Supporting Information:

Asymmetric Synthesis of 7-Membered-ring-bridged 3,4-Fused Tricyclic Indoles via Friedel–Crafts Alkylation/Annulation

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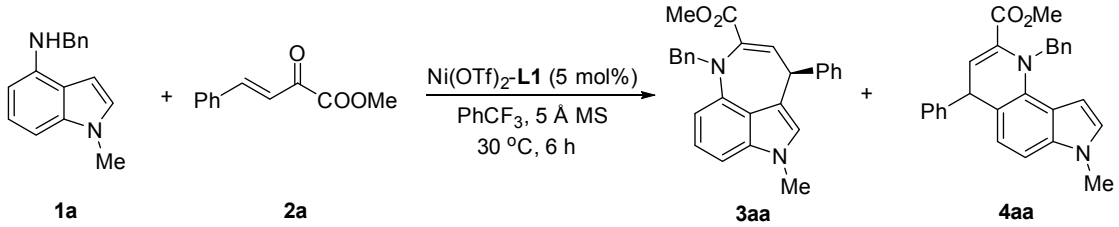
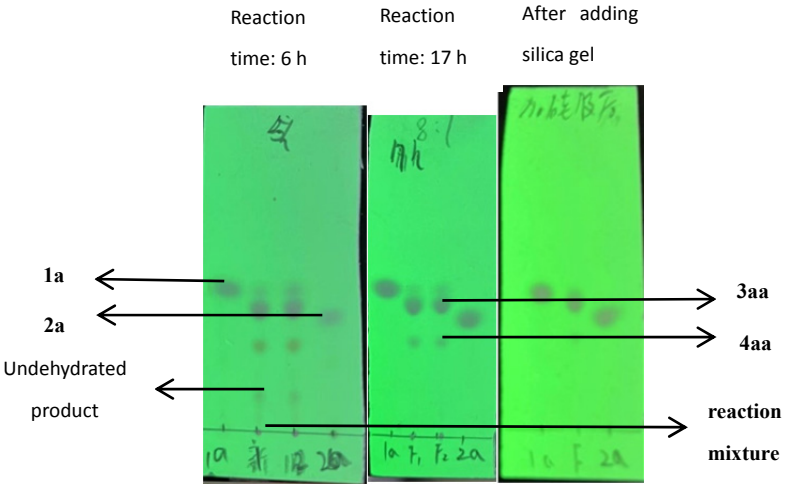
General information

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; sept = septet; m = multiplet; br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IC/IA/ODH/ASH/IF in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity HPLC instruments. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Single crystal X-ray crystallography data were obtained on Supernova Atlas S2 CCD detector. IR data were detected by Bruker Tensor II 400F. CH_2Cl_2 and $PhCF_3$ were purchased extra dry solvents.

General procedure for the synthesis of chiral 3,4-fused tricyclic indoles

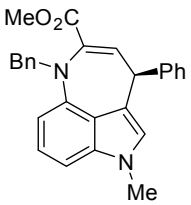


In a test tube, **L1** and $Ni(OTf)_2$ (5 mol%, 1:1) were added. Then β,γ-unsaturated α-ketoester **2a** (0.1 mmol, 19.0 mg), 5 Å MS (20 mg) and $PhCF_3$ (2.0 mL) were added at air atmosphere. After stirred at 30 °C for 0.5 hour, N-benzyl-1-methyl-1*H*-indol-4-amine **1a** (1.3 equiv., 30.7 mg) was added. The reaction mixture was stirred at 30 °C until β,γ-unsaturated α-ketoester **2a** was consumed (determined by TLC). Then, silica gel (1.0 g) was added and stirred for 1.5 h at 30 °C to promote dehydration completely. Finally, the reaction mixture was filtered and concentrated, and the residue was purified directly by flash column chromatography (Pet/EtOAc, 500/1~100/1, v/v) as eluent to afford the desired product **3aa**.



(**Figure S1.** Pet/EtOAc, 8/1, v/v).

Methyl (*S*)-1-benzyl-6-methyl-4-phenyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3aa)



Yellow solid, (36.7mg, 90% yield, 91% ee). m.p. = 153.5 – 156.3 °C.

R_f = 0.28 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -10.00 (c = 0.72, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.012 min, (minor) = 8.652 min.

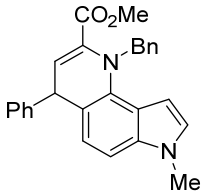
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 7.24 – 7.17 (m, 5H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 6.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.13 (s, 1H), 5.28 (d, *J* = 6.8, Hz, 1H), 4.85 (d, *J* = 14.0 Hz, 1H), 4.76 (d, *J* = 13.6 Hz, 1H), 3.64 (s, 3H), 3.61 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 142.5, 141.4, 138.4, 138.3, 137.8, 137.2, 128.9, 128.8, 128.6, 128.4, 127.3, 127.0, 123.1, 123.0, 120.6, 115.8, 104.9, 102.7, 54.2, 52.0, 42.3, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}N_2NaO_2^+$ 431.1730; found 431.1729.

IR(neat): 2922, 1721, 1635, 1578, 1496, 1461, 1421, 1395, 1322, 1264, 1227, 1148, 1070, 1030, 790, 769, 741, 702 cm^{-1}.

Methyl 1-benzyl-7-methyl-4-phenyl-4,7-dihydro-1*H*-pyrrolo[2,3-*h*]quinoline-2-carboxylate (4aa)



Yellow solid, (2.0 mg, 5% yield, 38% ee). m.p. ≥300 °C.

R_f = 0.18 (Pet/EtOAc, 8/1, v/v).

HPLC CHIRALPAK IA, n-hexane/2-propanol =90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: (minor) = 14.345 min, (major) = 17.138 min.

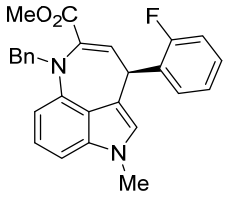
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.02 (m, 7H), 6.98 – 6.88 (m, 3H), 6.86 – 6.79 (m, 2H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 4.8 Hz, 1H), 5.32 (d, *J* = 14.8 Hz, 1H), 5.20 (d, *J* = 14.8 Hz, 1H), 4.73 (d, *J* = 4.8 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 146.0, 138.0, 137.4, 136.2, 134.6, 129.2, 128.7, 128.5, 128.3, 127.9, 127.5, 126.2, 123.7, 123.5, 119.6, 119.3, 105.3, 100.9, 54.9, 52.2, 43.8, 33.2.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}N_2NaO_2^+$ 431.1730; found 431.1726.

IR(neat): 1727, 1716, 1645, 1485, 1437, 1289, 1269, 1245, 1122, 1098, 780, 767, 746, 717, 698, 655, 589 cm^{-1}.

Methyl (*R*)-1-benzyl-4-(2-fluorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ab)



Yellow solid, (33.3 mg, 78% yield, 86% ee). m.p. = 74.5 – 76.5 °C.

R_f = 0.36 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -19.63 (c = 0.69, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 6.818 min, (minor) = 7.745 min.

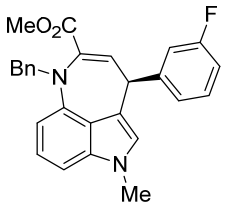
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.24 – 7.09 (m, 8H), 6.92 (dd, *J* = 6.6, 1.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.27 (s, 1H), 5.57 (d, *J* = 6.6 Hz, 1H), 4.87 (d, *J* = 13.8 Hz, 1H), 4.75 (d, *J* = 13.8 Hz, 1H), 3.64 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 160.8 (d, $J_{C\text{-}F}$ = 245.0 Hz), 141.5, 138.6 ,138.4, 137.5, 135.5, 130.23, 130.19, 129.4 (d, $J_{C\text{-}F}$ = 14.4 Hz), 129.0, 128.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.4, 127.4, 124.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 123.1, 122.8, 115.6 (d, $J_{C\text{-}F}$ = 21.8 Hz), 113.7, 104.8, 102.8, 54.1, 52.0, 35.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}FN_2NaO_2^+$ 449.1636; found 449.1628.

IR(neat): 3030, 1716, 1635, 1582, 1496, 1454, 1434, 1420, 1329, 1230, 1188, 1148, 1121, 1051, 932, 752, 730, 700 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(3-fluorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (*3*ac)



Yellow solid, (38.8 mg, 91% yield, 95% ee). m.p. = 65.1 – 68.2 °C.

R_f = 0.36 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -25.26 (c = 0.69, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.225 min, (minor) = 9.463 min.

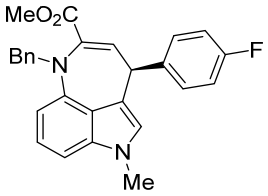
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.33 (m, 1H), 7.25 – 7.18 (m, 3H), 7.18 – 7.12 (m, 4H), 7.09 (dt, *J* = 10.2, 2.4 Hz, 1H), 7.04 (td, *J* = 8.4, 1.8 Hz, 1H), 6.91 (d, *J* = 6.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.21 (s, 1H), 5.26 (d, *J* = 6.0 Hz, 1H), 4.85 (d, *J* = 13.8, Hz, 1H), 4.77 (d, *J* = 13.8, Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 163.2(d, $J_{C\text{-}F}$ = 244.5 Hz), 145.22, 145.18, 141.2, 138.8, 138.4, 137.6, 135.9, 130.1 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.9, 128.4, 127.4, 124.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 120.5, 115.5 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.8, 113.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 105.0, 102.8, 54.1, 52.1, 41.9, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}FN_2NaO_2^+$ 449.1636; found 449.1633.

IR(neat): 3031, 1717, 1582, 1496, 1453, 1231, 1148, 767, 750, 730, 700 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(4-fluorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ad)



Yellow solid, (38.3 mg, 90% yield, 92% ee). m.p. = 143.5 – 146.6 °C.

R_f = 0.30 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -18.54 (c = 0.71, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.368 min, (minor) = 9.503 min.

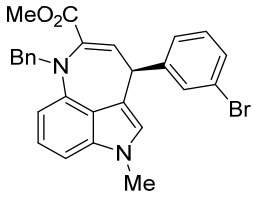
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.26 – 7.20 (m, 3H), 7.19 – 7.13 (m, 3H), 7.11 – 7.06 (m, 2H), 6.91 (d, *J* = 6.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 1.2 Hz, 1H), 5.26 (d, *J* = 6.0 Hz, 1H), 4.85 (d, *J* = 13.8 Hz, 1H), 4.77 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 161.9 (d, $J_{C\text{-}F}$ = 243.0 Hz), 141.3, 138.6, 138.4, 138.3(d, $J_{C\text{-}F}$ = 3.0 Hz), 137.7, 136.6, 130.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 128.9, 128.4, 127.4, 123.1, 120.5, 115.5 (d, $J_{C\text{-}F}$ = 21.0 Hz), 104.9, 102.8, 54.2, 52.1, 41.5, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}FN_2NaO_2^+$ 449.1636; found 449.1640.

IR(neat): 2922, 2852, 1716, 1606, 1497, 1460, 1262, 1226, 1187, 1148, 838, 798, 768, 731, 699 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(3-bromophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ae)



Yellow solid, (40.8 mg, 84% yield, 95% ee). m.p. = 64.7 – 69.4 °C.

R_f = 0.35 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -28.66 (c = 0.67, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.308 min, (minor) = 10.203 min.

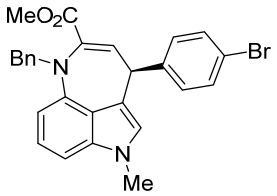
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (t, *J* = 1.8 Hz, 1H), 7.47 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.30 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.27 – 7.19 (m, 4H), 7.17 – 7.12 (m, 3H), 6.89 (d, *J* = 6.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.19 (s, 1H), 5.22 (d, *J* = 6.0, Hz, 1H), 4.84 (d, *J* = 13.8 Hz, 1H), 4.76 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 145.0, 141.2, 138.8, 138.3, 137.6, 135.7, 131.6, 130.3, 130.1, 128.9, 128.4, 127.4, 127.2, 123.2, 123.1, 122.8, 120.5, 114.8, 105.0, 102.8, 54.2, 52.1, 41.8, 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}BrN_2NaO_2^+$ 509.0835; found 509.0836.

IR(neat): 3030, 2925, 1717, 1633, 1580, 1497, 1461, 1421, 1399, 1327, 1231, 1148, 1072, 1052, 768, 731, 698 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(4-bromophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3af)



Yellow solid, (37.9 mg, 78% yield, 96% ee). m.p. = 74.3 – 77.4 °C.

R_f = 0.37 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -23.21 (c = 0.95, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.683 min, (minor) = 9.775 min.

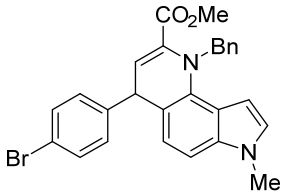
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.25 – 7.18 (m, 5H), 7.17 – 7.09 (m, 3H), 6.90 (d, *J* = 6.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 1H), 5.20 (d, *J* = 6.6 Hz, 1H), 4.83 (d, *J* = 13.8 Hz, 1H), 4.75 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 141.7, 141.2, 138.8, 138.4, 137.6, 135.9, 131.8, 130.3, 128.9, 128.4, 127.4, 123.2, 123.1, 120.7, 120.5, 114.9, 105.0, 102.8, 54.1, 52.1, 41.5, 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}BrN_2NaO_2^+$ 509.0835; found 509.0834.

IR(neat): 2925, 1717, 1633, 1580, 1497, 1461, 1421, 1327, 1231, 1148, 1072, 1052, 768, 731, 698 cm^{-1}.

Methyl 1-benzyl-4-(4-bromophenyl)-7-methyl-4,7-dihydro-1*H*-pyrrolo[2,3-*h*]quinoline-2-Carboxylate (4af)



Yellow solid, (7.7 mg, 16% yield). m.p. = 155.5 – 159.3 °C.

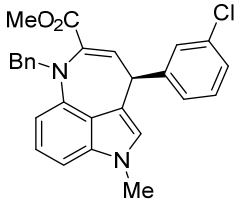
R_f = 0.15 (Pet/EtOAc, 8/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.17 (m, 3H), 7.15 – 7.07 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 3.0 Hz, 1H), 6.57 (dd, *J* = 25.8, 7.8 Hz, 3H), 6.17 (d, *J* = 4.8 Hz, 1H), 5.32 (d, *J* = 14.4 Hz, 1H), 5.13 (d, *J* = 14.4 Hz, 1H), 4.68 (d, *J* = 6.0 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.2, 145.0, 137.8, 137.4, 136.0, 134.9, 131.5, 130.3, 129.2, 128.4, 128.1, 127.6, 123.4, 122.6, 120.1, 119.7, 118.7, 105.6, 101.0, 54.7, 52.3, 43.3, 33.3.

IR(neat): 2922, 2853, 2158, 1724, 1646, 1490, 1482, 1453, 1305, 1290, 1265, 1237, 1183, 1119, 1104, 1094, 1076, 1008, 778, 747, 723, 699 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(3-chlorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ag)



Pale yellow solid, (35.8 mg, 81% yield, 96% ee).

R_f = 0.33 (Pet/EtOAc, 8/1, v/v). m.p. = 68.1 – 71.4 °C.

$[\alpha]_D^{26}$ = -30.93 (c = 0.72, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.178 min, (minor) = 9.853 min.

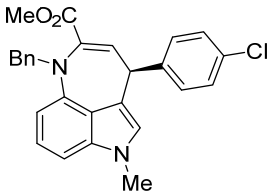
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.34 – 7.31 (m, 2H), 7.26 – 7.19 (m, 4H), 7.17 – 7.12 (m, 3H), 6.90 (d, *J* = 6.6 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 1H), 5.23 (d, *J* = 6.6 Hz, 1H), 4.84 (d, *J* = 13.8 Hz, 1H), 4.77 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 144.7, 141.2, 138.8, 138.4, 137.6, 135.8, 134.5, 130.0, 128.9, 128.7, 128.4, 127.4, 127.2, 126.8, 123.2, 123.1, 120.5, 114.8, 105.0, 102.8, 54.1, 52.1, 41.8, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}ClN_2NaO_2^+$ 465.1340; found 465.1344.

IR(neat): 3359, 2922, 2852, 1717, 1632, 1580, 1497, 1460, 1421, 1327, 1229, 1148, 768, 698 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(4-chlorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ah)



Pale yellow solid, (35.8 mg, 81% yield, 96% ee). m.p. = 109.7 – 112.5 °C.

R_f = 0.32 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -24.84 (c = 0.72, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.463 min, (minor) = 9.500 min.

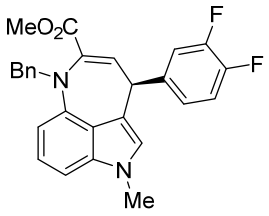
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 7.17 – 7.10 (m, 3H), 6.91 (d, *J* = 6.0 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.18 (s, 1H), 5.23 (d, *J* = 6.6 Hz, 1H), 4.84 (d, *J* = 13.8 Hz, 1H), 4.76 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 141.23, 141.17, 138.8, 138.4, 137.6, 136.1, 132.7, 129.9, 128.9, 128.8, 128.4, 127.4, 123.1, 120.5, 115.1, 105.0, 102.8, 54.1, 52.1, 41.5, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}ClN_2NaO_2^+$ 465.1340; found 465.1347.

IR(neat): 2920, 1737, 1712, 1581, 1498, 1454, 1393, 1319, 1262, 1234, 1188, 1157, 1047, 1014, 840, 771, 755, 745, 734, 698 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(3,4-difluorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ai)



Yellow solid, (27.5 mg, 62% yield, 96% ee). m.p. = 69.4 – 73.7 °C.

R_f = 0.35 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -33.93 (c = 1.18, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (minor) = 7.273 min, (major) = 9.675 min.

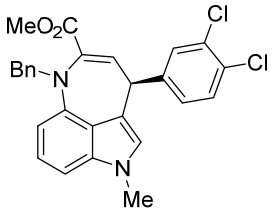
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 3H), 7.19 – 7.10 (m, 5H), 7.09 – 7.05 (m, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.22 (s, 1H), 5.18 (d, *J* = 6.6 Hz, 1H), 4.81 (d, *J* = 13.8 Hz, 1H), 4.76 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 150.5 (dd, $J_{C\text{-}F}$ = 246.0, 12.0 Hz), 149.4 (dd, $J_{C\text{-}F}$ = 244.5, 12.0 Hz), 141.2, 139.7 (t, $J_{C\text{-}F}$ = 3.0 Hz), 138.9, 138.4, 137.6, 135.4, 128.9, 128.4, 127.4, 124.4 (q, $J_{C\text{-}F}$ = 3.0 Hz), 123.2, 123.1, 120.4, 117.4 (t, $J_{C\text{-}F}$ = 18.0 Hz), 114.6, 105.0, 102.9, 54.1, 52.1, 41.2, 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}F_2N_2NaO_2^+$ 467.1542; found 467.1536.

IR(neat): 2922, 1417, 1633, 1607, 1580, 1497, 1460, 1421, 1326, 1238, 1149, 1051, 767, 732 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(3,4-dichlorophenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-Carboxylate (*3*aj)



Pale yellow solid, (35.7 mg, 75% yield, 97% ee). m.p. = 73.7 – 82.7 °C

R_f = 0.32 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -45.55 (c = 1.67, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.485 min, (minor) = 10.175 min.

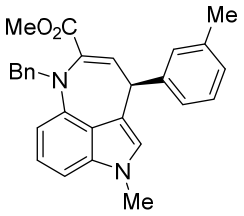
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.24 – 7.12 (m, 5H), 7.09 (dd, *J* = 7.2, 2.4 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.24 (s, 1H), 5.16 (d, *J* = 6.6 Hz, 1H), 4.81 (d, *J* = 13.8 Hz, 1H), 4.75 (d, *J* = 13.8 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 143.1, 141.1, 139.1, 138.4, 137.5, 134.9, 132.6, 130.9, 130.6, 130.5, 128.8, 128.4, 127.9, 127.4, 123.2, 120.4, 114.2, 105.1, 102.9, 54.1, 52.1, 41.1, 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}Cl_2N_2NaO_2^+$ 499.0951; found 499.0951.

IR(neat): 2922, 1717, 1633, 1580, 1497, 1462, 1421, 1401, 1326, 1231, 1148, 1053, 1029, 828, 766, 731, 698 cm^{-1}.

Methyl (*S*)-1-benzyl-6-methyl-4-(*m*-tolyl)-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ak)



Yellow solid, (33.8 mg, 80% yield, 88% ee). m.p. = 85.5 – 88.6 °C.

R_f = 0.27 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -2.67 (c = 0.75, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.148 min, (minor) = 9.178 min.

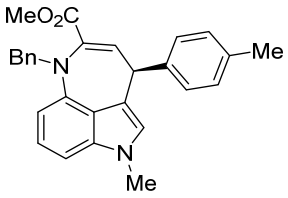
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.09 (m, 9H), 6.95 (d, *J* = 6.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 5.27 (d, *J* = 6.0, Hz, 1H), 4.87 (d, *J* = 14.0 Hz, 1H), 4.77 (d, *J* = 13.6 Hz, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 2.40 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 142.4, 141.4, 138.4, 138.3, 137.9, 137.6, 129.3, 128.9, 128.7, 128.4, 127.7, 127.3, 125.6, 123.1, 123.0, 120.7, 116.0, 104.8, 102.7, 54.2, 52.0, 42.4, 32.9, 21.7.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}N_2NaO_2^+$ 445.1886; found 445.1883.

IR(neat): 2947, 1717, 1633, 1580, 1497, 1460, 1421, 1327, 1231, 1148, 1072, 1052, 768, 698 cm^{-1}.

Methyl (*S*)-1-benzyl-6-methyl-4-(*p*-tolyl)-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3al)



Yellow solid, (38.0 mg, 90% yield, 93% ee). m.p. = 111.6 – 114.2 °C.

R_f = 0.27 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = 1.48 (c = 1.44, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.098 min, (minor) = 8.667 min.

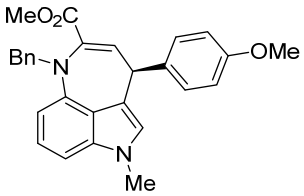
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 9H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 6.0 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.12 (s, 1H), 5.26 (d, *J* = 6.0 Hz, 1H), 4.85 (d, *J* = 13.8 Hz, 1H), 4.75 (d, *J* = 13.8 Hz, 1H), 3.63 (s, 3H), 3.60 (s, 3H), 2.40 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.9, 141.4, 139.4, 138.4, 138.3, 137.9, 137.6, 136.5, 129.4, 128.9, 128.5, 128.4, 127.3, 123.1, 123.0, 120.7, 116.0, 104.9, 102.6, 54.2, 52.0, 42.0, 32.9, 21.3.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}N_2NaO_2^+$ 445.1886; found 445.1886.

IR(neat): 3029, 2947, 1717, 1633, 1607, 1580, 1497, 1460, 1421, 1327, 1231, 1148, 1072, 768, 732, 698 cm^{-1}.

Methyl (*S*)-1-benzyl-4-(4-methoxyphenyl)-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3am)



Pale yellow solid, (29.3 mg, 67% yield, 95% ee). m.p. = 168.3 – 171.4 °C.

R_f = 0.18 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -5.49 (c = 0.60, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 8.547 min, (minor) = 10.473 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.25 – 7.16 (m, 5H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.98 – 6.89 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 1.2 Hz, 1H), 5.25 (d, *J* = 6.4,

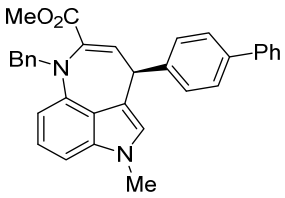
1H), 4.86 (d, *J* = 14.0 Hz, 1H), 4.76 (d, *J* = 14.0 Hz, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 3.60 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.9, 158.7, 141.4, 138.4, 138.2, 137.9, 137.7, 134.6, 129.6, 128.9, 128.4, 127.3, 123.1, 123.0, 120.6, 116.2, 114.1, 104.8, 102.7, 55.5, 54.2, 52.0, 41.6, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}N_2NaO_3^+$ 461.1836; found 461.1841.

IR(neat): 2924, 1717, 1633, 1581, 1497, 1460, 1421, 1327, 1230, 1148, 1071, 1052, 768, 732 cm^{-1}.

Methyl (*S*)-4-([1,1'-biphenyl]-4-*yl*)-1-benzyl-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3an)



Yellow solid, (35.8 mg, 73% yield, 95% ee). m.p. = 89.9 – 94.1 °C.

R_f = 0.32 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -17.14 (c = 1.65, $CHCl_3$).

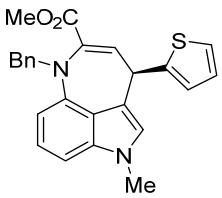
HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 8.448 min, (minor) = 11.053 min.

^1H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 4H), 7.52 – 7.44 (m, 4H), 7.43 – 7.36 (m, 1H), 7.24 – 7.12 (m, 6H), 7.01 (d, *J* = 6.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 6.6, Hz, 1H), 4.88 (d, *J* = 13.8 Hz, 1H), 4.79 (d, *J* = 13.8 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 165.9, 141.7, 141.4, 141.1, 140.0, 138.5, 138.4, 137.7, 136.8, 128.98, 128.95, 128.9, 128.4, 127.5, 127.4, 127.3, 127.2, 123.2, 123.1, 120.7, 115.5, 104.9, 102.7, 54.2, 52.0, 41.8, 32.9.

IR(neat): 2924, 1717, 1633, 1580, 1497, 1460, 1421, 1327, 1232, 1071, 1052, 768, 732, 698 cm^{-1}.

Methyl (*R*)-1-benzyl-6-methyl-4-(thiophen-2-*yl*)-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ao)



Yellow solid, (33.9 mg, 82% yield, 88% ee). m.p. = 65.4 – 71.5 °C.

R_f = 0.26 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = -12.03 (c = 1.69, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 7.647 min, (minor) = 8.822 min.

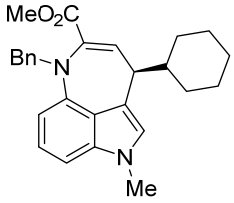
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.25 – 7.17 (m, 5H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.92 (d, *J* = 6.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.45 (s, 1H), 5.61 (d, *J* = 6.6 Hz, 1H), 4.84 (d, *J* = 13.8 Hz, 1H), 4.80 (d, *J* = 13.8 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.8, 145.7, 141.0, 138.5, 138.3, 137.7, 136.5, 128.8, 128.4, 127.3, 126.9, 125.4, 124.0, 123.14, 123.11, 120.3, 115.1, 105.0, 102.8, 54.1, 52.1, 37.3, 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{25}H_{22}N_2NaO_2S^+$ 437.1294; found 437.1291.

IR(neat): 2920, 2851, 1716, 1580, 1496, 1460, 1421, 1325, 1239, 1148, 1069, 767, 732, 697 cm^{-1}.

Methyl (*R*)-1-benzyl-4-cyclohexyl-6-methyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ap)



Yellow solid, (9.0 mg, 22% yield, 89% ee). m.p. = 135.2 – 138.4 °C.

R_f = 0.32 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{25}$ = -79.09 (c = 0.88, $CHCl_3$).

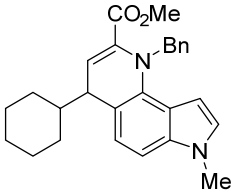
HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 9.382 min, (minor) = 12.107 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.59 (s, 1H), 4.78 (s, 2H), 3.68 (s, 3H), 3.62 (s, 3H), 3.25 (t, *J* = 8.8 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.91 (d, *J* = 13.2 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.22 – 1.11 (m, 2H), 1.09 – 0.79 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 141.5, 138.2, 137.8, 137.7, 135.5, 129.7, 128.3, 127.5, 123.2, 122.7, 120.0, 113.7, 104.0, 102.4, 54.0, 51.9, 42.4, 40.3, 32.9, 32.0, 31.7, 26.7, 26.5.

IR(neat): 2917, 2848, 1714, 1577, 1498, 1461, 1449, 1419, 1406, 1327, 1298, 1245, 1153, 1129, 1057, 769, 735, 714, 700 cm^{-1}.

Methyl 1-benzyl-4-cyclohexyl-7-methyl-4,7-dihydro-1*H*-pyrrolo[2,3-*h*]quinoline-2-carboxylate (4ap)



Yellow solid, (16.8 mg, 41% yield, 5% ee). m.p. = 168.0 – 170.2 °C.

R_f = 0.27 (Pet/EtOAc, 8/1, v/v).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 23.158 min, (minor) = 13.753 min.

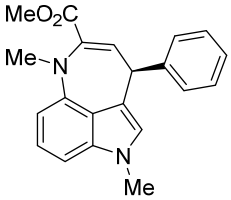
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 3H), 7.07 (d, J = 3.0 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 7.2 Hz, 2H), 6.76 (d, J = 3.0 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 6.42 (d, J = 6.6 Hz, 1H), 5.39 (d, J = 14.4 Hz, 1H), 5.14 (d, J = 15.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.92 (dd, J = 9.0, 7.2 Hz, 1H), 1.60 (d, J = 12.0 Hz, 1H), 1.51 (d, J = 9.6 Hz, 3H), 1.39 (d, J = 12.0 Hz, 3H), 1.10 – 0.95 (d, J = 12.0 Hz, 1H), 0.85 – 0.65 (m, 4H), 0.17 – 0.08 (m, 1H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 165.3, 138.0, 137.1, 135.9, 134.1, 129.4, 128.2, 127.7, 127.5, 126.1, 124.1, 120.3, 120.1, 104.3, 100.4, 54.1, 52.1, 45.8, 44.6, 33.2, 31.1, 30.2, 26.7, 26.1, 26.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{30}N_2NaO_2^+$ 437.2199; found 437.2198.

IR(neat): 2920, 2854, 1720, 1637, 1485, 1448, 1436, 1421, 1307, 1292, 1262, 1240, 1219, 1126, 1100, 1080, 1032, 789, 762, 746, 714, 705 cm^{-1}.

Methyl (*S*)-1,6-dimethyl-4-phenyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ba)



White solid, (25.9 mg, 78% yield, 84% ee). m.p. = 148.5 – 150.1 °C.

R_f = 0.40 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{26}$ = +6.82 (c = 0.440, $CHCl_3$).

HPLC CHIRALPAK IC, n-hexane/2-propanol =70/30, flow rate 0.8 mL/min, λ = 254 nm, retention time: (major) = 9.128 min, (minor) = 11.215 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.07 (s, 1H), 5.23 (d, *J* = 6.0Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 3.22 (s, 3H).

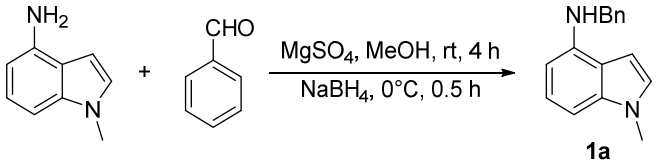
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 143.0, 141.9, 139.1, 138.3, 134.3, 128.8, 128.6, 127.0, 123.0, 119.8, 116.6, 103.3, 102.1, 52.1, 42.5, 38.7, 32.9.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{20}N_2NaO_2^+$ 355.1417; found 355.1411.

IR(neat): 2912, 1717, 1633, 1606, 1572, 1494, 1470, 1438, 1416, 1392, 1379, 1323, 1253, 1231, 1195, 1130, 1050, 935, 831, 769, 734, 702, 604, 518 cm^{-1}.

Synthesis of starting materials

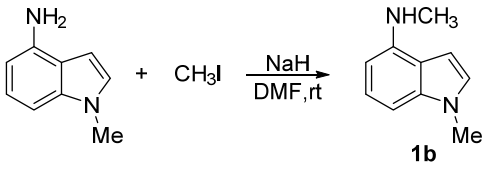
The synthesis of N-benzyl-1-methyl-1*H*-indol-4-amine (1a) [1]



1a

To a solution of 1-methyl-1*H*-indol-4-amine (5.0 g, 34.0 mmol) and benzaldehyde (4.0 g, 37.4 mmol) in MeOH (200 mL) was added $MgSO_4$ (40.9 g, 340.0 mmol) at room temperature. After 4 hours, the mixture was cooled to 0 °C, then treated with $NaBH_4$ (1.5 g, 40.8 mmol) in small portions. After stirring at 0 °C for 30 min, the reaction was quenched by water (300 mL), and then extracted with EtOAc (250 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 100/1, v/v) to afford **1a** as a white solid with 70% yield (5.6 g). The values of the NMR spectra are in accordance with reported literature data[1].

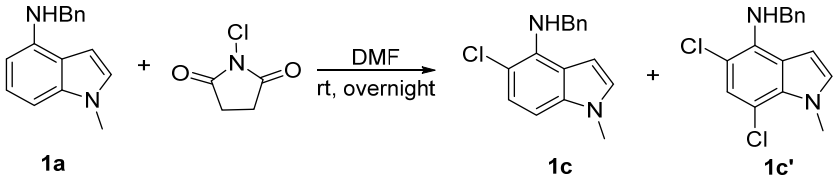
The synthesis of N,1-dimethyl-1*H*-indol-4-amine (1b)



1b

Methyl-1*H*-indol-4-amine (4.39 g, 30.0 mmol) were dissolved in DMF. Then, NaH (2.16 g, 90.0 mmol) was added at 0°C and stirred at 0°C for 30 minutes. After that, iodine-methane (1.87 mL, 30.0 mmol) was added. After the disappearance of 1-methyl-1*H*-indol-4-amine, the reaction was quenched by water (30 mL) and extracted with EtOAc (25 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 300/1, v/v) to afford **1b** as a white solid with 38% yield (1.8 g)

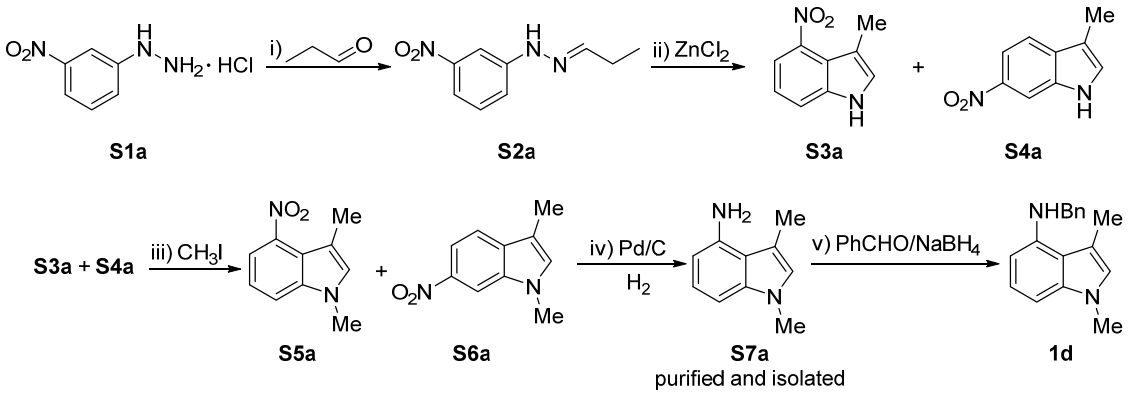
The synthesis of N-benzyl-5-chloro-1-methyl-1*H*-indol-4-amine (1c)



1a **1c** **1c'**

N-Benzyl-1-methyl-1*H*-indol-4-amine **1a** (1.9 g, 8.0 mmol) and NCS (1.6 g, 12.0 mmol) were added to a flask with DMF (30 mL) and stirred at room temperature overnight. At the end of the reaction, water and ethyl acetate were added to the reaction solution. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×50 mL). The combined organic layers were washed with water (3×50 mL) and dried over anhydrous Na_2SO_4. After filtration and removal of the solvents, the resulted residue was purified by silica gel column chromatography using Pet/EtOAc system (Pet/EtOAc = 500/1, v/v) to afford products **1c** and **1c'**.

The synthesis of N-benzyl-1,3-dimethyl-1*H*-indol-4-amine (1d)



i) To a solution of 3-nitrophenylhydrazine hydrochloride **S1a** (3.8 g, 20 mmol) in EtOH (100 mL) was added Et_3N (3.3 mL, 24 mmol) at room temperature. After 0.5 h, acetic acid was added to the reaction solution to adjust the pH to 6, and then n-propanal was added and stirred at room temperature for 3 h. Then, the reaction mixture was poured into ice water. The precipitation was then filtered, separated, washed with water and dried by air to afford **S2a**.

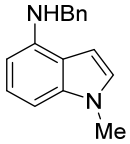
ii) Compound **S2a** (2.7 g, 14.0 mmol) was dissolved in toluene. Then, zinc chloride (5.7 g, 42.0 mmol) was added to the reaction solution and stirred overnight at 100°C. After the disappearance of **S2a**, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Then, water was added, and the reaction mixture was extracted with EtOAc (25 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and vacuum concentration results in a mixture that was directly used in the next step.[Note: **S3a** and **S4a** were difficult to separate because the polarity was too close.]

iii) Compounds (**S3a** + **S4a**) (1.9 g, 11.0 mmol) were dissolved in DMF. Then, NaH (0.8 g, 33.0 mmol) was added at 0°C and stirred at 0°C for 30 minutes. After that, iodine-methane (1.4 mL, 22.0 mmol) was added. After the disappearance of **S3a** and **S4a**, the reaction was quenched by water (30 mL) and extracted with EtOAc (25 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and vacuum concentration results in a mixture that is directly used in the next step.

iv) Compounds (**S5a** + **S6a**) (1.6 g, 8.4 mmol) were dissolved in EtOH. Then, Pd/C (1.8 g, 16.8 mmol) was added and the reaction was stirred under H_2 gas at room temperature overnight. After the reaction was complete, the reaction mixture was filtered and concentrated. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 500/1, v/v) to afford the product **S7a**.

v) Compound **S7a** (5.0 g, 34.0 mmol) [After many accumulations], benzaldehyde (3.8 mL, 37.4 mmol), and $MgSO_4$ (41.0 g, 340 mmol) were dissolved in MeOH (150 mL), and the reaction was stirred at room temperature for 4 h. Then, the reaction mixture was cooled to 0 °C and treated with $NaBH_4$ (1.5 g, 40.8 mmol). After stirring at 0 °C for another 30 min, the reaction was quenched by water (30 mL), and then extracted with EtOAc (25 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 400/1, v/v) to afford product **1d** as a white solid with 68% yield (5.8 g).

N-Benzyl-1-methyl-1*H*-indol-4-amine (1a)



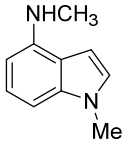
White solid. m.p. = 74.1 – 76.4 °C.

R_f = 0.35 (Pet/EtOAc, 8/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 3.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.43 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 4.54 (s, 2H), 4.34 (s, 1H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 139.9, 137.5, 128.7, 127.7, 127.3, 126.7, 123.2, 117.2, 99.9, 99.5, 97.1, 48.5, 33.1.

N,1-dimethyl-1*H*-indol-4-amine (1b)



Yellow solid. m.p. = 86.1 – 87.3 °C.

R_f = 0.29 (Pet/EtOAc, 8/1, v/v).

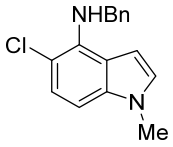
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 3.6 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.37 (d, *J* = 3.0 Hz, 1H), 6.30 (d, *J* = 7.2 Hz, 1H), 4.00 (s, 1H), 3.76 (s, 3H), 3.00 (s, 3H).

^{13}C{^{1}H} (150 MHz, $CDCl_3$) δ 142.8, 137.4, 126.6, 123.2, 117.3, 99.7, 98.7, 97.0, 33.2, 31.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{13}N_2^+$ 161.1073; found 161.1069.

IR(neat): 3418, 2901, 1587, 1499, 1411, 1398, 1351, 1279, 1161, 1078, 1053, 778, 732, 707 cm^{-1}.

N-Benzyl-5-chloro-1-methyl-1*H*-indol-4-amine (1c)



White solid. m.p. = 96.5 – 106.3 °C.

R_f = 0.42 (Pet/EtOAc, 8/1, v/v).

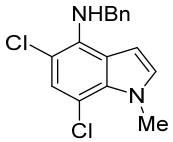
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 3.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 4.81 (s, 2H), 4.75 (s, 1H), 3.71 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 140.5, 138.1, 137.4, 128.8, 127.6, 127.5, 127.4, 123.1, 118.1, 110.4, 100.7, 100.4, 50.9, 33.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}ClN_2^+$ 271.0997; found 271.0995.

IR(neat): 2924, 1726, 1597, 1495, 1515, 1451, 1398, 1293, 1230, 1070, 781, 734, 699, 676 cm^{-1}.

N-Benzyl-3-chloro-1-methyl-1*H*-indol-4-amine (1c')



White solid. m.p. = 84.4 – 87.7 °C.

R_f = 0.48 (Pet/EtOAc, 8/1, v/v).

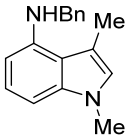
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 6.86 (d, *J* = 3.0 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 4.70 (s, 2H), 4.57 (s, 1H), 4.08 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 140.2, 137.2, 132.3, 130.5, 128.8, 127.53, 127.45, 123.7, 121.6, 110.8, 107.4, 100.6, 51.4, 37.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}Cl_2N_2^+$ 305.0607; found 305.0601.

IR(neat): 3400, 1567, 1508, 1492, 1443, 1427, 1357, 1338, 1311, 1287, 1252, 1042, 957, 845, 798, 738, 718, 705, 695 cm^{-1}.

N-Benzyl-1,3-dimethyl-1*H*-indol-4-amine (1d)



White solid. m.p. = 64.1 – 65.4 °C.

R_f = 0.29 (Pet/EtOAc, 8/1, v/v).

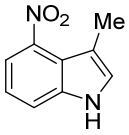
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.46-7.40 (m, 2H), 7.39-7.32 (m, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 4.90 (s, 1H), 4.52 (s, 2H), 3.70 (s, 3H), 2.60 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.6, 134.0, 138.5, 128.7, 127.5, 127.2, 125.0, 123.2, 116.2, 109.1, 99.9, 99.3, 48.5, 32.7, 13.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2^+$ 251.1543; found 251.1537.

IR(neat): 3427, 1607, 1581, 1550, 1503, 1452, 1418, 1342, 1279, 1166, 1070, 769, 730, 695 cm^{-1}.

3-Methyl-4-nitro-1*H*-indole (S3a)



Yellow solid. m.p. = 135.5 – 141.6 °C.

R_f = 0.05 (Pet/EtOAc, 8/1, v/v).

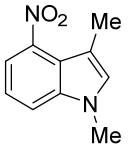
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.18 (m, 2H), 2.42 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 127.01, 120.75,120.1, 117.36, 117.01, 111.84, 13.21.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_9H_8N_2NaO_2^+$ 199.0478; found 199.0475.

IR(neat): 3354, 2921, 2852, 1528, 1510, 1465, 1353, 1315, 1282, 1087, 1055, 979, 798, 786, 730 cm^{-1}.

1,3-Dimethyl-4-nitro-1*H*-indole (S5a)



Yellow solid. m.p. = 102.1 – 104.2 °C.

R_f = 0.52 (Pet/EtOAc, 8/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 3.80 (s, 3H), 2.39 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 132.0, 120.4, 120.2, 116.8, 115.0, 110.1, 33.1, 13.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}N_2NaO_2^+$ 213.0634; found 213.0626.

IR(neat): 2922, 2854, 1542, 1514, 1473, 1375, 1350, 1328, 1293, 1211, 1060, 920, 794, 737, 632 cm^{-1}.

X-ray data

Figure S2. X-Ray crystal structure of (***S***)**-3af** (The crystal was obtained by slow evaporation of (***S***)**-3af** in a mixture of Pet/EtOAc/CH_2Cl_2). (CCDC:2225438):

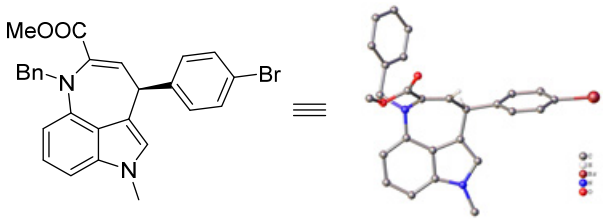


Table S1 Crystal data and structure refinement for (*S*)-3af.

Identification code	(***S***)**-3af**
Empirical formula	$C_{27}H_{23}BrN_2O_2$
Formula weight	487.40
Temperature/K	293
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5102(2)
b/Å	10.95350(10)
c/Å	22.7080(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2365.49(7)
Z	4
$\rho_{calc}g/cm^3$	1.3685
μ/mm^{-1}	2.570
F(000)	999.9
Crystal size/mm^3	0.15 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.78 to 143.1
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -27 ≤ l ≤ 22
Reflections collected	35613
Independent reflections	4590 [R_{int} = 0.0485, R_{sigma} = 0.0253]
Data/restraints/parameters	4590/0/291
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1017
Final R indexes [all data]	R_1 = 0.0457, wR_2 = 0.1031
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.71
Flack parameter	-0.01(2)

Figure S3. X-Ray crystal structure of **4af** (The crystal was obtained by slow evaporation of **4af** in a mixture of Pet/EtOAc/CH_2Cl_2) (CCDC:2225440):

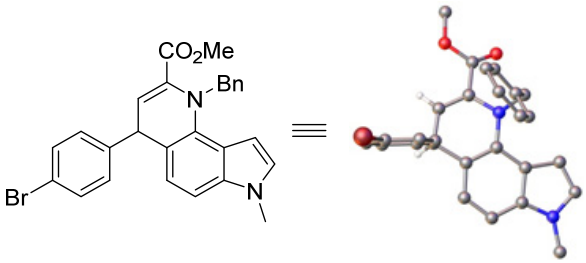


Table S2 Crystal data and structure refinement for 4af.

Identification code	**4af**
Empirical formula	$C_{27}H_{23}BrN_2O_2$
Formula weight	487.38
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	9.4265(4)
b/Å	10.3316(5)
c/Å	13.1925(5)
α/°	81.151(4)
β/°	78.346(3)
γ/°	64.360(4)
Volume/$Å^3$	1131.22(9)
Z	2
$\rho_{calc}g/cm^3$	1.431
μ/mm^{-1}	2.687
F(000)	500.0
Crystal size/mm^3	0.16 × 0.09 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.86 to 143.384
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -11 ≤ l ≤ 16
Reflections collected	9034
Independent reflections	4301 [R_{int} = 0.0205, R_{sigma} = 0.0280]
Data/restraints/parameters	4301/0/291
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.0972
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1010
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.68

Figure S4. X-Ray crystal structure of **1c** (The crystal was obtained by slow evaporation of **1c** in a mixture of Pet/EtOAc/CH_2Cl_2) (CCDC:2225441):

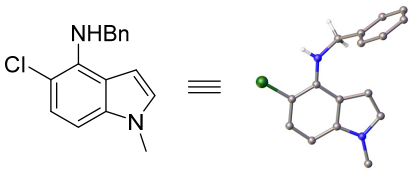


Table S3 Crystal data and structure refinement for 1c.

Identification code	**1c**
Empirical formula	$C_{16}H_{15}ClN_2$
Formula weight	270.75
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2358(3)
b/Å	5.6225(2)
c/Å	24.3001(8)
α/°	90
β/°	101.373(3)
γ/°	90
Volume/$Å^3$	1371.03(8)
Z	4
$\rho_{calc}g/cm^3$	1.312
μ/mm^{-1}	2.344
F(000)	568.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.422 to 143.038
Index ranges	-12 ≤ h ≤ 12, -6 ≤ k ≤ 3, -18 ≤ l ≤ 29
Reflections collected	5865
Independent reflections	2614 [R_{int} = 0.0396, R_{sigma} = 0.0380]
Data/restraints/parameters	2614/0/177
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0788, wR_2 = 0.2180
Final R indexes [all data]	R_1 = 0.0882, wR_2 = 0.2348
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.54

Figure S5. X-Ray crystal structure of **1c'** (The crystal was obtained by slow evaporation of **1c'** in a mixture of Pet/EtOAc/CH_2Cl_2) (CCDC:2225450):

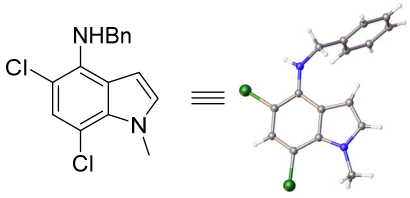


Table S4 Crystal data and structure refinement for 1c'.

Identification code	**1c'**
Empirical formula	$C_{16}H_{14}Cl_2N_2$
Formula weight	305.19
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5101(4)
b/Å	5.3886(2)
c/Å	23.0853(8)
α/°	90
β/°	95.195(3)
γ/°	90
Volume/$Å^3$	1425.95(9)
Z	4
$\rho_{calc}g/cm^3$	1.422
μ/mm^{-1}	4.004
F(000)	632.0
Crystal size/mm^3	0.15 × 0.06 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.69 to 142.674
Index ranges	-13 ≤ h ≤ 14, -6 ≤ k ≤ 2, -28 ≤ l ≤ 27
Reflections collected	5399
Independent reflections	2718 [R_{int} = 0.0219, R_{sigma} = 0.0344]
Data/restraints/parameters	2718/0/186
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0450, wR_2 = 0.1199
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.1271
Largest diff. peak/hole / e $Å^{-3}$	0.26/-0.31

Figure S6. X-Ray crystal structure of **1d** (The crystal was obtained by slow evaporation of **1d** in a mixture of Pet/EtOAc/CH_2Cl_2) (CCDC:2225454):

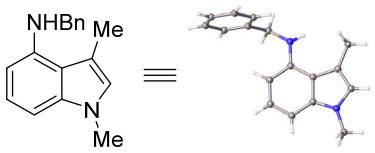
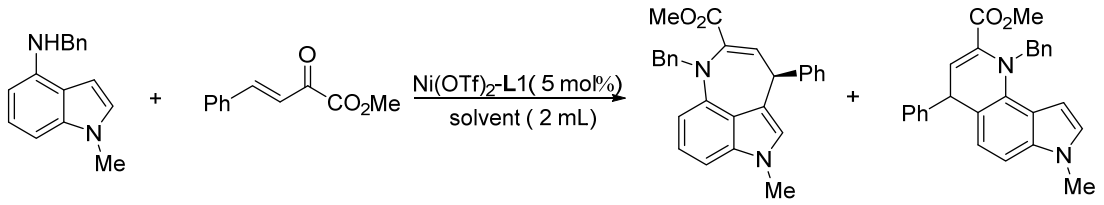


Table S5 Crystal data and structure refinement for 1d.

Identification code	**1d**
Empirical formula	$C_{17}H_{18}N_2$
Formula weight	250.33
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7952(4)
b/Å	5.4138(2)
c/Å	24.3400(8)
α/°	90
β/°	99.872(4)
γ/°	90
Volume/Å^3	1401.44(9)
Z	4
ρ_{calc}g/cm^3	1.186
μ/mm^{-1}	0.538
F(000)	536.0
Crystal size/mm^3	0.15 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.374 to 143.044
Index ranges	-13 ≤ h ≤ 13, -6 ≤ k ≤ 4, -18 ≤ l ≤ 29
Reflections collected	5862
Independent reflections	2654 [R_{int} = 0.0336, R_{sigma} = 0.0455]
Data/restraints/parameters	2654/0/178
Goodness-of-fit on F^2	1.162
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.1921
Final R indexes [all data]	R_1 = 0.0995, wR_2 = 0.2020
Largest diff. peak/hole / e Å^{-3}	0.16/-0.21

Optimization study

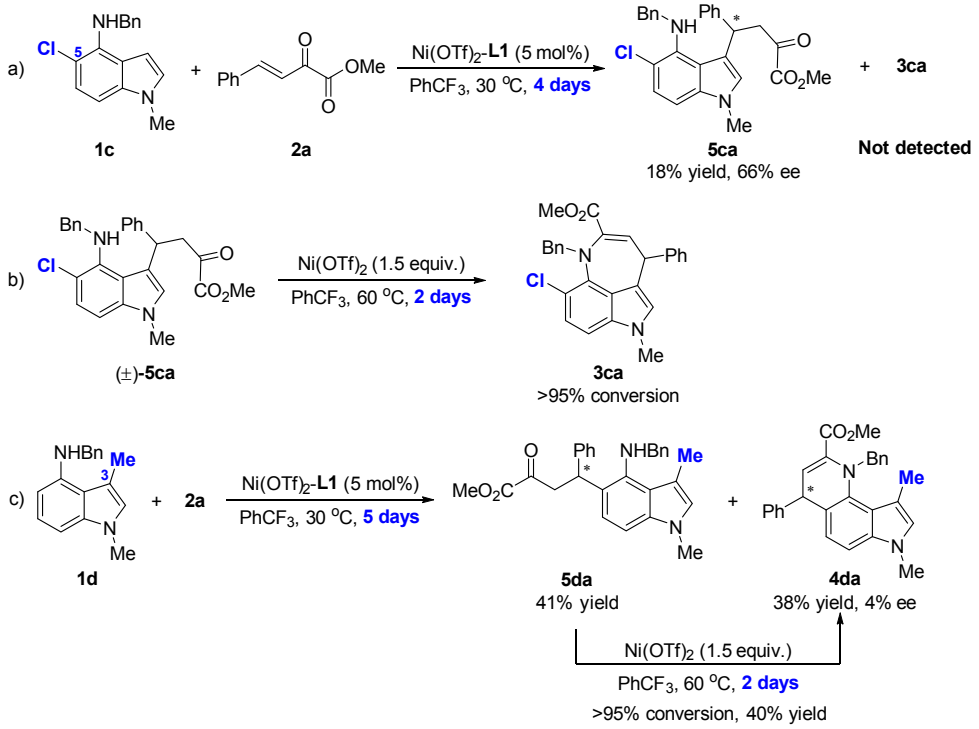


1a **2a** **3aa** **4aa**

Entry	**1a**: **2a**	Solvent	Additive	t (h)	Conv. [b](%)	**3aa**/**4aa**[b]	ee (**3aa**) [c](%)
1	1.5: 1	PhMe	-	8	38	81:19	66
2	1.5: 1	$PhCF_3$	-	6	86	86:14	89
3	1.5: 1	$PhCF_3$	3 Å MS (20 mg)	8	88	86:14	89
4	1.5: 1	$PhCF_3$	4 Å MS (20 mg)	6	91	87:13	76
5	1.5: 1	$PhCF_3$	5 Å MS (20 mg)	6	>95	91:9	90
6	1.5: 1	DCE	5 Å MS (20 mg)	6	94	86:14	72
7	1.5: 1	mesitylene	5 Å MS (20 mg)	6	64	89:11	86
8	1.3: 1	$PhCF_3$	5 Å MS (20 mg)	6	>95	91:9	91
9	2.0: 1	$PhCF_3$	5 Å MS (20 mg)	6	>95	91:9	90

[a]Reaction conditions: indole **1a**, **2a** (19.0 mg, 0.1 mmol), **L1** (3.4 mg, 0.005 mmol, 5 mol%), $Ni(OTf)_2$ (1.78 mg, 0.005 mmol, 5 mol%) in solvent (2 mL) for 6-8 h. [b] Determined by ^1H NMR spectra of the crude product. [c] Determined by chiral HPLC analysis.

Mechanism study



a) In a test tube, **L1** and $Ni(OTf)_2$ (5 mol%, 1:1) were added. Then β,γ-unsaturated α-ketoester **2a** (0.1 mmol) and $PhCF_3$ (2.0 mL) were added at air atmosphere. After stirred at 30 °C for 0.5 hour, the N-benzyl-5-chloro-1-methyl-1*H*-indol-4-amine **1c** (1.3 equiv., 35.0 mg) was added. The reaction mixture was stirred 4 d at 30 °C.

b) In a test tube, $Ni(OTf)_2$ (1.5 equiv) and $PhCF_3$ were added at air atmosphere. After stirred at 60 °C for 24 hour, product **5ca** (13.8 mg, 0.03 mmol) could be completely converted into **3ca (Figure S7)**. Finally, product **3ca** was purified directly by flash column chromatography (Pet/EtOAc, 100/1, v/v).

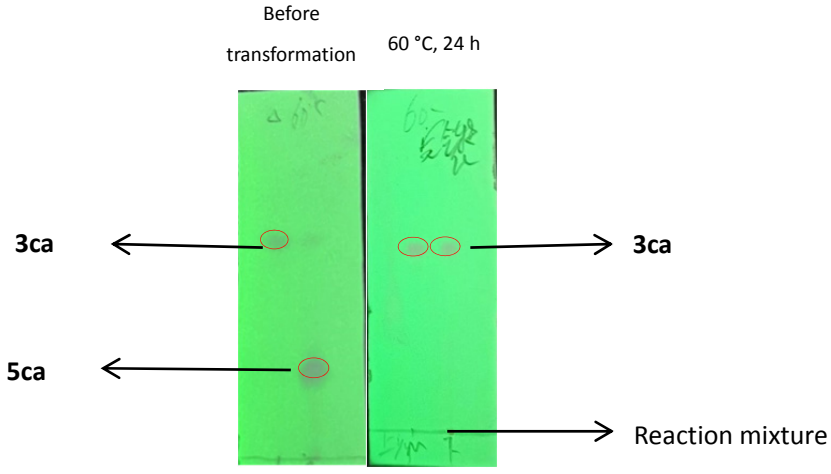
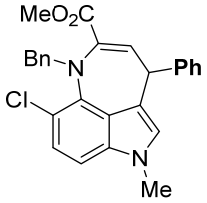


Figure S7. Pet/EtOAc, 5/1, v/v

c) In a test tube, **L1** and $Ni(OTf)_2$ (5 mol%, 1:1) were added. Then β,γ-unsaturated α-ketoester **2a** (0.1 mmol) and $PhCF_3$ (2.0 mL) were added at air atmosphere. After stirred at 30 °C for 0.5 hour, the N-benzyl-1,3-dimethyl-1*H*-indol-4-amine **1d** (1.3 equiv., 32.5 mg) was added. The reaction mixture was stirred at 30 °C 5 d. After flash column chromatography (Pet/EtOAc, 100/1, v/v), the pure product **4da** was obtained. Then $Ni(OTf)_2$ (1.5 equiv) and $PhCF_3$ were added to **5da** at air atmosphere. After stirred at 60 °C for 2d, product **5da** could be converted into **4da** (>95% conversion, 40% yield).

Methyl 1-benzyl-9-chloro-6-methyl-4-phenyl-4,6-dihydro-1*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (3ca)



Yellow solid, m.p. = 144.4 – 149.5 °C.

R_f = 0.35 (Pet/EtOAc, 8/1, v/v).

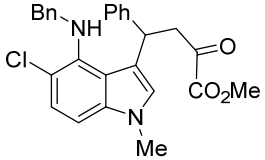
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 6H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.14 – 7.07 (m, 3H), 6.88 (d, J = 8.6 Hz, 1H), 5.85 (s, 1H), 5.02 (d, J = 14.4 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H), 4.20 (d, J = 3.6 Hz, 1H), 3.81 (s, 3H), 3.55 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 166.2, 143.3, 142.2, 139.4, 137.1, 137.0, 136.7, 129.3, 128.8, 128.7, 128.5, 127.5, 127.2, 125.1, 124.8, 124.5, 117.5, 115.8, 105.5, 57.7, 52.3, 42.3, 33.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}ClN_2NaO_2^+$ 465.1340; found 465.1338.

IR(neat): 2923, 1709, 1627, 1573, 1478, 1452, 1397, 1303, 1282, 1121, 1076, 1059, 1034, 780, 771, 757, 703 cm^{-1}.

Methyl 4-(4-(benzylamino)-5-chloro-1-methyl-1*H*-indol-3-*yl*)-2-oxo-4-phenylbutanoate (5ca)



Yellow solid (8.8 mg, 18% yield, 66% ee). m.p. ≥300 °C.

R_f = 0.085 (Pet/EtOAc, 8/1, v/v).

$[\alpha]_D^{23}$ = 5.07 (c = 0.50, $CHCl_3$).

HPLC CHIRALPAK ODH, n-hexane/2-propanol = 90/10, flow rate 0.8 mL/min, λ = 254 nm, retention time: (minor) = 23.262 min, (major) = 34.773 min.

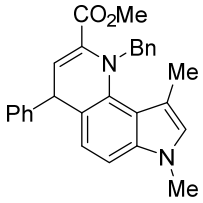
^{1}H NMR (600 MHz, $CDCl_3$) δ7.41 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 1H), 7.24 – 7.12 (m, 7H),6.92 (d, J = 9.0 Hz, 1H), 6.76 (s, 1H), 5.27 (t, J = 7.8 Hz, 1H), 4.23 (dd, *J* = 16.8, 13.2 Hz, 2H), 3.78 – 3.66 (m, 7H), 3.51 (dd, J = 17.4, 7.8 Hz, 1H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 192.5, 161.6, 143.7, 139.8, 139.2, 137.7, 128.7, 128.6, 128.5, 127.9, 127.7, 127.4, 126.8, 123.7, 122.2, 119.3, 117.1, 105.6, 55.3, 53.0, 47.3, 37.9, 33.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}ClN_2O_3^+$ 461.1626; found 461.1620.

IR(neat): 2923, 1727, 1603, 1490, 1452, 1413, 1230, 1268, 1063, 976, 783, 752, 699 cm^{-1}.

Methyl 1-benzyl-7,9-dimethyl-4-phenyl-4,7-dihydro-1*H*-pyrrolo[2,3-*h*]quinoline-2-carboxylate (4da)



Yellow solid (16.0 mg, 38% yield, 4% ee). m.p. = 67.4 – 75.6 °C.

R_f = 0.40 (Pet/EtOAc, 8/1, v/v).

HPLC CHIRALPAK ASH, n-hexane/2-propanol =90/10, flow rate 0.5 mL/min, λ = 254 nm, retention time: (major) = 10.972 min, (minor) = 13.618 min.

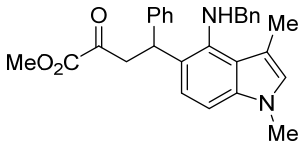
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.09 (m, 6H), 6.91 – 6.81 (m, 3H), 6.76 (d, *J* = 7.2 Hz, 2H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 4.89 (d, *J* = 14.0 Hz, 1H), 4.82 (d, *J* = 14.0 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 3H), 2.71 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1, 145.7, 138.1, 137.7, 137.4, 134.8, 129.5, 129.3, 128.5, 128.2, 127.6, 127.5, 126.4, 122.2, 120.5, 110.1, 105.7, 59.6, 52.1, 43.8, 32.9, 12.0.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}N_2NaO_2^+$ 445.1886; found 445.1881.

IR(neat): 2922, 2852, 1716, 1633, 1449, 1412, 1374, 1316, 1247, 1121, 1056, 1029, 825, 790, 767, 733, 701 cm^{-1}.

Methyl-4-(4-(benzylamino)-1,3-dimethyl-1*H*-indol-5-*yl*)-2-oxo-4-phenylbutanoate (5da)



Yellow solid (18.0 mg, 41% yield,). m.p. = 63.2 – 66.7 °C.

R_f = 0.38 (Pet/EtOAc, 8/1, v/v).

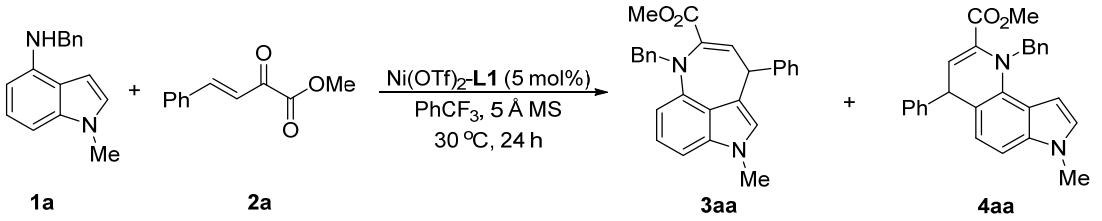
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.25 – 7.19 (m, 1H), 7.19 – 7.13 (m, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.23 (d, *J* = 7.6 Hz, 1H), 5.19 – 5.11 (m, 1H), 4.44 (s, 2H), 3.89-3.76 (m, 1H), 3.75 – 3.60 (m, 4H), 3.43 (s, 3H), 2.52 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.5, 161.0, 143.3, 140.9, 139.9, 138.4, 133.5, 128.8, 127.6, 127.3, 126.9, 126.8, 123.2, 115.7, 107.9, 100.0, 99.7, 77.4, 53.1, 48.6, 42.5, 34.9, 31.0, 12.5.

HRMS (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{28}H_{28}KN_2O_3^+$ 479.1732; found 479.1731.

IR(neat): 2922, 2852, 1728, 1660, 1632, 1595, 1516, 1451, 1398, 1292, 1234, 1069, 1040, 789, 736, 699 cm^{-1}.

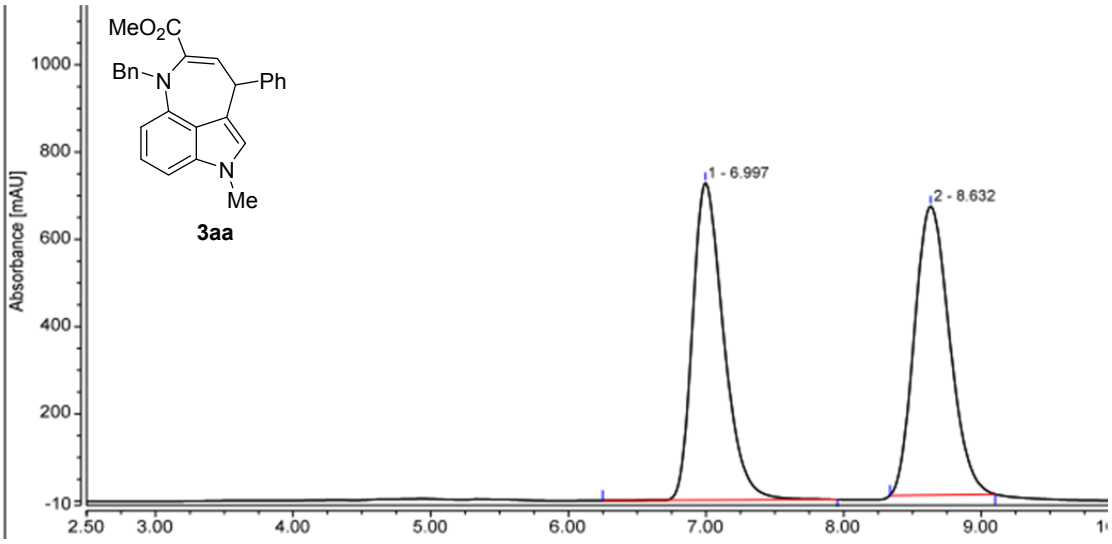
Gram-scale synthesis of 3aa



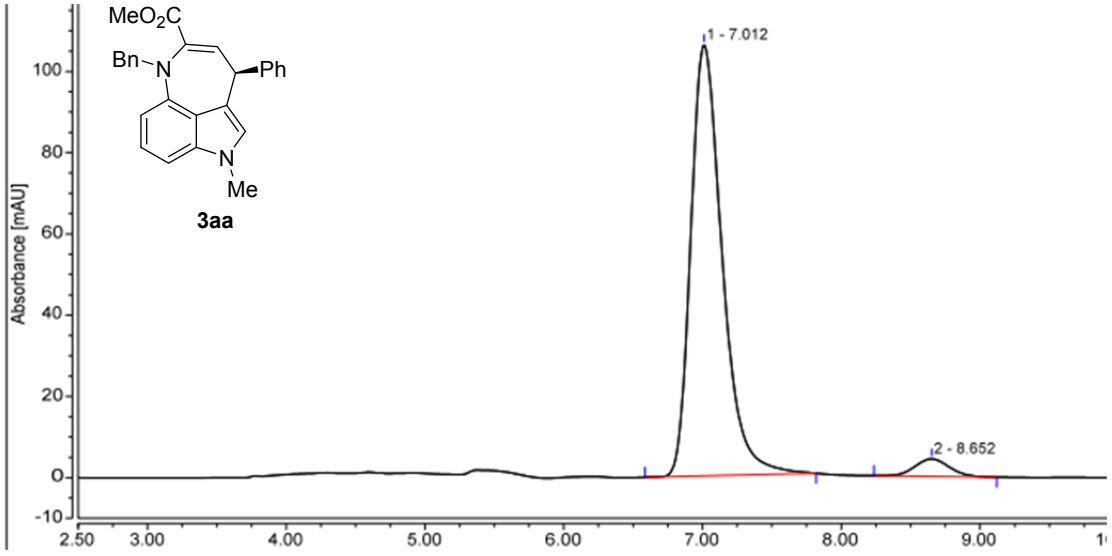
In a 50 mL round bottom flask, a mixture of $Ni(OTf)_2$ (17.8 mg, 0.05 mmol, 5.0 mol %), ligand **L1** (3.4 mg, 0.05 mmol, 5.0 mol %), 5 Å MS (200 mg) and β,γ-unsaturated α-ketoester **2a** (190.0 mg, 1.0 mmol) in $PhCF_3$ (15 mL) were stirred at room temperature for 30 minutes under the atmosphere. Then indole **1a** (307.0 mg, 1.3 mmol) in $PhCF_3$ (5.0 mL) was added. After 24 h, the reaction was complete (monitored by TLC). At the end of the reaction, the reaction mixture was filtered and concentrated, and the residue was purified directly by flash column chromatography (Pet/EtOAc, 500/1~100/1, v/v) as eluent to afford the desired product **3aa** (373.0 mg, 91% yield, 90% ee). Moreover, the crude NMR characterization showed that the conversion rate of substrate **3aa** was greater than 95%, and the ratio of product **3aa** to product **4aa** was 92:8.

HPLC Spectra

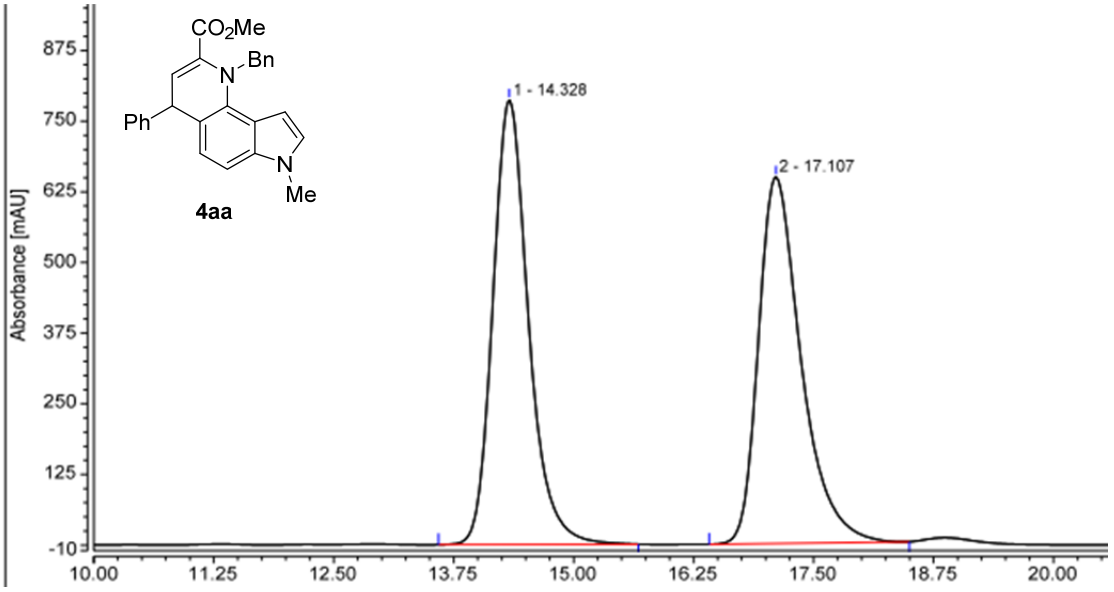
Figure S6. HPLC spectra of **3aa** and **3ap**



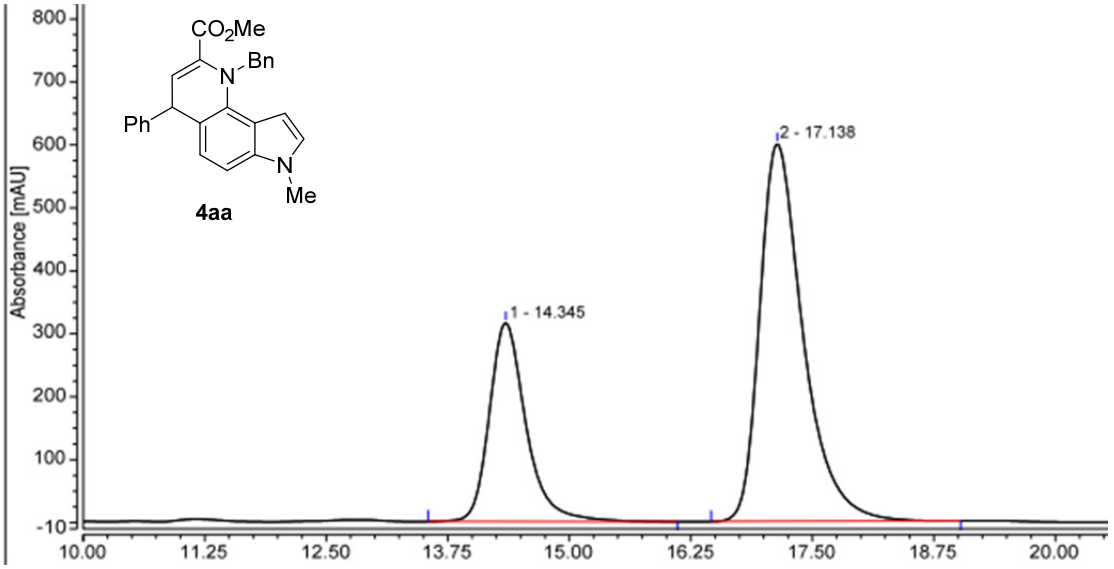
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	6.997	190.400	727.479	49.35	52.36
2	8.632	195.440	661.957	50.65	47.64
Total:		**385.840**	**1389.435**	**100.00**	**100.00**



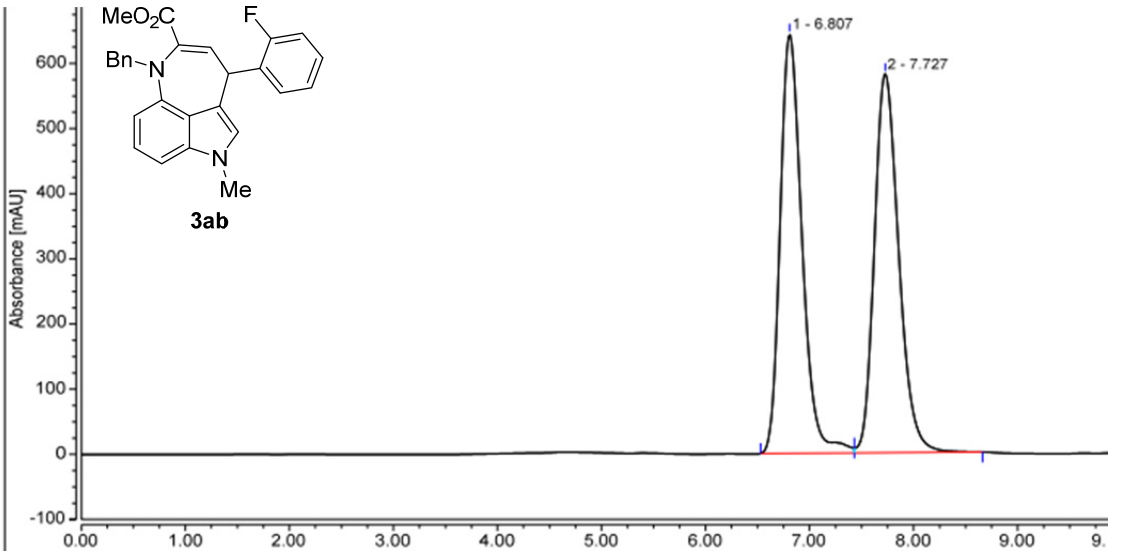
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.012	27.805	106.133	95.74	96.12
2	8.652	1.237	4.287	4.26	3.88
Total:		**29.043**	**110.421**	**100.00**	**100.00**



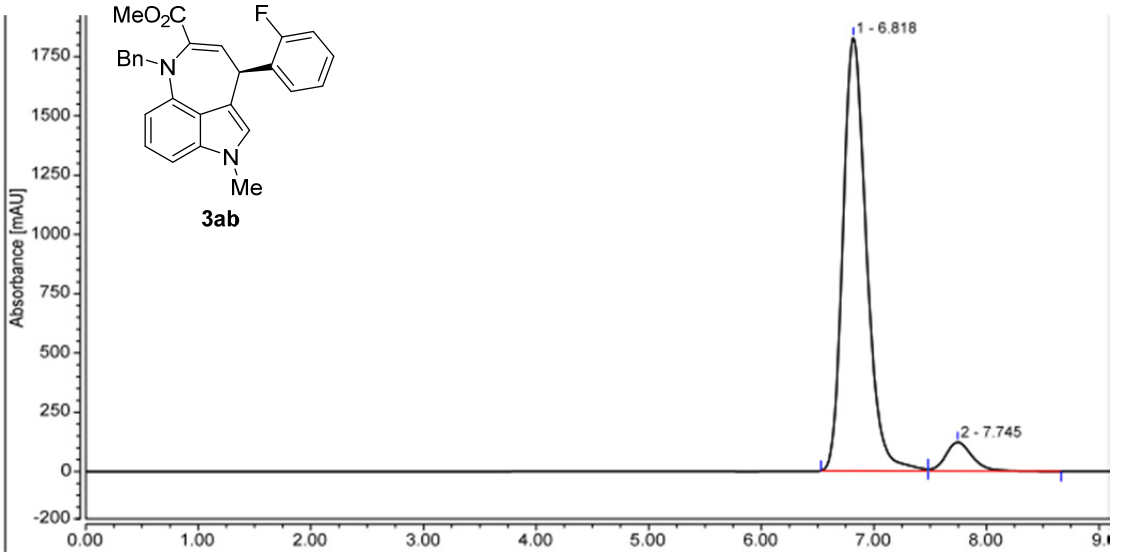
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.328	339.214	786.100	50.39	54.80
2	17.107	333.899	648.277	49.61	45.20
Total:		**673.112**	**1434.377**	**100.00**	**100.00**



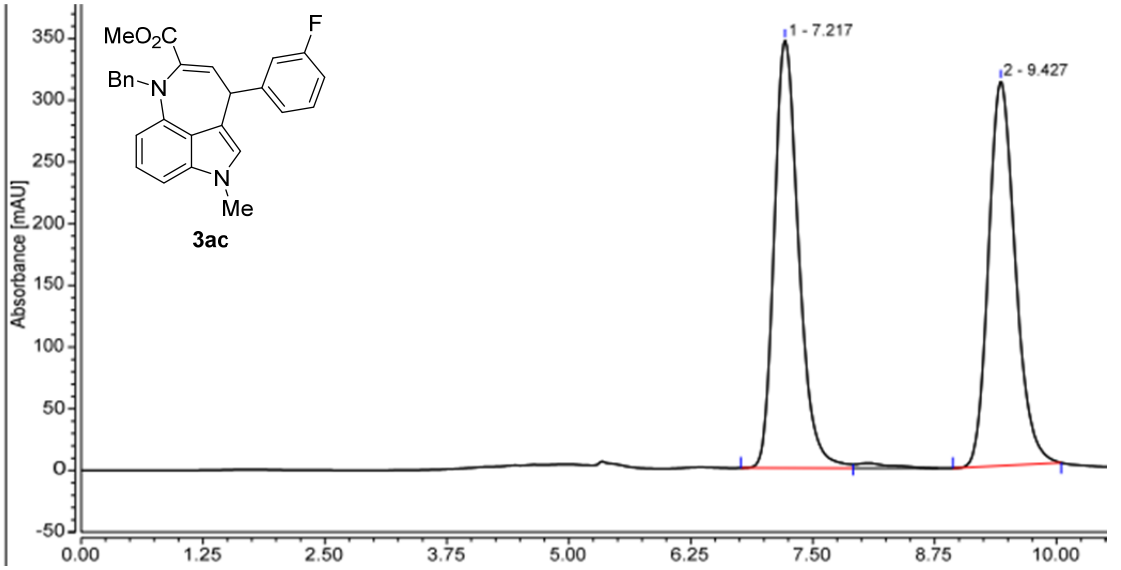
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.345	138.666	315.423	30.83	34.48
2	17.138	311.099	599.391	69.17	65.52
Total:		**449.765**	**914.813**	**100.00**	**100.00**



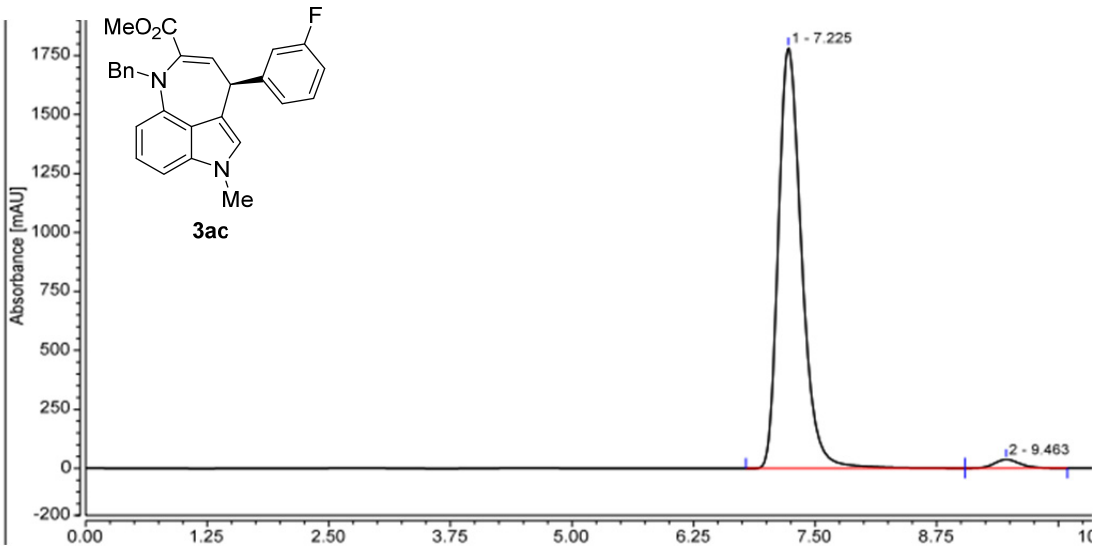
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	6.807	156.821	643.251	49.91	52.51
2	7.727	157.403	581.801	50.09	47.49
Total:		**314.224**	**1225.052**	**100.00**	**100.00**



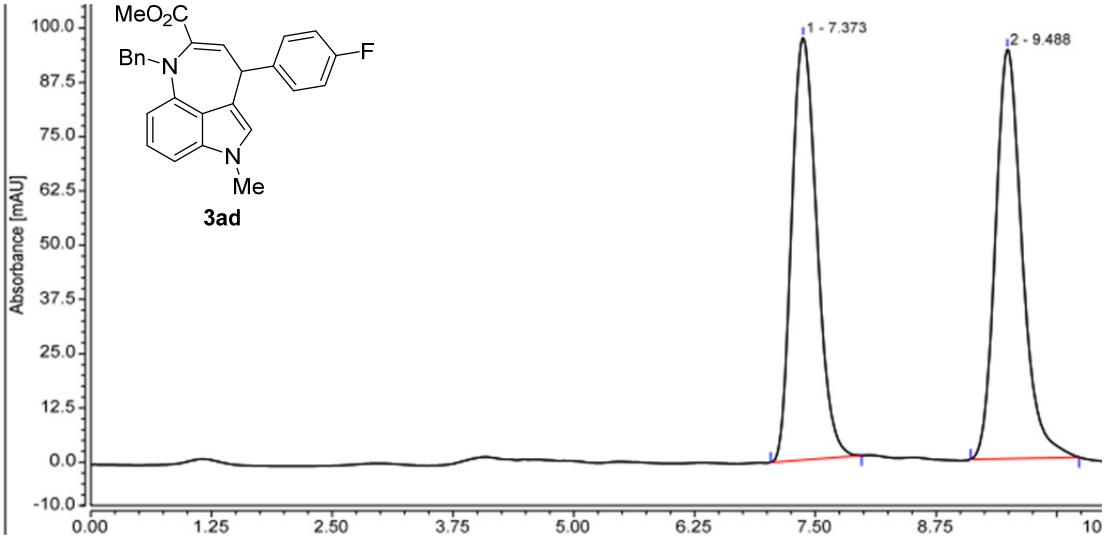
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	6.818	441.882	1827.350	92.99	93.75
2	7.745	33.304	121.723	7.01	6.25
Total:		**475.186**	**1949.074**	**100.00**	**100.00**



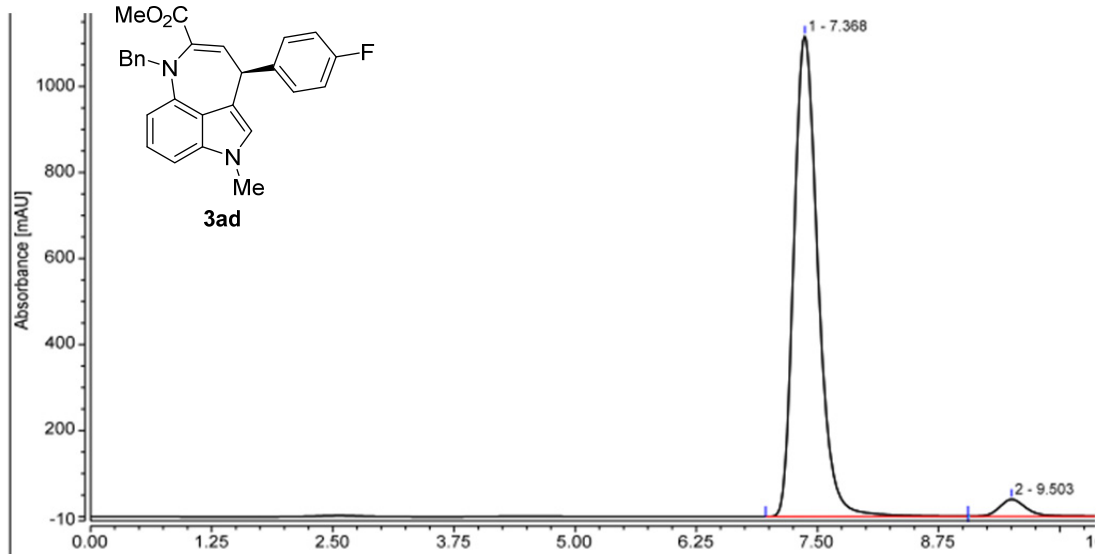
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.217	100.909	346.585	50.47	52.64
2	9.427	99.032	311.802	49.53	47.36
Total:		**199.942**	**658.387**	**100.00**	**100.00**



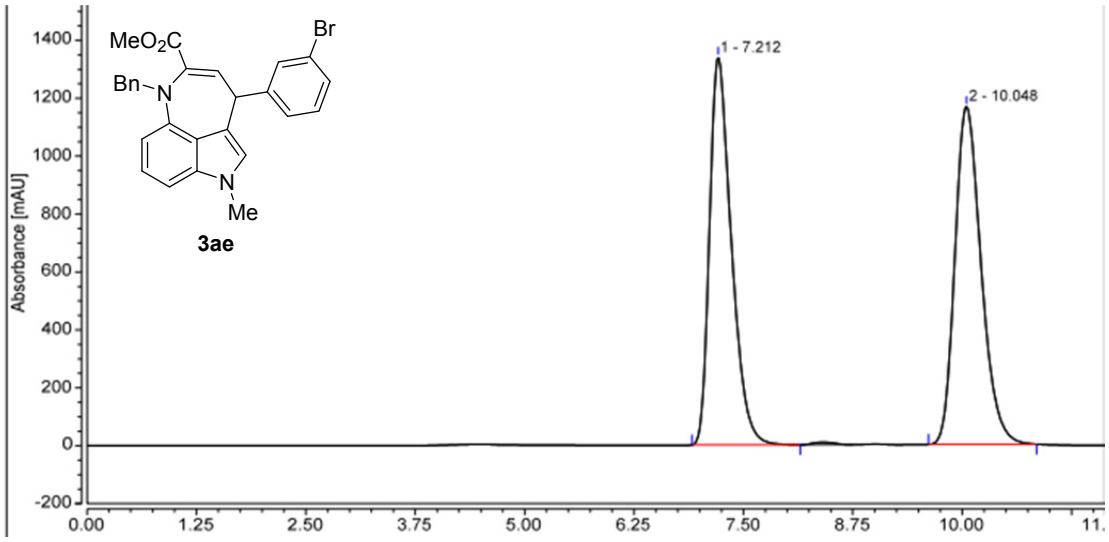
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.225	495.170	1783.498	97.72	97.96
2	9.463	11.537	37.133	2.28	2.04
Total:		**506.707**	**1820.630**	**100.00**	**100.00**



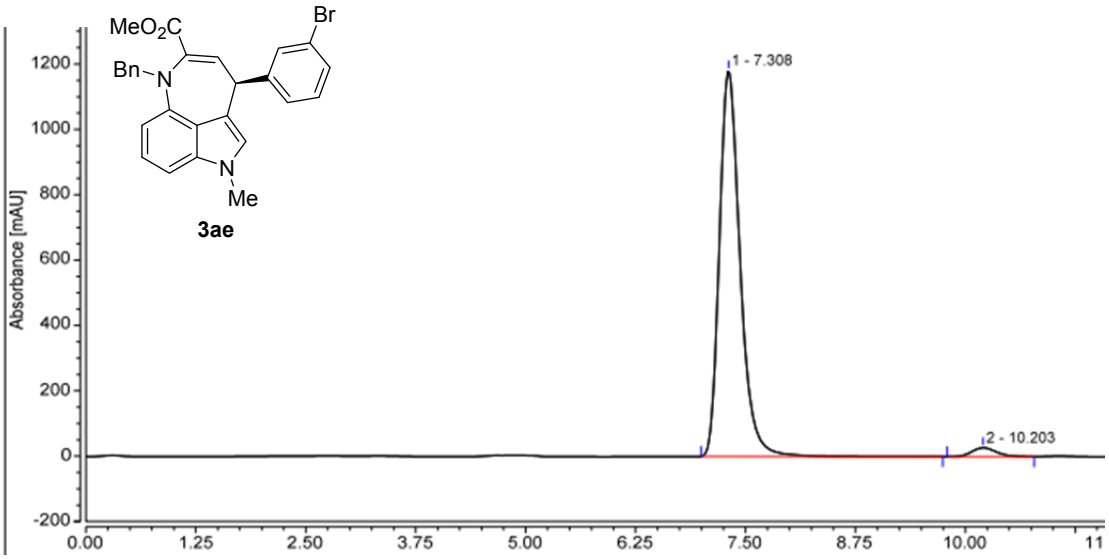
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.373	29.378	97.298	49.21	50.78
2	9.488	30.323	94.312	50.79	49.22
Total:		**59.701**	**191.611**	**100.00**	**100.00**



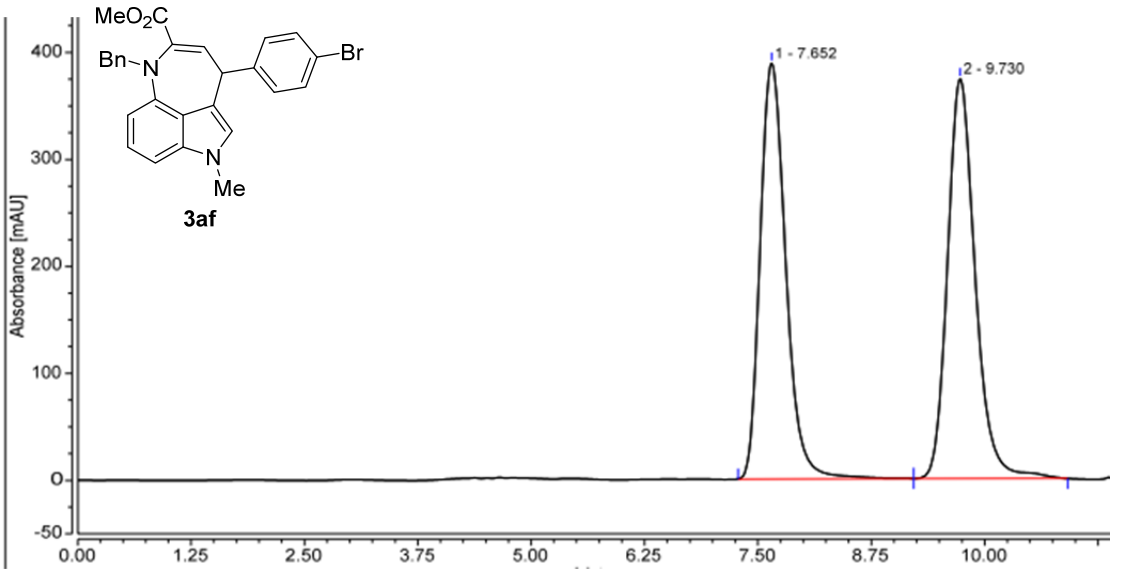
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.368	321.314	1116.792	96.20	96.61
2	9.503	12.676	39.232	3.80	3.39
Total:		**333.990**	**1156.024**	**100.00**	**100.00**



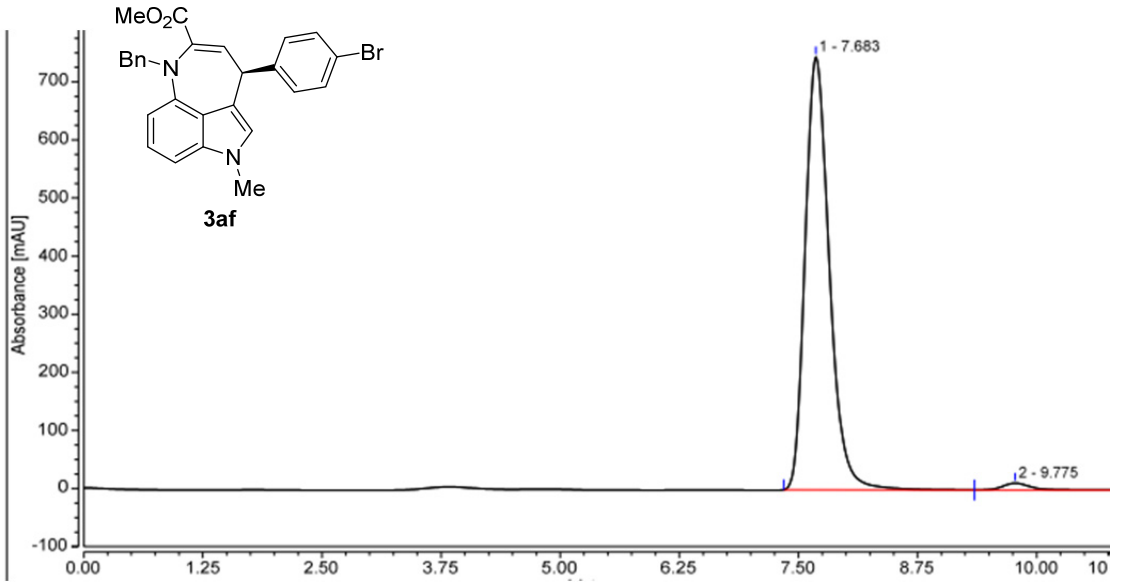
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.212	386.357	1338.614	48.78	53.42
2	10.048	405.649	1167.218	51.22	46.58
Total:		**792.006**	**2505.832**	**100.00**	**100.00**



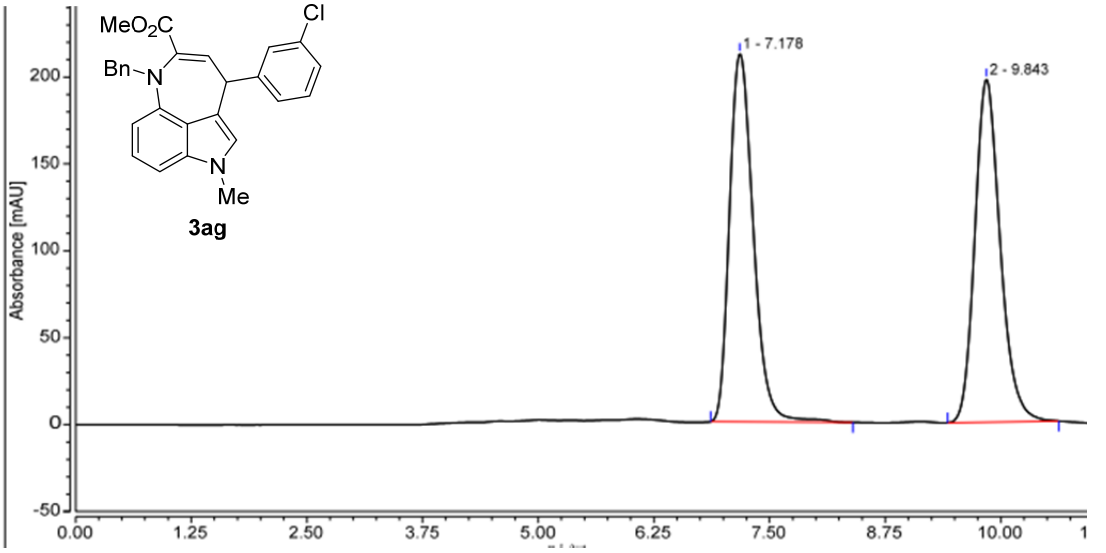
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.308	321.684	1179.702	97.37	97.76
2	10.203	8.703	26.982	2.63	2.24
Total:		**330.387**	**1206.684**	**100.00**	**100.00**



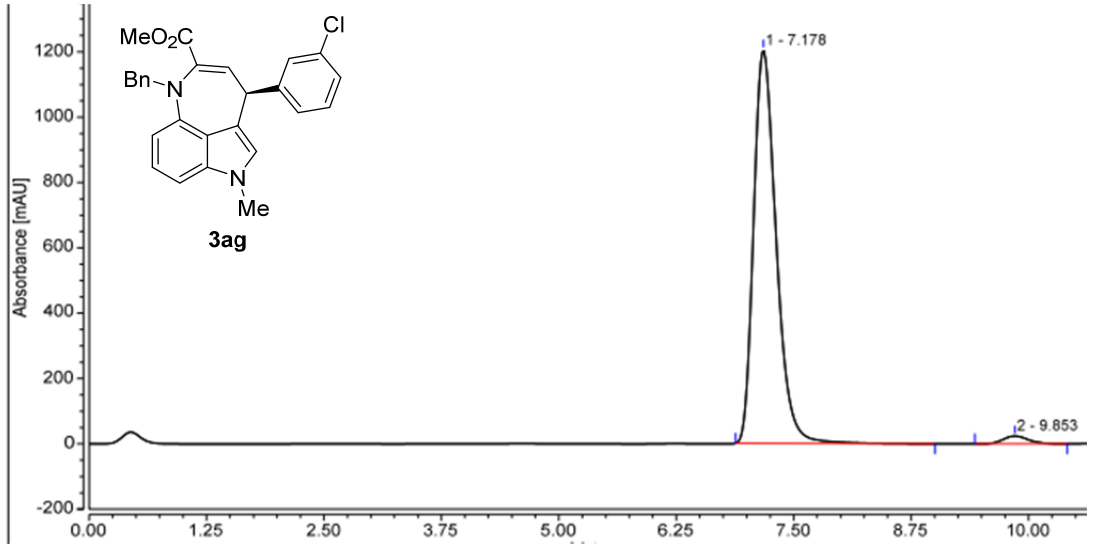
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.652	127.520	388.716	49.05	50.97
2	9.730	132.437	373.989	50.95	49.03
Total:		**259.956**	**762.705**	**100.00**	**100.00**



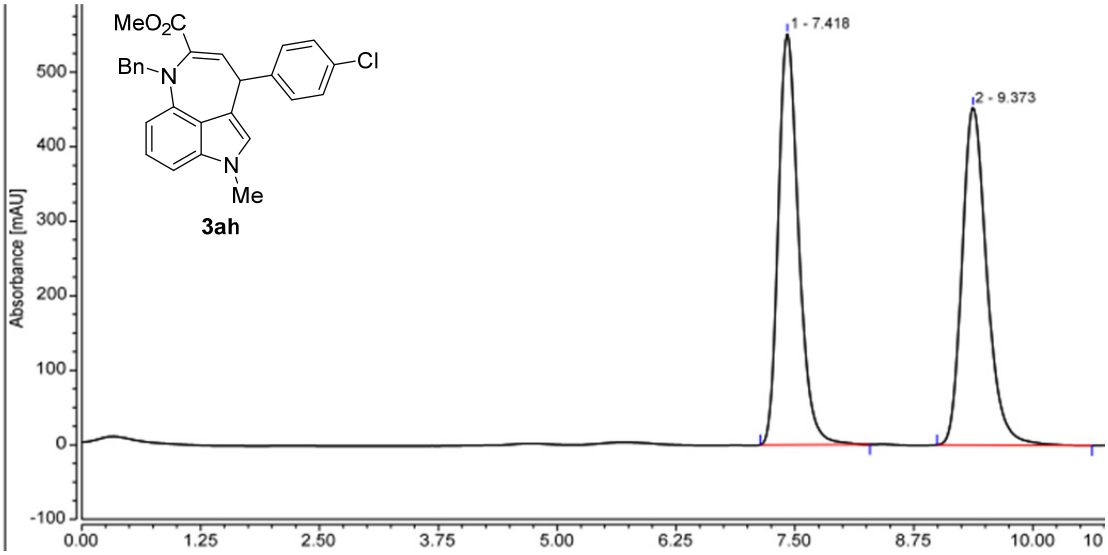
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.683	219.719	745.189	98.23	98.45
2	9.775	3.964	11.729	1.77	1.55
Total:		**223.683**	**756.918**	**100.00**	**100.00**



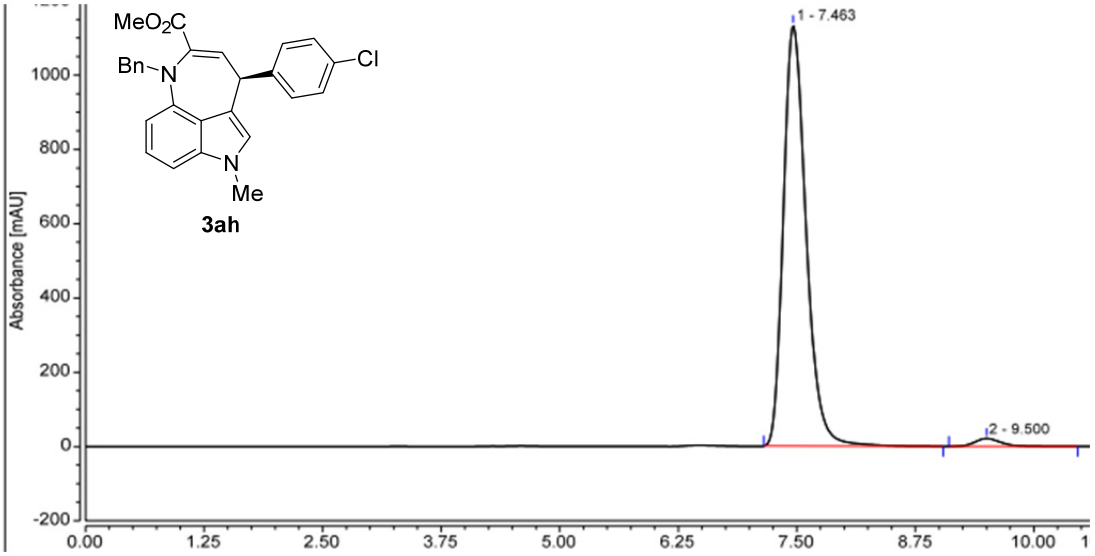
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.178	63.339	211.921	50.18	51.77
2	9.843	62.895	197.455	49.82	48.23
Total:		**126.233**	**409.376**	**100.00**	**100.00**



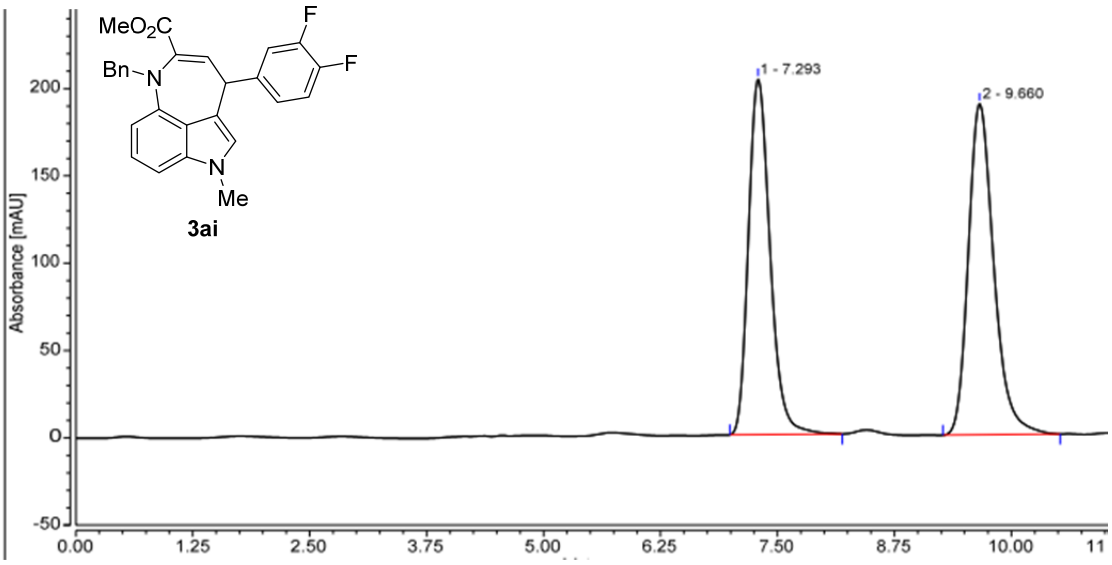
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.178	334.462	1203.869	97.82	98.06
2	9.853	7.466	23.838	2.18	1.94
Total:		**341.928**	**1227.708**	**100.00**	**100.00**



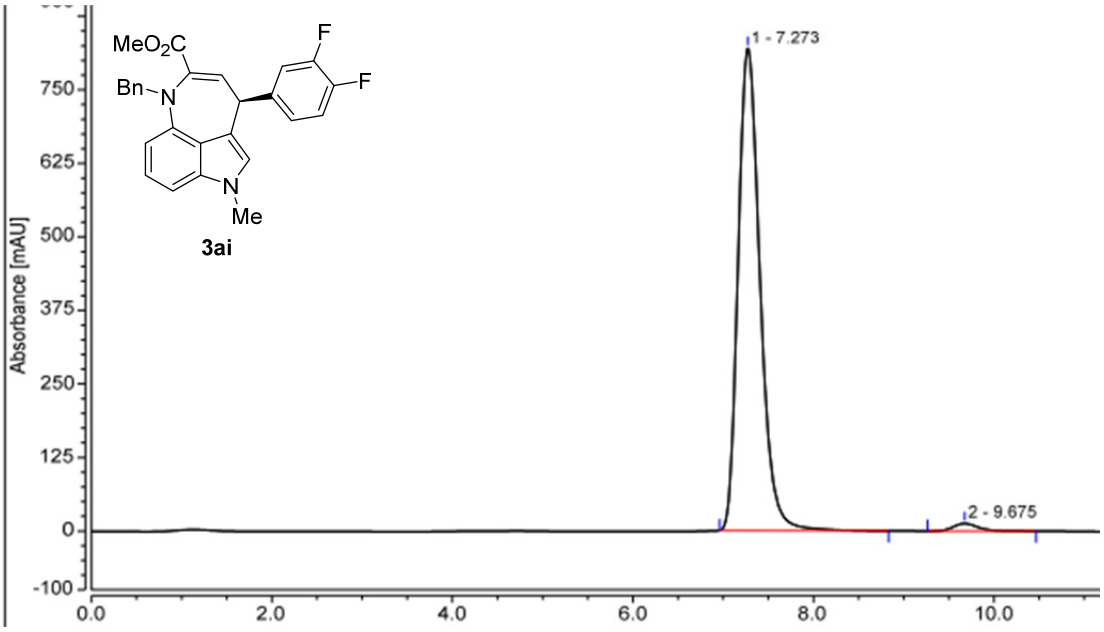
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.418	136.480	551.242	49.94	54.89
2	9.373	136.823	452.989	50.06	45.11
Total:		**273.303**	**1004.231**	**100.00**	**100.00**



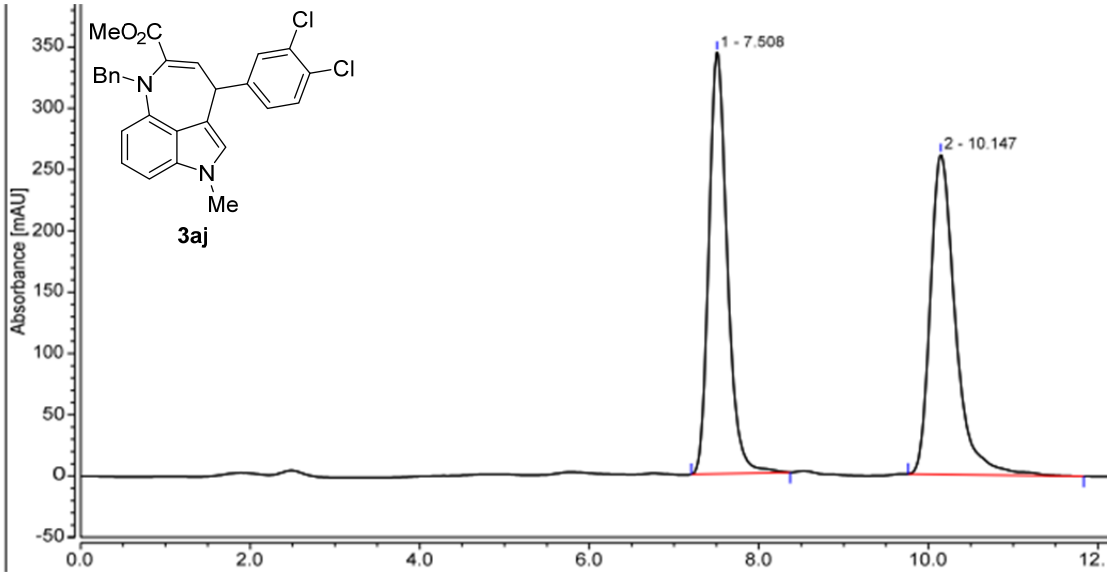
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.463	314.888	1132.369	97.92	98.16
2	9.500	6.698	21.244	2.08	1.84
Total:		**321.585**	**1153.613**	**100.00**	**100.00**



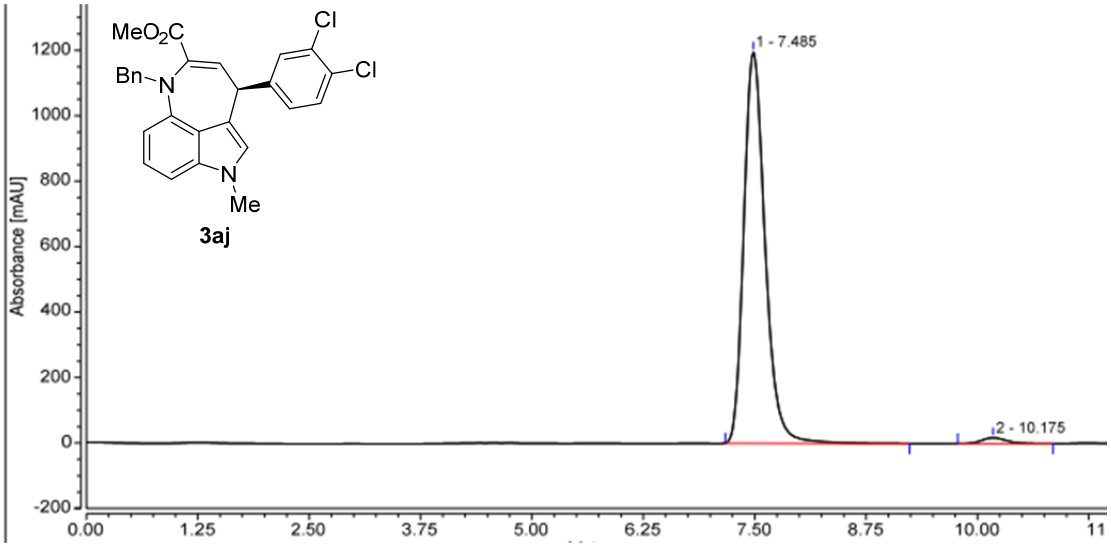
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.293	54.389	203.725	47.60	51.77
2	9.660	59.865	189.772	52.40	48.23
Total:		**114.254**	**393.497**	**100.00**	**100.00**



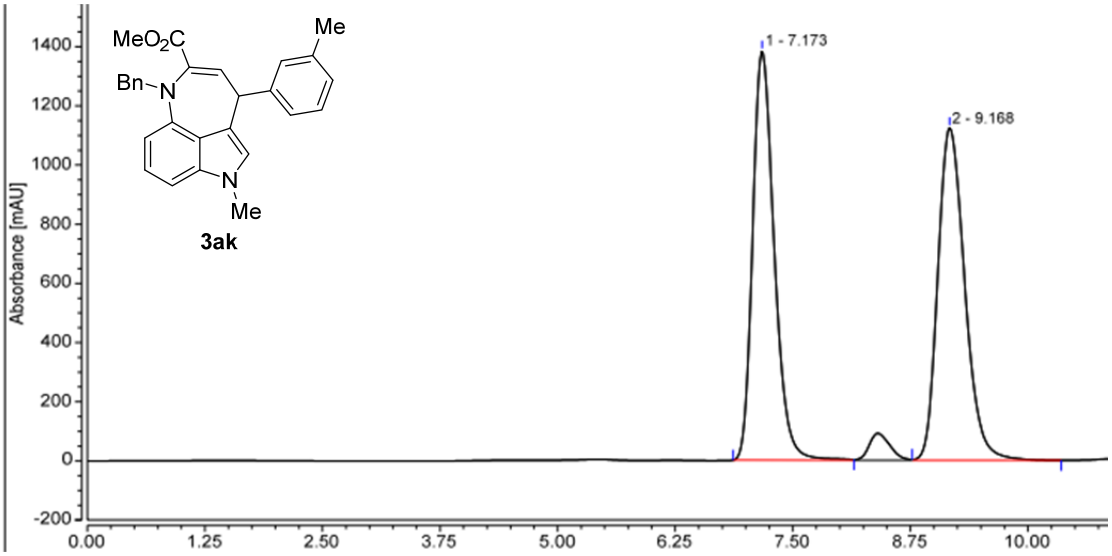
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.273	231.156	819.822	98.19	98.46
2	9.675	4.258	12.832	1.81	1.54
Total:		**235.414**	**832.654**	**100.00**	**100.00**



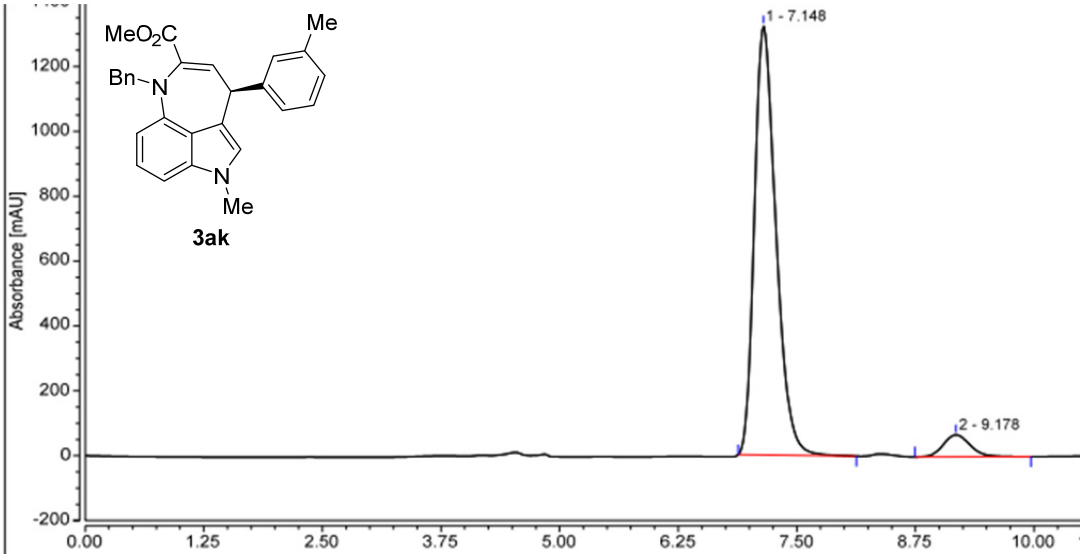
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.508	86.664	344.044	49.16	56.85
2	10.147	89.610	261.085	50.84	43.15
Total:		**176.274**	**605.130**	**100.00**	**100.00**



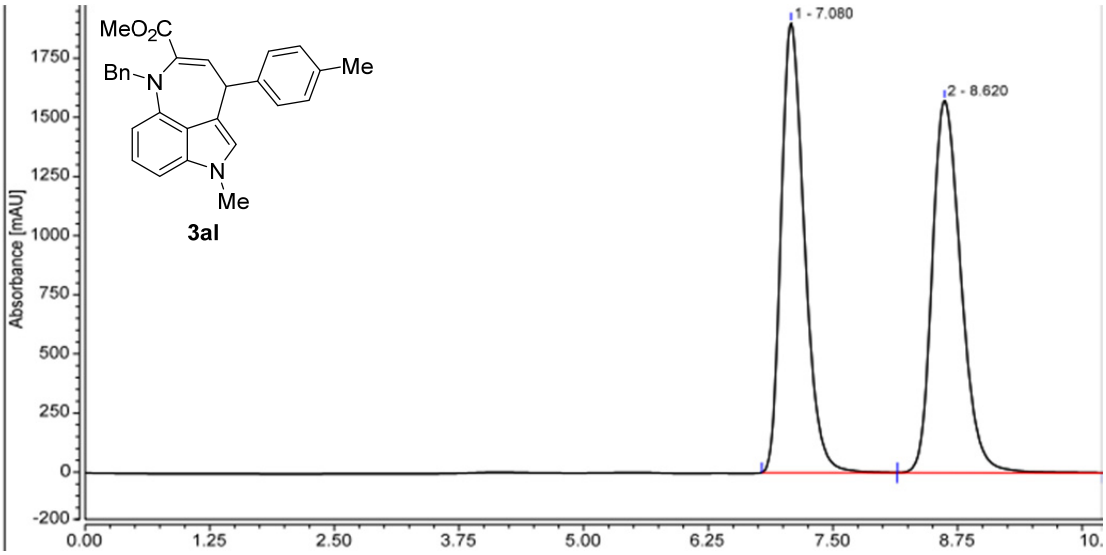
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.485	330.492	1194.822	98.25	98.53
2	10.175	5.899	17.841	1.75	1.47
Total:		**336.391**	**1212.662**	**100.00**	**100.00**



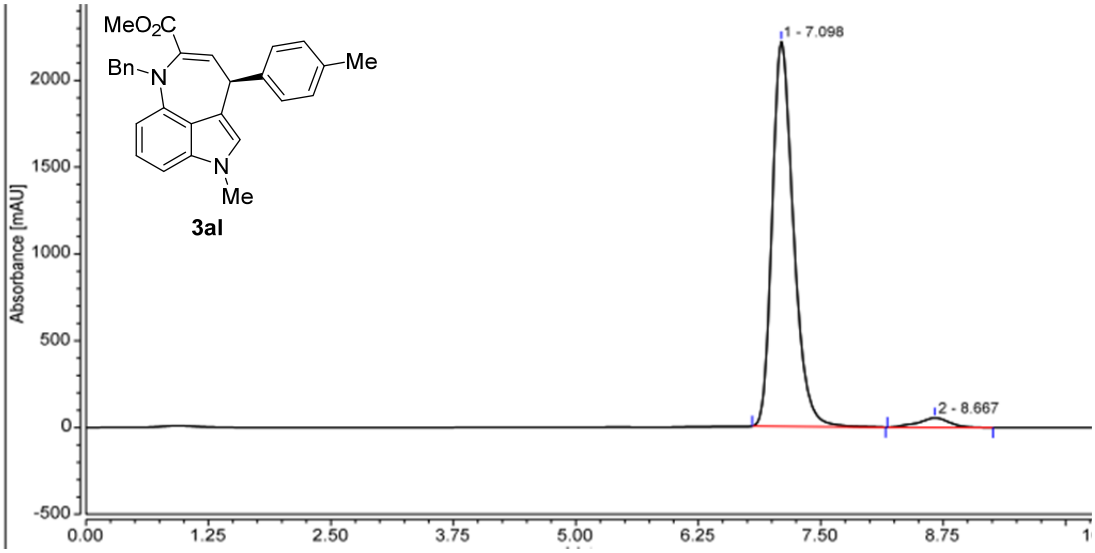
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.173	367.258	1382.716	49.62	55.17
2	9.168	372.894	1123.374	50.38	44.83
Total:		**740.152**	**2506.090**	**100.00**	**100.00**



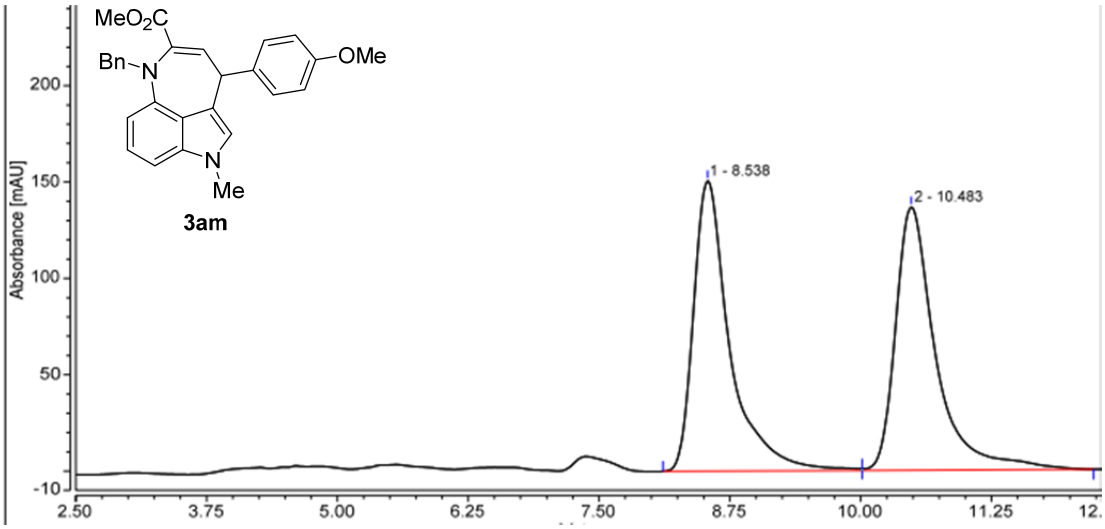
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.148	348.808	1322.561	94.05	95.14
2	9.178	22.065	67.513	5.95	4.86
Total:		**370.873**	**1390.074**	**100.00**	**100.00**



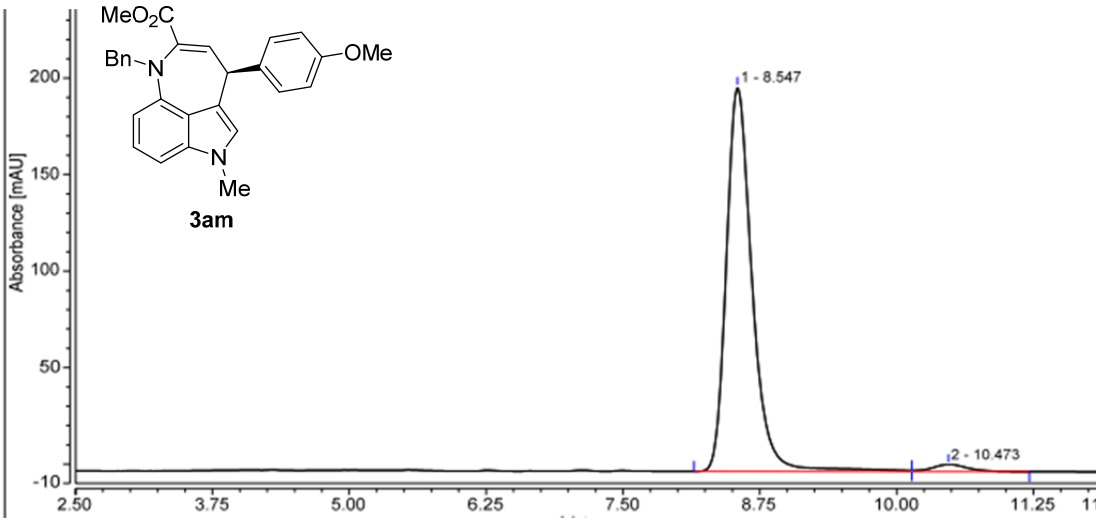
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.080	516.373	1900.918	49.53	54.69
2	8.620	526.246	1574.929	50.47	45.31
Total:		**1042.619**	**3475.847**	**100.00**	**100.00**



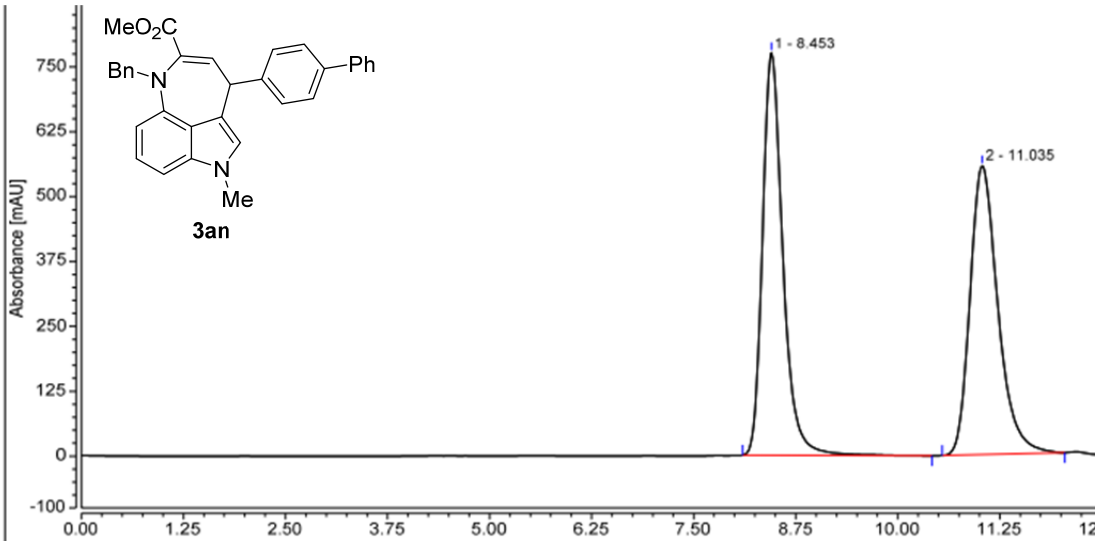
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.098	559.120	2216.898	96.52	97.60
2	8.667	20.153	54.542	3.48	2.40
Total:		**579.273**	**2271.440**	**100.00**	**100.00**



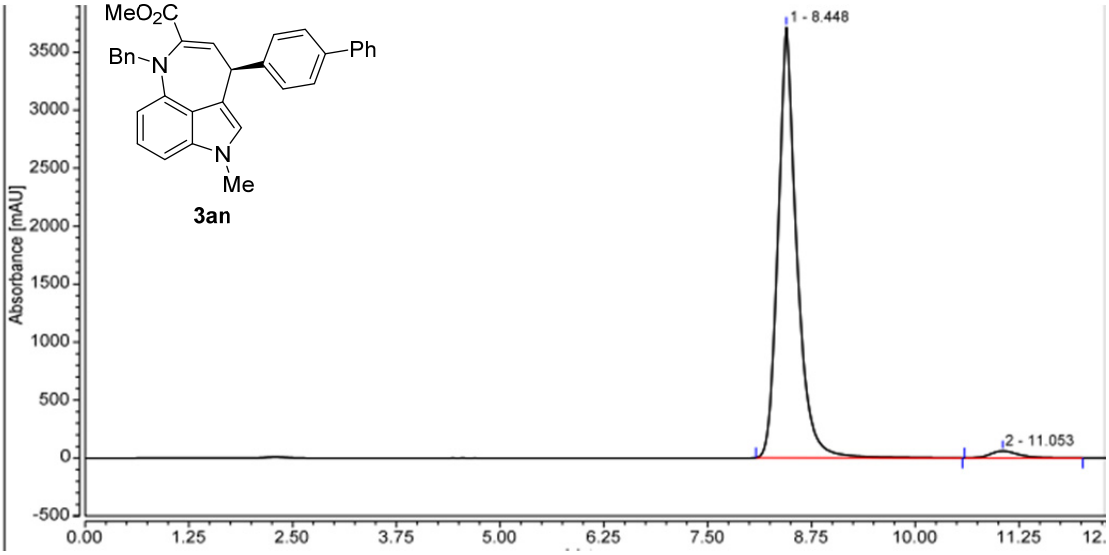
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.538	60.570	150.723	49.96	52.45
2	10.483	60.663	136.650	50.04	47.55
Total:		**121.233**	**287.373**	**100.00**	**100.00**



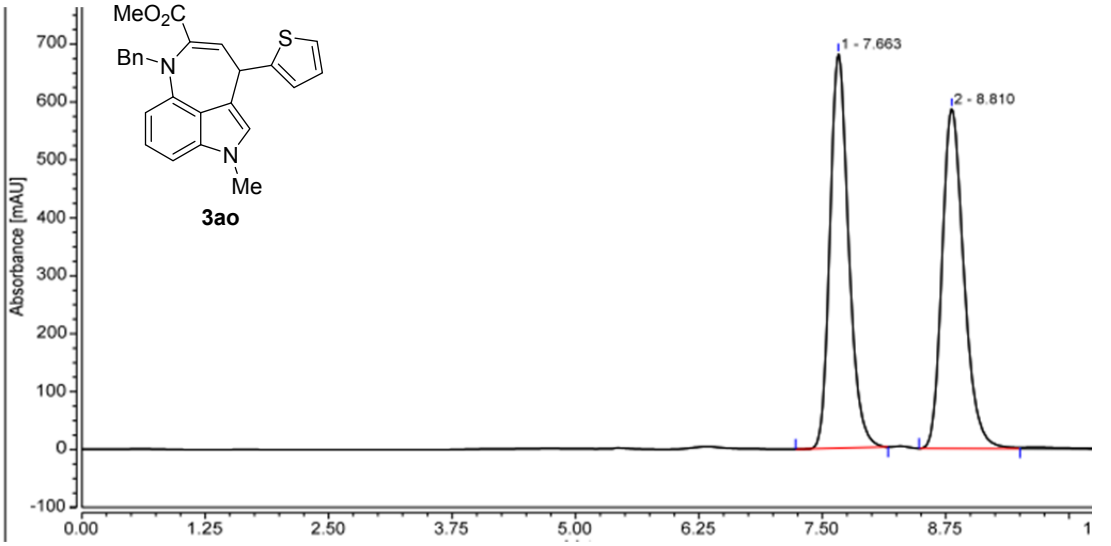
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.547	54.476	198.999	97.55	98.19
2	10.473	1.371	3.663	2.45	1.81
Total:		**55.847**	**202.661**	**100.00**	**100.00**



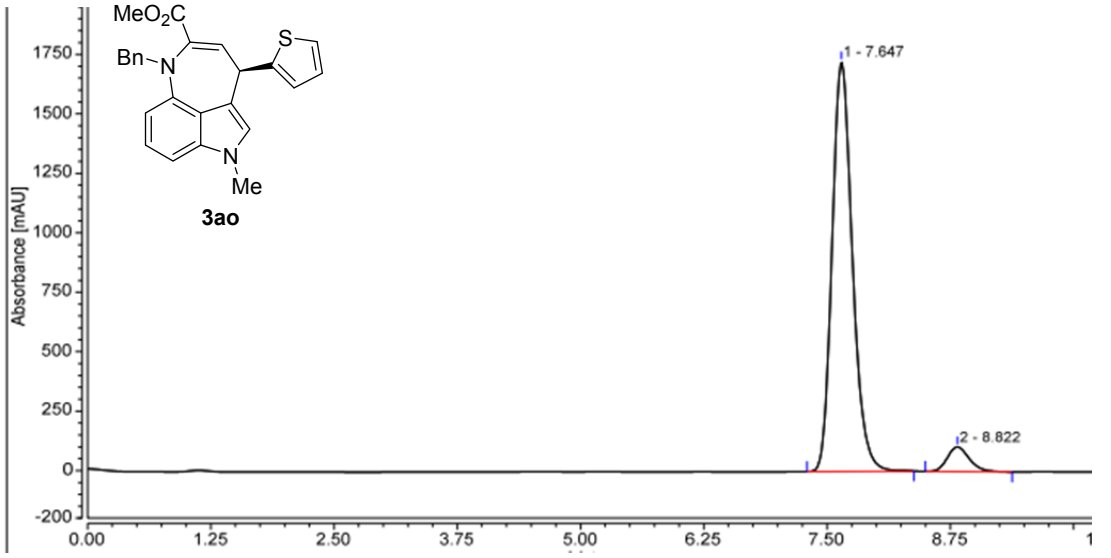
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.453	224.213	775.696	50.46	58.23
2	11.035	220.138	556.411	49.54	41.77
Total:		**444.351**	**1332.107**	**100.00**	**100.00**



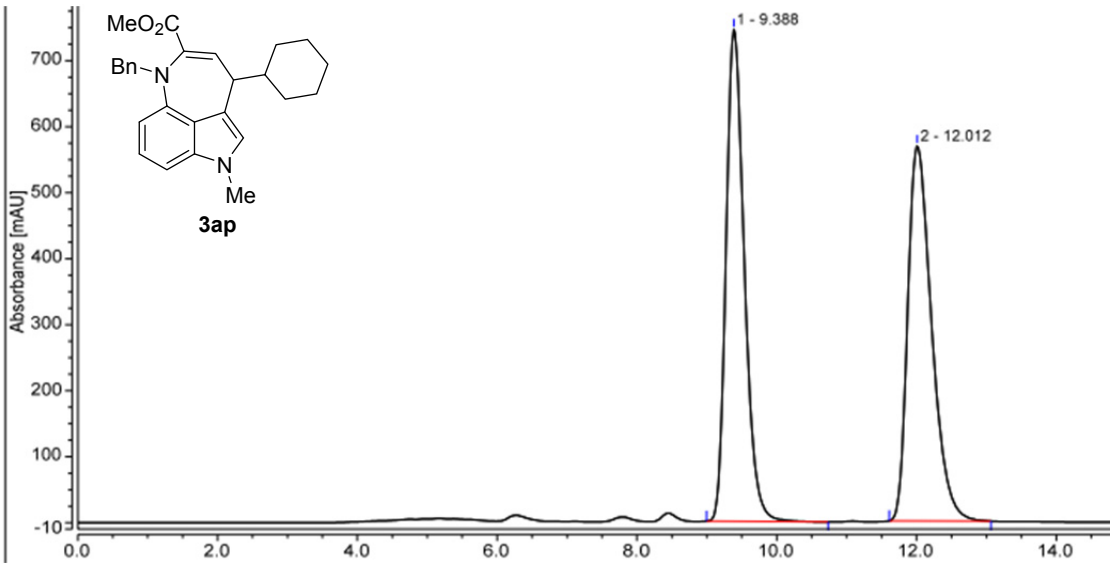
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.448	973.592	3713.103	97.59	98.40
2	11.053	24.074	60.186	2.41	1.60
Total:		**997.666**	**3773.290**	**100.00**	**100.00**



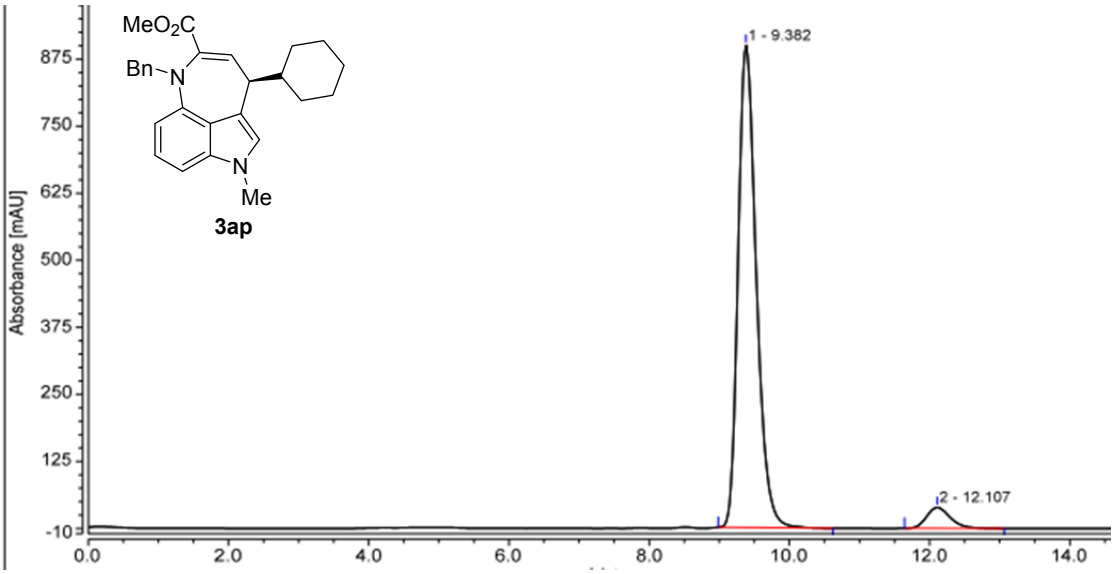
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.663	149.468	680.644	49.82	53.70
2	8.810	150.529	586.769	50.18	46.30
Total:		**299.996**	**1267.413**	**100.00**	**100.00**



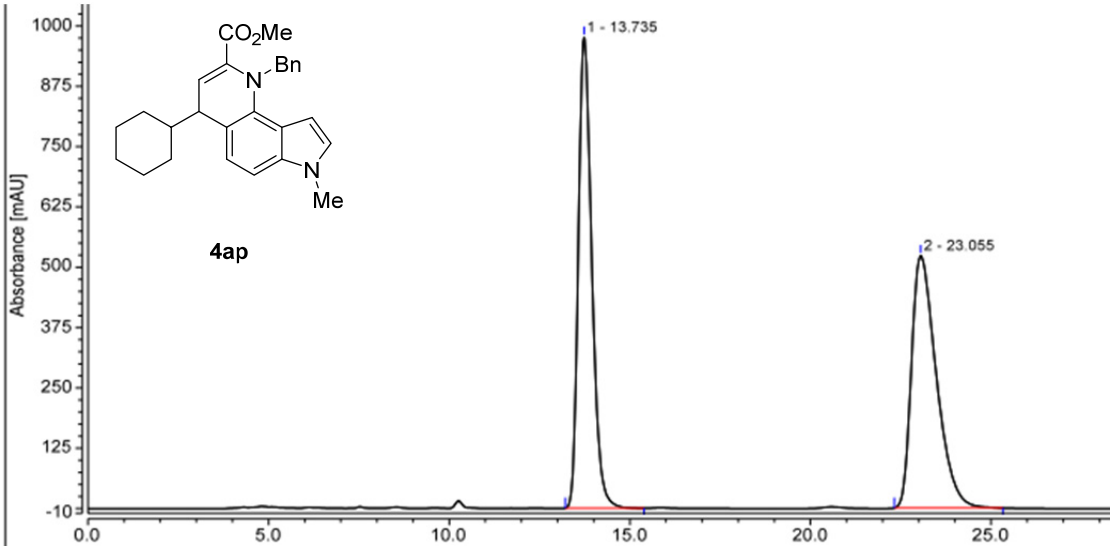
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.647	411.121	1722.365	93.86	94.33
2	8.822	26.896	103.536	6.14	5.67
Total:		**438.017**	**1825.901**	**100.00**	**100.00**



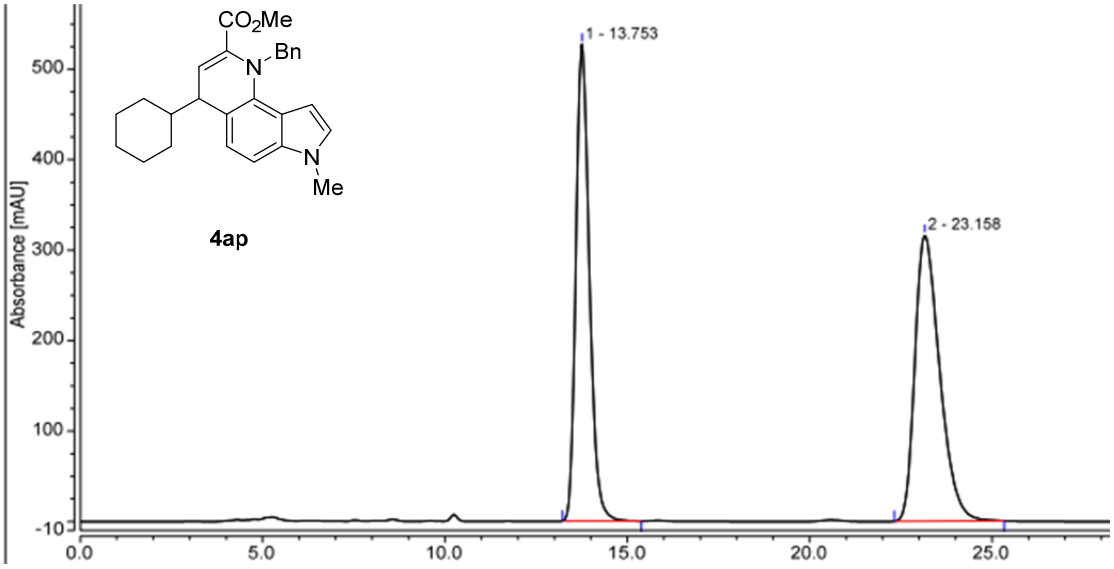
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.388	226.098	745.374	50.12	56.72
2	12.012	224.979	568.734	49.88	43.28
Total:		**451.077**	**1314.108**	**100.00**	**100.00**



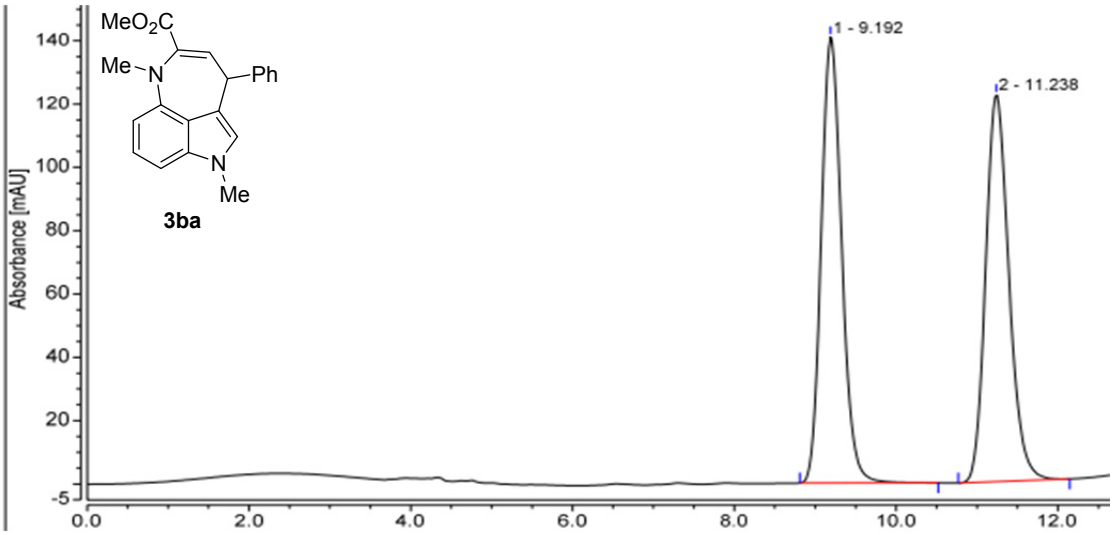
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.382	270.259	899.070	94.62	95.85
2	12.107	15.362	38.895	5.38	4.15
Total:		**285.622**	**937.965**	**100.00**	**100.00**



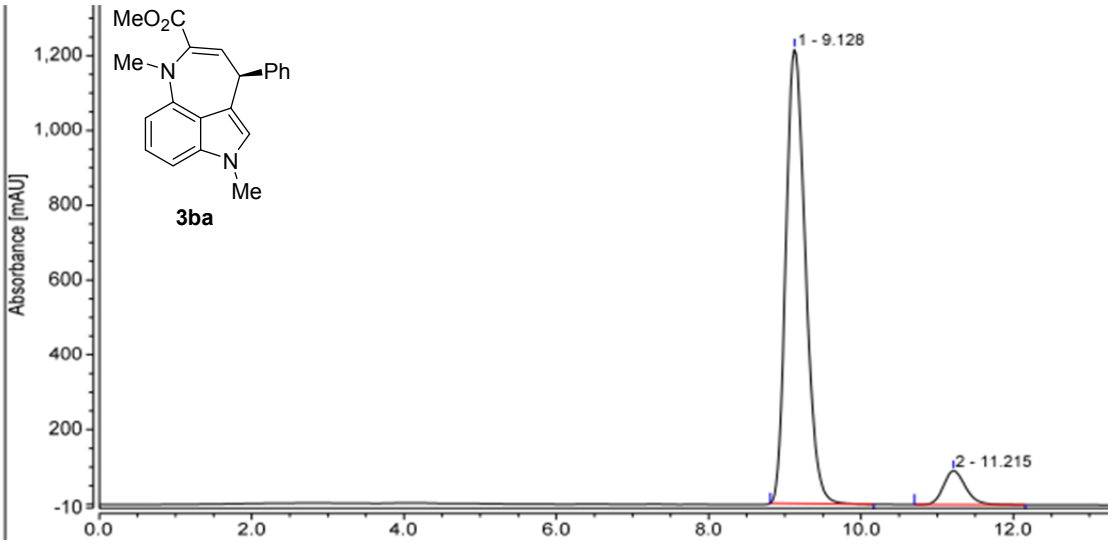
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.735	420.835	976.064	50.21	65.10
2	23.055	417.379	523.257	49.79	34.90
Total:		**838.214**	**1499.321**	**100.00**	**100.00**



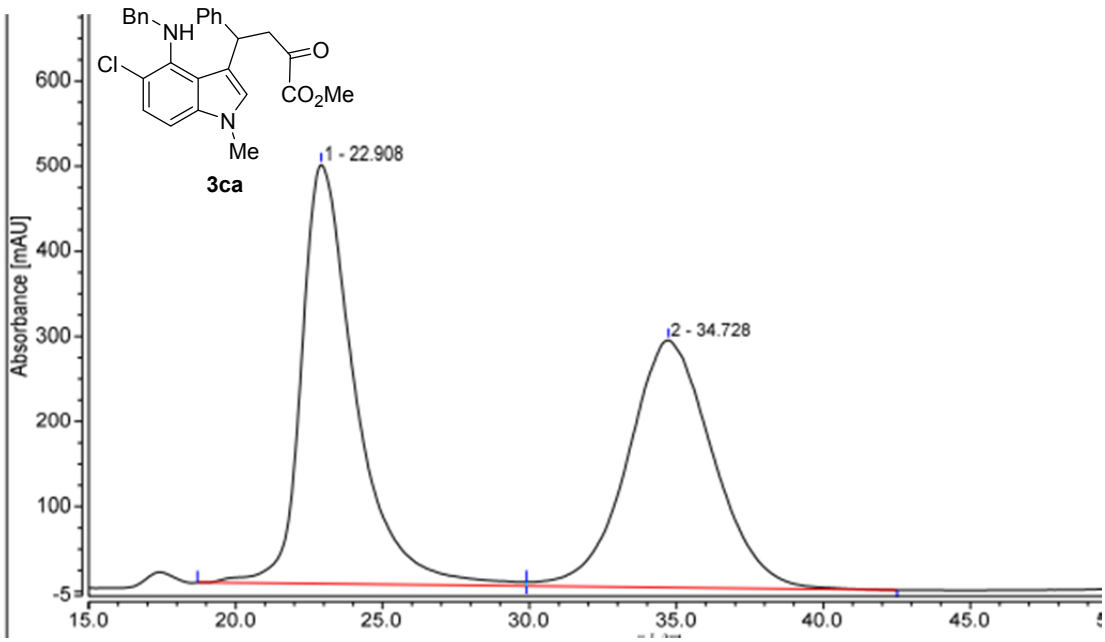
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.753	226.678	527.324	47.62	62.52
2	23.158	249.386	316.123	52.38	37.48
Total:		**476.065**	**843.448**	**100.00**	**100.00**



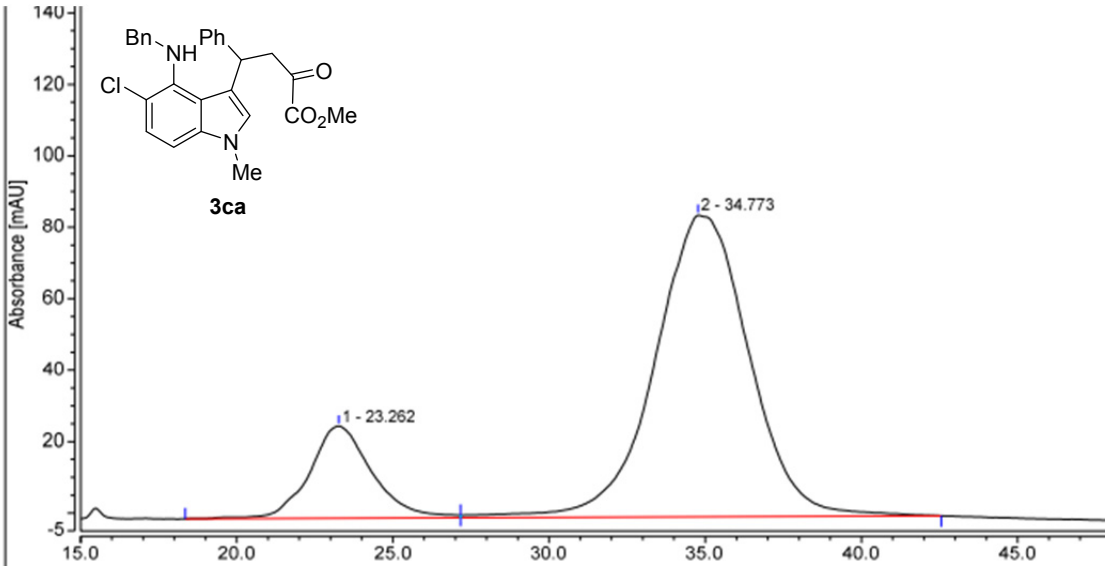
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.192	41.342	140.936	50.38	53.53
2	11.238	40.718	122.333	49.62	46.47
Total:		**82.060**	**263.269**	**100.00**	**100.00**



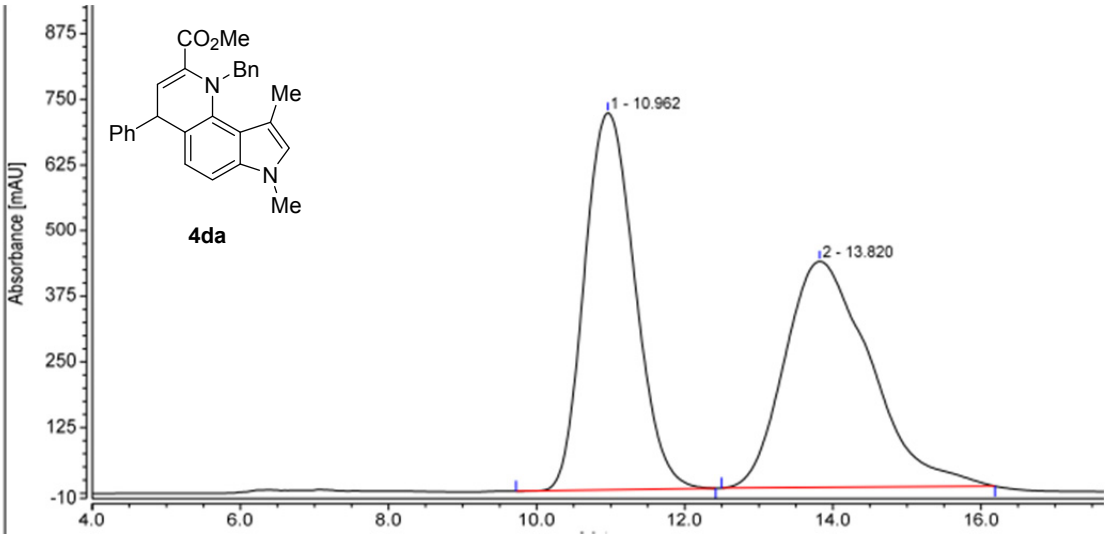
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.128	359.548	1214.701	92.19	93.07
2	11.215	30.471	90.427	7.81	6.93
Total:		**390.020**	**1305.128**	**100.00**	**100.00**



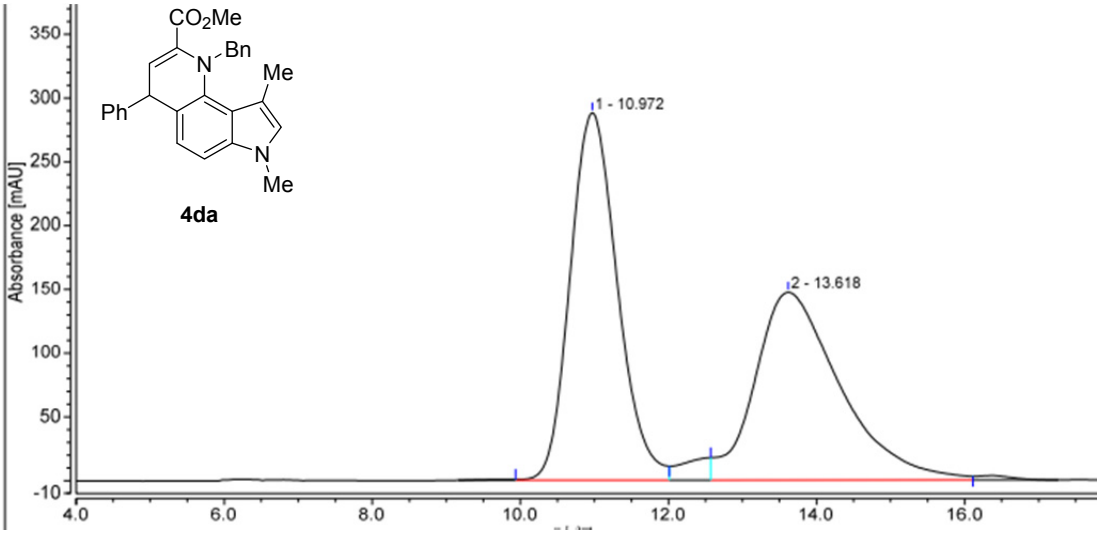
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	22.908	1046.828	492.488	51.73	62.91
2	34.728	976.886	290.358	48.27	37.09
Total:		**2023.714**	**782.847**	**100.00**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	23.262	59.644	25.776	16.77	23.39
2	34.773	295.964	84.421	83.23	76.61
Total:		**355.607**	**110.198**	**100.00**	**100.00**



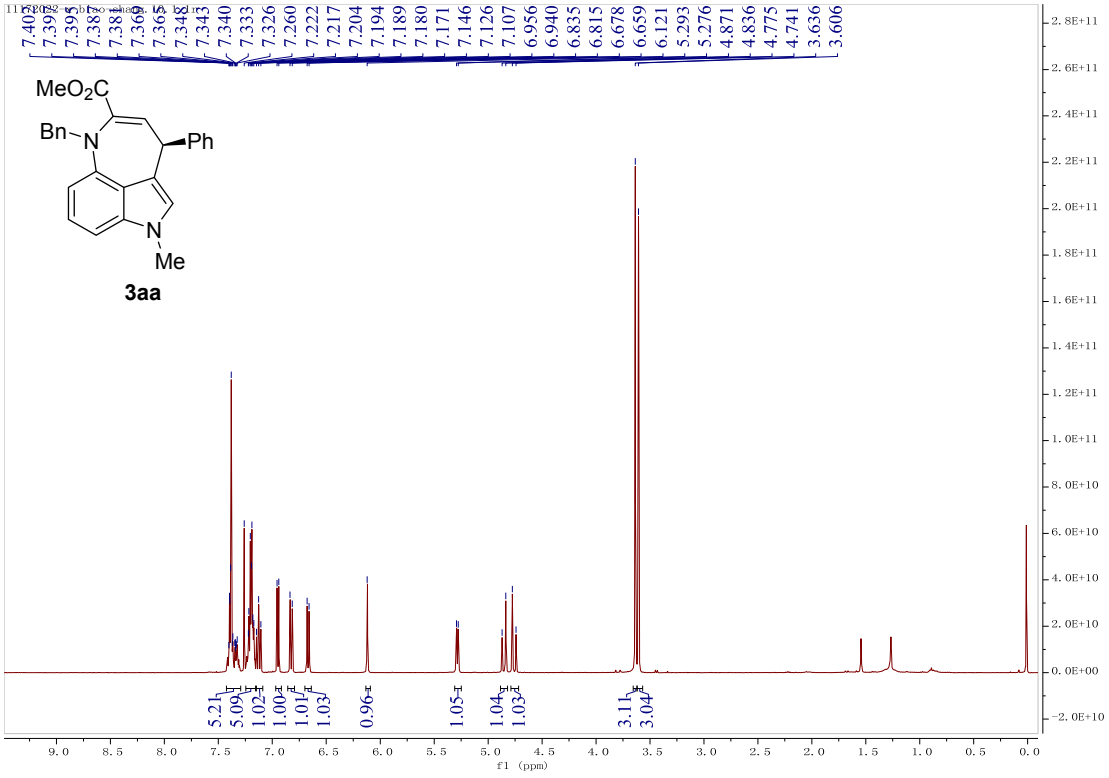
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.962	565.330	717.800	49.49	62.53
2	13.820	577.095	430.132	50.51	37.47
Total:		**1142.425**	**1147.932**	**100.00**	**100.00**



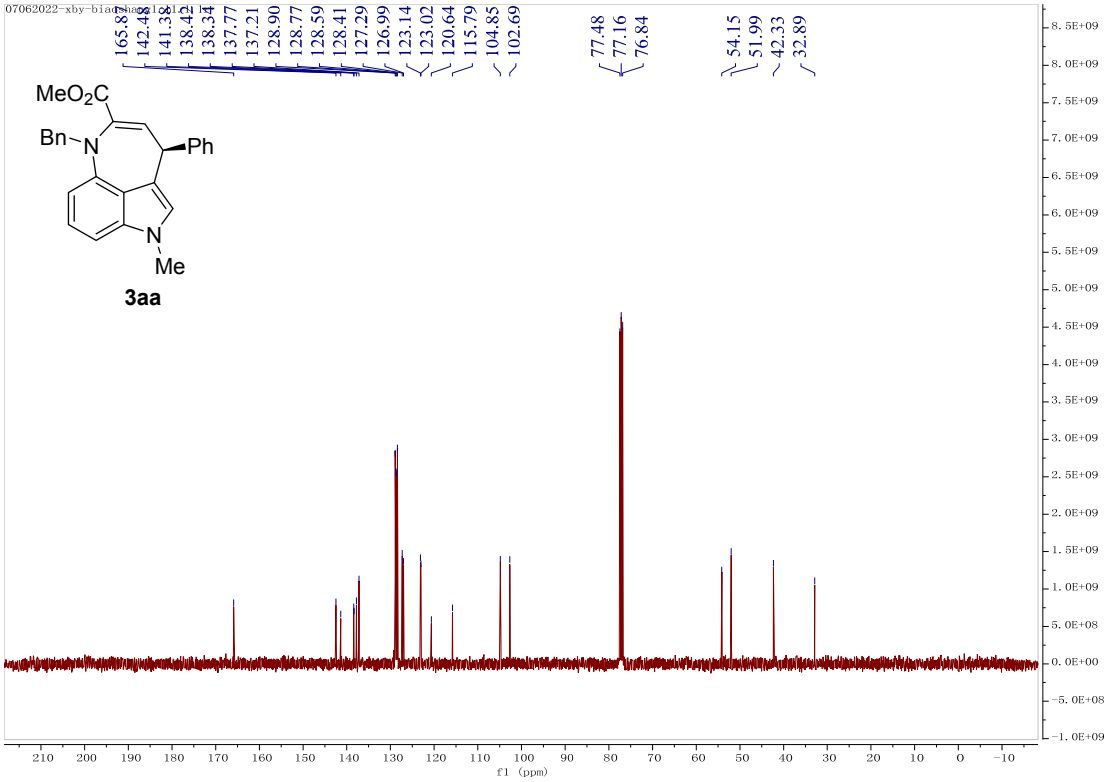
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.972	212.575	288.082	52.04	66.16
2	13.618	195.902	147.322	47.96	33.84
Total:		**408.476**	**435.405**	**100.00**	**100.00**

NMR Spectra

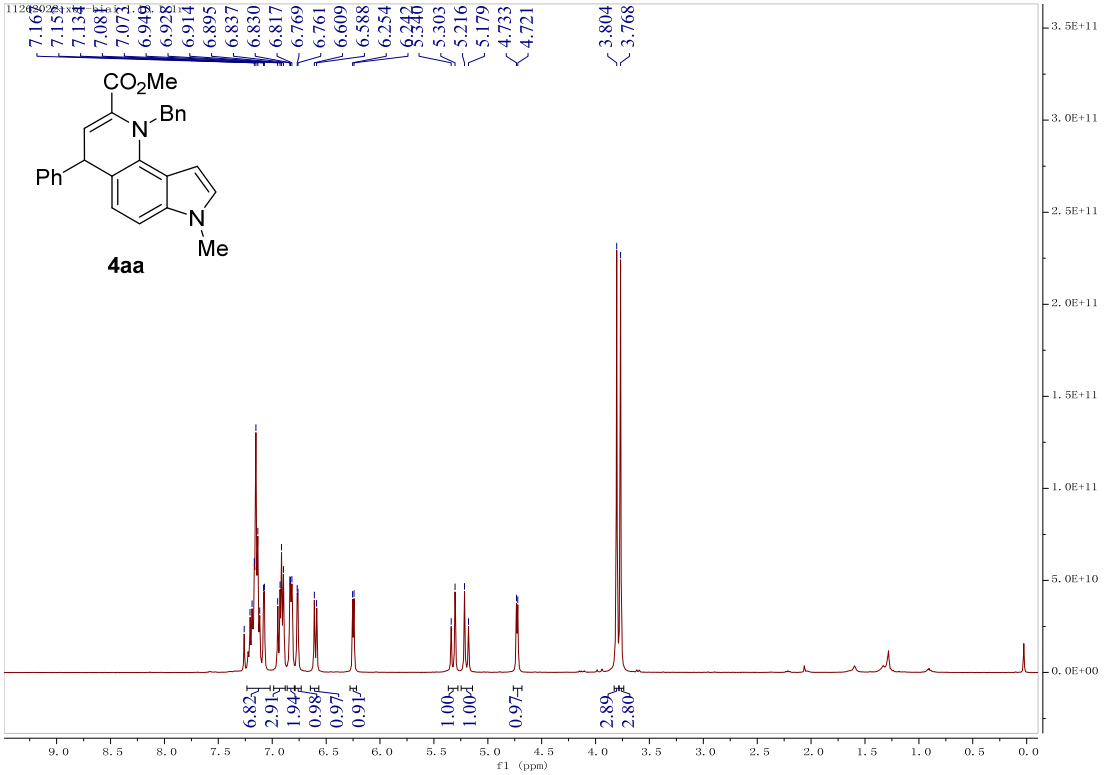
^{1}H NMR Spectrum of 3aa (400 MHz, $CDCl_3$)



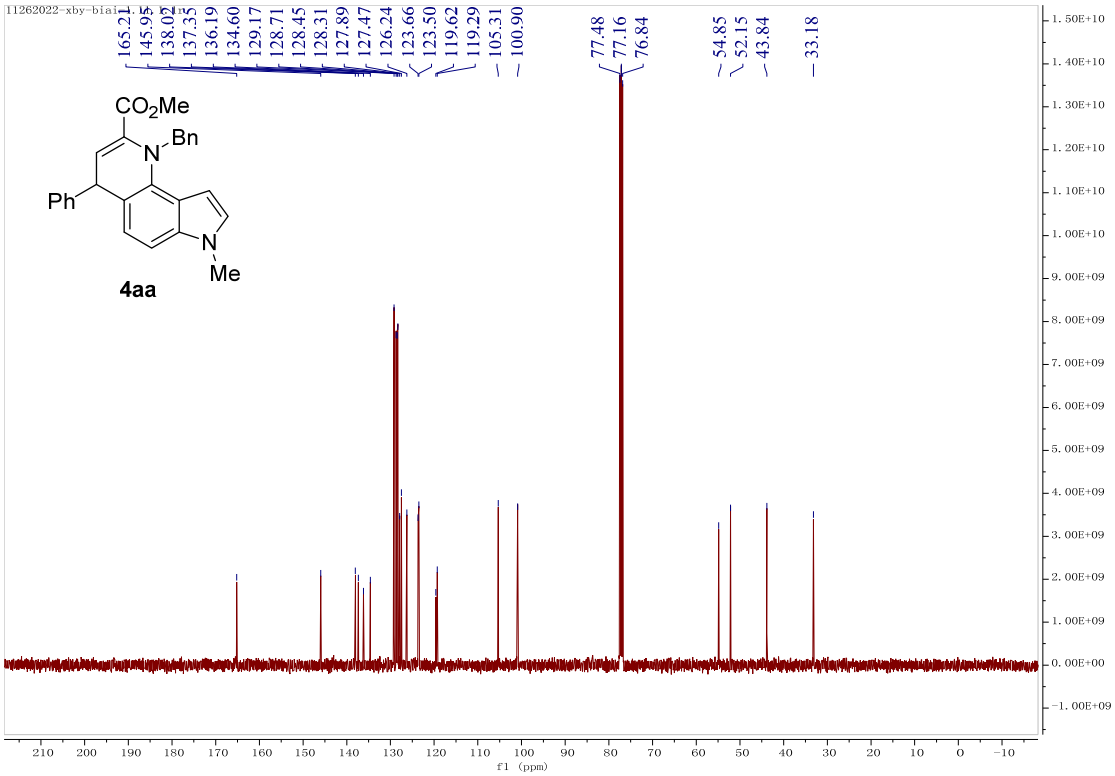
^{13}C{^{1}H} NMR Spectrum of 3aa (100 MHz, $CDCl_3$)



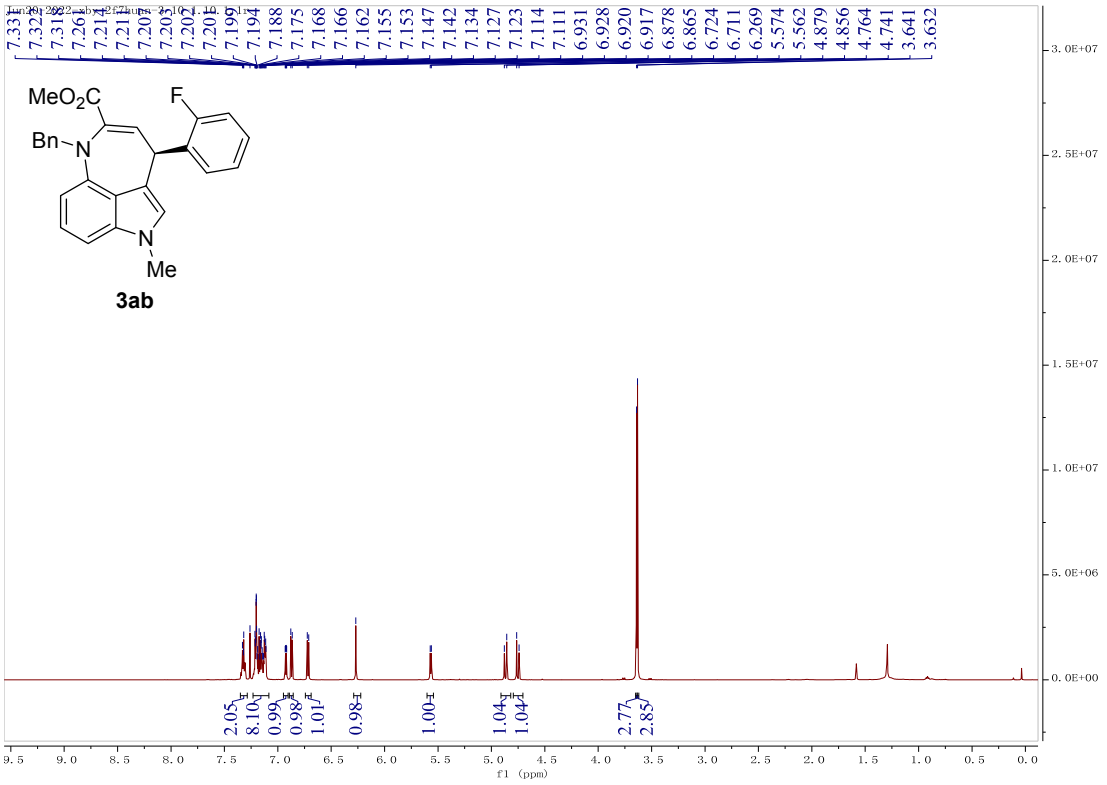
^{1}H NMR Spectrum of 4aa (400 MHz, $CDCl_3$)



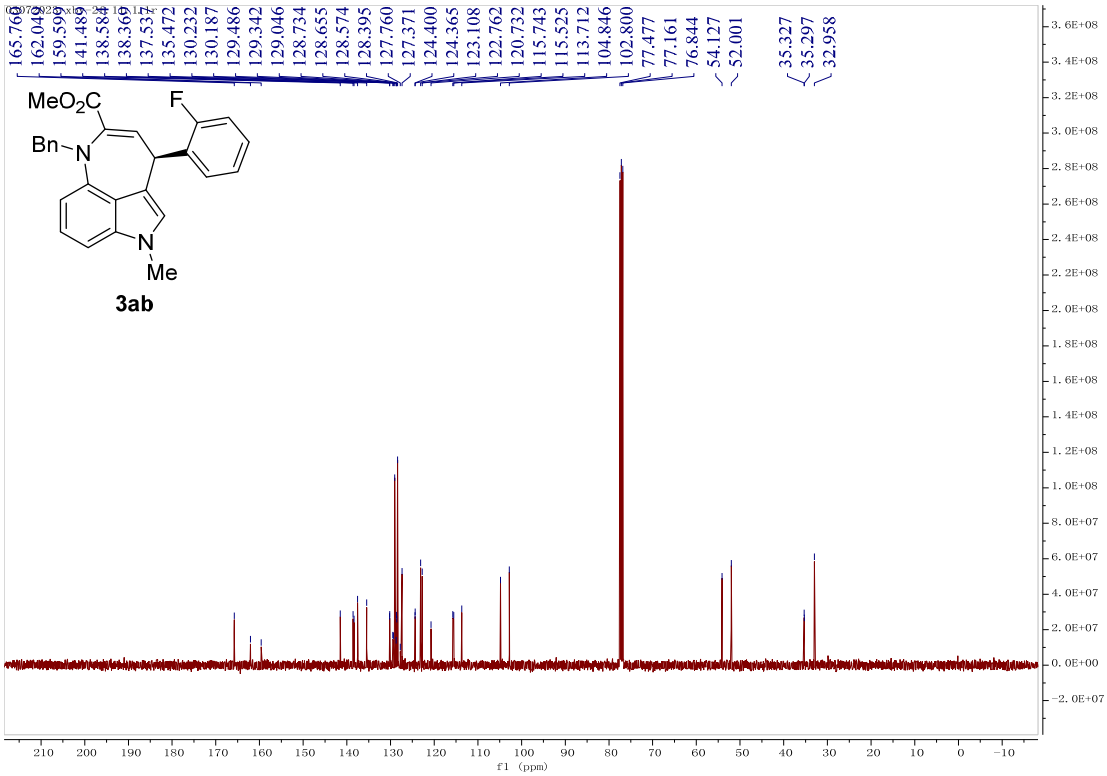
^{13}C{^{1}H} NMR Spectrum of 4aa (100 MHz, $CDCl_3$)



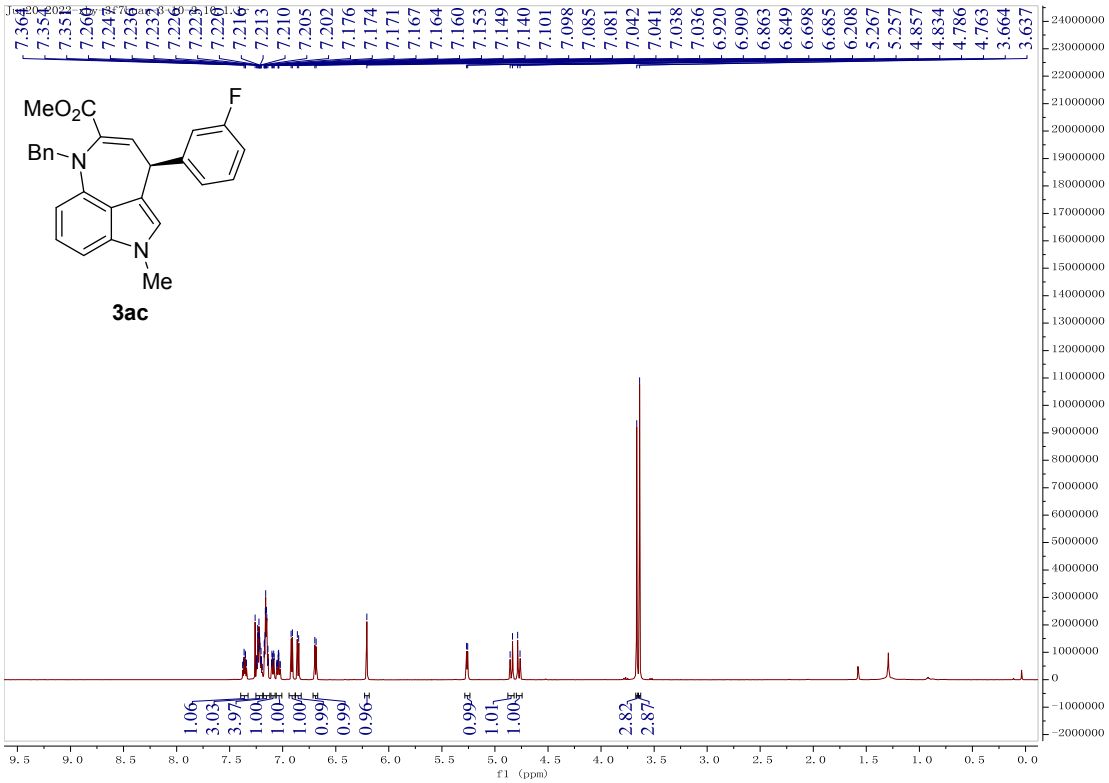
^{1}H NMR Spectrum of 3ab (600 MHz, $CDCl_3$)



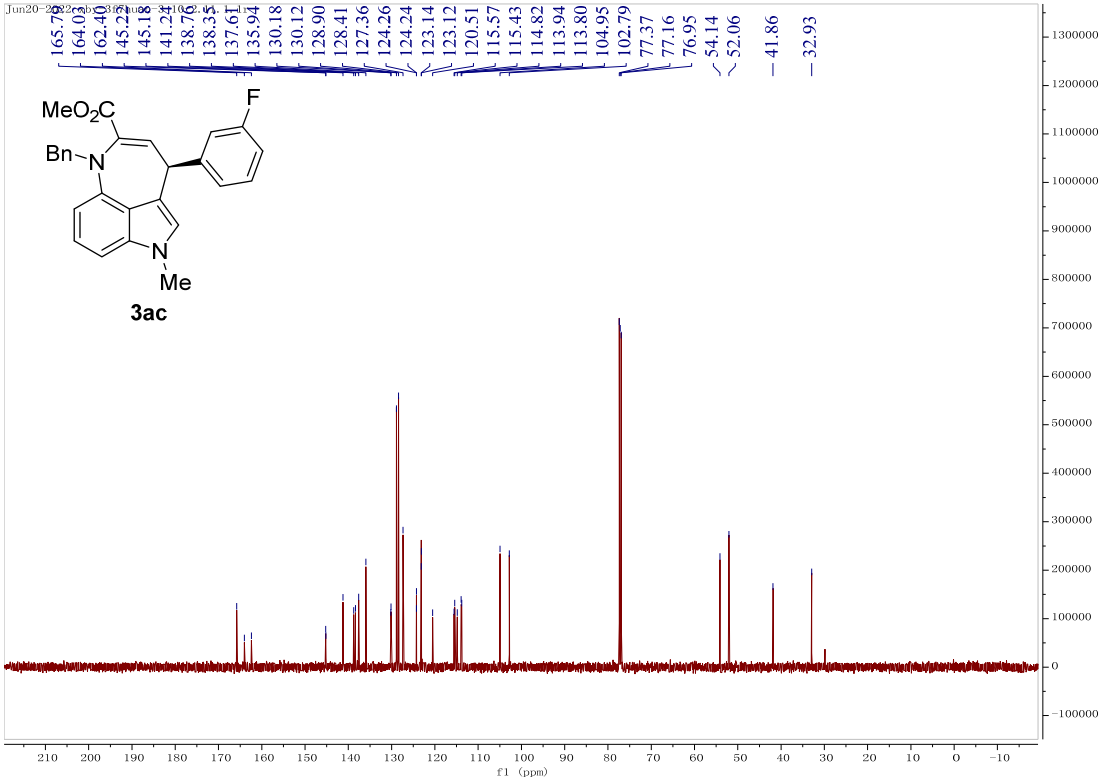
^{13}C{^{1}H} NMR Spectrum of 3ab (100 MHz, $CDCl_3$)



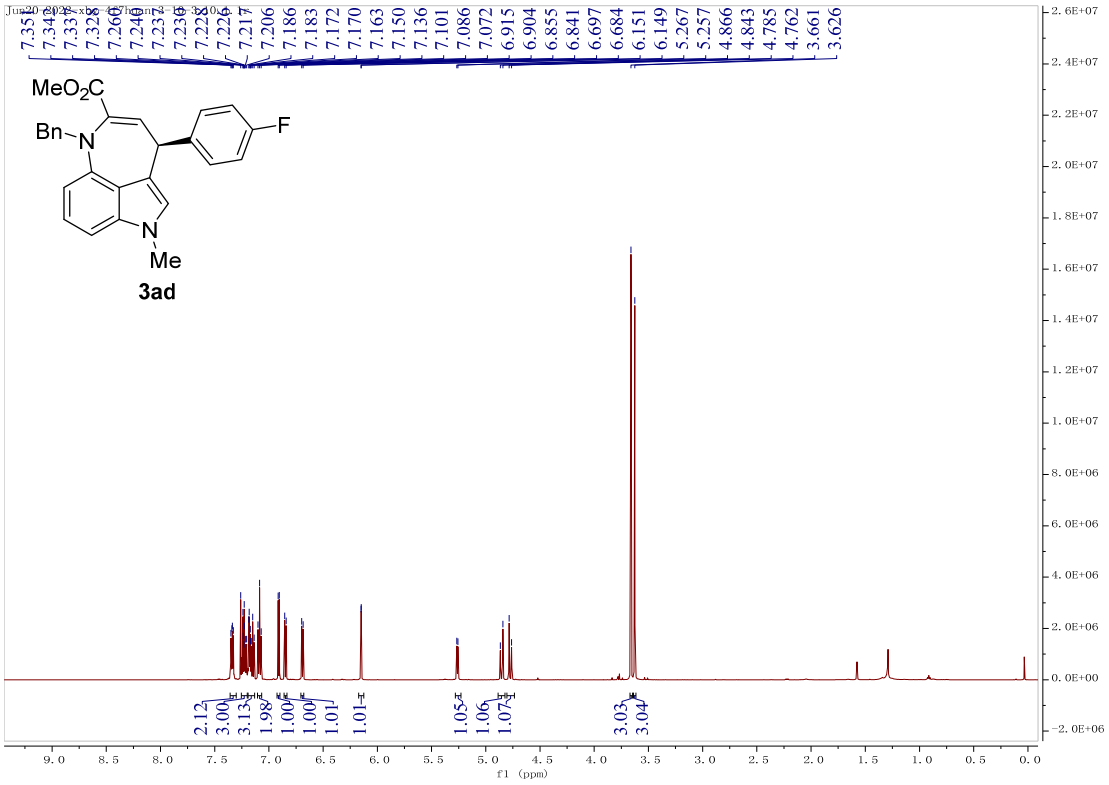
^{1}H NMR Spectrum of 3ac (600 MHz, $CDCl_3$)



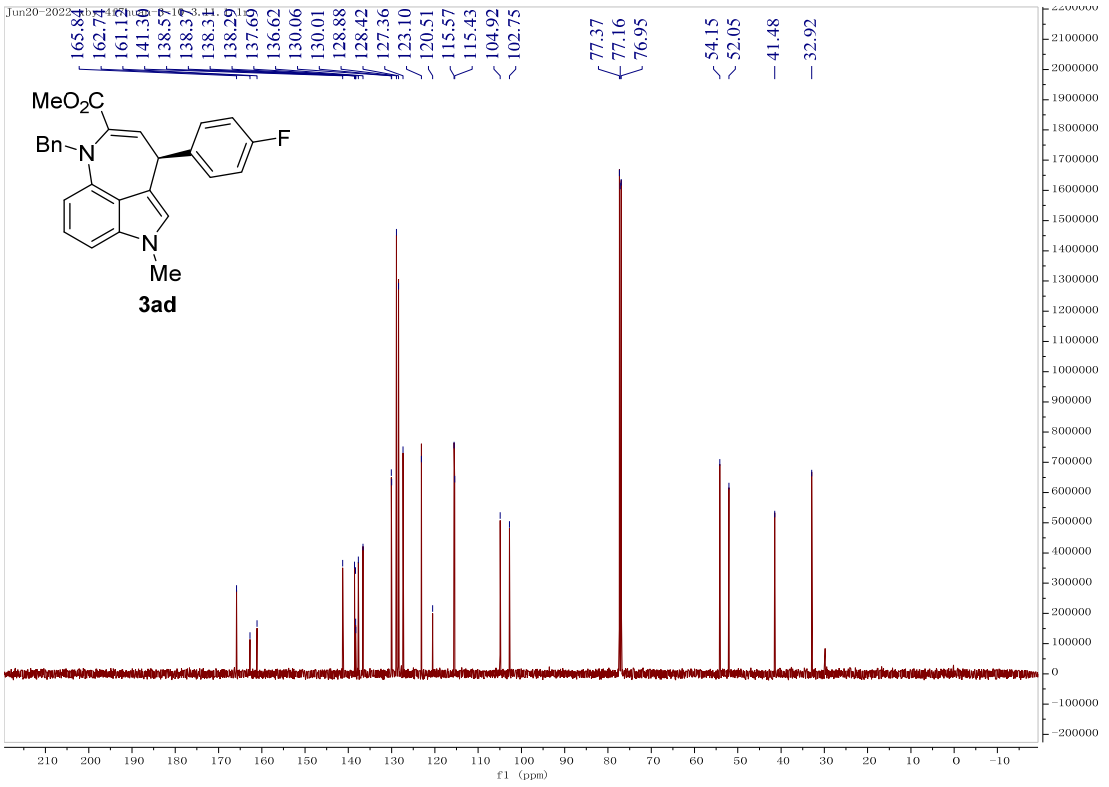
^{13}C{^{1}H} NMR Spectrum of 3ac (150 MHz, $CDCl_3$)



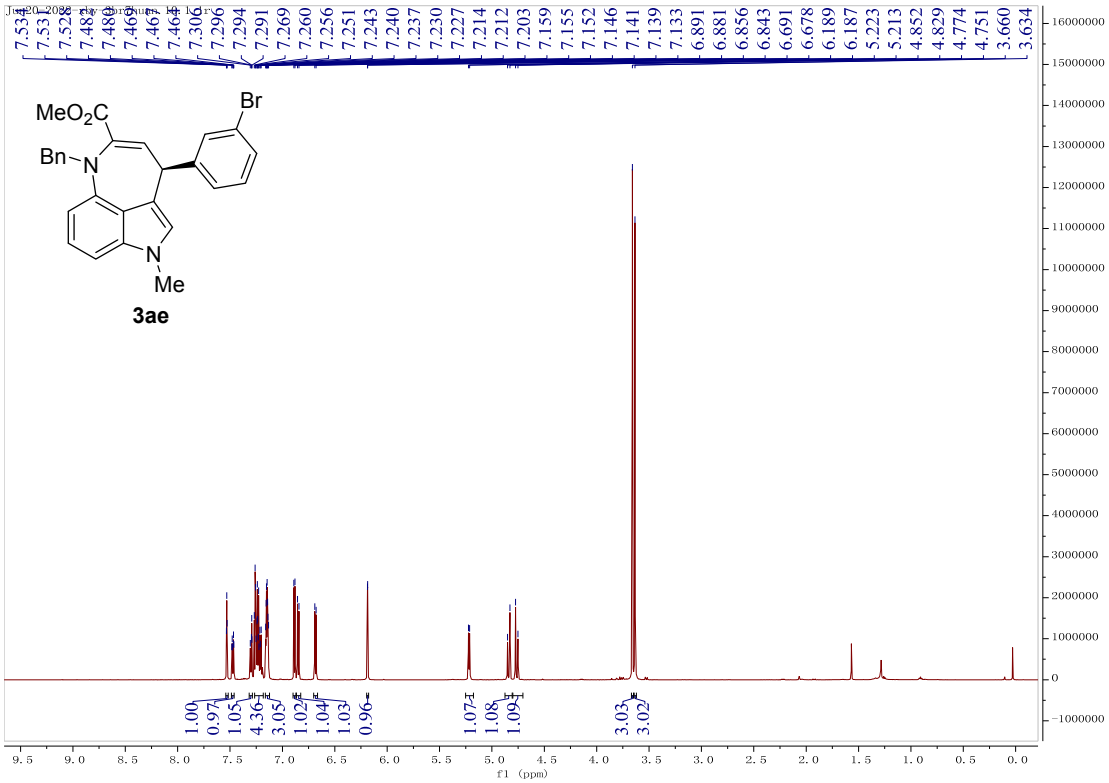
^{1}H NMR Spectrum of 3ad (600 MHz, $CDCl_3$)



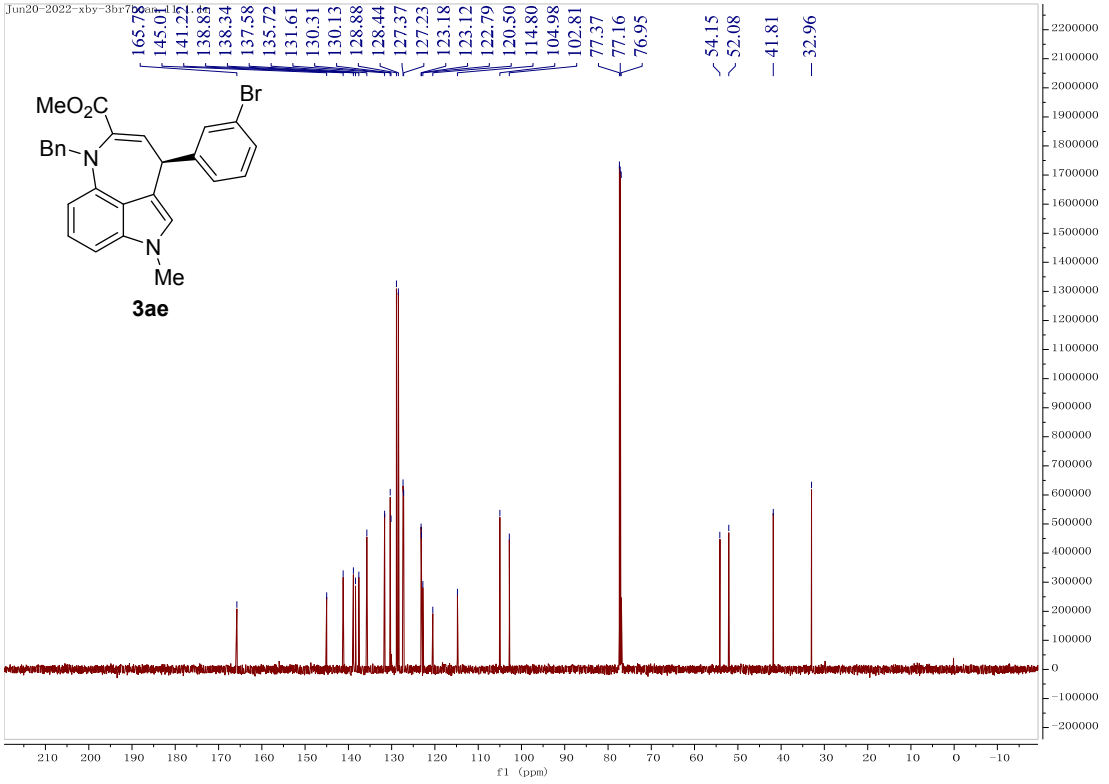
^{13}C{^{1}H} NMR Spectrum of 3ad (150 MHz, $CDCl_3$)



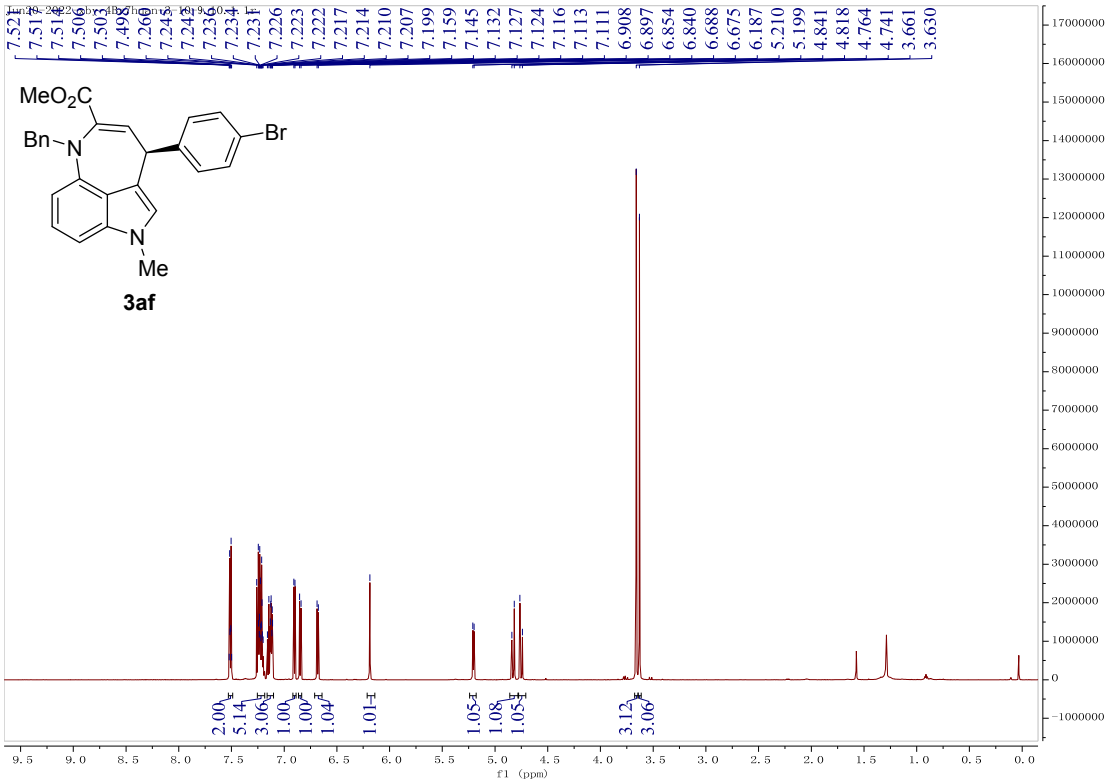
^{1}H NMR Spectrum of 3ae (600 MHz, $CDCl_3$)



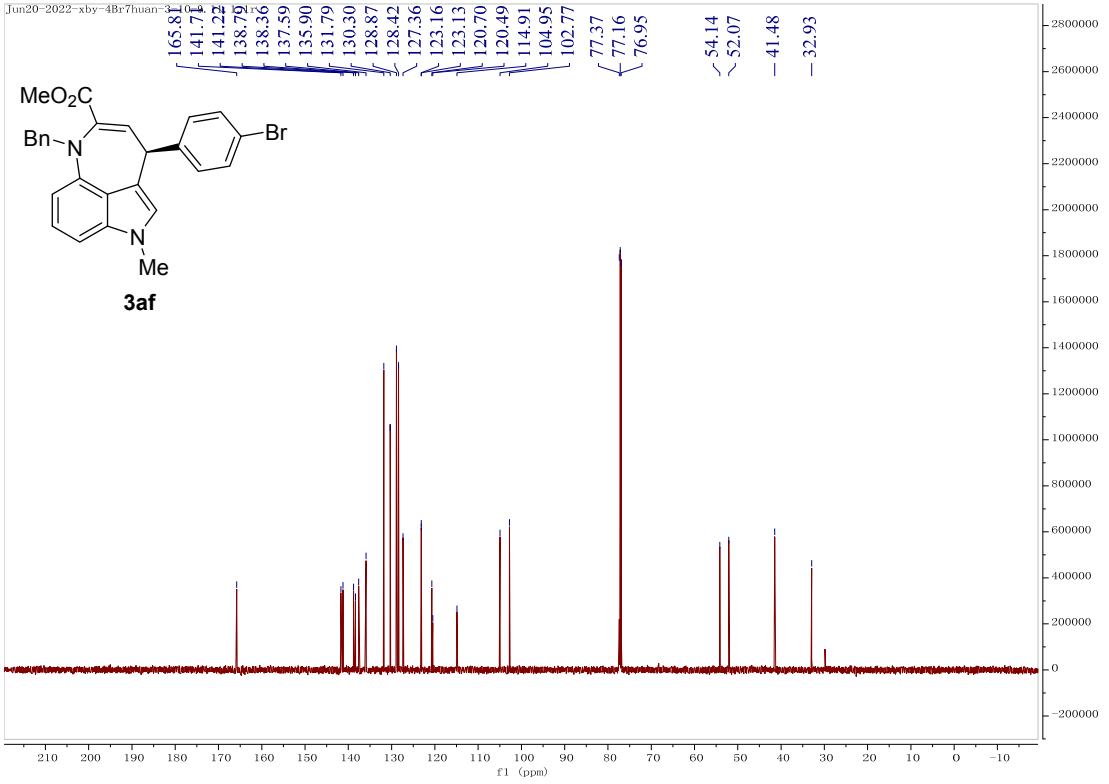
^{13}C{^{1}H} NMR Spectrum of 3ae (150 MHz, $CDCl_3$)



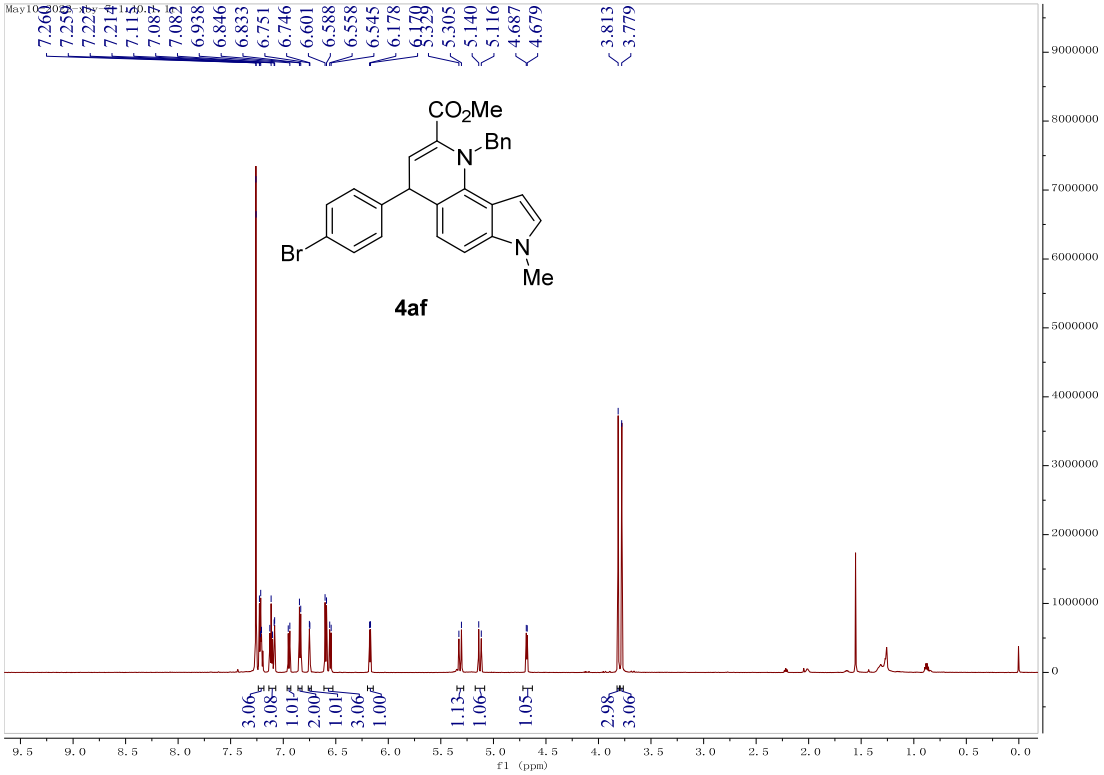
^{1}H NMR Spectrum of 3af (600 MHz, $CDCl_3$)



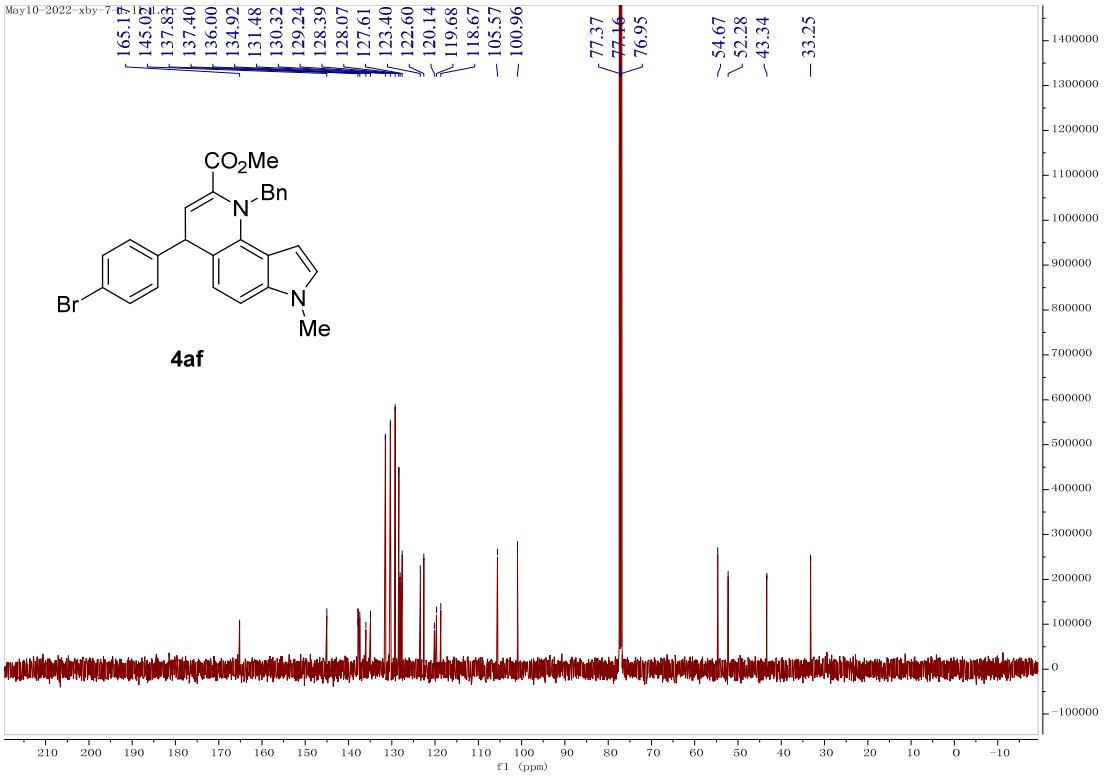
^{13}C{^{1}H} NMR Spectrum of 3af (150 MHz, $CDCl_3$)



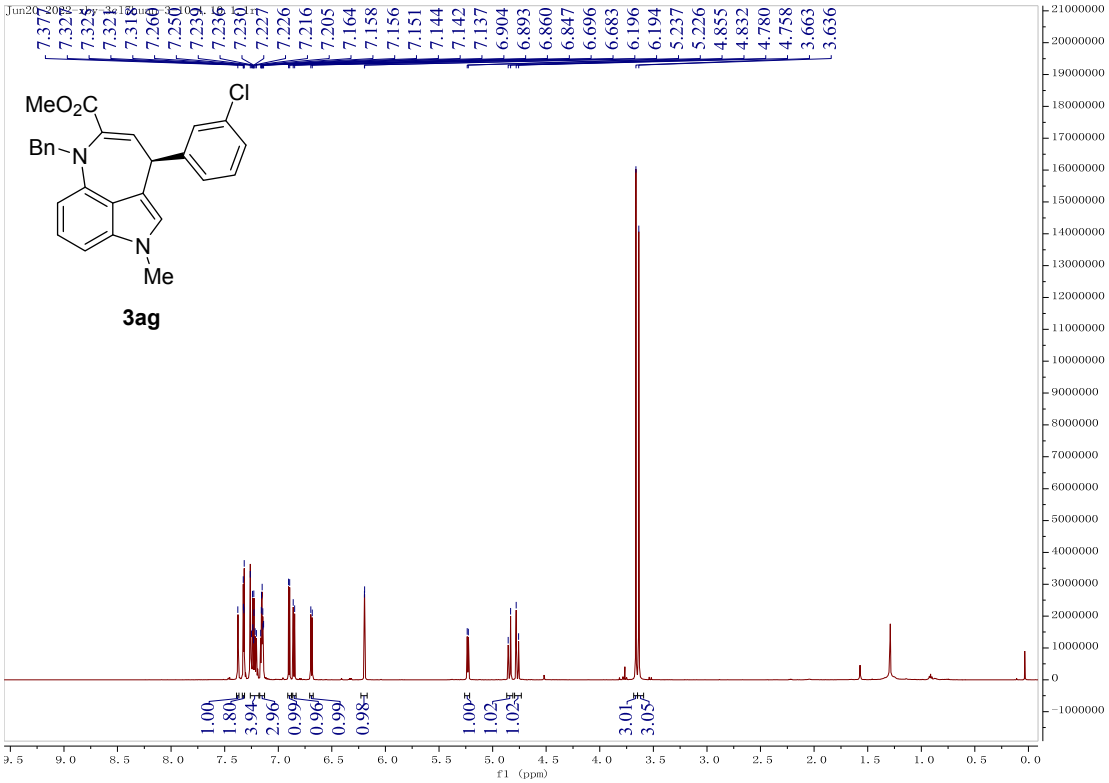
^{1}H NMR Spectrum of 4af (600 MHz, $CDCl_3$)



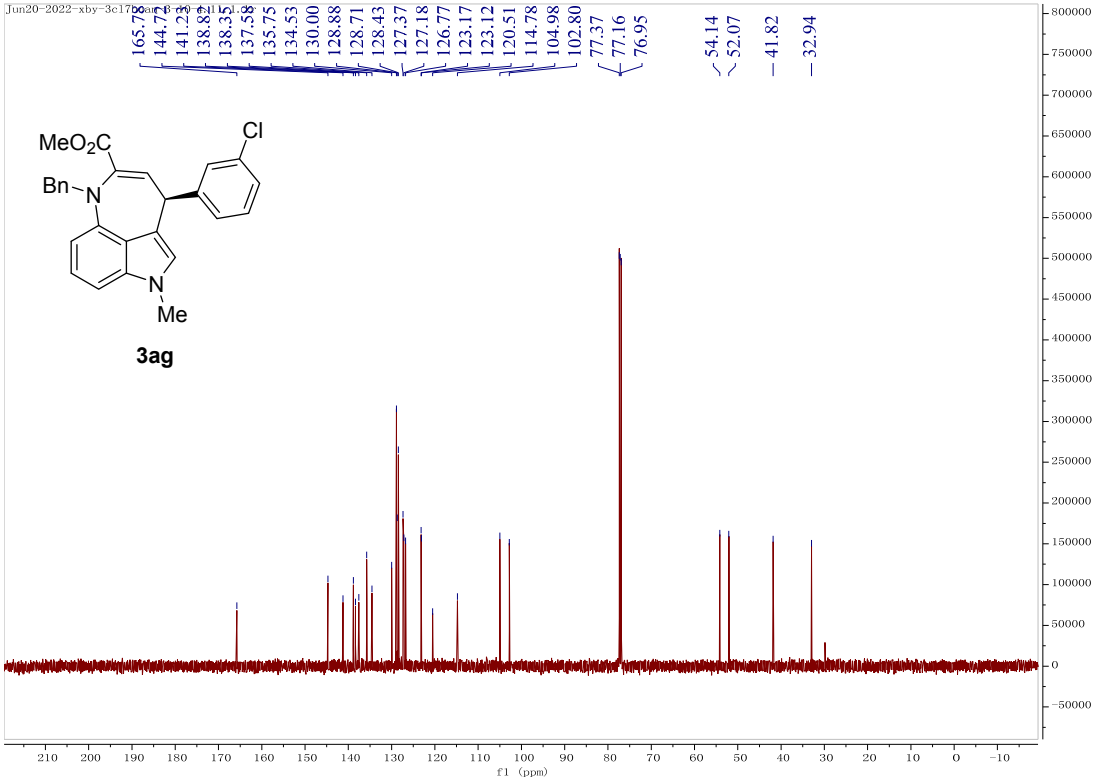
^{13}C{^{1}H} NMR Spectrum of 4af (150 MHz, $CDCl_3$)



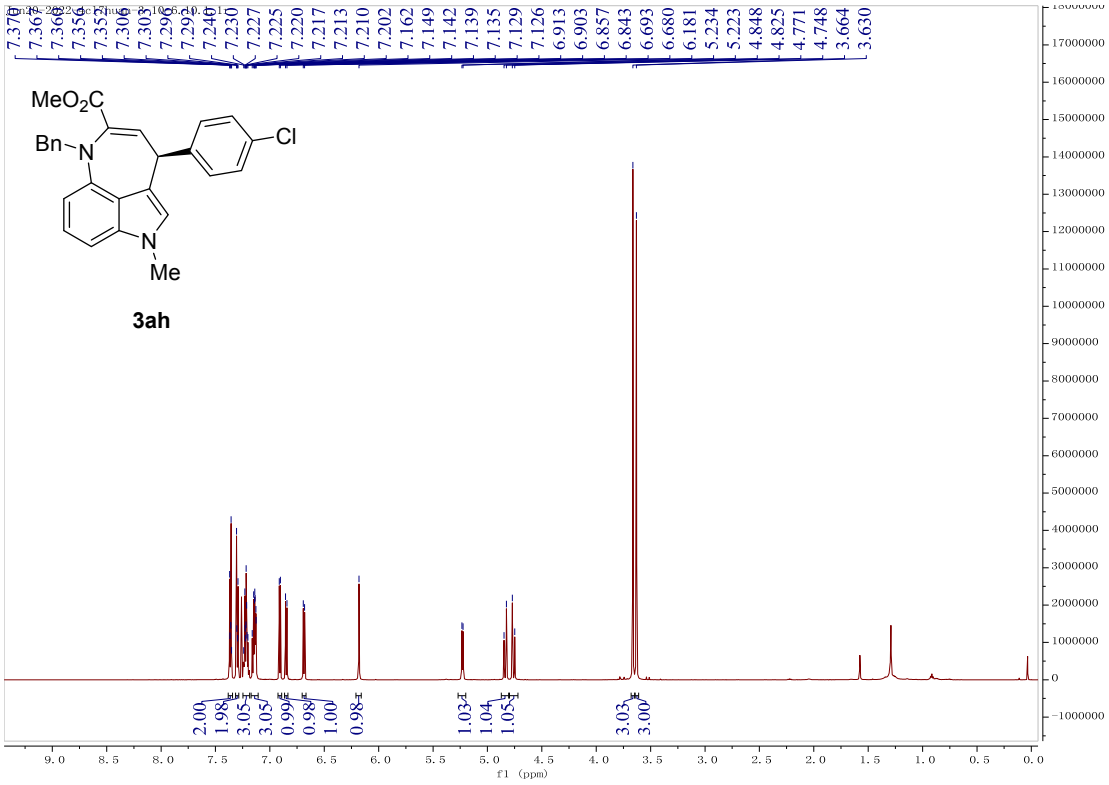
^{1}H NMR Spectrum of 3ag (600 MHz, $CDCl_3$)



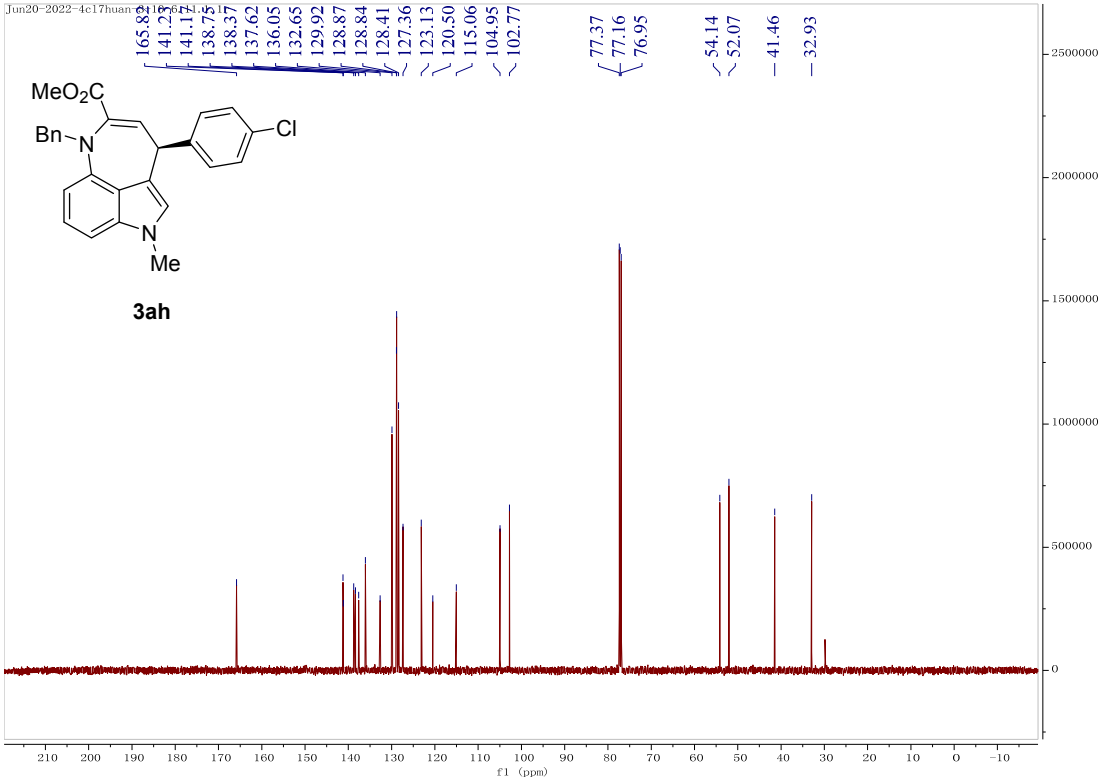
^{13}C{^{1}H} NMR Spectrum of 3ag (150 MHz, $CDCl_3$)



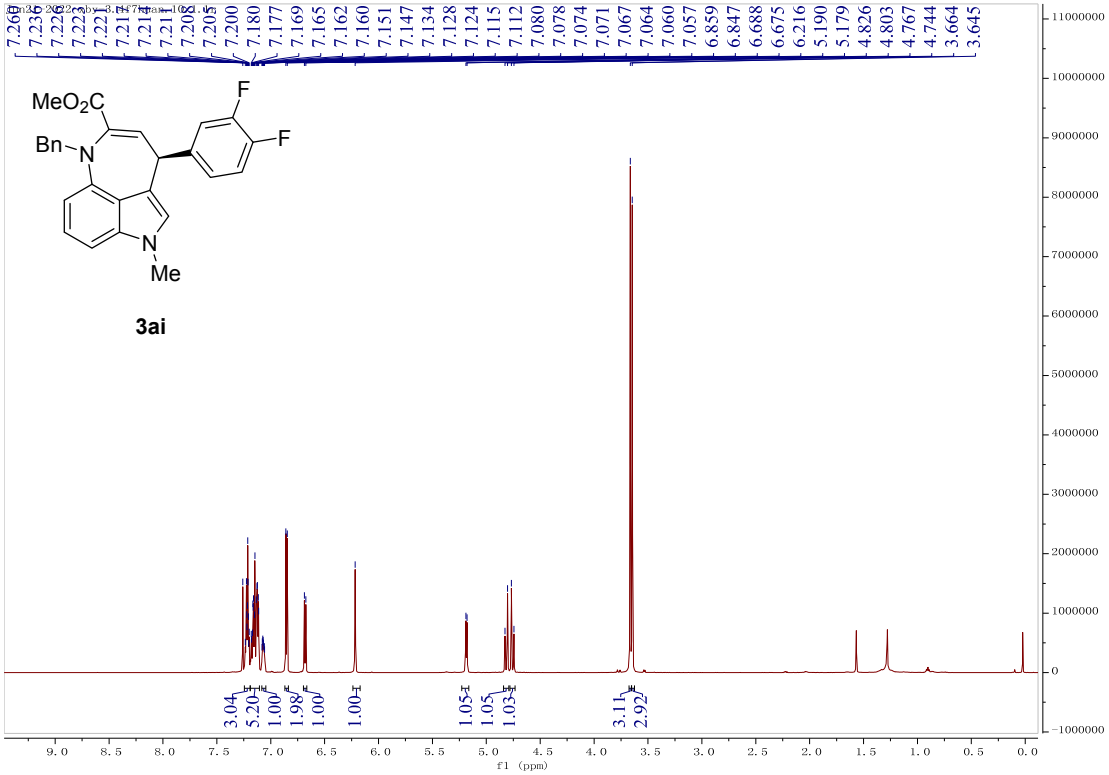
^{1}H NMR Spectrum of 3ah (600 MHz, $CDCl_3$)



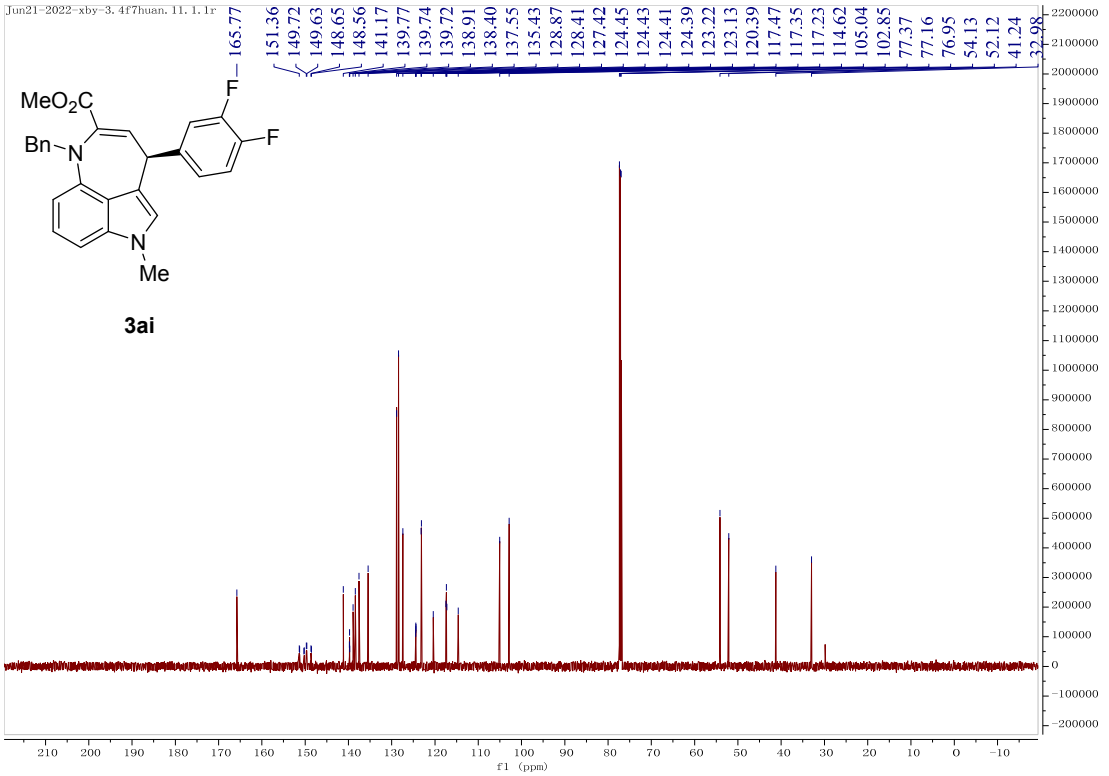
^{13}C{^{1}H} NMR Spectrum of 3ah (150 MHz, $CDCl_3$)



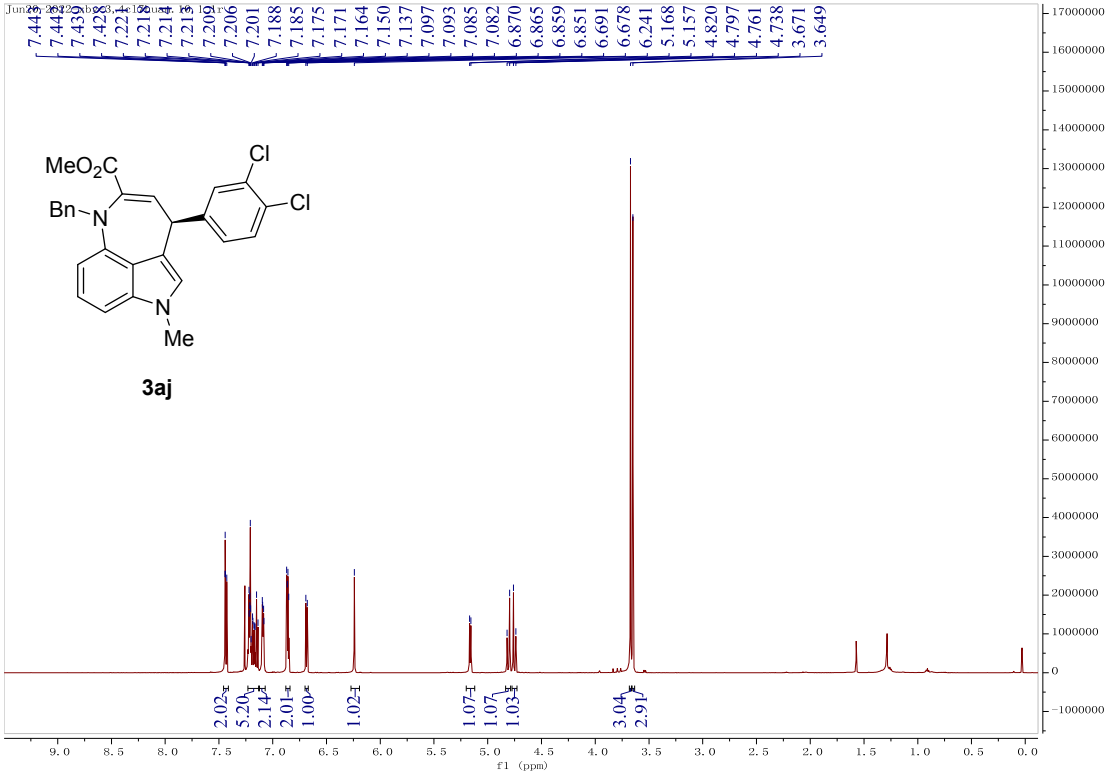
^{1}H NMR Spectrum of 3ai (600 MHz, $CDCl_3$)



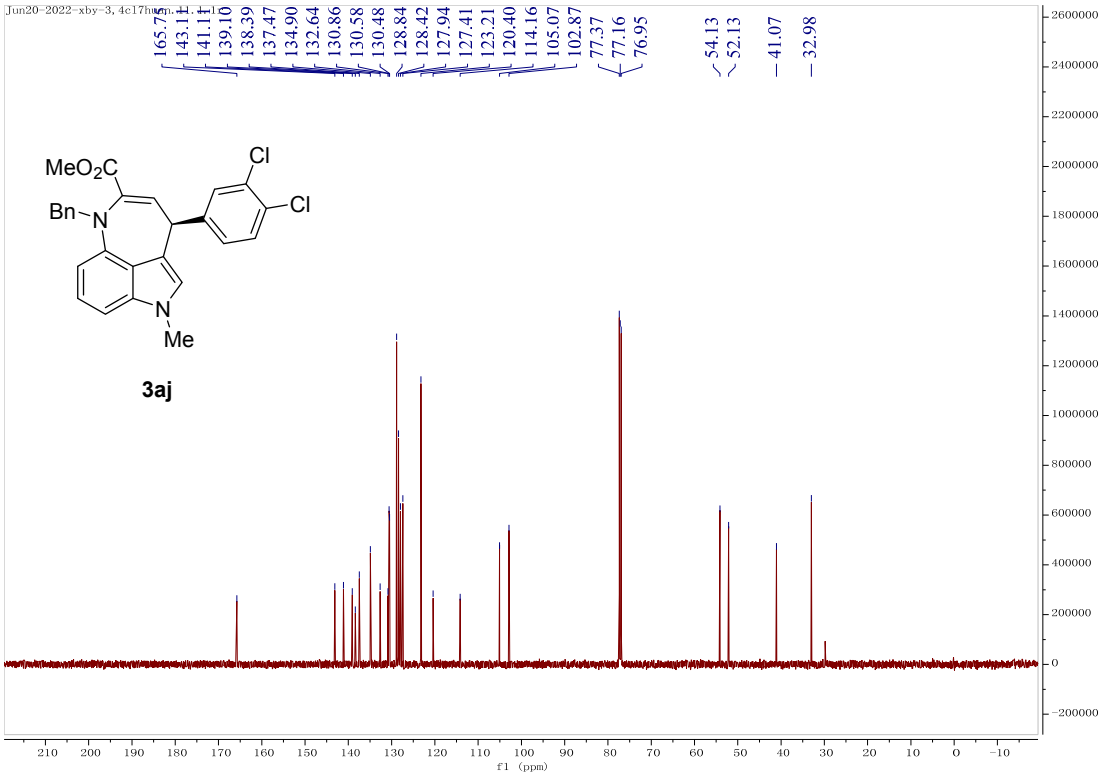
^{13}C{^{1}H} NMR Spectrum of 3ai(150 MHz, $CDCl_3$)



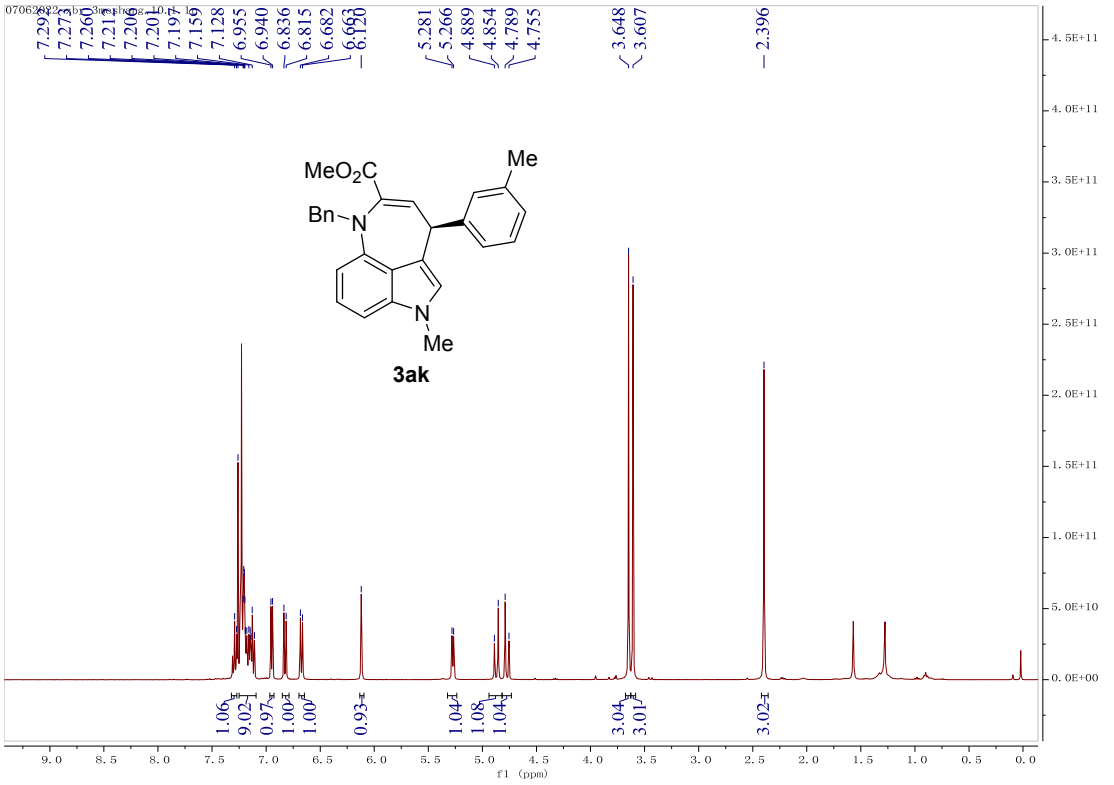
^{1}H NMR Spectrum of 3aj (600 MHz, $CDCl_3$)



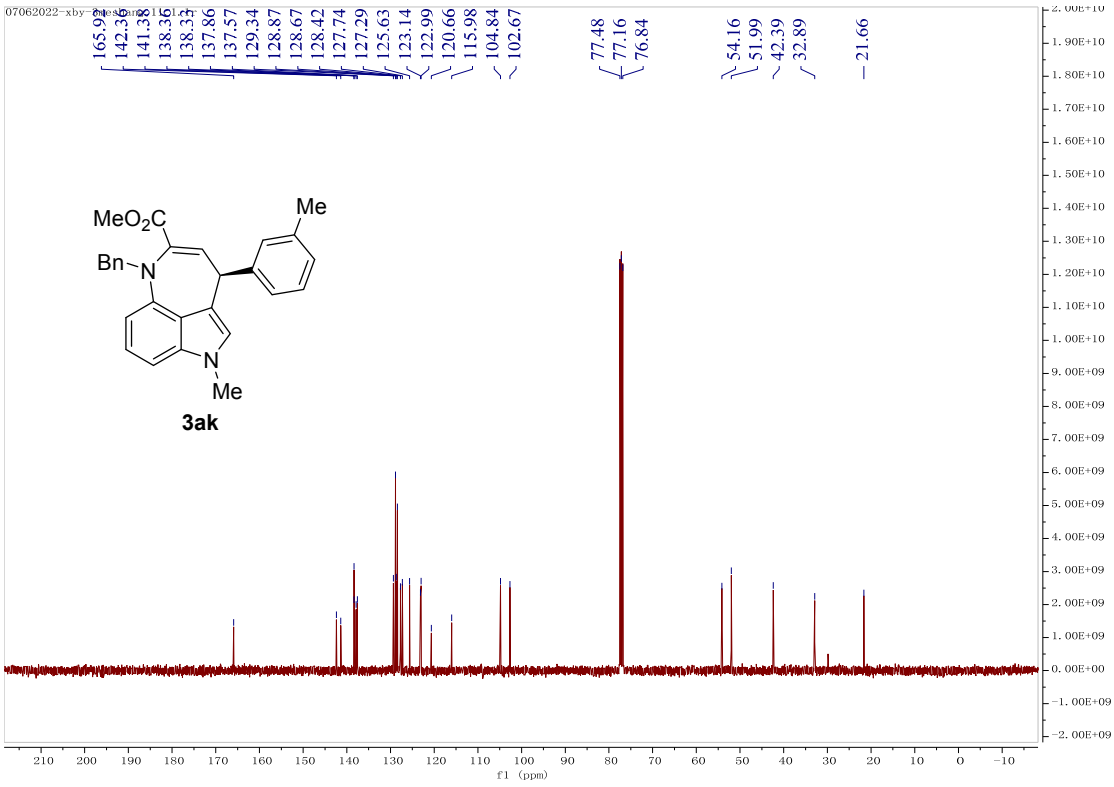
^{13}C{^{1}H} NMR Spectrum of 3aj (150 MHz, $CDCl_3$)



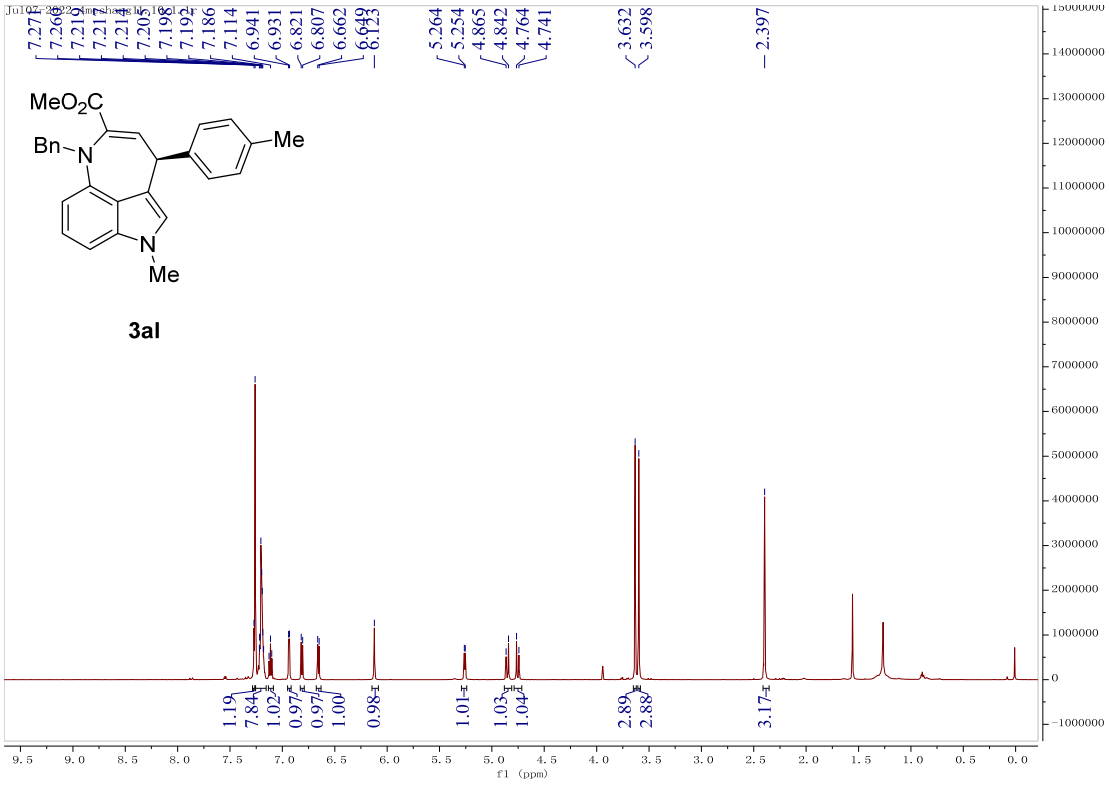
^{1}H NMR Spectrum of 3ak (400 MHz, $CDCl_3$)



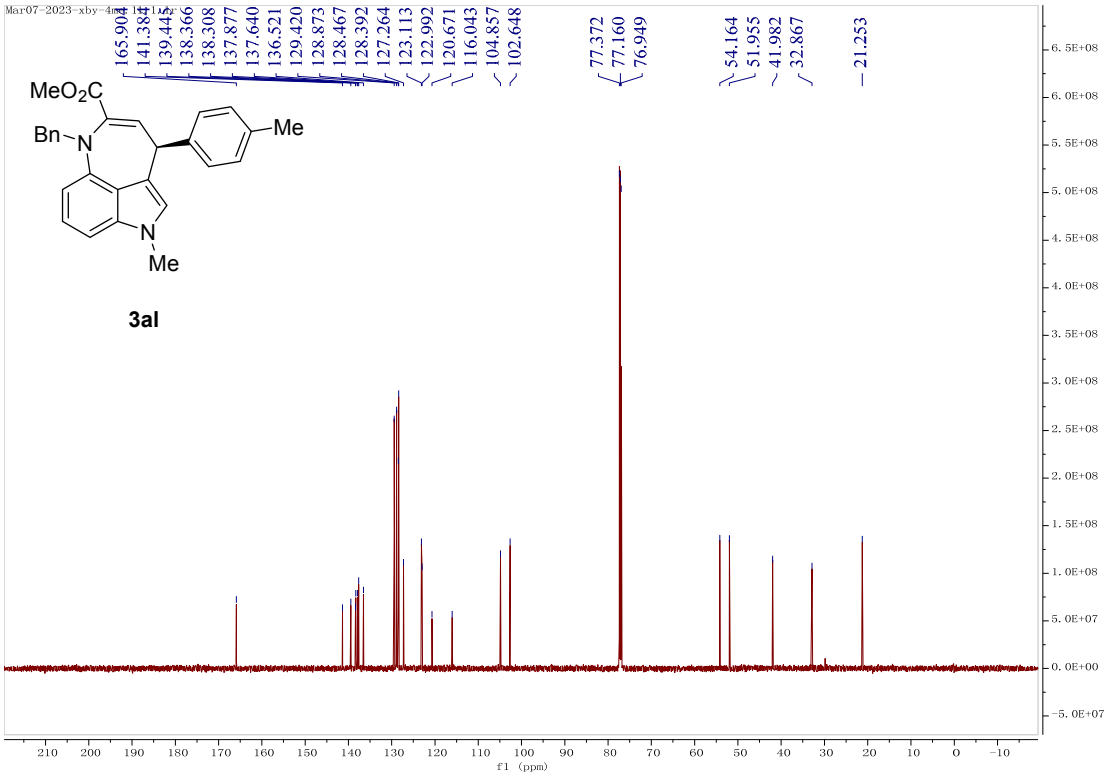
^{13}C{^{1}H} NMR Spectrum of 3ak (100 MHz, $CDCl_3$)



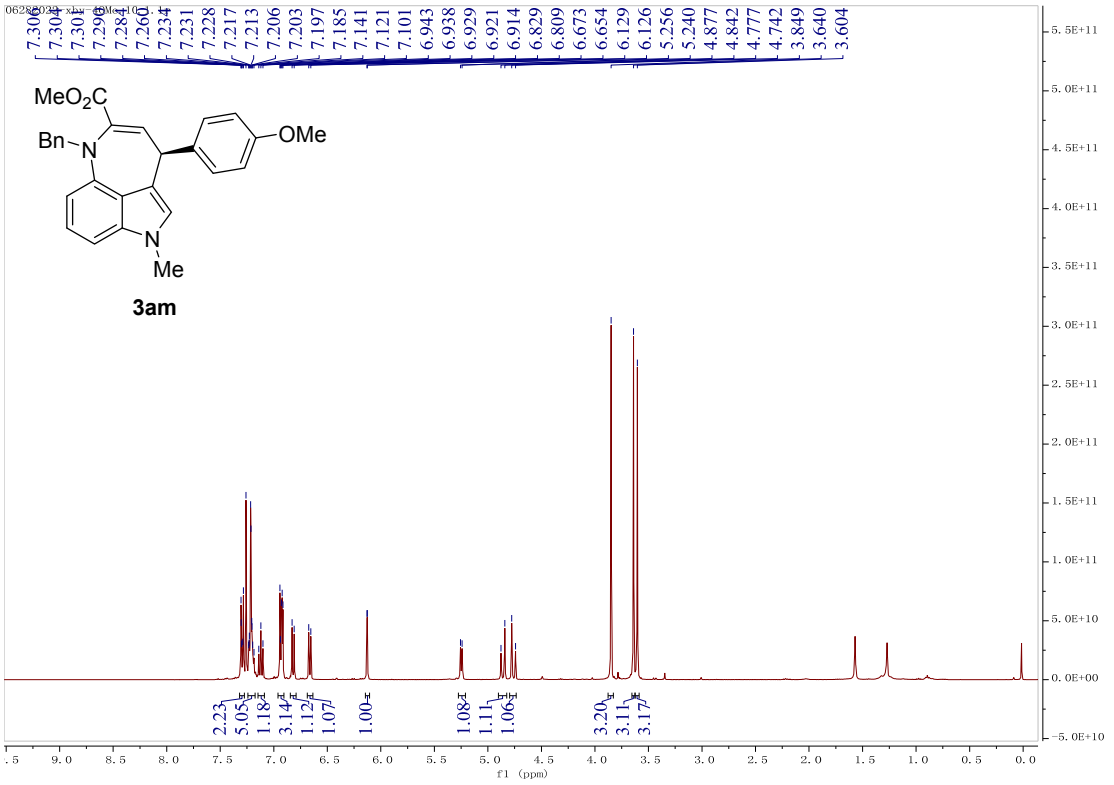
^{1}H NMR Spectrum of 3al (600 MHz, $CDCl_3$)



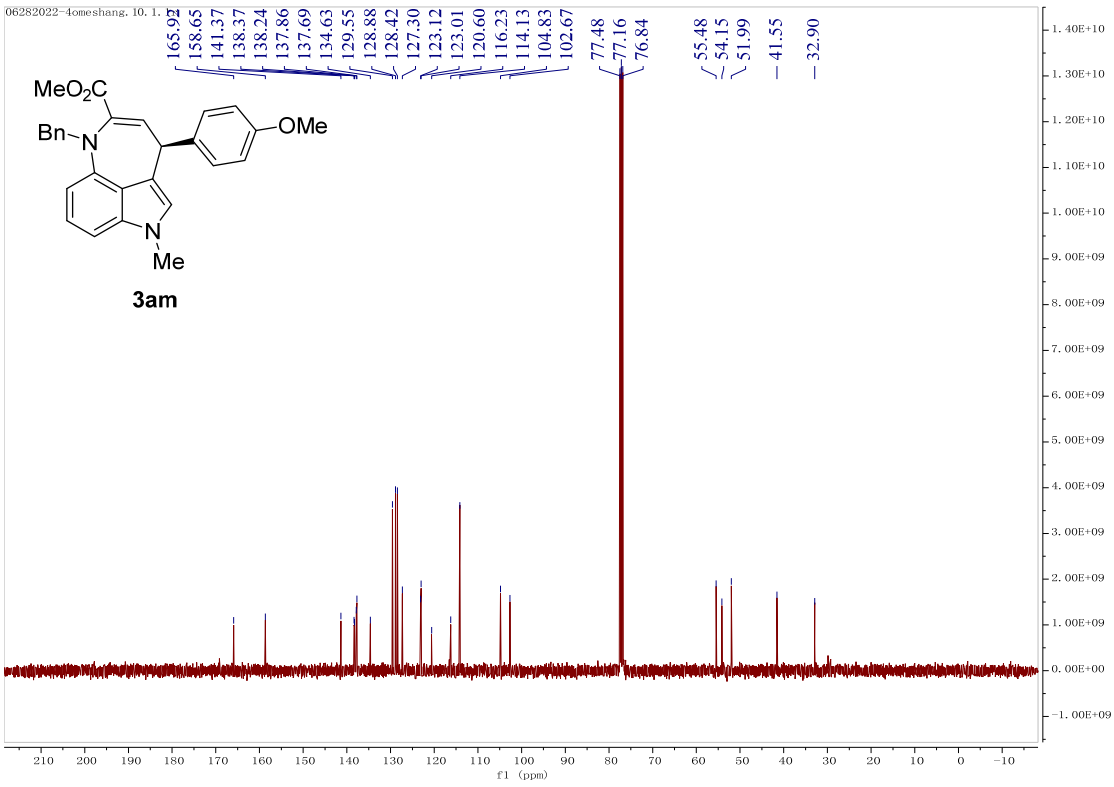
^{13}C{^{1}H} NMR Spectrum of 3al (150 MHz, $CDCl_3$)



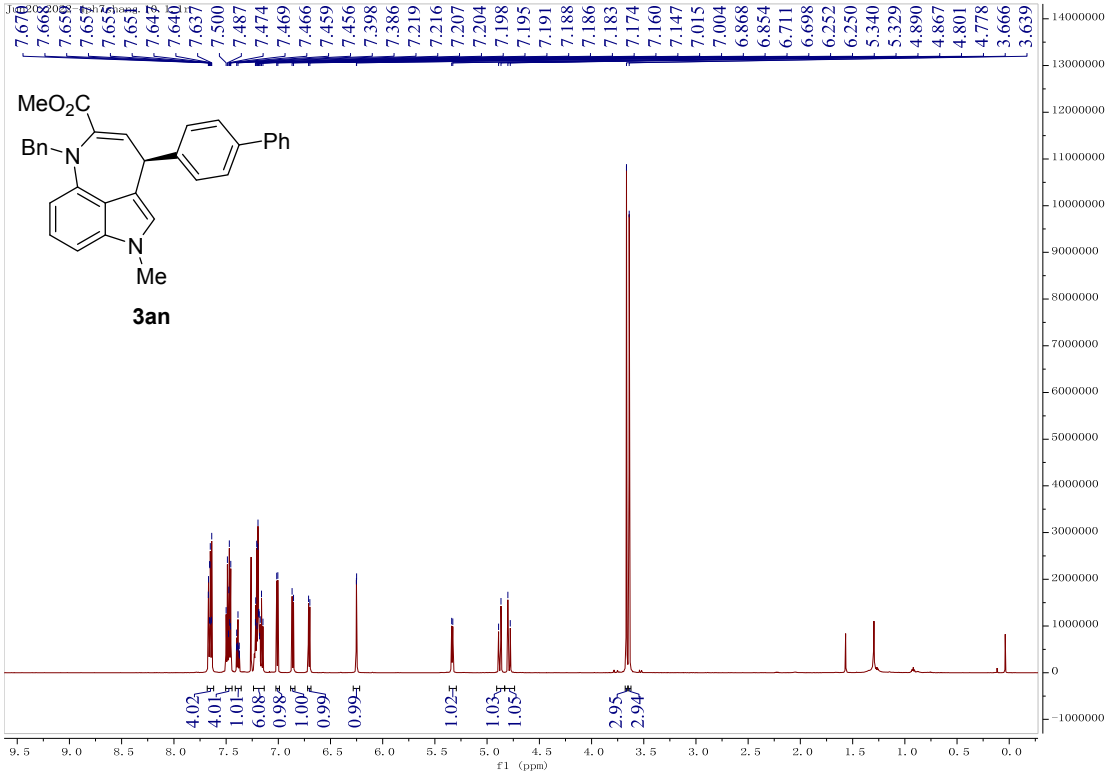
^{1}H NMR Spectrum of 3am (400 MHz, $CDCl_3$)



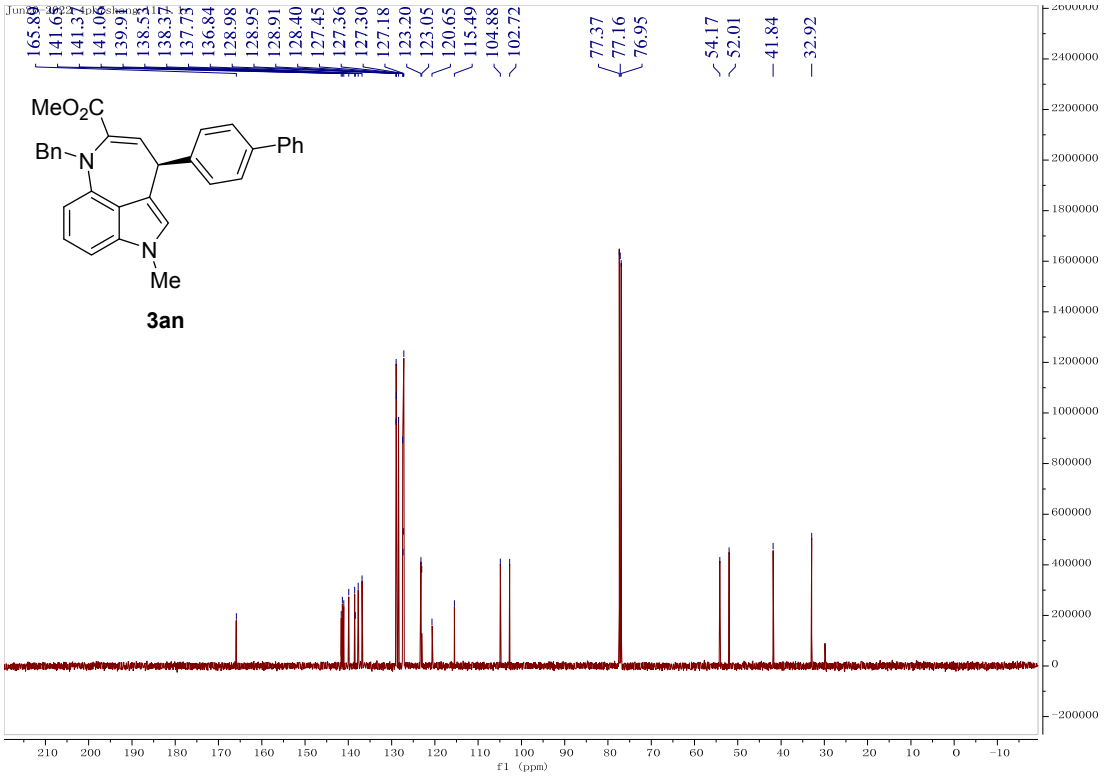
^{13}C{^{1}H} NMR Spectrum of 3am (100 MHz, $CDCl_3$)



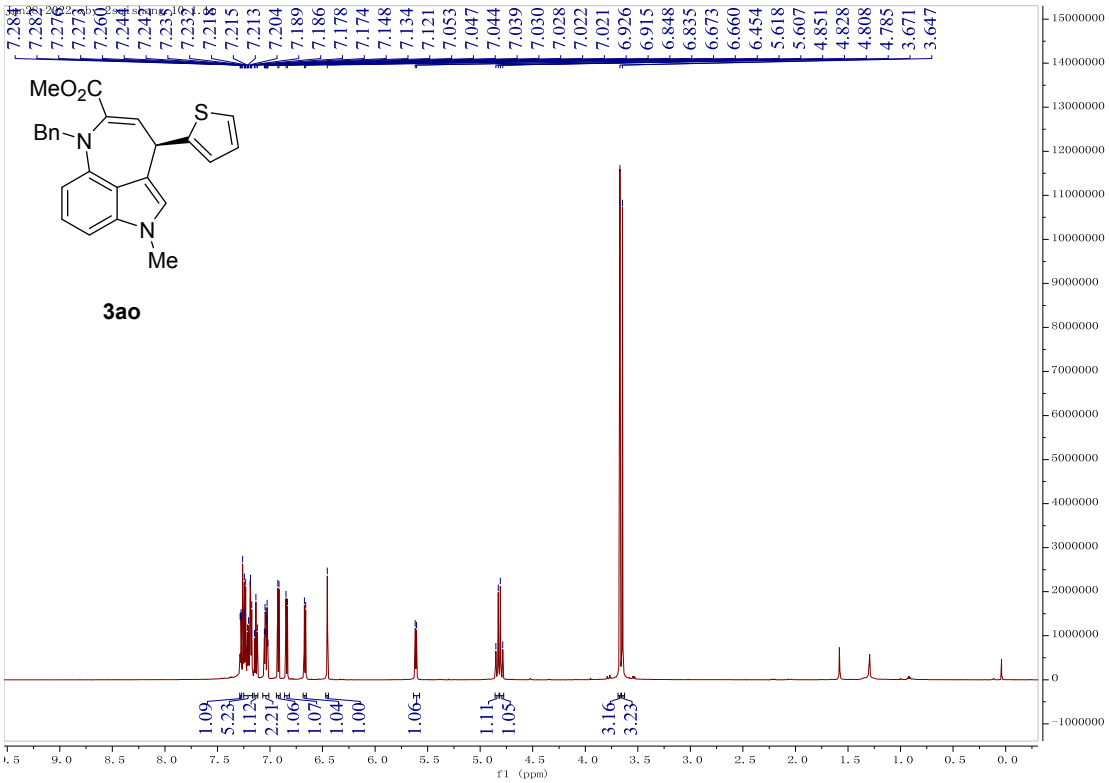
^{1}H NMR Spectrum of 3an (600 MHz, $CDCl_3$)



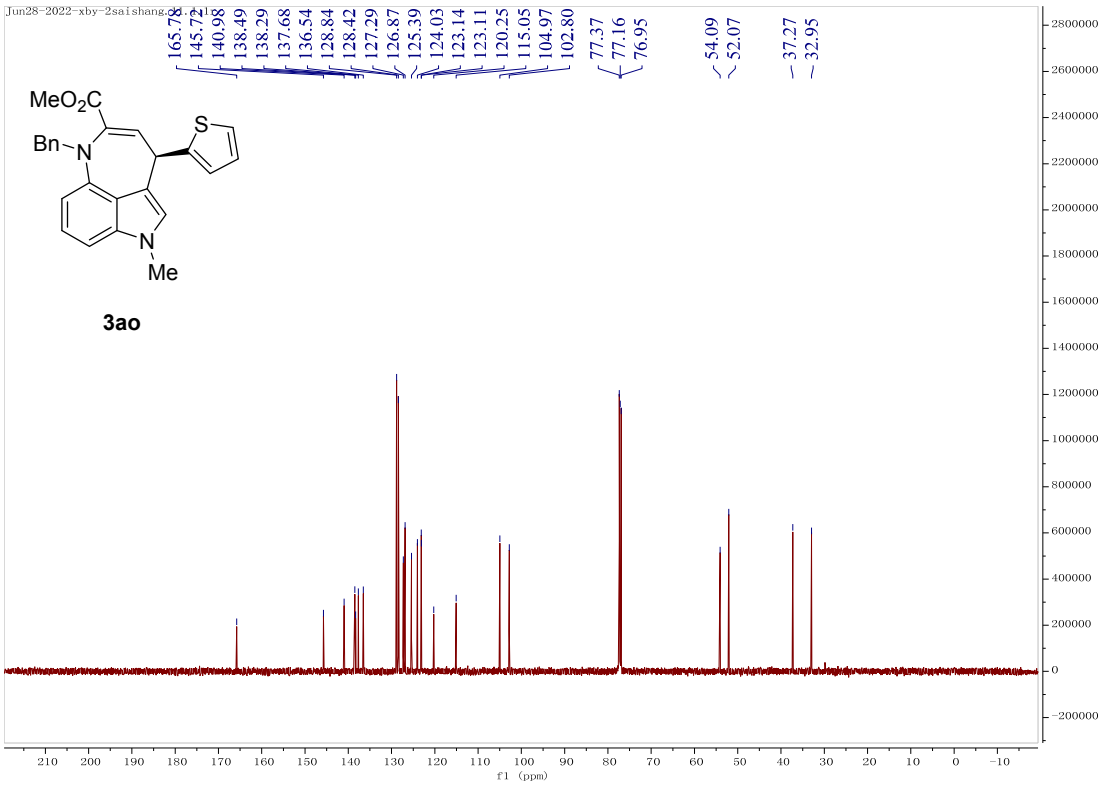
^{13}C{^{1}H} NMR Spectrum of 3an (150 MHz, $CDCl_3$)



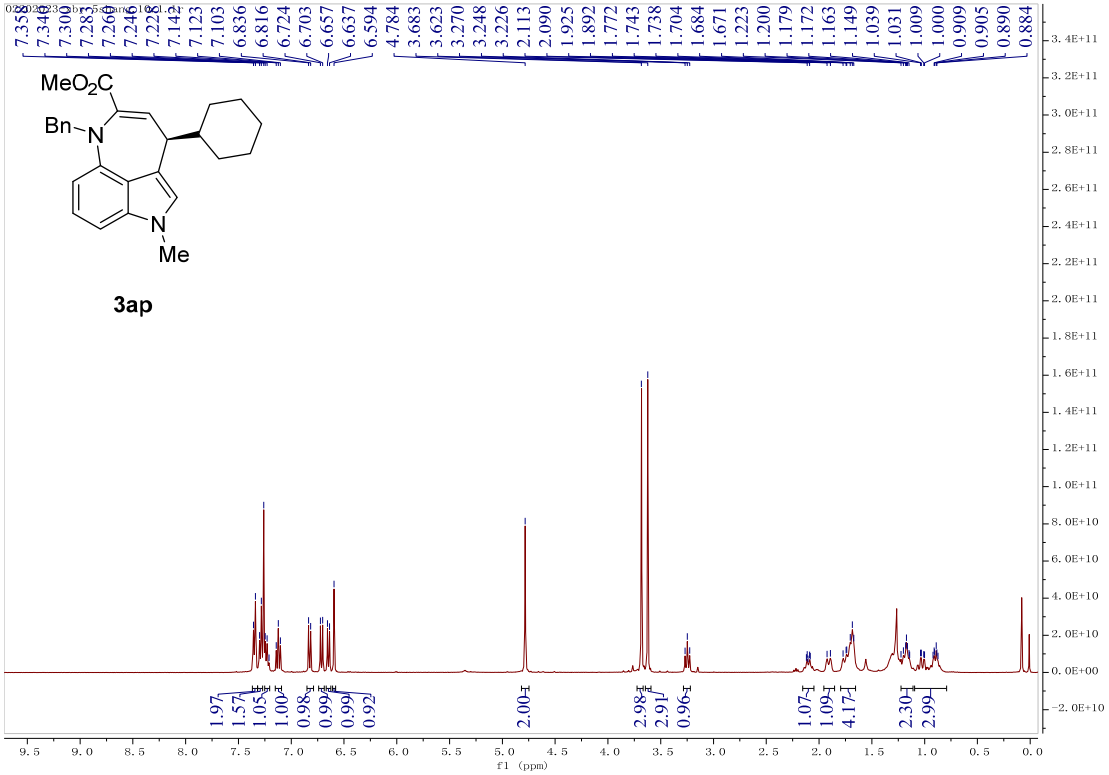
^{1}H NMR Spectrum of 3ao (600 MHz, $CDCl_3$)



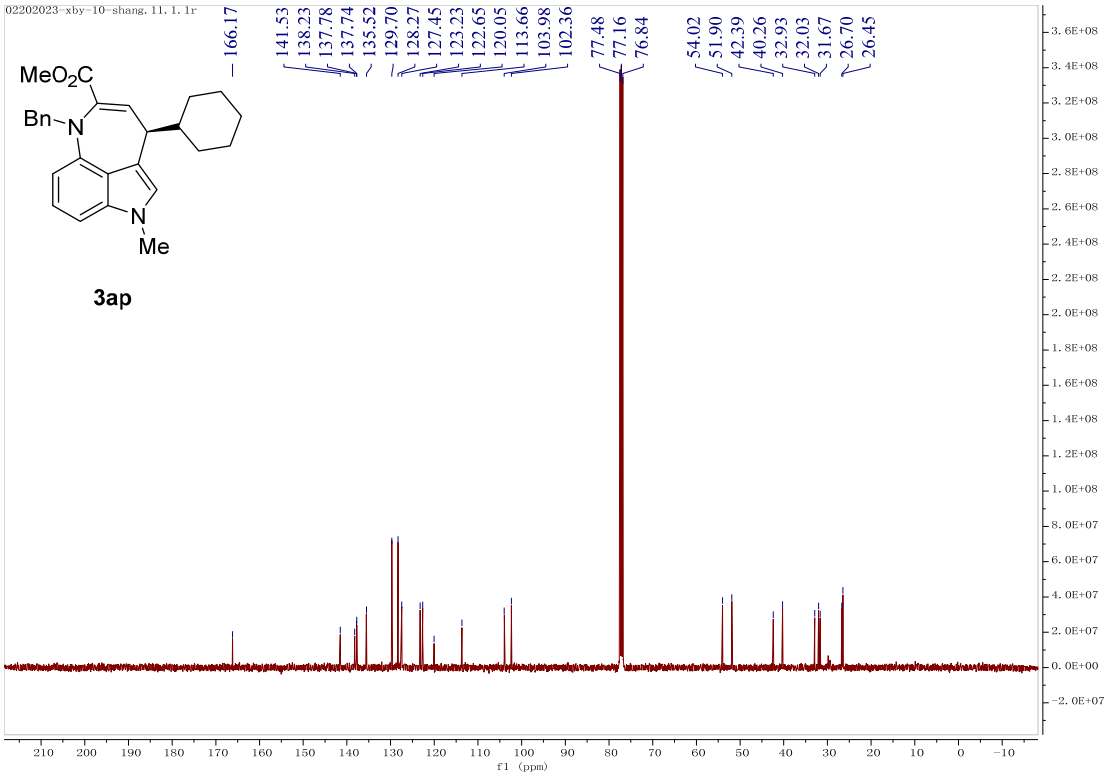
^{13}C{^{1}H} NMR Spectrum of 3ao (150 MHz, $CDCl_3$)



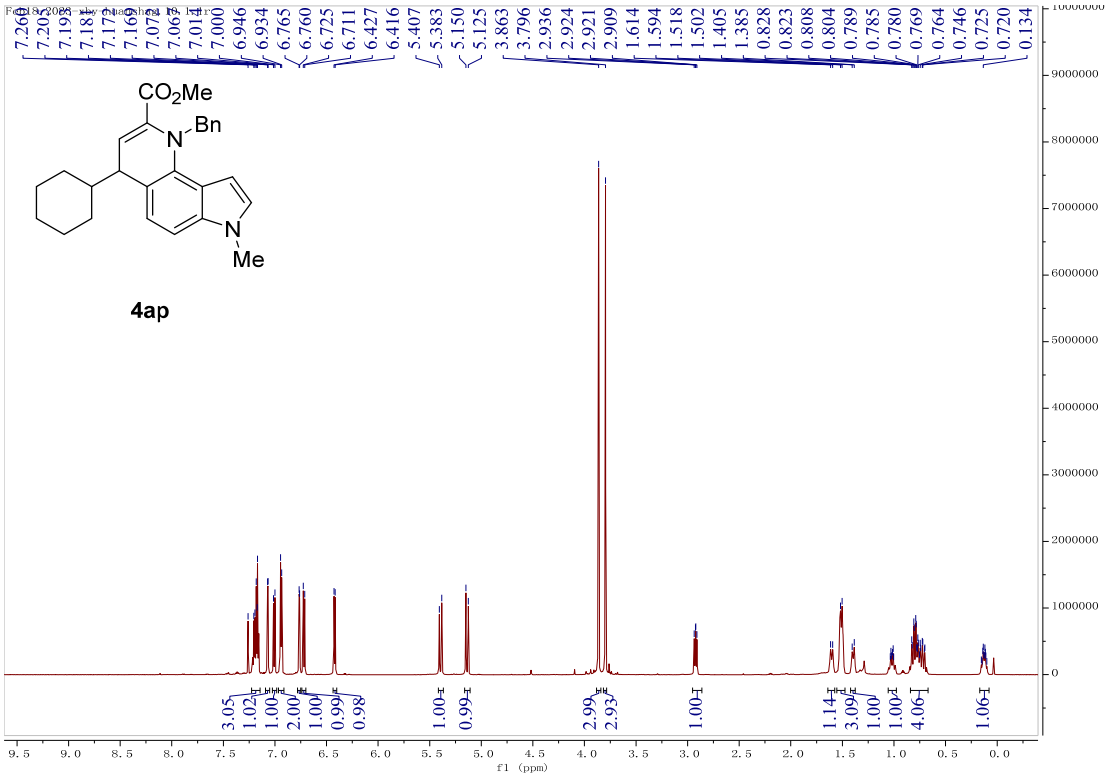
^{1}H NMR Spectrum of 3ap (400 MHz, $CDCl_3$)



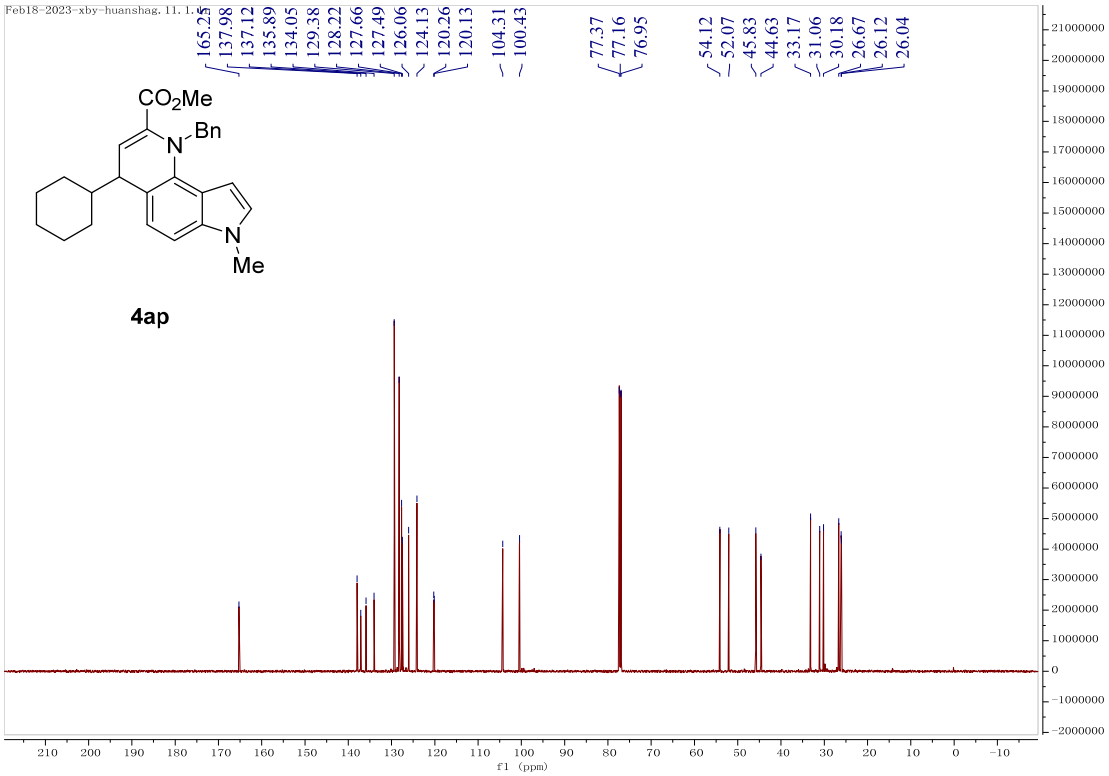
^{13}C{^{1}H} NMR Spectrum of 3ap (100 MHz, $CDCl_3$)



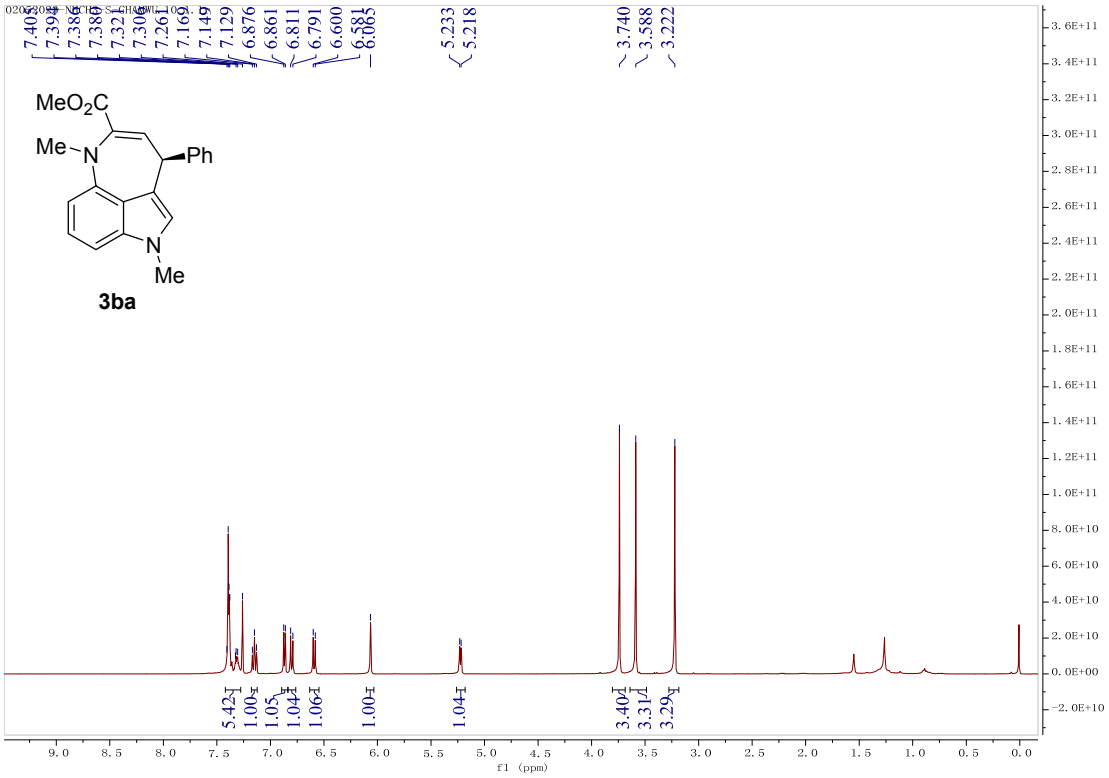
^{1}H NMR Spectrum of 4ap (600 MHz, $CDCl_3$)



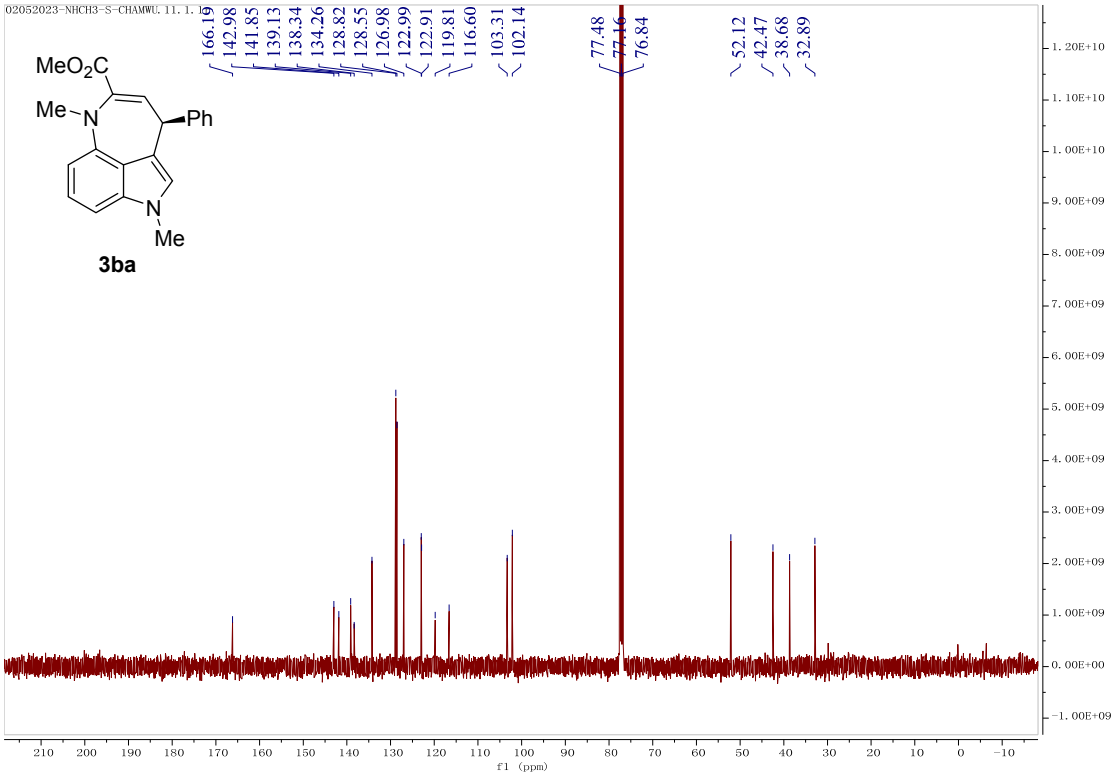
^{13}C{^{1}H} NMR Spectrum of 4ap (150 MHz, $CDCl_3$)



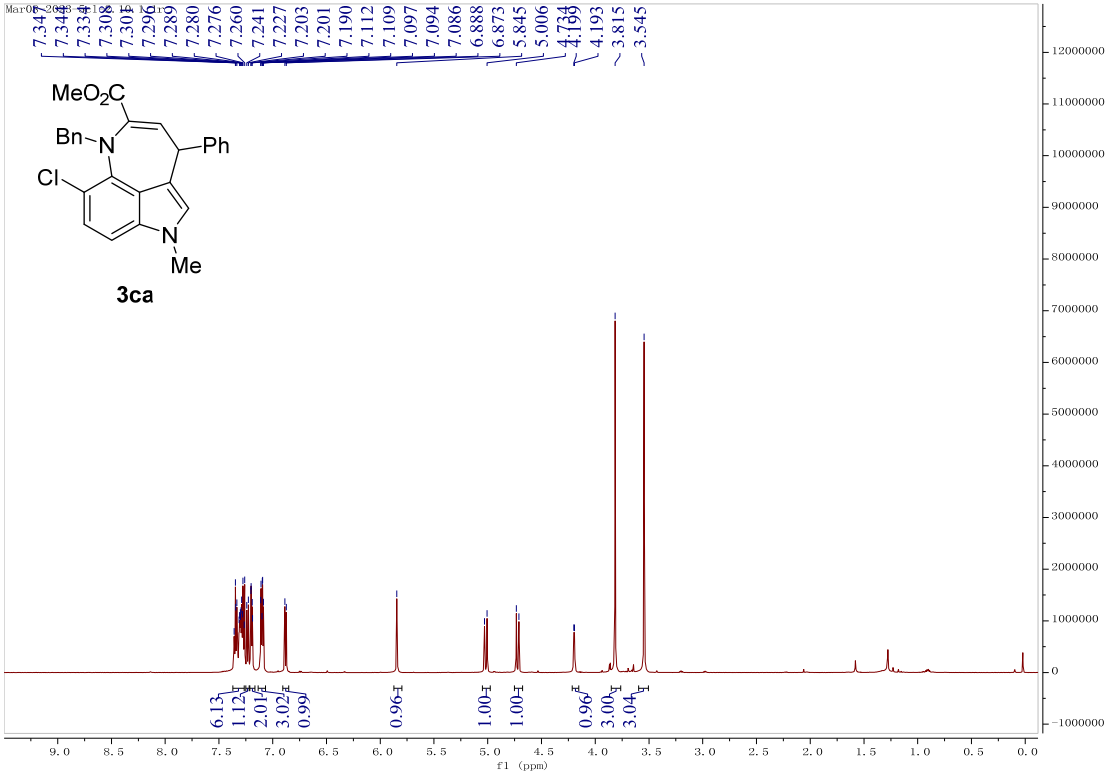
^{1}H NMR Spectrum of 3ba (400 MHz, $CDCl_3$)



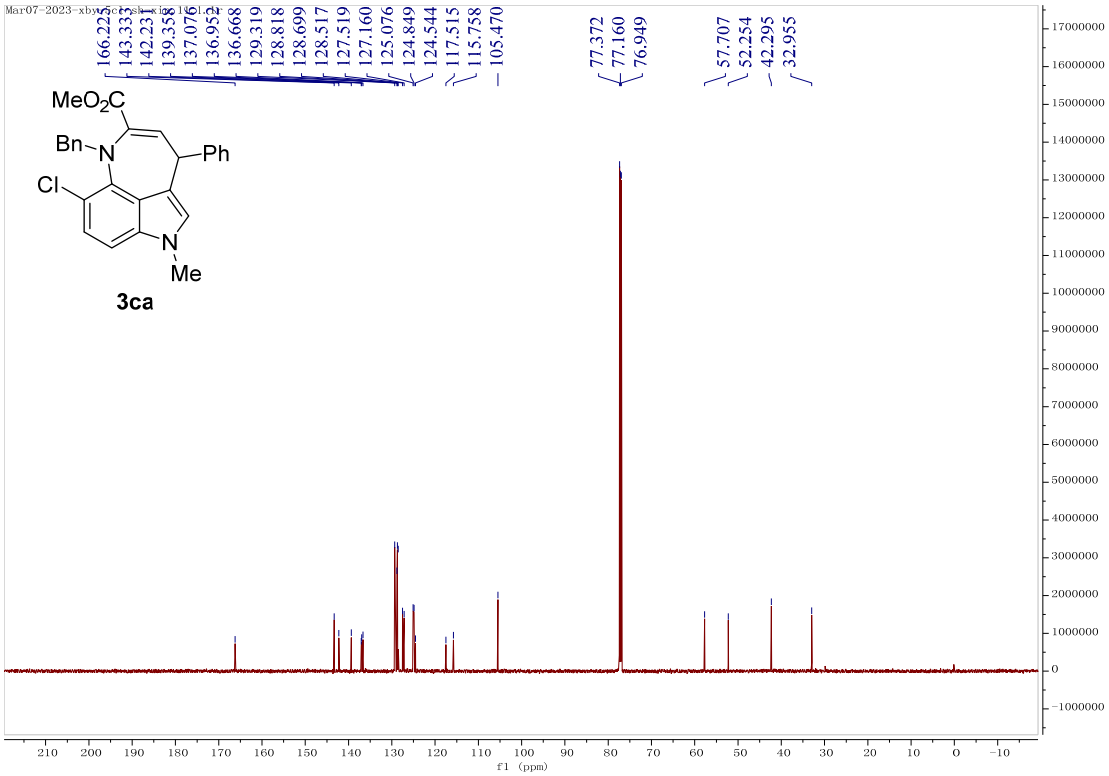
^{13}C{^{1}H} NMR Spectrum of 3ba (100 MHz, $CDCl_3$)



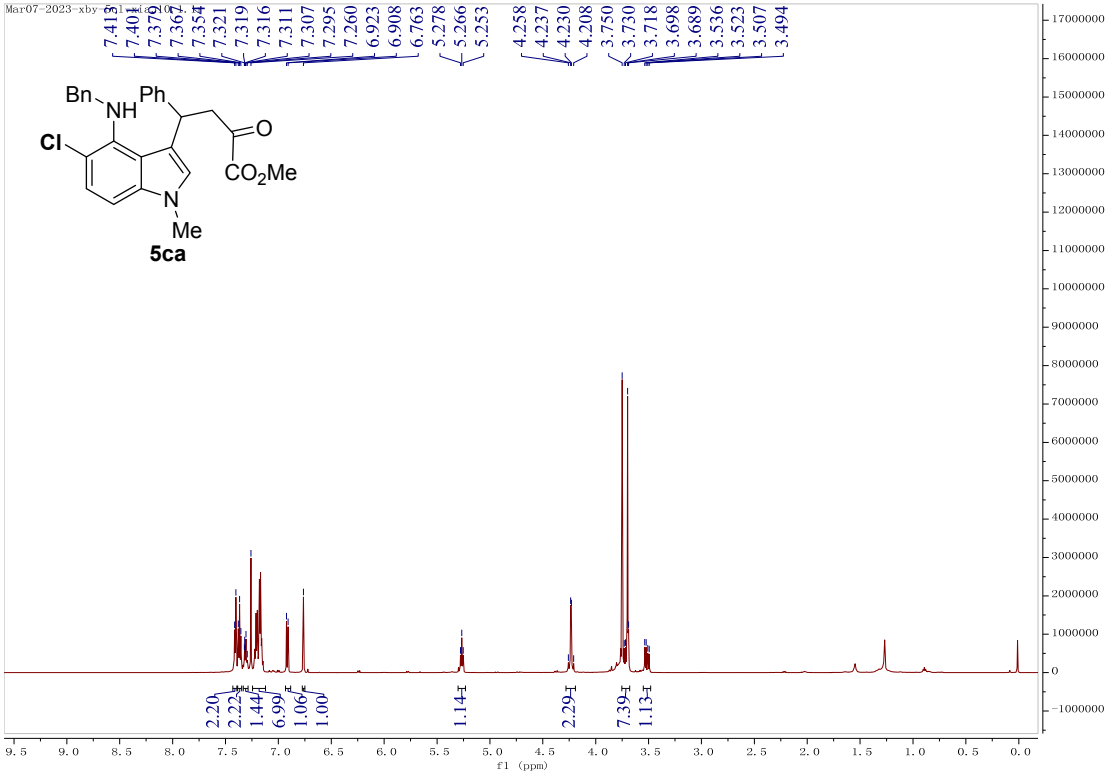
^{1}H NMR Spectrum of 3ca (600 MHz, $CDCl_3$)



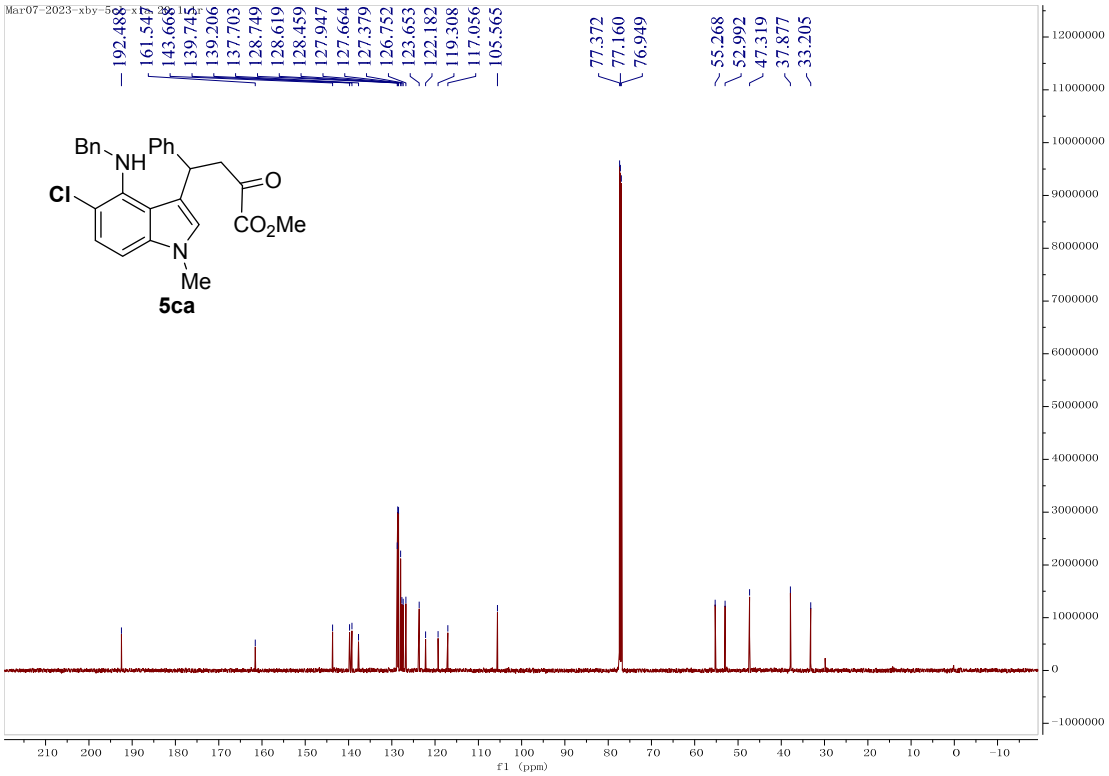
^{13}C{^{1}H} NMR Spectrum of 3ca (150 MHz, $CDCl_3$)



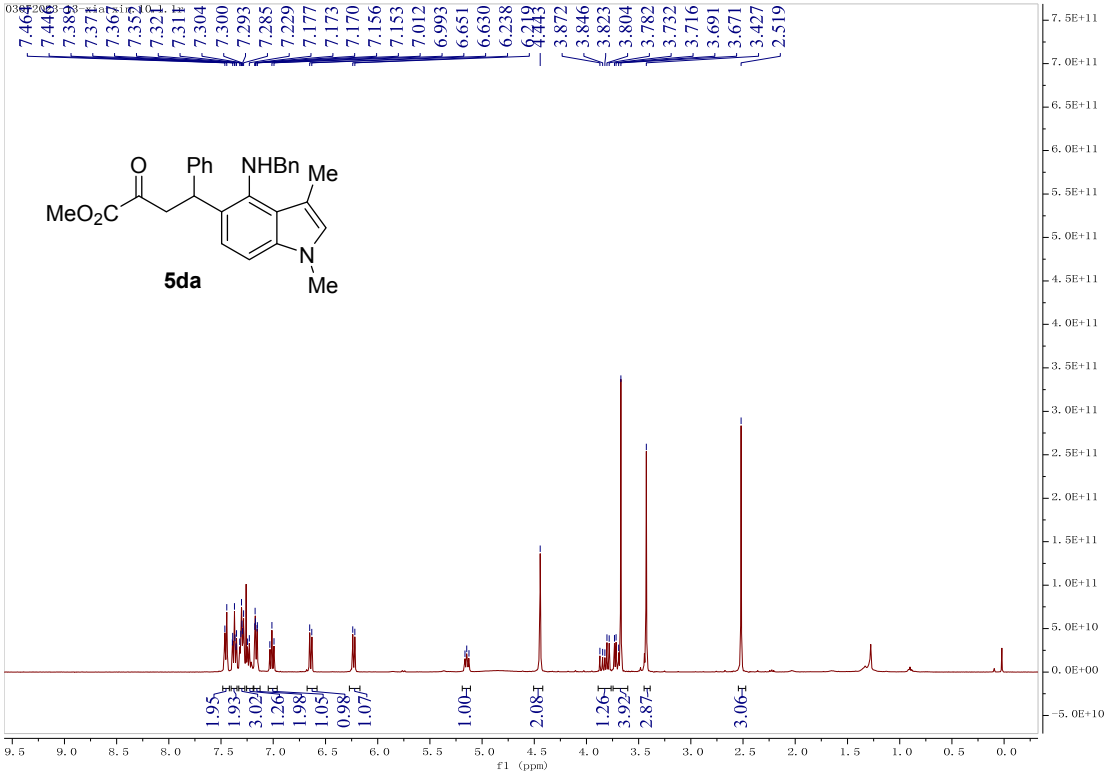
^{1}H NMR Spectrum of 5ca (600 MHz, $CDCl_3$)



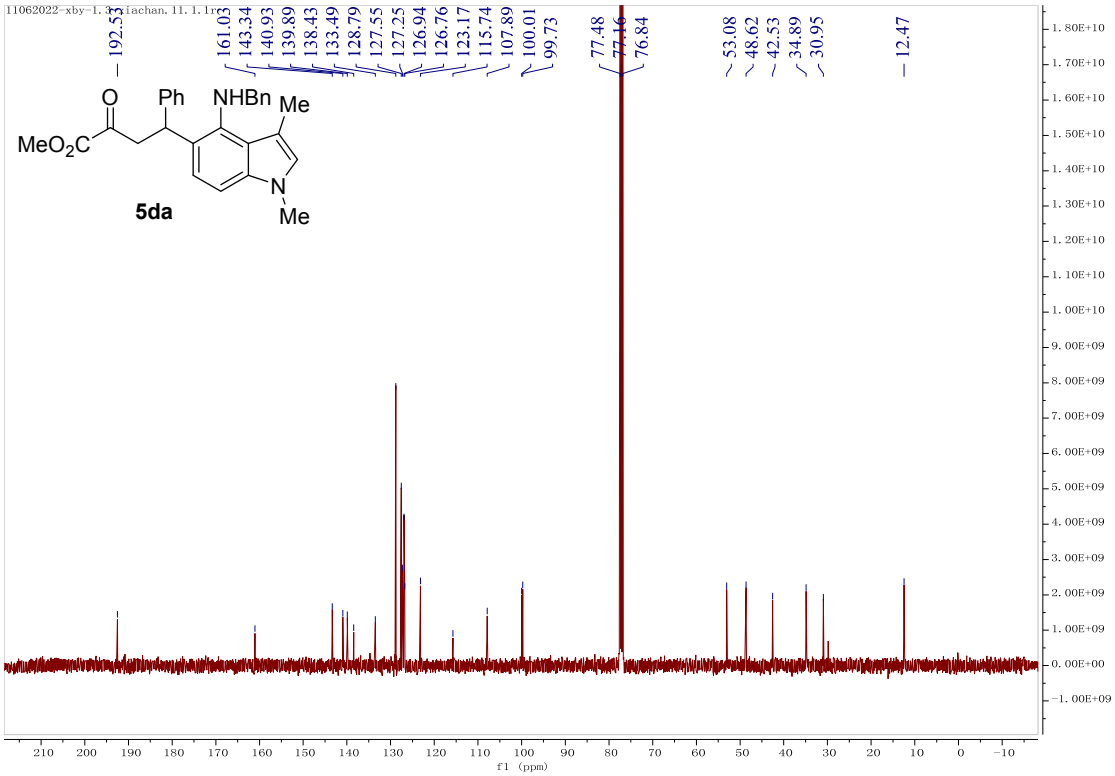
^{13}C{^{1}H} NMR Spectrum of 5ca (150 MHz, $CDCl_3$)



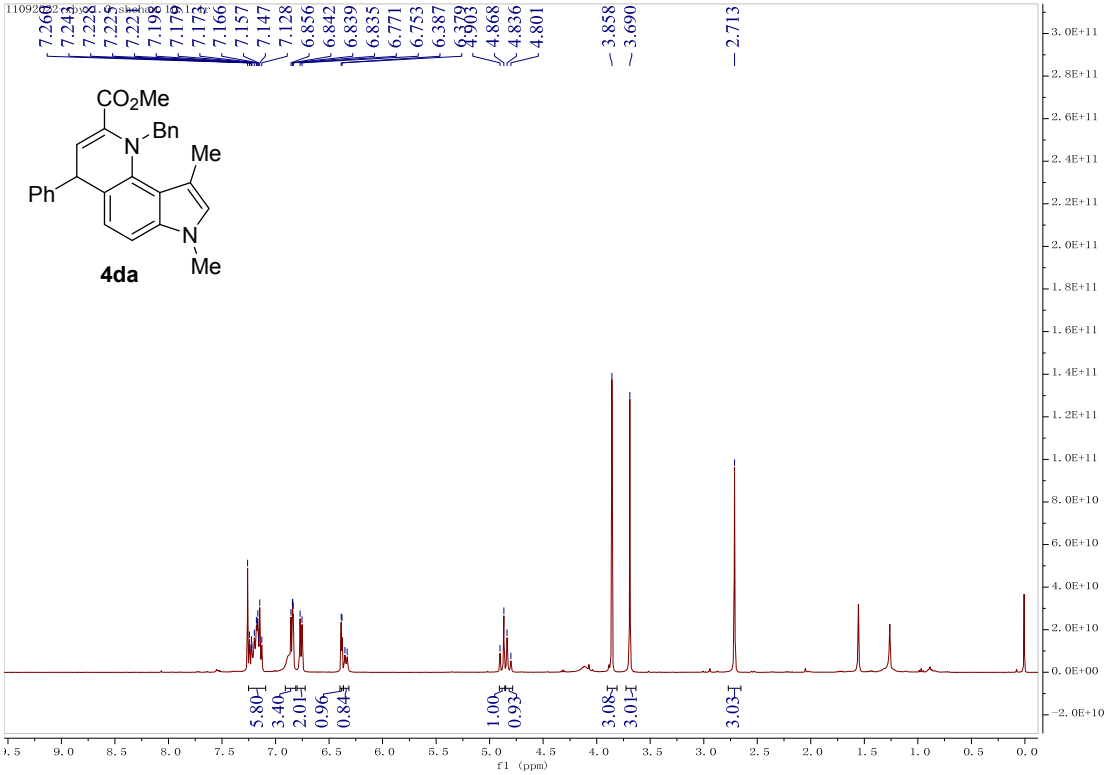
^{1}H NMR Spectrum of 5da (400 MHz, $CDCl_3$)



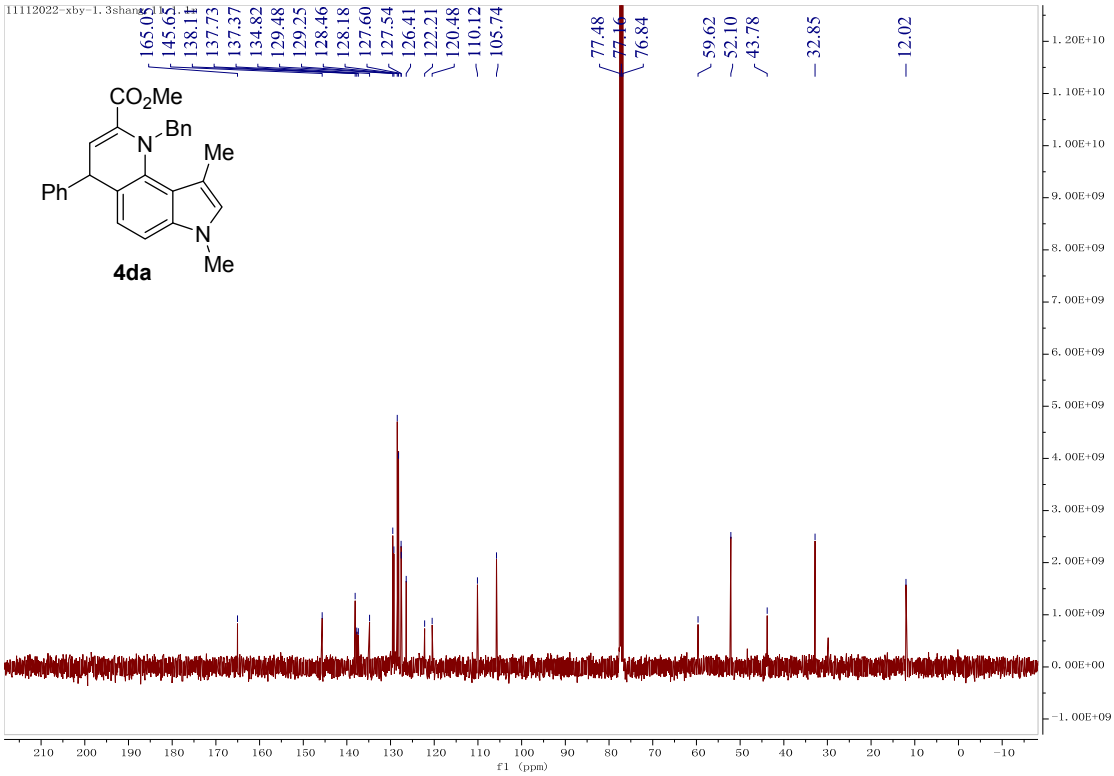
^{13}C{^{1}H}NMR Spectrum of 5da (100 MHz, $CDCl_3$)



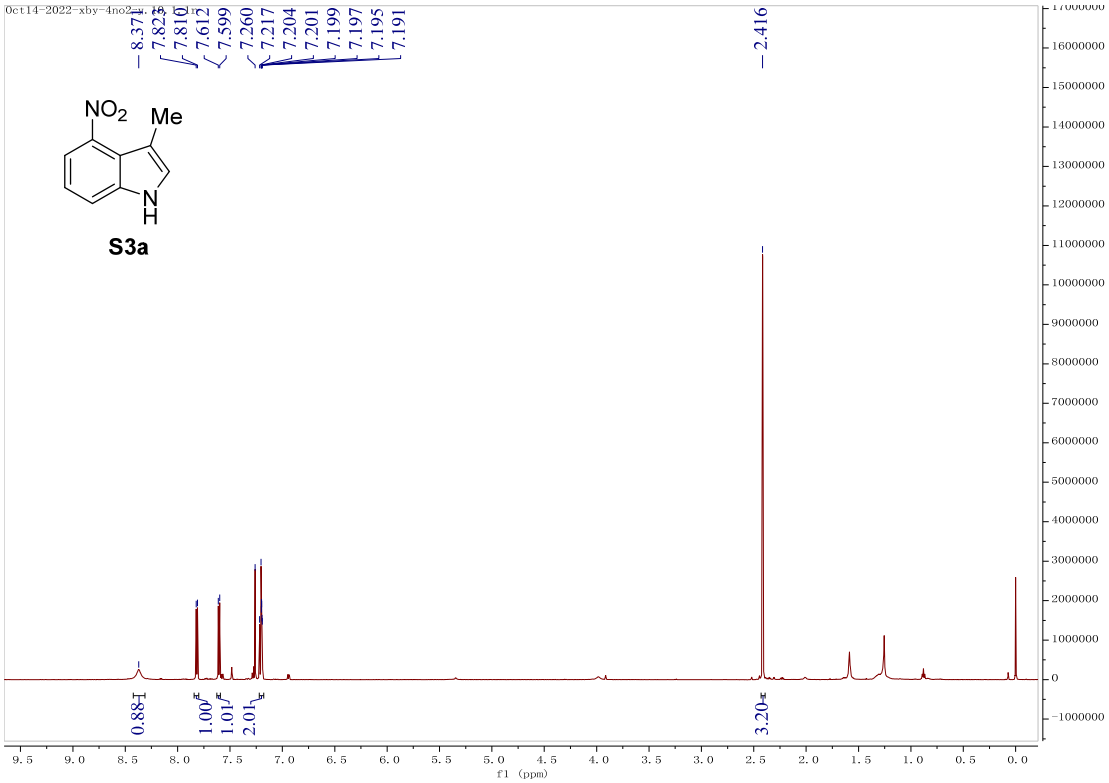
^{1}H NMR Spectrum of 4da (400 MHz, $CDCl_3$)



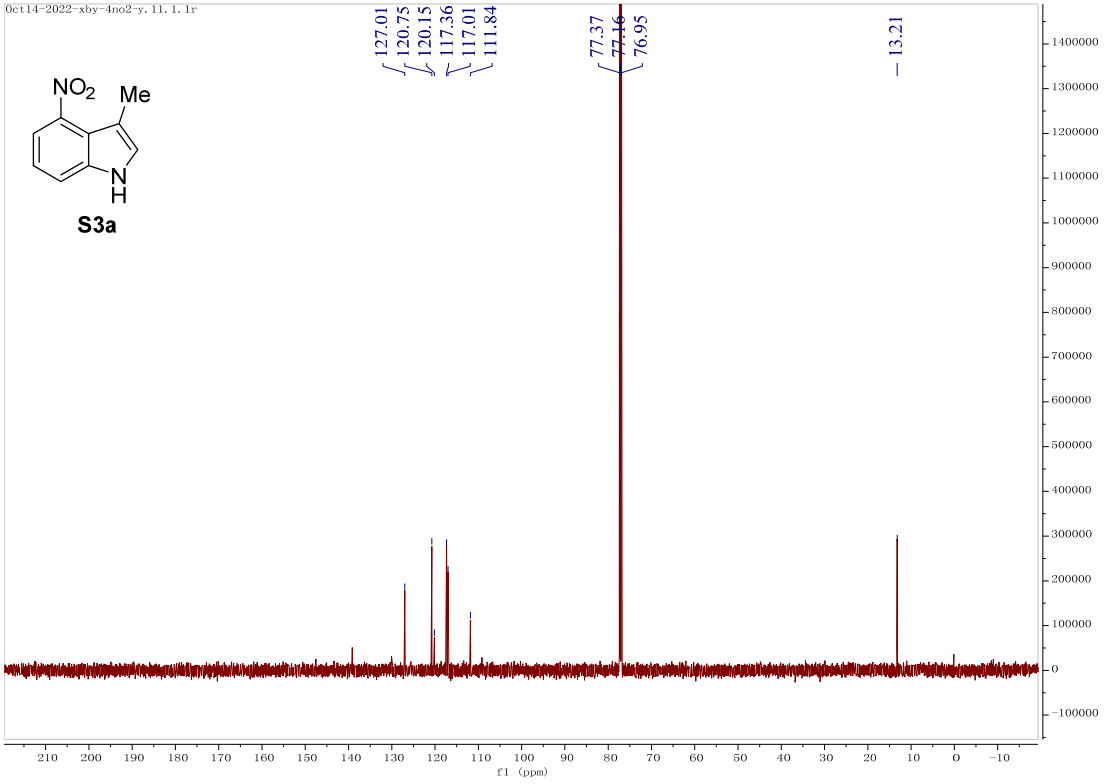
^{13}C{^{1}H} NMR Spectrum of 4da (100 MHz, $CDCl_3$)



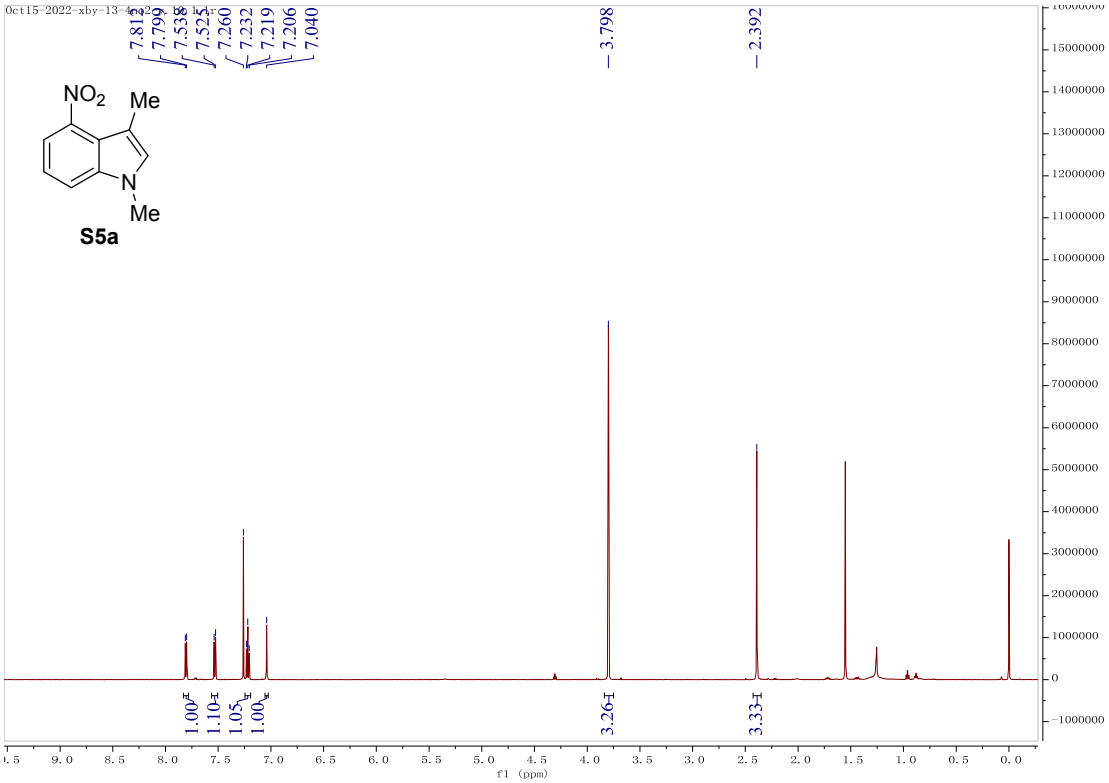
^{1}H NMR Spectrum of S3a(600 MHz, $CDCl_3$)



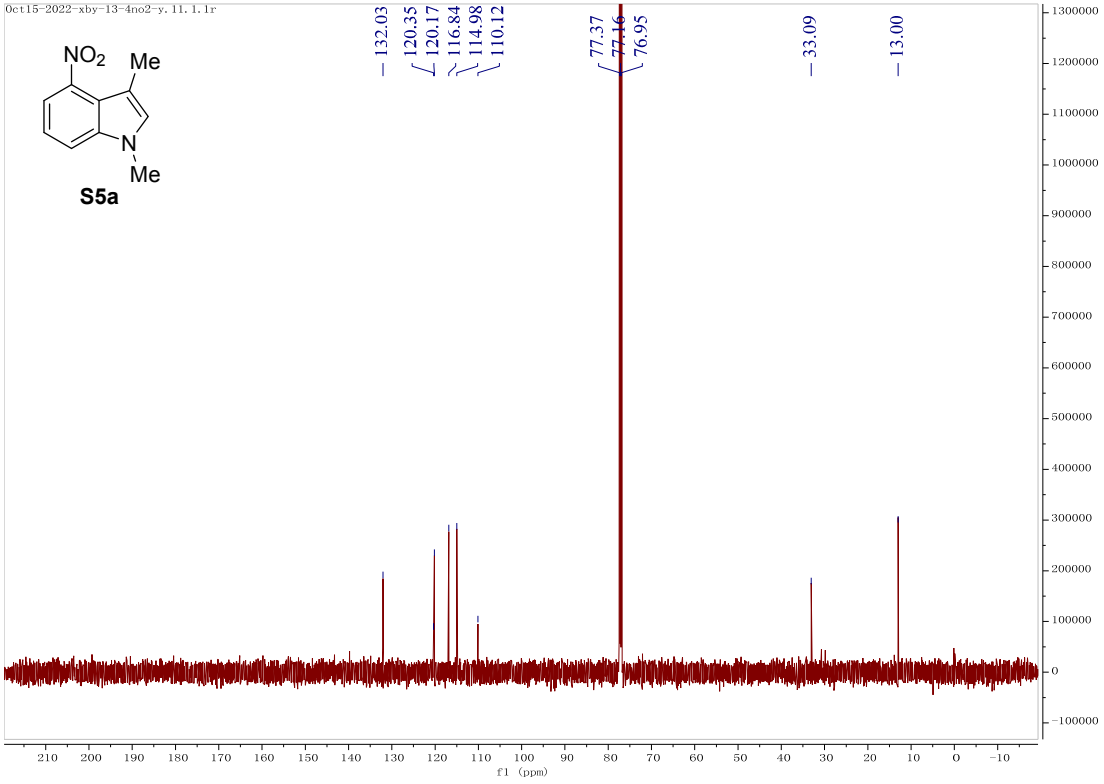
^{13}C{^{1}H} NMR Spectrum of S3a (150 MHz, $CDCl_3$)



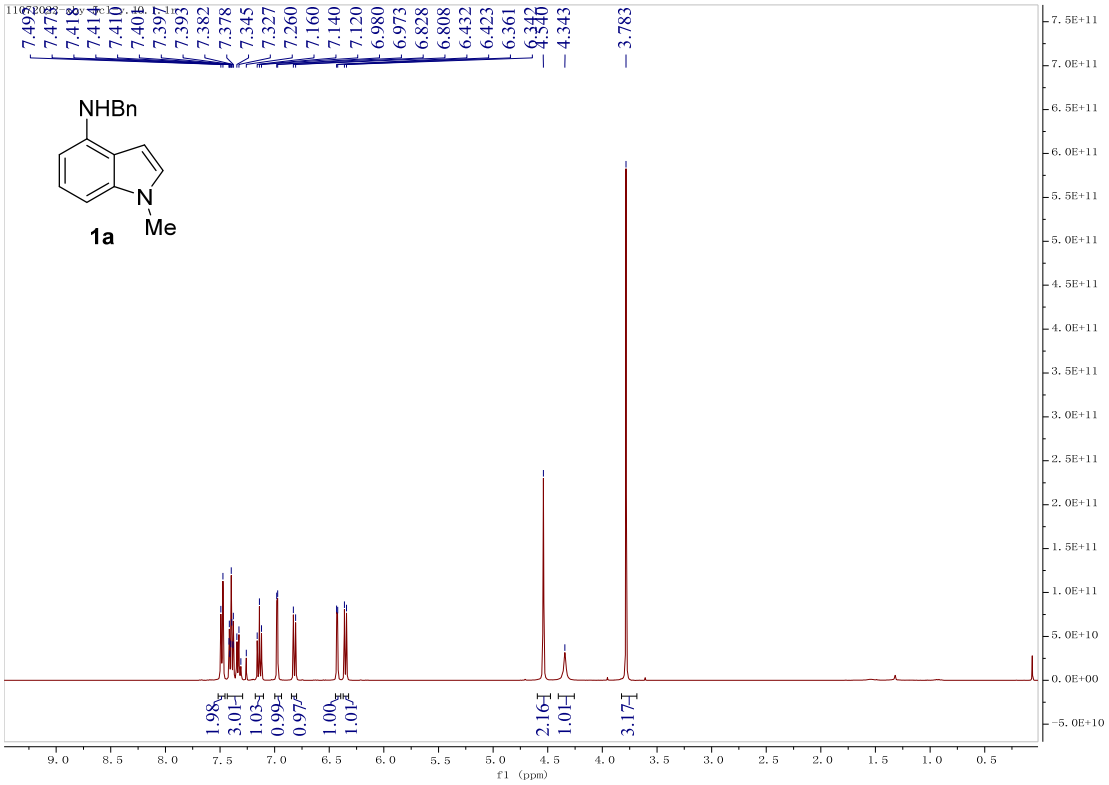
^{1}H NMR Spectrum of S5a (600 MHz, $CDCl_3$)



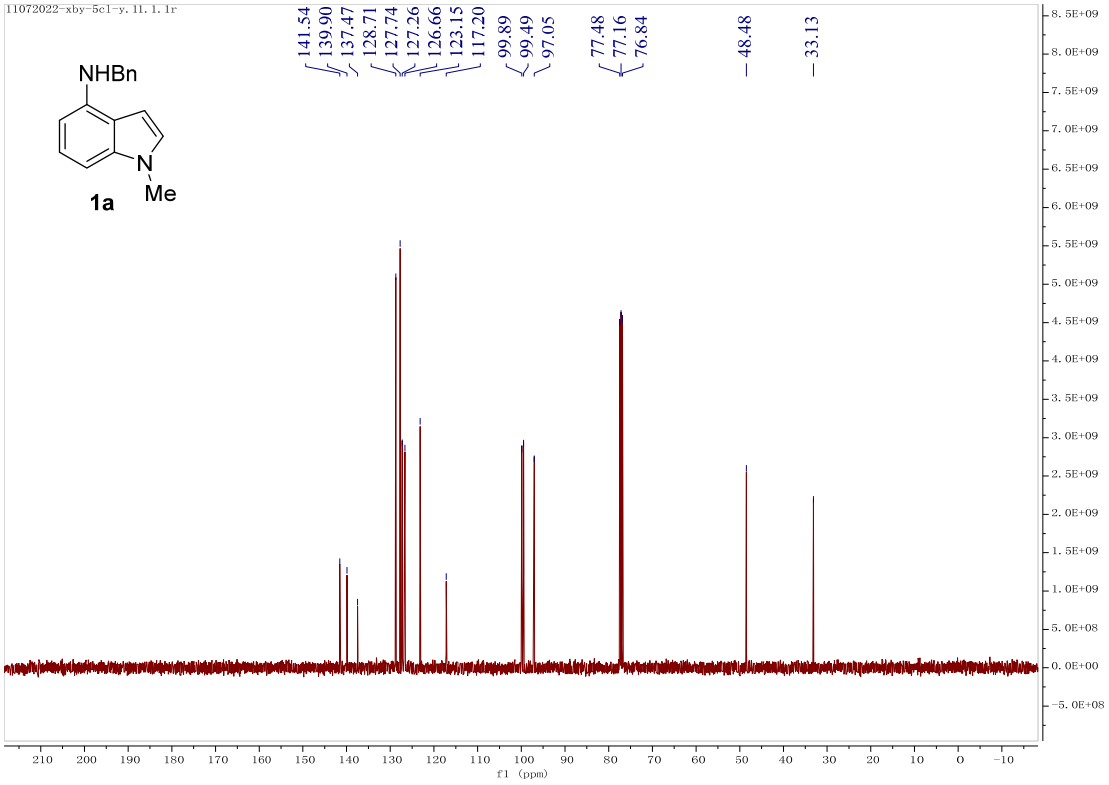
^{13}C{^{1}H} NMR Spectrum of S5a (150 MHz, $CDCl_3$)



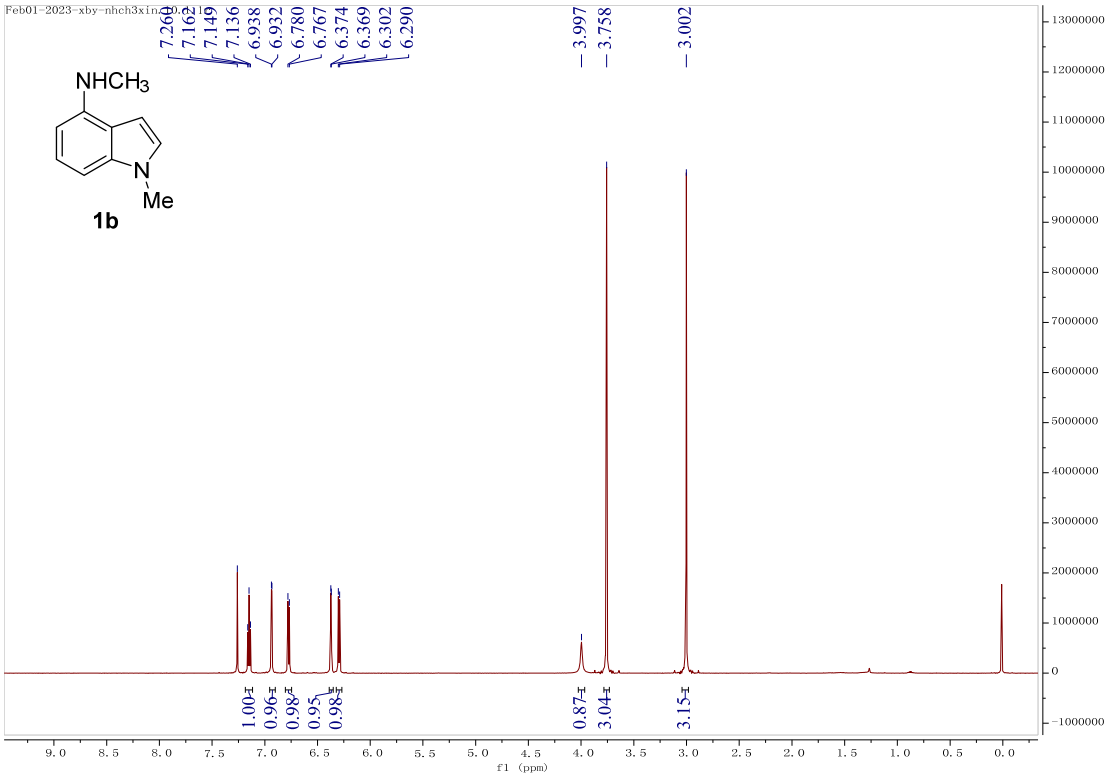
^{1}H NMR Spectrum of 1a (400 MHz, $CDCl_3$)



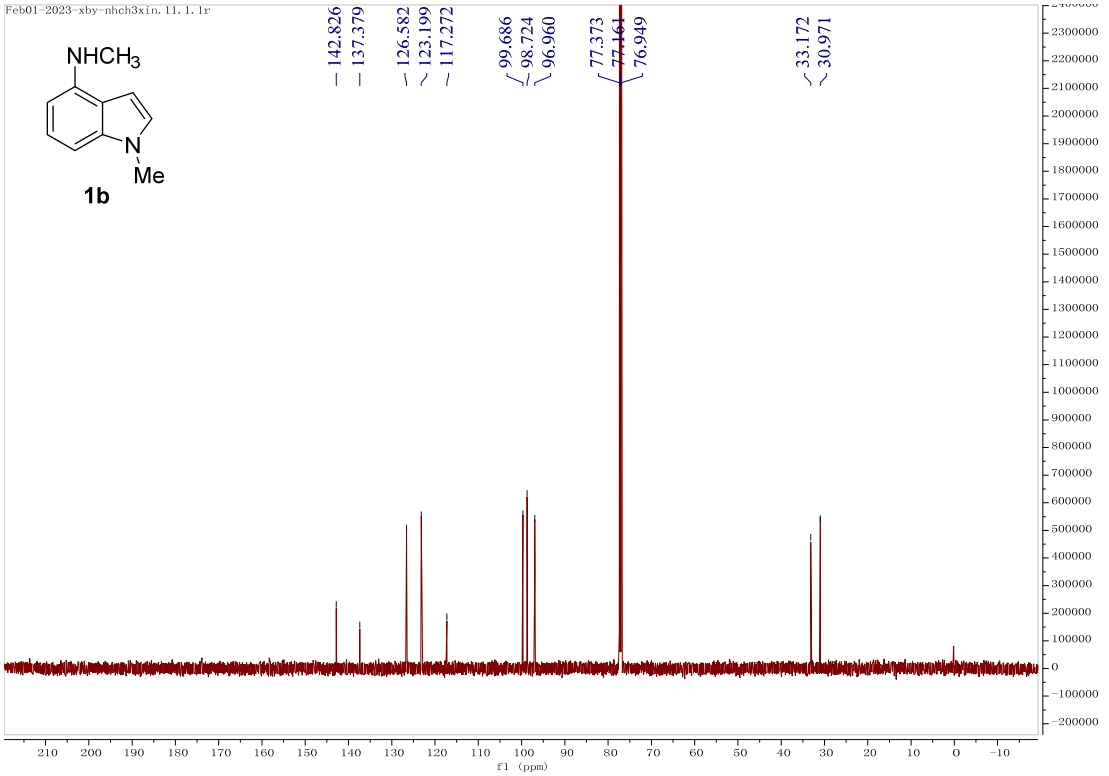
^{13}C{^{1}H} NMR Spectrum of 1a (100 MHz, $CDCl_3$)



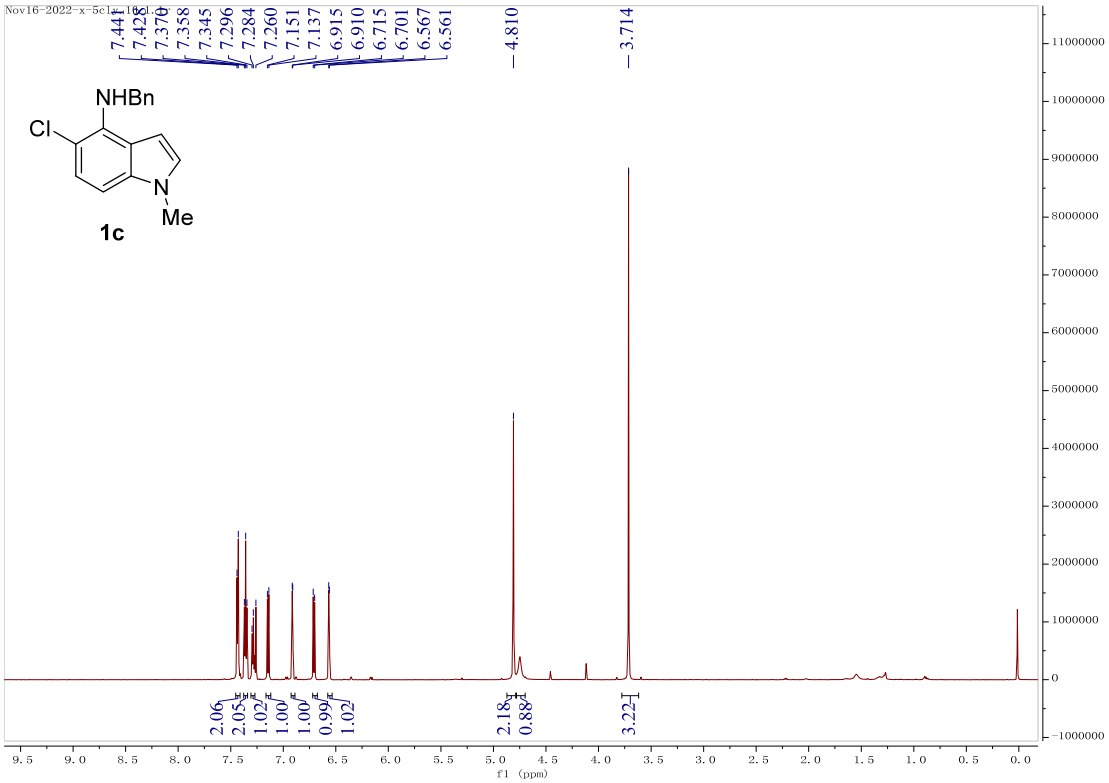
^{1}H NMR Spectrum of 1b (600 MHz, $CDCl_3$)



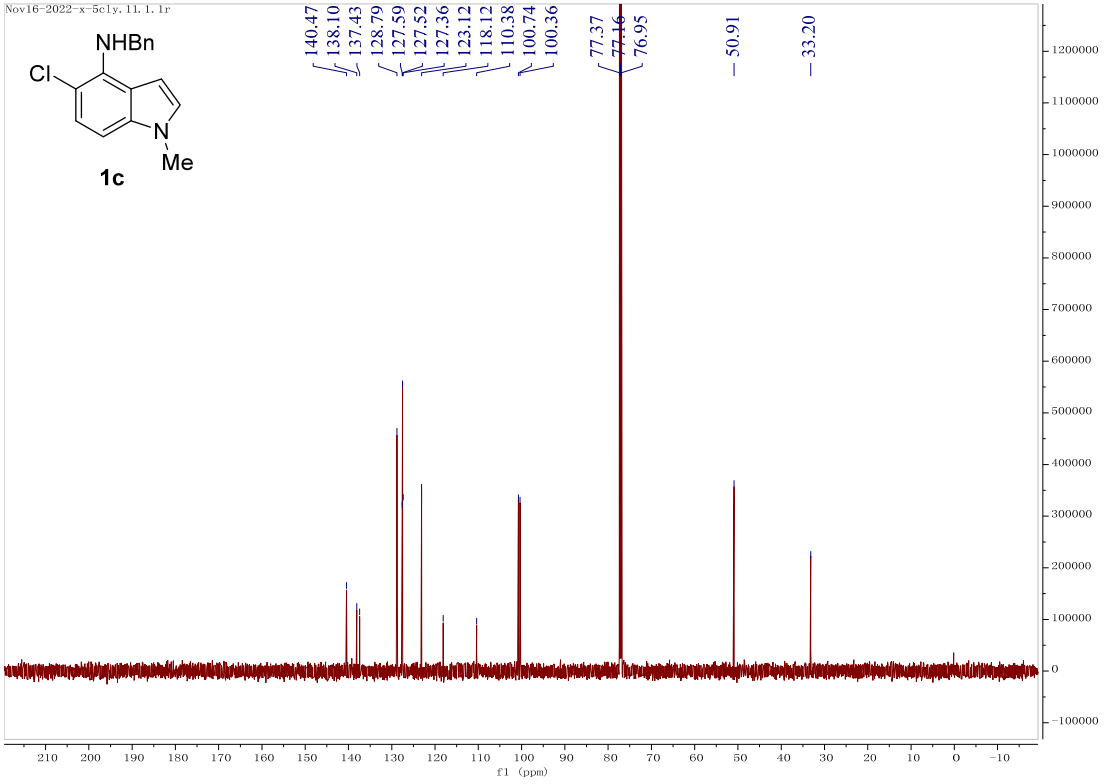
^{13}C{^{1}H} NMR Spectrum of 1b (150 MHz, $CDCl_3$)



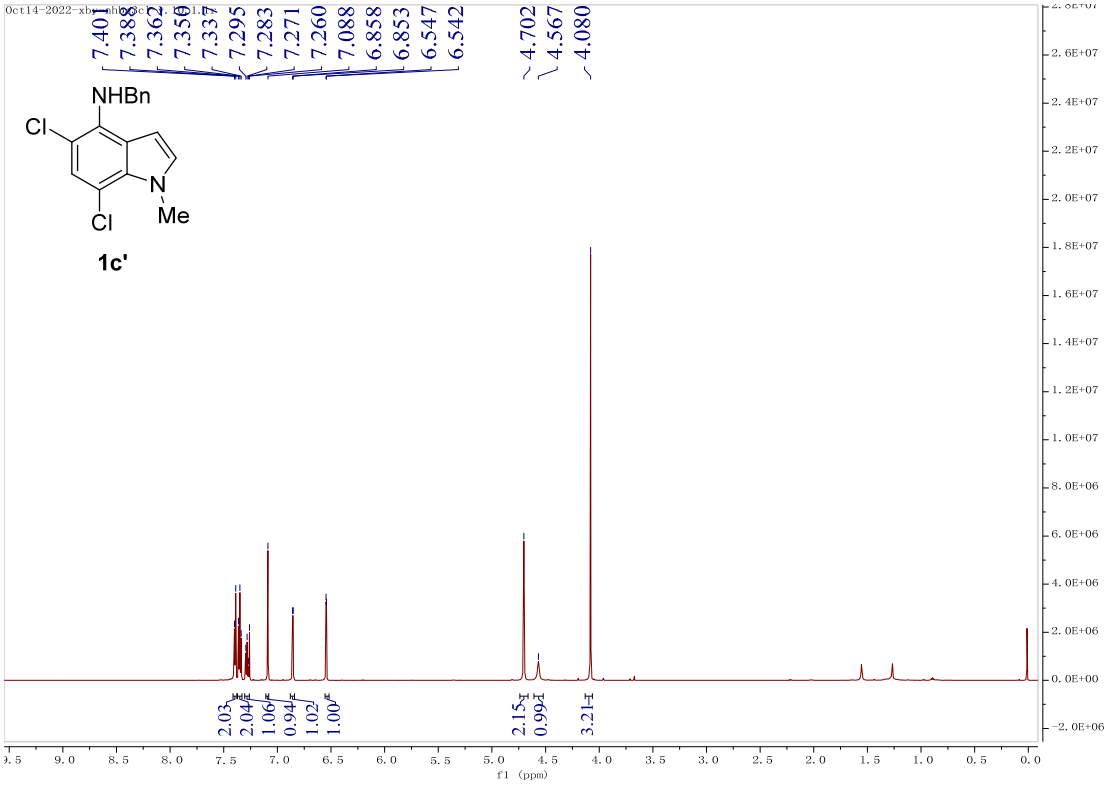
^{1}H NMR Spectrum of 1c (600 MHz, $CDCl_3$)



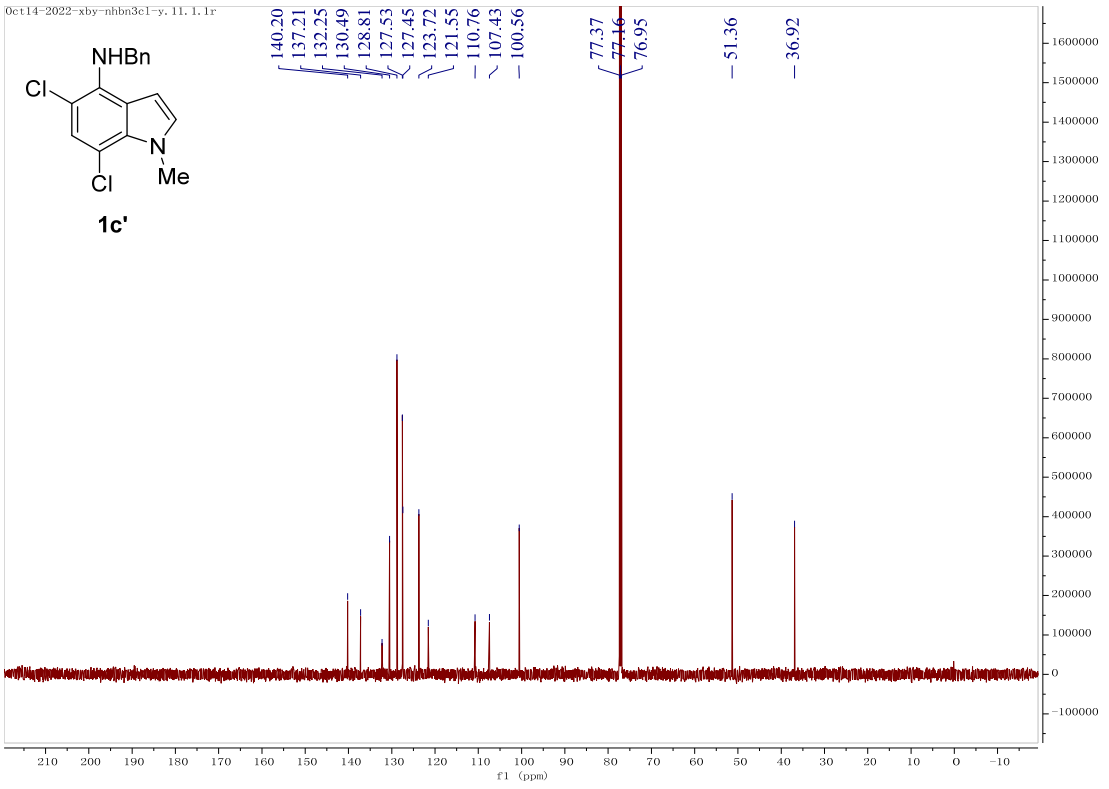
^{13}C{^{1}H} NMR Spectrum of 1c (150 MHz, $CDCl_3$)



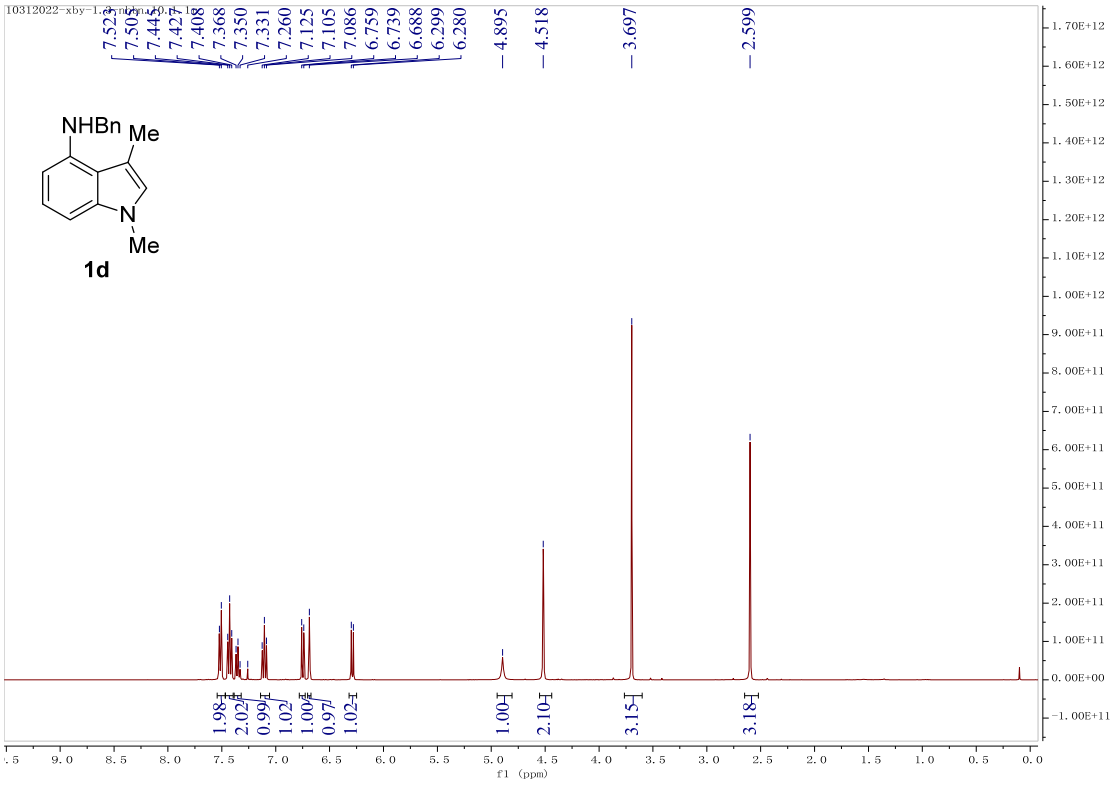
^{1}H NMR Spectrum of 1c' (600 MHz, $CDCl_3$)



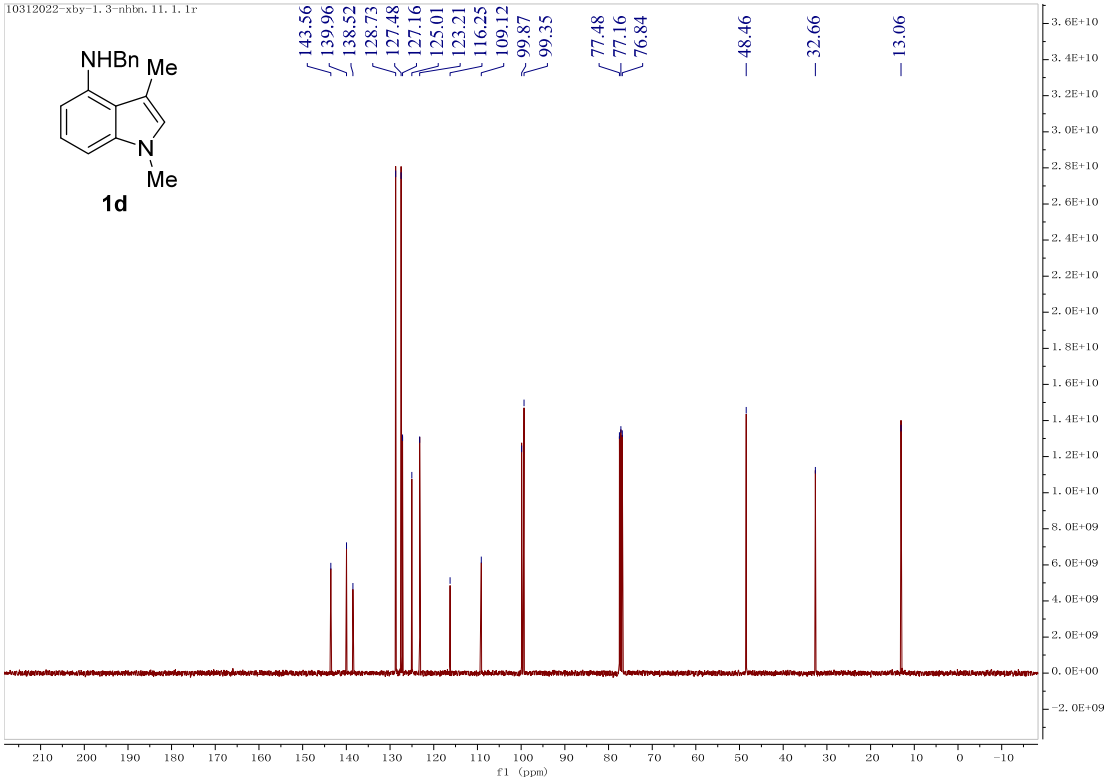
^{13}C{^{1}H} NMR Spectrum of 1c' (150 MHz, $CDCl_3$)



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



^{13}C{^{1}H} NMR Spectrum of 1d (100 MHz, $CDCl_3$)



Reference

[1] L. Cai, Y. Zhao, T. Huang, S. Meng, X. Jia, A. S. C. Chan and J. Zhao, *Org. Lett.*, 2019, **21**, 3538.