Supporting Information

Rh(III)-Catalyzed Regioselective C6-Arylation of 2-Pyridones with Diazonaphthalen-2(1*H*)-ones along with Directing Group Migration

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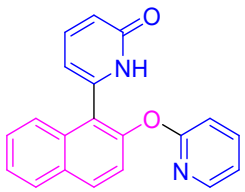
I. General experimental information

All reagents were purchased from commercial sources and were used without further purification. All solvents were purified and dried according to standard methods prior to use pyridones (**1**),[1] and diazonaphthoquinones (**2**),[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-TOF mode by using a BRUKER compact 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 3aa and spectroscopic data of 3aa-3ar

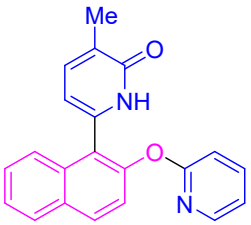
To a reaction tube equipped with a stir bar were added 2*H*-[1,2'-bipyridin]-2-one (**1a**, 34.4 mg, 0.2 mmol), HFIP (2 mL), 1-diazonaphthalen-2(1*H*)-one (**2a**, 51.1 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3aa** (50.9 mg, 81%). **3ba-3ar** were obtained in a similar manner.



3aa

6-(2-(Pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3aa)

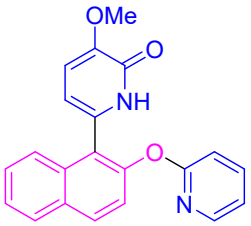
Eluent: dichloromethane/methanol (30:1). White solid (50.9 mg, 81%), mp 237.2-238.1 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.61 (br s, 1H), 8.14 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.91-7.90 (m, 1H), 7.78-7.77 (m, 1H), 7.69 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.53-7.50 (m, 2H), 7.44 (dd, J_1 = 9.0 Hz, J_2 = 6.6 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.02-7.00 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 9.0 Hz, 1H), 6.28 (d, J = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 163.7, 163.4, 149.9, 147.7, 141.0, 140.8, 140.0, 132.4, 131.8, 131.3, 128.5, 127.7, 126.0, 124.6, 122.9, 121.7, 119.9, 119.2, 112.1, 108.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}N_2O_2$ 315.1128; Found 315.1121.



3ba

3-Methyl-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ba)

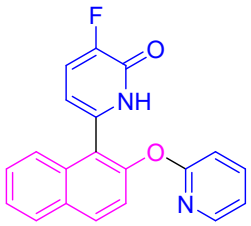
Eluent: dichloromethane/methanol (30:1). White solid (46.0 mg, 70%), mp 203.9-204.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (br s, 1H), 8.12 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.90-7.87 (m, 1H), 7.77-7.74 (m, 1H), 7.67-7.62 (m, 1H), 7.51-7.44 (m, 2H), 7.30-7.24 (m, 2H), 6.98 (dd, J_1 = 6.8 Hz, J_2 = 5.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.20 (d, J = 6.8 Hz, 1H), 2.10 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 163.9, 163.7, 149.9, 147.7, 139.8, 138.1, 138.0, 132.7, 131.5, 131.3, 128.9, 128.4, 127.5, 125.8, 124.8, 123.1, 121.6, 119.0, 112.0, 108.5, 16.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_2$ 329.1285; Found 329.1284.



3ca

3-Methoxy-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ca)

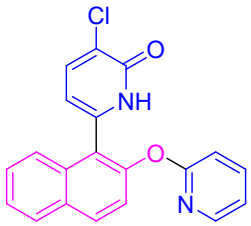
Eluent: dichloromethane/methanol (30:1). White solid (54.4 mg, 79%), mp 218.6-219.2 ºC. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.83 (s, 1H), 8.11 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 8.06 (d, J = 9.0 Hz, 1H), 8.02-8.01 (m, 1H), 7.81-7.78 (m, 1H), 7.57-7.54 (m, 3H), 7.35 (d, J = 9.0 Hz, 1H), 7.09 (dd, J_1 = 6.6 Hz, J_2 = 4.8 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 5.95 (d, J = 6.6 Hz, 1H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 163.7, 158.2, 150.0, 149.2, 147.9, 140.6, 133.5, 131.8, 131.1, 131.0, 128.6, 127.7, 126.0, 125.2, 123.7, 122.4, 119.5, 114.3, 111.7, 106.6, 55.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_3$ 345.1234; Found 345.1239.



3da

3-Fluoro-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3da)

Eluent: dichloromethane/methanol (30:1). White solid (61.8 mg, 93%), mp 239.2-240.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (br s, 1H), 8.14 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.92-7.88 (m, 1H), 7.77-7.69 (m, 2H), 7.55-7.50 (m, 2H), 7.24 (d, J = 8.8 Hz, 1H), 7.19 (dd, J_1 = 10.0 Hz, J_2 = 7.6 Hz, 1H), 7.04-6.98 (m, 2H), 6.20 (dd, J_1 = 7.6 Hz, J_2 = 3.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.6, 156.6 (d, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 152.1 (d, $^{1}J_{C\text{-}F}$ = 249.2 Hz), 150.1, 147.8, 140.1, 136.2 (d, $^{3}J_{C\text{-}F}$ = 5.8 Hz), 132.4, 132.0, 131.3, 128.5, 127.8, 126.0, 124.5, 122.3, 121.5, 121.4 (d, $^{2}J_{C\text{-}F}$ = 15.8 Hz), 119.4, 112.2, 106.9 (d, $^{4}J_{C\text{-}F}$ = 5.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -135.75 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}FN_2O_2$ 333.1034; Found 333.1032.

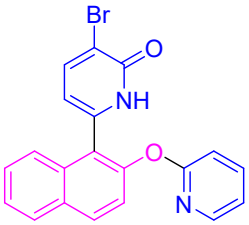


3ea

3-Chloro-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ea)

Eluent: dichloromethane/methanol (30:1). White solid (64.9 mg, 93%), mp 215.3-216.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (br s, 1H), 8.13 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.92-7.88 (m, 1H), 7.76-7.73 (m, 1H), 7.71-7.67 (m, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.53-7.49 (m, 2H), 7.24 (d, J = 8.8 Hz, 1H), 7.01 (dd, J_1 = 7.2 Hz, J_2 = 5.2 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.26 (d, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.6, 159.4, 150.0, 147.7, 140.1, 139.8, 138.7, 132.2, 132.1, 131.3, 128.5, 127.8,

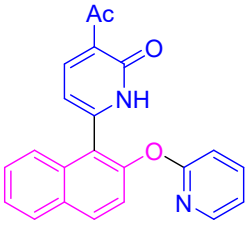
126.0, 125.5, 124.4, 122.2, 121.5, 119.4, 112.2, 108.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}ClN_2O_2$ 349.0738; Found 349.0729.



3fa

3-Bromo-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3fa)

Eluent: dichloromethane/methanol (30:1). White solid (62.9 mg, 80%), mp 211.2-212.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (br s, 1H), 8.12 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.92-7.88 (m, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.76-7.72 (m, 1H), 7.70-7.65 (m, 1H), 7.53-7.48 (m, 2H), 7.24 (d, J = 9.2 Hz, 1H), 7.02-6.99 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.20 (d, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.6, 159.5, 150.0, 147.7, 142.5, 140.8, 140.1, 132.13, 132.08, 131.3, 128.5, 127.8, 126.1, 124.4, 122.2, 121.6, 119.4, 115.6, 112.3, 108.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}BrN_2O_2$ 393.0233; Found 393.0230.

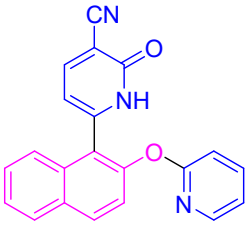


3ga

3-Acetyl-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ga)

Eluent: dichloromethane/methanol (30:1). Brown solid (61.3 mg, 86%), mp 111.8-112.4 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.04 (br s, 1H), 8.20 (d, J = 7.2 Hz, 1H), 8.11 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.90-7.89 (m, 1H), 7.68-7.64 (m, 2H), 7.51-7.45 (m, 2H), 7.28 (d, J = 9.0 Hz, 1H), 7.00-6.98 (m, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.44 (d, J = 7.2 Hz, 1H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.5, 163.5, 163.0, 149.8, 148.1, 147.7, 144.3, 139.9, 132.09, 132.05, 131.1, 128.5, 127.7, 126.0, 125.6,

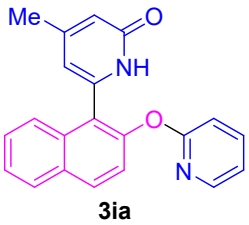
124.4, 122.1, 121.5, 119.3, 112.0, 109.2, 30.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_3$ 357.1234; Found 357.1231.



3ha

2-Oxo-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)-1,2-dihydropyridine-3-carbonitrile (3ha)

Eluent: dichloromethane/methanol (30:1). White solid (61.1 mg, 90%), mp 217.1-217.9 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 11.14 (br s, 1H), 8.13 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.93-7.91 (m, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.75-7.69 (m, 2H), 7.56-7.53 (m, 2H), 7.24 (d, J = 9.0 Hz, 1H), 7.05 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 163.4, 160.7, 150.2, 147.81, 147.79, 140.4, 132.9, 131.6, 131.2, 128.8, 128.2, 126.2, 124.0, 121.4, 121.2, 119.8, 115.4, 112.5, 108.5, 104.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}N_3O_2$ 340.1081; Found 340.1076.

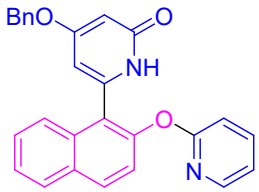


3ia

4-Methyl-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ia)

Eluent: dichloromethane/methanol (30:1). White solid (46.6 mg, 71%), mp 235.1-236.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (br s, 1H), 8.13 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.90-7.87 (m, 1H), 7.78-7.75 (m, 1H), 7.67 (td, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.26 (d, J = 8.8 Hz, 1H), 6.99 (dd, J_1 = 7.2 Hz, J_2 = 5.6 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.27 (s, 1H), 6.10 (d, J = 1.2 Hz, 1H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 163.75, 163.68, 152.4, 149.9, 147.7, 139.9, 132.5, 131.6, 131.2,

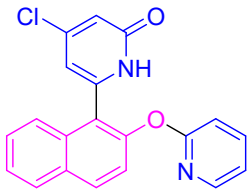
128.4, 127.6, 125.9, 124.7, 122.9, 121.6, 119.1, 118.2, 112.1, 111.1, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_2$ 329.1285; Found 329.1284.



3ja

4-(Benzyloxy)-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ja)

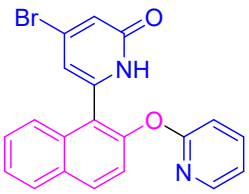
Eluent: dichloromethane/methanol (30:1). Yellowish solid (60.5 mg, 72%), mp 212.8-213.6 ºC. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.46 (s, 1H), 8.13 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 8.04-8.02 (m, 1H), 7.85-7.82 (m, 1H), 7.58-7.55 (m, 3H), 7.39-7.32 (m, 6H), 7.12 (dd, J_1 = 6.6 Hz, J_2 = 4.8 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 5.82-5.76 (m, 2H), 5.04 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.1, 165.2, 163.6, 149.8, 147.7, 141.0, 139.9, 135.3, 132.3, 131.7, 131.2, 128.7, 128.5, 128.4, 127.7, 127.6, 125.9, 124.7, 122.7, 121.6, 119.2, 112.1, 103.5, 97.4, 70.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}N_2O_3$ 421.1547; Found 421.1545.



3ka

4-Chloro-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ka)

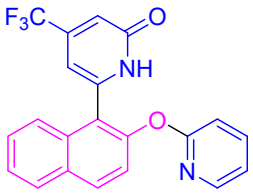
Eluent: dichloromethane/methanol (30:1). Yellowish solid (62.8 mg, 90%), mp 198.9-199.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (br s, 1H), 8.14 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.92-7.89 (m, 1H), 7.78-7.75 (m, 1H), 7.73-7.69 (m, 1H), 7.57-7.51 (m, 2H), 7.25 (d, J = 9.2 Hz, 1H), 7.05-6.99 (m, 2H), 6.51 (d, J = 2.0 Hz, 1H), 6.31 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.6, 162.6, 150.1, 147.9, 147.7, 141.6, 140.1, 132.2, 132.1, 131.2, 128.5, 127.9, 126.1, 124.3, 121.9, 121.5, 119.5, 118.5, 112.3, 110.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}ClN_2O_2$ 349.0738; Found 349.0739.



3la

4-Bromo-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3la)

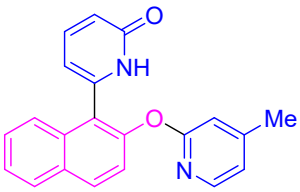
Eluent: dichloromethane/methanol (30:1). Yellowish solid (71.6 mg, 91%), mp 170.8-171.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.59 (br s, 1H), 8.11 (d, J = 3.2 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 6.0 Hz, 1H), 7.72-7.66 (m, 2H), 7.52-7.50 (m, 2H), 7.24 (d, J = 9.2 Hz, 1H), 7.02-6.95 (m, 2H), 6.65 (s, 1H), 6.42 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5, 162.6, 150.1, 147.7, 141.5, 140.0, 136.8, 132.2, 132.1, 131.1, 128.5, 127.9, 126.0, 124.4, 121.9, 121.6, 121.4, 119.4, 112.7, 112.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}BrN_2O_2$ 393.0233; Found 393.0240.



3ma

6-(2-(Pyridin-2-yloxy)naphthalen-1-yl)-4-(trifluoromethyl)pyridin-2(1*H*)-one (3ma)

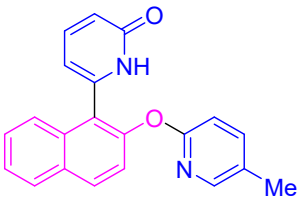
Eluent: dichloromethane/methanol (30:1). Brown solid (71.1 mg, 93%), mp 171.8-172.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.12 (br s, 1H), 8.09 (dd, J_1 = 5.2 Hz, J_2 = 2.0 Hz, 1H), 7.97 (d, J = 9.2 Hz, 1H), 7.91-7.87 (m, 1H), 7.70-7.64 (m, 2H), 7.54-7.49 (m, 2H), 7.27 (d, J = 8.8 Hz, 1H), 6.99 (dd, J_1 = 6.8 Hz, J_2 = 5.2 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.63 (s, 1H), 6.38 (d, J = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5, 162.9, 150.1, 147.7, 143.5, 142.3 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 140.0, 132.3, 132.1, 131.2, 128.6, 128.0, 126.1, 124.2, 122.2 (q, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 121.9, 121.5, 119.4, 117.2, 112.2, 103.9. ^{19}F NMR (565 MHz, $CDCl_3$): δ -66.61 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}F_3N_2O_2$ 383.1002; Found 383.1006.



3na

6-(2-((4-Methylpyridin-2-yl)oxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3na)

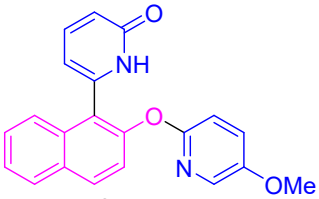
Eluent: dichloromethane/methanol (30:1). White solid (47.9 mg, 73%), mp 209.2-210.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (br s, 1H), 7.99-7.94 (m, 2H), 7.89-7.86 (m, 1H), 7.79-7.76 (m, 1H), 7.51-7.47 (m, 2H), 7.43 (dd, J_1 = 9.2 Hz, J_2 = 6.8 Hz, 1H), 7.24 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 5.2 Hz, 1H), 6.76 (s, 1H), 6.49 (d, J = 9.2 Hz, 1H), 6.27 (d, J = 6.8 Hz, 1H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.9, 163.7, 151.6, 150.0, 147.2, 141.2, 140.7, 132.4, 131.7, 131.2, 128.4, 127.6, 125.8, 124.6, 122.9, 121.6, 120.6, 119.8, 112.4, 108.5, 21.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_2O_2$ 329.1285; Found 329.1290.



3oa

6-(2-((5-Methylpyridin-2-yl)oxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3oa)

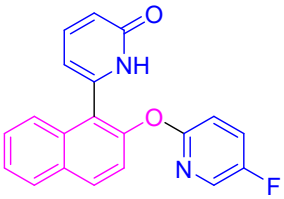
Eluent: dichloromethane/methanol (30:1). White solid (39.4 mg, 60%), mp 242.7-243.6 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.91 (br s, 1H), 7.95-7.94 (m, 2H), 7.89-7.88 (m, 1H), 7.79-7.77 (m, 1H), 7.52-7.48 (m, 3H), 7.44 (dd, J_1 = 9.0 Hz, J_2 = 6.6 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.50 (d, J = 9.6 Hz, 1H), 6.28 (d, J = 6.6 Hz, 1H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5, 162.0, 150.3, 147.4, 141.1, 140.8, 140.7, 132.4, 131.7, 131.2, 128.6, 128.4, 127.6, 125.8, 124.6, 122.9, 121.6, 119.9, 111.6, 108.5, 17.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_2$ 329.1285; Found 329.1284.



3pa

6-(2-((5-Methoxypyridin-2-yl)oxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3pa)

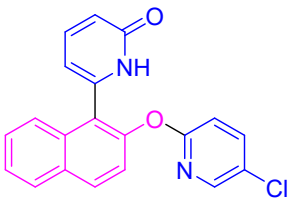
Eluent: dichloromethane/methanol (30:1). White solid (53.0 mg, 77%), mp 260.1-260.9 ºC. ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.99 (br s, 1H), 7.67-7.60 (m, 4H), 7.50 (d, J = 7.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.29-7.19 (m, 3H), 6.97 (d, J = 8.4 Hz, 1H), 6.55 (dd, J_1 = 9.0 Hz, J_2 = 1.2 Hz, 1H), 6.19-6.18 (m, 1H), 3.64 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 163.5, 155.2, 145.6, 144.7, 141.0, 135.4, 133.3, 131.1, 128.0, 127.4, 127.0, 124.7, 123.7, 123.2, 122.1, 119.6, 118.0, 114.9, 108.7, 56.1. HRMS (ESI-TOF) m/z: [M+H]$^{+}$ Calcd for $C_{21}H_{17}N_2O_3$ 345.1234; Found 345.1232.



3qa

6-(2-((5-Fluoropyridin-2-yl)oxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3qa)

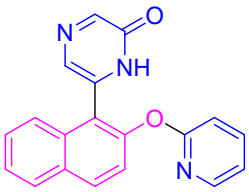
Eluent: dichloromethane/methanol (30:1). White solid (53.2 mg, 80%), mp 237.2-237.7 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.05 (br s, 1H), 8.01 (s, 1H), 7.69-7.63 (m, 4H), 7.52-7.39 (m, 3H), 7.25 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 9.2 Hz, 1H), 6.59 (d, J = 8.8 Hz, 1H), 6.25 (d, J = 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 163.3, 158.8 (d, $^{1}J_{C\text{-}F}$ = 252.8 Hz), 148.2, 145.2, 141.3, 136.3 (d, $^{2}J_{C\text{-}F}$ = 25.2 Hz), 133.2, 131.3, 128.1, 127.4, 127.2, 125.2 (d, $^{3}J_{C\text{-}F}$ = 5.6 Hz), 124.9 (d, $^{2}J_{C\text{-}F}$ = 19.8 Hz), 124.5, 123.3, 119.7, 117.9, 114.5, 109.0. ^{19}F NMR (565 MHz, DMSO-d_6): δ -128.16 (s). HRMS (ESI-TOF) m/z: [M+H]$^{+}$ Calcd for $C_{20}H_{14}FN_2O_2$ 333.1034; Found 333.1039.



3ra

6-(2-((5-Chloropyridin-2-yl)oxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ra)

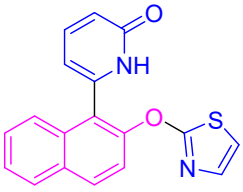
Eluent: dichloromethane/methanol (30:1). White solid (45.3 mg, 65%), mp 229.2-230.1 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.93 (br s, 1H), 8.05 (d, J = 2.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.91-7.90 (m, 1H), 7.75-7.73 (m, 1H), 7.62 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.53-7.50 (m, 2H), 7.43 (dd, J_1 = 9.0 Hz, J_2 = 6.6 Hz, 1H), 7.25 (d, J = 9.0 Hz, 1H), 6.91 (d, J = 9.0 Hz, 1H), 6.49 (d, J = 9.6 Hz, 1H), 6.24 (d, J = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 163.6, 161.9, 149.5, 146.1, 140.9, 140.8, 139.7, 132.4, 131.8, 131.3, 128.5, 127.8, 126.6, 126.1, 124.7, 122.9, 121.4, 119.9, 112.9, 108.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}ClN_2O_2$ 349.0738; Found 349.0734.



3sa

6-(2-(Pyridin-2-yloxy)naphthalen-1-yl)pyrazin-2(1*H*)-one (3sa)

Eluent: dichloromethane/methanol (30:1). Brownish solid (51.1 mg, 81%), mp 229.2-230.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.11 (br s, 1H), 8.09 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H), 8.03 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.90-7.87 (m, 1H), 7.76-7.73 (m, 1H), 7.71-7.67 (m, 1H), 7.55-7.50 (m, 2H), 7.44 (s, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.03-6.99 (m, 1H), 6.96 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.4, 156.9, 150.6, 148.1, 147.7, 140.1, 133.4, 132.4, 132.3, 131.2, 128.6, 127.9, 126.1, 126.0, 124.3, 121.4, 119.8, 119.5, 112.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}N_3O_2$ 316.1081; Found 316.1078.

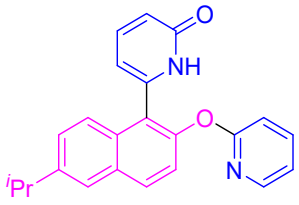


3ta

6-(2-(Thiazol-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ta)

Eluent: dichloromethane/methanol (30:1). White solid (50.6 mg, 79%), mp 259.1-260.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (br s, 1H), 8.00 (d, J = 6.0 Hz, 1H), 7.92-7.90 (m, 1H), 7.73-7.70 (m, 1H), 7.54-7.50

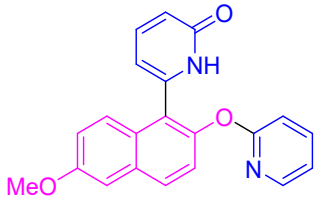
(m, 2H), 7.46-7.42 (m, 2H), 7.13 (d, J = 2.4 Hz, 1H), 6.79 (d, J = 2.4 Hz, 1H), 6.48 (dd, J_1 = 6.0 Hz, J_2 = 0.4 Hz, 1H), 6.26 (dd, J_1 = 4.4 Hz, J_2 = 0.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 173.6, 163.9, 150.5, 140.7, 140.3, 137.5, 132.4, 132.1, 131.6, 128.4, 127.9, 126.4, 124.9, 122.3, 120.13, 120.08, 113.7, 108.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}N_2O_2S$ 321.0692; Found 321.0694.



3ab

6-(6-Isopropyl-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ab)

Eluent: dichloromethane/methanol (30:1). White solid (58.5 mg, 82%), mp 226.9-227.7 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 10.21 (br s, 1H), 8.10 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.69-7.67 (m, 2H), 7.65-7.61 (m, 1H), 7.41-7.37 (m, 2H), 7.22 (d, J = 8.8 Hz, 1H), 6.96 (dd, J_1 = 6.8 Hz, J_2 = 5.6 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.44 (dd, J_1 = 9.2 Hz, J_2 = 0.8 Hz, 1H), 6.24 (dd, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 1H), 3.12-3.02 (m, 1H), 1.33 (d, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 163.85, 163.75, 149.3, 147.7, 146.5, 141.4, 140.7, 139.8, 131.5, 131.3, 131.0, 127.5, 124.7, 122.8, 121.6, 119.6, 119.0, 112.0, 108.5, 34.0, 23.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2O_2$ 357.1598; Found 357.1600.

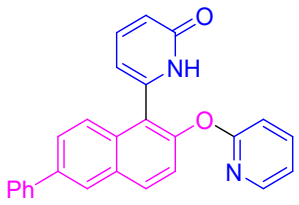


3ac

6-(6-Methoxy-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ac)

Eluent: dichloromethane/methanol (30:1). White solid (57.9 mg, 84%), mp 253.1-253.5 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ 9.78 (br s, 1H), 8.13 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.68-7.65 (m, 2H), 7.41 (dd, J_1 = 9.0 Hz, J_2 = 6.6 Hz, 1H), 7.23 (d, J = 9.0 Hz, 1H), 7.19-7.16 (m, 2H), 6.99 (dd, J_1 = 6.6 Hz, J_2 = 5.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.49-6.48 (m, 1H), 6.25-6.24 (m, 1H), 3.93 (s, 3H). $^{13}C\{^1H\}$ NMR

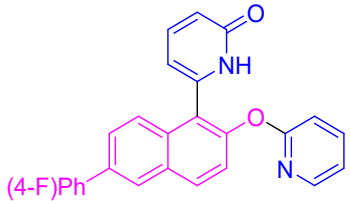
(100 MHz, $CDCl_3$): δ 163.8, 163.5, 157.7, 148.1, 147.7, 141.2, 140.7, 139.9, 132.6, 130.4, 127.5, 126.2, 123.1, 122.2, 120.2, 119.8, 119.0, 112.0, 108.4, 106.6, 55.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_3$ 345.1234; Found 345.1227.



3ad

6-(6-Phenyl-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ad)

Eluent: dichloromethane/methanol (30:1). White solid (64.0 mg, 82%), mp 246.4-247.2 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ 9.54 (br s, 1H), 8.15 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 8.10 (d, J = 1.8 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.79 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.72-7.69 (m, 3H), 7.50 (t, J = 7.8 Hz, 2H), 7.46 (dd, J_1 = 9.6 Hz, J_2 = 6.6 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.03 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.53 (d, J = 9.0 Hz, 1H), 6.30 (d, J = 6.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 163.7, 163.4, 149.9, 147.8, 140.9, 140.7, 140.4, 140.0, 138.8, 132.0, 131.6, 131.5, 129.0, 127.7, 127.4, 127.3, 126.2, 125.2, 122.9, 122.1, 120.0, 119.3, 112.1, 108.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{19}N_2O_2$ 391.1441; Found 391.1443.

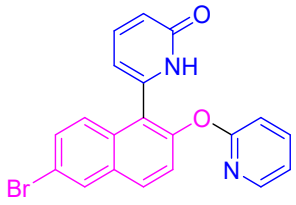


3ae

6-(6-(4-Fluorophenyl)-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ae)

Eluent: dichloromethane/methanol (30:1). White solid (61.3 mg, 75%), mp 238.7-239.7 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ 10.38 (br s, 1H), 8.12 (d, J = 4.2 Hz, 1H), 8.02-7.98 (m, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.69-7.63 (m, 4H), 7.41 (dd, J_1 = 9.0 Hz, J_2 = 7.2 Hz, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.17 (t, J = 8.4 Hz, 2H), 6.99 (t, J = 6.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 9.6 Hz, 1H), 6.27 (d, J = 7.2 Hz, 1H). $^{13}C\{^1H\}$ NMR

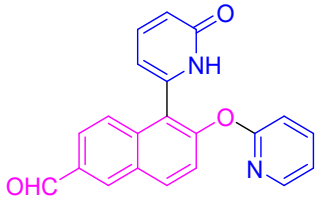
(150 MHz, $CDCl_3$): δ 163.9, 163.6, 162.7 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 149.9, 147.7, 141.1, 140.7, 139.9, 137.6, 136.5 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 131.8, 131.5 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 129.0, 128.9, 127.0, 126.0, 125.4, 122.9, 122.2, 119.8, 119.2, 115.9 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 112.1, 108.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.93 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{18}FN_2O_2$ 409.1347; Found 409.1344.



3af

6-(6-Bromo-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3af)

Eluent: dichloromethane/methanol (30:1). White solid (62.9 mg, 80%), mp 247.0-248.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (br s, 1H), 8.14 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H), 8.07 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.73-7.65 (m, 2H), 7.58 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.44 (dd, J_1 = 9.2 Hz, J_2 = 6.4 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 7.03 (dd, J_1 = 7.2 Hz, J_2 = 5.6 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 9.2 Hz, 1H), 6.24 (d, J = 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5, 163.4, 150.2, 147.7, 140.6, 140.4, 140.1, 132.4, 131.0, 130.7, 130.4, 126.4, 123.2, 122.9, 120.2, 120.0, 119.4, 112.2, 108.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}BrN_2O_2$ 393.0233; Found 393.0229.

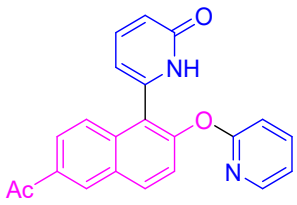


3ag

5-(6-Oxo-1,6-dihydropyridin-2-yl)-6-(pyridin-2-yloxy)-2-naphthaldehyde (3ag)

Eluent: dichloromethane/methanol (30:1). White solid (63.0 mg, 92%), mp 196.1-197.2 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.46 (br s, 1H), 10.17 (s, 1H), 8.39 (d, J = 1.2 Hz, 1H), 8.14-8.13 (m, 2H), 7.95 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.71-7.68 (m, 1H), 7.43 (dd, J_1 = 9.6 Hz, J_2 = 6.6 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 7.04-7.02 (m, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.47 (dd, J_1 = 9.6 Hz, J_2 = 1.2 Hz, 1H), 6.26

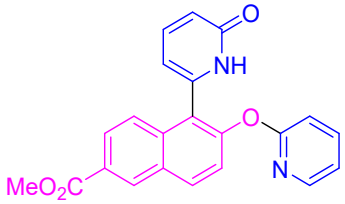
(dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 191.7, 163.7, 163.2, 152.6, 147.7, 140.7, 140.3, 140.1, 135.8, 134.1, 133.9, 133.1, 130.5, 125.8, 124.8, 123.3, 122.9, 120.2, 119.6, 112.3, 108.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}N_2O_3$ 343.1077; Found 343.1072.



3ah

6-(6-Acetyl-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ah)

Eluent: dichloromethane/methanol (30:1). White solid (64.1 mg, 90%), mp 216.2-217.0 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ 9.90 (br s, 1H), 8.51 (d, J = 1.8 Hz, 1H), 8.14 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 8.04 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.72-7.69 (m, 1H), 7.45 (dd, J_1 = 9.6 Hz, J_2 = 7.2 Hz, 1H), 7.35 (d, J = 9.0 Hz, 1H), 7.04 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 9.0 Hz, 1H), 6.26 (d, J = 7.2 Hz, 1H), 2.73 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 197.5, 163.5, 163.3, 152.1, 147.7, 140.7, 140.4, 140.1, 134.9, 134.4, 133.2, 130.4, 130.2, 125.8, 125.2, 123.0, 122.6, 120.2, 119.5, 112.3, 108.6, 26.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_3$ 357.1234; Found 357.1223.

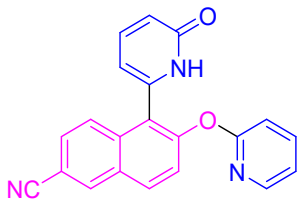


3ai

Methyl 5-(6-oxo-1,6-dihydropyridin-2-yl)-6-(pyridin-2-yloxy)-2-naphthoate (3ai)

Eluent: dichloromethane/methanol (30:1). White solid (67.8 mg, 91%), mp 220.3-221.3 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ 11.07 (br s, 1H), 8.61 (d, J = 1.2 Hz, 1H), 8.10 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 8.05-8.01 (m, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.65-7.62 (m, 1H), 7.39 (dd, J_1 = 9.6 Hz, J_2 = 7.2 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H), 6.99-6.97 (m, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.41 (dd, J_1 = 9.6 Hz, J_2 = 0.6 Hz, 1H), 6.24-6.23 (m,

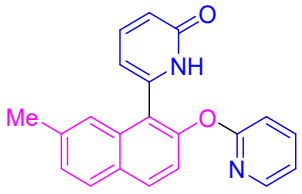
1H), 3.97 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 166.8, 164.2, 163.2, 151.8, 147.6, 140.8, 140.7, 139.9, 134.9, 132.8, 131.3, 130.2, 127.3, 126.8, 125.0, 122.8, 122.4, 119.8, 119.3, 112.2, 108.8, 52.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_4$ 373.1183; Found 373.1178.



3aj

5-(6-Oxo-1,6-dihydropyridin-2-yl)-6-(pyridin-2-yloxy)-2-naphthonitrile (3aj)

Eluent: dichloromethane/methanol (30:1). White solid (55.7 mg, 82%), mp 217.5-218.1 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.89 (br s, 1H), 8.70 (d, J = 1.2 Hz, 1H), 8.23 (d, J = 9.2 Hz, 1H), 8.14-8.12 (m, 1H), 7.86-7.82 (m, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 9.2 Hz, 1H), 7.44 (dd, J_1 = 8.8 Hz, J_2 = 6.8 Hz, 1H), 7.16-7.13 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.36 (d, J = 9.2 Hz, 1H), 6.11 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ 162.8, 162.6, 151.8, 147.3, 140.3, 134.5, 134.1, 131.3, 129.3, 127.7, 126.0, 123.7, 119.5, 118.9, 111.5, 107.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}N_3O_2$ 340.1081; Found 340.1077.

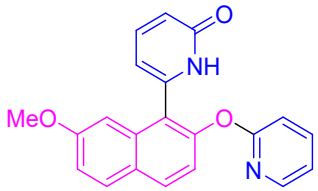


3ak

6-(7-Methyl-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ak)

Eluent: dichloromethane/methanol (30:1). White solid (49.9 mg, 76%), mp 238.2-239.1 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.03 (br s, 1H), 8.12 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.66-7.63 (m, 1H), 7.47 (s, 1H), 7.42 (dd, J_1 = 9.0 Hz, J_2 = 6.6 Hz, 1H), 7.32 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 6.97 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.47 (d, J = 9.6 Hz, 1H), 6.25 (d, J = 6.6 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 163.75,

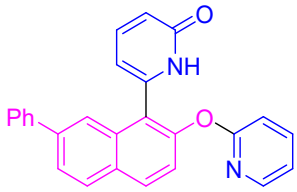
163.68, 150.0, 147.7, 141.4, 140.8, 139.8, 137.7, 132.7, 131.4, 129.5, 128.3, 128.1, 123.6, 122.3, 120.6, 119.7, 119.0, 112.0, 108.5, 22.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_2$ 329.1285; Found 329.1284.



3al

6-(7-Methoxy-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3al)

Eluent: dichloromethane/methanol (30:1). White solid (58.5 mg, 85%), mp 186.4-187.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (br s, 1H), 8.12 (d, J = 3.6 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 6.8 Hz, 1H), 7.14 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.01-6.91 (m, 3H), 6.47 (d, J = 9.2 Hz, 1H), 6.27 (d, J = 6.8 Hz, 1H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.8, 163.7, 159.0, 150.6, 147.7, 141.6, 140.7, 139.8, 134.0, 131.4, 130.0, 126.7, 121.9, 119.7, 119.1, 118.9, 118.2, 112.1, 108.3, 103.4, 55.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_3$ 345.1234; Found 345.1228.

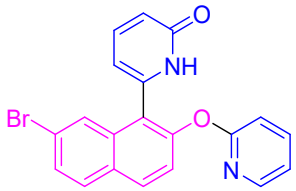


3am

6-(7-Phenyl-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3am)

Eluent: dichloromethane/methanol (30:1). White solid (67.2 mg, 86%), mp 228.5-229.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.22 (br s, 1H), 8.13-8.11 (m, 1H), 7.97-7.92 (m, 3H), 7.75 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.67-7.62 (m, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.45-7.33 (m, 4H), 7.24 (d, J = 5.2 Hz, 1H), 6.99-6.93 (m, 2H), 6.47 (d, J = 9.2 Hz, 1H), 6.28 (d, J = 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.8, 163.6, 150.4, 147.7, 141.2, 140.74, 140.47, 139.9, 132.8, 131.4, 130.4, 129.0, 127.8, 127.6, 125.7, 123.1, 122.5,

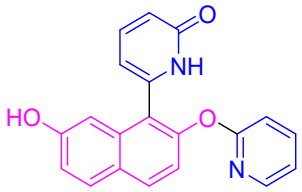
121.6, 119.9, 119.2, 112.1, 108.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{19}N_2O_2$ 391.1441; Found 391.1433.



3an

6-(7-Bromo-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3an)

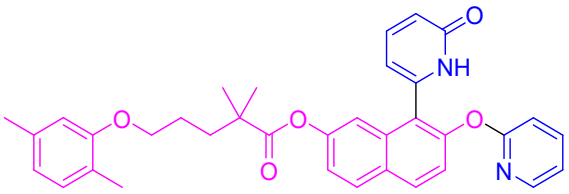
Eluent: dichloromethane/methanol (30:1). White solid (63.7 mg, 81%), mp 231.4-232.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (br s, 1H), 8.13 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 7.94-7.91 (m, 2H), 7.76 (d, J = 5.6 Hz, 1H), 7.69 (td, J_1 = 5.6 Hz, J_2 = 1.2 Hz, 1H), 7.59 (dd, J_1 = 5.6 Hz, J_2 = 1.2 Hz, 1H), 7.44 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 1H), 7.28 (d, J =6.0 Hz, 1H), 7.02 (dd, J_1 = 4.8 Hz, J_2 = 3.6 Hz, 1H), 6.97 (d, J = 5.6 Hz, 1H), 6.50-6.49 (m, 1H), 6.25-6.24 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 163.6, 163.4, 150.8, 147.7, 140.8, 140.4, 140.0, 133.7, 131.6, 130.0, 129.7, 129.4, 126.8, 122.3, 122.2, 122.1, 120.2, 119.4, 112.2, 108.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}BrN_2O_2$ 393.0233; Found 393.0234.



3ao

6-(7-Hydroxy-2-(pyridin-2-yloxy)naphthalen-1-yl)pyridin-2(1*H*)-one (3ao)

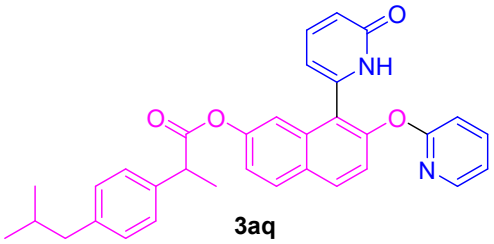
Eluent: dichloromethane/methanol (30:1). White solid (46.2 mg, 70%), mp 248.3-249.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.92 (br s, 1H), 10.00 (s, 1H), 8.12 (d, J = 3.6 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.79-7.75 (m, 1H), 7.41 (dd, J_1 = 8.8 Hz, J_2 = 6.8 Hz, 1H), 7.13-7.06 (m, 3H), 6.95 (d, J = 8.4 Hz, 1H), 6.88 (s, 1H), 6.32 (d, J = 9.2 Hz, 1H), 6.05 (d, J = 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.7, 163.6, 157.1, 150.2, 147.9, 143.0, 141.1, 140.6, 134.9, 131.1, 130.4, 125.7, 122.0, 119.5, 118.9, 118.7, 118.6, 111.7, 107.6, 106.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}N_2O_3$ 331.1077; Found 331.1074.



3ap

8-(6-Oxo-1,6-dihydropyridin-2-yl)-7-(pyridin-2-yloxy)naphthalen-2-yl 5-(2,5-dimethylphenoxy)- 2,2-dimethylpentanoate (3ap)

Eluent: dichloromethane/methanol (50:1). Brown solid (101.3 mg, 90%), mp 194.0-195.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.87 (br s, 1H), 8.14-8.08 (m, 3H), 7.83-7.79 (m, 1H), 7.39-7.32 (m, 2H), 7.27 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 7.11 (dd, J_1 = 7.2 Hz, J_2 = 5.2 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.27 (d, J = 9.2 Hz, 1H), 6.03 (br s, 1H), 3.96 (t, J = 6.0 Hz, 2H), 2.25 (s, 3H), 2.06 (s, 3H), 1.85-1.74 (m, 4H), 1.31 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.5, 163.8, 163.5, 156.9, 150.7, 150.4, 147.7, 140.80, 140.76, 140.0, 136.5, 133.2, 131.5, 130.4, 129.9, 129.2, 123.6, 122.6, 121.44, 121.36, 120.8, 119.9, 119.3, 115.7, 112.2, 112.0, 108.7, 67.7, 42.5, 37.1, 25.3, 25.1, 21.4, 15.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{35}H_{35}N_2O_5$ 563.2540; Found 563.2535.

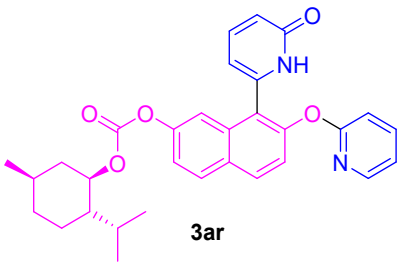


3aq

8-(6-Oxo-1,6-dihydropyridin-2-yl)-7-(pyridin-2-yloxy)naphthalen-2-yl 2-(4-isobutylphenyl)propanoate (3aq)

Eluent: dichloromethane/methanol (30:1). Brown solid (77.8 mg, 75%), mp 152.9-154.1 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.68 (br s, 1H), 8.08 (d, J = 3.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.81 (d, J =9.0 Hz, 1H), 7.62-7.59 (m, 1H), 7.37 (d, J =1.8 Hz, 1H), 7.33 (dd, J_1 = 9.6 Hz, J_2 = 7.2 Hz, 1H), 7.28 (d, J =7.8 Hz, 2H), 7.20 (d, J =9.0 Hz, 1H), 7.13-7.10 (m, 3H), 6.94 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 9.6 Hz, 1H), 6.19 (d, J = 6.6 Hz, 1H), 3.92 (q, J = 7.2 Hz, 1H), 2.46 (d, J = 7.2 Hz, 2H), 1.89-

1.82 (m, 1H), 1.58 (d, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 173.3, 164.1, 163.4, 150.6, 150.2, 147.6, 140.9, 140.7, 139.9, 137.1, 133.3, 131.4, 129.8, 129.6, 129.1, 127.3, 122.6, 121.4, 121.1, 119.7, 119.2, 115.7, 112.1, 108.8, 45.3, 45.1, 30.2, 22.4, 18.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{31}N_2O_4$ 519.2278; Found 519.2270.

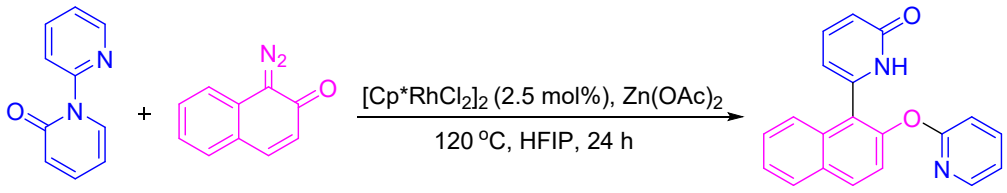


3ar

(1*R*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl (8-(6-oxo-1,6-dihydropyridin-2-yl)-7- (pyridin-2-yloxy) naphthalen-2-yl) carbonate (3ar)

Eluent: dichloromethane/methanol (30:1). Brown solid (80.0 mg, 78%), mp 207.2-207.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.51 (br s, 1H), 8.09 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.66-7.61 (m, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.42-7.36 (m, 2H), 7.24 (d, J = 8.8 Hz, 1H), 6.97 (dd, J_1 = 6.8 Hz, J_2 = 5.2 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 9.2 Hz, 1H), 6.24 (d, J = 6.4 Hz, 1H), 4.63 (td, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1H), 2.19-2.17 (m, 1H), 2.07-2.02 (m, 1H), 1.73-1.69 (m, 2H), 1.52-1.44 (m, 2H), 1.19-1.02 (m, 2H), 0.94-0.88 (m, 7H), 0.83 (d, J = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 163.9, 163.4, 153.1, 150.7, 150.3, 147.6, 140.8, 140.6, 139.9, 133.2, 131.4, 129.9, 129.1, 122.8, 121.5, 120.7, 119.9, 119.2, 115.3, 112.2, 108.7, 79.8, 47.0, 40.6, 34.0, 31.4, 26.2, 23.3, 22.0, 20.8, 16.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{33}N_2O_5$ 513.2384; Found 513.2385.

2. Gram-scale synthesis of 3aa

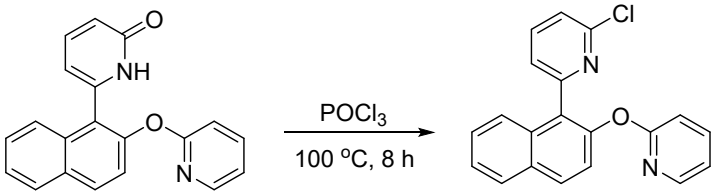


1a, 5 mmol **2a**, 7.5 mmol **3aa**, 1.26 g, 80%

To a reaction tube equipped with a stir bar were added 2*H*-[1,2'-bipyridin]-2-one (**1a**, 0.86 g, 5 mmol), HFIP (20 mL), 1-diazonaphthalen-2(1*H*)-one (**2a**, 1.28 g, 7.5 mmol), $[Cp^*RhCl_2]_2$ (77.3 mg, 0.125 mmol) and $Zn(OAc)_2$ (183.5 mg, 1 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 24 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3aa** (1.26 g, 80%).

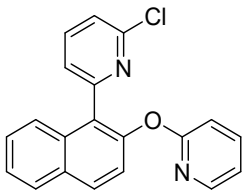
3. Structural elaborations of 3aa

3.1. Synthesis of 4[3]



3aa **4**, 87%

To a reaction tube equipped with a stir bar were added **3aa** (31.4 mg, 0.1 mmol) and $POCl_3$ (2 mL) with stirring. The resulting mixture was heated to reflux for 8 h in an oil bath. Upon completion, the reaction mixture was cooled to room temperature and poured into ice water. Then, saturated $NaHCO_3$ solution was added and crude material was extracted with ethyl acetate (5 mL × 3).The combined organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **4** (29.0 mg, 87%).

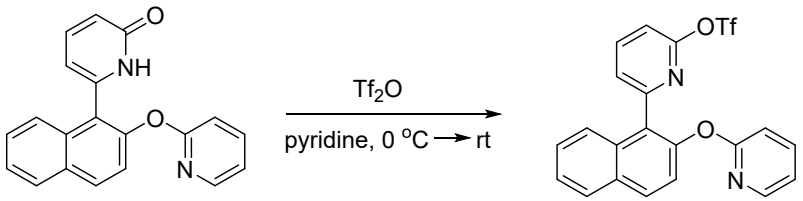


4

2-Chloro-6-(2-(pyridin-2-yloxy)naphthalen-1-yl)pyridine (4)

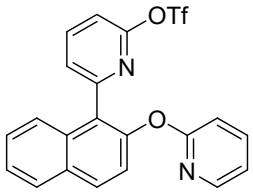
Yellowish solid, mp 139.6-140.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.82-7.79 (m, 1H), 7.58-7.50 (m, 3H), 7.41-7.34 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.25-7.18 (m, 2H), 6.86 (dd, J_1 = 6.8 Hz, J_2 = 5.6 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 162.8, 154.8, 149.9, 148.0, 146.6, 138.3, 137.7, 131.9, 130.4, 129.5, 127.1, 126.6, 126.0, 124.4, 124.3, 123.7, 121.8, 120.6, 117.4, 110.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}ClN_2O$ 333.0789; Found 333.0791.

3.2. Synthesis of 5[4]



3aa **5**, 85%

To a solution of **3aa** (31.4 mg, 0.1 mmol) in pyridine (0.5 mL), Tf_2O (42.3 mg, 0.15 mmol) was added dropwise at 0 °C, and the resulting solution was stirred at room temperature overnight. Upon completion, the resulting mixture was diluted with water, and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **5** (37.9 mg, 85%).



5

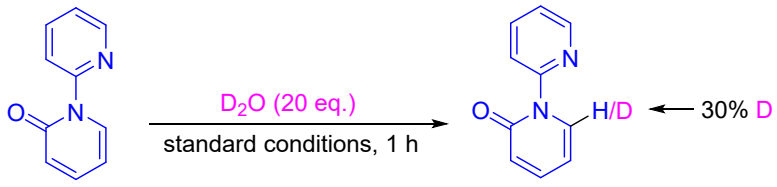
6-(2-(Pyridin-2-yloxy)naphthalen-1-yl)pyridin-2-yl trifluoromethanesulfonate (5)

Yellowish solid. mp 99.2-100.1 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-8.13 (m, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.90-7.85 (m, 2H), 7.67-7.65 (m, 1H), 7.61-7.56 (m, 2H), 7.49-7.44 (m, 2H), 7.32 (d, J = 9.0 Hz, 1H),

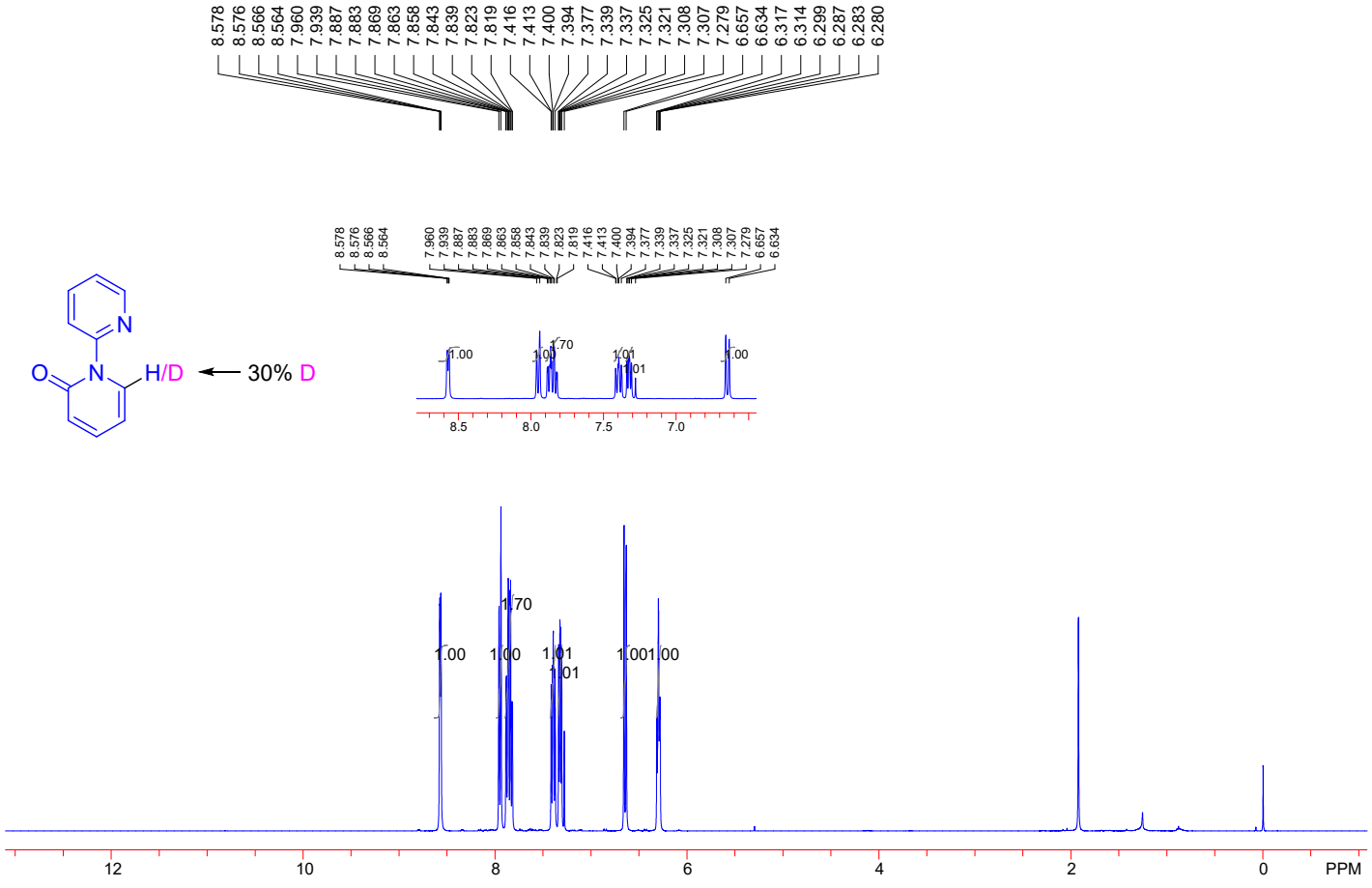
7.14 (d, J = 7.8 Hz, 1H), 6.94 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 163.7, 155.3, 155.1, 149.2, 147.7, 140.8, 139.5, 132.6, 131.4, 131.0, 128.2, 127.1, 127.0, 126.7, 125.6, 125.2, 121.6, 118.64 (d, $J_{C\text{-}F}$ = 318.3 Hz), 118.58, 113.7, 111.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.02 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}F_3N_2O_4S$ 447.0621; Found 447.0623.

III. Mechanism studies

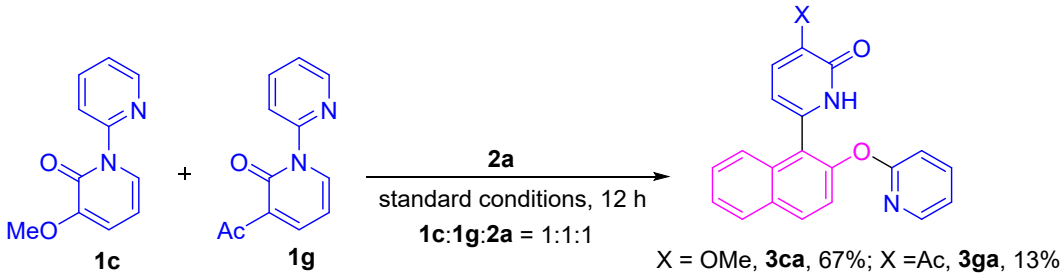
1. H/D exchange experiment



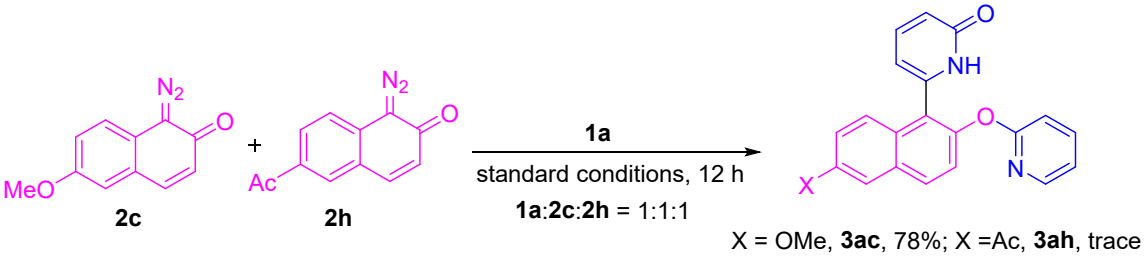
To a reaction tube equipped with a stir bar were added 2*H*-[1,2'-bipyridin]-2-one (**1a**, 34.4 mg, 0.2 mmol), HFIP (2 mL), D_2O (72.4 μL, 4 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) and $Zn(OAc)_2$ (7.3 mg, 0.04 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum dichloromethane/ethyl acetate (1:1) as eluent and ^{1}H NMR indicated that 30% hydrogen at the C6-position of **1a** was deuterated.



2. Electronic competition experiments

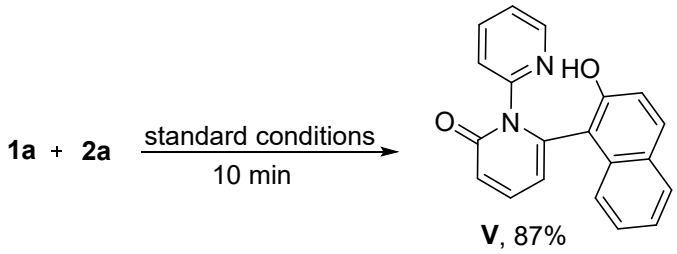


2.1 To a reaction tube equipped with a stir bar were added 3-methoxy-2*H*-[1,2'-bipyridin]-2-one (**1c**, 40.4 mg, 0.2 mmol), 3-acetyl-2*H*-[1,2'-bipyridin]-2-one (**1g**, 42.8 mg, 0.2 mmol), HFIP (2 mL), 1-diazonaphthalen-2(1*H*)-one (**2a**, 34.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) and $Zn(OAc)_2$ (7.3 mg, 0.04 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3ca** (46.1 mg, 67%) and **3ga** (9.3 mg, 13%).

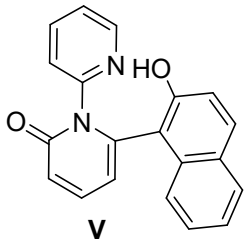


2.2 To a reaction tube equipped with a stir bar were added 1-diazo-6-methoxynaphthalen-2(1*H*)-one (**2c**, 40.0 mg, 0.2 mmol), 6-acetyl-1-diazonaphthalen-2(1*H*)-one (**2h**, 45.6 mg, 0.2 mmol), HFIP (2 mL), 2*H*-[1,2'-bipyridin]-2-one (**1a**, 34.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) and $Zn(OAc)_2$ (7.3 mg, 0.04 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3ac** (53.7 mg, 78%).

3. Isolation and transformation of intermediate V

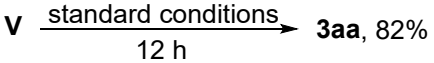


3.1 To a reaction tube equipped with a stir bar were added 2*H*-[1,2'-bipyridin]-2-one (**1a**, 34.4 mg, 0.2 mmol), HFIP (2 mL), 1-diazonaphthalen-2(1*H*)-one (**2a**, 51.1 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 10 min. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1-20:1) as eluent to afford **V** (54.7 mg, 87%).



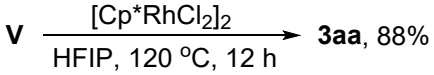
V

White solid, mp 260.9-261.4 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.01 (br s, 1H), 7.99 (br s, 1H), 7.65-7.61 (m, 4H), 7.51 (d, J = 8.0 Hz, 1H), 7.42-7.35 (m, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.06 (t, J = 6.0 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.58 (d, J = 8.8 Hz, 1H), 6.23 (d, J = 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 163.3, 152.1, 148.5, 145.3, 141.1, 137.7, 133.3, 131.1, 128.0, 127.4, 127.0, 124.7, 124.0, 123.4, 123.2, 119.7, 117.9, 114.7, 108.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}N_2O_2$ 315.1128; Found 315.1127.

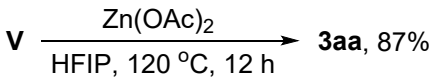


3.2 To a reaction tube equipped with a stir bar were added 6-(2-hydroxynaphthalen-1-yl)-2*H*-[1,2'-bipyridin]-2-one (**V**, 31.4 mg, 0.1 mmol), HFIP (1 mL), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Zn(OAc)_2$ (3.7 mg, 0.02 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the

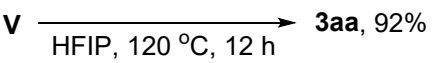
resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3aa** (25.8 mg, 82%).



3.3 To a reaction tube equipped with a stir bar were added 6-(2-hydroxynaphthalen-1-yl)-2*H*-[1,2'-bipyridin]-2-one (**V**, 31.4 mg, 0.1 mmol), HFIP (1 mL), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3aa** (27.7 mg, 88%).

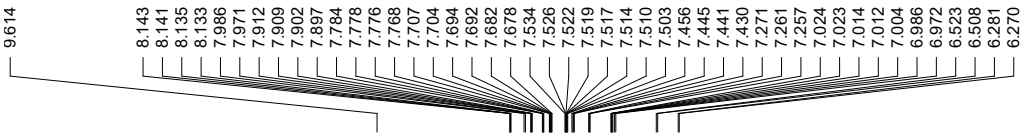


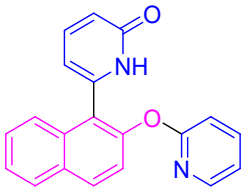
3.4 To a reaction tube equipped with a stir bar were added 6-(2-hydroxynaphthalen-1-yl)-2*H*-[1,2'-bipyridin]-2-one (**V**, 31.4 mg, 0.1 mmol), HFIP (1 mL), $Zn(OAc)_2$ (3.7 mg, 0.02 mmol) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, filtered through a pad of celite and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3aa** (27.3 mg, 87%).



3.5 To a reaction tube equipped with a stir bar were added 6-(2-hydroxynaphthalen-1-yl)-2*H*-[1,2'-bipyridin]-2-one (**V**, 31.4 mg, 0.1 mmol), HFIP (1 mL) with stirring. The mixture was stirred at 120 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature, and evaporated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (30:1) as eluent to afford **3aa** (28.9 mg, 92%).

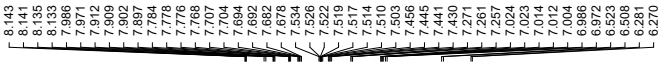
IV. Copies of NMR spectra of 3aa-3ar

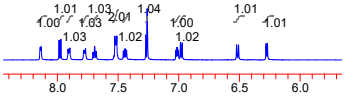


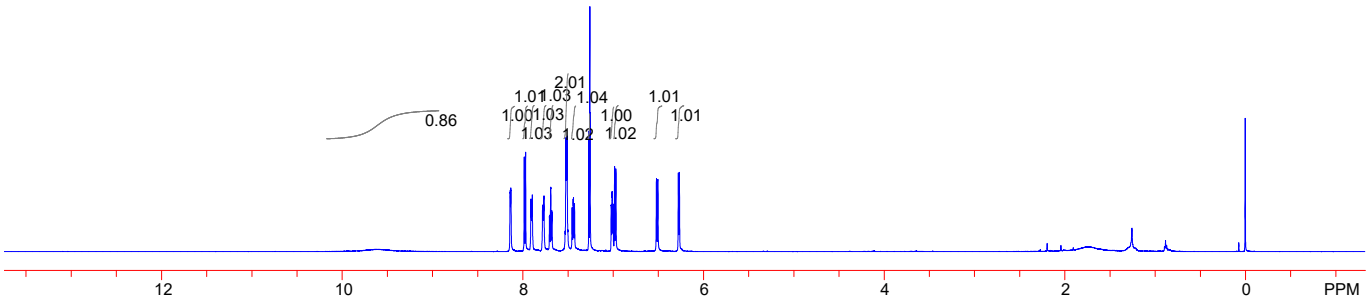


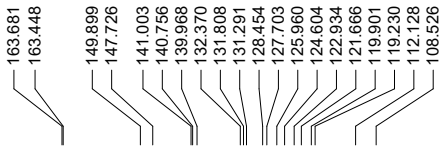
3aa

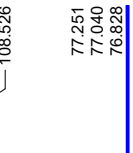
(600 MHz, $CDCl_3$)

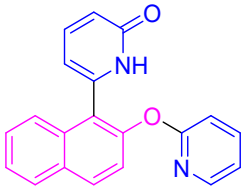






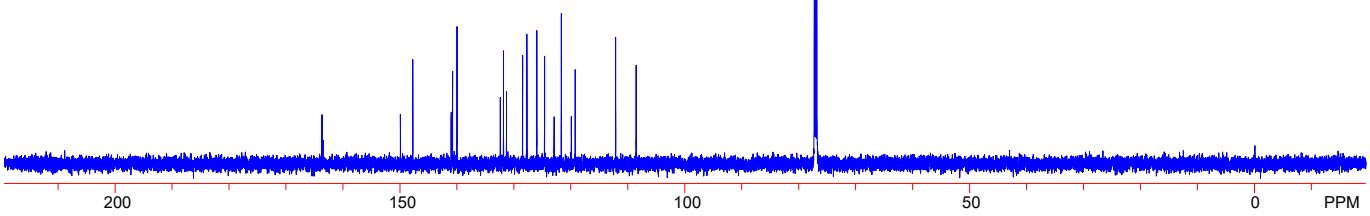


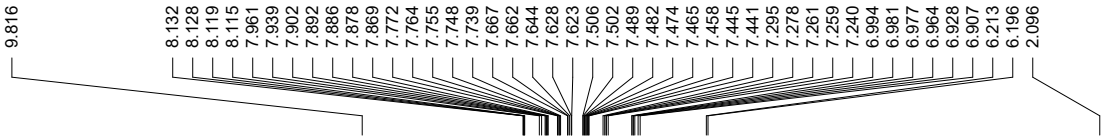


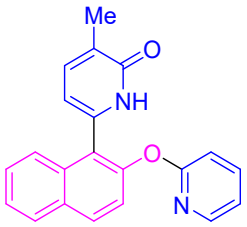


3aa

(150 MHz, $CDCl_3$)

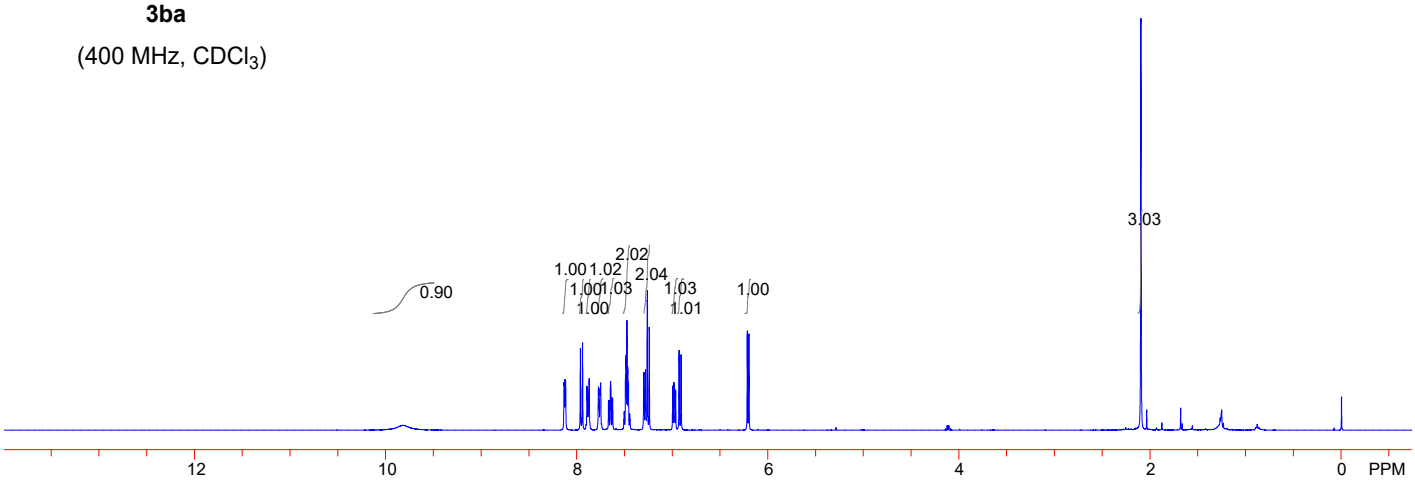


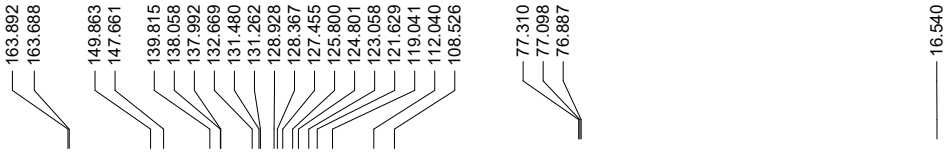


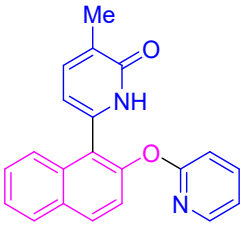


3ba

(400 MHz, $CDCl_3$)

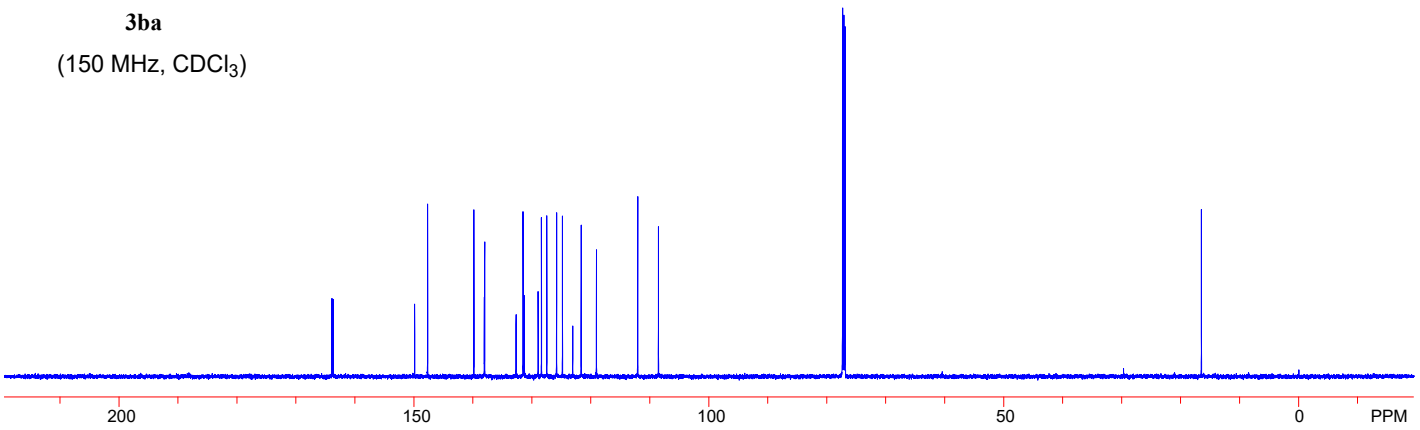


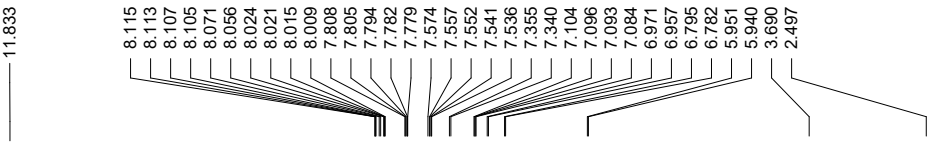


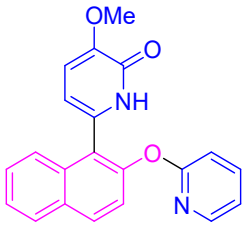


3ba

(150 MHz, $CDCl_3$)

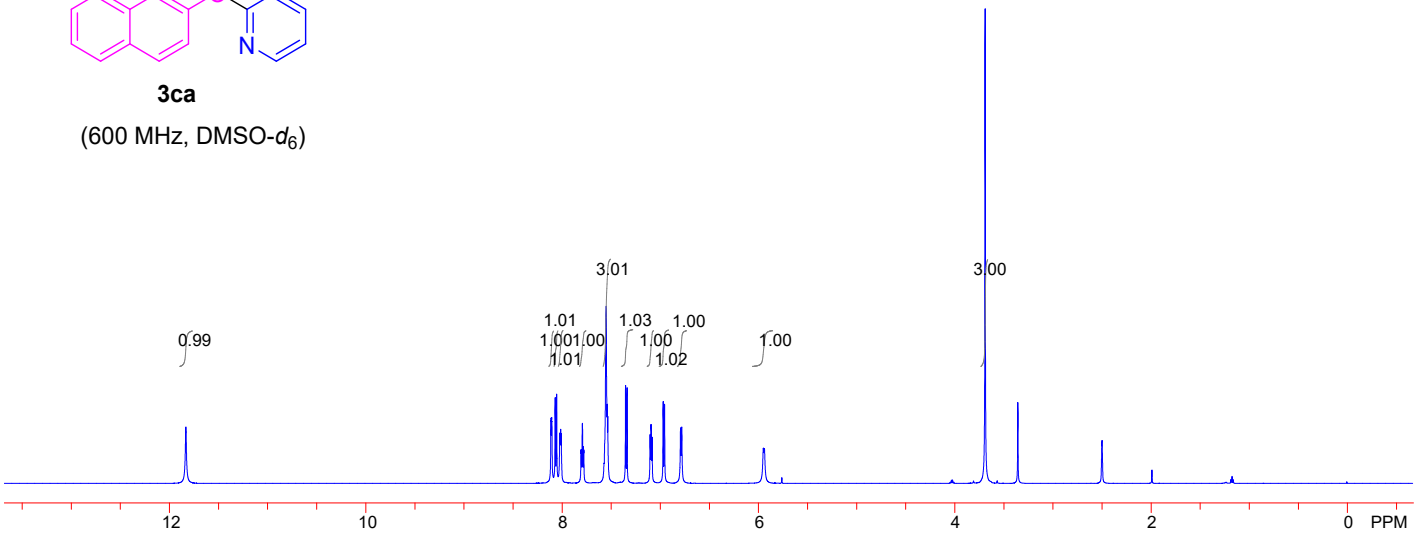


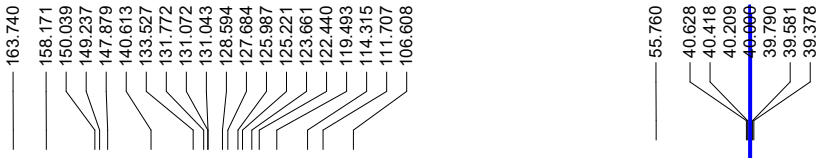


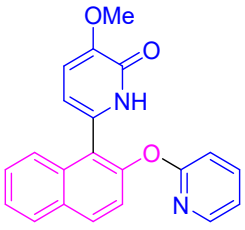


3ca

(600 MHz, DMSO-d_6)

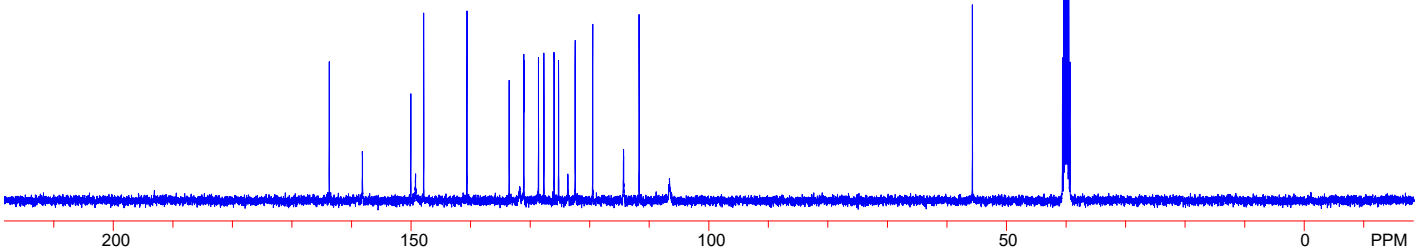


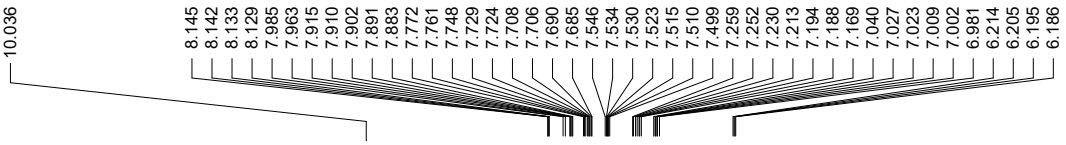


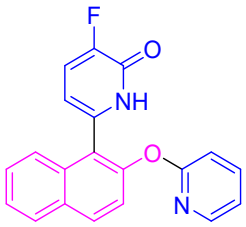


3ca

(100 MHz, DMSO-d_6)

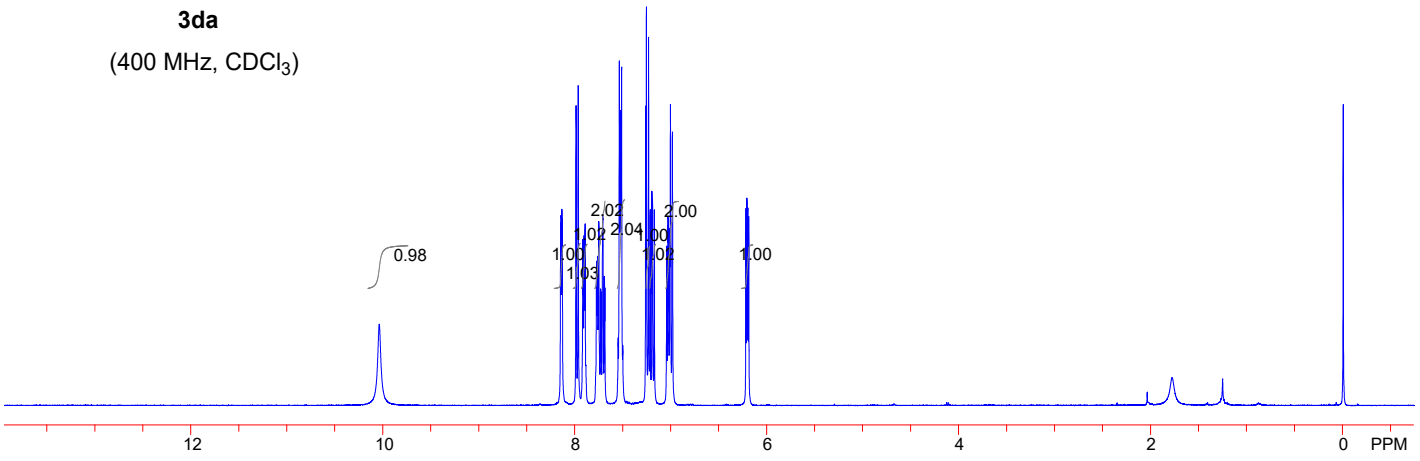


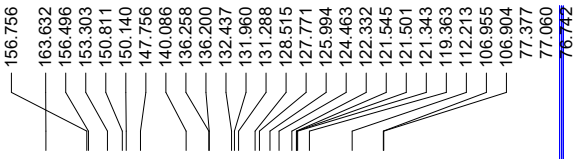


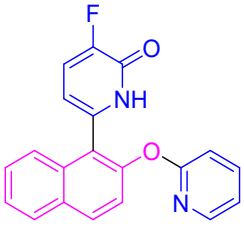


3da

(400 MHz, $CDCl_3$)

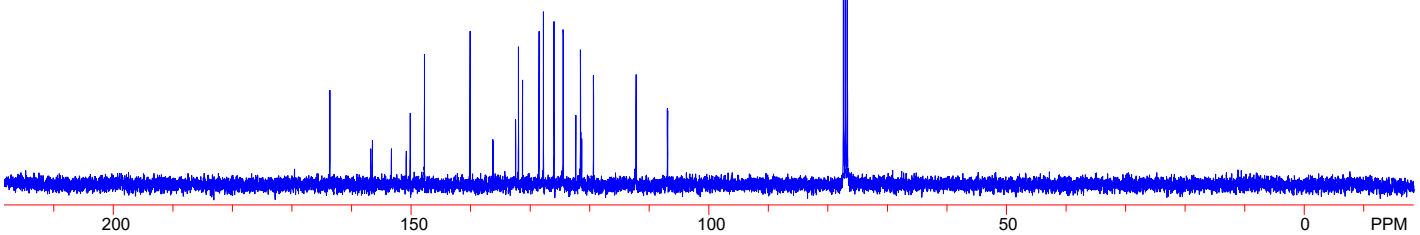


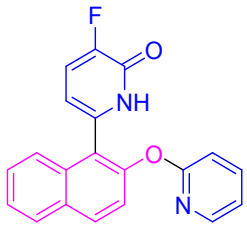




3da

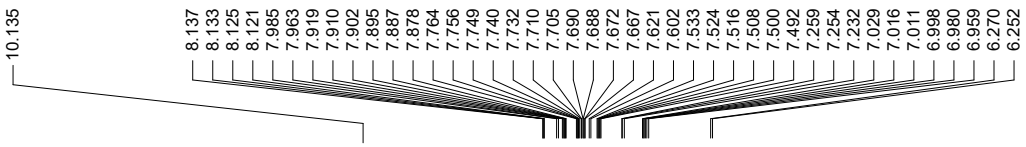
(100 MHz, $CDCl_3$)

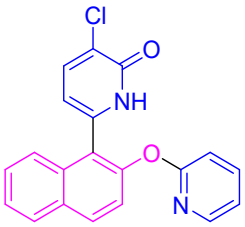




3da

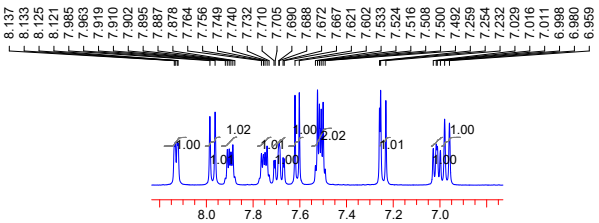
(376 MHz, $CDCl_3$)

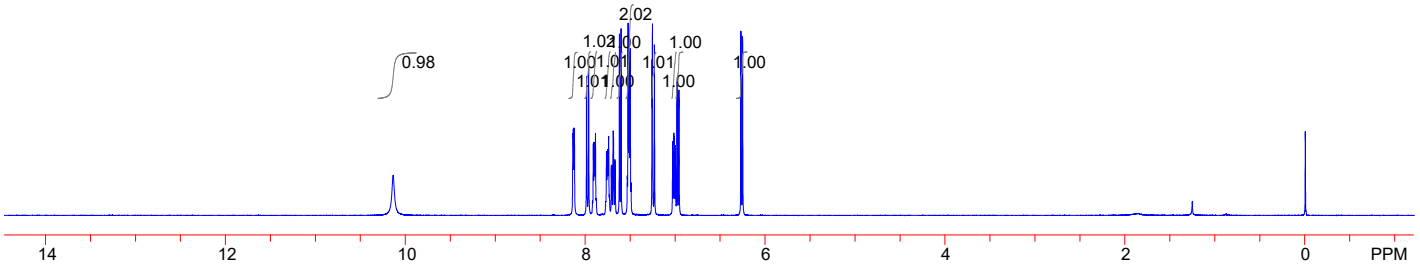


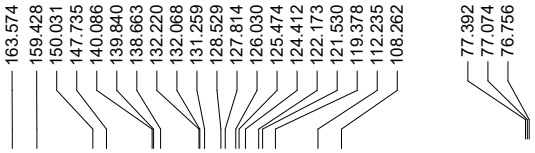


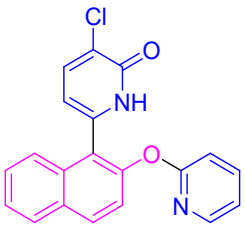
3ea

(400 MHz, $CDCl_3$)



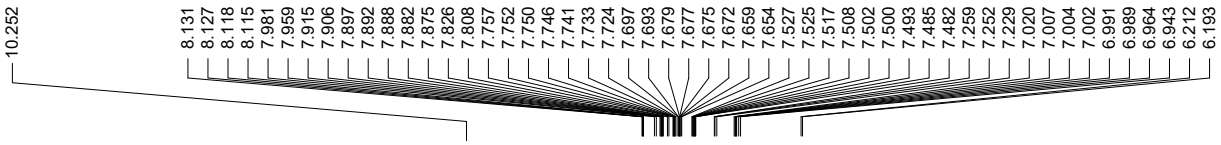


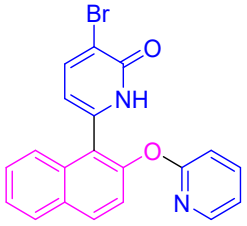




3ea

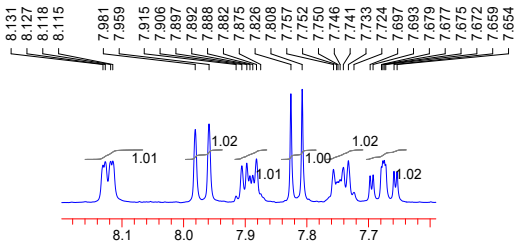
(100 MHz, $CDCl_3$)

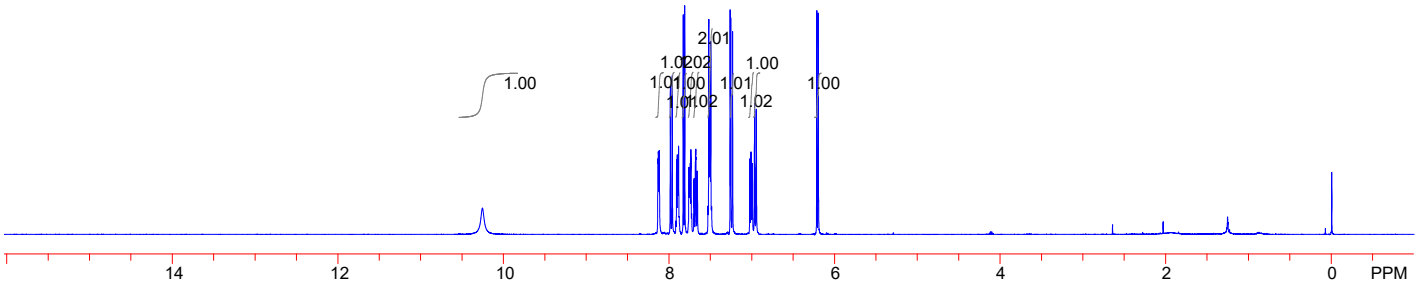


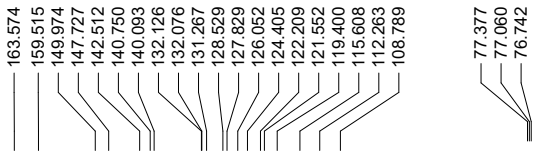


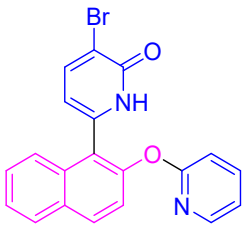
3fa

(400 MHz, $CDCl_3$)



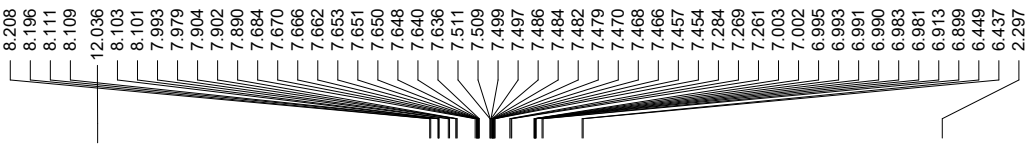


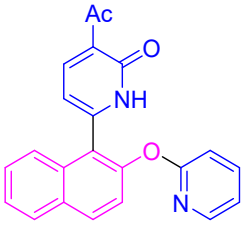




3fa

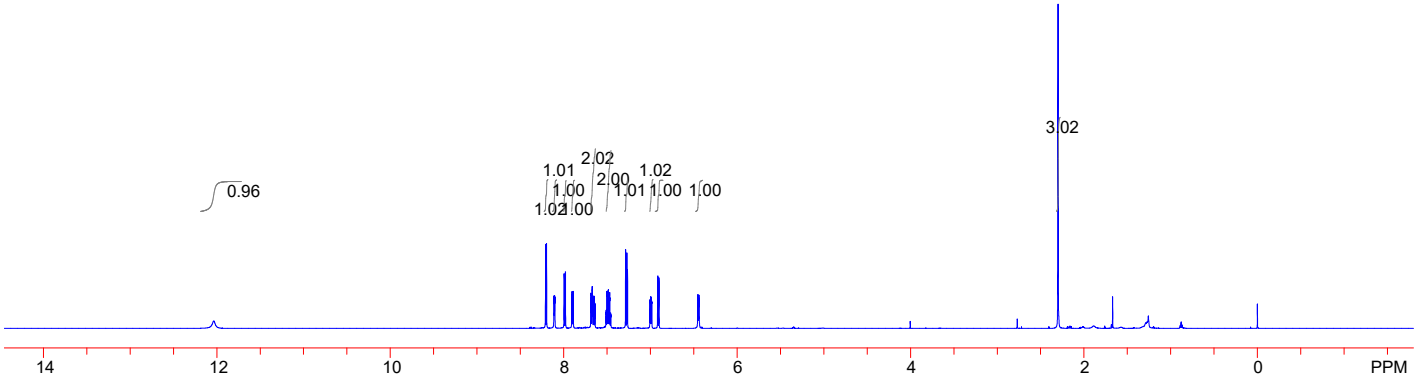
(100 MHz, $CDCl_3$)

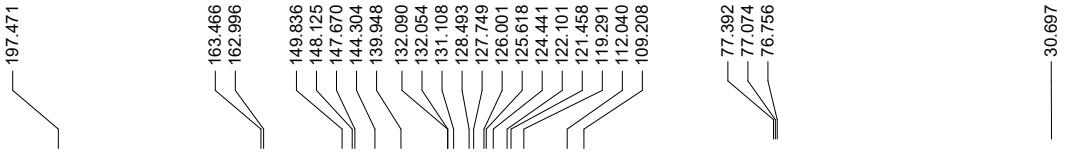


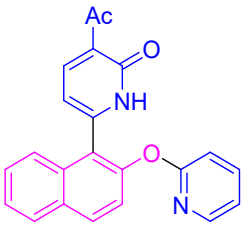


3ga

(600 MHz, $CDCl_3$)

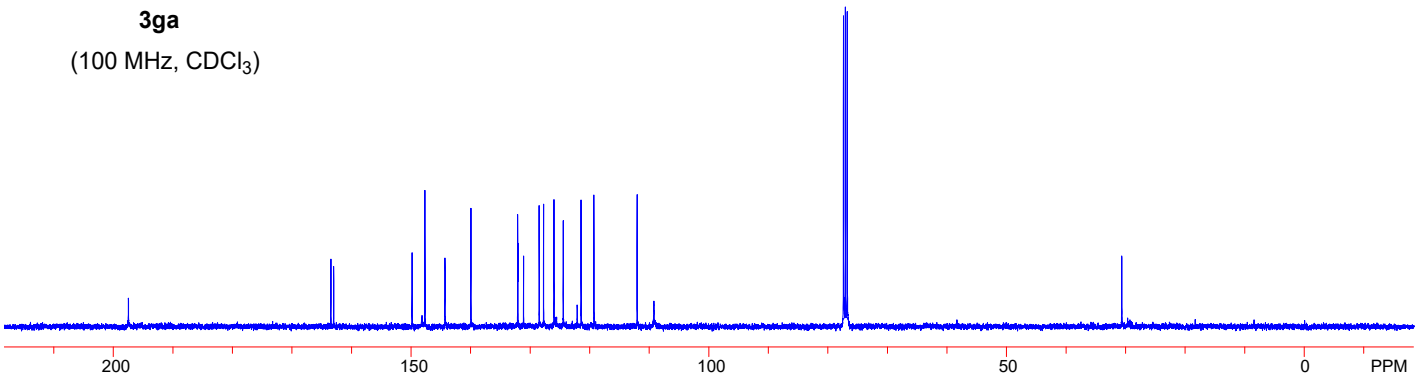


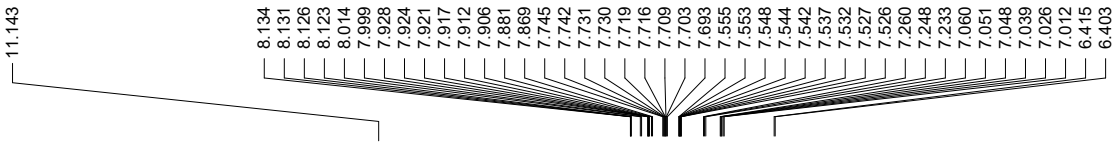


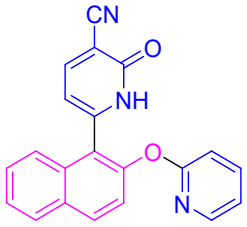


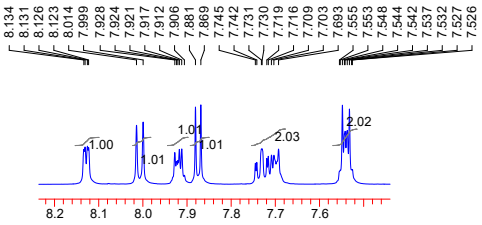
3ga

(100 MHz, $CDCl_3$)



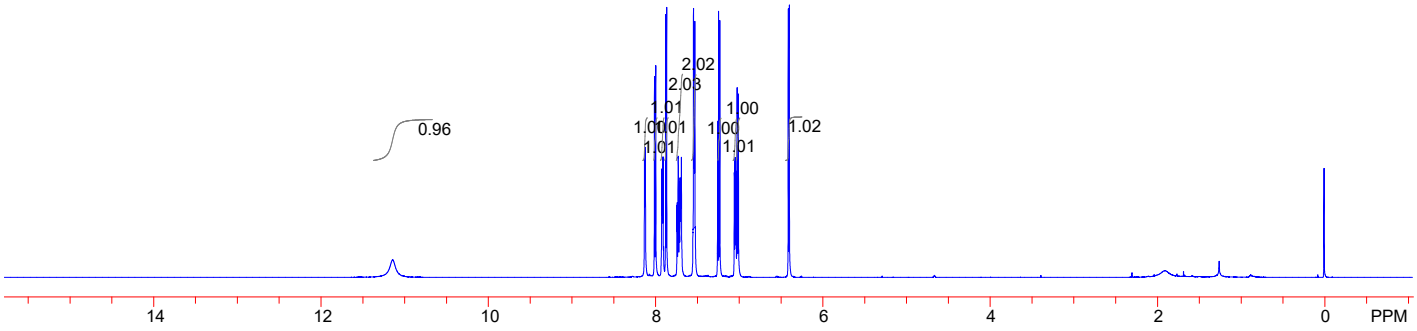


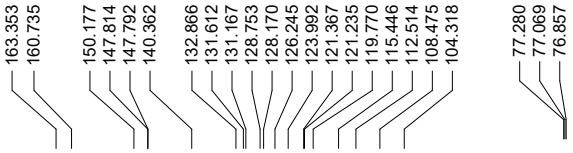


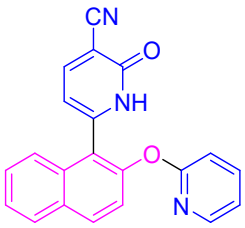


3ha

(600 MHz, $CDCl_3$)

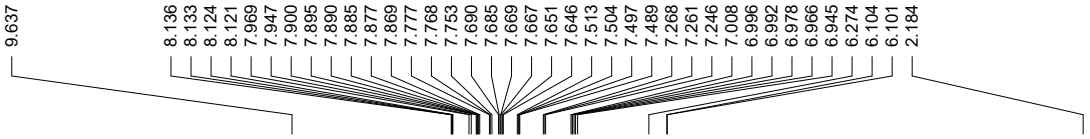


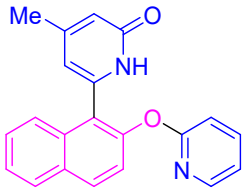




3ha

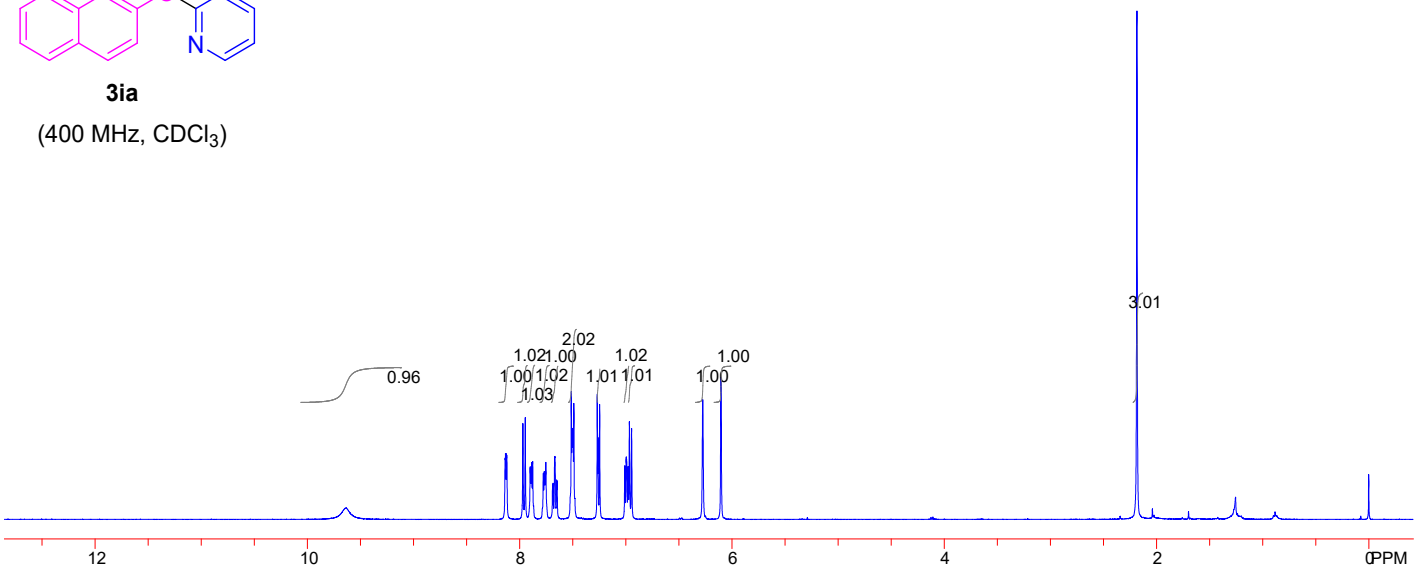
(150 MHz, $CDCl_3$)

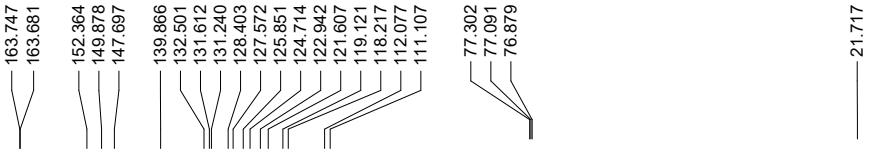


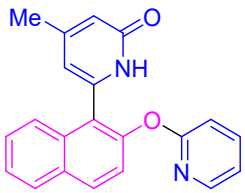


3ia

(400 MHz, $CDCl_3$)

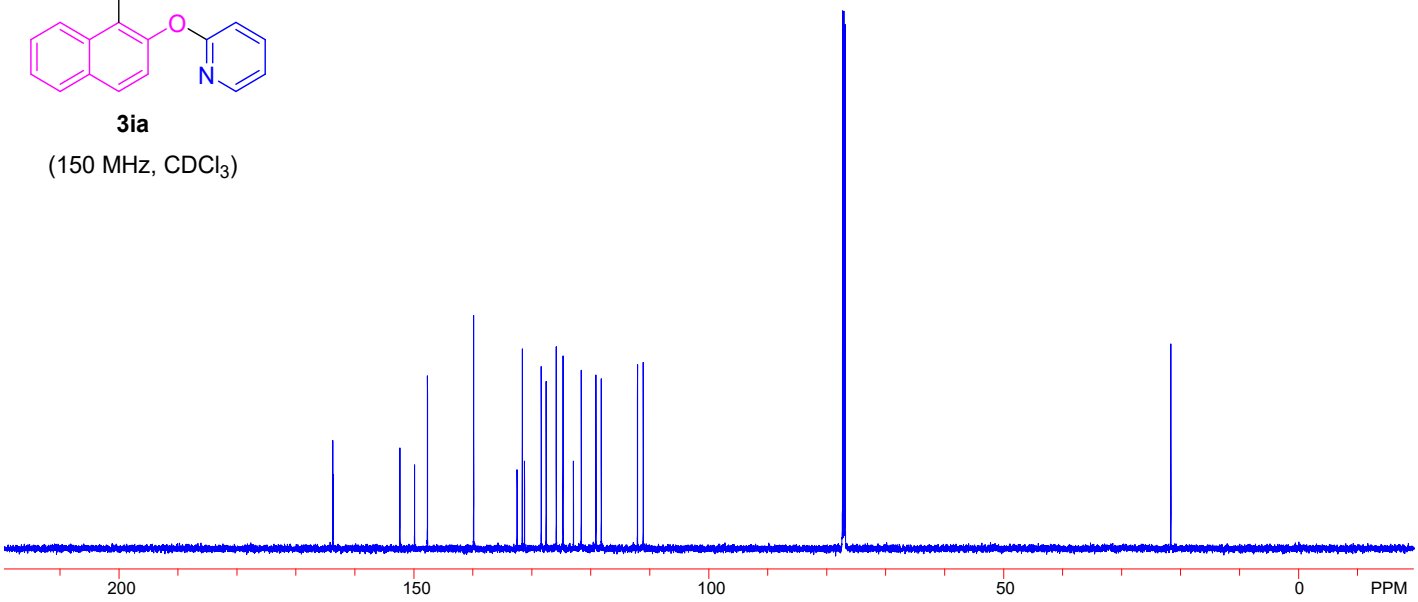


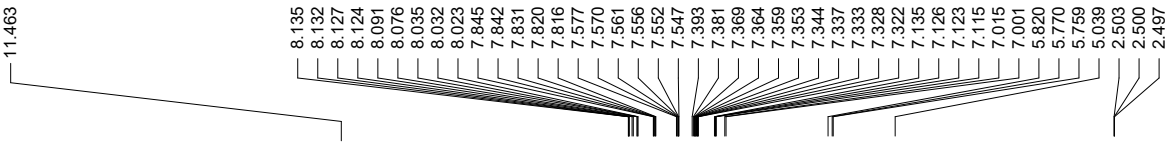


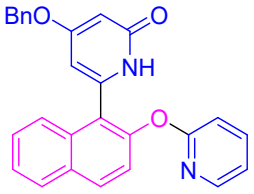


3ia

(150 MHz, $CDCl_3$)

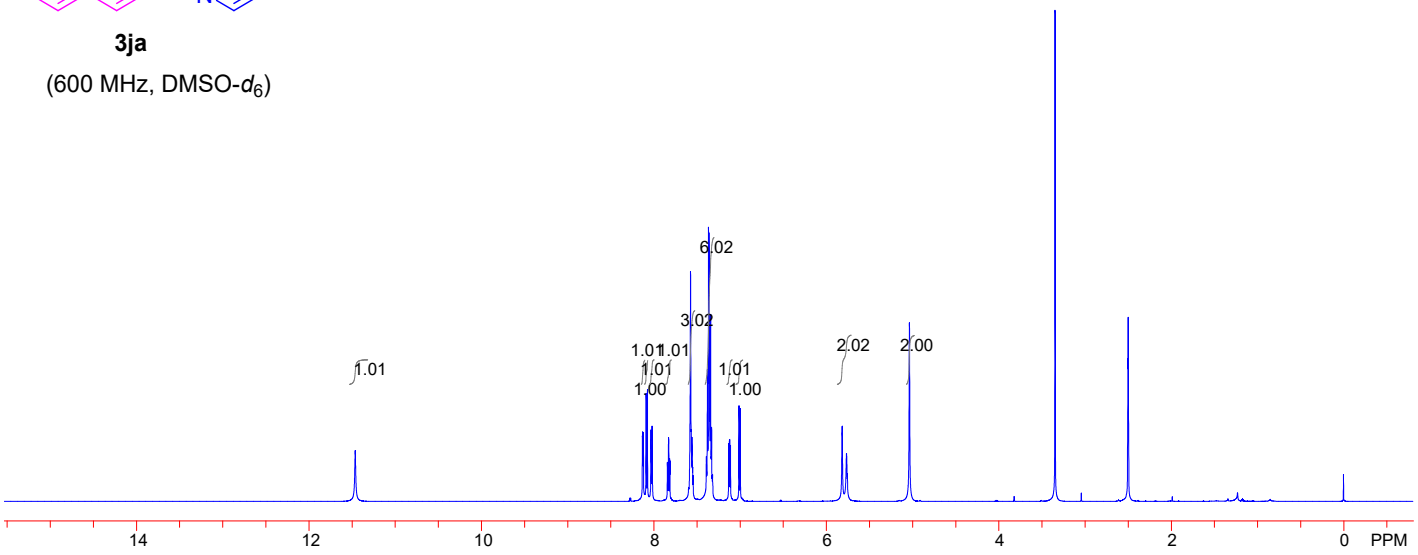


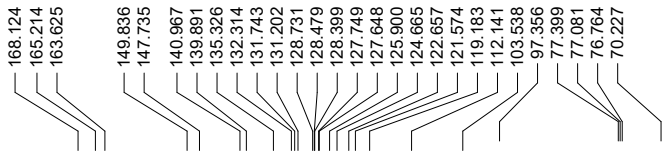


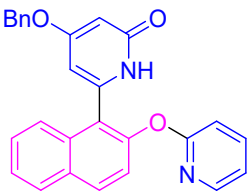


3ja

(600 MHz, DMSO-d_6)

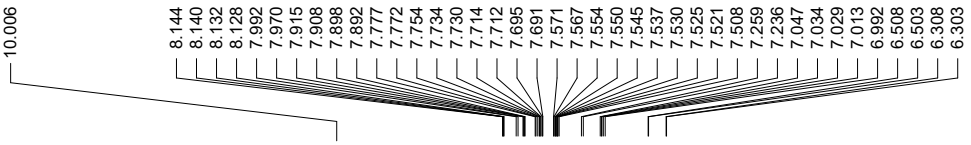


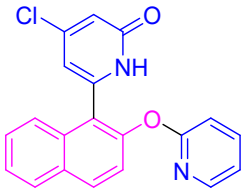




3ja

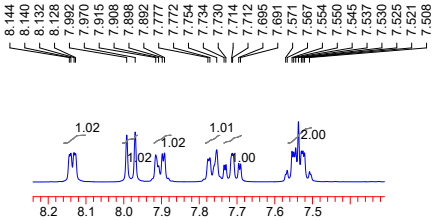
(100 MHz, $CDCl_3$)

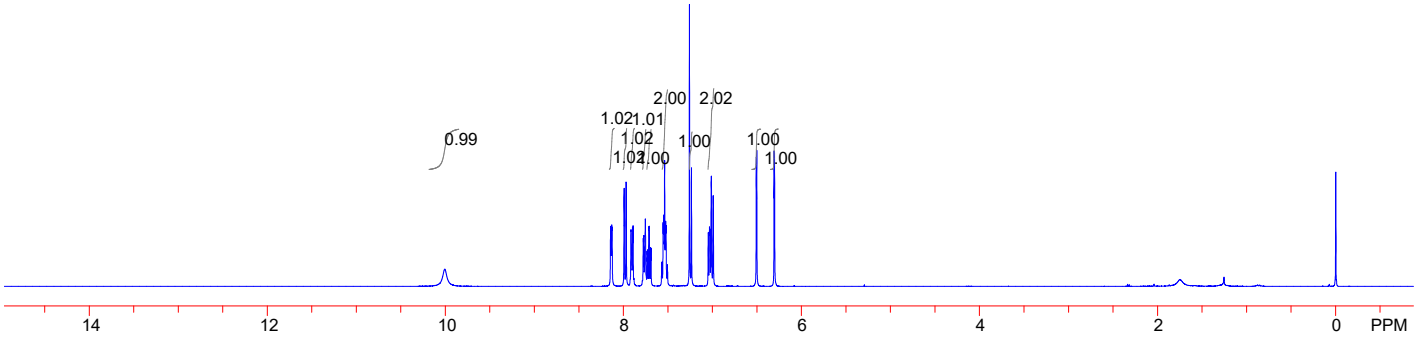


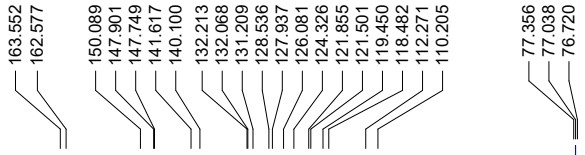


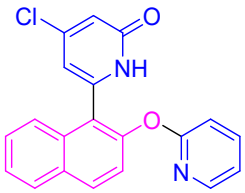
3ka

(400 MHz, $CDCl_3$)



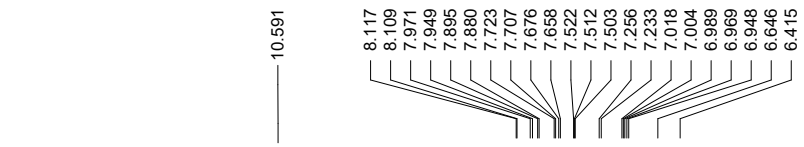


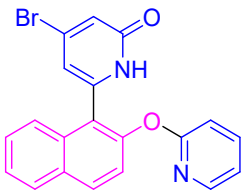




3ka

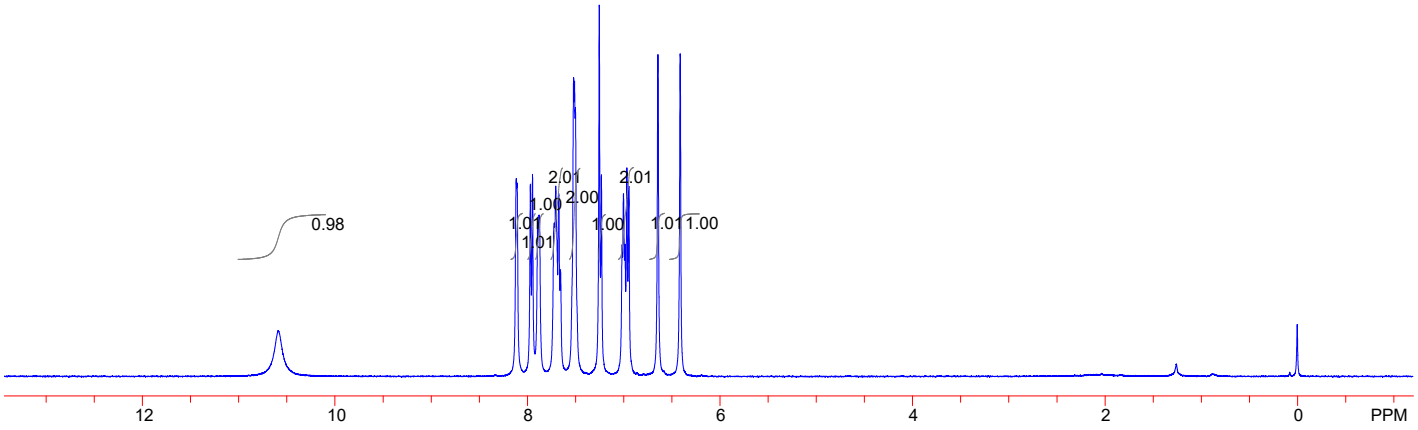
(100 MHz, $CDCl_3$)

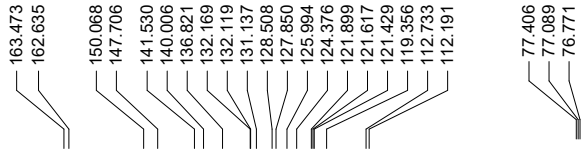


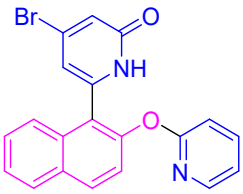


3la

(400 MHz, $CDCl_3$)

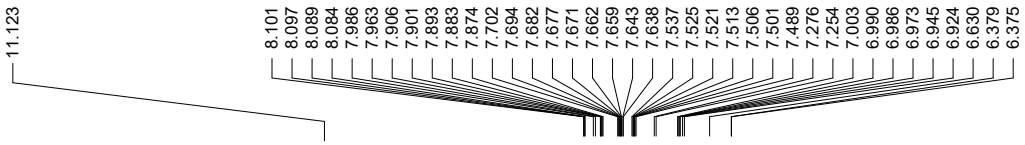


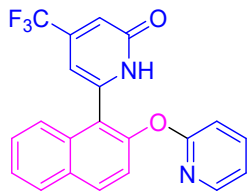




3la

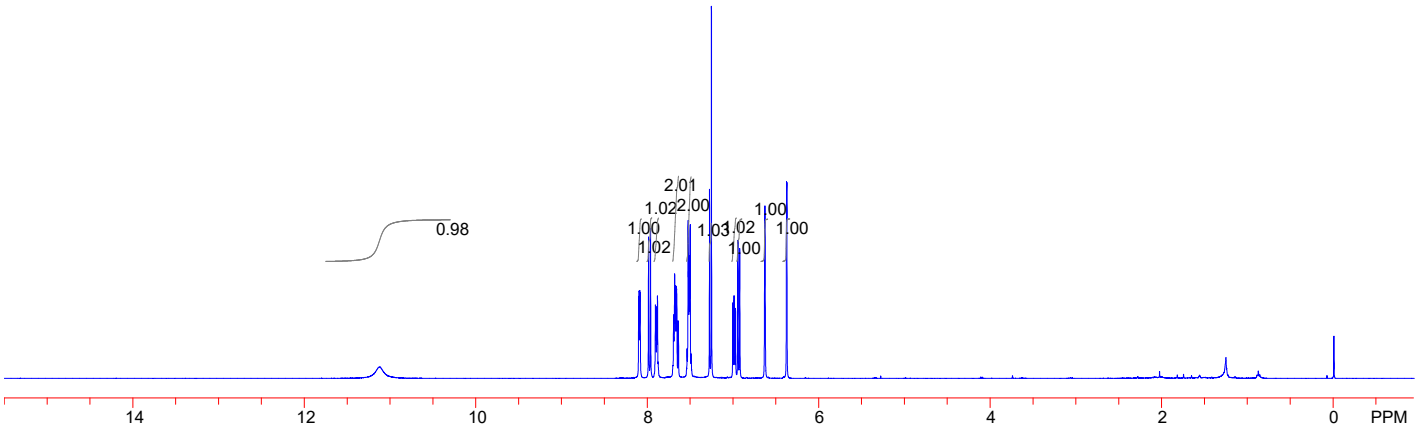
(100 MHz, $CDCl_3$)

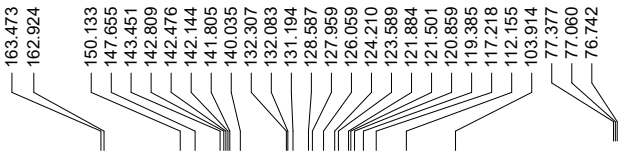


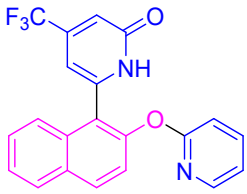


3ma

(400 MHz, $CDCl_3$)

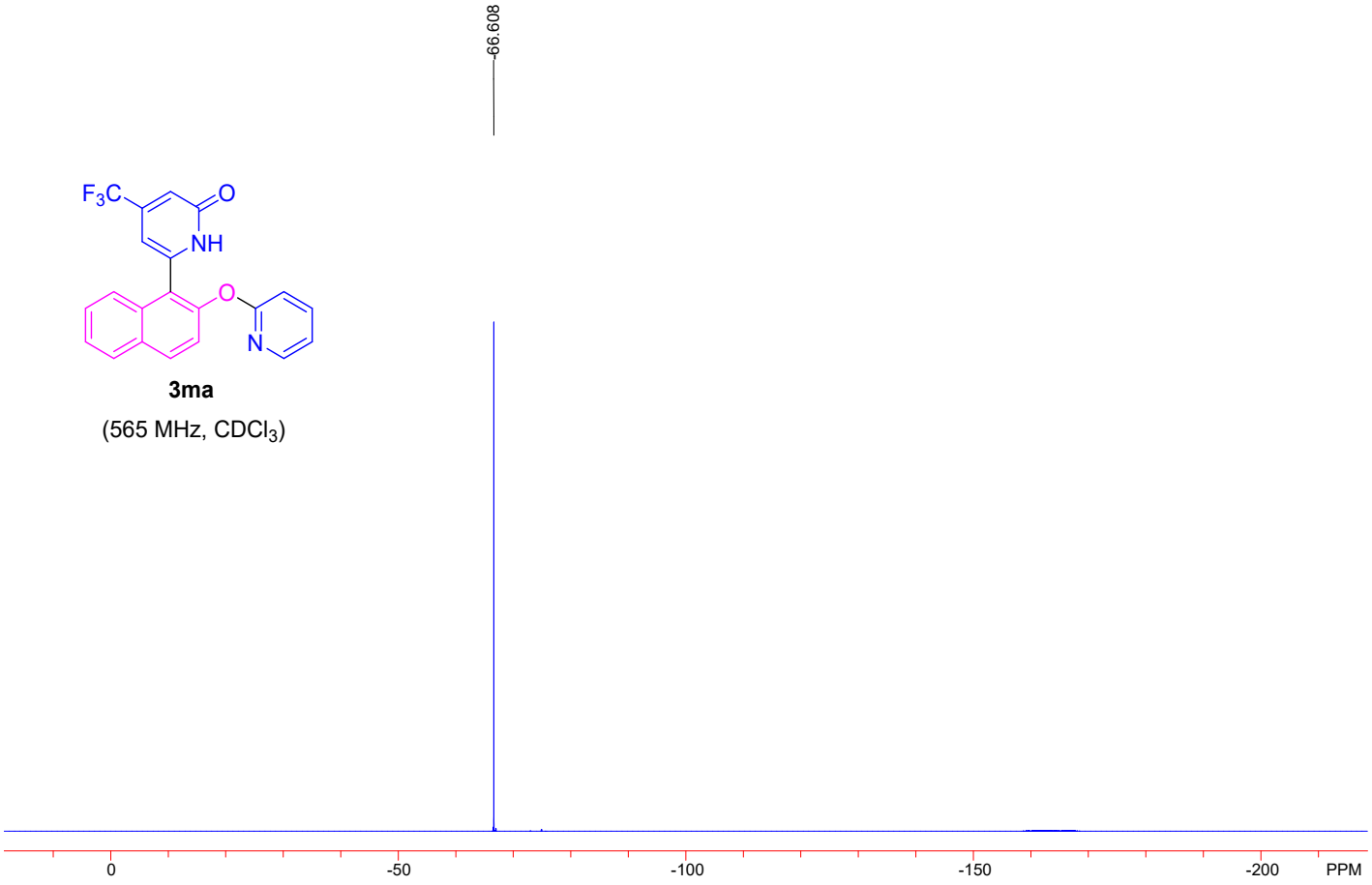






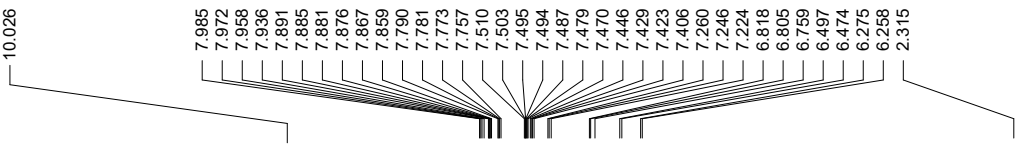
3ma

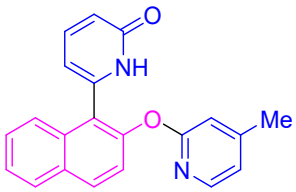
(100 MHz, $CDCl_3$)



3ma

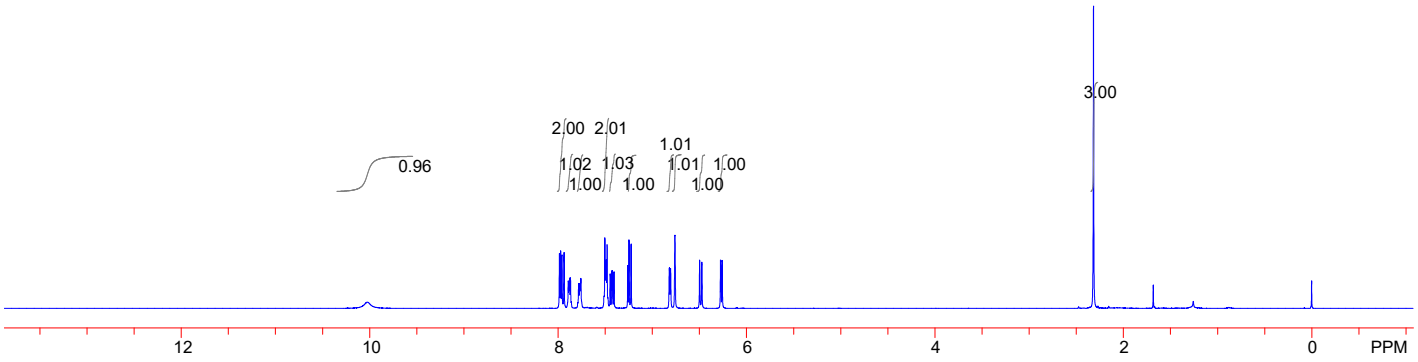
(565 MHz, $CDCl_3$)

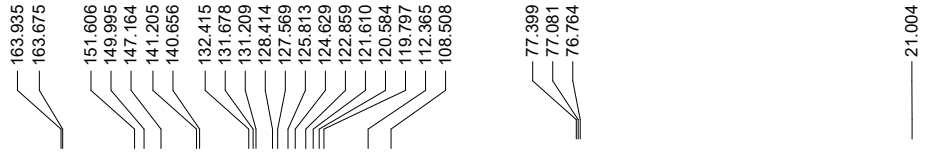


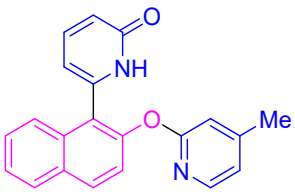


3na

(400 MHz, $CDCl_3$)

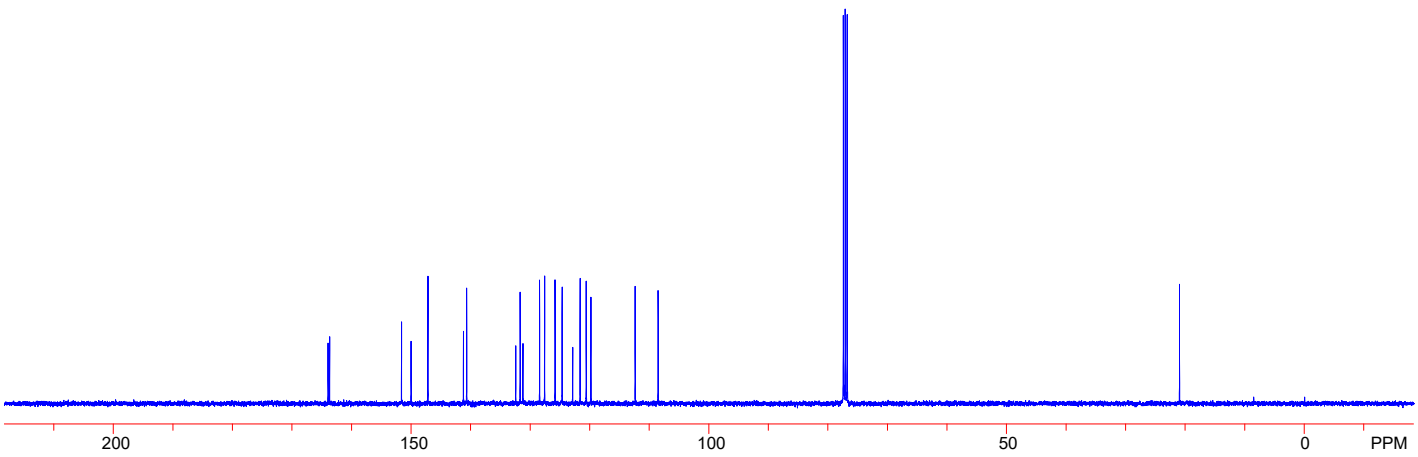


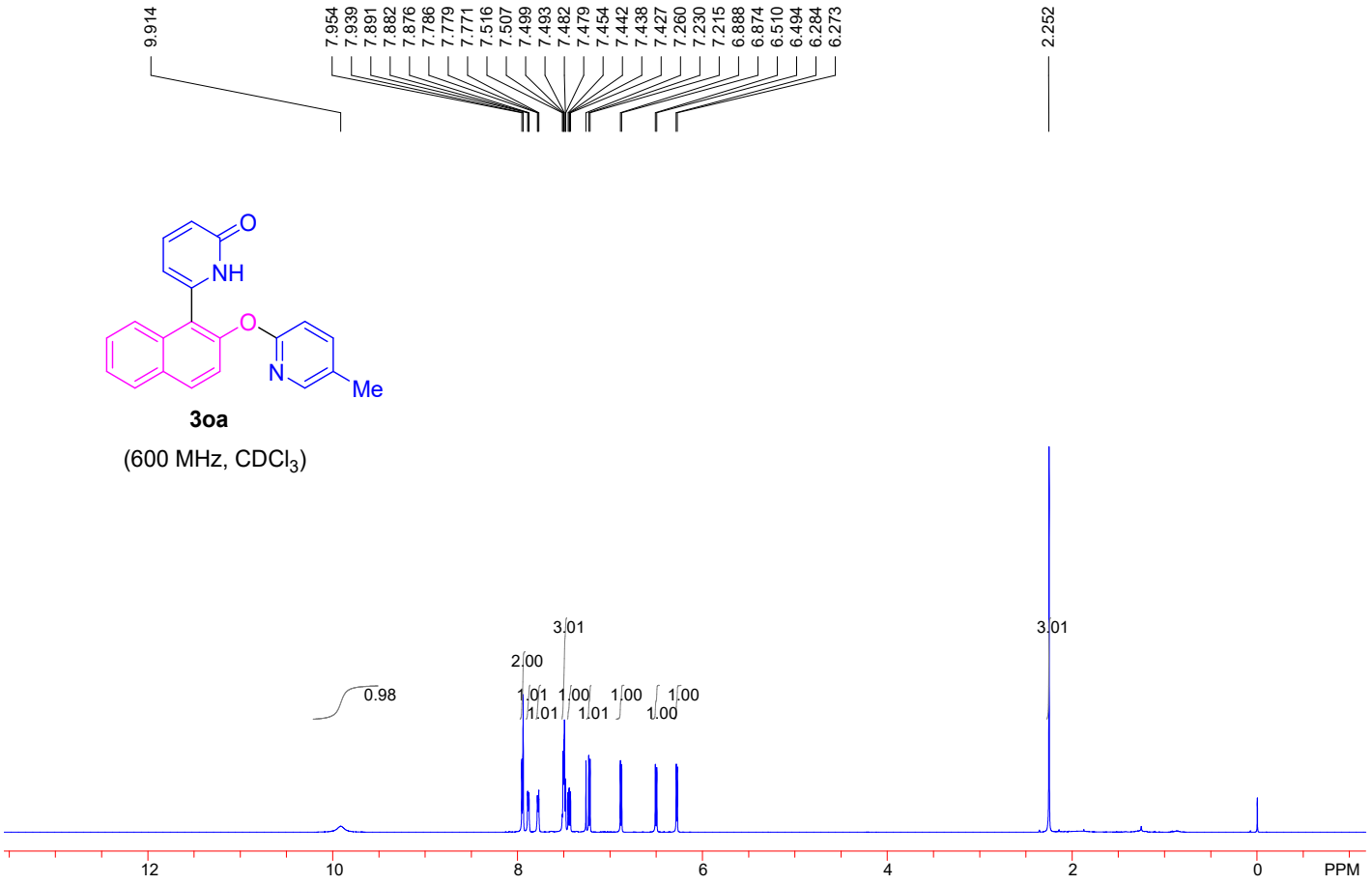


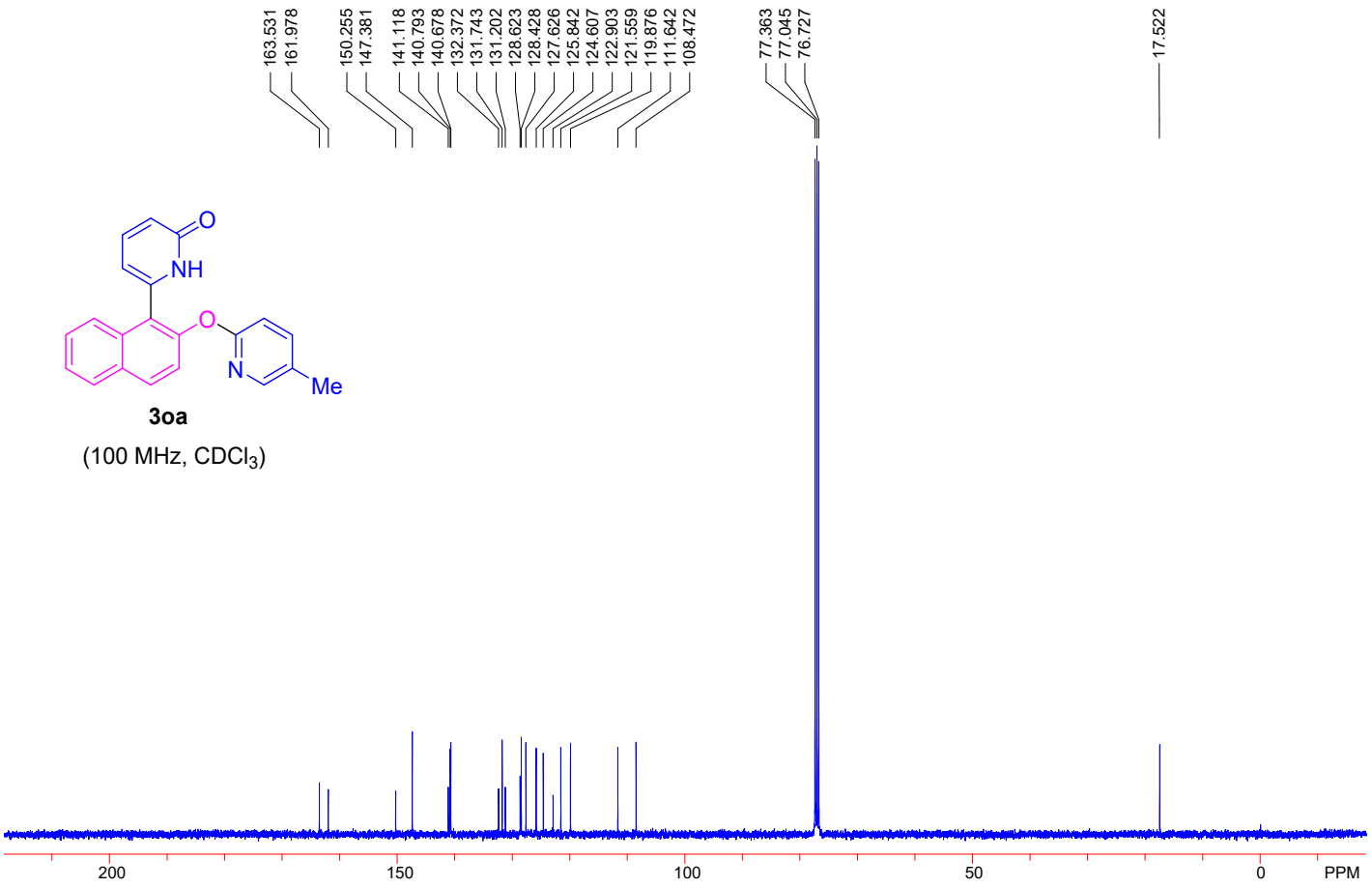


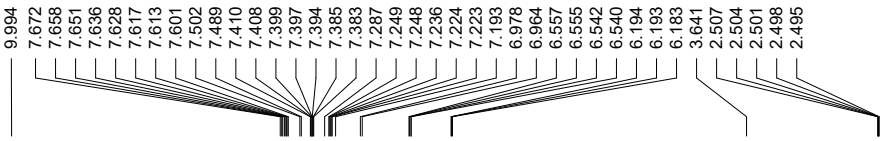
3na

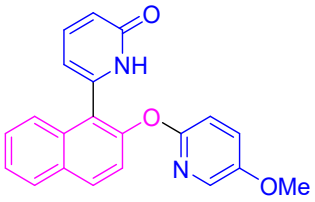
(100 MHz, $CDCl_3$)




9.914
7.954
7.939
7.891
7.882
7.876
7.786
7.779
7.771
7.516
7.507
7.499
7.493
7.482
7.479
7.454
7.442
7.438
7.427
7.260
7.230
7.215
6.888
6.874
6.510
6.494
6.284
6.273
2.252
O
NH
O
N
Me
3oa
(600 MHz, CDCl3)
3.01
2.00
0.98
1.01
1.01
1.00
1.01
1.00
1.00
1.00
3.01
12
10
8
6
4
2
0
PPM

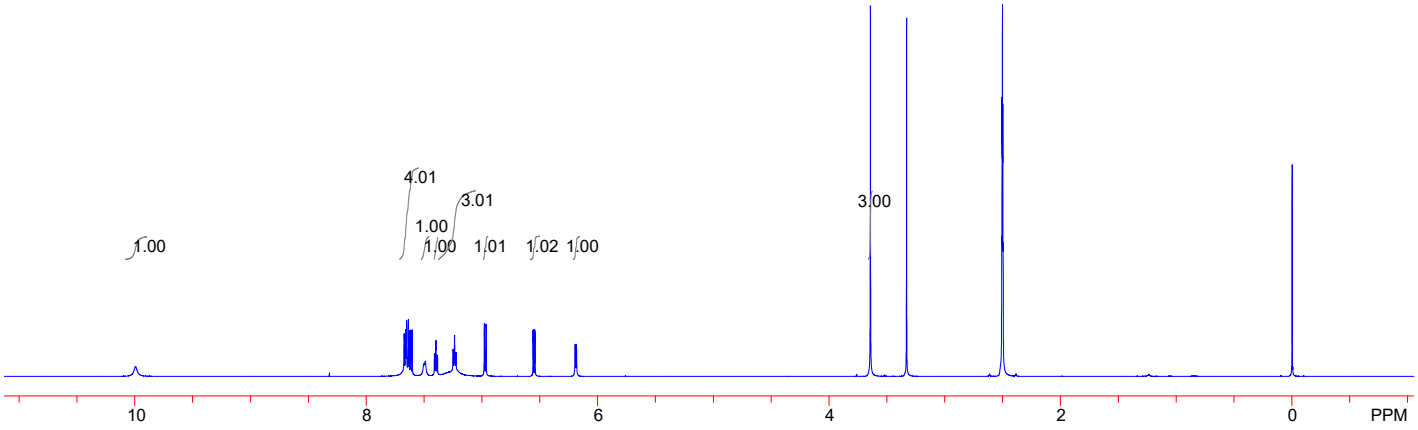

163.531
161.978
150.255
147.381
141.118
140.793
140.678
132.372
131.743
131.202
128.623
128.428
127.626
125.842
124.607
122.903
121.559
119.876
111.642
108.472
77.363
77.045
76.727
17.522
O
NH
O
N
Me
3oa
(100 MHz, CDCl3)
200
150
100
50
0
PPM

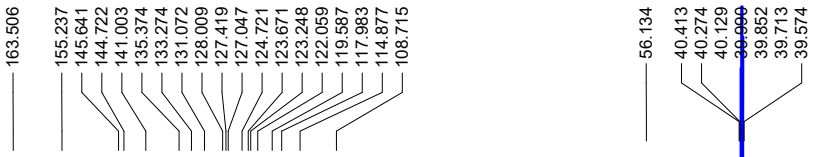


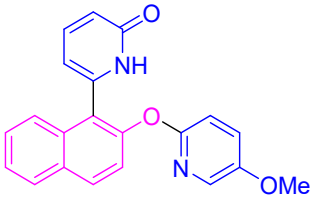


3pa

(600 MHz, DMSO-d_6)

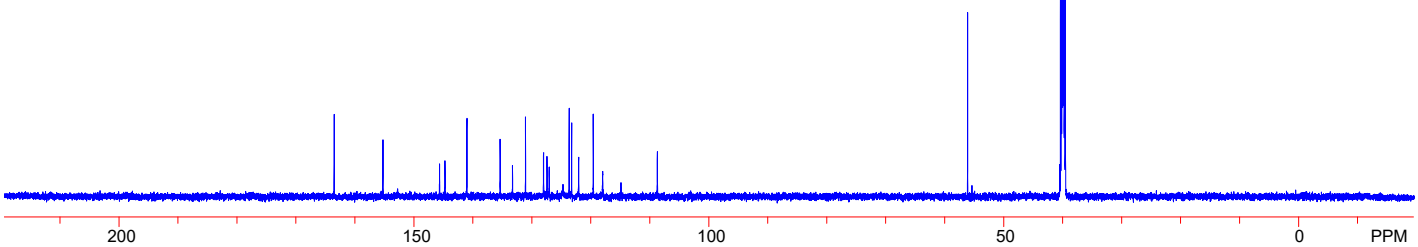


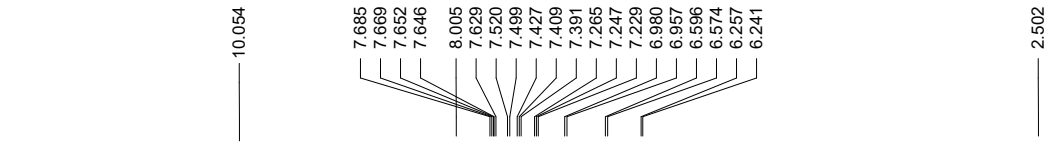


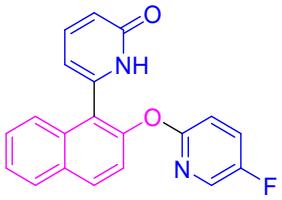


3pa

(150 MHz, DMSO-d_6)

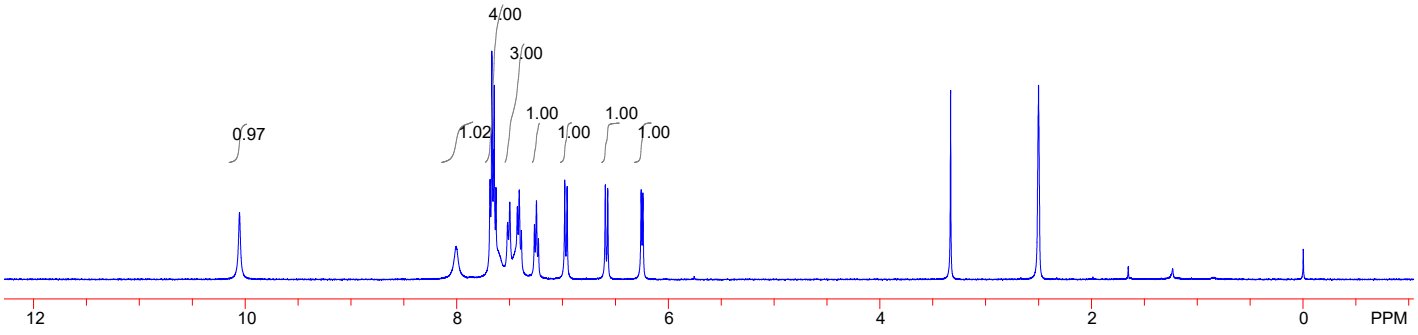


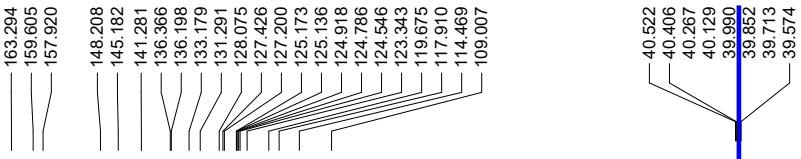


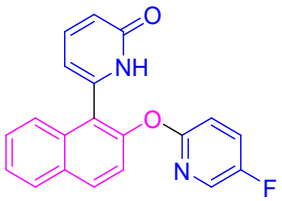


3qa

(400 MHz, DMSO-d_6)

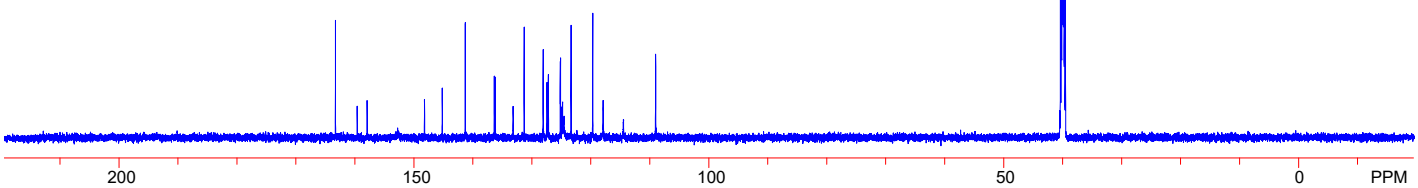


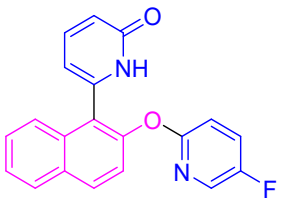




3qa

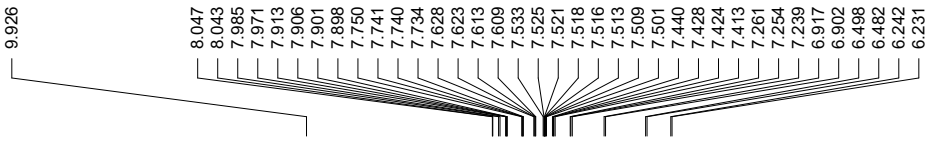
(150 MHz, DMSO-d_6)

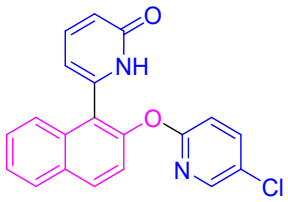




3qa

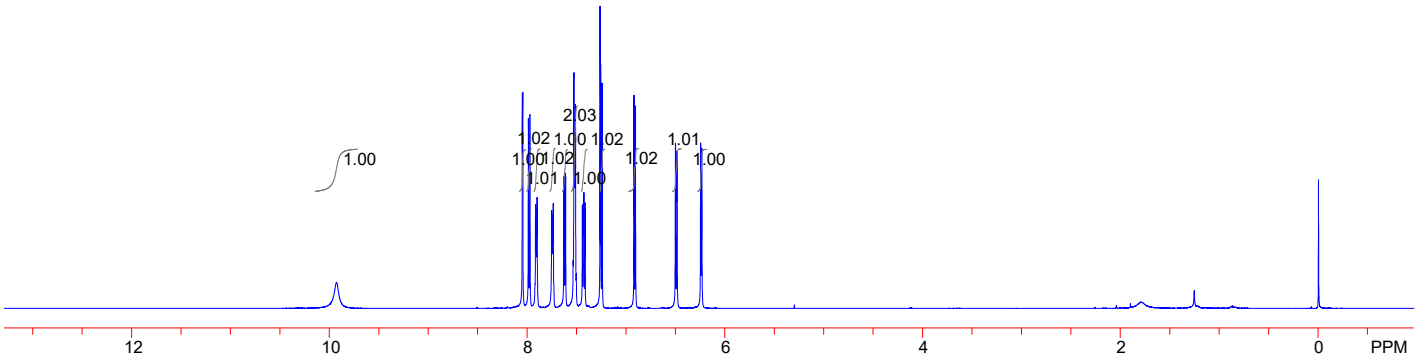
(565 MHz, DMSO-d_6)

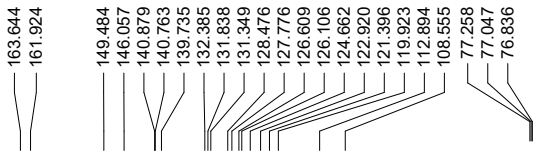


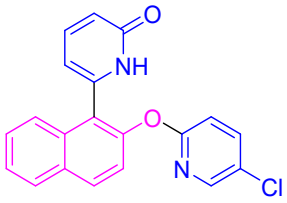


3ra

(600 MHz, $CDCl_3$)

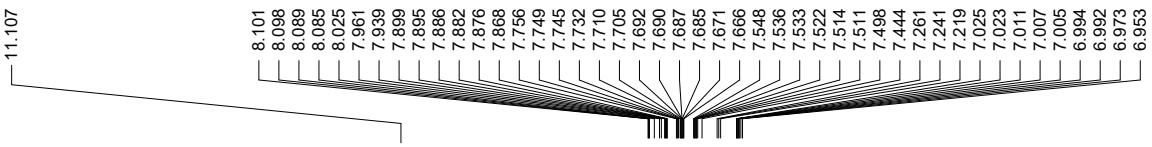


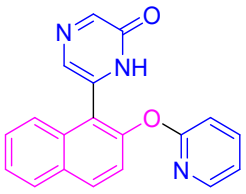




3ra

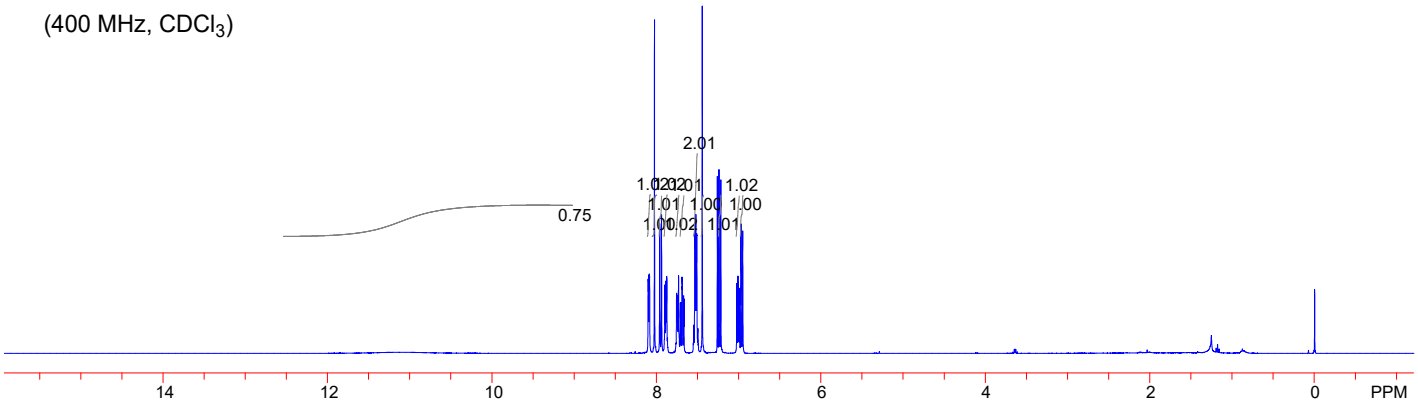
(150 MHz, $CDCl_3$)

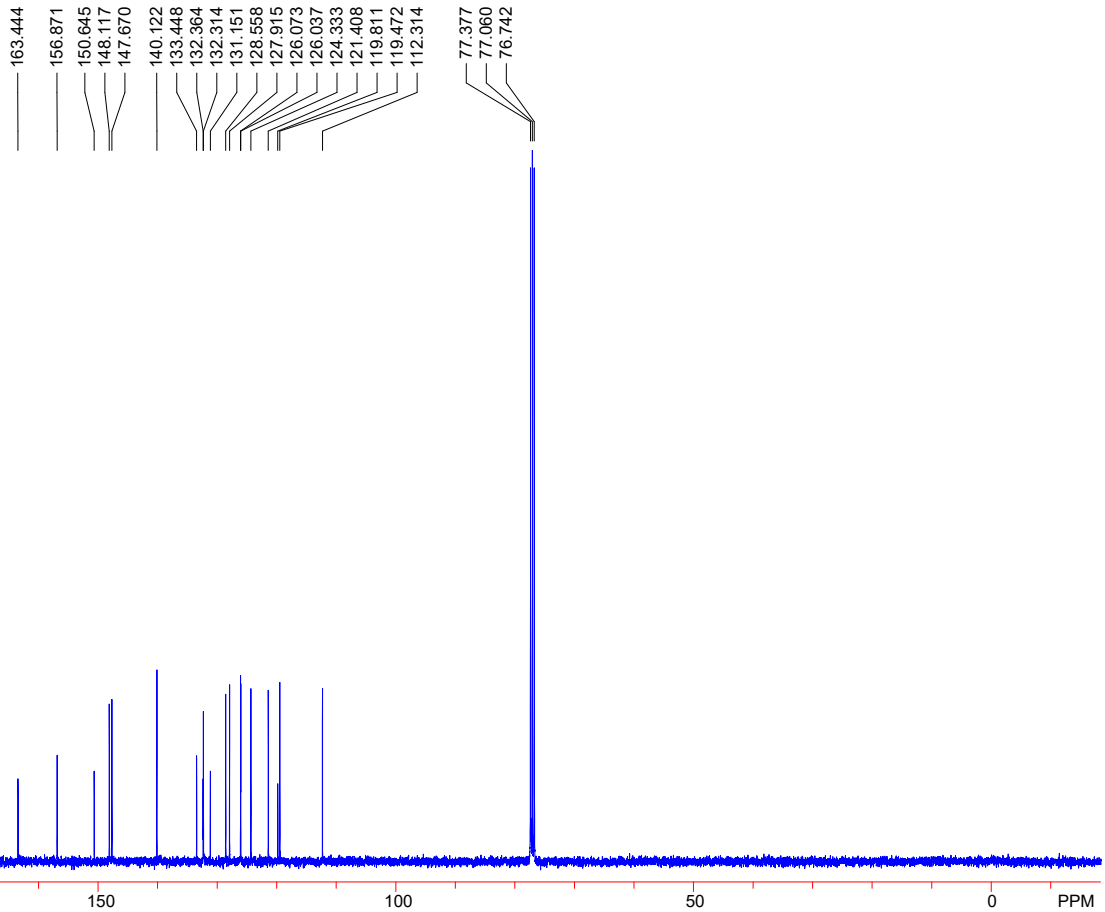


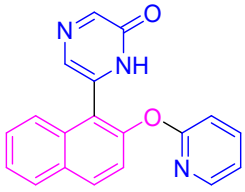


3sa

(400 MHz, $CDCl_3$)

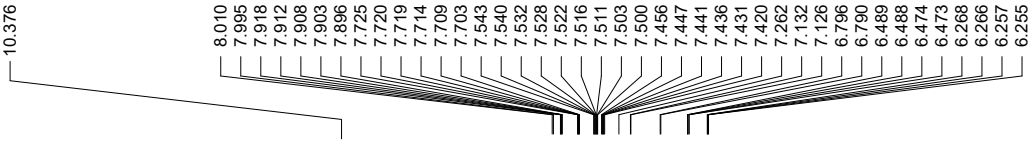


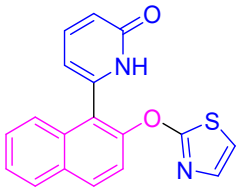




3sa

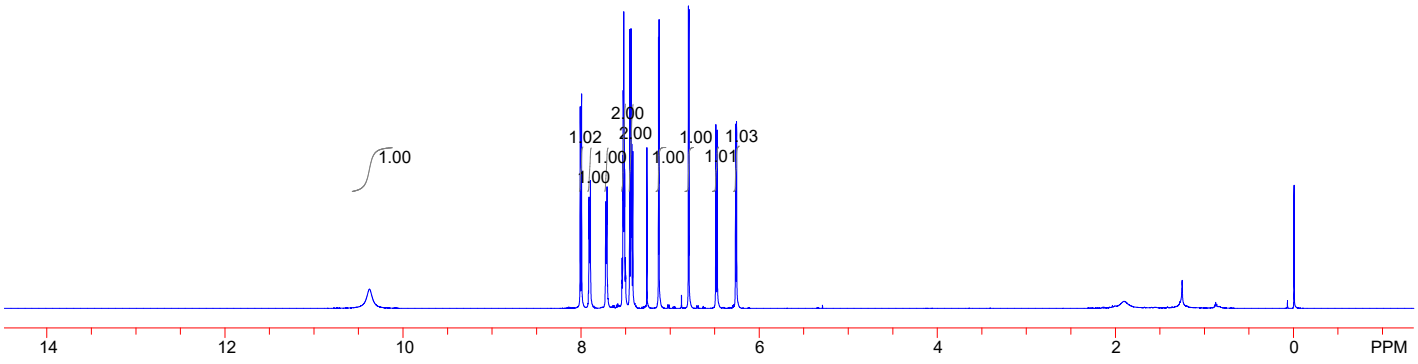
(100 MHz, $CDCl_3$)

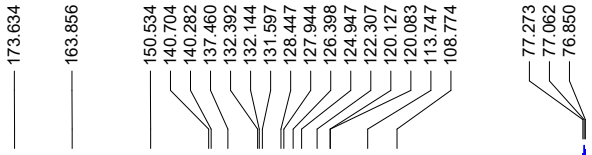


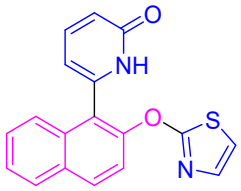


3ta

(400 MHz, $CDCl_3$)

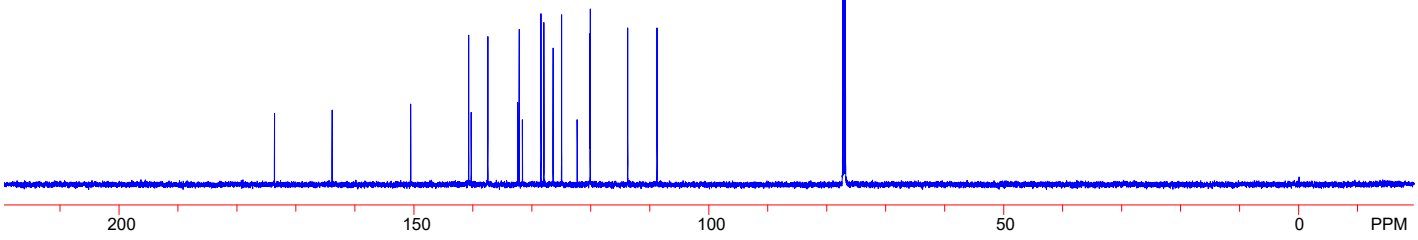


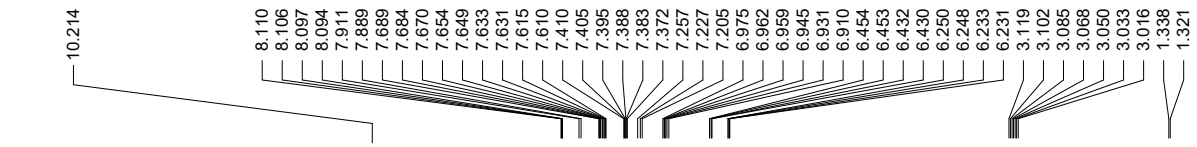


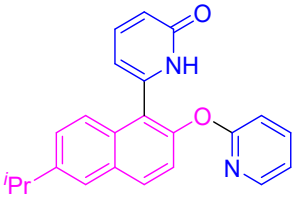


3ta

(150 MHz, $CDCl_3$)

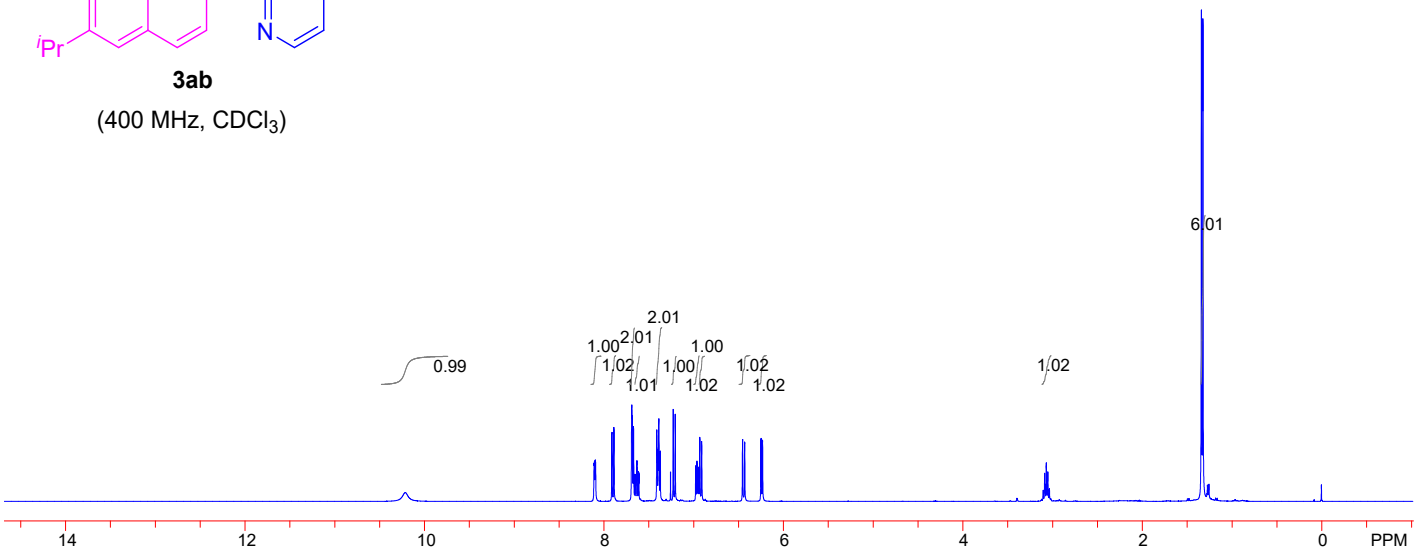


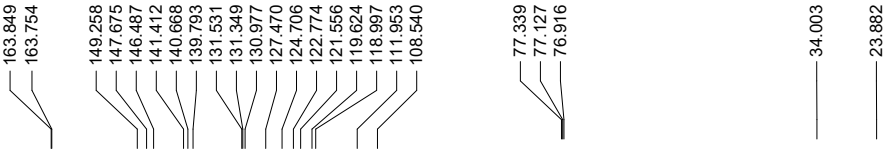


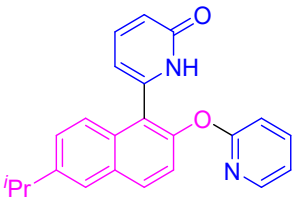


3ab

(400 MHz, $CDCl_3$)

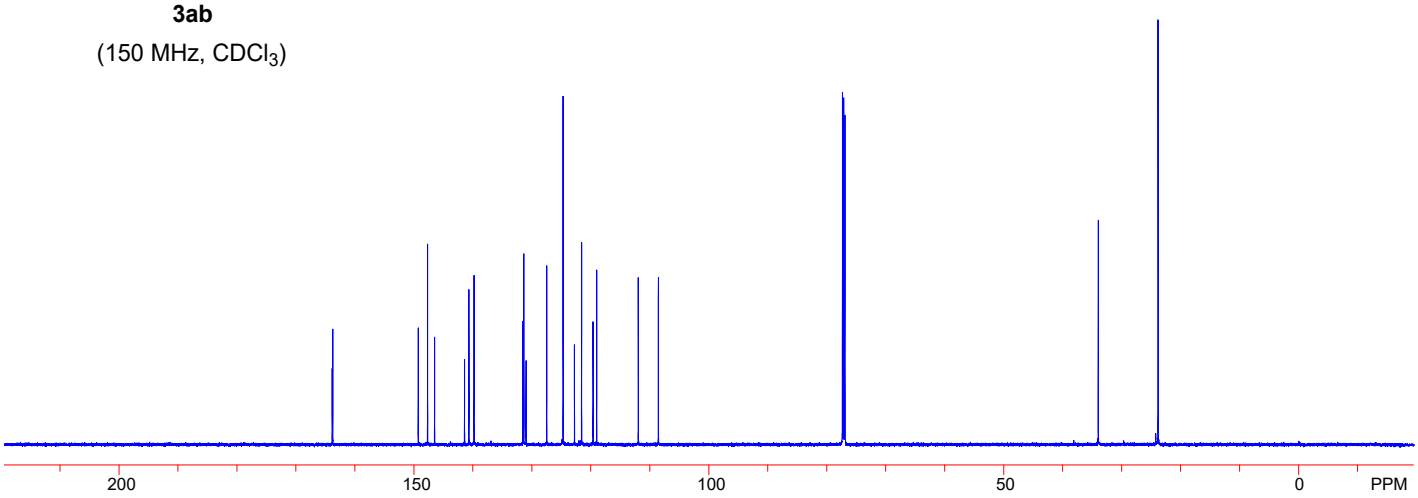


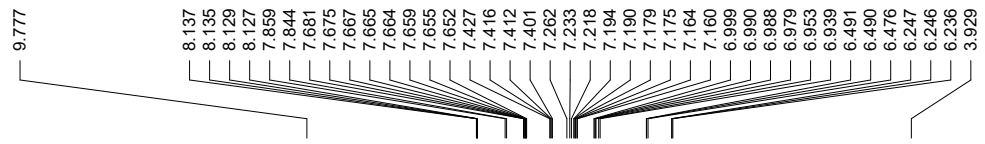


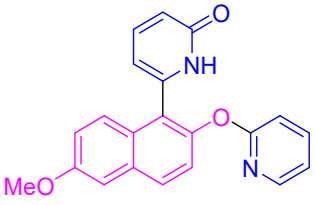


3ab

(150 MHz, $CDCl_3$)

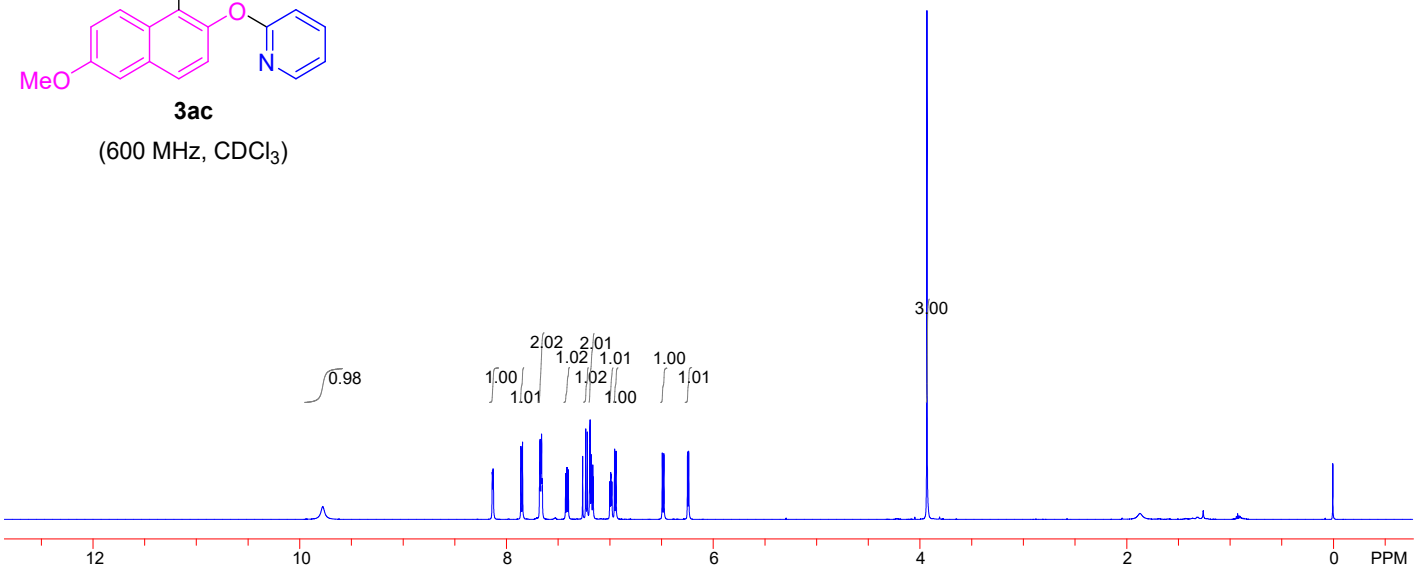


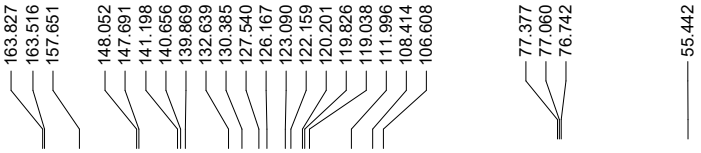


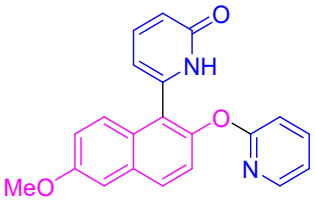


3ac

(600 MHz, $CDCl_3$)

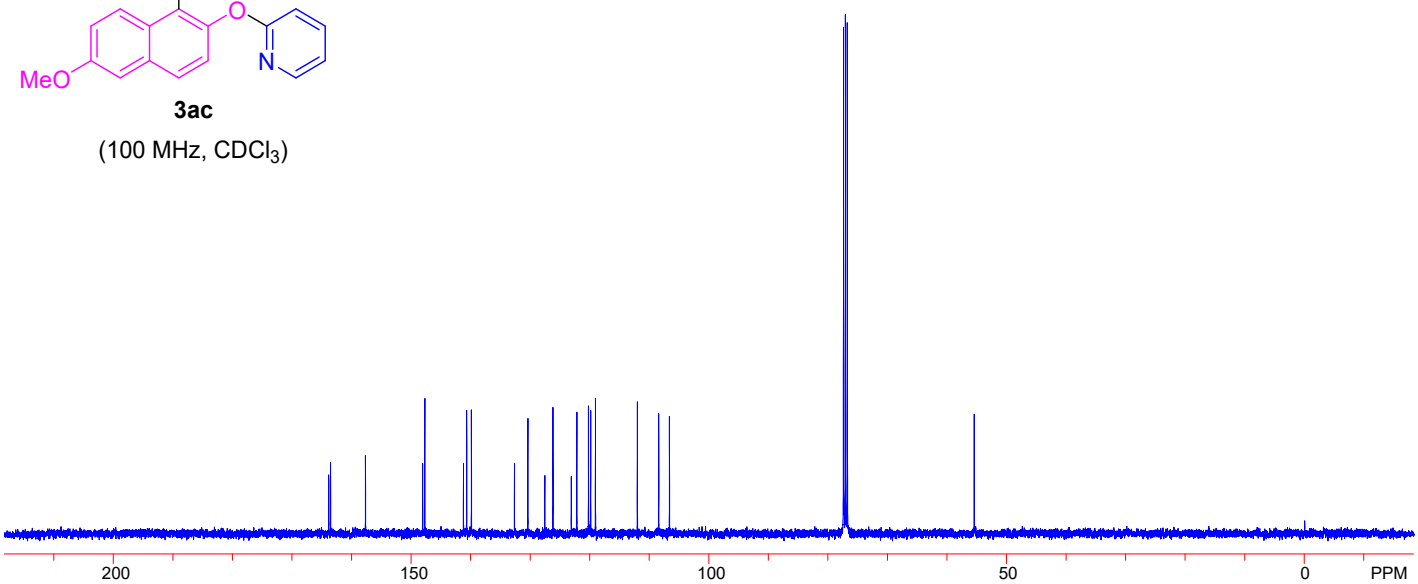


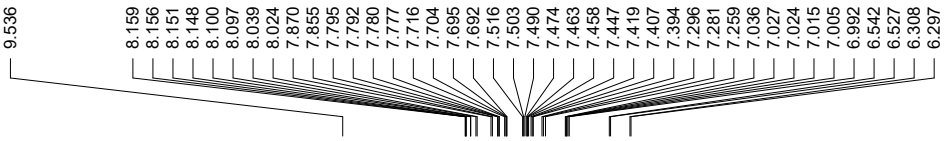


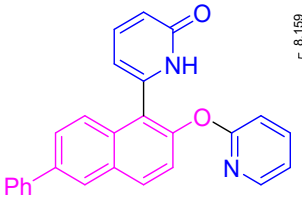


3ac

(100 MHz, $CDCl_3$)

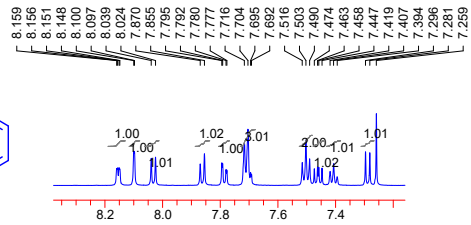


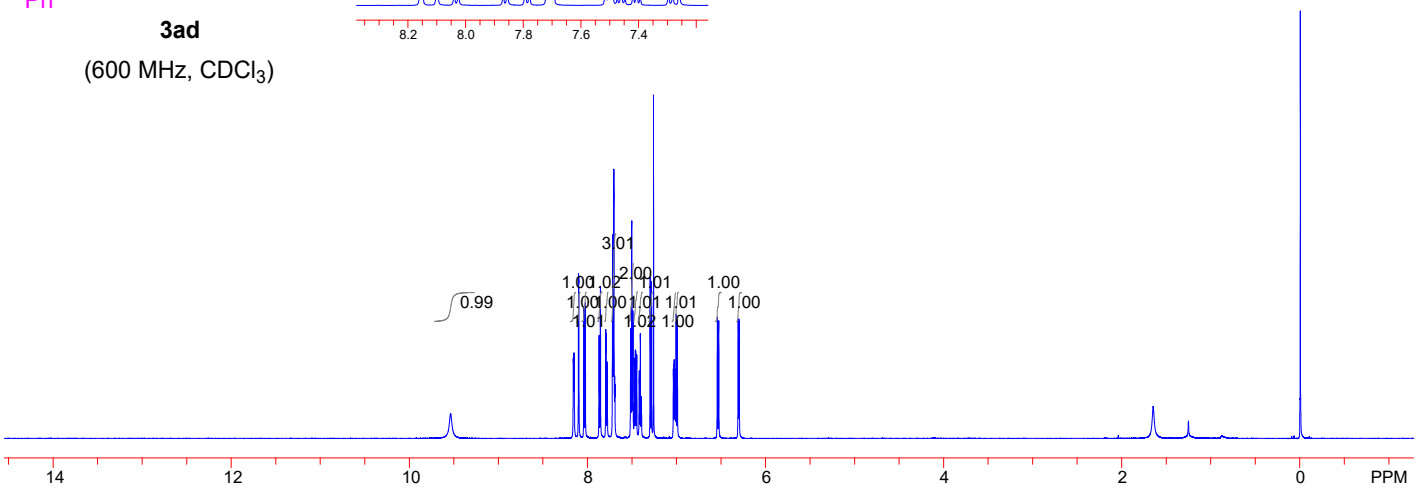


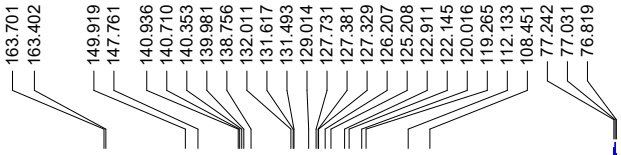


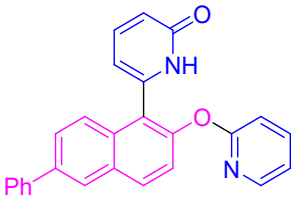
3ad

(600 MHz, $CDCl_3$)



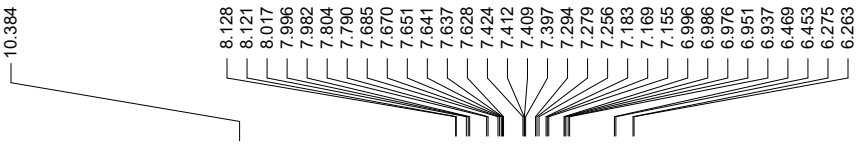


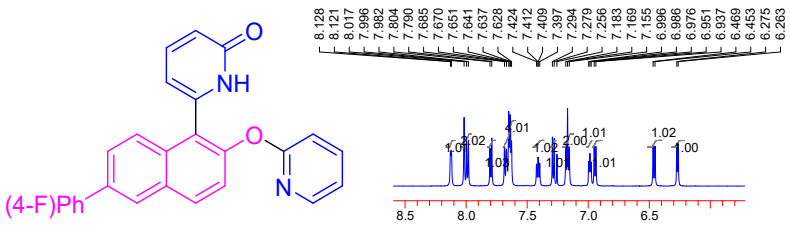




3ad

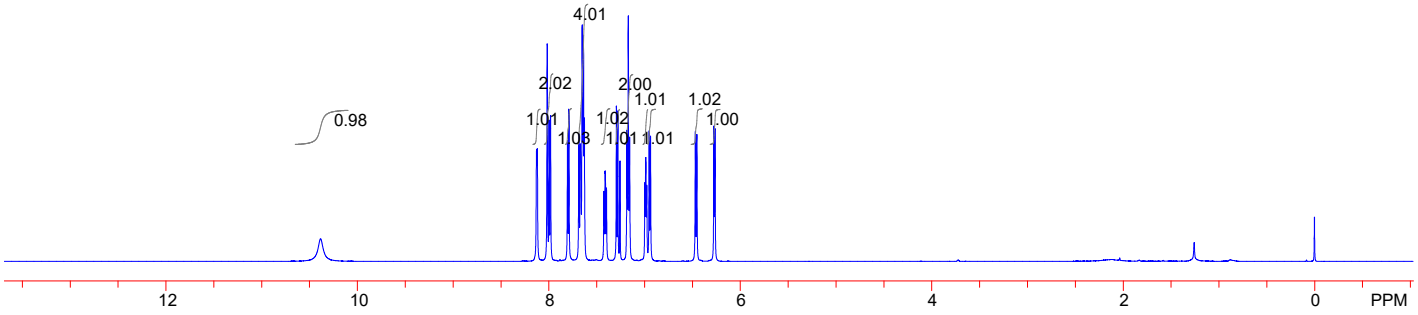
(150 MHz, $CDCl_3$)

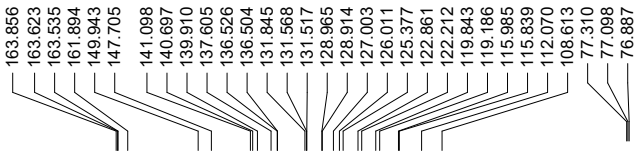


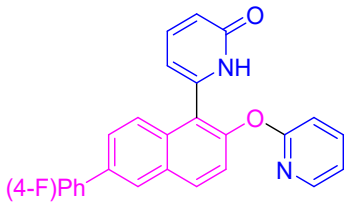


3ae

(600 MHz, $CDCl_3$)

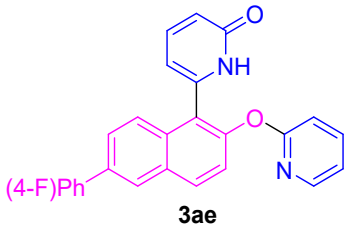






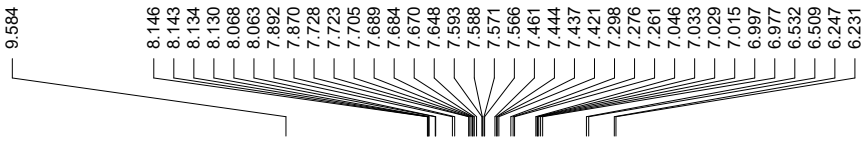
3ae

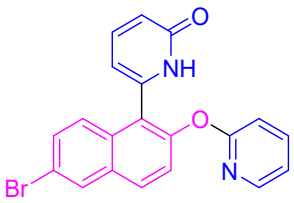
(150 MHz, $CDCl_3$)



3ae

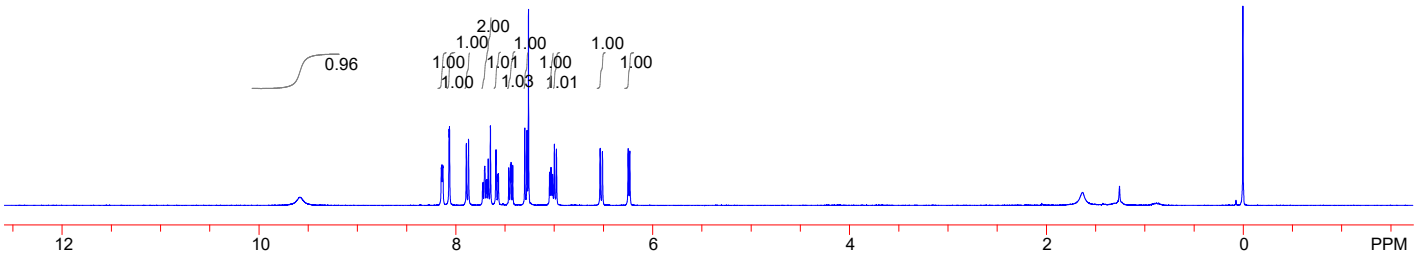
(376 MHz, $CDCl_3$)

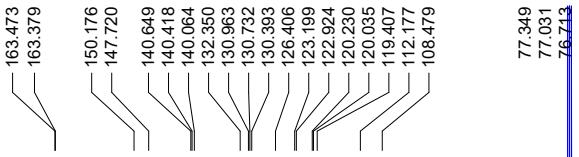


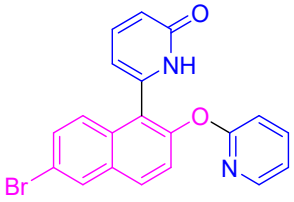


3af

(400 MHz, $CDCl_3$)

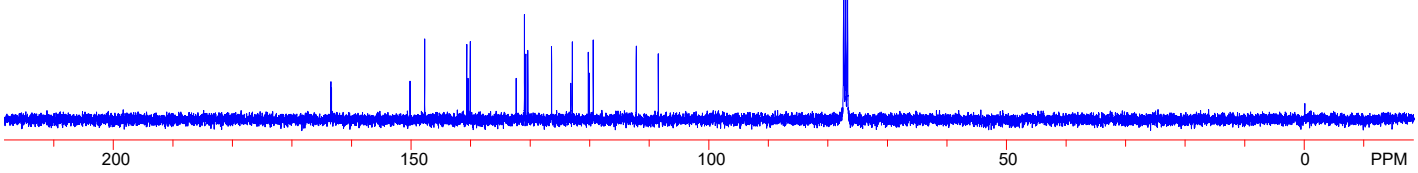


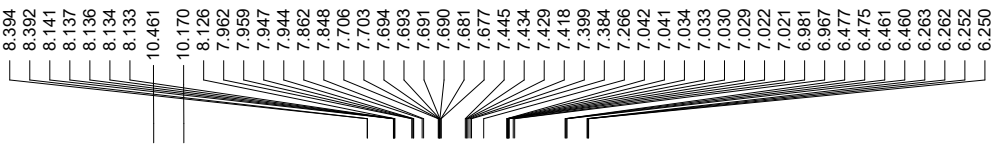


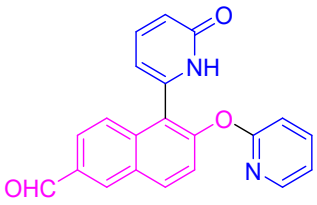


3af

(100 MHz, $CDCl_3$)

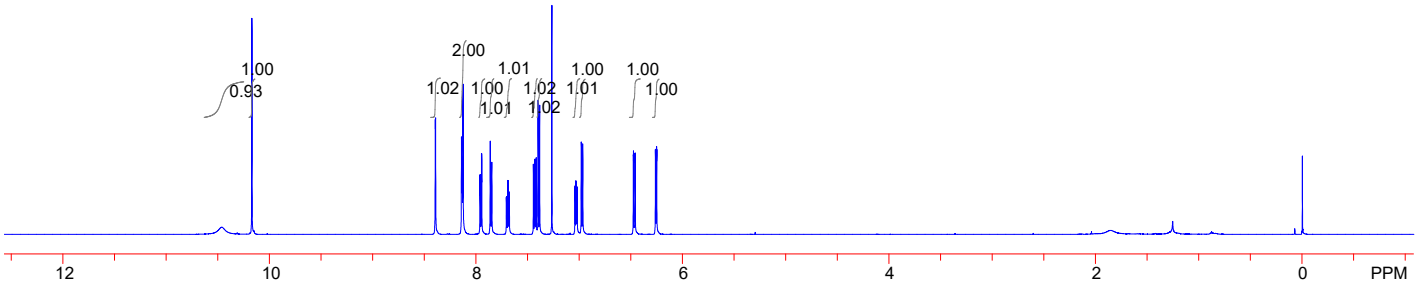


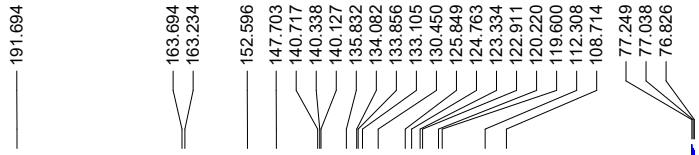


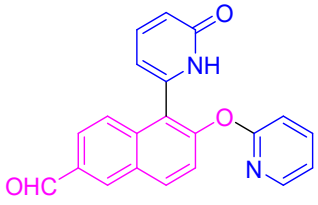


3ag

(600 MHz, $CDCl_3$)

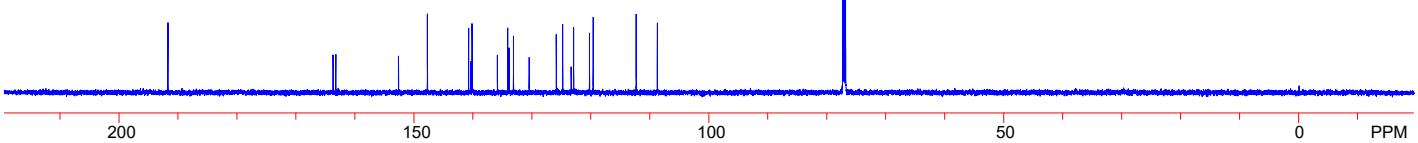


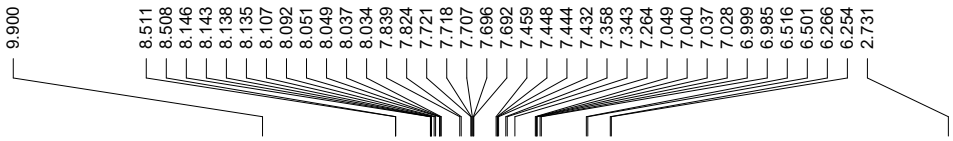


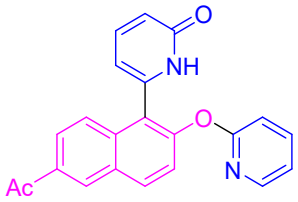


3ag

(150 MHz, $CDCl_3$)

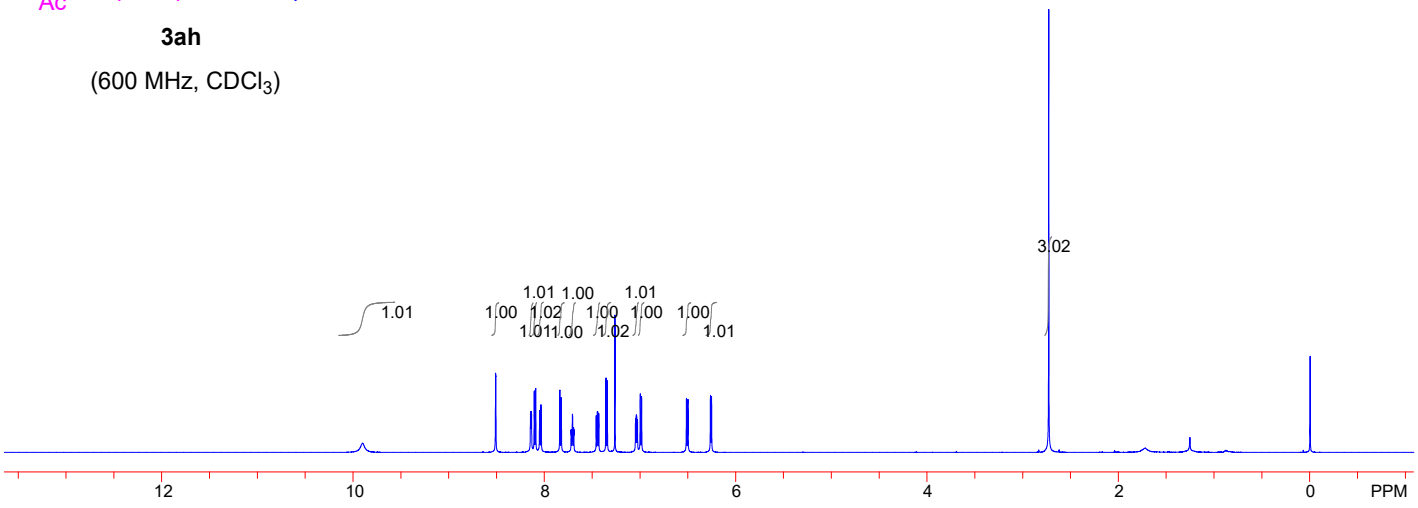


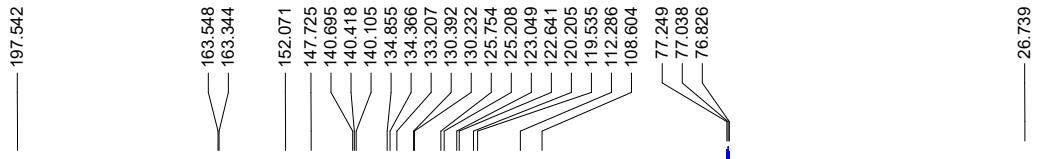


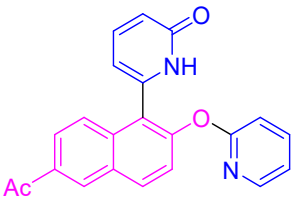


3ah

(600 MHz, $CDCl_3$)

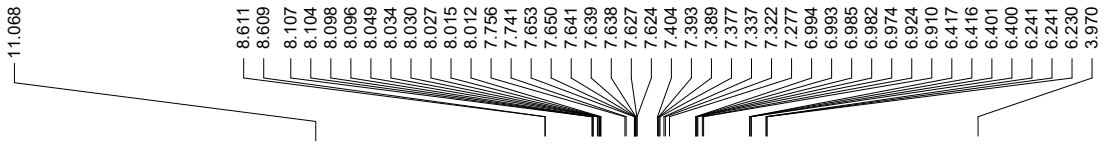


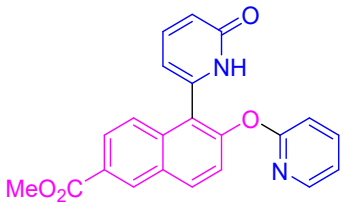




3ah

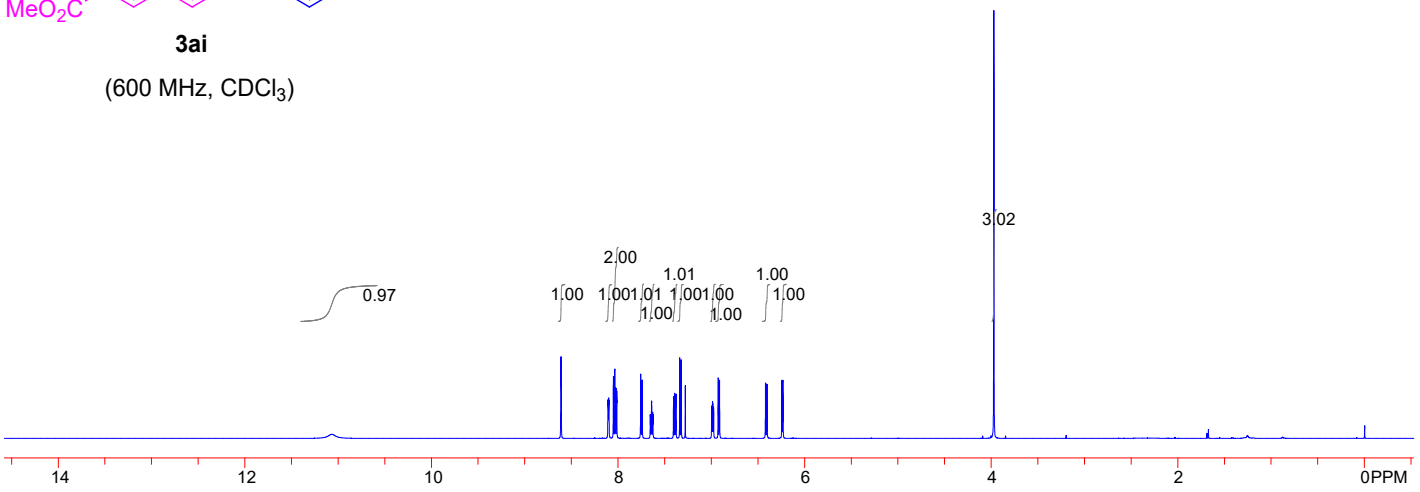
(150 MHz, $CDCl_3$)

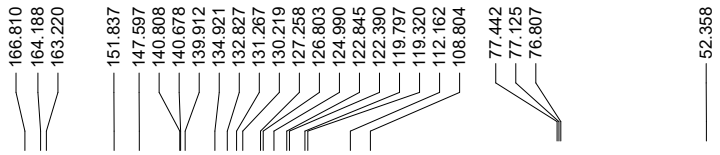


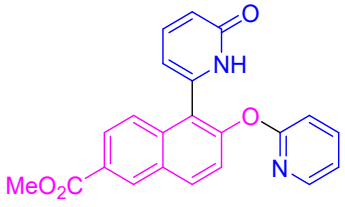


3ai

(600 MHz, $CDCl_3$)

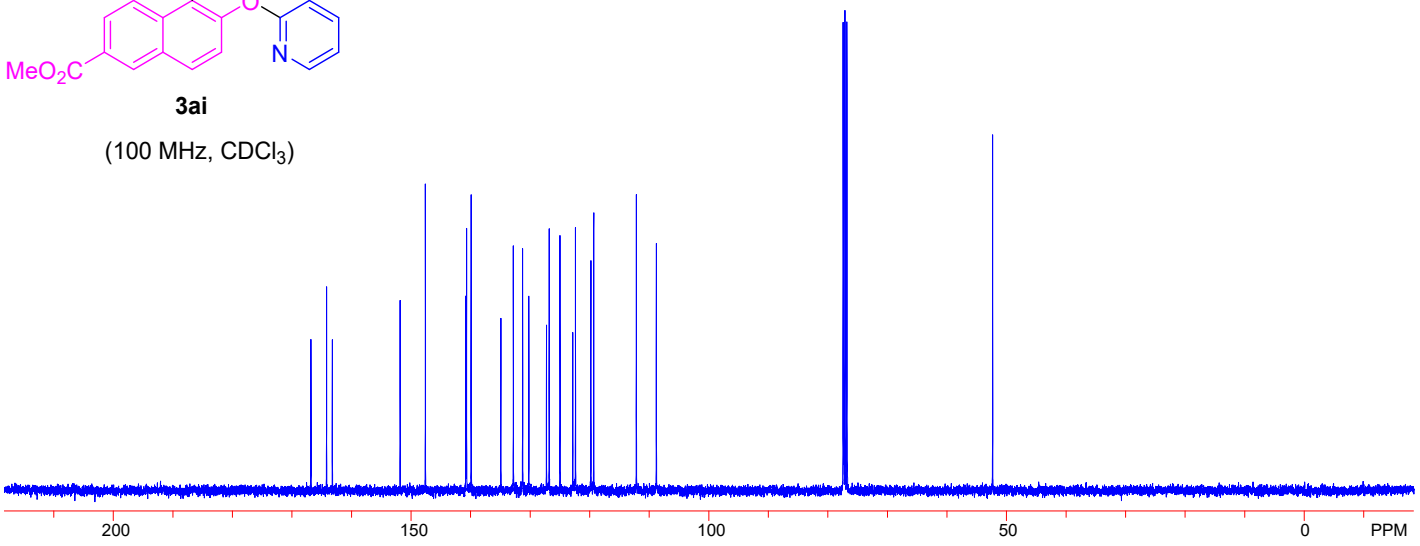


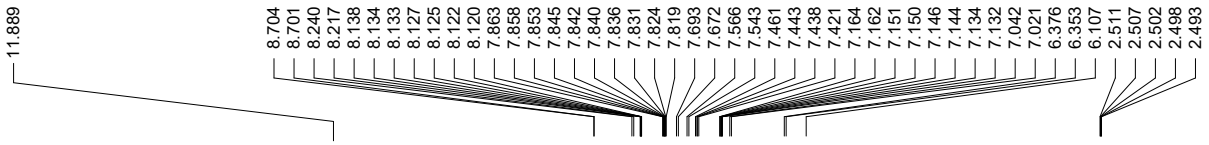


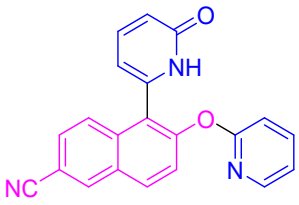


3ai

(100 MHz, $CDCl_3$)

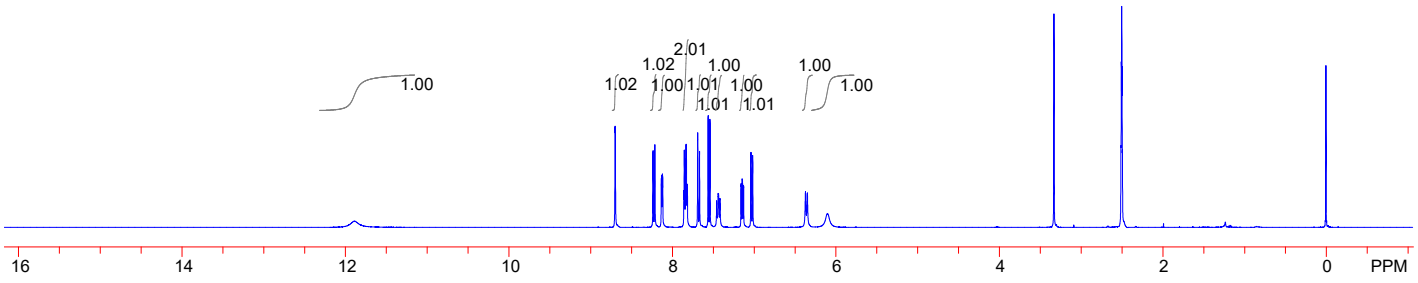


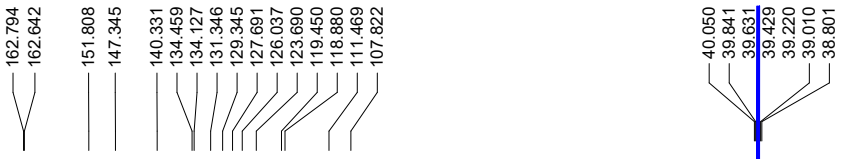


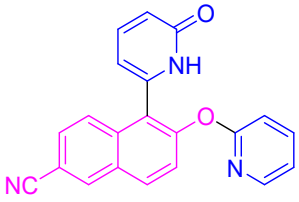


3aj

(400 MHz, DMSO-d_6)

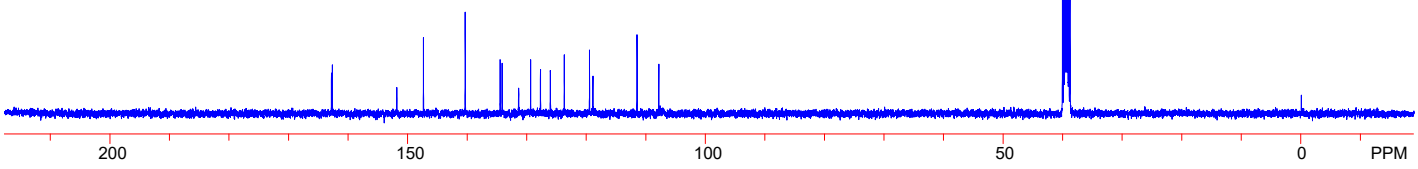


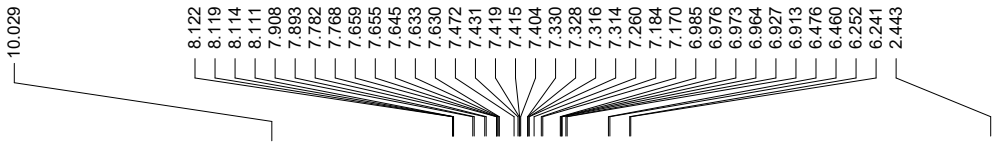


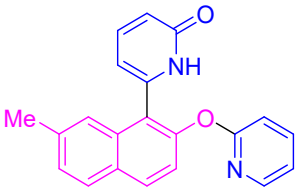


3aj

(100 MHz, DMSO-d_6)

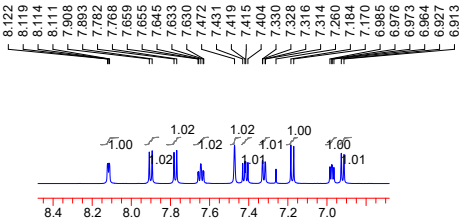


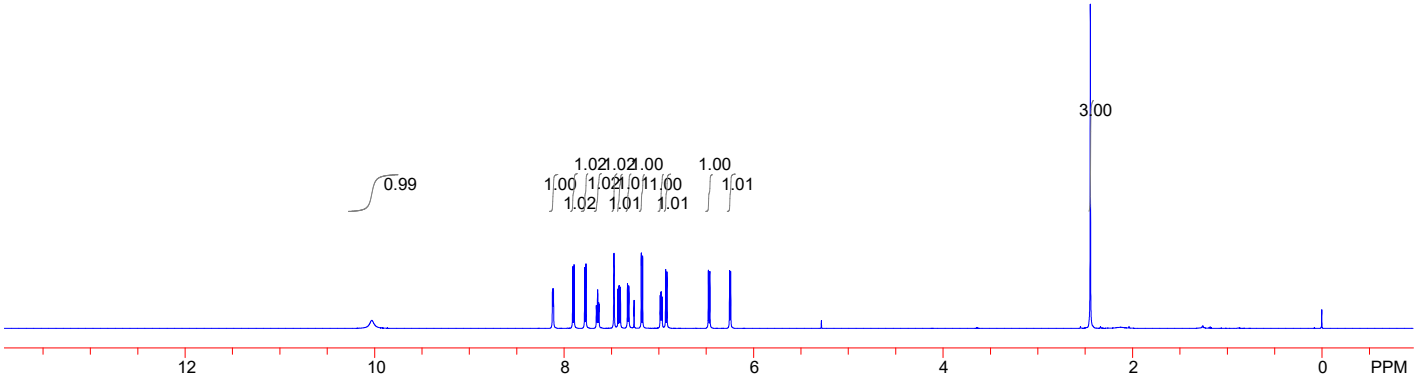


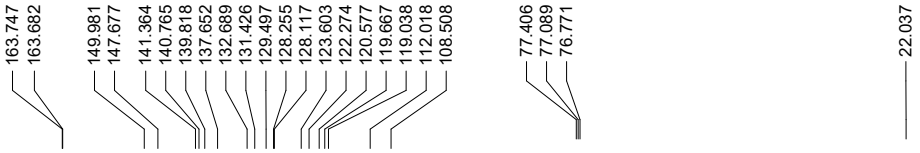


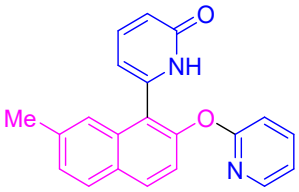
3ak

(600 MHz, $CDCl_3$)



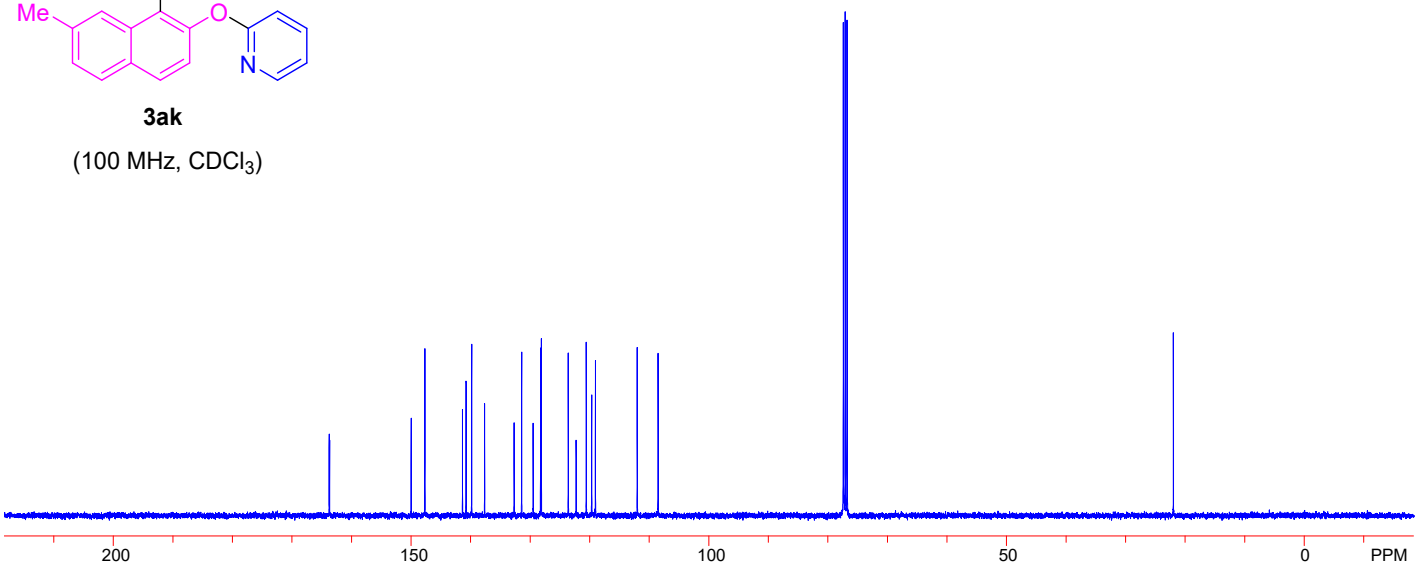


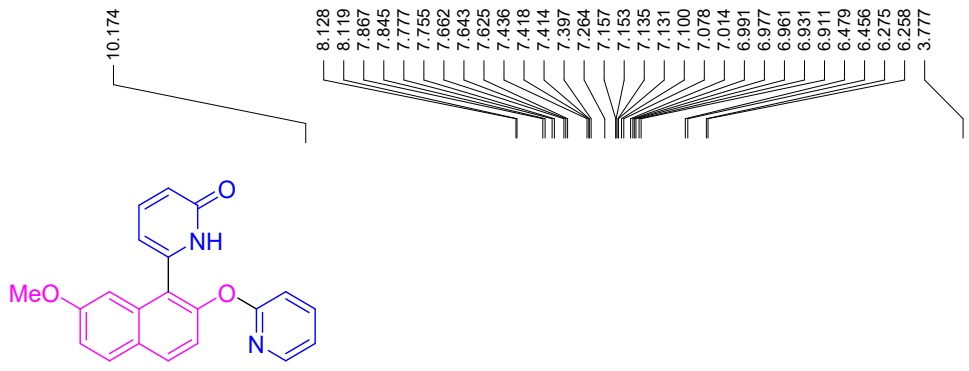




3ak

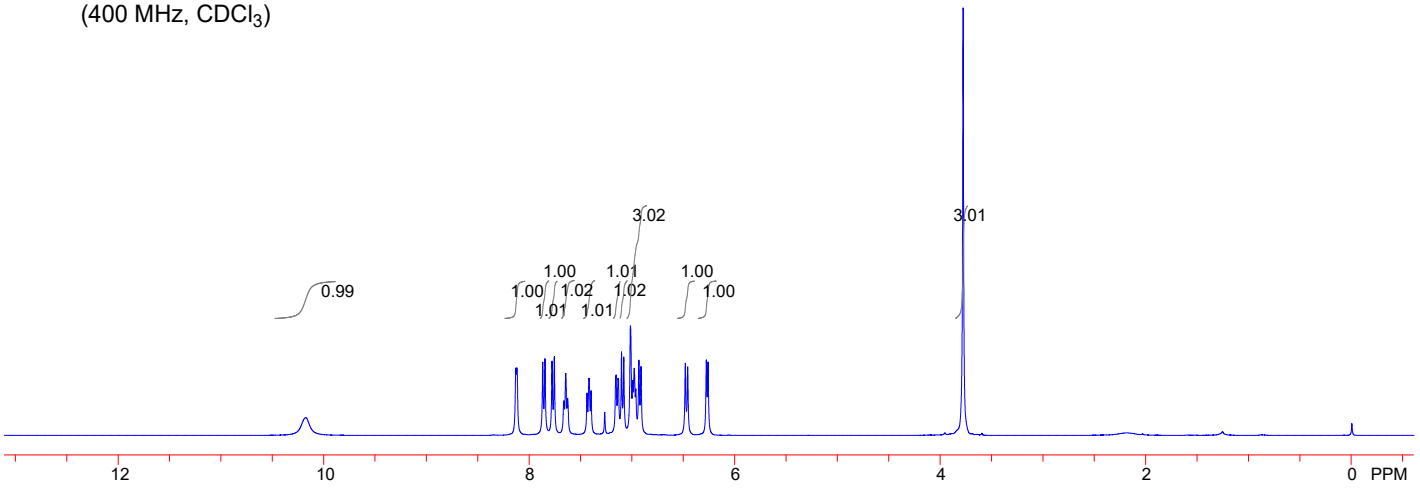
(100 MHz, $CDCl_3$)

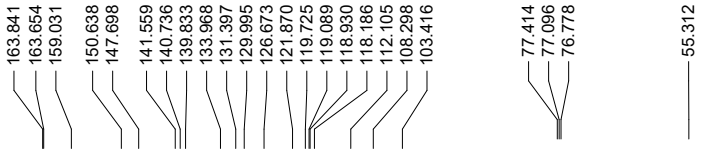


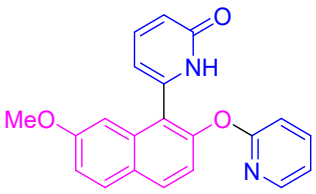


3al

(400 MHz, $CDCl_3$)

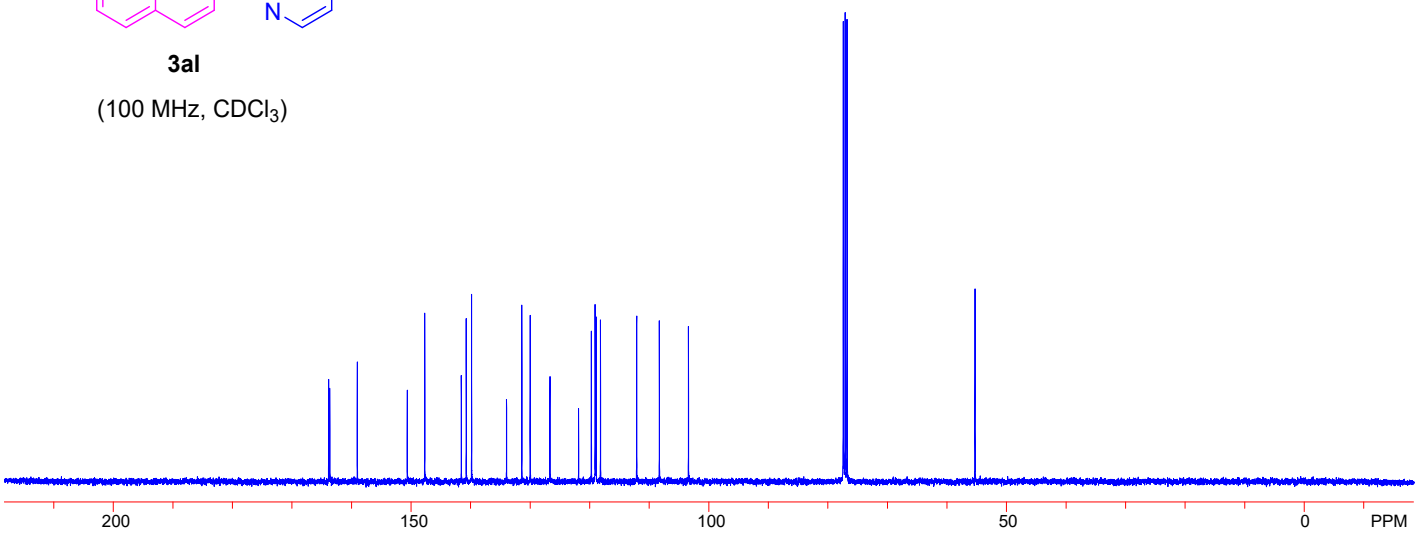


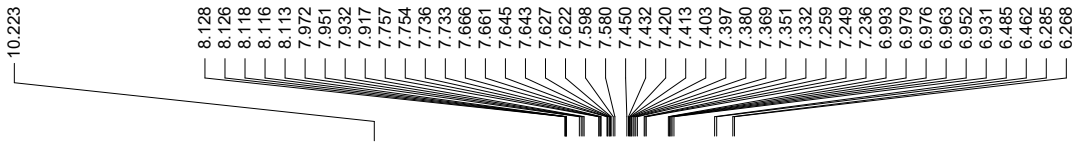


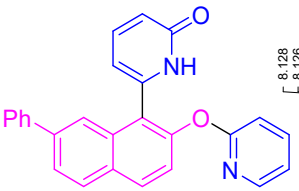


3al

(100 MHz, $CDCl_3$)

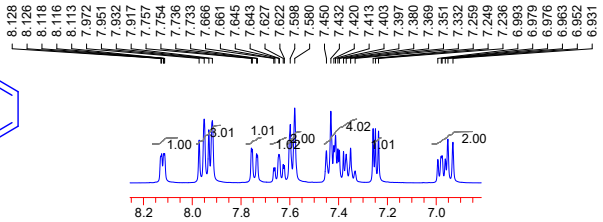


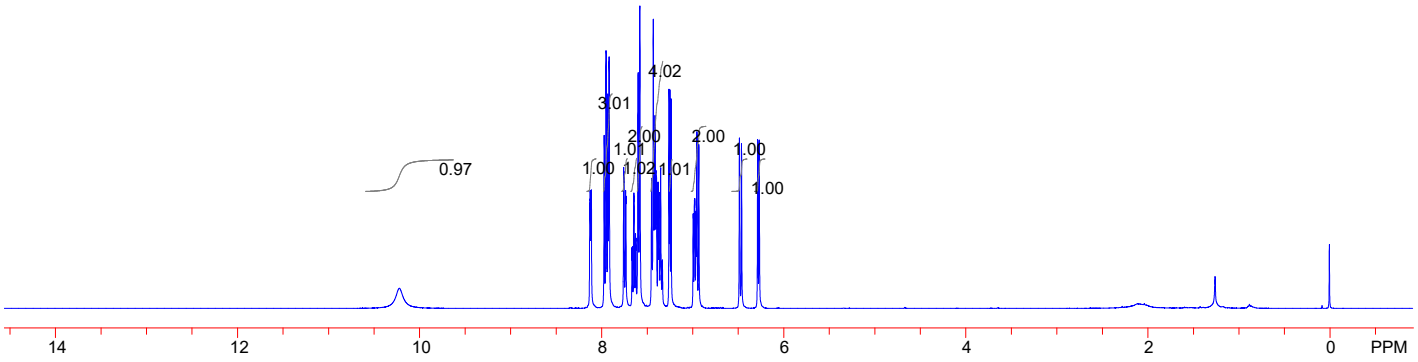


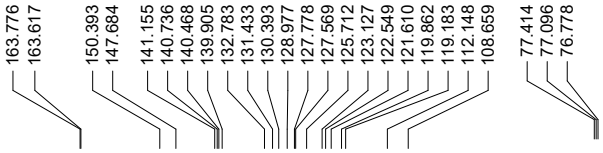


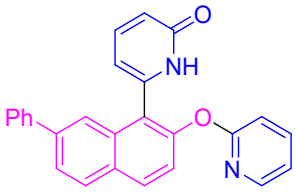
3am

(400 MHz, $CDCl_3$)



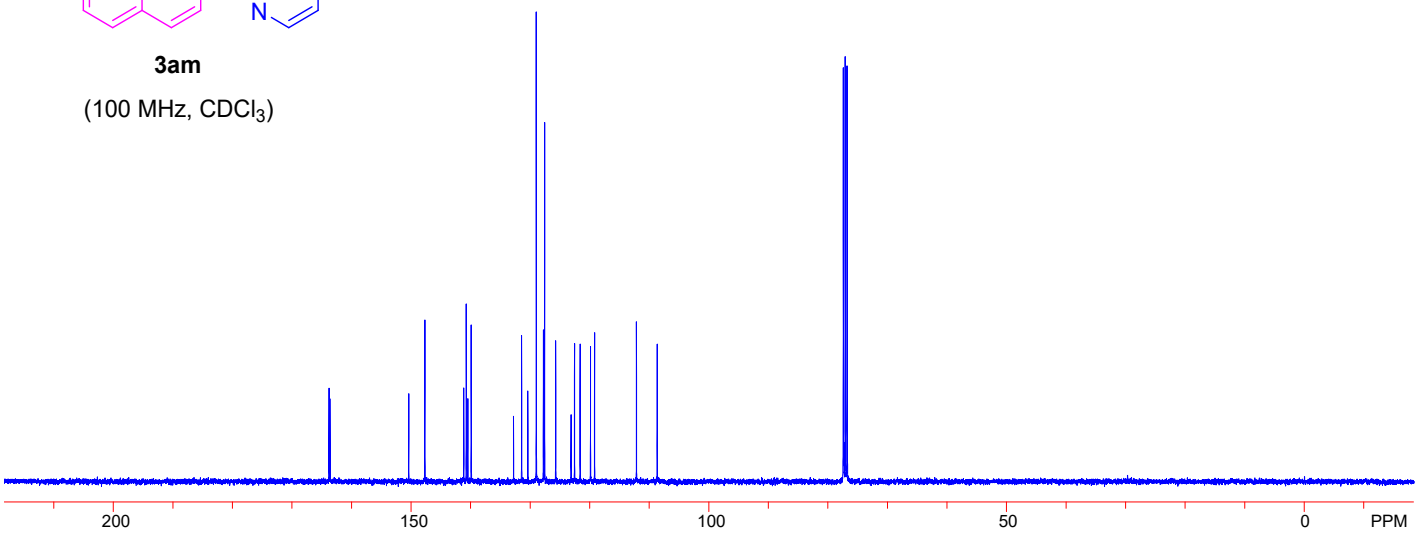


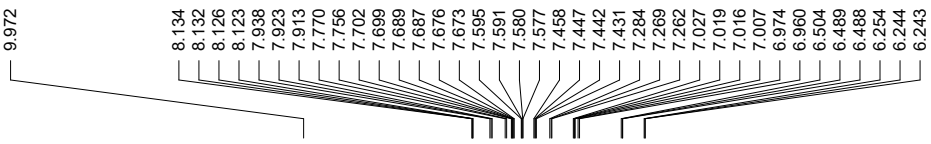


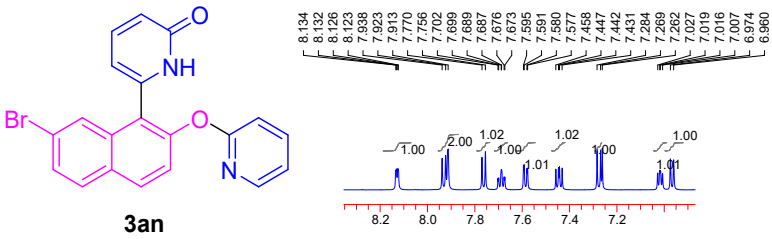


3am

(100 MHz, $CDCl_3$)

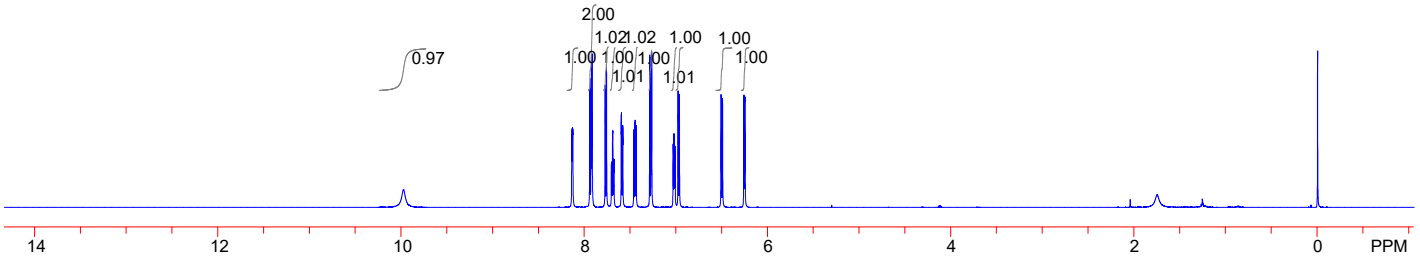


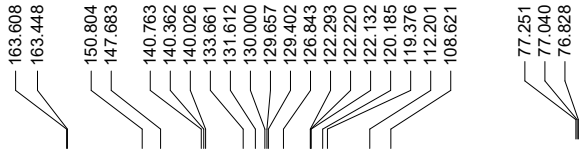


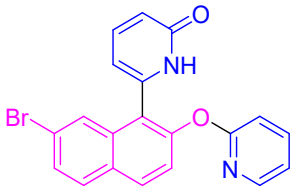


3an

(400 MHz, $CDCl_3$)

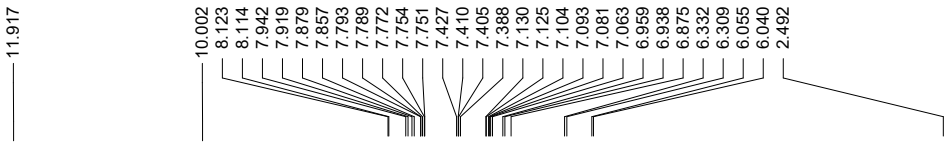


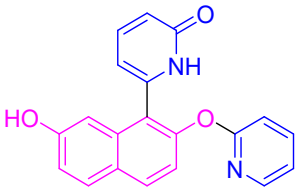




3an

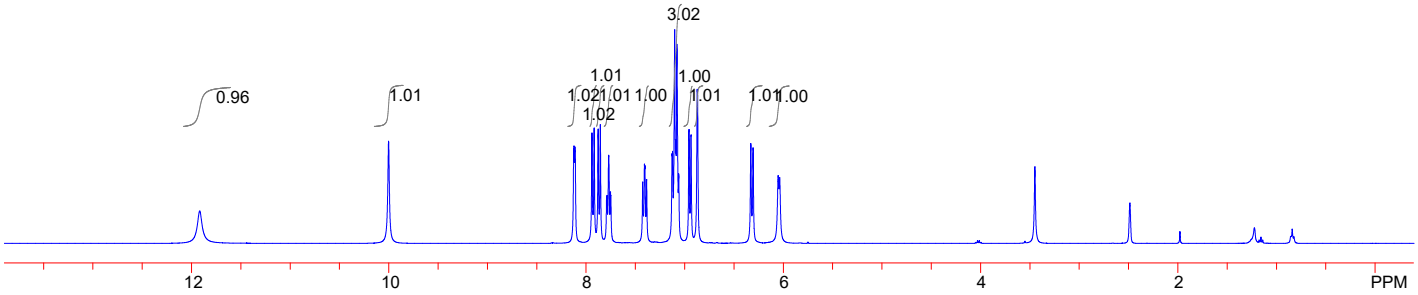
(150 MHz, $CDCl_3$)

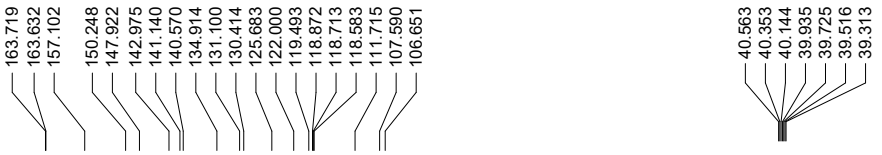


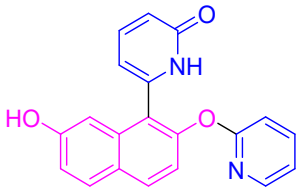


3ao

(400 MHz, $CDCl_3$)

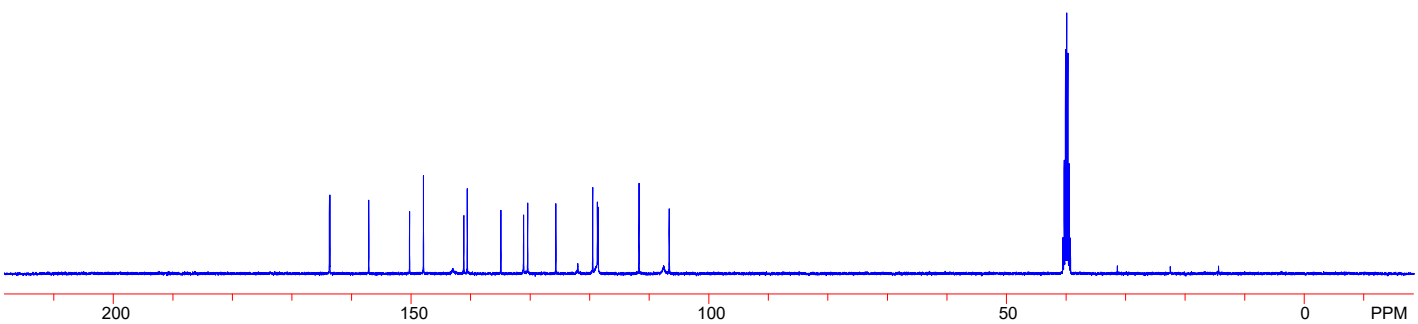


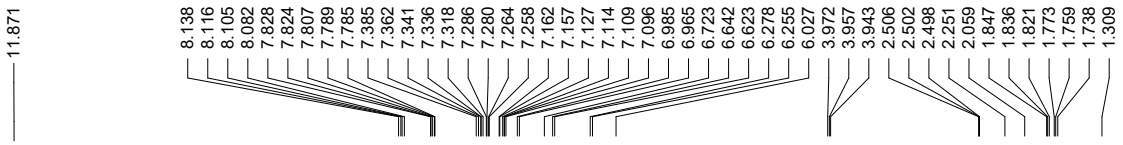


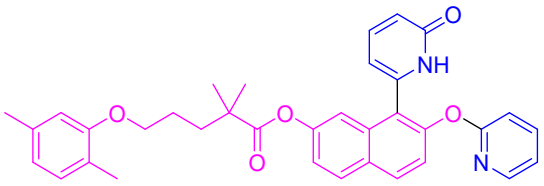


3ao

(100 MHz, $CDCl_3$)

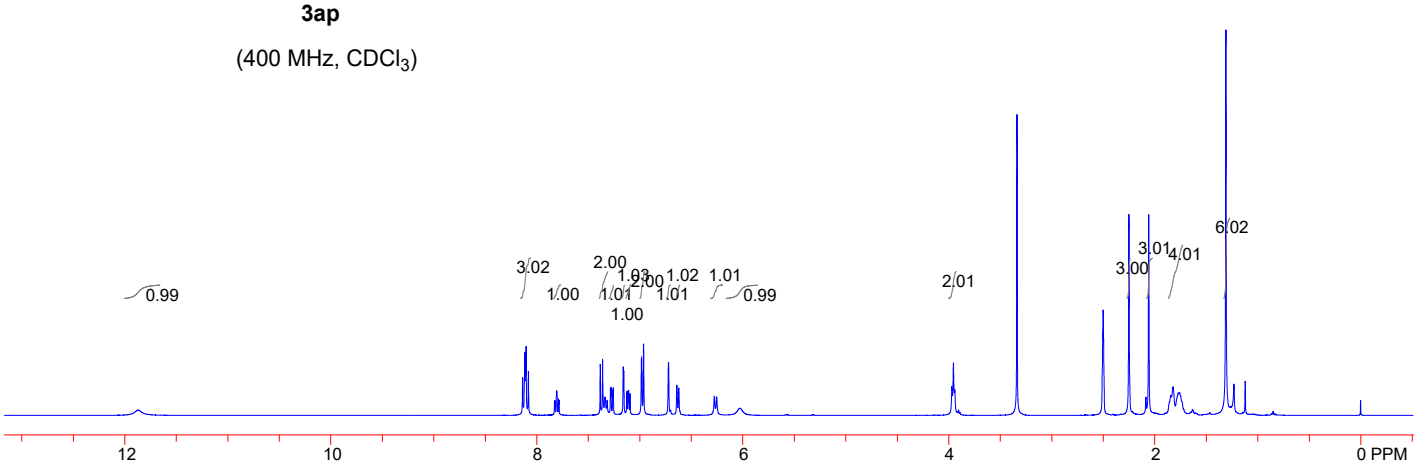


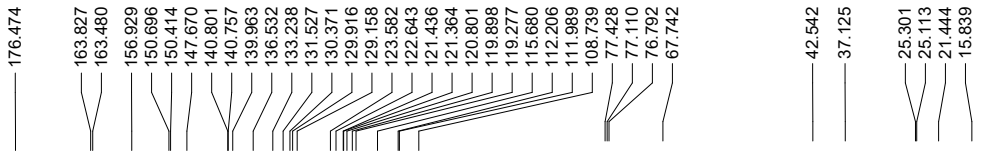


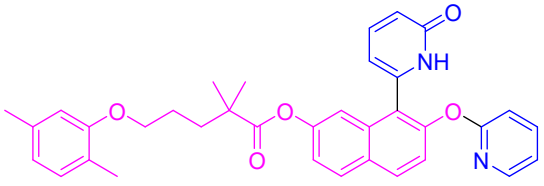


3ap

(400 MHz, $CDCl_3$)

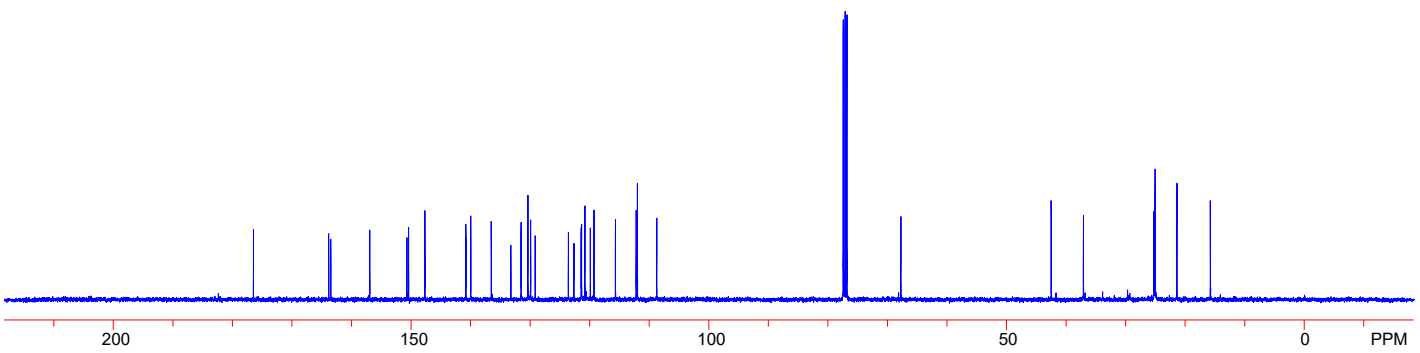


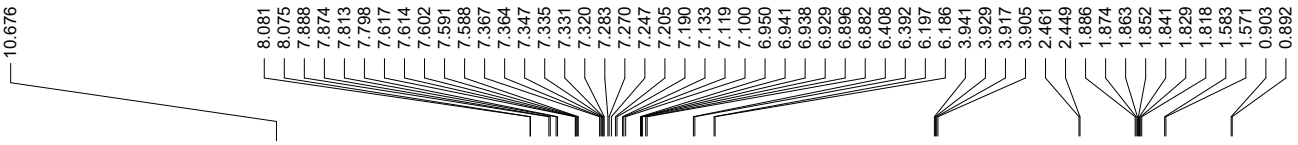


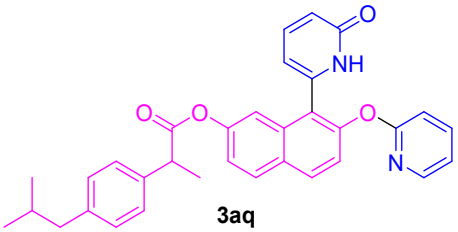


3ap

(100 MHz, $CDCl_3$)

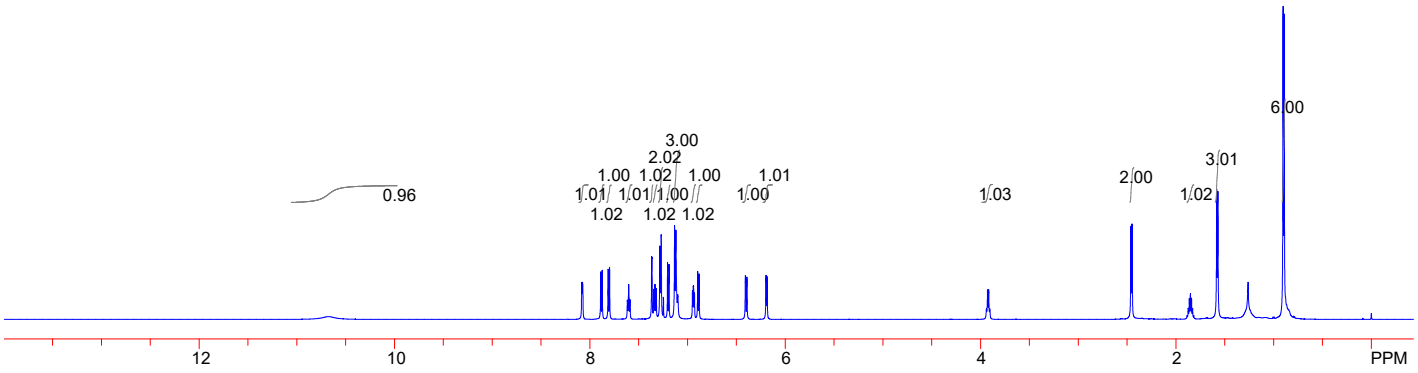


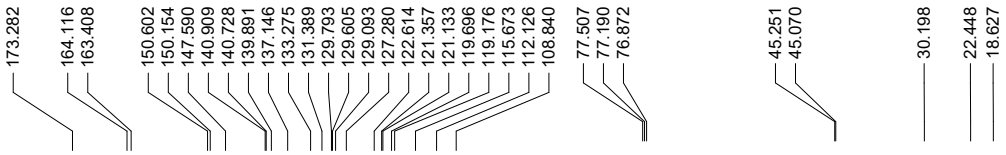


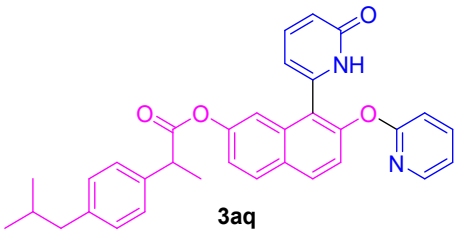


3aq

(600 MHz, $CDCl_3$)

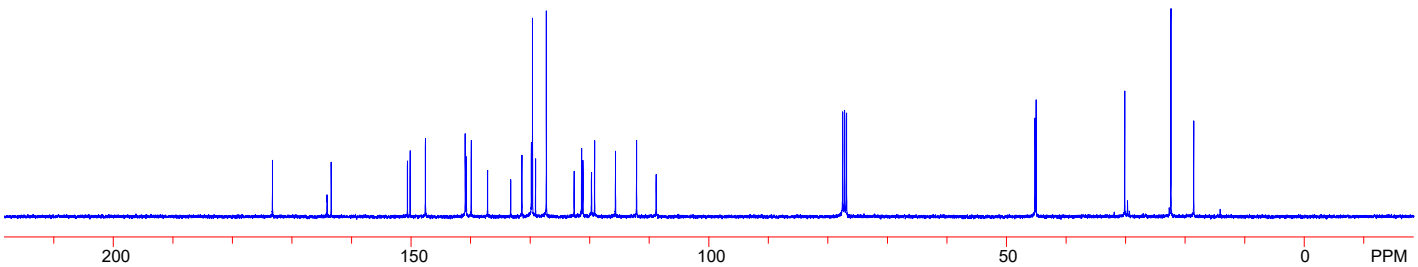


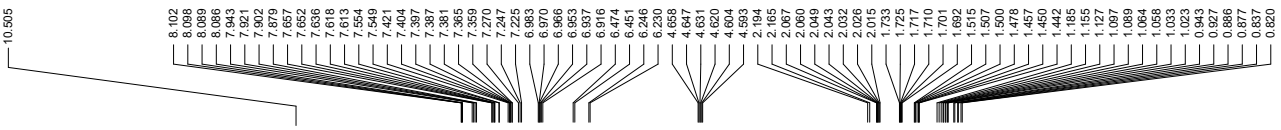


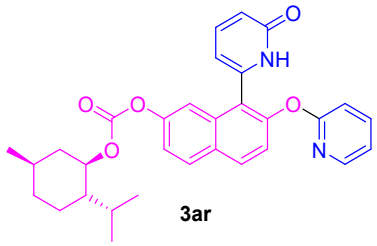


3aq

(100 MHz, $CDCl_3$)

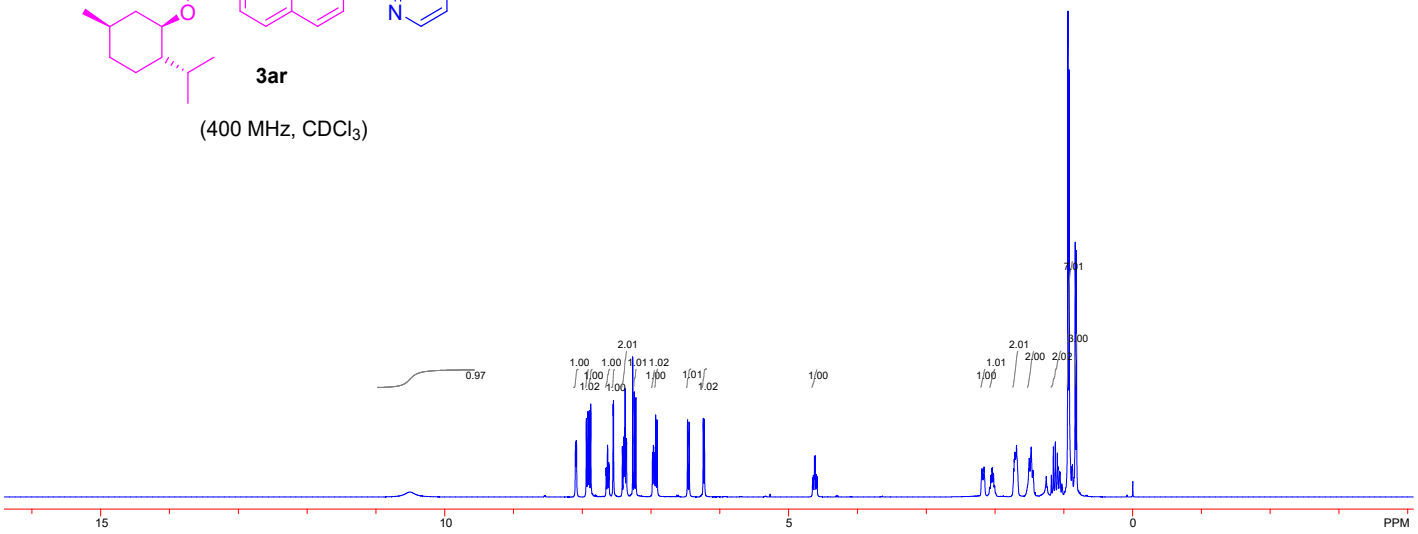


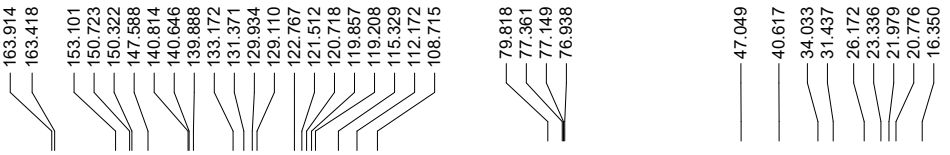


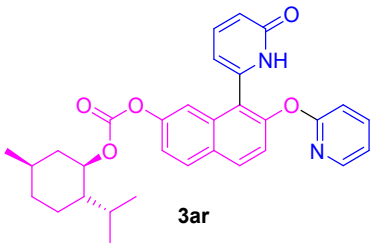


3ar

(400 MHz, $CDCl_3$)

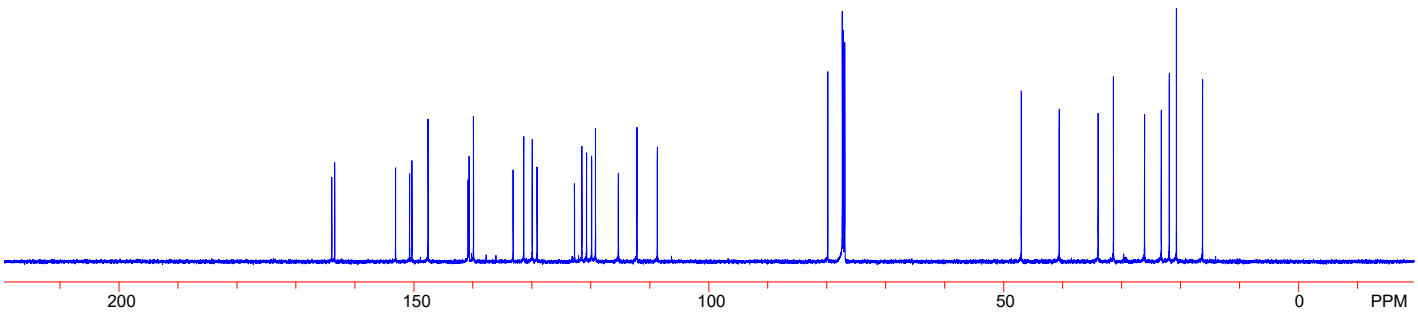




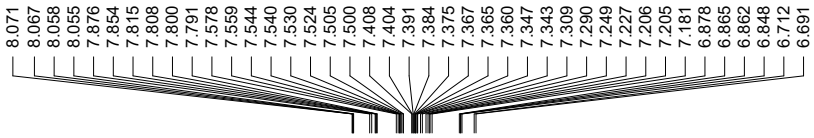


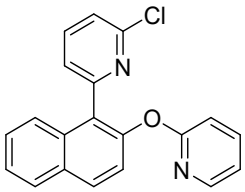
3ar

(150 MHz, $CDCl_3$)



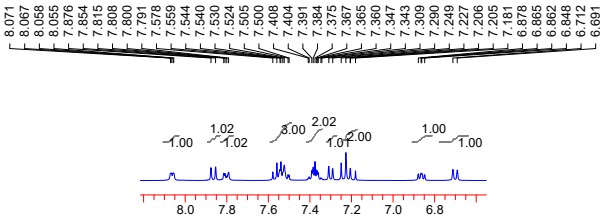
V. Copies of NMR spectra of 4 and 5

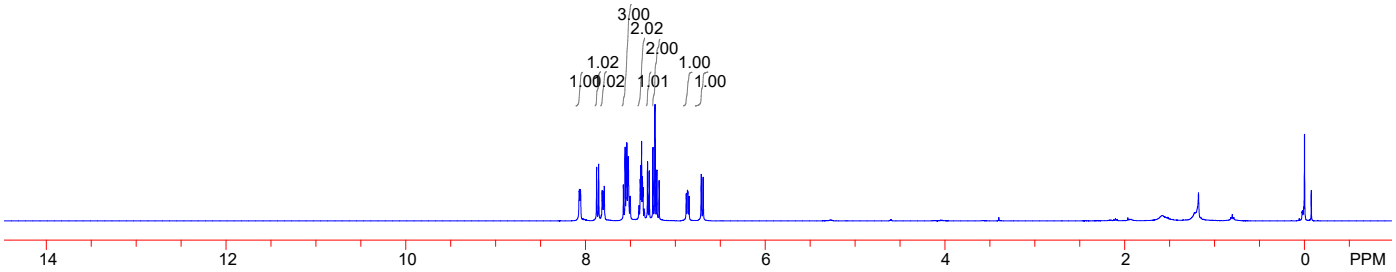


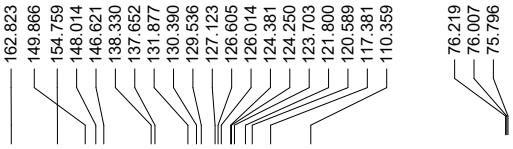


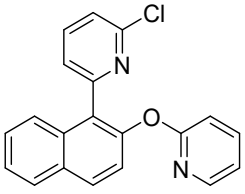
4

(400 MHz, $CDCl_3$)



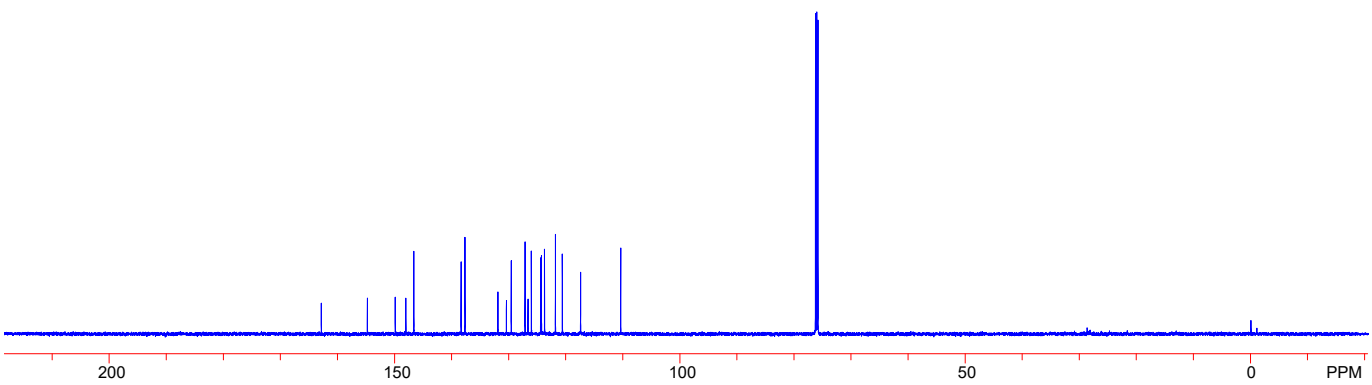


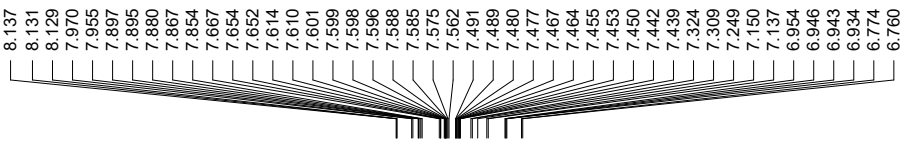


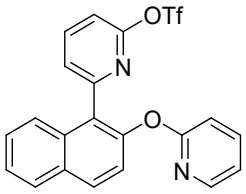


4

(150 MHz, $CDCl_3$)

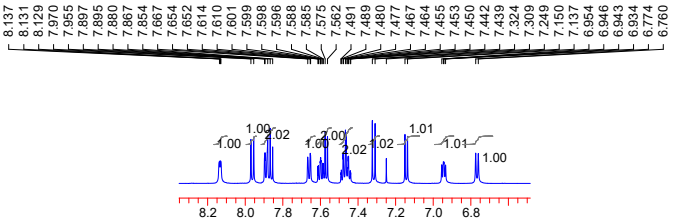


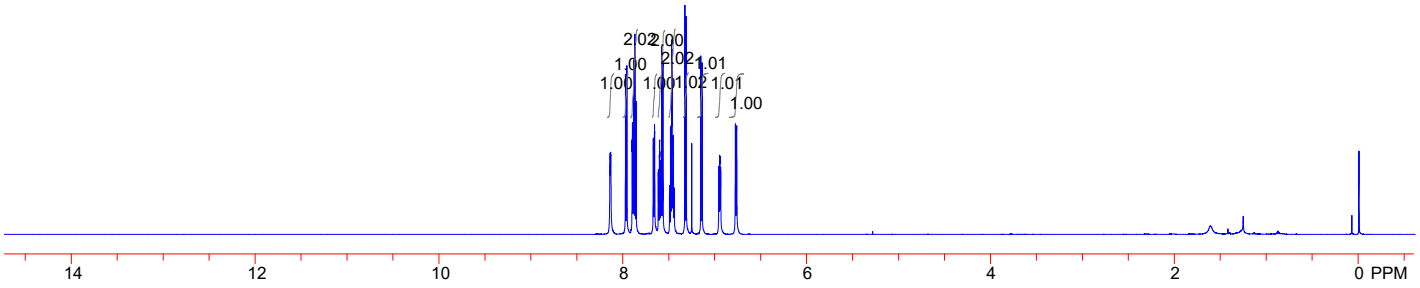


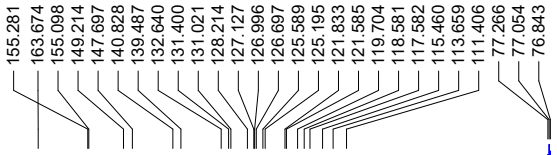


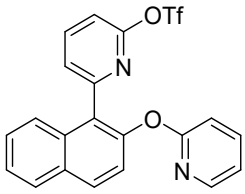
5

(600 MHz, $CDCl_3$)



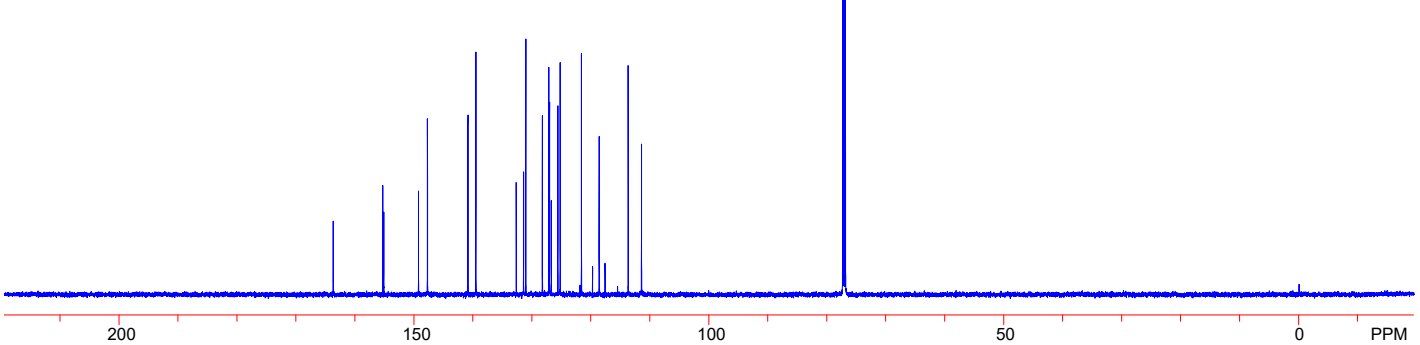


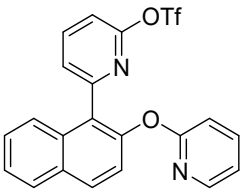




5

(150 MHz, $CDCl_3$)

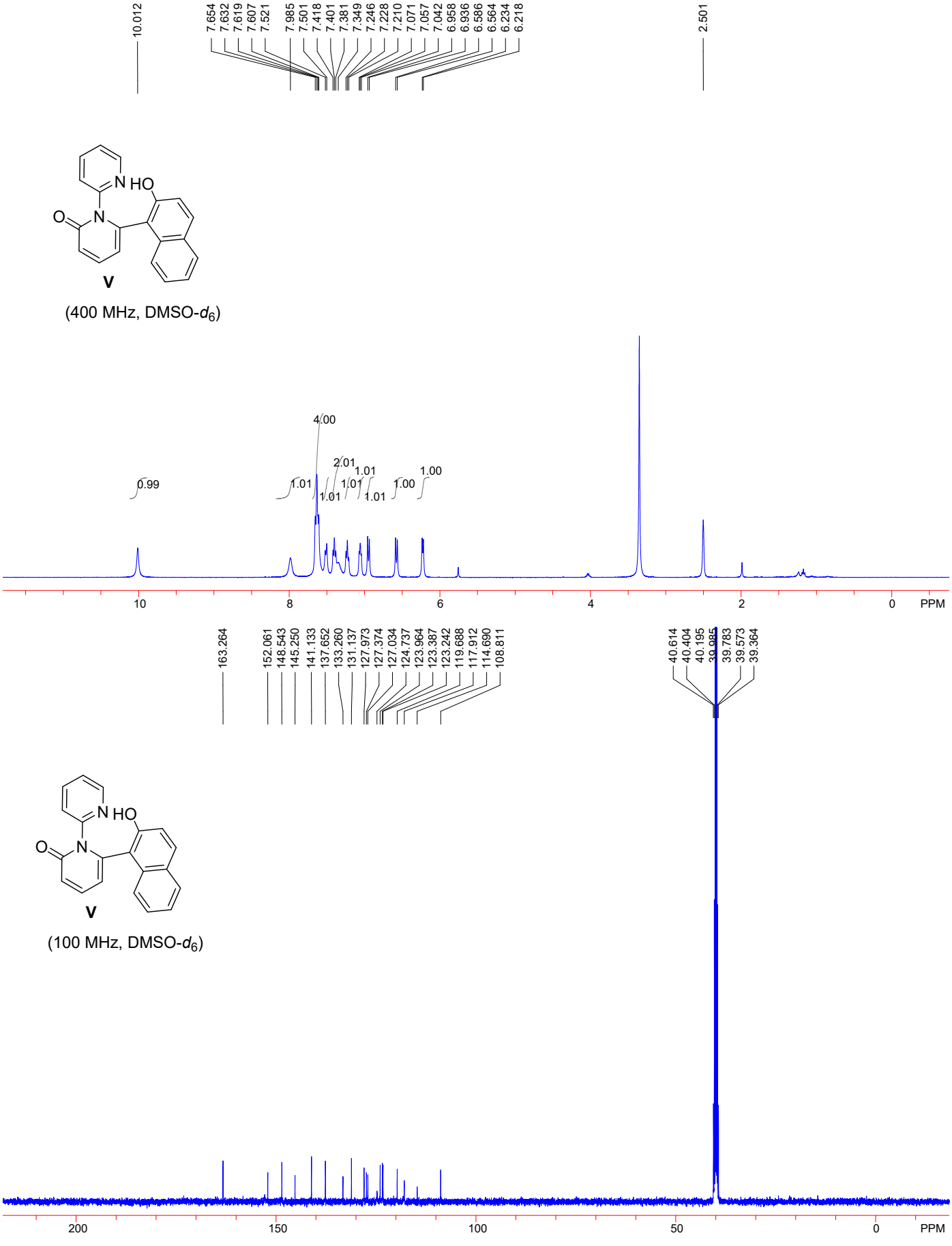




5

(376 MHz, $CDCl_3$)

VI. Copies of NMR spectra of V



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

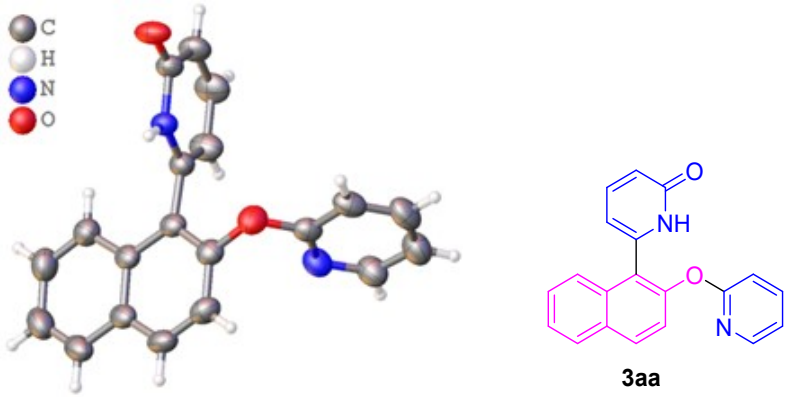


Fig. S1 X-ray crystal structure of **3aa** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an ethyl acetate/methanol (10:1) solution of **3aa**. Crystal data collection and refinement parameters of **3aa** 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 **3aa**

Empirical formula	$C_{20}H_{14}N_2O_2 \cdot 0.5OH$
Formula weight	322.84
Temp, K	293 (2)
Crystal system	monoclinic
Space group	C2/c
a, Å	13.7901(3)
b, Å	10.6650(2)
c, Å	22.1960(4)
α (°)	90
β (°)	101.160(2)
γ (°)	90
Volume, Å^3	3202.67(11)
Z	8
ρ_{calc}, g cm^{-3}	1.339
λ, Å	1.54184
μ, mm^{-1}	0.728
No. of data collected	6449
No. of unique data	3042
R_{int}	0.0139
Goodness-of-fit on F^2	1.044
R_1, wR_2 (I> =2σ(I))	0.0385, 0.1009
R_1, wR_2 (all data)	0.0426, 0.1051

VIII. X-ray crystal structure and data of V

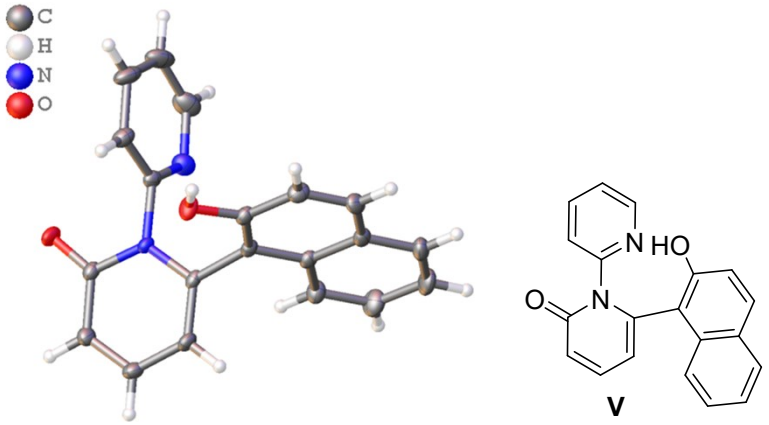


Fig. S2 X-ray crystal structure of **V** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a dichloromethane/methanol (9:10) solution of **V**. Crystal data collection and refinement parameters of **V** are summarized in Table S2. Intensity data were collected at 173 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 **V**

Empirical formula	$C_{20}H_{14}N_2O_2$
Formula weight	314.33
Temp, K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	9.0965(2)
b, Å	13.6340(2)
c, Å	13.1659(2)
α (°)	90
β (°)	109.138(2)
γ (°)	90
Volume, Å^3	1542.61(5)
Z	4
ρ_{calc}, g cm^{-3}	1.353
λ, Å	1.54184
μ, mm^{-1}	0.716
No. of data collected	6414
No. of unique data	2932
R_{int}	0.0210
Goodness-of-fit on F^2	1.040
R_1, wR_2 (I> =2σ(I))	0.0404, 0.1065
R_1, wR_2 (all data)	0.0448, 0.1103

IX. References

(1) (a) Mohanty, S. R.; Prusty, N.; Banjare, S. K.; Nanda, T,; Ravikumar, P. C. Overcoming the Challenges toward Selective C(6)−H Functionalization of 2-Pyridone with Maleimide through Mn(I)-Catalyst: Easy Access to All-Carbon Quaternary Center. *Org. Lett.* **2022**, *24*, 848-852. (b) Das, D.; Poddar, P.; Maity, S.; Samanta, R. Rhodium(III)-Catalyzed C6-Selective Arylation of 2-Pyridones and Related Heterocycles Using Quinone Diazides: Syntheses of Heteroarylated Phenols. *J. Org. Chem*. **2017**, 82, 3612-3621.

(2) Ghosh, B.; Samanta, R. Rh(III)-Catalyzed Straightforward Arylation of 8-Methyl/Formylquinolines Using Diazo Compounds. *Chem. Commun*. **2019**, *55*, 6886-6889.

(3) Huang, G.; Shan, Y.; Yu, J.-T.; Pan, C. Rh^{III}-Catalyzed C6-Selective Oxidative C−H/C−H Crosscoupling of 2-Pyridones with Thiophenes. *Chem. -Eur. J*. **2021**, *27*, 12294-12299.

(4) Xu, X.-H.; Wang, X.; Liu, G.-K.; Tokunaga, E.; Shibata, N. Regioselective Synthesis of Heteroaryl Triflones by LDA (Lithium Diisopropylamide)-Mediated Anionic Thia-Fries Rearrangement. *Org. Lett.* **2012**, *14*, 2544-2547.