Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Divergent Construction of Fused and Bridged Carbo-/Heterocyclic Scaffolds via Cascade Reactions of Aryl Azomethine Imines with Vinyl Cyclic Carbonates

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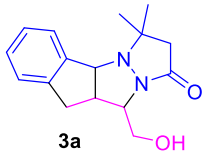
I. General experimental information

Commercial reagents were used without further purification. Aryl azomethine imines (**1**)[1] and 5-methylene-1,3-dioxan-2-one (**4**)[2] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. 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. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3v

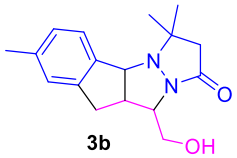
To a reaction tube equipped with a stir bar were charged with 2-benzylidene-3,3-dimethyl-5-oxopyrazolidin-2-ium-1-ide (**1a**, 40.4 mg, 0.2 mmol), 4-vinyl-1,3-dioxolan-2-one (**2**, 34.2 mg, 0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and TFE (2 mL). The mixture was stirred at 120 ℃ under air for 6 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 **3a**. **3b-3v** were obtained in a similar manner.



3a

10-(Hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3a)

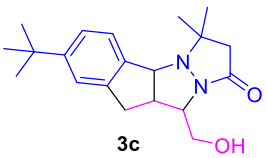
Eluent: petroleum ether/ethyl acetate (1:1). Yellowish oil (44.7 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29-7.25 (m, 3H), 7.22-7.21 (m, 1H), 5.55 (br s, 1H), 4.62 (d, J = 8.4 Hz, 1H), 3.99 (d, J = 12.0 Hz, 1H), 3.88 (dd, J_1 = 12.0 Hz, J_2 = 8.4 Hz, 1H), 3.23 (t, J = 9.0 Hz, 1H), 3.10 (dd, J_1 = 16.8 Hz, J_2 = 7.8 Hz, 1H), 2.85-2.79 (m, 3H), 2.37 (d, J = 15.6 Hz, 1H), 1.50 (s, 3H), 1.27 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.9, 142.5, 140.3, 128.4, 127.6, 125.5, 125.3, 64.0, 63.75, 63.69, 61.6, 49.7, 46.8, 34.3, 26.3, 19.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_2$ 273.1598; Found 273.1590.



3b

10-(Hydroxymethyl)-3,3,7-trimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3b)

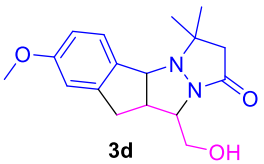
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (41.1 mg, 72%), mp 137.0-137.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.06 (s, 1H), 5.55 (dd, J_1 = 11.4 Hz, J_2 = 3.6 Hz, 1H), 4.61 (d, J = 8.4 Hz, 1H), 4.03-3.99 (m, 1H), 3.92-3.88 (m, 1H), 3.25 (t, J = 9.0 Hz, 1H), 3.07 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.86-2.81 (m, 2H), 2.77 (d, J = 16.2 Hz, 1H), 2.40 (d, J = 15.0 Hz, 1H), 2.36 (s, 3H), 1.54 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.0, 140.7, 138.6, 128.6, 126.1, 125.0, 64.1, 63.8, 61.6, 49.6, 47.2, 34.3, 26.2, 21.3, 19.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1750.



3c

7-(*tert*-Butyl)-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3c)

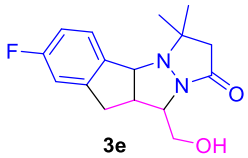
Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (43.8 mg, 67%), mp 190.4-191.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.25 (s, 1H), 7.20 (d, J = 7.8 Hz, 1H), 5.56 (dd, J_1 = 11.4 Hz, J_2 = 3.6 Hz, 1H), 4.62 (d, J = 8.4 Hz, 1H), 4.01 (td, J_1 = 12.6 Hz, J_2 = 2.4 Hz, 1H), 3.92-3.88 (m, 1H), 3.29 (t, J = 8.4 Hz, 1H), 3.11 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.88-2.81 (m, 3H), 2.39 (d, J = 15.6 Hz, 1H), 1.51 (s, 3H), 1.30 (s, 9H), 1.29 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.8, 151.9, 140.3, 139.5, 125.1, 124.7, 122.2, 63.8, 63.7, 63.6, 61.8, 49.8, 47.1, 34.7, 34.5, 31.5, 26.4, 19.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{20}H_{29}N_2O_2$ 329.2224; Found 329.2215.



3d

10-(Hydroxymethyl)-7-methoxy-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3d)

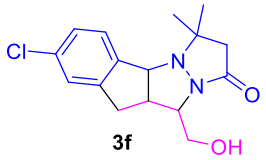
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (38.5 mg, 64%), mp 114.3-115.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (d, J = 8.4 Hz, 1H), 6.83 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.74 (d, J = 1.8 Hz, 1H), 5.57 (br s, 1H), 4.59 (d, J = 8.4 Hz, 1H), 4.00 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H), 3.89 (dd, J_1 = 12.6 Hz, J_2 = 8.4 Hz, 1H), 3.79 (s, 3H), 3.29 (t, J = 9.0 Hz, 1H), 3.09 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.87-2.78 (m, 3H), 2.39 (d, J = 15.0 Hz, 1H), 1.50 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.9, 160.3, 142.1, 134.4, 126.0, 114.3, 110.1, 63.8, 63.6, 63.5, 61.8, 55.5, 49.7, 47.5, 34.6, 26.4, 19.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_3$ 303.1703; Found 303.1704.



3e

7-Fluoro-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3e)

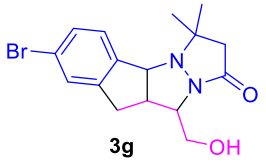
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (38.9 mg, 67%), mp 149.7-150.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, J_1 = 8.0 Hz, J_2 = 5.2 Hz, 1H), 6.98 (td, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.91 (d, J = 8.8 Hz, 1H), 5.47 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.60 (d, J = 8.0 Hz, 1H), 4.05-3.98 (m, 1H), 3.92-3.86 (m, 1H), 3.27 (t, J = 8.8 Hz, 1H), 3.12 (dd, J_1 = 16.4 Hz, J_2 = 7.2 Hz, 1H), 2.92-2.88 (m, 1H), 2.85-2.79 (m, 2H), 2.39 (d, J = 15.2 Hz, 1H), 1.50 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.0, 163.3 (d, $^{1}J_{C\text{-}F}$ = 244.1 Hz), 142.6 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 138.1 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 126.6 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 115.0 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 112.2 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 63.8, 63.7, 63.3, 61.5, 49.6, 47.3, 34.3 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 26.3, 19.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ -114.30 – -114.34 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}FN_2O_2$ 291.1503; Found 291.1503.



3f

7-Chloro-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3f)

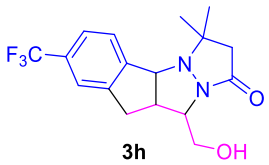
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (43.4 mg, 71%), mp 153.2-154.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.21 (s, 1H), 7.18 (d, J = 7.8 Hz, 1H), 5.47-5.45 (m, 1H), 4.59 (d, J = 7.8 Hz, 1H), 4.01 (t, J = 10.2 Hz, 1H), 3.88 (dd, J_1 = 12.6 Hz, J_2 = 8.4 Hz, 1H), 3.24 (t, J = 9.0 Hz, 1H), 3.10 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.87 (dd, J_1 = 15.6 Hz, J_2 = 7.8 Hz, 1H), 2.83-2.78 (m, 2H), 2.39 (d, J = 15.6 Hz, 1H), 1.49 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.0, 142.3, 141.1, 134.3, 128.0, 126.5, 125.6, 63.7, 63.6, 63.4, 61.5, 49.6, 47.0, 34.1, 26.3, 19.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}ClN_2O_2$ 307.1208; Found 307.1204.



3g

7-Bromo-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3g)

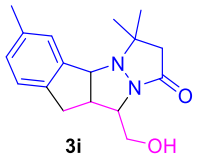
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (45.5 mg, 65%), mp 176.7-177.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, J = 7.8 Hz, 1H), 7.38 (s, 1H), 7.13 (d, J = 7.8 Hz, 1H), 5.44 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.57 (d, J = 8.4 Hz, 1H), 4.03-3.99 (m, 1H), 3.90-3.86 (m, 1H), 3.24 (t, J = 9.0 Hz, 1H), 3.12 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 1H), 2.88-2.79 (m, 3H), 2.39 (d, J = 15.0 Hz, 1H), 1.49 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 164.5, 144.9, 142.9, 130.2, 128.5, 128.0, 121.4, 63.3, 63.0, 62.3, 60.0, 49.8, 48.7, 35.0, 26.3, 19.7. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{16}H_{19}BrN_2NaO_2$ 373.0522; Found 373.0512.



3h

10-(Hydroxymethyl)-3,3-dimethyl-7-(trifluoromethyl)-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3h)

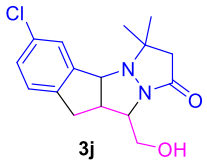
Eluent: petroleum ether/ethyl acetate (1:1). White solid (32.4 mg, 48%), mp 175.4-176.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 5.38-5.37 (m, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 4.04 (t, *J* = 10.8 Hz, 1H), 3.92-3.89 (m, 1H), 3.23 (t, *J* = 9.0 Hz, 1H), 3.18 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.93 (dd, J_1 = 16.2 Hz, J_2 = 8.4 Hz, 1H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 15.6 Hz, 1H), 2.41 (d, *J* = 15.6 Hz, 1H), 1.53 (s, 3H), 1.30 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): 165.0, 146.5, 141.1, 131.0 (q, $^{2}J_{C\text{-}F}$ = 32.9 Hz), 125.9, 124.9 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 271.4 Hz), 122.5 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 63.9, 63.8, 63.5, 61.3, 49.5, 46.8, 34.1, 26.4, 19.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.24 (s). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{20}F_3N_2O_2$ 341.1471; Found 341.1467.



3i

10-(Hydroxymethyl)-3,3,6-trimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3i)

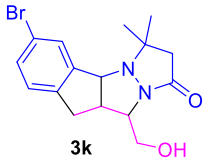
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (37.0 mg, 65%), mp 153.4-154.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 5.60 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.02-3.98 (m, 1H), 3.91-3.87 (m, 1H), 3.28 (t, *J* = 9.0 Hz, 1H), 3.08 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.86-2.82 (m, 2H), 2.78 (d, *J* = 16.8 Hz, 1H), 2.39 (d, *J* = 15.0 Hz, 1H), 2.34 (s, 3H), 1.51 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) : δ 165.0, 142.5, 137.5, 137.2, 129.5, 125.7, 125.3, 64.0, 63.9, 63.8, 61.6, 49.6, 47.0, 33.8, 26.3, 21.4, 19.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1749.



3j

6-Chloro-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3j)

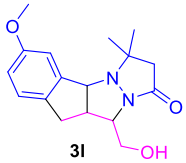
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (37.5 mg, 61%), mp 150.0-151.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H), 7.15 (d, J = 8.0 Hz, 1H), 5.42 (dd, J_1 = 10.8 Hz, J_2 = 4.0 Hz, 1H), 4.61 (d, J = 8.4 Hz, 1H), 4.05-3.99 (m, 1H), 3.92-3.86 (m, 1H), 3.23 (t, J = 9.2 Hz, 1H), 3.08 (dd, J_1 = 16.4 Hz, J_2 = 7.2 Hz, 1H), 2.90-2.82 (m, 2H), 2.78 (d, J = 16.8 Hz, 1H), 2.39 (d, J = 15.2 Hz, 1H), 1.52 (s, 3H), 1.27 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.1, 144.6, 138.6, 133.4, 128.8, 126.6, 125.6, 63.9, 63.8, 63.7, 61.4, 49.6, 47.0, 33.7, 26.3, 19.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}ClN_2O_2$ 307.1208; Found 307.1206.



3k

6-Bromo-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3k)

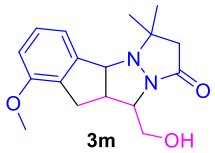
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (44.8 mg, 64%). mp 147.4-148.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.37 (s, 1H), 7.10 (d, J = 7.8 Hz, 1H), 5.42 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.62 (d, J = 8.4 Hz, 1H), 4.04-3.00 (m, 1H), 3.91-3.87 (m, 1H), 3.23 (t, J = 9.0 Hz, 1H), 3.06 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 1H), 2.87-2.82 (m, 2H), 2.76 (d, J = 16.8 Hz, 1H), 2.39 (d, J = 15.6 Hz, 1H), 1.52 (s, 3H), 1.27 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.1, 145.0, 139.2, 131.6, 128.6, 127.0, 121.4, 63.9, 63.8, 63.7, 61.4, 49.5, 46.9, 33.7, 26.4, 19.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}BrN_2O_2$ 351.0703; Found 351.0701.



3l

10-(Hydroxymethyl)-6-methoxy-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*] pyrazol-1-one (3l)

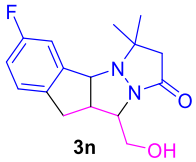
Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (11.5 mg, 19%), mp 114.7-115.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, J = 7.8 Hz, 1H), 6.83 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.78 (d, J = 1.8 Hz, 1H), 5.52-5.50 (m, 1H), 4.60 (d, J = 7.8 Hz, 1H), 4.01 (t, J = 10.8 Hz, 1H), 3.91-3.88 (m, 1H), 3.81 (s, 3H), 3.26 (t, J = 9.6 Hz, 1H), 3.05 (dd, J_1 = 15.6 Hz, J_2 = 7.2 Hz, 1H), 2.86-2.82 (m, 2H), 2.74 (d, J = 16.2 Hz, 1H), 2.39 (d, J = 15.0 Hz, 1H), 1.52 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.9, 159.7, 144.0, 132.1, 126.2, 114.7, 110.3, 64.1, 63.8, 63.7, 61.7, 55.5, 49.7, 47.3, 33.4, 26.4, 19.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_3$ 303.1703; Found 303.1696.



3m

10-(Hydroxymethyl)-8-methoxy-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*] pyrazol-1-one (3m)

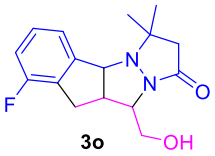
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (31.3 mg, 52%), mp 150.6-151.3 ℃. ^{1}H NMR (600MHz, $CDCl_3$): δ 7.28-7.26 (m, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 5.50 (br s, 1H), 4.64 (d, J = 8.4 Hz, 1H), 4.03-4.01 (m, 1H), 3. 89 (dd, J_1 = 12.6 Hz, J_2 = 8.4 Hz, 1H), 3.83 (s, 3H), 3.26 (t, J = 9.0 Hz, 1H), 2.97 (dd, J_1 = 16.2 Hz, J_2 = 6.6 Hz, 1H), 2.88-2.82 (m, 3H), 2.39 (d, J = 15.0 Hz, 1H), 1.51 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.9, 156.5, 144.3, 129.4, 128.3, 117.1, 109.4, 64.5, 63.9, 63.7, 61.6, 55.3, 49.7, 46.7, 31.1, 26.4, 19.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_3$ 303.1703; Found 303.1702.



3n

6-Fluoro-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]py razol-1-one (3n)

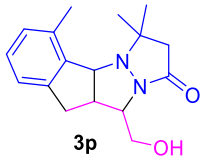
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (11.6 mg, 20%), mp 117.5-118.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (dd, J_1 = 8.4 Hz, J_2 = 6.0 Hz, 1H), 6.98-6.93 (m, 2H), 5.45 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.61 (d, J = 8.4 Hz, 1H), 4.04-4.00 (m, 1H), 3.91-3.87 (m, 1H), 3.24 (t, J = 8.4 Hz, 1H), 3.08 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.88 (q, J = 7.8 Hz, 1H), 2.83 (d, J = 15.6 Hz, 1H), 2.77 (d, J = 16.8 Hz, 1H), 2.39 (d, J = 15.0 Hz, 1H), 1.51 (s, 3H), 1.27 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.0, 162.8 (d, $^{1}J_{C\text{-}F}$ = 243.9 Hz), 144.8 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 135.5 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 126.6 (d, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 112.2 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 63.9 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 63.8, 63.7, 61.5, 49.6, 47.3, 33.5, 26.3, 19.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -115.2 – -115.3 (m). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}FN_2O_2$ 291.1503; Found 291.1500.



3o

8-Fluoro-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]py razol-1-one (3o)

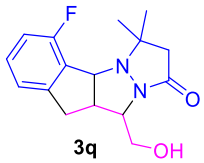
Eluent: petroleum ether/ethyl acetate (1:1). Yollow solid (29.7 mg, 51%), mp 148.7-149.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29-7.27 (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.96 (t, J = 9.0 Hz, 1H), 5.42 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.66 (d, J = 7.8 Hz, 1H), 4.06-4.02 (m, 1H), 3.92-3.88 (m, 1H), 3.26 (t, J = 8.4 Hz, 1H), 3.08 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 1H), 2.93-2.90 (m, 2H), 2.83 (d, J = 15.6 Hz, 1H), 2.40 (d, J = 15.6 Hz, 1H), 1.51 (s, 3H), 1.29 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.0, 159.7 (d, $^{1}J_{C\text{-}F}$ = 247.2 Hz), 146.1 (d, $^{3}J_{C\text{-}F}$ = 5.6 Hz), 129.8 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 126.8 (d, $^{2}J_{C\text{-}F}$ = 17.6 Hz), 120.9 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 114.7 (d, $^{2}J_{C\text{-}F}$ = 20.7 Hz), 64.2 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 63.8, 63.6, 61.4, 49.6, 46.8, 30.3, 26.4, 19.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ -117.50 – -117.53 (m). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}FN_2O_2$ 291.1503; Found 291.1504.



3p

10-(Hydroxymethyl)-3,3,5-trimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3p)

Eluent: petroleum ether/ethyl acetate (1:1). Orange solid (35.6 mg, 62%), mp 205.5-206.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.30 (dd, J_1 = 10.4 Hz, J_2 = 3.6 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 1H), 4.08-4.01 (m, 1H), 3.96-3.90 (m, 1H), 3.22 (t, *J* = 8.8 Hz, 1H), 3.01 (dd, J_1 = 16.0 Hz, J_2 = 6.8 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.78-2.74 (m, 2H), 2.48 (s, 3H), 2.27 (d, *J* = 14.8 Hz, 1H), 1.52 (s, 3H), 1.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.1, 140.6, 139.6, 136.1, 129.4, 128.7, 123.2, 66.8, 65.2, 64.3, 61.6, 49.5, 46.7, 33.5, 26.5, 19.9, 19.3. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1746.

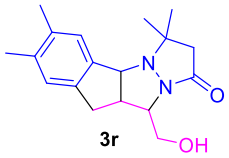


3q

5-Fluoro-10-(hydroxymethyl)-3,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3q)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (38.5 mg, 66%), mp 186.7-187.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 8.4 Hz, 1H), 5.49 (br s, 1H), 4.80 (d, *J* = 8.0 Hz, 1H), 4.01 (dd, J_1 = 12.4 Hz, J_2 = 2.4 Hz, 1H), 3.90 (dd, J_1 = 12.4 Hz, J_2 = 8.0 Hz, 1H), 3.39 (t, *J* = 8.4 Hz, 1H), 3.12 (dd, J_1 = 16.8 Hz, J_2 = 8.0 Hz, 1H), 2.95-2.89 (m, 2H), 2.86 (d, *J* = 16.0 Hz, 1H), 2.39 (d, *J* = 15.2 Hz, 1H), 1.47 (d, *J* = 2.0 Hz, 3H), 1.32 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.9, 160.1 (d, $^{1}J_{C\text{-}F}$ = 248.3 Hz), 144.6 (d, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 130.8 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 128.4 (d, $^{2}J_{C\text{-}F}$ = 14.3 Hz), 121.2 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 114.3 (d, $^{2}J_{C\text{-}F}$ = 20.7 Hz), 64.4, 63.2, 62.1 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 62.0, 50.0, 47.9, 35.1, 25.8 (d, $^{3}J_{C\text{-}F}$ =

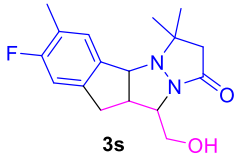
5.4 Hz), 19.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -116.08 – -116.11 (m). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}FN_2O_2$ 291.1503; Found 291.1502.



3r

10-(Hydroxymethyl)-3,3,6,7-tetramethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3r)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (38.9 mg, 65%), mp 181.5-182.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.01 (s, 1H), 7.00 (s, 1H), 5.56 (dd, J_1 = 10.8 Hz, J_2 = 3.0 Hz, 1H), 4.59 (d, J = 8.4 Hz, 1H), 4.02-3.98 (m, 1H), 3.91-3.87 (m, 1H), 3.25 (t, J = 9.0 Hz, 1H), 3.05 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.84-2.81 (m, 2H), 2.74 (d, J = 16.2 Hz, 1H), 2.39 (d, J = 15.6 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 1.53 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.9, 140.0, 137.8, 137.1, 136.2, 126.4, 126.0, 63.91, 63.89, 63.7, 61.8, 49.7, 47.1, 34.0, 26.4, 19.94, 19.88, 19.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_2$ 301.1911; Found 301.1903.

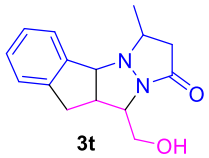


3s

7-Fluoro-10-(hydroxymethyl)-3,3,6-trimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3s)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (37.1 mg, 61%), mp 181.4-182.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.04 (d, J = 7.2 Hz, 1H), 6.86 (d, J = 9.6 Hz, 1H), 5.46 (dd, J_1 = 10.8 Hz, J_2 = 3.0 Hz, 1H), 4.58 (d, J = 7.8 Hz, 1H), 4.03-3.99 (m, 1H), 3.91-3.87 (m, 1H), 3.25 (t, J = 9.0 Hz, 1H), 3.07 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.88-2.83 (m, 2H), 2.76 (d, J = 16.2 Hz, 1H), 2.39 (d, J = 15.0 Hz, 1H), 2.27 (s, 3H), 1.52 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.0, 161.7 (d, $^1J_{C\text{-}F}$ = 243.9 Hz), 139.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 137.8 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 127.7 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 124.6 (d, $^2J_{C\text{-}F}$ = 18.5 Hz), 111.8 (d, $^2J_{C\text{-}F}$ = 23.1 Hz),

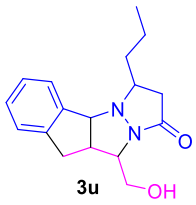
63.81, 63.78, 63.5, 61.5, 49.6, 47.3, 34.0 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 26.4, 19.7, 14.8 (d, $^{3}J_{C\text{-}F}$ = 4.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -117.93 – -117.96 (m). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{22}FN_2O_2$ 305.1660; Found 305.1655.



3t

10-(Hydroxymethyl)-3-methyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3t)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (34.6 mg, 67%), mp 123.7-124.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32-7.30 (m, 1H), 7.29-7.27 (m, 2H), 7.25-7.23 (m, 1H), 5.43-5.41 (m, 1H), 4.34 (d, *J* = 8.4 Hz, 1H), 4.04-4.00 (m, 1H), 3.93-3.90 (m, 1H), 3.46-3.41 (m, 1H), 3.39-3.35 (m, 1H), 3.15 (dd, J_1 = 16.2 Hz, J_2 = 7.8 Hz, 1H), 3.06-3.01 (m, 1H), 2.89 (dd, J_1 = 16.8 Hz, J_2 = 2.4 Hz, 1H), 2.74 (dd, J_1 = 15.6 Hz, J_2 = 7.2 Hz, 1H), 2.65-2.60 (m, 1H), 1.50 (d, *J* = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): 164.8, 141.3, 141.2, 128.8, 127.6, 125.6, 125.4, 73.4, 64.3, 63.2, 61.6, 46.8, 43.2, 34.8, 18.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2$ 259.1441; Found 259.1437.

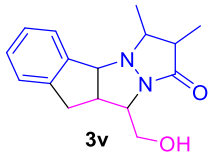


3u

10-(Hydroxymethyl)-3-propyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3u)

Eluent: petroleum ether/ethyl acetate (1:1). Orange solid (33.1 mg, 58%), mp 120.7-121.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.28 (m, 3H), 7.24-7.23 (m, 1H), 5.38 (dd, J_1 = 10.2 Hz, J_2 = 3.6 Hz, 1H), 4.36 (d, *J* = 9.0 Hz, 1H), 4.05-4.01 (m, 1H), 3.93-3.89 (m, 1H), 3.37-3.32 (m, 2H), 3.14 (dd, J_1 = 16.2 Hz, J_2 = 7.8 Hz, 1H), 3.04-3.00 (m, 1H), 2.87 (d, *J* = 16.2 Hz, 1H), 2.73 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 2.63-2.58 (m, 1H),

1.96-1.90 (m, 1H), 1.76-1.70 (m, 1H), 1.49-1.37 (m, 2H), 1.03 (t, J = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 165.0, 141.4, 141.2, 128.8, 127.6, 125.6, 125.4, 73.5, 67.6, 64.1, 61.5, 46.6, 41.0, 35.7, 34.6, 19.2, 14.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1753.

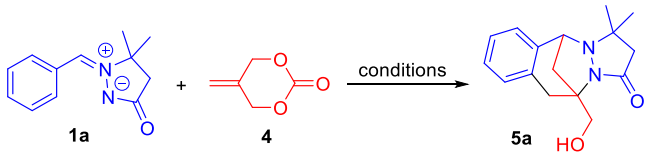


3v

10-(Hydroxymethyl)-2,3-dimethyl-2,3,4a,9,9a,10-hexahydro-1*H*-indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-1-one (3v)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (30.6 mg, 56%), mp 126.3-127.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.32 (m, 1H), 7.29-7.28 (m, 2H), 7.25-7.23 (m, 1H), 5.47 (dd, J_1 = 10.8 Hz, J_2 = 4.2 Hz, 1H), 4.32 (d, J = 8.4 Hz, 1H), 4.05-4.01 (m, 1H), 3.91-3.87 (m, 1H), 3.38 (t, J = 8.4 Hz, 1H), 3.15 (dd, J_1 = 16.8 Hz, J_2 = 8.4 Hz, 1H), 3.04-3.00 (m, 1H), 2.93-2.88 (m, 2H), 2.60-2.57 (m, 1H), 1.50 (d, J = 6.0 Hz, 3H), 1.22 (d, J = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 167.1, 141.3, 141.2, 128.8, 127.6, 125.6, 125.5, 73.3, 70.6, 64.2, 61.6, 47.8, 46.6, 34.7, 17.3, 12.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_2$ 273.1598; Found 273.1589.

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

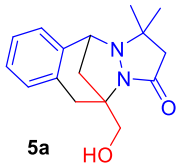


Entry	Catalyst (mol%)	Additive	Solvent	T (°C)	Yield (%)[b]
1[c]	[RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (5)	AgSbF$_6$	TFE	120	21
2	[RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (5)	AgSbF$_6$	TFE	120	40
3	[RhCp*Cl$_2$]$_2$ (5)	AgSbF$_6$	TFE	120	15
4	CoCp*(CO)I$_2$ (5)	AgSbF$_6$	TFE	120	ND
5	[IrCp*Cl$_2$]$_2$ (5)	AgSbF$_6$	TFE	120	trace
6	[Ru(*p*-cymene)Cl$_2$]$_2$ (5)	AgSbF$_6$	TFE	120	50
7	[Ru(*p*-cymene)Cl$_2$]$_2$ (5)	AgSbF$_6$	DCE	120	trace
8	[Ru(*p*-cymene)Cl$_2$]$_2$ (5)	AgSbF$_6$	MeOH	120	trace
9	[Ru(*p*-cymene)Cl$_2$]$_2$ (5)	AgSbF$_6$	HFIP	120	65
10	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgSbF$_6$	HFIP	120	66
11	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgSbF$_6$	HFIP	60	53
12	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgSbF$_6$	HFIP	80	72
13	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgSbF$_6$	HFIP	100	70
14	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgBF$_4$	HFIP	80	65
15	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	Ag$_2$CO$_3$	HFIP	80	22
16	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgOAc	HFIP	80	20
17	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	Cu(OAc)$_2$	HFIP	80	11
18	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	NaOAc	HFIP	80	67
19[d]	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgSbF$_6$	HFIP	80	76
20		AgSbF$_6$	HFIP	80	ND
21	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)		HFIP	80	trace
22[e]	[Ru(*p*-cymene)Cl$_2$]$_2$ (2.5)	AgSbF$_6$	HFIP	80	75

[a]Reaction conditions: **1a** (0.2 mmol), **4** (0.3 mmol), additive (0.02 mmol), solvent (2 mL), argon, 6 h. [b]Isolated yields. [c]Under air. [d]**4** (0.4 mmol). [e]8 h.

3. Typical procedure for the synthesis of 5a and spectroscopic data of 5a-5u

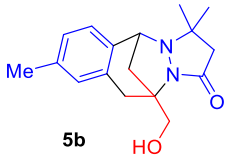
To a reaction tube equipped with a stir bar were charged with 2-benzylidene-3,3-dimethyl-5-oxopyrazolidin-2-ium-1-ide (**1a**, 40.4 mg, 0.2 mmol), 5-methylene-1,3-dioxan-2-one (**4**, 45.6 mg, 0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and HFIP (2 mL). The mixture was stirred at 80 ℃ under argon for 6 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 **5a**. **5b-5u** were obtained in a similar manner.



5a

11-(Hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5a)

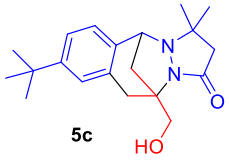
Eluent: petroleum ether/ethyl acetate (1:1). White solid (41.5 mg, 76%), mp 172.6-173.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (td, J_1 = 7.2 Hz, J_2 = 0.6 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 5.21 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H), 4.12 (d, J = 5.4 Hz, 1H), 4.08-4.05 (m, 2H), 3.50 (d, J = 17.4 Hz, 1H), 2.99 (d, J = 17.4 Hz, 1H), 2.60 (d, J = 15.0 Hz, 1H), 2.32 (d, J = 15.6 Hz, 1H), 2.26 (dd, J_1 = 11.4 Hz, J_2 = 4.8 Hz, 1H), 1.87 (d, J = 10.8 Hz, 1H), 1.22 (s, 3H) 1.15 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 166.8, 140.4, 133.5, 129.7, 128.2, 126.2, 126.1, 65.9, 65.8, 64.5, 56.0, 49.4, 38.7, 38.3, 24.9, 21.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_2$ 273.1598; Found 273.1595.



5b

11-(Hydroxymethyl)-3,3,8-trimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5b)

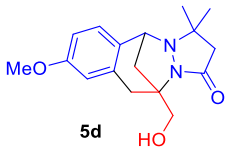
Eluent: petroleum ether/ethyl acetate (1:1). White solid (48.0 mg, 84%), mp 187.0-187.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.00 (s, 1H), 6.96 (s, 2H), 5.21 (br s, 1H), 4.10 (d, *J* = 5.4 Hz, 1H), 4.07-4.02 (m, 2H), 3.47 (d, *J* = 18.0 Hz, 1H), 2.94 (d, *J* = 18.0 Hz, 1H), 2.58 (d, *J* = 15.0 Hz, 1H), 2.33-2.30 (m, 4H), 2.25 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H), 1.85 (d, *J* = 10.8 Hz, 1H), 1.21 (s, 3H) 1.14 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 166.8, 138.0, 137.5, 133.2, 130.4, 126.9, 126.0, 66.0, 65.9, 64.5, 55.7, 49.4, 38.9, 38.2, 24.9, 21.7, 21.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1749.



5c

8-(*tert*-Butyl)-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5c)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (44.2 mg, 67%), mp 226.8-227.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 5.16 (t, *J* = 7.8 Hz, 1H), 4.10 (d *J* = 4.2 Hz, 1H), 4.06 (d, *J* = 7.2 Hz, 2H), 3.48 (d, *J* = 17.4 Hz, 1H), 2.98 (d, *J* = 18.0 Hz, 1H), 2.62 (d, *J* = 15.0 Hz, 1H), 2.31 (d, *J* = 15.0 Hz, 1H), 2.25 (dd, J_1 = 10.8 Hz, J_2 = 4.2 Hz, 1H), 1.85 (d, *J* = 11.4 Hz, 1H), 1.28 (s, 9H), 1.21 (s, 3H) 1.16 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.0, 151.1, 137.5, 132.7, 126.6, 125.6, 123.2, 66.2, 65.8, 64.5, 55.6, 49.4, 38.7, 38.4, 34.5, 31.4, 24.9, 21.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{20}H_{29}N_2O_2$ 329.2224; Found 329.2214.

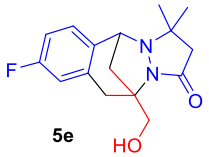


5d

11-(Hydroxymethyl)-8-methoxy-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5d)

Eluent: petroleum ether/ethyl acetate (1:1). Yollowish solid (47.1 mg, 78%), mp 138.3-139.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.99 (d, *J* = 7.8 Hz, 1H), 6.72 (s, 1H), 6.69 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 5.23 (br s,

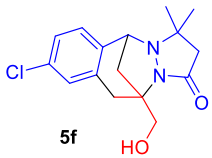
1H), 4.10 (d J = 4.8 Hz, 1H), 4.07-4.01 (m, 2H), 3.77 (s, 3H), 3.51 (d, J = 17.4 Hz, 1H), 2.96 (d, J = 18.0 Hz, 1H), 2.56 (d, J = 15.6 Hz, 1H), 2.35 (d, J = 15.0 Hz, 1H), 2.27 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H), 1.85 (d, J = 10.8 Hz, 1H), 1.22 (s, 3H) 1.11 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 166.8, 159.5, 134.9, 132.6, 127.3, 114.8, 111.9, 66.0, 65.7, 64.3, 55.5, 55.3, 49.5, 39.3, 38.5, 24.7, 22.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_3$ 303.1703; Found 303.1701.



5e

8-Fluoro-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5e)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (29.0 mg, 50%), mp 219.3-220.0 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.04 (dd, J_1 = 8.4 Hz, J_2 = 6.0, 1H), 6.89 (d, J = 9.6 Hz, 1H), 6.85 (td, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 5.16 (br s, 1H), 4.13 (d, J = 4.8 Hz, 1H), 4.09-4.05 (m, 2H), 3.49 (d, J = 18.0 Hz, 1H), 2.97 (d, J = 18.0 Hz, 1H), 2.61 (d, J = 15.0 Hz, 1H), 2.33 (d, J = 15.0 Hz, 1H), 2.27 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H), 1.84 (d, J = 11.4 Hz, 1H), 1.22 (s, 3H) 1.16 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 166.9, 162.4 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 136.4, 135.9 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 127.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 113.1 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 65.61, 65.59, 64.6, 55.3, 49.3, 38.8, 38.5, 25.0, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.04 – -114.10 (m). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{20}FN_2O_2$ 291.1503; Found 291.1501.

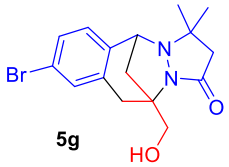


5f

8-Chloro-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5f)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (34.2 mg, 56%), mp 208.4-209.4 ℃. ^1H NMR (600 MHz, DMSO-d_6): δ 7.24 (s, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.18 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 5.16 (br s,

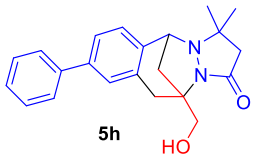
1H), 4.39 (d, *J* = 4.2 Hz, 1H), 3.94 (s, 2H), 3.13 (d, *J* = 17.4 Hz, 1H), 3.00 (d, *J* = 17.4 Hz, 1H), 2.36 (d, *J* = 15.0 Hz, 1H), 2.19 (dd, J_1 = 11.4 Hz, J_2 = 4.8 Hz, 1H), 2.15 (d, *J* = 15.6 Hz, 1H), 1.80 (d, *J* = 10.8 Hz, 1H), 1.14 (s, 3H) 1.11 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6): δ 167.4, 140.4, 137.0, 132.2, 129.3, 128.5, 126.1, 65.6, 64.2, 63.8, 54.7, 48.9, 38.6, 38.0, 25.1, 21.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}ClN_2O_2$ 307.1208; Found 307.1206.



5g

8-Bromo-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5g)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (41.8 mg, 60%), mp 198.5-199.4 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.30-7.27 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.13 (br s, 1H), 4.11 (d, *J* = 4.8 Hz, 1H), 4.06 (s, 2H), 3.47 (d, *J* = 18.0 Hz, 1H), 2.95 (d, *J* = 18.0 Hz, 1H), 2.61 (d, *J* = 15.2 Hz, 1H), 2.31(d, *J* = 15.2 Hz, 1H), 2.28-2.24 (m, 1H), 1.82 (d, *J* = 10.8 Hz, 1H), 1.21 (s, 3H) 1.17 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.9, 139.5, 135.9, 132.6, 129.4, 127.5, 121.8, 65.7, 65.5, 64.7, 55.4, 49.2, 38.4, 38.2, 25.1, 21.3. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}BrN_2O_2$ 351.0703; Found 351.0695.

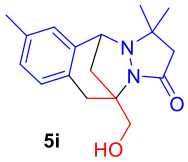


5h

11-(Hydroxymethyl)-3,3-dimethyl-8-phenyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5h)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (45.9 mg, 66%), mp 185.3-186.1 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.44-7.32 (m, 5H), 7.14 (d, *J* = 7.6 Hz, 1H), 5.18 (t, *J* = 7.2 Hz, 1H), 4.18 (d, *J* = 4.8 Hz, 1H), 4.09 (d, *J* = 6.8 Hz, 1H), 3.57 (d, *J* = 17.6 Hz, 1H), 3.05 (d, *J* = 17.6 Hz, 1H), 2.65 (d, *J* = 15.2 Hz, 1H), 2.35-2.28 (m, 3H), 1.90 (d, *J* = 11.2 Hz, 1H), 1.24 (s, 3H) 1.21 (s, 3H). $^{13}C\{^1H\}$ NMR (150

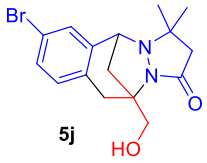
MHz, $CDCl_3$): δ 167.0, 141.3, 140.7, 139.6, 133.9, 128.8, 128.5, 127.4, 127.1, 126.4, 125.2, 66.1, 65.7, 64.7, 55.7, 49.4, 38.7, 38.5, 25.1, 21.4. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{22}H_{24}N_2NaO_2$ 371.1730; Found 371.1726.



5i

11-(Hydroxymethyl)-3,3,7-trimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5i)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (50.9 mg, 89%), mp 178.9-179.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.06 (d, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 5.20 (br s, 1H), 4.07-4.05 (m, 3H), 3.44 (d, *J* = 17.4 Hz, 1H), 2.93 (d, *J* = 18.0 Hz, 1H), 2.60 (d, *J* = 15.0 Hz, 1H), 2.31-2.29 (m, 4H), 2.24 (dd, J_1 = 11.4 Hz, J_2 = 4.8 Hz, 1H), 1.84 (d, *J* = 11.4 Hz, 1H), 1.21 (s, 3H) 1.17 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 166.9, 140.3, 135.9, 130.2, 129.6, 128.9, 126.7, 66.2, 65.8, 64.7, 56.0, 49.4, 38.7, 37.9, 24.9, 21.4, 21.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1745.

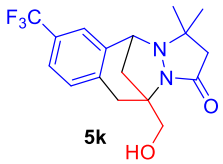


5j

7-Bromo-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5j)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (38.6 mg, 55%), mp 206.8-207.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 5.12 (br s, 1H), 4.08-4.06 (m, 3H), 3.42 (d, *J* = 18.0 Hz, 1H), 2.91 (d, *J* = 18.0 Hz, 1H), 2.63 (d, *J* = 15.6 Hz, 1H), 2.31 (d, *J* = 15.0 Hz, 1H), 2.25 (dd, J_1 = 11.4 Hz, J_2 = 5.4 Hz, 1H), 1.83 (d, *J* = 11.4 Hz, 1H), 1.21 (s, 3H) 1.19 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 166.9, 142.6, 132.5, 131.4, 131.0, 128.8, 119.7, 65.8, 65.5,

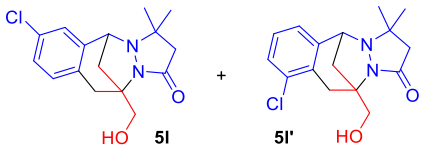
64.8, 55.6, 49.2, 38.3, 38.0, 25.1, 21.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{20}BrN_2O_2$ 351.0703; Found 351.0698.



5k

11-(Hydroxymethyl)-3,3-dimethyl-7-(trifluoromethyl)-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5k)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (27.3 mg, 40%), mp 176.4-177.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.32 (s, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 5.12 (dd, J_1 = 9.6 Hz, J_2 = 5.4 Hz, 1H), 4.19 (d, *J* = 4.8 Hz, 1H), 4.01-4.08 (m, 2H), 3.54 (d, *J* = 18.6 Hz, 1H), 3.03 (d, *J* = 18.0 Hz, 1H), 2.65 (d, *J* = 15.6 Hz, 1H), 2.33-2.28 (m, 2H), 1.85 (d, *J* = 11..4 Hz, 1H), 1.23 (s, 3H), 1.20 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.0, 141.4, 137.9, 130.2, 128.6 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 124.9 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 270.2 Hz), 122.6 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 65.8, 65.4, 64.9, 64.8, 55.6, 49.2, 38.5, 38.2, 25.2, 21.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.4 (s). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{20}F_3N_2O_2$ 341.1471; Found 341.1462.

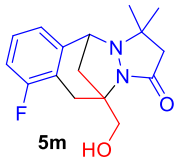


5l 5l'

7-Chloro-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one and 9-Chloro-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5l and 5l' as 1:1 mixture of diastereoisomers)

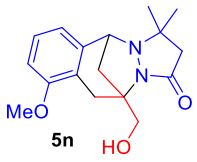
Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (40.5 mg, 66%, the ratio of two isomers = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.27 (m, 1H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.14-7.10 (m, 2H), 7.07 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 5.11 (br s, 2H), 4.14 (d, *J* = 5.2 Hz, 2H), 4.13-4.07 (m, 4H), 3.47-3.39 (m, 2H), 2.96-2.89 (m, 2H), 2.68-2.61 (m, 2H), 2.33-2.23 (m, 4H), 1.84-1.80 (m, 2H), 1.21-1.19 (m,

12H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 166.9, 166.8, 142.8, 142.3, 135.4, 131.94, 131.85, 131.7, 131.1, 128.8, 128.1, 127.6, 125.9, 124.1, 65.9, 65.7, 65.5, 65.4, 64.9, 64.8, 55.8, 55.6, 49.23, 49.17, 38.3, 37.9, 37.8, 37.7, 25.2, 25.1, 21.2, 20.8. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}ClN_2O_2$ 307.1208; Found 307.1205.



9-Fluoro-11-(hydroxymethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5m)

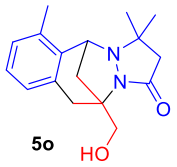
Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (31.8 mg, 55%), mp 178.4-179.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15 (td, J_1 = 7.8 Hz, J_2 = 5.4 Hz, 1H), 6.96-6.93 (m, 1H), 6.88 (d, J = 7.2 Hz, 1H), 5.09 (dd, J_1 = 9.6 Hz, J_2 = 5.4 Hz, 1H), 4.16 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 4.14-4.07 (m, 2H), 3.41 (d, J = 18.0 Hz, 1H), 2.91 (d, J = 18.6 Hz, 1H), 2.65 (d, J = 15.0 Hz, 1H), 2.31 (d, J = 15.0 Hz, 1H), 2.29-2.26 (m, 1H), 1.83 (d, J = 10.8 Hz, 1H), 1.22 (s, 3H) 1.19 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 166.9, 161.5 (d, $^{1}J_{C\text{-}F}$ = 246.2 Hz), 143.1 (d, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 127.9 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 121.2 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 120.8 (d, $^{2}J_{C\text{-}F}$ = 16.5 Hz), 114.8 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 65.5, 65.3, 64.8, 55.4 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 49.3, 38.2, 32.9, 25.1, 21.0. ^{19}F NMR (565 MHz,$CDCl_3$): δ -115.65 – -115.68 (m). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}FN_2O_2$ 291.1503; Found 291.1499.



11-(Hydroxymethyl)-9-methoxy-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5n)

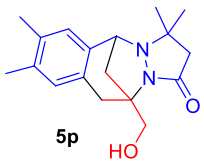
Eluent: petroleum ether/ethyl acetate (1:1). White solid (38.1 mg, 63%), mp 192.5-193.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15 (t, J = 8.4 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 7.2 Hz, 1H), 5.12 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H), 4.13-4.10 (m, 2H), 4.06 (dd, J_1 = 12.6 Hz, J_2 = 4.8 Hz, 1H), 3.79 (s, 3H), 3.31 (d, J =

18.6 Hz, 1H), 2.81 (d, *J* = 18.6 Hz, 1H), 2.63 (d, *J* = 15.0 Hz, 1H), 2.29 (d, *J* = 15.6 Hz, 1H), 2.25 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H), 1.82 (d, *J* = 11.4 Hz, 1H), 1.21 (s, 3H) 1.18 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 166.8, 158.0, 141.9, 127.3, 121.8, 117.9, 109.6, 65.71, 65.65, 64.7, 55.7, 55.2, 49.3, 38.2, 34.1, 25.0, 21.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_3$ 303.1703; Found 303.1695.



11-(Hydroxymethyl)-3,3,6-trimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5o)

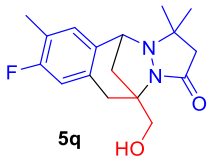
Eluent: petroleum ether/ethyl acetate (1:1). White solid (37.1 mg, 65%), mp 188.7-189.9 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.11 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.19 (t, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 5.4 Hz, 1H), 4.08 (d, *J* = 6.6 Hz, 2H), 3.43 (d, *J* = 17.4 Hz, 1H), 3.00 (d, *J* = 18.0 Hz, 1H), 2.67 (d, *J* = 15.0 Hz, 1H), 2.38 (s, 3H), 2.29 (d, *J* = 15.0 Hz, 1H), 2.23 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H), 1.81 (d, *J* = 10.8 Hz, 1H), 1.23 (s, 3H) 1.22 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz,$CDCl_3$): δ 167.0, 139.0, 133.4, 132.7, 128.1, 127.6, 66.0, 65.5, 64.9, 51.0, 49.3, 38.8, 38.1, 25.2, 20.8, 19.1. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{17}H_{22}N_2NaO_2$ 309.1573; Found 309.1570.



11-(Hydroxymethyl)-3,3,7,8-tetramethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5p)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (32.6 mg, 54%), mp 157.6-158.5 ℃. ^1H NMR (400 MHz,$CDCl_3$): δ 6.88 (s, 1H), 6.76 (s, 1H), 5.12 (t, *J* = 8.0 Hz, 1H), 3.98-3.96 (m, 3H), 3.35 (d, *J* = 17.6 Hz, 1H), 2.84 (d, *J* = 17.6 Hz, 1H), 2.53 (d, *J* = 15.6 Hz, 1H), 2.22 (d, *J* = 15.2 Hz, 1H), 2.18-2.15 (m, 4H), 2.13 (s, 3H), 1.76 (d, *J* = 10.8 Hz, 1H), 1.14 (s, 3H) 1.10 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$): δ 167.0,

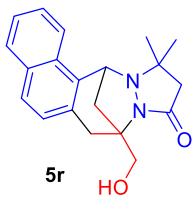
137.9, 136.5, 134.4, 130.9, 130.4, 127.2, 66.2, 65.9, 64.6, 55.6, 49.4, 38.9, 37.8, 24.9, 21.5, 19.5, 19.3. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_2$ 301.1911; Found 301.1902.



5q

8-Fluoro-11-(hydroxymethyl)-3,3,7-trimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5q)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (37.0 mg, 61%), mp 181.7-182.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.88 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 10.2 Hz, 1H), 5.16 (dd, J_1 = 9.6 Hz, J_2 = 5.4 Hz, 1H), 4.08-4.02 (m, 3H), 3.44 (d, *J* = 18.0 Hz, 1H), 2.93 (d, *J* = 18.0 Hz, 1H), 2.62 (d, *J* = 15.0 Hz, 1H), 2.31 (d, *J* = 15.0 Hz, 1H), 2.26-2.23 (m, 4H), 1.82 (d, *J* = 10.8 Hz, 1H), 1.21 (s, 3H) 1.17 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.0, 160.9 (d, $^1J_{C\text{-}F}$ = 243.9 Hz), 136.1 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 132.7 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 128.8 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 122.6 (d, $^2J_{C\text{-}F}$ = 17.6 Hz), 116.0 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 65.8, 65.7, 64.6, 55.3, 49.3, 38.7, 38.1, 25.0, 21.4, 14.2 (d, $^4J_{C\text{-}F}$ = 3.3 Hz). ^{19}F NMR (565 MHz,$CDCl_3$): δ -118.39 – -118.42 (m). HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{17}H_{21}FN_2NaO_2$ 327.1479; Found 327.1471.

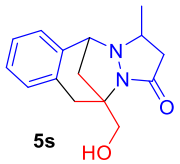


5r

8-(Hydroxymethyl)-12,12-dimethyl-7,11,12,14-tetrahydro-8*H*,10*H*-8,14-methanonaphtho[1,2-*d*]pyrazolo[1,2-*a*][1,2]diazepin-10-one (5r)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (36.6 mg, 57%), mp 221.3-224.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.30 (br s, 1H), 5.07 (d, *J* = 5.4 Hz, 1H), 4.17-4.13 (m, 2H), 3.62 (d, *J* = 17.4 Hz, 1H), 3.18 (d, *J* = 18.0 Hz, 1H), 2.59 (d, *J* = 15.0 Hz, 1H), 2.41 (dd, J_1

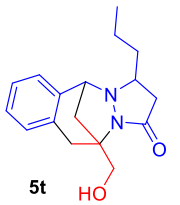
= 10.8 Hz, J_2 = 4.8 Hz, 1H), 2.38 (d, J = 15.6 Hz, 1H), 1.96 (d, J = 10.8 Hz, 1H), 1.32 (s, 3H) 1.08 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 166.8, 135.2, 132.4, 131.4, 129.6, 129.0, 128.1, 127.5, 126.7, 125.3, 121.4, 65.8, 64.8, 49.64, 49.55, 39.6, 38.7, 24.7, 21.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{20}H_{23}N_2O_2$ 323.1754; Found 323.1745.



5s

11-(Hydroxymethyl)-3-methyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5s)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (47.1 mg, 91%), mp 199.4-200.2 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.25-7.22 (m, 1H), 7.18-7.15 (m, 2H), 7.09 (d, J = 7.2 Hz, 1H), 4.85 (br s, 1H), 4.09 (s, 2H), 4.01 (d, J = 5.4 Hz, 1H), 3.42 (d, J = 17.4 Hz, 1H), 3.30-3.26 (m, 1H), 2.98 (d, J = 18.0 Hz, 1H), 2.55 (dd, J_1 = 15.6 Hz, J_2 = 12.6 Hz, 1H), 2.45 (dd, J_1 = 15.6 Hz, J_2 = 6.6 Hz, 1H), 2.17 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H), 1.88 (d, J = 11.4 Hz, 1H) 1.33 (d, J = 6.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 170.9, 140.1, 133.0, 129.7, 128.3, 126.4, 125.7, 68.8, 65.7, 62.5, 59.9, 42.1, 38.3, 35.9, 17.8. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2$ 259.1441; Found 259.1436.

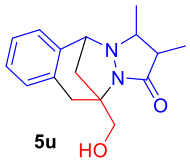


5t

11-(Hydroxymethyl)-3-propyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5t)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (40.8 mg, 71%), mp 176.9-177.4 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, J = 7.2 Hz, 1H), 7.18-7.15 (m, 2H), 7.09 (d, J = 7.2 Hz, 1H), 4.84 (t, J = 7.8 Hz, 1H), 4.09 (d, J = 7.2 Hz, 2H), 4.03 (d, J = 4.8 Hz, 1H), 3.42 (d, J = 18.0 Hz, 1H), 3.22-3.16 (m, 1H), 2.98 (d, J = 18.0 Hz, 1H), 2.56-2.46 (m, 2H), 2.16 (dd, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H), 1.87 (d, J = 11.4 Hz, 1H), 1.75-1.70

(m, 1H), 1.64-1.57 (m, 1H), 1.42-1.35 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 170.7, 140.3, 133.0, 129.7, 128.2, 126.4, 125.5, 68.4, 67.1, 65.7, 60.3, 40.6, 38.3, 35.9, 35.5, 19.7, 14.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2$ 287.1754; Found 287.1751.



5u

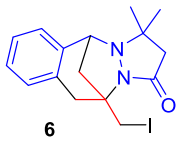
11-(Hydroxymethyl)-2,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (5u)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (32.0 mg, 59%), mp 184.9-185.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25-7.22 (m, 1H), 7.18-7.15 (m, 2H), 7.09 (d, J = 7.8 Hz, 1H), 4.83 (dd, J_1 = 10.2 Hz, J_2 = 5.4 Hz, 1H), 4.12 (dd, J_1 = 13.2 Hz, J_2 = 10.8 Hz, 1H), 4.04 (dd, J_1 = 12.6 Hz, J_2 = 5.4 Hz, 1H), 4.00 (d, J = 4.8 Hz, 1H), 3.42 (d, J = 17.4 Hz, 1H), 2.99 (d, J = 18.0 Hz, 1H), 2.79-2.75 (m, 1H), 2.52-2.49 (m, 1H), 2.14 (dd, J_1 = 11.4 Hz, J_2 = 4.8 Hz, 1H), 1.86 (d, J = 11.4 Hz, 1H), 1.32 (d, J = 6.6 Hz, 3H), 1.12 (d, J = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 173.3, 140.3, 133.1, 129.7, 128.3, 126.4, 125.6, 69.4, 68.5, 65.7, 59.7, 46.1, 38.3, 35.6, 16.7, 11.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_2$ 273.1598; Found 273.1593.

4. Structural elaborations of 5a

4.1. Synthesis of 6

To a reaction tube equipped with a stir bar were charged with **5a** (0.2 mmol, 54.4 mg) and toluene (10 mL). The resulting solution was then added with iodine (0.4 mmol, 103 mg), triphenylphosphine (0.6 mmol, 157 mg) and imidazole (0.6 mmol, 40 mg) under argon. The rsulting mixture was stirred at 110 ℃ for 6 h. Upon completion, it was cooled to room temperature, and then concentrated under reduced pressure. The residual was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to afford **6**.



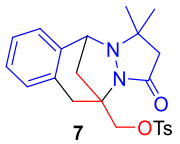
6

11-(Iodomethyl)-3,3-dimethyl-2,3,10,11-tetrahydro-1*H*,5*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-1-one (6)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (52.1 mg, 68%), mp 145.7-146.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.22 (m, 1H), 7.19-7.16 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 4.20 (d, *J* = 4.0 Hz, 1H), 3.91 (d, *J* = 10.4 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.69 (d, *J* = 16.8 Hz, 1H), 3.29 (d, *J* = 16.8 Hz, 1H), 2.62-2.58 (m, 1H), 2.23 (d, *J* = 15.6 Hz, 1H), 2.11 (d, *J* = 10.4 Hz, 1H), 1.94 (d, *J* = 15.6 Hz, 1H), 1.29 (s, 3H), 1.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.8, 136.5, 134.3, 129.4, 128.8, 128.5, 126.3, 62.2, 59.6, 58.4, 48.2, 45.6, 37.9, 27.9, 23.7, 11.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{16}H_{20}IN_2O$ 383.0615; Found 383.0614.

4.2. Synthesis of 7

To a reaction tube equipped with a stir bar were added **5a** (81.7 mg, 0.3 mmol), DMAP (110.0 mg, 0.9 mmol), *p*-TsCl (85.8 mg, 0.45 mmol) and DCM (1.5 mL). The resulting mixture was stirred at room temperature for 3 h. Upon completion, it was 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 **7**.



7

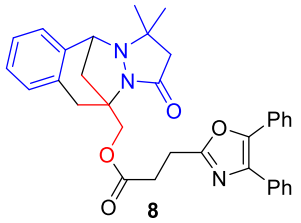
(3,3-Dimethyl-1-oxo-2,3,5,10-tetrahydro-1*H*,11*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-11-yl)methyl 4-methylbenzenesulfonate (7)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (94.6 mg, 74%), mp 182.8-183.5 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.23-7.20 (m, 1H), 7.17-7.13 (m, 2H), 7.09

(d, *J* = 7.8 Hz, 1H), 4.62 (d, *J* = 10.2 Hz, 1H), 4.52 (d, *J* = 10.2 Hz, 1H), 4.17 (d, *J* = 4.2 Hz, 1H), 3.42 (d, *J* = 16.8 Hz, 1H), 3.03 (d, *J* = 16.8 Hz, 1H), 2.51 (dd, J_1 = 11.4 Hz, J_2 = 3.6 Hz, 1H), 2.46 (s, 3H), 2.13 (d, *J* = 16.2 Hz, 1H), 2.08-2.04 (m, 2H), 1.20 (s, 3H), 1.12 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 170.1, 145.1, 137.4, 133.2, 132.6, 130.0, 129.6, 128.4, 128.11, 128.08, 126.4, 71.1, 62.0, 60.6, 57.4, 48.1, 40.9, 36.4, 26.2, 24.2, 21.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{27}N_2O_4S$ 427.1686; Found 427.1680.

4.3. Synthesis of 8[3]

To a reaction tube equipped with a stir bar were added **5a** (54.4 mg, 0.2 mmol), DCC (41.3 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol), oxaprozin (58.7 mg, 0.2 mmol) and DCM (1 mL). The resulting mixture was stirred at room temperature under air for 24 h. Upon completion, it was 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 **8**.



8

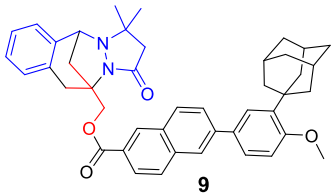
(3,3-Dimethyl-1-oxo-2,3,5,10-tetrahydro-1*H*,11*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-11-yl)methyl 3-(4,5-diphenyloxazol-2-yl)propanoate (8)

Eluent: petroleum ether/ethyl acetate (1:1). Colorless oil (71.3 mg, 65%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.34-7.30 (m, 6H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.03 (d, *J* = 4.2 Hz, 1H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.25-3.18 (m, 2H), 3.00-2.97 (m, 2H), 2.94 (d, *J* = 16.8 Hz, 1H), 2.47 (dd, J_1 = 10.8 Hz, J_2 = 4.2 Hz, 1H), 2.17-2.11 (m, 2H), 1.89 (d, *J* = 10.8 Hz, 1H), 1.21 (s, 3H), 1.13 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 171.5, 169.7, 161.7, 145.5, 138.0, 135.1, 133.4, 132.5, 129.7,

129.0, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 127.8, 126.5, 126.3, 65.3, 62.5, 60.8, 57.1, 48.4, 40.3, 37.0, 31.0, 25.6, 24.3, 23.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{34}H_{34}N_3O_4$ 548.2544; Found 548.2539.

4.4. Synthesis of 9

To a reaction tube equipped with a stir bar were added **5a** (54.4 mg, 0.2 mmol), DCC (41.3 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol), adapalene (82.5 mg, 0.2 mmol) and DCM (1 mL). The resulting mixture was stirred at room temperature for 24 h. Upon completion, it was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/ methanol (20:1) as eluent to afford **9**.



9

(3,3-Dimethyl-1-oxo-2,3,5,10-tetrahydro-1*H*,11*H*-5,11-methanobenzo[*d*]pyrazolo[1,2-*a*][1,2]diazepin-11-yl)methyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (9)

Eluent: dichloromethane/methanol (20:1). White solid (105.8 mg, 79%), mp 167.9-168.7 ^oC. ^1H NMR (600 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.27-7.24 (m, 1H), 7.20-7.18 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.02-4.96 (m, 2H), 4.21 (d, *J* = 4.2 Hz, 1H), 3.89 (s, 3H), 3.74 (d, *J* = 16.8 Hz, 1H), 3.12 (d, *J* = 16.8 Hz, 1H), 2.64 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 2.22 (d, *J* = 15.6 Hz, 1H), 2.18 (s, 6H), 2.15-2.10 (m, 5H), 1.80 (s, 6H), 1.29 (s, 3H), 1.20 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 170.4, 166.4, 159.0, 141.5, 139.0, 137.7, 136.1, 133.7, 133.0, 132.5, 131.3, 131.2, 129.8, 128.41, 128.35, 128.1, 126.7, 126.5, 126.4, 126.0, 125.8, 125.7, 124.8, 112.2, 65.9, 62.8, 60.2, 57.6, 55.2, 48.2, 40.9, 40.6, 37.23, 37.15, 36.9, 29.1, 26.5, 24.3. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{44}H_{47}N_2O_4$ 667.3530; Found 667.3519.

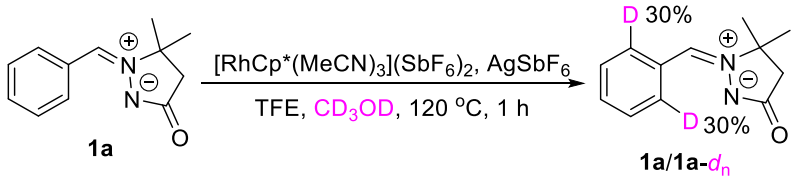
5. Gram-Scale Synthesis of 3a and 5a

To a reaction tube equipped with a stir bar were charged with **1a** (1.01g, 5.0 mmol), **2** (0.86 g, 7.5 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (104.0 mg, 0.125 mmol), $AgSbF_6$ (85.8 mg, 0.25 mmol) and TFE (10 mL). The mixture was stirred at 120 ℃ for 6 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 **3a** (0.91 g, 67%).

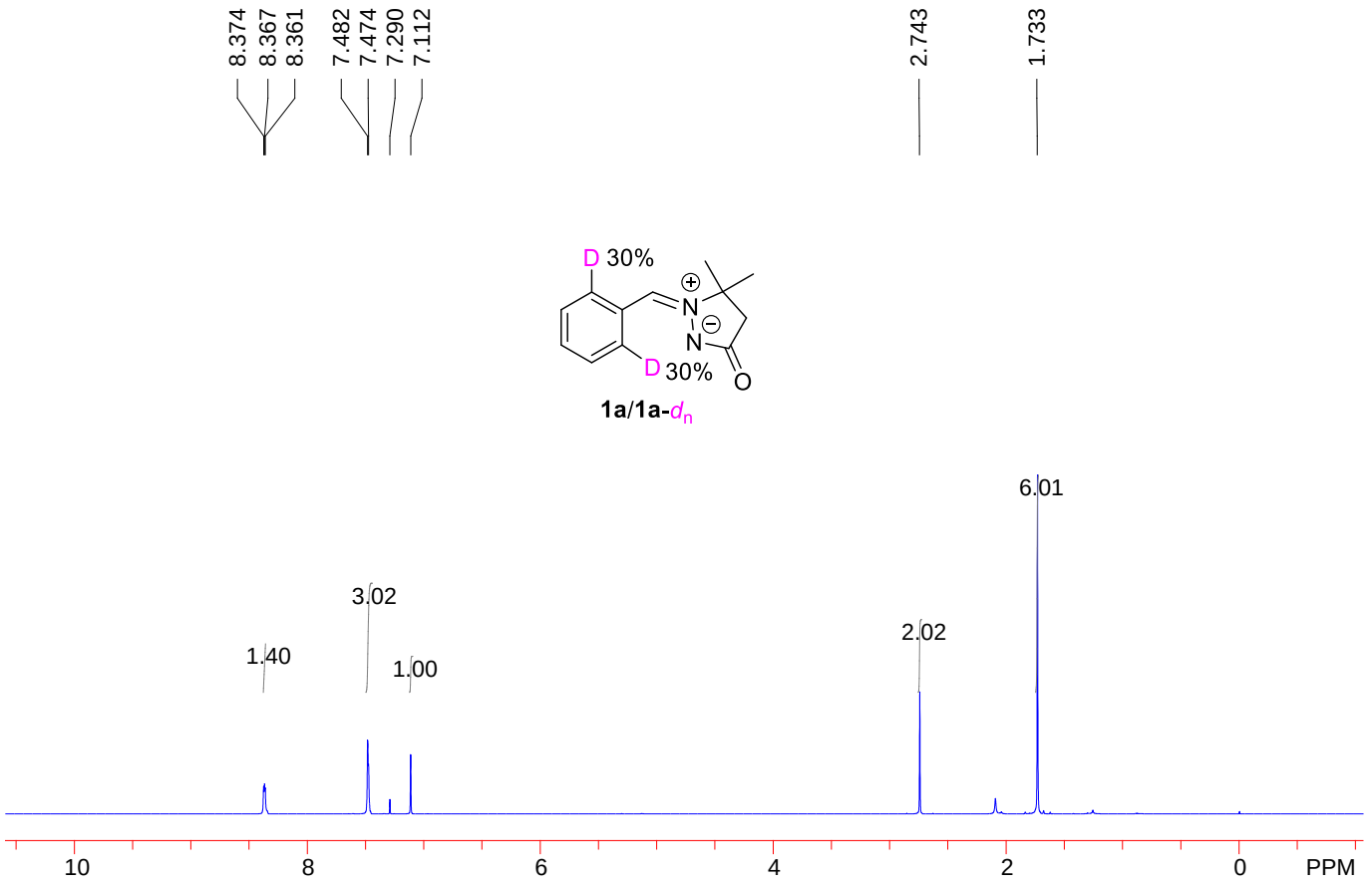
To a reaction tube equipped with a stir bar were charged with **1a** (1.01g, 5.0 mmol), **4** (1.14 g, 10.0 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (76.5 mg, 0.125 mmol), $AgSbF_6$ (171.7 g, 0.5 mmol) and HFIP (10 mL). The mixture was stirred at 80 ℃ under argon for 6 h. Upon completion, it was cooled to 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 **5a** (1.13 g, 83%).

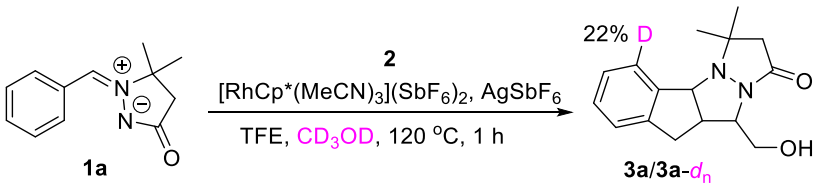
III. Mechanim studies

1. Studies on the reversibility of C−H bond activation

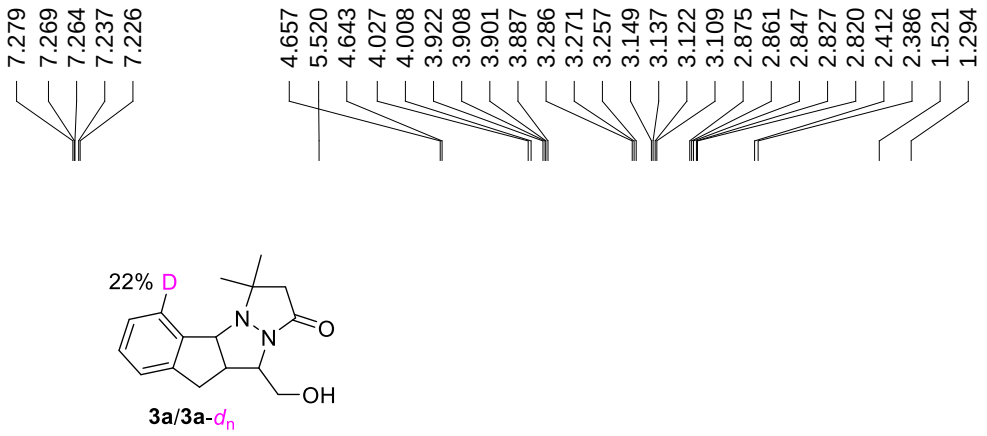


To a reaction tube equipped with a stir bar were charged with **1a** (40.4 mg, 0.2 mmol), CD_3OD (0.16 mL, 4 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and TFE (2 mL). The resulting mixture was stirred at 120 ℃ under air for 1 h. Afterwards, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel chromatography using ethyl acetate as eluent to give a mixture of **1a** and **1a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture, the deuteration ratio was determined to be 30%.

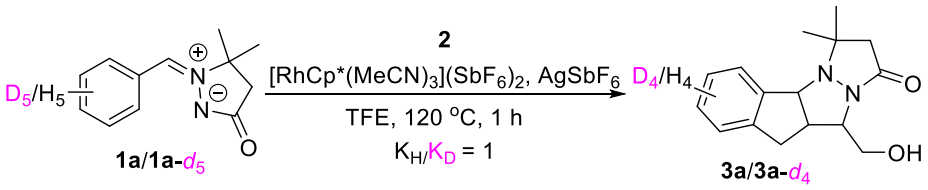




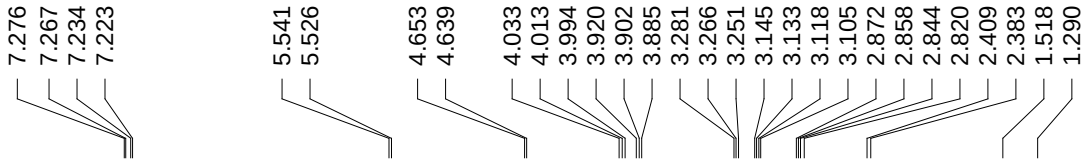
To a reaction tube equipped with a stir bar were charged with **1a** (40.4 mg, 0.2 mmol), **2** (34.2 mg, 0.3 mmol), CD_3OD (0.16 mL, 4 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and TFE (2 mL). The resulting mixture was stirred at 120 ℃ under air for 1 h. Afterwards, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to give a mixture of **3a** and **3a**-d_n. Upon analyzing the ^1H NMR spectrum of the mixture, the deuteration ratio was determined to be 22%.

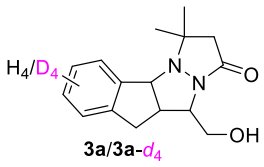


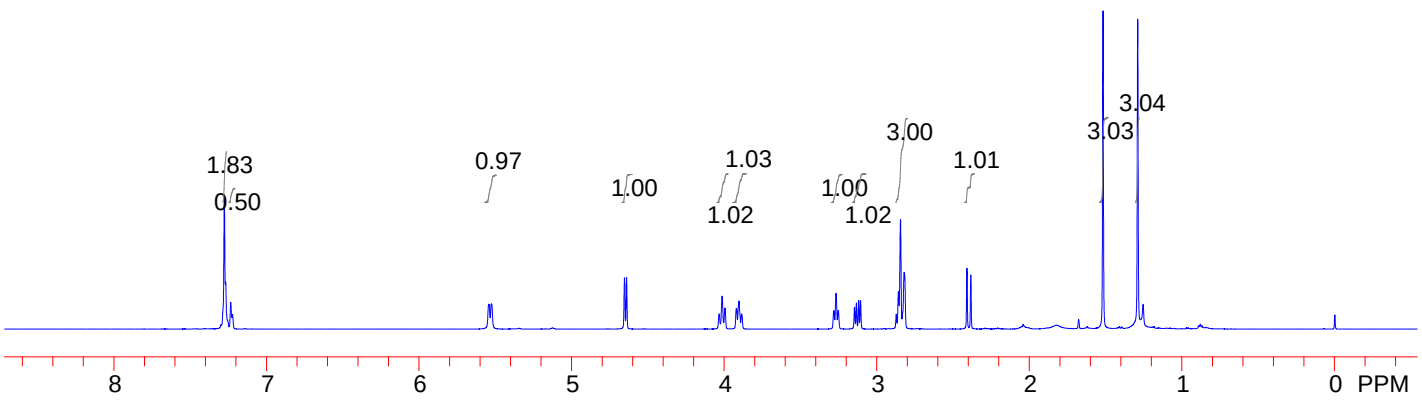
2. Kinetic isotope effect study



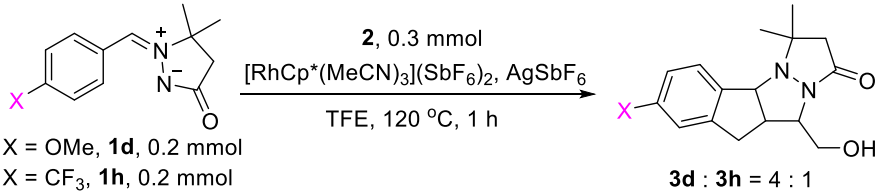
To a reaction tube equipped with a stir bar were added **1a** (40.4 mg, 0.2 mmol), **1a**-d_5 (41.5 mg, 0.2 mmol), TFE (2 mL), **2** (34.2 mg, 0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol) with stirring. The resulting mixture was stirred at 120 ℃ under air for 1 h. Afterwards, it was cooled to room temperature, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to afford a mixture of **3a** and **3a**-d_4. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **3a** to **3a**-d_4 was determined to be 0.5:0.5. Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be 1.



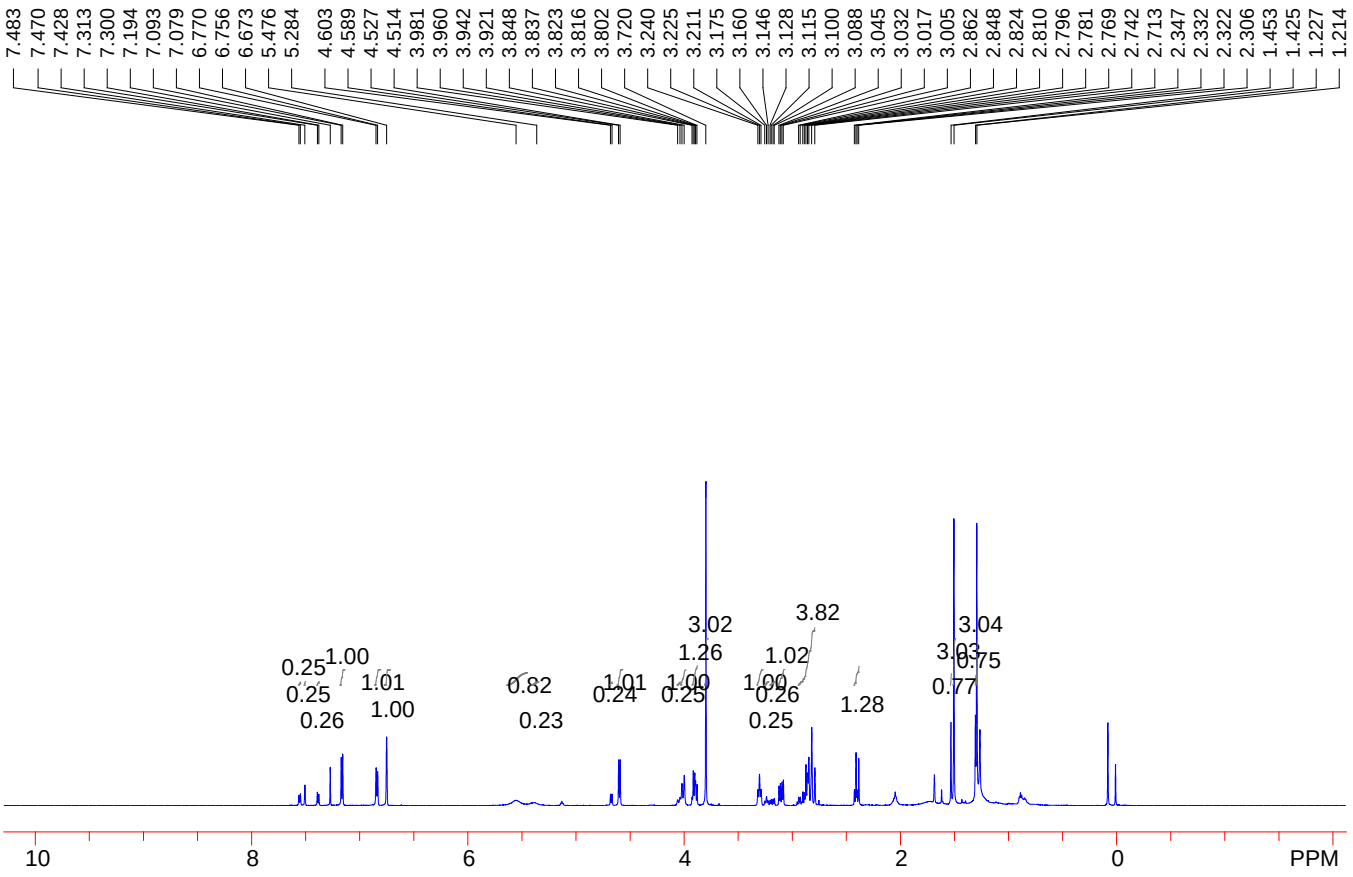




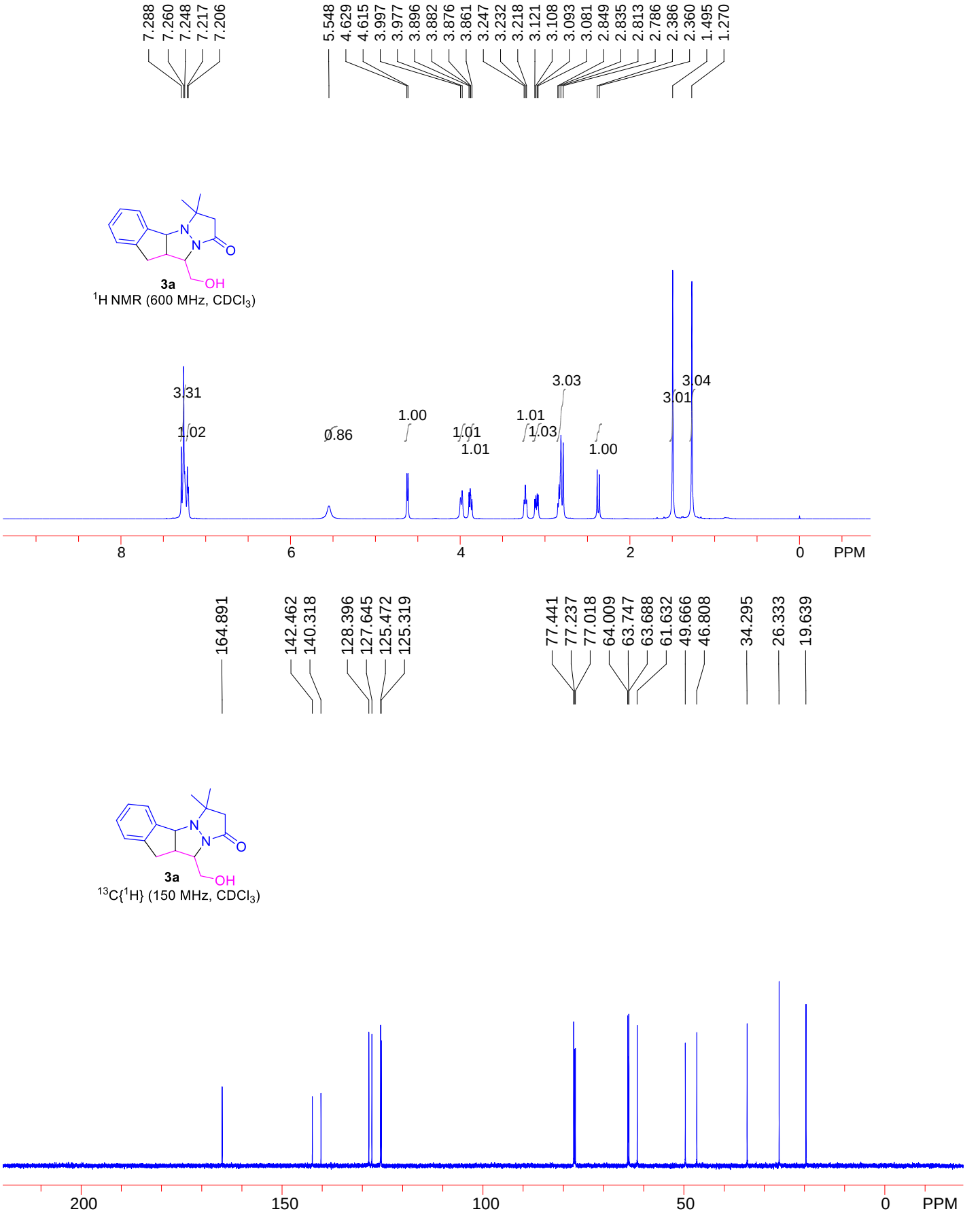
3. Competition experiment between 1d and 1h

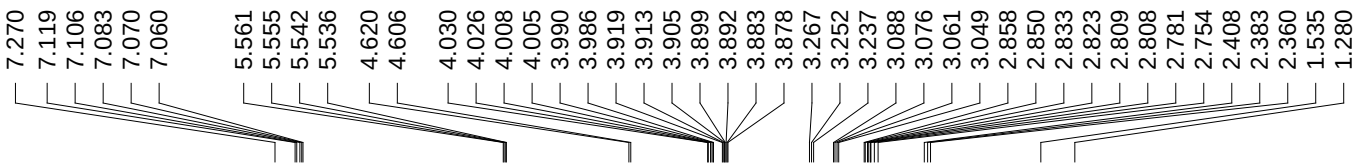


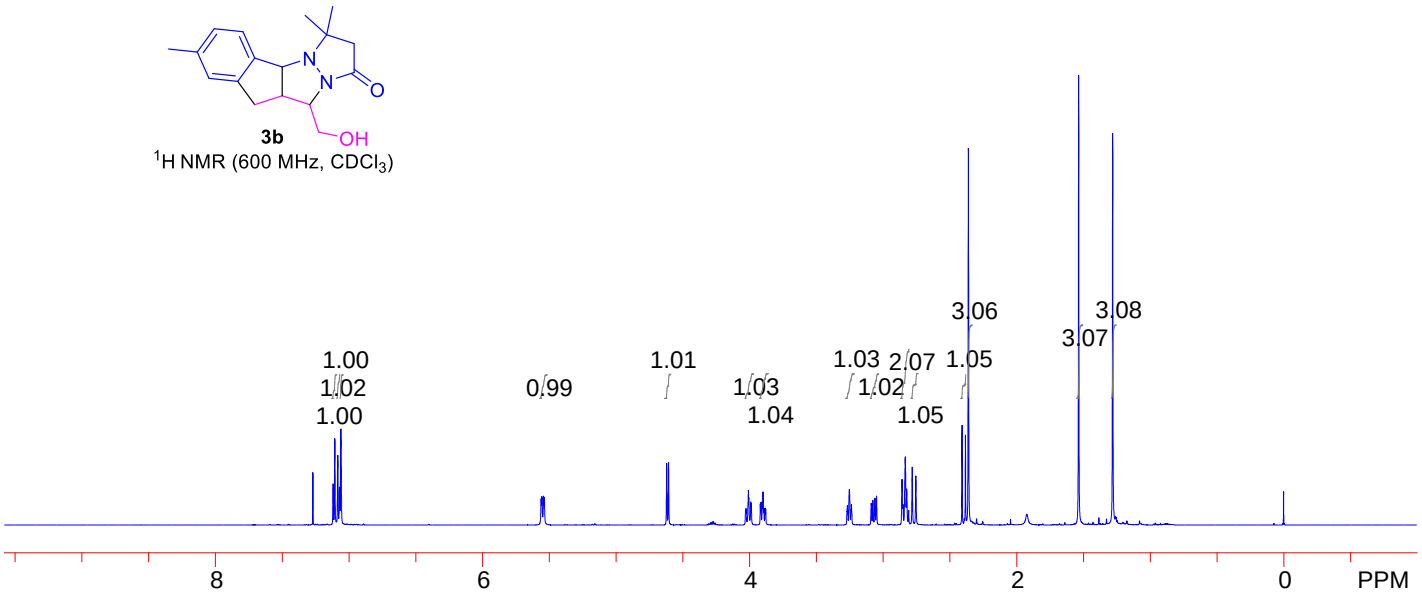
To a reaction tube equipped with a stir bar were added **1d** (46.5 mg, 0.2 mmol), **1h** (44.0 mg, 0.2 mmol), **2** (34.2 mg, 0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). The tube was then sealed, and the mixture was stirred at 120 ℃ under air for 1 h. 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 a mixture of **3d** and **3h**. Upon analyzing the ^1H NMR spectrum of the mixture, the ratio of **3d** to **3h** was determined to be about 4:1.

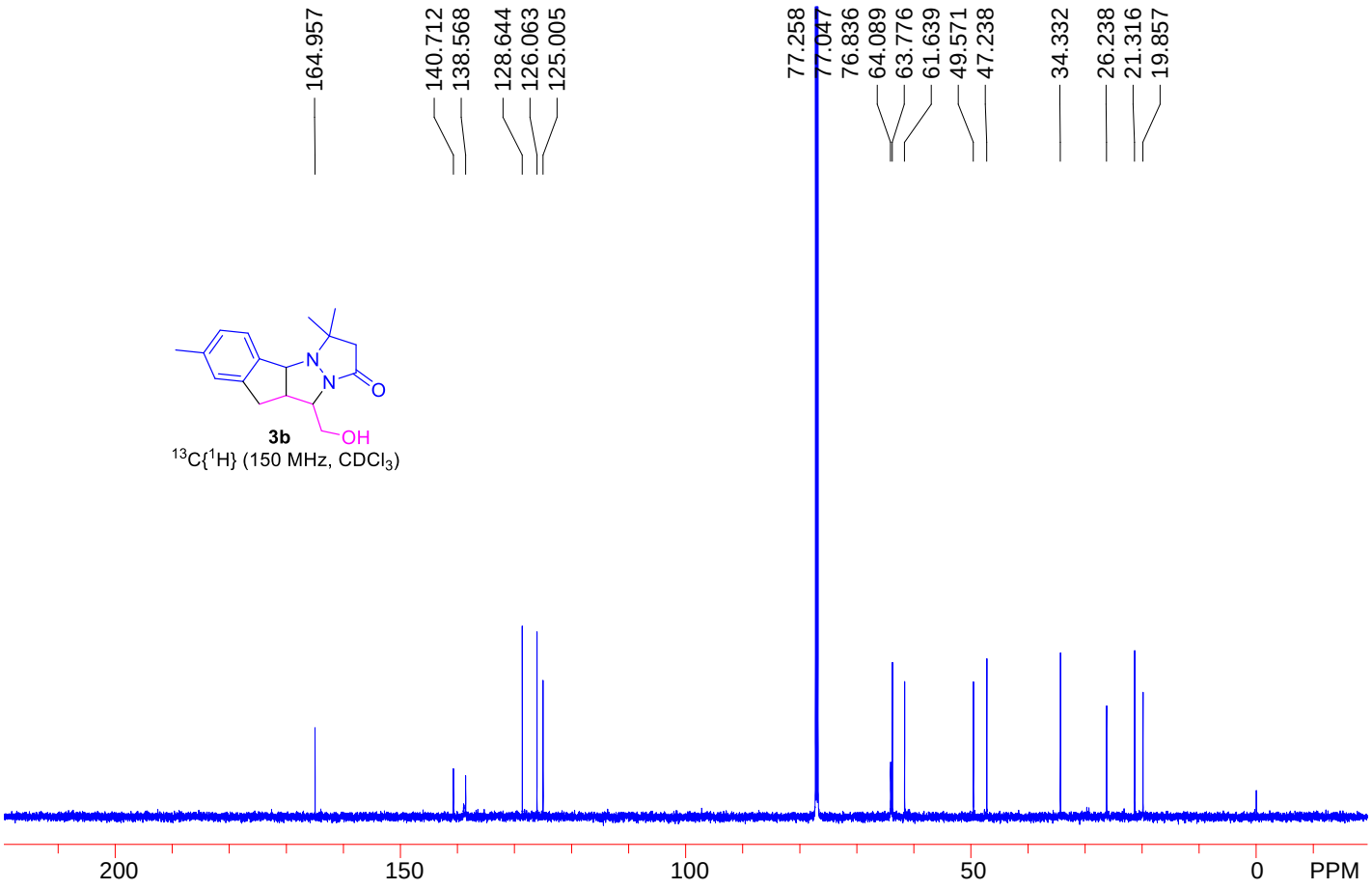


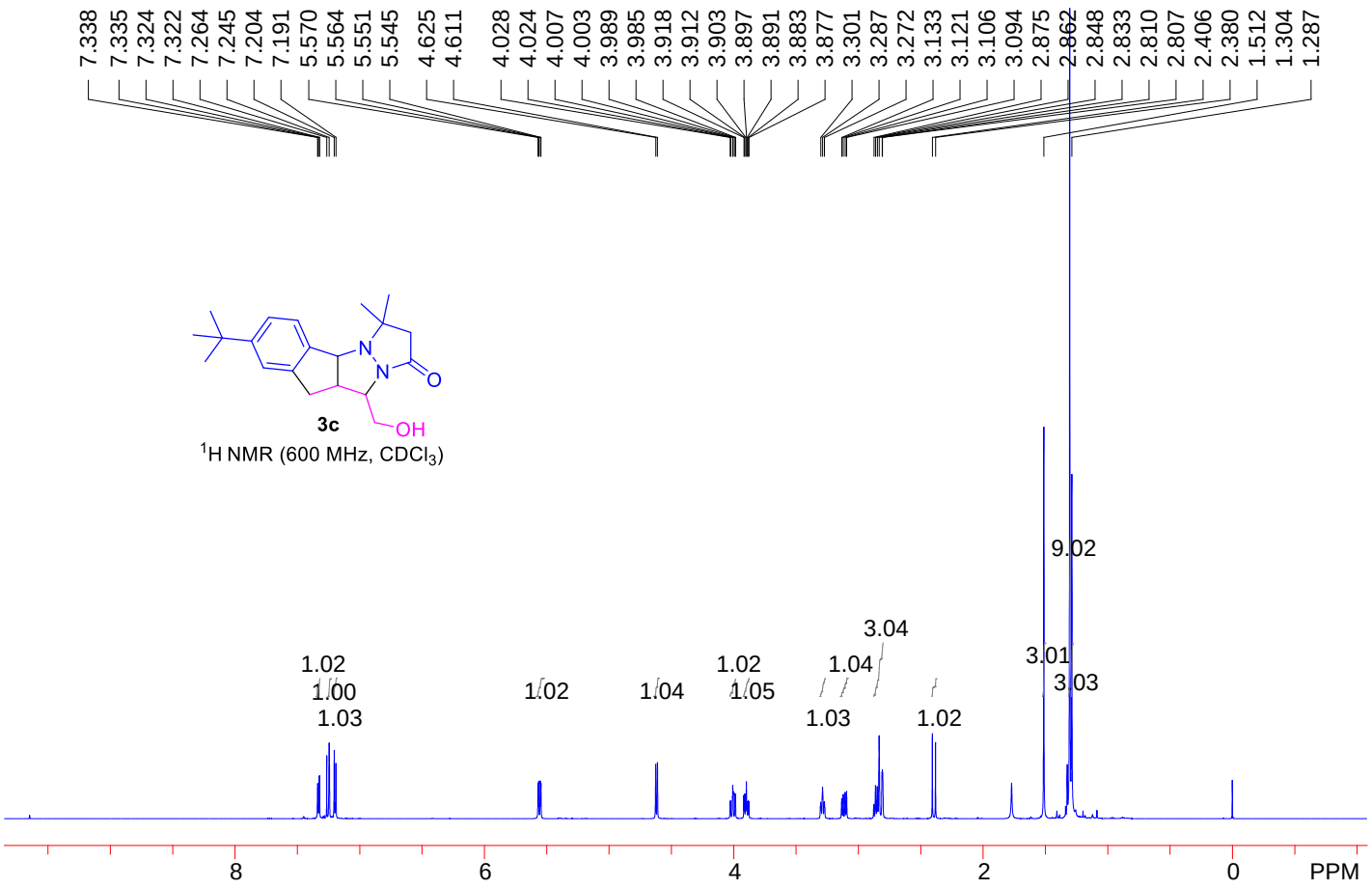
IV. Copies of NMR spectra of 3a-3v

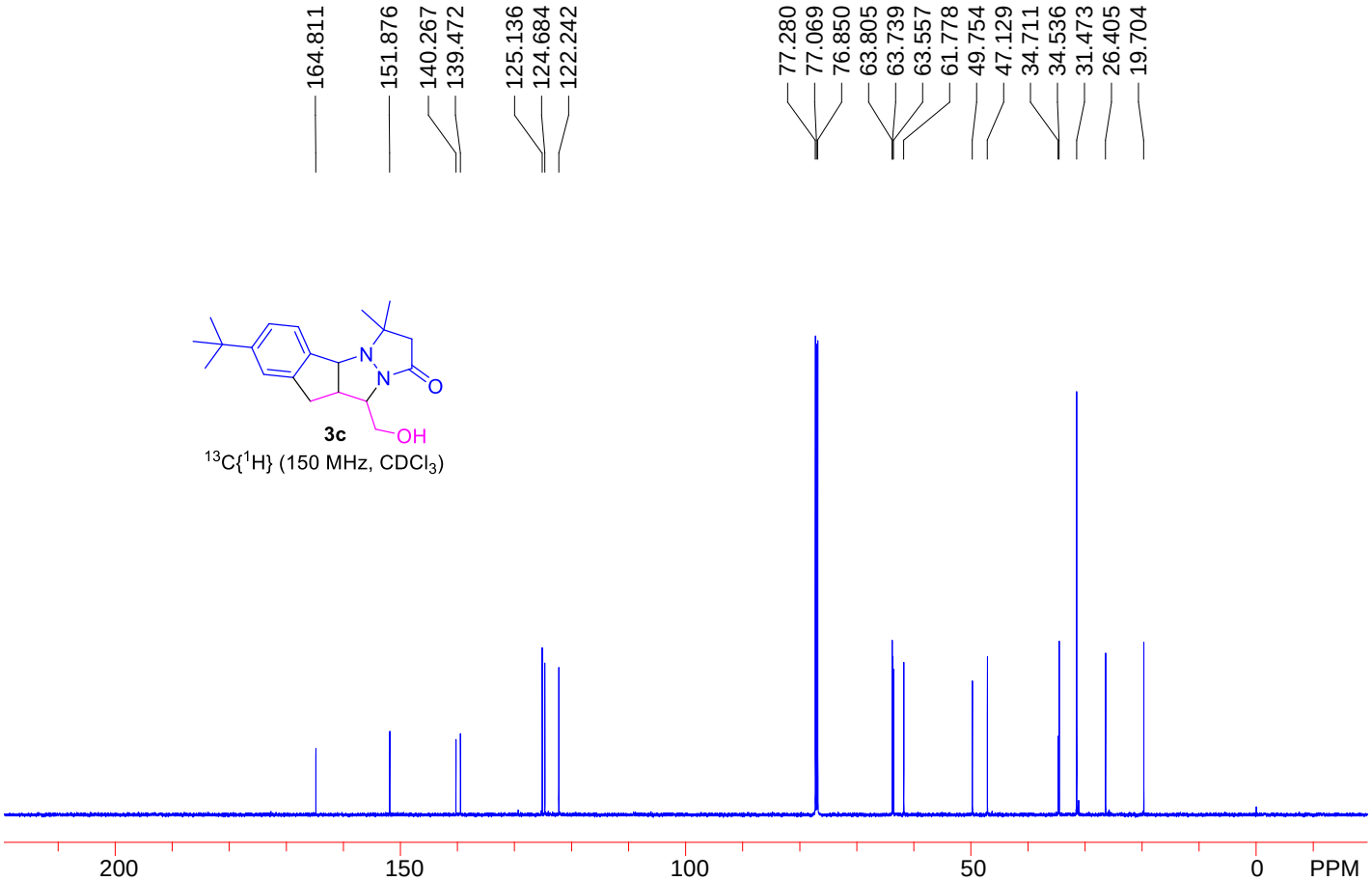


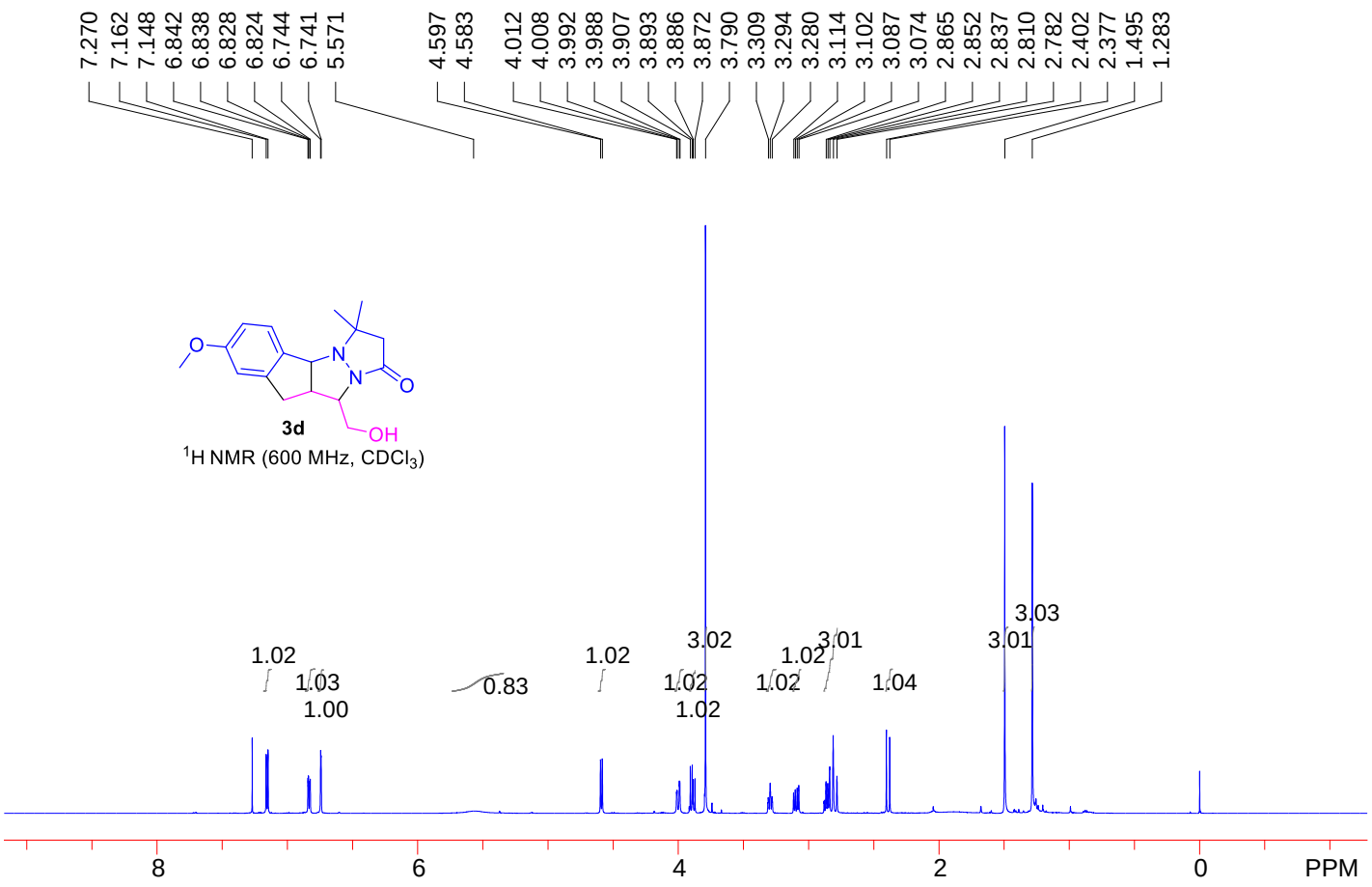

7.270
7.119
7.106
7.083
7.070
7.060
5.561
5.555
5.542
5.536
4.620
4.606
4.030
4.026
4.008
4.005
3.990
3.986
3.919
3.913
3.905
3.899
3.892
3.883
3.878
3.267
3.252
3.237
3.088
3.076
3.061
3.049
2.858
2.850
2.833
2.823
2.809
2.808
2.781
2.754
2.408
2.383
2.360
1.535
1.280

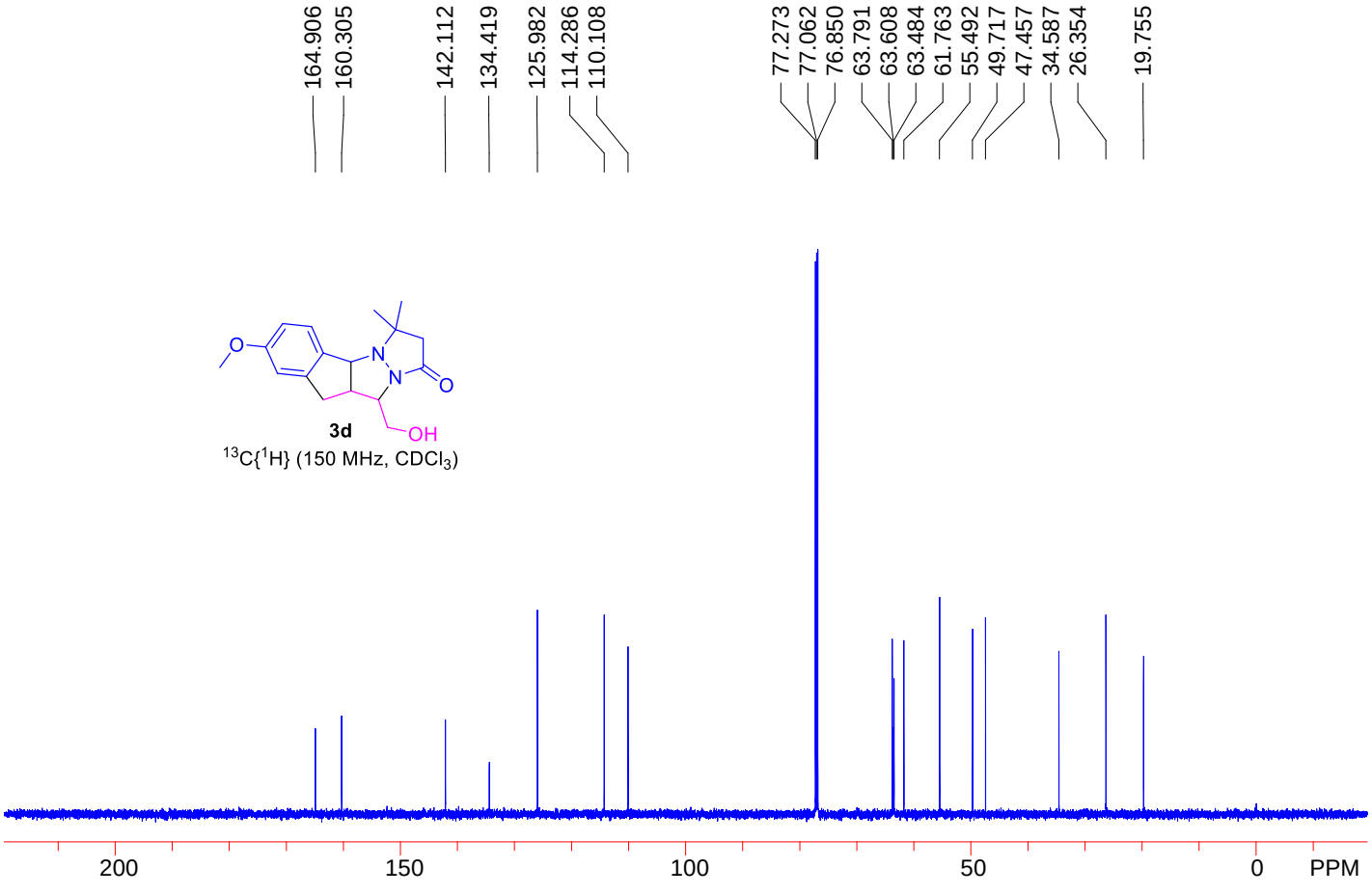

3b
1H NMR (600 MHz, CDCl3)
1.00
1.02
1.00
0.99
1.01
1.03
1.04
1.03
1.02
2.07
1.05
3.06
1.05
3.07
3.08
8
6
4
2
0
PPM

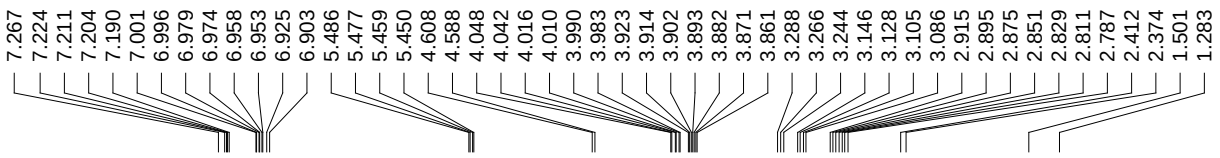

164.957
140.712
138.568
128.644
126.063
125.005
77.258
77.047
76.836
64.089
63.776
61.639
49.571
47.238
34.332
26.238
21.316
19.857
3b
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

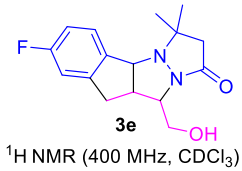

7.338
7.335
7.324
7.322
7.264
7.245
7.204
7.191
5.570
5.564
5.551
5.545
4.625
4.611
4.028
4.024
4.007
4.003
3.989
3.985
3.918
3.912
3.903
3.897
3.891
3.883
3.877
3.301
3.287
3.272
3.133
3.121
3.106
3.094
2.875
2.862
2.848
2.833
2.810
2.807
2.406
2.380
1.512
1.304
1.287
3c
1H NMR (600 MHz, CDCl3)
9.02
3.04
3.01
3.03
1.02
1.00
1.03
1.02
1.04
1.02
1.05
1.04
1.03
1.02
8
6
4
2
0
PPM


164.811
151.876
140.267
139.472
125.136
124.684
122.242
77.280
77.069
76.850
63.805
63.739
63.557
61.778
49.754
47.129
34.711
34.536
31.473
26.405
19.704
3c
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM


7.270
7.162
7.148
6.842
6.838
6.828
6.824
6.744
6.741
5.571
4.597
4.583
4.012
4.008
3.992
3.988
3.907
3.893
3.886
3.872
3.790
3.309
3.294
3.280
3.114
3.102
3.087
3.074
2.865
2.852
2.837
2.810
2.782
2.402
2.377
1.495
1.283
3d
1H NMR (600 MHz, CDCl3)
1.02
1.03
1.00
0.83
1.02
3.02
1.02
1.02
3.01
1.02
1.04
3.01
3.03
8
6
4
2
0
PPM

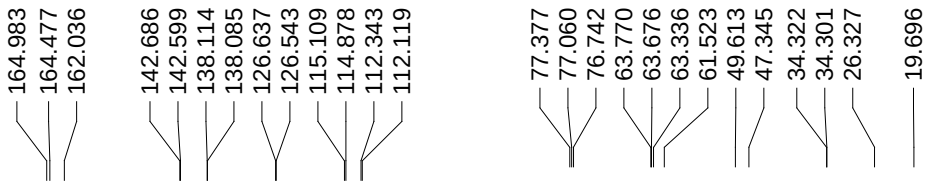

164.906
160.305
142.112
134.419
125.982
114.286
110.108
77.273
77.062
76.850
63.791
63.608
63.484
61.763
55.492
49.717
47.457
34.587
26.354
19.755
3d
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

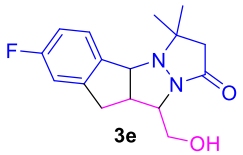




3e

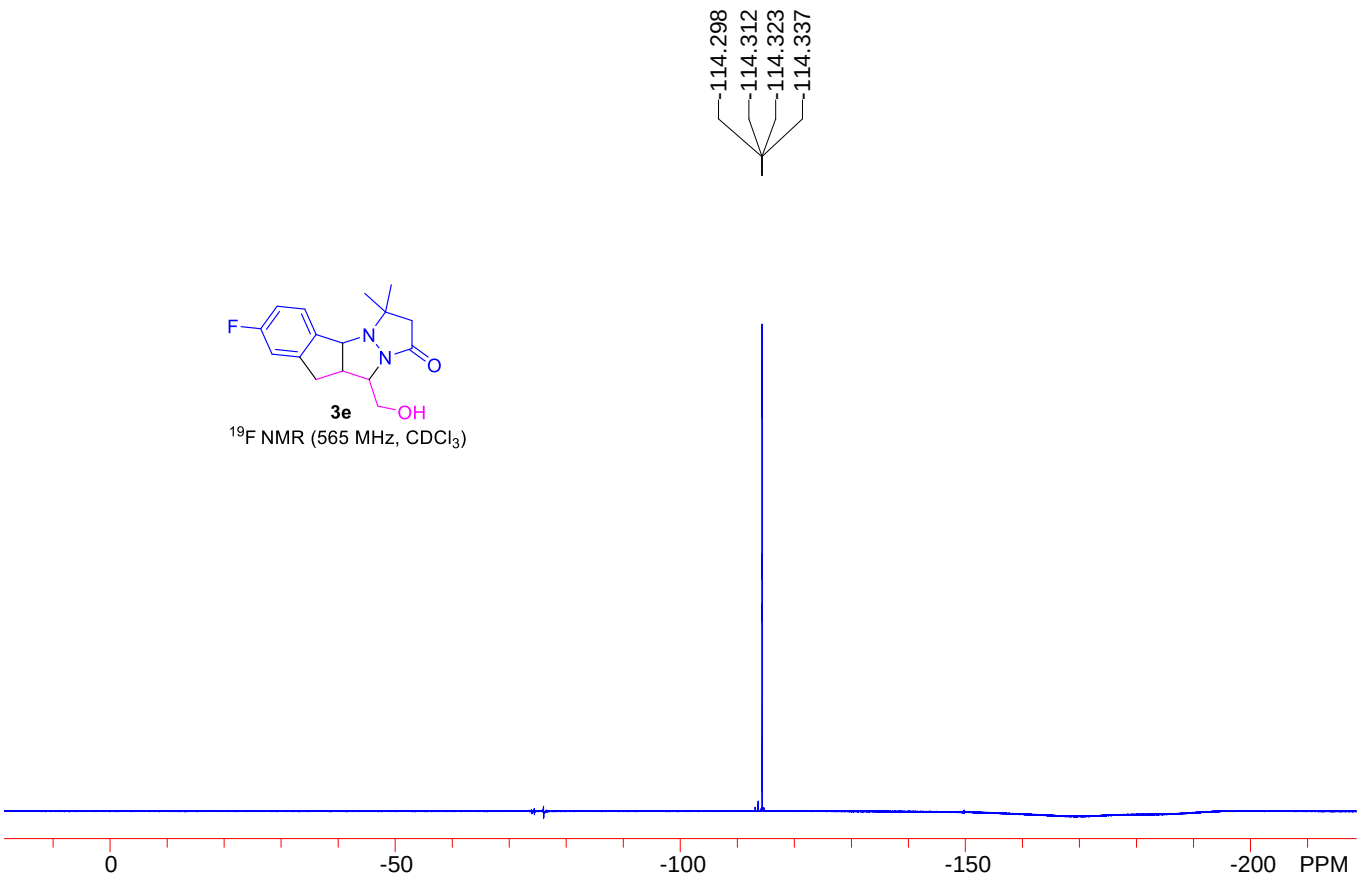
^{1}H NMR (400 MHz, $CDCl_3$)





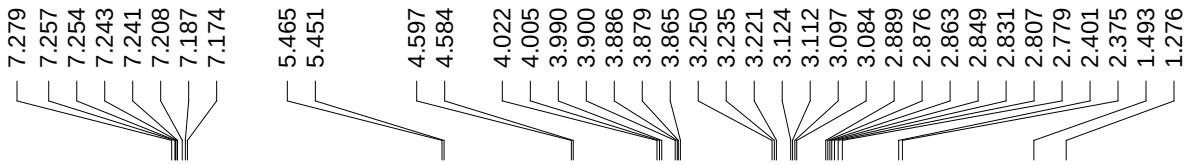
3e

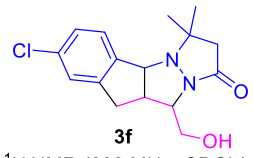
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



3e

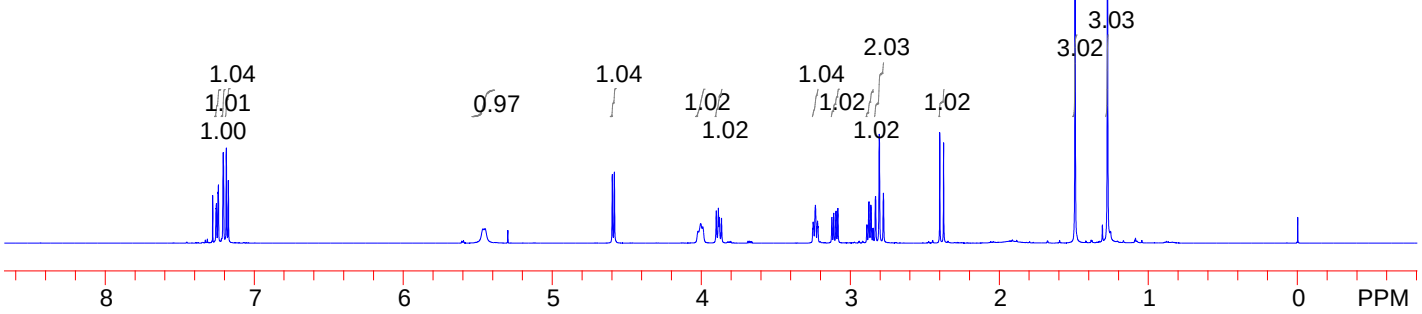
^{19}F NMR (565 MHz, $CDCl_3$)

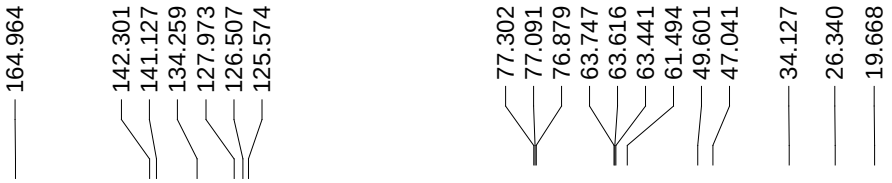


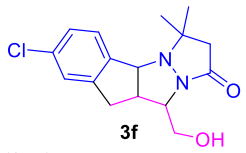


3f

^{1}H NMR (600 MHz, $CDCl_3$)

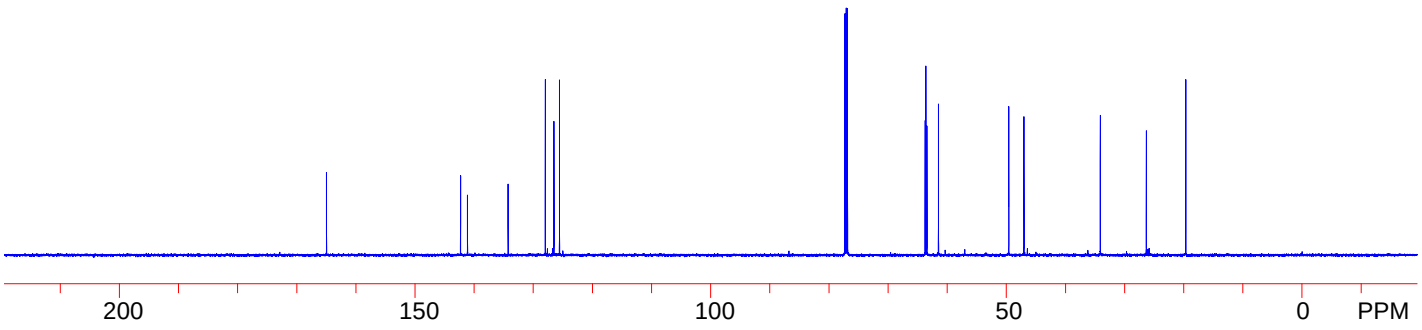


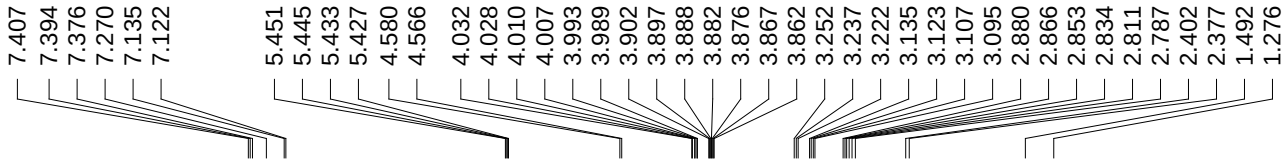


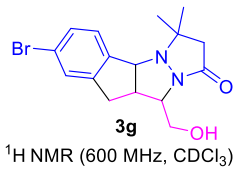


3f

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

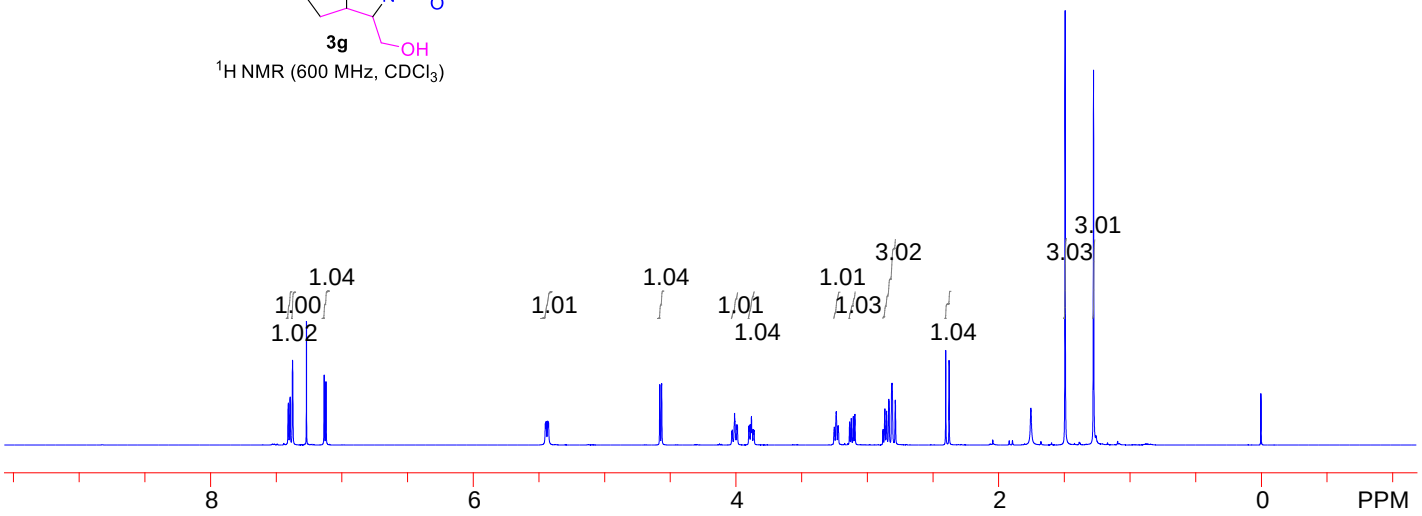


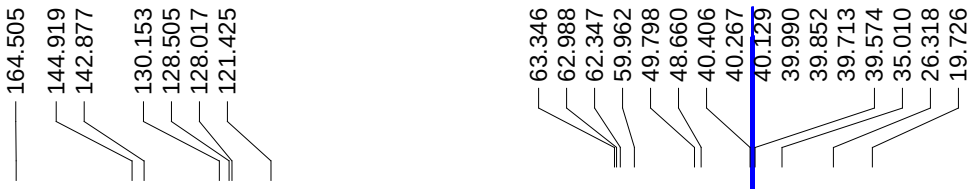


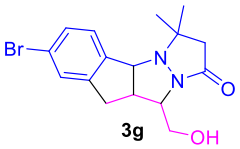


3g

^{1}H NMR (600 MHz, $CDCl_3$)

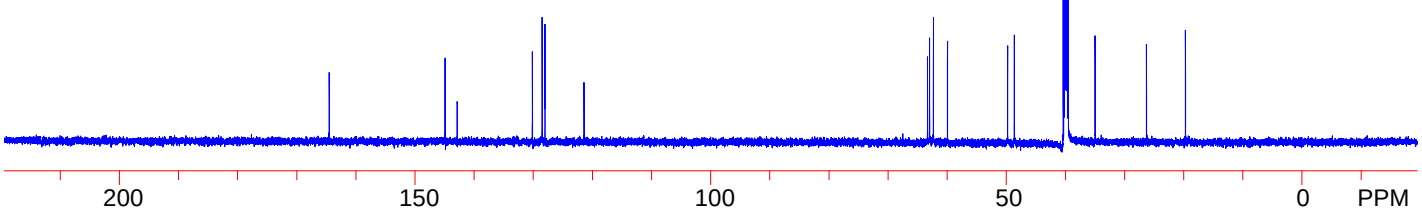


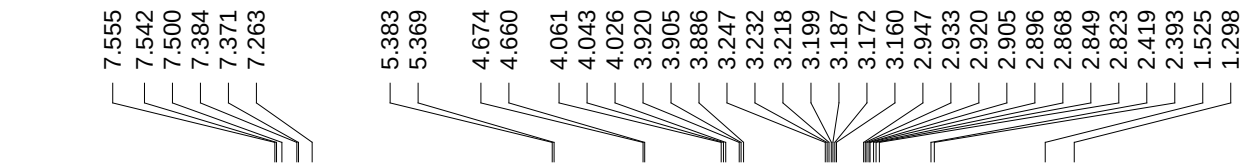


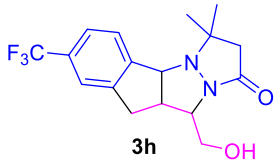


3g

$^{13}C\{^{1}H\}$ (150 MHz, DMSO-d_6)

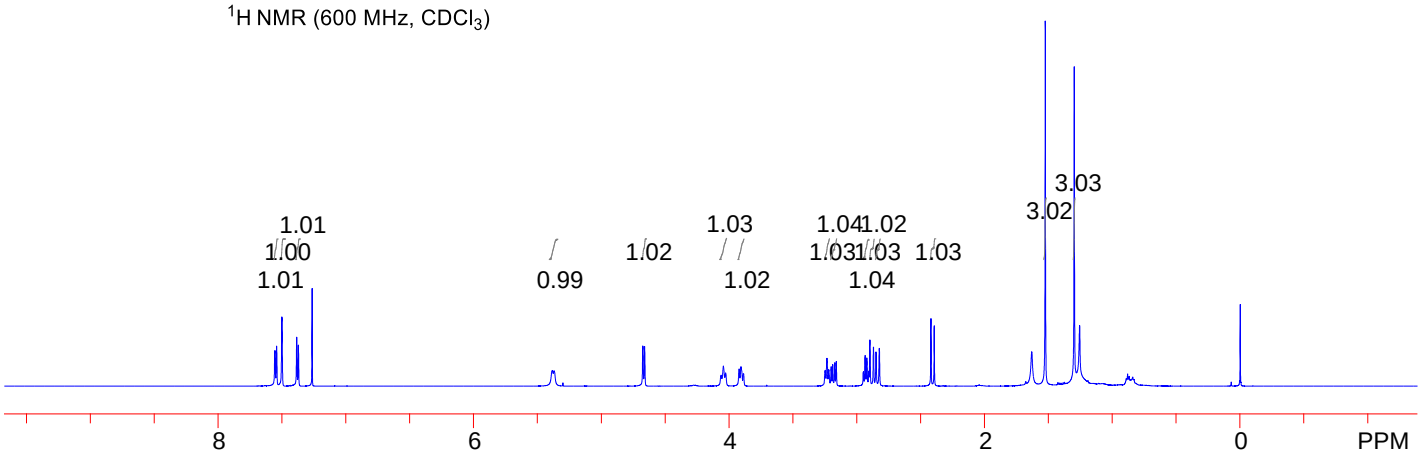


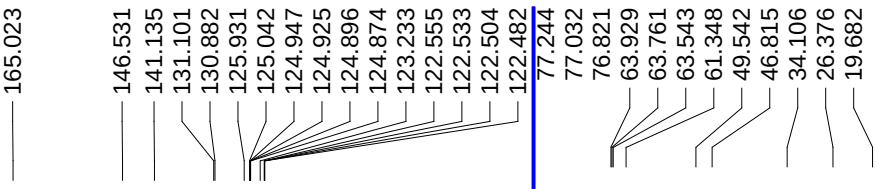


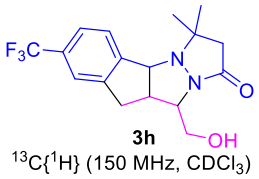


3h

^{1}H NMR (600 MHz, $CDCl_3$)

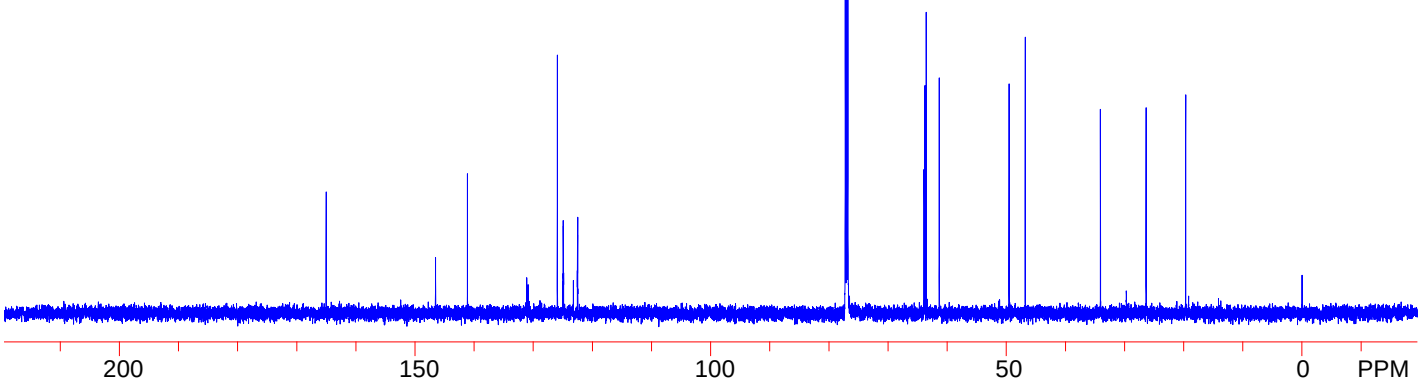


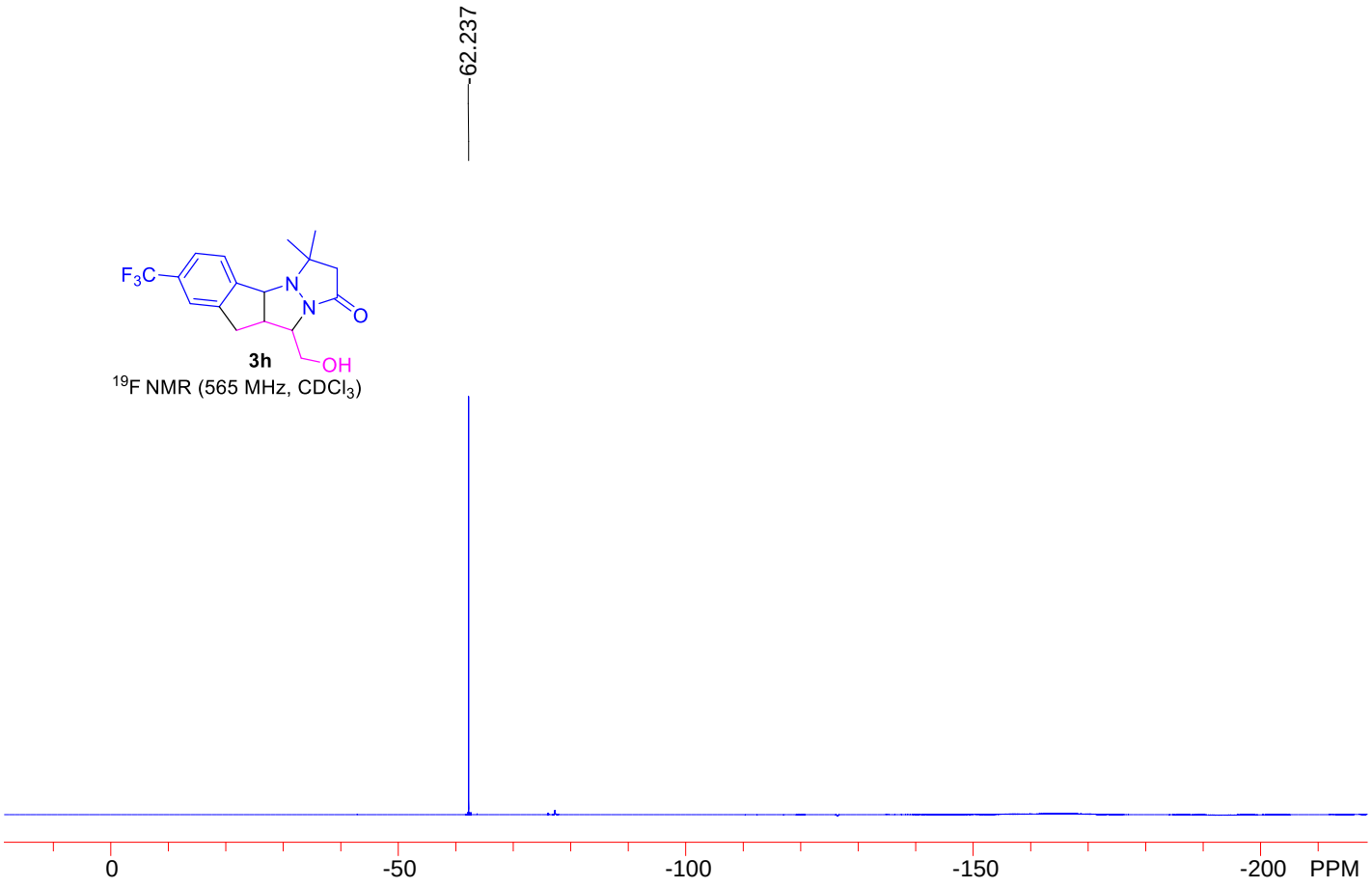


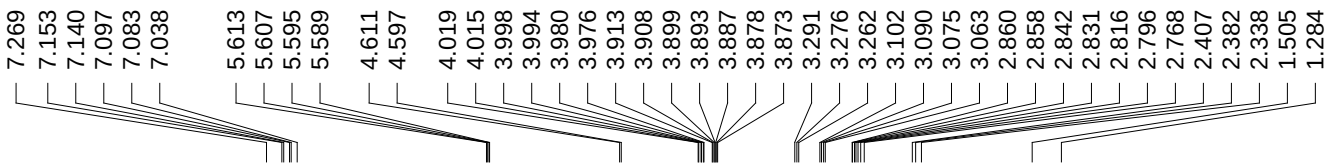


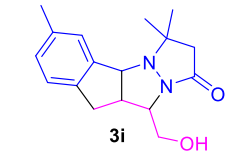
3h

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



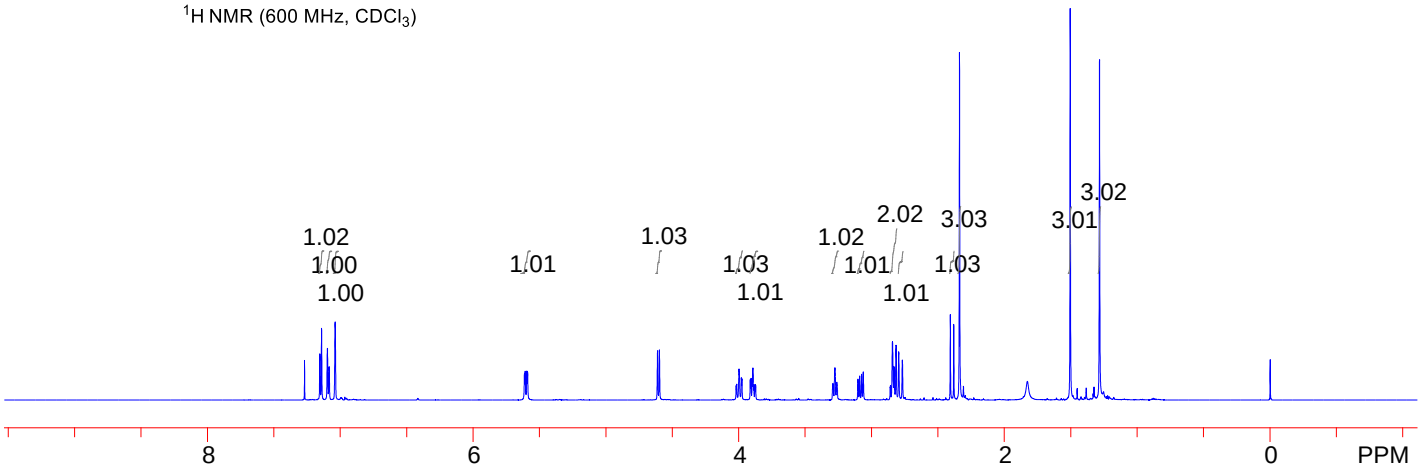

-62.237
F3C
N
N
O
OH
3h
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

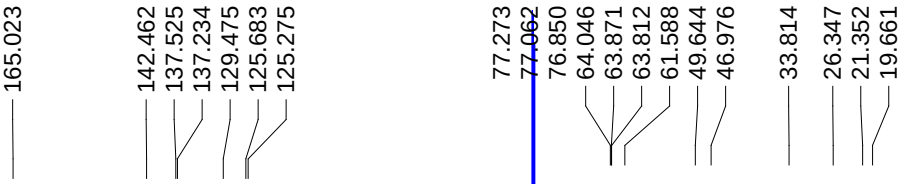


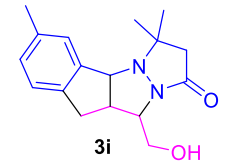


3i

^{1}H NMR (600 MHz, $CDCl_3$)

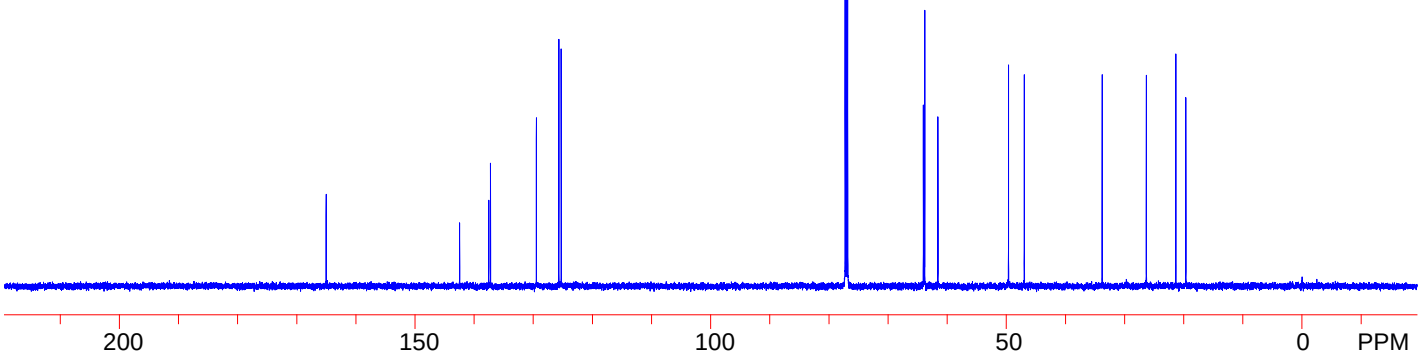


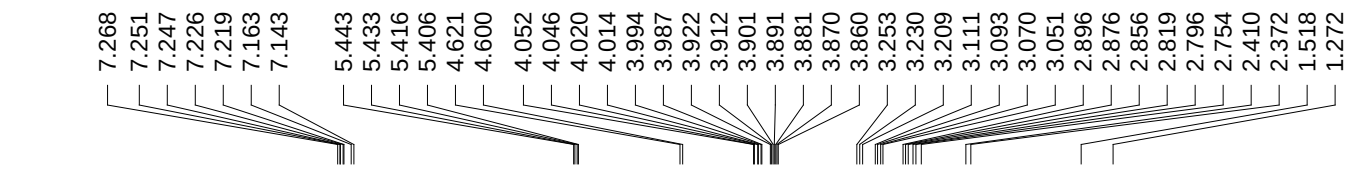


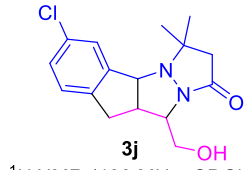


3i

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

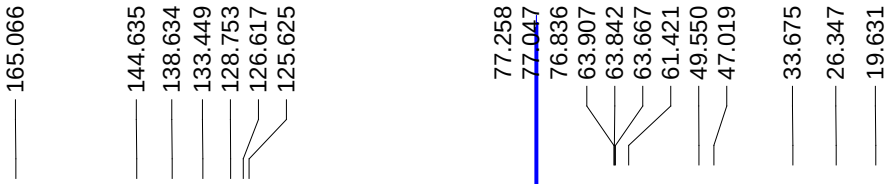


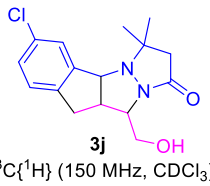




3j

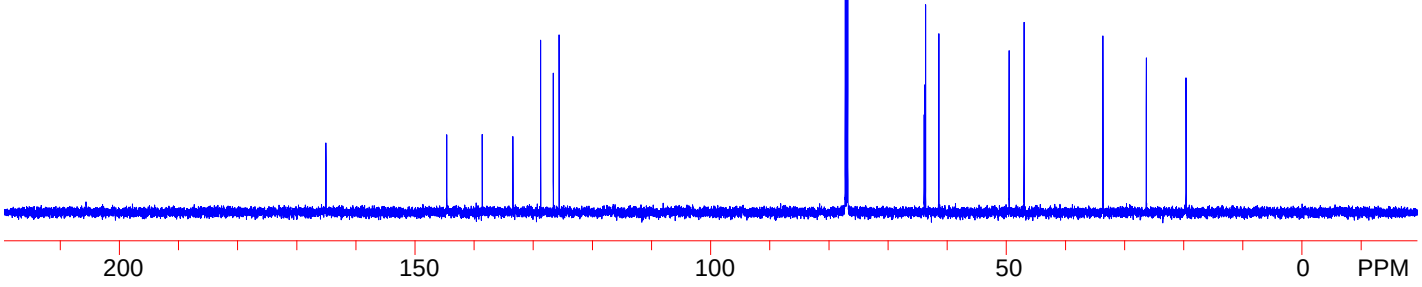
^{1}H NMR (400 MHz, $CDCl_3$)

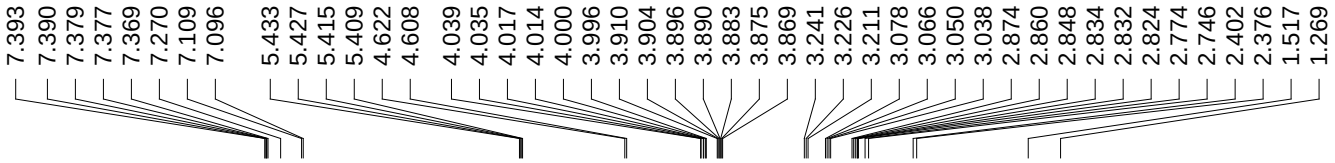


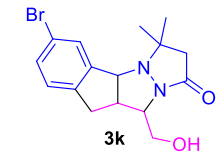


3j

^{13}C{^{1}H} (150 MHz, $CDCl_3$)

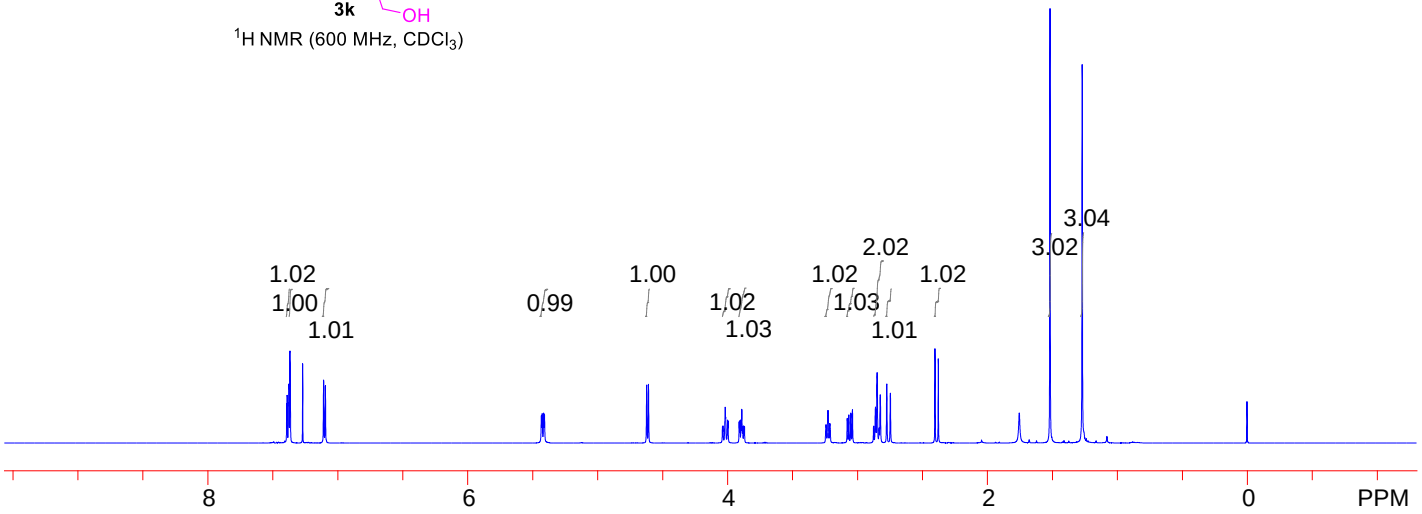


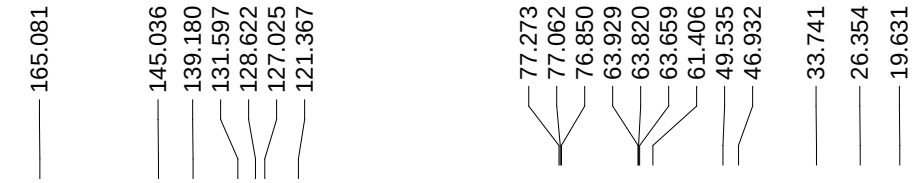


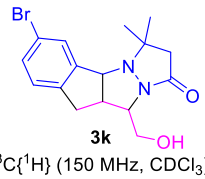


3k

^{1}H NMR (600 MHz, $CDCl_3$)

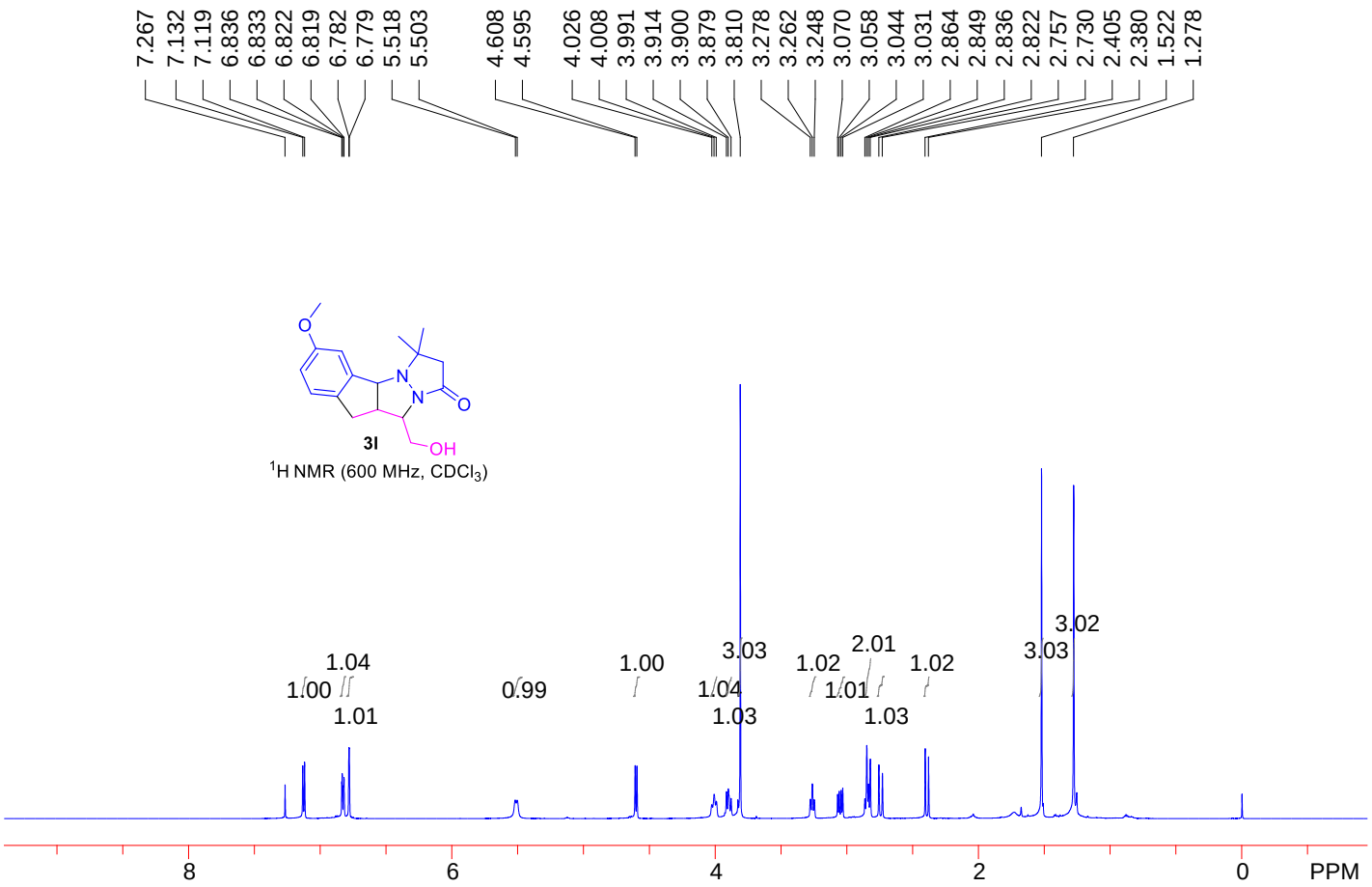


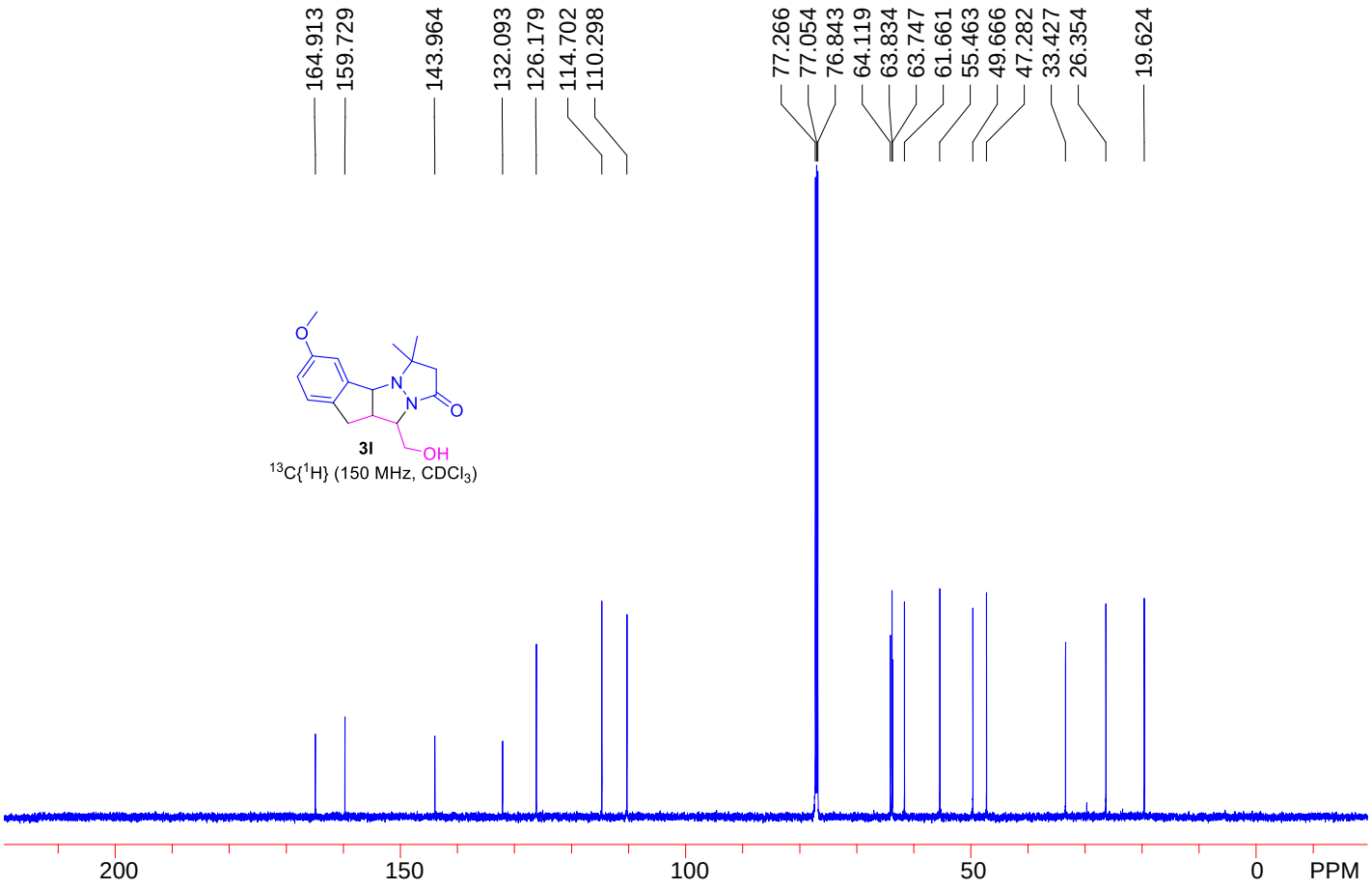


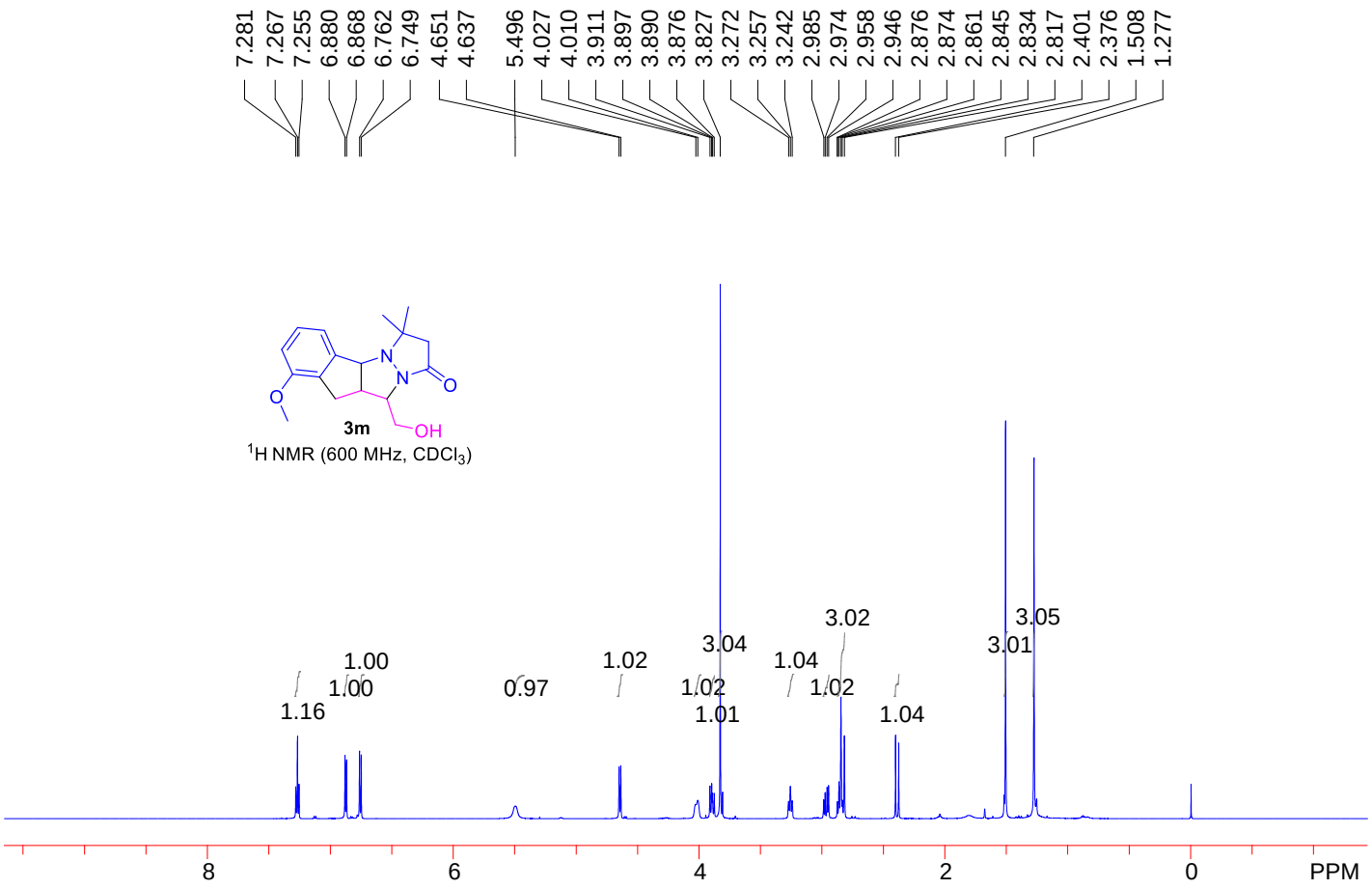


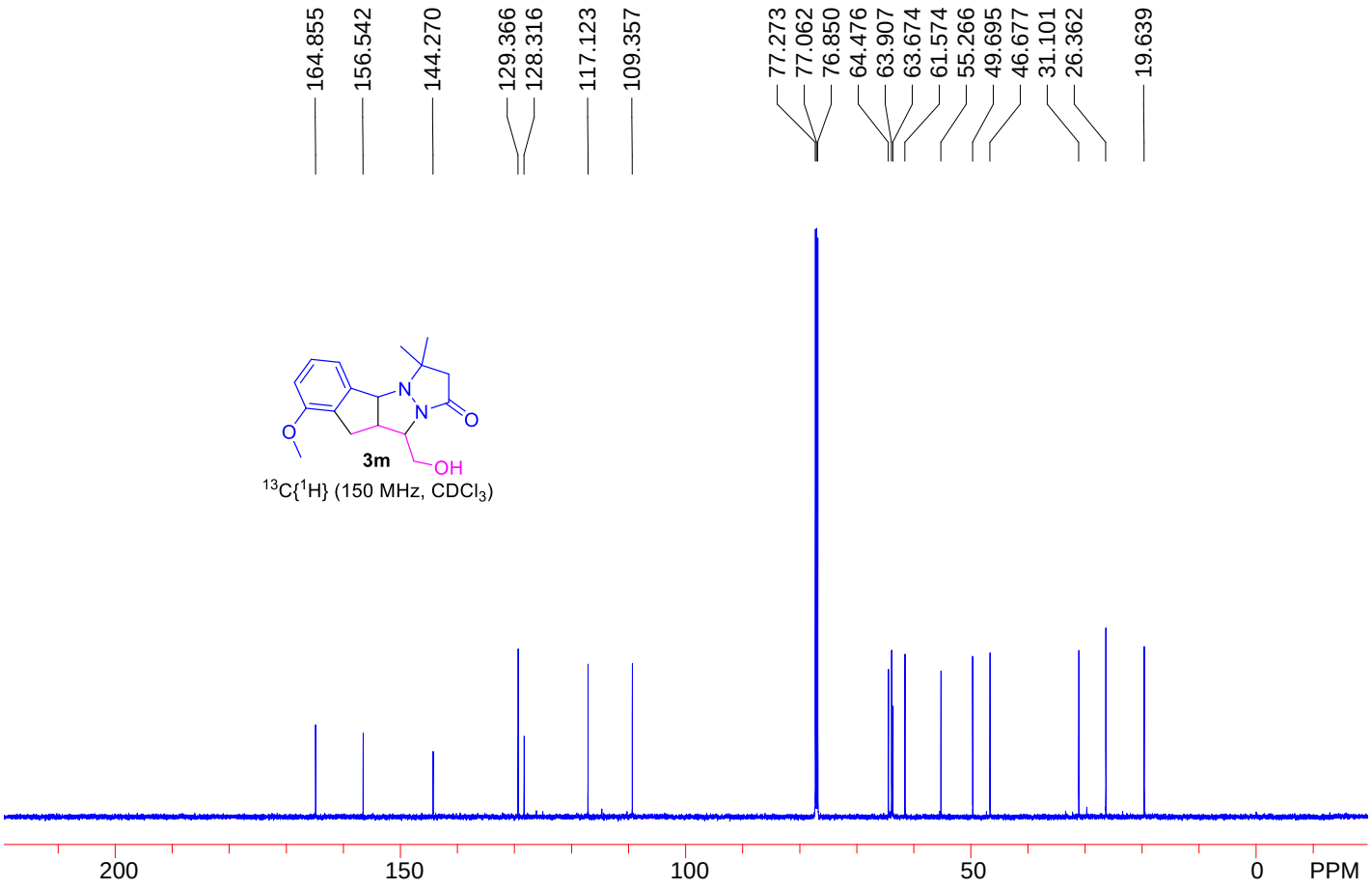
3k

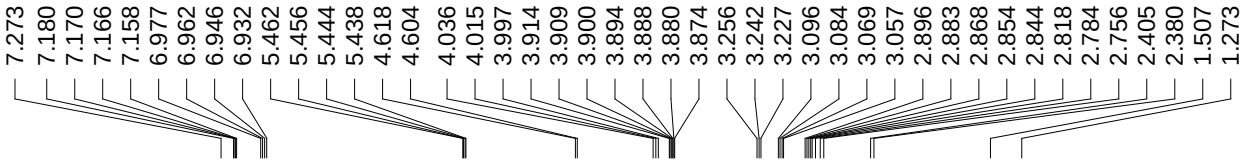
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

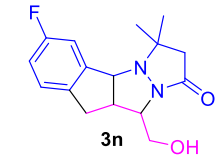

7.267
7.132
7.119
6.836
6.833
6.822
6.819
6.782
6.779
5.518
5.503
4.608
4.595
4.026
4.008
3.991
3.914
3.900
3.879
3.810
3.278
3.262
3.248
3.070
3.058
3.044
3.031
2.864
2.849
2.836
2.822
2.757
2.730
2.405
2.380
1.522
1.278
3l
^{1}H NMR (600 MHz, CDCl$_3$)
1.00
1.04
1.01
0.99
1.00
3.03
1.04
1.03
1.02
2.01
1.01
1.03
1.02
3.03
3.02
8
6
4
2
0
PPM


164.913
159.729
143.964
132.093
126.179
114.702
110.298
77.266
77.054
76.843
64.119
63.834
63.747
61.661
55.463
49.666
47.282
33.427
26.354
19.624
3l
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM


7.281
7.267
7.255
6.880
6.868
6.762
6.749
4.651
4.637
5.496
4.027
4.010
3.911
3.897
3.890
3.876
3.827
3.272
3.257
3.242
2.985
2.974
2.958
2.946
2.876
2.874
2.861
2.845
2.834
2.817
2.401
2.376
1.508
1.277
3m
OH
O
N
N
O
1H NMR (600 MHz, CDCl3)
1.16
1.00
1.00
0.97
1.02
1.02
3.04
1.01
1.04
1.02
3.02
1.04
3.01
3.05
8
6
4
2
0
PPM

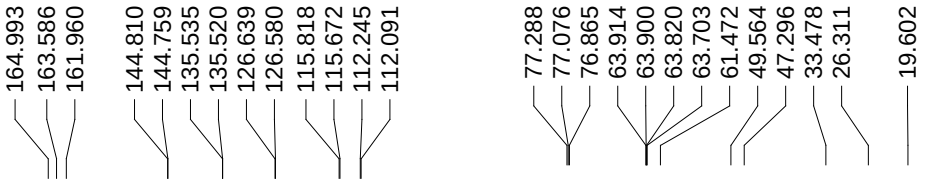

164.855
156.542
144.270
129.366
128.316
117.123
109.357
77.273
77.062
76.850
64.476
63.907
63.674
61.574
55.266
49.695
46.677
31.101
26.362
19.639
3m
OH
O
N
N
O
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

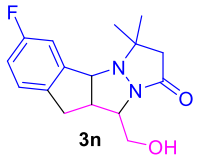




3n

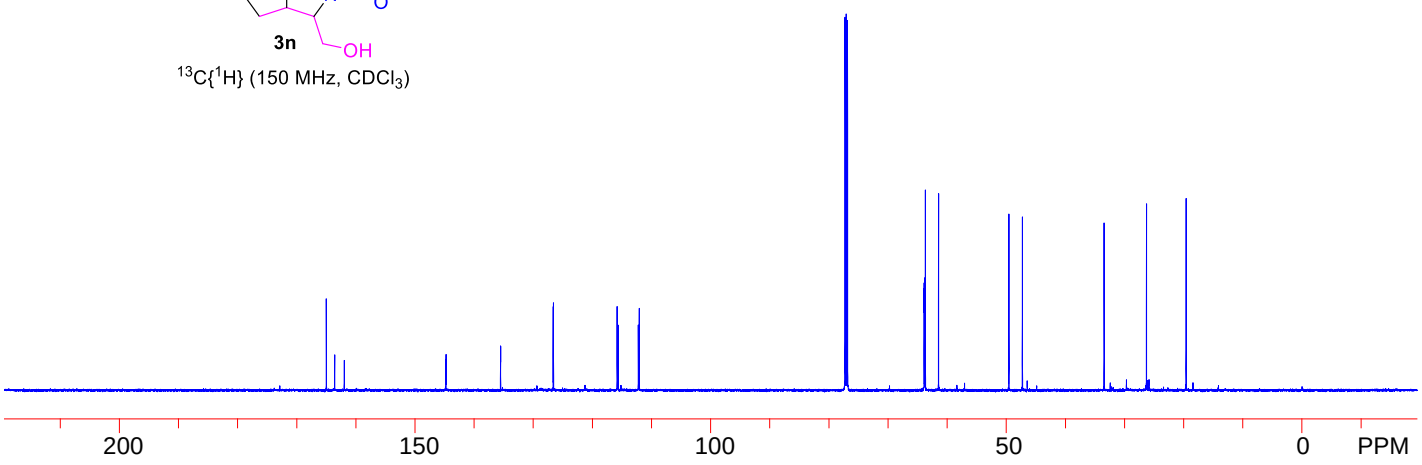
^{1}H NMR (600 MHz, $CDCl_3$)

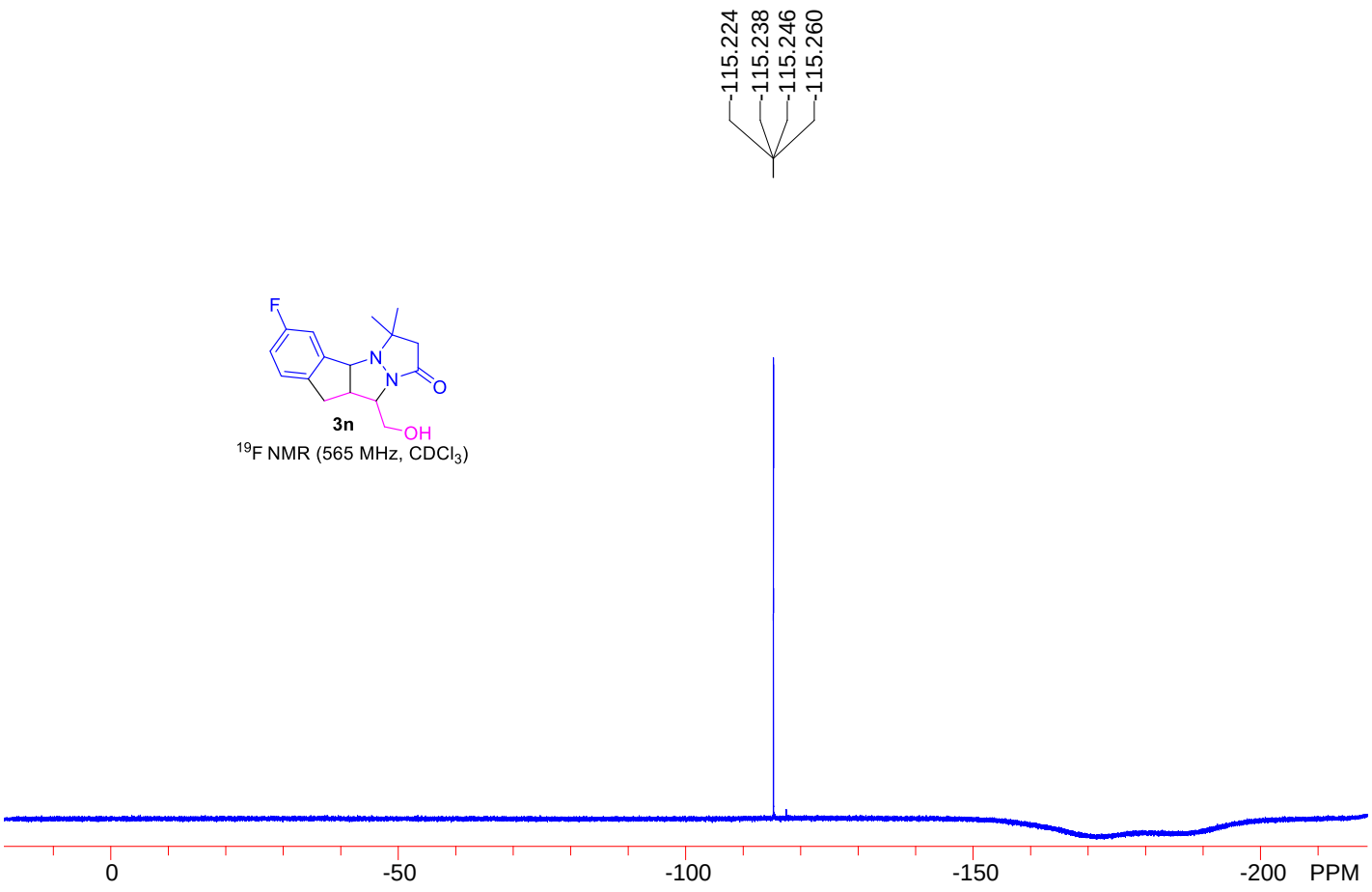




3n

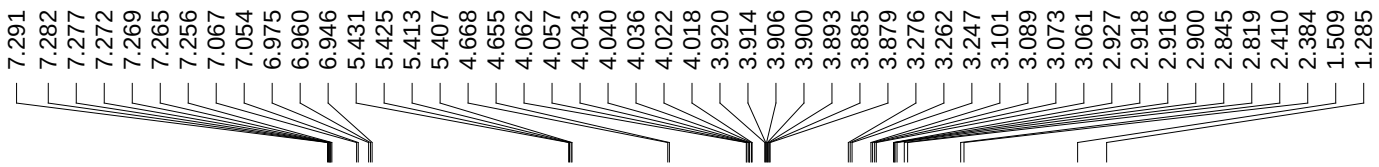
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

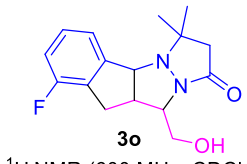




3n

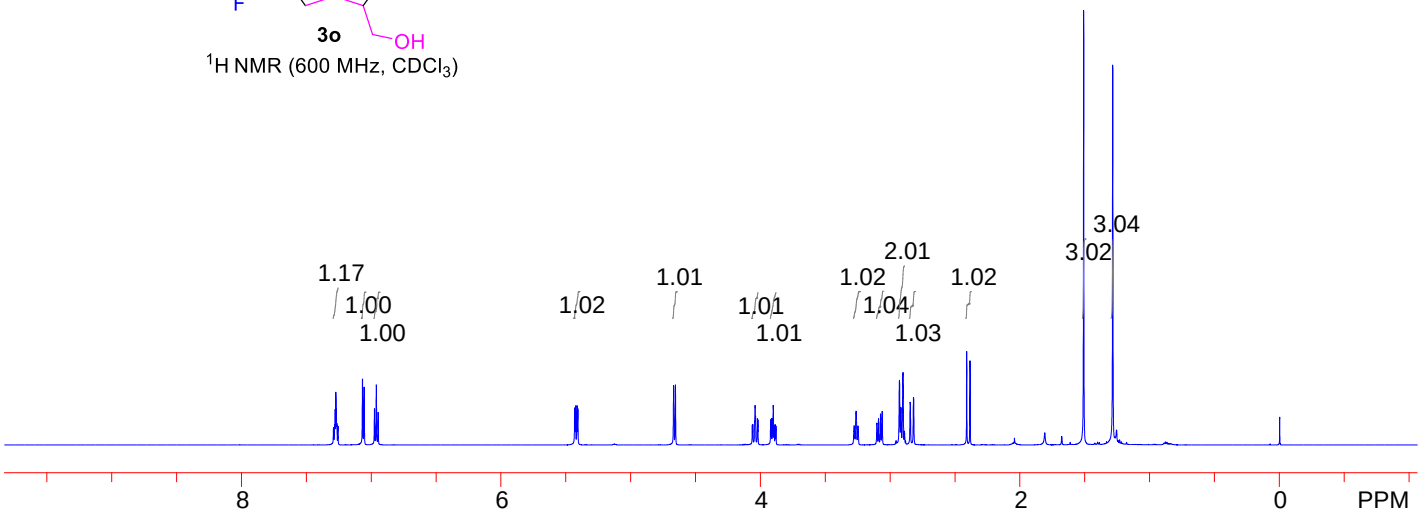
^{19}F NMR (565 MHz, $CDCl_3$)

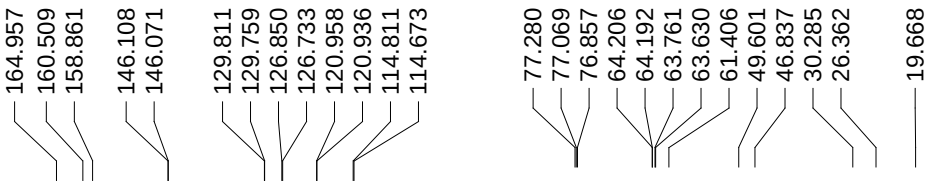


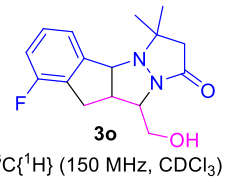


3o

^{1}H NMR (600 MHz, $CDCl_3$)

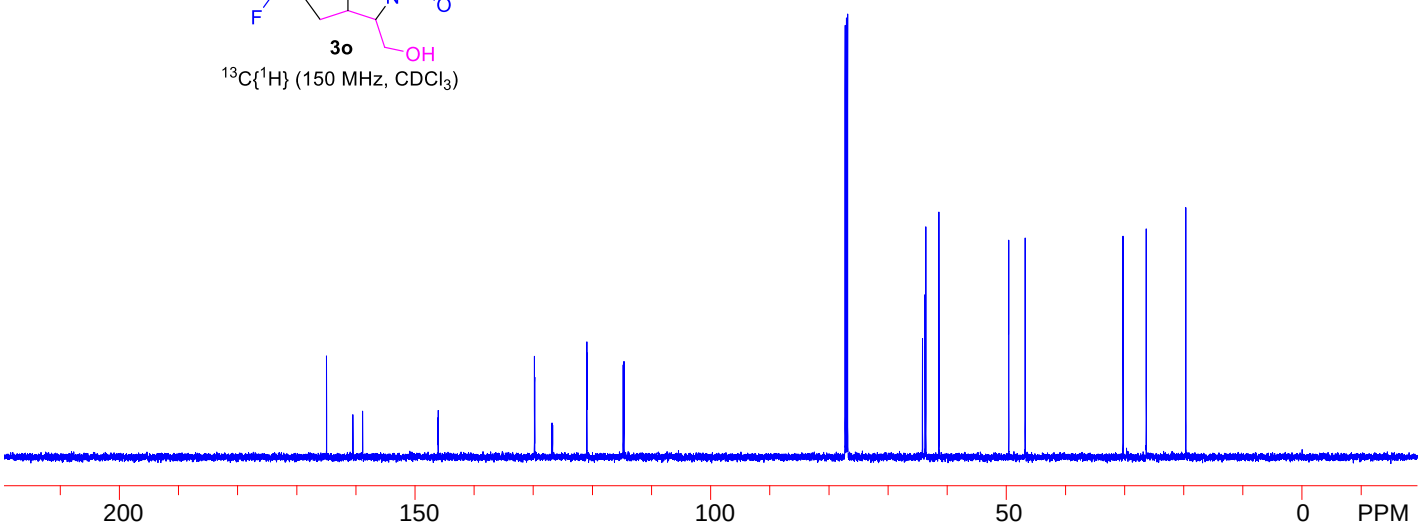


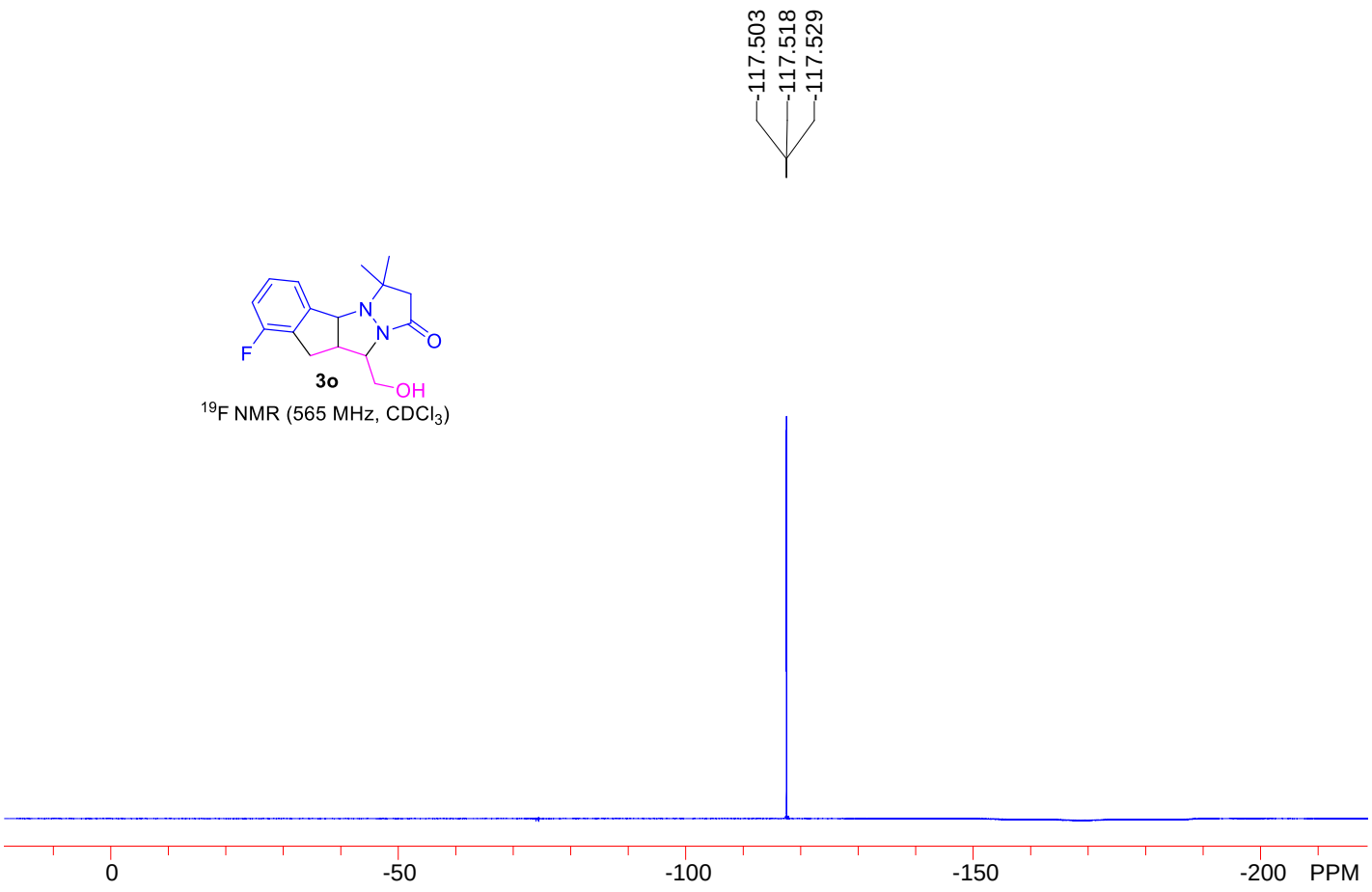




3o

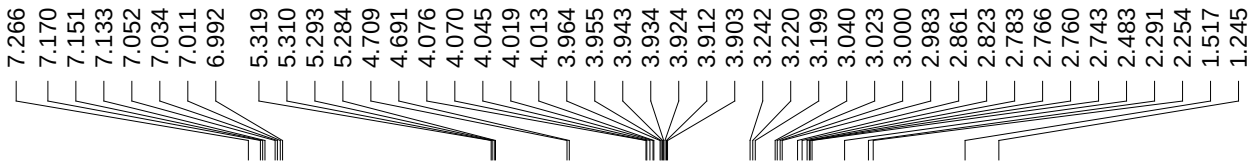
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

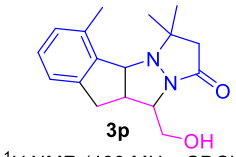




3o

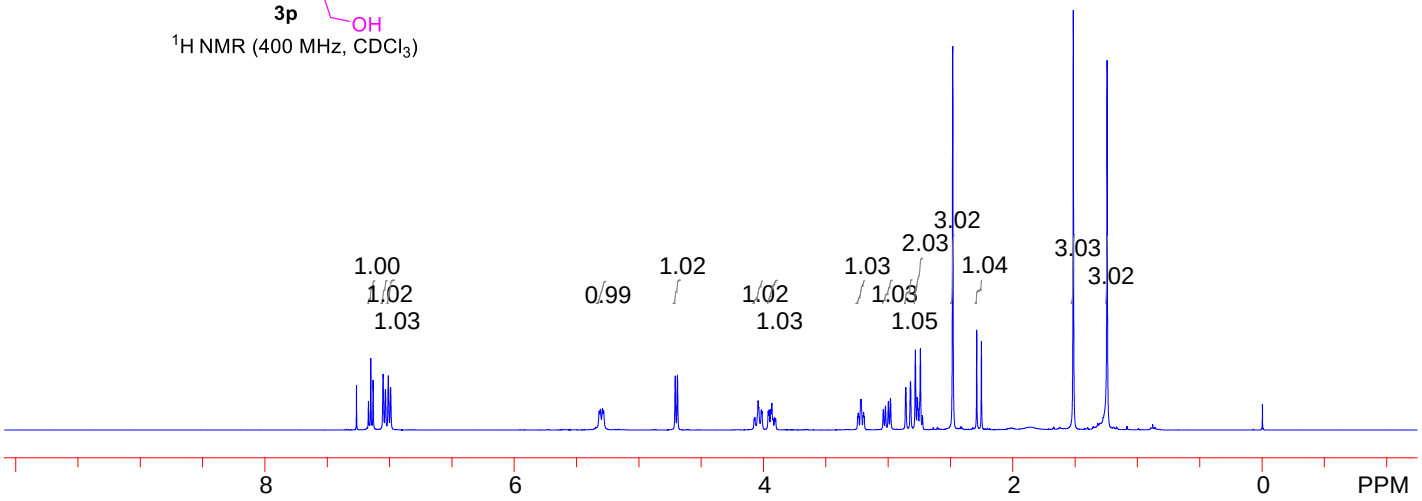
^{19}F NMR (565 MHz, $CDCl_3$)

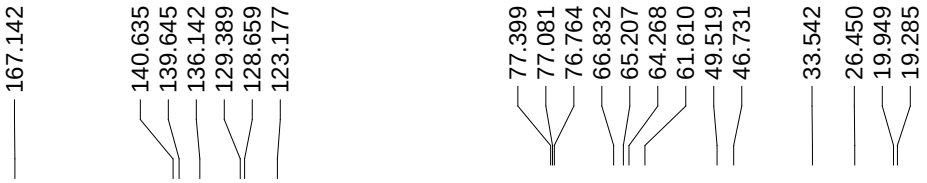


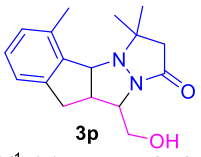


3p

^{1}H NMR (400 MHz, $CDCl_3$)

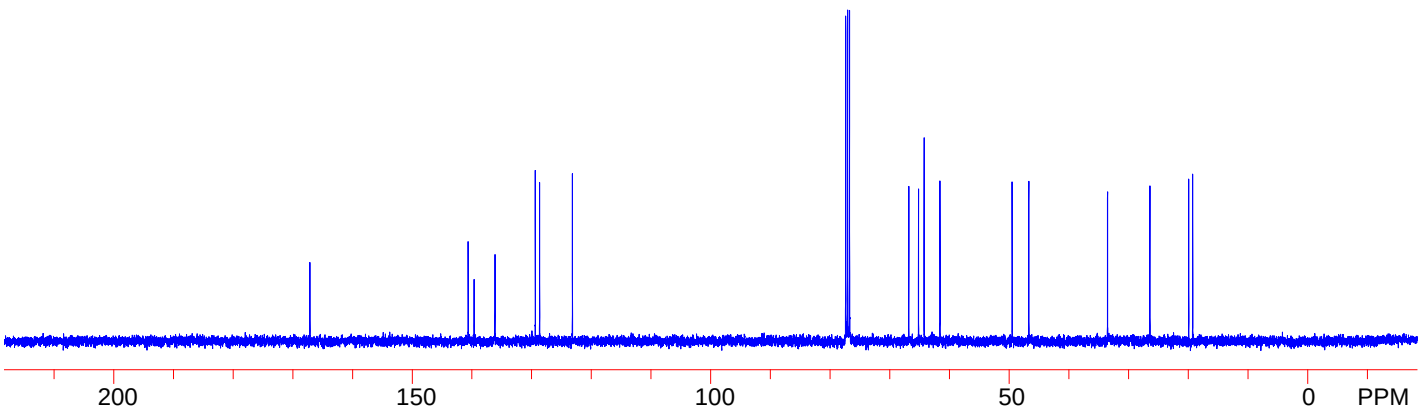


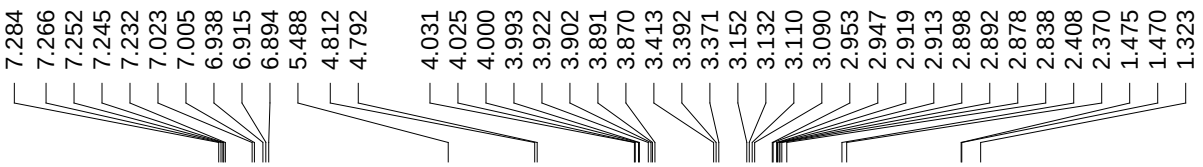


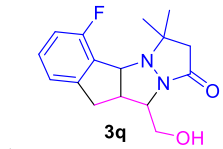


3p

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

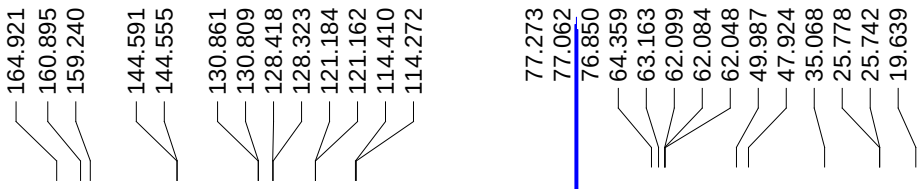


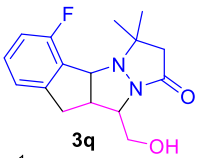




3q

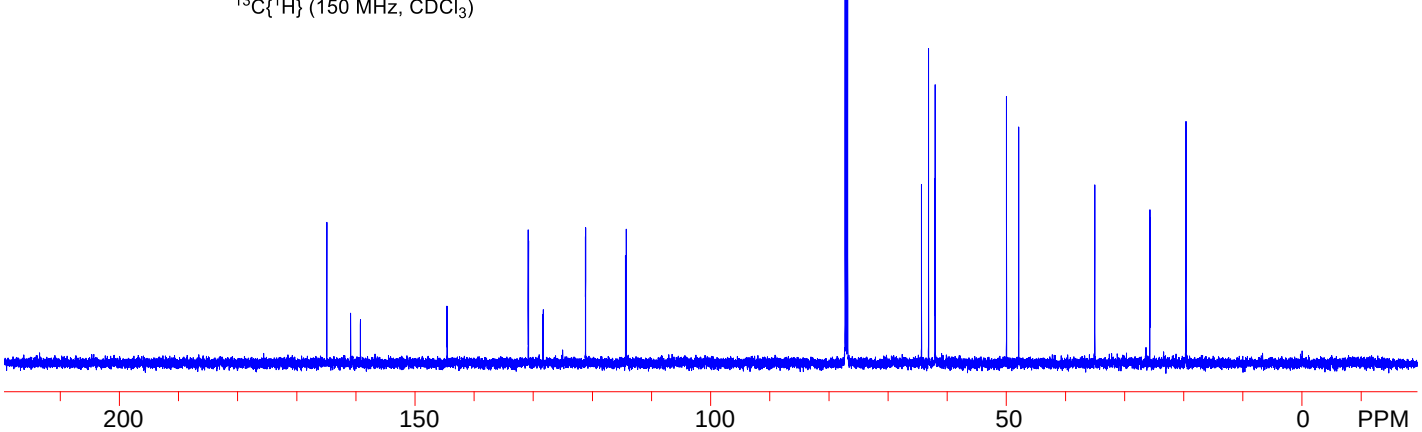
^{1}H NMR (400 MHz, $CDCl_3$)

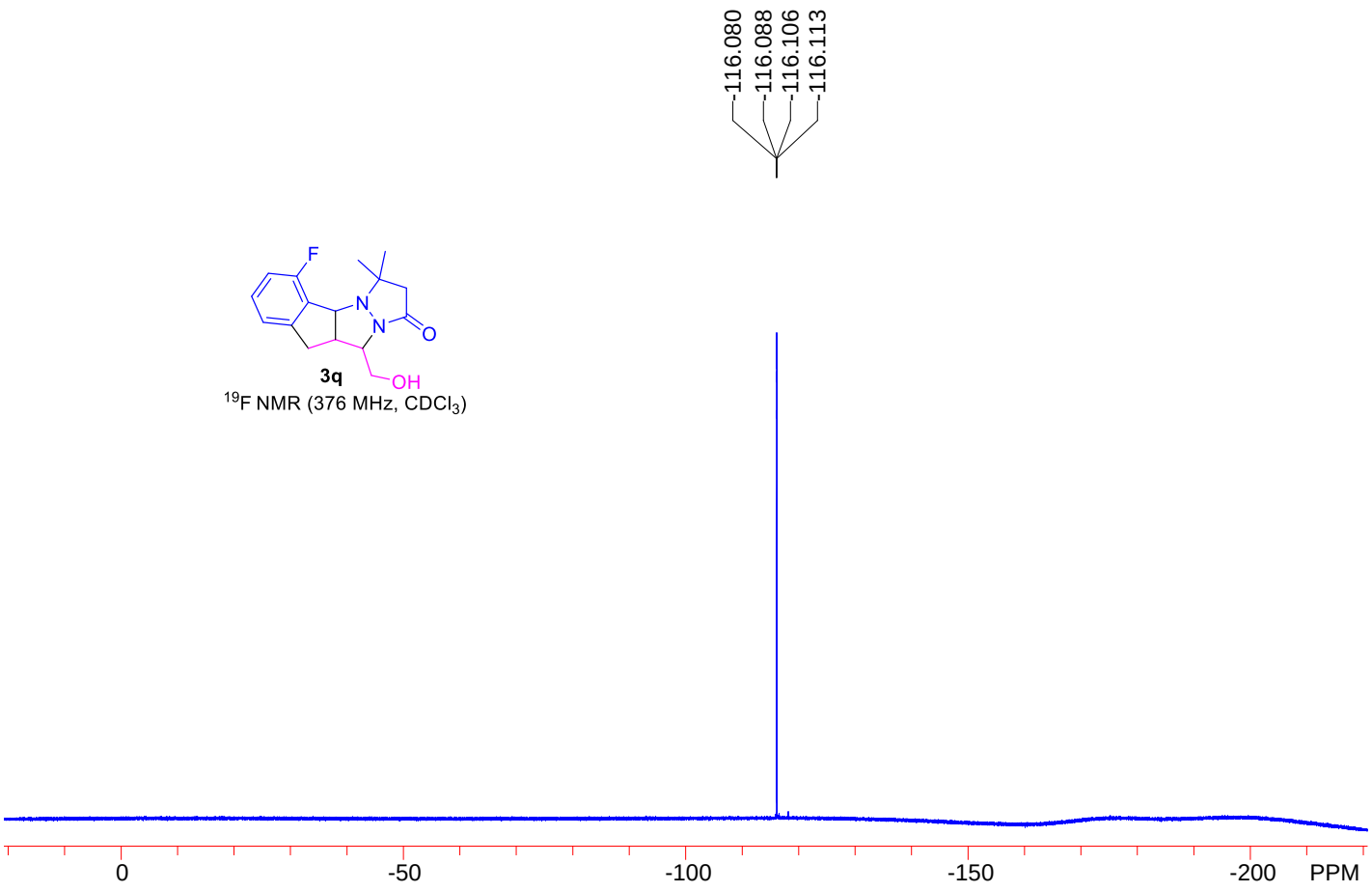




3q

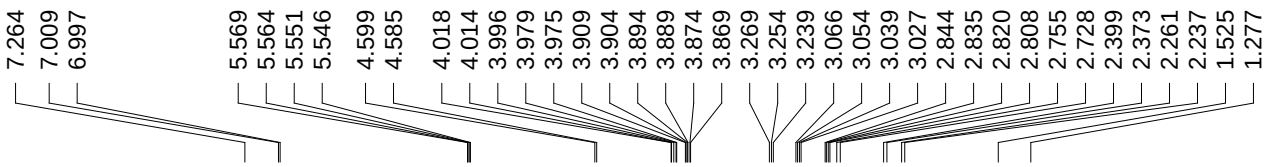
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

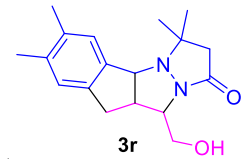




3q

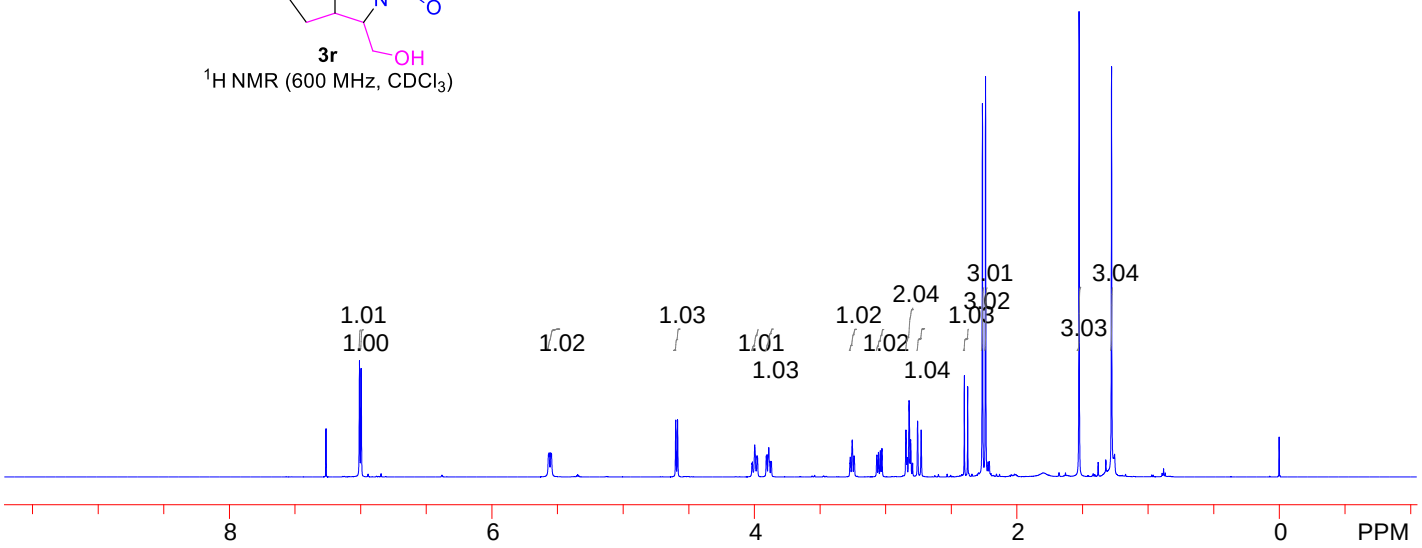
^{19}F NMR (376 MHz, $CDCl_3$)

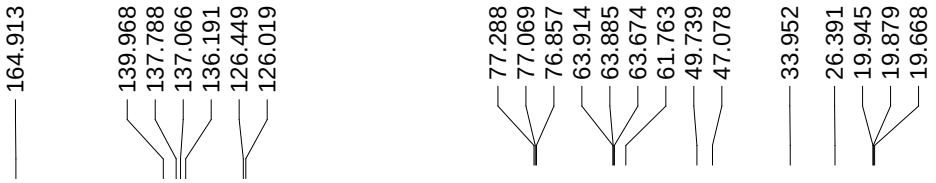


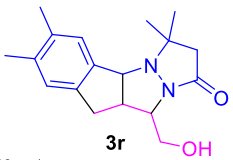


3r

^{1}H NMR (600 MHz, $CDCl_3$)

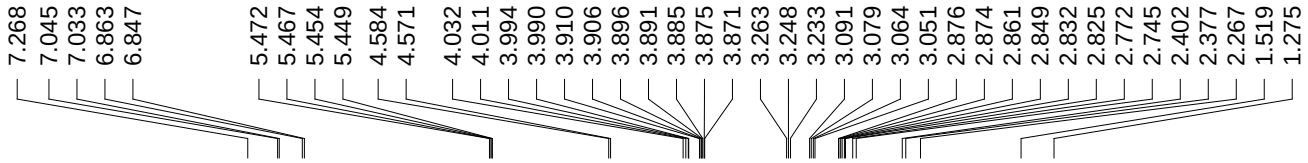


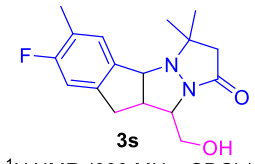




3r

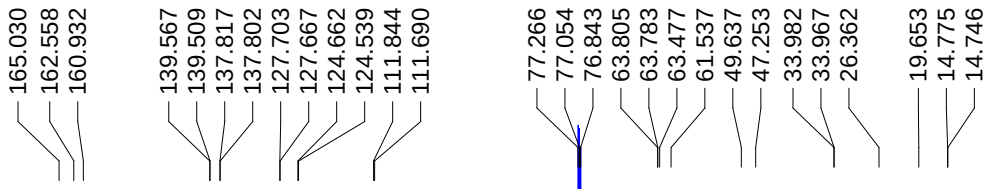
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

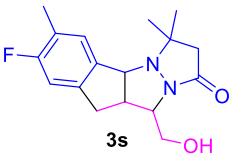




3s

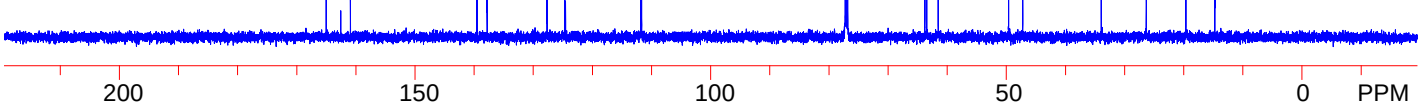
^{1}H NMR (600 MHz, $CDCl_3$)

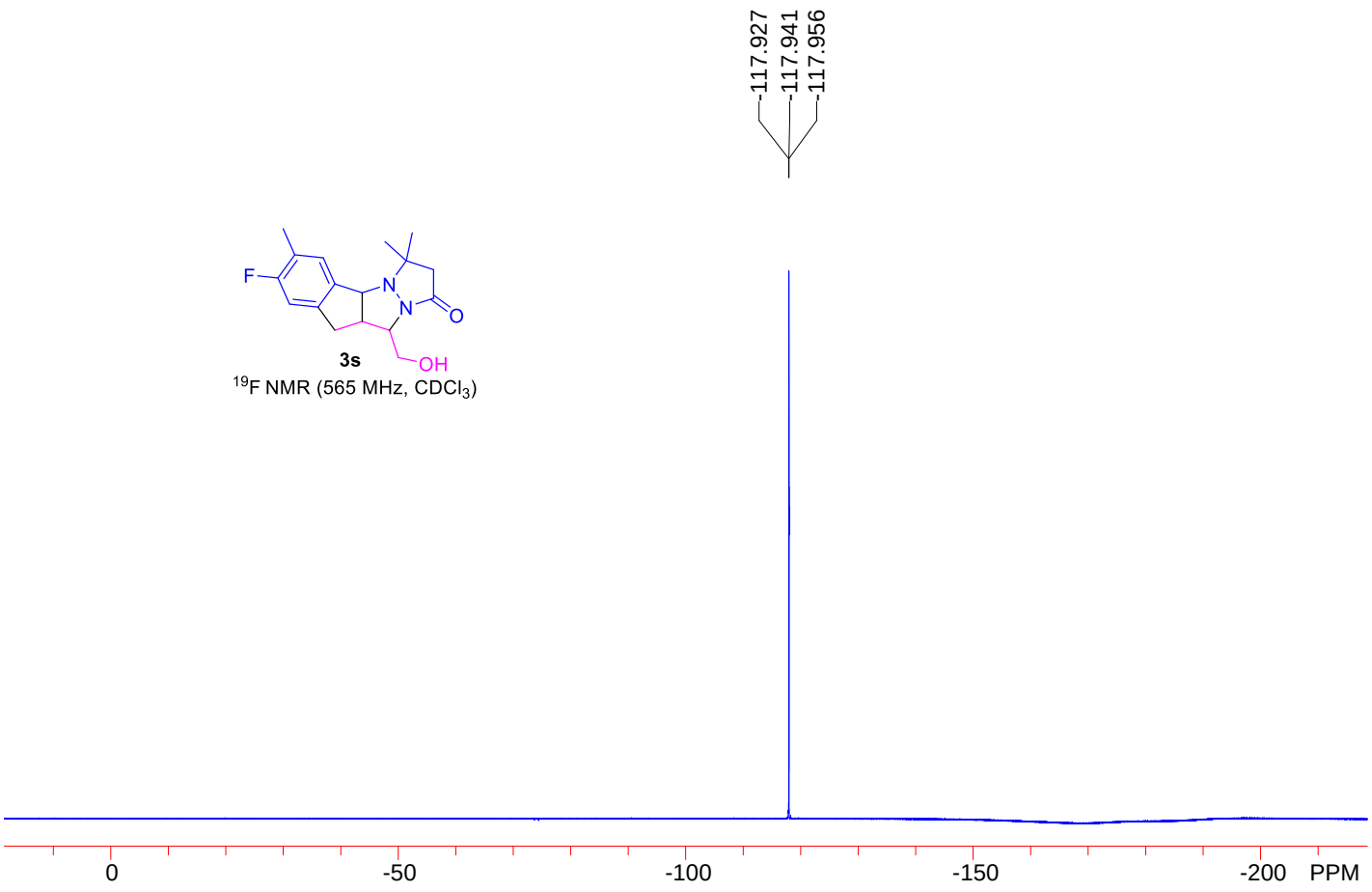




3s

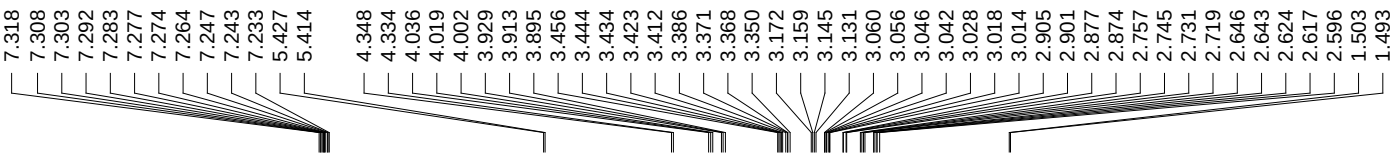
^{13}C{^{1}H} (150 MHz, $CDCl_3$)

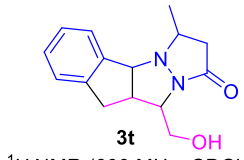




3s

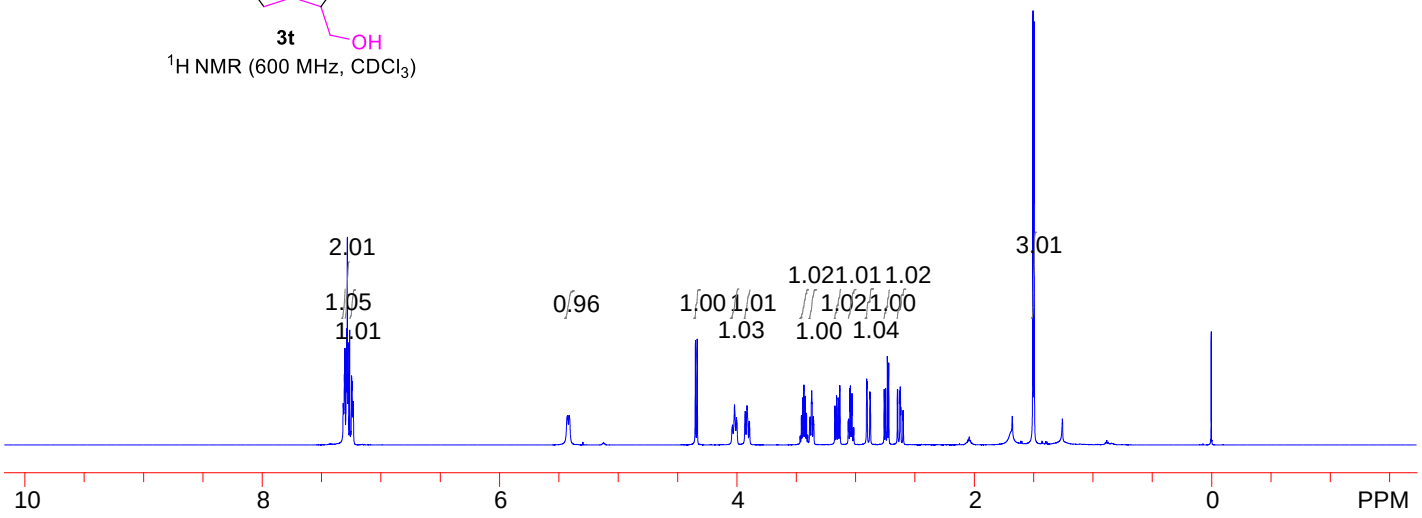
^{19}F NMR (565 MHz, $CDCl_3$)

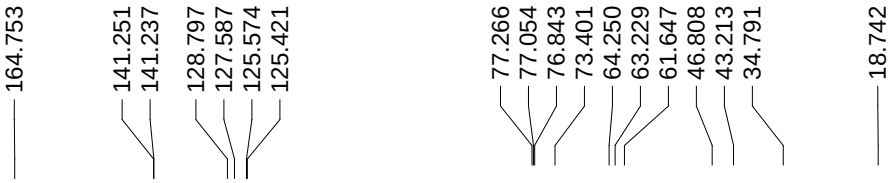


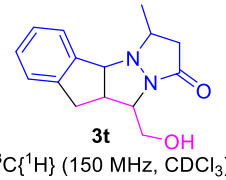


3t

^{1}H NMR (600 MHz, $CDCl_3$)

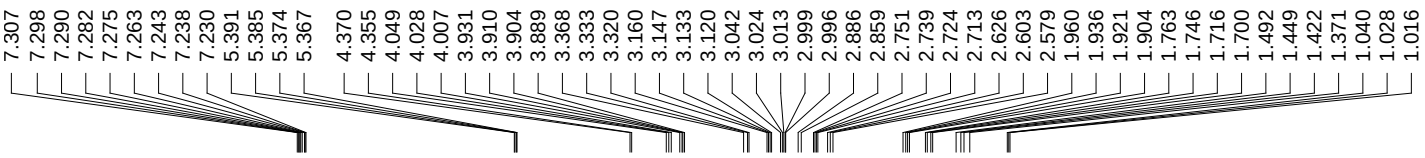


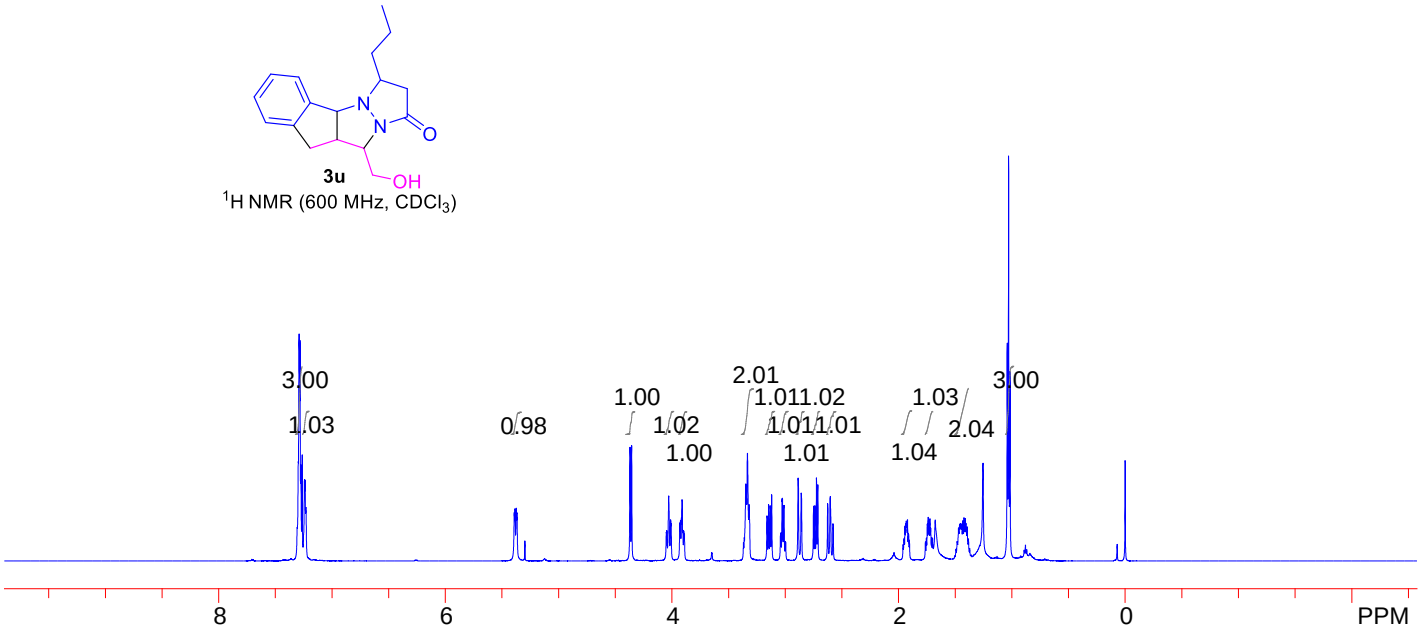


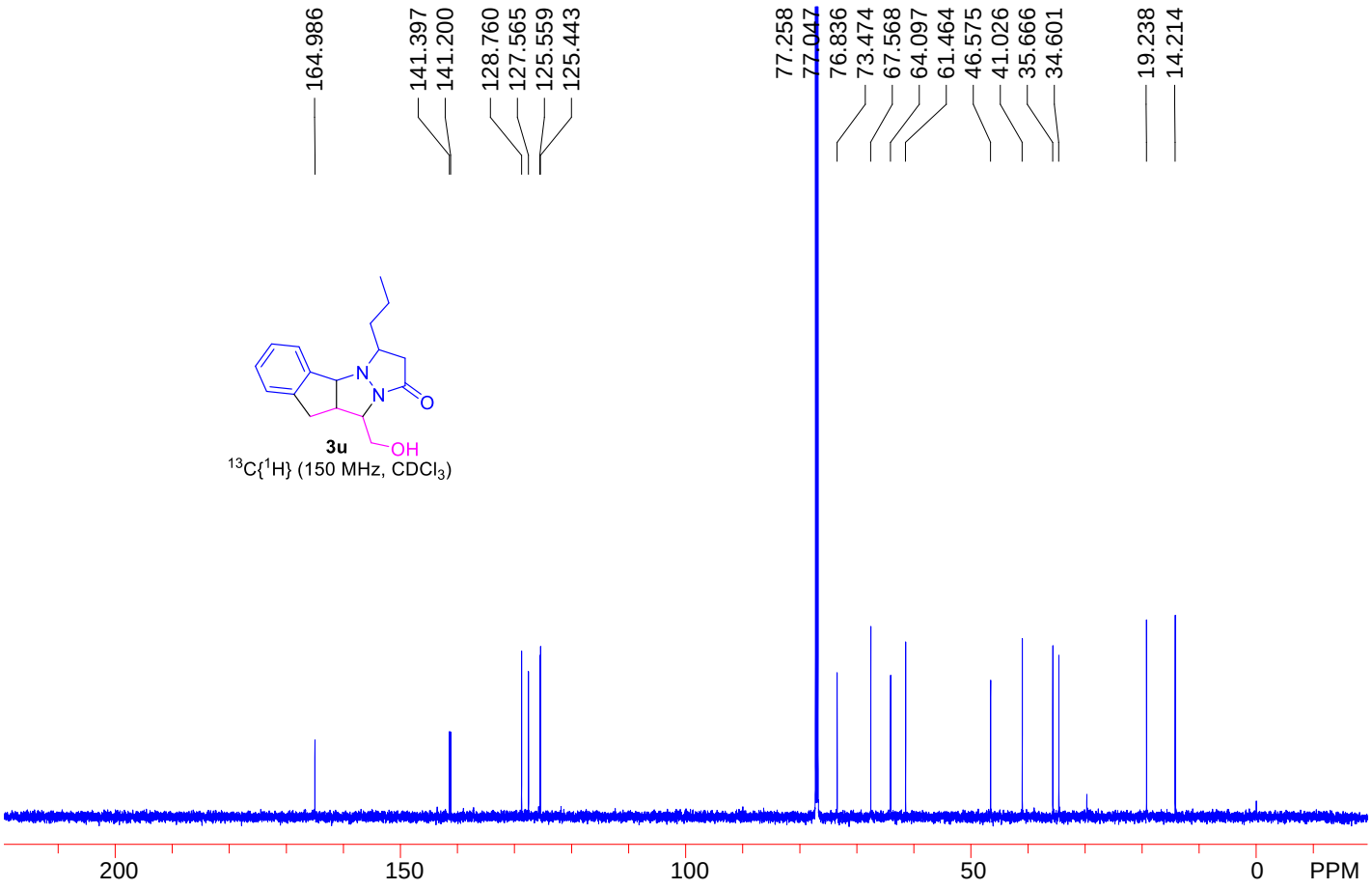


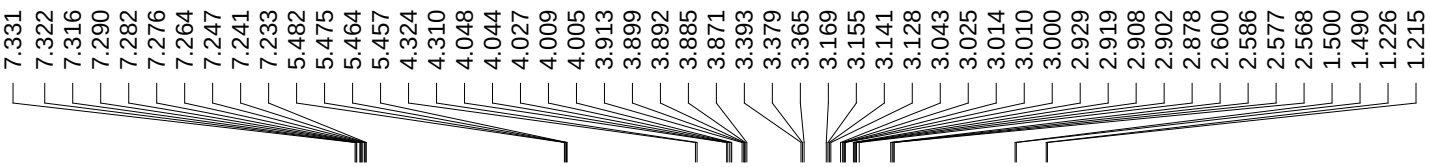
3t

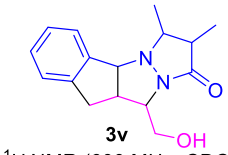
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)


7.307
7.298
7.290
7.282
7.275
7.263
7.243
7.238
7.230
5.391
5.385
5.374
5.367
4.370
4.355
4.049
4.028
4.007
3.931
3.910
3.904
3.889
3.368
3.333
3.320
3.160
3.147
3.133
3.120
3.042
3.024
3.013
2.999
2.996
2.886
2.859
2.751
2.739
2.724
2.713
2.626
2.603
2.579
1.960
1.936
1.921
1.904
1.763
1.746
1.716
1.700
1.492
1.449
1.422
1.371
1.040
1.028
1.016


3u
^{1}H NMR (600 MHz, CDCl$_3$)
3.00
1.03
0.98
1.00
1.02
1.00
2.01
1.01
1.02
1.01
1.01
1.03
1.04
2.04
3.00
8
6
4
2
0
PPM

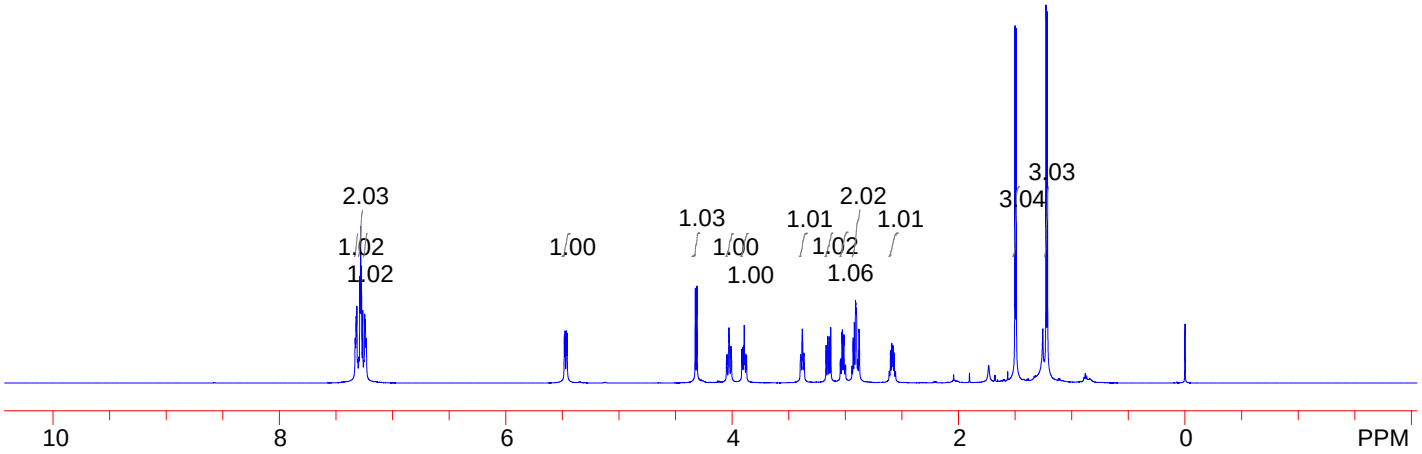

164.986
141.397
141.200
128.760
127.565
125.559
125.443
77.258
77.047
76.836
73.474
67.568
64.097
61.464
46.575
41.026
35.666
34.601
19.238
14.214
3u
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM

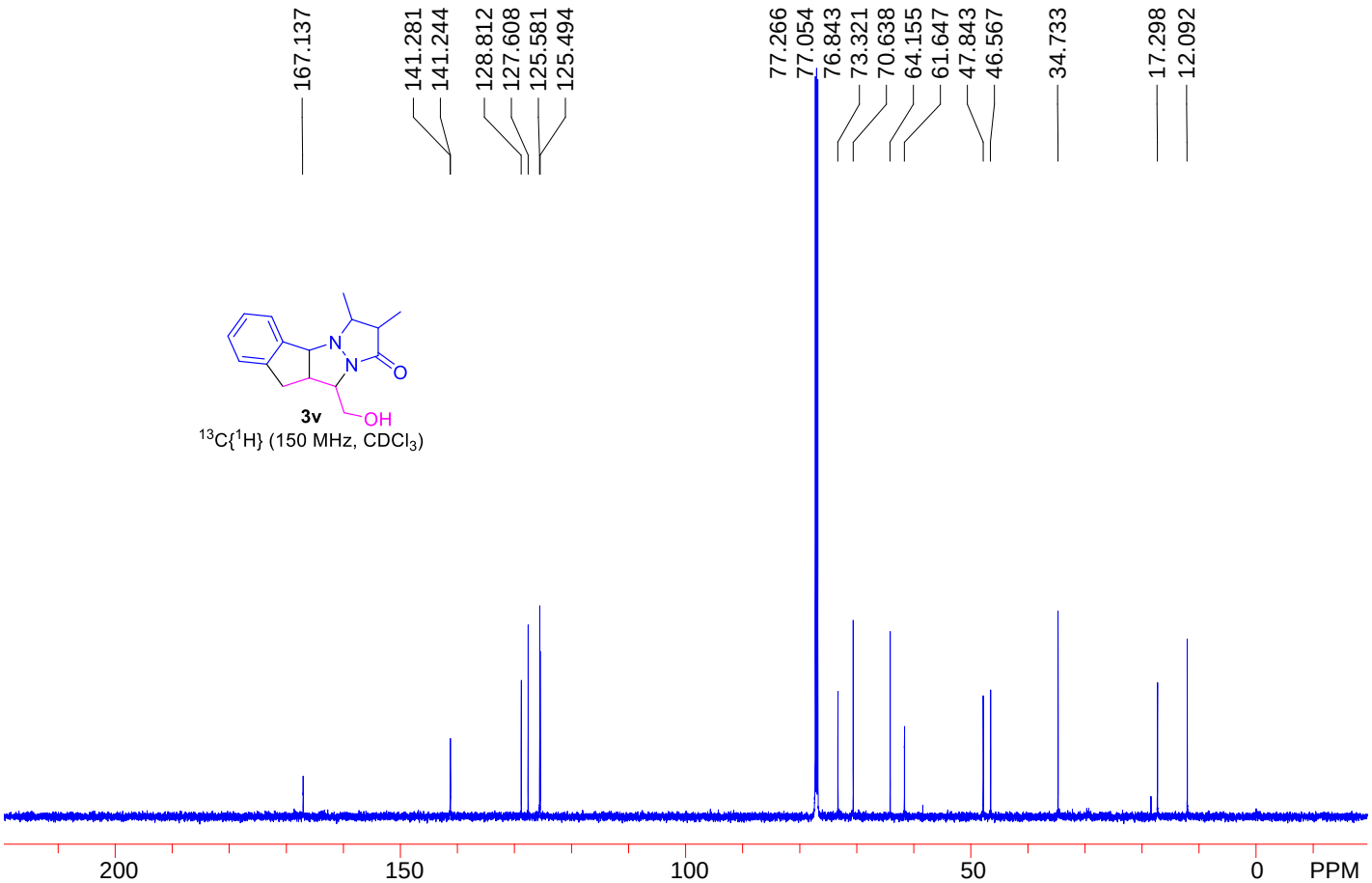




3v

^{1}H NMR (600 MHz, $CDCl_3$)

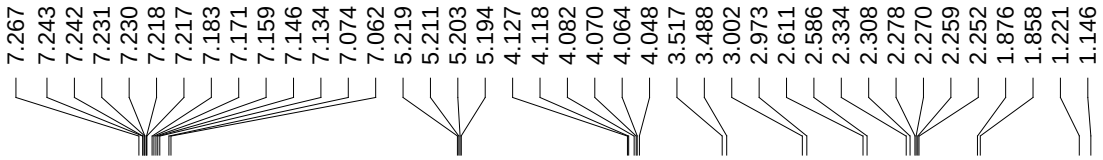


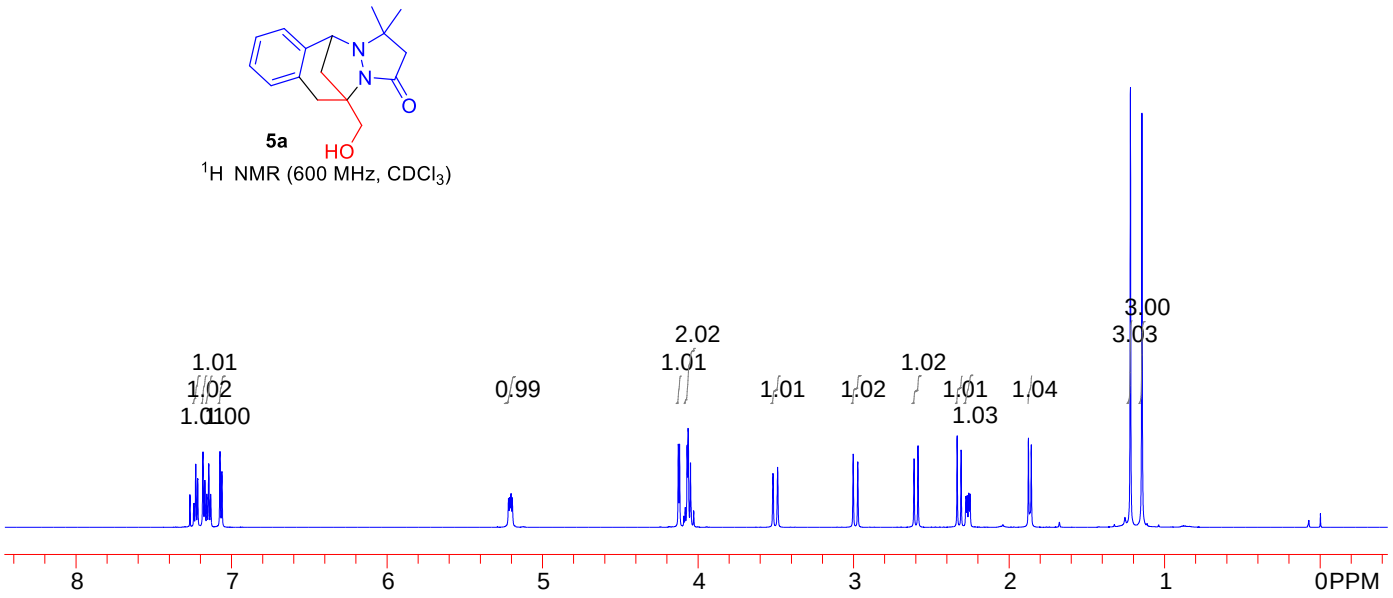


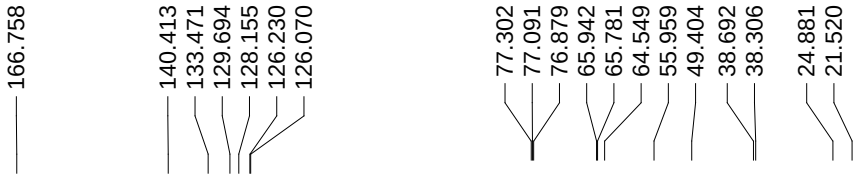
3v

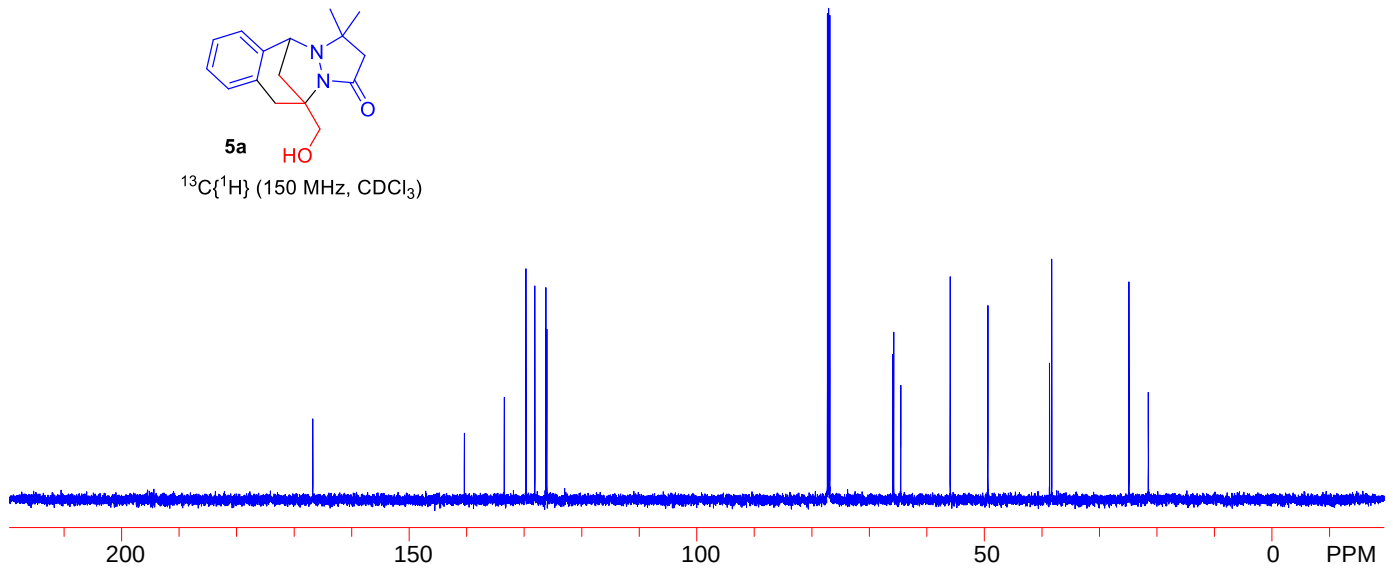
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

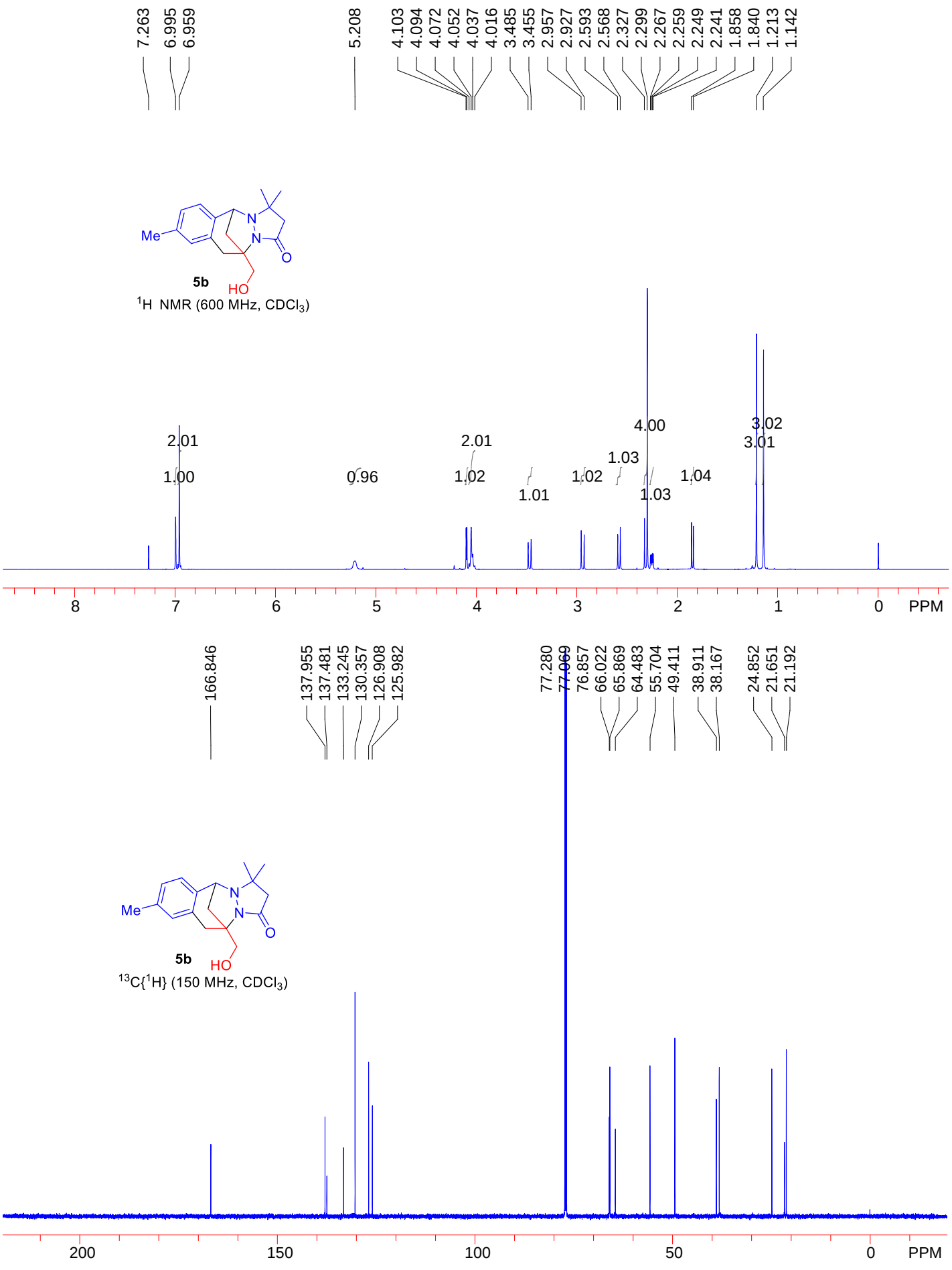
V. Copies of NMR spectra of 5a-5u

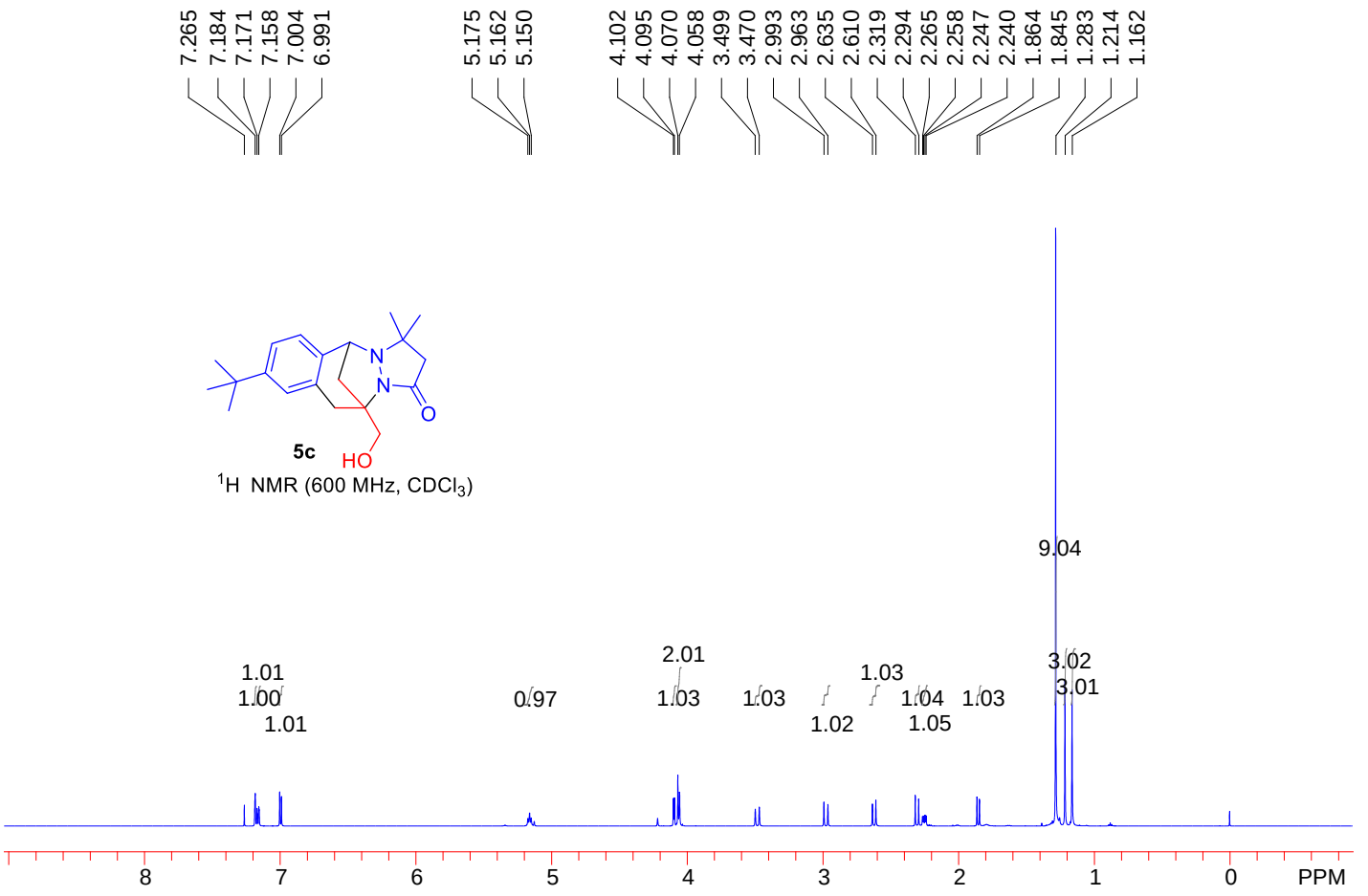


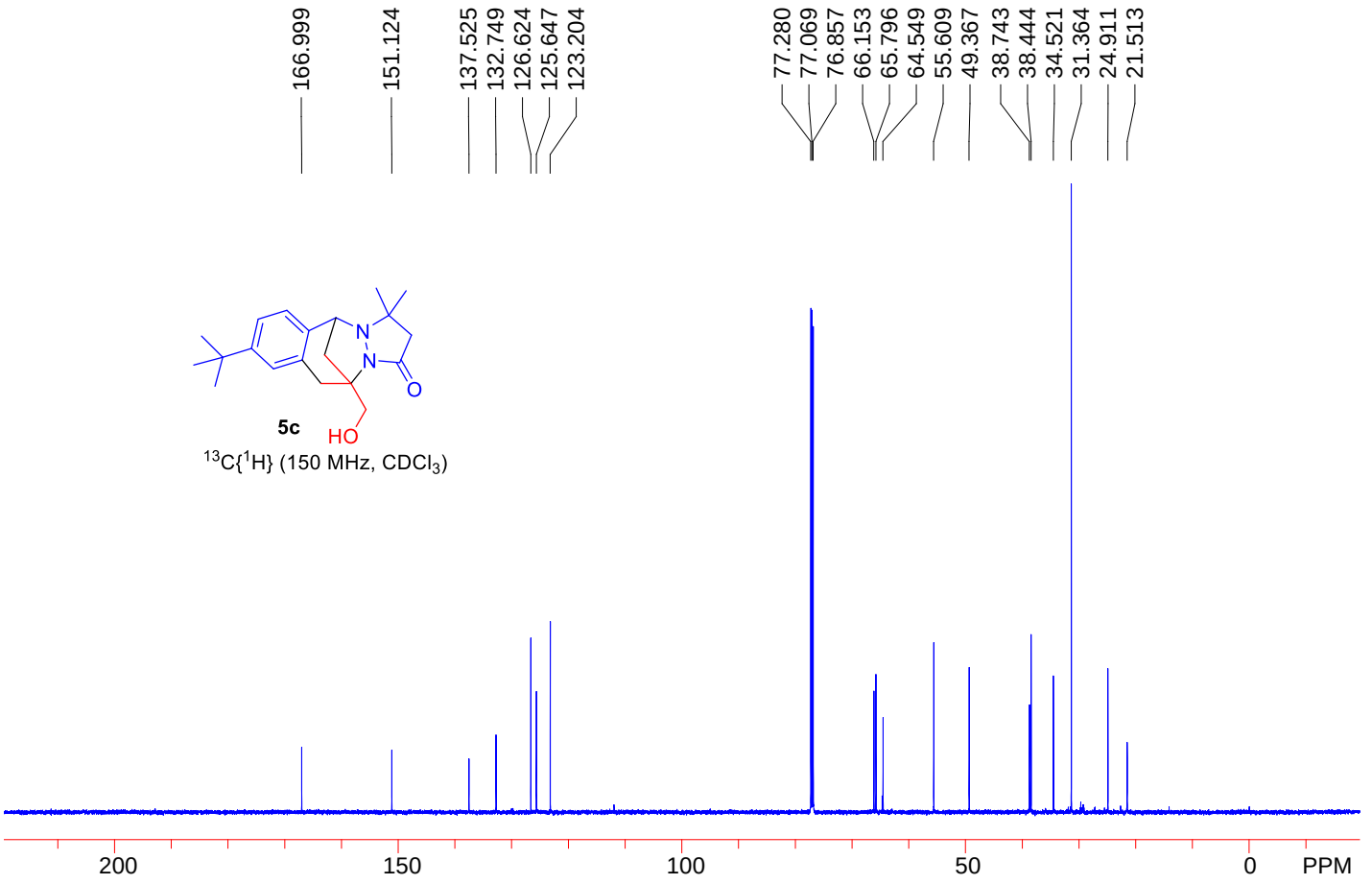


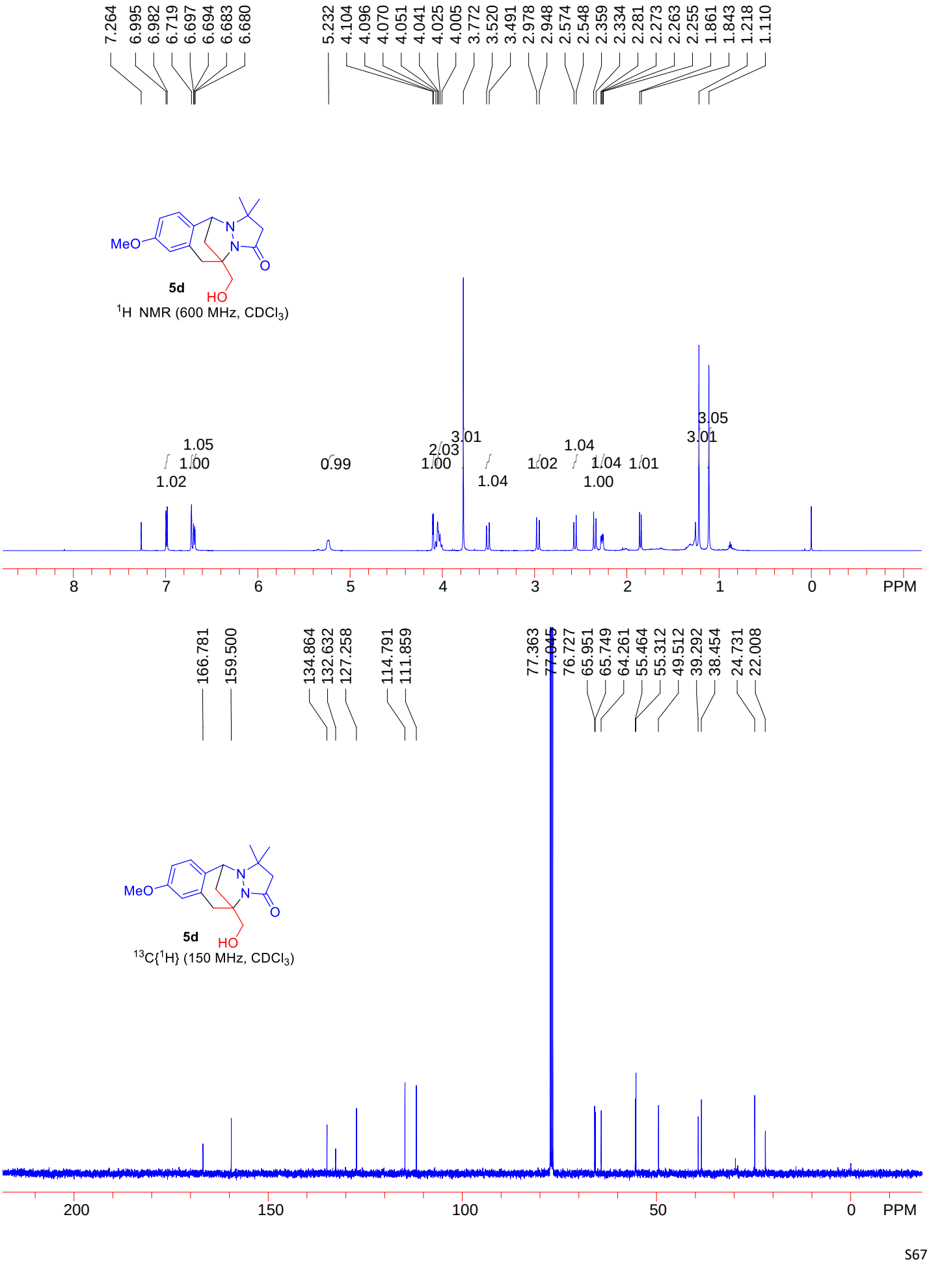


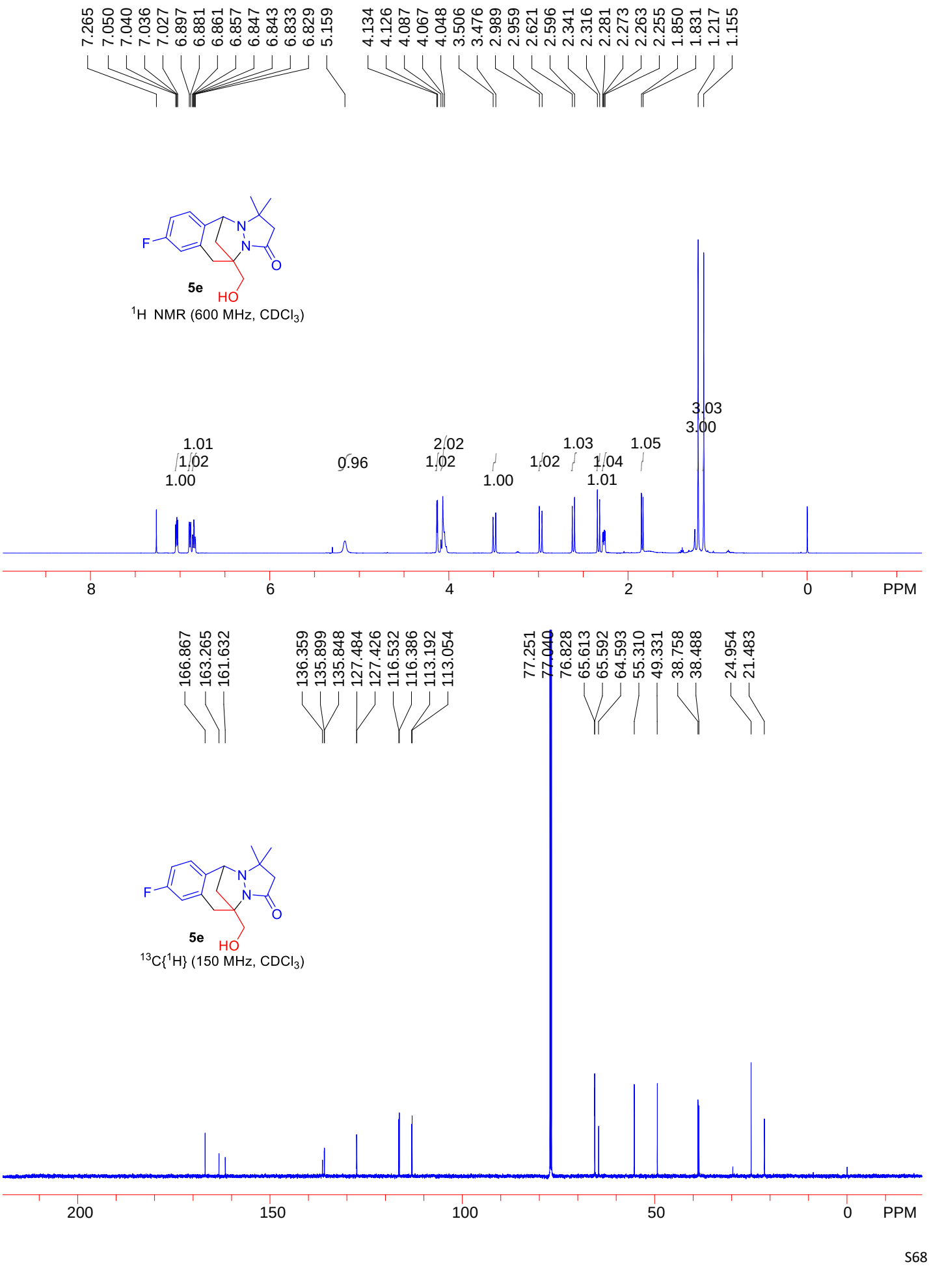


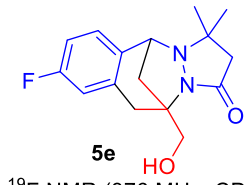

7.263
6.995
6.959
5.208
4.103
4.094
4.072
4.052
4.037
4.016
3.485
3.455
2.957
2.927
2.593
2.568
2.327
2.299
2.267
2.259
2.249
2.241
1.858
1.840
1.213
1.142
Me
N
N
O
HO
5b
1H NMR (600 MHz, CDCl3)
2.01
1.00
0.96
2.01
1.02
1.01
1.02
1.03
4.00
1.03
1.04
3.02
3.01
8
7
6
5
4
3
2
1
0
PPM
166.846
137.955
137.481
133.245
130.357
126.908
125.982
77.280
77.069
76.857
66.022
65.869
64.483
55.704
49.411
38.911
38.167
24.852
21.651
21.192
Me
N
N
O
HO
5b
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM


7.265
7.184
7.171
7.158
7.004
6.991
5.175
5.162
5.150
4.102
4.095
4.070
4.058
3.499
3.470
2.993
2.963
2.635
2.610
2.319
2.294
2.265
2.258
2.247
2.240
1.864
1.845
1.283
1.214
1.162
5c
HO
^{1}H NMR (600 MHz, CDCl$_3$)
9.04
1.01
1.00
1.01
0.97
2.01
1.03
1.03
1.02
1.03
1.04
1.05
1.03
3.02
3.01
8
7
6
5
4
3
2
1
0
PPM


166.999
151.124
137.525
132.749
126.624
125.647
123.204
77.280
77.069
76.857
66.153
65.796
64.549
55.609
49.367
38.743
38.444
34.521
31.364
24.911
21.513
5c
HO
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM

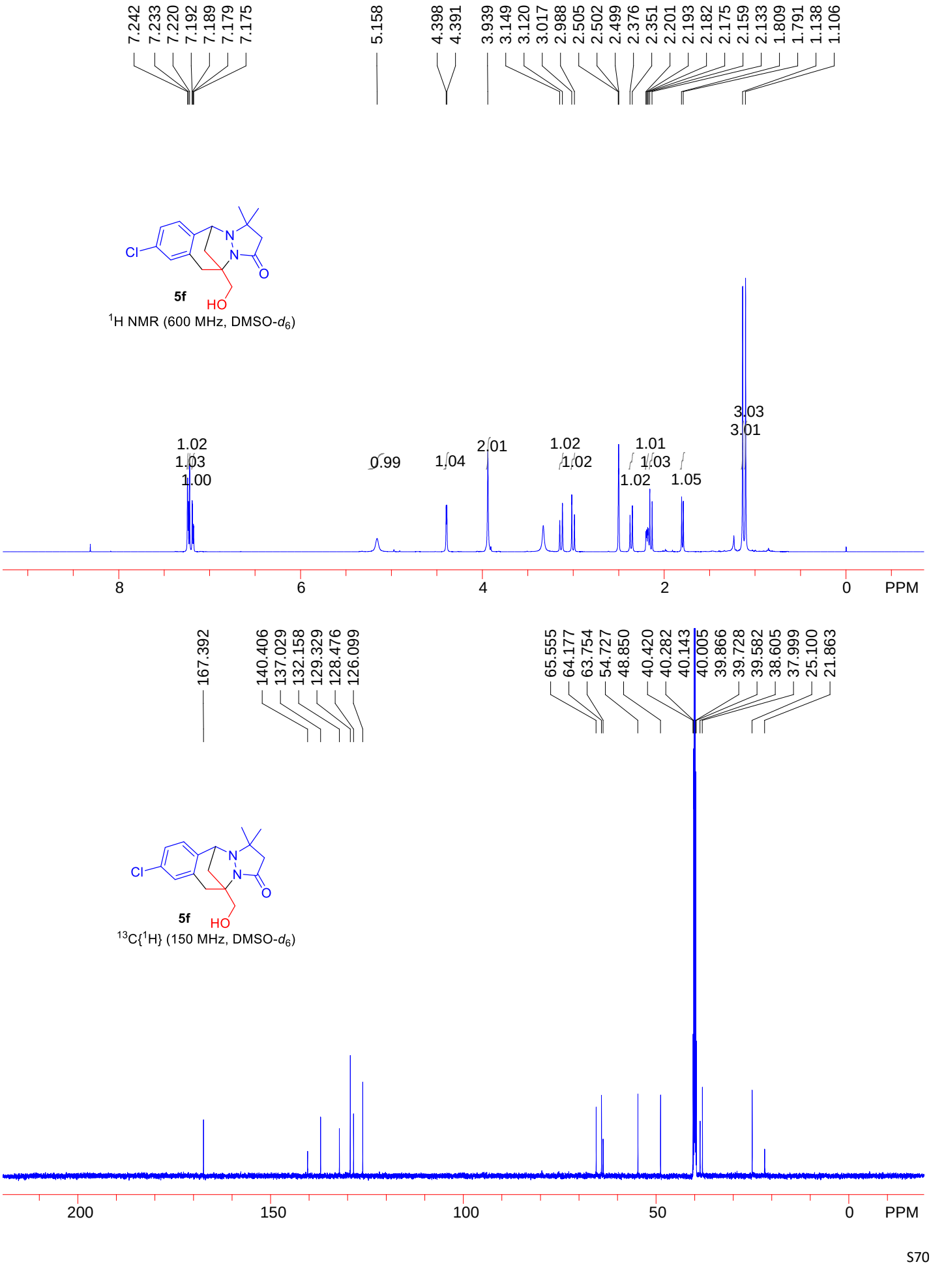

7.264
6.995
6.982
6.719
6.697
6.694
6.683
6.680
5.232
4.104
4.096
4.070
4.051
4.041
4.025
4.005
3.772
3.520
3.491
2.978
2.948
2.574
2.548
2.359
2.334
2.281
2.273
2.263
2.255
1.861
1.843
1.218
1.110
MeO
N
N
O
HO
5d
1H NMR (600 MHz, CDCl3)
1.05
1.00
1.02
0.99
2.03
1.00
3.01
1.04
1.02
1.04
1.00
1.04
1.01
3.05
3.01
8
7
6
5
4
3
2
1
0
PPM
166.781
159.500
134.864
132.632
127.258
114.791
111.859
77.363
77.045
76.727
65.951
65.749
64.261
55.464
55.312
49.512
39.292
38.454
24.731
22.008
MeO
N
N
O
HO
5d
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM


7.265
7.050
7.040
7.036
7.027
6.897
6.881
6.861
6.857
6.847
6.843
6.833
6.829
5.159
4.134
4.126
4.087
4.067
4.048
3.506
3.476
2.989
2.959
2.621
2.596
2.341
2.316
2.281
2.273
2.263
2.255
1.850
1.831
1.217
1.155
F
N
N
O
HO
5e
1H NMR (600 MHz, CDCl3)
1.01
1.02
1.00
0.96
2.02
1.02
1.00
1.02
1.03
1.04
1.01
1.05
3.03
3.00
8
6
4
2
0
PPM
166.867
163.265
161.632
136.359
135.899
135.848
127.484
127.426
116.532
116.386
113.192
113.054
77.251
77.040
76.828
65.613
65.592
64.593
55.310
49.331
38.758
38.488
24.954
21.483
F
N
N
O
HO
5e
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM



5e

^{19}F NMR (376 MHz, $CDCl_3$)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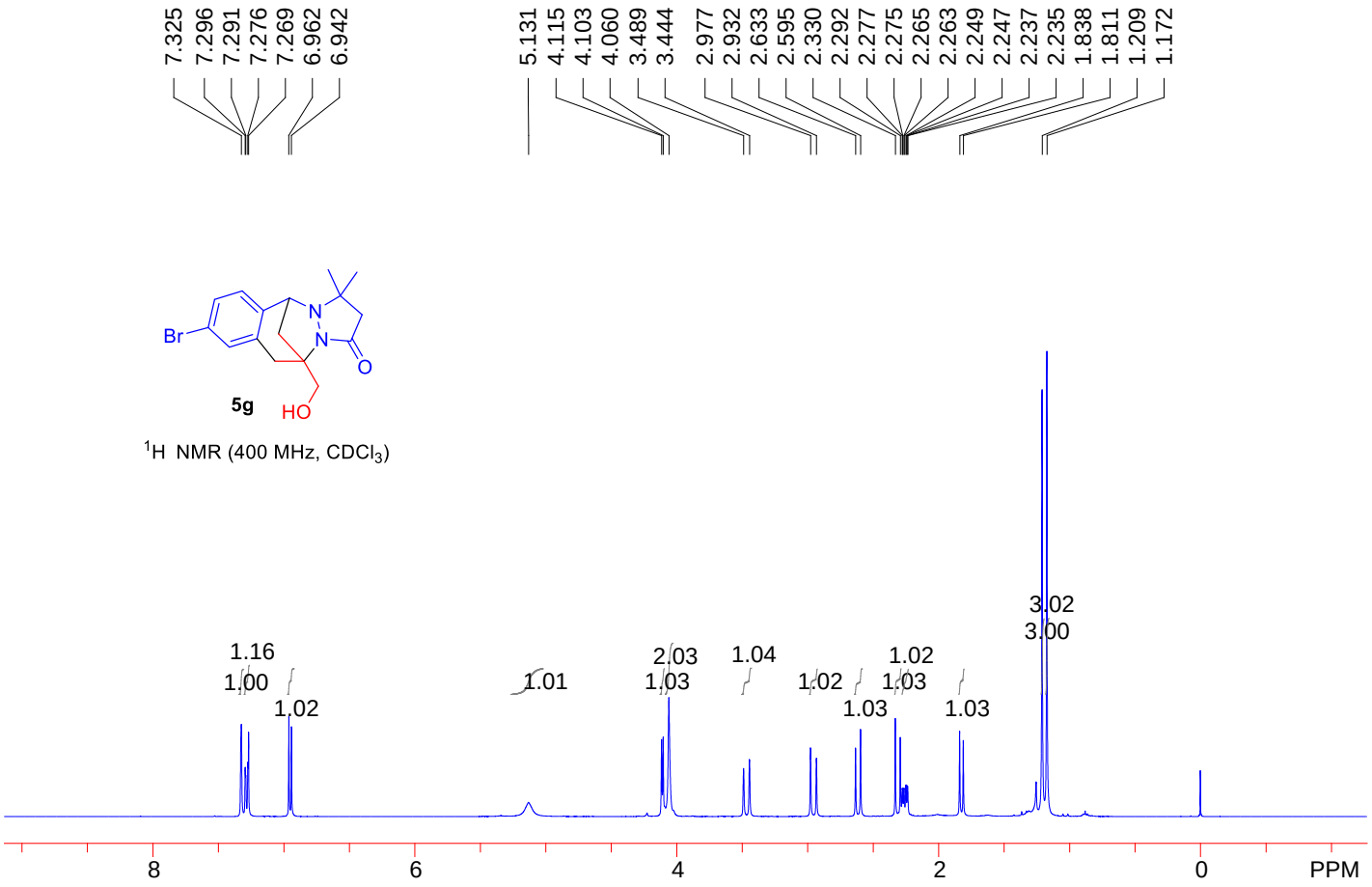
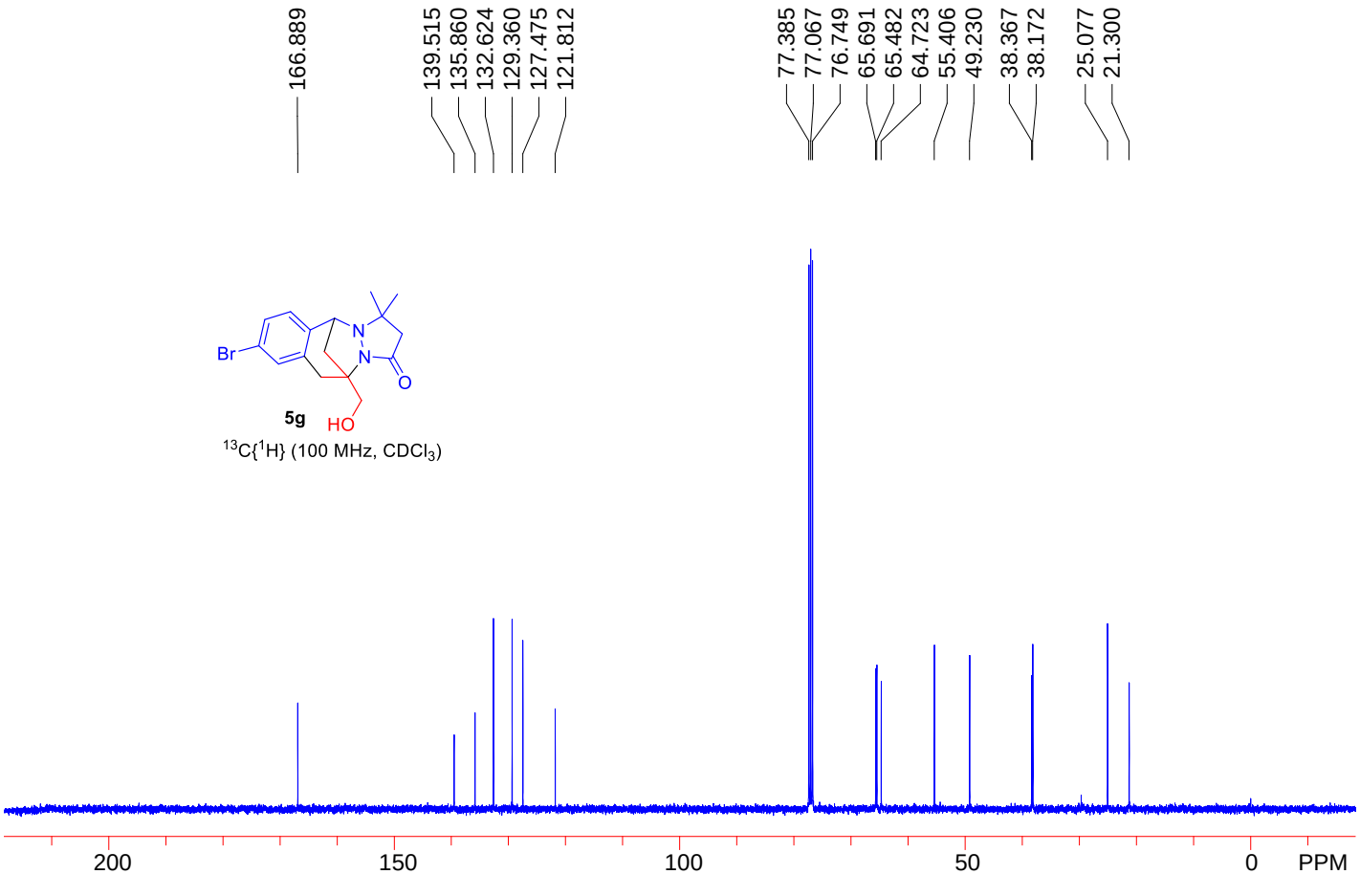
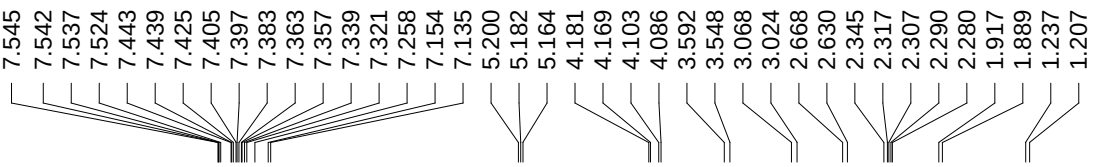
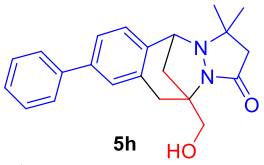
7.233
7.220
7.192
7.189
7.179
7.175
5.158
4.398
4.391
3.939
3.149
3.120
3.017
2.988
2.505
2.502
2.499
2.376
2.351
2.201
2.193
2.182
2.175
2.159
2.133
1.809
1.791
1.138
1.106
Cl
N
N
O
HO
5f
1H NMR (600 MHz, DMSO-d6)
1.02
1.03
1.00
0.99
1.04
2.01
1.02
1.02
1.02
1.01
1.03
1.02
1.05
3.03
3.01
8
6
4
2
0
PPM
167.392
140.406
137.029
132.158
129.329
128.476
126.099
65.555
64.177
63.754
54.727
48.850
40.420
40.282
40.143
40.005
39.866
39.728
39.582
38.605
37.999
25.100
21.863
Cl
N
N
O
HO
5f
13C{1H} (150 MHz, DMSO-d6)
200
150
100
50
0
PPM


7.325
7.296
7.291
7.276
7.269
6.962
6.942
5.131
4.115
4.103
4.060
3.489
3.444
2.977
2.932
2.633
2.595
2.330
2.292
2.277
2.275
2.265
2.263
2.249
2.247
2.237
2.235
1.838
1.811
1.209
1.172
Br
N
N
O
HO
5g
1H NMR (400 MHz, CDCl3)
1.16
1.00
1.02
1.01
2.03
1.03
1.04
1.02
1.02
1.03
1.03
3.02
3.00
8
6
4
2
0
PPM

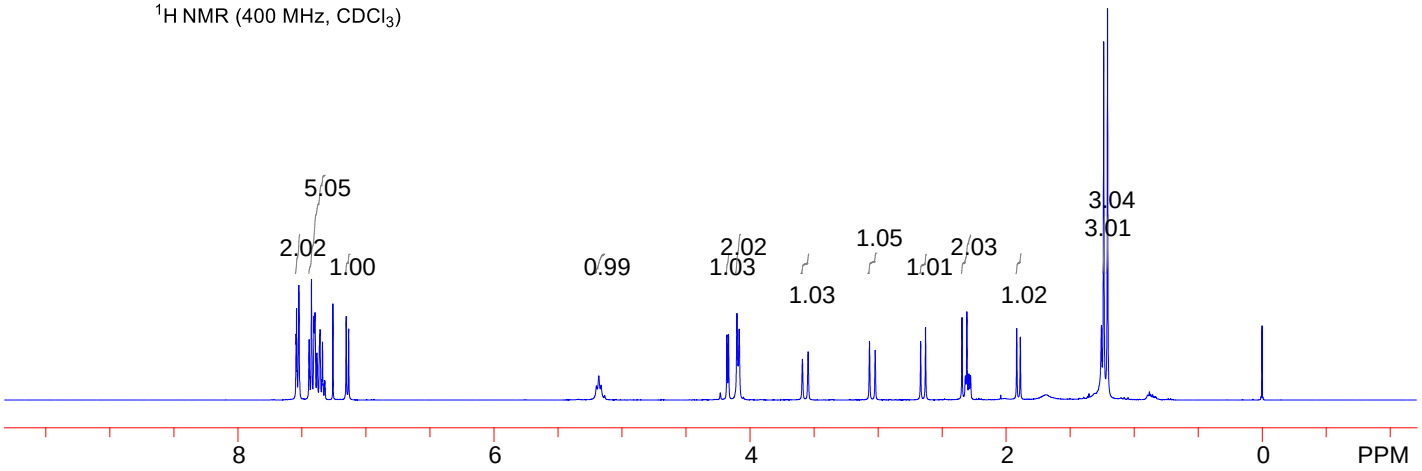

166.889
139.515
135.860
132.624
129.360
127.475
121.812
77.385
77.067
76.749
65.691
65.482
64.723
55.406
49.230
38.367
38.172
25.077
21.300
Br
N
N
O
HO
5g
13C{1H} (100 MHz, CDCl3)
200
150
100
50
0
PPM

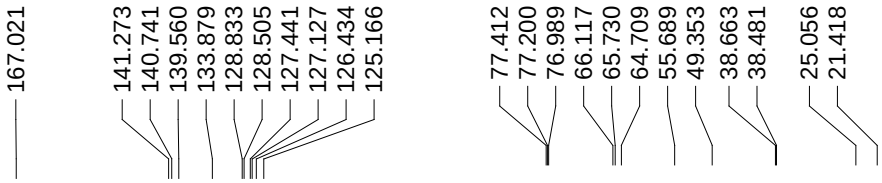


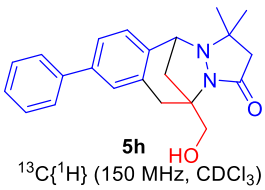


5h

^{1}H NMR (400 MHz, $CDCl_3$)

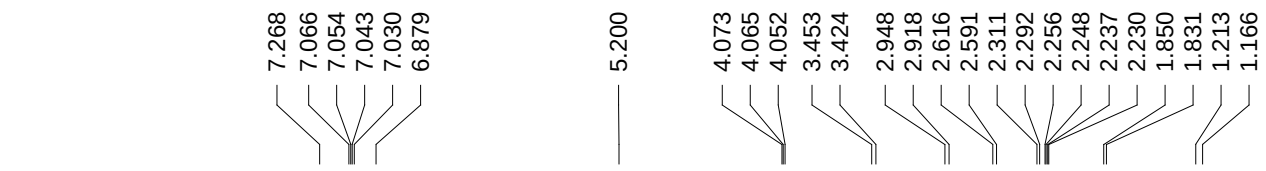


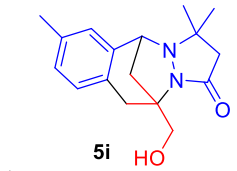




5h

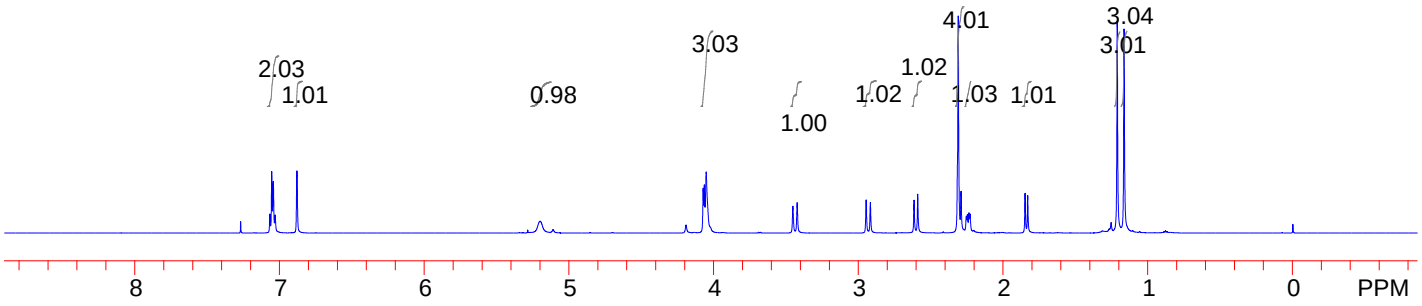
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

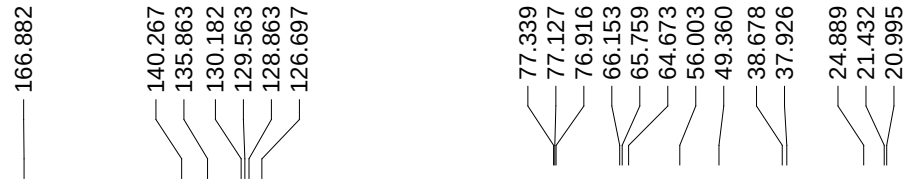


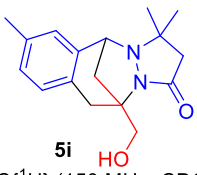


5i

^{1}H NMR (600 MHz, $CDCl_3$)

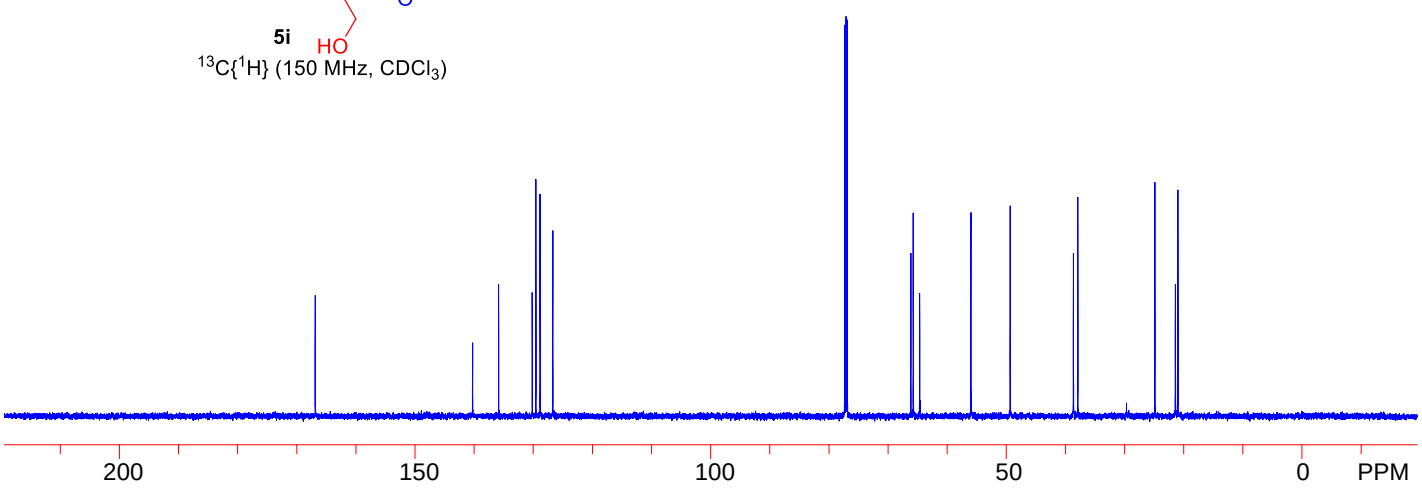


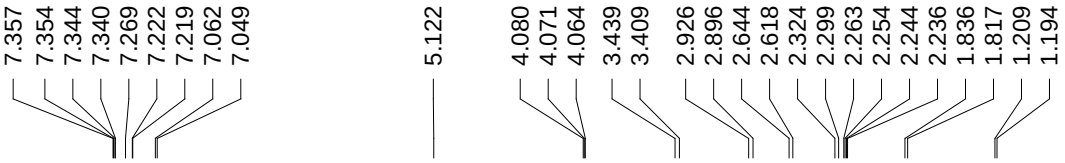


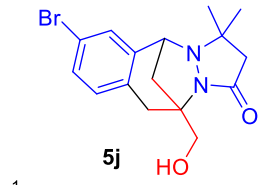


5i

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

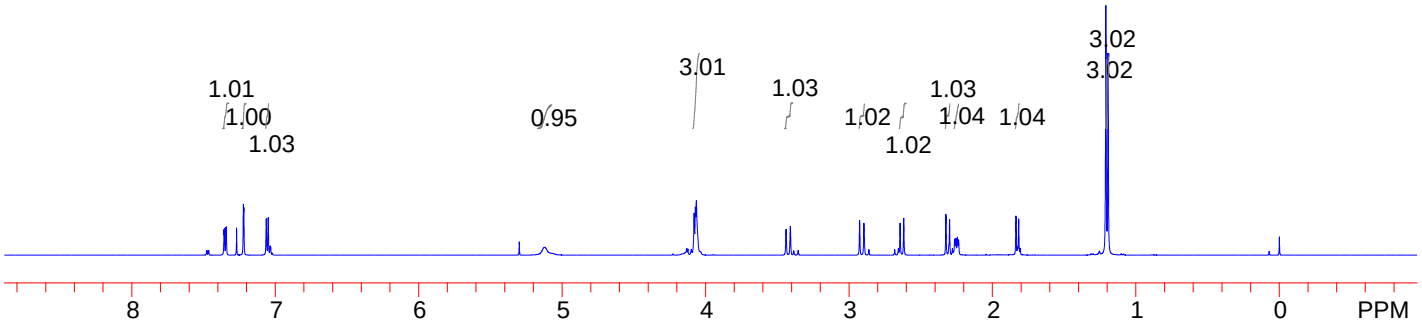


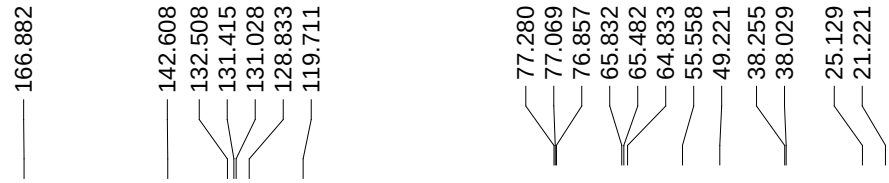


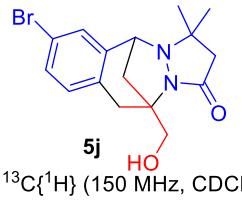


5j

^{1}H NMR (600 MHz, $CDCl_3$)

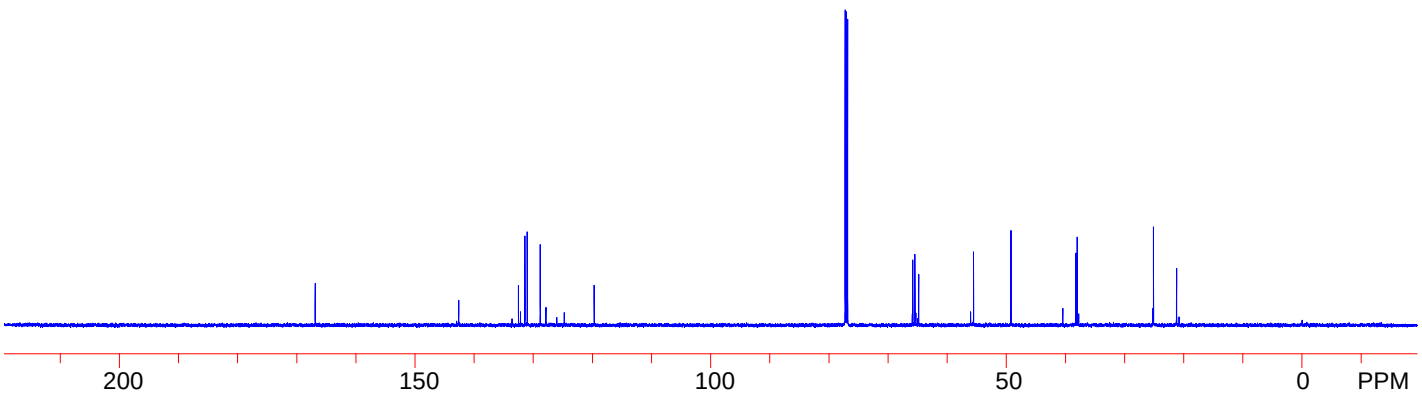


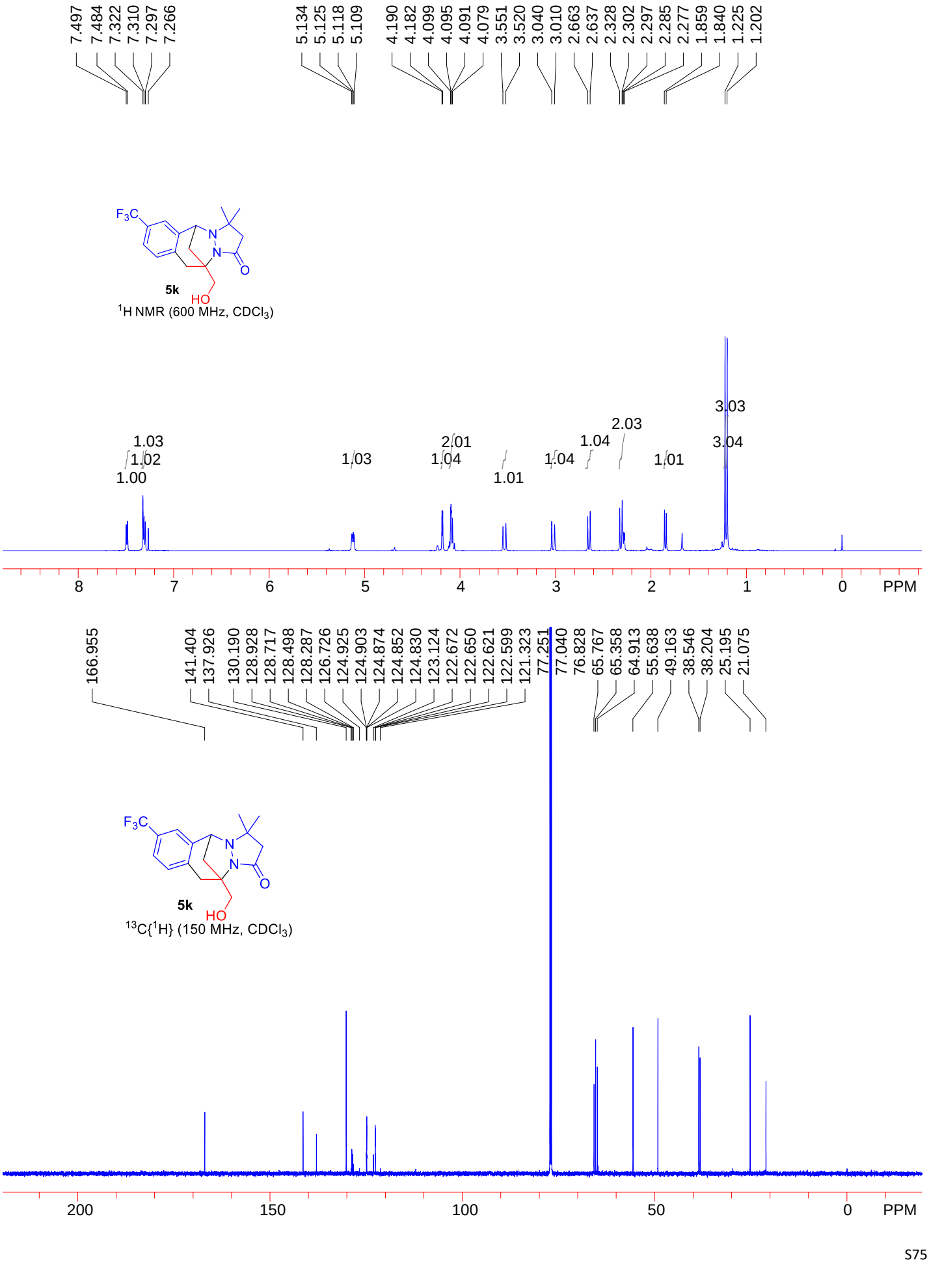




5j

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

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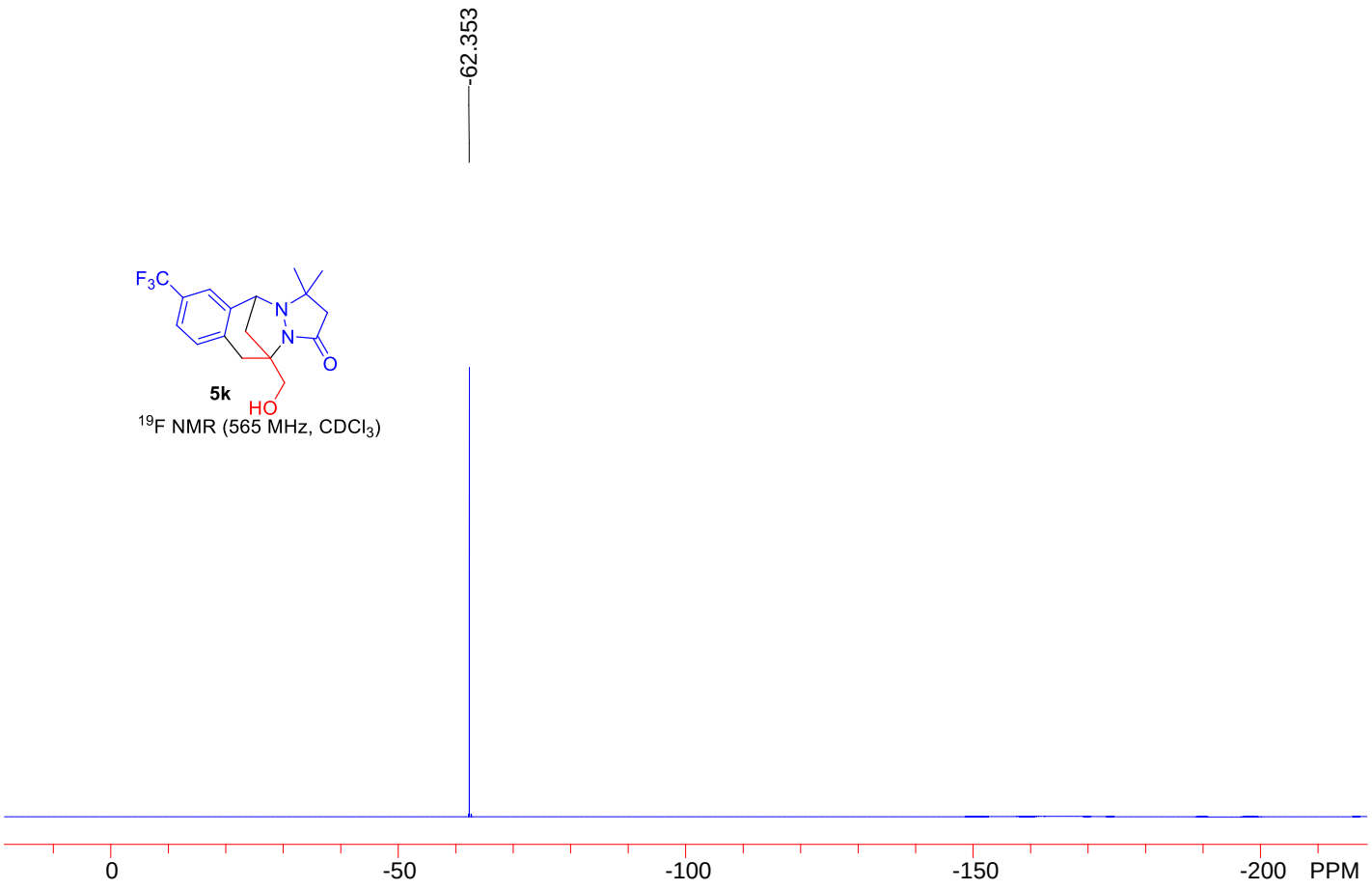
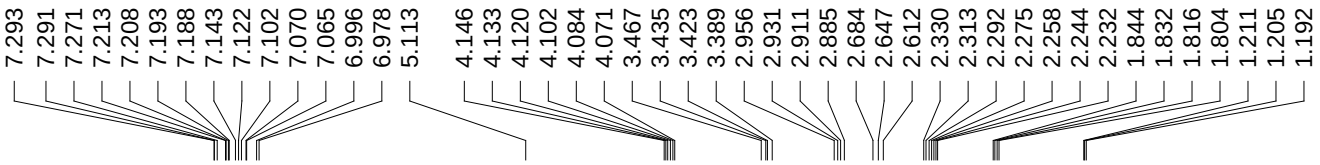
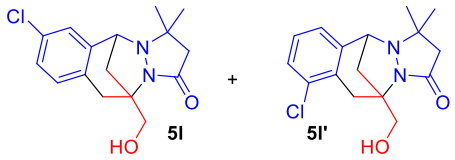
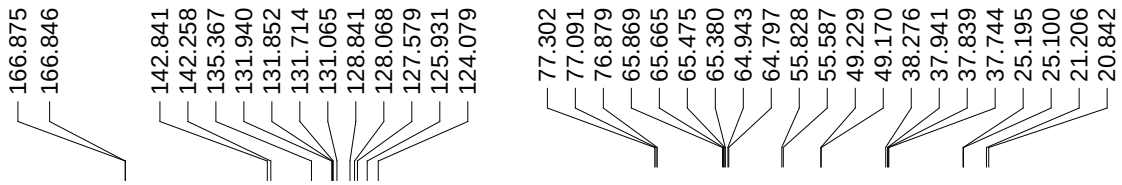
7.484
7.322
7.310
7.297
7.266
5.134
5.125
5.118
5.109
4.190
4.182
4.099
4.095
4.091
4.079
3.551
3.520
3.040
3.010
2.663
2.637
2.328
2.302
2.297
2.285
2.277
1.859
1.840
1.225
1.202
F3C
N
N
O
5k
HO
1H NMR (600 MHz, CDCl3)
1.03
1.02
1.00
1.03
2.01
1.04
1.01
1.04
1.04
2.03
1.01
3.03
3.04
8
7
6
5
4
3
2
1
0
PPM
166.955
141.404
137.926
130.190
128.928
128.717
128.498
128.287
126.726
124.925
124.903
124.874
124.852
124.830
123.124
122.672
122.650
122.621
122.599
121.323
77.251
77.040
76.828
65.767
65.358
64.913
55.638
49.163
38.546
38.204
25.195
21.075
F3C
N
N
O
5k
HO
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

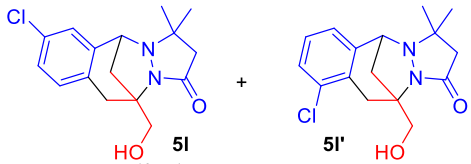

-62.353
F3C
N
N
O
HO
5k
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM



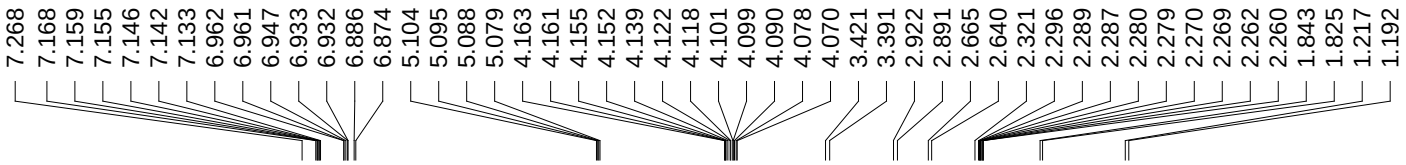


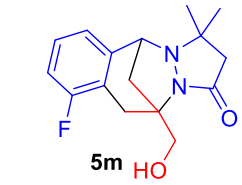
^{1}H NMR (400 MHz, $CDCl_3$)



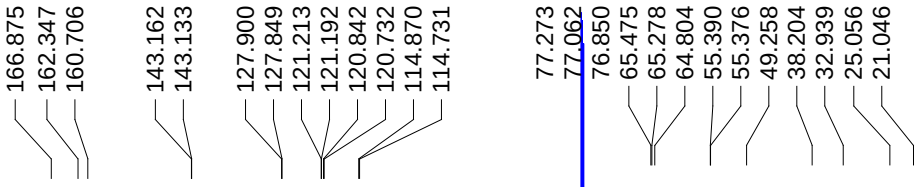


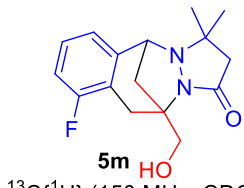
^{13}C{^{1}H} (150 MHz, $CDCl_3$)



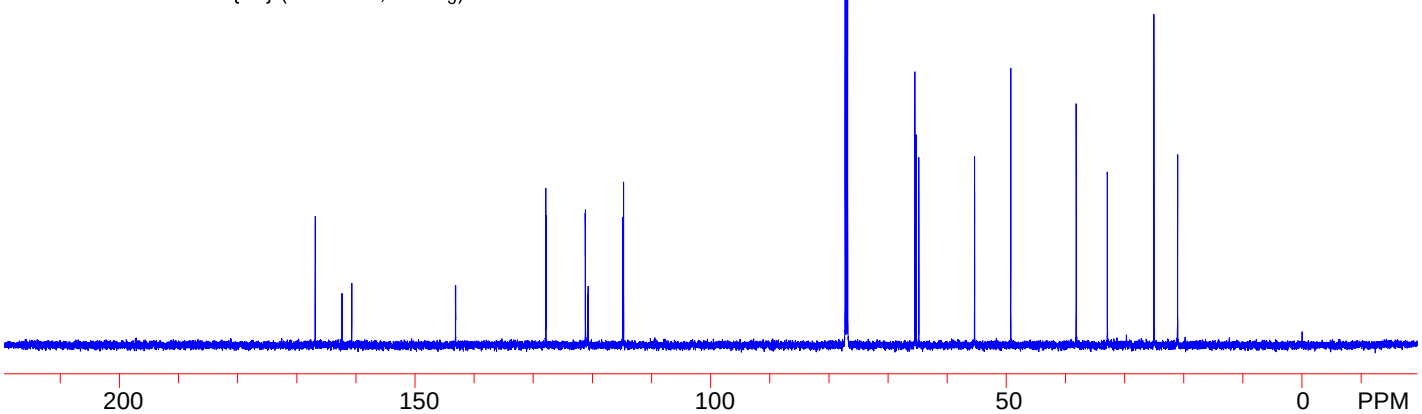


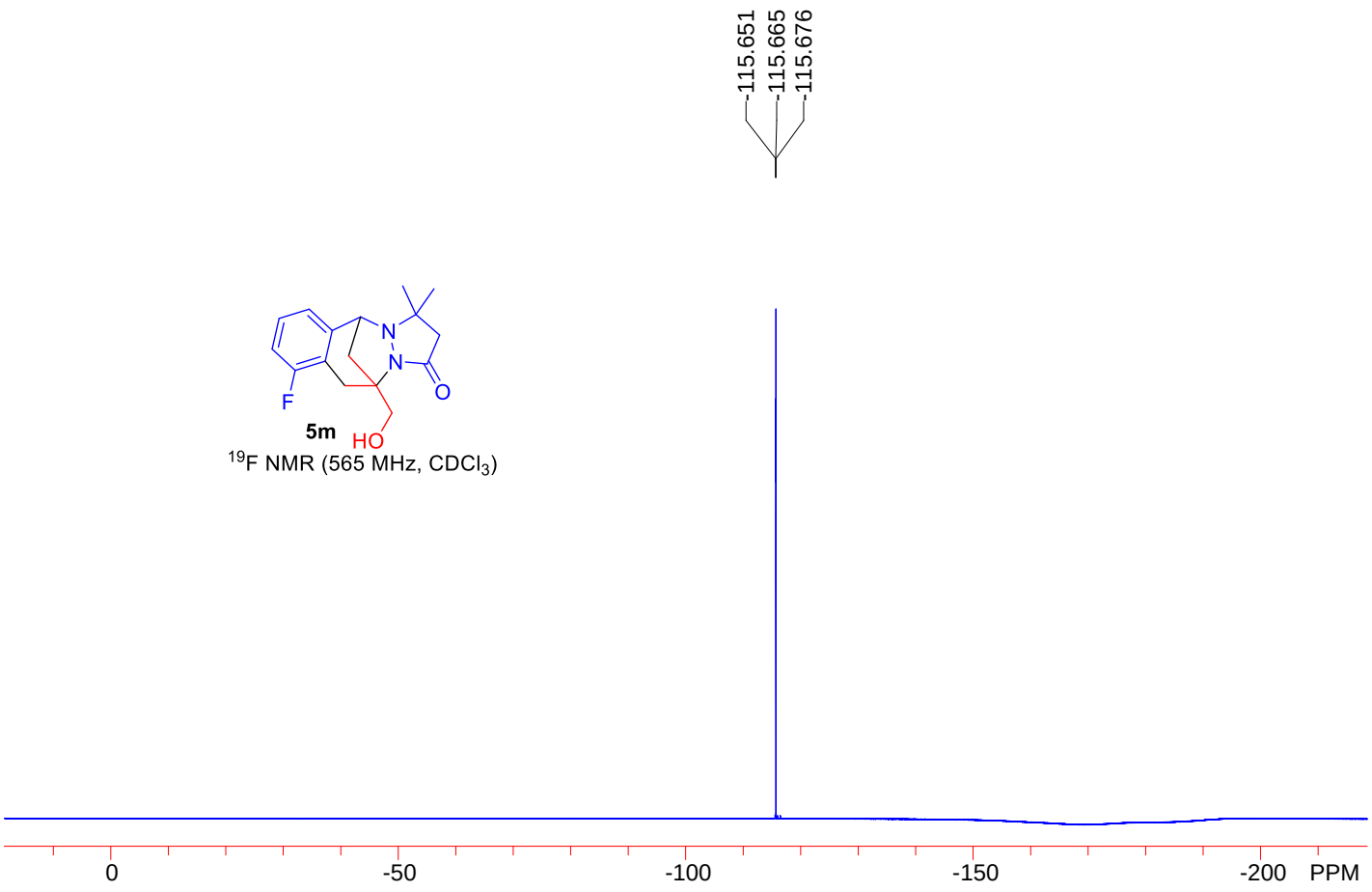
^{1}H NMR (600 MHz, $CDCl_3$)





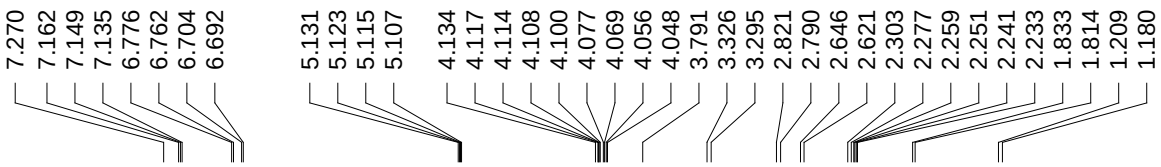
^{13}C{^{1}H} (150 MHz, $CDCl_3$)

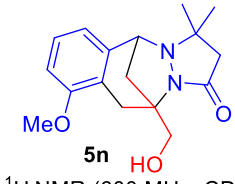




5m

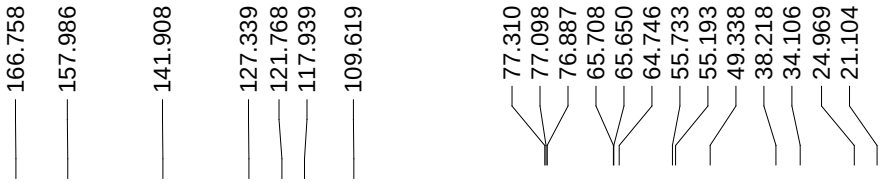
^{19}F NMR (565 MHz, $CDCl_3$)

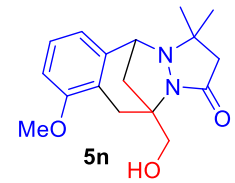




5n

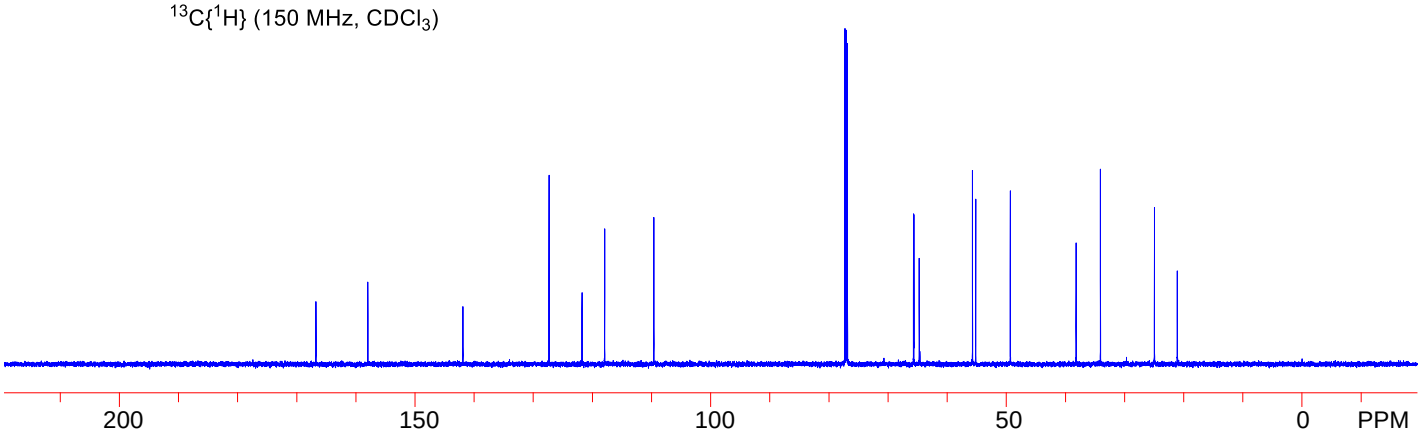
^{1}H NMR (600 MHz, $CDCl_3$)

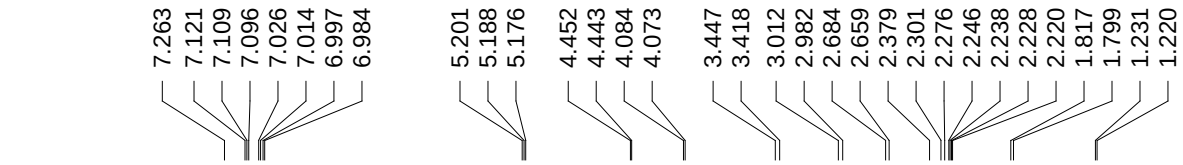


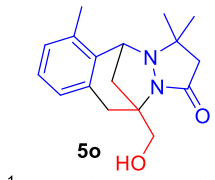


5n

^{13}C{^{1}H} (150 MHz, $CDCl_3$)

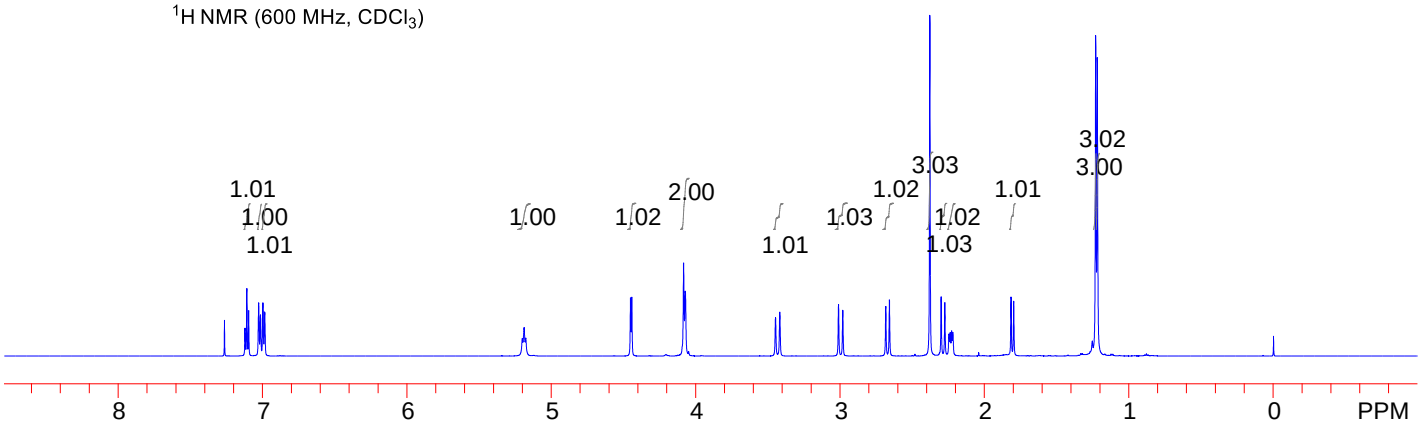


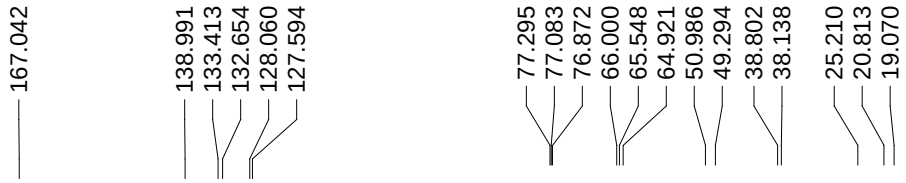


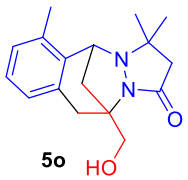


5o

^{1}H NMR (600 MHz, $CDCl_3$)

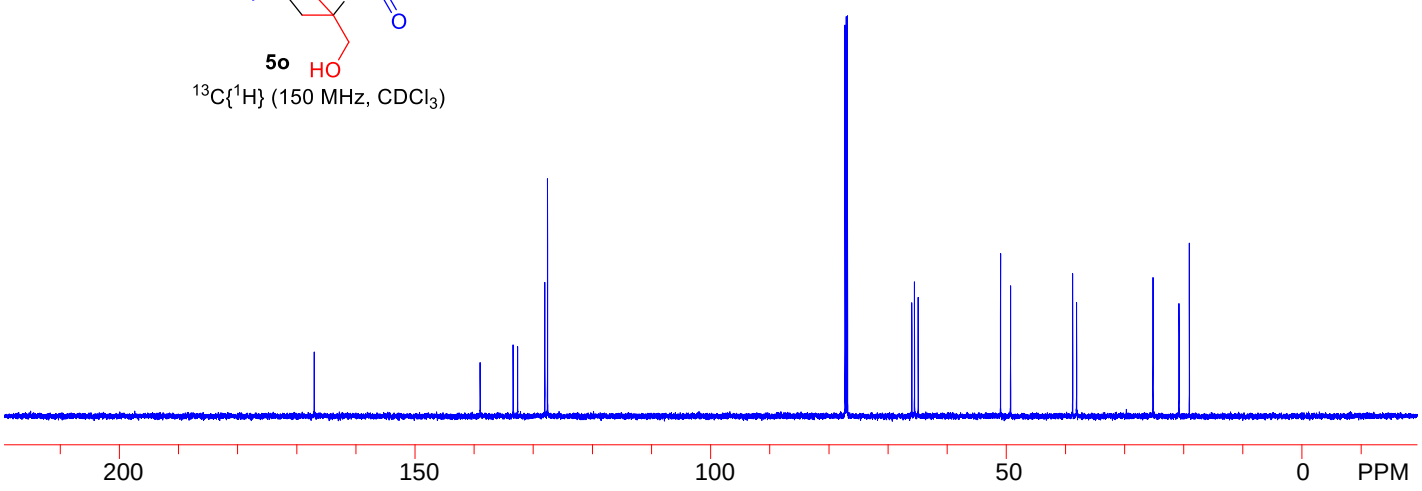


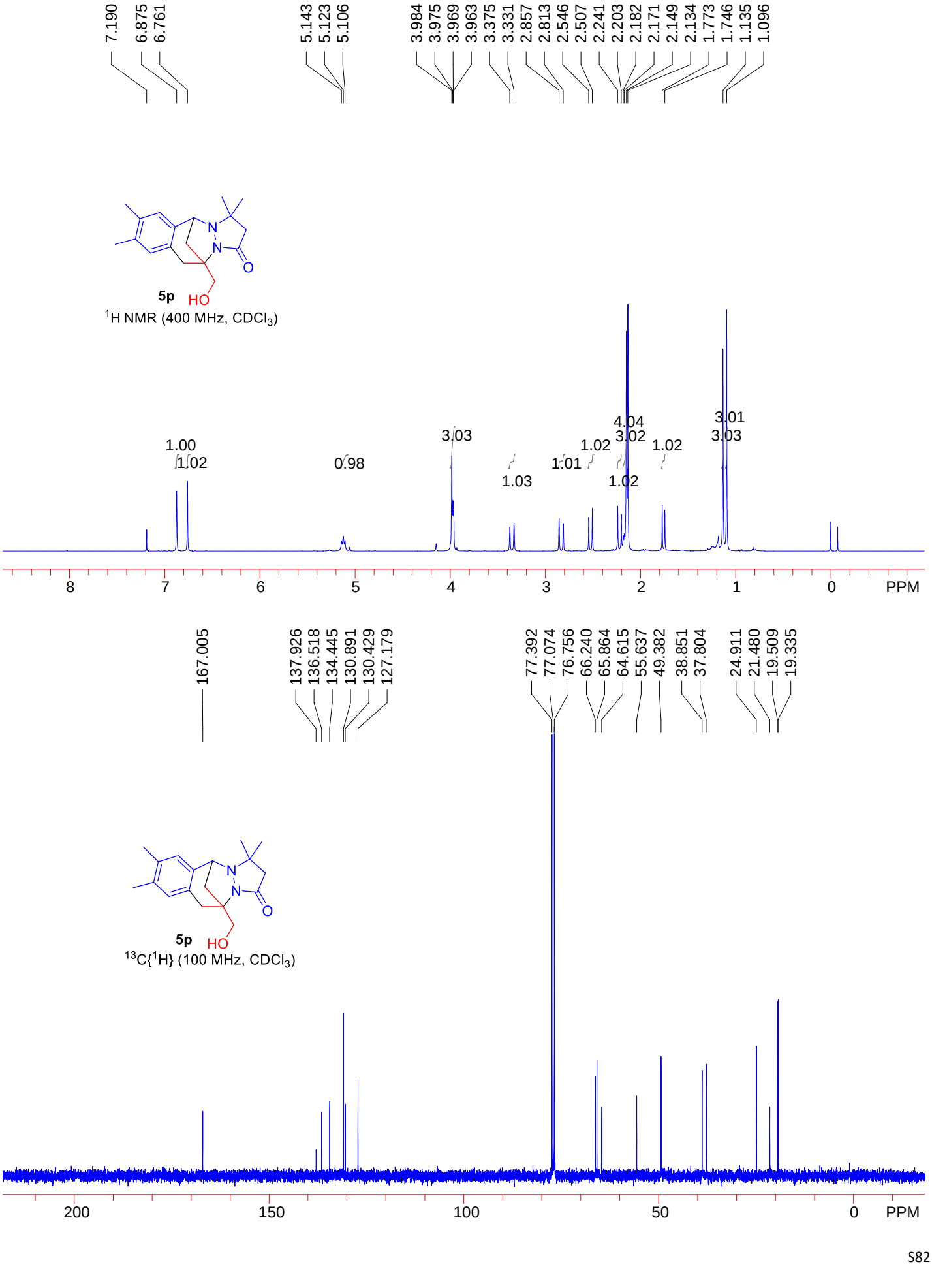




5o

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

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5.123
5.106
3.984
3.975
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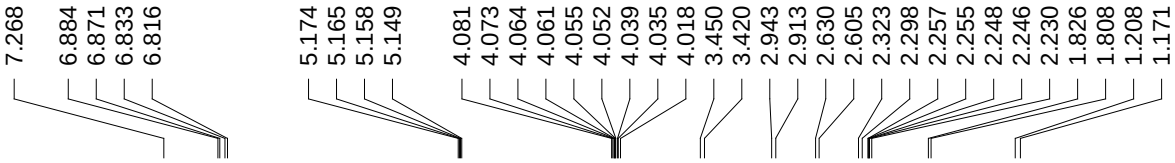
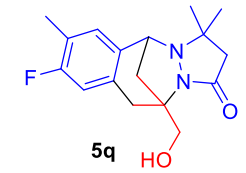
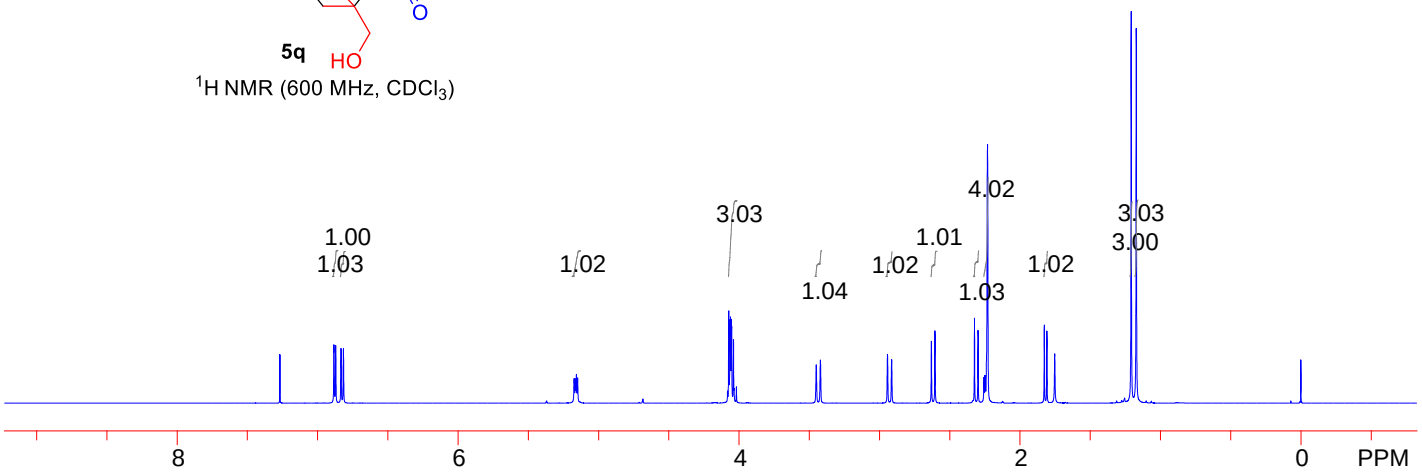
3.331
2.857
2.813
2.546
2.507
2.241
2.203
2.182
2.171
2.149
2.134
1.773
1.746
1.135
1.096
5p
HO
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.02
0.98
3.03
1.03
1.01
1.02
4.04
3.02
1.02
1.02
3.01
3.03
8
7
6
5
4
3
2
1
0
PPM
167.005
137.926
136.518
134.445
130.891
130.429
127.179
77.392
77.074
76.756
66.240
65.864
64.615
55.637
49.382
38.851
37.804
24.911
21.480
19.509
19.335
5p
HO
^{13}C{^{1}H} (100 MHz, CDCl$_3$)
200
150
100
50
0
PPM

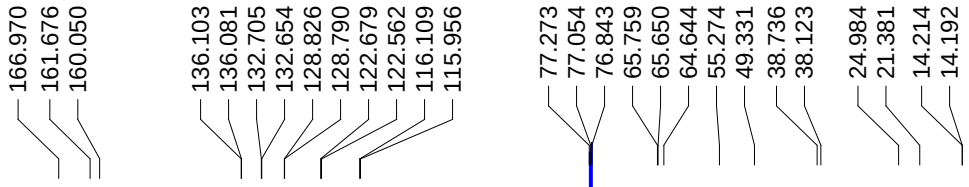


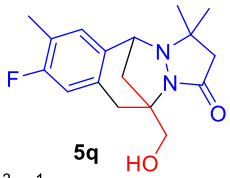


5q

^{1}H NMR (600 MHz, $CDCl_3$)

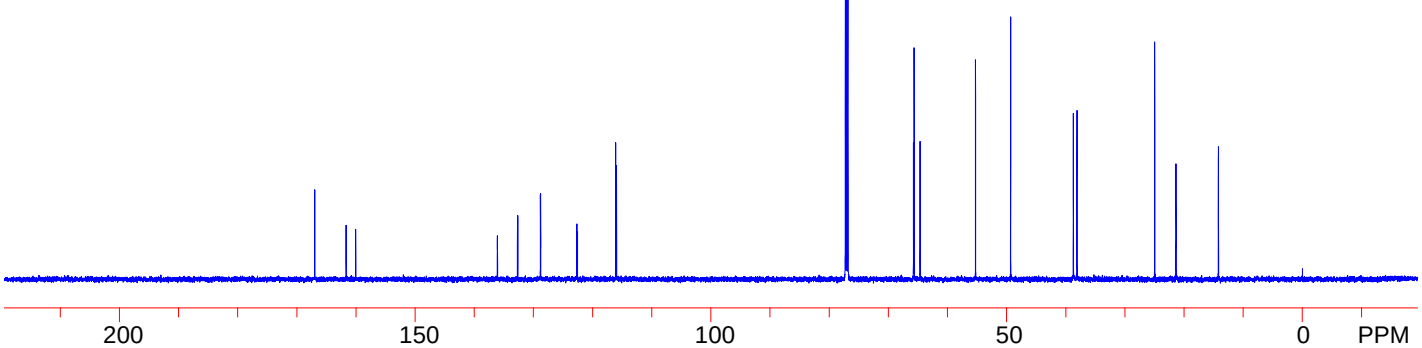


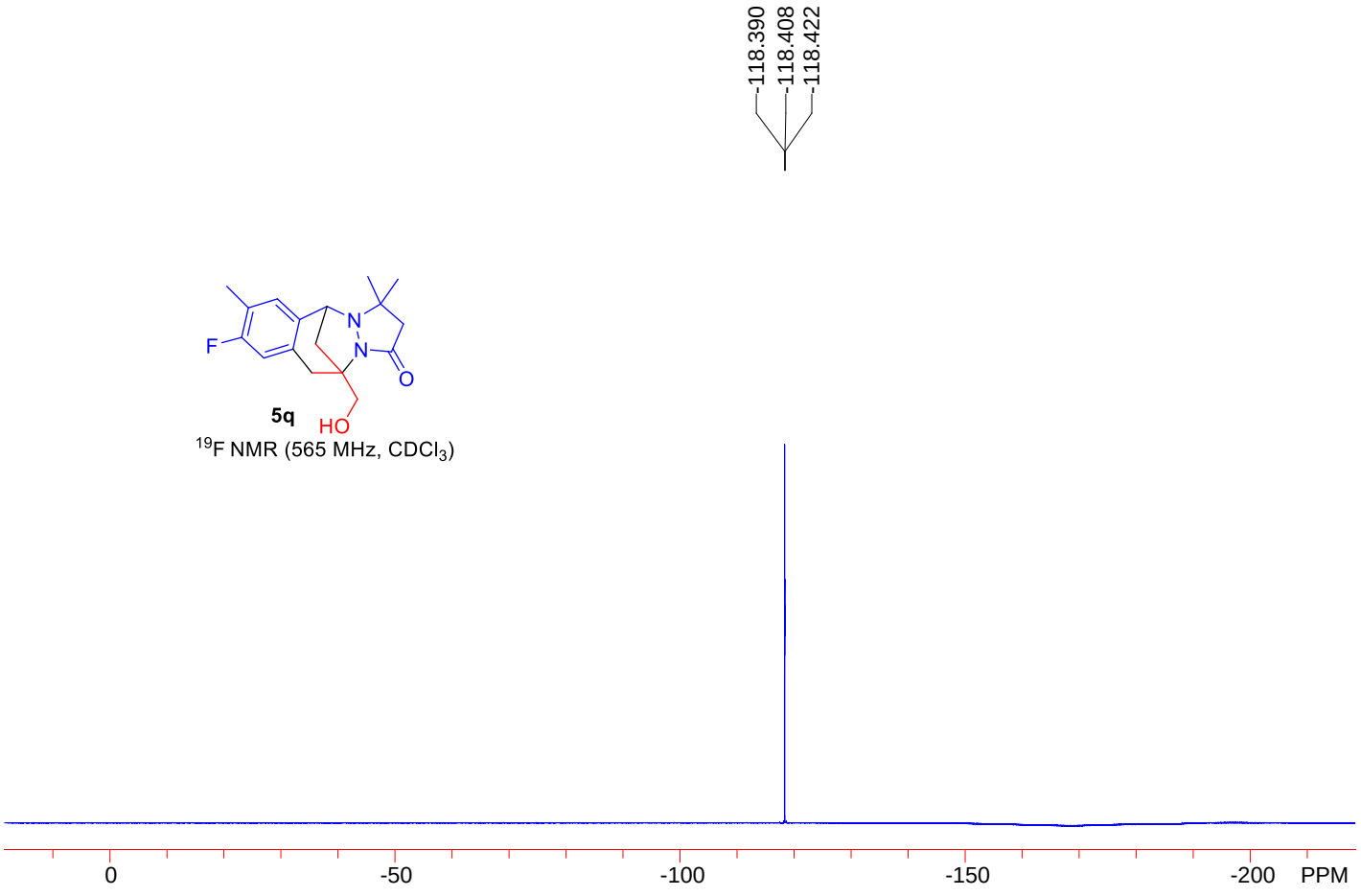




5q

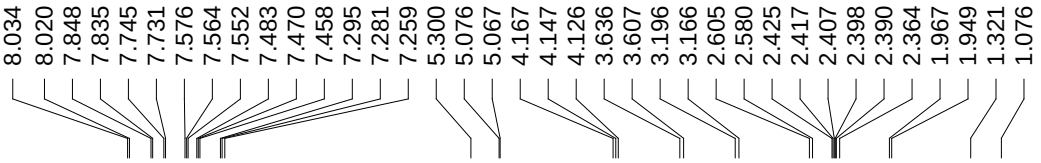
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

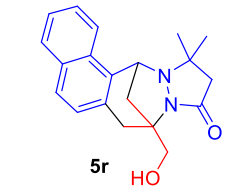




5q

^{19}F NMR (565 MHz, $CDCl_3$)





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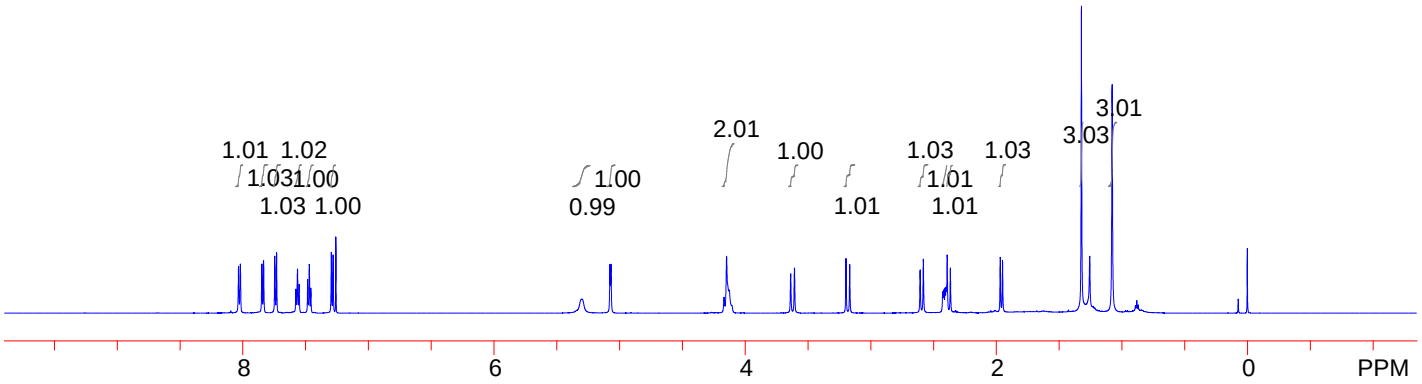
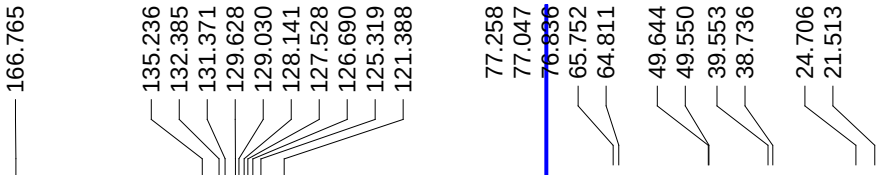
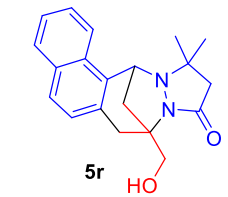
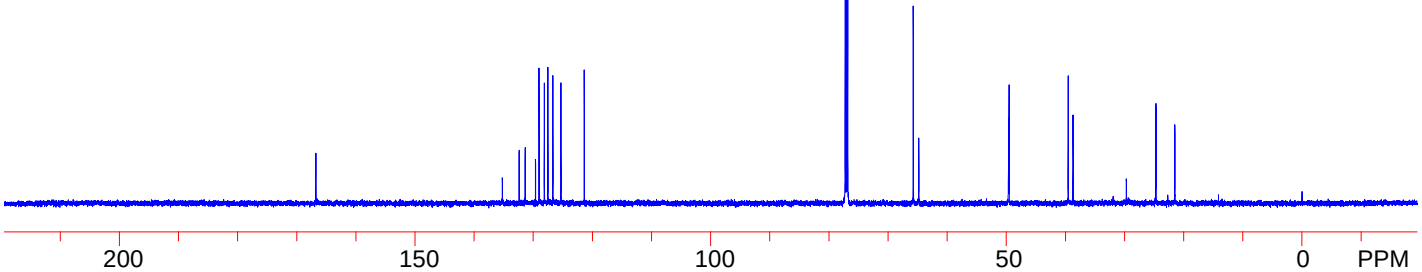
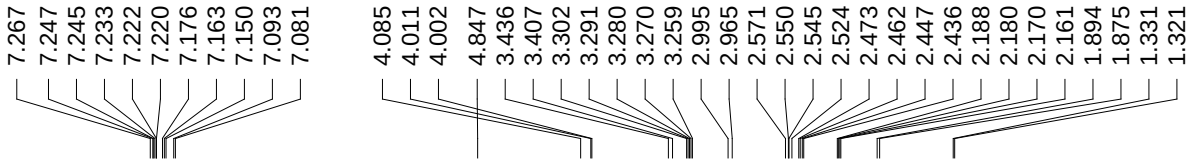


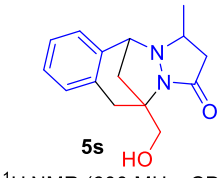




^{13}C{^{1}H} (150 MHz, $CDCl_3$)







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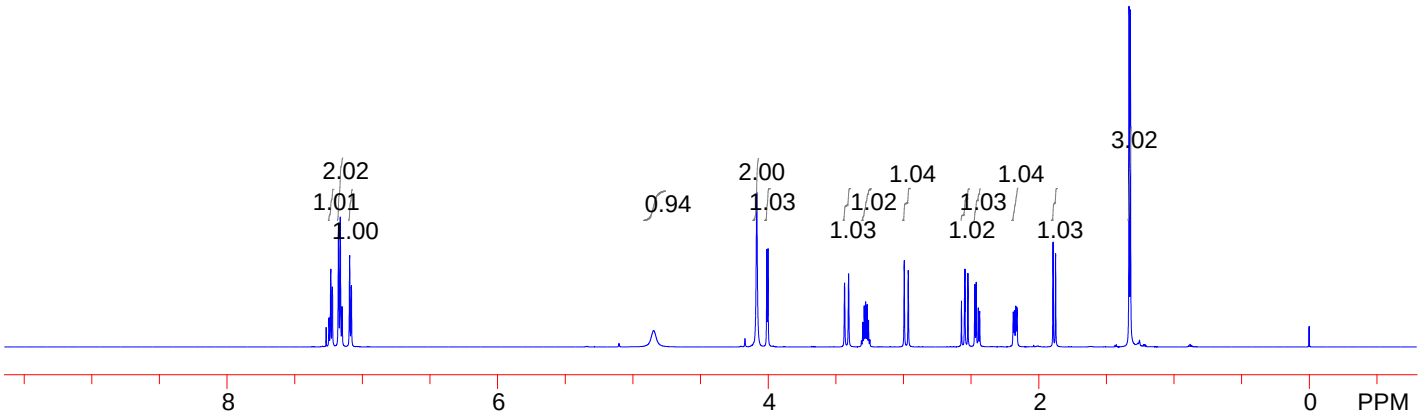
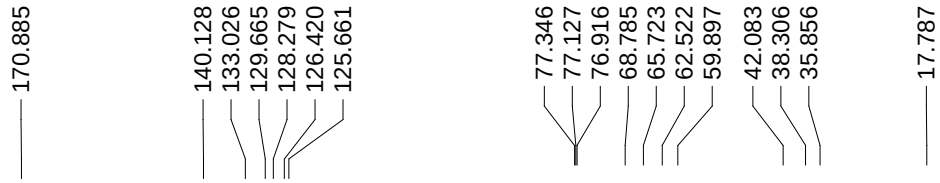
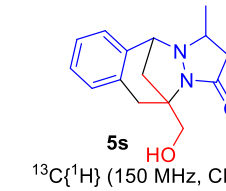
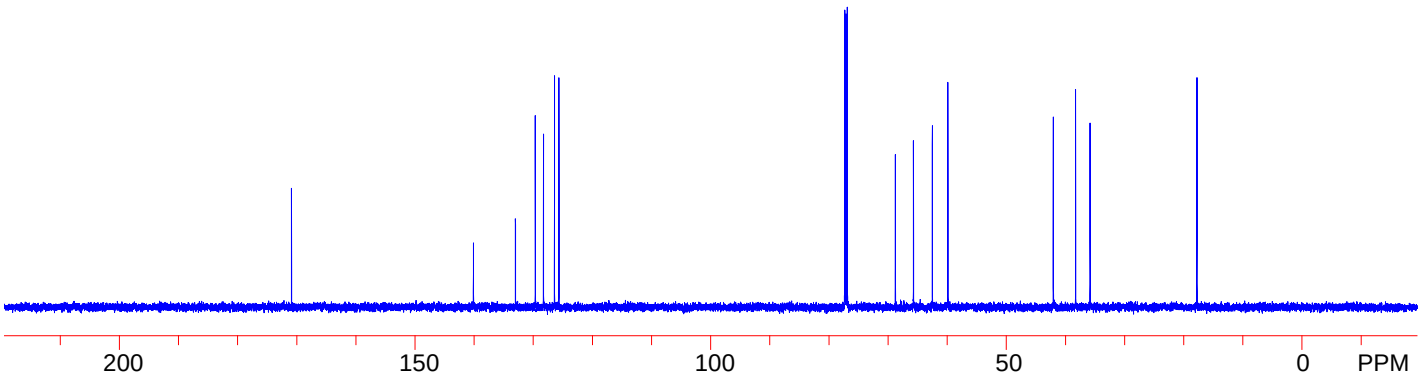
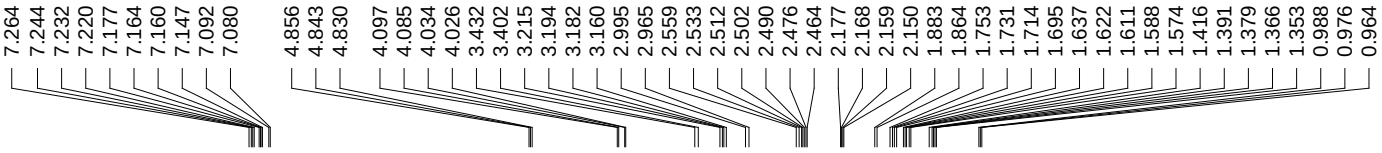


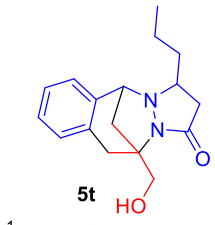




^{13}C{^{1}H} (150 MHz, $CDCl_3$)







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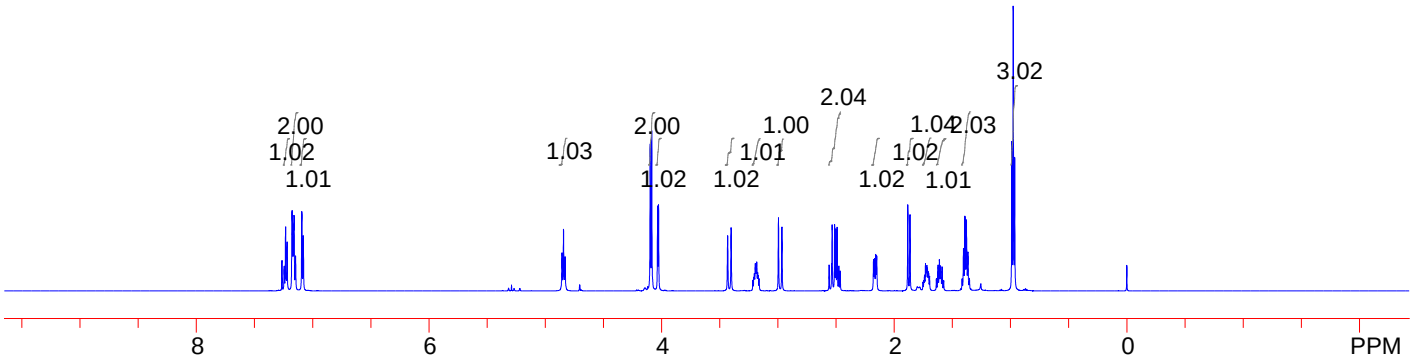
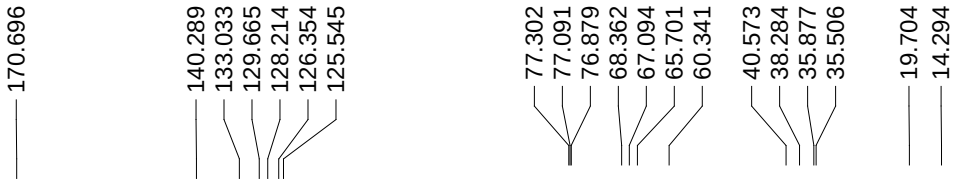
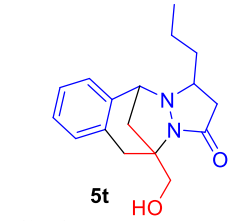
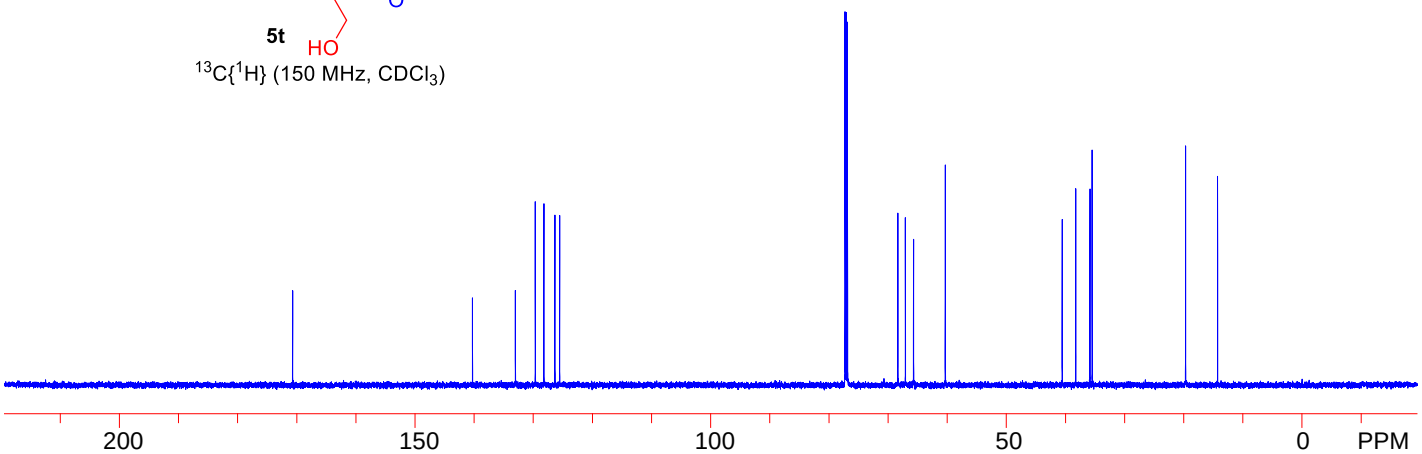
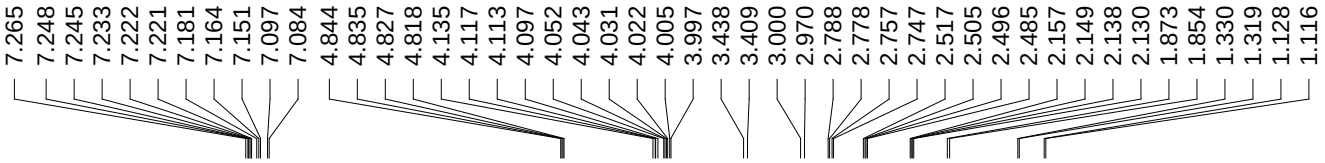


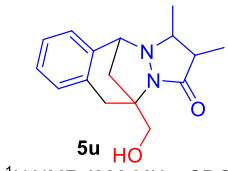




$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

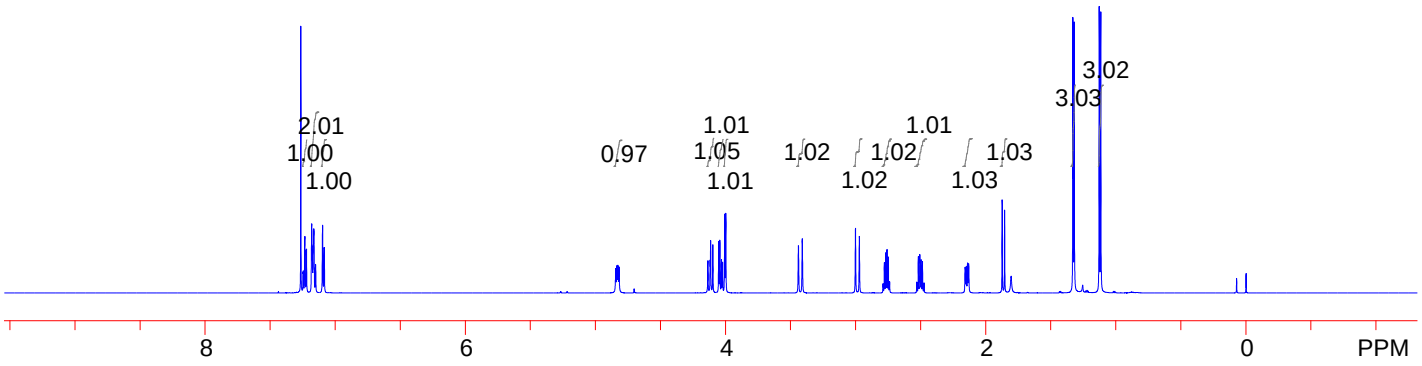


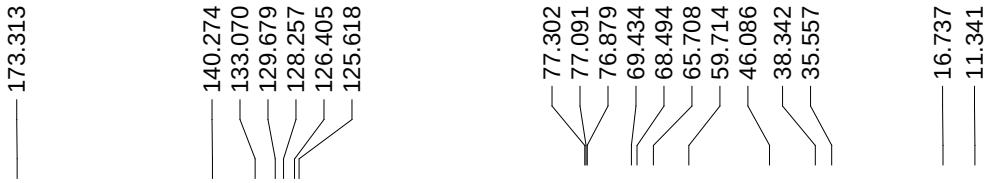


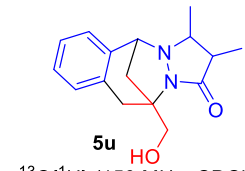


5u

^{1}H NMR (600 MHz, $CDCl_3$)







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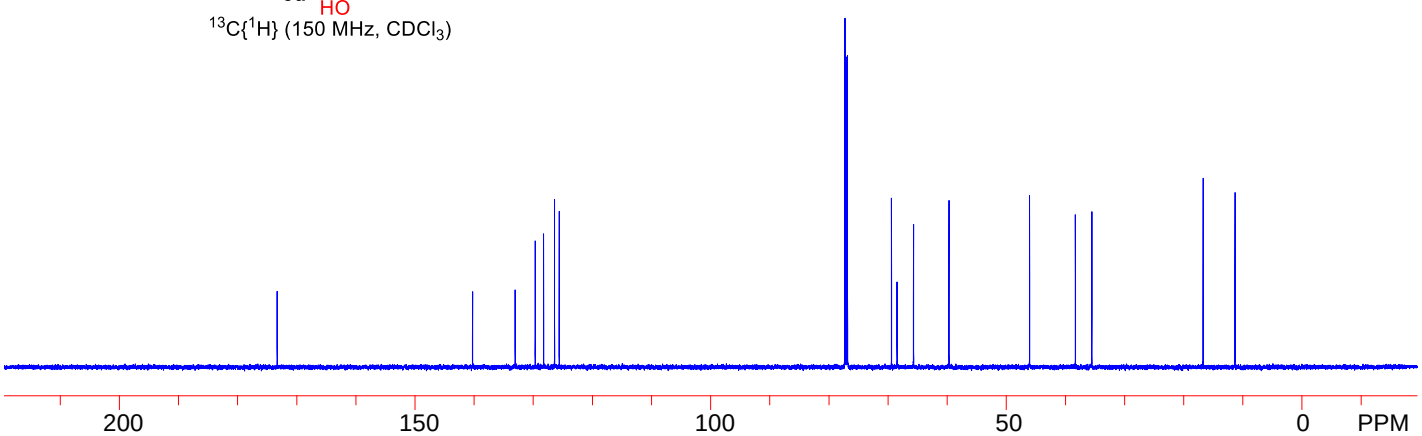
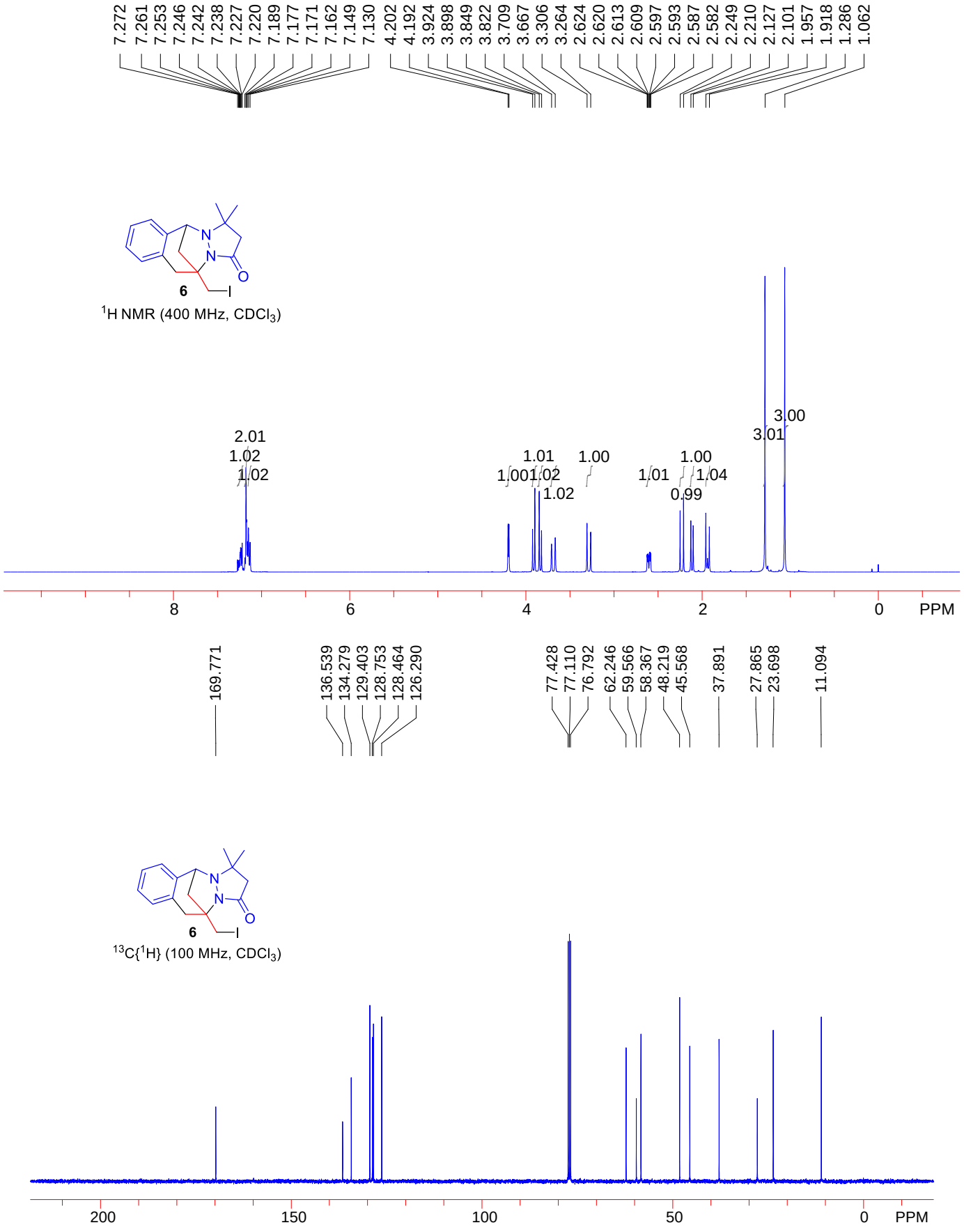
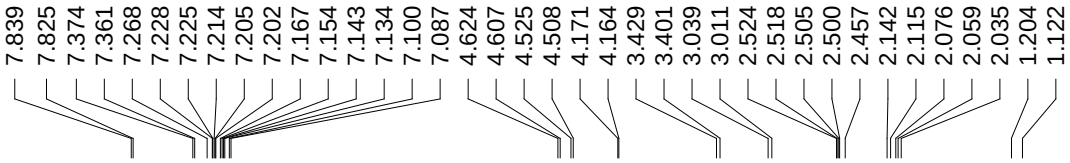
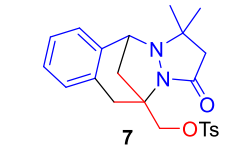
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



VI. Copies of NMR spectra of 6-9

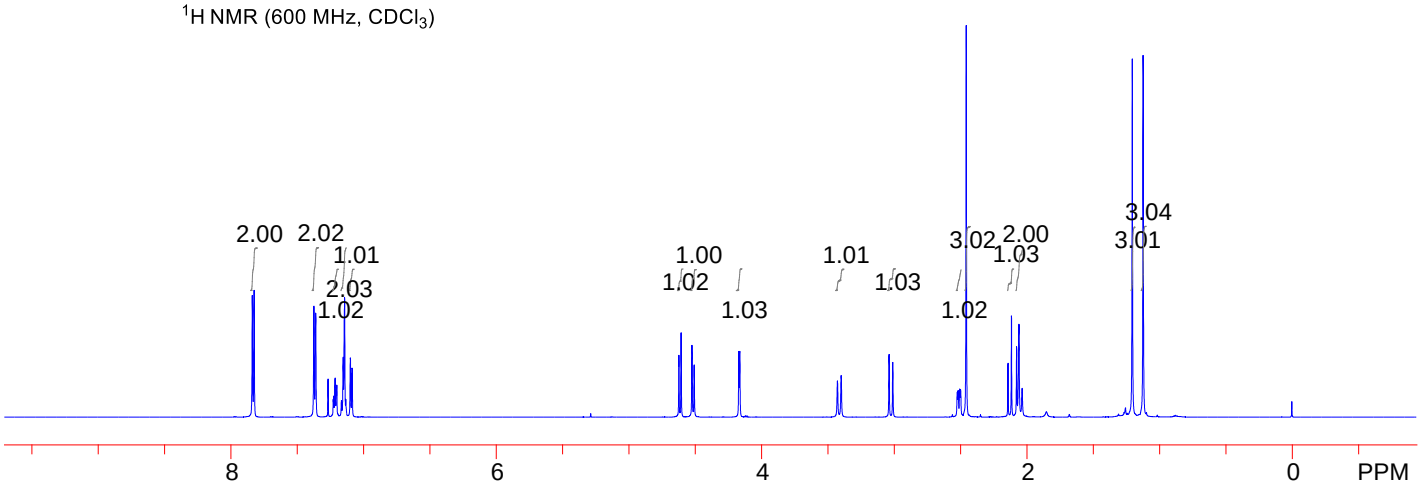


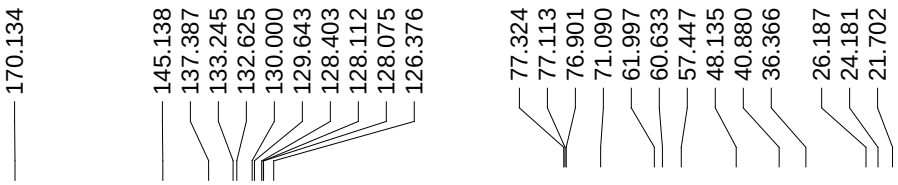


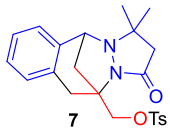


7

^{1}H NMR (600 MHz, $CDCl_3$)

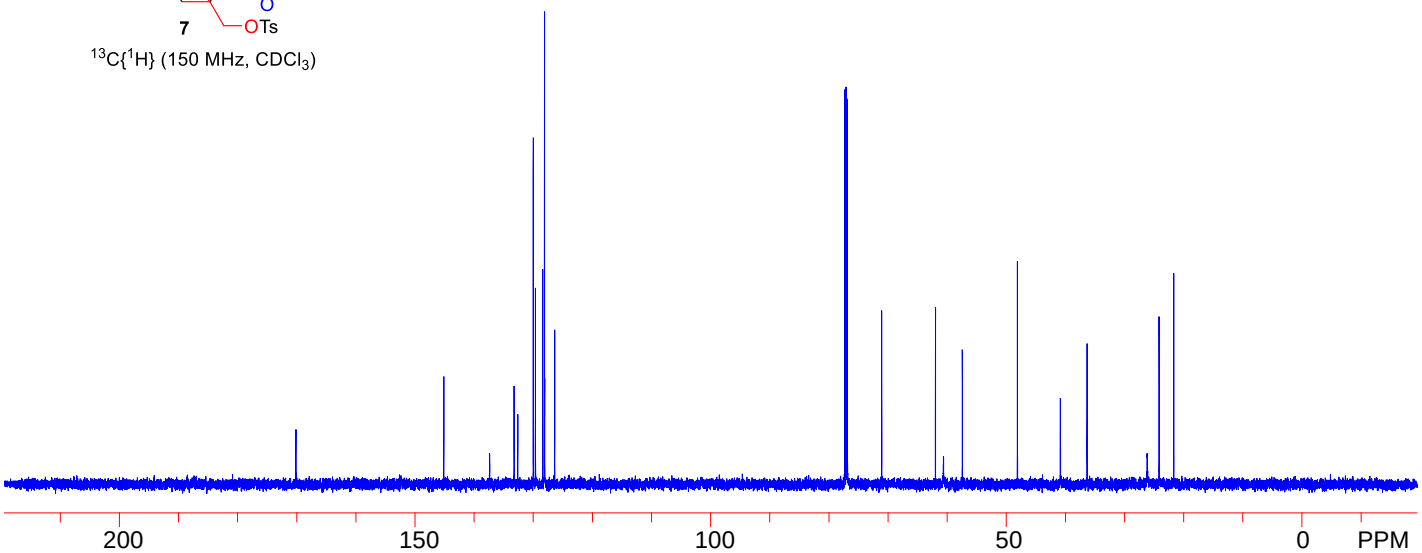


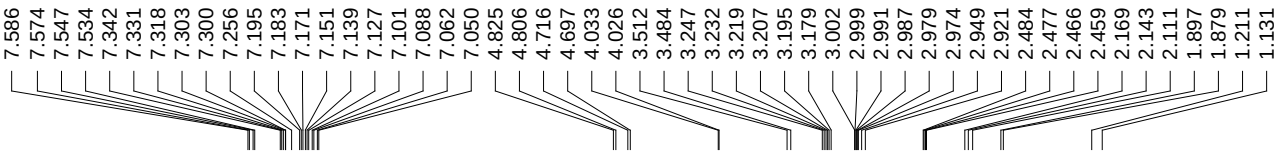


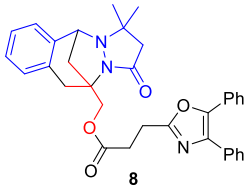


7

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

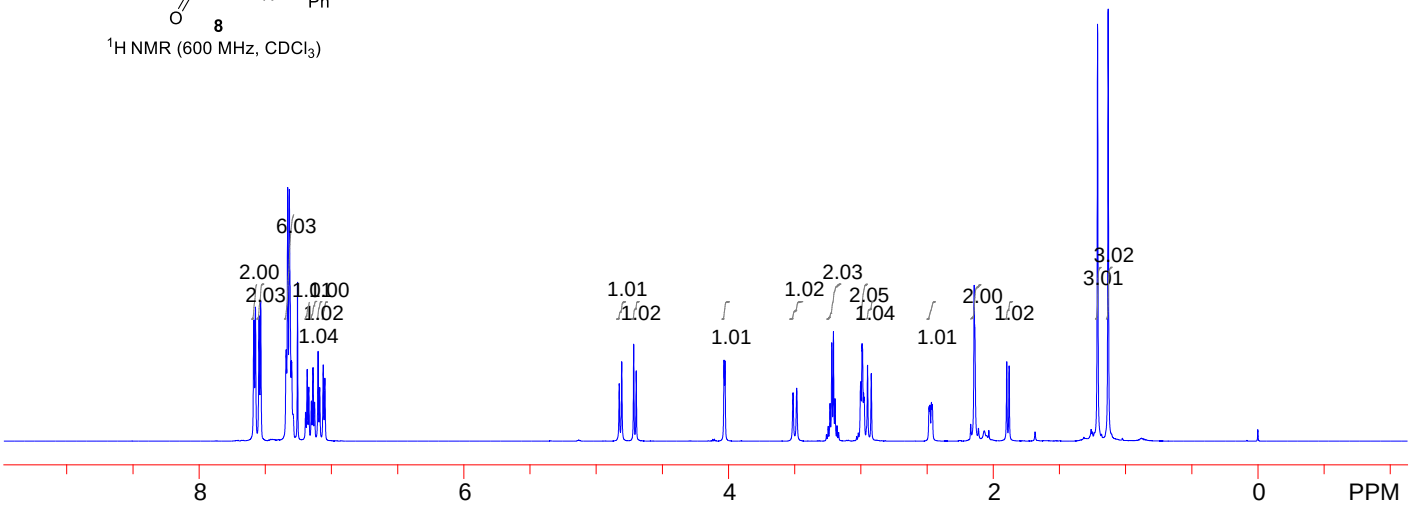


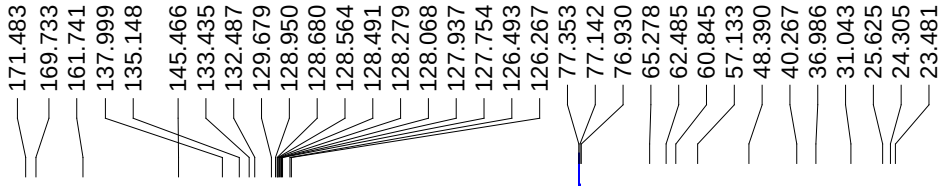


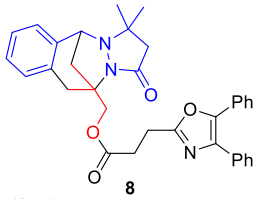


8

^{1}H NMR (600 MHz, $CDCl_3$)

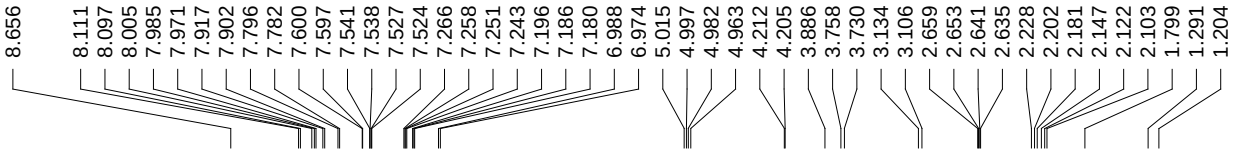


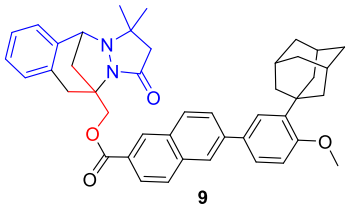




8

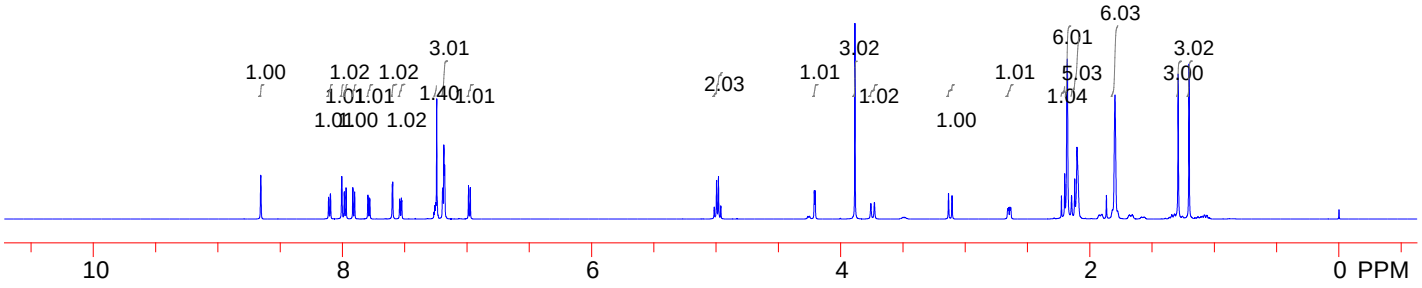
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

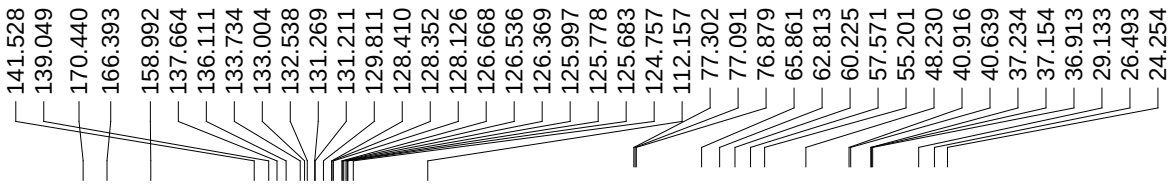


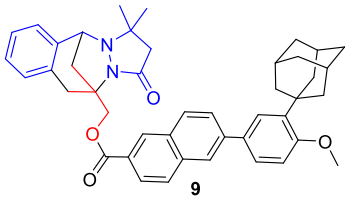


9

^{1}H NMR (600 MHz, $CDCl_3$)







9

^{13}C{^{1}H} (150 MHz, $CDCl_3$)

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

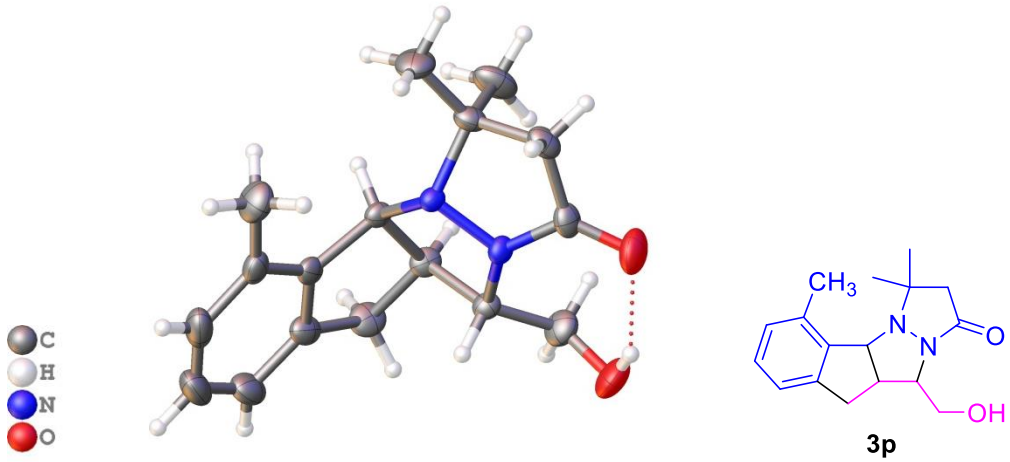


Figure S1. X-ray crystal structure of **3p** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a dichloromethane/chloroform (1:1) solution of **3p**. Crystal data collection and refinement parameters of **3p** 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 **3p**

Empirical formula	$C_{17}H_{22}N_2O_2$
Formula weight	286.36
Temp, K	293 (2)
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	10.6552(2)
b, Å	14.5864(2)
c, Å	9.8599(2)

α (°)	90
β (°)	104.578(2)
γ (°)	90
Volume, Å^3	1483.10(5)
Z	4
ρ_{calc}, g cm^{-3}	1.283
λ, Å	1.54184
μ, mm^{-1}	0.673
No. of data collected	10291
No. of unique data	2860
R_{int}	0.0372
Goodness-of-fit on F^2	1.090
R_1, wR_2 (I> 2σ(I))	0.0613, 0.1535
R_1, wR_2 (all data)	0.0659, 0.1596

VIII. X-ray crystal structure and data of 5a

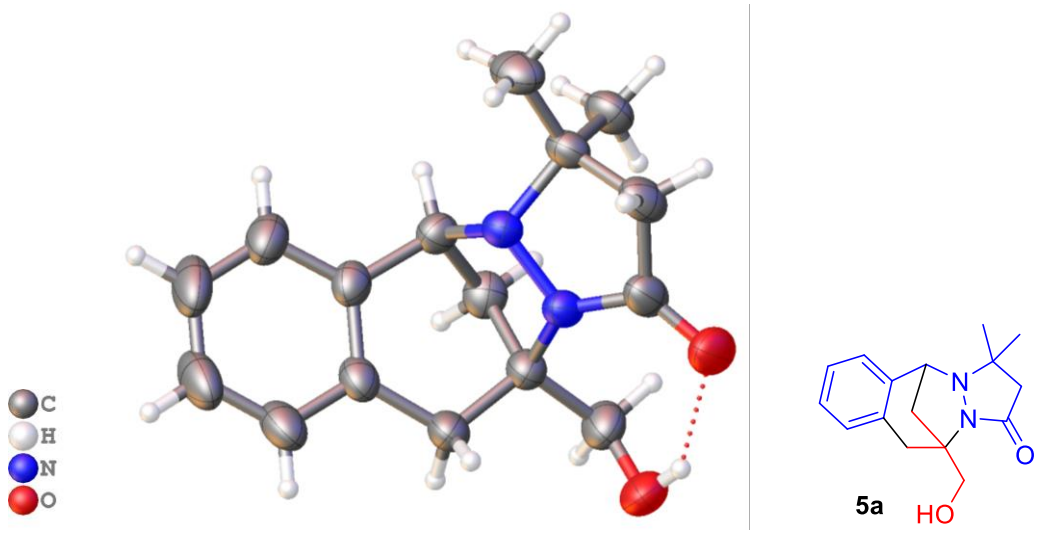


Figure S2. X-ray crystal structure of **5a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/dichloromethane (1:1) solution of **5a**. Crystal data collection and refinement parameters of **5a** 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 **5a**

Empirical formula	$C_{16}H_{20}N_2O_2$
Formula weight	272.34
Temp, K	293 (2)
Crystal system	triclinic
Space group	P-1
a, Å	7.2189(4)
b, Å	10.6828(5)

c, Å	10.8857(7)
α (°)	111.682(5)
β (°)	107.730(5)
γ (°)	94.966(4)
Volume, Å^3	724.00(8)
Z	2
ρ_{calc}, g cm^{-3}	1.249
λ, Å	1.54184
μ, mm^{-1}	0.665
No. of data collected	4574
No. of unique data	2736
R_{int}	0.0264
Goodness-of-fit on F^2	1.079
R_1, wR_2 ($I > 2\sigma(I)$)	0.0750, 0.1975
R_1, wR_2 (all data)	0.0801, 0.2050

IX. References

(1) M. Zhang, F. Wu, H. Wang, J. Wu and W. Chen, Copper-Catalyzed Sequential Azomethine Imine-Alkyne Cycloaddition and Umpolung Thiolation Reactions. *Adv. Synth. Catal.*, 2017, **359**, 2768–2772.

(2) S. Zhang, Y. Zheng, Z. Zhang, S. Chen, H. Xie, B. Shu, J. Song, Y. Liu, Y. Zeng and L. Zhang, Access to Branched Allylarenes via Rhodium(III)-Catalyzed C–H Allylation of (Hetero)arenes with 2-Methylidenetrimethylene Carbonate, *Org. Lett.*, 2021, **23**, 5719–5723.

(3) X. Wang, X. Xun, H. Song, Y. Liu and Q. Wang, Palladium Metallaphotoredox-Catalyzed 2-Arylation of Indole Derivatives, *Org. Lett.*, 2022, **24**, 4580–4585.