Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

An Unusual Reaction Mode of 1-Phenylpyrazolidinones toward Diazonaphthalen-2(1*H*)-ones Featuring with Cascade C(sp^2)−H and C(sp^3)−H Bond Cleavage

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I. General experimental information

Commercial reagents were used without further purification. 1-Phenylpyrazolidin-3-ones (**1**)[1], 1-diazonaphthalen-2(1*H*)-ones (**2**)[2] and $[RhCp^*Cl_2]_2$[3] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All 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. General Procedure for the Preparation of 1-Arylpyrazolidin-3-ones (1) and Diazonaphthalen-2(1*H*)-ones (2)

1.1 Preparation of 1-arylpyrazolidin-3-ones (1)[1]

To a solution of arylhydrazine hydrochloride (5 mmol) in dry pyridine (25 mL, 0.5 M) was added with 3-chloro-2,2-dimethylpropionyl chloride (5 mmol) at 0 ℃. It was allowed to warm to room temperature. Then, it was stirred at 100 ℃ for 8 h. The resulting mixture was cooled, neutralized to pH 2 using aqueous HCl (1 M), and extracted with DCM (30 mL × 3). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford the desired products.

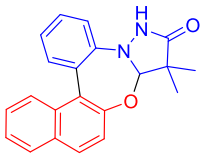
1.2 Preparation of diazonaphthalen-2(1*H*)-ones (2)[2]

To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (1.35 mmol) in MeCN (2 mL) was added with sodium azide (1.5 mmol) at -20 ℃ and the mixture was stirred for 30 min. Then, 2-naphthol (0.9 mmol) and triethylamine (1.8 mmol) in THF (4 mL) were added and the resulting mixture was stirred for 20 min. Upon completion, it was quenched with water and extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (5:1) as eluent to afford the desired compounds.

2. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3ii

To a reaction tube equipped with a stir bar were charged with 4,4-dimethyl-1-phenylpyrazolidin-3-one (**1a**, 57.0 mg, 0.3 mmol), MeCN (3 mL), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), AgOAc (100.1 mg, 0.6 mmol), TMBzOH (98.5 mg, 0.6 mmol), 4Å MS (50 mg) and 1-diazonaphthalen-2(1*H*)-one (**2a**, 76.5 mg, 0.45 mmol). The mixture was stirred at 100 ℃ under Ar for 12 h. Upon completion, it was cooled to room

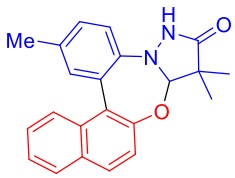
temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite, and then extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford product **3a**. **3b-3ii** were obtained in a similar manner.



3a

8,8-Dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3a)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (74.3 mg, 75%), mp 244.8-245.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.12 (m, 1H), 8.10 (s, 1H), 7.91-7.89 (m, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.57 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.50-7.47 (m, 3H), 7.42-7.39 (m, 1H), 7.28 (d, J = 9.0 Hz, 1H), 7.23 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 5.52 (s, 1H), 1.29 (s, 3H), 1.13 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 151.2, 146.5, 132.6, 132.0, 131.5, 130.2, 128.8, 128.6, 128.4, 126.9, 125.6, 125.4, 124.6, 122.8, 119.7, 115.9, 109.2, 43.6, 21.4, 18.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}N_2NaO_2$ 353.1260; found 353.1256.

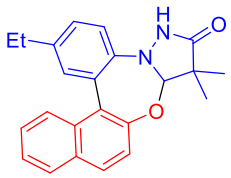


3b

8,8,14-Trimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3b)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (68.1 mg, 66%), mp 241.2-242.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.12 (m, 1H), 8.08 (s, 1H), 7.89-7.86 (m, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.51-7.45 (m, 2H), 7.37 (d, J = 1.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.25 (s, 1H), 7.19 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 5.45 (s, 1H), 2.39 (s, 3H), 1.27 (s, 3H), 1.12 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.3, 151.2, 144.1, 132.6,

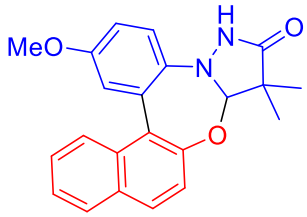
132.5, 132.2, 131.5, 130.1, 129.4, 128.6, 128.5, 126.8, 125.7, 125.4, 124.4, 119.8, 115.9, 108.9, 43.5, 21.5, 20.8, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{20}N_2NaO_2$ 367.1417; found 367.1405.



3c

14-Ethyl-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3c)

Eluent: petroleum ether/ethyl acetate (3:1). Light yellow solid (64.5 mg, 60%), mp 195.6-196.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15-8.13 (m, 1H), 7.90 (dd, J_1 = 7.2 Hz, J_2 = 3.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.52-7.47 (m, 3H), 7.41 (d, J = 1.8 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.23 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 5.54 (s, 1H), 2.70 (q, J = 7.8 Hz, 2H), 1.31 (s, 3H), 1.29 (t, J = 7.8 Hz, 3H), 1.15 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.2, 151.2, 144.2, 138.7, 132.6, 131.54, 131.46, 130.1, 128.59, 128.57, 128.2, 126.9, 125.6, 125.4, 124.5, 119.8, 115.8, 109.0, 43.5, 28.2, 21.5, 18.8, 15.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}N_2O_2$ 359.1754; found 359.1750.

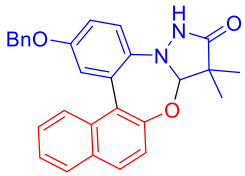


3d

14-Methoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3d)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (76.7 mg, 71%), mp 221.7-222.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.17-8.16 (m, 1H), 7.87-7.86 (m, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.49-7.45 (m, 2H), 7.34 (d, J = 9.0 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 7.13 (d, J = 2.4 Hz, 1H), 6.93 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz,

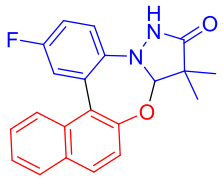
1H), 5.35 (s, 1H), 3.80 (s, 3H), 1.24 (s, 3H), 1.10 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 178.4, 155.4, 151.3, 139.9, 132.5, 131.4, 130.3, 128.6, 128.2, 127.0, 125.7, 125.5, 125.4, 119.9, 117.9, 116.9, 113.7, 108.6, 55.7, 43.3, 21.6, 18.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{20}N_2NaO_3$ 383.1366; found 383.1370.



3e

14-(Benzyloxy)-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3e)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (85.1 mg, 65%), mp 213.7-214.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 1H), 7.89-7.86 (m, 2H), 7.53 (s, 1H), 7.47-7.38 (m, 7H), 7.35 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.05 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 5.50 (s, 1H), 5.11 (d, J = 12.0 Hz, 1H), 5.07 (d, J = 12.0 Hz, 1H), 1.31 (s, 3H), 1.14 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 178.4, 154.5, 151.2, 140.2, 137.0, 132.5, 131.3, 130.4, 128.7, 128.6, 128.1, 128.0, 127.5, 127.1, 125.7, 125.43, 125.41, 119.8, 118.6, 116.9, 115.3, 108.9, 70.4, 43.3, 21.6, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}N_2O_3$ 437.1860; found 437.1863.

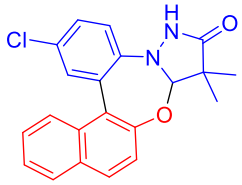


3f

14-Fluoro-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3f)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (68.9 mg, 66%), mp 239.2-240.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, J = 7.8 Hz, 1H), 7.95 (s, 1H), 7.91-7.89 (m, 2H), 7.54-7.49 (m, 2H), 7.44-7.42 (m, 1H), 7.31-7.30 (m, 2H), 7.11 (t, J = 7.2 Hz, 1H), 5.51 (s, 1H), 1.30 (s, 3H), 1.13 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz,

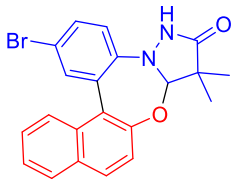
$CDCl_3$): δ 178.5, 158.8 (d, $^1J_{C-F}$ = 240.6 Hz), 151.4, 142.6 (d, $^4J_{C-F}$ = 2.1 Hz), 132.5, 131.2, 130.9, 128.7, 127.3, 127.2, 126.2 (d, $^3J_{C-F}$ = 7.7 Hz), 125.7, 125.1, 119.7, 118.6 (d, $^2J_{C-F}$ = 24.0 Hz), 117.1 (d, $^3J_{C-F}$ = 8.7 Hz), 115.2 (d, $^2J_{C-F}$ = 21.9 Hz), 109.1, 43.5, 21.5, 18.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -126.99 – -127.02 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}FN_2O_2$ 349.1347; found 349.1356.



3g

14-Chloro-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3g)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (84.1 mg, 77%), mp 259.2-260.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.56-7.50 (m, 4H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.37 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 5.56 (s, 1H), 1.32 (s, 3H), 1.14 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 151.4, 145.2, 132.5, 131.5, 131.2, 130.9, 128.7, 128.5, 128.2, 127.4, 127.0, 126.2, 125.7, 125.0, 119.7, 117.2, 109.3, 43.6, 21.3, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}ClN_2O_2$ 365.1051; found 365.1050.

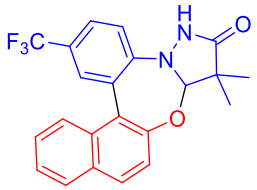


3h

14-Bromo-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3h)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (86.9 mg, 71%), mp 262.7-263.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 1.6 Hz, 1H), 7.57-7.51 (m, 4H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 5.56 (s, 1H), 1.32 (s, 3H), 1.14 (s, 3H). ^{13}C{^{1}H} NMR (150

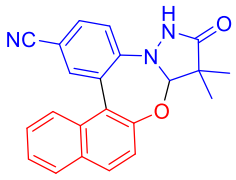
MHz, $CDCl_3$): δ 178.2, 151.4, 145.8, 134.3, 132.5, 131.5, 131.2, 131.0, 128.7, 127.5, 126.9, 126.6, 125.7, 125.0, 119.6, 117.6, 115.6, 109.3, 43.6, 21.3, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}BrN_2O_2$ 409.0546; found 409.0548.



3i

8,8-Dimethyl-14-(trifluoromethyl)-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3i)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (69.3 mg, 58%), mp 206.1-207.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 1.8 Hz, 1H), 7.66 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.56-7.51 (m, 2H), 7.32 (d, J = 9.0 Hz, 1H), 5.61 (s, 1H), 1.32 (s, 3H), 1.14 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.4, 151.6, 149.5, 132.6, 131.3, 131.1, 129.0 (q, $^3J_{C-F}$ = 3.3 Hz), 128.8, 127.6, 127.0, 125.79 (q, $^3J_{C-F}$ = 3.3 Hz), 125.78, 124.9 (q, $^2J_{C-F}$ = 32.9 Hz), 124.8, 124.3 (q, $^1J_{C-F}$ = 270.2 Hz), 119.6, 116.0, 109.6, 43.9, 21.0, 18.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.75 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}F_3N_2O_2$ 399.1315; found 399.1313.

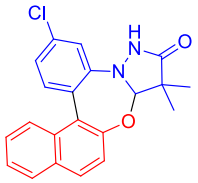


3j

8,8-Dimethyl-9-oxo-7a,8,9,10-tetrahydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepine-14-carbonitrile (3j)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (66.1 mg, 62%), mp 266.1-266.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.98-7.92 (m, 3H), 7.83 (d, J = 2.0 Hz, 1H), 7.65 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.59-7.52 (m, 3H), 7.31 (d, J = 8.8 Hz, 1H), 5.63 (s, 1H), 1.31 (s, 3H), 1.13 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz,

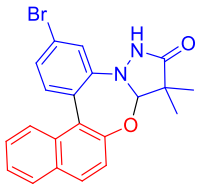
$CDCl_3$): δ 178.3, 151.3, 147.8, 134.7, 133.0, 132.6, 131.4, 130.6, 128.7, 127.4, 127.1, 125.6, 125.2, 123.0, 122.9, 119.6, 116.2, 109.3, 43.7, 21.2, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{17}N_3NaO_2$ 378.1213; found 378.1203.



3k

13-Chloro-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3k)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (78.6 mg, 72%), mp 213.4-214.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.3 (s, 1H), 8.12-8.08 (m, 2H), 8.02-8.00 (m, 1H), 7.63-7.56 (m, 3H), 7.49 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 5.70 (s, 1H), 1.24 (s, 3H), 1.01 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 176.3, 151.7, 148.9, 133.8, 133.6, 132.6, 131.2, 131.1, 129.3, 127.9, 127.2, 126.1, 125.0, 122.8, 122.5, 120.6, 116.1, 108.8, 43.6, 21.2, 19.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}ClN_2NaO_2$ 387.0871; found 387.0879.

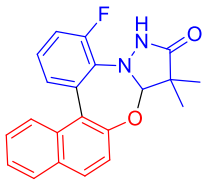


3l

13-Bromo-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3l)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (80.8 mg, 66%), mp 265.4-266.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.04 (m, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.65 (br s, 2H), 7.51-7.49 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 5.57 (s, 1H), 1.33 (s, 3H), 1.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.3, 151.3, 147.8, 133.2, 132.6, 131.3, 130.7, 128.7, 127.4, 127.2, 125.9, 125.6,

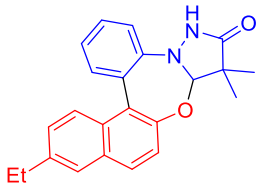
125.2, 123.5, 122.7, 119.7, 119.0, 109.4, 43.7, 21.2, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}BrN_2O_2$ 409.0546; found 409.0551.



3m

13-Fluoro-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3m)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (63.7 mg, 61%), mp 216.8-217.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.06 (m, 2H), 7.92-7.89 (m, 2H), 7.51-7.49 (m, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.15-7.11 (m, 2H), 5.38 (s, 1H), 1.34 (s, 3H), 1.27 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.3, 154.8 (d, $^1J_{C\text{-}F}$ = 250.0 Hz), 151.6, 132.8 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 132.6, 131.5, 130.8, 128.6, 128.5, 128.4, 128.0 (d, $^3J_{C\text{-}F}$ = 3.3 Hz), 127.6, 127.1, 125.5 (d, $^2J_{C\text{-}F}$ = 12.2 Hz), 123.2 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 119.6, 117.5 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 109.3, 44.0, 21.5, 17.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -126.91 – -126.96 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}FN_2O_2$ 349.1347; found 349.1338.

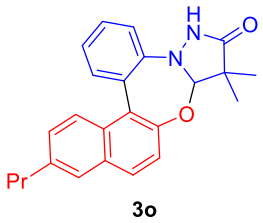


3n

3-Ethyl-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3n)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (73.1 mg, 68%), mp 245.4-246.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.02 (m, 2H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.67 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40-7.34 (m, 2H), 7.25-7.19 (m, 2H), 5.48 (s, 1H), 2.81 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 3H), 1.12 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 150.7, 146.5, 141.4, 132.9, 131.9,

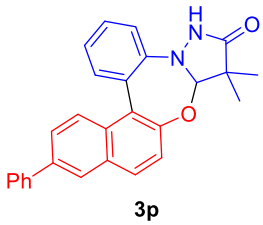
129.9, 129.7, 128.7, 128.1, 126.2, 125.5, 124.8, 122.8, 119.6, 115.8, 109.2, 43.6, 28.8, 21.4, 18.7, 15.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{22}N_2NaO_2$ 381.1573; found 381.1571.



3o

8,8-Dimethyl-3-propyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3o)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (73.7 mg, 66%), mp 217.8-218.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.80-7.78 (m, 2H), 7.66 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41-7.33 (m, 2H), 7.26-7.20 (m, 2H), 5.52 (s, 1H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.78-1.69 (m, 2H), 1.29 (s, 3H), 1.13 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 150.6, 146.5, 139.8, 132.8, 131.9, 129.9, 129.7, 128.7, 128.5, 128.1, 127.1, 125.4, 124.8, 122.8, 119.6, 115.8, 109.2, 43.6, 37.9, 24.4, 21.4, 18.7, 13.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{24}N_2NaO_2$ 395.1730; found 395.1719.

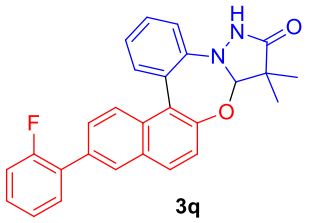


3p

8,8-Dimethyl-3-phenyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3p)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (74.3 mg, 61%), mp 259.6-260.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.67-7.64 (m, 4H), 7.53-7.52 (m, 1H), 7.43-7.41 (m, 3H), 7.36-7.31 (m, 2H), 7.25 (d, *J* = 9.0 Hz, 1H), 7.19-7.17 (m, 1H), 5.49 (s, 1H), 1.24 (s, 3H), 1.07 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.3, 151.3, 146.6, 140.6, 138.1, 132.9,

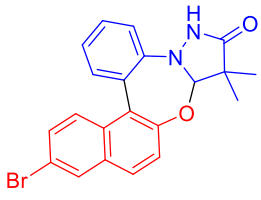
132.0, 130.6, 130.5, 129.0, 128.9, 128.3, 127.6, 127.4, 126.6, 126.3, 126.2, 124.6, 122.9, 120.2, 115.9, 109.2, 43.6, 21.4, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}N_2O_2$ 407.1754; found 407.1756.



3q

3-(2-Fluorophenyl)-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3q)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (91.6 mg, 72%), mp 251.2-252.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.8 Hz, 1H), 8.01 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.63 (dt, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.55 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.49 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.32-7.28 (m, 2H), 7.21-7.18 (m, 2H), 7.16-7.11 (m, 2H), 5.53 (s, 1H), 1.27 (s, 3H), 1.09 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.1, 160.0 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 151.5, 146.6, 133.0, 132.6, 132.0, 130.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.7, 130.6, 129.3 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 128.9, 128.7 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 128.6 (d, $^2J_{C\text{-}F}$ = 13.1 Hz), 128.4, 128.1 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 125.7, 124.56 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 124.55, 123.0, 120.2, 116.3 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 115.9, 109.4, 43.6, 21.4, 18.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.69 – -117.81 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}FN_2O_2$ 425.1660; found 425.1661.

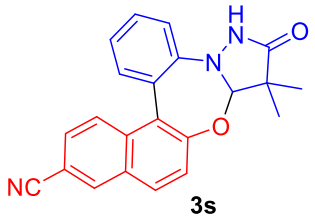


3r

3-Bromo-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3r)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (77.1 mg, 63%), mp 251.8-252.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.90 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.56-7.42 (m, 4H),

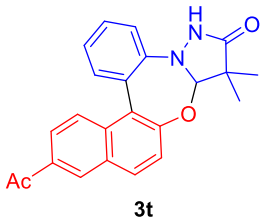
7.33-7.24 (m, 2H), 5.54 (s, 1H), 1.30 (s, 3H), 1.13 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 178.2, 151.4, 146.6, 133.7, 131.9, 130.5, 130.2, 130.0, 129.2, 129.1, 128.9, 127.4, 124.1, 123.0, 121.0, 119.6, 116.0, 109.2, 43.6, 21.4, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}BrN_2O_2$ 409.0546; found 409.0541.



3s

8,8-Dimethyl-9-oxo-7a,8,9,10-tetrahydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepine-3-carbo nitrile (3s)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (75.6 mg, 71%), mp 261.4-262.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.20 (s, 1H), 8.12-8.09 (m, 2H), 8.05 (d, J = 8.8 Hz, 1H), 7.71-7.69 (m, 1H), 7.52-7.47 (m, 3H), 7.41 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 5.63 (s, 1H), 1.20 (s, 3H), 0.95 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 176.3, 152.3, 147.5, 132.4, 131.7, 131.5, 131.1, 130.9, 129.7, 129.0, 127.8, 127.1, 123.4, 122.9, 121.5, 121.4, 116.6, 108.8, 43.4, 21.5, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}N_3O_2$ 356.1394; found 356.1376.

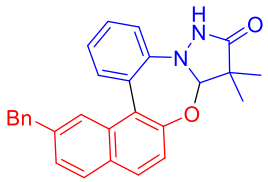


3t

3-Acetyl-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3t)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (78.2 mg, 70%), mp 259.1-260.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 1.2 Hz, 1H), 8.11 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.39-7.31 (m, 3H), 7.21-7.17 (m, 1H), 5.54 (s, 1H), 2.67 (s, 3H), 1.27 (s, 3H), 1.08 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 197.8, 178.1, 153.1, 146.6, 134.0, 133.9, 132.0, 131.9, 131.8, 130.6, 129.2, 128.9,

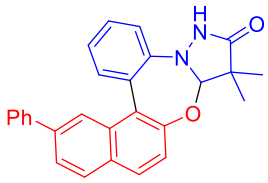
126.2, 124.9, 124.1, 123.1, 120.9, 116.0, 109.3, 43.6, 26.7, 21.4, 18.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}N_2NaO_3$ 395.1366; found 395.1371.



3u

2-Benzyl-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3u)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (78.2 mg, 62%), mp 213.4-214.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.90 (s, 1H), 7.83-7.79 (m, 2H), 7.52-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.32-7.23 (m, 4H), 7.21-7.16 (m, 4H), 5.54 (s, 1H), 4.08 (s, 2H), 1.29 (s, 3H), 1.13 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 151.4, 146.4, 140.7, 139.9, 131.8, 131.6, 131.2, 129.9, 128.9, 128.74, 128.71, 128.5, 127.9, 127.1, 126.2, 124.9, 124.7, 122.8, 119.1, 115.9, 109.1, 43.6, 42.3, 21.4, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}N_2O_2$ 421.1911; found 421.1910.

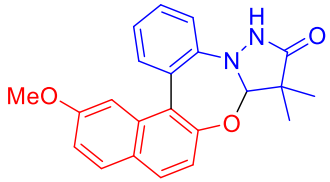


3v

8,8-Dimethyl-2-phenyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3v)

Eluent: petroleum ether/ethyl acetate (3:1). Light brown solid (64.6 mg, 53%), mp 146.8-147.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (d, J = 0.6 Hz, 1H), 8.16 (s, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.76 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.64-7.61 (m, 3H), 7.50-7.49 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.43-7.40 (m, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 7.24 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 5.52 (s, 1H), 1.29 (s, 3H), 1.15 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 151.6, 146.6, 141.1, 139.7, 131.9, 131.8,

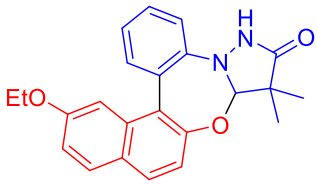
131.7, 129.9, 129.1, 128.9, 128.6, 127.6, 127.5, 125.3, 124.7, 123.6, 123.0, 119.8, 116.0, 109.2, 43.6, 21.4, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_2NaO_2$ 429.1573; found 429.1574.



3w

2-Methoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3w)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (78.9 mg, 73%), mp 261.1-262.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.64 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.53-7.51 (m, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.43-7.40 (m, 1H), 7.28 (s, 1H), 7.24 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.15 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 5.58 (s, 1H), 3.81 (s, 3H), 1.33 (s, 3H), 1.15 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.2, 158.7, 151.9, 146.5, 132.9, 131.3, 130.11, 130.07, 128.7, 128.1, 127.0, 125.0, 122.9, 118.0, 117.2, 116.0, 109.2, 104.2, 55.3, 43.5, 21.4, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_2O_3$ 361.1547; found 361.1542.

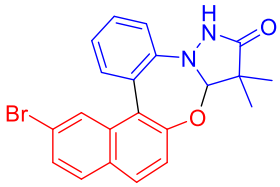


3x

2-Ethoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3x)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (84.2 mg, 75%), mp 217.8-218.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.79-7.77 (m, 2H), 7.62 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 8.8 Hz, 2H), 5.53 (s, 1H), 4.10-4.02 (m, 1H), 4.01-3.94 (m, 1H), 1.42 (t, J = 7.2 Hz, 3H), 1.30 (s, 3H), 1.13 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$):

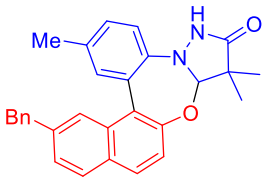
δ 178.4, 158.0, 151.9, 146.5, 132.9, 131.3, 130.1, 130.0, 128.7, 128.0, 127.0, 125.0, 122.8, 118.3, 117.1, 116.0, 109.1, 105.0, 63.5, 43.6, 21.4, 18.7, 14.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}N_2O_3$ 375.1703; found 375.1694.



3y

2-Bromo-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3y)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (67.3 mg, 55%), mp 275.1-275.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.2 (s, 1H), 8.15-8.11 (m, 2H), 8.06 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.54-7.49 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 5.66 (s, 1H), 1.22 (s, 3H), 0.97 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 176.3, 152.3, 147.5, 132.4, 131.7, 131.5, 131.1, 130.9, 129.7, 129.0, 127.8, 127.1, 123.4, 122.9, 121.5, 121.4, 116.6, 108.8, 43.4, 21.5, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}BrN_2O_2$ 409.0546; found 409.0543.

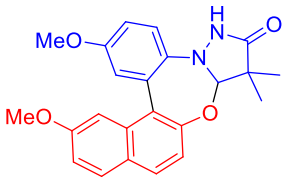


3z

2-Benzyl-8,8,14-trimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3z)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (78.2 mg, 60%), mp 184.9-185.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.92 (s, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.35-7.32 (m, 2H), 7.29-7.23 (m, 4H), 7.21-7.16 (m, 4H), 5.49 (s, 1H),4.07 (s, 2H), 2.33 (s, 3H), 1.27 (s, 3H), 1.12 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 151.4, 144.0, 140.7, 140.0, 132.5, 132.2, 131.7, 131.2, 129.8, 129.3, 129.0, 128.7, 128.6, 128.0, 127.1, 126.3,

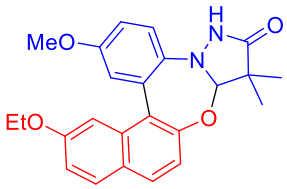
124.9, 124.5, 119.2, 115.9, 108.9, 43.5, 42.4, 21.5, 20.8, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{27}N_2O_2$ 435.2067; found 435.2064.



3aa

2,14-Dimethoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3aa)

Eluent: petroleum ether/ethyl acetate (3:1). Brown solid (71.4 mg, 61%), mp 228.3-229.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.54-7.52 (m, 2H), 7.41 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 2.8 Hz, 1H), 7.19-7.14 (m, 2H), 6.96 (dd, J_1 =8.8 Hz, J_2 = 2.4 Hz, 1H), 5.51 (s, 1H), 3.82 (s, 6H), 1.31 (s, 3H), 1.14 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.5, 158.7, 155.6, 152.0, 139.9, 132.7, 130.2, 128.0, 126.9, 126.0, 118.1, 117.4, 117.1, 116.7, 114.1, 108.7, 104.0, 55.7, 55.3, 43.3, 21.7, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}N_2O_4$ 391.1652; found 391.1653.

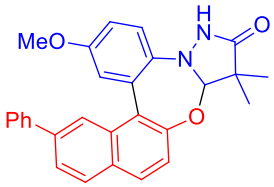


3bb

2-Ethoxy-14-methoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3bb)

Eluent: petroleum ether/ethyl acetate (3:1). Brown solid (52.1 mg, 43%), mp 125.6-126.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.53 (s, 1H), 7.50 (s, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.16-7.14 (m, 2H), 6.95 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 5.49 (s, 1H), 4.08-3.98 (m, 2H), 3.82 (s, 3H), 1.43 (t, J = 6.8 Hz, 3H), 1.30 (s, 3H), 1.13 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.4, 158.1, 155.6, 152.0, 139.9, 132.8, 130.15, 130.12, 128.0, 126.8, 126.1, 118.4, 117.2, 117.0, 116.8, 114.1, 108.7, 104.8,

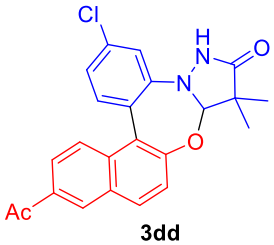
63.5, 55.7, 43.3, 21.7, 18.8, 14.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}N_2O_4$ 405.1809; found 405.1807.



3cc

14-Methoxy-8,8-dimethyl-2-phenyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3cc)

Eluent: petroleum ether/ethyl acetate (3:1). Light brown solid (77.2 mg, 59%), mp 203.4-204.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.75 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.63-7.62 (m, 2H), 7.46-7.41 (m, 3H), 7.38-7.35 (m, 2H), 7.32 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 3.0 Hz, 1H), 6.97 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 5.52 (s, 1H), 3.81 (s, 3H), 1.32 (s, 3H), 1.15 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.3, 155.6, 151.7, 141.0, 140.0, 139.8, 131.72, 131.67, 130.2, 129.2, 128.9, 128.4, 127.6, 127.5, 125.8, 125.3, 123.4, 119.9, 117.6, 117.0, 114.1, 108.9, 55.7, 43.3, 21.7, 18.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}N_2O_3$ 437.1860; found 437.1857.

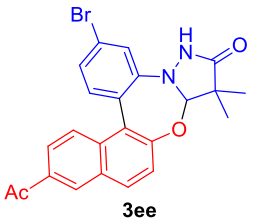


3dd

3-Acetyl-13-chloro-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3dd)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (63.4 mg, 52%), mp 262.5-263.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.10 (d, J = 9.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.53 (s, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.23 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 5.61 (s, 1H), 2.74 (s, 3H), 1.34 (s, 3H), 1.18

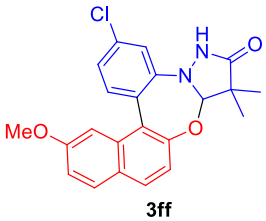
(s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 197.7, 178.1, 153.2, 147.8, 135.2, 134.2, 133.8, 133.0, 132.2, 131.8, 130.6, 127.9, 125.8, 125.2, 123.1, 122.4, 120.8, 116.4, 109.3, 43.8, 26.7, 21.2, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}ClN_2NaO_3$ 429.0976; found 429.0971.



3ee

3-Acetyl-13-bromo-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3ee)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (82.4 mg, 61%), mp 232.3-233.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.3 (s, 1H), 8.83 (s, 1H), 8.33 (d, J = 9.2 Hz, 1H), 8.09-8.04 (m, 2H), 7.60 (d, J = 8.8 Hz, 1H), 7.52 (s, 1H), 7.49-7.47 (m, 2H), 5.74 (s, 1H), 2.74 (s, 3H), 1.24 (s, 3H), 1.01 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6): δ 198.1, 176.2, 153.5, 148.9, 134.1, 133.9, 133.3, 133.1, 131.9, 131.6, 127.6, 125.6, 125.4, 122.8, 122.6, 121.7, 119.0, 108.8, 43.6, 27.2, 21.2, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}BrN_2O_3$ 451.0652; found 451.0645.

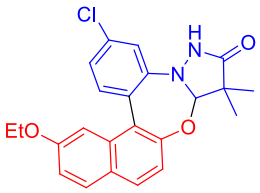


3ff

13-Chloro-2-methoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-b][1,3]oxazepin-9(10*H*)-one (3ff)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (73.3 mg, 62%), mp 240.7-241.5℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.81-7.78 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 2.0 Hz, 1H), 7.20 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 5.55 (s, 1H), 3.82 (s, 3H), 1.32 (s, 3H), 1.17 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 178.6, 158.8, 152.0, 147.7, 134.6, 132.8, 132.3,

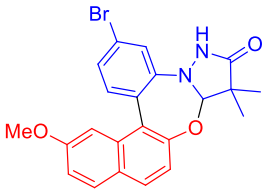
130.3, 130.2, 128.0, 126.1, 123.3, 122.8, 118.2, 117.1, 116.3, 109.1, 103.8, 55.3, 43.8, 21.2, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}ClN_2NaO_3$ 417.0976; found 417.0973.



3gg

13-Chloro-2-ethoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3gg)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (79.6 mg, 65%), mp 227.7-228.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.82-7.78 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.15 (d, J = 8.8 Hz, 2H), 5.57 (s, 1H), 4.11-3.96 (m, 2H), 1.44 (t, J = 6.8 Hz, 3H), 1.32 (s, 3H), 1.17 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.5, 158.2, 152.0, 147.7, 134.5, 132.8, 132.3, 130.3, 130.1, 128.0, 126.0, 123.4, 122.8, 118.5, 117.0, 116.3, 109.2, 104.6, 63.5, 43.7, 21.2, 18.8, 14.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{21}ClN_2NaO_3$ 431.1133; found 431.1135.

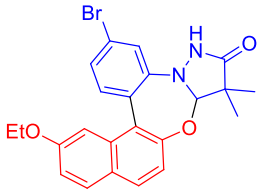


3hh

13-Bromo-2-methoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3hh)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (86.7 mg, 66%), mp 218.9-219.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.82-7.78 (m, 2H), 7.65 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.37-7.34 (m, 2H), 7.16 (d, J = 8.8 Hz, 2H), 5.56 (s, 1H), 3.82 (s, 3H), 1.32 (s, 3H), 1.17 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.5, 158.9, 152.0, 147.8, 132.7, 132.5, 130.4, 130.2, 128.0, 126.1, 125.8, 123.9, 122.6, 119.2, 118.2, 117.1, 109.2, 103.8, 55.3, 43.8, 21.2, 18.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}BrN_2O_3$ 439.0652; found

439.0650.



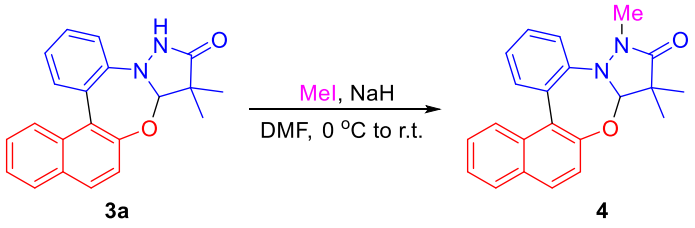
3ii

13-Bromo-2-ethoxy-8,8-dimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (3ii)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (74.6 mg, 55%), mp 229.8-228.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.81-7.78 (m, 2H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.35-7.34 (m, 2H), 7.16-7.14 (m, 2H), 5.56 (s, 1H), 4.08-4.04 (m, 1H), 4.02-3.98 (m, 1H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H), 1.17 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.5, 158.2, 151.9, 147.8, 132.8, 132.6, 130.4, 130.1, 128.0, 126.0, 125.8, 123.9, 122.5, 119.1, 118.5, 117.0, 109.2, 104.6, 63.6, 43.8, 21.2, 18.8, 14.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}BrN_2O_3$ 453.0808; found 453.0813.

3. Structural elaborations of 3a

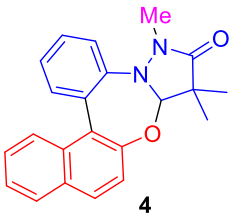
3.1 Synthesis of 4 from 3a[4]



3a **4**

To a reaction tube equipped with a stir bar were added NaH (5.8 mg, 0.24 mmol) in dry DMF (1 mL) and **3a** (66.0 mg, 0.2 mmol) in dry DMF (0.5 mL) in portions at 0 °C and stirred for 15 min. The reaction mixture was then warmed to room temperature and stirred for 1 h. After cooling to 0 °C again, MeI (15 μL, 0.24 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 30 min. Upon completion, it was cooled to 0 °C, quenched with saturated solution of NH_4Cl_2 (5 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and

brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford product **4** (34.4 mg, 50%).

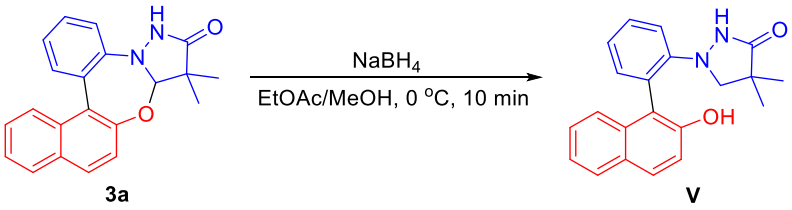


4

8,8,10-Trimethyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (4)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (34.4 mg, 50%), mp 196.4-197.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.18 (m, 1H), 7.93-7.89 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.53-7.47 (m, 2H), 7.43-7.39 (m, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.26-7.23 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.52 (s, 1H), 3.10 (s, 3H), 1.32 (s, 3H), 1.12 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.0, 151.2, 144.6, 132.6, 132.2, 131.4, 130.2, 128.63, 128.60, 128.4, 126.8, 125.7, 125.6, 125.4, 122.9, 119.8, 116.4, 108.2, 44.1, 31.5, 22.1, 18.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_2O_2$ 345.1598; found 345.1587.

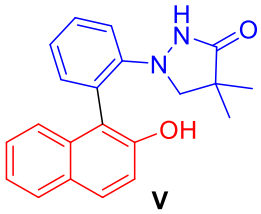
3.2. Synthesis of V from 3a[5]



3a **V**

To a reaction tube equipped with a stir bar were added **3a** (66.0 mg, 0.2 mmol), ethyl acetate (2 mL) and methanol (0.2 mL). It was then cooled to 0 °C and sodium borohydride (15.1 mg, 0.4 mmol) was added portionwise with stirring. The resulting mixture was stirred at 0 °C for 10 h. Upon completion, it was quenched with saturated solution of $NaHCO_3$ (5 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using

petroleum ether/ethyl acetate (3:1) as eluent to afford product **V** (29.9 mg, 45%).



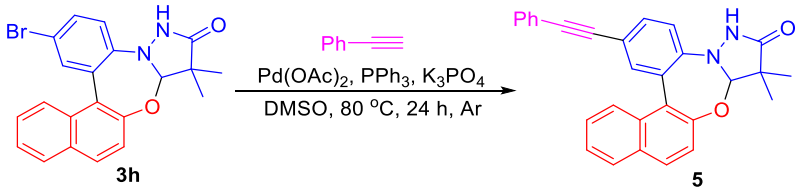
V

1-(2-(2-Hydroxynaphthalen-1-yl)phenyl)-4,4-dimethylpyrazolidin-3-one (V)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (29.9 mg, 45%), mp 221.7-222.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (t, *J* = 9.0 Hz, 2H), 7.77 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.42-7.38 (m, 2H), 7.37-7.35 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 3.19 (d, *J* = 11.4 Hz, 1H), 2.94 (d, *J* = 11.4 Hz, 1H), 1.02 (s, 3H), 0.99 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.6, 150.6, 149.9, 135.0, 133.3, 130.0, 129.8, 129.2, 128.3, 126.7, 126.1, 124.7, 124.2, 123.6, 119.6, 119.5, 116.2, 67.5, 40.4, 24.1, 22.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{20}N_2NaO_2$ 355.1417; found 355.1406.

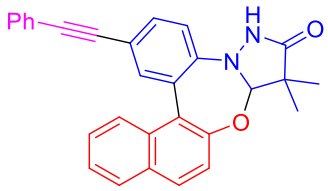
4. Structural elaborations of 3h

4.1 Synthesis of 5 from 3h[6]



3h **5**

To a reaction tube equipped with a stir bar were added **3h** (39.5 mg, 0.1 mmol), ethynylbenzene (16.5 μL, 0.15 mmol), PPh_3 (5.2 mg, 0.02 mmol), K_3PO_4 (25.5 mg, 0.12 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and DMSO (1 mL), and the resulting mixture was stirred at 80 ℃ under Ar for 24 h. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as the eluent to give **5** (33 mg, 77%).

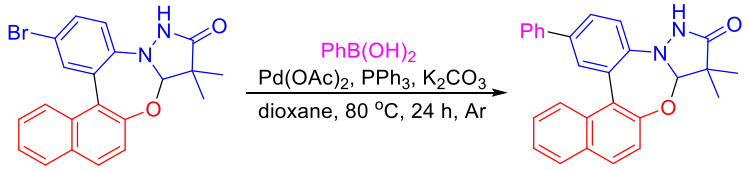


5

8,8-Dimethyl-14-(phenylethynyl)-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (5)

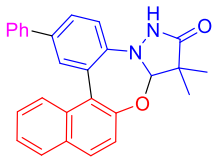
Eluent: petroleum ether/ethyl acetate (3:1). White solid (33 mg, 77%), mp 219.2-220.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 1H), 7.92-7.89 (m, 2H), 7.75 (d, J = 1.6 Hz, 1H), 7.68 (s, 1H), 7.59 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.56-7.47 (m, 5H), 7.35-7.30 (m, 4H), 5.58 (s, 1H), 1.32 (s, 3H), 1.15 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.2, 151.4, 146.6, 135.1, 132.6, 132.1, 131.6, 131.4, 130.6, 128.6, 128.4, 128.2, 127.5, 127.3, 125.6, 125.4, 124.7, 123.3, 119.6, 117.7, 116.0, 109.4, 89.3, 89.0, 43.8, 21.2, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}N_2O_2$ 431.1754; found 431.1740

4.2 Synthesis of 6 from 3h[7]



3h **6**

To a reaction tube equipped with a stir bar were added **3h** (40.8 mg, 0.1 mmol), phenylboronic acid (24.4 mg, 0.2 mmol), PPh_3 (15.7 mg, 0.06 mmol), K_2CO_3 (55.3 mg, 0.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and dioxane (1 mL). After the tube was sealed, the mixture was stirred at 80 ℃ under Ar for 24 h. Upon completion, it was diluted with ethyl acetate (10 mL) and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as the eluent to give **6** (26.9 mg, 66%).

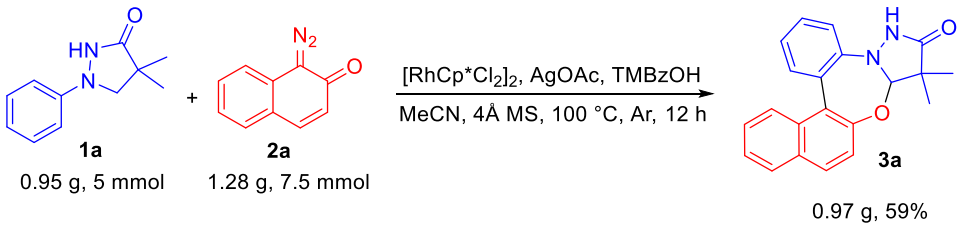


6

8,8-Dimethyl-14-phenyl-7a,8-dihydrobenzo[*d*]naphtho[1,2-*f*]pyrazolo[5,1-*b*][1,3]oxazepin-9(10*H*)-one (6)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (26.9 mg, 66%), mp 179.7-180.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19-8.17 (m, 1H), 7.93-7.89 (m, 2H), 7.83 (d, J = 1.8 Hz, 2H), 7.65 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H) 7.56 (d, J = 8.4 Hz, 1H), 7.51-7.48 (m, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.35-7.32 (m, 2H), 5.58 (s, 1H), 1.33 (s, 3H), 1.19 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 178.2, 151.4, 145.8, 140.2, 135.7, 132.7, 131.6, 130.6, 130.4, 128.9, 128.7, 128.3, 127.3, 127.17, 127.15, 126.8, 125.5, 124.9, 119.8, 116.4, 109.2, 43.7, 21.4, 18.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_2NaO_2$ 429.1573; found 429.1583.

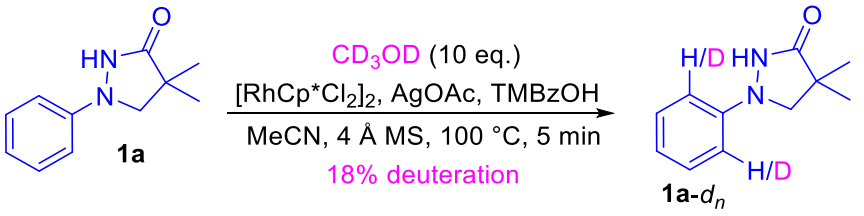
5. Gram-scale synthesis of 3a



To a reaction tube equipped with a stir bar were charged with 4,4-dimethyl-1-phenylpyrazolidin-3-one (**1a**, 0.95 g, 5 mmol), MeCN (30 mL), $[RhCp^*Cl_2]_2$ (30.9 mg, 0.05 mmol), AgOAc (1.67 g, 10 mmol), TMBzOH (1.64 g, 10 mmol), 4Å MS (500 mg) and 1-diazonaphthalen-2(1*H*)-one (**2a**, 1.28 g, 7.5 mmol). The mixture was stirred at 100 ℃ under Ar for 12 h. Upon completion, it was cooled to room temperature, quenched with saturated solution of $NaHCO_3$ (10 mL), and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford product **3a** (0.97 g, 59%).

III. Mechanism studies

1. H/D exchange experiment (I)



(a)

To a reaction tube equipped with a stir bar were charged with 4,4-dimethyl-1-phenylpyrazolidin-3-one (**1a**, 57.0 mg, 0.3 mmol), CH_3CN (3 mL), CD_3OD (0.24 mL, 3 mmol), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), AgOAc (100.1 mg, 0.6 mmol), TMBzOH (98.5 mg, 0.6 mmol) and 4Å MS (50 mg). The mixture was stirred at 100 ℃ under Ar for 5 min. It was then cooled to room temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford a mixture of **1a** and **1a**-d_n. Upon analyzing the ^1H NMR spectrum of the mixture as shown in Fig. S1, the deuteration percentage was determined as 18%.

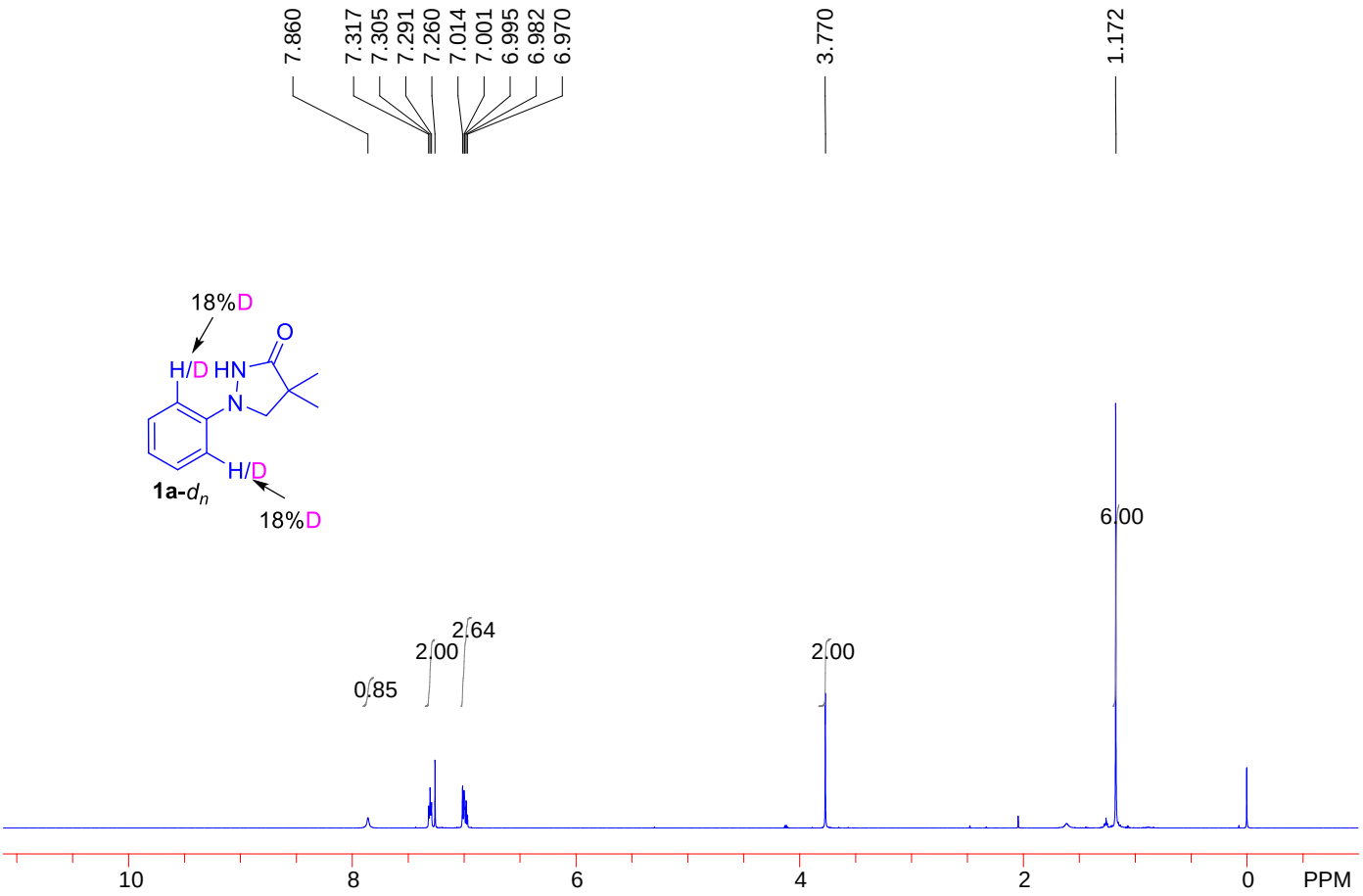
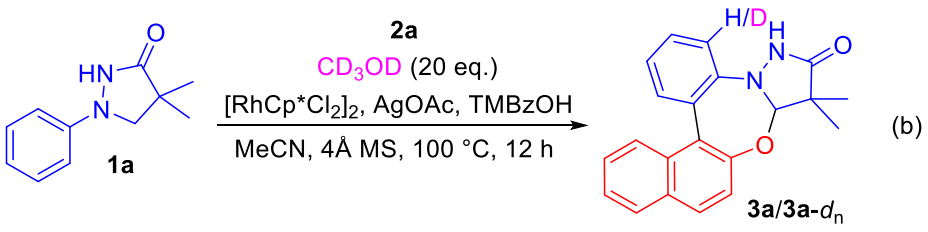


Fig. S1 The ^{1}H NMR spectrum of the products obtained from the H/D exchange experiment (I)

2. H/D exchange experiment (II)



To a reaction tube equipped with a stir bar were charged with 4,4-dimethyl-1-phenylpyrazolidin-3-one (**1a**, 57.0 mg, 0.3 mmol), MeCN (3 mL), CD_3OD (0.48 mL, 6 mmol), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), AgOAc (100.1 mg, 0.6 mmol), TMBzOH (98.5 mg, 0.6 mmol), 4Å MS (50 mg) and 1-diazonaphthalen-2(1*H*)-one (**2a**, 76.5 mg, 0.45 mmol). The mixture was stirred at 100 ℃ under Ar for 12 h. Upon completion, it was cooled to room temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite, and then extracted with ethyl acetate (10 mL × 3). The combined organic

layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to give a mixture of **3a** and **3a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture as shown in Fig. S2, the deuteration percentage was determined as 56%.

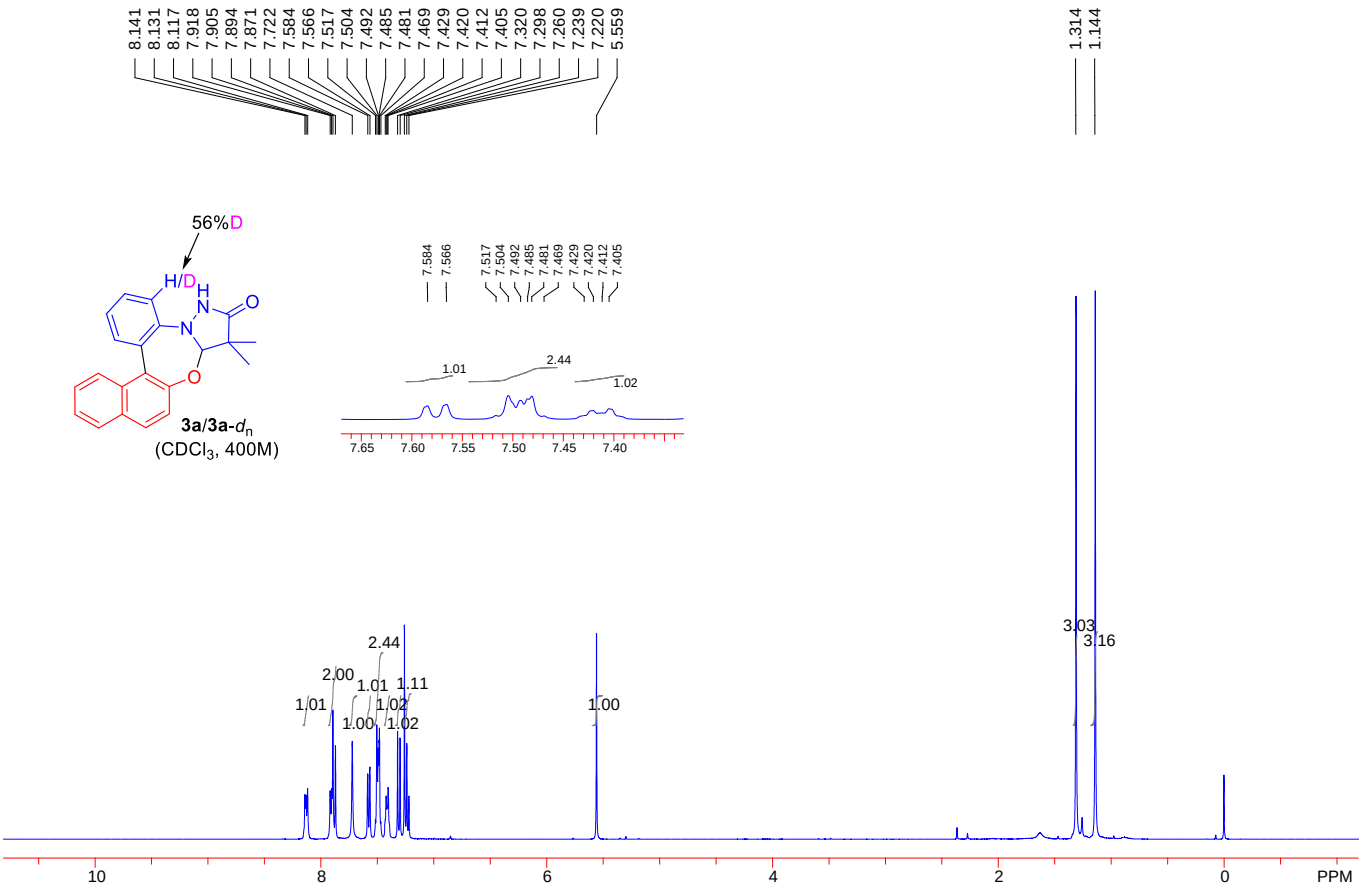
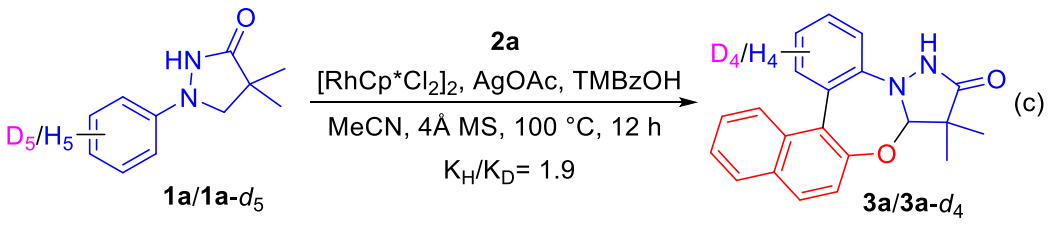


Fig. S2 The ^{1}H NMR spectrum of the products obtained from the H/D exchange experiment (II)

3. Intermolecular kinetic isotope effect study



To a reaction tube equipped with a stir bar were charged with 4,4-dimethyl-1-phenylpyrazolidin-3-one (**1a,** 57.0 mg, 0.3 mmol) and 4,4-dimethyl-1-(phenyl-2,3,4,5,6-d_5)-pyrazolidin-3-one (**1a**-d_5, 58.5 mg, 0.3 mmol)**,**

MeCN (3 mL), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), AgOAc (100.1 mg, 0.6 mmol), TMBzOH (98.5 mg, 0.6 mmol), 4Å MS (50 mg), and 1-diazonaphthalen-2(1*H*)-one (**2a**, 76.5 mg, 0.45 mmol). The mixture was stirred at 100 ℃ under Ar for 12 h. Upon completion, it was cooled to room temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite, and then extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to give a mixture of **3a** and **3a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture as shown in Fig. S3, the ratio of **3a** and **3a**-d_4 was determined as 0.65:0.35. Accordingly, the intermolecular KIE value (k_H/k_D) was calculated as about 1.9.

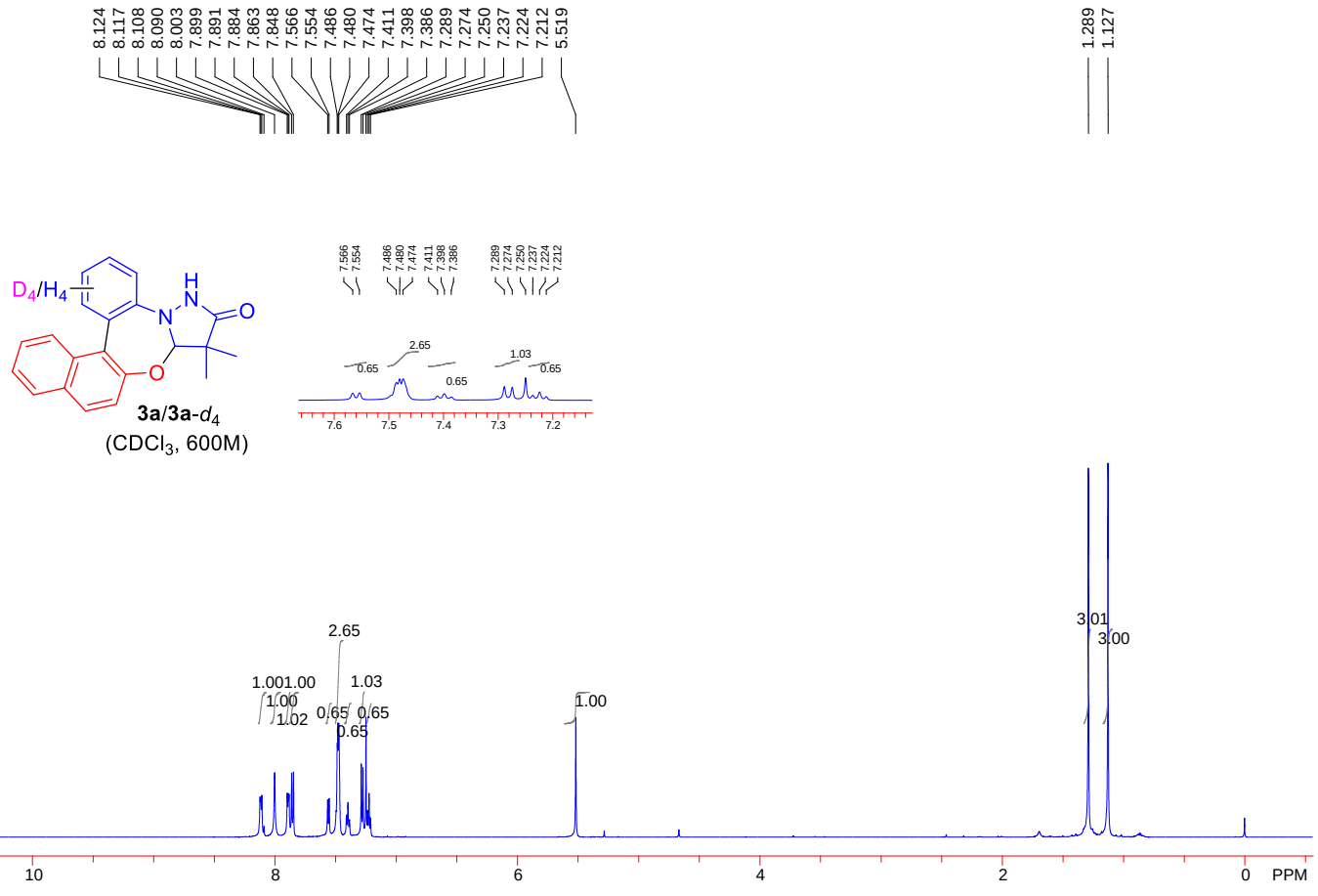
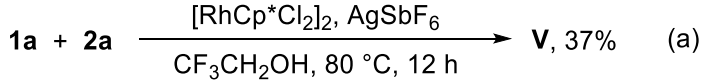


Fig. S3 The ^{1}H NMR spectrum of the products obtained from the intermolecular KIE experiment

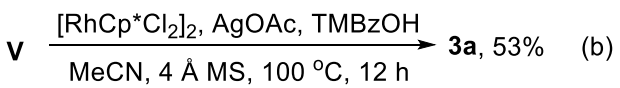
4. Competition experiment between 1d and 1i

To a reaction tube equipped with a stir bar were charged with 1-(4-methoxyphenyl)-4,4-dimeth ylpyrazolidin-3-one (**1d**, 66.0 mg, 0.3 mmol), 4,4-dimethyl-1-(4-(trifluoromethyl)phenyl)pyrazolidin-3-one (**1i**, 77.4 mg, 0.3 mmol), MeCN (3 mL), $[RhCp^*Cl_2]_2$ (4.7 mg, 0.0075 mmol), AgOAc (100.1 mg, 0.6 mmol), TMBzOH (98.5 mg, 0.6 mmol), 4Å MS (50 mg), and 1-diazonaphthalen-2(1*H*)-one (**2a**, 51.0 mg, 0.3 mmol). The mixture was stirred at 100 °C under Ar for 12 h. Upon completion, it was cooled to room temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite, and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3d** (73.5 mg, 68%) and **3i** (10.7 mg, 9%).

5. Preparation and transformation of intermediate V

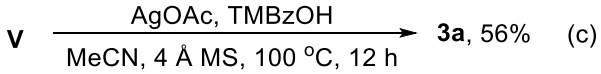


To a reaction tube equipped with a stir bar were charged with 4,4-dimethyl-1-phenylpyrazolidin-3-one (**1a**, 57.0 mg, 0.3 mmol), CF_3CH_2OH (3 mL), $[RhCp^*Cl_2]_2$ (7.4 mg, 0.012 mmol), $AgSbF_6$ (16.5 mg, 0.048 mmol) and 1-diazonaphthalen-2(1*H*)-one (**2a**, 51.0 mg, 0.3 mmol). The mixture was stirred at 80 °C under Ar for 12 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to afford **V** (36.9 mg, 37%).

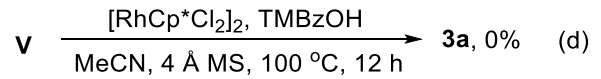


To a reaction tube equipped with a stir bar were charged with **V** (66.4 mg, 0.2 mmol), MeCN (2 mL), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), AgOAc (66.8 mg, 0.4 mmol), TMBzOH (65.7 mg, 0.4 mmol) and 4Å MS (30 mg). The mixture was stirred at 100 ℃ under Ar for 12 h. Upon completion, it was cooled to room

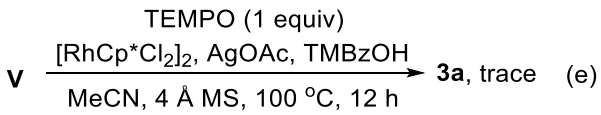
temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite, and then extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3a** (35.0 mg, 53%).



To a reaction tube equipped with a stir bar were charged with **V** (66.4 mg, 0.2 mmol), MeCN (2 mL), AgOAc (66.8 mg, 0.4 mmol), TMBzOH (65.7 mg, 0.4 mmol) and 4Å MS (30 mg). The mixture was stirred at 100 ℃ under Ar for 12 h. Upon completion, it was cooled to room temperature, quenched with saturated solution of $NaHCO_3$ (5 mL), filtered through a pad of celite, and then extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3a** (37.0 mg, 56%).

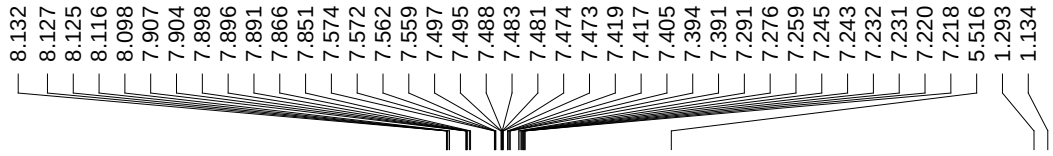


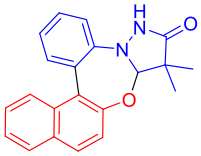
To a reaction tube equipped with a stir bar were charged with **V** (66.4 mg, 0.2 mmol), MeCN (2 mL), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), TMBzOH (65.7 mg, 0.4 mmol) and 4Å (30 mg). The mixture was stirred at 100 ℃ under Ar for 12 h, from which the formation of **3a** was not observed (TLC).



To a reaction tube equipped with a stir bar were charged with **V** (66.4 mg, 0.2 mmol), MeCN (2 mL), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), AgOAc (66.8 mg, 0.4 mmol), TMBzOH (65.7 mg, 0.4 mmol), 4Å MS (30 mg) and TEMPO (31.3 mg, 0.2 mmol). The mixture was stirred at 100 ℃ under Ar for 12 h, from which only trace amount of **3a** was formed as observed by TLC.

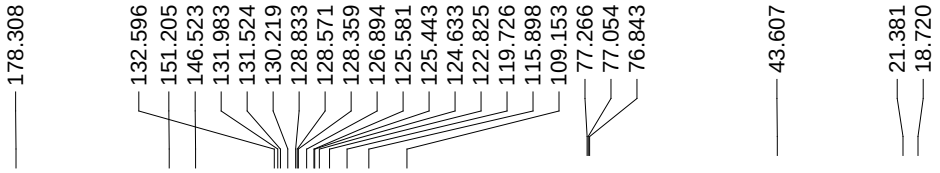
IV. Copies of NMR spectra of 3a-3ii

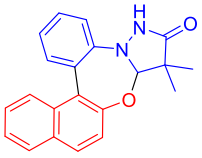




3a

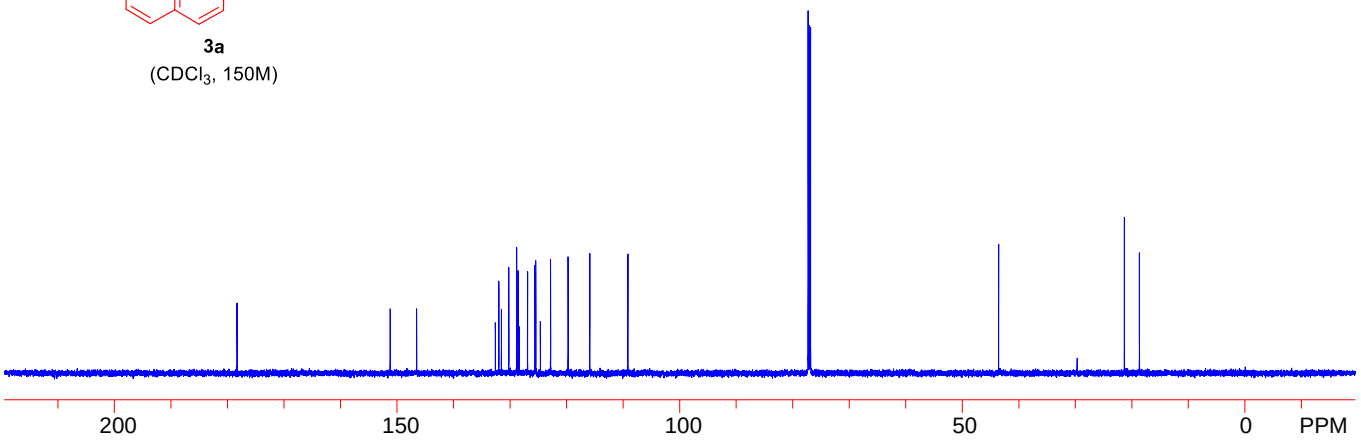
($CDCl_3$, 600M)

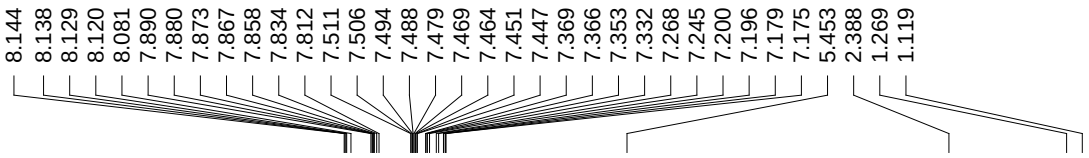


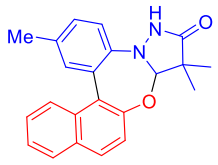


3a

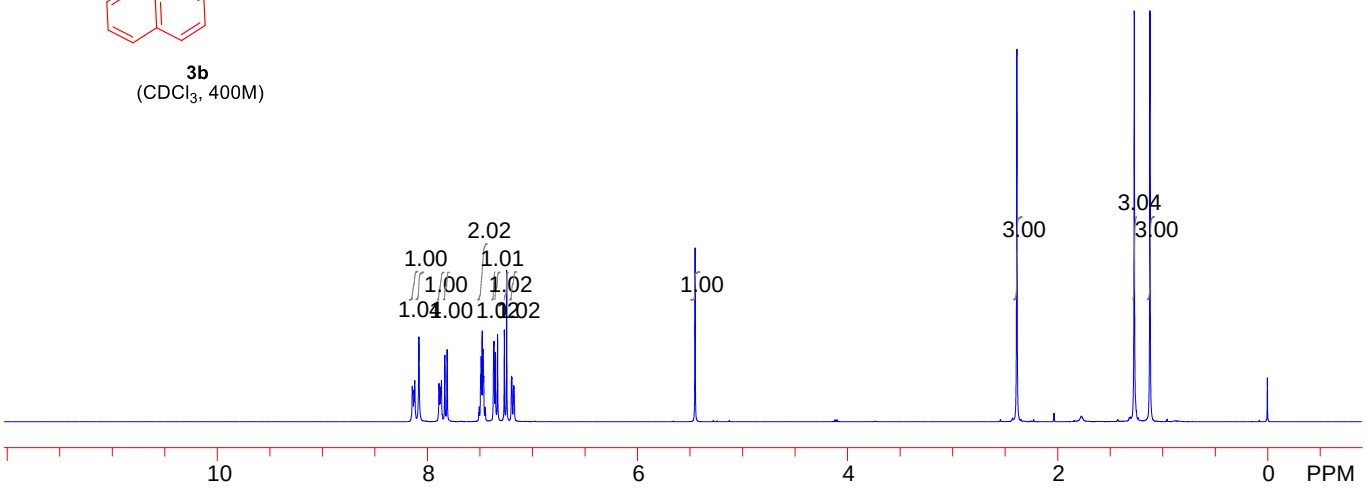
($CDCl_3$, 150M)

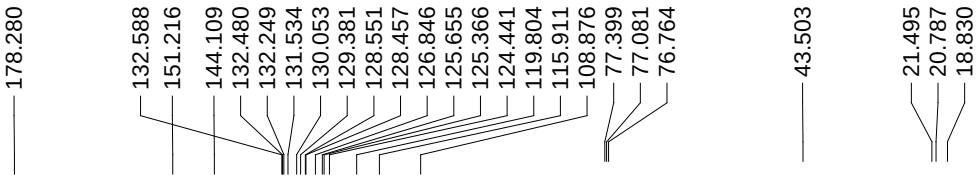


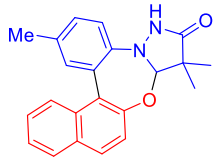




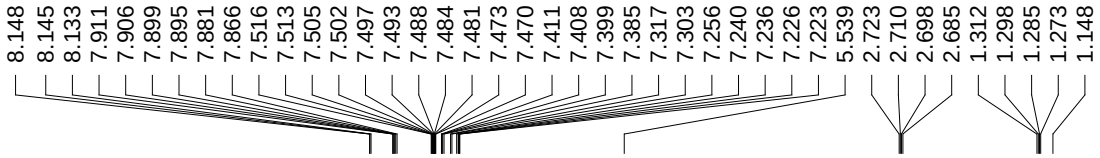
3b
($CDCl_3$, 400M)

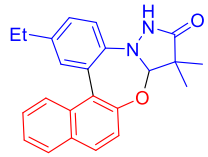




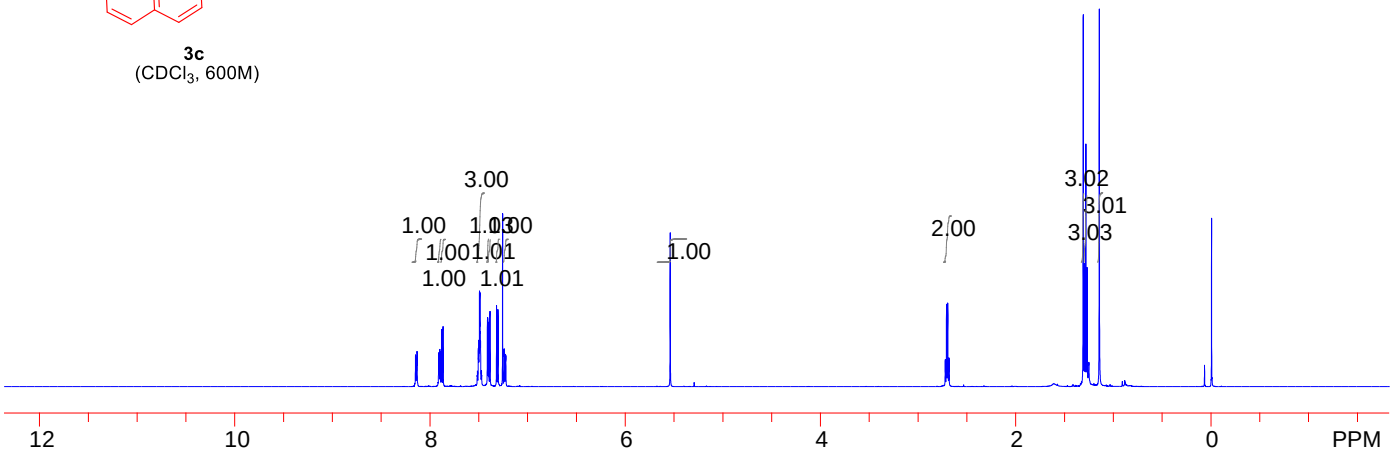


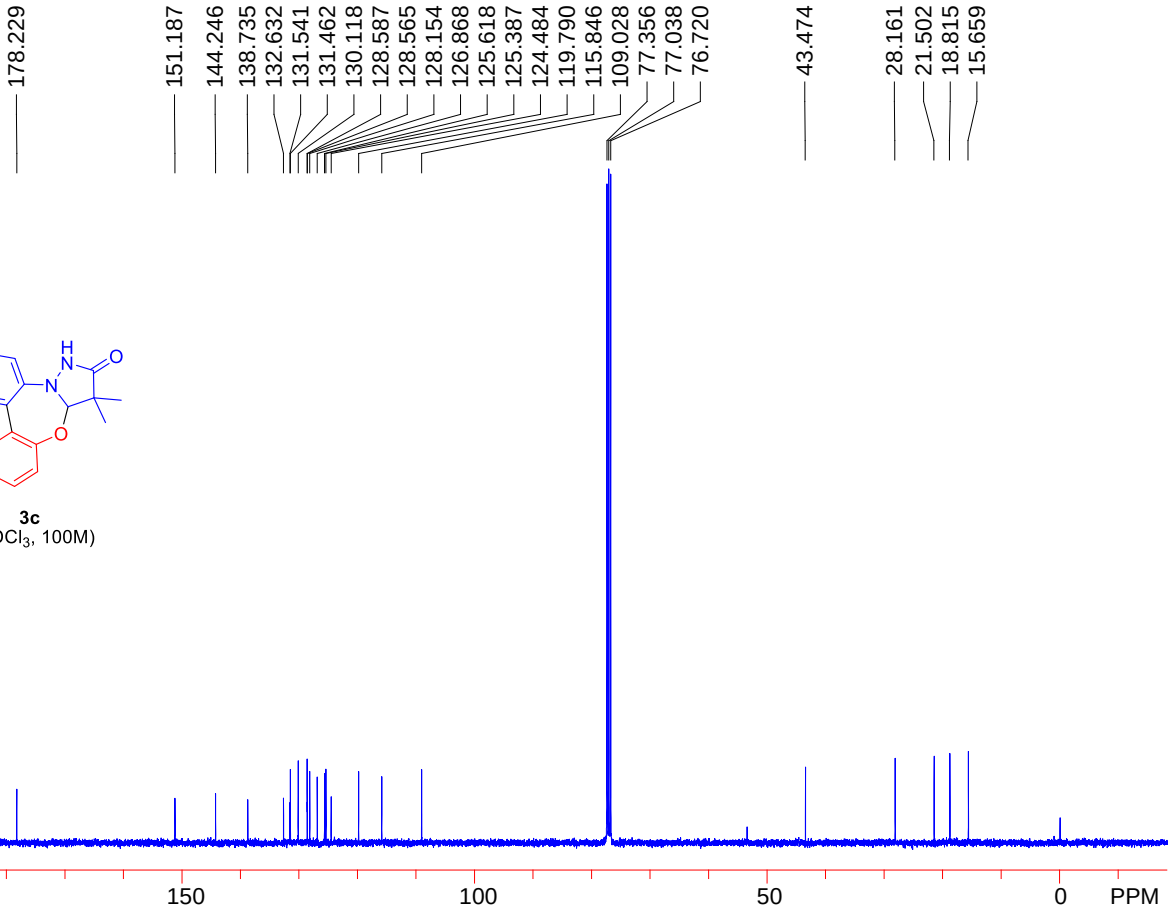
3b
($CDCl_3$, 100M)



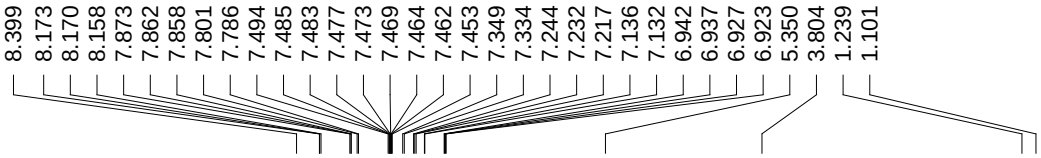


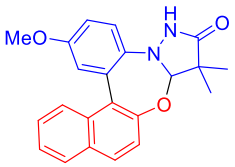
3c
($CDCl_3$, 600M)



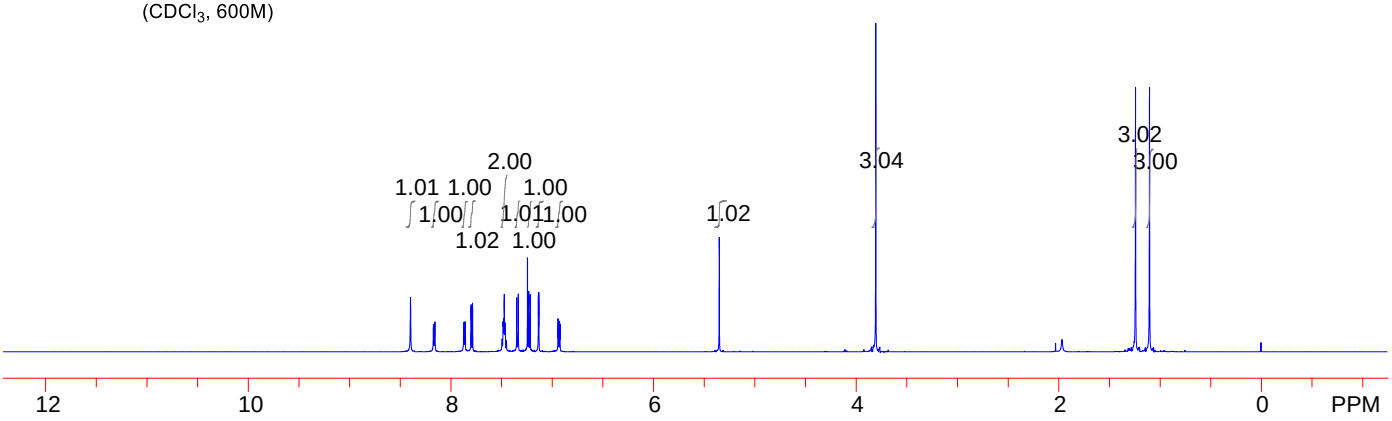


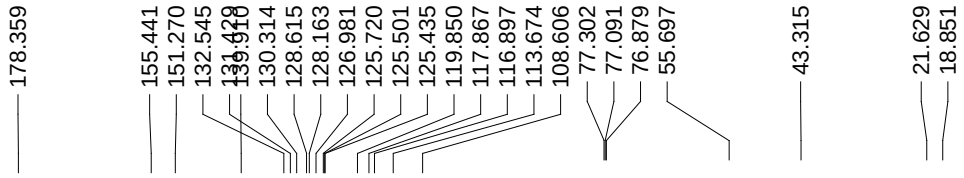
3c
($CDCl_3$, 100M)

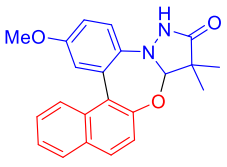




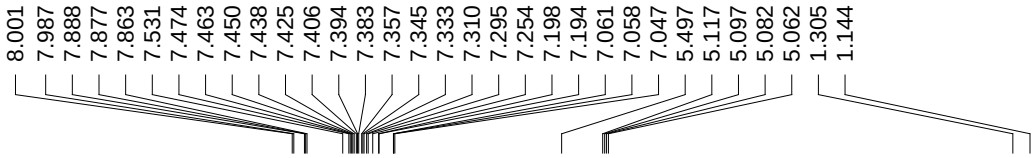
3d
($CDCl_3$, 600M)

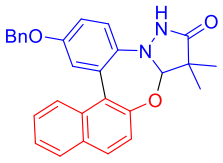




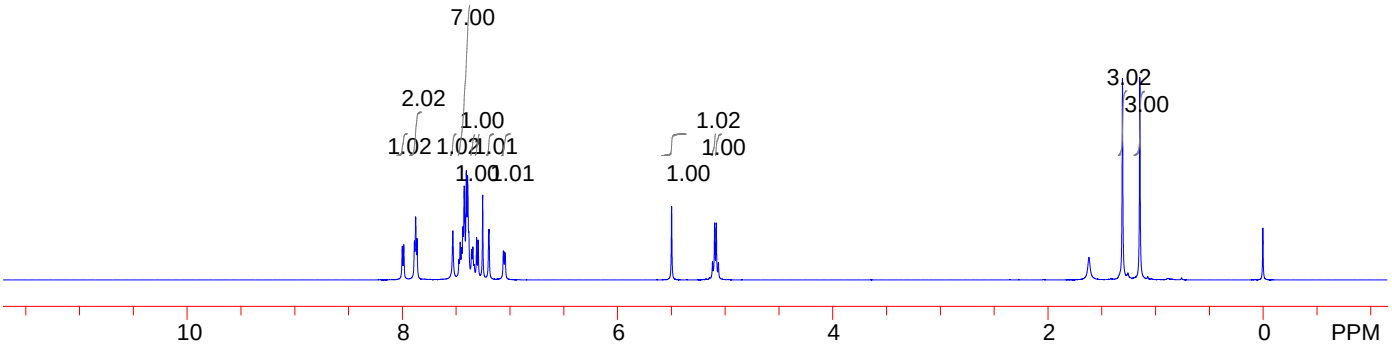


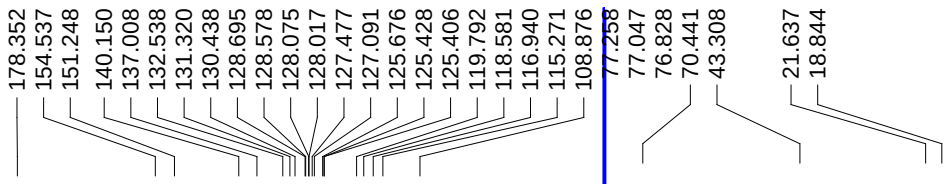
3d
($CDCl_3$, 150M)

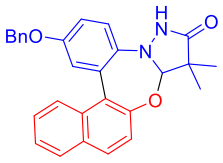




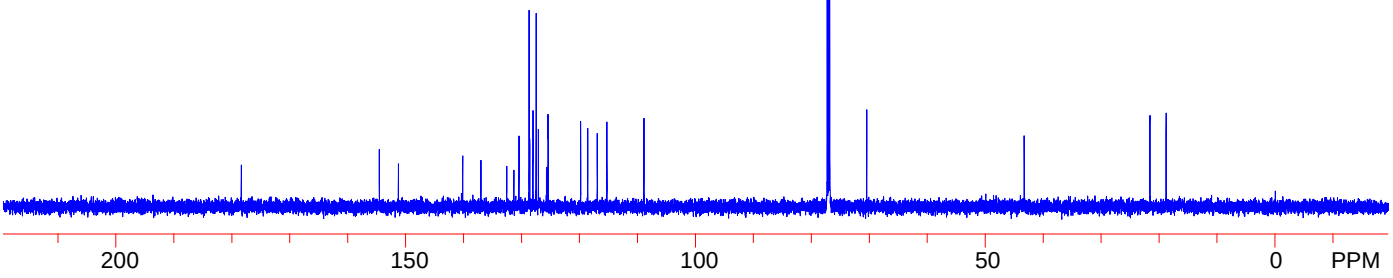
3e
($CDCl_3$, 600M)

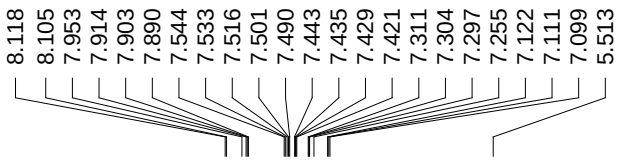


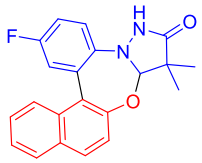




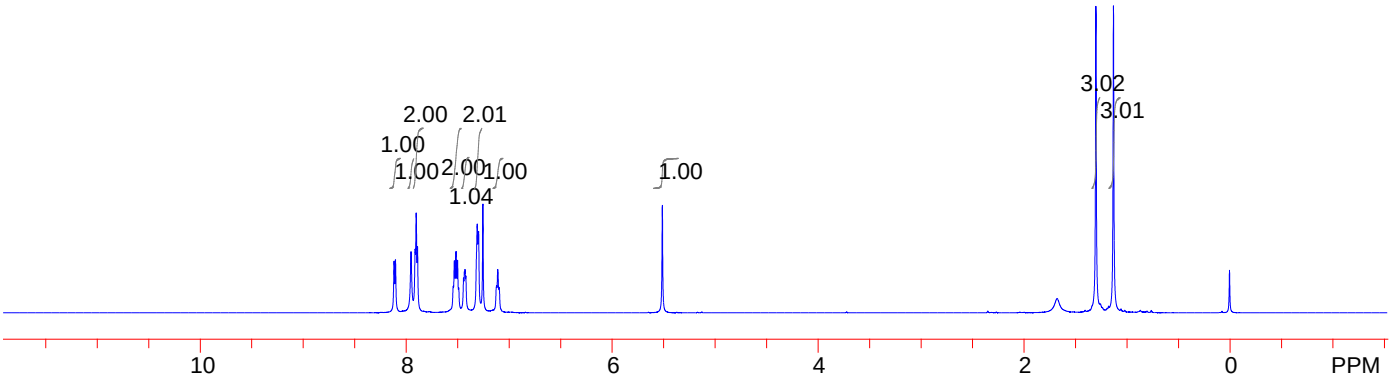
3e
($CDCl_3$, 150M)

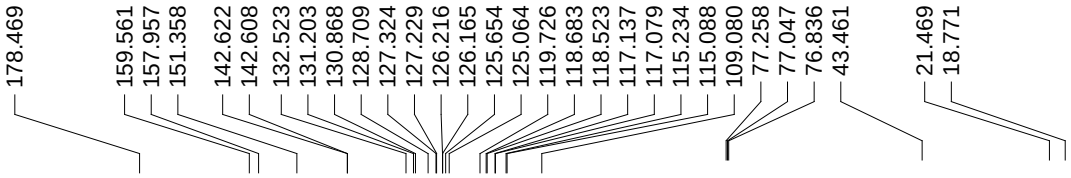


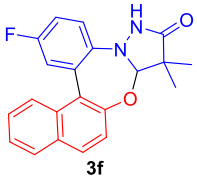




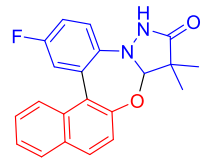
3f
($CDCl_3$, 600M)



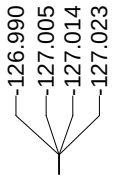


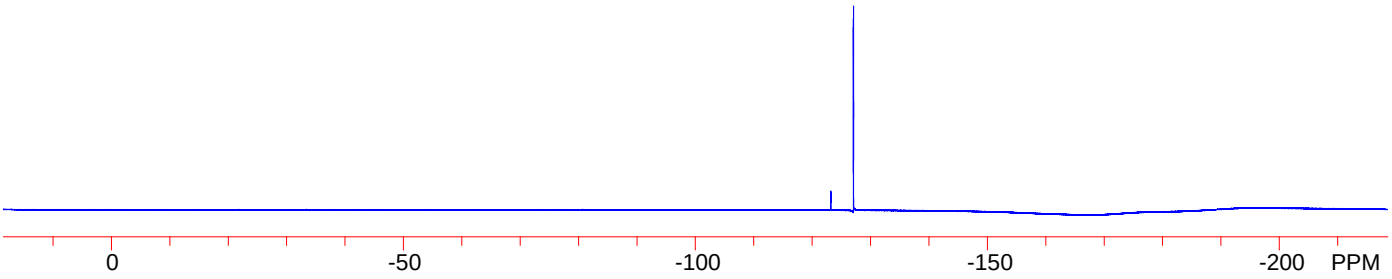


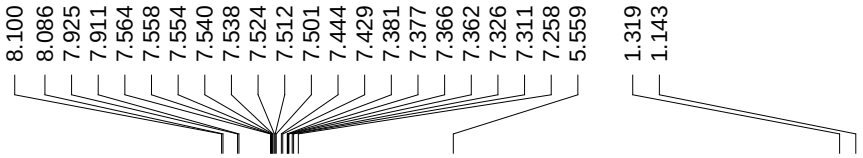
3f
($CDCl_3$, 150M)

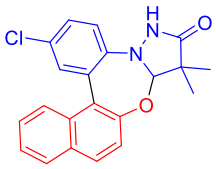


3f
($CDCl_3$, 565M)

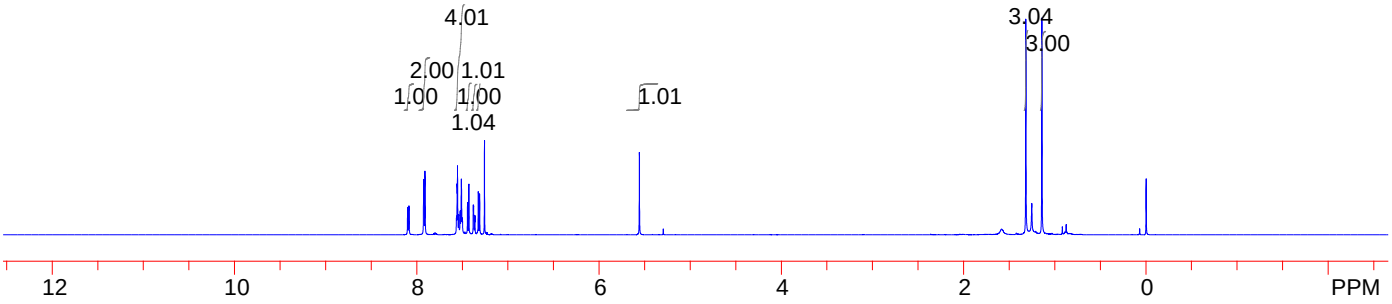


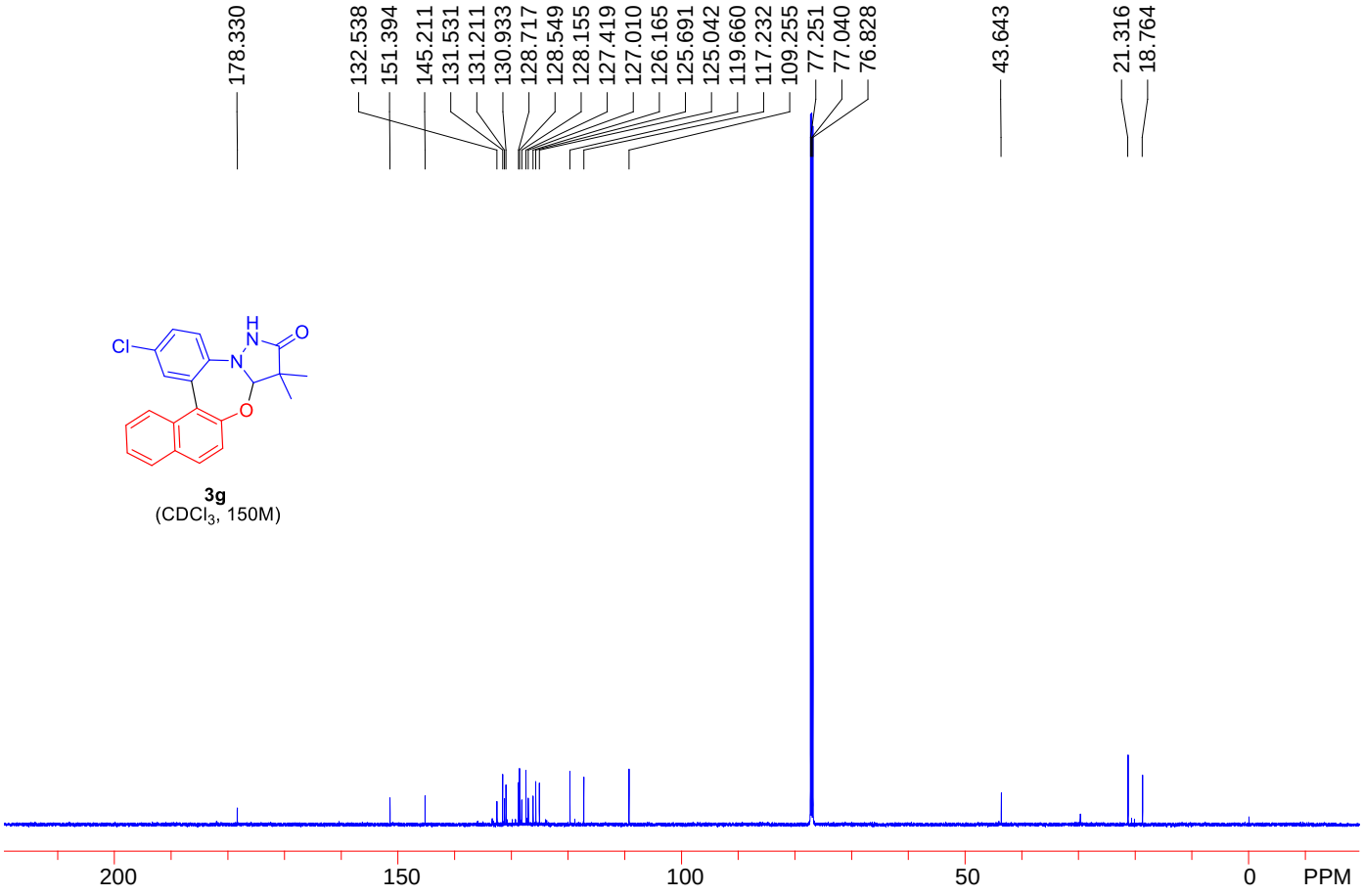




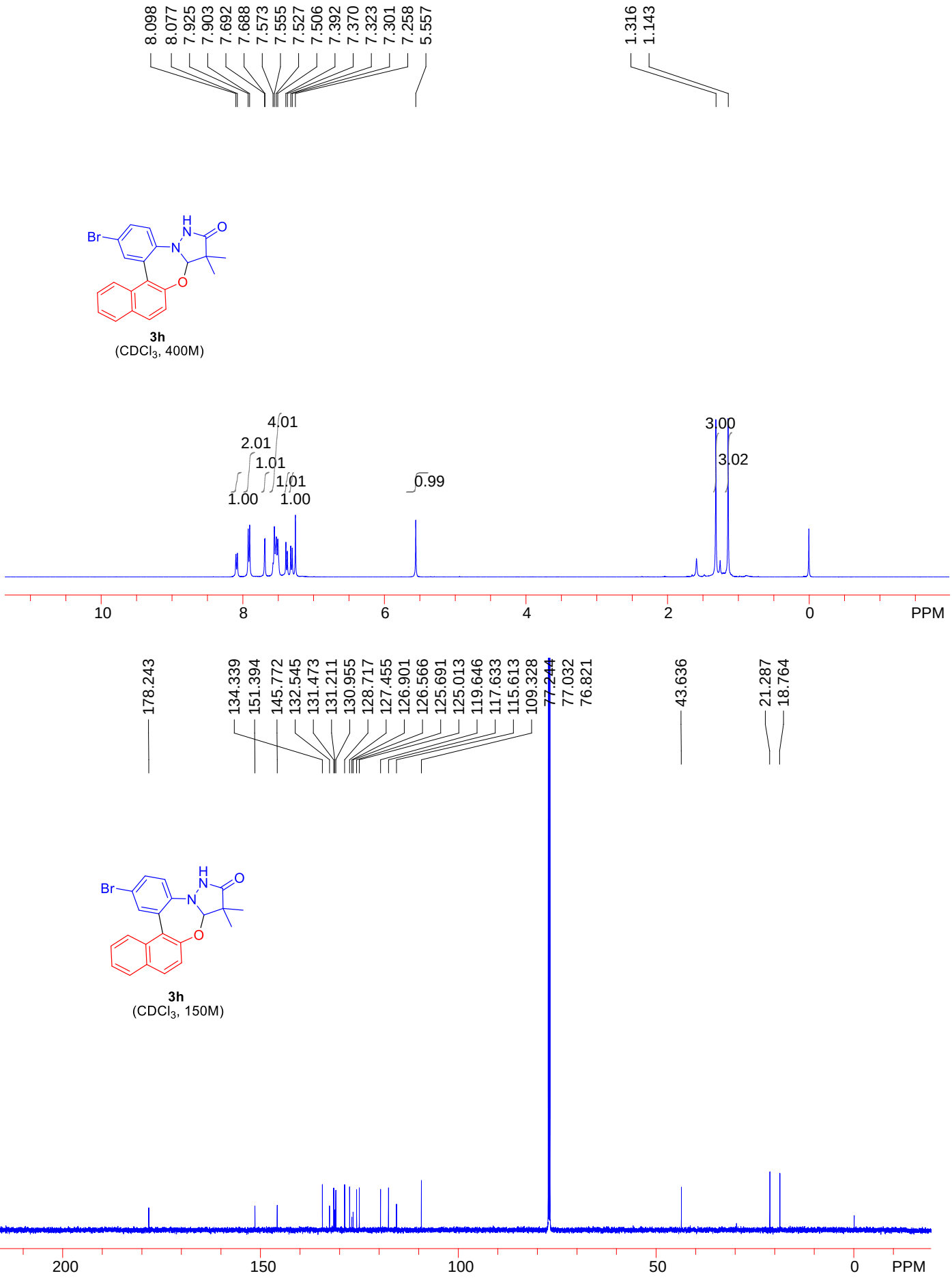


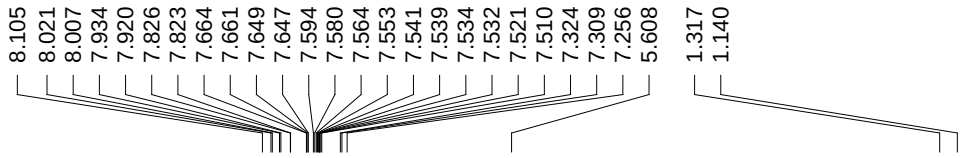
3g
($CDCl_3$, 600M)

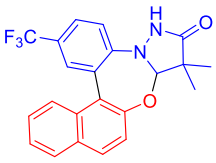




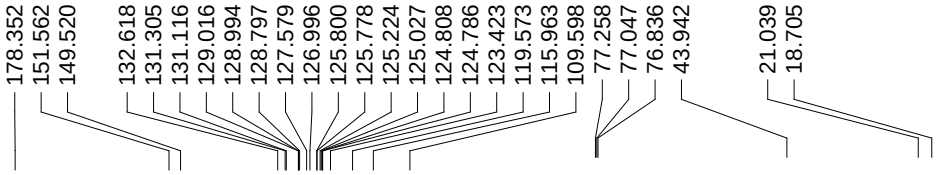
3g
($CDCl_3$, 150M)

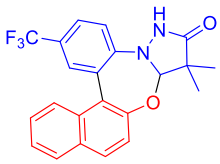

8.098
8.077
7.925
7.903
7.692
7.688
7.573
7.555
7.527
7.506
7.392
7.370
7.323
7.301
7.258
5.557
1.316
1.143
Br
H
N
N
O
O
3h
(CDCl3, 400M)
4.01
2.01
1.01
1.01
1.00
1.00
0.99
3.00
3.02
10
8
6
4
2
0
PPM
178.243
134.339
151.394
145.772
132.545
131.473
131.211
130.955
128.717
127.455
126.901
126.566
125.691
125.013
119.646
117.633
115.613
109.328
77.244
77.032
76.821
43.636
21.287
18.764
Br
H
N
N
O
O
3h
(CDCl3, 150M)
200
150
100
50
0
PPM



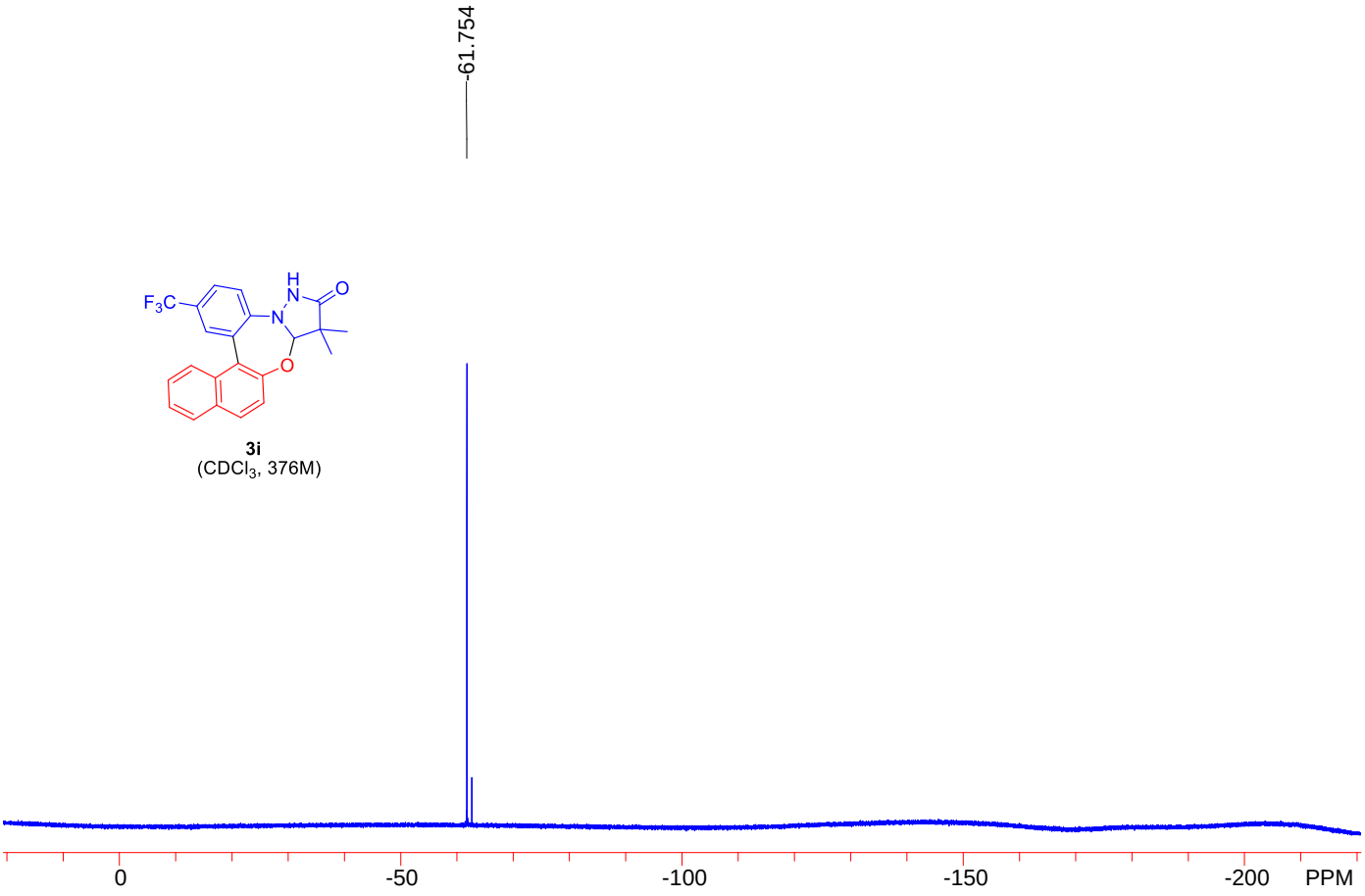


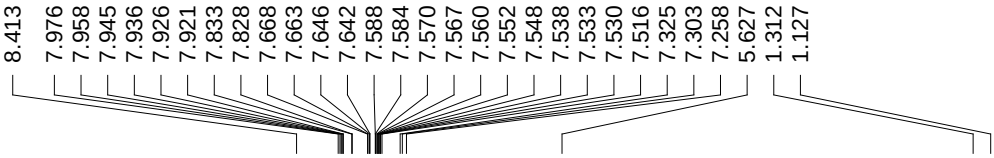
3i
($CDCl_3$, 600M)

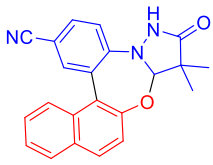




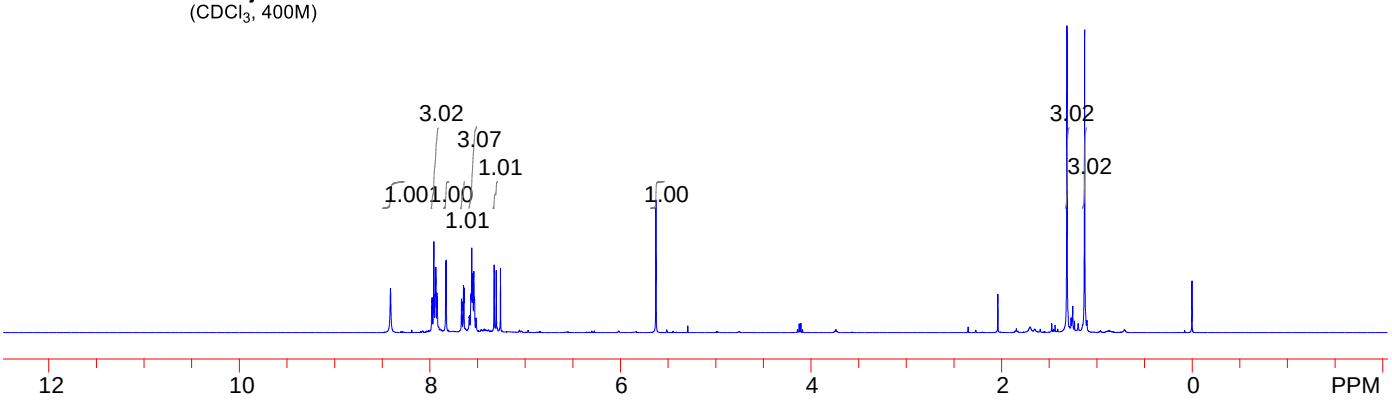
3i
($CDCl_3$, 150M)

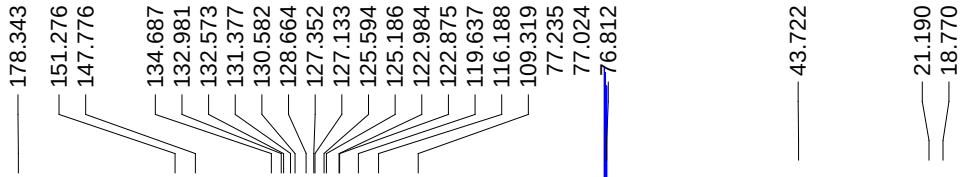

-61.754
F3C
H
N
N
O
O
3i
(CDCl3, 376M)
0
-50
-100
-150
-200
PPM

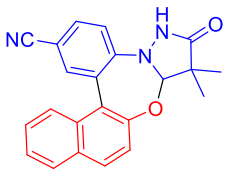




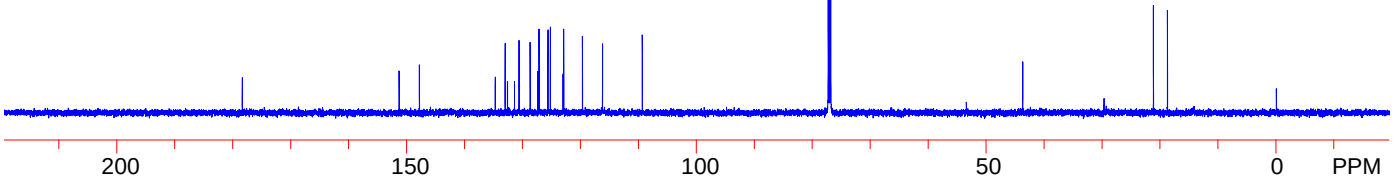
3j
($CDCl_3$, 400M)

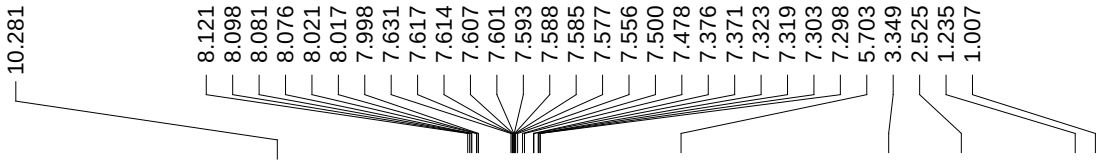


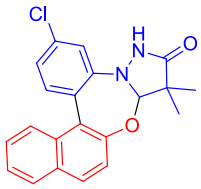




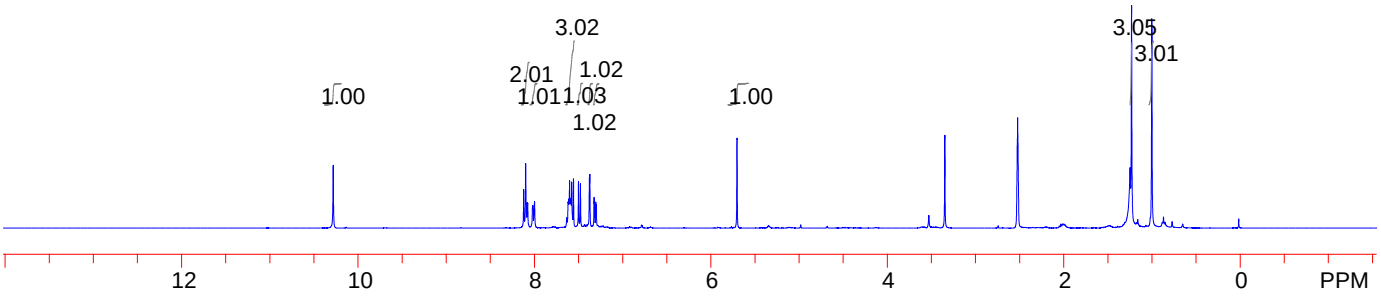
3j
($CDCl_3$, 150M)

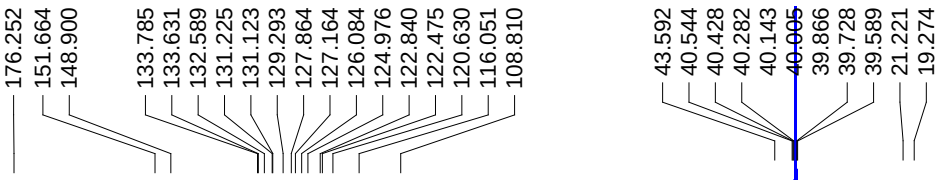


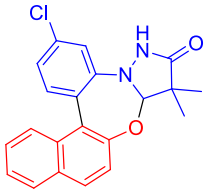




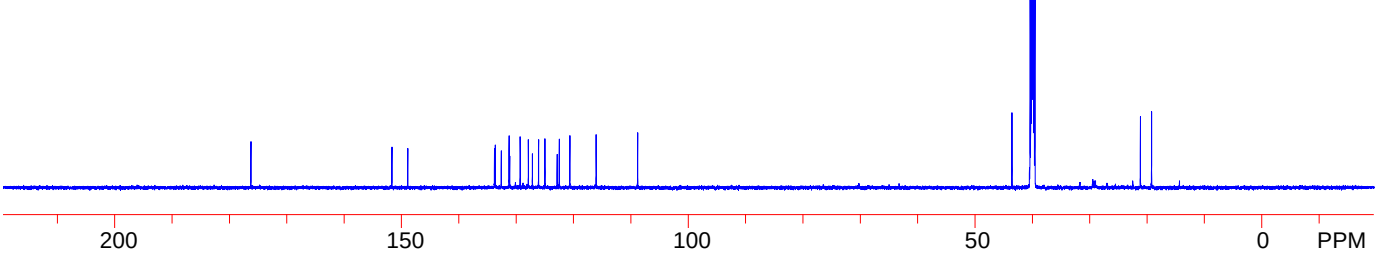
3k
(DMSO-d_6, 400M)

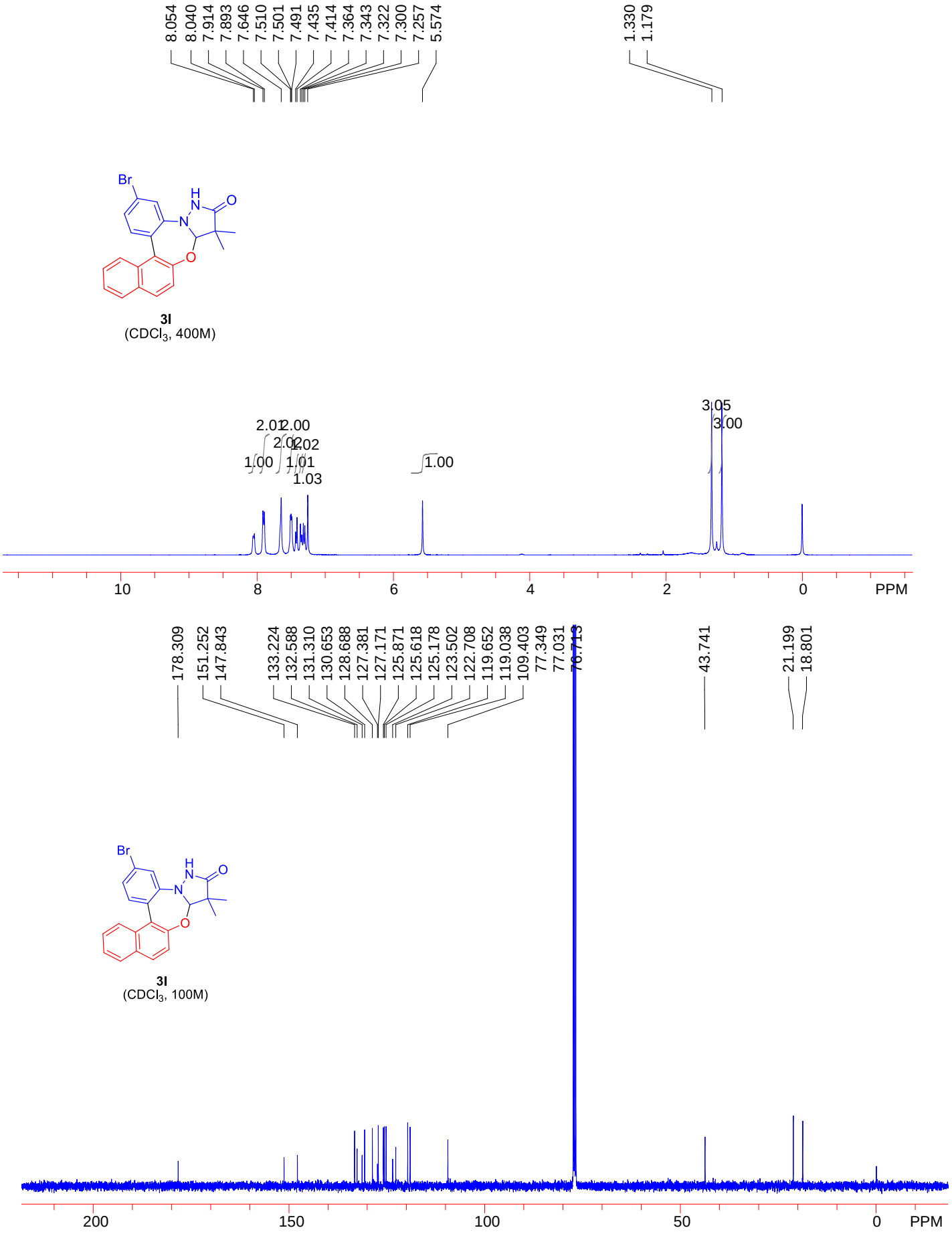






3k
(DMSO-d_6, 150M)

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7.646
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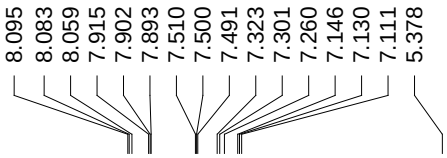
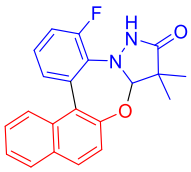
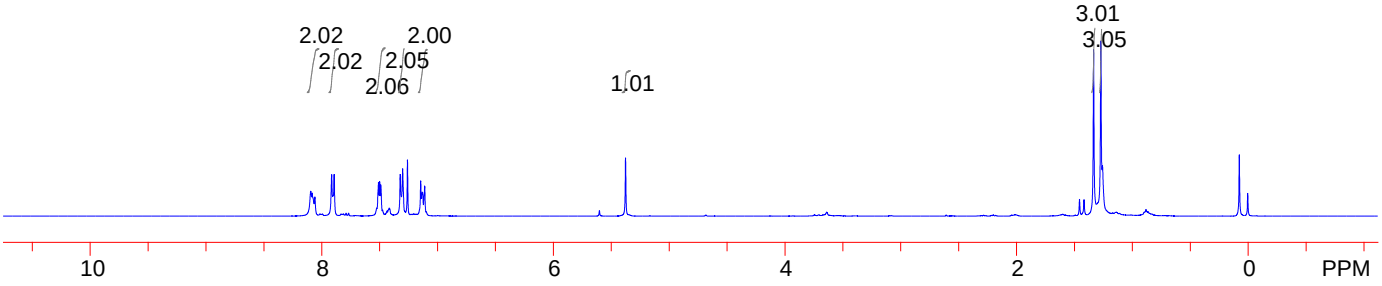
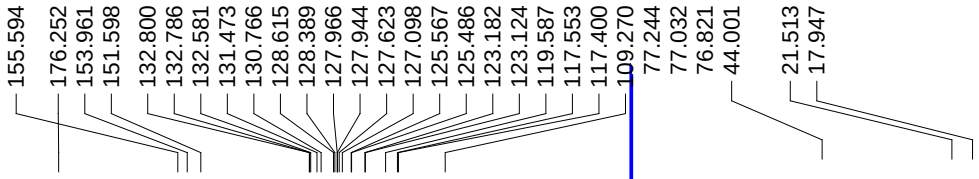
7.501
7.491
7.435
7.414
7.364
7.343
7.322
7.300
7.257
5.574
1.330
1.179
Br
H
N
O
N
O
3l
(CDCl3, 400M)
2.01
2.00
2.02
2.02
1.00
1.01
1.03
1.00
3.05
3.00
10
8
6
4
2
0
PPM
178.309
151.252
147.843
133.224
132.588
131.310
130.653
128.688
127.381
127.171
125.871
125.618
125.178
123.502
122.708
119.652
119.038
109.403
77.349
77.031
76.713
43.741
21.199
18.801
Br
H
N
O
N
O
3l
(CDCl3, 100M)
200
150
100
50
0
PPM

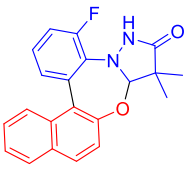




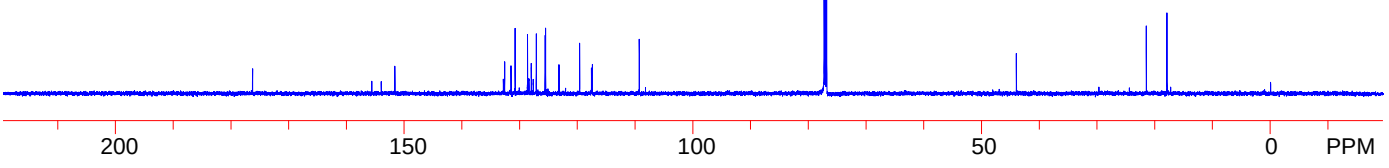
3m
($CDCl_3$, 400M)



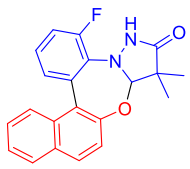




3m
($CDCl_3$, 150M)

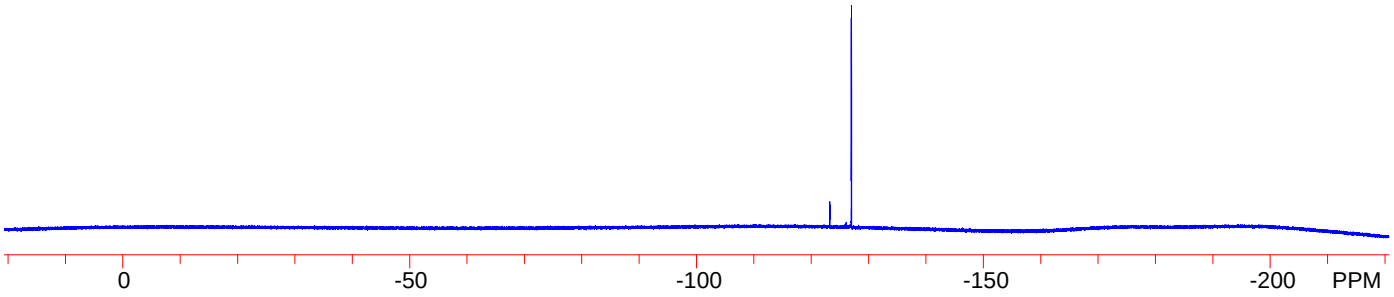


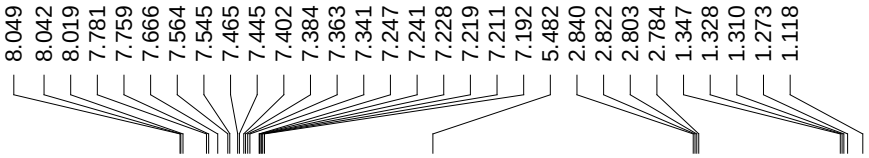
126.910
126.936
126.962

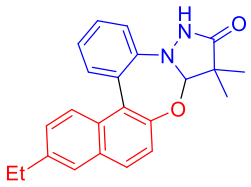


3m

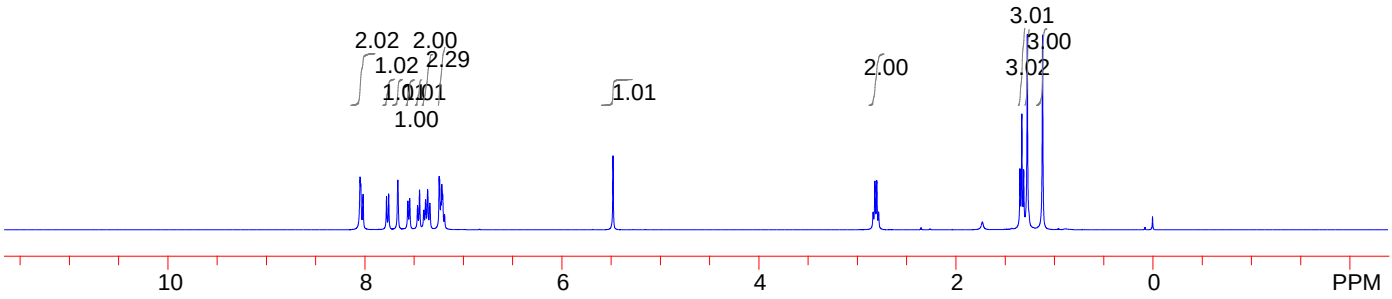
($CDCl_3$, 376M)

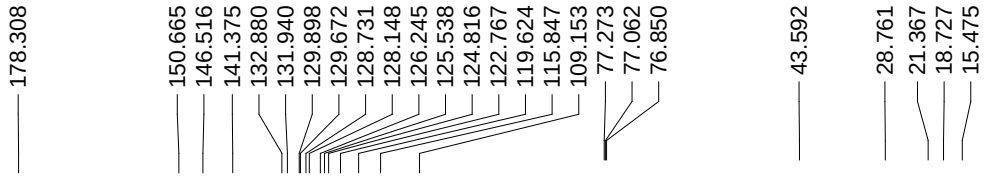


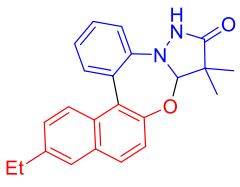




3n
($CDCl_3$, 400M)







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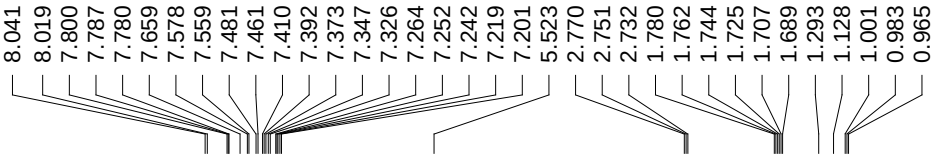
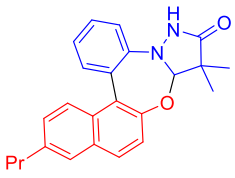
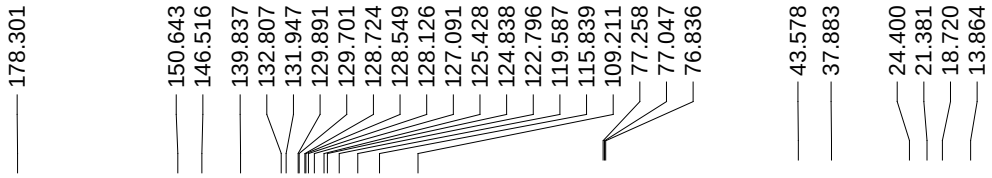
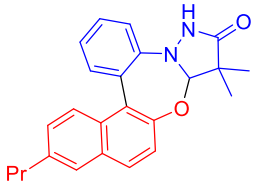


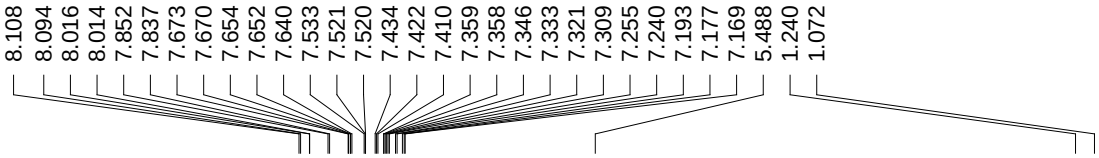


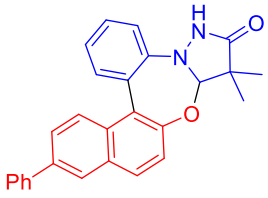
3o
($CDCl_3$, 400M)



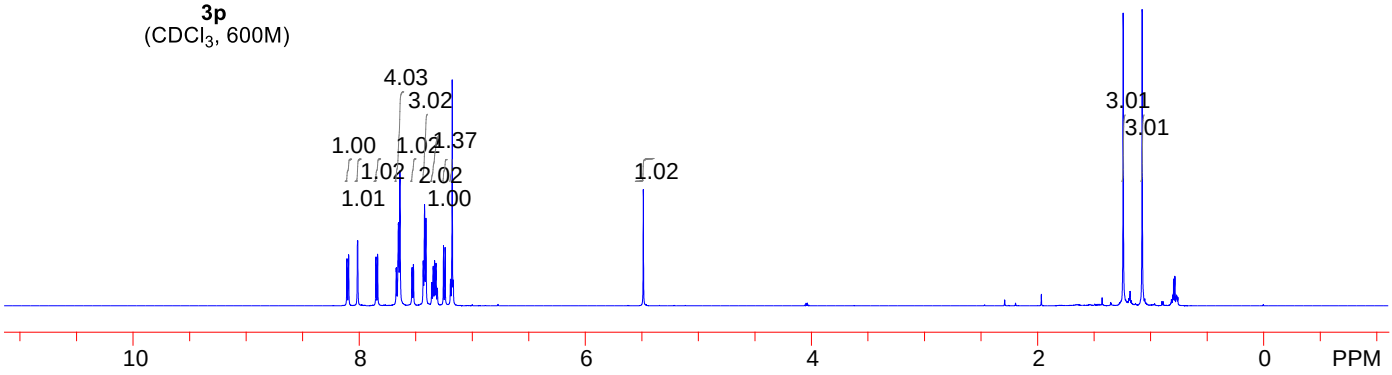


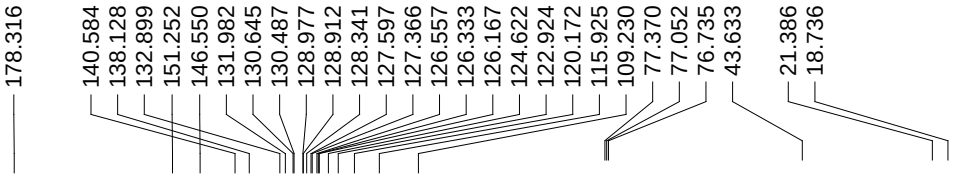
3o
($CDCl_3$, 150M)

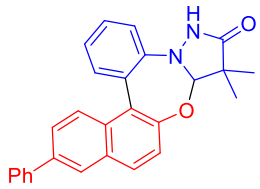




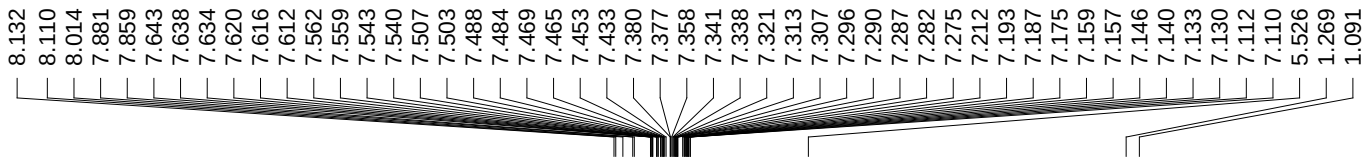
3p
($CDCl_3$, 600M)

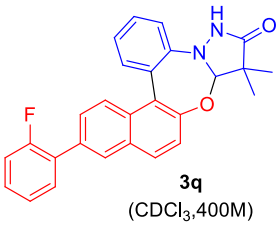




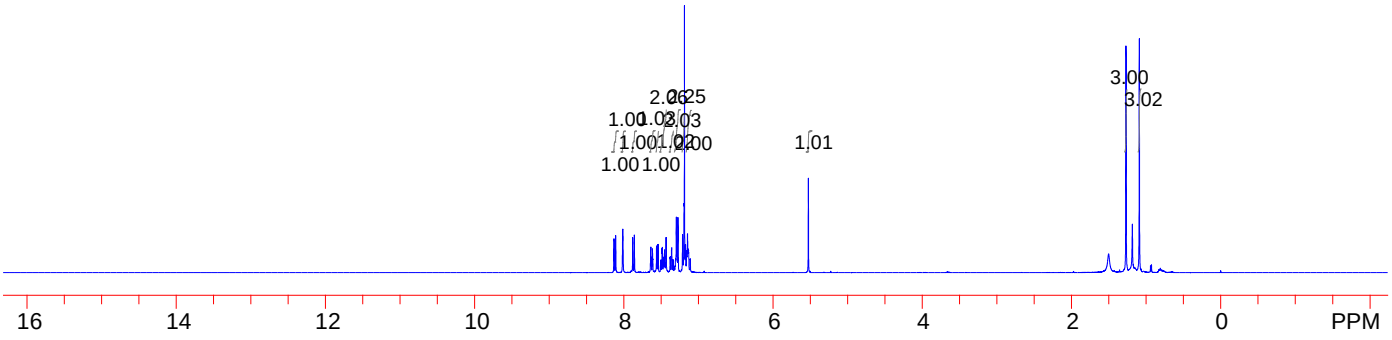


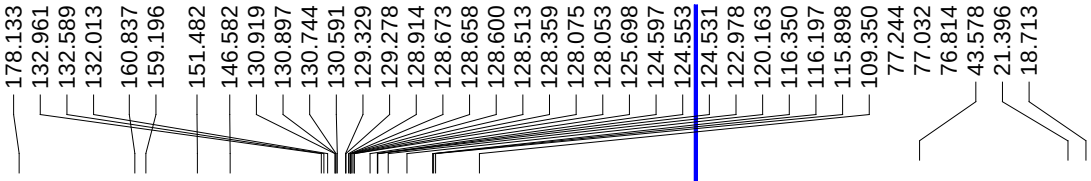
3p
($CDCl_3$,100M)

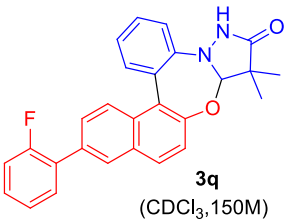




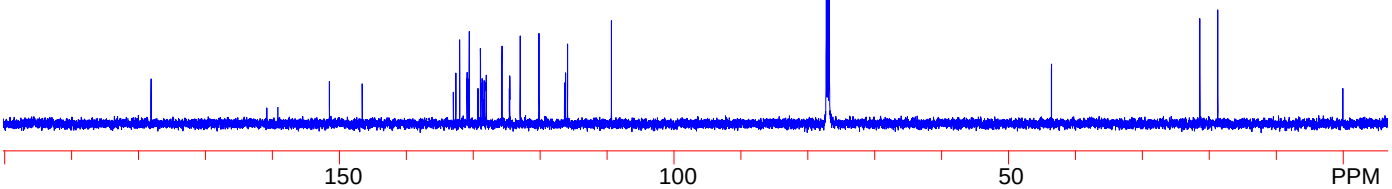
3q
($CDCl_3$,400M)

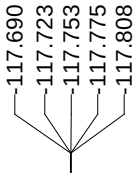


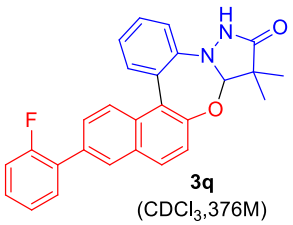




3q
($CDCl_3$,150M)

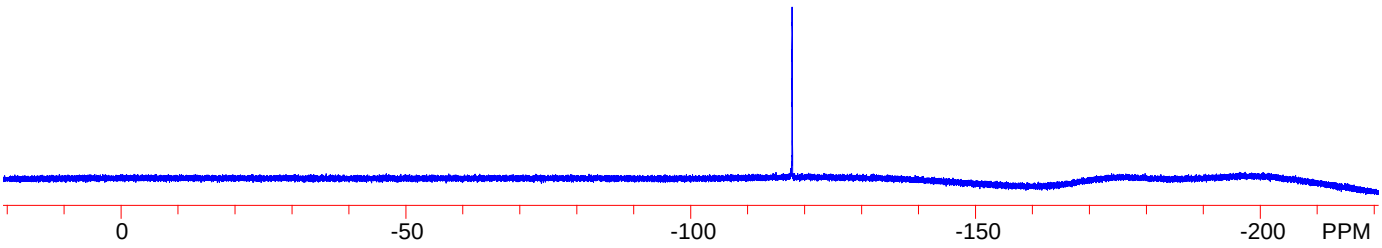


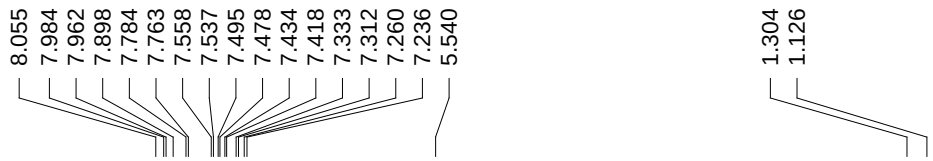


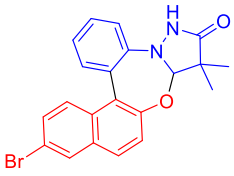


3q

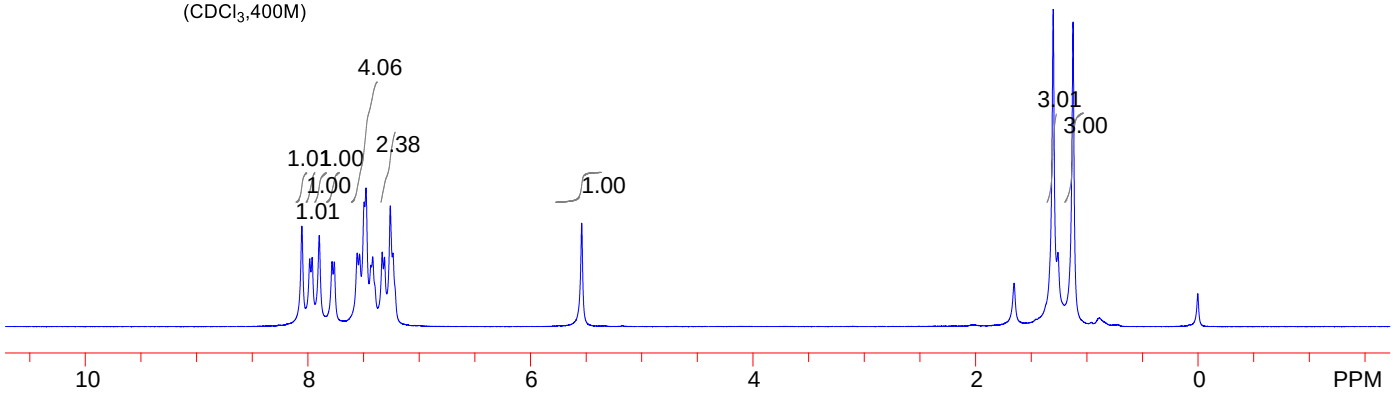
($CDCl_3$,376M)

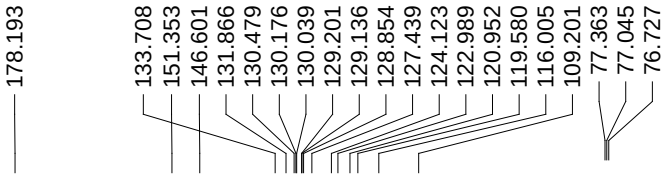


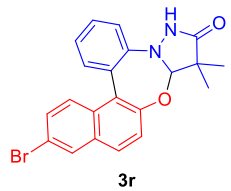




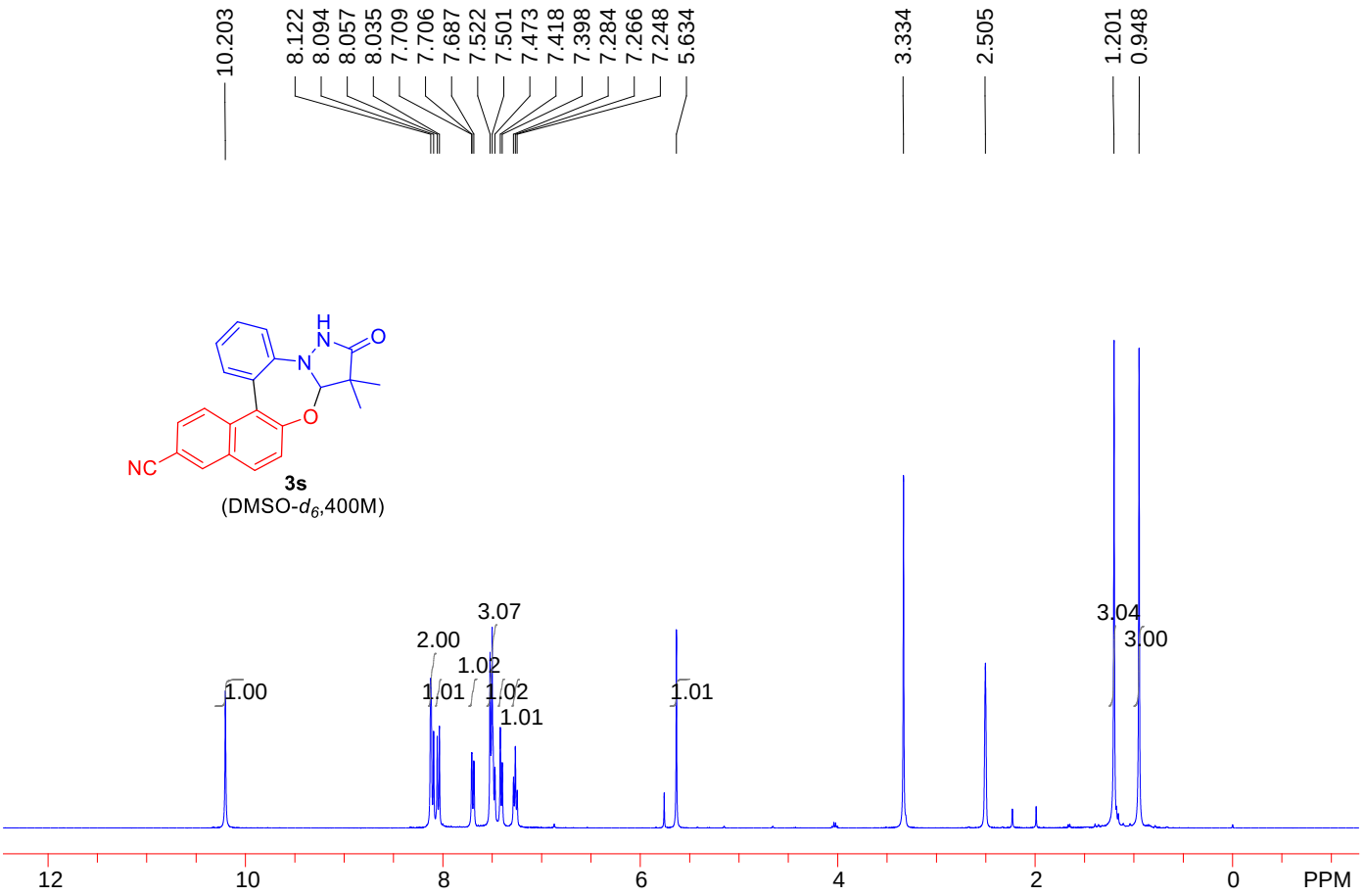
3r
($CDCl_3$,400M)







3r
($CDCl_3$,100M)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3s
(DMSO-d6,400M)
1.00
2.00
1.01
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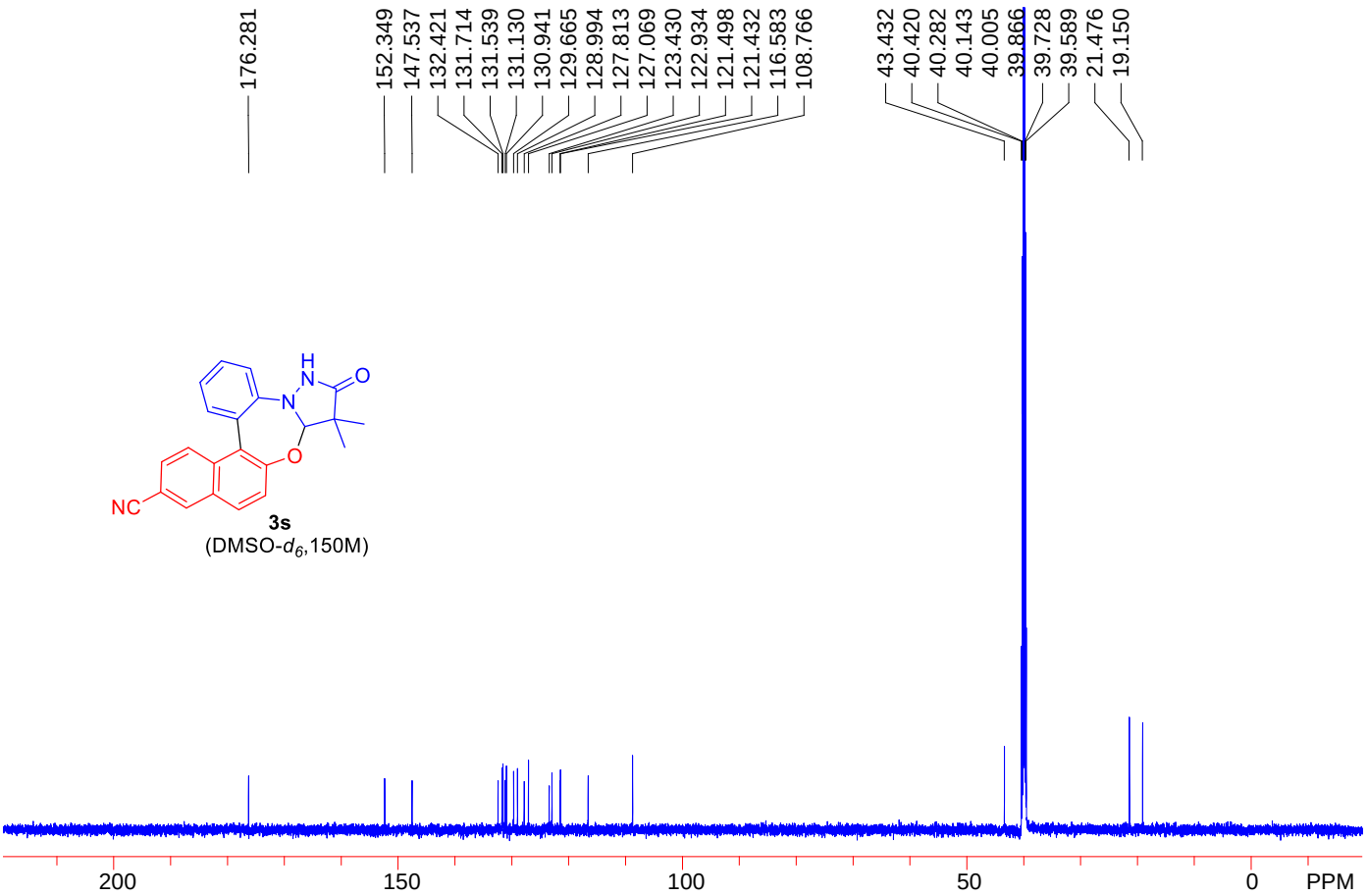
PPM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40.143
40.005
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39.728
39.589
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19.150
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(DMSO-d6,150M)
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150
100
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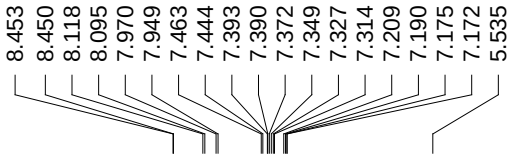
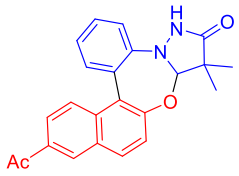
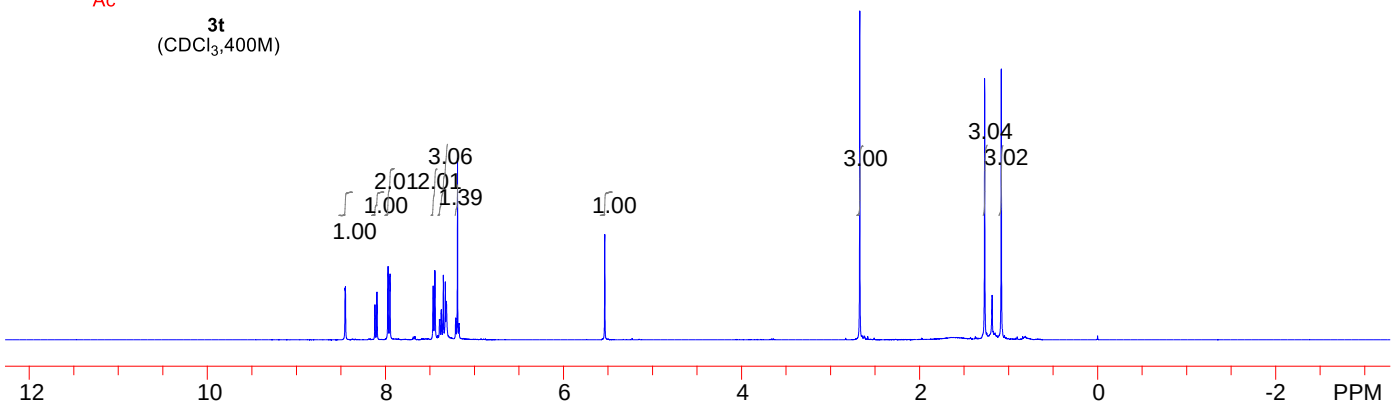
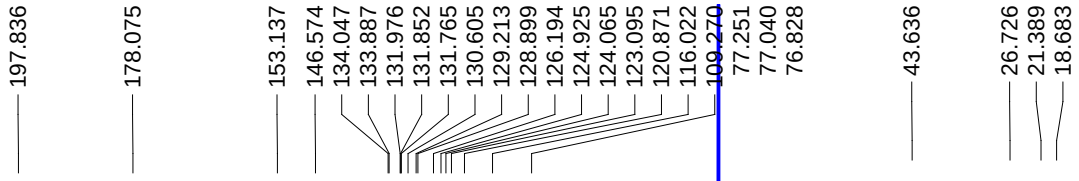
0
PPM

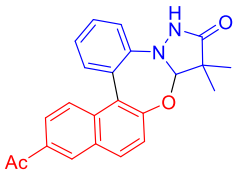




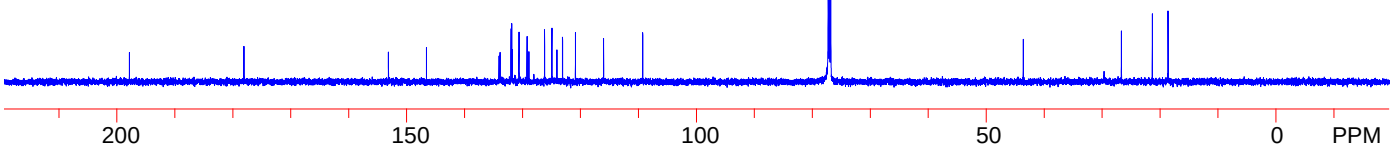
3t
($CDCl_3$,400M)

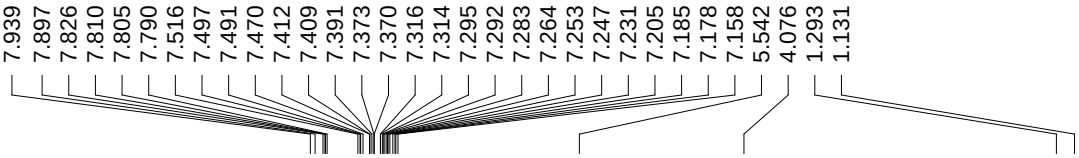


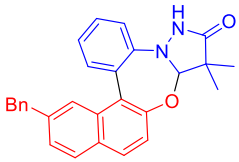




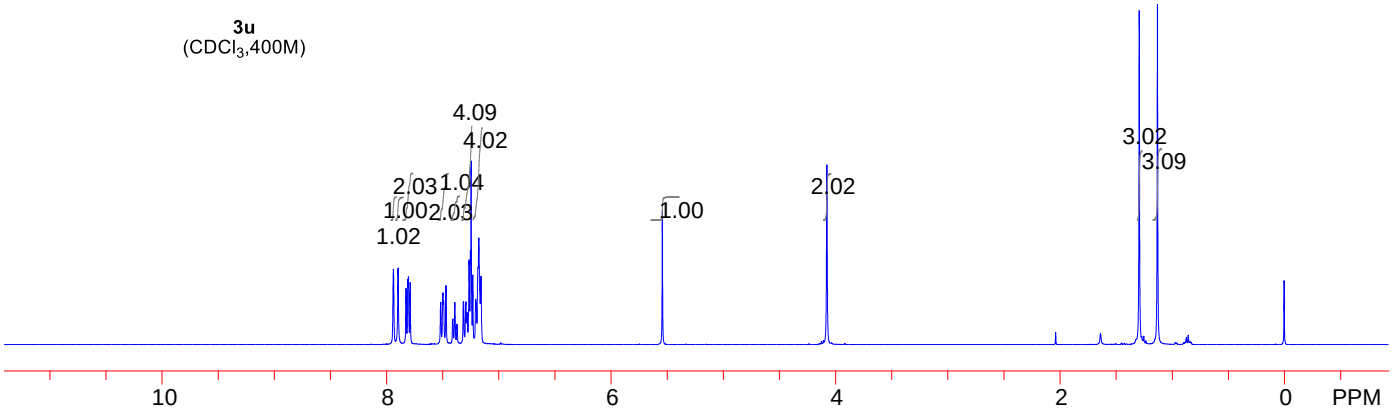
3t
($CDCl_3$,150M)

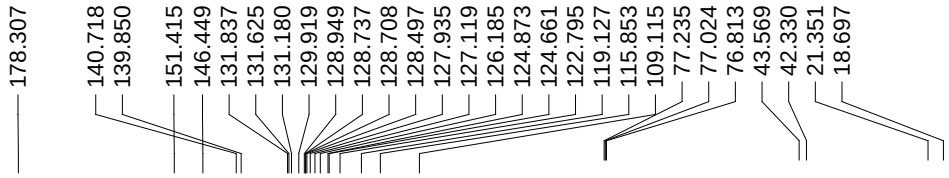


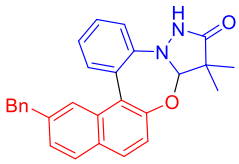




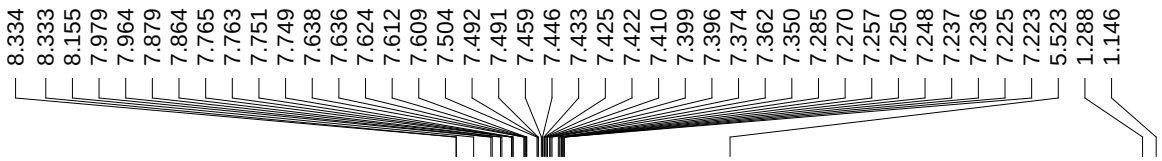
3u
($CDCl_3$,400M)

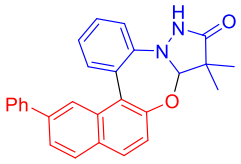




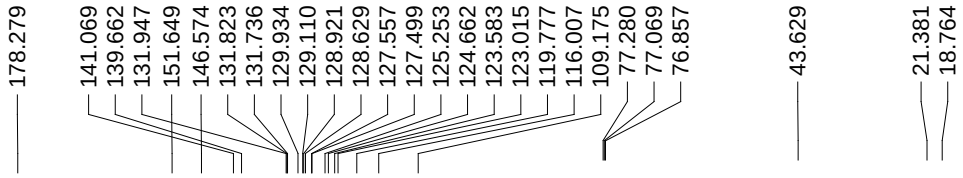


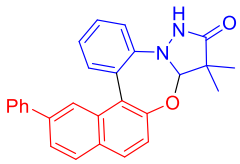
3u
($CDCl_3$,150M)





3v
($CDCl_3$,600M)





3v
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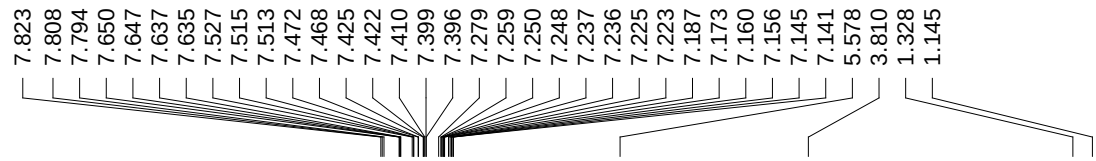
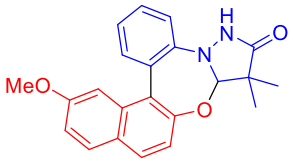
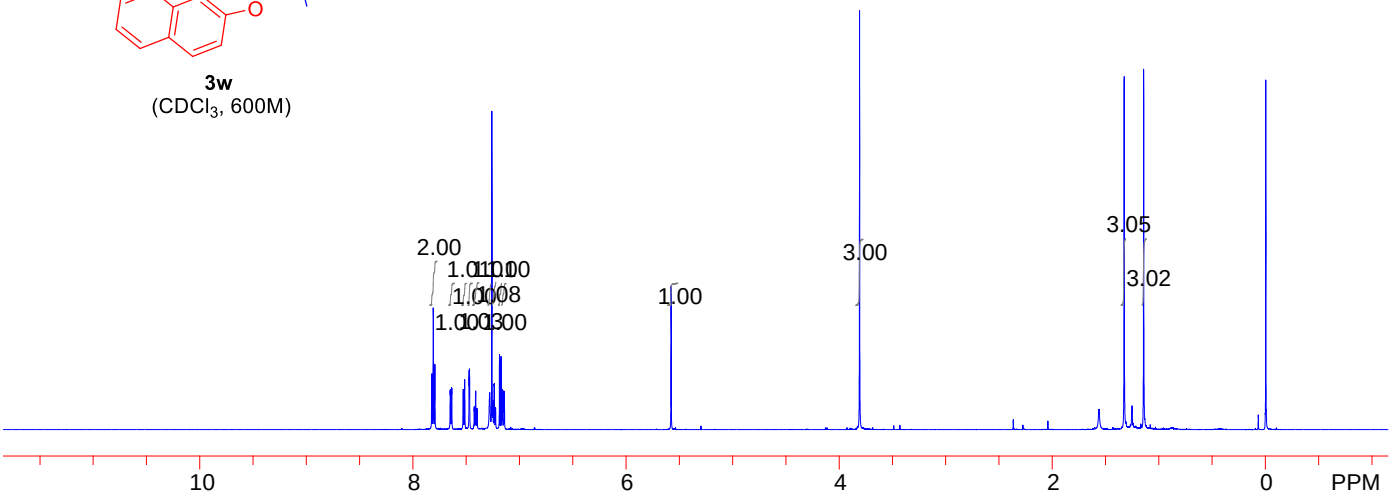
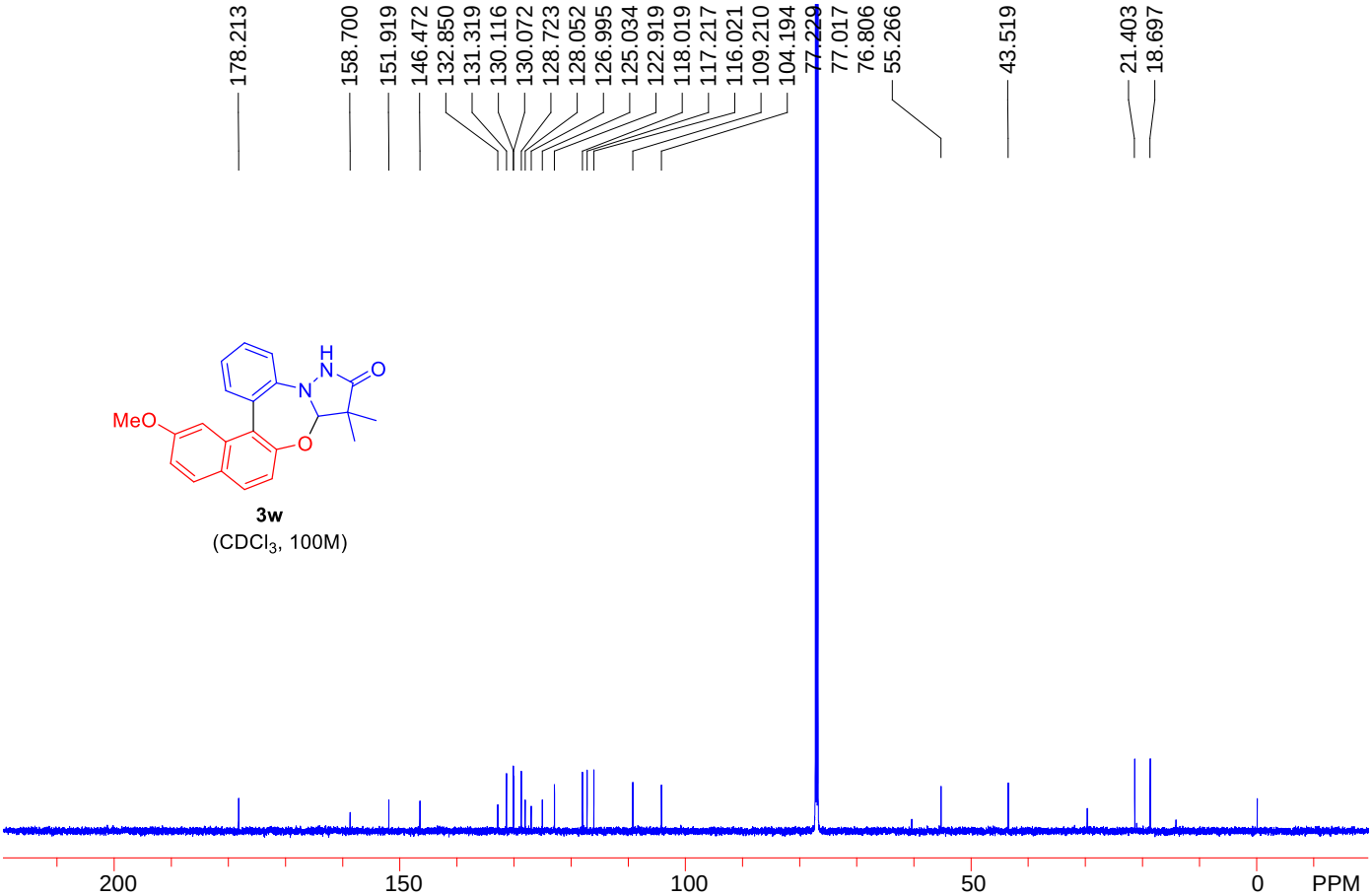




3w
($CDCl_3$, 600M)





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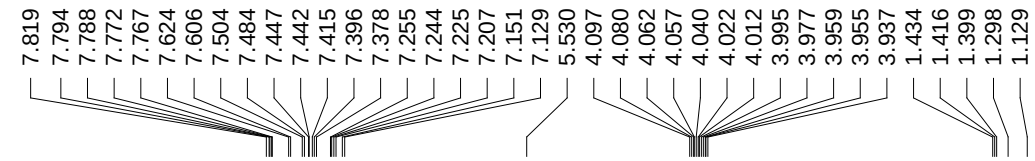

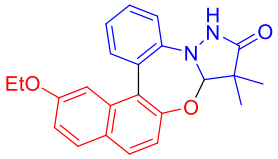

3x
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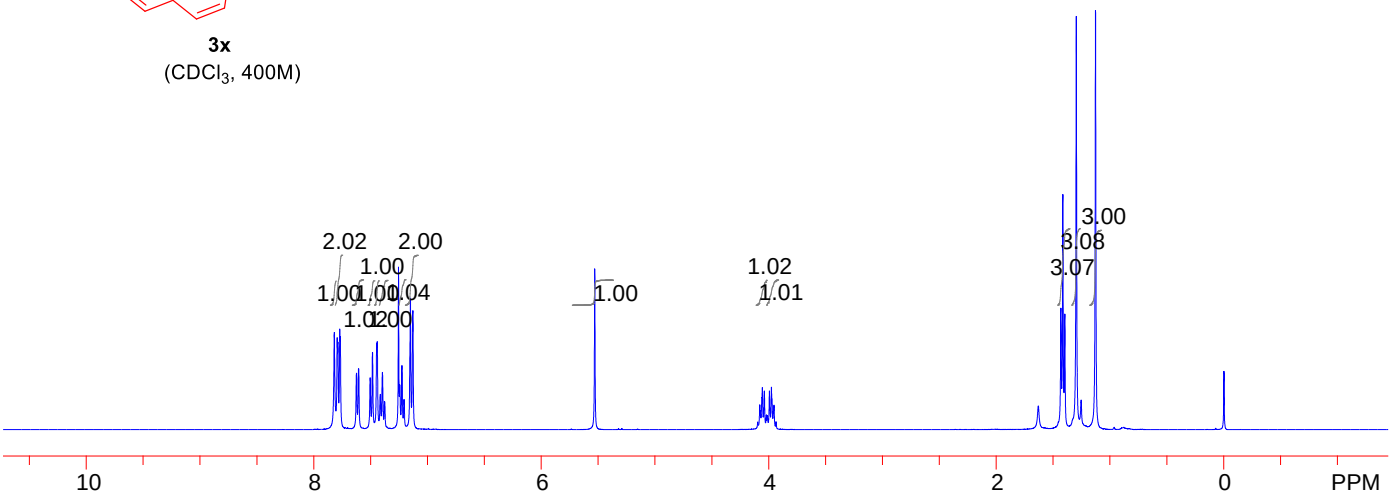

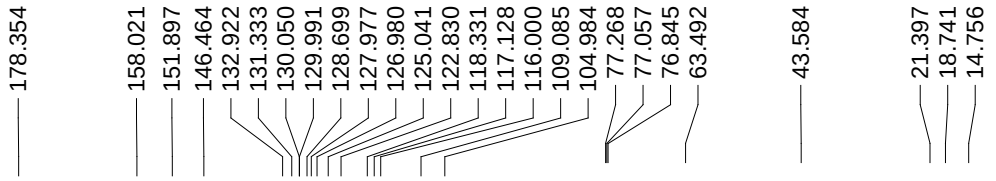

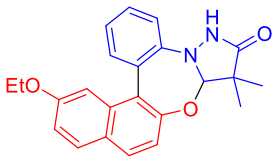

3x
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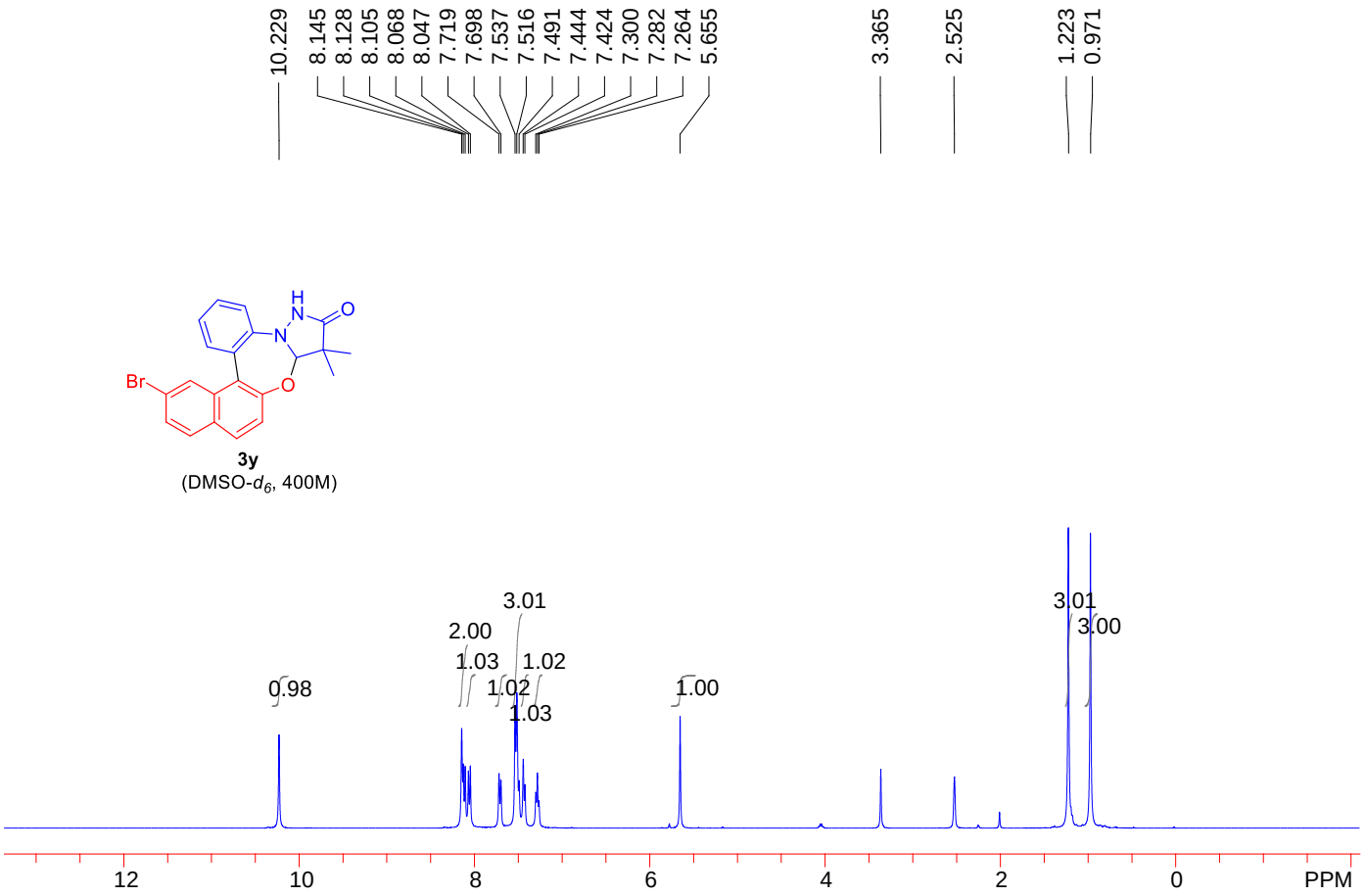
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H
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3y
(DMSO-d6, 400M)
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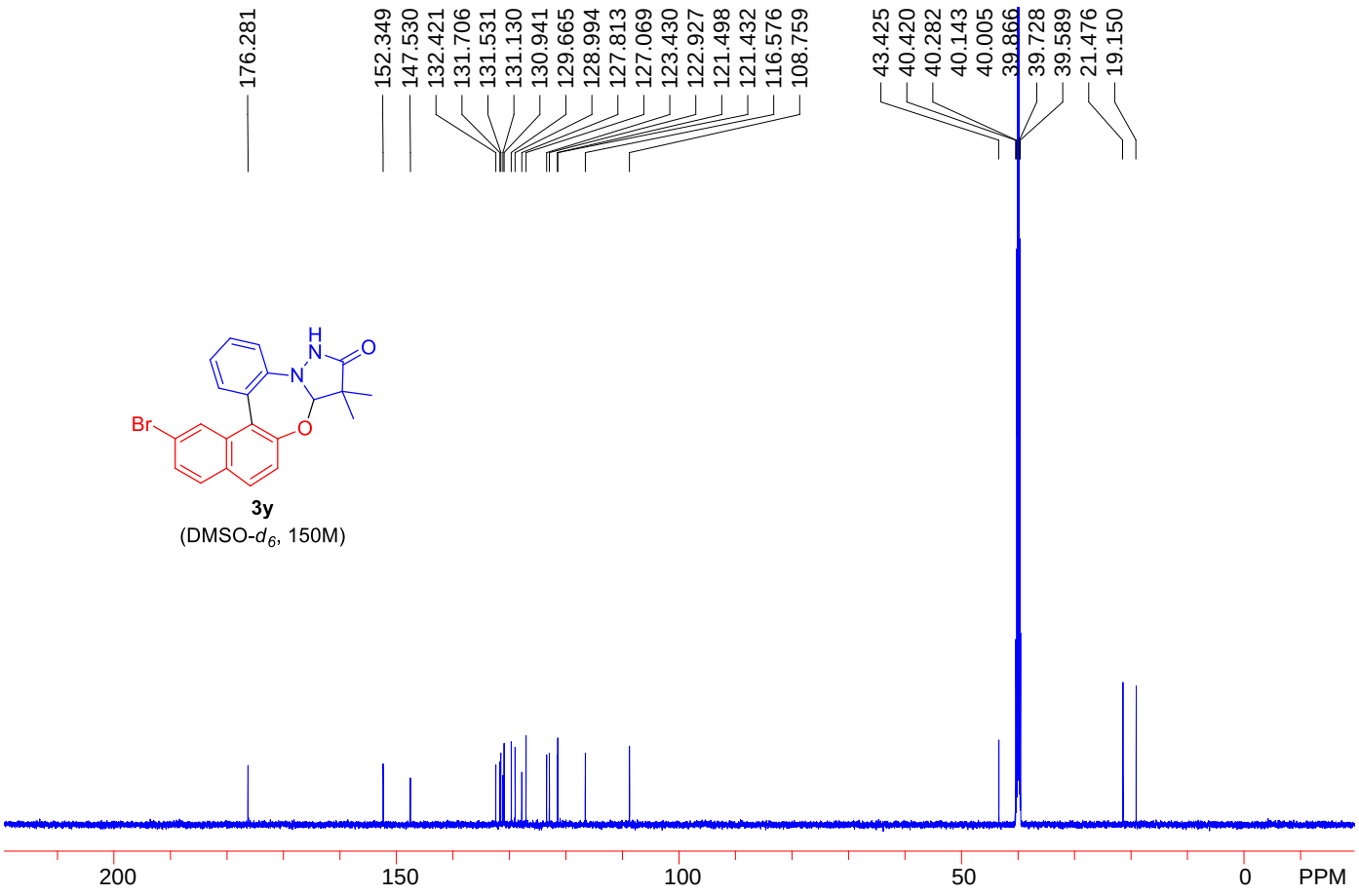
2
0
PPM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40.282
40.143
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39.866
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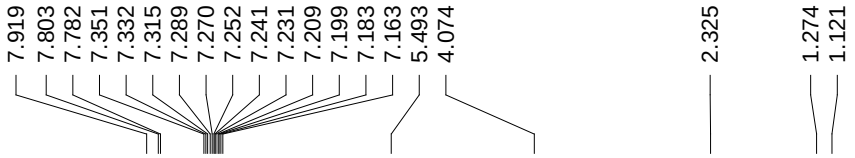
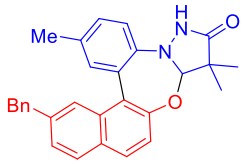
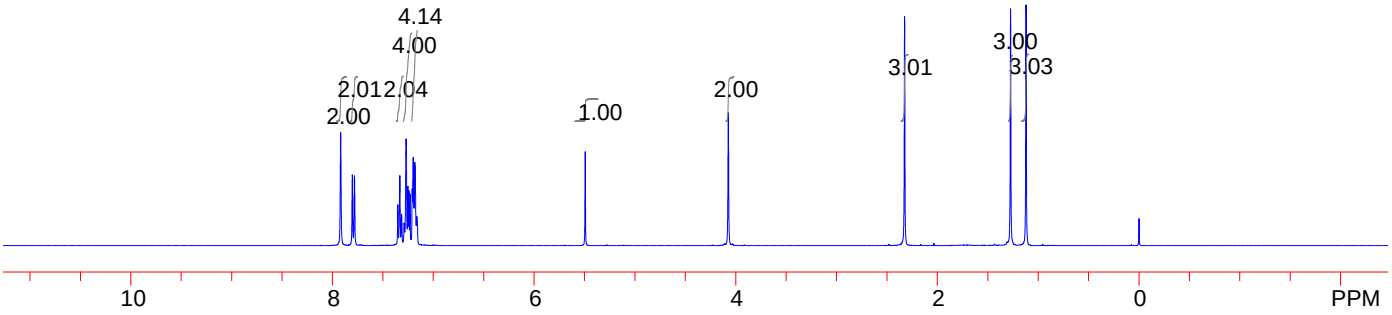
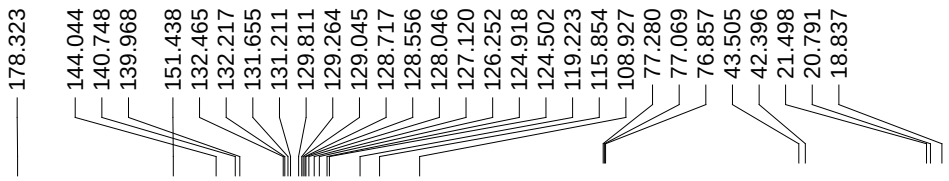
39.589
21.476
19.150
Br
O
N
H
O
3y
(DMSO-d6, 150M)
200
150
100
50
0
PPM

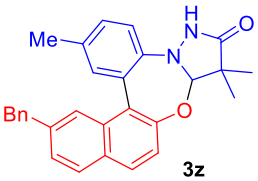




3z
($CDCl_3$, 400M)

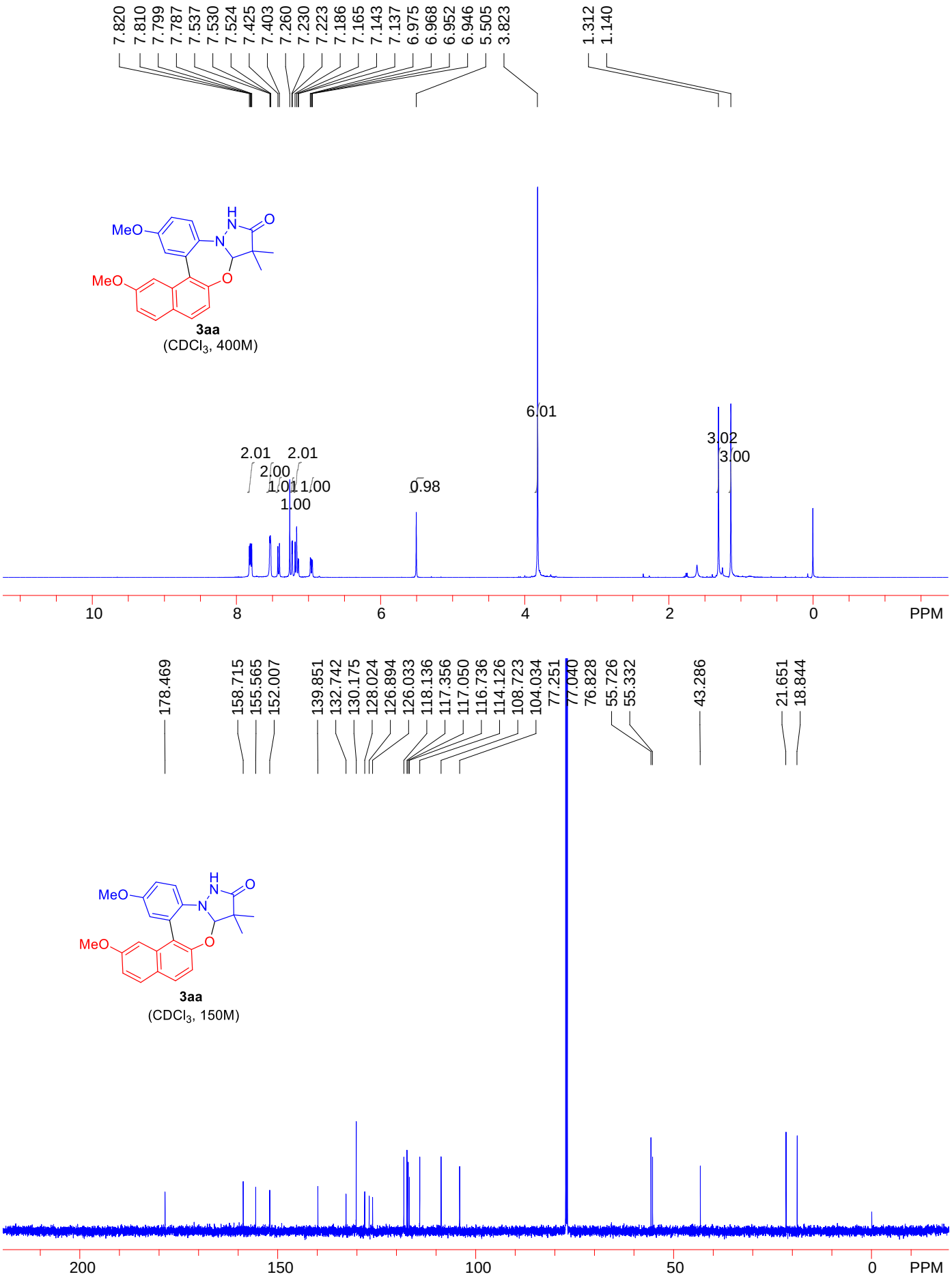


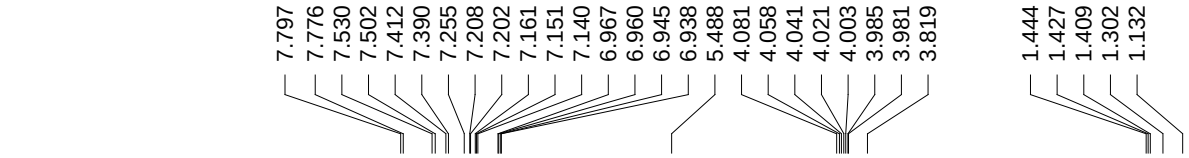


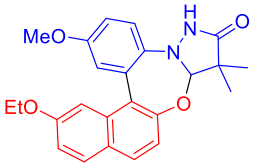


3z

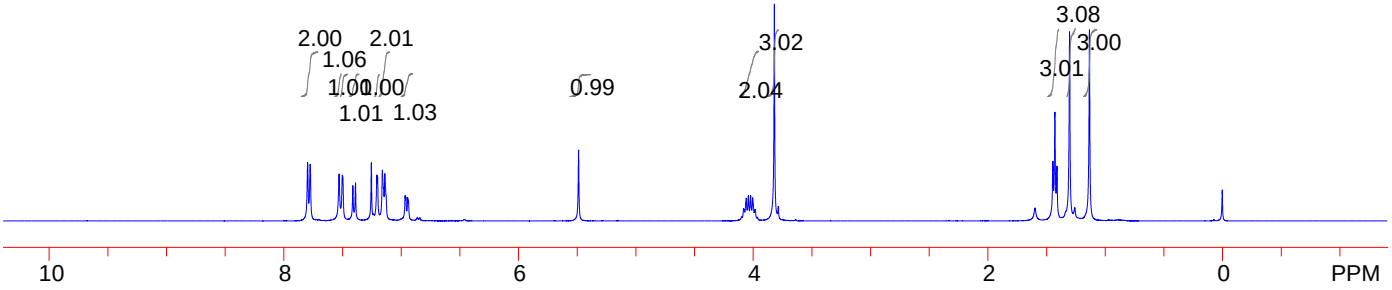
($CDCl_3$, 150 M)

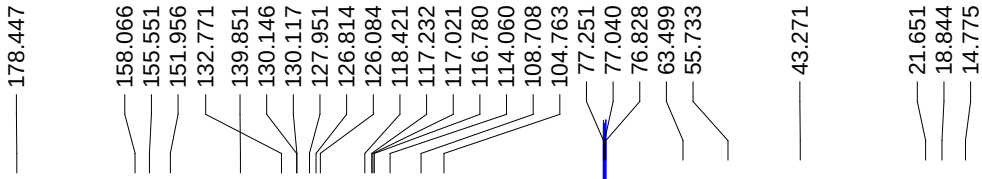

7.820
7.810
7.799
7.787
7.537
7.530
7.524
7.425
7.403
7.260
7.230
7.223
7.186
7.165
7.143
7.137
6.975
6.968
6.952
6.946
5.505
3.823
1.312
1.140
MeO
MeO
H
N
N
O
O
3aa
(CDCl3, 400M)
6.01
3.02
3.00
2.01
2.01
2.00
1.01
1.00
1.00
0.98
10
8
6
4
2
0
PPM
178.469
158.715
155.565
152.007
139.851
132.742
130.175
128.024
126.894
126.033
118.136
117.356
117.050
116.736
114.126
108.723
104.034
77.251
77.040
76.828
55.726
55.332
43.286
21.651
18.844
MeO
MeO
H
N
N
O
O
3aa
(CDCl3, 150M)
200
150
100
50
0
PPM

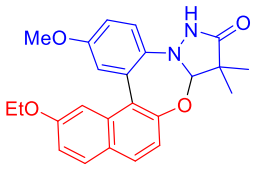




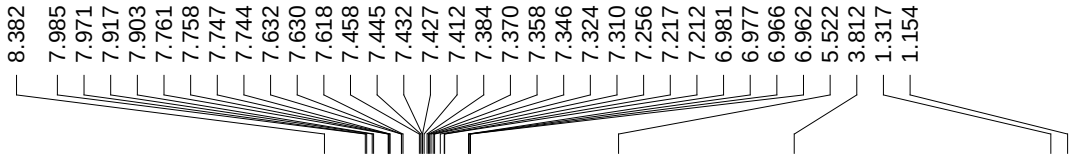
3bb
($CDCl_3$, 400M)

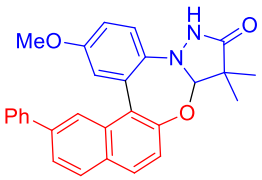




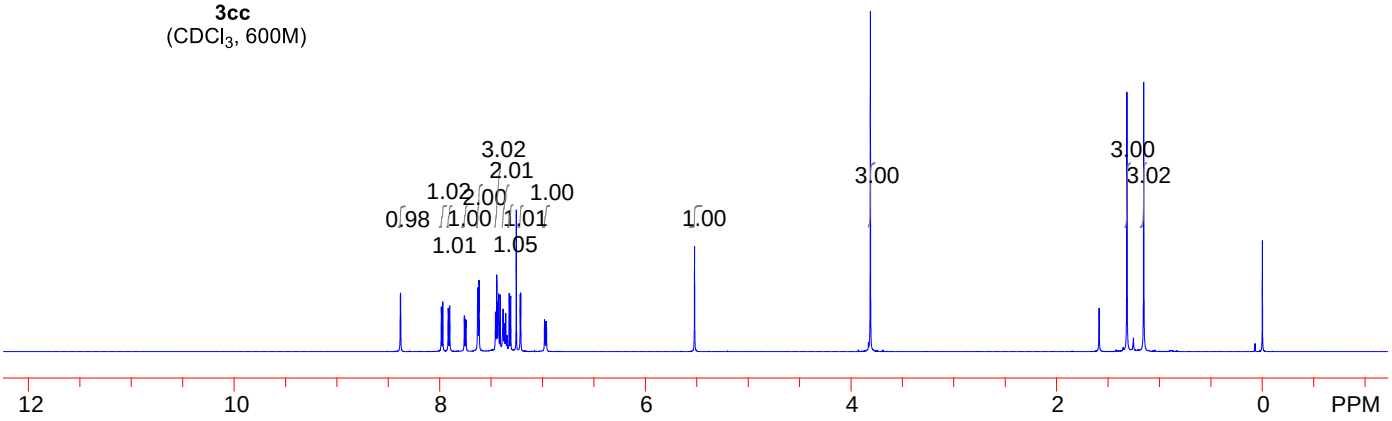


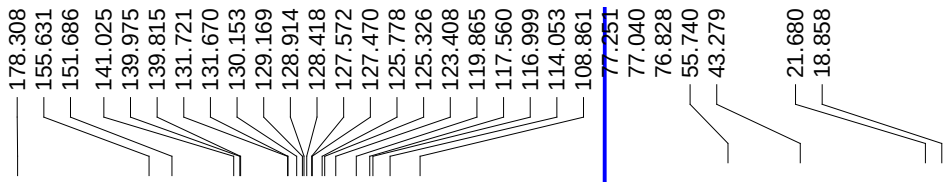
3bb
($CDCl_3$, 150M)

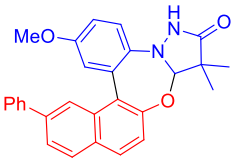




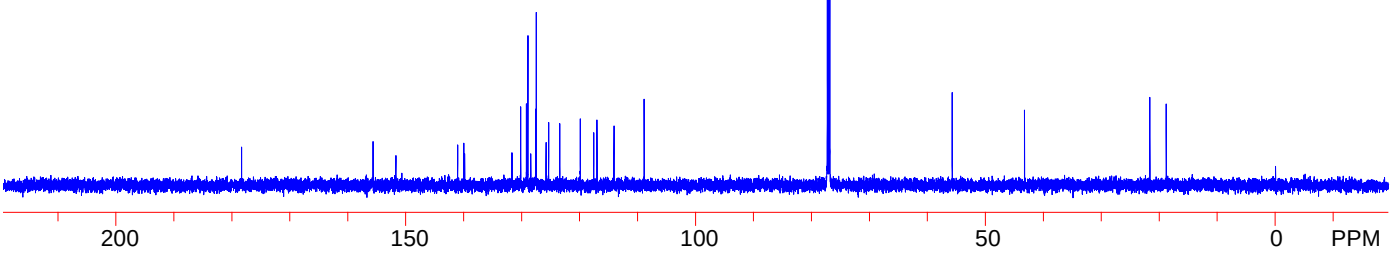
3cc
($CDCl_3$, 600M)

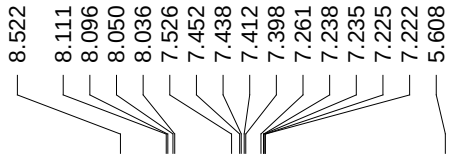


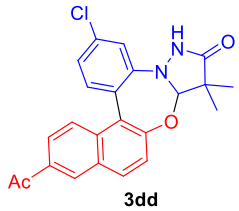




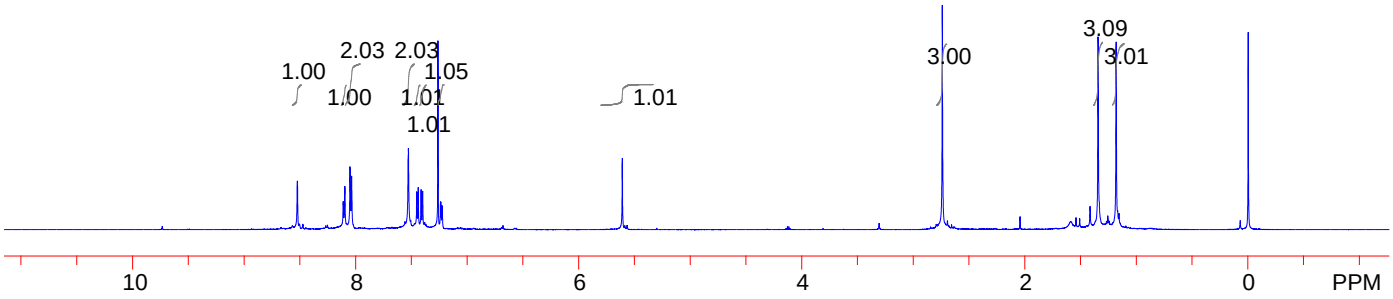
3cc
($CDCl_3$, 150M)

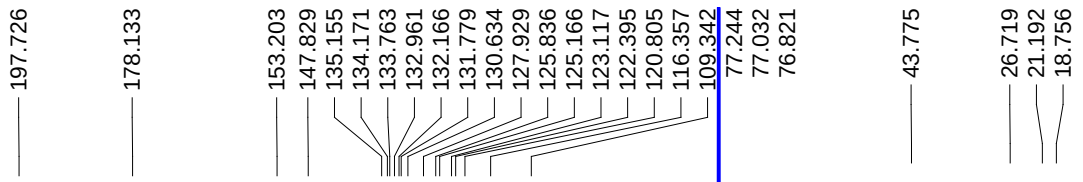


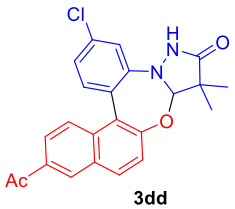




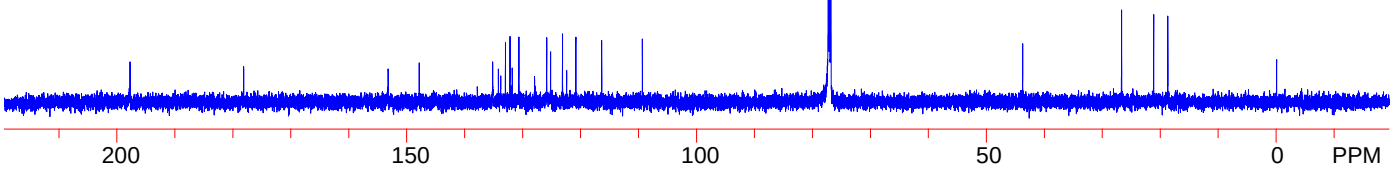
3dd
($CDCl_3$, 600M)

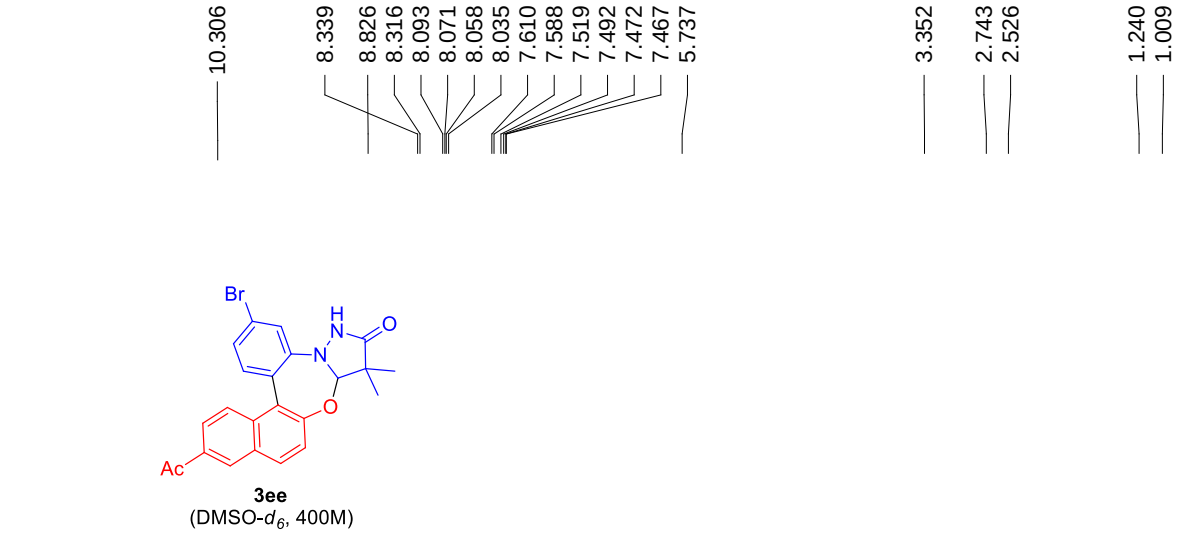




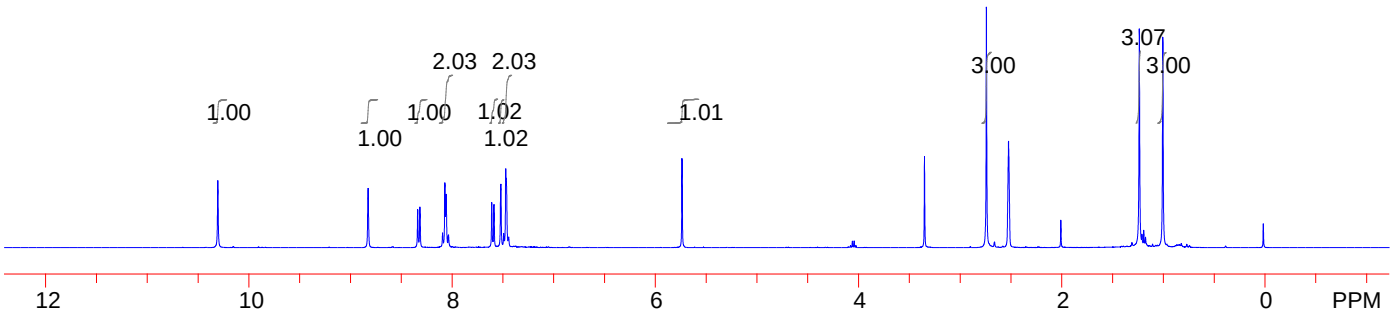


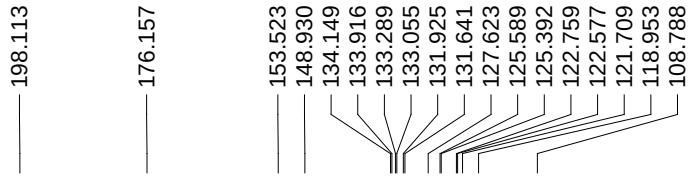
3dd
($CDCl_3$, 150M)

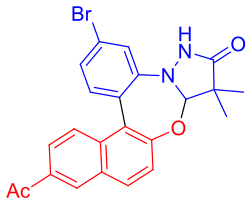




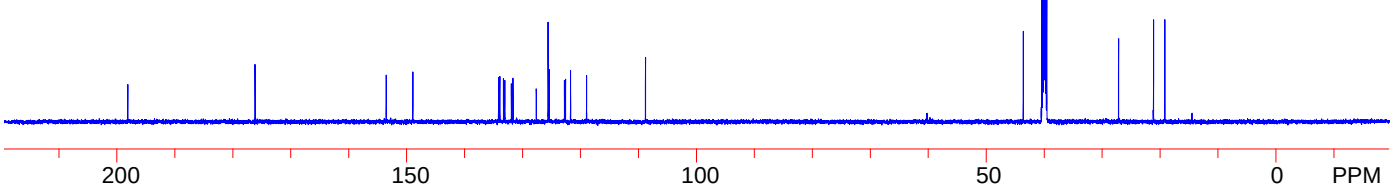
3ee
(DMSO-d_6, 400M)

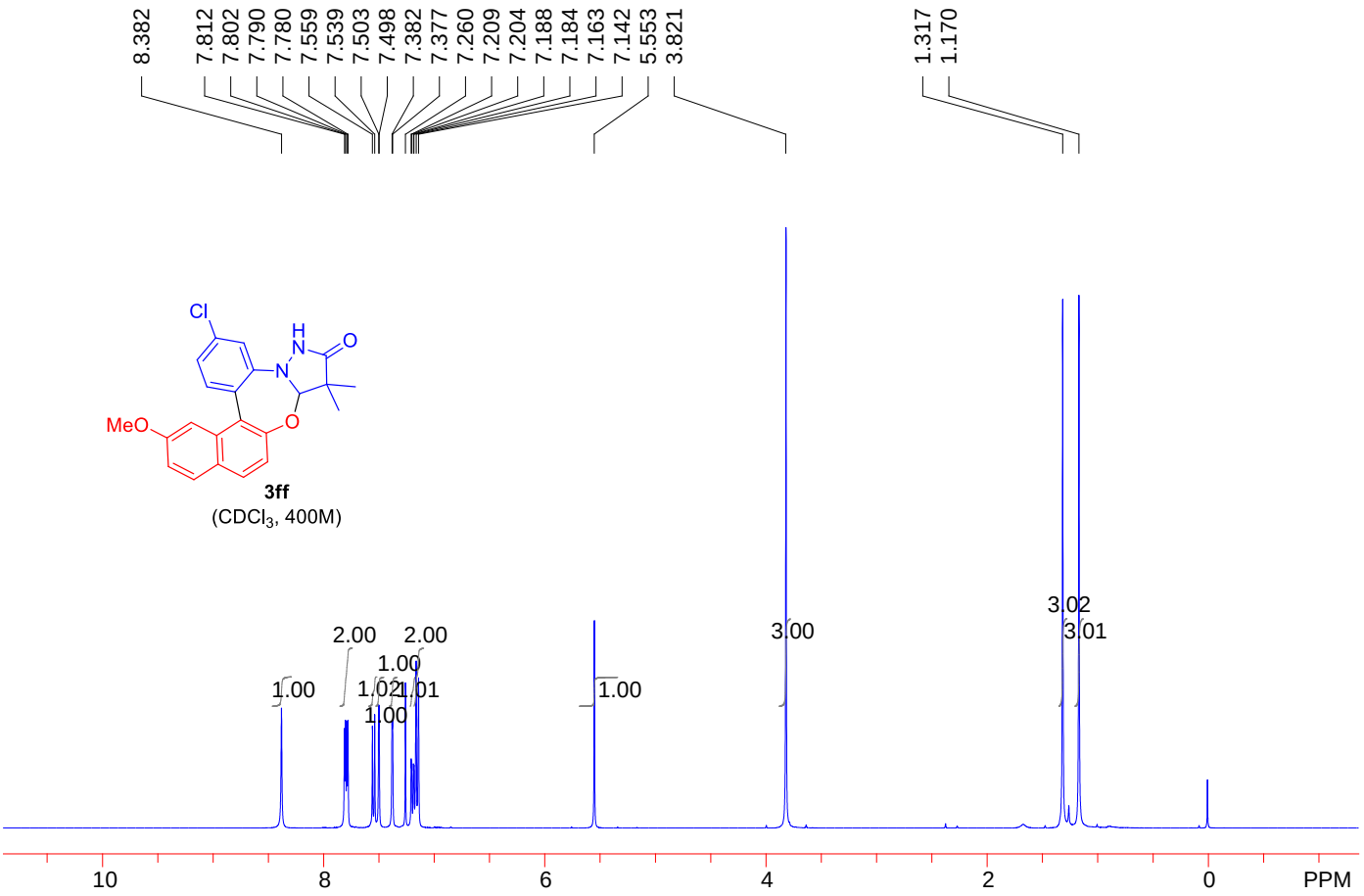


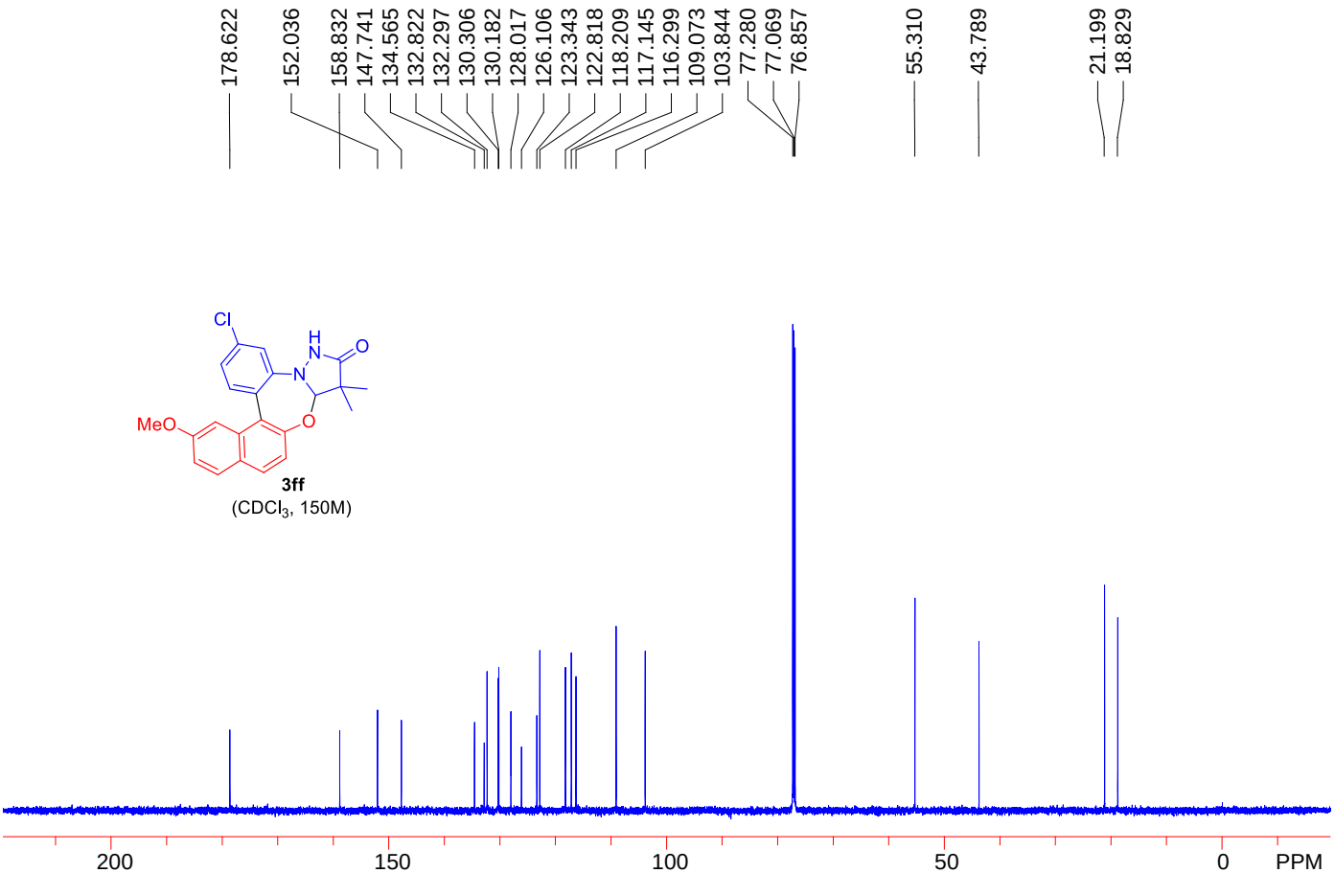


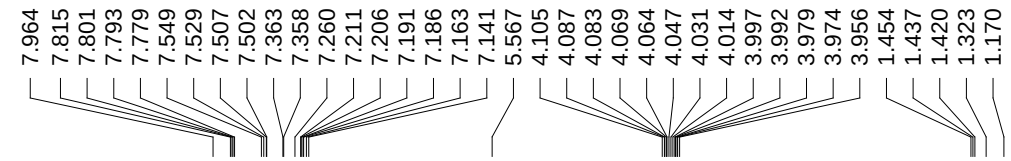


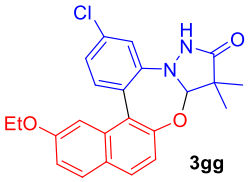
3ee
(DMSO-d_6, 150M)




8.382
7.812
7.802
7.790
7.780
7.559
7.539
7.503
7.498
7.382
7.377
7.260
7.209
7.204
7.188
7.184
7.163
7.142
5.553
3.821
1.317
1.170
Cl
H
N
N
O
MeO
O
3ff
(CDCl3, 400M)
1.00
2.00
2.00
1.00
1.02
1.01
1.00
1.00
3.00
3.02
3.01
10
8
6
4
2
0
PPM

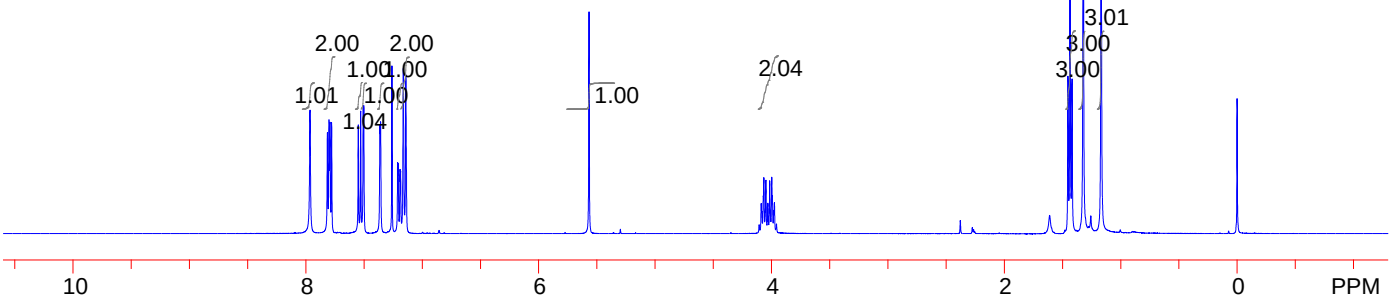

178.622
152.036
158.832
147.741
134.565
132.822
132.297
130.306
130.182
128.017
126.106
123.343
122.818
118.209
117.145
116.299
109.073
103.844
77.280
77.069
76.857
55.310
43.789
21.199
18.829
Cl
H
N
N
O
MeO
O
3ff
(CDCl3, 150M)
200
150
100
50
0
PPM

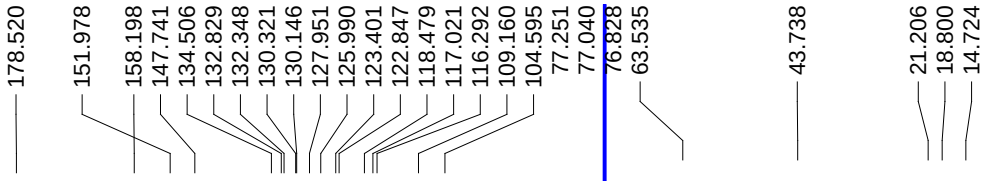


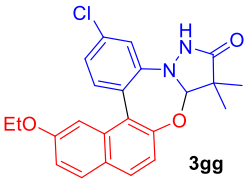


3gg

($CDCl_3$, 400M)

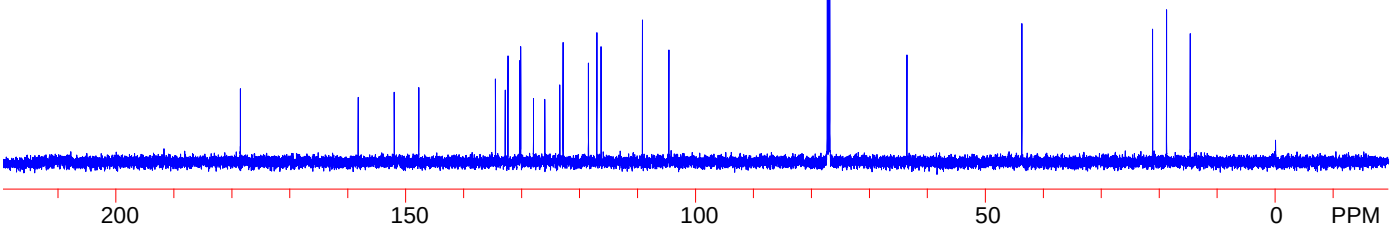


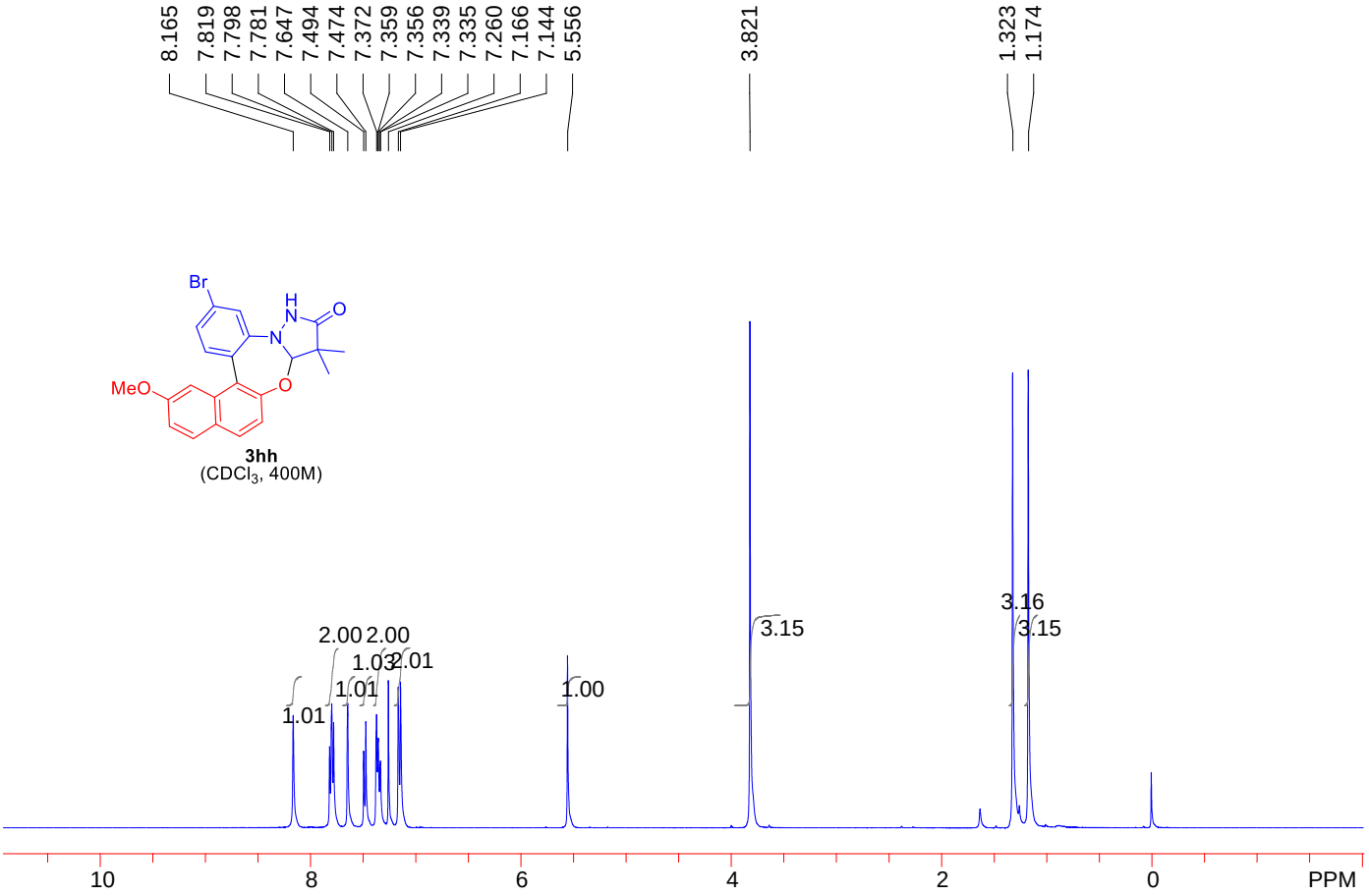


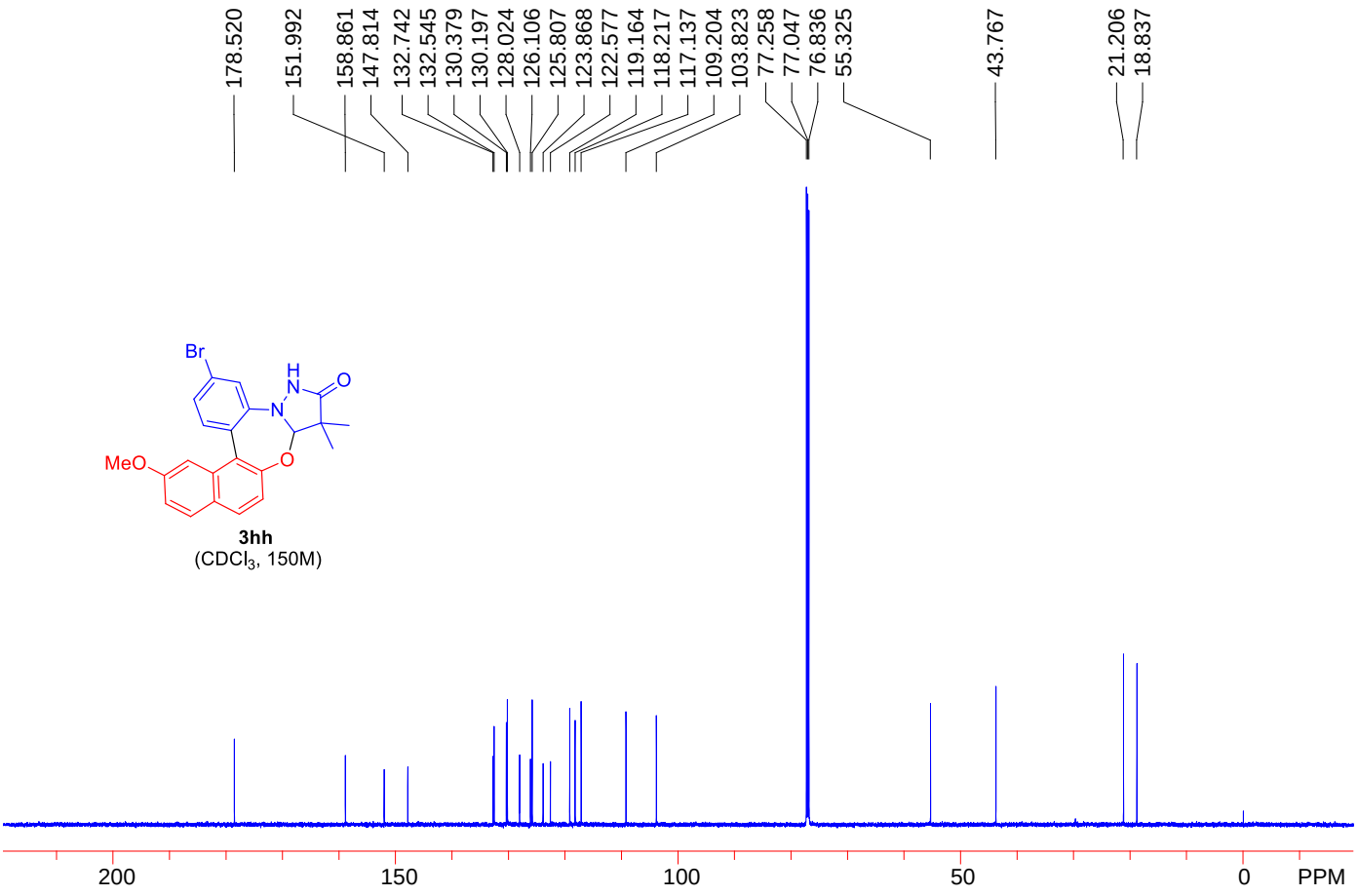


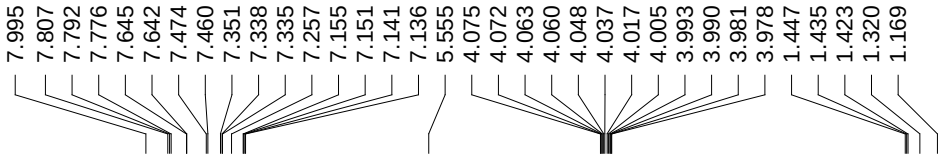
3gg

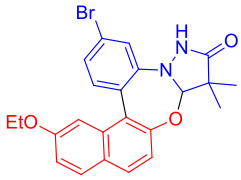
($CDCl_3$, 400M)



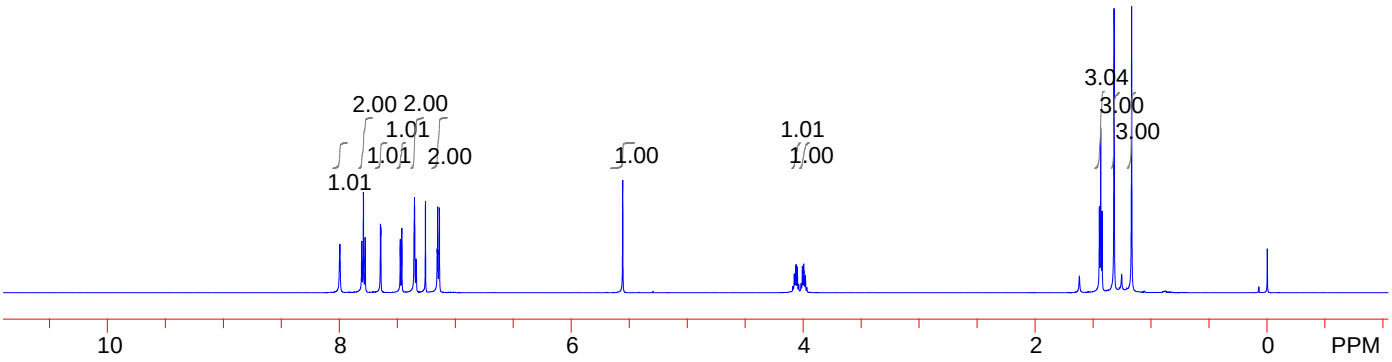

8.165
7.819
7.798
7.781
7.647
7.494
7.474
7.372
7.359
7.356
7.339
7.335
7.260
7.166
7.144
5.556
3.821
1.323
1.174
Br
H
N
N
O
MeO
O
3hh
(CDCl3, 400M)
2.00
2.00
1.03
2.01
1.01
1.01
1.00
3.15
3.16
3.15
10
8
6
4
2
0
PPM

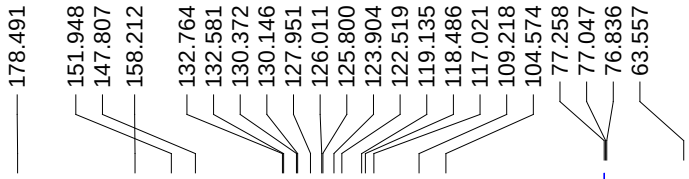

178.520
151.992
158.861
147.814
132.742
132.545
130.379
130.197
128.024
126.106
125.807
123.868
122.577
119.164
118.217
117.137
109.204
103.823
77.258
77.047
76.836
55.325
43.767
21.206
18.837
Br
H
N
N
O
MeO
O
3hh
(CDCl3, 150M)
200
150
100
50
0
PPM

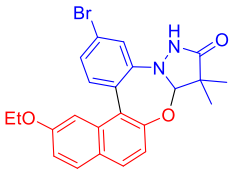




3ii
($CDCl_3$, 600M)

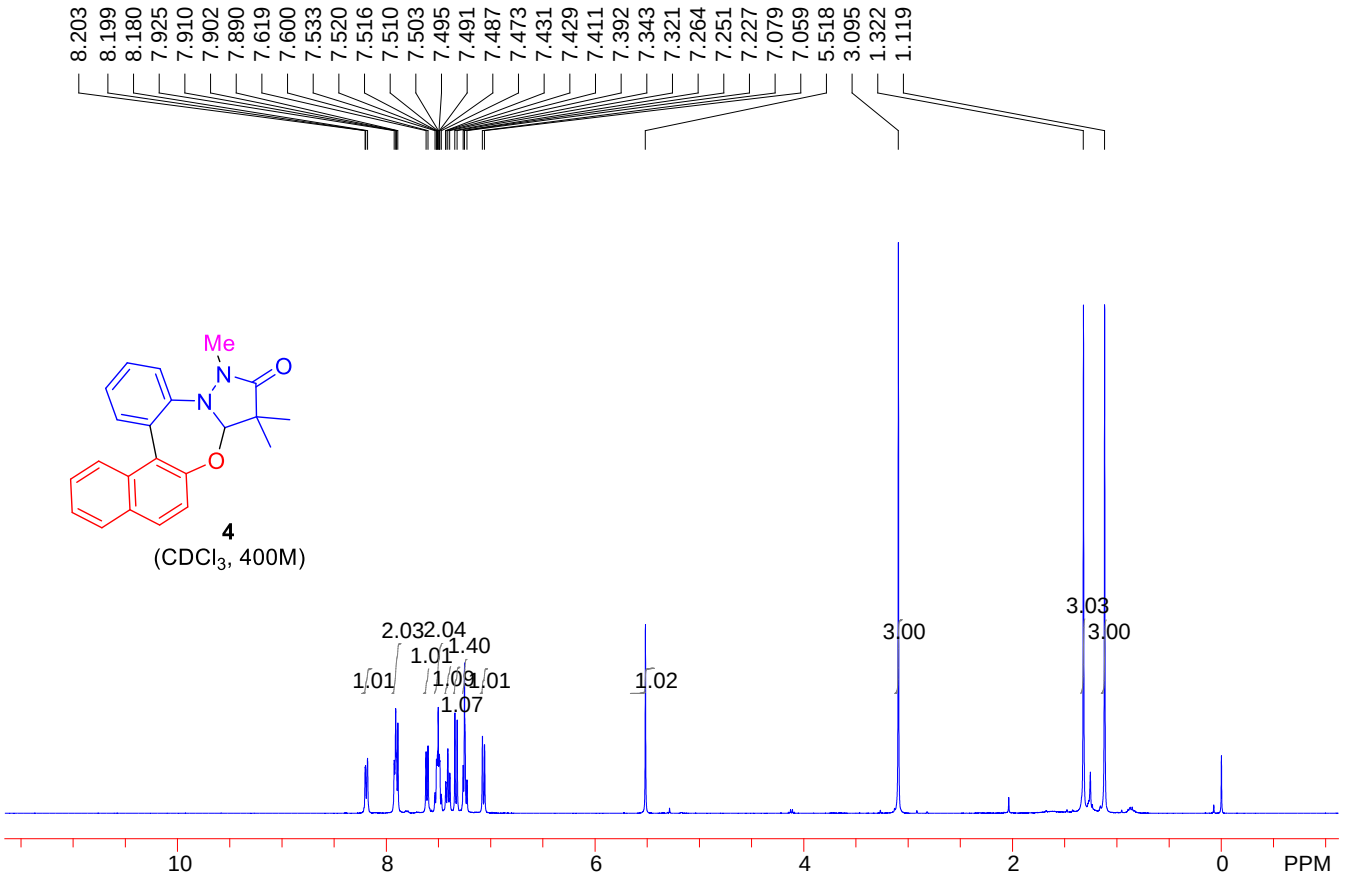


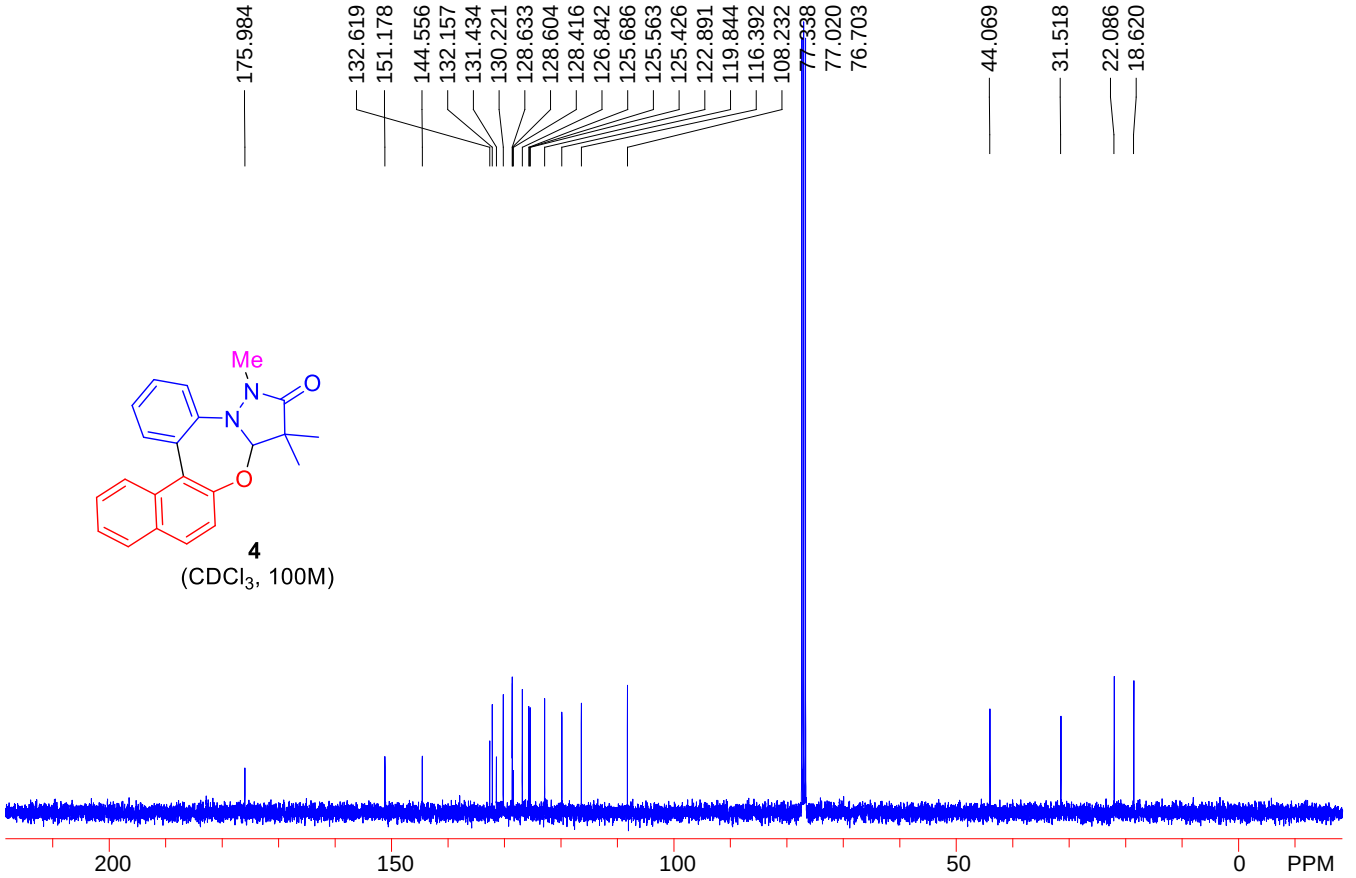


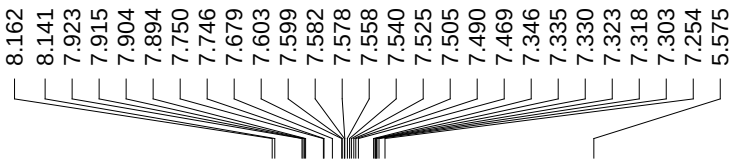


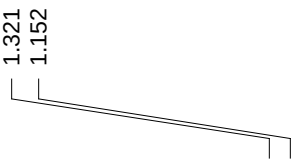
3ii
($CDCl_3$, 150M)

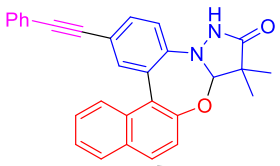
V. Copies of NMR spectra of 4-6





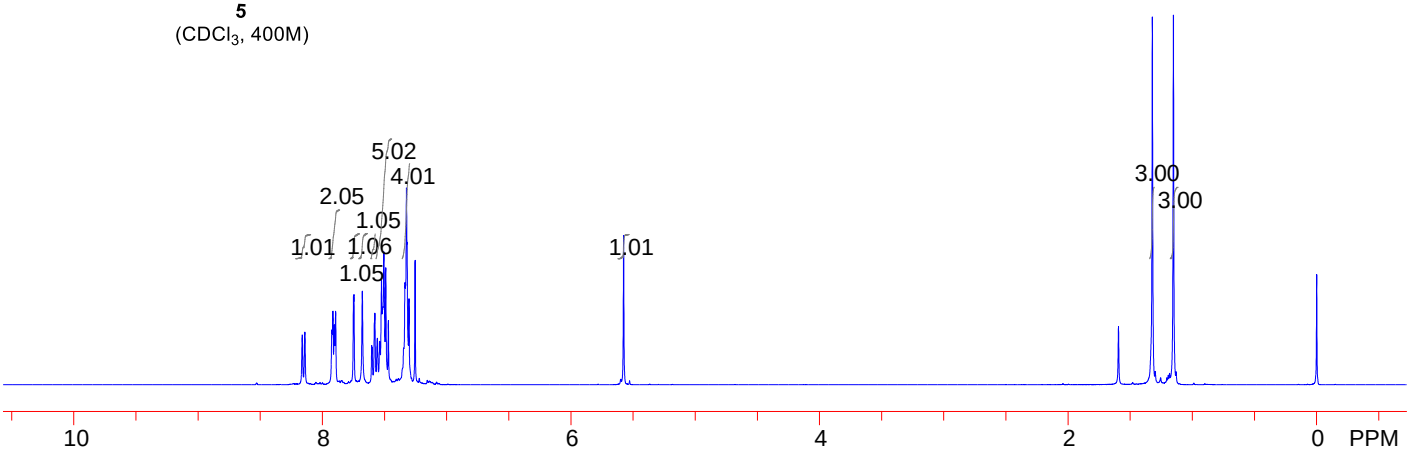


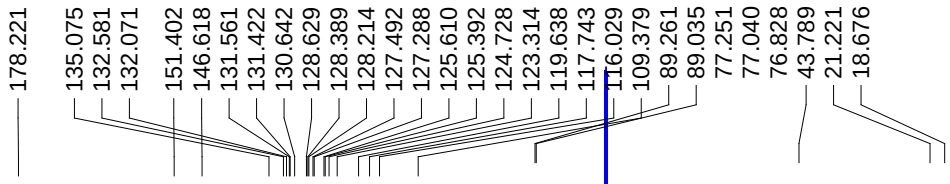


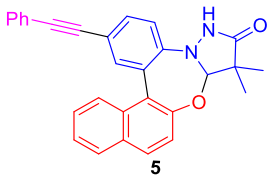


5

(CDCl$_3$, 400M)

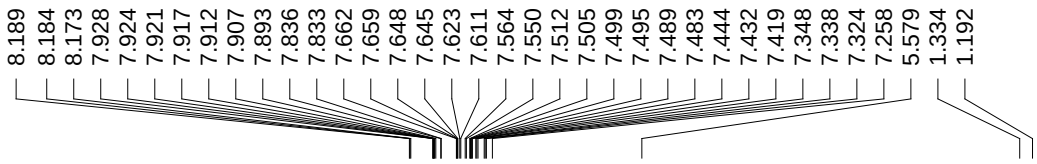


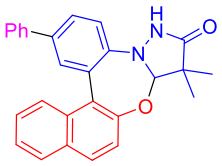




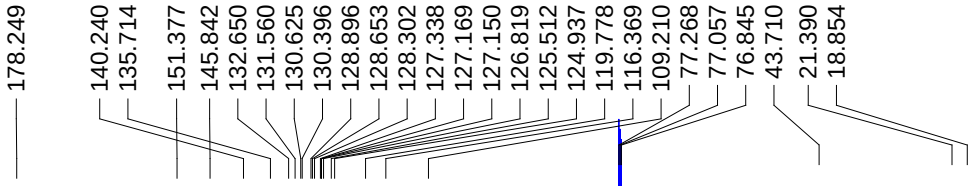
5

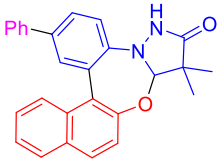
(CDCl$_3$, 150M)





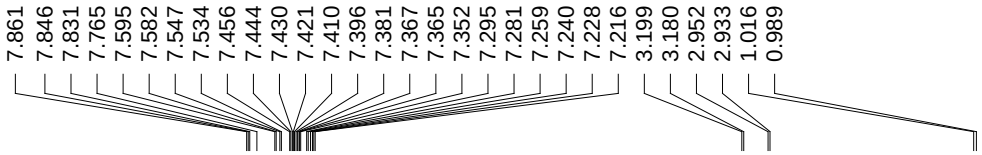
6
($CDCl_3$, 600M)

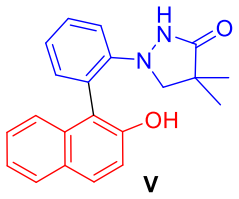




6
($CDCl_3$, 150M)

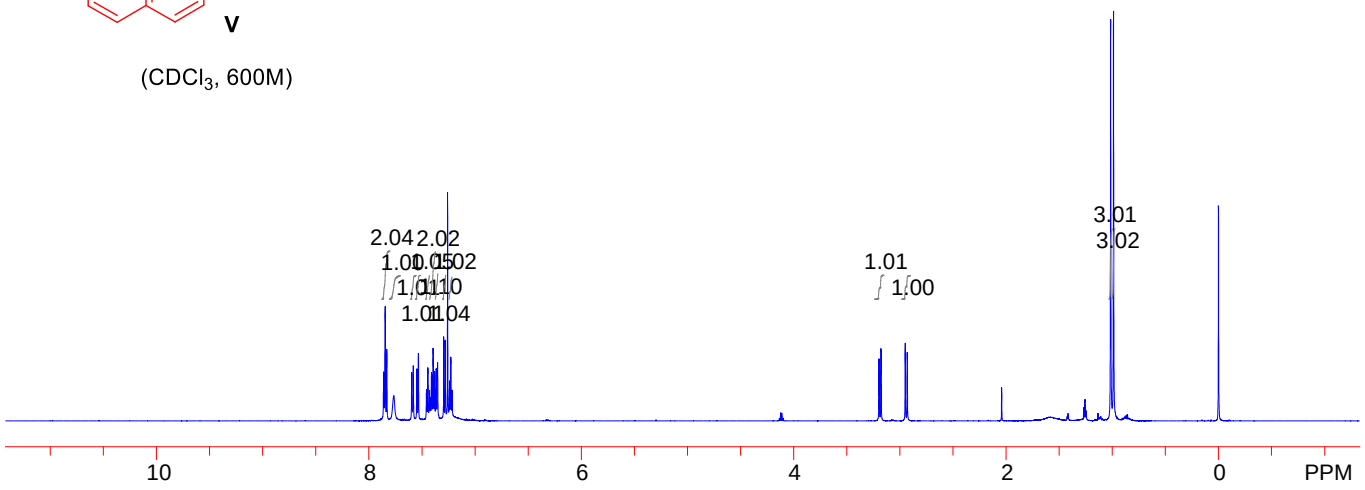
VI. Copies of NMR spectra of V

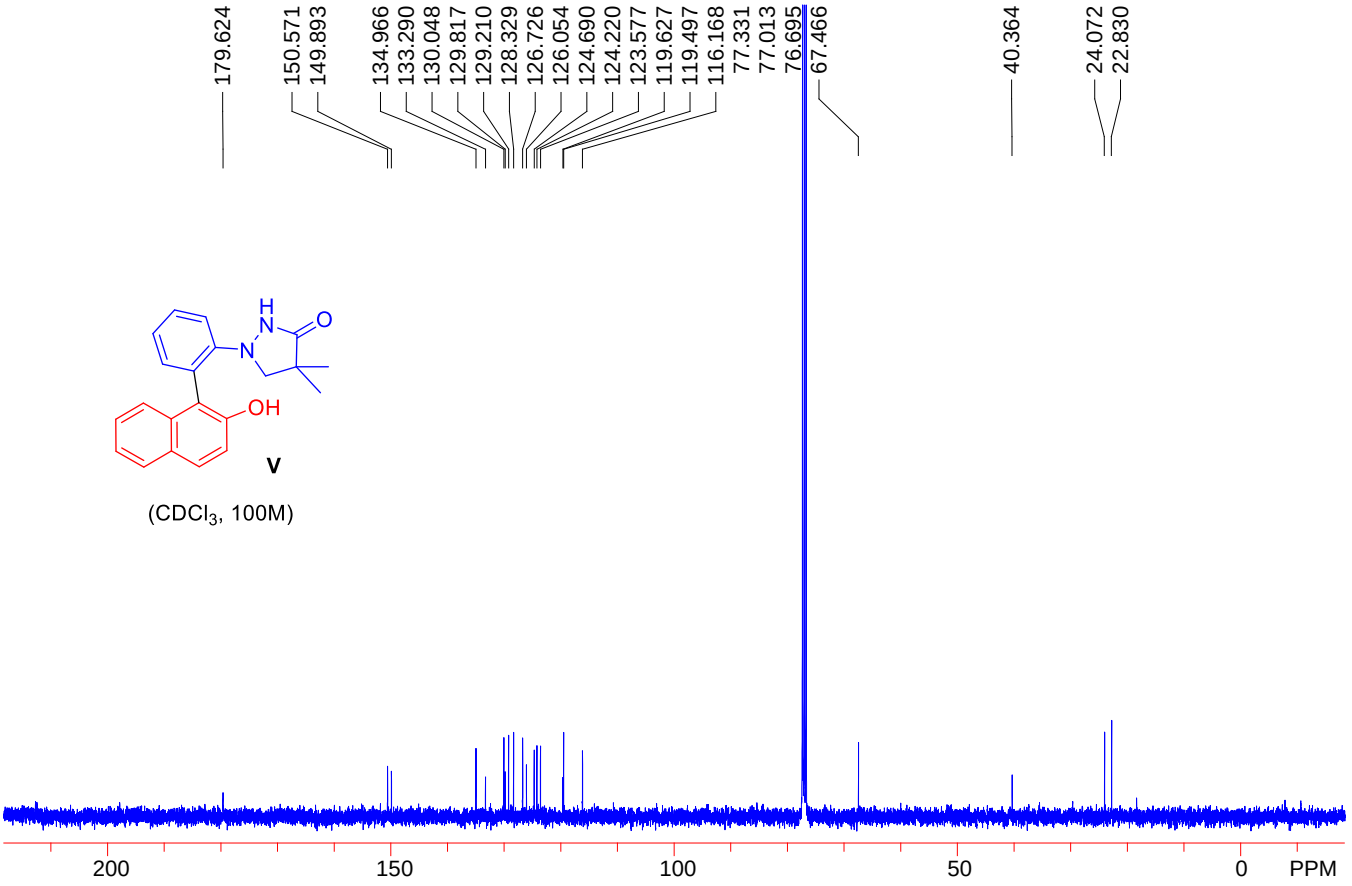




V

($CDCl_3$, 600M)





V

($CDCl_3$, 100M)

VII. X-ray crystal structure and data of 3a

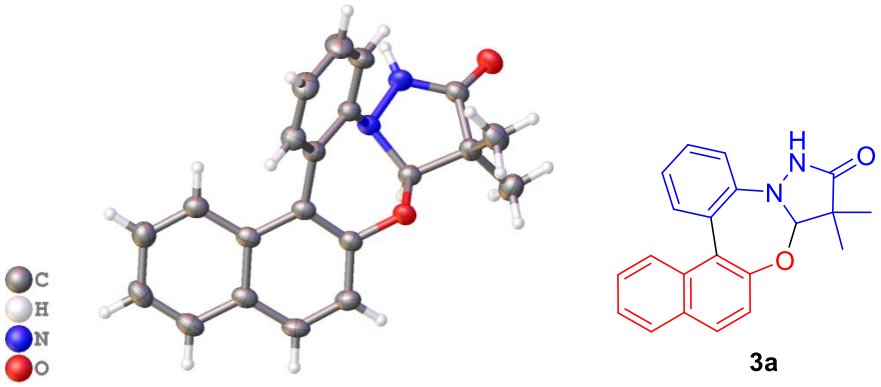


Fig. S4 X-ray crystal structure of **3a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a dichloromethane/ethyl acetate (3:1) solution of **3a**. Crystal data collection and refinement parameters of **3a** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. 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	$C_{21}H_{18}N_2O_2$
Formula weight	330.37
Temp, K	293 (2)
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.0718(2)
b, Å	9.9479(2)
c, Å	18.1789(3)
α (°)	90
β (°)	99.428(2)
γ (°)	90
Volume, Å^3	1618.40(6)

Z	4
d_{calc}, g cm^{-3}	1.356
λ, Å	1.54184
μ, mm^{-1}	0.705
No. of data collected	7072
No. of unique data	3076
R_{int}	0.0186
Goodness-of-fit on F^2	1.098
R_1, wR_2 ($I > 2\sigma(I)$)	0.0501, 0.1252
R_1, wR_2 (all data)	0.0539, 0.1286

VIII. X-ray crystal structure and data of 3m

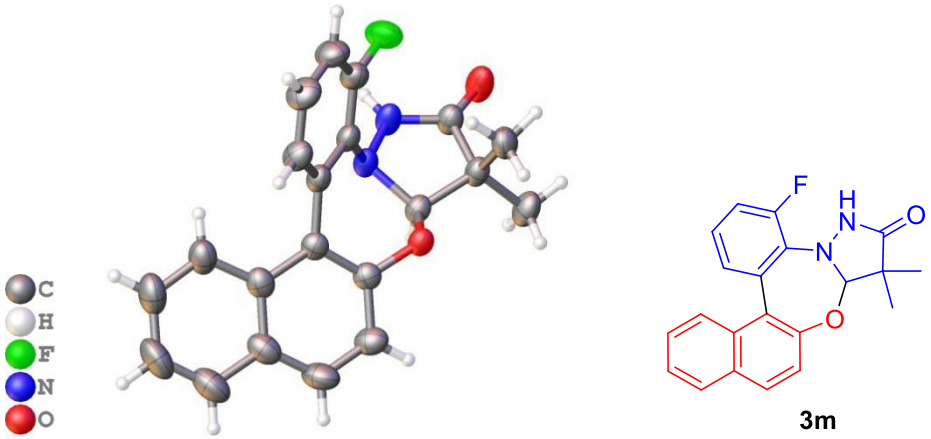


Fig. S5 X-ray crystal structure of **3m** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a chloroform solution of **3m**. Crystal data collection and refinement parameters of **3m** are summarized in Table S2. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S2 Crystallographic data and structure refinement results of **3m**

Empirical formula	$2(C_{21}H_{17}FN_2O_2)$, $CHCl_3$
Formula weight	816.10
Temp, K	293 (2)
Crystal system	monoclinic
Space group	C2/c
a, Å	27.3194(10)
b, Å	9.9217(2)
c, Å	18.9017(7)
α (°)	90
β (°)	131.359(6)
γ (°)	90

Volume, Å^3	3845.5(3)
Z	4
d_{calc}, g cm^{-3}	1.410
λ, Å	1.54184
μ, mm^{-1}	2.654
No. of data collected	9180
No. of unique data	3671
R_{int}	0.0135
Goodness-of-fit on F^2	1.040
R_1, wR_2 ($I > 2\sigma(I)$)	0.0472, 0.1295
R_1, wR_2 (all data)	0.0523, 0.1343

IX. X-ray crystal structure and data of V

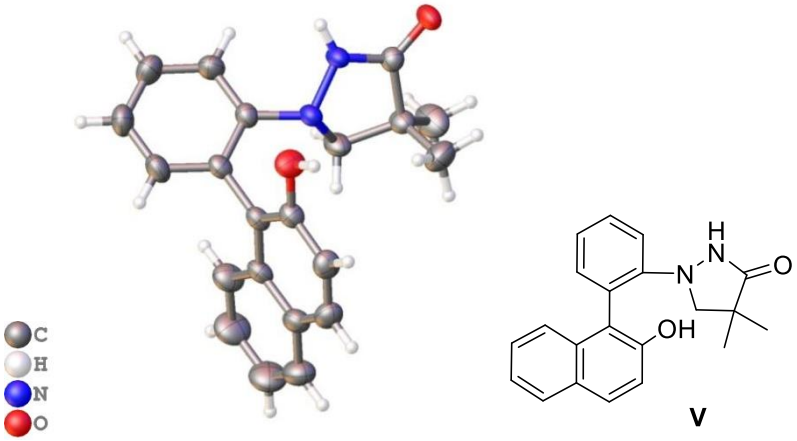


Fig. S6 X-ray crystal structure of **V** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an acetonitrile solution of **V**. Crystal data collection and refinement parameters of **V** are summarized in Table S3. Intensity data were collected at 295 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S3 Crystallographic data and structure refinement results of **V**

Empirical formula	$2(C_{21}H_{20}N_2O_2)$
Formula weight	664.78
Temp, K	295.2 (6)
Crystal system	triclinic
Space group	P-1
a, Å	10.8576(3)
b, Å	10.8630(3)
c, Å	15.5793(4)
α (°)	79.820(2)
β (°)	75.401(3)
γ (°)	89.673(2)

Volume, Å^3	1748.74(9)
Z	2
d_{calc}, g cm^{-3}	1.262
λ, Å	1.54184
μ, mm^{-1}	0.653
No. of data collected	14094
No. of unique data	6647
R_{int}	0.0258
Goodness-of-fit on F^2	1.264
R_1, wR_2 ($I > 2\sigma(I)$)	0.0500, 0.1492
R_1, wR_2 (all data)	0.0664, 0.1539

X. References

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