Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Directing Group Assisted ZnI_2-Catalyzed Cyclopropanation of Indoles *via* 2-Furylcarbenoids

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General information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and the compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on 400 MHz or 100 MHz spectrometers, the spectra were recorded in $CDCl_3$ as the solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to either the residual solvent peak or TMS as an internal standard. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded on FT-IR instrument and are reported in wave numbers (cm^{-1}). HRMS were performed on FT-ICRMS mass instrument (ESI). Substrates **1a**-**1r** and **2a**-**2k** were prepared according to the literature procedures.[1, 2, 3]

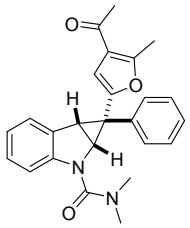
General procedure for the reaction of indoles and ene-yne-ketones

Indoles **1** (0.20 mmol, 1.0 equiv), ene-yne-ketones **2** (0.22 mmol, 1.1 equiv), ZnI_2 (0.02 mmol, 10 mol %) and freshly distilled DCE (2 mL) were added to an oven-dried tube equipped with a stir bar. The reaction vessel was placed in an oil bath preheated to 30 °C. Upon completion of the reaction monitored by TLC analysis, the reaction was cooled to ambient temperature. The reaction mixture was then concentrated and purified by flash chromatography (EA/PE = 1/5) to yield the desired products. The procedure for the gram scale reaction of **1j** was the same with this.

Procedure for the synthesis of Product 4aa

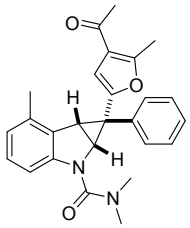
3aa (0.20 mmol), K^{t}OBu (224.4 mg, 10 equiv) and 2 mL MeOH were added to an oven-dried 10 mL pressure tube equipped with a stir bar. After stirring at 100 °C for 24 h, the reaction was cooled to ambient temperature. Then, the reaction mixture was quenched by water and extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography (EA/PE = 1/6).

1-(4-acetyl-5-methylfuran-2-yl)-N,N-dimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3aa).



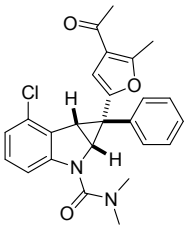
The title compound was prepared via the general procedure and purified by silica gel column chromatography (PE/EA = 5:1). An amorphous solid; yield 99% (79.2 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.27−7.20 (m, 1H), 7.18−7.07 (m, 4H), 6.94 (dt, *J* = 7.2, 1.2 Hz, 1H), 5.87 (s, 1H), 4.59 (d, *J* = 6.8 Hz, 1H), 3.48 (d, *J* = 6.8 Hz, 1H), 3.05 (s, 6H), 2.37 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.1, 157.6, 147.6, 145.0, 141.4, 129.3, 128.7, 127.5, 126.8, 126.4, 124.8, 121.8, 121.4, 115.5, 111.7, 54.2, 38.2, 37.0, 28.9, 26.1, 14.3; IR (KBr): 3056, 2922, 1670, 1565, 1477, 1376, 1264, 754, 634 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{25}H_{25}N_2O_3]$: 401.1862, found for 401.1862.

1-(4-acetyl-5-methylfuran-2-yl)-N,N,6-trimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3ba).



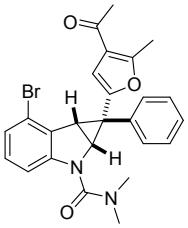
An amorphous solid; yield 99% (82.0 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.30 (m, 2H), 7.28−7.23 (m, 1H), 7.22−7.18 (m, 2H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.89 (s, 1H), 4.54 (d, *J* = 6.8 Hz, 1H), 3.45 (d, *J* = 6.8 Hz, 1H), 3.04 (s, 6H), 2.47 (s, 3H), 2.34 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.1, 157.7, 147.7, 144.5, 141.5, 134.4, 128.7, 128.4, 127.6, 126.8, 126.6, 122.6, 121.4, 112.7, 111.0, 54.0, 38.2, 35.2, 28.9, 26.1, 18.5, 14.2; IR (KBr): 3059, 2926, 1657, 1598, 1448, 1388, 1245, 777, 631 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{26}N_2O_3Na]$: 437.1836, found for 437.1833.

1-(4-acetyl-5-methylfuran-2-yl)-6-chloro-N,N-dimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3ca).



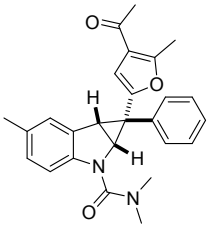
An amorphous solid; yield 86% (74.6 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.31 (m, 2H), 7.30−7.21 (m, 3H), 7.07−7.01 (m, 2H), 6.97−6.91 (m, 1H), 5.98 (s, 1H), 4.57 (d, *J* = 6.8 Hz, 1H), 3.63 (d, *J* = 6.8 Hz, 1H), 3.09 (s, 6H), 2.38 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.9, 158.7, 157.9, 147.5, 146.2, 140.7, 130.6, 128.8, 128.8, 128.2, 127.1, 126.9, 121.6, 121.5, 113.9, 111.2, 54.2, 38.2, 35.4, 28.9, 26.3, 14.3; IR (KBr): 3061, 2929, 1674, 1600, 1449, 1388, 1245, 778, 701 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{23}ClN_2O_3Na]$: 457.1289, found for 457.1292.

1-(4-acetyl-5-methylfuran-2-yl)-N,N,5-trimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3da).



An amorphous solid; yield 84% (80.3 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.31 (m, 2H), 7.30−7.23 (m, 3H), 7.13−7.06 (m, 2H), 6.97 (t, *J* = 8.0 Hz, 1H), 5.98 (s, 1H), 4.56 (d, *J* = 6.8 Hz, 1H), 3.59 (d, *J* = 6.8 Hz, 1H), 3.09 (s, 6H), 2.38 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.9, 158.7, 157.8, 147.5, 145.9, 140.7, 130.3, 128.9, 128.9, 127.2, 127.1, 124.6, 121.5, 119.3, 114.5, 111.2, 53.8, 38.2, 37.1, 28.9, 26.4, 14.3; IR (KBr): 3060, 2927, 1674, 1565, 1447, 1384, 1238, 762, 702 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{23}BrN_2O_3Na]$: 501.0784, found for 501.0791.

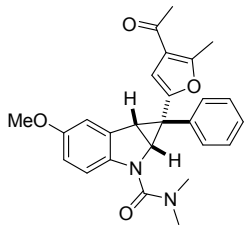
1-(4-acetyl-5-methylfuran-2-yl)-6-bromo-N,N-dimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3ea).



An amorphous solid; yield 99% (82.0 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.28 (m, 2H), 7.27−7.20 (m, 2H), 7.18−7.12 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H),

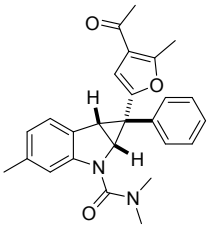
6.92 (d, J = 8.4 Hz, 1H), 5.90 (s, 1H), 4.56 (d, J = 6.4 Hz, 1H), 3.43 (d, J = 6.4 Hz, 1H), 3.04 (s, 6H), 2.37 (s, 3H), 2.31 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.0, 159.2, 157.6, 147.7, 142.7, 141.5, 131.3, 129.4, 128.7, 128.1, 126.7, 126.4, 125.3, 121.4, 115.2, 111.6, 54.2, 38.2, 36.8, 28.9, 26.4, 20.9, 14.3; IR (KBr): 3059, 2925, 1672, 1448, 1389, 1231, 1075, 758, 701 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{26}N_2O_3Na]$: 437.1836, found for 437.1836.

1-(4-acetyl-5-methylfuran-2-yl)-5-methoxy-N,N-dimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3fa).



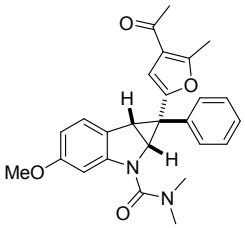
An amorphous solid; yield 99% (85.1 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.28 (m, 2H), 7.26−7.20 (m, 1H), 7.17−7.08 (m, 3H), 7.00 (d, J = 2.8 Hz, 1H), 6.69 (dd, J = 8.8, 2.8 Hz, 1H), 5.95 (s, 1H), 4.56 (d, J = 6.8 Hz, 1H), 3.77 (s, 3H), 3.45 (d, J = 6.8 Hz, 1H), 3.06 (s, 6H), 2.38 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.9, 159.4, 157.6, 155.3, 147.6, 141.4, 138.8, 130.4, 128.7, 126.8, 126.3, 121.5, 116.3, 113.0, 111.4, 110.7, 55.9, 54.6, 38.2, 37.0, 28.9, 26.7, 14.3; IR (KBr): 3058, 2926, 1664, 1565, 1485, 1379, 1234, 756, 701 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{26}N_2O_4Na]$: 453.1785, found for 453.1786.

1-(4-acetyl-5-methylfuran-2-yl)-N,N,4-trimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3ga).



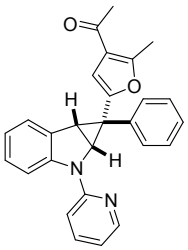
An amorphous solid; yield 99% (82.0 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.36−7.30 (m, 2H), 7.29−7.20 (m, 2H), 7.13 (d, J = 7.2 Hz, 2 H), 7.00 (s, 1H), 6.76 (d, J = 7.6 Hz, 1H), 5.86 (s, 1H), 4.56 (d, J = 6.4 Hz, 1H), 3.43 (d, J = 6.4 Hz, 1H), 3.05 (s, 6H), 2.38 (s, 3H), 2.27 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.1, 159.2, 157.6, 147.7, 145.3, 141.6, 137.4, 128.7, 126.7, 126.5, 126.3, 124.3, 122.7, 121.5, 116.2, 111.7, 54.5, 38.2, 36.8, 28.9, 26.3, 21.7, 14.3; IR (KBr): 2955, 2923, 1672, 1545, 1460, 1378, 1262, 741, 700 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{26}N_2O_3Na]$: 437.1836, found for 437.1836.

1-(4-acetyl-5-methylfuran-2-yl)-4-methoxy-N,N-dimethyl-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxamide (cis-3ha).



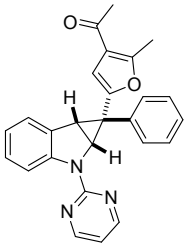
An amorphous solid; yield 98% (85.1 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.30 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.26−7.24 (m, 1H), 7.15−7.10 (m, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.92 (s, 1H), 4.57 (d, *J* = 6.8 Hz, 1H), 3.73 (s, 3H), 3.42 (d, *J* = 6.8 Hz, 1H), 3.06 (s, 6H), 2.39 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.0, 159.7, 159.0, 157.6, 147.8, 146.4, 141.5, 128.7, 126.6, 126.3, 124.9, 121.7, 121.5, 111.7, 108.4, 101.4, 55.5, 54.8, 38.2, 36.5, 28.9, 26.3, 14.3; IR (KBr): 3059, 2926, 1661, 1600, 1494, 1376, 1221, 767, 700 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{26}N_2O_4Na]$: 453.1785, found for 453.1785.

1-(2-methyl-5-(1-phenyl-2-(pyridin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3ia).



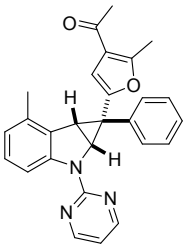
An amorphous solid; yield 90% (74.7 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39−8.31 (m, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.68−7.59 (m, 1H), 7.47−7.39 (m, 1H), 7.38−7.30 (m, 2H), 7.28−7.22 (m, 1H), 7.17−7.08 (m, 4H), 6.92−6.82 (m, 2H), 5.78 (s, 1H), 4.56 (d, *J* = 6.8 Hz, 1H), 3.56 (d, *J* = 6.8 Hz, 1H), 2.16 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 157.8, 155.0, 148.0, 147.2, 145.2, 142.1, 137.4, 129.5, 128.7, 127.8, 126.5, 126.0, 124.9, 121.2, 120.5, 115.8, 113.9, 111.6, 110.3, 52.8, 37.1, 28.8, 25.6, 14.0; IR (KBr): 3056, 2920, 1676, 1590, 1483, 1437, 1231, 752, 698 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{23}N_2O_2]$: 407.1754, found for 407.1756.

1-(2-methyl-5-(1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3ja).



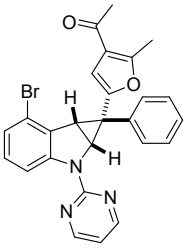
An amorphous solid; yield 99% (80.6 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.38−7.32 (m, 2H), 7.30−7.26 (m, 2H), 7.25−7.22 (m, 1H), 7.17−7.13 (m, 1H), 6.95 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.81 (t, *J* = 4.8 Hz, 1H), 5.75 (s, 1H), 5.22 (d, *J* = 6.4 Hz, 1H), 3.53 (d, *J* = 6.4 Hz, 1H), 2.16 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.8, 157.7, 157.6, 147.8, 143.7, 142.0, 130.6, 128.6, 127.5, 126.7, 126.6, 124.8, 121.5, 121.2, 115.6, 112.6, 111.1, 51.9, 35.9, 28.8, 27.2, 14.0; IR (KBr): 2918, 2850, 1580, 1484, 1441, 1232, 1132, 752, 636 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{22}N_3O_2]$: 408.1707, found for: 408.1708.

1-(2-methyl-5-(6-methyl-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3ka).



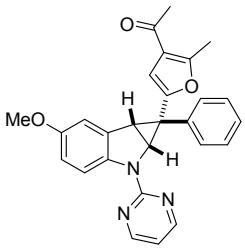
An amorphous solid; yield 99% (83.3 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.8 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.39−7.33 (m, 2H), 7.32−7.21 (m, 3H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.82−6.75 (m, 2H), 5.71 (s, 1H), 5.14 (d, *J* = 6.8 Hz, 1H), 3.45 (d, *J* = 6.8 Hz, 1H), 2.50 (s, 3H), 2.16 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.8, 157.7, 157.6, 148.0, 143.6, 142.1, 134.3, 129.5, 128.7, 127.7, 126.9, 126.6, 122.5, 121.3, 113.1, 112.6, 110.6, 52.0, 34.3, 28.8, 27.2, 18.8, 14.0; IR (KBr): 3036, 2998, 1713, 1579, 1468, 1423, 1221, 776, 629 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_2]$: 422.1863, found for: 422.1864.

1-(5-(6-bromo-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3la).



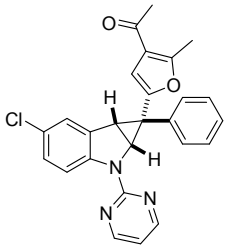
An amorphous solid; yield 84% (81.5 mg); dr =12:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 4.8 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.44−7.30 (m, 4H), 7.29−7.23 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 5.81 (s, 1H), 5.17 (d, *J* = 6.4 Hz, 1H), 3.58 (d, *J* = 6.4 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.7, 157.8, 157.7, 147.8, 144.7, 141.1, 131.3, 129.0, 128.8, 127.5, 127.0, 124.2, 121.3, 119.3, 114.4, 113.1, 110.6, 51.2, 35.8, 28.8, 27.2, 14.1; IR (KBr): 3057, 2921, 1713, 1677, 1576, 1453, 1230, 798, 627 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{21}BrN_3O_2]$: 486.0812, found for: 486.0813.

1-(5-(5-methoxy-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3ma).



An amorphous solid; yield 86% (75.4 mg); dr =8:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.8 Hz, 2H), 7.88 (d, *J* = 2.4 Hz, 1H), 7.38−7.27 (m, 3H), 7.26−7.19 (m, 3H), 6.80 (t, *J* = 4.8 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.77 (s, 1H), 5.17 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.44 (d, *J* = 6.8 Hz, 1H), 2.18 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 159.7, 159.6, 157.8, 157.6, 148.0, 145.1, 142.1, 128.6, 126.7, 126.5, 124.7, 123.1, 121.3, 112.7, 111.1, 106.8, 102.6, 55.5, 52.6, 35.3, 28.8, 27.5, 14.1; IR (KBr): 3035, 2998, 1676, 1580, 1486, 1430, 1224, 736, 631 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_3]$: 438.1812, found for: 438.1814.

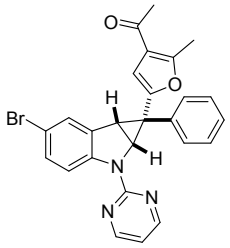
1-(5-(5-chloro-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3na).



An amorphous solid; yield 96% (84.7 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 4.8 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.38−7.30 (m, 2H), 7.29−7.20 (m, 3H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 5.80 (s, 1H), 5.20 (d, *J* = 6.8 Hz, 1H), 3.76 (d, *J* = 6.4 Hz, 1H), 2.18 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.5, 157.9, 157.7, 147.5, 142.3, 141.4, 132.3, 128.7, 127.4, 126.8, 126.7, 126.3, 124.8, 121.3, 116.5, 113.0, 111.1, 52.1, 35.3,

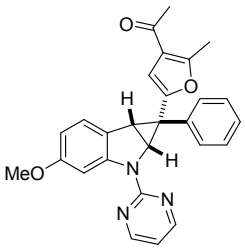
28.9, 27.2, 14.0; IR (KBr): 3054, 2919, 1676, 1578, 1478, 1422, 1231, 737, 634 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{21}ClN_3O_2]$: 442.1317, found for: 442.1319.

1-(5-(5-bromo-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3oa).



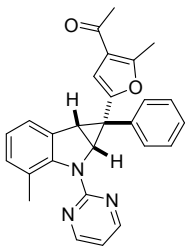
An amorphous solid; yield 97% (94.1 mg); dr > 20:1; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.38−7.30 (m, 2H), 7.28−7.20 (m, 4H), 6.82 (t, *J* = 4.8 Hz, 1H), 5.79 (s, 1H), 5.18 (d, *J* = 6.8 Hz, 1H), 3.47 (d, *J* = 6.4 Hz, 1H), 2.18 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.5, 157.9, 157.7, 147.5, 142.3, 141.4, 132.8, 130.3, 128.7, 127.7, 126.8, 121.3, 117.0, 113.6, 113.0, 111.1, 52.0, 35.2, 28.9, 27.2, 14.0; IR (KBr): 3055, 3000, 1714, 1579, 1477, 1362, 1222, 737, 630 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{21}BrN_3O_2]$: 486.0812, found for: 486.0811.

1-(5-(4-methoxy-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethan-1-one (cis-3pa).



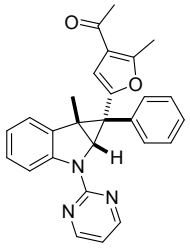
An amorphous solid; yield 78% (68.2 mg); dr =5:1; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.8 Hz, 2H), 7.88 (d, *J* = 2.4 Hz, 1H), 7.38−7.27 (m, 3H), 7.26−7.21 (m, 3H), 6.80 (t, *J* = 4.8 Hz, 1H), 6.49 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.77 (s, 1H), 5.17 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.44 (d, *J* = 6.8 Hz, 1H), 2.18 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 159.7, 159.6, 157.8, 157.6, 148.0, 145.1, 142.1, 128.6, 126.7, 126.5, 124.9, 123.1, 121.3, 112.7, 111.1, 106.8, 102.6, 55.5, 52.6, 35.3, 28.9, 27.5, 14.1; IR (KBr): 3036, 2957, 1659, 1578, 1490, 1439, 1220, 798, 699 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_3]$: 438.1812, found for: 438.1814.

1-(2-methyl-5-(3-methyl-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3qa).



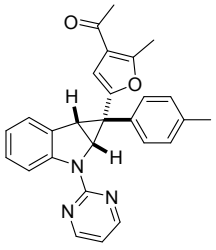
An amorphous solid; yield 99% (83.3 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 2H), 7.37−7.27 (m, 3H), 7.26−7.18 (m, 3H), 6.93 (d, *J* = 4.4 Hz, 2H), 6.83 (t, *J* = 4.8 Hz, 1H), 6.07 (s, 1H), 5.16 (d, *J* = 6.4 Hz, 1H), 3.51 (d, *J* = 6.4 Hz, 1H), 2.21, (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 161.0, 157.7, 157.6, 147.6, 142.0, 141.9, 131.6, 130.0, 128.6, 127.0, 126.7, 126.6, 123.2, 122.4, 121.1, 113.9, 111.6, 54.3, 36.2, 29.0, 27.6, 21.4, 14.1; IR (KBr): 3034, 2959, 1675, 1576, 1421, 1372, 1231, 749, 634 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_2]$: 422.1863, found for 422.1867.

1-(2-methyl-5-(6b-methyl-1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3ra).



An amorphous solid; yield 98% (82.5 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 4.8 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.64−7.62 (m, 2H), 7.46−7.31 (m, 3H), 7.29−7.22 (m, 1H), 7.17−7.09 (m, 1H), 6.98 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.78 (t, *J* = 4.8 Hz, 1H), 5.57 (s, 1H), 5.19 (s, 1H), 2.09, (s, 3H), 1.96 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 160.0, 157.7, 157.1, 150.1, 143.4, 138.6, 135.2, 129.9, 128.7, 127.5, 127.1, 123.2, 121.4, 121.1, 115.4, 112.9, 109.5, 53.7, 36.7, 31.9, 28.8, 15.4, 14.0; IR (KBr): 3050, 2960, 1674, 1575, 1421, 1372, 1231, 737, 634 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_2]$: 422.1863, found for 422.1867.

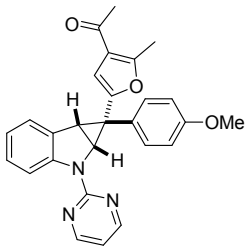
1-(2-methyl-5-(2-(pyrimidin-2-yl)-1-(p-tolyl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3jb).



An amorphous solid; yield 99% (83.3 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ

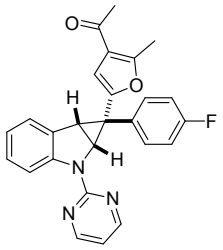
8.54 (d, J = 4.8 Hz, 2H), 8.16 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.21−7.10 (m, 5H), 6.93 (dt, J = 7.6, 0.8 Hz, 1H), 6.78 (t, J = 4.8 Hz, 1H), 5.72 (s, 1H), 5.16 (d, J = 6.4 Hz, 1H), 3.48 (d, J = 6.8 Hz, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 159.8, 157.7, 157.6, 148.1, 143.8, 138.9, 136.3, 130.6, 129.4, 127.5, 126.8, 124.8, 121.5, 121.2, 115.6, 112.6, 110.9, 51.8, 35.6, 28.8, 26.9, 21.1, 14.1; IR (KBr): 3048, 2926, 1676, 1579, 1484, 1443, 1231, 751, 637 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_2]$: 422.1863, found for 422.1865.

1-(5-(1-(4-methoxyphenyl)-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3jc).



An amorphous solid; yield 85% (74.3 mg); dr = 6:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 4.8 Hz, 2H), 8.16 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.31−7.25 (m, 2H), 7.17−7.10 (m, 1H), 6.97−6.86 (m, 3H), 6.79 (t, J = 4.8 Hz, 1H), 5.71 (s, 1H), 5.14 (d, J = 6.8 Hz, 1H), 3.79 (s, 3H), 3.47 (d, J = 6.8 Hz, 1H), 2.15 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.9, 158.5, 157.6, 157.5, 148.4, 143.8, 133.8, 130.6, 128.4, 127.5, 124.8, 121.5, 121.2, 115.6, 114.1, 112.6, 110.5, 55.4, 51.5, 35.1, 28.8, 26.8, 14.1; IR (KBr): 3048, 2836, 1675, 1580, 1484, 1443, 1250, 752, 637 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_3]$: 438.1812, found for 438.1813.

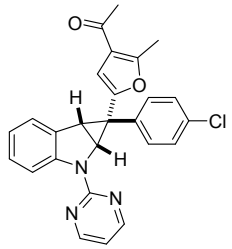
1-(5-(1-(4-fluorophenyl)-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3jd).



An amorphous solid; yield 96% (81.6 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 4.8 Hz, 2H), 8.17 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.32−7.26 (m, 2H), 7.18−7.12 (m, 1H), 7.07−7.00 (m, 2H), 6.95 (dt, J = 7.2, 0.8 Hz, 1H), 6.81 (t, J = 4.8 Hz), 5.72 (s, 1H), 5.14 (d, J = 6.8 Hz, 1H), 3.47 (d, J = 6.8 Hz, 1H), 2.16 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 161.6 ($J_{C\text{-}F}$ = 244 Hz), 159.8, 157.8, 157.7, 147.8, 143.7, 137.5, 137.5, 130.3, 128.8 ($J_{C\text{-}F}$ = 8 Hz), 127.6, 124.9,

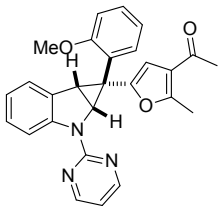
121.6, 121.2, 115.6, 115.4, 112.7, 110.8, 51.7, 35.5, 28.8, 26.7, 14.0; IR (KBr): 3050, 2961, 1677, 1580, 1484, 1443, 1229, 753, 637 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{21}FN_3O_2]$: 426.1612, found for 426.1611.

1-(5-(1-(4-chlorophenyl)-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3je).



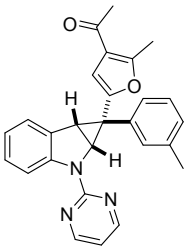
An amorphous solid; yield 93% (82.0 mg); dr > 20:1; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.32−7.26 (m, 2H), 7.21−7.11 (m, 3H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 4.8 Hz, 1H), 5.73 (s, 1H), 5.14 (d, *J* = 6.4 Hz, 1H), 3.47 (d, *J* = 6.4 Hz, 1H), 2.15 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.7, 157.8, 157.7, 147.4, 143.7, 140.5, 132.5, 130.2, 128.7, 128.2, 127.7, 124.9, 121.6, 121.3, 115.6, 112.8, 111.2, 51.9, 35.9, 28.8, 26.7, 14.0; IR (KBr): 3049, 2956, 1676, 1580, 1484, 1442, 1231, 751, 637 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{21}ClN_3O_2]$: 442.1317, found for 442.1318.

1-(5-(1-(2-methoxyphenyl)-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)-2-methylfuran-3-yl)ethanone (cis-3jf).



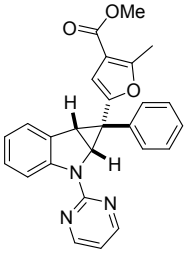
An amorphous solid; yield 69% (60.3 mg); dr = 2.5:1; ^1H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52−7.46 (m, 1H), 7.31−7.25 (m, 1H), 7.18−7.12 (m, 1H), 7.02 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.97 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.92-6.86 (m, 1H), 6.79 (t, *J* = 4.8 Hz, 1H), 5.68 (s, 1H), 5.22 (d, *J* = 6.8 Hz, 1H), 3.94 (s, 3H), 3.41 (d, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 160.2, 158.8, 157.5, 148.8, 144.0, 131.9, 130.9, 129.0, 128.4, 127.3, 124.8, 121.4, 121.3, 120.7, 115.5, 112.4, 111.2, 109.8, 55.6, 50.6, 33.3, 28.8, 24.9, 14.0; IR (KBr): 2932, 2836, 1674, 1580, 1485, 1443, 1251, 754, 633 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_3]$: 438.1812, found for 438.1811.

1-(2-methyl-5-(2-(pyrimidin-2-yl)-1-(m-tolyl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3jg).



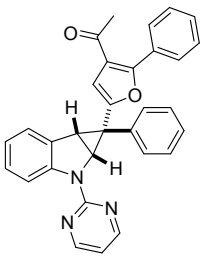
An amorphous solid; yield 96% (80.9 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.8 Hz, 1H), 7.25−7.18 (m, 1H), 7.16−7.10 (m, 1H), 7.08−7.00 (m, 3H), 6.92 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.76 (t, *J* = 4.8 Hz, 1H), 5.74 (s, 1H), 5.18 (d, *J* = 6.4 Hz, 1H), 3.48 (d, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 2.15 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.8, 157.7, 157.6, 148.0, 143.7, 141.9, 138.3, 130.7, 128.6, 127.5, 127.4, 127.3, 124.8, 123.8, 121.5, 121.3, 115.6, 112.6, 111.2, 51.9, 36.0, 28.8, 27.1, 21.6, 14.0; IR (KBr): 3038, 2919, 1675, 1579, 1485, 1443, 1229, 753, 638 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{27}H_{24}N_3O_2]$: 422.1863, found for 422.1865.

methyl-2-methyl-5-(1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-carboxylate (cis-3jh).



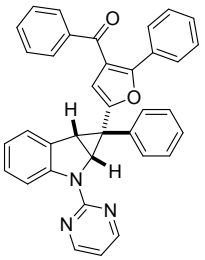
An amorphous solid; yield 99% (83.8 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35−7.29 (m, 2H), 7.26−7.19 (m, 3H), 7.17−7.10 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 4.8 Hz, 1H), 5.86 (s, 1H), 5.18 (d, *J* = 6.8 Hz, 1H), 3.61 (s, 3H), 3.51 (d, *J* = 6.8 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.8, 158.6, 157.6, 148.0, 143.7, 142.2, 130.5, 128.6, 127.5, 126.7, 126.5, 124.9, 121.6, 115.6, 113.2, 112.7, 111.2, 52.0, 51.0, 35.9, 27.1, 13.5; IR (KBr): 3004, 2254, 1713, 1580, 1443, 1228, 1047, 735, 630 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{26}H_{22}N_3O_3]$: 424.1656, found for 424.1657.

1-(2-phenyl-5-(1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)ethanone (cis-3ji).



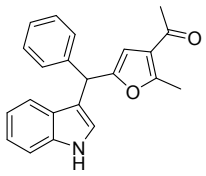
An amorphous solid; yield 49% (46.0 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.8 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.45−7.40 (m, 2H), 7.37−7.29 (m, 4H), 7.28−7.20 (m, 4H), 7.17-7.12 (m, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 4.8 Hz, 1H), 5.95 (s, 1H), 5.26 (d, *J* = 6.4 Hz, 1H), 3.59 (d, *J* = 6.4 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 159.7, 157.7, 155.5, 149.1, 143.6, 141.8, 130.6, 129.9, 129.2, 128.7, 128.2, 127.9, 127.7, 126.8, 126.7, 124.8, 122.1, 121.7, 115.8, 113.3, 112.8, 51.9, 51.0, 35.9, 29.6; IR (KBr): 2999, 2921, 1707, 1579, 1441, 1356, 1219, 754, 698 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{31}H_{24}N_3O_2]$: 470.1863, found for 470.1865.

phenyl(2-phenyl-5-(1-phenyl-2-(pyrimidin-2-yl)-1,1a,2,6b-tetrahydrocyclopropa[b]indol-1-yl)furan-3-yl)methanone (cis-3jj).



An amorphous solid; yield 90% (95.6 mg); dr > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.8 Hz, 2H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.41−7.20 (m, 12H), 7.19−7.12 (m, 3H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.76 (t, *J* = 4.8 Hz, 1H), 5.92 (s, 1H), 5.29 (d, *J* = 6.4 Hz, 1H), 3.61 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 159.7, 157.7, 155.0, 148.4, 143.7, 141.8, 138.0, 132.5, 131.0, 129.8, 128.7, 128.1, 128.0, 127.6, 127.2, 126.6, 126.5, 125.0, 121.7, 121.0, 115.6, 115.0, 112.8, 52.1, 36.2, 27.2; IR (KBr): 2918, 2284, 1648, 1578, 1482, 1441, 1232, 753, 693 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{36}H_{26}N_3O_2]$: 532.2020, found for 532.2016.

1-(5-((1H-indol-3-yl)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-on(4aa).

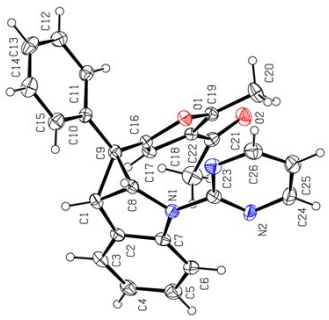


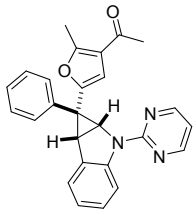
Yellow oil; yield 61% (40.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (br, 1H), 7.38-7.36 (m, 2H), 7.34−7.26 (m, 5H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 6.16 (s, 1H), 5.60 (s, 1H), 2.55 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 157.8, 154.9, 141.2, 136.5, 128.5, 128.4, 126.9, 126.6, 123.4, 122.3, 122.0, 119.6, 119.4, 116.8, 111.2, 108.0, 42.4, 29.2, 14.6; IR (KBr): 3414, 2252, 1669, 1564, 1455, 1228, 909, 732, 649 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd for $[C_{22}H_{20}NO_2]$: 330.1489, found for 330.1486.

Reference

1**.** S. Xu, X. Huang, X. Hong and B. Xu, *Org*. *Lett*., 2012, **14**, 4614.
2. D. J. Schipper, M. Hutchinson and K. Fagnou, *J*. *Am*. *Chem*. *Soc*., 2010, **132**, 6910.
3. Y. Xia, S.-L. Qu, Q. Xiao, Z.-X. Wang, P.-Y. Qu, L. Chen, Z. Liu, L.-M. Tian, Z.-X. Huang, Y. Zhang and J.-B. Wang, *J*. *Am*. *Chem*. *Soc*., 2013, **135**, 13502.

The X-Ray Crystallographic Data of *cis*-3ja

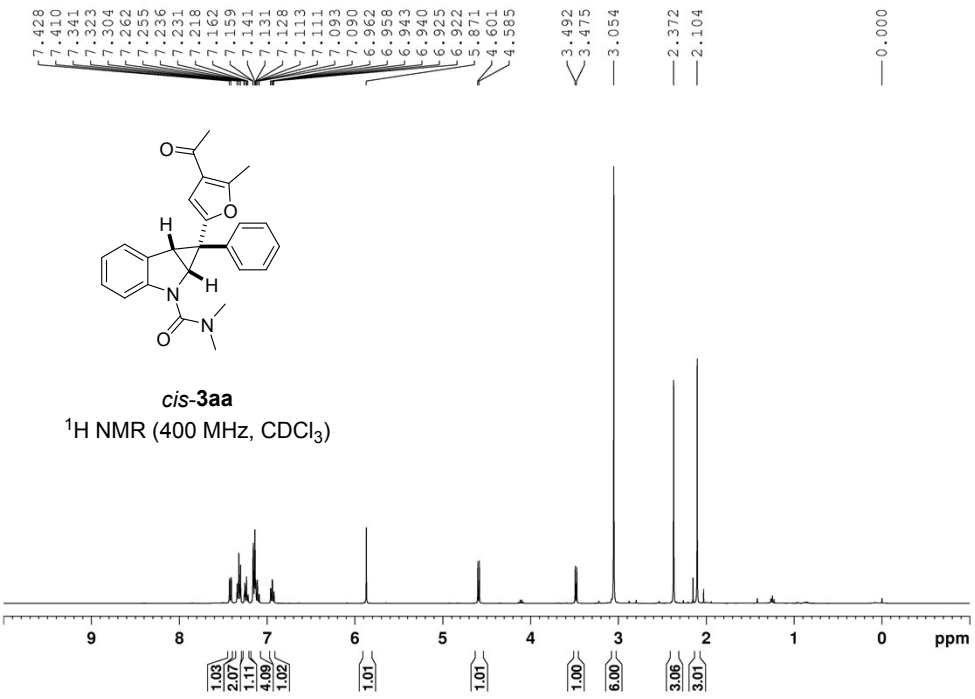




The crystal structure *cis-**3ja*** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1574775.

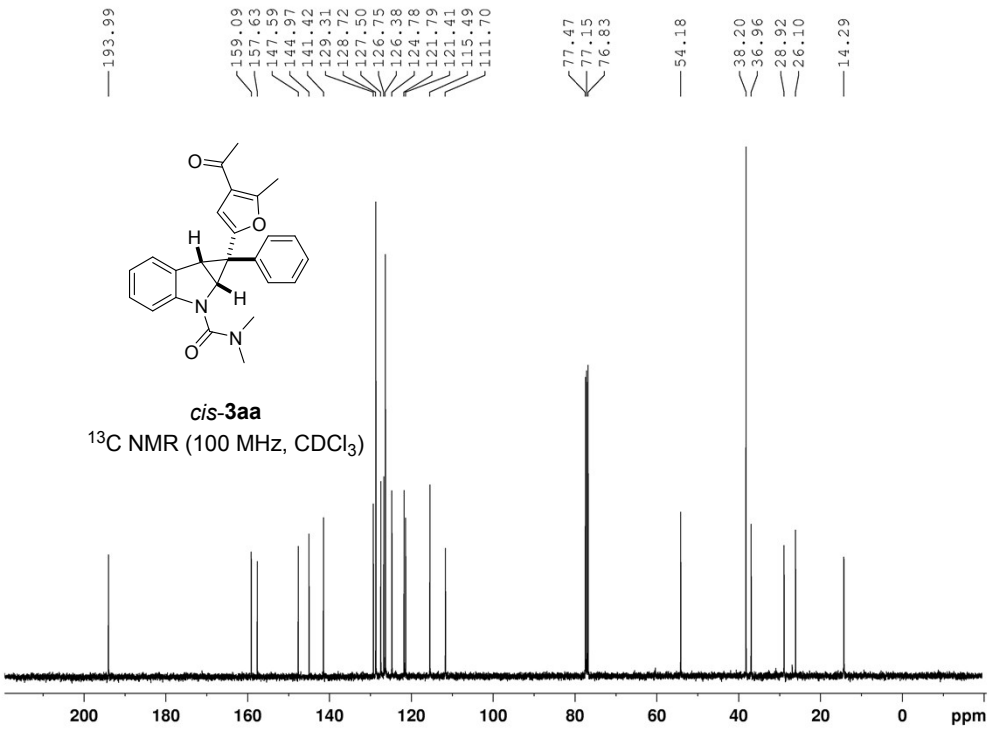
Bond precision:	C-C = 0.0051 A	Wavelength=0.71070	
Cell:	a=7.6842(9)	b=19.978(2)	c=13.7517(18)
	alpha=90	beta=98.473(12)	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	2088.1(4)	2088.0(4)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C26 H21 N3 O2	C26 H21 N3 O2	
Sum formula	C26 H21 N3 O2	C26 H21 N3 O2	
Mr	407.46	407.46	
Dx,g cm-3	1.296	1.296	
Z	4	4	
Mu (mm-1)	0.084	0.084	
F000	856.0	856.0	
F000’	856.34		
h,k,lmax	9, 24, 16	9, 24, 16	
Nref	4100	4101	
Tmin,Tmax	0.983,0.988	0.707,1.000	
Tmin’	0.983		
Correction method= # Reported T Limits: Tmin=0.707 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.998		Theta(max)= 26.020	
R(reflections)= 0.0669(1995)		wR2(reflections)= 0.1605(4101)	
S = 1.028		Npar= 308	
Displacement ellipsoids are drawn at 30% probability level			

Copies of ^{1}H and ^{13}C NMR



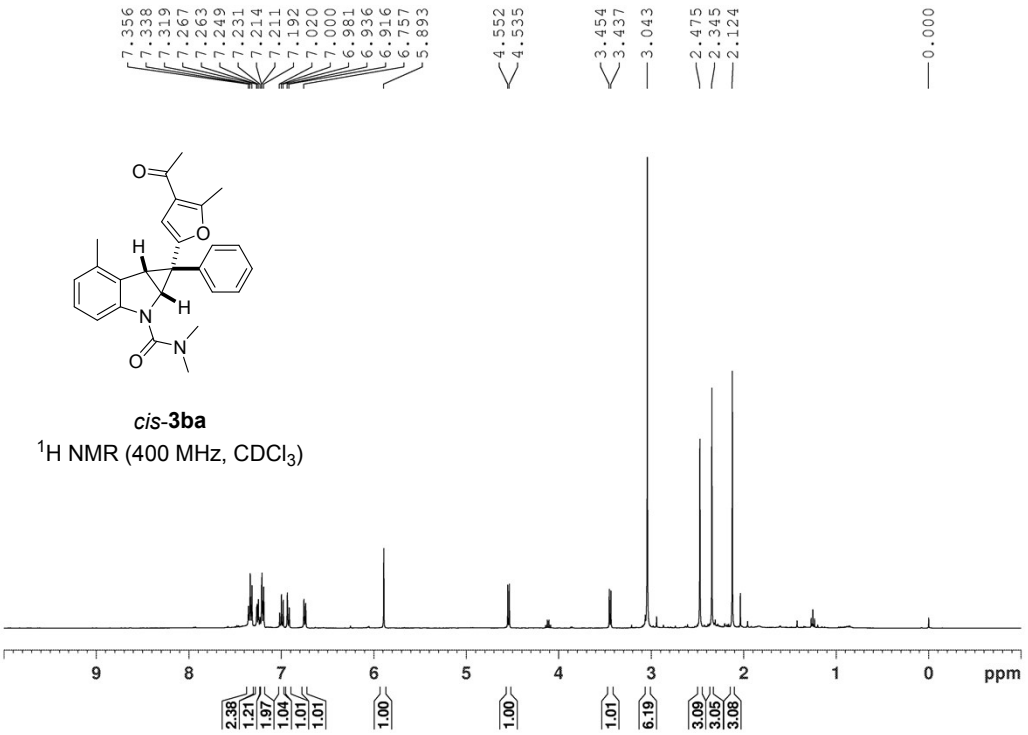
cis-**3aa**

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



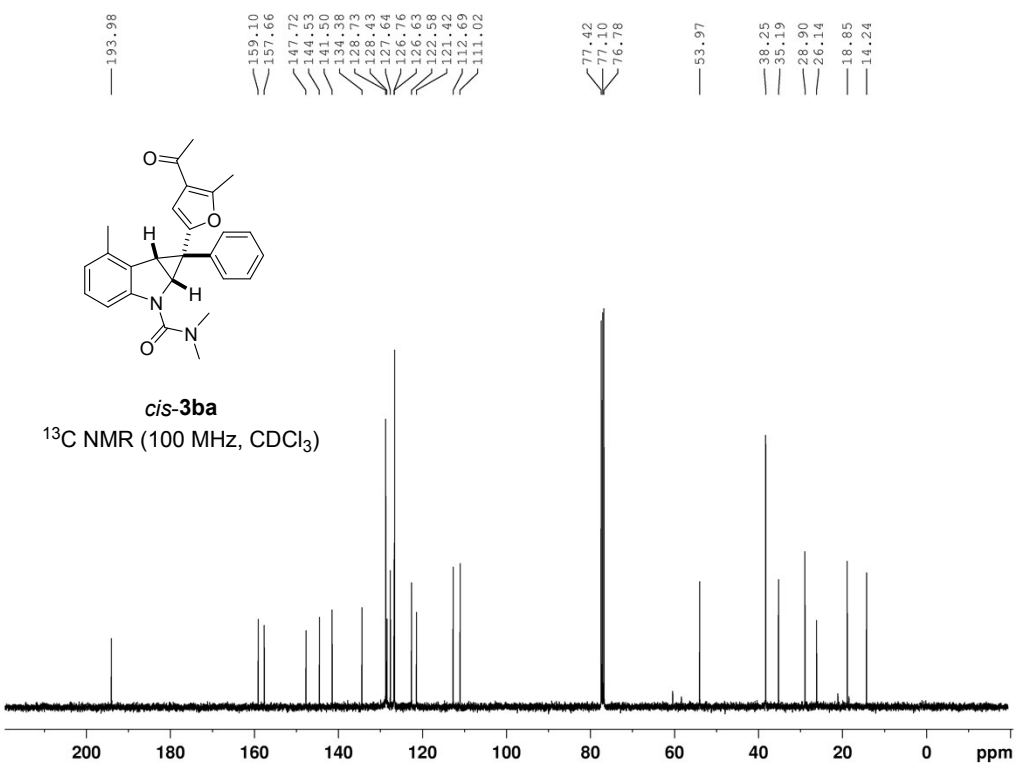
cis-**3aa**

^{13}C NMR (100 MHz, $CDCl_3$)



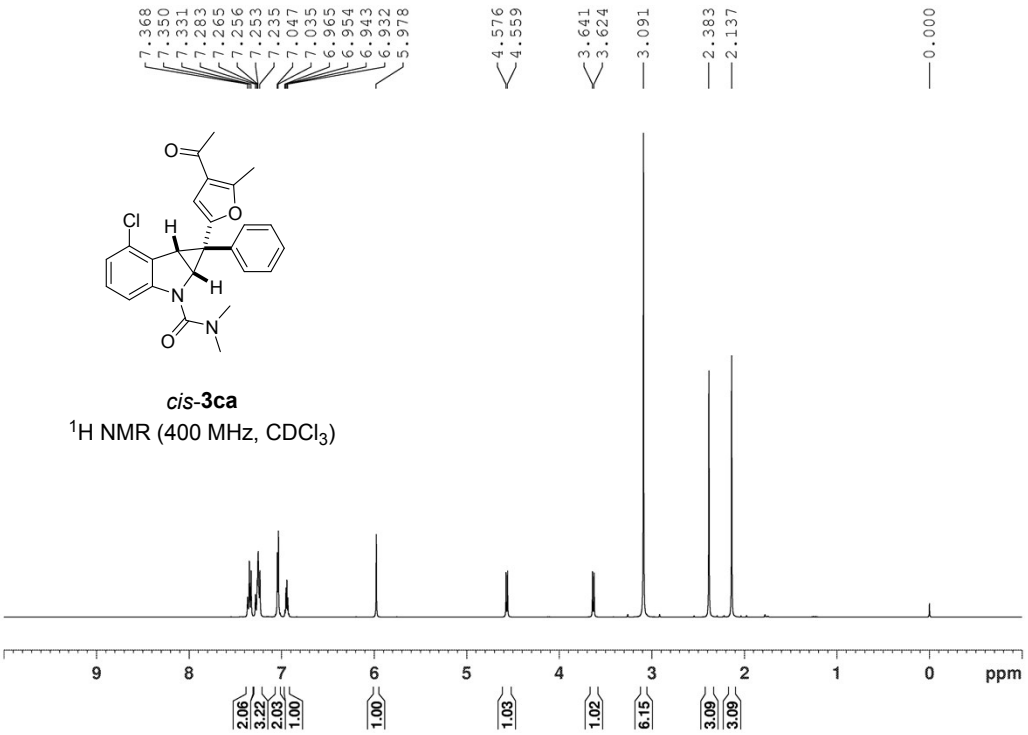
cis-**3ba**

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



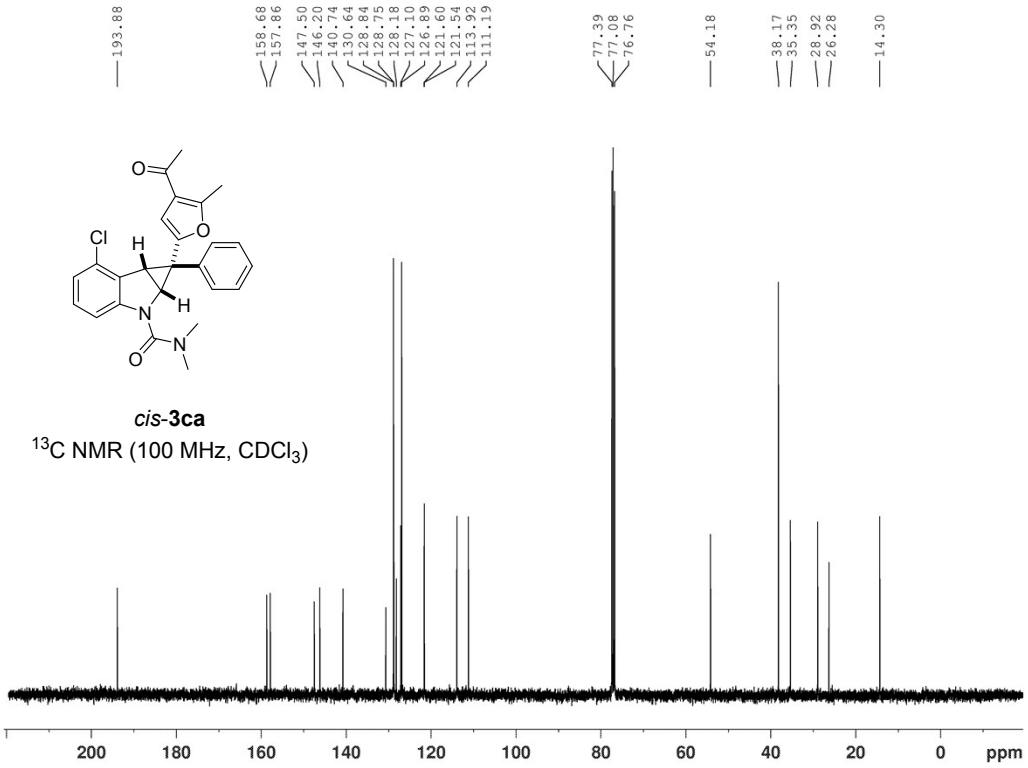
cis-**3ba**

^{13}C NMR (100 MHz, $CDCl_3$)



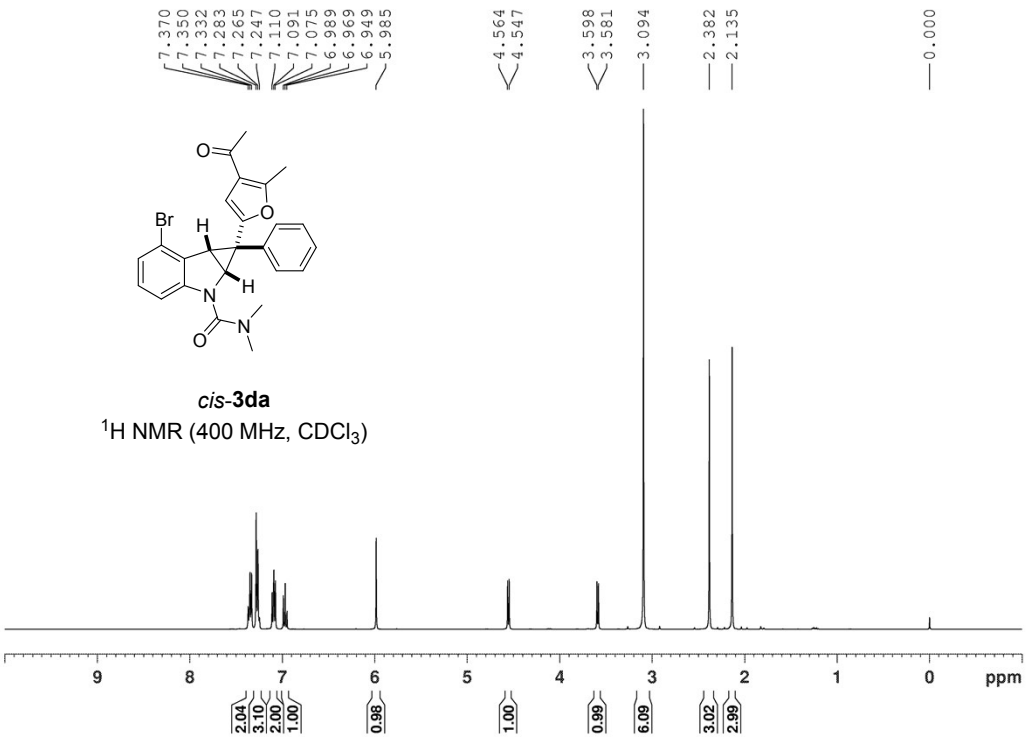
***cis*-3ca**

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



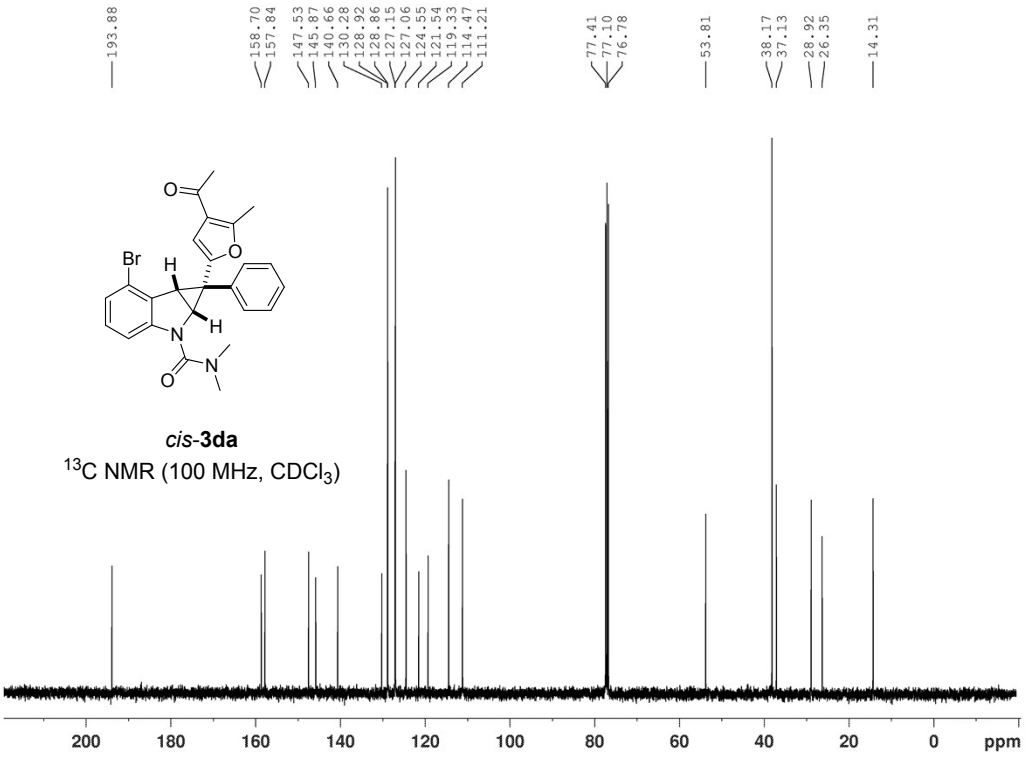
***cis*-3ca**

^{13}C NMR (100 MHz, $CDCl_3$)



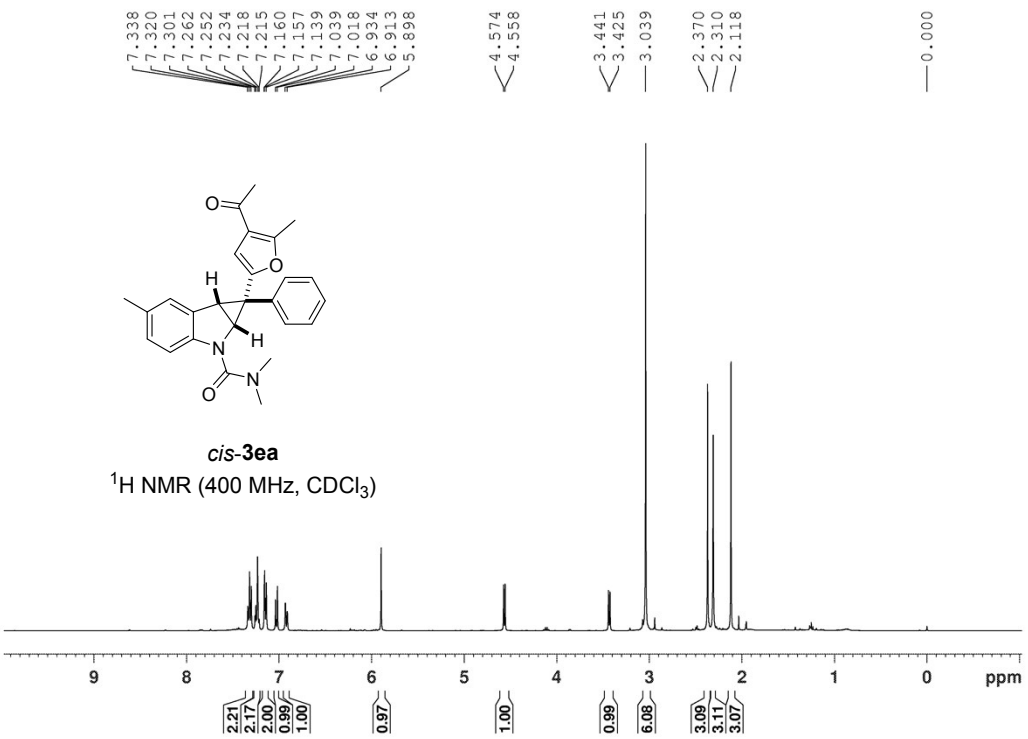
***cis*-3da**

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



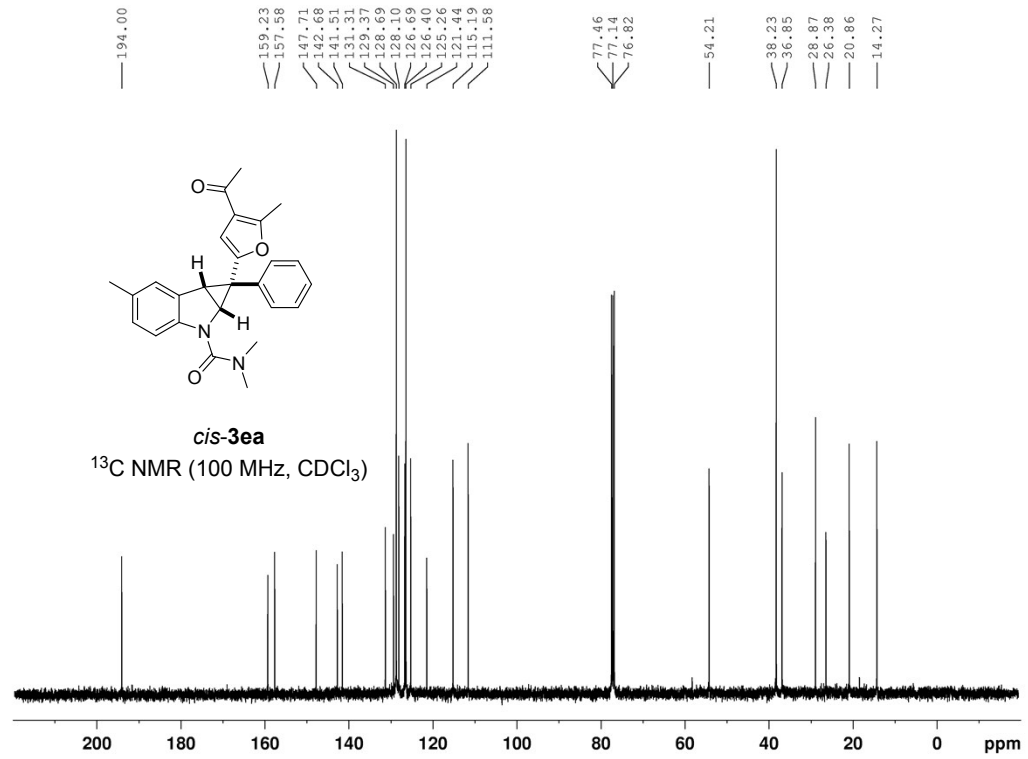
***cis*-3da**

^{13}C NMR (100 MHz, $CDCl_3$)



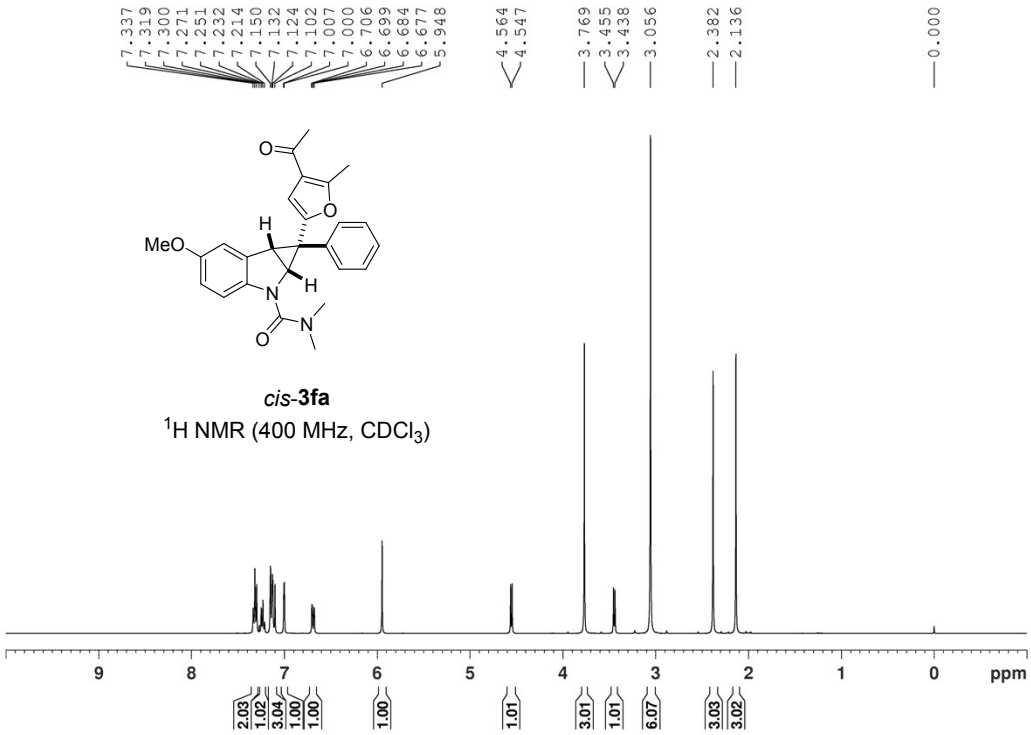
cis-**3ea**

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



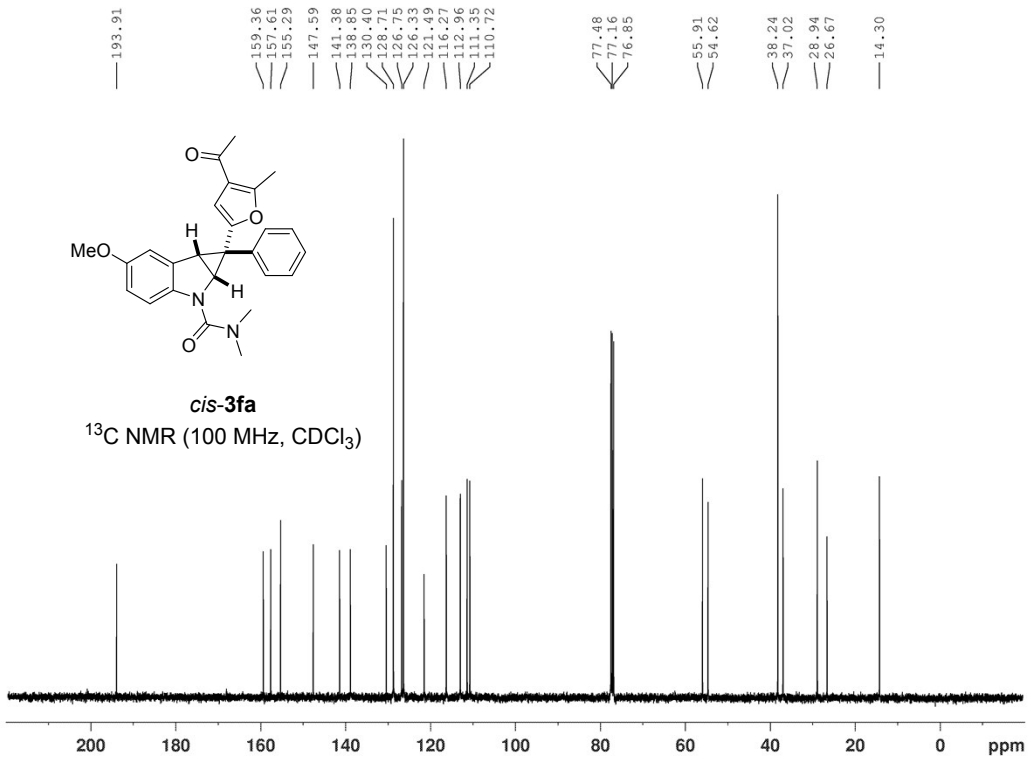
cis-**3ea**

^{13}C NMR (100 MHz, $CDCl_3$)



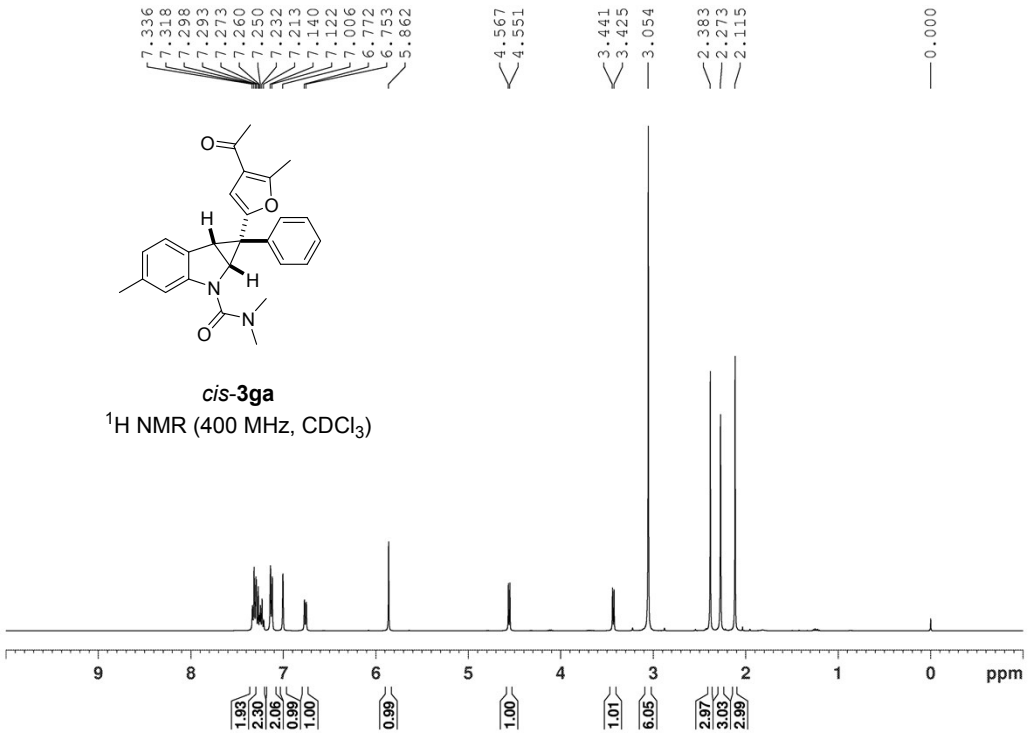
cis-**3fa**

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



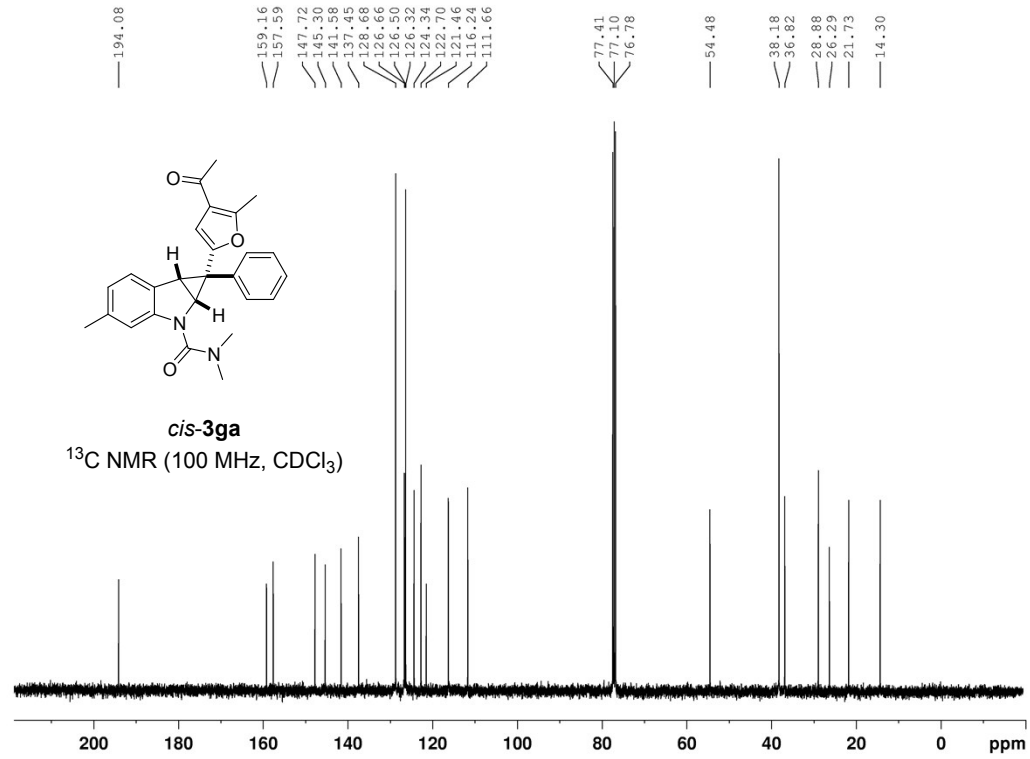
cis-**3fa**

^{13}C NMR (100 MHz, $CDCl_3$)



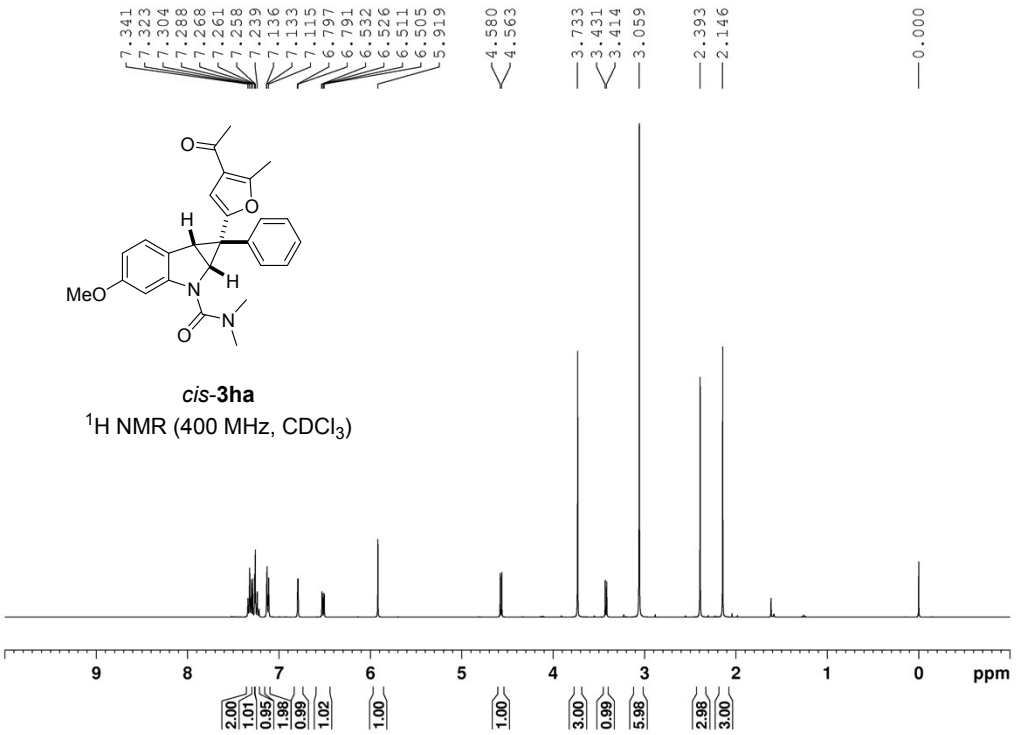
cis-**3ga**

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



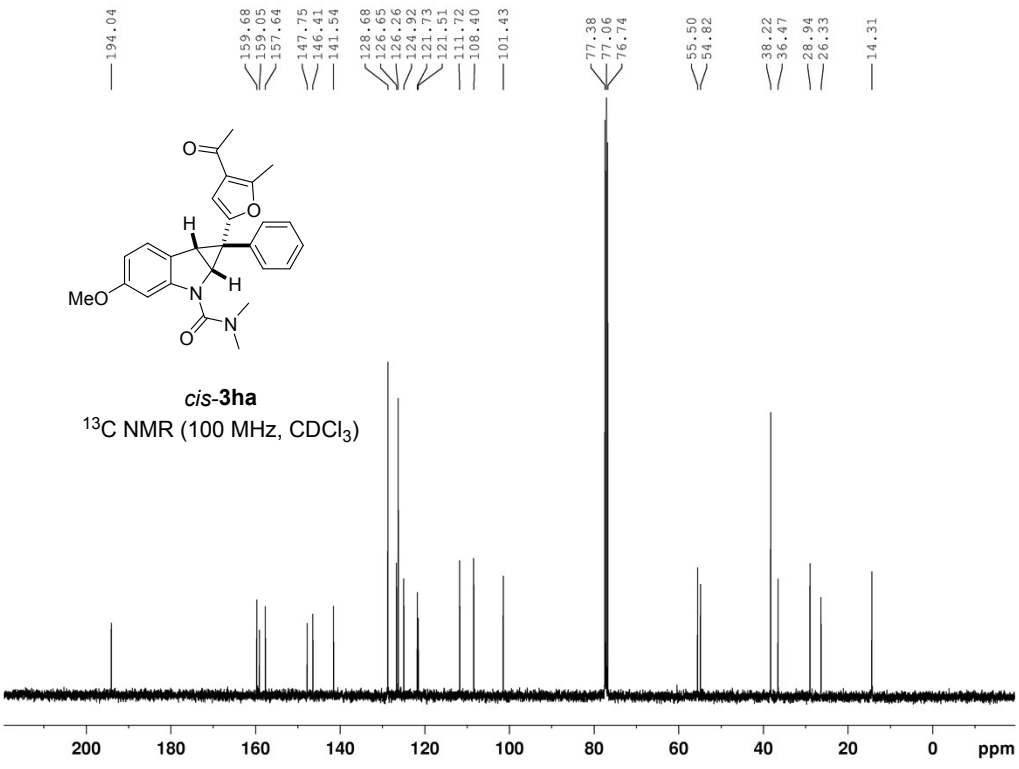
cis-**3ga**

^{13}C NMR (100 MHz, $CDCl_3$)



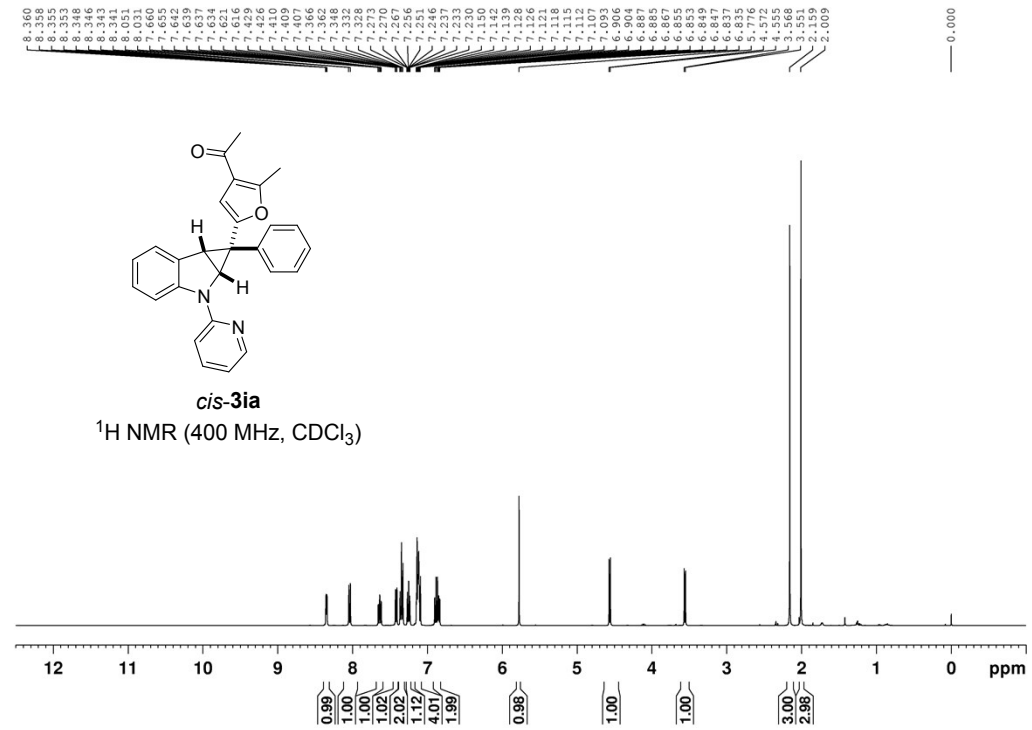
cis-**3ha**

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



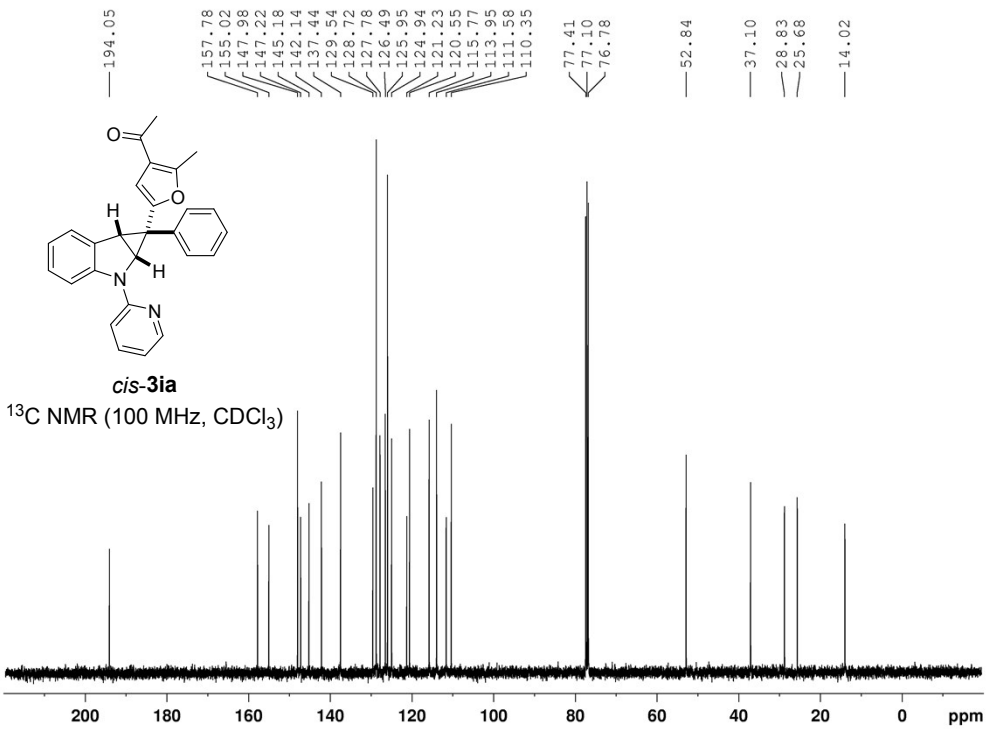
cis-**3ha**

^{13}C NMR (100 MHz, $CDCl_3$)



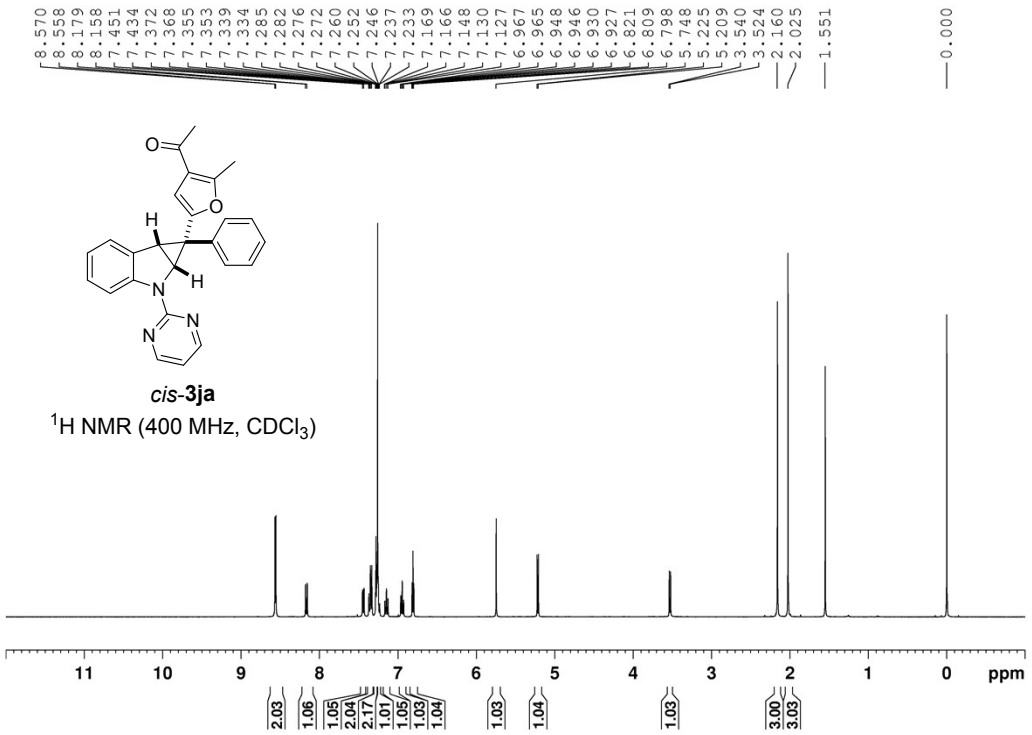
cis-**3ia**

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



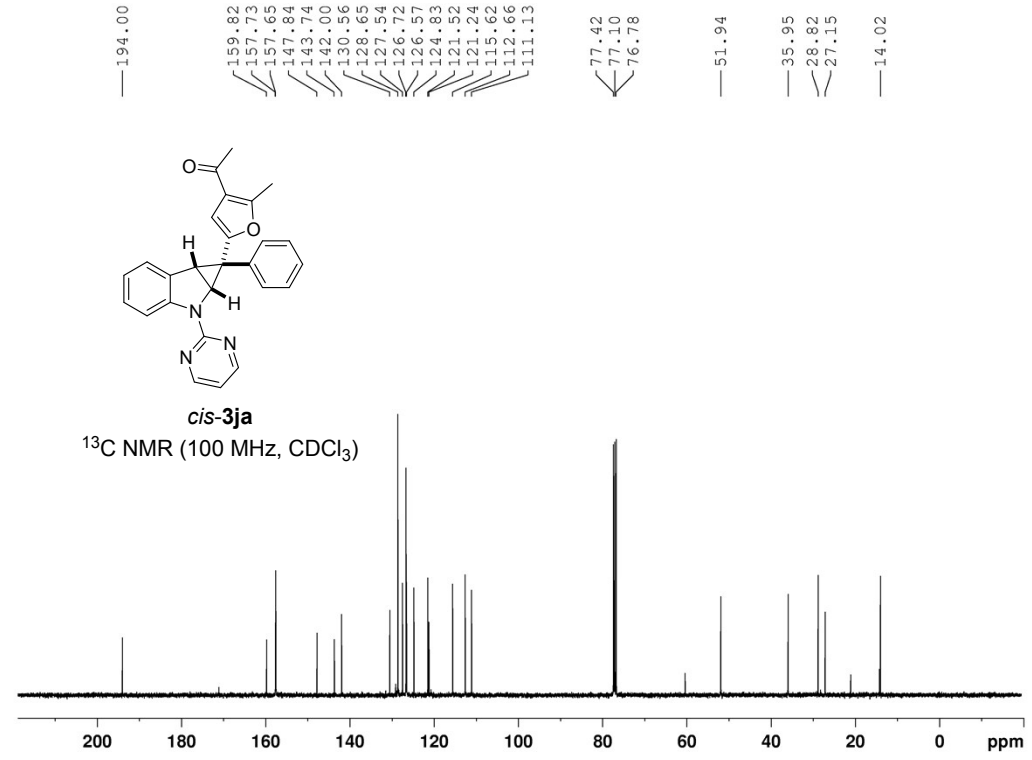
cis-**3ia**

^{13}C NMR (100 MHz, $CDCl_3$)



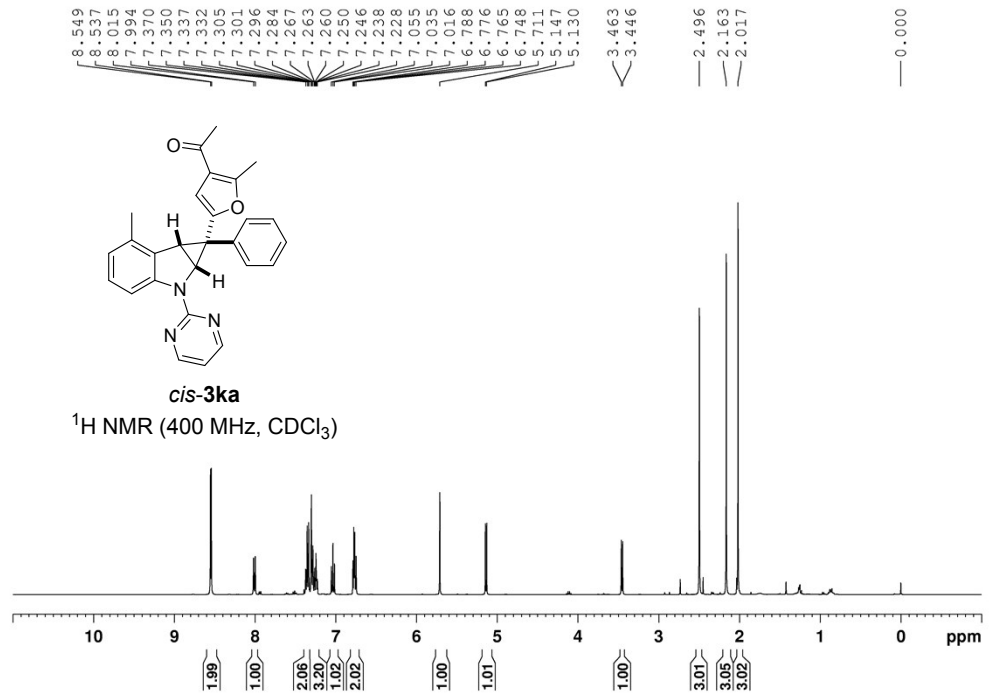
cis-**3ja**

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



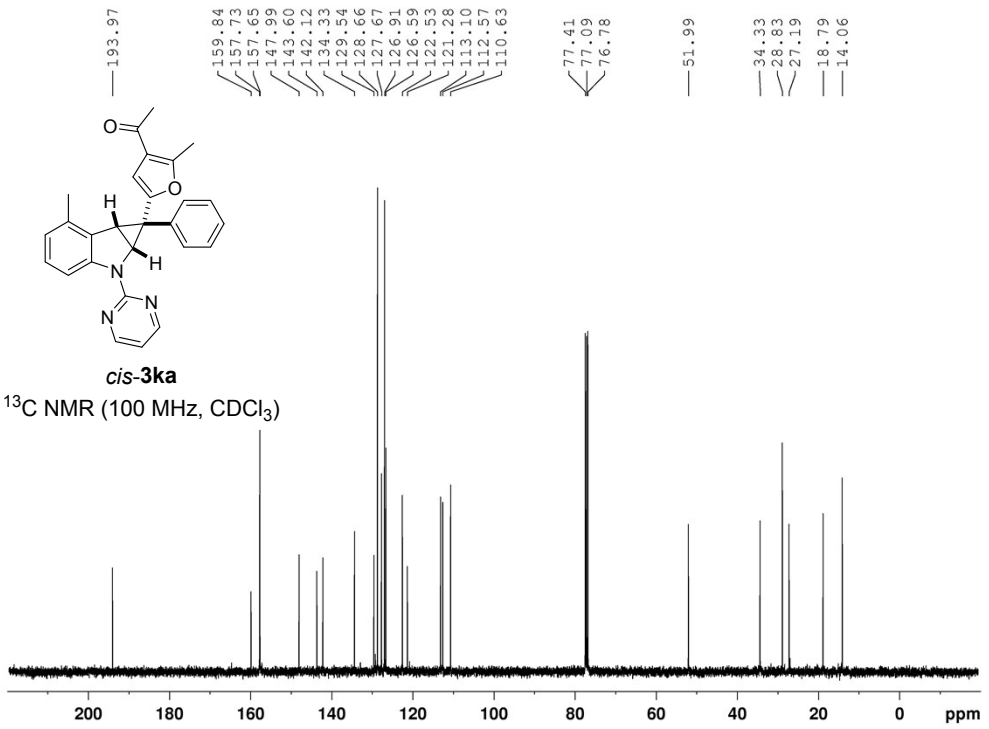
cis-**3ja**

^{13}C NMR (100 MHz, $CDCl_3$)



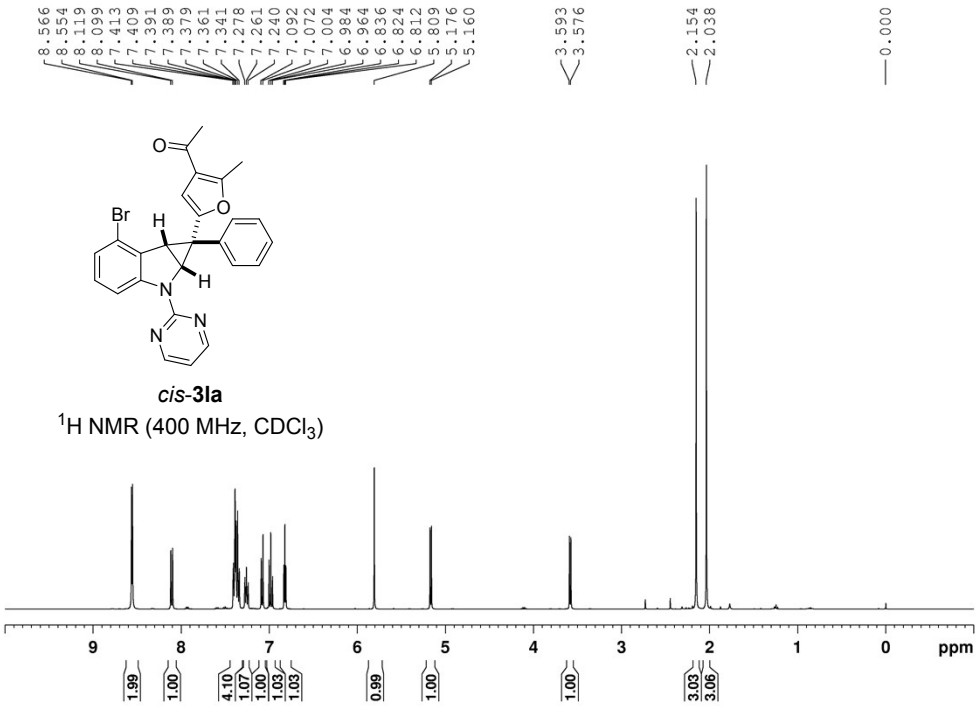
cis-**3ka**

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



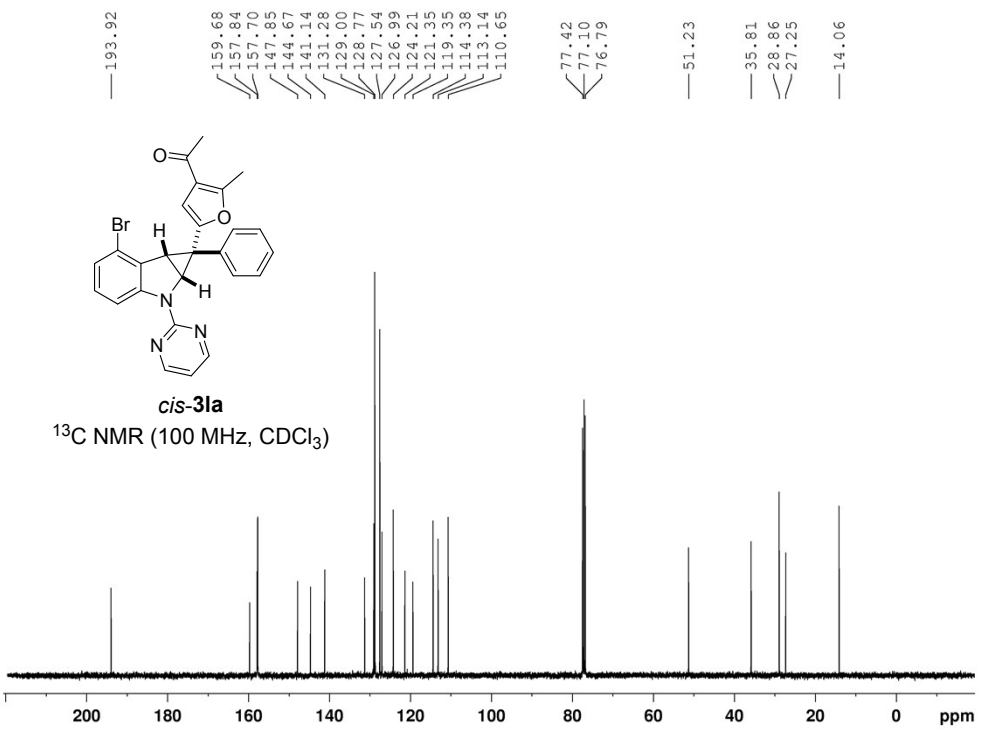
cis-**3ka**

^{13}C NMR (100 MHz, $CDCl_3$)



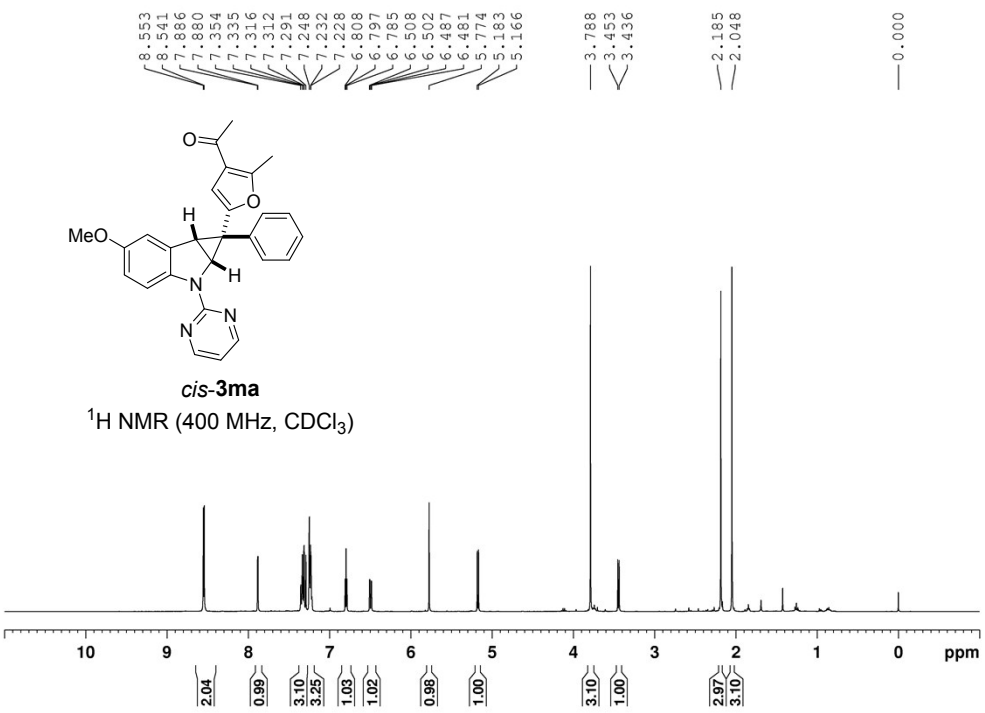
cis-**3la**

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



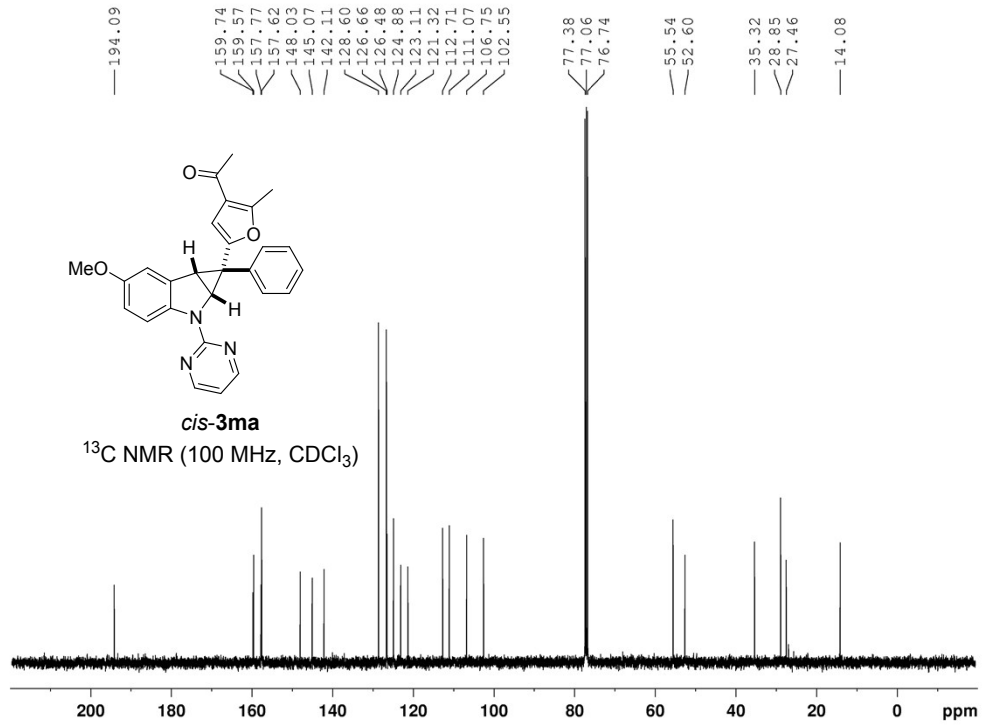
cis-**3la**

^{13}C NMR (100 MHz, $CDCl_3$)



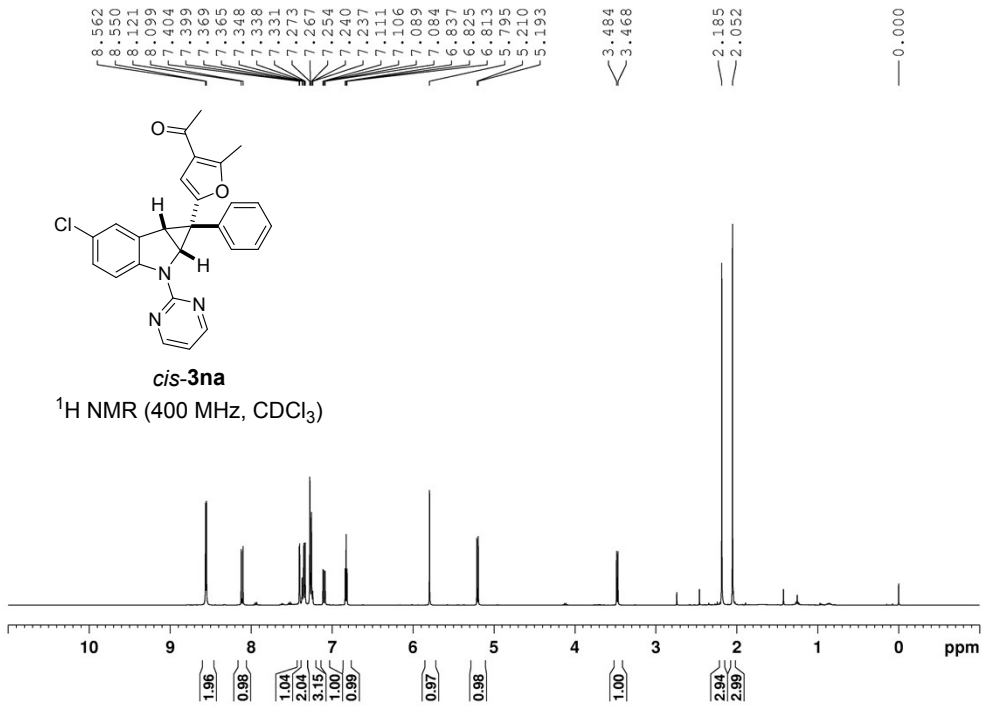
cis-**3ma**

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



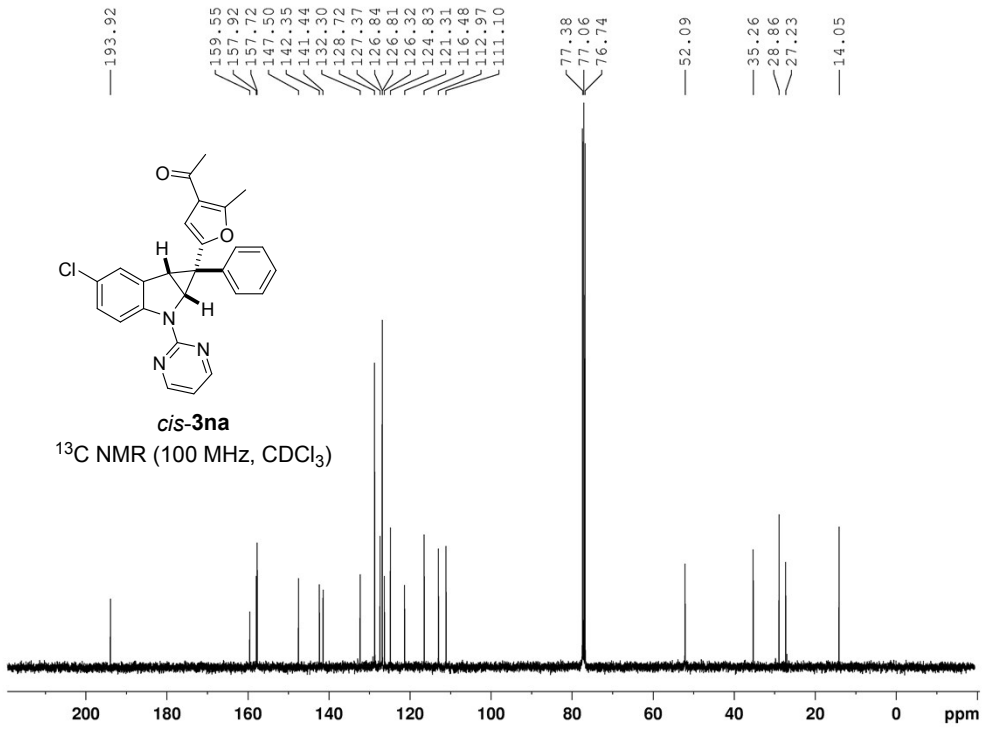
cis-**3ma**

^{13}C NMR (100 MHz, $CDCl_3$)



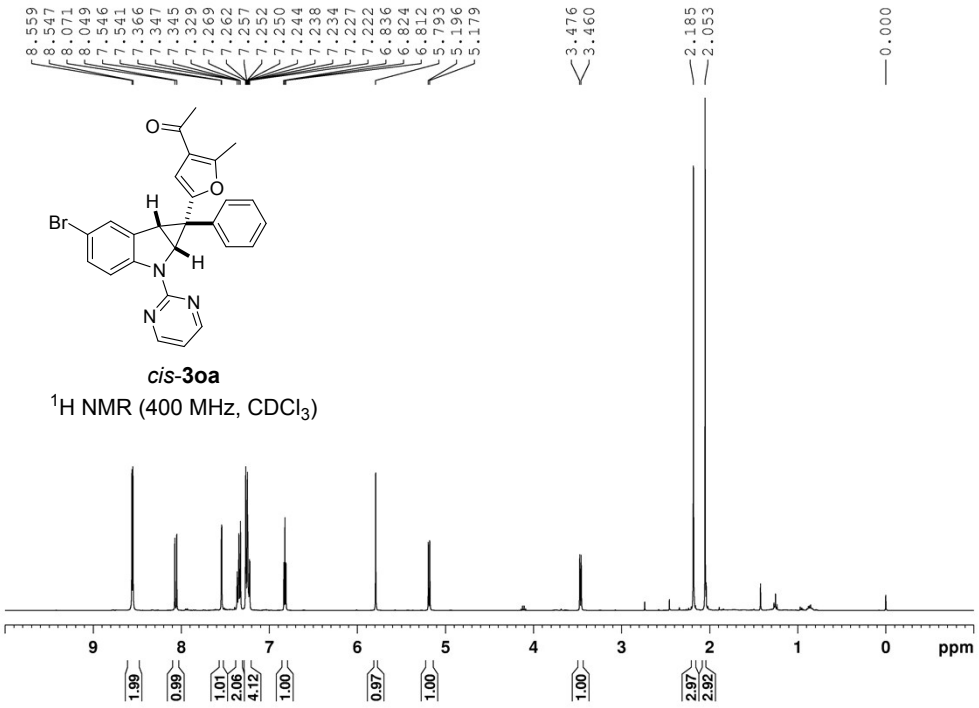
cis-**3na**

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



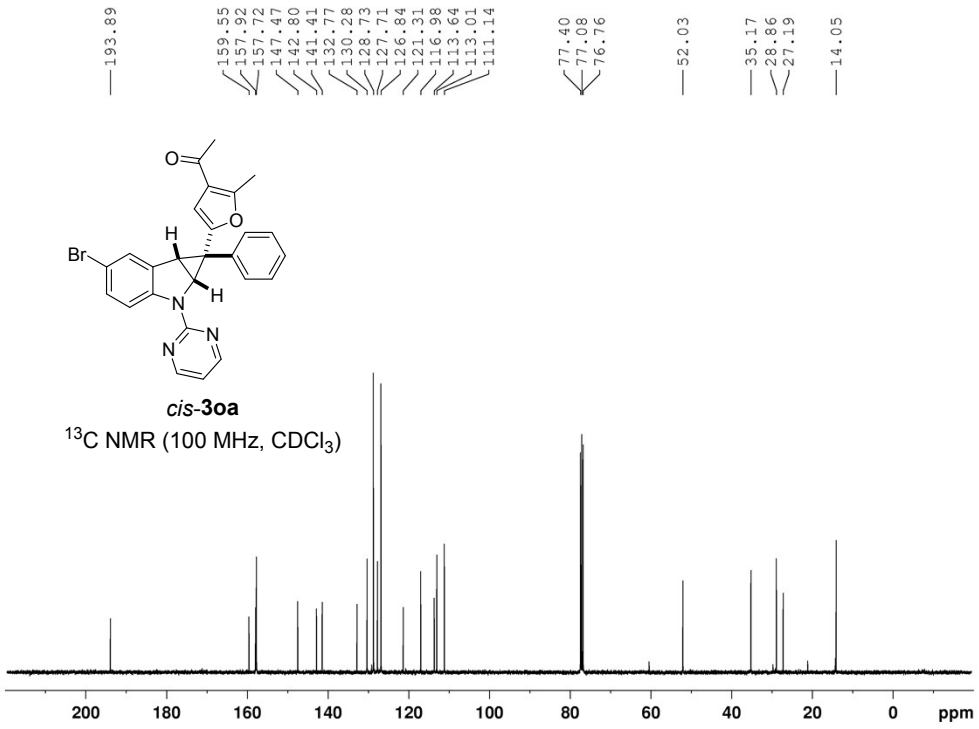
cis-**3na**

^{13}C NMR (100 MHz, $CDCl_3$)



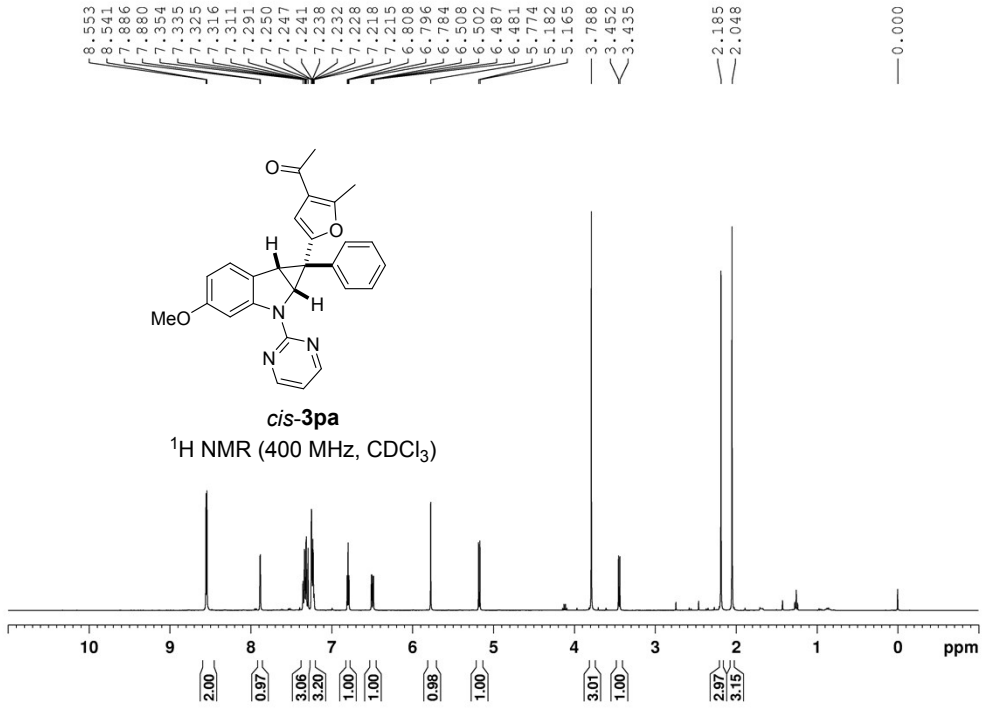
cis-**3oa**

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



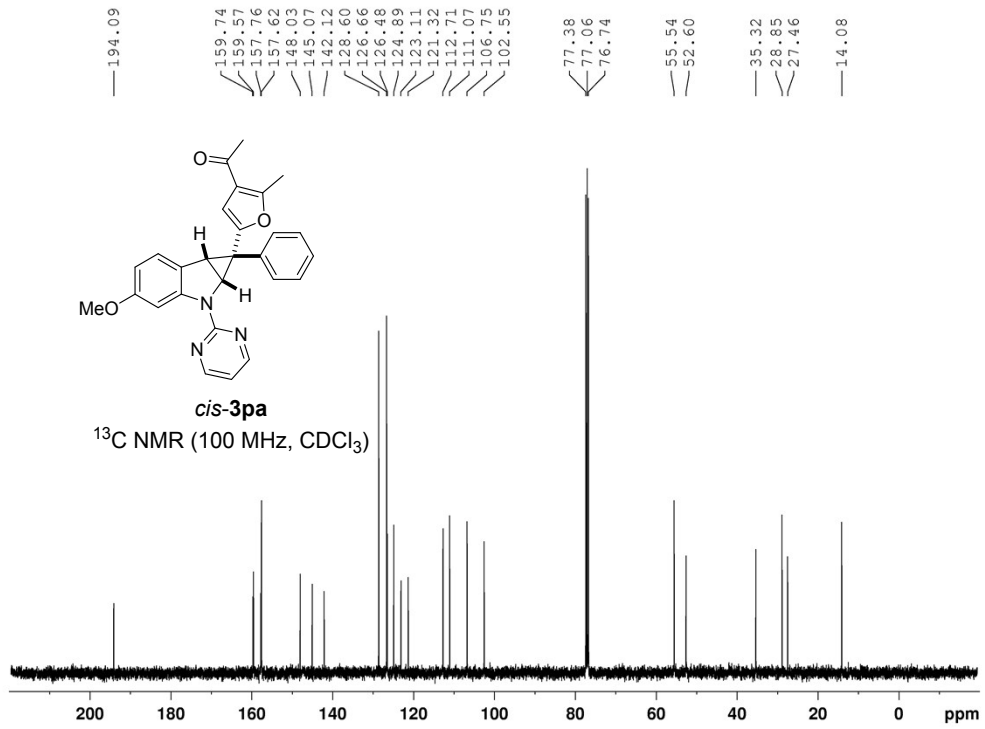
cis-**3oa**

^{13}C NMR (100 MHz, $CDCl_3$)



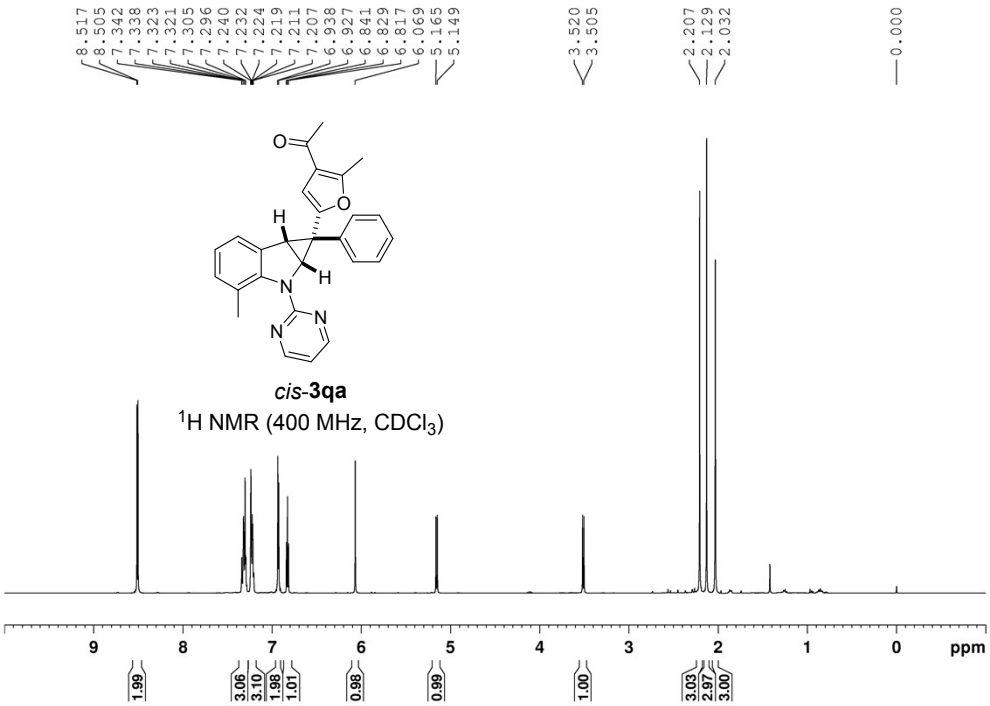
cis-**3pa**

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



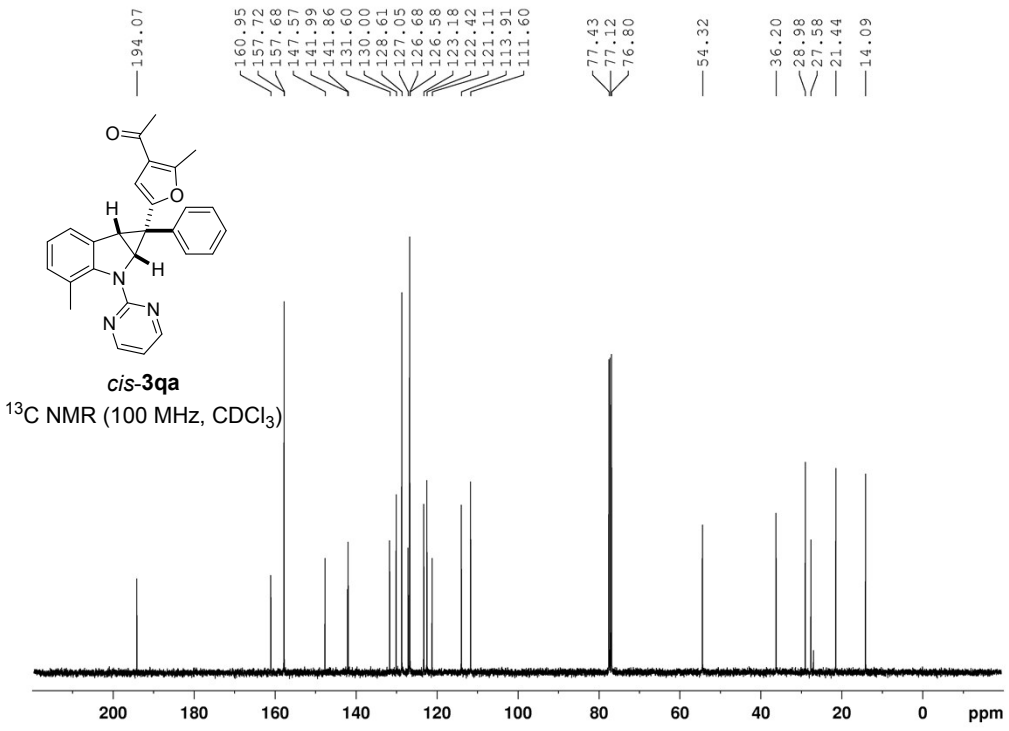
cis-**3pa**

^{13}C NMR (100 MHz, $CDCl_3$)



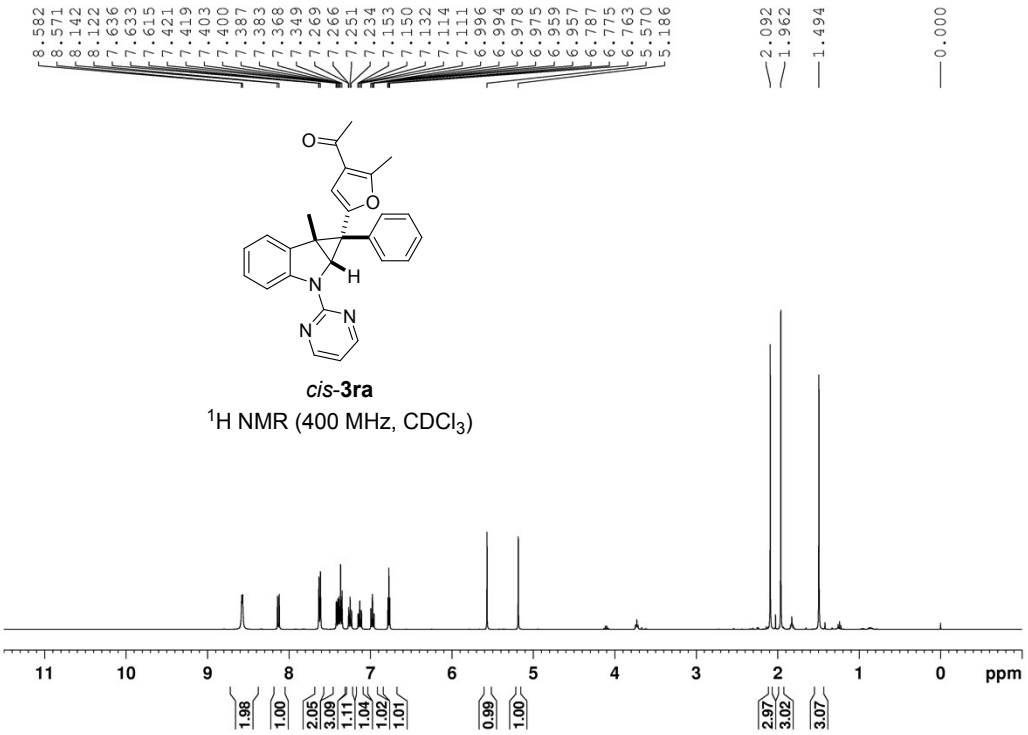
cis-**3qa**

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



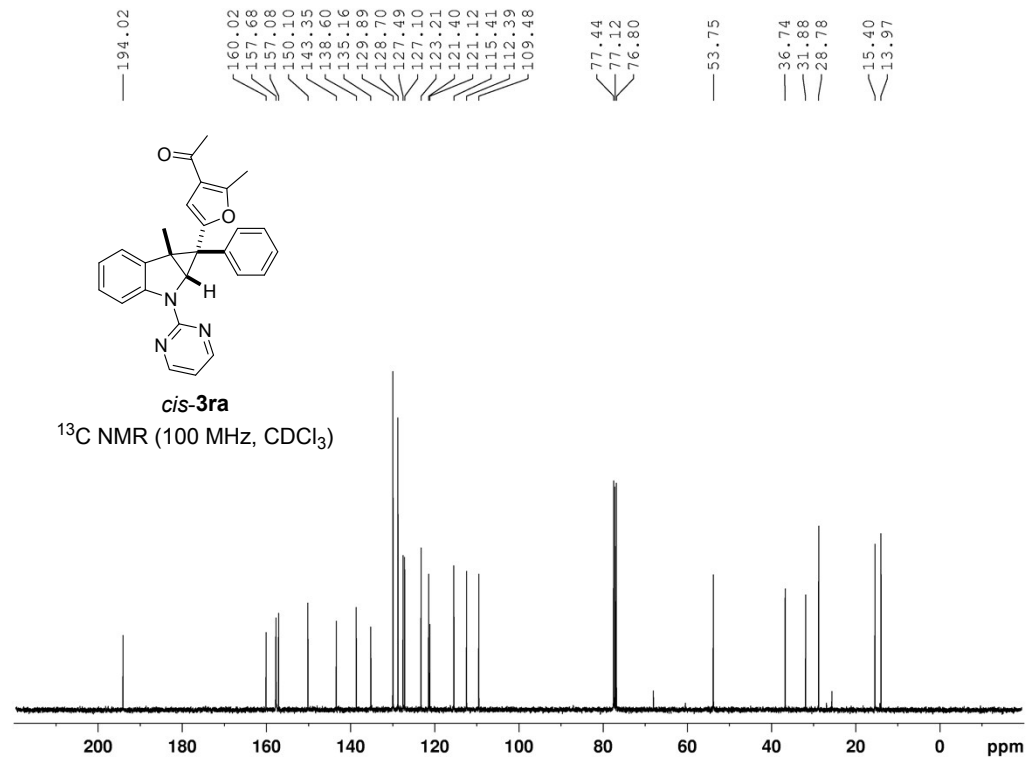
cis-**3qa**

^{13}C NMR (100 MHz, $CDCl_3$)



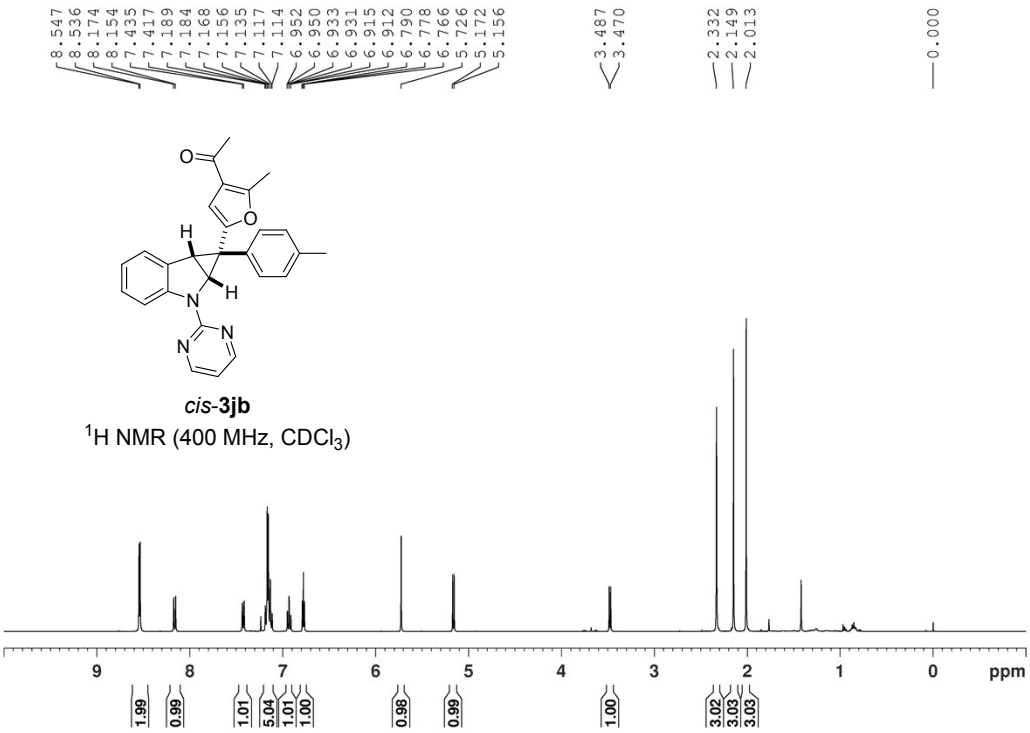
cis-**3ra**

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



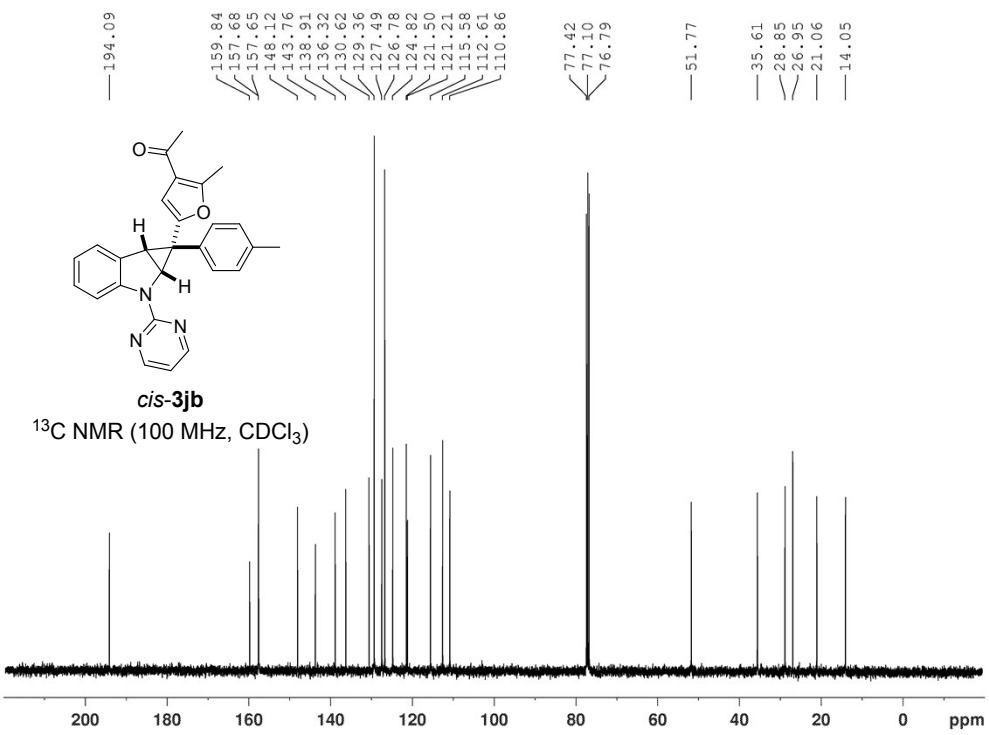
cis-**3ra**

^{13}C NMR (100 MHz, $CDCl_3$)



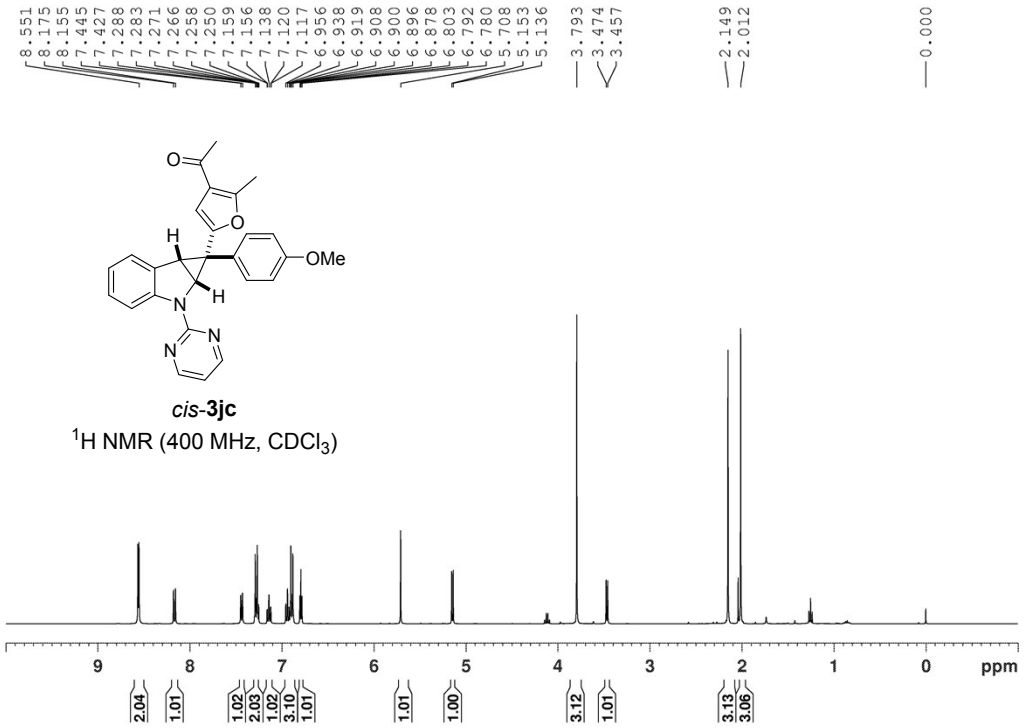
***cis*-3jb**

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



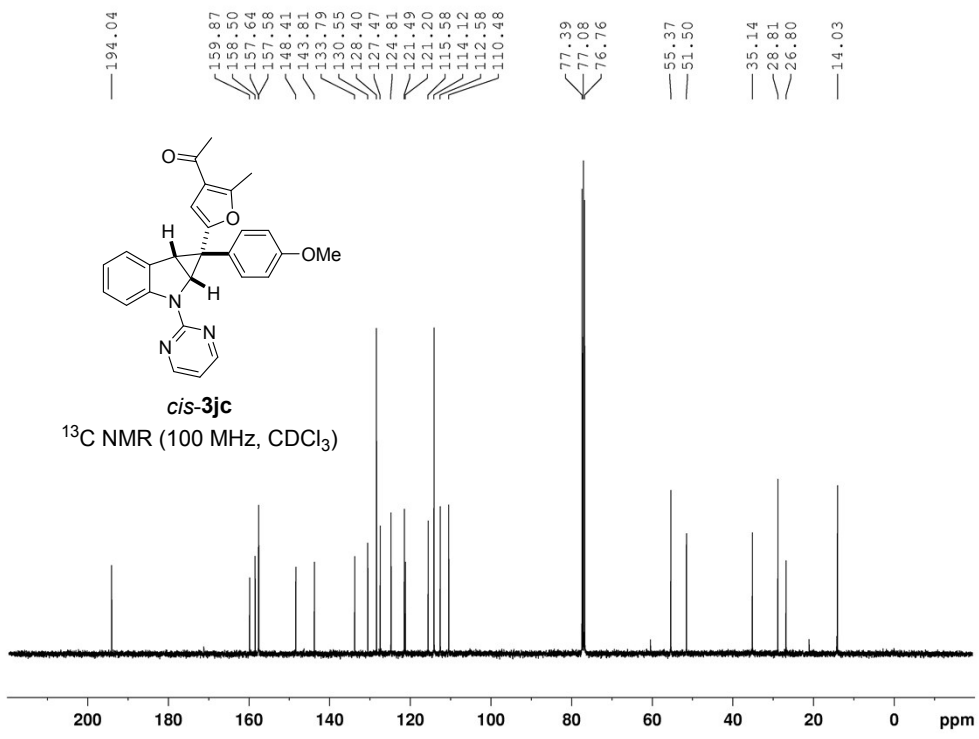
***cis*-3jb**

^{13}C NMR (100 MHz, $CDCl_3$)



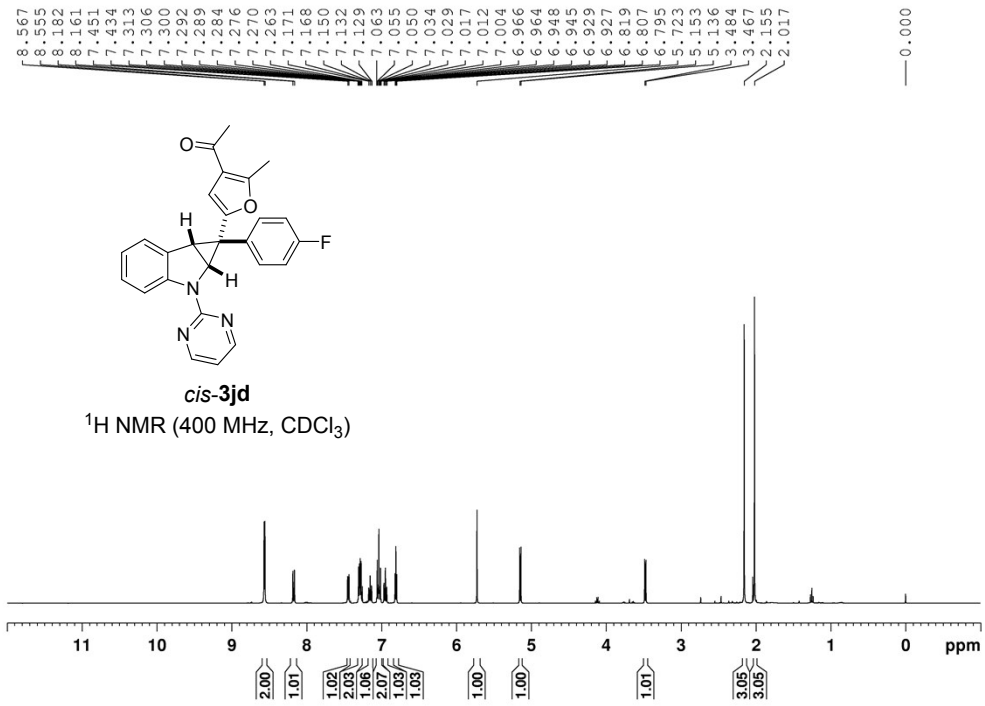
cis-**3jc**

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



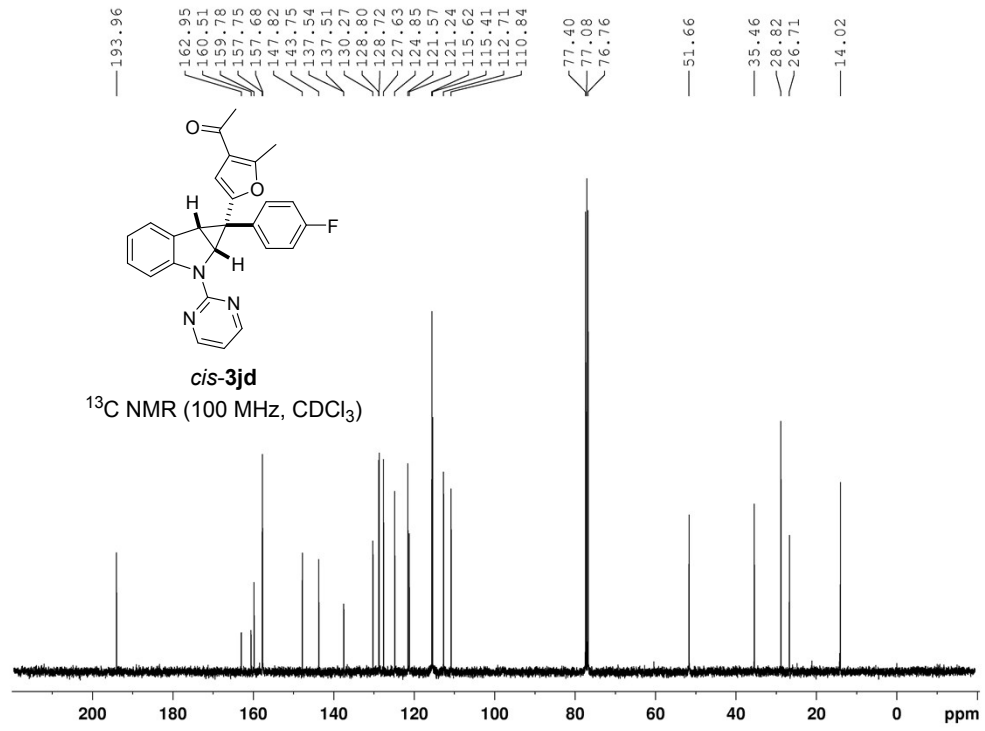
cis-**3jc**

^{13}C NMR (100 MHz, $CDCl_3$)



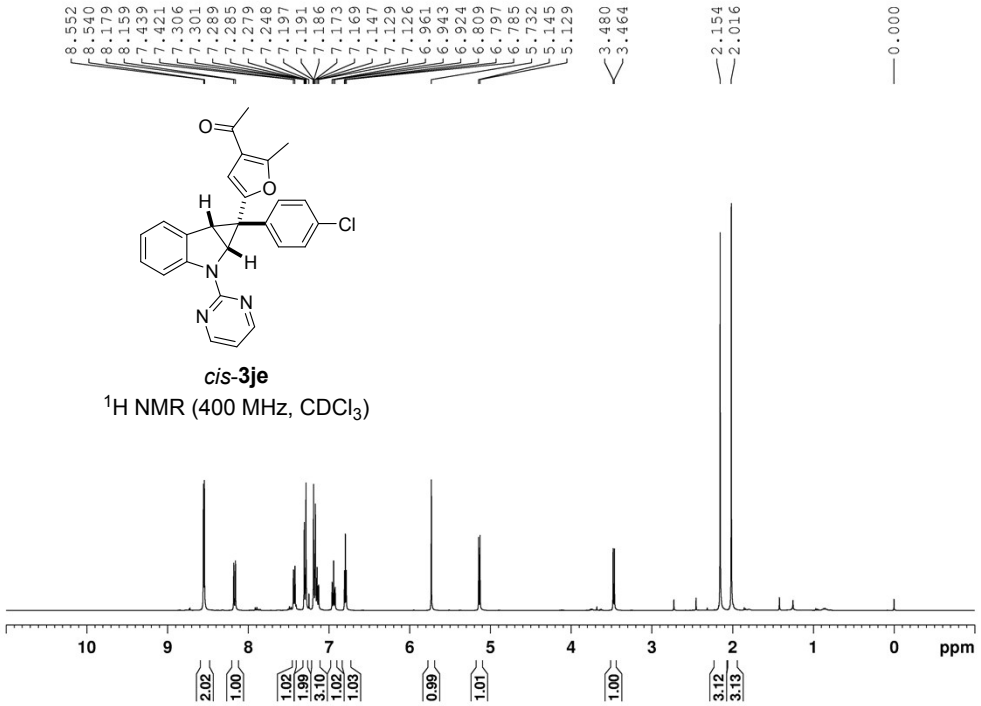
cis-**3jd**

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



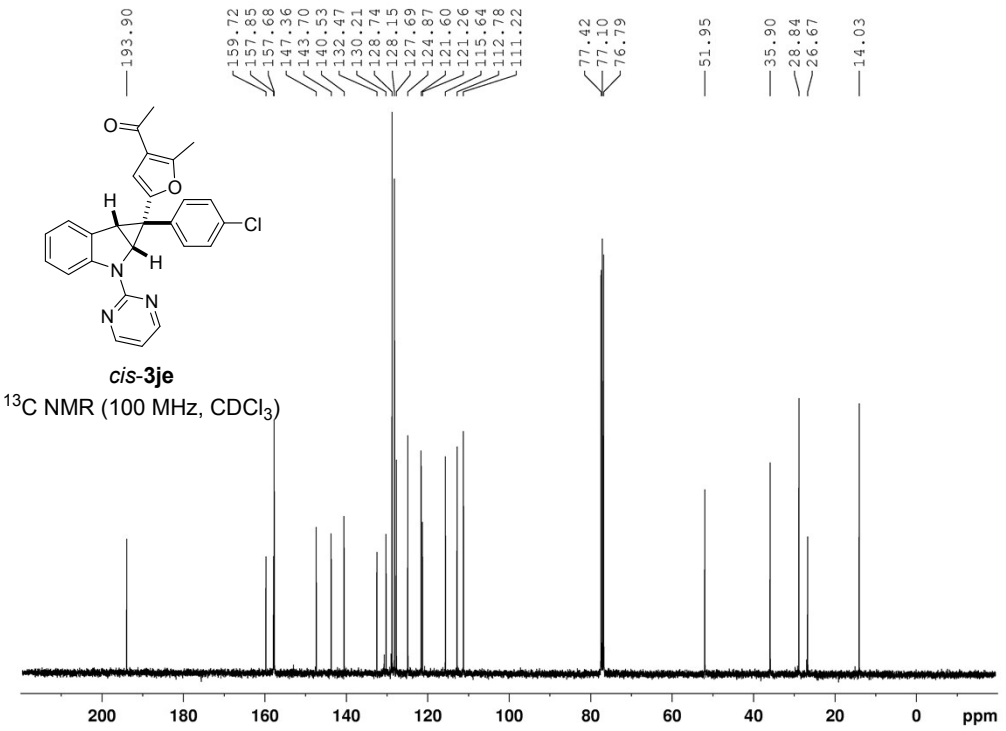
cis-**3jd**

^{13}C NMR (100 MHz, $CDCl_3$)



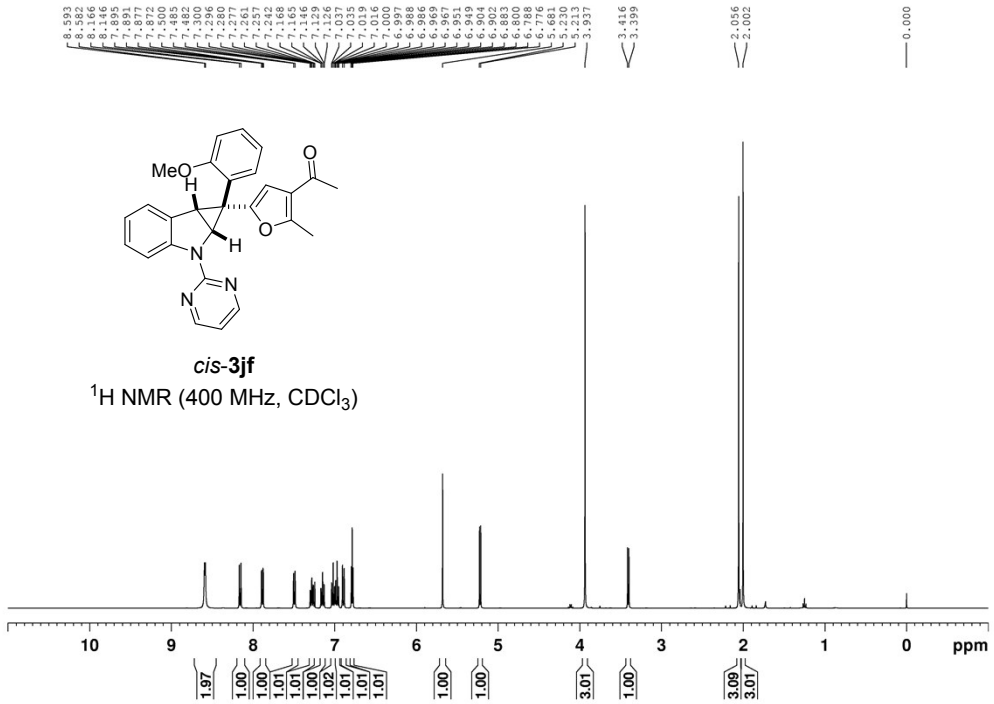
cis-**3je**

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



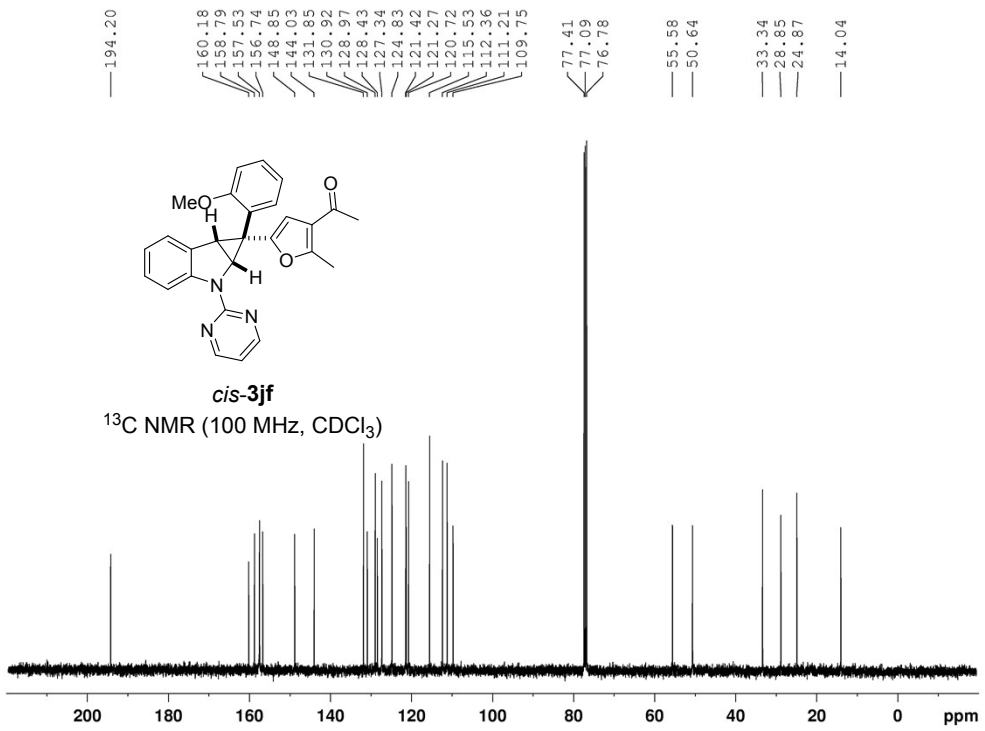
cis-**3je**

^{13}C NMR (100 MHz, $CDCl_3$)



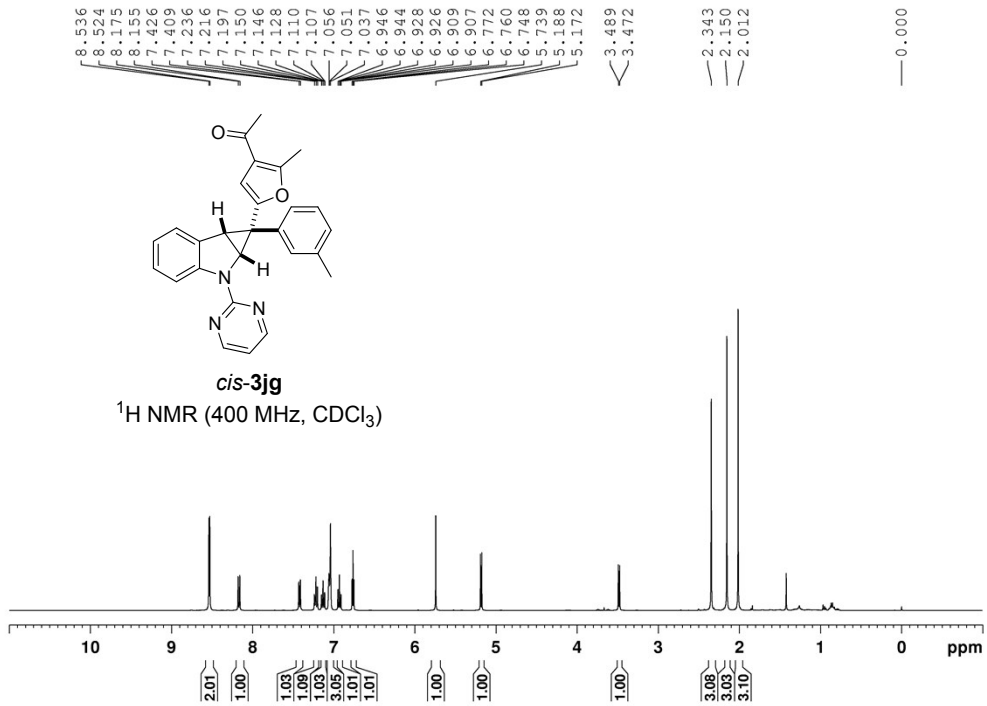
cis-**3jf**

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



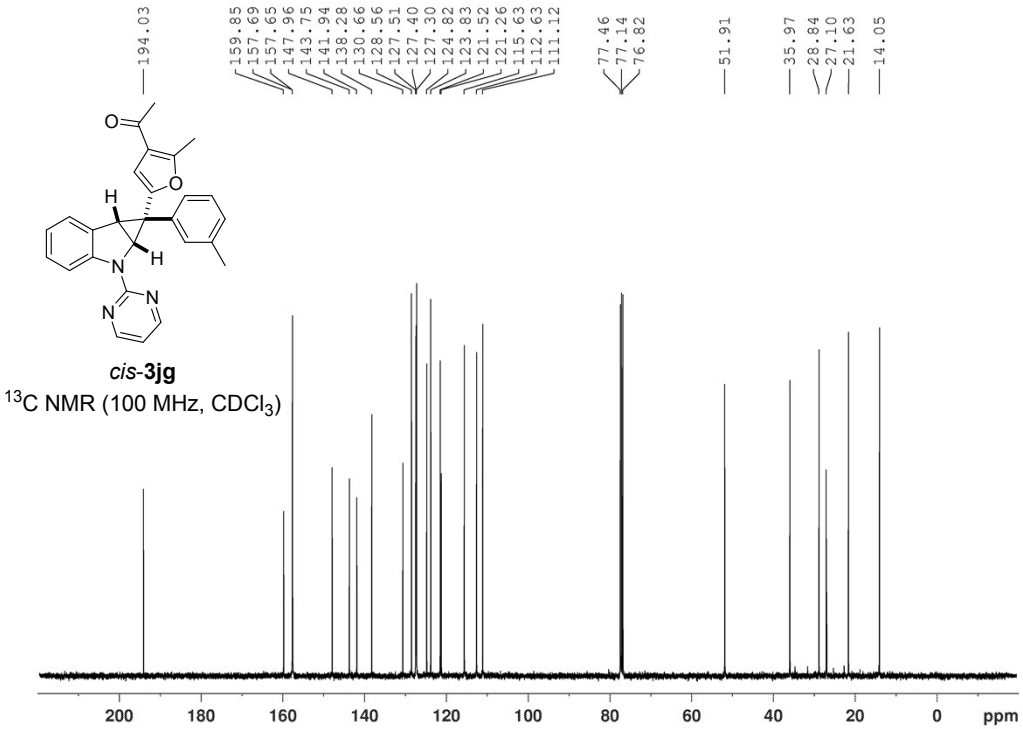
cis-**3jf**

^{13}C NMR (100 MHz, $CDCl_3$)



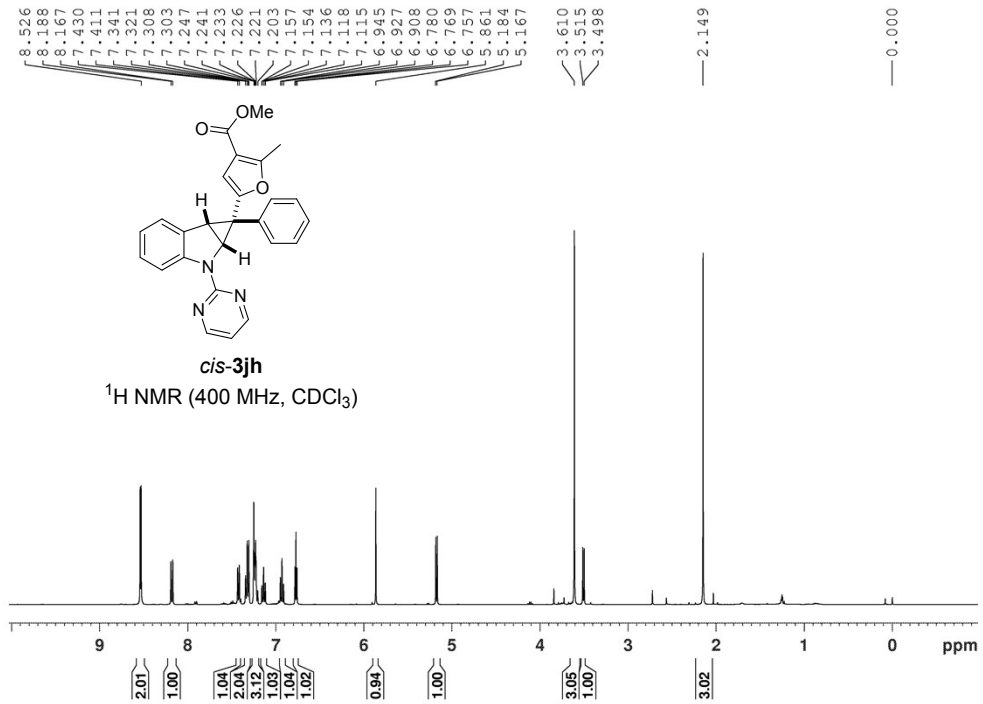
cis-**3jg**

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



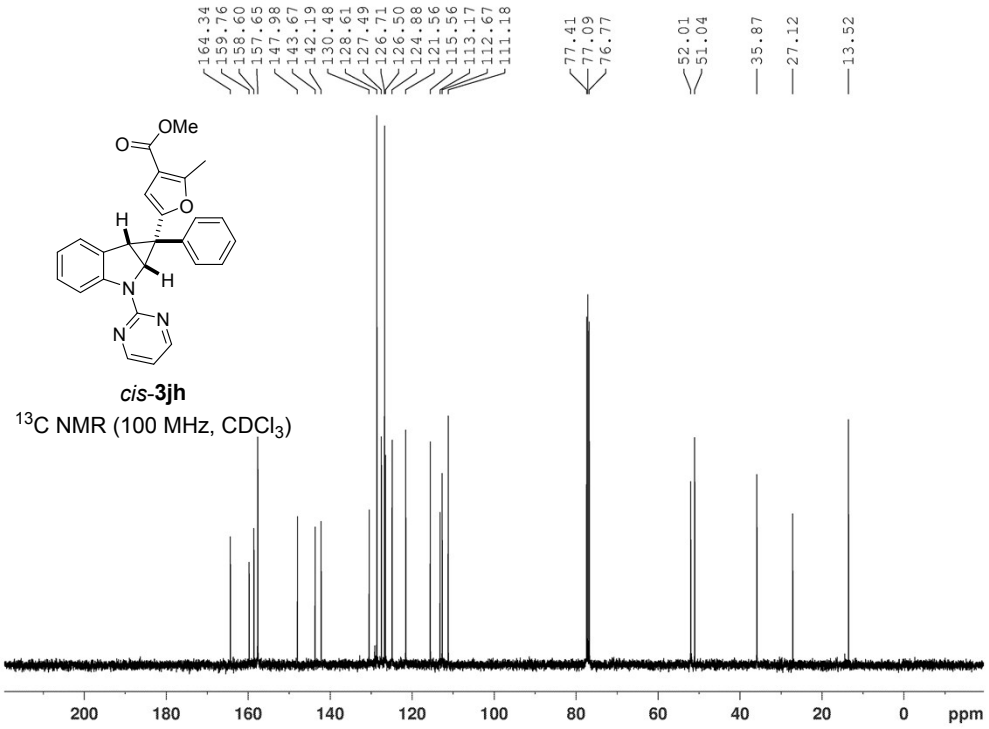
cis-**3jg**

^{13}C NMR (100 MHz, $CDCl_3$)



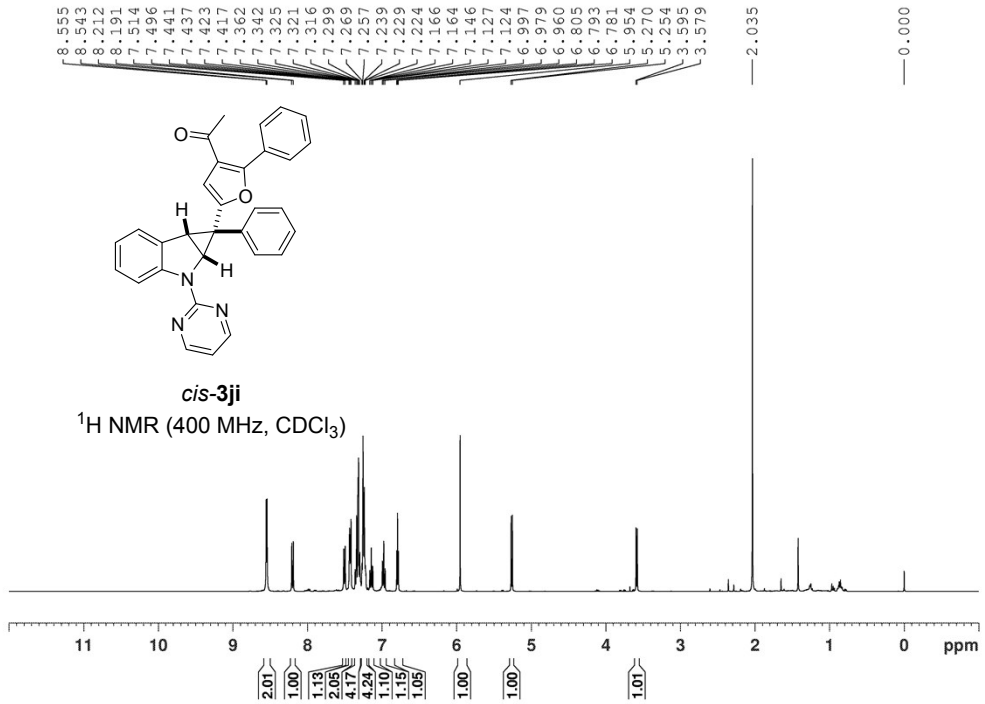
cis-**3jh**

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



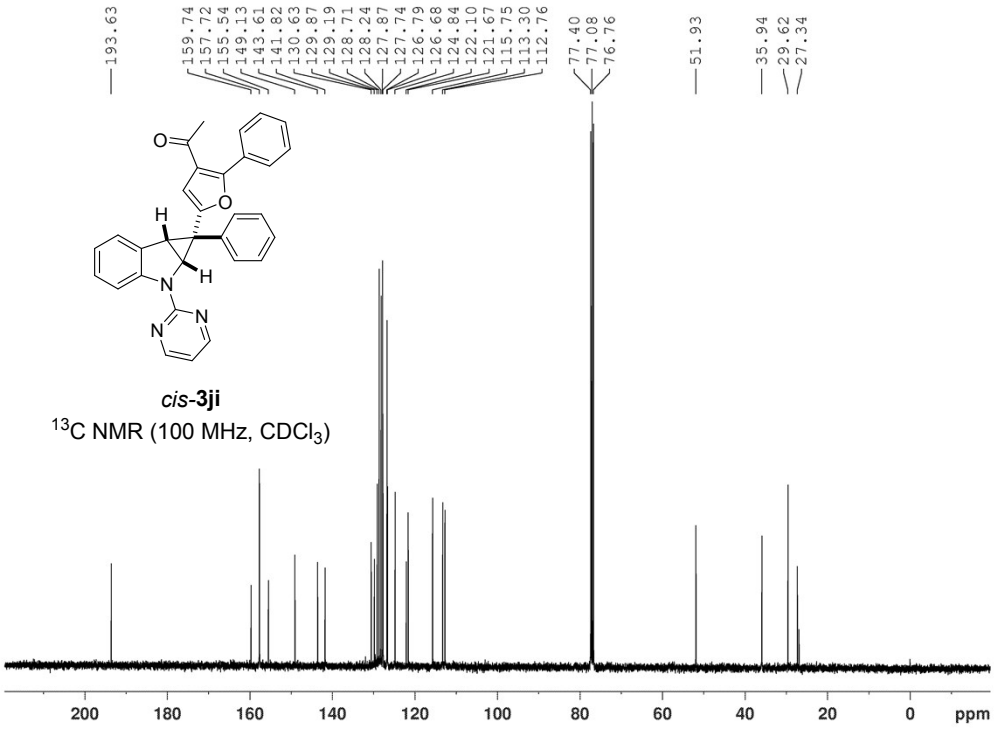
cis-**3jh**

^{13}C NMR (100 MHz, $CDCl_3$)



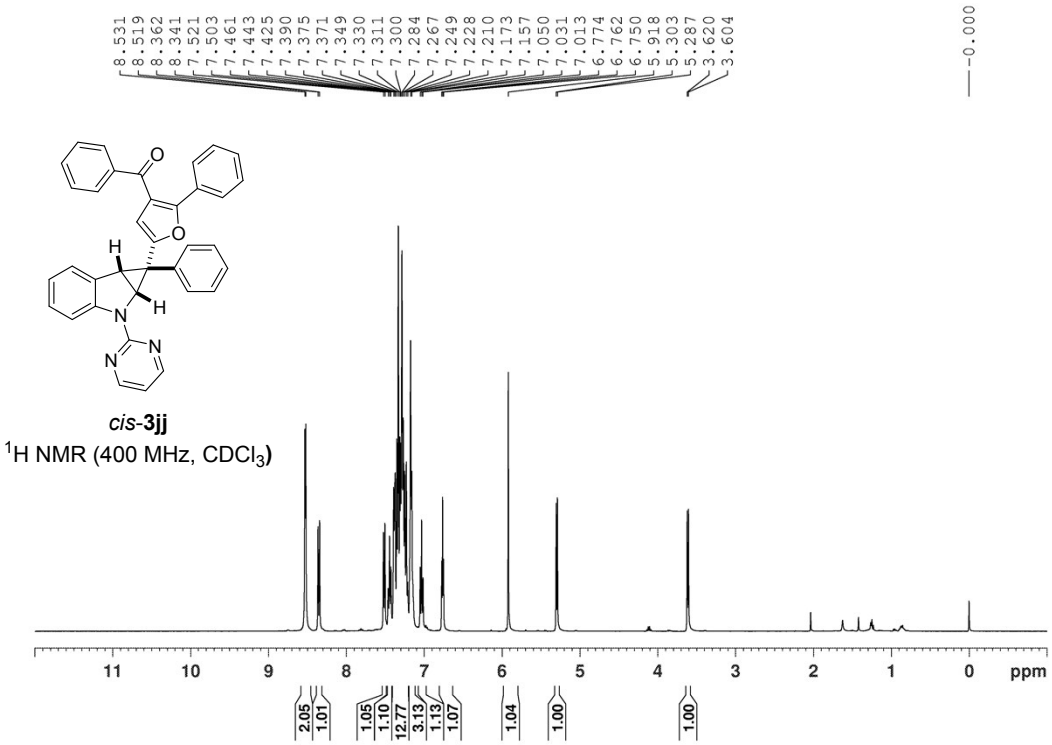
cis-**3ji**

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



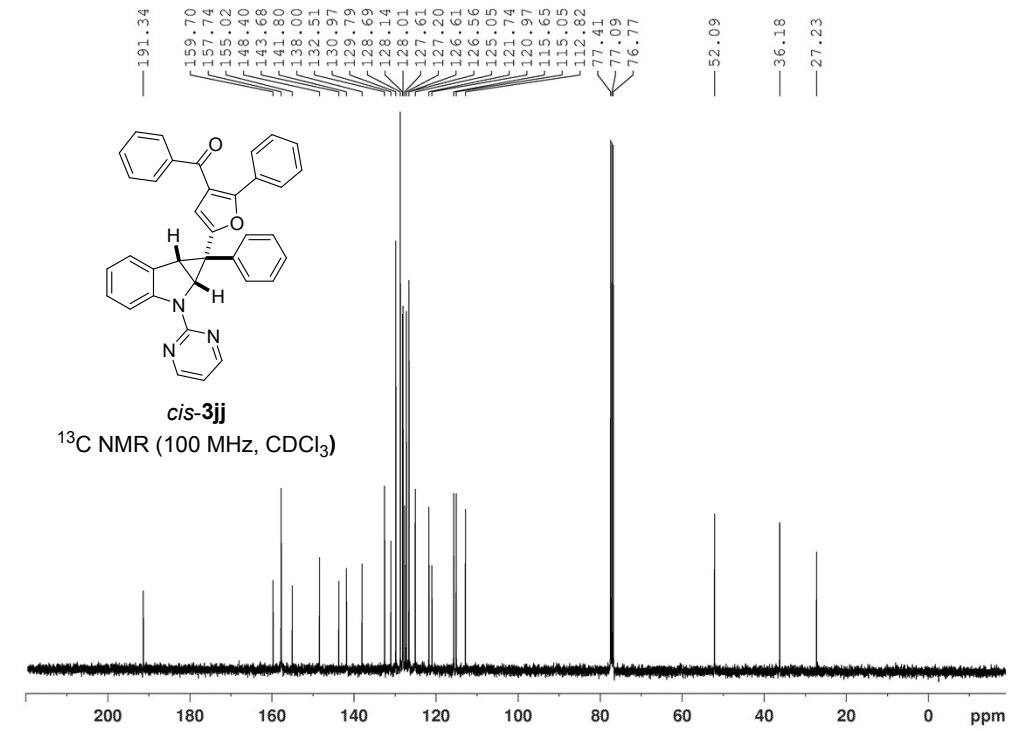
cis-**3ji**

^{13}C NMR (100 MHz, $CDCl_3$)



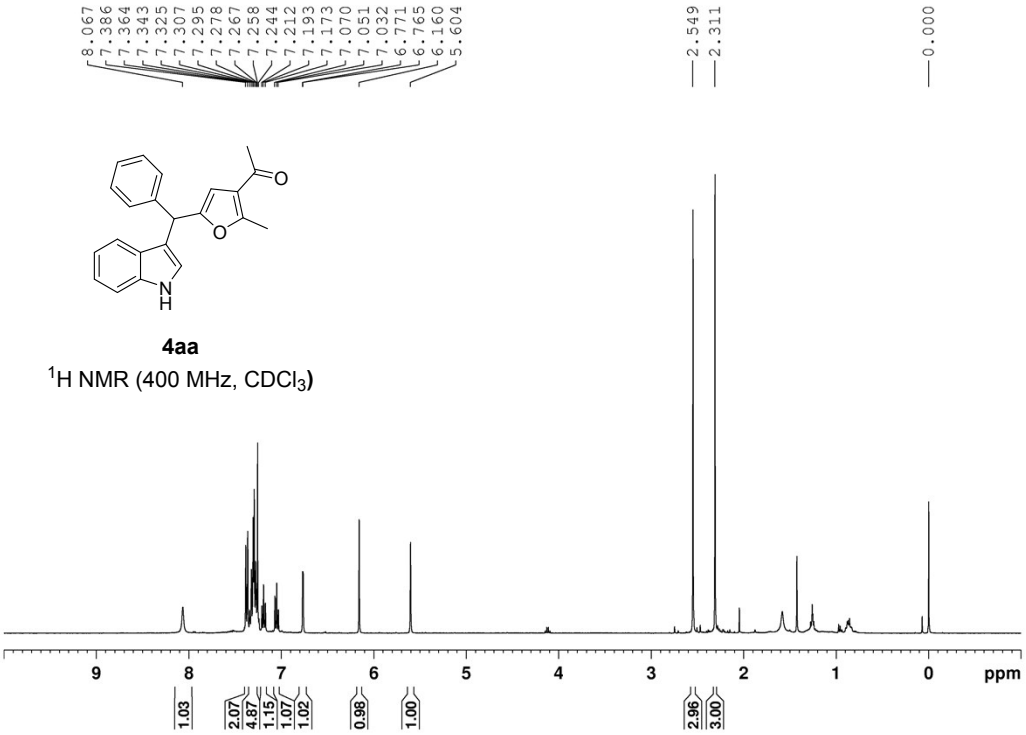
cis-**3jj**

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



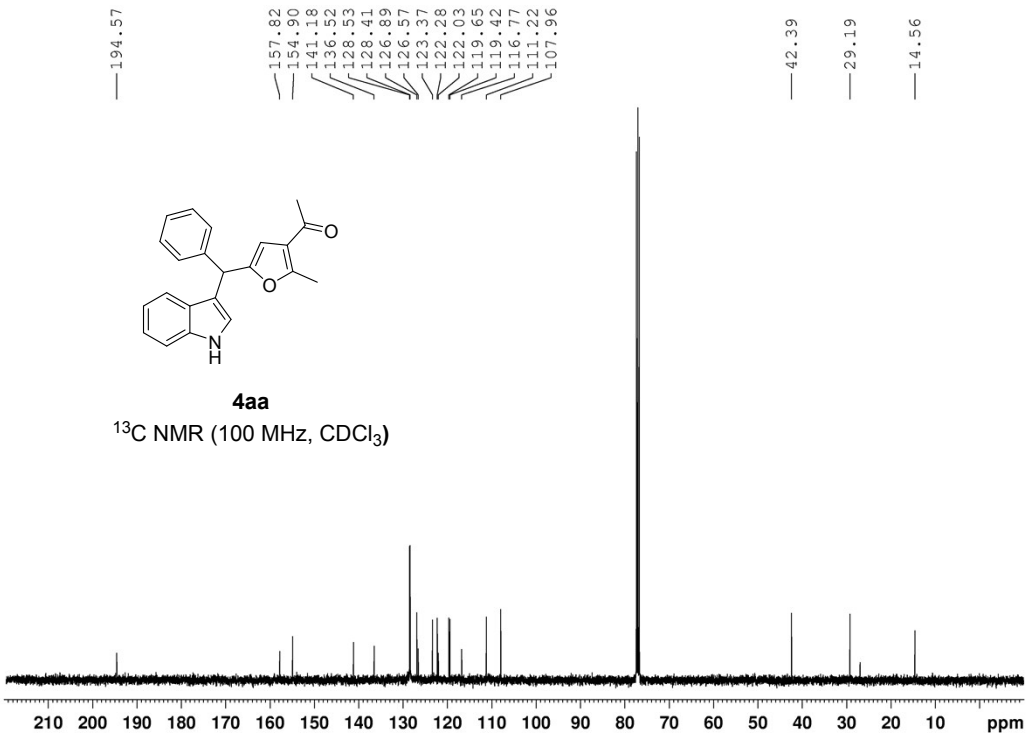
cis-**3jj**

^{13}C NMR (100 MHz, $CDCl_3$)



4aa

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



4aa

^{13}C NMR (100 MHz, $CDCl_3$)