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Supporting Information for

Ir-Catalyzed Intermolecular Asymmetric Allylic Dearomatization Reaction of Indoles

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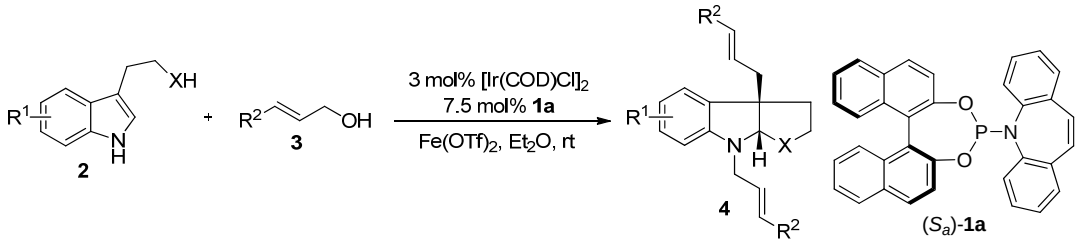
General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were freshly distilled according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on Varian instrument (282 MHz and 376 MHz, respectively) and referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

General procedure for iridium-catalyzed intermolecular asymmetric allylic dearomatization reaction of indoles:



A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $[Ir(COD)Cl]_2$ (4.0 mg, 0.006 mmol, 3 mol%), (S_a)-**1a** (7.6 mg, 0.015 mmol, 7.5 mol%), indole derivative **2** (0.20 mmol, 100 mol%), allylic alcohol (0.60 mmol, 300 mol%), $Fe(OTf)_2$ (70.8 mg, 0.20 mmol, 100 mol%), ether (2 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the mixture was quenched with water, and extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was

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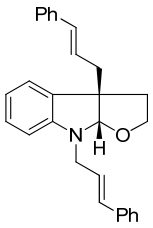
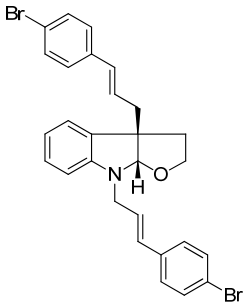
purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product **4**. The characterization data of the products are summarized below.



4aa[1]. Yellow oil, 97% yield, 94% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, v = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 11.42 min, t (minor) = 14.76 min]; $[\alpha]_D^{19}$ = +107.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12-2.25 (m, 2H), 2.62 (dd, J = 8.4, 13.8 Hz, 1H), 2.79 (dd, J = 6.0, 13.8 Hz, 1H), 3.48-3.57 (m, 1H), 3.96-4.01 (m, 1H), 4.07 (d, J = 5.4 Hz, 2H), 5.36 (s, 1H), 6.03-6.21 (m, 2H), 6.42-6.57 (m, 3H), 6.69 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 6.9 Hz, 2H), 7.21-7.27 (m, 10H).



4ab. Yellow oil, 92% yield, 95% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, v = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 18.93 min, t (minor) = 39.01 min]; $[\alpha]_D^{20}$ = +97.4 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15-2.19 (m, 2H), 2.58 (dd, J = 9.0, 13.8 Hz, 1H), 2.80 (dd, J = 5.1, 13.8 Hz, 1H), 3.48-3.56 (m, 1H), 3.95-4.05 (m, 3H), 5.33 (s, 1H), 5.96-6.15 (m, 2H), 6.33-6.45 (m, 3H), 6.70 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 7.06-7.12 (m, 4H), 7.32-7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 41.8, 46.3, 56.4, 66.9, 100.9, 105.3, 117.5, 120.9, 121.0, 123.2, 126.5, 126.9, 127.6, 127.7, 128.3, 130.3, 131.5, 131.6,

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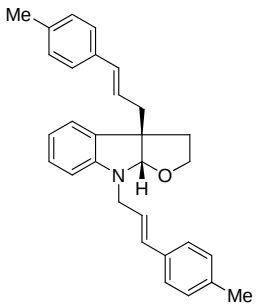
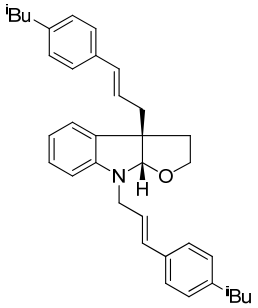
131.7, 132.0, 135.6, 136.0, 150.1. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1261, 1091, 1019, 865, 799, 689, 664; HRMS (ESI) calcd for $C_{28}H_{26}Br_2NO$ $[M+H]^+$: 550.0376. Found: 550.0356.



4ac. Yellow oil, 77% yield, 94% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.20 min, t (minor) = 16.05 min]; $[\alpha]_D^{21}$ = +109.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09-2.20 (m, 2H), 2.30 (s, 3H), 2.32 (s, 3H), 2.59 (dd, J = 9.0, 13.8 Hz, 1H), 2.75 (dd, J = 6.0, 13.8 Hz, 1H), 3.47-3.56 (m, 1H), 3.97 (t, J = 7.2 Hz, 1H), 4.05 (d, J = 5.7 Hz, 2H), 5.35 (s, 1H), 5.97-6.15 (m, 2H), 6.37-6.53 (m, 3H), 6.67 (t, J = 7.5 Hz, 1H), 7.01-7.17 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 40.0, 41.8, 46.6, 56.4, 66.9, 101.2, 105.4, 117.3, 123.3, 124.7, 124.9, 126.0, 126.2, 128.2, 129.1, 129.2, 131.5, 132.5, 132.8, 134.0, 134.5, 136.8, 137.0, 150.2. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1260, 1088, 1018, 865, 797, 702, 664; HRMS (ESI) calcd for $C_{30}H_{32}NO$ $[M+H]^+$: 422.2484. Found: 422.2470.



4ad. Yellow oil, 93% yield, 91% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, v = 1.0 mL·min^{-1}, λ = 220 nm, t (major) = 7.11 min, t (minor) = 9.20 min]; $[\alpha]_D^{23}$ = +68.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ

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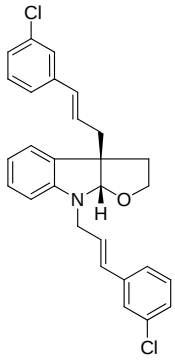
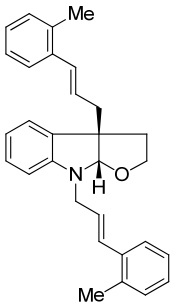
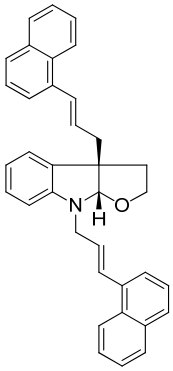
0.88-0.90 (m, 12H), 1.78-1.89 (m, 2H), 2.11-2.23 (m, 2H), 2.42-2.45 (m, 4H), 2.61 (dd, *J* = 8.4, 14.0 Hz, 1H), 2.73-2.78 (m, 1H), 3.49-3.55 (m, 1H), 3.95-3.99 (m, 1H), 4.06 (d, *J* = 7.2 Hz, 2H), 5.36 (s, 1H), 6.02-6.18 (m, 2H), 6.40-6.45 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.66-6.70 (m, 1H), 7.00-7.10 (m, 6H), 7.15-7.20 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.34, 22.36, 30.2, 40.0, 41.8, 45.1, 46.6, 56.4, 66.9, 101.2, 105.4, 117.3, 123.3, 124.8, 124.9, 125.9, 126.1, 128.2, 129.2, 129.3, 131.6, 132.6, 132.9, 134.3, 134.8, 140.8, 140.9, 150.2. IR (thin film): ν_{max} (cm^{-1}) = 3048, 2961, 2921, 2867, 1606, 1510, 1490, 1463, 1260, 1158, 1017, 966, 943, 798, 740, 687; HRMS (ESI) calcd for $C_{36}H_{44}NO$ $[M+H]^+$: 506.3417. Found: 506.3407.



4ae. Yellow oil, 94% yield, 95% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 13.30 min, t (minor) = 23.91 min]; $[\alpha]_D^{19}$ = +67.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16-2.20 (m, 2H), 2.62 (dd, *J* = 8.8, 14.0 Hz, 1H), 2.78 (dd, *J* = 6.4, 14.0 Hz, 1H), 3.49-3.55 (m, 1H), 3.97-4.01 (m, 1H), 4.05-4.07 (m, 2H), 5.32 (s, 1H), 6.04-6.11 (m, 1H), 6.15-6.22 (m, 1H), 6.34-6.48 (m, 3H), 6.71 (t, *J* = 7.6 Hz, 1H), 7.02-7.05 (m, 1H), 7.08-7.16 (m, 7H), 7.227-7.230 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 41.6, 46.4, 56.4, 67.0, 101.1, 105.4, 117.6, 123.3, 124.2, 124.4, 126.0, 126.2, 127.18, 127.24, 127.4, 127.5, 128.4, 129.6, 129.7, 130.2, 131.8, 132.1, 134.3, 134.4, 138.6, 139.0, 150.1. IR (thin film): ν_{max} (cm^{-1}) = 3025, 2965, 2922, 2867, 1681, 1593, 1564, 1488, 1425, 1358, 1261, 1077, 1042, 1011, 961, 875, 773, 740, 683, 635; HRMS (ESI) calcd for $C_{28}H_{26}Cl_2NO$ $[M+H]^+$: 462.1386. Found: 462.1374.



4af. Yellow oil, 71% yield, 93% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.95 min, t (minor) = 10.85 min]; $[\alpha]_D^{18}$ = +109.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13-2.20 (m, 2H), 2.22 (s, 3H), 2.25 (s, 3H), 2.64 (dd, *J* = 8.4, 14.0 Hz, 1H), 2.76-2.82 (m, 1H), 3.51-3.57 (m, 1H), 3.97-4.01 (m, 1H), 4.08-4.10 (m, 2H), 5.39 (s, 1H), 5.90-5.98 (m, 1H), 6.01-6.08 (m, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 7.03-7.10 (m, 8H), 7.25-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 40.1, 42.1, 47.0, 56.4, 66.9, 101.4, 105.4, 117.3, 123.4, 125.67, 125.7, 126.0, 127.06, 127.1, 127.2, 127.3, 128.2, 129.8, 130.06, 130.09, 131.2, 132.4, 135.0, 135.2, 136.0, 136.5, 150.1. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1412, 1261, 1092, 1020, 866, 799, 702, 689, 667; HRMS (ESI) calcd for $C_{30}H_{32}NO$ $[M+H]^+$: 422.2478. Found: 422.2469.



4ag. Yellow oil, 86% yield, 89% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 19.80 min, t (minor) = 30.59 min]; $[\alpha]_D^{17}$ = +81.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18-2.30 (m, 2H), 2.72-2.77 (m, 1H), 2.88-2.94 (m, 1H), 3.56-3.63 (m, 1H), 4.01-4.05 (m, 1H), 4.18-4.19 (m, 2H), 5.51 (s, 1H), 6.04-6.11 (m, 1H), 6.14-6.21 (m,

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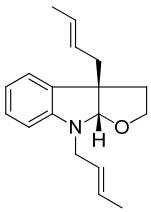
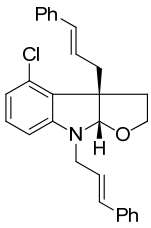
1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.71-6.75 (m, 1H), 7.08-7.16 (m, 3H), 7.19-7.27 (m, 3H), 7.31-7.44 (m, 6H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.75-7.79 (m, 2H), 7.88-7.90 (m, 1H), 7.96-7.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 42.2, 47.0, 56.6, 66.9, 101.5, 105.5, 117.5, 123.5, 123.7, 123.9, 125.46, 125.50, 125.6, 125.8, 125.9, 127.5, 127.6, 128.31, 128.33, 128.9, 129.1, 129.3, 130.6, 130.96, 131.0, 132.4, 133.41, 133.44, 134.6, 135.1, 150.3. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1412, 1261, 1091, 1019, 865, 798, 702, 663; HRMS (ESI) calcd for $C_{36}H_{32}NO$ $[M+H]^+$: 494.2478. Found: 494.2467.

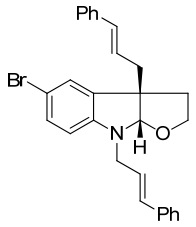


4ah[1]. Yellow oil, 82% yield, 85% ee [Phenomenex Lu X 5u Cellulose-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 50/1, *v* = 0.51 mL · min^{-1}, λ = 254 nm, t (major) = 7.58 min, t (minor) = 8.75 min]; $[\alpha]_D^{20}$ = +102.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (d, *J* = 6.4 Hz, 3H), 1.68 (d, *J* = 8.0 Hz, 3H), 2.02-2.14 (m, 2H), 2.38 (dd, *J* = 8.0, 13.6 Hz, 1H), 2.51 (dd, *J* = 6.0, 13.6 Hz, 1H), 3.43-3.49 (m, 1H), 3.83-3.84 (m, 2H), 3.90-3.95 (m, 1H), 5.23 (s, 1H), 5.26-5.34 (m, 1H), 5.42-5.54 (m, 2H), 5.62-5.70 (m, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 6.63-6.67 (m, 1H), 7.01-7.08 (m, 2H).

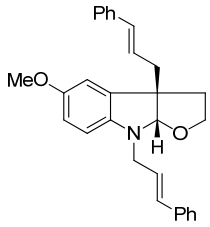


4ba. Yellow oil, 93% yield, 96% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 10.70 min, t (minor) = 12.59 min]; $[\alpha]_D^{23}$ = +70.7 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06-2.14 (m, 1H), 2.58-2.63 (m, 2H), 3.28-3.33 (m, 1H), 3.51-3.57 (m, 1H), 3.97-4.06 (m, 3H), 5.40 (s, 1H), 5.86-5.94 (m, 1H), 6.04-6.10 (m, 1H), 6.27 (d, *J* =

8.0 Hz, 1H), 6.44 (d, *J* = 13.6 Hz, 1H), 6.48 (d, *J* = 10.5 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 7.09-7.12 (m, 2H), 7.16-7.23 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8, 39.2, 46.4, 57.4, 66.9, 100.7, 103.7, 118.2, 125.0, 126.0, 126.1, 126.3, 127.1, 127.31, 127.34, 128.4, 128.5, 129.8, 130.2, 131.8, 132.8, 136.5, 137.2, 152.0. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1598, 1261, 1091, 1019, 965, 867, 799, 733, 692; HRMS (ESI) calcd for $C_{28}H_{27}ClNO$ $[M+H]^+$: 428.1776. Found: 428.1765.

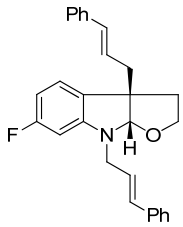


4ca. Yellow oil, 83% yield, 94% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 15.00 min, t (minor) = 19.06 min]; $[\alpha]_D^{23}$ = +27.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09-2.21 (m, 2H), 2.59 (dd, *J* = 8.8, 13.6 Hz, 1H), 2.78 (dd, *J* = 6.0, 14.0 Hz, 1H), 3.48-3.54 (m, 1H), 3.96-4.08 (m, 3H), 5.35 (s, 1H), 5.97-6.14 (m, 2H), 6.28 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 7.15-7.26 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 41.5, 46.5, 56.5, 66.9, 101.0, 106.7, 108.8, 125.1, 125.3, 126.1, 126.2, 126.28, 126.29, 127.4, 128.4, 128.5, 130.9, 131.9, 133.4, 134.8, 136.5, 137.0, 149.3. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1412, 1260, 1090, 1019, 865, 798, 702, 664; HRMS (ESI) calcd for $C_{28}H_{27}BrNO$ $[M+H]^+$: 472.1271. Found: 472.1258.

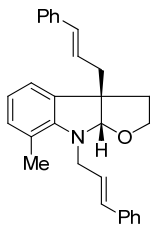


4da. Yellow oil, 93% yield, 95% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 28.16 min, t (minor) = 36.10 min]; $[\alpha]_D^{18}$ = +58.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ

2.12-2.23 (m, 2H), 2.61 (dd, *J* = 8.4, 13.6 Hz, 1H), 2.77 (dd, *J* = 6.4, 14.8 Hz, 1H), 3.51-3.57 (m, 1H), 3.73 (s, 3H), 3.96-4.04 (m, 3H), 5.34 (s, 1H), 6.04-6.12 (m, 1H), 6.15-6.22 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.64-6.66 (m, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 7.18-7.27 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 41.6, 47.4, 56.0, 56.6, 67.0, 101.8, 105.8, 111.0, 112.4, 125.9, 126.1, 126.3, 127.2, 127.3, 128.4, 128.5, 128.7, 131.6, 133.1, 134.0, 136.8, 137.2, 144.6, 152.5. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1412, 1260, 1090, 1019, 865, 798, 688; HRMS (ESI) calcd for $C_{29}H_{30}NO_2$ $[M+H]^+$: 424.2271. Found: 424.2262.



4ea. Yellow oil, 91% yield, 91% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 13.46 min, t (minor) = 16.36 min]; $[\alpha]_D^{23}$ = +96.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09-2.21 (m, 2H), 2.59 (dd, *J* = 8.8, 14.0 Hz, 1H), 2.75-2.80 (m, 1H), 3.49-3.56 (m, 1H), 3.97-4.09 (m, 3H), 5.37 (s, 1H), 6.00-6.15 (m, 3H), 6.32-6.36 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.95-6.98 (m, 1H), 7.18-7.27 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 41.9, 46.4, 55.9, 67.0, 93.4 (*J* = 27.0 Hz), 101.6, 103.1 (*J* = 22.9 Hz), 123.7 (*J* = 10.6 Hz), 125.1, 125.7, 126.1, 126.3, 127.3, 127.4, 127.7, 128.5, 128.6, 132.0, 133.2, 136.6, 137.1, 151.7 (*J* = 12.2 Hz), 164.0 (*J* = 241.7 Hz). IR (thin film): ν_{max} (cm^{-1}) = 2963, 1413, 1261, 1091, 1019, 865, 798, 688, 664; HRMS (ESI) calcd for $C_{28}H_{27}FNO$ $[M+H]^+$: 412.2071. Found: 412.2065.



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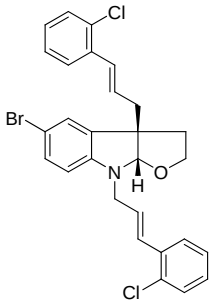
4fa. Yellow oil, 90% yield, 83% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 13.86 min, t (minor) = 14.75 min]; $[\alpha]_D^{23}$ = +88.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08-2.12 (m, 1H), 2.16-2.23 (m, 1H), 2.38 (s, 3H), 2.58-2.64 (m, 1H), 2.72-2.77 (m, 1H), 3.52-3.58 (m, 1H), 3.92-3.96 (m, 1H), 4.14-4.20 (m, 1H), 4.27-4.33 (m, 1H), 5.26 (s, 1H), 6.05-6.12 (m, 1H), 6.19-6.26 (m, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 17.6 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 7.15-7.26 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 40.1, 42.3, 50.3, 56.0, 66.4, 103.0, 118.5, 119.2, 121.3, 126.0, 126.1, 126.3, 127.2, 127.29, 127.32, 128.4, 128.5, 131.4, 131.5, 133.2, 134.1, 136.8, 137.2, 148.5. IR (thin film): ν_{max} (cm^{-1}) = 2963, 2869, 1594, 1494, 1469, 1422, 1358, 1327, 1294, 1260, 1222, 1088, 1019, 964, 866, 798, 739, 692; HRMS (ESI) calcd for $C_{29}H_{30}NO_2$ $[M+H]^+$: 408.2322. Found: 408.2312.



4ci. Yellow oil, 90% yield, 98% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 100/1, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 13.82 min, t (minor) = 27.51 min]; $[\alpha]_D^{22}$ = +21.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10-2.25 (m, 2H), 2.65 (dd, *J* = 9.0, 14.1 Hz, 1H), 2.83 (dd, *J* = 5.7, 13.5 Hz, 1H), 3.50-3.58 (m, 1H), 4.01 (t, *J* = 7.5 Hz, 1H), 4.07 (d, *J* = 5.4 Hz, 2H), 5.39 (s, 1H), 5.91-6.12 (m, 2H), 6.31 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 7.08-7.19 (m, 6H), 7.25-7.30 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 41.6, 46.8, 56.4, 66.9, 101.3, 106.8, 108.9, 126.2, 126.7, 126.8, 128.2, 128.3, 128.4, 129.47, 129.51, 129.9, 131.0, 132.6, 132.8, 134.7, 134.8, 135.2, 149.1. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1261, 1092, 1020, 865, 799, 685; HRMS (ESI) calcd for

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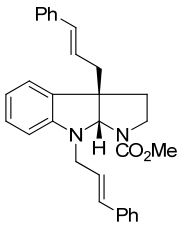
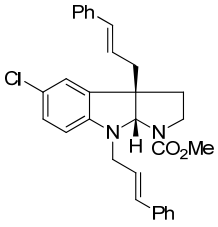
$C_{28}H_{25}BrCl_2NO$ $[M+H]^+$: 540.0491. Found: 540.0465.

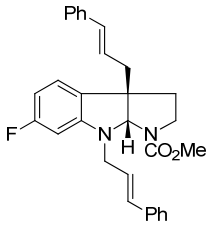


4ga. Yellow oil, 87% yield, 90% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 0.5 mL · min^{-1}, λ = 254 nm, t (major) = 10.99 min, t (minor) = 12.55 min]; $[\alpha]_D^{17}$ = +218.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03-2.14 (m, 2H), 2.53-2.61 (m, 1H), 2.66-2.72 (m, 1H), 3.08-3.17 (m, 1H), 3.66-4.34 (m, 6H), 5.38 and 5.54 (s, 1H), 5.95-6.19 (m, 2H), 6.39-6.58 (m, 3H), 6.67-6.71 (m, 1H), 7.04-7.12 (m, 2H), 7.22-7.23 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.2, 37.4, 42.4, 42.6, 45.4, 45.6, 48.2, 52.4, 56.2, 57.4, 60.4, 83.9, 84.4, 106.4, 117.3, 117.6, 122.8, 125.3, 125.4, 126.05, 126.10, 126.2, 126.9, 127.1, 127.2, 128.4, 128.5, 131.2, 131.9, 132.2, 133.4, 136.7, 137.0, 137.1, 149.99, 155.05, 156.0. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1261, 1091, 1020, 865, 798, 701, 663; HRMS (ESI) calcd for $C_{30}H_{31}N_2O_2$ $[M+H]^+$: 451.2380. Found: 451.2371.



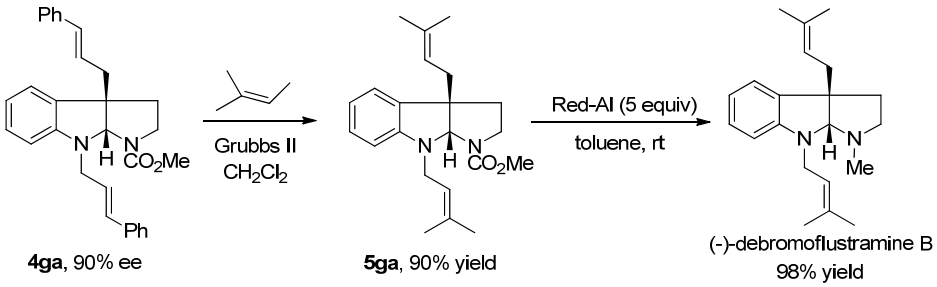
4ha. Yellow oil, 92% yield, 88% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 0.5 mL · min^{-1}, λ = 254 nm, t (major) = 10.78 min, t (minor) = 12.25 min]; $[\alpha]_D^{25}$ = +140.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06-2.10 (m, 2H), 2.54 (dd, J = 8.8, 14.0 Hz, 1H), 2.65-2.70 (m, 1H), 3.08-3.15 (m, 1H), 3.66 and 3.71 (s, 3H), 3.78-4.29 (m, 3H), 5.40 and 5.56 (s, 1H), 5.95-6.13 (m, 2H), 6.34 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 6.50-6.54 (m, 1H), 7.00-7.04 (m, 2H), 7.20-7.23 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.2, 37.4, 42.2, 42.4, 45.3, 45.5, 48.2, 52.5, 56.2, 57.5, 83.9, 84.4, 107.1, 121.8, 122.1, 123.0, 124.6, 124.8,

125.4, 126.1, 126.2, 127.2, 127.3, 128.3, 128.4, 128.5, 131.5, 133.8, 134.1, 136.5, 136.8, 136.9, 148.6, 154.9, 155.9. IR (thin film): ν_{max} (cm^{-1}) = 2953, 1736, 1698, 1600, 1489, 1446, 1382, 1318, 1240, 1211, 1152, 1098, 1045, 1029, 965, 936, 877, 802, 766, 736, 693; HRMS (ESI) calcd for $C_{30}H_{30}ClN_2O_2$ $[M+H]^+$: 485.1990. Found: 485.1981.



4ia. Yellow oil, 97% yield, 86% ee [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, *v* = 0.5 mL · min^{-1}, λ = 254 nm, t (major) = 11.23 min, t (minor) = 13.00 min]; $[\alpha]_D^{26}$ = +147.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07-2.09 (m, 2H), 2.50-2.56 (m, 1H), 2.62-2.67 (m, 1H), 3.08-3.15 (m, 1H), 3.65 and 3.70 (s, 3H), 3.75-4.29 (m, 3H), 5.38 and 5.55 (s, 1H), 5.99-6.16 (m, 2H), 6.34-6.56 (m, 3H), 6.75-6.79 (m, 2H), 7.19-7.22 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.9, 37.3, 42.0, 42.2, 45.3, 45.4, 48.7, 52.3, 56.2, 57.4, 84.4, 84.9, 106.5, 106.6, 110.2, 110.5, 114.2, 114.4, 124.6, 124.7, 125.8, 126.0, 126.2, 127.1, 127.2, 128.3, 128.4, 131.4, 133.6, 136.6, 136.9, 146.1, 154.9, 155.1, 155.9, 157.4. IR (thin film): ν_{max} (cm^{-1}) = 2953, 1736, 1697, 1600, 1492, 1445, 1381, 1264, 1241, 1204, 1138, 1104, 1072, 1045, 964, 907, 867, 802, 767, 734, 693; HRMS (ESI) calcd for $C_{30}H_{31}FN_2O_2$ $[M+H]^+$: 469.2286. Found: 469.2272.

Synthesis of (-)-debromoflustramine B



A 25 mL flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask was added **4ga** (58.5 mg, 0.13 mmol). The vessel was placed

under vacuum and the atmosphere exchanged with argon three times before the addition of CH_2Cl_2 (5 mL) and 2-methyl-2-butene (91.0 mg, 1.30 mmol). Then the mixture was heated to reflux after Grubbs II (11.1 mg, 0.013 mmol) was added. After the reaction was almost complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by silica sel column chromatography (PE/EA = 15/1) to afford the desired product **5ga**[2] as a colorless liquid (41.9 mg, 90% yield). Analytical data for **5ga**: $[\alpha]_D^{28}$ = +281.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.68-1.76 (m, 9H), 2.03 (s, 2H), 2.38 (d, *J* = 7.2 Hz, 2H), 3.02-3.11 (m, 1H), 3.70-4.22 (m, 6H), 5.05-5.34 (m, 3H), 6.36-6.39 (m, 1H), 6.45 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 6.9 Hz, 1H).

A flame-dried 25mL round bottom flask was cooled to room temperature and filled with argon. To this flask was added **5ga** (35.4 mg, 0.1 mmol), the atmosphere exchanged with argon three times before the addition of toluene (5 mL) and the slow addition of Red-Al (0.5 mmol, 70 wt% in toluene, 0.14 mL)[3]. After the reaction was complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by silica sel column chromatography (PE/EA = 1/2) to afford the desired product **(-)-debromoflustramine B** as a colorless liquid (29.0 mg, 98% yield). Analytical data for **(-)-debromoflustramine B**: $[\alpha]_D^{25}$ = +85.68 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3H), 1.65 (s, 3H), 1.70 (s, 3H), 1.71 (s, 3H), 1.89-1.95 (m, 1H), 2.03-2.12 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 2.54-2.61 (m, 1H), 2.67-2.74 (m, 1H), 3.80 (dd, *J* = 6.9, 15.9 Hz, 1H), 3.94 (dd, *J* = 5.7, 15.9 Hz, 1H), 4.30 (s, 1H), 4.96 (t, *J* = 6.9 Hz, 1H), 5.17 (t, *J* = 6.0 Hz, 1H), 6.42 (d, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H).

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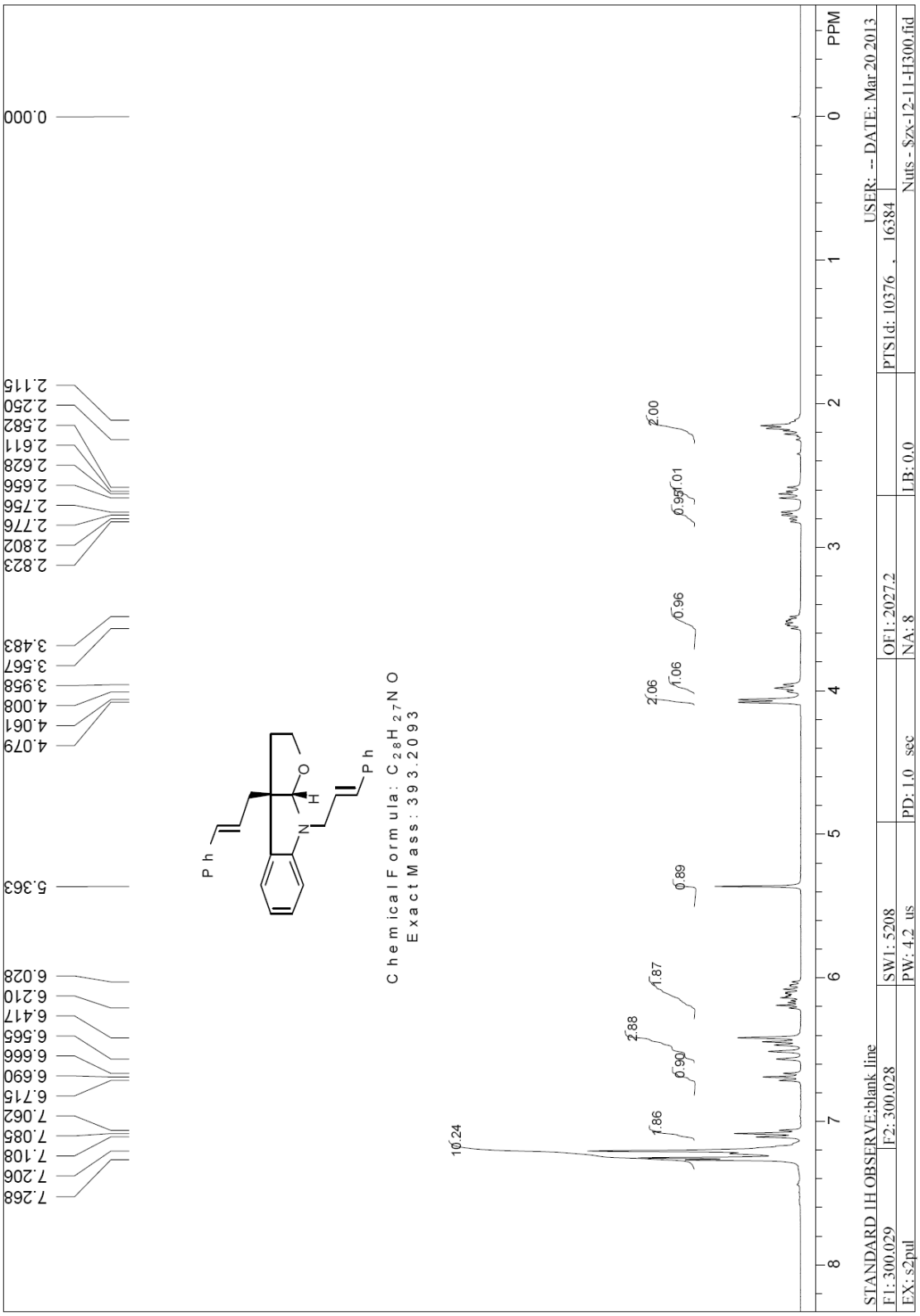
References

[1] X. Zhang, Z.-P. Yang, C. Liu and S.-L. You, *Chem. Sci.*, 2013, **4**, 3239.

[2] (a) A. V. Dix, C. M. Meseck, A. J. Lowe and M. O. Mitchell, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 2522; (b) A. W. Schammel, B. W. Boal, L. Zu, T. Mesganaw and N. K. Garg, *Tetrahedron,* 2010, **66**, 4687.

[3] (a) G. H. Tan, X. Zhu and A. Ganesan, *Org. Lett.*, 2003, **5**, 1801; (b) T. Newhouse and P. S. Baran, *J. Am. Chem. Soc.*, 2008, **130**, 10886; (c) Z. Zhang and J. C. Antilla, *Angew. Chem. Int. Ed.*, 2012, **51**, 11778.

Compound **4aa**'s ^{1}H NMR Spectra



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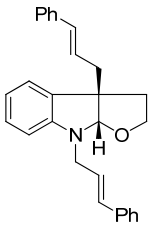

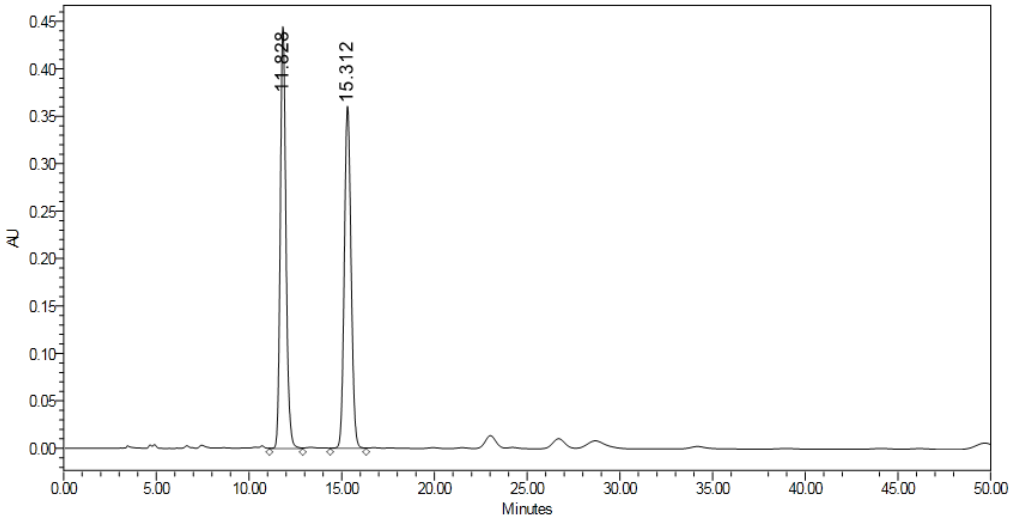

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1	11.828	9452089	50.74
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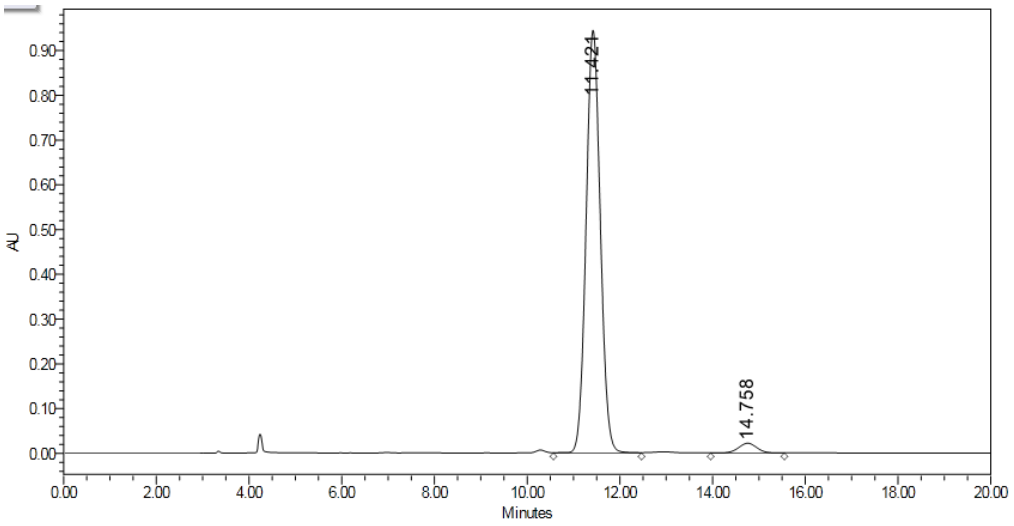

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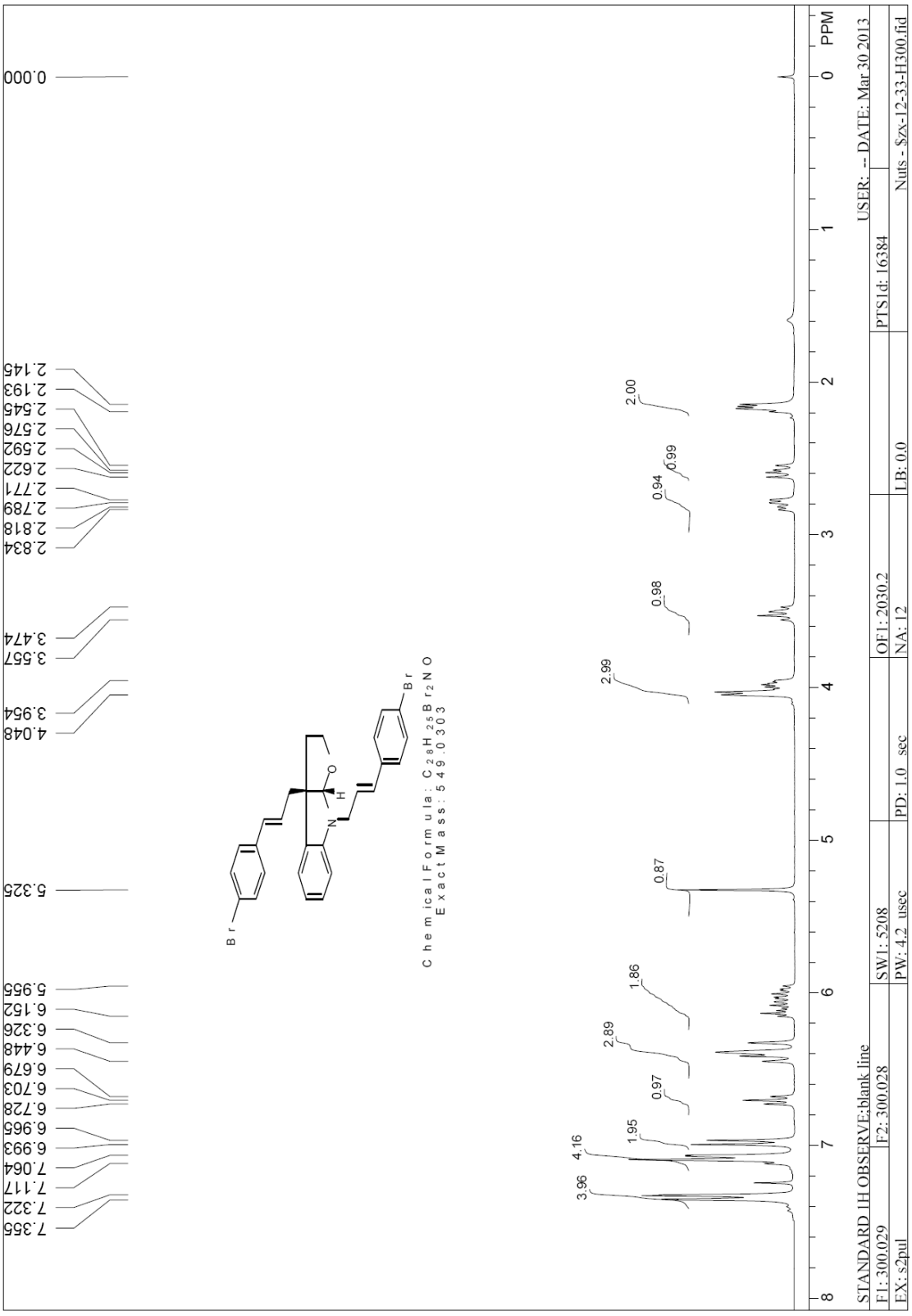
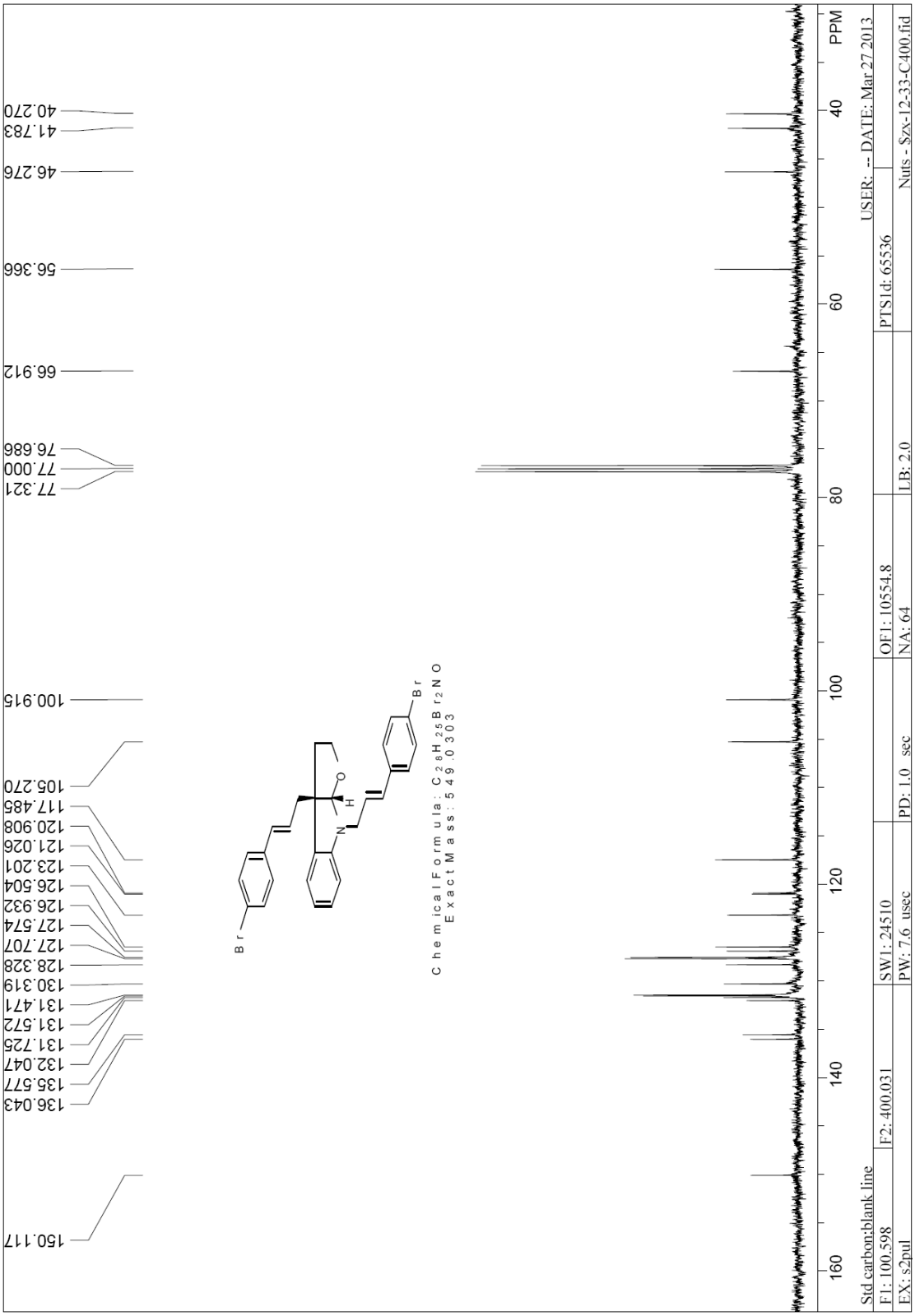
1	11.421	20145695	97.14
2	14.758	593923	2.86

Compound **4ab**'s ^{1}H NMR Spectra



Compound **4ab**'s ^{13}C NMR Spectra



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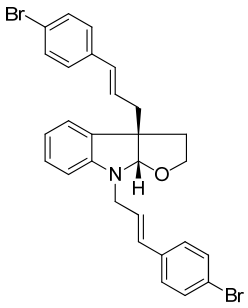

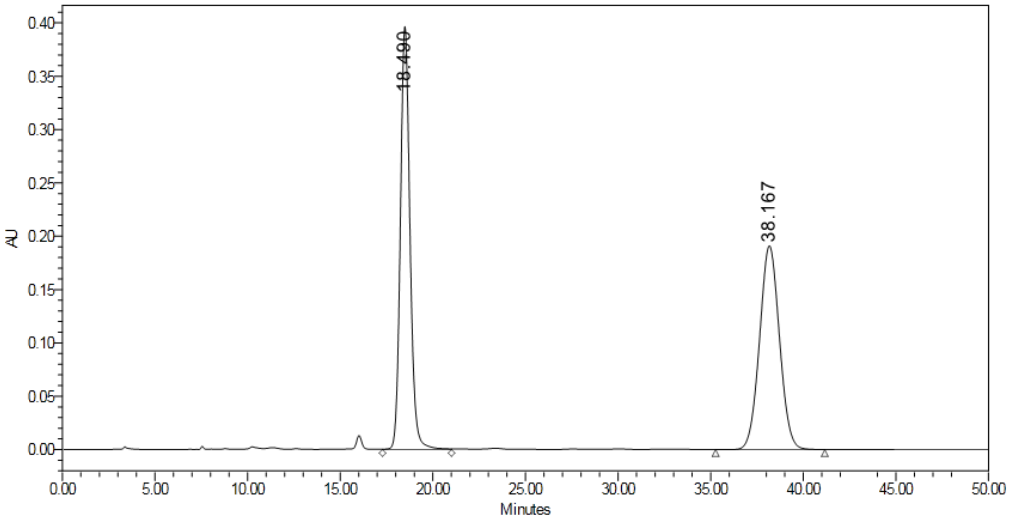

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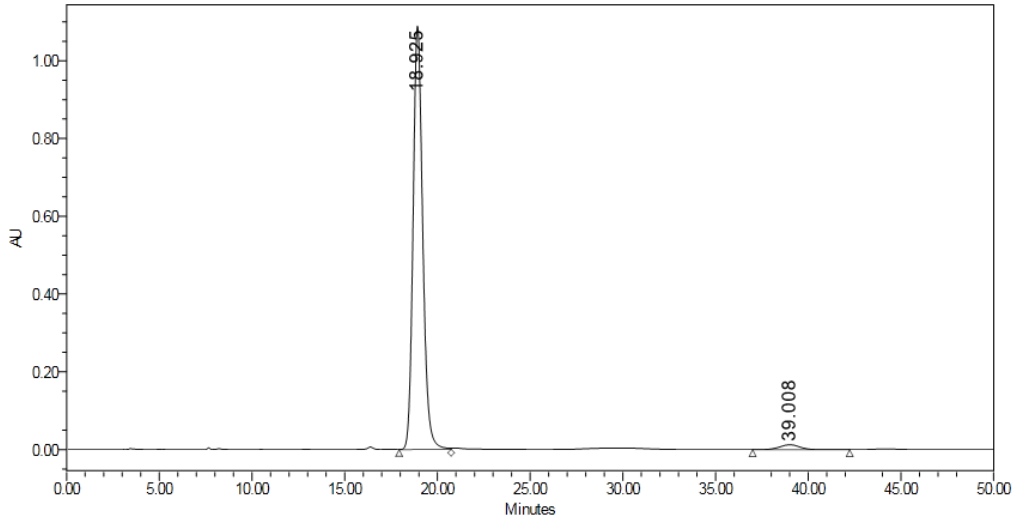
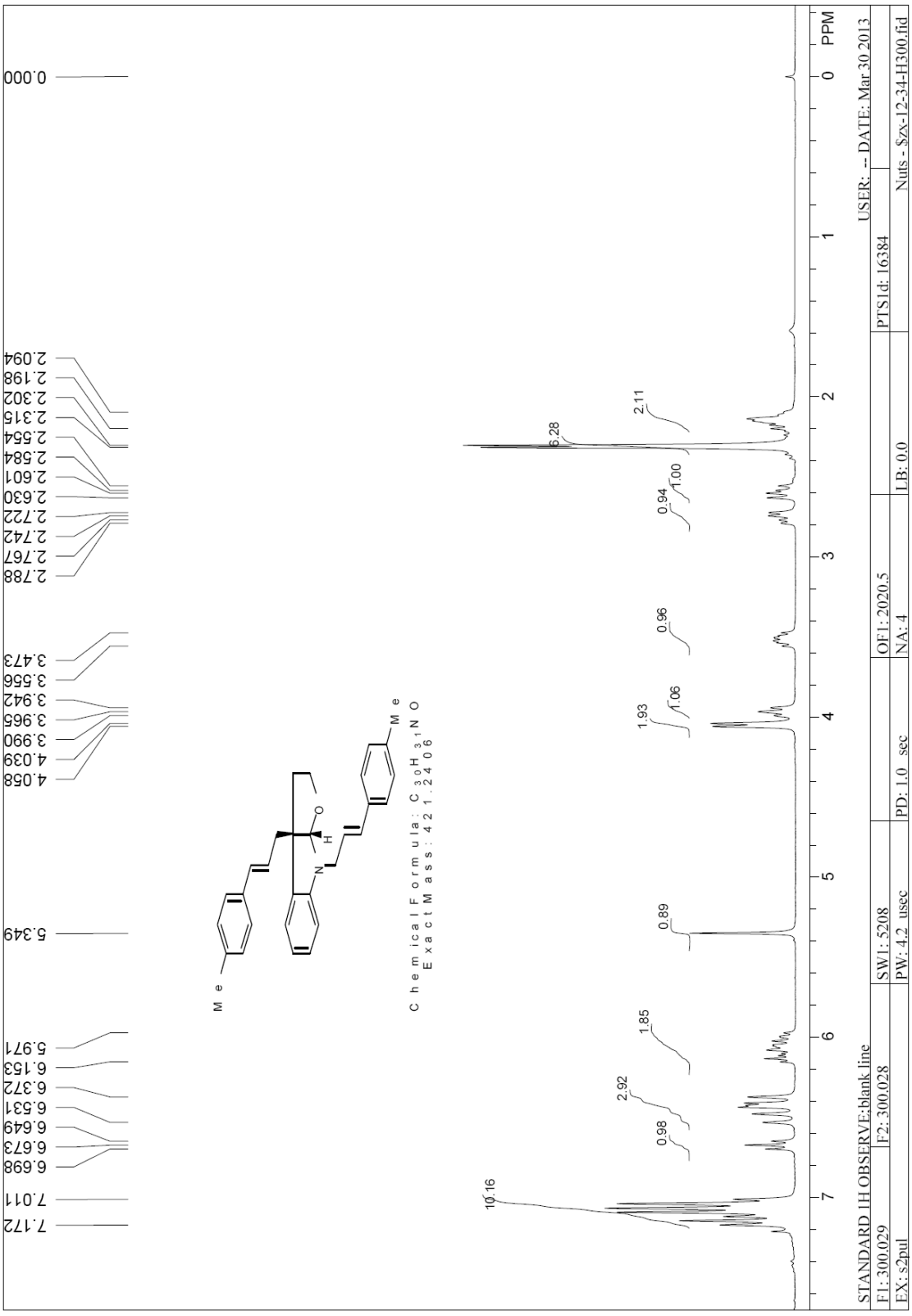
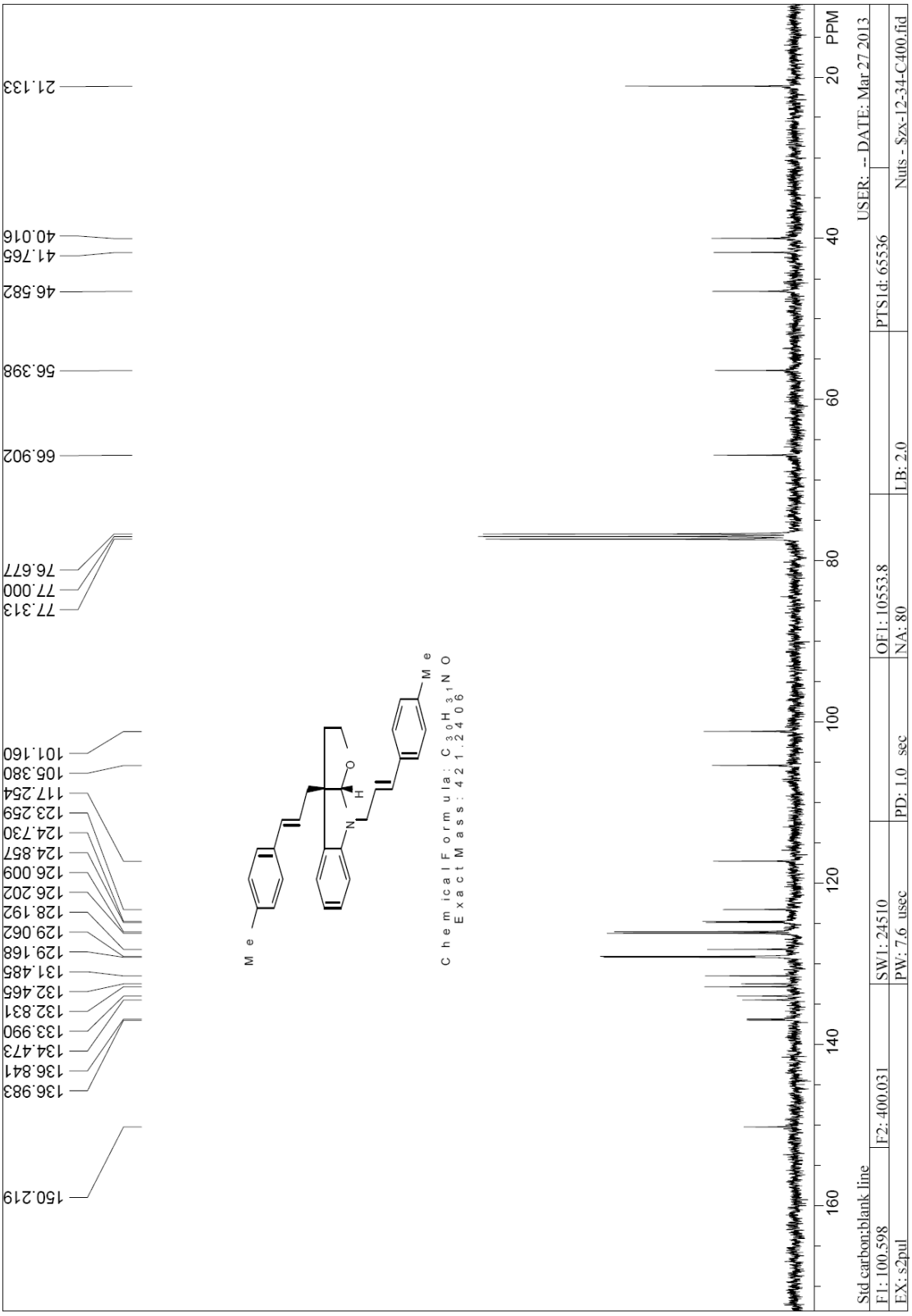


	RT (min)	Area (μV*sec)	% Area
1	18.925	39389524	97.70
2	39.008	926642	2.30

Compound **4ac**'s ^{1}H NMR Spectra



Compound **4ac**'s ^{13}C NMR Spectra



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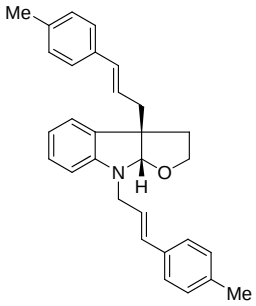

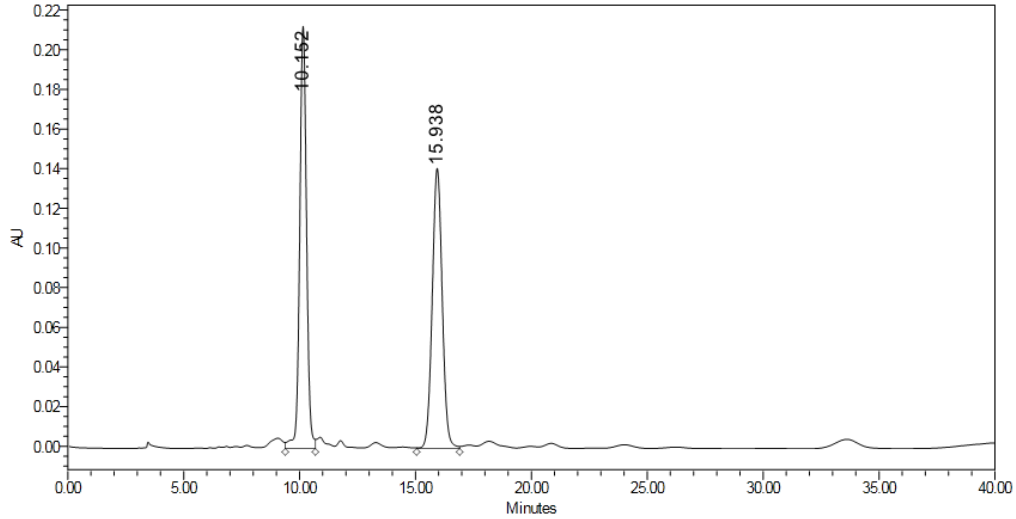

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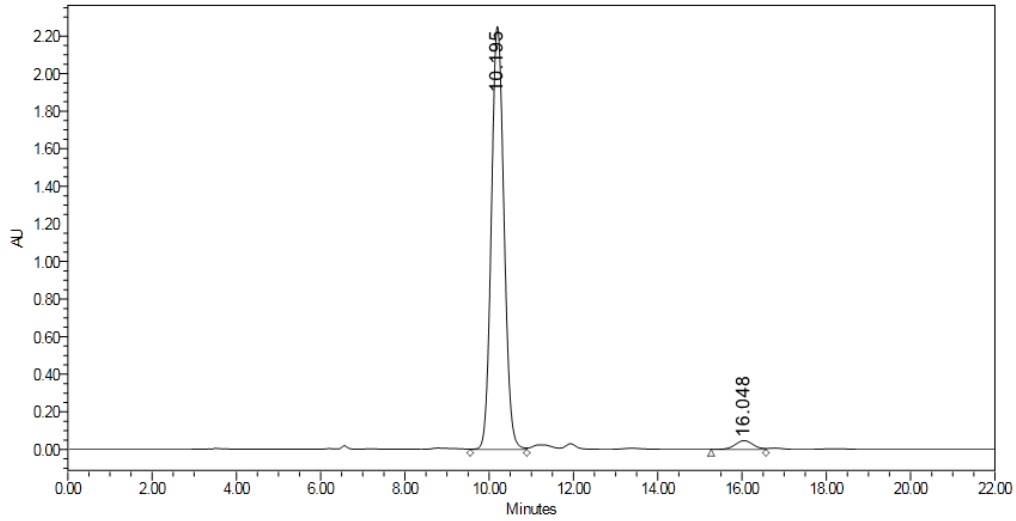

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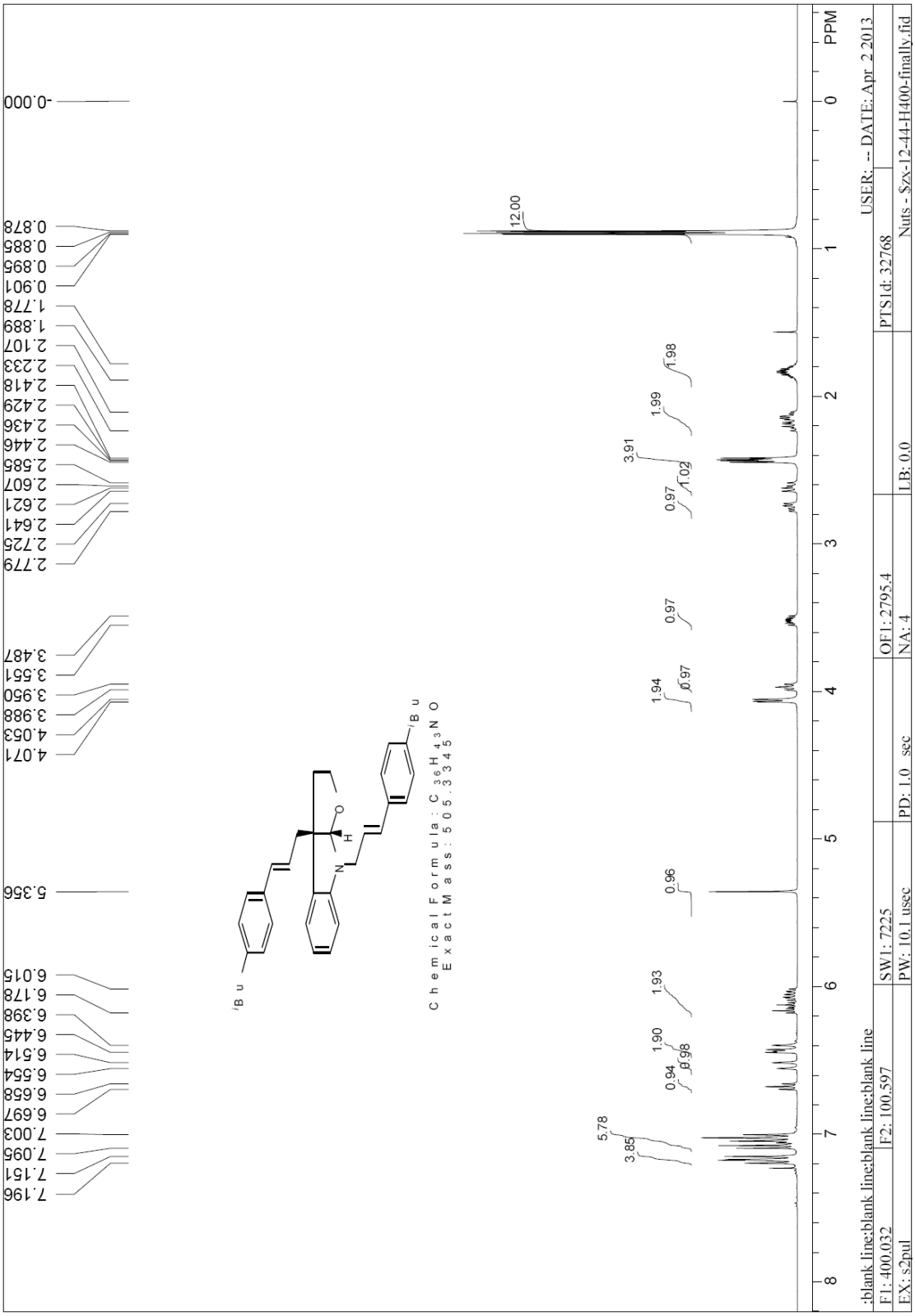
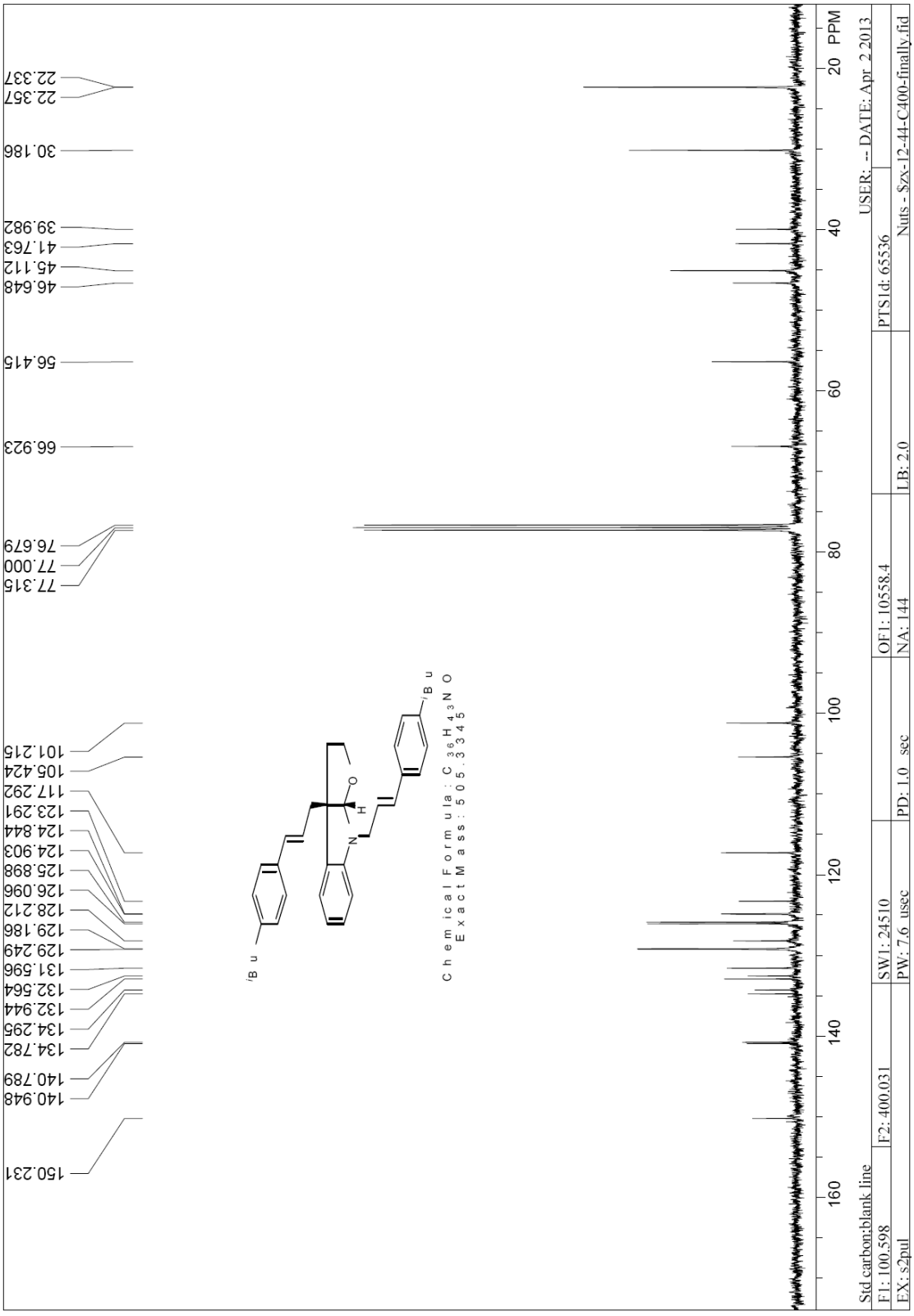
1	10.195	46959161	97.16
2	16.048	1372722	2.84

Compound **4ad**'s ^{1}H NMR Spectra



Compound **4ad**'s ^{13}C NMR Spectra



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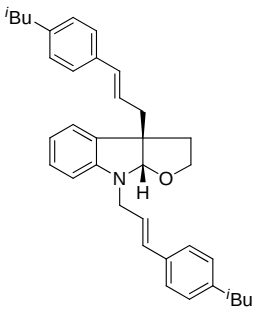
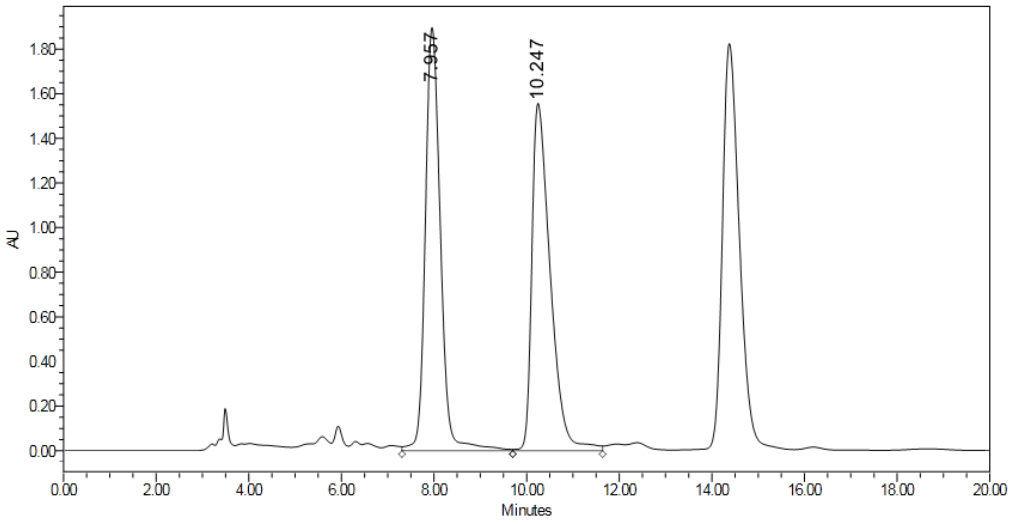
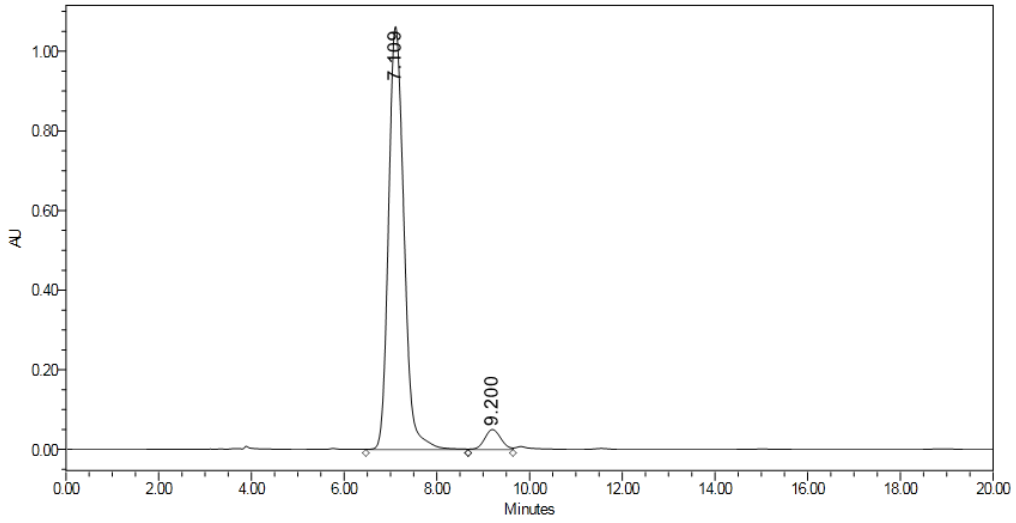


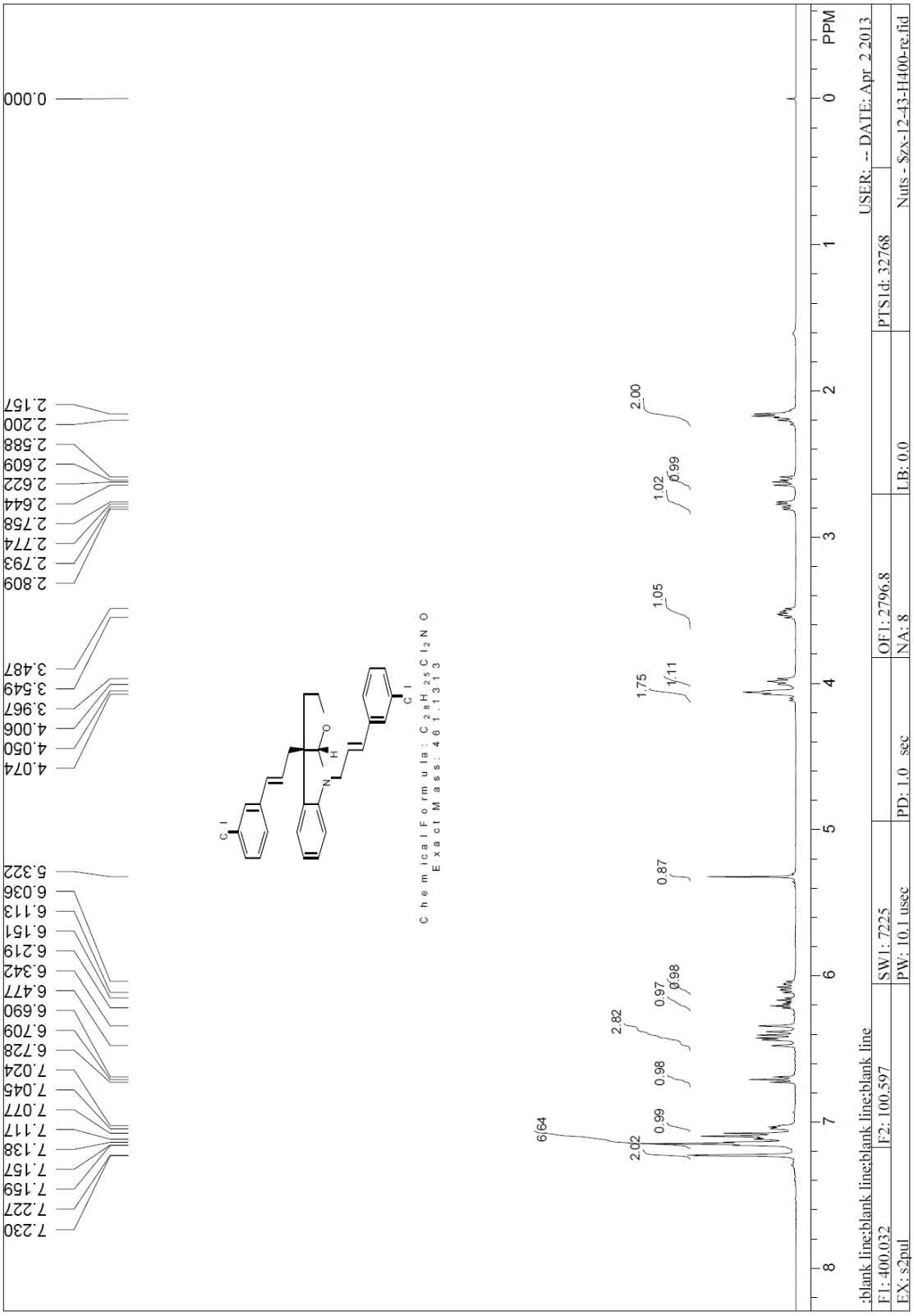


	RT (min)	Area (μV*sec)	% Area
1	7.957	43107495	50.09
2	10.247	42949687	49.91

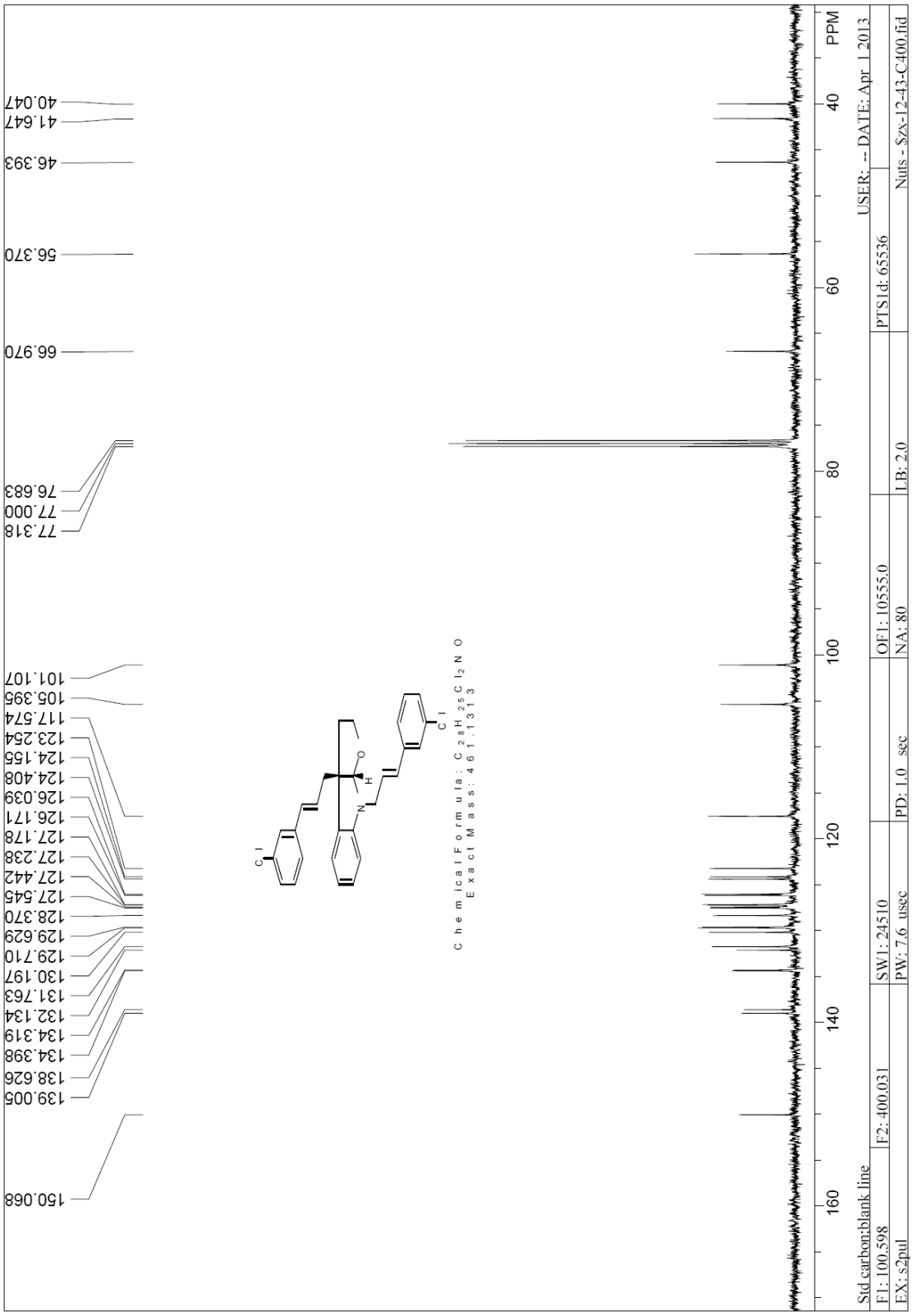


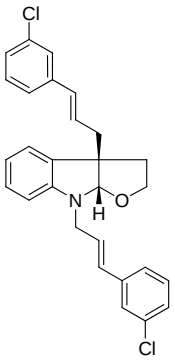
	RT (min)	Area (μV*sec)	% Area
1	7.109	24547497	95.27
2	9.200	1217438	4.73

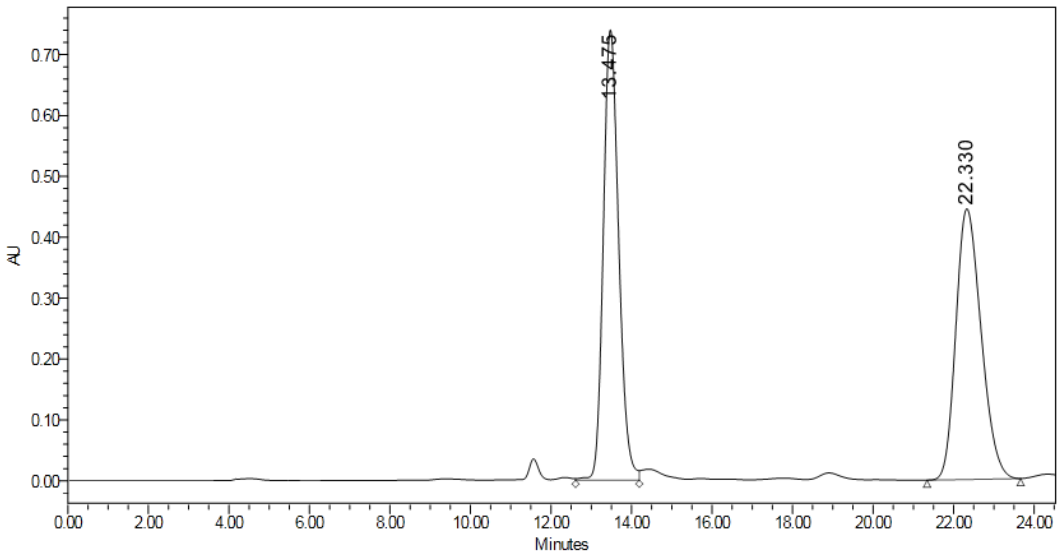
Compound **4ae**'s ^{1}H NMR Spectra



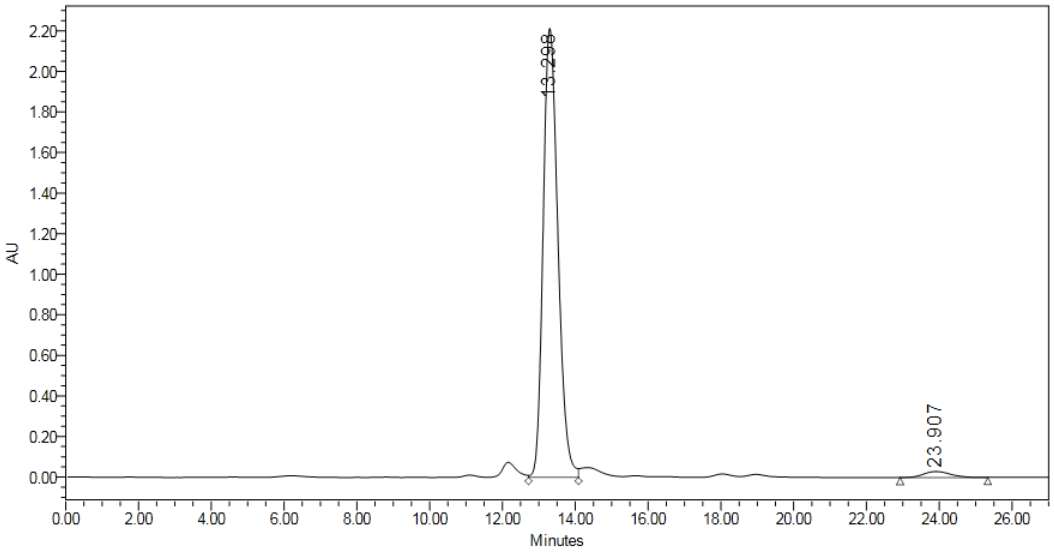
Compound **4ae**'s ^{13}C NMR Spectra





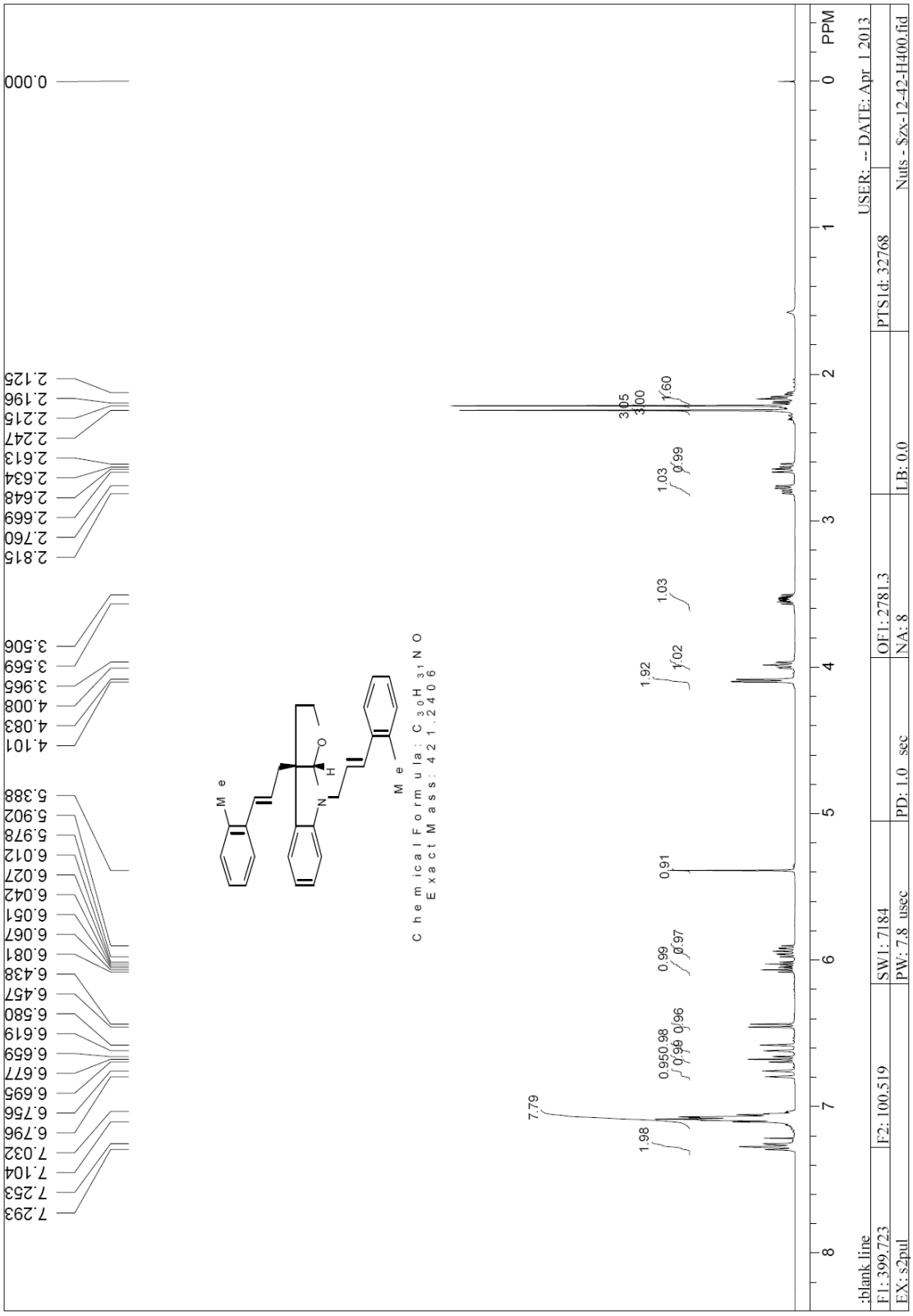


	RT (min)	Area (μV*sec)	% Area
1	13.475	19651125	50.36
2	22.330	19371859	49.64

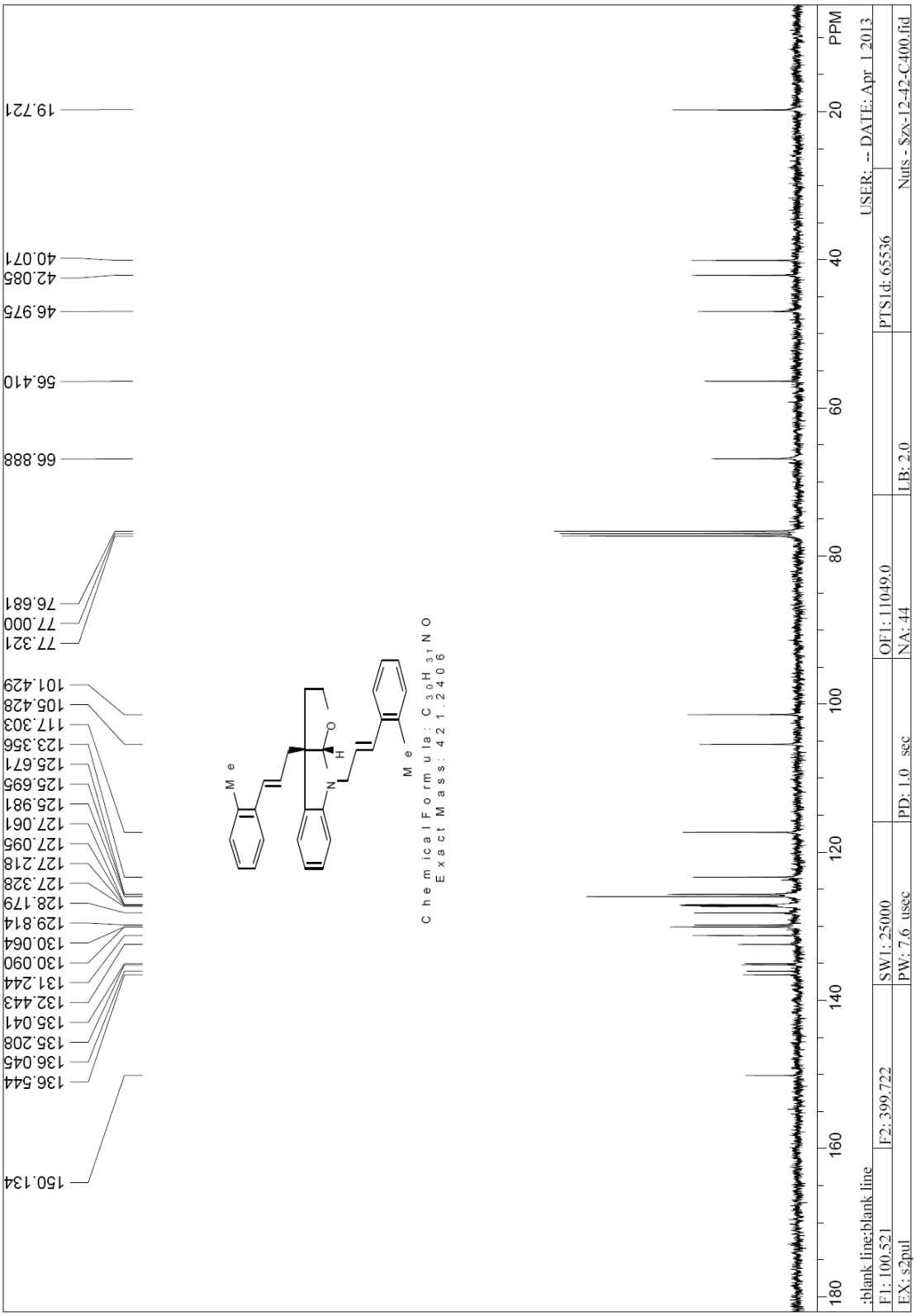


	RT (min)	Area (μV*sec)	% Area
1	13.298	62400850	97.67
2	23.907	1488451	2.33

Compound **4af**'s ^{1}H NMR Spectra



Compound **4af**'s ^{13}C NMR Spectra



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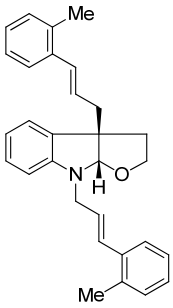
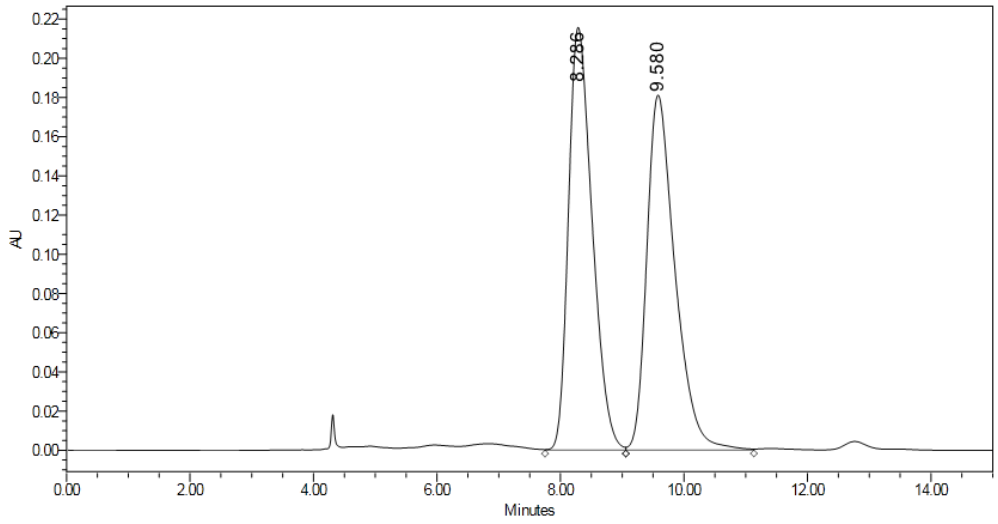
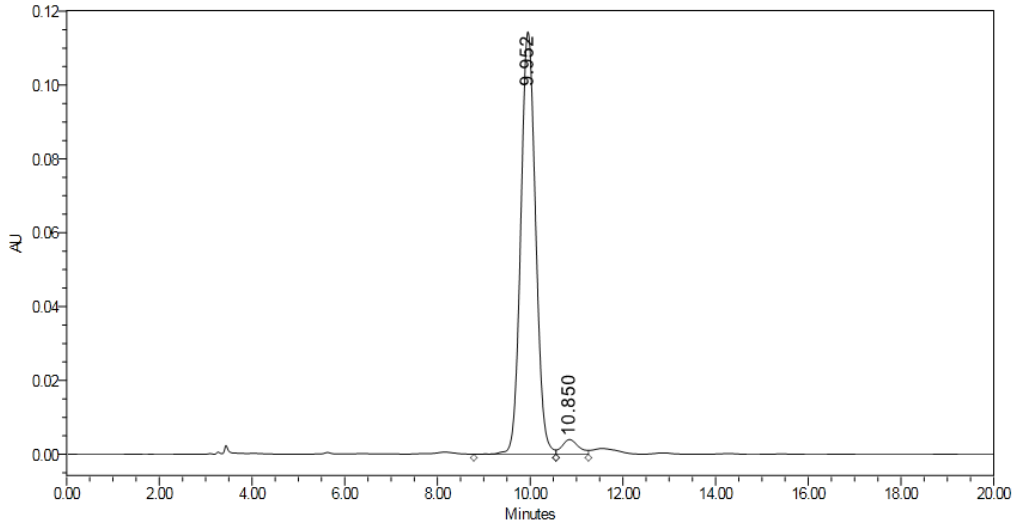


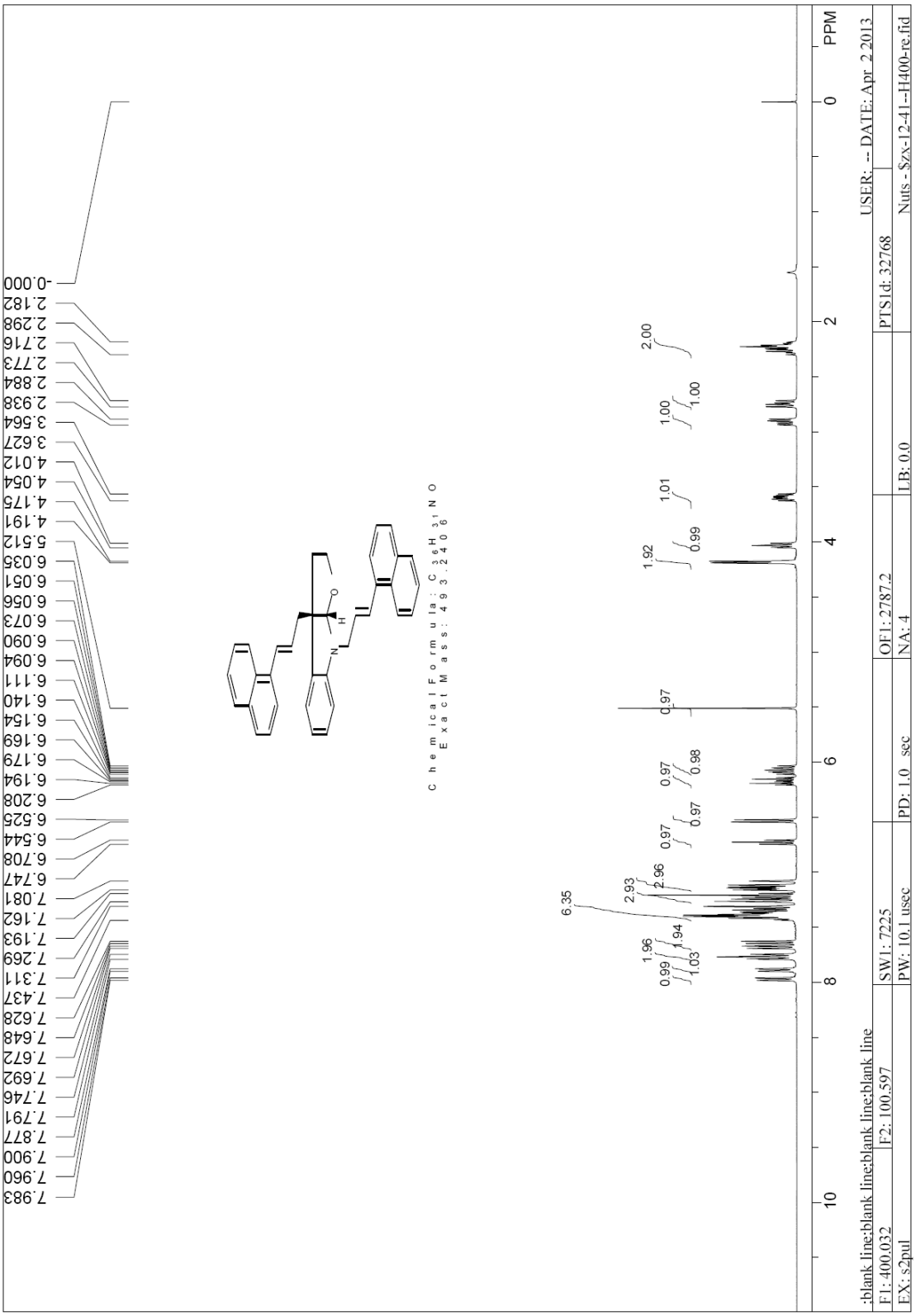


	RT (min)	Area (μV*sec)	% Area
1	8.286	5766018	50.04
2	9.580	5756505	49.96

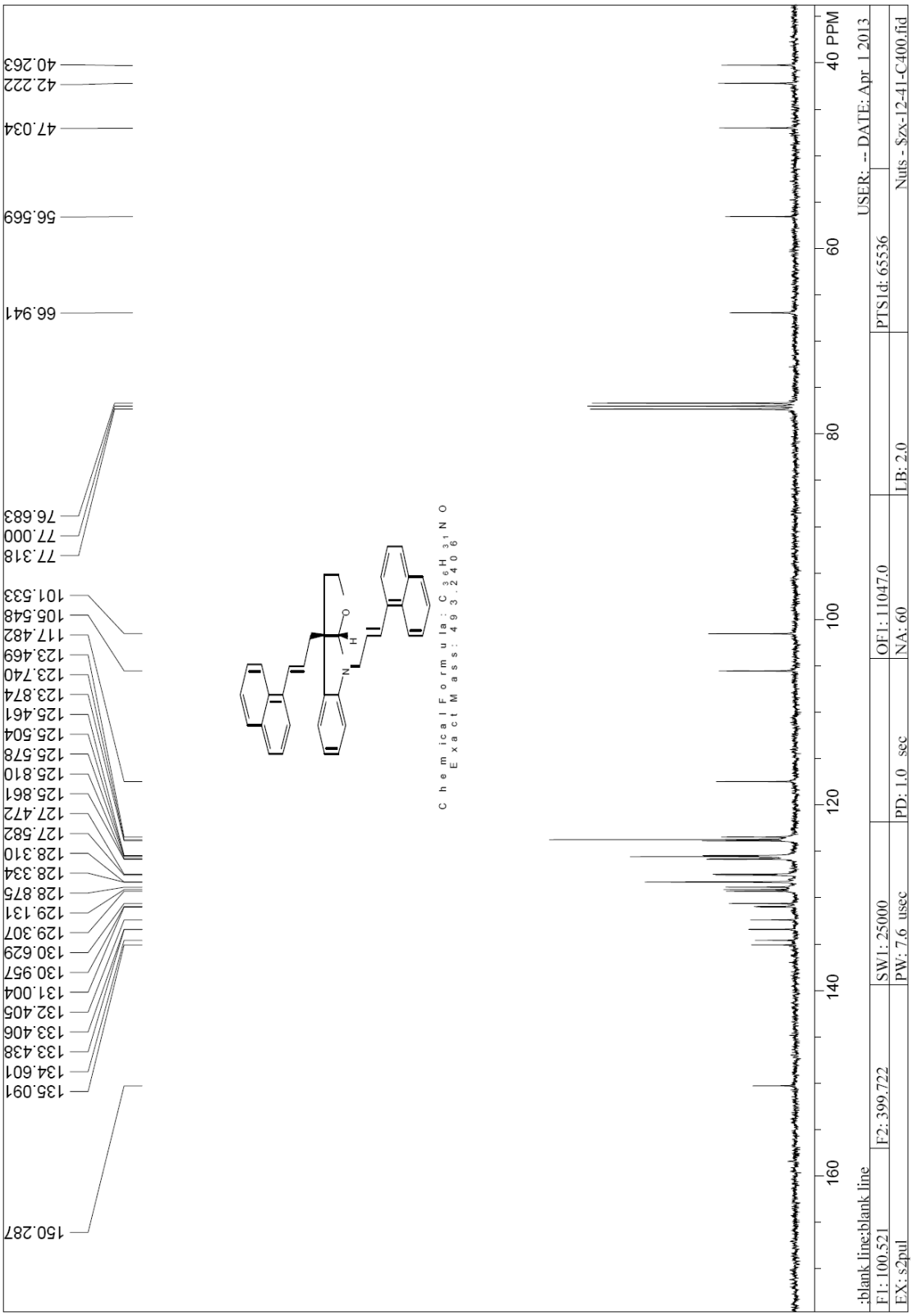


	RT (min)	Area (μV*sec)	% Area
1	9.952	2543446	96.23
2	10.850	99716	3.77

Compound **4ag**'s ^{1}H NMR Spectra



Compound **4ag**'s ^{13}C NMR Spectra



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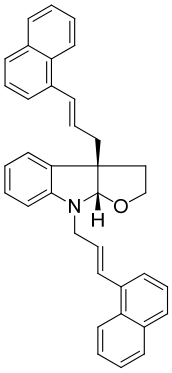
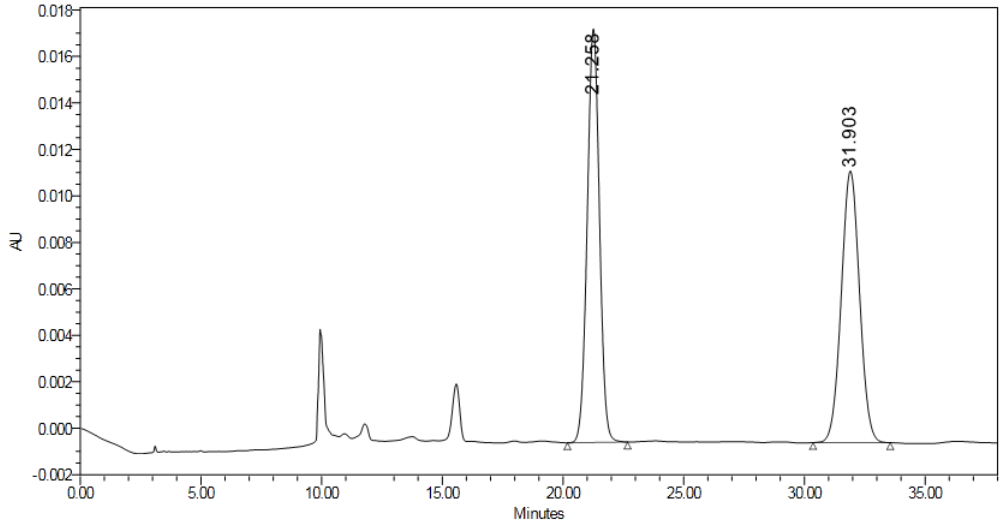
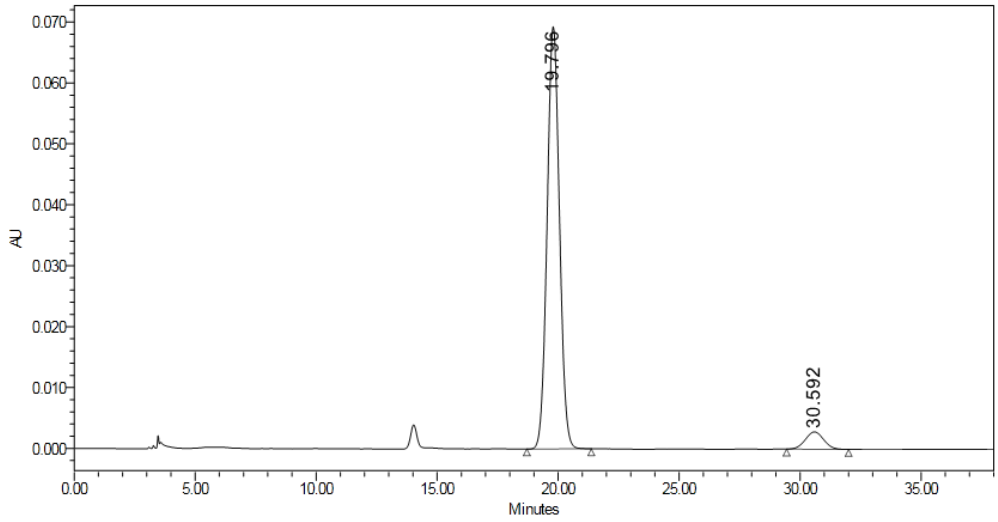


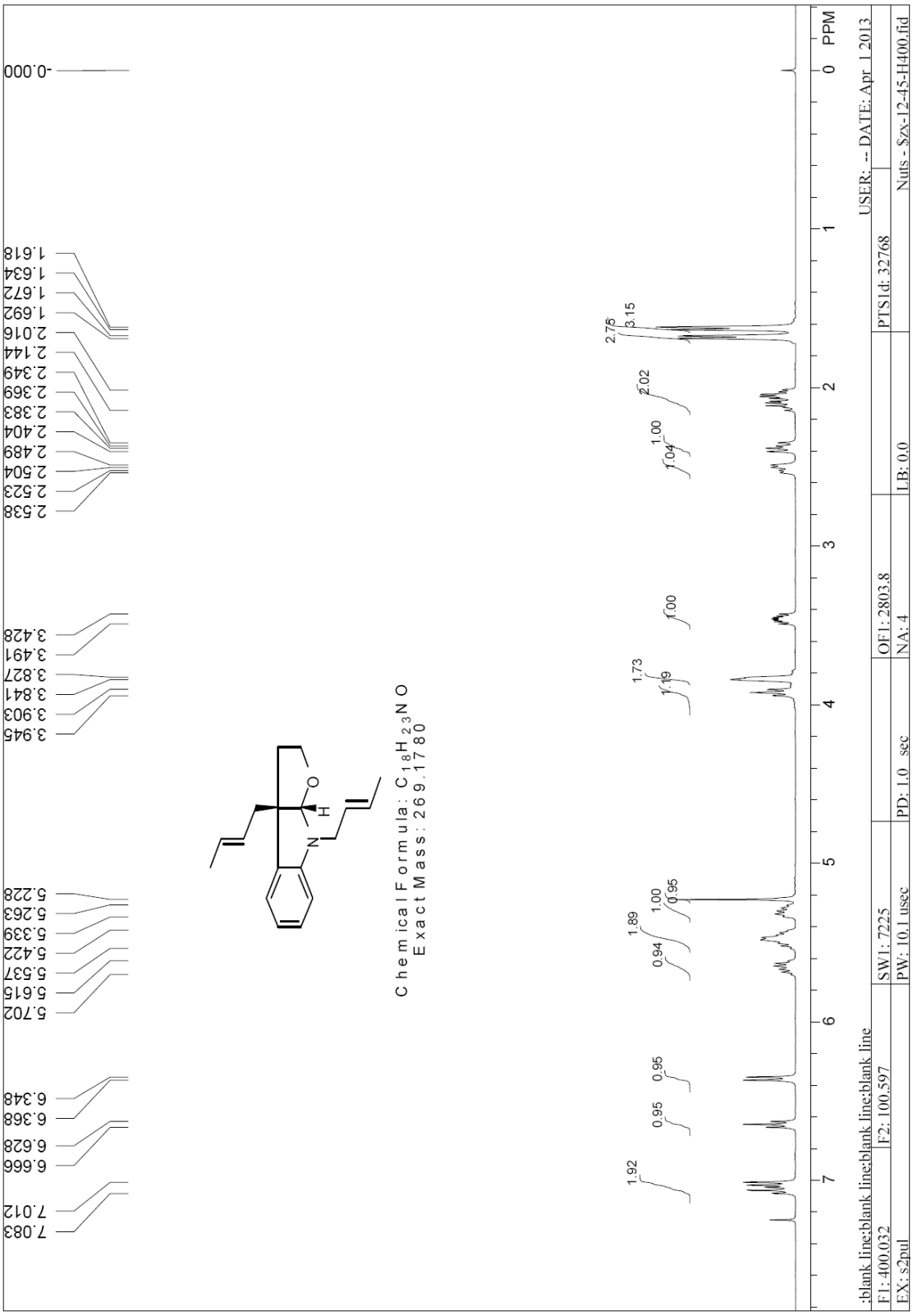


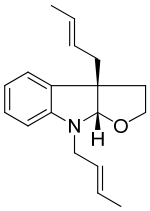
	RT (min)	Area (μV*sec)	% Area
1	21.258	626673	50.45
2	31.903	615500	49.55

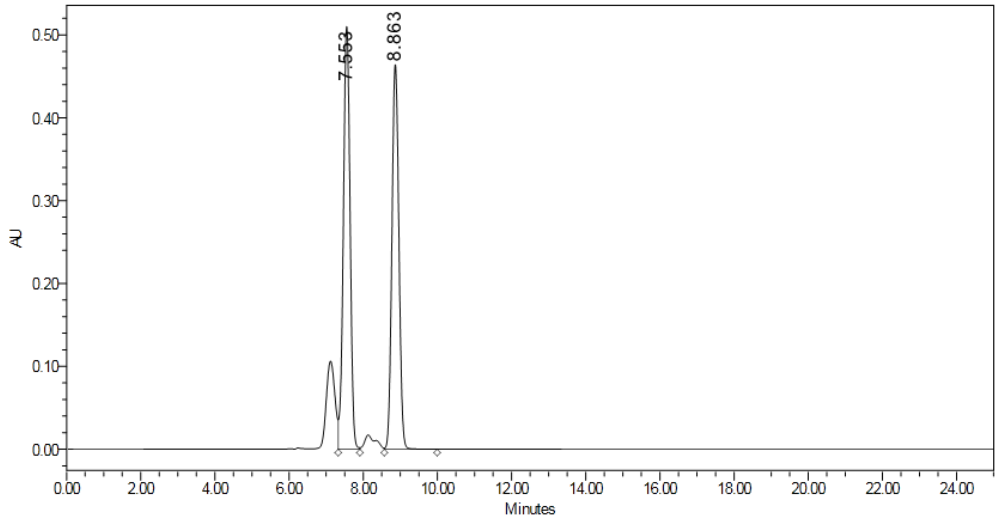


	RT (min)	Area (μV*sec)	% Area
1	19.796	2454157	94.24
2	30.592	149891	5.76

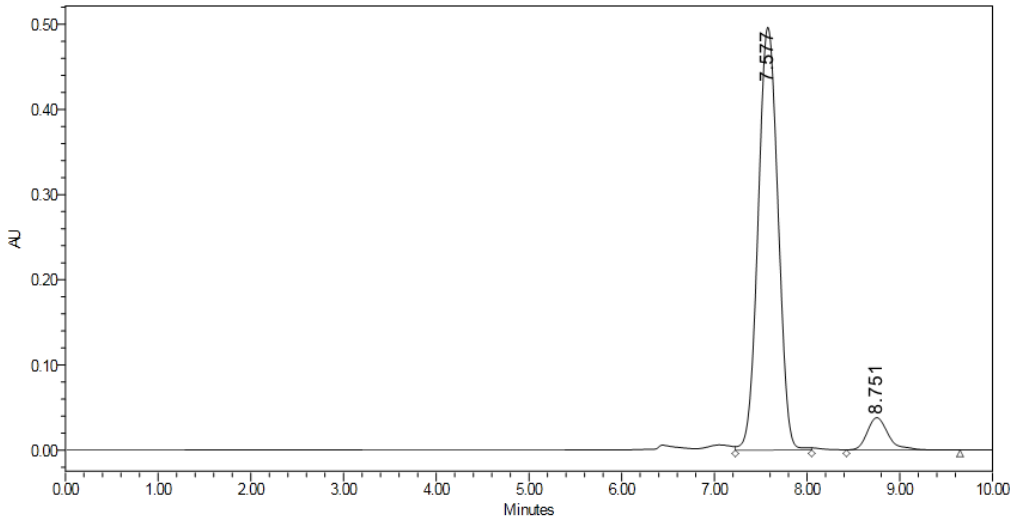
Compound **4ah**'s ^{1}H NMR Spectra





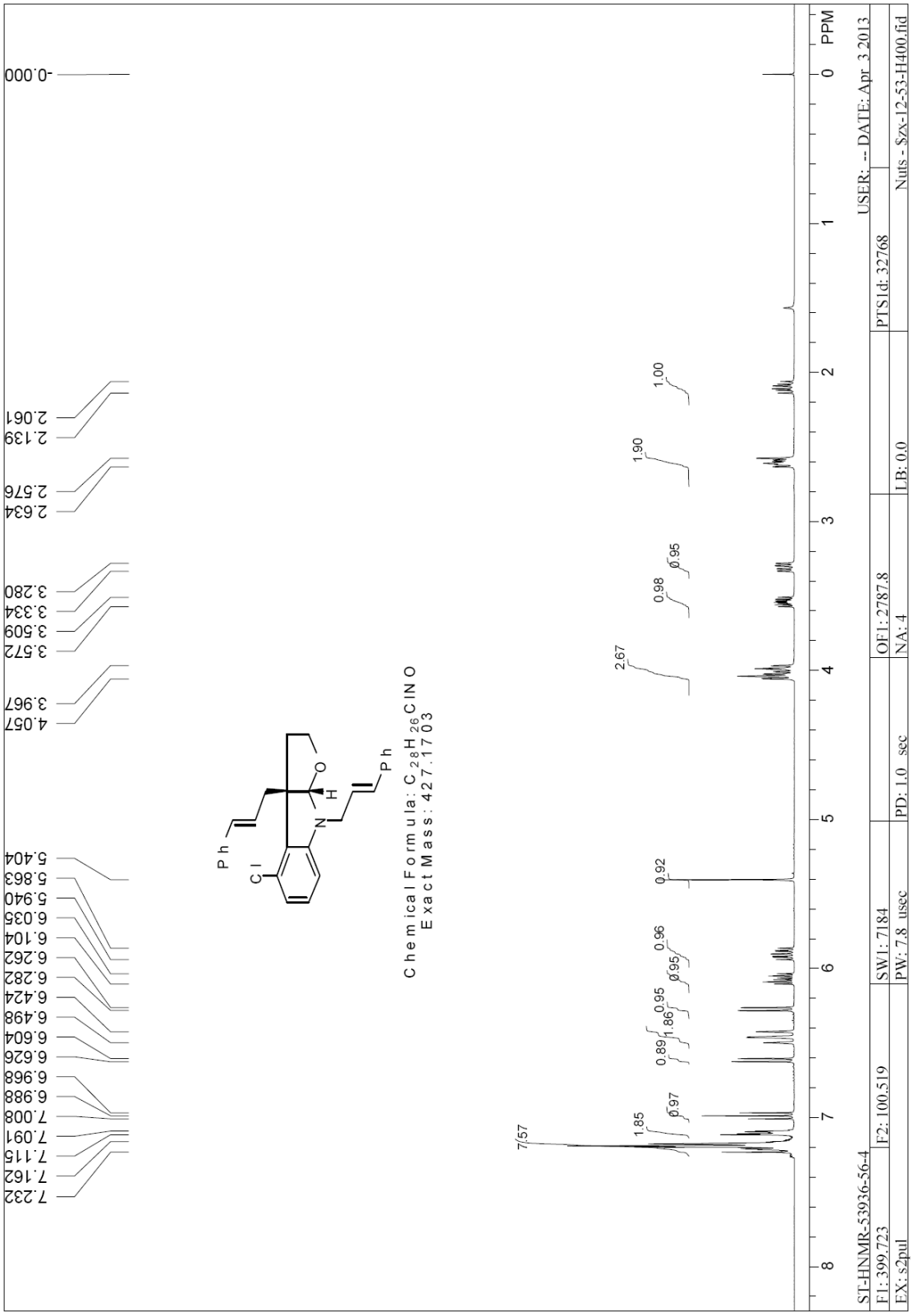


	RT (min)	Area (μV*sec)	% Area
1	7.553	6404908	51.49
2	8.863	6034737	48.51

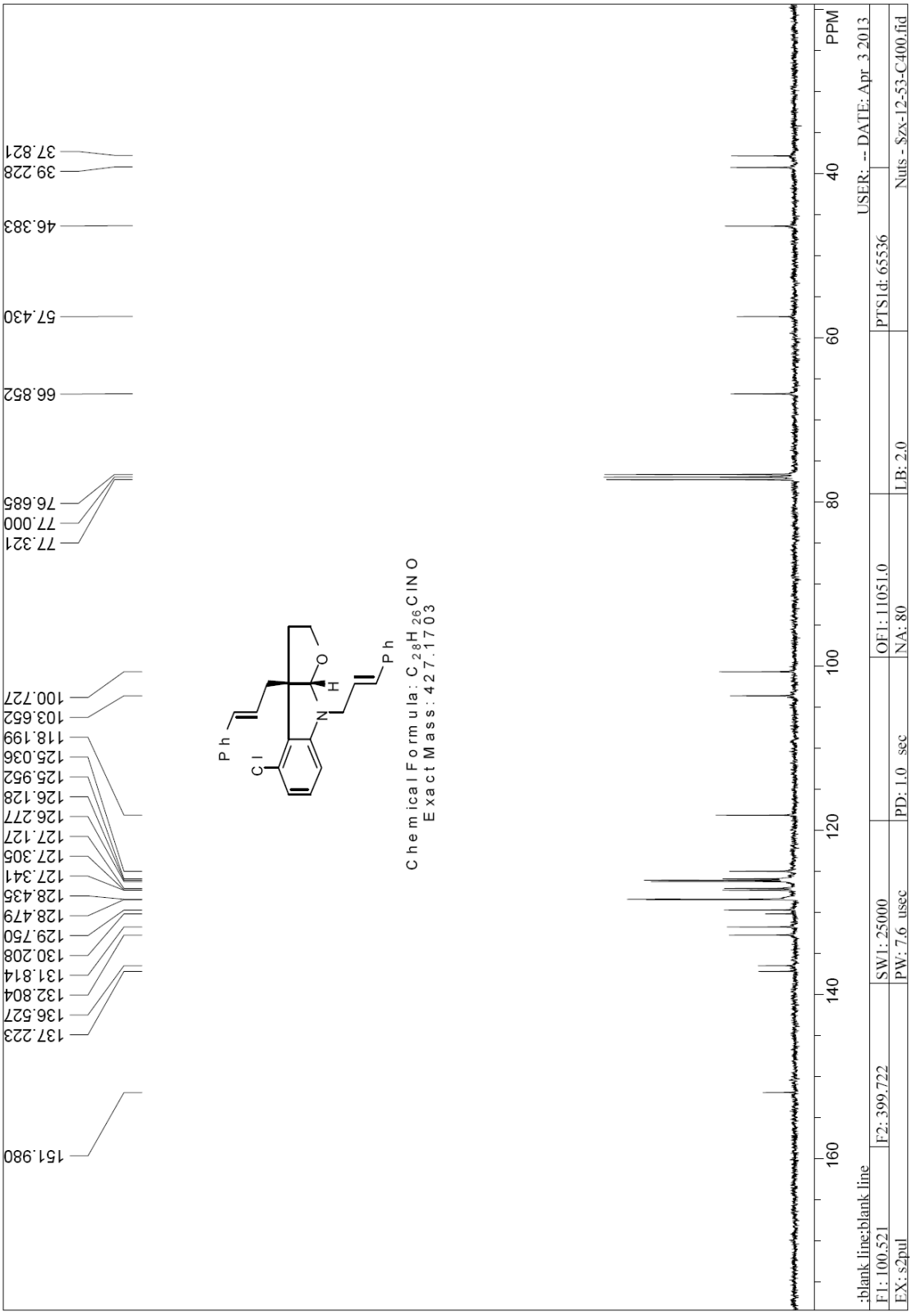


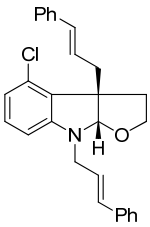
	RT (min)	Area (μV*sec)	% Area
1	7.577	7400943	92.58
2	8.751	592818	7.42

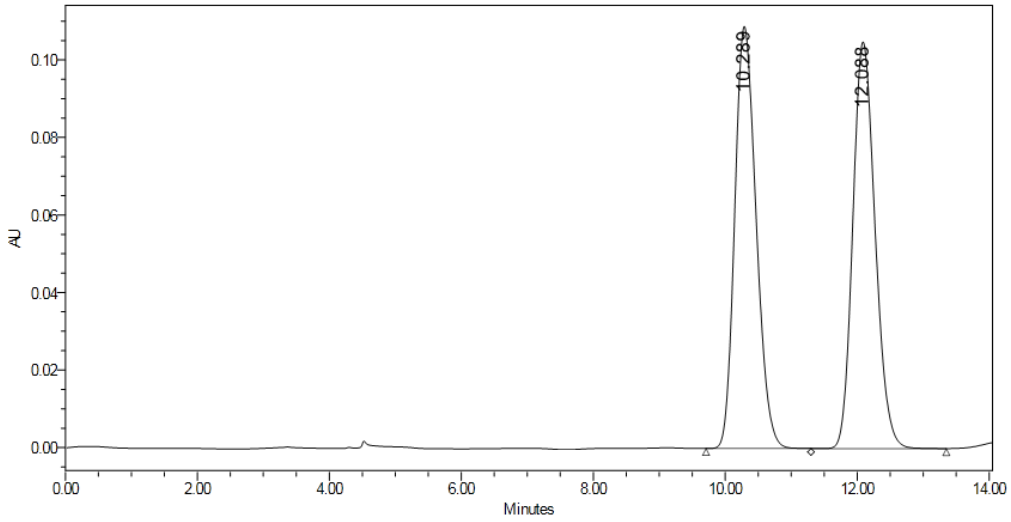
Compound **4ba**'s ^{1}H NMR Spectra



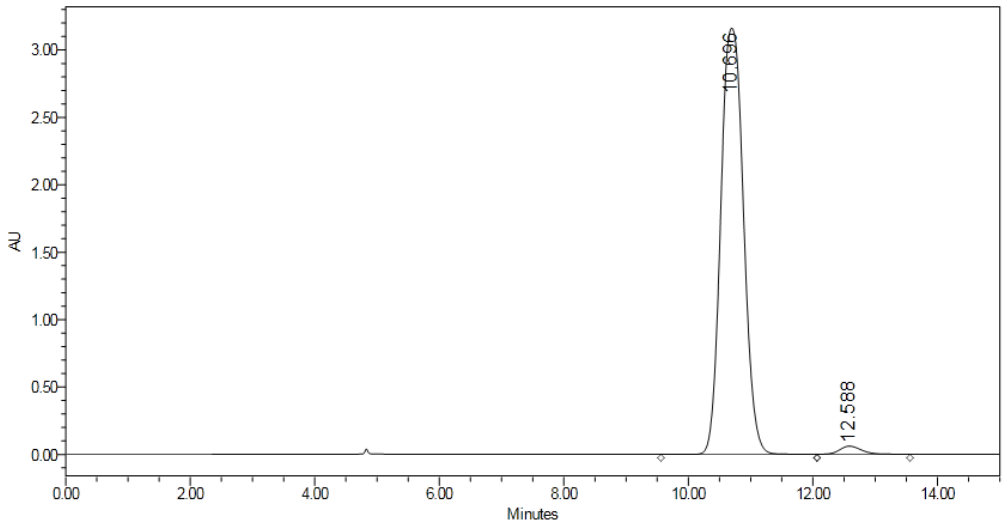
Compound **4ba**'s ^{13}C NMR Spectra





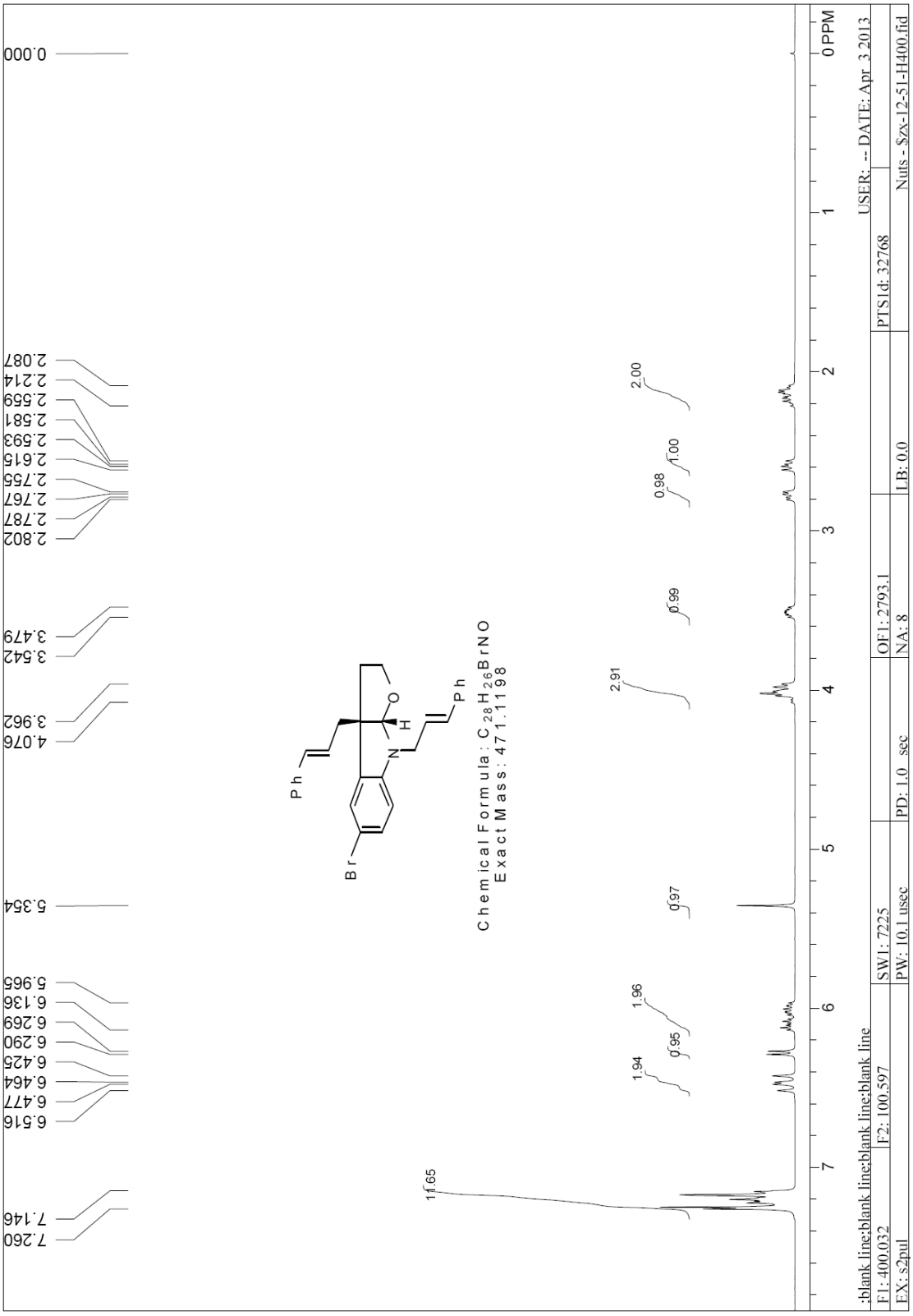


	RT (min)	Area (μV*sec)	% Area
1	10.289	2452908	49.90
2	12.088	2462418	50.10

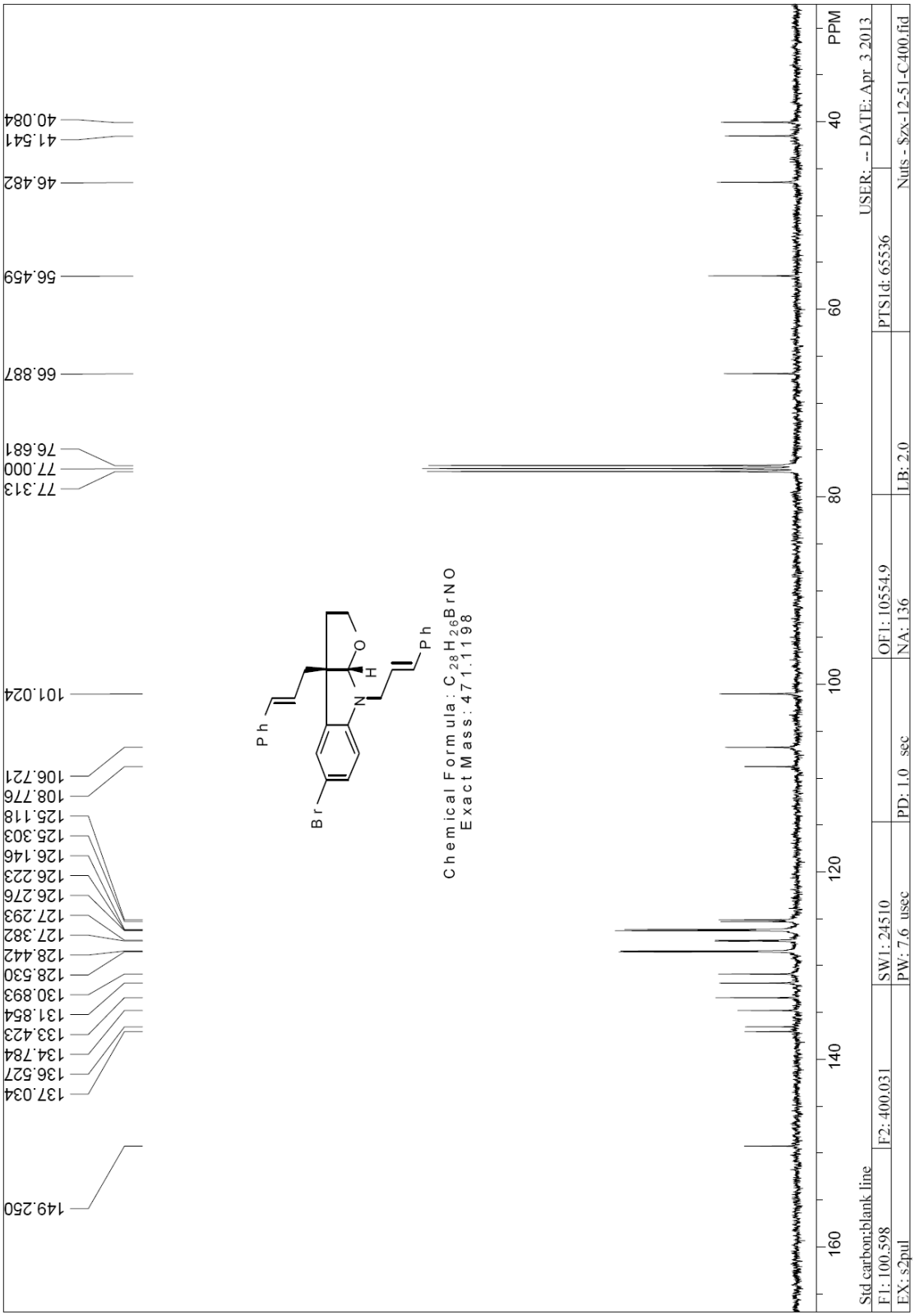


	RT (min)	Area (μV*sec)	% Area
1	10.696	79959773	98.17
2	12.588	1494184	1.83

Compound **4ca**'s ^{1}H NMR Spectra



Compound **4ca**'s ^{13}C NMR Spectra



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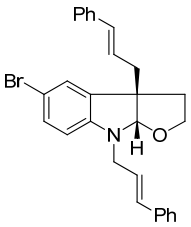
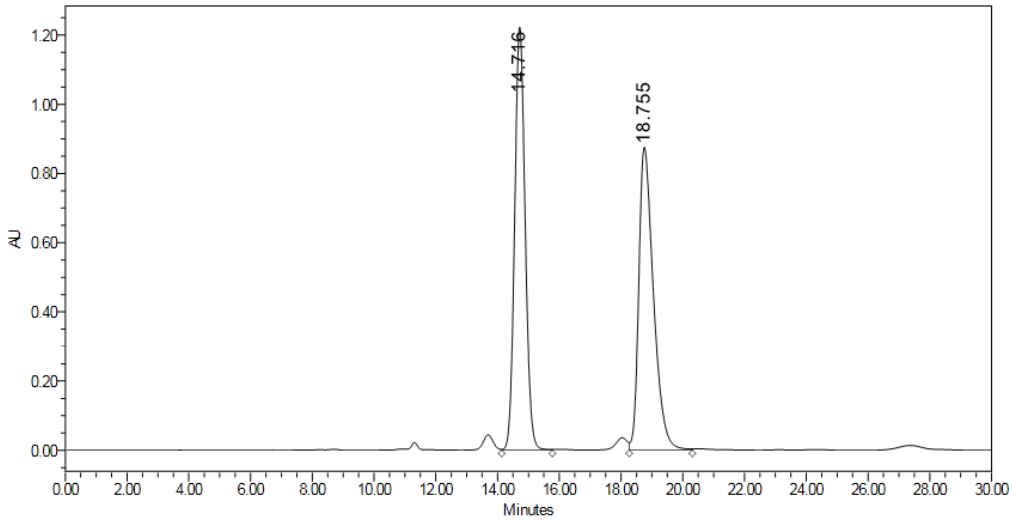
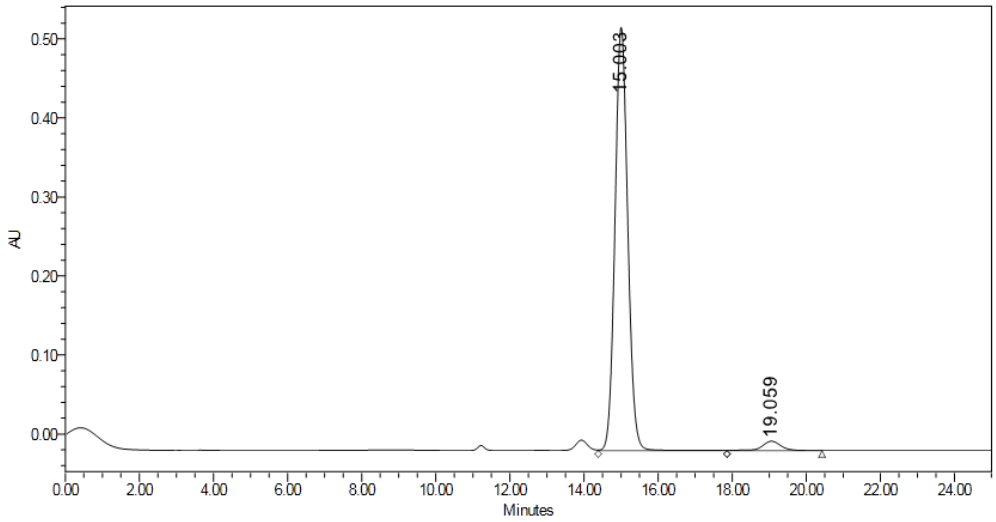


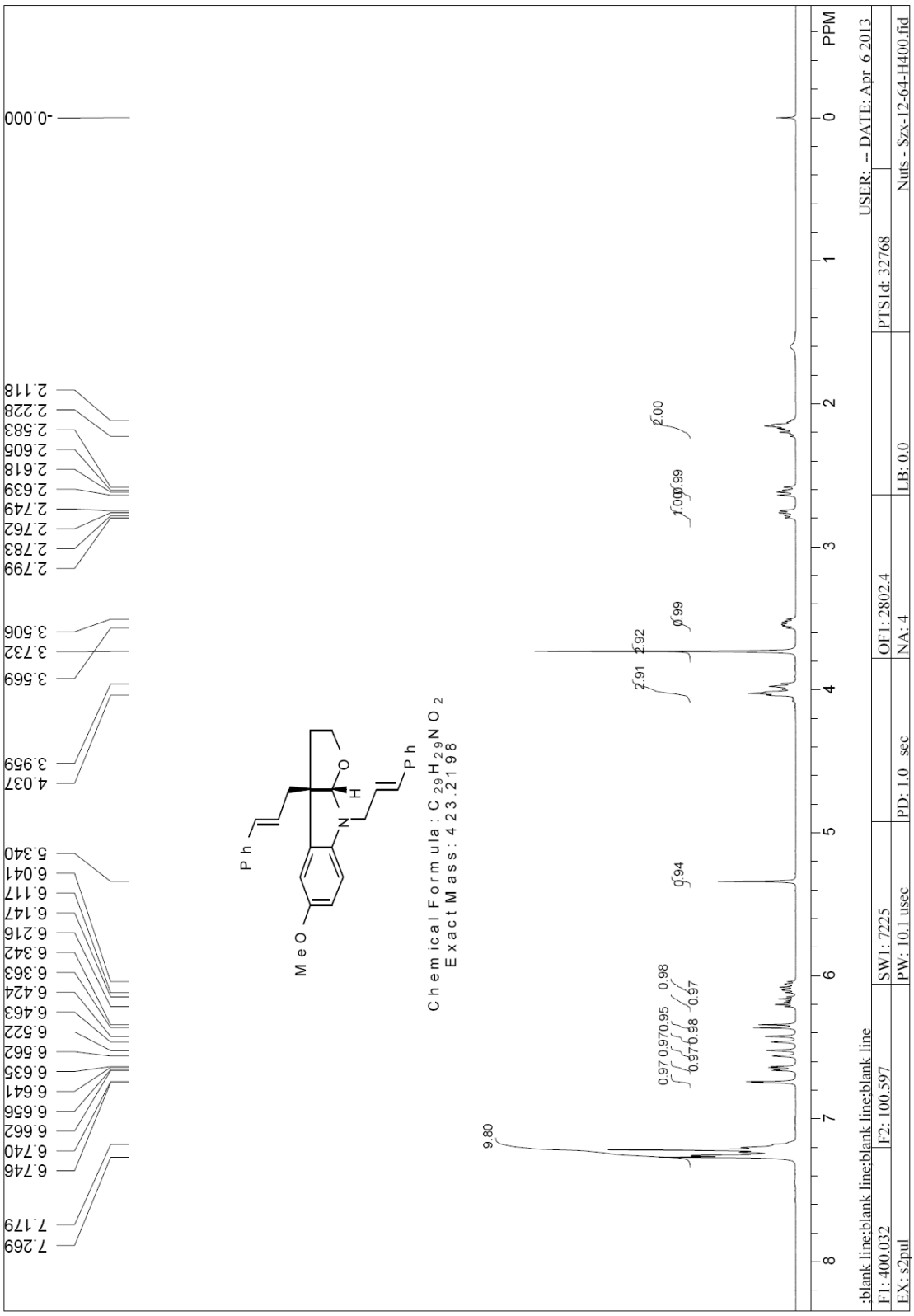


	RT (min)	Area (μV*sec)	% Area
1	14.716	28861592	50.05
2	18.755	28809458	49.95

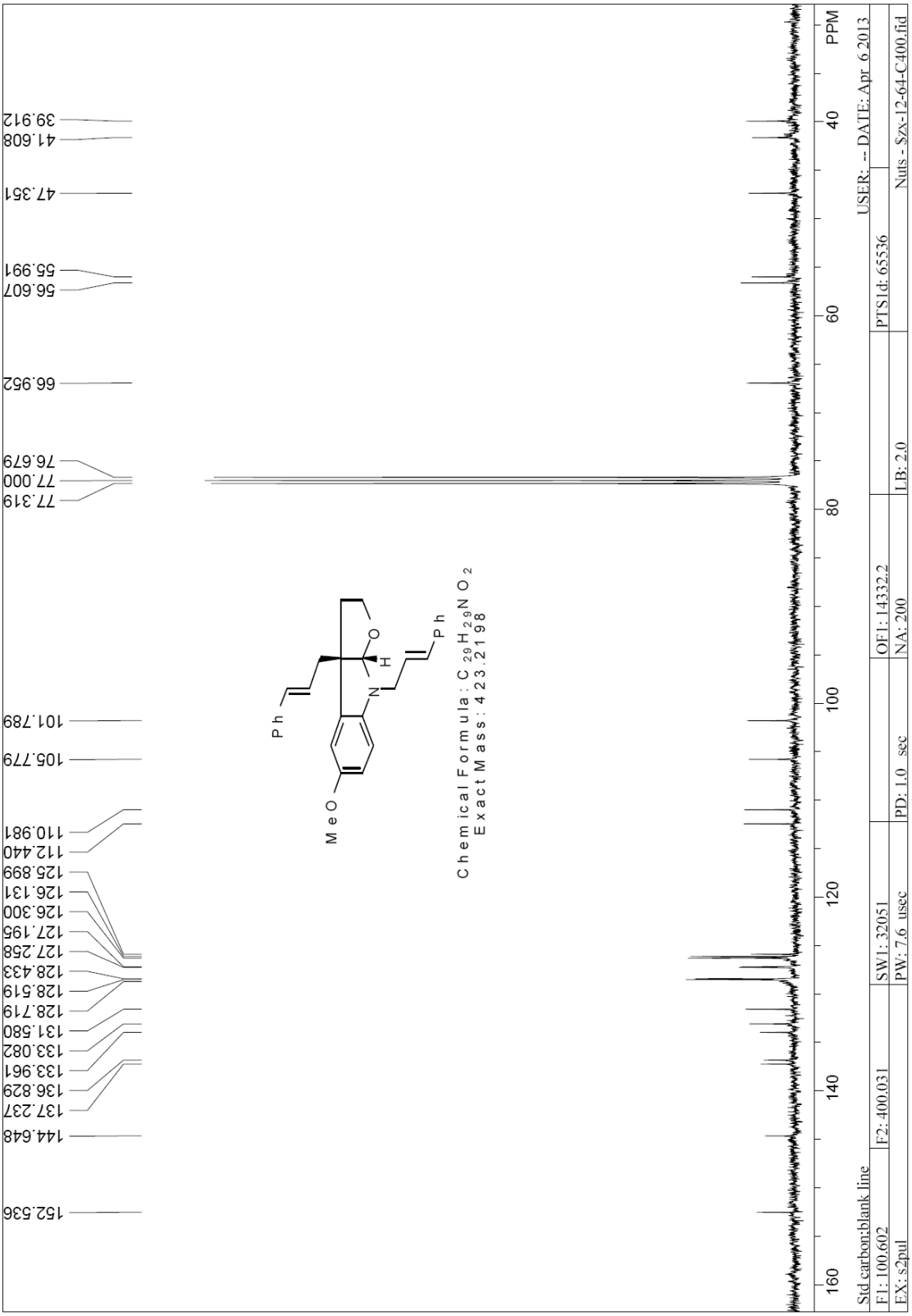


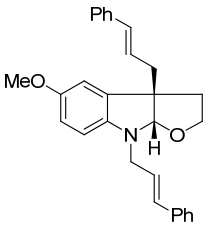
	RT (min)	Area (μV*sec)	% Area
1	15.003	12787952	96.88
2	19.059	411504	3.12

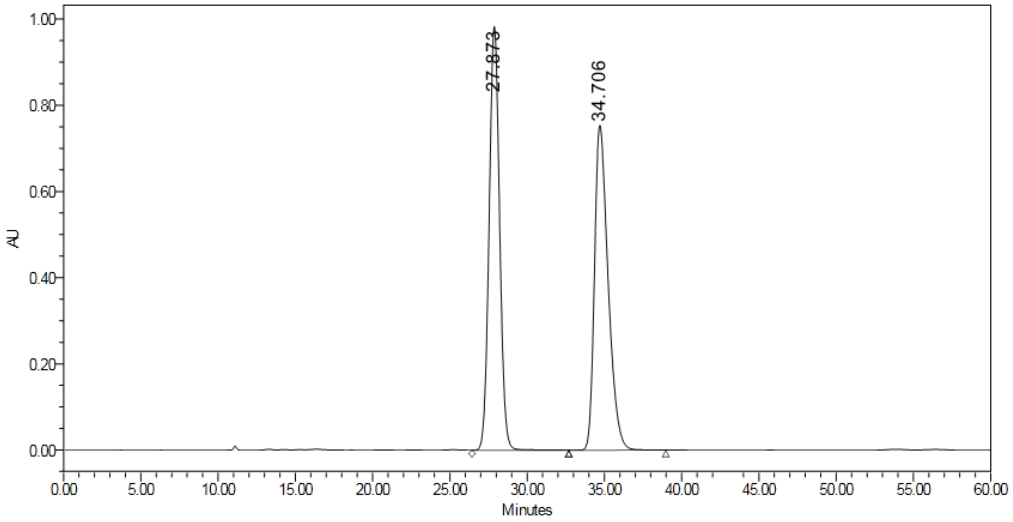
Compound **4da**'s ^{1}H NMR Spectra



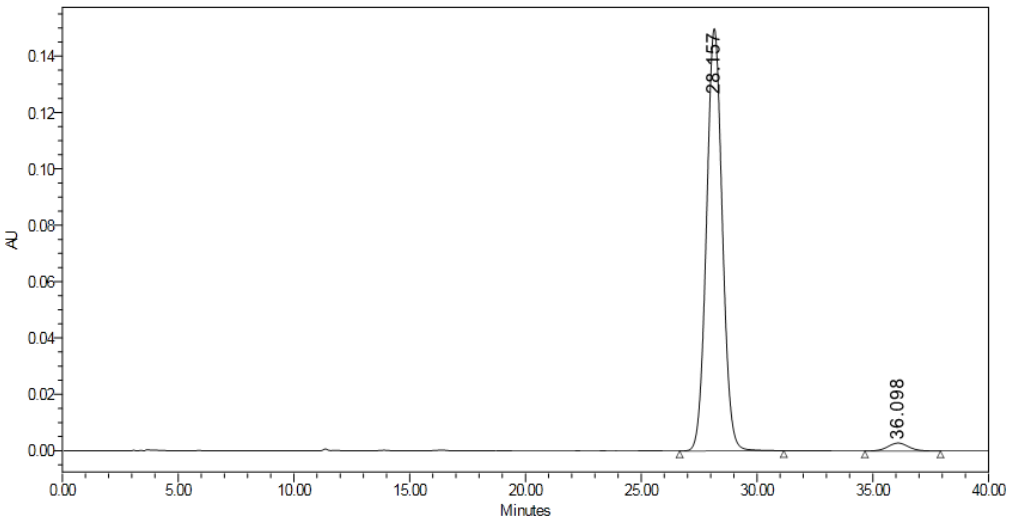
Compound **4da**'s ^{13}C NMR Spectra





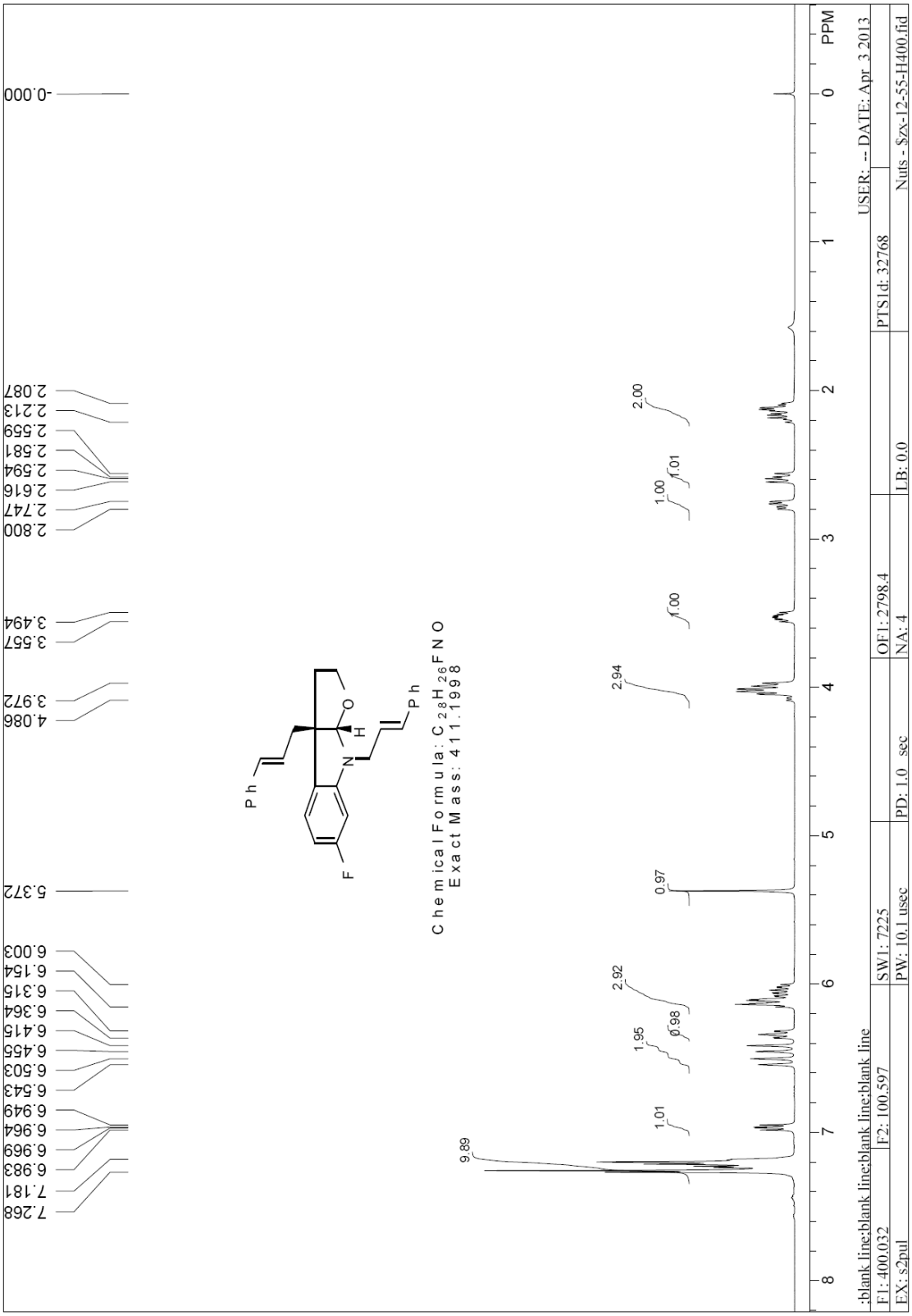


	RT (min)	Area (μV*sec)	% Area
1	27.873	46168421	50.00
2	34.706	46176519	50.00

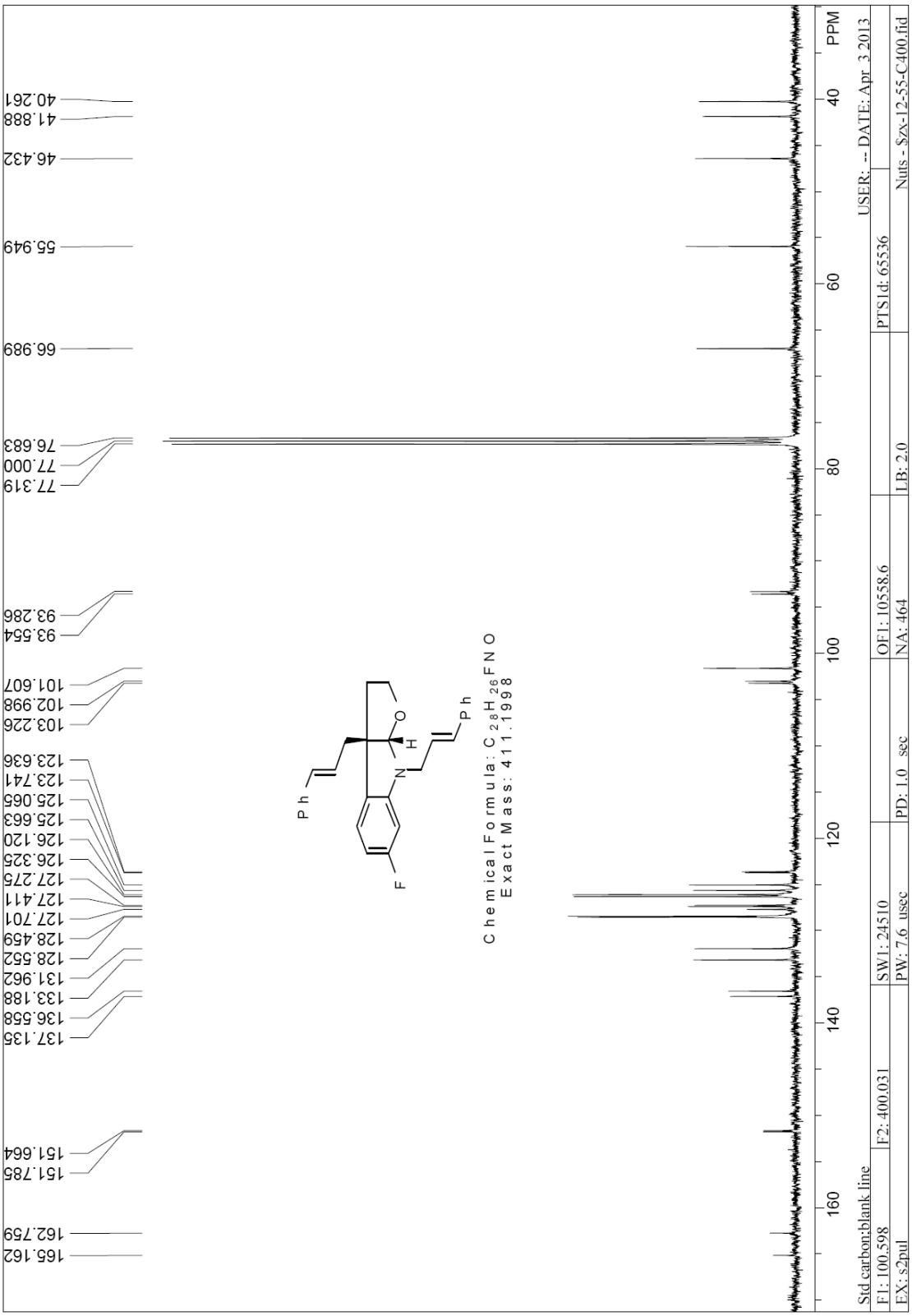


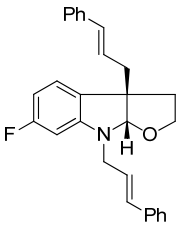
	RT (min)	Area (μV*sec)	% Area
1	28.157	7119307	97.64
2	36.098	172449	2.36

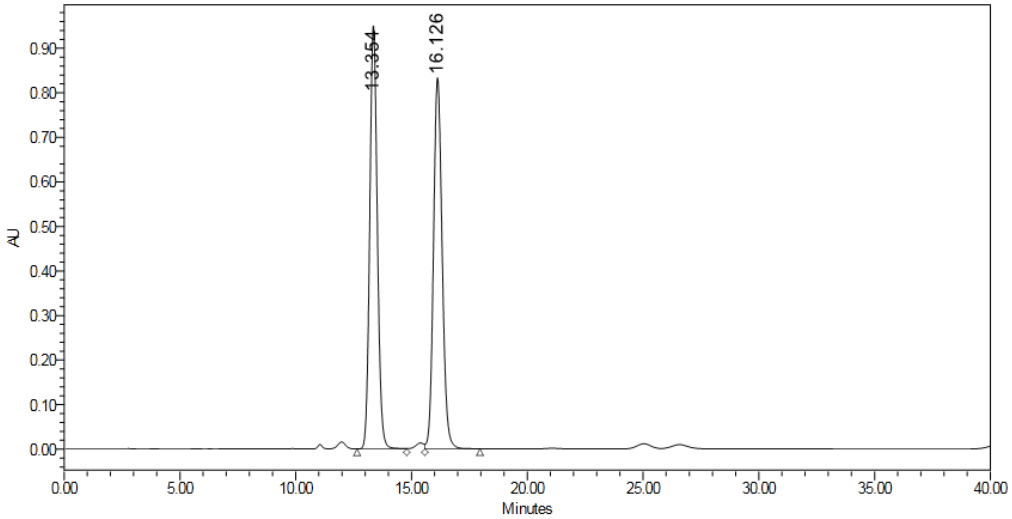
Compound **4ea**'s ^{1}H NMR Spectra



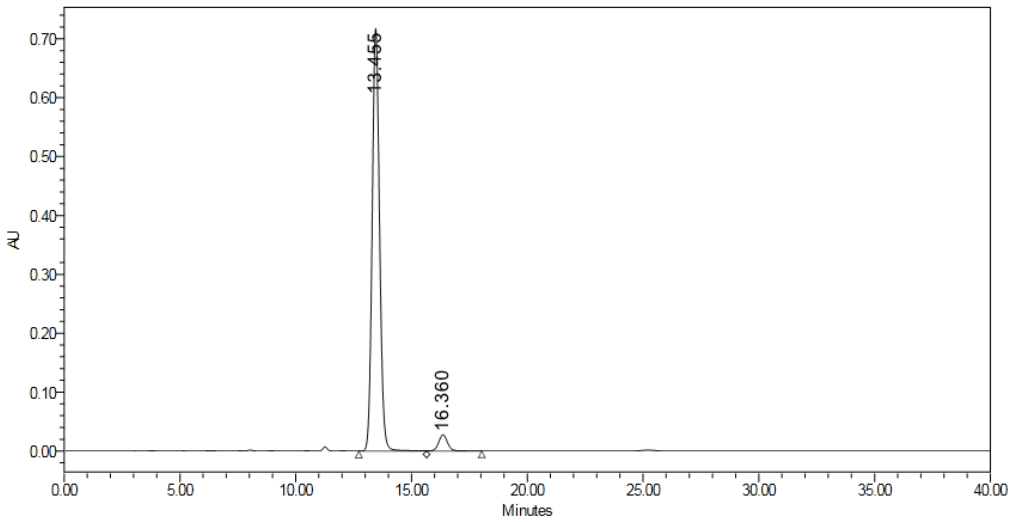
Compound **4ea**'s ^{13}C NMR Spectra





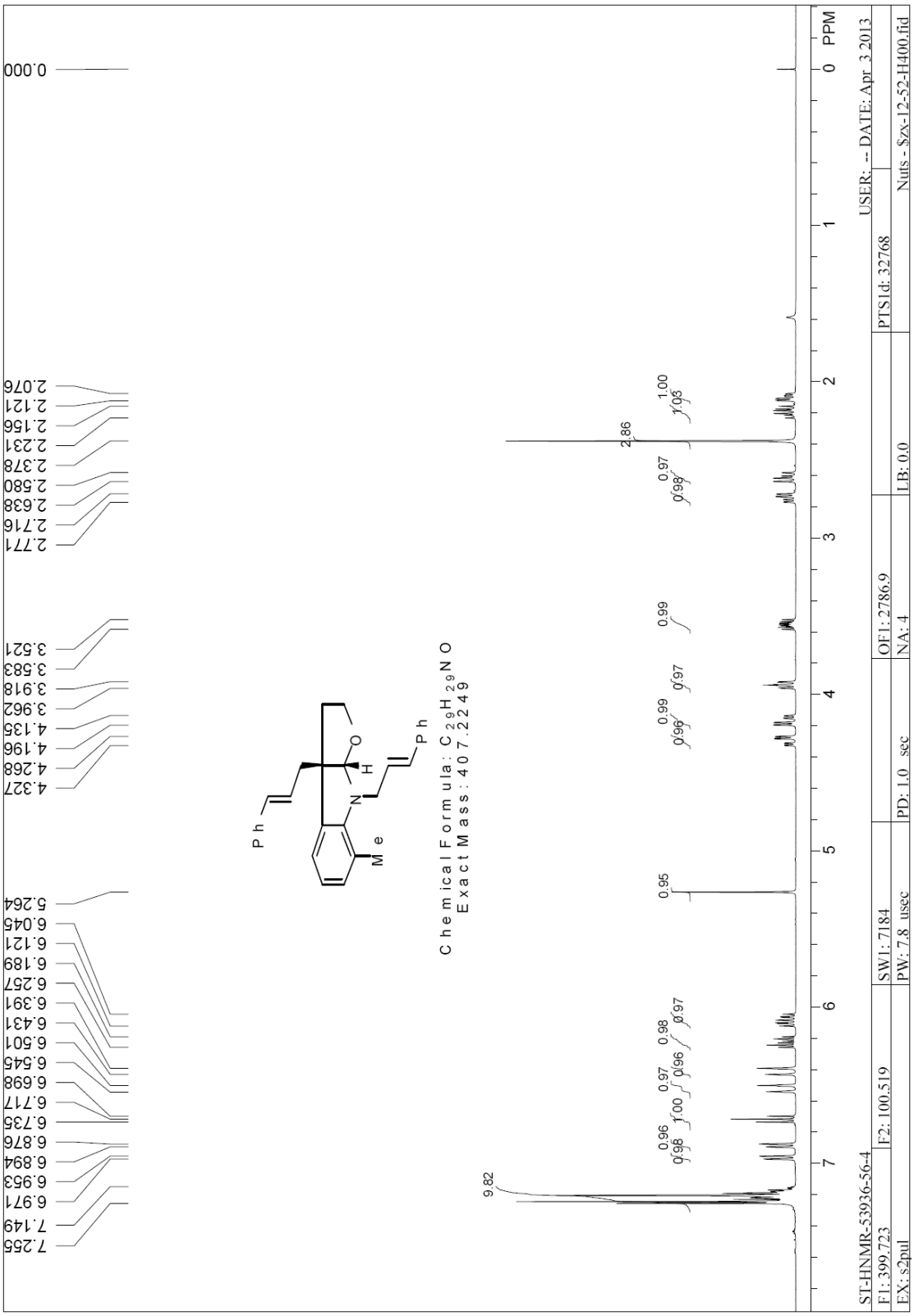


	RT (min)	Area (μV*sec)	% Area
1	13.354	21617009	49.95
2	16.126	21657225	50.05

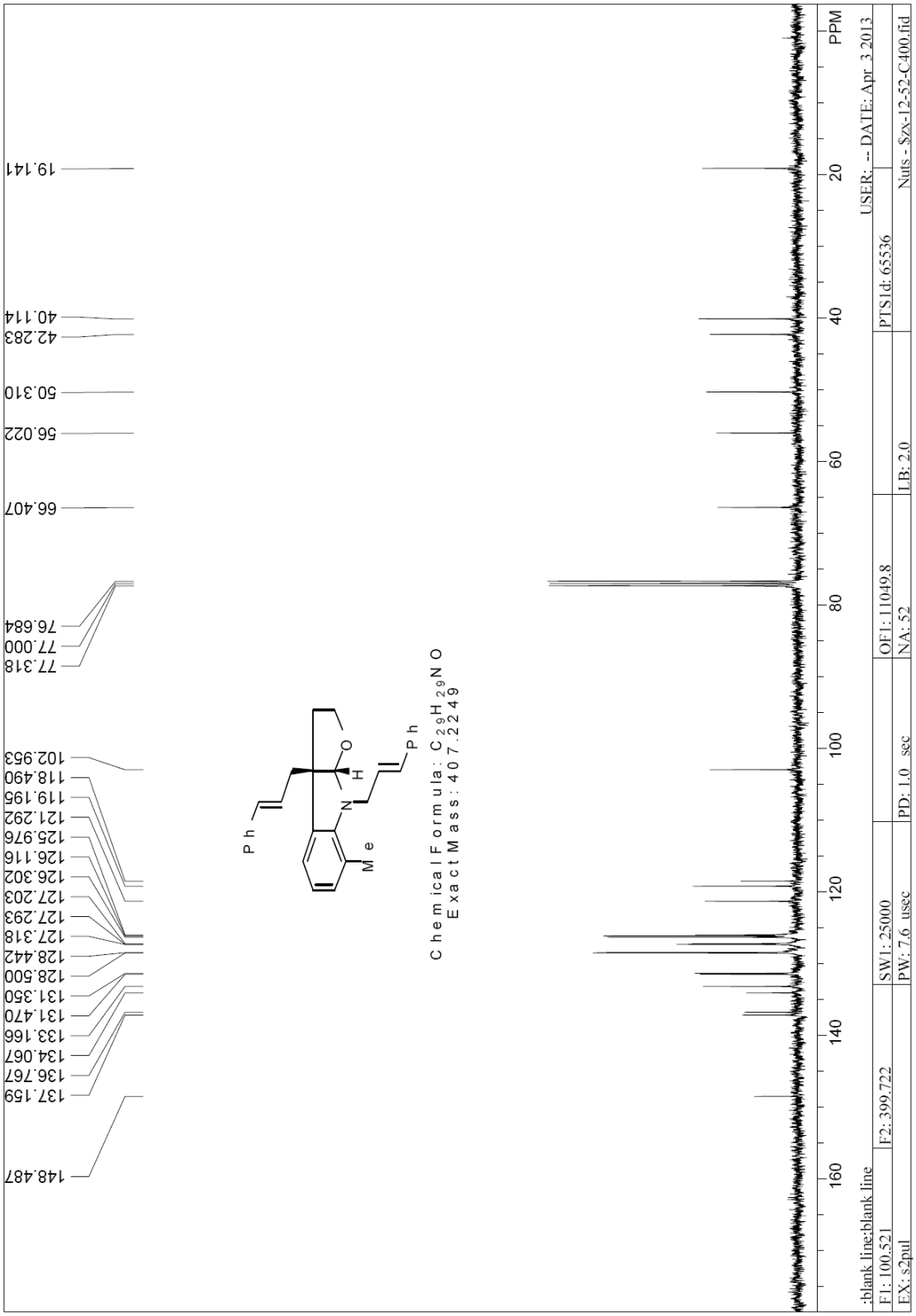


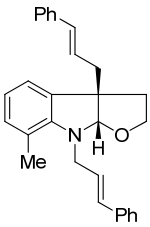
	RT (min)	Area (μV*sec)	% Area
1	13.455	15901995	95.57
2	16.360	736464	4.43

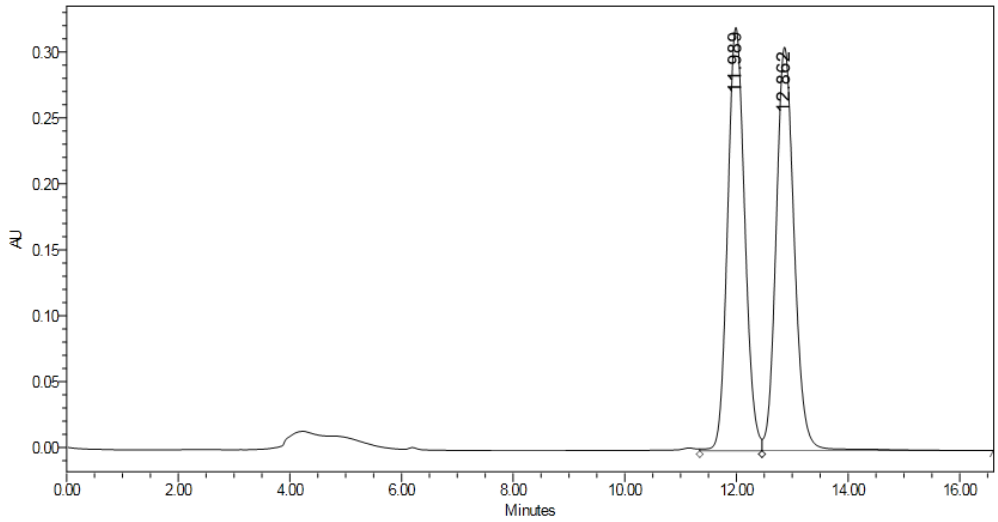
Compound **4fa**'s ^{1}H NMR Spectra



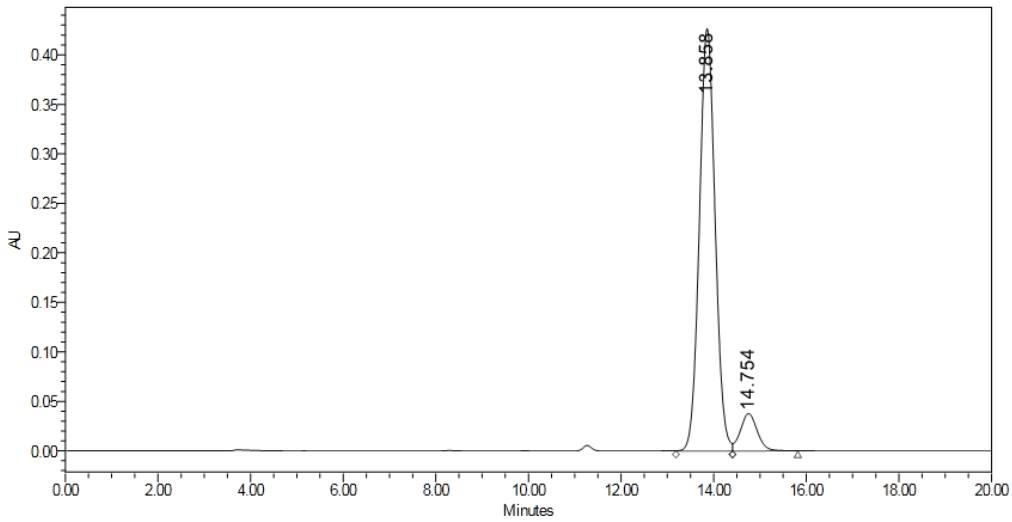
Compound **4fa**'s ^{13}C NMR Spectra





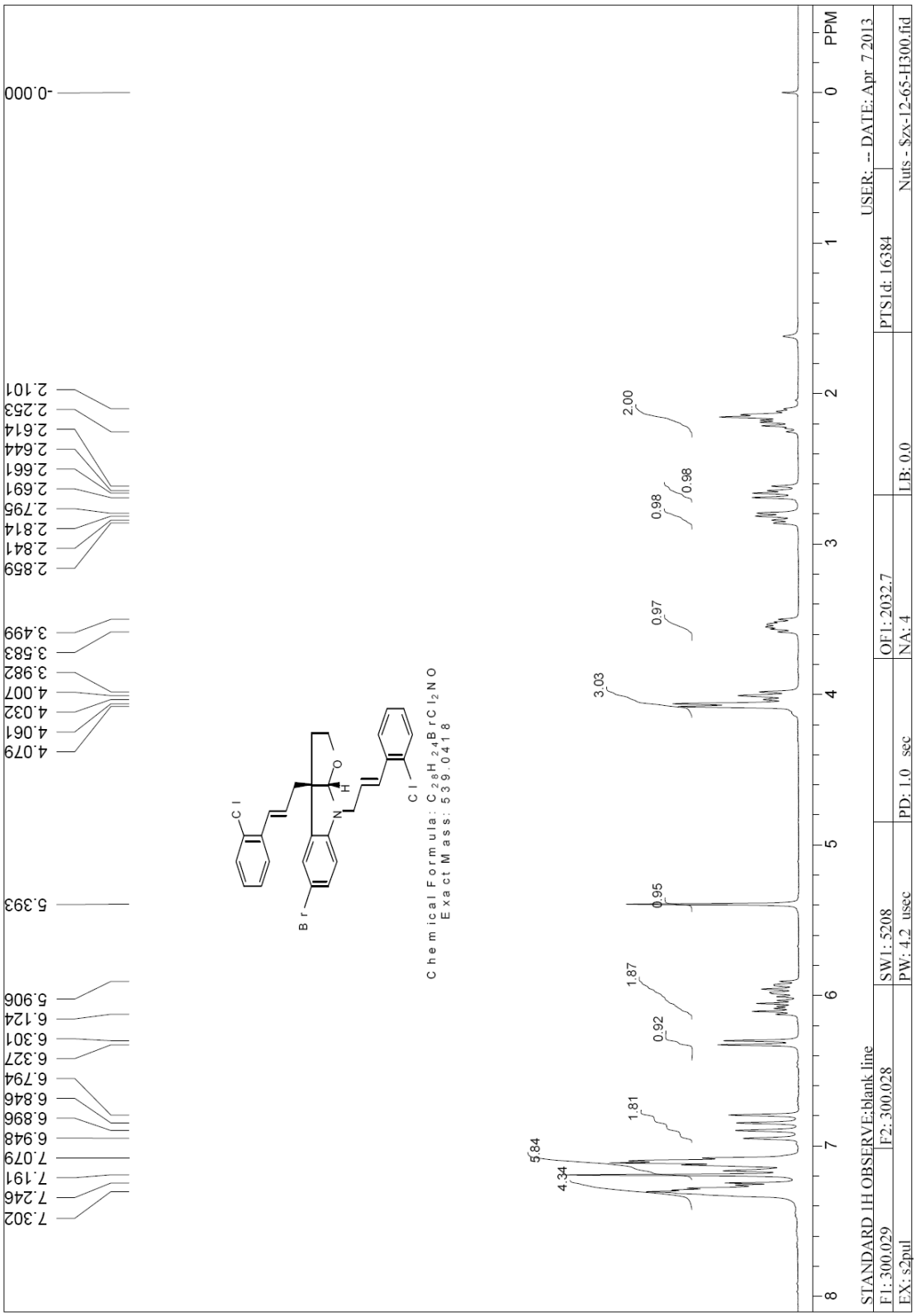


	RT (min)	Area (μV*sec)	% Area
1	11.989	6836705	49.66
2	12.862	6929806	50.34

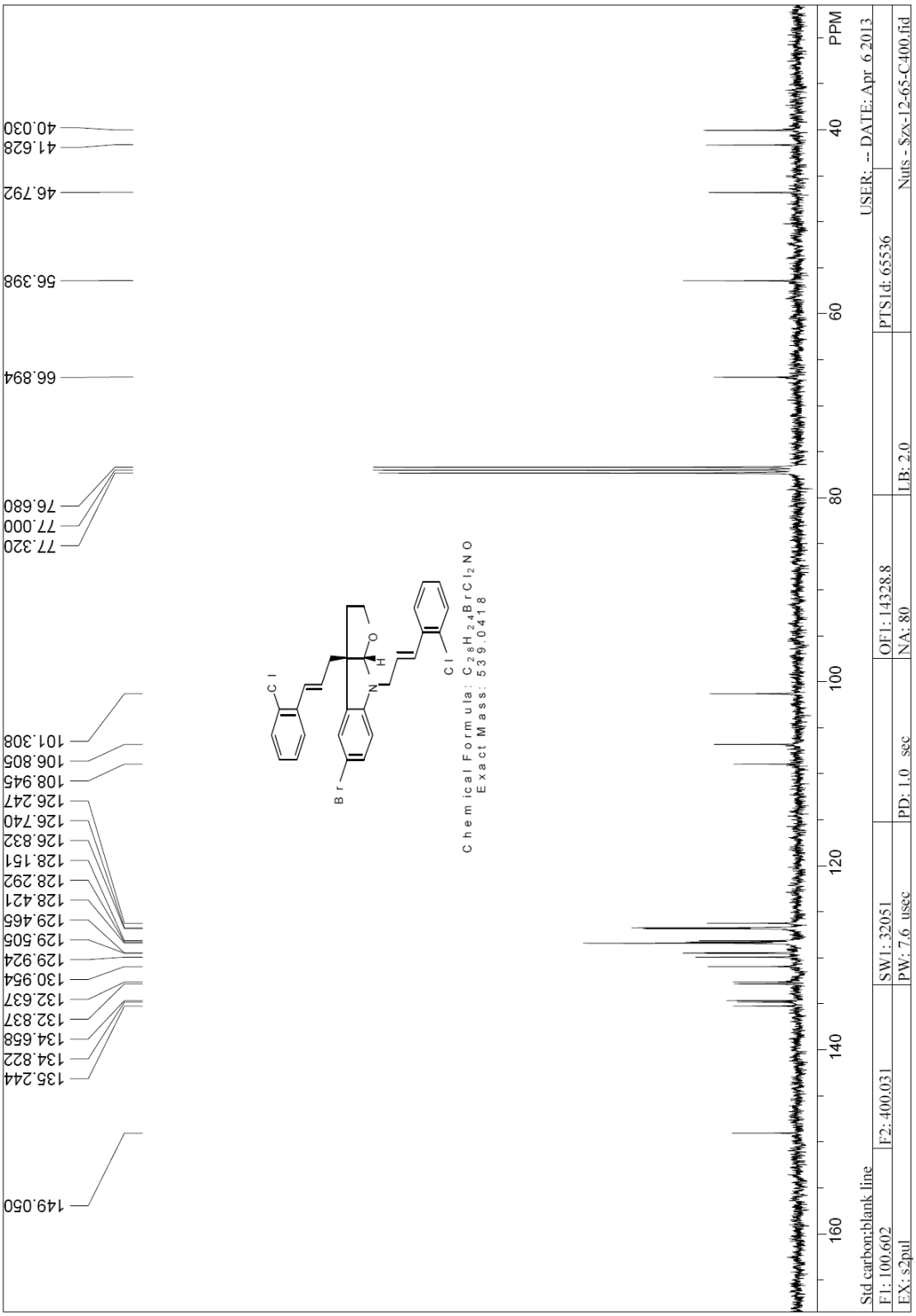


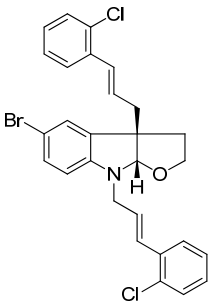
	RT (min)	Area (μV*sec)	% Area
1	13.858	10071358	91.39
2	14.754	948998	8.61

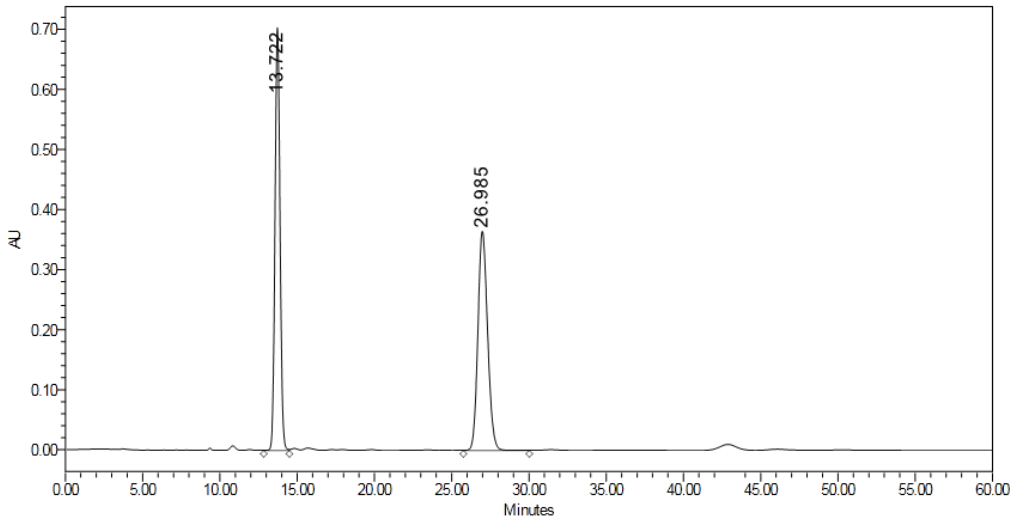
Compound **4ci**'s ^{1}H NMR Spectra



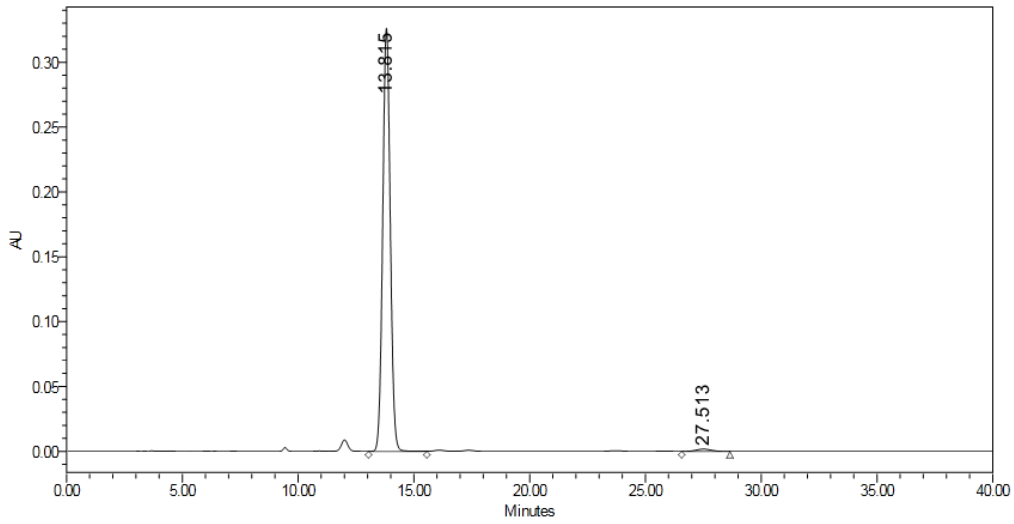
Compound **4ci**'s ^{13}C NMR Spectra





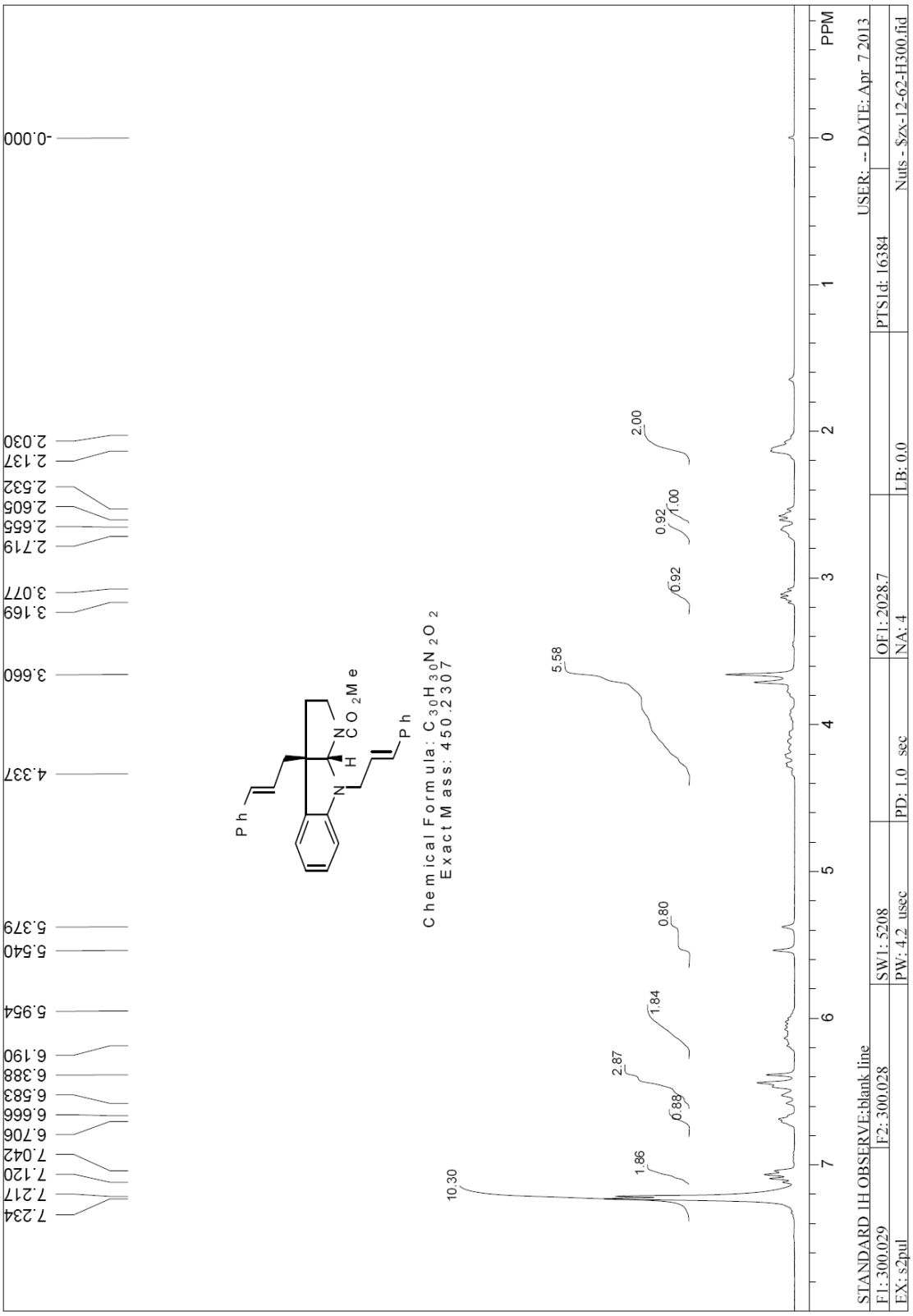


	RT (min)	Area (μV*sec)	% Area
1	13.722	15849786	49.96
2	26.985	15874520	50.04

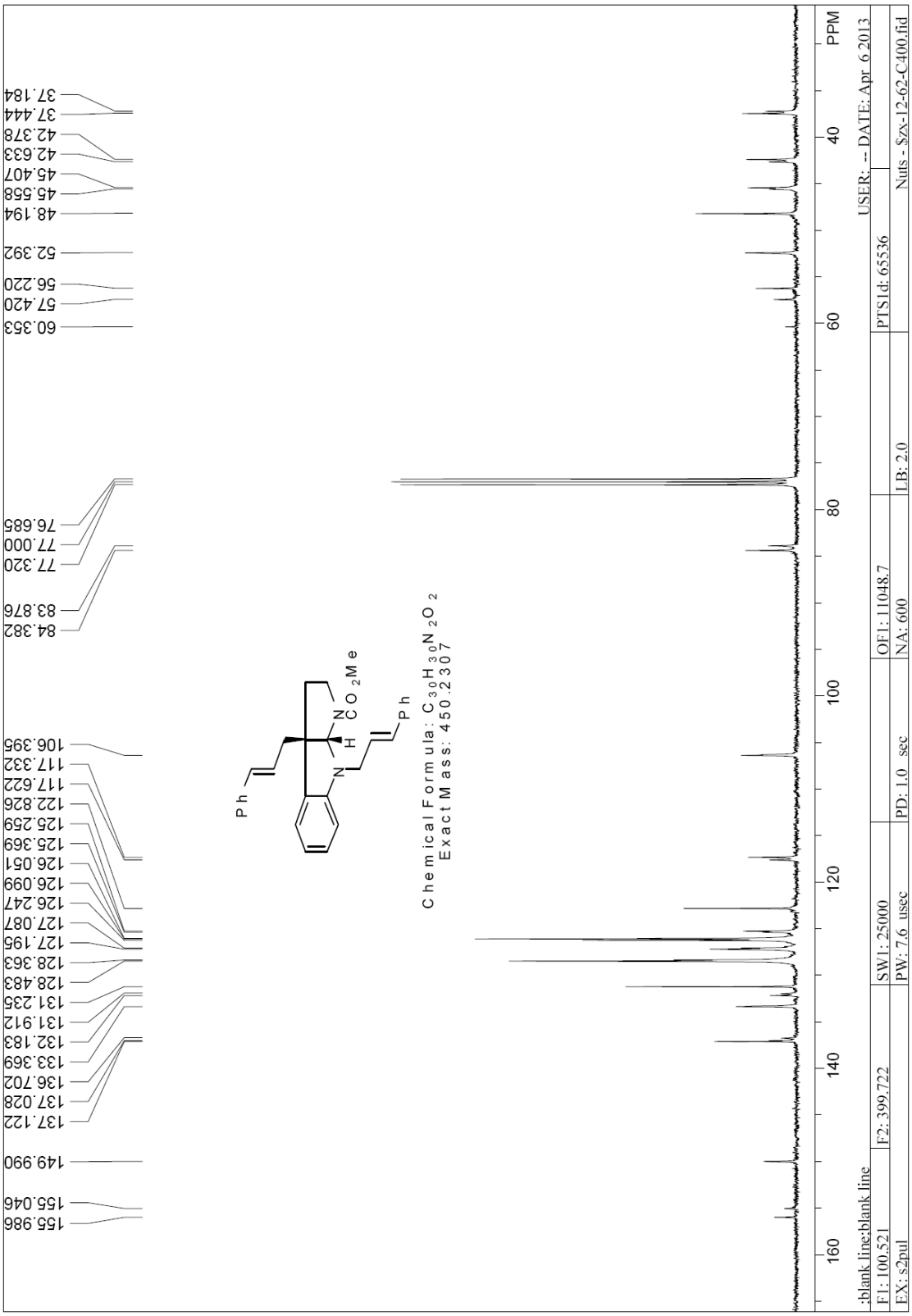


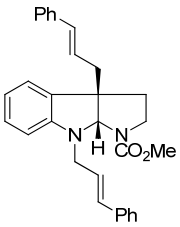
	RT (min)	Area (μV*sec)	% Area
1	13.815	7392553	98.97
2	27.513	77083	1.03

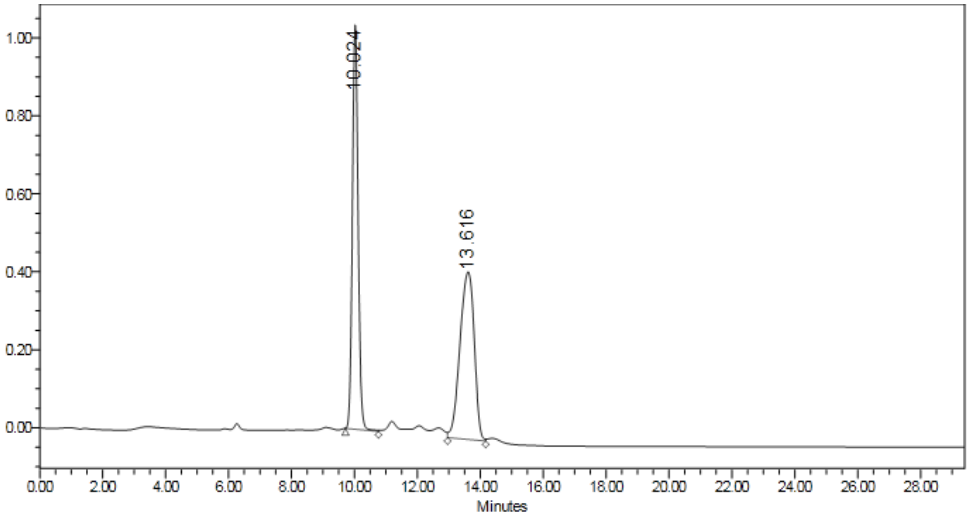
Compound **4ga**'s ^{1}H NMR Spectra



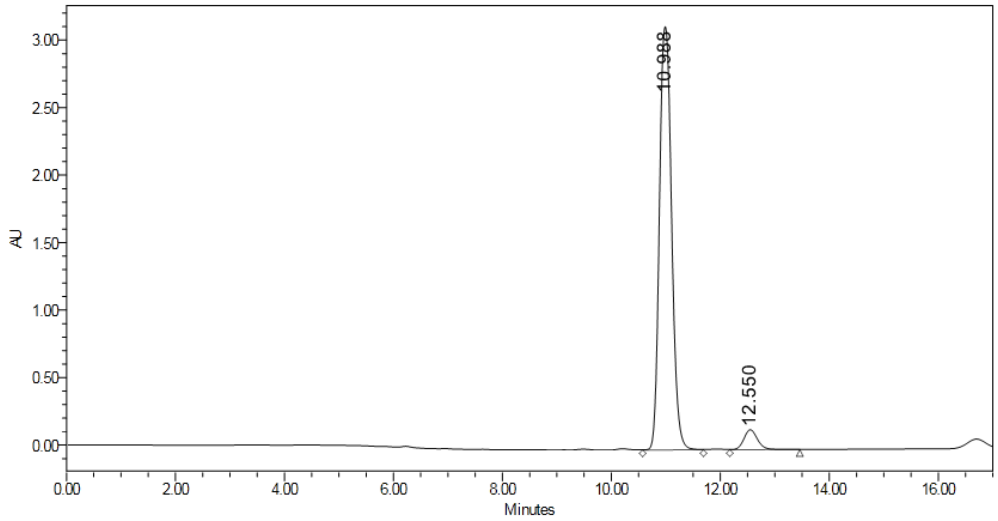
Compound **4ga**'s ^{13}C NMR Spectra





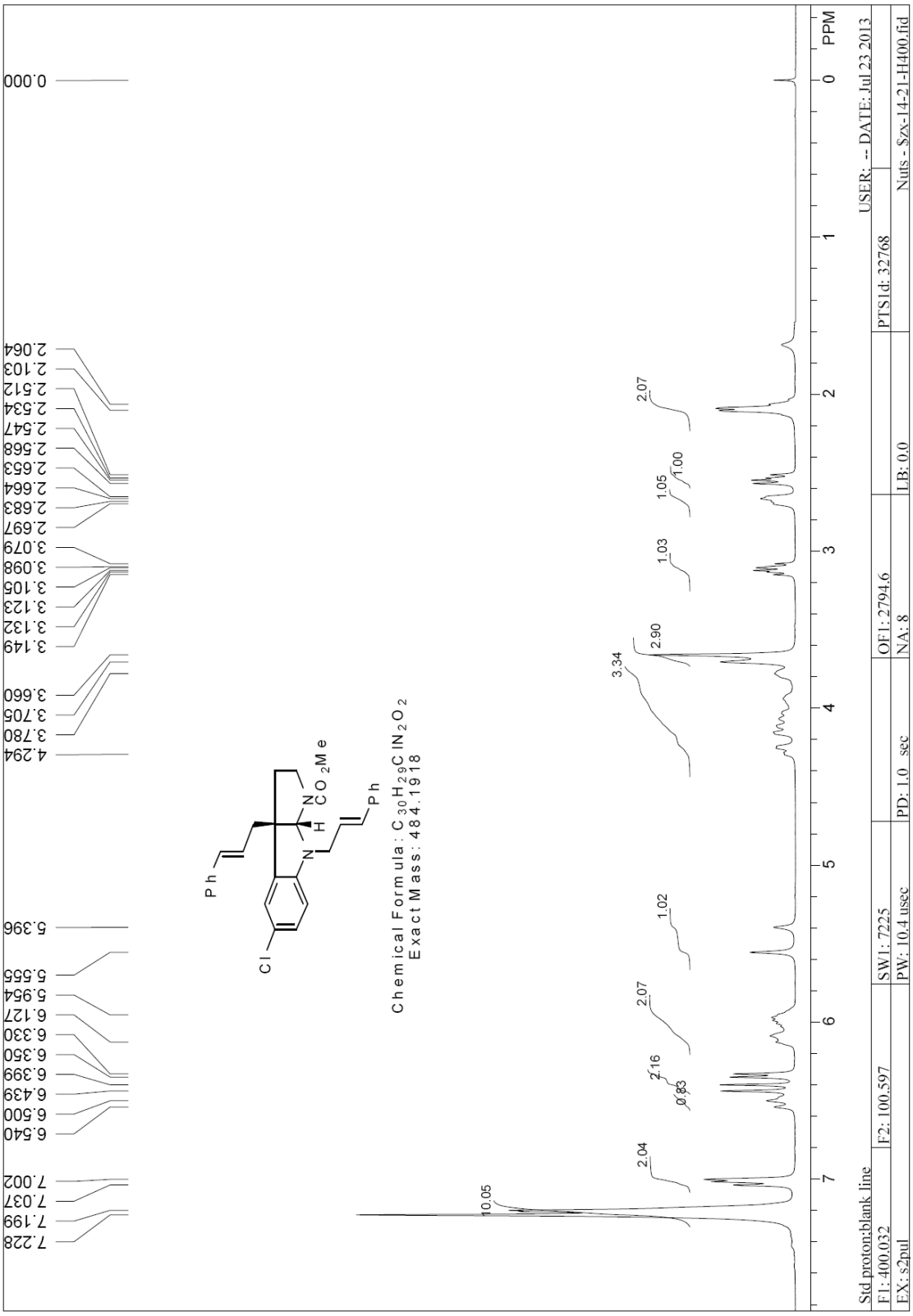


	RT (min)	Area (μV*sec)	% Area
1	10.024	13097253	49.17
2	13.616	13541732	50.83

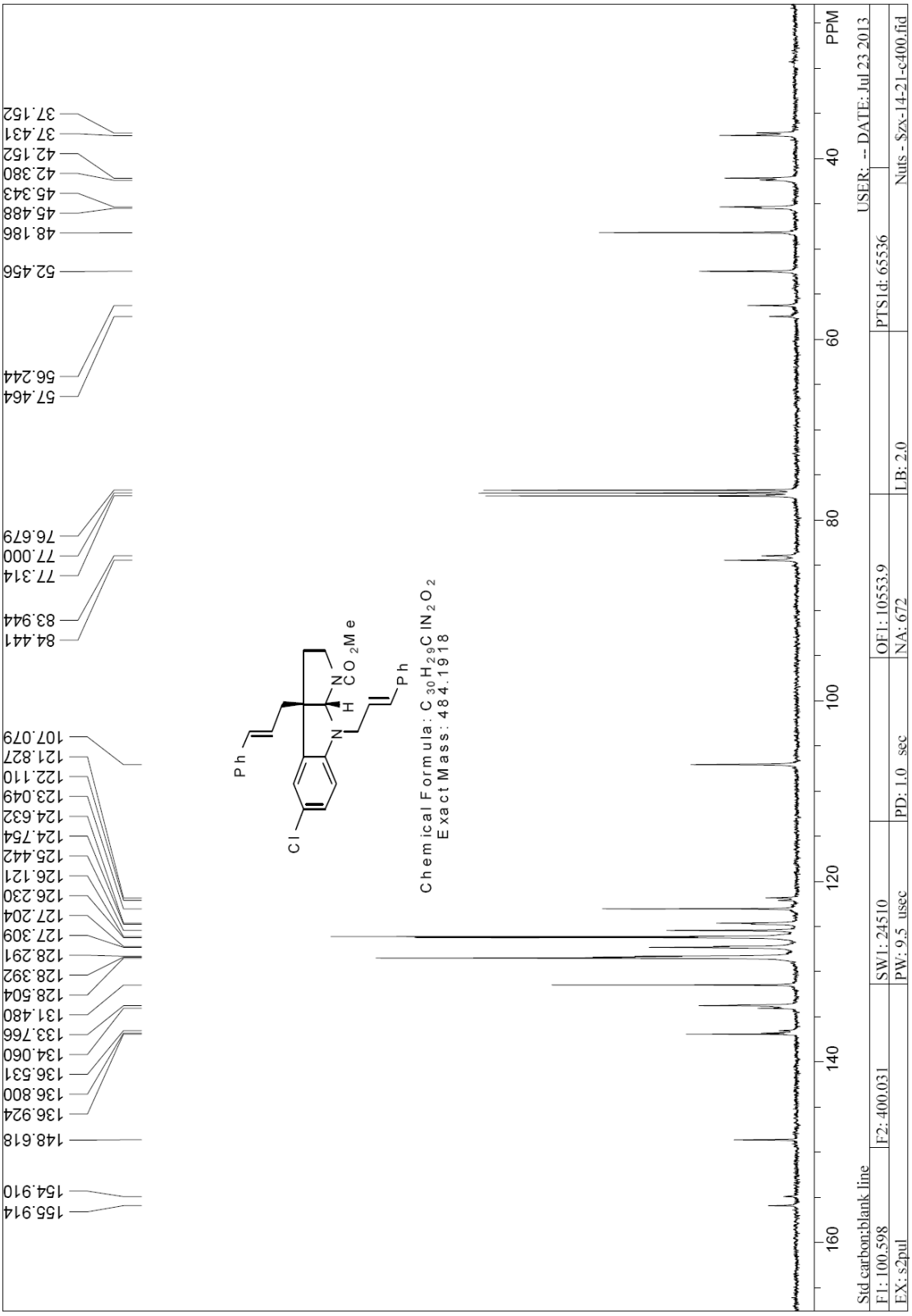


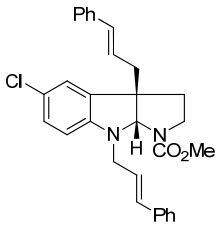
	RT (min)	Area (μV*sec)	% Area
1	10.988	48464867	95.04
2	12.550	2530103	4.96

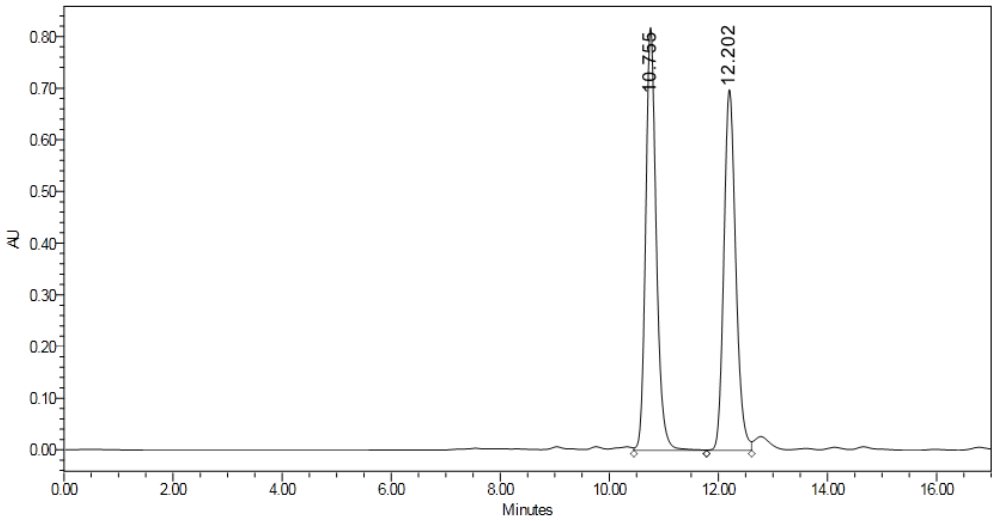
Compound **4ha**'s ^{1}H NMR Spectra



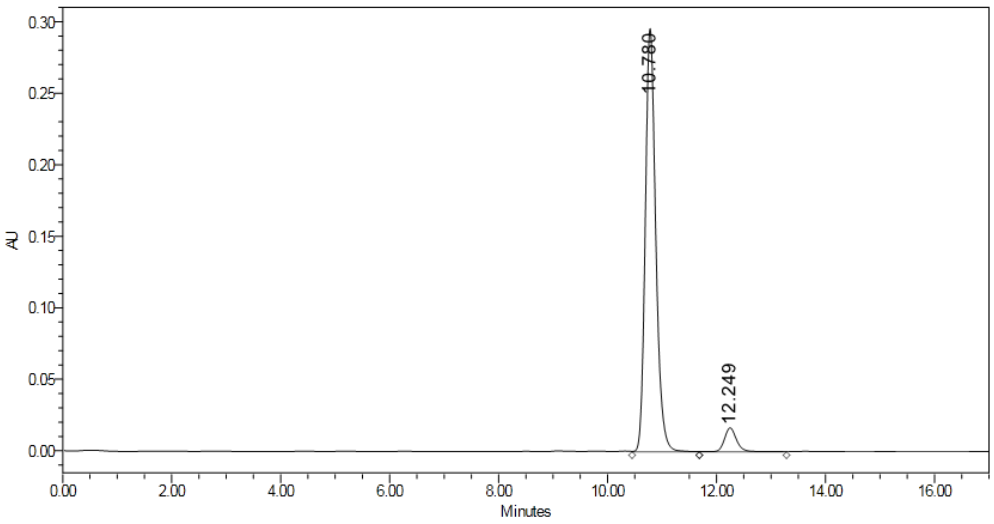
Compound **4ha**'s ^{13}C NMR Spectra





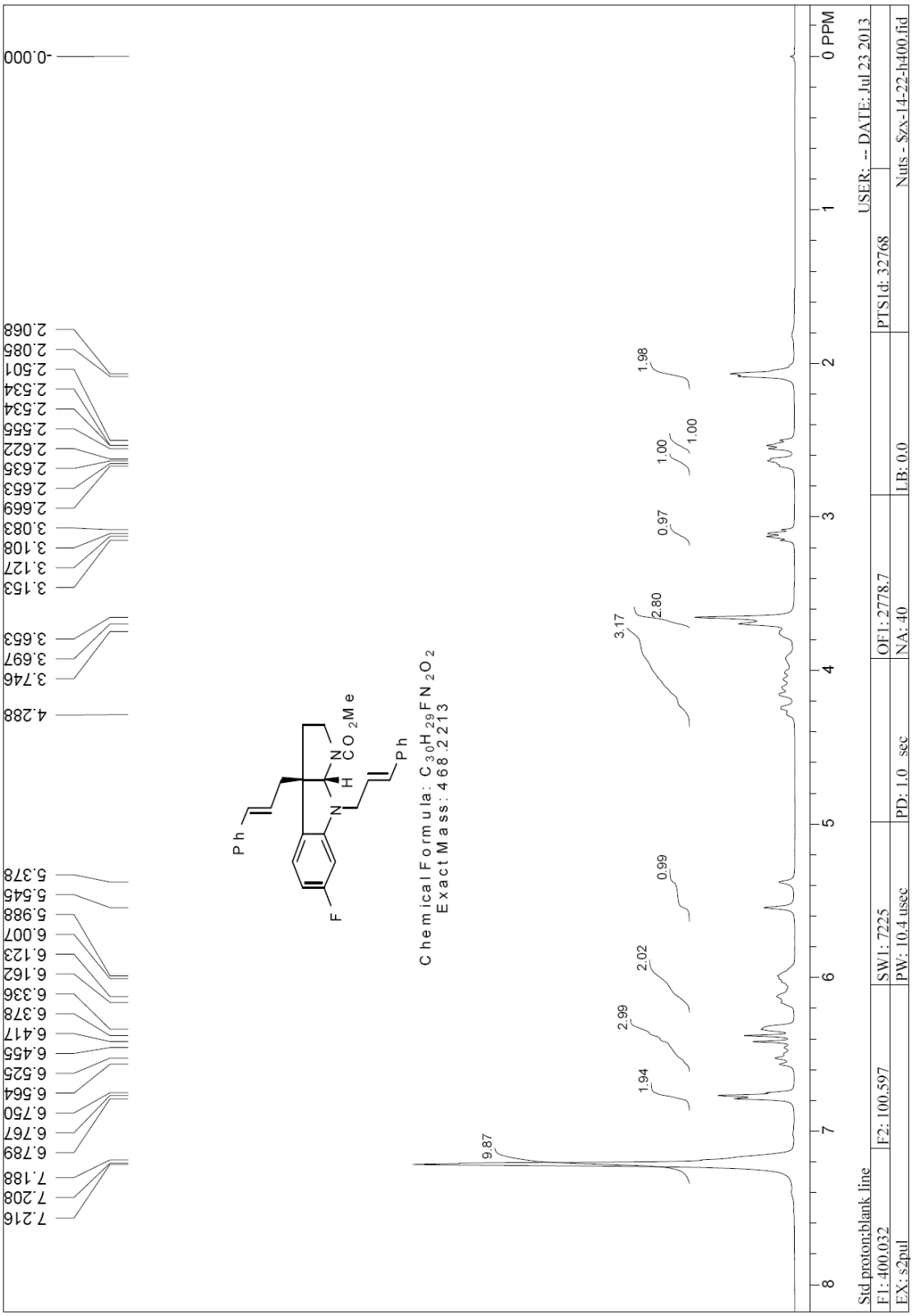


	RT (min)	Area (μV*sec)	% Area
1	10.755	11041804	51.05
2	12.202	10586031	48.95

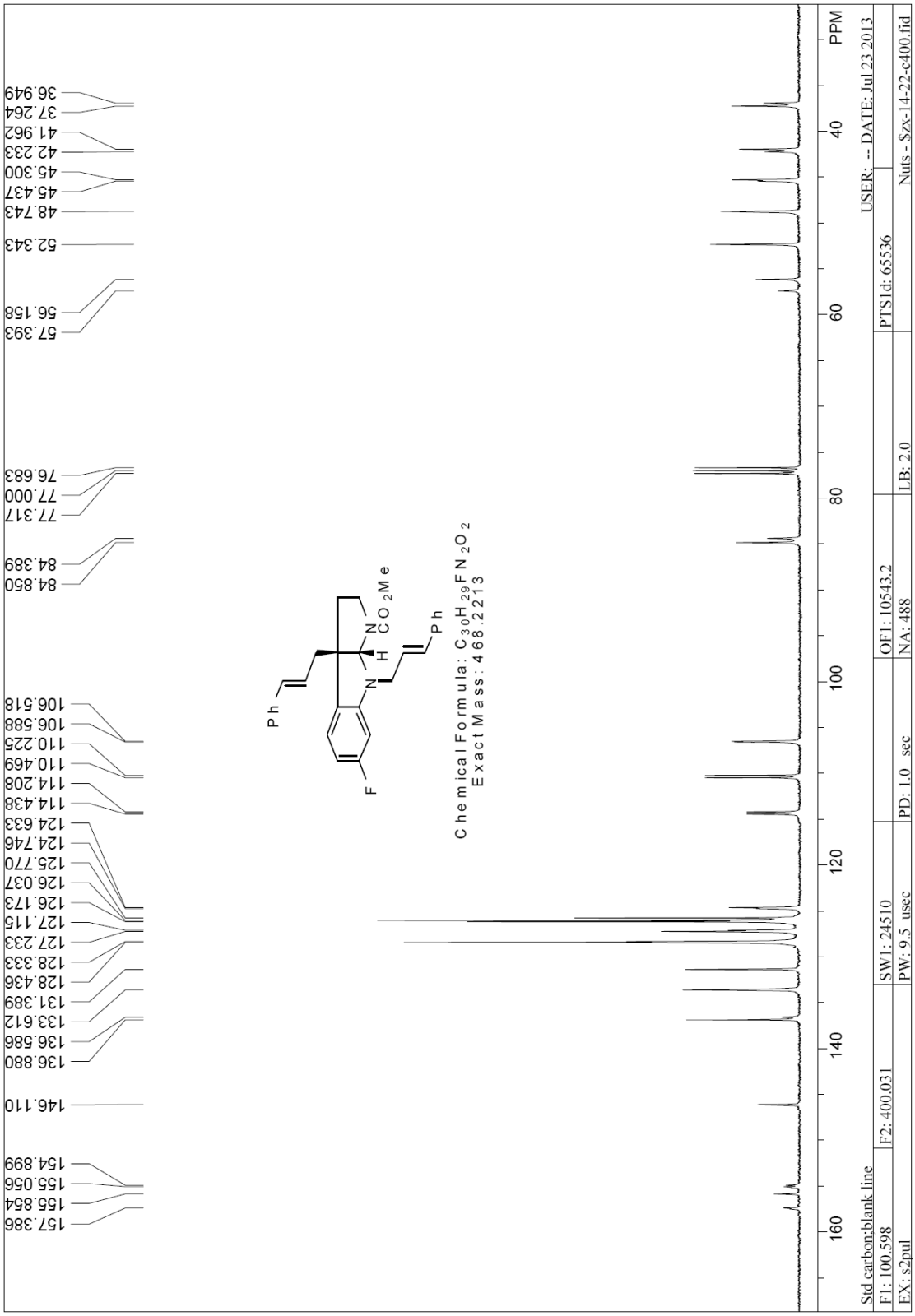


	RT (min)	Area (μV*sec)	% Area
1	10.780	3946302	93.86
2	12.249	258241	6.14

Compound **4ia**'s ^{1}H NMR Spectra



Compound **4ia**'s ^{13}C NMR Spectra



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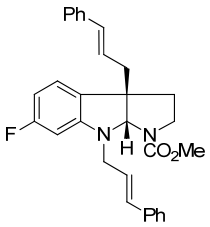
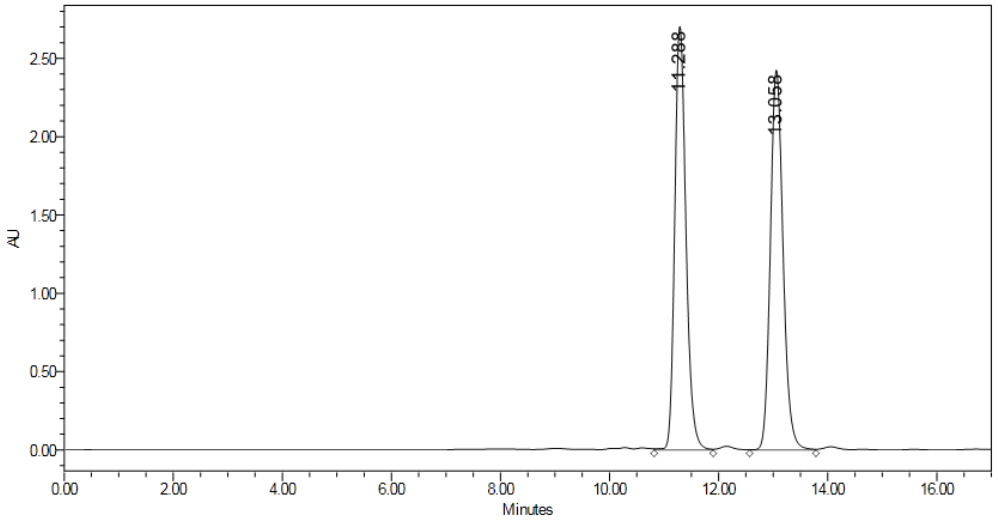
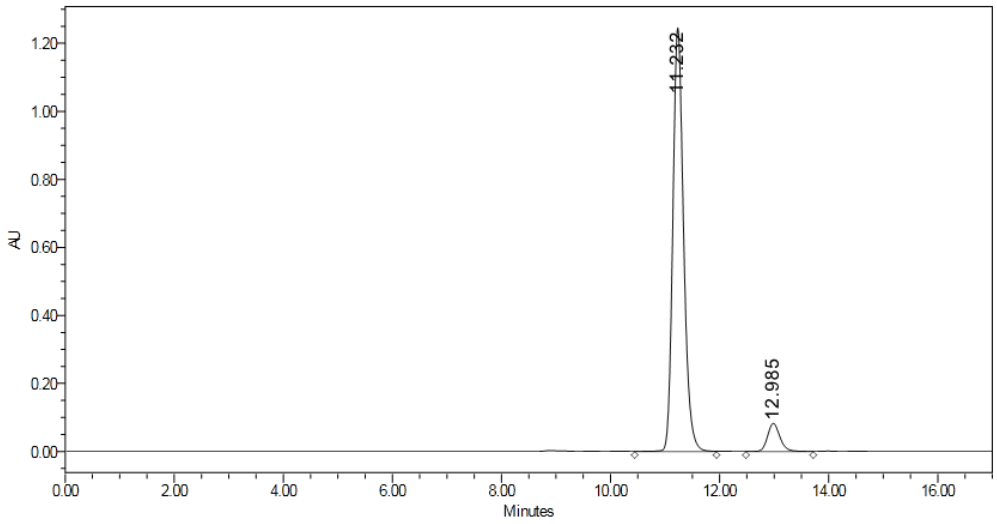


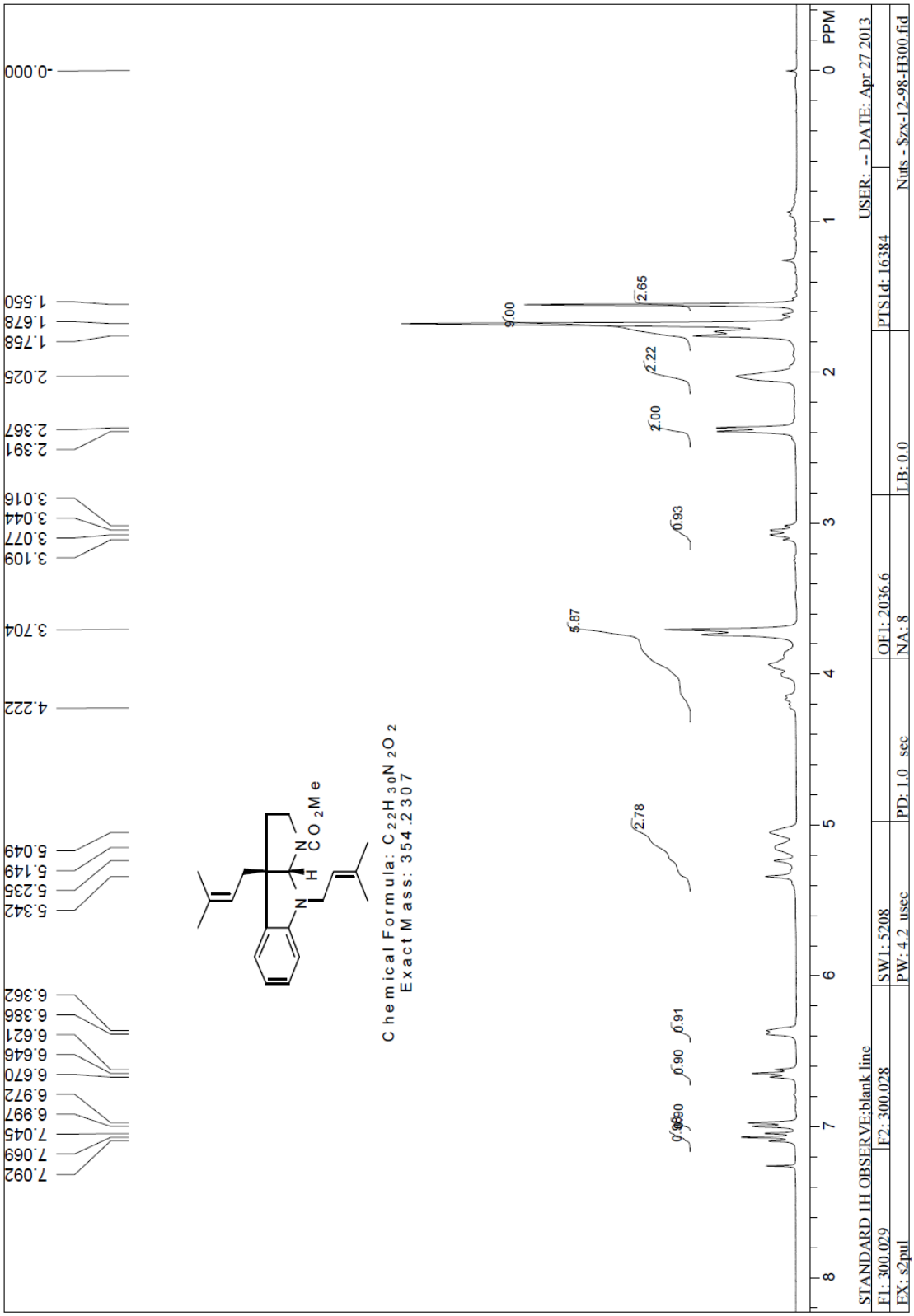


	RT (min)	Area (μV*sec)	% Area
1	11.288	38665031	49.61
2	13.058	39268850	50.39



	RT (min)	Area (μV*sec)	% Area
1	11.232	17075103	92.85
2	12.985	1314498	7.15

Compound **5ga**'s ^{1}H NMR Spectra



(-)-**debromoflustramine B**'s ^{1}H NMR Spectra