Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


*Supporting Information for*

# Enantioselective Synthesis of 4,5,6,7-Tetrahydroindoles *via* Olefin Cross-Metathesis/Intramolecular Friedel–Crafts Alkylation Reaction of Pyrroles

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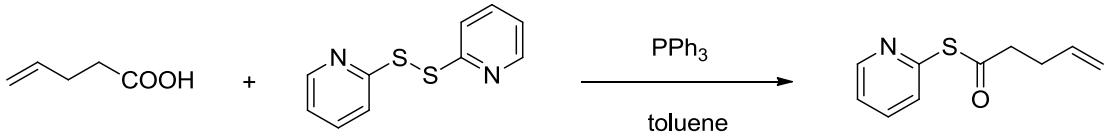
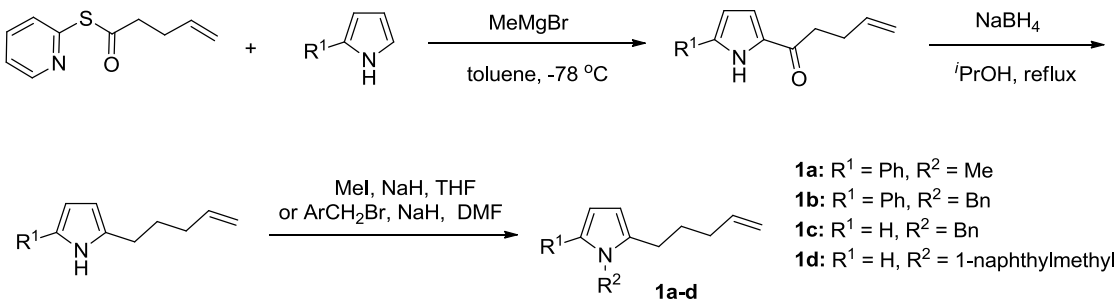
**General Methods**. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protonic solvent signals. 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).

## Experimental Sections:

### General procedure for preparation of 1a-d




A dry three-necked flask was charged with 4-pentenoic acid (20 g, 200 mmol, 1.0 equiv), toluene (300 mL), 2, 2'-dithiodipyridine (52.8 g, 240 mmol, 1.2 equivs) and triphenylphosphine (62.9 g, 240 mmol, 1.2 equivs). The mixture was then stirred at room temperature for 1 hour. When the reaction was complete (monitored by TLC), the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 10: 1) to afford S-pyridin-2-yl pent-4-enethioate (20.4 g, 53% yield).

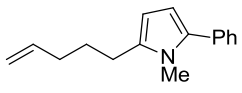



MeMgBr (1.5 equivs, 3M in $Et_2O$) was added dropwise to a solution of pyrrole

or 2-phenyl pyrrole (1.0 equiv, 0.1 M) in toluene at -78 $^{o}$C in a dry three-necked flask. After the reaction was stirred at room temperature for 1 hour, S-pyridin-2-yl pent-4-enethioate (1.5 equiv, 1.0 mol/L) in toluene was added slowly to the reaction mixture at -78 $^{o}$C. Then the reaction mixture was stirred at room temperature. When the reaction was complete (monitored by TLC), it was quenched by saturated $NH_4Cl$ (aq.) at 0 $^{o}$C and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, and filtered. After the solvent was removed under reduced pressure, the residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 50: 1) to afford acylated pyrrole.

The acylated pyrrole was dissolved in $^{i}$PrOH (0.5 mol/L), and then sodium borohydride (2.0 equiv) was added. The reaction mixture was refluxed until pyrrole was fully consumed (monitored by TLC). After the solvent was evaporated under reduced pressure, the crude product was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 50: 1) to afford the alkylated pyrrole.

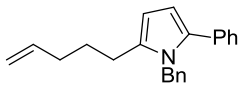
To a suspension of NaH (3.0 equivs) in THF (0.1 M) or DMF (0.1 M) in a dry three-necked flask was added alkylated pyrrole (1.0 equiv) in THF or DMF slowly at 0 $^{o}$C. After the mixture was stirred at room temperature for 1 hour, MeI (3.0 equivs) or $ArCH_2Br$ (1.5 equivs) was added dropwise at 0 $^{o}$C. The reaction was stirred at room temperature until alkylated pyrrole was fully consumed (monitored by TLC). It was quenched by water at 0 $^{o}$C and extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. After the solvent was removed under reduced pressure, the residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 1/100-1/500) to afford **1a-d**.




**1-Methyl-2-(pent-4-en-1-yl)-5-phenyl-1H-pyrrole (1a)**

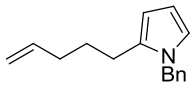
Yellow liquid (1.2 g, 22% yield over three steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/100, v/v). Analytical data for **1a**: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.74-1.84 (m, 2H), 2.21 (dt, $J_1$ = 6.9 Hz, $J_2$ = 7.5 Hz, 2H), 2.62 (t, $J$ = 8.1 Hz, 2H), 3.51 (s, 3H), 5.02 (d, $J$ = 10.2 Hz, 1H), 5.07 (d, $J$ = 17.1 Hz, 1H), 5.82-5.91 (m, 1H), 5.97 (d, $J$ = 3.3 Hz, 1H), 6.15 (d, $J$ = 3.6 Hz, 1H),

7.23-7.30 (m, 1H), 7.35-7.38 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 26.4, 27.7, 31.6, 33.5, 105.3, 107.4, 114.9, 126.4, 128.3, 128.7, 133.9, 134.1, 134.9, 138.4; IR (film) 2931, 1640, 1601, 1511, 1455, 1308, 992, 910, 749, 698 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{16}H_{20}N$ $(M+H)^+$ requires *m/z* 226.1590, found *m/z* 226.1594.



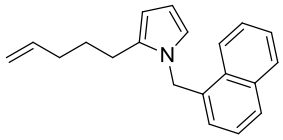

**1-Benzyl-2-(pent-4-en-1-yl)-5-phenyl-1H-pyrrole (1b)**

Yellow solid (276 mg, 10% yield over three steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/250, v/v). Analytical data for **1b**: m.p. = 43-44 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.68-1.75 (m, 2H), 2.08 (dt, $J_1$ = 6.9 Hz, $J_2$ = 7.2 Hz, 2H), 2.43 (t, $J$ = 7.8 Hz, 2H), 4.92 (d, $J$ = 9.6 Hz, 1H), 4.97 (d, $J$ = 16.8 Hz, 1H), 5.13 (s, 2H), 5.71-5.76 (m, 1H), 6.07 (d, $J$ = 3.0 Hz, 1H), 6.25 (d, $J$ = 3.9 Hz, 1H), 6.90 (d, $J$ = 6.9 Hz, 2H), 7.20-7.31 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 26.0, 27.6, 33.4, 47.5, 106.0, 108.1, 114.7, 125.6, 126.6, 126.9, 128.3, 128.7, 128.8, 133.7, 134.5, 134.8, 138.4, 139.1; IR (film) 2931, 1601, 1495, 1450, 1360, 1312, 1074, 1027, 913, 749, 726, 698 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{22}H_{24}N$ $(M+H)^+$ requires *m/z* 302.1903, found *m/z* 302.1910.




**1-Benzyl-2-(pent-4-en-1-yl)-1H-pyrrole (1c)**

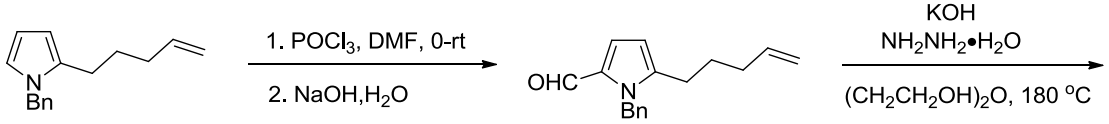
Yellow liquid (1.1 g, 22% yield over three steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/300, v/v). Analytical data for **1c**: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.61-1.71 (m, 2H), 2.07 (dt, $J_1$ = 7.2 Hz, $J_2$ = 6.9 Hz, 2H), 2.46 (t, $J$ = 7.5 Hz, 2H), 4.93 (d, $J$ = 9.9 Hz, 1H), 4.98 (d, $J$ = 16.8 Hz, 1H), 5.03 (s, 2H), 5.71-5.80 (m, 1H), 5.97 (s, 1H), 6.13 (t, $J$ = 3.0 Hz, 1H), 6.61 (s, 1H), 6.98 (d, $J$ = 7.5 Hz, 2H), 7.24-7.32 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 25.5, 27.9, 33.3, 50.2, 106.0, 107.1, 114.7, 120.8, 126.3, 127.3, 128.6, 133.2, 138.4, 138.5; IR (film) 2931, 2860, 1703, 1640, 1495, 1453, 1428, 1355, 1295, 1074, 1029, 992, 910, 695 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{16}H_{20}N$ $(M+H)^+$ requires *m/z* 226.1590, found *m/z* 226.1591.



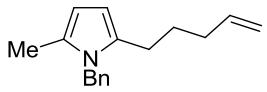
**1-(Naphthalen-1-ylmethyl)-2-(pent-4-en-1-yl)-1H-pyrrole (1d)**

Yellow liquid (400 mg, 18% yield over three steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/300, v/v). Analytical data for **1d**: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.63-1.73 (m, 2H), 2.03 (dt, $J_1$ = 6.9 Hz, $J_2$ = 7.5 Hz, 2H), 2.46 (t, $J$ = 7.8 Hz, 2H), 4.88 (d, $J$ = 11.1 Hz, 1H), 4.93 (d, $J$ = 17.7 Hz, 1H), 5.39 (s, 2H), 5.64-5.78 (m, 1H), 6.04 (m, 1H), 6.16-6.18 (m, 1H), 6.55-6.59 (m, 2H), 7.30 (t, $J$ = 7.8 Hz, 1H), 7.44-7.52 (m, 2H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.82-7.88 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 25.4, 27.8, 33.2, 47.8, 105.9, 107.2, 114.7, 120.9, 122.2, 123.7, 125.6, 125.7, 126.3, 127.7, 128.8, 130.2, 133.2, 133.3, 133.9, 138.2; IR (film) 2929, 2858, 1639, 1486, 1428, 1297, 1076, 991, 910, 791, 769, 702 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{20}H_{22}N$ $(M+H)^+$ requires *m/z* 276.1747, found *m/z* 276.1749.

**Procedure for preparation of 1e-f**




**1c**

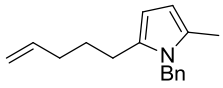



**1e**

92% yield

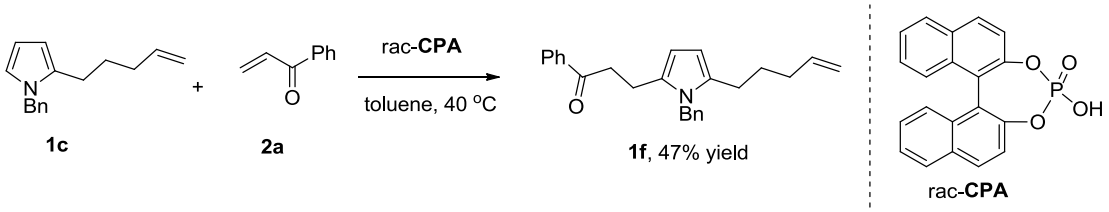
To a solution of **1c** (450 mg, 2 mmol) in DMF (10 mL) in a dry three-necked flask was added $POCl_3$ (367 mg, 2.4 mmol, 1.2 equiv) dropwise at 0 °C. After the reaction mixture was stirred at room temperature for 4 hours, it was slowly adjusted by the addition of saturated NaOH (aq.) to pH >7 at 0 °C. Then the reaction was stirred at 60 °C for 2 hours. After the reaction was complete (monitored by TLC), the mixture was extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and filtrated. The solvent was removed in vacuo to afford the crude product which was used in the next step without purification.

KOH (400 mg, 7.1 mmol) and hydrazine hydrate (2 mL, 80%) were added to a solution of 1-benzyl-5-(pent-4-en-1-yl)-1H-pyrrole-2-carbaldehyde in diethylene glycol ether (5 mL). The reaction mixture was stirred at 180 $^{o}$C. After the reaction was complete (monitored by TLC), it was quenched with $H_2O$ and extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtrated and concentrated in vacuo. The crude product was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 1/100) to afford pyrrole **1e** (274 mg, 57% yield over two steps).

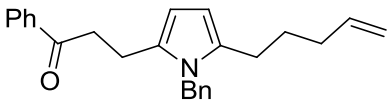


**1-Benzyl-2-methyl-5-(pent-4-en-1-yl)-1H-pyrrole (1e)**

Yellow liquid (274 mg, 92% yield), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/100, v/v). Analytical data for **1e**: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.60-1.70 (m, 2H), 2.05 (dt, $J_1$ = 6.9 Hz, $J_2$ = 7.8 Hz, 2H), 2.12 (s, 3H), 2.45 (t, $J$ = 7.5 Hz, 2H), 4.92 (d, $J$ = 10.2 Hz, 1H), 4.97 (d, $J$ = 17.4 Hz, 1H), 5.01 (s, 2H), 5.71-5.80 (m, 1H), 5.89 (s, 2H), 6.86 (d, $J$ = 7.5 Hz, 2H), 7.22-7.31 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 12.3, 26.0, 28.0, 33.3, 46.5, 104.5, 105.5, 114.6, 125.6, 127.0, 128.0, 128.7, 132.6, 138.5, 138.7; IR (film) 3102, 2930, 2859, 1640, 1495, 1416, 1354, 1299, 1029,1018, 991, 910, 727, 695 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{17}H_{22}N$ $(M+H)^+$ requires *m/z* 240.1747, found *m/z* 240.1749.



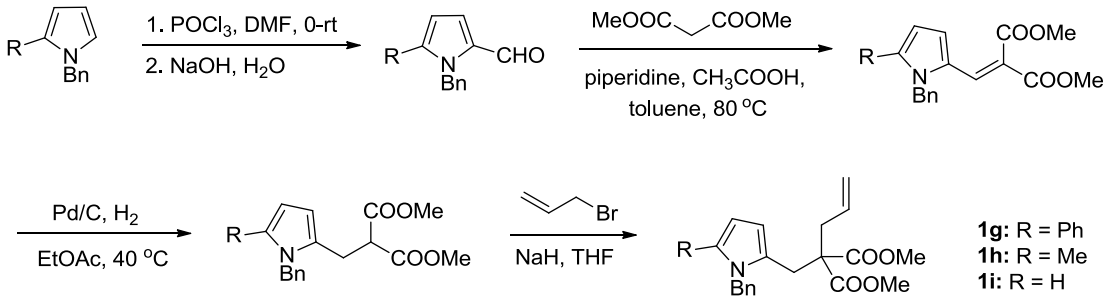

To a solution of **1c** (450 mg, 2 mmol) in toluene (10 mL) was added the enone **2a** (290 mg, 2.2 mmol) and racemic phosphoric acid (35 mg, 0.1 mmol, 5 mol%). The mixture was stirred at 40 $^{o}$C for 12 hours. After the reaction was complete (monitored by TLC), the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 1/50) to afford **1f** (187 mg, 47% yield).



**3-(1-Benzyl-5-(pent-4-en-1-yl)-1H-pyrrol-2-yl)-1-phenylpropan-1-one (1f)**

Yellow solid (187 mg, 47% yield), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/25, v/v). Analytical data for **1f**: m.p. = 58-59 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.62-1.72 (m, 2H), 2.08 (app q, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 2.89 (t, *J* = 8.4 Hz, 2H), 3.18-3.23 (m, 2H), 4.92 (d, *J* = 9.3 Hz, 1H), 4.97 (d, *J* = 17.4 Hz, 1H), 5.08 (s, 2H), 5.69-5.82 (m, 1H), 5.93-5.96 (m, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 7.17-7.29 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.8, 25.8, 27.8, 33.3, 37.7, 46.4, 104.4, 104.6, 114.7, 125.5, 127.0, 127.9, 128.4, 128.6, 131.2, 132.9, 136.6, 138.3, 138.4, 199.0; IR (film) 2928, 1682, 1494, 1418, 1351, 1273, 1193, 1006, 973, 909, 731, 697, 686, 642 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{25}H_{28}NO(M+H)^+$ requires *m/z* 358.2165, found *m/z* 358.2167.

**General procedure for preparation of 1g-i**



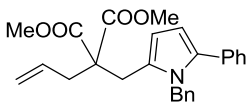

In a dry three-necked flask, $POCl_3$ (2.0 equiv.) was added to a solution of *N*-Bn pyrrole (1.0 equiv, 0.7 M) in DMF at 0 $^{o}$C. After the mixture was stirred at room temperature for 4 hours, it was slowly adjusted by the addition of saturated NaOH (aq.) to pH >7 at 0 $^{o}$C. Then the mixture was stirred at 80 $^{o}$C for 2 hours. After the reaction was complete (monitored by TLC), the mixture was quenched with water and extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. After the solvent was removed in vacuo, the residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 1/100)

to afford pyrrole aldehyde.

The pyrrole aldehyde (1.0 equiv) was dissolved in toluene (0.3 mol/L) and methyl malonate (1.1 equivs), piperidine (1.0 equiv) and AcOH (0.1 equiv) were added. The mixture was stirred at 60 $^{o}$C for 12 hours. After the reaction was complete (monitored by TLC), the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 1/5) to afford dimethyl (pyrrol-methylene)malonate.

The mixture of dimethyl (pyrrol-methylene)malonate (1.0 equiv, 0.4 mol/L) and Pd/C (10%, 0.1 equiv.) in ethyl acetate under 1 atm of $H_2$ was stirred at 40 $^{o}$C. After the reaction was complete (monitored by TLC), the reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The solvent was evaporated under reduced pressure to afford the crude product, which was directly used in the next step.

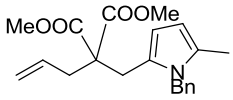
To a suspension of NaH (3.0 equivs) in THF (0.3 M) in a dry three-necked flask was added the aforementioned product in THF (1 mol/L) slowly at 0 $^{o}$C. The mixture was stirred at room temperature for 1 hour. After allyl bromide (1.5 equivs) was added at 0 $^{o}$C, the reaction was stirred at room temperature. When the reaction was complete (monitored by TLC), it was quenched with water at 0 $^{o}$C and extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. After the solvent was removed in vacuo, the crude product was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate = 1/20) to afford **1**.




**Dimethyl 2-allyl-2-((1-benzyl-1H-pyrrol-2-yl)methyl) malonate (1g)**

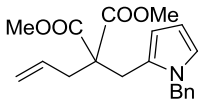
White solid (1.3 g, 40% yield over four steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v). Analytical data for **1g**: m.p. = 85-86$^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.77 (d, *J* = 7.2 Hz, 2H), 3.13 (s, 2H), 3.69 (s, 6H), 5.02 (d, *J* = 10.8 Hz, 1H), 5.03 (d, *J* = 16.2 Hz, 1H), 5.05 (s, 2H), 5.50-5.61 (m, 1H), 6.03 (d, *J* = 3.6 Hz, 1H), 6.21 (d, *J* = 3.3 Hz, 1H), 6.79 (d, *J* = 6.9

Hz, 2H), 7.15-7.27 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 29.4, 37.1, 47.4, 52.5, 58.0, 108.3, 108.7, 119.1, 125.5, 126.9, 127.0, 128.2, 128.3, 128.7, 128.9, 132.5, 133.6, 135.2, 138.9, 171.3; IR (film) 2923, 2853, 1731, 1438, 1295, 1204, 1060, 1027, 943, 756, 738, 700 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{26}H_{28}NO_4(M+H)^+$ requires *m/z* 418.2013, found *m/z* 418.1997.




**Dimethyl 2-allyl-2-((1-benzyl-5-methyl-1H-pyrrol-2-yl)methyl) malonate (1h)**

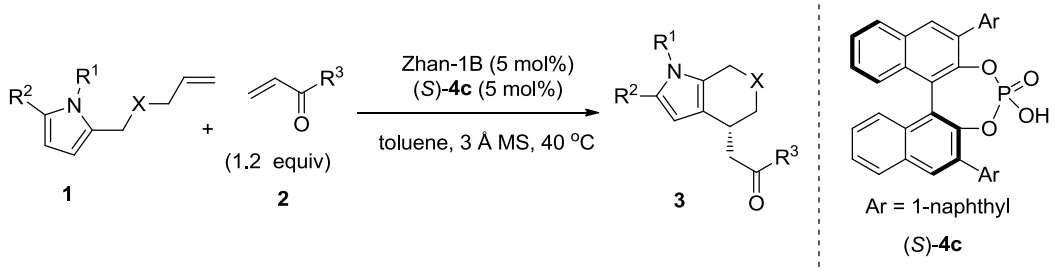
White solid (36% yield over four steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v). Analytical data for **1h**: m.p. = 51-52 $^{o}$C; $^1$H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.73 (d, *J* = 7.2 Hz, 2H), 3.14 (s, 2H), 3.68 (s, 6H), 5.00-5.05 (m, 2H), 5.03 (s, 2H), 5.53-5.59 (m, 1H), 5.85-5.88 (m, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 7.21-7.30 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 12.5, 29.2, 36.9, 46.4, 52.4, 58.0, 106.3, 106.8, 119.0, 125.5, 125.9, 127.0, 128.7, 132.5, 138.4, 171.3; IR (film) 2952, 1729, 1438, 1301, 1198, 1155, 1067, 1027, 1001, 934, 861, 748, 730, 695, 671 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{21}H_{26}NO_4(M+H)^+$ requires *m/z* 356.1856, found *m/z* 356.1845.



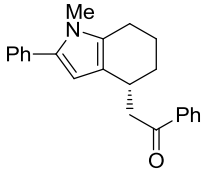

**Dimethyl 2-allyl-2-((1-benzyl-1H-pyrrol-2-yl)methyl) malonate (1i)**

Colourless liquid (2.8 g, 23% yield over four steps), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v). Analytical data for **1i**: $^1$H NMR (300 MHz, $CDCl_3$) δ 2.71 (d, *J* = 7.2 Hz, 2H), 3.14 (s, 2H), 3.68 (s, 6H), 4.99-5.04 (m, 2H), 5.05 (s, 2H), 5.54-5.63 (m, 1H), 5.93 (d, *J* = 1.8 Hz, 2H), 6.10-6.12 (m, 1H), 6.60 (dd, $J_1$ = 1.8 Hz, $J_2$ = 2.7 Hz, 1H), 6.93 (d, *J* = 6.9 Hz, 2H), 7.23-7.32 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 28.7, 36.9, 50.2, 52.5, 58.1, 107.5, 108.2, 119.1, 121.7, 126.2, 126.7, 127.3, 128.6, 132.4, 138.3, 171.2; IR (film) 2981, 1731, 1480, 1434, 1292, 1211, 1136, 1075, 923, 705 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{20}H_{24}NO_4(M+H)^+$ requires *m/z* 342.1700, found *m/z* 342.1691.

**General procedure for the enantioselective synthesis of 4,5,6,7-tetrahydroindole**



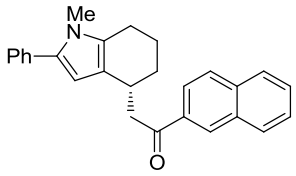

To a solution of pyrrole olefin **1** (0.2 mmol, 1.0 equiv) in toluene (2 mL) were added enone **2** (1.2 equivs or 2.0 equivs) and 3Å MS (100 mg), then chiral phosphoric acid (*S*)-**4c** (6.0 mg, 0.01 mmol, 5 mol%) and Zhan-1B (7.3 mg, 0.01 mmol, 5 mol%) were added in one portion. The reaction was stirred at 40 °C. After the reaction was complete (monitored by TLC), it was quenched with water and extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. After the solvent was removed in vacuo, the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/25 - 1/9) to afford tetrahydroindole **3**



**(*R*)-2-(1-Methyl-2-phenyl-4,5,6,7-tetrahydro-1H-indol-4-yl)-1-phenylethanone (3a)**

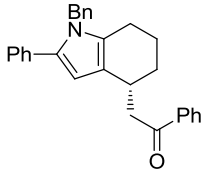
Yellow liquid (39.5 mg, 60% yield, 72% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/30, v/v). Analytical data for **3a**: $[\alpha]_D^{20}$ = +29.2 (c = 0.5 Acetone, 72% *ee*). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.40-1.50 (m, 1H), 1.79-1.88 (m, 1H), 1.97-2.04 (m, 2H), 2.61 (t, $J$ = 6.0 Hz, 2H), 3.09 (dd, $J_1$ = 8.1 Hz, $J_2$ = 15.9 Hz, 1H), 3.35-3.49 (m, 2H), 3.49 (s, 3H), 6.07 (s, 1H), 7.23-7.30 (m, 1H), 7.33-7.38 (m, 4H), 7.43-7.48 (m, 2H), 7.55 (t, $J$ = 7.2 Hz, 1H), 8.01 (d, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.6, 22.3, 29.8, 30.0, 31.3, 45.5, 105.7, 120.7, 126.4, 128.1, 128.3, 128.5, 130.0, 132.9, 133.4, 133.5, 137.4, 200.0; IR (film) 2923, 2852, 1680, 1599, 1515, 1447, 1357, 1277, 1201, 988, 751, 689 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{23}H_{24}NO$ $(M+H)^+$ requires *m/z* 330.1852, found *m/z* 330.1856. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major)

= 7.63 min, t (minor) = 6.99 min.



**(*R*)-2-(1-Methyl-2-phenyl-4,5,6,7-tetrahydro-1H-indol-4-yl)-1-(naphthalen-2-yl)ethanone (3b)**

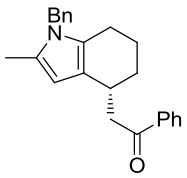
Yellow solid (33.7 mg, 44% yield, 67% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/35, v/v). Analytical data for **3b**: m.p. = 55-56 $^{o}$C; $[\alpha]_D^{20}$ = +89.7 (c = 0.5 Acetone, 67% *ee*). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.34-1.53 (m, 1H), 1.74-1.79 (m, 1H), 1.91-2.00 (m, 2H), 2.52-2.56 (m, 2H), 3.15 (dd, $J_1$ = 9.9 Hz, $J_2$ = 17.4 Hz, 1H), 3.42-3.47 (m, 2H), 3.42 (s, 3H), 6.03 (s, 1H), 7.15-7.20 (m, 1H), 7.25-7.30 (m, 4H), 7.43-7.53 (m, 2H), 7.77-7.87 (m, 3H), 8.01 (d, *J* = 7.8 Hz, 1H), 8.44 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.7, 22.3, 29.9, 30.2, 31.3, 45.6, 105.7, 120.8, 124.0, 126.4, 126.7, 127.7, 128.3, 128.4, 128.5, 129.6, 129.8, 130.0, 132.5, 133.4, 133.6, 134.8, 135.5, 200.0; IR (film) 3056, 2922, 2851, 1674, 1626, 1599, 1514, 1467, 1358, 1280, 1178, 1122, 861, 818, 750, 699 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{27}H_{26}NO(M+H)^+$ requires *m/z* 380.2009, found *m/z* 380.2008. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 11.24 min, t (minor) = 10.28 min.



**(*R*)-2-(1-Benzyl-2-phenyl-4,5,6,7-tetrahydro-1H-indol-4-yl)-1-phenylethanone (3c)**

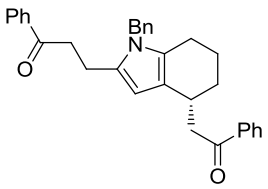
Yellow solid (75.2 mg, 93% yield, 84% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/30, v/v). Analytical data for **3c**: m.p. = 104-105 $^{o}$C; $[\alpha]_D^{20}$ = +21.5 (c = 0.5 Acetone, 84% *ee*). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.42-1.45 (m, 1H), 1.70-1.77 (m, 1H), 1.86-2.02 (m, 2H), 2.37-2.41 (m, 2H), 3.10 (dd, $J_1$ = 8.1 Hz, $J_2$ = 15.9 Hz, 1H), 3.39-3.46 (m, 2H), 5.09 (s, 2H), 6.14 (s,1H), 6.96 (d, *J* = 7.2 Hz, 2H), 7.22-7.33 (m, 8H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 6.9 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.6, 22.2, 29.9, 30.1, 45.6, 47.4, 106.3, 121.3, 125.7, 126.5, 126.9, 128.1, 128.3, 128.4, 128.5, 128.6, 129.9, 132.8, 133.5, 133.8, 137.4, 139.0, 200.1; IR (film) 3028, 2916, 1686, 1598, 1494, 1447, 1401, 1358, 1199, 1027, 990, 918, 794, 761, 742,

685, 624 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{29}H_{28}NO$ $(M+H)^+$ requires *m/z* 406.2165, found *m/z* 406.2170. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 0.5 mL/min, λ = 254 nm, t (major) = 14.52 min, t (minor) = 15.40 min.




**(*R*)-2-(1-Benzyl-2-methyl-4,5,6,7-tetrahydro-1H-indol-4-yl)-1-phenylethanone (3d)**

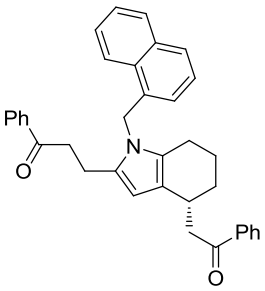
Yellow solid (38.6 mg, 56% yield, 84% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/30, v/v). Analytical data for **3d**: m.p. = 50-51 °C; $[\alpha]_D^{20}$ = +0.9 (c = 0.5 Acetone, 84% *ee*). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.34-1.44 (m, 1H), 1.68-1.77 (m, 1H), 1.87-1.99 (m, 2H), 2.12 (s, 3H), 2.38-2.41 (m, 2H), 3.04 (dd, $J_1$ = 8.4 Hz, $J_2$ = 15.6 Hz, 1H), 3.32-3.38 (m, 2H), 4.95 (s, 2H), 5.79 (s, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 7.20-7.32 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.53-7.58 (m, 1H), 8.02 (d, *J* = 7.5 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 12.0, 21.7, 22.0, 30.0, 30.1, 45.7, 46.5, 103.9, 119.7, 125.8, 126.9, 127.3, 128.1, 128.5, 128.6, 132.8, 137.4, 138.5, 200.2; IR (film) 2923, 2853, 1679, 1597, 1447, 1355, 1276, 1205, 1000, 752, 728, 690 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{24}H_{26}NO$ $(M+H)^+$ requires *m/z* 344.2009, found *m/z* 344.2016. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 27.66 min, t (minor) = 20.06 min.




**(*R*)-3-(1-Benzyl-4-(2-oxo-2-phenylethyl)-4,5,6,7-tetrahydro-1H-indol-2-yl)-1-phenylpropan-1-one (3e)**

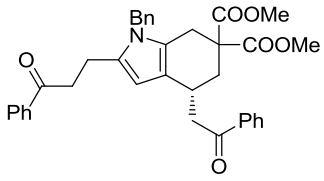
Yellow solid (81.7 mg, 88% yield, 80% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3e**: m.p. = 102-103 °C; $[\alpha]_D^{20}$ = +15.2 (c = 0.5 Acetone, 80% *ee*). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.40-1.43 (m, 1H), 1.74-1.77 (m, 1H), 1.87-2.00 (m, 2H), 2.42-2.46 (m, 2H), 2.86-2.91 (m, 2H), 3.05 (dd, $J_1$ = 7.8 Hz, $J_2$ = 15.3 Hz, 1H), 3.13-3.18 (m, 2H), 3.33-3.42 (m, 2H), 5.02 (s, 2H), 5.83 (s, 1H), 6.92 (d, *J* = 6.9 Hz, 2H), 7.19-7.32 (m, 3H), 7.39-7.58 (m, 6H), 7.85 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 6.9 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.7, 21.6, 21.9, 30.1,

30.2, 38.0, 45.7, 46.4, 103.1, 119.9, 125.7, 127.0, 127.8, 127.9, 128.2, 128.5, 128.7, 130.7, 132.8, 133.0, 136.7, 137.5, 138.5, 199.1, 200.2; IR (film) 2927, 1678, 1597, 1448, 1351, 1298, 1284, 1204, 1179, 973, 755, 726, 692 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{33}H_{32}NO_2$ $(M+H)^+$ requires *m/z* 462.2428, found *m/z* 462.2430. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 25.34 min, t (minor) = 18.36 min.



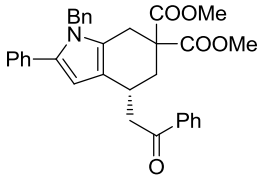

**(*R*)-3-(1-(Naphthalen-1-ylmethyl)-4-(2-oxo-2-phenylethyl)-4, 5,6,7-tetrahydro-1H-indol-2-yl)-1-phenylpropan-1-one (3f)**

Yellow solid (75.7 mg, 74% yield, 82% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3f**: m.p. = 96-97 $^oC$; $[\alpha]_D^{20}$ = +3.6 (c = 0.5 Acetone, 82% *ee*). $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.43-1.46 (m, 1H), 1.67-1.75 (m, 1H), 1.85-1.89 (m, 1H), 1.98-2.04 (m, 1H), 2.38-2.42 (m, 2H), 2.85-2.91 (m, 2H), 3.08 (dd, $J_1$ = 7.8 Hz, $J_2$ = 15.6 Hz, 1H), 3.20 (t, *J* = 7.2 Hz, 2H), 3.38-3.47 (m, 2H), 5.47 (s, 2H), 5.92 (s, 1H), 6.40 (d, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 3H), 7.45-7.61 (m, 6H), 7.72-7.80 (m, 3H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.99-8.05 (m, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 20.6, 21.6, 30.1, 30.2, 38.0, 44.2, 45.7, 103.3, 120.1, 122.1, 122.4, 125.7, 125.8, 126.3, 127.5, 127.9, 128.1, 128.2, 128.4, 128.5, 128.9, 130.1, 130.9, 132.8, 132.9, 133.4, 133.8, 136.6, 137.5, 199.0, 200.3; IR (film) 2930, 1735, 1681, 1596, 1447, 1359, 1278, 1203, 973, 795, 771, 749, 690 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{36}H_{34}NO_2$ $(M+H)^+$ requires *m/z* 512.2584, found *m/z* 512.2582. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 25.36 min, t (minor) = 20.16 min.




**(*R*)-Dimethyl 1-benzyl-4-(2-oxo-2-phenylethyl)-2-(3-oxo-3-phenylpropyl)-4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3g)**

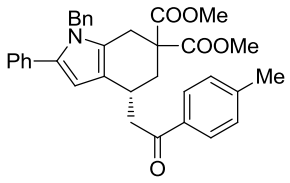
Yellow solid (56.6 mg, 49% yield, 85% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v). Analytical data for **3g**: m.p. = 62-63 $^{o}$C; $[\alpha]_D^{20}$ = +30.3 (c = 0.5 Acetone, 85% *ee*). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.80 (dd, $J_1$ = 10.8 Hz, $J_2$= 12.0 Hz, 1H), 2.60-2.75 (m, 4H), 2.80-2.89 (m, 3H), 3.01-3.13 (m, 2H), 3.66-3.68 (m, 1H), 3.69 (s, 6H), 5.05 (s, 2H), 5.75 (s, 1H), 6.97 (d, *J* = 7.5 Hz, 2H), 7.20-7.33 (m, 3H), 7.38-7.59 (m, 6H), 7.81 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.5, 27.5, 27.9, 35.7, 37.8. 45.5, 46.6, 52.7, 52.8, 54.4, 102.9, 118.4, 124.2, 125.8, 127.2, 127.9, 128.1, 128.4, 128.5, 128.7, 131.8, 132.9, 133.0, 136.6, 137.2, 138.0, 170.7, 172.1, 199.0, 199.3; IR (film) 3674, 2988, 2901, 1732, 1681, 1448, 1250, 1205, 1066, 733, 690 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{36}H_{36}NO_6(M+H)^+$ requires *m/z* 578.2537, found *m/z* 578.2535. The enantiomeric excess was determined by Phenomenex Lu X 5u Cellulose-2 (0.46cm x 25 cm), Hexanes / IPA = 70 / 30, 0.7 mL/min, λ = 214 nm, t (major) = 49.54 min, t (minor) = 59.21 min




**(*R*)-Dimethyl 1-benzyl-4-(2-oxo-2-phenylethyl)-2-phenyl -4,5-dihydro-1H- indole-6,6(7H)-dicarboxylate (3h)**

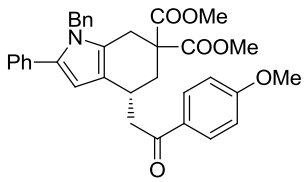
Yellow solid (61.2 mg, 59% yield, 92% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3h**: m.p. = 60-61 $^{o}$C; $[\alpha]_D^{20}$ = +52.8 (c = 0.5 Acetone, 92% *ee*). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.85 (dd, $J_1$ = 10.5 Hz, $J_2$ = 13.2 Hz, 1H), 2.74 (dd, $J_1$ = 4.8 Hz, $J_2$ = 13.2 Hz, 1H), 2.80 (AB, *J* = 16.2 Hz, 1H), 3.10 (dd, $J_1$ = 7.5 Hz, $J_2$ = 16.5 Hz, 1H), 3.25 (AB, *J* = 15.6 Hz, 1H), 3.43-3.58 (m, 2H), 3.66 (s, 3H), 3.67 (s, 3H), 5.10 (s, 2H), 6.07 (s, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 7.17-7.35 (m, 8H), 7.44-7.49 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.4, 28.0, 35.6, 45.4, 47.5, 52.7, 52.8, 54.4, 105.9, 119.8, 125.7, 126.3, 126.7, 127.0, 128.1, 128.3, 128.5, 128.6, 128.7, 133.0, 133.1, 134.8, 137.1, 138.5, 170.7, 172.1, 199.1; IR (film) 2951, 1731, 1682, 1599, 1448, 1356, 1247, 1075,

757, 730, 691 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{33}H_{32}NO_5(M+H)^+$ requires *m/z* 552.2275, found *m/z* 552.2269. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 95 / 5, 0.8 mL/min, λ = 254 nm, t (major) = 60.75 min, t (minor) = 69.06 min.




**(*R*)-Dimethyl 1-benzyl-4-(2-oxo-2-(p-tolyl)ethyl)-2-phenyl -4,5- dihydro-1H-indole-6,6(7H)-dicarboxylate (3i)**

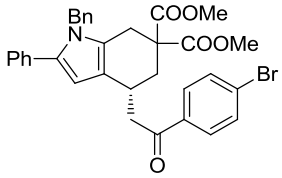
Yellow solid (63.9 mg, 60% yield, 90% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3i**: m.p. = 59-60 $^oC$; $[\alpha]_D^{20}$ = +47.9 (c = 0.5 Acetone, 90% *ee*). $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.75-1.88 (m, 1H), 2.40 (s, 3H), 2.70-2.82 (m, 2H), 3.07 (dd, $J_1$ = 7.5 Hz, $J_2$ = 16.5 Hz, 1H), 3.25 (d, $J$ = 15.9 Hz, 1H), 3.40-3.57 (m, 2H), 3.66 (s, 3H), 3.67 (s, 3H), 5.09 (s, 2H), 6.06 (s, 1H), 6.99 (d, $J$ = 7.2 Hz, 2H), 7.18-7.34 (m, 10H), 7.91 (d, $J$ = 8.4 Hz, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 21.6, 27.4, 28.0, 35.6, 45.2, 47.5, 52.6, 52.7, 54.4, 105.9, 119.9, 125.7, 126.2, 126.7, 127.0, 128.1, 128.2, 128.4, 128.6, 129.2, 133.1, 134.7, 134.8, 138.5, 143.7, 170.7, 172.1, 198.7; IR (film) 2952, 1731, 1679, 1433, 1246, 1201, 1176, 813, 758, 731, 697 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{34}H_{34}NO_5(M+H)^+$ requires *m/z* 536.2431, found *m/z* 536.2433. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 33.7 min, t (minor) = 39.91 min.




**(*R*)-Dimethyl 1-benzyl-4-(2-(4-methoxyphenyl)-2-oxoethyl)-2-phenyl-4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3j)**

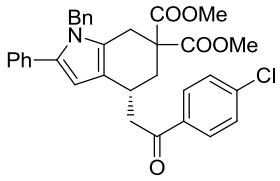
Yellow solid (62.3 mg, 57% yield, 88% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3j**: m.p. = 56-57 $^oC$; $[\alpha]_D^{20}$ = +37.8 (c = 0.5 Acetone, 88% *ee*). $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.80-1.88 (m, 1H), 2.70-2.82 (m, 2H), 3.01-3.09 (m, 1H), 3.25 (d, $J$ = 15.3 Hz, 1H), 3.06 (dd, $J_1$ = 5.4 Hz, $J_2$ = 16.5 Hz, 1H), 3.53-3.68 (m, 1H), 3.67 (s, 3H), 3.68 (s, 3H), 3.88 (s, 3H), 5.10 (s, 2H), 6.06 (s, 1H), 6.95 (d, $J$ = 8.7 Hz,

2H), 7.01 (d, $J$ = 8.1 Hz, 2H), 7.23-7.36 (m, 8H), 8.01 (d, $J$ = 9.0 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.5, 28.0, 35.6, 44.9, 47.4, 52.6, 52.7, 54.4, 55.3, 105.9, 113.6, 119.9, 125.6, 126.2, 126.6, 127.0, 128.2, 128.4, 128.6, 128.8, 130.3, 133.1, 134.7, 138.5, 163.3, 170.6, 172.1, 197.6; IR (film) 3700, 2954, 2902, 1731, 1674, 1599, 1511, 1451, 1435, 1251, 1205, 1168, 1075, 1029, 982, 831, 759, 730, 698 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{34}H_{34}NO_6(M+H)^+$ requires *m/z* 552.2381, found *m/z* 552.2378. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 56.37 min, t (minor) = 65.28 min.



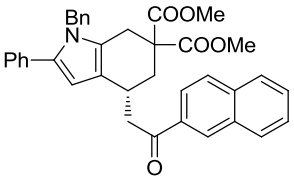

**(*R*)-Dimethyl 1-benzyl-4-(2-(4-bromophenyl)-2-oxoethyl)-2-phenyl -4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3k)**

Yellow solid (90.8 mg, 76% yield, 93% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3k**: m.p. = 68-69 $^{o}$C; $[\alpha]_D^{20}$ = +51.6 (c = 0.5 Acetone, 93% *ee*). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.83 (dd, $J_1$ = 10.8 Hz, $J_2$ = 12.9 Hz, 1H), 2.69-2.82 (m, 2H), 3.06 (dd, $J_1$ = 7.5 Hz, $J_2$ = 17.1 Hz, 1H), 3.25 (d, $J$ = 16.2 Hz, 1H), 3.42 (dd, $J_1$ = 5.7 Hz, $J_2$ = 17.1 Hz, 1H), 3.53-3.54 (m, 1H), 3.67 (s, 3H), 3.68 (s, 3H), 5.09 (s, 2H), 6.02 (s, 1H), 6.99 (d, $J$ = 7.2 Hz, 2H), 7.20-7.35 (m, 8H), 7.61 (d, $J$ = 8.7 Hz, 2H), 7.87 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.4, 28.0, 35.5, 45.3, 47.5, 52.7, 52.8, 54.4, 105.8, 119.6, 125.7, 126.3, 126.8, 127.1, 128.2, 128.3, 128.5, 128.7, 129.6, 131.9, 133.0, 134.9, 135.8, 138.5, 170.6, 172.1, 198.1; IR (film) 2928, 1729, 1680, 1434, 1247, 1205, 1173, 731, 697 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{33}H_{31}BrNO_5(M+H)^+$ requires *m/z* 600.1380, found *m/z* 600.1379. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 95 / 5, 0.8 mL/min, λ = 254 nm, t (major) = 75.35 min, t (minor) = 66.30 min.




**(*R*)-Dimethyl 1-benzyl-4-(2-(4-chlorophenyl)-2-oxoethyl)-2-phenyl -4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3l)**

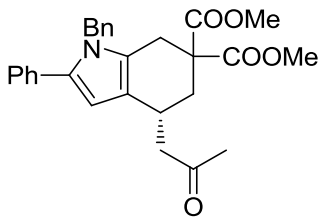
Yellow solid (75.8 mg, 68% yield, 91% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3l**: m.p. = 72-73 $^{o}$C; $[\alpha]_D^{20}$ = +52.1 (c = 0.5 Acetone, 91% *ee*). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.83 (dd, $J_1$ = 8.1 Hz, $J_2$ = 12.9 Hz, 1H), 2.69-2.82 (m, 2H), 3.07 (dd, $J_1$ = 7.8 Hz, $J_2$ = 17.1 Hz, 1H), 3.25 (d, $J$ = 16.2 Hz, 1H), 3.43 (dd, $J_1$ = 5.7 Hz, $J_2$ = 16.8 Hz, 1H), 3.53-3.57 (m, 1H), 3.66 ( s, 3H), 3.67 (s, 3H), 5.10 (s, 2H), 6.03 (s, 1H), 6.99 (d, $J$ =7.5 Hz, 2H), 7.19-7.27 (m, 6H), 7.33 (t, $J$ = 7.2 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 7.95 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.4, 28.0, 35.5, 45.3, 47.5, 52.7, 52.8, 54.4, 105.8, 119.6, 125.6, 126.2, 126.8, 127.0, 128.3, 128.4, 128.6, 128.8, 129.5, 133.0, 134.9, 135.4, 138.4, 139.4, 170.6, 172.0, 197.9; IR (film) 2951, 1731, 1683, 1587, 1433, 1397, 1247, 1200, 1174, 1089, 983, 817, 759, 731, 698 cm$^{-1}$; HRMS (ESI) exact mass calcd for $C_{33}H_{31}ClNO_5(M+H)^+$ requires *m/z* 556.1885, found *m/z* 556.1880. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (major) = 74.39 min, t (minor) = 80.71 min.




**(*R*)-Dimethyl 1-benzyl-4-(2-(naphthalen-2-yl)-2-oxoethyl) -2-phenyl -4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3m)**

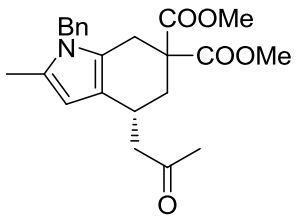
Yellow solid (58.0 mg, 51% yield, 90% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3m**: m.p. = 63-64 $^{o}$C; $[\alpha]_D^{20}$ = +58.7 (c = 0.5 Acetone, 90% *ee*). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.85-1.93 (m, 1H), 2.76-2.84 (m, 2H), 3.20-3.30 (m, 2H), 3.57-3.67 (m, 2H), 3.63 (s, 6H), 5.11 (s, 2H), 6.11 (s, 1H), 7.00 (d, $J$ = 7.2 Hz, 2H), 7.19-7.36 (m, 8H), 7.55-7.63 (m, 2H), 7.87-7.98 (m, 3H), 8.10 (d, $J$ = 8.7 Hz, 1H), 8.53 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.6, 28.0, 35.6, 45.4, 47.5, 52.7, 52.8, 54.4, 105.9, 119.8, 123.9, 125.7, 126.3, 126.7, 127.0, 127.7, 128.3, 128.4, 128.5,

128.6, 128.8, 129.5, 129.7, 132.5, 133.1, 134.5, 134.9, 135.5, 138.5, 170.7, 172.1, 199.0; IR (film) 2951, 1730, 1680, 1448, 1246, 1202, 1174, 1030, 757, 730, 696 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{37}H_{34}NO_5(M+H)^+$ requires *m/z* 572.2431, found *m/z* 572.2430. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 95 / 5, 0.8 mL/min, λ = 254 nm, t (major) = 87.55 min, t (minor) = 97.88 min.




**(*R*)-Dimethyl 1-benzyl-4-(2-oxopropyl)-2-phenyl-4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3n)**

Yellow liquid (81.1mg, 88% yield, 88% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3n**: $[\alpha]_D^{20}$ = +29.9 (c = 0.5 Acetone, 88% *ee*). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.71-1.79 (m, 1H), 2.22 (s, 3H), 2.53-2.66 (m, 2H), 2.79 (dd, $J_1$ = 1.5 Hz, $J_2$ = 15.9 Hz, 1H), 2.90 (dd, $J_1$ = 6.0 Hz, $J_2$ = 17.1 Hz, 1H), 3.23 (d, *J* = 15.3 Hz, 1H), 3.33-3.41 (m, 1H), 3.66 (s, 3H), 3.68 (s, 3H), 5.04 (AB, *J* = 17.1 Hz, 1H), 5.11 (AB, *J* = 17.1 Hz, 1H),6.00 (s, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 7.18-7.34 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 27.1, 27.9, 30.4, 35.4, 47.4, 50.3, 52.6, 52.7, 54.3, 105.7, 119.5, 125.6, 126.1, 126.8, 127.0, 128.2, 128.4, 128.6, 133.0, 134.8, 138.4, 170.6, 171.9, 208.0; IR (film) 2953, 2924, 1732, 1603, 1434, 1357, 1249, 1088, 1030, 973, 760, 731, 699, 665 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{28}H_{30}NO_5$ $(M+H)^+$ requires *m/z* 460.2118, found *m/z* 460.2120. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 97 / 3, 1.0 mL/min, λ = 254 nm, t (major) = 31.74 min, t (minor) = 34.03 min.



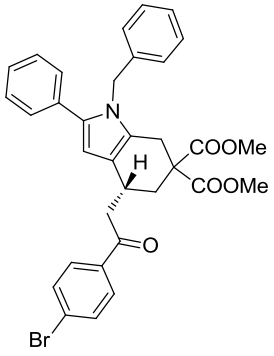

**(*R*)-Dimethyl 1-benzyl-2-methyl-4-(2-oxopropyl) -4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate (3o)**

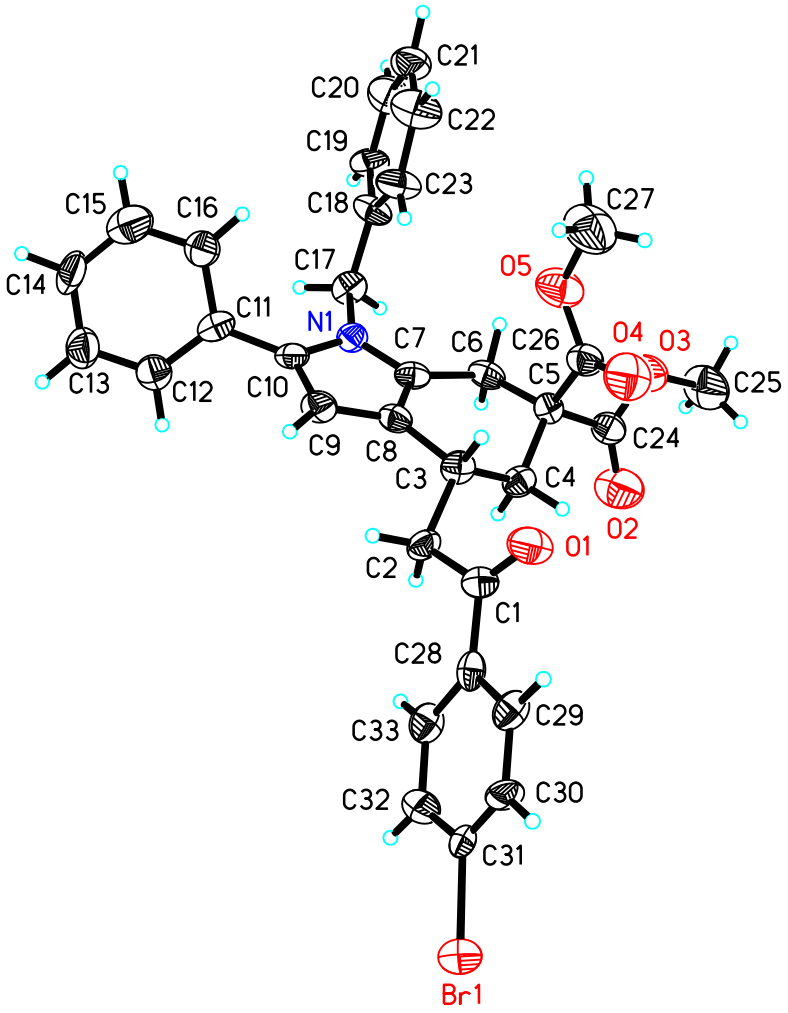
Yellow liquid (59.2 mg, 75% yield, 69% *ee*), following silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v). Analytical data for **3o**: $[\alpha]_D^{20}$ = +8.8 (c = 0.5 Acetone, 69% *ee*). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.71 (dd, $J_1$ = 11.1 Hz, $J_2$ = 13.2 Hz, 1H), 2.07 (s, 3H), 2.21 (s,

3H), 2.46-2.64 (m, 2H), 2.76-2.85 (m, 2H), 3.23-3.28 (m, 2H), 3.66 (s, 3H), 3.69 (s, 3H), 4.97 (s, 2H), 5.65 (s, 1H), 6.94 (d, $J$ = 7.5 Hz, 2H), 7.21-7.33 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 11.9, 27.2, 27.8, 30.3, 35.5, 46.5, 50.5, 52.6, 52.7, 54.4, 103.6, 117.9, 123.6, 125.7, 127.0, 128.4, 128.5, 138.0, 170.6, 172.1, 208.2; IR (film) 2952, 2925, 1732, 1496, 1432, 1401, 1357, 1249, 1086, 1050, 731, 698, 665 $cm^{-1}$; HRMS (ESI) exact mass calcd for $C_{23}H_{28}NO_5(M+H)^+$ requires *m/z* 398.1962, found *m/z* 398.1969. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 15.51 min, t (minor) = 12.65 min.

**_X_-Ray structure of enantiopure 3k**

(*R*)-dimethyl 1-benzyl-4-(2-(4-bromophenyl)-2-oxoethyl)-2-phenyl-4,5-dihydro-1H-indole-6,6(7H)-dicarboxylate [CCDC 1045810 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk /data request/cif.]

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C22
C19
C23
C18
C27
C15
C16
C17
O5
C14
C11
N1
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C26
O4
O3
C5
C25
C13
C12
C10
C9
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C1
C28
C29
C33
C30
C32
C31
Br1

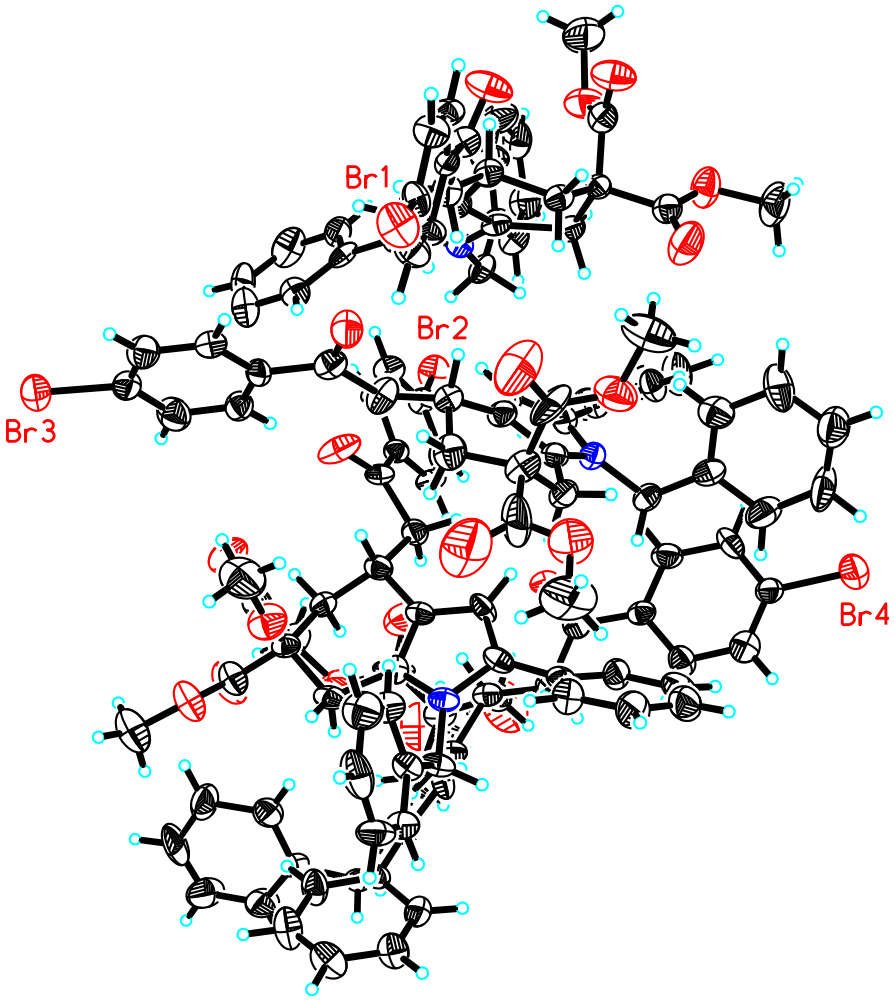
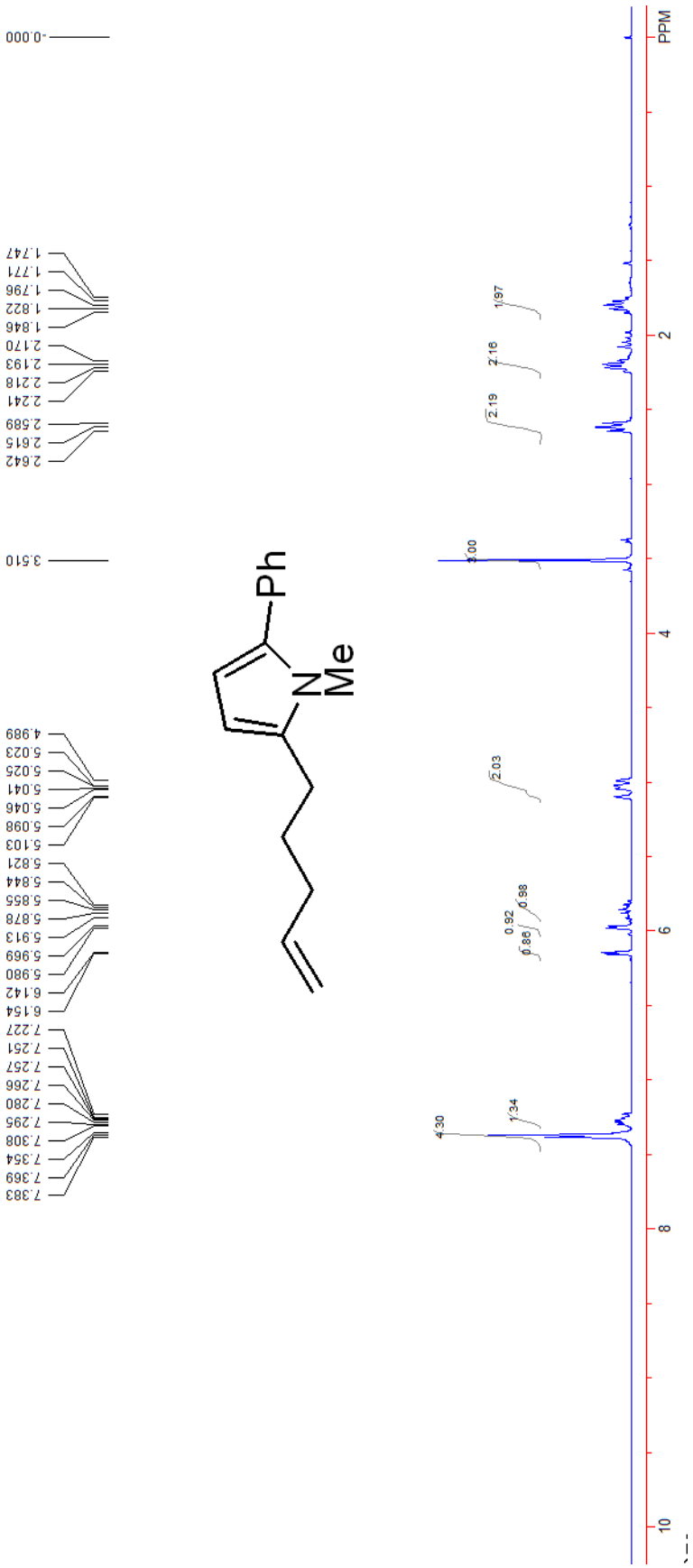
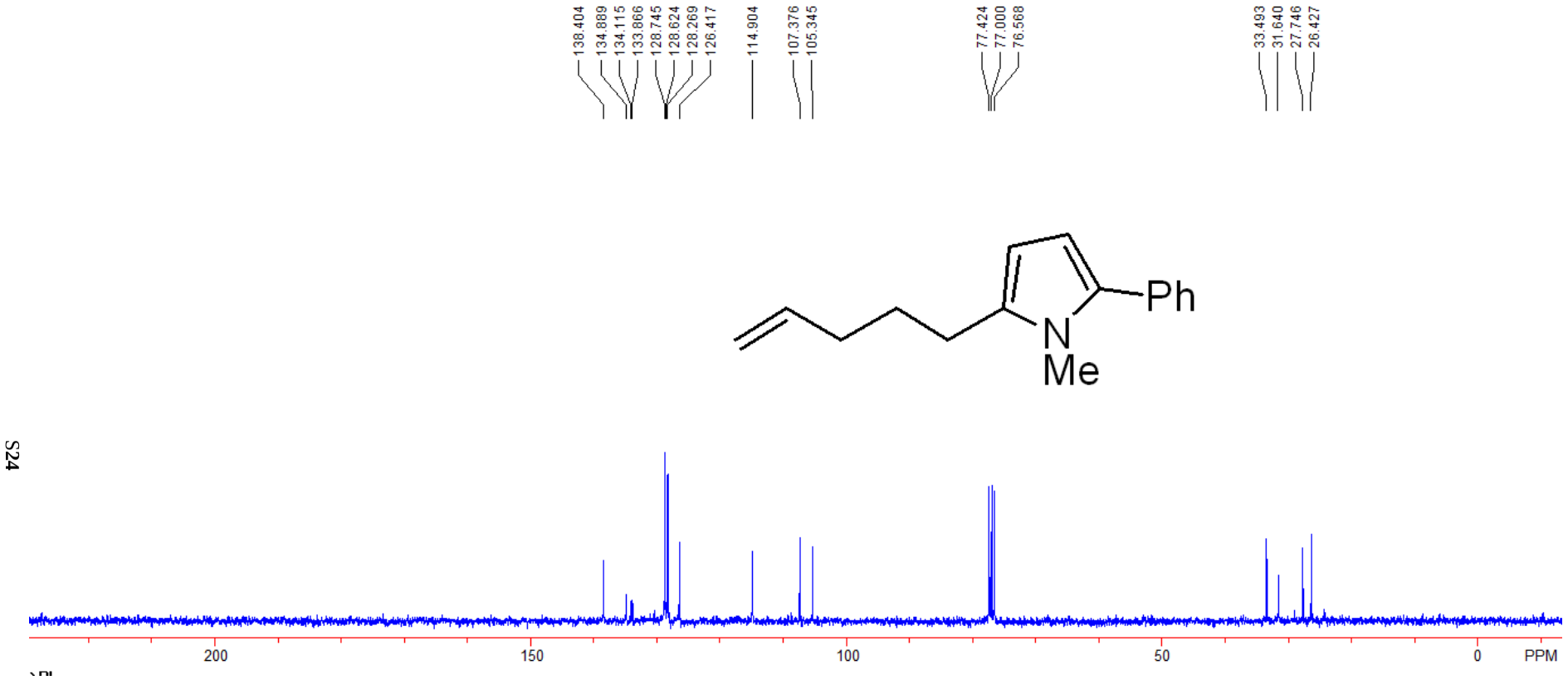

Br1
Br2
Br3
Br4

Table 1. Crystal data and structure refinement for cd214165.

| | | |
|---|---|---|
| Identification code | cd214165 | |
| Empirical formula | C33 H30 Br N O5 | |
| Formula weight | 600.49 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | I 2 2 2 | |
| Unit cell dimensions | a = 15.713(12) Å | = 90°. |
| | b = 28.08(2) Å | = 90°. |
| | c = 28.507(18) Å | = 90 °. |
| Volume | 12578(15) $Å^3$ | |
| Z | 16 | |
| Density (calculated) | 1.268 $Mg/m^3$ | |
| Absorption coefficient | 1.346 $mm^{-1}$ | |
| F(000) | 4960 | |
| Crystal size | 0.156 x 0.142 x 0.103 $mm^3$ | |
| Theta range for data collection | 1.018 to 25.499 °. | |
| Index ranges | 0<=h<=19, -34<=k<=26, -34<=l<=34 | |
| Reflections collected | 18429 | |
| Independent reflections | 11716 [R(int) = 0.0600] | |
| Completeness to theta = 25.242 ° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7457 and 0.5761 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11716 / 0 / 725 | |
| Goodness-of-fit on $F^2$ | 0.891 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0686, wR2 = 0.1544 | |
| R indices (all data) | R1 = 0.1326, wR2 = 0.1759 | |
| Absolute structure parameter | 0.031(9) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.715 and -0.377 e. $Å^{-3}$ | |

$^{1}$H NMR and $^{13}$C NMR Spectra of **1a**

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76.568
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Me
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50
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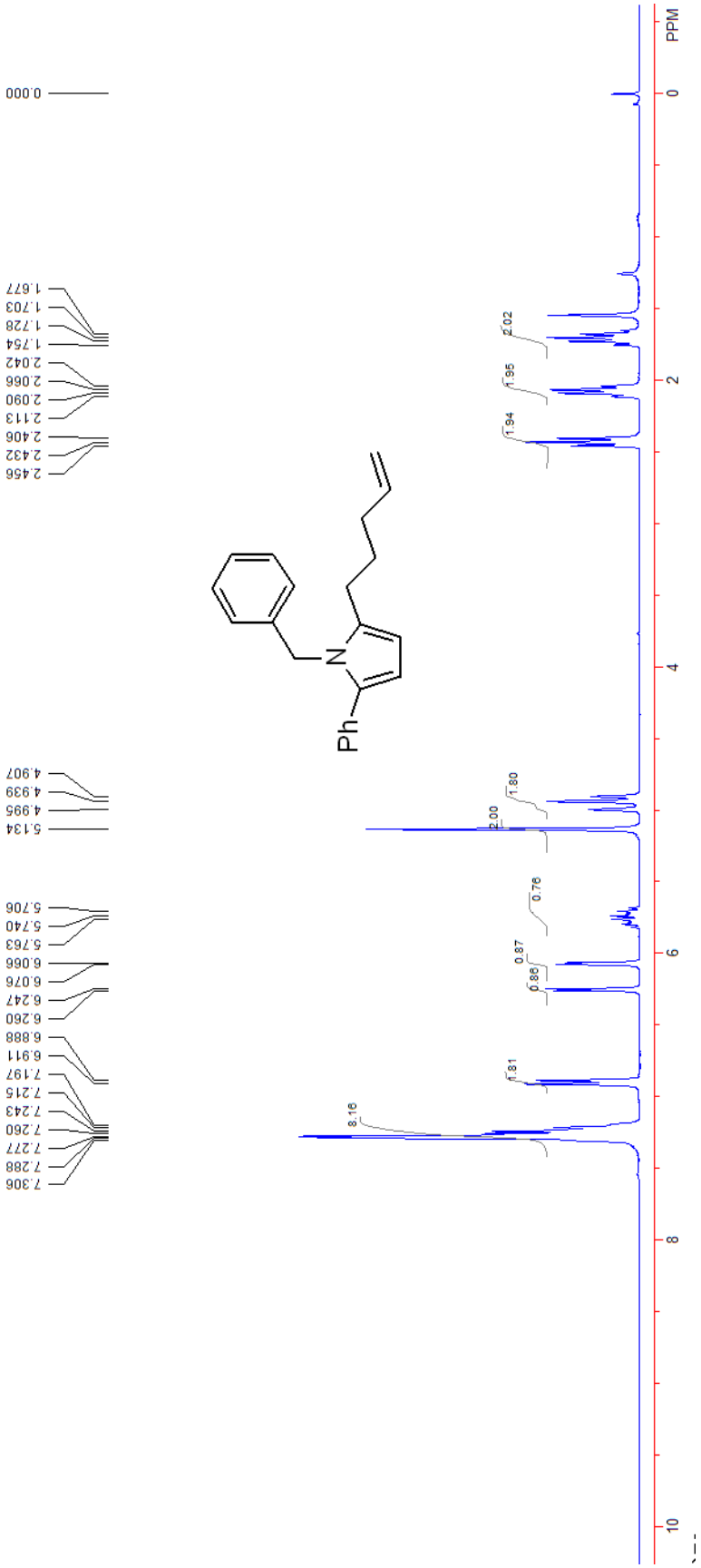
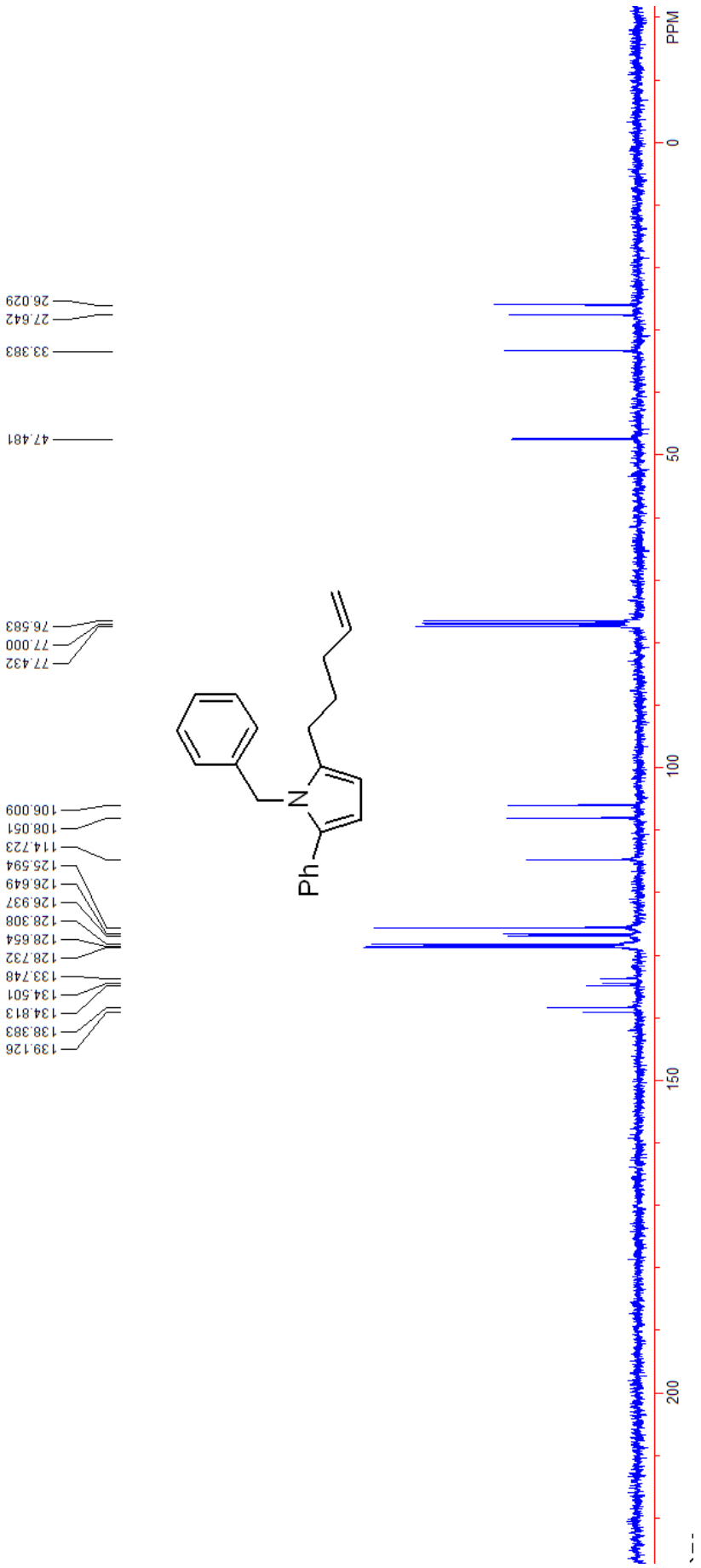
PPM

$^{1}$H NMR and $^{13}$C NMR Spectra of **1b**

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108.051
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126.649
126.937
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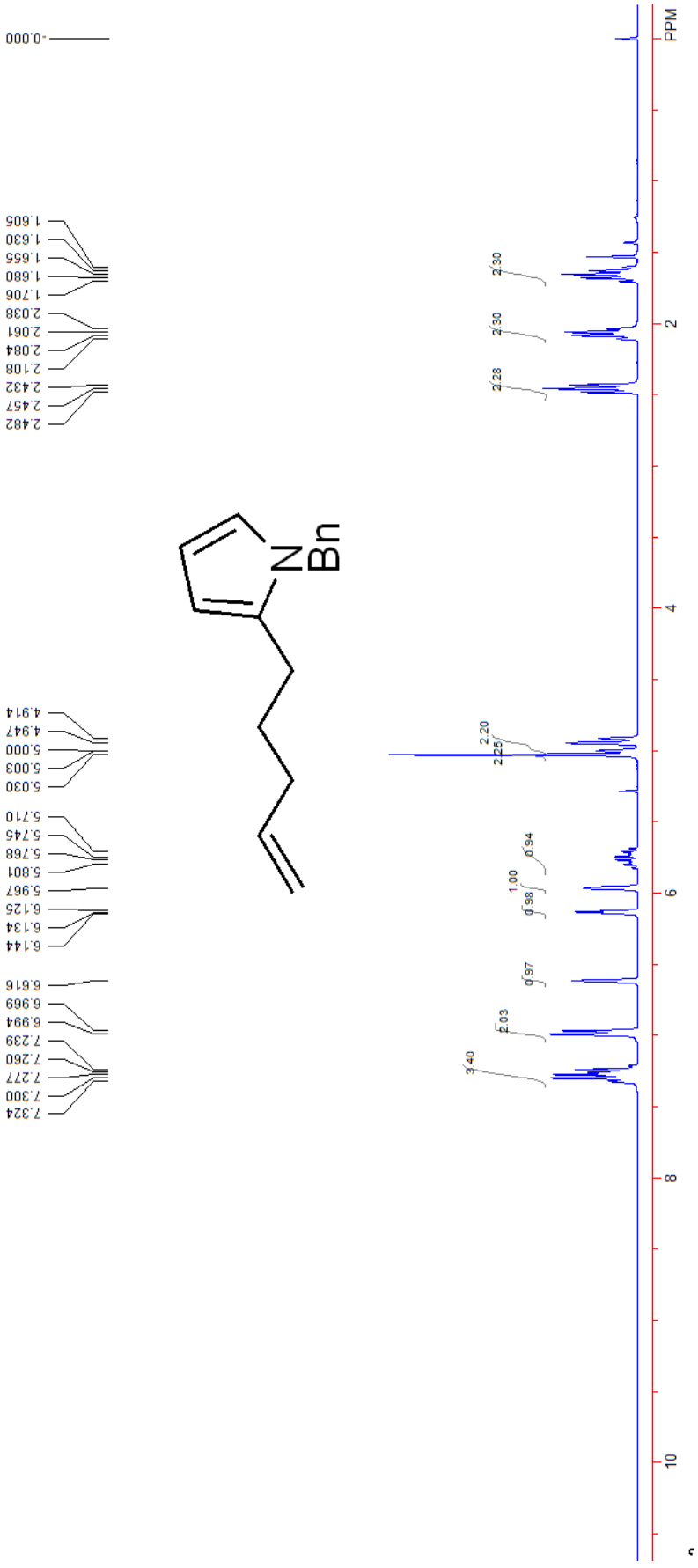
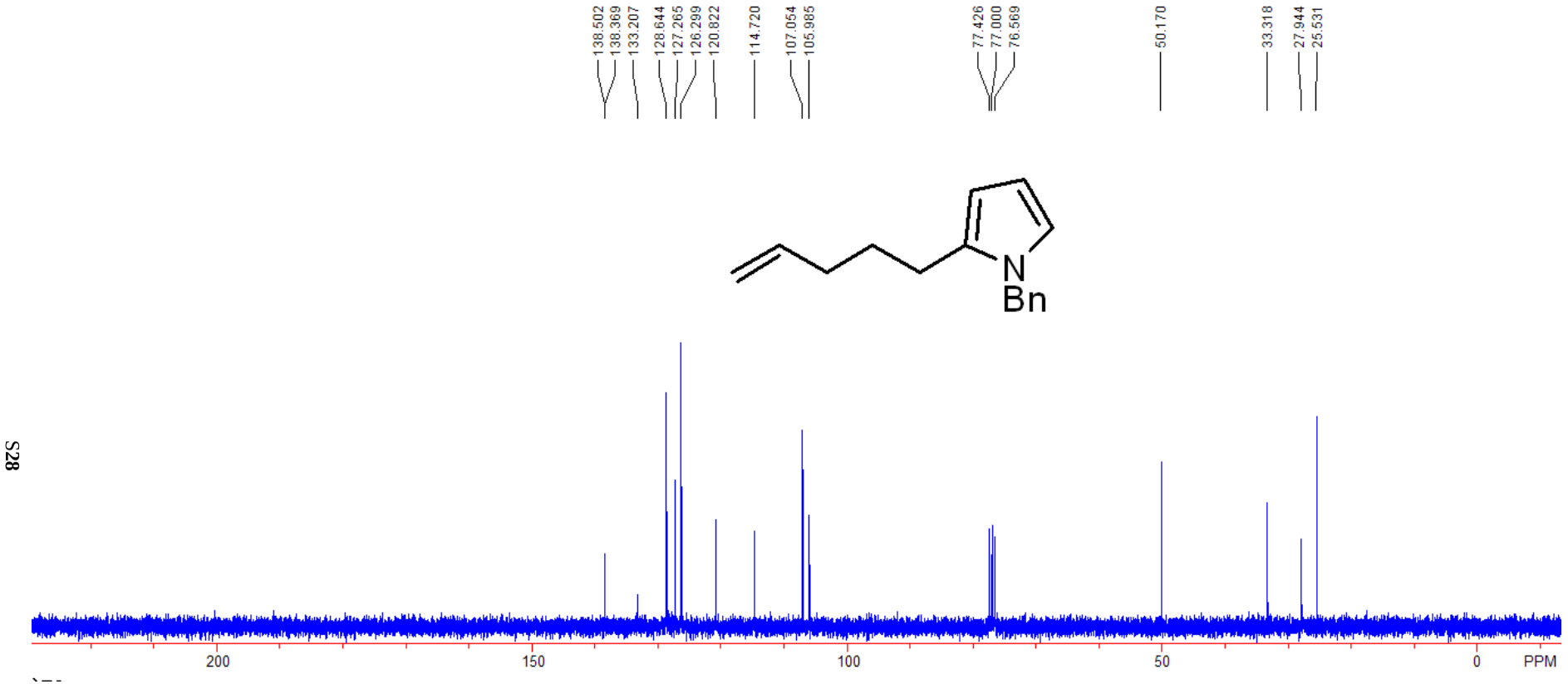
134.813
138.383
139.126

$^{1}$H NMR and $^{13}$C NMR Spectra of **1c**

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105.985
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77.000
76.569
50.170
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Bn
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150
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50
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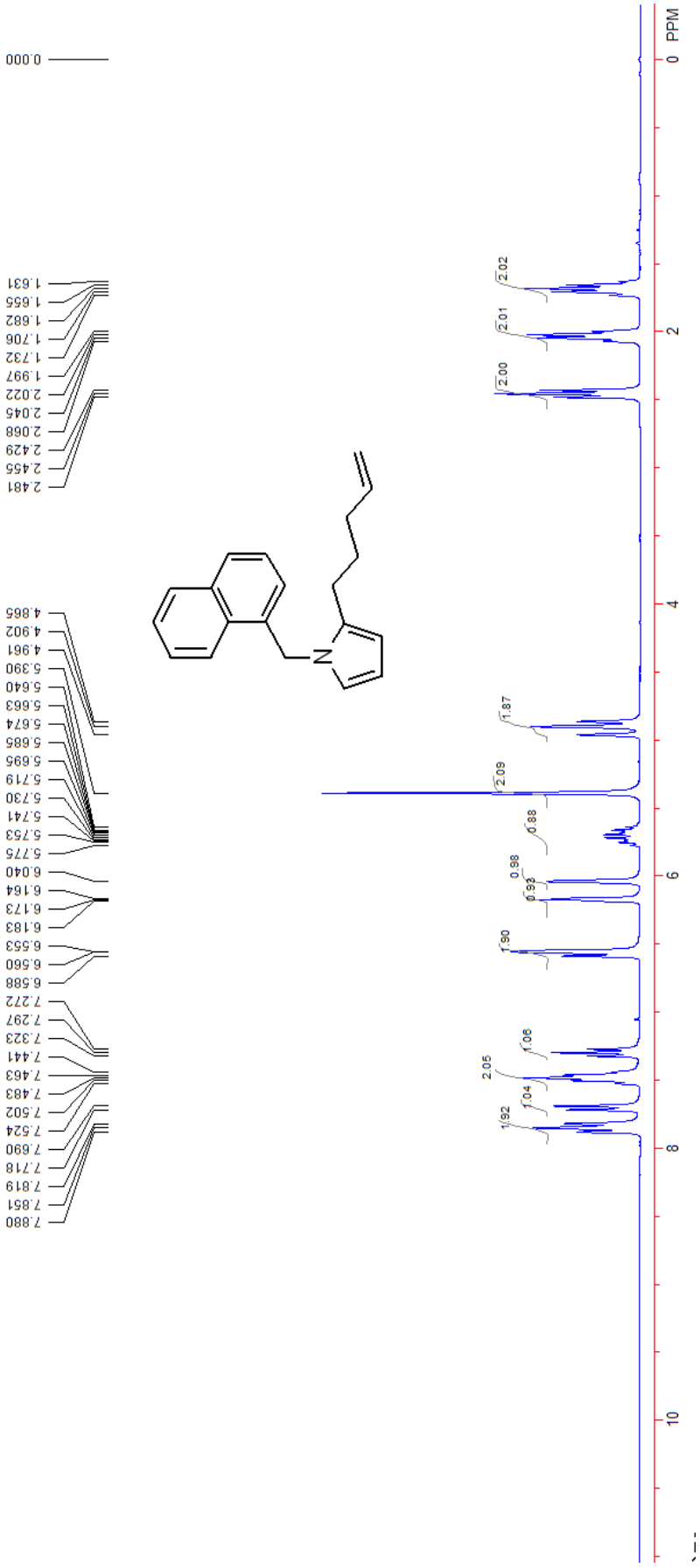
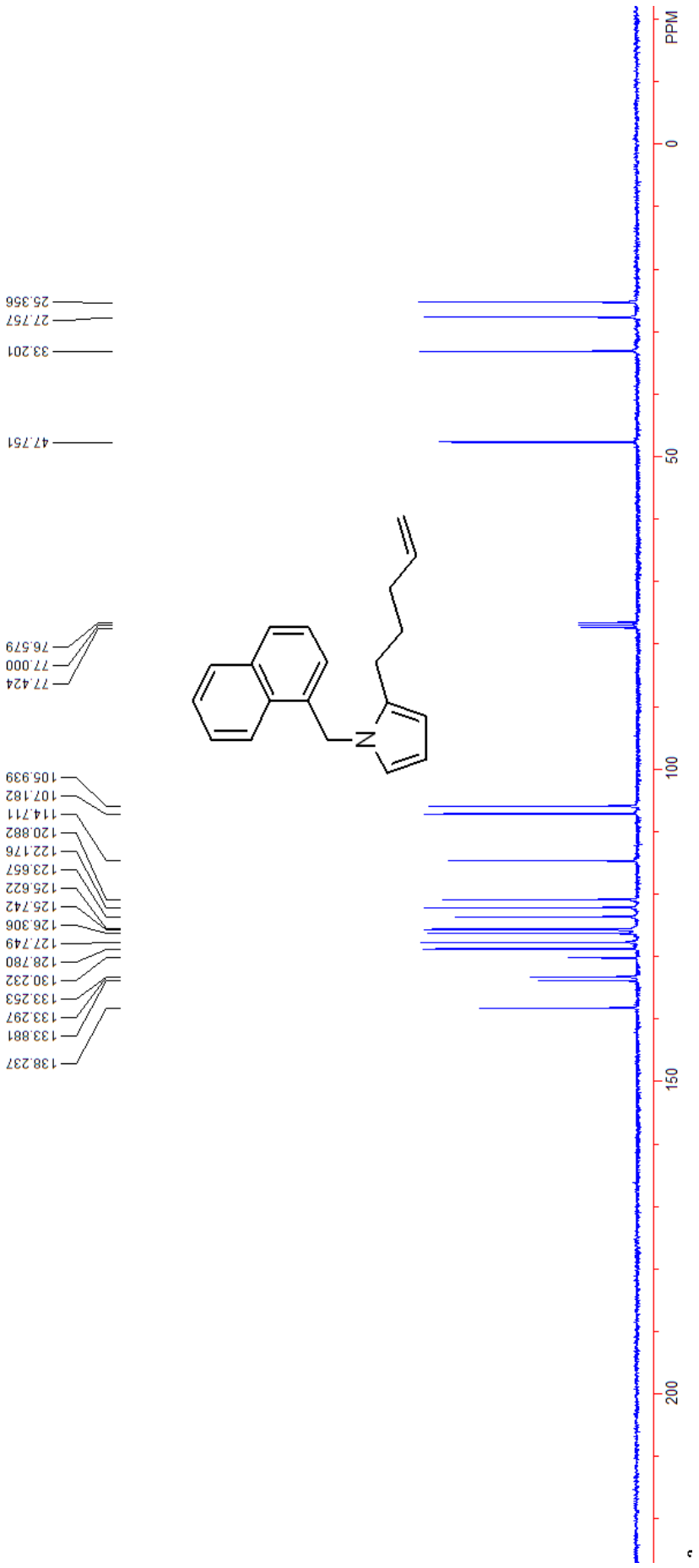
PPM

$^{1}$H NMR and $^{13}$C NMR Spectra of **1d**

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122.176
123.657
125.622
125.742
126.306
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130.232
133.253
133.297
133.881
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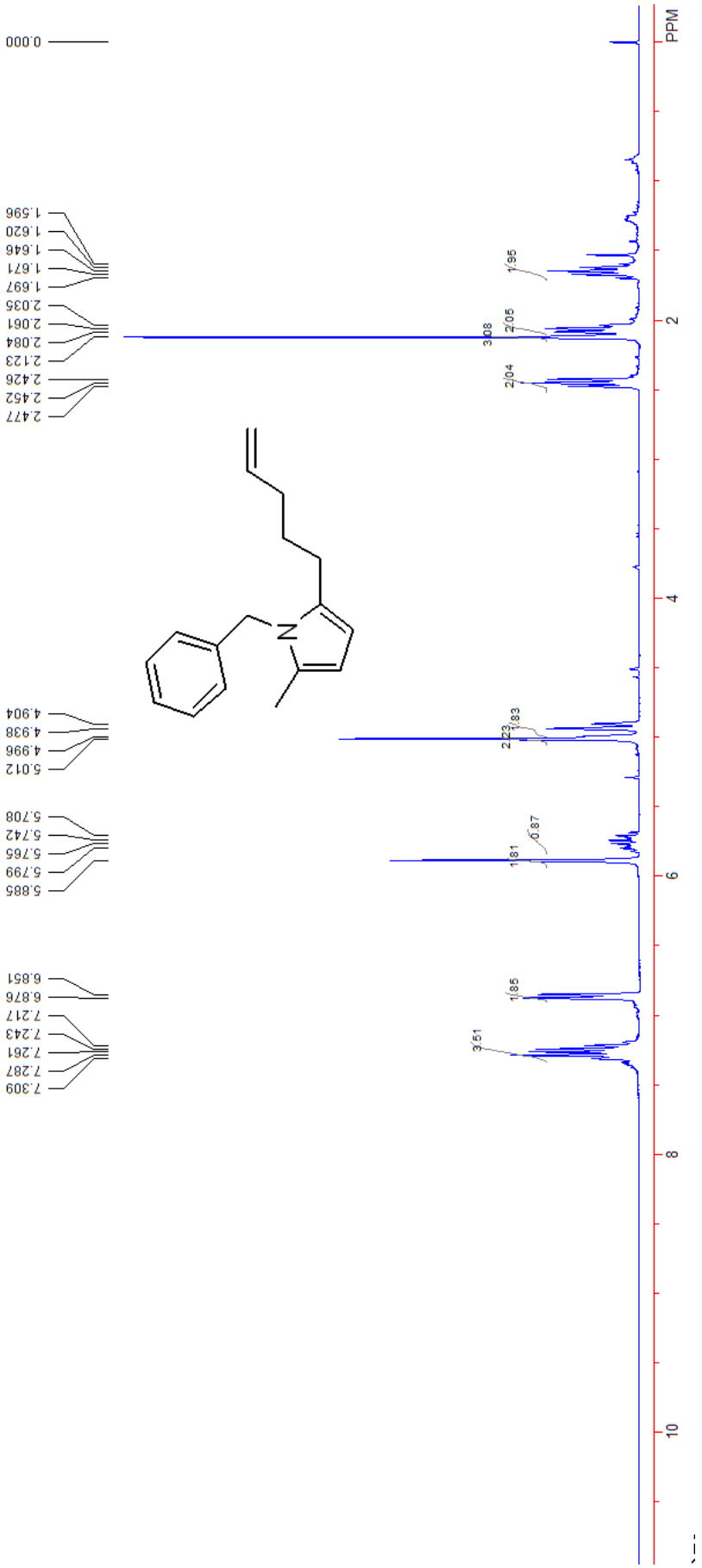
N

$^{1}$H NMR and $^{13}$C NMR Spectra of **1e**

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77.000
77.420
104.455
105.500
114.649
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127.994
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PPM
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50
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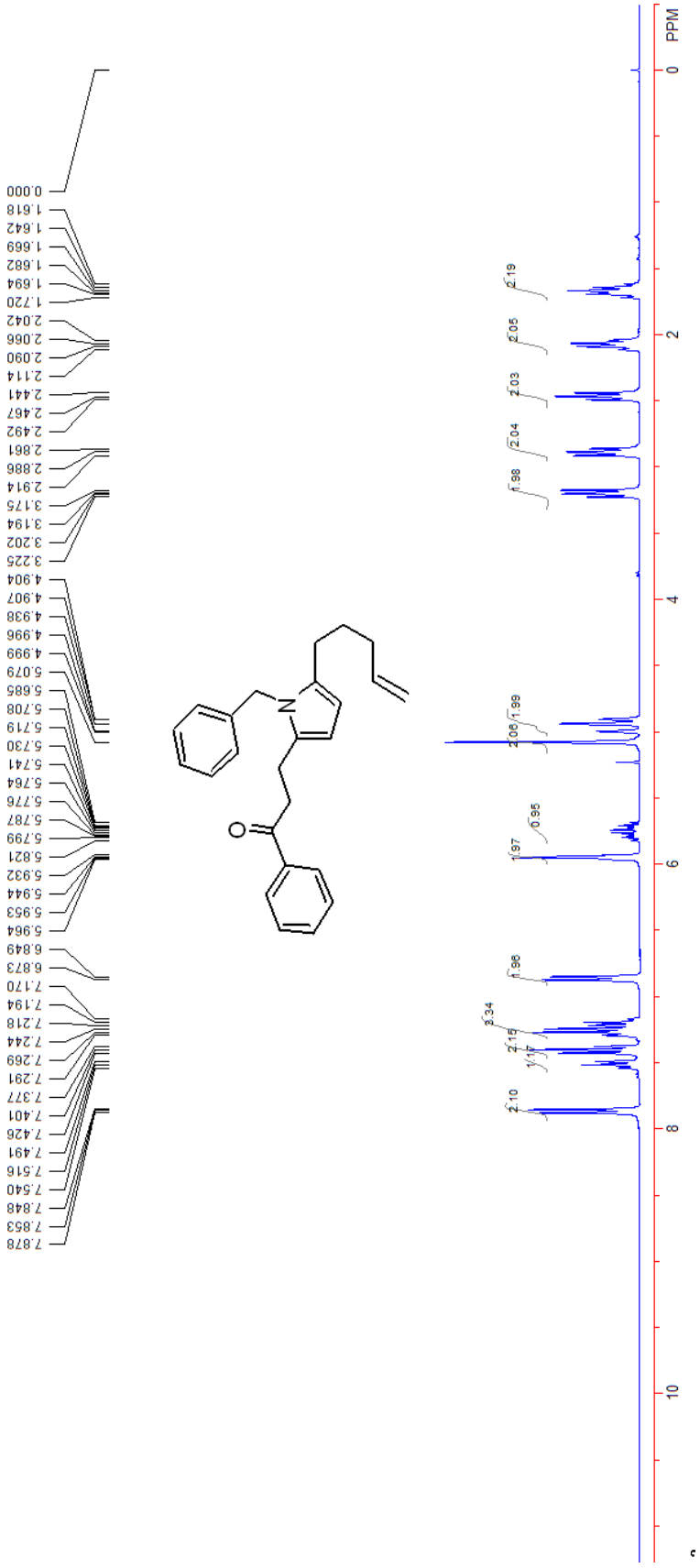
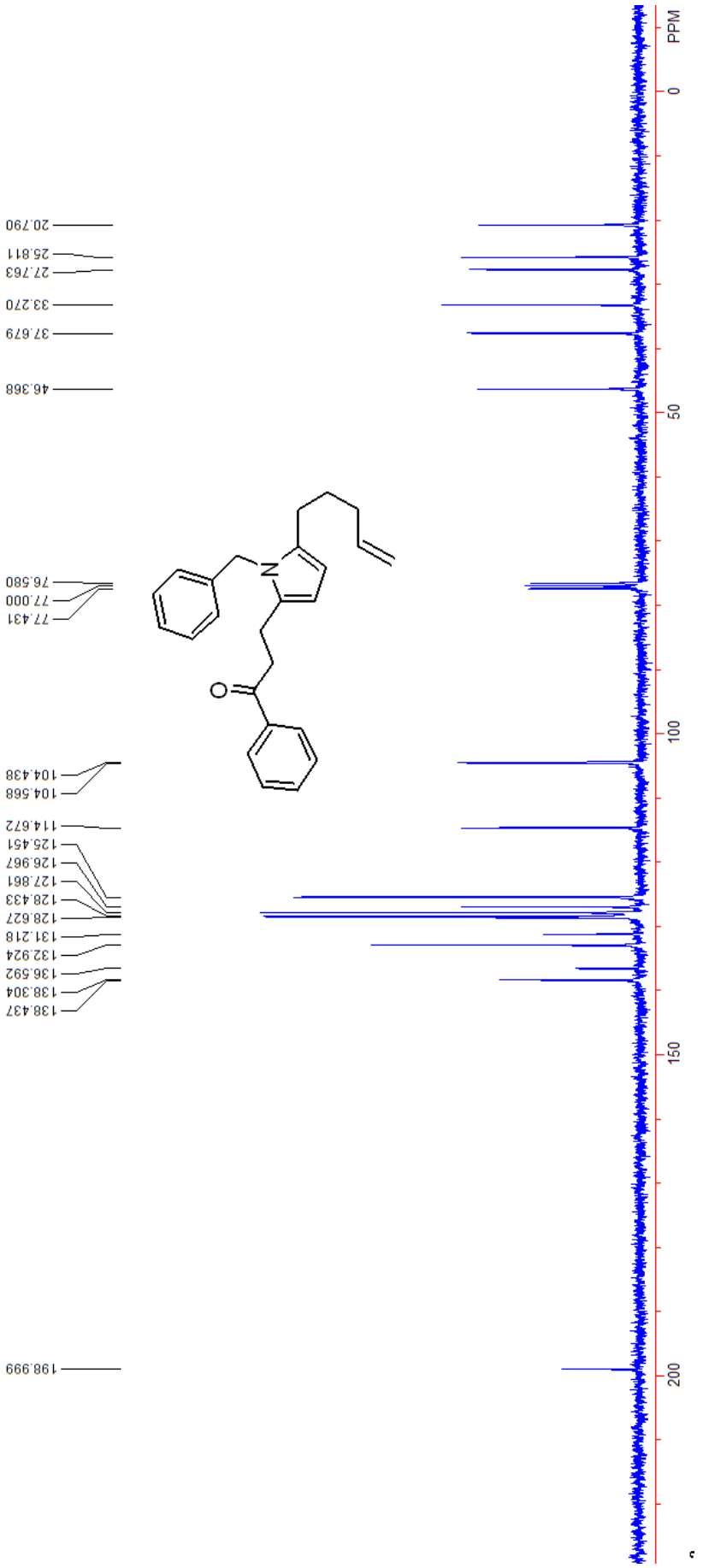
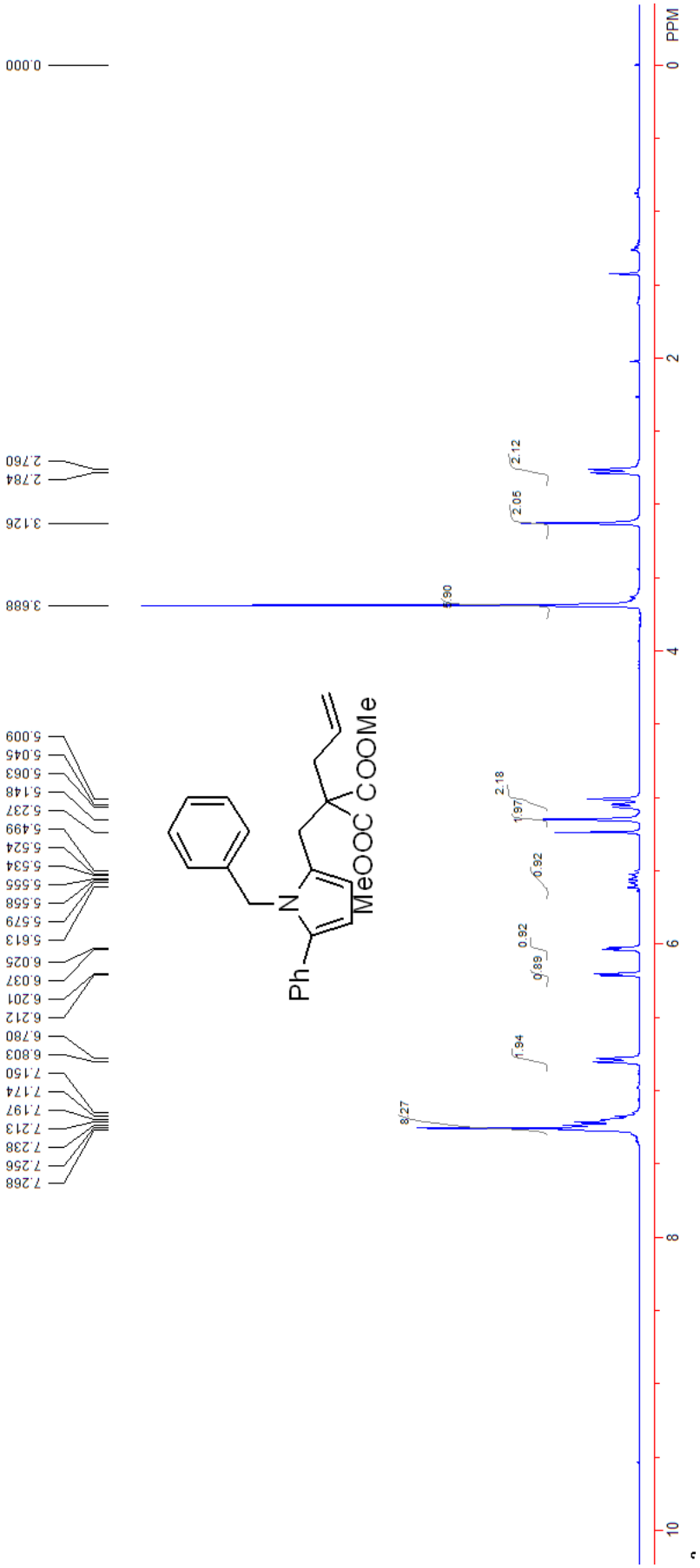
150
200

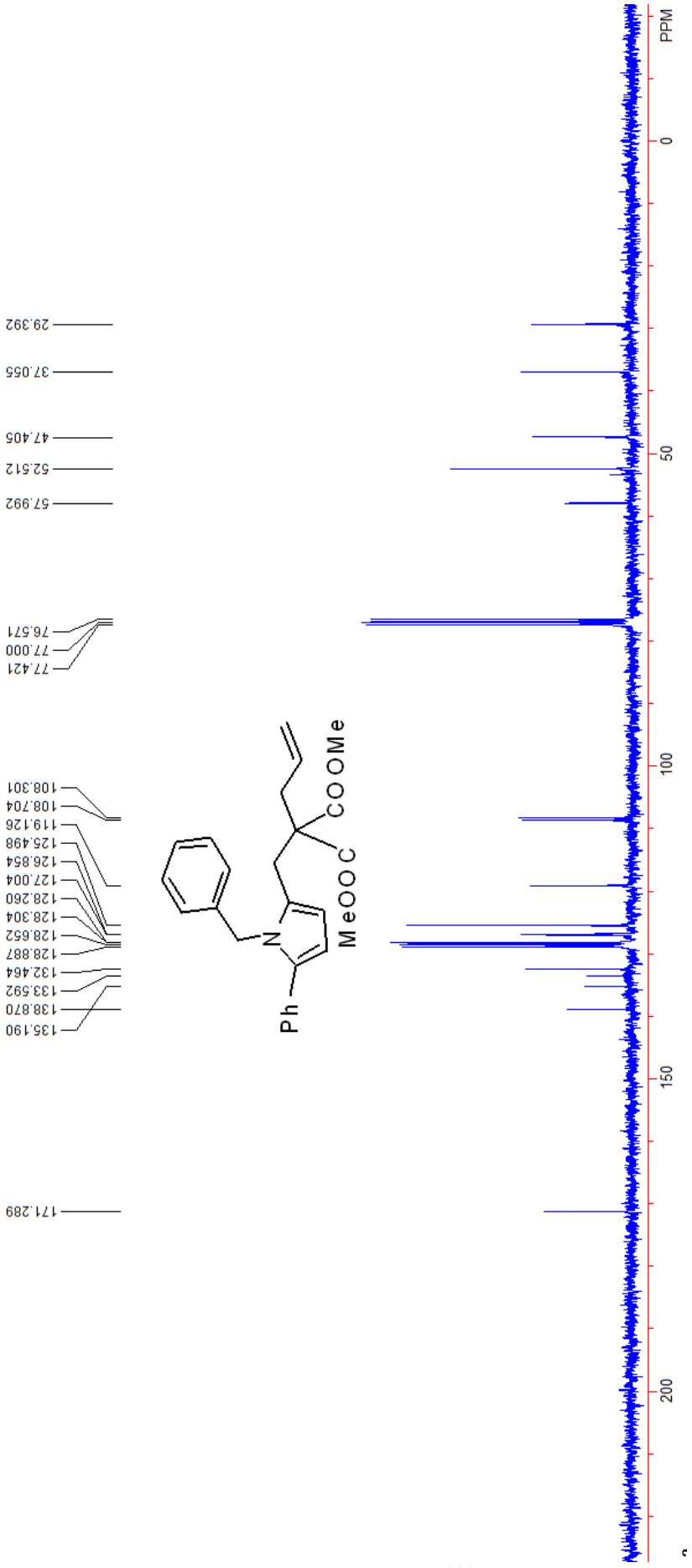
$^{1}$H NMR and $^{13}$C NMR Spectra of **1f**



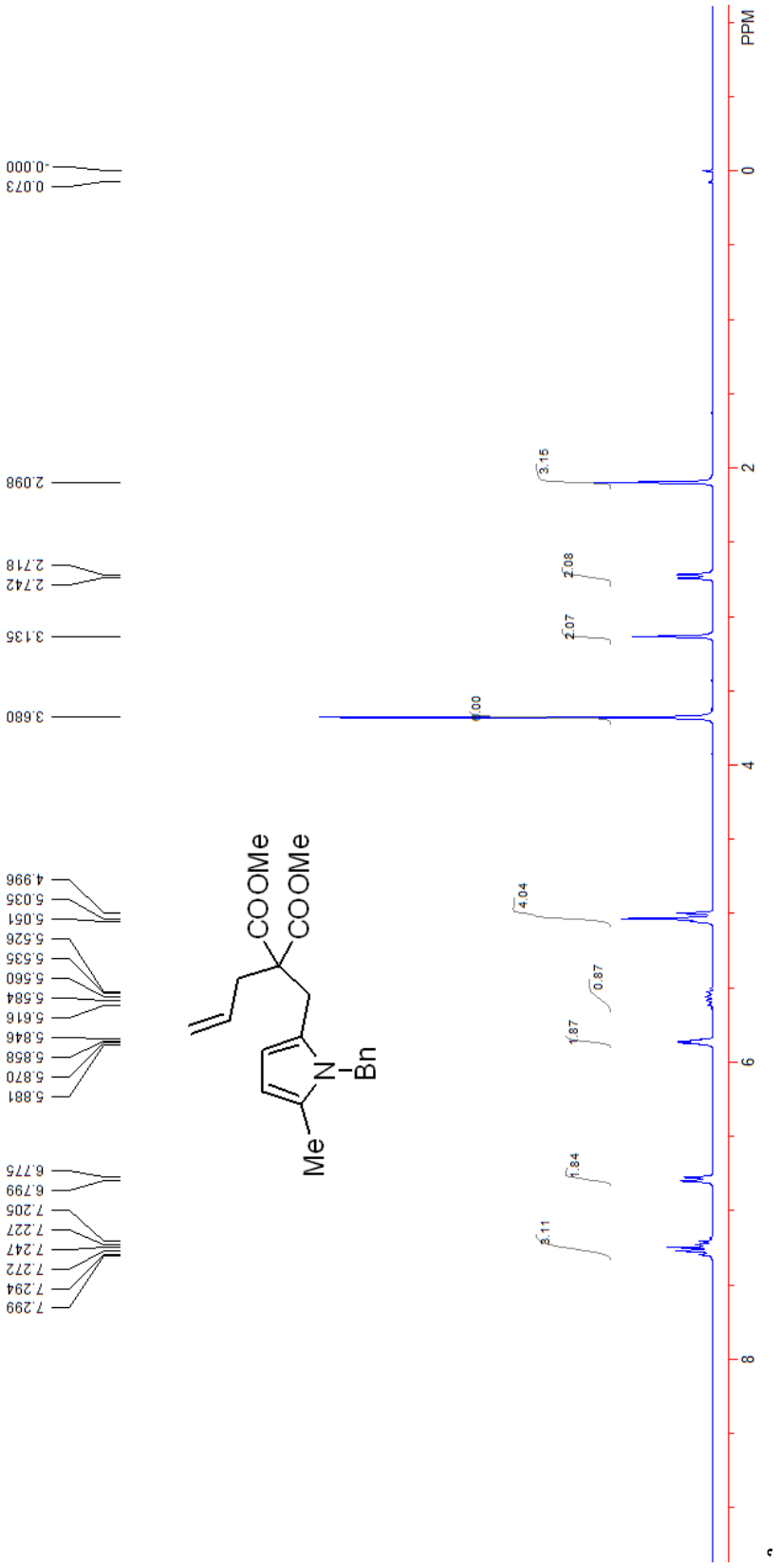

PPM
0
50
100
150
200
198.999
138.437
138.304
136.592
132.924
131.218
128.627
128.433
127.861
126.967
126.451
114.672
104.568
104.438
77.431
77.000
76.580
46.368
37.679
33.270
27.763
25.811
20.790
N
O

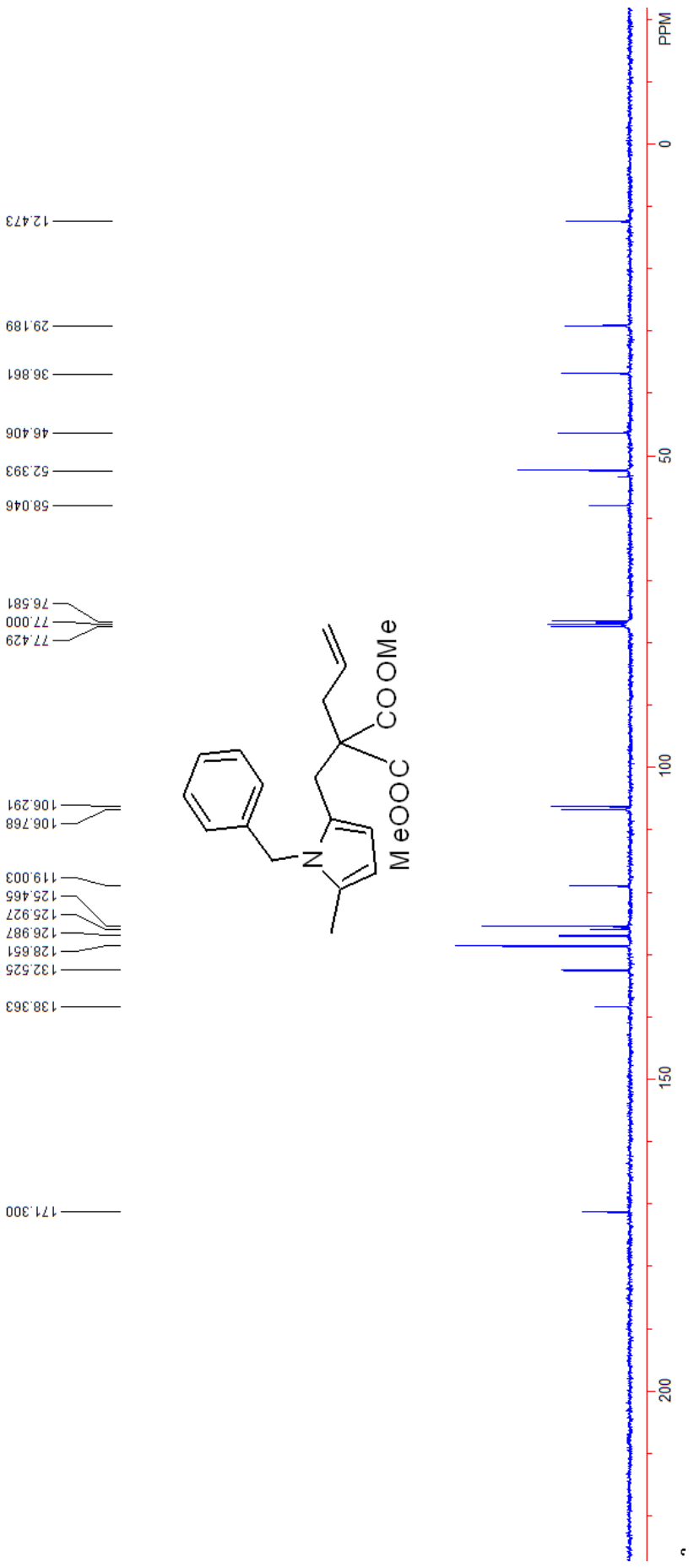
$^{1}$H NMR and $^{13}$C NMR Spectra of **1g**



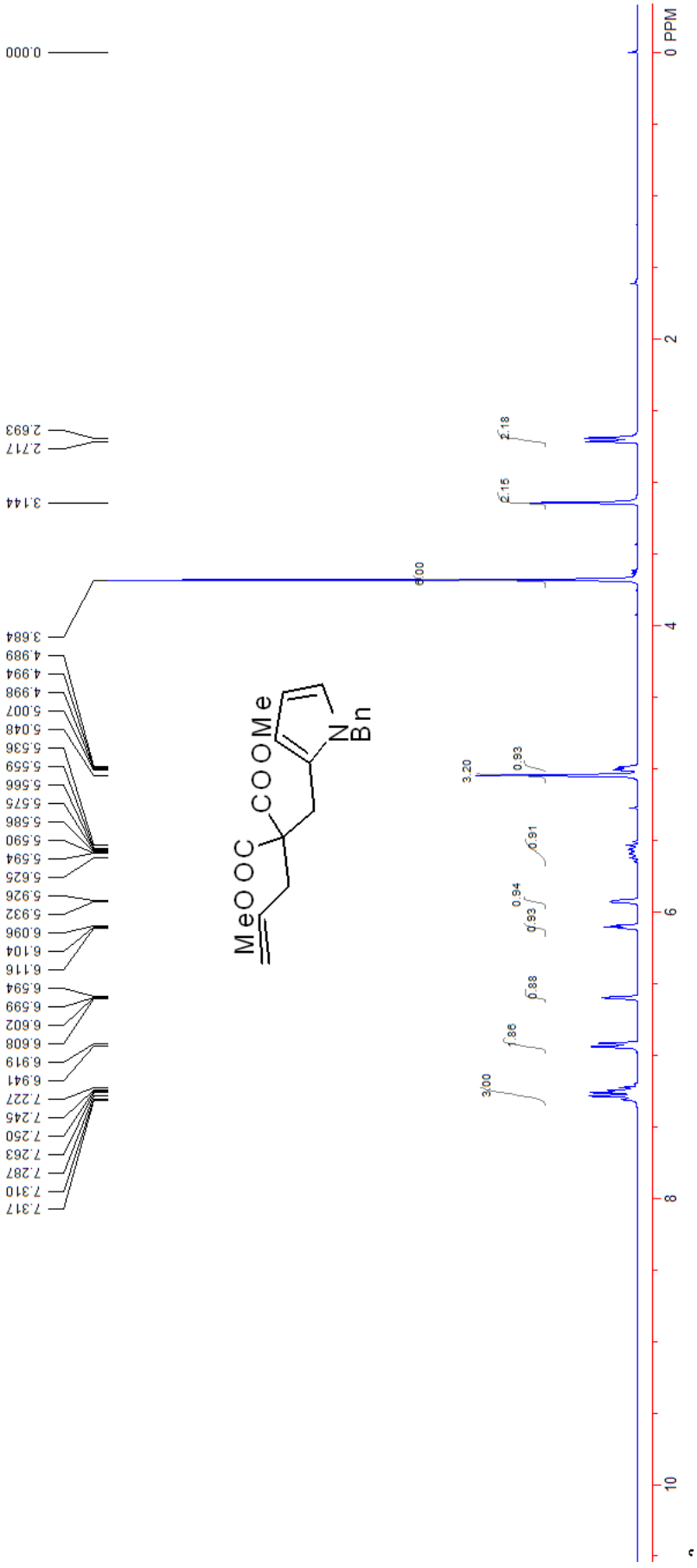

29.392
37.055
47.405
52.512
57.992
76.571
77.000
77.421
108.301
108.704
119.126
125.498
126.854
127.004
128.260
128.304
128.652
128.887
132.464
133.592
138.870
135.190
171.289
PPM
0
50
100
150
200
N
Ph
MeOOC
COOMe

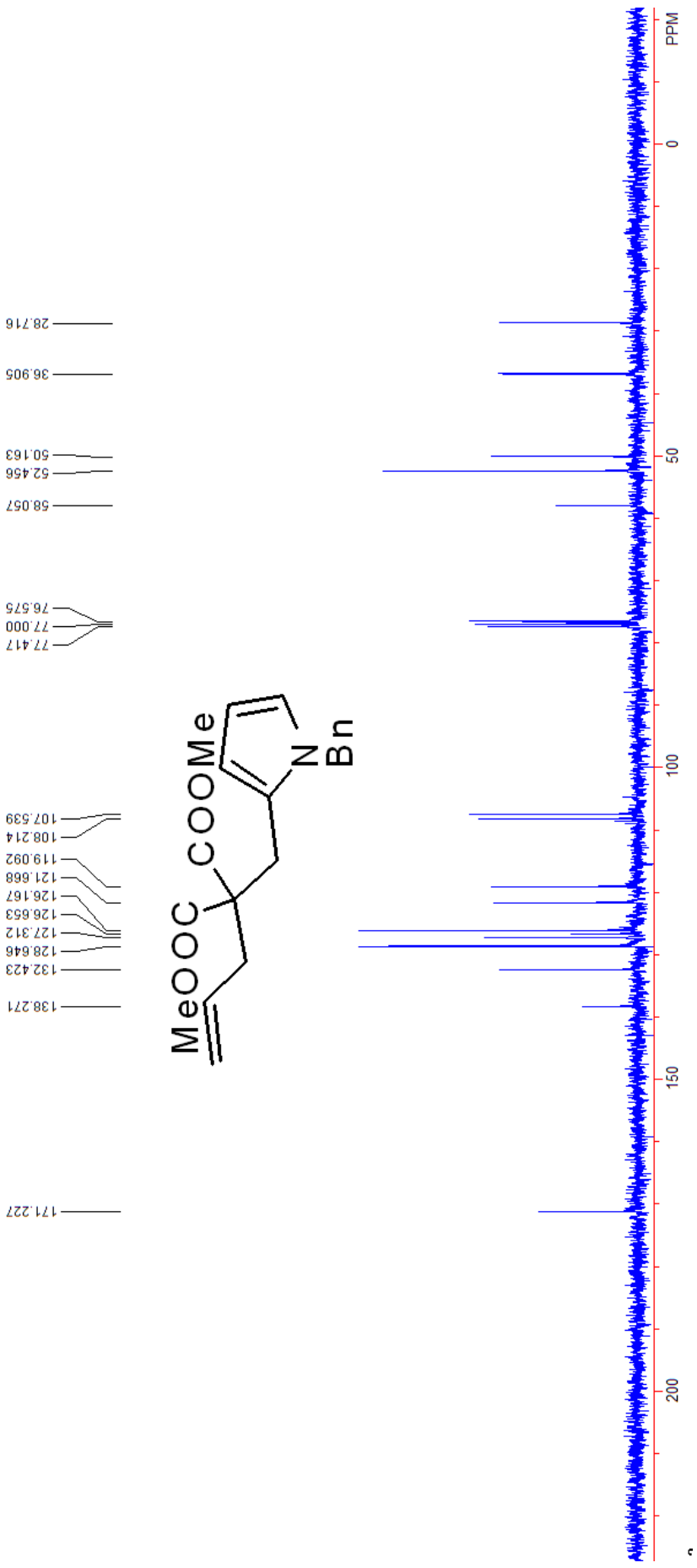
$^{1}$H NMR and $^{13}$C NMR Spectra of **1h**



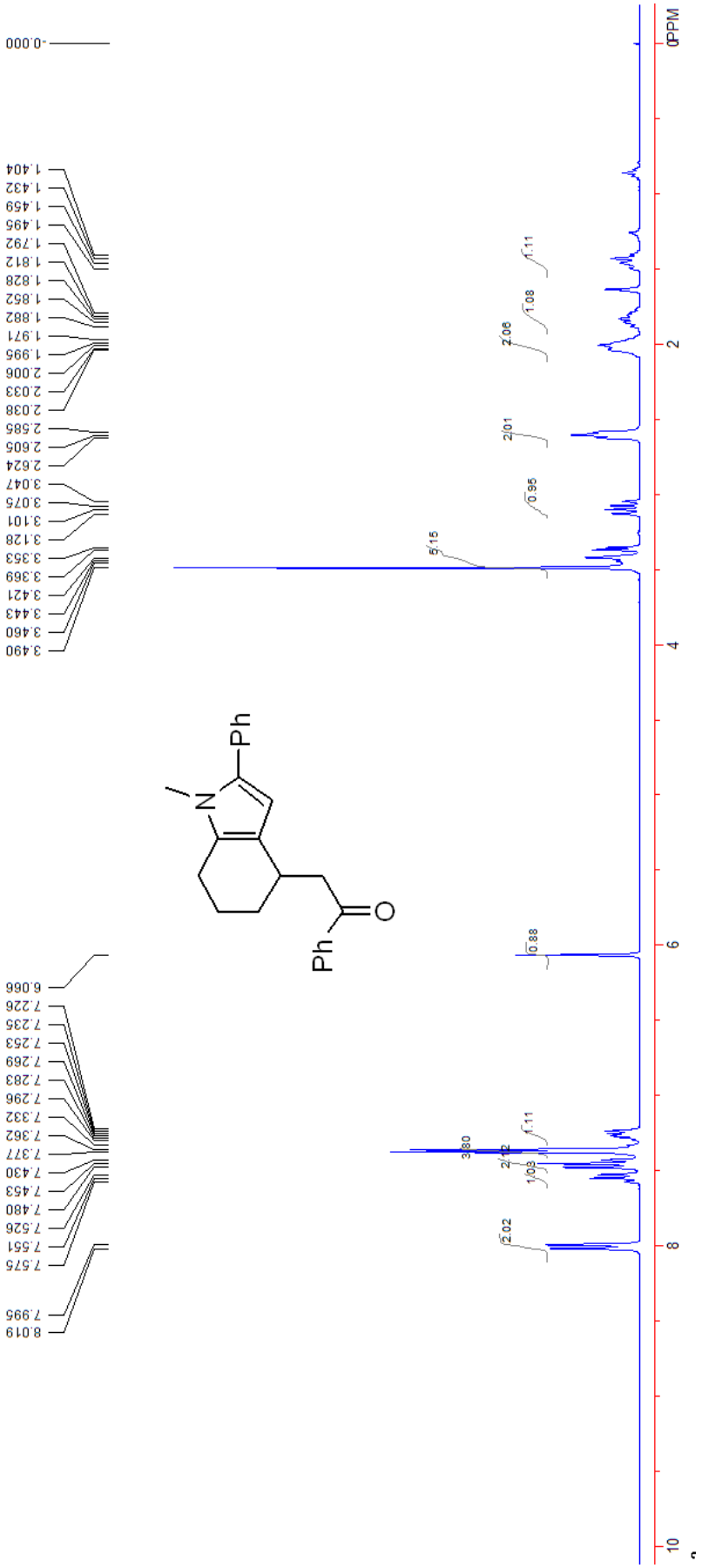

12.473
29.189
36.861
46.406
52.393
58.046
76.581
77.000
77.429
106.291
106.768
119.003
125.465
125.927
126.987
128.651
132.525
138.363
171.300
N
COOMe
MeOOC
PPM
0
50
100
150
200

$^{1}$H NMR and $^{13}$C NMR Spectra of **1i**



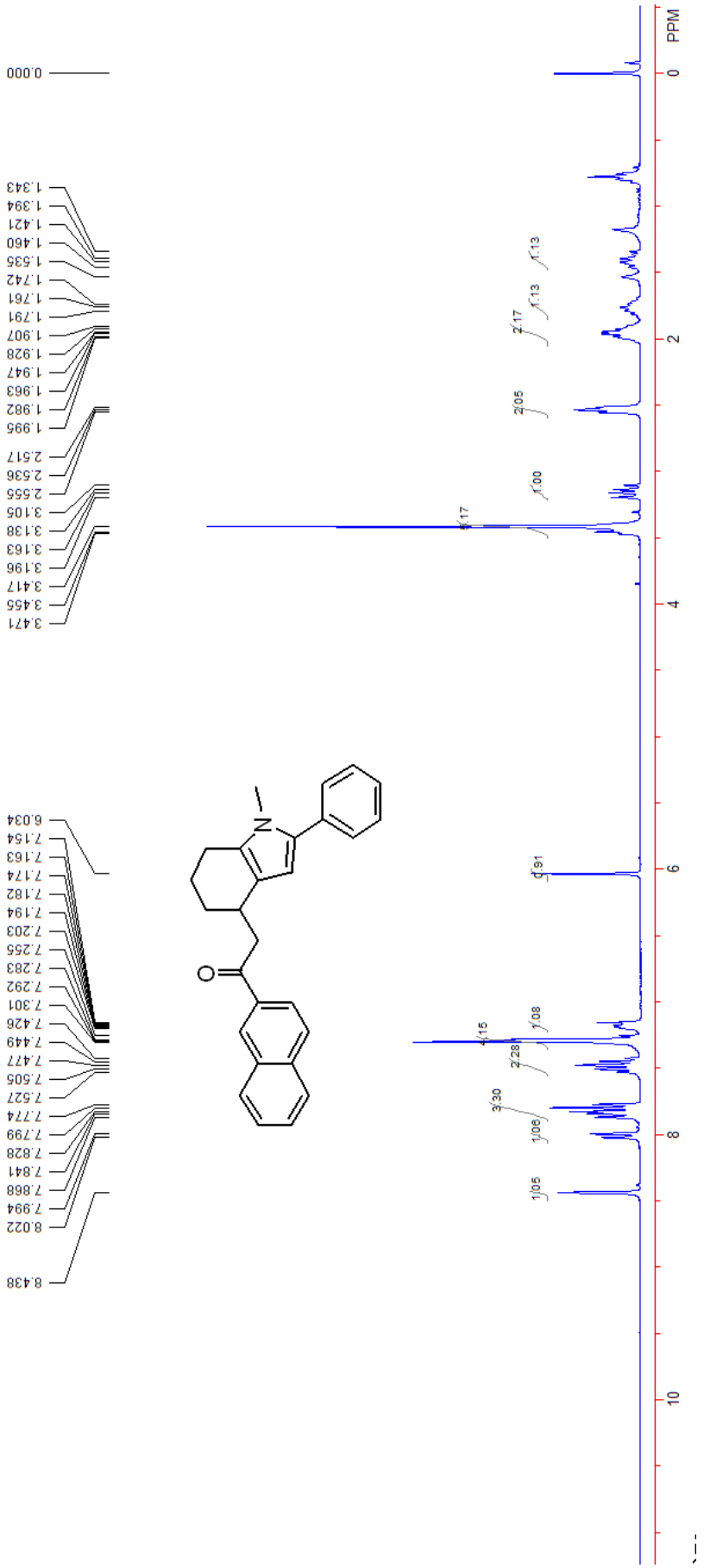

28.716
36.905
50.163
52.456
58.057
76.575
77.000
77.417
107.539
108.214
119.092
121.668
126.167
126.653
127.312
128.646
132.423
138.271
171.227
MeOOC
COOMe
N
Bn
PPM
0
50
100
150
200

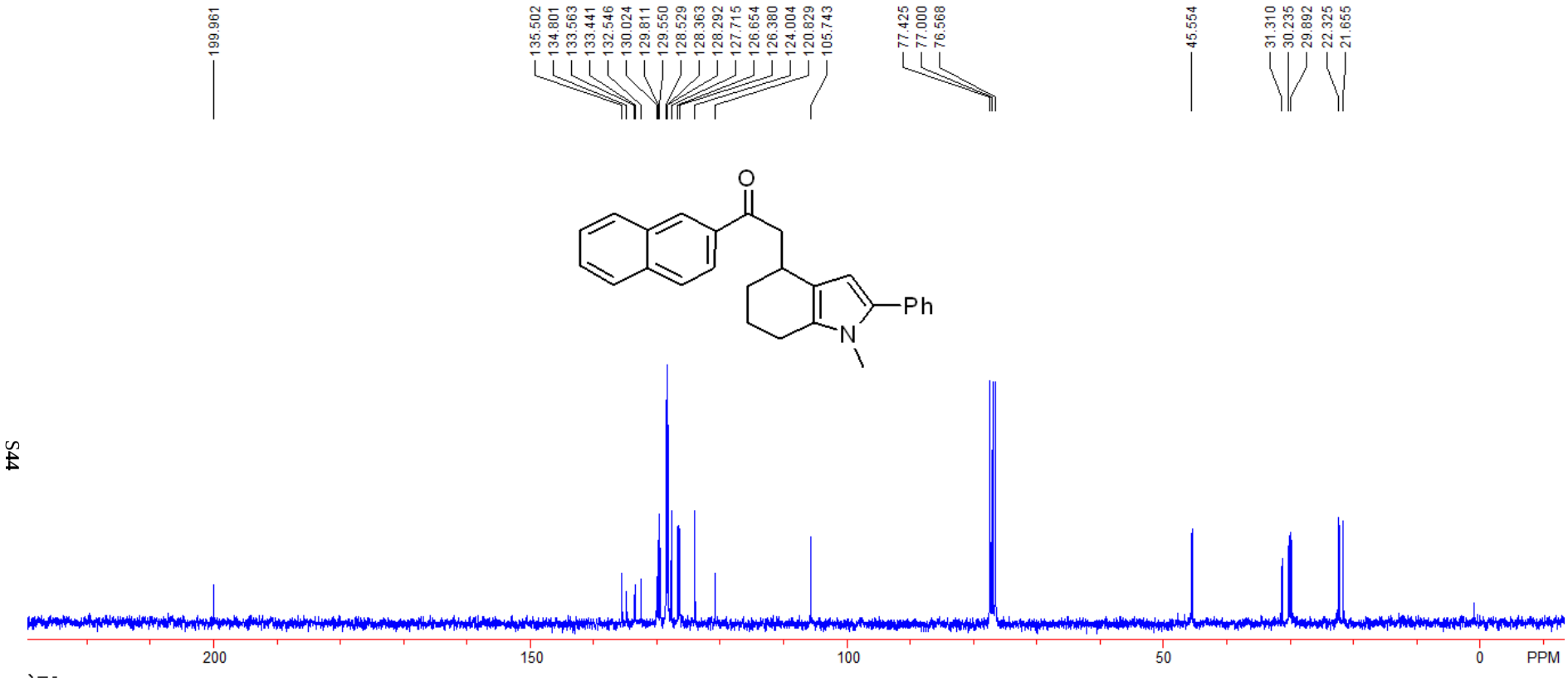
$^{1}$H NMR and $^{13}$C NMR Spectra of **3a**



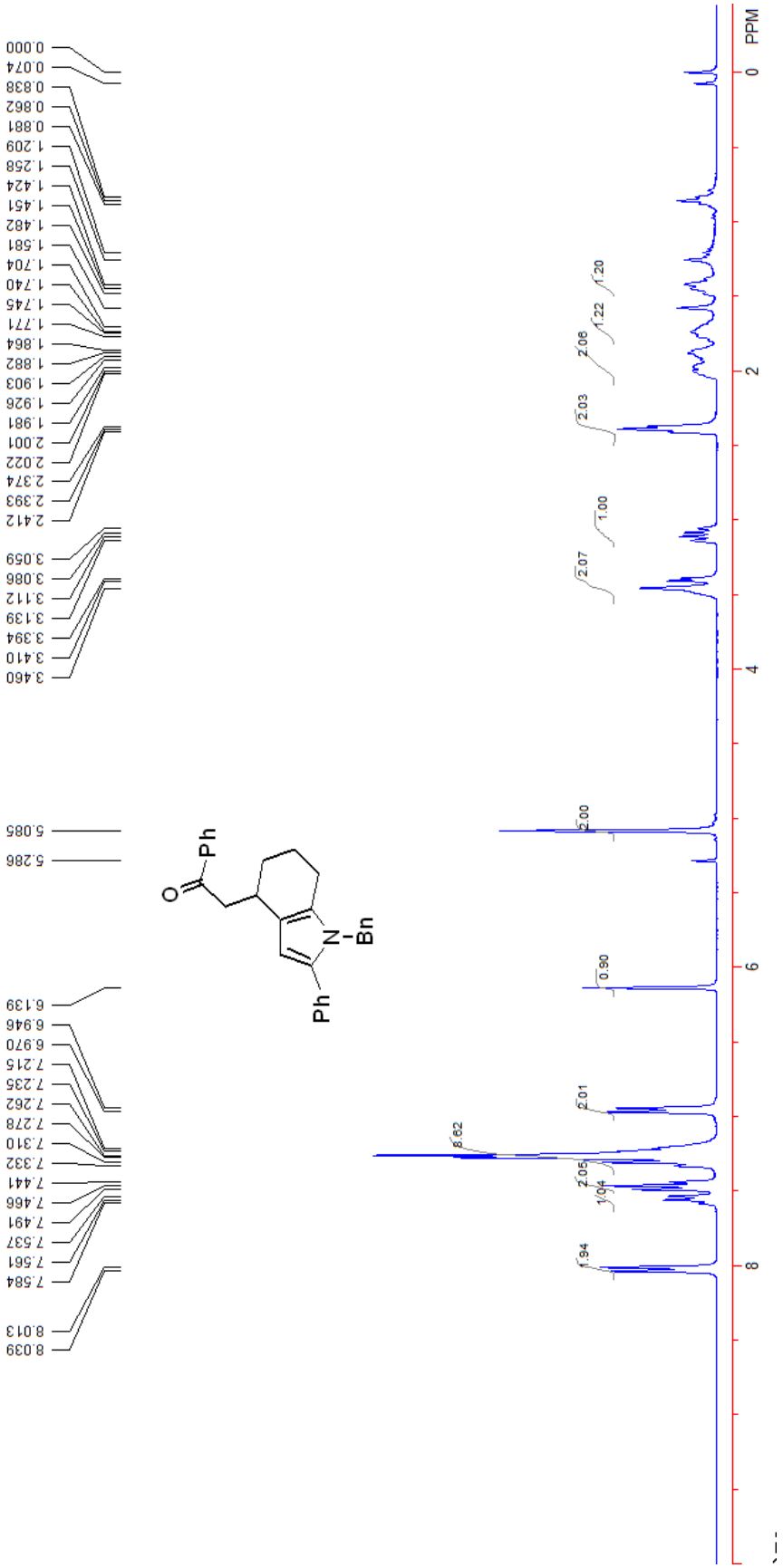

PPM
0
50
100
150
200
21.624
22.281
29.844
29.993
31.307
45.481
76.577
77.000
77.419
105.662
120.736
126.368
128.120
128.270
128.507
129.990
132.863
133.364
137.373
133.508
200.029
Ph
N
Ph
O

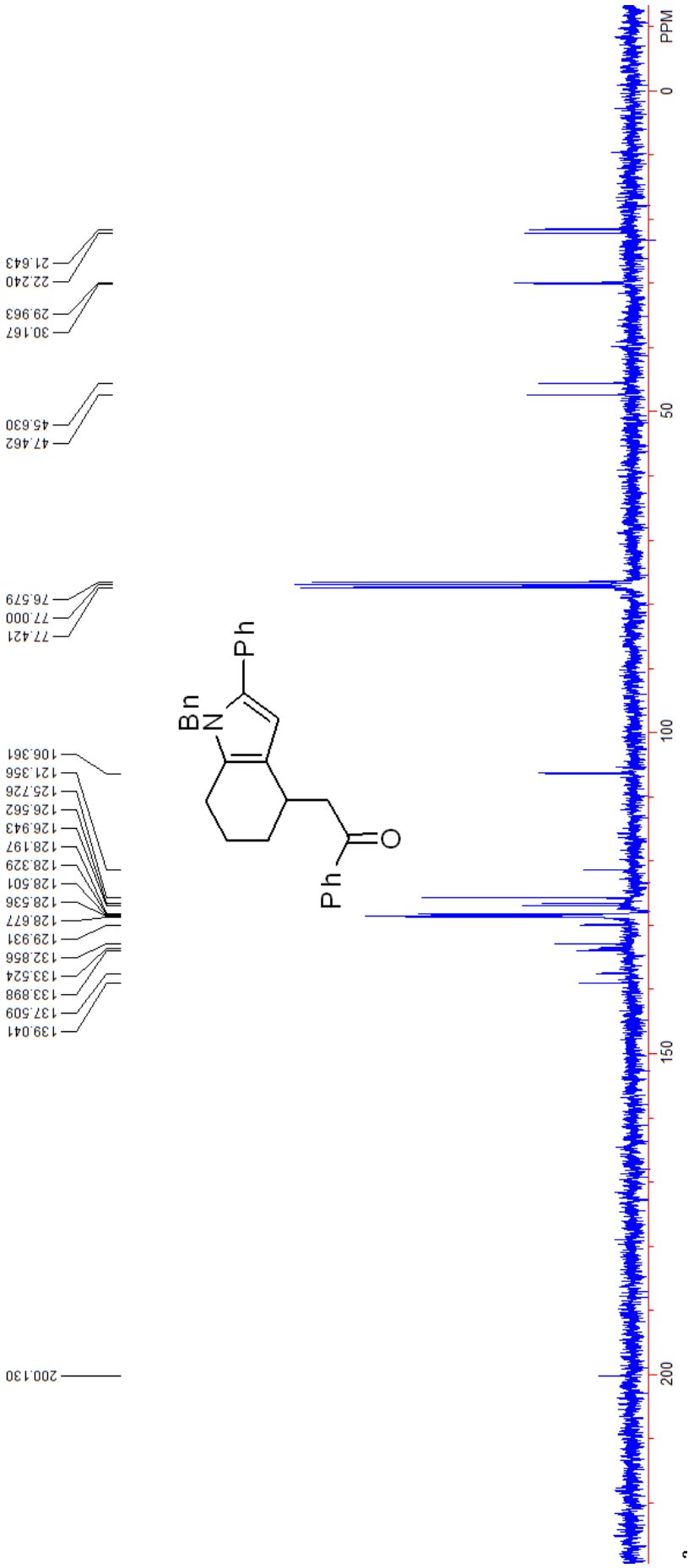
$^{1}$H NMR and $^{13}$C NMR Spectra of **3b**



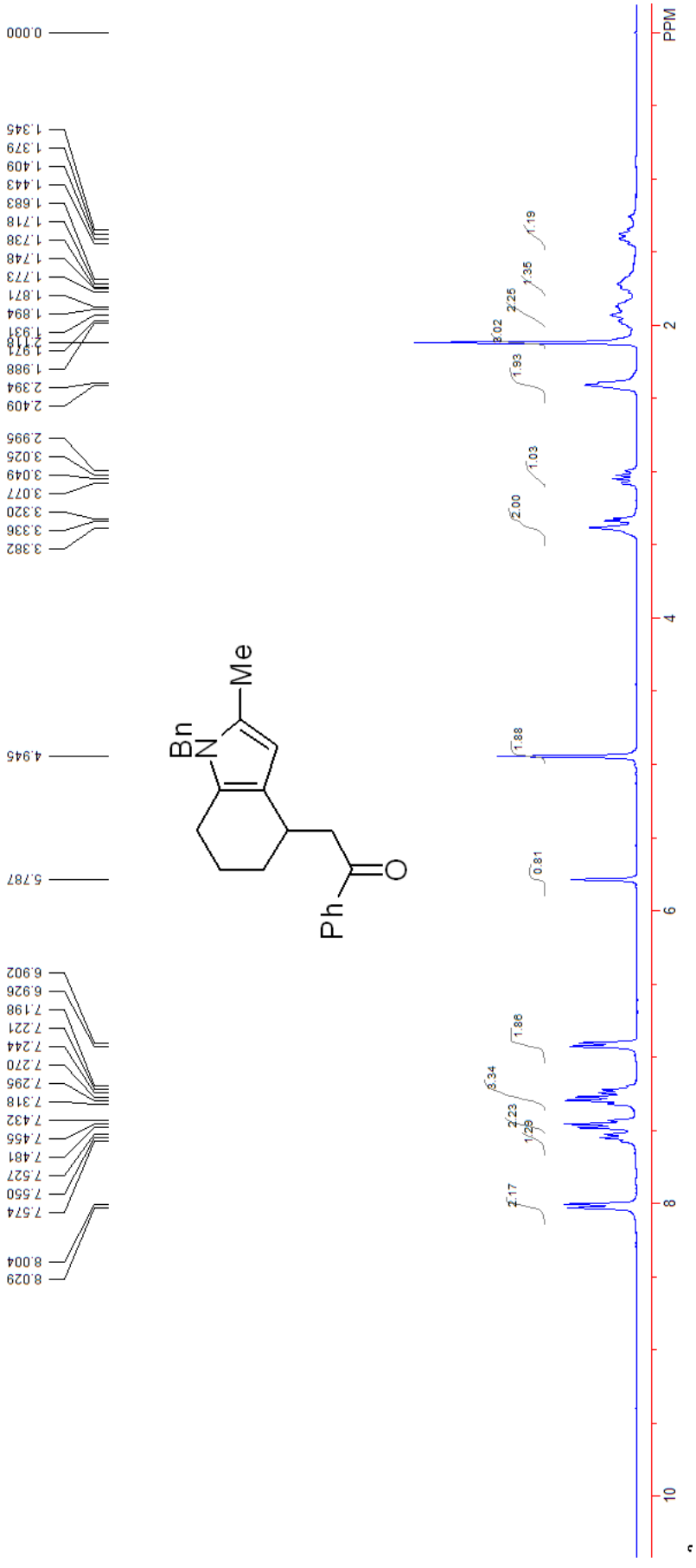

199.961
135.502
134.801
133.563
133.441
132.546
130.024
129.811
129.550
128.529
128.363
128.292
127.715
126.654
126.380
124.004
120.829
105.743
77.425
77.000
76.568
45.554
31.310
30.235
29.892
22.325
21.655
O
Ph
N
200
150
100
50
0
PPM

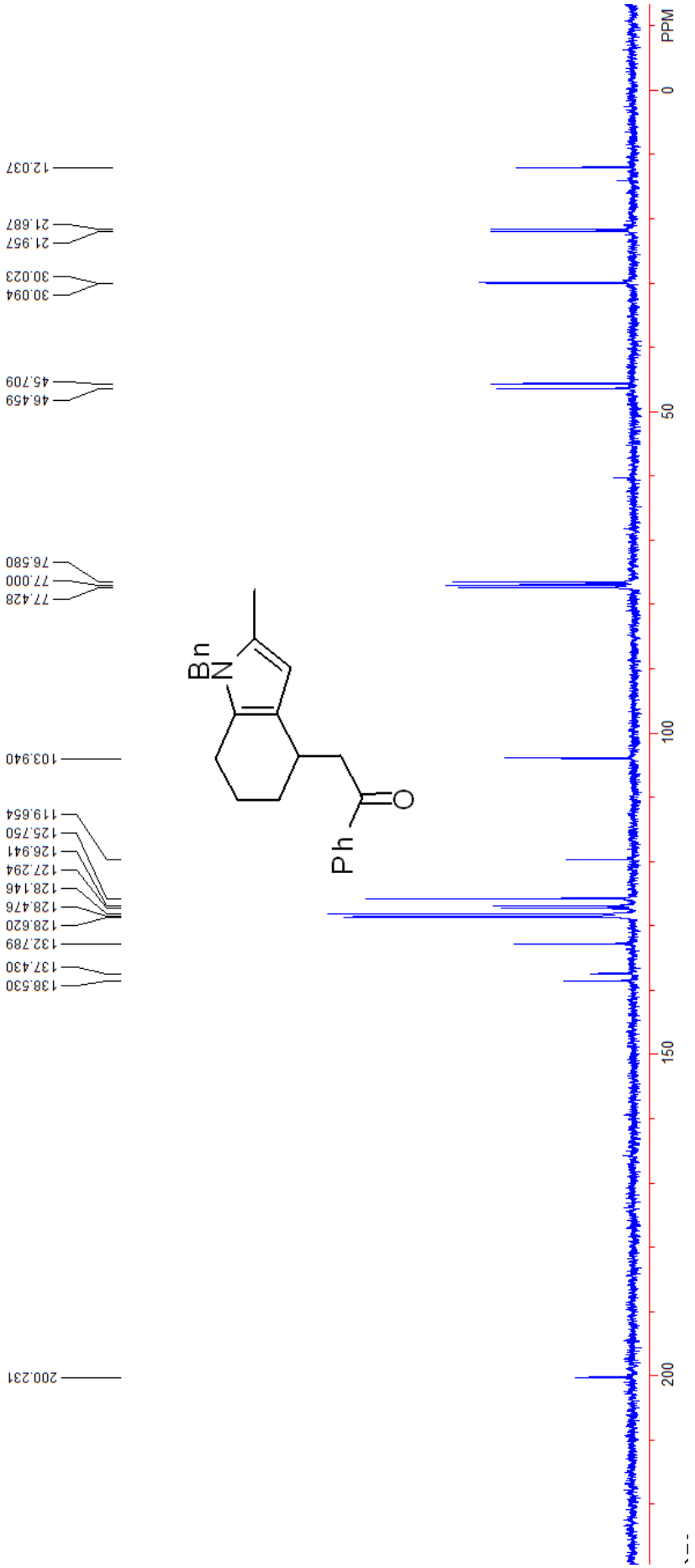
$^{1}$H NMR and $^{13}$C NMR Spectra of **3c**



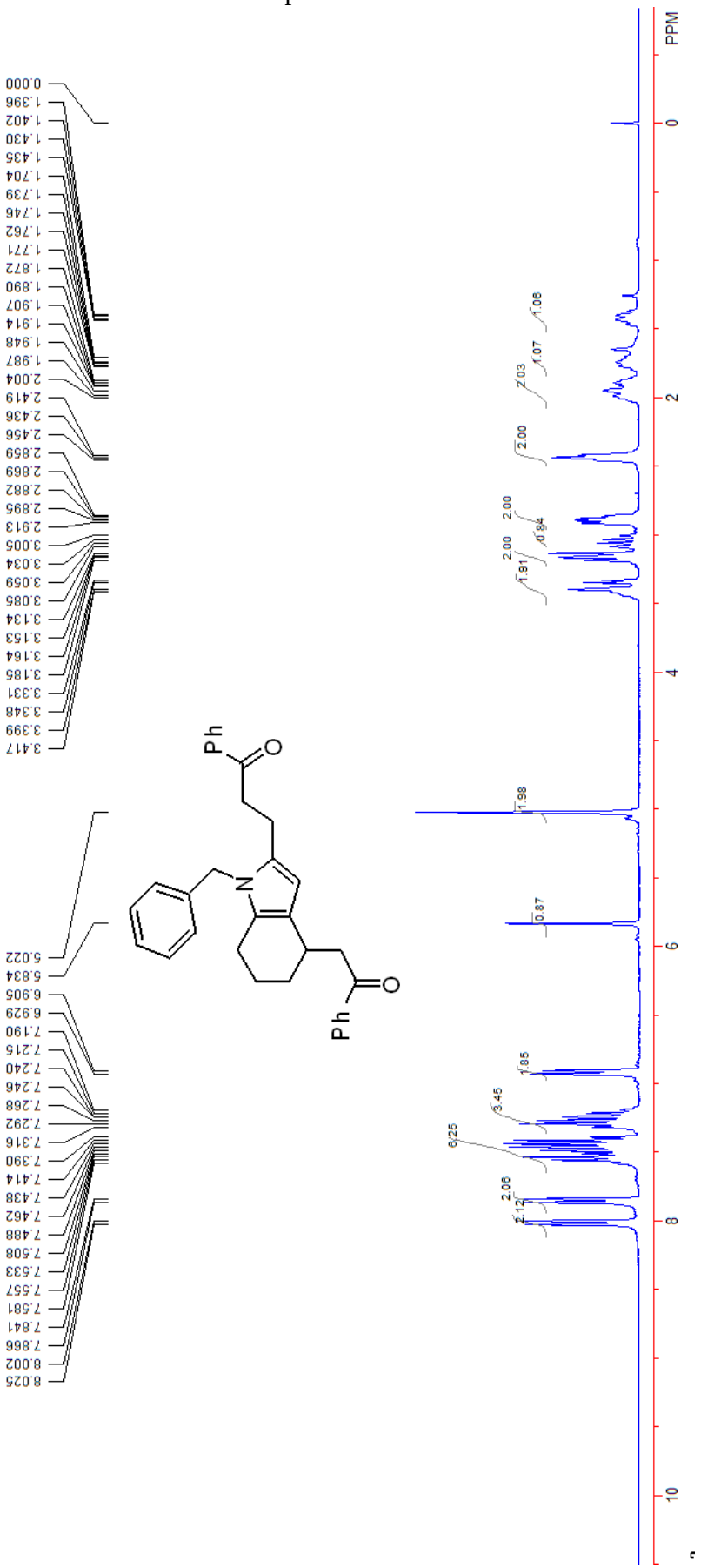

21.643
22.240
29.963
30.167
45.630
47.462
76.579
77.000
77.421
106.361
121.356
125.726
126.562
126.943
128.197
128.329
128.501
128.536
128.677
129.931
132.856
133.524
133.898
137.509
139.041
200.130
Bn
N
Ph
Ph
O
PPM
0
50
100
150
200

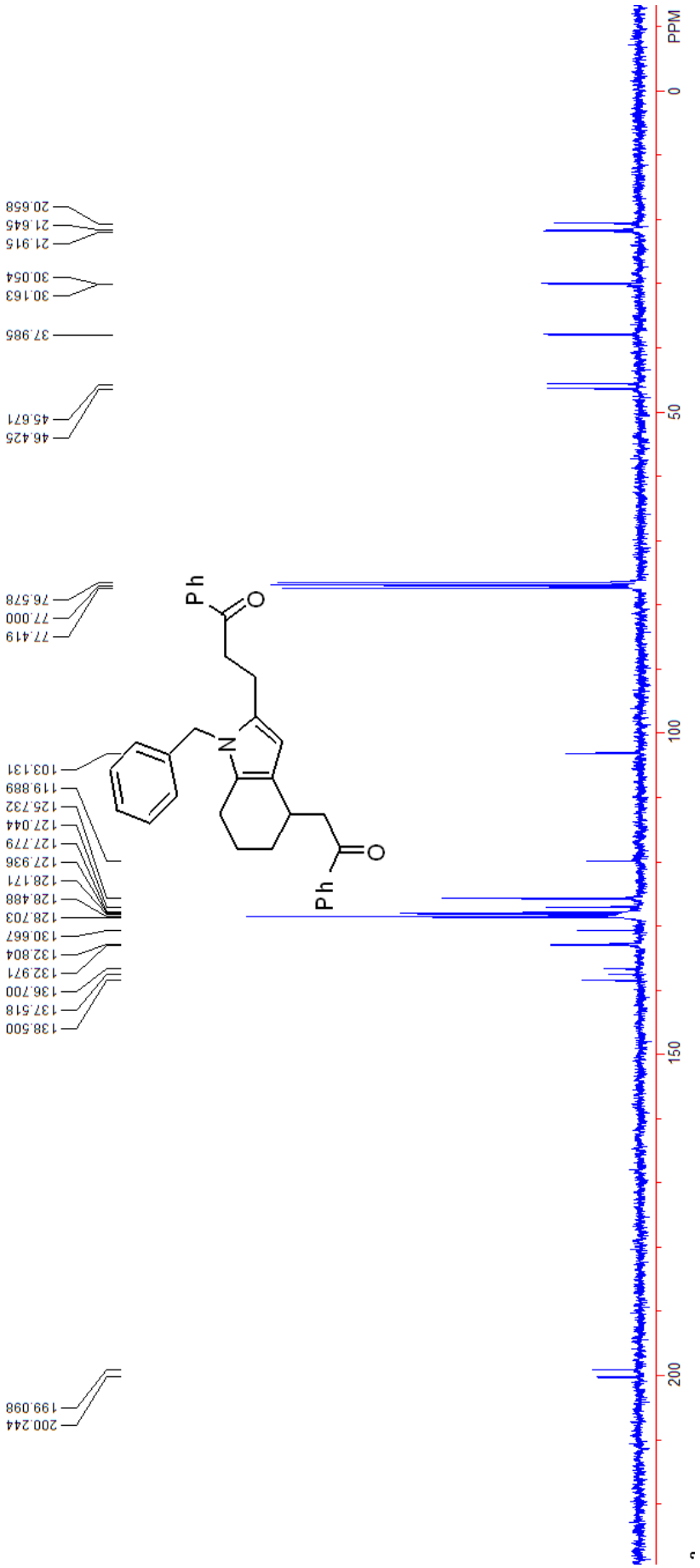
$^{1}$H NMR and $^{13}$C NMR Spectra of **3d**



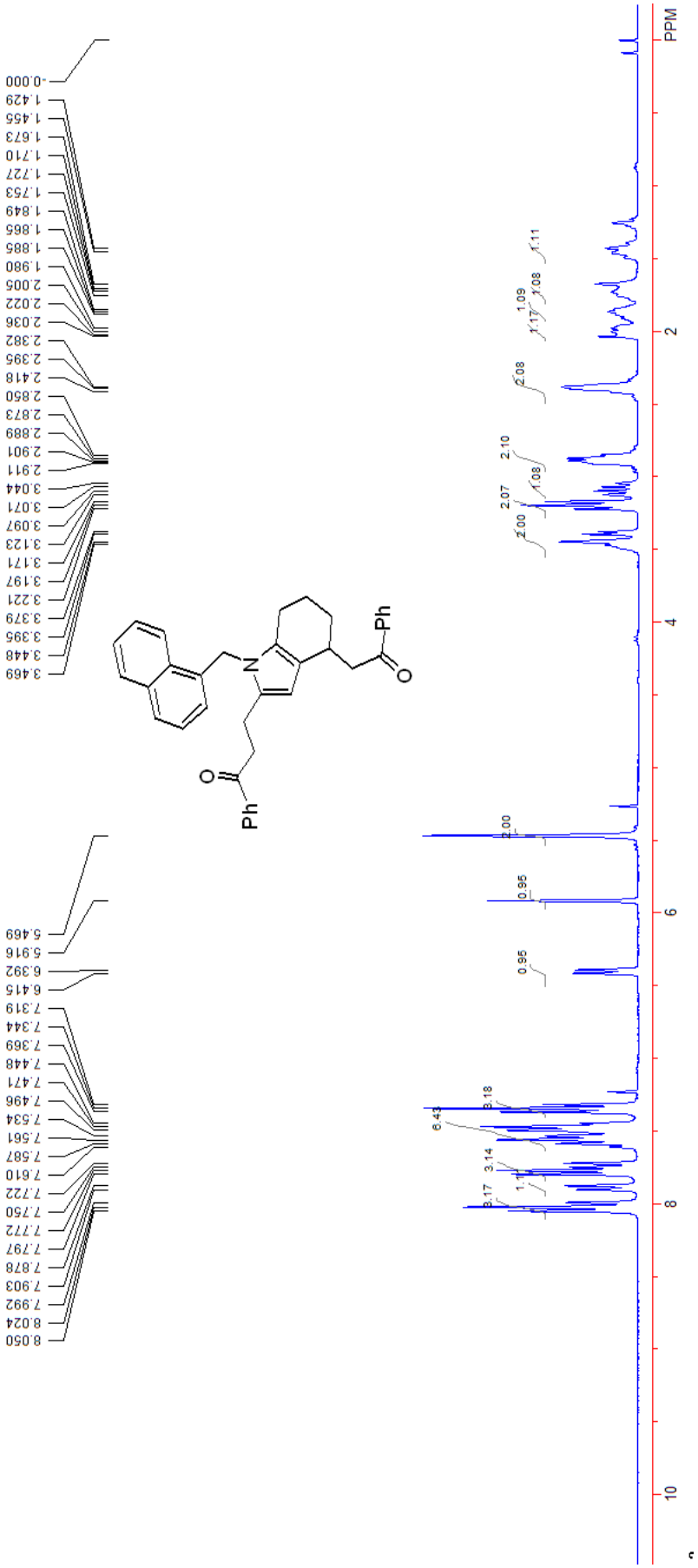

12.037
21.687
21.957
30.023
30.094
45.709
46.459
76.580
77.000
77.428
103.940
119.654
125.750
126.941
127.294
128.146
128.476
128.620
132.789
137.430
138.530
200.231
Bn
N
Ph
O
PPM
0
50
100
150
200

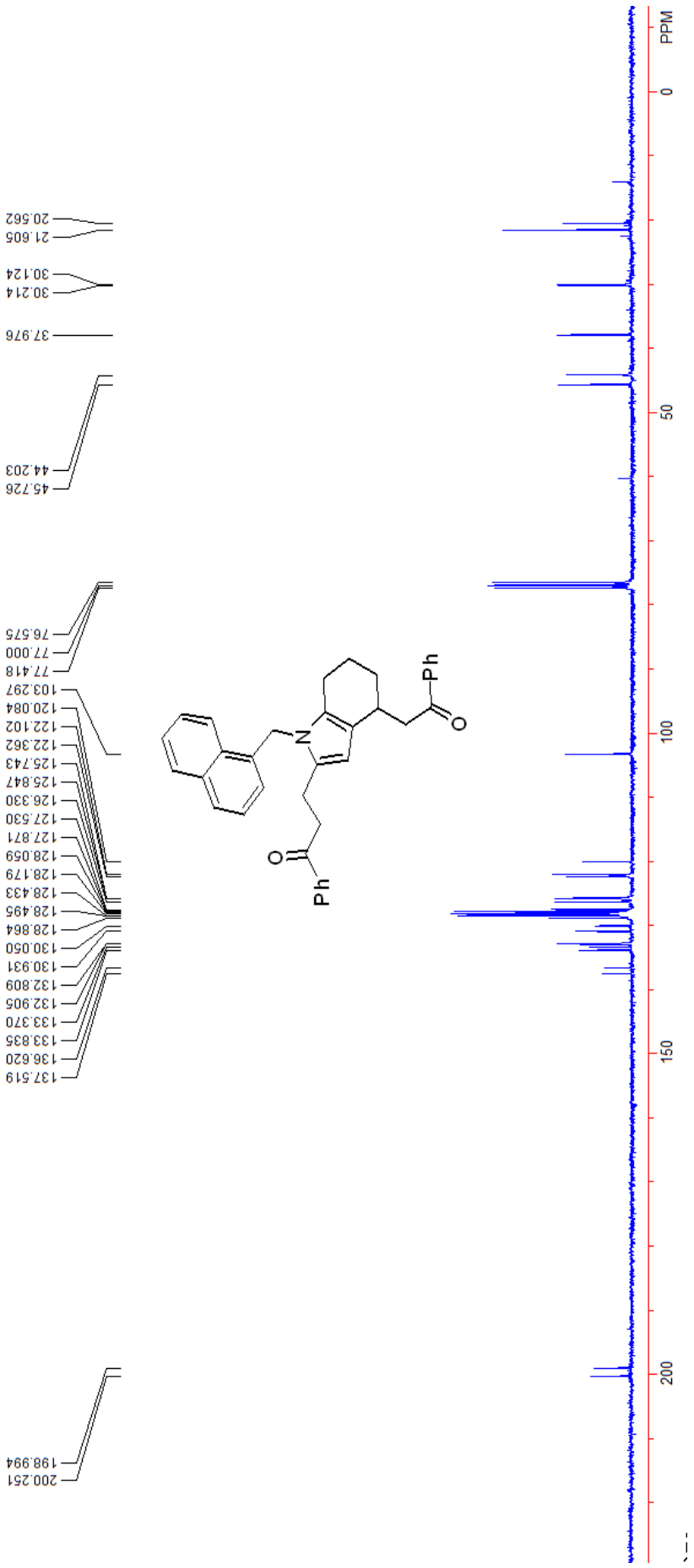
$^{1}$H NMR and $^{13}$C NMR Spectra of **3e**



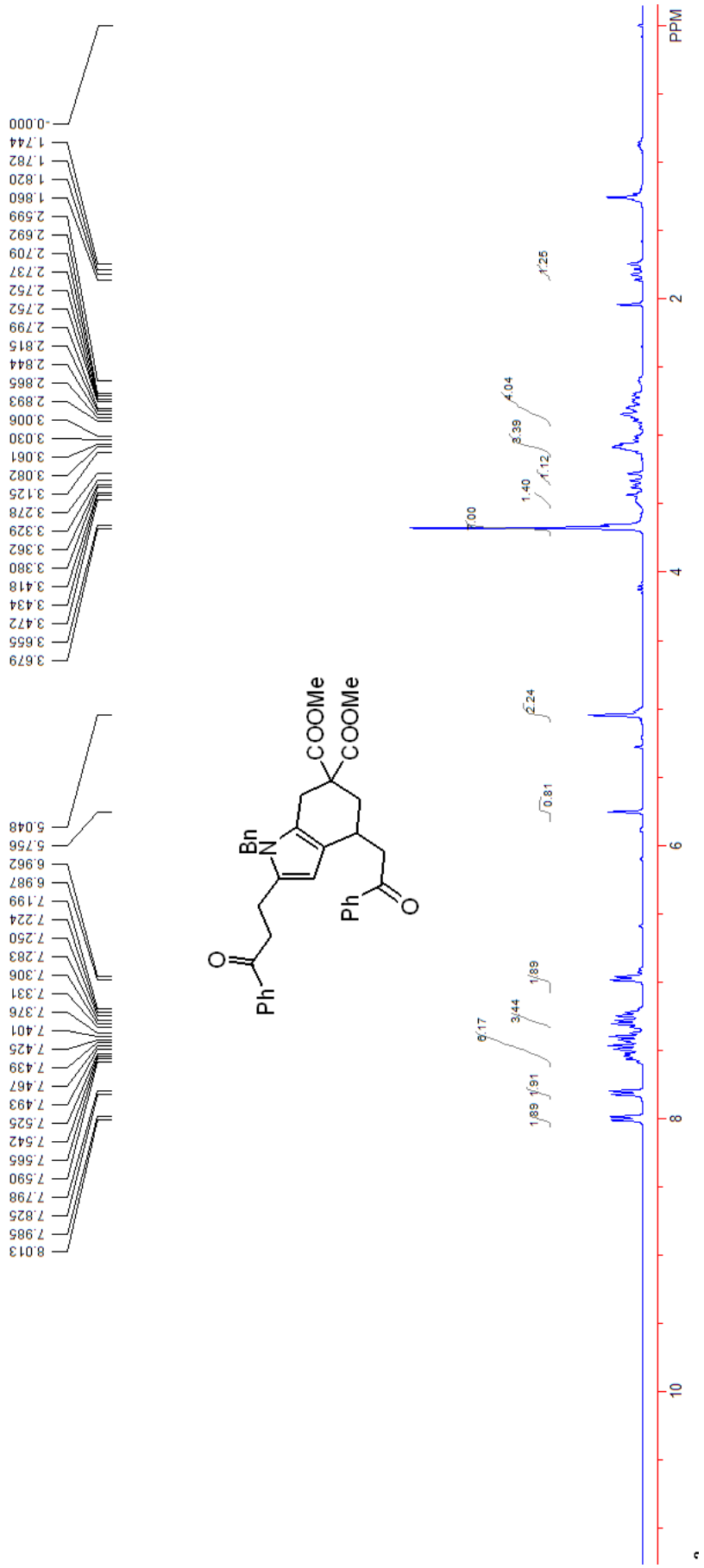

20.658
21.645
21.915
30.054
30.163
37.985
45.671
46.425
76.578
77.000
77.419
103.131
119.889
125.732
127.044
127.779
127.936
128.171
128.488
128.703
130.667
132.804
132.971
136.700
137.518
138.500
199.098
200.244
Ph
O
N
Ph
O
PPM
0
50
100
150
200

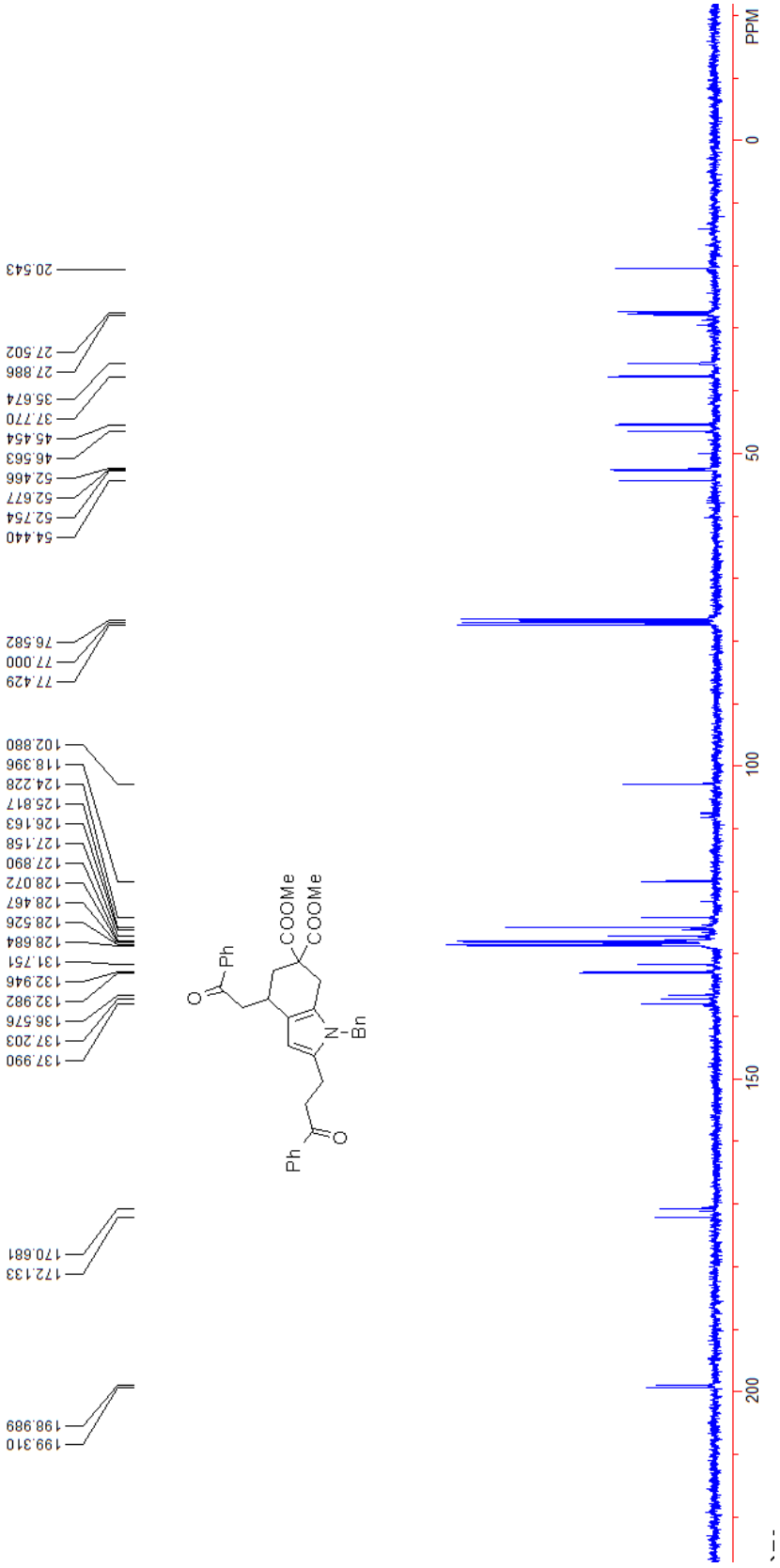
$^{1}$H NMR and $^{13}$C NMR Spectra of **3f**



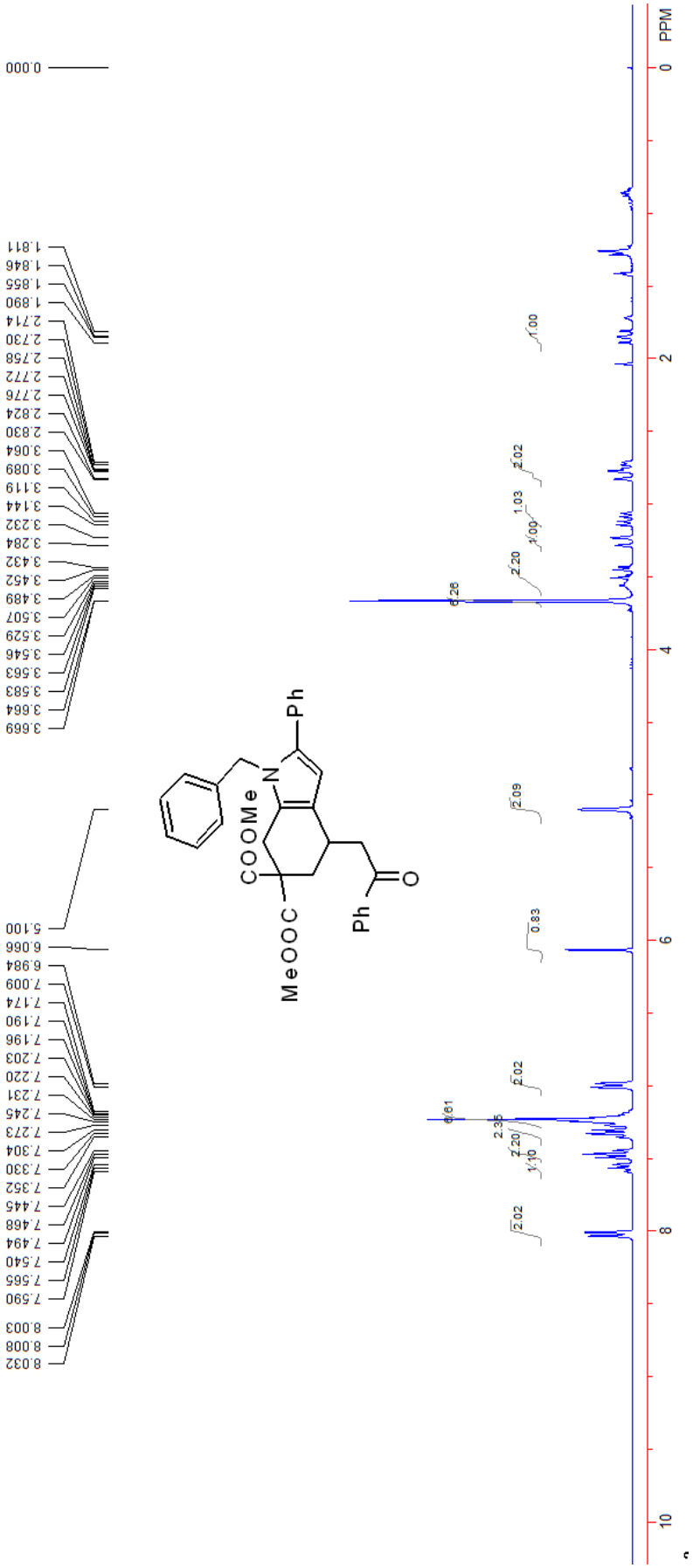

PPM
0
50
100
150
200
20.562
21.605
30.124
30.214
37.976
44.203
45.726
76.575
77.000
77.418
103.297
120.084
122.102
122.362
125.743
125.847
126.330
127.530
127.871
128.059
128.179
128.433
128.495
128.864
130.050
130.931
132.809
132.905
133.370
133.835
136.620
137.519
198.994
200.251
O
N
Ph
O
Ph

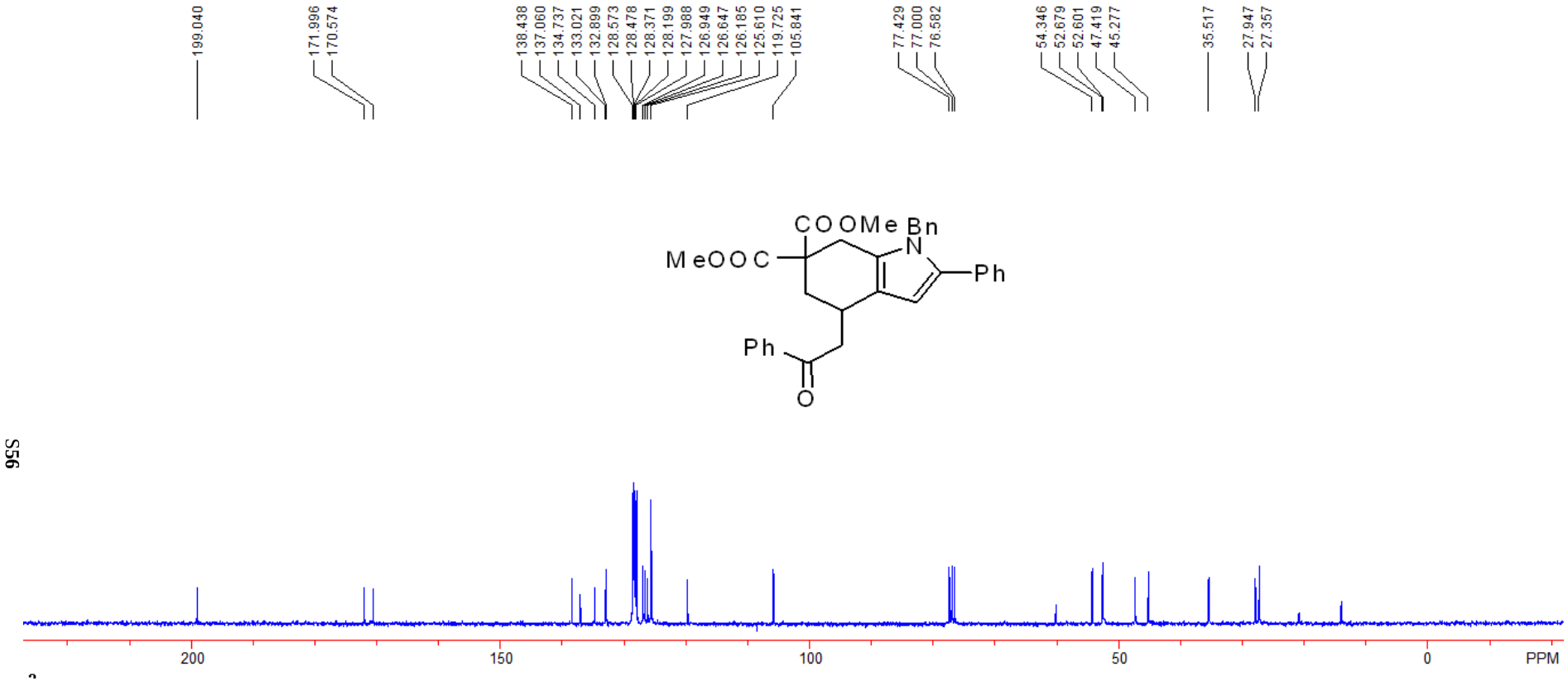
$^{1}$H NMR and $^{13}$C NMR Spectra of **3g**



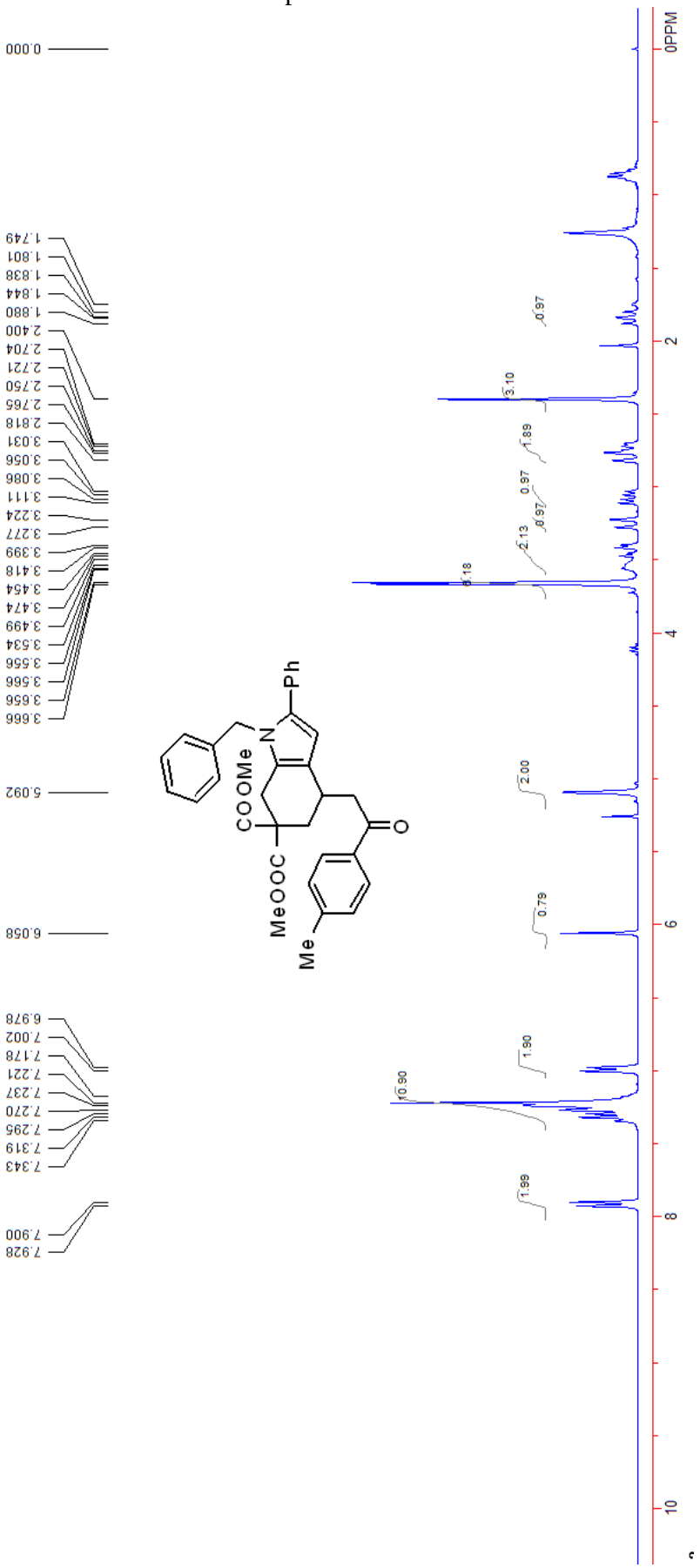

20.543
27.502
27.886
35.674
37.770
45.454
46.563
52.466
52.677
52.754
54.440
76.582
77.000
77.429
102.880
118.396
124.228
125.817
126.163
127.158
127.890
128.072
128.467
128.526
128.684
131.751
132.946
132.982
136.576
137.203
137.990
170.681
172.133
198.989
199.310
COOMe
COOMe
Ph
Ph
O
O
N
Bn
PPM
0
50
100
150
200

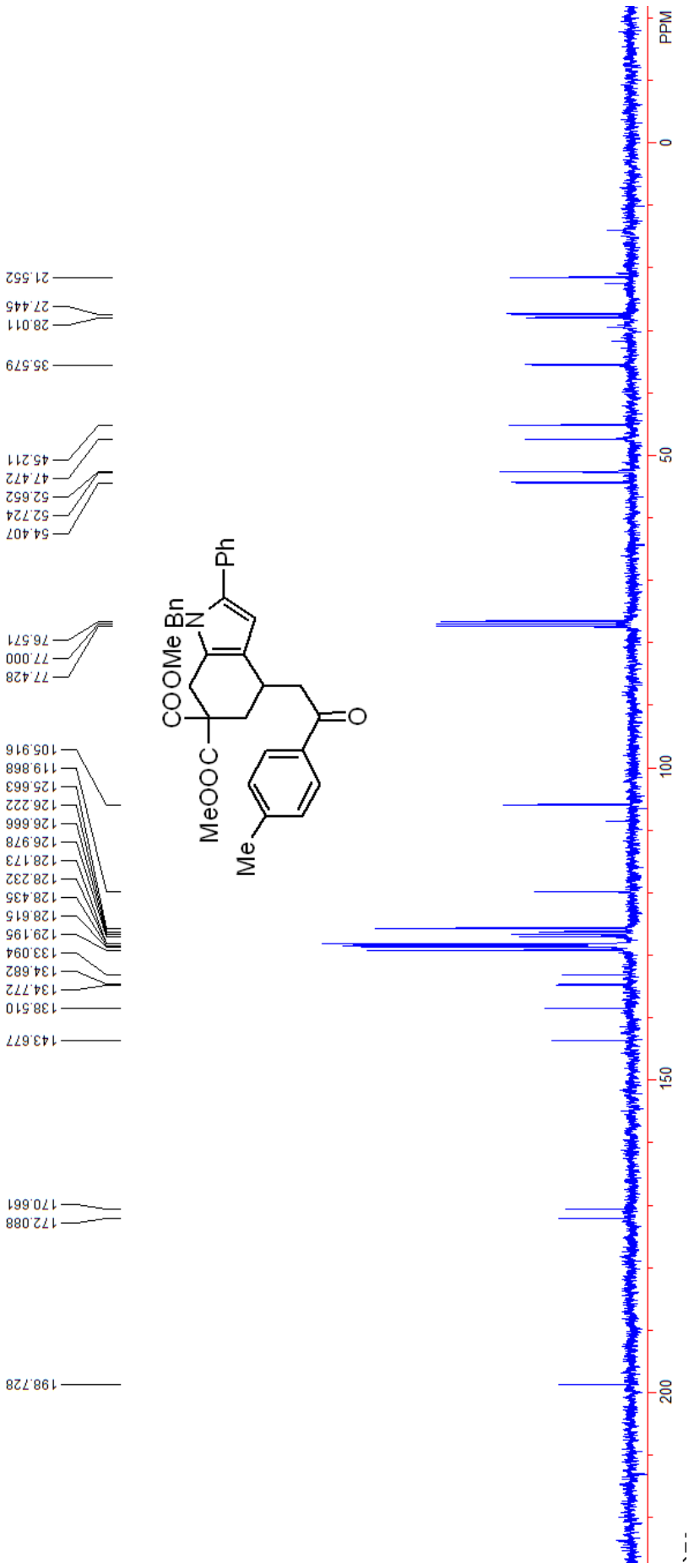
$^{1}$H NMR and $^{13}$C NMR Spectra of **3h**



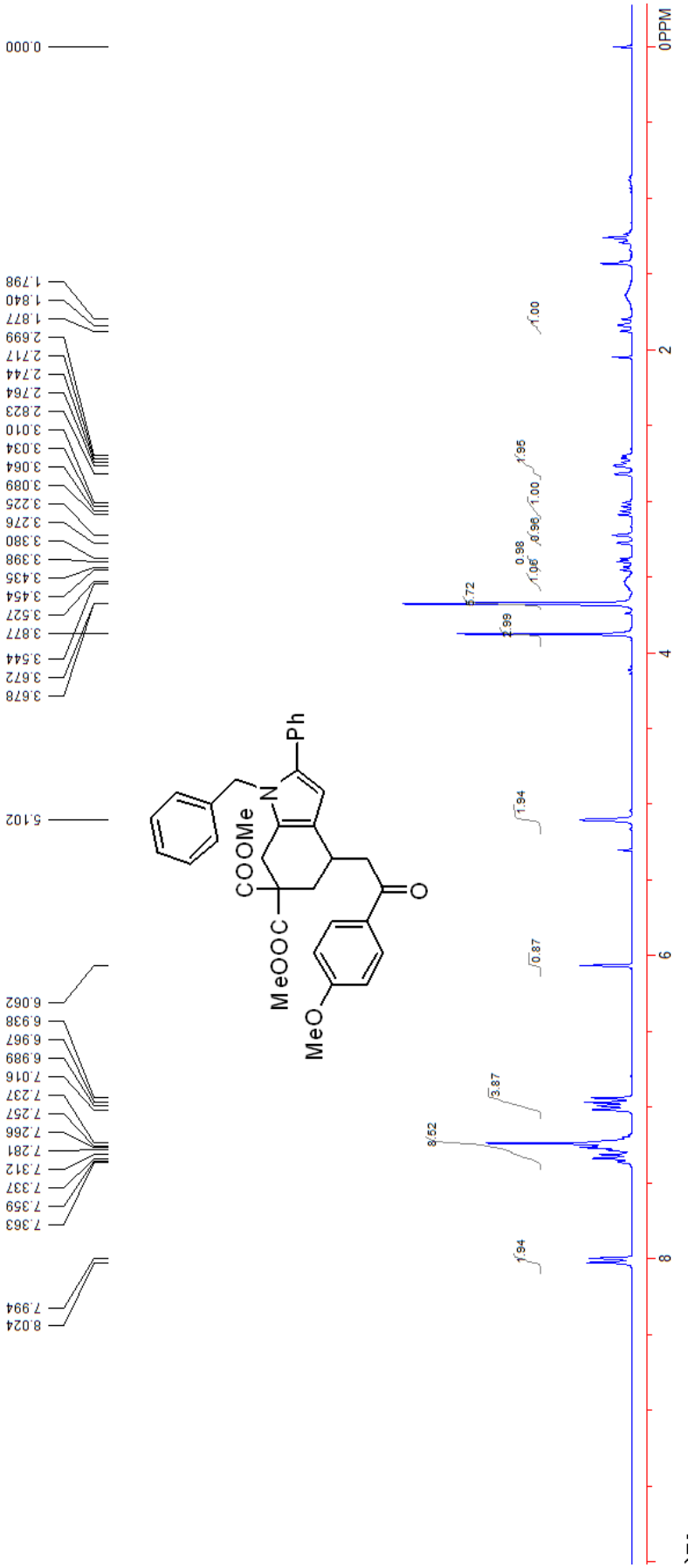

199.040
171.996
170.574
138.438
137.060
134.737
133.021
132.899
128.573
128.478
128.371
128.199
127.988
126.949
126.647
126.185
125.610
119.725
105.841
77.429
77.000
76.582
54.346
52.679
52.601
47.419
45.277
35.517
27.947
27.357
COOMe
Bn
N
MeOOC
Ph
Ph
O
200
150
100
50
0
PPM

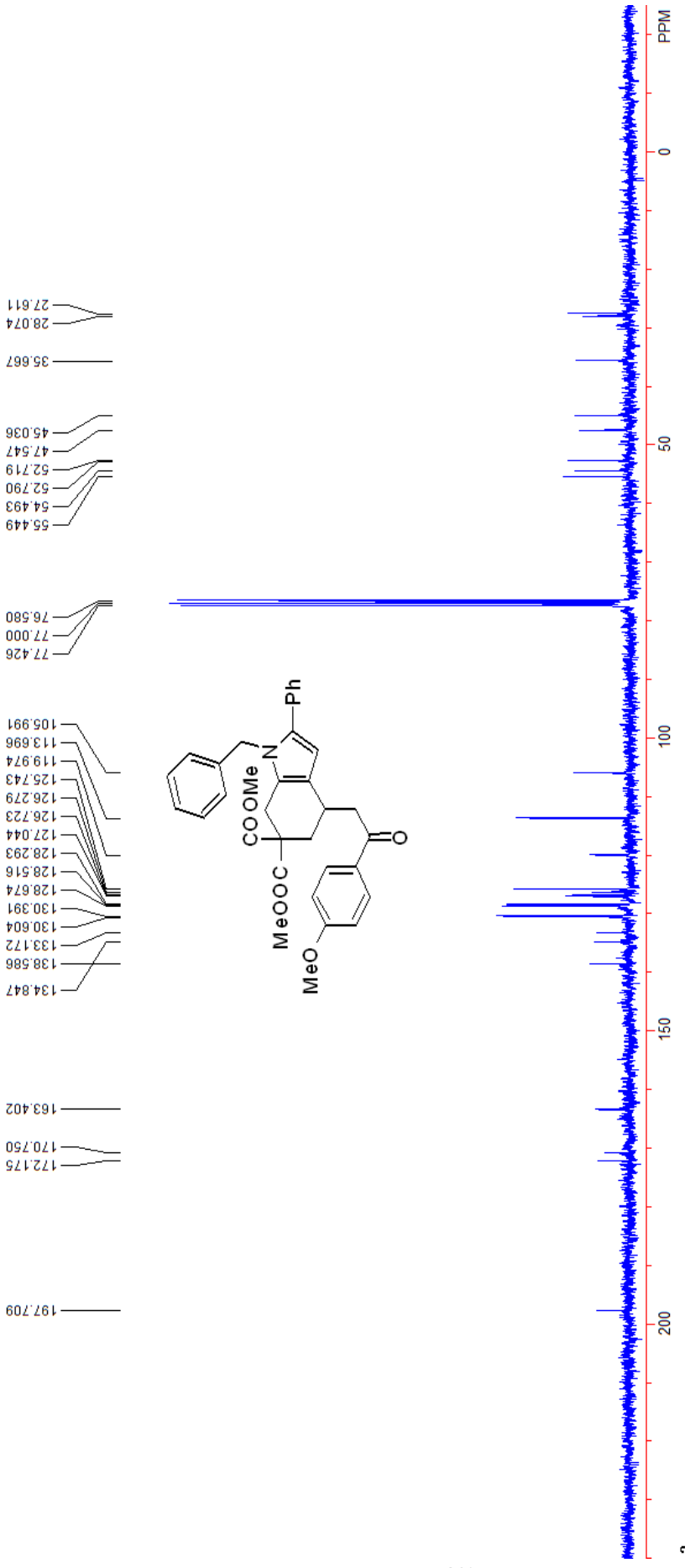
$^{1}$H NMR and $^{13}$C NMR Spectra of **3i**



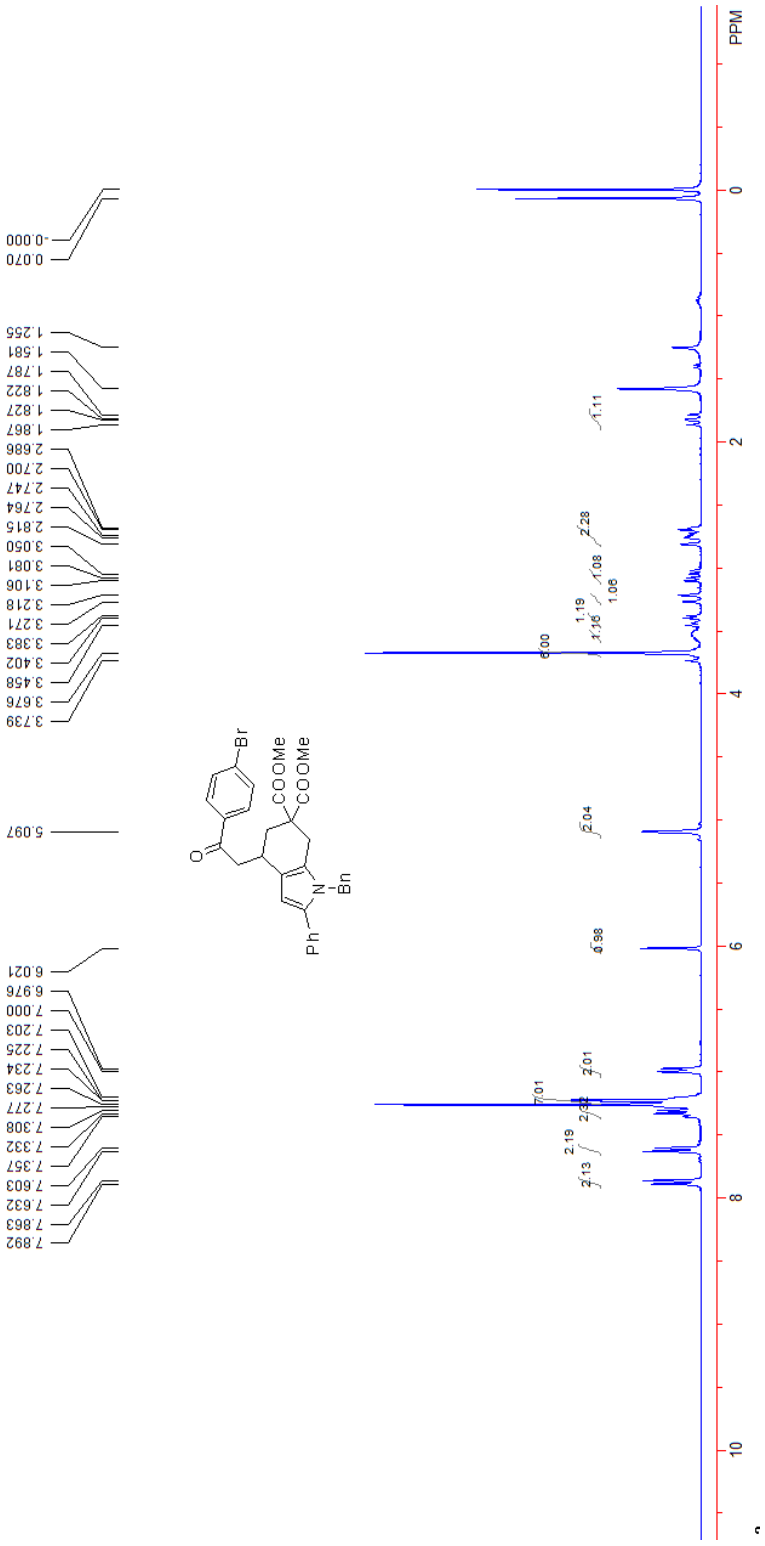

21.552
27.445
28.011
35.579
45.211
47.472
52.652
52.724
54.407
76.571
77.000
77.428
105.916
119.868
125.663
126.222
126.666
126.978
128.173
128.232
128.435
128.615
129.195
133.094
134.682
134.772
138.510
143.677
170.661
172.088
198.728
COOMe
Bn
N
Ph
MeOOC
O
Me
PPM
0
50
100
150
200

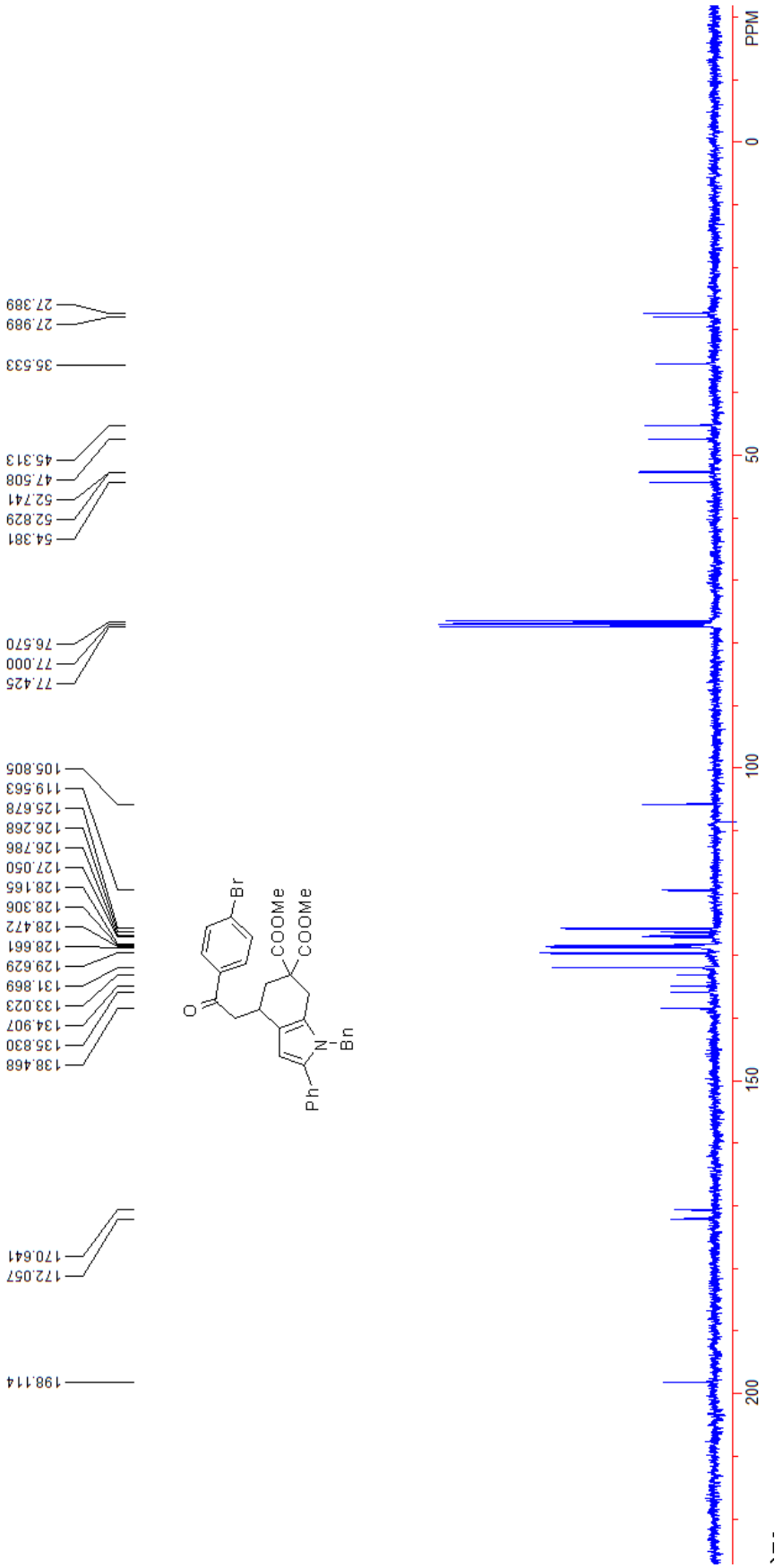
$^{1}$H NMR and $^{13}$C NMR Spectra of **3j**



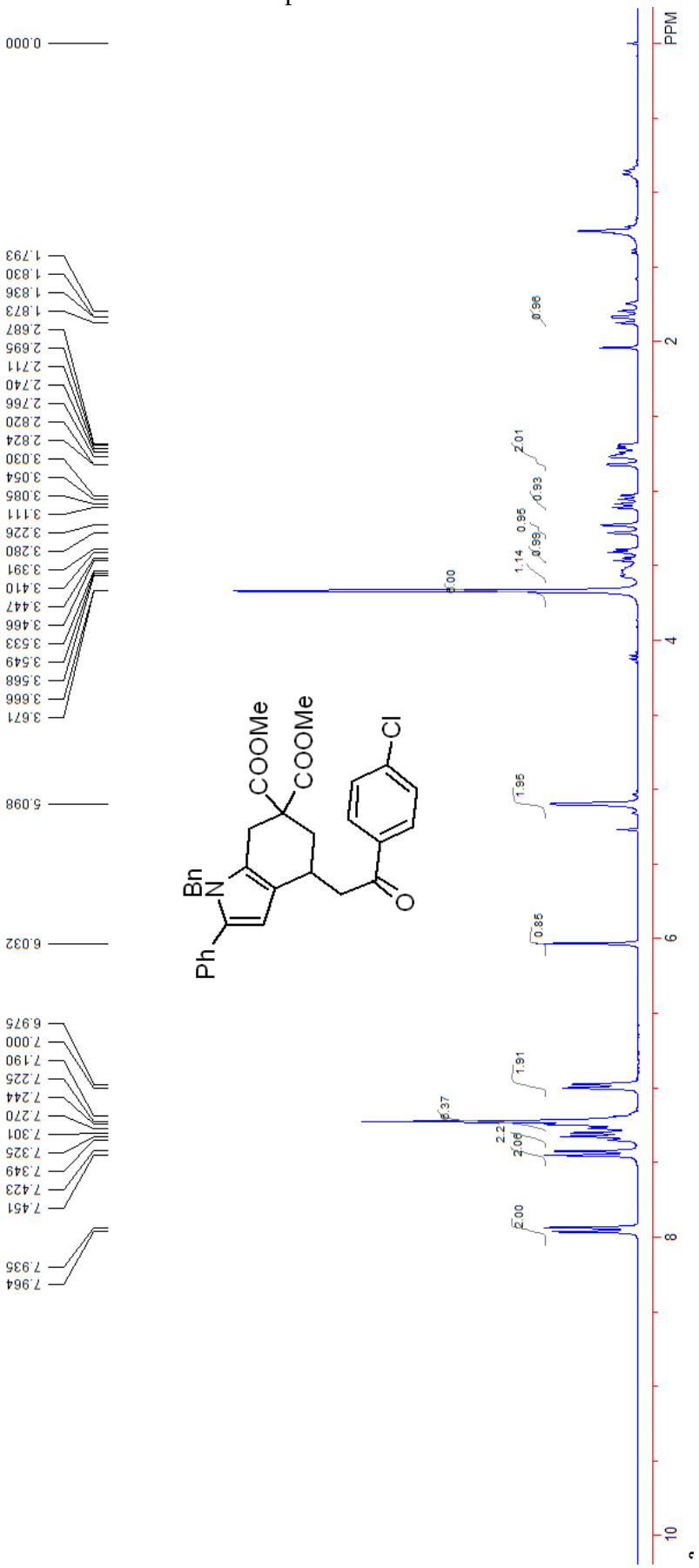

27.611
28.074
35.667
45.036
47.547
52.719
52.790
54.493
55.449
76.580
77.000
77.426
105.991
113.696
119.974
125.743
126.279
126.723
127.044
128.293
128.516
128.674
130.391
130.604
133.172
138.586
134.847
163.402
170.750
172.175
197.709
Ph
N
COOMe
MeOOC
MeO
O
PPM
0
50
100
150
200

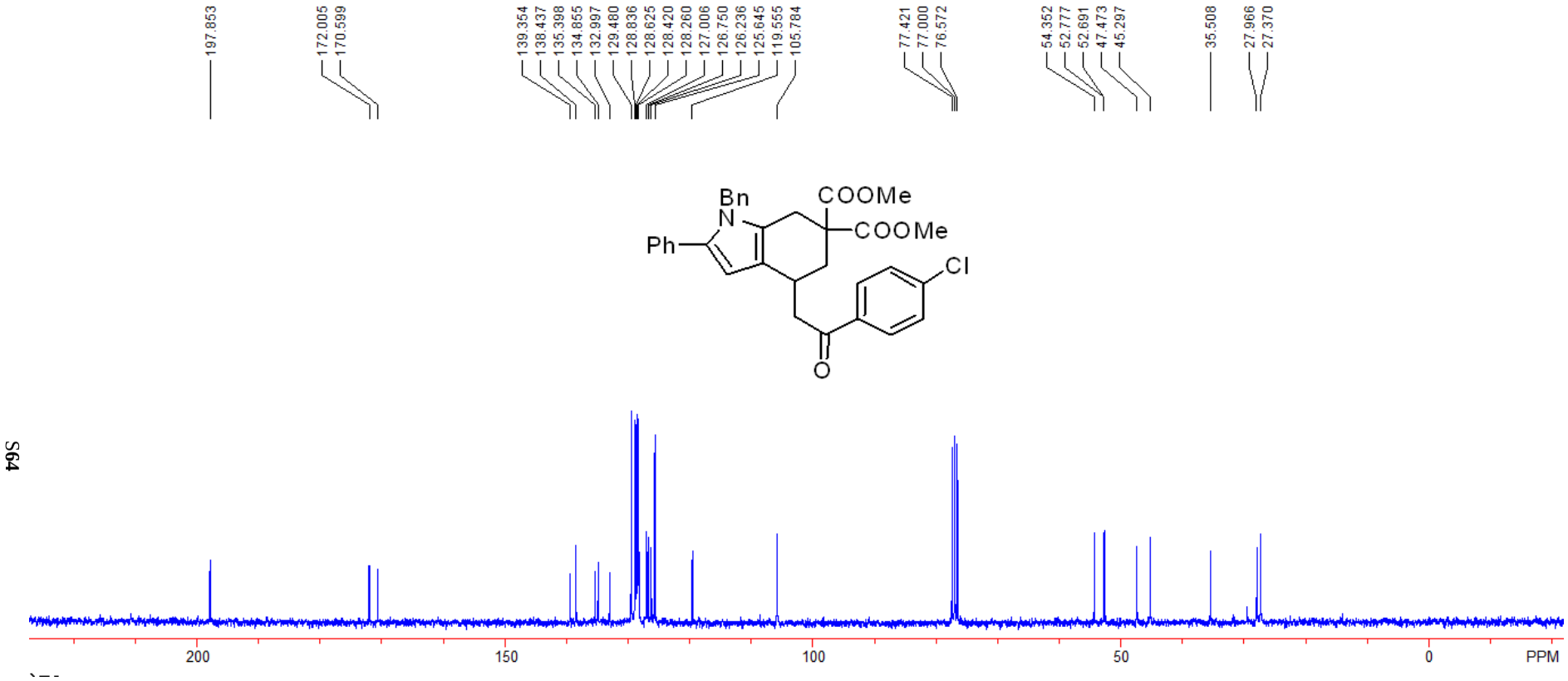
$^{1}$H NMR and $^{13}$C NMR Spectra of **3k**



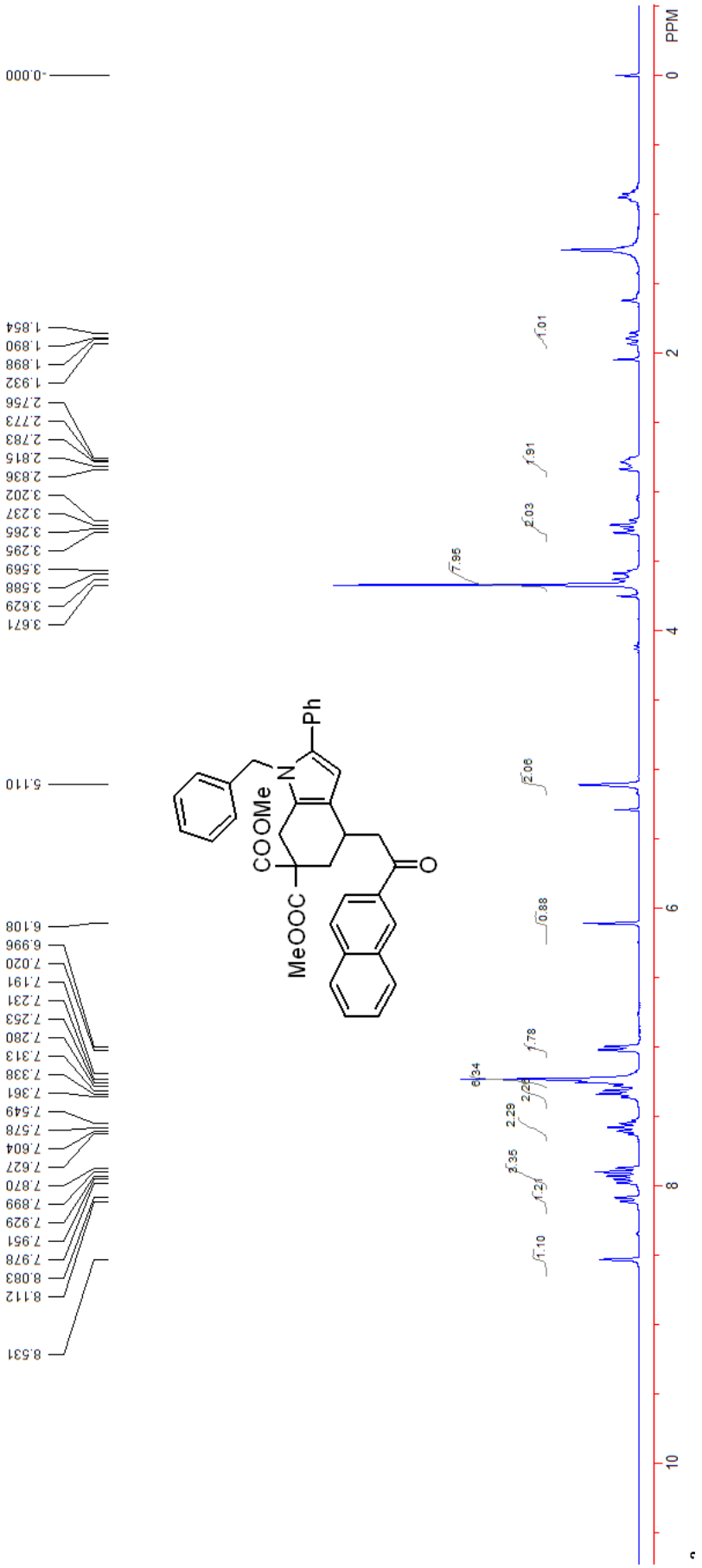

198.114
172.057
170.641
138.468
135.830
134.907
133.023
131.869
129.629
128.661
128.472
128.306
128.165
127.050
126.786
126.268
125.678
119.563
105.805
77.425
77.000
76.570
54.381
52.829
52.741
47.508
45.313
35.533
27.989
27.389
Br
COOMe
COOMe
O
N
Bn
Ph
PPM
0
50
100
150
200

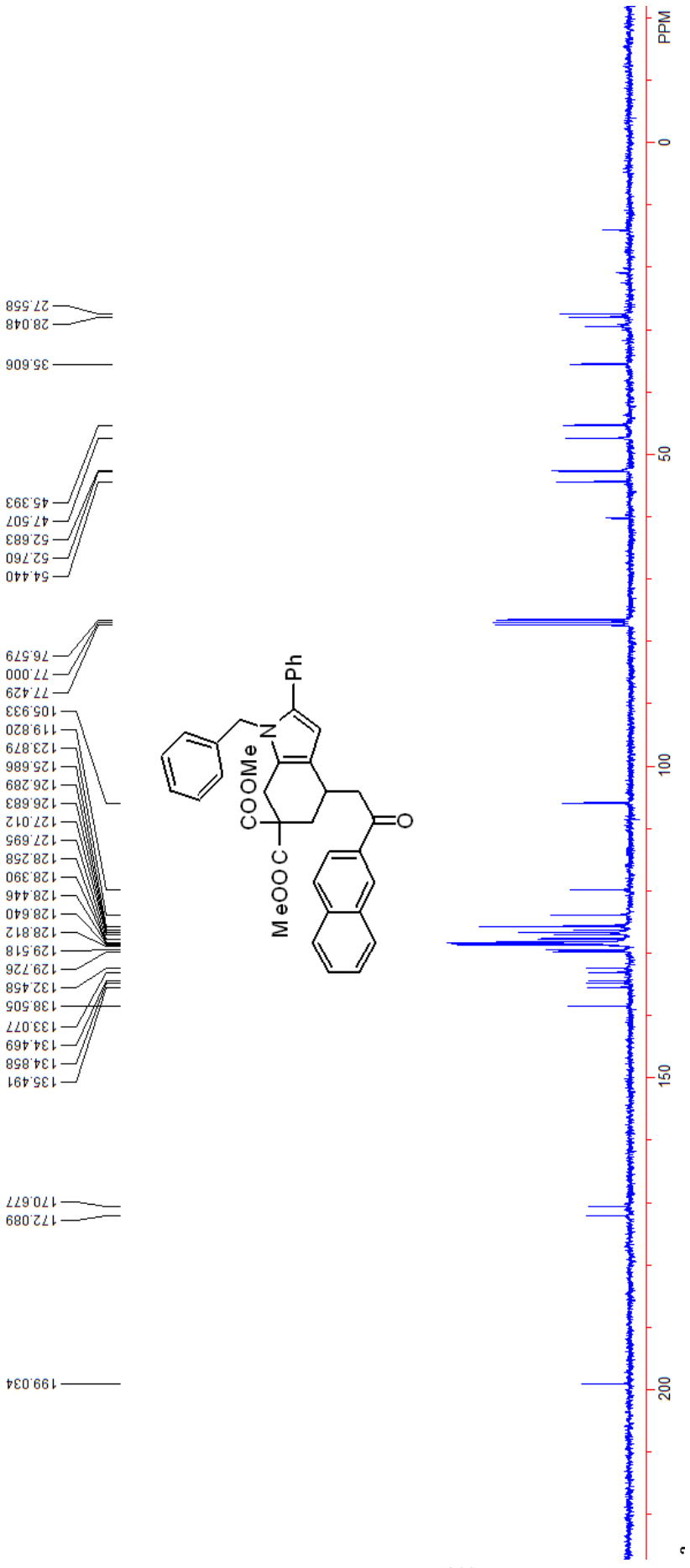
$^{1}$H NMR and $^{13}$C NMR Spectra of **3l**



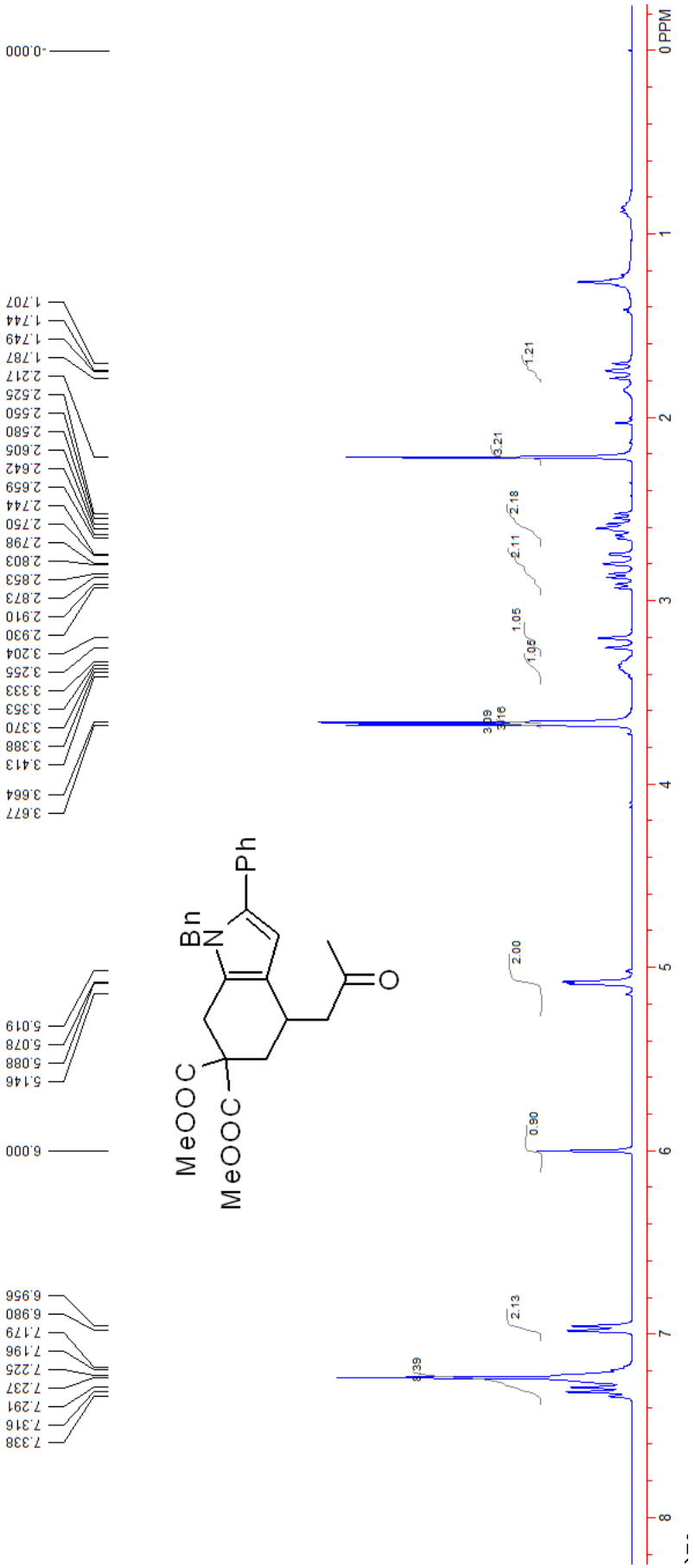

197.853
172.005
170.599
139.354
138.437
135.398
134.855
132.997
129.480
128.836
128.625
128.420
128.260
127.006
126.750
126.236
125.645
119.555
105.784
77.421
77.000
76.572
54.352
52.777
52.691
47.473
45.297
35.508
27.966
27.370
Bn
N
Ph
COOMe
COOMe
Cl
O
200
150
100
50
0
PPM

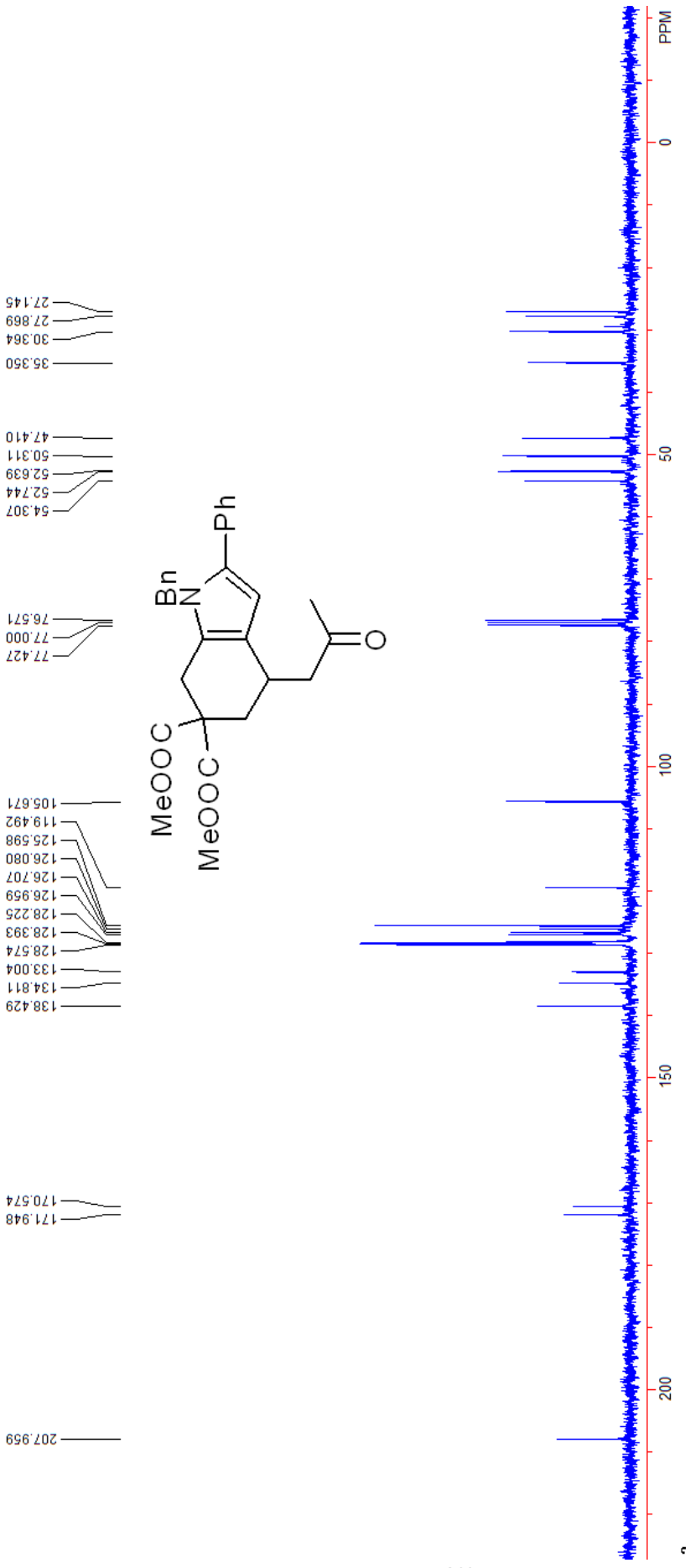
$^{1}$H NMR and $^{13}$C NMR Spectra of **3m**



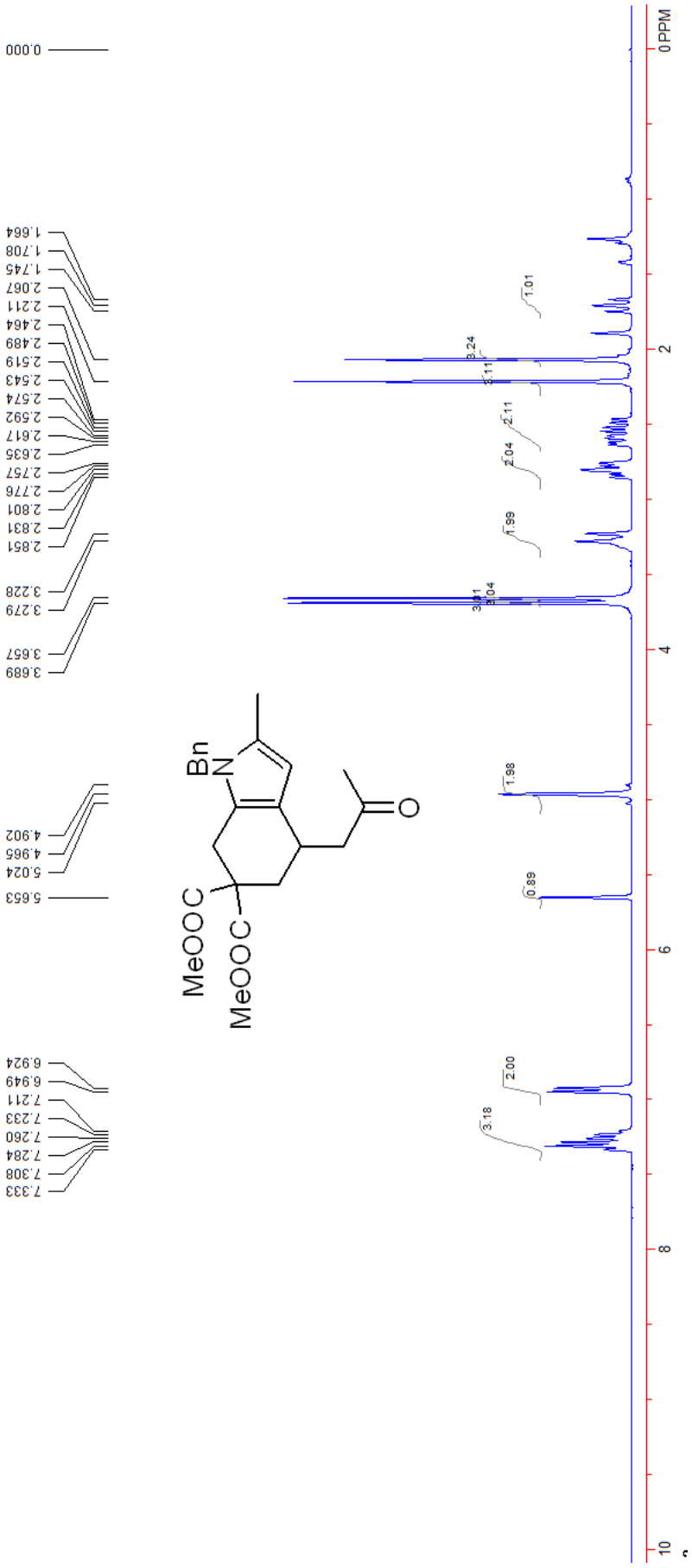

27.558
28.048
35.606
45.393
47.507
52.683
52.760
54.440
76.579
77.000
77.429
105.933
119.820
123.879
125.686
126.289
126.683
127.012
127.695
128.258
128.390
128.446
128.640
128.812
129.518
129.726
132.458
138.505
133.077
134.469
134.858
135.491
170.677
172.089
199.034
COOMe
N
Ph
MeOOC
O
PPM
0
50
100
150
200

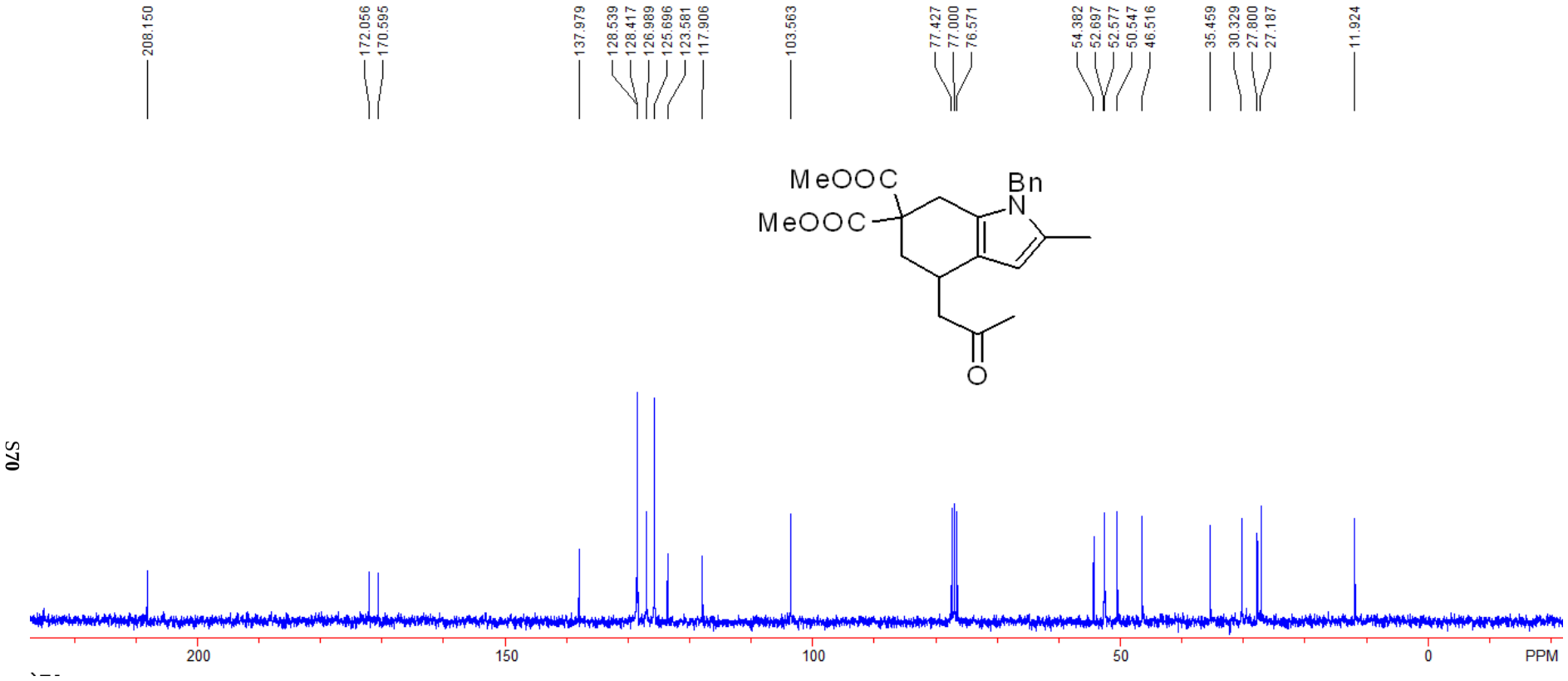
$^{1}$H NMR and $^{13}$C NMR Spectra of **3n**



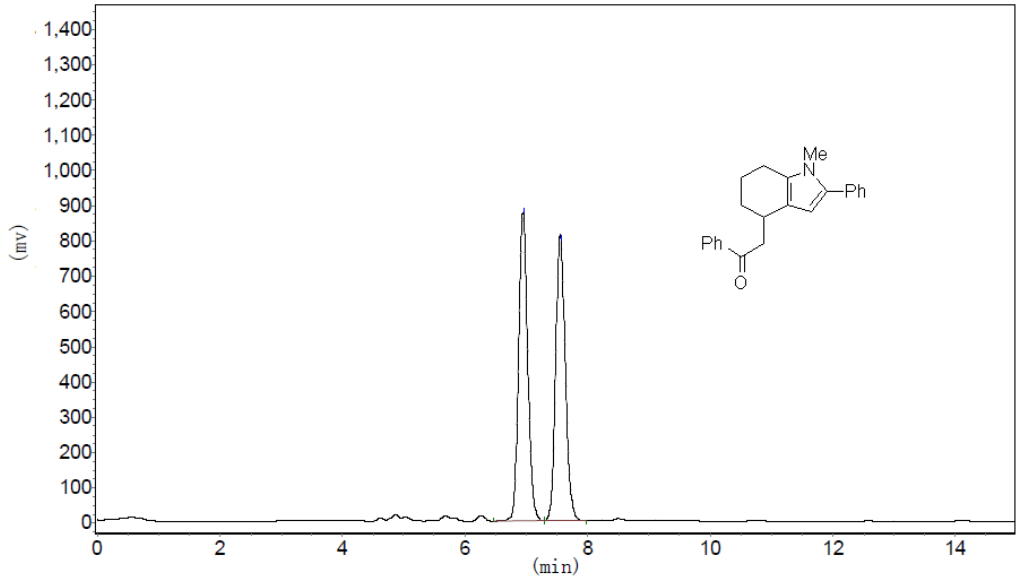

27.145
27.869
30.364
35.350
47.410
50.311
52.639
52.744
54.307
76.571
77.000
77.427
105.671
119.492
125.598
126.080
126.707
126.959
128.225
128.393
128.574
133.004
134.811
138.429
170.574
171.948
207.959
Bn
N
Ph
O
MeOOC
MeOOC
PPM
0
50
100
150
200

$^{1}$H NMR and $^{13}$C NMR Spectra of **3o**

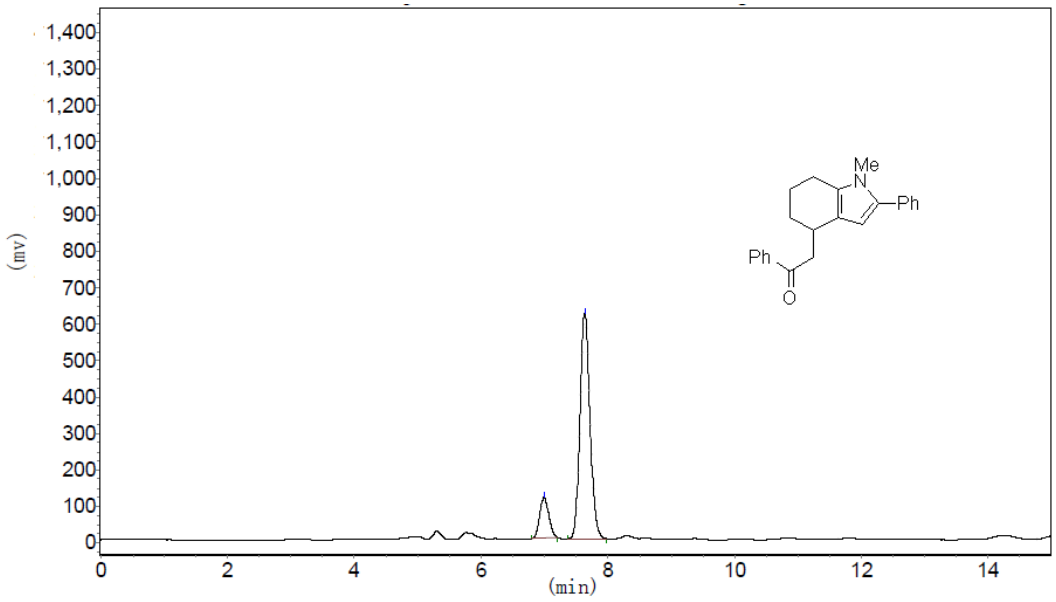



208.150
172.056
170.595
137.979
128.539
128.417
126.989
125.696
123.581
117.906
103.563
77.427
77.000
76.571
54.382
52.697
52.577
50.547
46.516
35.459
30.329
27.800
27.187
11.924
MeOOC
MeOOC
Bn
N
O
S70
200
150
100
50
0
PPM

## HPLC Chromatograph of 3a

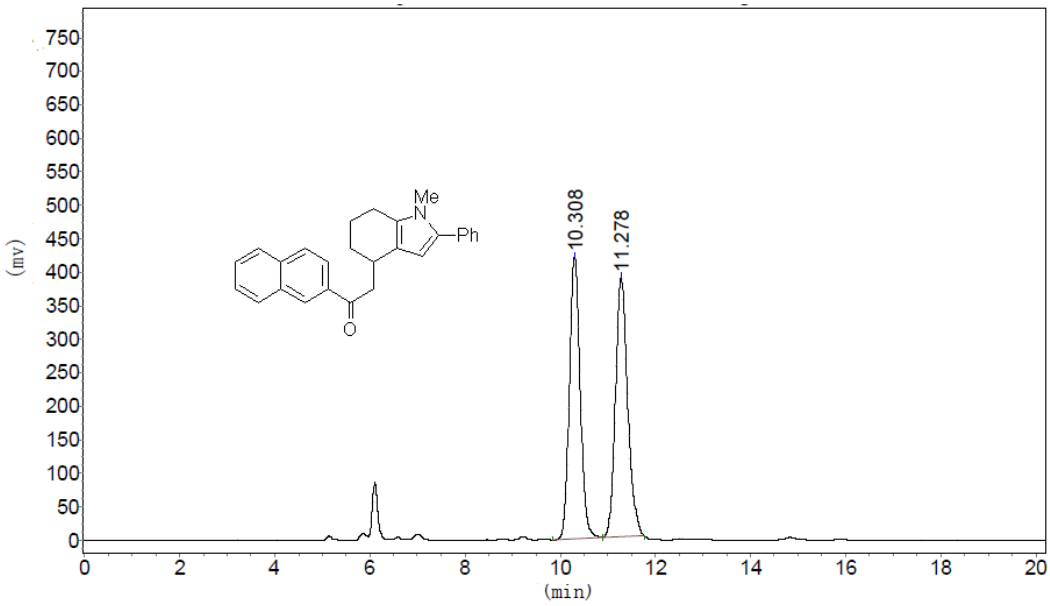



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 6.948 | 874963.000 | 9054563.000 | 50.2750 |
| 2 | 7.565 | 807482.813 | 8955519.000 | 49.7250 |
| **Total** | | 1682445.813 | 18010082.000 | 100.0000 |

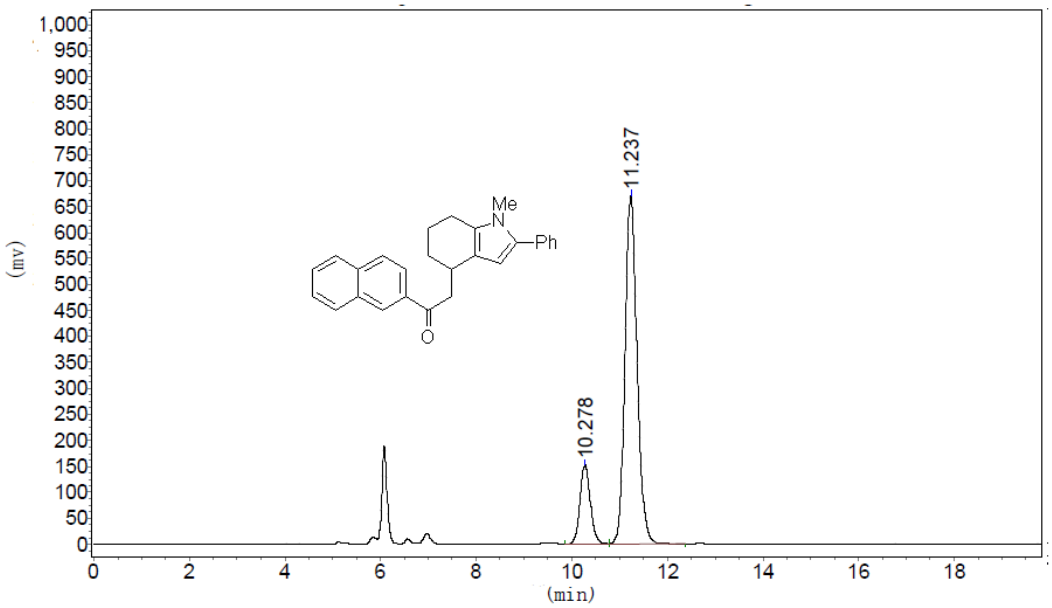



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 6.993 | 111384.266 | 1109007.500 | 13.9978 |
| 2 | 7.630 | 618690.750 | 6813725.500 | 86.0022 |
| **Total** | | 730075.016 | 7922733.000 | 100.0000 |

## HPLC Chromatograph of 3b

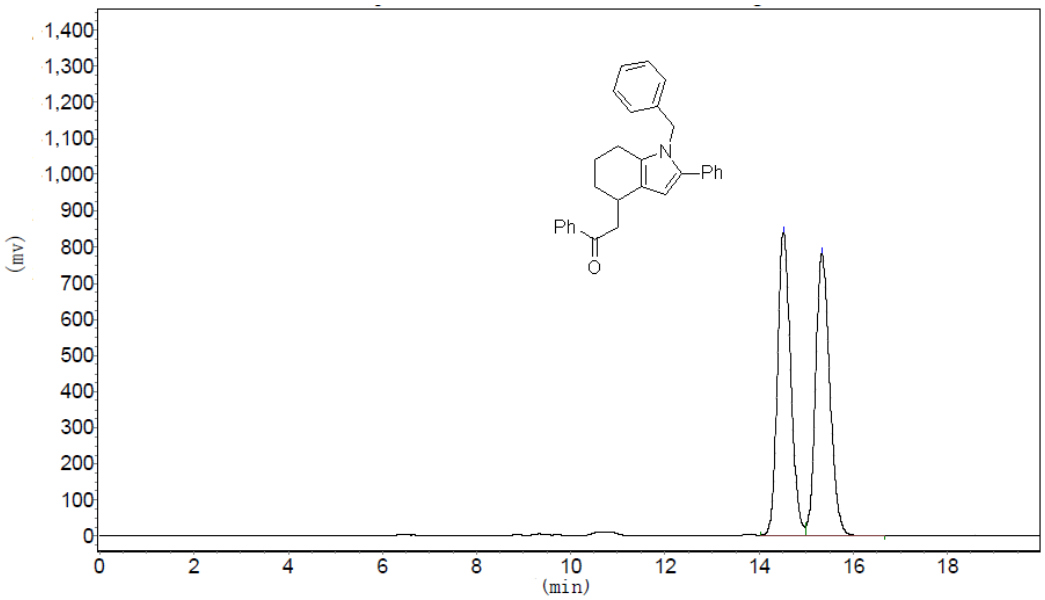



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 10. 308 | 419986. 875 | 6630831. 000 | 49. 2029 |
| 2 | 11. 278 | 386581. 531 | 6845678. 000 | 50. 7971 |
| **Total** | | 806568. 406 | 13476509. 000 | 100. 0000 |

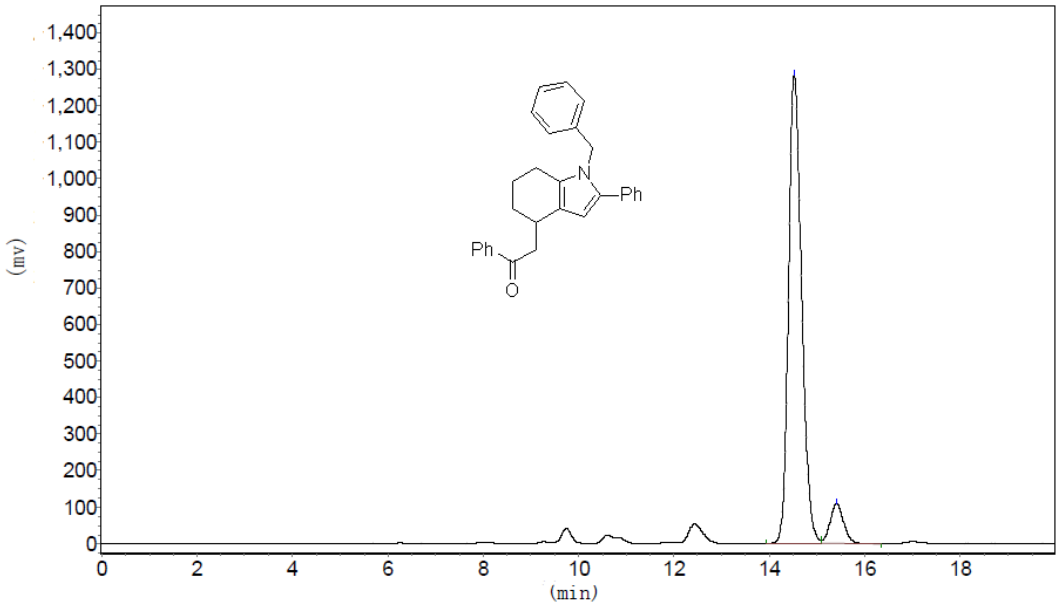



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 10. 278 | 151755. 094 | 2326352. 000 | 16. 4622 |
| 2 | 11. 237 | 670158. 688 | 11805160. 000 | 83. 5378 |
| **Total** | | 821913. 781 | 14131512. 000 | 100. 0000 |

## HPLC Chromatograph of 3c

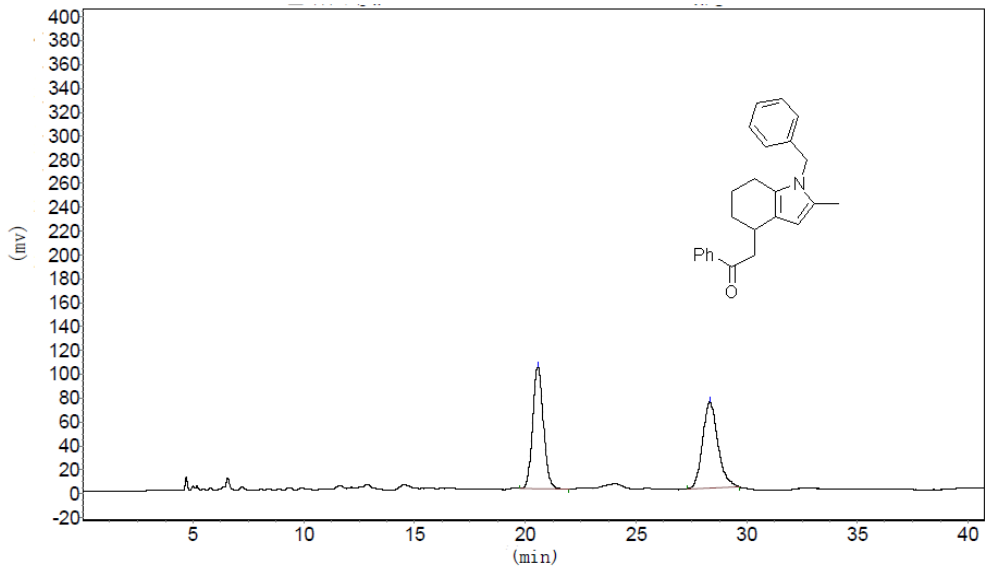



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 14. 515 | 841126. 813 | 16380837. 000 | 49. 8906 |
| 2 | 15. 332 | 783242. 500 | 16452659. 000 | 50. 1094 |
| **Total** | | 1624369. 313 | 32833496. 000 | 100. 0000 |

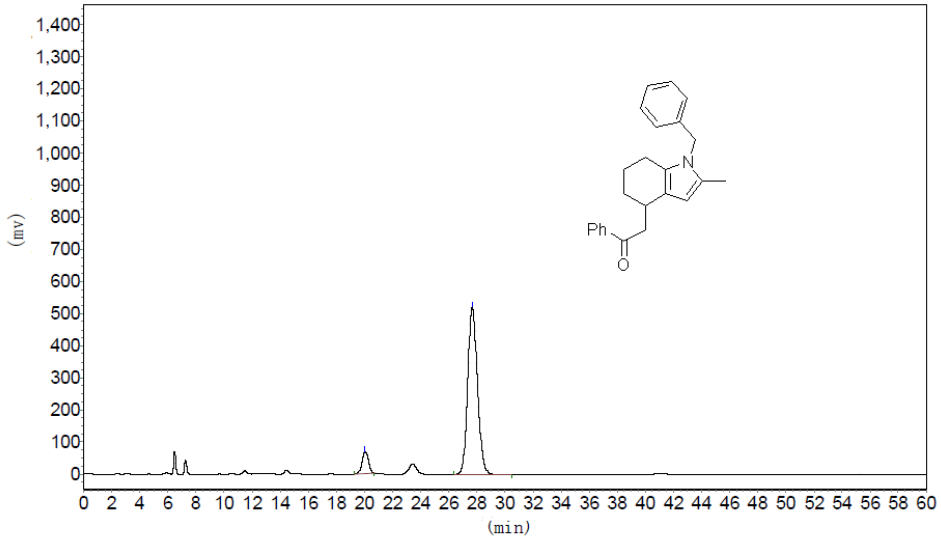



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 14. 517 | 1282834. 625 | 24389950. 000 | 91. 8480 |
| 2 | 15. 403 | 107808. 141 | 2164726. 750 | 8. 1520 |
| **Total** | | 1390642. 766 | 26554676. 750 | 100. 0000 |

## HPLC Chromatograph of 3d

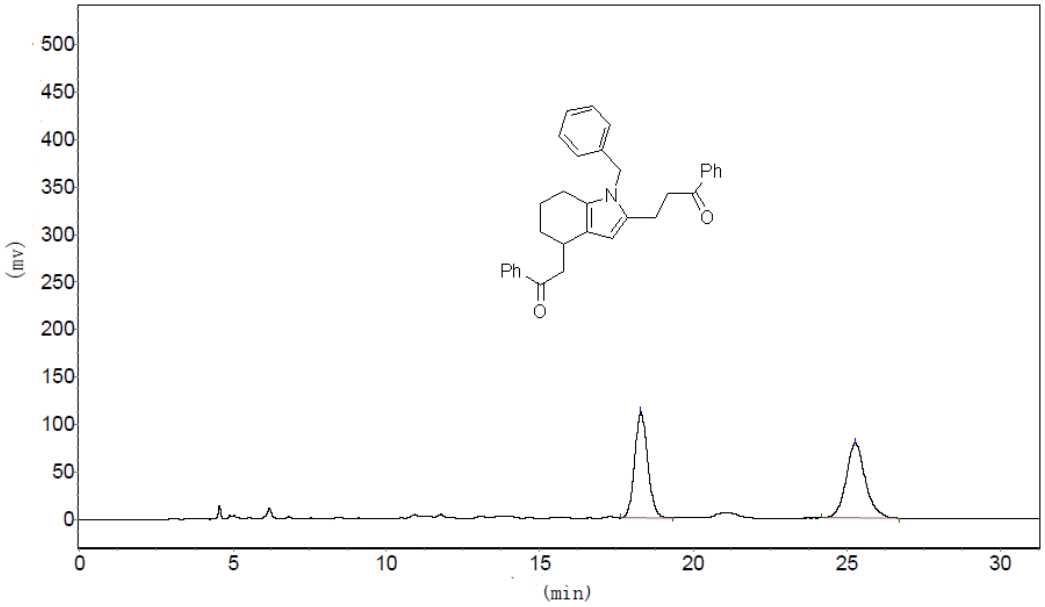



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 20.565 | 102504.070 | 3481336.750 | 49.8784 |
| 2 | 28.327 | 72086.125 | 3498306.250 | 50.1216 |
| Total | | 174590.195 | 6979643.000 | 100.0000 |

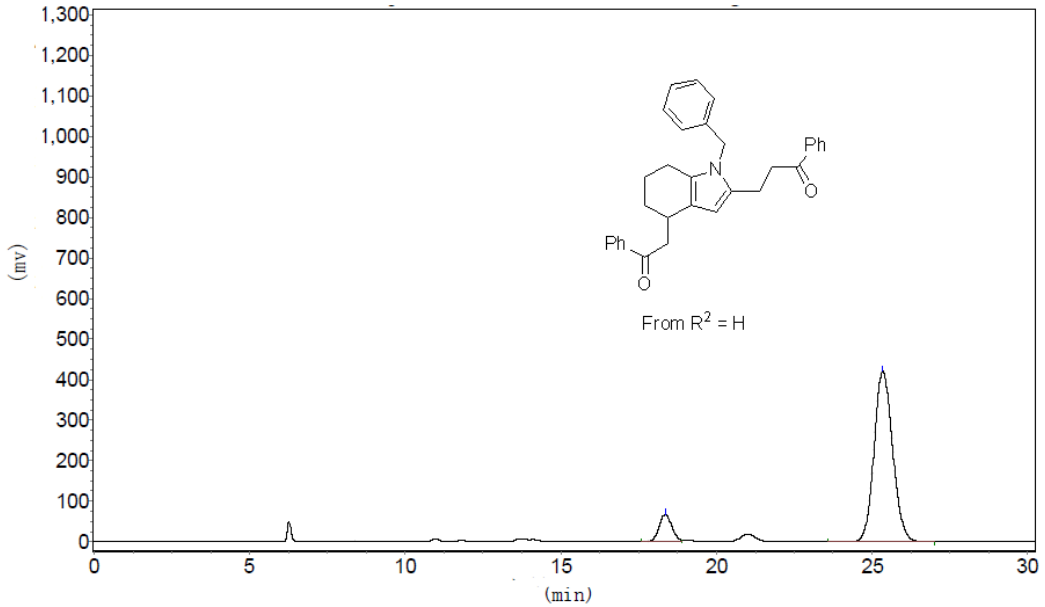



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 20.058 | 68956.156 | 2213508.250 | 8.1304 |
| 2 | 27.662 | 522879.969 | 25011430.000 | 91.8696 |
| Total | | 591836.125 | 27224938.250 | 100.0000 |

## HPLC Chromatograph of 3e

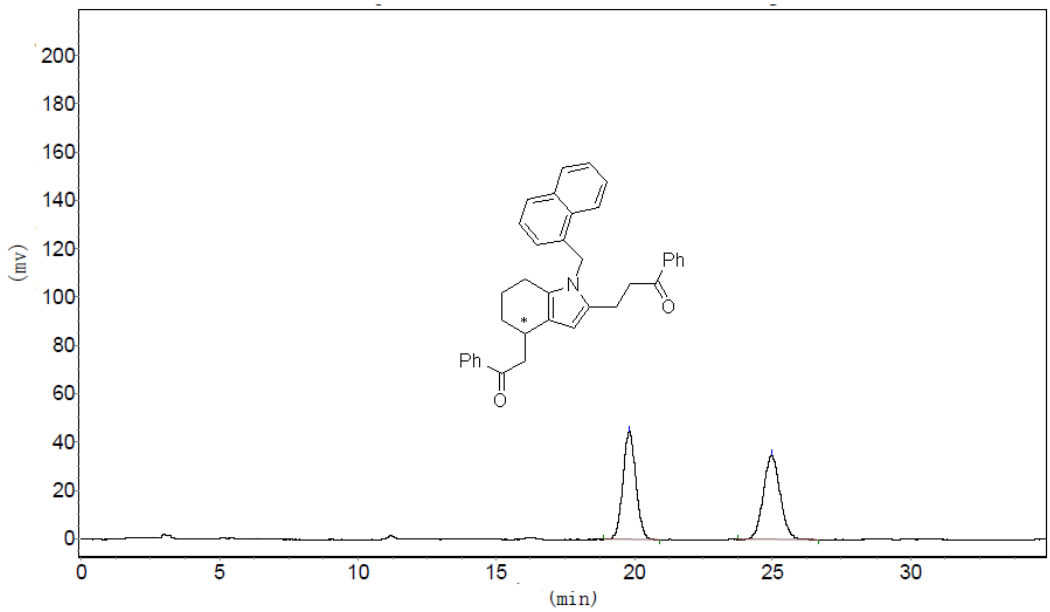



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 18. 293 | 111326. 563 | 3328729. 750 | 49. 2491 |
| 2 | 25. 287 | 78488. 508 | 3430229. 250 | 50. 7509 |
| Total | | 189815. 070 | 6758959. 000 | 100. 0000 |

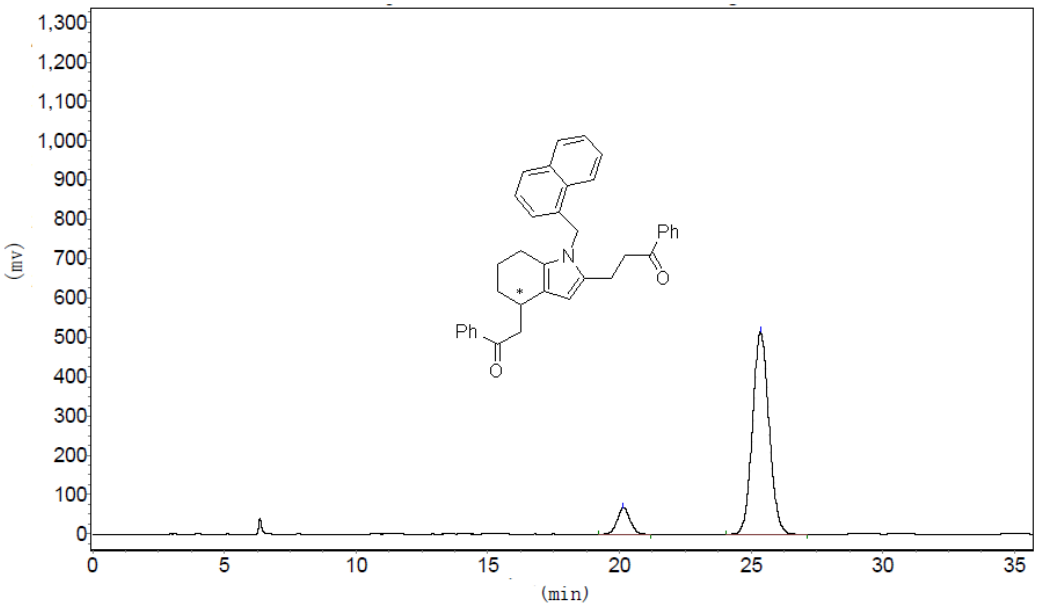



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 18. 362 | 67416. 938 | 1956712. 375 | 10. 0189 |
| 2 | 25. 340 | 422568. 156 | 17573402. 000 | 89. 9810 |
| Total | | 489985. 094 | 19530114. 375 | 100. 0000 |

## HPLC Chromatograph of 3f

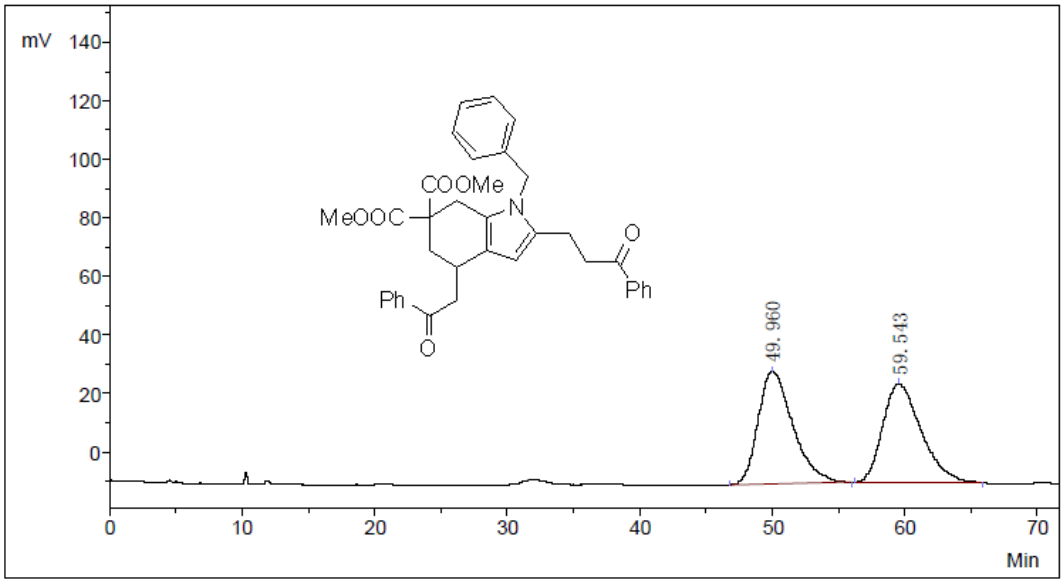



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 19. 818 | 44671. 621 | 1460307. 875 | 49. 8882 |
| 2 | 24. 965 | 35003. 121 | 1466855. 000 | 50. 1118 |
| **Total** | | 79674. 742 | 2927162. 875 | 100. 0000 |

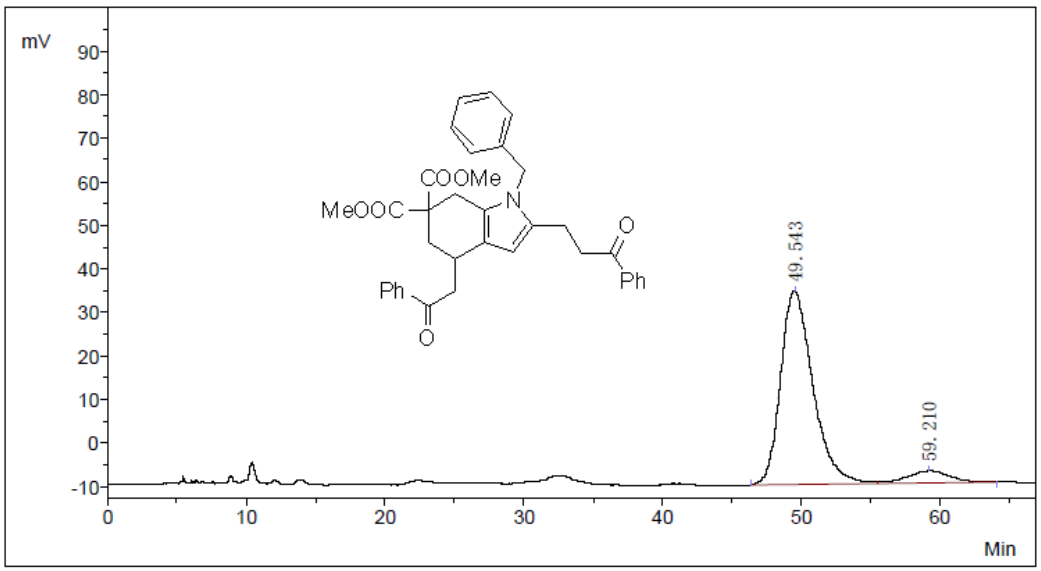



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 20. 158 | 66185. 547 | 2258200. 500 | 9. 2074 |
| 2 | 25. 358 | 515310. 750 | 22267806. 000 | 90. 7926 |
| **Total** | | 581496. 297 | 24526006. 500 | 100. 0000 |

## HPLC Chromatograph of 3g

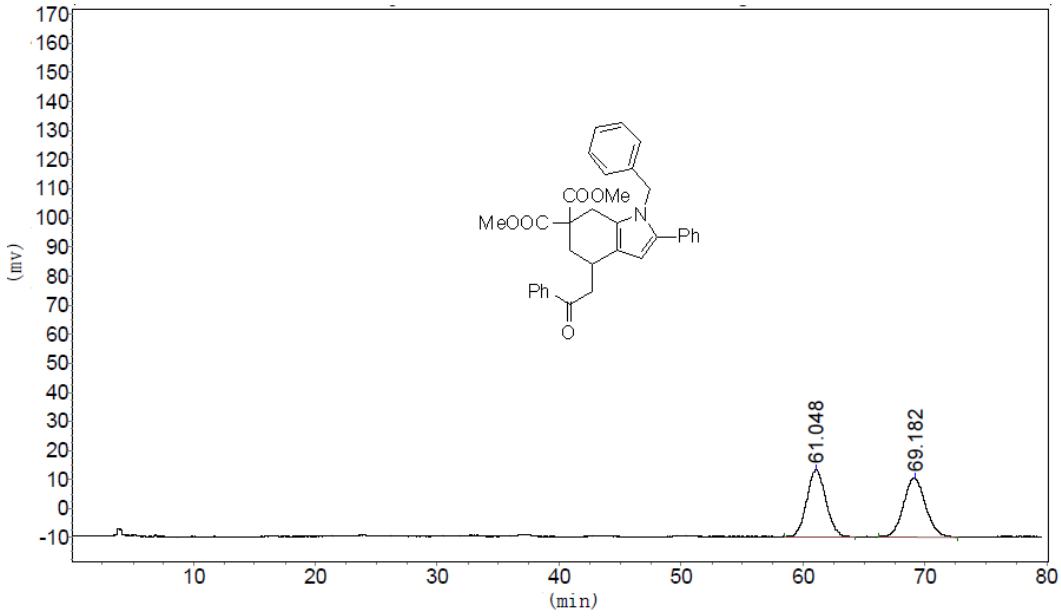



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | Unknown | 49.960 | 38385.5 | 6991874.9 | 50.6854 |
| 2 | 2 | Unknown | 59.543 | 33587.5 | 6802773.0 | 49.3146 |
| Total | | | | 71973.1 | 13794647.9 | 100.0000 |

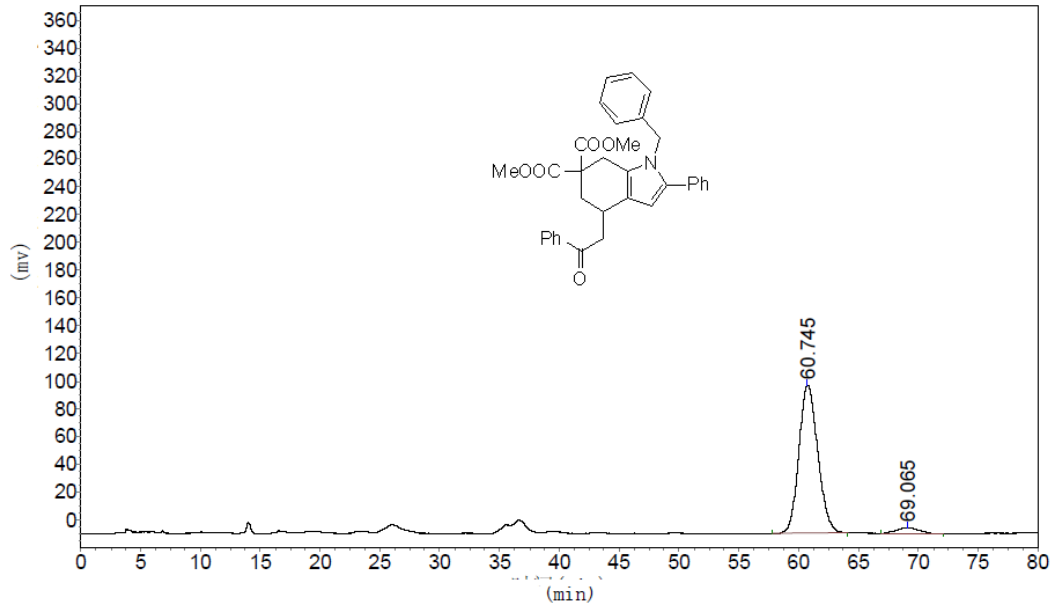



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | Unknown | 49.543 | 44528.0 | 7172282.6 | 92.6021 |
| 2 | 2 | Unknown | 59.210 | 2797.3 | 572986.1 | 7.3979 |
| Total | | | | 47325.3 | 7745268.7 | 100.0000 |

## HPLC Chromatograph of 3h

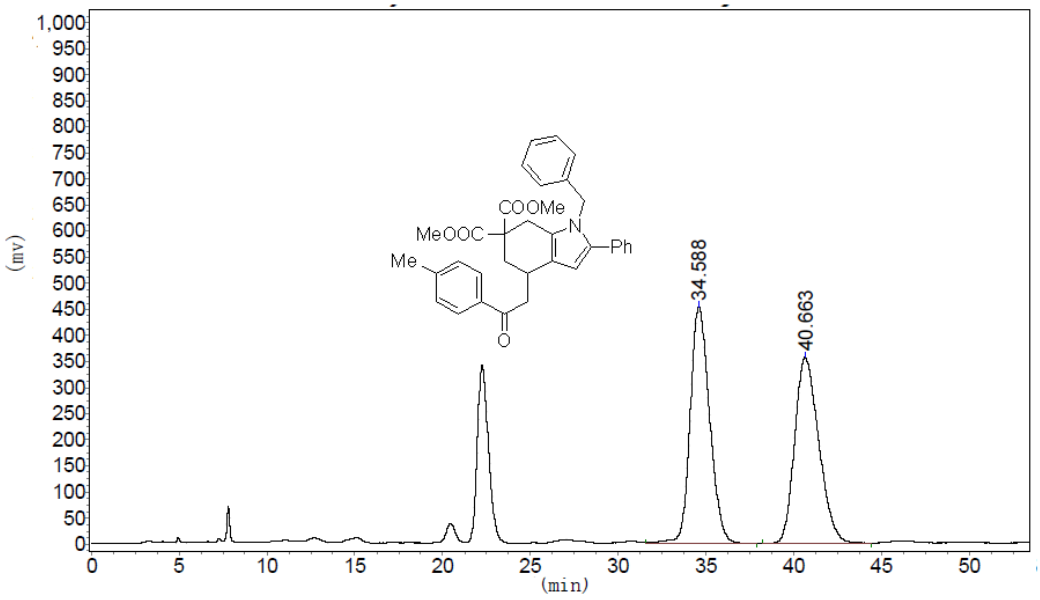



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 61.048 | 23056.500 | 2530019.250 | 49.7122 |
| 2 | 69.182 | 20290.648 | 2559312.250 | 50.2878 |
| **Total** | | 43347.148 | 5089331.500 | 100.0000 |

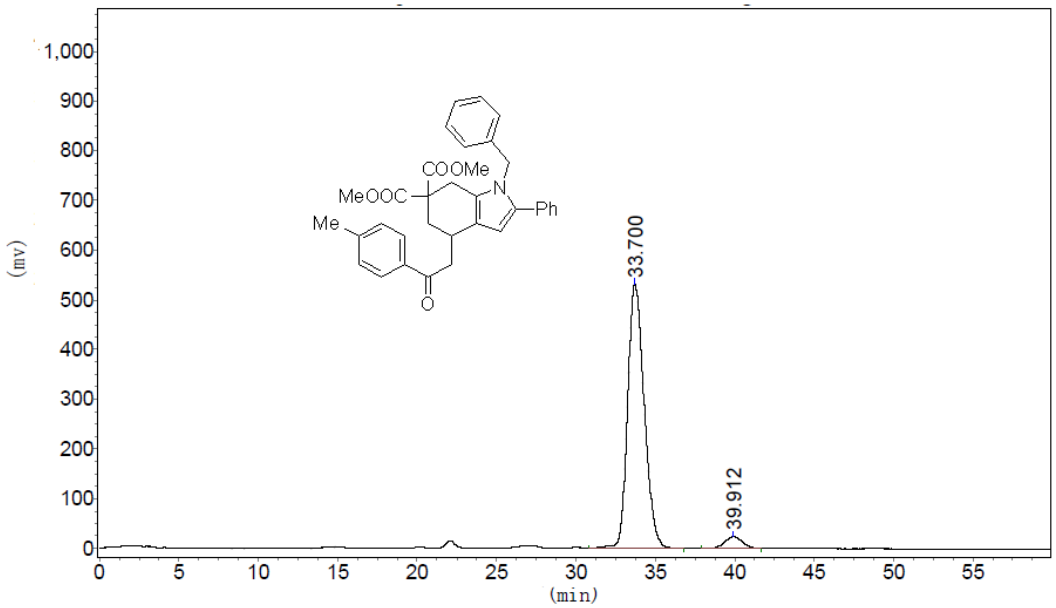



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 60.745 | 106340.891 | 11745743.000 | 95.8073 |
| 2 | 69.065 | 4203.947 | 514020.625 | 4.1927 |
| **Total** | | 110544.838 | 12259763.625 | 100.0000 |

## HPLC Chromatograph of 3i

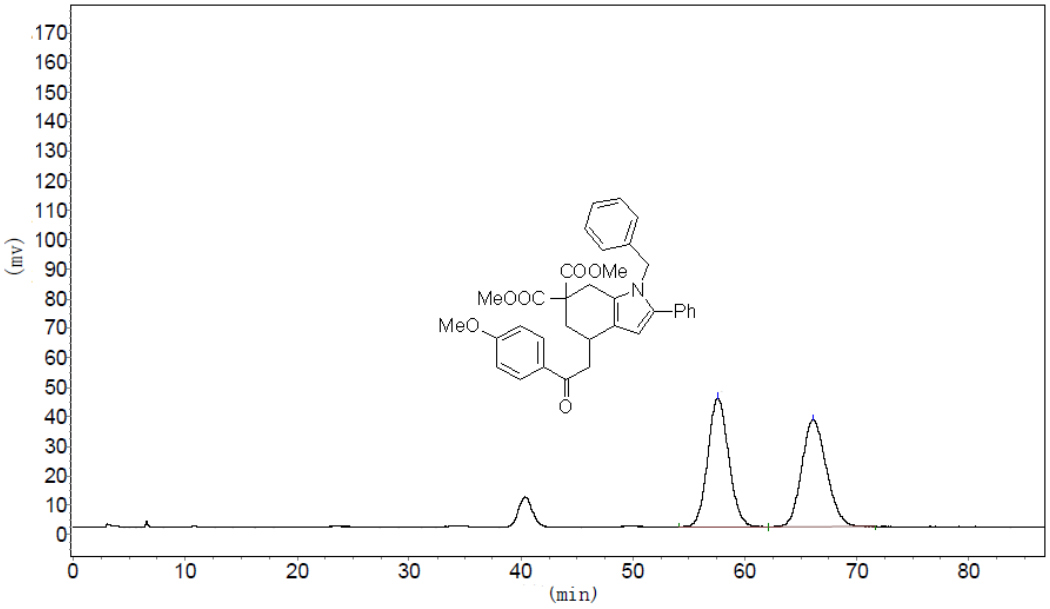



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 34. 588 | 453643. 031 | 34809344. 000 | 50. 3315 |
| 2 | 40. 663 | 356532. 719 | 34350784. 000 | 49. 6685 |
| **Total** | | 810175. 750 | 69160128. 000 | 100. 0000 |

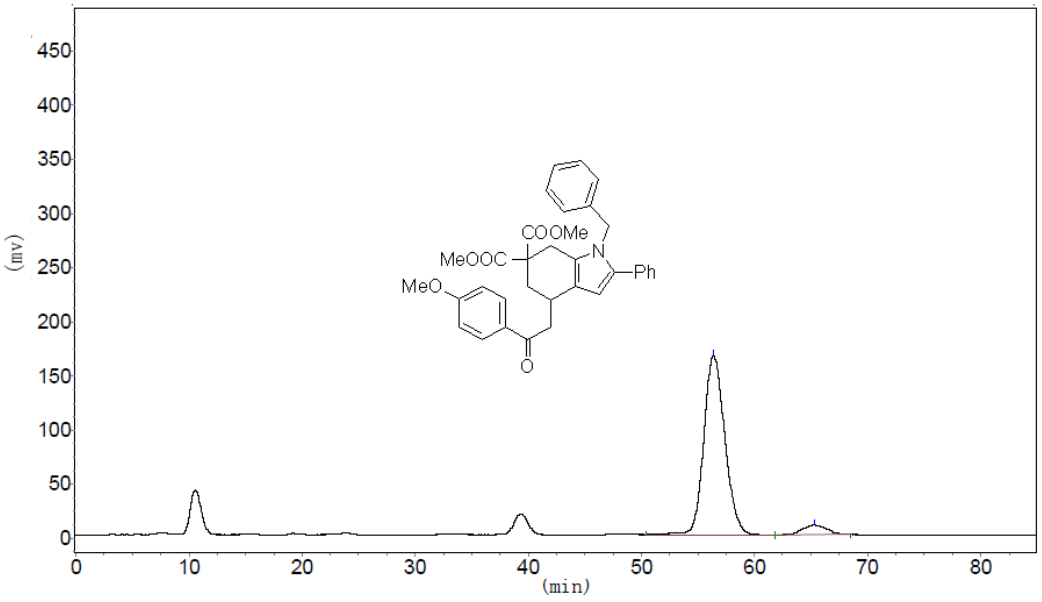



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 33. 700 | 531798. 500 | 38787344. 000 | 95. 2259 |
| 2 | 39. 912 | 24402. 662 | 1944589. 000 | 4. 7741 |
| **Total** | | 556201. 162 | 40731933. 000 | 100. 0000 |

## HPLC Chromatograph of 3j

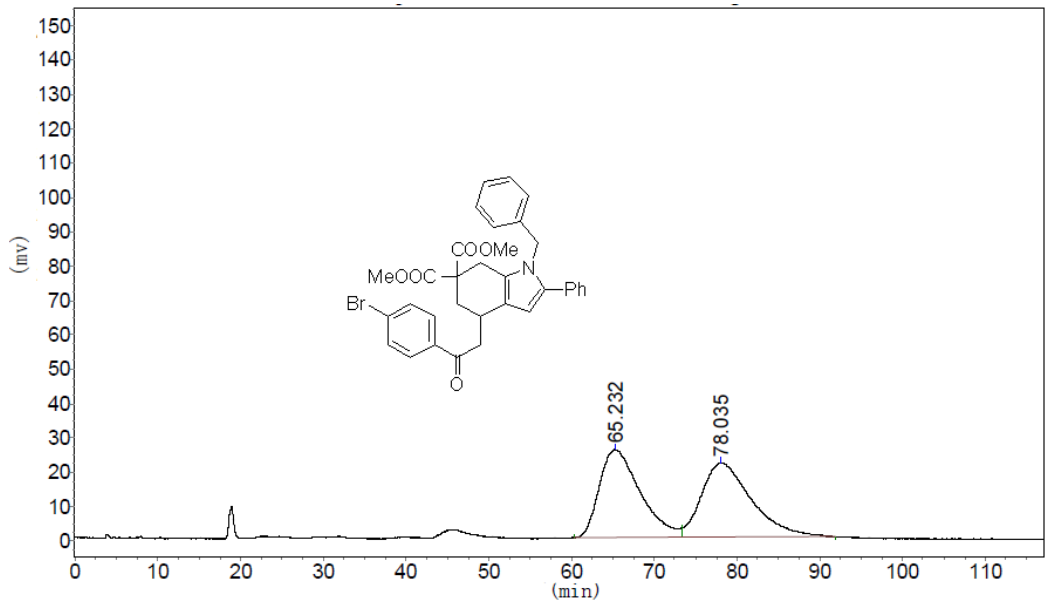



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 57.580 | 43708.070 | 5695279.500 | 50.2071 |
| 2 | 66.132 | 36177.227 | 5648286.500 | 49.7929 |
| **Total** | | 79885.297 | 11343566.000 | 100.0000 |

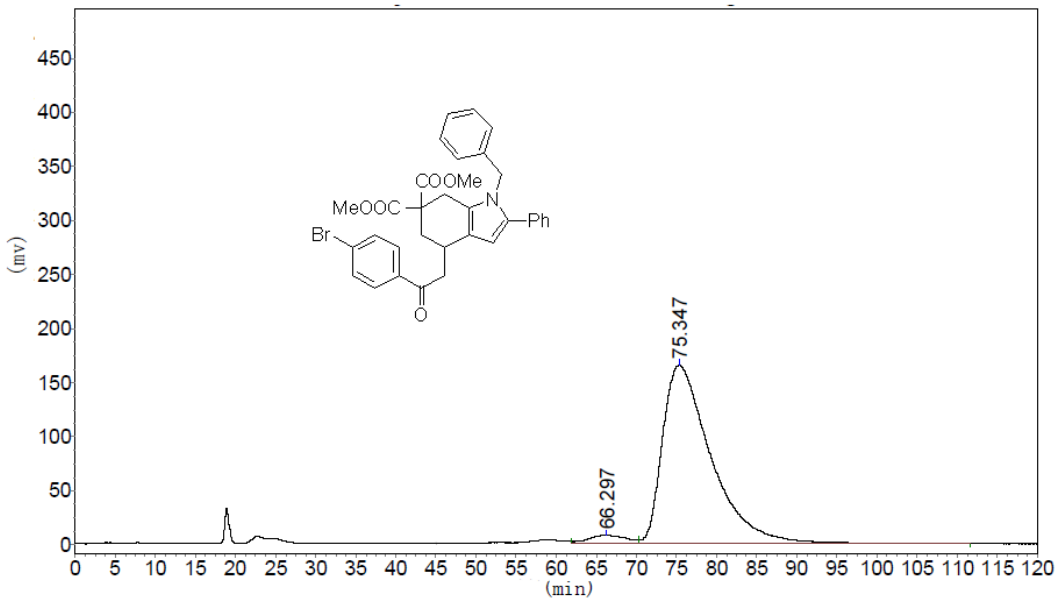



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 56.372 | 166133.656 | 21694434.000 | 94.1665 |
| 2 | 65.275 | 9015.061 | 1343944.625 | 5.8335 |
| **Total** | | 175148.717 | 23038378.625 | 100.0000 |

## HPLC Chromatograph of 3k

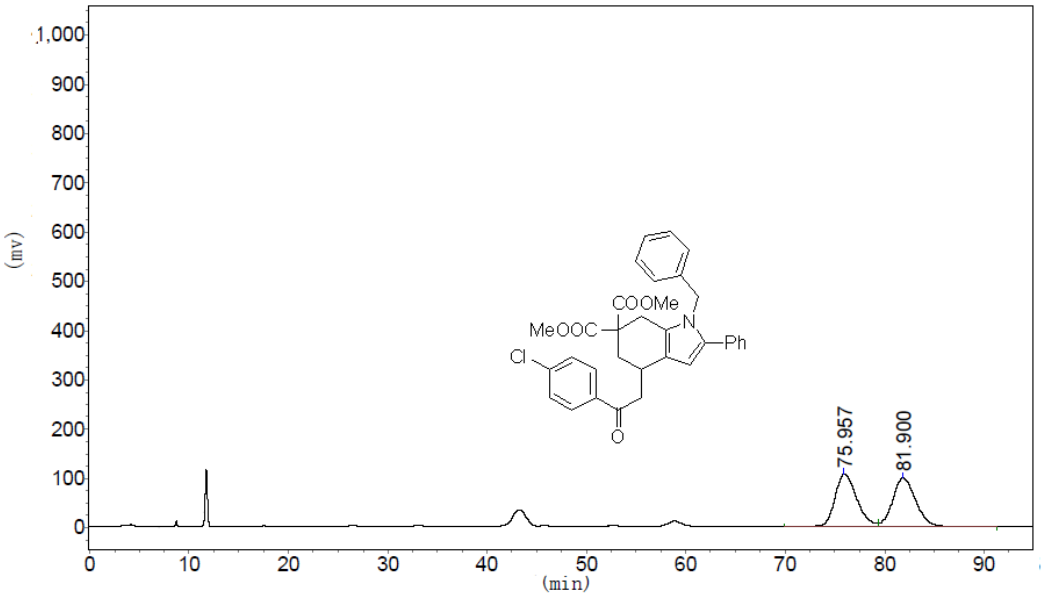



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 65. 232 | 25568. 416 | 8740805. 000 | 49. 3063 |
| 2 | 78. 035 | 21537. 629 | 8986759. 000 | 50. 6937 |
| **Total** | | 47106. 045 | 17727564. 000 | 100. 0000 |

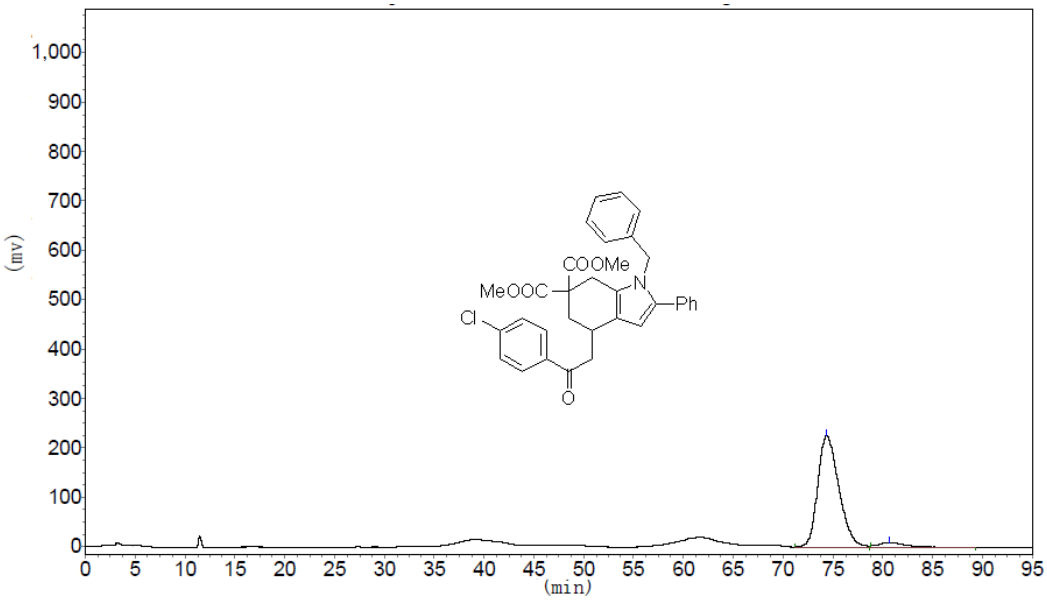



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 66. 297 | 7622. 033 | 2506388. 250 | 3. 4773 |
| 2 | 75. 347 | 164784. 438 | 69572360. 000 | 96. 5227 |
| **Total** | | 172406. 470 | 72078748. 250 | 100. 0000 |

## HPLC Chromatograph of 3l

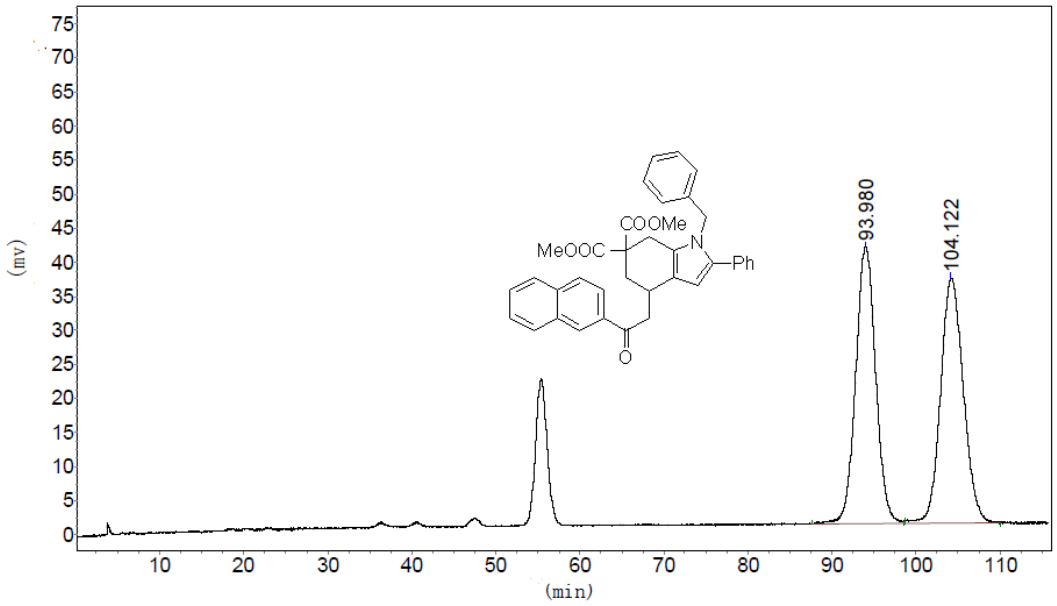



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 75. 957 | 107664. 406 | 16382757. 000 | 50. 3222 |
| 2 | 81. 900 | 98957. 242 | 16172999. 000 | 49. 6778 |
| **Total** | | 206621. 648 | 32555756. 000 | 100. 0000 |

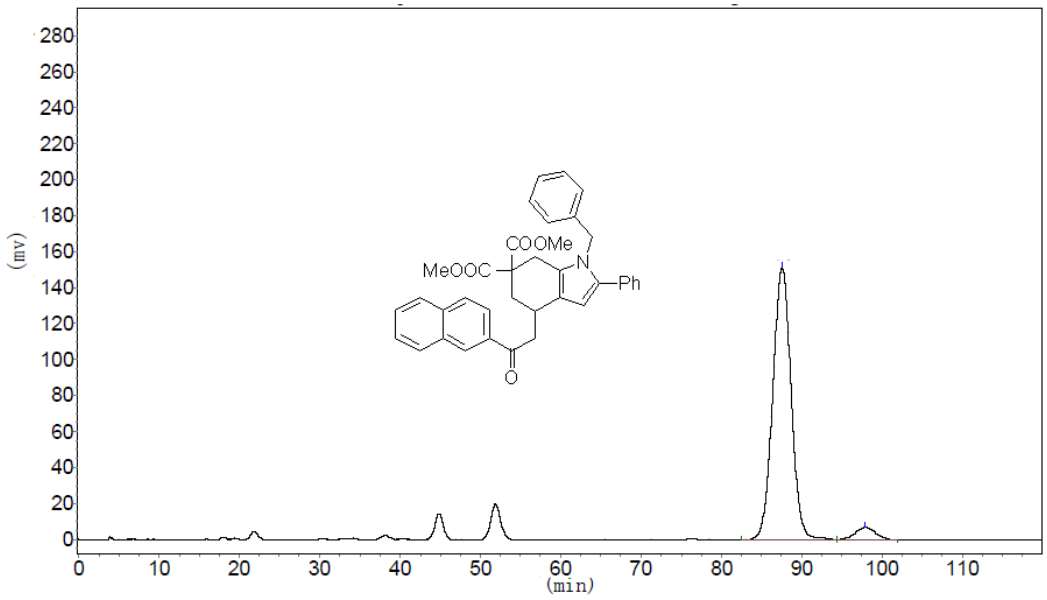



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 74. 392 | 225183. 922 | 32867570. 000 | 95. 3988 |
| 2 | 80. 713 | 9254. 096 | 1585253. 000 | 4. 6012 |
| **Total** | | 234438. 018 | 34452823. 000 | 100. 0000 |

## HPLC Chromatograph of 3m

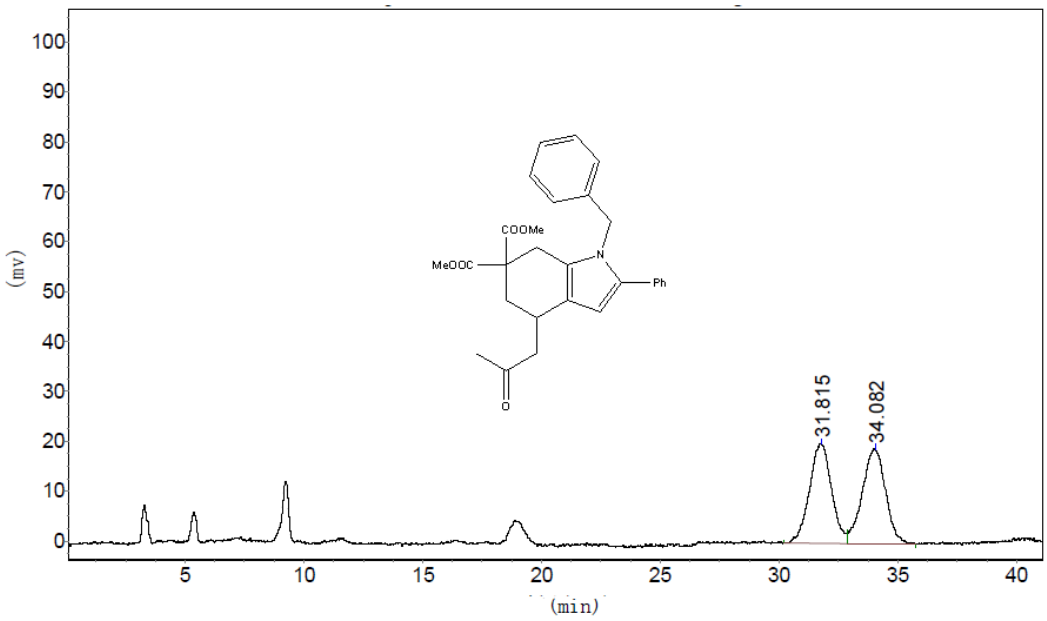



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 93.980 | 40626.441 | 6679924.000 | 49.8489 |
| 2 | 104.122 | 35979.207 | 6720421.500 | 50.1511 |
| **Total** | | 76605.648 | 13400345.500 | 100.0000 |

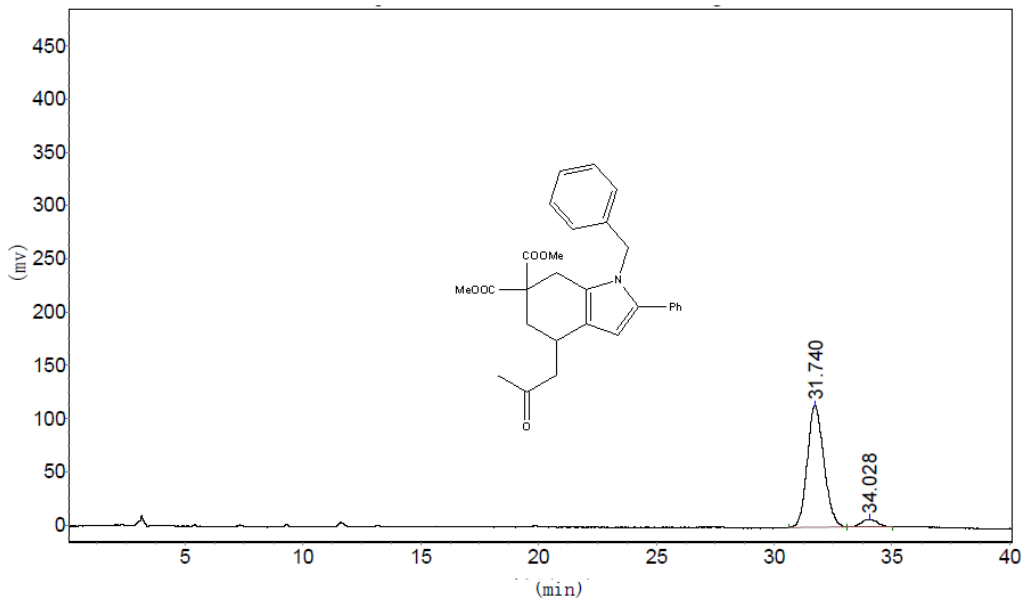



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 87.553 | 151237.656 | 23885472.000 | 95.1186 |
| 2 | 97.878 | 6988.942 | 1225792.500 | 4.8814 |
| **Total** | | 158226.599 | 25111264.500 | 100.0000 |

## HPLC Chromatograph of 3n

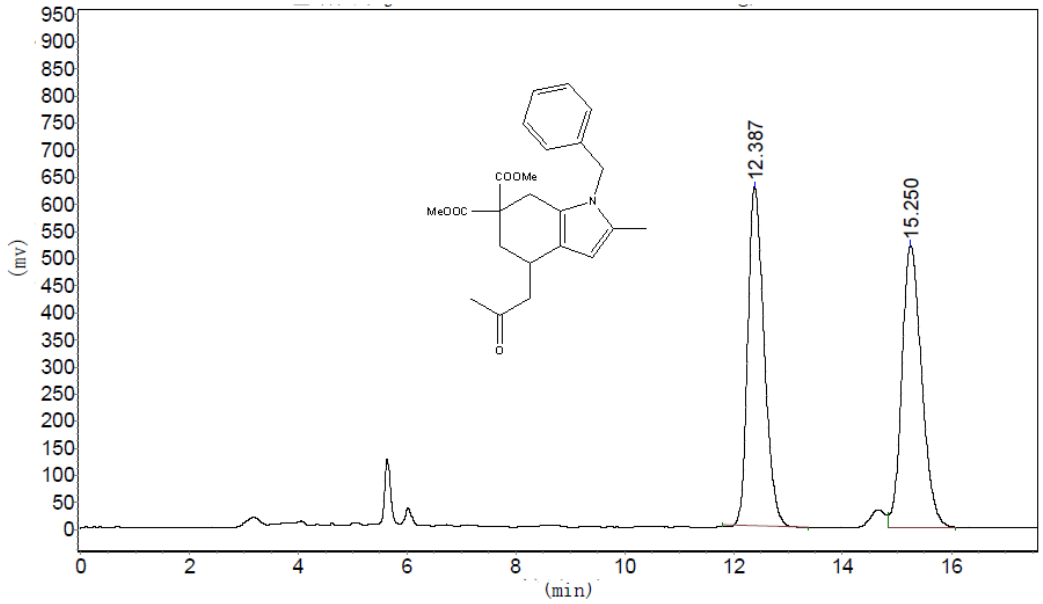



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 31.815 | 20447.604 | 1378868.750 | 50.7072 |
| 2 | 34.082 | 19316.811 | 1340405.750 | 49.2928 |
| **Total** | | 39764.414 | 2719274.500 | 100.0000 |

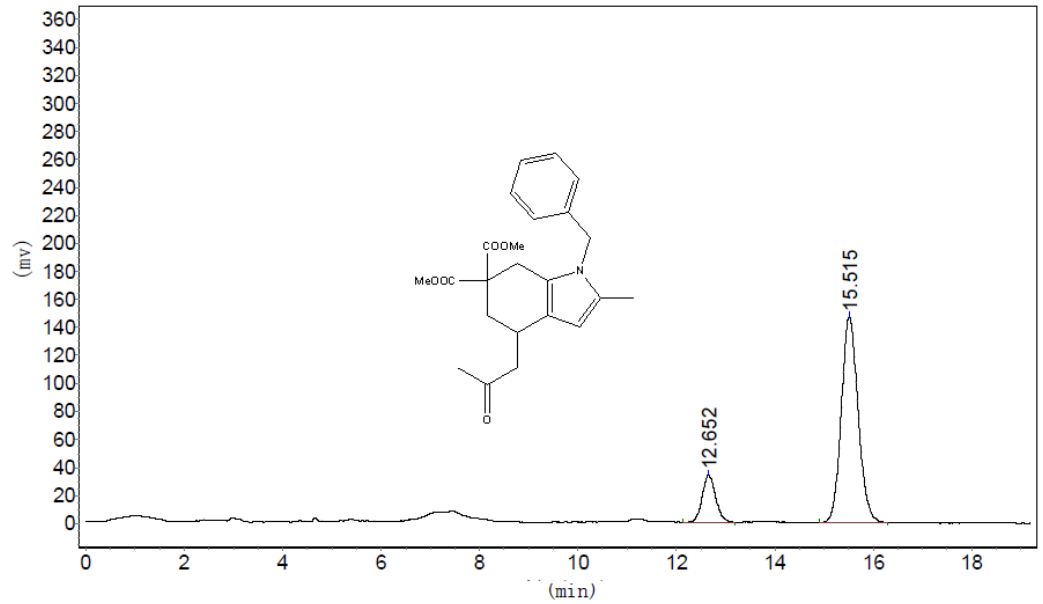



| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 31.740 | 113780.242 | 5621866.500 | 94.0474 |
| 2 | 34.028 | 7160.040 | 355826.281 | 5.9526 |
| **Total** | | 120940.282 | 5977692.781 | 100.0000 |

## HPLC Chromatograph of 3o




| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 12. 387 | 623705. 000 | 12927950. 000 | 49. 5356 |
| 2 | 15. 250 | 519027. 188 | 13170336. 000 | 50. 4644 |
| **Total** | | 1142732. 188 | 26098286. 000 | 100. 0000 |




| Peak No. | R. Time | Peak Height | Peak Area | Percent |
|---|---|---|---|---|
| 1 | 12. 652 | 33594. 027 | 637341. 938 | 15. 5484 |
| 2 | 15. 515 | 146662. 516 | 3461745. 000 | 84. 4516 |
| **Total** | | 180256. 543 | 4099086. 938 | 100. 0000 |