Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Enantioselective Construction of 2,2'-Bisindolylmethane Scaffold via Catalytic Asymmetric Reactions of 2-Indolylmethanols with 3-Alkylindoles

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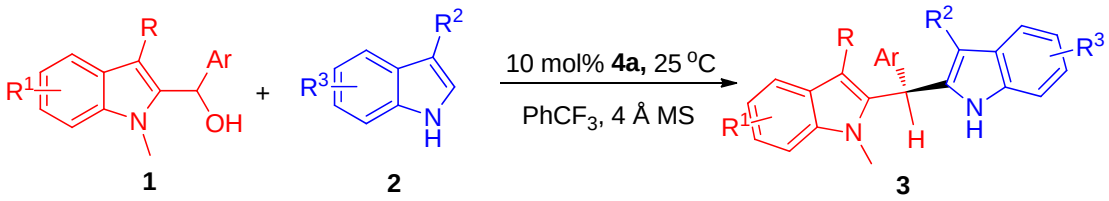
Contents:

General information:

^{1}H and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a micrOTOF-Q Ⅱ HRMS/MS instrument (Bruker). Enantiomeric ratios (er) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak OD-H columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. Analytic grade solvents for the column chromatography and commercially available reagents were used as received. All starting materials commercially available were used directly. Substrates **1** were synthesized according to the literature method.[1]

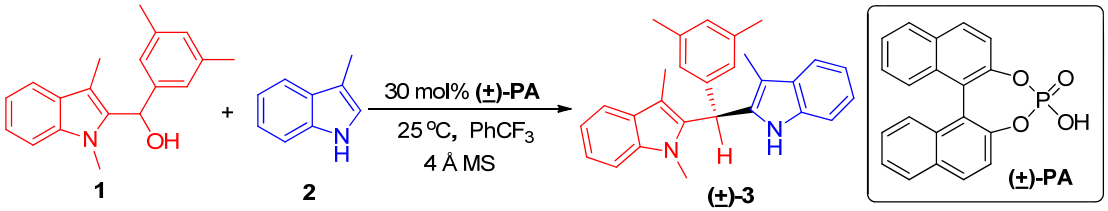
General procedure for the catalytic asymmetric reactions of 2-indolylmethanols with 3-alkylindoles:



Benzotrifluoride (0.5 mL) was added to the mixture of 2-indolylmethanols **1** (0.05 mmol), 3-alkylindoles **2** (0.05 mmol), the catalyst **4a** (0.005 mmol), and 4 Å molecular sieves (50 mg). After being stirred at 25 °C for 16 h, the reaction mixture was filtered to remove the molecular sieves, and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure products **3**.

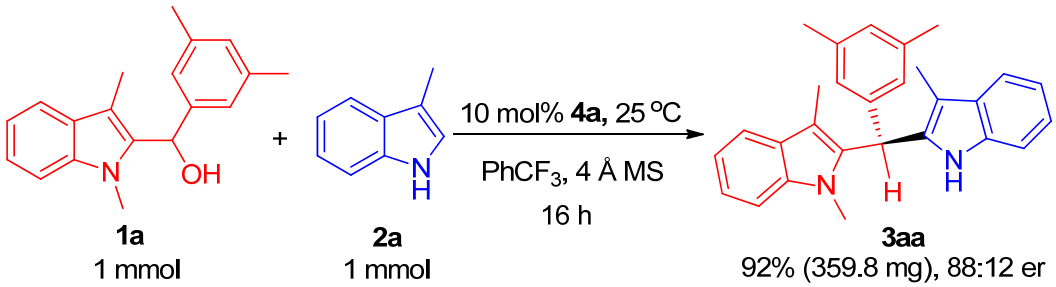
[1] S. Qi, C. Y. Liu, J. Y. Ding, F. S. Han, *Chem. Commun*. **2014**, *50*, 8605.

General procedure for the synthesis of racemic products:



Benzotrifluoride (0.5 mL) was added to the mixture of 2-indolylmethanols **1** (0.05 mmol), 3-alkylindoles **2** (0.05 mmol), the racemic phosphoric acid **(±)-PA** (0.015 mmol), and 4 Å molecular sieves (50 mg). After being stirred at 25 °C for 16 h, the reaction mixture was filtered to remove the molecular sieves, and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure products **(±)-3**. These products were used as racemic standards for HPLC determination.

Procedure for large scale synthesis of product 3aa:



Benzotrifluoride (5 mL) was added to the mixture of 2-indolylmethanol **1a** (1 mmol), 3-methylindole **2a** (1 mmol), the catalyst **4a** (0.1 mmol), and 4 Å molecular sieves (250 mg). After being stirred at 25 °C for 16 h, the reaction mixture was filtered to remove the molecular sieves, and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure product **3aa**.

Characterization of products:

(*S*)-2-((3,5-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-1,3-dimethyl-1H-indole (3aa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 90% (17.7 mg); pale yellow solid; m.p. 78-80 ^{o}C; $[\alpha]_D^{20}$ = -2.2(c 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 3H), 7.34 – 7.27 (m, 2H), 7.25 (s, 1H), 7.20 – 7.14 (m, 3H), 6.96 (s, 1H), 6.83 (s, 2H), 6.03 (s, 1H), 3.56 (s, 3H), 2.30 (s, 6H), 2.20 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.4, 135.7, 133.9, 133.6, 131.7, 128.5, 127.8, 127.7, 125.3, 120.4, 120.3, 118.2, 117.8, 117.4, 117.3, 109.8, 108.0, 107.8, 107.4, 39.6, 29.1, 20.3, 7.6, 7.5; IR (KBr): 3436, 3053, 2961, 2917, 2850, 2359, 1600, 1459, 1100, 1013, 803, 737 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{28}N_2\text{-}H)^-$ requires m/z 391.2174, found m/z 391.2188; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 5.153 (major), t_R = 5.770 (minor).

(*S*)-1,3-dimethyl-2-((3-methyl-1H-indol-2-yl)(phenyl)methyl)-1H-indole (3ba): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 98% (17.9 mg); pale yellow solid; m.p. 96-98 ^{o}C; $[\alpha]_D^{20}$ = -11.6 (c 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 3H), 7.36 (d, *J* = 4.7 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.31 (t, *J* = 4.3 Hz, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.25 – 7.22 (m, 1H), 7.20 (d, *J* = 1.3 Hz, 1H), 7.18 (s, 1H), 7.18 – 7.15 (m, 2H), 7.15 – 7.12 (m, 1H), 6.09 (s, 1H), 3.57 (s, 3H), 2.20 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.7, 134.0, 133.6, 131.3, 128.5, 127.8, 127.7, 127.6, 126.1, 120.6, 120.5, 118.3, 117.9, 117.4, 117.3, 109.8, 108.1, 107.8, 107.5, 39.7, 29.0, 7.7, 7.6; IR (KBr): 3435, 2917, 2855, 2360, 2340, 1600, 1458, 1101, 739, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}N_2\text{-}H)^-$ requires m/z 363.1856, found m/z 363.1880; Enantiomeric ratio: 81:19, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 6.957 (major), t_R = 8.433 (minor).

(*S*)-1,3-dimethyl-2-((3-methyl-1H-indol-2-yl)(m-tolyl)methyl)-1H-indole (3ca): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 74% (14.0 mg); pale yellow solid; m.p. 80-82 ^{o}C; $[\alpha]_D^{20}$ =-1.9 (c 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 9.0, 5.9 Hz, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.17 – 7.10 (m, 4H), 7.03 (s, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.04 (s, 1H), 3.55 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.5, 135.7, 133.9, 133.7, 131.5, 128.5, 128.2, 127.7, 127.6, 126.9, 124.7, 120.5, 120.4, 118.2, 117.8, 117.4, 117.3, 109.8, 108.0, 107.8, 107.5, 39.6, 29.0, 20.5, 7.7, 7.6; IR (KBr): 3435, 2963, 2918, 2855, 1604, 1459, 1262, 1096, 1020, 738 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{26}N_2\text{-}H)^-$ requires m/z 377.2018, found m/z 377.2012; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T =30 ^{o}C, 254 nm): t_R = 6.010 (major), t_R =7.040 (minor).

(*S*)-1,3-dimethyl-2-((3-methyl-1H-indol-2-yl)(p-tolyl)methyl)-1H-indole (3da): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h ; yield: 89% (16.8 mg); pale yellow solid; m.p. 177-179 ^{o}C; $[\alpha]_D^{20}$ =-1.8 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.8, 4.6 Hz, 3H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.17 – 7.11 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.03 (s, 1H), 3.54 (s, 3H), 2.37 (s, 3H), 2.17 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.5, 133.9, 133.7, 131.6, 128.5, 128.5, 127.7, 127.5, 120.5, 120.4, 118.2, 117.8, 117.4, 117.3, 109.8, 108.0, 107.8, 107.4, 39.3, 29.0, 20.1, 7.7, 7.5. IR (KBr): 3411, 3047, 2962, 2921, 2854, 1721, 1612, 1261, 1097, 1014, 803, 744 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{26}N_2\text{-}H)^-$ requires m/z 377.2018, found m/z 377.2010. Enantiomeric ratio: 84:16, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 6.043 (major), t_R = 7.013 (minor).

(*S*)-2-((3,4-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-1,3-dimethyl-1H-indole (3ea): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h ; yield: 98% (19.2 mg); pale yellow solid; m.p. 179-181 ^{o}C; $[\alpha]_D^{20}$ =-1.8 (c 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 3H), 7.28

(d, *J* = 8.0 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.11 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.01 (s, 1H), 3.54 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.8, 135.7, 134.4, 133.8, 133.8, 131.8, 129.0, 128.7, 128.5, 127.7, 124.9, 120.4, 120.3, 118.2, 117.7, 117.4, 117.3, 109.7, 107.9, 107.8, 107.3, 39.3, 29.1, 18.8, 18.4, 7.6, 7.5; IR (KBr):3436, 2963, 2922, 2854, 1600, 1262, 1096, 1020, 800, 736 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{28}N_2\text{-}H)^-$ requires m/z 391.2174, found m/z 391.2174; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 5.510 (major), t_R = 6.270 (minor).

(*S*)-5-bromo-2-((3,5-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-1,3-dimeth yl-1H-indole (3fa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h ; yield: 70% (16.5 mg); pale yellow solid; m.p. 88-90 ^oC; $[\alpha]_D^{20}$ =-18.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 – 7.11 (m, 3H), 6.93 (s, 1H), 6.80 (s, 2H), 5.99 (s, 1H), 3.54 (s, 3H), 2.26 (s, 6H), 2.17 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.4, 135.7, 133.9, 133.8, 131.7, 128.5, 127.8, 127.7, 125.3, 120.4, 120.3, 118.2, 117.8, 117.4, 117.3, 109.8, 108.0, 107.8, 107.4, 39.6, 29.1, 20.4, 7.6, 7.6.; IR (KBr): 3436, 2962, 2924, 2853, 2360, 1609, 1261, 1069, 1021, 737 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{27}BrN_2\text{-}H)^-$ requires m/z 469.1280, found m/z 469.1280; Enantiomeric ratio: 88:12, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 5.120 (major), t_R = 5.770 (minor).

(*S*)-2-((3,5-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-1,3,6-trimethyl-1H-i ndole (3ga): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h ; yield: 76% (15.5 mg); pale yellow solid; m.p. 201-203 ^oC; $[\alpha]_D^{20}$ = -18.5 (c 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 10.0, 6.9 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.14 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.08 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.93 (s, 1H), 6.80 (s, 2H), 5.97 (s, 1H), 3.50 (s, 3H), 2.52 (s, 3H), 2.26 (s, 6H), 2.16 (s, 3H), 1.79 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$)

δ 138.5, 137.3, 136.1, 133.8, 133.1, 131.8, 130.3, 128.5, 127.7, 125.6, 125.3, 120.2, 119.5, 18.1, 117.3, 117.1, 109.8, 107.9, 107.8, 107.3, 39.6, 29.0, 20.9, 20.3, 7.7, 7.5; IR(KBr): 3419, 2963, 2915, 2855, 1599, 1460, 1261, 1097, 803, 739 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{30}N_2\text{-}H)^-$ requires m/z 405.2331, found m/z 405.2369; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 5.493 (major), t_R = 6.260 (minor).

(*S*)-2-((3,5-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-1,3,7-trimethyl-1H-indole (3ha): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 80% (16.2 mg); pale yellow solid; m.p. 89-91^oC; $[\alpha]_D^{20}$ = -5.3 (c 0.13, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.24 (dd, *J* = 5.8, 3.0 Hz, 1H), 7.19 – 7.09 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 4.5 Hz, 2H), 6.80 (s, 2H), 5.96 (s, 1H), 3.81 (s, 3H), 2.75 (s, 3H), 2.26 (s, 6H), 2.17 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.3, 134.6, 134.2, 133.9, 131.7, 128.5, 128.4, 127.7, 125.3, 123.8, 120.3, 119.6, 118.1, 117.8, 117.3, 115.5, 109.8, 108.4, 107.3, 39.6, 31.9, 20.4, 19.7, 7.7, 7.6; IR (KBr): 3439, 2963, 2916, 2856, 1600, 1459, 1262, 1101, 1022, 801, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{30}N_2\text{-}H)^-$ requires m/z 405.2331, found m/z 405.2337; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.397 (minor), t_R = 4.877 (major).

(*S*)-2-((3,5-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-3-ethyl-1-methyl-1H-indol (3ia): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 80% (16.2 mg); pale yellow solid; m.p. 211-213 ^oC; $[\alpha]_D^{20}$ = -6.0 (c 0.12, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.17 – 7.09 (m, 3H), 6.92 (s, 1H), 6.80 (s, 2H), 6.04 (s, 1H), 3.49 (s, 3H), 2.40 (d, *J* = 7.3 Hz, 2H), 2.25 (s, 6H), 2.15 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.3, 136.0, 133.9, 133.3, 131.7, 128.5, 127.7, 126.8, 125.3, 120.4, 120.3, 118.2, 117.8, 117.8, 117.3, 114.9, 109.8, 108.0, 107.4, 39.4, 29.3, 20.3, 16.4, 14.2, 7.7;

IR (KBr): 3435, 3051, 2961, 2920, 2851, 1616, 1262, 1102, 1013, 807 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{30}N_2\text{-}H)^-$ requires m/z 405.2331, found m/z 405.2344; Enantiomeric ratio: 83:17, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol= 85/15, flowrate 1.0mL/min, T= 30°C, 254 nm): t_R = 5.883 (major), t_R = 6.727 (minor).

(*S*)-2-((1,3-dimethyl-1H-indol-2-yl)(3,5-dimethylphenyl)methyl)-5-methoxy-3-methyl-1H-indole (3ab): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 72% (17.0 mg); pale yellow solid; m.p. 85-87 °C; $[\alpha]_D^{20}$ = -16.7 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.31 (s, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.96 (s, 1H), 6.79 (s, 2H), 5.97 (s, 1H), 3.54 (s, 3H), 2.28 (s, 6H), 2.12 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.5, 135.7, 133.3, 133.2, 132.4, 130.3, 128.0, 127.7, 125.3, 123.1, 120.6, 120.0, 117.8, 117.4, 111.5, 111.2, 108.1, 107.8, 107.1, 39. 6, 29.0, 28.7, 20.4, 7.6, 7.5; IR (KBr): 3435, 2963, 2922, 2853, 1600, 1464, 1262, 1197, 1021, 800, 738 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{27}BrN_2\text{-}H)^-$ requires m/z 469.1280, found m/z 469.1286; Enantiomeric ratio: 81:19, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.130 (minor), t_R = 7.230 (major).

(*S*)-2-((3,5-dimethylphenyl)(3-methyl-1H-indol-2-yl)methyl)-4-methoxy-3-methyl-1H-indole (3ac): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h ; yield: 76% (16.1 mg); pale yellow solid; m.p. 80-82 °C; $[\alpha]_D^{20}$ = -33.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.39 (s, 1H), 7.27 (d, *J* = 6.5 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.12 (dd, *J* = 11.8, 5.4 Hz, 2H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.92 (s, 1H), 6.82 – 6.75 (m, 3H), 5.95 (s, 1H), 3.87 (s, 3H), 3.52 (s, 3H), 2.25 (s, 6H), 2.10 (d, *J* = 9.6 Hz, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 138.4, 137.4, 135.7, 133.7, 132.6, 129.0, 128.9, 127.8, 127.7, 125.3, 120.4, 117.7, 117.4, 110.5, 110.3, 108.0, 107.8, 107.2, 99.3, 54.9, 39.7, 29.1, 28.7, 20.4, 7.6, 7.6; IR (KBr): 3401, 2963, 2923, 2854, 1719, 1599, 1261, 1097,

1022, 800 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{30}N_2O\text{-}H)^-$ requires m/z 421.2274, found m/z 421.2276; Enantiomeric ratio: 78:22, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 6.207 (minor), t_R = 7.317 (major).

(*S*)-2-((3,5-dimethylphenyl)(3-ethyl-1H-indol-2-yl)methyl)-1,3-dimethyl-1H-indole (3ad): Flash column chromatography eluent, petroleum ether/ethyl acetate =30/1; Reaction time = 16 h; yield: 75% (15.2 mg); pale yellow solid; m.p. 90-92 ^oC; $[\alpha]_D^{20}$ = -15.5 (c 0.28, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.51 (s, 1H), 7.28 (s, 1H), 7.25 – 7.20 (m, 2H), 7.16 – 7.08 (m, 3H), 6.92 (s, 1H), 6.78 (s, 2H), 6.01 (s, 1H), 3.53 (s, 3H), 2.67 (d, *J* = 7.6 Hz, 2H), 2.25 (s, 6H), 1.80 (s, 3H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.3, 135.7, 134.1, 133.9, 131.1, 127.8, 127.6, 125.3, 120.4, 120.2, 118.1, 117.7, 117.7, 117.4, 113.9, 109.9, 108.0, 107.8, 39.5, 29.1, 20.3, 16.6, 13.7, 7.7; IR (KBr): 3429, 3052, 2962, 2918, 2855, 1610, 1261, 1099, 1013, 809, 738 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{30}N_2\text{-}H)^-$ requires m/z 405.2331, found m/z 405.2329; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 7.303 (major), t_R = 8.443 (minor).

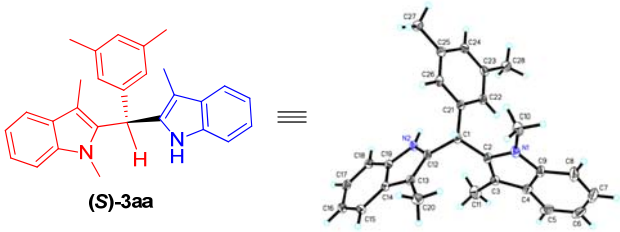
(*S*)-2-((1,3-dimethyl-1H-indol-2-yl)(p-tolyl)methyl)-5-methoxy-3-methyl-1H-indole (3cc): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 72% (14.7 mg); pale yellow solid; m.p. 75-77 ^oC; $[\alpha]_D^{20}$ =-6.1 (c 0.24, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.12 (dd, *J* = 11.4, 8.4 Hz, 4H), 7.03 (dd, *J* = 21.2, 5.2 Hz, 3H), 6.80 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.01 (s, 1H), 3.88 (s, 3H), 3.53 (s, 3H), 2.37 (s, 3H), 2.14 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 135.7, 135.5, 133.7, 132.6, 129.0, 128.9, 128.5, 127.7, 127.5, 120.5, 117.8, 117.4, 110.5, 110.3, 108.0, 107.8, 107.2, 99.3, 54.9, 39.4, 29.0, 20.1, 7.6; IR (KBr): 3436, 2920, 2855, 2360, 1624, 1598, 1483, 1215, 803, 738 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{28}N_2O\text{-}H)^-$ requires m/z 407.2124, found m/z 407.2127; Enantiomeric ratio: 77:23, determined by HPLC (Daicel Chirapak OD-H,

hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 7.530 (minor), t_R = 8.230 (major).

(*S*)-2-((3,5-dimethylphenyl)(3-ethyl-1H-indol-2-yl)methyl)-1,3,7-trimethyl-1H-indole (3hd): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 81% (17.1 mg); pale yellow solid; m.p. 179-181 ^{o}C; $[\alpha]_D^{20}$ = -22.7 (c 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 6.3, 2.6 Hz, 1H), 7.52 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.15 – 7.10 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.0 Hz, 2H), 6.78 (s, 2H), 5.97 (s, 1H), 3.81 (s, 3H), 2.74 (s, 3H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.24 (d, *J* = 8.1 Hz, 6H), 1.73 (s, 3H), 1.14 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.2, 134.4, 134.1, 131.1, 128.5, 127.7, 125.4, 123.8, 120.2, 119.6, 118.1, 117.8, 117.7, 115.5, 113.8, 109.9, 108.4, 39.5, 31.9, 20.3, 19.7, 16.6, 13.7, 7.8; IR (KBr): 3448, 2963, 2924, 2852, 1600, 1262, 1096, 1022, 807, 704 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{32}N_2\text{-}H)^-$ requires m/z 419.2487, found m/z 419.2509; Enantiomeric ratio: 84:16 , determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.180 (minor), t_R = 5.027 (major).

2-((1H-indol-2-yl)(phenyl)methyl)-3-methyl-1H-indole (8): Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1; Reaction time = 16 h; yield: 80% (13.4mg); pale yellow solid; m.p. 90-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.66 (s, 1H), 7.59 – 7.51 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 4H),7.23 (d, J = 7.2 Hz, 1H), 7.18–7.08 (m, 4H), 6.22 (s, 1H), 5.90 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.7, 136.2, 135.3, 133.3, 129.3, 128.9, 128.6, 128.4, 127.4, 121.9, 121.8, 120.4, 120.0, 119.4, 118.6, 110.8, 108.7, 102.6, 42.8, 8.6. IR(KBr): 3397, 3054, 2963, 2920, 1618, 1492, 1288, 1099, 1020, 741 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2\text{-}H)^-$ requires m/z 335.1548, found m/z 335.1550. Enantiomeric ratio: 53:47, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T =30 ^{o}C, 254 nm): t_R = 7.367(major), t_R =12.893(minor).

X-ray single crystal data for compound 3aa

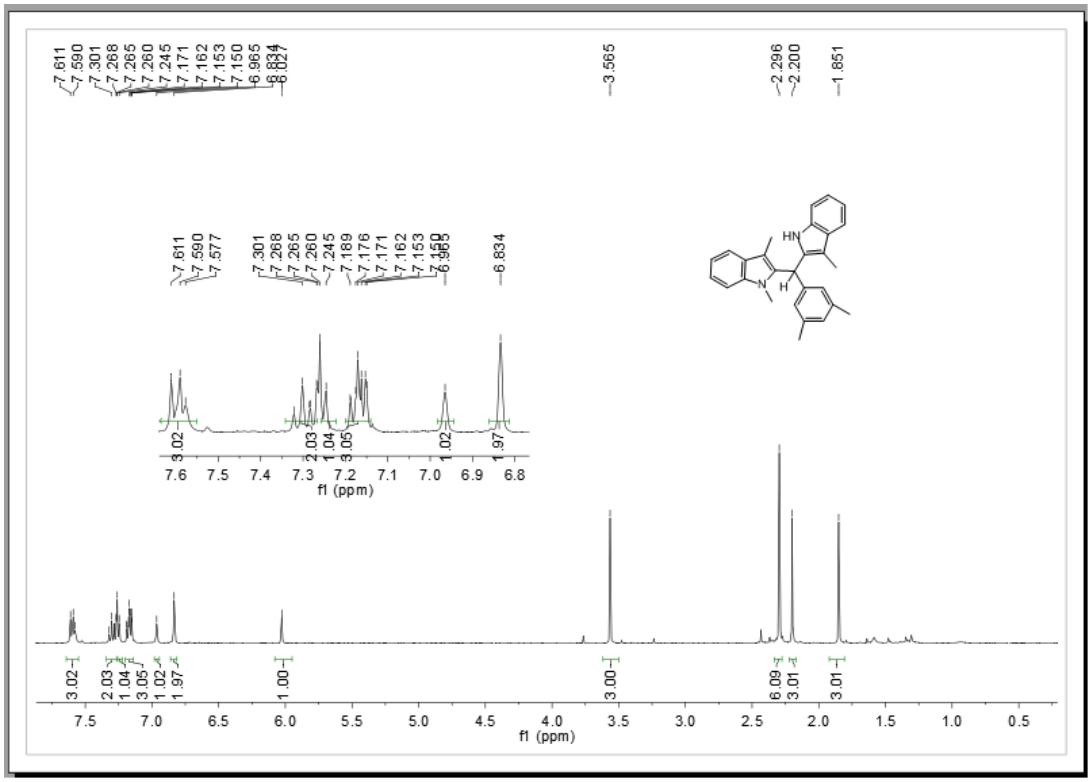


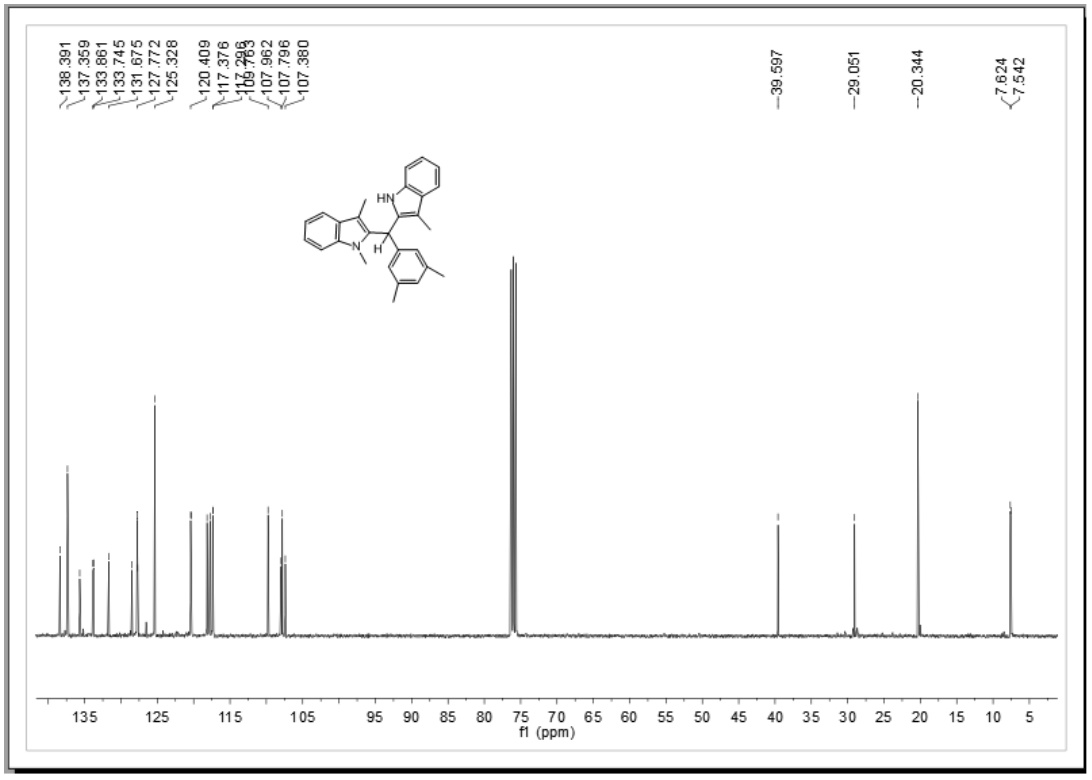
(*S*)-3aa

Empirical formula	C28 H28 N2	
Formula weight	392.52	
Temperature	130 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.20980(10) Å	α= 90°.
	b = 8.35700(10) Å	β= 105.3780(10)°.
	c = 14.8849(2) Å	γ = 90°.
Volume	1104.62(2) $Å^3$	
Z	2	
Density (calculated)	1.180 Mg/m^3	
Absorption coefficient	0.522 mm^{-1}	
F(000)	420	
Crystal size	0.15 x 0.1 x 0.06 mm^3	
Theta range for data collection	3.079 to 69.612°.	
Index ranges	-11<=h<=11, -10<=k<=8, -18<=l<=17	
Reflections collected	8154	
Independent reflections	3399 [R(int) = 0.0382]	
Completeness to theta = 67.679°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.5183	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3399 / 1 / 276	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1186	
R indices (all data)	R1 = 0.0446, wR2 = 0.1193	
Absolute structure parameter	0.1(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.232 and -0.203 $e.Å^{-3}$	

NMR Spectra of products

3aa





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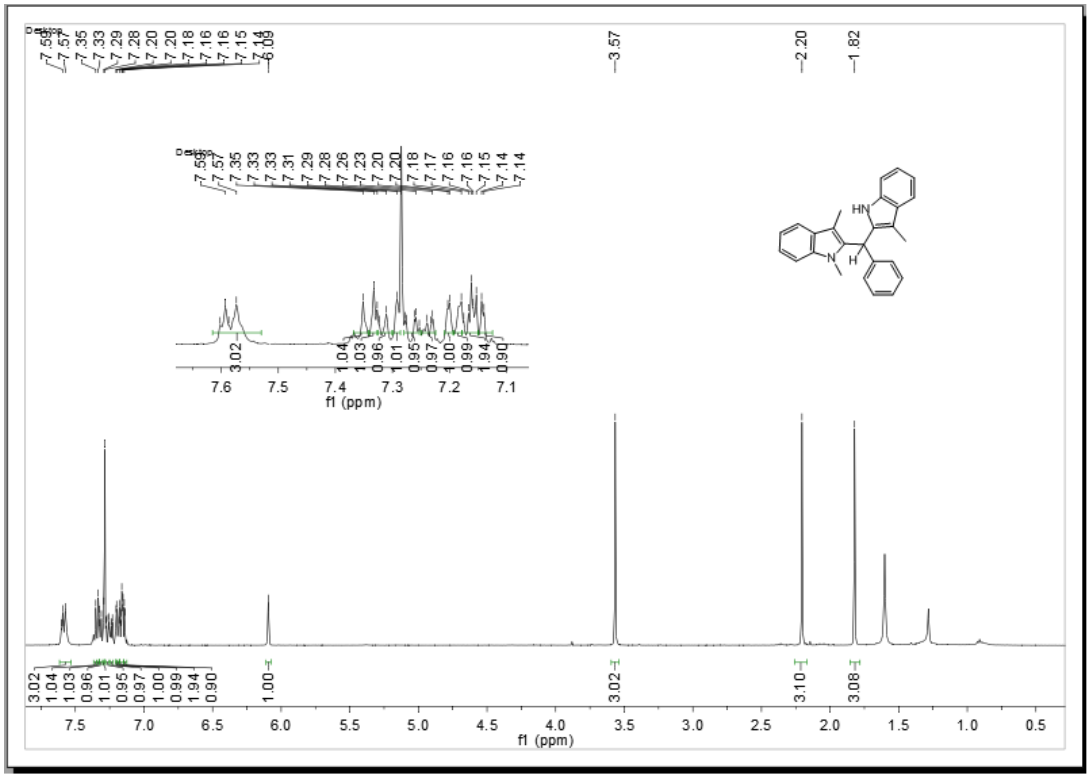
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1.82
HN
N
H
3.02
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1.03
0.96
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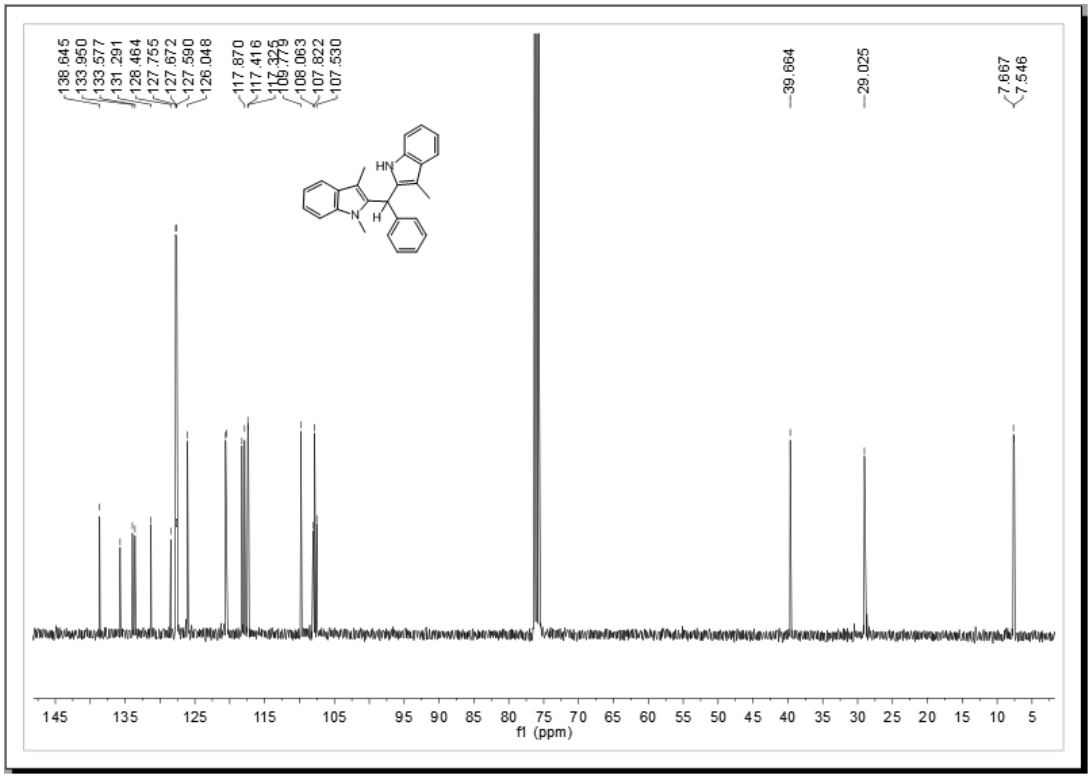
f1 (ppm)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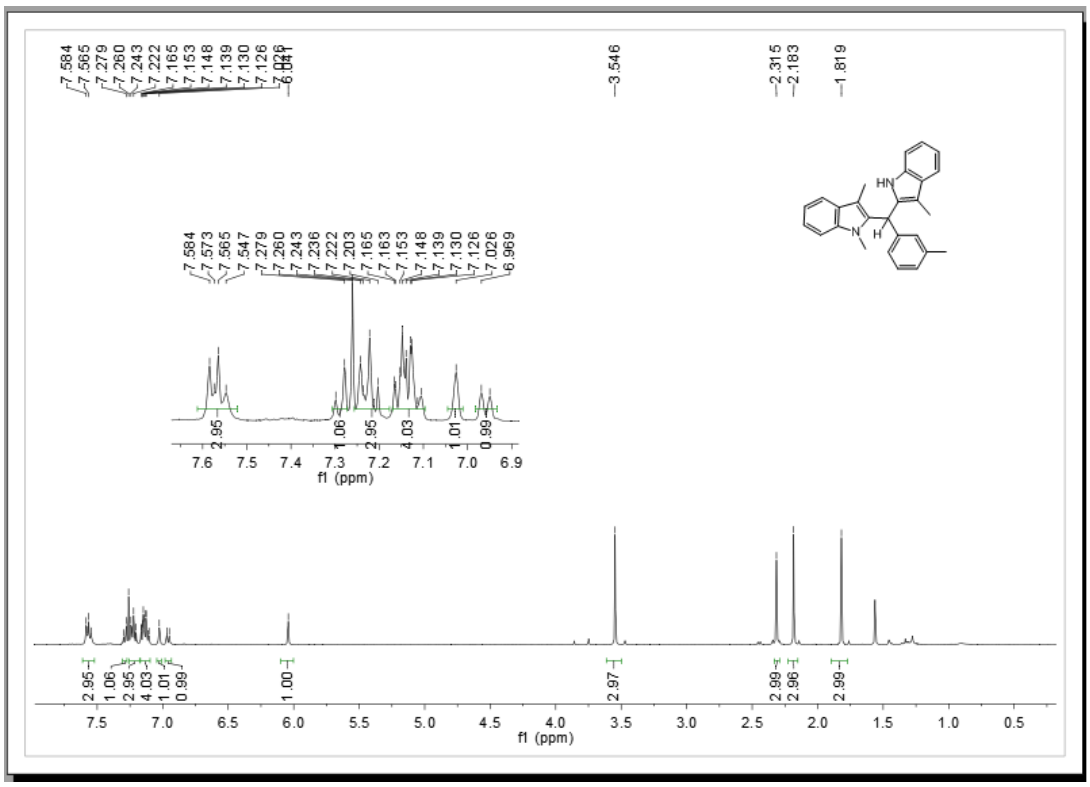
H
f1 (ppm)

3ca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H
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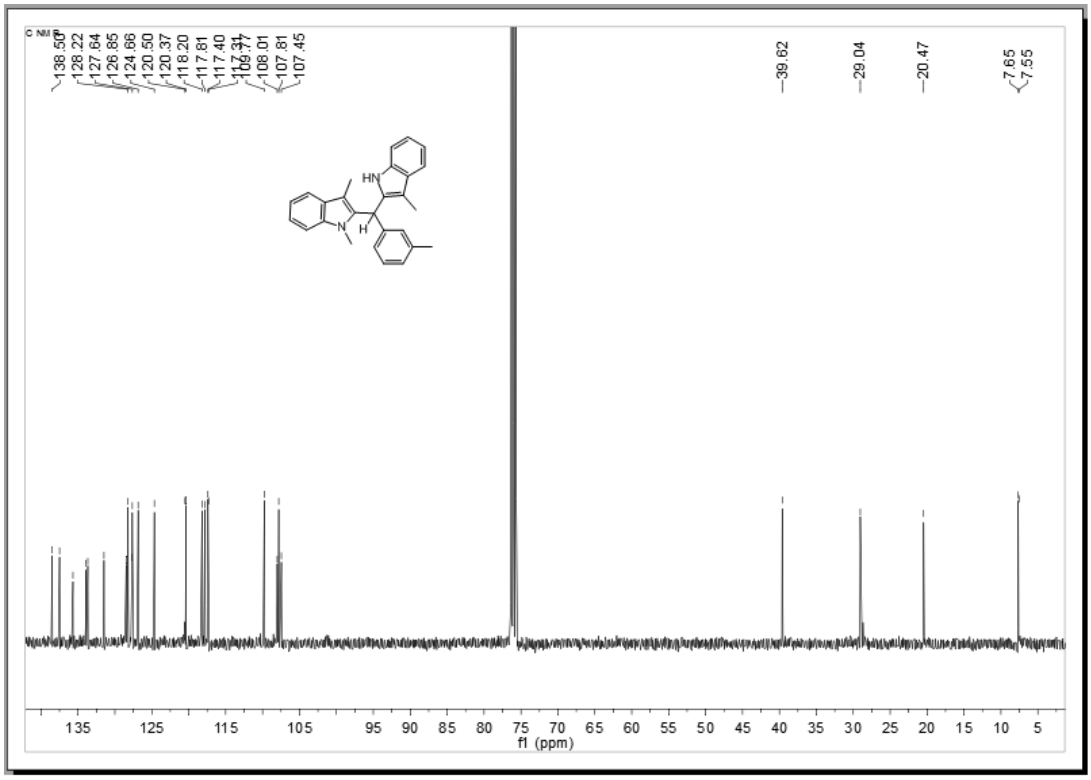
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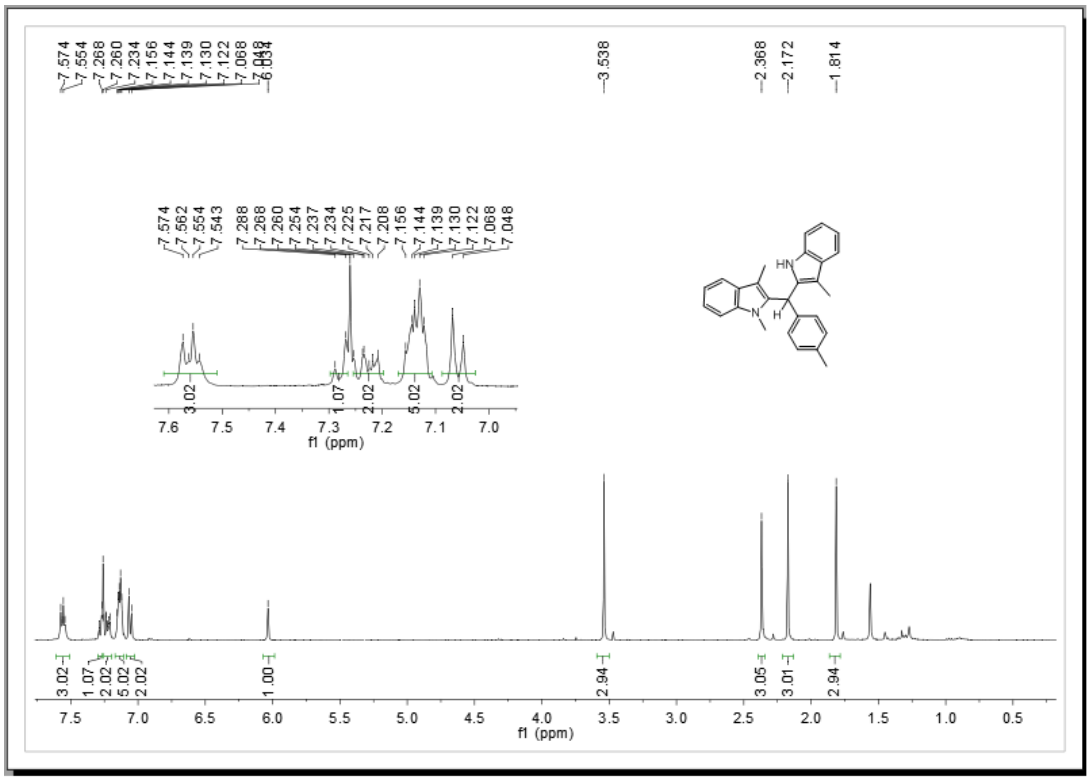
HN
N
H
f1 (ppm)

3da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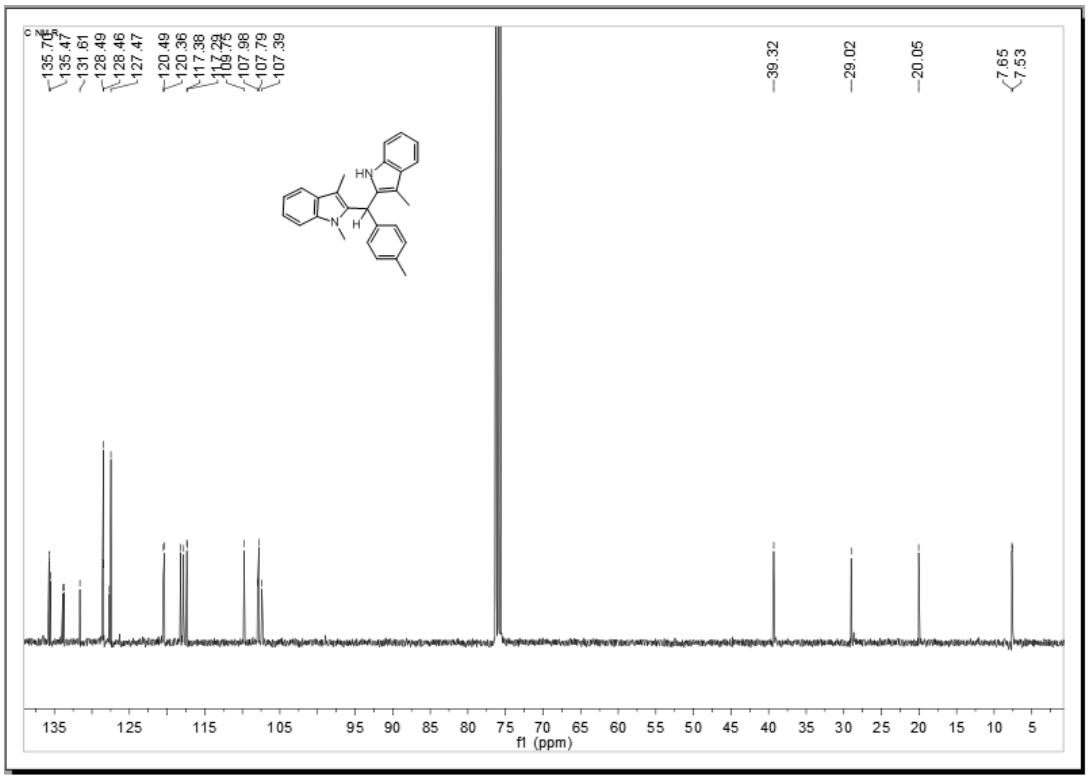
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7.53
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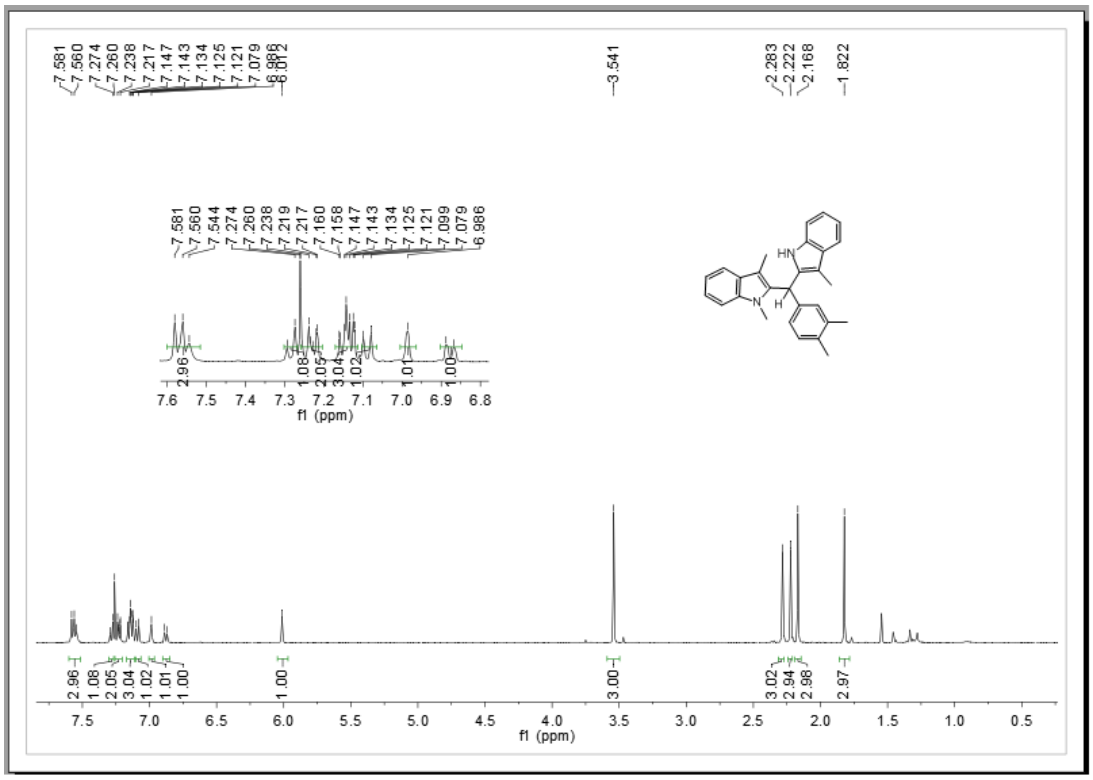
N
H
f1 (ppm)

3ea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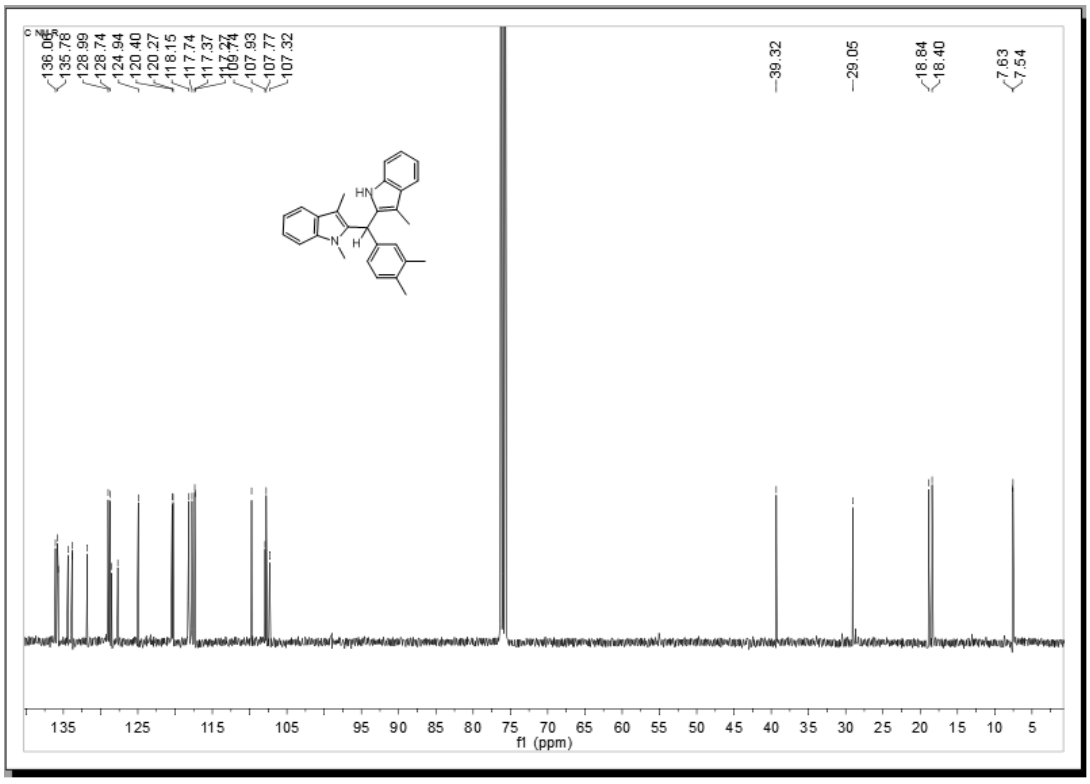
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7.54
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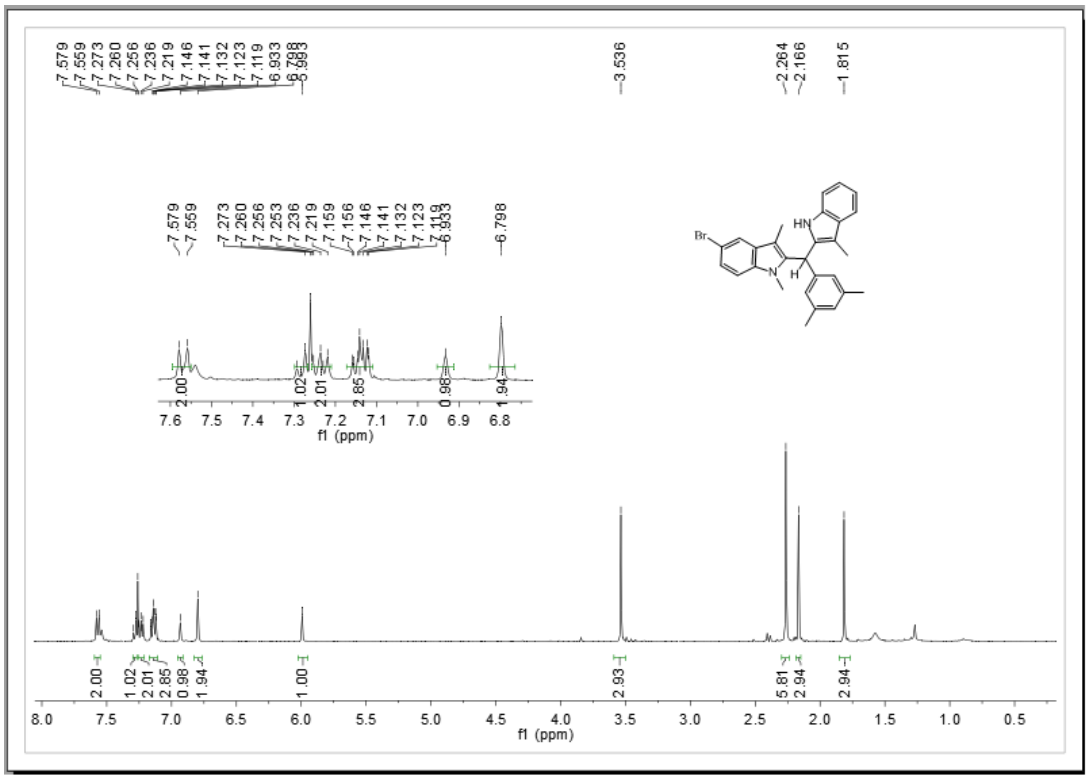
N
H
f1 (ppm)

3fa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N
H
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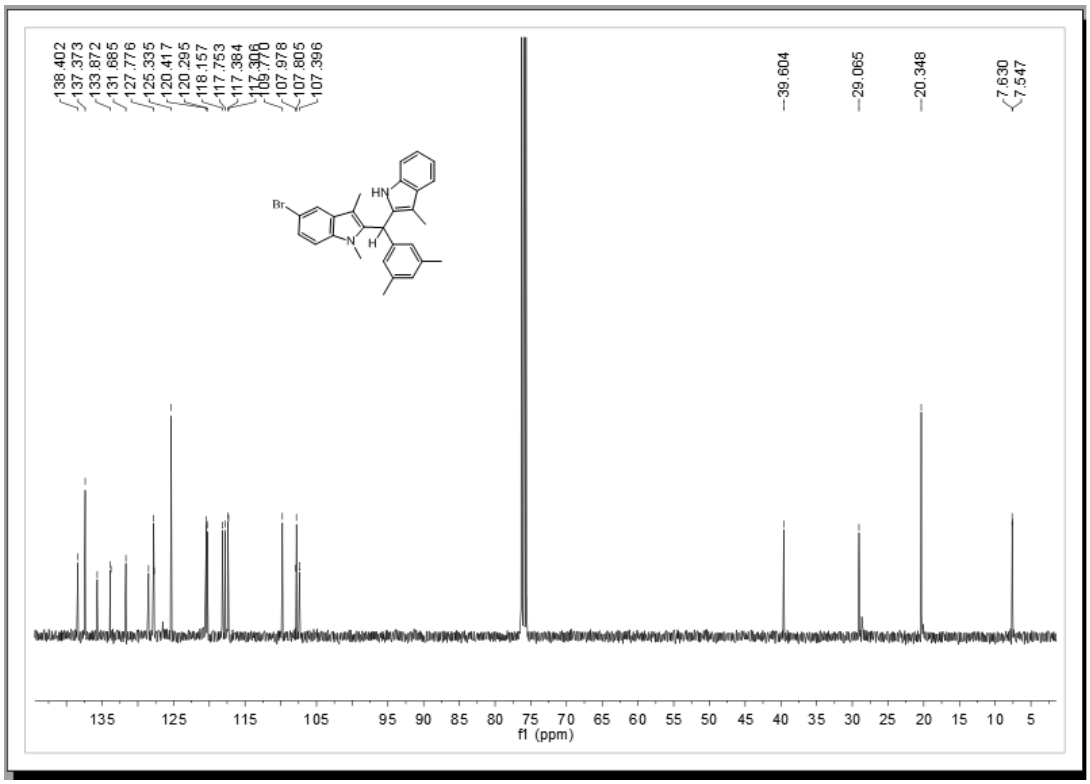
2.94
f1 (ppm)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H
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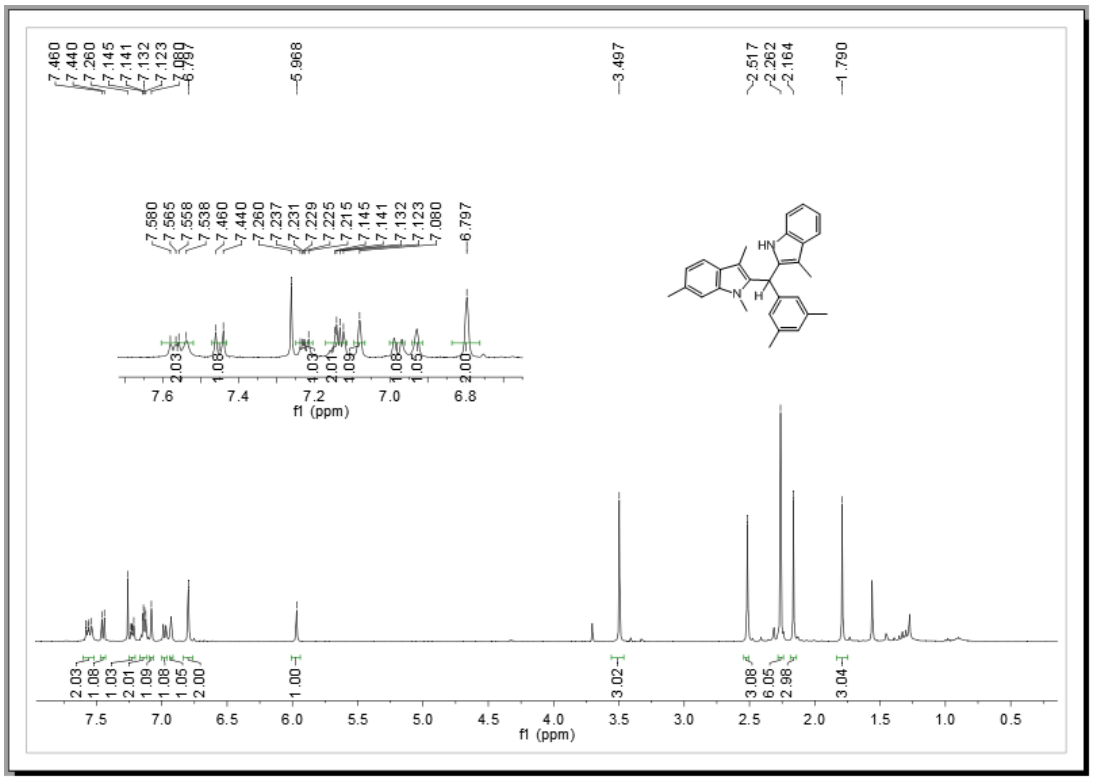
3ga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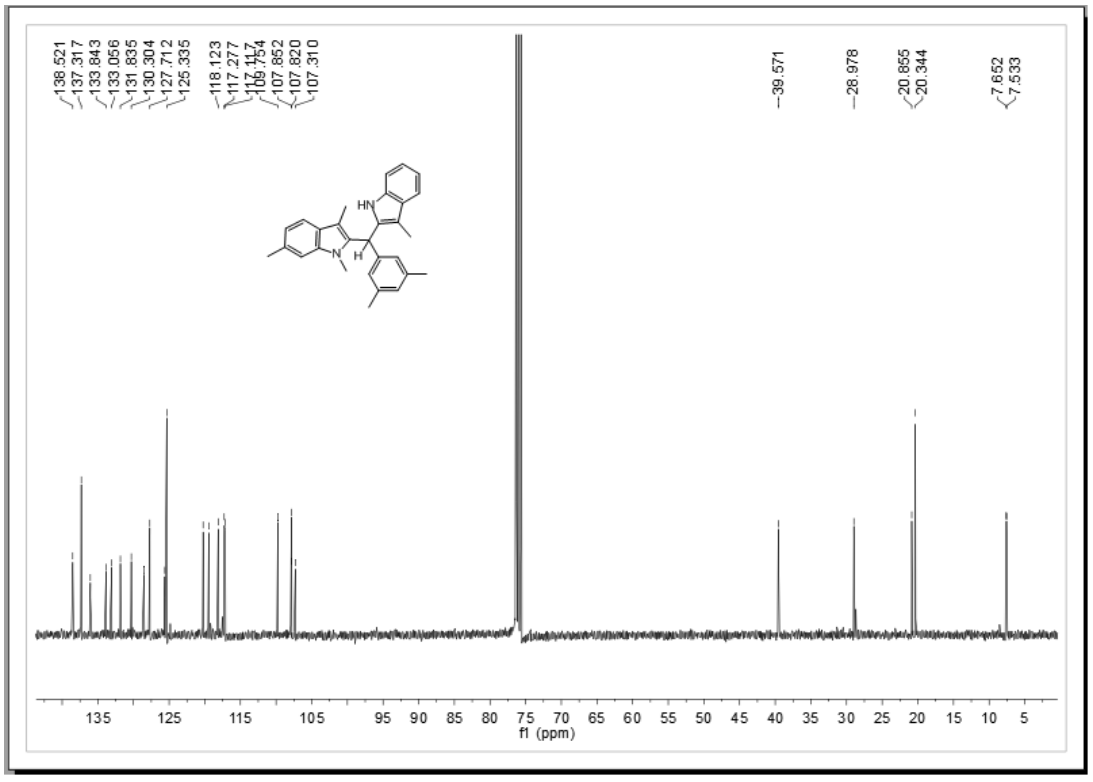
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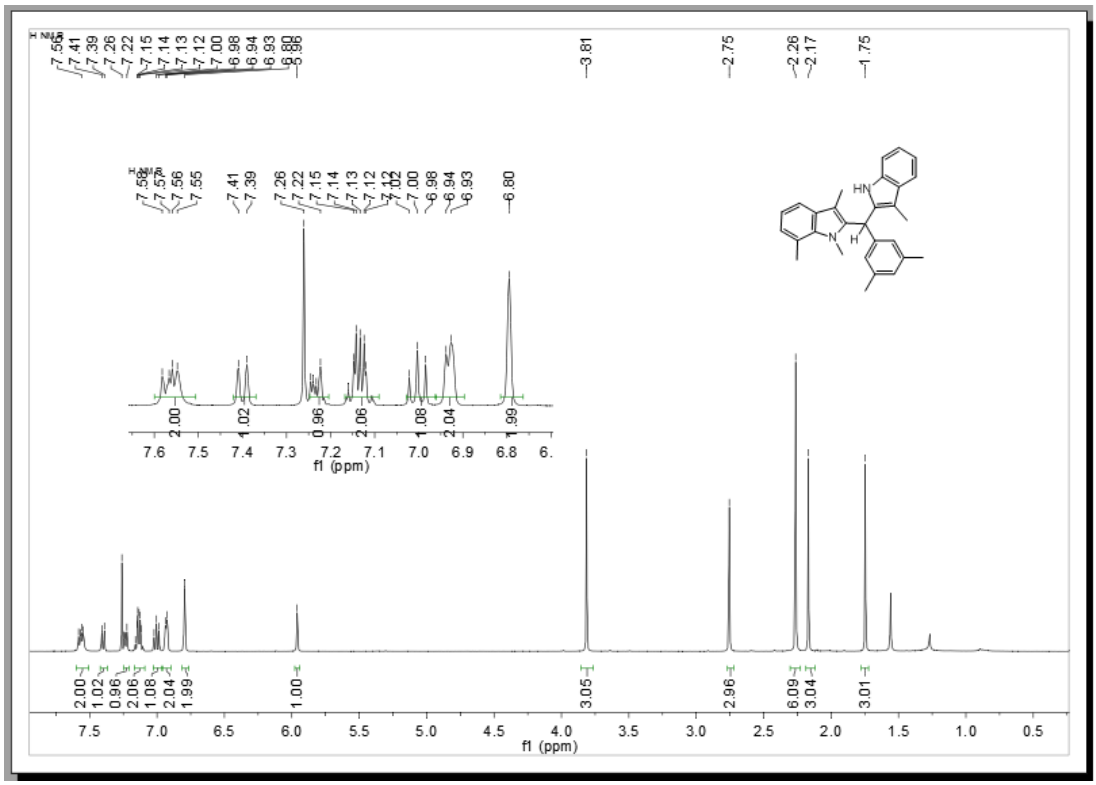
H
f1 (ppm)

3ha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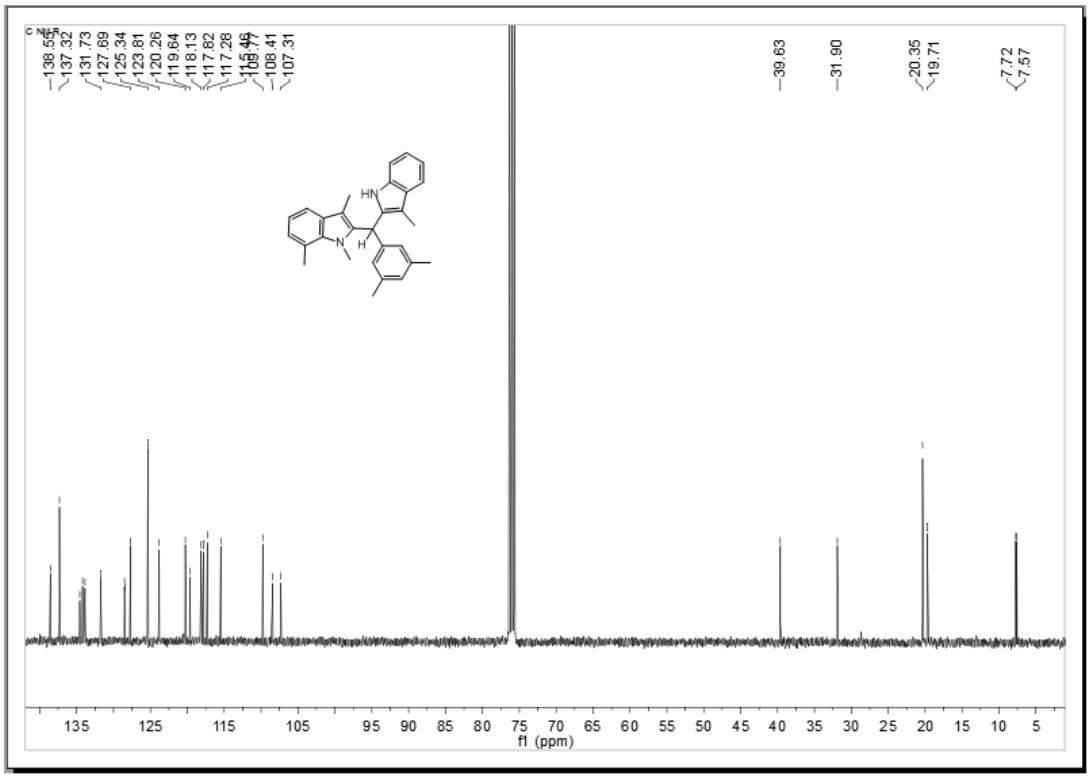
f1 (ppm)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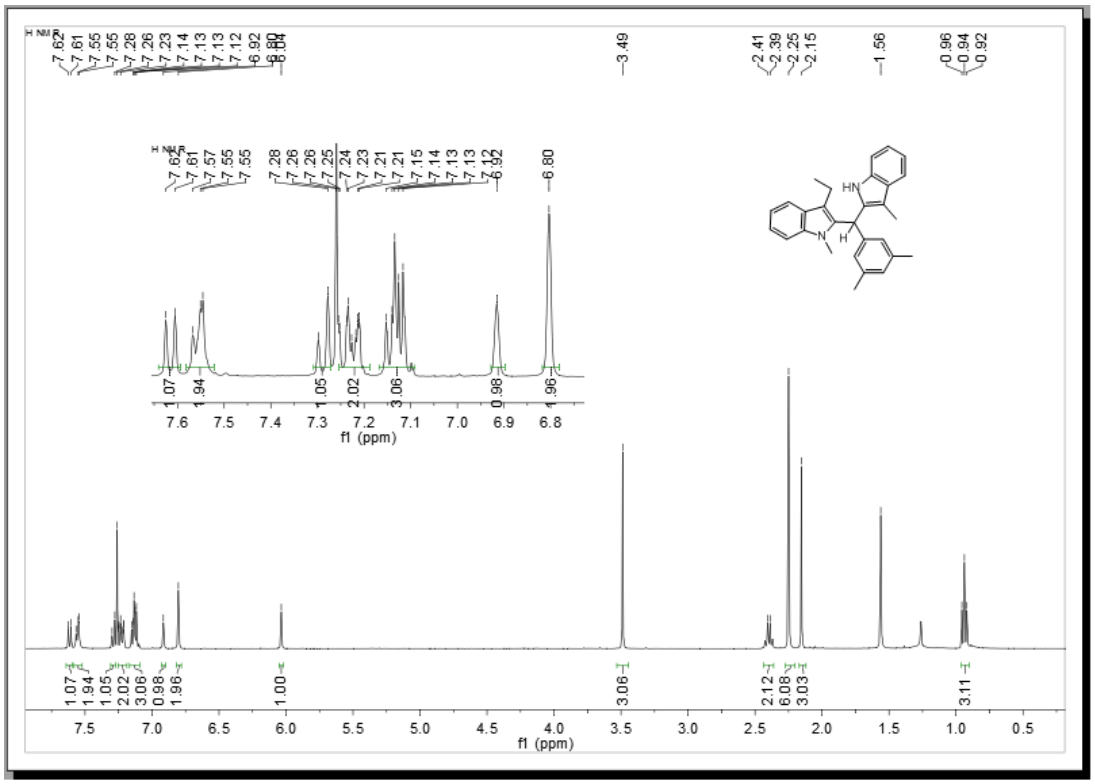
H
f1 (ppm)

3ia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0.94
0.92
HN
N
H
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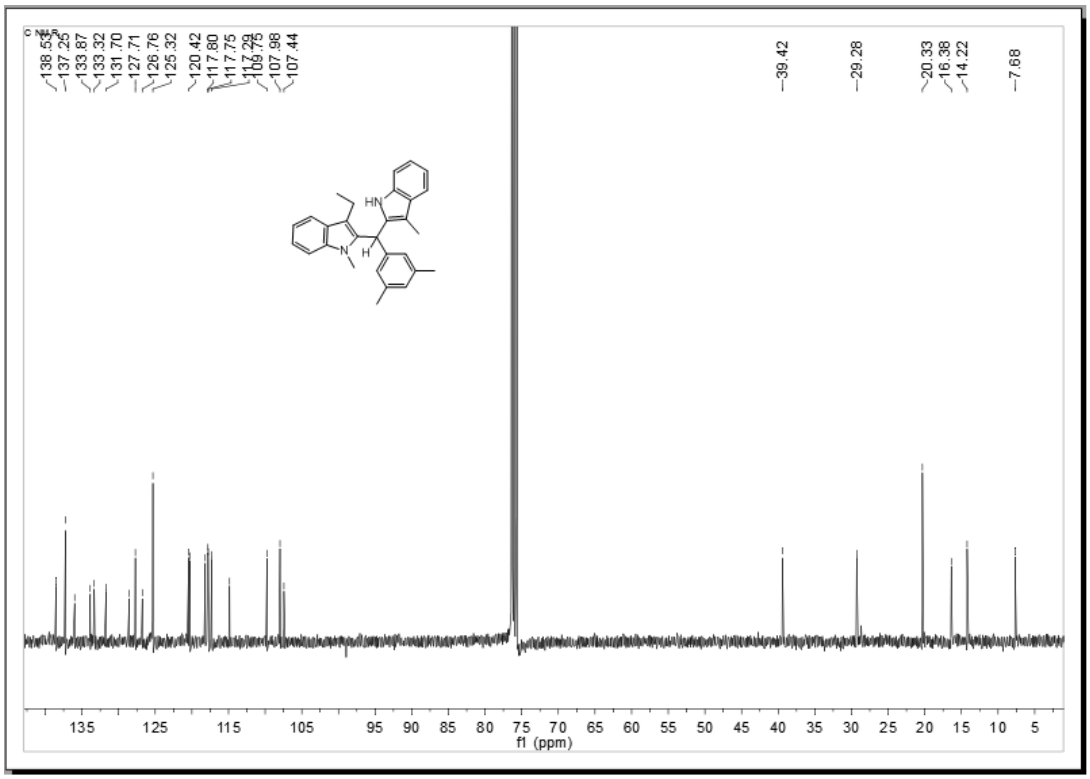
f1 (ppm)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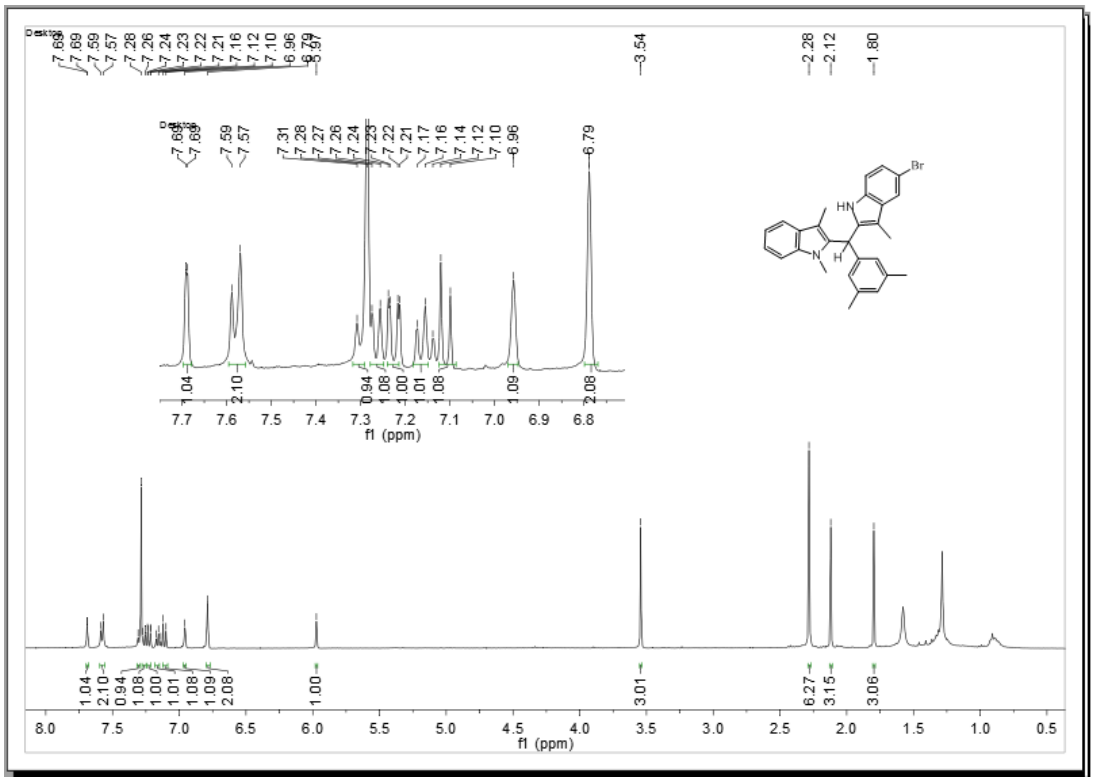
3ab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N
H
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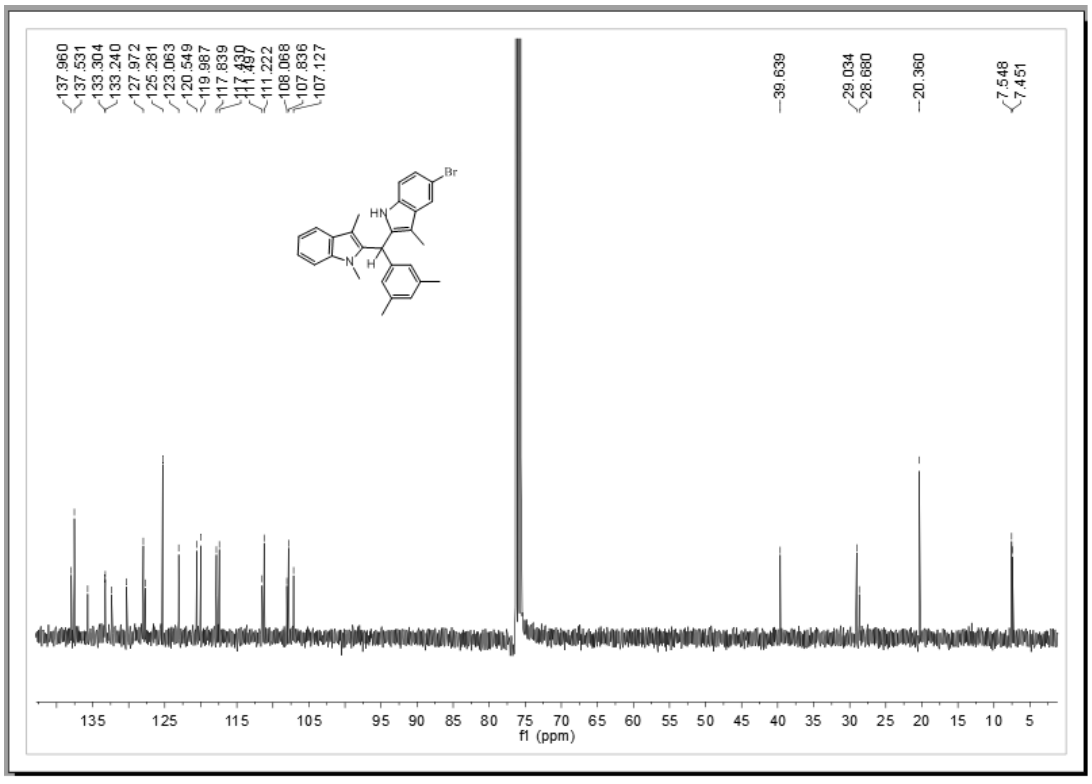
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111.222
108.068
107.836
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20.360
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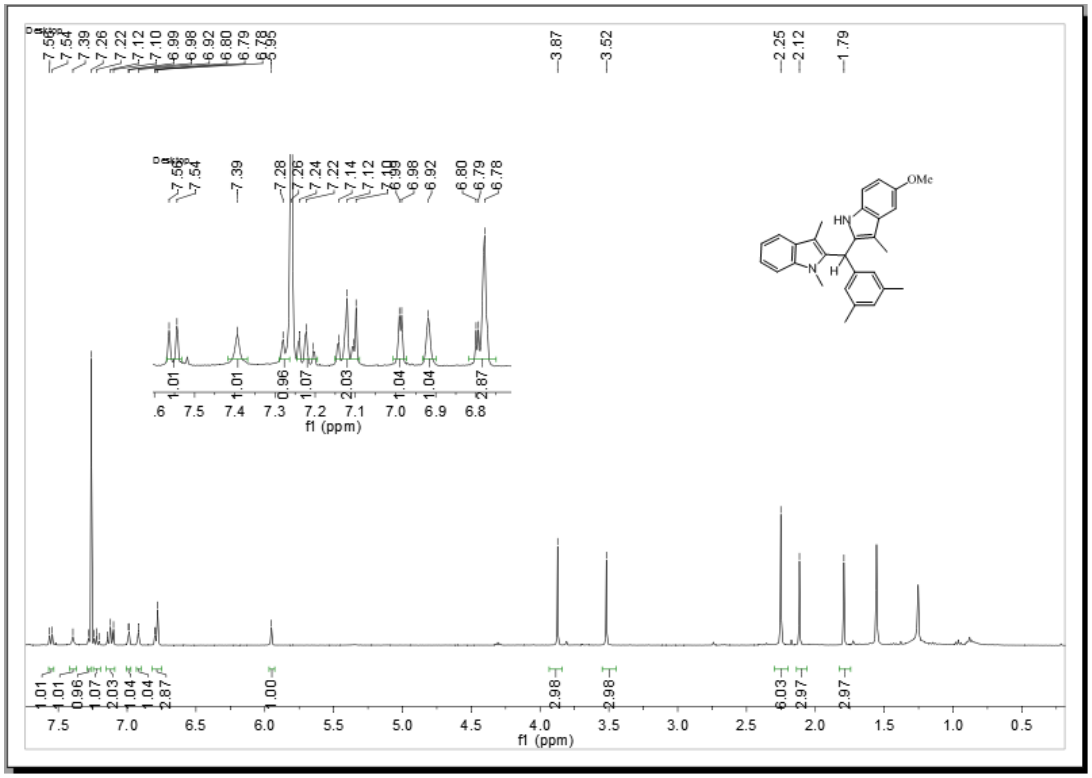
7.451
Br
HN
N
H
f1 (ppm)

3ac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5.95
3.87
3.52
2.25
2.12
1.79
OMe
HN
N
H
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1.01
0.96
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2.98
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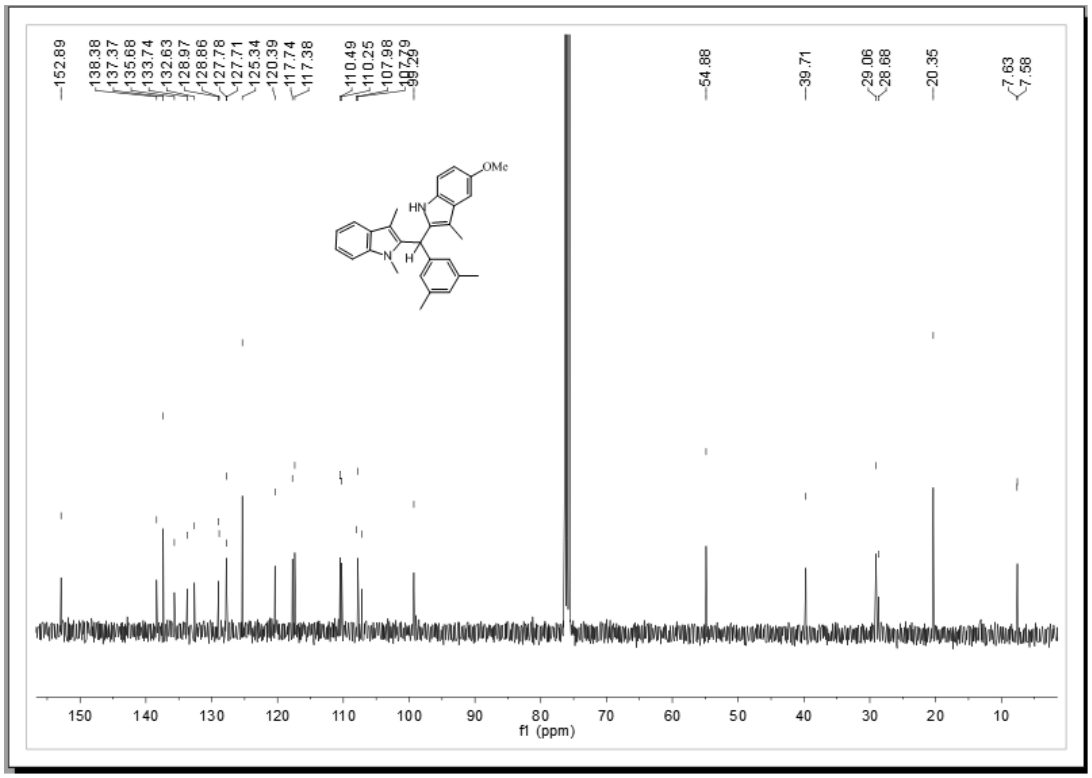
2.97
f1 (ppm)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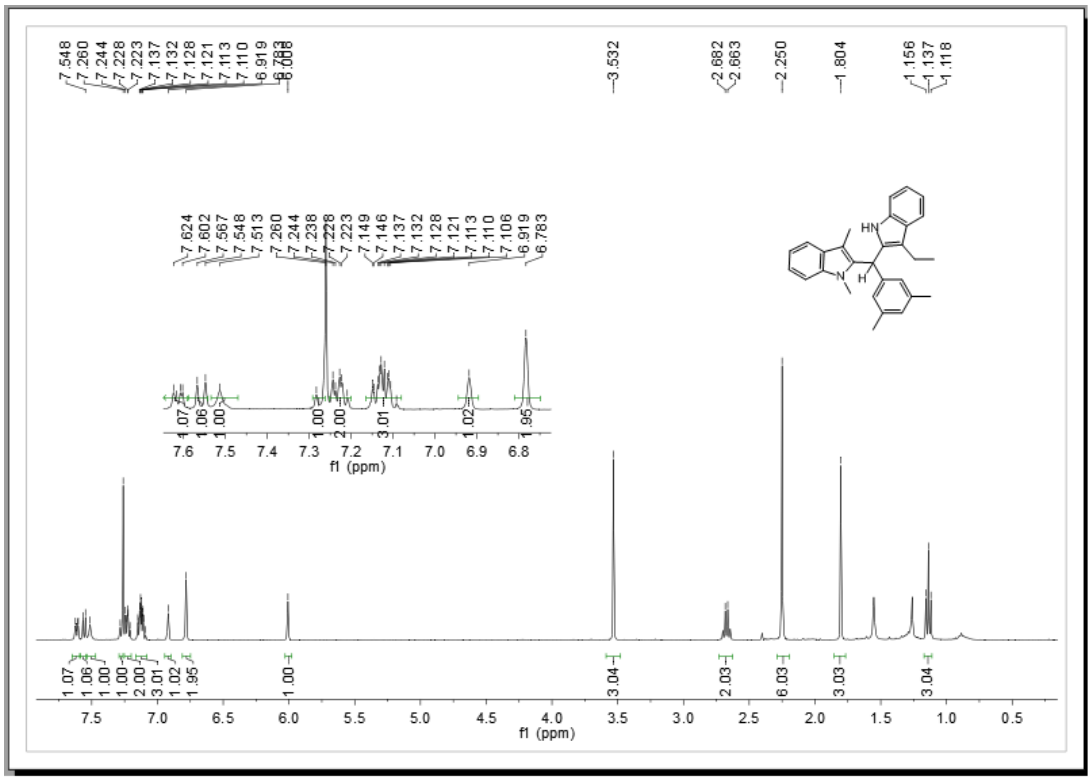
OMe
HN
N
H
f1 (ppm)

3ad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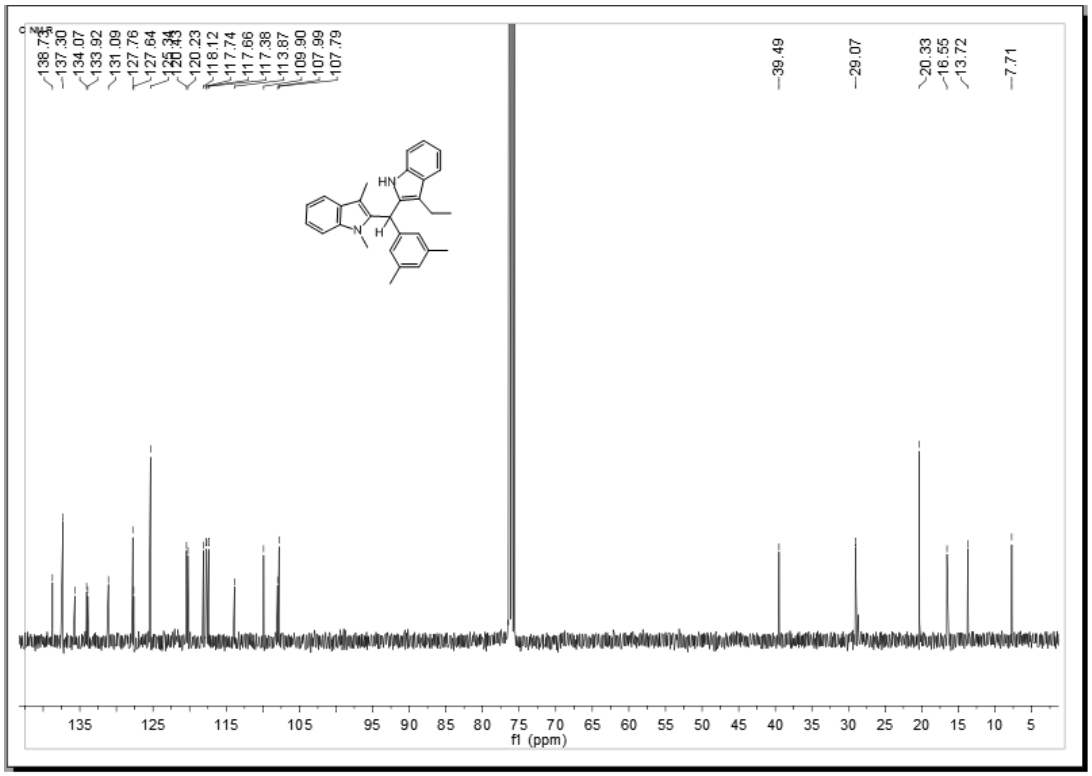
HN
N
H
f1 (ppm)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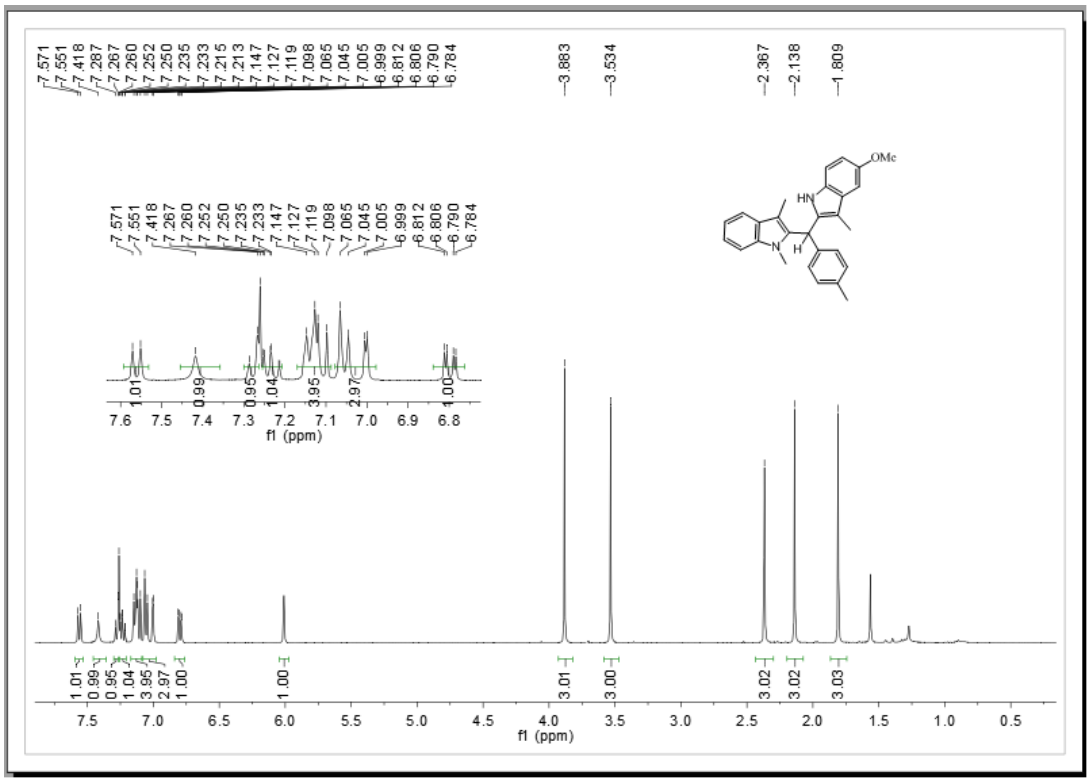
H
f1 (ppm)

3cc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OMe
HN
N
H
1.01
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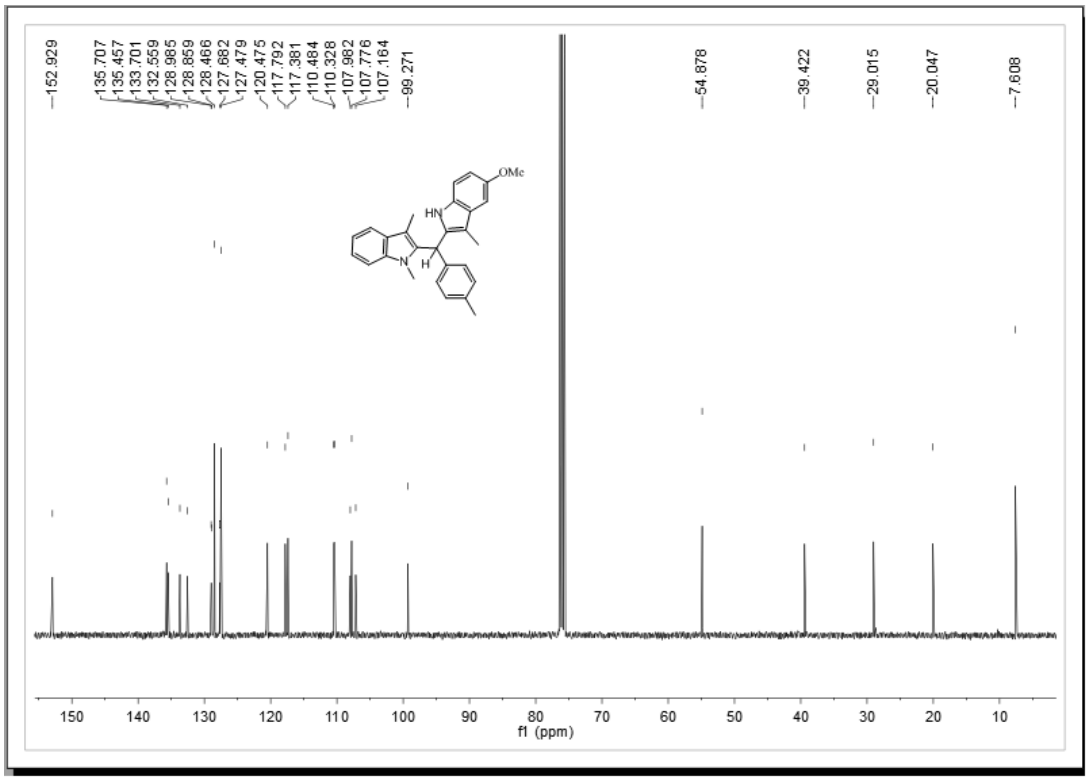
3.01
3.00
3.02
3.02
3.03
f1 (ppm)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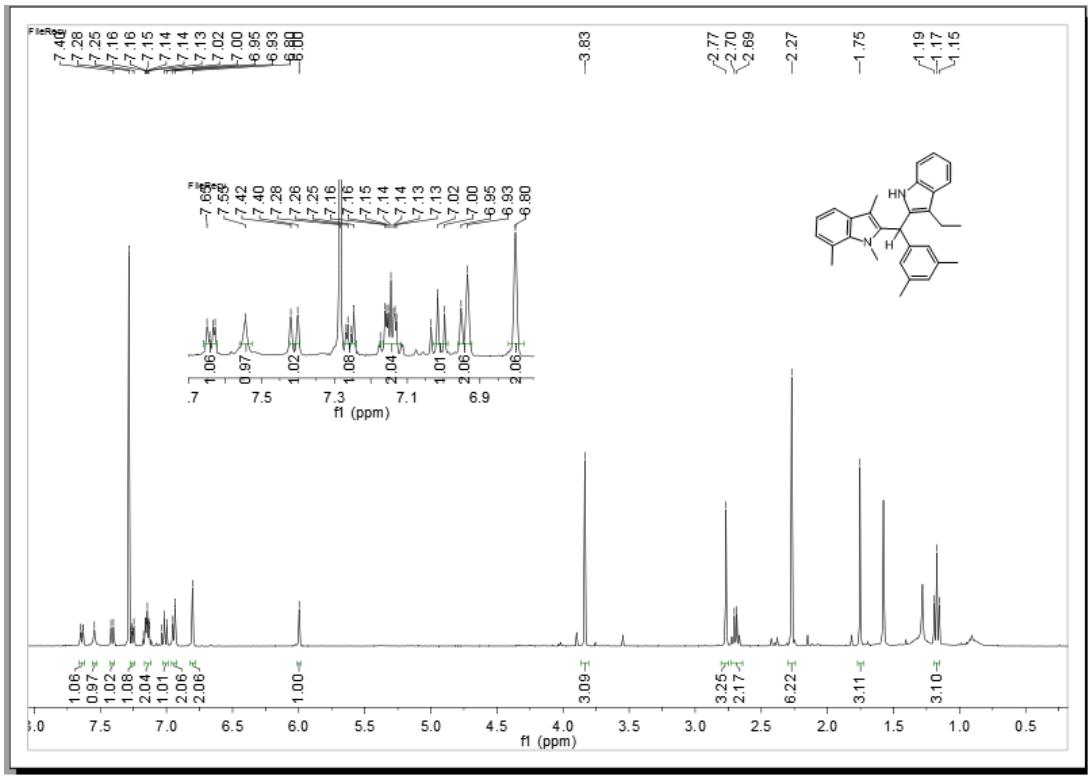
OMe
HN
N
H
f1 (ppm)

3hd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3.83
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2.70
2.69
2.27
1.75
1.19
1.17
1.15
HN
N
H
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0.97
1.02
1.08
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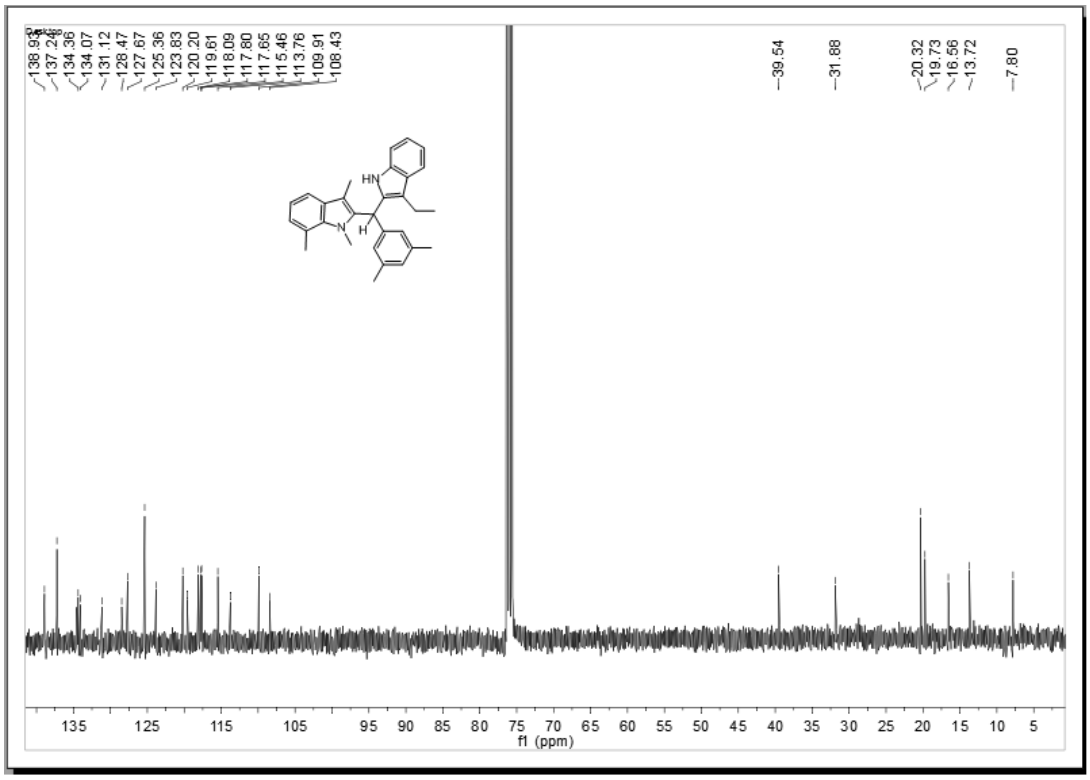
3.09
3.25
2.17
6.22
3.11
3.10
f1 (ppm)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117.65
115.46
113.76
109.91
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39.54
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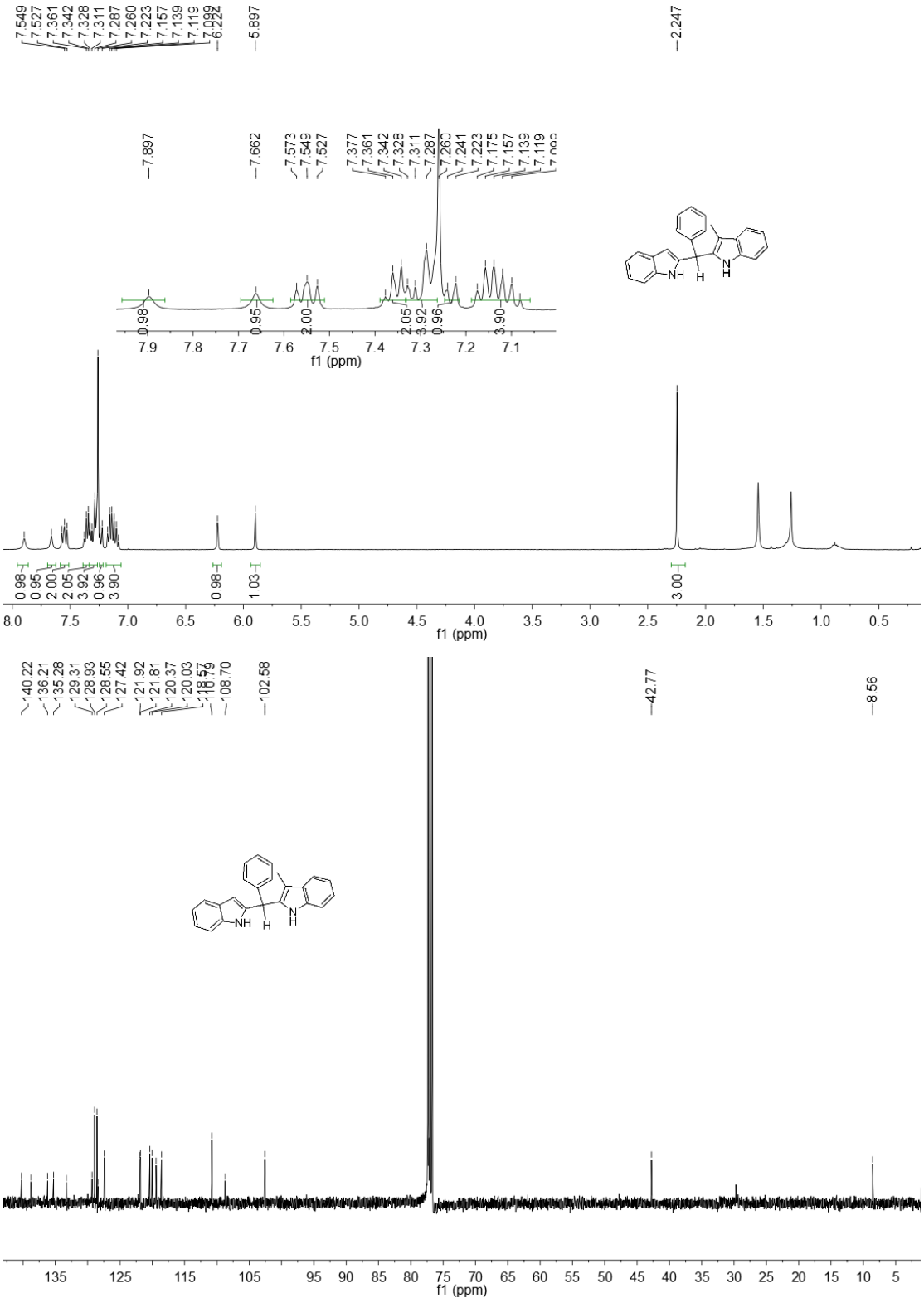
20.32
19.73
16.56
13.72
7.80
HN
N
H
f1 (ppm)

Compound 8: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7.157
7.139
7.119
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5.897
2.247
7.897
7.662
7.573
7.549
7.527
7.377
7.361
7.342
7.328
7.311
7.287
7.260
7.241
7.223
7.175
7.157
7.139
7.119
0.98
0.95
2.00
2.05
3.92
0.96
3.90
f1 (ppm)
NH
H
N
0.98
0.95
2.00
2.05
3.92
0.96
3.90
0.98
1.03
3.00
f1 (ppm)
140.22
136.21
135.28
129.31
128.93
128.55
127.42
121.92
121.81
120.37
120.03
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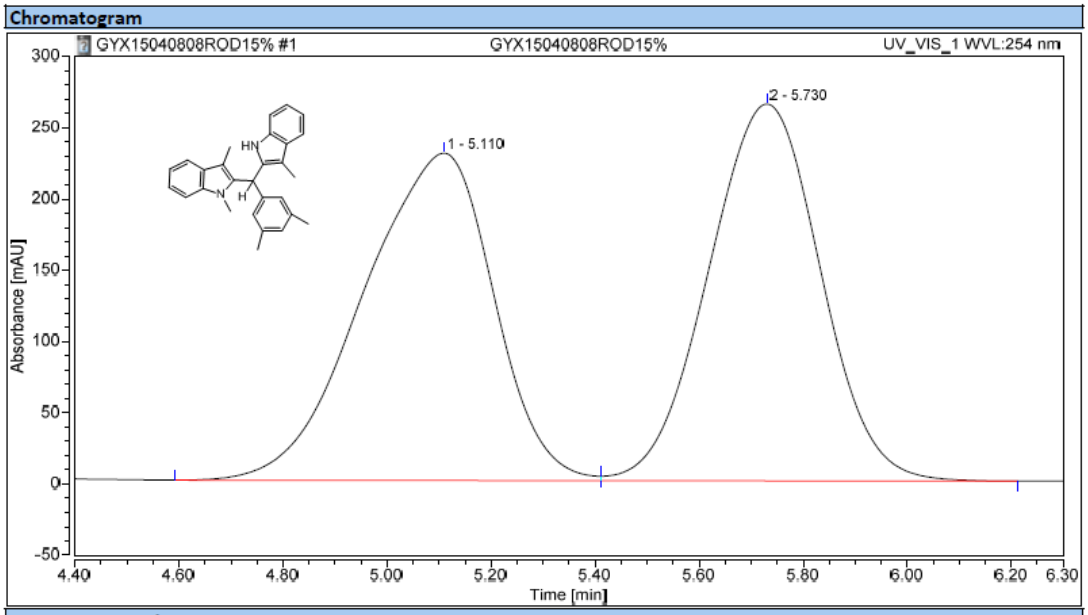
108.70
102.58
42.77
8.56
NH
H
N
f1 (ppm)

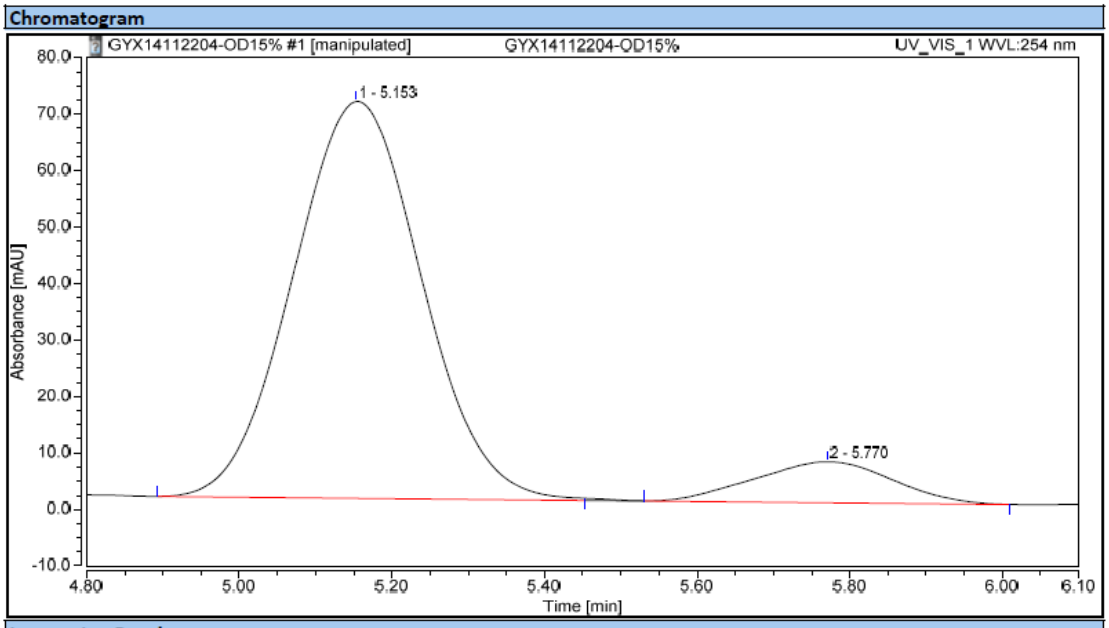
HPLC Spectra of products

3aa



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.110	66.788	229.706	50.31	46.48	n.a.
2		5.730	65.961	264.518	49.69	53.52	n.a.
Total:			**132.749**	**494.224**	**100.00**	**100.00**	

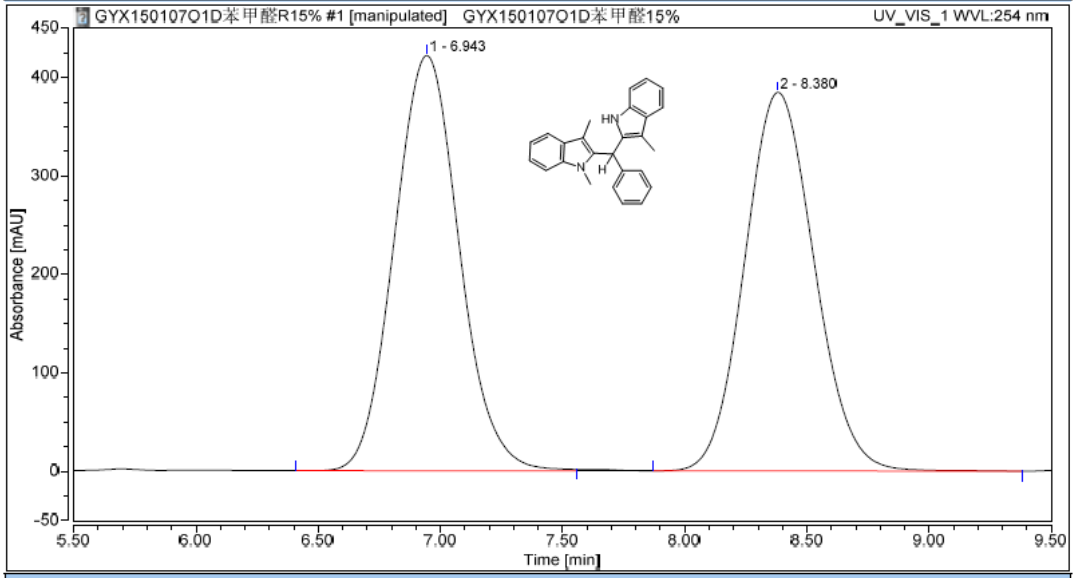


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.153	13.715	70.270	90.00	90.62	n.a.
2		5.770	1.524	7.271	10.00	9.38	n.a.
Total:			**15.239**	**77.541**	**100.00**	**100.00**	

3ba

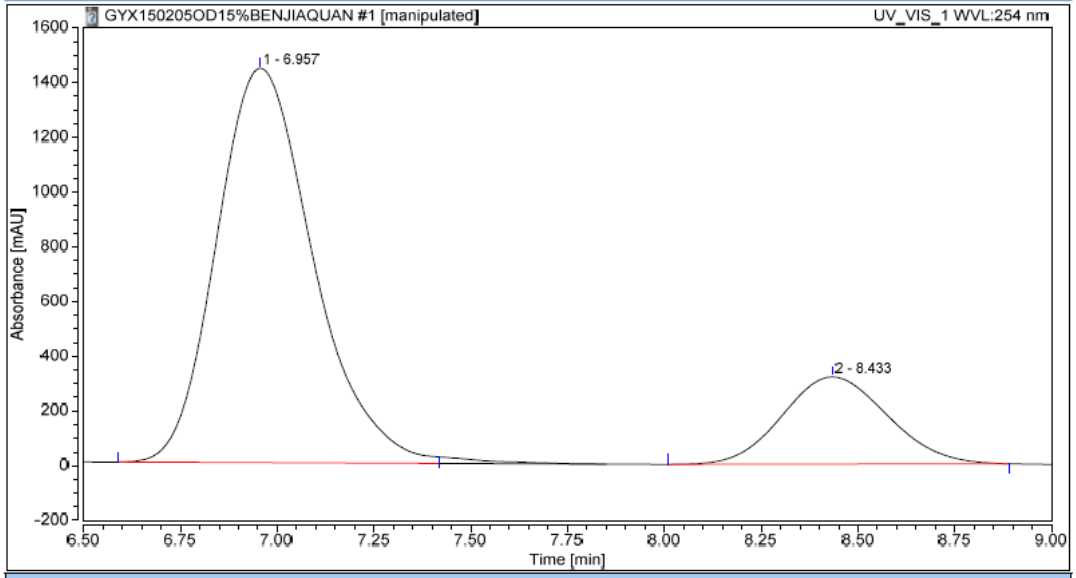
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.943	129.983	421.647	50.60	52.31	n.a.
2		8.380	126.892	384.389	49.40	47.69	n.a.
Total:			256.874	806.037	100.00	100.00	

Chromatogram

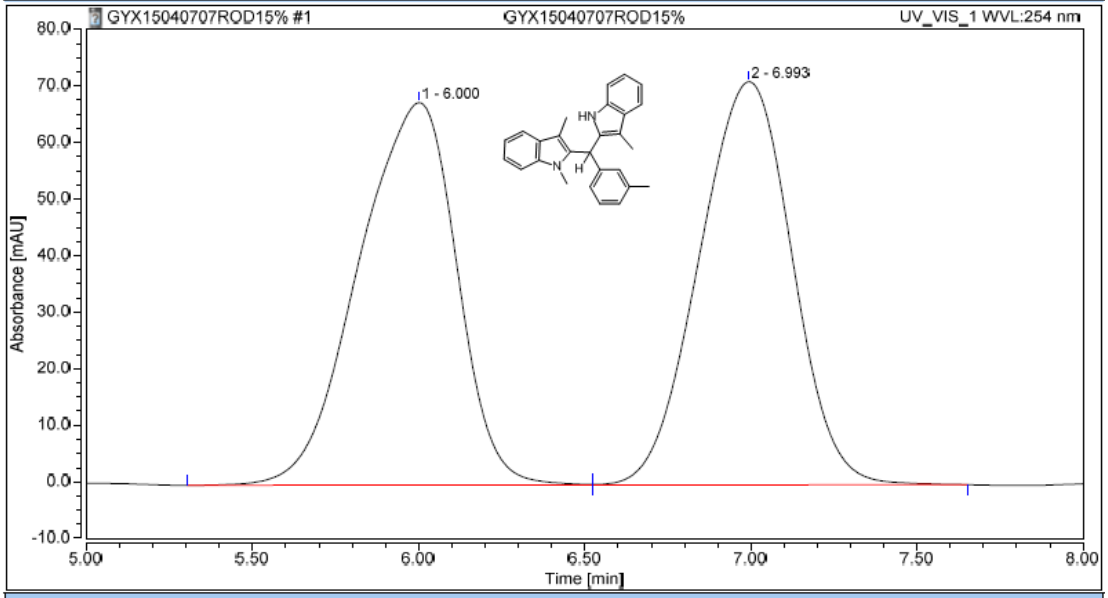


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.957	415.309	1441.953	80.59	81.92	n.a.
2		8.433	100.037	318.318	19.41	18.08	n.a.
Total:			515.346	1760.271	100.00	100.00	

3ca

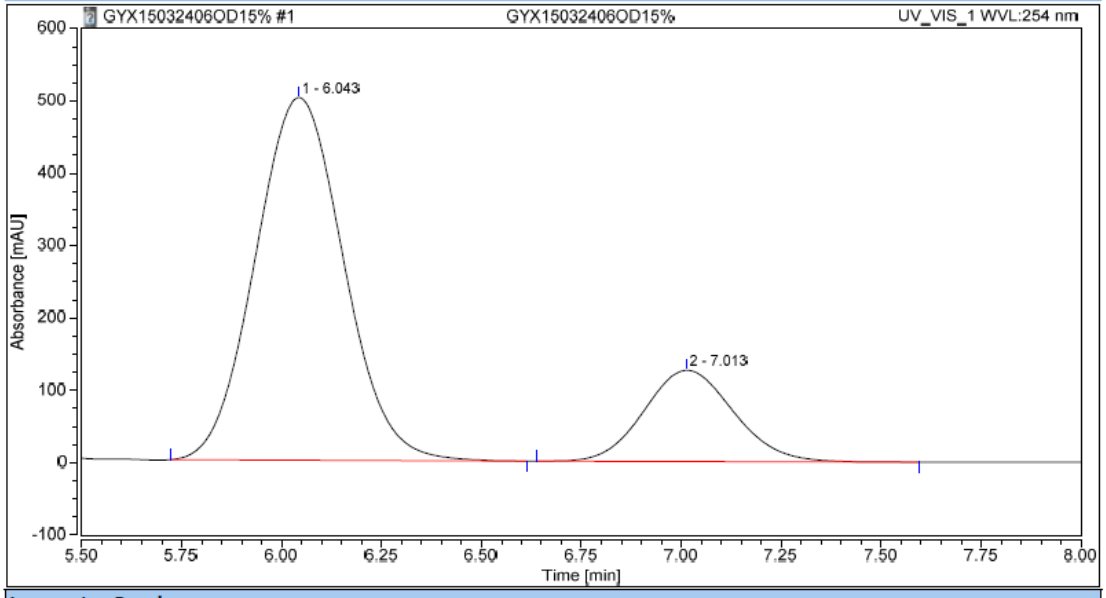
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.000	23.179	67.644	50.05	48.68	n.a.
2		6.993	23.129	71.312	49.95	51.32	n.a.
Total:			**46.309**	**138.956**	**100.00**	**100.00**	

Chromatogram

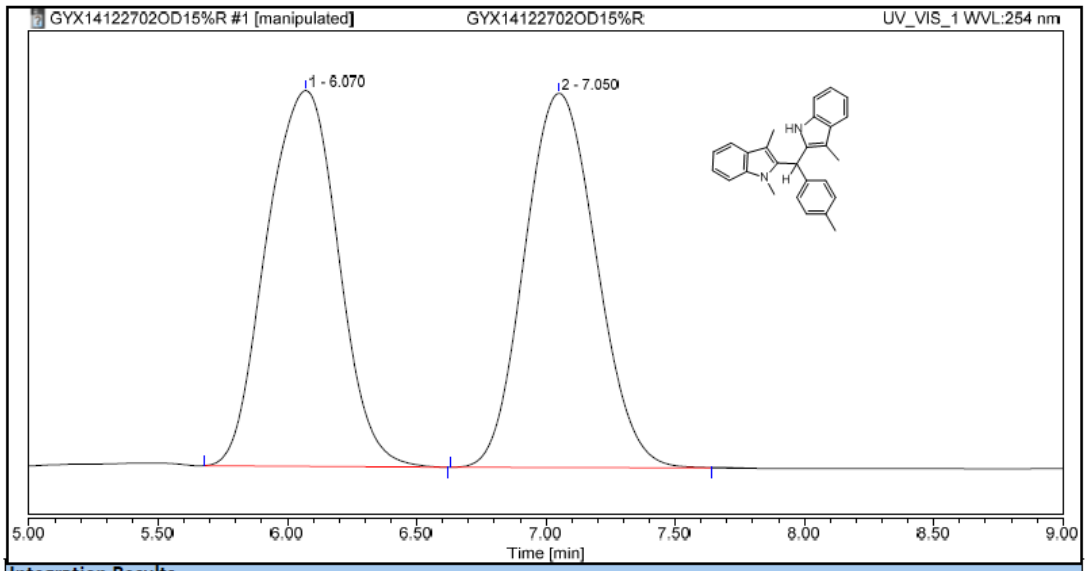


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.043	128.300	501.205	79.66	79.90	n.a.
2		7.013	32.762	126.115	20.34	20.10	n.a.
Total:			**161.062**	**627.320**	**100.00**	**100.00**	

3da

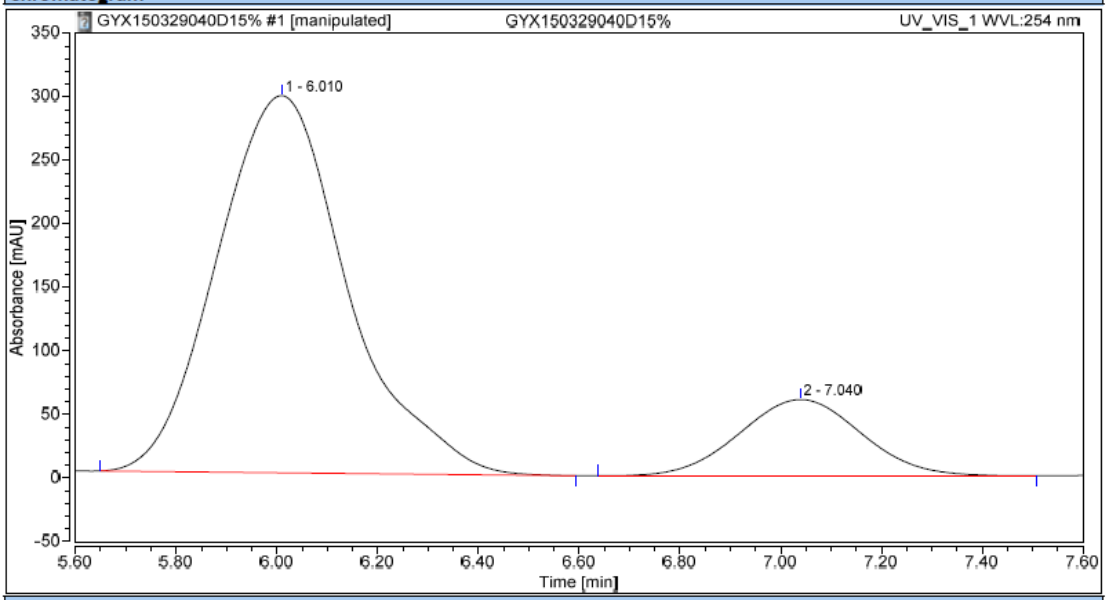
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.070	551.973	1712.115	50.16	50.10	n.a.
2		7.050	548.433	1705.047	49.84	49.90	n.a.
Total:			**1100.407**	**3417.162**	**100.00**	**100.00**	

Chromatogram

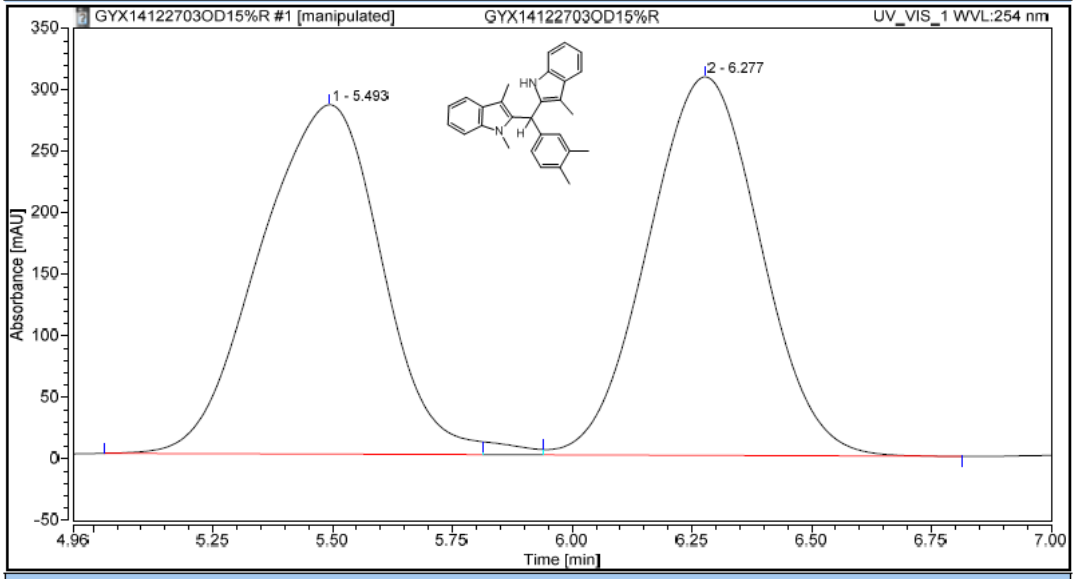


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.010	88.937	296.781	84.10	83.19	n.a.
2		7.040	16.820	59.980	15.90	16.81	n.a.
Total:			**105.757**	**356.762**	**100.00**	**100.00**	

3ea

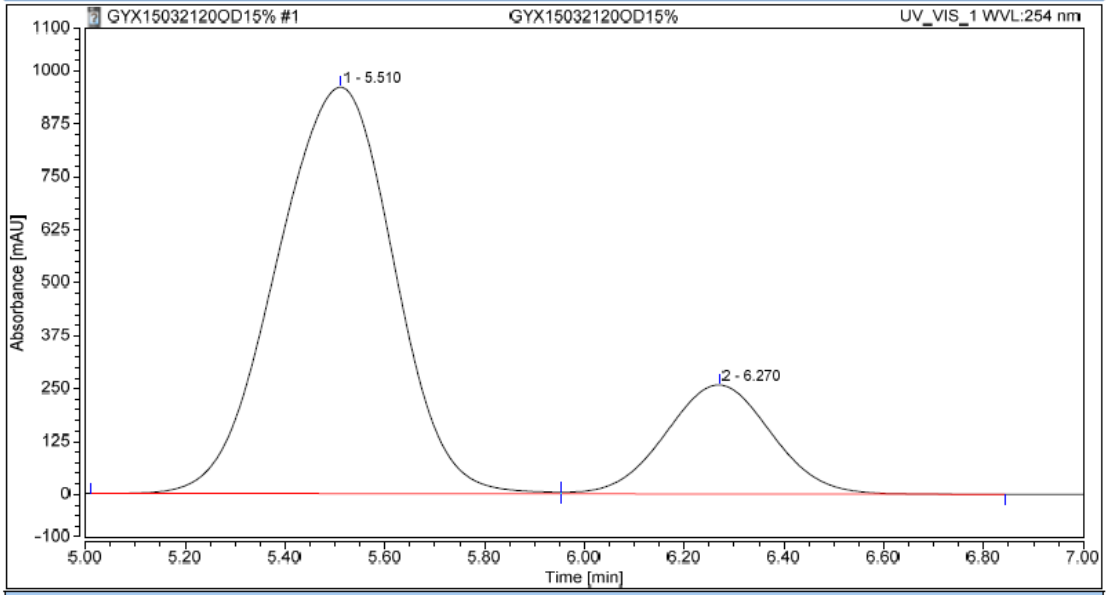
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.493	83.365	283.951	49.86	47.99	n.a.
2		6.277	83.832	307.719	50.14	52.01	n.a.
Total:			**167.197**	**591.671**	**100.00**	**100.00**	

Chromatogram

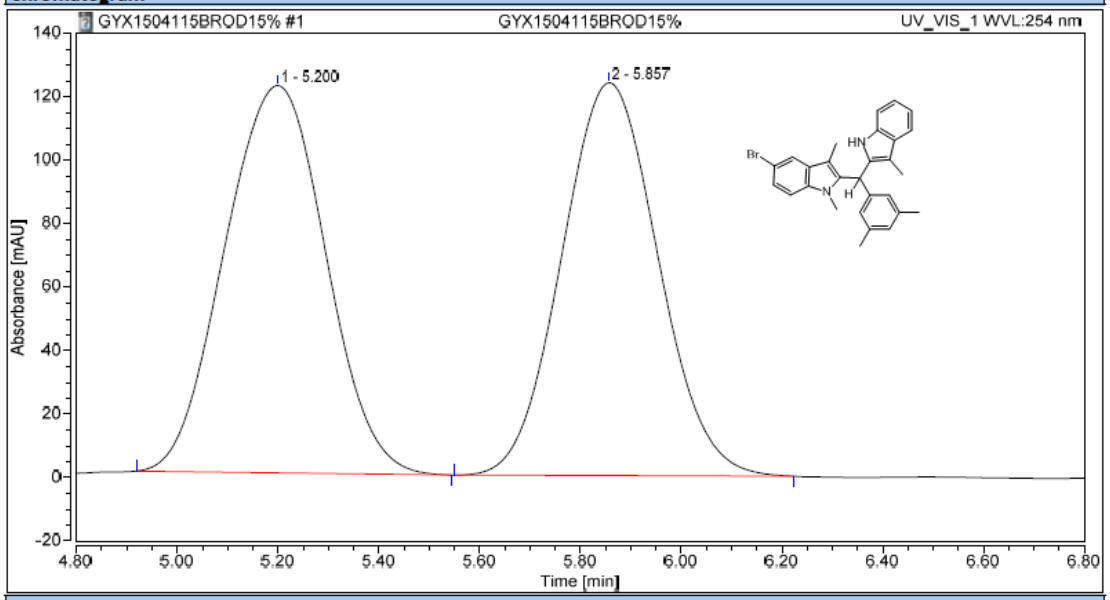


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.510	261.481	959.451	80.44	78.84	n.a.
2		6.270	63.587	257.506	19.56	21.16	n.a.
Total:			**325.068**	**1216.957**	**100.00**	**100.00**	

3fa

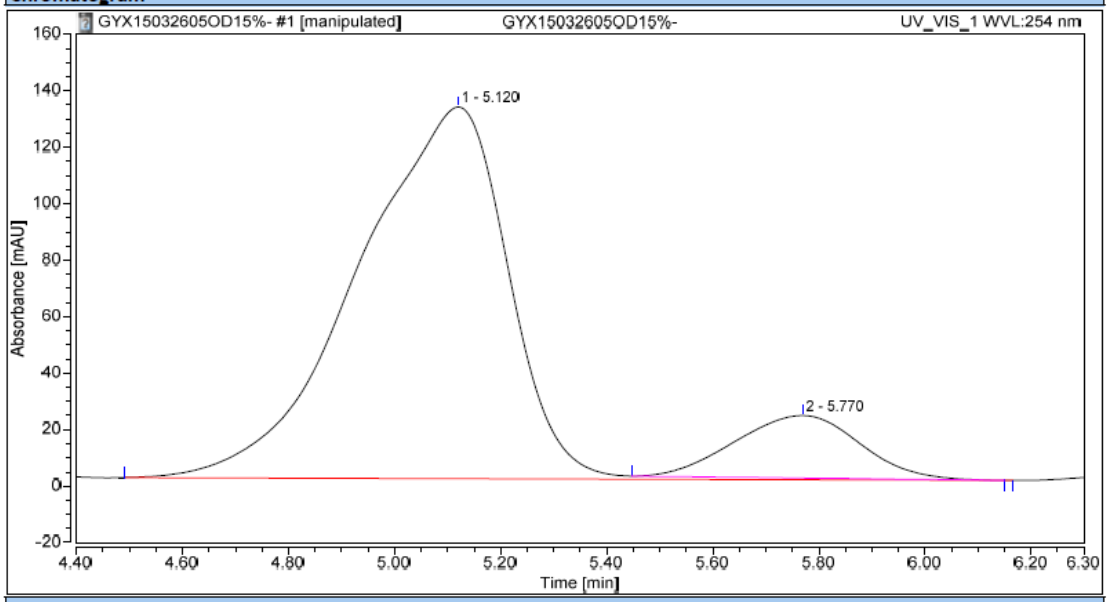
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.200	28.330	122.114	50.82	49.65	n.a.
2		5.857	27.421	123.858	49.18	50.35	n.a.
Total:			**55.751**	**245.972**	**100.00**	**100.00**	

Chromatogram

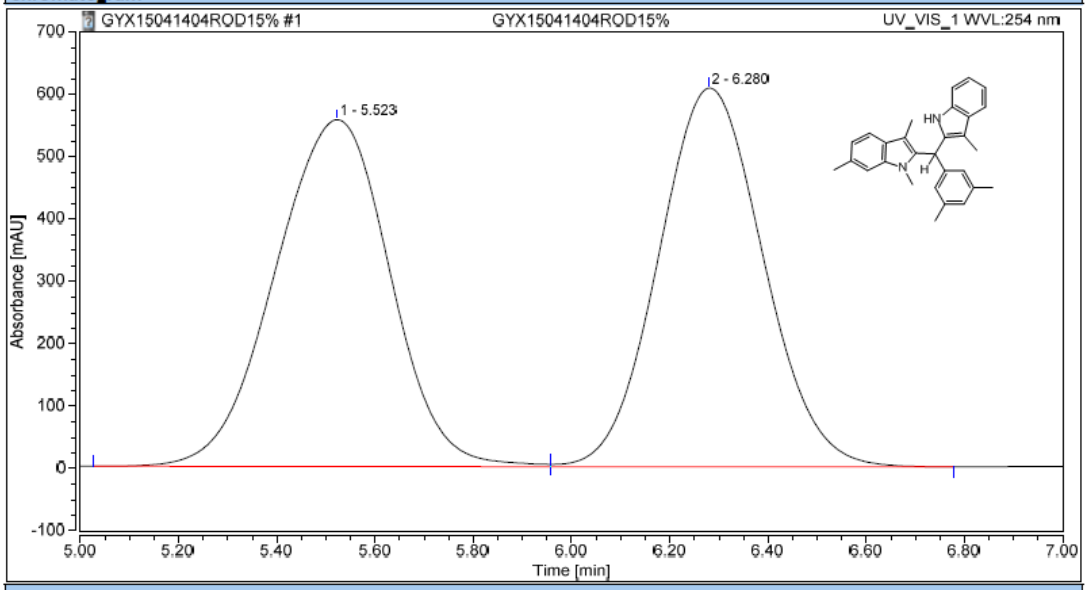


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.120	43.485	131.663	87.87	85.61	n.a.
2		5.770	6.004	22.130	12.13	14.39	n.a.
Total:			**49.489**	**153.793**	**100.00**	**100.00**	

3ga

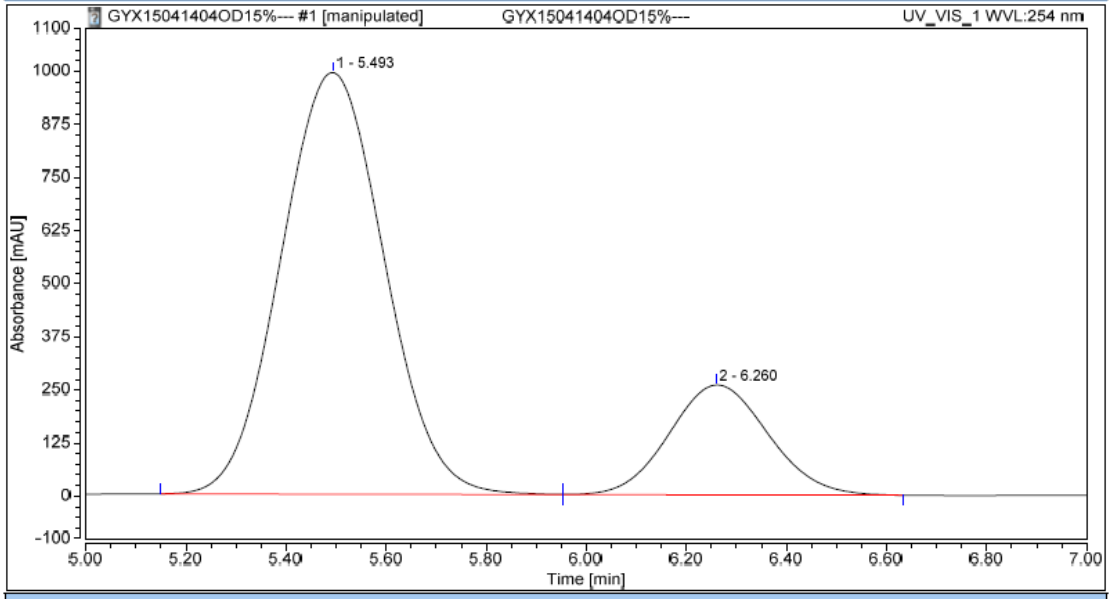
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.523	150.863	556.473	50.13	47.80	n.a.
2		6.280	150.063	607.618	49.87	52.20	n.a.
Total:			**300.925**	**1164.091**	**100.00**	**100.00**	

Chromatogram

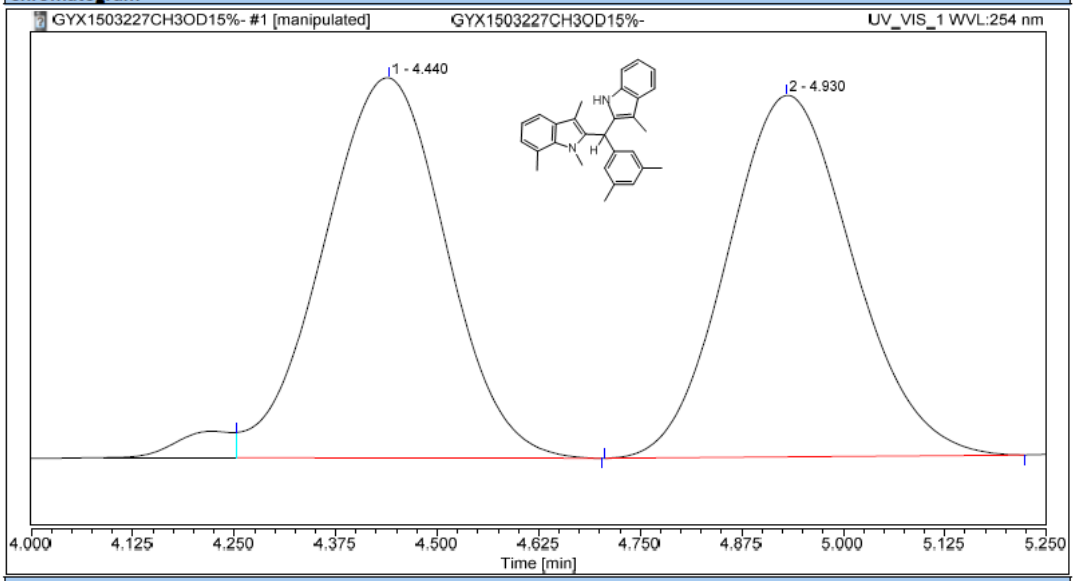


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.493	237.330	992.546	79.98	79.33	n.a.
2		6.260	59.400	258.644	20.02	20.67	n.a.
Total:			**296.729**	**1251.190**	**100.00**	**100.00**	

3ha

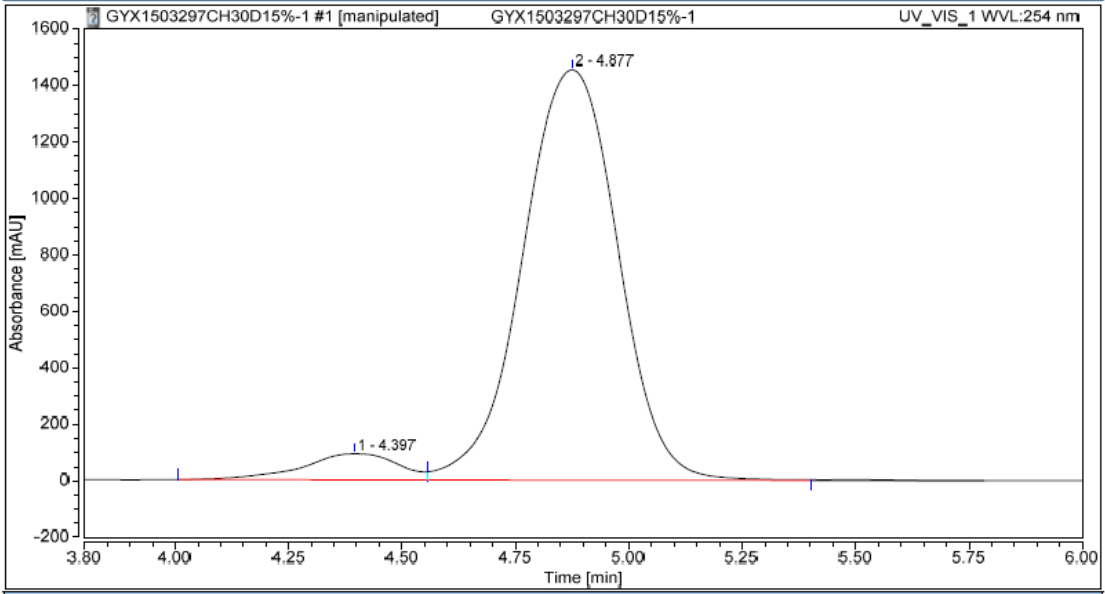
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.440	21.647	123.625	50.71	51.26	n.a.
2		4.930	21.042	117.528	49.29	48.74	n.a.
Total:			**42.689**	**241.153**	**100.00**	**100.00**	

Chromatogram

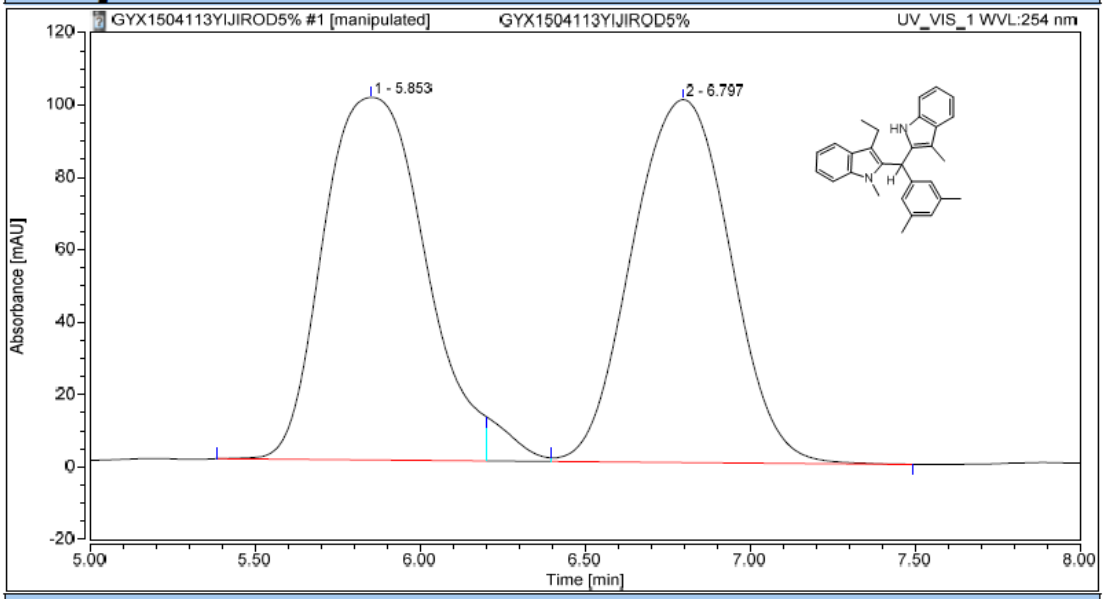


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.397	22.513	92.471	5.99	5.98	n.a.
2		4.877	353.431	1452.716	94.01	94.02	n.a.
Total:			**375.944**	**1545.187**	**100.00**	**100.00**	

3ia

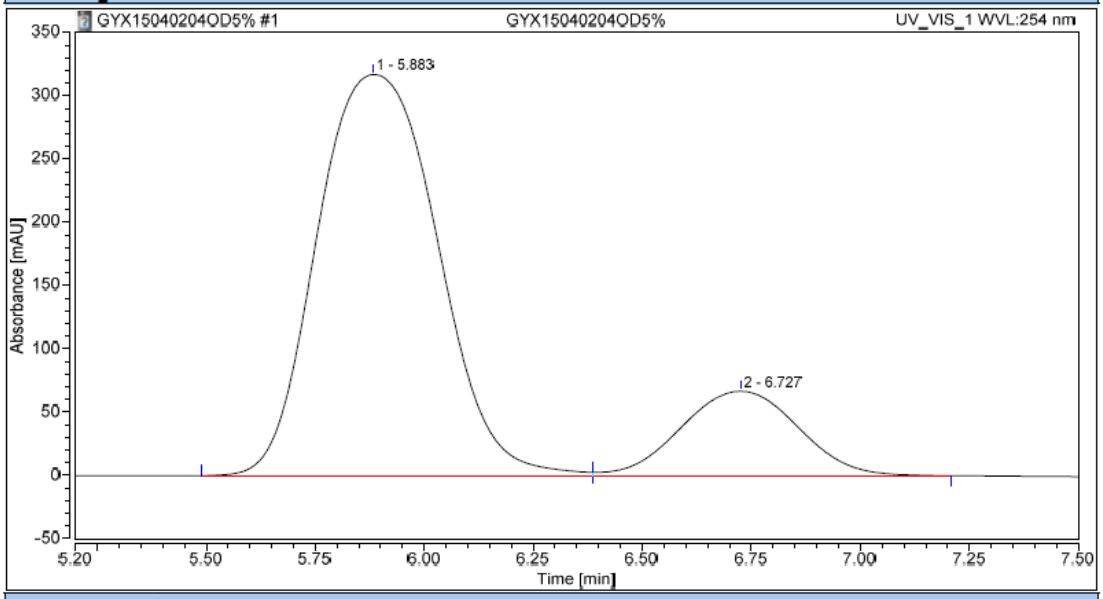
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.853	35.699	100.133	50.78	49.98	n.a.
2		6.797	34.609	100.209	49.22	50.02	n.a.
Total:			**70.308**	**200.342**	**100.00**	**100.00**	

Chromatogram

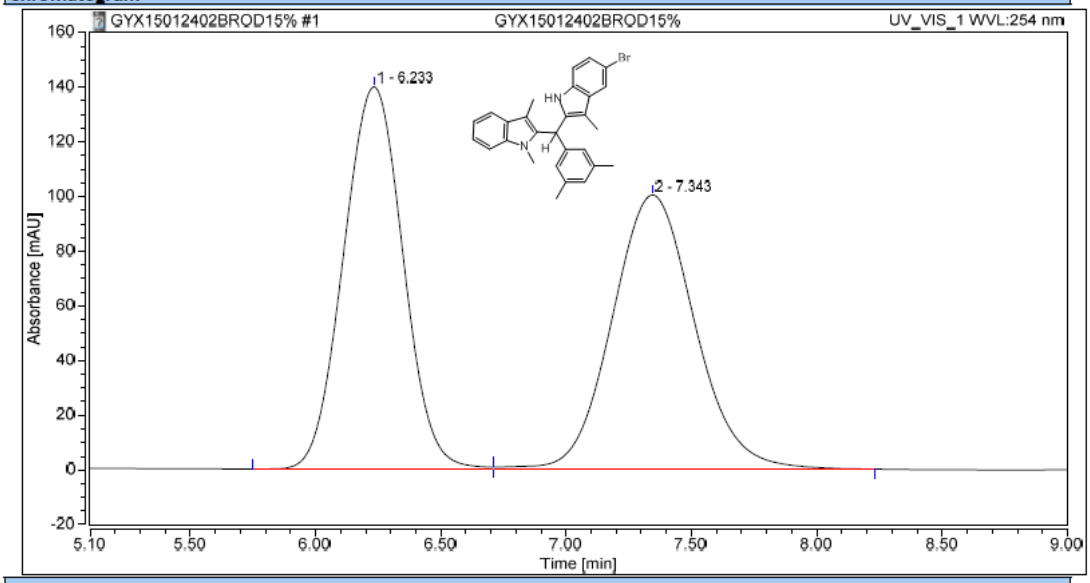


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.883	101.289	316.915	82.98	82.61	n.a.
2		6.727	20.774	66.704	17.02	17.39	n.a.
Total:			**122.063**	**383.619**	**100.00**	**100.00**	

3ab

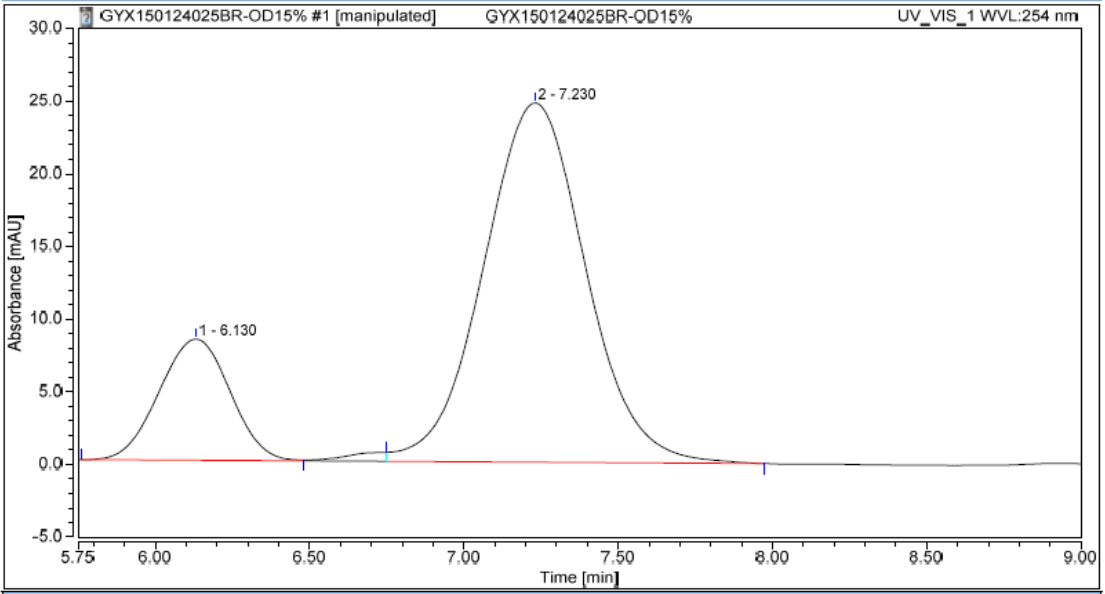
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.233	38.523	139.871	50.15	58.24	n.a.
2		7.343	38.295	100.272	49.85	41.76	n.a.
Total:			**76.817**	**240.143**	**100.00**	**100.00**	

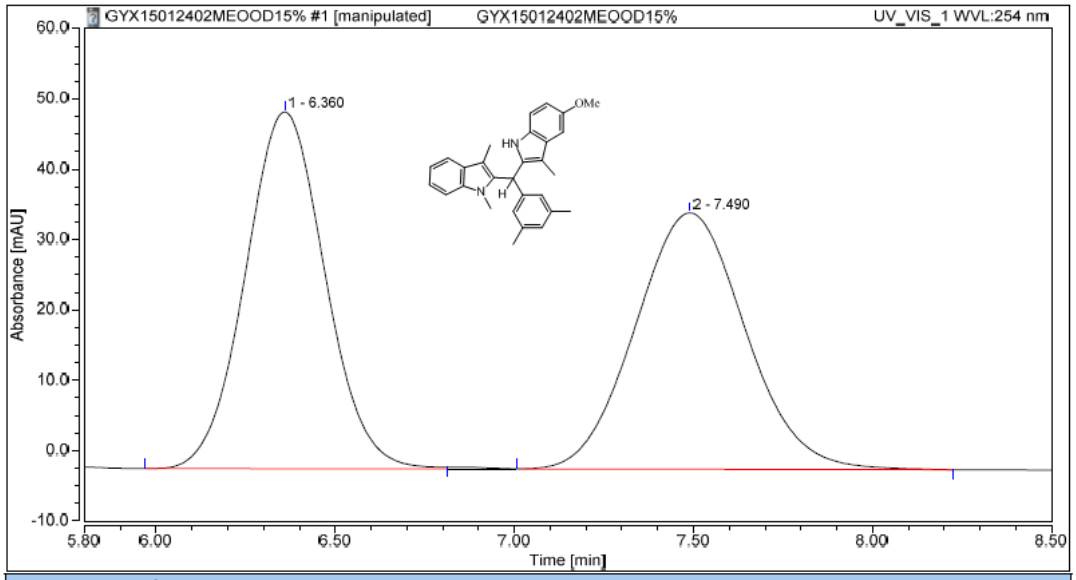
Chromatogram



Integration Results

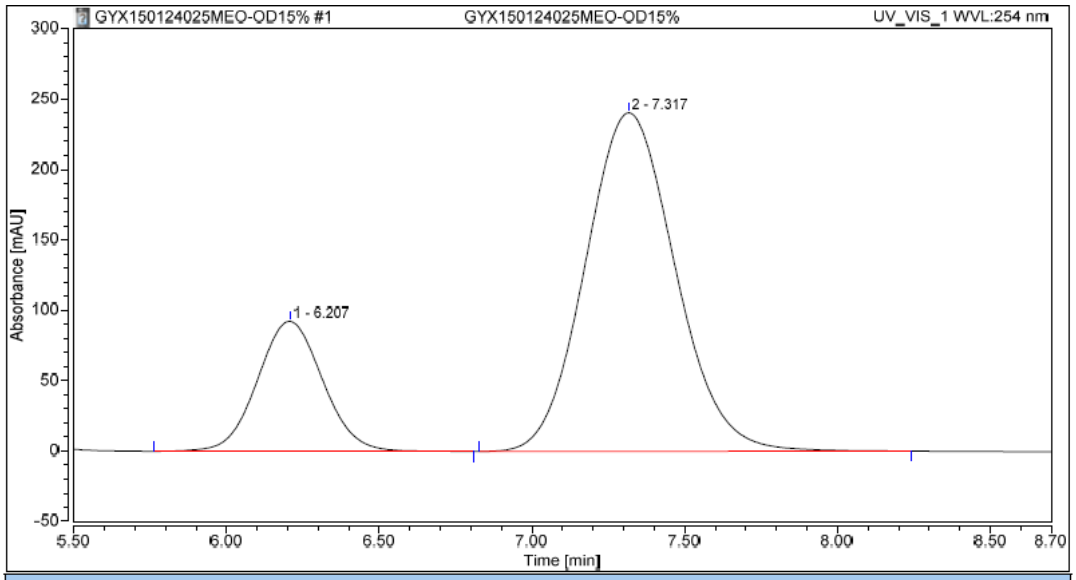
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.130	2.221	8.337	18.94	25.21	n.a.
2		7.230	9.501	24.736	81.06	74.79	n.a.
Total:			**11.722**	**33.073**	**100.00**	**100.00**	

3ac



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.360	13.058	50.717	50.16	58.19	n.a.
2		7.490	12.973	36.447	49.84	41.81	n.a.
Total:			**26.031**	**87.164**	**100.00**	**100.00**	

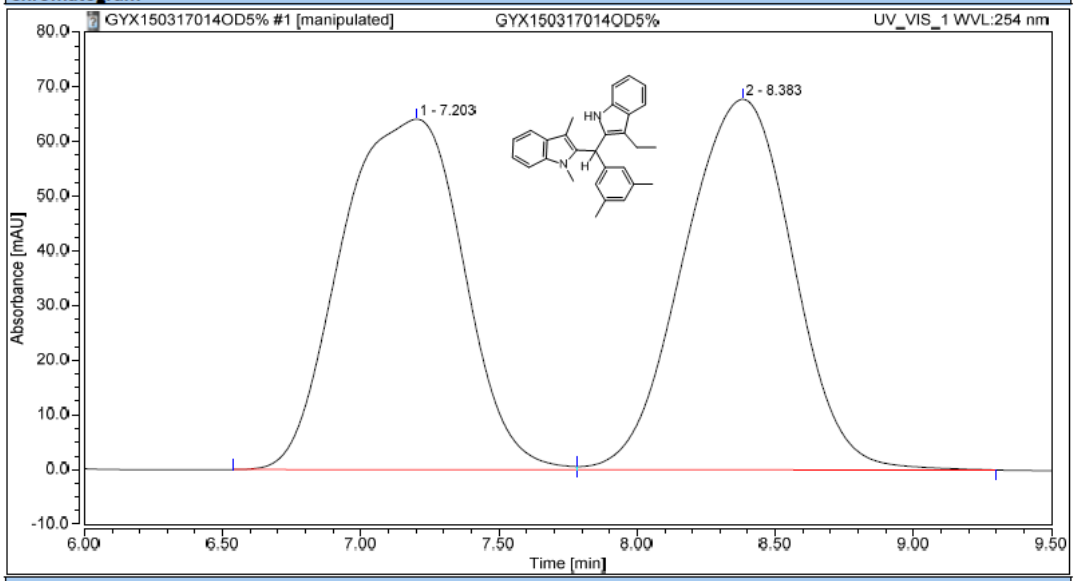


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.207	22.886	92.406	21.82	27.76	n.a.
2		7.317	81.978	240.517	78.18	72.24	n.a.
Total:			**104.864**	**332.923**	**100.00**	**100.00**	

3ad

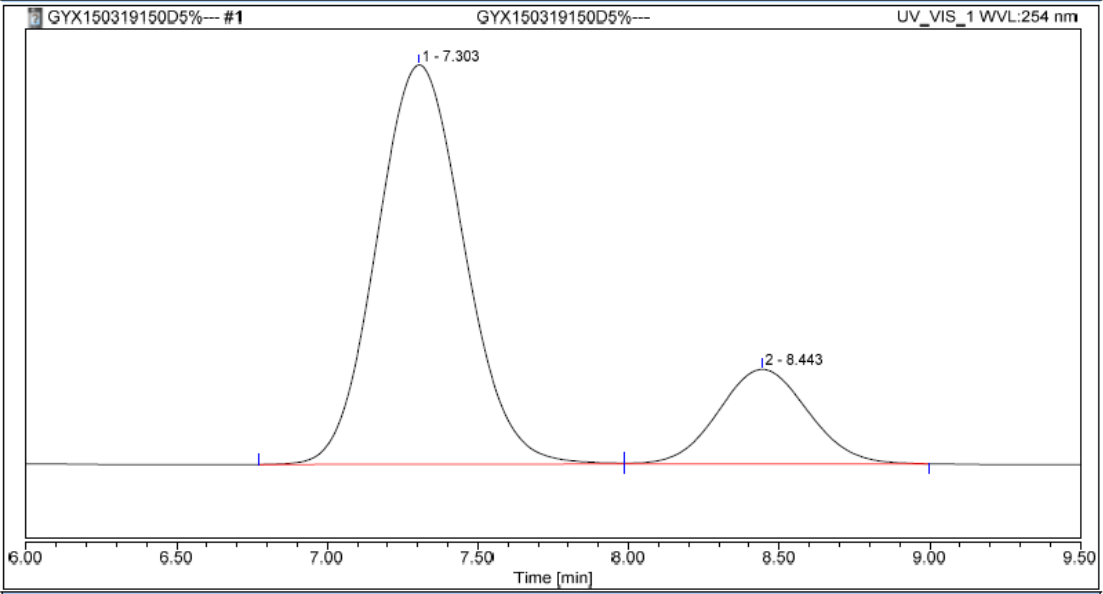
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.203	32.813	64.119	51.28	48.61	n.a.
2		8.383	31.174	67.781	48.72	51.39	n.a.
Total:			**63.987**	**131.901**	**100.00**	**100.00**	

Chromatogram

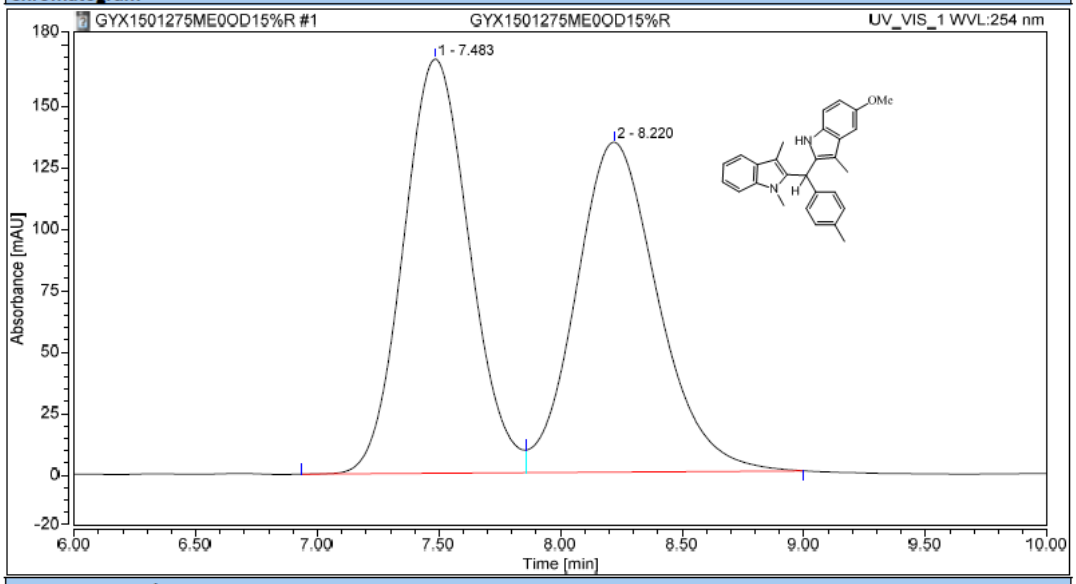


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.303	92.455	275.091	80.38	80.85	n.a.
2		8.443	22.563	65.144	19.62	19.15	n.a.
Total:			**115.018**	**340.236**	**100.00**	**100.00**	

3cc

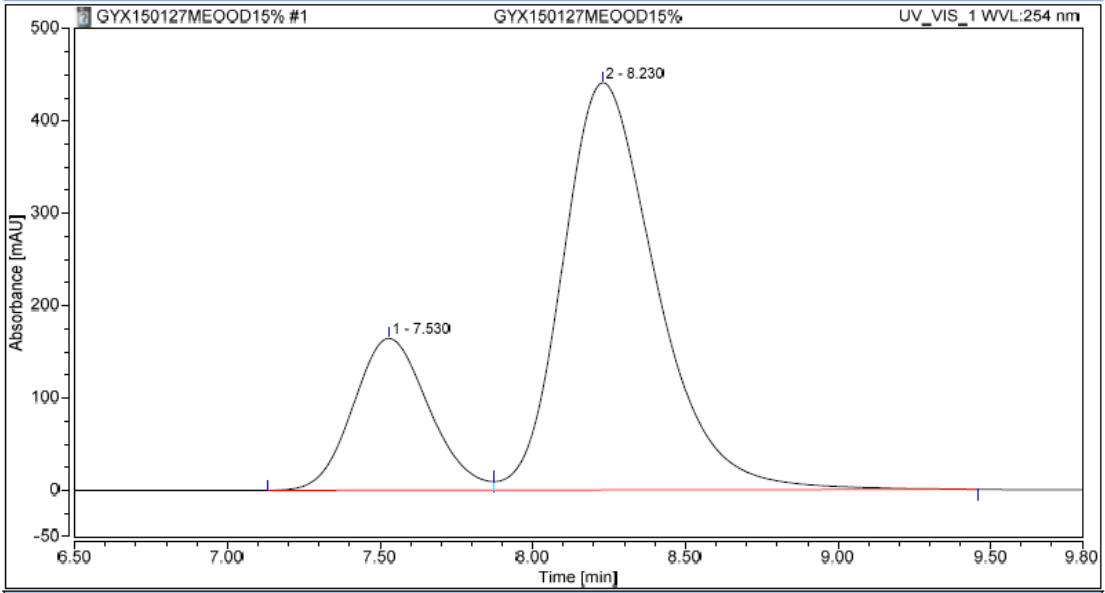
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.483	52.954	168.225	50.29	55.66	n.a.
2		8.220	52.334	134.005	49.71	44.34	n.a.
Total:			**105.288**	**302.230**	**100.00**	**100.00**	

Chromatogram

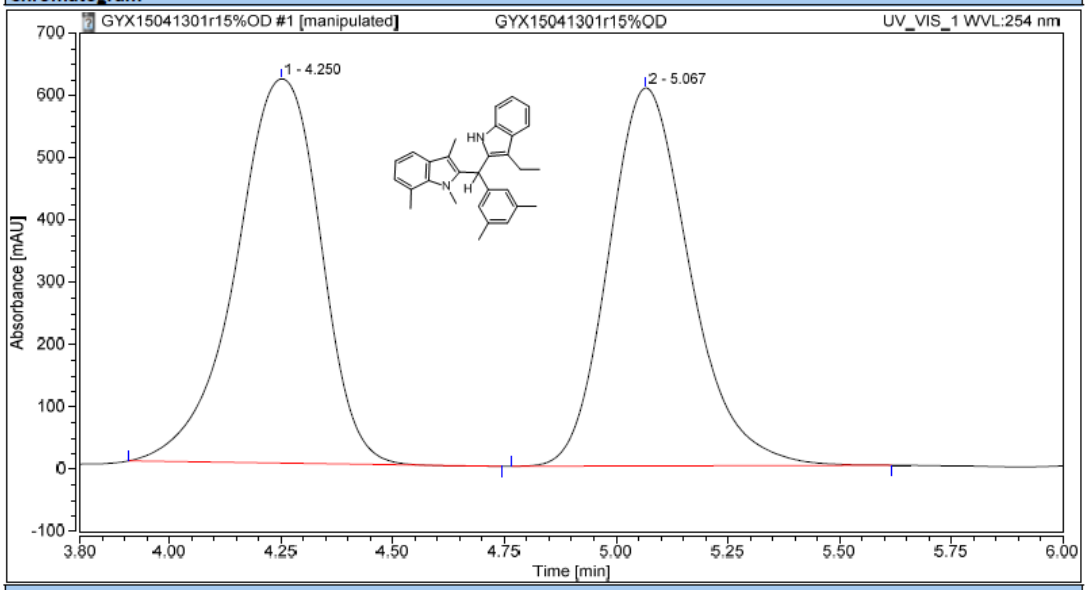


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.530	47.209	164.297	23.16	27.16	n.a.
2		8.230	156.668	440.657	76.84	72.84	n.a.
Total:			**203.876**	**604.954**	**100.00**	**100.00**	

3hd

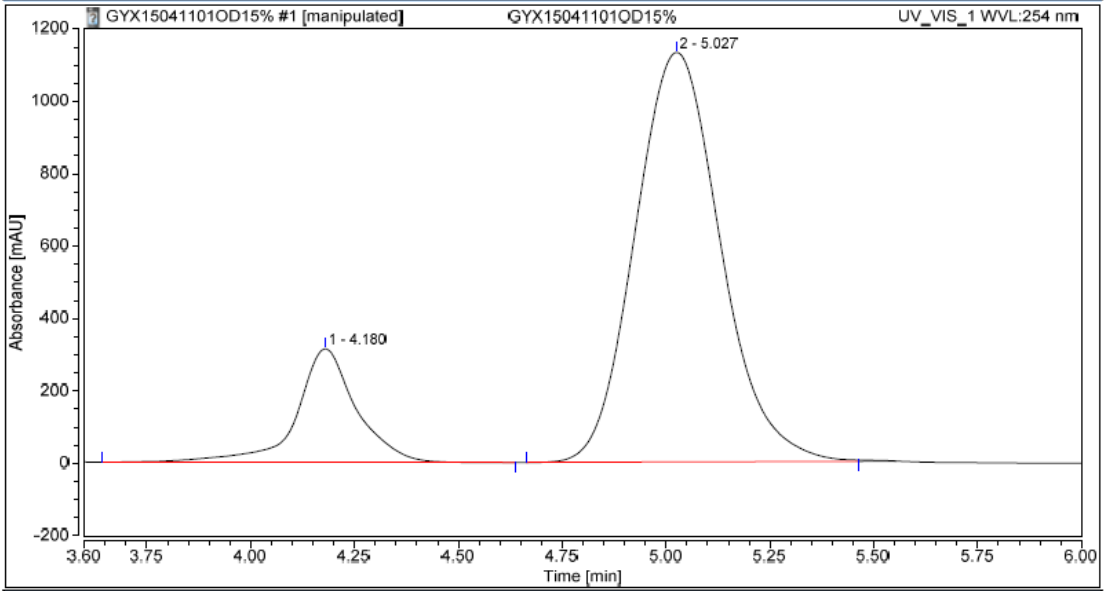
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.250	135.920	617.174	51.41	50.41	n.a.
2		5.067	128.461	607.220	48.59	49.59	n.a.
Total:			**264.380**	**1224.394**	**100.00**	**100.00**	

Chromatogram

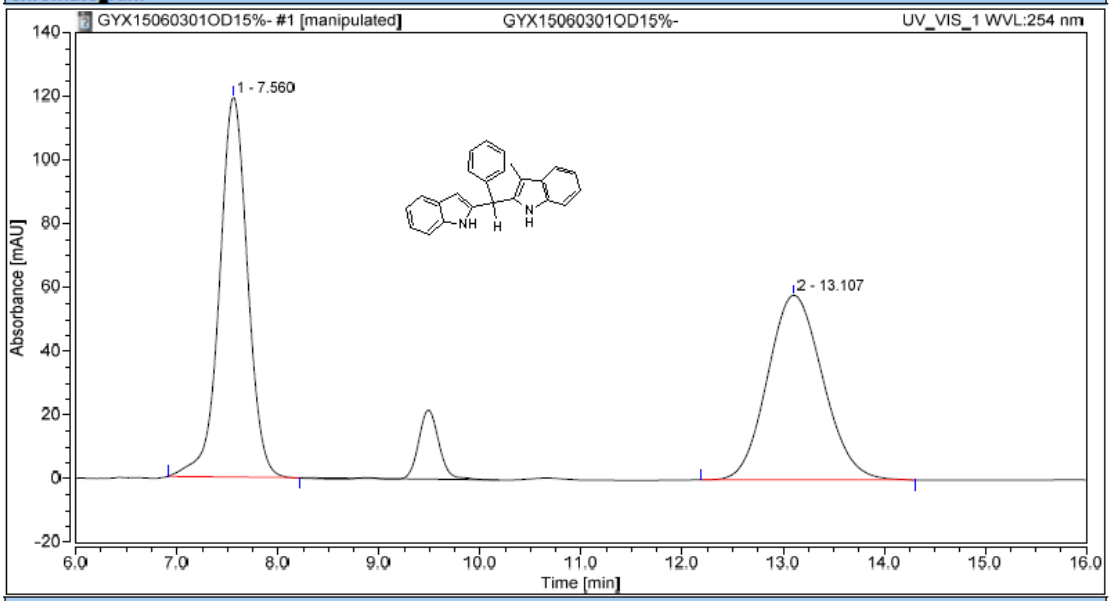


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.180	52.247	313.503	16.26	21.70	n.a.
2		5.027	269.166	1131.022	83.74	78.30	n.a.
Total:			**321.413**	**1444.525**	**100.00**	**100.00**	

Compound 8:

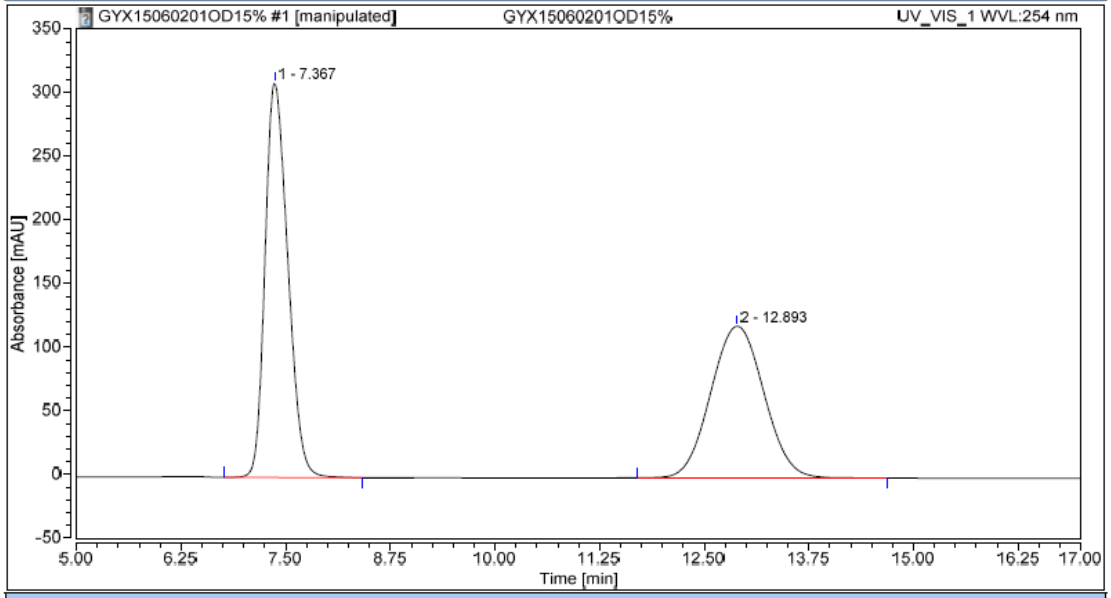
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.560	38.405	119.346	51.13	67.30	n.a.
2		13.107	36.708	57.978	48.87	32.70	n.a.
Total:			**75.113**	**177.324**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.367	97.635	309.939	52.56	72.20	n.a.
2		12.893	88.116	119.367	47.44	27.80	n.a.
Total:			**185.751**	**429.306**	**100.00**	**100.00**	