Photochemical α-Carboxyalkylation of Tryptophols and Tryptamines via C–H Functionalization

Zhiqiang Pan, Yuchang Liu, Fengchi Hu, Qinglong Liu, Wenbin Shang, and Chengfeng Xia*

Key Laboratory of Medicinal Chemistry for Natural Resource (Ministry of Education and Yunnan Province), School of Chemical Science and Technology, Yunnan University

Supporting Information

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1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvent were treated according to general methods. Flash column chromatography with was performed using 200 - 300 mesh silica gel. All reactions were carried out in flame - dried glassware under a dry argon atmosphere, glassware was dried in an oven at 150 °C or flame dried and cooled under a dry atmosphere. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp. ^{1}H NMR spectra were recorded on Bruker 600 (600 MHz) spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet or unresolved, br = broad, dd = doublet of doublets, q = quartet, coupling constant (s) in Hz, integration). ^{13}C NMR spectra were recorded on Bruker 600 (151 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass spectra were measured on a MS spectrometer.

2. Photochemical reaction setup

An oven dried glass tube equipped with a stirring bar and filled with argon, two parallel LED lamps (Ouying-5301, Blue LEDs, 12 W) are placed perpendicular to the sidewall of the glass tube, so that the glass tube can be equally exposed to the LEDs (at approximately 5 cm away from the light source, 44.5 mW/cm^2).

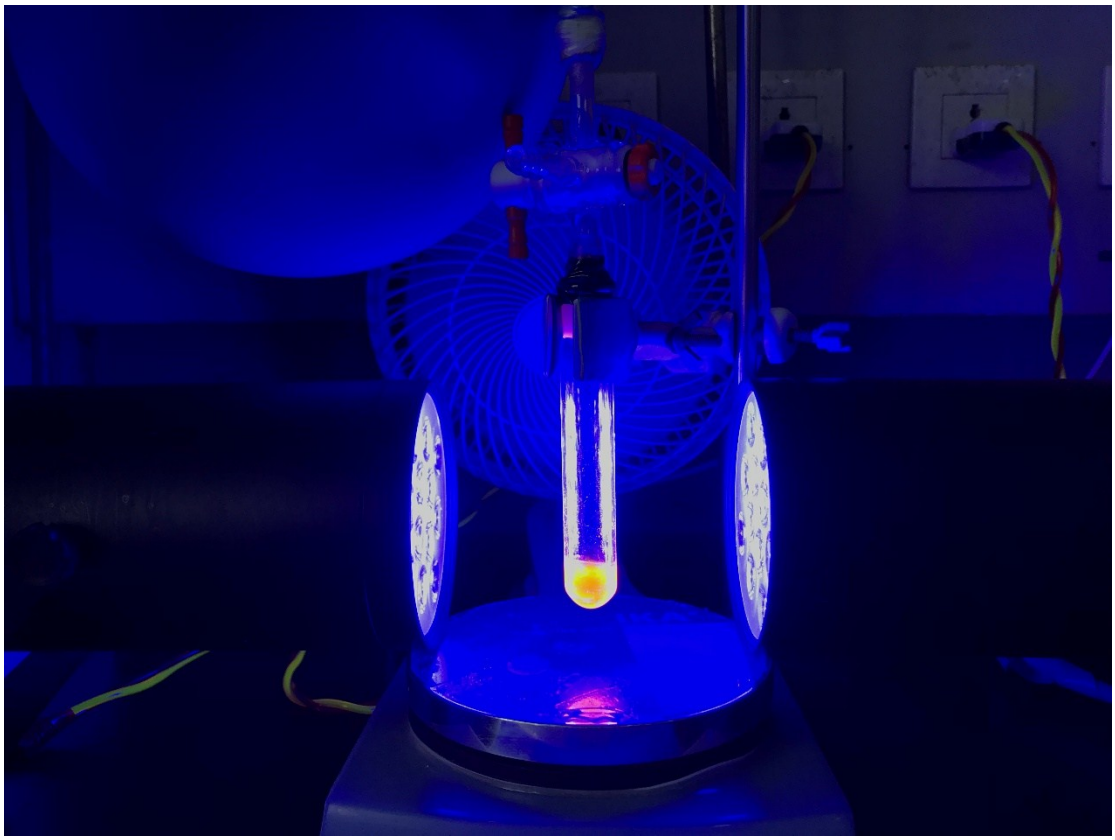


Figure S1. Details for the photochemical reaction setup.

3. Stern-Volmer Fluorescence Quenching Data

Fluorescence quenching experiments were performed on a Fluorescence Spectrophotometer F-4500. In a typical experiment, a 0.5 mM solution of $Ir(dmppy)_2(dtbbpy)PF_6$ in DCE was added to the appropriate amount of methyl bromoacetate **2a** in an 1.0 cm quartz cuvette. $Ir[(dmppy)_2(dtbbpy)]PF_6$ was excited at 385 nm, and emission was measured at 590 nm. Emission intensities were recorded using 5 μM $Ir[(dmppy)_2(dtbbpy)]PF_6$ and the appropriate amount of methyl bromoacetate **2a**. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected.

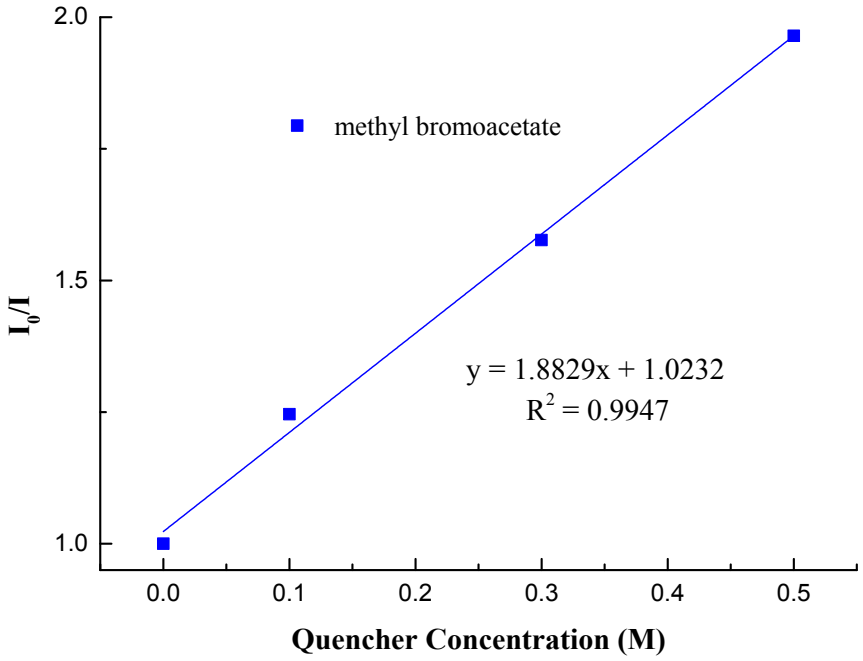
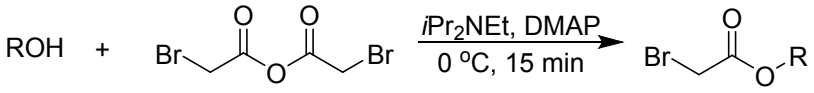


Figure S2. Stern-Volmer plots for methyl bromoacetate **2a** using $Ir(dmppy)_2(dtbbpy)PF_6$ as photocatalyst

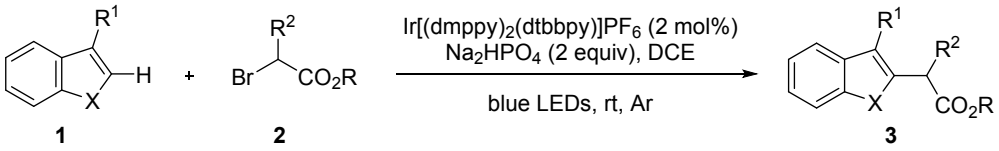
4. Experimental section

4.1 General procedure for preparation of α-bromo-aliphatates 2-S1 – 2-S4.



To a stirred solution of the requisite alcohol (0.35 mmol), 4-dimethyl-aminopyridine (DMAP, 0.035 mmol) and bromoacetic anhydride (0.35 mmol) in CH_2Cl_2 (3 mL) at 0 °C, a solution of *i*Pr_2NEt (0.35 mmol) in CH_2Cl_2 (1 mL) was added dropwise via syringe. The reaction mixture was stirred at 0 °C for 15 min, diluted with EtOAc, washed sequentially with 1N $KHSO_4$, conc. $NaHCO_3$, and brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The resultant product was immediately purified by flash chromatography.

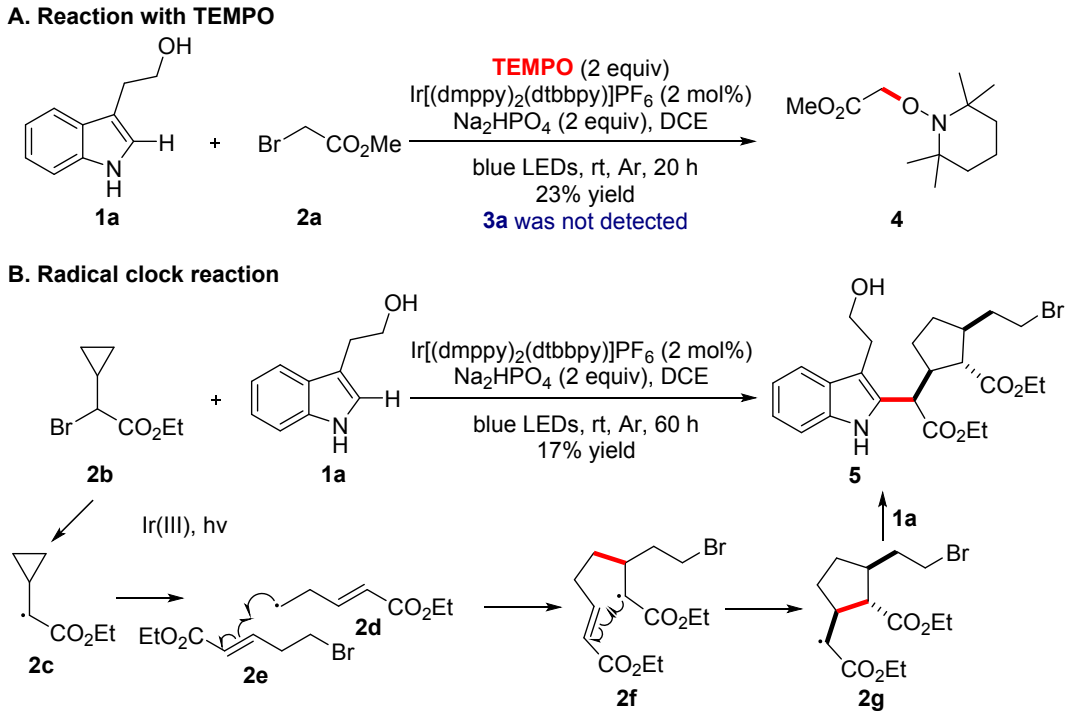
4.2 General procedure for preparation of C2 selective alkylated indole derivatives.



An oven dried glass tube equipped with a stirring bar was charged with indole derivatives **1** (0.5 mmol), α-bromo-aliphatates **2** (1.0 mmol), $Ir[(dmppy)_2(dtbbpy)]PF_6$ (0.01 mmol), Na_2HPO_4 (1.0 mmol) and 1.0 mL DCE (or a mixture of DCM and MeOH (1:1) as indicated). The reaction mixture was degassed three times by applying vacuum, and backfilling with argon while stirring vigorously. The reaction mixture was placed at approximately 5 cm away from two parallel LED lamps (Ouying-5301, Blue LEDs, 12 W, 44.5 mW/cm^2). After the reaction was complete (detected by TLC analysis), the mixture was concentrated in vacuo and purified by silica gel column chromatography to afford product **3**.

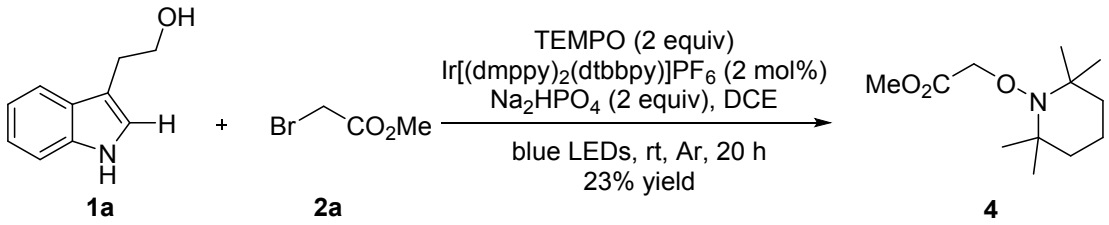
For compounds **3au, 3aw** – **3ba**, the reactions were conducted in a mixture of DCE/MeOH (1:1).

5 Controlled experiments



Scheme S1. A) TEMPO trapping experiment; B) Radical clock experiment.

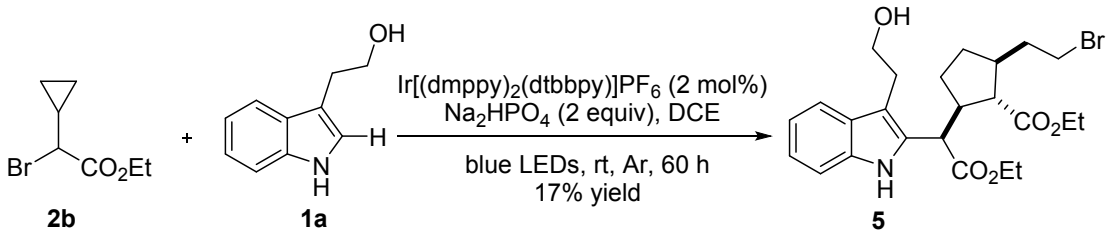
5.1 TEMPO trapping experiment



An oven dried glass tube equipped with a stirring bar was charged with tryptophol **1a** (81 mg, 0.5 mmol), methyl bromoacetate **2** (95 μL, 1.0 mmol), $Ir[(dmppy)_2(dtbbpy)]PF_6$ (9.7 mg, 0.01 mmol), Na_2HPO_4 (141 mg, 1.0 mmol), TEMPO (156 mg, 1.0 mmol) and 1.0 mL DCE. The reaction mixture was degassed three times by applying vacuum, and backfilling with argon while stirring vigorously. The reaction mixture was placed at approximately 5 cm away from two parallel LED lamps (Ouying-5301, Blue LEDs, 12 W, 44.5 mW/cm^2). After the reaction was complete (20 h), the mixture was concentrated in vacuo and purified by silica gel column chromatography to afford 53 mg product **4**, 23% yield. Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 2H), 3.73 (s, 3H),

1.59-1.50 (m, 1H), 1.45-1.38 (m, 4H), 1.33-1.25 (m, 1H), 1.14 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 75.4, 60.0, 51.5, 39.7, 32.7, 20.1, 17.0; HRMS (ESI) calcd for $C_{12}H_{24}NO_3$ [M + H]$^+$: 230.1751, Found: 230.1756; The product was purified as a pale yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 15.

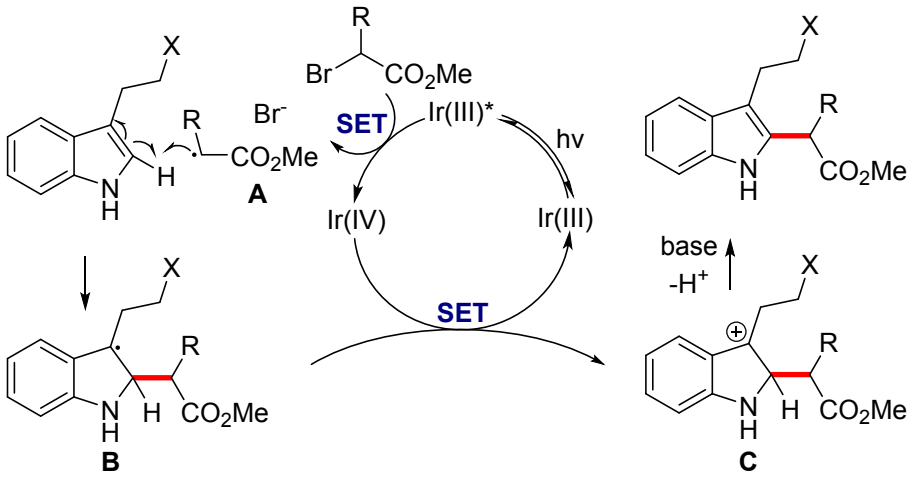
5.2 Radical clock experiment



2b **1a** **5**

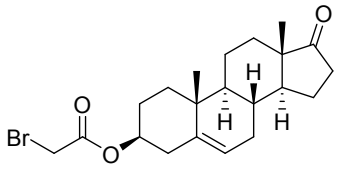
An oven dried glass tube equipped with a stirring bar was charged with tryptophol **1a** (403 mg, 2.5 mmol), methyl bromoacetate **2b** (207 mg, 0.14 mL, 1.0 mmol), Ir[(dmppy)$_2$(dtbbpy)]PF$_6$ (9.7 mg, 0.01 mmol), Na_2HPO_4 (141 mg, 1.0 mmol), and 3.0 mL DCE. The reaction mixture was degassed three times by applying vacuum, and backfilling with argon while stirring vigorously. The reaction mixture was placed at approximately 5 cm away from two parallel LED lamps (Blue LEDs, 12 W, 44.5 mW/cm^2). After the reaction was complete (96 h), the mixture was concentrated in vacuo and purified by silica gel column chromatography to afford 42 mg product **5**, 17% yield. Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 4.29-4.23 (m, 1H), 4.17-4.08 (m, 4H), 3.88-3.84 (m, 2H), 3.42 (t, *J* = 7.2 Hz, 2H), 3.38-3.05 (m, 1H), 3.02-2.93 (m, 1H), 2.90-2.80 (m, 1H), 2.71-2.68 (m, 1H), 2.53-2.48 (m, 1H), 2.04-1.90 (m, 3H), 1.59-1.49 (m, 1H), 1.40-1.37 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.16-1.09 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.0, 135.8, 131.8, 128.1, 122.3, 119.7, 118.8, 110.9, 110.2, 62.9, 61.5, 60.7, 51.0, 45.7, 44.0, 43.1, 39.4, 31.4, 31.2, 30.0, 27.7, 14.2, 13.9; HRMS (ESI) calcd for $C_{24}H_{33}BrNO_5$ [M + H]$^+$: 494.1537, Found: 494.1545; The product was purified as a colorless oil by silica gel column chromatography with dichloromethane/acetone = 25 : 1.

6. Proposed mechanism.

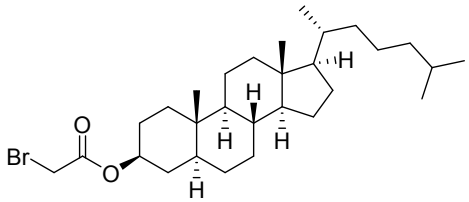


Scheme S2. Proposed photochemical catalytic cycle.

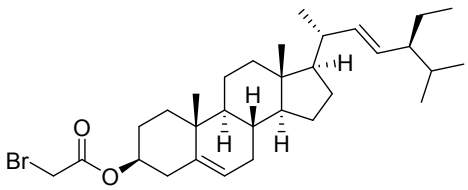
7. Characterizations of synthetic products



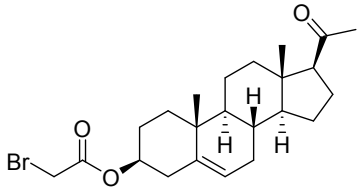
2-S1, 134 mg, 94% yield, Mp = 128 - 130 °C; Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 5.42 (d, *J* = 4.7 Hz, 1H), 4.71 - 4.65 (m, 1H), 3.81 (s, 2H), 2.48 - 2.43 (m, 1H), 2.40 - 2.34 (m, 2H), 2.14 - 2.06 (m, 2H), 1.97 - 1.83 (m, 4H), 1.69 - 1.64 (m, 4H), 1.56 - 1.45 (m, 3H), 1.32 - 1.24 (m, 2H), 1.19 - 1.14 (m, 1H), 1.05 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 220.9, 166.7, 139.5, 122.3, 75.8, 51.7, 50.1, 47.5, 37.7, 36.8, 36.7, 35.8, 31.5, 31.4, 30.8, 27.4, 26.3, 21.9, 20.3, 19.3, 13.5; HRMS (ESI) calcd for $C_{21}H_{29}BrO_3Na$ $[M + Na]^+$: 431.1192, Found: 431.1196; The product was purified as a white solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 5.



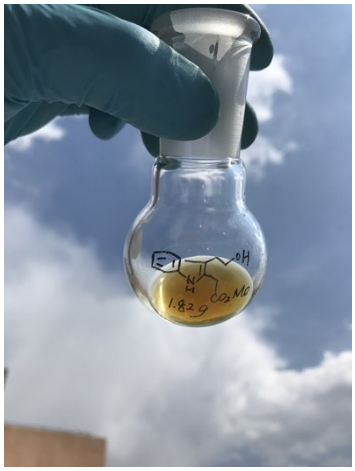
2-S2, 174 mg, 98% yield, Mp = 156 - 158 °C; Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 4.78 - 4.73 (m, 1H), 3.79 (s, 2H), 1.97 - 1.95 (m, 1H), 1.84 - 1.81 (m, 2H), 1.79 - 1.73 (m, 1H), 1.67 - 1.60 (m, 2H), 1.53 - 1.46 (m, 3H), 1.43 - 1.39 (m, 1H), 1.37 - 1.20 (m, 10H), 1.19 - 0.96 (m, 11H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.8 Hz, 3H), 0.86 (d, *J* = 2.8 Hz, 3H), 0.82 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 76.0, 56.4, 56.3, 54.2, 44.6, 42.6, 40.0, 39.5, 36.7, 36.2, 35.8, 35.5, 35.4, 33.7, 32.0, 28.6, 28.2, 28.0, 27.2, 26.4, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 12.2, 12.1; HRMS (ESI) calcd for $C_{29}H_{49}BrO_2Na$ $[M + Na]^+$: 531.2808, Found: 531.2808; The product was purified as a white solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 4.



2-S3, 177 mg, 95% yield, Mp = 162 - 164 °C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.39 (d, *J* = 4.1 Hz, 1H), 5.16 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.04 - 5.00 (dd, *J* = 15.1, 8.8 Hz, 1H), 4.70 - 4.65 (m, 1H), 3.81 (s, 2H), 2.36 (d, *J* = 7.7 Hz, 2H), 2.06 - 1.95 (m, 3H), 1.90 - 1.86 (m, 2H), 1.71 - 1.60 (m, 2H), 1.56 - 1.49 (m, 5H), 1.47 - 1.38 (m, 3H), 1.29 - 1.12 (m, 6H), 1.03 - 1.02 (m, 7H), 0.98 - 0.91 (m, 1H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.82 - 0.79 (m, 6H), 0.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 139.2, 138.3, 135.8, 129.3, 123.1, 76.1, 56.8, 56.0, 51.2, 50.0, 42.2, 40.5, 39.6, 37.8, 36.9, 36.6, 31.9, 31.8, 28.9, 27.5, 26.3, 25.4, 24.4, 21.2, 21.1, 21.0, 19.3, 19.0, 12.2, 12.1; HRMS (ESI) calcd for $C_{31}H_{49}BrO_2Na$ $[M + Na]^+$: 555.2808, Found: 555.2810; The product was purified as a white solid by silica gel column chromatography with ethyl acetate /petroleum = 1 : 5.



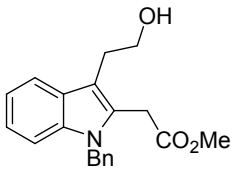
2-S4, 148 mg, 97% yield, Mp = 142 - 144 °C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.39 (d, *J* = 4.4 Hz, 1H), 4.70 - 4.65 (m, 1H), 3.81 (s, 2H), 2.55 (t, *J* = 9.1 Hz, 1H), 2.36 (d, *J* = 7.8 Hz, 2H), 2.20 - 2.14 (m, 1H), 2.12 (s, 3H), 2.06 - 1.98 (m, 2H), 1.91 - 1.87 (m, 2H), 1.70 - 1.51 (m, 5H), 1.51 - 1.42 (m, 3H), 1.26 - 1.19 (m, 1H), 1.18 - 1.13 (m, 2H), 1.02 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.4, 166.7, 139.2, 122.8, 76.0, 63.7, 56.8, 49.9, 44.0, 38.8, 37.7, 36.9, 36.6, 31.8, 31.7, 31.5, 27.5, 26.3, 24.5, 22.9, 21.0, 19.3, 13.2; HRMS (ESI) calcd for $C_{23}H_{33}BrO_3Na$ $[M + Na]^+$: 459.1505, Found: 459.1507; The product was purified as a white solid by silica gel column chromatography with acetone/petroleum ether = 1 : 5.



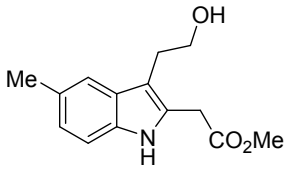
3a, 98 mg, 84% yield (1.82 g, 78% yield for 10 mmol scale). Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 3.86 - 3.84 (m, 4H), 3.74 (s, 3H), 3.00 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 135.9, 128.0, 127.9, 122.2, 119.6, 118.5, 110.9, 110.0, 62.7, 52.5, 31.8, 27.7; HRMS (ESI) calcd for $C_{13}H_{15}NO_3Na$ $[M + Na]^+$: 256.0944, Found: 256.0946; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

3b, 121 mg, 98% yield. Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 3.82 (s, 2H), 3.75 (s, 3H), 3.63 (t, *J* = 6.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 1.93 - 1.89 (m, 2H), 1.64 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 135.8, 128.0, 126.6, 121.9, 119.3, 118.6, 113.1, 110.8, 61.8, 52.4, 32.9, 31.7, 19.9; HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ $[M + Na]^+$: 270.1101, Found: 270.1103; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

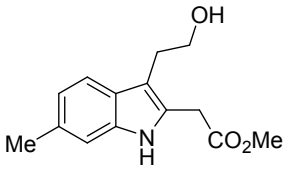
3c, 115 mg, 93% yield, Mp = 65 - 67 ^{o}C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.24 - 7.21 (m, 1H), 7.12 - 7.09 (m, 1H), 3.86 (s, 2H), 3.83 (t, *J* = 6.0 Hz, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 3.01 (t, *J* = 6.0 Hz, 2H), 1.95 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 137.2, 130.3, 127.2, 121.9, 119.3, 118.6, 110.1, 109.1, 62.7, 52.5, 30.9, 29.9, 28.1; HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ $[M + Na]^+$: 270.1101, Found: 270.1098; The product was purified as a pale yellow solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.



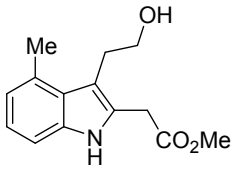
3d, 158 mg, 98% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.25 - 7.20 (m, 4H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 2H), 5.34 (s, 2H), 3.88 (t, *J* = 5.9 Hz, 2H), 3.77 (s, 2H), 3.52 (s, 3H), 3.04 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 137.5, 137.2, 130.2, 128.8, 127.5, 127.4, 126.0, 122.3, 119.6, 118.8, 111.1, 109.6, 62.6, 52.4, 46.9, 30.9, 28.3; HRMS (ESI) calcd for $C_{20}H_{21}NO_3Na$ $[M + Na]^+$: 346.1414, Found: 346.1415; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 2.



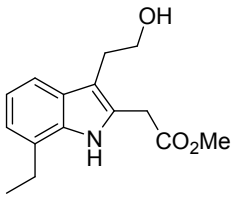
3e, 100 mg, 81% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.33 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 3.85 (t, *J* = 6.2 Hz, 2H), 3.82 (s, 2H), 3.74 (s, 3H), 2.97 (t, *J* = 6.2 Hz, 2H), 2.45 (s, 3H), 1.79 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 134.2, 128.9, 128.3, 128.1, 123.7, 118.2, 110.6, 109.5, 62.7, 52.4, 31.8, 27.7, 21.5; HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ $[M + Na]^+$: 270.1101, Found: 270.1103; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.



3f, 110 mg, 89% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 3.85 (t, *J* = 6.1 Hz, 2H), 3.81 (s, 2H), 3.73 (s, 3H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.45 (s, 3H), 1.80 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 136.1, 132.0, 127.2, 125.9, 121.3, 118.1, 110.9, 109.8, 62.7, 52.4, 31.8, 27.8, 21.7; HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ $[M + Na]^+$: 270.1101, Found: 270.1102; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

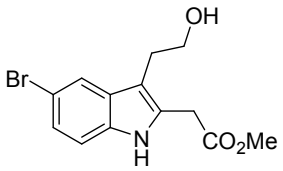


3g, 96 mg, 78% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.1 Hz, 1H), 3.85 - 3.83 (m, 4H), 3.74 (s, 3H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.67 (s, 3H), 1.73 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 136.2, 130.2, 128.1, 126.3, 122.0, 121.6, 110.3, 108.9, 64.0, 52.4, 31.7, 28.8, 20.4; HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ $[M + Na]^+$: 270.1101, Found: 270.1100; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

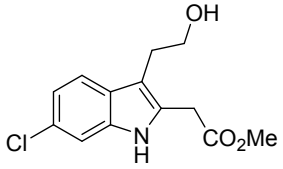


3h, 98 mg, 75% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.1 Hz, 1H), 3.86 - 3.84 (m, 4H), 3.75 (s, 3H), 3.00 (t, *J* = 6.2 Hz, 2H), 2.88 (q, *J* = 7.6 Hz, 2H), 1.67 (br, 1H), 1.38 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 134.7, 127.7, 127.6, 126.3, 120.8, 120.0, 116.2, 110.4, 62.7, 52.5, 31.8, 27.8, 24.0, 13.8; HRMS (ESI) calcd for $C_{15}H_{19}NO_3Na$ $[M + Na]^+$: 284.1257, Found: 284.1261; The product was purified as a yellow oil by silica gel column chromatography with ethyl

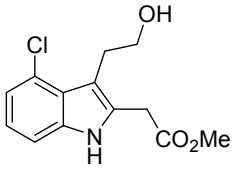
acetate/petroleum ether = 1 : 1.5.



3i, 103 mg, 66% yield. Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.26 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 3.83 - 3.81 (m, 4H), 3.75 (s, 3H), 2.94 (t, *J* = 6.2 Hz, 2H), 1.68 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 134.4, 129.8, 129.3, 124.9, 121.1, 112.9, 112.3, 109.8, 62.6, 52.5, 31.6, 27.5; HRMS (ESI) calcd for $C_{13}H_{14}BrNO_3Na$ $[M + Na]^+$: 334.0049, Found: 334.0052; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 2.5.

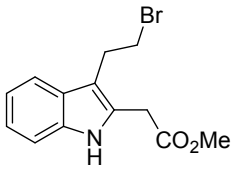


3j, 85 mg, 64% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 1.2 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.83 - 3.81 (m, 4H), 3.75 (s, 3H), 2.96 (t, *J* = 6.2 Hz, 2H), 1.69 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 136.1, 128.6, 128.0, 126.6, 120.3, 119.3, 110.8, 110.2, 62.6, 52.5, 31.7, 27.6; HRMS (ESI) calcd for $C_{13}H_{14}ClNO_3Na$ $[M + Na]^+$: 290.0554, Found: 290.0556; The product was purified as a pale yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

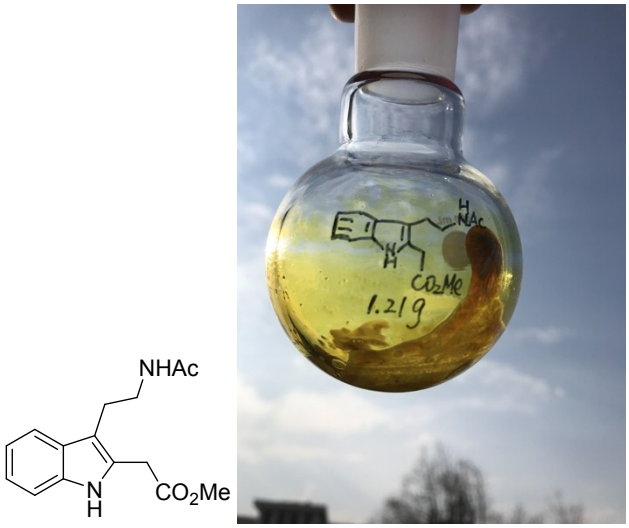


3k, 89 mg, 67% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.22 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.06 - 7.03 (m, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 2H), 3.75 (s, 3H), 3.22 (t, *J* = 6.3 Hz, 2H), 1.72 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 137.3, 129.5, 125.8, 124.5, 122.4, 120.8, 110.1, 109.7, 63.9, 52.4, 31.4, 28.1; HRMS (ESI) calcd for $C_{13}H_{14}ClNO_3Na$ [M +

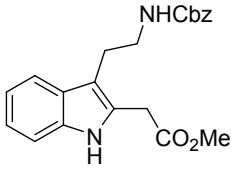
Na]$^+$: 290.0554, Found: 290.0556; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 2.



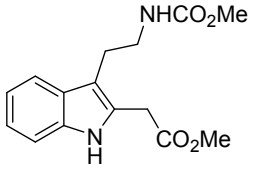
3l, 94 mg, 64% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* =7.5 Hz, 1H), 3.84 (s, 2H), 3.76 (s, 3H), 3.59 (t, *J* = 7.6 Hz, 2H), 3.31 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 135.7, 127.7, 127.5, 122.2, 119.7, 118.1, 111.0, 110.8, 52.4, 32.8, 31.7, 28.3; HRMS (ESI) calcd for $C_{13}H_{14}BrNO_2Na$ [M + Na]$^+$: 318.0100, Found: 318.0102; The product was purified as a pale yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 4.



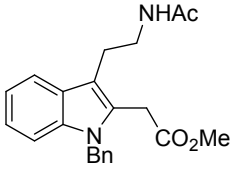
3m, 130 mg, 95% yield (1.21 g, 88% yield for 5 mmol scale), Mp = 95 - 97 °C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.19 - 7.16 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.00 (br, 1H), 3.79 (s, 2H), 3.75 (s, 3H), 3.56 (dd, *J* = 12.4, 6.1 Hz, 2H), 2.94 (t, *J* = 6.0 Hz, 2H), 1.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 170.5, 135.9, 127.9, 127.6, 122.2, 119.6, 118.5, 111.0, 110.7, 52.5, 39.9, 31.7, 24.0, 23.1; HRMS (ESI) calcd for $C_{15}H_{18}N_2O_3Na$ [M + Na]$^+$: 297.1210, Found: 297.1208; The product was purified as a yellow solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1 to EtOAc.



3n, 156 mg, 85% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.37 - 7.32 (m, 6H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 6.8 Hz, 1H), 5.10 (s, 2H), 4.94 (s, 1H), 3.76 (s, 2H), 3.68 (s, 3H), 3.48 (d, *J* = 6.0 Hz, 2H), 2.96 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 156.4, 136.7, 135.8, 128.5, 128.1, 128.0, 127.5, 122.7, 122.1, 119.6, 118.4, 110.9, 110.4, 66.6, 52.4, 41.4, 31.6, 24.5; HRMS (ESI) calcd for $C_{21}H_{22}N_2O_4Na$ $[M + Na]^+$: 389.1472, Found: 389.1472; The product was purified as a pale yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

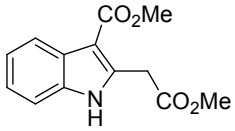


3o, 110 mg, 76% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 4.90 (br, 1H), 3.79 (s, 2H), 3.74 (s, 3H), 3.66 (s, 3H), 3.45 - 3.44 (m, 2H), 2.95 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 157.1, 135.9, 127.8, 127.6, 122.1, 119.6, 118.4, 110.9, 110.4, 52.4, 52.0, 41.4, 31.6, 24.6; HRMS (ESI) calcd for $C_{15}H_{18}N_2O_4Na$ $[M + Na]^+$: 313.1159, Found: 313.1162; The product was purified as a pale yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

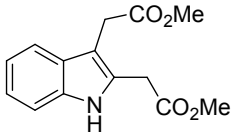


3p, 160 mg, 88% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.32 - 7.21 (m, 6H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.36 (br, 1H), 5.37 (s, 2H), 3.77 (s, 2H), 3.65 (dd, *J* = 12.0, 6.0 Hz, 2H), 3.58 (s, 3H), 3.03 (t, *J* = 6.0 Hz, 2H), 1.91 (s,

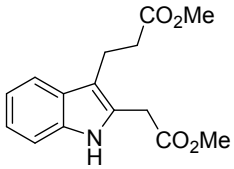
3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 170.4, 137.4, 137.2, 129.5, 128.8, 127.4, 127.3, 125.9, 122.4, 119.7, 118.8, 111.8, 109.6, 52.4, 46.9, 39.6, 30.6, 24.5, 23.0; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_3$ $[M + H]^+$: 365.1860, Found: 365.1856; The product was purified as an orange oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1.5 : 1.



3q, 105 mg, 85% yield, Mp = 122 - 124 °C; Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.11 - 8.09 (m, 1H), 7.38 - 7.36 (m, 1H), 7.25 - 7.22 (m, 2H), 4.38 (s, 2H), 3.94 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 166.1, 138.6, 134.8, 126.4, 122.9, 121.9, 121.5, 111.2, 105.2, 52.5, 50.9, 32.1; HRMS (ESI) calcd for $C_{13}H_{13}NO_4Na$ $[M + Na]^+$: 270.0737, Found: 270.0738; The product was purified as a white solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 3.

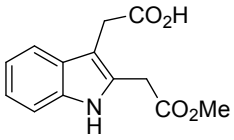


3r, 103 mg, 79% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 2H), 3.76 (s, 3H), 3.73 (s, 2H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 170.8, 135.5, 128.1, 127.9, 122.1, 119.8, 118.5, 110.9, 106.1, 52.5, 52.0, 31.6, 30.0; HRMS (ESI) calcd for $C_{14}H_{15}NO_4Na$ $[M + Na]^+$: 284.0893, Found: 284.0898; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 4.

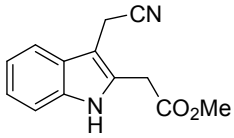


3s, 94 mg, 68% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 3.86 (s,

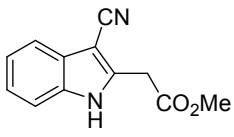
2H), 3.75 (s, 3H), 3.64 (s, 3H), 3.06 (t, J = 7.5 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 171.1, 135.8, 127.6, 126.9, 121.9, 119.4, 118.3, 112.0, 110.9, 52.3, 51.5, 34.8, 31.5, 19.5; HRMS (ESI) calcd for $C_{15}H_{17}NO_4Na$ $[M + Na]^+$: 298.1050, Found: 298.1049; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/dichloromethane = 1 : 100.



3t, 106 mg, 86% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 7.1 Hz, 1H), 7.12 (t, J = 7.1 Hz, 1H), 3.84 (s, 2H), 3.73 (s, 3H), 3.72 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 170.9, 135.4, 128.3, 127.7, 122.3, 120.0, 118.4, 110.9, 105.5, 52.4, 31.6, 29.9; HRMS (ESI) calcd for $C_{13}H_{13}NO_4Na$ $[M + Na]^+$: 270.0737, Found: 270.0741; The product was purified as a brown oil by silica gel column chromatography with ethyl acetate/petroleum ether = 2 : 1.

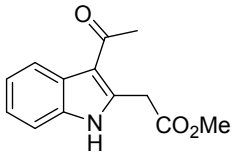


3u, 72 mg, 63% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.3 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 3.86 (s, 2H), 3.79 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 135.3, 128.0, 126.8, 122.8, 120.4, 117.8, 117.6, 111.2, 101.7, 52.6, 31.5, 12.9; HRMS (ESI) calcd for $C_{13}H_{12}N_2O_2Na$ $[M + Na]^+$: 251.0791, Found: 251.0788; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 3.

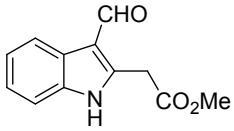


3v, 76 mg, 71% yield, Mp = 95 - 97 ^{o}C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.31 - 7.25 (m, 2H), 4.08 (s, 2H), 3.83

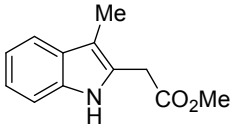
(s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 139.2, 134.7, 127.0, 124.0, 122.3, 119.3, 115.4, 111.8, 86.5, 52.8, 31.8; HRMS (ESI) calcd for $C_{12}H_{10}N_2O_2Na$ $[M + Na]^+$: 237.0634, Found: 237.0636; The product was purified as a pale yellow solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 2.



3w, 62 mg, 54% yield, Mp = 125 - 127 °C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.29 - 7.24 (m, 2H), 4.38 (s, 2H), 3.80 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.9, 171.7, 138.8, 134.9, 125.9, 122.7, 122.1, 120.5, 114.8, 111.8, 52.4, 32.7, 31.5; HRMS (ESI) calcd for $C_{13}H_{13}NO_3Na$ $[M + Na]^+$: 254.0788, Found: 254.0783; The product was purified as an orange solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 3.

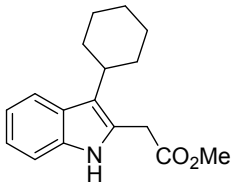


3x, 55 mg, 51% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.90 (s, 1H), 8.09 - 8.08 (m, 1H), 7.35 - 7.33 (m, 1H), 7.22 - 7.19 (m, 2H), 4.20 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 184.5, 170.4, 140.4, 135.1, 126.0, 123.8, 122.9, 120.1, 114.6, 111.5, 52.8, 31.3; HRMS (ESI) calcd for $C_{12}H_{11}NO_3Na$ $[M + Na]^+$: 240.0631, Found: 240.0630; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 2.

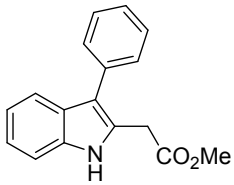


3y, 79 mg, 78% yield, Mp = 65 - 67 °C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 2H), 3.75 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 135.7, 128.8,

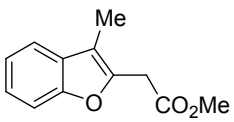
126.2, 121.8, 119.2, 118.5, 110.6, 109.0, 52.3, 31.7, 8.4; HRMS (ESI) calcd for $C_{12}H_{13}NO_2Na$ [M + Na]$^+$: 226.0838, Found: 226.0839; The product was purified as a yellow solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 10.



3z, 96 mg, 71% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 3.83 (s, 2H), 3.74 (s, 3H), 2.75 - 2.71 (m, 1H), 1.95 - 1.86 (m, 4H), 1.81 (d, *J* = 12.6 Hz, 3H), 1.45 - 1.32 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 135.9, 127.0, 125.0, 121.4, 120.1, 119.1, 118.9, 110.9, 52.3, 36.6, 33.1, 32.0, 27.3, 26.3; HRMS (ESI) calcd for $C_{17}H_{21}NO_2Na$ [M + Na]$^+$: 294.1465, Found: 294.1465; The product was purified as a pale brown oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 12.

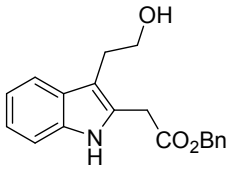


3aa, 119 mg, 90% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 - 7.47 (m, 4H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.36 - 7.33 (m, 1H), 7.24 - 7.21 (m, 1H), 7.15 - 7.12 (m, 1H), 3.92 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 135.7, 134.5, 129.7, 128.7, 127.4, 126.7, 126.4, 122.4, 120.1, 119.3, 116.4, 110.9, 52.4, 32.0; HRMS (ESI) calcd for $C_{17}H_{15}NO_2Na$ [M + Na]$^+$: 288.0995, Found: 288.0997; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 10.

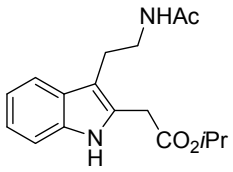


3ab, 92 mg, 90% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.25 - 7.19 (m, 2H), 3.78 (s, 2H), 3.72 (s, 3H), 2.20 (s, 3H). ^{13}C NMR

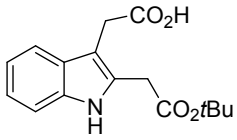
(151 MHz, $CDCl_3$) δ 169.5, 154.2, 145.9, 129.9, 124.0, 122.3, 119.1, 112.9, 111.0, 52.3, 32.6, 7.9; HRMS (ESI) calcd for $C_{12}H_{12}O_3Na$ $[M + Na]^+$: 227.0679, Found: 227.0682; The product was purified as a colorless oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 3.



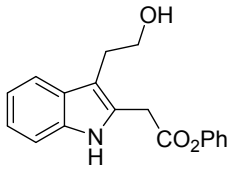
3ac, 133 mg, 86% yield. Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.39 - 7.34 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 5.17 (s, 2H), 3.87 (s, 2H), 3.84 (t, *J* = 6.2 Hz, 2H), 2.99 (t, *J* = 6.2 Hz, 2H), 1.72 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 135.9, 135.3, 128.7, 128.6, 128.4, 128.0, 127.9, 122.1, 119.6, 118.5, 110.9, 110.1, 67.3, 62.7, 32.0, 27.7; HRMS (ESI) calcd for $C_{19}H_{19}NO_3Na$ $[M + Na]^+$: 332.1257, Found: 332.1253; The product was purified as a brown oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 2.5.



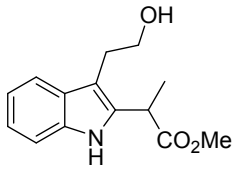
3ad, 124 mg, 82% yield. Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.87 (br, 1H), 5.08 - 504 (m, 1H), 3.75 (s, 2H), 3.57 - 3.54 (m, 2H), 3.95 (t, *J* = 6.4 Hz, 2H), 1.90 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.9, 170.5, 135.8, 127.9, 127.8, 122.2, 119.7, 118.4, 110.9, 110.7, 69.4, 39.8, 32.1, 24.0, 23.2, 21.8; HRMS (ESI) calcd for $C_{17}H_{22}N_2O_3Na$ $[M + Na]^+$: 325.1523, Found: 325.1521; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate /petroleum = 1.5 : 1.



3ae, 127 mg, 88% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 3.74 (s, 2H), 3.73 (s, 2H), 1.46 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 170.0, 135.4, 129.1, 127.8, 122.1, 119.8, 118.4, 110.9, 105.1, 82.4, 32.8, 30.1, 28.0; HRMS (ESI) calcd for $C_{16}H_{19}NO_4Na$ $[M+Na]^+$: 312.1206, Found: 312.1209; The product was purified as a red oil by silica gel column chromatography ethyl acetate /petroleum = 1 : 4.

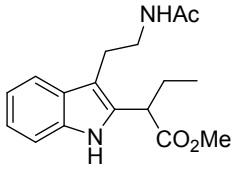


3af, 105 mg, 71% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.25-7.23 (m, 1H), 7.20-7.18 (m, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 4.07 (s, 2H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.06 (t, *J* = 6.2 Hz, 2H), 1.67 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 150.5, 136.0, 129.5, 128.0, 127.4, 126.2, 122.3, 121.4, 119.7, 118.5, 111.0, 110.4, 62.7, 32.1, 27.7; HRMS (ESI) calcd for $C_{18}H_{17}NO_3Na$ $[M+Na]^+$: 318.1101, Found: 318.1096; The product was purified as a brown oil by silica gel column chromatography ethyl acetate/petroleum ether = 1 : 2.5.

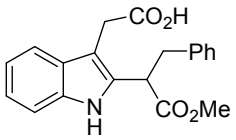


3ag, 101 mg, 82% yield. Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.20 - 7.18 (m, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 3.88 - 3.86 (m, 2H), 3.72 (s, 3H), 3.09 - 3.04 (m, 1H), 3.02 - 2.97 (m, 1H), 1.89 (br, 1H), 1.58 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.7, 135.8, 133.9, 128.0, 122.1, 119.6, 118.6, 111.0, 108.6, 62.8, 52.5, 36.9, 27.7, 18.8; HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ [M +

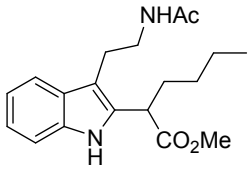
Na]$^+$: 270.1101, Found: 270.1103; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.



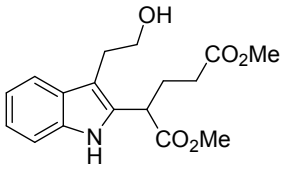
3ah, 139 mg, 92% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.66 (br, 1H), 3.85 (t, *J* = 7.7 Hz, 1H), 3.73 (s, 3H), 3.67 - 3.63 (m, 1H), 3.46 - 3.40 (m, 1H), 3.03 - 3.00 (m, 1H), 2.92 - 2.87 (m, 1H), 2.13 - 2.06 (m, 1H), 1.92 (s, 3H), 1.88 - 1.83 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 170.1, 135.8, 131.9, 127.9, 122.2, 119.6, 118.5, 111.0, 110.4, 52.3, 44.3, 40.1, 27.2, 24.1, 23.2, 11.9; HRMS (ESI) calcd for $C_{17}H_{22}N_2O_3Na$ [M + Na]$^+$: 325.1523, Found: 325.1520; The product was purified as a yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.



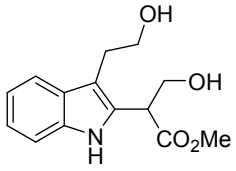
3ai, 131 mg, 78% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.21-7.15 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 2H), 4.20 (t, *J* = 7.7 Hz, 1H), 3.60 (s, 3H), 3.56 (d, *J* = 15.9 Hz, 1H), 7.47 (d, *J* = 16.0 Hz, 1H), 3.32 (dd, *J* = 13.2, 8.4 Hz, 1H), 3.14 (dd, *J* = 13.8, 7.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 173.6, 137.8, 135.5, 132.1, 128.8, 128.5, 127.6, 126.9, 122.4, 119.9, 118.7, 111.1, 105.5, 52.3, 45.2, 40.3, 29.6; HRMS (ESI) calcd for $C_{20}H_{19}NO_4Na$ [M+Na]$^+$:360.1206, Found: 360.1205; The product was purified as an orange oil by silica gel column chromatography ethyl acetate/petroleum ether = 1 : 4.



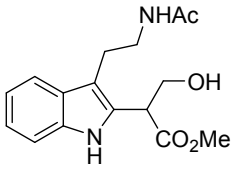
3aj, 121 mg, 73% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.72 (br, 1H), 3.92 (t, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.66 - 3.62 (m, 1H), 3.45 - 3.40 (m, 1H), 3.03 - 2.99 (m, 1H), 2.90 - 2.86 (m, 1H), 2.10 - 2.04 (m, 1H), 1.91 (s, 3H), 1.85 - 1.79 (m, 1H), 1.34 - 1.28 (m, 2H), 1.27 - 1.22 (m, 2H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 170.1, 135.8, 132.2, 127.9, 122.2, 119.6, 118.5, 111.0, 110.2, 52.3, 42.8, 40.1, 33.4, 29.5, 24.1, 23.2, 22.4, 13.8; HRMS (ESI) calcd for $C_{19}H_{26}N_2O_3Na$ $[M + Na]^+$: 353.1836, Found: 353.1837; The product was purified as an yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1.5 : 1.



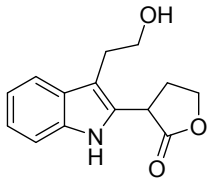
3ak, 129 mg, 81% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.20 - 7.17 (m, 1H), 7.12 - 7.09 (m, 1H), 4.13 (t, *J* = 6.1 Hz, 1H), 3.88 (t, *J* = 8.1 Hz, 2H), 3.71 (s, 3H), 3.61 (s, 3H), 3.06 - 3.02 (m, 1H), 2.98 - 2.93 (m, 1H), 2.40 - 2.34 (m, 1H), 2.33 - 2.30 (m, 2H), 2.26 - 2.20 (m, 1H), 1.91 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 173.0, 136.0, 131.3, 127.9, 122.4, 119.6, 118.7, 111.0, 110.5, 62.8, 52.5, 51.7, 41.6, 31.2, 28.2, 27.7; HRMS (ESI) calcd for $C_{17}H_{21}NO_5Na$ $[M + Na]^+$: 342.1312, Found: 342.1307; The product was purified as an orange oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.



3al, 72 mg, 55% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 4.19 - 4.17 (m, 1H), 4.14 - 4.11 (m, 1H), 4.02 - 4.00 (m, 1H), 3.88 - 3.85 (m, 2H), 3.72 (s, 3H),3.01 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 135.9, 130.4, 127.6, 122.4, 119.6, 118.5, 111.1, 110.6, 63.9, 62.4, 52.6, 44.6, 27.5; HRMS (ESI) calcd for $C_{14}H_{17}NO_4Na$ $[M + Na]^+$: 286.1050, Found: 286.1048; The product was purified as an orange oil by silica gel column chromatography with dichloromethane/ethyl acetate = 1 : 3.

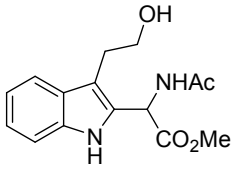


3am, 93 mg, 61% yield. Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.86 (br, 1H), 4.19-4.16 (m, 1H), 4.15 (t, *J* = 5.0 Hz, 1H), 4.06-4.04 (m, 1H), 3.75 (s, 3H), 3.55 (q, *J* = 6.7 Hz, 2H), 3.02-3.00 (m, 1H), 2.95-2.90 (m, 1H), 1.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 170.4, 135.8, 129.9, 127.7, 122.3, 119.7, 118.5, 111.2, 64.0, 52.6, 44.7, 40.2, 24.2, 23.1; HRMS (ESI) calcd for $C_{16}H_{20}N_2O_4Na$ $[M+Na]^+$: 327.1315, Found: 327.1319; The product was purified as a yellow oil by silica gel column chromatography acetone/dichloromethane = 1 : 2.

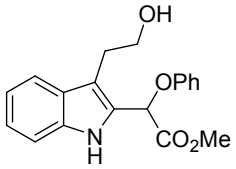


3an, 93 mg, 76% yield, Mp = 120 - 122 ^{o}C; Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 4.51 (t, *J* = 8.8 Hz, 1H), 4.36 - 4.31 (m, 1H), 4.26 - 4.22 (m, 1H), 3.88 - 3.81 (m, 2H), 3.06 - 3.01 (m, 1H), 2.96 - 2.92 (m, 1H), 2.79 - 2.74 (m, 1H), 2.54 - 2.46 (m, 1H), 2.06 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 136.0, 130.0, 127.9, 122.5, 119.7, 118.4, 111.3, 111.2, 67.1, 62.4, 38.2, 30.4, 27.9; HRMS (ESI) calcd for $C_{14}H_{15}NO_3Na$ $[M + Na]^+$: 268.0944, Found:

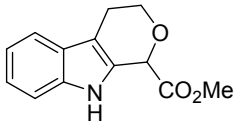
268.0945; The product was purified as a yellow solid by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.



3ao, 65 mg, 45% yield. Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 6.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 5.79 (d, *J* = 6.4 Hz, 1H), 3.97-3.88 (m, 2H), 3.72 (s, 3H), 3.09 (t, *J* = 5.6 Hz, 2H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 170.4, 135.7, 129.7, 127.8, 122.9, 119.8, 118.8, 111.5, 111.3, 62.6, 53.2, 50.2, 27.2, 22.8; HRMS (ESI) calcd for $C_{15}H_{18}N_2O_4Na$ $[M + Na]^+$: 313.1159, Found: 313.1166; The product was purified as a pale yellow oil by silica gel column chromatography with acetone/dichloromethane = 1 : 3.

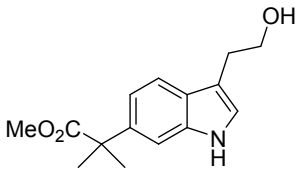


3ap, 78 mg, 48% yield. Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 3.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.04 - 6.98 (m, 3H), 5.56 (s, 1H), 4.07 - 4.01 (m, 1H), 3.96 - 3.90 (m, 1H), 3.78 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 156.2, 136.1, 129.6, 127.4, 122.9, 122.2, 121.9, 119.3, 118.7, 117.0, 112.1, 111.1, 97.0, 67.3, 52.6, 25.5; HRMS (ESI) calcd for $C_{19}H_{20}NO_4Na$ $[M + H]^+$: 326,1387, Found: 326.1396; The product was purified as an pale yellow oil by silica gel column chromatography with acetone/petroleum ether = 1 : 3.

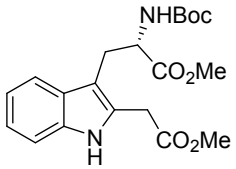


3aq, 74 mg, 64% yield. Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 5.49 (s,

1H), 4.33 - 4.28 (m, 1H), 4.13 - 4.07 (m, 1H), 3.88 (s, 3H), 2.95-2.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 136.0, 127.2, 126.6, 122.5, 119.8, 118.4, 111.2, 109.2, 71.6, 64.6, 52.8, 21.6; HRMS (ESI) calcd for $C_{13}H_{14}NO_3$ $[M + H]^+$: 232.0968, Found: 232.0976; The product was purified as a colorless oil by silica gel column chromatography with acetone/dichloromethane = 1 : 25.

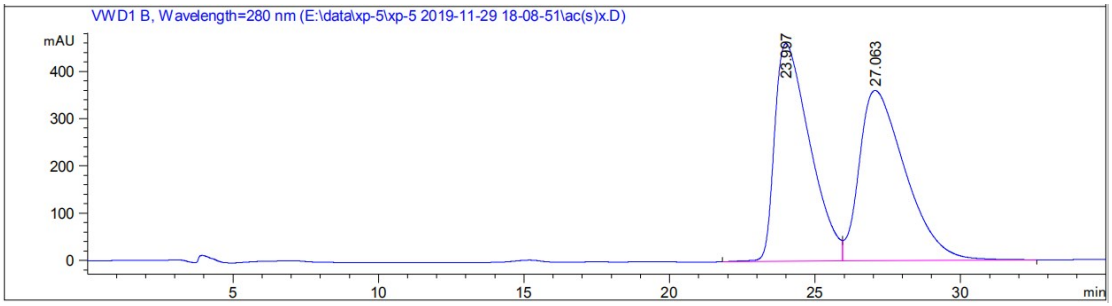


3ar, 20 mg, 15% yield. Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 1.2 Hz, 1H), 7.13 (t, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.64 (s, 3H), 3.03 (t, *J* = 6.4 Hz, 2H), 1.64 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 139.1, 136.5, 126.1, 122.8, 118.8, 117.8, 112.2, 108.1, 62.6, 52.2, 46.5, 28.8, 26.9; HRMS (ESI) calcd for $C_{15}H_{20}NO_3$ $[M + H]^+$: 262.1438, Found: 262.1437; The product was purified as a colorless oil by silica gel column chromatography with acetone/dichloromethane = 1 : 30.

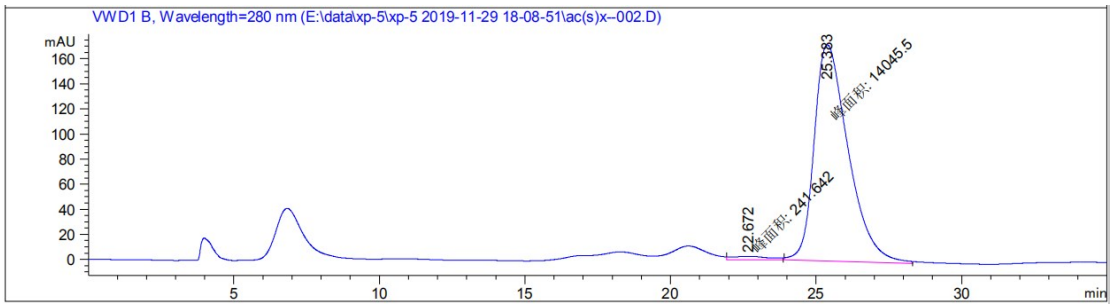


3as, 142 mg, 73% yield, $[\alpha]_D^{20}$ –9.0 (*c* 1.0, $CHCl_3$). Analytical data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.18 (d, *J* = 7.3 Hz, 1H), 4.62 (d, *J* = 6.7 Hz, 1H), 3.79 (s, 2H), 3.76 (s, 3H), 3.64 (s, 3H), 3.25 (d, *J* = 5.5 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 171.0, 155.2, 135.7, 128.3, 128.2, 122.1, 119.7, 118.6, 110.8, 107.7, 79.8, 54.2, 52.4, 52.3, 31.5, 28.3, 27.2; HRMS (ESI) calcd for $C_{20}H_{26}N_2O_6Na$ $[M + Na]^+$: 413.1683, Found: 413.1686; The product was purified as an orange oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

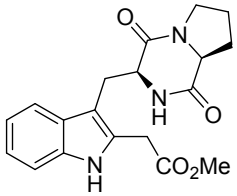
Conditions: HPLC (Daicel ChiralPak AD-H column, 25 ºC, 90:10 hexane/*i*PrOH, flow rate: 0.80 mL/min, λ = 280 nm)



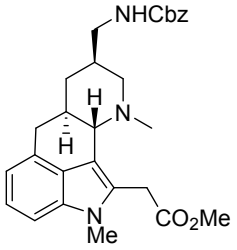
No.	RT	Area	Height	% Area
1	23.997	3.86584e4	461.02029	49.3548
2	27.063	3.96692e4	360.43457	50.6452



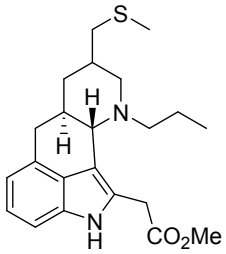
No.	RT	Area	Height	% Area
1	22.672	241.64189	2.61686	1.6913
2	25.383	1.40455e4	172.42592	98.3087



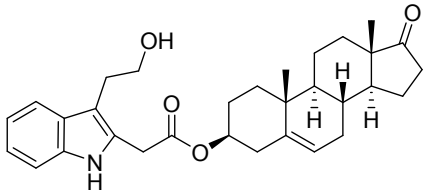
3at, 94 mg, 53% yield, $[\alpha]_D^{20}$ -58.7 (*c* 1.0, $CHCl_3$). Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 - 7.20 (m, 1H), 7.13 - 7.11 (m, 1H), 6.10 (s, 1H), 4.43 (dd, *J* = 11.0, 2.6 Hz, 1H), 4.07 (t, *J* = 7.6 Hz, 1H), 3.86 (d, *J* = 16.2 Hz, 1H), 3.78 - 3.73 (m, 5H), 3.69 - 3.64 (m, 1H), 3.61 - 3.57 (m, 1H), 2.94 - 2.89 (dd, *J* = 15.0, 11.4p Hz, 1H), 2.35 - 2.29 (m, 1H), 2.09 - 1.99 (m, 2H), 1.94 - 1.86 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 169.5, 165.8, 136.0, 128.7, 127.3, 122.8, 120.2, 118.3, 111.2, 107.8, 59.3, 54.7, 52.7, 45.5, 31.9, 28.3, 25.6, 22.7; HRMS (ESI) calcd for $C_{19}H_{21}N_3O_4Na$ $[M + Na]^+$: 378.1424, Found: 378.1423; The product was purified as a pale yellow oil by silica gel column chromatography with acetone/dichloromethane = 1 : 4.



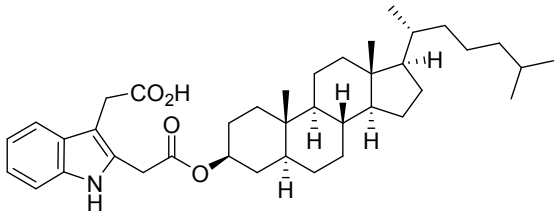
3au, 159 mg, 67% yield, $[\alpha]_D^{20}$ -52.5 (*c* 1.0, $CHCl_3$). Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 - 7.35 (m, 4H), 7.34 - 7.30 (m, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 6.9 Hz, 1H), 5.25 (br, 1H), 5.14 (dd, *J* = 27.2, 12.2 Hz, 2H), 3.76 (d, *J* = 8.3 Hz, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 3.56 - 3.54 (m, 1H), 3.43 - 3.41 (m, 1H), 3.37 - 3.34 (m, 1H), 3.28 - 3.17 (m, 3H), 2.76 (s, 3H), 2.70 - 2.64 (m, 3H), 2.47 - 2.43 (m, 1H), 1.28 - 1.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 156.9, 136.4, 134.8, 128.6, 128.2, 128.1, 126.2, 125.0, 122.8, 113.2, 107.5, 107.2, 67.6, 67.0, 60.2, 52.4, 44.1, 41.7, 38.4, 35.0, 30.9, 30.8, 30.1, 30.0, 24.7; HRMS (ESI) calcd for $C_{28}H_{34}N_3O_4$ $[M + H]^+$: 476.2544, Found: 476.2543; The product was purified as a brown oil by silica gel column chromatography with acetone/dichloromethane = 1 : 1.



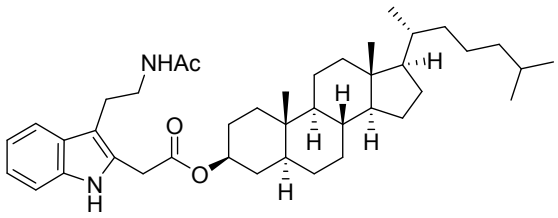
3av, 183 mg, 95% yield, Mp = 196 - 198 °C, $[\alpha]_D^{20}$ –19.0 (*c* 1.0, $CHCl_3$); Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 6.7 Hz, 1H), 3.77 - 3.66 (m, 7H), 3.37 (t, *J* = 12.5 Hz, 1H), 3.21 (s, 3H), 3.03 - 3.01 (m, 2H), 2.76 (d, *J* = 12.5 Hz, 1H), 2.63 - 2.60 (m, 2H), 2.43 - 2.40 (m, 1H), 2.16 (s, 3H), 1.91 - 1.85 (m, 1H), 1.70 (br, 1H), 1.32 - 1.26 (m, 1H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 133.0, 128.8, 125.6, 124.3, 123.0, 113.5, 109.4, 105.9, 65.1, 56.7, 54.7, 52.4, 38.0, 37.7, 32.3, 31.8, 31.7, 23.5, 16.1, 15.5, 11.3; HRMS (ESI) calcd for $C_{22}H_{31}N_2O_2S$ $[M + H]^+$: 387.2101, Found: 387.2104; The product was purified as a yellow solid by silica gel column chromatography with acetone/petroleum ether = 1.5 : 1.



3aw, 135 mg, 55% yield, $[\alpha]_D^{20}$ +10.2 (*c* 1.0, $CHCl_3$). Analytical data:^1H NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.40 (d, *J* = 4.9 Hz, 1H), 4.68 - 4.63 (m, 1H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.81 (s, 2H), 3.00 (t, *J* = 6.0 Hz, 2H), 2.48 - 2.44 (m, 1H), 2.37 - 2.32 (m, 2H), 2.12 - 2.07 (m, 2H), 1.97 - 1.92 (m, 1H), 1.89 - 1.83 (m, 3H), 1.67 - 1.61 (m, 4H), 1.57 - 1.44 (m, 2H), 1.31 - 1.25 (m, 3H), 1.16 - 1.12 (m, 1H), 1.04 (s, 3H), 1.02 - 0.99 (m, 1H), 0.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.0, 170.3, 139.6, 135.9, 128.3, 128.0, 122.2, 122.1, 119.6, 118.4, 110.9, 109.8, 75.1, 62.7, 51.7, 50.1, 47.5, 37.9, 36.9, 36.7, 35.8, 32.3, 31.4, 31.3, 30.8, 27.7, 27.6, 21.9, 20.3, 19.3, 13.6; HRMS (ESI) calcd for $C_{31}H_{39}NO_4Na$ $[M + Na]^+$: 512.2771, Found: 512.2771; The product was purified as a pale yellow oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 1.5.

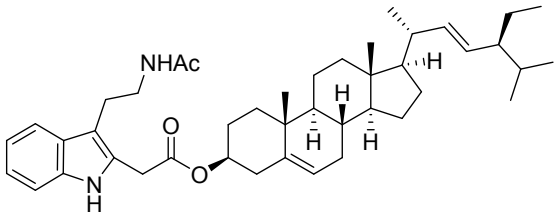


3ax, 232 mg, 77% yield, $[\alpha]_D^{20}$ -38.2 (*c* 1.0, $CHCl_3$). Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 - 7.15 (m, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 4.77 - 4.71 (m, 1H), 3.79 (s, 2H), 3.73 (s, 2H), 1.98 - 1.96 (m, 1H), 1.85 - 1.80 (m, 2H), 1.74 - 1.71 (m, 1H), 1.66 - 1.64 (m, 1H), 1.60 - 1.50 (m, 5H), 1.49 - 1.46 (m, 1H), 1.37 - 1.33 (m, 6H), 1.26 - 1.23 (m, 4H), 1.14 - 1.07 (m, 6H), 1.00 - 0.98 (m, 4H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 2.7 Hz, 3H), 0.89 (d, *J* = 2.7 Hz, 3H), 0.81 (s, 3H), 0.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 170.2, 135.4, 128.7, 127.8, 122.1, 119.9, 118.4, 110.9, 105.3, 75.4, 56.4, 56.3, 54.2, 44.7, 42.6, 40.0, 39.5, 36.7, 36.2, 35.8, 35.5, 35.5, 33.9, 32.1, 32.0, 30.0, 28.6, 28.2, 28.0, 27.4, 24.2, 23.9, 22.8, 22.6, 21.2, 18.7, 12.2, 12.1; HRMS (ESI) calcd for $C_{39}H_{57}NO_4Na$ $[M + Na]^+$: 626.4180, Found: 626.4183; The product was purified as a brown oil by silica gel column chromatography with ethyl acetate/petroleum ether = 1 : 4.

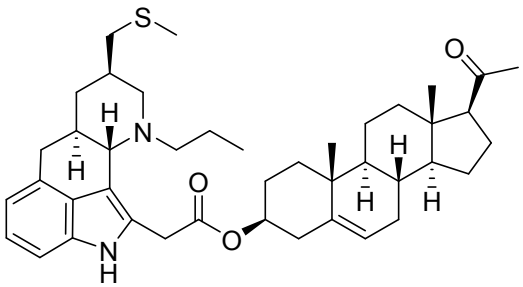


3ay, 227 mg, 72% yield, $[\alpha]_D^{20}$ -33.6 (*c* 1.0, $CHCl_3$). Analytical data:^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.01 (br, 1H), 4.77-4.72 (m, 1H), 3.75 (s, 2H), 3.56-3.55 (m, 2H), 2.94 (t, *J* = 6.1 Hz, 2H), 1.97-1.95 (m, 1H), 1.91 (s, 3H), 1.83-1.79 (m, 2H), 1.76-1.74 (m, 1H), 1.67-1.64 (m, 1H), 1.61-1.56 (m, 1H), 1.54-1.46 (m, 5H), 1.42-1.40 (m, 1H), 1.35-1.31 (m, 4H), 1.27-1.24 (m, 4H), 1.14-1.06 (m, 7H), 1.05-0.97 (m, 4H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 2.6 Hz, 3H), 0.86 (d, *J* = 2.6 Hz, 3H), 0.83 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 170.4, 135.8, 127.9, 127.8, 122.2, 119.7, 118.4, 110.9, 110.6, 75.4, 56.4, 56.3, 54.2, 44.7, 42.6, 40.0, 39.9, 39.5, 36.7, 36.2, 35.8, 35.5, 34.0, 32.2, 32.0, 28.6, 28.2, 28.0, 27.5, 24.2, 24.0, 23.8, 23.1, 22.8, 22.6, 21.2, 18.7, 12.2, 12.1; HRMS (ESI) calcd for $C_{41}H_{62}N_2O_3Na$ $[M + Na]^+$: 653.4653, Found: 653.4656; The

product was purified as a brown oil by silica gel column chromatography with ethyl acetate/petroleum ether = 2 : 1.



3az, 223 mg, 68% yield, $[\alpha]_D^{20}$ -22.3 (*c* 1.0, $CHCl_3$). Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.02 (br, 1H), 5.37 - 5.37 (m, 1H), 5.17 - 5.13 (m, 1H), 5.04 - 5.00 (m, 1H), 4.67 - 4.64 (m, 1H), 3.77 (s, 2H), 3.37 - 3.54 (m, 2H), 2.95 (t, *J* = 6.2 Hz, 2H), 2.37 - 2.32 (m, 2H), 2.05 - 2.02 (m, 1H), 2.00 - 1.96 (m, 2H), 1.91 (s, 3H), 1.90 - 1.87 (m, 3H), 1.72 - 1.62 (m, 2H), 1.55 - 1.51 (m, 4H), 1.47 - 1.40 (m, 3H), 1.27 - 1.23 (m, 2H), 1.19 - 1.12 (m, 4H), 1.03 - 1.01 (m, 6H), 1.00 - 0.91 (m, 2H), 0.85 (d, *J* = 6.1 Hz, 3H), 0.82 - 0.79 (m, 6H), 0.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 170.4, 139.2, 138.3, 135.8, 129.4, 127.9, 127.8, 123.1, 122.2, 119.7, 118.4, 110.9, 110.6, 75.6, 56.8, 56.0, 51.2, 50.0, 42.2, 40.5, 39.9, 39.6, 38.1, 36.9, 36.6, 32.1, 31.9, 31.9, 28.9, 27.8, 25.4, 24.3, 23.9, 23.0, 21.2, 21.1, 21.0, 19.3, 19.0, 12.2, 12.1; HRMS (ESI) calcd for $C_{43}H_{62}N_2O_3Na$ $[M + Na]^+$: 677.4653, Found: 677.4655; The product was purified as a pule yellow oil by silica gel column chromatography with ethyl acetate /petroleum = 2 : 1.

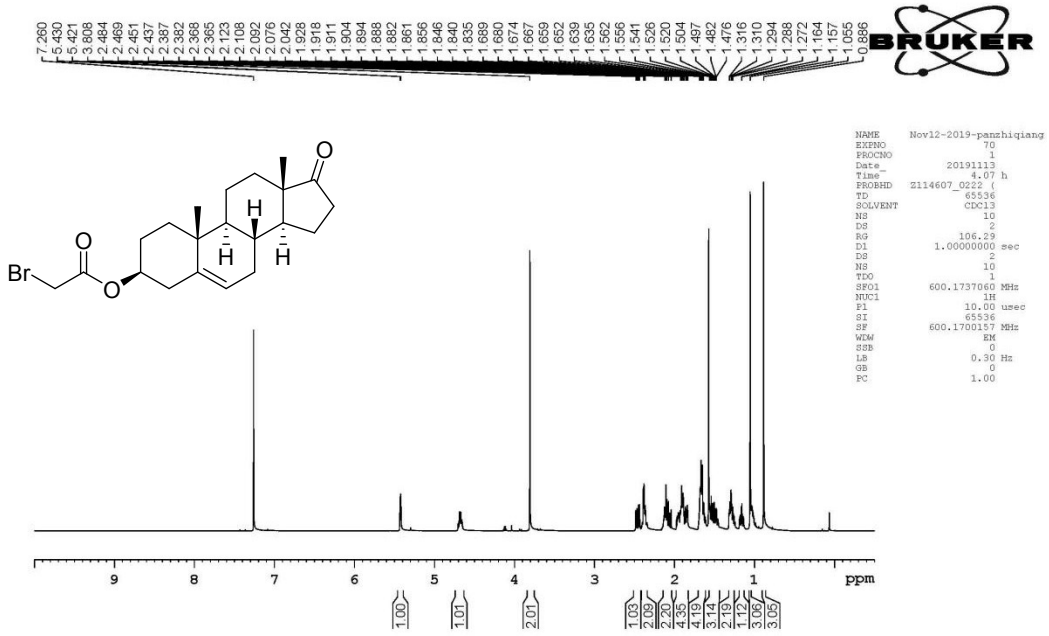


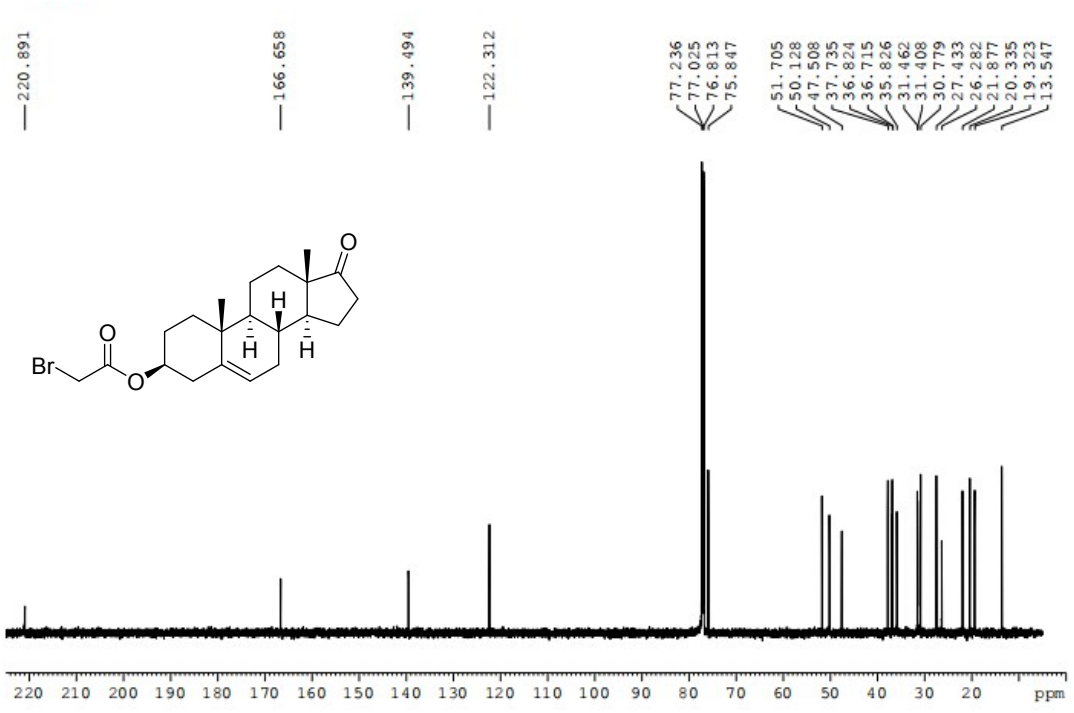
3ba, 225 mg, 67% yield, $[\alpha]_D^{20}$ -10.1 (*c* 1.0, $CHCl_3$). Analytical data: ^1H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.14 - 7.12 (m, 2H), 6.92 (d, *J* = 6.5 Hz, 1H), 5.38 (d, *J* = 4.6 Hz, 1H), 4.69 - 4.64 (m, 1H), 3.76 (s, 2H), 3.30 - 3.24 (m, 2H), 3.00 (s, 1H), 2.88 (s, 1H), 2.81 (d, *J* = 12.5 Hz, 2H), 2.67 (s, 1H), 2.57 - 2.52 (m, 3H), 2.48 - 2.44 (m, 1H), 2.36 (d, *J* = 7.7 Hz, 2H), 2.15 (s, 3H), 2.12 (s, 3H), 2.06 - 2.04 (m, 3H), 1.90 - 1.87 (m, 2H), 1.70 - 1.67 (m, 2H), 1.64 - 1.55 (m, 6H), 1.51

- 1.42 (m, 4H), 1.25 - 1.20 (m, 2H), 1.17 - 1.13 (m, 3H), 1.02 (s, 3H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.4, 170.0, 139.4, 133.2, 126.6, 123.5, 123.5, 122.8, 122.6, 113.4, 110.0, 108.3, 75.0, 63.9, 63.7, 58.5, 56.8, 55.3, 49.9, 44.0, 40.6, 39.1, 38.8, 38.0, 37.0, 36.6, 34.8, 34.2, 32.4, 31.8, 31.8, 31.5, 27.8, 25.8, 24.5, 22.9, 21.0, 19.3, 17.2, 16.1, 13.2, 12.0; HRMS (ESI) calcd for $C_{42}H_{59}N_2O_3S$ $[M + H]^+$: 671.4241, Found: 671.4246; The product was purified as a yellow oil by silica gel column chromatography with acetone/petroleum ether = 1 : 1.5.

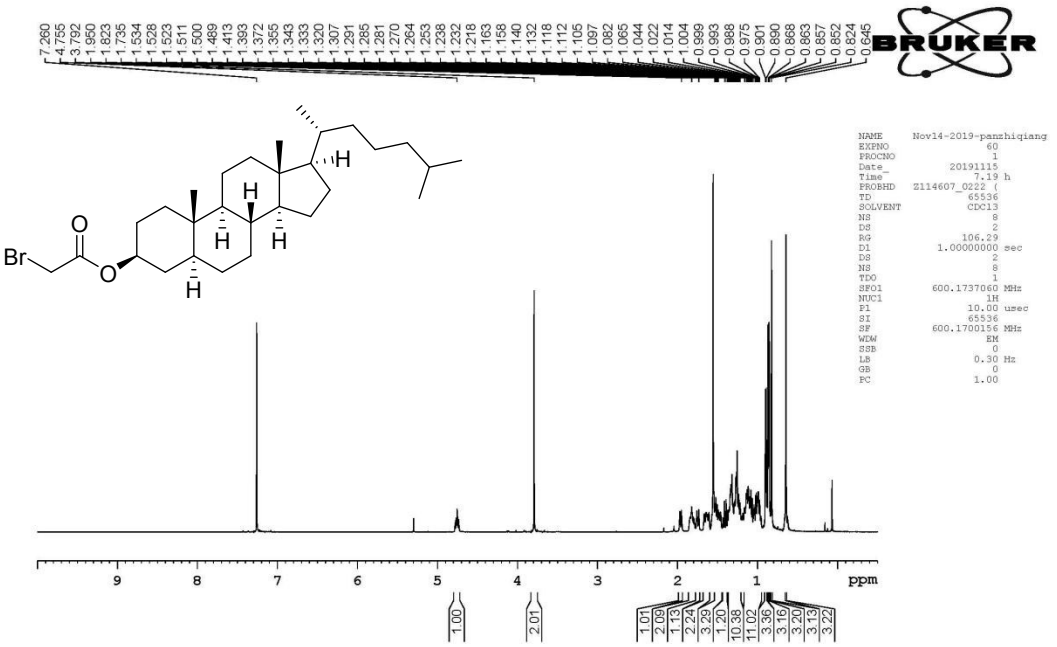
8. Copies of NMR Spectra

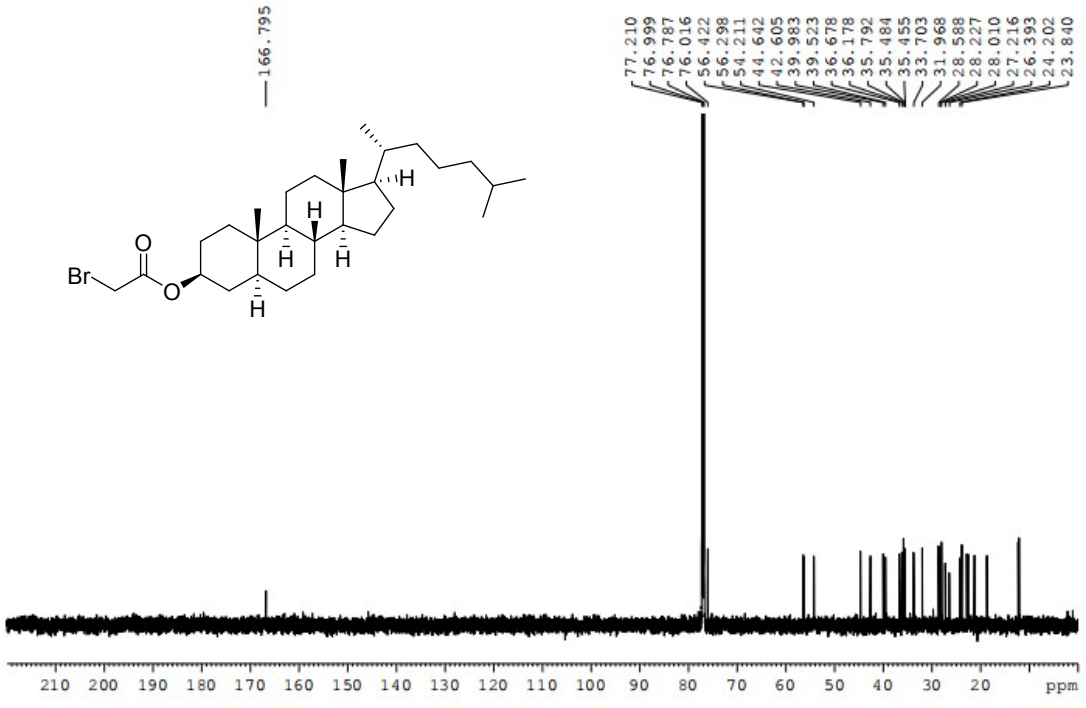
Copies of NMR spectra of **2-S1**



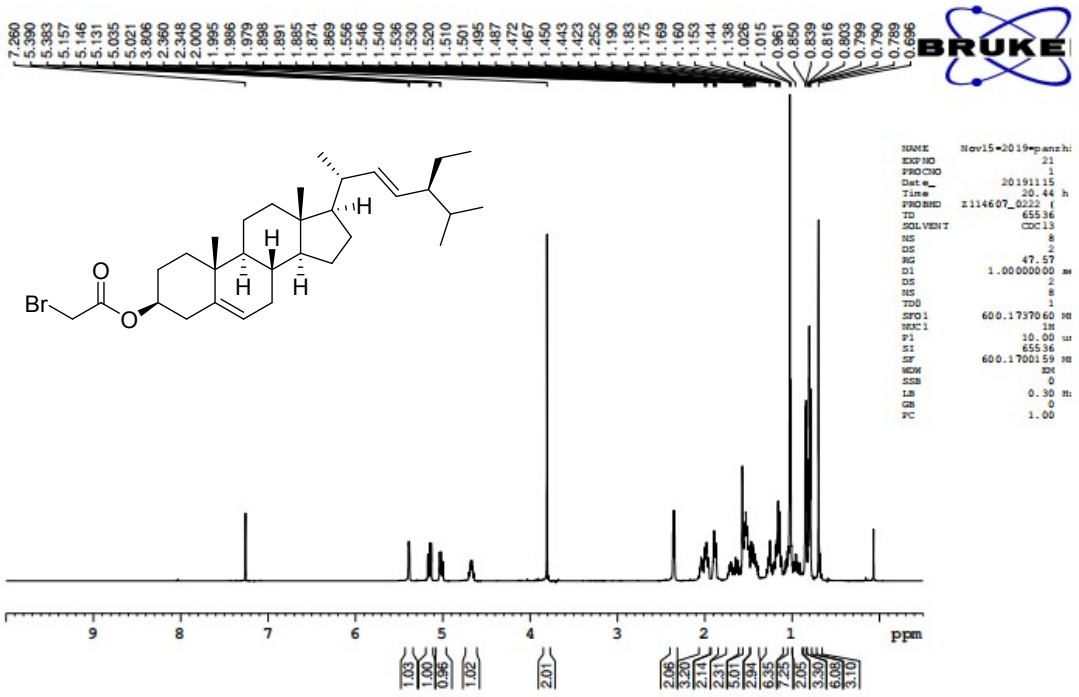


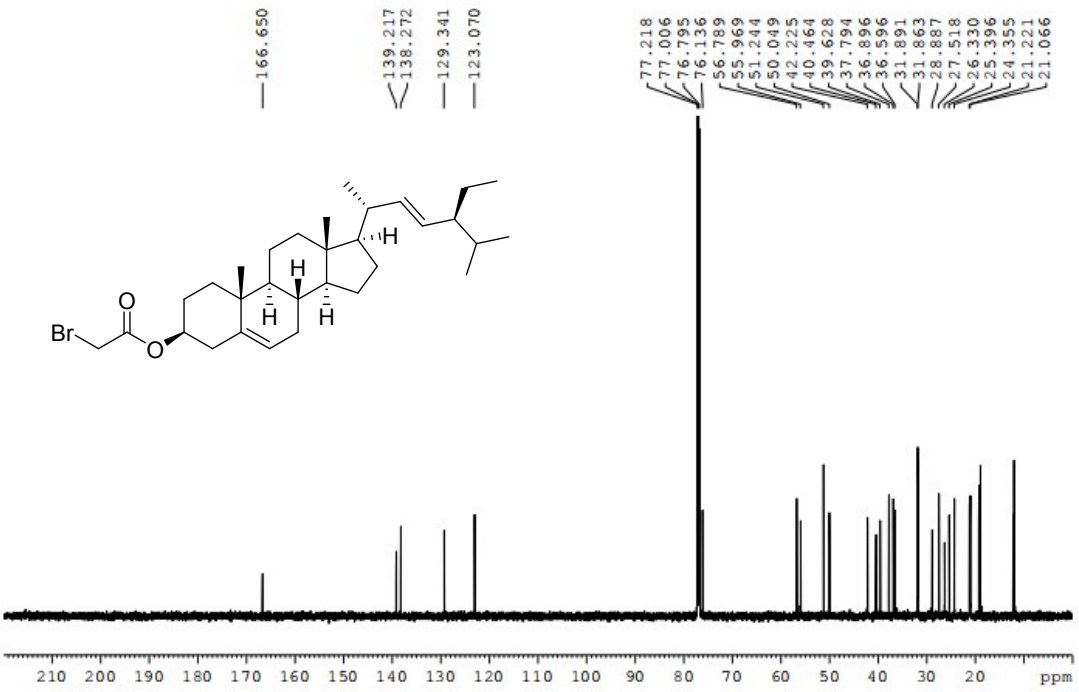
Copies of NMR spectra of **2-S2**



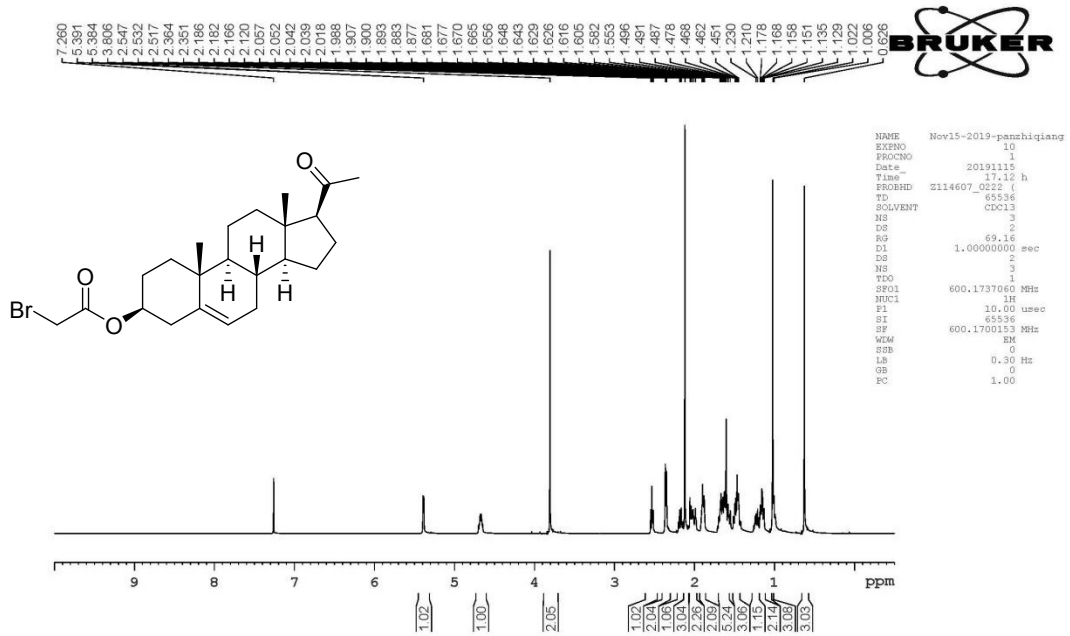


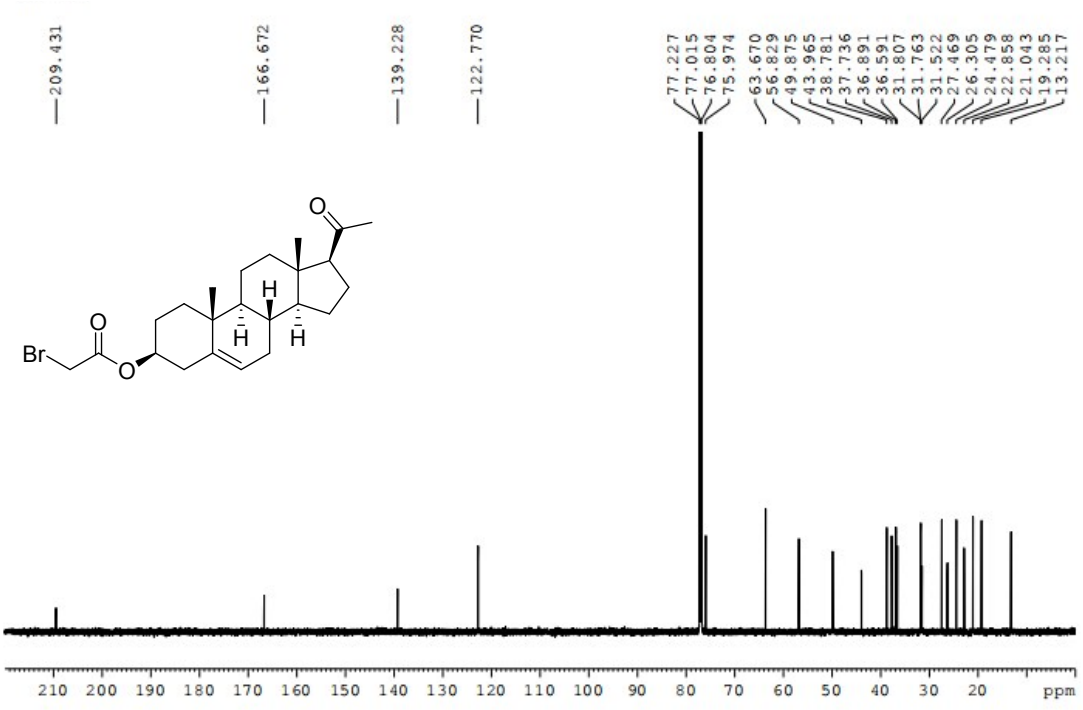
Copies of NMR spectra of **2-S3**



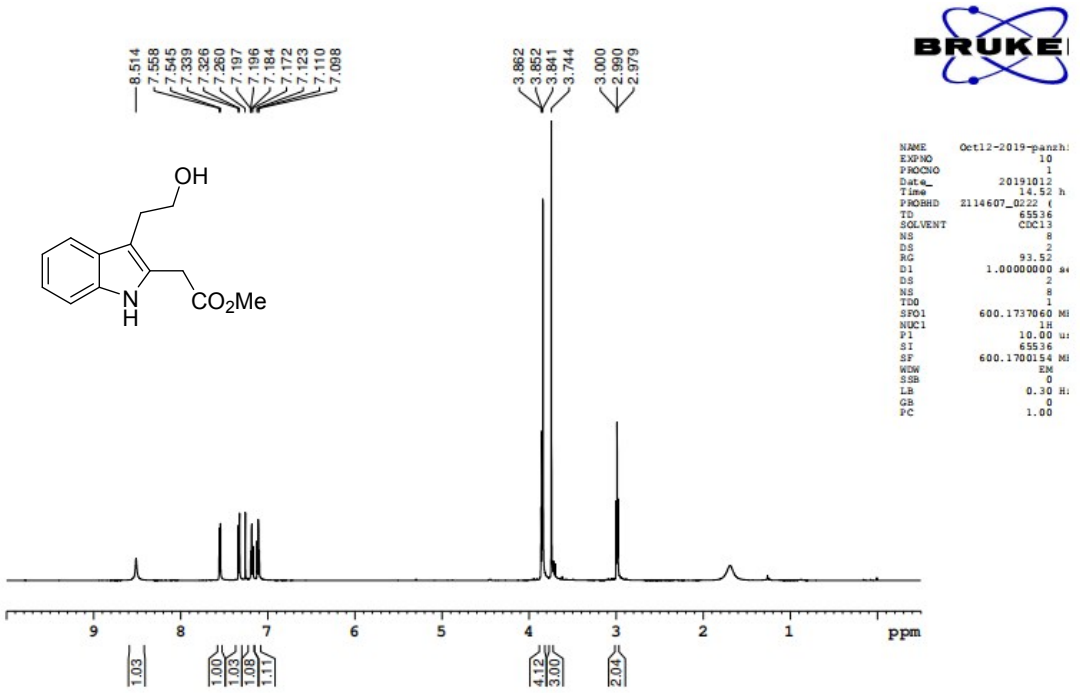


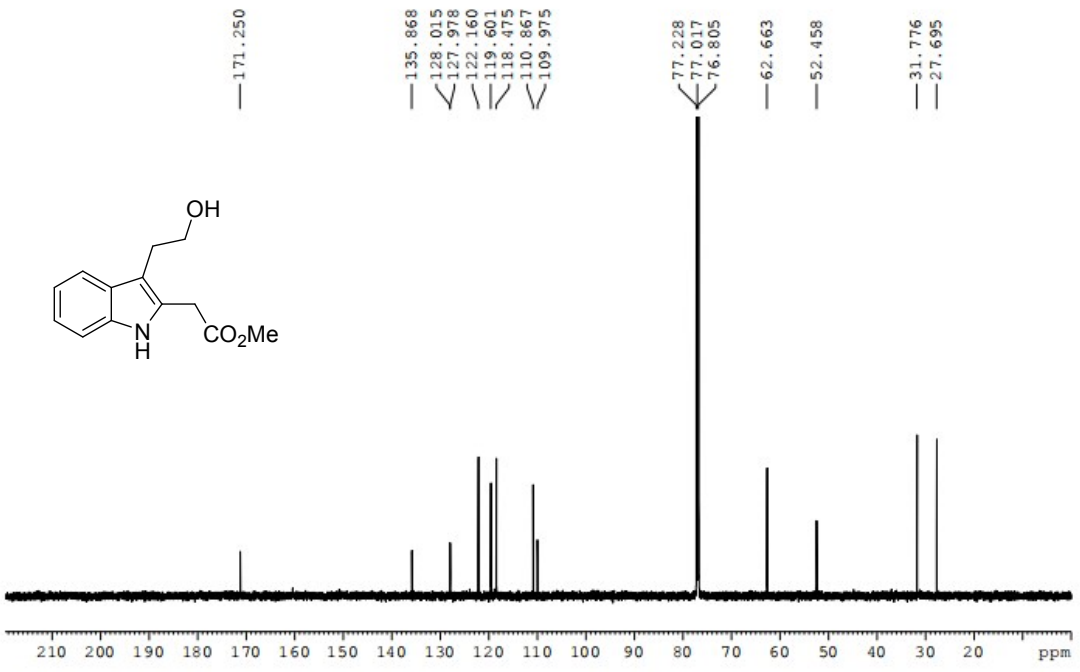
Copies of NMR spectra of **2-S4**



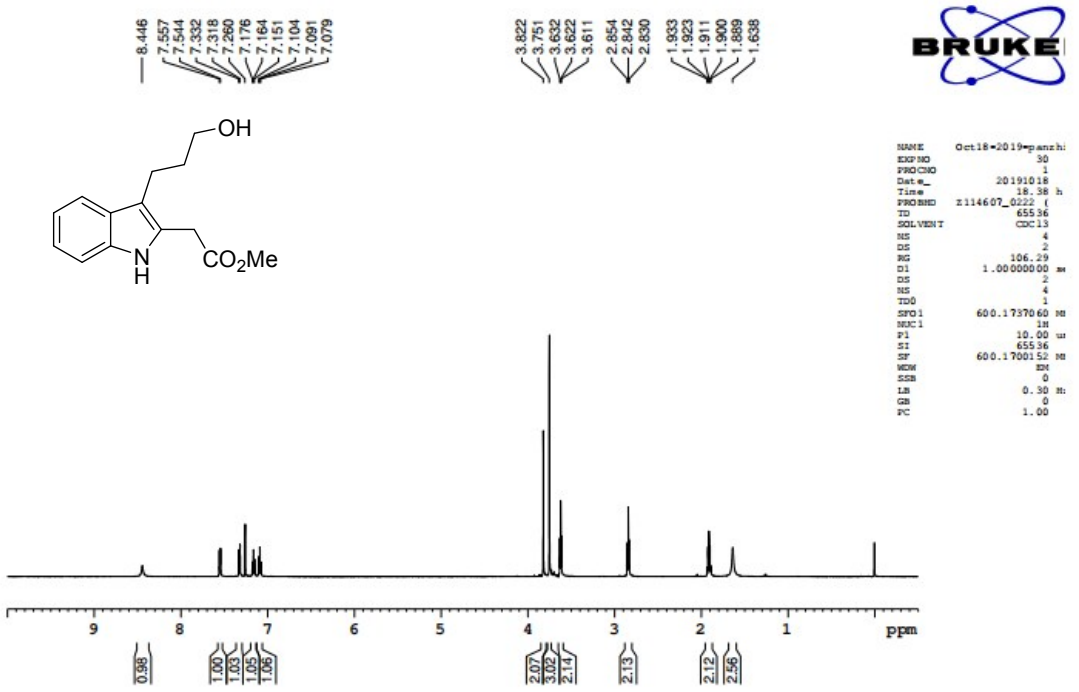


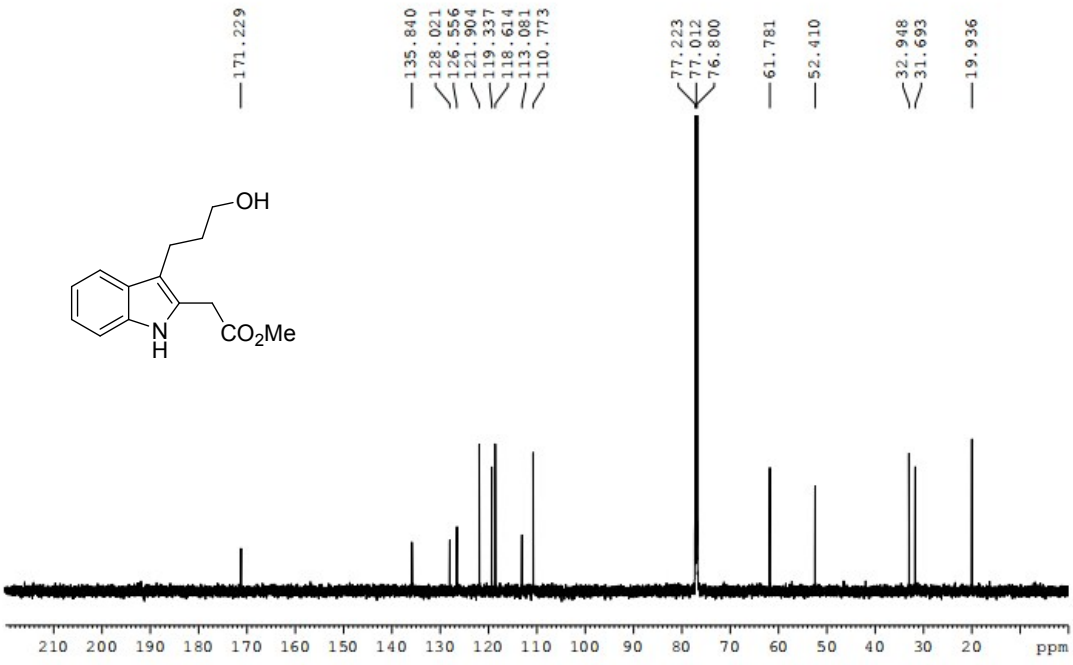
Copies of NMR spectra of **3a**



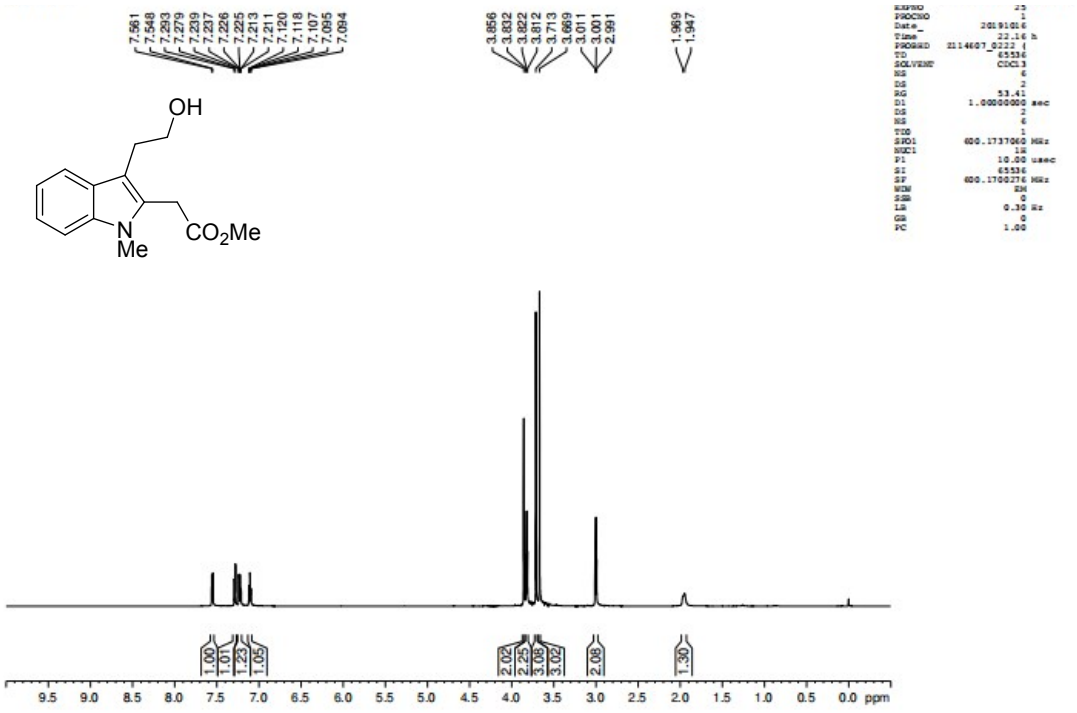


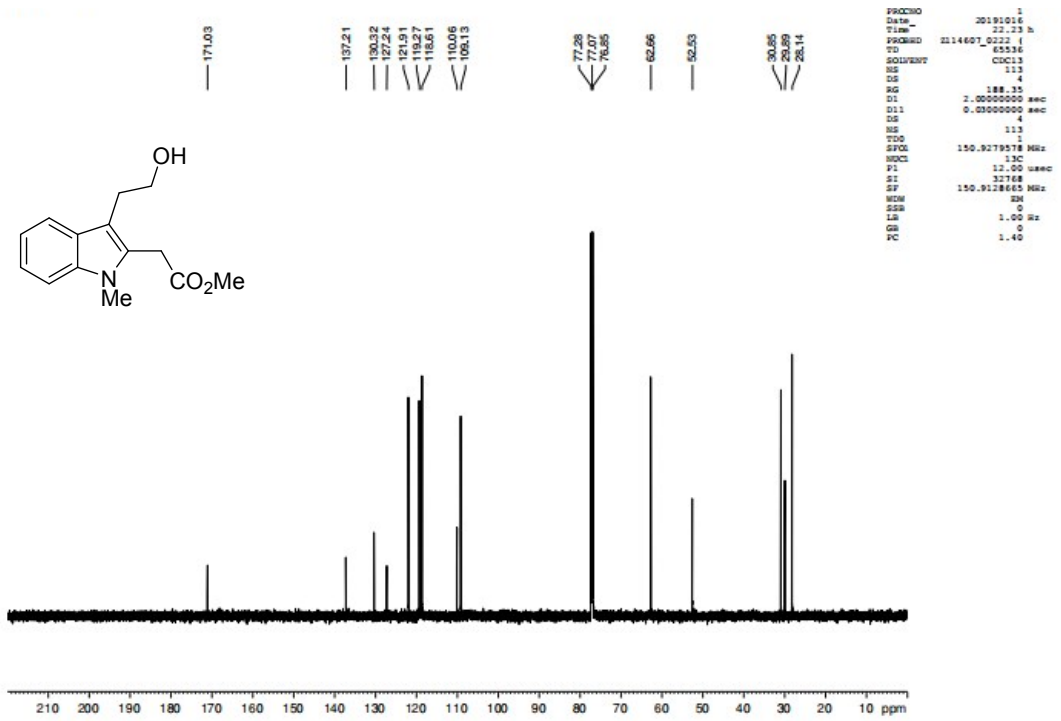
Copies of NMR spectra of **3b**



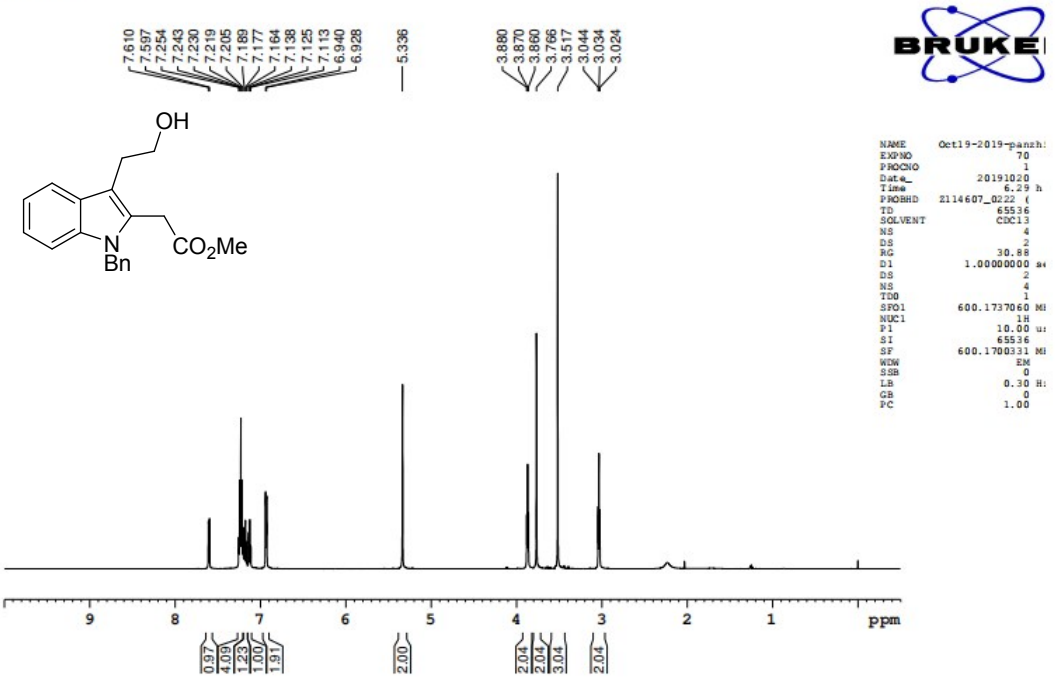


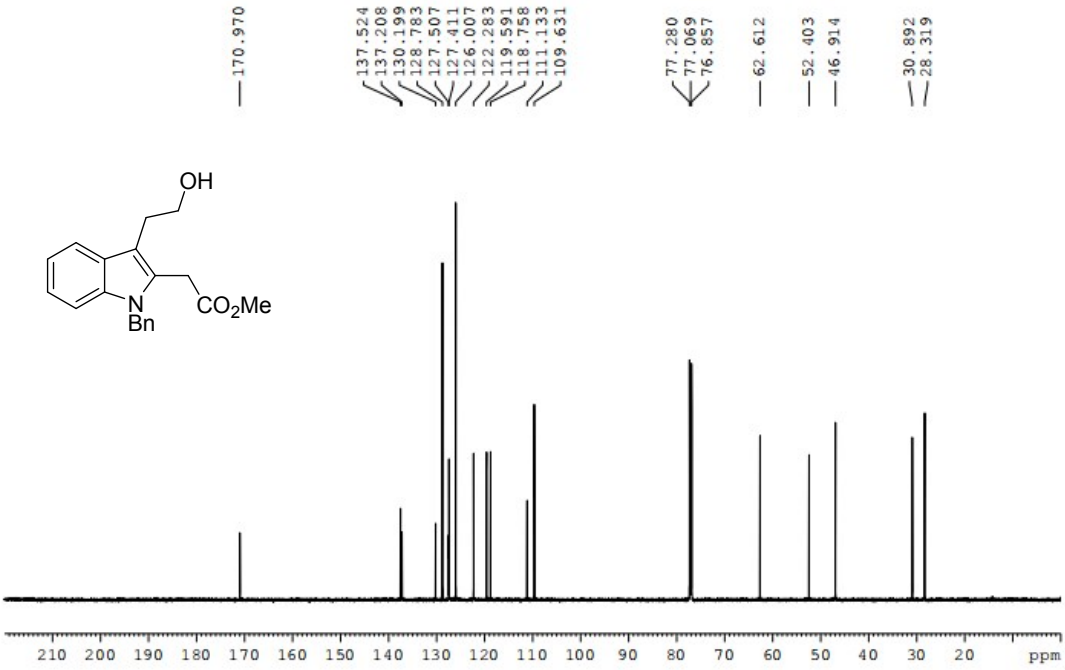
Copies of NMR spectra of **3c**



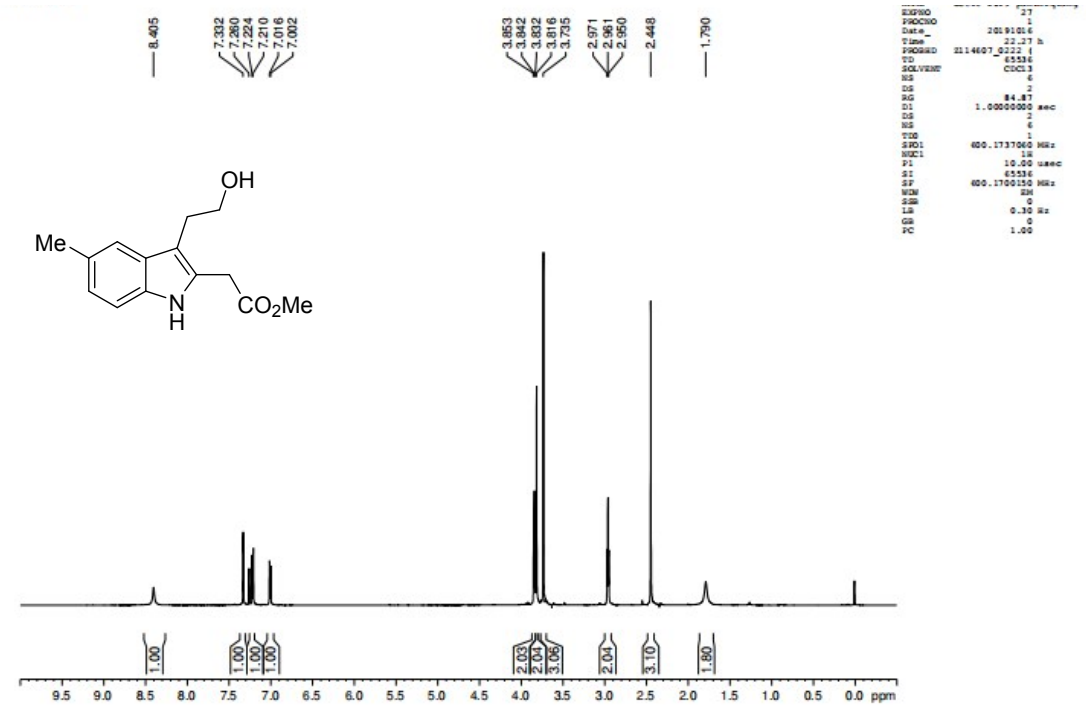


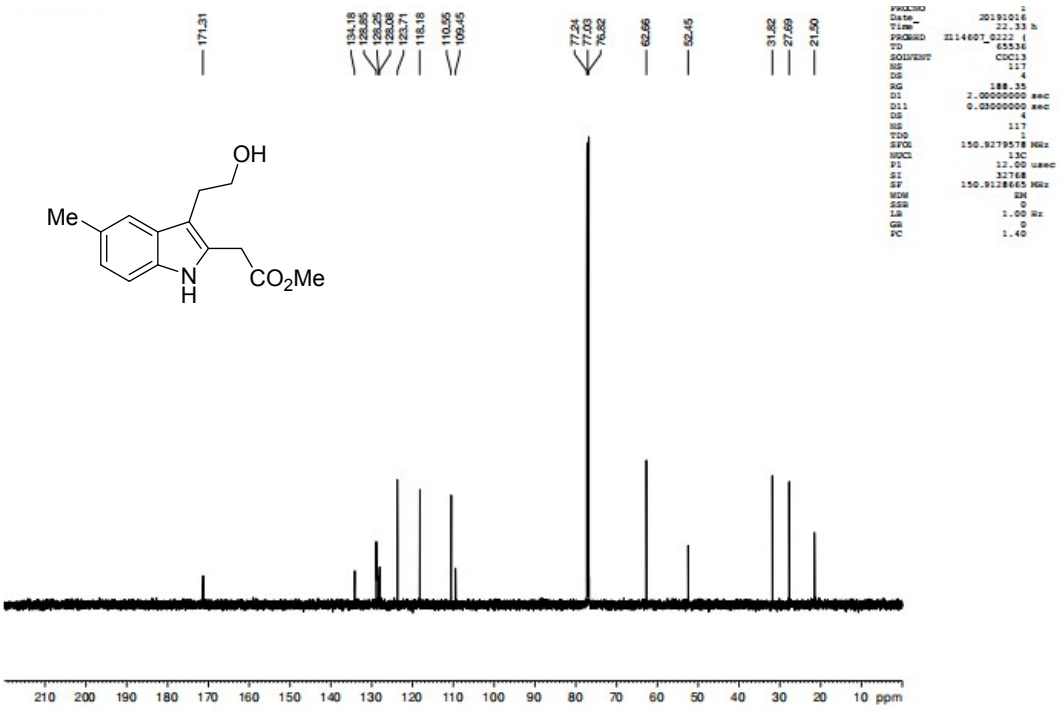
Copies of NMR spectra of **3d**



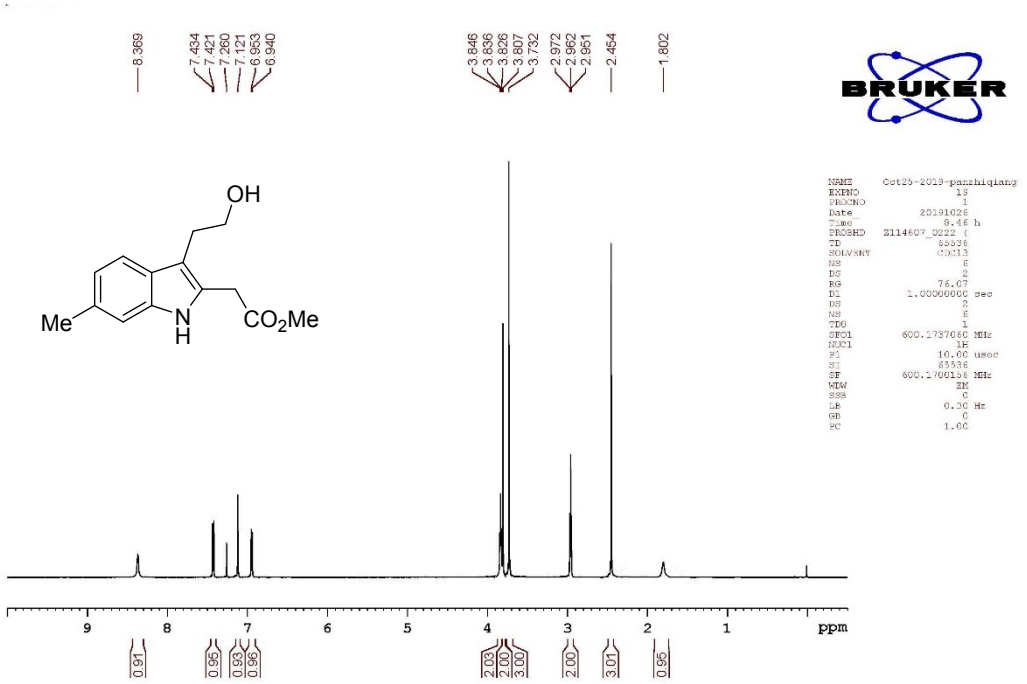


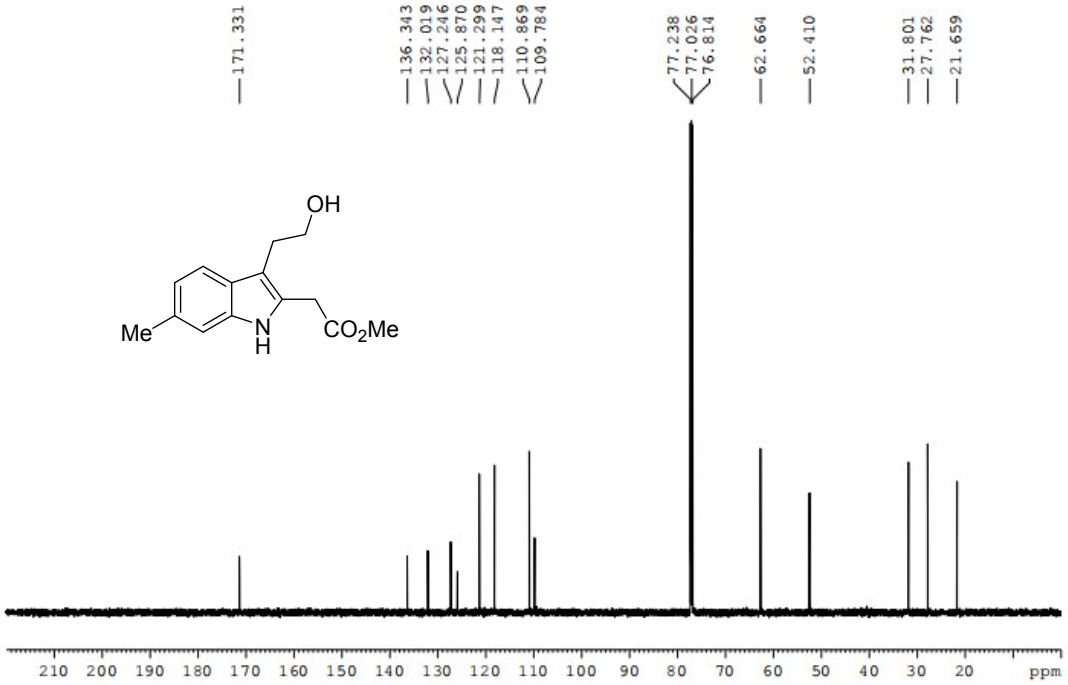
Copies of NMR spectra of **3e**



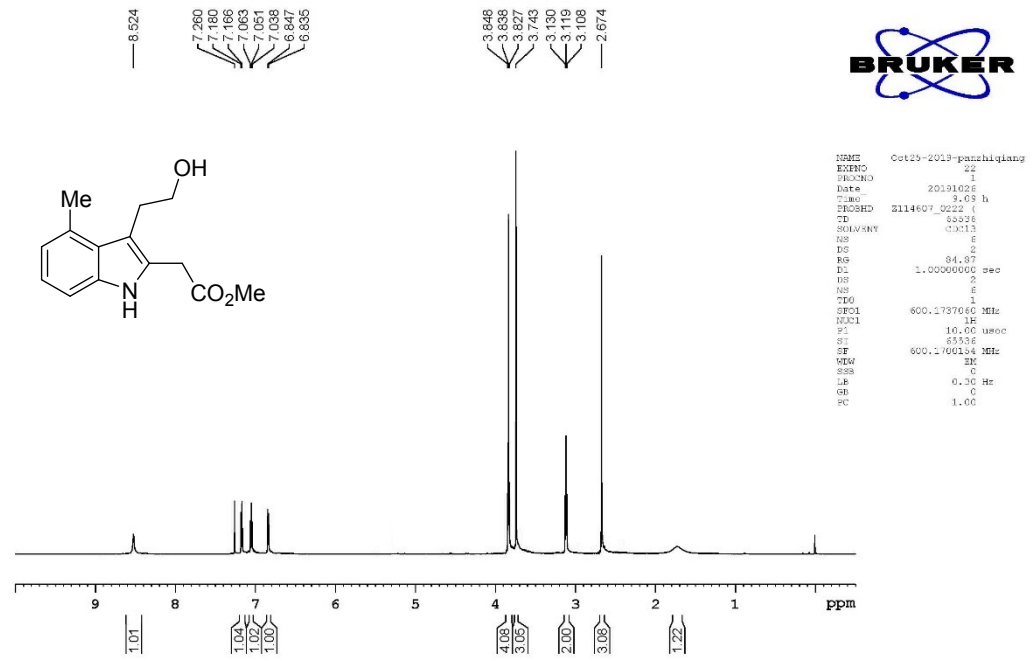


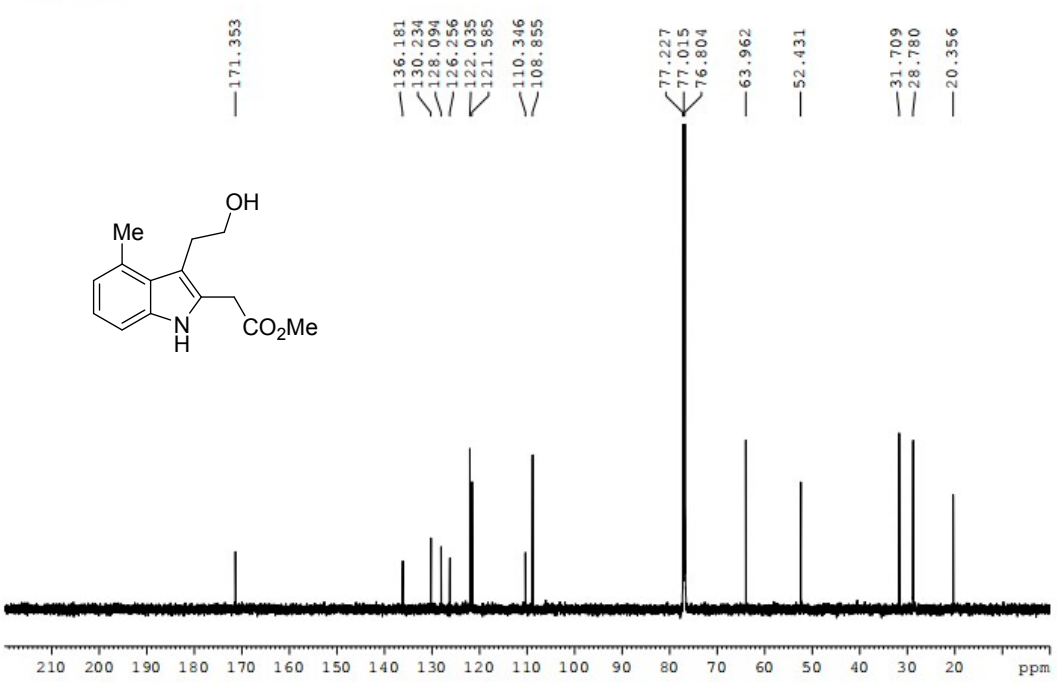
Copies of NMR spectra of **3f**



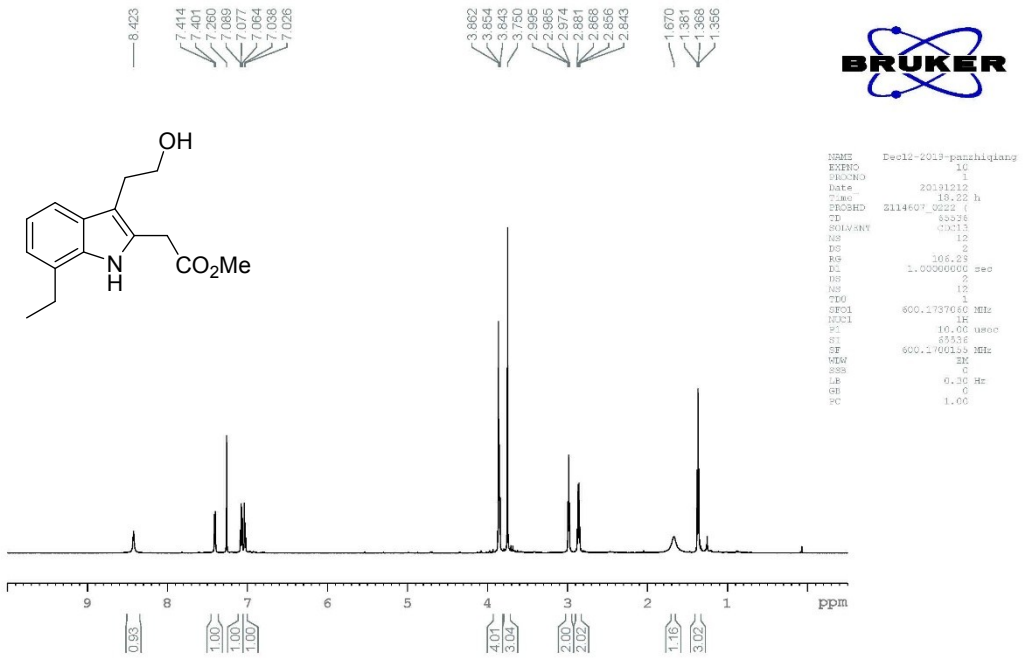


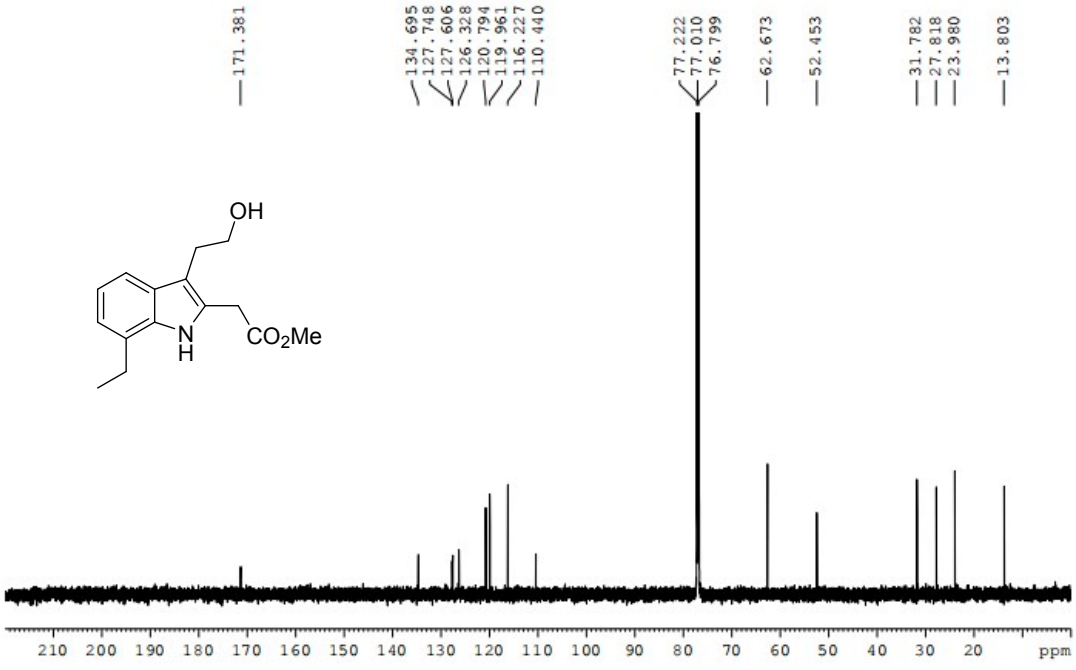
Copies of NMR spectra of **3g**



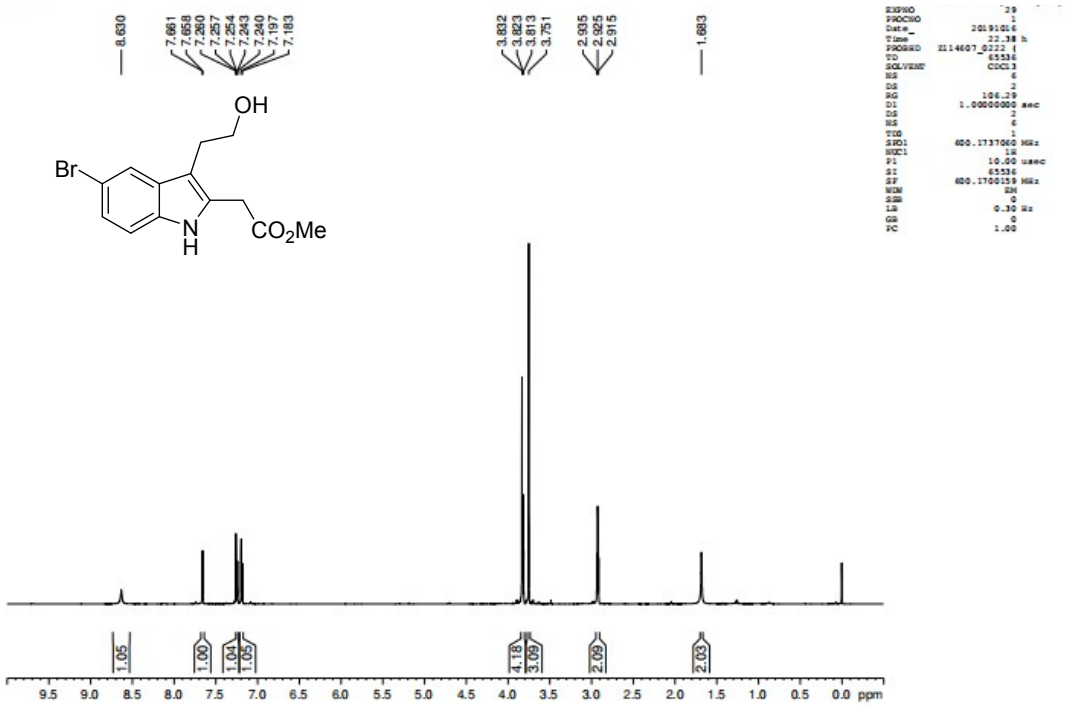


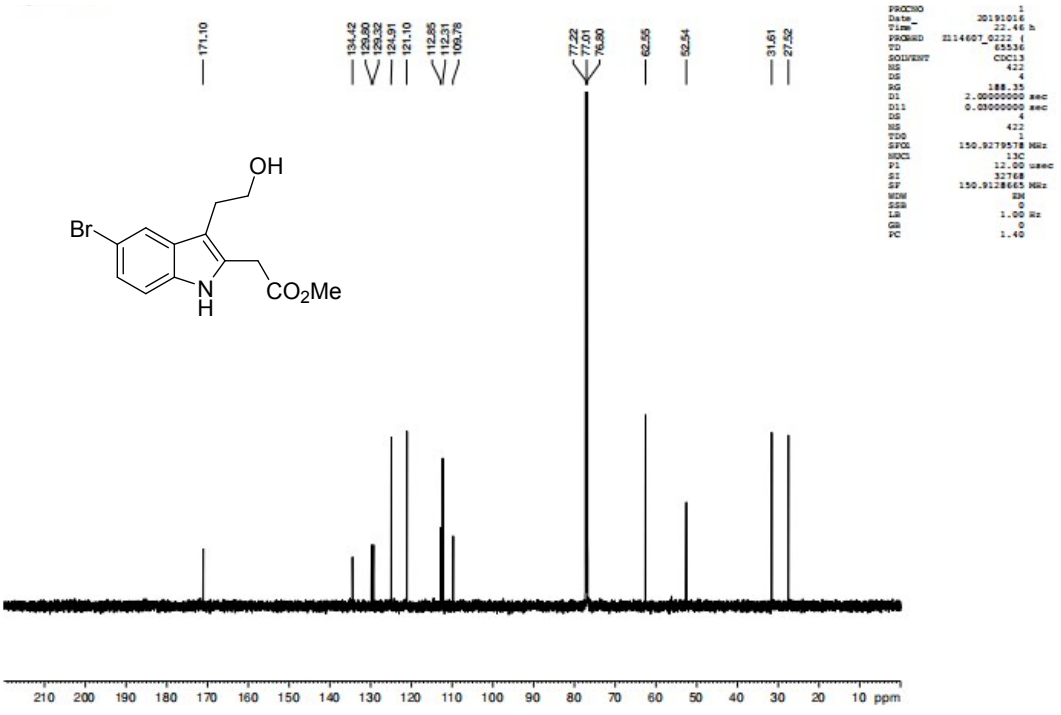
Copies of NMR spectra of **3h**



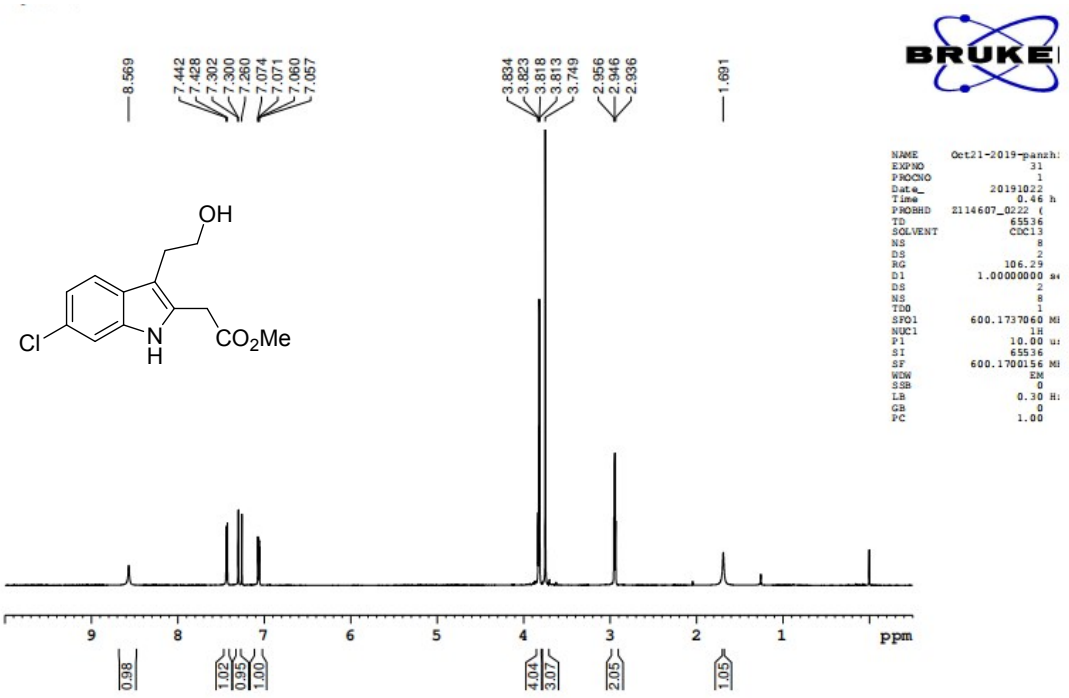


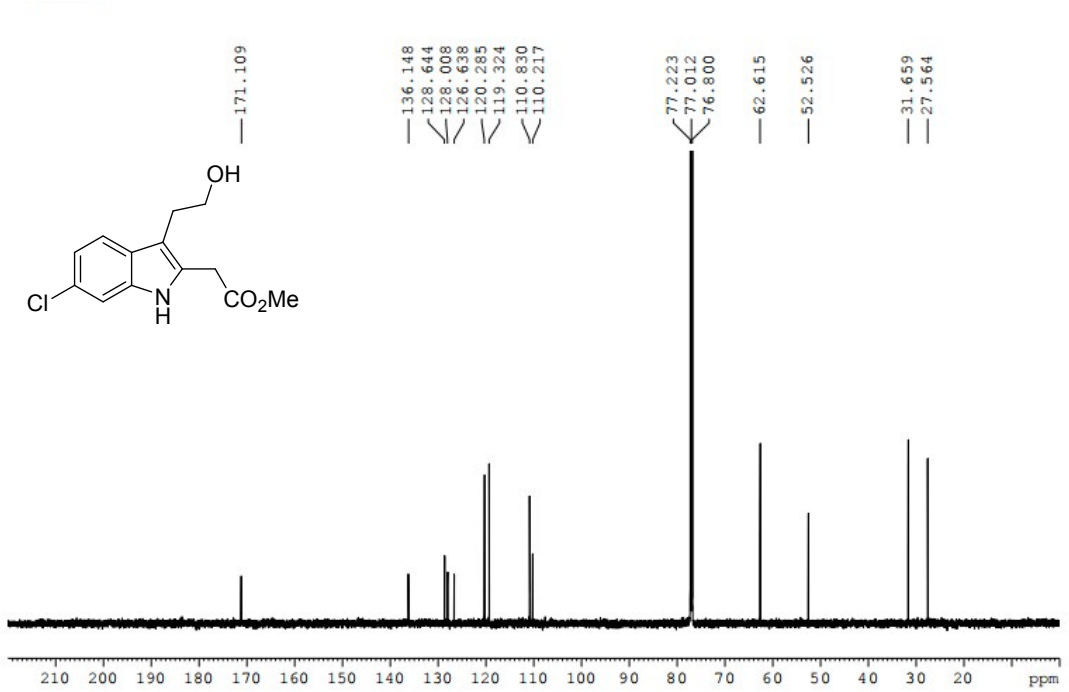
Copies of NMR spectra of **3i**



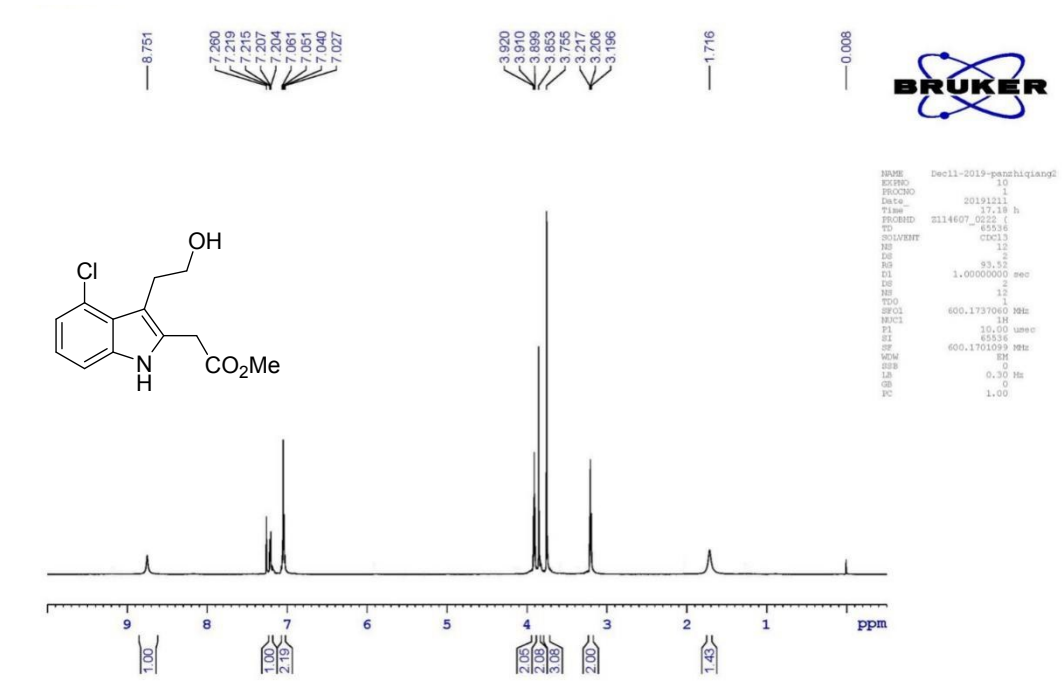


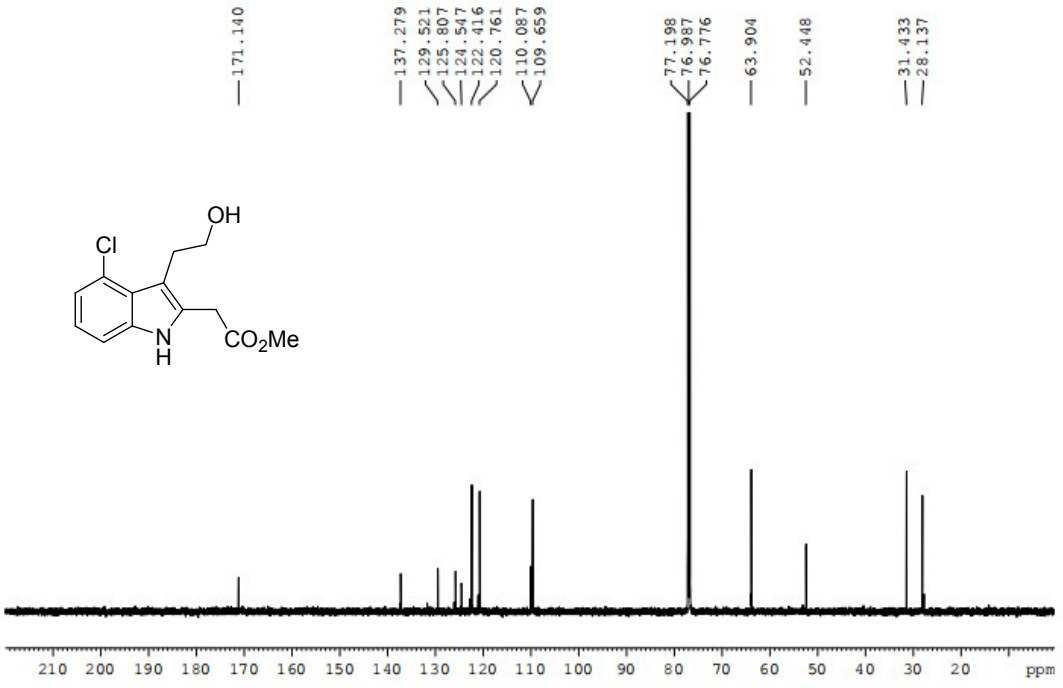
Copies of NMR spectra of **3j**



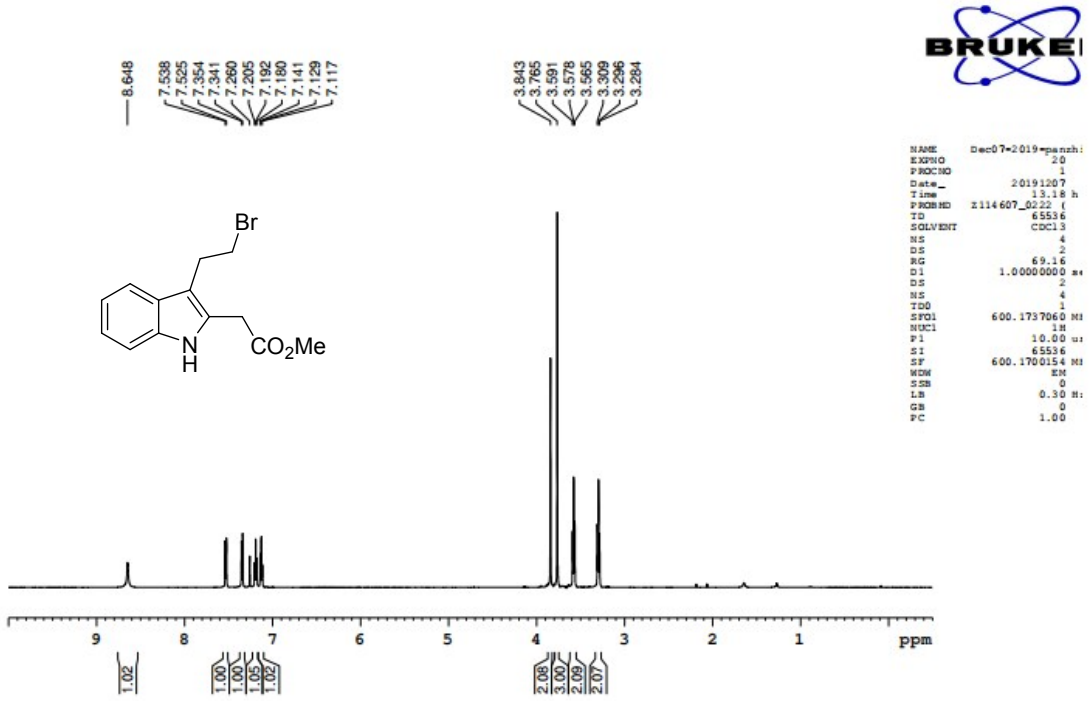


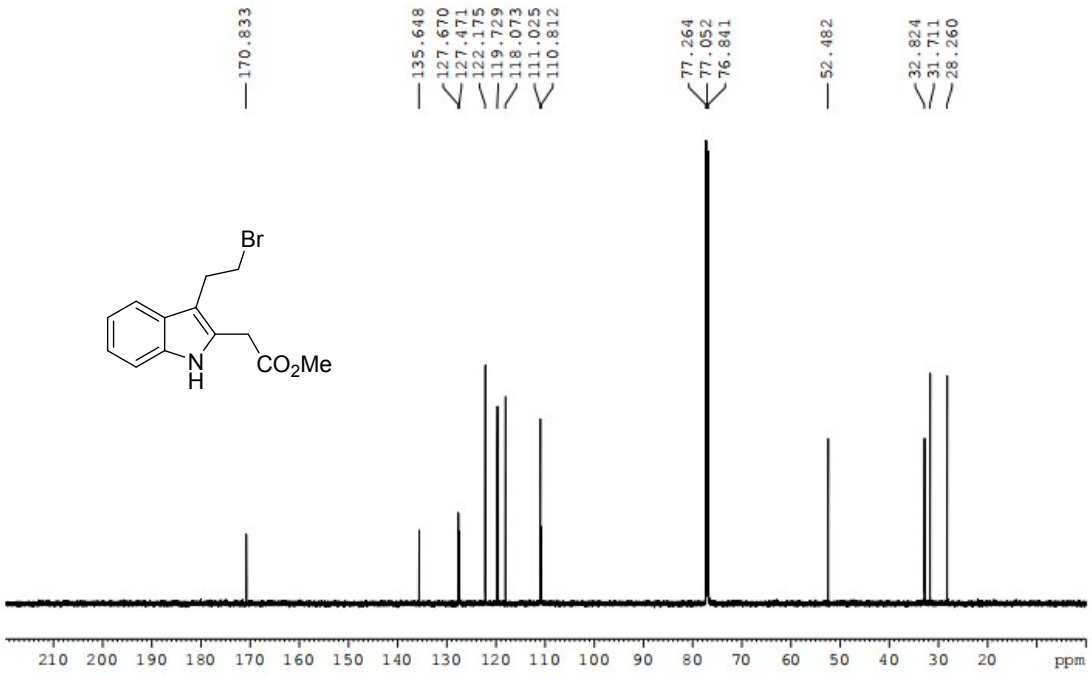
Copies of NMR spectra of **3k**



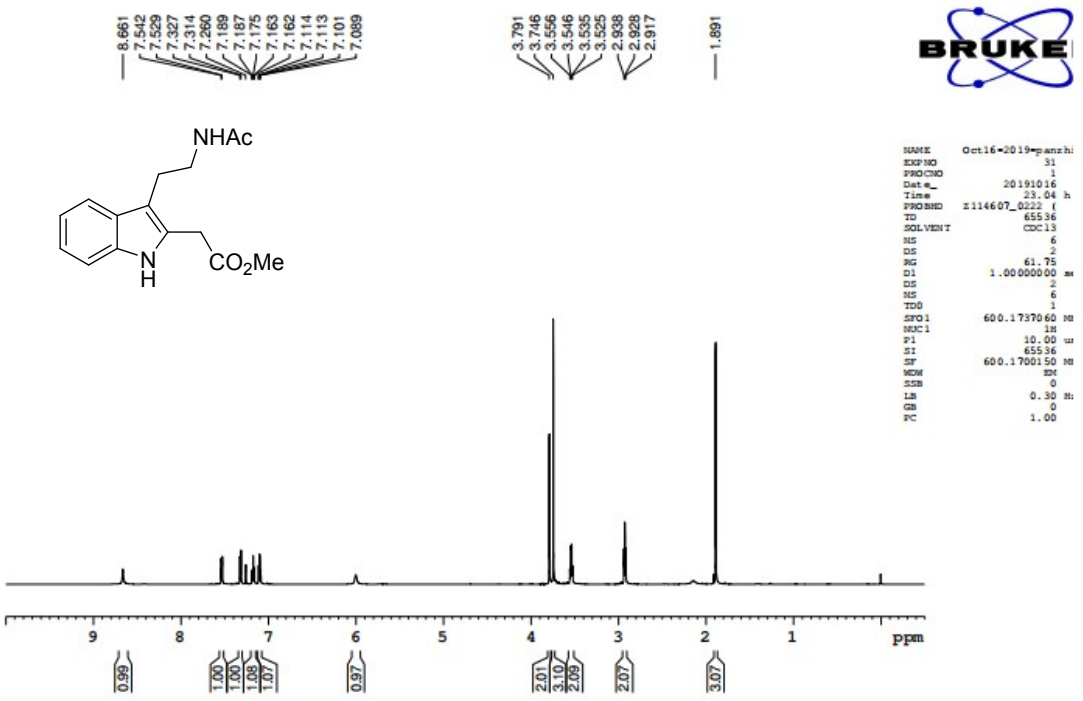


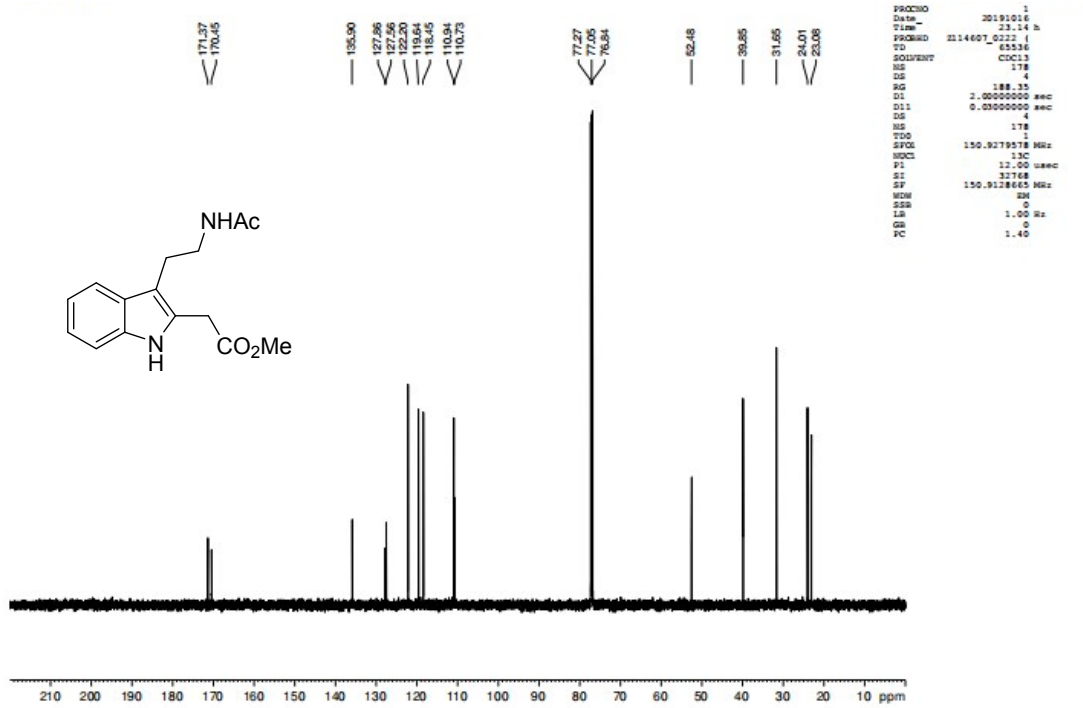
Copies of NMR spectra of **3l**



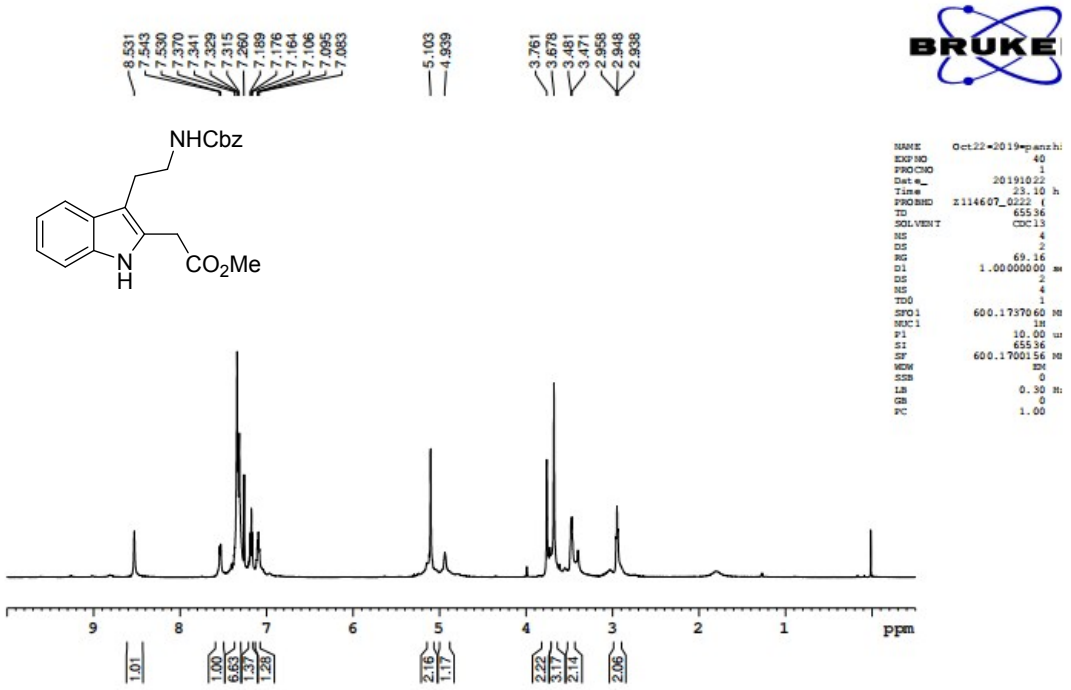


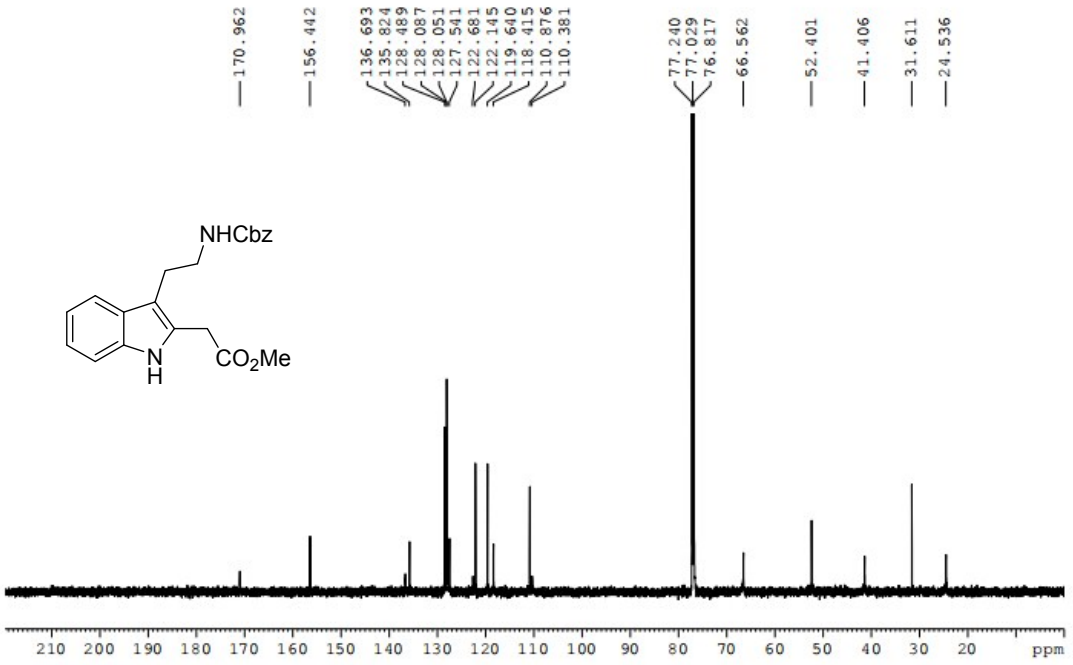
Copies of NMR spectra of **3m**



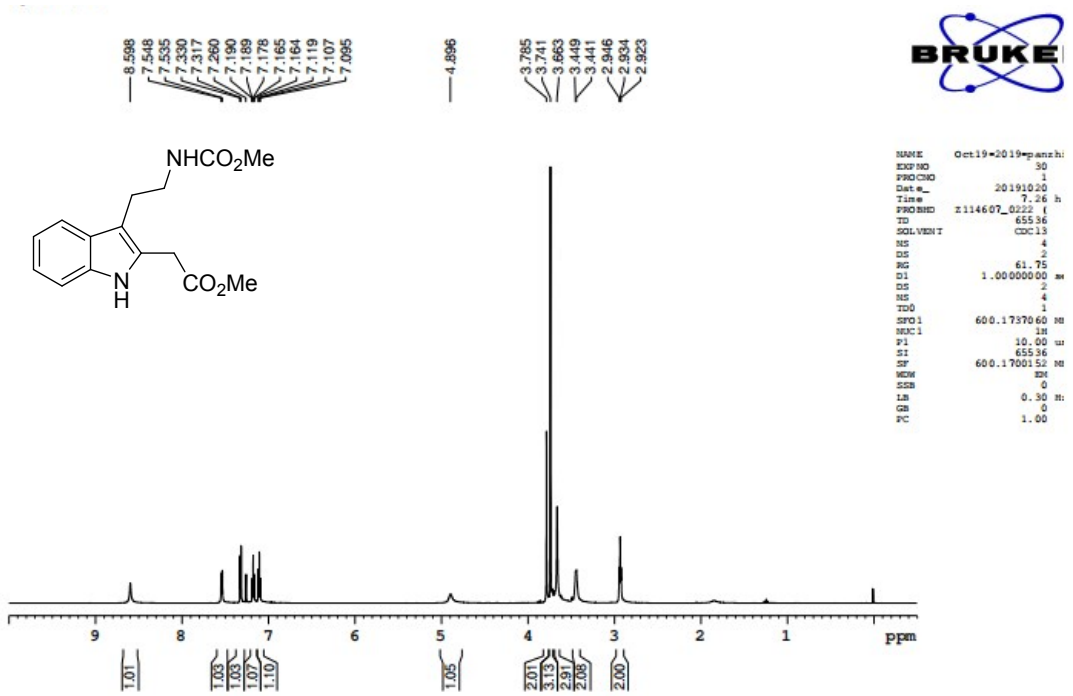


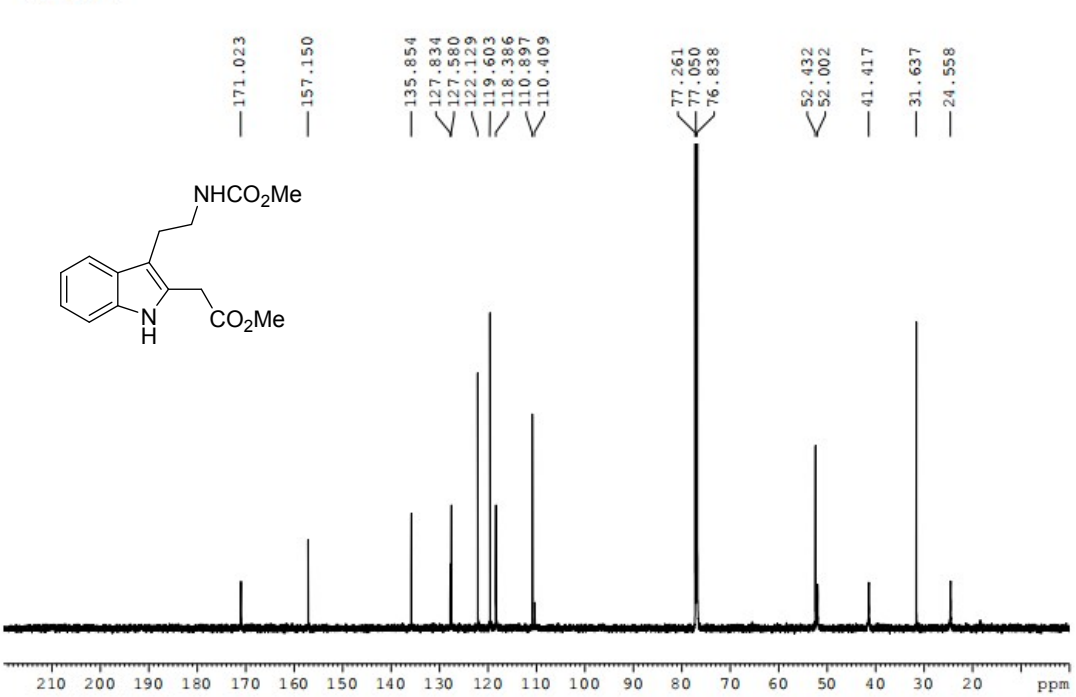
Copies of NMR spectra of **3n**



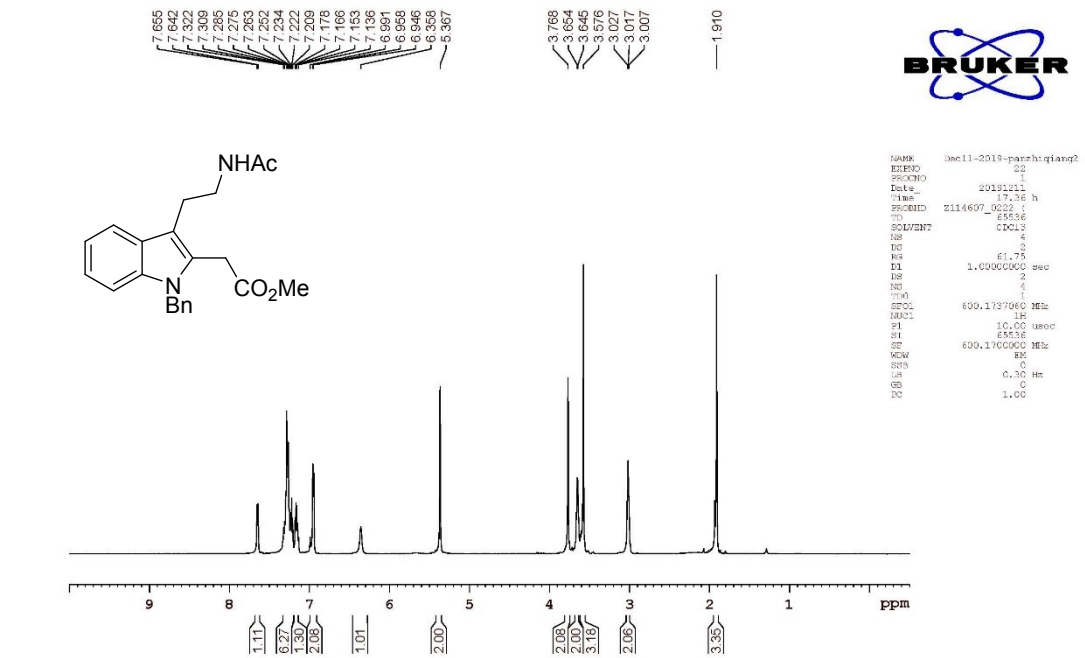


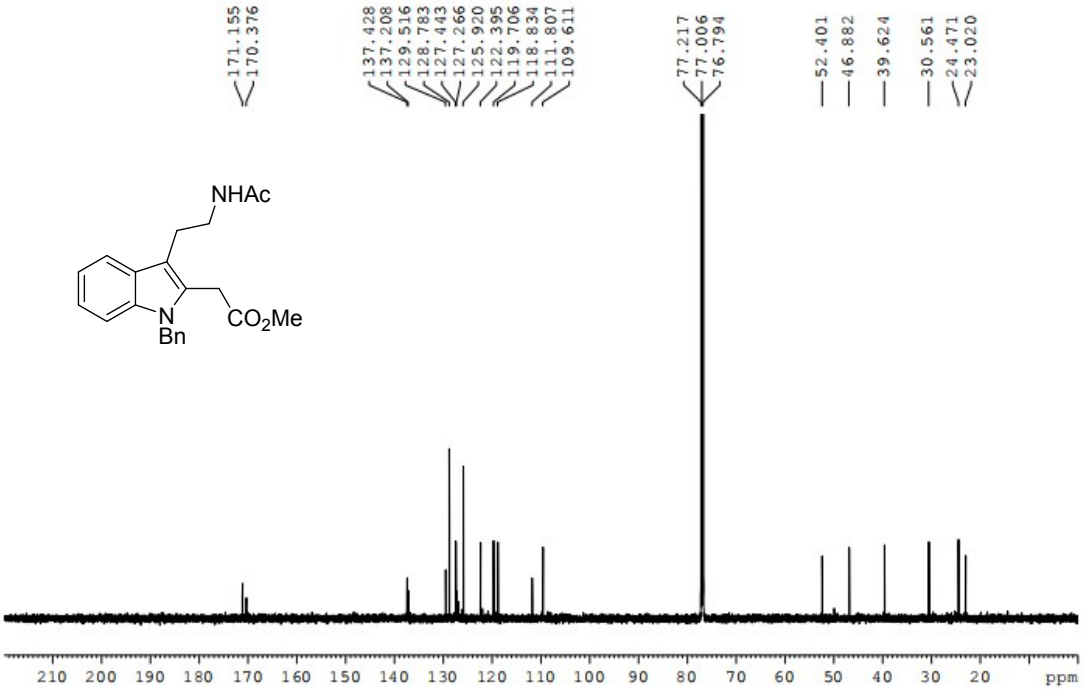
Copies of NMR spectra of **3o**



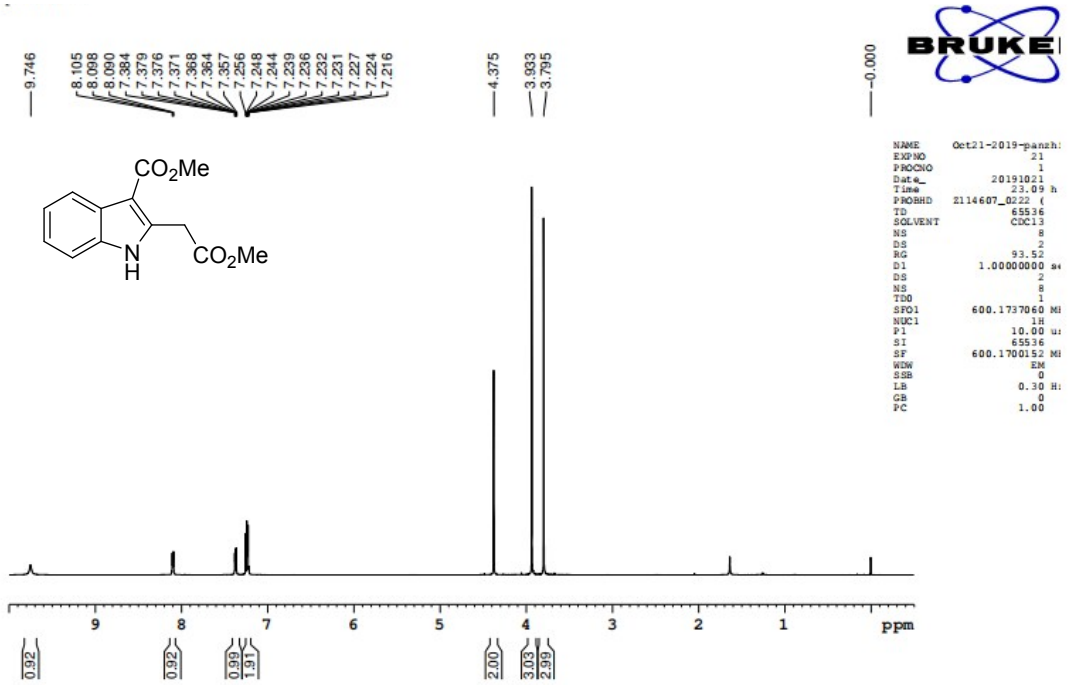


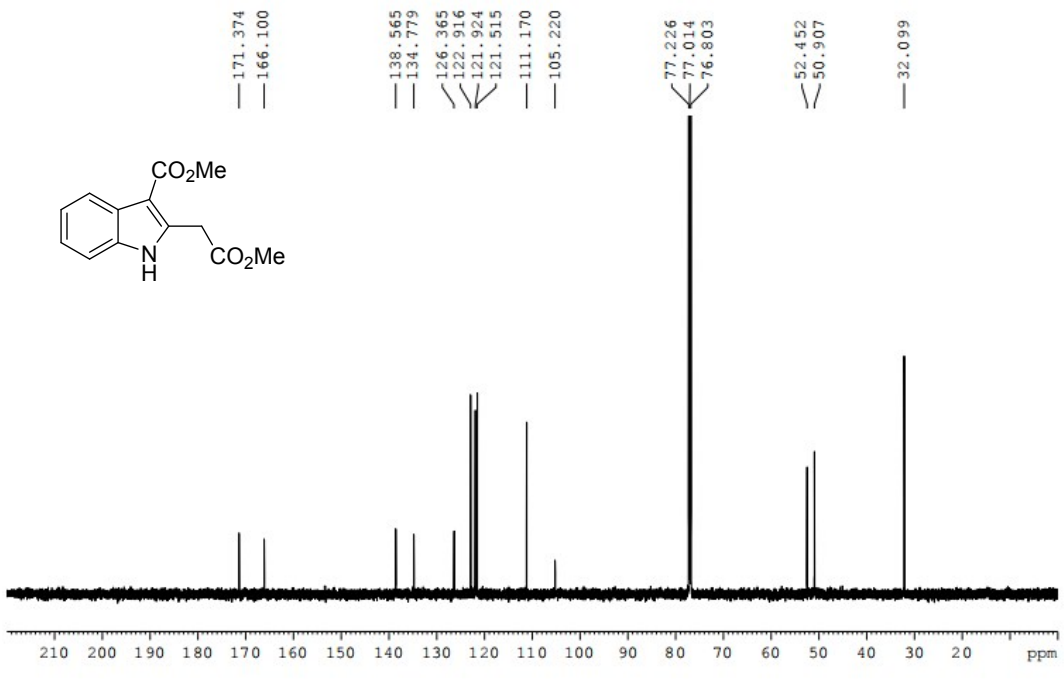
Copies of NMR spectra of **3p**



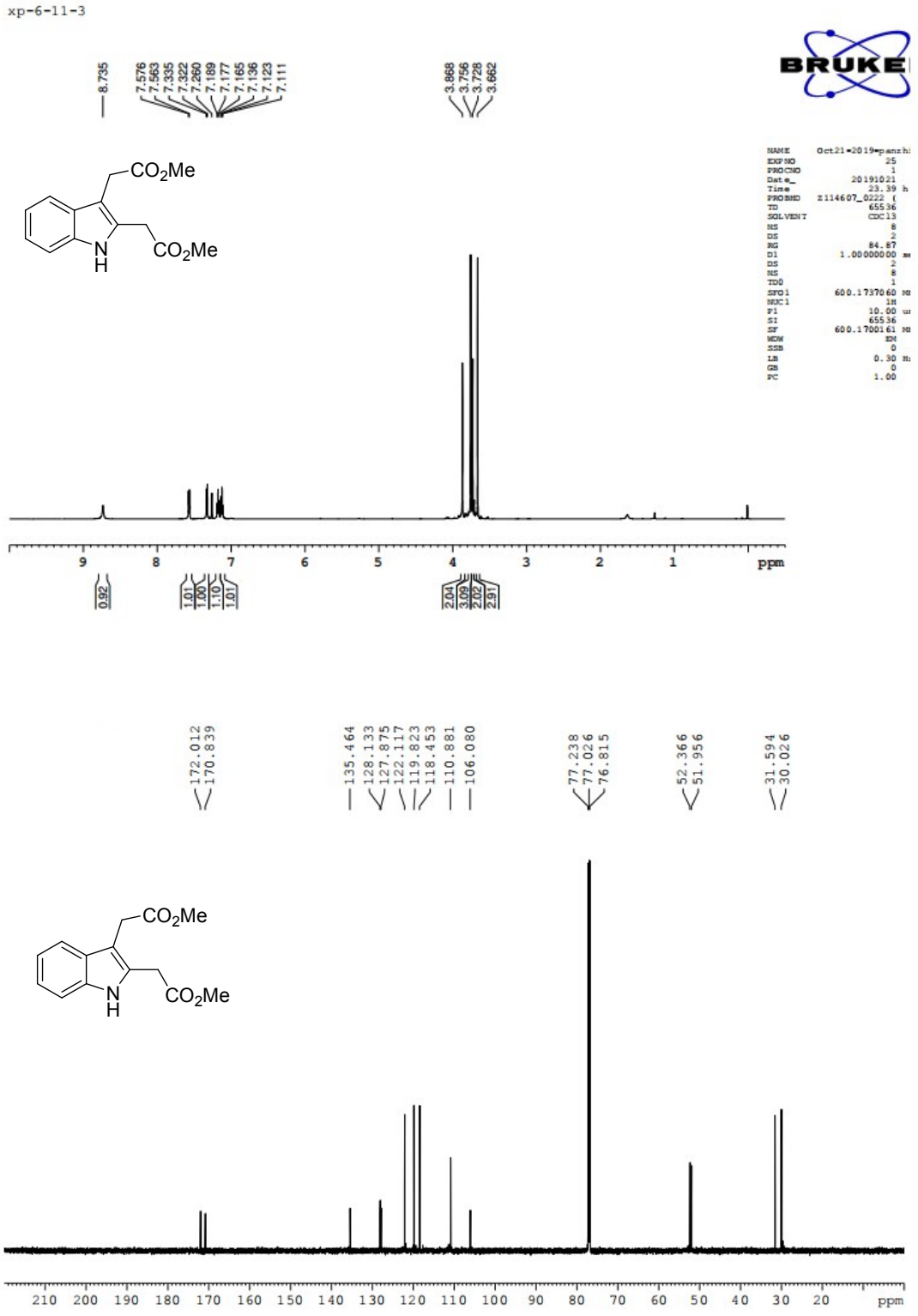


Copies of NMR spectra of **3q**

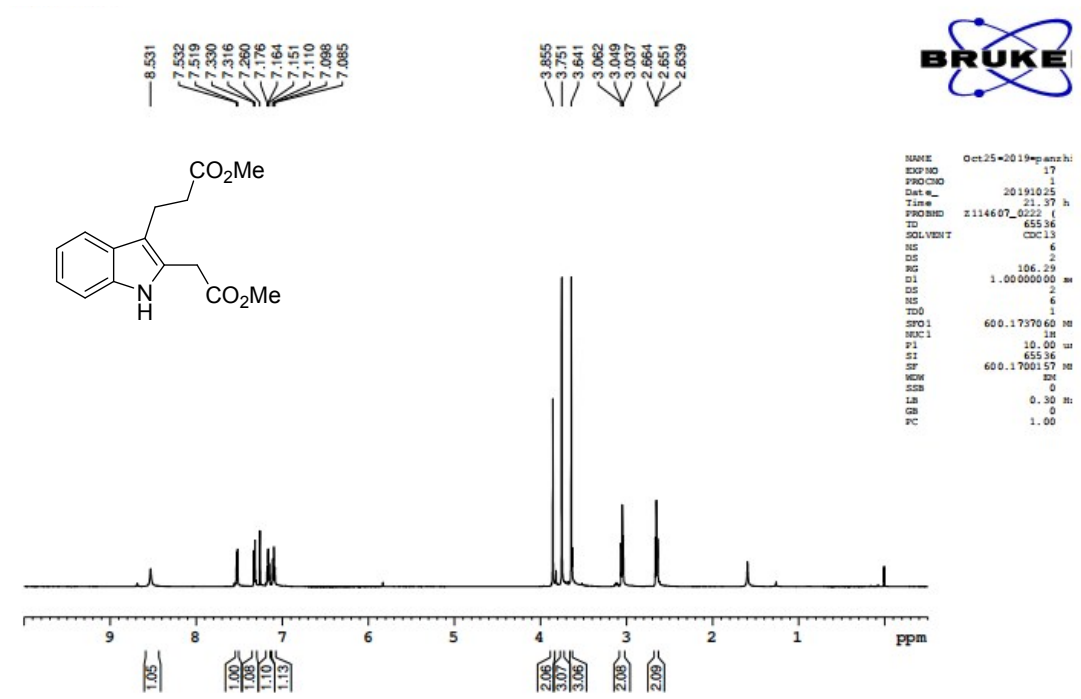


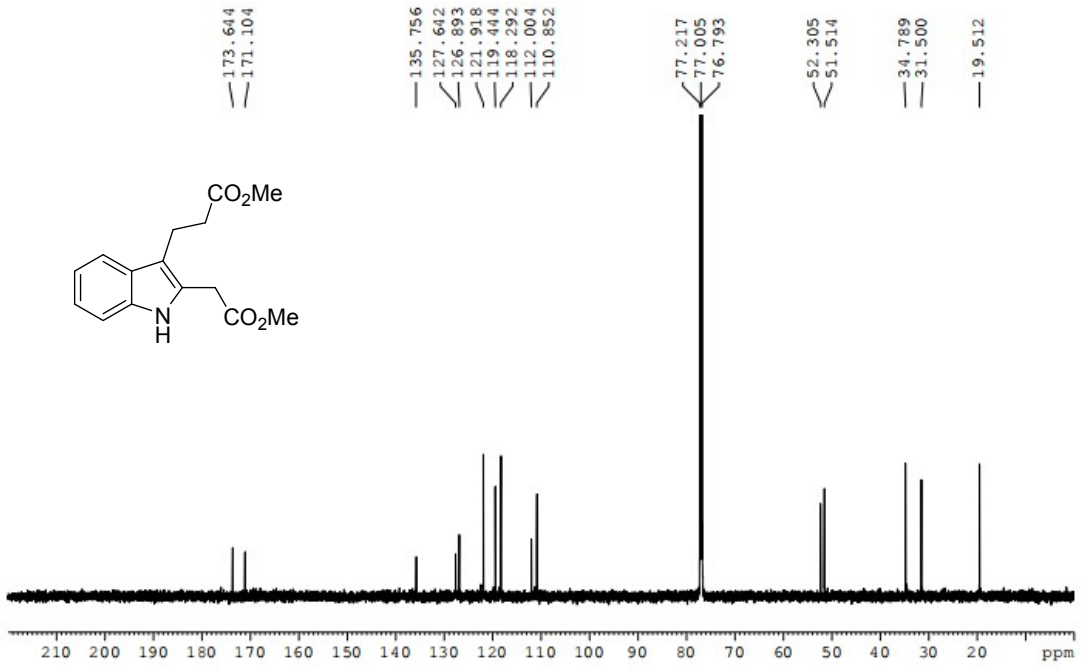


Copies of NMR spectra of **3r**

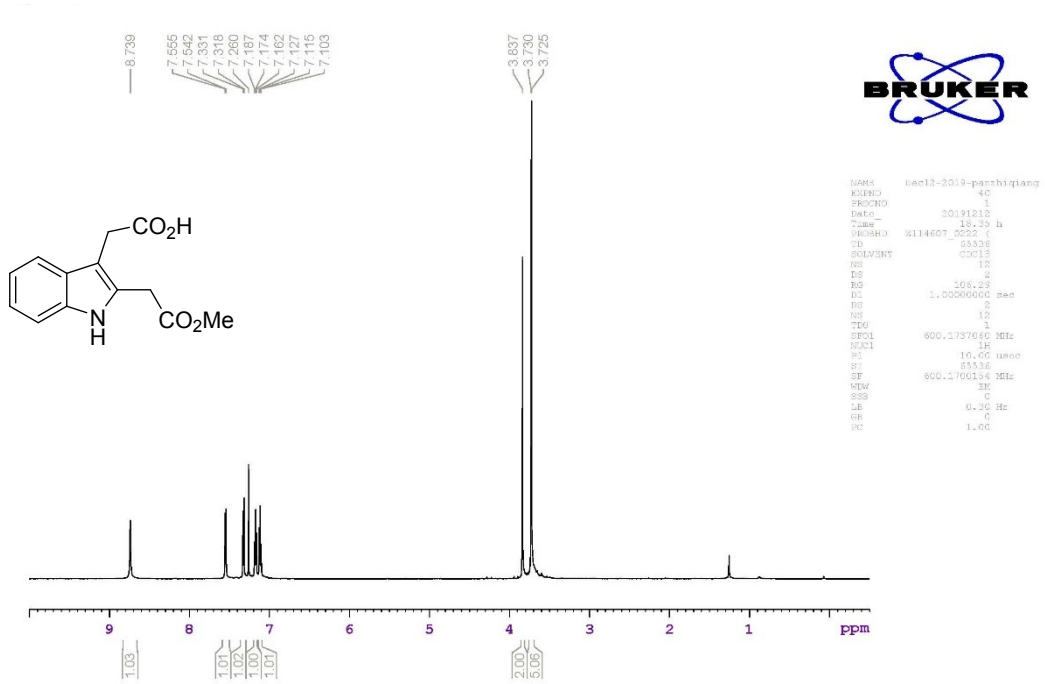


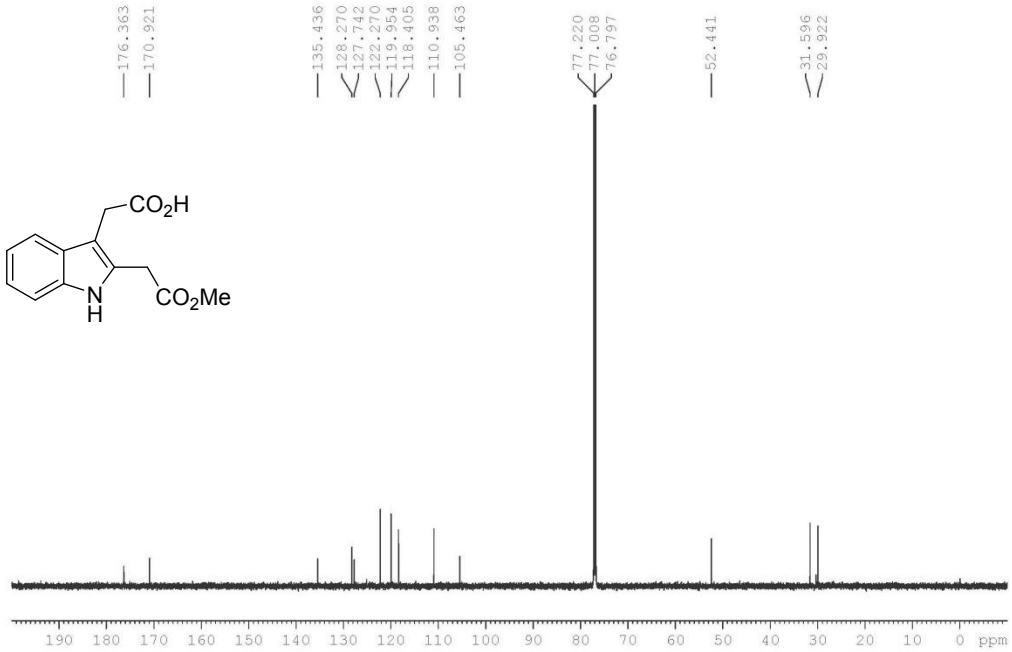
Copies of NMR spectra of **3s**



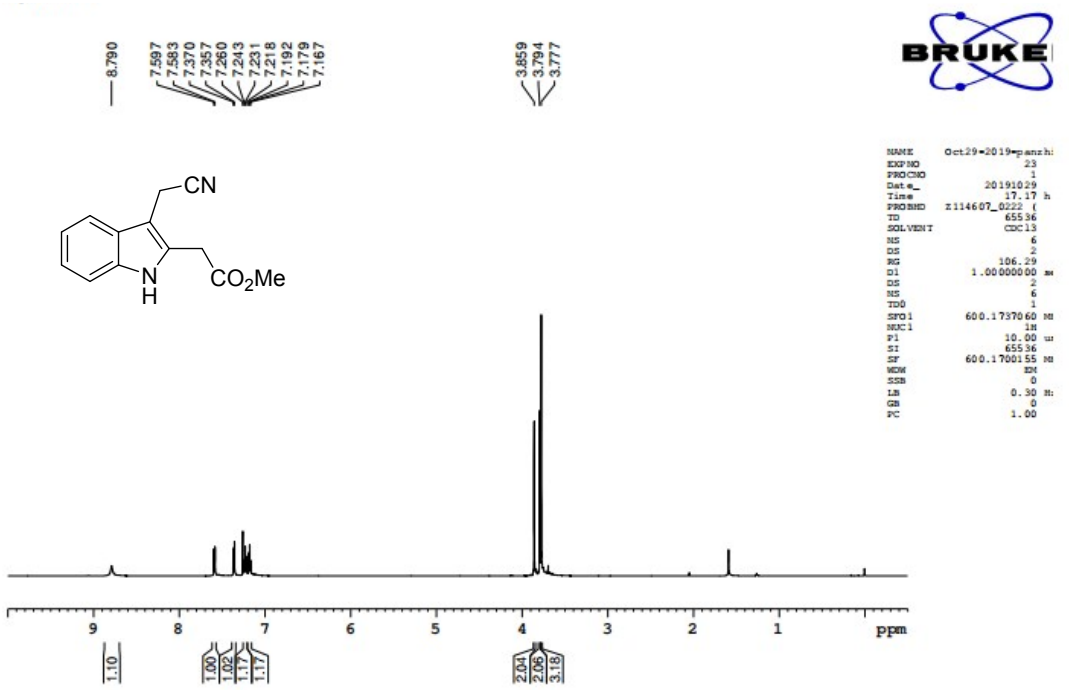


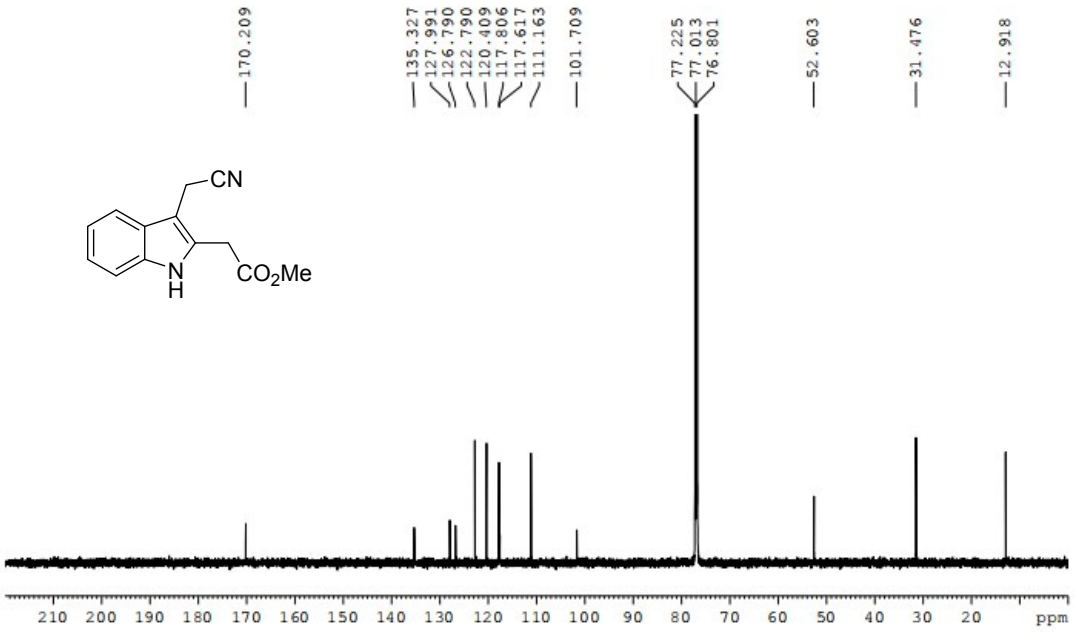
Copies of NMR spectra of **3t**



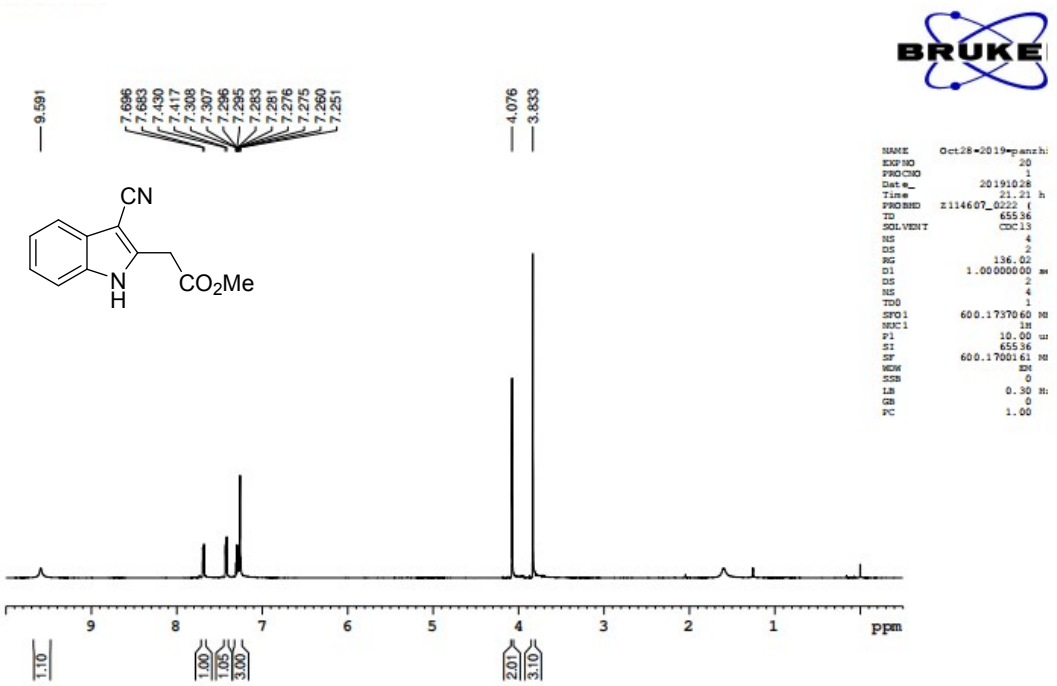


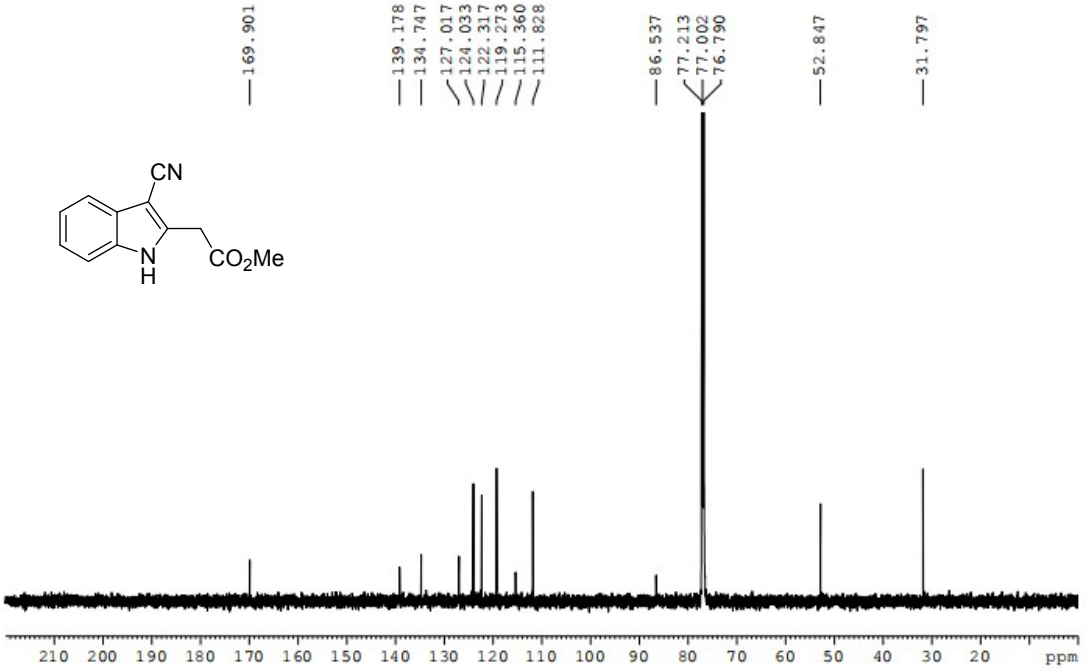
Copies of NMR spectra of **3u**



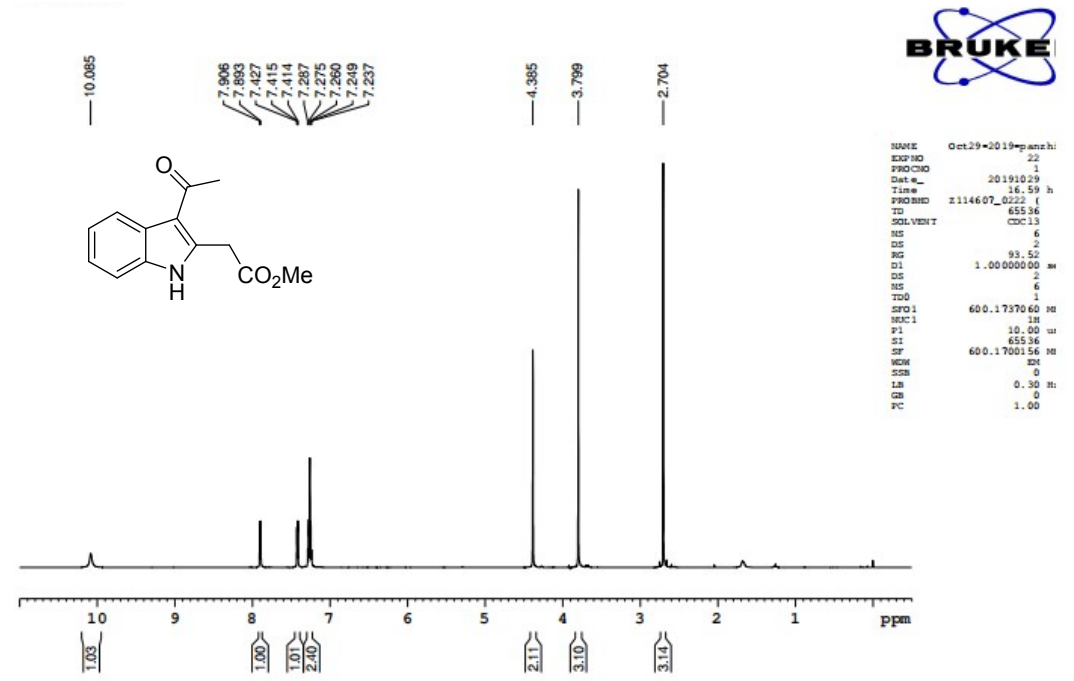


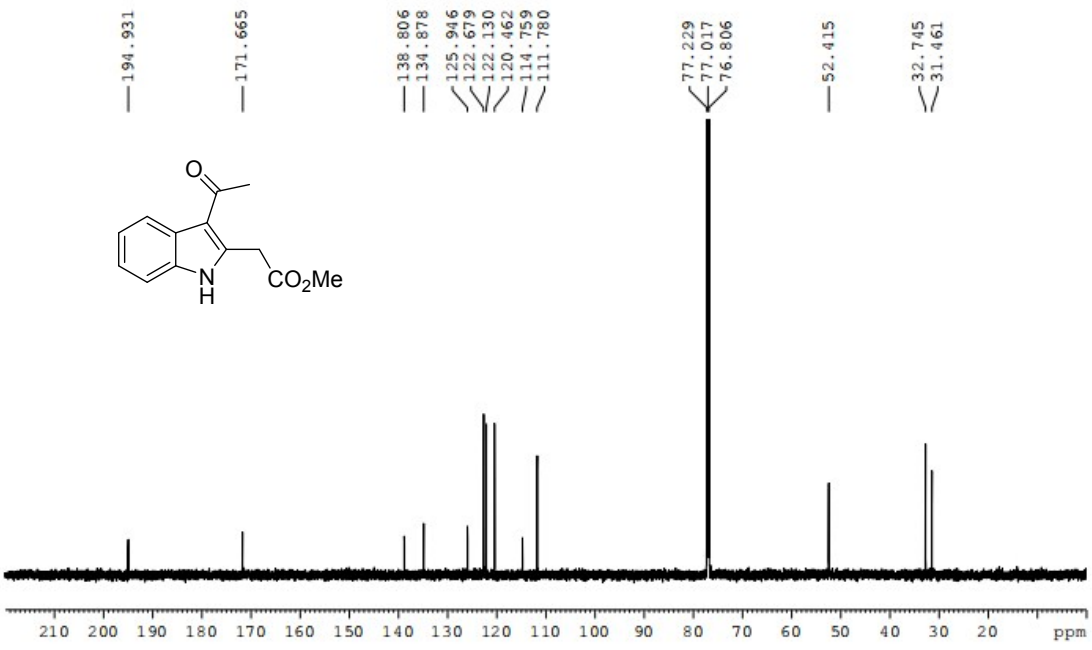
Copies of NMR spectra of **3v**



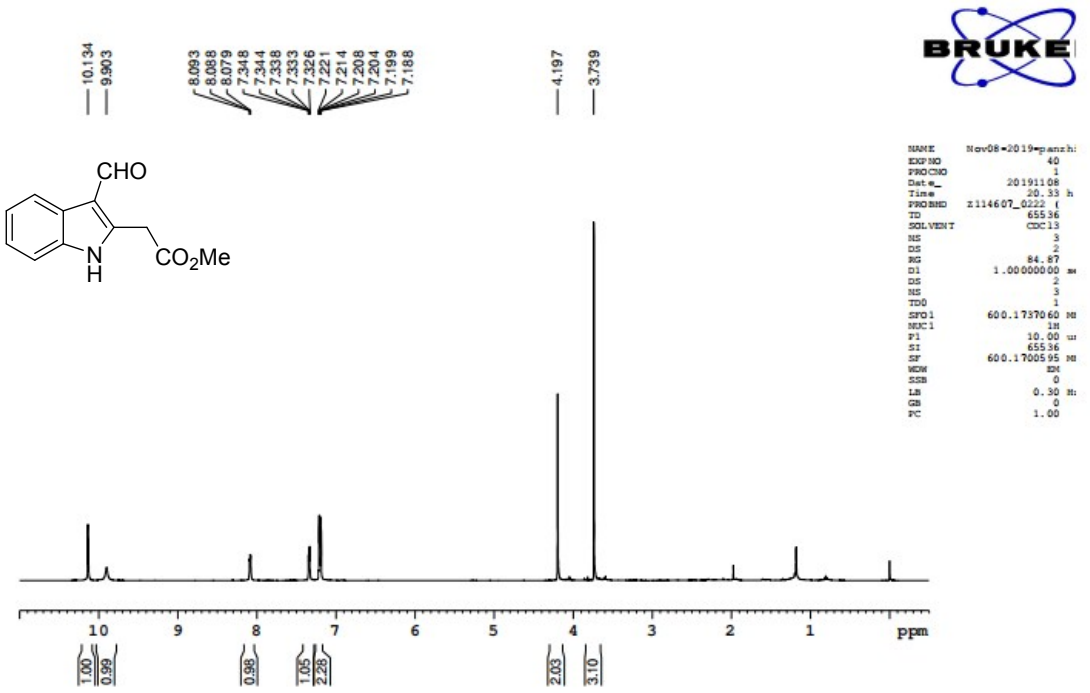


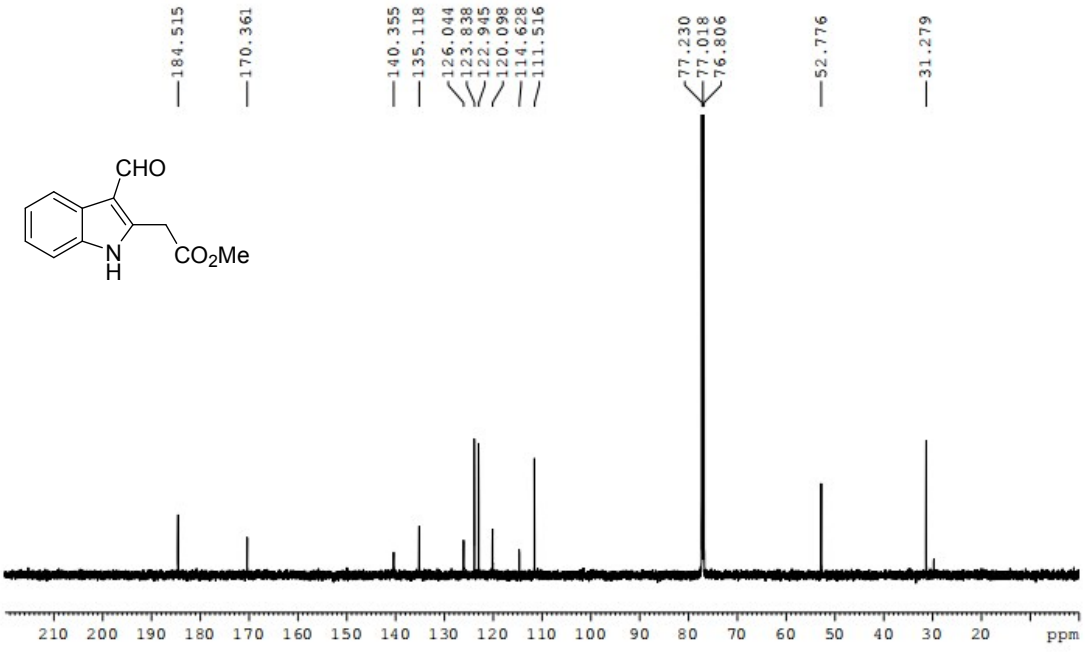
Copies of NMR spectra of **3w**



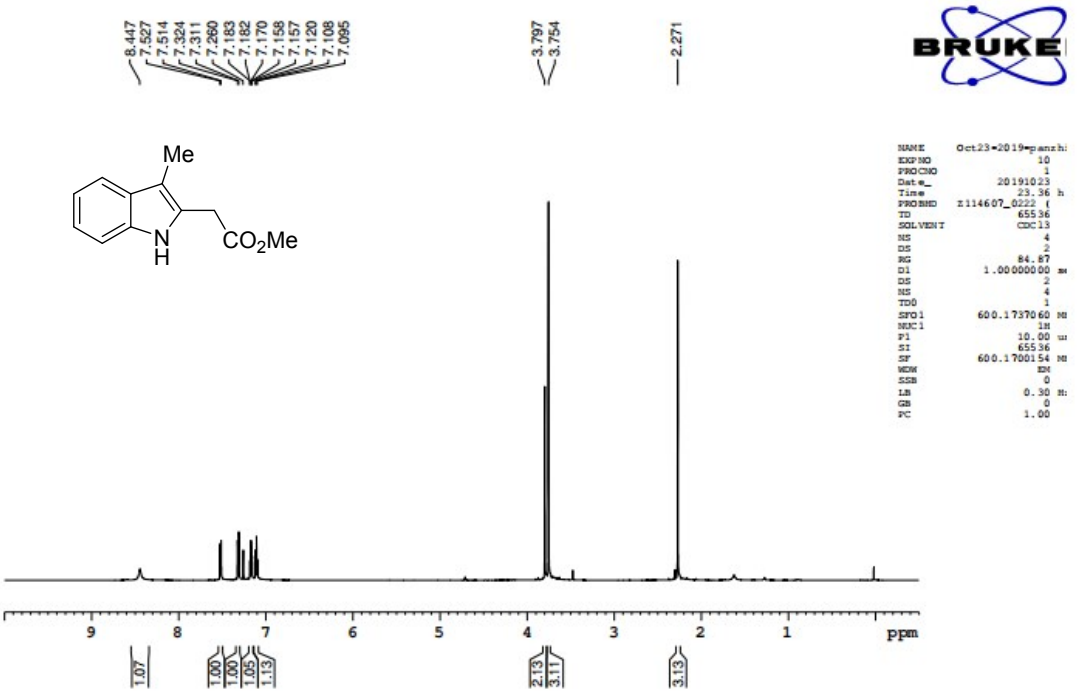


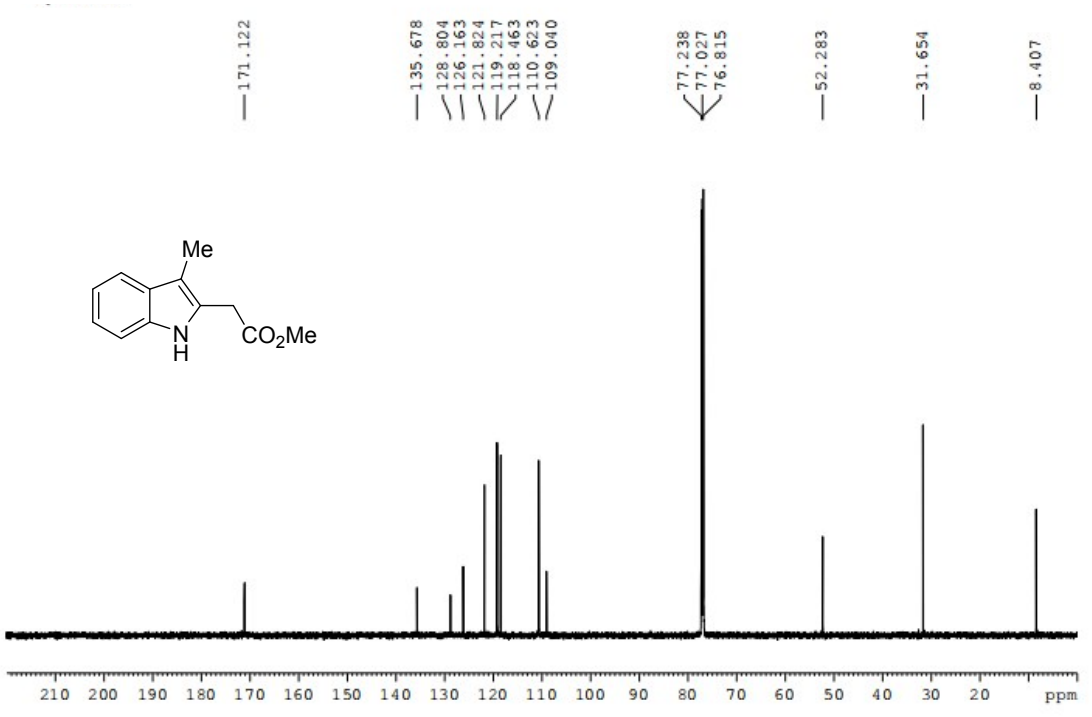
Copies of NMR spectra of **3x**



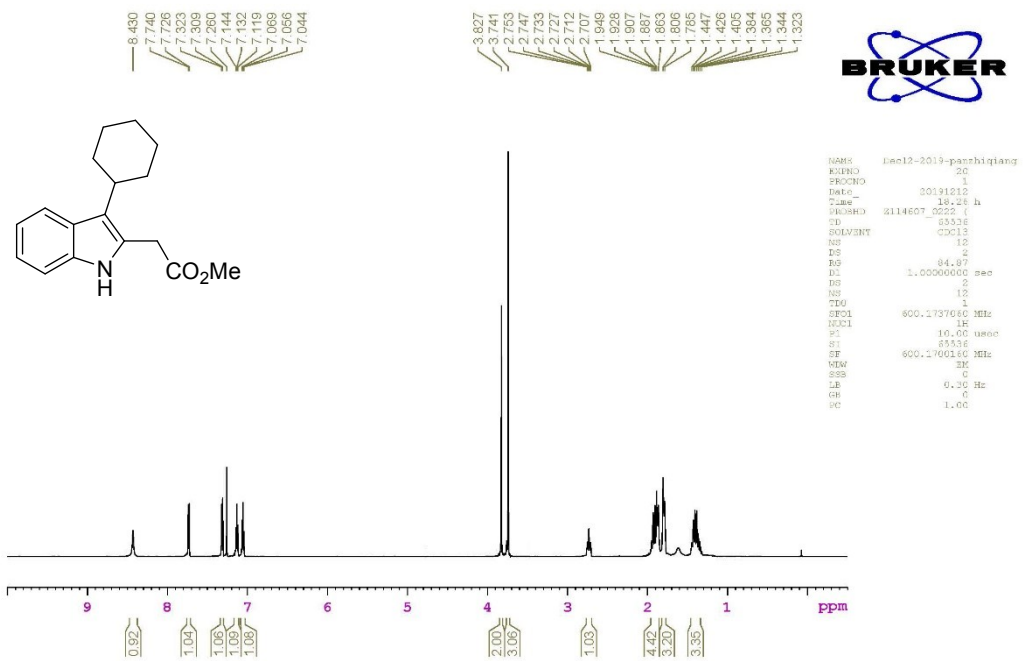


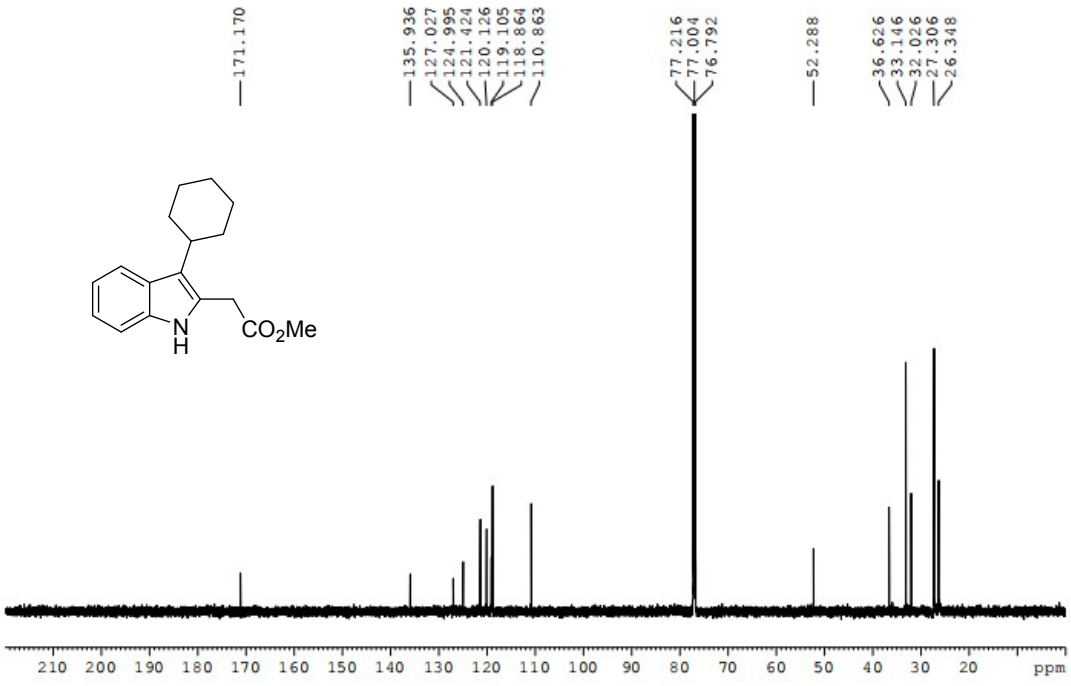
Copies of NMR spectra of **3y**



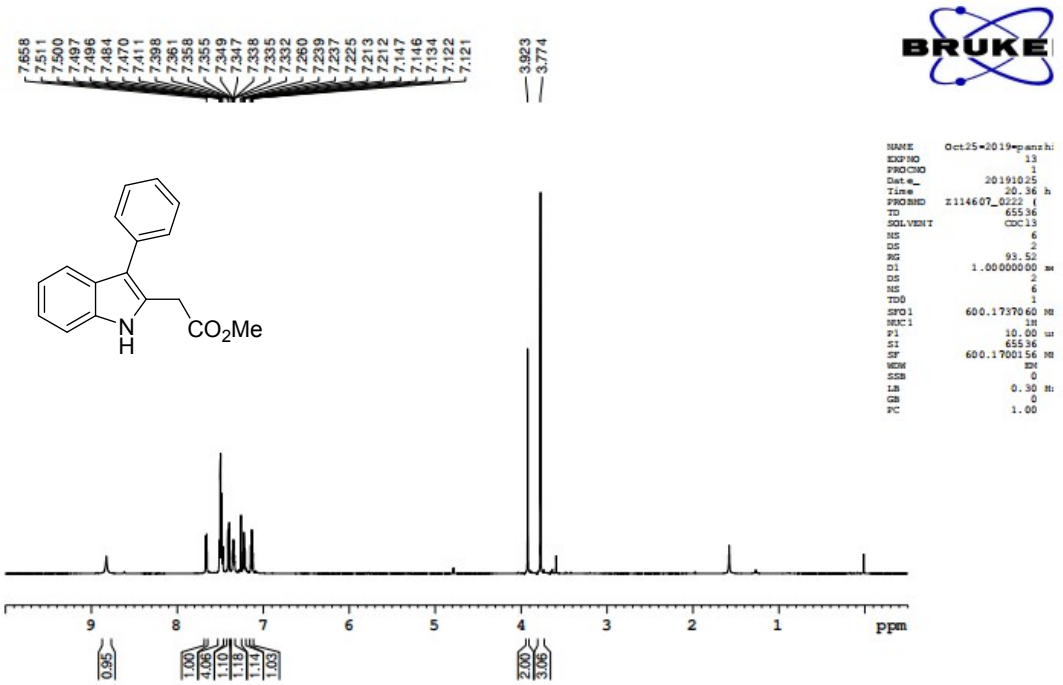


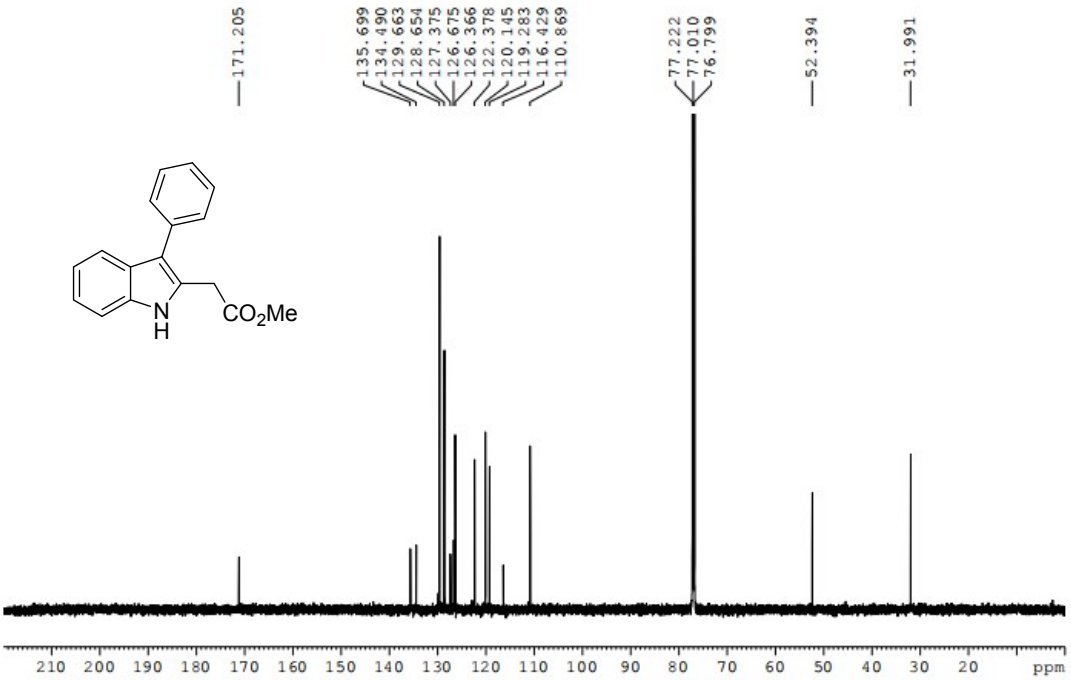
Copies of NMR spectra of **3z**



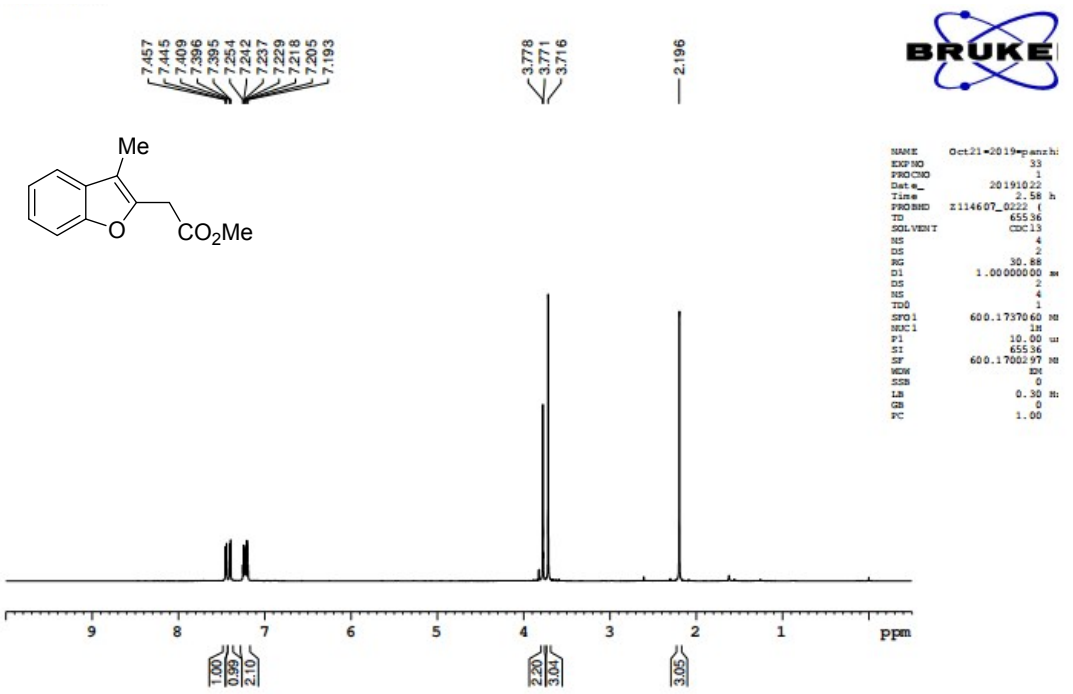


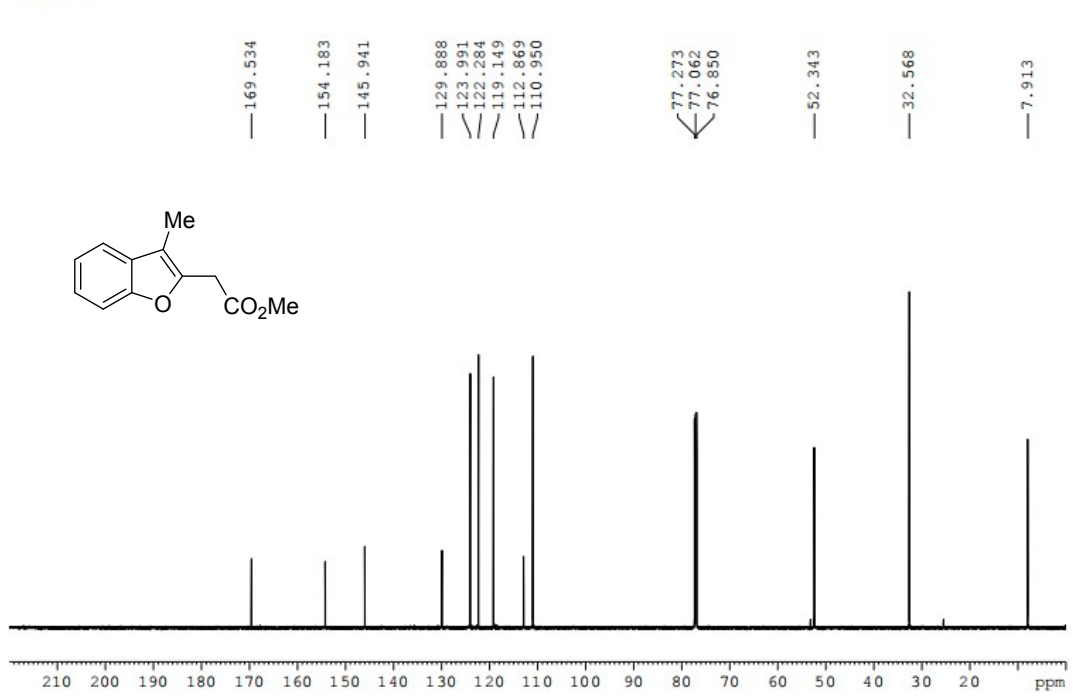
Copies of NMR spectra of **3aa**



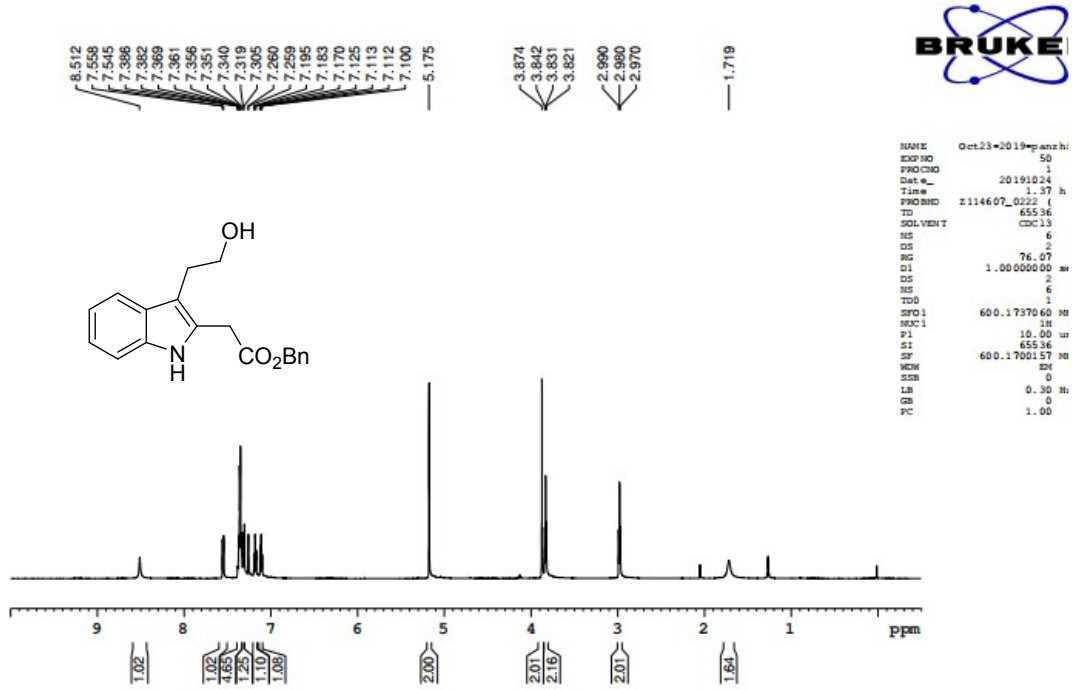


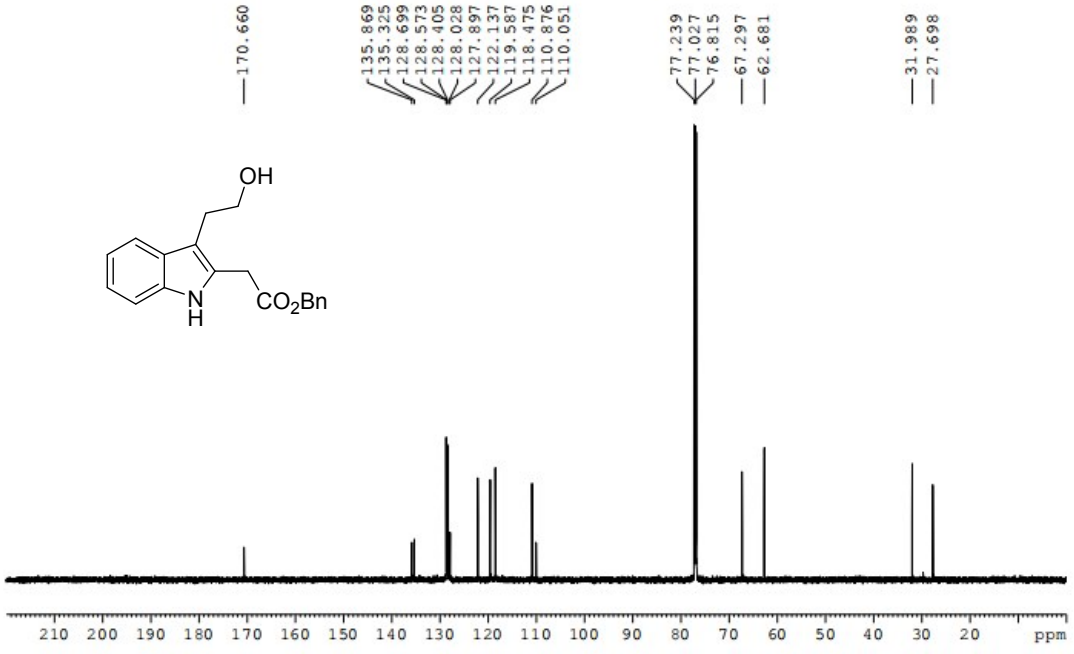
Copies of NMR spectra of **3ab**



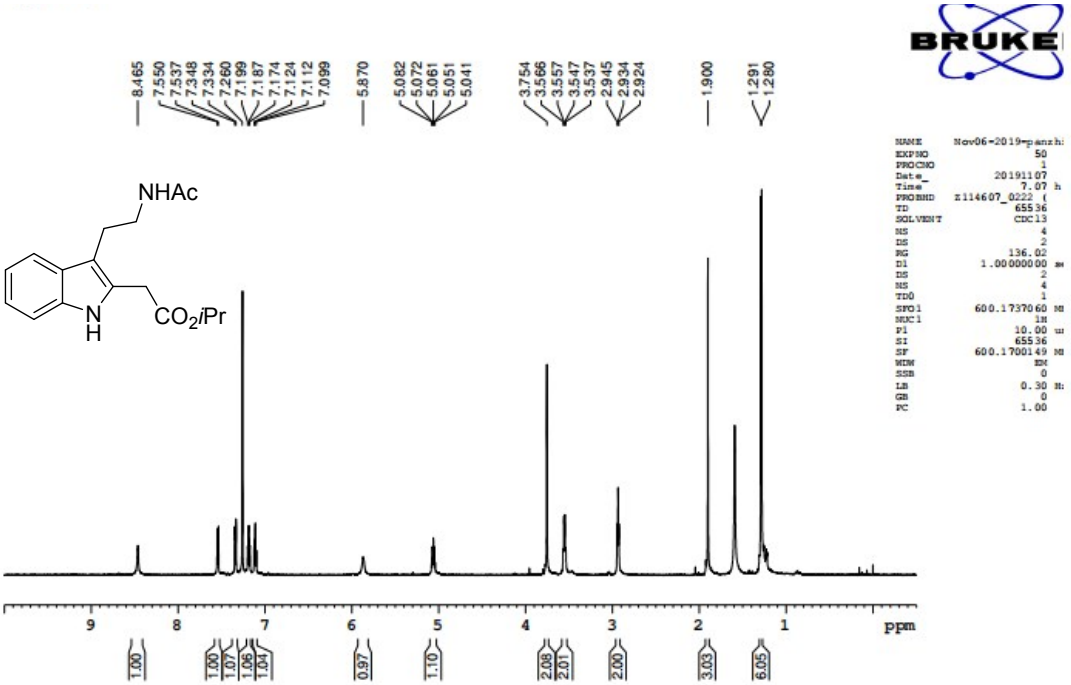


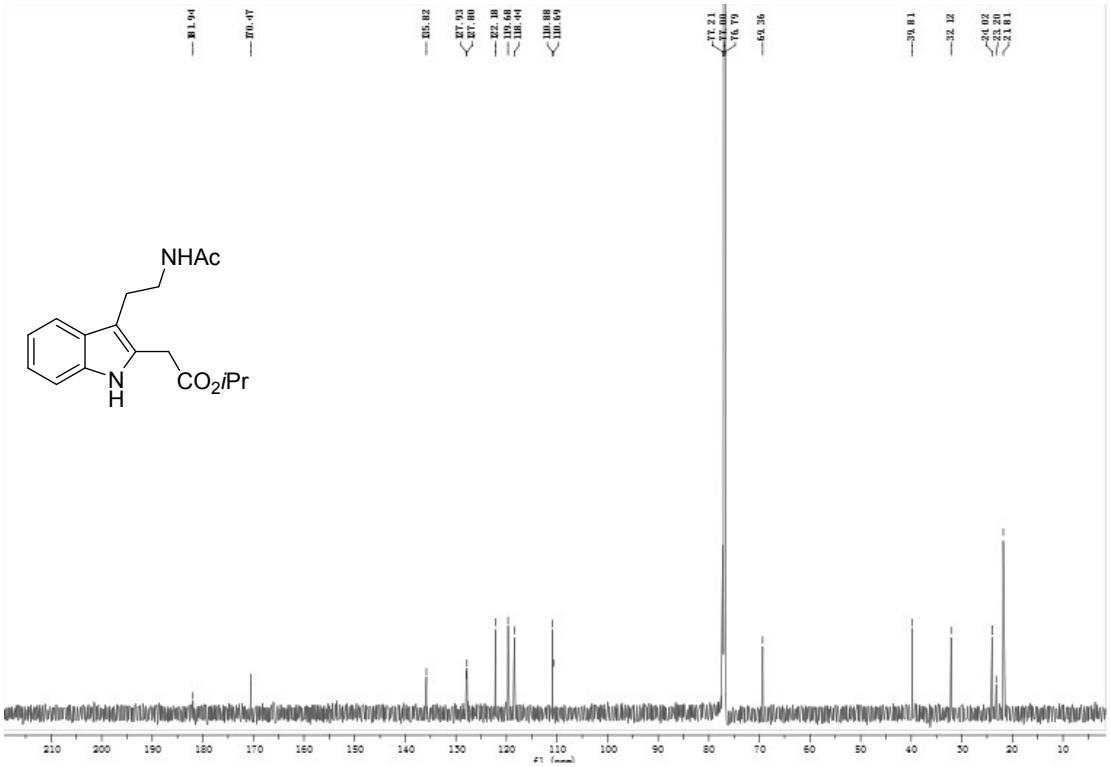
Copies of NMR spectra of **3ac**



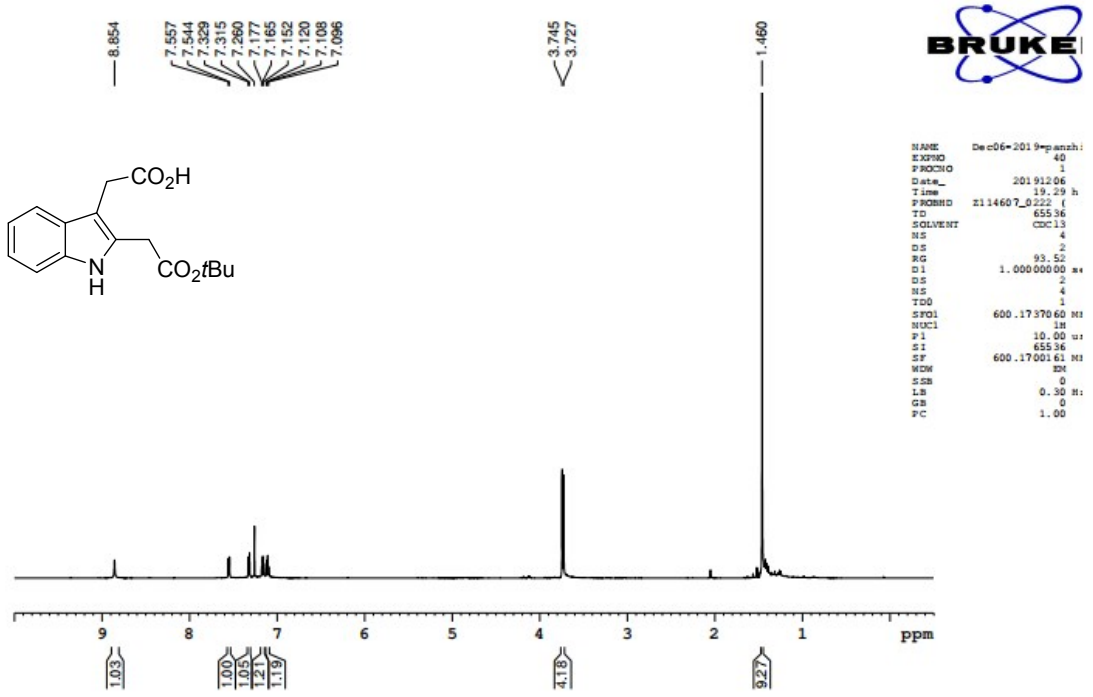


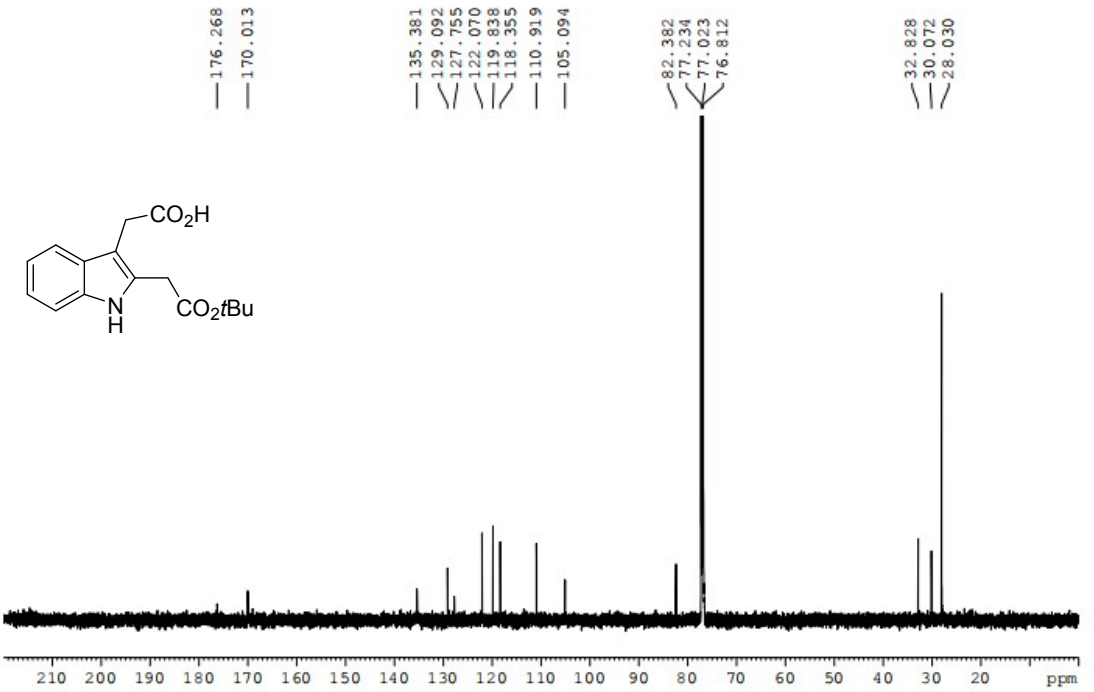
Copies of NMR spectra of **3ad**



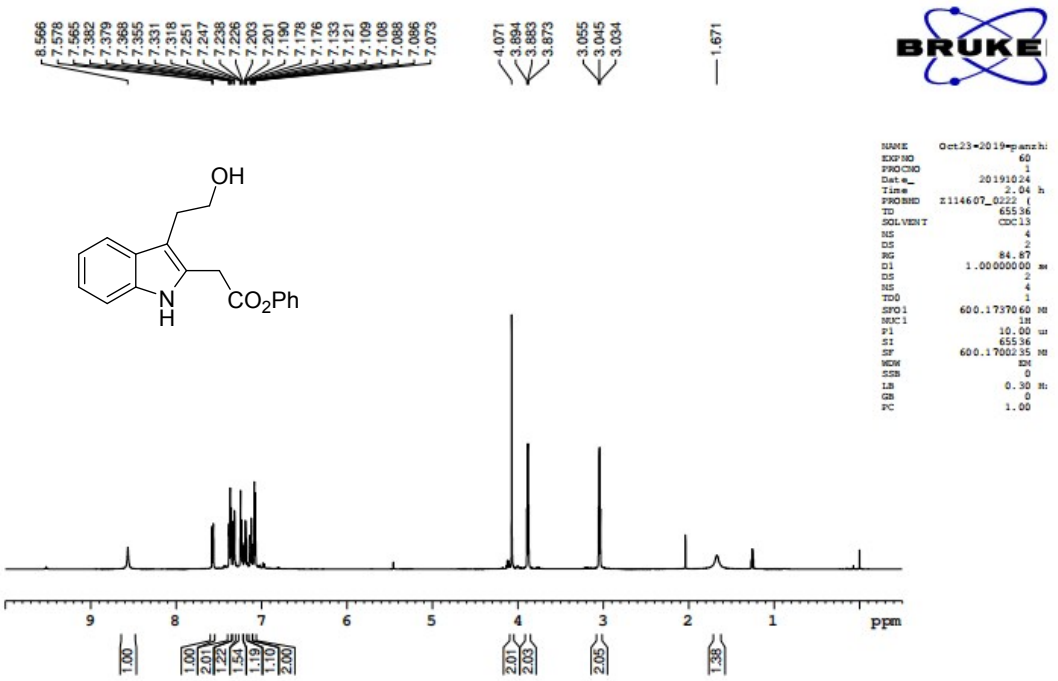


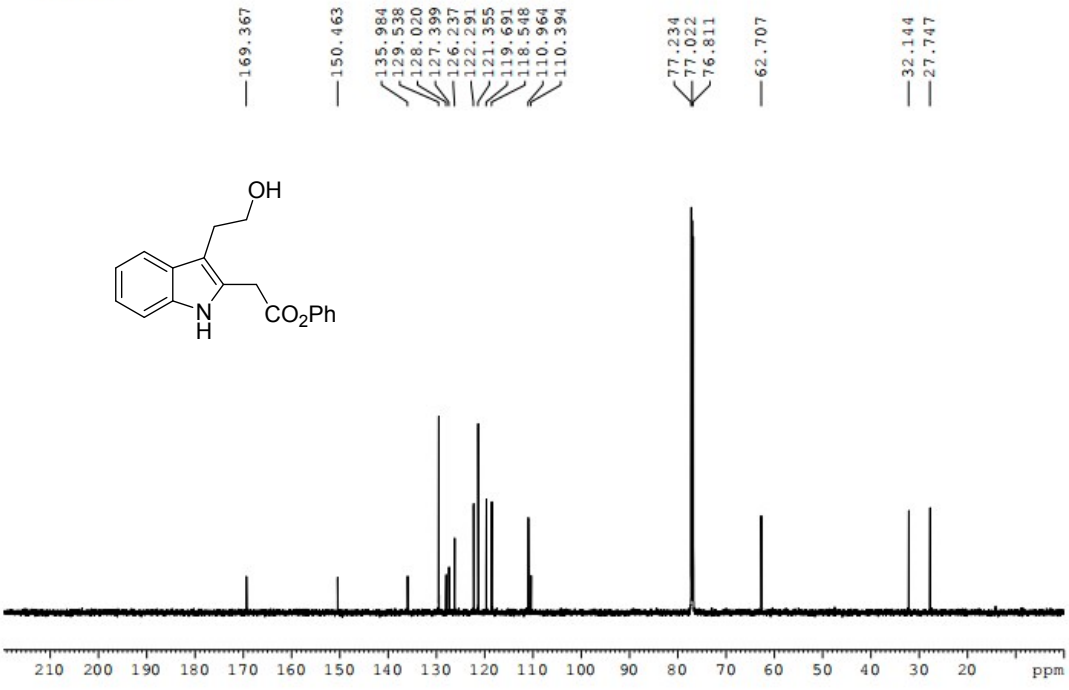
Copies of NMR spectra of **3ae**



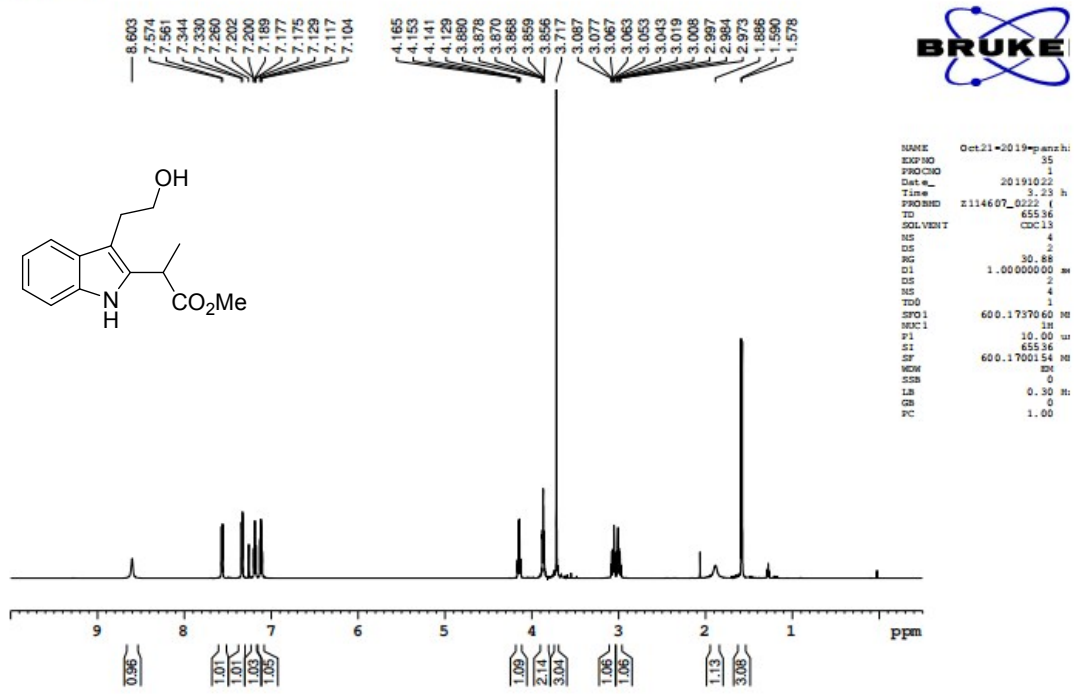


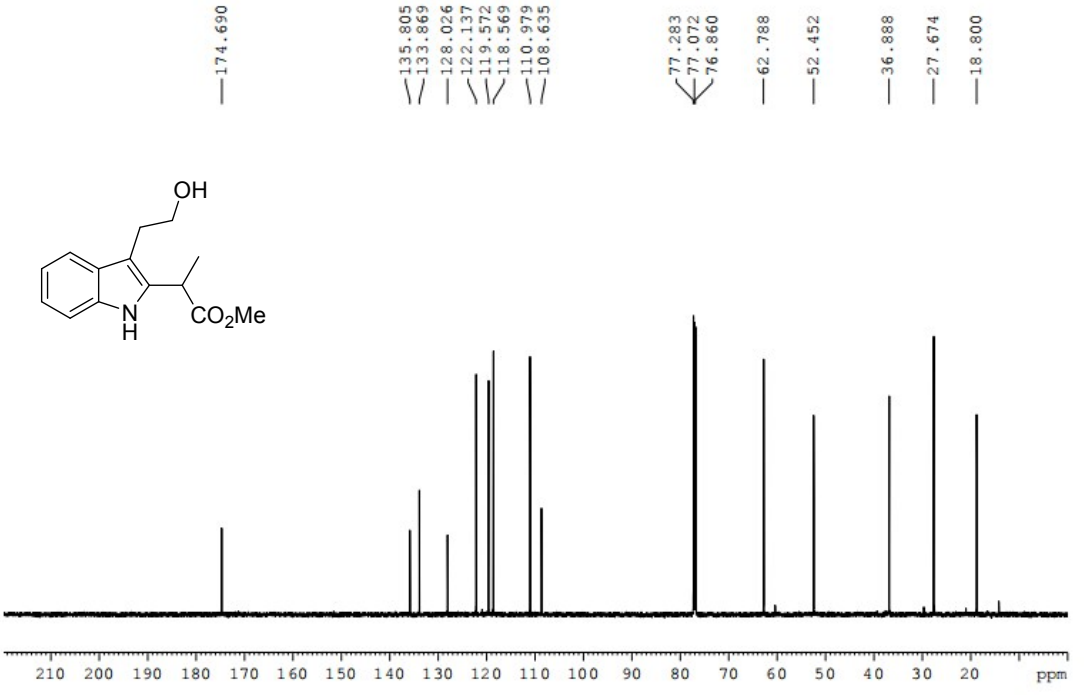
Copies of NMR spectra of **3af**



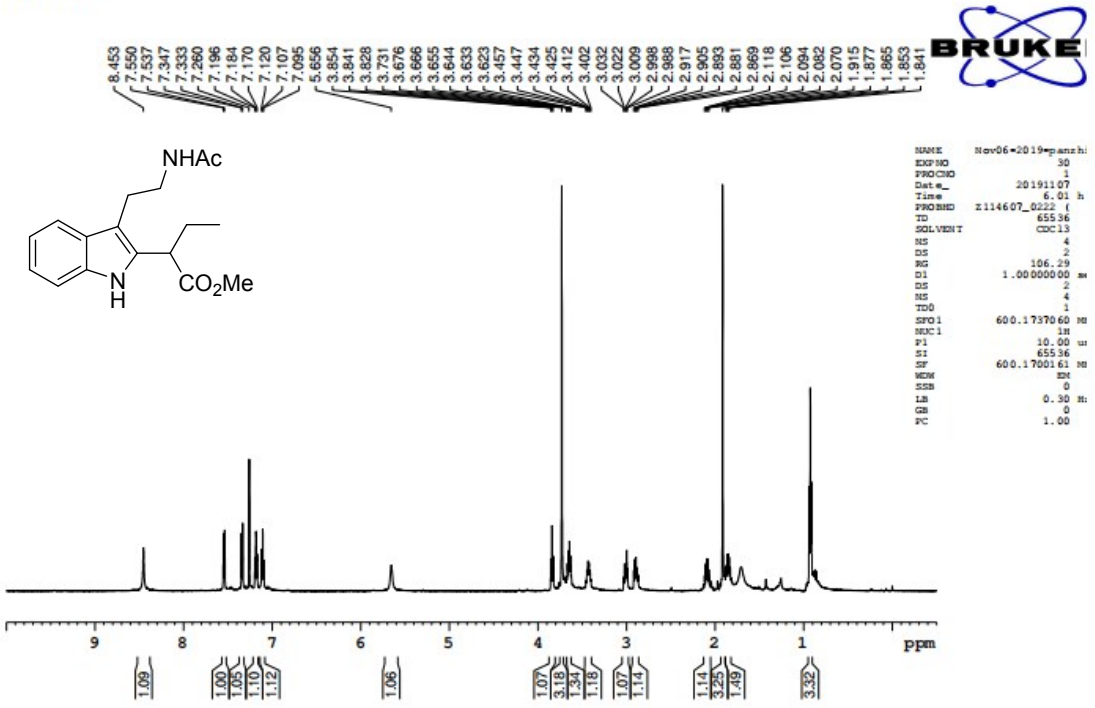


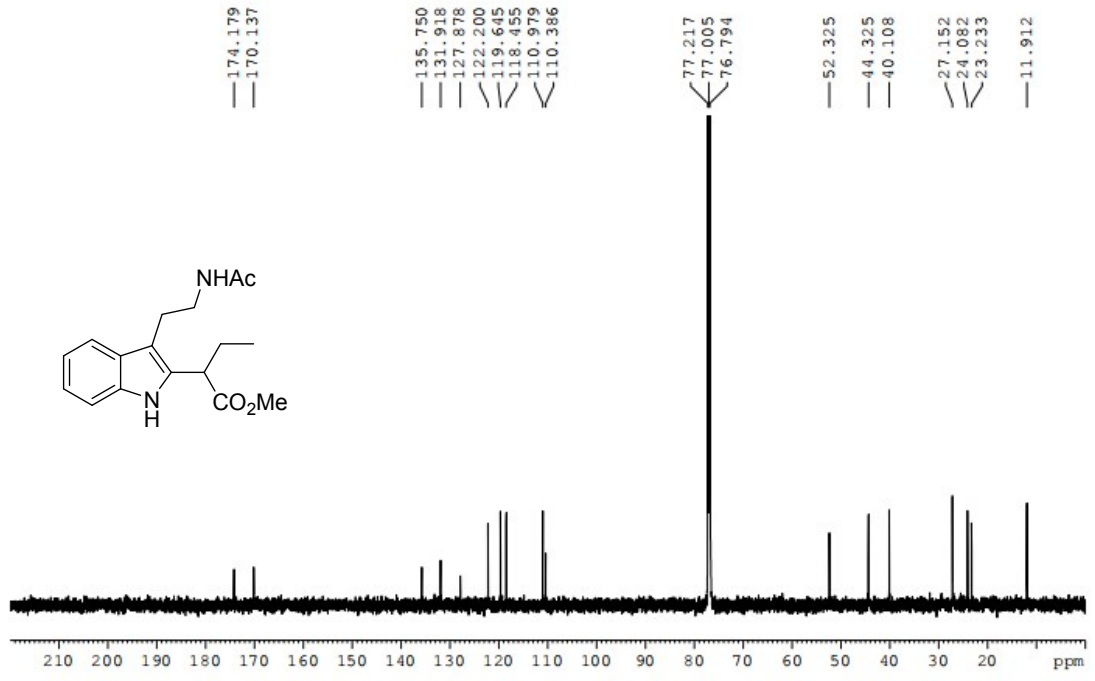
Copies of NMR spectra of **3ag**



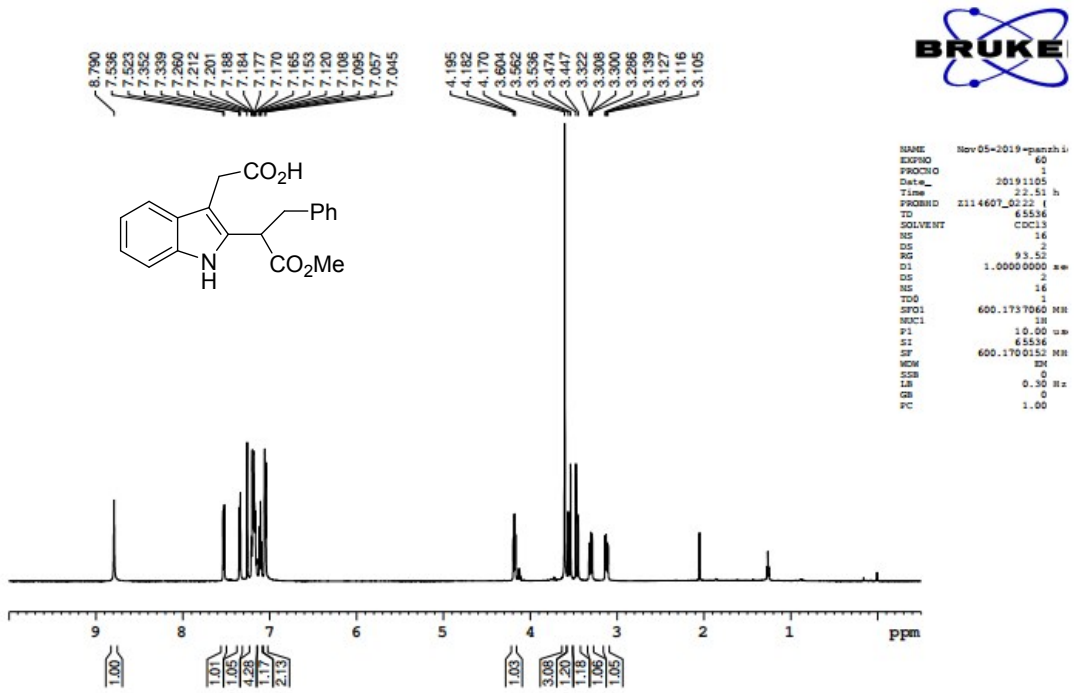


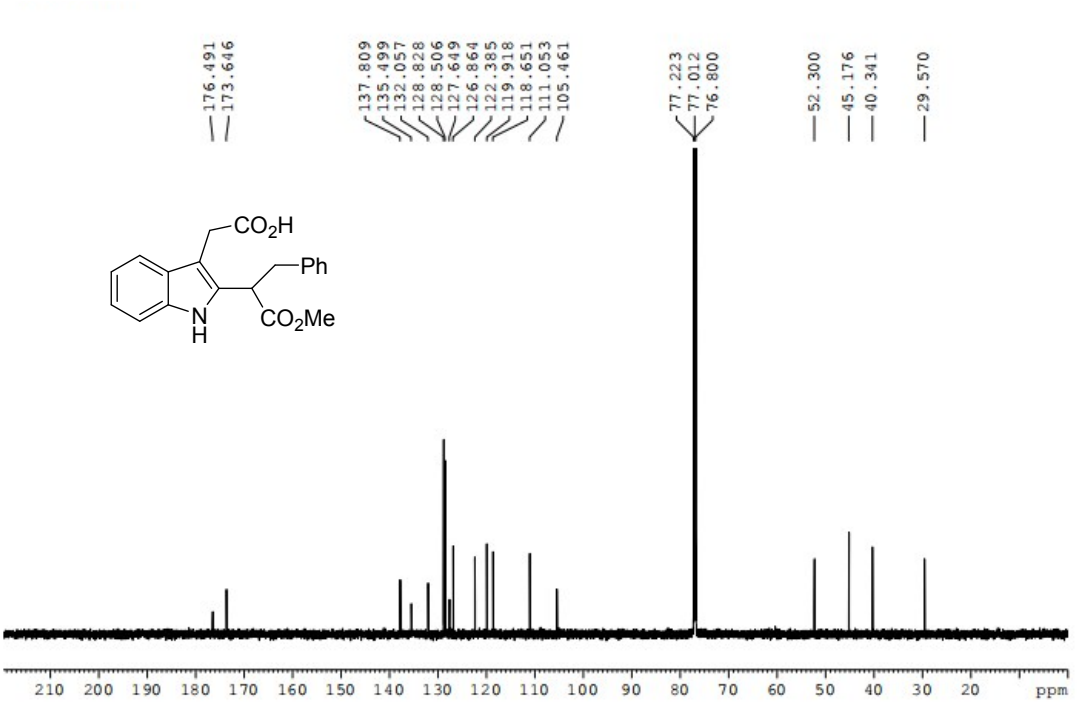
Copies of NMR spectra of **3ah**



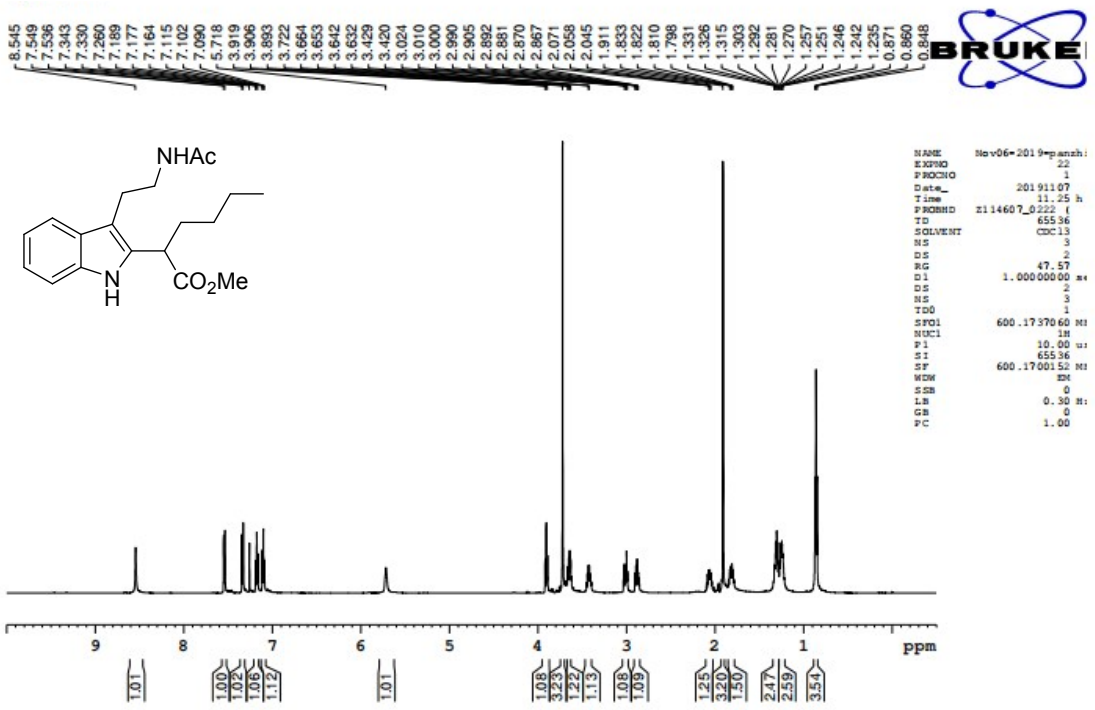


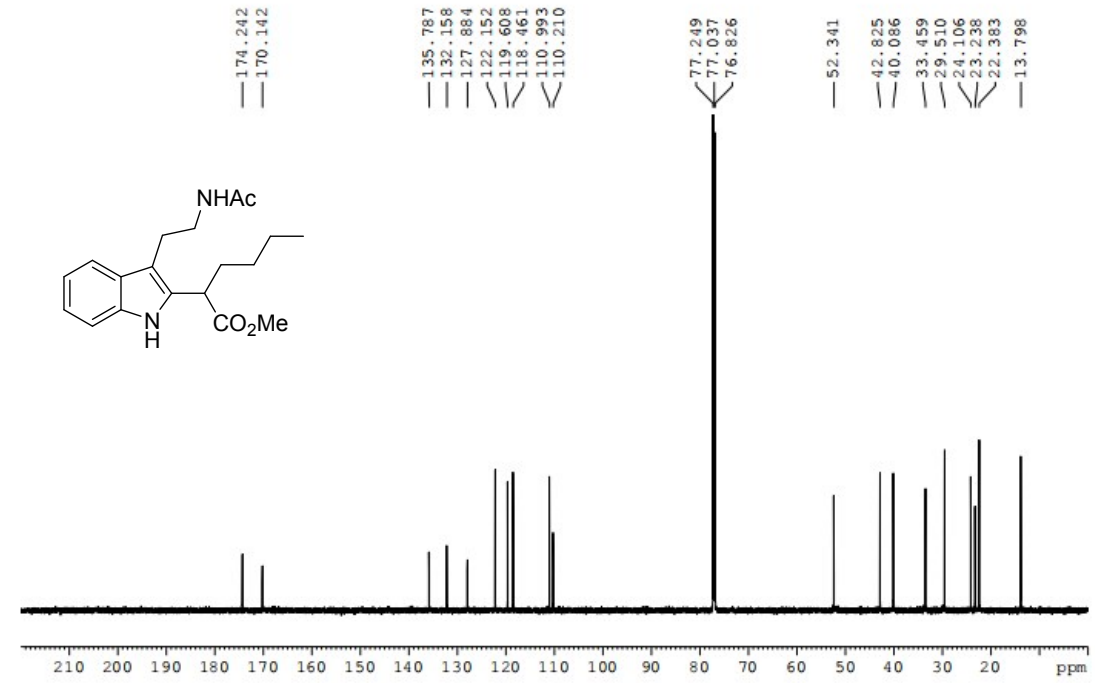
Copy of NMR spectra of **3ai**



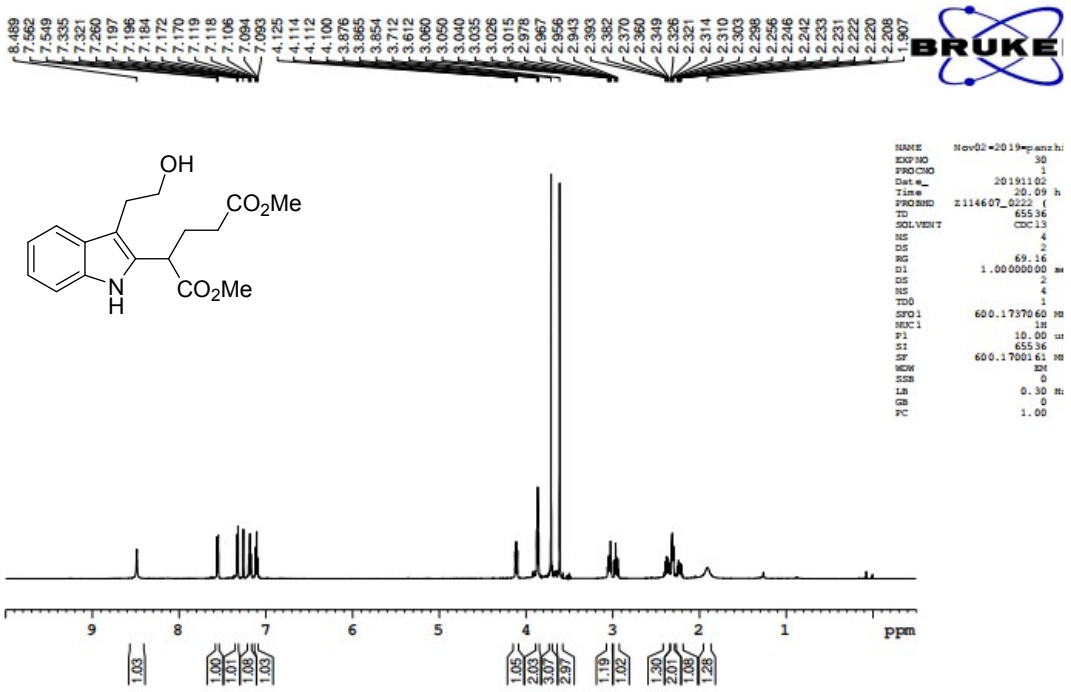


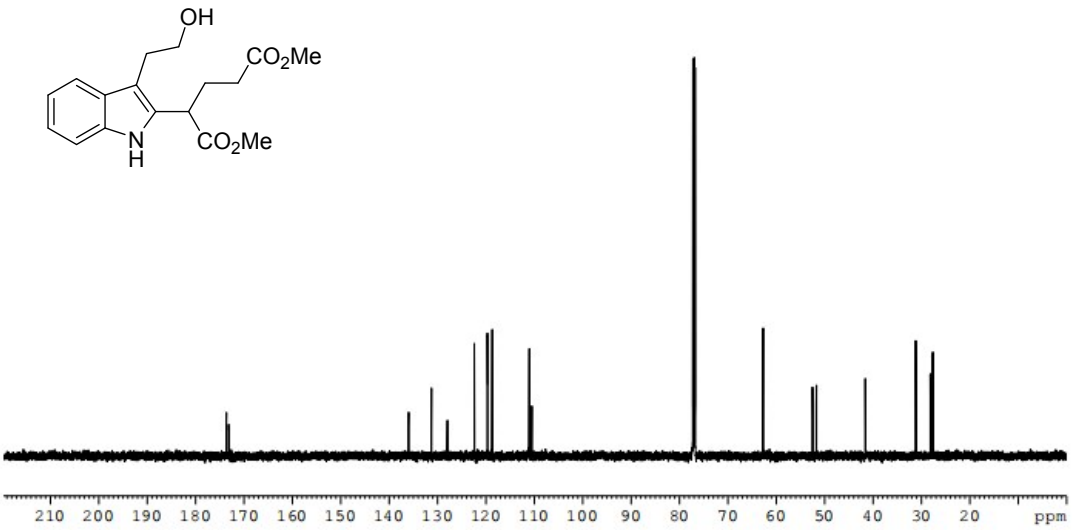
Copies of NMR spectra of **3aj**



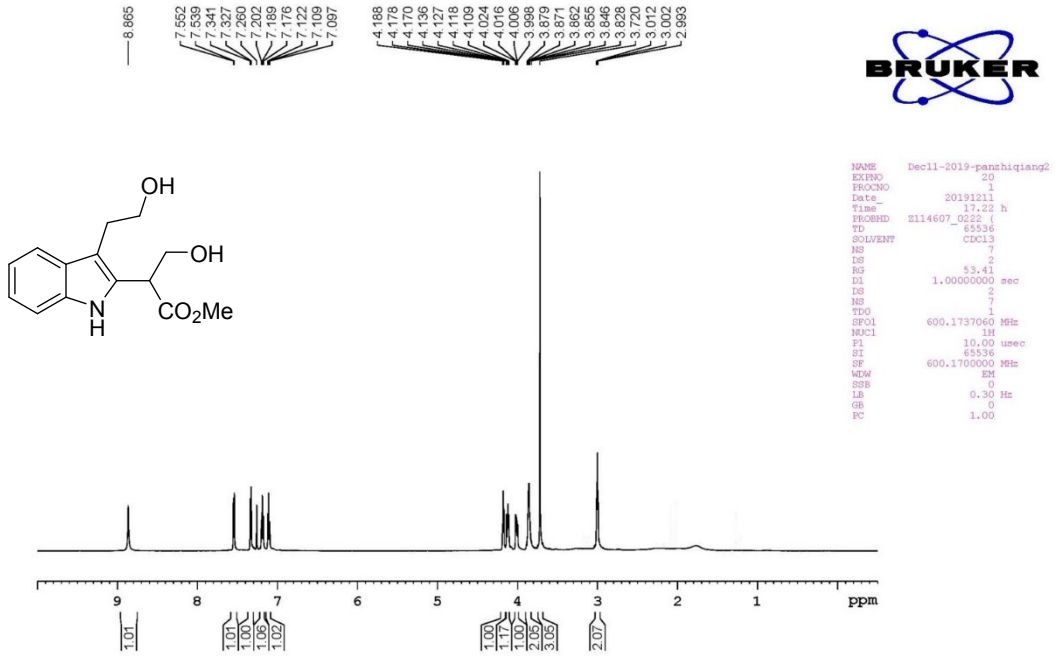


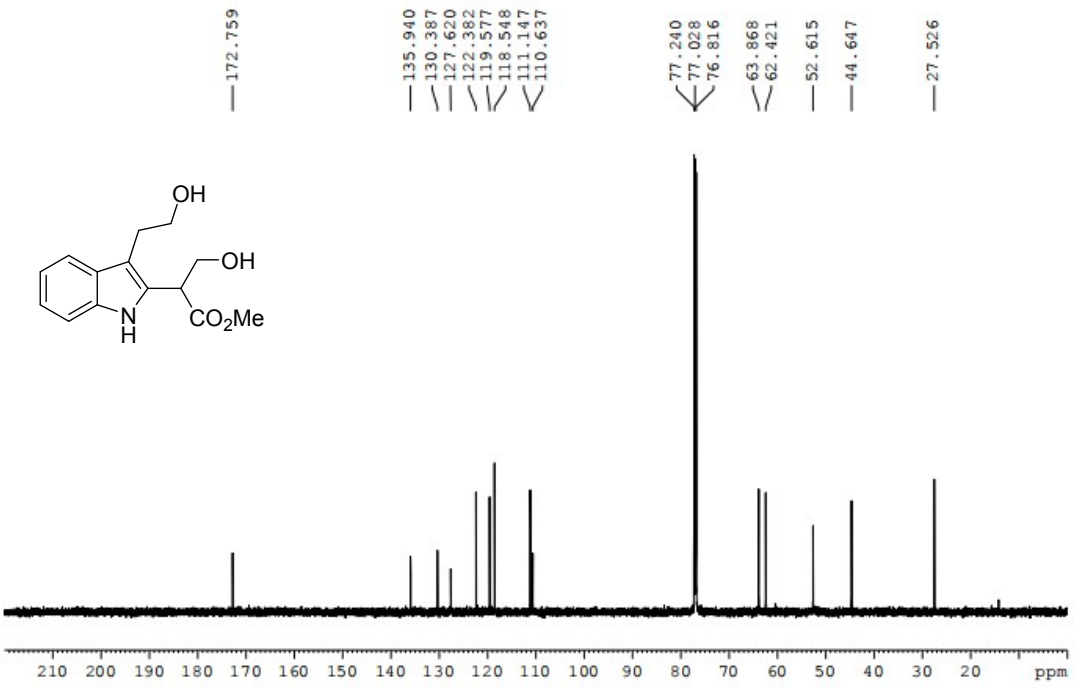
Copies of NMR spectra of **3ak**



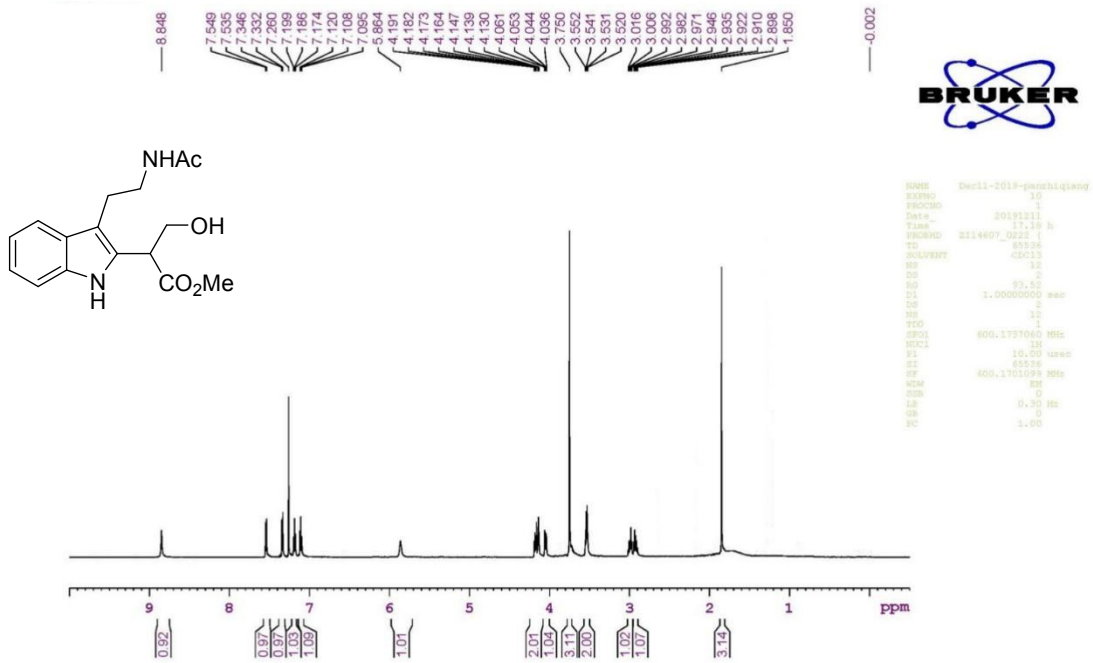


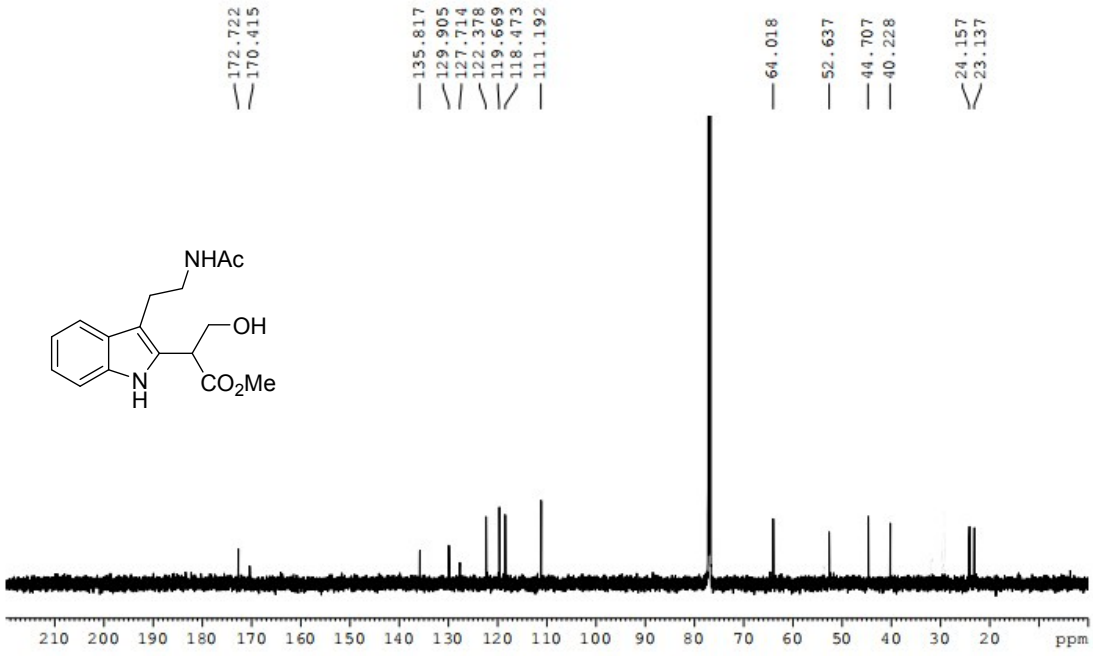
Copies of NMR spectra of **3al**



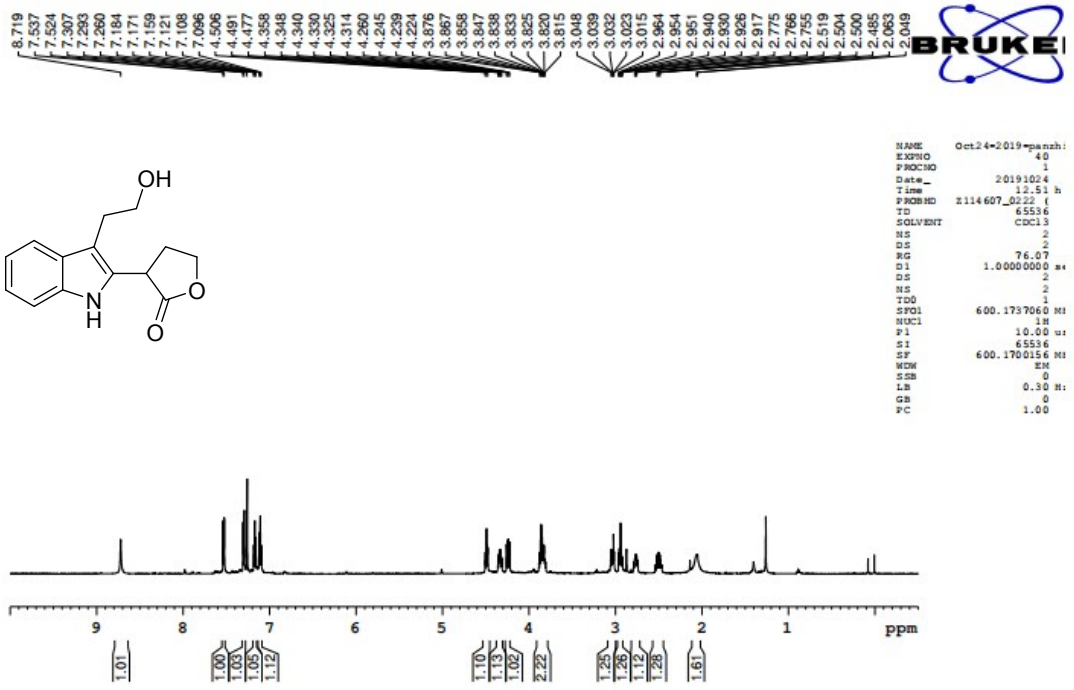


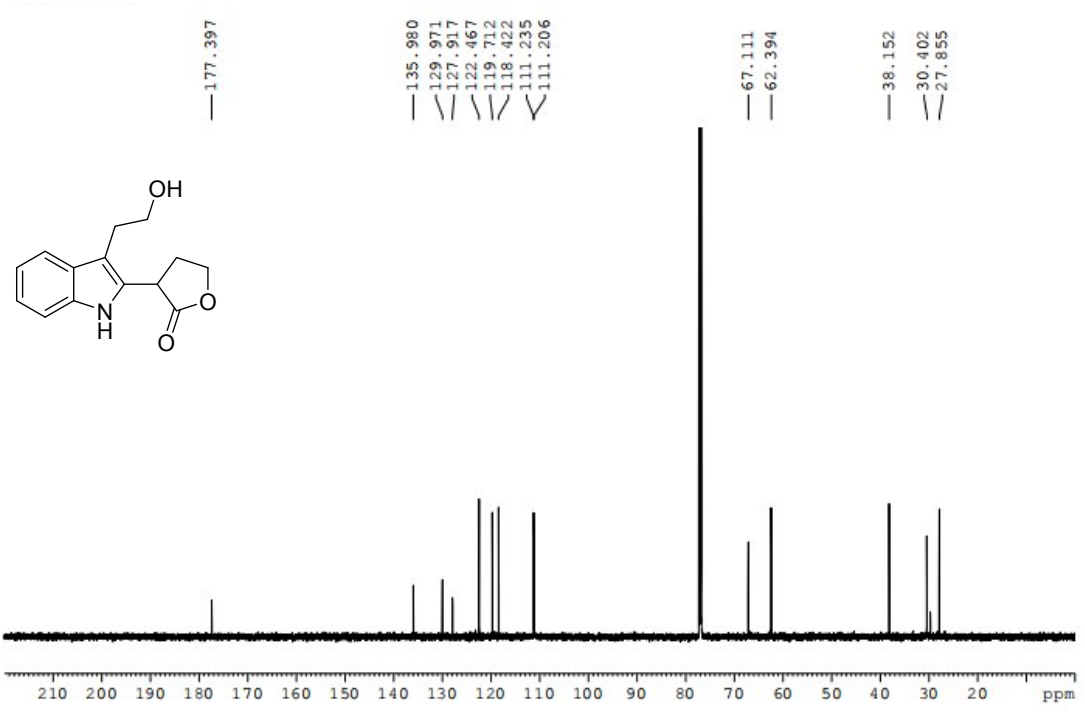
Copy of NMR spectra of **3m**



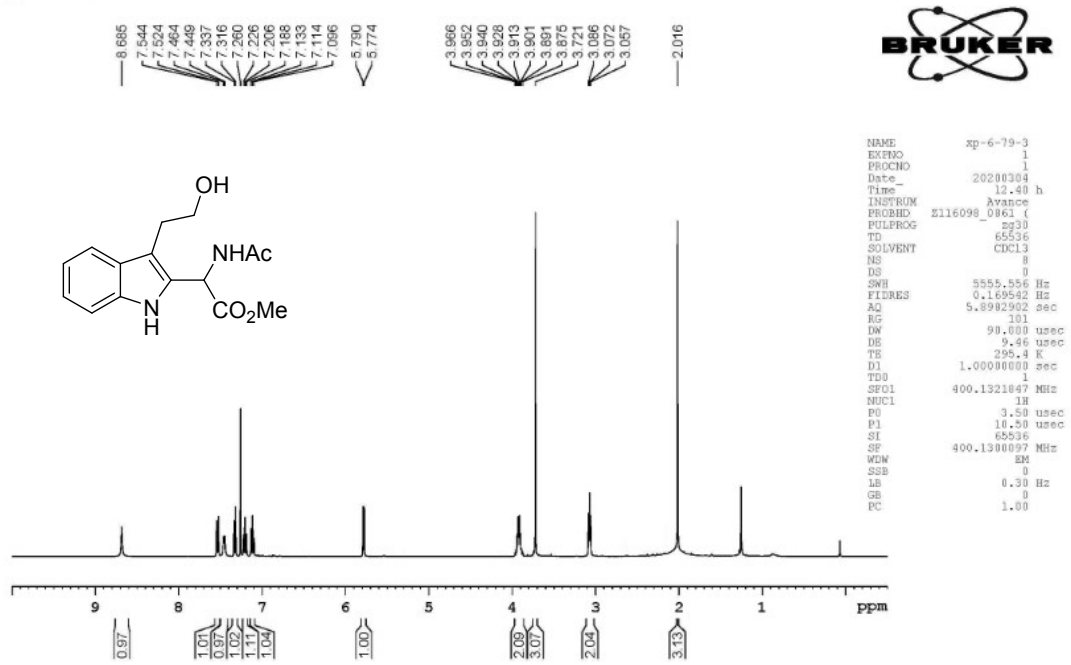


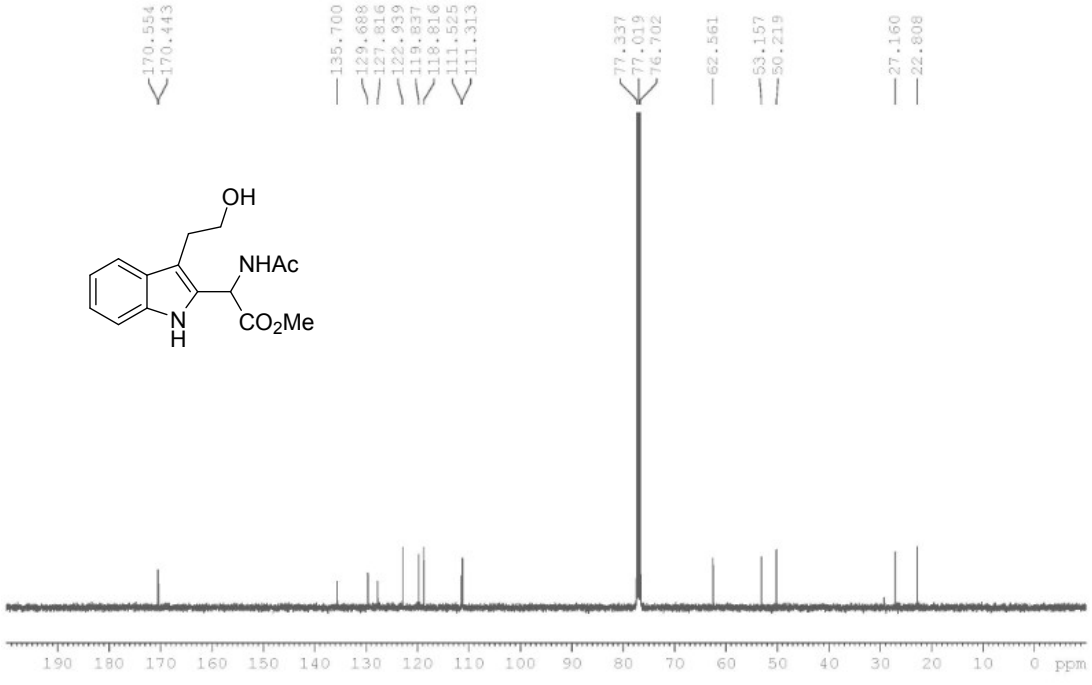
Copies of NMR spectra of **3an**



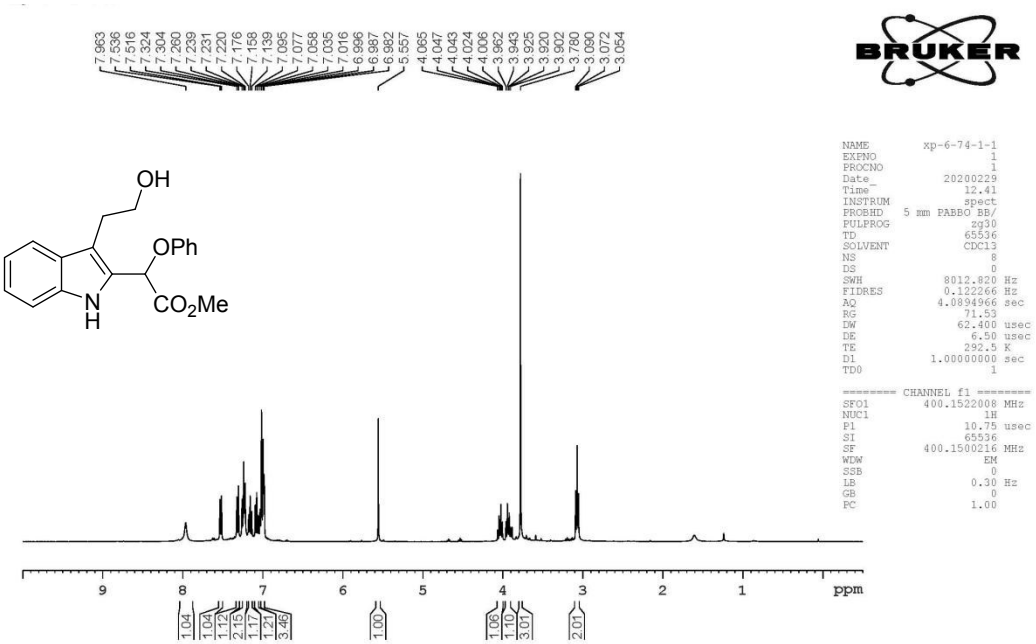


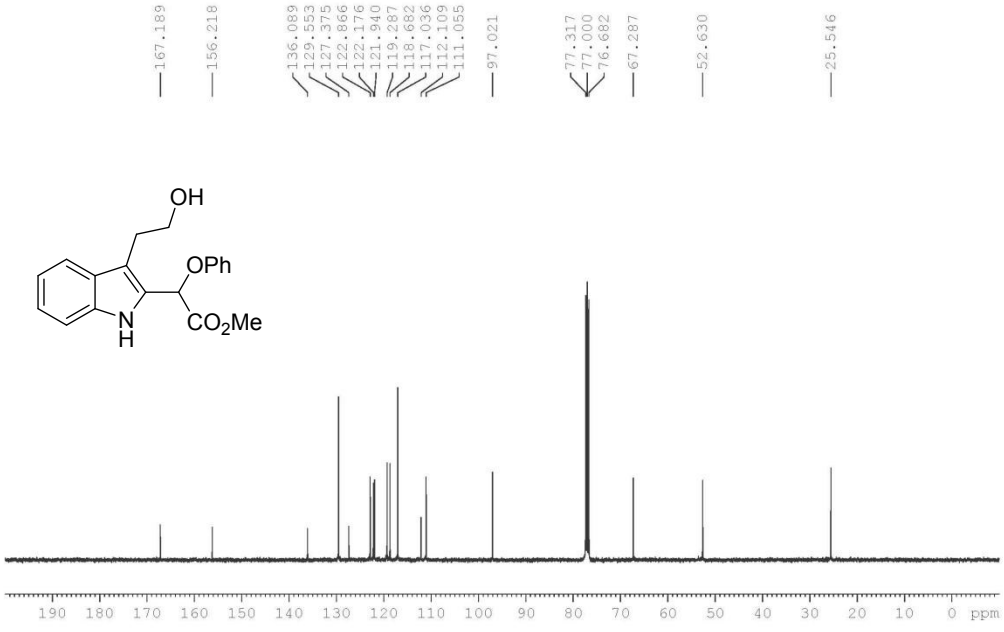
Copies of NMR spectra of **3ao**



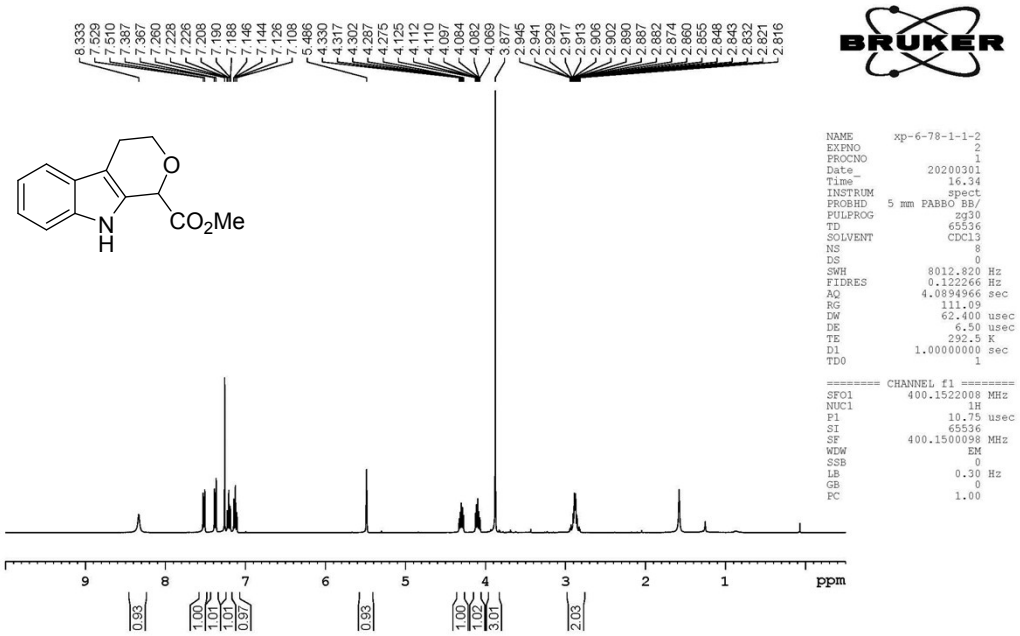


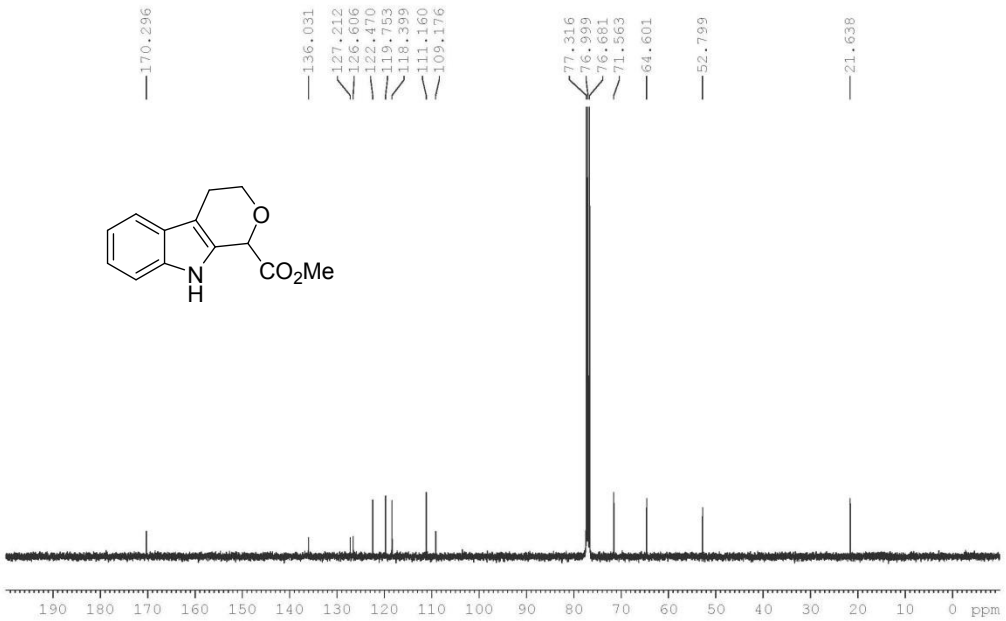
Copies of NMR spectra of **3ap**



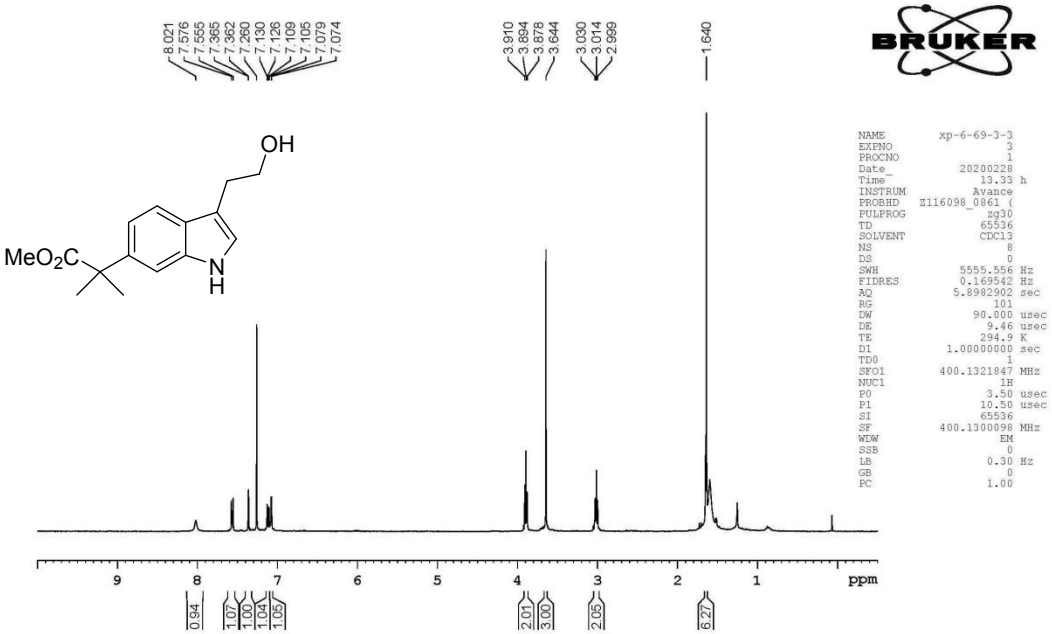


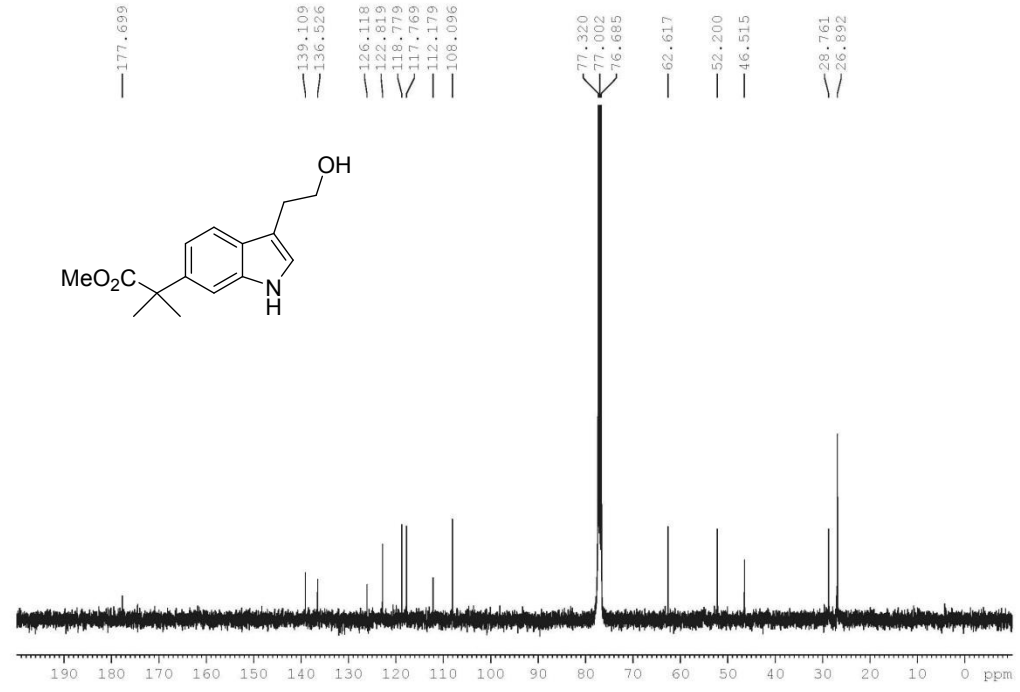
Copies of NMR spectra of **3aq**



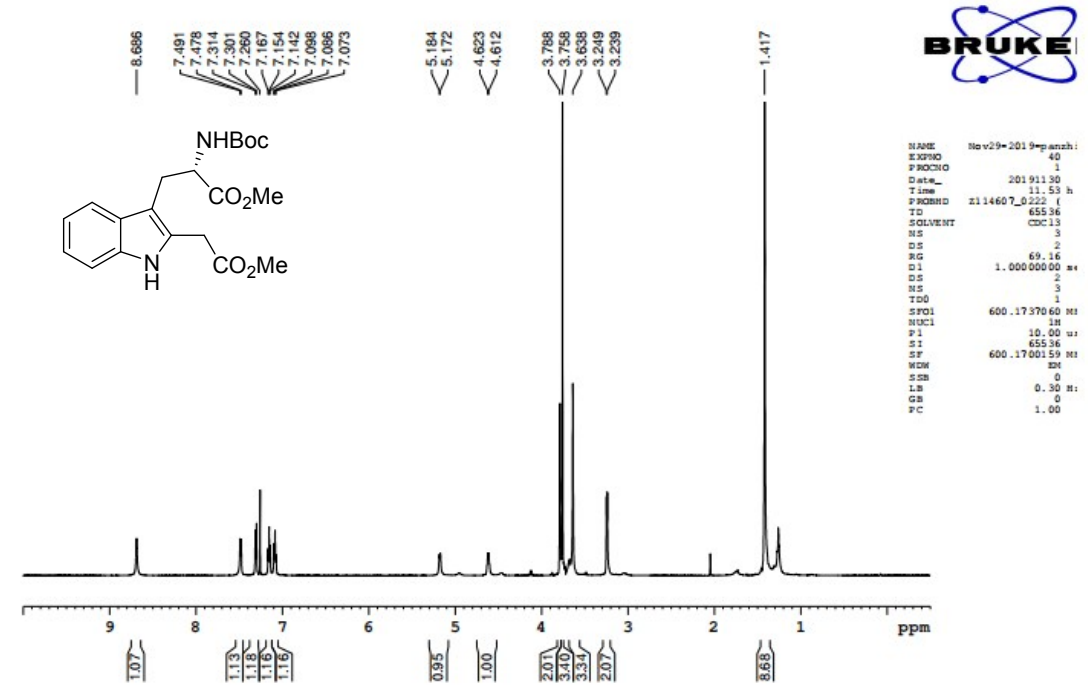


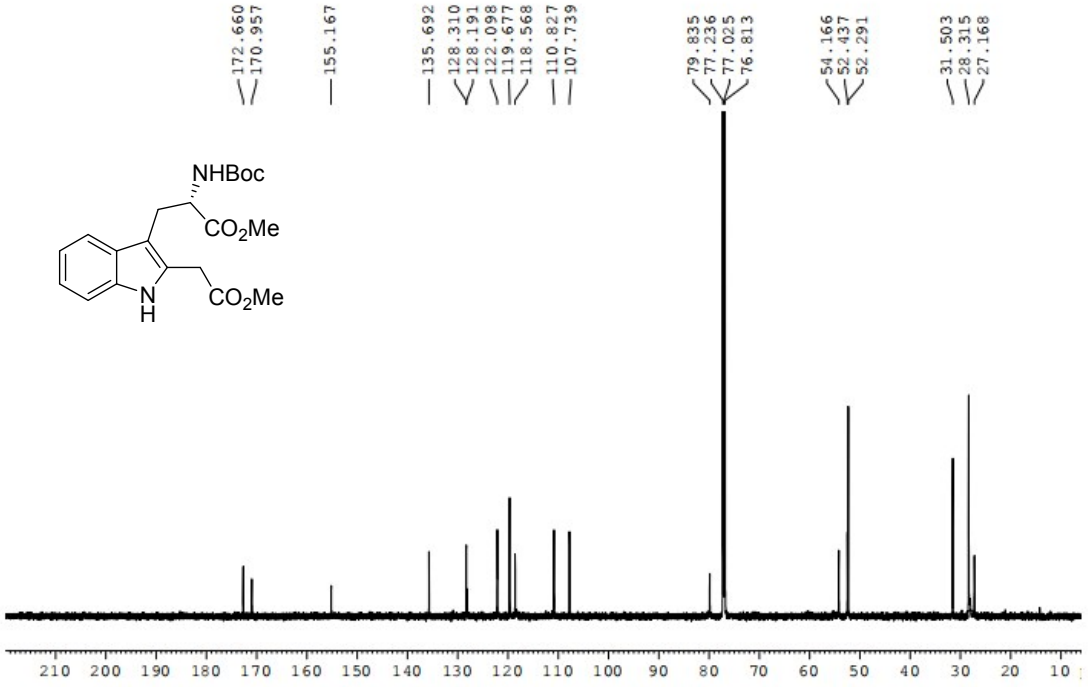
Copies of NMR spectra of **3ar**



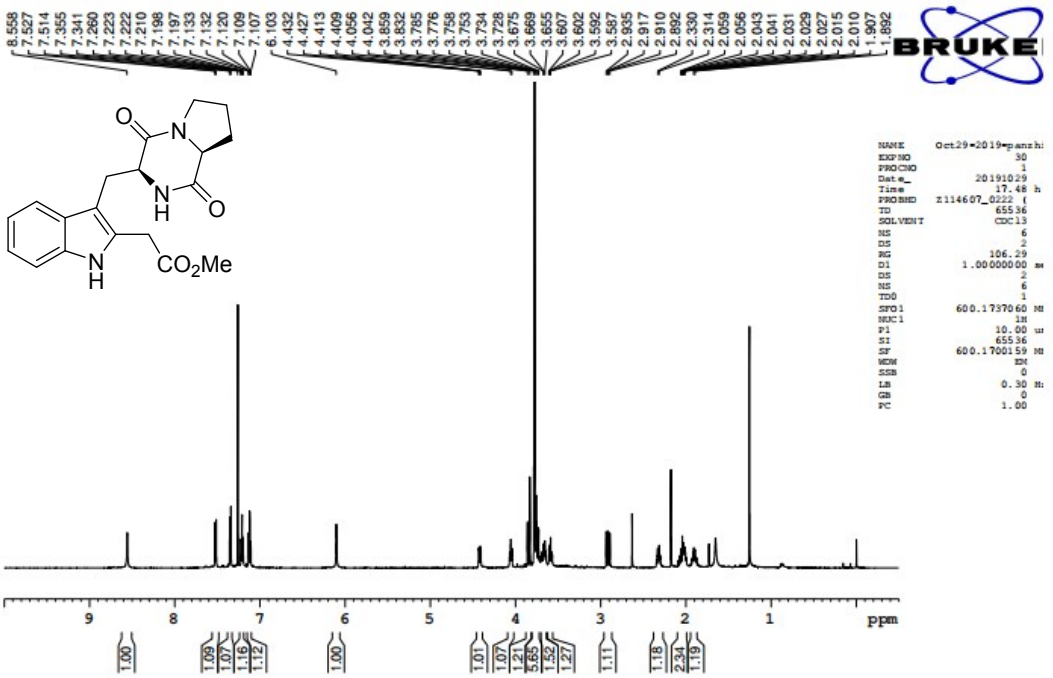


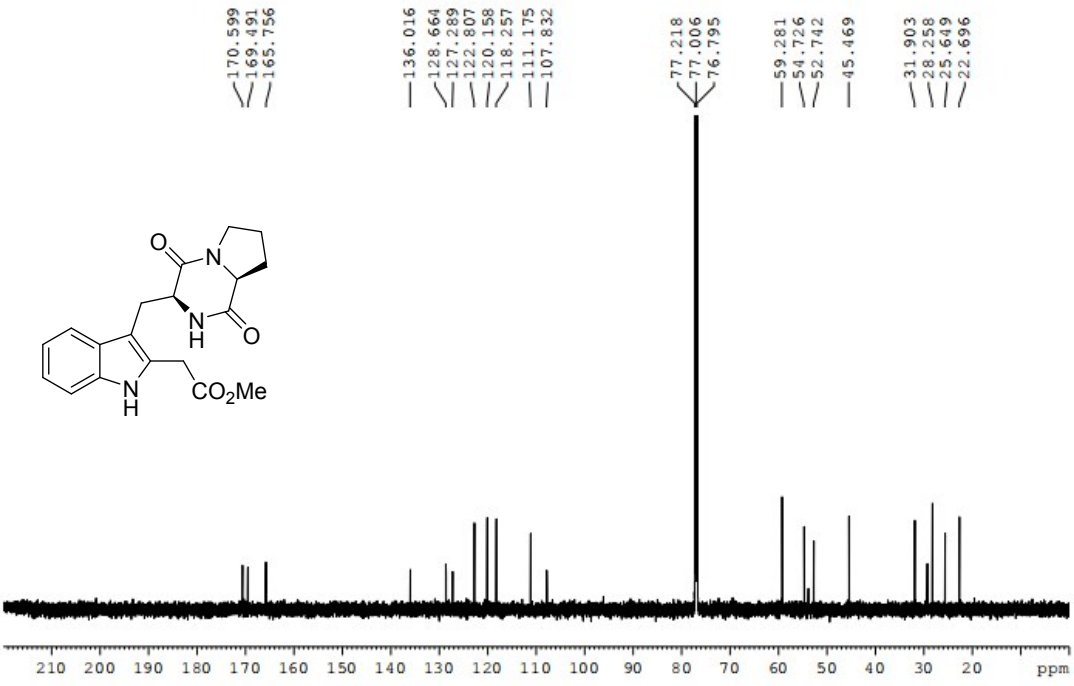
Copies of NMR spectra of **3as**



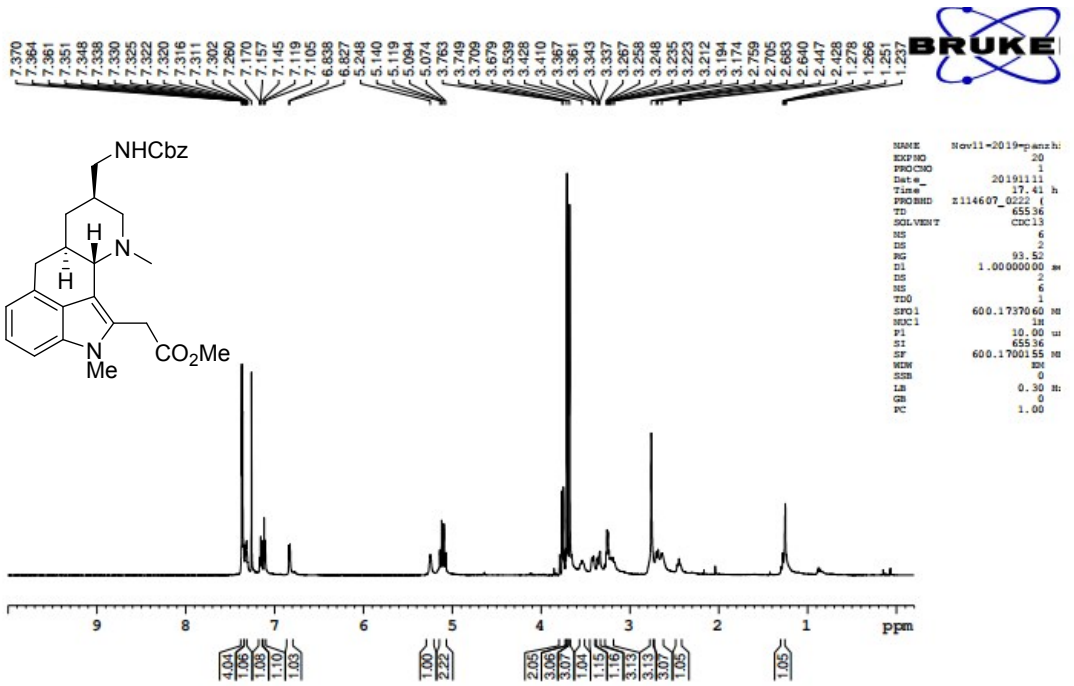


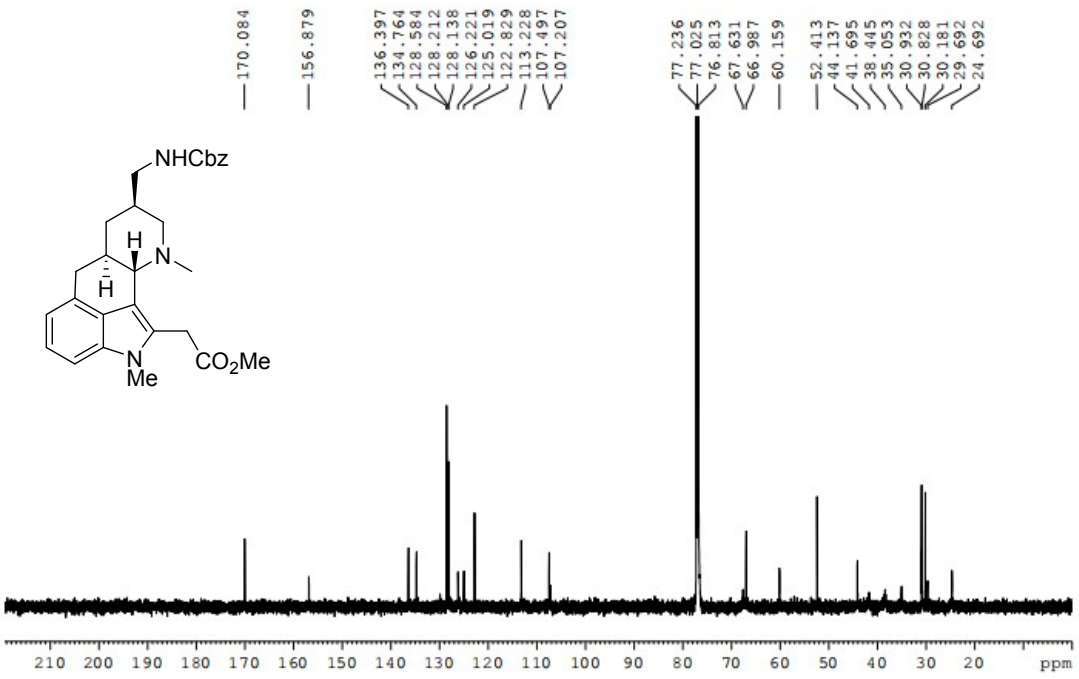
Copies of NMR spectra of **3at**



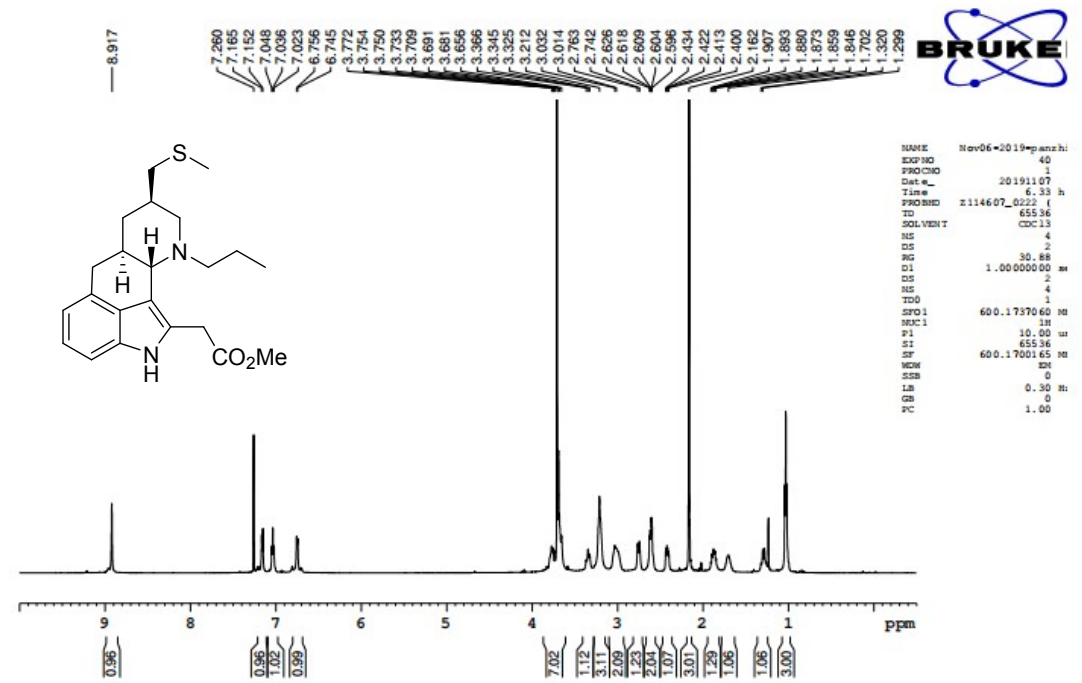


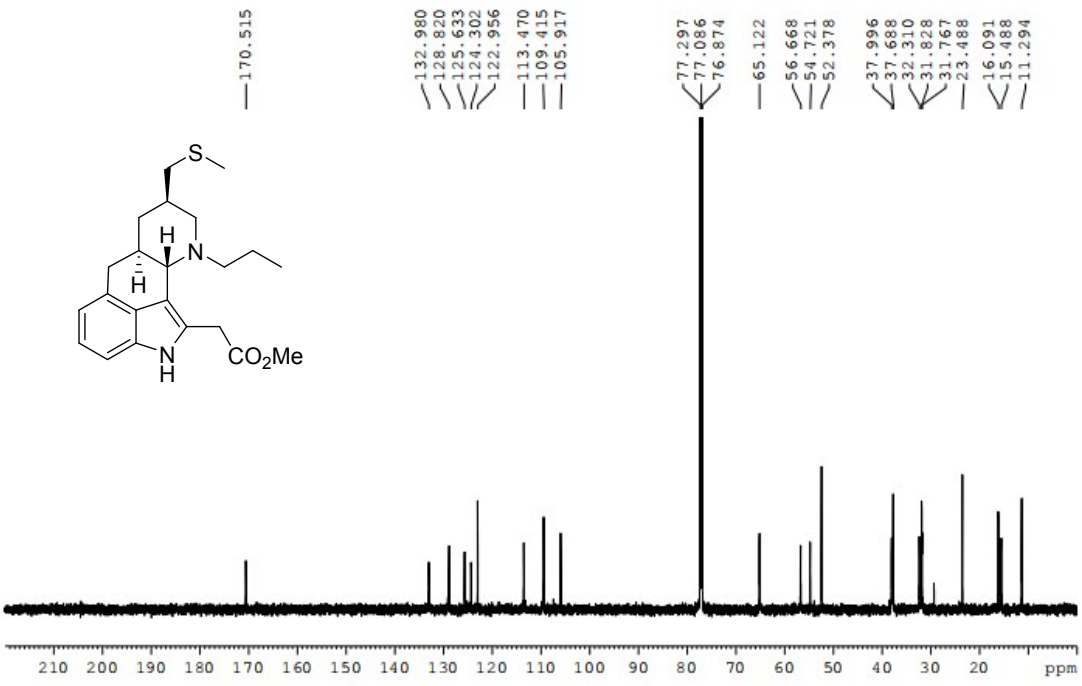
Copies of NMR spectra of **3au**



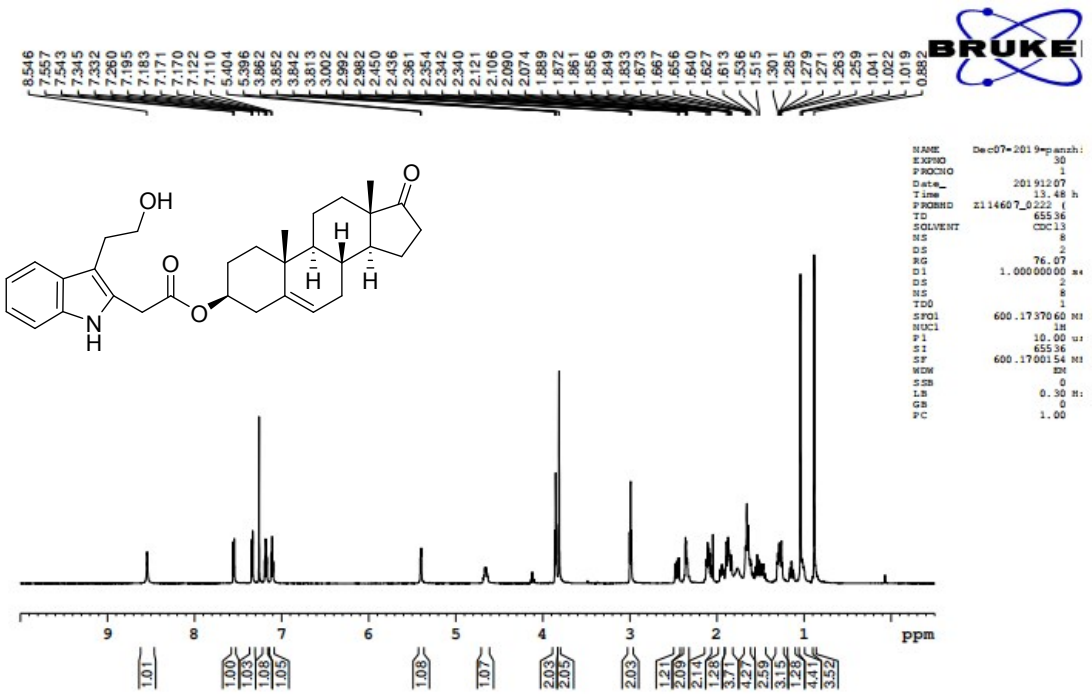


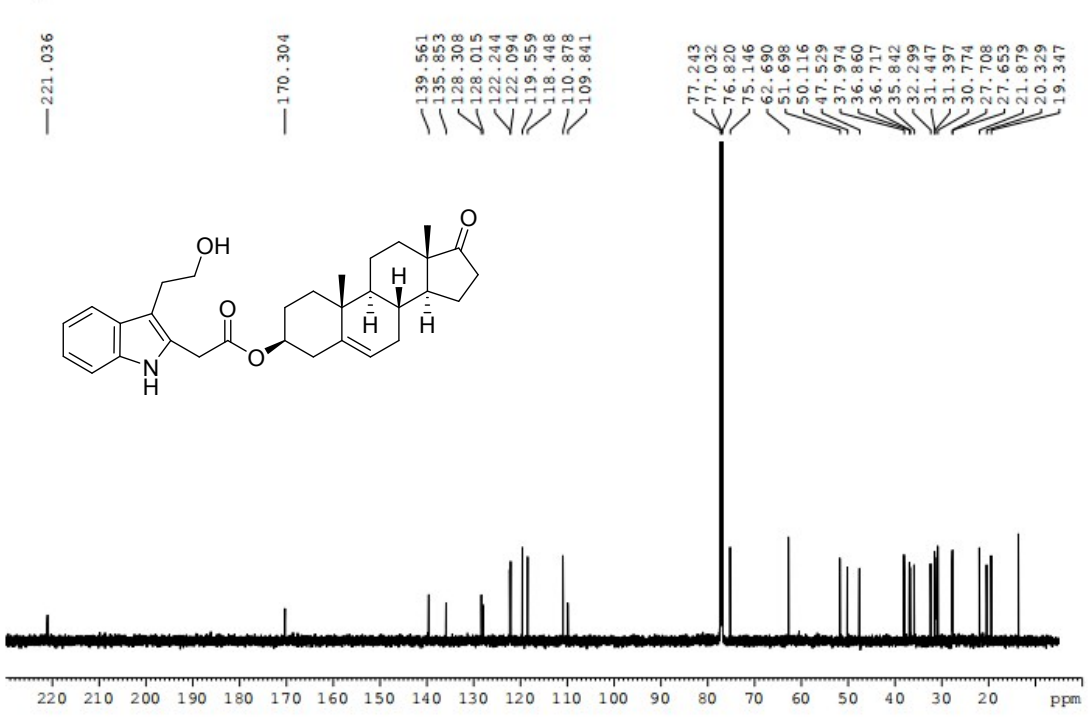
Copies of NMR spectra of **3av**



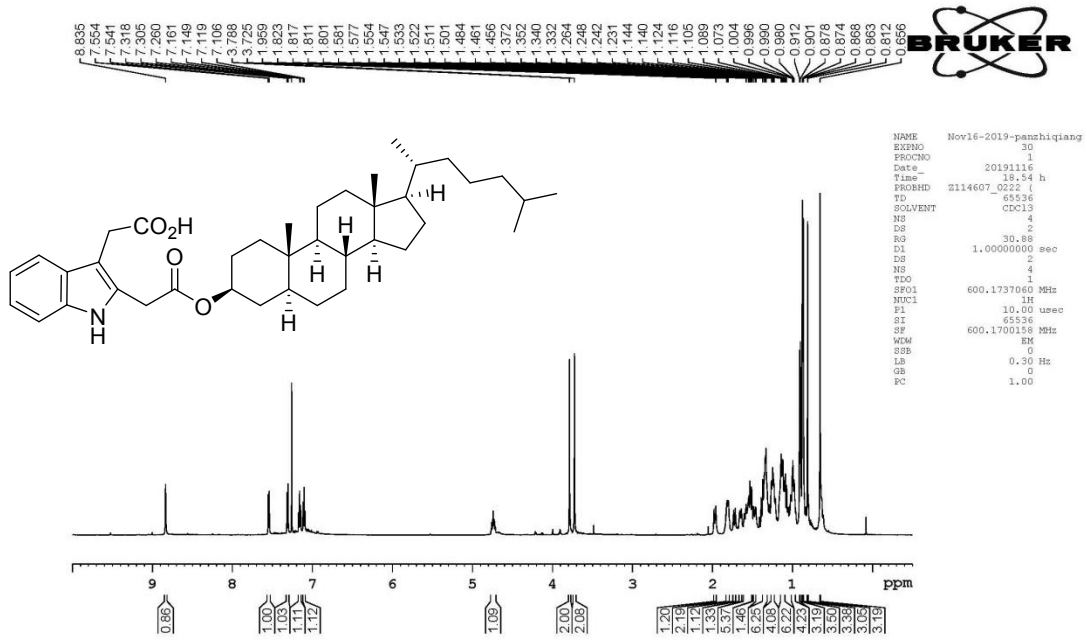


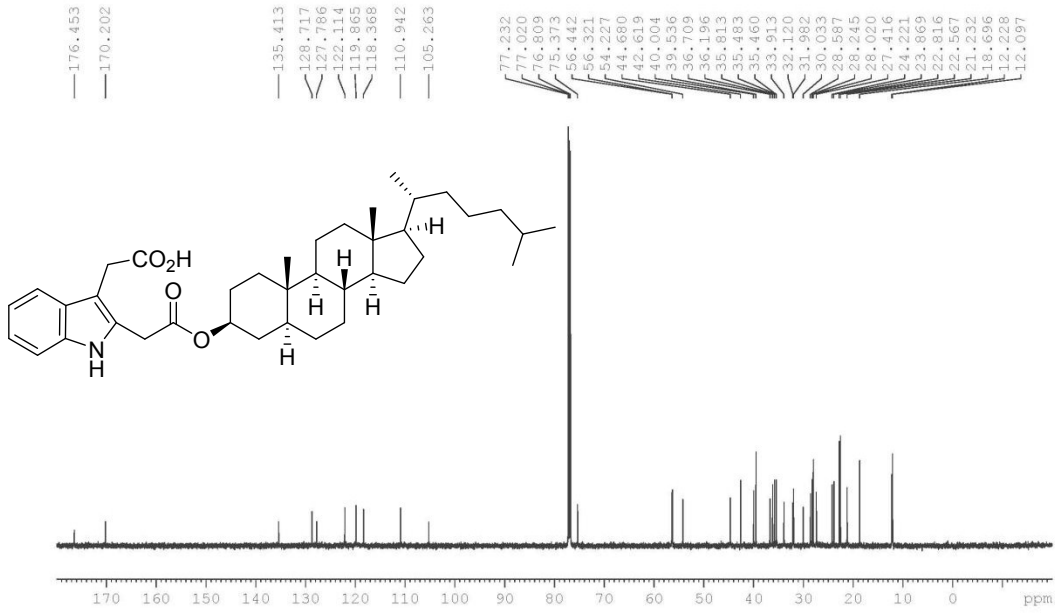
Copies of NMR spectra of **3aw**



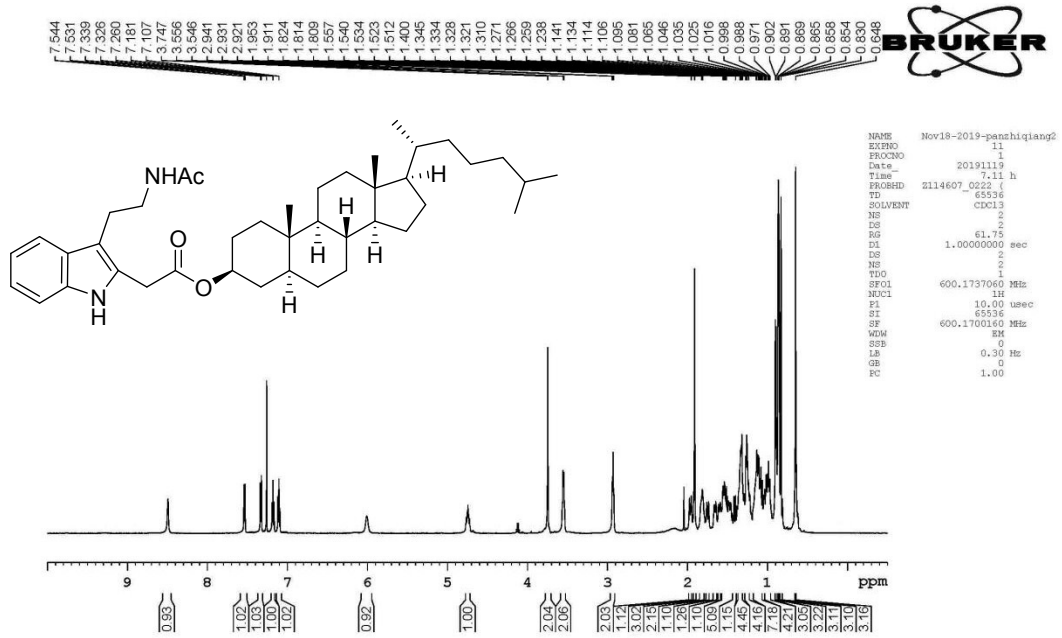


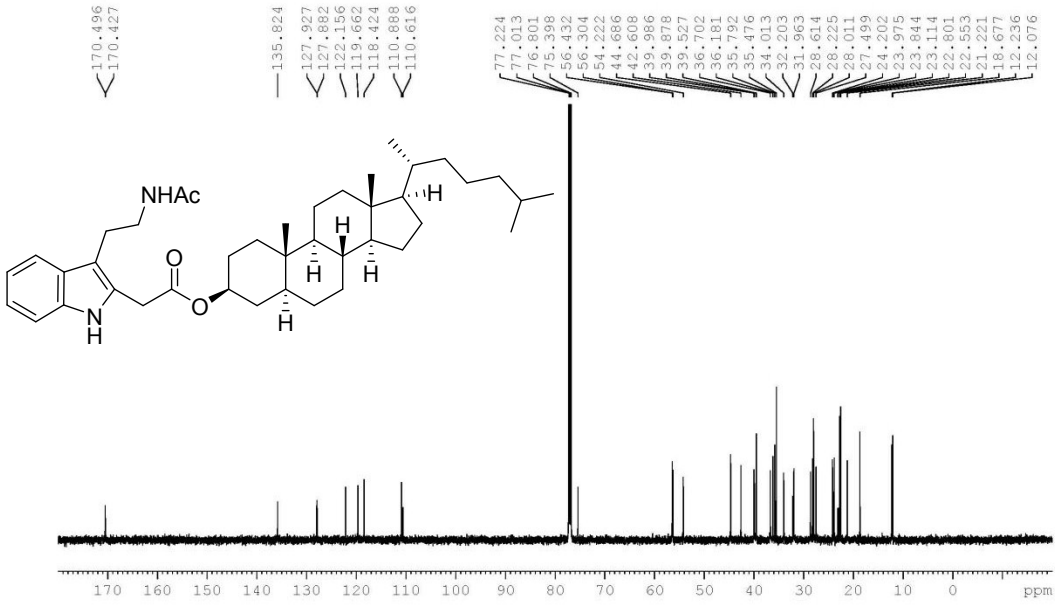
Copies of NMR spectra of **3ax**



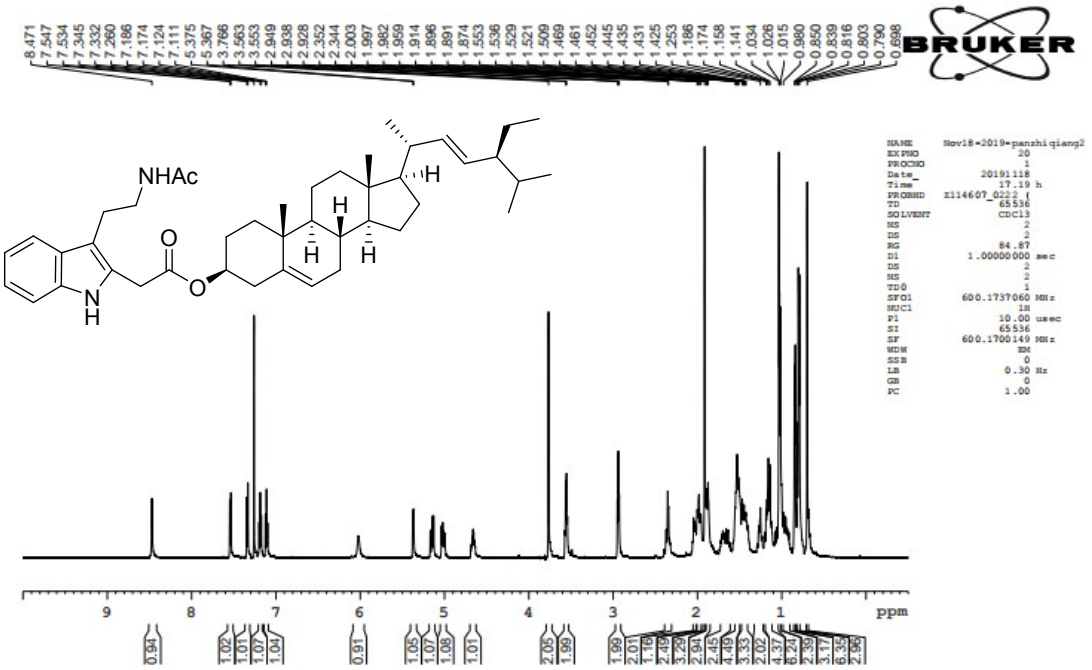


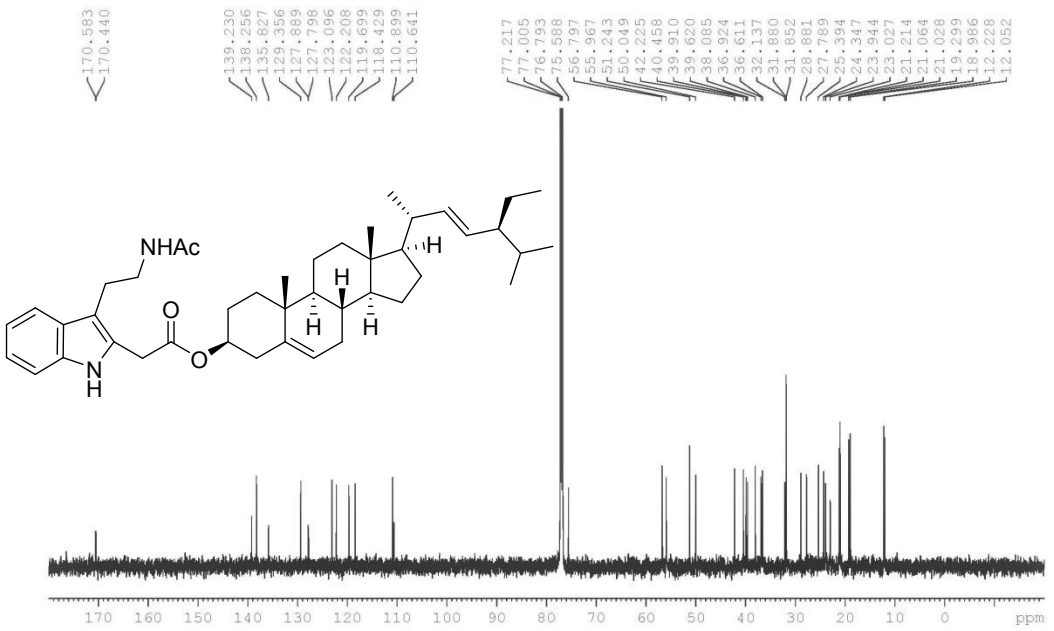
Copies of NMR spectra of **3ay**



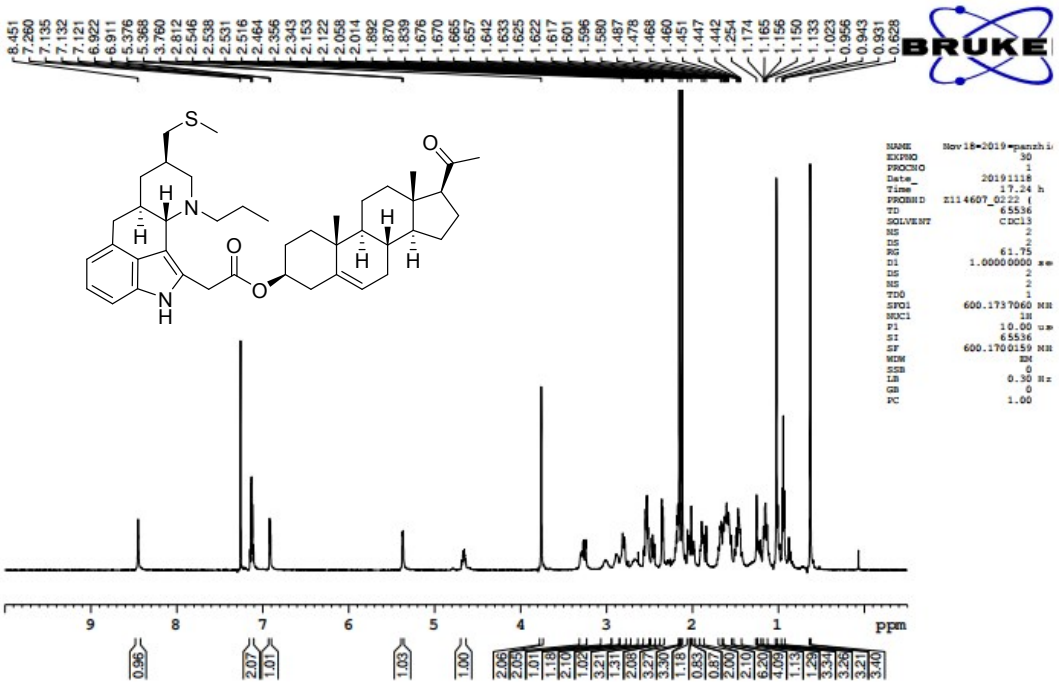


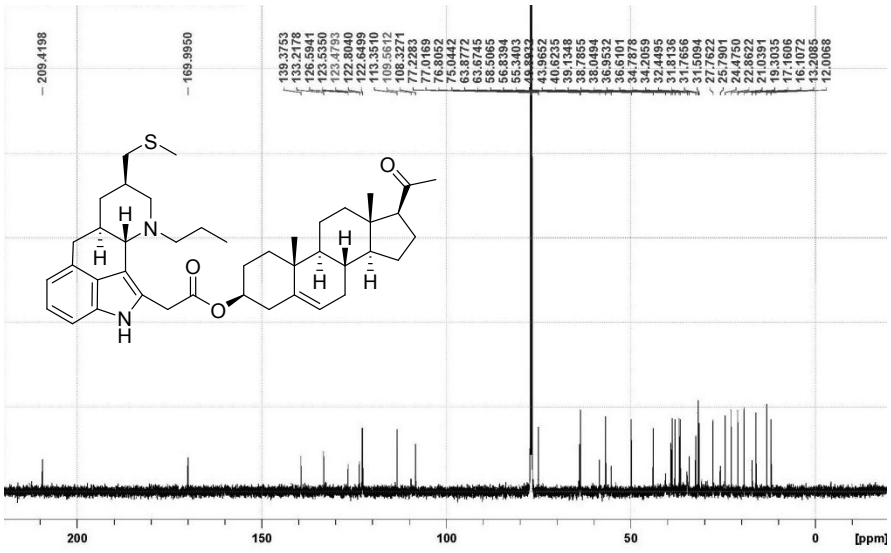
Copies of NMR spectra of **3az**



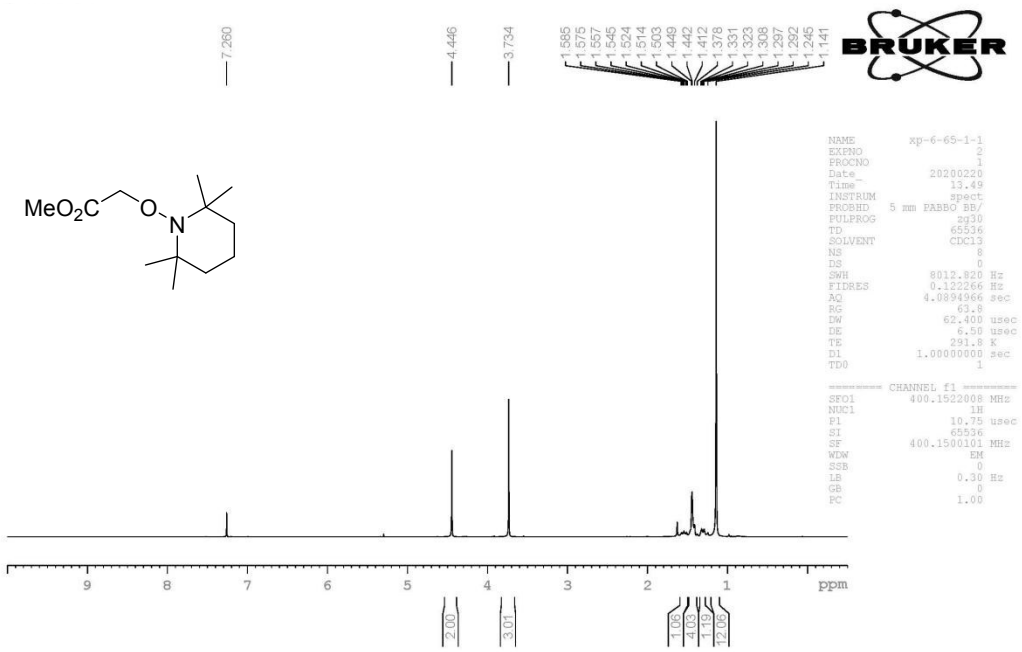


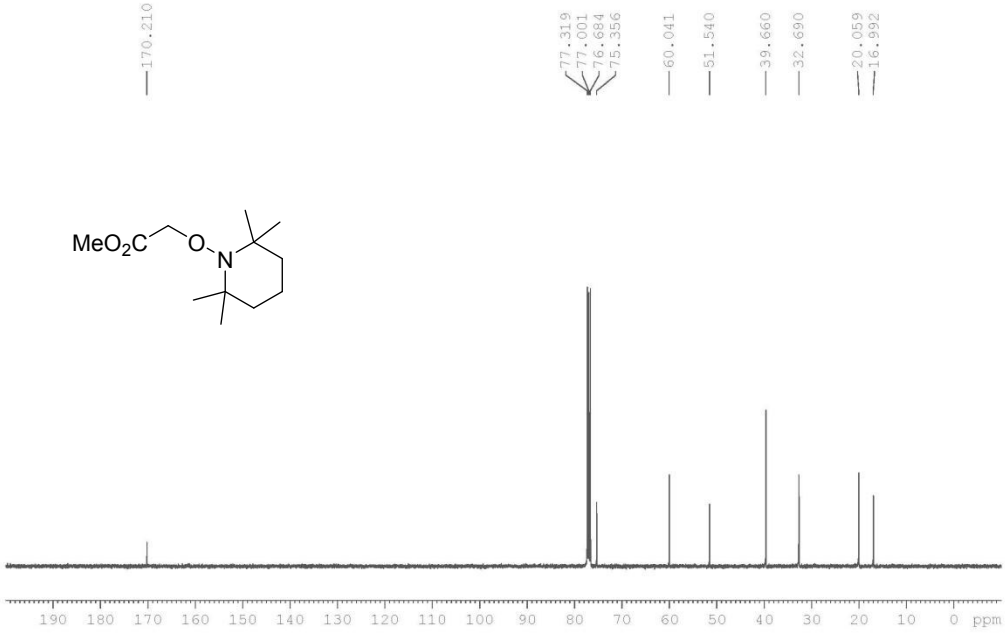
Copies of NMR spectra of **3ba**



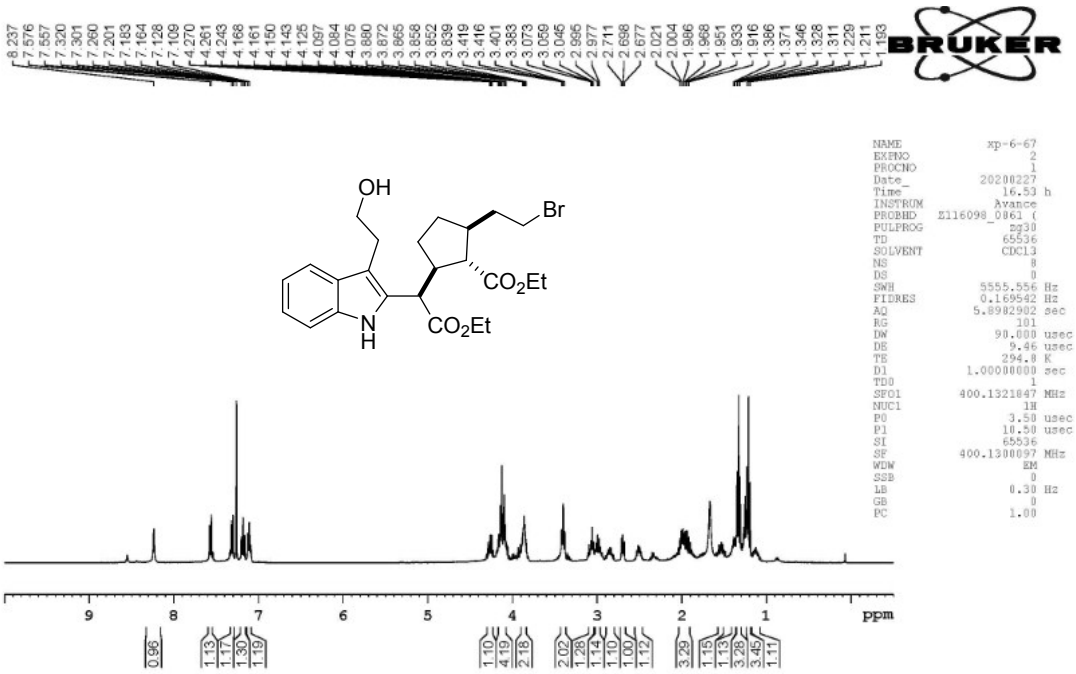


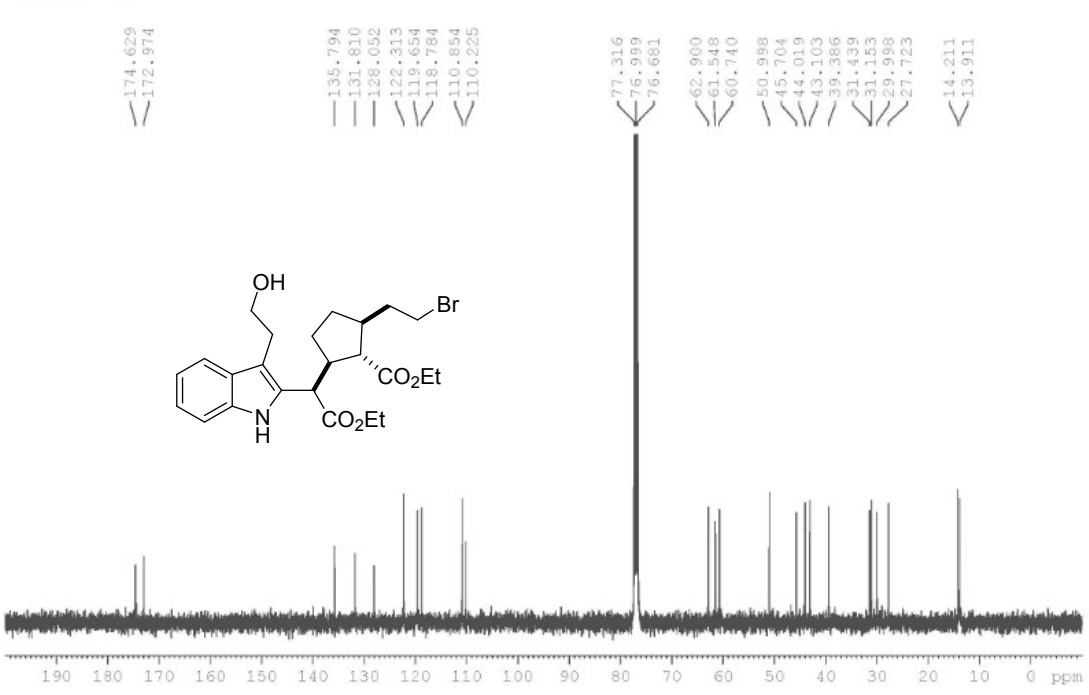
Copies of NMR spectra of **4**

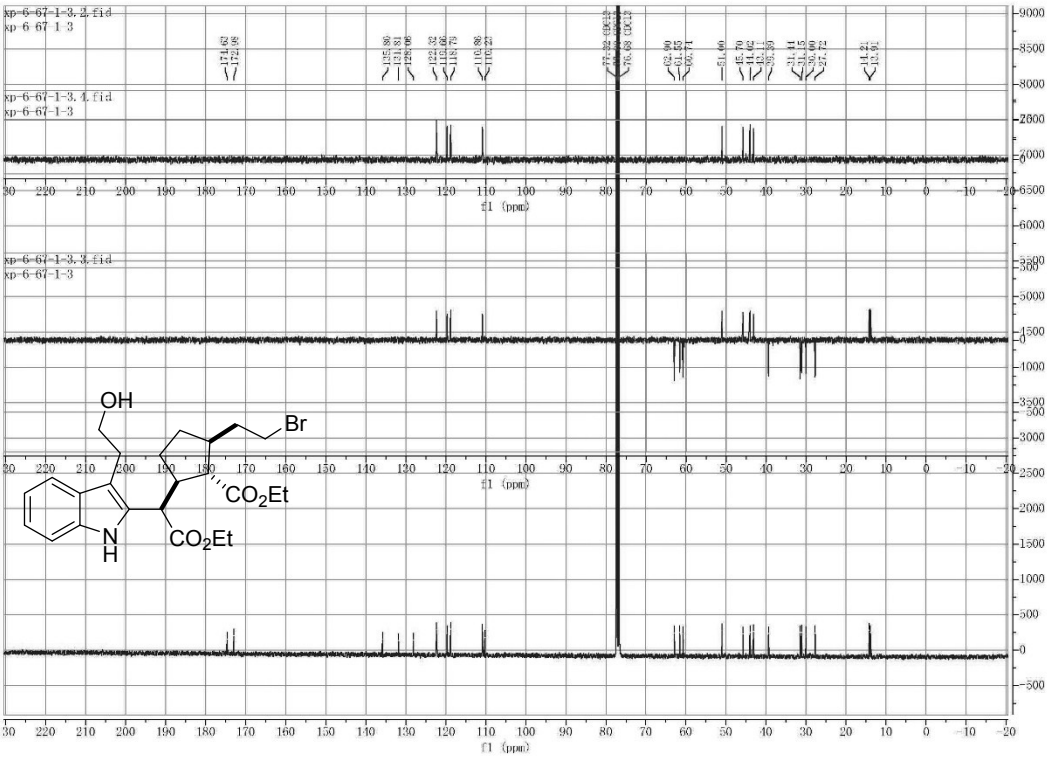




Copies of NMR spectra of **5**



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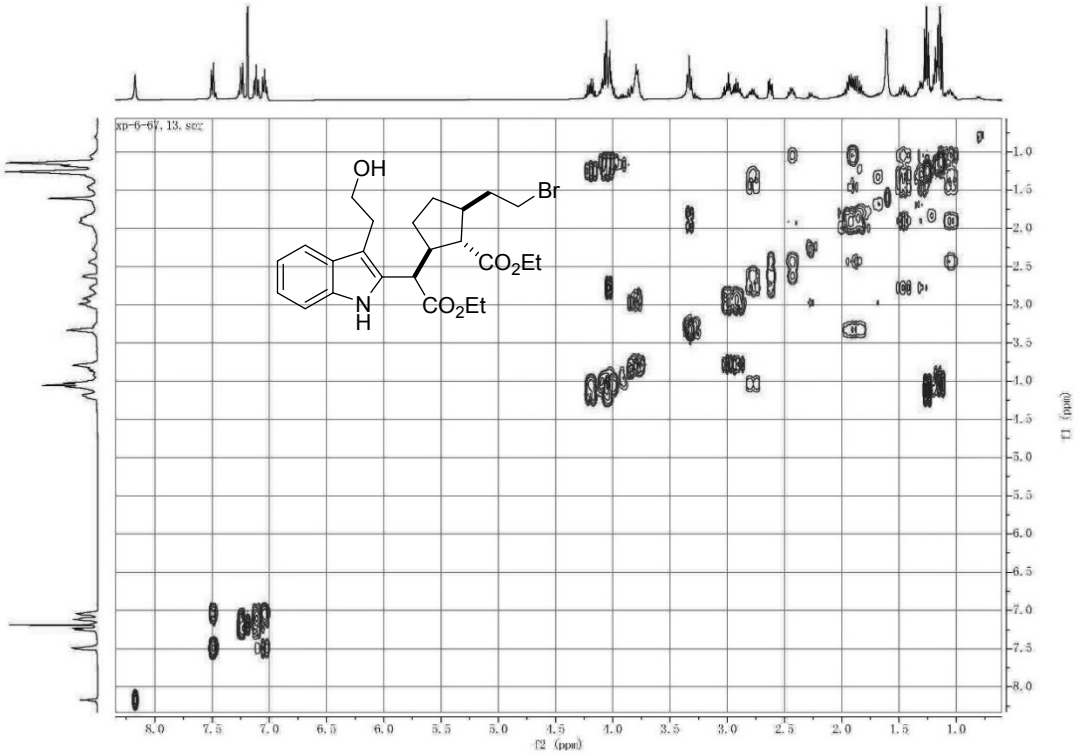
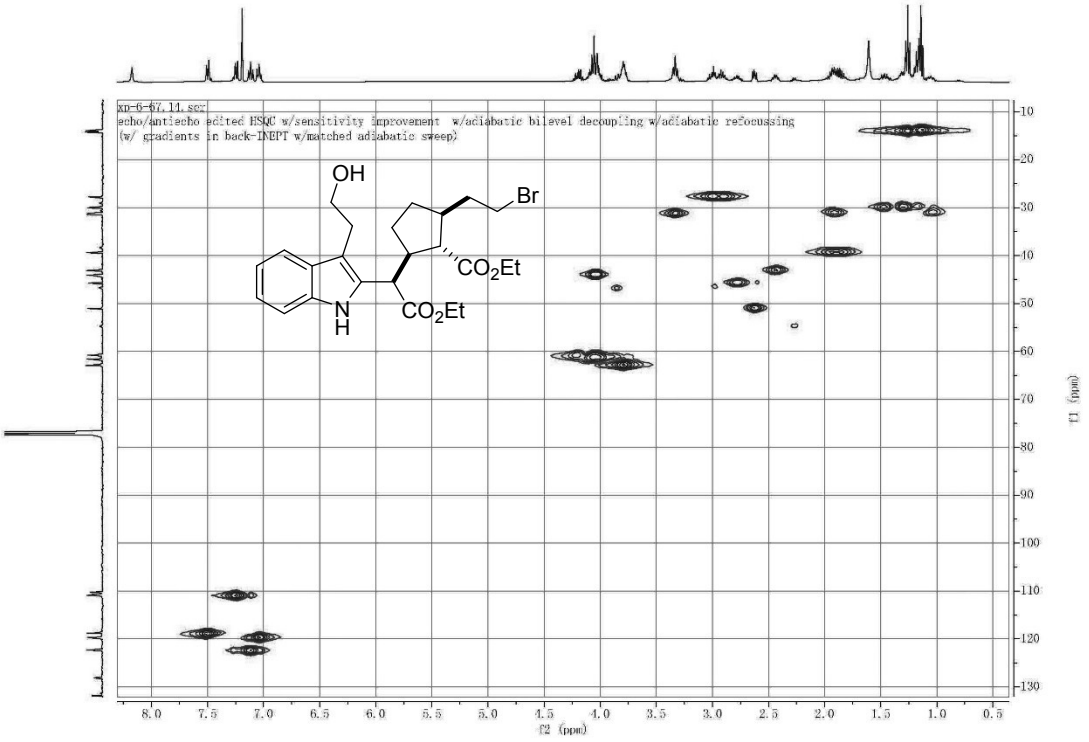
Br
CO2Et
CO2Et
N
H
f1 (ppm)


OH
Br
CO2Et
CO2Et
N
H
f2 (ppm)
f1 (ppm)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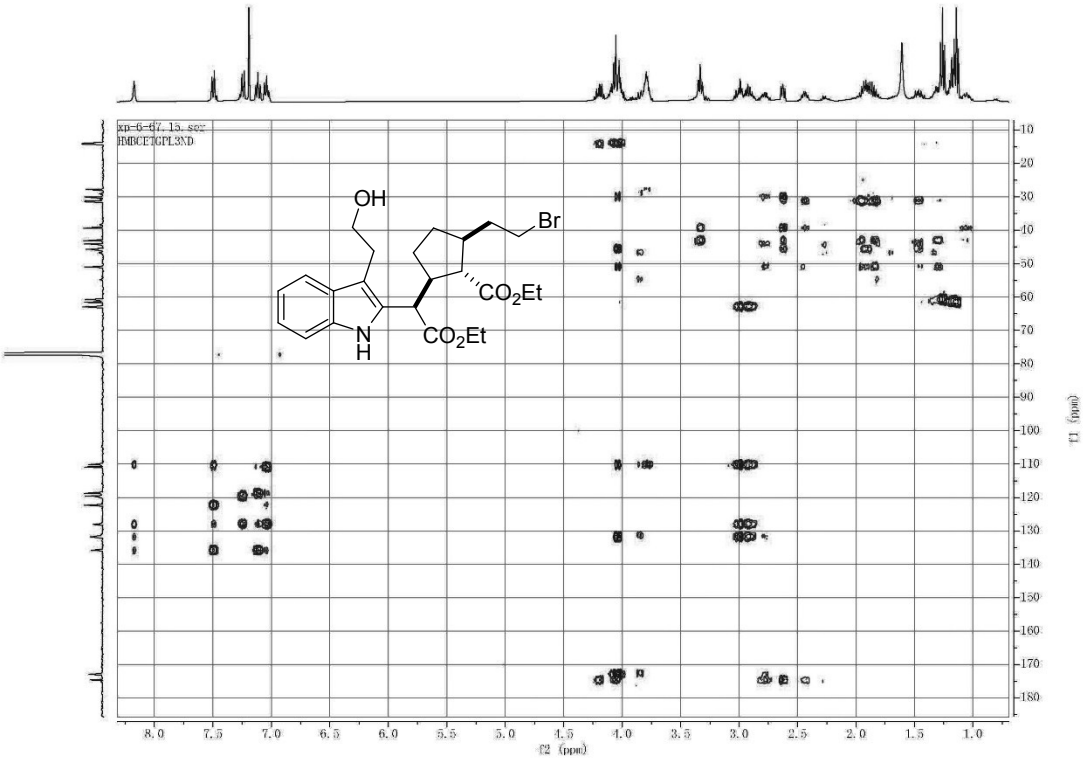
echo/antiecho edited HSQC w/sensitivity improvement w/adiabatic bilevel decoupling w/adiabatic refocussing
(w/ gradients in back-INEPT w/matched adiabatic sweep)
OH
Br
CO2Et
CO2Et
N
H
f2 (ppm)
f1 (ppm)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Br
CO2Et
CO2Et
N
H
f2 (ppm)
f1 (ppm)