Electronic Supplementary Material (ESI) for Green Chemistry.

Water-Promoted Synthesis of Fused Bicyclic Triazolines and Naphthols from Oxa(aza)bicyclic Alkenes and the Transformation via Novel Ring-Opening/Rearrangement Reaction

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1. Experimental Procedures

General Experimental. Unless otherwise noted, reactions were carried out in single-neck or two-neck flask round bottom flasks, with magnetic stirring. Air- or water-sensitive liquids and solutions were transferred via syringe. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 40 Torr (house vacuum). Analytical thin layer chromatography (TLC) was performed with Silicycle normal phase glass plates (0.25 mm, 60-A pore size, 230-400 mesh). Visualization was done under a 254 nm UV light source. Purification of reaction products was generally done by flash chromatography with Silicycle 230-400 mesh silica gel.

Materials. Unless otherwise indicated, all reagents and solvents were purchased for commercial suppliers and used without additional purification. Distilled water was used in the reactions. Oxa(aza)bicyclic alkenes[1] were prepared according to literature procedures.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 23 °C with a Varian Mercury NMR spectrometer. Recorded shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents ($CHCl_3$: δ 7.26, CD_2HOD: δ 3.30). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0, CD_3OD: δ 49.2). Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), and coupling constant (*J*, Hz). HRMS (ion trap) were obtained from mass spectrometer (ESI) and MS were recorded using EI at 70 eV. Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected.

The procedure for 1-(4-chlorobutyl)-1,4-dihydro-1,4-epoxynaphthalene (1ac) : A dry 2 L three-neck round bottom flask was fitted with two dry 250 mL pressure equalizing addition funnels. The flask was charged with 2,2'-bipyridine (270 mg, 1.74 mmol, 0.005 equiv) and dry THF (540 mL), and the solution was cooled to 0 ºC. Furan (37.3 mL, 387.14 mmol, 3.7 equiv) was added in one portion via addition funnel, and the resulting solution was held at 0 ºC for 30 minutes. A solution of *n*-BuLi (2.07 M in hexanes, 149 mL, 307.8 mmol, 3.0 equiv) was added to the addition funnel via cannula, and then added dropwise to the reaction flask. The mixture was allowed to stir at 0 ºC in an ice bath for 2 h before 1-bromo-3-chlorobutane (10.26 mL, 102.6 mmol, 1.0 equiv) was added dropwise. The reaction remained in the bath and was allowed to warm slowly 0 - 23 ºC over 12 h. The reaction was quenched with a saturated, aqueous solution of NH_4Cl (270 mL), and then hexanes (270 mL) were added. The layers were separated, and the aqueous layer was extracted with hexanes (350 mL x 3). The organic layer was washed with brine (275 mL x 2). The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by fractional vacuum distillation, 77–80 ºC at 2 mmHg yielding 2-(3-chlorobutyl)furan as a yellow oil (10.2 g, 78% yield)[2]. To a 100 mL round-bottomed flask with a reflux condenser tube, 10 mL 2-(3-chlorobutyl)furan and 10 mL DME were added. Taking two 25 mL dropping bottles, one with 4 mL *iso*-amyl nitrite and 10 mL DME (A), another with 2-aminobenzoic acid (2.75 g, 0.02 mol) dissolved by 10 mL DME (B). Then 1 mL A and 1 mL B were added to the refluxing 2-(3-chlorobutyl)furan solution per 4 minute. Firstly, the A was added, then the B. The solution became red brown, giving off gas when the reagents were added. Let the mixture refluxing until the solution did not release gas after all the reactants were added (about 15 min). After completion 2% sodium hydroxide (25 mL) was added to the mixture and transferred to separating funnel to rinse, which we can get the organic phase and the aqueous solution extracted three times by 15 mL petroleum ether. Then the extractive solution and the organic phase were mixed together. The mixture was washed by water (15 mL x 4) and dried by anhydrous magnesium sulfate. After completion the reaction mixture was concentrated in vacuo and the solvents were removed, the crude mixture was purified by flash chromatography gave 1-(4-chlorobutyl)-1,4-dihydro-1,4-epoxynaphthalene (**1ac**) a yellow oil (1.32 g, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 6.4 Hz, 1H), 7.09 – 6.91 (m, 3H), 6.80 (d, *J* = 5.5 Hz, 1H), 5.67 (s, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.49 – 2.24 (m, 2H), 2.01 – 1.91 (m, 2H), 1.86 – 1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.4, 144.6, 144.4, 124.9, 124.8, 120.0, 119.2, 92.6, 81.7, 44.8, 32.9, 28.4, 22.2. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{16}ClO$: 235.0890, found: 235.0883.

The general procedure (A) for new compounds of 3a-t and 7a-c: The substrate oxa(aza)benzonorbornadienes **1** (0.2 mmol), sodium azide (0.4 mmol), haloalkane **2** (9.7 mmol) and *n*-Bu_4NOAc (0.01 mmol, 5 mol %) were added to 10.0 mL round-bottomed flask, followed by addition of 2.0 mL H_2O. The mixture was stirred at 65 ºC for 12 h. The solution was then extracted with EtOAc, the combined organic layers were dried over $MgSO_4$, filtered, and evaporated under vacuum. The residue was purified by column chromatography (Silica Gel: 200-300 mesh) to afford the desired product **3** and **7**.

The procedure for new compounds of 3u and **3u':** The substrate cyclopentadiene **1ab** (0.2 mL), sodium azide (0.2 mmol), DCE (9.7 mmol) and *n*-Bu_4NOAc (0.01 mmol) were added 10.0 mL round-bottomed flask, followed by addition of 2.0 mL H_2O. The mixture was stirred at 65 ºC for 12 h. The solution was then extracted with EtOAc, the combined organic layers

were dried over $MgSO_4$, filtered, and evaporated under vacuum. The residue was purified by column chromatography (Silica Gel: 200-300 mesh) to afford the desired product **3u** and **3u′**.

The procedure for new compounds of 3v: The substrate 1-(4-chlorobutyl)-1,4-dihydro-1,4-epoxynaphthalene **1ac** (0.1 mL), sodium azide (0.4 mmol) and *n*-Bu_4NOAc (0.01 mmol) were added to 10.0 mL round-bottomed flask, followed by addition of 0.3 mL H_2O. The mixture was stirred at 70 °C for 16 h. The solution was then extracted with EtOAc, the combined organic layers were dried over $MgSO_4$, filtered, and evaporated under vacuum. The residue was purified by column chromatography (Silica Gel: 200-300 mesh) to afford the desired product **3v**.

The general procedure (B) for the compounds of 4a-i: The substrate oxa(aza)benzonorbornadienes **1** (0.1 mmol) was added to 10.0 mL round-bottomed flask, followed by addition of 2.05 mL solvent ($ClF_2CCOOCH_2CH_3$ and H_2O, V : V = 0.05 : 2). The mixture was stirred at 80 °C for 12 h. Concentration in vacuum followed by purification by flash column chromatography (Silica Gel: 200-300 mesh) to afford the desired product **4**.

Typical procedure (C) for new compound of 5:

The substrate 1-(2-chloroethyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole **3a** (0.2 mmol, 0.0498 g) and Cs_2CO_3 (0.4 mmol, 0.1303 g) was added to 10 mL flask, followed by addition of 2 mL CH_3CH_2OH. The mixture was stirred at 65 °C for 24h. Concentration in vacuum followed by purification by flash column chromatography (Silica Gel: 200-300 mesh) to afford the desired product 1-vinyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (**5**).

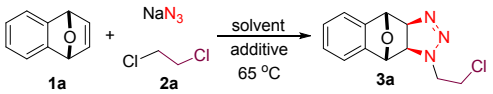
Typical procedure (D) for new compound of 6:

The substrate 1-(2-chloroethyl)-10-tosyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole **3e** (0.2 mmol, 0.0804 g) and Cs_2CO_3 (0.4 mmol, 0.1303 g) was added to 10 mL flask, followed by addition of 2 mL CH_3CH_2OH. The mixture was stirred at 65 °C for 24h. Concentration in vacuum followed by purification by flash column chromatography (Silica Gel: 200-300 mesh) to afford the desired product 1-vinyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (**6**).

Typical procedure (E) for new compounds of 7d-f:

The substrate bicyclic triazoline (0.2 mmol) was added to a flame-dried 50.0 mL round-bottomed flask with stir bar. The flask was sealed under nitrogen and bromobenzene (4.0 mL) was added. $BF_3{\cdot}OEt_2$ (0.06 mmol, 0.0085 g) was diluted to 0.2 mL by the Et_2O and added dropwise until the bubble disappears. The mixture was stirred at room temperature for 0.2 h. Concentration in vacuum followed by purification by flash column chromatography (Silica Gel: 200-300 mesh) to afford the desired product (**7d-f**).

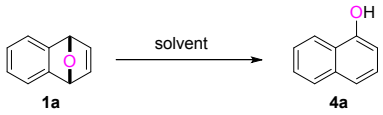
Table S1. Initial investigations on multicomponent cycloaddition reaction in Water.[a]



Entry	Solvent	Additive (mol %)	Time (h)	Yield[b] (%)
1	CH_3OH	-	24	n.r.
2	THF	-	24	n.r.
3	toluene	-	24	n.r.
4	DCE	-	24	n.r.
5	DCE	CuI (5)	24	n.r.
6	water	-	12	11
7	water	-	24	34
8[c]	water	-	24	56
9	water	Bu_4NBr (10)	12	68
10	water	Bu_4NBF_4 (10)	12	82
11	water	Bu_4NOAc (10)	12	85
12	water	Bu_4NOAc (5)	12	**98**
13	water	Bu_4NOAc (2)	12	66
14[d]	water	Bu_4NOAc (5)	12	42
15[e]	water	Bu_4NOAc (5)	12	40
16[f]	water	Bu_4NOAc (5)	12	33

[a] The reaction was carried out using oxabicyclic alkenes (0.2 mmol), sodium azide (0.4 mmol), and DCE (9.7 mmol) in solvent (2 mL) at 65 °C. DCE = $ClCH_2CH_2Cl$. [b] Isolated yield. [c] The reaction was performed at 90 °C. [d] DCE (10 mmol) in 0.3 mL H_2O . [e] DCE (9 mmol) in 0.3 mL H_2O. [f] DCE (5mmol) in 0.3 mL H_2O.

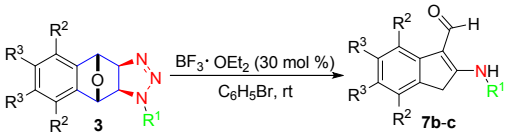
Table S2. Initial investigations on ring-opening reaction of oxa(aza)bicyclic alkene in water. [a]



Entry	Solvent	Temp (°C)	Yield (%)
1	water	85	n.r.
2	chlorocyclohexane	85	n.r.
3	water / chlorocyclohexane	85	84(n.r.[c])
4[b]	water / *tert*-butyl chloride	65	77
5	**water / $ClF_2CCOOCH_2CH_3$**	**65**	**99**
6	$ClF_2CCOOCH_2CH_3$	65	36
7	water / $CH_3COOCH_2CH_3$	65	n.r.
8	$ClF_2CCOOCH_2CH_3$ / CH_3CH_2OH	65	n.r.
9	$ClF_2CCOOCH_2CH_3$ / isopropanol	65	n.r.
10	$ClF_2CCOOCH_2CH_3$ / toluene	65	n.r.
11	$ClF_2CCOOCH_2CH_3$ / 1,4-dioxane	65	n.r.
12	water / $CF_3COOCH_2CH_3$	65	94
13	water / $CCl_3COOCH_2CH_3$	65	92
14	water/ F_3CCH_2OH	65	n.r.
15[d]	**Water/$ClF_2CCOOCH_2CH_3$**	**80**	**99**
16[e]	Water / 1,4-dioxane	**65**	**99**

[a] The reaction was carried out using oxabicyclic alkenes (0.1 mmol) in solvent (ratio of various solvent = 1:1 v/v, 2 mL) for 12 h. [b] The reaction was performed for 3 h. [c] The reaction was performed at 65 °C. [d] Water/$ClF_2CCOOCH_2CH_3$ = 1 : 0.025 v/v, 2.05 mL , 80 °C. [e] HCl (2 eq) had been added in the reaction system.

Table S3. Synthesis of indene **7d–f** via BF_3-induced cascade ring-opening reaction of bicyclic triazolines. [a]

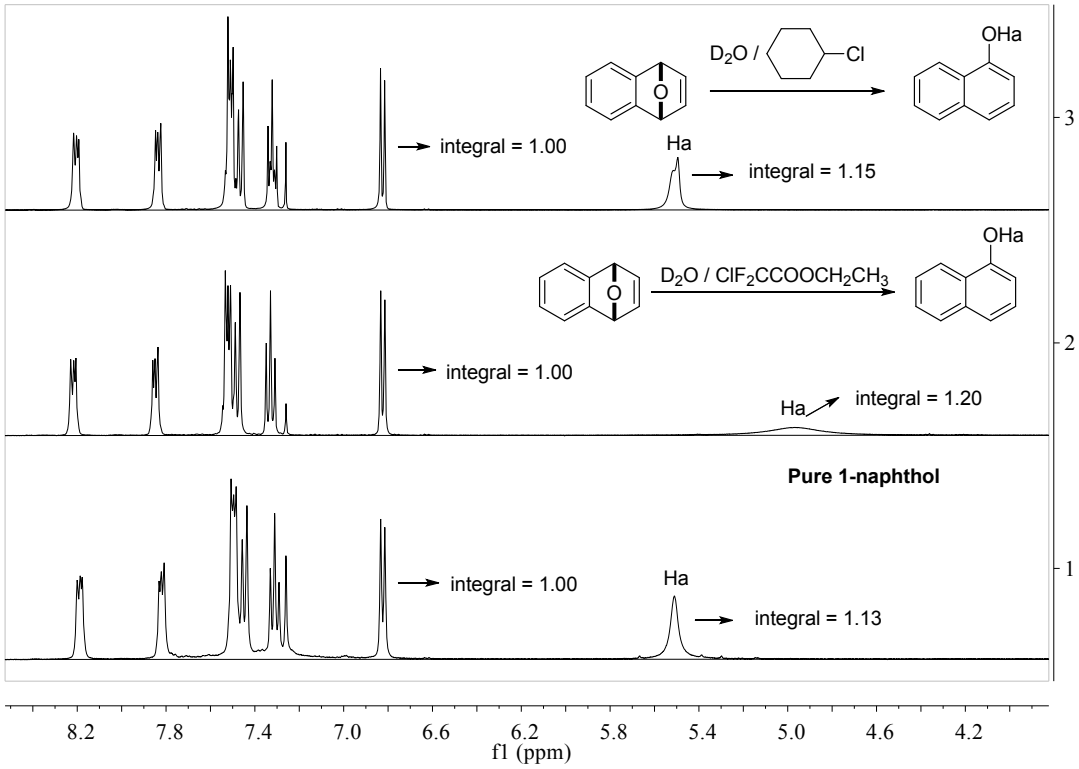


7d: $R^1 = (CH_2)_3CH_3$, $R^2 = R^3 = H$
7e: $R^1 = (CH_2)_{11}CH_3$, $R^2 = R^3 = H$
7f: $R^1 = (CH_2)_3CH_3$, $R^2 = OMe$, $R^3 = H$

Entry	Cat. (eq)	solvent	Time (h)	Prod.	Yield[b] (%)
1	-	CH_2Cl_2	24	**7d**	n.r.
2	$FeCl_3$ (0.1)	CH_2Cl_2	24	**7d**	n.r.
3	$BF_3{\cdot}OEt_2$ (0.3)	CH_2Cl_2	0.2	**7d**	34
4	TfOH (1.0)	CH_2Cl_2	0.2	**7d**	n.r.
5	$BF_3{\cdot}OEt_2$ (0.3)	toluene	0.2	**7d**	52
6	$BF_3{\cdot}OEt_2$ (0.3)	C_6H_5Br	0.2	**7d**	70
7	$BF_3{\cdot}OEt_2$ (0.3)	C_6H_5Br	0.2	**7e**	74
8	$BF_3{\cdot}OEt_2$ (0.3)	C_6H_5Br	0.2	**7f**	68

[a] The reaction was performed at room temperature. [b] Isolated yield.

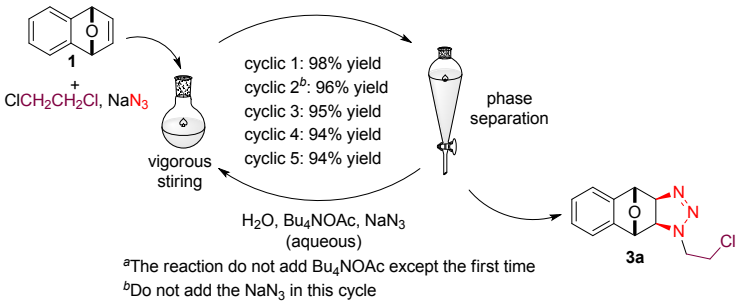
Scheme S1. Deuterium-labeling experiments. [a]

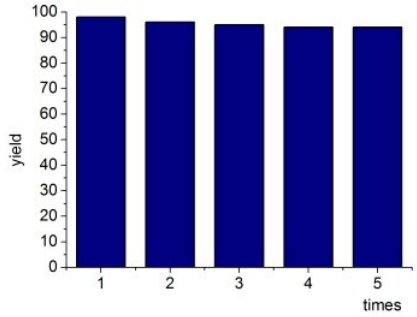


[a] ^1H NMR spectra of the naphthol produced in D_2O over chlorocyclohexane (3) and $ClF_2CCOOCH_2CH_3$ (2). The spectrum for pure naphthol (1) is also shown for comparison. Reaction conditions: oxabicyclic alkene (0.1 mmol); 1 mL D_2O; 1mL haloalkane; 65 °C; t = 12 h.

The H of the O-H could been seen in the the spectrum for pure naphthol (see scheme S1 (1)). While using the D_2O to replace the H_2O, the H of the O-H in the naphthol was stell in the spectrum (see scheme S1 (2 and 3)).

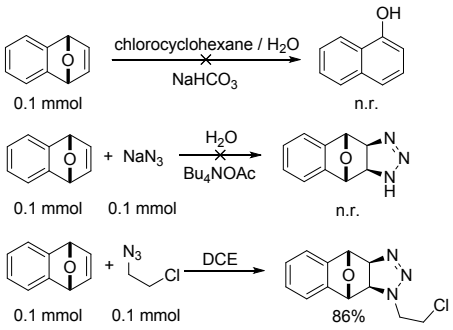
Scheme S2. A simple isolation and recycling of the aqueous phase. [a]



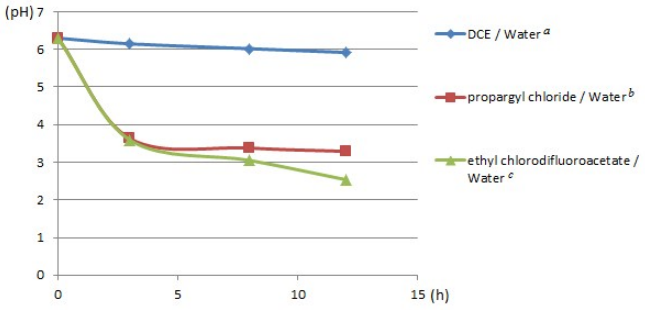


Recycling experiments have been performed under aqueous biphasic conditions. The substrates **1** (0.1 mmol), NaN_3 (0.4 mmol) and $ClCH_2CH_2Cl$ (9.7 mmol) were added to a solution (H_2O, 2 mL) of the Bu_4NOAc (5 mmol %), and the mixture was stirred at 65 °C for 12 h. When the stirring was stopped, the mixture separated slowly into two distinct phases. Following the facile separation of the mixture in a separating funnel, the aqueous phase was returned to the reaction flask, and another batch of reactants was added. The cyclic 2 do not add the NaN_3, but just using NaN_3 which recovery by the last aqueous phase.

Scheme S3. The control experiments of cycloaddition.

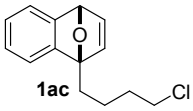


Scheme S4. The pH of the aqueous layer in different haloalkane/Water system.

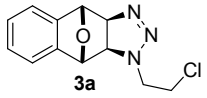


[a]DCE / Water = 1 : 1 v/v, 65 °C. [b]Propargyl chloride / Water = 1 : 1 v/v, 65 °C. [c]Ethyl chlorodifluoroacetate / Water = 0. 025 : 1 v/v, 80 °C

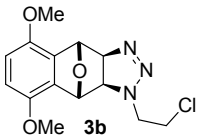
2. Characterization data



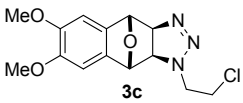
1-(4-chlorobutyl)-1,4-dihydro-1,4-epoxynaphthalene (1ac). Following the procedure for 1-(4-chlorobutyl)-1,4-dihydro-1,4-epoxynaphthalene, **1ac** was obtained as a yellow oil (1.32 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 6.4 Hz, 1H), 7.09 – 6.91 (m, 3H), 6.80 (d, *J* = 5.5 Hz, 1H), 5.67 (s, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.49 – 2.24 (m, 2H), 2.01 – 1.91 (m, 2H), 1.86 – 1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.4, 144.6, 144.4, 124.9, 124.8, 120.0, 119.2, 92.6, 81.7, 44.8, 32.9, 28.4, 22.2. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{16}ClO$: 235.0890, found: 235.0883.



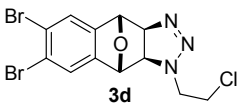
1-(2-Chloroethyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3a). Following the general procedure **(A)**, **3a** was obtained as a yellow oil (48.8 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.23 (ddd, *J* = 12.7, 6.8, 1.2 Hz, 2H), 5.66 (s, 1H), 5.47 (s, 1H), 4.94 (d, *J* = 8.7 Hz, 1H), 4.15 (dt, *J* = 14.8, 6.0 Hz, 1H), 4.02 (dt, *J* = 14.8, 6.2 Hz, 1H), 3.85 (dd, *J* = 13.8, 7.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 142.9, 127.9, 127.6, 120.4, 120.4, 87.5, 83.2, 82.6, 63.7, 49.8, 42.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{12}H_{13}ClN_3O$: 250.0747, found: 250.0747.



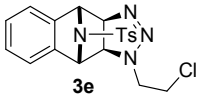
1-(2-Chloroethyl)-5,8-dimethoxy-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3b). Following the general procedure **(A)**, **3b** was obtained as a white solid (47.6 mg, 77%). m.p. 116.0-117.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (q, *J* = 8.8 Hz, 2H), 5.74 (s, 1H), 5.51 (s, 1H), 4.89 (d, *J* = 8.7 Hz, 1H), 4.06 (dt, *J* = 14.0, 6.2 Hz, 1H), 3.96 – 3.89 (m, 1H), 3.79 – 3.75 (m, 3H), 3.74 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 147.3, 132.1, 131.8, 112.3, 111.8, 87.1, 81.4, 80.6, 63.1, 56.1, 55.9, 49.7, 42.3. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{17}ClN_3O_3$: 310.0958, found: 310.0966.



1-(2-Chloroethyl)-6,7-dimethoxy-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3c). Following the general procedure **(A)**, **3c** was obtained as a yellow oil (33.4 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.86 (s, 1H), 5.59 (s, 1H), 5.41 (s, 1H), 4.88 (d, *J* = 8.7 Hz, 1H), 4.12 (dt, *J* = 14.5, 5.9 Hz, 1H), 3.99 (dt, *J* = 14.8, 6.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.82 (dd, *J* = 13.2, 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.9, 148.7, 135.4, 135.0, 104.8, 104.7, 87.8, 83.4, 82.8, 63.9, 56.2, 49.8, 42.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{17}ClN_3O_3$: 310.0958, found: 310.0956.

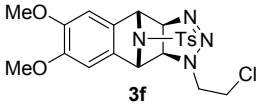


6,7-Dibromo-1-(2-chloroethyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3d). Following the general procedure **(A)**, **3d** was obtained as a white solid (80.2 mg, 99%). m.p. 114.0-115.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 19.5 Hz, 1H), 7.59 (d, *J* = 19.5 Hz, 1H), 5.66 (d, *J* = 19.3 Hz, 1H), 5.48 (d, *J* = 19.4 Hz, 1H), 4.98 (dd, *J* = 19.3, 8.5 Hz, 1H), 4.22 – 4.11 (m, 1H), 4.10 – 4.00 (m, 1H), 3.94 – 3.81 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 143.9, 125.8, 124.1, 123.8, 87.1, 82.7, 82.2, 63.5, 49.9, 42.9. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{12}H_{11}Br_2ClN_3O$: 405.8957, found: 405.8953.



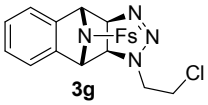
3e

1-(2-Chloroethyl)-10-tosyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3e). Following the general procedure **(A)**, **3e** was obtained as a white solid (35.4 mg, 44%). m.p. 102.0-103.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 6.2 Hz, 1H), 7.05 – 6.98 (m, 5H), 5.38 (s, 1H), 5.23 (s, 1H), 4.86 (d, *J* = 8.9 Hz, 1H), 4.18 (dt, *J* = 14.7, 5.7 Hz, 1H), 3.96 (dt, *J* = 14.7, 6.5 Hz, 1H), 3.87 – 3.80 (m, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 141.5, 141.2, 135.1, 129.1, 127.9, 127.8, 127.6, 121.5, 121.4, 87.7, 67.6, 66.6, 63.8, 49.4, 42.7, 21.4. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{19}H_{20}ClN_4O_2S$: 403.0995, found: 403.0995.



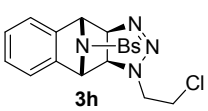
3f

1-(2-Chloroethyl)-6,7-dimethoxy-10-tosyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3f). Following the general procedure **(A)**, **3f** was obtained as a white solid (58.2 mg, 63%). m.p. 134.0-135.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.68 (s, 1H), 6.62 (s, 1H), 5.30 (s, 1H), 5.14 (s, 1H), 4.82 (d, *J* = 8.9 Hz, 1H), 4.13 (dt, *J* = 14.7, 5.7 Hz, 1H), 3.96 – 3.88 (m, 2H), 3.84 – 3.81 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 148.6, 143.5, 135.6, 134.0, 133.7, 129.1, 128.0, 106.0, 105.8, 88.1, 67.9, 66.9, 64.0, 56.3, 56.2, 49.4, 42.8, 21.4. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{21}H_{24}ClN_4O_4S$: 463.1207, found: 463.1222.



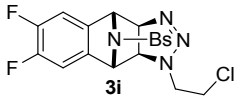
3g

1-(2-Chloroethyl)-10-((4-fluorophenyl)sulfonyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3g). Following the general procedure **(A)**, **3g** was obtained as a white solid (70.7 mg, 87%). m.p. 122.0-123.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.6, 5.1 Hz, 2H), 7.09 (d, *J* = 6.1 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.86 (t, *J* = 8.5 Hz, 2H), 5.38 (s, 1H), 5.22 (s, 1H), 4.86 (d, *J* = 8.9 Hz, 1H), 4.18 (dt, *J* = 14.6, 5.6 Hz, 1H), 4.01 – 3.92 (m, 1H), 3.85 (t, *J* = 6.0 Hz, 2H), 3.82 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (d, J_{CF} = 253.8 Hz), 141.1 (d, J_{CF} = 31.3 Hz), 134.16 (d, J_{CF} = 2.5 Hz), 130.6, 130.5, 128.2, 127.9, 121.5 (d, J_{CF} = 8.8 Hz), 115.8, 115.6, 87.8, 67.7, 66.8, 63.9, 49.5, 42.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.3. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{18}H_{17}ClFN_4O_2S$: 407.0745, found: 407.0733.



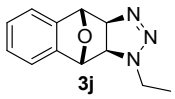
3h

10-((4-Bromophenyl)sulfonyl)-1-(2-chloroethyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3h). Following the general procedure **(A)**, **3h** was obtained as a white solid (85.7 mg, 92%). m.p. 108.0-109.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (q, *J* = 8.7 Hz, 4H), 7.09 – 7.00 (m, 4H), 5.37 (s, 1H), 5.21 (s, 1H), 4.86 (d, *J* = 9.0 Hz, 1H), 4.17 (dt, *J* = 14.8, 5.7 Hz, 1H), 3.97 (dt, *J* = 14.8, 6.3 Hz, 1H), 3.84 (dd, *J* = 14.2, 7.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 141.0, 137.1, 131.7, 129.2, 128.1, 127.8, 127.7, 121.6, 121.5, 87.7, 67.7, 66.8, 63.8, 49.5, 42.8. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{18}H_{17}BrClN_4O_2S$: 466.9944, found: 466.9958.



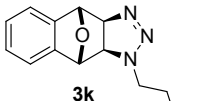
3i

10-((4-Bromophenyl)sulfonyl)-1-(2-chloroethyl)-6,7-difluoro-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3i). Following the general procedure **(A)**, **3i** was obtained as a white solid (72.3 mg, 72%). m.p. 132.0-133.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (q, *J* = 8.7 Hz, 4H), 7.04 (dd, *J* = 8.4, 6.8 Hz, 1H), 6.97 (dd, *J* = 8.4, 6.8 Hz, 1H), 5.37 (s, 1H), 5.22 (s, 1H), 4.88 (d, *J* = 8.9 Hz, 1H), 4.12 (dt, *J* = 13.1, 5.5 Hz, 1H), 3.98 – 3.92 (dt, *J* = 13.1, 5.5 Hz, 1H), 3.83 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 137.9, 137.6, 137.2, 132.1, 129.3, 128.4, 111.9, 111.8, 111.7, 87.6, 67.2, 66.6, 63.9, 49.8, 43.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -139.7 (d, *J* = 18.8 Hz), -140.0 (d, *J* = 18.8 Hz). HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{18}H_{15}BrClF_2N_4O_2S$: 502.9756, found: 502.9748.



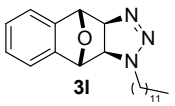
3j

1-Ethyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3j). Following the general procedure **(A)**, **3j** was obtained as a yellow oil (19.4 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.22 (dt, *J* = 14.8, 7.4 Hz, 2H), 5.65 (s, 1H), 5.40 (s, 1H), 4.87 (d, *J* = 8.8 Hz, 1H), 3.87 (dq, *J* = 14.5, 7.3 Hz, 1H), 3.74 (d, *J* = 8.7 Hz, 1H), 3.73 – 3.67 (m, 1H), 1.38 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 143.2, 127.9, 127.6, 120.4, 86.5, 83.5, 82.6, 63.1, 43.0, 14.0. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{12}H_{14}N_3O$: 216.1137, found: 216.1129.



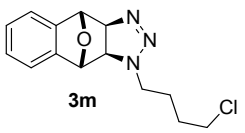
3k

1-Butyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3k). Following the general procedure **(A)**, **3k** was obtained as a white solid (25.3 mg, 52%). m.p. 84.0-85.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 6.8 Hz, 1H), 7.25 – 7.20 (m, 2H), 5.65 (s, 1H), 5.40 (s, 1H), 4.86 (d, *J* = 8.9 Hz, 1H), 3.82 (dt, *J* = 14.9, 5.9 Hz, 1H), 3.73 (d, *J* = 8.9 Hz, 1H), 3.65 (m, 1H), 1.74 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.44 (dd, *J* = 14.9, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 143.2, 127.9, 127.5, 120.4, 120.3, 86.4, 83.5, 82.4, 63.3, 47.9, 30.6, 20.0, 13.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{18}N_3O$: 244.1450, found: 244.1433.



3l

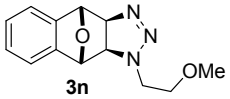
1-Dodecyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3l). Following the general procedure **(A)**, **3l** was obtained as a white solid (65.4 mg, 92%). m.p. 89.0-90.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.4 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.23 (dt, *J* = 7.9, 6.0 Hz, 2H), 5.65 (s, 1H), 5.39 (s, 1H), 4.87 (d, *J* = 8.9 Hz, 1H), 3.87 – 3.76 (m, 1H), 3.73 (d, *J* = 8.9 Hz, 1H), 3.68 – 3.58 (m, 1H), 1.82 – 1.67 (m, 2H), 1.40 – 1.20 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 143.2, 127.9, 127.5, 120.4, 120.3, 86.4, 83.5, 82.4, 63.3, 48.2, 31.9, 29.6, 29.5, 29.3, 28.6, 26.8, 22.7, 14.1. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{22}H_{34}N_3O$: 356.2702, found: 356.2708.



3m

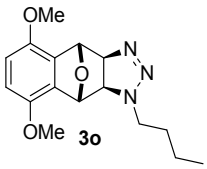
1-(4-Chlorobutyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3m). Following the general procedure **(A)**, **3m** was obtained as a yellow oil (51.5 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.7 Hz, 1H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.22 (dd, *J* = 7.5, 6.0 Hz,

2H), 5.65 (s, 1H), 5.41 (s, 1H), 4.88 (d, J = 8.8 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.74 – 3.67 (m, 2H), 3.62 (t, J = 5.8 Hz, 2H), 1.93 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 143.0, 127.9, 127.6, 120.4, 86.7, 83.4, 82.3, 63.2, 47.3, 44.5, 29.5, 25.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{17}ClN_3O$: 278.1060, found: 278.1041.



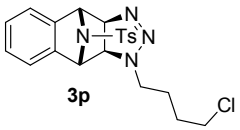
3n

1-(2-Methoxyethyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3n). Following the general procedure **(A)**, **3n** was obtained as a yellow oil (10.8 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 6.1 Hz, 1H), 7.27 (d, J = 2.8 Hz, 1H), 7.23 – 7.19 (m, 2H), 5.65 (s, 1H), 5.48 (s, 1H), 4.88 (d, J = 8.9 Hz, 1H), 3.92 (t, J = 4.7 Hz, 2H), 3.83 (d, J = 8.8 Hz, 1H), 3.76 – 3.65 (m, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.3, 127.7, 127.5, 120.4, 120.3, 86.9, 83.4, 82.9, 71.8, 64.3, 58.9, 48.3. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{13}H_{16}N_3O_2$: 246.1243, found: 246.1225.



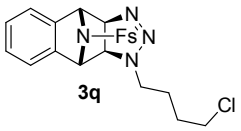
3o

5,8-Dimethoxy-1-propyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3o). Following the general procedure **(A)**, **3o** was obtained as a yellow oil (25.5 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 – 6.66 (m, 2H), 5.81 (s, 1H), 5.54 (s, 1H), 4.89 (d, J = 8.8 Hz, 1H), 3.83 (t, J = 2.8 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.77 (d, J = 2.8 Hz, 1H), 3.73 (d, J = 8.9 Hz, 1H), 1.78 – 1.70 (m, 2H), 1.44 (dd, J = 15.0, 7.5 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 131.5, 131.2, 111.2, 110.6, 85.0, 80.6, 79.4, 61.9, 55.1, 54.9, 46.8, 29.6, 19.0, 12.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{16}H_{22}N_3O_3$: 304.1661, found: 304.1648.



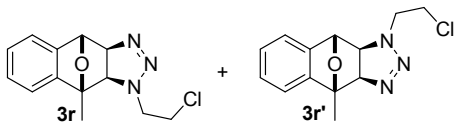
3p

1-(4-Chlorobutyl)-10-tosyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3p). Following the general procedure **(A)**, **3p** was obtained as a white solid (56.8 mg, 66%). m.p. 135.0-136.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 6.3 Hz, 1H), 7.02 (d, J = 3.2 Hz, 1H), 7.01 – 6.97 (m, 4H), 5.34 (s, 1H), 5.14 (s, 1H), 4.78 (d, J = 9.0 Hz, 1H), 3.77 (dd, J = 13.6, 6.7 Hz, 1H), 3.64 (dt, J = 12.8, 7.5 Hz, 4H), 2.27 (s, 3H), 1.96 – 1.89 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 141.7, 141.4, 135.2, 129.1, 127.9, 127.8, 127.5, 121.4, 87.0, 67.7, 66.6, 63.6, 47.1, 44.6, 29.5, 25.7, 21.4. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{21}H_{24}ClN_4O_2S$: 431.1308, found: 431.1300.

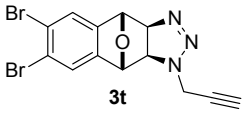


3q

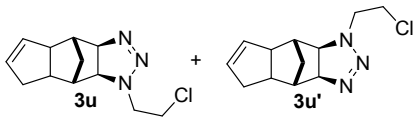
10-((4-Fluorophenyl)sulfonyl)-1-(4-chlorobutyl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (3q). Following the general procedure **(A)**, **3q** was obtained as a white solid (58.2 mg, 67%). m.p. 145.0-146.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.9, 5.7 Hz, 2H), 7.08 (d, J = 6.5 Hz, 1H), 7.05 – 6.97 (m, 3H), 6.86 (t, J = 8.5 Hz, 2H), 5.37 (s, 1H), 5.16 (s, 1H), 4.81 (d, J = 9.0 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.71 (t, J = 6.8 Hz, 1H), 3.68 (d, J = 8.9 Hz, 1H), 3.64 (t, J = 5.5 Hz, 2H), 1.98 – 1.88 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8 (d, J_{CF} = 253.8 Hz), 141.2 (d, J_{CF} = 51.8 Hz), 134.1 (d, J_{CF} = 3.0 Hz), 130.5 (d, J_{CF} = 9.4 Hz), 128.1, 127.8, 121.5, 115.8, 115.6, 86.9, 67.7, 66.7, 63.6, 47.1, 44.6, 29.5, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.4. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{20}H_{21}ClFN_4O_2S$: 435.1058, found: 435.1048.



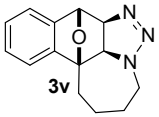
1-(2-chloroethyl)-9-methyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3r) and 1-(2-chloroethyl)-4-methyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-d][1,2,3]triazole (3r'). Following the general procedure **(A)**, **3r** and **3r′** was obtained as a yellow oil (48.4 mg, **3r** : **3r' =** 37% : 55%). ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.34 – 7.14 (m, 4H), 5.60, 5.37 (s, 1H), 5.03, 4.70 (d, *J* = 8.8 Hz, 1H), 4.33 – 3.99 (m, 2H), 3.90 – 3.80 (m, 2H), 3.77 (d, *J* = 4.7 Hz, 1H), 1.95, 1.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.8, 146.0, 144.3, 143.3, 127.9, 127.8, 127.6, 127.5, 120.4, 120.2, 119.5, 119.3, 90.8, 90.4, 90.2, 88.7, 81.8, 81.6, 66.4, 65.7, 51.6, 49.9, 42.8, 42.1, 13.8. HRMS *m/z* (EI) [M – N$_2$]$^+$ calcd for $C_{13}H_{15}ClNO$: 236.0837, found: 236.0839.



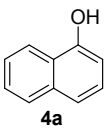
6,7-dibromo-1-(prop-2-yn-1-yl)-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (3t). Following the general procedure **(A)**, **3t** was obtained as a white solid (54.8 mg, 72%). m.p. 97.0-97.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (s, 1H), 7.57 (s, 1H), 5.63 (s, 1H), 5.46 (s, 1H), 4.95 (d, *J* = 8.7 Hz, 1H), 4.67 (dd, *J* = 17.9, 2.3 Hz, 1H), 4.44 (dd, *J* = 17.8, 2.3 Hz, 1H), 3.84 (d, *J* = 8.6 Hz, 1H), 2.36 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.4, 144.0, 126.0, 125.8, 124.1, 123.8, 88.1, 82.5, 82.0, 73.8, 62.4, 38.4. HRMS *m/z* (EI) [M + H]$^+$ calcd for $C_{13}H_{10}Br_2N_3O$: 381.9191, found: 381.9190.



1-(2-chloroethyl)-1,3a,4,4a,7,7a,8,8a-octahydro-4,8-methanoindeno[5,6-*d*][1,2,3]triazole (3u) and 1-(2-chloroethyl)-1,3a,4,4a,5,7a,8,8a-octahydro-4,8-methanoindeno[5,6-*d*][1,2,3]triazole (3u′). Following the procedure for new compounds of **3u** and **3u'**, **3u** and **3u'** was obtained as a colourless oil (39.8 mg, **3r** : **3r' =** 1 : 1, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.67 – 5.35 (m, 2H), 4.30, 4.25 (d, *J* = 9.6, 1H), 3.88 – 3.51 (m, 4H), 3.21, 3.13 (d, *J* = 9.6 Hz, 1H), 3.07 (s, 1H), 2.74 – 2.29 (m, 3H), 2.27 – 2.10 (m, 2H), 1.24 (d, *J* = 10.4 Hz, 1H), 1.05 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 131.4, 131.3, 131.2, 131.0, 83.4, 80.2, 59.9, 57.1, 51.5, 51.4, 50.0, 49.8, 46.1, 45.5, 44.4, 44.0, 42.4, 42.1, 40.9, 40.6, 35.0, 34.9, 32.2, 32.0. HRMS *m/z* (EI) [M – N$_2$+H]$^+$ calcd for $C_{12}H_{17}ClN$: 210.1050, found: 210.1046.

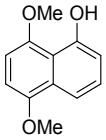


2,3,4,4a^1,6a,7-hexahydro-1*H*-12-oxa-4a,5,6-triaza-7,11b-methanonaphtho[3,2,1-*cd*]azulene (**3v**). Following the procedure for new compounds of **3v**, **3v** was obtained as a white solid (36.5 mg, 38%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.27 (m, 1H), 7.22 – 7.13 (m, 3H), 5.57 (s, 1H), 4.89 (d, *J* = 9.1 Hz, 1H), 3.71 (d, *J* = 9.1 Hz, 1H), 3.61 – 3.48 (m, 2H), 1.70 (dt, *J* = 13.0, 6.5 Hz, 4H), 0.94 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.1, 144.4, 127.7, 127.4, 120.1, 119.3, 91.5, 88.7, 82.7, 65.4, 47.4, 31.9, 22.6, 14.1. HRMS *m/z* (EI) [M + H]$^+$ calcd for $C_{14}H_{16}N_3O$: 241.1293, found: 242.1289.



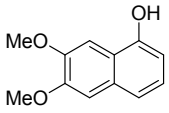
1-Naphthol (4a). Following the general procedure **(B)**, **4a** was obtained as a white solid (14.3 mg, 99%). m.p. 94.0-95.0 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 – 8.17 (m, 1H), 7.88 – 7.80 (m, 1H), 7.54 – 7.49 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 7.4 Hz, 1H),

5.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 134.7, 127.6, 126.4, 125.8, 125.2, 124.3, 121.5, 120.7, 108.6. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{10}H_7O$: 143.05, found: 143.10.



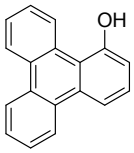
4b

5,8-Dimethoxy-1-naphthol (4b). Following the general procedure **(B)**, **4b** was obtained as a white solid (19.2 mg, 94%). m.p. 155.0-156.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.66 (q, *J* = 8.4 Hz, 2H), 4.01 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.2, 150.0, 128.3, 127.3, 115.6, 112.9, 111.3, 103.2, 102.9, 56.3, 55.7. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{12}H_{11}O_3$: 203.07, found: 202.88.



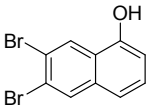
4c

6,7-Dimethoxy-1-naphthol (4c). Following the general procedure **(B)**, **4c** was obtained as a white solid (19.4 mg, 95%). m.p. 168.0-169.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 5.94 (s, 1H), 3.99 (d, *J* = 3.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.7, 148.8, 130.7, 124.2, 119.5, 119.0, 107.3, 106.2, 100.7, 55.8, 55.7. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{12}H_{11}O_3$: 203.07, found: 202.82.



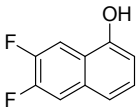
4d

Triphenylen-1-ol (4d). Following the general procedure **(B)**, **4d** was obtained as a white solid (17.8 mg, 73%). m.p. 178.0-180.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 – 9.59 (m, 1H), 8.72 – 8.56 (m, 3H), 8.30 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.58 (m, 4H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 5.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 132.8, 130.3, 130.1, 129.7, 129.5, 128.9, 127.4, 127.1, 126.9, 126.8, 126.6, 124.0, 123.2, 122.8, 118.9, 116.2, 114.7. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{18}H_{11}O$: 243.08, found: 243.25.



4e

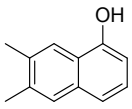
6,7-Dibromo-1-naphthol (4e). Following the general procedure **(B)**, **4e** was obtained as a white solid (20.4 mg, 68%). m.p. 143.0-144.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.09 (s, 1H), 7.36 – 7.28 (m, 2H), 6.82 (dd, *J* = 6.5, 1.6 Hz, 1H), 5.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 134.4, 131.9, 127.4, 127.0, 124.2, 122.9, 121.3, 119.4, 109.6. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{10}H_5Br_2O$: 298.87, found: 298.80.



4f

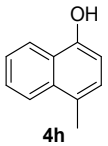
6,7-Difluoro-1-naphthol (4f). Following the general procedure **(B)**, **4f** was obtained as a white solid (15.7 mg, 87%). m.p. 133.0-134.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.08 (s, 1H), 7.36 – 7.27 (m, 2H), 6.81 (dd, *J* = 6.5, 1.6 Hz, 1H), 5.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 151.0 (dd, J_{CF} = 5.3 Hz, J_{CF} = 2.2 Hz), 150.5 (dd, J_{CF} = 247.7 Hz, J_{CF} = 14.7 Hz), 149.6 (dd, J_{CF} = 246.9 Hz, J_{CF} = 15.1 Hz), 131.8 (dd, J_{CF} = 7.6 Hz, J_{CF} = 1.3 Hz), 126.4 (d, J_{CF} = 2.3 Hz), 121.1 (d, J_{CF} = 7.6 Hz), 119.9 (dd, J_{CF} = 4.8 Hz, J_{CF} = 1.6 Hz), 113.3 (d, J_{CF} = 16.7 Hz), 108.7 (d,

J_{CF} = 1.9 Hz), 108.6 (d, J_{CF} = 17.9 Hz) ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.8 (d, J_{CF} = 24.6 Hz), -137.4 (d, J_{CF} = 20.4 Hz). MS *m/z* (EI) [M - H]$^-$ calcd for $C_{10}H_5F_2O$: 179.03, found: 179.12.



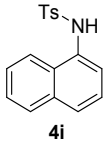
4g

6,7-Dimethyl-1-naphthol (4g). Following the general procedure **(B)**, **4g** was obtained as a white solid (16.0 mg, 93%). m.p. 128.0-129.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.58 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 136.1, 135.0, 133.7, 127.3, 124.9, 123.0, 120.9, 119.7, 107.8, 20.3, 20.1. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{12}H_{11}O$: 171.08, found: 171.11.



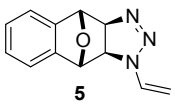
4h

4-Methyl-1-naphthol (4h). Following the general procedure **(B)**, **4h** was obtained as a white solid (15.3 mg, 97%). m.p. 85.0-86.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.49 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 5.42 (s, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 133.5, 126.6, 126.2, 126.1, 124.9, 124.5, 124.2, 122.0, 108.1, 18.8. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{11}H_9O$: 157.07, found: 157.09.



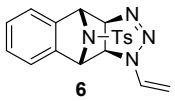
4i

4-Methyl-N-(naphthalen-1-yl)benzenesulfonamide (4i). Following the general procedure **(B)**, **4i** was obtained as a white solid (29.4 mg, 99%). m.p. 161.0-162.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J* = 12.9, 6.9 Hz, 2H), 7.40 – 7.31 (m, 2H), 7.15 (s, 2H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.3, 134.2, 131.4, 129.5, 128.8, 128.3, 127.3, 127.1, 126.6, 126.2, 125.4, 122.6, 121.5, 21.5. MS *m/z* (EI) [M - H]$^-$ calcd for $C_{17}H_{14}NO_2S$: 296.07, found: 297.07.



5

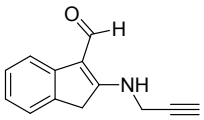
1-Vinyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epoxynaphtho[2,3-*d*][1,2,3]triazole (5). Following the typical procedure **(C)**, **5** was obtained as a white solid (42.2 mg, 99%). m.p. 81.0-82.0 °C (yield, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.8, 2.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 5.72 (s, 1H), 5.62 (s, 1H), 4.97 (d, *J* = 8.4 Hz, 1H), 4.33 (dd, *J* = 6.3, 1.4 Hz, 1H), 4.30 (s, 1H), 3.94 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 142.8, 132.2, 128.1, 127.9, 120.6, 120.4, 88.2, 87.3, 83.3, 80.7, 59.7. HRMS *m/z* (EI) [M + H]$^+$ calcd for $C_{12}H_{12}N_3O$: 214.0980, found: 214.0974.



6

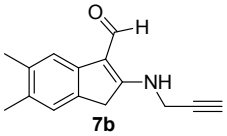
10-Tosyl-1-vinyl-3a,4,9,9a-tetrahydro-1*H*-4,9-epiminonaphtho[2,3-*d*][1,2,3]triazole (6). Following the typical procedure **(D)**, **6** was obtained as a white solid (72.5 mg, 99%). m.p. 88.0-89.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 16.0, 9.2 Hz, 1H), 7.13

(dd, *J* = 5.5, 2.3 Hz, 1H), 7.08 (dd, *J* = 5.4, 2.7 Hz, 1H), 7.06 – 7.03 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.43 (s, 1H), 5.38 (s, 1H), 4.88 (d, *J* = 8.7 Hz, 1H), 4.31 (ddd, *J* = 17.5, 12.6, 1.5 Hz, 2H), 3.86 (d, *J* = 8.7 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 141.5, 141.4, 135.3, 131.9, 129.2, 128.1, 127.9, 127.8, 121.6, 121.5, 88.8, 87.6, 67.6, 64.9, 60.3, 21.4. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{19}H_{19}N_4O_2S$: 367.1229, found: 367.1240.



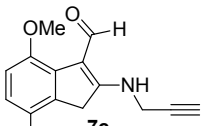
7a

2-(Prop-2-yn-1-ylamino)-1*H*-indene-3-carbaldehyde (7a). Following the general procedure **(A)**, **7a** was obtained as a white solid (19.71 mg, 50%). m.p.77.0-78.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 9.60 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.03 (td, *J* = 7.5, 0.9 Hz, 1H), 4.12 (dd, *J* = 5.9, 2.4 Hz, 2H), 3.71 (s, 2H), 2.35 (dd, *J* = 5.4, 2.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.4, 169.2, 142.3, 132.9, 127.3, 123.9, 122.4, 115.2, 111.1, 77.8, 73.0, 35.6, 34.3. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{13}H_{12}NO$: 198.0919, found: 198.0907.



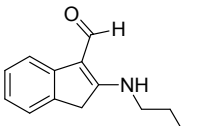
7b

5,6-dimethyl-2-(prop-2-yn-1-ylamino)-1*H*-indene-3-carbaldehyde (7b). Following the general procedure **(A)**, **7b** was obtained as a white solid (16.7 mg, 37%). m.p.77.0-78.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 9.56 (s, 1H), 7.20 (s, 1H), 7.06 (s, 1H), 4.09 (d, *J* = 3.1 Hz, 2H), 3.63 (s, 2H), 2.32 (t, *J* = 2.4 Hz, 1H), 2.27 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 169.3, 139.9, 135.35, 130.5, 125.2, 116.6, 111.0, 77.9, 72.9, 35.3, 34.3, 20.1, 19.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{15}H_{16}NO$: 226.1232, found: 226.1223.



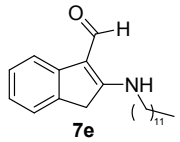
7c

4,7-dimethoxy-2-(prop-2-yn-1-ylamino)-1*H*-indene-3-carbaldehyde (7c). Following the general procedure **(A)**, **7c** was obtained as a white solid (22.6 mg, 44%). m.p.62.5-63.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 10.00 (s, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.48 (d, *J* = 8.7 Hz, 1H), 4.09 (s, 2H), 3.82 (s, 6H), 3.63 (s, 2H), 2.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 169.5, 149.7, 147.4, 130.9, 121.0, 110.7, 104.4, 77.9, 76.1, 72.9, 55.8, 55.5, 34.3, 33.6. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{15}H_{16}NO_3$: 258.1130, found: 258.1124.



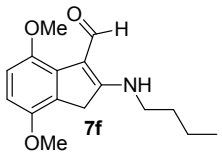
7d

2-(Butylamino)-1*H*-indene-3-carbaldehyde (7d). Following the typical procedure **(E)**, **7d** was obtained as a white solid (30.11 mg, 70%). m.p. 70.0-71.0 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 9.55 (s, 1H), 7.33 (d, *J* = 6.4 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 3.67 (s, 2H), 3.39 (t, *J* = 7.1 Hz, 2H), 1.66 (dt, *J* = 14.9, 7.3 Hz, 2H), 1.45 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 182.3, 173.5, 143.5, 134.3, 128.1, 125.0, 123.4, 115.7, 110.8, 46.2, 36.6, 32.8, 21.0, 14.1. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{14}H_{18}NO$: 216.1388, found: 216.1383.



7e

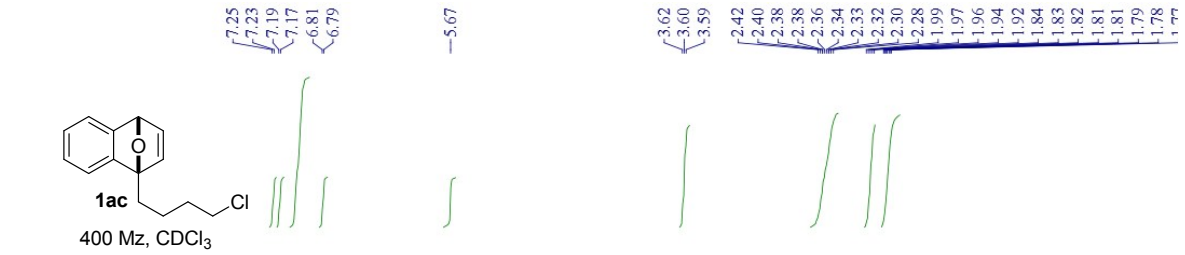
2-(Dodecylamino)-1*H*-indene-3-carbaldehyde (7e). Following the general procedure **(E)**, **7e** was obtained as a white solid (48.43 mg, 74%). m.p.76.0-77.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 9.66 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 9.5 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 3.59 (s, 2H), 3.34 (dd, *J* = 13.5, 6.9 Hz, 2H), 1.71 – 1.66 (m, 2H), 1.40 – 1.26 (m, 18H), 0.87 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.1, 170.4, 142.8, 132.4, 127.3, 123.9, 122.0, 121.1, 114.8, 45.5, 35.7, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 26.8, 22.7, 14.1. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{22}H_{34}NO$: 328.2640, found: 328.2631.



7f

2-(Butylamino)-4,7-dimethoxy-1*H*-indene-3-carbaldehyde (7f). Following the general procedure **(E)**, **7f** was obtained as a white solid (37.42 mg, 68%). m.p. 56-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 9.93 (s, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.47 (d, *J* = 8.8 Hz, 1H), 3.83 (d, *J* = 4.9 Hz, 6H), 3.55 (s, 2H), 3.36 (dd, *J* = 13.5, 6.8 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.48 – 1.41 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.1, 170.8, 149.7, 147.4, 136.2, 132.3, 120.6, 110.8, 104.1, 55.9, 55.5, 45.2, 33.6, 31.7, 20.0, 13.7. HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{16}H_{22}NO_3$: 276.1600, found: 276.1592.

3. Copies of ^{1}H and ^{13}C NMR spectra of **1ac**, **3a–v**, **4a–i** and **7a–f**, and ^{19}F NMR spectra for **3g**, **3i**, **3q** and **4f.**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7.23
7.19
7.17
6.81
6.79
5.67
3.62
3.60
3.59
2.42
2.40
2.38
2.38
2.36
2.34
2.33
2.32
2.30
2.28
1.99
1.97
1.96
1.94
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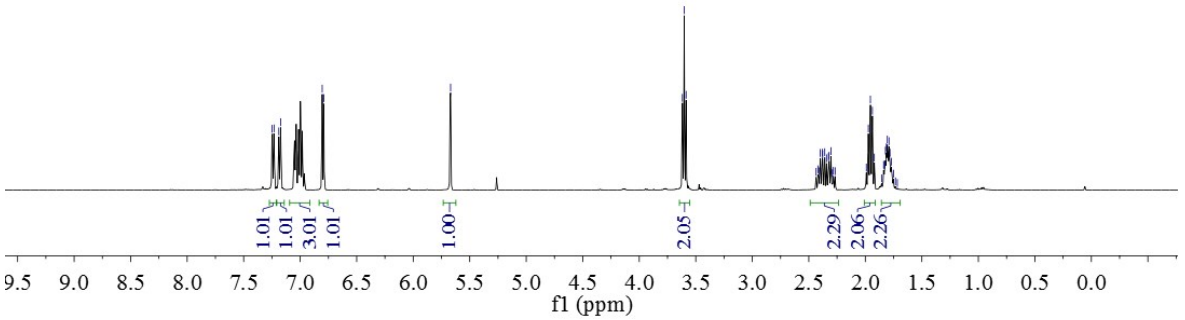
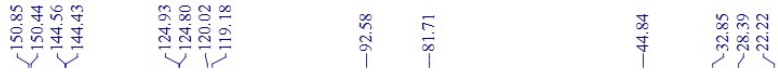
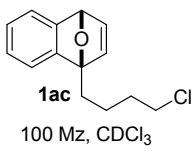
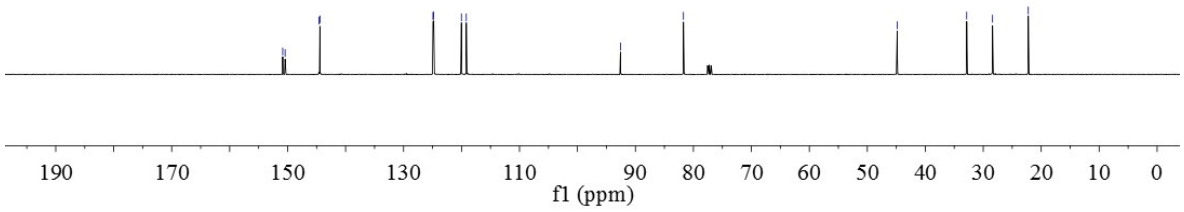
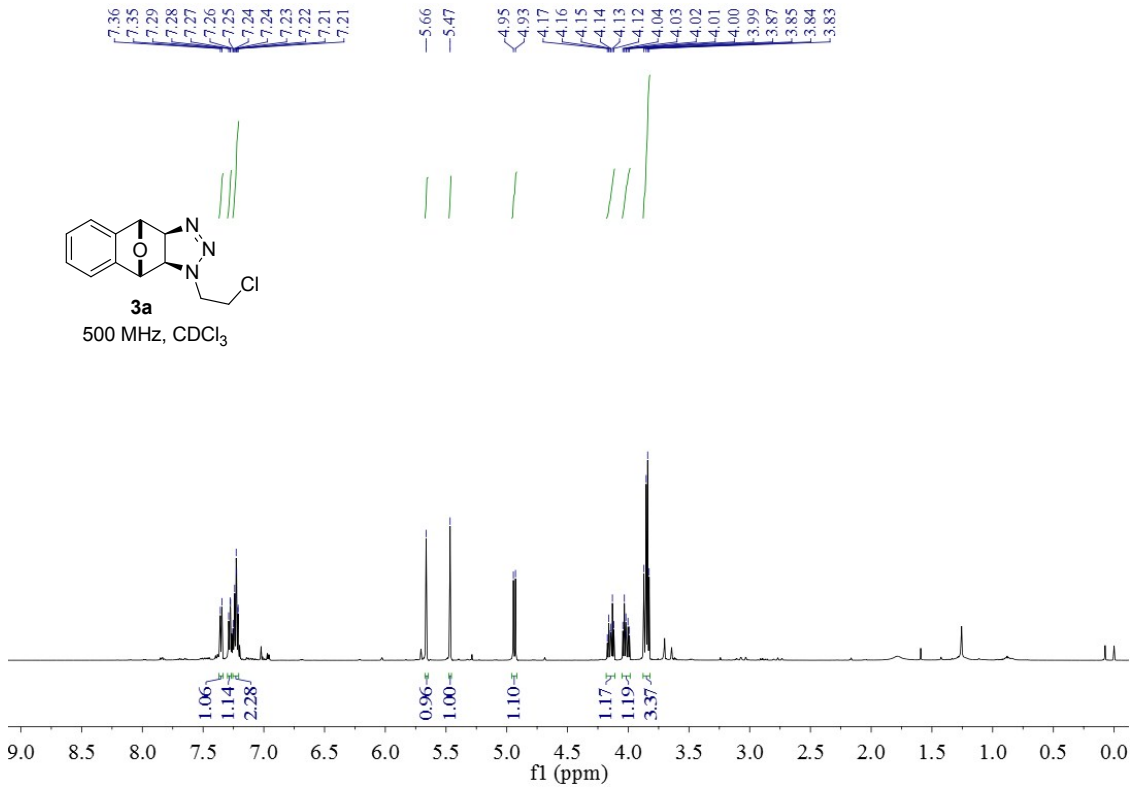
1.79
1.78
O
1ac
Cl
400 Mz, CDCl3

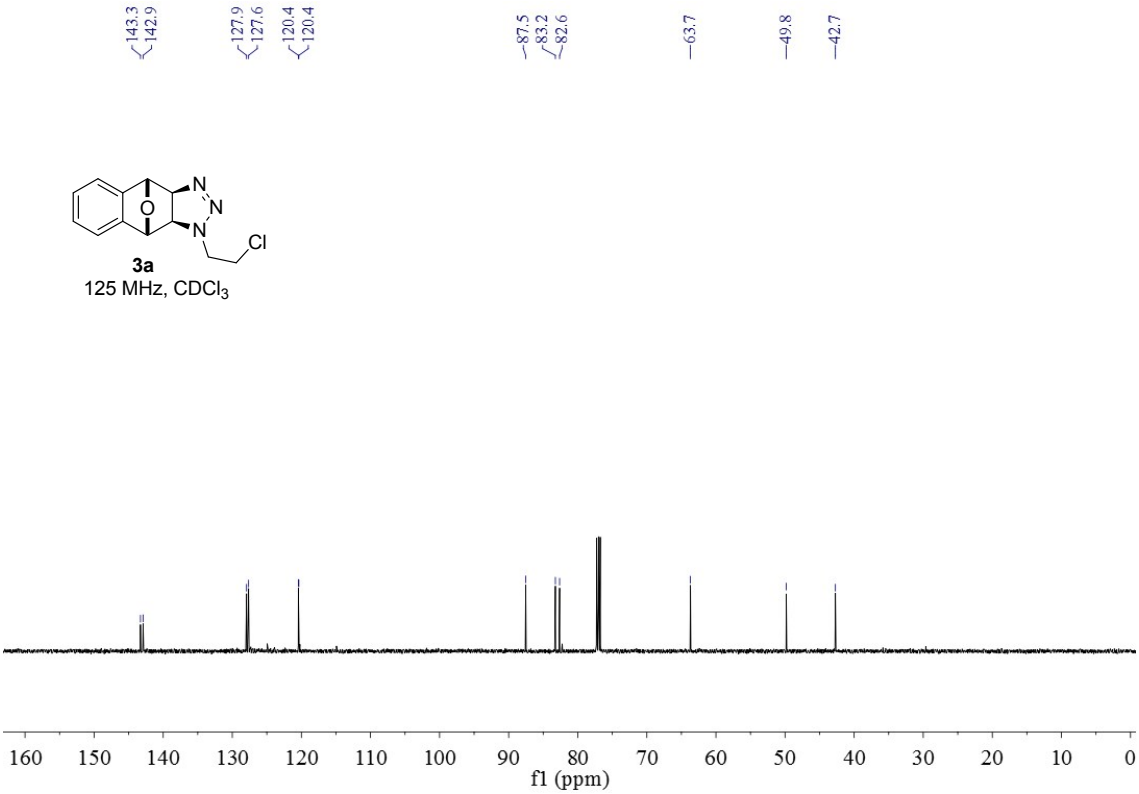

1.01
1.01
3.01
1.01
1.00
2.05
2.29
2.06
2.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

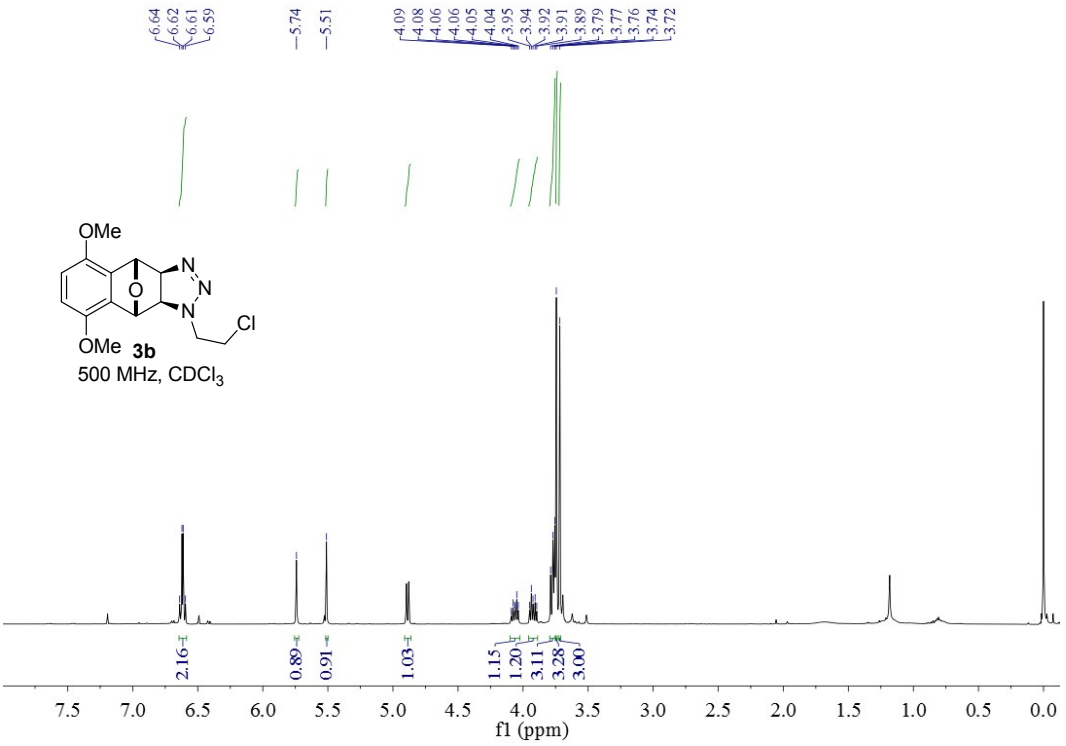

150.85
150.44
144.56
144.43
124.93
124.80
120.02
119.18
92.58
81.71
44.84
32.85
28.39
22.22


O
1ac
Cl
100 Mz, CDCl3

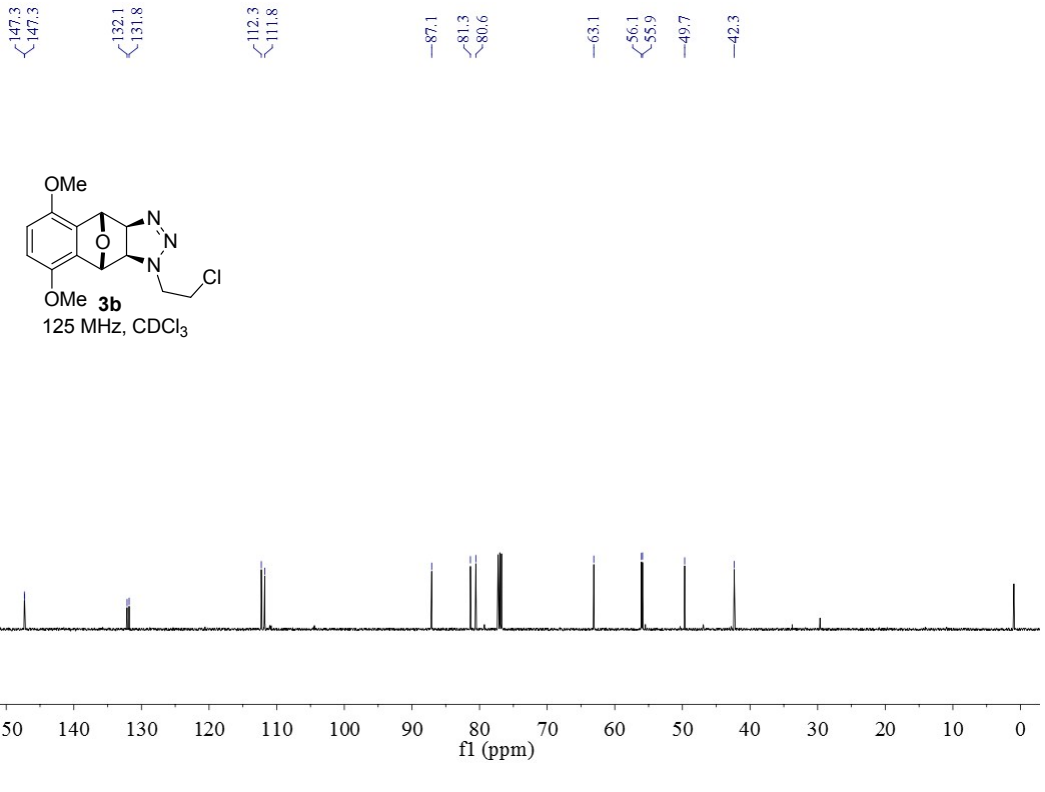

190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.36
7.35
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.21
5.66
5.47
4.95
4.93
4.17
4.16
4.15
4.14
4.13
4.12
4.04
4.03
4.02
4.01
4.00
3.99
3.87
3.85
3.84
3.83
N
N
N
O
Cl
3a
500 MHz, CDCl3
1.06
1.14
2.28
0.96
1.00
1.10
1.17
1.19
3.37
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

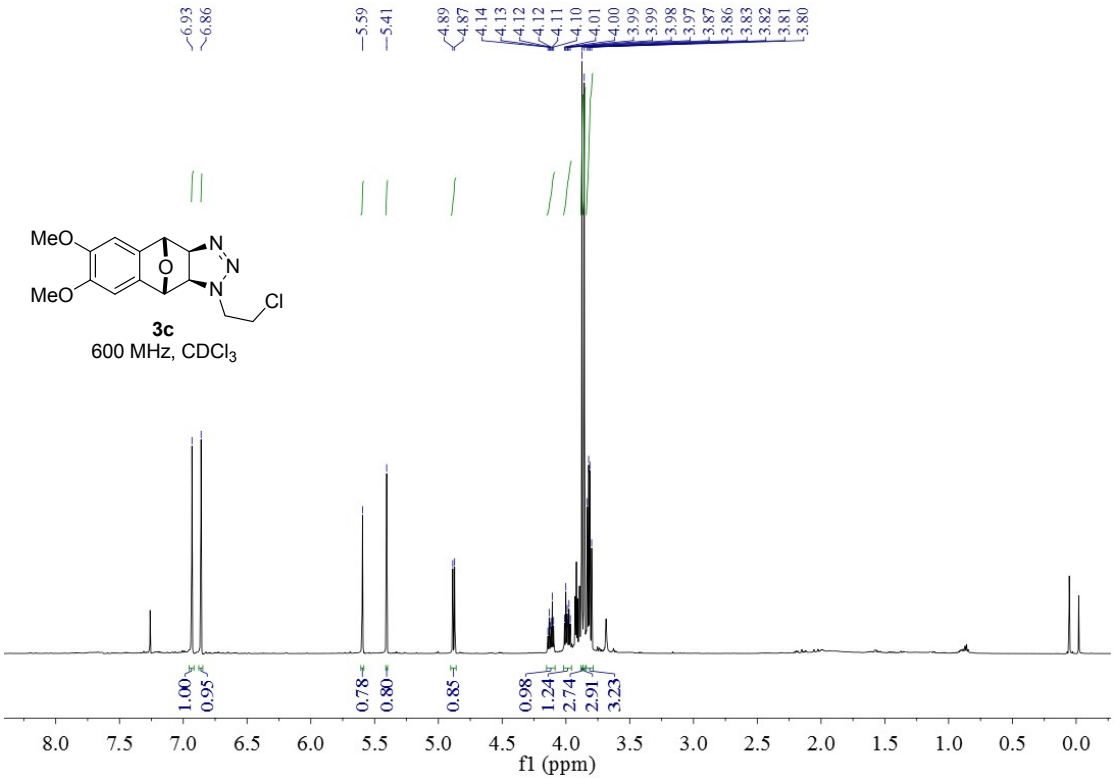

143.3
142.9
127.9
127.6
120.4
120.4
87.5
83.2
82.6
63.7
49.8
42.7
N
N
N
O
Cl
3a
125 MHz, CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



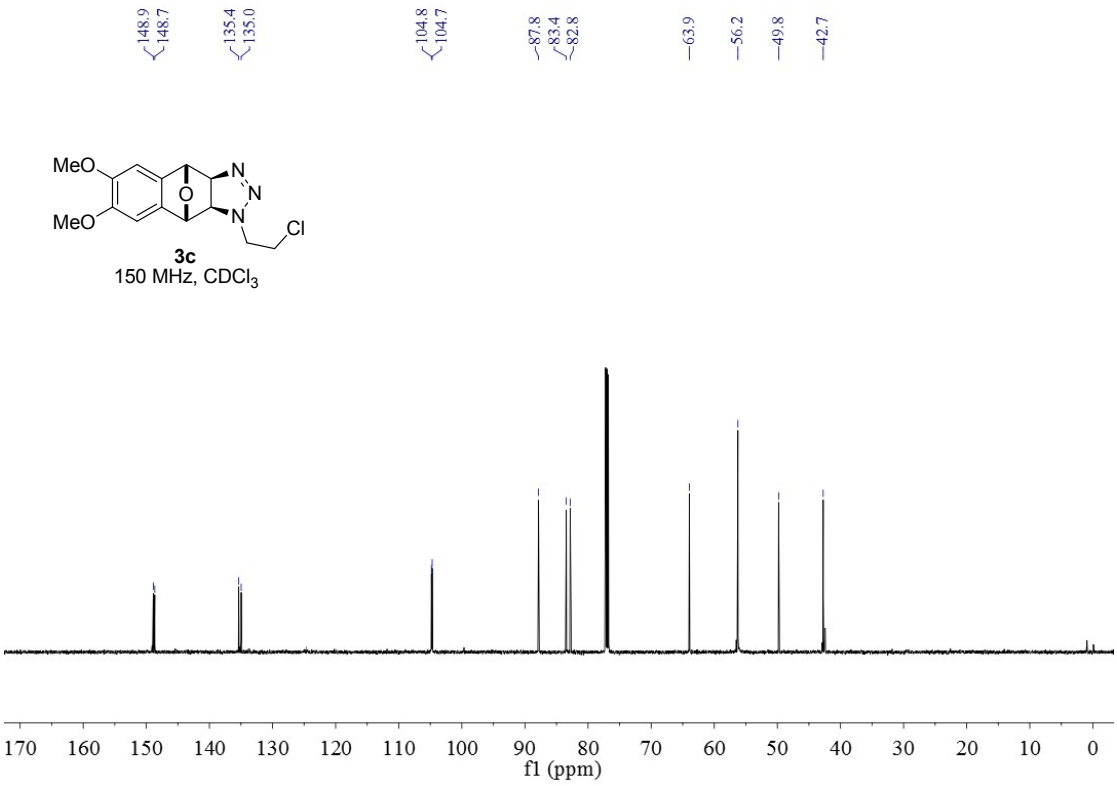
3b
500 MHz, $CDCl_3$



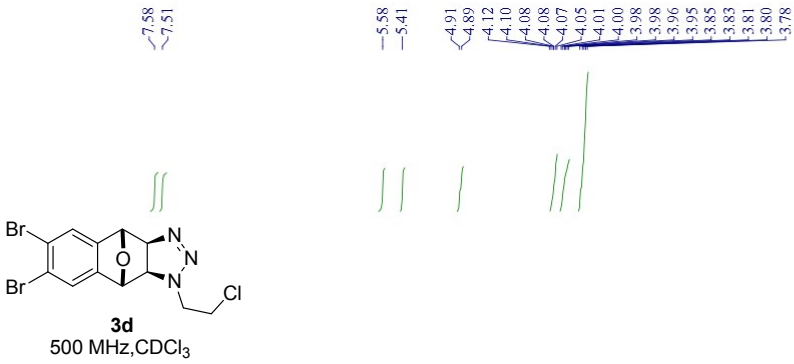
3b
125 MHz, $CDCl_3$



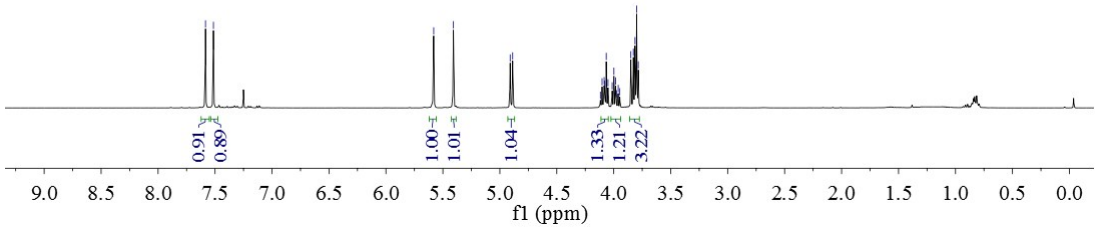
3c
600 MHz, $CDCl_3$



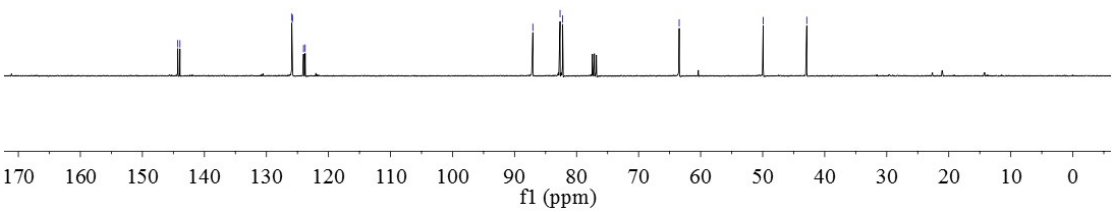
3c
150 MHz, $CDCl_3$



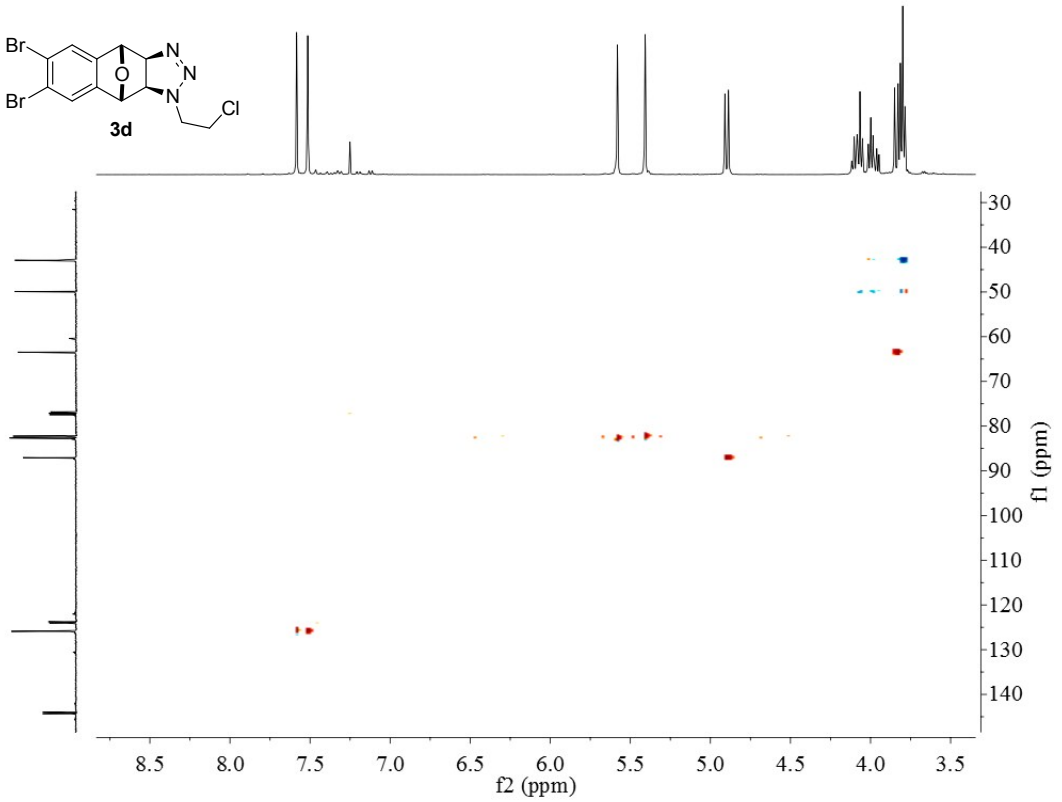
3d
500 MHz,$CDCl_3$

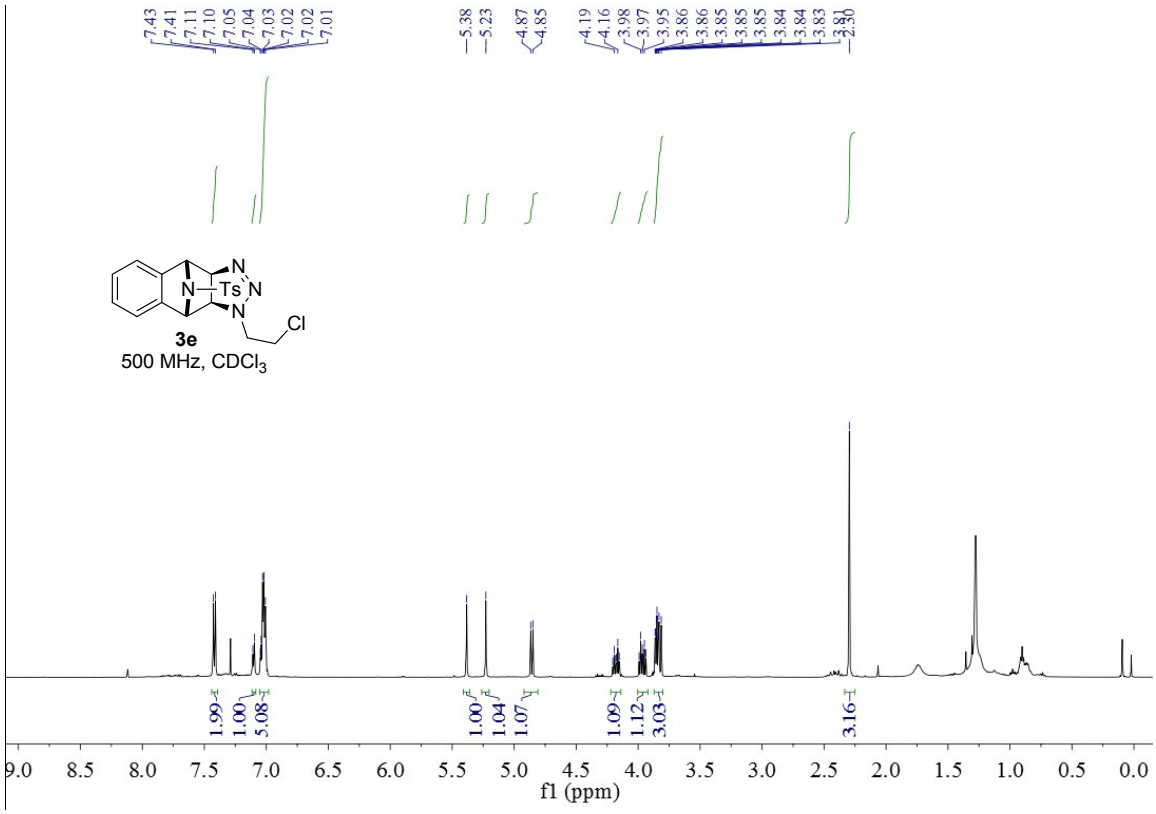


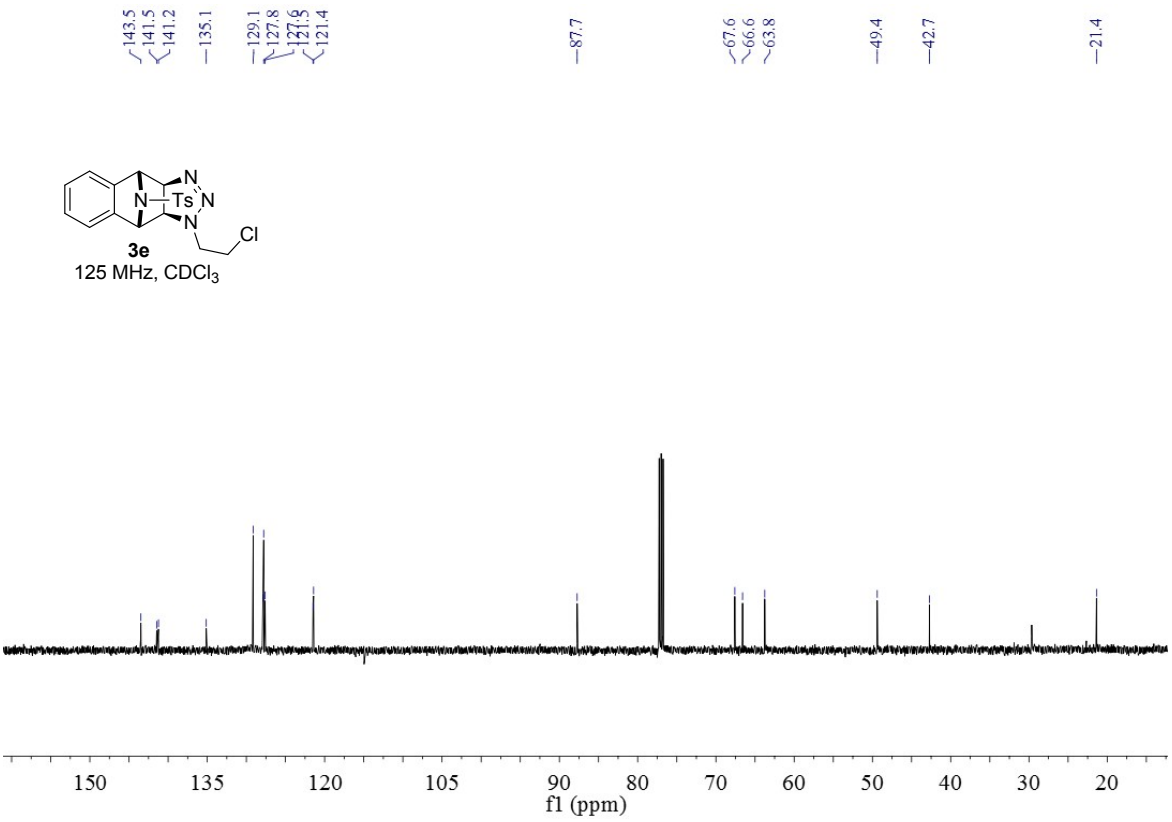
3d
125 MHz, $CDCl_3$

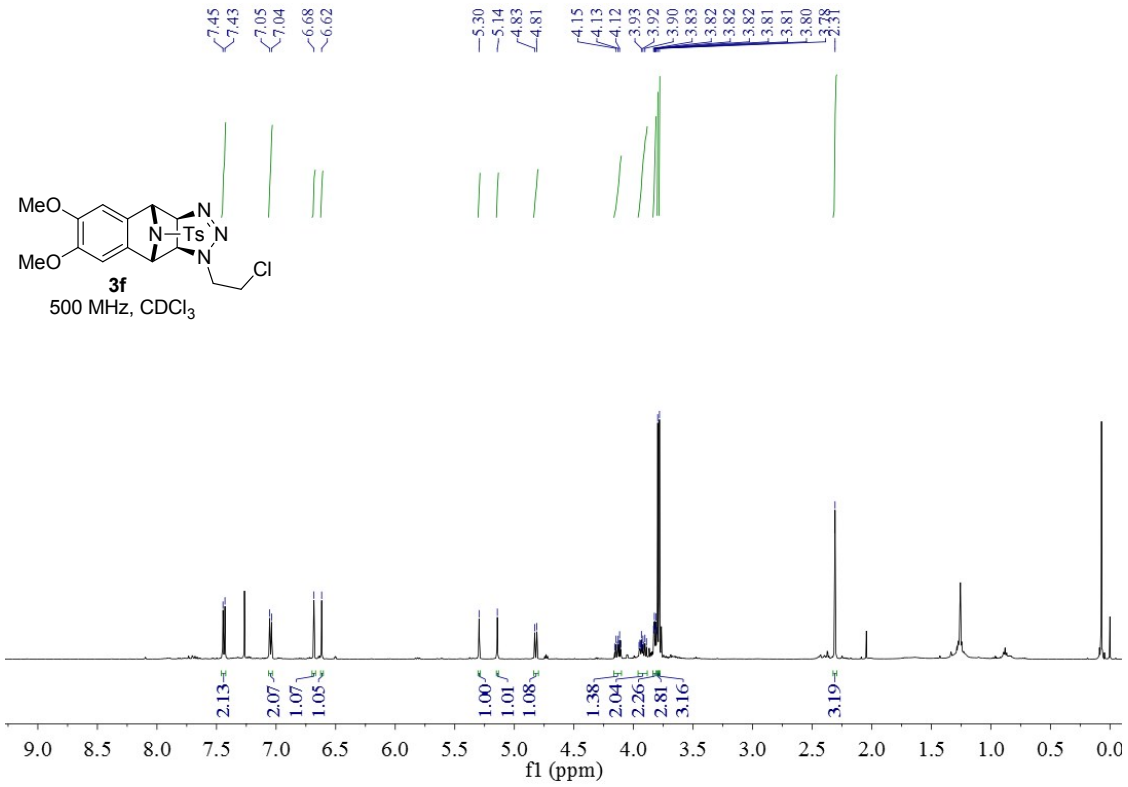


4. HSQC spectra of 3d




7.43
7.41
7.11
7.10
7.05
7.04
7.03
7.02
7.02
7.01
5.38
5.23
4.87
4.85
4.19
4.16
3.98
3.97
3.95
3.86
3.86
3.85
3.85
3.85
3.84
3.84
3.83
3.81
2.30
N
N
Ts
N
N
Cl
3e
500 MHz, CDCl3
1.99
1.00
5.08
1.00
1.04
1.07
1.09
1.12
3.03
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.5
141.5
141.2
135.1
129.1
127.8
127.6
121.5
121.4
87.7
67.6
66.6
63.8
49.4
42.7
21.4
N
N
Ts
N
N
Cl
3e
125 MHz, CDCl3
150
135
120
105
90
80
70
60
50
40
30
20
f1 (ppm)


7.45
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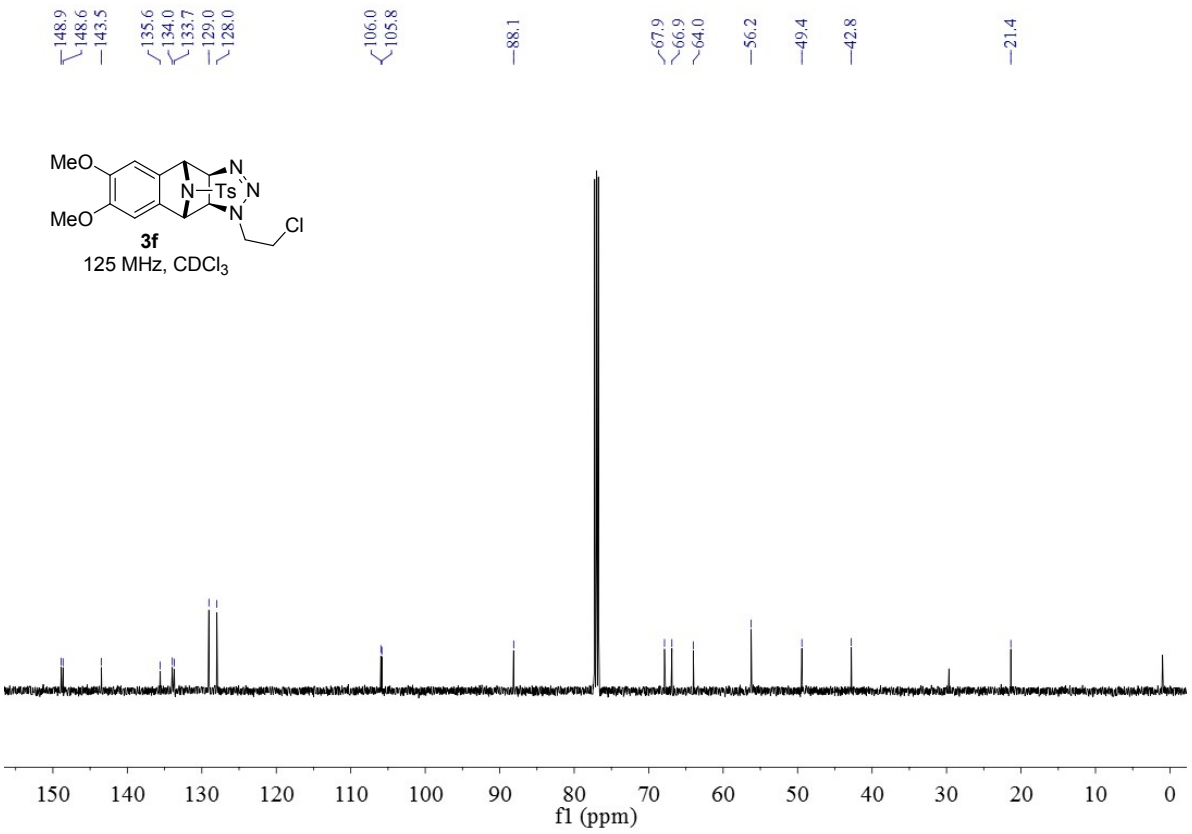
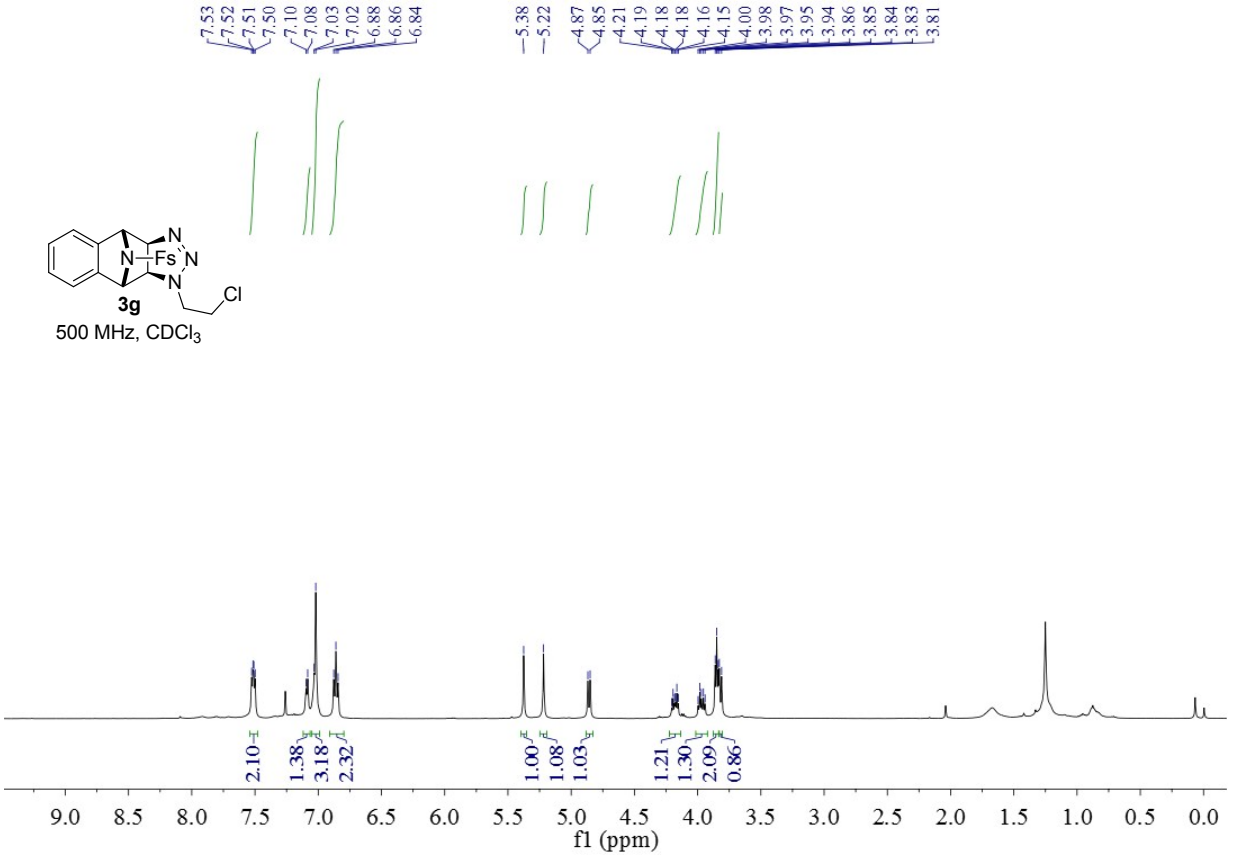
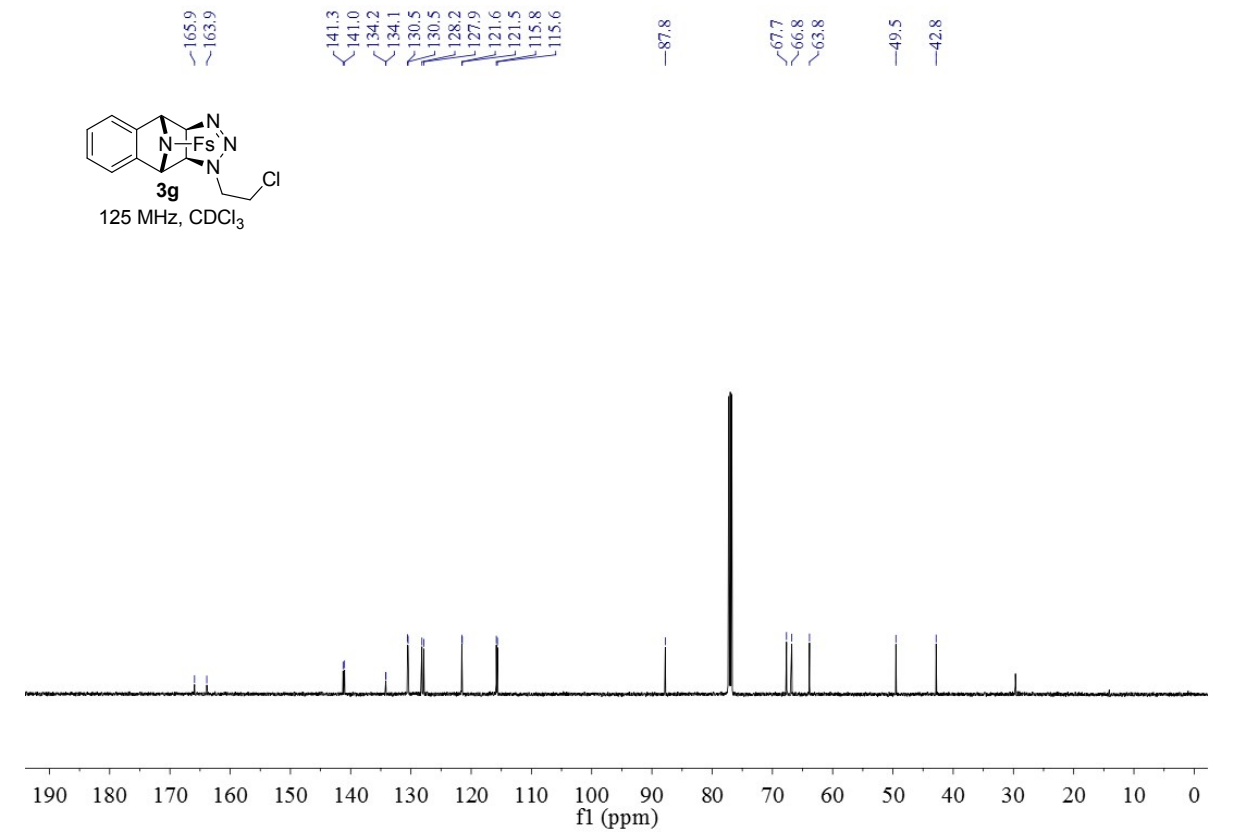
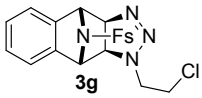
7.05
7.04
6.68
6.62
5.30
5.14
4.83
4.81
4.15
4.13
4.12
3.93
3.92
3.90
3.83
3.82
3.82
3.82
3.81
3.81
3.80
3.78
2.31
MeO
MeO
N
N
Ts
N
N
Cl
3f
500 MHz, CDCl3
2.13
2.07
1.07
1.05
1.00
1.01
1.08
1.38
2.04
2.26
2.81
3.16
3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.9
148.6
143.5
135.6
134.0
133.7
129.0
128.0
106.0
105.8
88.1
67.9
66.9
64.0
56.2
49.4
42.8
21.4
MeO
MeO
N
N
Ts
N
N
Cl
3f
125 MHz, CDCl3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.53
7.52
7.51
7.50
7.10
7.08
7.03
7.02
6.88
6.86
6.84
5.38
5.22
4.87
4.85
4.21
4.19
4.18
4.18
4.16
4.15
4.00
3.98
3.97
3.95
3.94
3.86
3.85
3.84
3.83
3.81
N
N
Fs
N
N
Cl
3g
500 MHz, CDCl3
2.10
1.38
3.18
2.32
1.00
1.08
1.03
1.21
1.30
2.09
0.86
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

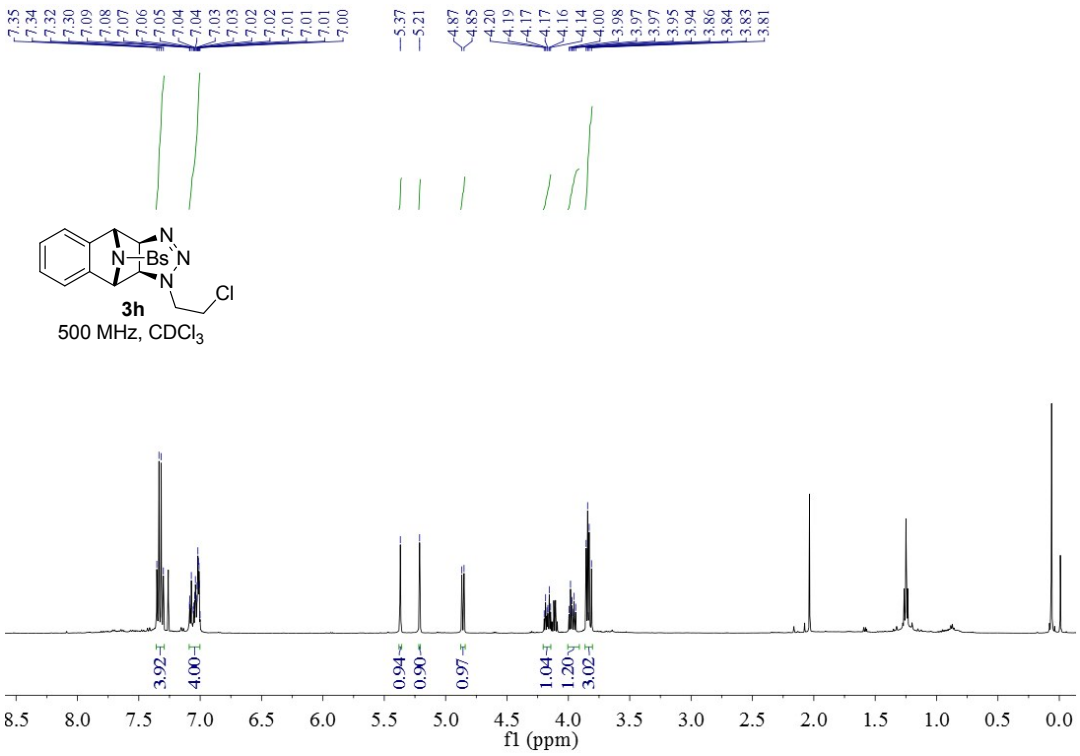

165.9
163.9
141.3
141.0
134.2
134.1
130.5
130.5
128.2
127.9
121.6
121.5
115.8
115.6
87.8
67.7
66.8
63.8
49.5
42.8
N
N
Fs
N
N
Cl
3g
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

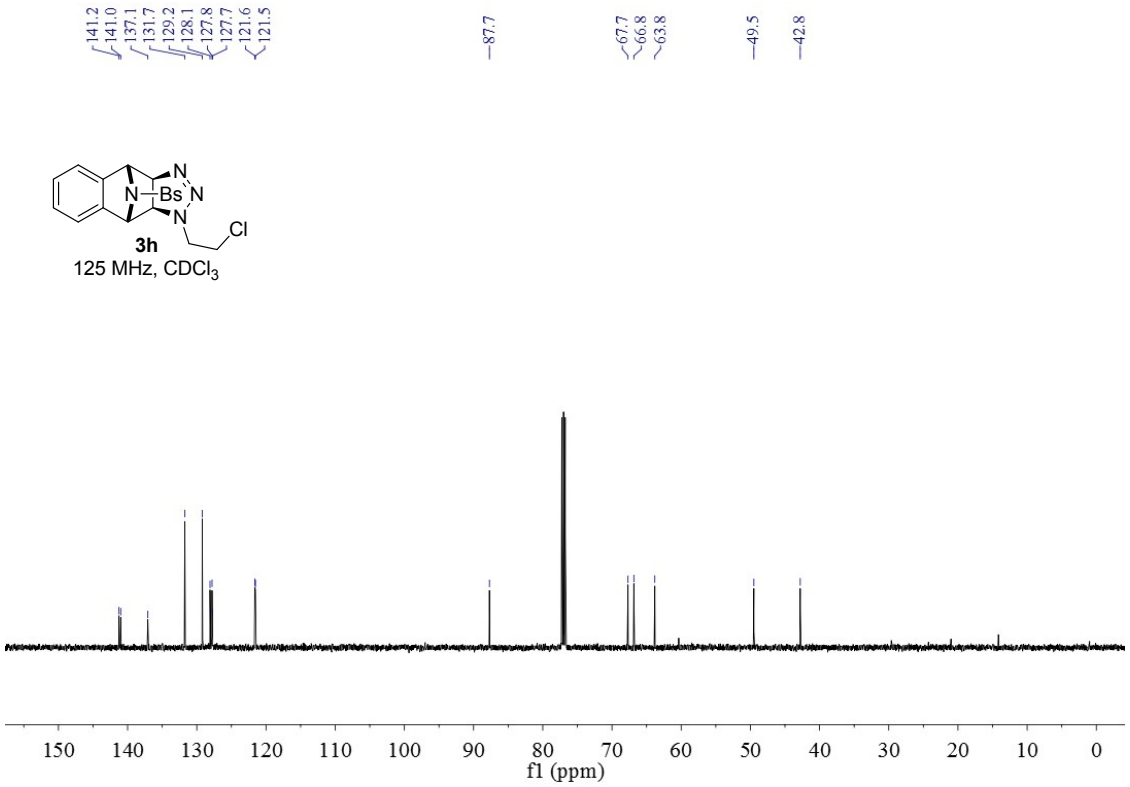


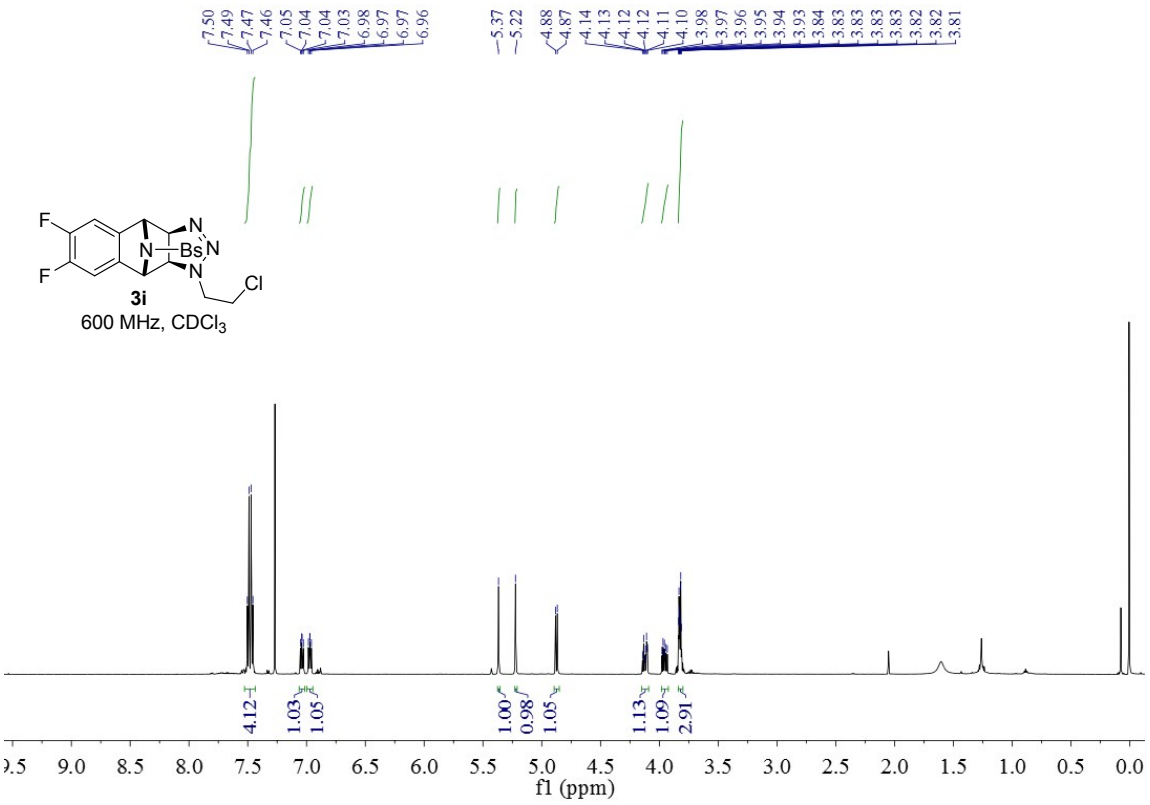
3g

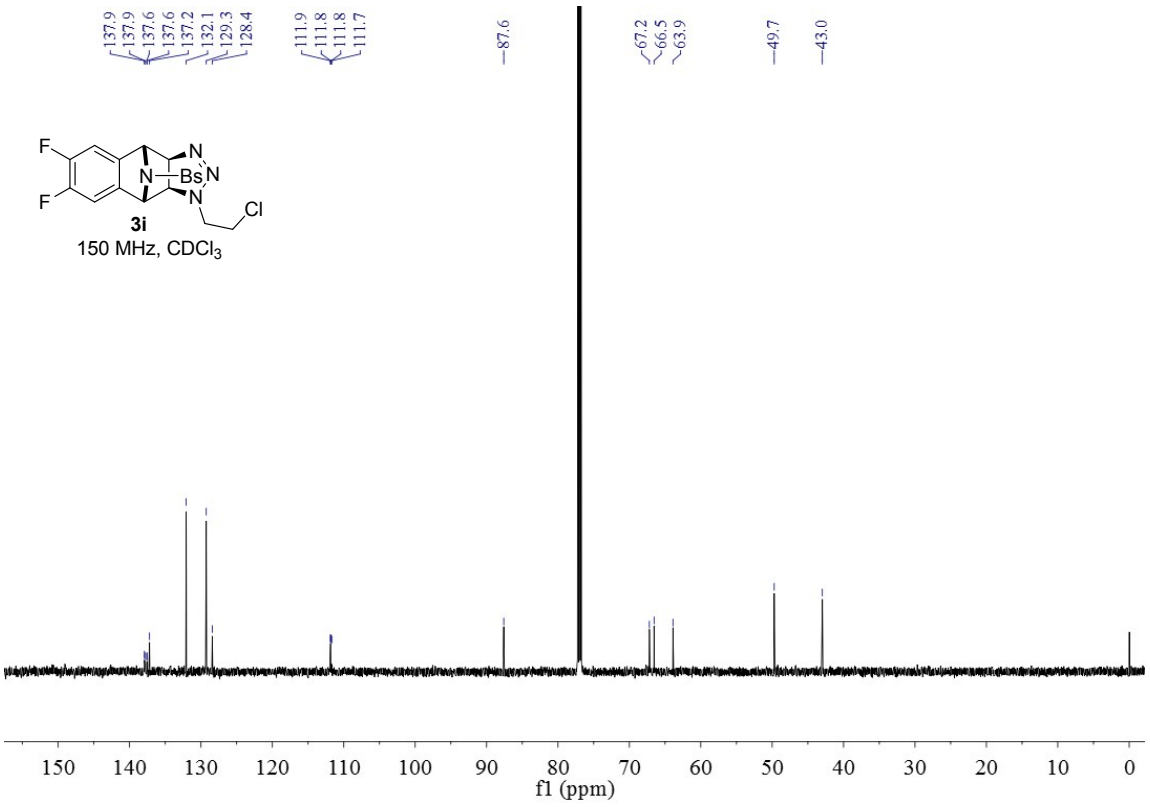
^{19}F NMR

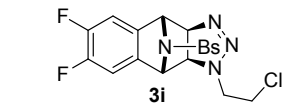
376 MHz, $CDCl_3$


7.35
7.34
7.32
7.30
7.09
7.08
7.07
7.06
7.05
7.04
7.04
7.03
7.03
7.02
7.02
7.01
7.01
7.01
7.00
5.37
5.21
4.87
4.85
4.20
4.19
4.17
4.17
4.16
4.14
4.00
3.98
3.97
3.97
3.95
3.94
3.86
3.84
3.83
3.81
N
N
Bs
N
N
Cl
3h
500 MHz, CDCl3
3.92
4.00
0.94
0.90
0.97
1.04
1.20
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.2
141.0
137.1
131.7
129.2
128.1
127.8
127.7
121.6
121.5
87.7
67.7
66.8
63.8
49.5
42.8
N
N
Bs
N
N
Cl
3h
125 MHz, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.50
7.49
7.47
7.46
7.05
7.04
7.04
7.03
6.98
6.97
6.97
6.96
5.37
5.22
4.88
4.87
4.14
4.13
4.12
4.12
4.11
4.10
3.98
3.97
3.96
3.95
3.94
3.93
3.84
3.83
3.83
3.83
3.83
3.82
3.82
3.81
F
F
N
N
Bs
N
N
Cl
3i
600 MHz, CDCl3
4.12
1.03
1.05
1.00
0.98
1.05
1.13
1.09
2.91
f1 (ppm)

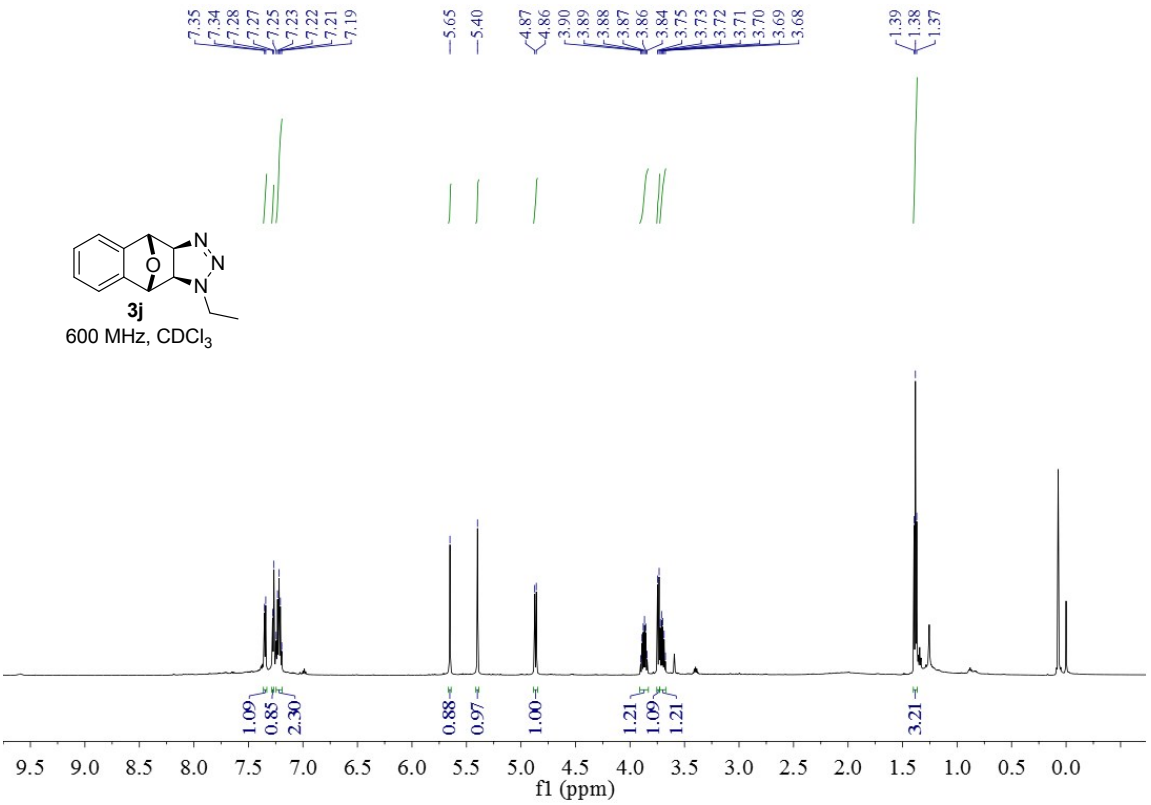

137.9
137.9
137.6
137.6
137.2
132.1
129.3
128.4
111.9
111.8
111.8
111.7
87.6
67.2
66.5
63.9
49.7
43.0
F
F
N
N
Bs
N
N
Cl
3i
150 MHz, CDCl3
f1 (ppm)



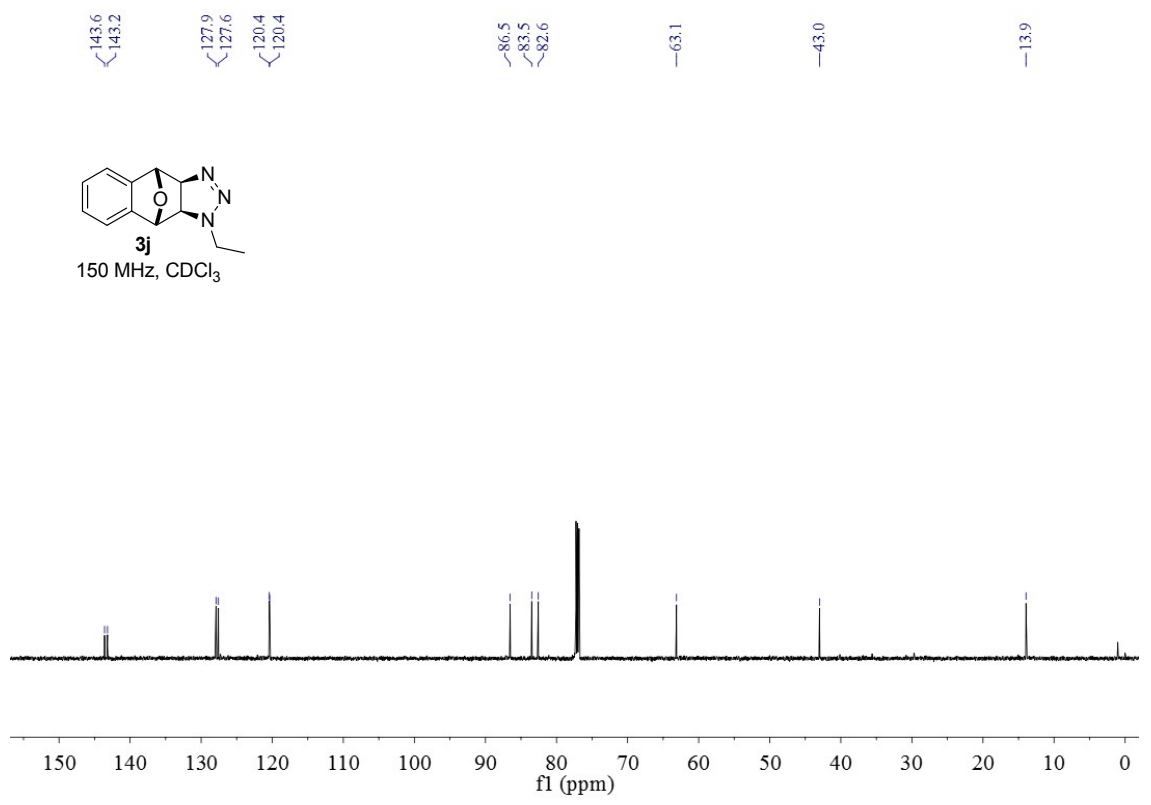
3i

^{19}F NMR

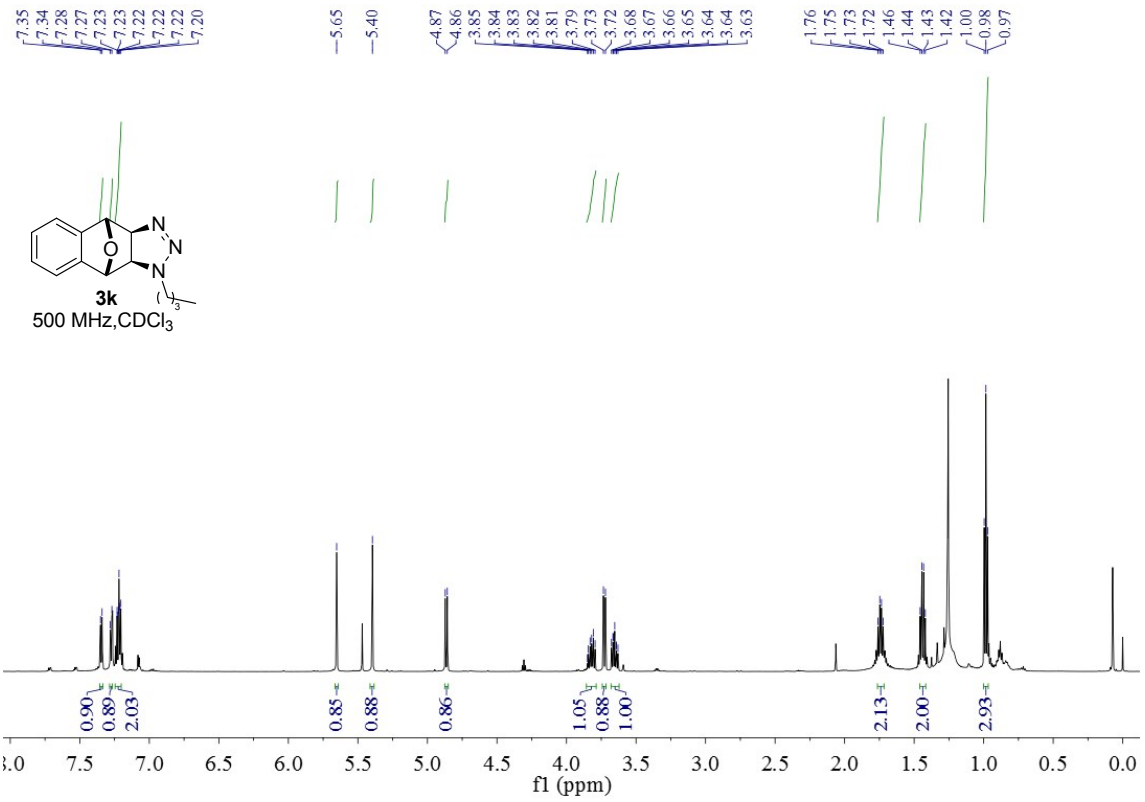
376 MHz, $CDCl_3$

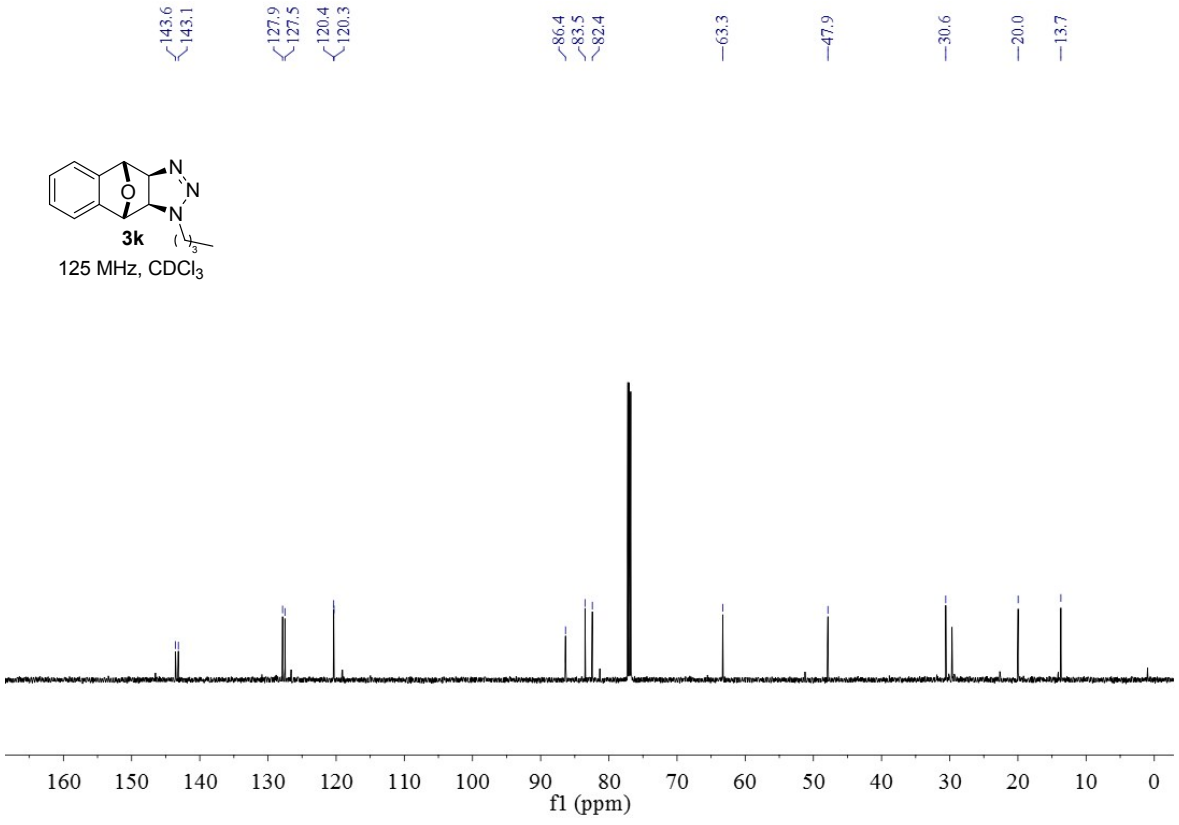


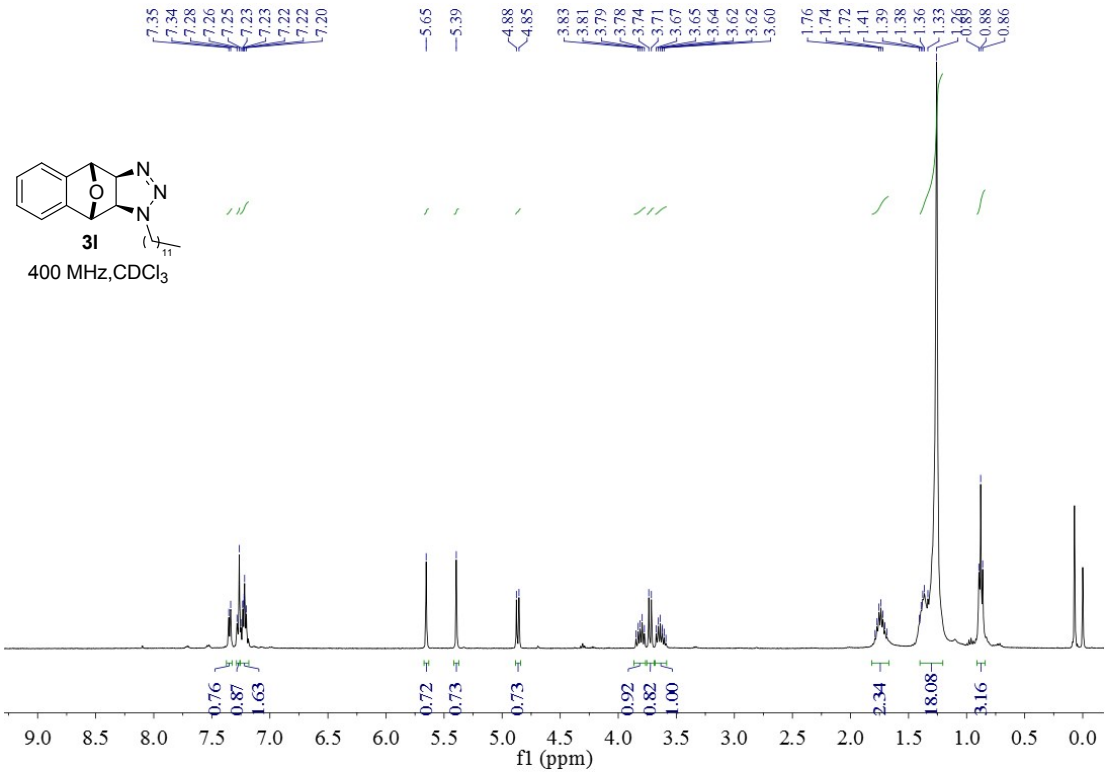
3j
600 MHz, $CDCl_3$



3j
150 MHz, $CDCl_3$

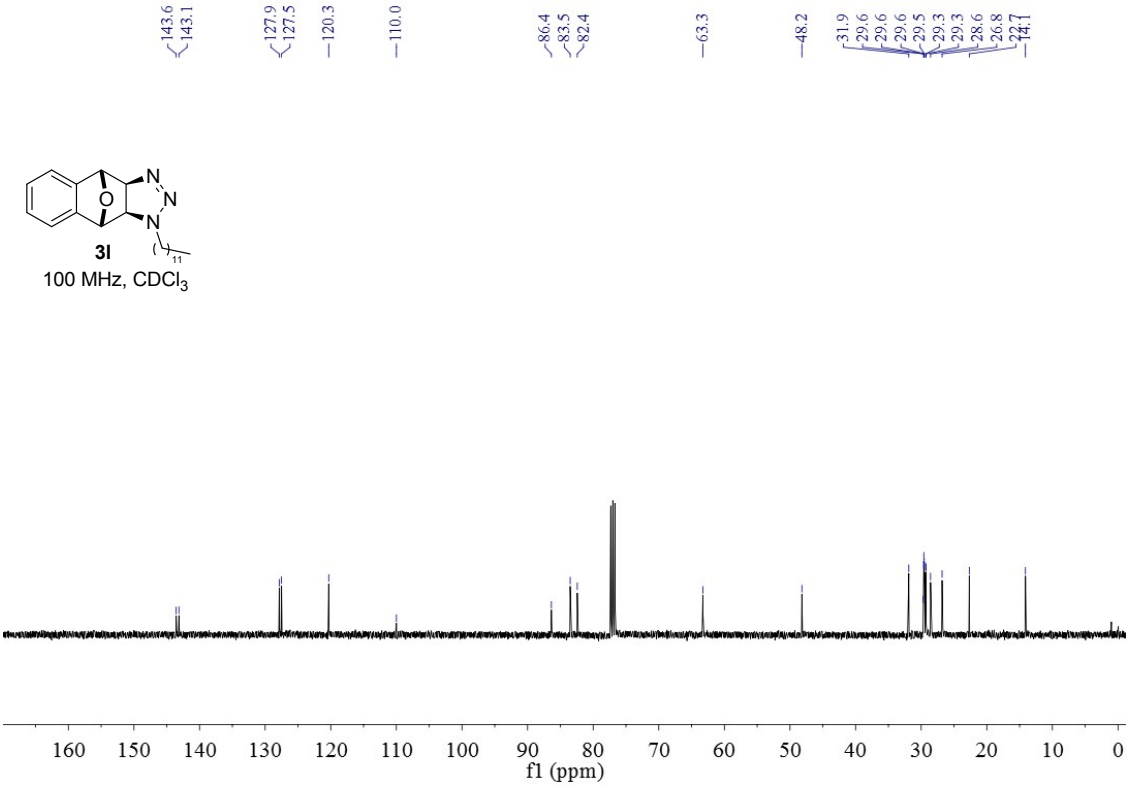

7.35
7.34
7.28
7.27
7.23
7.23
7.22
7.22
7.22
7.20
5.65
5.40
4.87
4.86
3.85
3.84
3.83
3.82
3.81
3.79
3.73
3.72
3.68
3.67
3.66
3.65
3.64
3.64
3.63
1.76
1.75
1.73
1.72
1.46
1.44
1.43
1.42
1.00
0.98
0.97
O
N
N
N
3k
500 MHz,CDCl3
0.90
0.89
2.03
0.85
0.88
0.86
1.05
0.88
1.00
2.13
2.00
2.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.6
143.1
127.9
127.5
120.4
120.3
86.4
83.5
82.4
63.3
47.9
30.6
20.0
13.7
O
N
N
N
3k
125 MHz, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



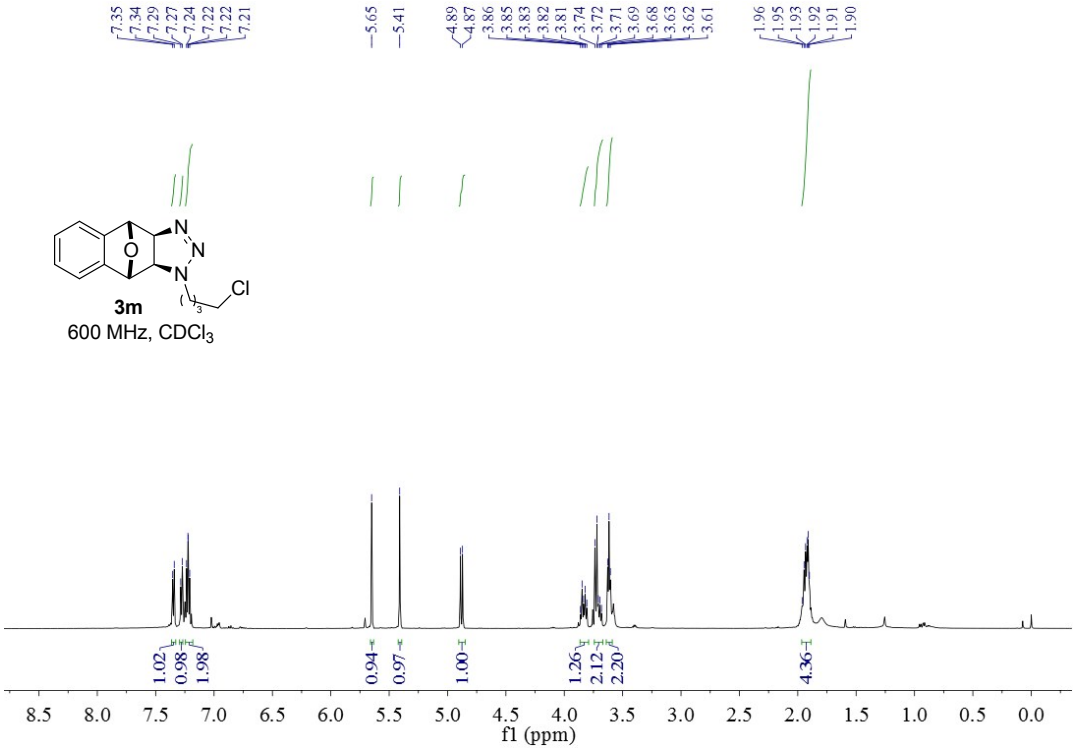
3l

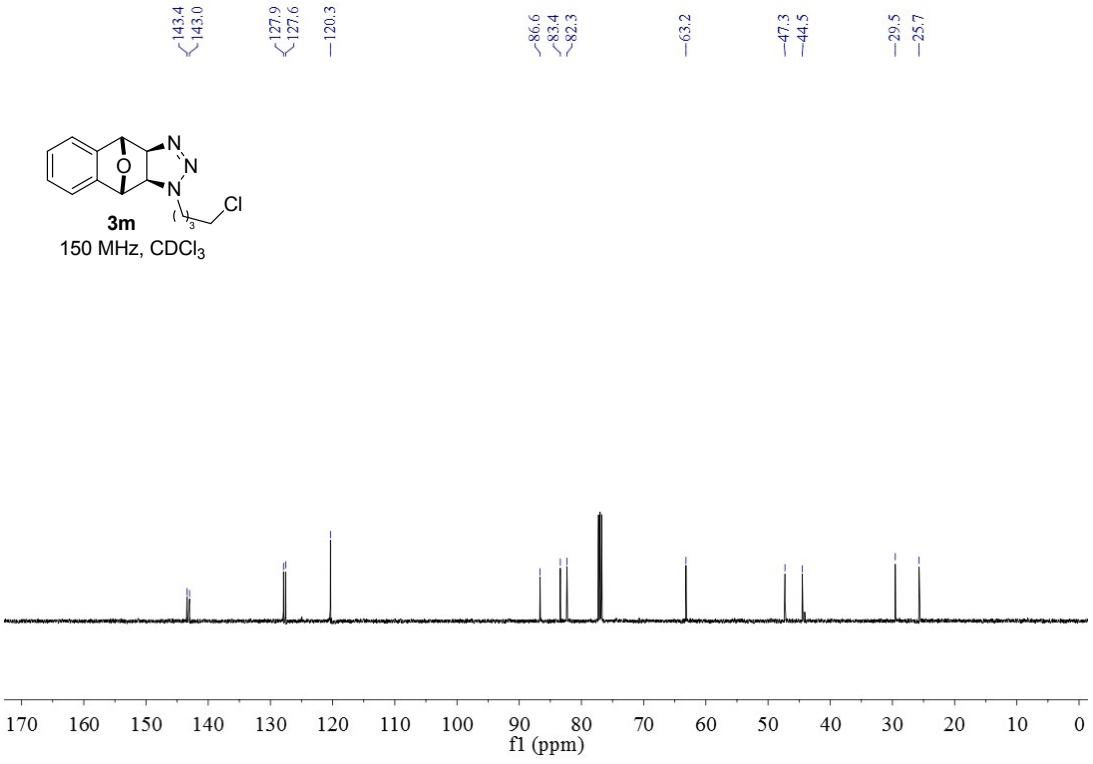
400 MHz,$CDCl_3$

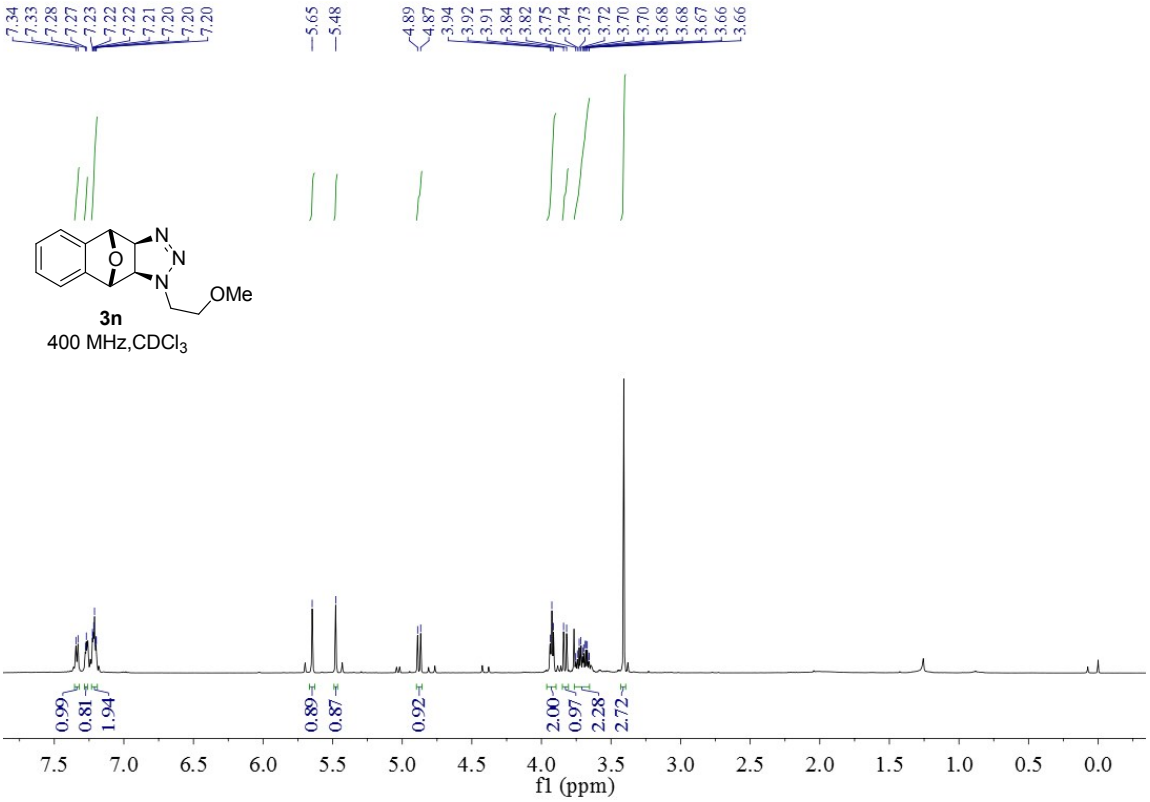


3l

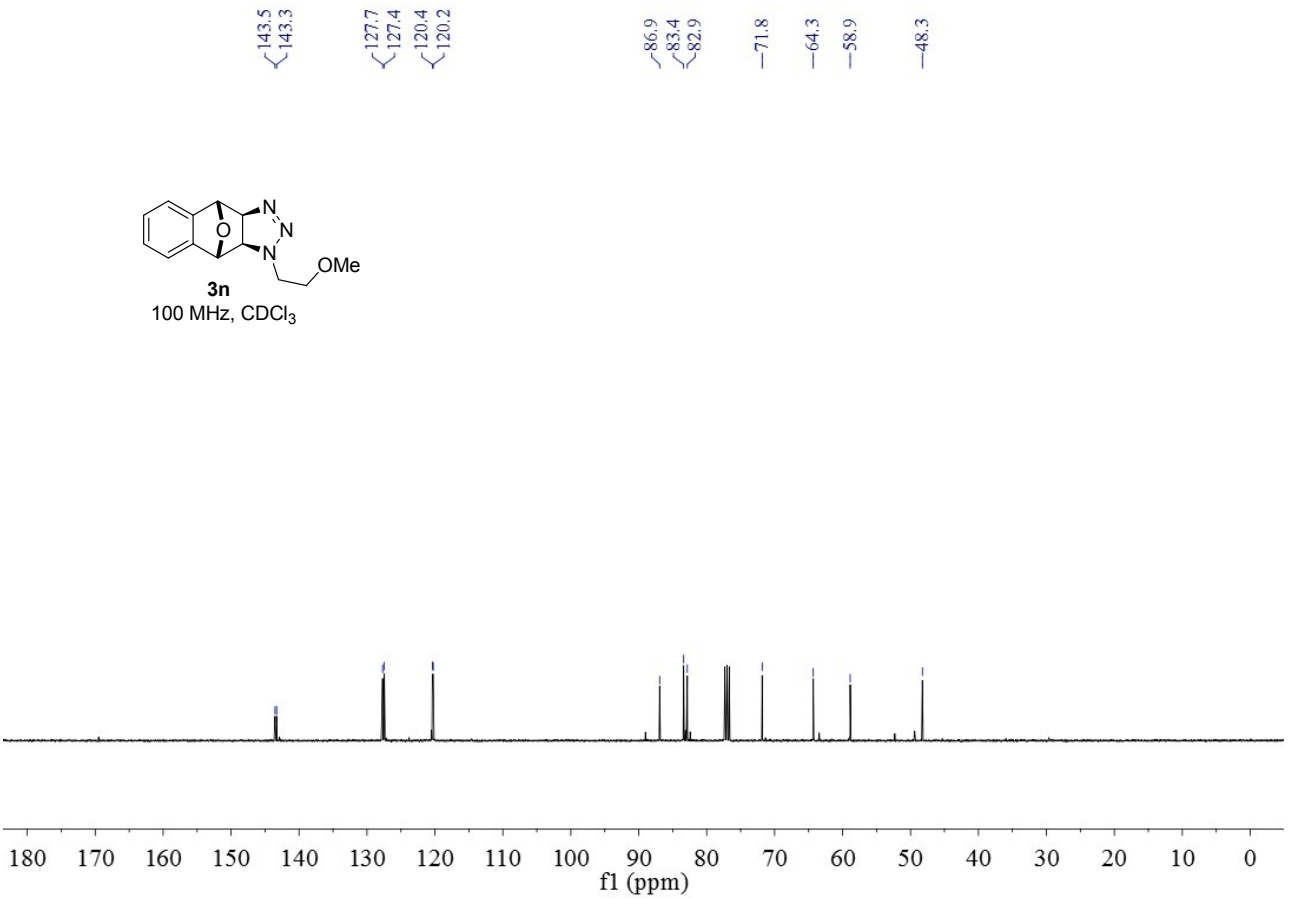
100 MHz, $CDCl_3$


7.35
7.34
7.29
7.27
7.24
7.22
7.22
7.21
5.65
5.41
4.89
4.87
3.86
3.85
3.83
3.82
3.81
3.74
3.72
3.71
3.69
3.68
3.63
3.62
3.61
1.96
1.95
1.93
1.92
1.91
1.90
N
N
O
N
Cl
3
3m
600 MHz, CDCl3
1.02
0.98
1.98
0.94
0.97
1.00
1.26
2.12
2.20
4.36
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

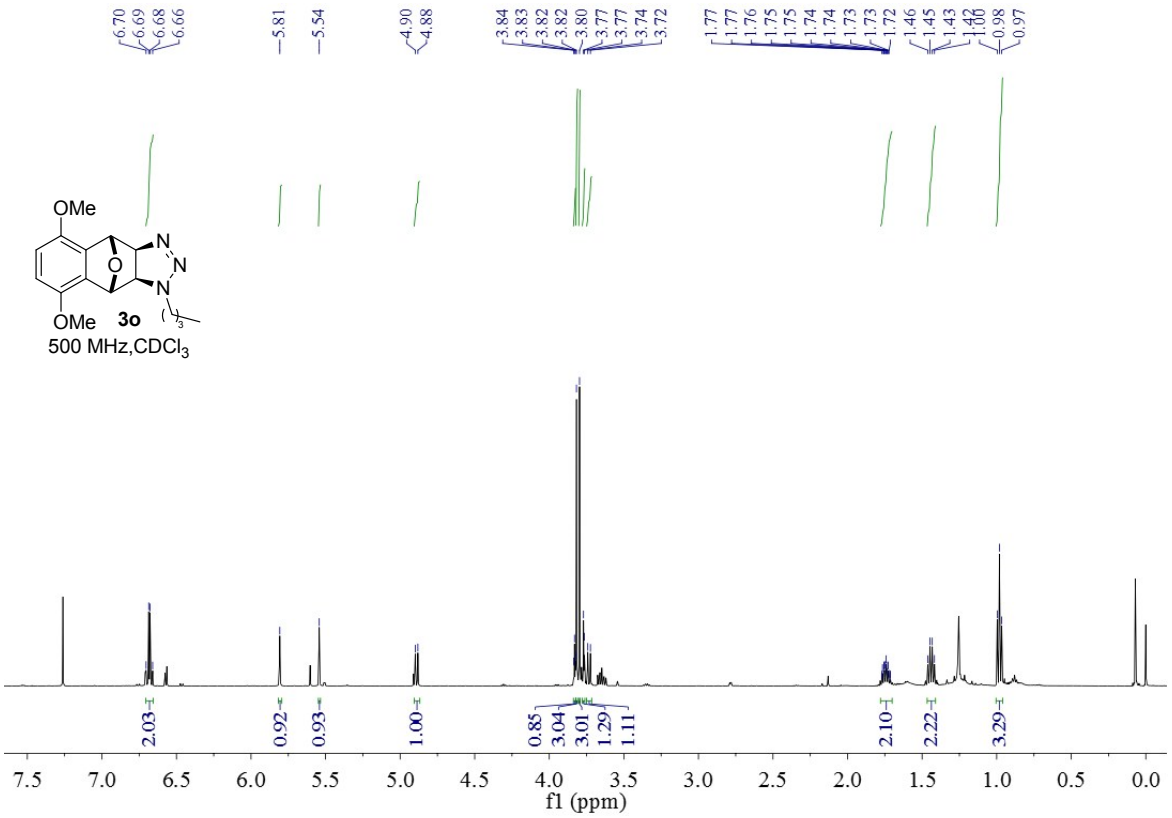

143.4
143.0
127.9
127.6
120.3
86.6
83.4
82.3
63.2
47.3
44.5
29.5
25.7
N
N
O
N
Cl
3
3m
150 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

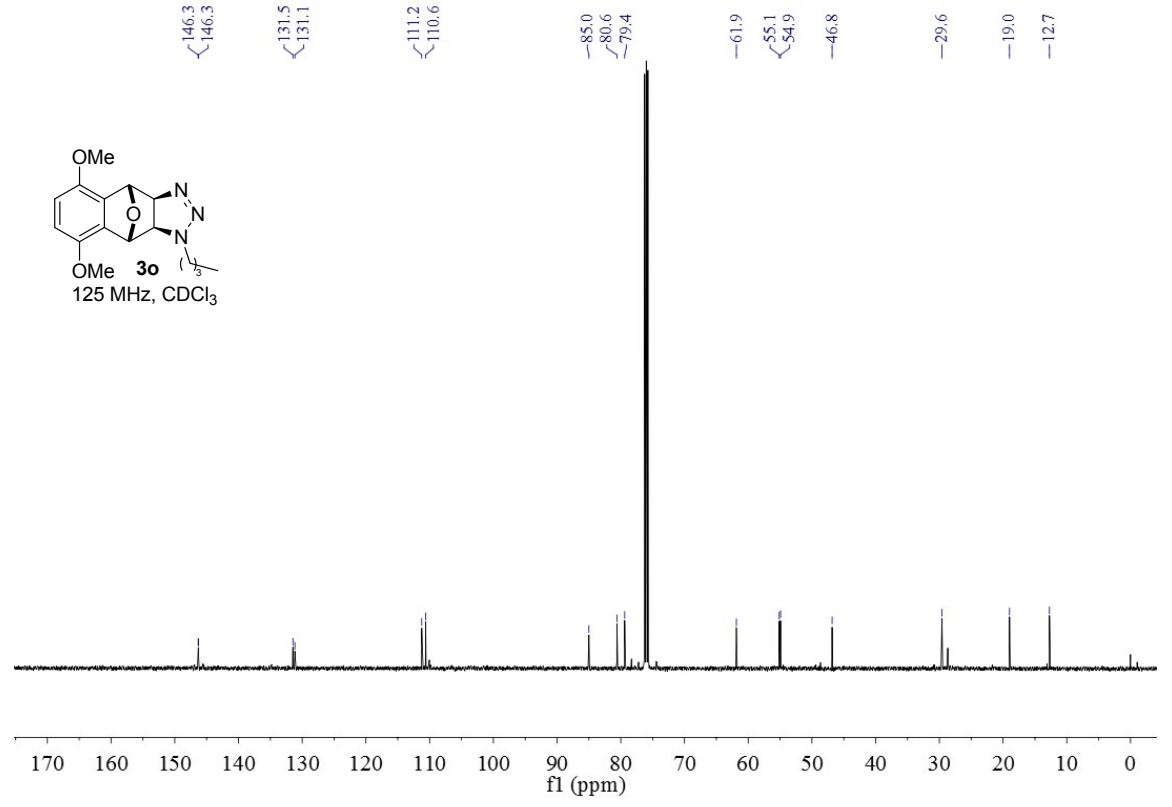


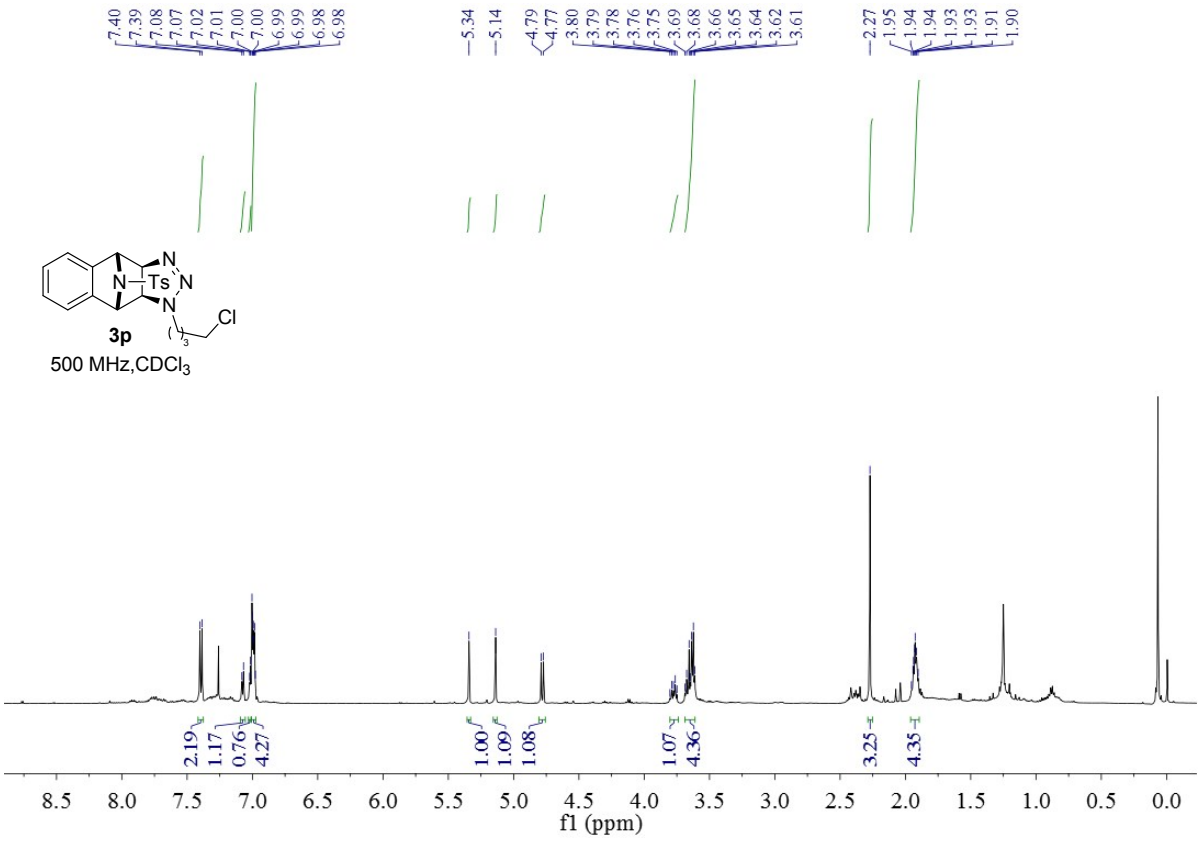
3n
400 MHz,$CDCl_3$

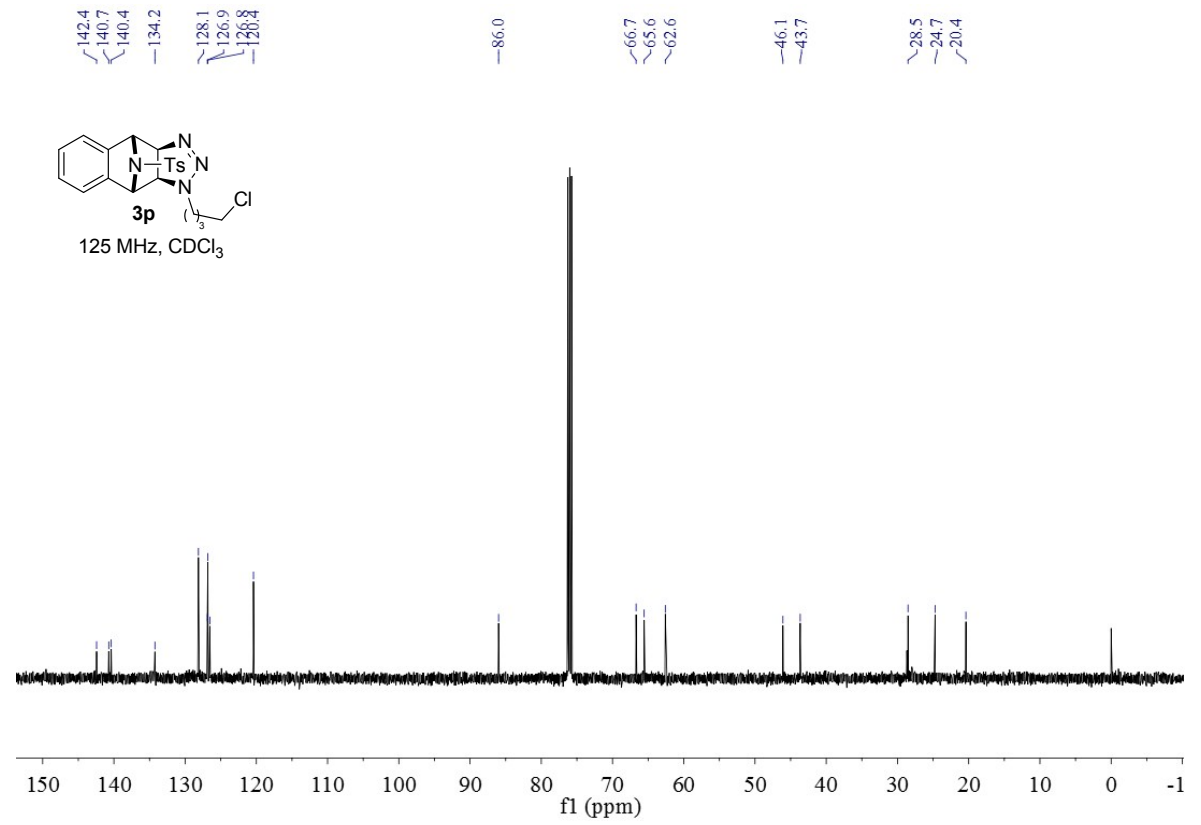


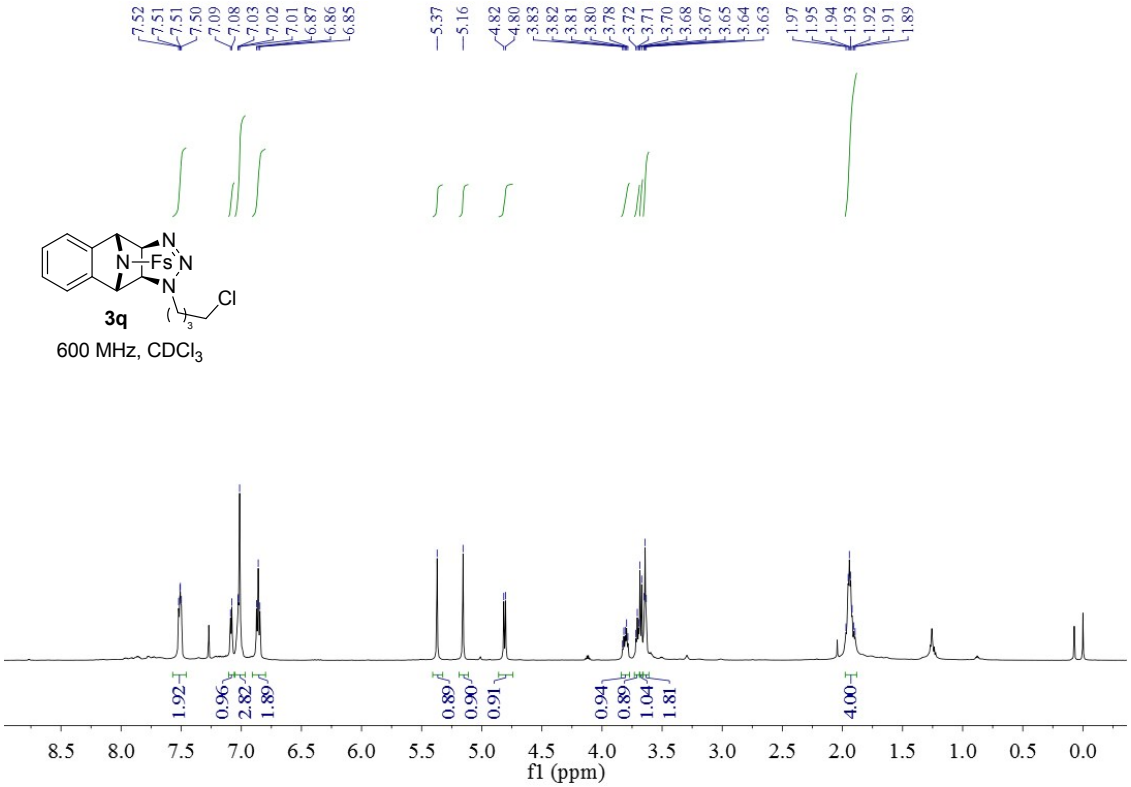
3n
100 MHz, $CDCl_3$

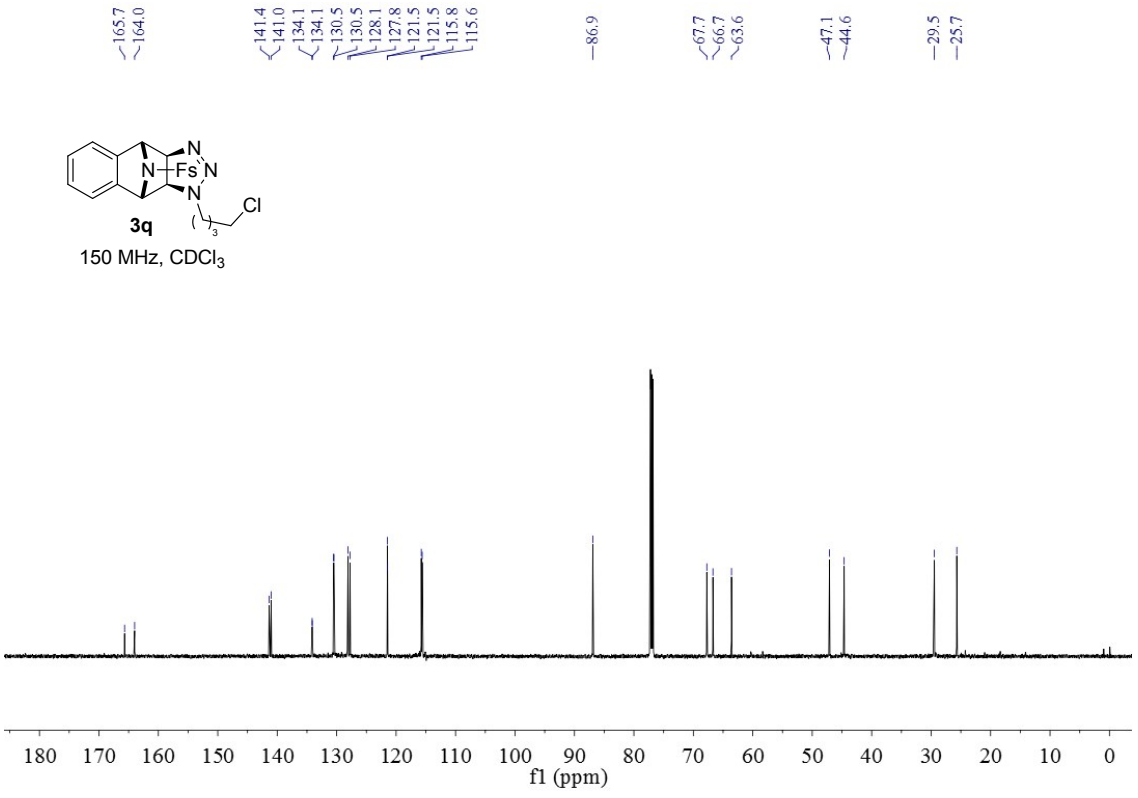

OMe
OMe
3o
500 MHz,CDCl3
f1 (ppm)

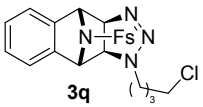

OMe
OMe
3o
125 MHz, CDCl3
f1 (ppm)


7.40
7.39
7.08
7.07
7.02
7.01
7.00
7.00
6.99
6.99
6.98
6.98
5.34
5.14
4.79
4.77
3.80
3.79
3.78
3.76
3.75
3.69
3.68
3.66
3.65
3.64
3.62
3.61
2.27
1.95
1.94
1.94
1.93
1.93
1.91
1.90
N
N
Ts
N
N
Cl
3
3p
500 MHz,CDCl3
2.19
1.17
0.76
4.27
1.00
1.09
1.08
1.07
4.36
3.25
4.35
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.4
140.7
140.4
134.2
128.1
126.9
126.8
120.4
86.0
66.7
65.6
62.6
46.1
43.7
28.5
24.7
20.4
N
N
Ts
N
N
Cl
3
3p
125 MHz, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.52
7.51
7.51
7.50
7.09
7.08
7.03
7.02
7.01
6.87
6.86
6.85
5.37
5.16
4.82
4.80
3.83
3.82
3.81
3.80
3.78
3.72
3.71
3.70
3.68
3.67
3.65
3.64
3.63
1.97
1.95
1.94
1.93
1.92
1.91
1.89
N
N
Fs
N
N
Cl
3
3q
600 MHz, CDCl3
1.92
0.96
2.82
1.89
0.89
0.90
0.91
0.94
0.89
1.04
1.81
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

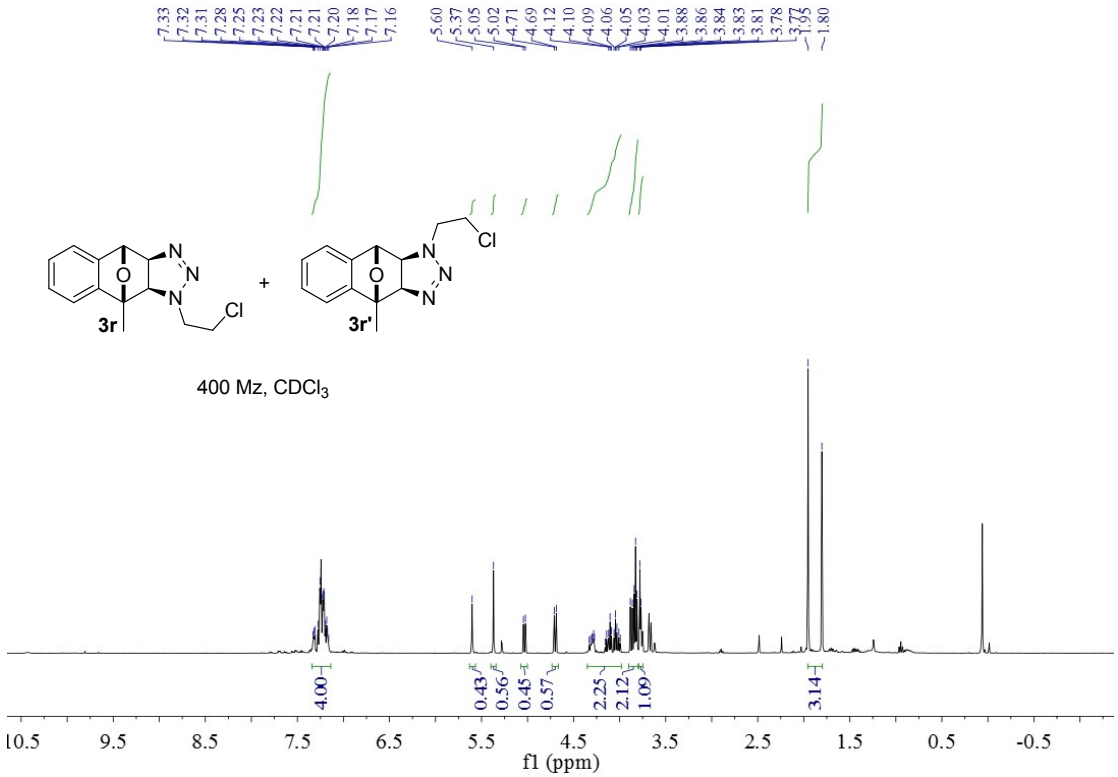

165.7
164.0
141.4
141.0
134.1
134.1
130.5
130.5
128.1
127.8
121.5
121.5
115.8
115.6
86.9
67.7
66.7
63.6
47.1
44.6
29.5
25.7
N
N
Fs
N
N
Cl
3
3q
150 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

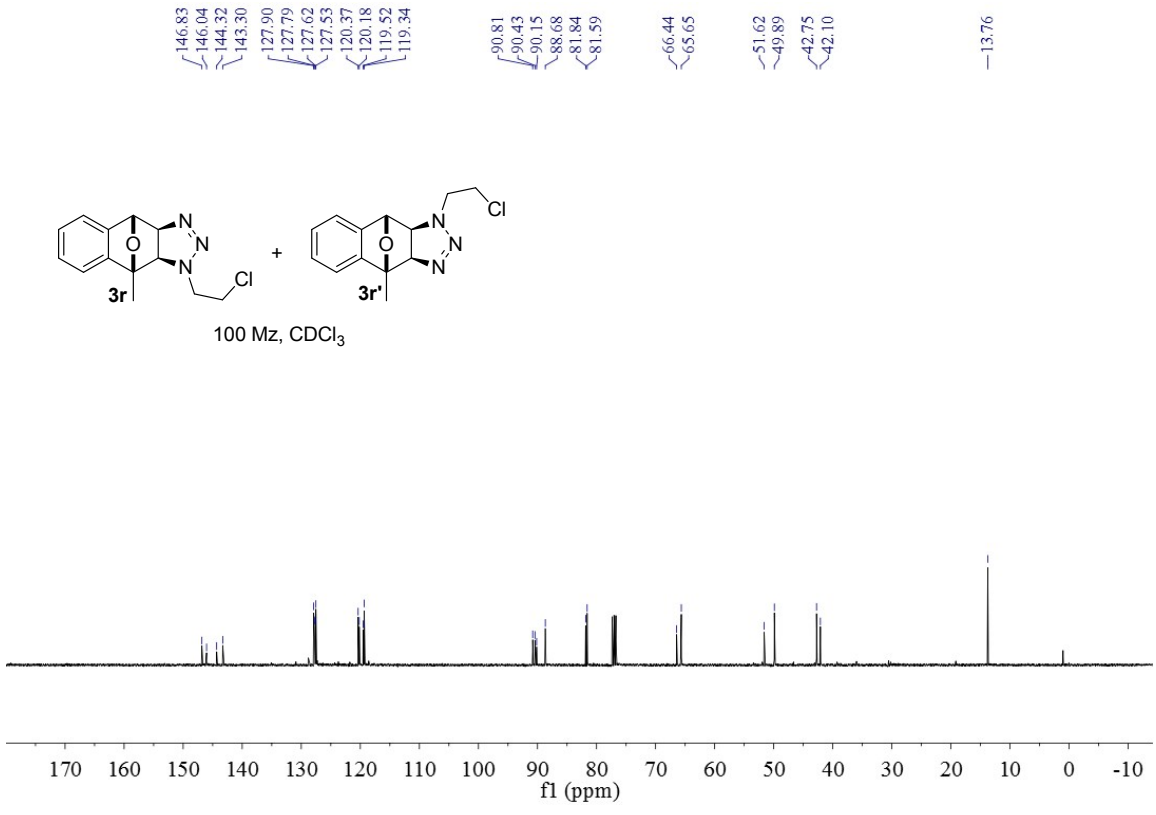


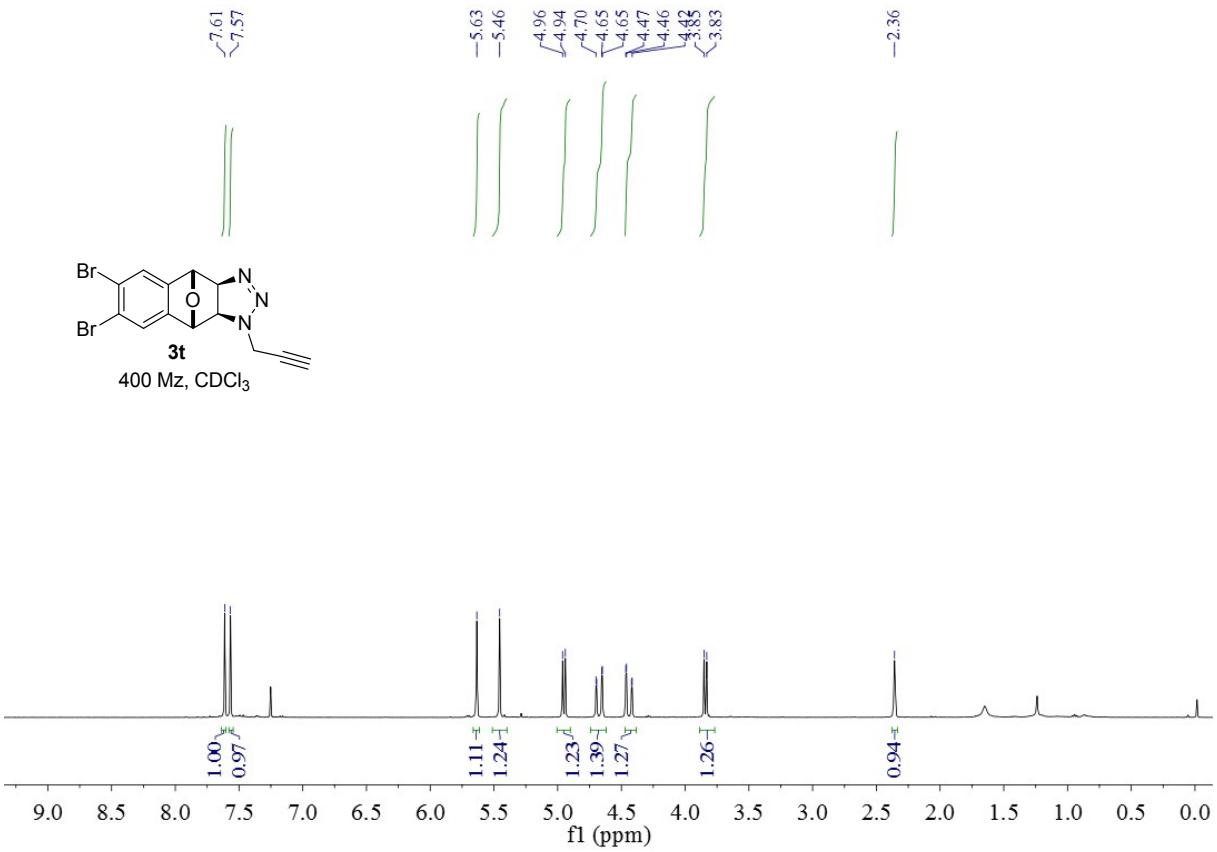
3q

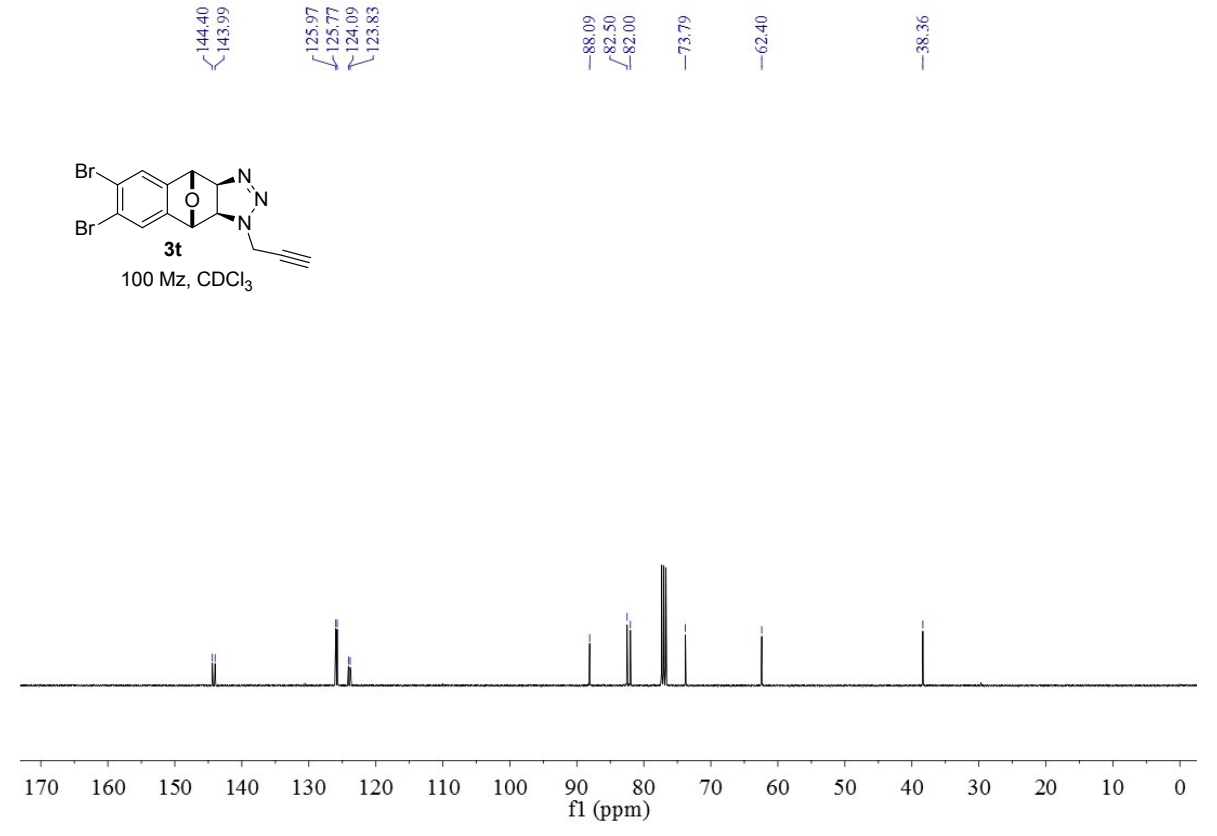
^{19}F NMR

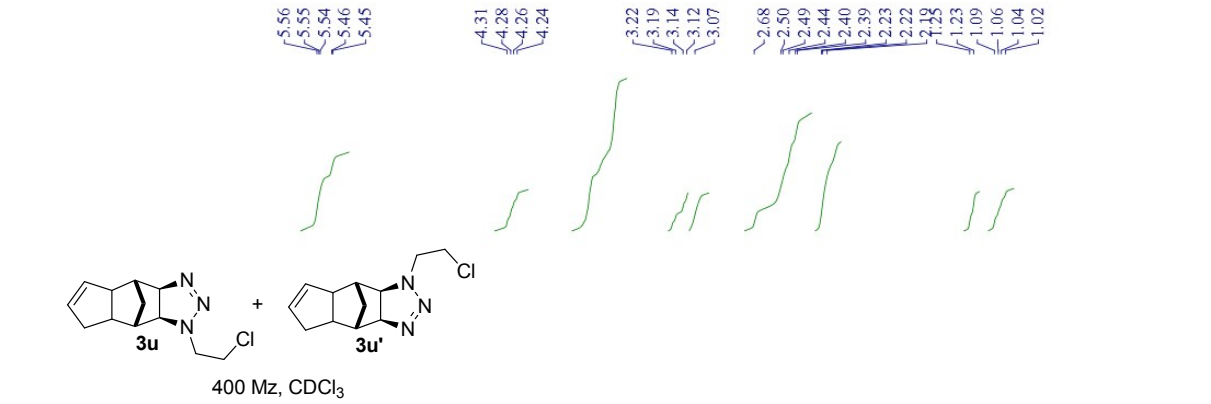
376 MHz, $CDCl_3$

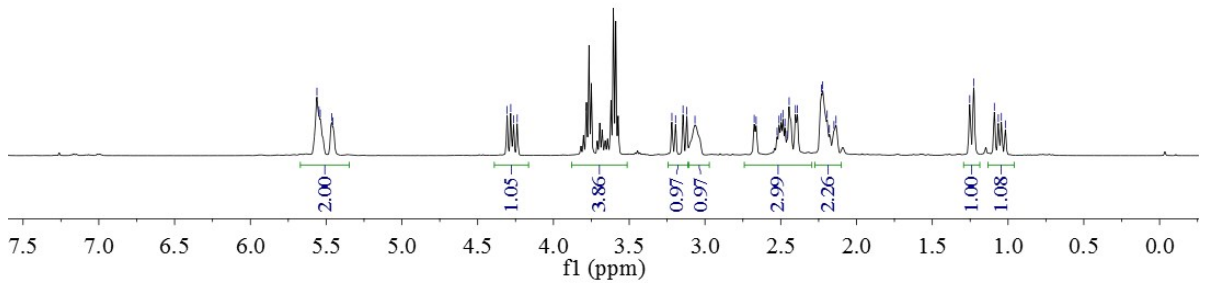

7.33
7.32
7.31
7.28
7.25
7.23
7.22
7.21
7.21
7.20
7.18
7.17
7.16
5.60
5.37
5.05
5.02
4.71
4.69
4.12
4.10
4.09
4.06
4.05
4.03
4.01
3.88
3.86
3.84
3.83
3.81
3.78
3.77
1.95
1.80
Cl
3r
+
Cl
3r'
400 Mz, CDCl3
4.00
0.43
0.56
0.45
0.57
2.25
2.12
1.09
3.14
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

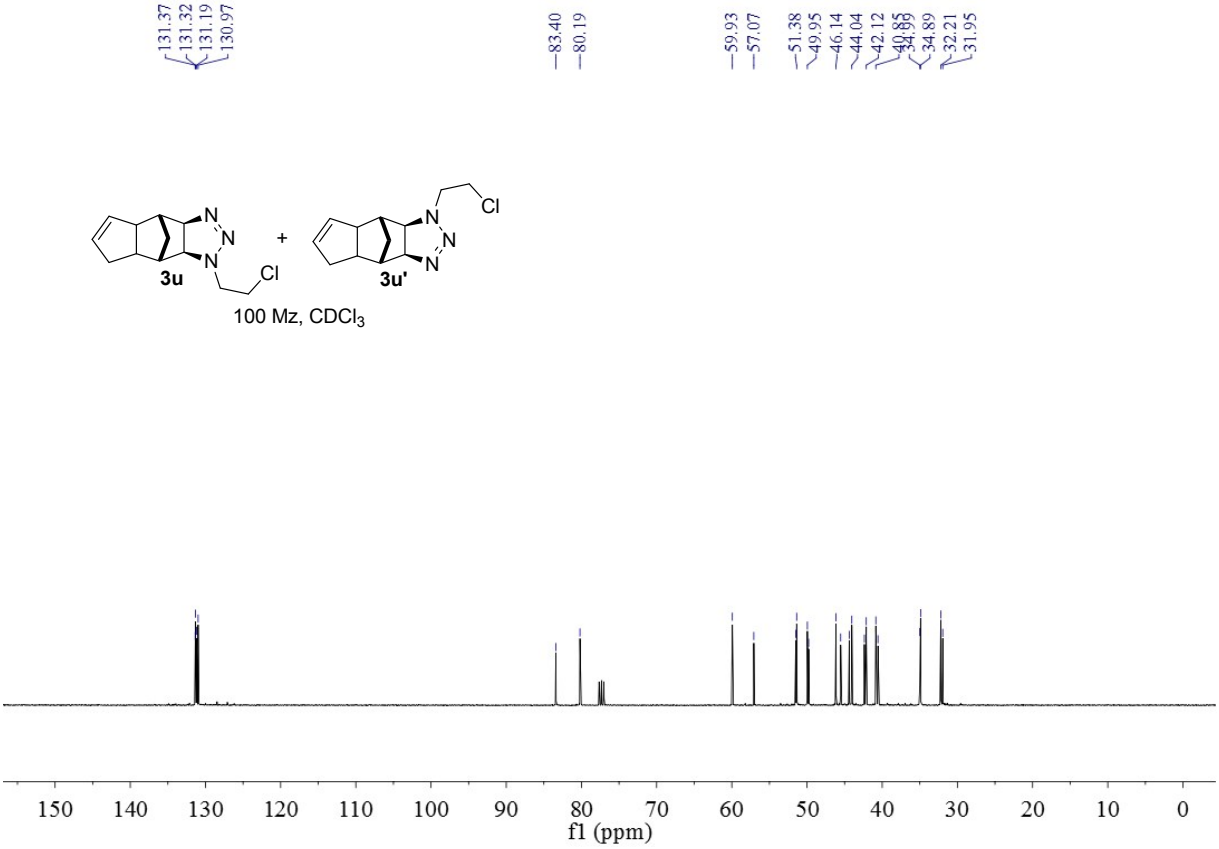

146.83
146.04
144.32
143.30
127.90
127.79
127.62
127.53
120.37
120.18
119.52
119.34
90.81
90.43
90.15
88.68
81.84
81.59
66.44
65.65
51.62
49.89
42.75
42.10
13.76
Cl
3r
+
Cl
3r'
100 Mz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

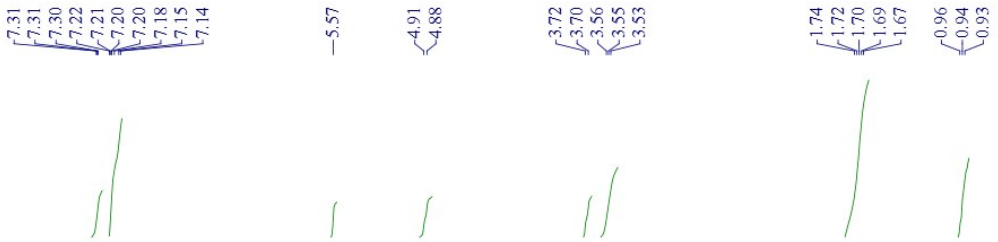

7.61
7.57
5.63
5.46
4.96
4.94
4.70
4.65
4.65
4.47
4.46
3.85
3.83
2.36
Br
Br
O
N
N
N
3t
400 Mz, CDCl3
1.00
0.97
1.11
1.24
1.23
1.39
1.27
1.26
0.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

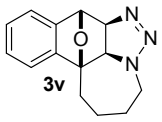

144.40
143.99
125.97
125.77
124.09
123.83
88.09
82.50
82.00
73.79
62.40
38.36
Br
Br
O
N
N
N
3t
100 Mz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5.56
5.55
5.54
5.46
5.45
4.31
4.28
4.26
4.24
3.22
3.19
3.14
3.12
3.07
2.68
2.50
2.49
2.44
2.40
2.39
2.23
2.22
1.23
1.09
1.06
1.04
1.02
N
N
N
Cl
3u
+
N
N
N
Cl
3u'
400 Mz, CDCl3


2.00
1.05
3.86
0.97
0.97
2.99
2.26
1.00
1.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

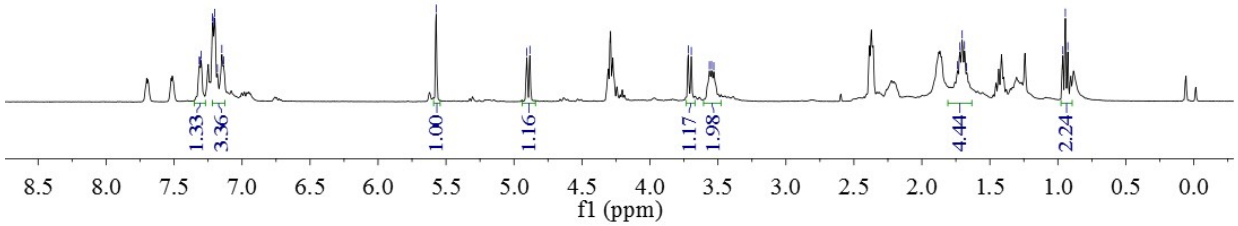

131.37
131.32
131.19
130.97
83.40
80.19
59.93
57.07
51.38
49.95
46.14
44.04
42.12
34.89
32.21
31.95
N
N
N
Cl
3u
+
N
N
N
Cl
3u'
100 Mz, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

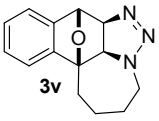




3v

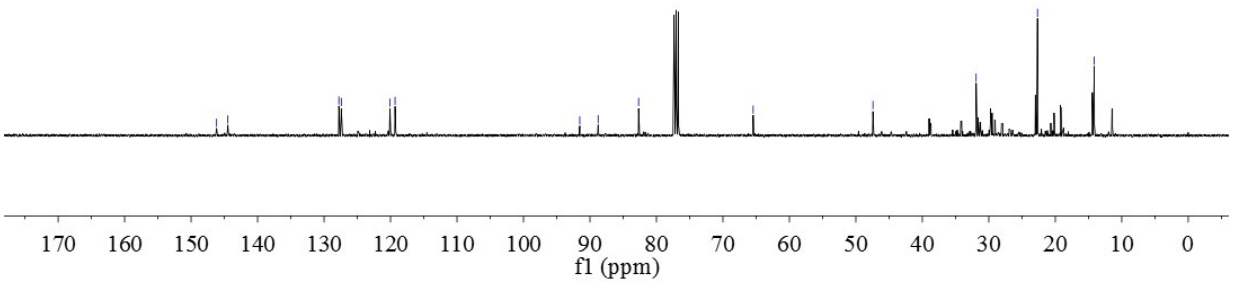
400 Mz, $CDCl_3$

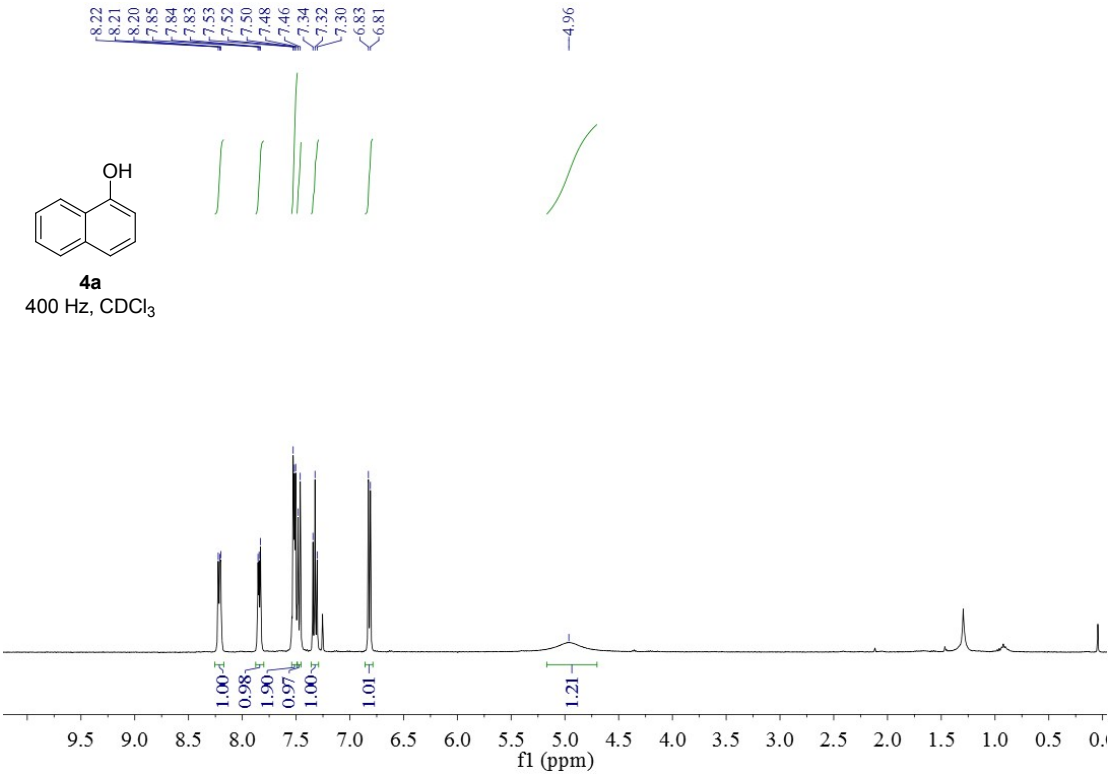




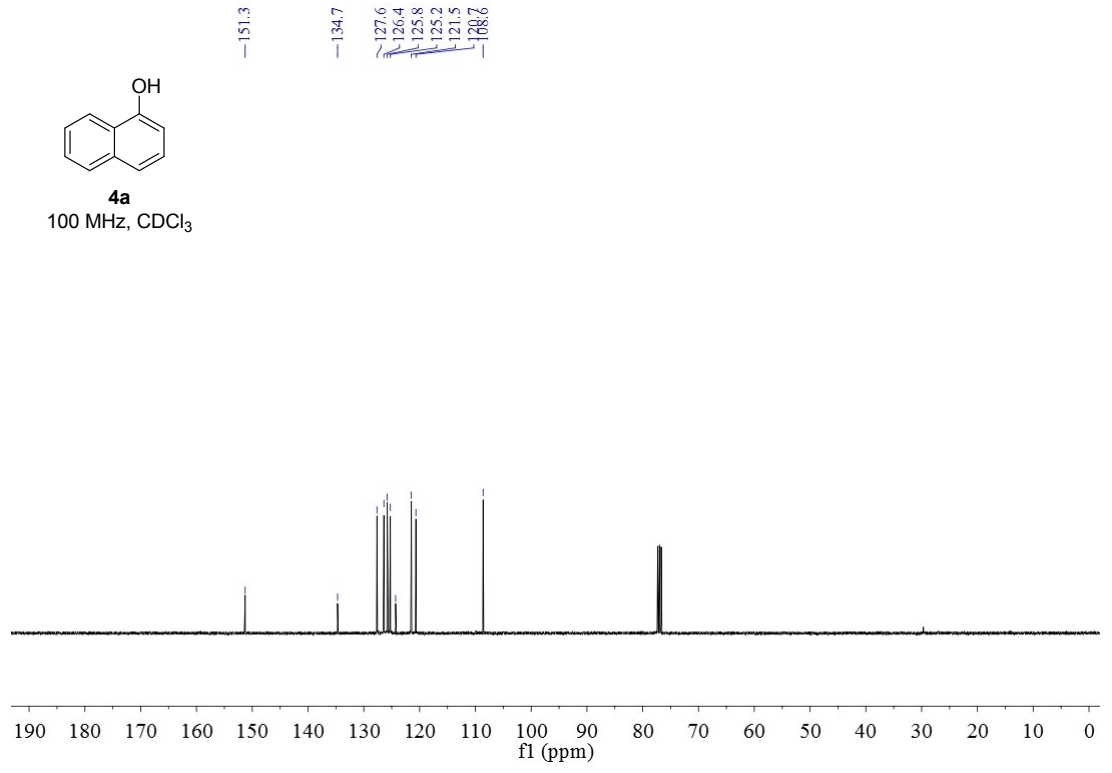
3v

100 Mz, $CDCl_3$

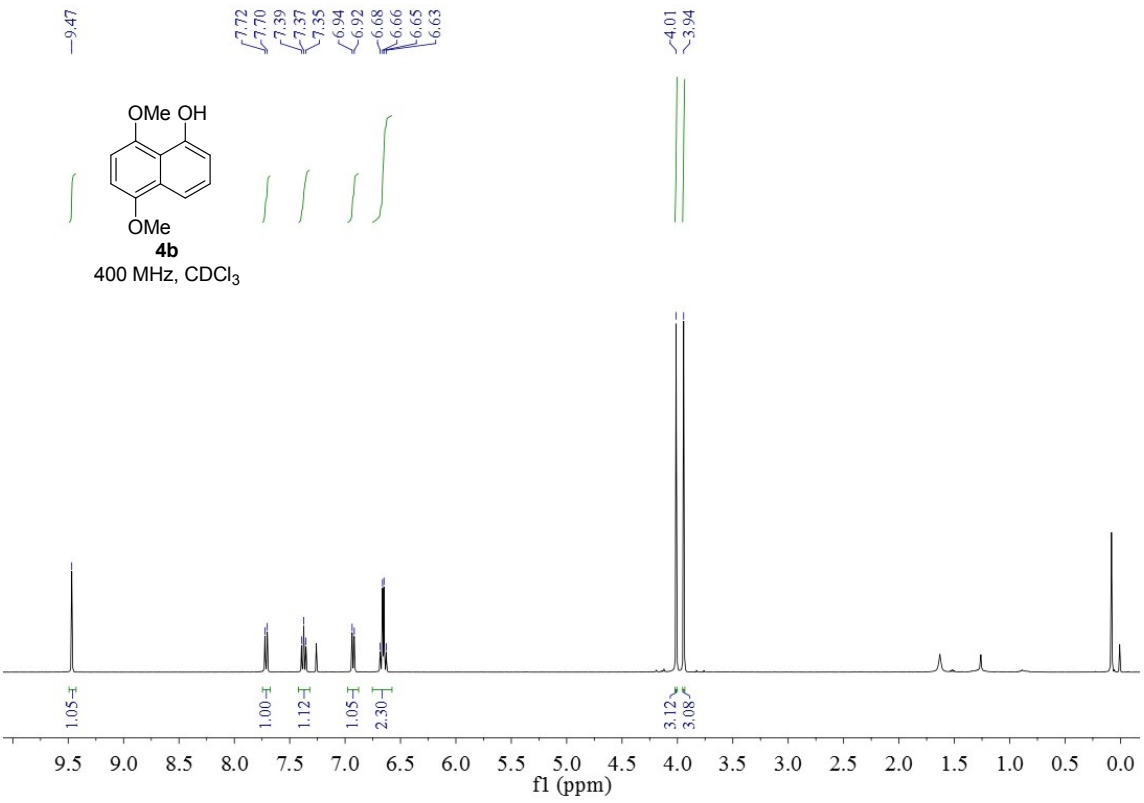


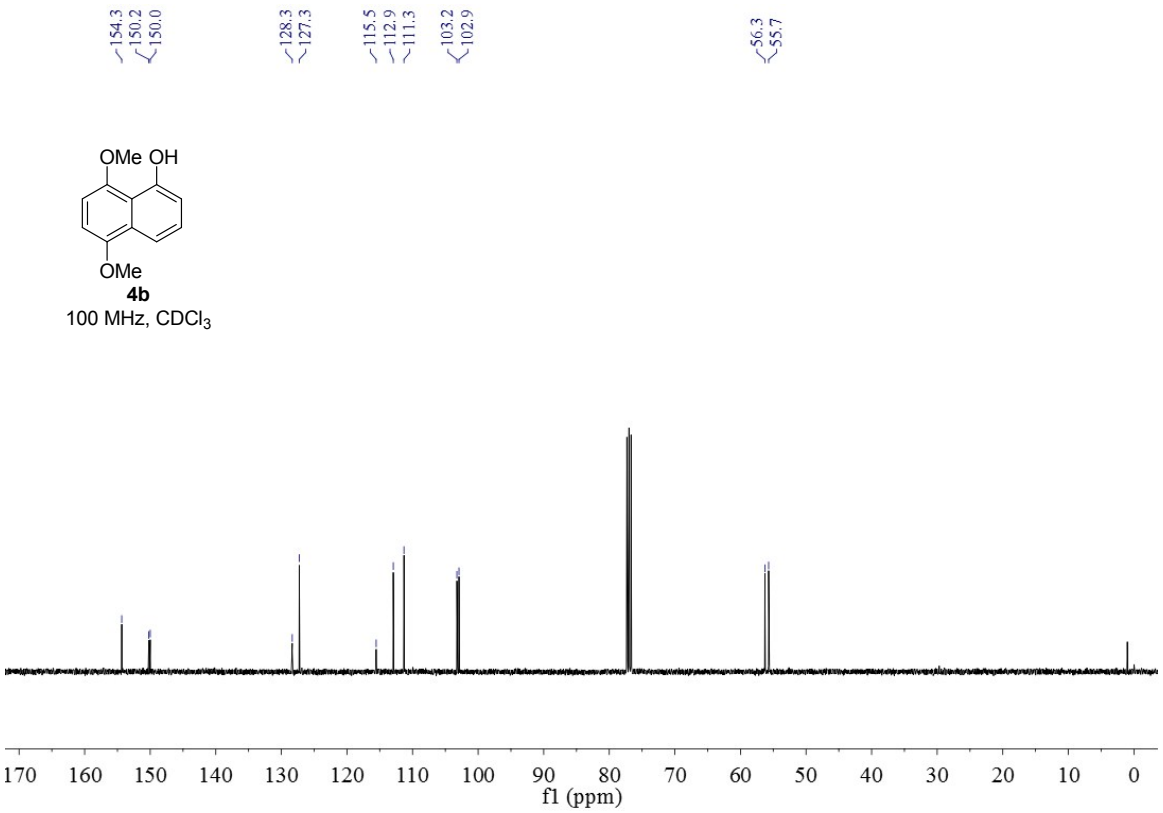


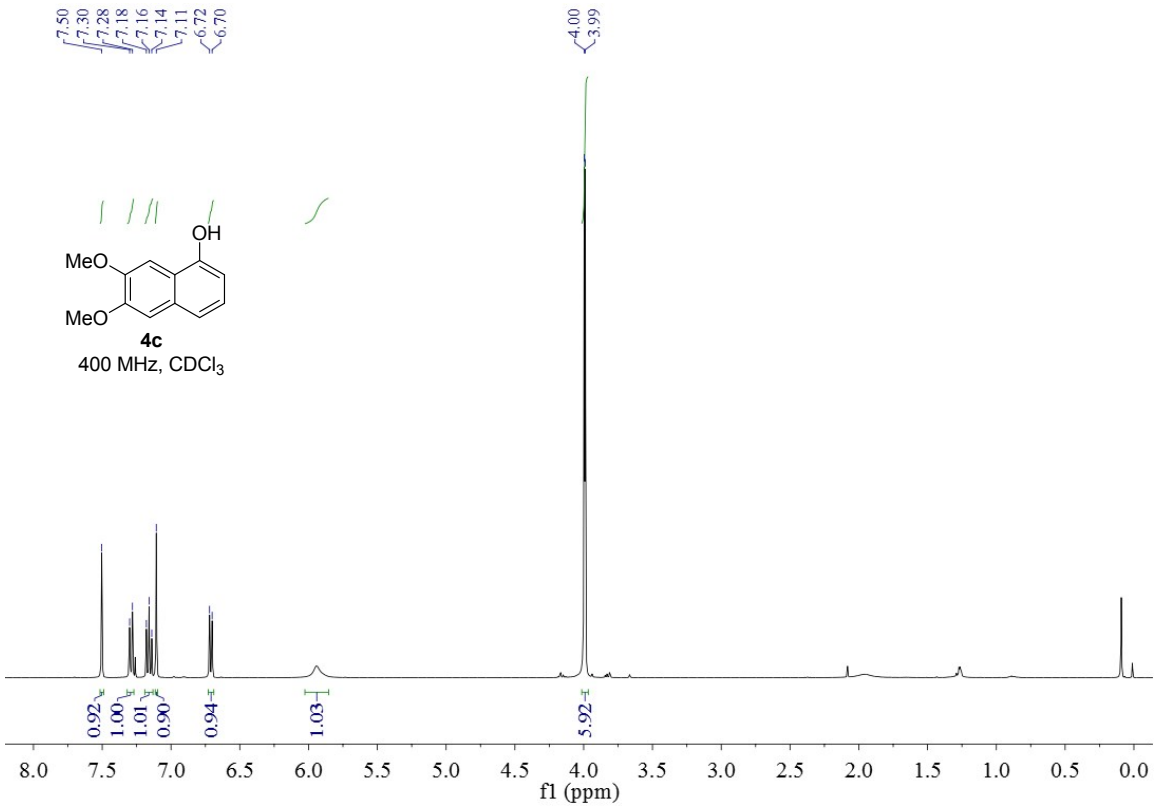
4a
400 Hz, $CDCl_3$



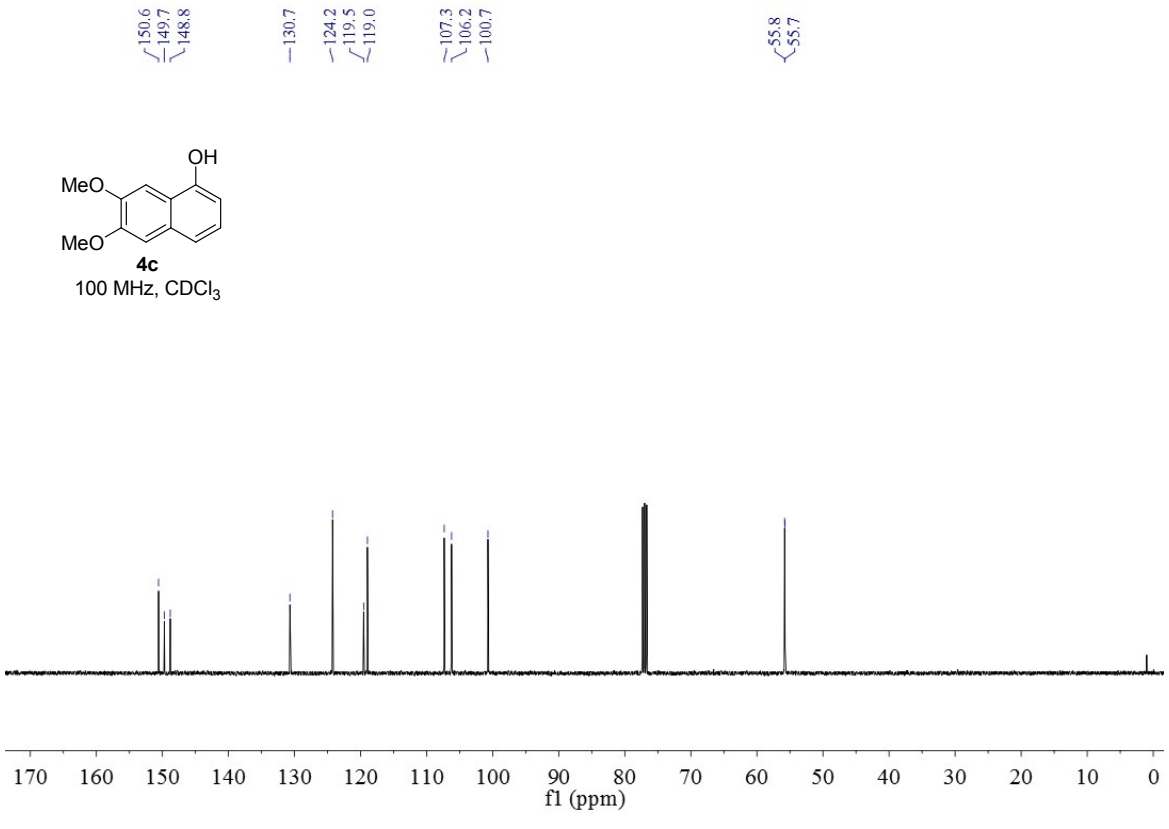
4a
100 MHz, $CDCl_3$


9.47
7.72
7.70
7.39
7.37
7.35
6.94
6.92
6.68
6.66
6.65
6.63
4.01
3.94
OMe OH
OMe
4b
400 MHz, CDCl3
1.05
1.00
1.12
1.05
2.30
3.12
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

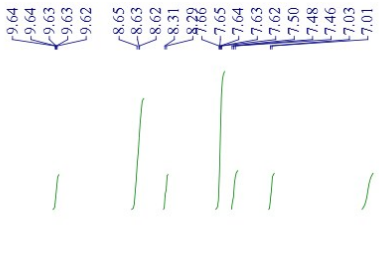

154.3
150.2
150.0
128.3
127.3
115.5
112.9
111.3
103.2
102.9
56.3
55.7
OMe OH
OMe
4b
100 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

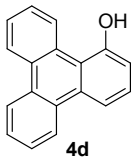


4c
400 MHz, $CDCl_3$

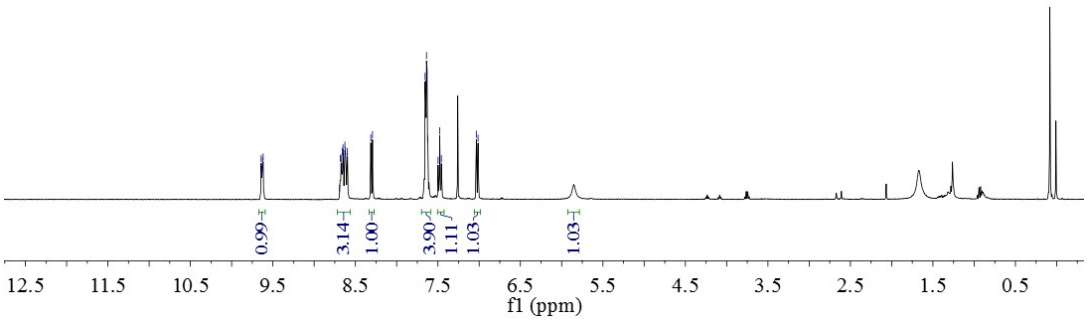


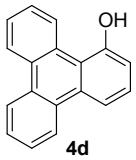
4c
100 MHz, $CDCl_3$



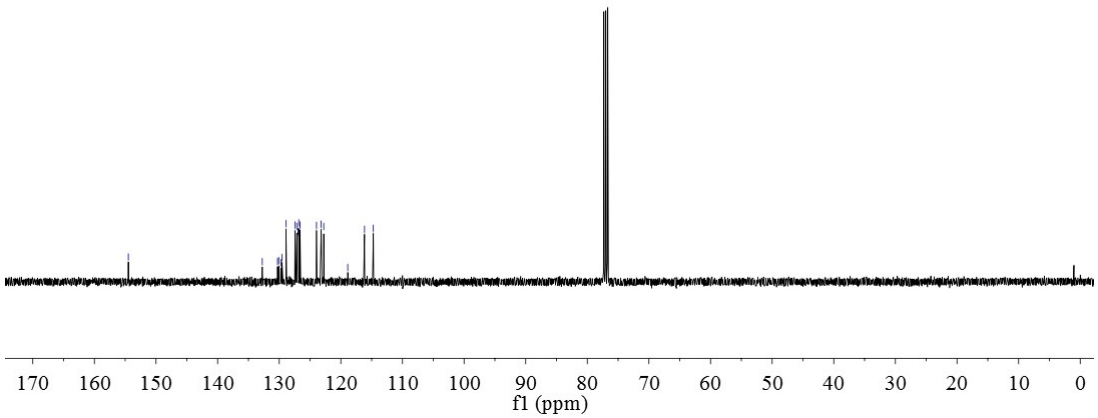


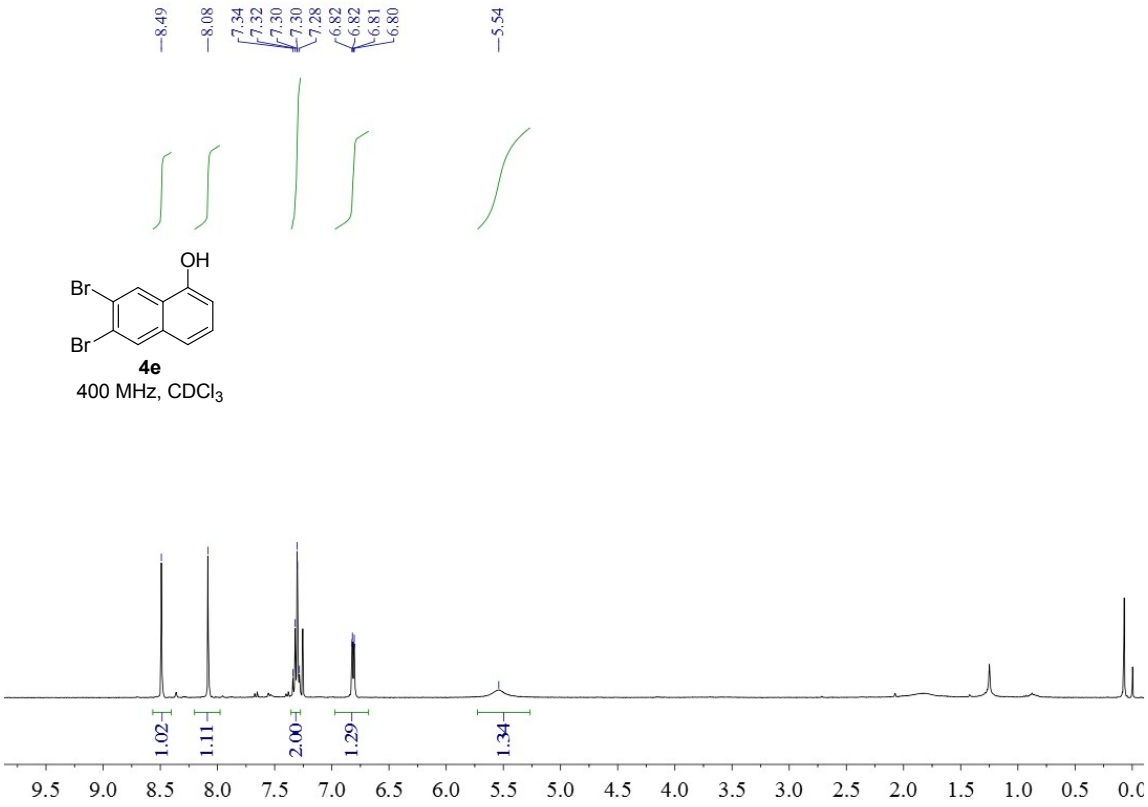
4d
400 MHz, $CDCl_3$





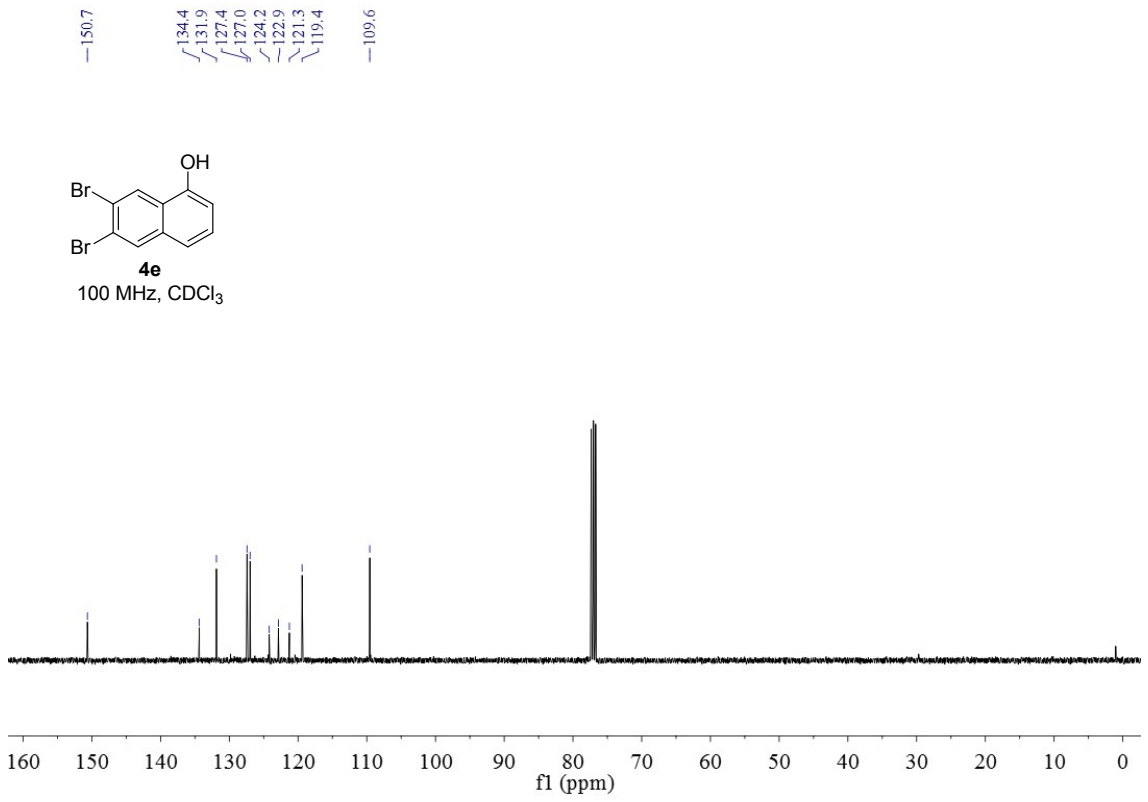
4d
100 MHz, $CDCl_3$





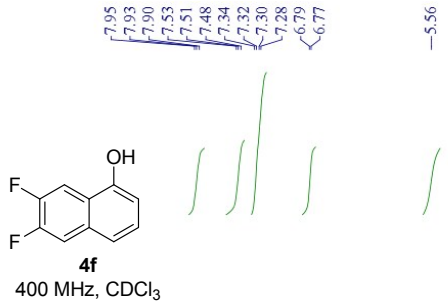
4e

400 MHz, $CDCl_3$



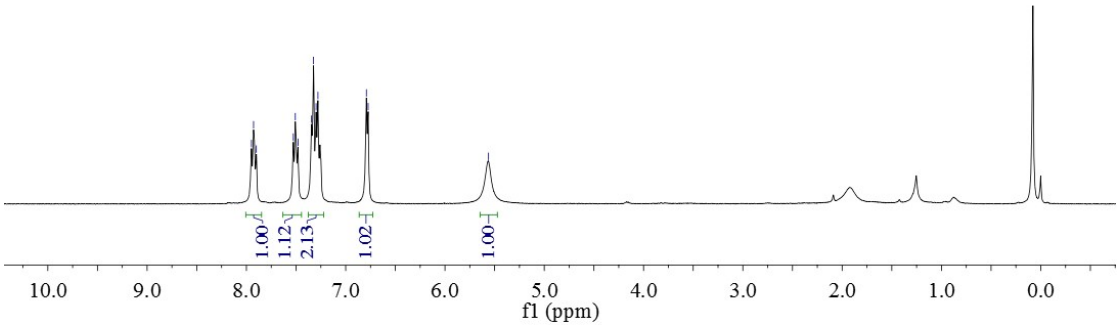
4e

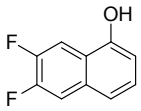
100 MHz, $CDCl_3$



4f

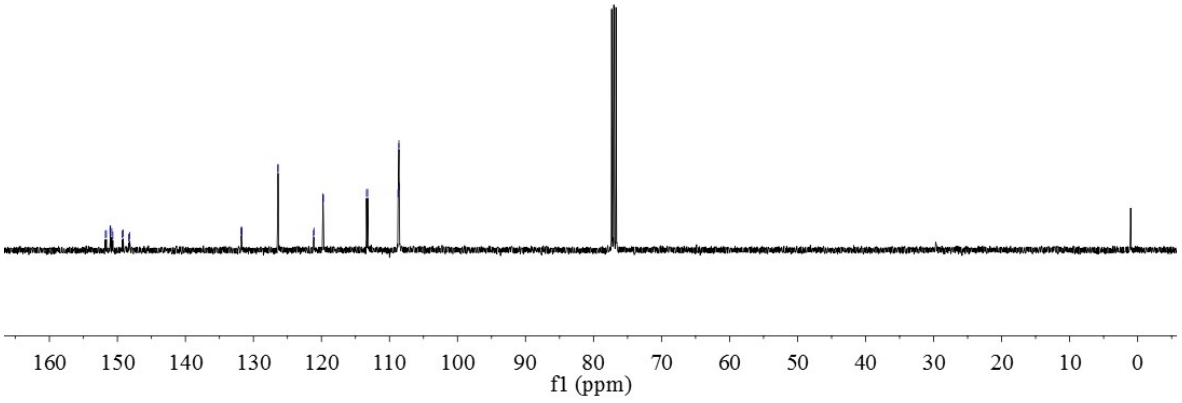
400 MHz, $CDCl_3$

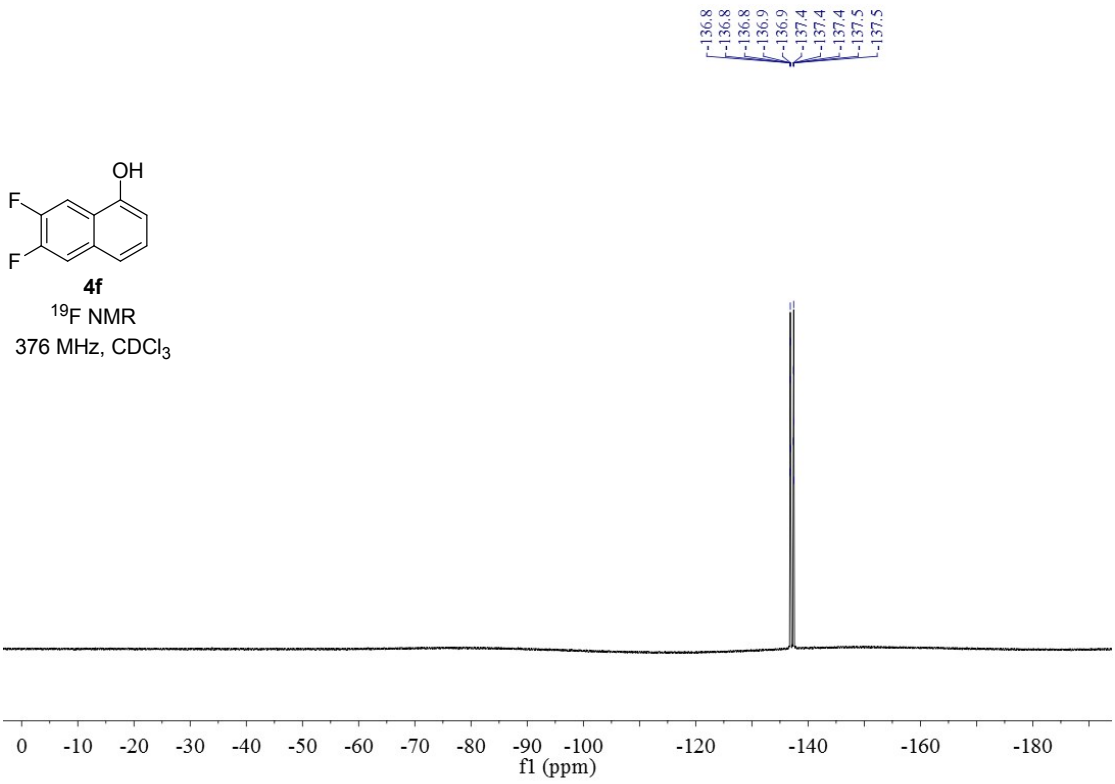


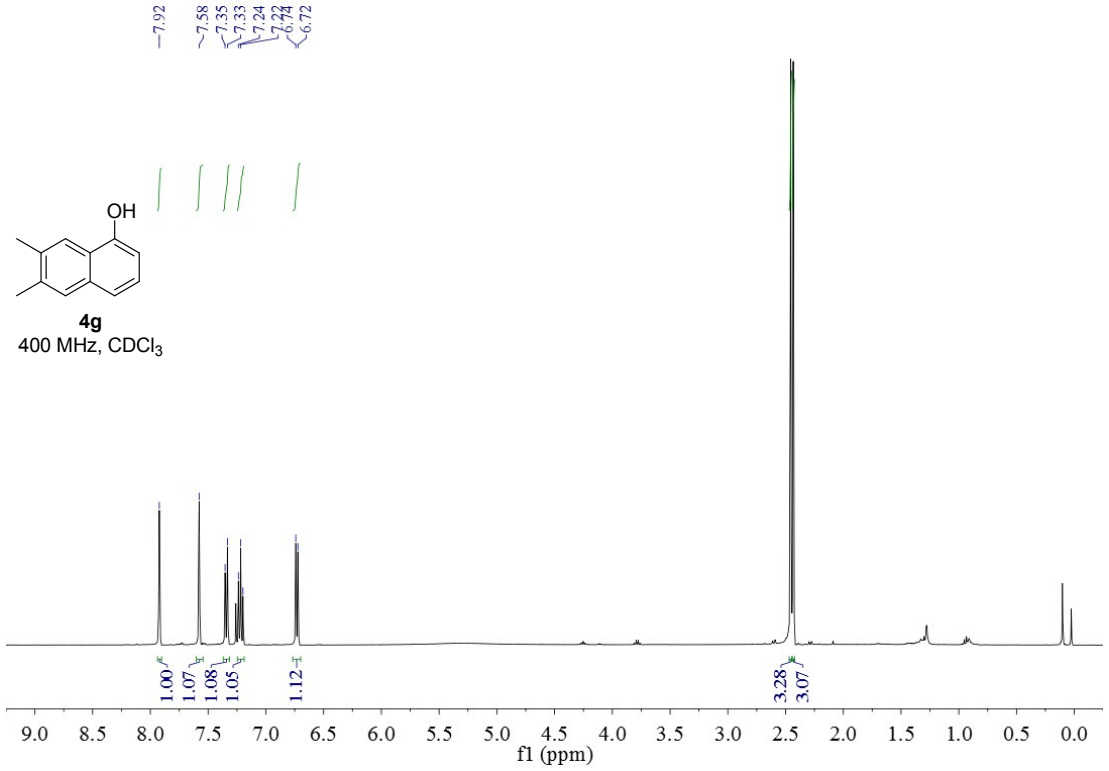


4f

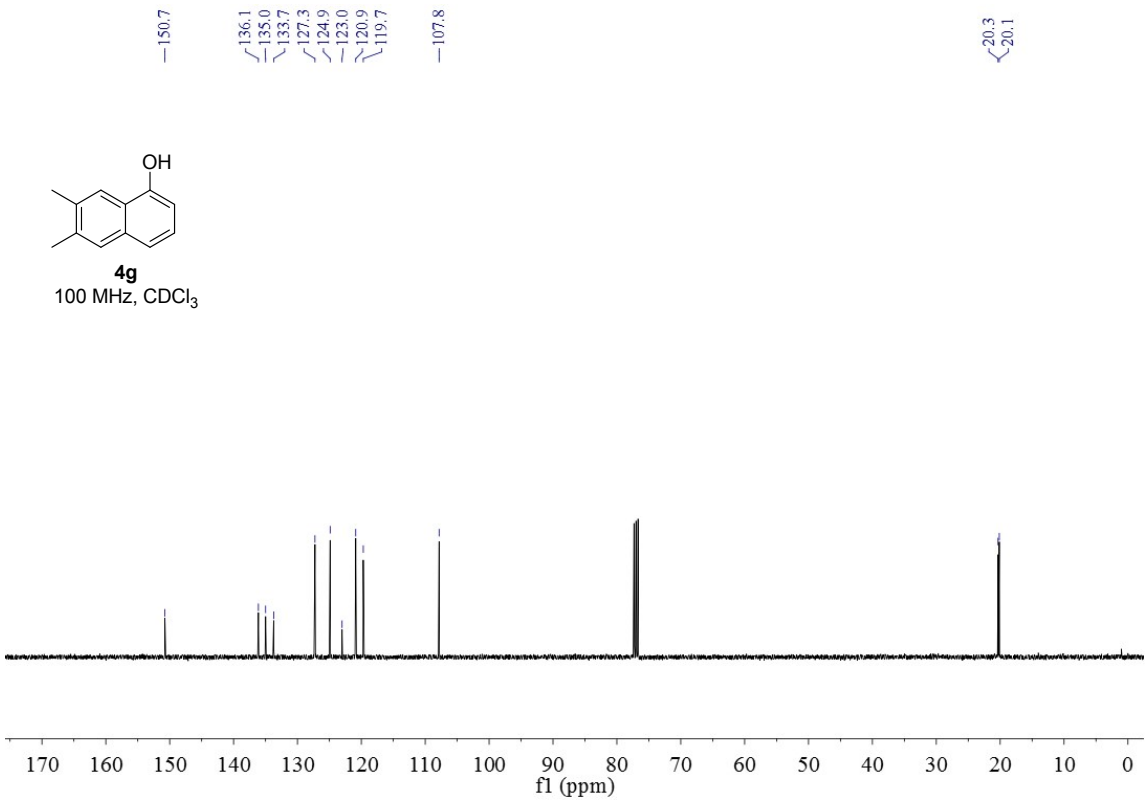
100 MHz, $CDCl_3$



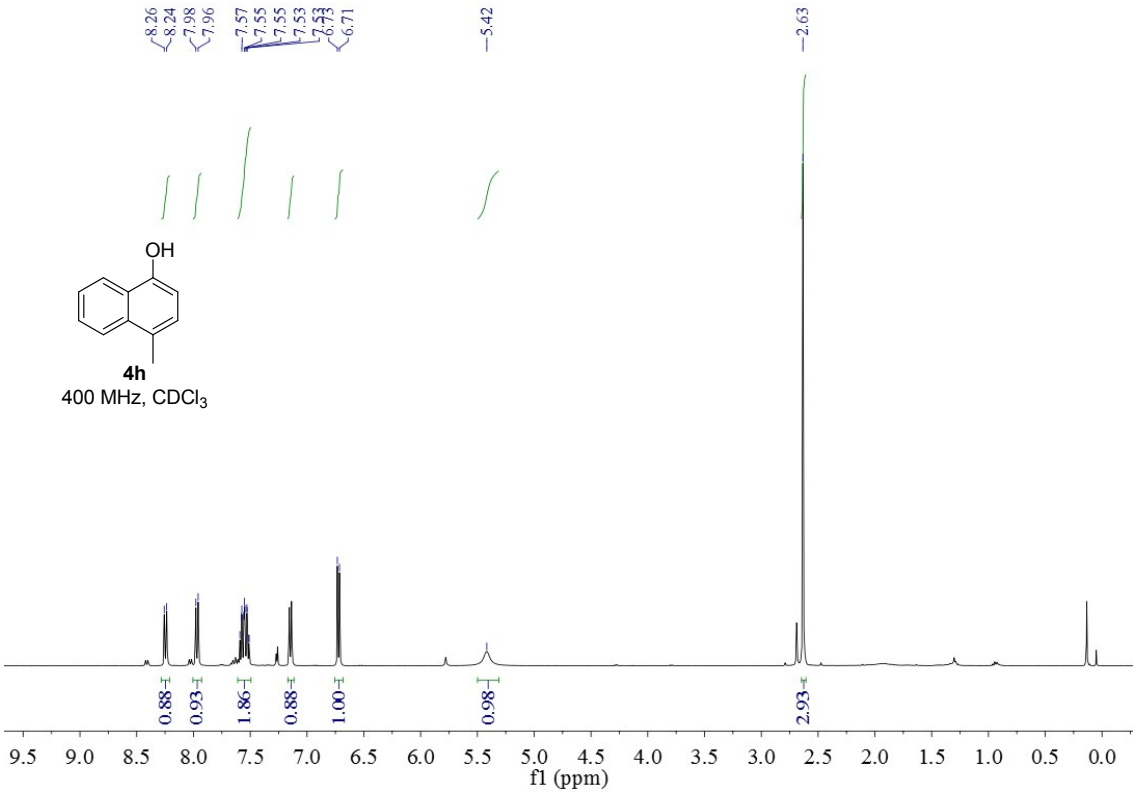

-136.8
-136.8
-136.8
-136.9
-136.9
-137.4
-137.4
-137.4
-137.5
-137.5
OH
F
F
4f
19F NMR
376 MHz, CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
f1 (ppm)

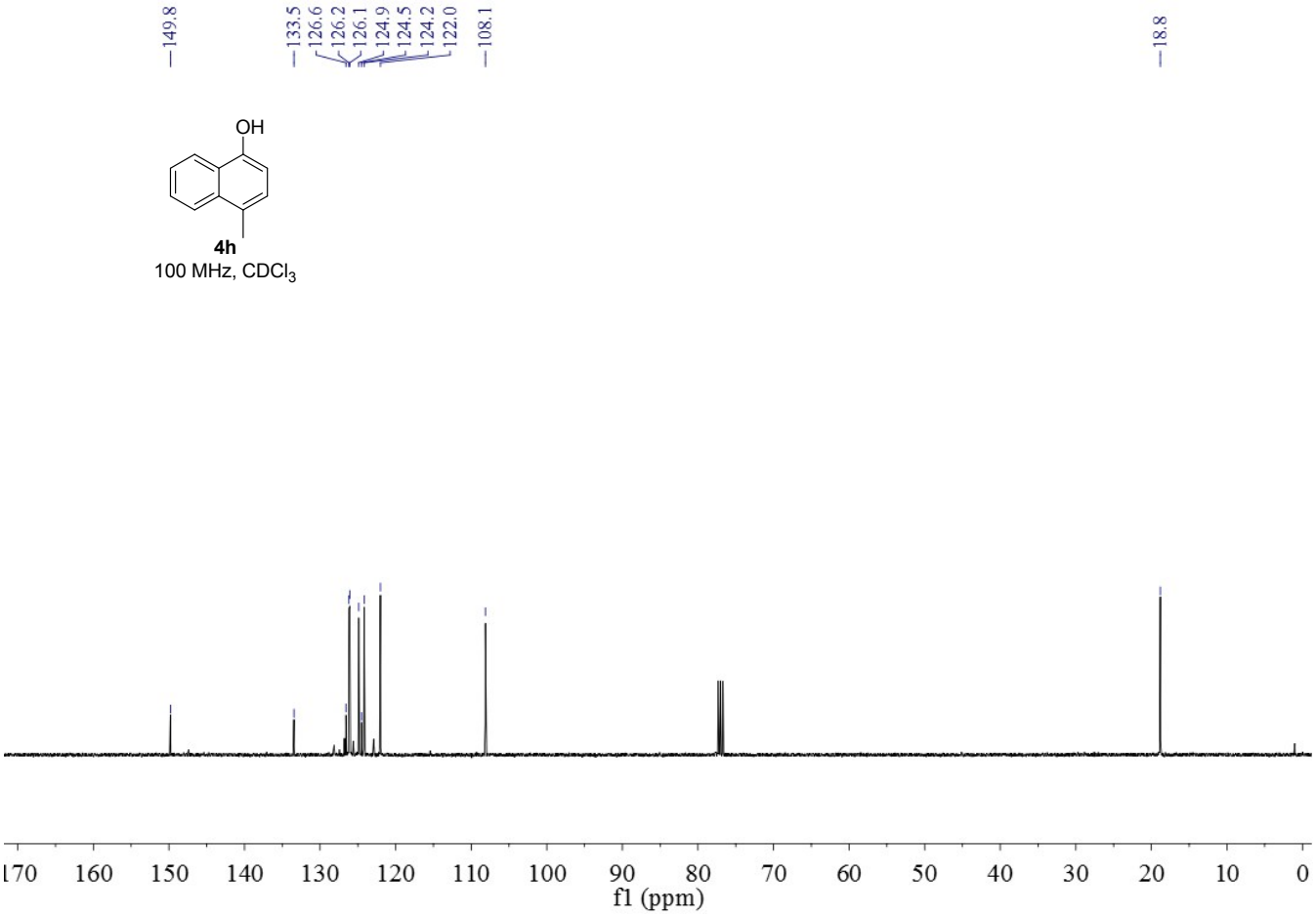


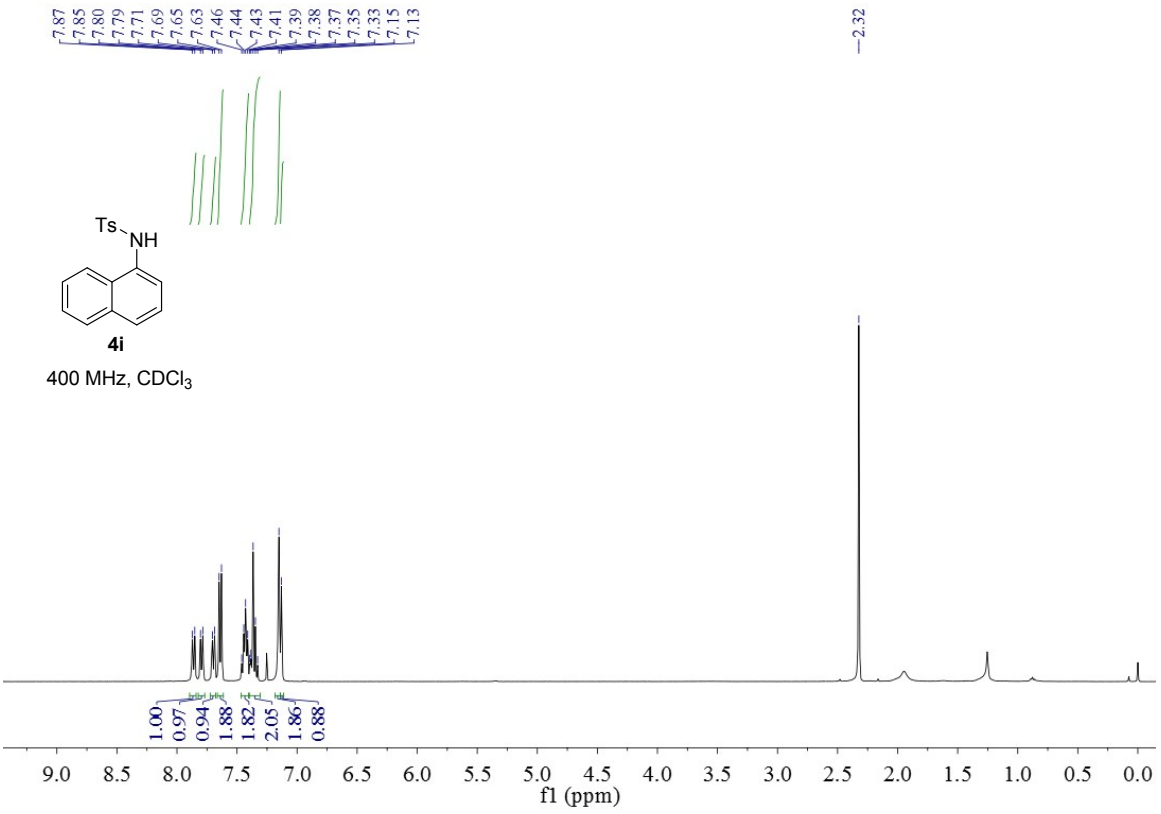
4g
400 MHz, $CDCl_3$



4g
100 MHz, $CDCl_3$

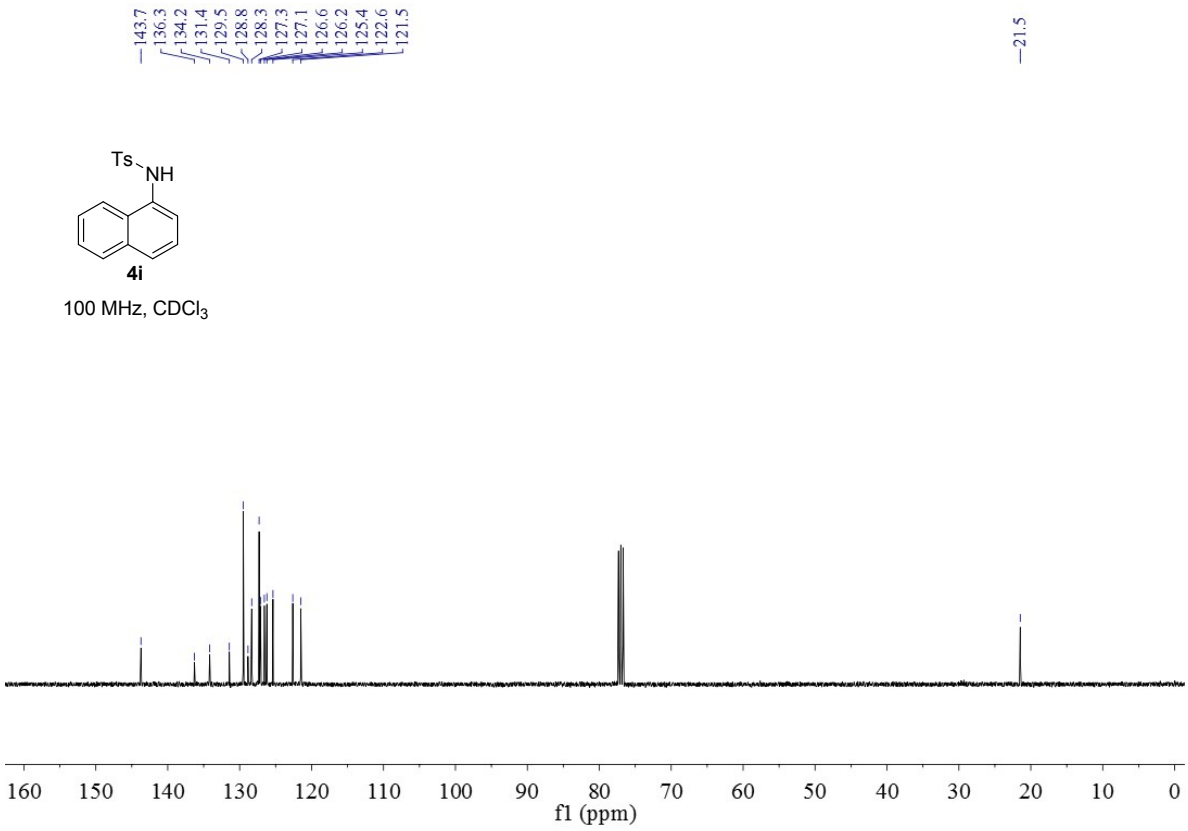

8.26
8.24
7.98
7.96
7.57
7.55
7.55
7.53
7.53
6.71
5.42
2.63
OH
4h
400 MHz, CDCl3
0.88
0.93
1.86
0.88
1.00
0.98
2.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.8
133.5
126.6
126.2
126.1
124.9
124.5
124.2
122.0
108.1
18.8
OH
4h
100 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



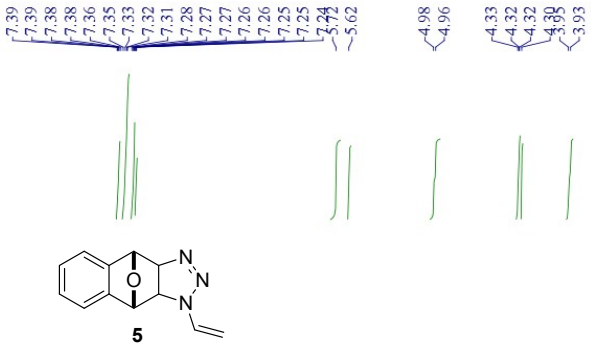
4i

400 MHz, $CDCl_3$



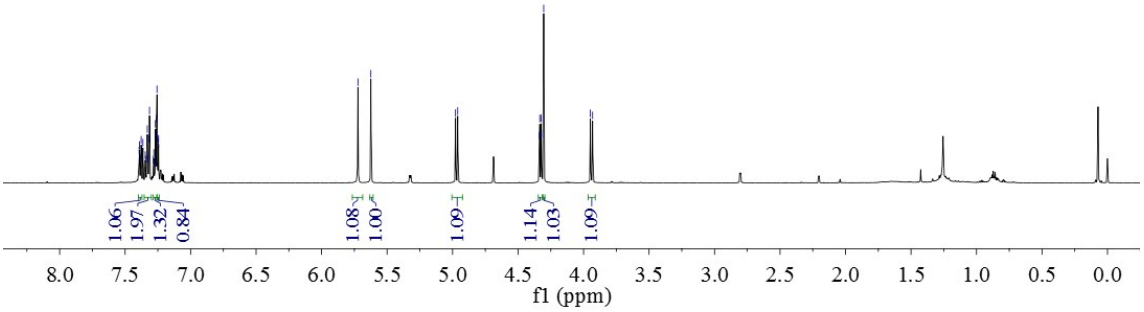
4i

100 MHz, $CDCl_3$



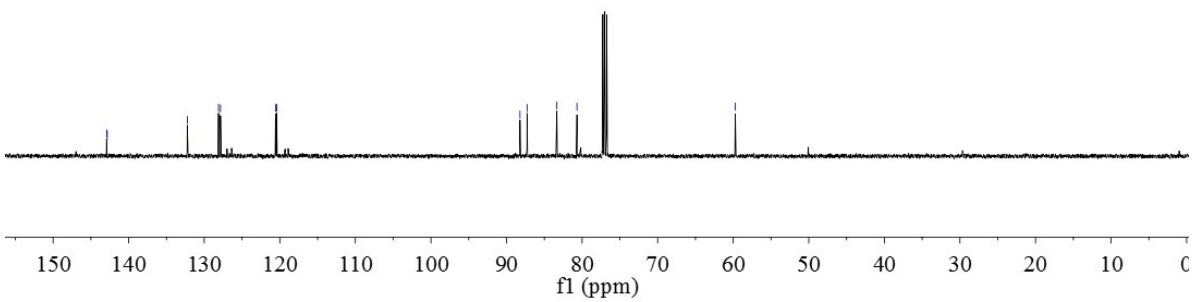
5

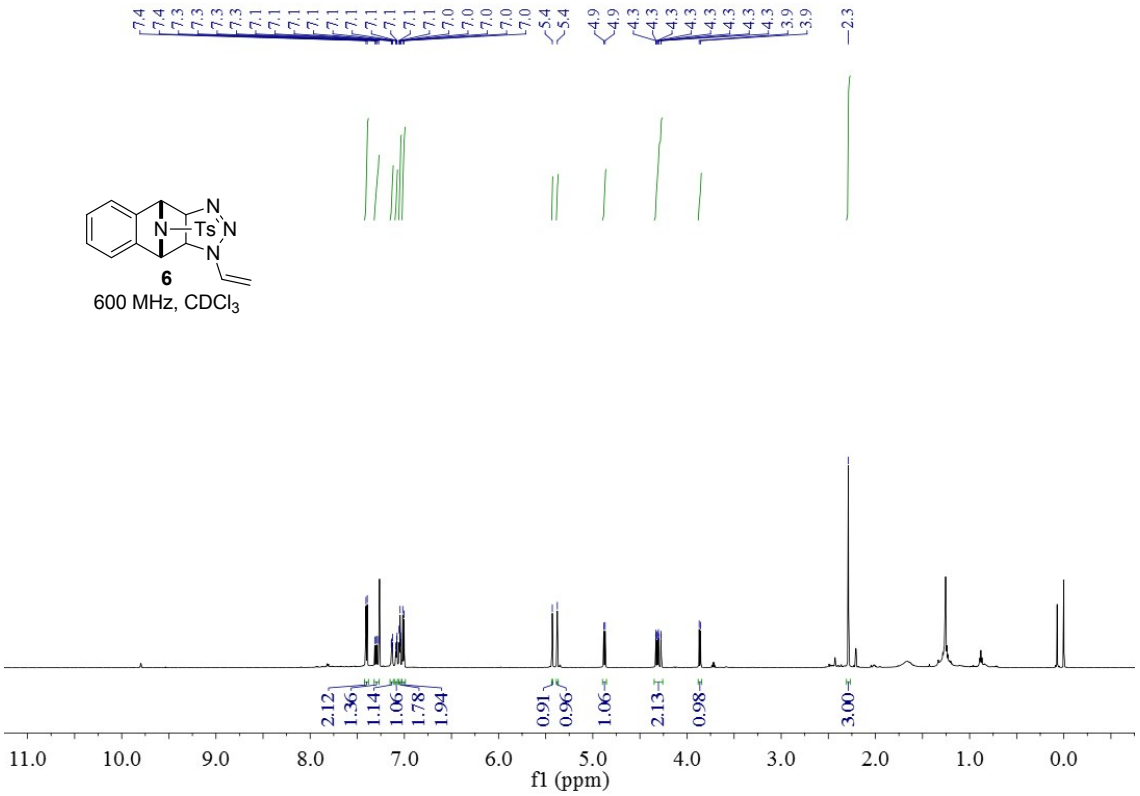
500 MHz, $CDCl_3$

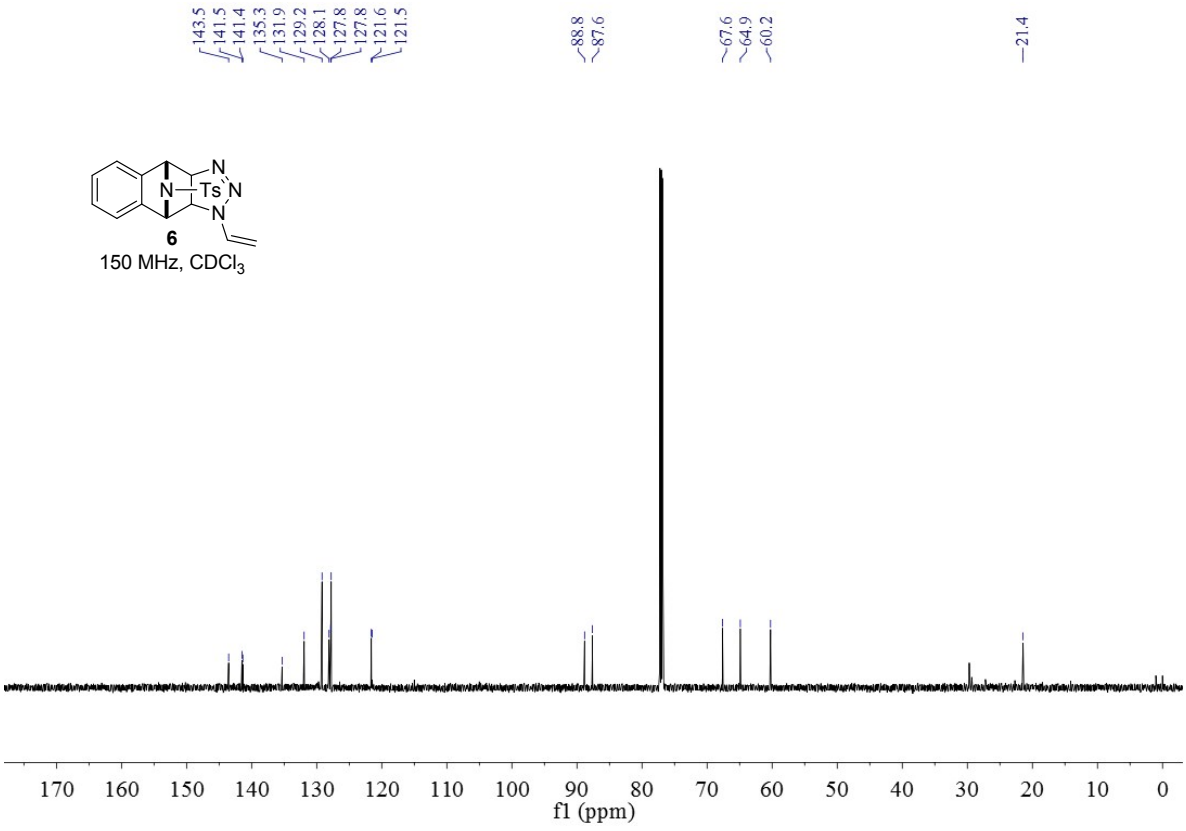


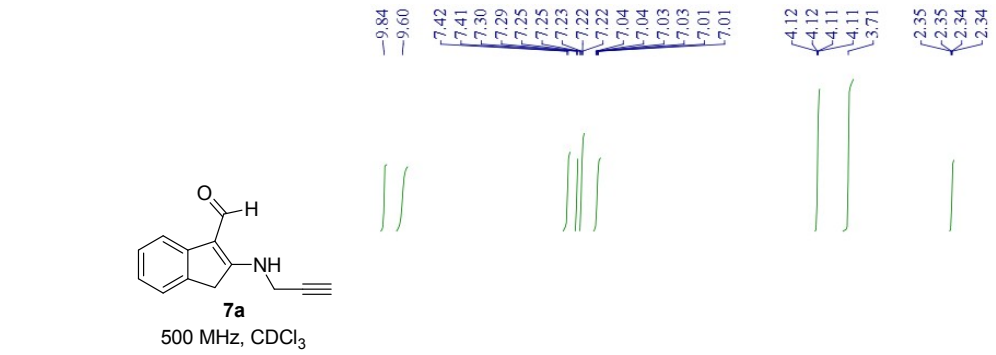
5

125 MHz, $CDCl_3$



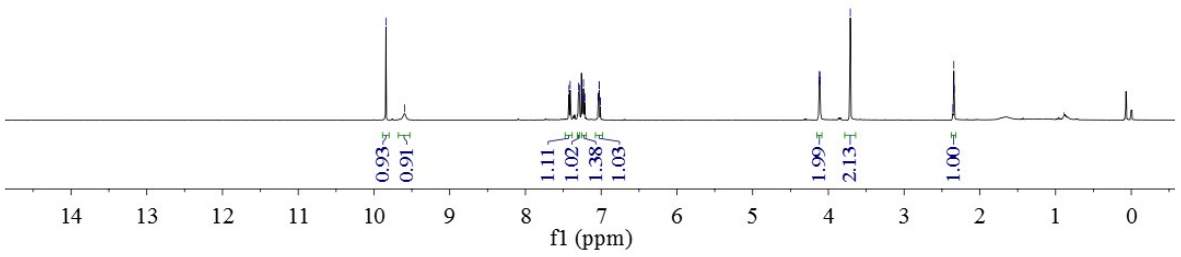

7.4
7.4
7.3
7.3
7.3
7.3
7.1
7.1
7.1
7.1
7.1
7.1
7.1
7.1
7.1
7.1
7.0
7.0
7.0
7.0
7.0
5.4
5.4
4.9
4.9
4.3
4.3
4.3
4.3
4.3
4.3
4.3
3.9
3.9
2.3
N
N
Ts
N
N
6
600 MHz, CDCl3
2.12
1.36
1.14
1.06
1.78
1.94
0.91
0.96
1.06
2.13
0.98
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

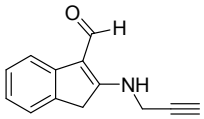

143.5
141.5
141.4
135.3
131.9
129.2
128.1
127.8
127.8
121.6
121.5
88.8
87.6
67.6
64.9
60.2
21.4
N
N
Ts
N
N
6
150 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7a

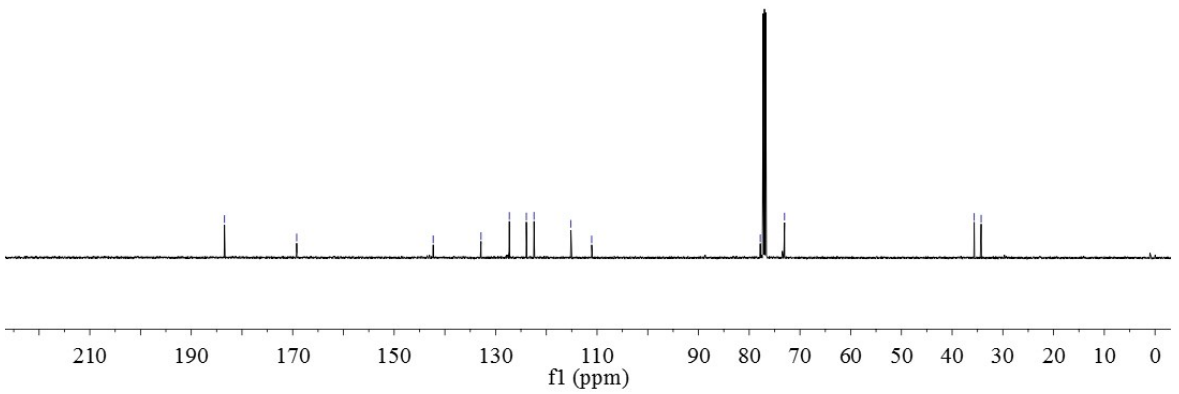
500 MHz, $CDCl_3$

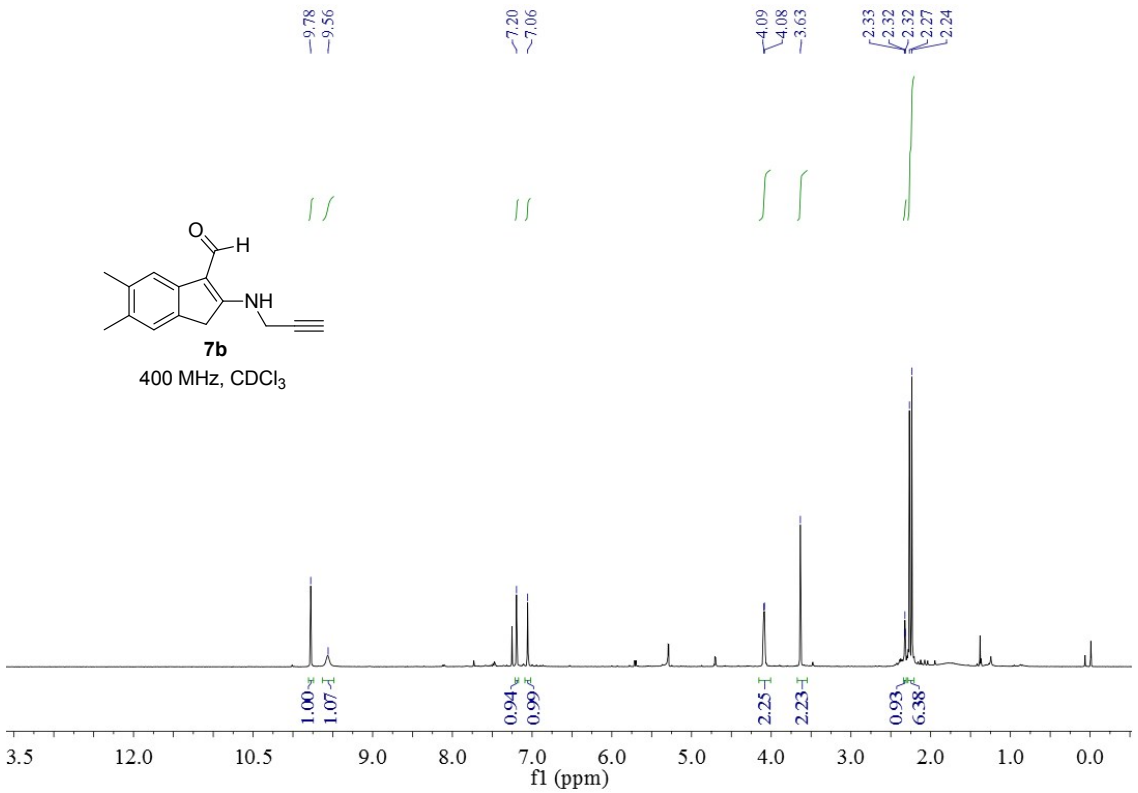




7a

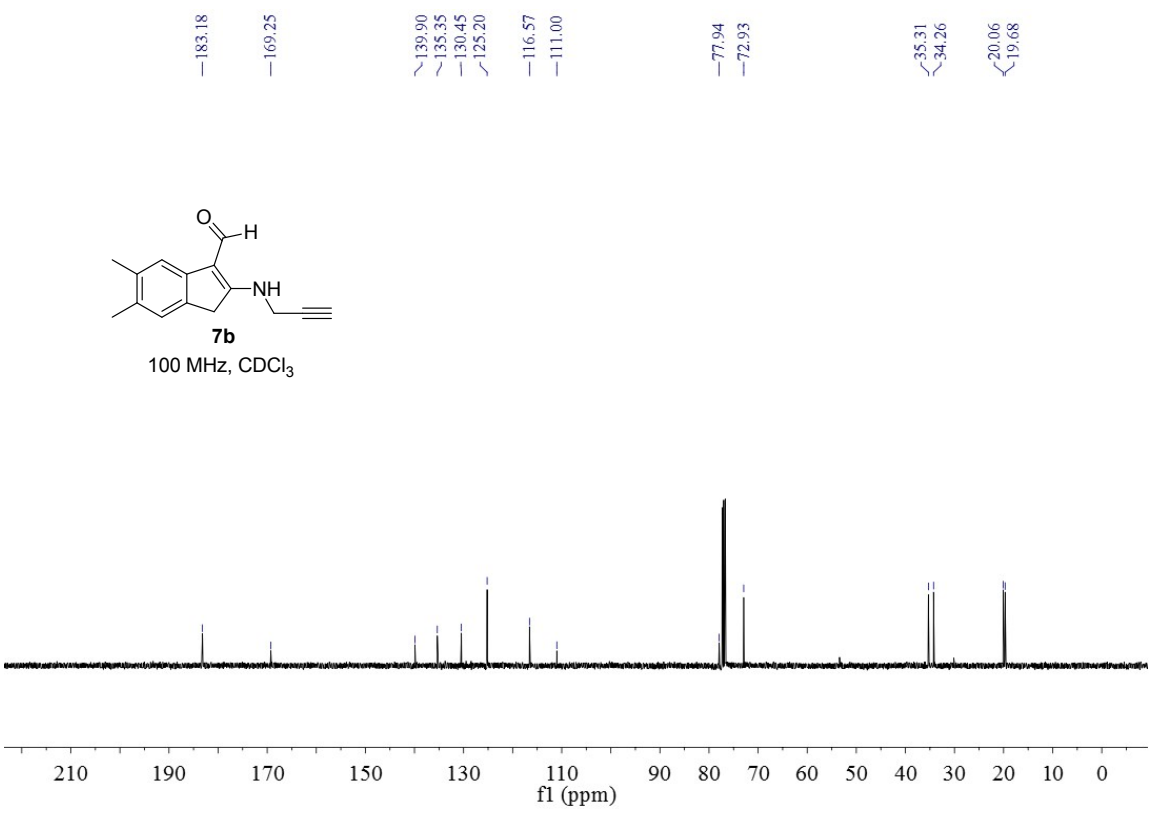
125 MHz, $CDCl_3$





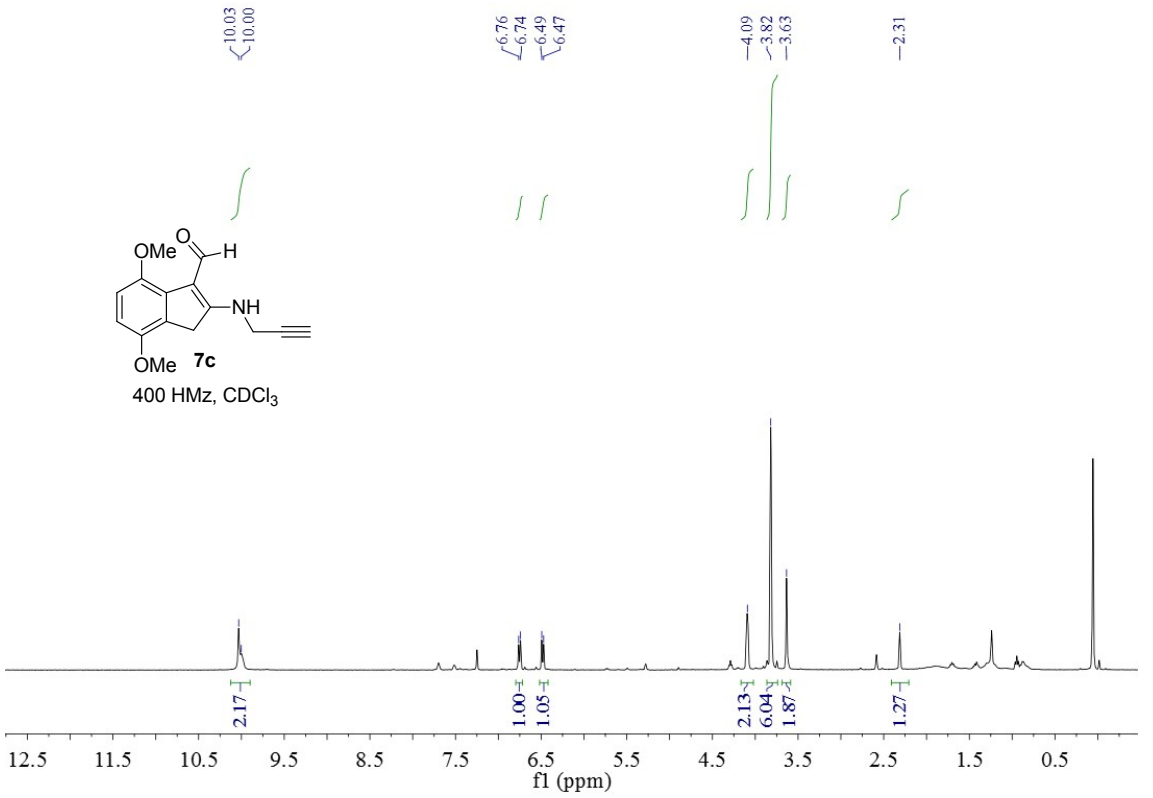
7b

400 MHz, $CDCl_3$



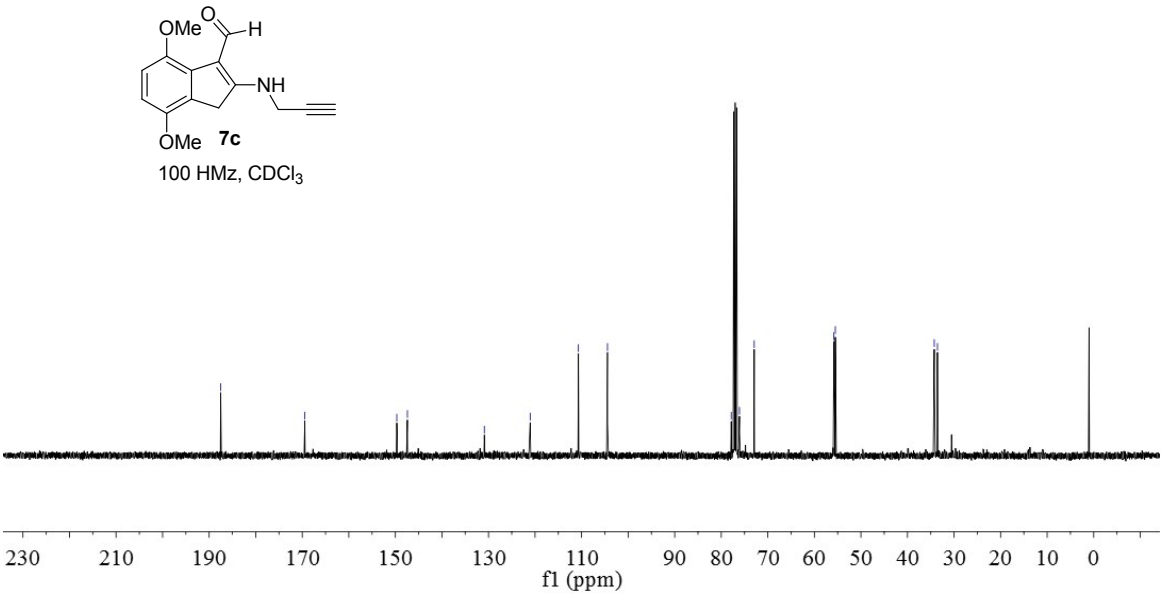
7b

100 MHz, $CDCl_3$



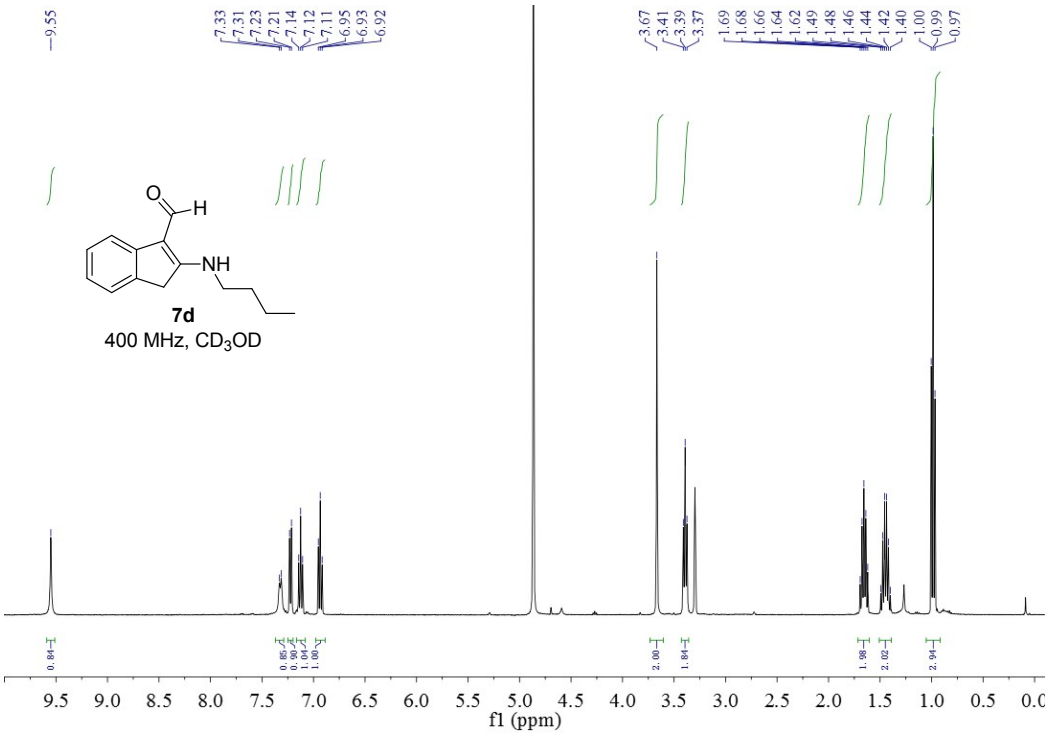
7c

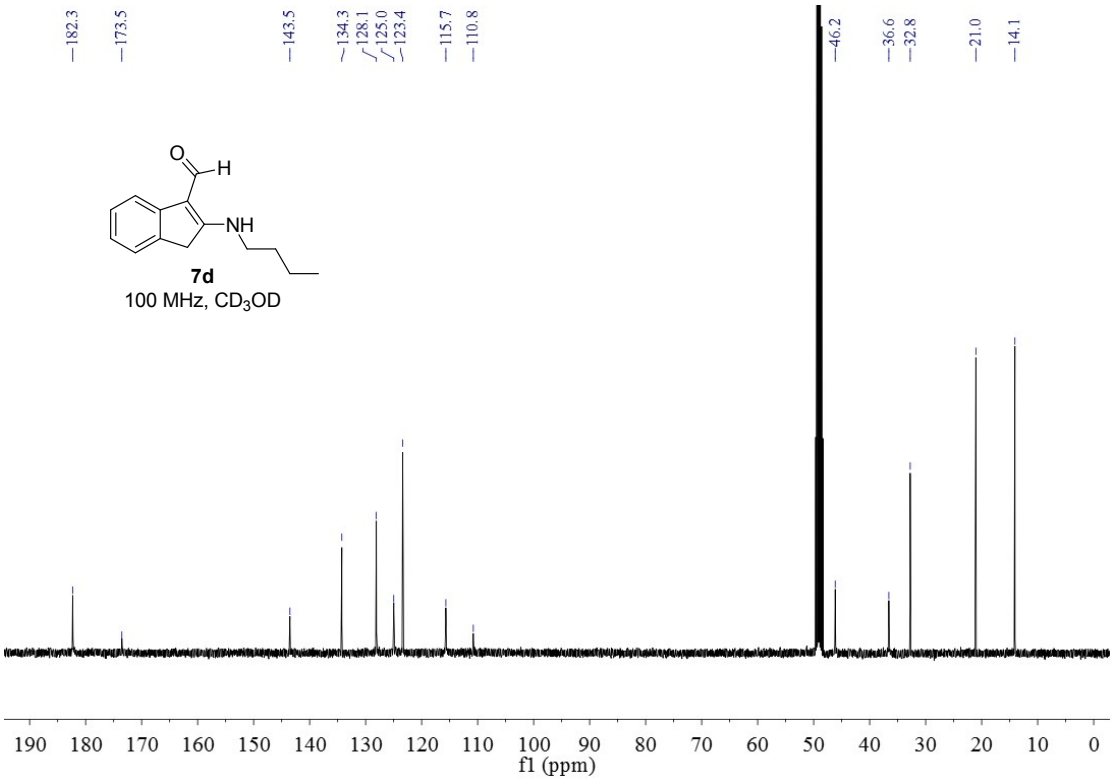
400 HMz, $CDCl_3$



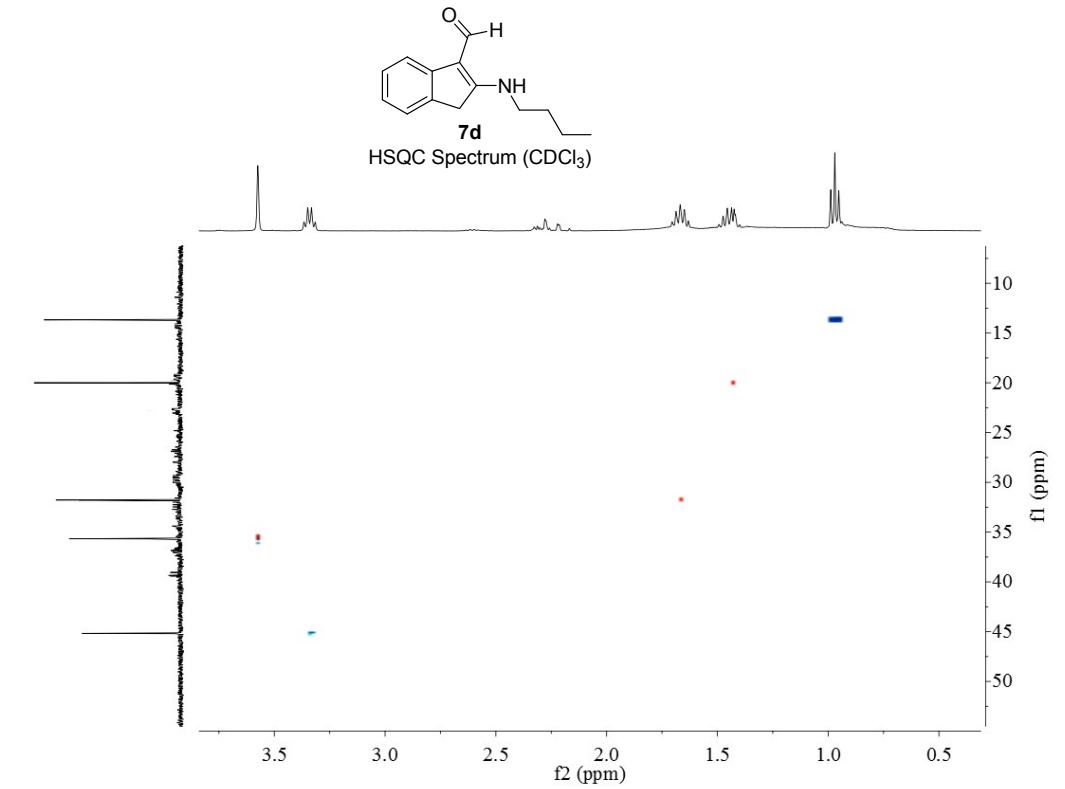
7c

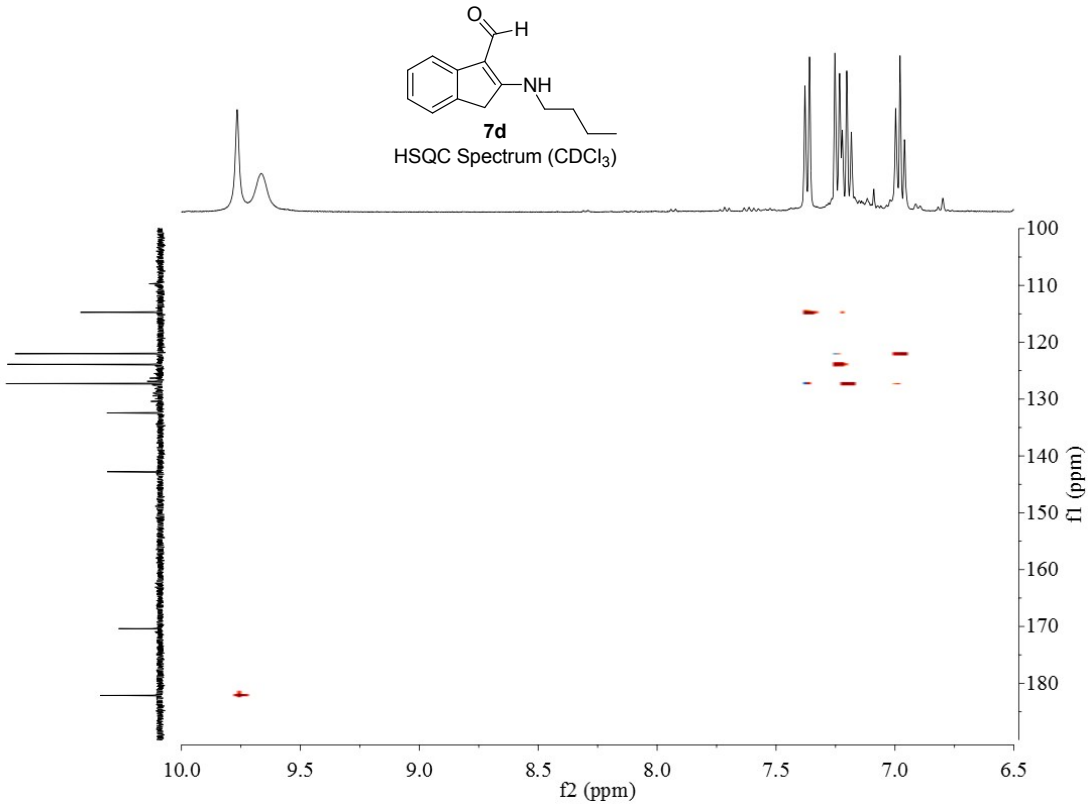
100 HMz, $CDCl_3$

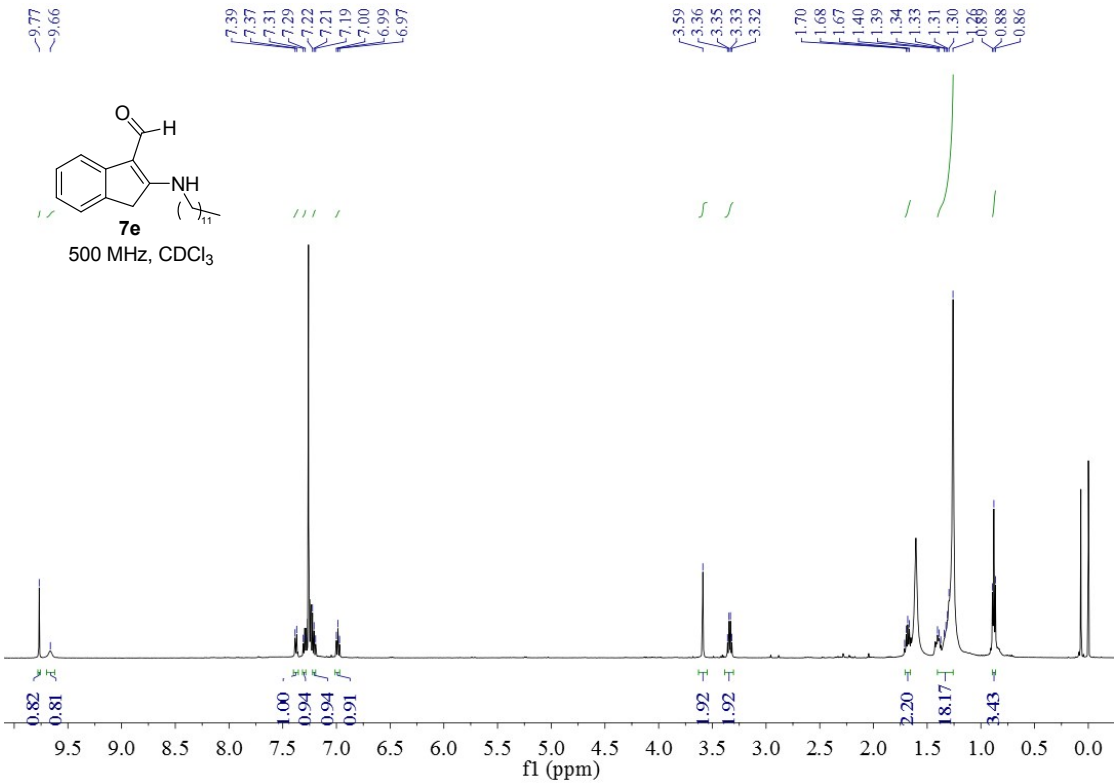

9.55
7.33
7.31
7.23
7.21
7.14
7.12
7.11
6.95
6.93
6.92
3.67
3.41
3.39
3.37
1.69
1.68
1.66
1.64
1.62
1.49
1.48
1.46
1.44
1.42
1.40
1.00
0.99
0.97
O
H
NH
7d
400 MHz, CD3OD
f1 (ppm)

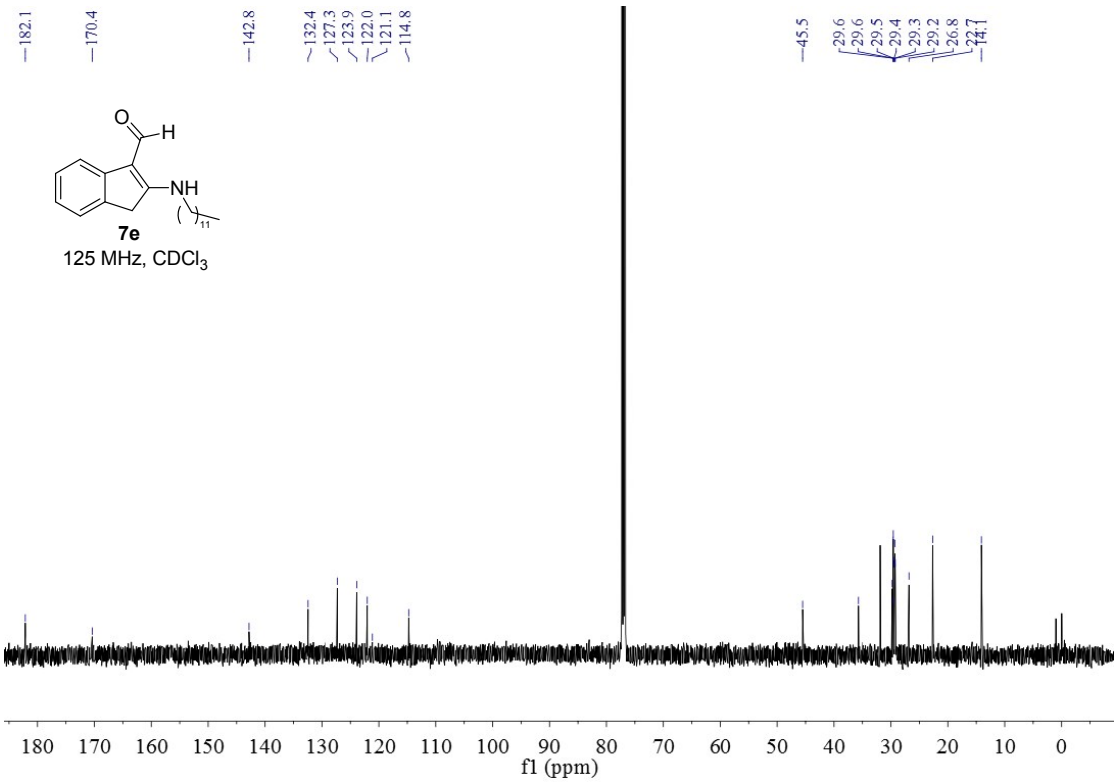

182.3
173.5
143.5
134.3
128.1
125.0
123.4
115.7
110.8
46.2
36.6
32.8
21.0
14.1
O
H
NH
7d
100 MHz, CD3OD
f1 (ppm)

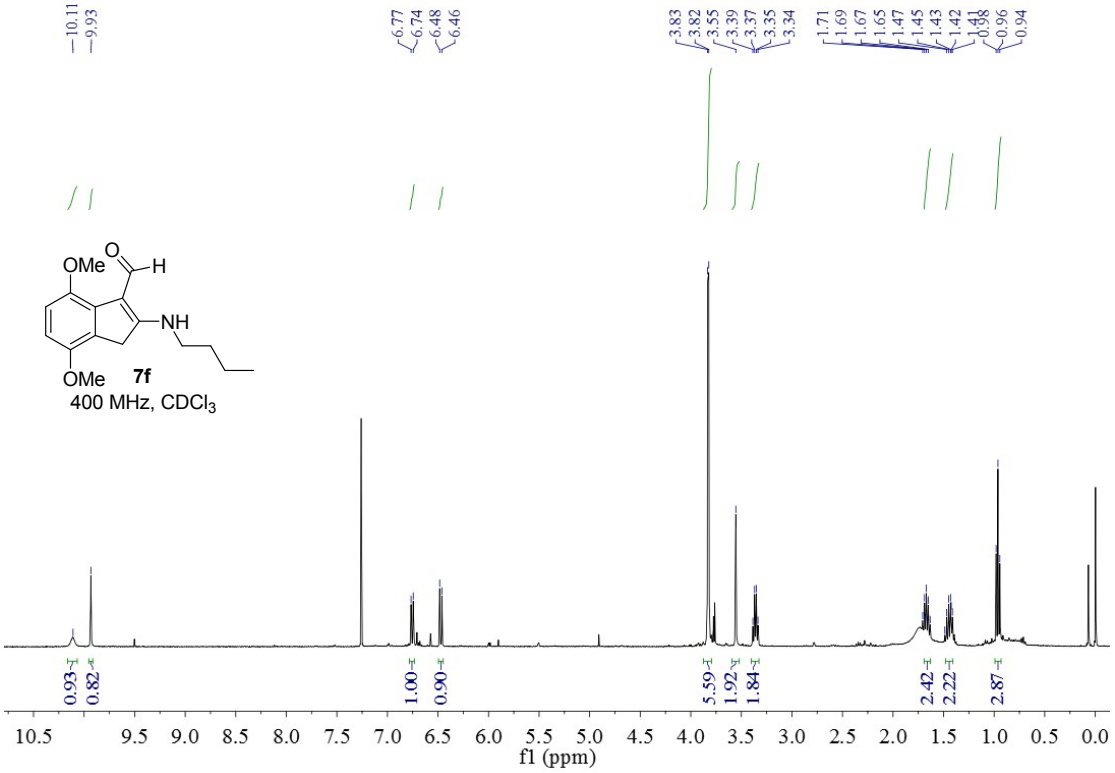
5. HSQC spectra of 7d

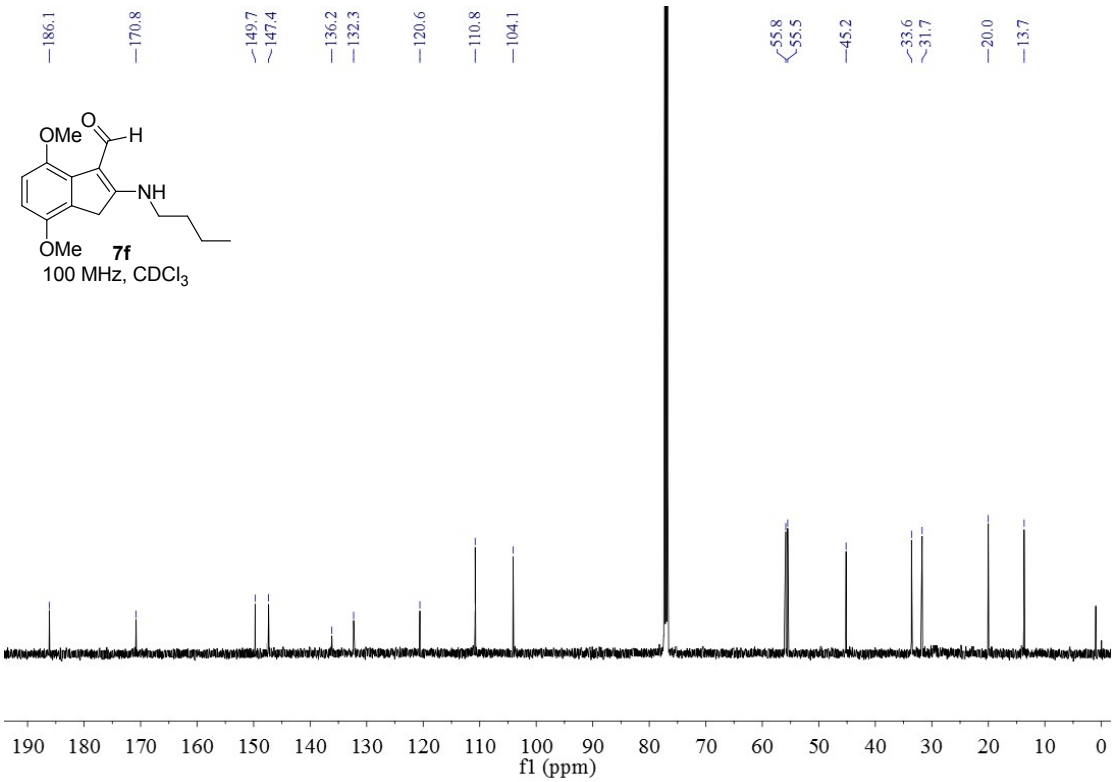





9.77
9.66
7.39
7.37
7.31
7.29
7.22
7.21
7.19
7.00
6.99
6.97
3.59
3.36
3.35
3.33
3.32
1.70
1.68
1.67
1.40
1.39
1.34
1.33
1.31
1.30
0.88
0.86
O
H
NH
11
7e
500 MHz, CDCl3
0.82
0.81
1.00
0.94
0.94
0.91
1.92
1.92
2.20
18.17
3.43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


182.1
170.4
142.8
132.4
127.3
123.9
122.0
121.1
114.8
45.5
29.6
29.6
29.5
29.4
29.3
29.2
26.8
14.1
O
H
NH
11
7e
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.11
9.93
6.77
6.74
6.48
6.46
3.83
3.82
3.55
3.39
3.37
3.35
3.34
1.71
1.69
1.67
1.65
1.47
1.45
1.43
1.42
1.41
0.98
0.96
0.94
OMe
O
H
NH
OMe
7f
400 MHz, CDCl3
0.93
0.82
1.00
0.90
5.59
1.92
1.84
2.42
2.22
2.87
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


186.1
170.8
149.7
147.4
136.2
132.3
120.6
110.8
104.1
55.8
55.5
45.2
33.6
31.7
20.0
13.7
OMe
O
H
NH
OMe
7f
100 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6. References

1 (a) E. Wolthuis, *J. Org. Chem*., 1961, **26**, 2215; (b) H. Hart, C. Lai, G. C. Nwokogu, S. Shamouilian, *Tetrahedron*, 1987, **43**, 5203; (c) G. Stork, E. E. van Tamelen, L. J. Friedman, A. W. Burgstahler, *J. Am. Chem. Soc.*, 1953, **75**, 384; (d) D. B. Millward, G. Sammis, R. M. Waymouth, *J. Org. Chem*., 2000, **65**, 3902; (e) M. Lautens, K. Fagnou,; V. Zunic, *Org. Lett.*, 2002, **4**, 3465.

2. A. L. Silberstein, S. D. Ramgren, N. K. Garg, *Org. Lett.*, 2012, **14**, 3796.