Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Unsymmetrical Diaryl Oxindoles/Isoquinolinediones Using 2-Phenoxy-1*H*-benzo[*d*]imidazoles as Integrated Diarylating Reagent

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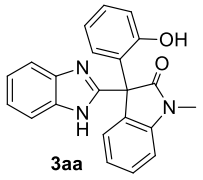
I. General experimental information

Commercial reagents were used without further purification. 2-Phenoxy-1*H*-benzo[*d*]imidazoles (**1**)[1], diazooxindoles (**2**)[2], diazo homophthalimides (**4**)[3] and $[RhCp^*Cl_2]_2$ [4] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Typical procedure for the synthesis of 3aa and spectroscopic data of 3aa-3am

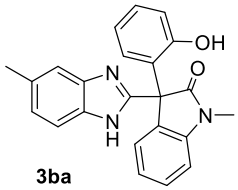
To a reaction tube equipped with a stir bar were added 2-phenoxy-1*H*-benzo[*d*]imidazole (**1a**, 42.1 mg, 0.2 mmol), TFE (2 mL), 3-diazo-1-methylindolin-2-one (**2a**, 52.0 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol) and NaOAc (24.0 mg, 0.3 mmol) with stirring. The mixture was stirred at 60 ℃ (oil bath) under air for 1 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3aa** (61.1 mg, 86%). **3ba-3am** were obtained in a similar manner.



3aa

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3aa)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (61.1 mg, 86%), mp 253.3-254.8 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.16 (s, 1H), 9.68 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.13-7.11 (m, 2H), 7.06-7.04 (m, 2H), 6.74-6.72 (m, 2H), 6.60 (d, J = 7.2 Hz, 1H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 175.9, 155.2, 151.2, 144.2, 142.7, 135.6, 130.9, 129.5, 129.4, 128.5, 127.3, 126.7, 122.7, 122.6, 121.6, 119.4, 119.2, 116.3, 112.4, 108.6, 57.5, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}N_3O_2$ 356.1394; Found 356.1392.

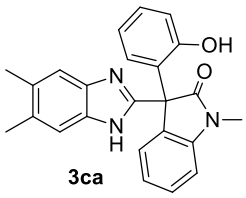


3ba

3-(2-Hydroxyphenyl)-1-methyl-3-(5-methyl-1*H*-benzo[*d*]imidazol-2-yl)indolin-2-one and 3-(2-hydroxyphenyl)-1-methyl-3-(6-methyl-1*H*-benzo[*d*]imidazol-2-yl)indolin-2-one (3ba)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (55.1 mg, 75%, the ratio of two products: 0.6:0.4), mp 257.7-258.8 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.01 (s, 1H), 9.66 (s, 1H), 7.42 (d, J = 7.8 Hz, 0.6H), 7.38-7.35 (m, 0.8H), 7.32-7.28 (m, 2.6H), 7.11 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.05-7.03 (m, 2H), 7.00 (d,

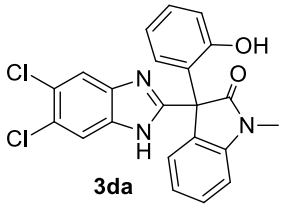
J = 8.4 Hz, 0.4H), 6.94 (d, *J* = 8.4 Hz, 0.6H), 6.73-6.70 (m, 2H), 6.57-6.56 (m, 1H), 3.22 (s, 3H), 2.39 (s, 1.8H), 2.37 (s, 1.2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6): δ 176.0, 155.2, 150.9, 150.5, 144.2, 143.1, 140.8, 135.9, 133.6, 132.0, 130.9, 130.4, 129.6, 129.4, 128.5, 127.5, 126.7, 124.1, 123.2, 122.5, 119.4, 118.9, 118.8, 116.3, 112.1, 111.9, 108.6, 57.4, 27.1, 21.85, 21.75. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1555.



3ca

3-(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3ca)

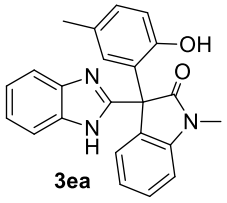
Eluent: petroleum ether/ethyl acetate (3:1). White solid (58.2 mg, 76%), mp 296.6-297.5 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.91 (br s, 1H), 9.66 (s, 1H), 7.31-7.27 (m, 4H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.05-7.01 (m, 2H), 6.73-6.69 (m, 2H), 6.54 (d, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 2.27 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6): δ 176.1, 155.2, 150.0, 144.2, 141.3, 134.2, 131.3, 130.9, 129.9, 129.6, 129.3, 128.4, 127.6, 126.7, 122.5, 119.3, 119.2, 116.2, 112.3, 108.5, 57.4, 27.1, 20.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}N_3O_2$ 384.1707; Found 384.1705.



3da

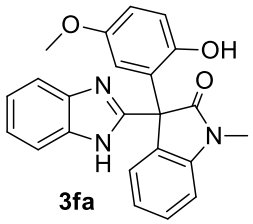
3-(5,6-Dichloro-1*H*-benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3da)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (51.8 mg, 61%), mp 241.2-242.9 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.48 (br s, 1H), 9.74 (s, 1H), 7.88 (br s, 1H), 7.69 (br s, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.17-7.13 (m, 1H), 7.08-7.05 (m, 2H), 6.77-6.74 (m, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 3.24 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ 175.4, 155.3, 154.2, 144.1, 142.3, 135.1, 130.5, 129.6, 129.3, 128.8, 126.9, 126.7, 125.2, 124.3, 122.8, 120.5, 119.5, 116.4, 113.5, 108.8, 57.5, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{16}Cl_2N_3O_2$ 424.0614; Found 424.0604.



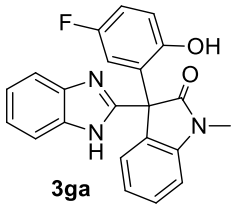
3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxy-5-methylphenyl)-1-methylindolin-2-one (3ea)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (50.2 mg, 68%), mp 270.4-271.9 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.16 (br s, 1H), 9.44 (s, 1H), 7.55-7.51 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.16-7.13 (m, 2H), 7.06-7.03 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.47 (s, 1H), 3.22 (s, 3H), 2.08 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.9, 153.1, 151.4, 144.1, 142.7, 135.6, 131.1, 129.82, 129.80, 128.5, 127.8, 126.9, 126.7, 122.6, 121.6, 119.2, 116.3, 112.4, 108.6, 57.6, 27.1, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1556.



3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxy-5-methoxyphenyl)-1-methylindolin-2-one (3fa)

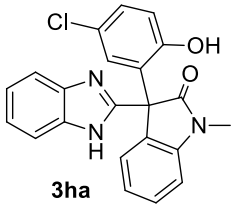
Eluent: petroleum ether/ethyl acetate (3:1). White solid (46.3 mg, 60%), mp 195.2-196.4 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.17 (br s, 1H), 9.21 (s, 1H), 7.56-7.50 (m, 2H), 7.39-7.38 (m, 1H), 7.31-7.30 (m, 1H), 7.17-7.14 (m, 2H), 7.06-7.05 (m, 2H), 6.75 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.17 (s, 1H), 3.54 (s, 3H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 175.7, 152.3, 151.1, 149.1, 144.2, 142.6, 135.6, 130.7, 128.6, 128.0, 126.7, 122.8, 122.6, 121.7, 119.2, 116.7, 116.4, 113.4, 112.3, 108.7, 57.5, 55.8, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_3$ 386.1499; Found 386.1497.



3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(5-fluoro-2-hydroxyphenyl)-1-methylindolin-2-one (3ga)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (61.2 mg, 82%), mp 198.1-199.4 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.26 (br s, 1H), 9.75 (s, 1H), 7.59-7.53 (m, 2H), 7.42 (d, *J* = 6.6 Hz, 1H), 7.34-7.32 (m,

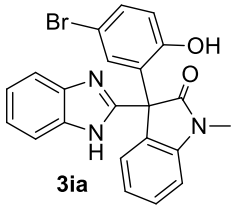
1H), 7.19-7.16 (m, 2H), 7.09-7.06 (m, 2H), 7.01 (td, J_1 = 8.4 Hz, J_2 = 3.0 Hz, 1H), 6.74 (dd, J_1 = 9.0 Hz, J_2 = 4.8 Hz, 1H), 6.41 (dd, J_1 = 10.2 Hz, J_2 = 3.6 Hz, 1H), 3.24 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 175.3, 155.6 (d, $^1J_{C\text{-}F}$ = 232.6 Hz), 151.7, 150.7, 144.2, 142.7, 135.6, 130.4, 128.8, 128.4 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 126.6, 122.9, 122.8, 121.8, 119.3, 117.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 116.0 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 112.4, 108.8, 57.3, 27.1. ^{19}F NMR (376 MHz, DMSO-d_6): δ -125.41 – -125.47 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}FN_3O_2$ 374.1299; Found 374.1295.



3ha

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(5-chloro-2-hydroxyphenyl)-1-methylindolin-2-one (3ha)

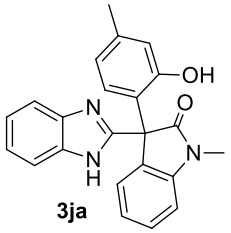
Eluent: petroleum ether/ethyl acetate (3:1). White solid (58.5 mg, 75%), mp 246.2-247.6 ℃. ^1H NMR (600 MHz, DMSO-d_6): δ 12.27 (s, 1H), 10.09 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.23 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H), 7.21-7.16 (m, 2H), 7.10-7.07 (m, 2H), 6.78 (d, J = 9.0 Hz, 1H), 6.63 (d, J = 2.4 Hz, 1H), 3.25 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 175.2, 154.5, 150.6, 144.2, 142.7, 135.5, 130.3, 129.3, 129.1, 129.0, 128.8, 126.6, 122.9, 122.84, 122.79, 121.8, 119.3, 118.0, 112.4, 108.8, 57.3, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}ClN_3O_2$ 390.1004; Found 390.1000.



3ia

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(5-bromo-2-hydroxyphenyl)-1-methylindolin-2-one (3ia)

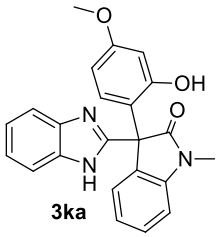
Eluent: petroleum ether/ethyl acetate (3:1). White solid (69.5 mg, 80%), mp 286.9-287.6 ℃. ^1H NMR (600 MHz, DMSO-d_6): δ 12.25 (s, 1H), 10.10 (s, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.34-7.31 (m, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.08-7.06 (m, 2H), 6.74-6.71 (m, 2H), 3.23 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 175.2, 154.9, 150.6, 144.2, 142.7, 135.5, 132.2, 131.8, 130.4, 129.6, 128.8, 126.6, 122.9, 122.8, 121.8, 119.3, 118.6, 112.4, 110.3, 108.8, 57.3, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrN_3O_2$ 434.0499; Found 434.0503.



3ja

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxy-4-methylphenyl)-1-methylindolin-2-one (3ja)

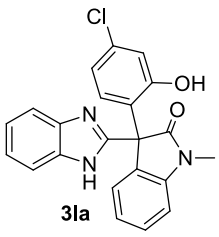
Eluent: petroleum ether/ethyl acetate (3:1). White solid (53.2 mg, 72%), mp 178.3-179.6 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.13 (s, 1H), 9.56 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.05-7.02 (m, 2H), 6.57-6.54 (m, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 176.0, 155.1, 151.4, 144.1, 142.7, 138.9, 135.6, 131.1, 129.4, 128.4, 126.7, 124.5, 122.7, 122.6, 121.6, 120.1, 119.2, 116.9, 112.4, 108.6, 57.3, 27.1, 21.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1551.



3ka

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxy-4-methoxyphenyl)-1-methylindolin-2-one (3ka)

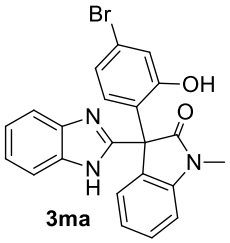
Eluent: petroleum ether/ethyl acetate (3:1). White solid (44.7 mg, 58%), mp 195.2-196.4 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.12 (br s, 1H), 9.71 (s, 1H), 7.52-7.50 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.14 (br s, 2H), 7.07-7.03 (m, 2H), 6.50 (d, *J* = 8.8 Hz, 1H), 6.34 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 2.4 Hz, 1H), 3.65 (s, 3H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 176.1, 160.4, 156.3, 151.5, 144.0, 142.7, 135.6, 131.3, 130.1, 128.4, 126.6, 122.6, 121.6, 121.1, 119.8, 119.2, 118.9, 112.3, 108.6, 104.7, 102.3, 57.0, 55.5, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_3$ 386.1499; Found 386.1497.



3la

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(4-chloro-2-hydroxyphenyl)-1-methylindolin-2-one (3la)

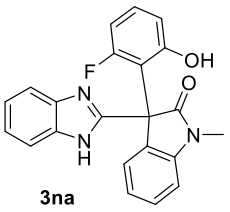
Eluent: petroleum ether/ethyl acetate (3:1). White solid (47.6 mg, 61%), mp 206.8-208.0 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.21 (br s, 1H), 10.28 (s, 1H), 7.56-7.51 (m, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.33-7.31 (m, 1H), 7.16-7.15 (m, 2H), 7.08-7.05 (m, 2H), 6.84 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.4, 156.3, 150.8, 144.2, 142.7, 135.6, 133.4, 131.0, 130.5, 128.7, 126.61, 126.58, 122.9, 122.8, 121.7, 119.33, 119.26, 116.0, 112.4, 108.8, 57.1, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}ClN_3O_2$ 390.1004; Found 390.1002.



3ma

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(4-bromo-2-hydroxyphenyl)-1-methylindolin-2-one (3ma)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (49.5 mg, 57%), mp 202.8-203.6 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.19 (br s, 1H), 10.25 (s, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.35-7.31 (m, 2H), 7.18-7.12 (m, 2H), 7.08-7.05 (m, 2H), 6.96 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.88 (d, J = 1.8 Hz, 1H), 6.56 (d, J = 8.4 Hz, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.4, 156.4, 150.7, 144.2, 142.7, 135.6, 132.5, 131.3, 130.4, 128.7, 127.0, 126.6, 122.8, 122.7, 122.2, 121.7, 119.3, 118.8, 112.4, 108.8, 57.1, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrN_3O_2$ 434.0499; Found 434.0490.

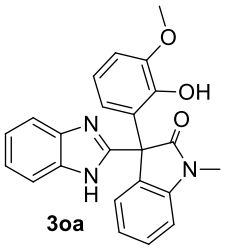


3na

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-fluoro-6-hydroxyphenyl)-1-methylindolin-2-one (3na)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (46.3 mg, 62%), mp 274.5-276.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.33 (br s, 1H), 10.23 (s, 1H), 7.44 (br s, 2H), 7.35-7.31 (m, 2H), 7.18-7.03 (m, 5H), 6.63-6.58 (m, 2H), 3.16 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 174.7, 162.0 (d, $^{1}J_{C\text{-}F}$ = 244.2 Hz), 157.5, 152.2, 144.1, 142.7, 136.0, 130.5, 129.9 (d, $^{3}J_{C\text{-}F}$ = 11.6 Hz), 128.9, 126.3, 122.9, 122.3, 121.2, 119.0 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 114.4 (d, $^{2}J_{C\text{-}F}$ = 13.1 Hz), 112.7, 111.8, 108.9, 107.2 (d, $^{2}J_{C\text{-}F}$ = 24.8 Hz), 54.4, 27.1. ^{19}F

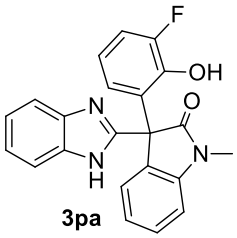
NMR (376 MHz, DMSO-d_6): δ -110.30 (dd, J_1 = 11.7 Hz, J_2 = 6.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_3$ 374.1299; Found 374.1308.



3oa

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxy-3-methoxyphenyl)-1-methylindolin-2-one (3oa)

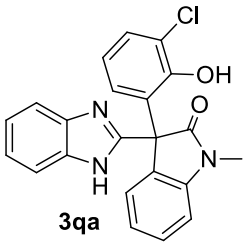
Eluent: petroleum ether/ethyl acetate (3:1). White solid (45.5 mg, 59%), mp 195.3-196.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.15 (br s, 1H), 8.88 (s, 1H), 7.52 (br s, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.15 (br s, 2H), 7.07-7.04 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 8.0 Hz, 1H), 6.23 (d, J = 7.6 Hz, 1H), 3.71 (s, 3H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.7, 151.4, 148.3, 144.6, 144.1, 142.7, 135.6, 131.0, 128.6, 127.2, 126.7, 122.6, 121.7, 121.6, 121.2, 119.5, 119.1, 112.3, 112.0, 108.7, 57.5, 56.4, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_3$ 386.1499; Found 386.1497.



3pa

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(3-fluoro-2-hydroxyphenyl)-1-methylindolin-2-one (3pa)

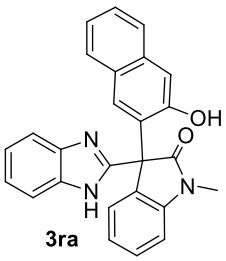
Eluent: petroleum ether/ethyl acetate (3:1). White solid (53.8 mg, 72%), mp 174.2-175.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (br s, 1H), 9.97 (s, 1H), 7.54 (br s, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.35-7.31 (m, 1H), 7.16-7.06 (m, 5H), 6.79-6.74 (m, 1H), 6.47 (d, J = 8.0 Hz, 1H), 3.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.4, 152.2 (d, $^1J_{C\text{-}F}$ = 237.0 Hz), 150.1, 144.0, 143.0 (d, $^2J_{C\text{-}F}$ = 16.4 Hz), 142.6, 135.5, 130.5, 130.3 (d, $^4J_{C\text{-}F}$ = 1.9 Hz), 128.8, 126.6, 125.0, 122.8, 121.6, 119.5 (d, $^3J_{C\text{-}F}$ = 6.9 Hz), 119.3, 118.4, 115.9 (d, $^2J_{C\text{-}F}$ = 17.9 Hz), 112.3, 108.9, 57.5 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 27.2. ^{19}F NMR (376 MHz, DMSO-d_6): δ -135.30 – -135.34 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}FN_3O_2$ 374.1299; Found 374.1297.



3qa

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(3-chloro-2-hydroxyphenyl)-1-methylindolin-2-one (3qa)

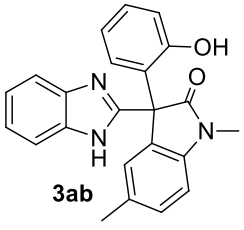
Eluent: petroleum ether/ethyl acetate (3:1). White solid (56.9 mg, 73%), mp 267.4-268.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.24 (br s, 1H), 9.81 (br s, 1H), 7.54 (br s, 2H), 7.38-7.32 (m, 3H), 7.16-7.06 (m, 4H), 6.82 (t, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 3.26 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.7, 151.1, 151.0, 144.0, 142.7, 135.6, 130.3, 130.1, 129.9, 128.9, 128.5, 126.6, 122.9, 122.7, 122.0, 121.7, 120.9, 119.2, 112.4, 109.1, 57.9, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}ClN_3O_2$ 390.1004; Found 390.1002.



3ra

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(3-hydroxynaphthalen-2-yl)-1-methylindolin-2-one (3ra)

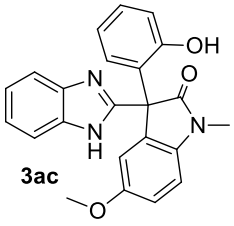
Eluent: petroleum ether/ethyl acetate (3:1). White solid (43.0 mg, 53%), mp 250.0-251.8 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.30 (br s, 1H), 10.11 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.58-7.55 (m, 2H), 7.43-7.38 (m, 2H), 7.34 (t, J = 7.8 Hz, 1H), 7.28 (s, 1H), 7.24-7.20 (m, 3H), 7.11-7.05 (m, 3H), 3.29 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 175.8, 153.6, 151.2, 144.3, 142.8, 135.7, 134.5, 130.9, 130.1, 129.2, 128.7, 128.2, 127.7, 127.0, 126.6, 125.8, 123.7, 122.8, 122.7, 121.7, 119.3, 112.4, 110.2, 108.8, 58.1, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}N_3O_2$ 406.1550; Found 406.1552.



3ab

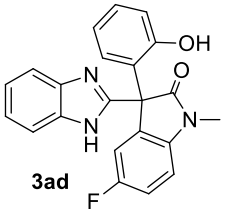
3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-1,5-dimethylindolin-2-one (3ab)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (45.8 mg, 62%), mp > 300 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.12 (br s, 1H), 9.66 (s, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.17-7.10 (m, 5H), 6.94 (d, J = 7.8 Hz, 1H), 6.74-6.72 (m, 2H), 6.60 (d, J = 7.2 Hz, 1H), 3.20 (s, 3H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.9, 155.2, 151.3, 142.7, 141.9, 135.6, 131.4, 130.9, 129.6, 129.4, 128.8, 127.5, 127.2, 122.7, 121.6, 119.4, 119.2, 116.4, 112.4, 108.4, 57.6, 27.1, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1551.



3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-5-methoxy-1-methylindolin-2-one (3ac)

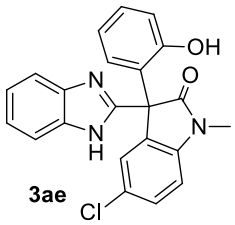
Eluent: petroleum ether/ethyl acetate (3:1). White solid (43.9 mg, 57%), mp 298.7-299.9 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.16 (br s, 1H), 9.68 (s, 1H), 7.57-7.50 (m, 2H), 7.15-7.12 (m, 3H), 6.98-6.96 (m, 2H), 6.89 (d, J = 8.4 Hz, 1H), 6.75-6.74 (m, 2H), 6.63 (d, J = 7.2 Hz, 1H), 3.69 (s, 3H), 3.20 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.5, 155.7, 155.4, 151.3, 142.7, 137.8, 135.6, 132.3, 129.54, 129.49, 127.2, 122.7, 121.6, 119.4, 119.2, 116.4, 114.4, 112.3, 108.9, 57.9, 55.9, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_3$ 386.1499; Found 386.1504.



3-(1*H*-Benzo[*d*]imidazol-2-yl)-5-fluoro-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3ad)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (57.5 mg, 77%), mp 219.8-220.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (br s, 1H), 9.76 (s, 1H), 7.55 (br s, 2H), 7.20-7.13 (m, 5H), 7.09-7.06 (m, 1H), 6.77-6.74 (m, 2H), 6.61 (d, J = 6.8 Hz, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 175.5, 158.8 (d, $^1J_{C\text{-}F}$ = 234.5 Hz), 155.2, 150.6, 142.6, 140.5, 135.5, 132.7 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 129.7, 129.6, 126.7, 122.9, 121.7, 121.1, 119.5, 119.3, 118.9, 116.3, 114.8 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 114.3 (d, $^2J_{C\text{-}F}$ = 25.7 Hz), 112.4,

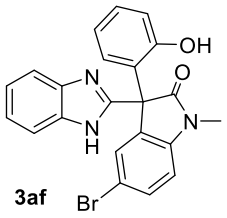
109.5 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 57.8, 27.3. ^{19}F NMR (376 MHz, DMSO-d_6): δ -113.08 – -113.14 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}FN_3O_2$ 374.1299; Found 374.1301.



3ae

3-(1H-Benzo[*d*]imidazol-2-yl)-5-chloro-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3ae)

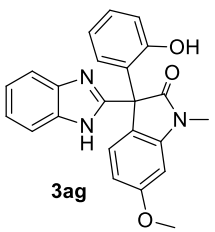
Eluent: petroleum ether/ethyl acetate (3:1). White solid (49.9 mg, 64%), mp 237.4-238.8 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.26 (s, 1H), 9.80 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.33 (d, J = 2.0 Hz, 1H), 7.21-7.12 (m, 3H), 7.10 (d, J = 8.4 Hz, 1H), 6.77-6.74 (m, 2H), 6.62-6.60 (m, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.5, 155.2, 150.5, 143.2, 142.6, 135.6, 132.9, 129.8, 129.6, 128.5, 126.65, 126.55, 126.4, 122.9, 121.8, 119.6, 119.3, 116.3, 112.4, 110.2, 57.6, 27.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}ClN_3O_2$ 390.1004; Found 390.1003.



3af

3-(1*H*-Benzo[*d*]imidazol-2-yl)-5-bromo-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3af)

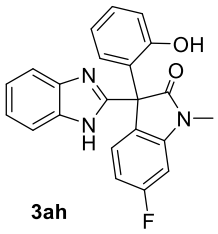
Eluent: petroleum ether/ethyl acetate (3:1). White solid (48.6 mg, 56%), mp 253.3-254.3 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.24 (br s, 1H), 9.78 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.52 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 7.19-7.14 (m, 3H), 7.07 (d, J = 8.4 Hz, 1H), 6.77-6.75 (m, 2H), 6.60 (d, J = 7.2 Hz, 1H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 175.4, 155.2, 150.5, 143.6, 142.6, 135.7, 133.2, 131.3, 129.8, 129.6, 129.1, 126.7, 122.9, 121.8, 119.6, 119.3, 116.3, 114.3, 112.4, 110.8, 57.5, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrN_3O_2$ 434.0499; Found 434.0493.



3ag

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-6-methoxy-1-methylindolin-2-one (3ag)

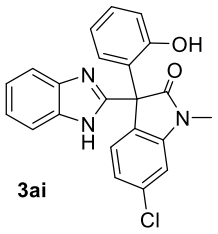
Eluent: petroleum ether/ethyl acetate (3:1). White solid (40.1 mg, 52%), mp 271.3-272.7 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.13 (br s, 1H), 9.67 (s, 1H), 7.57-7.51 (m, 2H), 7.25 (d, J = 7.8 Hz, 1H), 7.16-7.13 (m, 3H), 6.74-6.72 (m, 3H), 6.62 (br s, 2H), 3.81 (s, 3H), 3.24 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 176.4, 160.4, 155.2, 151.6, 145.3, 142.7, 135.7, 129.4, 129.3, 127.6, 127.3, 122.8, 122.6, 121.6, 119.4, 119.1, 116.3, 112.3, 107.1, 96.2, 57.0, 55.9, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_3$ 386.1499; Found 386.1501.



3ah

3-(1*H*-Benzo[*d*]imidazol-2-yl)-6-fluoro-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3ah)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (53.0 mg, 71%), mp 278.5-279.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.21 (br s, 1H), 9.75 (s, 1H), 7.55 (br s, 2H), 7.32 (dd, J_1 = 8.0 Hz, J_2 = 5.6 Hz, 1H), 7.15-7.11 (m, 3H), 7.05 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 6.87-6.82 (m, 1H), 6.76-6.73 (m, 2H), 6.58 (d, J = 8.0 Hz, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 176.2, 163.0 (d, $^{1}J_{C\text{-}F}$ = 241.4 Hz), 155.1, 150.9, 145.9 (d, $^{3}J_{C\text{-}F}$ = 12.2 Hz), 142.6, 135.7, 129.54, 129.49, 127.9 (d, $^{3}J_{C\text{-}F}$ = 10.1 Hz), 127.2, 126.6, 122.8, 121.7, 119.5, 119.2, 116.3, 112.4, 108.4 (d, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 97.4 (d, $^{2}J_{C\text{-}F}$ = 28.7 Hz), 57.0, 27.3. ^{19}F NMR (376 MHz, DMSO-d_6): δ -113.09 – -113.16 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}FN_3O_2$ 374.1299; Found 374.1303.

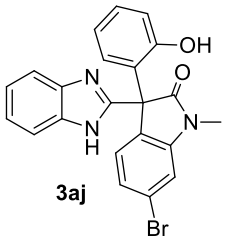


3ai

3-(1*H*-Benzo[*d*]imidazol-2-yl)-6-chloro-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3ai)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (51.5 mg, 66%), mp 298.5-299.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (br s, 1H), 9.76 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 1.6 Hz, 1H), 7.18-7.09 (m, 4H), 6.76-6.73 (m, 2H), 6.58 (d, J = 6.8 Hz, 1H),

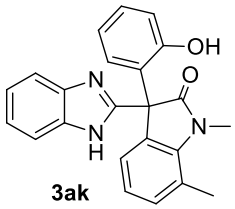
3.24 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ 176.0, 155.1, 150.5, 145.7, 142.6, 135.7, 133.2, 129.7, 129.6, 129.5, 127.9, 126.9, 122.9, 122.2, 121.7, 119.5, 119.3, 116.3, 112.4, 109.1, 57.1, 27.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}ClN_3O_2$ 390.1004; Found 390.1000.



3aj

3-(1*H*-Benzo[*d*]imidazol-2-yl)-6-bromo-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3aj)

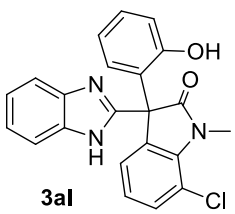
Eluent: petroleum ether/ethyl acetate (3:1). White solid (49.5 mg, 57%), mp 233.5-234.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (br s, 1H), 9.75 (s, 1H), 7.55-7.50 (m, 2H), 7.34 (s, 1H), 7.26-7.22 (m, 2H), 7.16-7.12 (m, 3H), 6.74 (t, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 7.2 Hz, 1H), 3.23 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ 175.8, 155.1, 150.4, 145.8, 142.5, 135.7, 130.2, 129.6, 129.5, 128.3, 126.8, 125.2, 122.9, 121.8, 121.5, 119.5, 119.2, 116.2, 112.4, 111.8, 57.2, 27.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrN_3O_2$ 434.0499; Found 434.0495.



3ak

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)-1,7-dimethylindolin-2-one (3ak)

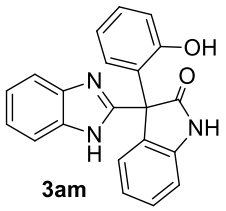
Eluent: petroleum ether/ethyl acetate (3:1). White solid (59.9 mg, 81%), mp 187.5-188.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.16 (br s, 1H), 9.71 (s, 1H), 7.55 (br s, 2H), 7.19-7.12 (m, 4H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.76-6.74 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 3.52 (s, 3H), 2.59 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6): δ 176.6, 155.2, 151.4, 142.7, 141.8, 135.6, 132.1, 131.4, 129.5, 129.4, 127.6, 124.9, 122.7, 122.4, 121.6, 119.6, 119.4, 119.2, 116.4, 112.4, 57.0, 30.2, 19.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1553.



3al

3-(1*H*-Benzo[*d*]imidazol-2-yl)-7-chloro-3-(2-hydroxyphenyl)-1-methylindolin-2-one (3al)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (49.1 mg, 63%), mp 179.8-180.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.27 (s, 1H), 9.84 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.21-7.13 (m, 3H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.77-6.72 (m, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 3.56 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 176.4, 155.0, 150.2, 142.6, 139.9, 135.7, 133.7, 130.5, 129.7, 129.6, 127.1, 126.0, 123.8, 123.0, 121.8, 119.5, 119.3, 116.2, 114.3, 112.5, 57.2, 30.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}ClN_3O_2$ 390.1004; Found 390.1001.



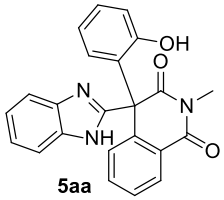
3am

3-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(2-hydroxyphenyl)indolin-2-one (3am)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (51.2 mg, 75%), mp 199.3-200.2 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.11 (br s, 1H), 10.73 (s, 1H), 9.69 (s, 1H), 7.57-7.52 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.16-7.13 (m, 3H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.77-6.74 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 177.5, 155.5, 151.7, 142.7, 135.5, 131.9, 129.6, 129.4, 128.4, 127.3, 126.9, 122.6, 121.9, 121.6, 119.4, 119.1, 118.4, 116.4, 112.3, 109.6, 58.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}N_3O_2$ 342.1237; Found 342.1233.

2. Typical procedure for the synthesis of 5aa and spectroscopic data of 5aa-5ac

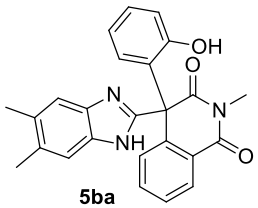
To a reaction tube equipped with a stir bar were added 2-phenoxy-1*H*-benzo[*d*]imidazole (**1a**, 42.1 mg, 0.2 mmol), TFE (2 mL), 4-diazo-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (**4a**, 60.4 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol) and NaOAc (24.0 mg, 0.3 mmol) with stirring. The mixture was stirred at 60 ℃ (oil bath) under air for 1 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1) as eluent to afford **5aa** (61.3 mg, 80%). **5ba-5ac** were obtained in a similar manner.



5aa

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(2-hydroxyphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5aa)

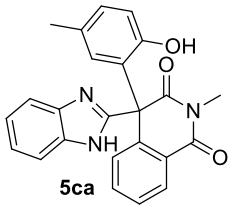
Eluent: petroleum ether/ethyl acetate (2:1). White solid (61.3 mg, 80%), mp 206.6-207.5 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.31 (br s, 1H), 9.88 (s, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.55-7.49 (m, 3H), 7.22-7.13 (m, 4H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.79-6.74 (m, 2H), 3.32 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 172.7, 164.6, 154.2, 151.4, 142.5, 140.8, 135.7, 133.6, 130.4, 130.3, 129.8, 129.6, 128.0, 127.7, 125.0, 123.3, 122.0, 119.6, 119.4, 116.2, 112.6, 57.4, 27.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}N_3O_3$ 384.1343; Found 384.1340.



5ba

4-(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-2-yl)-4-(2-hydroxyphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5ba)

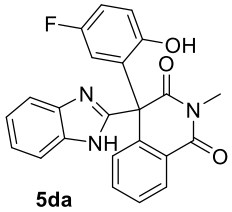
Eluent: petroleum ether/ethyl acetate (2:1). White solid (50.2 mg, 61%), mp 207.5-208.5 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.02 (br, 1H), 9.84 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.52-7.50 (m, 1H), 7.29 (s, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.742-6.737 (m, 2H), 3.32 (s, 3H), 2.27 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 172.7, 164.7, 154.2, 150.3, 141.2, 140.9, 134.2, 133.5, 131.9, 130.4, 130.3, 130.2, 129.7, 129.6, 128.0, 127.7, 124.9, 119.5, 119.3, 116.2, 112.5, 57.4, 27.8, 20.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_3$ 412.1656; Found 412.1653.



5ca

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(2-hydroxy-5-methylphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5ca)

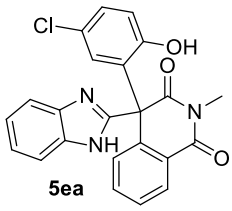
Eluent: petroleum ether/ethyl acetate (2:1). White solid (58.8 mg, 74%), mp 205.2-206.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.31 (s, 1H), 9.63 (s, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.54-7.48 (m, 3H), 7.21 (t, J = 7.6 Hz, 1H), 7.17-7.11 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.62 (s, 1H), 3.30 (s, 3H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 172.7, 164.7, 152.0, 151.5, 142.5, 140.9, 135.6, 133.5, 130.4, 130.1, 130.0, 128.0, 127.8, 127.6, 124.9, 123.3, 121.9, 119.6, 116.1, 112.6, 57.4, 27.8, 20.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}N_3O_3$ 398.1499; Found 398.1506.



5da

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(5-fluoro-2-hydroxyphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5da)

Eluent: petroleum ether/ethyl acetate (2:1). White solid (55.4 mg, 69%), mp 210.4-211.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.40 (br s, 1H), 9.94 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.55-7.52 (m, 3H), 7.22-7.20 (m, 2H), 7.16 (d, J = 7.6 Hz, 1H), 7.09 (td, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 6.76 (dd, J_1 = 8.8 Hz, J_2 = 4.8 Hz, 1H), 6.67 (dd, J_1 = 10.0 Hz, J_2 = 2.8 Hz, 1H), 3.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 172.1, 164.5, 155.5 (d, $^{1}J_{C\text{-}F}$ = 232.9 Hz), 150.9, 150.7 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 142.5, 140.2, 135.6, 133.8, 131.3 (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 130.1, 128.3, 127.9, 125.0, 123,5, 122.1, 119.7, 117.5 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 116.5 (d, $^{2}J_{C\text{-}F}$ = 24.9 Hz), 116.0 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 112.6, 57.3, 27.8. ^{19}F NMR (376 MHz, DMSO-d_6): δ -125.04 – -125.10 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}FN_3O_3$ 402.1248; Found 402.1252.

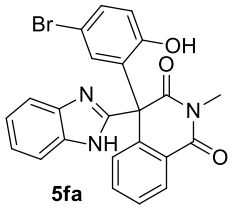


5ea

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(5-chloro-2-hydroxyphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5ea)

Eluent: petroleum ether/ethyl acetate (2:1). White solid (66.9 mg, 80%), mp 204.3-205.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.38 (s, 1H), 10.27 (s, 1H), 8.17-8.15 (m, 1H), 7.67-7.63 (m, 1H), 7.58-7.52 (m, 3H),

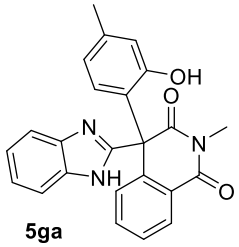
7.30 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.25-7.16 (m, 3H), 6.79-6.77 (m, 2H), 3.32 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 172.1, 164.5, 153.4, 150.7, 142.5, 140.1, 135.6, 133.8, 131.9, 130.0, 129.6, 129.2, 128.3, 127.9, 125.0, 123.5, 122.9, 122.2, 119.7, 117.8, 112.7, 57.3, 27.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}ClN_3O_3$ 418.0953; Found 418.0952.



5fa

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(5-bromo-2-hydroxyphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5fa)

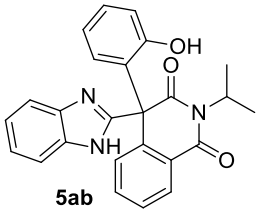
Eluent: petroleum ether/ethyl acetate (2:1). White solid (65.6 mg, 71%), mp 207.3-208.6 ℃. ^1H NMR (600 MHz, DMSO-d_6): δ 12.37 (s, 1H), 10.28 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.57-7.52 (m, 3H), 7.41 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.18-7.14 (m, 2H), 6.89 (d, J = 1.8 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 3.31 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 172.1, 164.5, 153.8, 150.7, 142.5, 140.1, 135.5, 133.9, 132.6, 132.4, 131.9, 130.0, 128.3, 127.9, 125.0, 123.5, 122.2, 119.7, 118.4, 112.7, 110.4, 57.3, 27.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}BrN_3O_3$ 462.0448; Found 462.0442.



5ga

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(2-hydroxy-4-methylphenyl)-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (5ga)

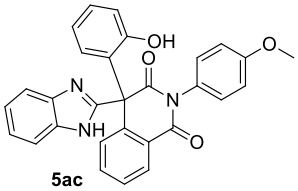
Eluent: petroleum ether/ethyl acetate (2:1). White solid (53.3 mg, 67%), mp 186.2-187.9 ℃. ^1H NMR (600 MHz, DMSO-d_6): δ 12.28 (br s, 1H), 9.76 (s, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.55-7.53 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.19-7.15 (m, 3H), 6.67 (s, 2H), 6.57 (s, 1H), 3.32 (s, 3H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 172.8, 164.7, 154.1, 151.6, 142.5, 141.0, 139.3, 135.6, 133.5, 130.4, 129.4, 128.0, 127.7, 127.6, 124.9, 123.2, 121.9, 120.0, 119.4, 116.8, 112.5, 57.2, 27.8, 21.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}N_3O_3$ 398.1499; Found 398.1494.



5ab

4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(2-hydroxyphenyl)-2-isopropylisoquinoline-1,3(2*H*,4*H*)-dione (5ab)

Eluent: petroleum ether/ethyl acetate (2:1). White solid (72.4 mg, 88%), mp 193.1-194.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.26 (s, 1H), 9.83 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.60-7.56 (m, 1H), 7.55-7.53 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.22-7.17 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.16-5.06 (m, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 172.3, 164.7, 154.3, 151.5, 142.6, 140.7, 135.6, 133.3, 130.4, 130.0, 129.7, 129.5, 127.9, 127.8, 125.6, 123.2, 121.9, 119.6, 119.2, 116.2, 112.6, 58.0, 45.5, 20.3, 19.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_3$ 412.1656; Found 412.1659.



5ac

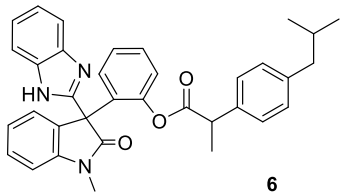
4-(1*H*-Benzo[*d*]imidazol-2-yl)-4-(2-hydroxyphenyl)-2-(4-methoxyphenyl)isoquinoline-1,3(2*H*,4*H*)-dione (5ac)

Eluent: petroleum ether/ethyl acetate (2:1). White solid (51.4 mg, 54%), mp 245.8-246.5 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.23 (s, 1H), 10.06 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.54-7.52 (m, 2H), 7.22-7.21 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 7.2 Hz, 1H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 172.5, 164.7, 159.4, 154.3, 151.4, 142.6, 140.8, 135.7, 133.8, 130.6, 130.4, 130.1, 129.8, 129.5, 128.8, 128.1, 128.0, 125.2, 123.3, 122.0, 119.6, 119.4, 116.4, 114.7, 112.7, 58.0, 55.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}N_3O_4$ 476.1605; Found 476.1623.

3. Structural elaborations of 3aa

3.1 Synthesis of product 6

To a round bottom flask were added **3aa** (71.1 mg, 0.2 mmol) and DCM (2 mL) with stirring. Then, DCC (41.3 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol) and ibuprofen (41.3 mg, 0.2 mmol) were added. The mixture was then stirred at room temperature for 12 h. Upon completion, it was washed with water, dried over anhydrous Na_2SO_4, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **6** as a mixture of two diastereoisomers: **isomer 1** (50.9 mg, 47%), **isomer 2** (29.8 mg, 27%).



6

2-(3-(1*H*-Benzo[*d*]imidazol-2-yl)-1-methyl-2-oxoindolin-3-yl)phenyl 2-(4-isobutylphenyl)propanoate (6)

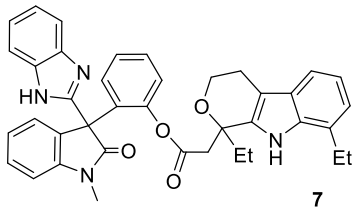
Isomer 1: Eluent: petroleum ether/ethyl acetate (3:1). White solid (50.9 mg, 47%), mp 242.1-243.5 ℃. ^{1}H NMR (400 MHz,$CDCl_3$): δ 10.14 (s, 1H), 7.80-7.78 (m, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.39-7.37 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27-7.23 (m, 2H), 7.21-7.15 (m, 2H), 7.05-7.00 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.86-6.82 (m, 3H), 3.35-3.27 (m, 4H), 2.41 (d, *J* = 6.8 Hz, 2H), 1.85-1.79 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.0, 172.1, 149.8, 148.1, 142.9, 142.5, 140.9, 136.4, 134.1, 131.1, 129.9, 129.5, 129.4, 129.2, 129.0, 127.3, 127.1, 126.0, 124.0, 123.5, 123.4, 122.2, 120.2, 111.2, 108.5, 57.0, 45.0, 44.6, 30.2, 27.0, 22.4, 18.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{34}N_3O_3$ 544.2595; Found 544.2601.

Isomer 2: Eluent: petroleum ether/ethyl acetate (3:1). White solid (29.8 mg, 27%), mp 239.3-240.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.80-7.78 (m, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.40-7.35 (m, 2H), 7.24-7.16 (m, 5H), 7.09 (3H, overlapping with $CHCl_3$), 7.03 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.80 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.37 (s, 3H), 3.20 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.86-1.81 (m, 1H), 0.98 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 175.7, 171.7, 149.8, 148.5, 143.0, 142.7, 140.9, 136.9, 134.0, 131.2, 129.71, 129.65, 129.6, 129.3, 129.0, 127.6, 127.0, 126.0, 124.1, 123.6, 123.4, 122.2, 120.2, 111.2, 108.4, 57.2, 45.1, 44.5,

30.2, 27.0, 22.4, 17.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{34}N_3O_3$ 544.2595; Found 544.2585.

3.2 Synthesis of product 7

To a round bottom flask were added **3aa** (71.1 mg, 0.2 mmol) and DCM (2 mL) with stirring. Then, DCC (41.3 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol) and etodolac (57.5 mg, 0.2 mmol) were added. The mixture was stirred at room temperature for 12 h. Upon completion, it was washed with water, dried over anhydrous Na_2SO_4, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **7** as a mixture of two diastereoisomers: **isomer 1** (51.1 mg, 41%), **isomer 2** (61.3 mg, 49%).



7

2-(3-(1*H*-benzo[*d*]imidazol-2-yl)-1-methyl-2-oxoindolin-3-yl)phenyl 2-(1,8-diethyl-1,3,4,9-tetrahydro-pyrano[3,4-*b*]indol-1-yl)acetate (7)

Isomer 1: Eluent: petroleum ether/ethyl acetate (3:1). White solid (51.1 mg, 41%), mp 148.9-149.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.50 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.34-7.31 (m, 2H), 7.18-7.11 (m, 3H), 7.09(t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 6.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.56 (t, *J* = 7.2 Hz, 1H), 4.03-4.00 (m, 1H), 3.88-3.85(m, 1H), 3.31 (s, 3H), 2.85-2.80 (m, 2H), 2.77-2.74 (m, 3H), 2.52 (d, *J* = 17.4 Hz, 1H), 2.06-2.02 (m, 1H), 1.94-1.90 (m, 1H), 1.32 (t, *J* = 7.8 Hz, 3H), 0.80 (t, *J* = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR (600 MHz, $CDCl_3$): δ 175.9, 170.3, 149.1, 147.4, 142.8, 142.1, 135.0, 134.7, 133.8, 131.5, 130.3, 129.4, 129.0, 128.7, 127.2, 126.6, 126.2, 123.81, 123.78, 123.6, 122.3, 120.3, 120.1, 119.7, 115.9, 111.1, 108.4, 108.2, 74.4, 60.7, 57.0, 42.0, 30.5, 27.1, 24.0, 22.5, 13.7, 7.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{37}N_4O_4$ 625.2809; Found 625.2780.

Isomer 2: Eluent: petroleum ether/ethyl acetate (3:1). White solid (61.3 mg, 49%), mp 178.7-179.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.54 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.38-7.34 (m, 3H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.23-7.18 (m, 3H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.91-6.90 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.04-4.01 (m, 1H), 3.88-3.85 (m,

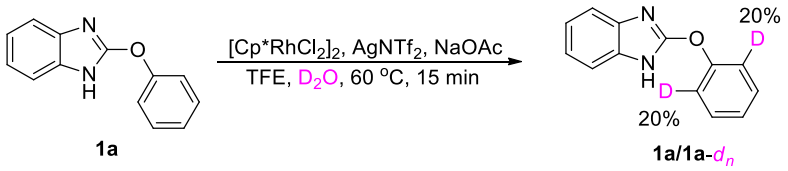
1H), 3.20 (s, 3H), 2.90 (d, *J* = 16.8 Hz, 1H), 2.85-2.82 (m, 3H), 2.73-2.70 (m, 1H), 2.49 (d, *J* = 16.8 Hz, 1H), 1.98-1.94 (m, 1H), 1.74-1.71 (m, 1H), 1.33 (t, *J* = 7.8 Hz, 3H), 0.68 (t, *J* = 7.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (600 MHz, $CDCl_3$): δ 175.8, 170.1, 149.3, 147.5, 142.9, 142.6, 134.63, 134.56, 133.9, 131.3, 130.3, 129.33, 129.27, 129.2, 127.4, 126.7, 126.5, 126.1, 124.0, 123.6, 123.5, 122.3, 120.7, 120.3, 119.8, 116.0, 111.1, 109.2, 108.6, 74.6, 60.7, 56.9, 42.6, 31.0, 26.9, 24.1, 22.4, 13.9, 7.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{37}N_4O_4$ 625.2809; Found 625.2806.

4. Gram-scale synthesis of 3aa

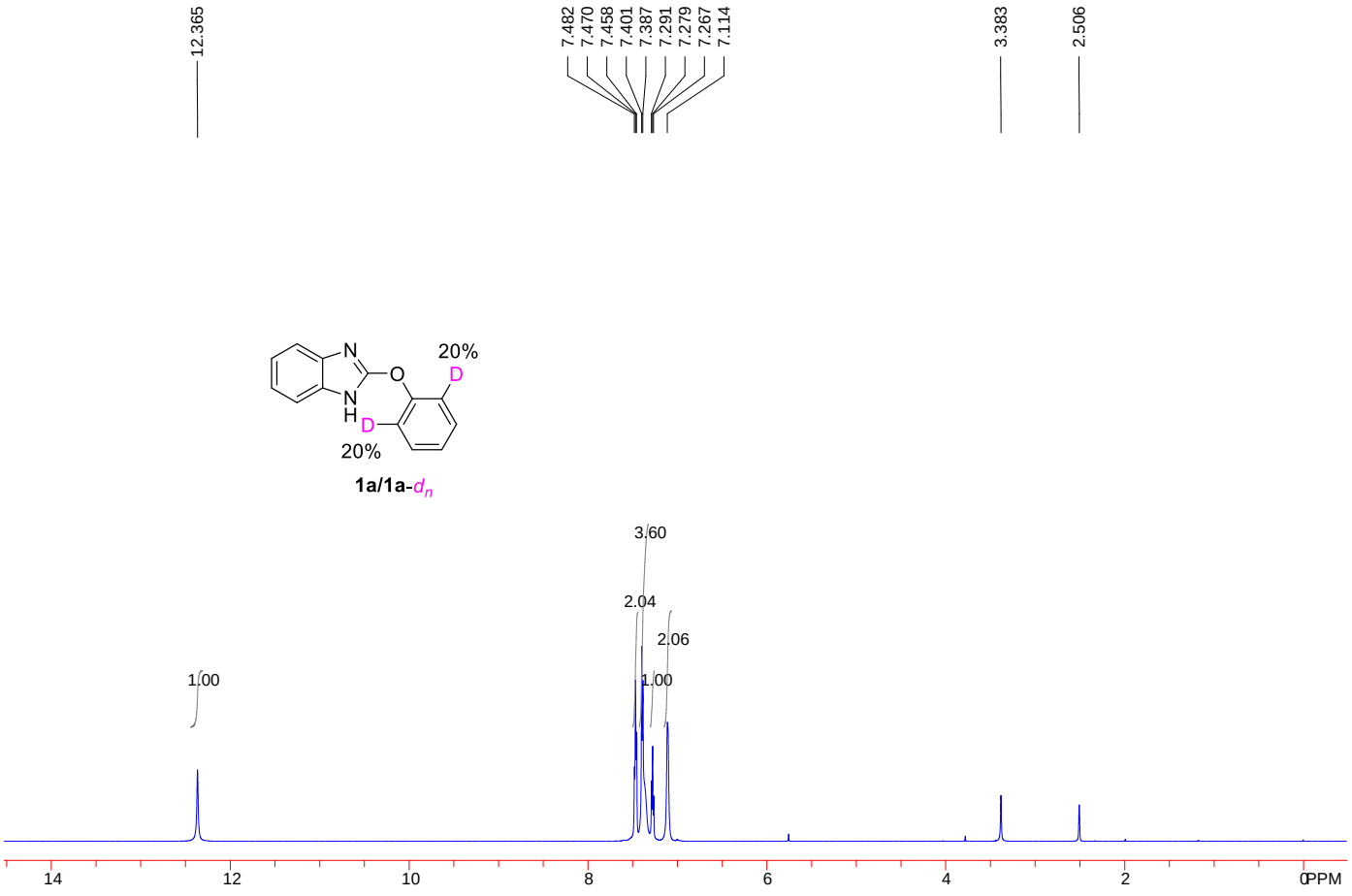
To a reaction tube equipped with a stir bar were added 2-phenoxy-1*H*-benzo[*d*]imidazole (**1a**, 1.05 g, 5 mmol), TFE (30 mL), 3-diazo-1-methylindolin-2-one (**2a**, 1.3 g, 7.5 mmol), $[RhCp^*Cl_2]_2$ (46.4 mg, 0.075 mmol), $AgNTf_2$ (194.0 mg, 0.5 mmol) and NaOAc (600.2 mg, 7.5 mmol) with stirring. The mixture was stirred at 60 °C (oil bath) under air for 4 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3aa** (1.58 g, 89%).

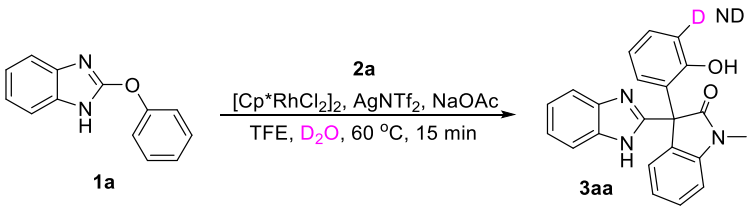
III. Mechanism studies

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

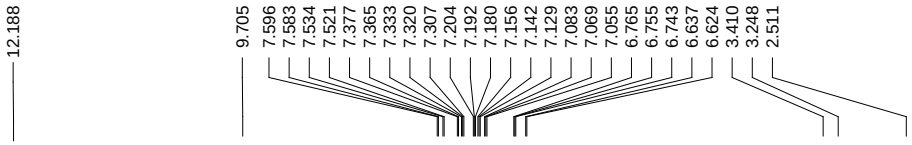


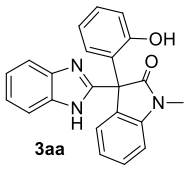
To a reaction tube equipped with a stir bar were charged with 2-phenoxy-1*H*-benzo[*d*]imidazole (**1a**, 42.1 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol), NaOAc (24.0 mg, 0.3 mmol), TFE (2 mL) and D_2O (72 μL, 4 mmol). The tube was sealed, and the mixture was stirred at 60 ℃ (oil bath) under air for 15 min. Upon analyzing the ^1H NMR spectrum of the resulting mixture, the deuteration percentage at the *ortho* positions of the phenyl moiety of **1a** was calculated as 20%.

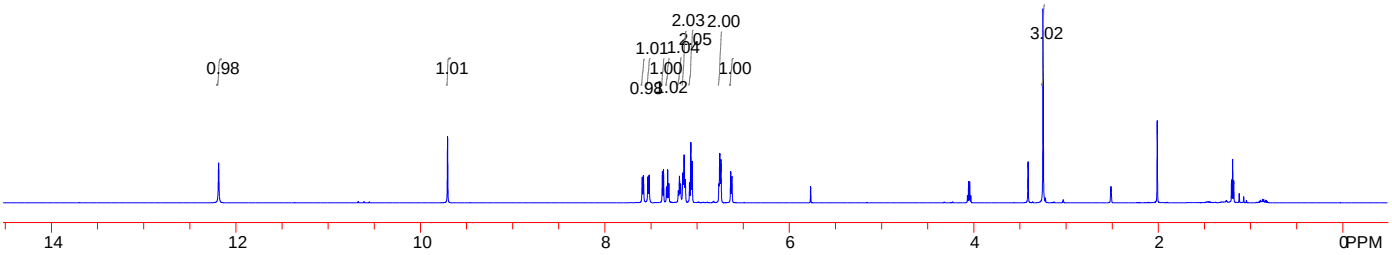




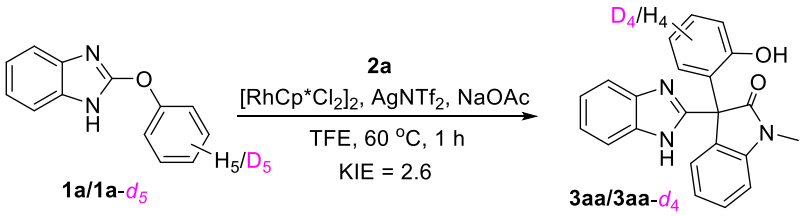
To a reaction tube equipped with a stir bar were added 2-phenoxy-1*H*-benzo[*d*]imidazole (**1a**, 42.1 mg, 0.2 mmol), TFE (2 mL), 3-diazo-1-methylindolin-2-one (**2a**, 52.0 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol) and NaOAc (24.0 mg, 0.3 mmol) with stirring. The mixture was stirred at 60 ℃ (oil bath) under air for 15 min. Then, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **3aa**. Upon analyzing its ^1H NMR spectrum, no deuteration was observed.



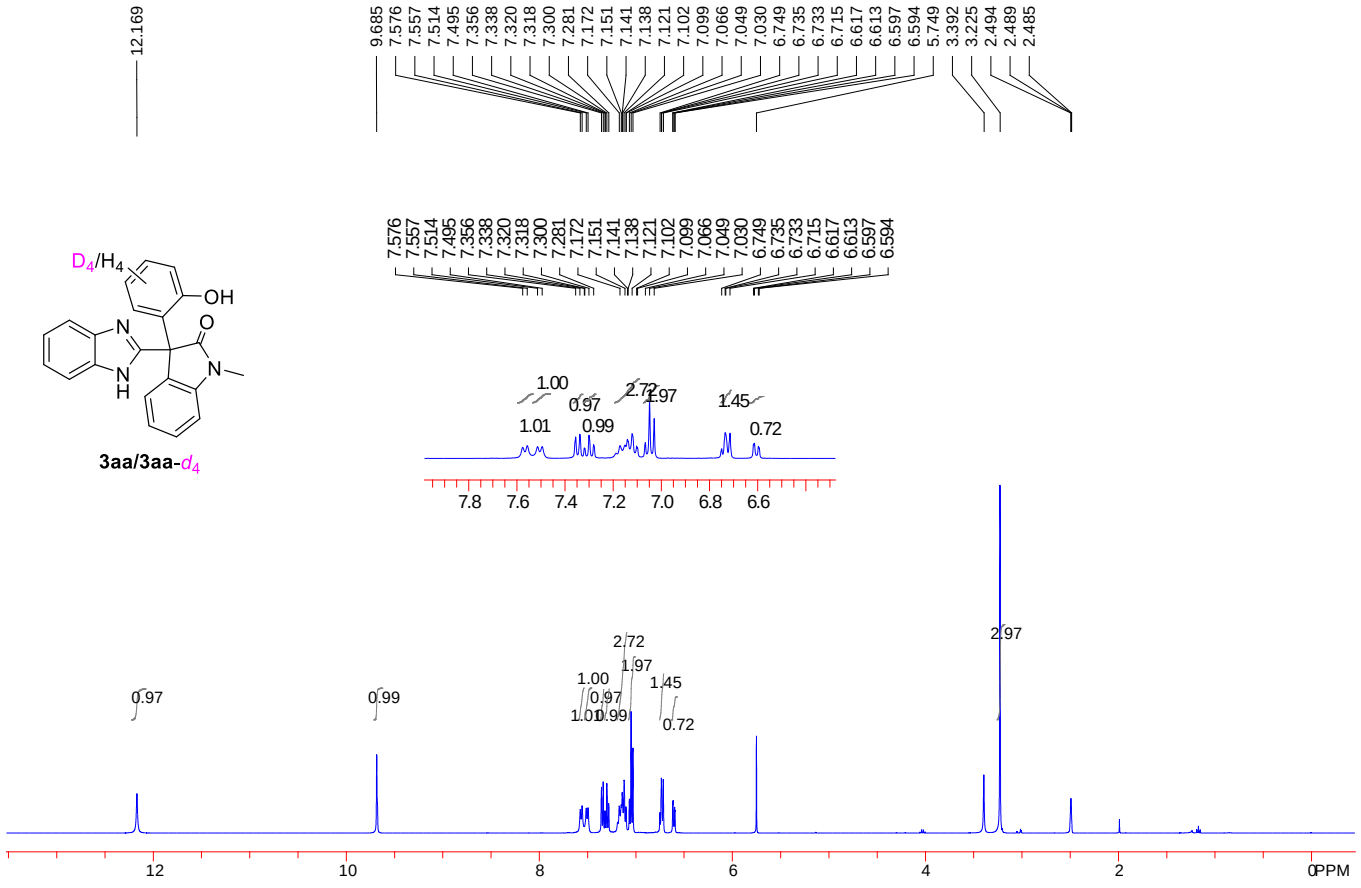




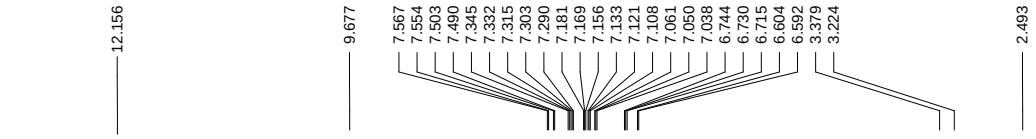
2. Kinetic isotope effect study

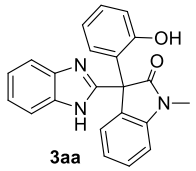


To a reaction tube equipped with a stir bar were added **1a** (42.1 mg, 0.2 mmol), **1a**-d_5 (43.0 mg, 0.2 mmol), TFE (2 mL), **2a** (34.6 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol) and NaOAc (24.0 mg, 0.3 mmol) with stirring. The mixture was stirred at 60 °C under air for 1 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford a mixture of **3aa** and **3aa**-d_4. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **3aa** to **3aa**-d_4 was determined as 0.72:0.28. Accordingly, the intermolecular KIE value (k_H/k_D) was calculated to be 2.6.



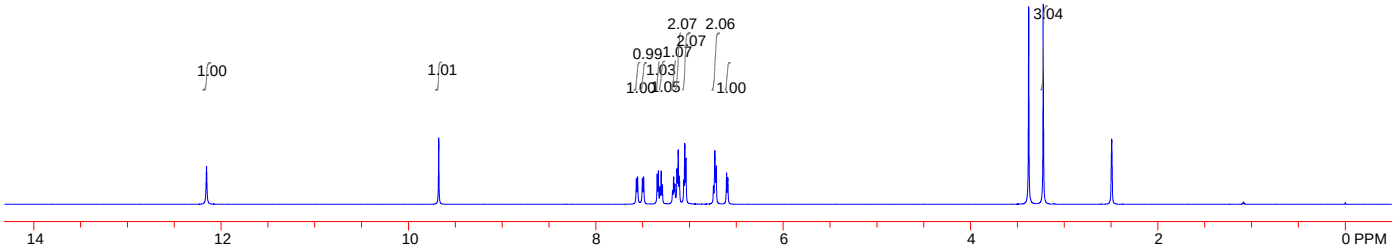
IV. NMR spectra of 3aa-3am

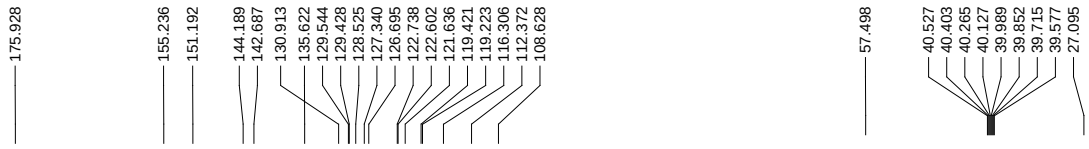


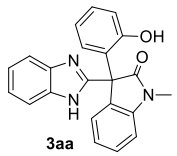


3aa

^{1}H NMR (600 MHz, DMSO-d_6)

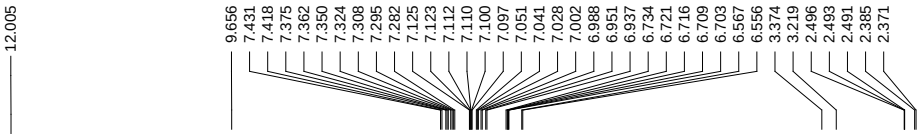


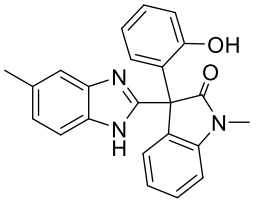




3aa

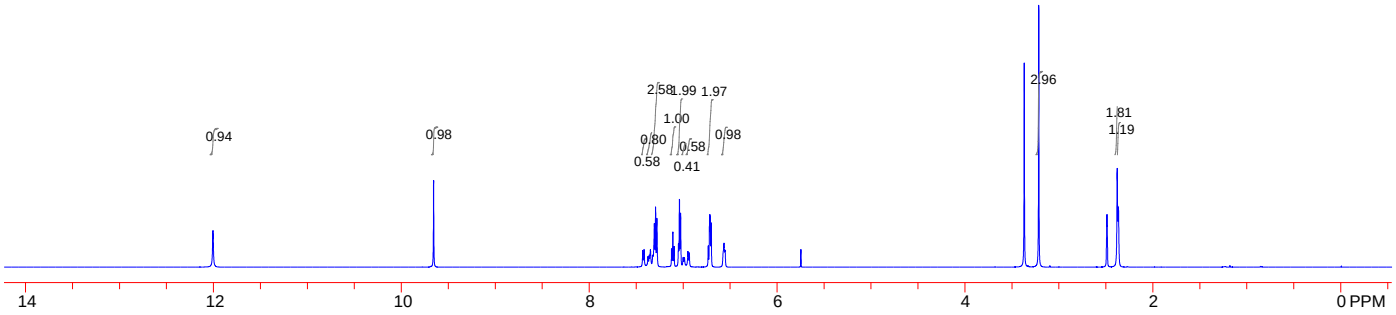
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

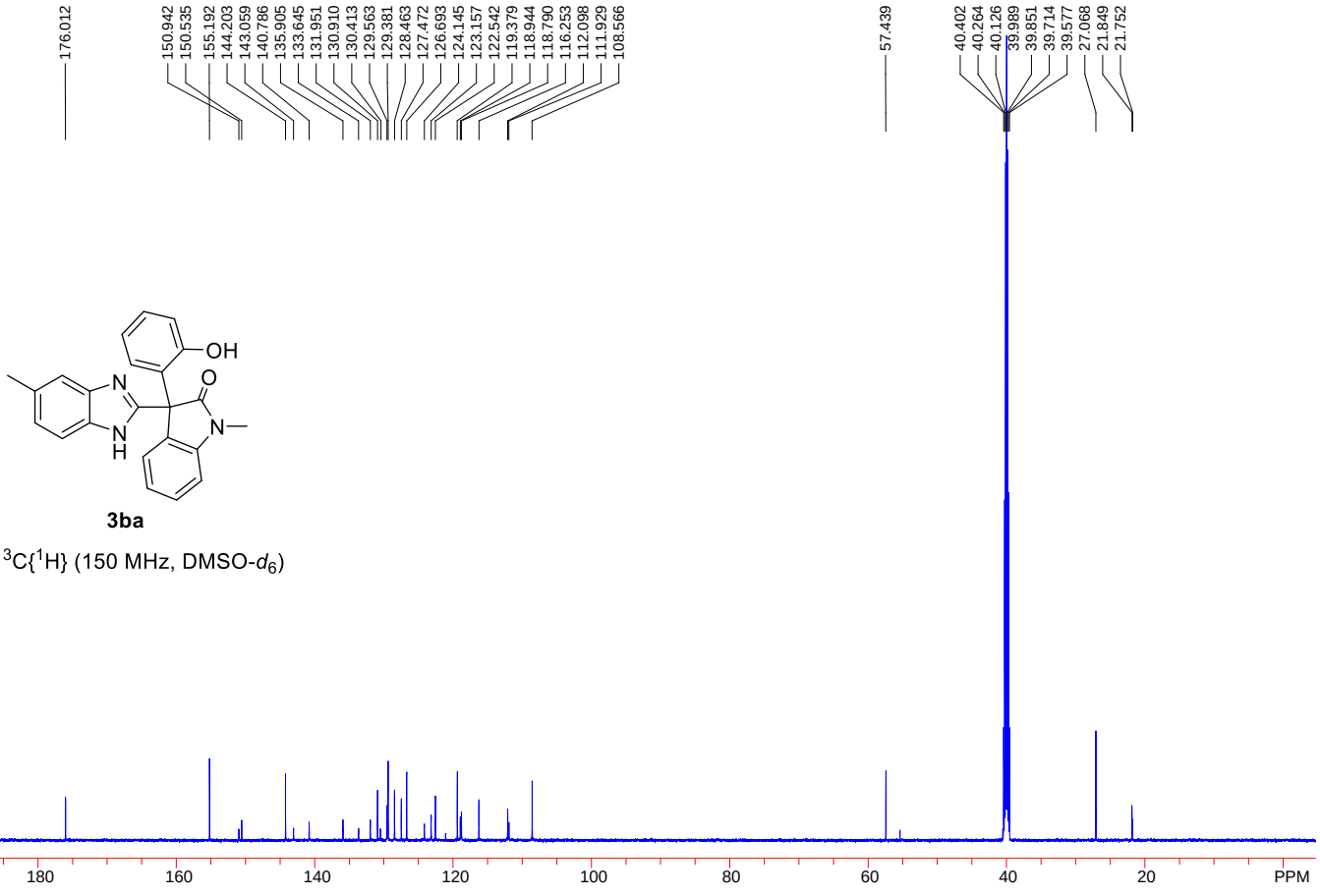




3ba

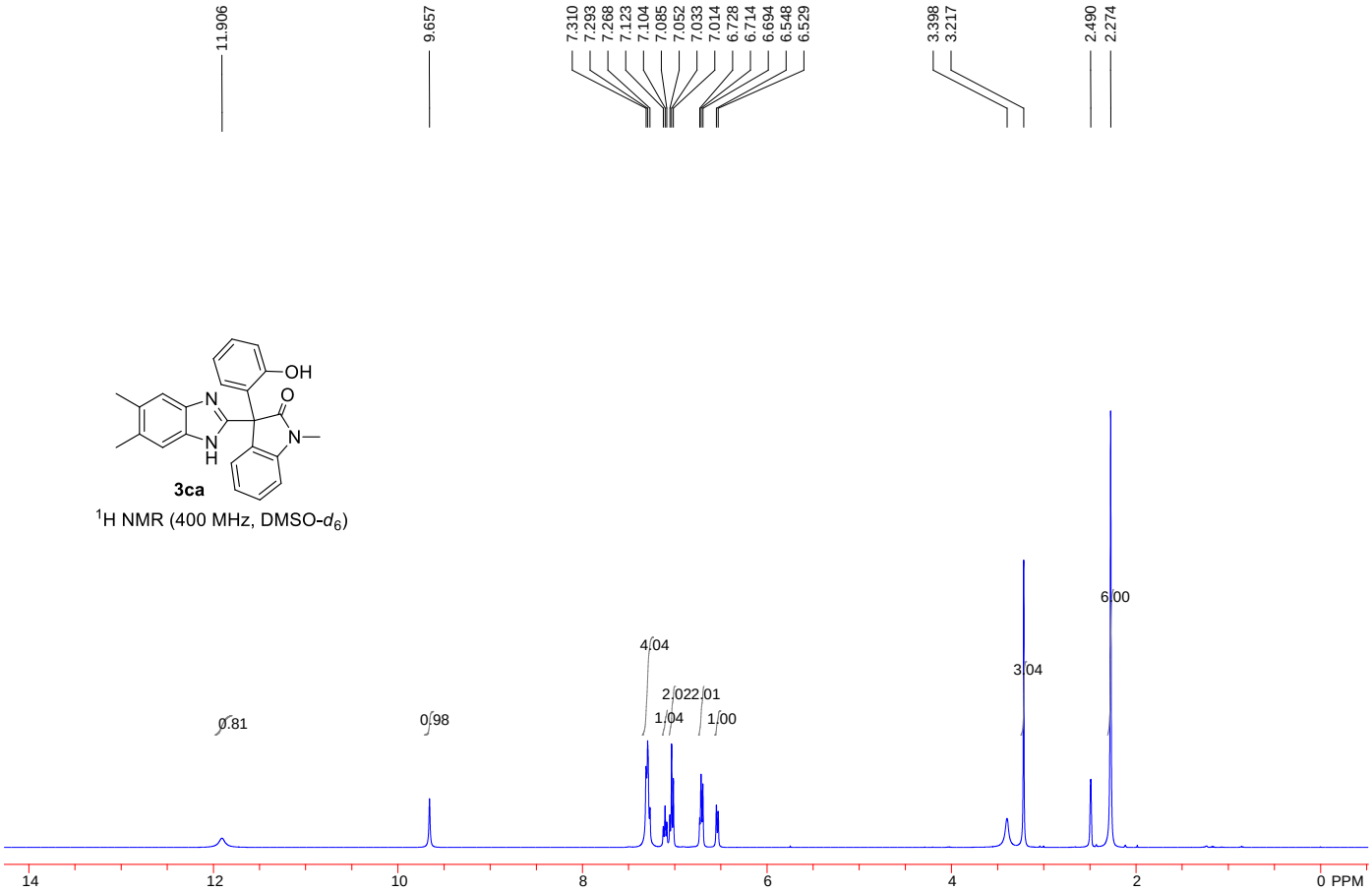
^{1}H NMR (600 MHz, DMSO-d_6)





3ba

^{13}C{^{1}H} (150 MHz, DMSO-d_6)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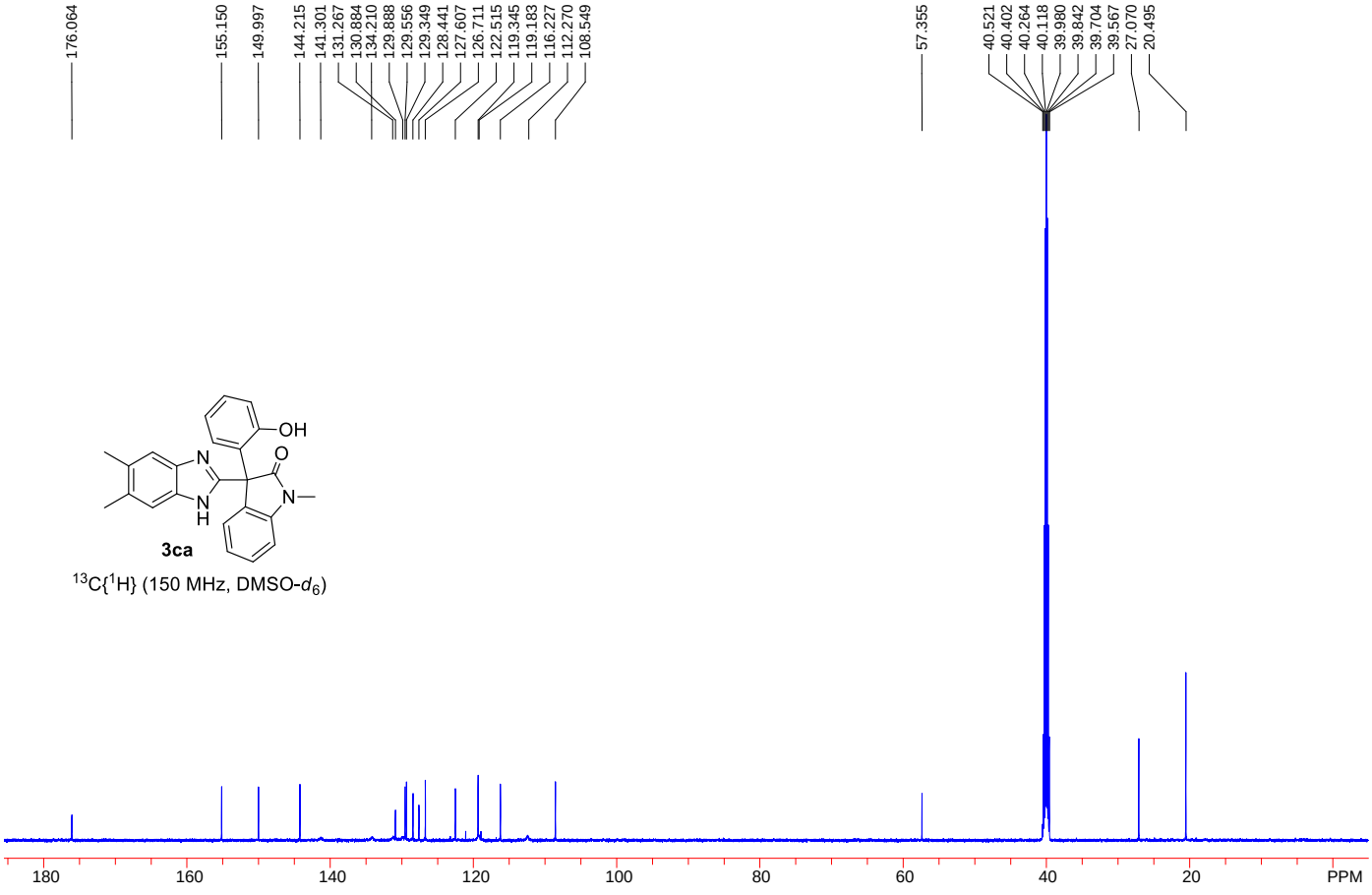
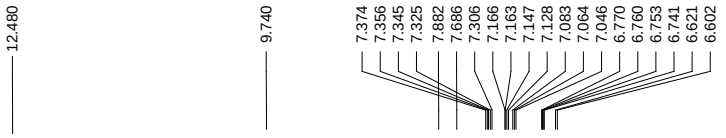
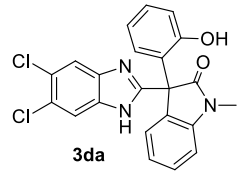
9.657
7.310
7.293
7.268
7.123
7.104
7.085
7.052
7.033
7.014
6.728
6.714
6.694
6.548
6.529
3.398
3.217
2.490
2.274
OH
N
O
N
H
N
3ca
^{1}H NMR (400 MHz, DMSO-d_6)
0.81
0.98
4.04
2.02
2.01
1.04
1.00
3.04
6.00
14
12
10
8
6
4
2
0 PPM

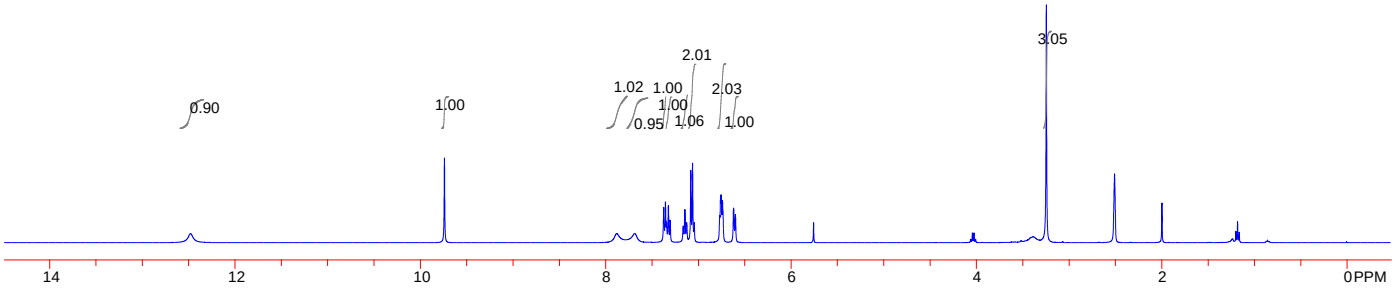

176.064
155.150
149.997
144.215
141.301
131.267
130.884
134.210
129.888
129.556
129.349
128.441
127.607
126.711
122.515
119.345
119.183
116.227
112.270
108.549
57.355
40.521
40.402
40.264
40.118
39.980
39.842
39.704
39.567
27.070
20.495
OH
N
O
N
H
N
3ca
^{13}C{^{1}H} (150 MHz, DMSO-d_6)
180
160
140
120
100
80
60
40
20
PPM

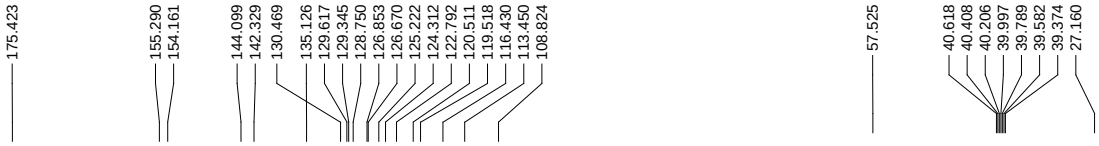


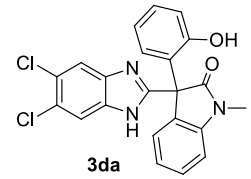


3da

^{1}H NMR (400 MHz, DMSO-d_6)

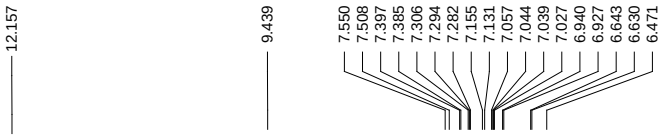


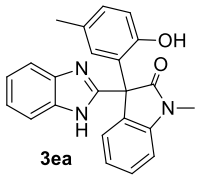




3da

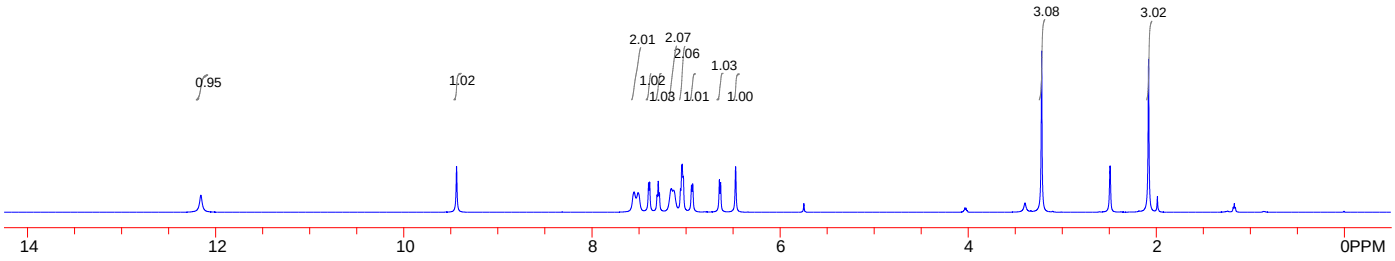
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

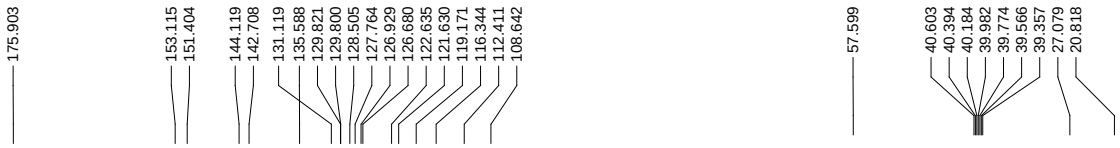


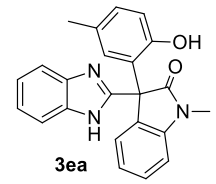


3ea

^{1}H NMR (600 MHz, DMSO-d_6)

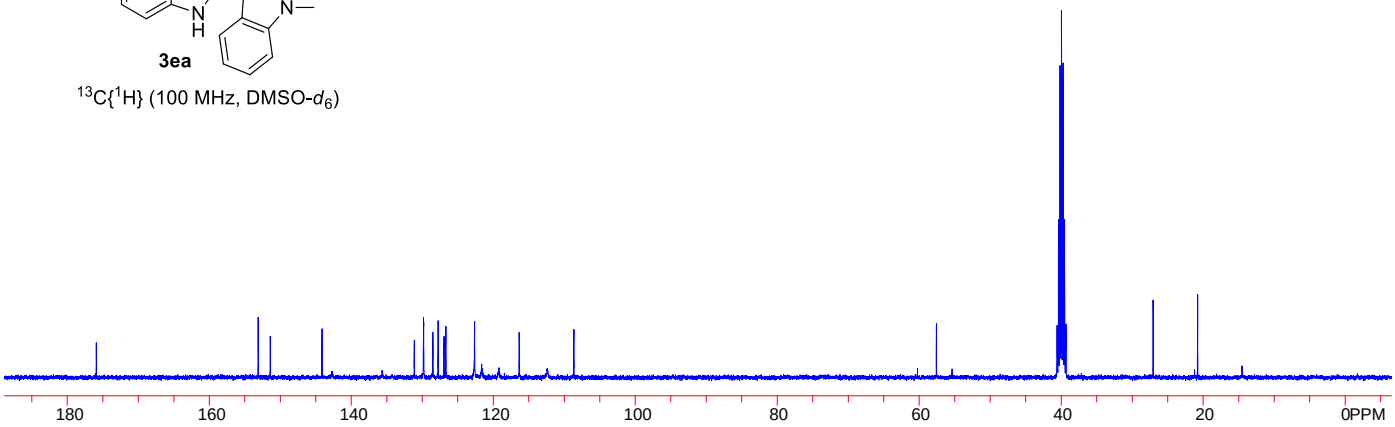


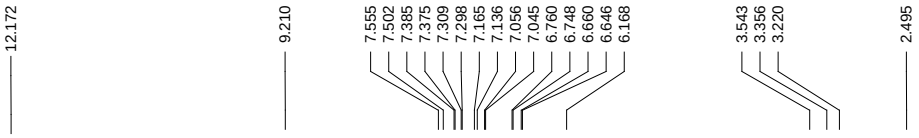


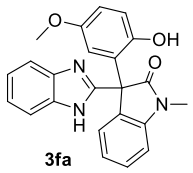


3ea

^{13}C{^{1}H} (100 MHz, DMSO-d_6)

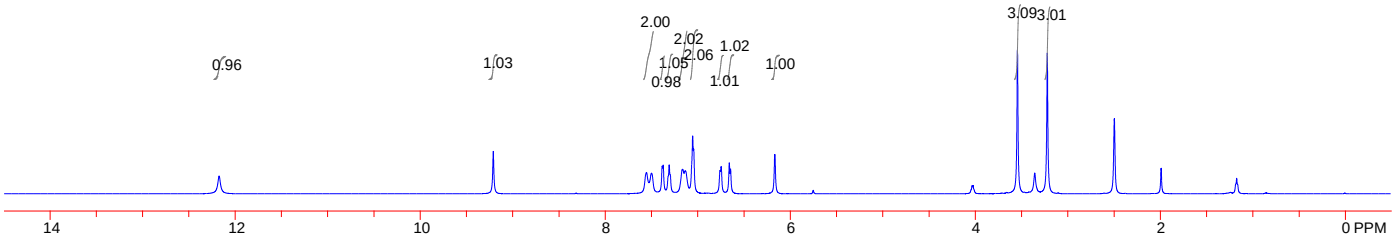


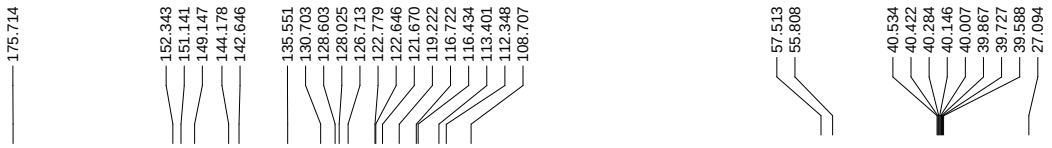


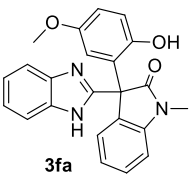


3fa

^{1}H NMR (600 MHz, DMSO-d_6)

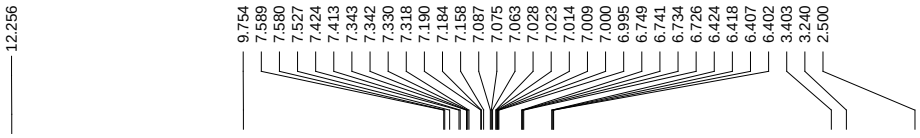


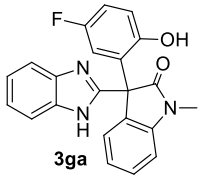




3fa

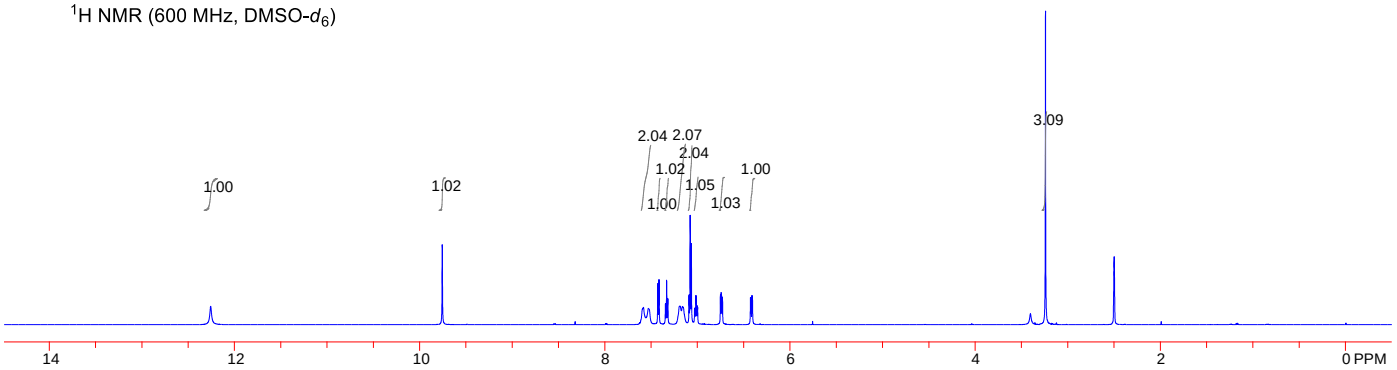
^{13}C{^{1}H} (150 MHz, DMSO-d_6)

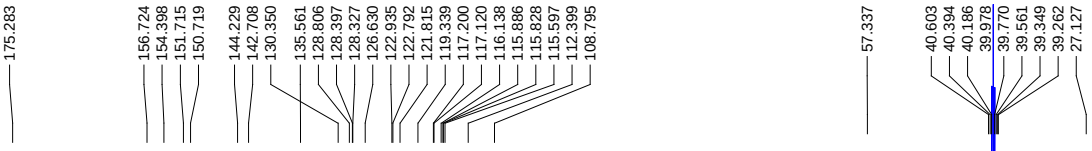


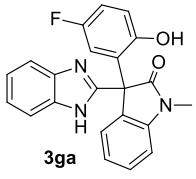


3ga

^{1}H NMR (600 MHz, DMSO-d_6)

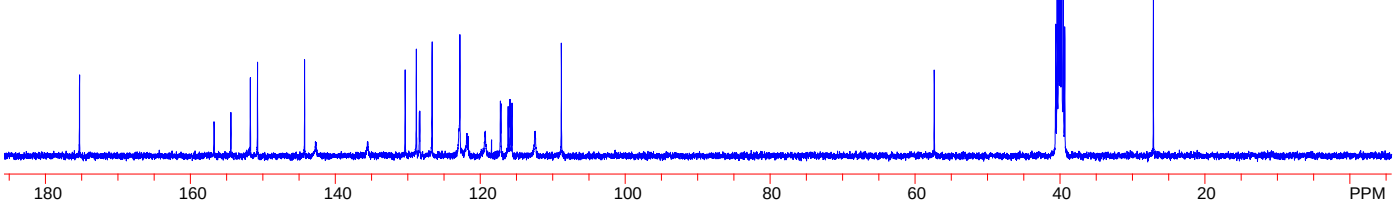


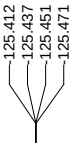


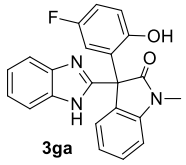


3ga

^{13}C{^{1}H} (100 MHz, DMSO-d_6)

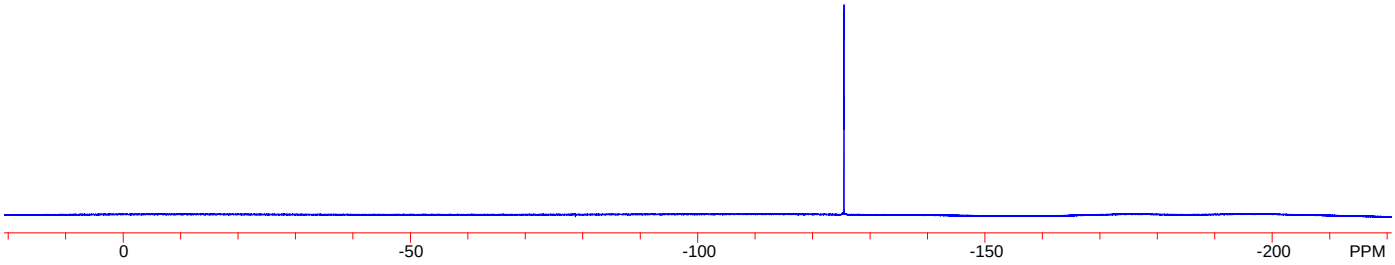


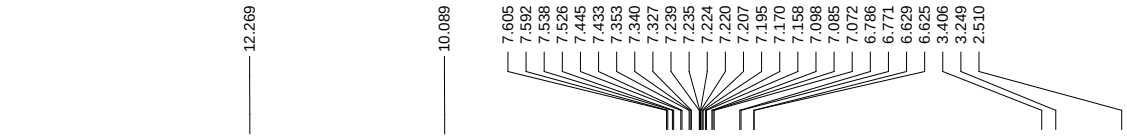


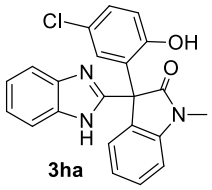


3ga

^{19}F NMR (376 MHz, DMSO-d_6)

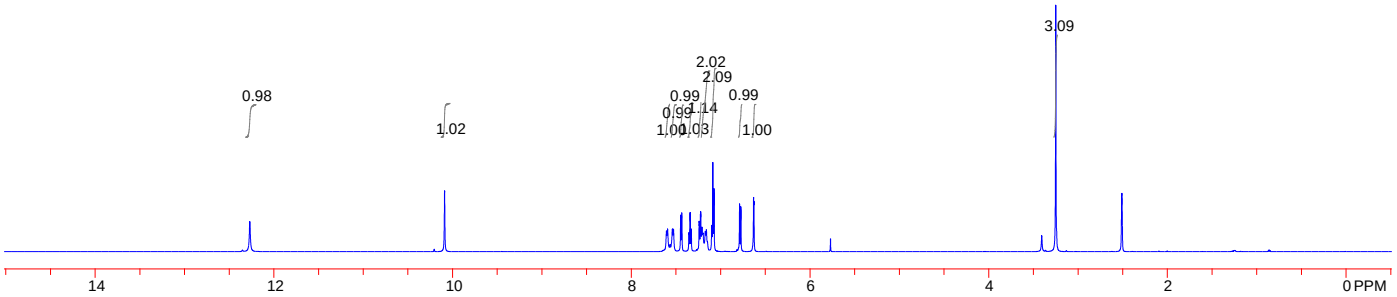


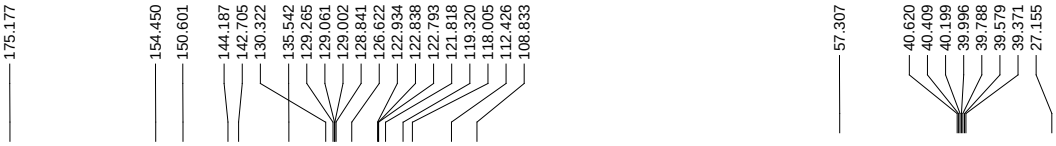


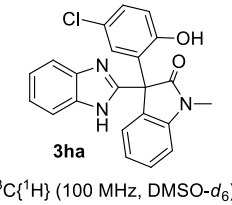


3ha

^{1}H NMR (600 MHz, DMSO-d_6)

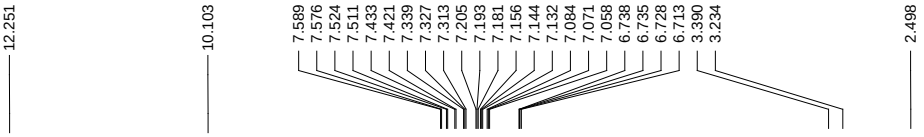


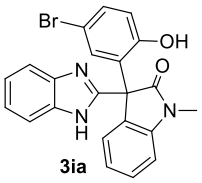




3ha

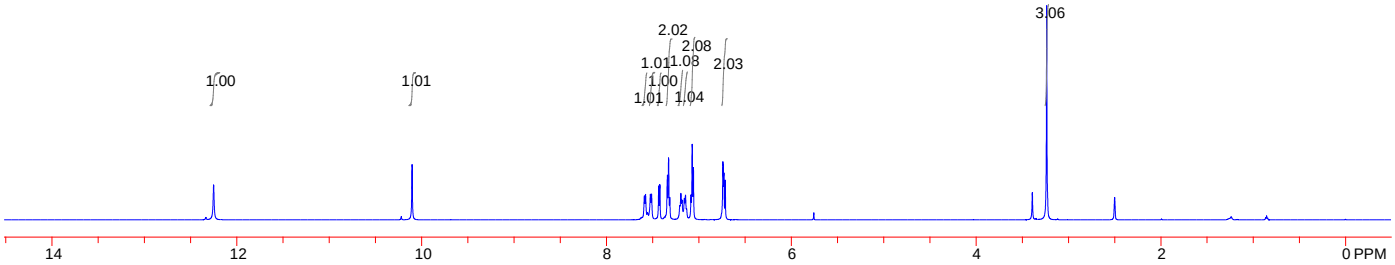
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

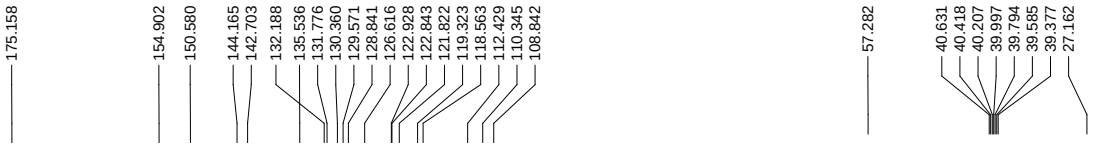


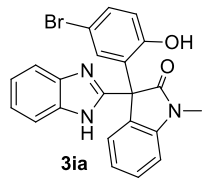


3ia

^{1}H NMR (600 MHz, DMSO-d_6)

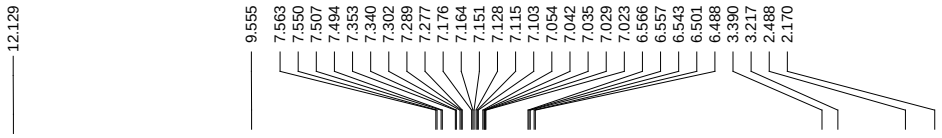


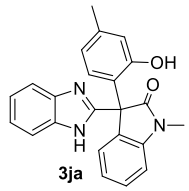




3ia

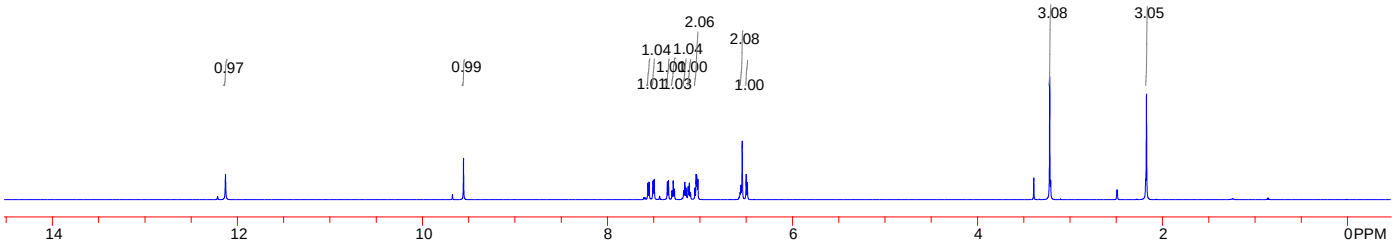
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

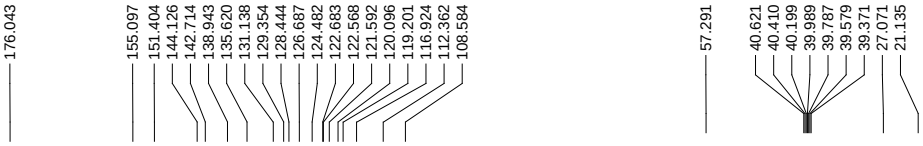


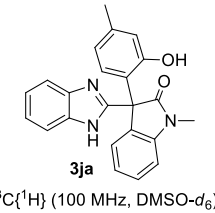


3ja

^{1}H NMR (600 MHz, DMSO-d_6)

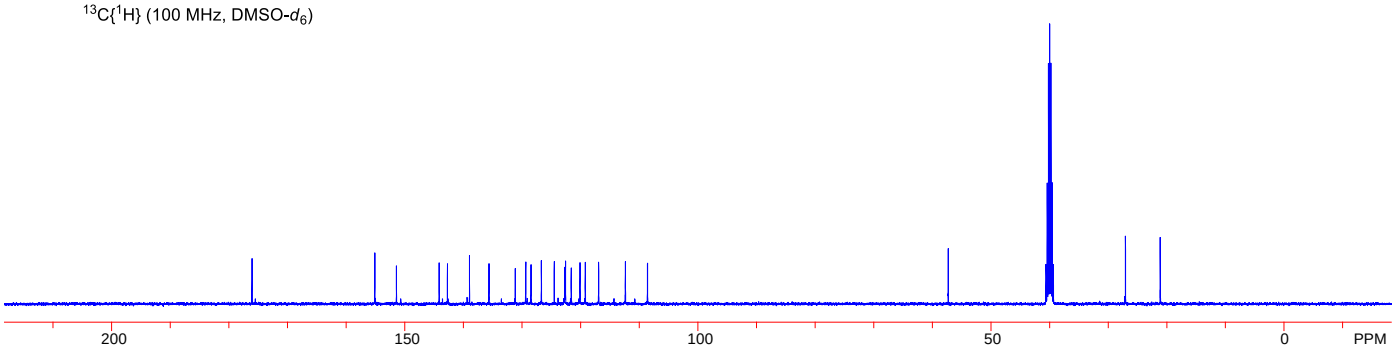


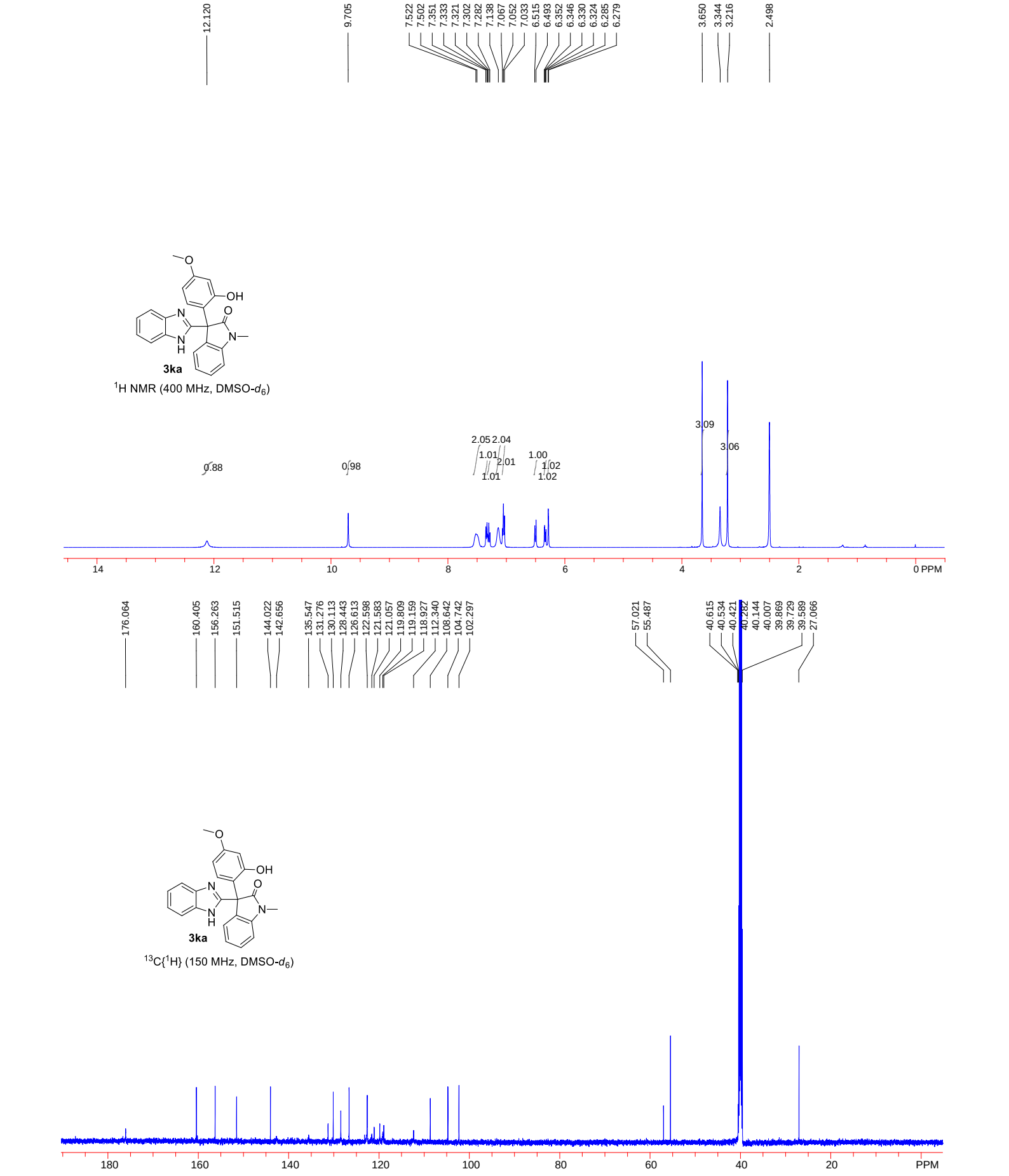


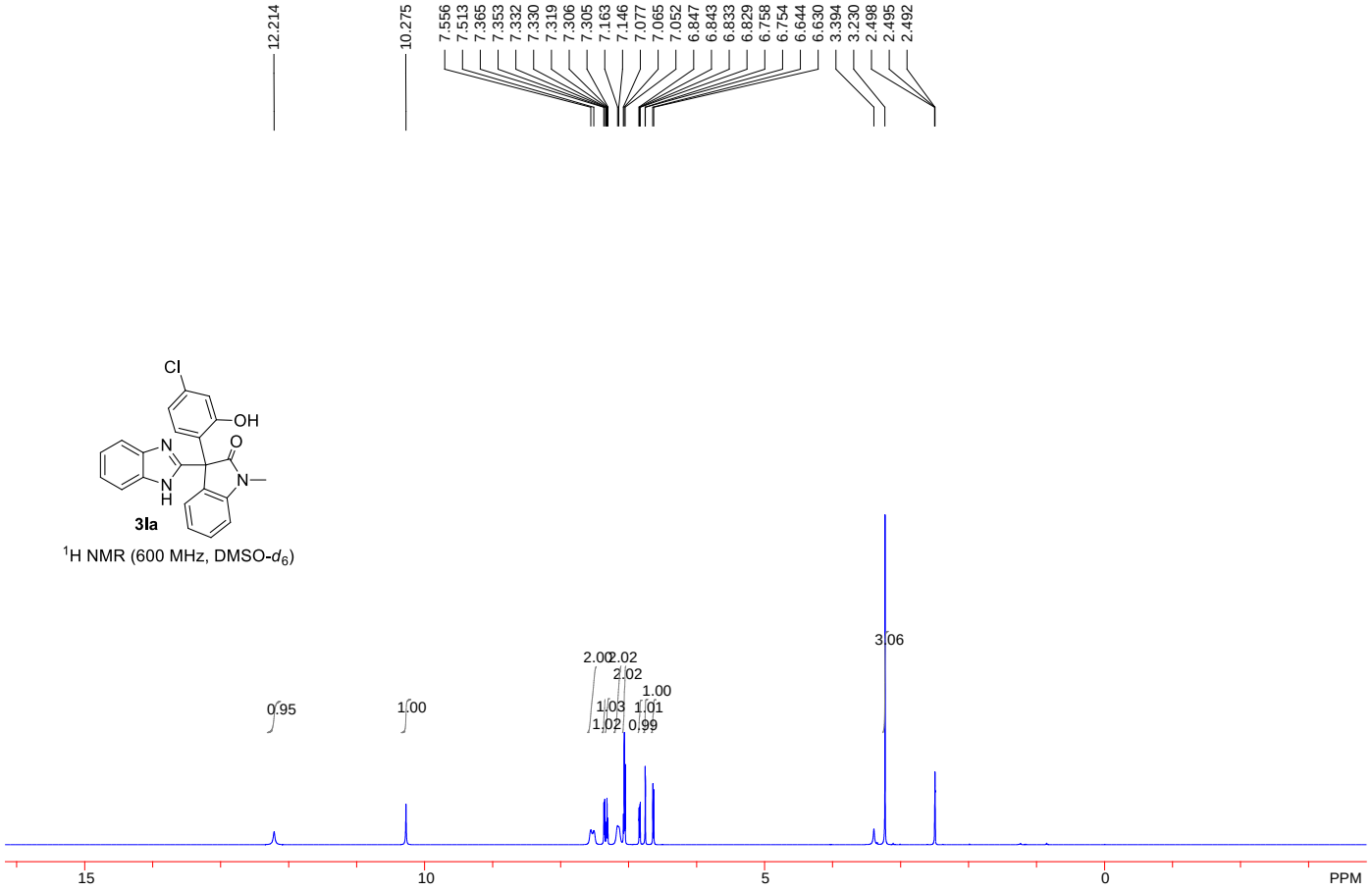


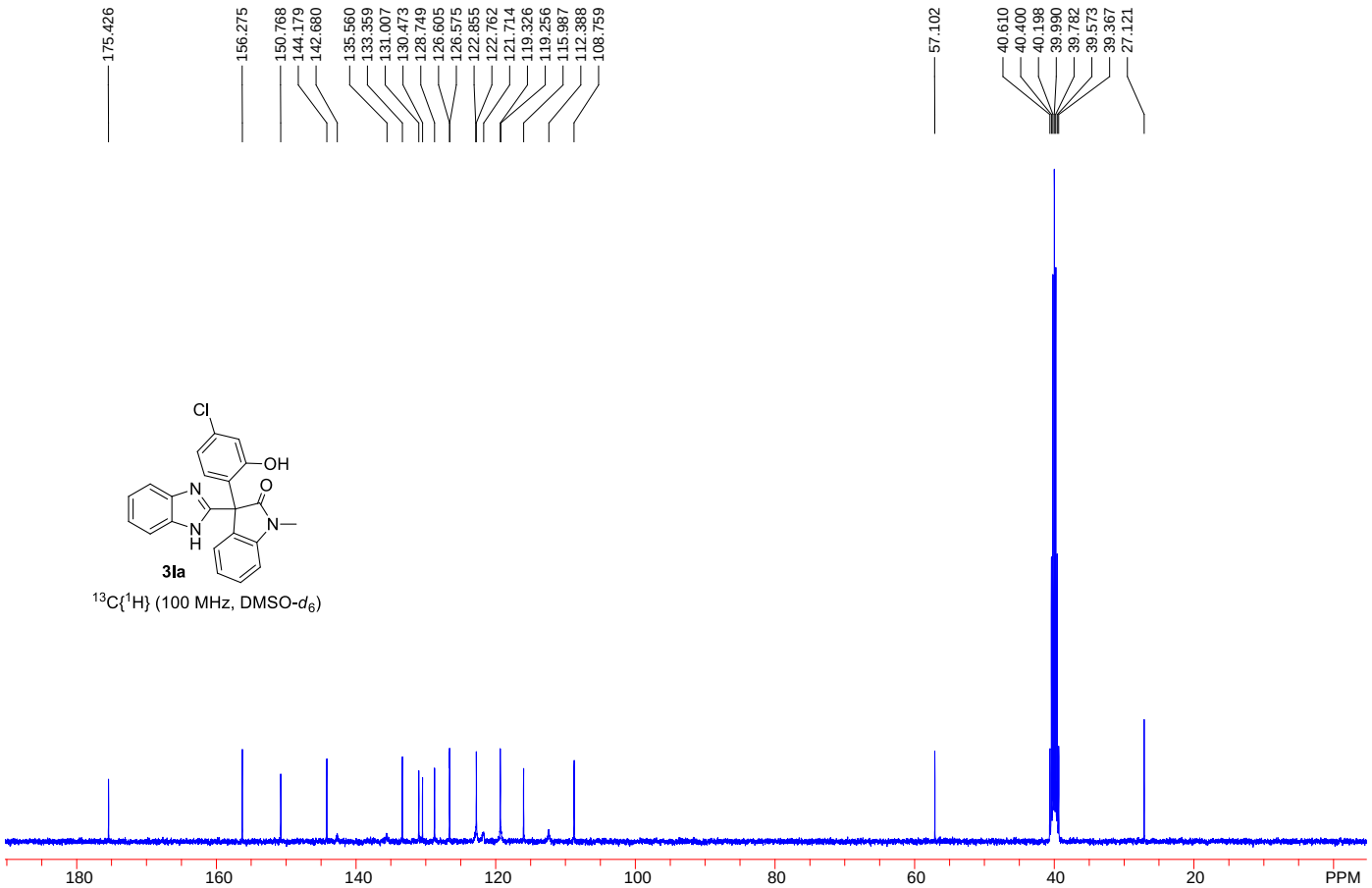
3ja

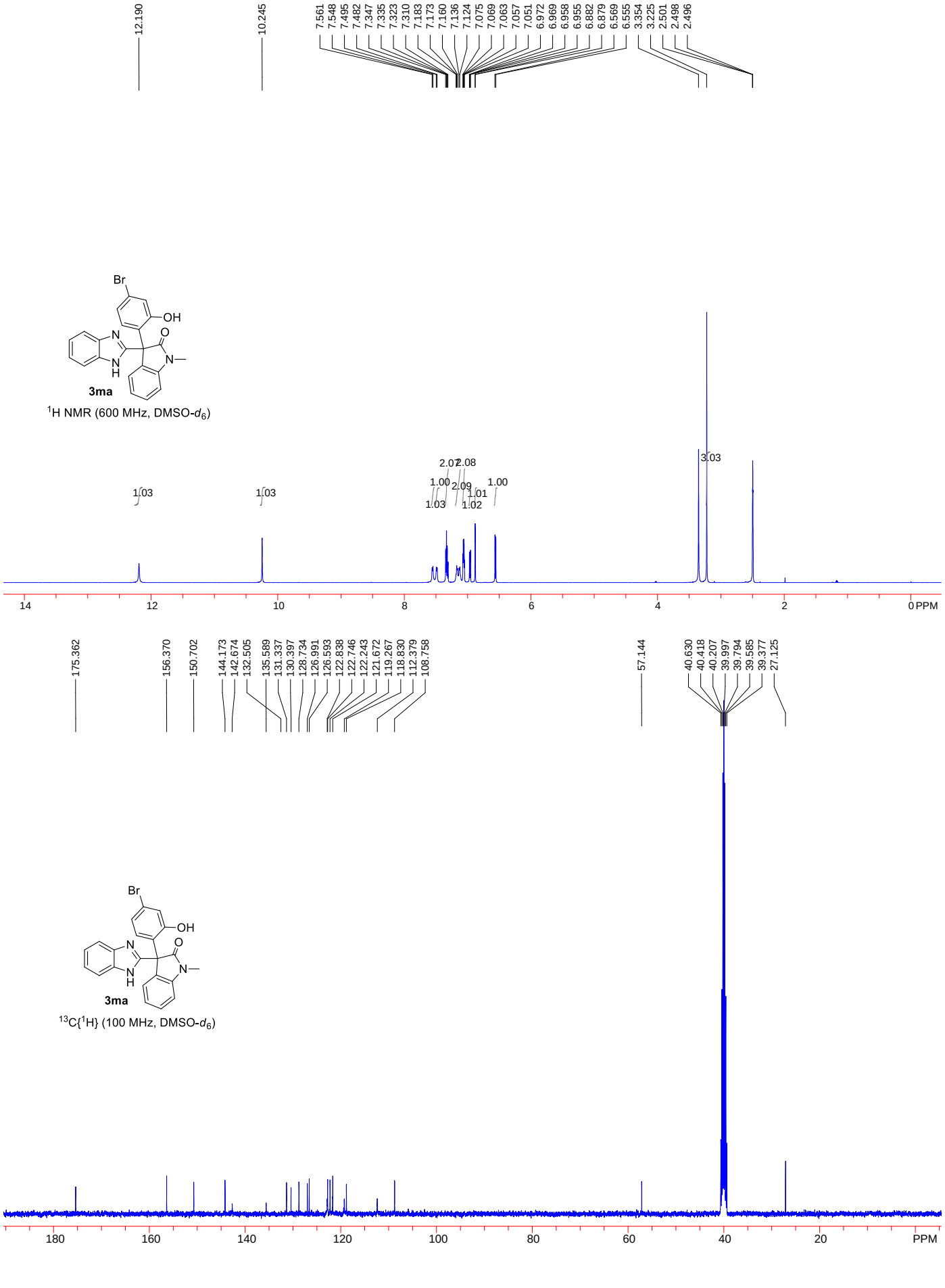
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

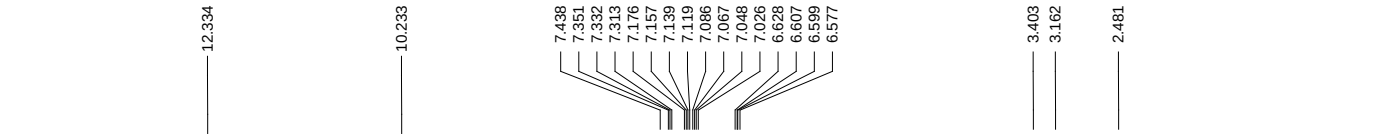


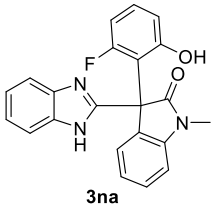

12.120
9.705
7.522
7.502
7.351
7.333
7.321
7.302
7.282
7.138
7.067
7.052
7.033
6.515
6.493
6.352
6.346
6.330
6.324
6.285
6.279
3.650
3.344
3.216
2.498
OH
O
N
N
H
O
N
3ka
1H NMR (400 MHz, DMSO-d6)
0.88
0.98
2.05
2.04
1.01
2.01
1.01
1.00
1.02
1.02
3.09
3.06
14
12
10
8
6
4
2
0 PPM
176.064
160.405
156.263
151.515
144.022
142.656
135.547
131.276
130.113
128.443
126.613
122.598
121.583
121.057
119.809
119.159
118.927
112.340
108.642
104.742
102.297
57.021
55.487
40.615
40.534
40.421
40.282
40.144
40.007
39.869
39.729
39.589
27.066
OH
O
N
N
H
O
N
3ka
13C{1H} (150 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM


12.214
10.275
7.556
7.513
7.365
7.353
7.332
7.330
7.319
7.306
7.305
7.163
7.146
7.077
7.065
7.052
6.847
6.843
6.833
6.829
6.758
6.754
6.644
6.630
3.394
3.230
2.498
2.495
2.492
Cl
OH
N
O
N
H
N
3la
^{1}H NMR (600 MHz, DMSO-d_6)
3.06
2.00
2.02
2.02
1.00
1.03
1.01
1.02
0.99
0.95
1.00
15
10
5
0
PPM


175.426
156.275
150.768
144.179
142.680
135.560
133.359
131.007
130.473
128.749
126.605
126.575
122.855
122.762
121.714
119.326
119.256
115.987
112.388
108.759
57.102
40.610
40.400
40.198
39.990
39.782
39.573
39.367
27.121
Cl
OH
N
O
N
H
N
3la
^{13}C{^{1}H} (100 MHz, DMSO-d_6)
180
160
140
120
100
80
60
40
20
PPM

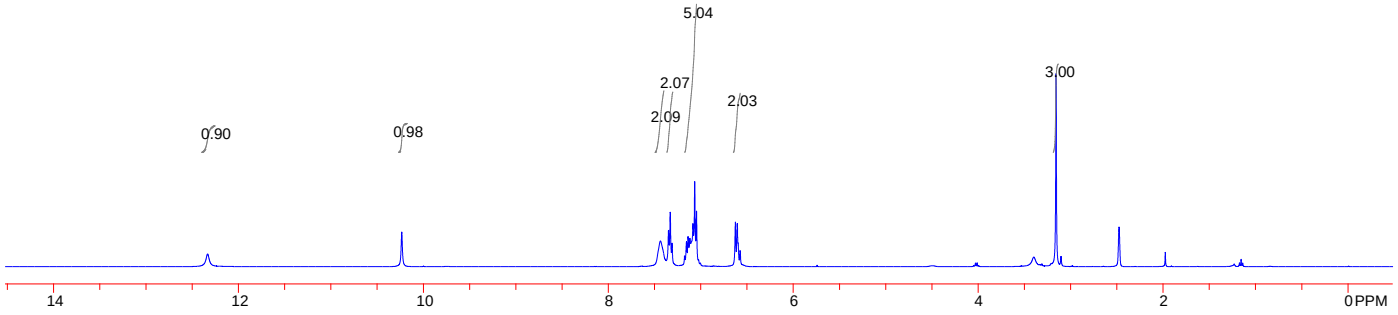

12.190
10.245
7.561
7.548
7.495
7.482
7.347
7.335
7.323
7.310
7.183
7.173
7.160
7.136
7.124
7.075
7.069
7.063
7.057
7.051
6.972
6.969
6.958
6.955
6.882
6.879
6.569
6.555
3.354
3.225
2.501
2.498
2.496
Br
OH
N
O
N
H
N—
3ma
1H NMR (600 MHz, DMSO-d6)
1.03
1.03
2.07
2.08
1.00
2.09
1.01
1.00
1.03
1.02
3.03
14
12
10
8
6
4
2
0 PPM
175.362
156.370
150.702
144.173
142.674
132.505
135.589
131.337
130.397
128.734
126.991
126.593
122.838
122.746
122.243
121.672
119.267
118.830
112.379
108.758
57.144
40.630
40.418
40.207
39.997
39.794
39.585
39.377
27.125
Br
OH
N
O
N
H
N—
3ma
13C{1H} (100 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM

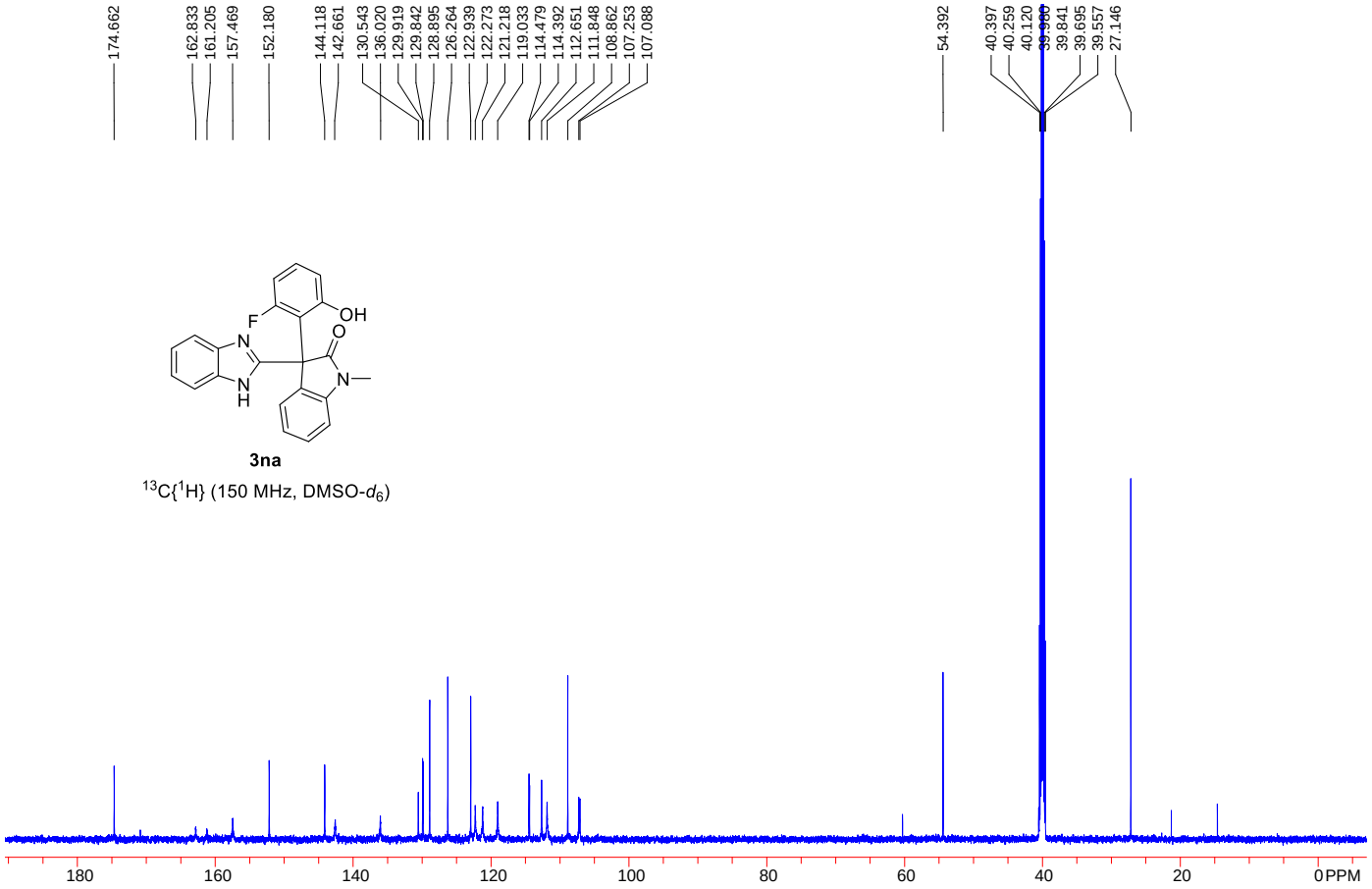




3na

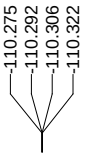
^{1}H NMR (400 MHz, DMSO-d_6)

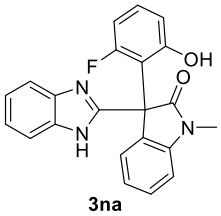




3na

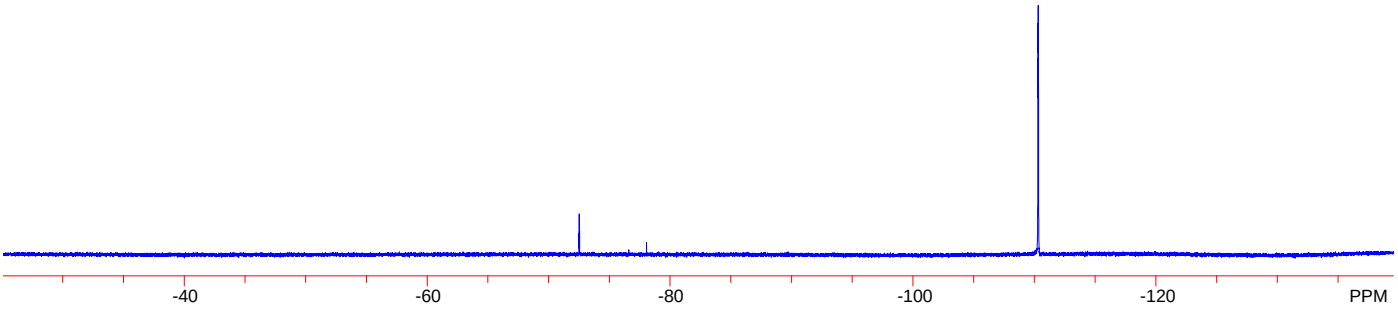
^{13}C{^{1}H} (150 MHz, DMSO-d_6)

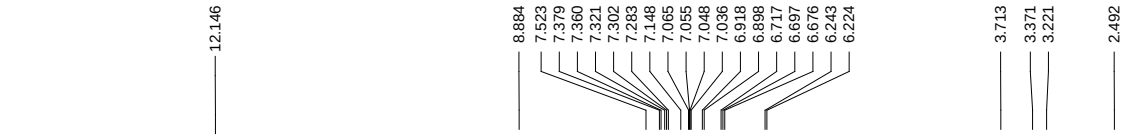


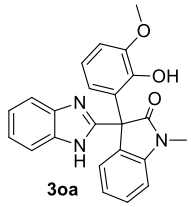


3na

^{19}F NMR (565 MHz, DMSO-d_6)

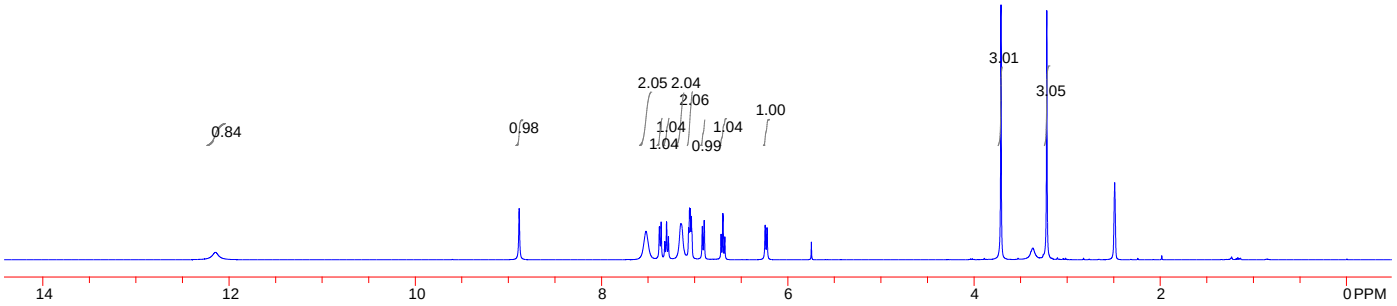


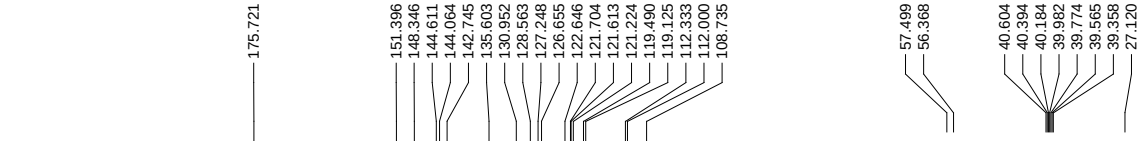


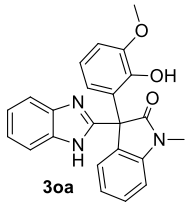


3oa

^{1}H NMR (400 MHz, DMSO-d_6)

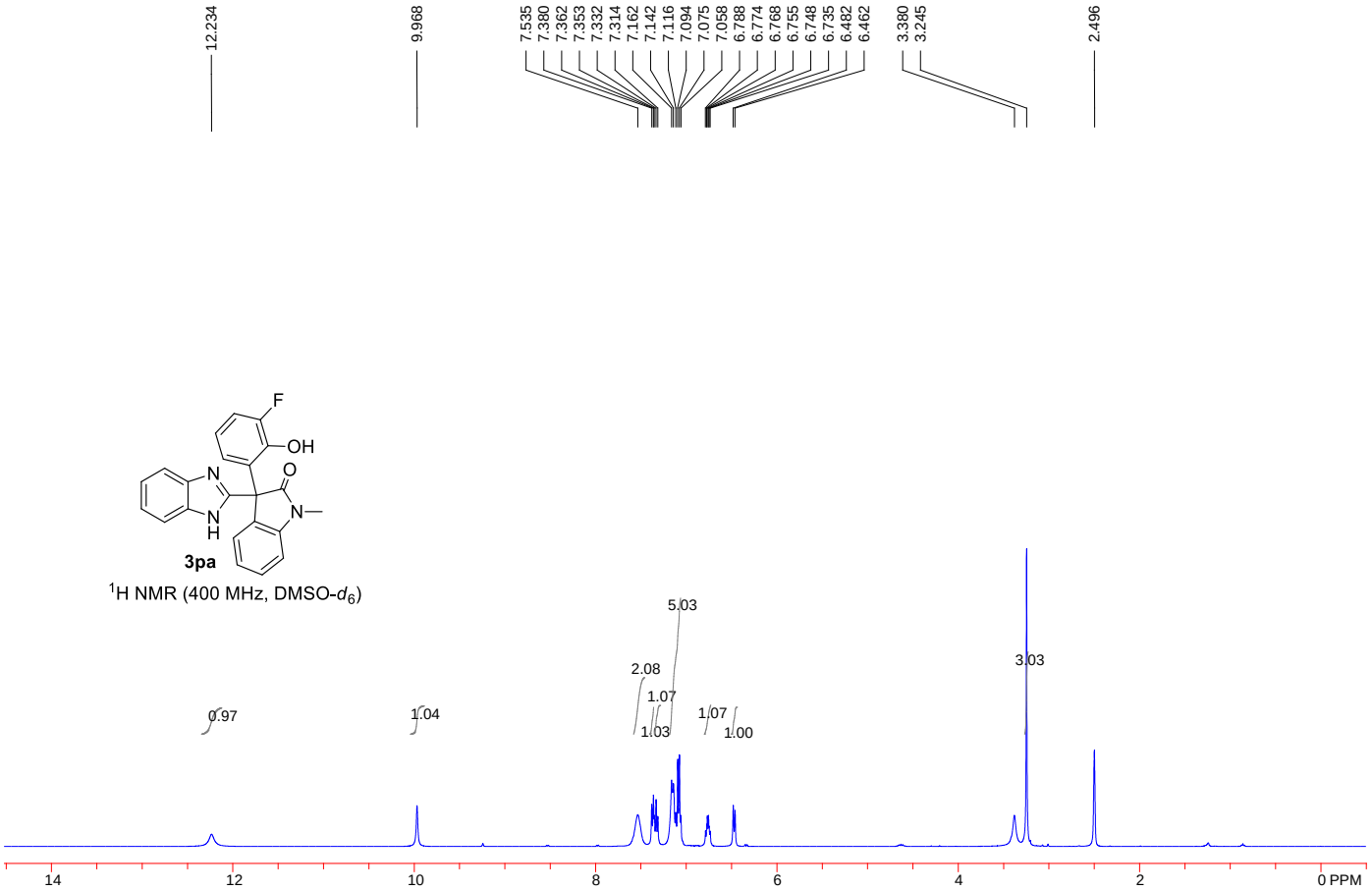


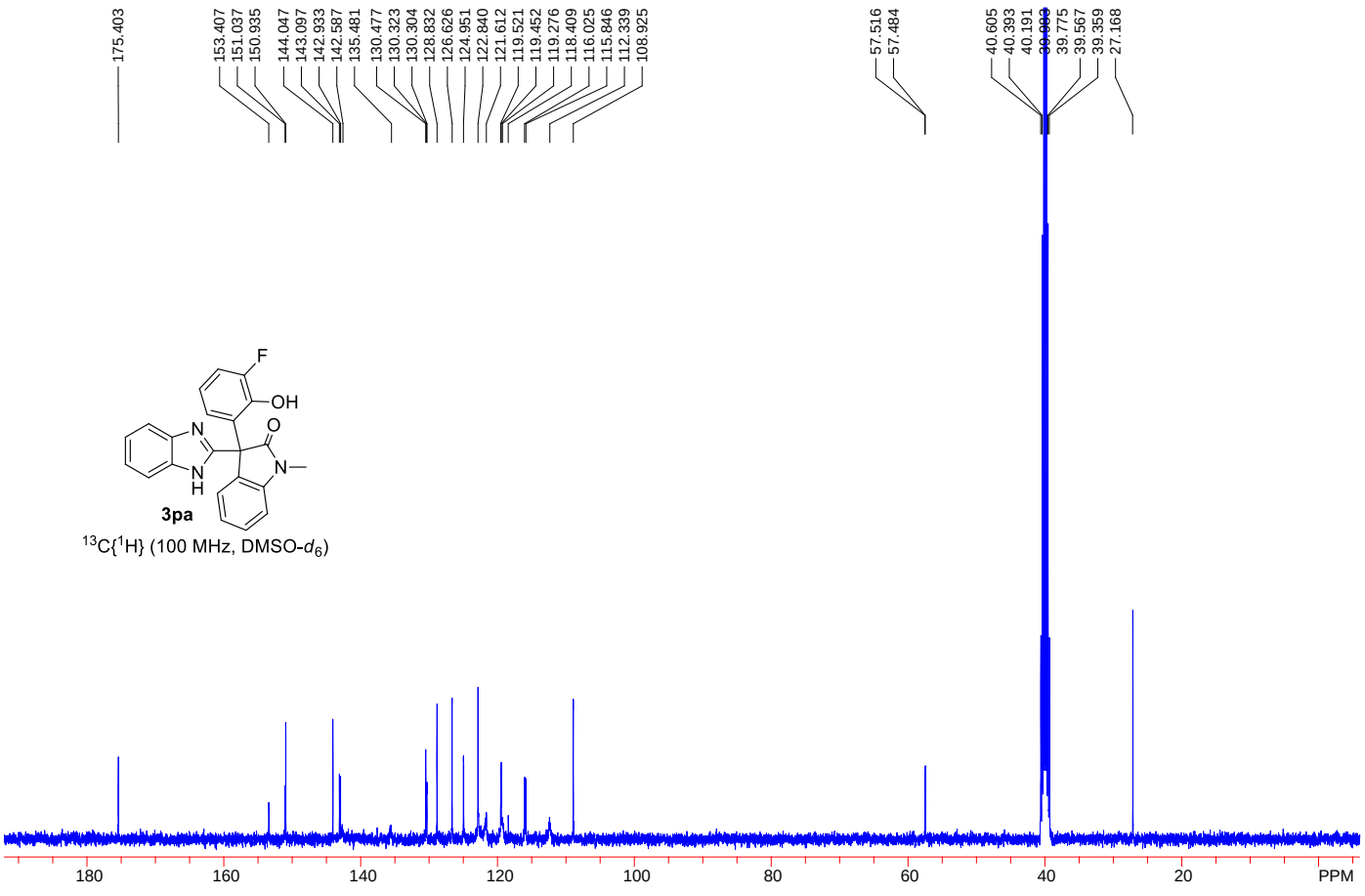


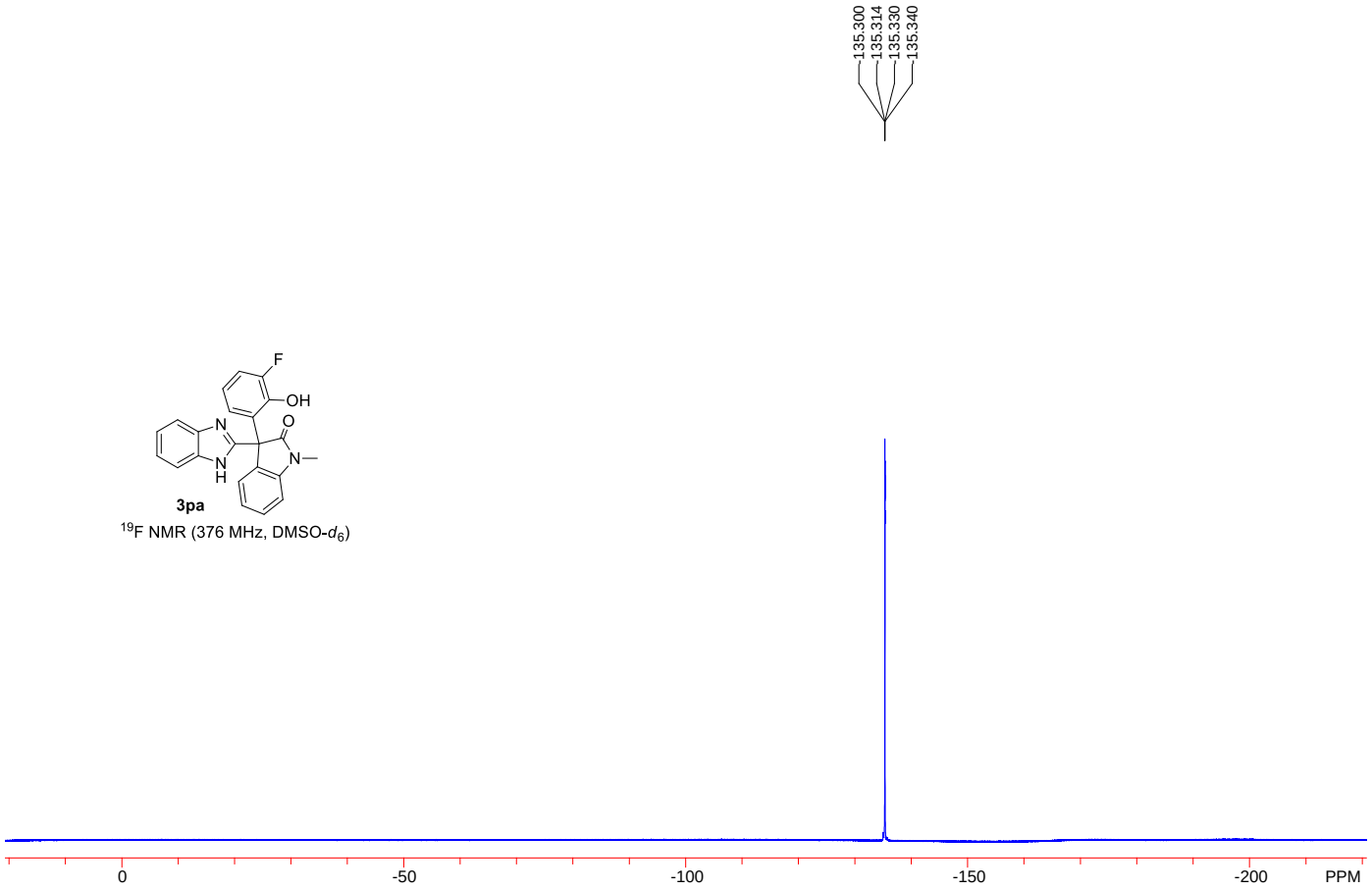


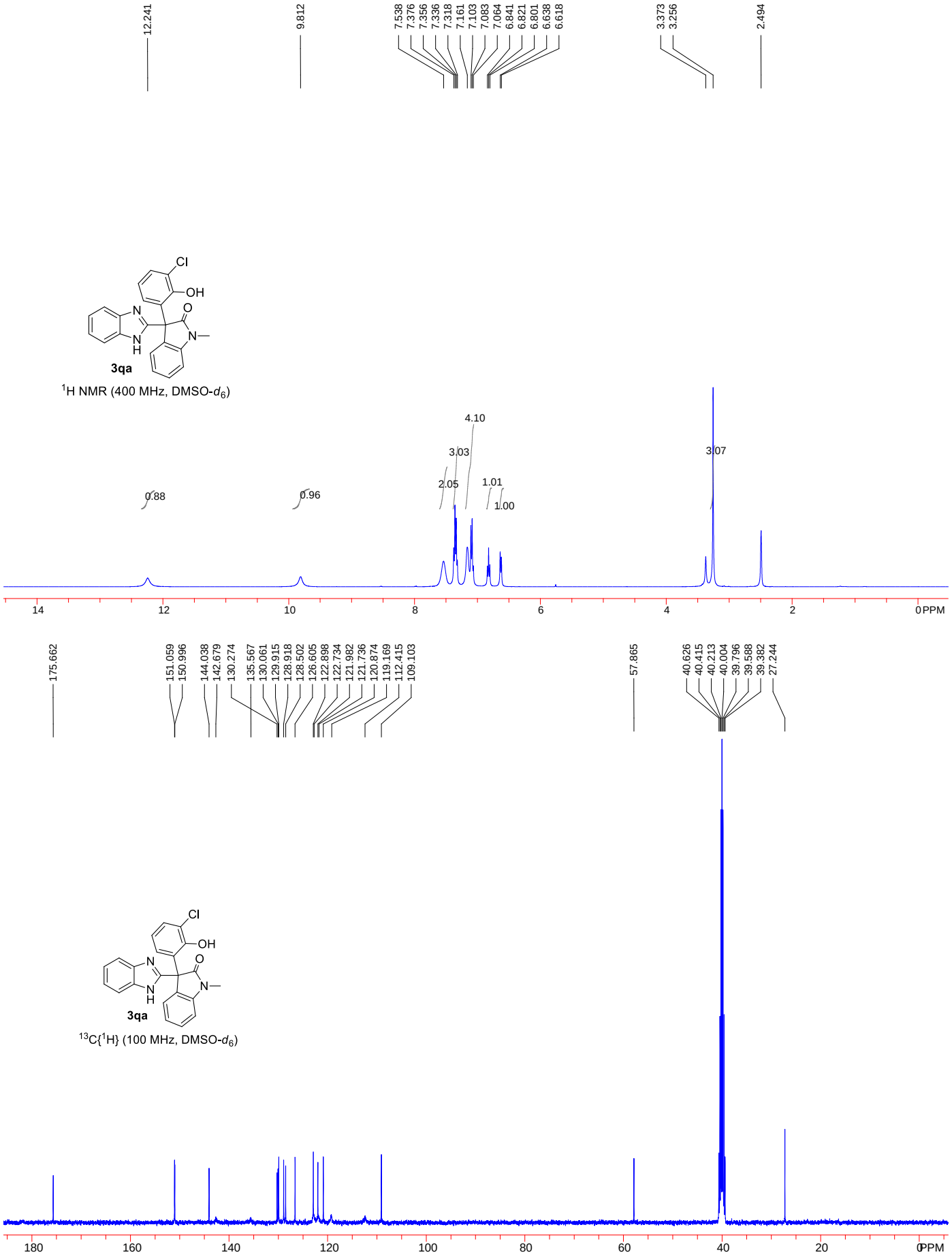
3oa

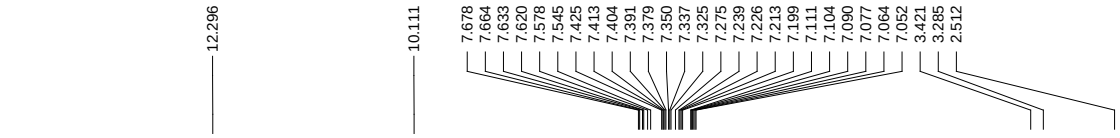
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

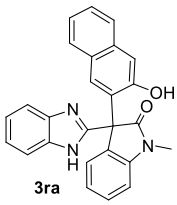

12.234
9.968
7.535
7.380
7.362
7.353
7.332
7.314
7.162
7.142
7.116
7.094
7.075
7.058
6.788
6.774
6.768
6.755
6.748
6.735
6.482
6.462
3.380
3.245
2.496
F
OH
O
N
N
H
N
3pa
^{1}H NMR (400 MHz, DMSO-d_6)
5.03
2.08
1.07
1.03
1.07
1.00
3.03
0.97
1.04
14
12
10
8
6
4
2
0 PPM


175.403
153.407
151.037
150.935
144.047
143.097
142.933
142.587
135.481
130.477
130.323
130.304
128.832
126.626
124.951
122.840
121.612
119.521
119.452
119.276
118.409
116.025
115.846
112.339
108.925
57.516
57.484
40.605
40.393
40.191
39.775
39.567
39.359
27.168
F
OH
O
N
N
H
N
3pa
^{13}C{^{1}H} (100 MHz, DMSO-d_6)
180
160
140
120
100
80
60
40
20
PPM


135.300
135.314
135.330
135.340
F
OH
O
N
N
H
N
3pa
^{19}F NMR (376 MHz, DMSO-d_6)
0
-50
-100
-150
-200
PPM

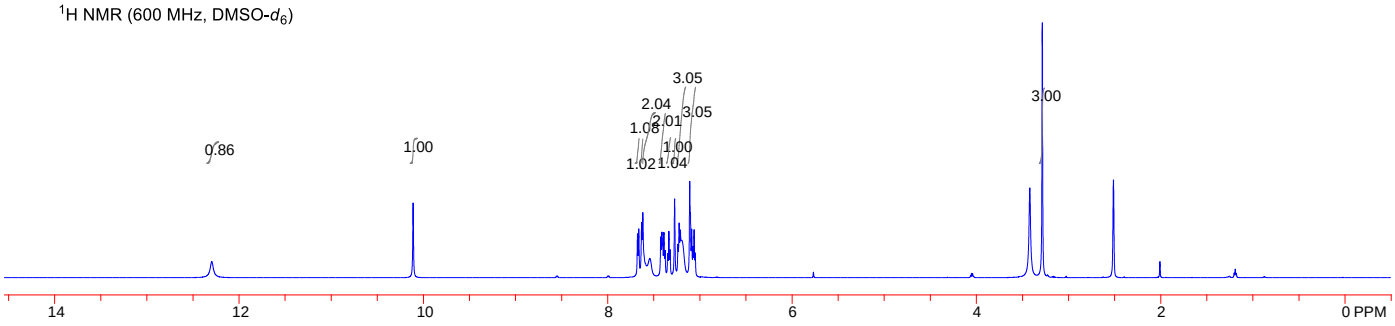

12.241
9.812
7.538
7.376
7.356
7.336
7.318
7.161
7.103
7.083
7.064
6.841
6.821
6.801
6.638
6.618
3.373
3.256
2.494
Cl
OH
O
N
H
N
3qa
^{1}H NMR (400 MHz, DMSO-d_6)
4.10
3.03
2.05
1.01
1.00
3.07
0.88
0.96
14
12
10
8
6
4
2
0 PPM
175.662
151.059
150.996
144.038
142.679
130.274
135.567
130.061
129.915
128.918
128.502
126.605
122.898
122.734
121.982
121.736
120.874
119.169
112.415
109.103
57.865
40.626
40.415
40.213
40.004
39.796
39.588
39.382
27.244
Cl
OH
O
N
H
N
3qa
^{13}C{^{1}H} (100 MHz, DMSO-d_6)
180
160
140
120
100
80
60
40
20
0 PPM

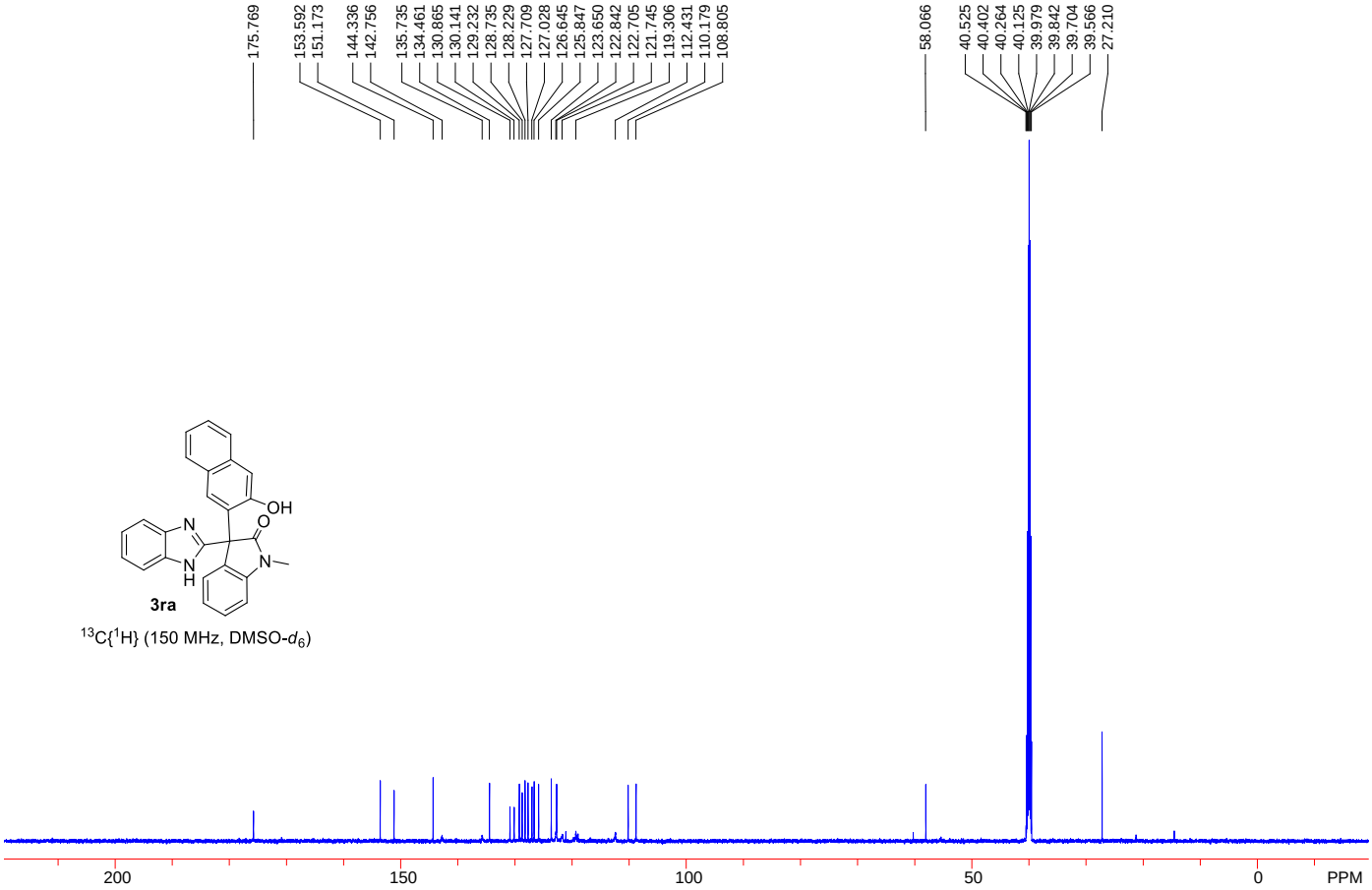




3ra

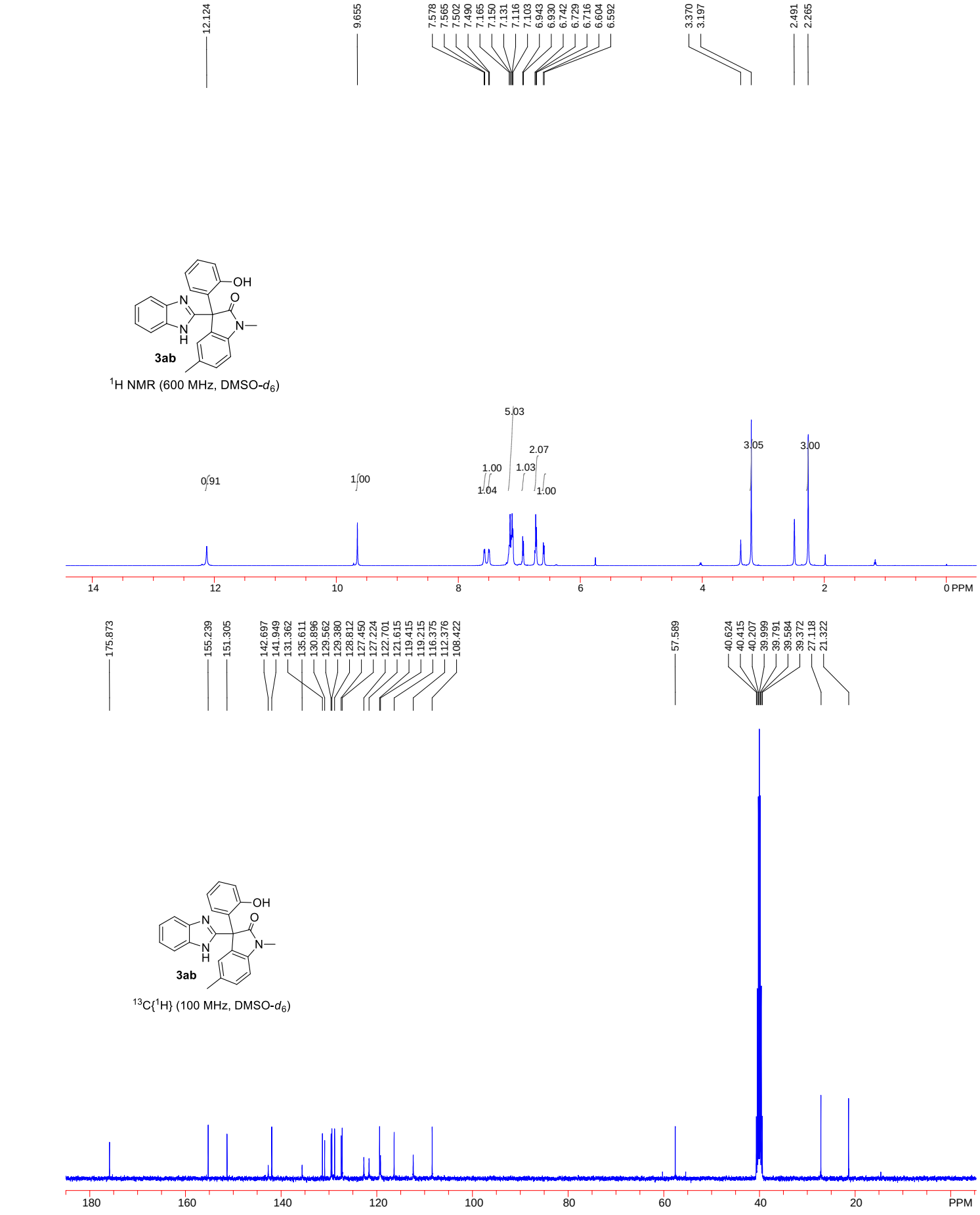
^{1}H NMR (600 MHz, DMSO-d_6)

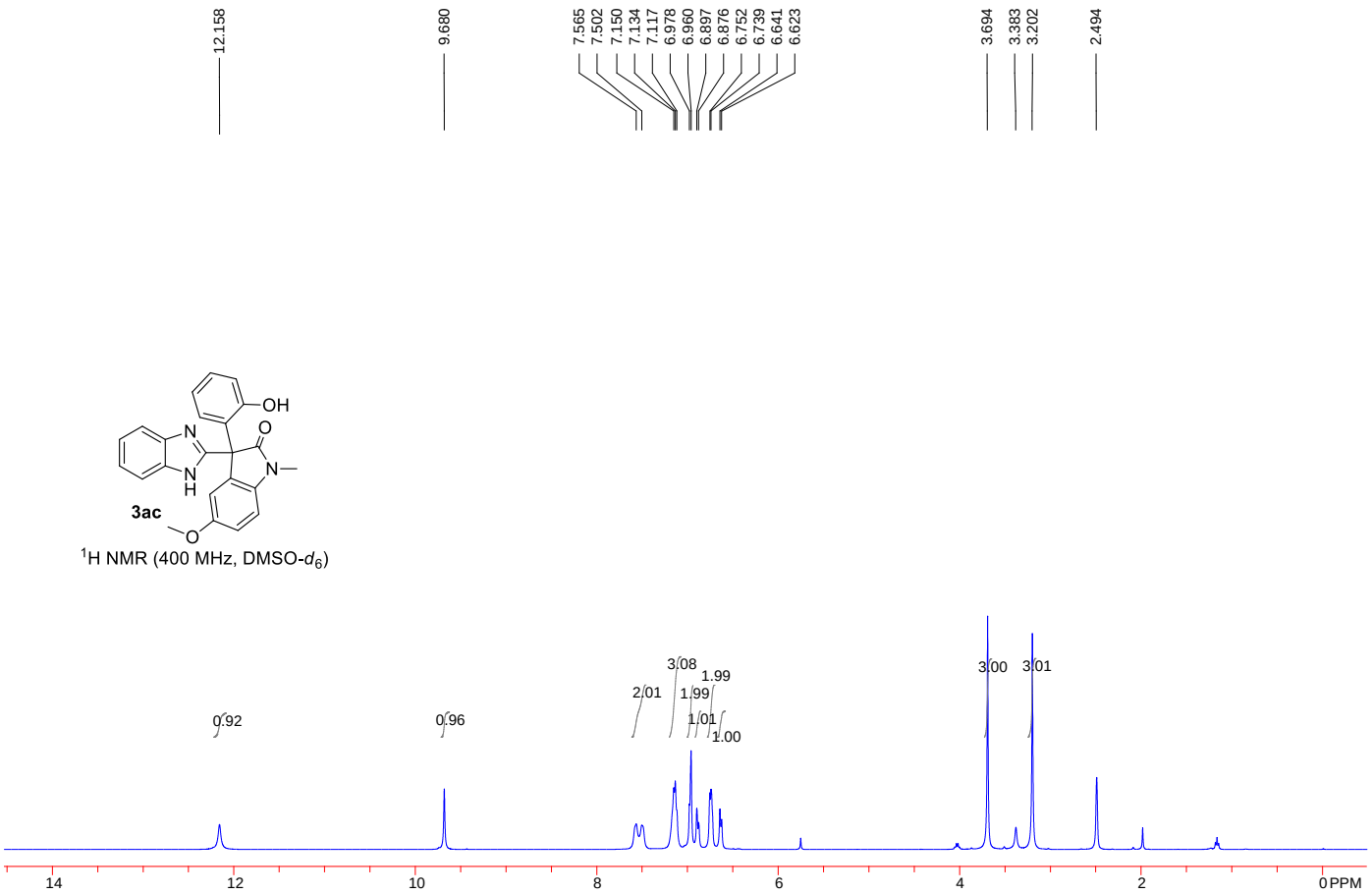




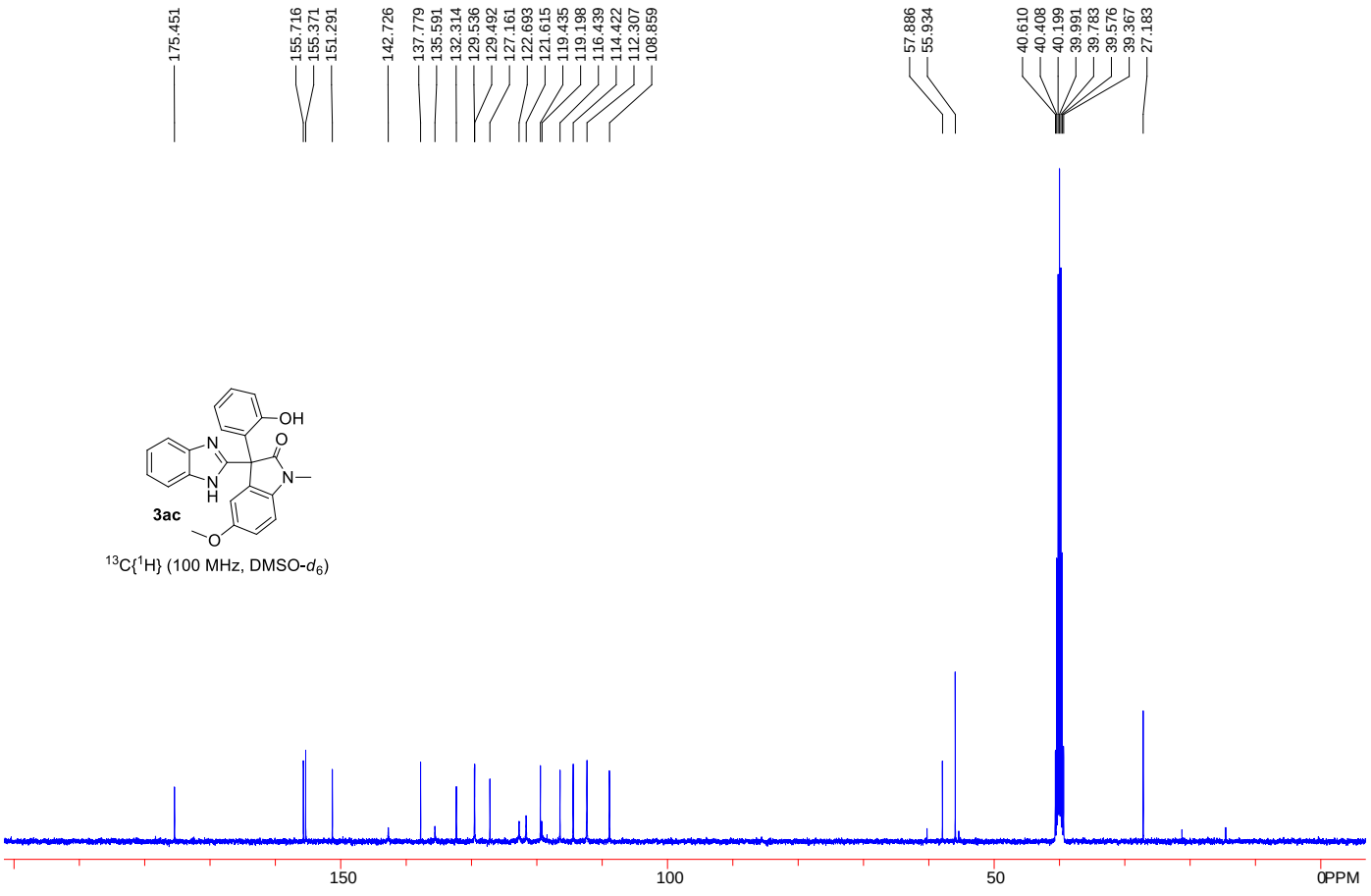
3ra

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

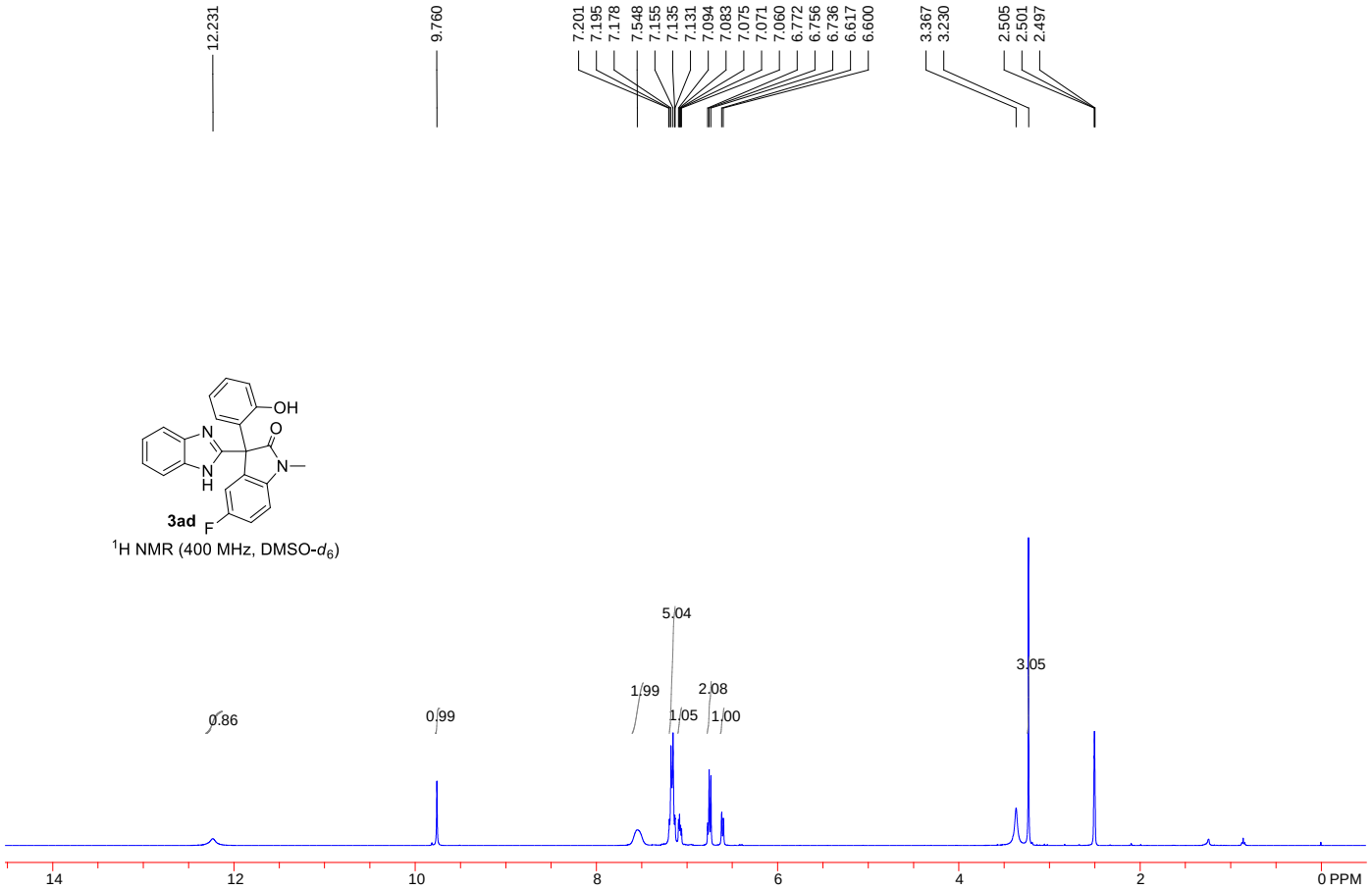

12.124
9.655
7.578
7.565
7.502
7.490
7.165
7.150
7.131
7.116
7.103
6.943
6.930
6.742
6.729
6.716
6.604
6.592
3.370
3.197
2.491
2.265
OH
O
N
N
H
N
3ab
1H NMR (600 MHz, DMSO-d6)
5.03
3.05
3.00
2.07
1.00
1.03
0.91
1.00
1.04
1.00
14
12
10
8
6
4
2
0 PPM
175.873
155.239
151.305
142.697
141.949
131.362
135.611
130.896
129.562
129.380
128.812
127.450
127.224
122.701
121.615
119.415
119.215
116.375
112.376
108.422
57.589
40.624
40.415
40.207
39.999
39.791
39.584
39.372
27.118
21.322
OH
O
N
N
H
N
3ab
13C{1H} (100 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM

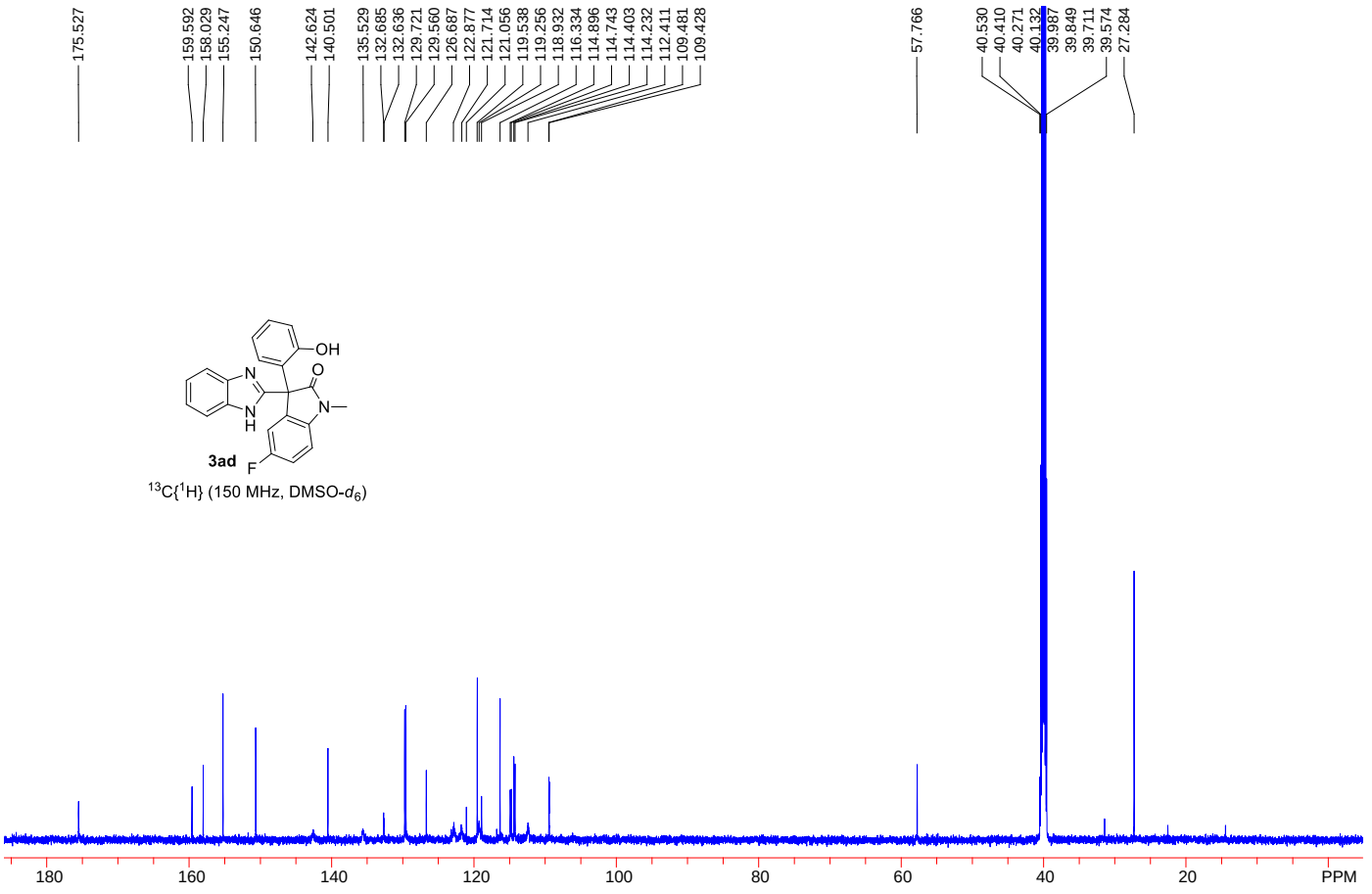


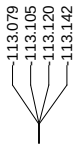
^{1}H NMR (400 MHz, DMSO-d_6)

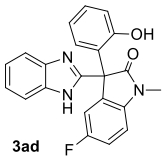


^{13}C{^{1}H} (100 MHz, DMSO-d_6)


12.231
9.760
7.201
7.195
7.178
7.548
7.155
7.135
7.131
7.094
7.083
7.075
7.071
7.060
6.772
6.756
6.736
6.617
6.600
3.367
3.230
2.505
2.501
2.497
OH
O
N
N
H
N
F
3ad
^{1}H NMR (400 MHz, DMSO-d_6)
5.04
3.05
1.99
2.08
0.86
0.99
1.05
1.00
14
12
10
8
6
4
2
0 PPM

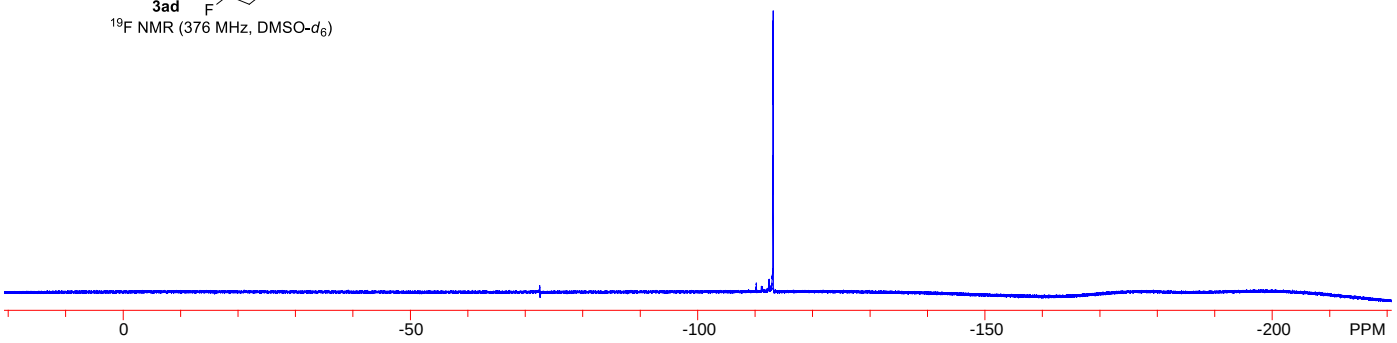

175.527
159.592
158.029
155.247
150.646
142.624
140.501
135.529
132.685
132.636
129.721
129.560
126.687
122.877
121.714
121.056
119.538
119.256
118.932
116.334
114.896
114.743
114.403
114.232
112.411
109.481
109.428
57.766
40.530
40.410
40.271
40.132
39.987
39.849
39.711
39.574
27.284
OH
O
N
N
H
N
F
3ad
^{13}C{^{1}H} (150 MHz, DMSO-d_6)
180
160
140
120
100
80
60
40
20
PPM

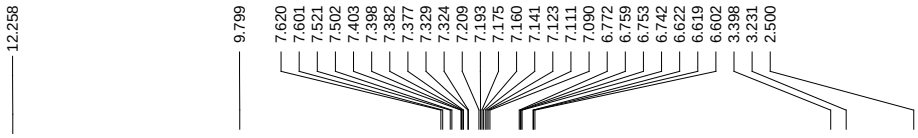


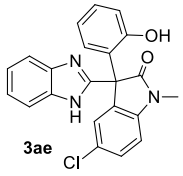


3ad

^{19}F NMR (376 MHz, DMSO-d_6)

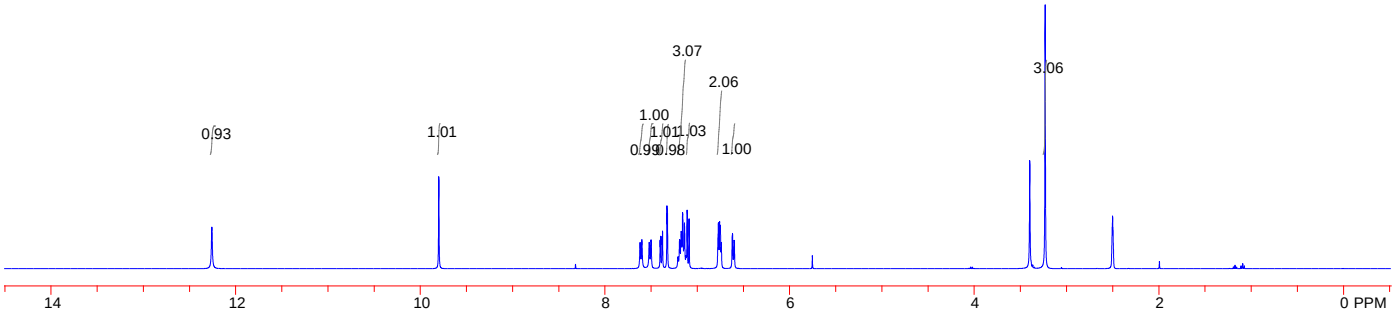


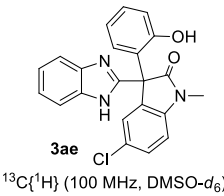




3ae

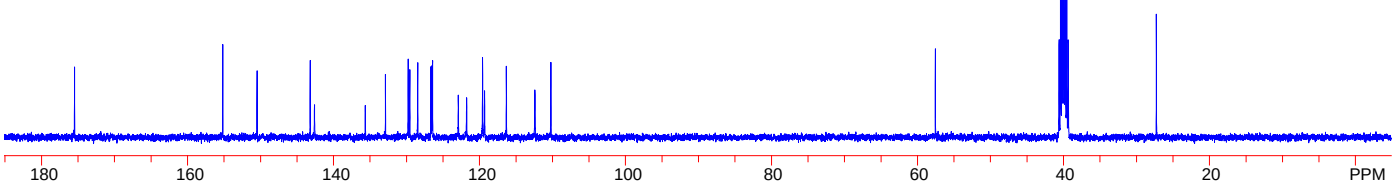
^{1}H NMR (400 MHz, DMSO-d_6)

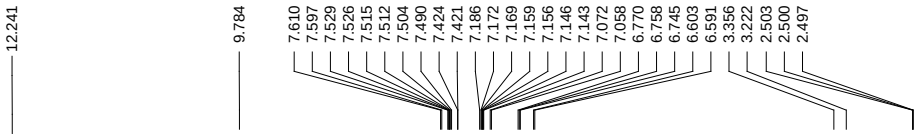


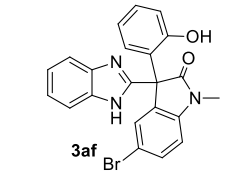


3ae

^{13}C{^{1}H} (100 MHz, DMSO-d_6)

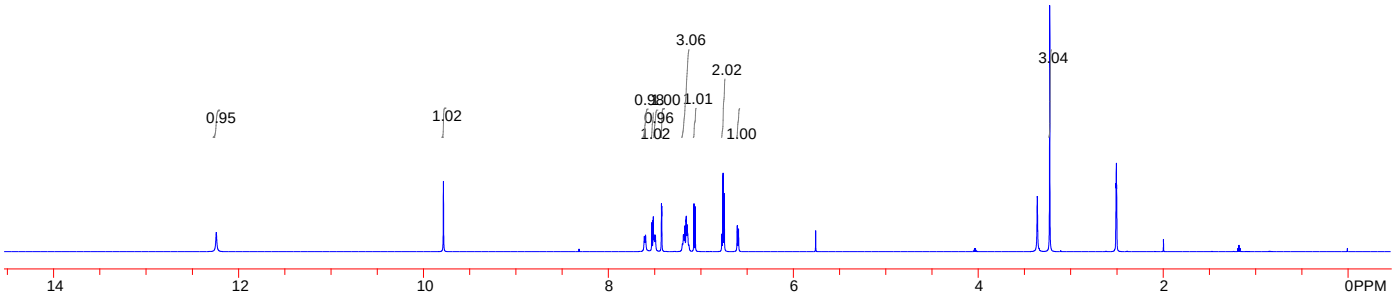


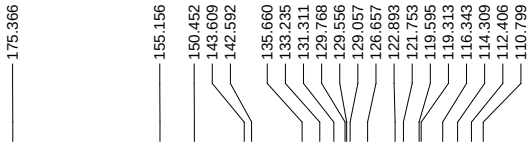


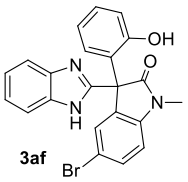


3af

^{1}H NMR (600 MHz, DMSO-d_6)

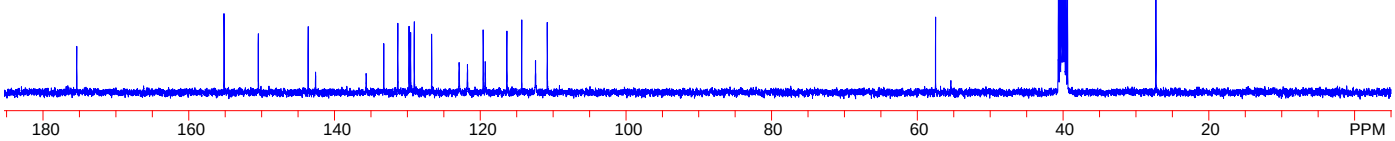


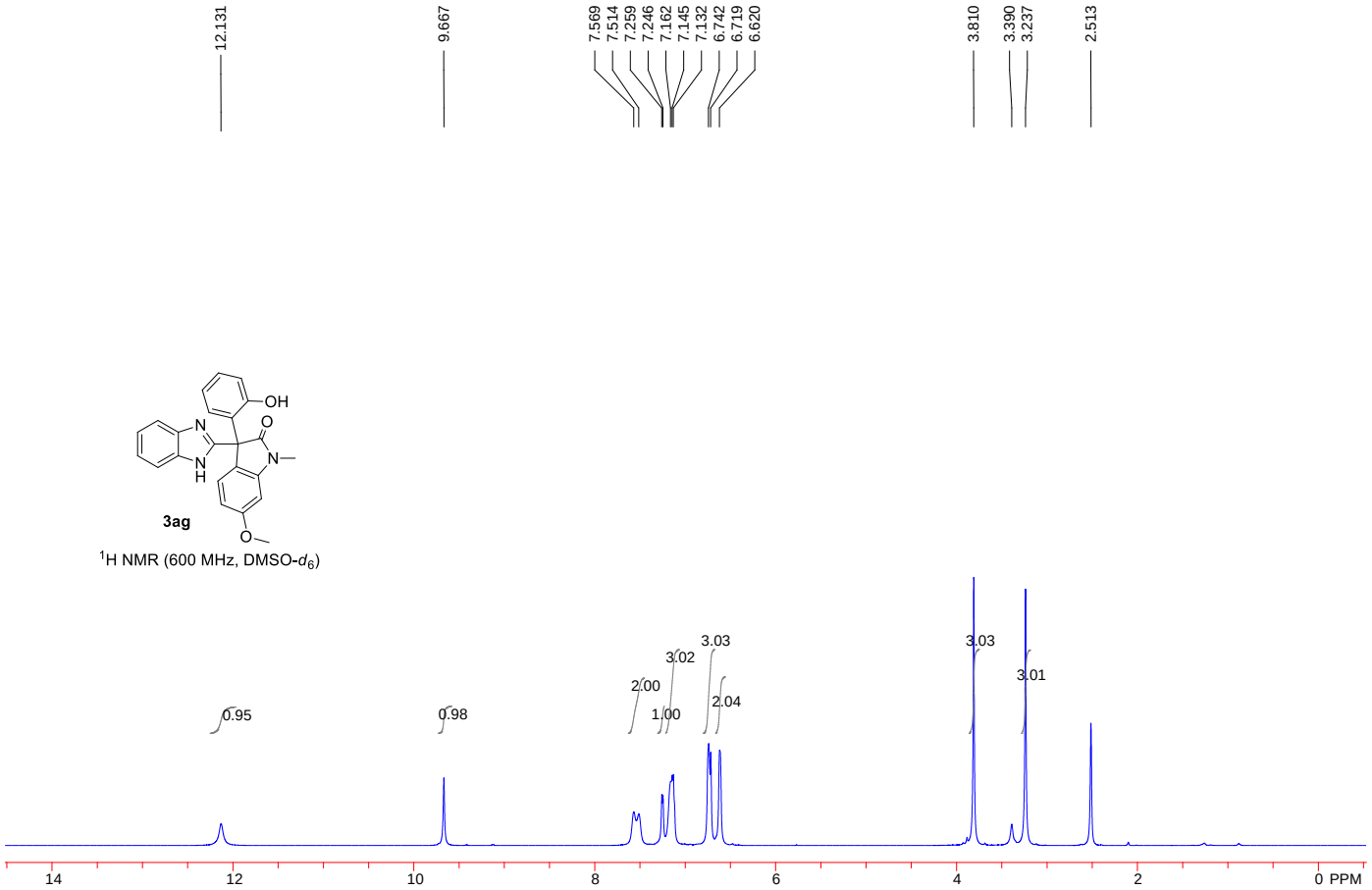


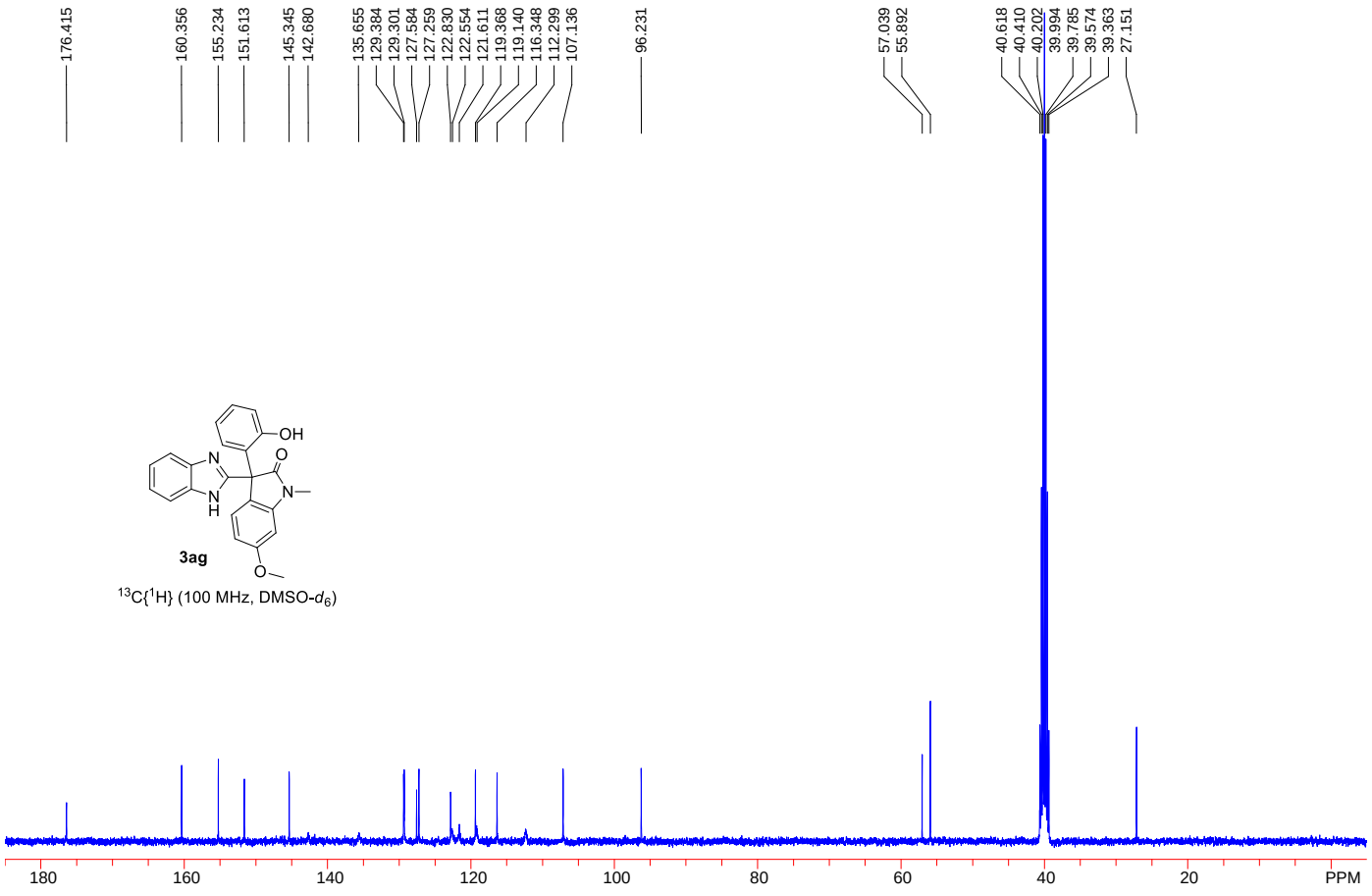


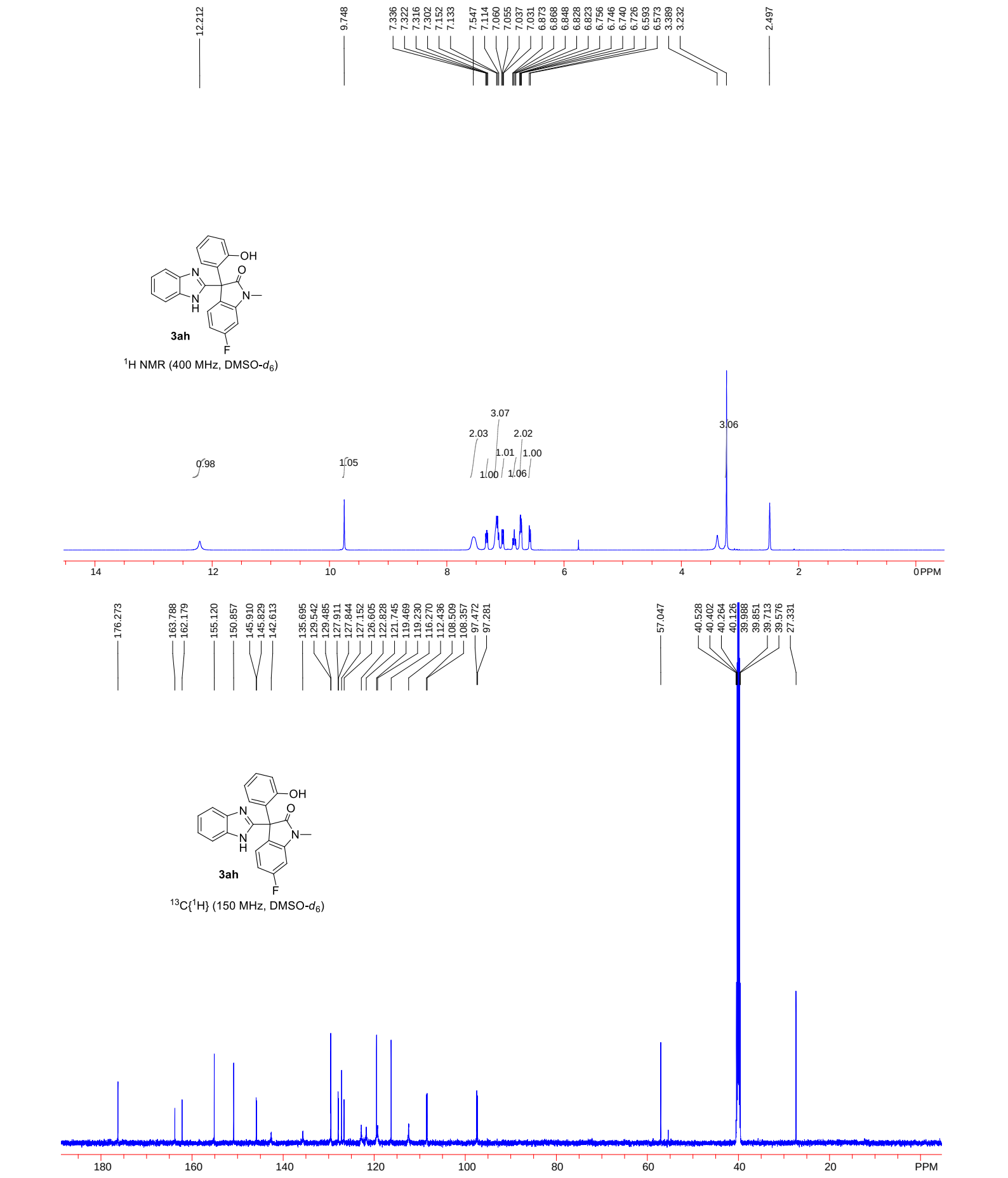
3af

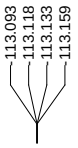
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

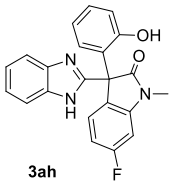



12.131
9.667
7.569
7.514
7.259
7.246
7.162
7.145
7.132
6.742
6.719
6.620
3.810
3.390
3.237
2.513
OH
O
N
H
N
O
3ag
^{1}H NMR (600 MHz, DMSO-d_6)
0.95
0.98
2.00
3.02
3.03
1.00
2.04
3.03
3.01
14
12
10
8
6
4
2
0 PPM


176.415
160.356
155.234
151.613
145.345
142.680
135.655
129.384
129.301
127.584
127.259
122.830
122.554
121.611
119.368
119.140
116.348
112.299
107.136
96.231
57.039
55.892
40.618
40.410
40.202
39.994
39.785
39.574
39.363
27.151
OH
O
N
H
N
O
3ag
^{13}C{^{1}H} (100 MHz, DMSO-d_6)
180
160
140
120
100
80
60
40
20
PPM

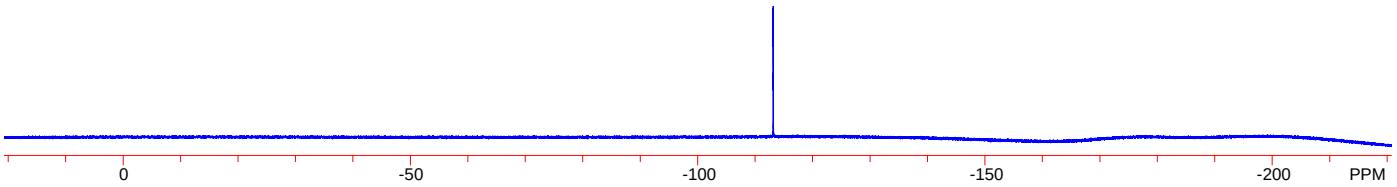

12.212
9.748
7.336
7.322
7.316
7.302
7.152
7.133
7.547
7.114
7.060
7.055
7.037
7.031
6.873
6.868
6.848
6.828
6.823
6.756
6.746
6.740
6.726
6.593
6.573
3.389
3.232
2.497
OH
O
N
N
H
N
F
3ah
1H NMR (400 MHz, DMSO-d6)
3.07
2.03
2.02
1.01
1.00
3.06
0.98
1.05
1.00
1.06
14
12
10
8
6
4
2
0 PPM
176.273
163.788
162.179
155.120
150.857
145.910
145.829
142.613
135.695
129.542
129.485
127.911
127.844
127.152
126.605
122.828
121.745
119.469
119.230
116.270
112.436
108.509
108.357
97.472
97.281
57.047
40.528
40.402
40.264
40.126
39.988
39.851
39.713
39.576
27.331
OH
O
N
N
H
N
F
3ah
13C{1H} (150 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM



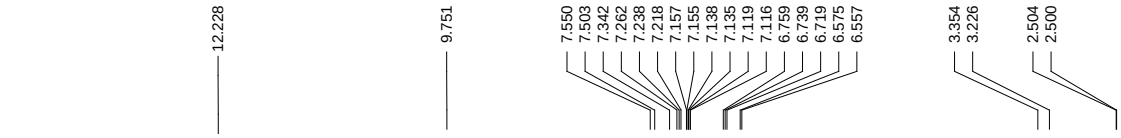


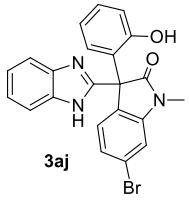
3ah

^{19}F NMR (376 MHz, DMSO-d_6)



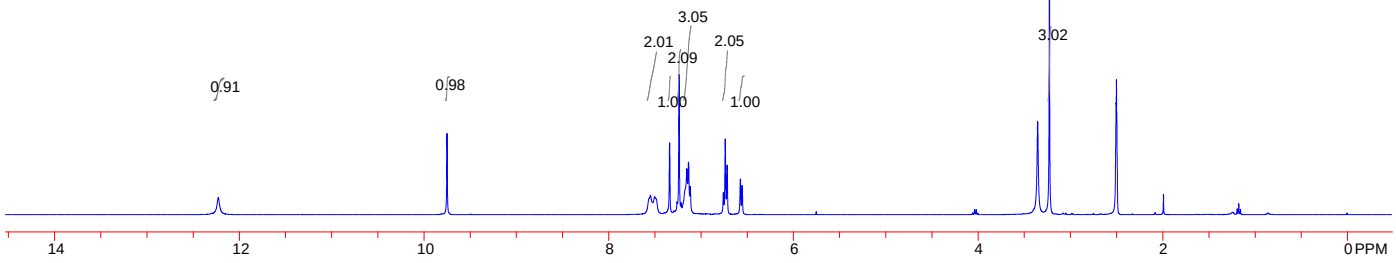

12.234
9.762
7.579
7.560
7.511
7.492
7.314
7.294
7.227
7.223
7.183
7.158
7.154
7.135
7.117
7.097
7.093
6.761
6.745
6.725
6.587
6.570
3.380
3.236
2.497
OH
O
N
N
H
N
Cl
3ai
1H NMR (400 MHz, DMSO-d6)
4.06
2.09
3.04
0.99
1.00
1.01
1.03
1.02
0.99
1.00
14
12
10
8
6
4
2
0 PPM
175.954
155.114
150.541
145.701
142.615
135.666
133.179
129.741
129.617
129.535
127.941
126.911
122.876
122.227
121.736
119.505
119.267
116.252
112.425
109.135
57.134
40.622
40.409
40.198
39.996
39.788
39.580
39.372
27.294
OH
O
N
N
H
N
Cl
3ai
13C{1H} (100 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM

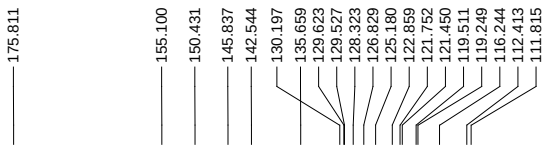


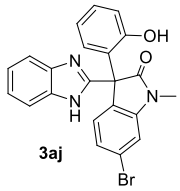


3aj

^{1}H NMR (400 MHz, DMSO-d_6)

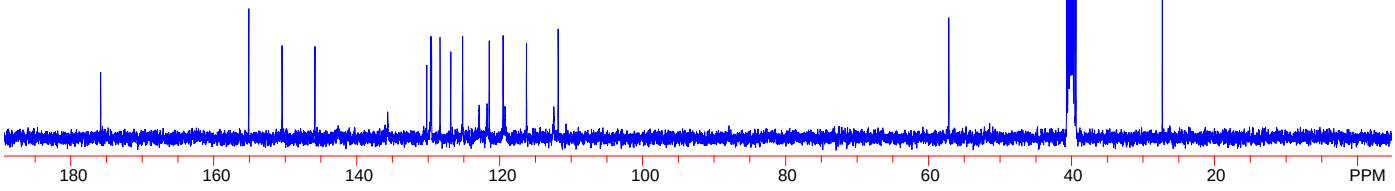


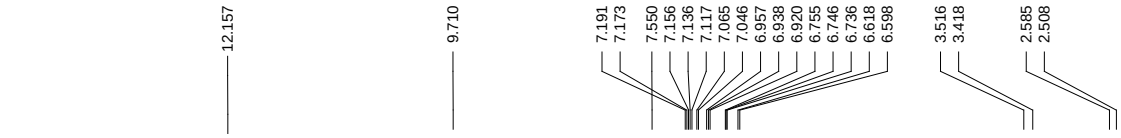


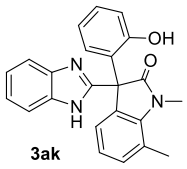


3aj

^{13}C{^{1}H} (100 MHz, DMSO-d_6)

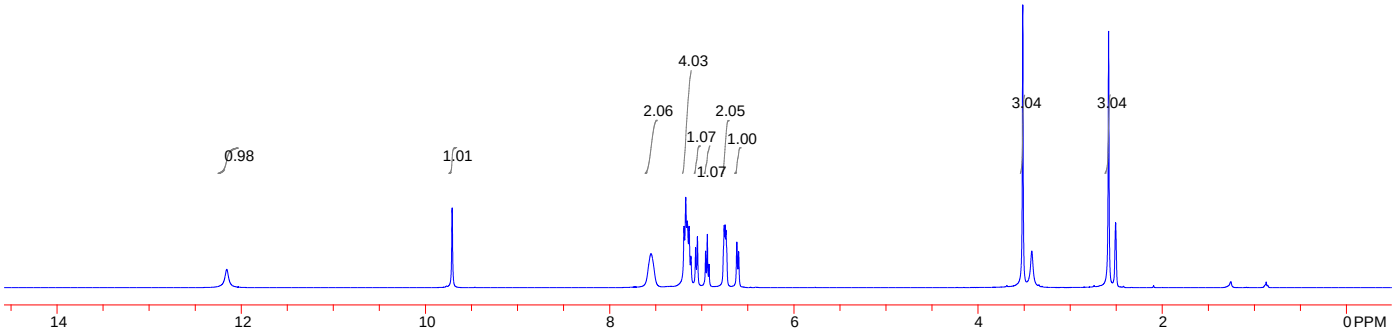


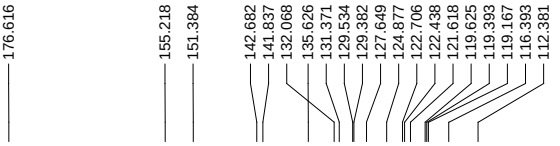


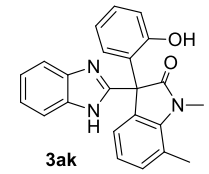


3ak

^{1}H NMR (400 MHz, DMSO-d_6)

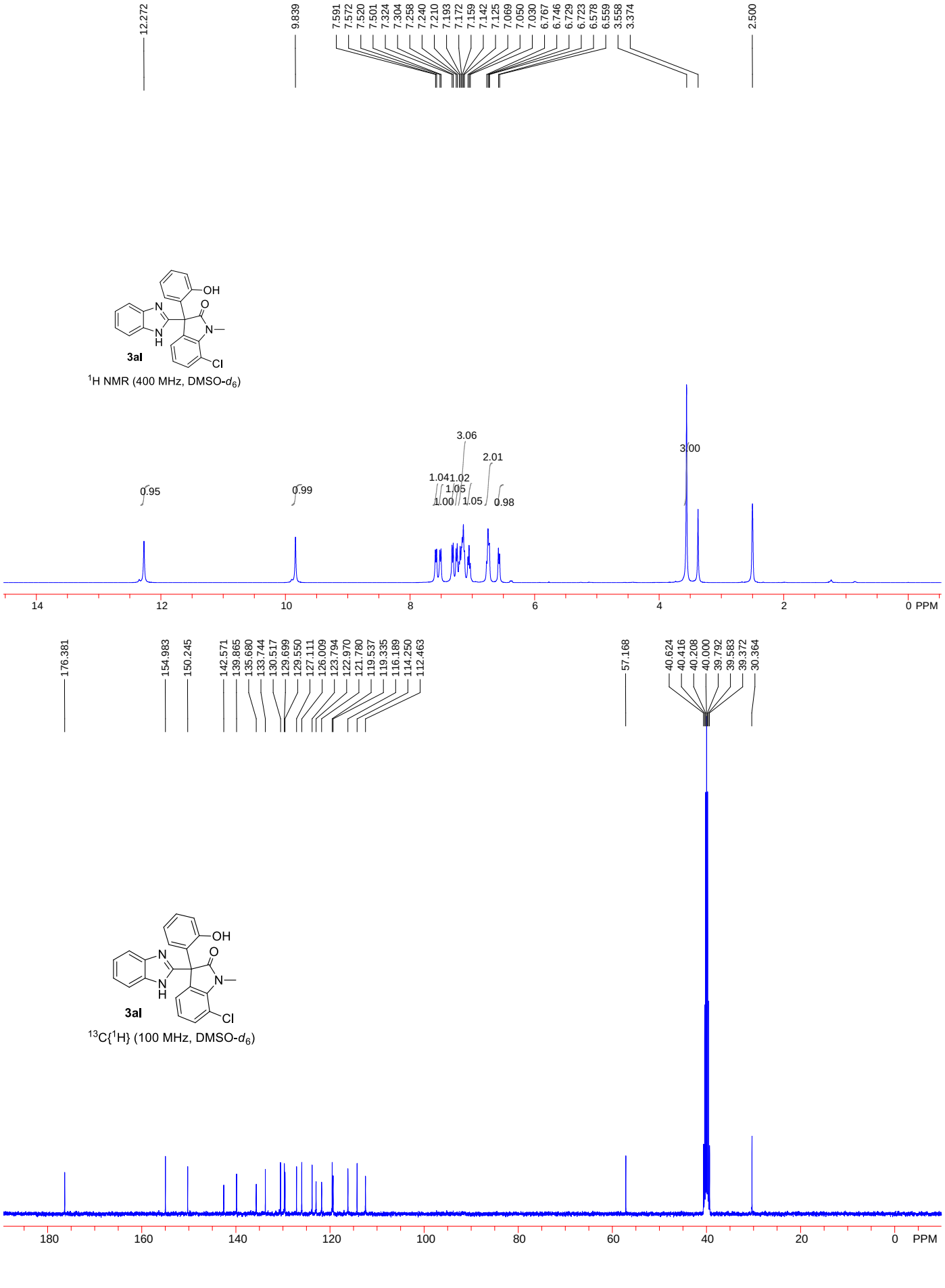


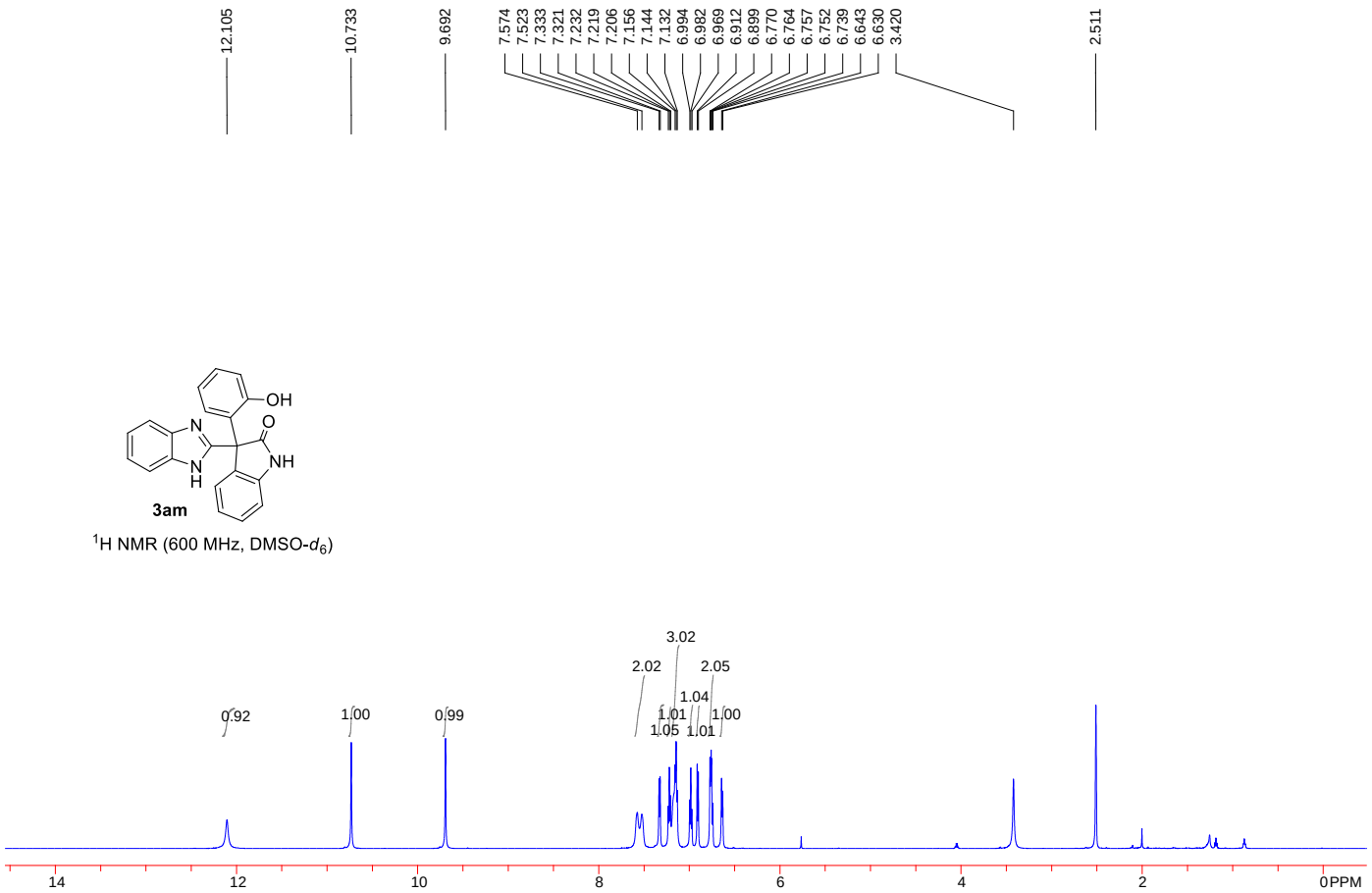




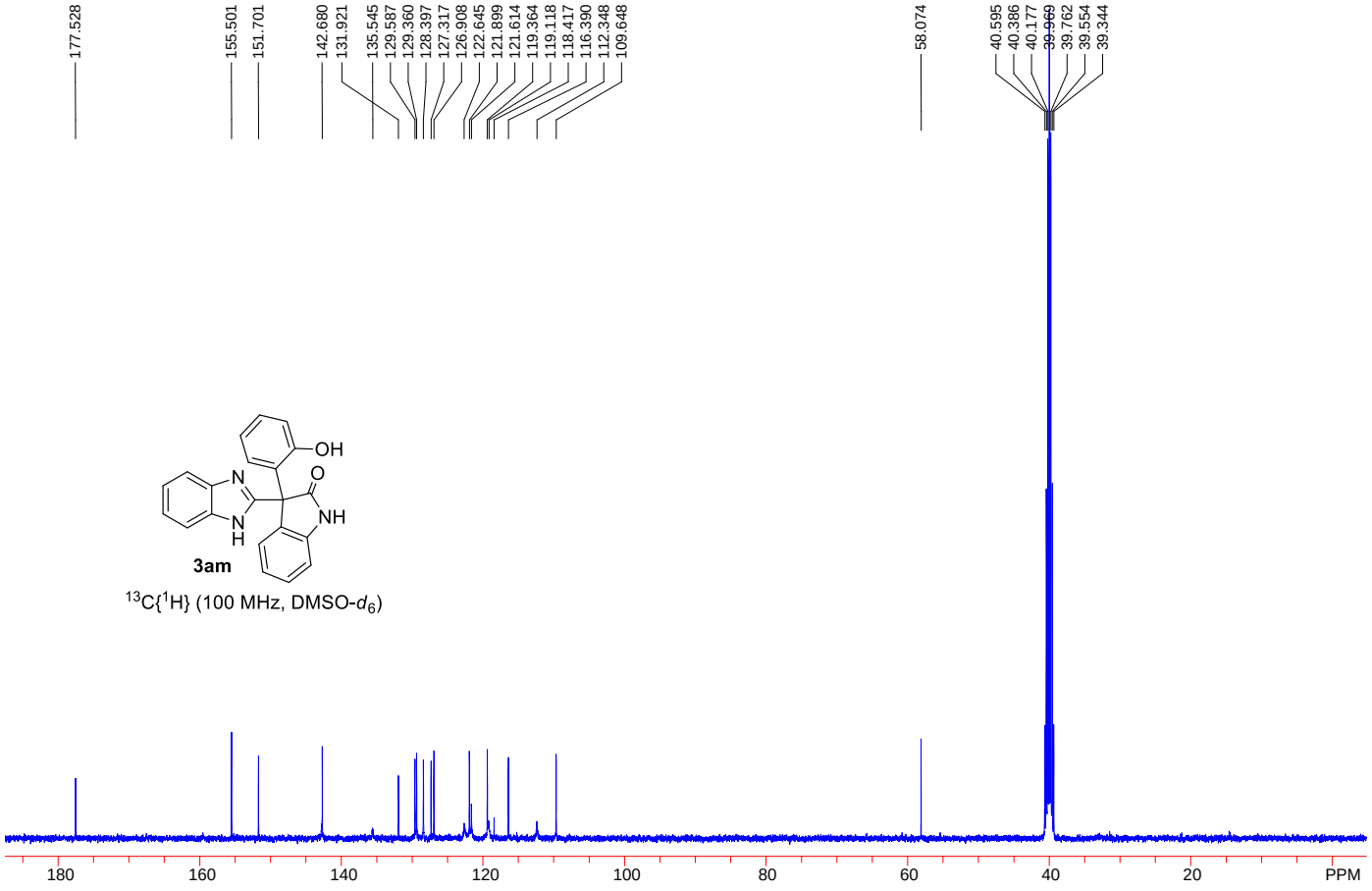
3ak

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


12.272
9.839
7.591
7.572
7.520
7.501
7.324
7.304
7.258
7.240
7.210
7.193
7.172
7.159
7.142
7.125
7.069
7.050
7.030
6.767
6.746
6.729
6.723
6.578
6.559
3.558
3.374
2.500
OH
O
N
N
H
N
Cl
3al
1H NMR (400 MHz, DMSO-d6)
3.06
2.01
3.00
1.04
1.02
1.05
1.00
1.05
0.95
0.99
0.98
14
12
10
8
6
4
2
0 PPM
176.381
154.983
150.245
142.571
139.865
135.680
133.744
130.517
129.699
129.550
127.111
126.009
123.794
122.970
121.780
119.537
119.335
116.189
114.250
112.463
57.168
40.624
40.416
40.208
40.000
39.792
39.583
39.372
30.364
OH
O
N
N
H
N
Cl
3al
13C{1H} (100 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
0 PPM

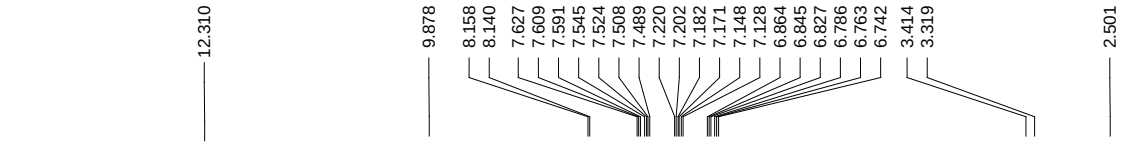


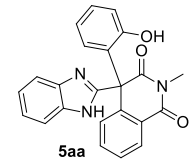
^{1}H NMR (600 MHz, DMSO-d_6)



^{13}C{^{1}H} (100 MHz, DMSO-d_6)

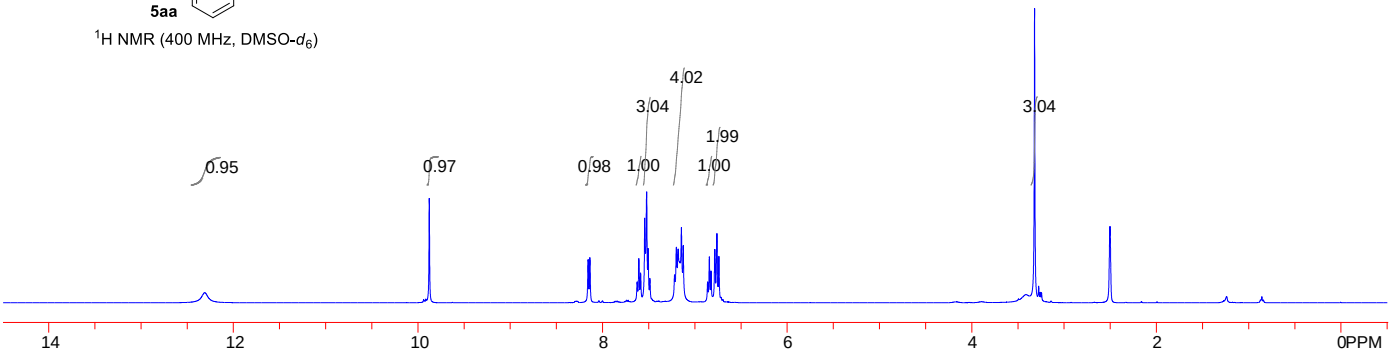
V. NMR spectra of 5aa-5ac

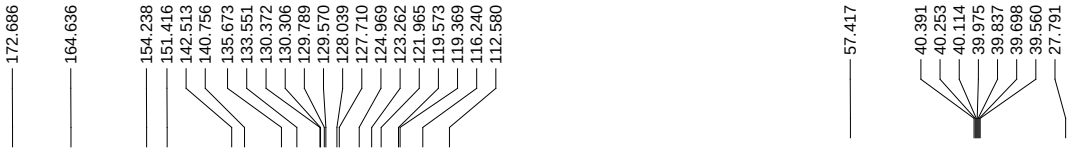


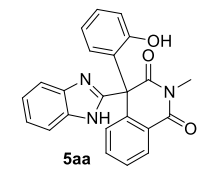


5aa

^{1}H NMR (400 MHz, DMSO-d_6)

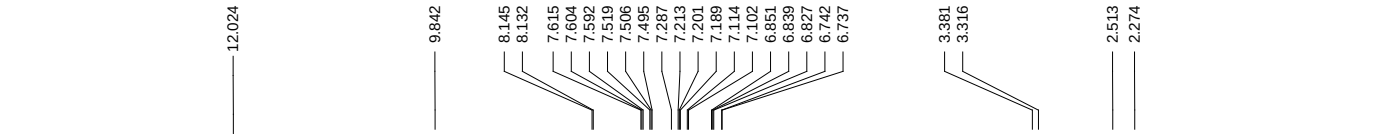


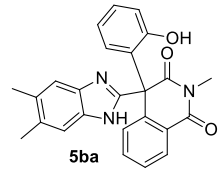




5aa

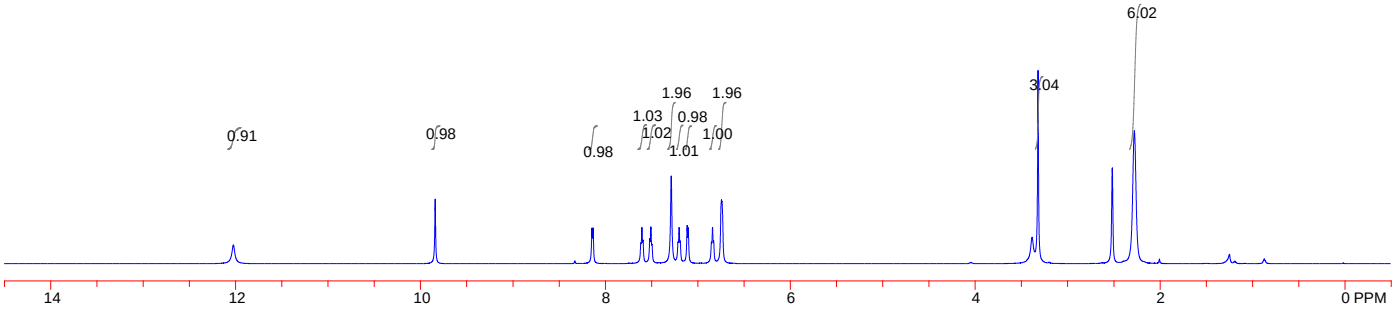
^{13}C{^{1}H} (150 MHz, DMSO-d_6)

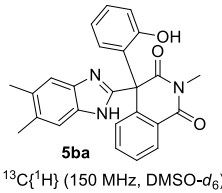




5ba

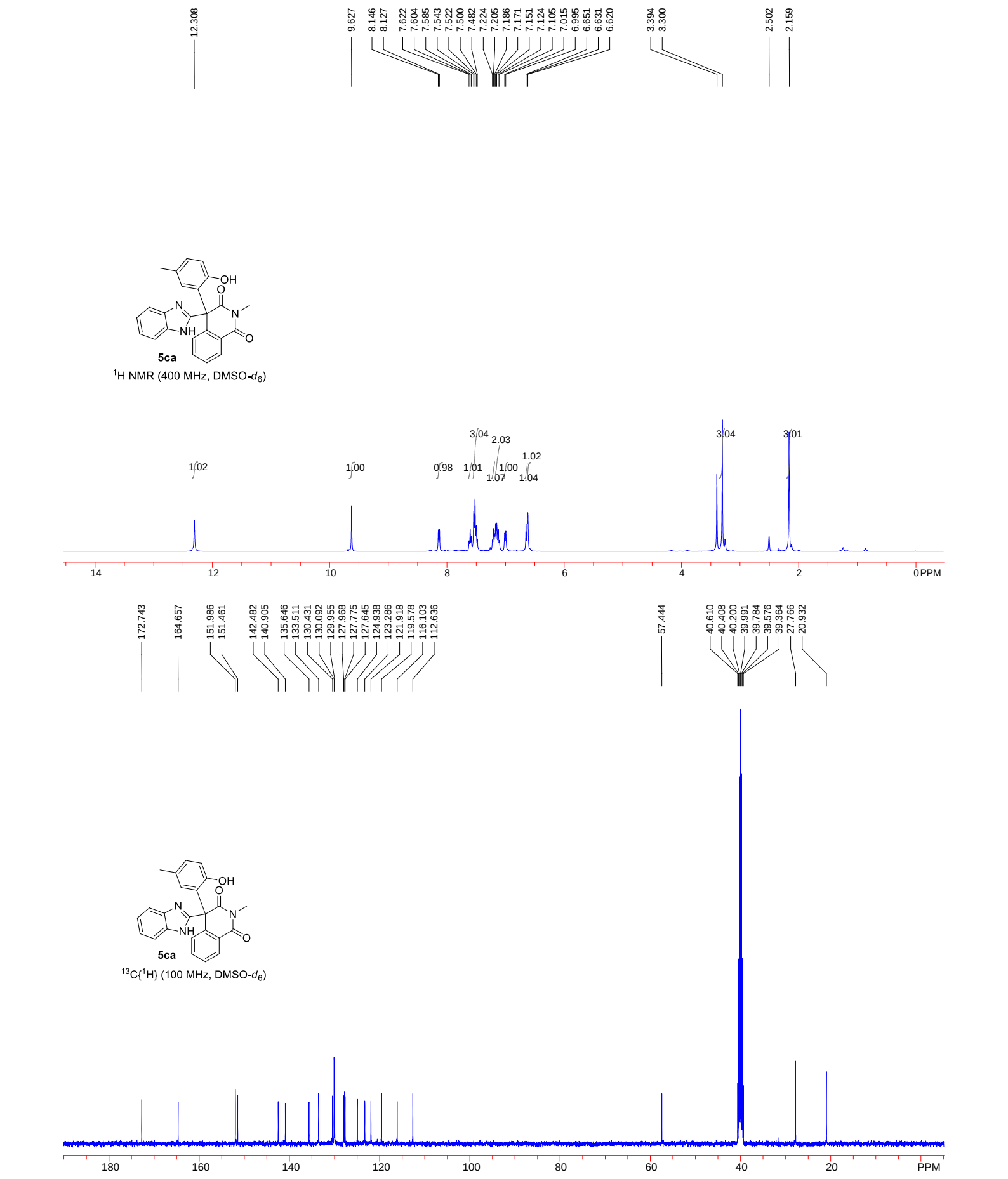
^{1}H NMR (600 MHz, DMSO-d_6)

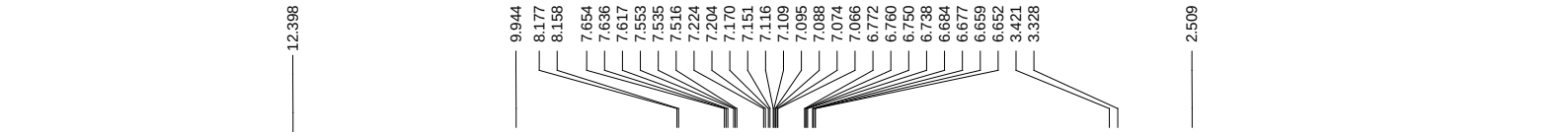


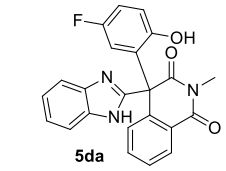


5ba

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

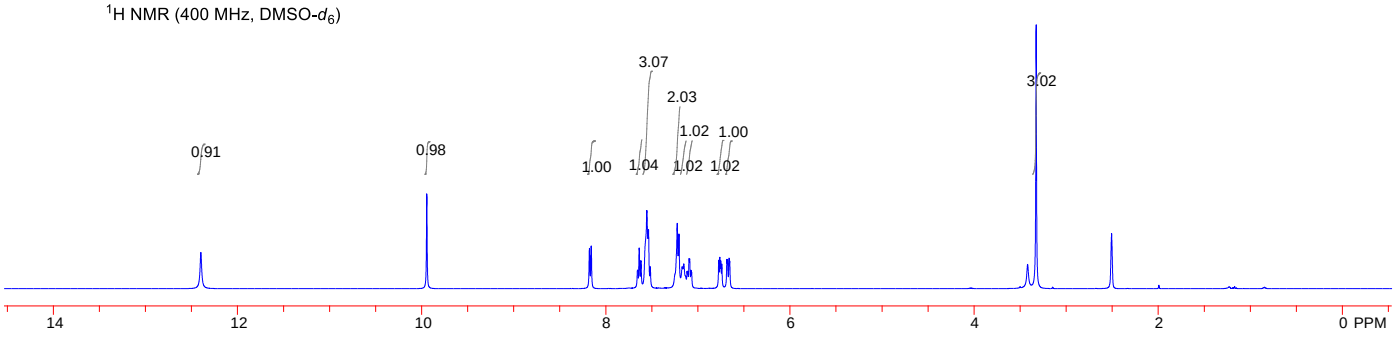

12.308
9.627
8.146
8.127
7.622
7.604
7.585
7.543
7.522
7.500
7.482
7.224
7.205
7.186
7.171
7.151
7.124
7.105
7.015
6.995
6.651
6.631
6.620
3.394
3.300
2.502
2.159
OH
O
N
NH
N
O
5ca
1H NMR (400 MHz, DMSO-d6)
1.02
1.00
0.98
1.01
3.04
2.03
1.07
1.00
1.02
1.04
3.04
3.01
14
12
10
8
6
4
2
0 PPM
172.743
164.657
151.986
151.461
142.482
140.905
135.646
133.511
130.431
130.092
129.955
127.968
127.775
127.645
124.938
123.286
121.918
119.578
116.103
112.636
57.444
40.610
40.408
40.200
39.991
39.784
39.576
39.364
27.766
20.932
OH
O
N
NH
N
O
5ca
13C{1H} (100 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM

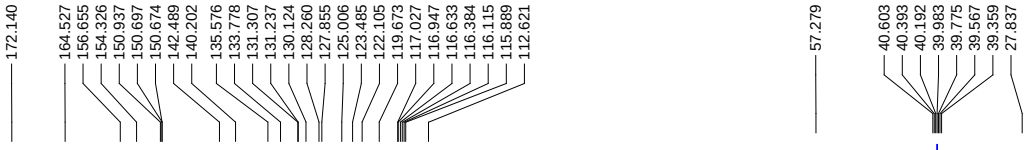


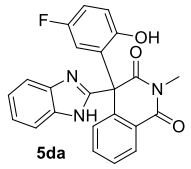


5da

^{1}H NMR (400 MHz, DMSO-d_6)

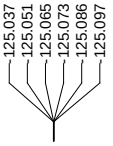


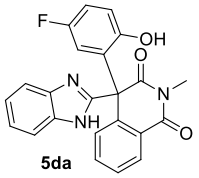




5da

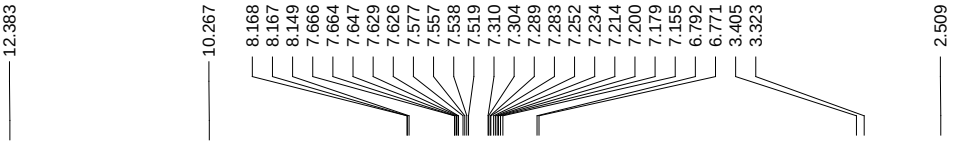
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

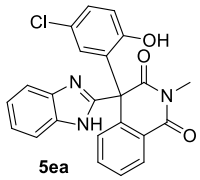




5da

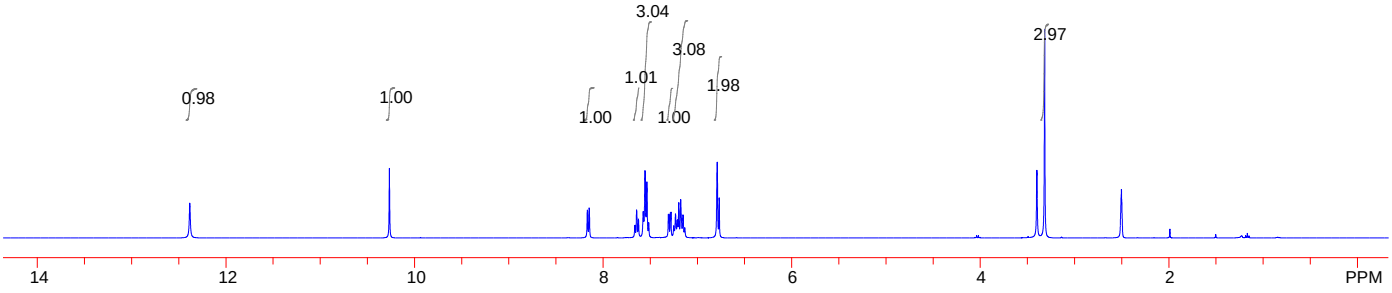
^{19}F NMR (376 MHz, DMSO-d_6)

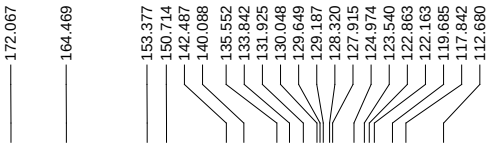


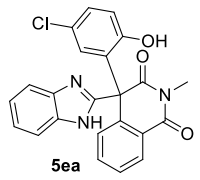


5ea

^{1}H NMR (400 MHz, DMSO-d_6)

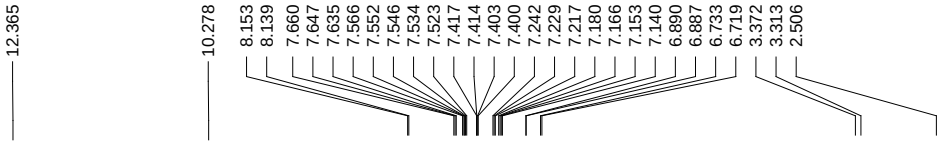


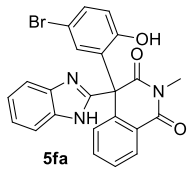




5ea

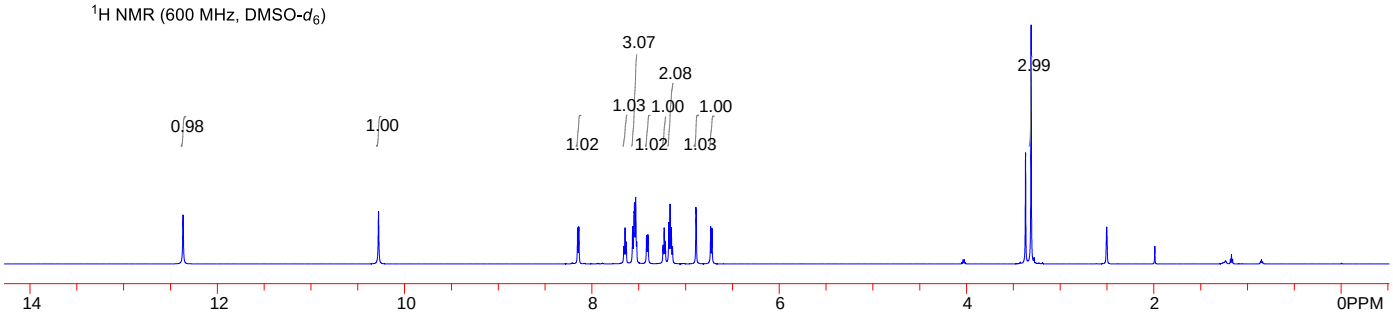
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

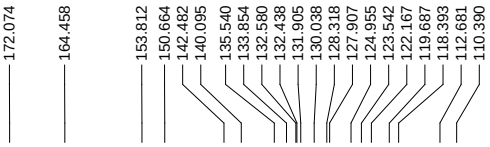


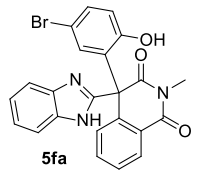


5fa

^{1}H NMR (600 MHz, DMSO-d_6)

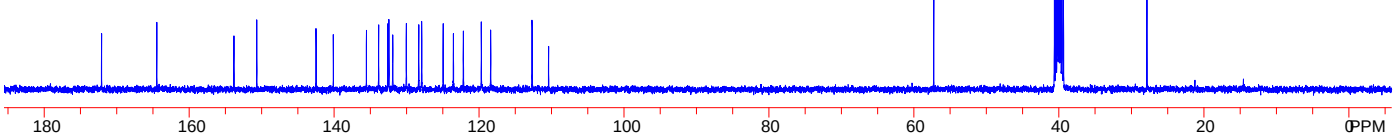


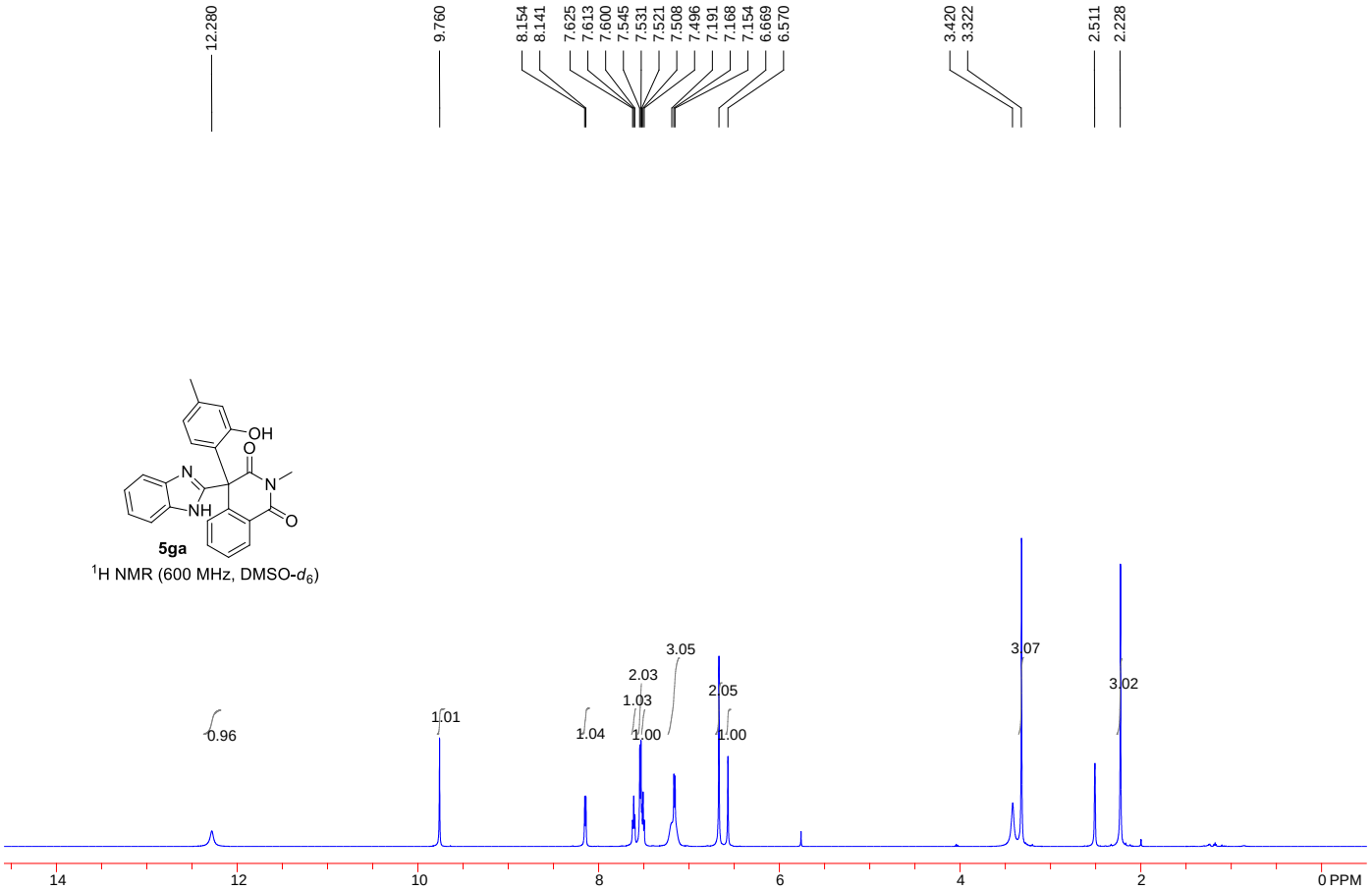


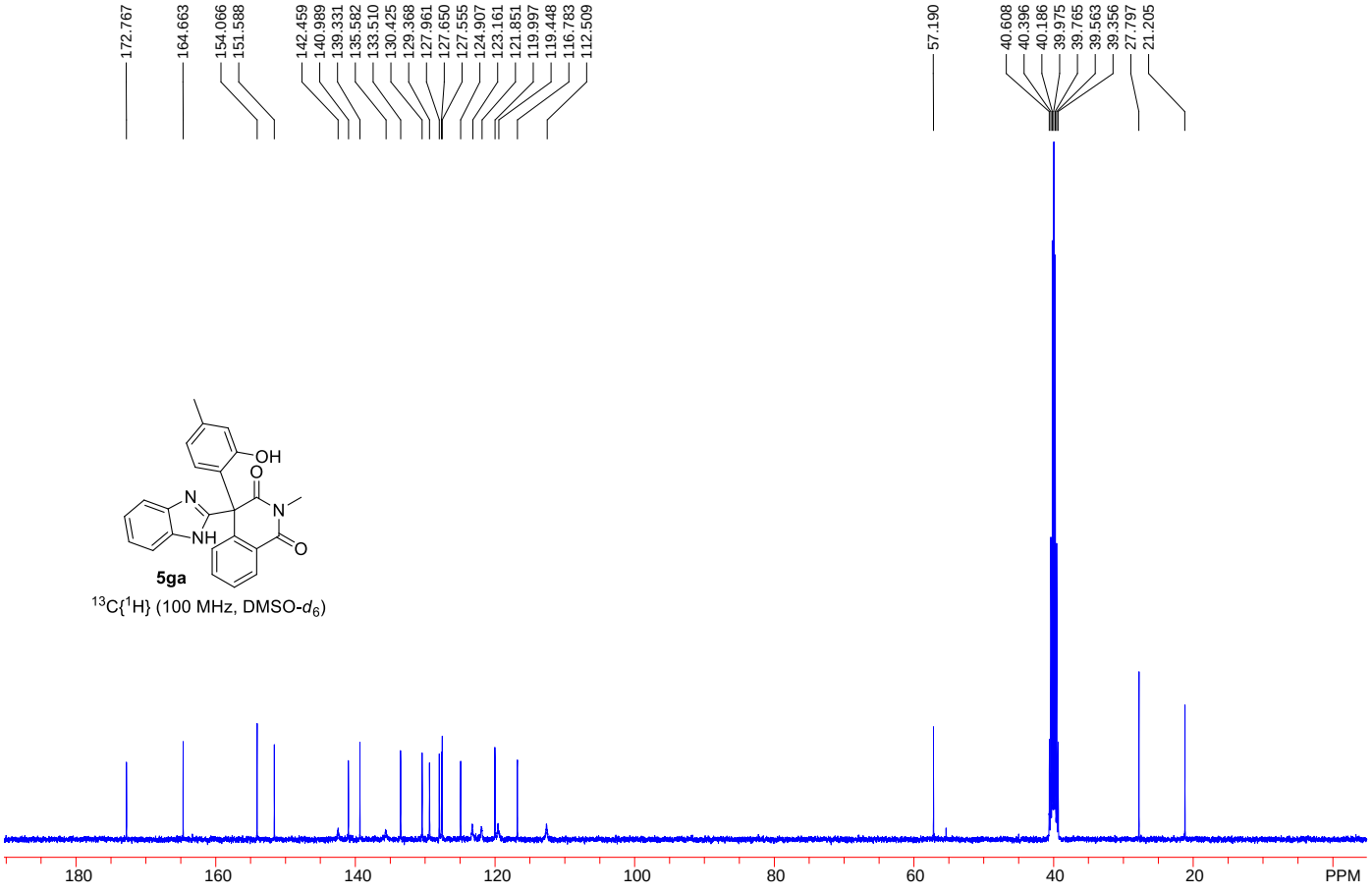


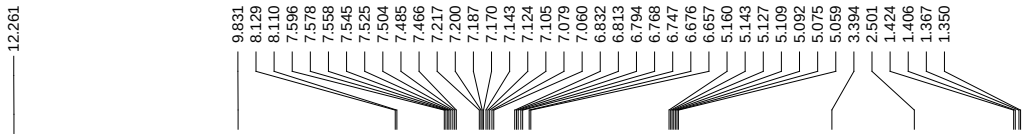
5fa

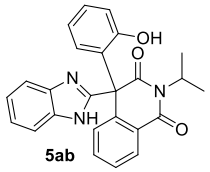
^{13}C{^{1}H} (100 MHz, DMSO-d_6)




12.280
9.760
8.154
8.141
7.625
7.613
7.600
7.545
7.531
7.521
7.508
7.496
7.191
7.168
7.154
6.669
6.570
3.420
3.322
2.511
2.228
OH
O
N
NH
N
O
5ga
1H NMR (600 MHz, DMSO-d6)
0.96
1.01
1.04
2.03
1.03
1.00
3.05
2.05
1.00
3.07
3.02
14
12
10
8
6
4
2
0 PPM

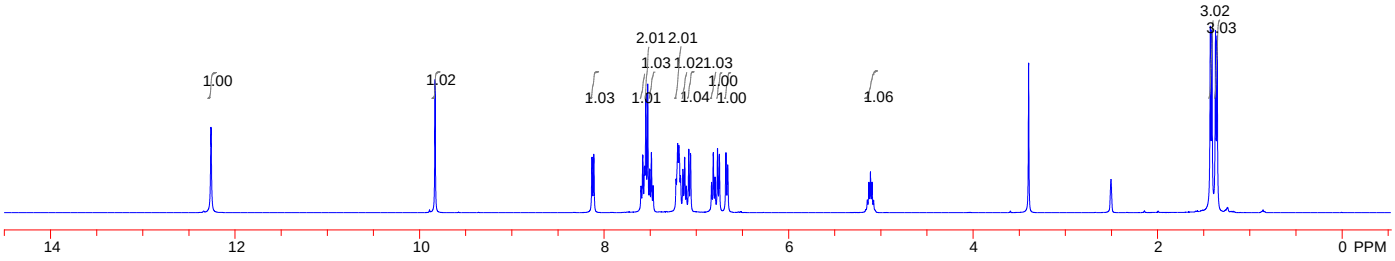

172.767
164.663
154.066
151.588
142.459
140.989
139.331
135.582
133.510
130.425
129.368
127.961
127.650
127.555
124.907
123.161
121.851
119.997
119.448
116.783
112.509
57.190
40.608
40.396
40.186
39.975
39.765
39.563
39.356
27.797
21.205
OH
O
N
NH
N
O
5ga
13C{1H} (100 MHz, DMSO-d6)
180
160
140
120
100
80
60
40
20
PPM

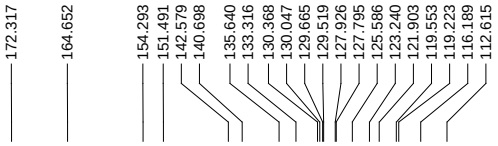


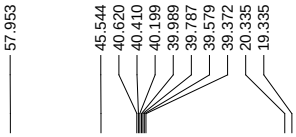


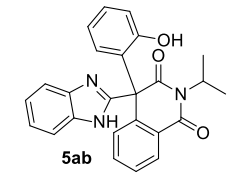
5ab

^{1}H NMR (400 MHz, DMSO-d_6)



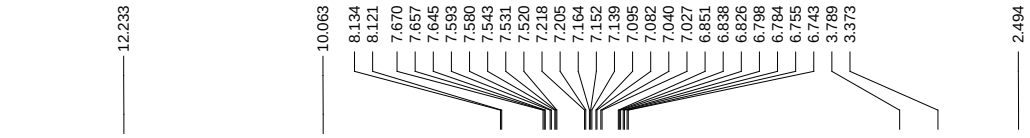


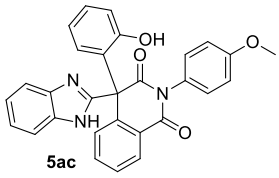




5ab

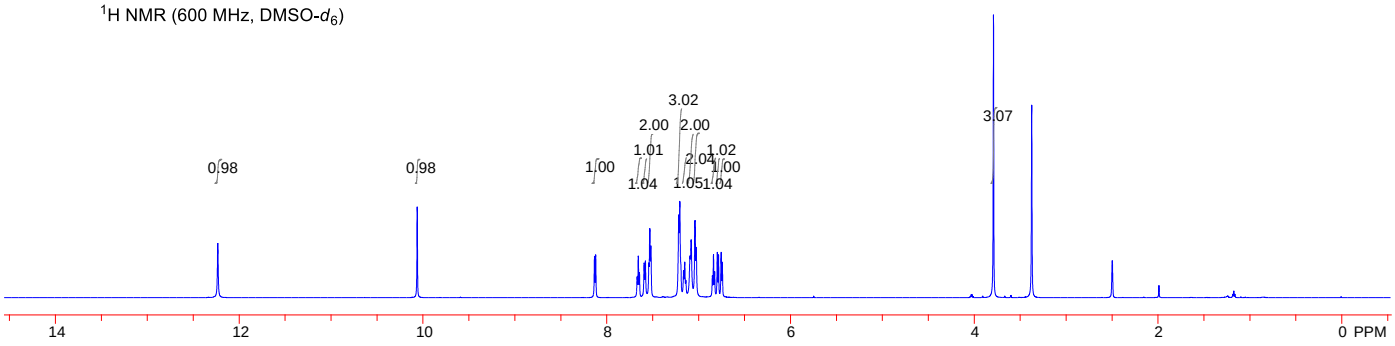
^{13}C{^{1}H} (100 MHz, DMSO-d_6)

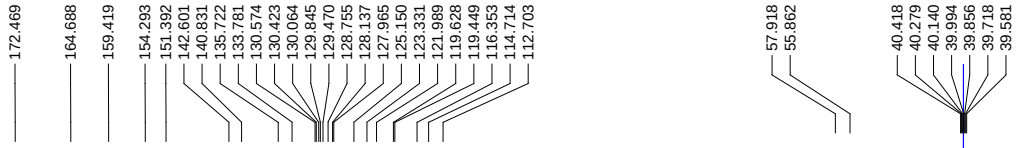


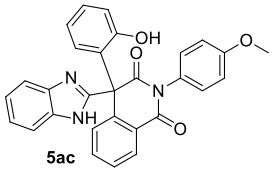


5ac

^{1}H NMR (600 MHz, DMSO-d_6)

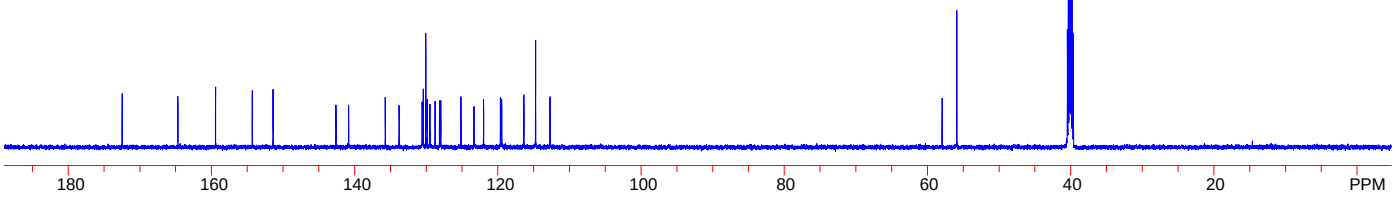




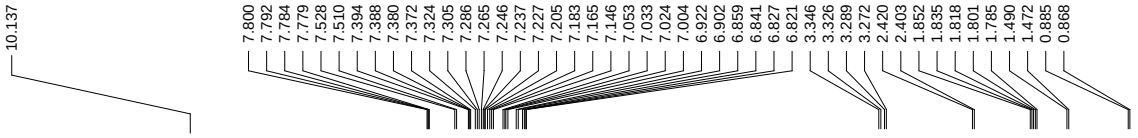


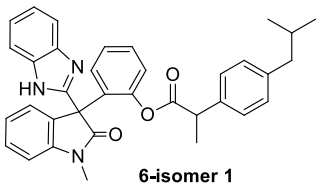
5ac

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



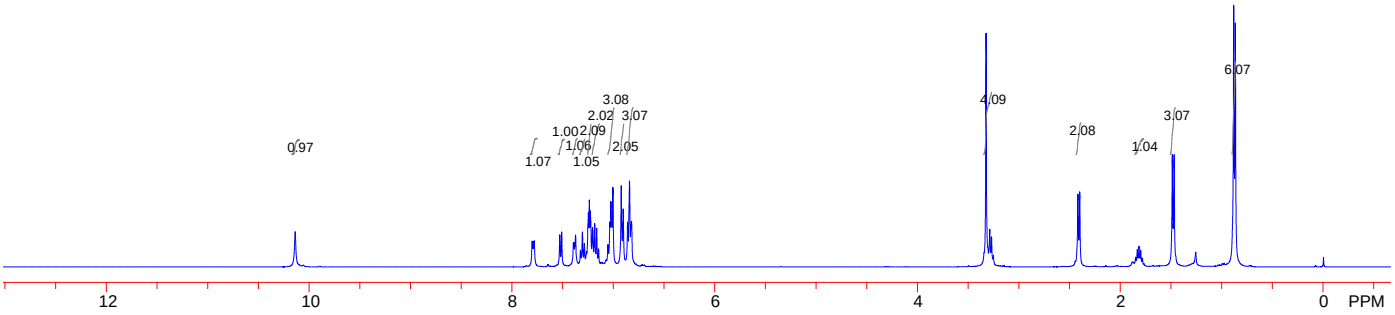
VI. NMR spectra of 6 and 7

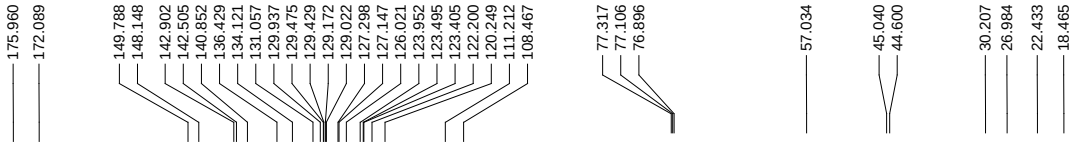


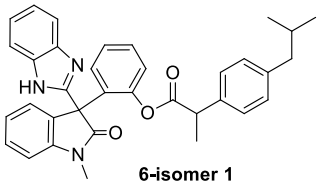


6-isomer 1

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

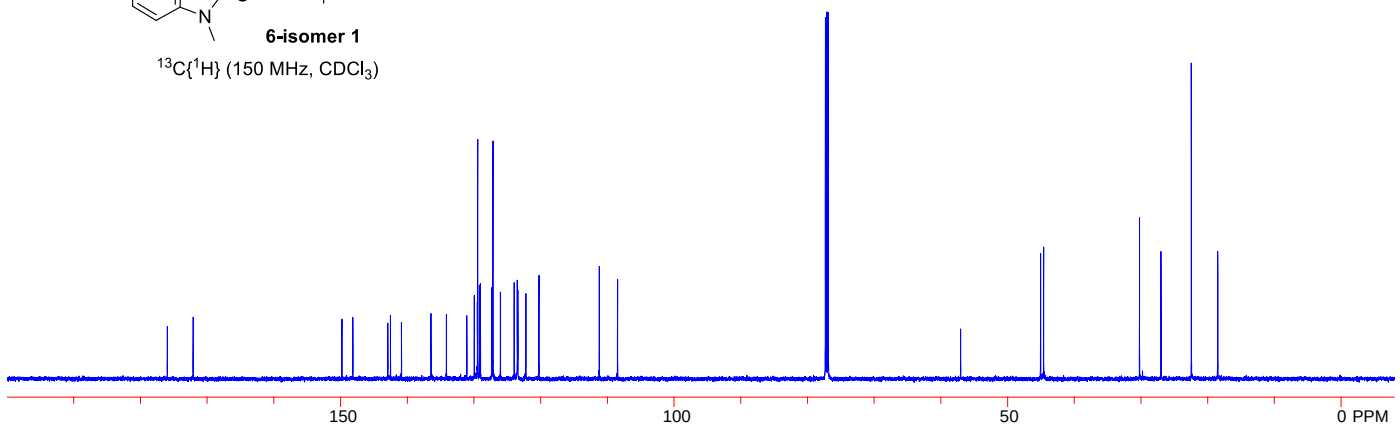


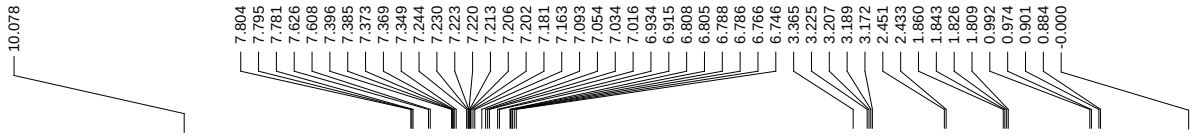


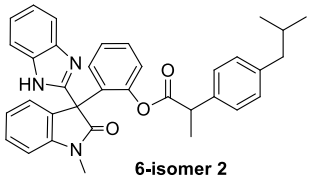


6-isomer 1

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

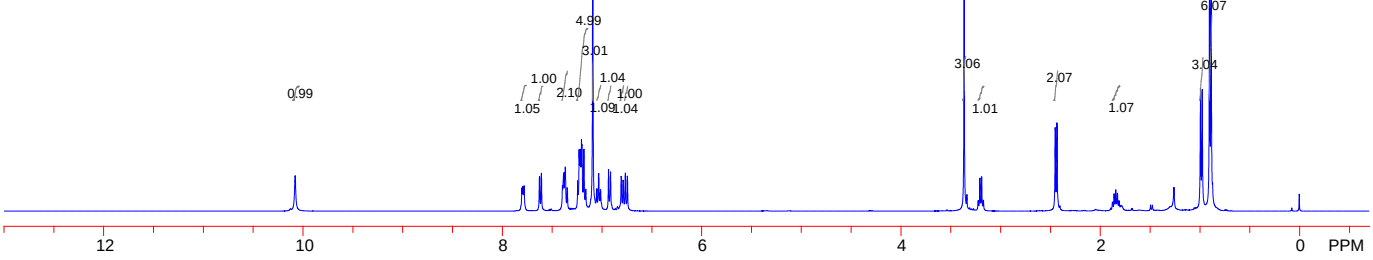


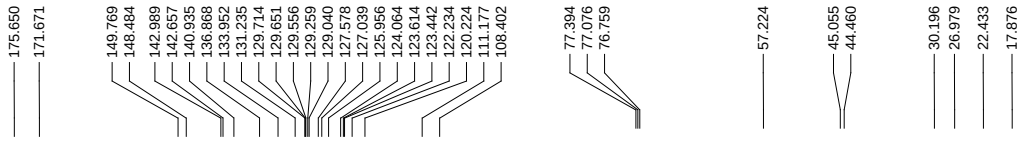


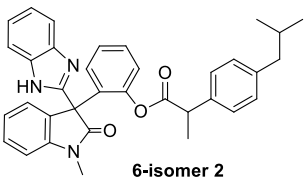


6-isomer 2

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

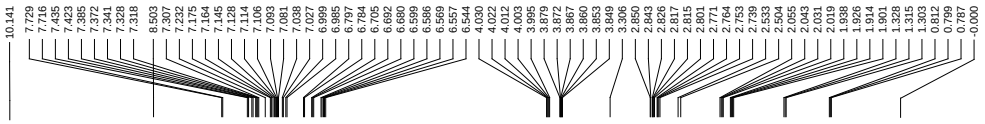


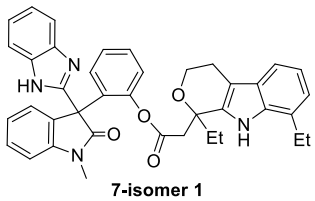




6-isomer 2

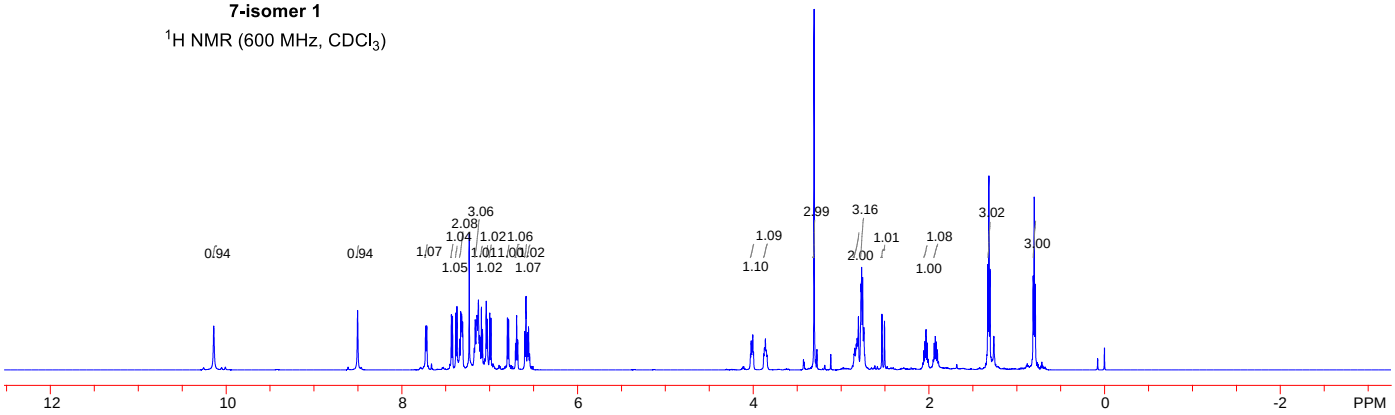
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

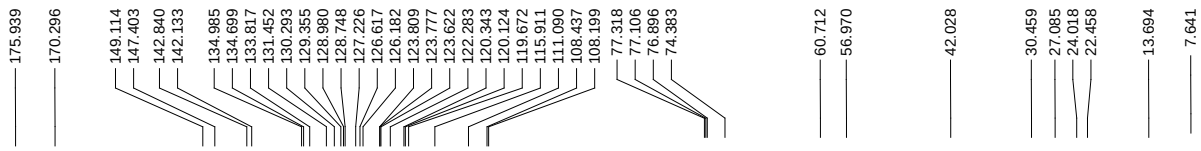


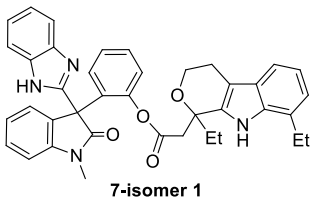


7-isomer 1

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

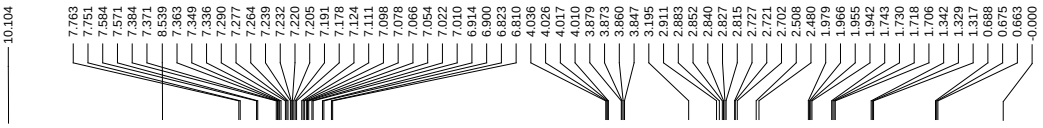


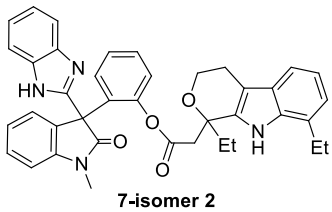




7-isomer 1

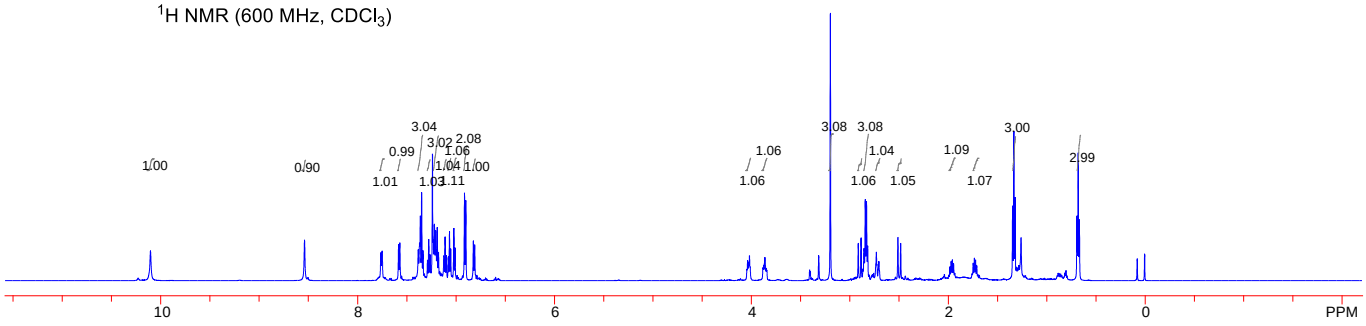
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

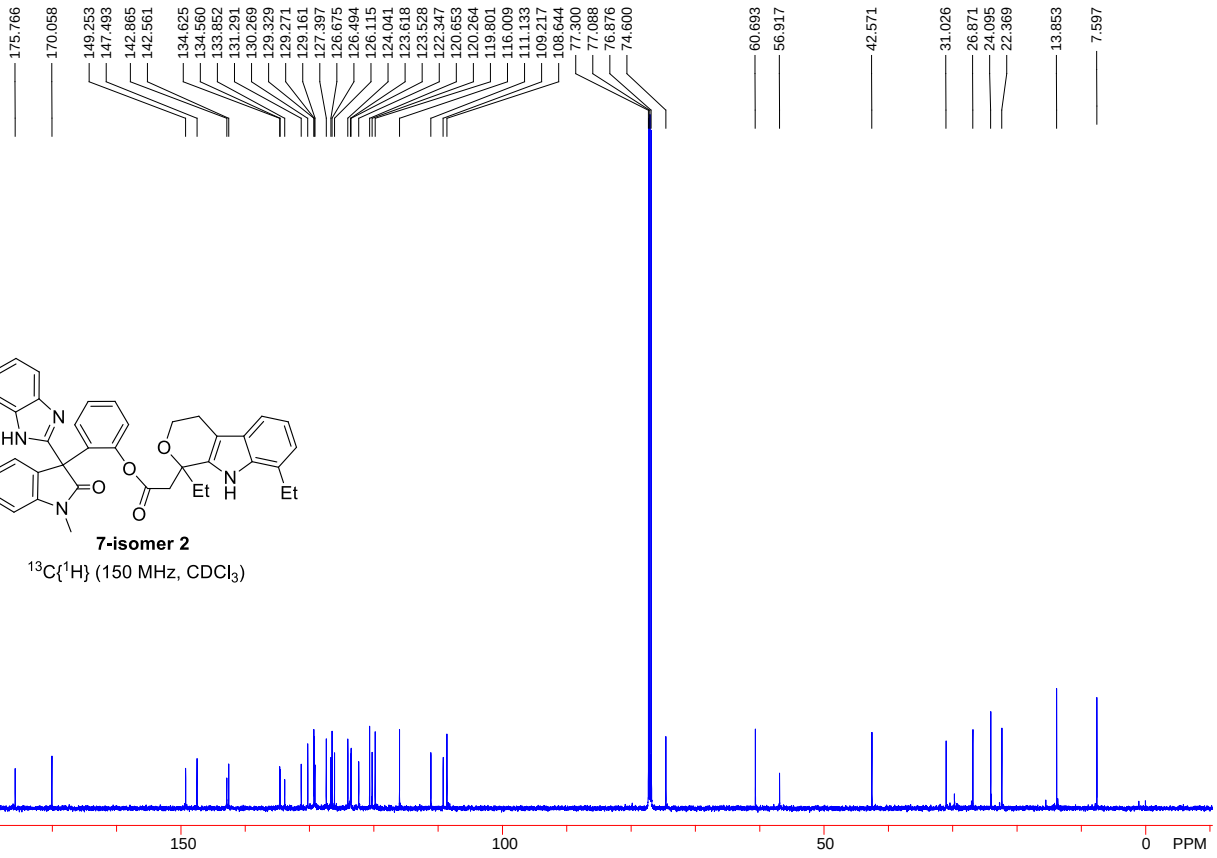




7-isomer 2

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





7-isomer 2

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

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

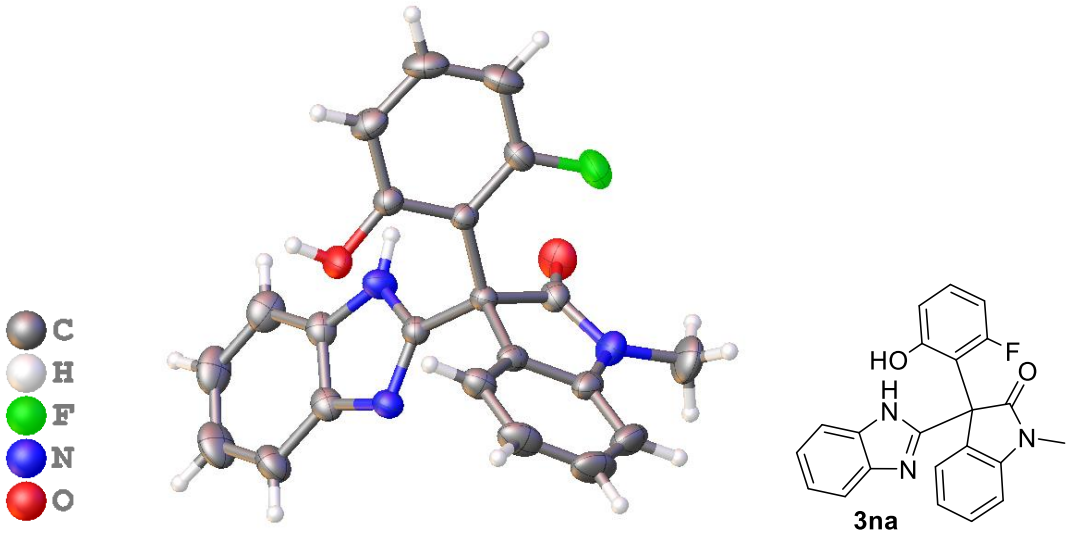


Figure S1. X-ray crystal structure of **3na** with 50% ellipsoid probability

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

Empirical formula	2 ($C_{22}H_{16}FN_3O_2$)
Formula weight	746.75
Temp, K	293.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a, Å	18.2786(2)
b, Å	11.9317(2)
c, Å	16.8004(2)
α (°)	90

β (°)	90
γ (°)	90
Volume, Å^3	3664.08(9)
Z	4
ρ_{calc}, g cm^{-3}	1.354
λ, Å	1.54184
μ, mm^{-1}	0.789
No. of data collected	13760
No. of unique data	5541
R_{int}	0.0289
Goodness-of-fit on F^2	1.048
R_1, wR_2 (I> 2σ(I))	0.0475, 0.1290
R_1, wR_2 (all data)	0.0494, 0.1316

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

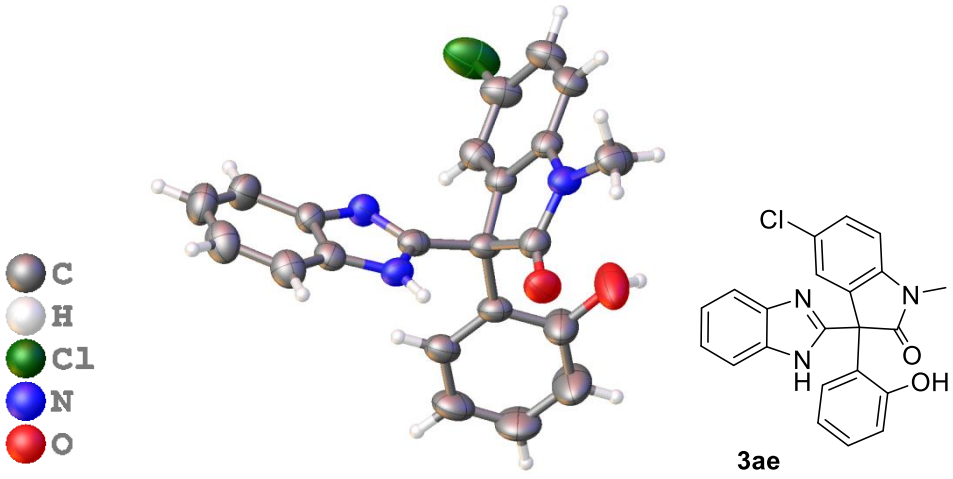


Figure S2. X-ray crystal structure of **3ae** with 50% ellipsoid probability

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

Table S2. Crystallographic data and structure refinement results of **3ae**

Empirical formula	$C_{22}H_{16}ClN_3O_2$
Formula weight	389.83
Temp, K	293(2)
Crystal system	triclinic
Space group	P-1
a, Å	10.0502(4)
b, Å	11.7456(4)
c, Å	13.2442(5)
α (°)	109.804(4)

β (°)	100.969(3)
γ (°)	104.033(3)
Volume, Å^3	1362.01(10)
Z	2
ρ_{calc}, g cm^{-3}	0.951
λ, Å	1.54184
μ, mm^{-1}	1.374
No. of data collected	10916
No. of unique data	5159
R_{int}	0.0298
Goodness-of-fit on F^2	1.058
R_1, wR_2 (I> 2σ(I))	0.0822, 0.2271
R_1, wR_2 (all data)	0.0922, 0.2353

IX. References

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