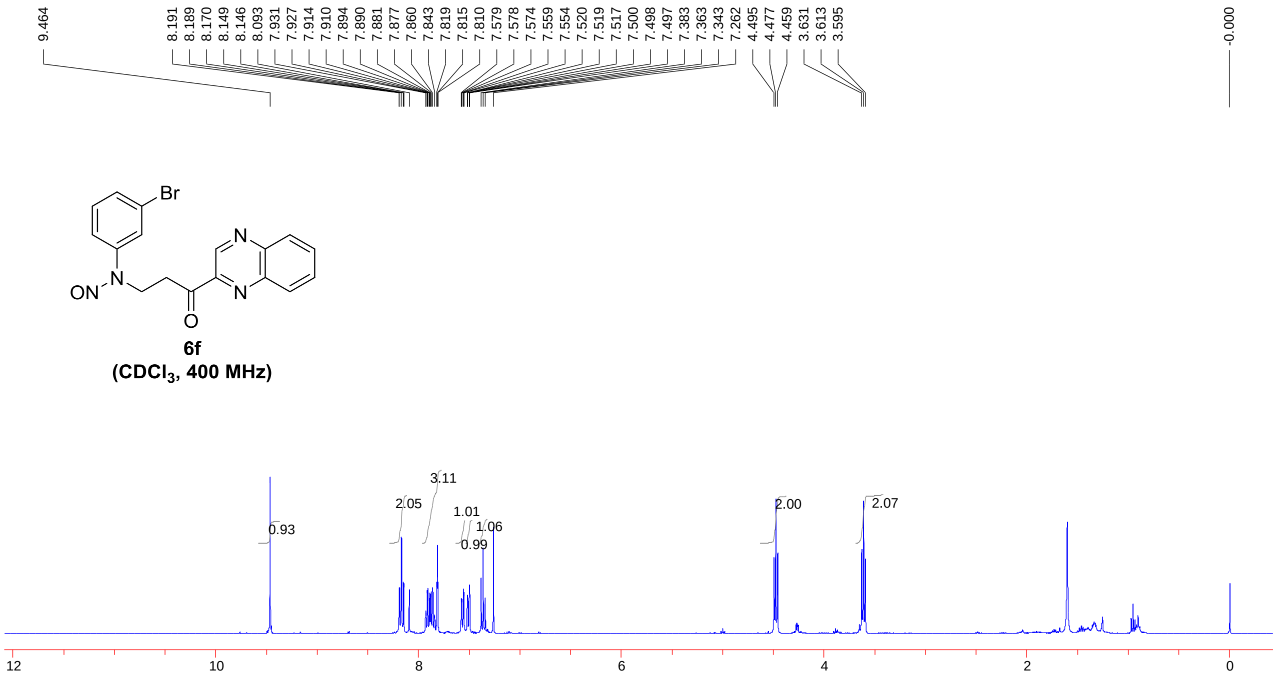
6d
($CDCl_3$, 150 MHz)

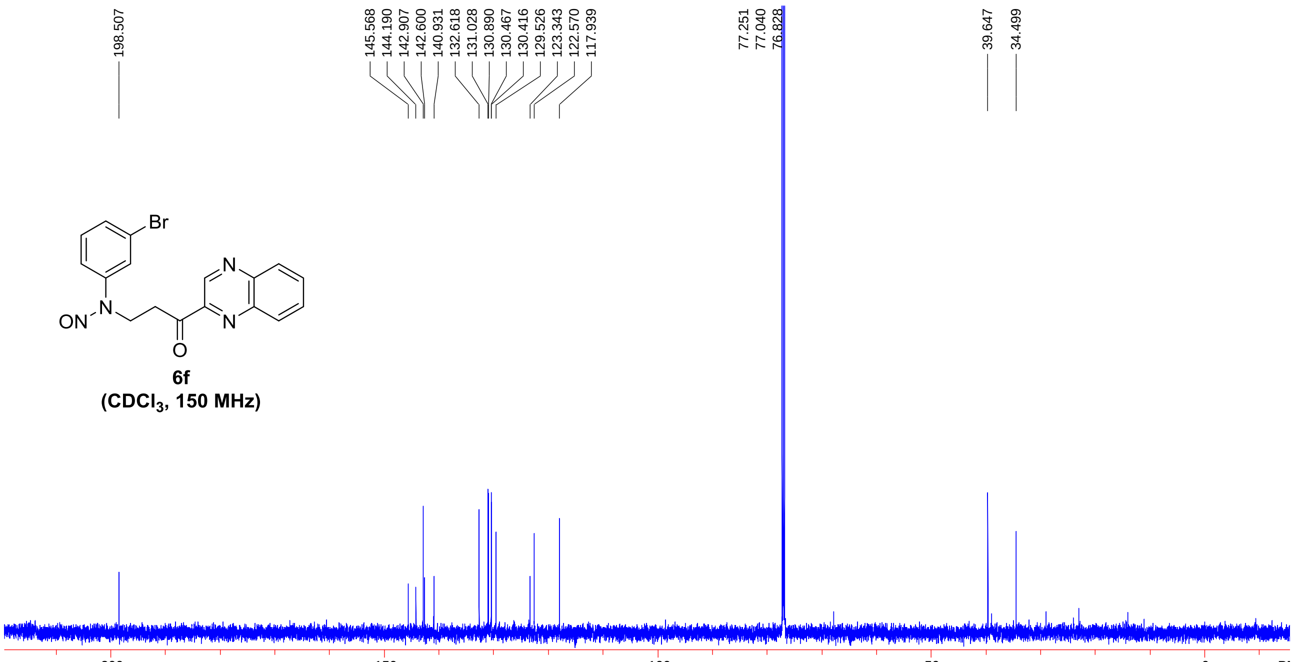


6e
(CDCl$_3$, 400 MHz)



6e
(CDCl$_3$, 150 MHz)


9.464
8.191 8.189 8.170 8.149 8.146 8.093 7.931 7.927 7.914 7.910 7.894 7.890 7.881 7.877 7.860 7.843 7.819 7.815 7.810 7.579 7.578 7.574 7.559 7.554 7.520 7.519 7.517 7.500 7.498 7.497 7.383 7.363 7.343 7.262
4.495 4.477 4.459
3.631 3.613 3.595
-0.000
Br
N
N
ON
N
O
6f
(CDCl3, 400 MHz)
0.93
2.05
3.11
1.01
0.99
1.06
2.00
2.07
12
10
8
6
4
2
0


198.507
145.568 144.190 142.907 142.600 140.931 132.618 131.028 130.890 130.467 130.416 129.526 123.343 122.570 117.939
77.251 77.040 76.828
39.647 34.499
Br
N
N
ON
N
O
6f
(CDCl3, 150 MHz)
200
150
100
50
0

VI. X-ray Crystal Structures and Data of 3a

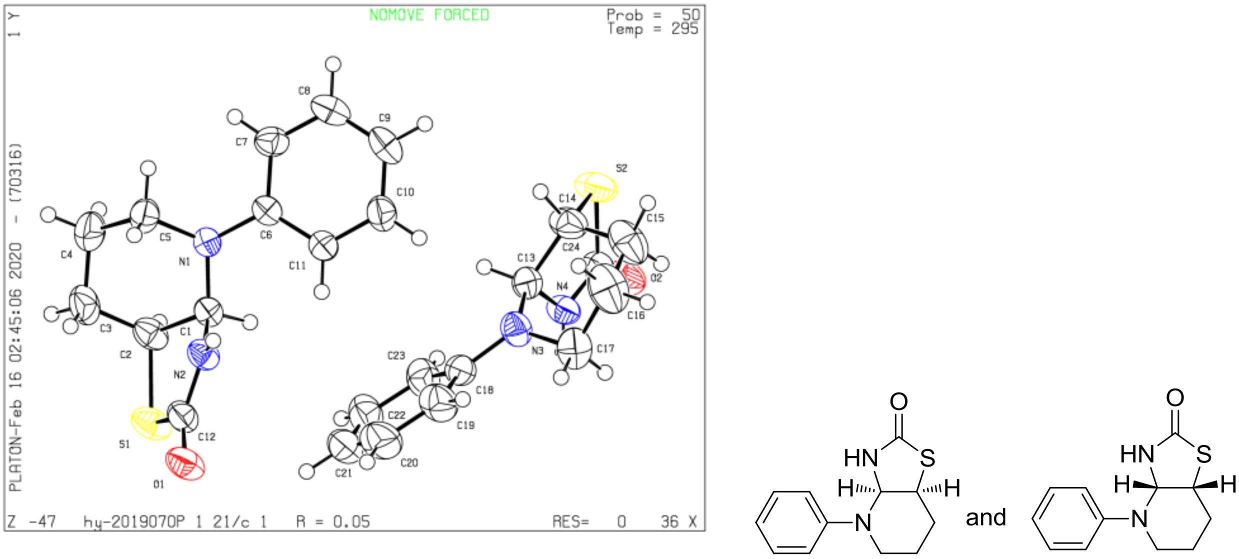


Fig. S6 X-ray structure of **3a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction was obtained by slow evaporation of the solvent from a CH_3CN solution of **3a**. Crystal data collection and refinement parameters of **3a** are summarized in Table S1. Intensity data were collected at 298 K on a SuperNova Dualdiffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3a**

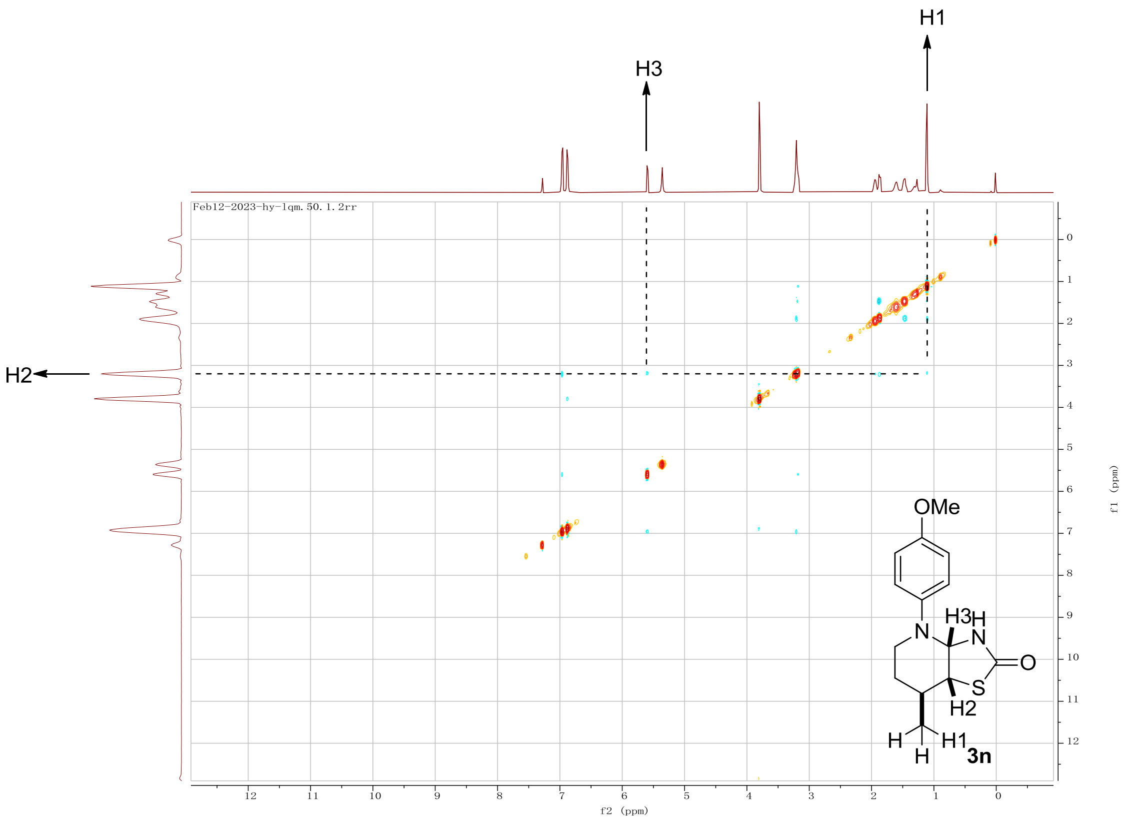
Empirical formula	$C_{12}H_{14}N_2OS$
Formula weight	234.08
Temp, K	295.25(16)
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	10.7386(4)
b, Å	13.7675(5)
c, Å	15.6087(5)

α (°)	90
β (°)	90.917(3)
γ (°)	90
Volume, Å^3	2307.35(14)
Z	4
d_{calc}, g cm^{-3}	1.349
λ, Å	0.71073
μ, mm^{-1}	0.260
No. of data collected	18532
No. of unique data	5454/0/289
R_{int}, R_{sigma}	0.0307, 0.0344
Goodness-of-fit on F^2	1.039
R_1, wR_2 ($I > 2\sigma(I)$)	0.0473, 0.1072
R_1, wR_2 (all data)	0.0730, 0.1199

VII. Copies of ^{1}H-^{1}H NOESY spectra of 3m and 3n

According to the cross-peaks of **3m**-Me-H1 to **3m**-H2 and **3m**-H2 to **3m**-H3 appeared on the ^{1}H-^{1}H NOESY spectrum of **3m**, we could deduce that **3m**-Me, **3m**-H2 and **3m**-H3 were located at the same side.

According to the cross-peaks of **3n**-Me-H1 to **3n**-H2 and **3n**-H2 to **3n**-H3 appeared on the ^{1}H-^{1}H NOESY spectrum of **3n**, we could deduce that **3n**-Me, **3n**-H2 and **3n**-H3 were located at the same side.



VIII. Details of DFT Calculations

All calculations have been performed using the DFT method implemented in the commercial Gaussian 16[3] program package. Molecular geomtetries of the model complexes were optimized applying the M062X(D3)[4-5] functional with the 6-31G(d)[6] basis set with the SMD[7] continuum solvation model in DMF. As soon as the convergences of optimizations were obtained, the frequency calculations ate the same level have been performed to identify all the stationary points as minima. All transition states were further confirmed by vibrational analysis and characterized by the only one imaginary frequency. Furthermore intrinsic reaction coordinate (IRC)[8] calculations were performed to confirm that the optimized transition states correctly connect the relevant reactants and products. Additionally, the single-point energies for all stationary points have also been calculated at the M062x(D3)/6-311+G(d,p) level in tetrahydrofuran solvent to provide more accurate energy information. All energies discussed in the following parts are Gibbs free energies calculated at 298.15 K unless otherwise stated. All of the optimized geometries mentioned were built by Gaussview 6.0.[9]

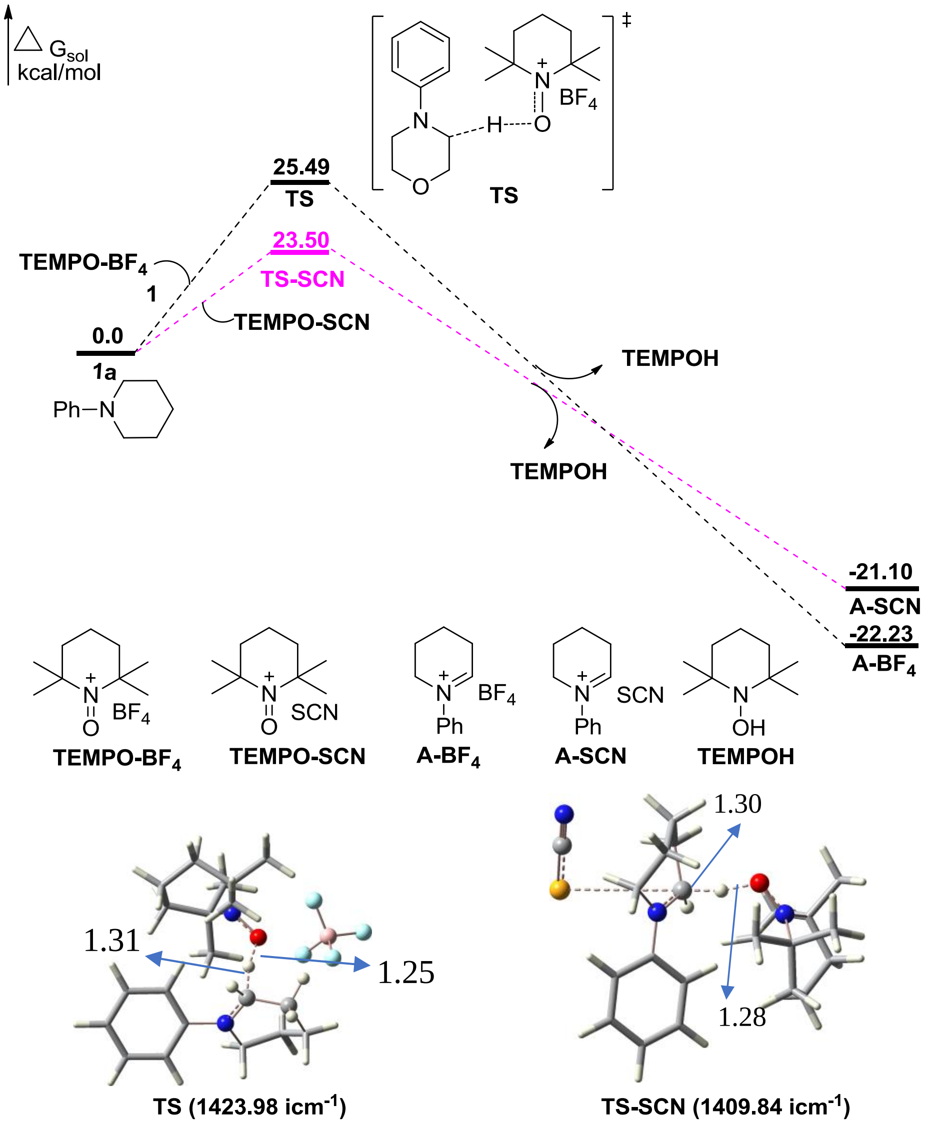


Fig. S7 Computational investigation on the rate determining step for the formation of **5a**

Considering that KSCN as additive can improve the yield of the reaction for the formation of **5a**, calculations of the rate determining step (hydride abstraction from α-carbon of piperidine **1a** by $TEMPO^+$ acts as the initial step for the formation of iminium intermediate **A-BF$_4$**) with a SCN ion was conducted (Fig. S7). It requires a free energy barrier of 23.50 kcal/mol (**TS-SCN**), which is lower than that with a BF_4^- (25.49 kcal/mol, **TS**). This result shows that SCN ion is favorable for rate determining step to further improve the formation of product **5a**.

Coordinates of Stationary Points

Cartesian coordinates (in Å), *E*sol (in kcal/mol), Gibbs free energies (G_{sol}, in kcal/mol) and the number of imaginary vibrational frequencies (N_{imag}) for the stationary points computed at the M062x(D3)/6-311+G(d,p) level in tetrahydrofuran solvent.

Table S2

	G_{sol}	Thermal correction to Gibbs Free Energy (TCG)	E_{sol}	$\triangle G_{sol}=E_{sol}+TCG$	N_{imag}
1a	-482.532186	0.205377	-482.8663901	-482.6610131	0
TEMPOBF$_4$	-907.560626	0.239119	-908.0964087	-907.8572897	0
TS	-1390.055065	0.463005	-1390.940679	-1390.477674	-1423.98
A-BF$_4$	-906.26548	0.201725	-906.75148	-906.549755	0
TEMPOH	-483.857679	0.241618	-484.2455952	-484.0039772	0
TEMPOSCN	-974.216089	0.232562	-974.6467954	-974.4142334	0
TS-SCN	-1456.710647	0.455251	-1457.49304	-1457.037789	-1409.84
A-SCN	-972.917917	0.198948	-973.3038418	-973.1048938	0

1a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.627068	-1.034849	0.728272
2	6	0	-1.290588	-1.248985	0.021580
3	6	0	-1.290582	1.248964	-0.021599
4	6	0	-2.627103	1.034865	-0.728225
5	6	0	-3.499836	-0.000011	0.000022
6	1	0	-0.711261	-1.997745	0.570064
7	1	0	-1.453507	-1.642836	-0.994604
8	1	0	-4.152277	-0.498259	-0.724600

9	1	0	-2.413312	-0.693931	1.747918
10	1	0	-1.453432	1.642786	0.994611
11	1	0	-0.711285	1.997742	-0.570094
12	1	0	-2.413402	0.694002	-1.747900
13	1	0	-3.146437	1.994146	-0.813607
14	1	0	-4.152305	0.498210	0.724638
15	1	0	-3.146399	-1.994125	0.813738
16	7	0	-0.534599	-0.000009	-0.000061
17	6	0	0.841660	-0.000007	-0.000036
18	6	0	1.575784	-1.166974	-0.311524
19	6	0	1.575756	1.166976	0.311478
20	6	0	2.966111	-1.157784	-0.304174
21	1	0	1.055791	-2.077794	-0.587120
22	6	0	2.966080	1.157801	0.304206
23	1	0	1.055728	2.077787	0.587034
24	6	0	3.680838	0.000010	0.000037
25	1	0	3.495996	-2.073318	-0.554153
26	1	0	3.495947	2.073338	0.554209
27	1	0	4.766035	0.000020	0.000070

TEMPOBF$_4$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.397426	1.062156	1.028407
2	6	0	1.251253	1.310309	0.034497
3	6	0	1.226574	-1.342304	-0.006801
4	6	0	2.752917	-1.351203	0.301708

5	6	0	3.386066	0.037380	0.476936
6	1	0	3.761511	0.391607	-0.489976
7	1	0	2.008659	0.750321	2.000988
8	1	0	3.260452	-1.888896	-0.503313
9	1	0	2.860915	-1.941537	1.216162
10	1	0	4.250263	-0.041608	1.140523
11	1	0	2.888846	2.027460	1.180408
12	7	0	0.936947	-0.009629	-0.655832
13	6	0	0.825048	-2.432030	-0.983990
14	1	0	-0.252066	-2.408867	-1.168078
15	1	0	1.360814	-2.342691	-1.932344
16	1	0	1.088188	-3.388797	-0.525983
17	6	0	0.390955	-1.452185	1.280896
18	1	0	-0.665658	-1.273089	1.083697
19	1	0	0.523543	-2.482015	1.624445
20	1	0	0.738413	-0.792070	2.075334
21	6	0	1.646811	2.299447	-1.060587
22	1	0	0.828756	2.469633	-1.762137
23	1	0	1.880736	3.245306	-0.566655
24	1	0	2.530607	1.963576	-1.610548
25	6	0	-0.053541	1.764609	0.704213
26	1	0	0.177916	2.705997	1.211661
27	1	0	-0.830915	1.940149	-0.041538
28	1	0	-0.423034	1.051314	1.441754
29	8	0	0.476123	0.020317	-1.744613
30	9	0	-3.141172	1.369923	-0.180811
31	9	0	-2.651953	-0.160034	1.452915
32	9	0	-4.038248	-0.733520	-0.275725
33	9	0	-1.802062	-0.424677	-0.653793
34	5	0	-2.919139	0.015355	0.087676

TS

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.294035	3.731387	0.714658
2	6	0	0.889327	2.398075	1.190433
3	6	0	0.322091	1.698119	-1.285344
4	6	0	-0.830743	2.737062	-1.320464
5	6	0	-1.027615	3.520203	-0.015313
6	1	0	-1.719028	2.982320	0.644442
7	1	0	1.005371	4.248896	0.061154
8	1	0	-1.763745	2.225399	-1.579749
9	1	0	-0.611759	3.431110	-2.139035
10	1	0	-1.496405	4.483772	-0.235249
11	1	0	0.158962	4.363899	1.597862
12	7	0	0.683062	1.384127	0.123032
13	6	0	-0.094866	0.405354	-1.981903
14	1	0	0.736446	-0.300348	-2.034529
15	1	0	-0.943238	-0.064515	-1.473361
16	1	0	-0.412761	0.662475	-2.996867
17	6	0	1.595784	2.233227	-1.965836
18	1	0	2.411087	1.517378	-1.830083
19	1	0	1.396086	2.357774	-3.035160
20	1	0	1.901864	3.202438	-1.563358
21	6	0	0.182454	1.903755	2.458979
22	1	0	0.588429	0.941465	2.784471
23	1	0	0.354676	2.632033	3.256417

24	1	0	-0.897761	1.801936	2.313909
25	6	0	2.392597	2.519468	1.459504
26	1	0	2.550547	3.247044	2.262273
27	1	0	2.806209	1.554502	1.761393
28	1	0	2.923200	2.862453	0.566939
29	8	0	0.969003	0.187496	0.419191
30	9	0	2.916080	-1.825660	0.553734
31	9	0	3.635668	0.211013	-0.230325
32	9	0	4.777905	-1.697229	-0.764051
33	9	0	2.719203	-1.314207	-1.675494
34	5	0	3.508652	-1.153937	-0.523912
35	6	0	0.190219	-2.321775	1.981730
36	6	0	-0.813255	-1.352998	1.373043
37	6	0	-1.285261	-2.878800	-0.509643
38	6	0	0.192676	-3.201699	-0.360957
39	1	0	-1.290579	-0.686426	2.095415
40	1	0	-0.003823	-0.483113	0.829969
41	1	0	-0.211067	-2.631264	2.953648
42	1	0	-1.884420	-3.769119	-0.281029
43	1	0	-1.530012	-2.558423	-1.527524
44	1	0	0.810173	-2.353285	-0.679234
45	1	0	0.421370	-4.048116	-1.015479
46	1	0	1.110025	-1.762505	2.177759
47	7	0	-1.678188	-1.791410	0.405585
48	6	0	-2.861936	-1.076346	0.117579
49	6	0	-2.945911	0.299593	0.368256
50	6	0	-3.955748	-1.740733	-0.450382
51	6	0	-4.118354	0.991019	0.087046
52	1	0	-2.078523	0.838195	0.740532
53	6	0	-5.122087	-1.036376	-0.733169

54	1	0	-3.904420	-2.805430	-0.651521
55	6	0	-5.214319	0.327456	-0.462740
56	1	0	-4.162501	2.059359	0.279321
57	1	0	-5.966507	-1.564306	-1.165519
58	1	0	-6.125838	0.870637	-0.690303
59	6	0	0.488497	-3.536705	1.095512
60	1	0	-0.138410	-4.383579	1.397940
61	1	0	1.531728	-3.832927	1.219557

A-BF_4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.334671	2.046614	-0.553745
2	6	0	-0.361012	0.939240	-0.694182
3	6	0	0.846218	2.016310	1.042074
4	6	0	0.686633	3.355856	0.328106
5	6	0	-0.634720	3.421804	-0.462972
6	1	0	-0.482088	0.136982	-1.416327
7	1	0	-0.442220	3.784252	-1.475001
8	1	0	-1.874289	1.841822	0.381138
9	1	0	0.070064	1.866357	1.800468
10	1	0	1.821505	1.907891	1.512159
11	1	0	1.540560	3.482164	-0.343908
12	1	0	0.739633	4.147100	1.079453
13	1	0	-1.333507	4.118603	0.004376
14	1	0	-2.060501	2.001552	-1.364114
15	7	0	0.686191	0.922166	0.057258

16	6	0	1.652980	-0.144775	0.000945
17	6	0	3.007611	0.176343	-0.056238
18	6	0	1.208207	-1.463272	-0.000116
19	6	0	3.936892	-0.855904	-0.128944
20	1	0	3.328712	1.213702	-0.064279
21	6	0	2.153219	-2.484182	-0.076283
22	1	0	0.147565	-1.682805	0.071569
23	6	0	3.511957	-2.184499	-0.139357
24	1	0	4.994581	-0.619344	-0.182828
25	1	0	1.820729	-3.517254	-0.074954
26	1	0	4.242130	-2.985795	-0.193991
27	9	0	-1.731111	-0.565047	0.996330
28	9	0	-2.857181	-0.414654	-0.986367
29	9	0	-3.760691	-1.597366	0.757422
30	9	0	-1.923618	-2.404159	-0.346724
31	5	0	-2.580540	-1.252110	0.104753

TEMPOH

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.111062	1.407950	0.487168
2	6	0	-1.271376	-0.062919	0.054293
3	6	0	1.282615	-0.029881	0.048116
4	6	0	1.309596	1.513864	-0.133804
5	6	0	-0.076241	2.124778	-0.371195
6	1	0	-0.351059	2.032876	-1.428392
7	1	0	-0.800635	1.457769	1.538934

8	1	0	1.968995	1.773565	-0.969393
9	1	0	1.754401	1.955229	0.766167
10	1	0	-0.055880	3.194890	-0.140171
11	1	0	-2.090688	1.895595	0.424774
12	7	0	0.013761	-0.514059	-0.546650
13	6	0	2.423026	-0.644142	-0.769028
14	1	0	2.513734	-1.718712	-0.588214
15	1	0	2.255212	-0.478712	-1.839281
16	1	0	3.369959	-0.168463	-0.492792
17	6	0	1.481982	-0.424973	1.519130
18	1	0	1.305277	-1.497198	1.652751
19	1	0	2.513911	-0.208975	1.819092
20	1	0	0.822850	0.128752	2.193261
21	6	0	-2.308960	-0.166379	-1.068898
22	1	0	-2.327181	-1.185346	-1.469746
23	1	0	-3.310458	0.074044	-0.695755
24	1	0	-2.068361	0.520325	-1.887638
25	6	0	-1.756038	-0.908810	1.238709
26	1	0	-2.676423	-0.464060	1.634432
27	1	0	-1.976889	-1.932518	0.927385
28	1	0	-1.026226	-0.943810	2.050594
29	8	0	0.012847	-1.940176	-0.529248
30	1	0	0.139110	-2.172364	-1.462424

TEMPOSCN

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	2.312163	-1.031080	-1.013858
2	6	0	1.113219	-1.302853	-0.091061
3	6	0	1.054124	1.349062	-0.025595
4	6	0	2.595666	1.378565	-0.243850
5	6	0	3.255123	-0.000853	-0.395814
6	1	0	3.578196	-0.361080	0.587578
7	1	0	1.976599	-0.713078	-2.004102
8	1	0	3.048541	1.913320	0.594986
9	1	0	2.750072	1.979878	-1.144399
10	1	0	4.155079	0.095175	-1.007589
11	1	0	2.823026	-1.989063	-1.146882
12	7	0	0.739772	0.006315	0.590136
13	6	0	0.582959	2.423196	0.938115
14	1	0	-0.503019	2.387387	1.055854
15	1	0	1.061174	2.325449	1.915915
16	1	0	0.864027	3.387886	0.508283
17	6	0	0.292878	1.463303	-1.358741
18	1	0	-0.770936	1.268474	-1.224815
19	1	0	0.431704	2.498455	-1.683259
20	1	0	0.694276	0.815739	-2.137945
21	6	0	1.457057	-2.295821	1.018493
22	1	0	0.599873	-2.484357	1.666587
23	1	0	1.736329	-3.233275	0.532183
24	1	0	2.299191	-1.950018	1.624628
25	6	0	-0.144122	-1.768323	-0.839782
26	1	0	0.128344	-2.702785	-1.339514
27	1	0	-0.961408	-1.958666	-0.141777
28	1	0	-0.478593	-1.053148	-1.592112
29	8	0	0.207558	-0.040589	1.644932
30	16	0	-4.594294	0.023852	-0.329798

31	6	0	-3.111469	-0.078841	0.164463
32	7	0	-1.886889	-0.163649	0.572645

TS-SCN

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.822598	0.363801	-1.571002
2	6	0	-2.927644	-0.847231	-1.267039
3	6	0	-2.794120	0.328176	1.081829
4	6	0	-2.998952	1.712403	0.412186
5	6	0	-3.176002	1.666772	-1.113077
6	1	0	-2.202024	1.773771	-1.605561
7	1	0	-4.800611	0.239170	-1.093885
8	1	0	-2.146568	2.354665	0.657973
9	1	0	-3.880596	2.165175	0.878158
10	1	0	-3.780405	2.518940	-1.436966
11	1	0	-3.999511	0.374670	-2.651242
12	7	0	-2.321214	-0.659672	0.076419
13	6	0	-1.767575	0.416116	2.207541
14	1	0	-1.710218	-0.525517	2.759830
15	1	0	-0.772833	0.675212	1.828677
16	1	0	-2.087491	1.210418	2.888654
17	6	0	-4.110285	-0.216214	1.670303
18	1	0	-3.955244	-1.228226	2.059256
19	1	0	-4.416962	0.435037	2.495426
20	1	0	-4.919602	-0.236015	0.936612
21	6	0	-1.793943	-0.958701	-2.294653

22	1	0	-1.146890	-1.813172	-2.075020
23	1	0	-2.238136	-1.116904	-3.281369
24	1	0	-1.184365	-0.050307	-2.332976
25	6	0	-3.734034	-2.149757	-1.256287
26	1	0	-4.161095	-2.315632	-2.250592
27	1	0	-3.088620	-2.997096	-1.006124
28	1	0	-4.550393	-2.098793	-0.529988
29	8	0	-1.422335	-1.490785	0.417345
30	6	0	1.557036	-2.472788	-0.093082
31	6	0	1.046068	-1.055326	-0.197587
32	6	0	2.376765	-0.645162	1.794533
33	6	0	1.627638	-1.846728	2.366118
34	1	0	0.836666	-0.682192	-1.203474
35	1	0	-0.264643	-1.124437	0.127855
36	1	0	2.585704	-2.457379	-0.478068
37	1	0	3.398537	-0.921767	1.502519
38	1	0	2.430991	0.162602	2.525348
39	1	0	0.619359	-1.514775	2.636651
40	1	0	2.123758	-2.166242	3.286394
41	1	0	0.972628	-3.108779	-0.762214
42	7	0	1.656129	-0.142419	0.614541
43	6	0	1.529483	1.241407	0.382970
44	6	0	0.389373	1.744742	-0.257129
45	6	0	2.542571	2.119374	0.786734
46	6	0	0.275271	3.106810	-0.508017
47	1	0	-0.424524	1.073403	-0.520316
48	6	0	2.412137	3.481899	0.537139
49	1	0	3.437655	1.737386	1.266772
50	6	0	1.285111	3.983010	-0.112197
51	1	0	-0.619193	3.483319	-0.996458

52	1	0	3.206191	4.154231	0.847002
53	1	0	1.190083	5.047607	-0.299687
54	6	0	1.543861	-2.999274	1.355239
55	1	0	2.386966	-3.683139	1.485723
56	1	0	0.628697	-3.568856	1.539976
57	16	0	2.899690	-0.824879	-0.980933
58	6	0	4.443715	-0.616936	-1.571089
59	7	0	5.535525	-0.456538	-1.971433

A-SCN

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.330478	-0.888236	-0.836611
2	6	0	0.936723	-0.399327	-0.958636
3	6	0	0.539667	-1.662236	1.011375
4	6	0	1.245829	-2.861403	0.381352
5	6	0	2.356566	-2.416518	-0.590879
6	1	0	0.592075	0.223032	-1.779539
7	1	0	2.241242	-2.927190	-1.549271
8	1	0	2.766353	-0.378228	0.034680
9	1	0	1.214880	-1.070727	1.636973
10	1	0	-0.323744	-1.950730	1.607442
11	1	0	0.496376	-3.461410	-0.143040
12	1	0	1.649733	-3.473605	1.191040
13	1	0	3.344031	-2.671225	-0.200877
14	1	0	2.906031	-0.601280	-1.716271
15	7	0	0.075102	-0.758495	-0.067565

16	6	0	-1.291215	-0.305019	-0.098931
17	6	0	-2.316826	-1.228005	0.093418
18	6	0	-1.553478	1.041842	-0.332881
19	6	0	-3.634503	-0.785414	0.043328
20	1	0	-2.091413	-2.277221	0.258344
21	6	0	-2.877957	1.468500	-0.380876
22	1	0	-0.734113	1.743988	-0.464185
23	6	0	-3.916532	0.559763	-0.191738
24	1	0	-4.441461	-1.497189	0.183508
25	1	0	-3.093414	2.517400	-0.556971
26	1	0	-4.946891	0.899118	-0.225574
27	16	0	2.011006	2.715919	-0.395727
28	6	0	1.497628	1.962858	0.996920
29	7	0	1.117177	1.408457	1.959041

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