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Rhodium-catalyzed three-component C(sp^3)/C(sp^2)−H activation enabled by two-fold directing groups strategy

Fu-Cheng Hou, Jia-Le Zhang, Zi-Rui Wang, and Zhong-Yuan Li*

Anhui Laboratory of Molecule-Based Materials; Key Laboratory of Functional Molecular Solids, Ministry of Education; School of Chemistry and Materials Science, Anhui Normal University, Wuhu, 241002, China.

E-mail: zhongyuanli@ahnu.edu.cn

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1. General

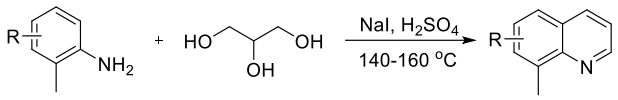
Experimental: Unless otherwise noted, all the reactions were set up under N_2 atmosphere utilizing glassware that was flame-dried and cooled under vacuum. All non-aqueous manipulations were using standard Schlenk techniques. Reactions were monitored using thin-layer chromatography (TLC) on Silica Gel plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Silica-gel flash column chromatography was performed using 200–300 mesh silica gel.

Materials: Unless otherwise indicated, starting catalysts and materials were obtained from Energy Chemicals, Bidepharm and J&K Scientific. Moreover, commercially available reagents were used without additional purification.

Instrumentation: ^{1}H NMR spectra were recorded at 400 MHz NMR spectrometers using TMS as an internal standard, ^{13}C NMR spectra were recorded at 100 MHz spectrometers using TMS as an internal standard, and were fully decoupled by broad band proton decoupling. ^{1}H NMR chemical shifts are reported in parts per million (ppm) and are referenced to residual protium in the NMR solvent (δ 0.00 for TMS). ^{13}C NMR chemical shifts are reported in parts per million (ppm) and are referenced to the carbon resonances of the solvent residual peak (δ 77.16 for $CDCl_3$). Data for ^{1}H NMR and ^{13}C NMR are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz) and integration. High-resolution mass spectra (HRMS) were obtained using ESI-TOF in positive mode.

2. Preparation of Substrates

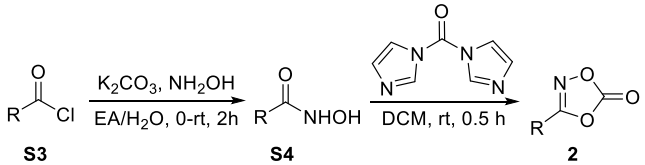
The synthesis of substrates **1**.[1]



S1 **S2** **1**

To a 50 mL one-neck round flask equipped with a stirring bar were added 2-methyl aniline (**S1**, 10 mmol), glycerine (**S2**, 1.2 equiv.), NaI (0.13 mmol) and 80% H_2SO_4 (4.5 mmol) at 140 °C. The reaction mixture was allowed to stir at the same temperature for 6 h. The mixture was neutralized with 25% aq. NaOH solution and pH was adjusted to 9−10. The mixed solution was extracted with ethyl acetate (50 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20 : 1) as eluant to obtain substrates **1**.

The synthesis of substrates **2.**[2]

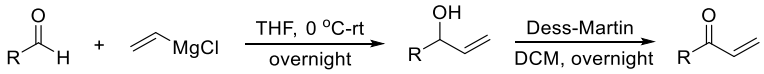


S3 **S4** **2**

To a stirred biphasic mixture of $NH_2OH·HCl$ (10 mmol, 2.0 equiv) in ethyl acetate (40 mL) and H_2O (20 mL) was added K_2CO_3 (10 mmol, 2.0 equiv). The solution was cooled to 0 °C followed by dropwise addition of acid chloride (5 mmol), and then warmed to room temperature and stirred for additional 1.5 h. The reaction mixture was extracted with ethyl acetate (25 mL × 2) and dried over anhydrous Na_2SO_4. Dried over anhydrous Na_2SO_4, filtration and removed all of organic solvent. The crude product (**S4**) was directly used for the next step without purification.

To a stirred mixture of hydroxamic acid (**S4**) in CH_2Cl_2 (50 mL) was added 1,1'-carbonyldiimidazole (5.5 mmol, 1.1 equiv). The residue was stirred for 30 min. The reaction was quenched with 1 M HCl (15 mL) and extracted with CH_2Cl_2 (25 mL × 2). The combined organic phase was washed with H_2O (50 mL), dried over anhydrous Na_2SO_4 and removed all of organic solvent to afford crude 3-aryl substituted 1,4,2-dioxazol-5-ones. The crude product was purified through a short silica gel chromatography quickly (petroleum ether/ethyl acetate = 20 : 1) to get pure products of **2**.

The synthesis of substrates 3.[3]



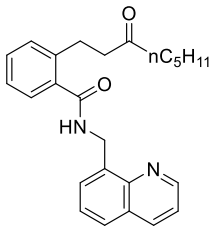
To a 50 mL of Schlenk flask equipped with a magnetic stirring bar was evacuated and backfilled with nitrogen for three times. Then the flask was added aldehyde (3 mmol) in dry THF (5 mL) and cooled to 0 °C in an ice-water bath. After that, vinyl magnesium chloride (2.0 M solution in THF, 3.6 mmol) was added dropwise. The mixture was warmed to room temperature and stirred overnight. Saturated NH_4Cl solution (20 mL) was added to quench the reaction and the aqueous layer was extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was dissolved in CH_2Cl_2 (10 mL) and Dess-Martin periodinane (4.0 mmol) was added. The mixture was stirred at room temperature for overnight. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel with petroleum ether/ethyl acetate (50 : 1) as eluant to get the desired products **3**.

3. General procedure for rhodium-catalyzed three-component C(sp^3)/C(sp^2)−H activation enabled by two-fold directing groups

To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added substrate **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and acid (**A6**, 0.3 equiv.) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1** (0.2 mmol), **3** (1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give the corresponding products **4**.

4. Characterization of products

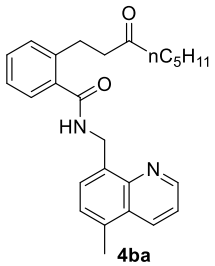
2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4aa

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2a** (65.7 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), **A6** (15.4 mg, 0.06 mmol) and $AgSbF_6$ (6.8 mg, 0.02 mmol) afforded **4aa** (52.6 mg, 68% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.3, 1.8 Hz, 1H), 8.19 (dd, J = 8.3, 1.9 Hz, 1H), 7.82 (dd, J = 7.0, 1.5 Hz, 1H), 7.78 (dd, J = 8.3, 1.6 Hz, 1H), 7.56–7.47 (m, 2H), 7.44 (dd, J = 8.3, 4.3 Hz, 1H), 7.33–7.25 (m, 2H), 7.21–7.13 (m, 2H), 5.17 (d, J = 6.1 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.18 (t, J = 7.5 Hz, 2H), 1.50–1.40 (m, 2H), 1.32–1.22 (m, 2H), 1.22–1.12 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.7, 149.8, 147.0, 139.7, 136.8, 136.7, 136.0, 130.4, 130.0, 129.7, 128.6, 127.9, 127.2, 126.7, 126.3, 121.4, 44.4, 42.8, 41.7, 31.5, 27.8, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{28}N_2O_2$ $[M+H]^+$ 389.2224; found 389.2239.

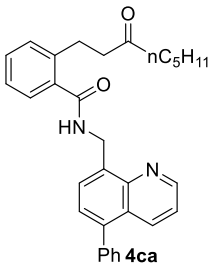
2-(3-oxooctyl)-*N*-((5-methylquinolin-8-yl)methyl)benzamide



4ba

By following the general procedure, the reaction of **1b** (31.4 mg, 0.2 mmol) with **2a** (65.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.3 mg, 0.005 mmol), **A6** (15.8 mg, 0.06 mmol) and $AgSbF_6$ (7.1 mg, 0.02 mmol) afforded **4ba** (45.2 mg, 56% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 4.1, 1.8 Hz, 1H), 8.36 (dd, J = 8.5, 1.8 Hz, 1H), 7.70 (d, J = 7.1 Hz, 1H), 7.49–7.42 (m, 2H), 7.34 (dd, J = 7.1, 1.0 Hz, 1H), 7.31–7.25 (m, 2H), 7.20–7.12 (m, 2H), 5.12 (d, J = 6.1 Hz, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.68 (s, 3H), 2.64 (t, J = 7.6 Hz, 2H), 2.17 (t, J = 7.5 Hz, 2H), 1.49–1.40 (m, 2H), 1.30–1.20 (m, 2H), 1.21–1.13 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.7, 149.3, 147.3, 139.7, 136.9, 134.7, 134.1, 133.2, 130.5, 129.9, 129.5, 128.1, 127.2, 127.0, 126.3, 120.9, 44.4, 42.8, 41.8, 31.5, 27.9, 23.5, 22.6, 18.7, 14.1; **HRMS** (ESI) Calcd for $C_{26}H_{30}N_2O_2$ $[M+H]^+$ 403.2380; found 403.2399.

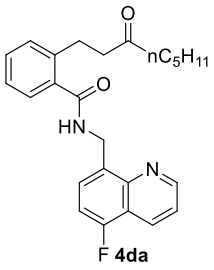
2-(3-oxooctyl)-*N*-((5-phenylquinolin-8-yl)methyl)benzamide



4ca

By following the general procedure, the reaction of **1c** (43.8 mg, 0.2 mmol) with **2a** (65.9 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (2.9 mg, 0.005 mmol), **A6** (15.5 mg, 0.06 mmol) and $AgSbF_6$ (8.1 mg, 0.02 mmol) afforded **4ca** (63.1 mg, 68% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.2, 1.8 Hz, 1H), 8.28 (dd, J = 8.6, 1.9 Hz, 1H), 7.86 (d, J = 7.3 Hz, 1H), 7.56–7.43 (m, 7H), 7.39 (dd, J = 8.6, 4.2 Hz, 1H), 7.33 (dd, J = 7.5, 1.6 Hz, 1H), 7.31–7.27 (m, 1H), 7.22–7.14 (m, 2H), 5.20 (d, J = 6.1 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H), 2.23 (t, J = 7.5 Hz, 2H), 1.52–1.42 (m, 2H), 1.28–1.21 (m, 2H), 1.21–1.13 (m, 2H), 0.84 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.7, 149.6, 147.2, 140.6, 139.8, 139.2, 136.8, 135.3, 135.1, 130.5, 130.1 (2C), 130.0, 129.1, 128.6 (2C), 127.9, 127.22, 127.18, 127.1, 126.3, 121.3, 44.5, 42.8, 41.8, 31.5, 27.8, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{31}H_{32}N_2O_2$ $[M+H]^+$ 465.2537; found 465.2560.

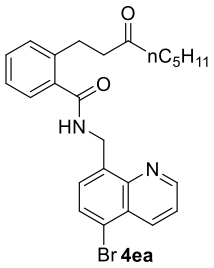
***N*-((5-Fluoroquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4da

By following the general procedure, the reaction of **1d** (32.0 mg, 0.2 mmol) with **2a** (65.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), **A6** (15.2 mg, 0.06 mmol) and $AgSbF_6$ (7.2 mg, 0.02 mmol) afforded **4da** (44.6 mg, 55% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.3, 1.9 Hz, 1H), 8.46 (dd, J = 8.5, 1.9 Hz, 1H), 7.78 (dd, J = 8.1, 5.9 Hz, 1H), 7.51 (dd, J = 8.5, 4.3 Hz, 1H), 7.35 (t, J = 6.1 Hz, 1H), 7.31–7.26 (m, 2H), 7.22–7.13 (m, 3H), 5.11 (d, J = 6.3 Hz, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H), 1.51–1.41 (m, 2H), 1.31–1.23 (m, 2H), 1.22–1.13 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 169.7, 157.55 (d, J = 255.4 Hz), 150.7, 147.3, 139.7, 136.7, 132.3 (d, J = 4.7 Hz), 130.4, 130.1, 130.0, 129.3 (d, J = 8.7 Hz), 127.2, 126.3, 121.4 (d, J = 2.5 Hz), 119.5 (d, J = 16.7 Hz), 110.0 (d, J = 19.3 Hz), 44.4, 42.8, 41.2, 31.5, 27.7, 23.5, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.9; **HRMS** (ESI) Calcd for $C_{25}H_{27}FN_2O_2$ $[M+H]^+$ 407.2129; found 407.2149.

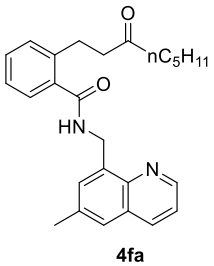
***N*-((5-Bromoquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4ea

By following the general procedure, the reaction of **1e** (44.2 mg, 0.2 mmol) with **2a** (65.6 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol), **A6** (15.7 mg, 0.06 mmol) and $AgSbF_6$ (8.3 mg, 0.02 mmol) afforded **4ea** (46.3 mg, 57% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.3, 1.8 Hz, 1H), 8.58 (dd, J = 8.6, 1.8 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.55 (dd, J = 8.6, 4.2 Hz, 1H), 7.35 (t, J = 5.7 Hz, 1H), 7.31–7.26 (m, 2H), 7.21–7.13 (m, 2H), 5.12 (d, J = 6.3 Hz, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.5 Hz, 2H), 1.51–1.41 (m, 2H), 1.31–1.23 (m, 2H), 1.23–1.13 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 169.8, 150.4, 147.6, 139.7, 136.7, 136.3, 136.2, 130.40, 130.38, 130.1, 130.0, 128.0, 127.2, 126.3, 122.5, 121.7, 44.3, 42.8, 41.3, 31.5, 27.7, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}BrN_2O_2$ $[M+H]^+$ 467.1329; found 467.1350.

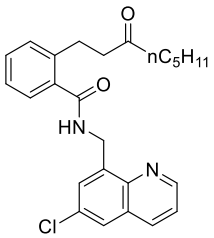
***N*-((6-Methylquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4fa

By following the general procedure, the reaction of **1f** (32.0 mg, 0.2 mmol) with **2a** (65.9 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.5 mg, 0.005 mmol), **A6** (15.6 mg, 0.06 mmol) and $AgSbF_6$ (8.2 mg, 0.02 mmol) afforded **4fa** (57.1 mg, 71% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (dd, J = 4.3, 1.9 Hz, 1H), 8.09 (dd, J = 8.3, 1.8 Hz, 1H), 7.66 (d, J = 2.1 Hz, 1H), 7.56–7.47 (m, 1H), 7.39 (dd, J = 8.3, 4.3 Hz, 1H), 7.31–7.25 (m, 2H), 7.21–7.13 (m, 2H), 5.12 (d, J = 6.1 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H), 2.54 (s, 3H), 2.18 (t, J = 7.5 Hz, 2H), 1.50–1.41 (m, 2H), 1.30–1.22 (m, 2H), 1.22–1.14 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.6, 148.9, 145.6, 139.7, 136.8, 136.6, 136.1, 135.5, 132.0, 130.5, 130.0, 128.8, 127.2, 126.6, 126.3, 121.4, 44.4, 42.8, 41.7, 31.5, 27.8, 23.5, 22.6, 21.7, 14.1; **HRMS** (ESI) Calcd for $C_{26}H_{30}N_2O_2$ $[M+H]^+$ 403.2380; found 403.2397.

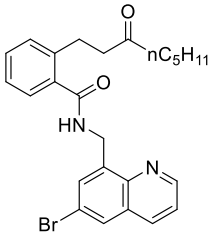
***N*-((6-Chloroquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4ga

By following the general procedure, the reaction of **1g** (35.4 mg, 0.2 mmol) with **2a** (65.1 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol), **A6** (15.8 mg, 0.06 mmol) and $AgSbF_6$ (8.3 mg, 0.02 mmol) afforded **4ga** (49.5 mg, 58% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 4.3, 1.8 Hz, 1H), 8.11 (dd, J = 8.3, 1.9 Hz, 1H), 7.81–7.75 (m, 2H), 7.46 (dd, J = 8.3, 4.2 Hz, 1H), 7.44–7.36 (m, 1H), 7.33–7.27 (m, 2H), 7.22–7.14 (m, 2H), 5.14 (d, J = 6.3 Hz, 2H), 2.93 (t, J = 7.4 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.23 (t, J = 7.4 Hz, 2H), 1.52–1.42 (m, 2H), 1.32–1.23 (m, 2H), 1.23–1.14 (m, 2H), 0.86 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.8, 149.9, 145.3, 139.7, 138.2, 136.5, 135.8, 132.3, 130.4, 130.2, 130.1, 129.3, 127.2, 126.32, 126.27, 122.2, 44.3, 42.8, 41.1, 31.5, 27.7, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}ClN_2O_2$ $[M+H]^+$ 423.1834; found 423.1853.

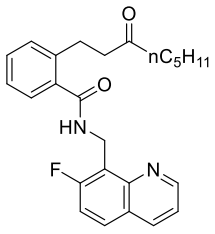
***N*-((6-Bromoquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4ha

By following the general procedure, the reaction of **1h** (44.2 mg, 0.2 mmol) with **2a** (65.6 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.3 mg, 0.06 mmol) and $AgSbF_6$ (7.6 mg, 0.02 mmol) afforded **4ha** (43.8 mg, 47% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.3, 1.8 Hz, 1H), 8.10 (dd, J = 8.4, 1.8 Hz, 1H), 7.95 (d, J = 2.3 Hz, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.46 (dd, J = 8.3, 4.3 Hz, 1H), 7.40 (t, J = 5.6 Hz, 1H), 7.33–7.27 (m, 2H), 7.22–7.15 (m, 2H), 5.14 (d, J = 6.3 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.23 (t, J = 7.5 Hz, 2H), 1.52–1.42 (m, 2H), 1.32–1.23 (m, 2H), 1.23–1.14 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.8, 150.1, 145.6, 139.7, 138.3, 136.6, 135.7, 132.8, 130.4, 130.1, 129.8, 129.7, 127.2, 126.3, 122.2, 120.5, 44.3, 42.9, 41.1, 31.5, 27.7, 23.6, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}BrN_2O_2$ $[M+H]^+$ 467.1329; found 467.1352.

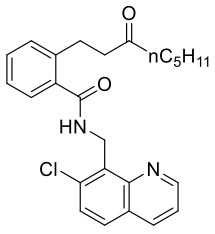
***N*-((7-Fluoroquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4ia

By following the general procedure, the reaction of **1i** (32.0 mg, 0.2 mmol) with **2a** (65.4 mg, 0.4 mmol), **3a** (152 μL, 1 mmol), $[Cp^*RhCl_2]_2$ (3.5 mg, 0.005 mmol), **A6** (15.6 mg, 0.06 mmol) and $AgSbF_6$ (7.8 mg, 0.02 mmol) afforded **4ia** (55.2 mg, 63% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93–8.89 (m, 1H), 8.19 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.79 (dd, *J* = 9.1, 5.9 Hz, 1H), 7.51–7.34 (m, 3H), 7.31–7.26 (m, 2H), 7.21–7.11 (m, 2H), 5.24 (d, *J* = 6.0 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.52–1.43 (m, 2H), 1.31–1.23 (m, 2H), 1.23–1.14 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 169.4, 160.2 (d, *J* = 251.4 Hz), 150.8, 148.1 (d, *J* = 8.7 Hz), 139.8, 136.7 (2C), 130.5, 130.0, 129.3 (d, *J* = 10.5 Hz), 127.2, 126.2, 125.6, 120.6 (d, *J* = 2.5 Hz), 120.2 (d, *J* = 14.9 Hz), 117.5 (d, *J* = 26.9 Hz), 44.5, 42.8, 33.6 (d, *J* = 5.4 Hz), 31.5, 27.9, 23.5, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.8; **HRMS** (ESI) Calcd for $C_{25}H_{27}FN_2O_2$ $[M+H]^+$ 407.2129; found 407.2149.

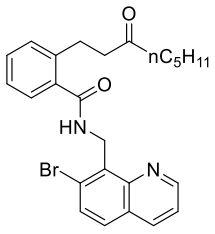
***N*-((7-Chloroquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4ja

By following the general procedure, the reaction of **1j** (35.6 mg, 0.2 mmol) with **2a** (65.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.3 mg, 0.06 mmol) and $AgSbF_6$ (7.6 mg, 0.02 mmol) afforded **4ja** (39.6 mg, 47% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.3, 2.1 Hz, 1H), 8.17 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.30–7.26 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.41 (d, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.52–1.43 (m, 2H), 1.31–1.24 (m, 2H), 1.23–1.15 (m, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 169.4, 150.8, 147.8, 139.8, 136.8, 136.7, 135.4, 133.5, 130.4, 130.0, 128.6, 128.6, 127.22, 127.16, 126.2, 121.5, 44.5, 42.9, 38.0, 31.5, 27.9, 23.6, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}ClN_2O_2$ $[M+H]^+$ 423.1834; found 423.1852.

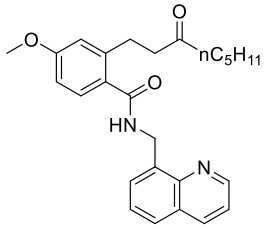
***N*-((7-Bromoquinolin-8-yl)methyl)-2-(3-oxooctyl)benzamide**



4ka

By following the general procedure, the reaction of **1k** (44.3 mg, 0.2 mmol) with **2a** (65.8 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), **A6** (15.7 mg, 0.06 mmol) and $AgSbF_6$ (8.4 mg, 0.02 mmol) afforded **4ka** (37.3 mg, 40% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.30–7.25 (m, 2H), 7.24–7.17 (m, 2H), 7.14 (td, *J* = 7.4, 1.4 Hz, 1H), 5.43 (d, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.30–2.24 (m, 2H), 1.53–1.43 (m, 2H), 1.31–1.24 (m, 2H), 1.23–1.15 (m, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 169.4, 150.7, 147.8, 139.8, 136.8, 136.7, 135.7, 131.5, 130.4, 130.0, 128.7, 127.6, 127.2, 126.2, 126.0, 121.7, 44.5, 42.9, 40.9, 31.5, 27.9, 23.6, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}BrN_2O_2$ $[M+H]^+$ 467.1329; found 467.1341.

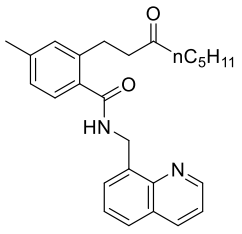
4-Methoxy-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ab

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2b** (77.2 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), **A6** (15.3 mg, 0.06 mmol) and $AgSbF_6$ (8.6 mg, 0.02 mmol) afforded **4ab** (45.9 mg, 55% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55–7.49 (m, 1H), 7.47–7.41 (m, 2H), 7.30–7.26 (m, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.15 (d, *J* = 6.1 Hz, 2H), 3.77 (s, 3H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.51–1.42 (m, 2H), 1.30–1.23 (m, 2H), 1.23–1.14 (m, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 169.4, 160.7, 149.8, 147.1, 142.3, 136.8, 136.2, 129.7, 129.1, 128.9, 128.7, 127.9, 126.7, 121.4, 115.9, 111.4, 55.4, 44.4, 42.8, 41.7, 31.5, 28.2, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{26}H_{30}N_2O_3$ $[M+H]^+$ 419.2329; found 419.2347.

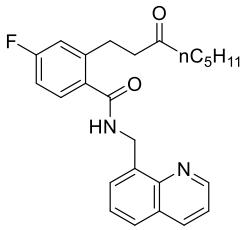
4-Methyl-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ac

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2c** (70.8 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.2 mg, 0.06 mmol) and $AgSbF_6$ (8.3 mg, 0.02 mmol) afforded **4ac** (46.6 mg, 58% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.52 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.49–7.41 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 5.15 (d, *J* = 6.1 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.18 (t, *J* = 7.4 Hz, 2H), 1.50–1.41 (m, 2H), 1.31–1.22 (m, 2H), 1.22–1.12 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 169.8, 149.8, 147.0, 140.1, 139.8, 136.7, 136.1, 133.9, 131.2, 129.7, 128.7, 127.9, 127.3, 126.9, 126.7, 121.3, 44.5, 42.8, 41.7, 31.5, 27.9, 23.5, 22.6, 21.4, 14.1; **HRMS** (ESI) Calcd for $C_{26}H_{30}N_2O_2$ $[M+H]^+$ 403.2380; found 403.2396.

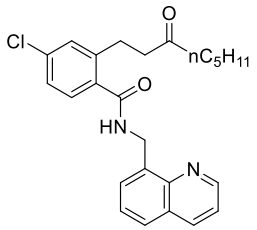
4-Fluoro-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ad

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2d** (72.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), **A6** (15.7 mg, 0.06 mmol) and $AgSbF_6$ (8.1 mg, 0.02 mmol) afforded **4ad** (35.7 mg, 44% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.84–7.77 (m, 2H), 7.57–7.50 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 (dd, *J* = 8.5, 5.8 Hz, 1H), 6.89 (dd, *J* = 9.9, 2.6 Hz, 1H), 6.84 (td, *J* = 8.3, 2.6 Hz, 1H), 5.15 (d, *J* = 6.1 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.50–1.41 (m, 2H), 1.31–1.23 (m, 2H), 1.23–1.13 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.2, 168.8, 163.3 (d, *J* = 249.6 Hz), 149.8, 147.0, 142.9 (d, *J* = 8.0 Hz), 136.8, 135.9, 133.0 (d, *J* = 3.3 Hz), 129.8, 129.2 (d, *J* = 8.7 Hz), 128.7, 128.0, 126.7, 121.4, 117.2 (d, *J* = 21.4 Hz), 113.2 (d, *J* = 21.4 Hz), 43.9, 42.8, 41.8, 31.5, 27.6, 23.5, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.9; **HRMS** (ESI) Calcd for $C_{25}H_{27}FN_2O_2$ $[M+H]^+$ 407.2129; found 407.2146.

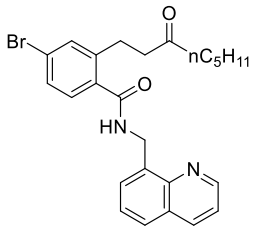
4-Chloro-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ae

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2e** (78.9 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), **A6** (15.2 mg, 0.06 mmol) and $AgSbF_6$ (8.6 mg, 0.02 mmol) afforded **4ae** (43.1 mg, 51% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.3, 1.9 Hz, 1H), 8.20 (dd, J = 8.3, 1.9 Hz, 1H), 7.84–7.77 (m, 2H), 7.62–7.50 (m, 2H), 7.45 (dd, J = 8.3, 4.3 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 7.13 (dd, J = 8.3, 2.1 Hz, 1H), 5.15 (d, J = 6.1 Hz, 2H), 2.89 (t, J = 7.5 Hz, 2H), 2.64 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.5 Hz, 2H), 1.50–1.41 (m, 2H), 1.30–1.23 (m, 2H), 1.22–1.14 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.1, 168.7, 149.8, 147.0, 141.9, 136.8, 135.8, 135.7, 135.2, 130.4, 129.8, 128.7, 128.6, 128.0, 126.7, 126.4, 121.4, 43.9, 42.8, 41.8, 31.5, 27.5, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}ClN_2O_2$ $[M+H]^+$ 423.1834; found 423.1854.

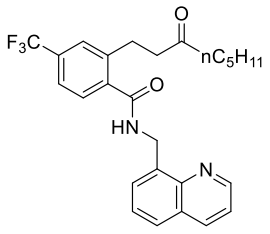
4-Bromo-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4af

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2f** (96.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.3 mg, 0.005 mmol), **A6** (15.8 mg, 0.06 mmol) and $AgSbF_6$ (7.9 mg, 0.02 mmol) afforded **4af** (59.6 mg, 64% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.3, 1.8 Hz, 1H), 8.20 (dd, J = 8.3, 1.8 Hz, 1H), 7.85–7.75 (m, 2H), 7.58 (t, J = 5.9 Hz, 1H), 7.53 (dd, J = 8.4, 6.9 Hz, 1H), 7.45 (dd, J = 8.3, 4.2 Hz, 1H), 7.34 (d, J = 2.0 Hz, 1H), 7.29 (dd, J = 8.1, 2.0 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 5.14 (d, J = 6.1 Hz, 2H), 2.88 (t, J = 7.5 Hz, 2H), 2.64 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.4 Hz, 2H), 1.50–1.41 (m, 2H), 1.30–1.23 (m, 2H), 1.23–1.14 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.2, 168.8, 149.8, 147.0, 142.1, 136.8, 135.8, 135.7, 133.3, 129.8, 129.4, 128.8, 128.7, 128.0, 126.7, 124.1, 121.4, 44.0, 42.8, 41.9, 31.5, 27.4, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}BrN_2O_2$ $[M+H]^+$ 467.1329; found 467.1346.

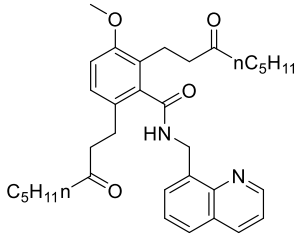
2-(3-Oxooctyl)-*N*-(quinolin-8-ylmethyl)-4-(trifluoromethyl)benzamide



4ag

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2g** (92.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), **A6** (15.8 mg, 0.06 mmol) and $AgSbF_6$ (7.6 mg, 0.02 mmol) afforded **4ag** (27.4 mg, 30% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 4.3, 1.9 Hz, 1H), 8.20 (dd, J = 8.3, 1.9 Hz, 1H), 7.85–7.78 (m, 2H), 7.66 (t, J = 6.3 Hz, 1H), 7.54 (dd, J = 8.3, 6.8 Hz, 1H), 7.48–7.37 (m, 4H), 5.17 (d, J = 6.1 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.4 Hz, 2H), 1.50–1.41 (m, 2H), 1.30–1.23 (m, 2H), 1.22–1.14 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.0, 168.5, 149.9, 147.0, 140.6, 140.3, 136.8, 135.6, 131.8 (q, J = 32.7 Hz), 129.8, 128.7, 128.1, 127.7, 127.1 (q, J = 4.0 Hz), 126.7, 123.8 (q, J = 273.6 Hz), 123.3 (q, J = 4.0 Hz), 121.5, 43.9, 42.8, 41.9, 31.5, 27.5, 23.5, 22.6, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9; **HRMS** (ESI) Calcd for $C_{26}H_{27}F_3N_2O_2$ $[M+H]^+$ 457.2097; found 457.2117.

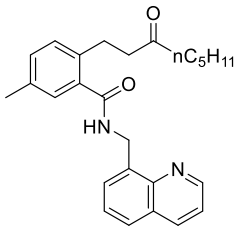
3-Methoxy-2,6-bis(3-oxooctyl)-N-(quinolin-8-ylmethyl)benzamide



4ah

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2h** (77.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), **A6** (15.4 mg, 0.06 mmol) and $AgSbF_6$ (7.9 mg, 0.02 mmol) afforded **4ah** (49.3 mg, 45% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.86 (dd, J = 4.2, 1.8 Hz, 1H), 8.18 (dd, J = 8.3, 1.9 Hz, 1H), 7.83 (dd, J = 7.0, 1.4 Hz, 1H), 7.77 (dd, J = 8.3, 1.6 Hz, 1H), 7.51 (dd, J = 8.3, 6.9 Hz, 1H), 7.43 (dd, J = 8.3, 4.3 Hz, 1H), 7.30 (t, J = 6.3 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 5.15 (d, J = 6.1 Hz, 2H), 3.73 (s, 3H), 2.75–2.64 (m, 2H), 2.60 (t, J = 7.4 Hz, 2H), 2.54–2.43 (m, 4H), 2.17 (t, J = 7.6 Hz, 2H), 2.11 (t, J = 7.4 Hz, 2H), 1.52–1.38 (m, 4H), 1.33–1.14 (m, 8H), 0.92–0.84 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.9, 210.5, 169.3, 155.9, 149.9, 146.9, 138.9, 136.7, 135.8, 129.9, 129.6, 128.6, 128.2, 128.0, 126.7, 126.4, 121.4, 110.8, 55.6, 44.5, 42.80, 42.76, 42.5, 41.4, 31.6, 31.5, 26.8, 23.6, 23.5, 22.60, 22.57, 22.3, 14.09, 14.06; **HRMS** (ESI) Calcd for $C_{34}H_{44}N_2O_4$ $[M+H]^+$ 545.3374; found 545.3396.

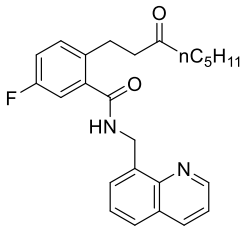
5-Methyl-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ai

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2i** (70.9 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.5 mg, 0.06 mmol) and $AgSbF_6$ (8.3 mg, 0.02 mmol) afforded **4ai** (59.9 mg, 74% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.48–7.41 (m, 2H), 7.13 (s, 1H), 7.10–7.04 (m, 2H), 5.17 (d, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 2.16 (t, *J* = 7.5 Hz, 2H), 1.49–1.39 (m, 2H), 1.29–1.22 (m, 2H), 1.22–1.13 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 169.9, 149.8, 147.0, 136.69, 136.67, 136.4, 136.1, 135.9, 130.6, 130.3, 129.6, 128.6, 127.9, 127.8, 126.7, 121.3, 44.4, 42.8, 41.6, 31.5, 27.3, 23.5, 22.5, 20.9, 14.0; **HRMS** (ESI) Calcd for $C_{26}H_{30}N_2O_2$ $[M+H]^+$ 403.2380; found 403.2398.

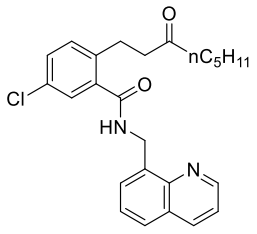
5-Fluoro-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4aj

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2j** (72.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol), **A6** (15.2 mg, 0.06 mmol) and $AgSbF_6$ (8.4 mg, 0.02 mmol) afforded **4aj** (59.3 mg, 73% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.83–7.76 (m, 2H), 7.61–7.50 (m, 2H), 7.45 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.18–7.07 (m, 2H), 7.03 (ddd, *J* = 9.6, 7.9, 1.6 Hz, 1H), 5.15 (d, *J* = 6.1 Hz, 2H), 2.95–2.88 (m, 2H), 2.71–2.65 (m, 2H), 2.28–2.22 (m, 2H), 1.54–1.45 (m, 2H), 1.33–1.25 (m, 2H), 1.25–1.17 (m, 2H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.3, 168.4 (d, *J* = 3.3 Hz), 161.4 (d, *J* = 246.3 Hz), 149.8, 147.0, 139.3 (d, *J* = 4.4 Hz), 136.8, 135.8, 129.8, 128.7, 128.0, 127.7 (d, *J* = 8.7 Hz), 127.0 (d, *J* = 16.7 Hz), 126.7, 122.8 (d, *J* = 3.3 Hz), 121.4, 116.8 (d, *J* = 23.3 Hz), 42.9, 42.6, 41.8, 31.5, 23.6, 22.6, 20.9 (d, *J* = 3.6 Hz), 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.5; **HRMS** (ESI) Calcd for $C_{25}H_{27}FN_2O_2$ $[M+H]^+$ 407.2129; found 407.2148.

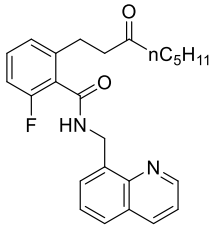
5-Chloro-2-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ak

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2k** (78.8 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), **A6** (15.5 mg, 0.06 mmol) and $AgSbF_6$ (7.8 mg, 0.02 mmol) afforded **4ak** (52.3 mg, 62% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.84–7.78 (m, 2H), 7.57–7.50 (m, 2H), 7.46 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.24 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 5.15 (d, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.16 (t, *J* = 7.4 Hz, 2H), 1.49–1.40 (m, 2H), 1.30–1.22 (m, 2H), 1.22–1.13 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.3, 168.3, 149.9, 147.0, 138.3, 138.2, 136.8, 135.7, 132.0, 131.9, 129.9, 129.8, 128.7, 128.1, 127.2, 126.7, 121.5, 44.0, 42.8, 41.9, 31.5, 27.1, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}ClN_2O_2$ $[M+H]^+$ 423.1834; found 423.1852.

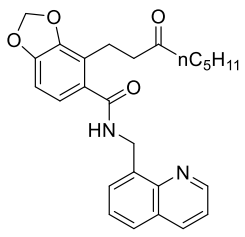
2-Fluoro-6-(3-oxooctyl)-*N*-(quinolin-8-ylmethyl)benzamide



4al

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2l** (72.4 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.3 mg, 0.005 mmol), **A6** (15.7 mg, 0.06 mmol) and $AgSbF_6$ (8.2 mg, 0.02 mmol) afforded **4al** (37.4 mg, 46% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47–7.35 (m, 2H), 7.25–7.17 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 8.8 Hz, 1H), 5.21 (d, *J* = 6.1 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.14 (t, *J* = 7.5 Hz, 2H), 1.49–1.39 (m, 2H), 1.30–1.22 (m, 2H), 1.21–1.13 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.1, 164.9, 159.3 (d, *J* = 246.7 Hz), 149.7, 146.8, 141.9 (d, *J* = 2.9 Hz), 136.8, 135.7, 130.6 (d, *J* = 8.7 Hz), 129.7, 128.6, 127.9, 126.7, 125.6 (d, *J* = 3.3 Hz), 125.3 (d, *J* = 17.8 Hz), 121.4, 113.6 (d, *J* = 22.2 Hz), 44.0, 42.7, 41.6, 31.5, 27.4 (d, *J* = 2.2 Hz), 23.5, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.1; **HRMS** (ESI) Calcd for $C_{25}H_{27}FN_2O_2$ $[M+H]^+$ 407.2129; found 407.2149.

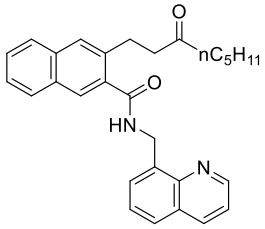
6-(3-Oxooctyl)-*N*-(quinolin-8-ylmethyl)benzo[d][1,3]dioxole-5-carboxamide



4am

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2m** (82.9 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.8 mg, 0.06 mmol) and $AgSbF_6$ (8.6 mg, 0.02 mmol) afforded **4am** (54.4 mg, 63% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.82–7.75 (m, 2H), 7.55–7.48 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 2H), 5.13 (d, *J* = 6.1 Hz, 2H), 2.95–2.88 (m, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.53–1.43 (m, 2H), 1.32–1.24 (m, 2H), 1.24–1.16 (m, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 168.8, 149.8, 148.3, 147.0, 146.5, 136.7, 136.1, 131.2, 129.6, 128.6, 127.8, 126.7, 122.0, 121.5, 121.3, 106.1, 101.3, 42.6, 42.4, 41.7, 31.5, 23.6, 22.6, 21.5, 14.1; **HRMS** (ESI) Calcd for $C_{26}H_{28}N_2O_4$ $[M+H]^+$ 433.2122; found 433.2144.

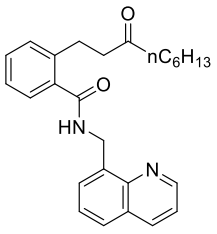
3-(3-Oxooctyl)-*N*-(quinolin-8-ylmethyl)-2-naphthamide



4an

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2n** (85.2 mg, 0.4 mmol), **3a** (152 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), **A6** (15.9 mg, 0.06 mmol) and $AgSbF_6$ (8.7 mg, 0.02 mmol) afforded **4an** (31.5 mg, 36% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.86 (d, *J* = 7.0 Hz, 1H), 7.83–7.78 (m, 2H), 7.76–7.71 (m, 2H), 7.64–7.52 (m, 3H), 7.50–7.39 (m, 3H), 5.22 (d, *J* = 6.1 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.15 (t, *J* = 7.4 Hz, 2H), 1.48–1.39 (m, 2H), 1.28–1.20 (m, 2H), 1.19–1.11 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 169.7, 149.8, 147.1, 136.8 (2C), 136.0, 135.4, 134.0, 131.4, 129.8, 129.0, 128.7, 128.0 (2C), 127.4, 127.2, 127.0, 126.7, 126.1, 121.4, 44.3, 42.8, 41.9, 31.5, 28.0, 23.5, 22.6, 14.1; **HRMS** (ESI) Calcd for $C_{29}H_{30}N_2O_2$ $[M+H]^+$ 439.2380; found 439.2401.

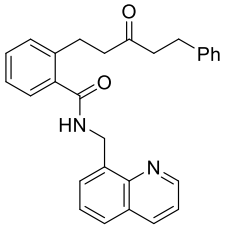
2-(3-Oxononyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ao

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2a** (65.6 mg, 0.4 mmol), **3o** (140 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.5 mg, 0.005 mmol), **A6** (15.8 mg, 0.06 mmol) and $AgSbF_6$ (8.1 mg, 0.02 mmol) afforded **4ao** (54.7 mg, 68% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55–7.40 (m, 3H), 7.33–7.24 (m, 2H), 7.20–7.12 (m, 2H), 5.17 (d, *J* = 6.3 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.49–1.39 (m, 2H), 1.31–1.15 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 169.7, 149.8, 147.0, 139.7, 136.8, 136.7, 136.0, 130.4, 130.0, 129.7, 128.6, 127.9, 127.1, 126.7, 126.3, 121.3, 44.4, 42.8, 41.7, 31.7, 29.0, 27.8, 23.8, 22.6, 14.2; **HRMS** (ESI) Calcd for $C_{26}H_{30}N_2O_2$ $[M+H]^+$ 403.2380; found 403.2402.

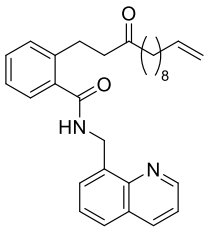
2-(3-Oxo-5-phenylpentyl)-*N*-(quinolin-8-ylmethyl)benzamide



4ap

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2a** (65.7 mg, 0.4 mmol), **3p** (160.0 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), **A6** (15.3 mg, 0.06 mmol) and $AgSbF_6$ (8.4 mg, 0.02 mmol) afforded **4ap** (64.1 mg, 76% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.81 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.74 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.52–7.38 (m, 3H), 7.32–7.24 (m, 4H), 7.22–7.09 (m, 5H), 5.15 (d, *J* = 6.1 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.48 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.3, 169.7, 149.8 (2C), 141.2, 139.6, 136.8 (2C), 136.0, 130.5, 130.0, 129.8, 128.7, 128.6 (2C), 128.5 (2C), 128.0, 127.2, 126.7, 126.4, 126.2, 121.4, 44.5, 44.2, 41.7, 29.7, 27.8; **HRMS** (ESI) Calcd for $C_{28}H_{26}N_2O_2$ $[M+H]^+$ 423.2067; found 423.2088.

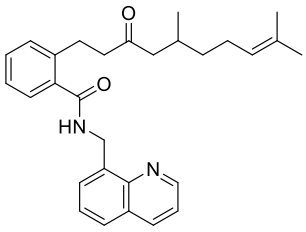
2-(3-Oxotridec-12-en-1-yl)-*N*-(quinolin-8-ylmethyl)benzamide



4aq

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2a** (65.9 mg, 0.4 mmol), **3q** (194.1 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.3 mg, 0.005 mmol), **A6** (15.7 mg, 0.06 mmol) and $AgSbF_6$ (7.5 mg, 0.02 mmol) afforded **4aq** (47.3 mg, 52% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55–7.41 (m, 3H), 7.32–7.25 (m, 2H), 7.20–7.13 (m, 2H), 5.81 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.17 (d, *J* = 6.1 Hz, 2H), 5.03–4.96 (m, 1H), 4.95–4.90 (m, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.18 (t, *J* = 7.4 Hz, 2H), 2.07–1.99 (m, 2H), 1.49–1.40 (m, 2H), 1.39–1.32 (m, 2H), 1.30–1.15 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 169.7, 149.8, 147.0, 139.7, 139.3, 136.8, 136.7, 136.0, 130.4, 130.0, 129.7, 128.6, 127.9, 127.1, 126.7, 126.3, 121.4, 114.3, 44.4, 42.8, 41.7, 33.9, 29.5, 29.4, 29.3, 29.2, 29.0, 27.8, 23.8; **HRMS** (ESI) Calcd for $C_{30}H_{36}N_2O_2$ $[M+H]^+$ 457.2850; found 457.2873.

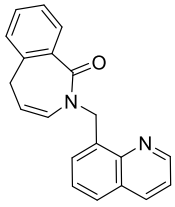
2-(5,9-Dimethyl-3-oxodec-8-en-1-yl)-*N*-(quinolin-8-ylmethyl)benzamide



4ar

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2a** (65.5 mg, 0.4 mmol), **3r** (166.4 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.3 mg, 0.06 mmol) and $AgSbF_6$ (7.9 mg, 0.02 mmol) afforded **4ar** (54.9 mg, 64% yield). White solid (petroleum ether/ethyl acetate = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.84–7.76 (m, 2H), 7.55–7.41 (m, 3H), 7.32–7.28 (m, 1H), 7.28–7.25 (m, 1H), 7.21–7.12 (m, 2H), 5.17 (d, *J* = 6.1 Hz, 2H), 5.08–5.02 (m, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.64 (td, *J* = 7.3, 2.6 Hz, 2H), 2.20 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.02 (dd, *J* = 15.8, 8.1 Hz, 1H), 1.96–1.86 (m, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.27–1.16 (m, 1H), 1.15–1.04 (m, 1H), 0.80 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.3, 169.7, 149.8, 147.0, 139.7, 136.8, 136.7, 136.1, 131.5, 130.5, 130.0, 129.7, 128.6, 127.9, 127.1, 126.7, 126.3, 124.5, 121.3, 50.2, 45.0, 41.7, 37.1, 29.0, 27.7, 25.8, 25.6, 19.8, 17.8; **HRMS** (ESI) Calcd for $C_{29}H_{34}N_2O_2$ $[M+H]^+$ 433.2693; found 433.2717.

2-(Quinolin-8-ylmethyl)-2,5-dihydro-*1H*-benzo[c]azepin-1-one

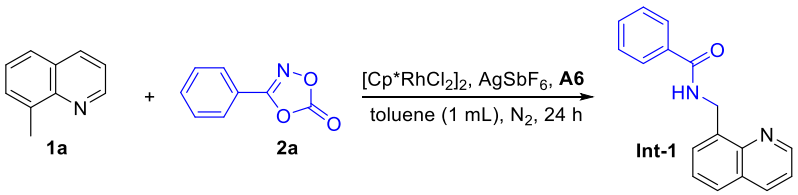


4as

By following the general procedure, the reaction of **1a** (27 μL, 0.2 mmol) with **2a** (65.4 mg, 0.4 mmol), **3s** (56.1 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), **A6** (15.5 mg, 0.06 mmol) and $AgSbF_6$ (8.4 mg, 0.02 mmol) afforded **4as** (25.2 mg, 42% yield). Colorless oil (petroleum ether/ethyl acetate = 5 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.3, 1.9 Hz, 1H), 8.17 (dd, J = 8.3, 1.9 Hz, 1H), 7.95 (dd, J = 7.8, 1.6 Hz, 1H), 7.78–7.71 (m, 2H), 7.55–7.49 (m, 1H), 7.46–7.37 (m, 2H), 7.32 (td, J = 7.6, 1.4 Hz, 1H), 7.09 (dd, J = 7.6, 1.3 Hz, 1H), 6.21 (d, J = 7.6 Hz, 1H), 5.70 (s, 2H), 5.62 (dt, J = 7.6, 7.3 Hz, 1H), 3.27 (d, J = 7.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 149.7, 146.6, 143.5, 136.4, 135.4, 134.2, 131.7, 131.5, 130.5, 128.4, 128.0, 127.4, 126.7, 126.6, 126.2, 121.3, 118.0, 48.0, 31.7; **HRMS** (ESI) Calcd for $C_{20}H_{16}N_2O$ $[M+H]^+$ 301.1335; found 301.1350.

5. Mechanistic study

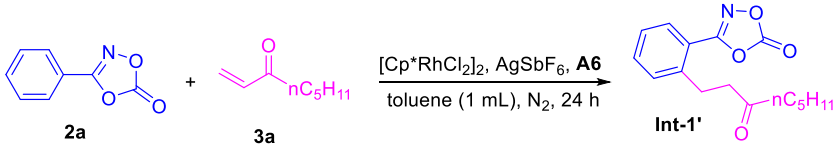
5.1 Synthesis of **Int-1** via Rh-catalyzed C–H activation of **1a** and **2a**



1a + 2a → Int-1

To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added substrate **2a** (65.7 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), $AgSbF_6$ (8.7 mg, 0.02 mmol) and **A6** (15.6 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1a** (27 μL, 0.2 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (5 : 1) as the eluent to give the **Int-1** (45.2 mg, 86% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.96 (dd, J = 4.3, 1.9 Hz, 1H), 8.19 (dd, J = 8.3, 1.9 Hz, 1H), 7.97 (br, 1H), 7.82–7.74 (m, 4H), 7.54–7.42 (m, 3H), 7.41–7.35 (m, 2H), 5.20 (d, J = 6.1 Hz, 2H).[4]

5.2 Synthesis of **Int-1'** via Rh-catalyzed C–H activation of **2a** and **3a**

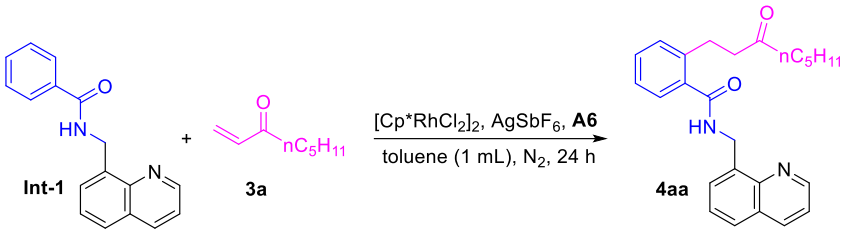


2a + 3a → Int-1'

To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added substrate **2a** (65.8 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (8.7 mg, 0.02

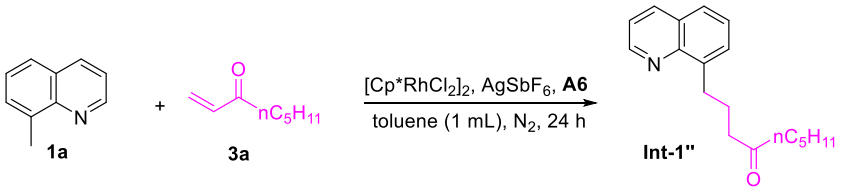
mmol) and **A6** (15.6 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **3a** (152 µL, 1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature, while no desired product was obtained.

5.3 Synthesis of **4aa** via Rh-catalyzed C–H activation of **Int-1** and **3a**



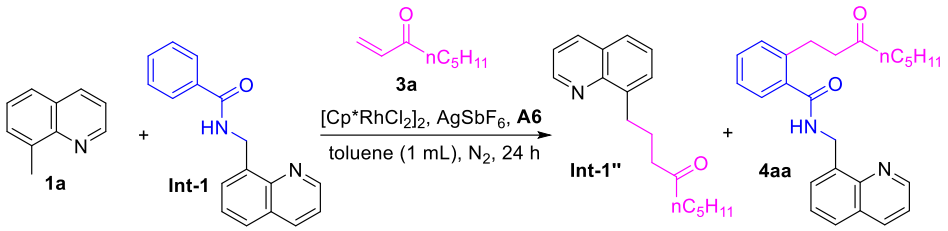
To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added **Int-1** (52.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.3 mg, 0.005 mmol), $AgSbF_6$ (8.6 mg, 0.02 mmol) and **A6** (15.4 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **3a** (152 µL, 1.0 mmol), and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (2 : 1) as the eluent to give the **4aa** (34.9 mg, 45% yield).

5.4 Synthesis of **Int-1''** via Rh-catalyzed C–H activation of **1a** and **3a**



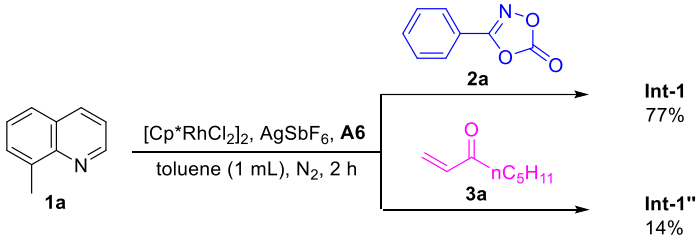
To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), $AgSbF_6$ (8.7 mg, 0.02 mmol) and **A6** (15.3 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1a** (27 µL, 0.2 mmol), **3a** (152 µL, 1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10 : 1) as the eluent to give the **Int-1''** (21.5 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.3, 1.9 Hz, 1H), 8.14 (dd, J = 8.3, 1.9 Hz, 1H), 7.68 (dd, J = 8.1, 1.8 Hz, 1H), 7.56 (dd, J = 7.1, 1.6 Hz, 1H), 7.50–7.44 (m, 1H), 7.39 (dd, J = 8.3, 4.3 Hz, 1H), 3.31–3.25 (m, 2H), 2.51 (t, J = 7.4 Hz, 2H), 2.38 (t, J = 7.4 Hz, 2H), 2.14–2.04 (m, 2H), 1.60–1.51 (m, 2H), 1.34–1.21 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H).[5]

5.5 Competing reaction of **Int-1** and **1a** with **3a**



To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added substrate **Int-1** (52.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 0.005 mmol), $AgSbF_6$ (8.3 mg, 0.02 mmol) and **A6** (15.3 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1a** (27 μL, 0.2 mmol), **3a** (152 μL, 1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10 : 1 to 2 : 1) as the eluent to give the **Int-1''** (21.3 mg, 40% yield) and **4aa** (37.2 mg, 48% yield).

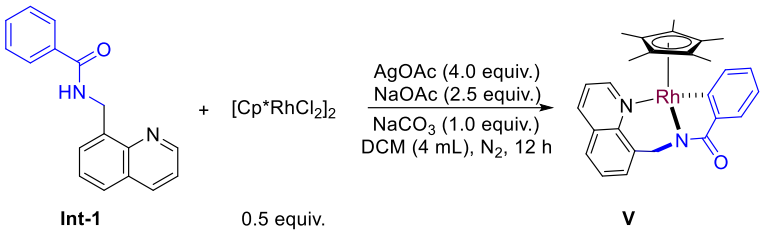
5.6 Rh-catalyzed C–H activation of **1a** with **2a** and **3a** for 2 h



To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added substrate **2a** (65.8 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (8.7 mg, 0.02 mmol) and **A6** (15.3 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1a** (27 μL, 0.2 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 2 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (2 : 1) as the eluent to give the **Int-1** (40.5 mg, 77% yield).

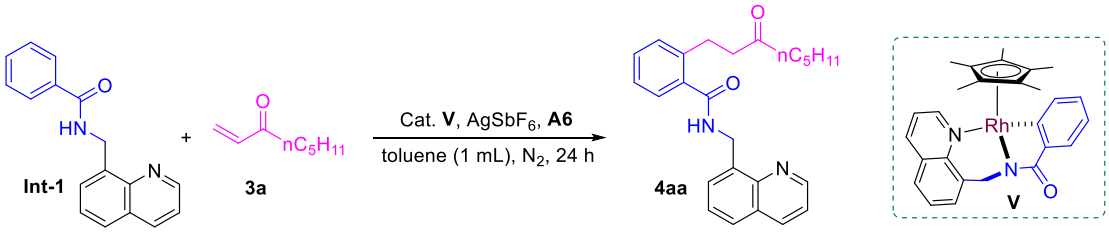
To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (8.7 mg, 0.02 mmol) and **A6** (15.4 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1a** (28 μL, 0.2 mmol), **3a** (152 μL, 1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 2 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10 : 1) as the eluent to give the **Int-1''** (7.1 mg, 14% yield).

5.7 Synthesis of Rh-complex **V**



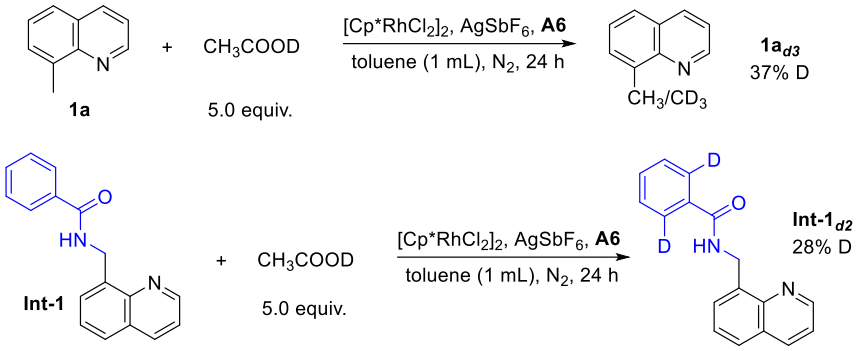
To a 25 mL of Schlenk tube equipped with a magnetic stirring bar were added **Int-1** (26.6 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (30.0 mg, 0.05 mmol), AgOAc (66.8 mg, 0.4 mmol), $NaCO_3$ (11.0 mg, 0.1 mmol) and NaOAc (20.5 mg, 0.25 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, CH_2Cl_2 (4.0 mL) were added subsequently. After stirring at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel very quickly with ethyl acetate/methanol (20 : 1) as the eluent to obtain the product (28.1 mg, 56%). Orange solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, J = 4.9 Hz, 1H), 7.94 (dd, J = 7.4, 1.1 Hz, 1H), 7.68 (dd, J = 7.1, 1.4 Hz, 1H), 7.63 (dd, J = 8.3, 1.8 Hz, 1H), 7.56 (dd, J = 7.4, 1.6 Hz, 1H), 7.34–7.30 (m, 1H), 7.30–7.26 (m, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.07 (td, J = 7.4, 1.3 Hz, 1H), 6.65 (dd, J = 8.3, 5.0 Hz, 1H), 5.83 (d, J = 16.9 Hz, 1H), 4.90 (d, J = 16.6 Hz, 1H), 1.43 (s, 15H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1 (d, J = 3.6 Hz), 171.2 (d, J = 32.7 Hz), 154.9, 145.6, 145.3, 139.2, 138.9, 133.5, 130.9, 130.1, 129.5, 127.4, 126.8, 126.7, 123.1, 120.5, 95.0 (d, J = 5.8 Hz), 48.9, 9.0; **HRMS** (ESI) Calcd for $C_{27}H_{28}N_2ORh$ $[M+H]^+$ 499.1252; found 499.1265.

5.8 Synthesis of **4aa** via Rh-complex-catalyzed C–H activation of **Int-1** and **3a**



To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added **Int-1** (52.6 mg, 0.2 mmol), Rh-complex **V** (2.5 mg, 0.01 mmol), $AgSbF_6$ (8.5 mg, 0.02 mmol) and **A6** (15.5 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **3a** (152 μL, 1.0 mmol), and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (2 : 1) as the eluent to give the **4aa** (33.3 mg, 43% yield).

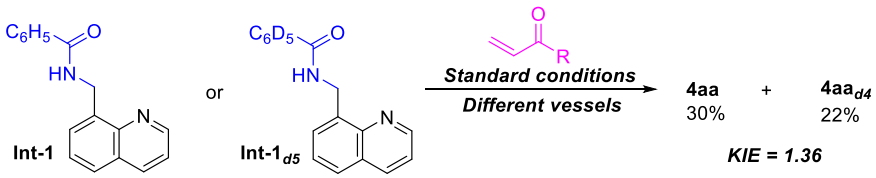
5.9 H/D Scrambling experiments of **1a** and **Int-1**



To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol), $AgSbF_6$ (8.7 mg, 0.02 mmol) and **A6** (15.4 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **1a** (0.2 mmol), CH_3COOD (5.0 equiv., 1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give the corresponding product. The ratio of H/D was determined by ^1H NMR spectra.

To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added **Int-1** (52.3 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (8.5 mg, 0.02 mmol) and **A6** (15.3 mg, 0.06 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, CH_3COOD (5.0 equiv., 1.0 mmol) and toluene (1.0 mL) were added subsequently. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give the corresponding product. The ratio of H/D was determined by ^1H NMR spectra.

5.10 KIE experiments of **Int-1** and **Int-1$_{d5}$** with **3a**



To a 10 mL of Schlenk tube equipped with a magnetic stirring bar were added **Int-**1 (26.2 mg, 0.1 mmol) or **Int$_{d5}$** (52.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), $AgSbF_6$ (3.9 mg, 0.01 mmol) and **A6** (7.6 mg, 0.03 mmol) under air. The mixture was then evacuated and backfilled with nitrogen for three times. After that, **3a** (30 μL, 0.2 mmol), and toluene (0.5 mL) were added subsequently. After stirring at 120 °C for 6 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the yields of **4aa** (30%) and **4aa$_{d4}$** (22%) were obtained by crude NMR with 1,3,5-trimethoxybenzene as the internal standard, respectively. The KIE ratio was calculated as 1.36.

6. References

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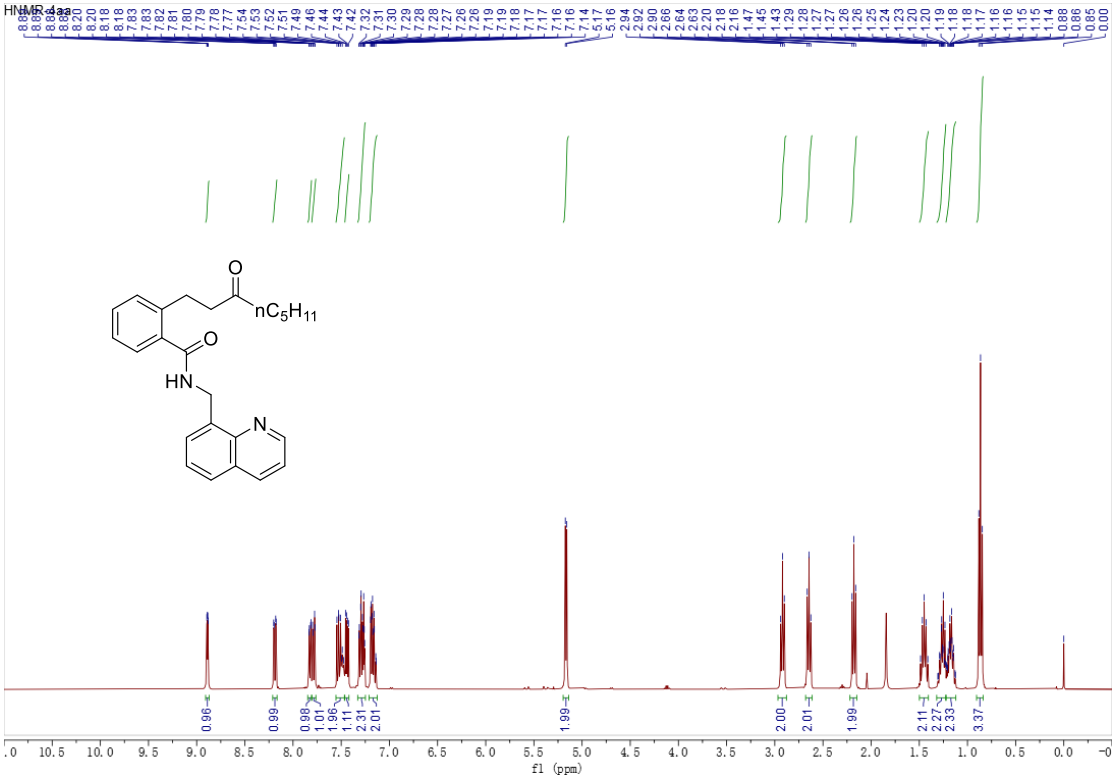
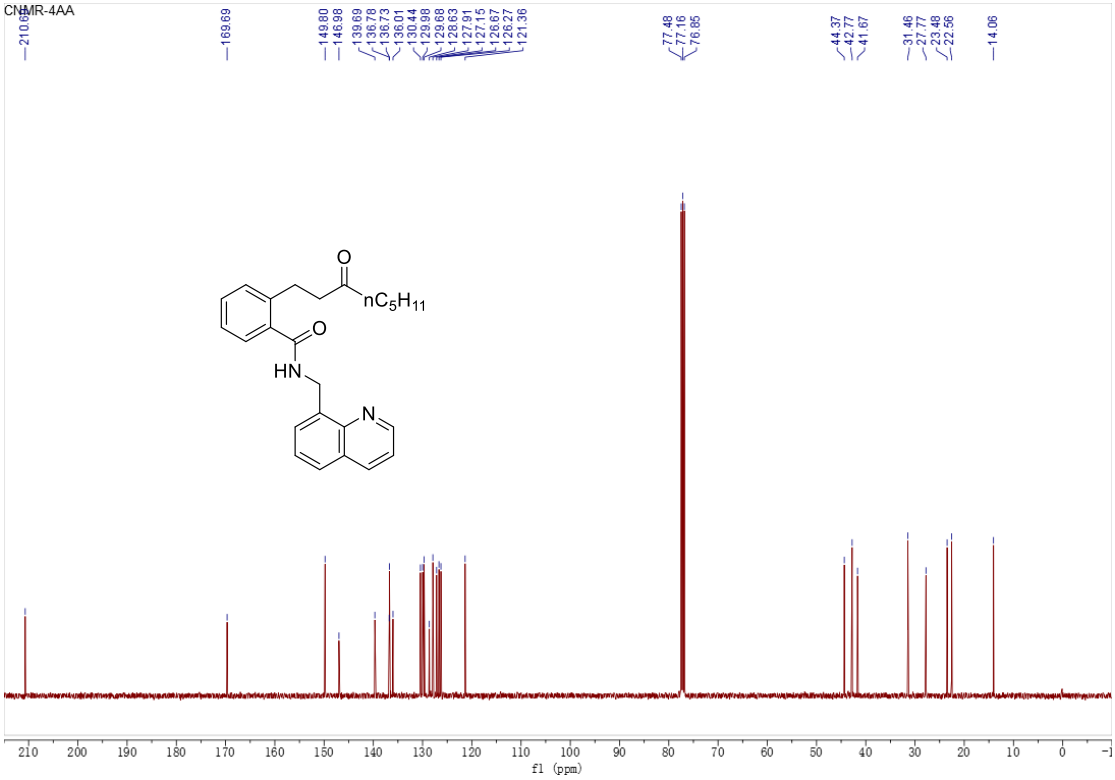
7. NMR Spectra of 4aa-4as and V

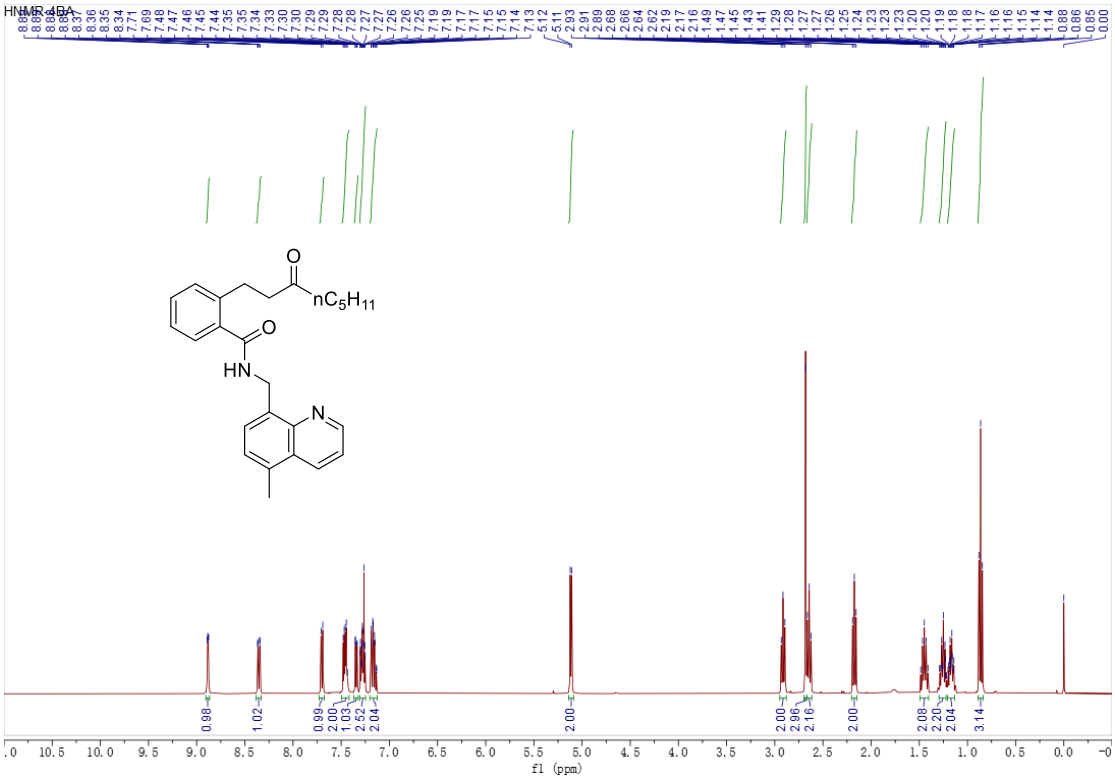
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4aa**



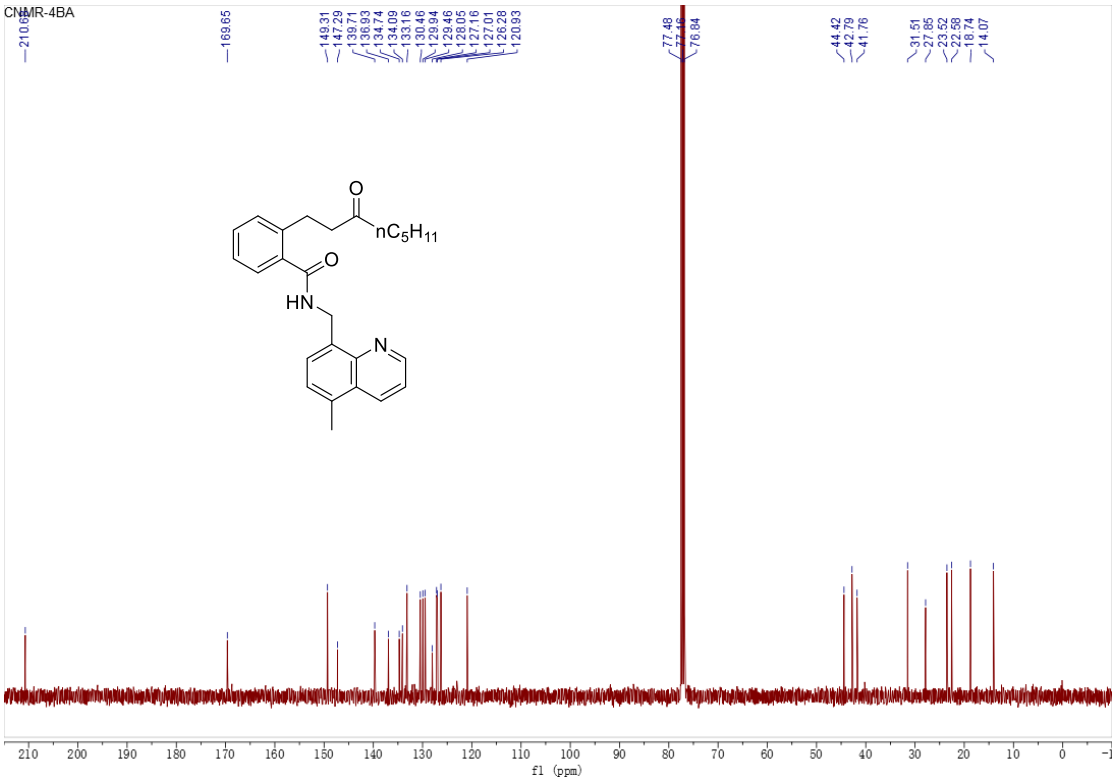
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4aa**



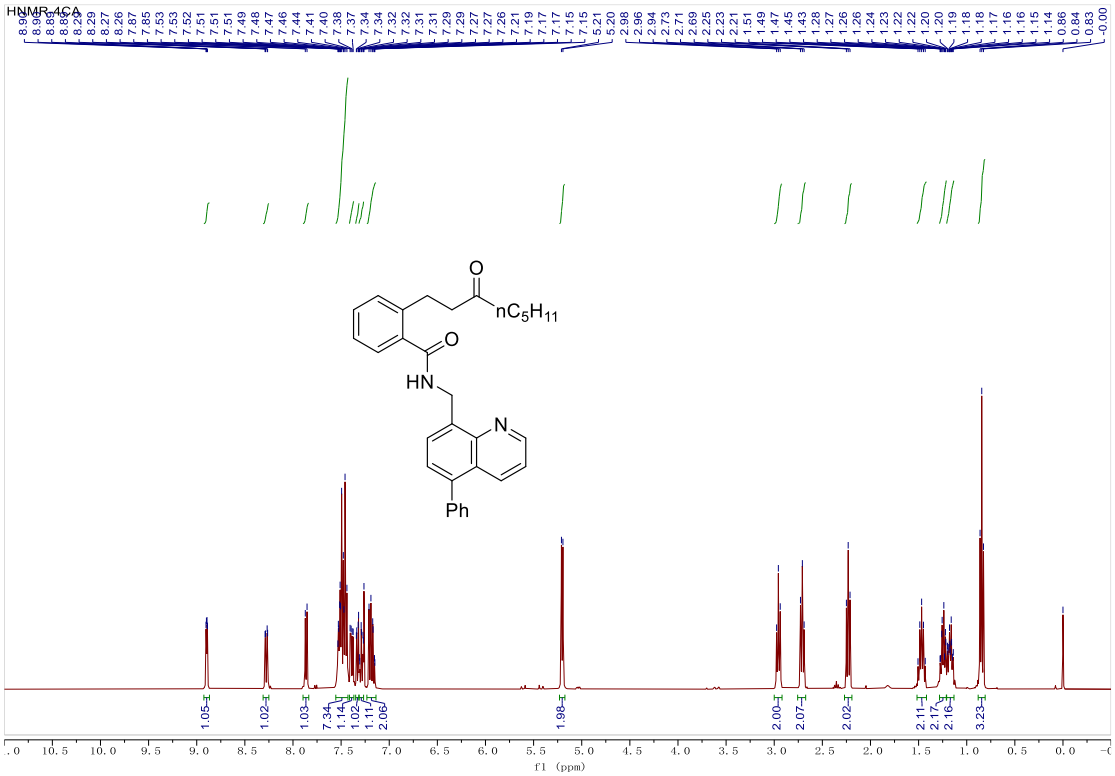
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ba**



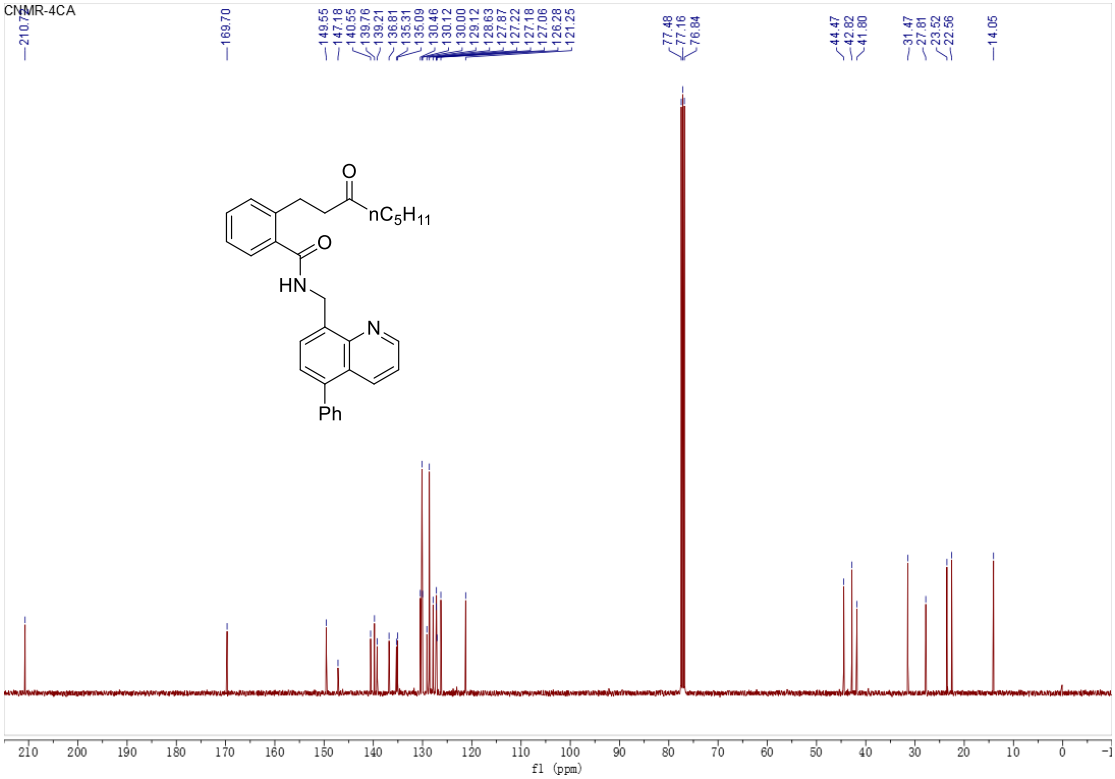
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ba**



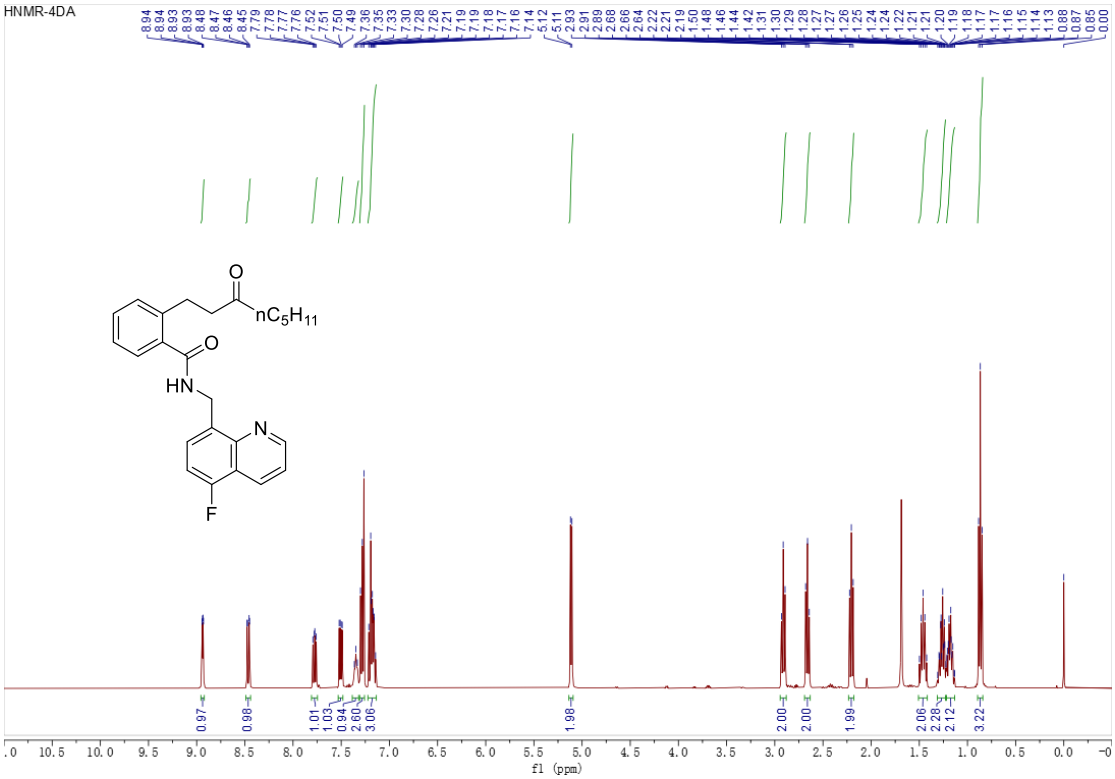
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ca**



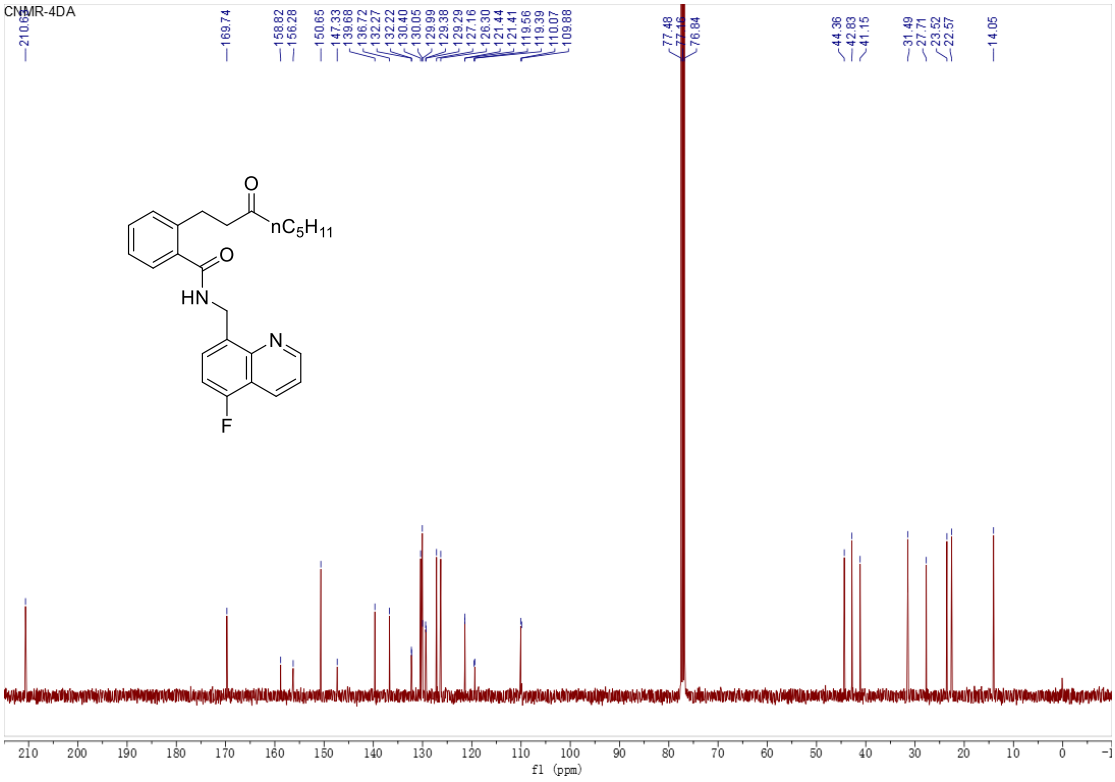
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ca**



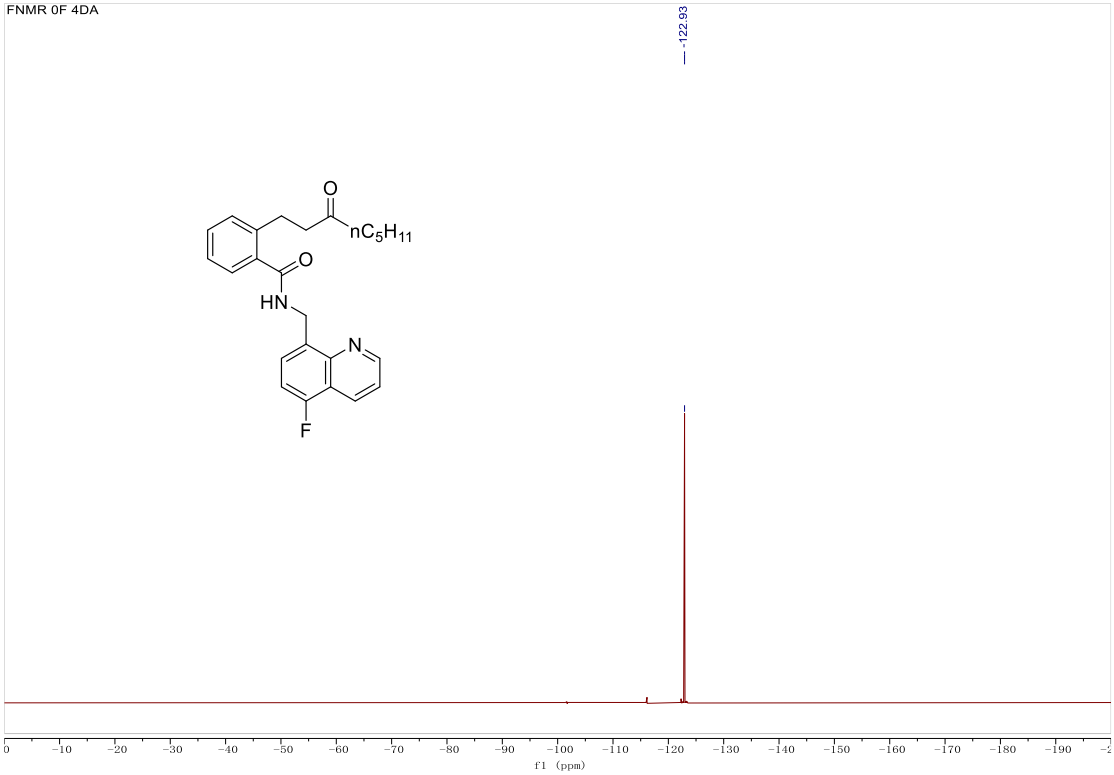
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4da**



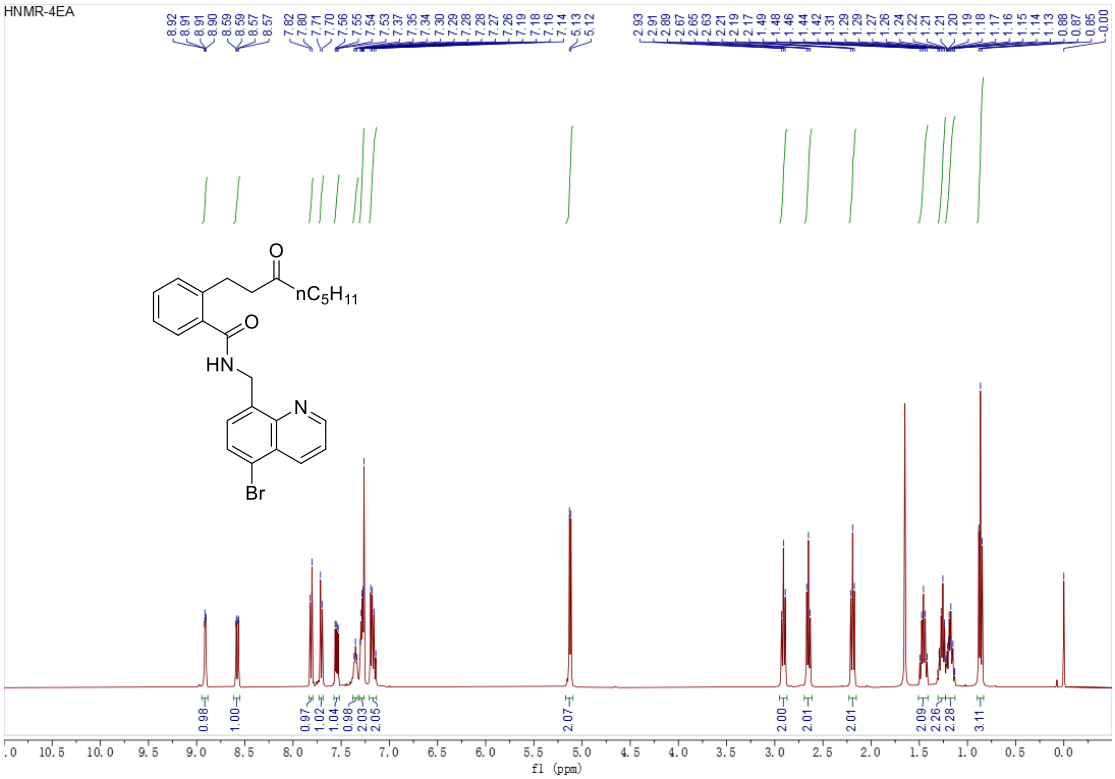
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4da**



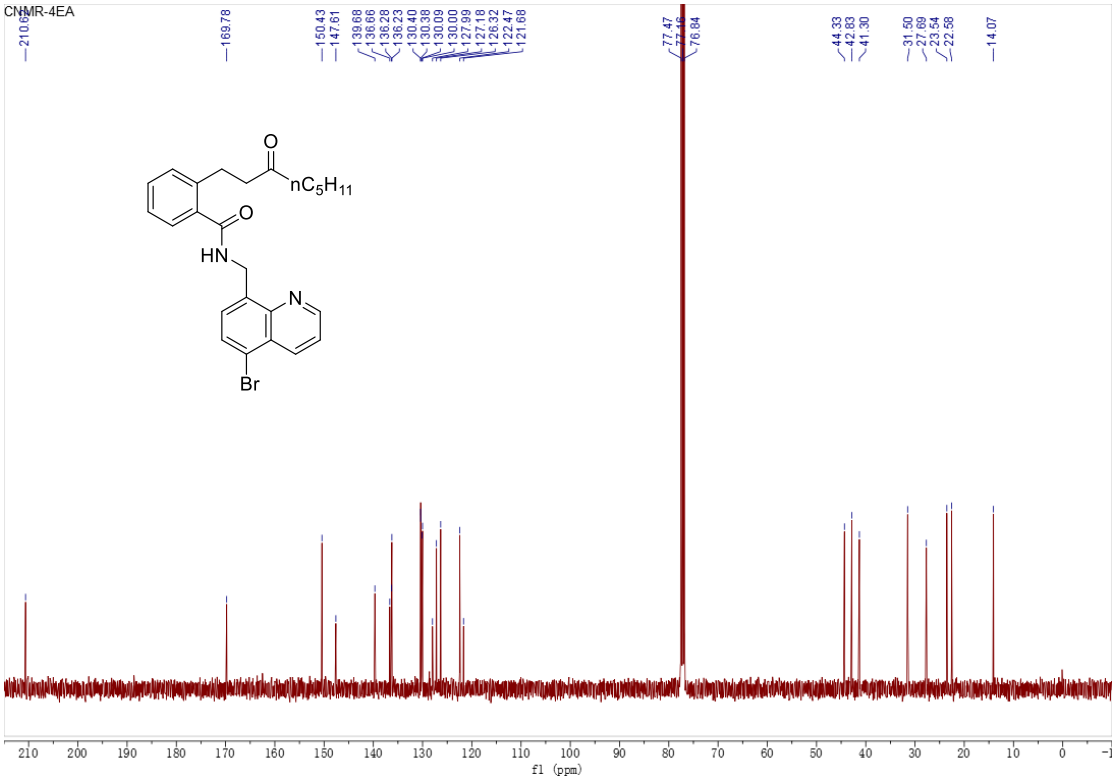
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4da**



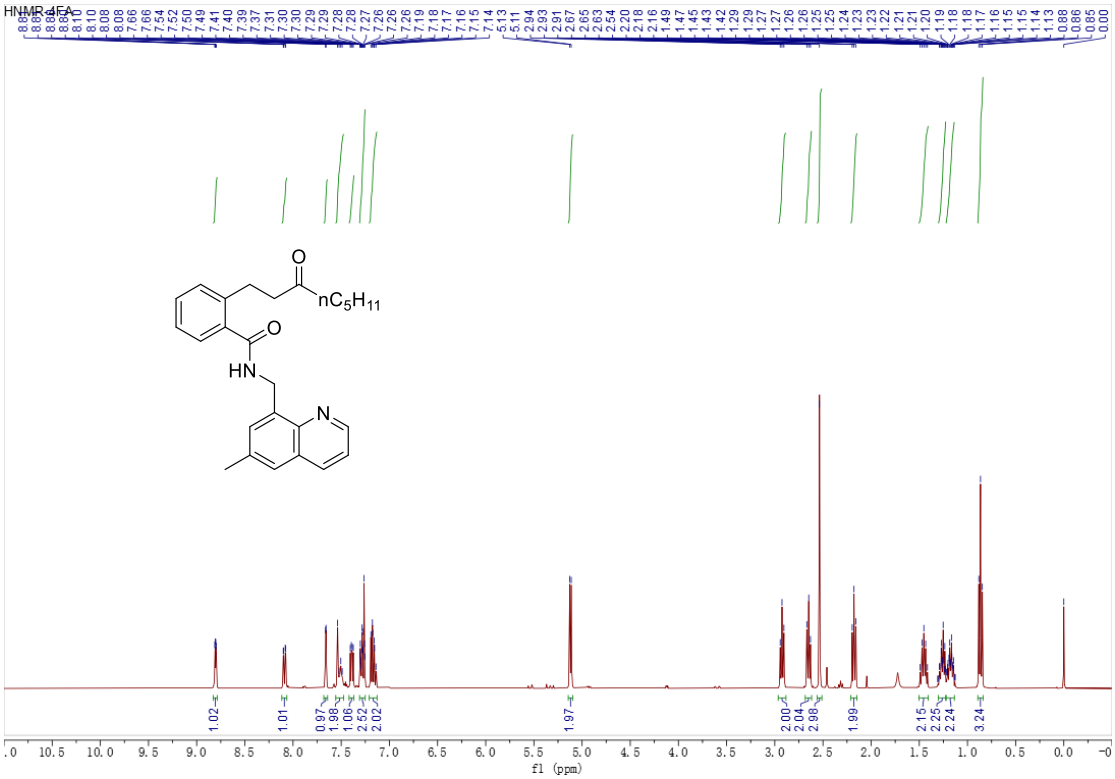
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ea**



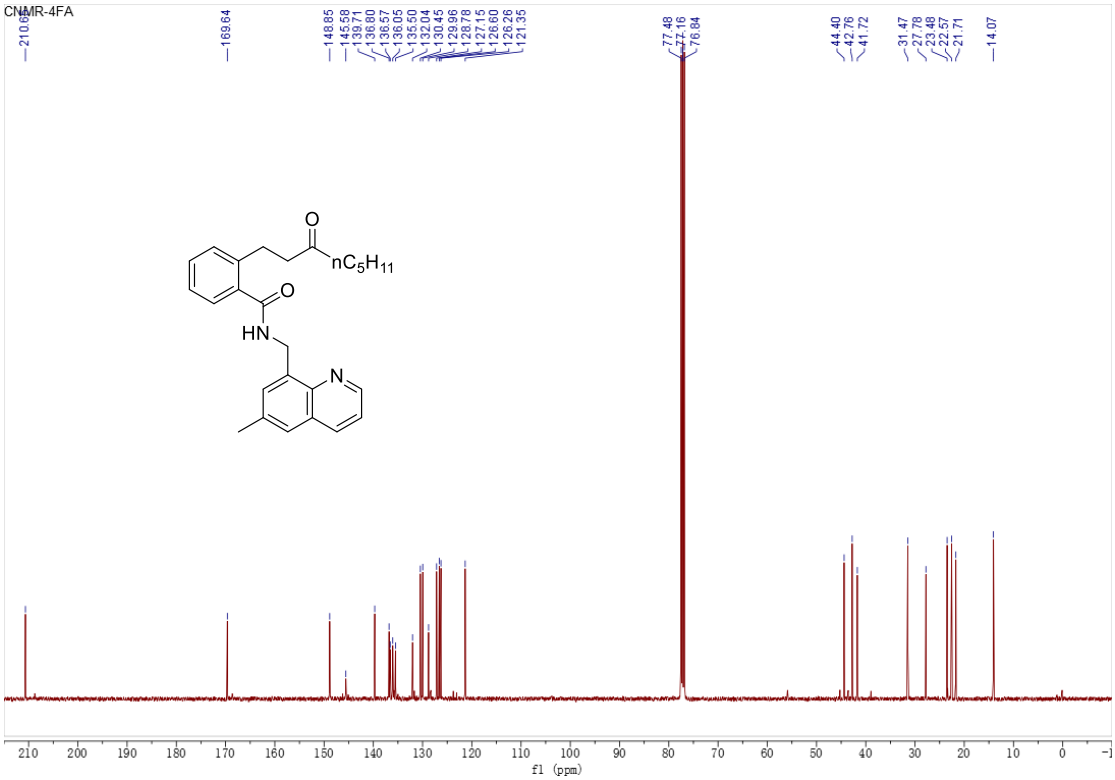
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ea**



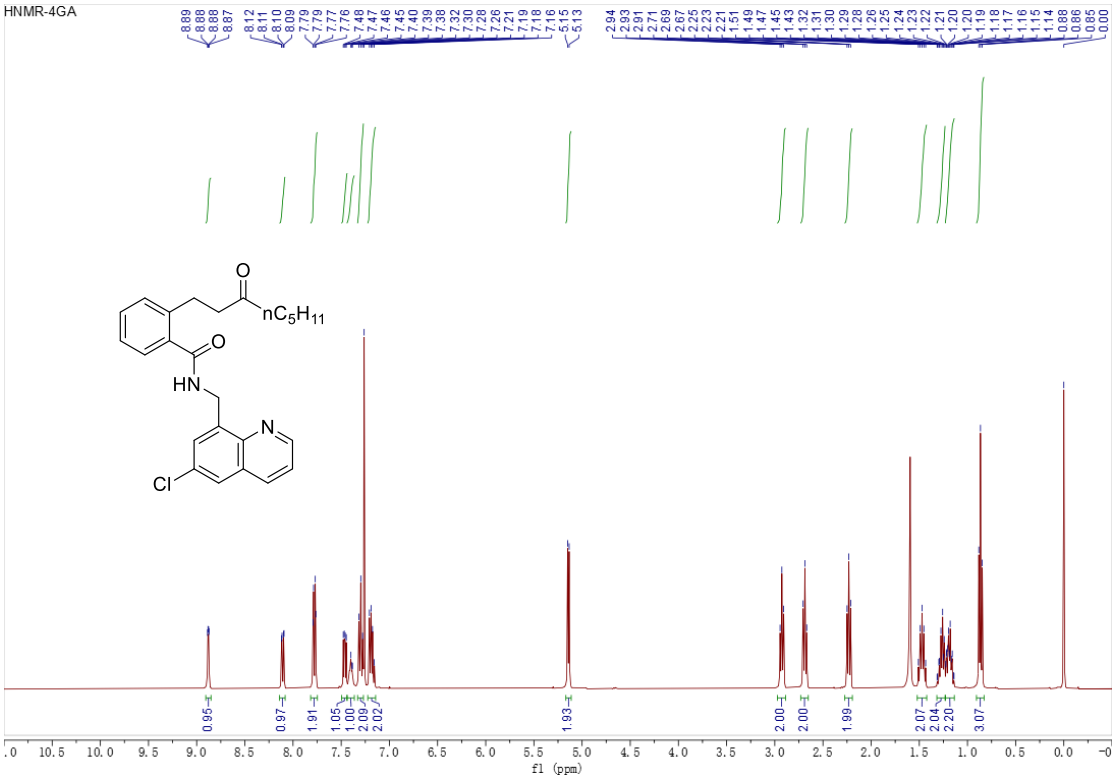
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4fa**



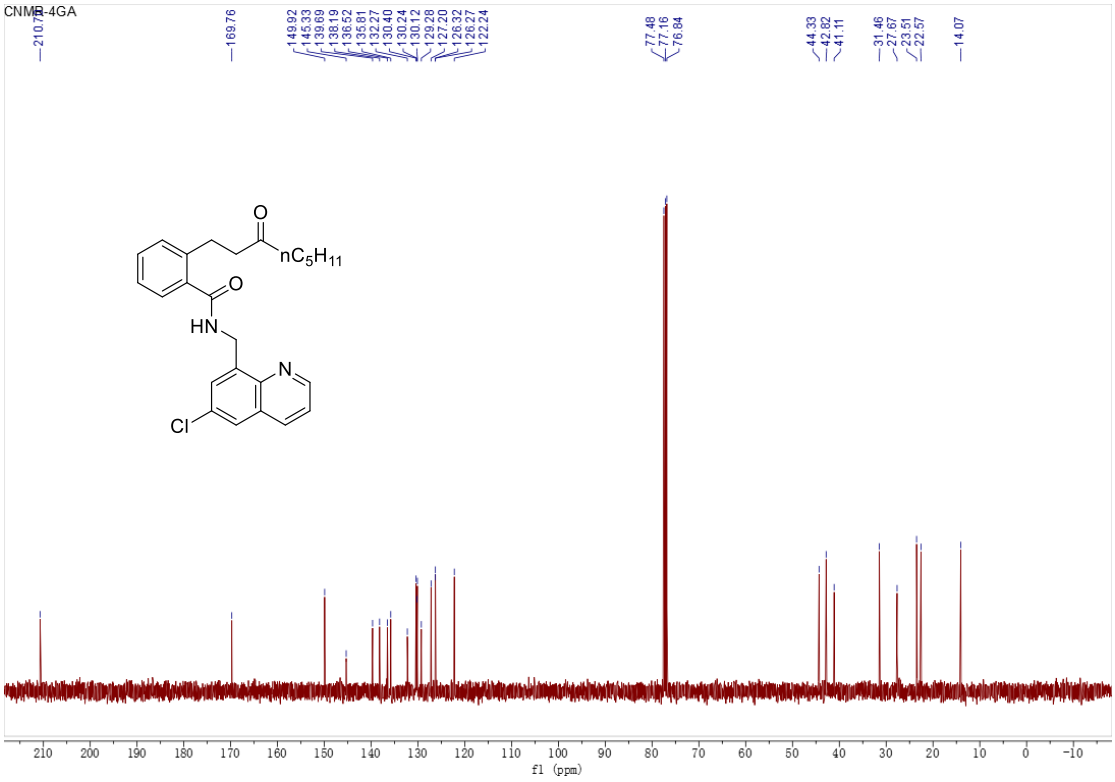
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4fa**



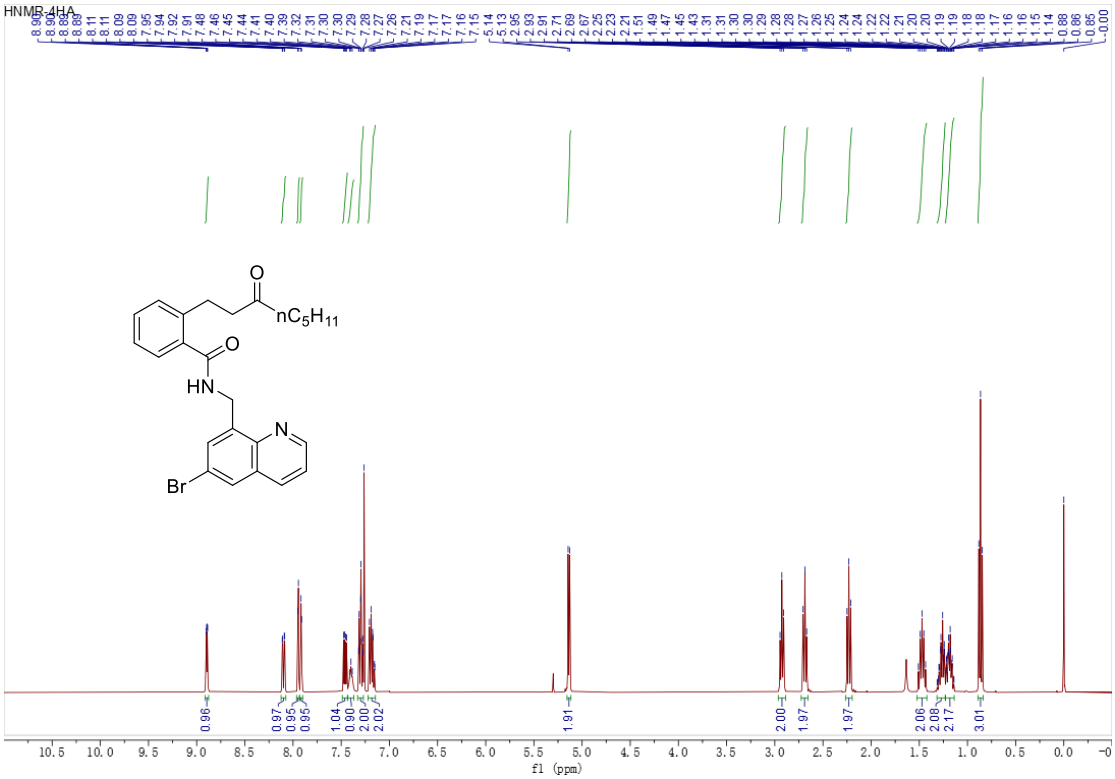
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ga**



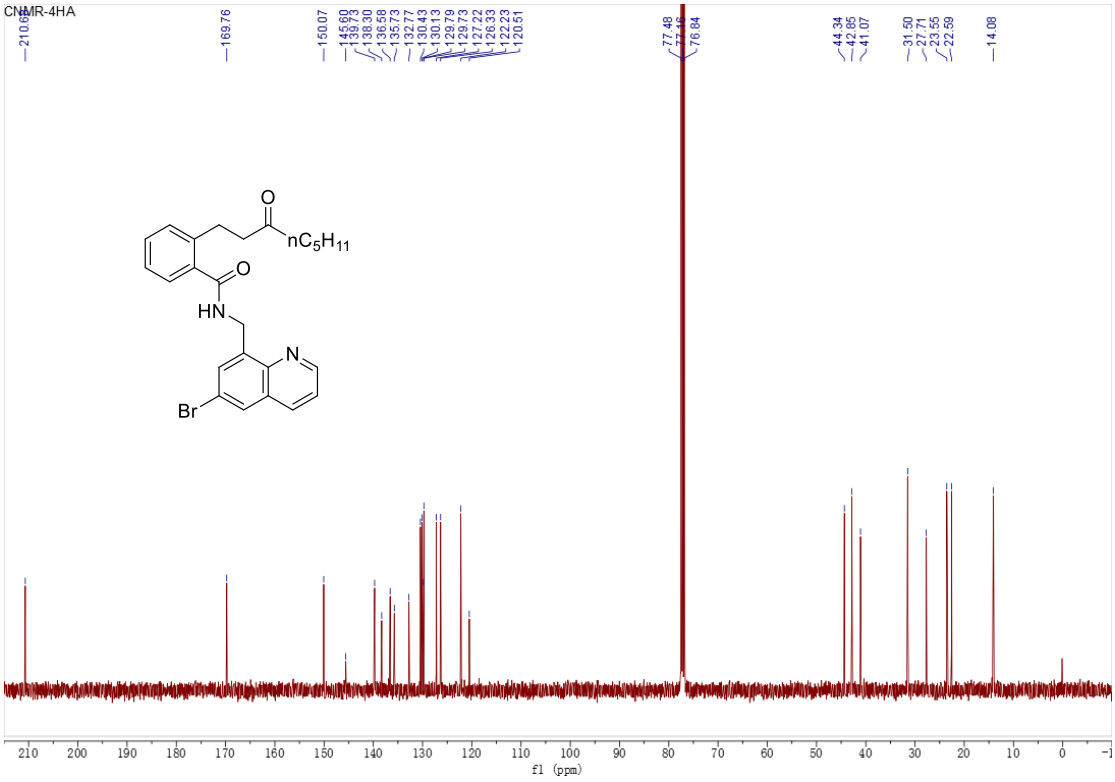
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ga**



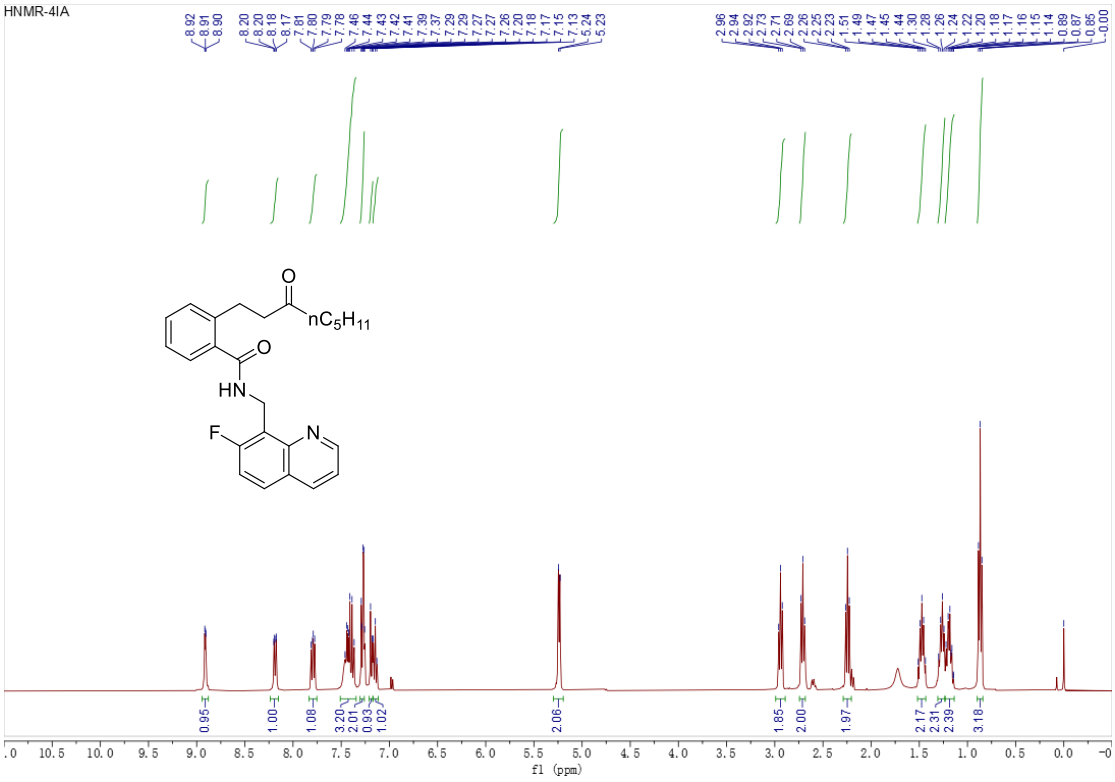
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ha**



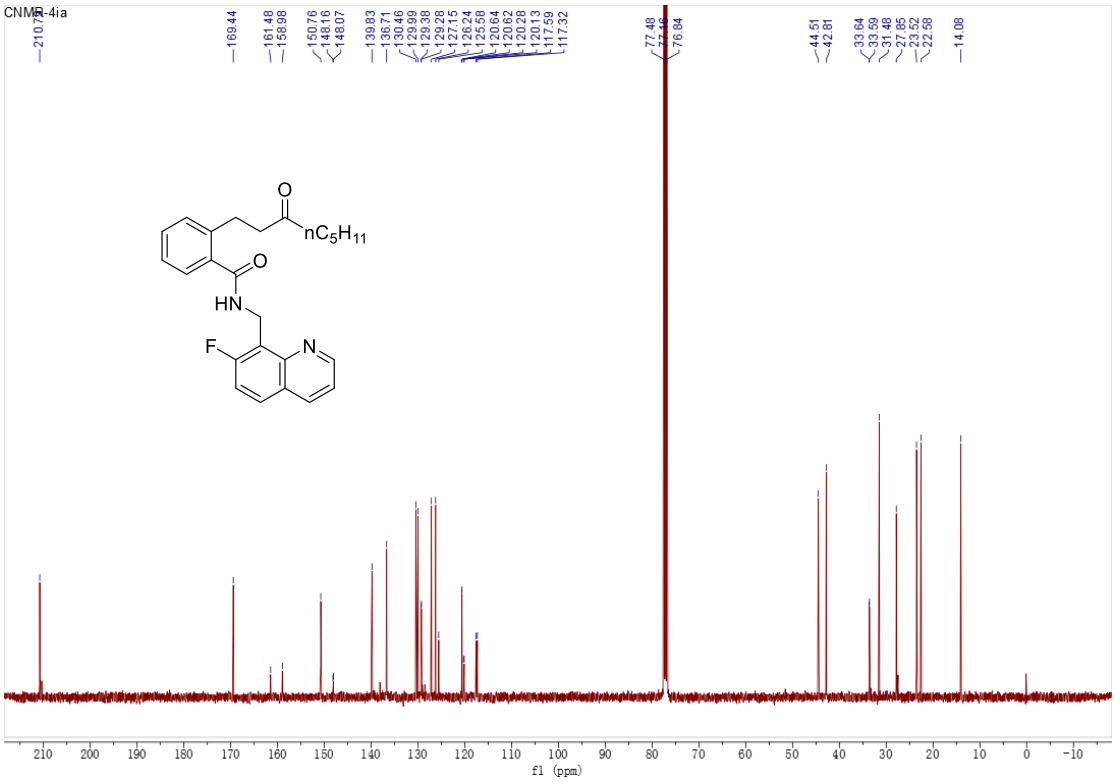
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ha**



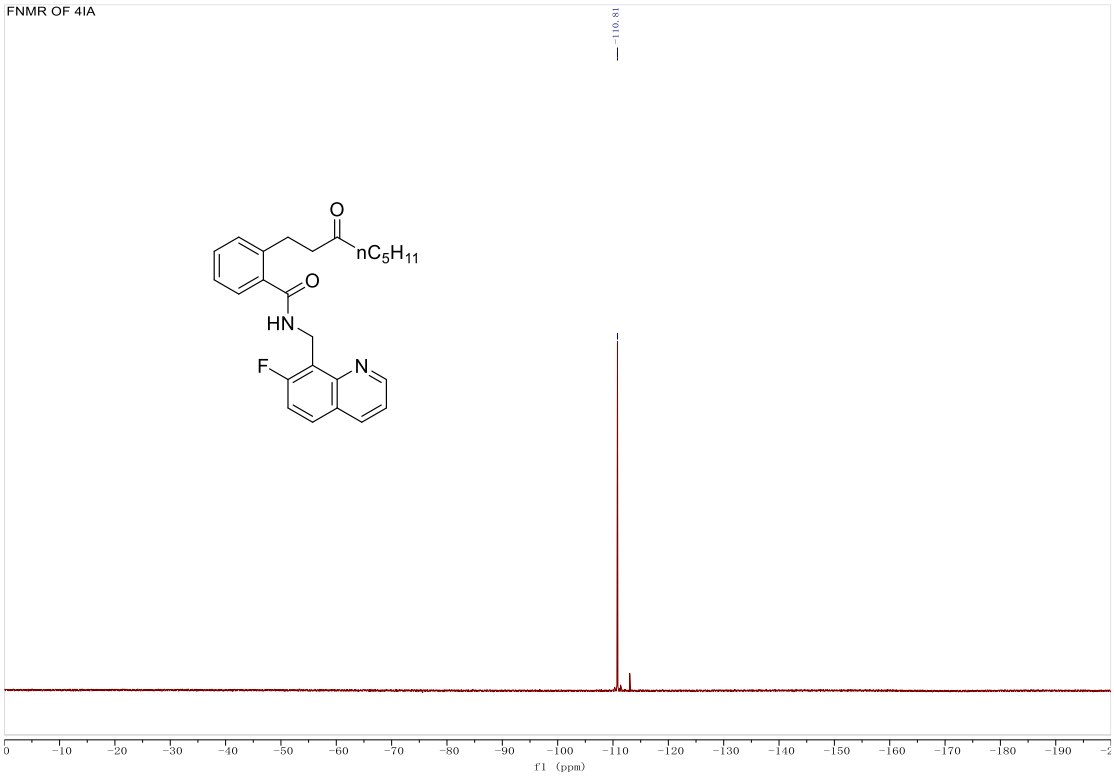
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ia**



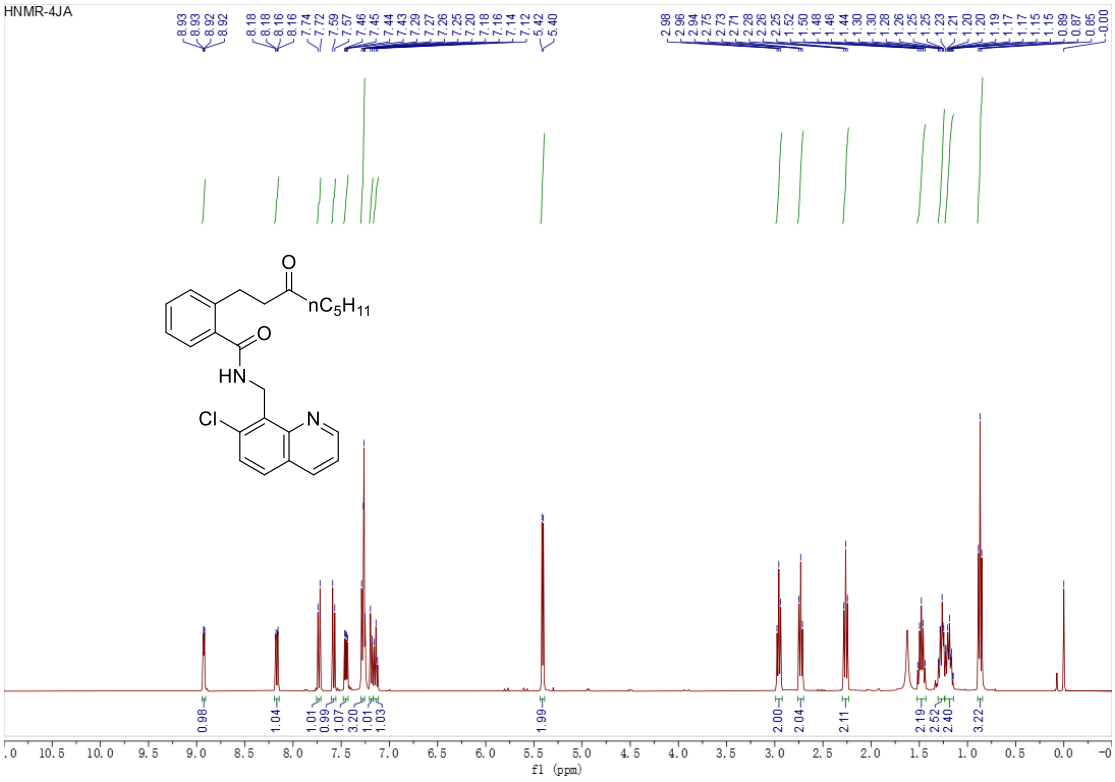
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ia**



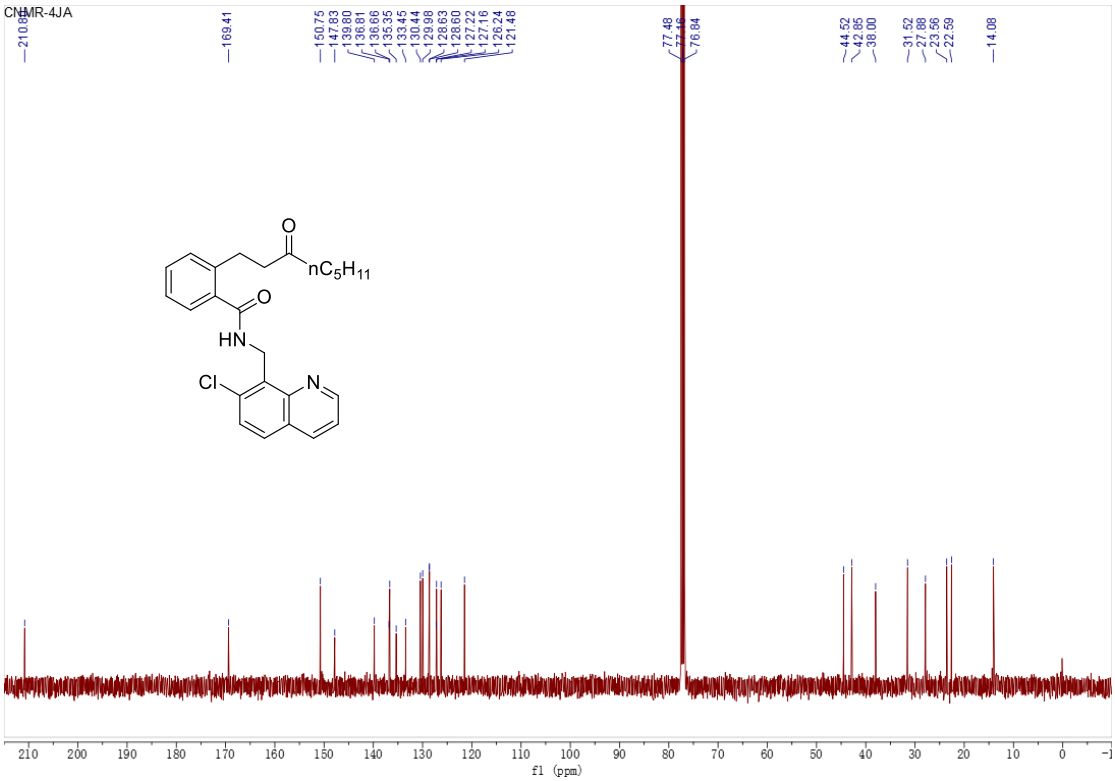
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4ia**



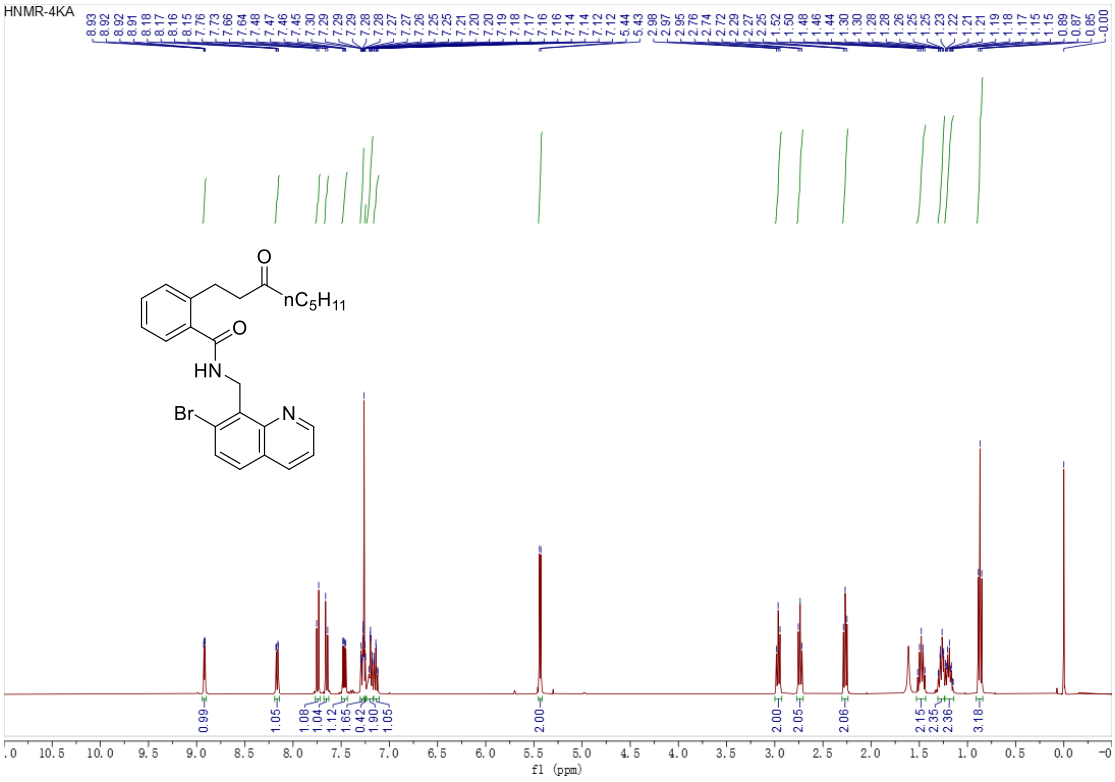
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ja**



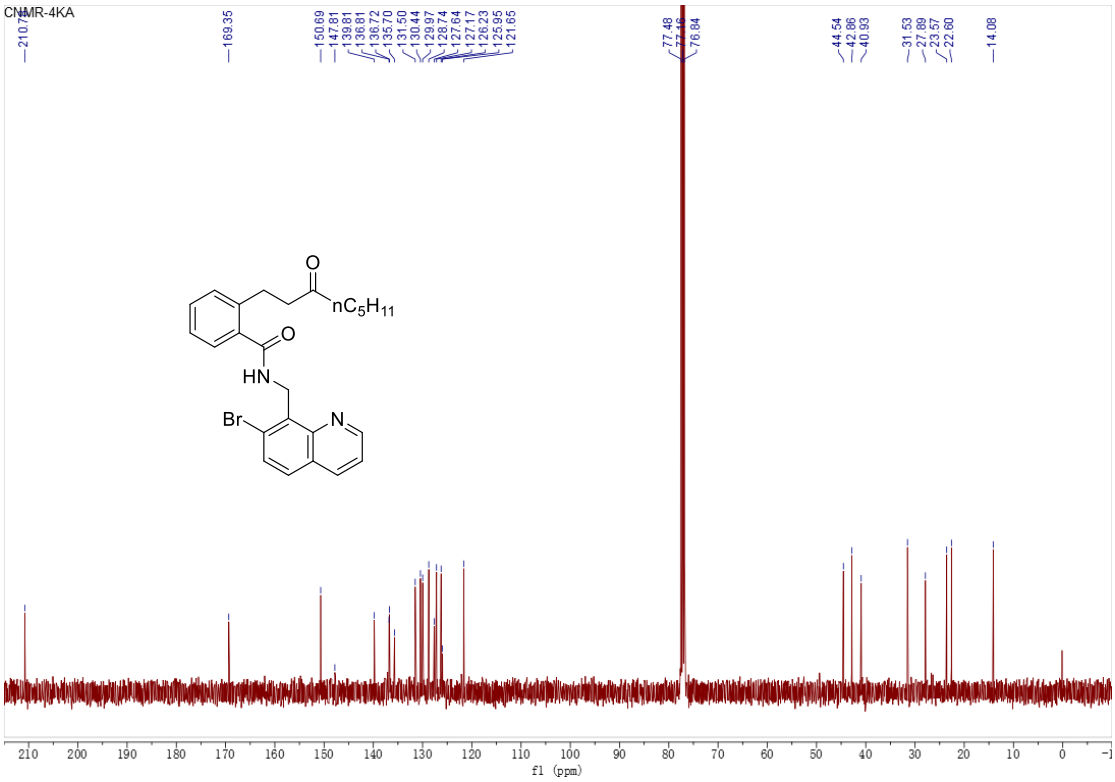
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ja**



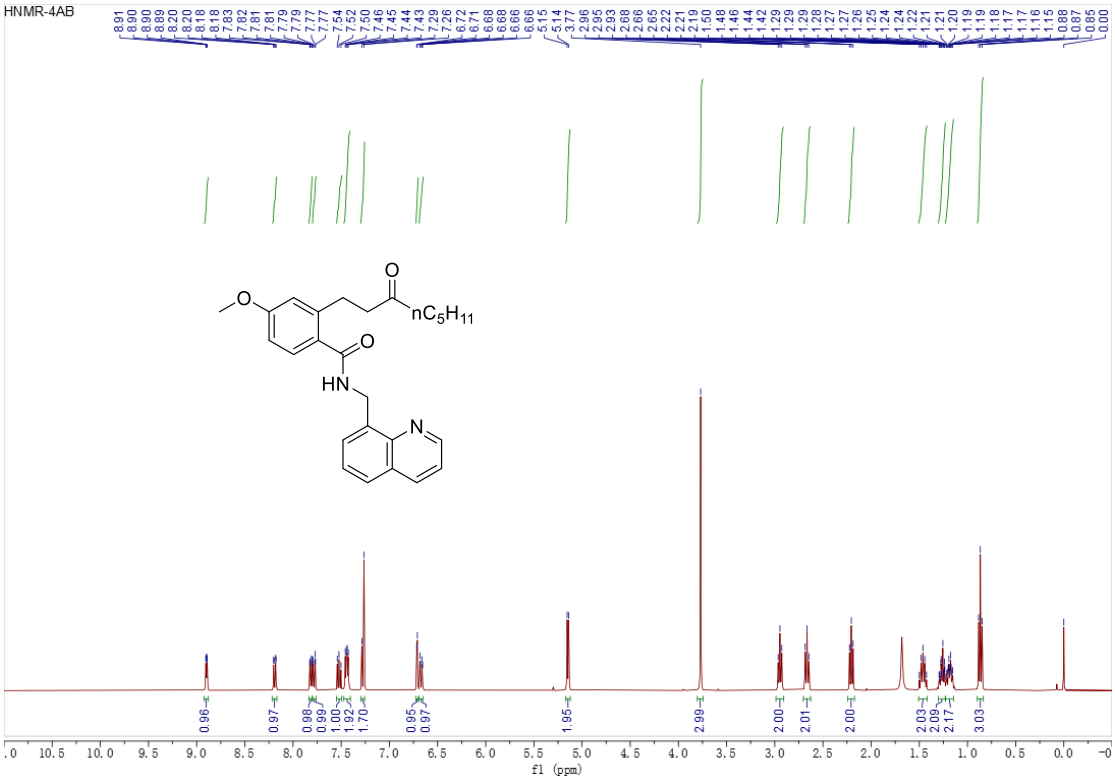
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ka**



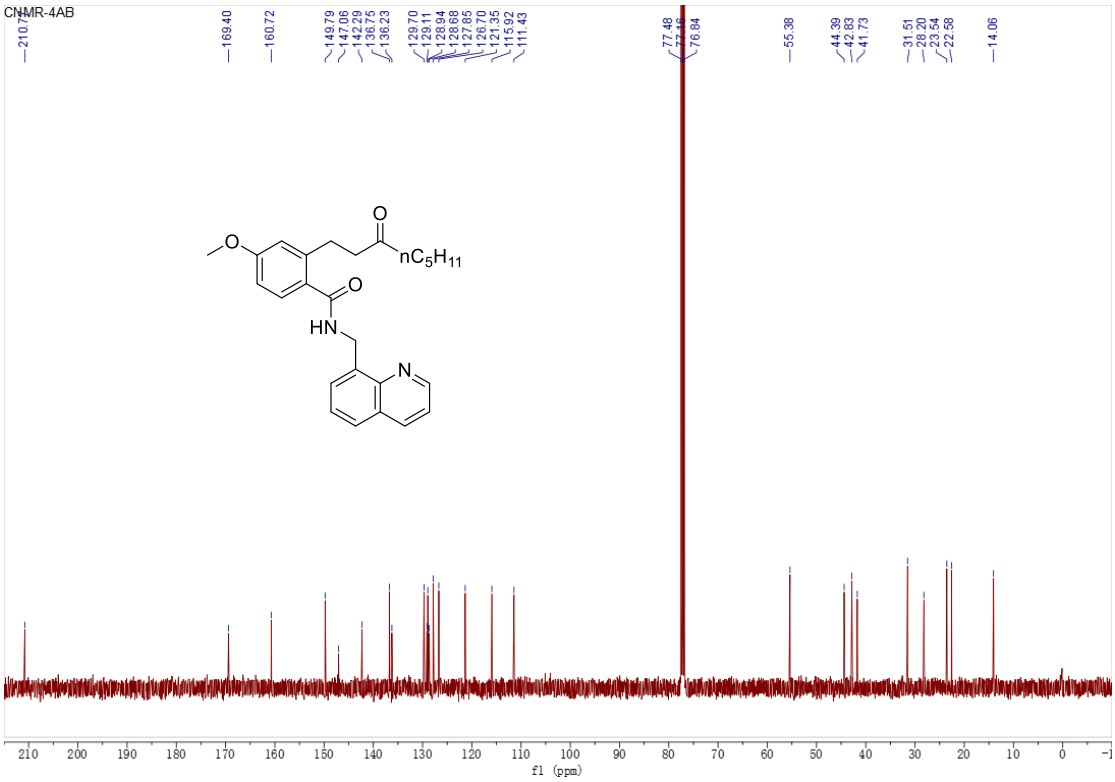
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ka**



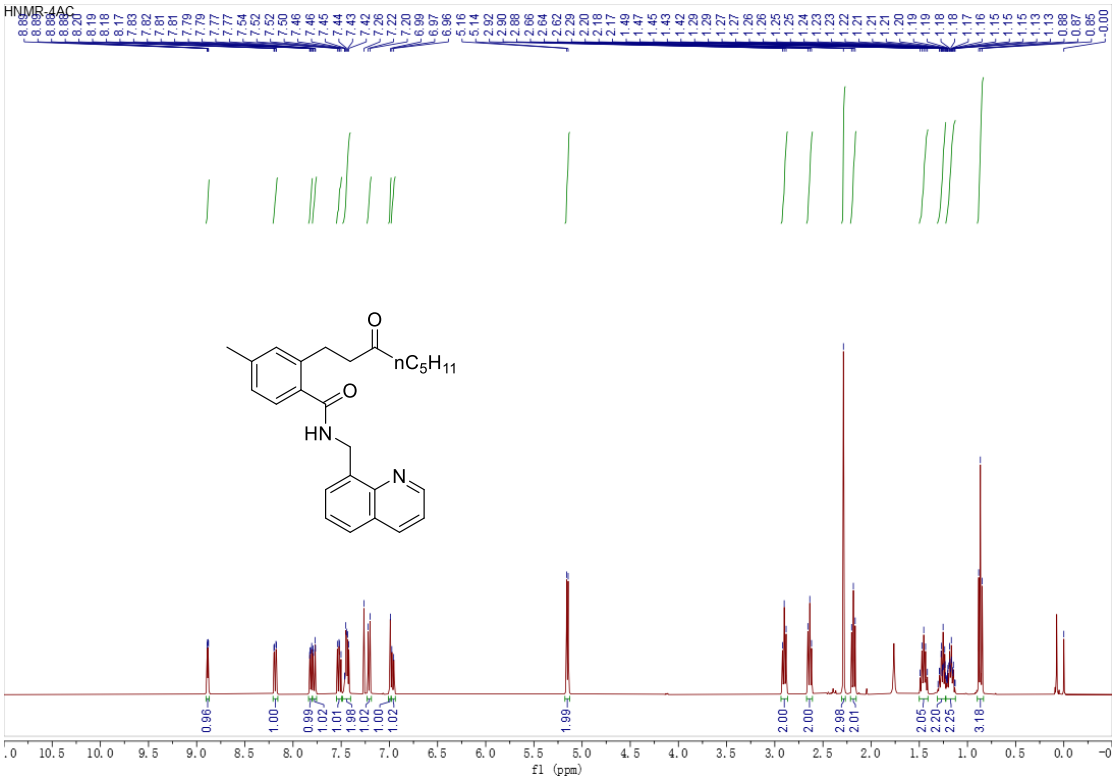
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ab**



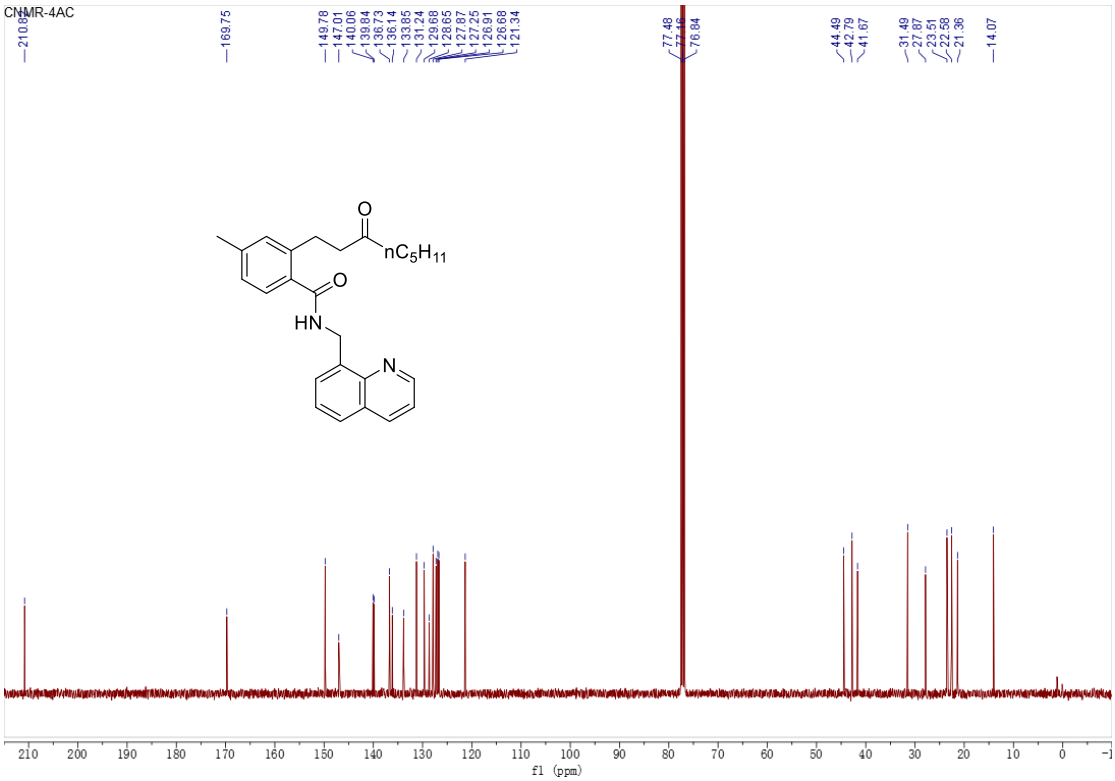
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ab**



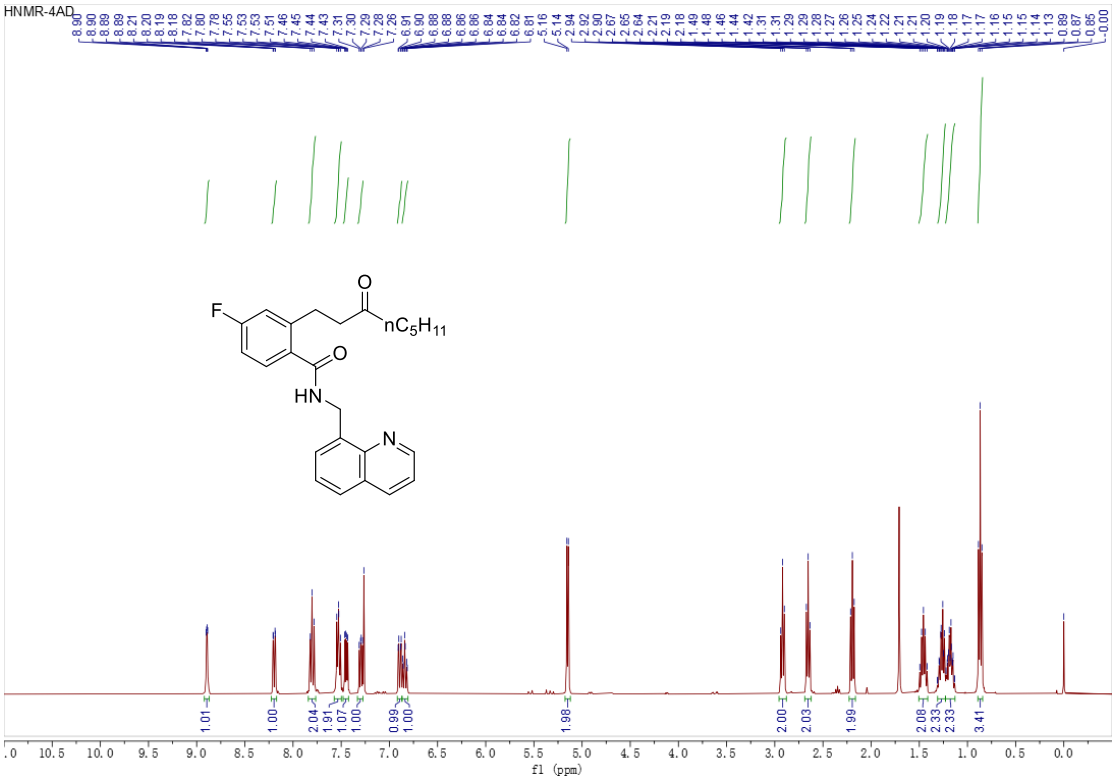
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ac**



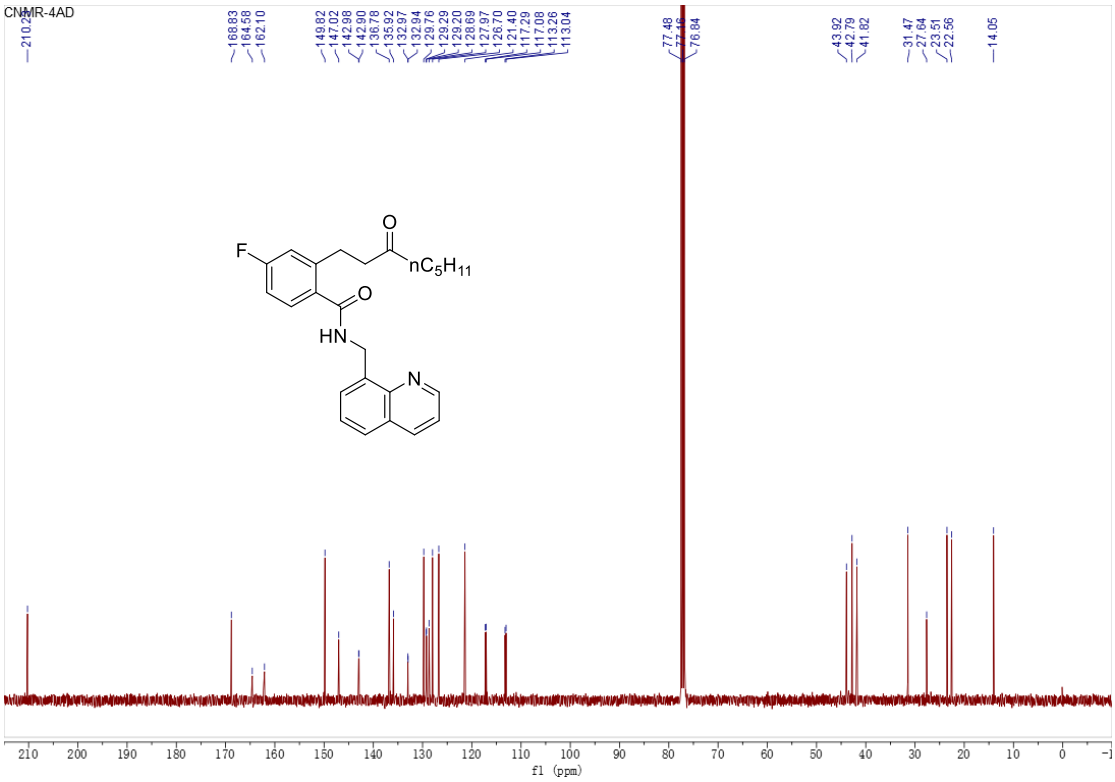
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ac**



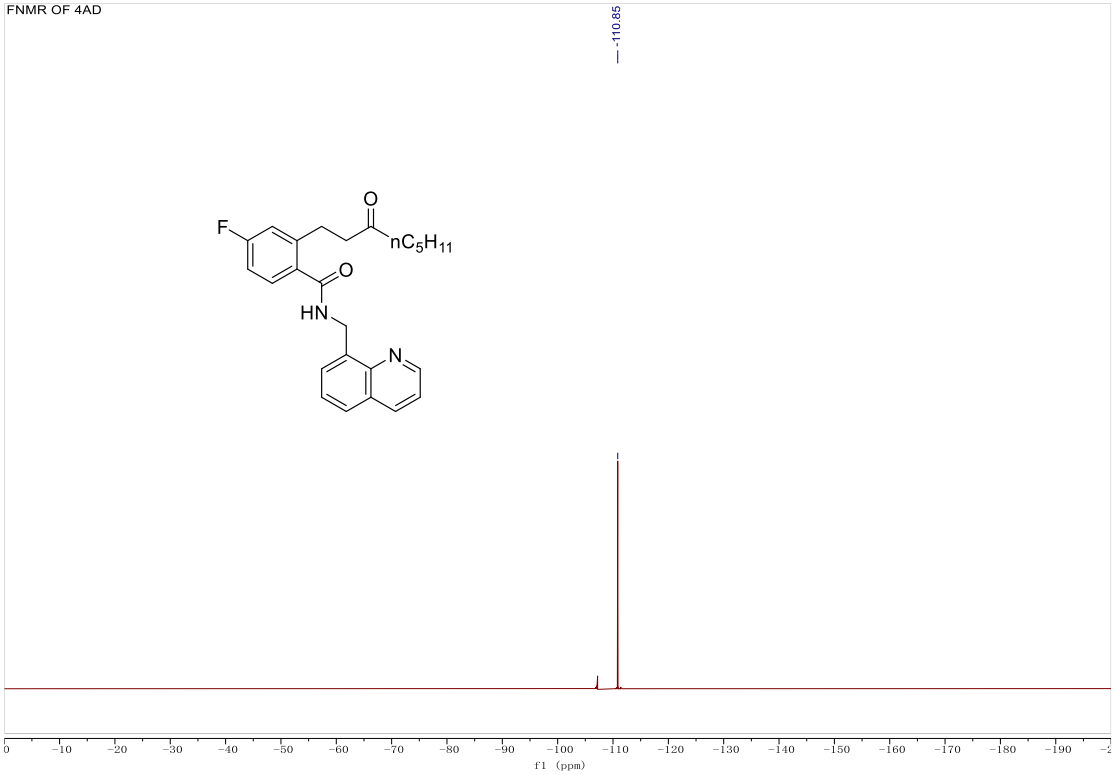
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ad**



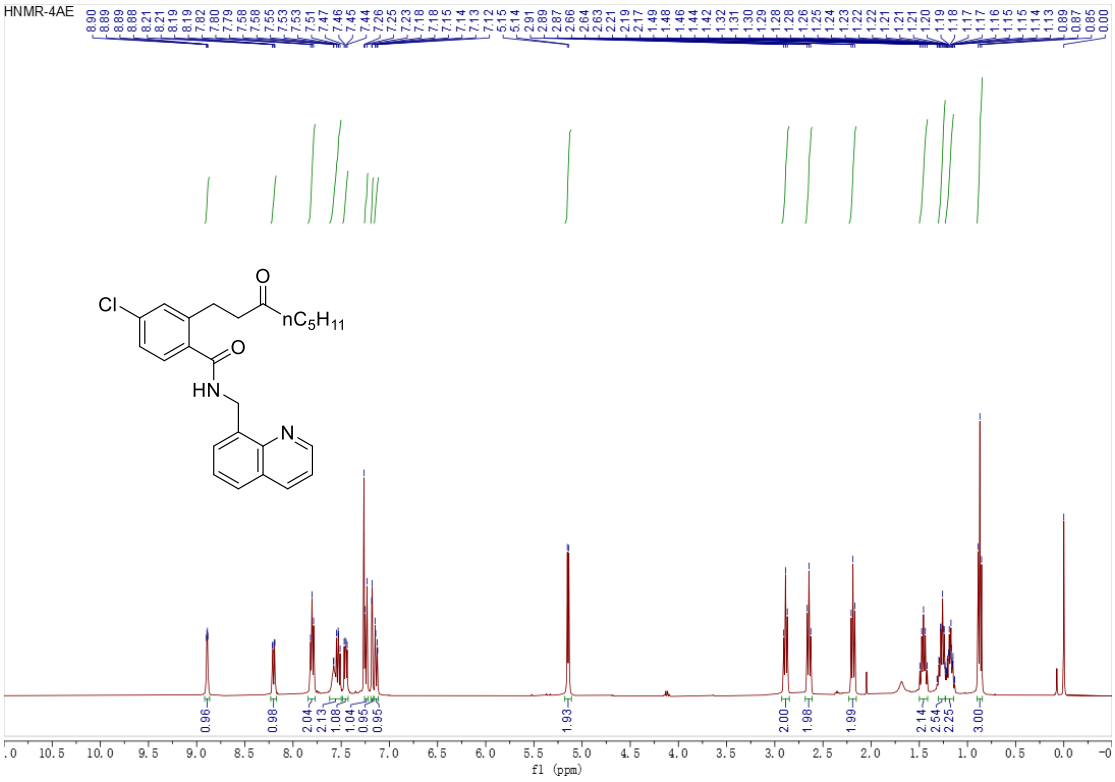
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ad**



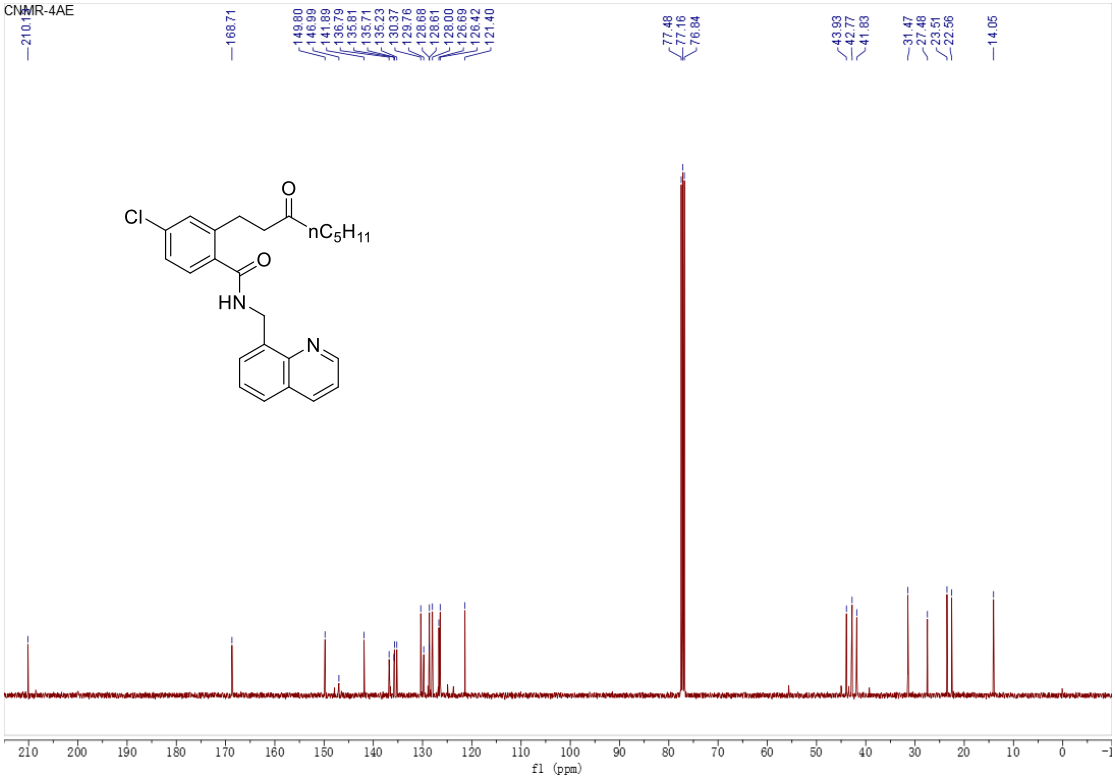
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4ad**



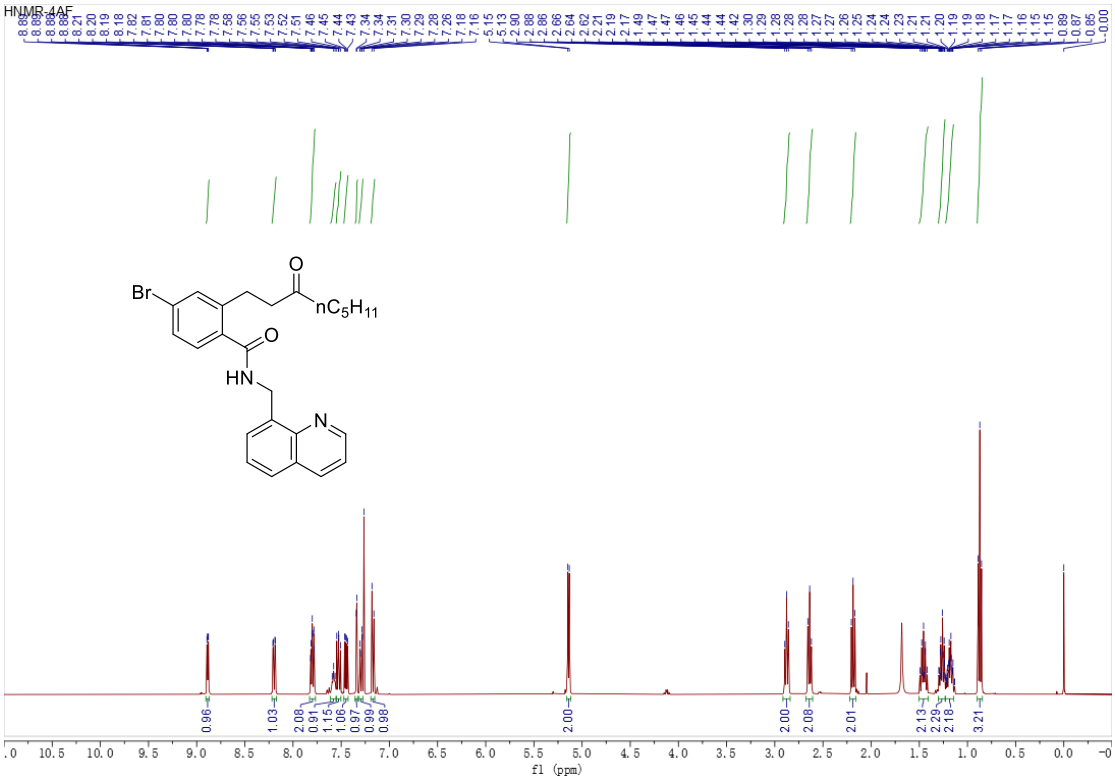
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ae**



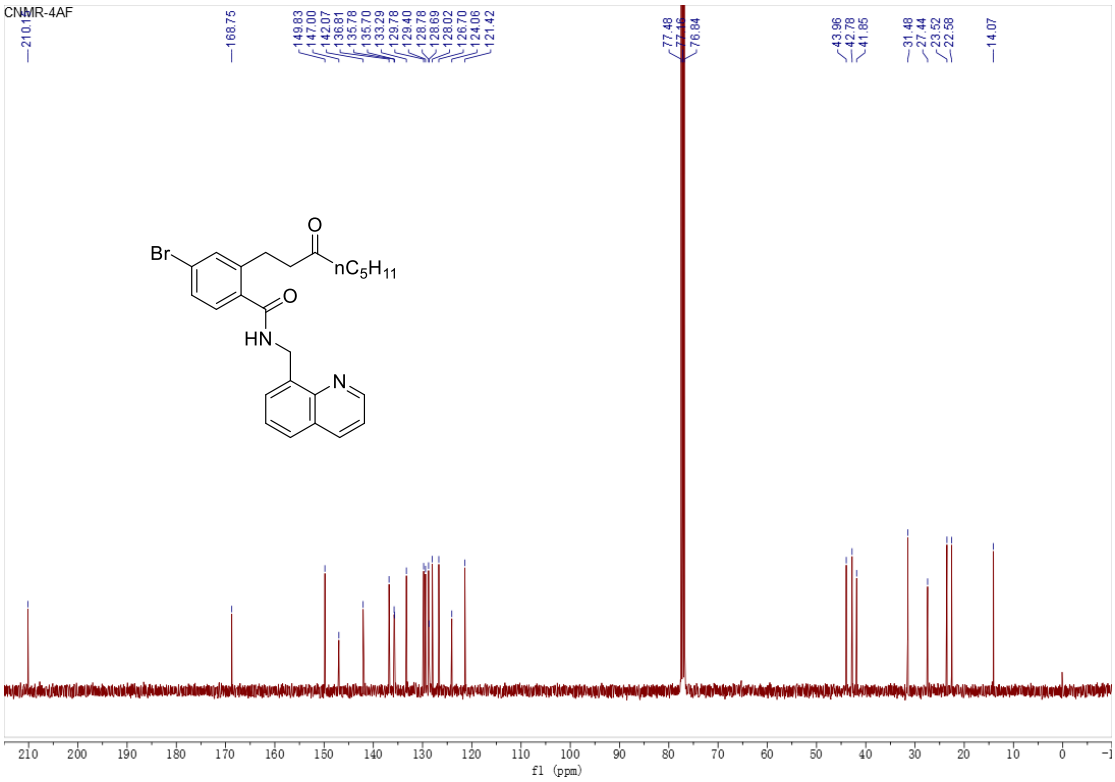
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ae**



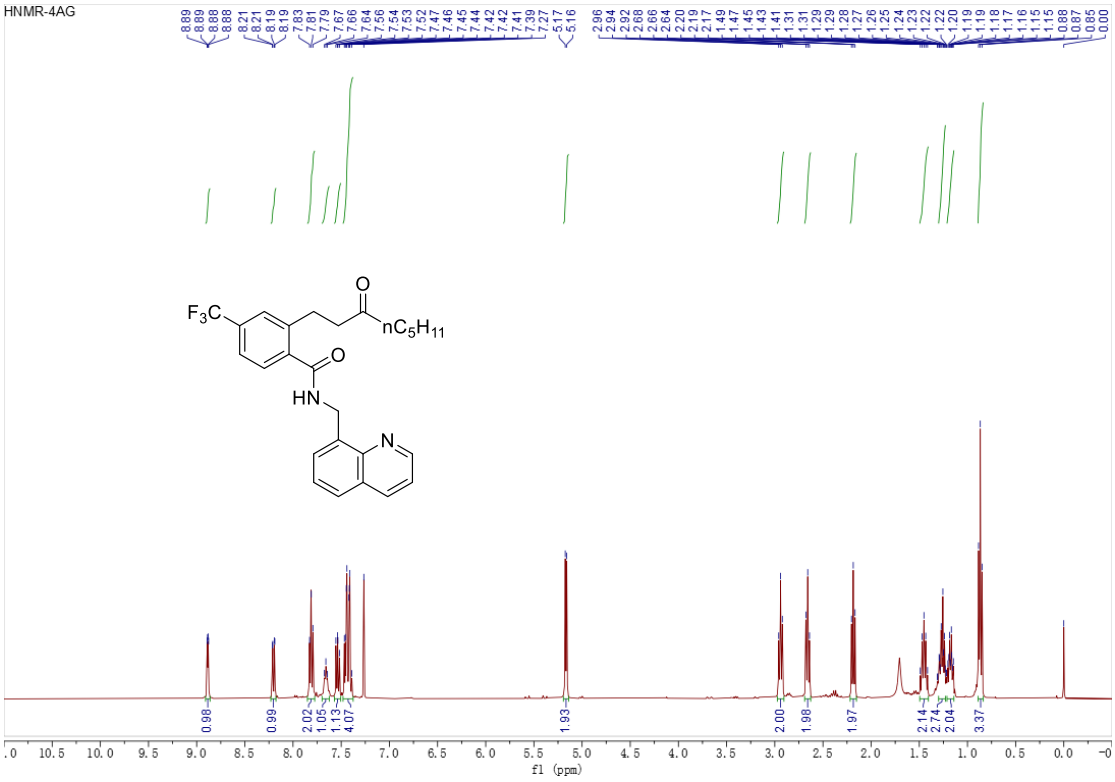
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4af**



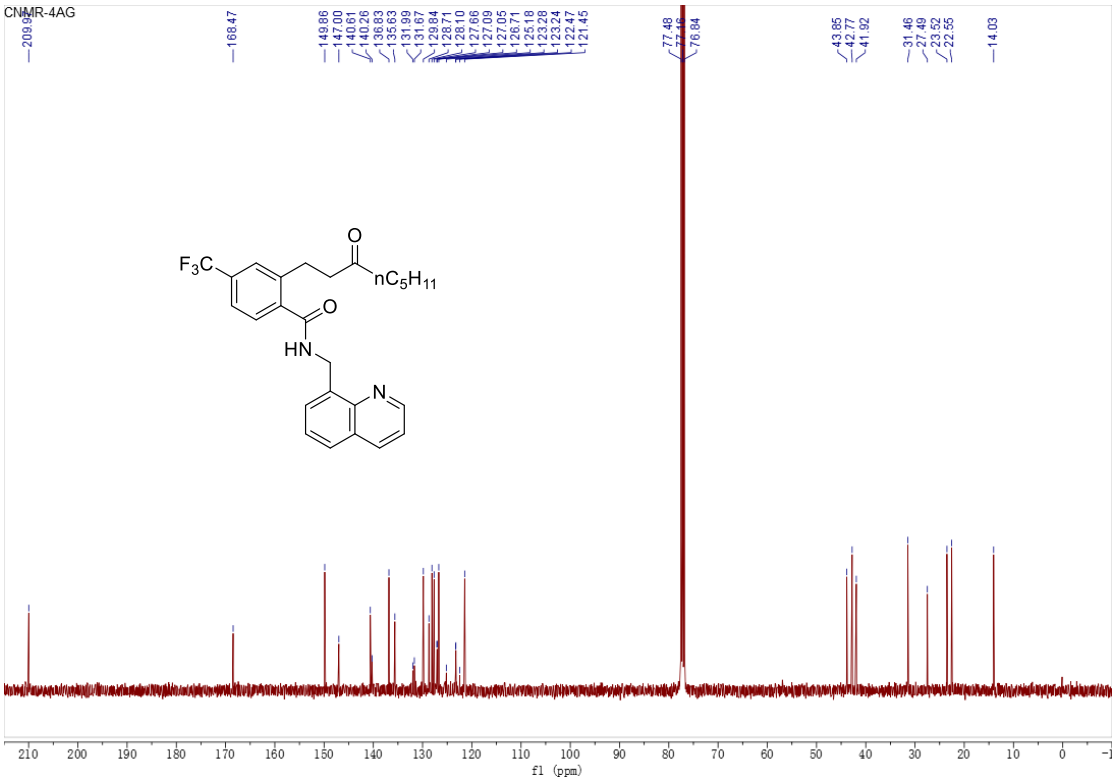
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4af**



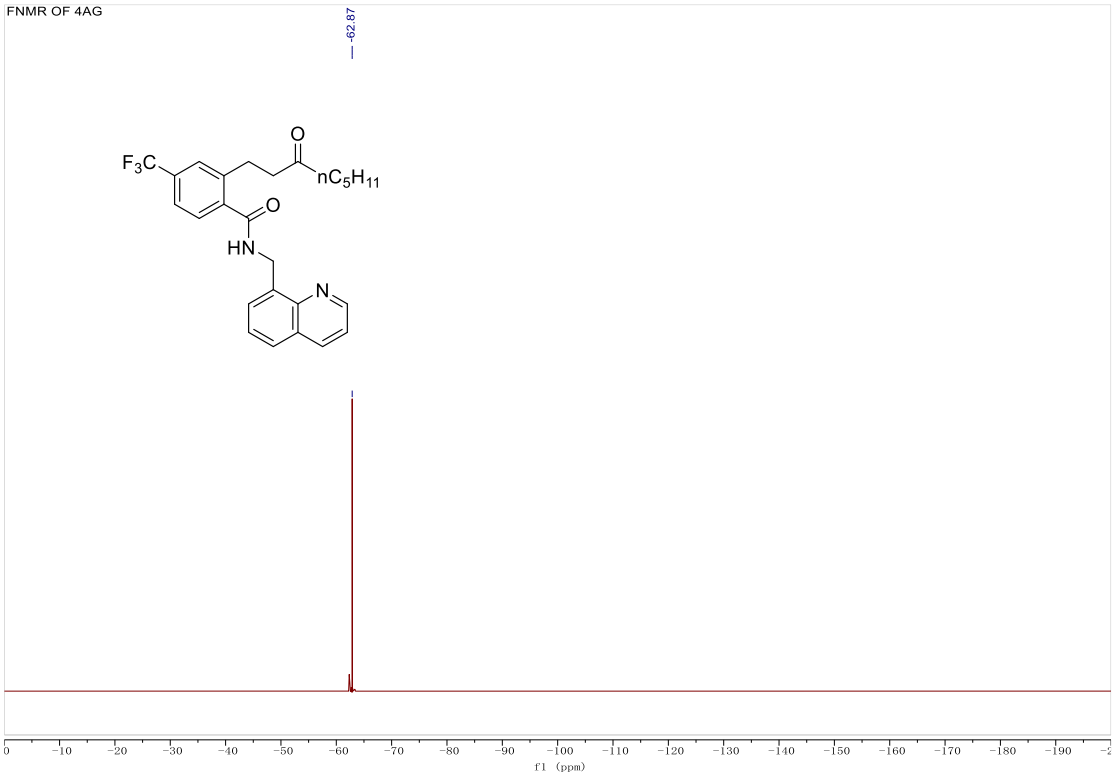
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ag**



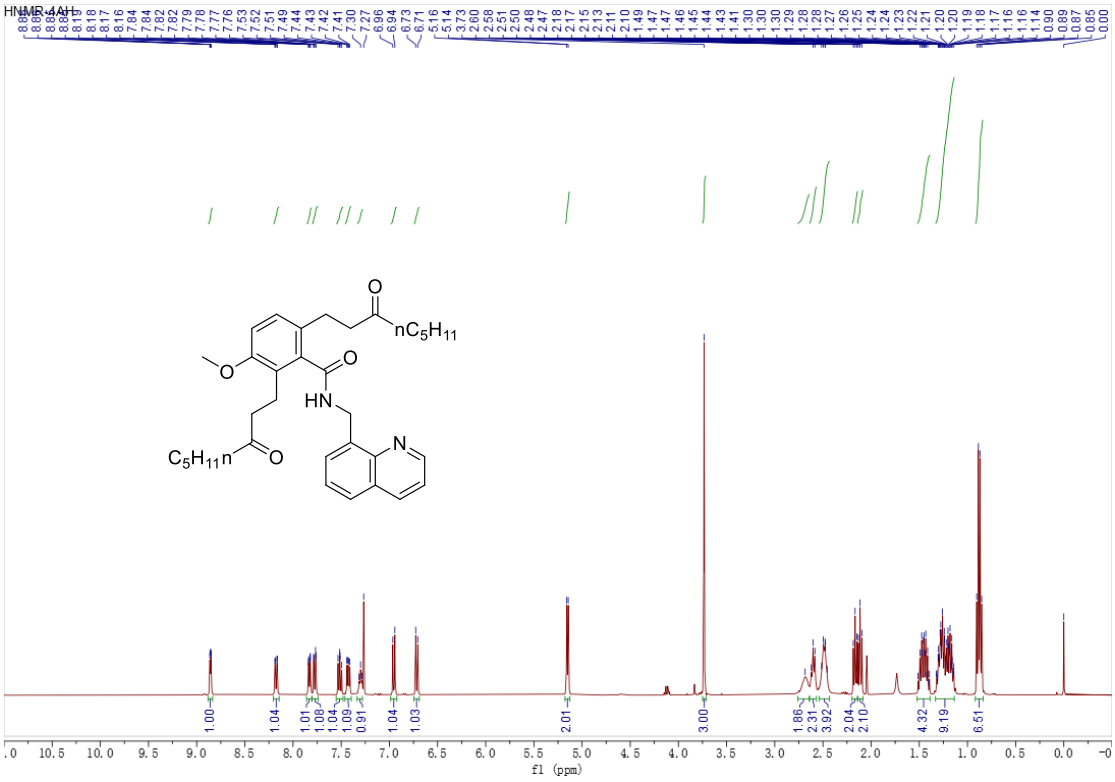
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ag**



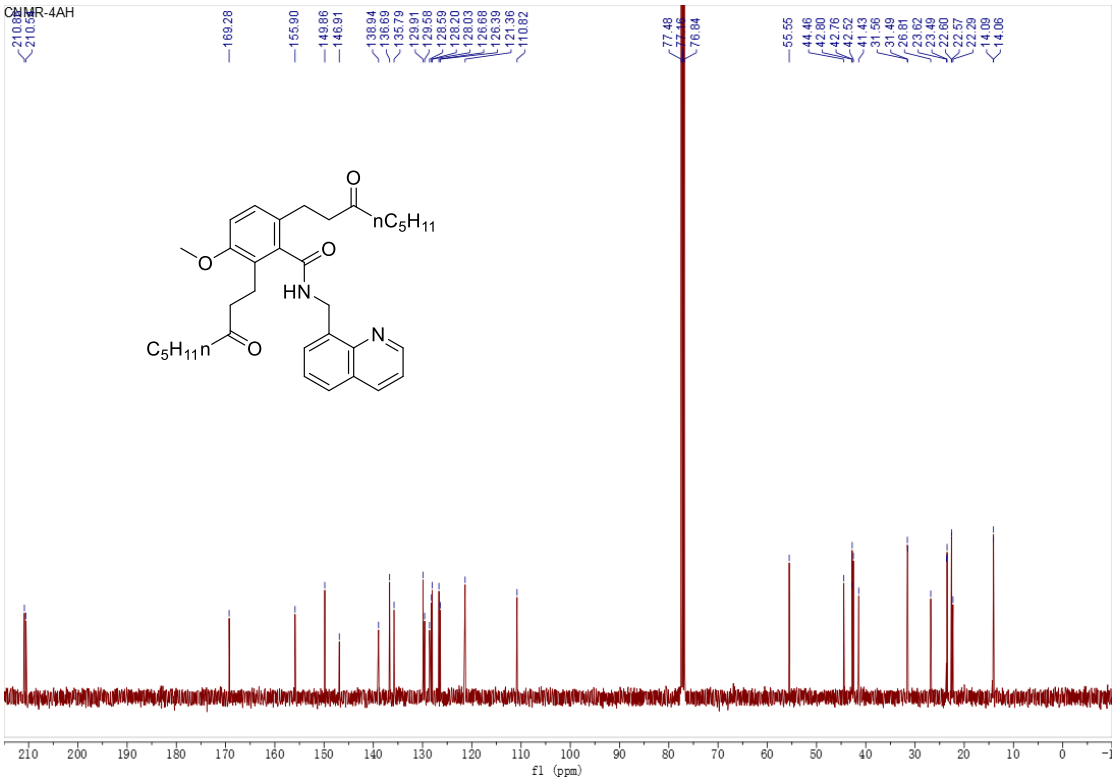
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4ag**



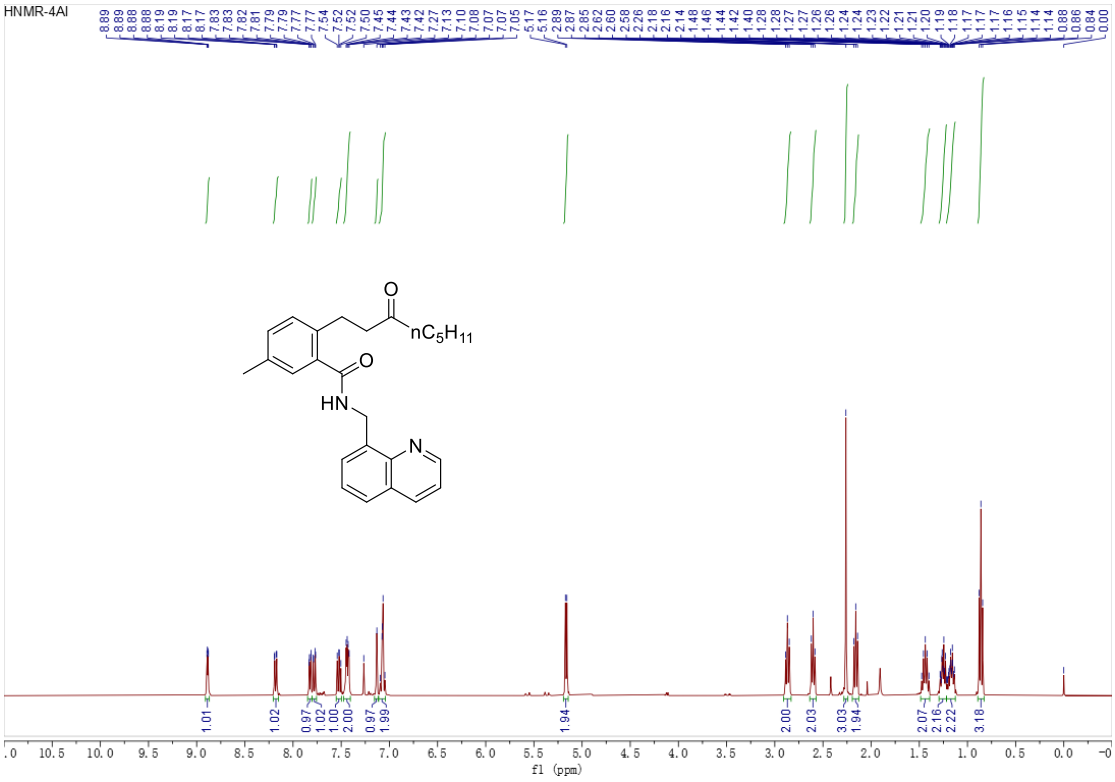
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ah**



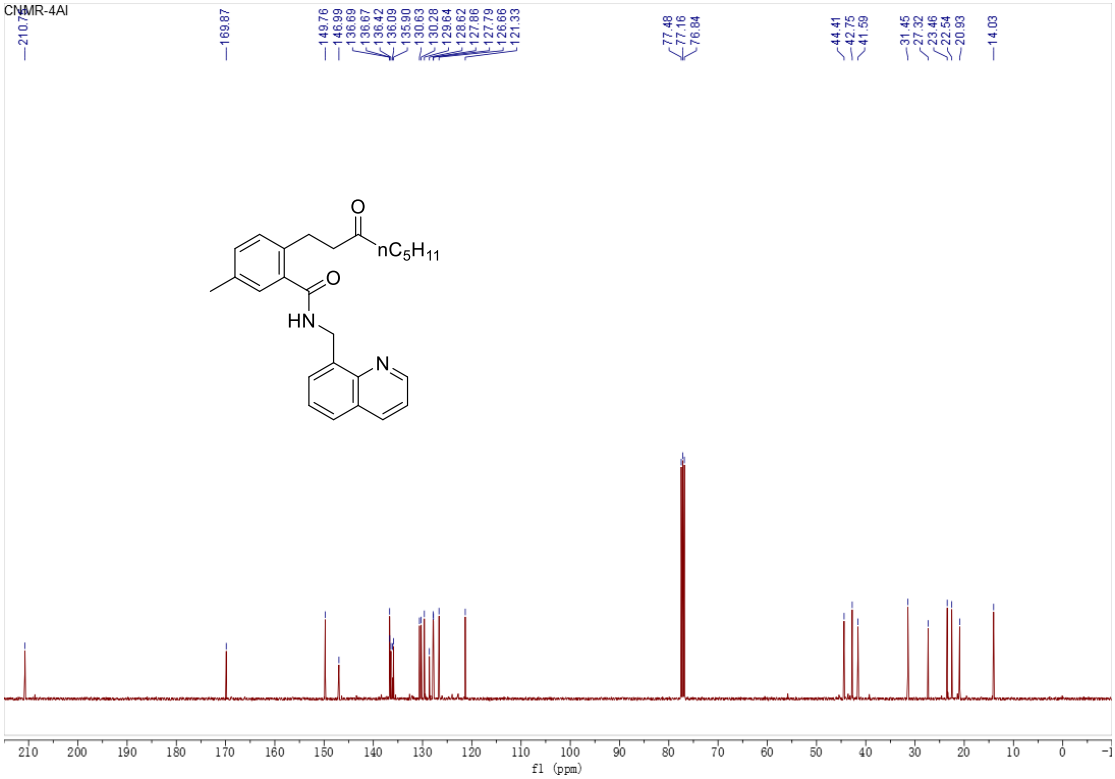
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ah**



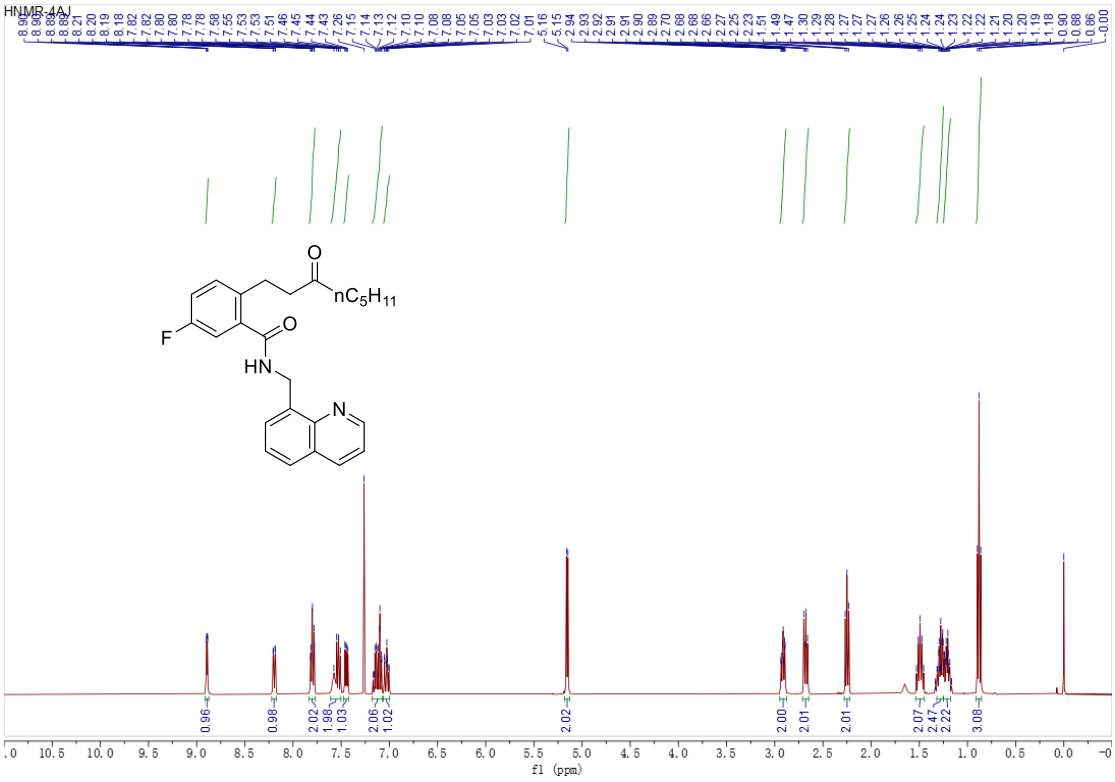
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ai**



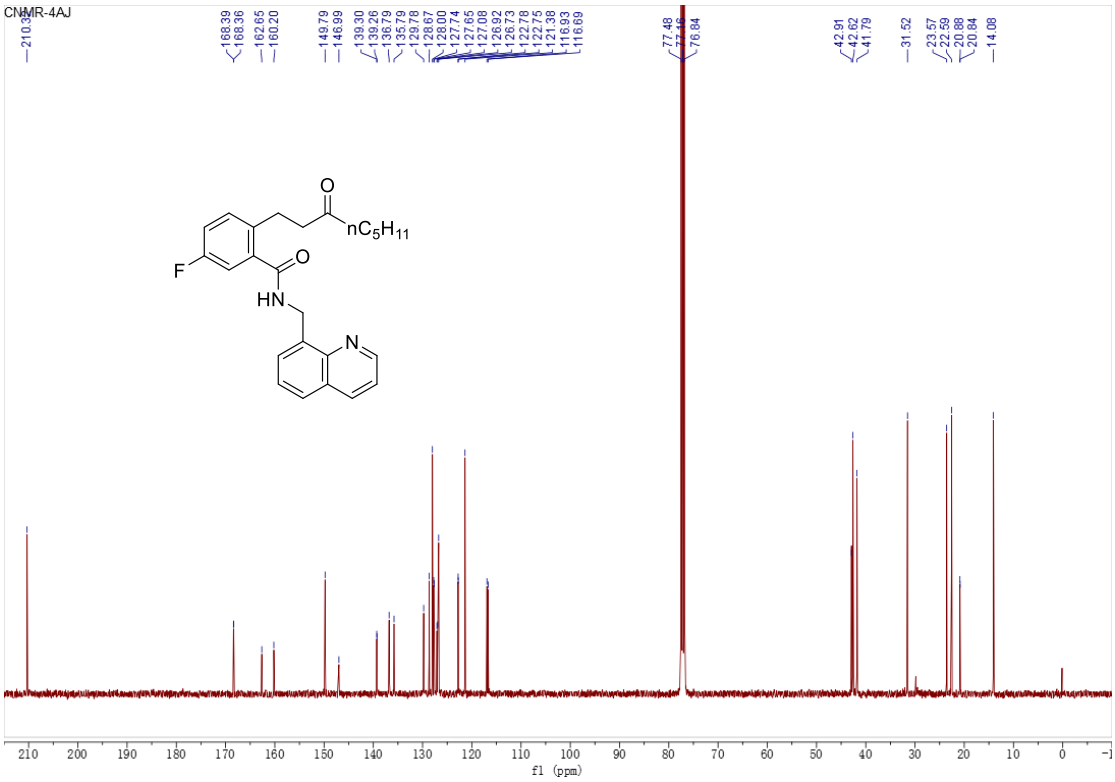
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ai**



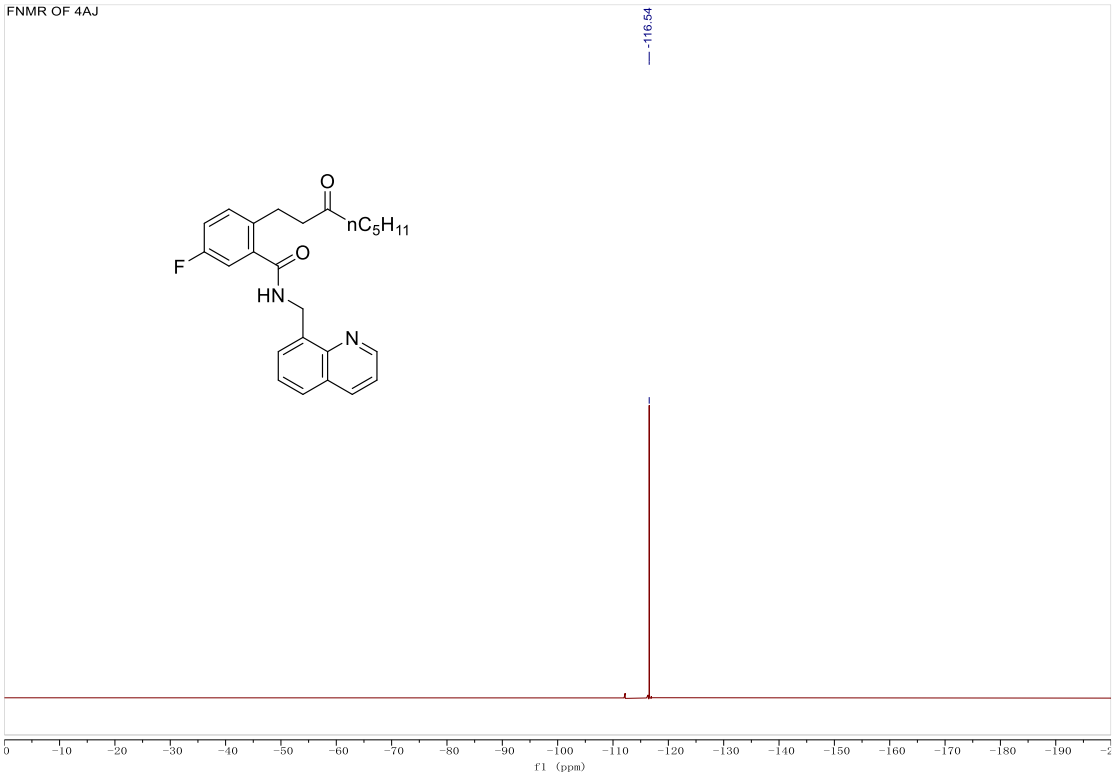
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4aj**



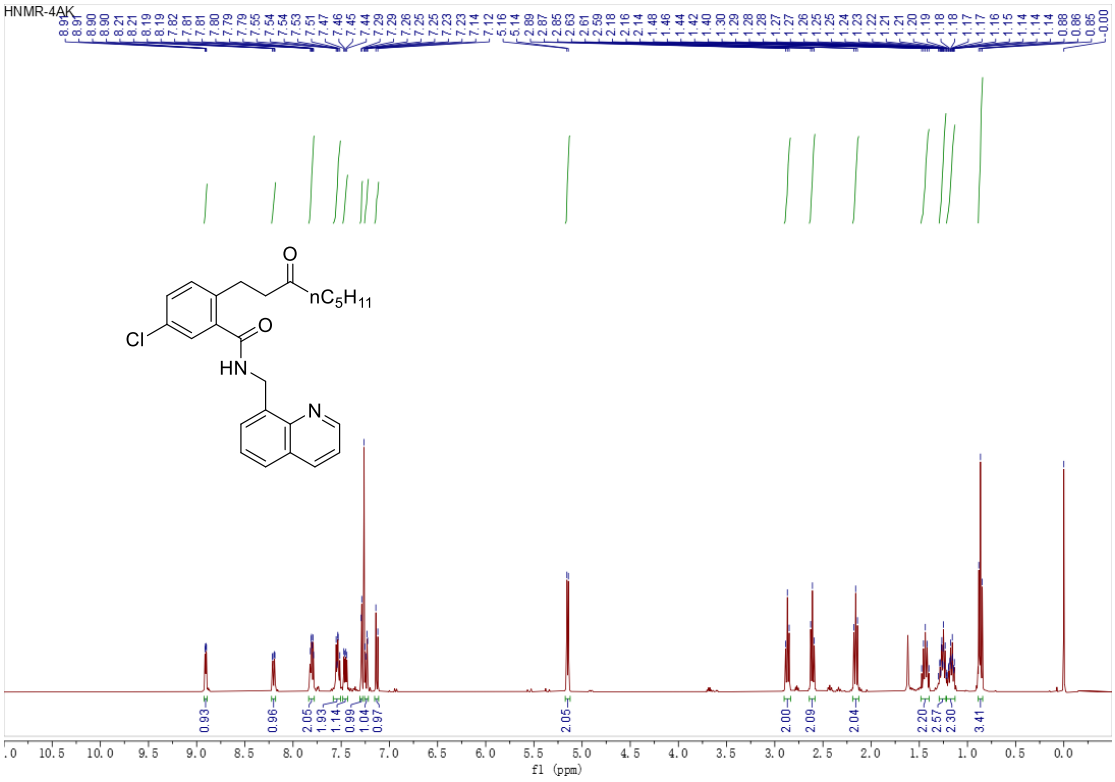
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4aj**



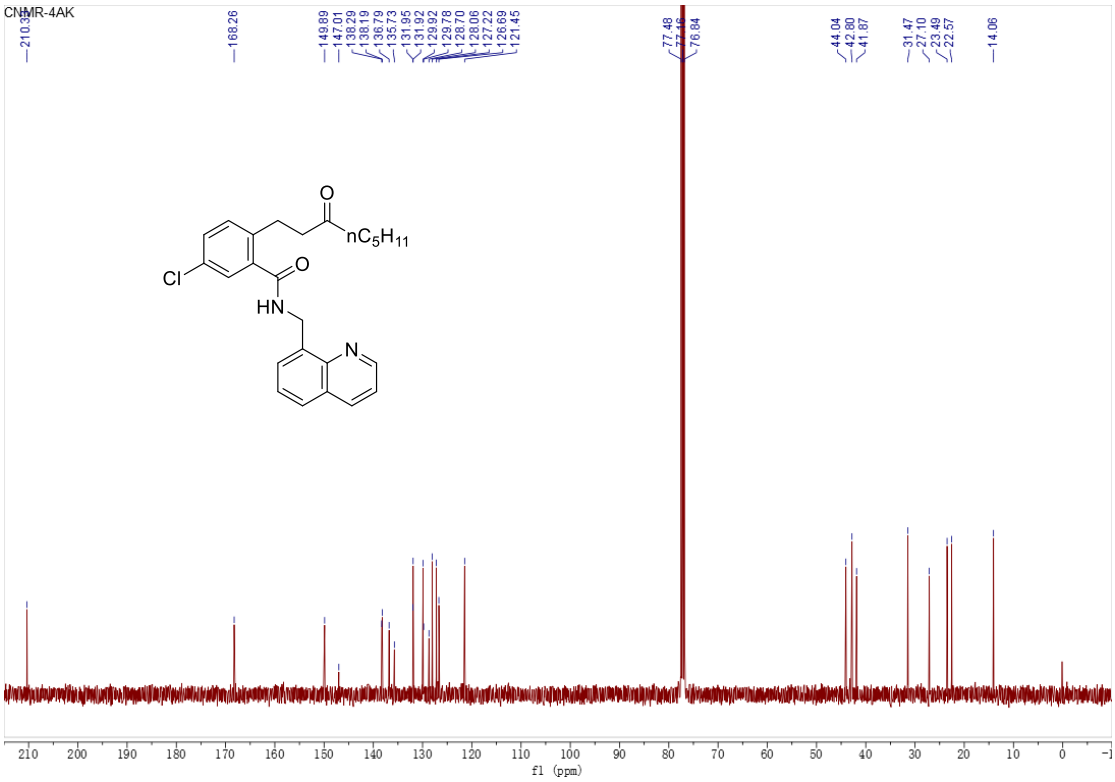
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4aj**



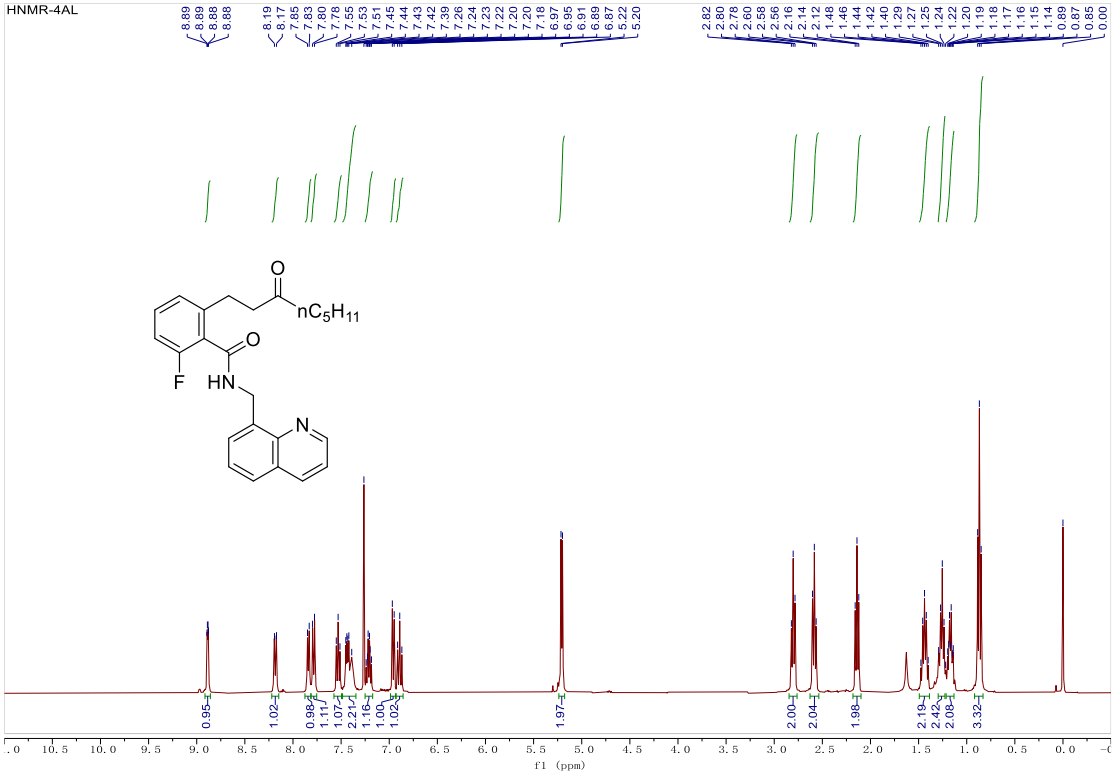
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ak**



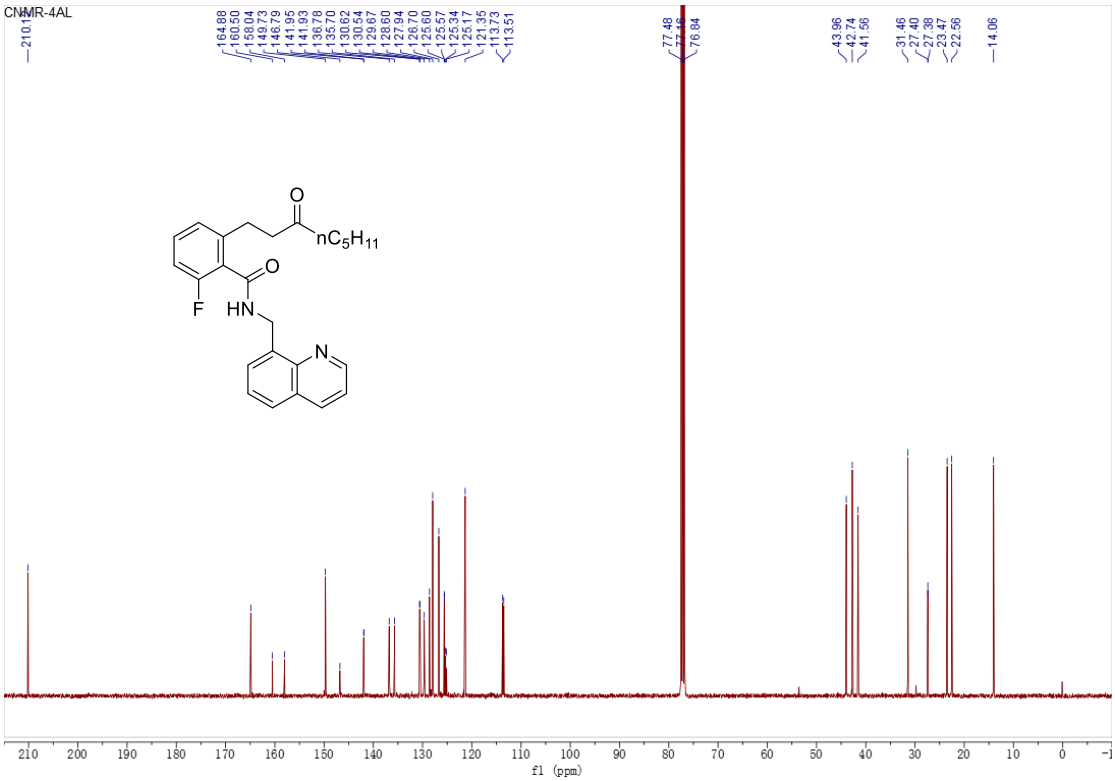
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ak**



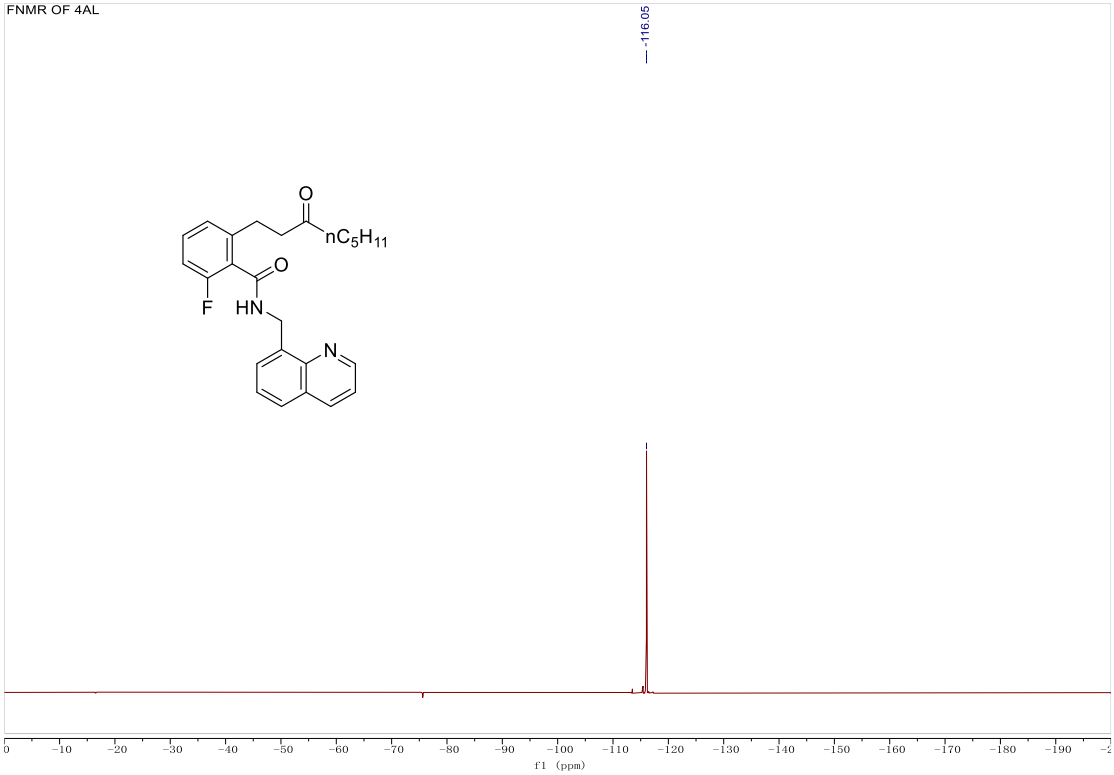
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4al**



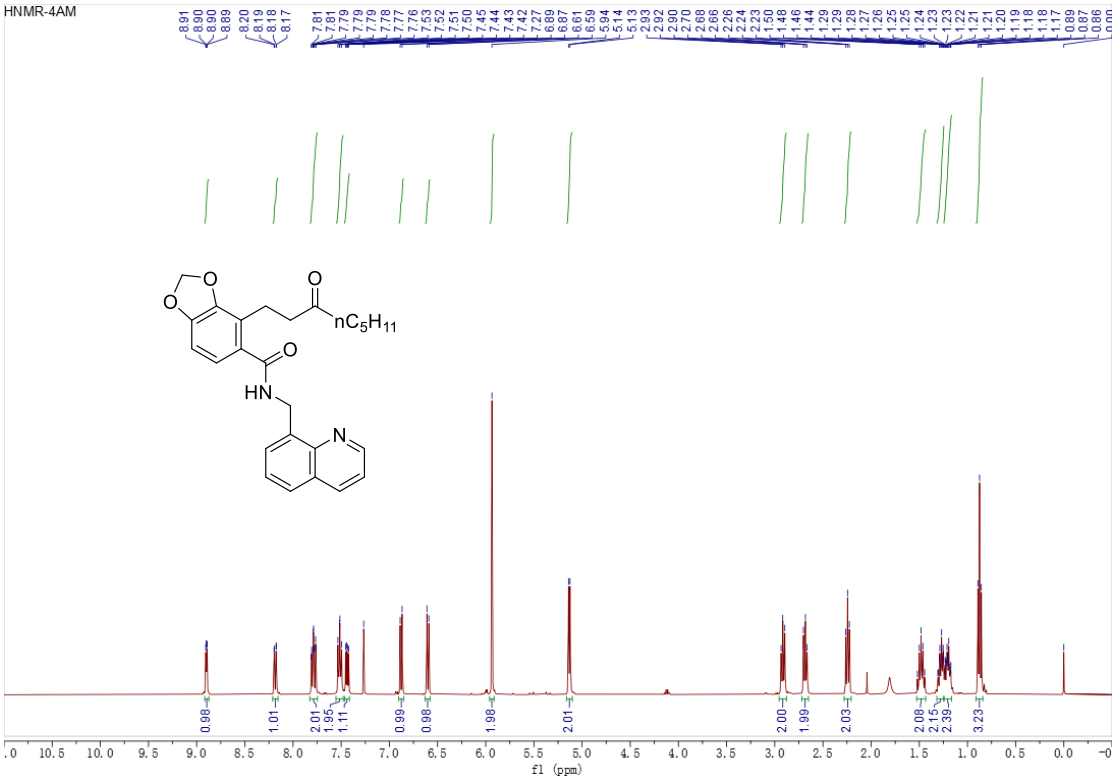
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4al**



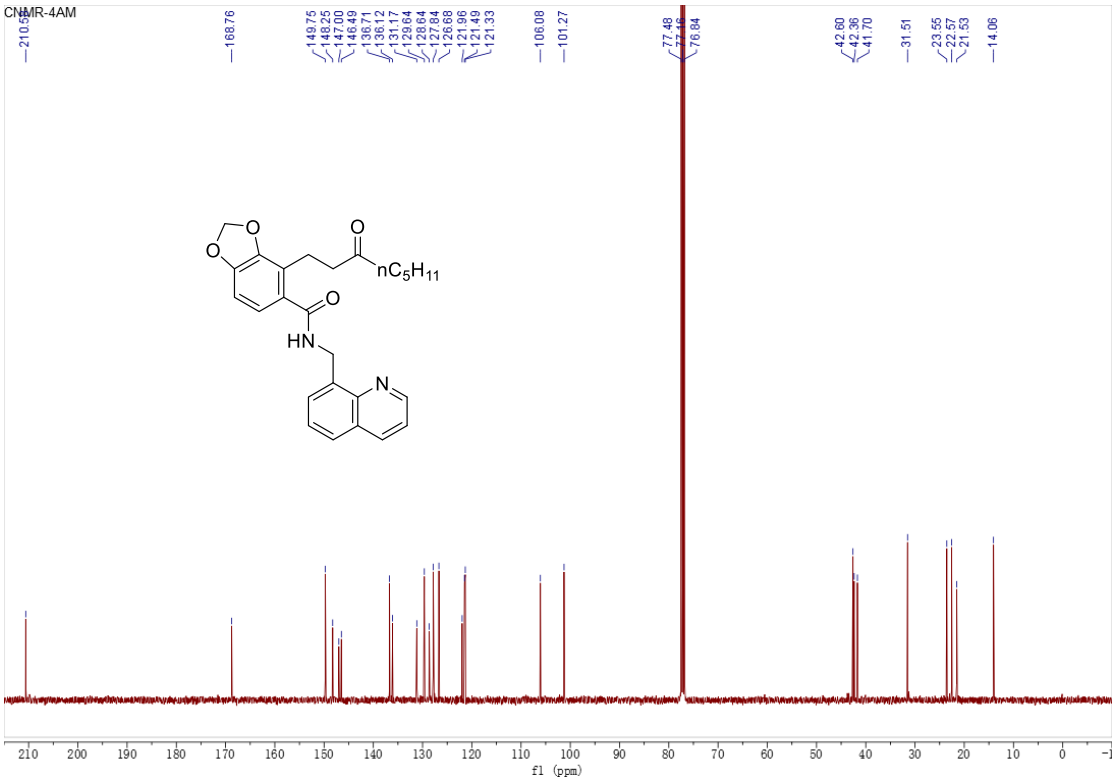
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4al**



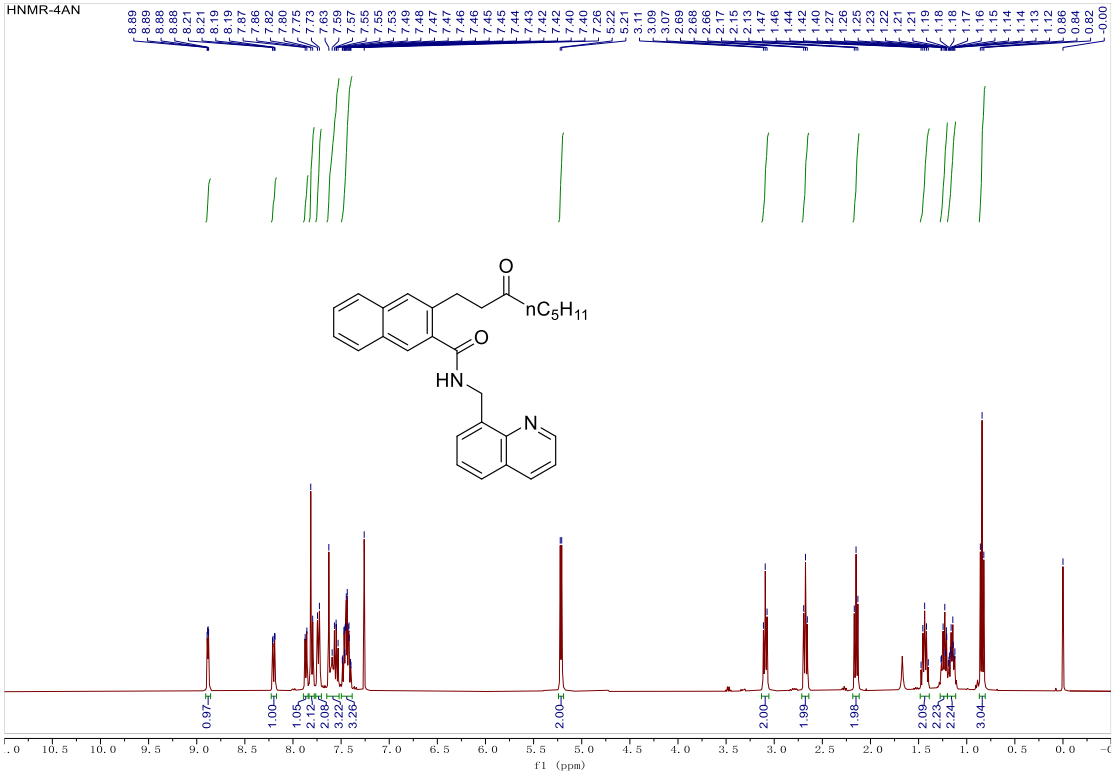
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4am**



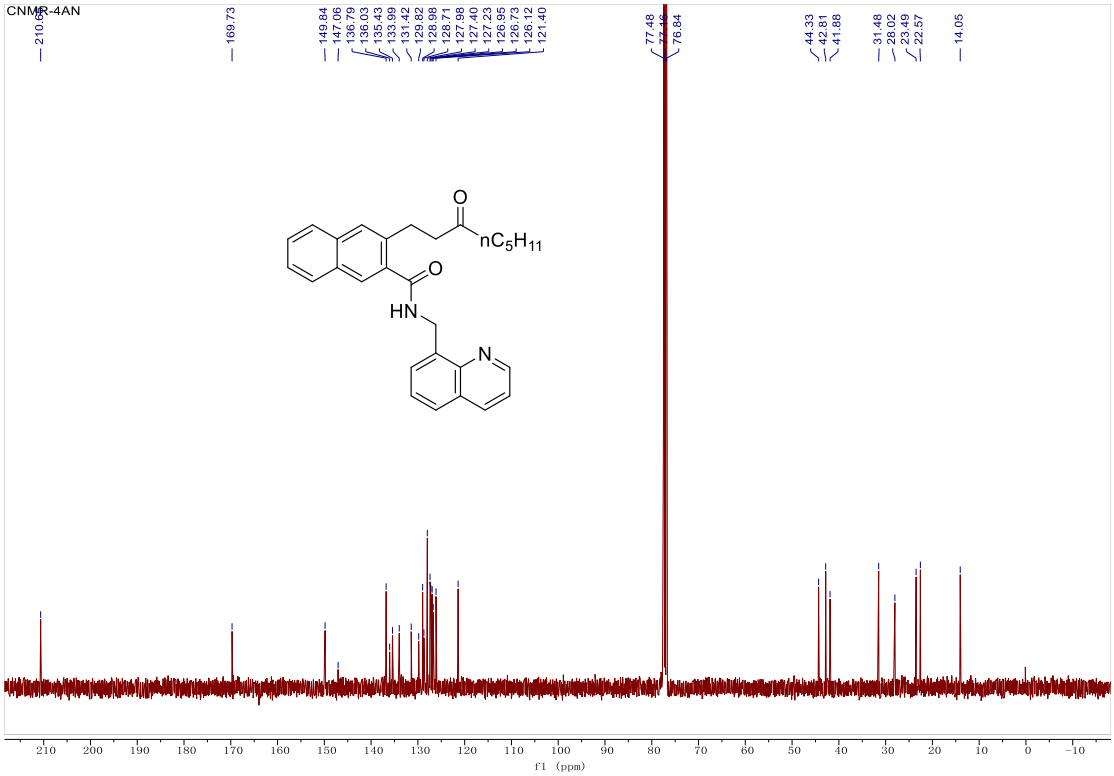
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4am**



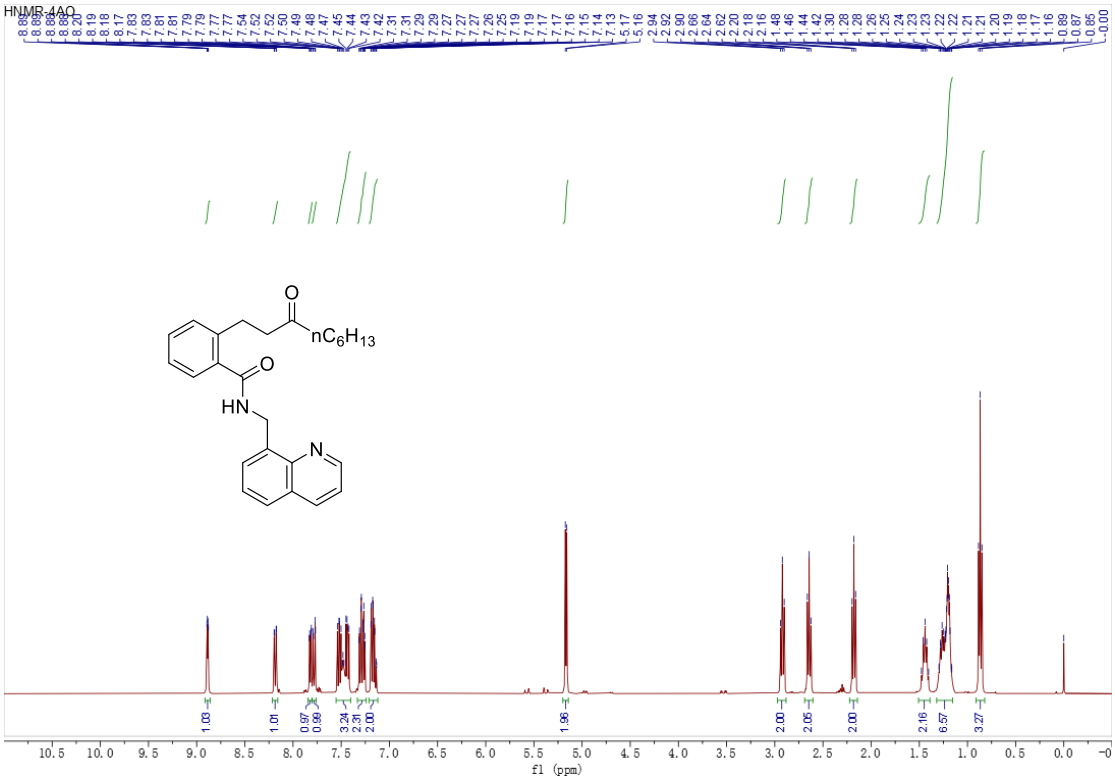
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4an**



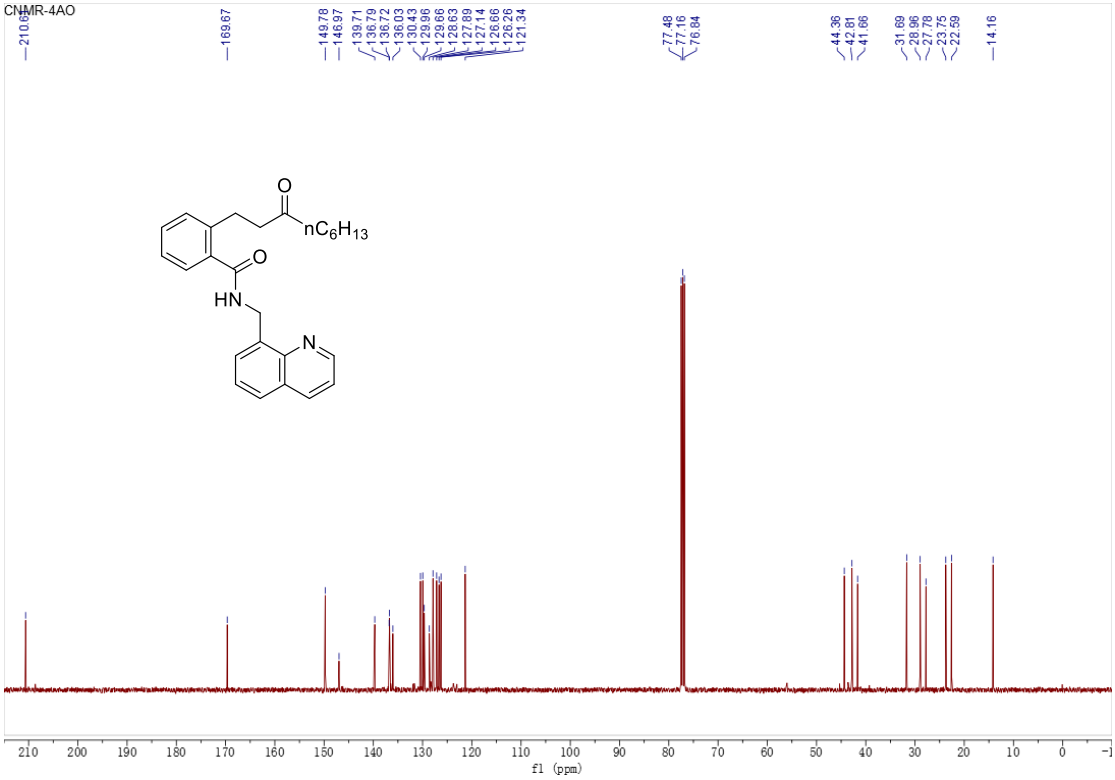
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4an**



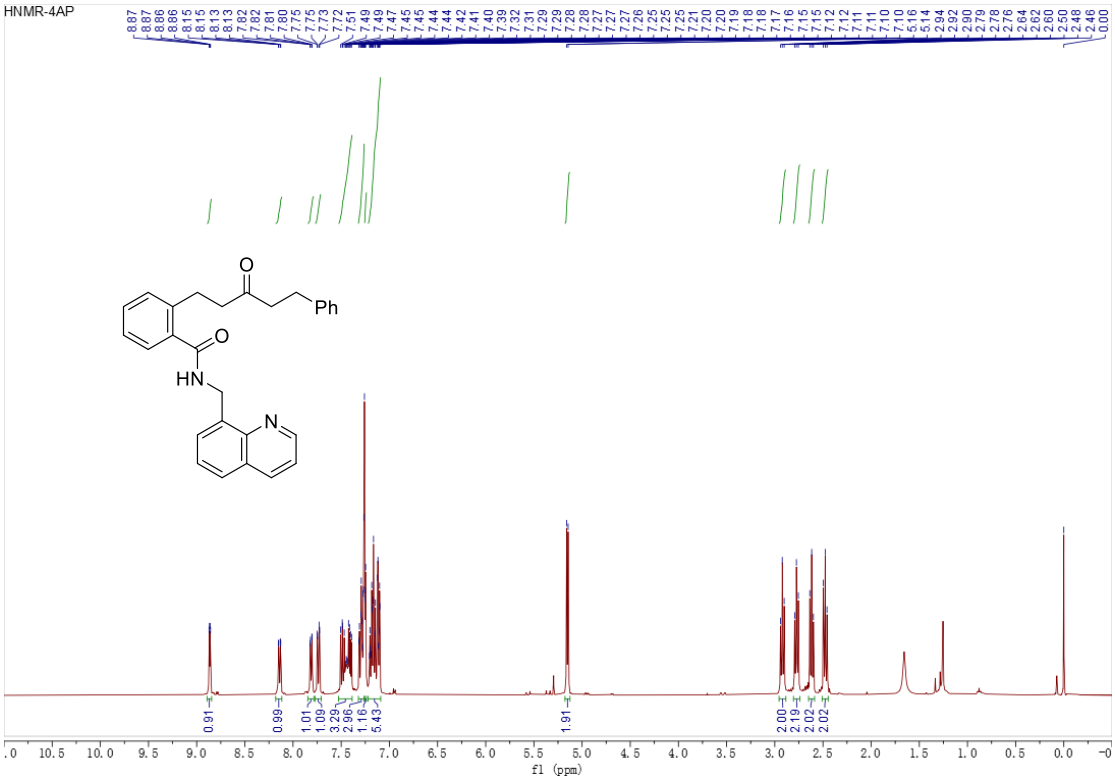
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ao**



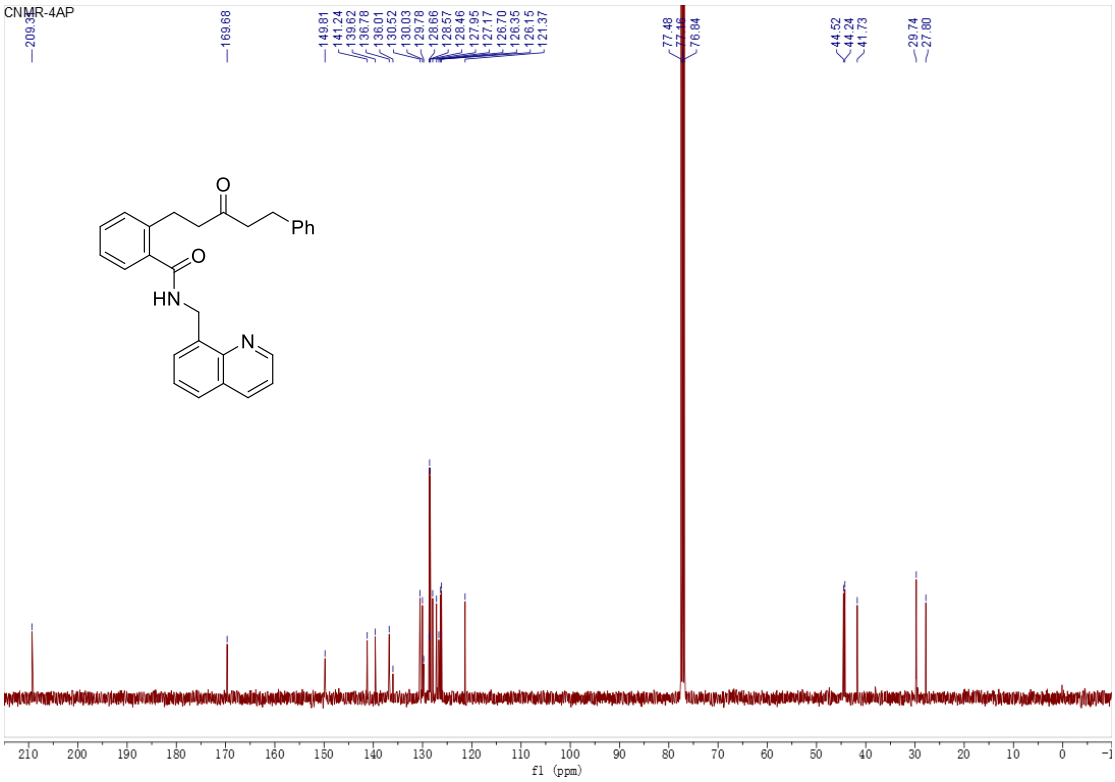
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ao**



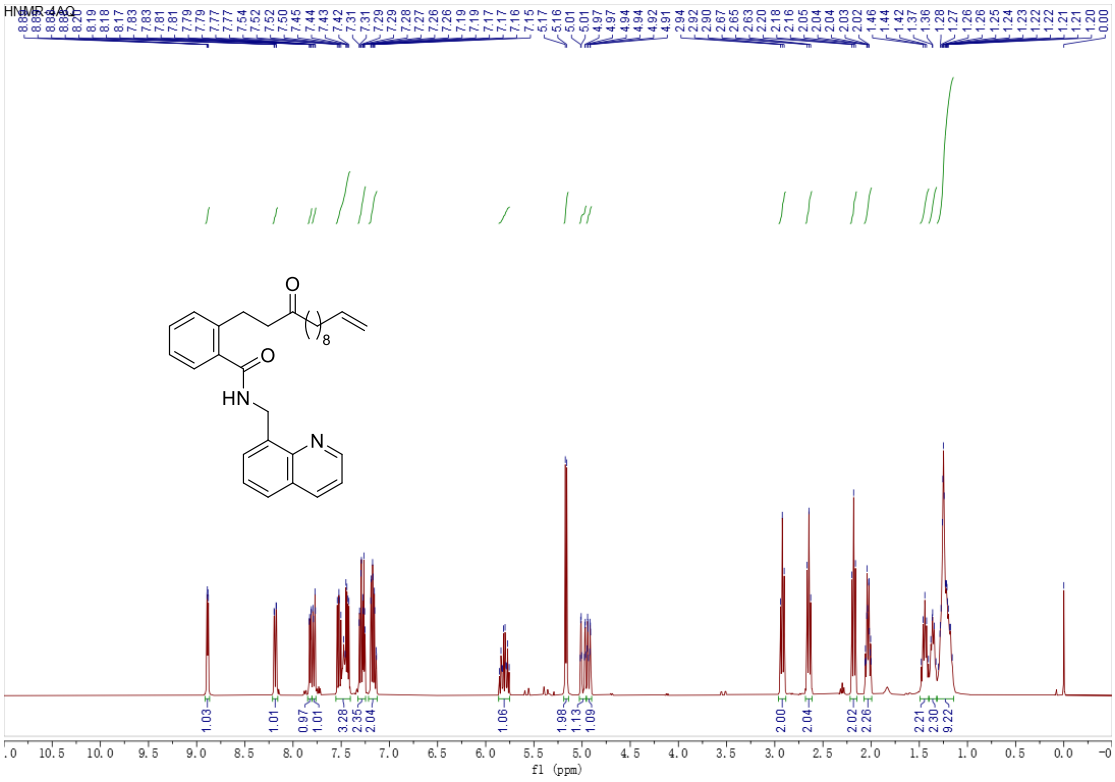
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ap**



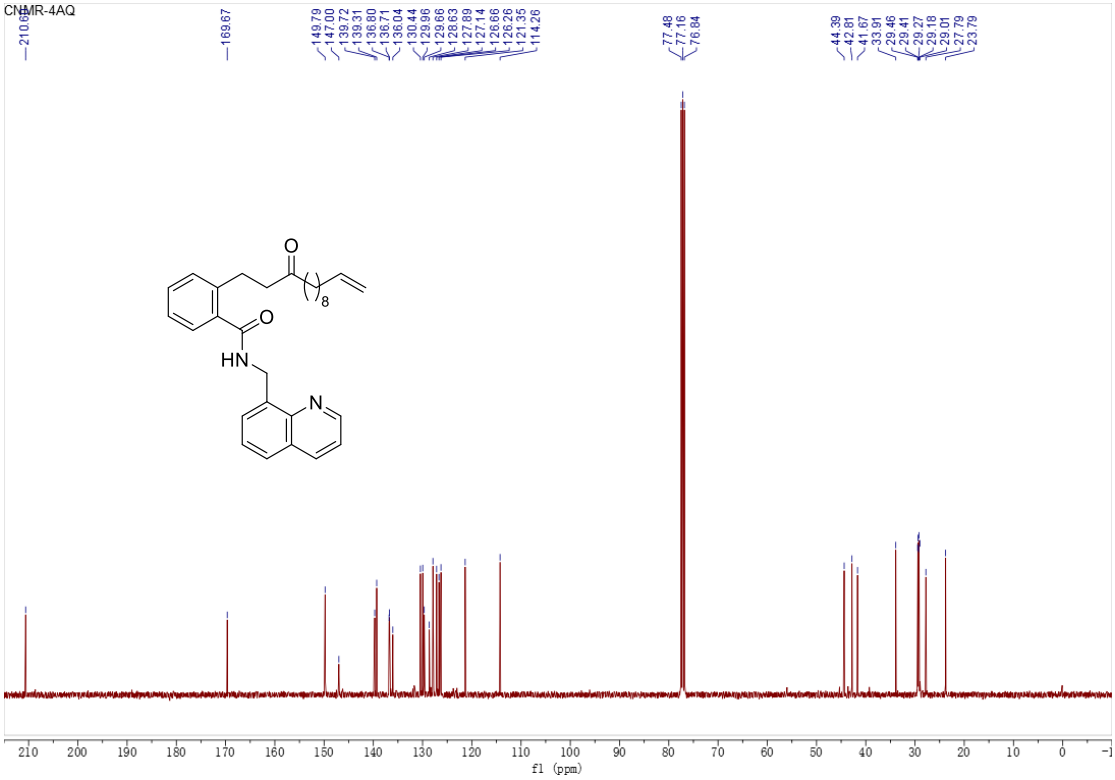
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ap**



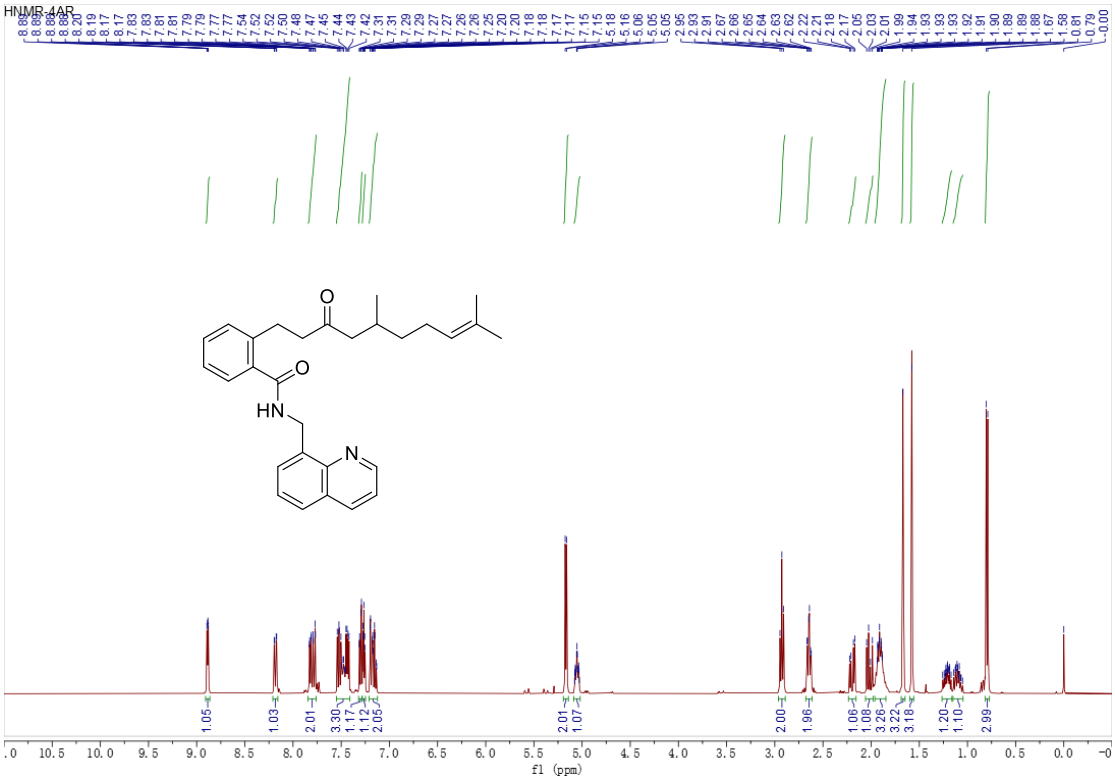
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4aq**



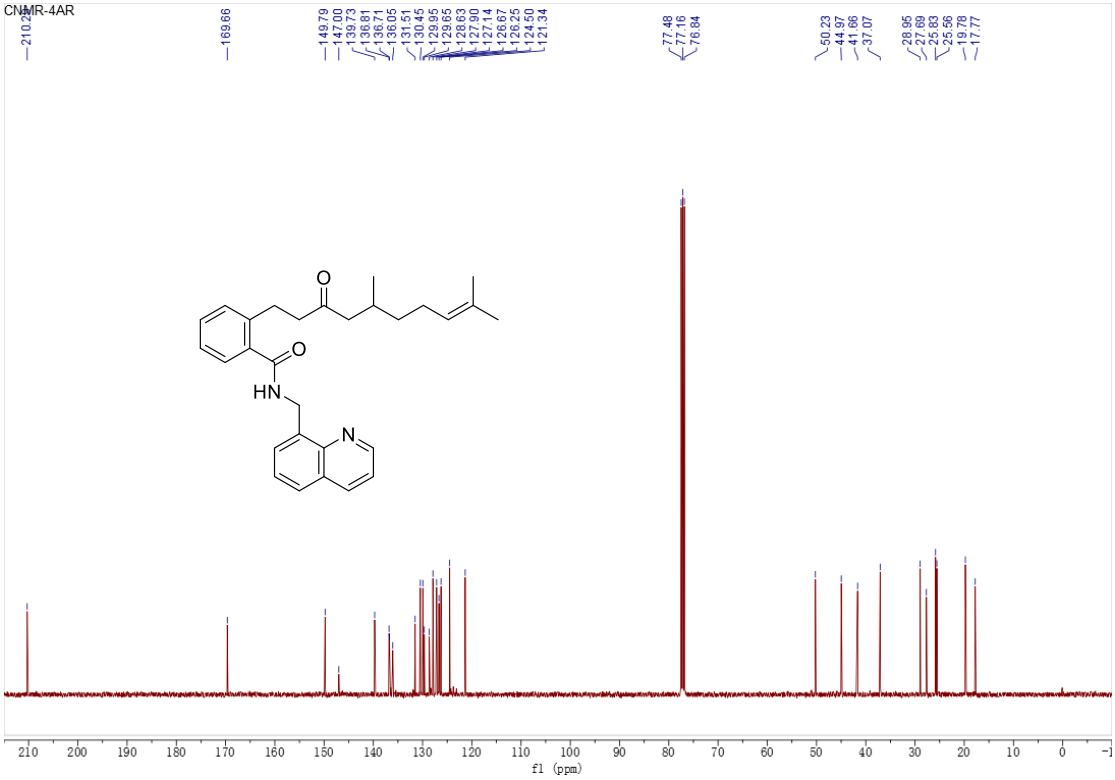
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4aq**



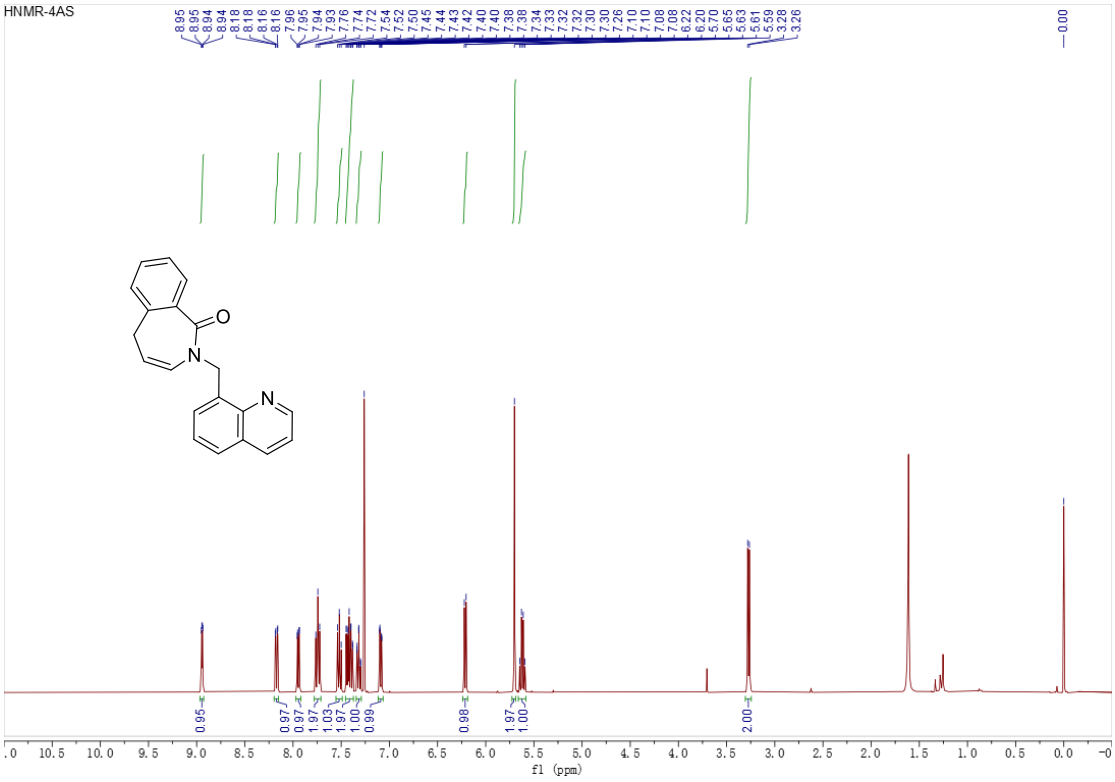
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ar**



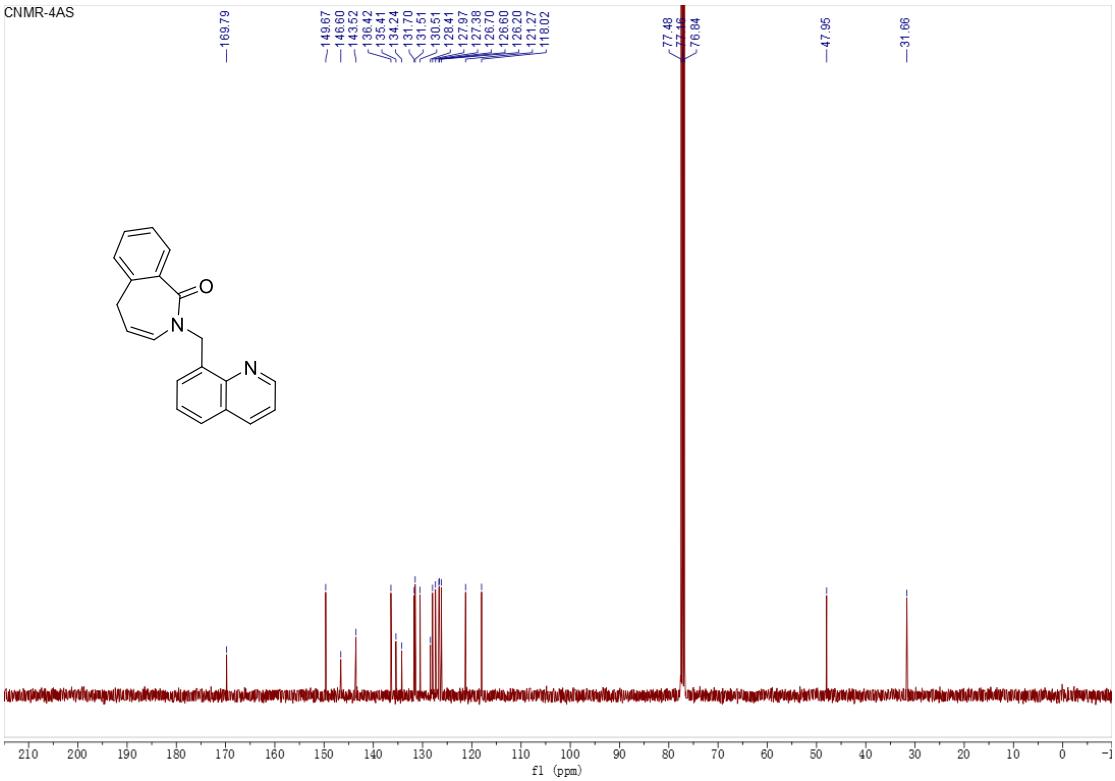
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4ar**



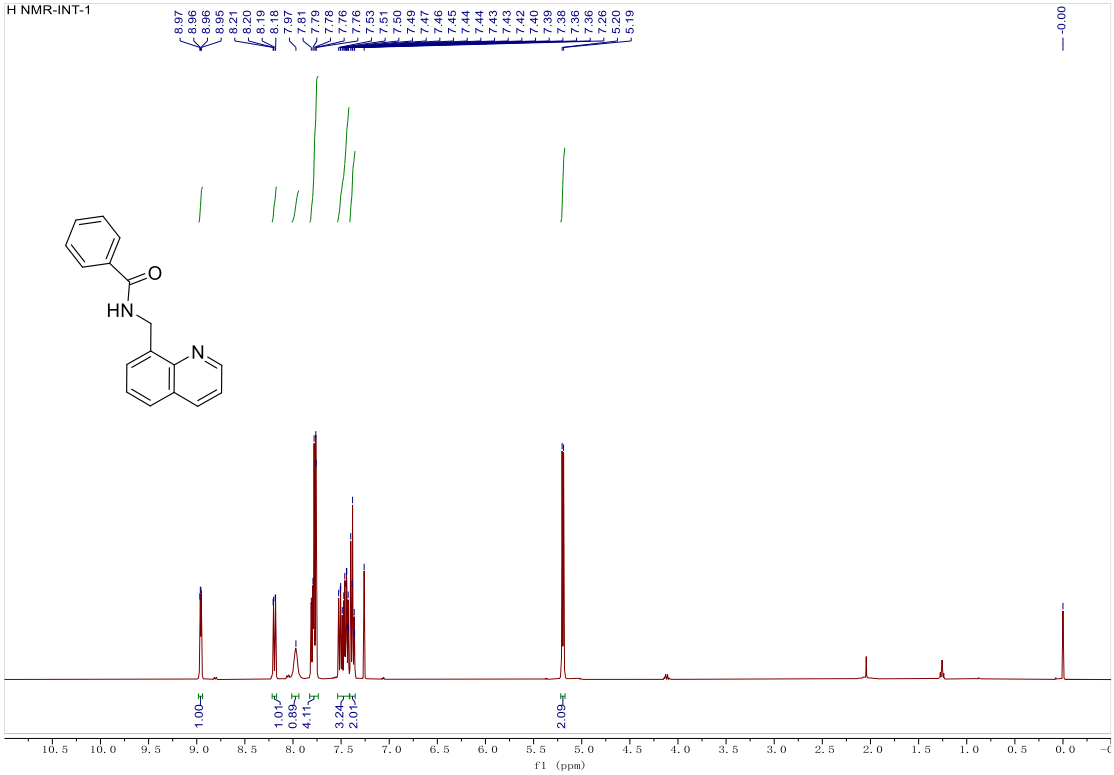
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4as**



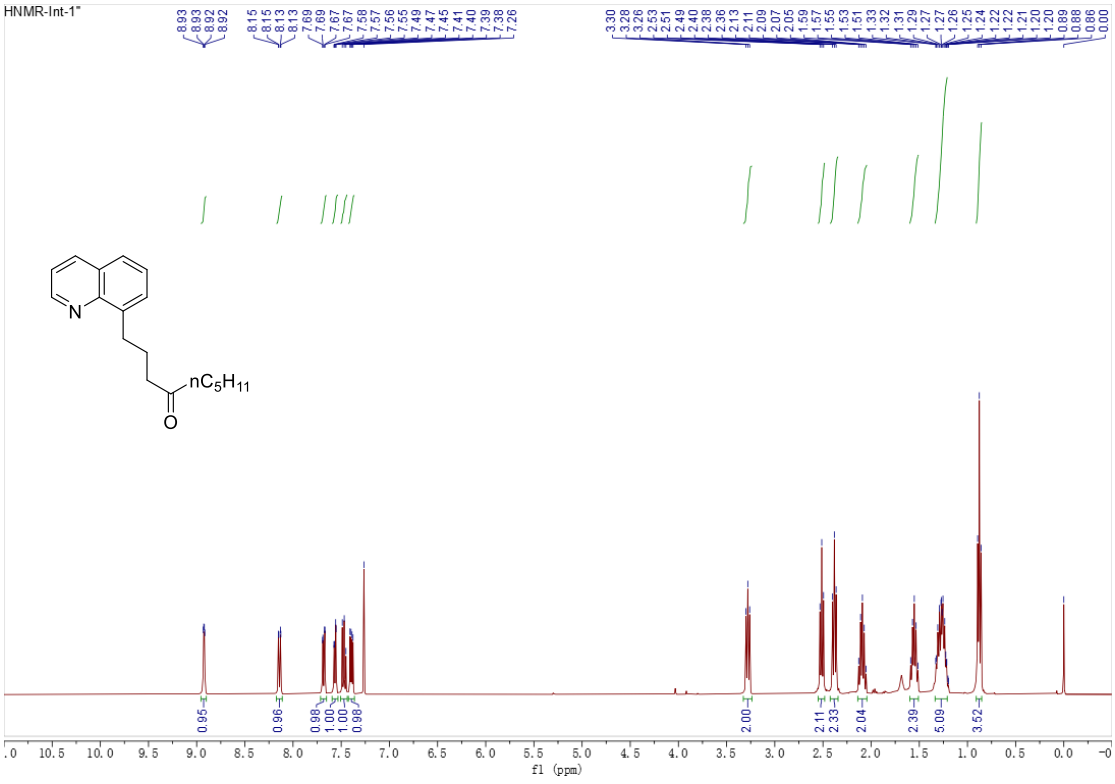
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4as**



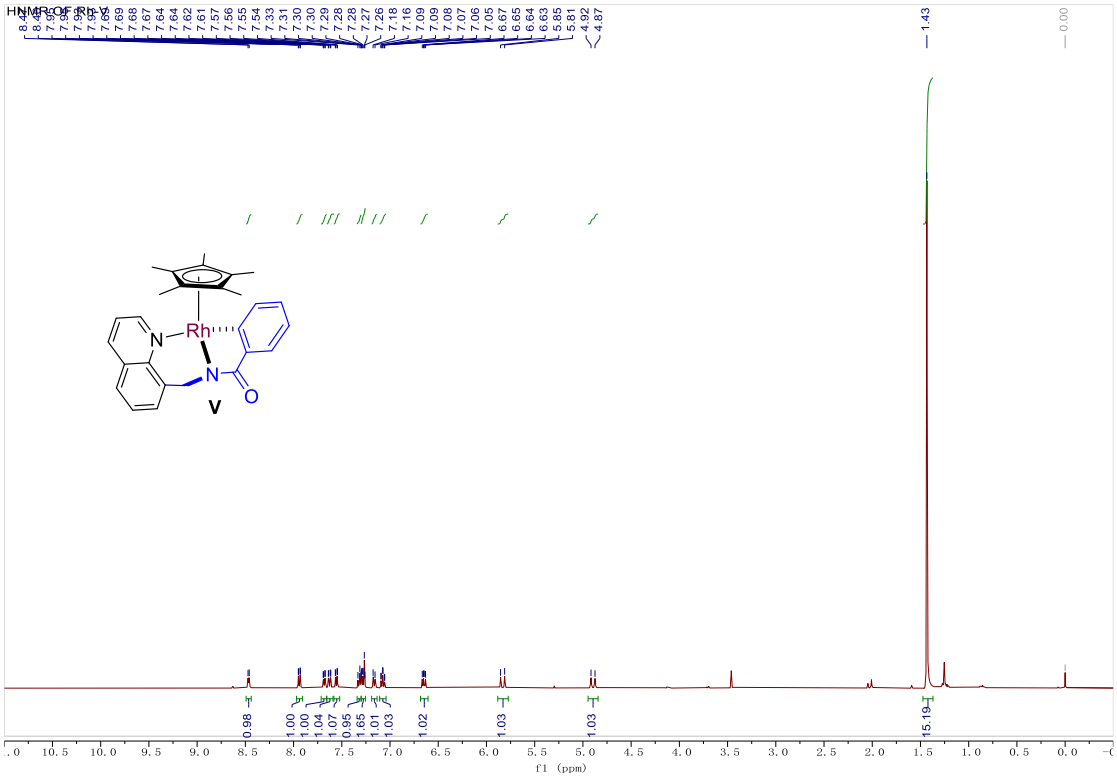
^{1}H NMR (400 MHz, $CDCl_3$) of compound **Int-1**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **Int-1''**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **V**



^{13}C NMR (101 MHz, $CDCl_3$) of compound **V**