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Supporting Information

Co(III)-Catalyzed Stereospecific Synthesis of (*E*)-Homoallylic Alcohols with 4-vinyl-1,3-dioxan-2-ones: Late-Stage C−H Homoallylation of indole derivatives

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1. General information.

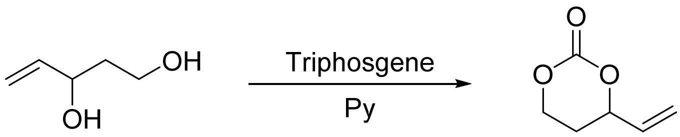
All reactions involving air- and moisture-sensitive reagents were carried out under a nitrogen atmosphere. Toluene, DME, DCM, 1, 2- dichloroethane, 1, 4- dioxane and THF were distilled from appropriate drying agents prior to use. TFE (2,2,2-trifluoroethanol) and HFIP (hexafluoroisopropanol) were purchased from Energy, which were used without further purification. Other chemicals were purchased from Sigma-Aldrich and Energy, which were used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230~400 mesh) was used for column chromatography. 2-pyrimidylindoles,[1] 2-pyridylindoles,[2] and 4-vinyl-1,3-dioxan-2-ones[3] were prepared according to the literatures.

NMR: Spectra were recorded on a 400 MHz (Varian Unity Inova-400 or Bruker Ascend 400) NMR spectrometer. Chemical shifts (δ) are reported in ppm and quoted relative to the residual solvent peaks in $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm) and coupling constants (*J*) are given in Hertz (Hz). Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broadened).

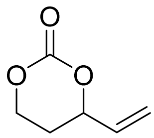
HRMS: High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer with an ESI source.

2. Experimental procedures.

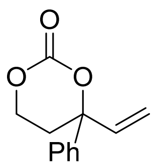
Genaral procedure for synthesis of carbonate 2[3]



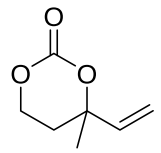
To a solution of diol (510.3 mg, 5.0 mmol, 1.0 equiv) and pyridine (1.6 mL, 20 mmol, 4.0 equiv) in CH_2Cl_2 (25.0 mL) was added triphosgene (1.0 M in CH_2Cl_2, 2.5 mL, 0.5 equiv) at 0 °C. The reaction was stirred under N_2 atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl (1.0 mL), and extracted with CH_2Cl_2 (3x25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica (petrol ether/ ethyl acetate, 2:1) to afford the corresponding carbonate as light yellow oil (435.4 mg, 3.4 mmol, 68% yield).



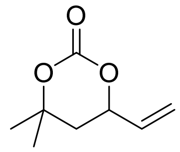
2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.92-5.84 (m, 1H), 5.46 – 5.34 (m, 2H), 5.01 – 4.96 (m, 1H), 4.48 – 4.37 (m, 2H), 2.24 – 2.17 (m, 1H), 2.06 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.6, 134.2, 118.5, 78.8, 66.4, 27.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_9O_3$ 129.0552; Found 129.0548.



2b: Purification by column chromatography (petrol ether/ethyl acetate, 4:1) was used to afford **2b** as light yellow oil (622.4 mg, 3.1 mmol, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 – 7.39 (m, 4H), 7.36 – 7.33 (m, 1H), 6.09 – 6.04 (m, 1H), 5.41 (d, *J* = 8.0 Hz, 1H), 5.35 (d, *J* = 8.0 Hz, 1H), 4.45 – 4.41 (m, 1H), 4.27 – 4.23 (m, 1H), 2.51 – 2.47 (m, 1H), 2.45 – 2.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.53, 140.46, 138.95, 129.04, 128.49, 124.91, 116.19, 85.54, 64.98, 31.62. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}O_3$ 205.0865; Found 205.0861.

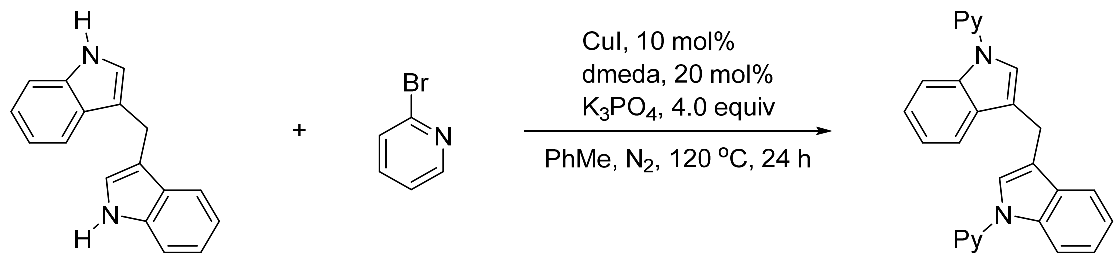


2c: Purification by column chromatography (petrol ether/ethyl acetate, 4:1) was used to afford **2c** as light yellow oil (447.5 mg, 3.2 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.86 – 5.79 (m, 1H), 5.37 – 5.29 (m, 2H), 4.36 – 4.33 (m, 2H), 2.13 – 2.06 (m, 1H), 2.00 (dt, *J* = 14.4, 3.8 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.9, 138.8, 116.0, 82.7, 65.0, 31.7, 27.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_{11}O_3$ 143.0708; Found 143.0702.



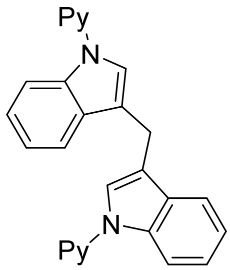
2d: Purification by column chromatography (petrol ether/ethyl acetate, 6:1) was used to afford **2d** as white solid (663.3 mg, 4.3 mmol, 85% yield); m.p. = 82-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.90 – 5.81 (m, 1H), 5.42 (d, *J* = 16.0 Hz, 1H), 5.30 (d, *J* = 16.0 Hz, 1H), 4.97 – 4.91 (m, 1H), 2.03 – 1.99 (m, 1H), 1.89 – 1.83 (m, 1H), 1.50 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.1, 134.5, 118.4, 80.8, 76.2, 38.9, 29.9, 26.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{13}O_3$ 157.0865; Found 157.0869.

Genaral procedure for synthesis of bis(*N*-pyridyl)-3,3'-diindolylmethane.



A mixture of 3,3'-diindolylmethane (0.98 g, 4.0 mmol), 2-bromopyridine (1.57 g, 10.0 mmol), CuI (76.2 mg, 0.4 mmol, 10.0 mol%), *N*,*N*'-dimethyl-ethylenediamine (70.5 mg, 0.8 mmol, 20.0 mol%), K_3PO_4 (3.40 g, 16.0 mmol) in toluene (10 mL) was vigorously stirred at 120 °C under nitrogen atmosphere for 24 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (30 mL) and washed with H_2O (2×10 mL). The aqueous phase was extracted with EtOAc (2×50 mL), and the combined organic phase was dried over Na_2SO_4.

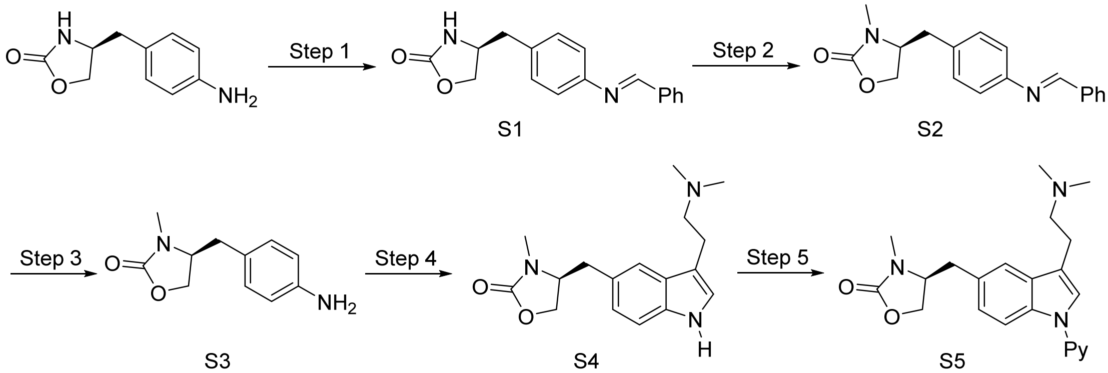
After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel to give N-pyridyl 3,3'-diindolylmethane (0.70 g, 1.76 mmol, 44%) as a white solid.



m.p. = 148-150 ºC;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 4.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 8.0, 4.0 Hz, 2H), 4.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.7, 148.9, 138.4, 135.7, 130.3, 124.0, 123.4, 121.1, 119.7, 119.5, 118.0, 114.3, 113.5, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}N_4$ 401.1766; Found 401.1748.

Genaral procedure for synthesis of zolmitriptan derivative S5.

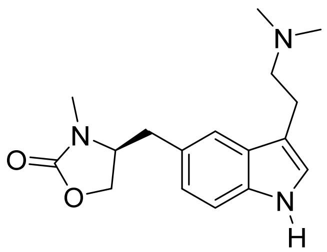


5-(4-aminobenzyl)oxazolidin-2-one (1.92 g, 10 mmol, 1.0 equiv) and benzaldehyde (1.0 mL, 10.2 mmol, 1.02 equiv) were dissolved in 20 mL ethanol in a flame dried Schlenk flask under argon atmosphere. The reaction was fluxed for 10 h. After cooling the mixture to room temperature, the crude solid **S1** was collected by filtration, which could be used directly for next step.

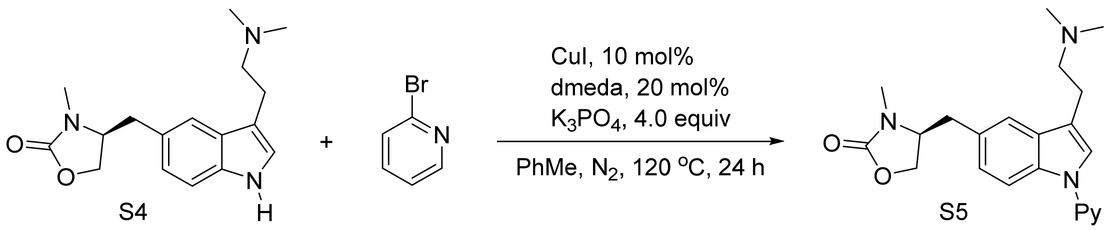
To a solution of **S1** in THF (25 mL), sodium hydride (0.4 g, 60% dispersion in mineral oil, 10 mmol, 1.0 equiv) was added in one portion at 0 °C. After 0.5 h, CH_3I (0.65 mL, 10.5 mmol, 1.05 equiv) was added in a drop wise fashion. The reaction was left to stir for 10 h at room temperature. The reaction mixture was then quenched with H_2O (0.5 mL), and the solvent was removed under vacuum. Ethanol (20 mL) was added, and the crude solid **S2** was collected by filtration, which could be used directly for next step.

To a solution of **S2** in 100 mL of MeOH were added $NH_2OH{\cdot}HCl$ (3.47 g, 50 mmol, 5.0 equiv) and anhydrous NaOAc (7.38 g, 90 mmol, 9.0 equiv). The mixture was stirred overnight at room temperature. The solvent was removed. The residue was diluted with 0.1 M NaOH solution, and extracted with ethyl acetate (3x50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue **S3** was obtained, which could be used directly for next step.

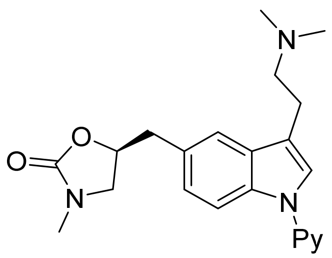
Follow the reported procedure,[4] **S3** could be converted into **S4** (572.2 mg, 1.9 mmol, 19%) as pale yellow semi-solid liquid compound.



S4: The crude product was purified by column chromatography ($CHCl_3$/MeOH, 10:1) to afford **S4** as pale yellow semi-solid liquid (572.2 mg, 1.9 mmol, 19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (s, 1H), 7.36 (s, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.15 (t, J = 8.0 Hz, 1H), 4.06 – 4.03 (m, 1H), 3.99 – 3.93 (m, 1H), 3.20 (dd, J = 16.0, 8.0 Hz, 1H), 2.98 (d, J = 8.0 Hz, 2H), 2.93 (s, 3H), 2.81 – 2.69 (m, 3H), 2.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.77, 135.57, 127.85, 125.85, 123.04, 122.74, 118.97, 113.15, 111.82, 66.82, 60.00, 58.89, 45.17, 38.44, 29.61, 23.39. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{23}N_3O_2Na$ 324.1688; Found 324.1678.

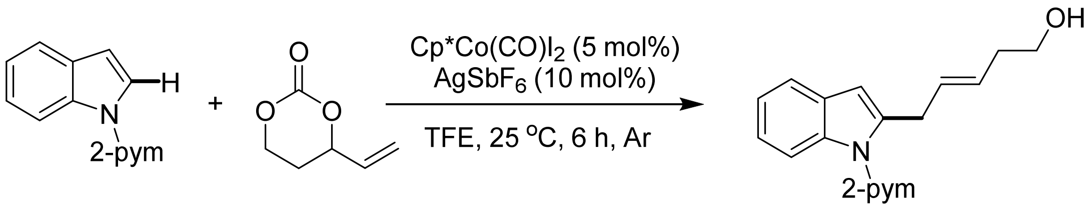


A mixture of **S4** (301.2 mg, 1.0 mmol), 2-bromopyridine (188.3 mg, 1.2 mmol), CuI (19.1 mg, 0.1 mmol, 10.0 mol%), *N*,*N*'-dimethyl-ethylenediamine (17.6 mg, 0.2 mmol, 20.0 mol%), K_3PO_4 (849.0 mg, 4.0 mmol) in toluene (10 mL) was vigorously stirred at 120 °C under nitrogen atmosphere for 24 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (30 mL) and washed with H_2O (2×10 mL). The aqueous phase was extracted with EtOAc (2×50 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel to give **S5** (98.3 mg, 0.26 mmol, 26%) as pale yellow semi-solid liquid.



S5 26% ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 4.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.16 – 7.13 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.18 (t, *J* = 8.0 Hz, 1H), 4.06 (t, *J* = 8.0 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.28 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.97 (t, *J* = 8.0 Hz, 2H), 2.93 (s, 3H), 2.83 – 2.78 (m, 1H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.7, 152.5, 149.0, 138.5, 134.6, 130.8, 127.9, 124.3, 123.9, 119.9, 119.4, 117.1, 114.2, 113.9, 66.9, 59.9, 59.0, 45.6, 38.7, 29.7, 23.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{26}N_4O_2Na$ 401.1953; Found 401.1952.

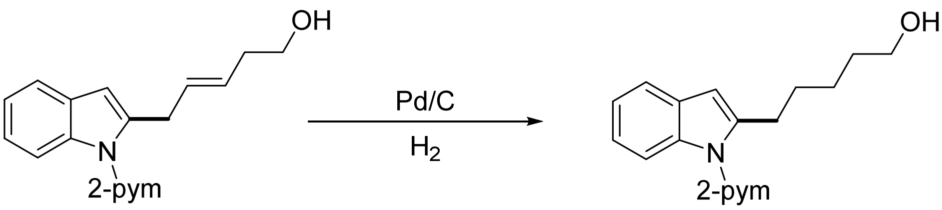
Experimental procedure for synthesis of homoallylic alcohol 3aa.



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

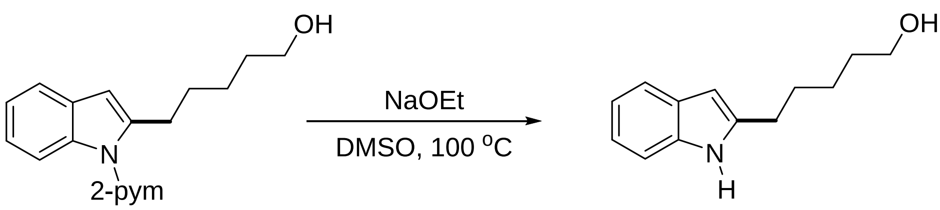
A mixture of *N*-(2-pyrimidyl)indole **1a** (39.0 mg, 0.2 mmol, 1.0 equiv), **2a** (25.6 mg, 0.2 mmol, 1.0 equiv), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol, 5 mol%), and $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mmol%) in TFE (1.0 ml) was stirred under argon at 25 °C for 6 hours. The solvent was removed under reduced pressure. The contents were subjected to flash chromatography (petrol ether/ethyl acetate, 2:1) to give the product as light pale yellow oil (51.4 mg, 0.18 mmol, 92%).

Derivatization of homoallylic alcohol 3aa.



3aa **9**, 78%

In a 50 ml of round-bottom flask was added **3aa** (72.6 mg, 0.26 mol), catalytic amount of Pd/C (30 wt%, 10 mol%), and EtOH (20 mL). The air in the flask was exchanged to hydrogen, using pump and hydrogen balloon for three times. Another hydrogen balloon was connected to the flask and the mixture was stirred vigorously at room temperature for 12 hours. After that, the crude mixture was concentrated in vacuo and purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **9** as colorless oil (57.0 mg, 0.20 mmol, 78%).

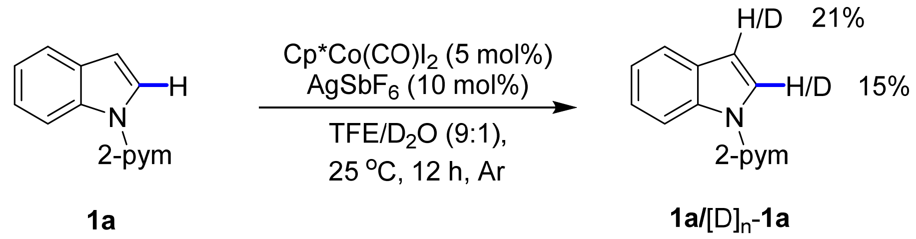


9 **10**, 83%

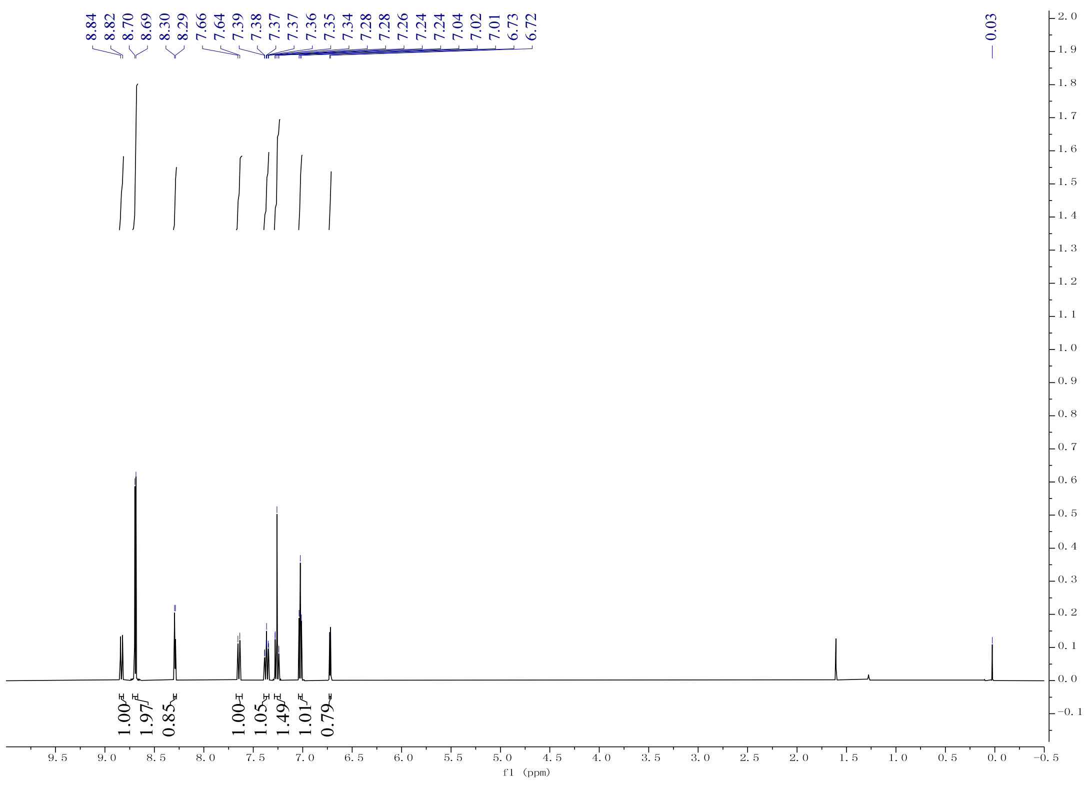
A mixture of **9** (36.5 mg, 0.13 mmol) and sodium ethoxide (26.5 mg, 0.39 mmol) in DMSO (1 mL) was stirred at 100 °C under Ar atmosphere for 20 h. After cooling to ambient temperature, the reaction mixture was quenched with H_2O (1.0 mL). The aqueous phase was extracted with EtOAc (3x2 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **10** as white solid (21.9 mg, 0.11 mmol, 83%).

3. Mechanistic studies

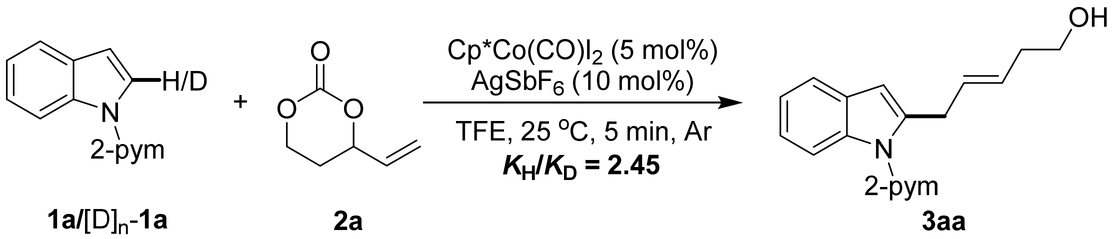
H/D scrambling experiments.



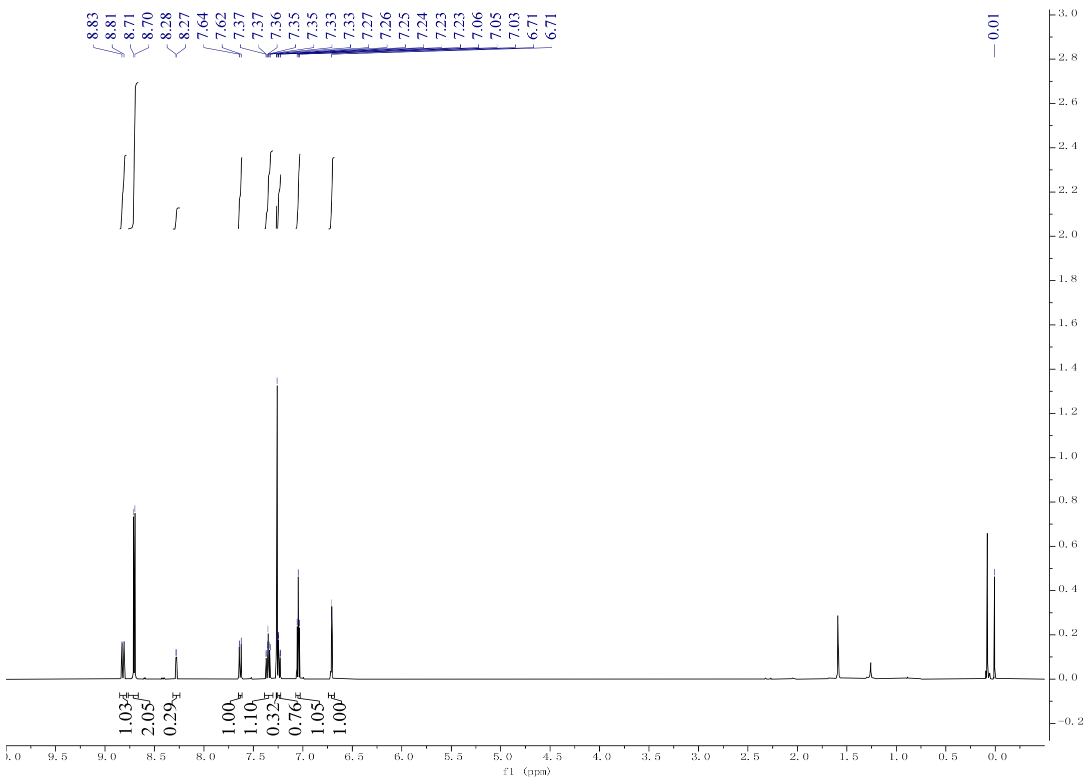
A mixture of *N*-(2-pyrimidyl)indole **1a** (39 mg, 0.2 mmol), Cp*Co(CO)I_2 (4.8 mg, 5 mol%), and $AgSbF_6$ (6.9 mg, 10 mmol%) were added to an oven-dried sealed tube (35 mL) equipped with a magnetic stir bar under argon atmosphere. TFE (0.9 mL) and D_2O (0.1 mL) were then added *via* syringe. The reaction mixture was stirred at room temperature for 12 h. After that, the solvent was removed in vacuo and the mixture was purified by column chromatography on silica gel (petrol ether/ethyl acetate, 20:1) to afford $[D]_n$-**1a** (37.4 mg, 96%) as a white solid.



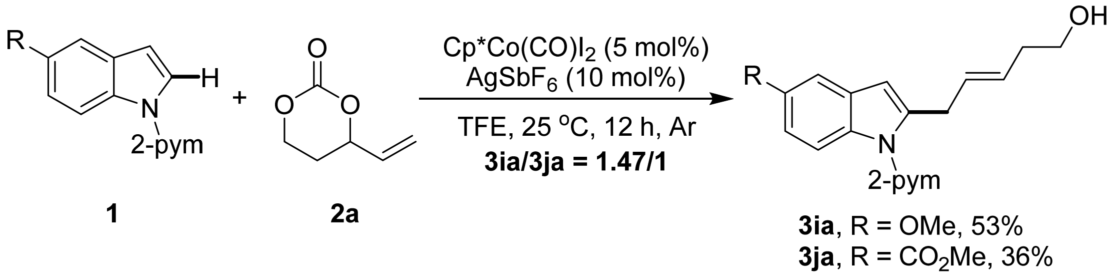
KIE by parallel experiments.



A mixture of **1a** (39.0 mg, 0.2 mmol, 1.0 equiv) or **[2-D]-1a** (39.0 mg, 0.2 mmol, 1.0 equiv), **2a** (25.6 mg, 0.2 mmol, 1.0 equiv), $Cp^*Co(CO)I_2$ (4.8 mg, 0.01 mmol, 5 mol%), and $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mmol%) in TFE (1.0 mL) was stirred separately under argon at room temperature for 5 minutes. The mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of celite. The filtrate was combined and removed under reduced pressure. The residue was purified by column chromatography (petrol ether/ethyl acetate, 20:1) to give the recovery mixture of **1a and [2-D]-1a** as white solids. Analysis by ^1H NMR showed the KIE value of 2.45.



Intramolecular competition experiment between 1i and 1j.



A mixture of **1i** (45.0 mg, 0.2 mmol, 1.0 equiv), **1j** (50.6 mg, 0.2 mmol, 1.0 equiv), **2a** (25.6 mg, 0.2 mmol, 1 equiv), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol, 5 mol %), and $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mmol %) in TFE (1.0 mL) was stirred under argon at room temperature for 12 hours. The mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of celite. The filtrate was removed under reduced pressure and the residue was purified by column chromatography (petrol ether/ethyl acetate, 2:1 to 3:2) to give the **3ia** (32.8 mg, 0.11 mmol, 53%) and **3ja** (24.3 mg, 0.01mmol, 36%) as light pale yellow oil, respectively.

4. Computational studies.

Computational details.

The geometries were optimized at the density functional B3LYP-D3(BJ)[5–8] level of theory. The Stuttgart/Dresden ECP[9] together with the valence basis functions were chosen only for the metal element and 6-31G(d)[10–13] for the rest. The natures of all intermediates and transition states were confirmed by analytic computation of their vibrational frequencies. Transition-state (TS) structures were verified to connect with reactants and products by following normal modes associated with the corresponding imaginary frequencies.[14] The free energies at 298.15 K were obtained after vibrational frequency computations.

Single-point energies based on the B3LYP geometries were calculated using the B97D3[15,16] functional with the Def2TZVP[17] basis set (LANL08(f)[18, 19] for the cobalt atom). Solvation effects in 2,2,2-trifluoroethanol were treated by the implicit solvation model SMD.[20] All calculations were performed with the Gaussian09 program.[21]

TABLE S1: B97D3 single point energies *E* and free energies *G* (in Hartree) of species.

Species	E	G
INT1-SS	-1620.59424515	-1620.11133515
TS1-SS	-1620.58205577	-1620.09815476
INT2-SS (II-SS)	-1620.59015922	-1620.10571922
TS2-SS	-1620.58908485	-1620.10228085
INT3-E	-1620.59907161	-1620.11305761
INT1-RS	-1620.59607162	-1620.11623362
TS1-RS	-1620.57996840	-1620.09938840
INT2-RS (II-RS)	-1620.58801606	-1620.10598706
TS2-RS	-1620.58907775	-1620.10386875
INT3-Z	-1620.60018924	-1620.11578724

Cartesian XYZ coordinates

66

INT1-SS

C	3.939702	0.131295	-1.117426
C	3.592008	-0.948258	-0.269217
C	4.489676	-1.952978	0.080403
C	5.778245	-1.858251	-0.448947
C	6.147608	-0.798084	-1.291842
C	5.238646	0.201852	-1.632290
C	2.766113	0.973949	-1.259817
C	1.749376	0.447273	-0.521187
H	4.197580	-2.765273	0.731816
H	6.508173	-2.621949	-0.199870
H	7.159199	-0.757393	-1.683667
H	5.530985	1.019059	-2.284874
H	2.718143	1.874086	-1.857496
N	2.238931	-0.742938	0.079620
C	1.369598	-1.524136	0.766959
C	0.850999	-3.355095	2.009159
C	-0.822564	-1.768780	1.454631
C	-0.485209	-2.952473	2.093511
H	1.194630	-4.270893	2.484177
H	-1.831959	-1.385327	1.449575
H	-1.228451	-3.529390	2.629542
N	1.774083	-2.654399	1.353092
N	0.089209	-1.042009	0.783681
C	-1.675164	2.229815	0.426639
C	-0.511487	2.823859	-0.211463
C	-1.246797	1.594351	1.610233
C	0.599481	2.660618	0.662959
C	0.182058	1.794099	1.730251
C	-3.097176	2.427428	0.007691
H	-3.469707	3.353372	0.465821

H	-3.742367	1.612576	0.338555
H	-3.204268	2.552060	-1.073551
C	-0.533357	3.638845	-1.468095
H	-0.843613	4.669929	-1.257606
H	-1.237787	3.236236	-2.202529
H	0.453907	3.679953	-1.935447
C	1.917993	3.354323	0.572744
H	1.862323	4.268172	1.179784
H	2.160657	3.651955	-0.448277
H	2.736316	2.742508	0.953359
C	1.044816	1.333335	2.862656
H	1.059517	2.080823	3.665587
H	2.075935	1.174732	2.535744
H	0.676552	0.397852	3.291627
C	-2.131092	0.944818	2.626937
H	-3.007678	0.470781	2.177134
H	-2.495755	1.711690	3.323111
H	-1.591939	0.206717	3.225849
C	-1.465048	0.147234	-1.740940
Co	-0.093888	0.762875	-0.038255
C	-0.164334	0.109776	-2.163737
H	0.277619	0.947252	-2.688520
H	0.376185	-0.828978	-2.229716
H	-2.047634	1.045835	-1.906142
C	-2.287687	-1.072152	-1.445113
C	-3.225346	-1.433552	-2.593258
H	-1.641566	-1.924395	-1.208808
C	-4.258157	-2.412634	-2.066179
H	-3.729246	-0.537464	-2.973630
H	-2.653790	-1.874937	-3.415142

H	-5.006233	-2.673710	-2.814729
H	-3.791920	-3.333554	-1.696535
O	-3.056404	-0.781239	-0.251204
C	-4.378549	-1.064915	-0.071260
O	-4.932679	-0.627741	0.903293
O	-5.004729	-1.809005	-0.987218

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TS1-SS

C	-3.762017713	-0.2118305586	-1.2874545371
C	-3.3920255291	0.9851996367	-0.6195820459
C	-4.3084310366	1.9945239212	-0.3304858272
C	-5.6259567741	1.7836267446	-0.7364911295
C	-6.0152189716	0.6090948125	-1.4062217328
C	-5.0947855968	-0.3936156566	-1.6869537968
C	-2.5826587234	-1.0237047264	-1.4088606008
C	-1.5233155184	-0.3755299656	-0.8188611093
H	-4.0050560192	2.8984388295	0.1789881975
H	-6.3674400296	2.5496926116	-0.5330041653
H	-7.0508591347	0.4870545171	-1.7070076036
H	-5.3972696601	-1.3005723543	-2.2013533623
H	-2.5242346635	-1.9695689611	-1.9302349533
N	-2.0169509333	0.8734396423	-0.3434189367
C	-1.2028700142	1.6693337203	0.4107664484
C	-0.7559262759	3.5818946646	1.5486928149
C	0.8785730848	1.8695042506	1.3864103801
C	0.5288123306	3.1276295782	1.855287816
H	-1.1083641258	4.5521860416	1.8895284961
H	1.8530752243	1.4408941503	1.5666607898
H	1.2267696096	3.7191337709	2.4346811714

N	-1.6183810956	2.8662783356	0.8247321037
N	0.0178197874	1.1233062415	0.6692025506
C	1.5179797913	-2.326825186	0.7065143498
C	0.2676286394	-2.850520363	0.2145016975
C	1.2332325505	-1.4833648804	1.8084601503
C	-0.7742159681	-2.4267138616	1.1164284099
C	-0.1984896625	-1.5328742836	2.0511729504
C	2.888311562	-2.6652958765	0.2118762285
H	3.3215125996	-3.4467898037	0.8491670908
H	3.5517057777	-1.7984217332	0.2480855636
H	2.8749239402	-3.0561651575	-0.809126702
C	0.1127820518	-3.8157091594	-0.9210400717
H	0.2756969067	-4.8466351327	-0.583023931
H	0.8354585464	-3.6194421125	-1.7189750801
H	-0.8889574805	-3.7687876422	-1.3557657507
C	-2.2009221436	-2.871948064	1.1093741977
H	-2.3450660224	-3.6243377805	1.8952264056
H	-2.4840860324	-3.3270476104	0.1596704388
H	-2.8903698717	-2.0472586196	1.3052010071
C	-0.9222984514	-0.8188120285	3.149842274
H	-0.8910293125	-1.4041661406	4.0772366491
H	-1.9736513686	-0.6572418756	2.8963123649
H	-0.4708685267	0.1538530538	3.3636187206
C	2.2511881469	-0.8290529908	2.6898541422
H	3.0608424142	-0.3569748099	2.1273366393
H	2.7036477093	-1.5893809984	3.3399805423
H	1.7999635803	-0.0810311234	3.3462336549
C	1.315585027	-0.4094106922	-1.5341382177
Co	0.1747795355	-0.7758370671	0.1026196062
C	0.0029388634	-0.2964373016	-2.0794557856

H	-0.3481153317	-1.1162411359	-2.6944893634
H	-0.32617549	0.6813609593	-2.4258774467
H	1.839958922	-1.3357087044	-1.749253565
C	2.2234870914	0.7842177594	-1.4675979482
C	3.2072185244	0.8962114896	-2.6244185914
H	1.6310481724	1.7054412444	-1.3926887216
C	4.119693515	2.0808282011	-2.3567080389
H	3.7852333615	-0.0318232756	-2.7013037834
H	2.6776170418	1.0457441298	-3.5709939456
H	4.9770109891	2.1064340094	-3.0309383699
H	3.5747240466	3.0268441432	-2.4493057818
O	2.9940044532	0.6557744342	-0.2468122744
C	4.1119057519	1.3959618424	-0.0076378071
O	4.5608052855	1.4221319145	1.1095912217
O	4.6871846432	2.0439069834	-1.0253950968

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INT2-SS

C	3.513733	0.253159	-1.419553
C	3.241557	-0.923969	-0.670012
C	4.231821	-1.587204	0.058945
C	5.516844	-1.058652	-0.003479
C	5.815748	0.096300	-0.760249
C	4.827287	0.758018	-1.469109
C	2.277613	0.701976	-1.966081
C	1.261422	-0.145991	-1.561480
H	4.010165	-2.487689	0.616926
H	6.316341	-1.557035	0.535609
H	6.836163	0.464210	-0.784294
H	5.052664	1.649186	-2.046521

H	2.144234	1.523905	-2.657367
N	1.871619	-1.178431	-0.774882
C	1.117308	-1.938362	0.108486
C	0.751363	-3.811758	1.326929
C	-0.872016	-2.077961	1.262990
C	-0.508115	-3.342670	1.706493
H	1.125360	-4.772102	1.671489
H	-1.816969	-1.611302	1.509257
H	-1.169379	-3.926045	2.335609
N	1.557298	-3.124045	0.508989
N	-0.038306	-1.350596	0.496671
C	-1.187796	2.235011	0.769016
C	0.063182	2.631100	0.205500
C	-0.908923	1.330595	1.843333
C	1.123857	2.079082	1.032974
C	0.533723	1.259477	2.009411
C	-2.537445	2.729544	0.358749
H	-2.699718	3.728843	0.783045
H	-3.334537	2.078929	0.719318
H	-2.625998	2.825637	-0.727514
C	0.235417	3.602489	-0.921951
H	0.155895	4.635364	-0.560029
H	-0.534911	3.467444	-1.687452
H	1.211304	3.497285	-1.402196
C	2.586432	2.363044	0.903290
H	2.880136	3.099774	1.661893
H	2.840905	2.776834	-0.072940
H	3.199515	1.471122	1.058894
C	1.250638	0.451808	3.047610
H	1.307370	0.996013	3.998401

H	2.273753	0.219555	2.737803
H	0.735338	-0.492715	3.248184
C	-1.912460	0.752625	2.789745
H	-2.858275	0.503008	2.303645
H	-2.131059	1.491626	3.572540
H	-1.525102	-0.134698	3.298354
C	-1.241850	0.237253	-1.485580
Co	-0.120424	0.569999	0.072082
C	-0.079243	-0.357895	-2.284032
H	0.019799	0.094764	-3.275426
H	-0.203846	-1.436517	-2.438234
H	-1.549386	1.205210	-1.890622
C	-2.439804	-0.679333	-1.358716
C	-3.454650	-0.567336	-2.488042
H	-2.103296	-1.721577	-1.284757
C	-4.709325	-1.320047	-2.090880
H	-3.698058	0.485850	-2.671948
H	-3.032734	-0.980491	-3.410431
H	-5.510984	-1.221765	-2.823622
H	-4.507745	-2.386448	-1.932182
O	-3.094080	-0.390767	-0.087548
C	-4.435928	-0.369025	0.113627
O	-4.862649	0.020007	1.172480
O	-5.249785	-0.768276	-0.871766

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TS2-SS

C	-3.9469237058	-1.3668597129	-0.6612008343
C	-2.8649791537	-1.9968019661	-1.373570707
C	-1.8432366154	-1.1056665776	-1.4931818991

C	-3.5504300176	-0.0354968029	-0.389040312
H	-2.8610222697	-2.9995162447	-1.7797708452
N	-0.187384981	1.3092043202	-0.7233105358
C	0.666397322	-1.5369174049	-1.3487172967
C	-0.5552348821	-1.2608614032	-2.2240962676
H	-0.6931780595	-2.0910052371	-2.9286032282
H	-0.3614572307	-0.3705081551	-2.835763057
H	0.6043819738	-2.4448168707	-0.7525021449
C	1.9195020848	-1.2809966332	-1.9420239921
C	3.2029228409	-1.9786135784	-1.6484724355
H	3.2188221829	-2.3756674968	-0.6304417443
O	4.6203162511	-0.0516079445	-0.942251217
O	2.4099642396	0.4613994732	-1.0659011559
O	3.854794705	1.8314147539	-0.0398154545
C	3.6191354188	0.8102980789	-0.6533682362
H	3.2645917584	-2.8408286969	-2.3303592031
N	-2.2285120944	0.1122642729	-0.8755733704
C	-1.5326547674	1.3102226503	-0.9187362667
N	-2.2561500691	2.4135017609	-1.1235878822
C	-1.619566495	3.5803768034	-1.1900409293
H	-2.2422979894	4.4597916639	-1.3356224289
C	-0.2303924173	3.6740262461	-1.0935425842
H	0.2957360564	4.6169870499	-1.1780299838
C	0.4529428364	2.4958565609	-0.8475148958
H	1.5265807138	2.4701645515	-0.7101484382
C	-4.3734691793	0.853850838	0.3039970513
C	-5.1993424443	-1.8189141528	-0.2242566912
C	-6.0233986976	-0.9398279072	0.4694335213
C	-5.613247385	0.3792245998	0.7289131182
H	-6.2790531479	1.0507633328	1.26162516

H	-5.515971799	-2.8376854718	-0.4256222355
H	-6.9981654095	-1.2723530294	0.8117617851
H	-4.0807487844	1.8807517198	0.4768764333
C	-0.075065519	0.3532967973	2.0049873569
C	1.2866474543	0.7834456286	2.0769484975
C	-0.0953942264	-1.0470977423	1.7234287164
C	-1.2640775827	1.2288155609	2.2305986548
C	2.1167411493	-0.3872221618	1.955955655
C	1.7608337511	2.1692639571	2.3855926861
C	1.2767784512	-1.5059256379	1.7175904194
C	-1.2938550525	-1.9400099424	1.6923897477
H	-1.3847270966	1.3877993671	3.3098158247
H	-1.1415283569	2.2157664063	1.776141669
H	-2.1864699021	0.780638848	1.8601411681
C	3.5966365207	-0.431298739	2.1579781534
H	1.9655261421	2.2701453025	3.4592164144
H	2.6758360047	2.4041063291	1.8381374444
H	1.0042835016	2.9152394472	2.1272523578
C	1.7021446027	-2.9394184152	1.6743246635
H	-1.4184373444	-2.4180761415	2.6728554344
H	-2.2103944172	-1.393734022	1.4691799209
H	-1.1923274854	-2.7330857859	0.9486244651
H	3.7961287405	-0.6791893752	3.2089738286
H	4.0792571354	-1.1968570371	1.5462030491
H	4.0697726923	0.5266866853	1.9429704854
H	2.7544498227	-3.0491997827	1.4021128435
H	1.5789888699	-3.3855148227	2.6697786143
H	1.0988644916	-3.5352467393	0.9836930421
Co	0.9201278988	-0.0957994484	0.1560073554
C	4.420843962	-1.0901239687	-1.9131342428

H	5.337913948	-1.6781599633	-1.8676223426
H	4.3503682465	-0.637443714	-2.9096096979
H	1.9127978087	-0.7427662802	-2.8883279814

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INT3-E

C	-4.036786	-1.278252	-0.586823
C	-3.029463	-1.901092	-1.405003
C	-1.978518	-1.045501	-1.526970
C	-3.565005	0.013778	-0.253344
H	-3.094326	-2.872548	-1.876774
N	-0.197238	1.340006	-0.740216
C	0.492846	-1.663976	-1.607886
C	-0.747724	-1.208690	-2.347071
H	-0.973624	-1.971150	-3.103907
H	-0.520480	-0.289624	-2.899910
H	0.392064	-2.548214	-0.985345
C	1.719061	-1.247726	-2.020483
C	3.056443	-1.878944	-1.785553
H	3.104705	-2.421266	-0.838372
O	4.566098	-0.124706	-0.793137
O	2.495221	0.802135	-0.855974
O	4.188199	1.806037	0.236465
C	3.734066	0.897741	-0.434348
H	3.172318	-2.638254	-2.575575
N	-2.262739	0.138811	-0.800736
C	-1.555090	1.334730	-0.861380
N	-2.296745	2.434045	-1.006011
C	-1.683618	3.613010	-1.080003
H	-2.326466	4.485081	-1.172910

C	-0.294770	3.719493	-1.055705
H	0.219171	4.668602	-1.147243
C	0.412486	2.543772	-0.873159
H	1.492021	2.514702	-0.802747
C	-4.314029	0.888889	0.536364
C	-5.283239	-1.707666	-0.110428
C	-6.030436	-0.843457	0.680911
C	-5.549421	0.438842	0.997795
H	-6.156940	1.102271	1.605087
H	-5.654516	-2.696888	-0.359807
H	-6.999974	-1.156971	1.054417
H	-3.972010	1.891246	0.756074
C	-0.016672	0.205651	1.922363
C	1.350856	0.632517	2.002070
C	-0.037388	-1.170694	1.564450
C	-1.190452	1.071148	2.237053
C	2.183561	-0.540518	1.853965
C	1.825203	2.002686	2.365128
C	1.336878	-1.630254	1.540170
C	-1.230444	-2.069917	1.519535
H	-1.235490	1.207769	3.325299
H	-1.098710	2.068069	1.798254
H	-2.133320	0.628063	1.919874
C	3.646171	-0.621661	2.141847
H	2.054991	2.045517	3.437862
H	2.730109	2.262193	1.809148
H	1.058903	2.755447	2.162744
C	1.754023	-3.059843	1.414540
H	-1.302688	-2.615302	2.469801
H	-2.159938	-1.518862	1.380469

H	-1.161508	-2.812064	0.721994
H	3.765440	-0.939360	3.186688
H	4.157232	-1.351363	1.511487
H	4.146153	0.339010	2.021955
H	2.818901	-3.160331	1.196597
H	1.568862	-3.568624	2.370002
H	1.185624	-3.601553	0.654067
Co	1.035152	-0.083600	0.067017
C	4.247050	-0.924562	-1.935070
H	5.153938	-1.508266	-2.101302
H	4.096157	-0.275303	-2.805860
H	1.731672	-0.439608	-2.749397

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INT1-RS

C	3.504102	-0.109761	-1.066156
C	3.109911	0.776215	-0.034754
C	3.948902	1.761344	0.477721
C	5.228760	1.845500	-0.073285
C	5.645470	0.976993	-1.094784
C	4.793137	-0.003320	-1.599239
C	2.380626	-0.987239	-1.348072
C	1.349366	-0.660307	-0.519002
H	3.617086	2.430375	1.259998
H	5.913456	2.601820	0.297193
H	6.648492	1.073235	-1.498854
H	5.120869	-0.669848	-2.391509
H	2.370939	-1.750355	-2.112829
N	1.783079	0.422837	0.288677
C	0.900446	0.971292	1.157766

C	0.276172	2.510048	2.703556
C	-1.254886	0.854836	1.977838
C	-1.010344	1.957837	2.776337
H	0.548064	3.376418	3.300604
H	-2.214043	0.351295	1.971355
H	-1.774212	2.364846	3.426757
N	1.228942	2.014943	1.921282
N	-0.317031	0.353305	1.159008
C	-2.011511	-2.443860	0.673870
C	-1.558851	-2.937768	-0.599265
C	-0.887277	-2.463123	1.554877
C	-0.163718	-3.205188	-0.521314
C	0.266209	-2.891668	0.818695
C	-3.433196	-2.139891	1.041858
H	-3.985559	-3.062461	1.258723
H	-3.496044	-1.513739	1.936009
H	-3.966014	-1.626394	0.235710
C	-2.413607	-3.222660	-1.794362
H	-2.541240	-4.307385	-1.898091
H	-3.411682	-2.787757	-1.704870
H	-1.959610	-2.868363	-2.725259
C	0.651202	-3.842067	-1.602088
H	0.386007	-4.902947	-1.692529
H	0.471959	-3.379266	-2.577833
H	1.718439	-3.782137	-1.387863
C	1.627398	-3.107162	1.399937
H	1.666804	-4.073322	1.918625
H	2.398191	-3.094467	0.628764
H	1.876275	-2.328010	2.125587
C	-0.881502	-2.146107	3.016120

H	-1.755425	-1.568313	3.322943
H	-0.891125	-3.082440	3.588042
H	0.016226	-1.595120	3.307845
C	-1.895168	0.030798	-1.436591
Co	-0.465622	-1.152726	-0.083768
C	-0.690777	-0.178338	-2.054154
H	-0.511939	-1.046088	-2.677982
H	0.016125	0.635148	-2.147189
H	-2.699950	-0.688317	-1.539543
C	-2.352025	1.380644	-0.955544
C	-3.251065	2.087333	-1.969500
H	-2.898135	1.277075	-0.007331
O	-1.201489	2.201653	-0.739647
C	-3.636616	3.428213	-1.366390
H	-2.695680	2.213660	-2.904662
H	-4.154632	1.506579	-2.181776
C	-1.340880	3.538502	-0.480279
H	-4.048052	4.111002	-2.111950
H	-4.375163	3.299052	-0.567488
O	-2.509935	4.121500	-0.785015
O	-0.424230	4.150055	-0.009636

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TS1-RS

C	-3.479536	-0.864164	-1.362324
C	-3.124514	-1.479844	-0.134654
C	-3.969850	-2.361467	0.534533
C	-5.202028	-2.626778	-0.063938
C	-5.574608	-2.033436	-1.283177
C	-4.723774	-1.152016	-1.941233

C	-2.382397	-0.021763	-1.761612
C	-1.392151	-0.086915	-0.813340
H	-3.677526	-2.822618	1.467621
H	-5.885899	-3.313922	0.423985
H	-6.541169	-2.270329	-1.716108
H	-5.013435	-0.695108	-2.882410
H	-2.322404	0.525590	-2.692147
N	-1.841552	-0.995221	0.190148
C	-1.098567	-1.156090	1.317905
C	-0.656081	-2.146113	3.314276
C	0.807732	-0.502454	2.437709
C	0.519263	-1.398695	3.453853
H	-0.962396	-2.859982	4.074782
H	1.690823	0.121408	2.461457
H	1.170585	-1.506564	4.312114
N	-1.457021	-2.035726	2.256615
N	0.004140	-0.356224	1.370361
C	1.166410	2.809954	-0.386044
C	-0.070965	2.781477	-1.117523
C	0.866424	2.623084	0.988977
C	-1.148774	2.718304	-0.160621
C	-0.577191	2.562314	1.125041
C	2.519257	3.091153	-0.957755
H	2.708652	4.171689	-0.920445
H	3.315367	2.598875	-0.394362
H	2.599326	2.789703	-2.005303
C	-0.207381	2.969043	-2.597714
H	-0.166866	4.033261	-2.861089
H	0.598510	2.468983	-3.143889
H	-1.157948	2.576995	-2.966332

C	-2.610716	2.846793	-0.442795
H	-2.939518	3.859522	-0.176828
H	-2.842153	2.688384	-1.496293
H	-3.204882	2.138900	0.140591
C	-1.339006	2.415505	2.405017
H	-1.598425	3.399502	2.814736
H	-2.272482	1.867374	2.248170
H	-0.759533	1.886600	3.166077
C	1.848193	2.713170	2.117228
H	2.803721	2.238170	1.875376
H	2.062450	3.766490	2.338551
H	1.459950	2.270253	3.037272
C	1.544879	-0.037381	-1.129994
Co	0.112692	0.964852	-0.095656
C	0.357219	-0.552597	-1.719802
H	0.056811	-0.163200	-2.684959
H	0.133352	-1.606524	-1.577483
H	2.072501	0.705500	-1.720228
C	2.473394	-0.998972	-0.431133
C	3.688598	-0.367309	0.221427
H	1.927670	-1.605961	0.299238
O	2.911780	-1.909995	-1.475680
C	4.608173	-1.486831	0.672530
H	4.205204	0.276285	-0.499917
H	3.394565	0.251637	1.074099
C	4.094822	-2.591035	-1.441011
H	5.558504	-1.115513	1.060376
H	4.129200	-2.094260	1.452019
O	4.953474	-2.340015	-0.426727
O	4.366603	-3.365436	-2.311192

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INT2-RS

C	-3.147760	-0.798099	-1.728365
C	-2.975063	-1.454291	-0.478180
C	-4.057361	-1.913214	0.276437
C	-5.324584	-1.723345	-0.265108
C	-5.519468	-1.093516	-1.514650
C	-4.443873	-0.628893	-2.252485
C	-1.857253	-0.409936	-2.185716
C	-0.903193	-0.782550	-1.252810
H	-3.909474	-2.422670	1.219661
H	-6.188985	-2.083732	0.283598
H	-6.527917	-0.978332	-1.897883
H	-4.589805	-0.141587	-3.211394
H	-1.625110	0.026507	-3.148340
N	-1.606681	-1.457610	-0.197565
C	-1.023267	-1.621249	1.045083
C	-0.817582	-2.687587	3.034789
C	0.669183	-0.935073	2.446448
C	0.301599	-1.914149	3.357678
H	-1.197973	-3.443214	3.716816
H	1.498715	-0.260627	2.618079
H	0.846448	-2.054929	4.283068
N	-1.468743	-2.557634	1.875187
N	-0.015331	-0.752873	1.303615
C	0.749932	2.739040	-0.050361
C	-0.426809	2.586430	-0.838608
C	0.418332	2.372142	1.294681
C	-1.531865	2.271189	0.053699

C	-1.013489	2.122278	1.349862
C	2.058813	3.269659	-0.540900
H	1.989716	4.359201	-0.652684
H	2.873684	3.061096	0.153957
H	2.327567	2.861599	-1.519070
C	-0.521634	2.886947	-2.303470
H	-0.568591	3.970107	-2.472925
H	0.350788	2.510349	-2.846746
H	-1.414312	2.444942	-2.750574
C	-2.976841	2.169488	-0.322462
H	-3.507087	3.067348	0.018832
H	-3.115866	2.095154	-1.401080
H	-3.467182	1.305745	0.135937
C	-1.790260	1.765830	2.579444
H	-2.076693	2.668351	3.133555
H	-2.709399	1.228286	2.329314
H	-1.207874	1.140087	3.262709
C	1.312427	2.492941	2.489713
H	2.355125	2.268683	2.251681
H	1.284232	3.520530	2.874955
H	0.994003	1.841495	3.307843
C	1.515554	-0.037865	-0.960546
Co	0.052014	0.760421	0.049784
C	0.575814	-1.089103	-1.555876
H	0.677369	-1.153200	-2.642026
H	0.797150	-2.085915	-1.161201
H	1.836356	0.679241	-1.721528
C	2.732566	-0.655740	-0.312052
C	3.773705	0.299673	0.235882
H	2.429640	-1.352203	0.480485

O	3.334185	-1.486622	-1.350796
C	5.008360	-0.506114	0.594932
H	4.028765	1.054931	-0.514754
H	3.385656	0.814164	1.120107
C	4.665891	-1.745611	-1.464543
H	5.834900	0.122682	0.930817
H	4.785342	-1.235749	1.385279
O	5.506697	-1.203738	-0.553462
O	5.075429	-2.416963	-2.367544

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TS2-RS

C	3.878155	1.055958	1.069542
C	3.435527	-0.177436	0.534023
C	4.265233	-0.986378	-0.243951
C	5.558829	-0.527930	-0.488179
C	6.014624	0.695974	0.030841
C	5.184154	1.492995	0.811086
C	2.776616	1.621668	1.807344
C	1.705813	0.789835	1.694071
H	3.934618	-1.947045	-0.615244
H	6.230135	-1.139410	-1.082741
H	7.030201	1.017997	-0.176212
H	5.536709	2.437243	1.214568
H	2.792339	2.536118	2.385156
N	2.071719	-0.317689	0.889328
C	1.305491	-1.450928	0.671331
C	1.242336	-3.736386	0.561316
C	-0.731847	-2.467005	0.280453
C	-0.139477	-3.715274	0.378074

H	1.803382	-4.667465	0.588843
H	-1.790028	-2.363912	0.069021
H	-0.729199	-4.618393	0.279338
N	1.947352	-2.619120	0.725282
N	-0.022449	-1.318991	0.390643
C	-1.102407	1.876574	-1.754897
C	0.253130	1.362729	-1.757576
C	-1.967454	0.826868	-2.178095
C	0.194301	0.005667	-2.195347
C	-1.180550	-0.351207	-2.395630
C	-1.499161	3.295645	-1.490607
H	-1.481846	3.871482	-2.424368
H	-2.512694	3.366312	-1.086163
H	-0.813754	3.789595	-0.796881
C	1.490333	2.163932	-1.503870
H	1.751897	2.737411	-2.402424
H	1.355125	2.876077	-0.686488
H	2.342465	1.532061	-1.249437
C	1.358775	-0.895952	-2.443294
H	1.566784	-0.918193	-3.520672
H	2.264373	-0.553675	-1.941494
H	1.152664	-1.925092	-2.137090
C	-1.705401	-1.678700	-2.849681
H	-1.920797	-1.661411	-3.925351
H	-0.978620	-2.476275	-2.675071
H	-2.627468	-1.938333	-2.322855
C	-3.450696	0.901320	-2.323192
H	-3.881031	1.691330	-1.704149
H	-3.702561	1.120989	-3.368884
H	-3.922957	-0.045557	-2.053952

C	-0.656391	1.499896	1.318938
Co	-0.924179	0.301302	-0.385659
C	0.350771	0.912985	2.300488
H	0.446264	1.564338	3.178772
H	0.010860	-0.059138	2.674036
H	-0.304186	2.417513	0.851567
C	-2.033648	1.533649	1.653117
C	-2.673317	0.969112	2.880213
H	-2.629918	2.291373	1.150328
O	-2.727969	0.154171	0.444407
C	-4.118194	0.530726	2.628342
H	-2.096358	0.136158	3.292089
H	-2.676897	1.763967	3.641675
C	-3.541016	-0.842349	0.740781
H	-4.628990	0.327432	3.569650
H	-4.671785	1.310395	2.091161
O	-4.216048	-0.704021	1.899292
O	-3.700910	-1.831947	0.049483

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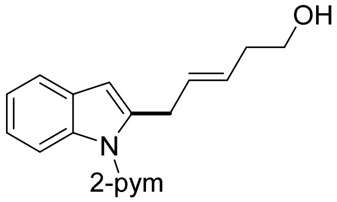
INT3-Z

C	-3.962489	-0.805860	1.119671
C	-3.434664	0.289165	0.394814
C	-4.186037	0.970635	-0.564660
C	-5.483322	0.519912	-0.800772
C	-6.020130	-0.573523	-0.099017
C	-5.270453	-1.240111	0.863236
C	-2.935144	-1.251750	2.025737
C	-1.826158	-0.486892	1.833085
H	-3.797038	1.838208	-1.080929

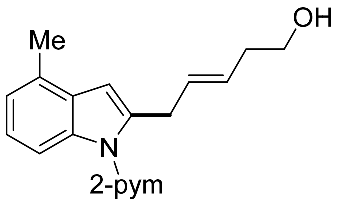
H	-6.094526	1.036379	-1.534037
H	-7.036293	-0.893206	-0.306570
H	-5.687005	-2.079779	1.410963
H	-3.025974	-2.036104	2.765274
N	-2.087163	0.448549	0.802248
C	-1.286701	1.529006	0.449215
C	-1.204898	3.780575	0.026228
C	0.758835	2.467930	-0.067428
C	0.174553	3.721359	-0.150193
H	-1.760901	4.709678	-0.073627
H	1.818708	2.344696	-0.262457
H	0.775664	4.594223	-0.374038
N	-1.915393	2.698695	0.340352
N	0.044949	1.347358	0.204025
C	1.117025	-2.207028	-1.335052
C	-0.230131	-1.664069	-1.439431
C	2.015238	-1.285771	-1.923661
C	-0.135687	-0.416177	-2.109860
C	1.258309	-0.124271	-2.327313
C	1.467347	-3.558878	-0.800706
H	1.331498	-4.311271	-1.588206
H	2.510291	-3.609183	-0.479111
H	0.828515	-3.854567	0.035562
C	-1.486047	-2.393070	-1.082683
H	-1.725483	-3.116085	-1.873199
H	-1.388695	-2.952426	-0.149553
H	-2.336675	-1.719109	-0.976423
C	-1.267942	0.450809	-2.548509
H	-1.416381	0.314238	-3.627444
H	-2.202727	0.194197	-2.050795

H	-1.060150	1.512182	-2.388307
C	1.828715	1.092202	-2.984919
H	2.132276	0.858832	-4.013200
H	1.095545	1.900697	-3.032697
H	2.705557	1.457059	-2.441853
C	3.490613	-1.442252	-2.067342
H	3.918313	-2.018559	-1.244269
H	3.707902	-1.975504	-3.002251
H	3.990072	-0.473178	-2.100567
C	0.486428	-1.399151	1.819339
Co	1.005728	-0.359464	-0.296919
C	-0.520360	-0.540759	2.549611
H	-0.707945	-0.979862	3.537892
H	-0.123931	0.463315	2.732533
H	0.068523	-2.272342	1.328834
C	1.831162	-1.355660	2.004995
C	2.587257	-0.425742	2.906358
H	2.429822	-2.136408	1.541048
O	2.792059	0.047668	0.280024
C	4.038035	-0.120911	2.491207
H	2.046884	0.512835	3.068060
H	2.624963	-0.923564	3.888921
C	3.548117	1.083571	0.483136
H	4.631534	0.105980	3.377806
H	4.482078	-0.990241	1.991639
O	4.205931	1.044196	1.671968
O	3.715183	2.040945	-0.261876

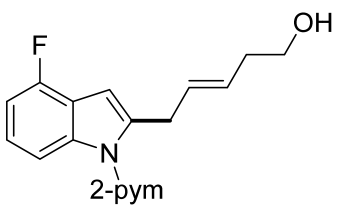
5. Characterization of the Products.



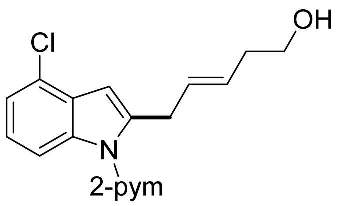
3aa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3aa** as pale yellow oil (51.4 mg, 92%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, *J* = 8.0 Hz, 2H), 8.21(d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 4.0 Hz, 1H), 7.25 – 7.13 (m, 3H), 6.48 (s, 1H), 5.77 – 5.69 (m, 1H), 5.43 – 5.36 (m, 1H), 3.92 (d, *J* = 4.0 Hz, 2H), 3.53 (t, *J* = 4.0 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.59 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 140.1, 137.2, 130.7, 129.3, 128.2, 122.8, 121.9, 119.9, 117.3, 113.7, 106.5, 61.9, 35.9, 32.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{17}N_3ONa$ 302.1269; Found 302.1265.



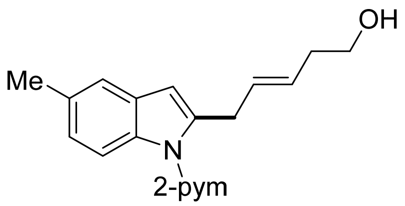
3ba: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ba** as pale yellow oil (50.4 mg, 86%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 4.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 5.77 – 5.68 (m, 1H), 5.43 – 5.33 (m, 1H), 3.92 (d, *J* = 8.0 Hz, 2H), 3.51 (t, *J* = 4.0 Hz, 2H), 2.55 (s, 3H), 2.24 – 2.19 (m, 2H), 1.59 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 139.4, 136.9, 130.9, 129.3, 128.8, 128.1, 122.8, 122.3, 117.3, 111.2, 104.9, 61.9, 36.0, 32.8, 18.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3ONa$ 316.1426; Found 316.1420.



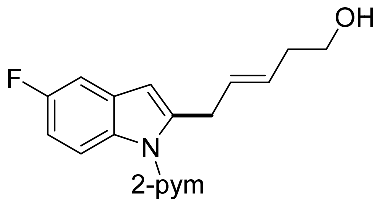
3ca: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ca** as pale yellow oil (52.9 mg, 89%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, *J* = 4.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.09 (m, 2H), 6.88 – 6.84 (m, 1H), 6.57 (s, 1H), 5.73 – 5.66 (m, 1H), 5.43 – 5.36 (m, 1H), 3.89 (d, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 4.0 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.71 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 158.1, 155.6 (d, *J* = 244.0 Hz), 140.3, 139.5 (d, *J* = 10.0 Hz), 130.2, 128.6, 123.2 (d, *J* = 7.0 Hz), 118.10 (d, *J* = 22.0 Hz), 117.8, 109.8 (d, *J* = 4.0 Hz), 107.0 (d, *J* = 18.0 Hz), 101.8, 62.0, 35.9, 32.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}FN_3O$ 298.1356; Found 298.1355.



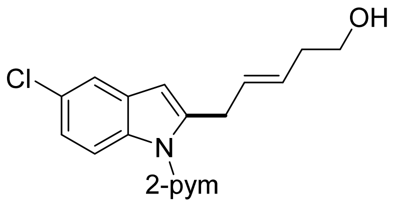
3da: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3da** as pale yellow oil (56.4 mg, 90%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, *J* = 4.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.11 (m, 3H), 6.60 (s, 1H), 5.75 – 5.68 (m, 1H), 5.44 – 5.37 (m, 1H), 3.91 (d, *J* = 8.0 Hz, 2H), 3.55 – 3.51 (m, 2H), 2.25 – 2.20 (m, 2H), 1.44 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 158.0, 141.0, 137.8, 130.3, 128.6, 127.9, 125.2, 123.3, 121.6, 117.8, 112.4, 104.5, 62.0, 36.0, 32.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}ClN_3O$ 314.1060; Found 314.1053.



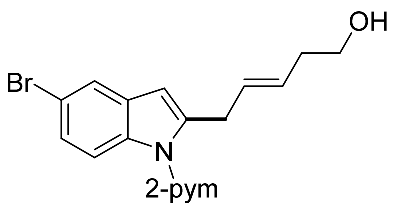
3ea: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ea** as pale yellow oil (53.4 mg, 91%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.10 (t, *J* = 4.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.41 (s, 1H), 5.75 – 5.68 (m, 1H), 5.42 – 5.34 (m, 1H), 3.90 (d, *J* = 8.0 Hz, 2H), 3.51 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.23 – 2.18 (m, 2H), 1.70 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 158.2, 140.1, 135.4, 131.2, 130.9, 129.5, 128.0, 124.1, 119.8, 117.0, 113.6, 106.3, 61.9, 35.9, 32.9, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3ONa$ 316.1426; Found 316.1422.



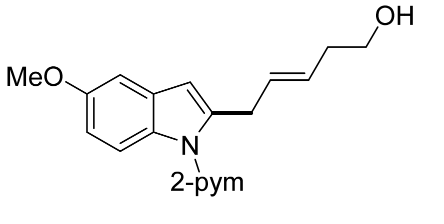
3fa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3fa** as pale yellow oil (51.1 mg, 86%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (d, *J* = 4.0 Hz, 2H), 8.18 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.97 – 6.91 (m, 1H), 6.43 (s, 1H), 5.75 – 5.68 (m, 1H), 5.45 – 5.36 (m, 1H), 3.90 (d, *J* = 4.0 Hz, 2H), 3.53 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.62 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.1 (d, *J* = 236.0 Hz), 158.3, 158.1, 141.9, 133.5, 130.5, 130.0 (d, *J* = 10.0 Hz), 128.5, 117.4, 114.9 (d, *J* = 9.0 Hz), 110.4 (d, *J* = 25.0 Hz), 106.3 (d, *J* = 4.0 Hz), 105.1 (d, *J* = 23.0 Hz), 62.0, 36.0, 33.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}FN_3ONa$ 320.1175; Found 320.1167.



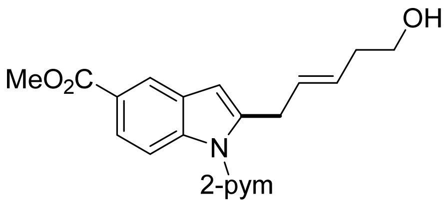
3ga: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ga** as pale yellow oil (57.0 mg, 91%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (d, *J* = 4.0 Hz, 2H), 8.14 (d, *J* = 12.0 Hz, 1H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.41 (s, 1H), 5.73 – 5.66 (m, 1H), 5.44 – 5.37 (m, 1H), 3.89 (d, *J* = 4.0 Hz, 2H), 3.52 (t, *J* = 8.0 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.59 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 158.0, 141.7, 135.5, 130.4, 130.3, 128.6, 127.3, 122.8, 119.4, 117.6, 115.0, 105.8, 62.0, 35.9, 32.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}ClN_3ONa$ 336.0880; Found 336.0869.



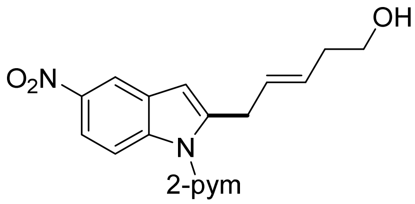
3ha: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ha** as pale yellow oil (59.2 mg, 83%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 4.0 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (t, *J* = 4.0 Hz, 1H), 6.41 (s, 1H), 5.74 – 5.66 (m, 1H), 5.45 – 5.35 (m, 1H), 3.90 (d, *J* = 4.0 Hz, 2H), 3.53 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.62 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 157.8, 141.6, 135.9, 131.0, 130.4, 128.6, 125.5, 122.5, 117.6, 115.5, 115.1, 105.8, 62.0, 36.0, 32.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}BrN_3ONa$ 380.0374; Found 380.0359.



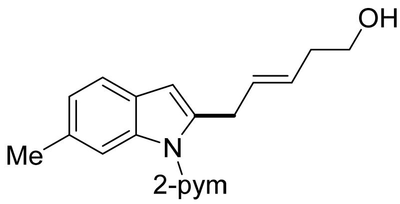
3ia: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ia** as pale yellow oil (51.3 mg, 83%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 4.0 Hz, 1H), 7.01 (d, *J* = 4.0 Hz, 1H), 6.85 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.41 (s, 1H), 5.77 – 5.67 (m, 1H), 5.45 – 5.35 (m, 1H), 3.90 (d, *J* = 4.0 Hz, 2H), 3.85 (s, 3H), 3.52 (t, *J* = 8.0 Hz, 2H), 2.24 – 2.19 (m, 1H), 1.59 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.2, 158.2, 155.5, 140.8, 132.0, 130.9, 130.0, 128.1, 117.0, 114.9, 111.7, 106.5, 102.4, 61.9, 55.8, 36.0, 33.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3O_2Na$ 332.1375; Found 332.1380.



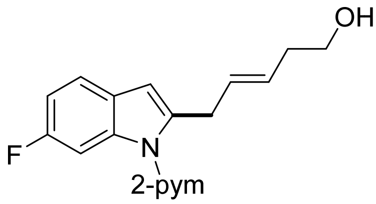
3ja: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **3ja** as pale yellow oil (61.4 mg, 91%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, *J* = 8.0 Hz, 2H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 4.0 Hz, 1H), 6.54 (s, 1H), 5.72 – 5.63 (m, 1H), 5.43 – 5.35 (m, 1H), 3.93 (s, 3H), 3.89 (d, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 8.0 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.55 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.1, 158.5, 157.9, 141.7, 139.8, 130.1, 128.9, 128.7, 124.2, 123.7, 122.4, 118.0, 113.3, 106.8, 62.0, 52.0, 35.9, 32.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{19}N_3O_3Na$ 360.1324; Found 360.1338.



3ka: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **3ka** as white solid (51.2 mg, 79%, *E/Z* > 20:1); m.p. = 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, *J* = 4.0 Hz, 2H), 8.44 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 4.0 Hz, 1H), 6.61 (s, 1H), 5.72 – 5.65 (m, 1H), 5.47 – 5.39 (m, 1H), 3.91 (d, *J* = 8.0 Hz, 2H), 3.55 (t, *J* = 4.0 Hz, 2H), 2.26 – 2.21 (m, 2H), 1.43 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.6, 157.6, 143.8, 143.1, 140.2, 129.5, 129.3, 128.8, 118.5, 118.1, 116.4, 113.7, 107.0, 62.0, 36.0, 32.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}N_4O_3Na$ 347.1120; Found 347.1131.

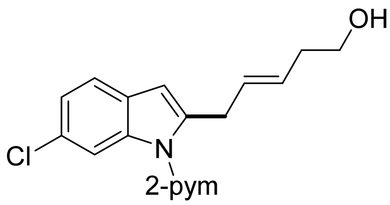


3la: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3la** as pale yellow oil (54.5 mg, 93%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 4.0 Hz, 2H), 8.00 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 4.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 5.74 – 5.67 (m, 1H), 5.41 – 5.32 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.23 – 2.18 (m, 2H), 1.56 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 158.2, 139.3, 137.5, 132.6, 130.9, 128.0, 127.0, 123.4, 119.6, 117.2, 113.6, 106.3, 61.9, 35.9, 32.7, 22.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3ONa$ 316.1426; Found 316.1432.

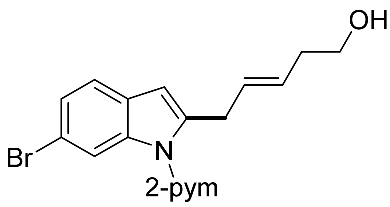


3ma: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ma** as pale yellow oil (49.9 mg, 84%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 8.0 Hz, 2H), 8.01 (dd, *J* = 12.0, 4.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.44 (s, 1H), 5.75 – 5.68 (m, 1H), 5.44 – 5.37 (m, 1H), 3.90 (d, *J* =

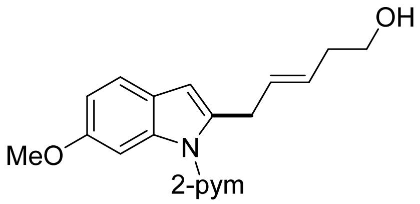
8.0 Hz, 2H), 3.53 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.46 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.3 (d, *J* = 236.0 Hz), 158.3, 158.1, 140.6 (d, *J* = 4.0 Hz), 137.2 (d, *J* = 13.0 Hz), 130.7, 128.3, 125.6, 120.3 (d, *J* = 10.0 Hz), 117.5, 110.1 (d, *J* = 24.0 Hz), 106.3, 101.3 (d, *J* = 29.0 Hz), 62.0, 36.0, 33.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}FN_3ONa$ 320.1175; Found 320.1167.



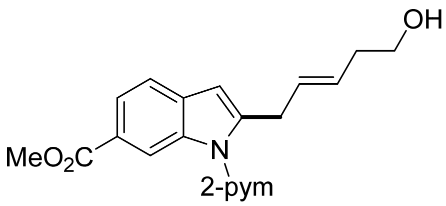
3na: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3na** as pale yellow oil (52.6 mg, 84%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 4.0 Hz, 2H), 8.27 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.44 (s, 1H), 5.73 – 5.67 (m, 1H), 5.44 – 5.36 (m, 1H), 3.89 (d, *J* = 8.0 Hz, 2H), 3.53 (t, *J* = 8.0 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.49 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 158.0, 141.0, 137.5, 130.4, 128.6, 128.5, 127.8, 122.4, 120.6, 117.6, 114.1, 106.3, 62.0, 36.0, 32.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}ClN_3ONa$ 336.0880; Found 336.0894.



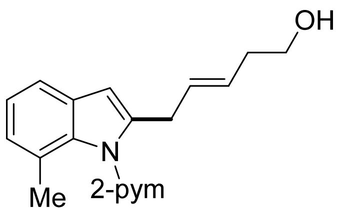
3oa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3oa** as pale yellow oil (62.1 mg, 87%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, *J* = 8.0 Hz, 2H), 8.42 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.18 (t, *J* = 4.0 Hz, 1H), 6.44 (s, 1H), 5.74 – 5.66 (m, 1H), 5.44 – 5.36 (m, 1H), 3.89 (d, *J* = 8.0 Hz, 2H), 3.55 – 3.51 (m, 2H), 2.25 – 2.20 (m, 2H), 1.42 (s, OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 157.9, 141.0, 137.8, 130.4, 128.5, 128.1, 125.1, 121.0, 117.6, 116.9, 116.3, 106.3, 62.0, 36.0, 32.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_3O$ 358.0555; Found 358.0569.



3pa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3pa** as pale yellow oil (52.6 mg, 85%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 4.0 Hz, 2H), 7.84 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 4.0 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.40 (s, 1H), 5.73 – 5.66 (m, 1H), 5.44 – 5.31 (m, 1H), 3.88 (d, *J* = 4.0 Hz, 2H), 3.86 (s, 3H), 3.51 (t, *J* = 8.0 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.44 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 156.9, 139.0, 138.0, 131.1, 127.9, 123.4, 120.3, 117.2, 110.7, 106.4, 98.8, 62.0, 55.9, 36.0, 32.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3O_2Na$ 332.1375; Found 332.1362.

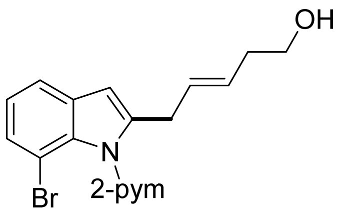


3qa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **3qa** as pale yellow oil (62.0 mg, 92%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (s, 1H), 8.82 (d, *J* = 8.0 Hz, 2H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 4.0 Hz, 1H), 6.51 (s, 1H), 5.73 – 5.66 (m, 1H), 5.45 – 5.37 (m, 1H), 3.92 (m, 5H), 3.52 (t, *J* = 8.0 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.58 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.3, 158.5, 157.8, 143.7, 136.5, 133.0, 129.9, 128.8, 124.3, 123.1, 119.5, 117.9, 115.8, 106.3, 62.0, 52.0, 35.9, 32.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{19}N_3O_3Na$ 360.1324; Found 360.1311.

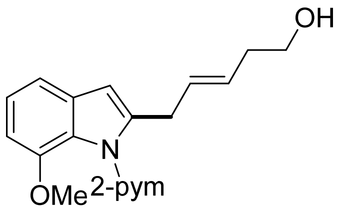


3ra: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **3ra** as pale yellow oil (53.4 mg, 91%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d,

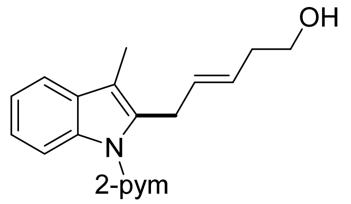
J = 4.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 4.0 Hz, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.44 (s, 1H), 5.58 – 5.51 (m, 1H), 5.20 – 5.13 (m, 1H), 3.50 – 3.47 (m, 4H), 2.15–2.10 (m, 2H), 1.92 (s, 3H), 1.71 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.0, 158.5, 139.8, 136.9, 130.1, 129.5, 128.4, 125.2, 121.7, 121.4, 119.4, 118.2, 104.3, 61.8, 35.9, 30.9, 20.0. HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_{18}H_{19}N_3ONa$ 316.1426; Found 316.1420.



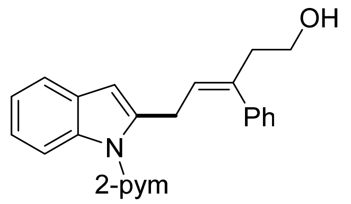
3sa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **3sa** as pale yellow oil (60.0 mg, 84%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0, 1.0 Hz, 1H), 7.38 (t, J = 4.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.45 (s, 1H), 5.59 – 5.51 (m, 1H), 5.24 – 5.16 (m, 1H), 3.54 – 3.50 (m, , 2H), 3.43 (d, J = 8.0 Hz, 2H), 2.18 – 2.13 (m, 2H), 1.92 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.6, 157.8, 141.3, 135.3, 131.7, 129.3, 129.0, 127.0, 122.2, 120.2, 119.6, 104.5, 103.6, 61.8, 35.9, 30.7. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{17}H_{17}BrN_3O$ 358.0555; Found 358.0554.



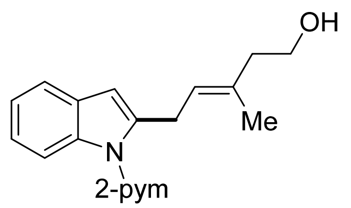
3ta: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **3ta** as pale yellow oil (53.2 mg, 86%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (d, J = 4.0 Hz, 2H), 7.29 (t, J = 4.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.41 (s, 1H), 5.59 – 5.52 (m, 1H), 5.20 – 5.12 (m, 1H), 3.62 (s, 3H), 3.49 (d, J = 8.0 Hz, 4H), 2.15 – 2.10 (m, 2H), 1.92 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.9, 157.9, 146.9, 139.7, 130.8, 130.1, 128.4, 127.4, 121.6, 119.2, 113.2, 104.4, 103.9, 61.8, 55.8, 35.9, 30.6. HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_{18}H_{19}N_3O_2Na$ 332.1375; Found 332.1382.



3ua: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3ua** as pale yellow oil (53.9 mg, 92%, *E/Z* = 12:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (d, *J* = 4.0 Hz, 2H), 8.17 – 8.15 (m, 1H), 7.54 – 7.50 (m, 1H), 7.25-7.21 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 5.68 – 5.61 (m, 1H), 5.23 – 5.15 (m, 1H), 3.89 (d, *J* = 4.0 Hz, 2H), 3.41 (t, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.15 – 2.10 (m, 2H), 1.53 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 158.2, 136.3, 134.4, 131.5, 130.4, 126.8, 123.0, 121.6, 118.2, 117.1, 113.7, 113.4, 61.7, 35.9, 29.2, 8.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3ONa$ 316.1426; Found 316.1429.

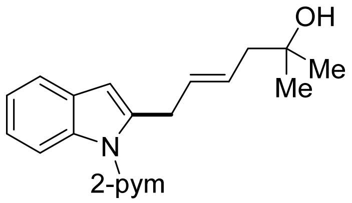


3ab: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ab** as pale yellow oil (27.7 mg, 39%, *Z/E* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 4.0 Hz, 2H), 8.06 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.41 (m, 2H), 7.38 – 7.31 (m, 3H), 7.28 – 7.23 (m, 2H), 6.99 (t, *J* = 4.0 Hz, 1H), 6.19 (t, *J* = 8.0 Hz, 1H), 3.75 – 3.70 (m, 4H), 2.98 (t, *J* = 8.0 Hz, 2H), 1.51 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.2, 157.8, 142.4, 137.4, 136.0, 131.2, 128.8, 128.5, 127.2, 126.6, 124.1, 122.8, 122.0, 119.6, 119.0, 116.5, 115.9, 61.5, 33.5, 24.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{21}N_3ONa$ 378.1582; Found 378.1574.

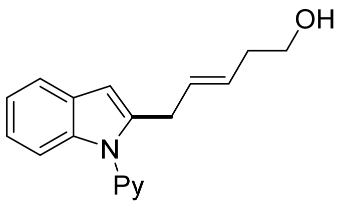


3ac: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 6:1) to afford **3ac** as pale yellow oil (44.0 mg, 75%, *Z/E* = 1.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 – 8.78 (m, 2H), 8.26 – 8.21 (m, 1H), 7.54 – 7.51 (m, 1H), 7.24 – 7.13 (m, 3H), 6.46 (s, 1H), 5.57 –

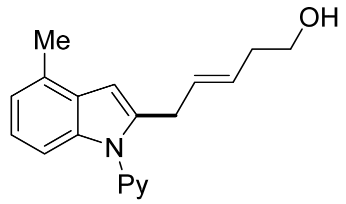
5.42 (m, 1H), 3.94 – 3.90 (m, 2H), 3.70 – 3.64 (m, 2H), 2.43 – 2.24 (m, 2H), 1.77 – 1.70 (m, 3H), 1.50 – 1.43 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, (141.0, 140.6), 137.2, (133.6, 133.4), 129.3, 124.7, 122.7, 121.9, 119.9, (117.2, 117.2), (113.9, 113.7), (106.1, 106.0), (60.8, 60.3), 42.7, 35.3, (28.8, 28.6), 23.6, 16.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3ONa$ 316.1426; Found 316.1424.



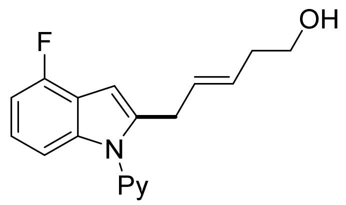
3ad: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 6:1) to afford **3ad** as pale yellow oil (51.0 mg, 83%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 4.0 Hz, 2H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.14 (t, *J* = 4.0 Hz, 1H), 6.49 (s, 1H), 5.75 – 5.68 (m, 1H), 5.55 – 5.47 (m, 1H), 3.95 (d, *J* = 4.0 Hz, 2H), 2.14 (d, *J* = 8.0 Hz, 2H), 1.50 (OH, 1H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3, 140.1, 137.2, 131.9, 129.3, 127.5, 122.8, 122.0, 119.9, 117.3, 113.9, 106.6, 70.5, 46.9, 33.0, 29.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}N_3ONa$ 330.1582; Found 330.1574.



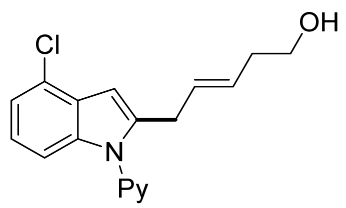
5aa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5aa** as pale yellow oil (48.4 mg, 87%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.65 (d, *J* = 8.0 Hz, 1H), 7.88 (td, *J* = 7.6, 2.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34-7.30 (m, 2H), 7.16-7.11 (m, 2H), 6.46 (s, 1H), 5.63 – 5.56 (m, 1H), 5.29 – 5.21 (m, 1H), 3.60 (d, *J* = 4.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.66 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ : 151.6, 149.7, 139.4, 138.5, 137.5, 130.1, 128.6, 128.4, 122.3, 122.0, 121.3, 120.8, 120.2, 110.2, 103.3, 61.9, 35.9, 31.1. $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O$ 279.1497; Found 279.1489.



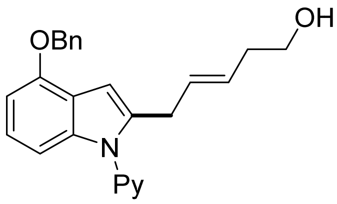
5ba: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ba** as pale yellow oil (45.6 mg, 78%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.88 (td, *J* = 8.0, 2.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 5.64 – 5.56 (m, 1H), 5.28 – 5.20 (m, 1H), 3.62 (d, *J* = 4.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.56 (s, 3H), 2.20 – 2.15 (m, 2H) 1.67 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.7, 149.6, 138.8, 138.4, 137.3, 130.3, 129.7, 128.3, 128.3, 122.2, 122.1, 121.4, 121.1, 107.9, 101.8, 61.9, 35.9, 31.2, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2ONa$ 315.1473; Found 315.1468.



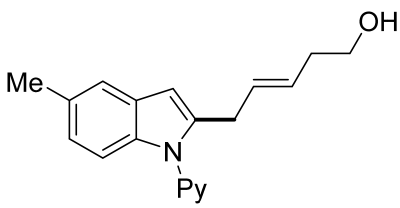
5ca: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ca** as pale yellow oil (52.7 mg, 89%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.89 (td, *J* = 8.0, 2.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.24 – 7.19 (m, 2H), 6.86 (td, *J* = 9.2, 2.4 Hz, 1H), 6.41 (s, 1H), 5.61 – 5.54 (m, 1H), 5.29 – 5.22 (m, 1H), 3.56 (d, *J* = 4.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.78 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.9 (d, *J* = 245 Hz), 151.2, 149.8, 140.1 (d, *J* = 11.0 Hz), 139.5, 138.7, 129.6, 128.8, 122.7, 122.4 (d, *J* = 7.0 Hz), 121.4, 117.4 (d, *J* = 23.0 Hz), 106.4 (d, *J* = 3.0 Hz), 105.7 (d, *J* = 19.0 Hz), 98.9, 61.9, 35.9, 31.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O$ 297.1403; Found 297.1414.



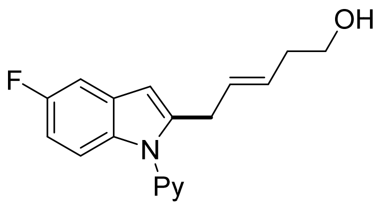
5da: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5da** as pale yellow oil (56.2 mg, 90%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.65 (dd, *J* = 4.8, 20 Hz, 1H), 7.90 (td, *J* = 7.6, 2.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 5.62 – 5.55 (m, 1H), 5.29 – 5.22 (m, 1H), 3.58 (d, *J* = 8.0 Hz, 2H), 3.51 (t, *J* = 8.0 Hz, 2H), 2.20 – 2.15 (m, 2H), 1.85 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.1, 149.8, 140.3, 138.7, 138.2, 129.5, 128.9, 127.3, 125.5, 122.8, 122.6, 121.5, 120.6, 108.9, 101.6, 61.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}ClN_2ONa$ 335.0927; Found 335.0939.



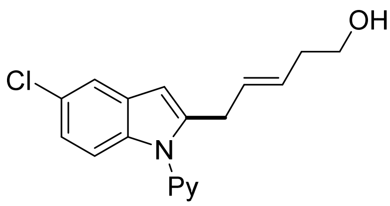
5ea: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ea** as pale yellow oil (69.9 mg, 91%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.87 (td, *J* = 7.6, 2.0 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.43 – 7.39 (m, 3H), 7.36 – 7.30 (m, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.65 – 6.63 (m, 2H), 5.63 – 5.56 (m, 1H), 5.28 – 5.21 (m, 3H), 3.59 (d, *J* = 8.0 Hz, 2H), 3.49 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.70 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 151.7, 149.6, 139.0, 138.4, 137.9, 137.7, 130.2, 128.6, 128.3, 127.9, 127.5, 122.7, 122.3, 121.4, 119.3, 104.0, 102.5, 100.6, 70.2, 61.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{24}N_2O_2Na$ 407.1735; Found 407.1741.



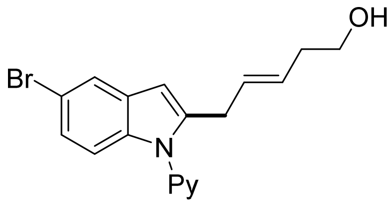
5fa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5fa** as pale yellow oil (45.0 mg, 77%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 4.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.38 (s, 1H), 5.62 – 5.55 (m, 1H), 5.27 – 5.19 (m, 1H), 3.59 (d, *J* = 8.0 Hz, 2H), 3.48 (t, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.19 – 2.13 (m, 2H), 1.81 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.7, 149.6, 139.4, 138.4, 135.9, 130.2, 130.1, 128.9, 128.3, 123.4, 122.1, 121.1, 120.0, 109.9, 103.0, 61.9, 35.9, 31.1, 21.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2ONa$ 315.1473; Found 315.1463.



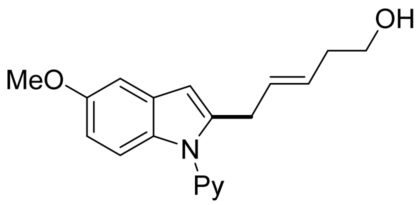
5ga: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ga** as pale yellow oil (38.5 mg, 65%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.89 (td, *J* = 8.0, 2.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.24 – 7.19 (m, 2H), 6.86 (td, *J* = 9.2, 2.4 Hz, 1H), 6.41 (s, 1H), 5.61 – 5.53 (m, 1H), 5.29 – 5.22 (m, 1H), 3.56 (d, *J* = 4.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.78 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.6 (d, *J* = 234.0 Hz), 151.3, 149.8, 141.1, 138.6, 134.1, 129.6, 129.1, 129.0 (d, *J* = 10.0 Hz), 122.5, 121.2, 111.0 (d, *J* = 10.0 Hz), 109.9 (d, *J* = 26.0 Hz), 105.2 (d, *J* = 23.0 Hz), 103.2 (d, *J* = 4.0 Hz), 61.9, 35.9, 31.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O$ 297.1403; Found 297.1395.



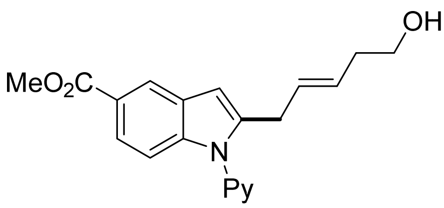
5ha: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ha** as pale yellow oil (53.7 mg, 86%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.89 (td, *J* = 8.0, 2.0 Hz, 1H), 7.52 (d, *J* = 4.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.39 (s, 1H), 5.60 – 5.53 (m, 1H), 5.29 – 5.22 (m, 1H), 3.56 (d, *J* = 4.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.82 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.1, 149.8, 140.9, 138.7, 136.0, 129.6, 129.5, 128.8, 126.3, 122.6, 122.1, 121.3, 119.6, 111.3, 102.8, 61.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}ClN_2ONa$ 335.0927; Found 335.0931.



5ia: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ia** as pale yellow oil (44.2 mg, 62%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.90 (td, *J* = 7.6, 2.0 Hz, 1H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.22 – 7.15 (m, 2H), 6.39 (s, 1H), 5.62 – 5.53 (m, 1H), 5.29 – 5.22 (m, 1H), 3.57 (d, *J* = 8.0 Hz, 2H), 3.51 (t, *J* = 8.0 Hz, 2H), 2.20 – 2.15 (m, 2H), 1.64 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.1, 149.8, 140.8, 138.7, 136.3, 130.3, 129.6, 128.8, 124.7, 122.7, 122.6, 121.3, 114.0, 111.8, 102.7, 61.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}BrN_2ONa$ 379.0422; Found 379.0428.

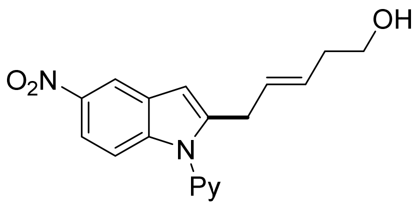


5ja: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ja** as pale yellow oil (50.5 mg, 82%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.87 (td, *J* = 7.6, 2.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 7.2, 4.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.38 (s, 1H), 5.63 – 5.56 (m, 1H), 5.29 – 5.21 (m, 1H), 3.85 (s, 3H), 3.59 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.15 (m, 2H), 1.68 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.9, 151.7, 149.6, 140.0, 138.5, 132.7, 130.1, 129.2, 128.4, 122.1, 121.0, 111.5, 111.1, 103.2, 102.4, 61.9, 56.0, 35.9, 31.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2O_2Na$ 331.1422; Found 331.1410.

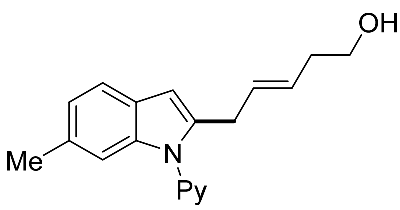


5ka: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5ka** as pale yellow oil (66.6 mg, 99%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (dd,

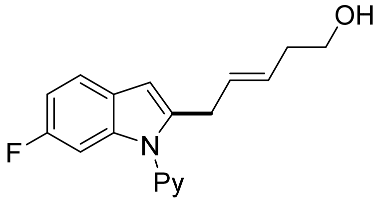
J = 5.2, 2.0 Hz, 1H), 8.32 (d, J = 2.0 Hz, 1H), 7.91 (td, J = 7.6, 2.0 Hz, 1H), 7.83 (dd, J = 8.4, 1.8 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.37 (dd, J = 8.0, 4.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 6.53 (s, 1H), 5.61 – 5.54 (m, 1H), 5.29 – 5.22 (m,, 1H), 3.92 (s, 3H), 3.57 (d, J = 4.0 Hz, 2H), 3.51 (t, J = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.69 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.2, 151.0, 149.9, 141.0, 140.1, 138.7, 129.4, 128.9, 128.1, 123.5, 123.0, 122.9, 122.8, 121.5, 109.9, 104.1, 61.9, 52.0, 35.9, 31.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2O_3Na$ 359.1372; Found 359.1377.



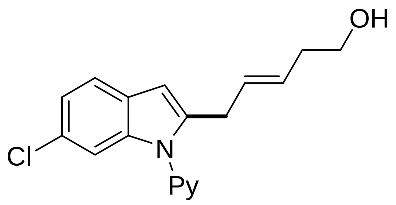
5la: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5la** as white solid (61.4 mg, 95%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (dd, J = 5.2, 2.0 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.02 (dd, J = 8.8, 2.4 Hz, 1H), 7.96 (td, J = 7.6, 2.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 6.61 (s, 1H), 5.61 – 5.54 (m, 1H), 5.33 – 5.25 (m, 1H), 3.57 (d, J = 8.0 Hz, 2H), 3.52 (t, J = 4.0 Hz, 2H), 2.22 – 2.17 (m, 2H), 1.60 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.4, 150.1, 143.1, 142.5, 140.5, 139.0, 129.5, 128.7, 127.9, 123.4, 121.5, 117.7, 117.1, 110.2, 104.6, 61.9, 35.9, 31.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}N_3O_3Na$ 346.1168; Found 346.1167.



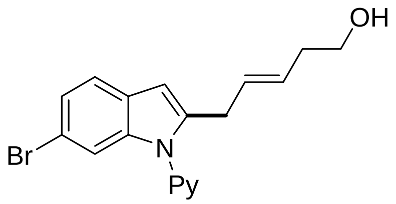
5ma: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5ma** as pale yellow oil (42.1 mg, 72%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, J = 5.2, 2.0 Hz, 1H), 7.89 (td, J = 7.6, 2.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 8.0, 4.0 Hz, 1H), 7.11 (s, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 5.61 – 5.54 (m, 1H), 5.26 – 5.19 (m, 1H), 3.57 (d, J = 8.0 Hz, 2H), 3.49 (t, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.18 – 2.13 (m, 2H), 1.75 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.7, 149.7, 138.7, 138.5, 138.0, 131.8, 130.2, 128.3, 126.3, 122.4, 122.2, 121.4, 119.8, 110.3, 103.1, 61.9, 35.9, 31.1, 21.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2ONa$ 315.1473; Found 315.1481.



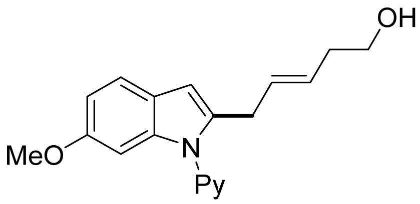
5na: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5na** as pale yellow oil (56.9 mg, 96%, *E/Z* > 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.65 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.90 (td, *J* = 8.0, 2.0 Hz, 1H), 7.46 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.02 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.89 (td, *J* = 9.2, 2.4 Hz, 1H), 6.42 (s, 1H), 5.61 – 5.54 (m, 1H), 5.28 – 5.21 (m, 1H), 3.56 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.67 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.0 (d, *J* = 236.0 Hz), 151.2, 149.8, 139.8 (d, *J* = 3.0 Hz), 138.7, 137.6 (d, *J* = 12.0 Hz), 129.8, 128.6, 124.9, 122.6, 121.1, 120.8 (d, *J* = 10.0 Hz), 109.2 (d, *J* = 24.0 Hz), 103.1, 97.2 (d, *J* = 27.0 Hz), 61.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O$ 297.1403; Found 297. 1408.



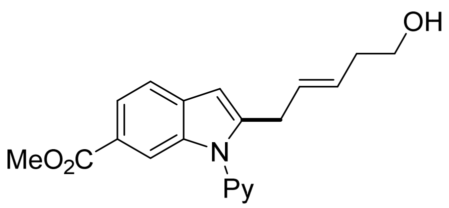
5oa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5oa** as pale yellow oil (52.4 mg, 84%, *E/Z* > 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.65 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.91 (td, *J* = 7.6, 2.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.10 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.42 (s, 1H), 5.60 – 5.53 (m, 1H), 5.29 – 5.21 (m, 1H), 3.56 (d, *J* = 4.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.68 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.0, 149.9, 140.2, 138.7, 137.9, 129.6, 128.8, 127.9, 127.1, 122.7, 121.4, 121.3, 121.0, 110.4, 103.2, 61.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O$ 313.1108; Found 313.1097.



5pa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5pa** as pale yellow oil (66.2 mg, 93%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.65 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.91 (td, *J* = 7.8, 2.0 Hz, 1H), 7.44 – 7.34 (m, 4H), 7.24 – 7.21 (m, 1H), 6.42 (s, 1H), 5.60 – 5.53 (m, 1H), 5.28 – 5.21 (m, 1H), 3.55 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.74 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.0, 149.9, 140.2, 138.8, 138.3, 129.5, 128.8, 127.4, 124.0, 122.7, 121.4, 121.3, 115.5, 113.3, 103.2, 61.9, 35.9, 31.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}BrN_2ONa$ 379.0422; Found 379.0418.

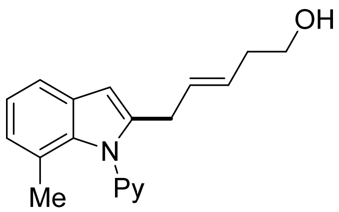


5qa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5qa** as pale yellow oil (50.5 mg, 82%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.88 (td, *J* = 8.0, 2.0 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.34 – 7.31 (m, 1H), 6.84 – 6.79 (m, 2H), 6.37 (s, 1H), 5.60 – 5.53 (m, 1H), 5.25 – 5.18 (m, 1H), 3.77 (s, 3H), 3.54 (d, *J* = 8.0 Hz, 2H), 3.48 (t, *J* = 8.0 Hz, 2H), 2.17 – 2.12 (m, 2H), 1.75 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.5, 151.6, 149.7, 138.5, 138.3, 138.2, 130.2, 128.3, 122.8, 122.3, 121.2, 120.7, 110.0, 103.1, 94.8, 61.9, 55.9, 35.9, 31.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2O_2Na$ 331.1422; Found 331.1424.

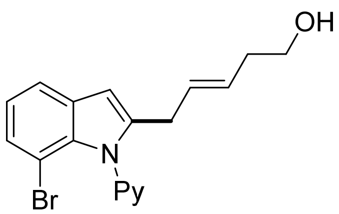


5ra: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5ra** as pale yellow oil (65.2 mg, 97%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (dd, *J* = 5.2, 2.0 Hz, 1H), 8.00 (s, 1H), 7.93 (td, *J* = 7.6, 2.0 Hz, 1H), 7.83 (d, *J* = 12.0 Hz, 1H), 7.58 (d,

J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 6.50 (s, 1H), 5.62 – 5.54 (m, 1H), 5.31 – 5.24 (m, 1H), 3.88 (s, 3H), 3.60 (d, J = 4.0 Hz, 2H), 3.51 (t, J = 8.0 Hz, 2H), 2.20 – 2.15 (m, 2H), 1.73 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.2, 150.8, 149.9, 143.2, 138.8, 137.0, 132.4, 129.2, 129.1, 123.6, 122.9, 122.0, 121.6, 119.7, 112.4, 103.4, 61.9, 52.0, 35.9, 31.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1552; Found 337.1554.

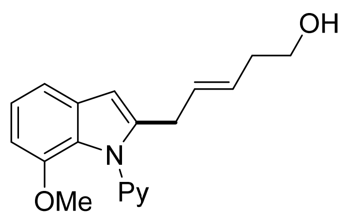


5sa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5sa** as pale yellow oil (50.8 mg, 87%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (dd, J = 5.2, 1.6 Hz, 1H), 7.84 (td, J = 7.6, 2.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.42 (s, 1H), 5.59 – 5.52 (m, 1H), 5.21 – 5.13 (m, 1H), 3.55 (s, 2H), 3.28 (s, 2H), 2.20 – 2.15 (m, 3H), 1.82 (s, 3H), 1.72 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.1, 149.0, 139.9, 137.9, 137.0, 130.0, 129.1, 128.7, 124.7, 124.5, 123.6, 121.2, 120.6, 118.2, 102.5, 61.8, 35.9, 30.8, 19.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2ONa$ 315.1473; Found 315.1462.

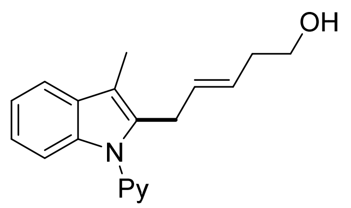


5ta: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5ta** as pale yellow oil (57.7 mg, 81%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (dd, J = 5.0, 1.8 Hz, 1H), 7.84 (td, J = 7.6, 2.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.28 – 7.26 (m, 1H), 6.97 (t, J = 8.0 Hz, 1H), 6.43 (s, 1H), 5.59 – 5.51 (m, 1H), 5.26 – 5.18 (m, 1H), 3.56 (d, J = 8.0 Hz, 2H), 3.27 (s, 2H), 2.21 – 2.16 (m, 2H), 2.05 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.2, 148.9, 141.6, 137.8, 134.8, 131.3, 129.1, 126.7, 125.8, 124.0, 121.5, 119.5, 103.9, 102.4, 61.8, 35.9, 30.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for

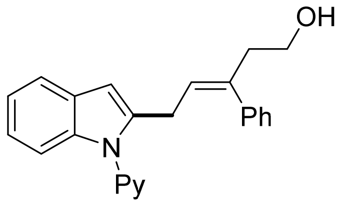
$C_{18}H_{18}BrN_2O$ 357.0603; Found 357.0606.



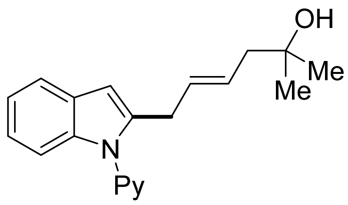
5ua: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5ua** as pale yellow oil (56.7 mg, 92%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.78 (td, *J* = 7.6, 2.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.28 – 7.26 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.40 (s, 1H), 5.59 – 5.52 (m, 1H), 5.22 – 5.14 (m, 1H), 3.56 (s, 3H), 3.53 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J* = 8.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.95 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.9, 148.0, 146.8, 140.1, 137.0, 130.6, 130.0, 128.4, 127.1, 123.9, 122.6, 120.8, 113.2, 103.8, 102.8, 61.8, 55.6, 35.9, 30.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2$ 309.1603; Found 309.1606.



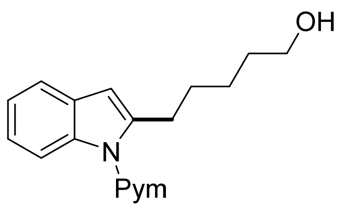
5va: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **5va** as pale yellow oil (52.6 mg, 90%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.86 (td, *J* = 7.6, 2.0 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.18 – 7.12 (m, 2H), 5.53 – 5.46 (m, 1H), 5.10 – 5.02 (m, 1H), 3.59 (d, *J* = 8.0 Hz, 2H), 3.43 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.12 – 2.07 (m, 2H), 1.71 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.9, 149.6, 138.4, 136.8, 134.3, 130.5, 129.4, 127.5, 122.1, 122.0, 121.3, 120.3, 118.5, 110.7, 110.1, 61.7, 35.9, 28.2, 8.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2ONa$ 315.1473; Found 315.1469.



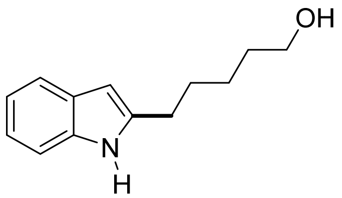
5ab: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5ab** as pale yellow oil (31.2 mg, 44%, *Z/E* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 4.0 Hz, 1H), 7.55 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.25 – 7.20 (m, 2H), 7.13 – 7.10 (m, 1H), 6.18 (t, *J* = 8.0 Hz, 1H), 3.75 (d, *J* = 8.0 Hz, 2H), 3.70 (t, *J* = 8.0 Hz, 2H), 2.98 (t, *J* = 8.0 Hz, 2H), 1.63 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.6, 149.1, 142.3, 138.4, 137.2, 135.7, 130.2, 129.2, 128.5, 127.2, 126.6, 123.5, 123.2, 121.1, 119.8, 119.3, 118.2, 114.5, 113.2, 61.5, 33.4, 24.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O$ 355.1810; Found 355.1809.



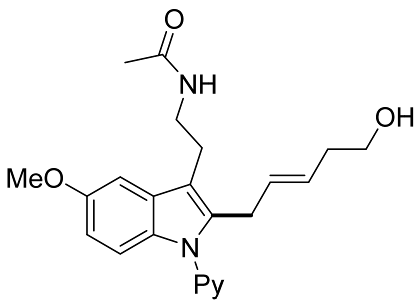
5ac: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **5ac** as pale yellow oil (58.2 mg, 95%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.88 (td, *J* = 7.6, 2.0 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 6.46 (s, 1H), 5.64 – 5.57 (m, 1H), 5.45 – 5.36 (m, 1H), 3.64 (d, *J* = 4.0 Hz, 2H), 2.10 (d, *J* = 8.0 Hz, 2H), 1.58 (OH, 1H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.5, 149.7, 139.6, 138.4, 137.4, 131.1, 128.6, 127.7, 122.2, 122.0, 121.1, 120.8, 120.2, 110.2, 103.3, 70.5, 46.8, 31.2, 29.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{22}N_2ONa$ 329.1630; Found 329.1634.



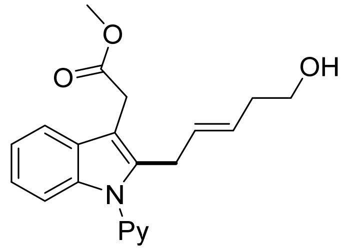
6: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **6** as colorless oil (43.9 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, *J* = 4.0 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.13 (m, 3H), 6.47 (s, 1H), 3.60 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.59 – 1.53 (m, 2H), 1.47 – 1.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 158.3, 142.1, 137.1, 129.4, 122.5, 121.9, 119.8, 117.2, 113.7, 105.7, 63.0, 32.6, 29.3, 28.9, 25.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}N_3O$ 282.1606; Found 282.1614.



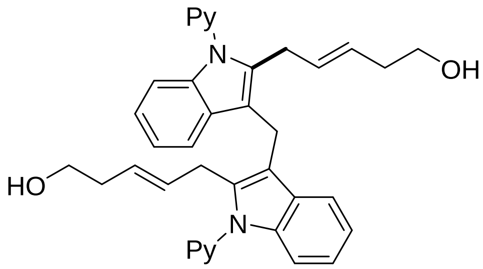
7: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **7** as colorless solid (33.7 mg, 83%); m.p. = 66-67 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.24 (s, 1H), 3.66 (t, *J* = 4.0 Hz, 2H), 2.77 (t, *J* = 4.0 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.66 – 1.59 (m, 2H), 1.51 – 1.42 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.8, 136.0, 128.9, 121.0, 119.8, 119.7, 110.5, 99.5, 62.9, 32.5, 29.0, 28.2, 25.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{17}NONa$ 226.1208; Found 226.1210.



8: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **8** as pale yellow oil (70.8 mg, 90%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (d, *J* = 4.0 Hz, 1H), 7.87 (td, *J* = 7.6, 2.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 7.4, 5.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.85 (brs, 1H), 5.49 – 5.42 (m, 1H), 5.15 – 5.10 (m, 1H), 3.86 (s, 3H), 3.58 (d, *J* = 4.0 Hz, 2H), 3.55 – 3.50 (m, 2H), 3.45 – 3.41 (m, 2H), 2.96 (t, *J* = 8.0 Hz, 2H), 2.20 (OH, 1H), 2.09 – 2.05 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.6, 154.9, 151.6, 149.6, 138.6, 136.1, 132.0, 130.0, 129.2, 128.2, 122.2, 121.3, 111.8, 111.8, 111.2, 100.6, 61.7, 56.1, 40.1, 35.9, 28.3, 24.5, 23.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{27}N_3O_3Na$ 416.1950; Found 416.1960.

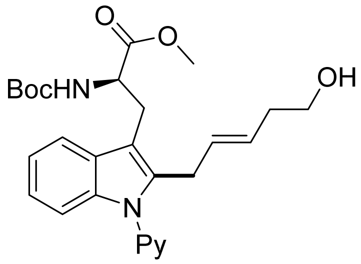


9: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **9** as pale yellow oil (51.1 mg, 73%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.88 (td, *J* = 7.6, 2.0 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.20 – 7.14 (m, 2H), 5.53 – 5.46 (m, 1H), 5.13 – 5.05 (m, 1H), 3.79 (s, 2H), 3.68 (s, 3H), 3.63 (d, *J* = 4.0 Hz, 2H), 3.46 – 3.43 (m, 2H), 2.12 – 2.07 (m, 2H), 1.98 (OH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.4, 151.4, 149.7, 138.5, 136.8, 136.2, 129.8, 128.4, 128.1, 122.4, 121.6, 120.8, 118.6, 110.3, 107.7, 61.7, 52.1, 35.9, 30.5, 28.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{22}N_2O_3Na$ 373.1528; Found 373.1513.

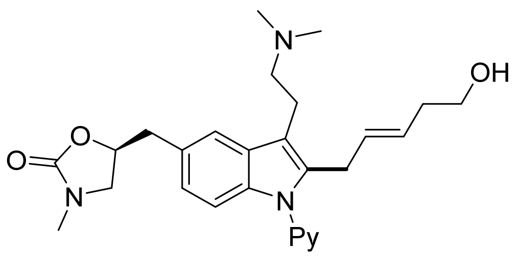


10: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **10** as pale yellow oil (62.5 mg, 55%, *E/Z* > 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (d, *J* = 4.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.13 – 7.05 (m, 4H), 5.30 – 5.23 (m, 2H), 4.92 – 4.85 (m, 2H), 4.29 (s, 2H), 3.62 (d, *J* = 8.0 Hz, 4H), 3.30 (t, *J* = 8.0 Hz, 4H), 2.23 (OH, 2H), 1.96 – 1.92 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.8, 149.6, 138.5, 136.9, 135.0, 129.5, 129.1, 127.9, 122.2, 122.0, 121.7, 120.5, 119.1, 113.6, 110.1, 61.5, 35.7, 28.3, 19.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{37}N_4O_2$

569.2917; Found 569.2929.



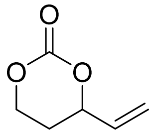
11: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **11** as pale yellow oil (53.7 mg, 56%, *E/Z* = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (d, *J* = 4.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.25 – 7.24 (m, 1H), 7.15 – 7.13 (m, 2H), 5.47 – 5.41 (m, 1H), 5.24 – 5.22 (m, 1H), 5.11 – 5.04 (m, 1H), 4.66 – 4.61 (m, 1H), 3.73 – 3.61 (m, 5H), 3.42 (s, 2H), 3.33 – 3.28 (m, 2H), 2.08 – 2.04 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, 173.0, 155.3, 151.5, 149.6, 138.5, 136.9, 136.3, 129.9, 128.7, 128.4, 122.4, 121.6, 120.7, 118.5, 110.1, 109.3, 80.0, 61.7, 54.3, 52.5, 35.9, 28.4, 28.1, 27.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{34}N_3O_5$ 480.2498; Found 480.2484.



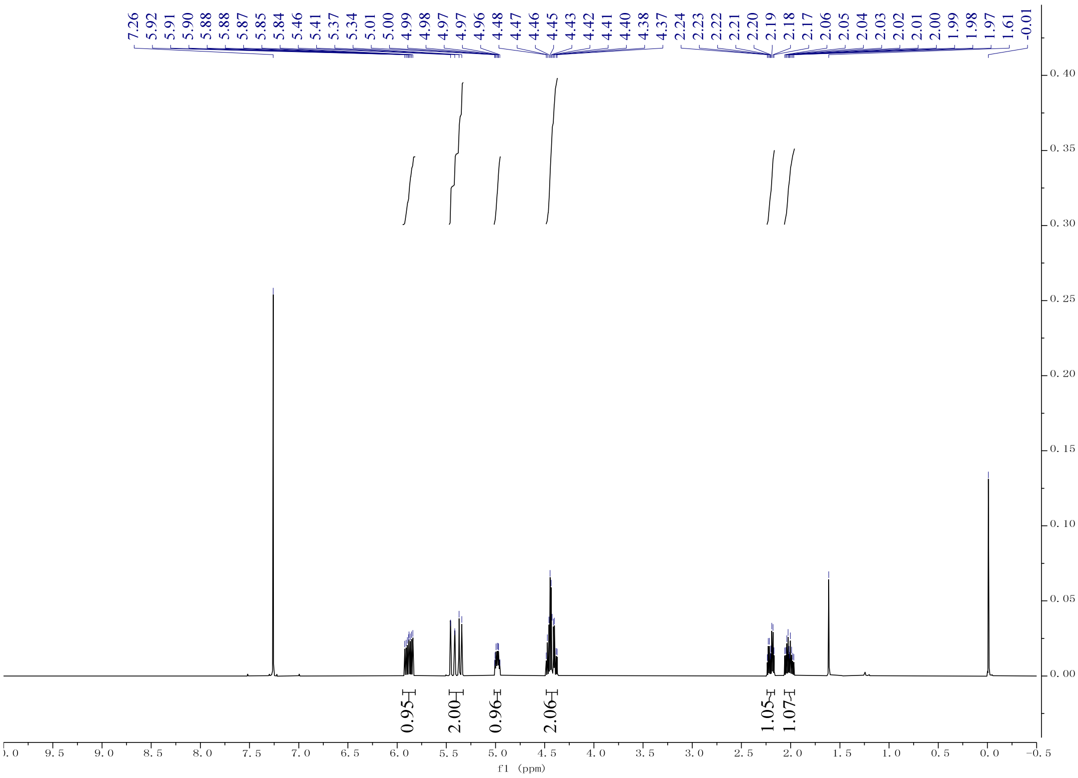
12: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:2) to afford **12** as colorless oil (61.9 mg, 67%, *E/Z* = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 – 8.61 (m, 1H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.0, 4.0 Hz, 1H), 5.53 – 5.47 (m, 1H), 5.29 – 5.21 (m, 1H), 4.17 (t, *J* = 8.0 Hz, 1H), 4.04 (t, *J* = 8.0 Hz, 1H), 3.99 – 3.95 (m, 1H), 3.57 (d, *J* = 8.0 Hz, 2H), 3.49 (t, *J* = 8.0 Hz, 2H), 3.21 – 3.17 (m, 1H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.93 (s, 3H), 2.84 – 2.78 (m, 1H), 2.77 – 2.67 (m, 2H), 2.52 (s, 1H), 2.50 (s, 5H), 2.14 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.7, 151.3, 149.7, 138.6, 136.0, 135.7, 129.6, 128.9, 128.9, 127.3, 123.4, 122.4, 121.4, 118.4, 111.6, 110.8, 66.7, 61.7, 59.4, 58.8, 44.8, 38.3, 36.0, 29.6, 28.8, 22.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{34}N_4O_3Na$ 485.2529;

Found 485.2534.

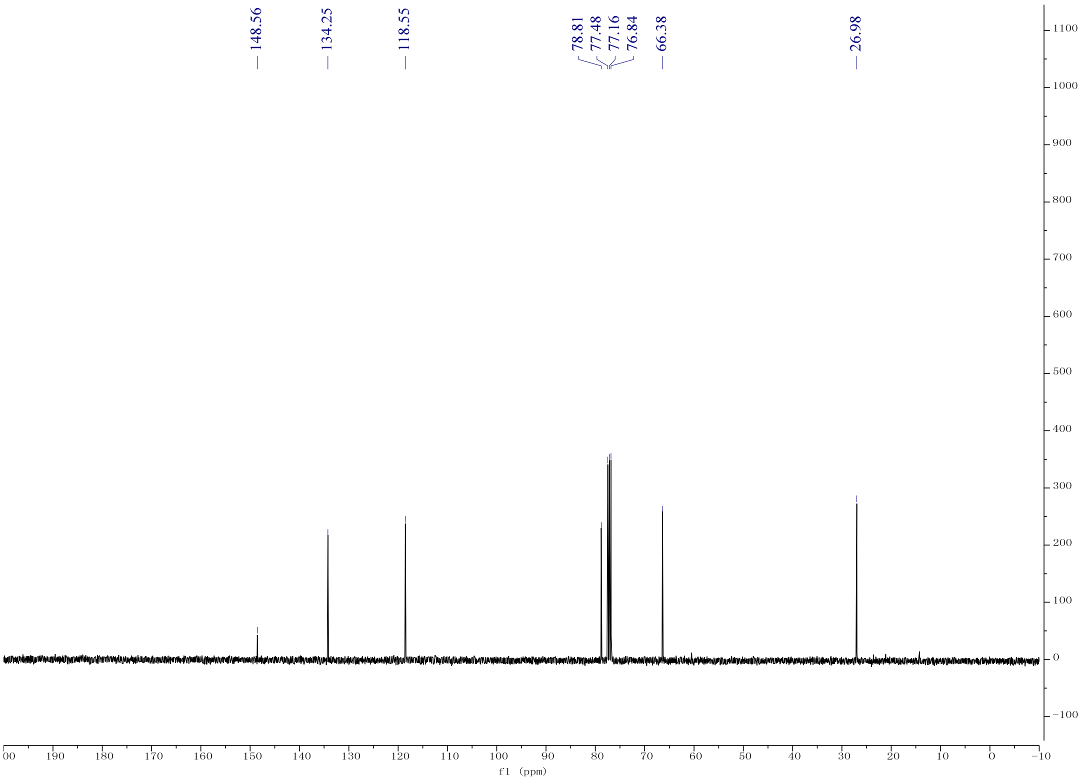
6. NMR Chart.

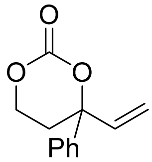


^{1}H NMR (400 MHz, $CDCl_3$) Compound **2a**



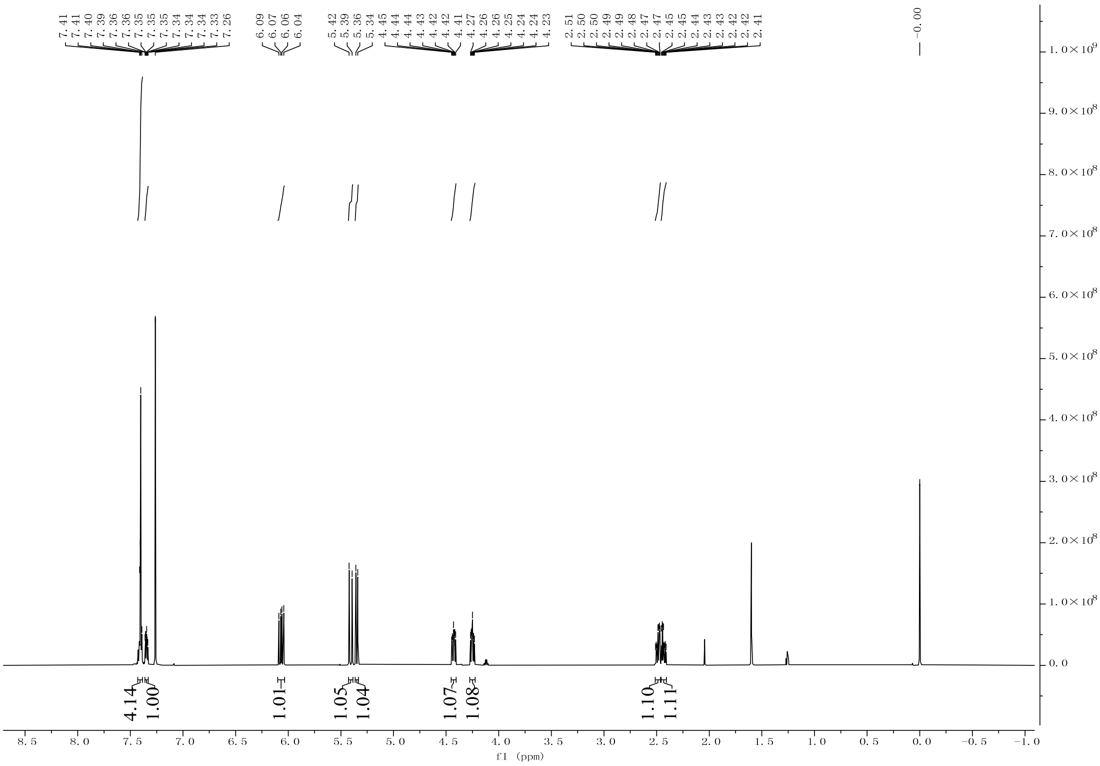
^{13}C NMR (101 MHz, $CDCl_3$) Compound **2a**



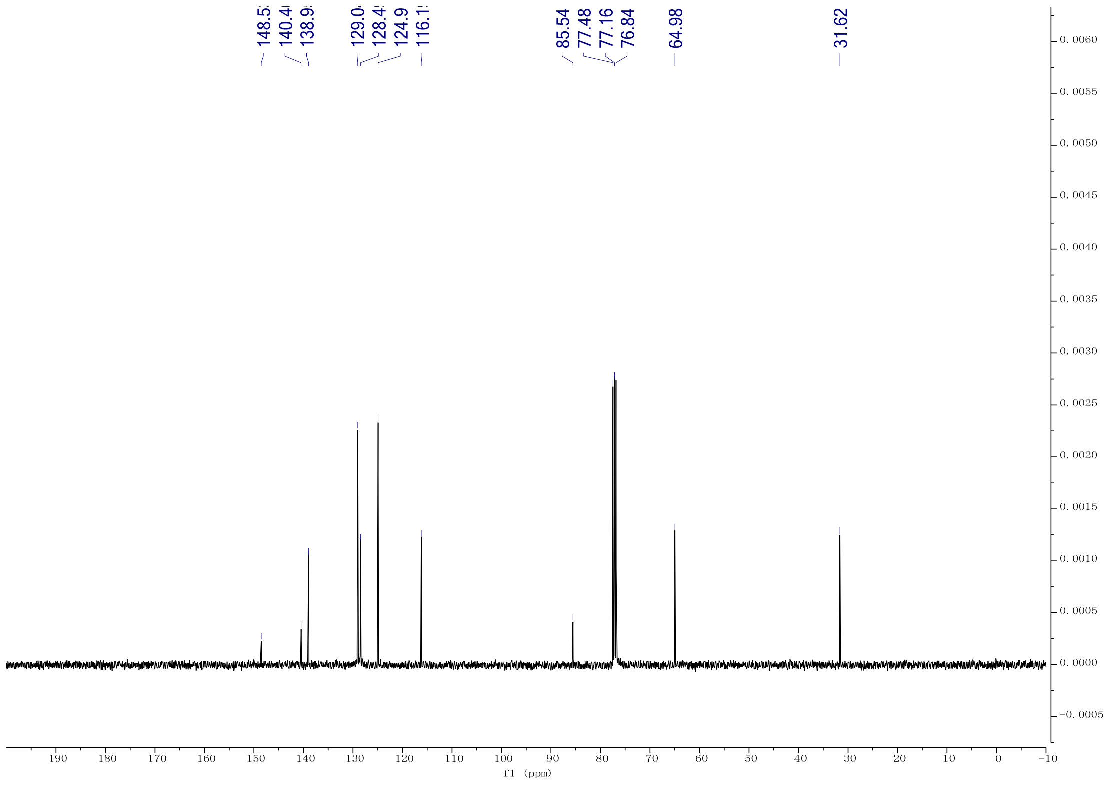


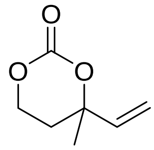
Ph

^{1}H NMR (400 MHz, $CDCl_3$) Compound **2b**

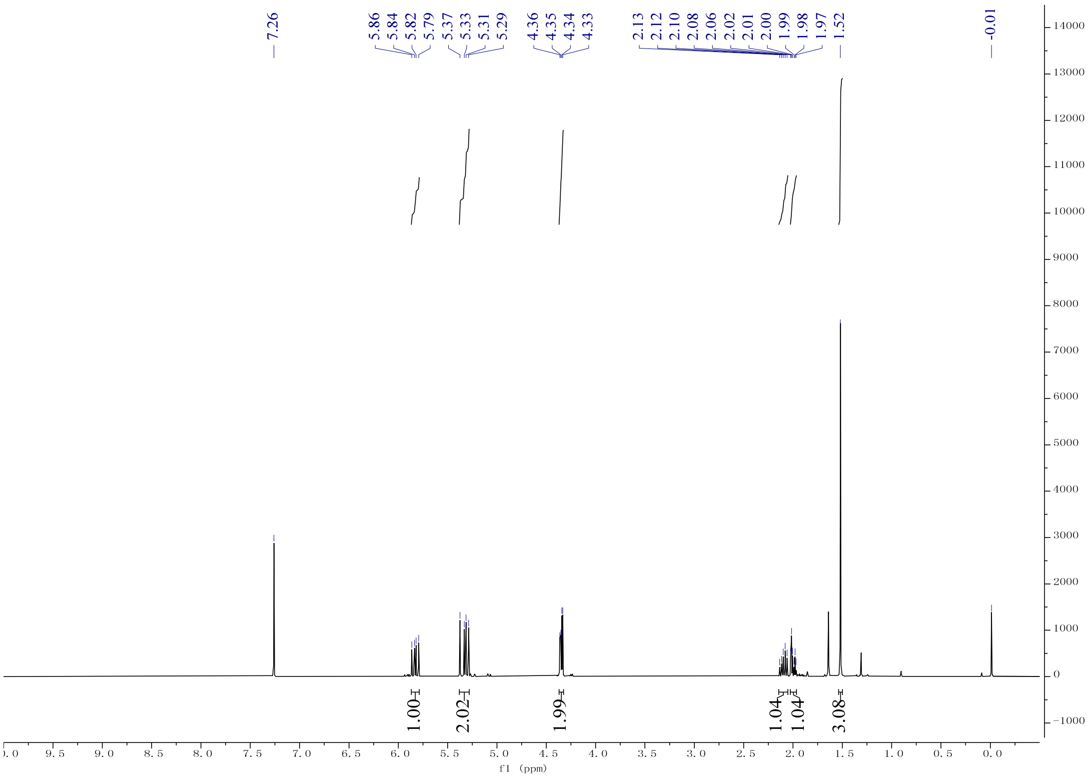


^{13}C NMR (101 MHz, $CDCl_3$) Compound **2b**

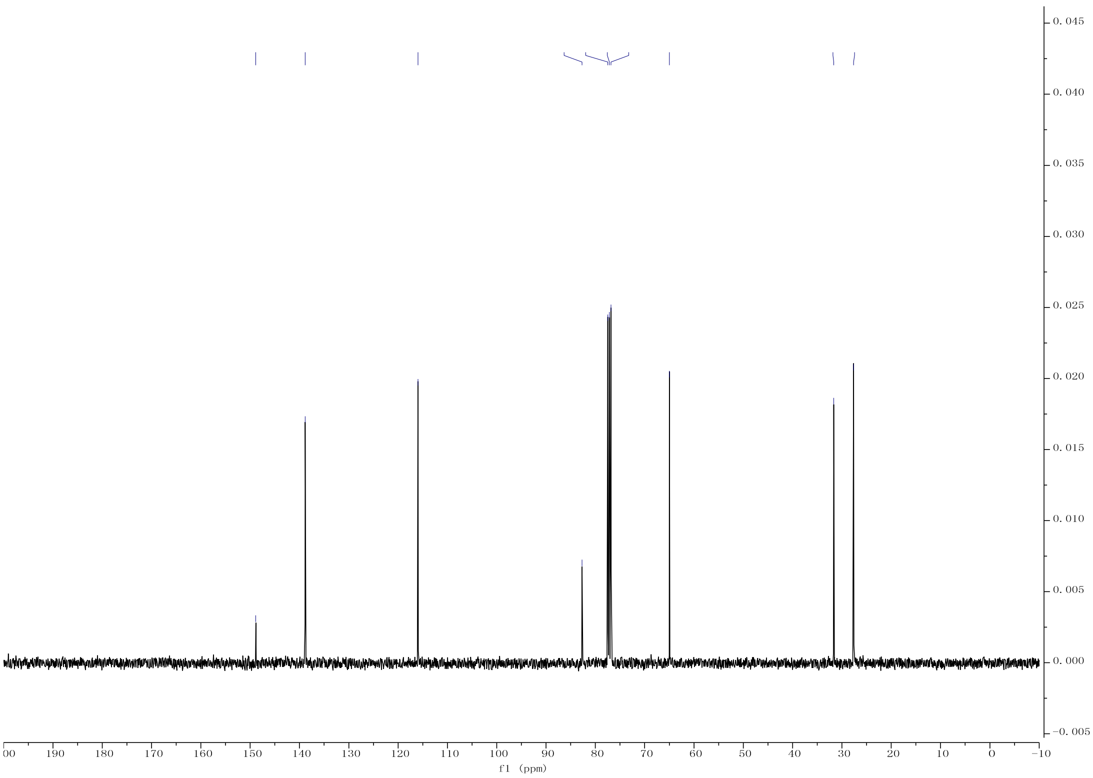


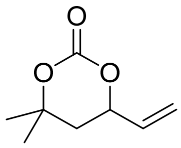


[1]H NMR (400 MHz, $CDCl_3$) Compound **2c**

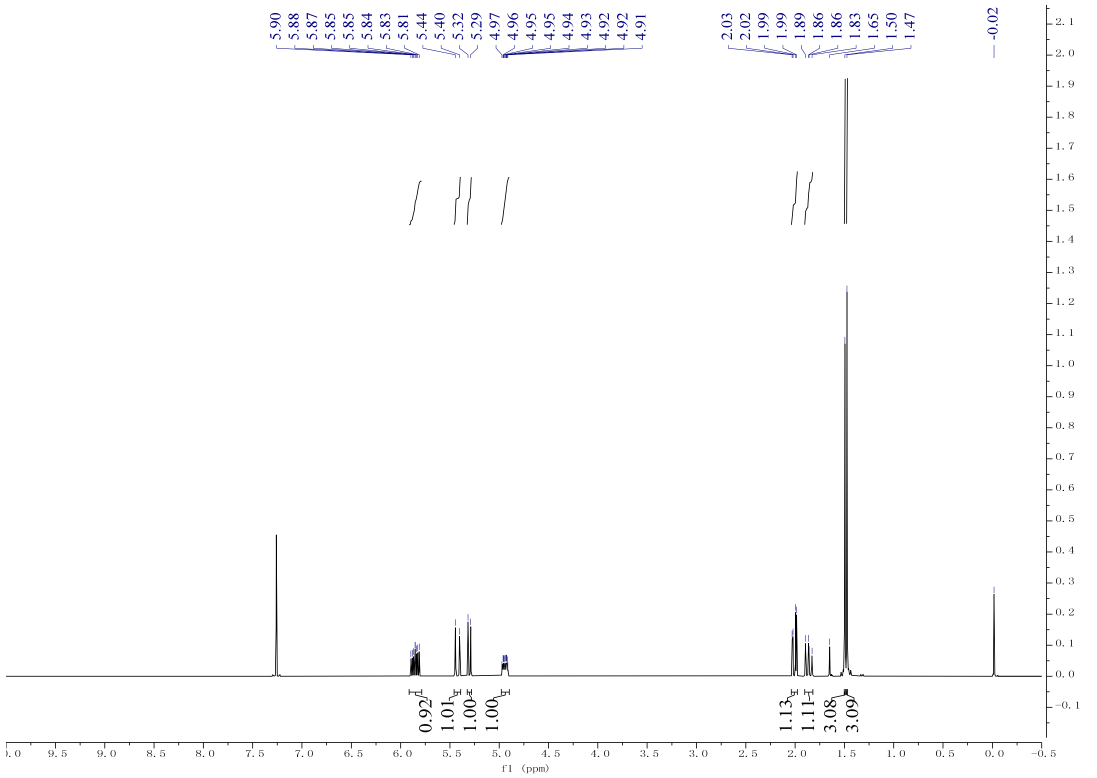


[13]C NMR (101 MHz, $CDCl_3$) Compound **2c**

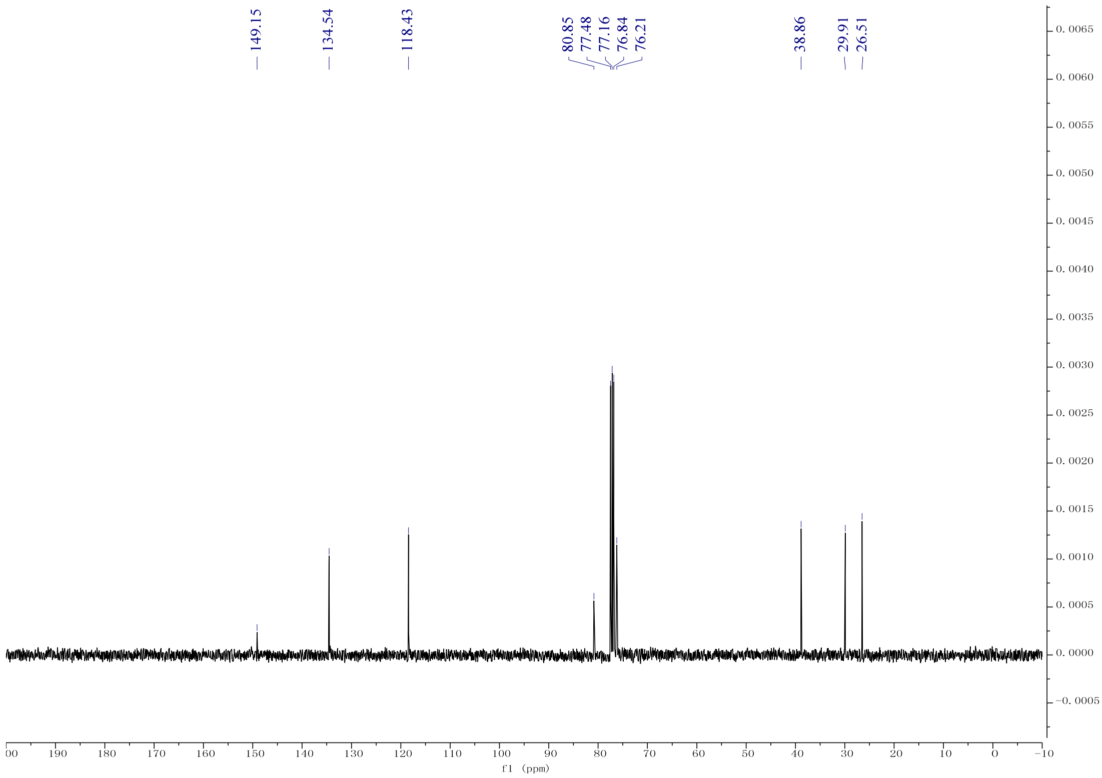


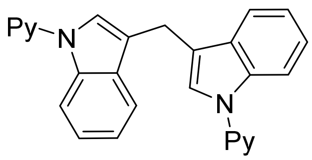


[1]H NMR (400 MHz, $CDCl_3$) Compound **2d**

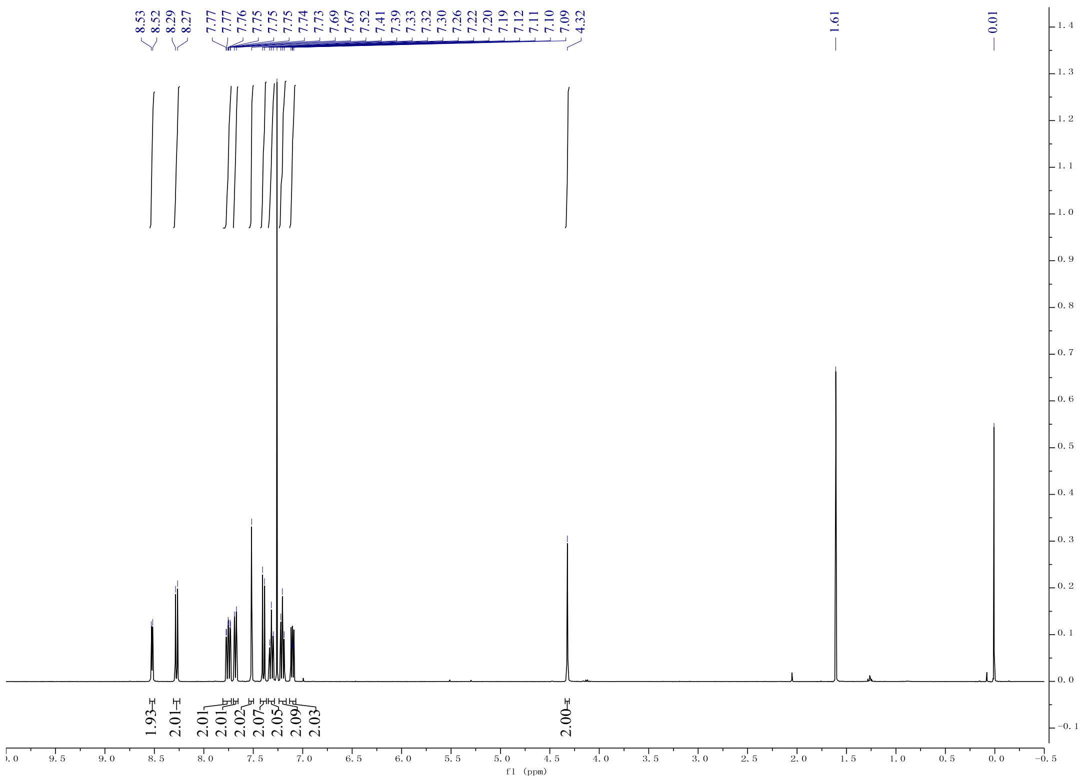


[13]C NMR (101 MHz, $CDCl_3$) Compound **2d**

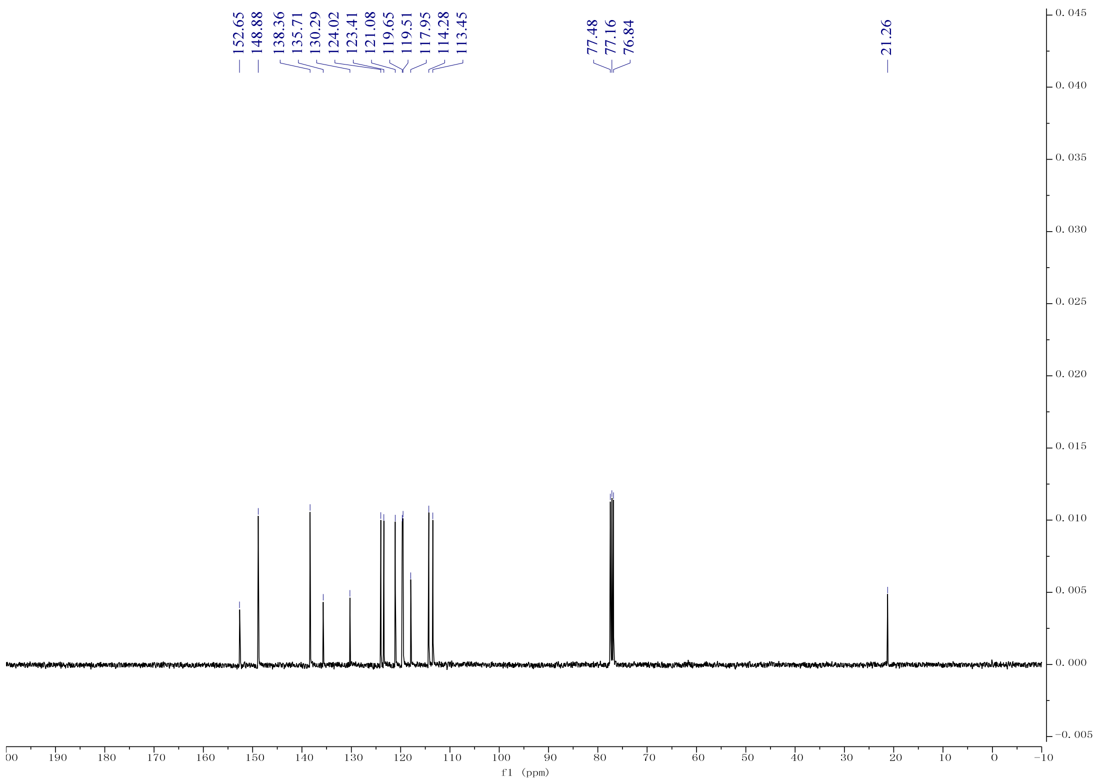


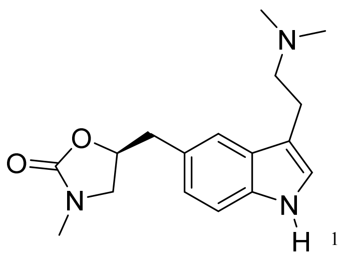


^{1}H NMR (400 MHz, $CDCl_3$) Compound ***N*-pyridyl DIM**

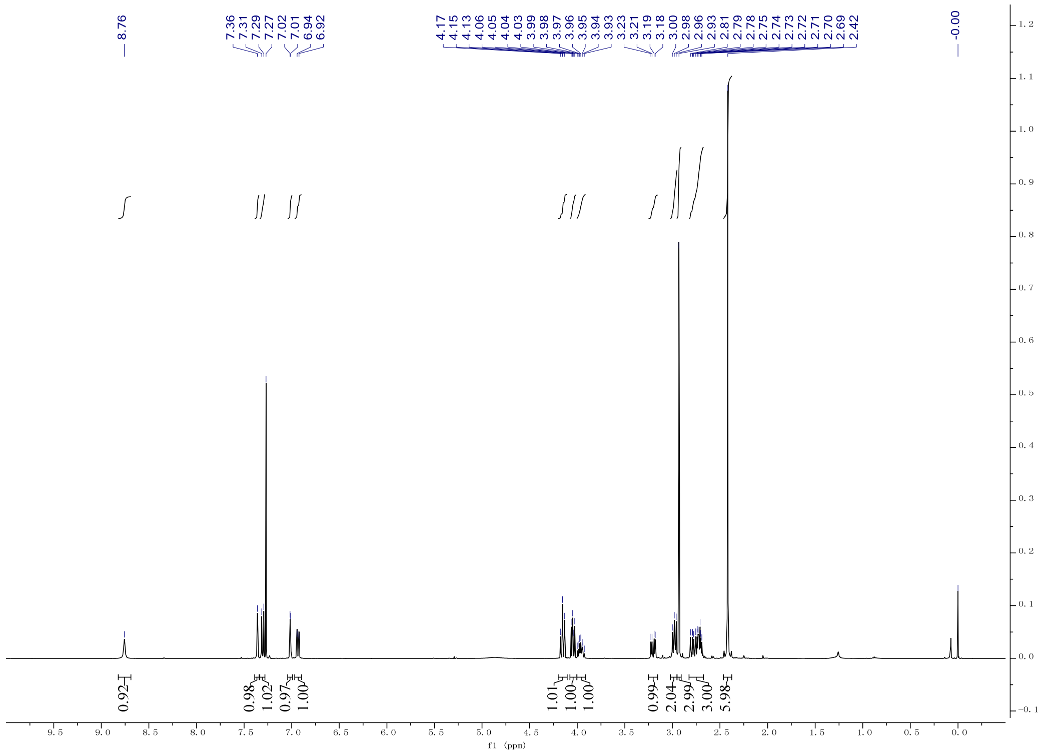


^{13}C NMR (101 MHz, $CDCl_3$) Compound ***N*-pyridyl DIM**

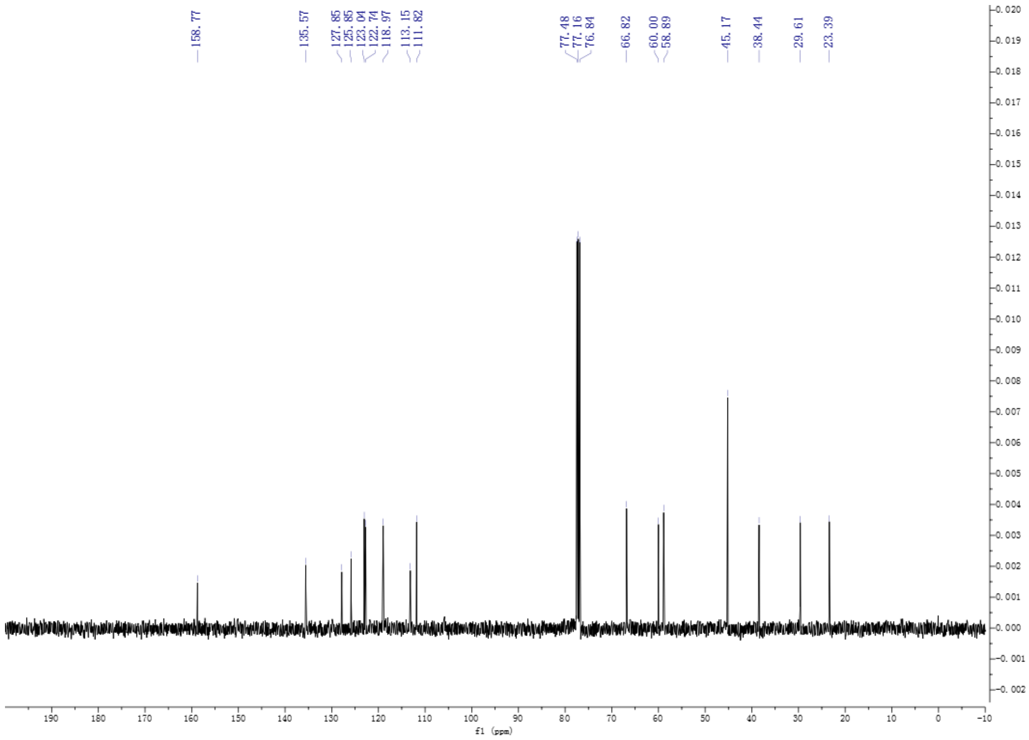


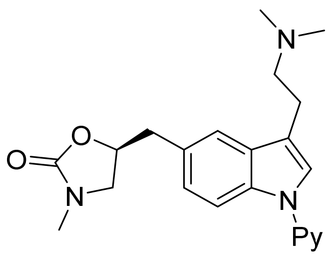


^{1}H NMR (400 MHz, $CDCl_3$) Compound **S4**

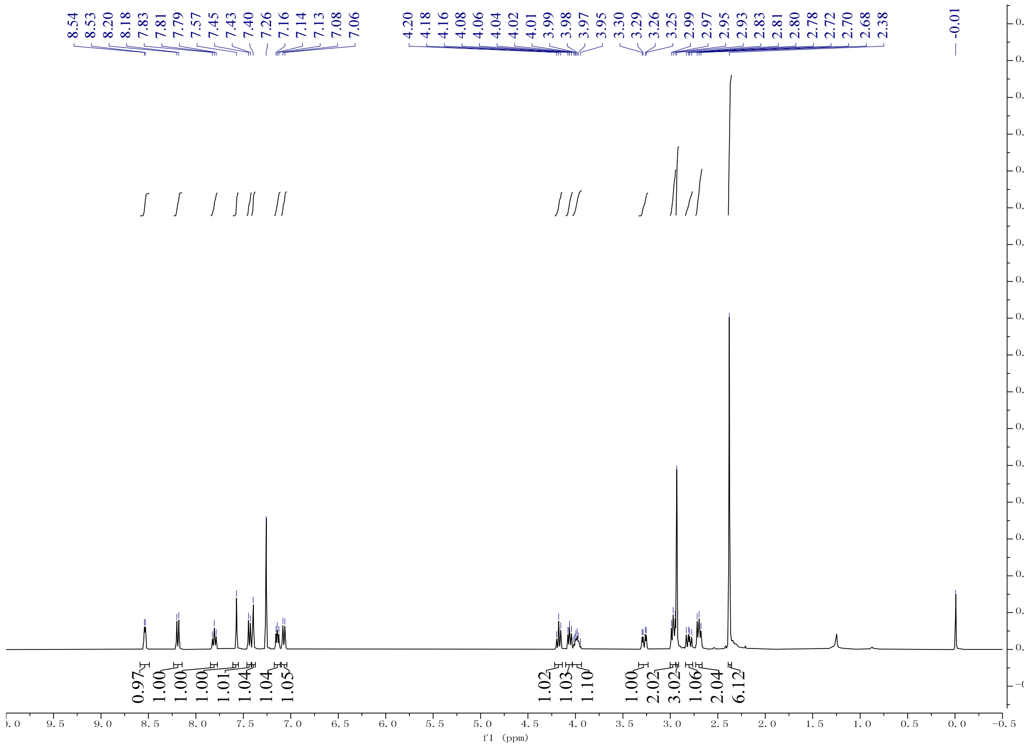


^{13}C NMR (101 MHz, $CDCl_3$) Compound **S4**

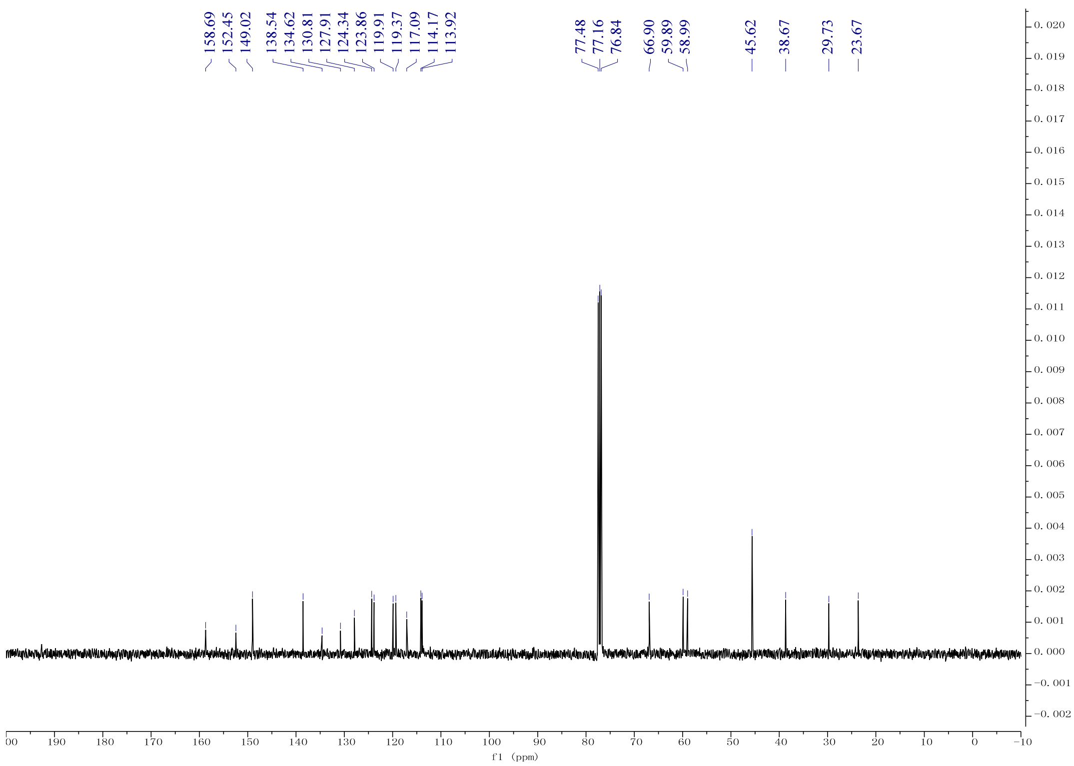


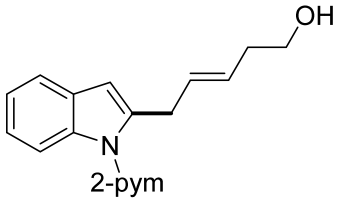


¹H NMR (400 MHz, $CDCl_3$) Compound ***N*-pyridyl zolmitriptan**

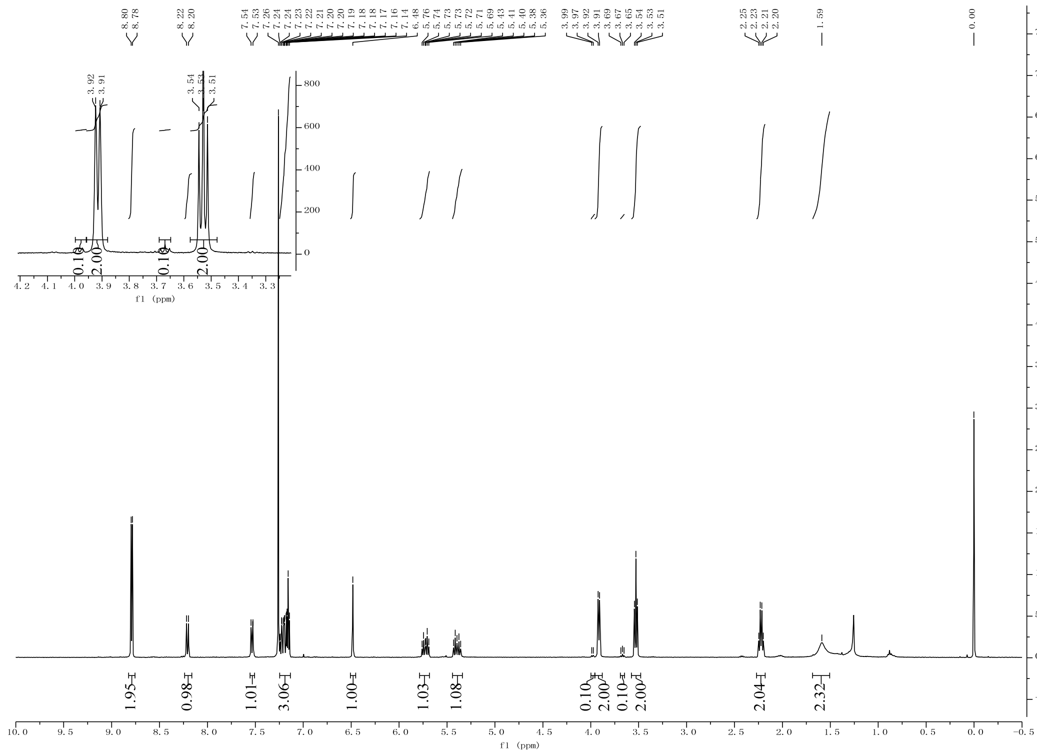


¹³C NMR (101 MHz, $CDCl_3$) Compound ***N*-pyridyl zolmitriptan**

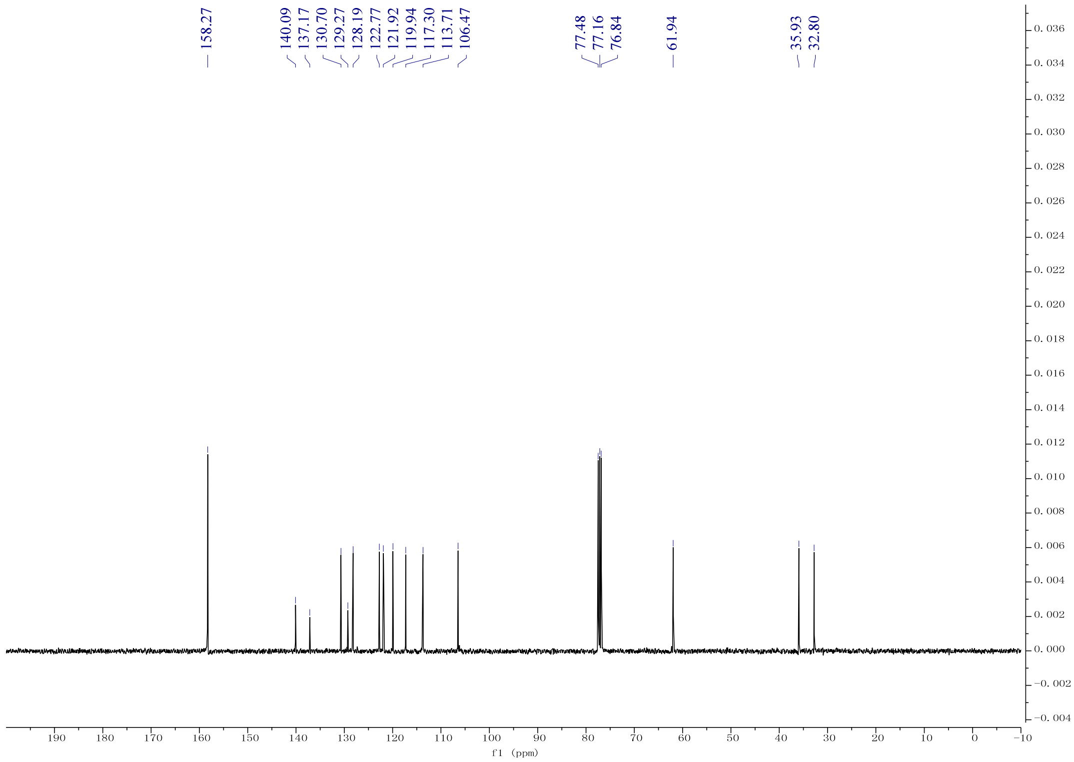


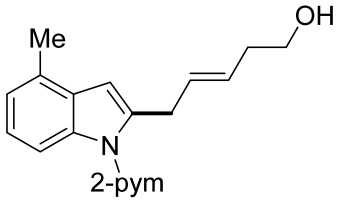


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3aa**

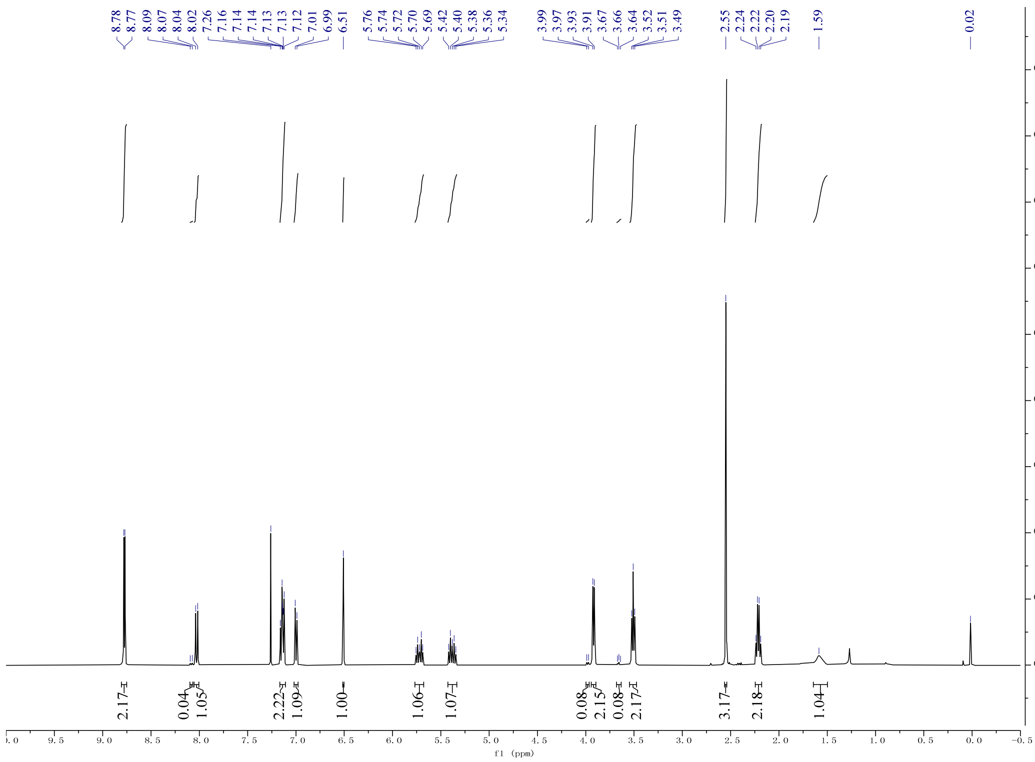


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3aa**

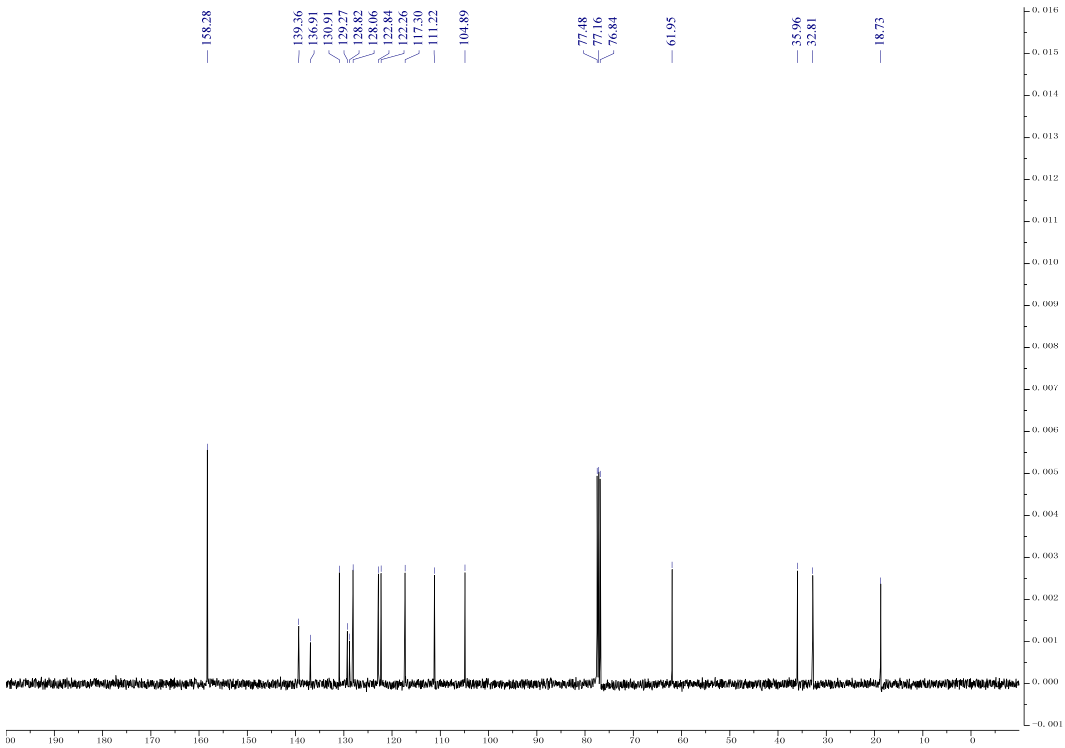


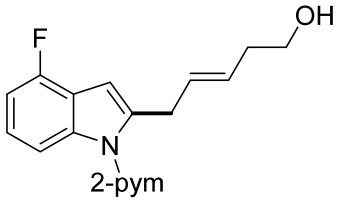


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ba**

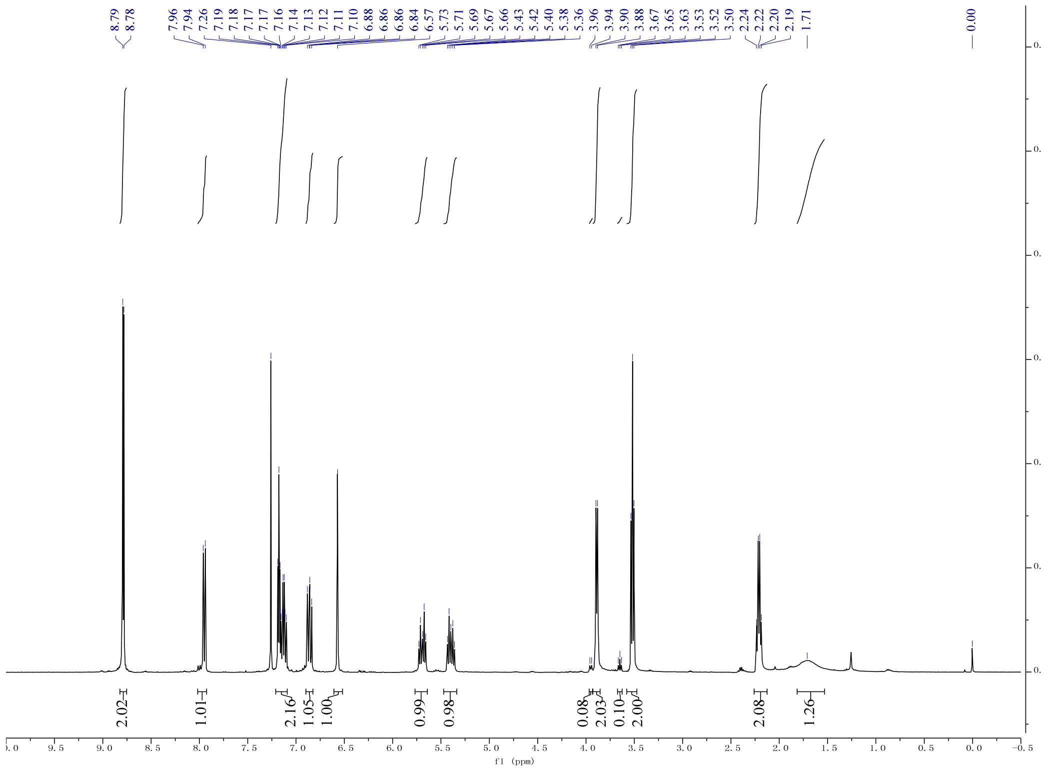


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ba**

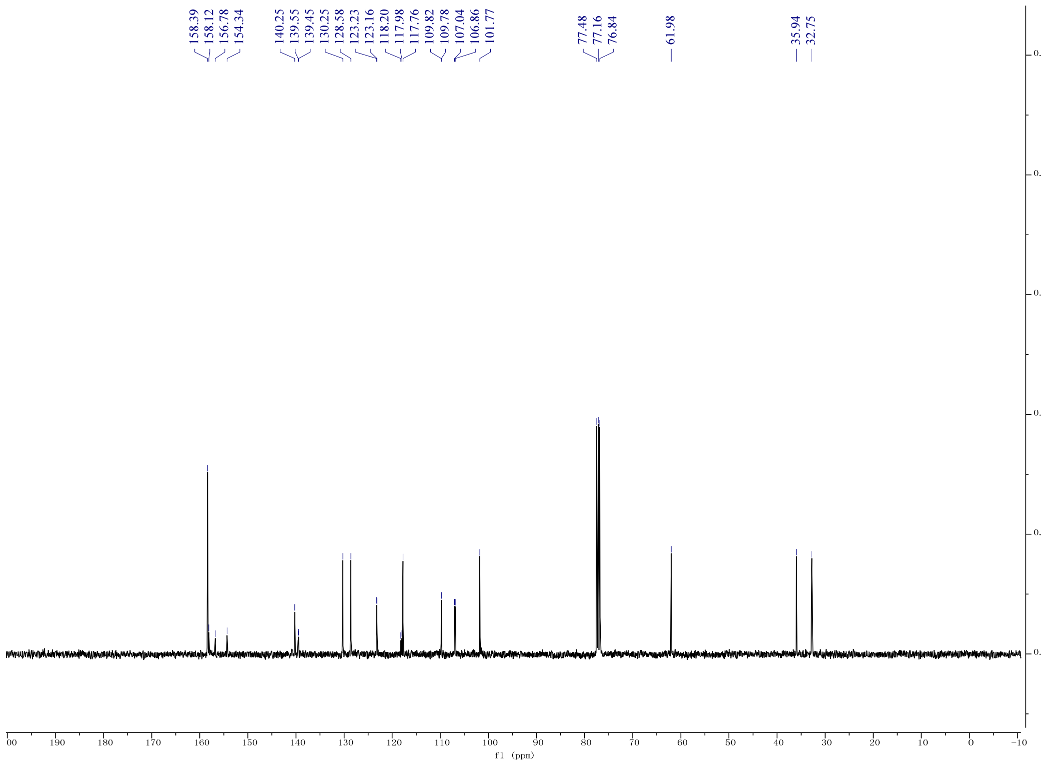


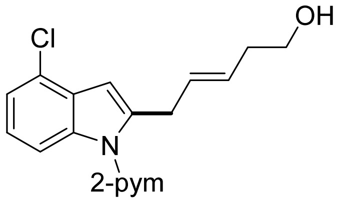


^{1}H NMR (400 MHz, CDCl$_3$) Compound **3ca**

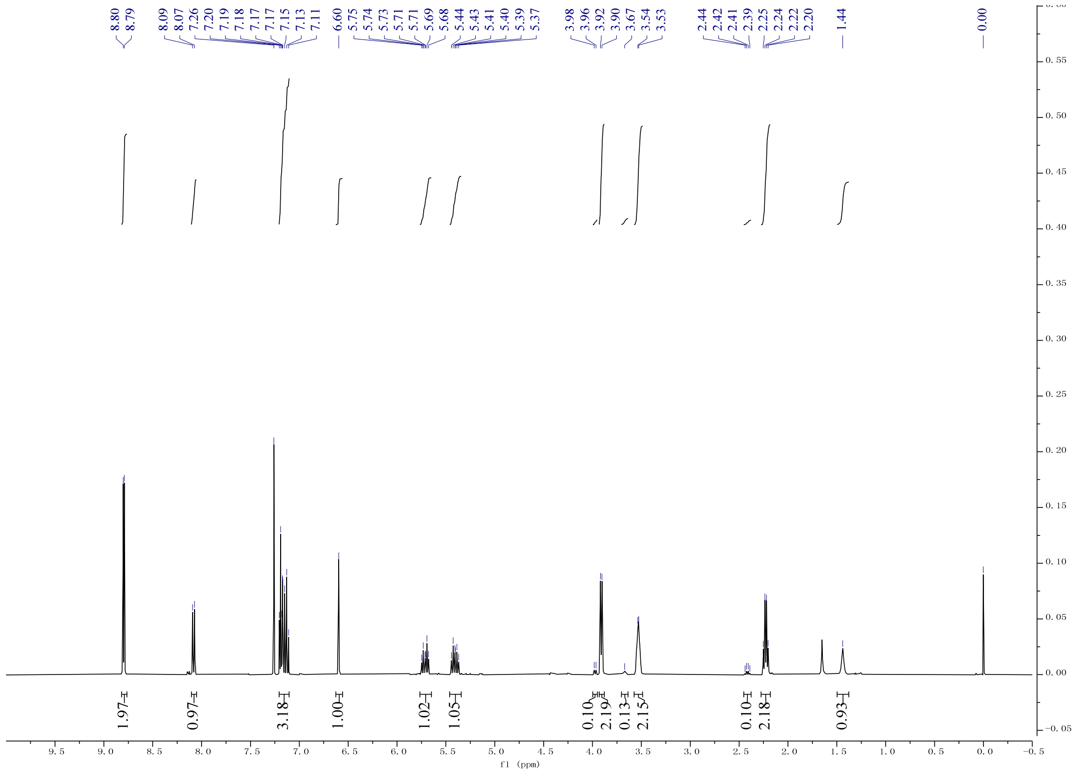


^{13}C NMR (101 MHz, CDCl$_3$) Compound **3ca**

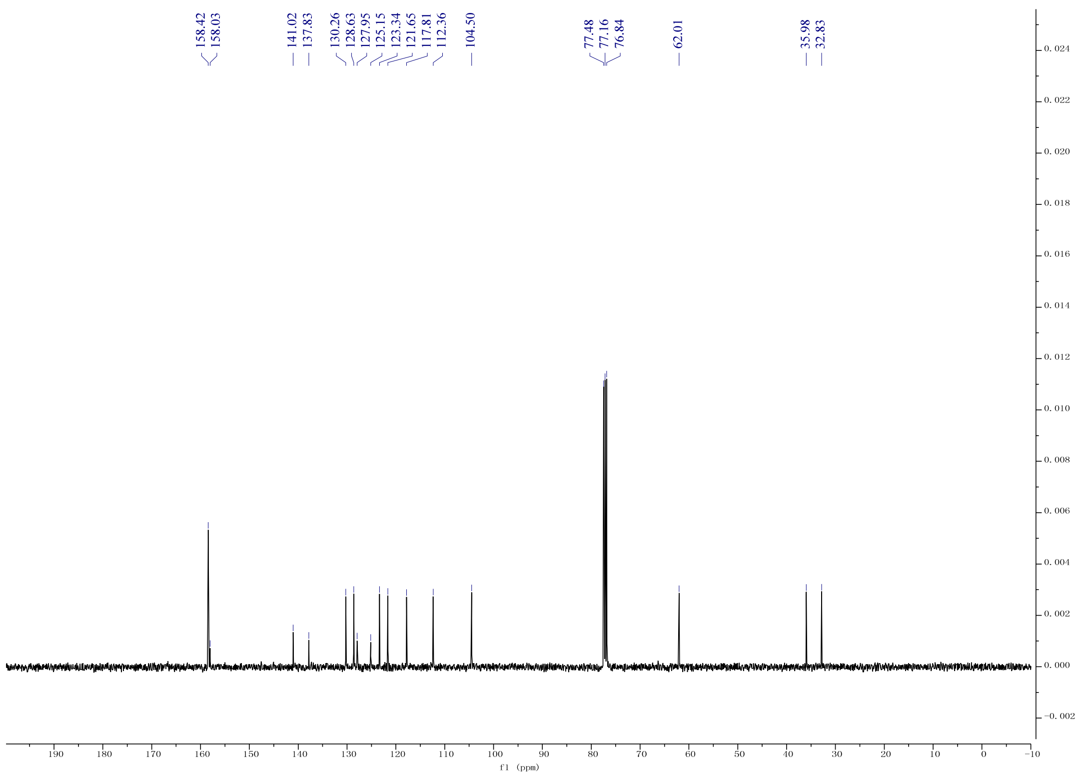


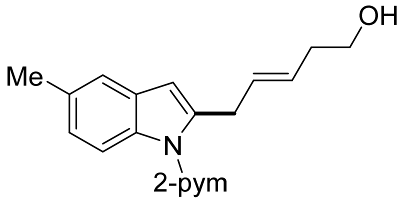


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3da**

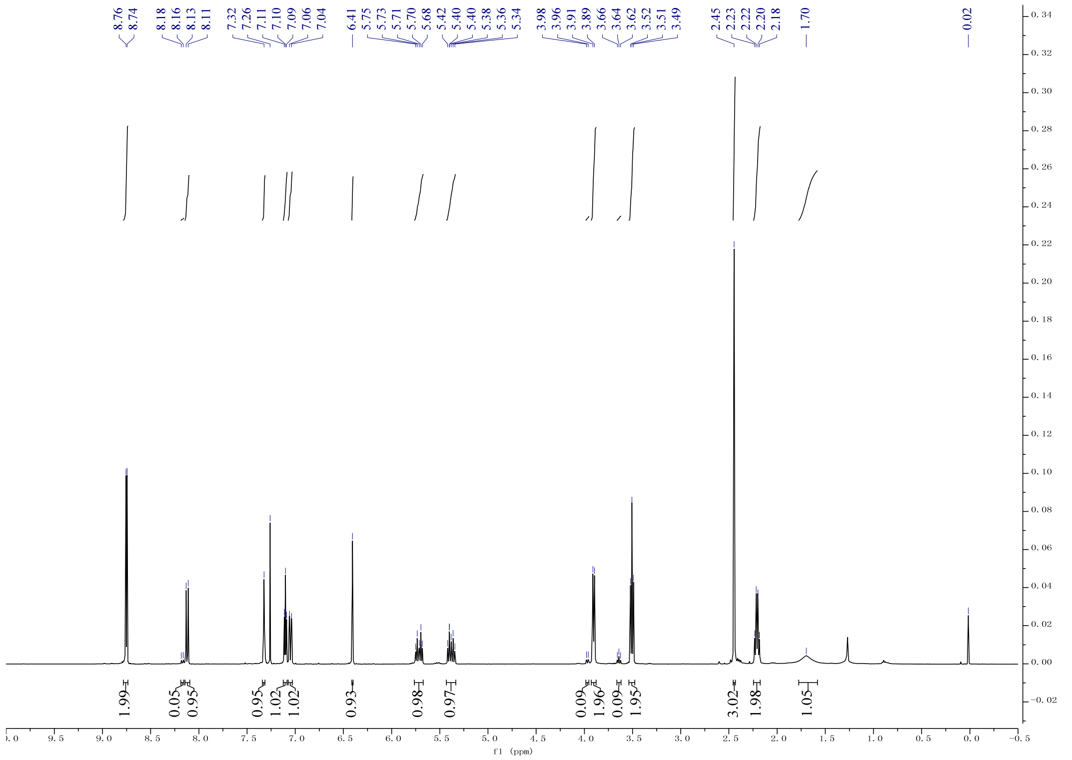


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3da**

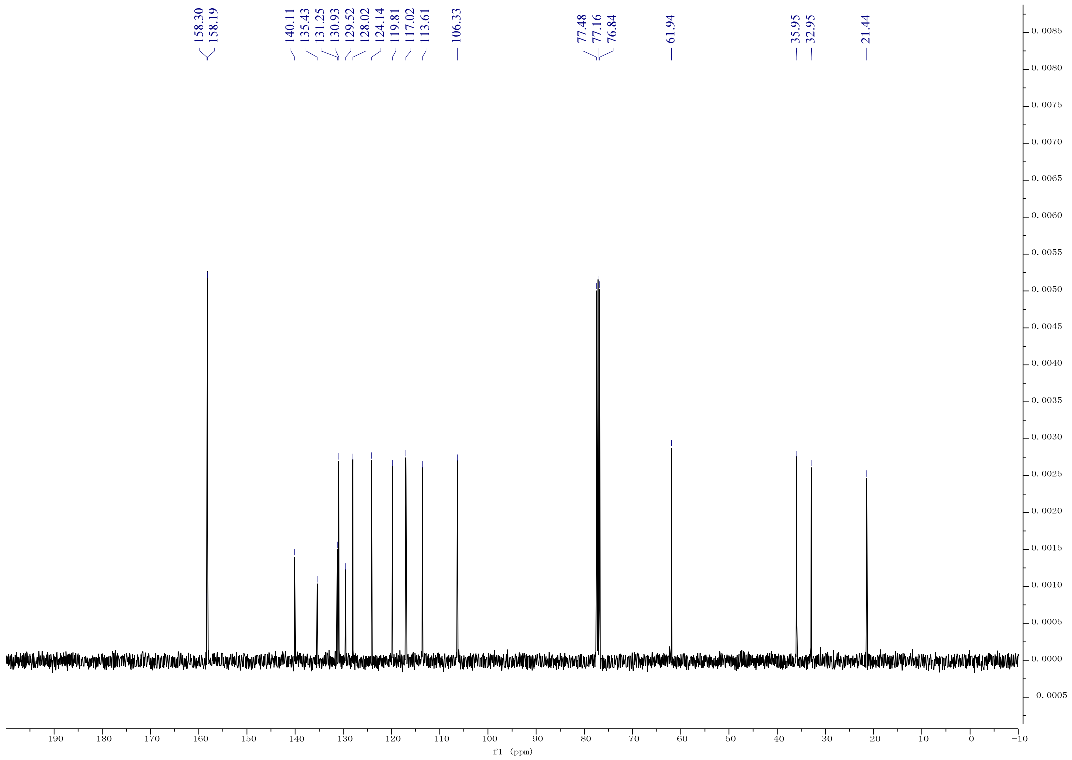


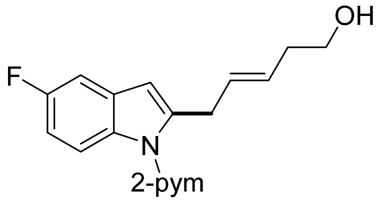


[1]H NMR (400 MHz, $CDCl_3$) Compound **3ea**

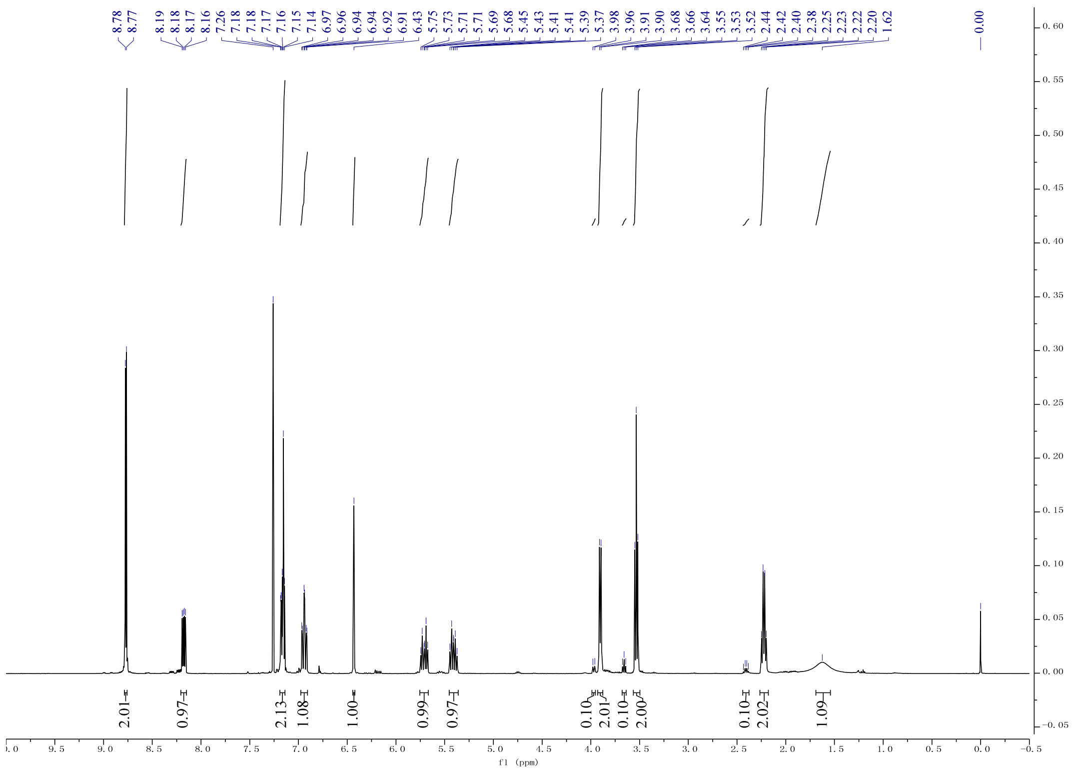


[13]C NMR (101 MHz, $CDCl_3$) Compound **3ea**

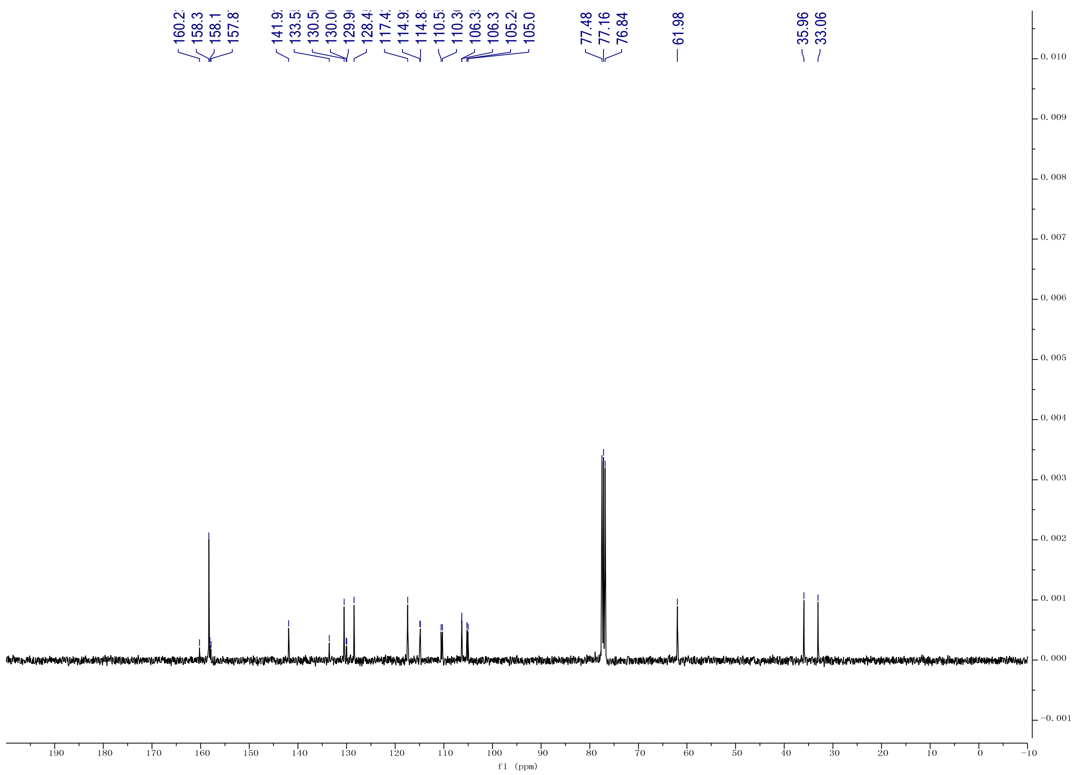


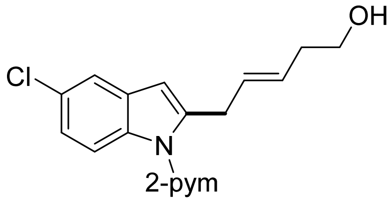


[1]H NMR (400 MHz, $CDCl_3$) Compound **3fa**

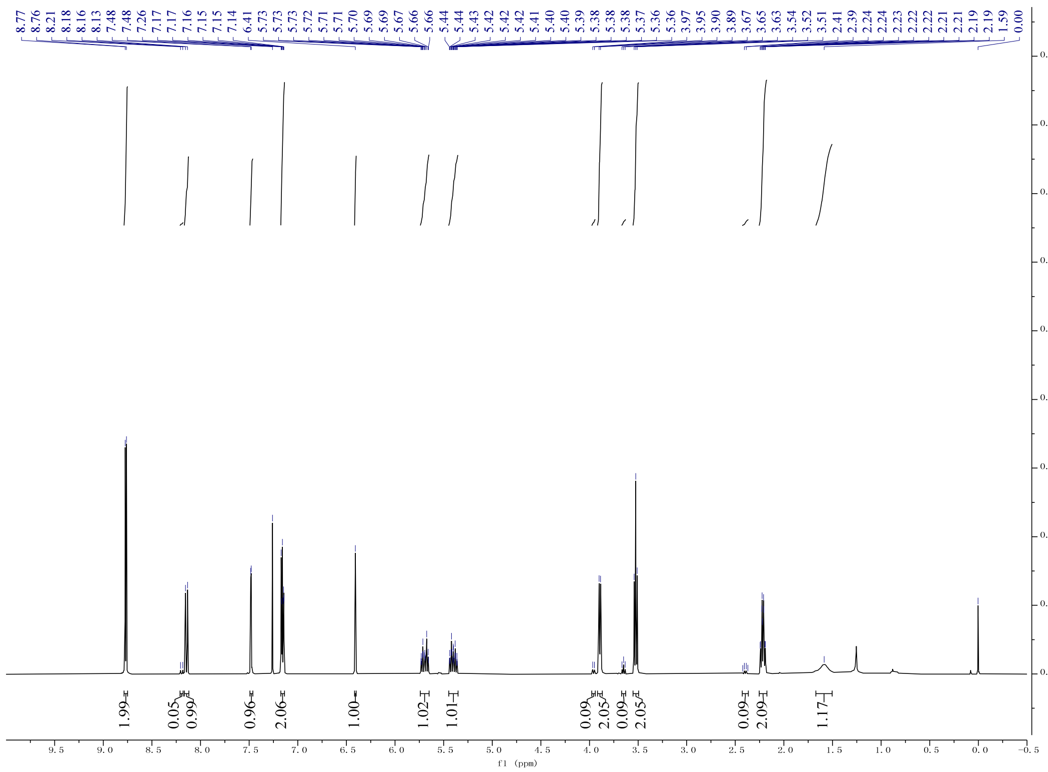


[13]C NMR (101 MHz, $CDCl_3$) Compound **3fa**

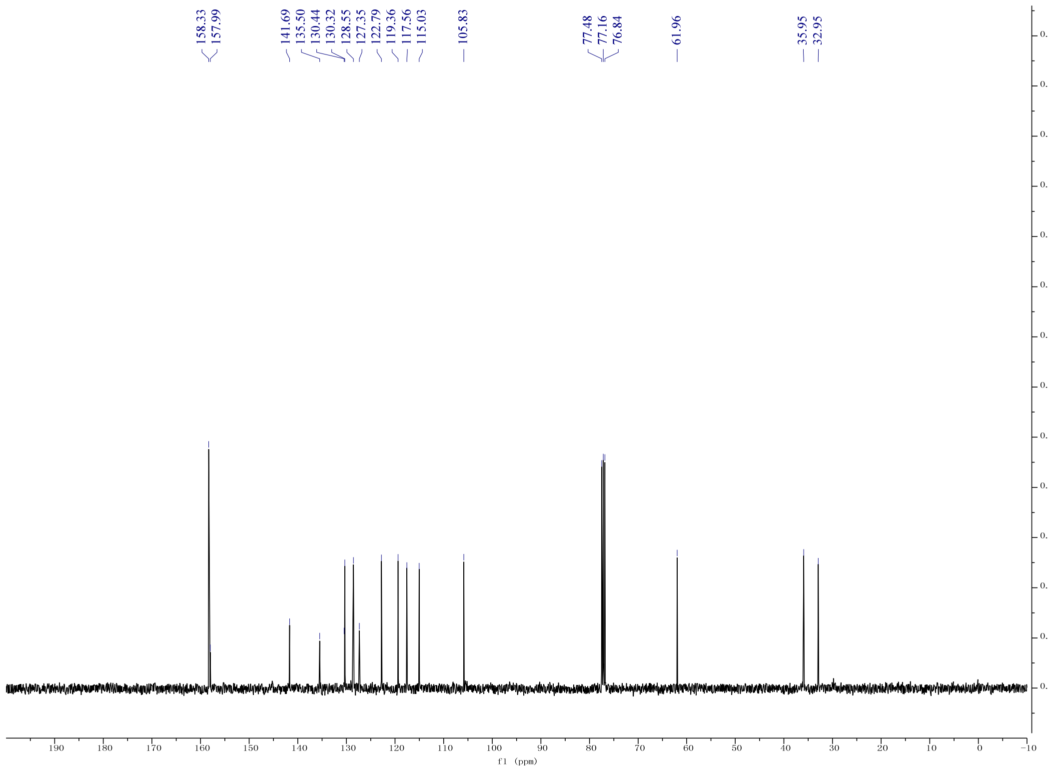


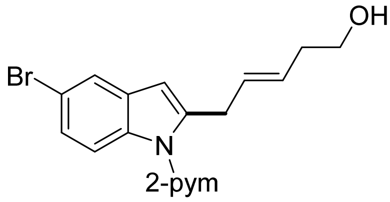


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ga**

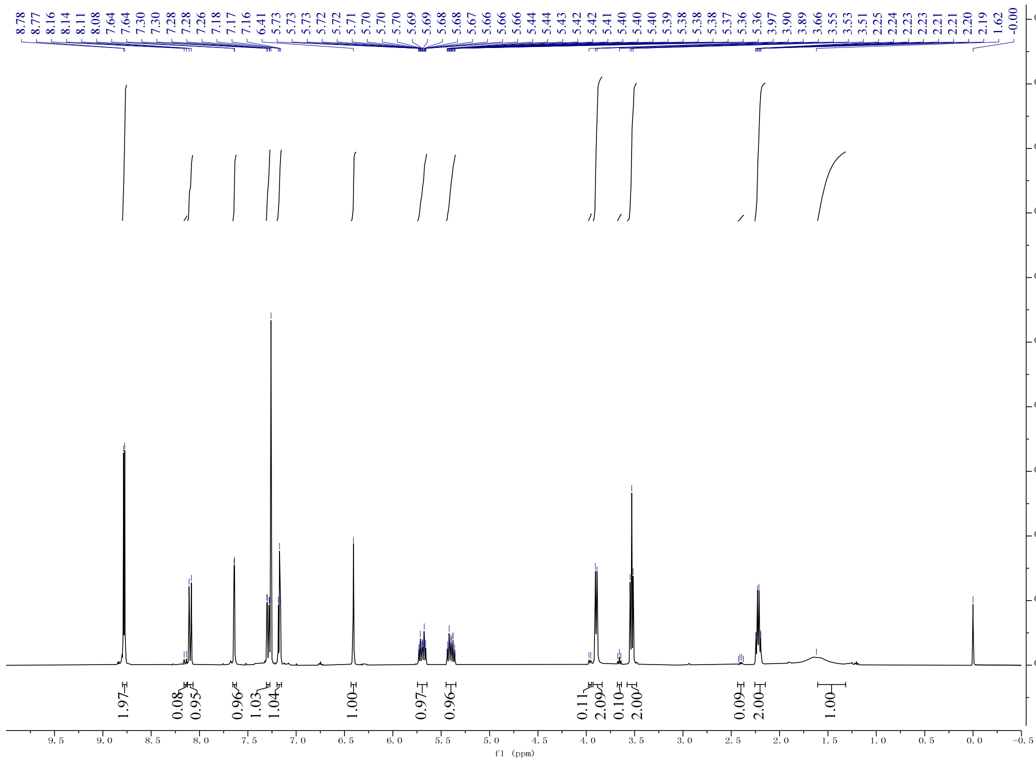


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ga**

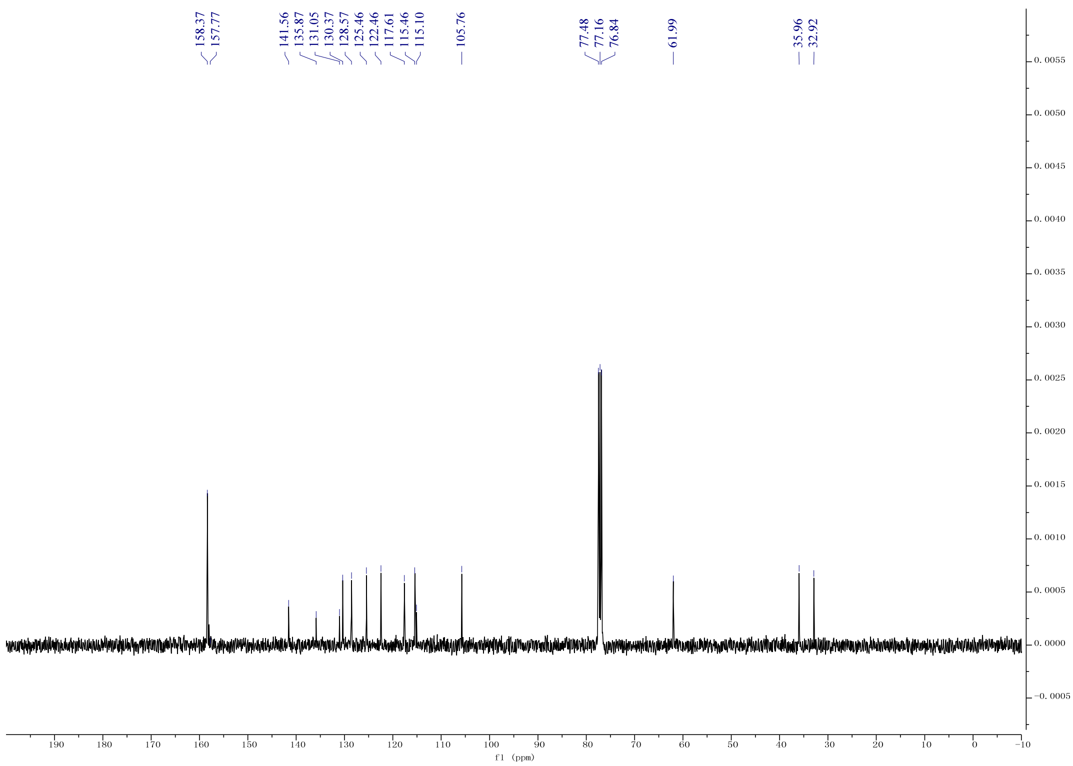


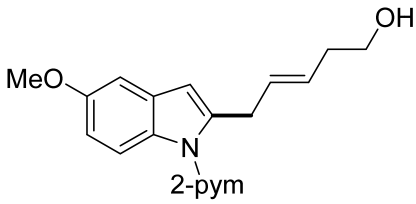


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ha**

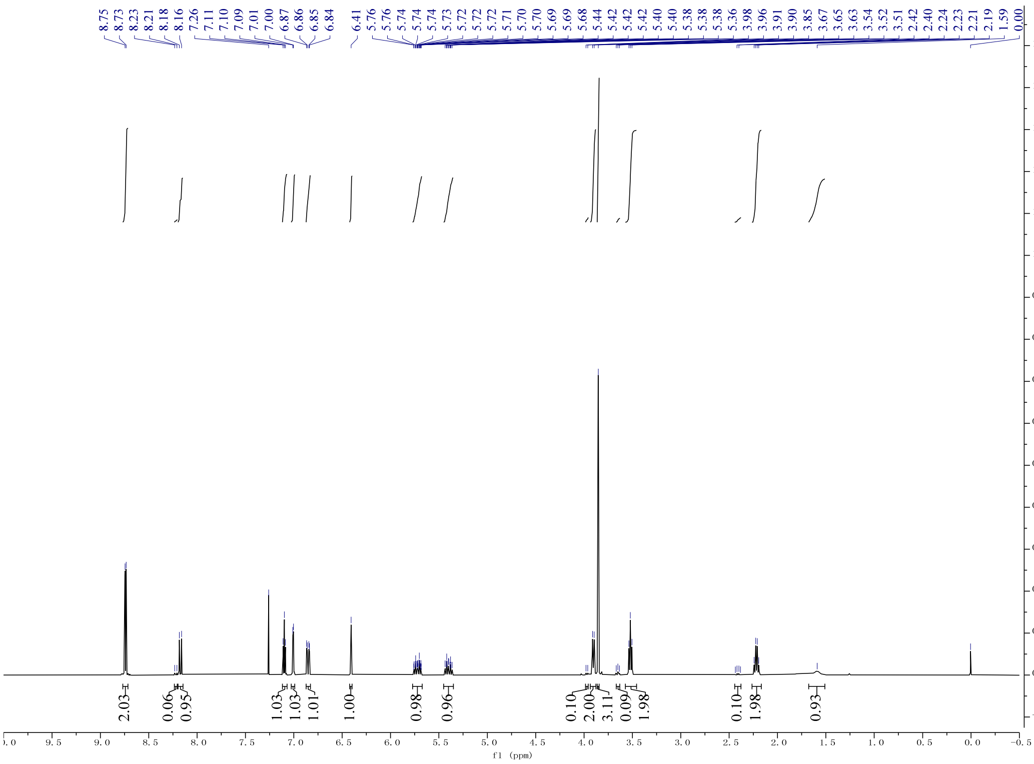


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ha**

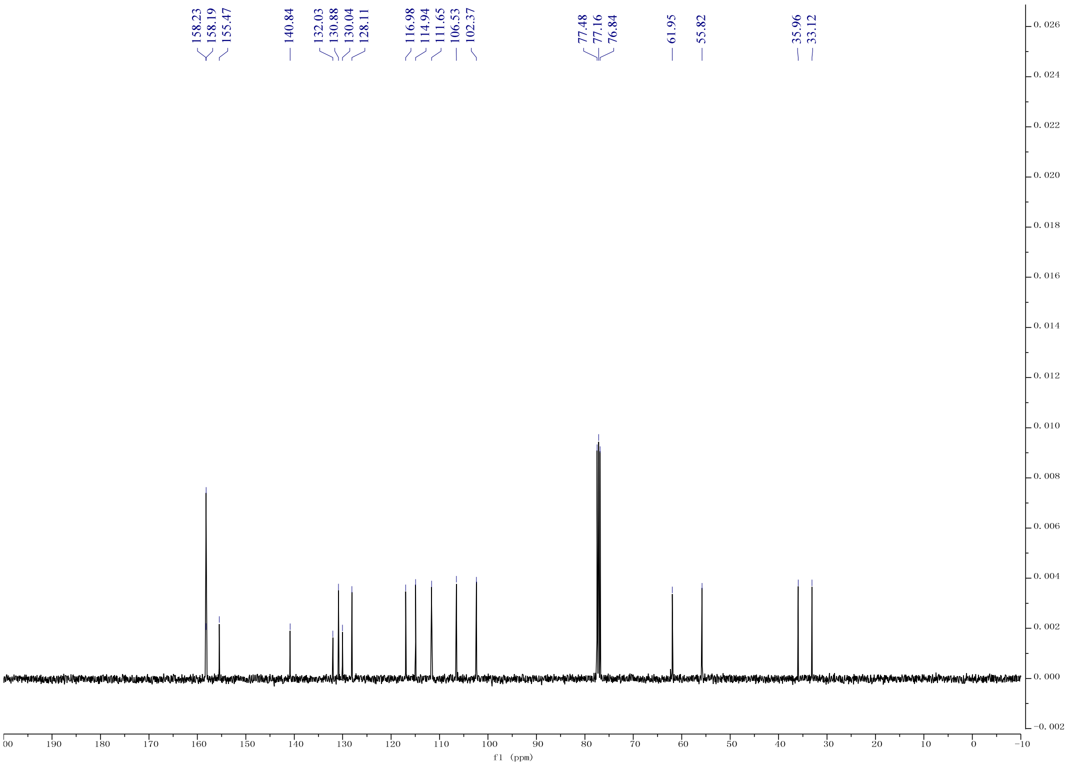


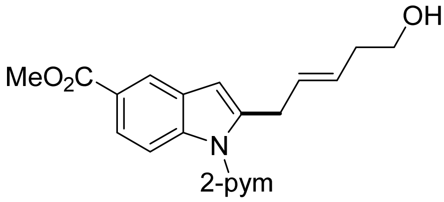


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ia**

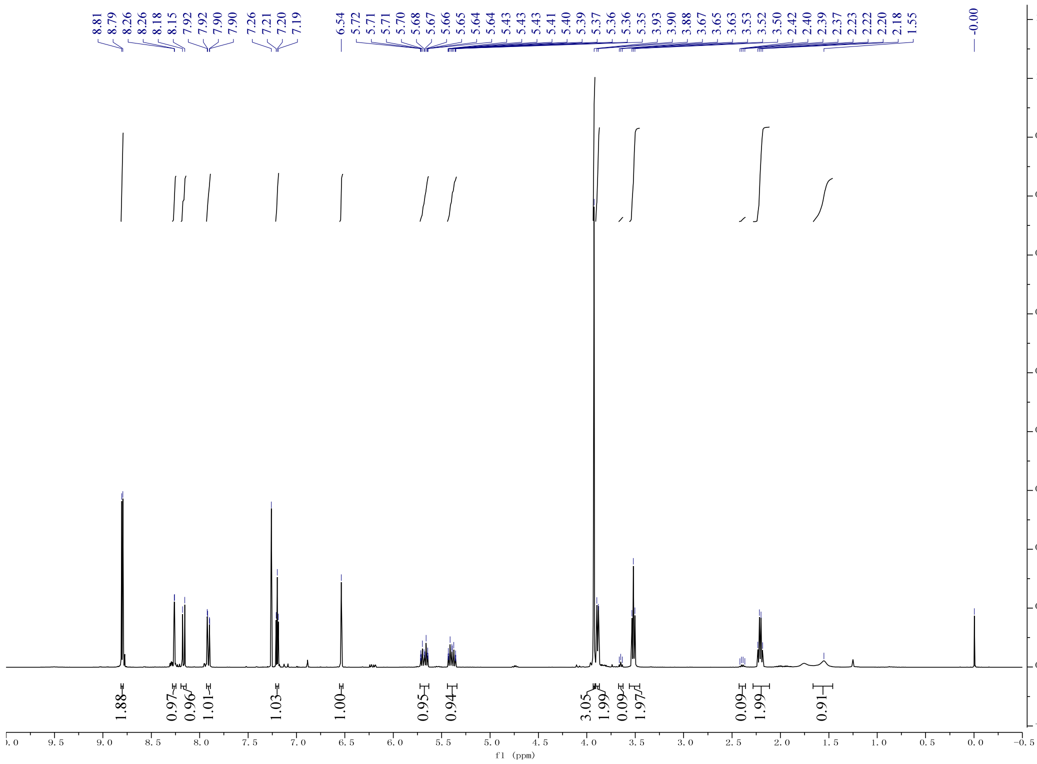


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ia**





^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ja**



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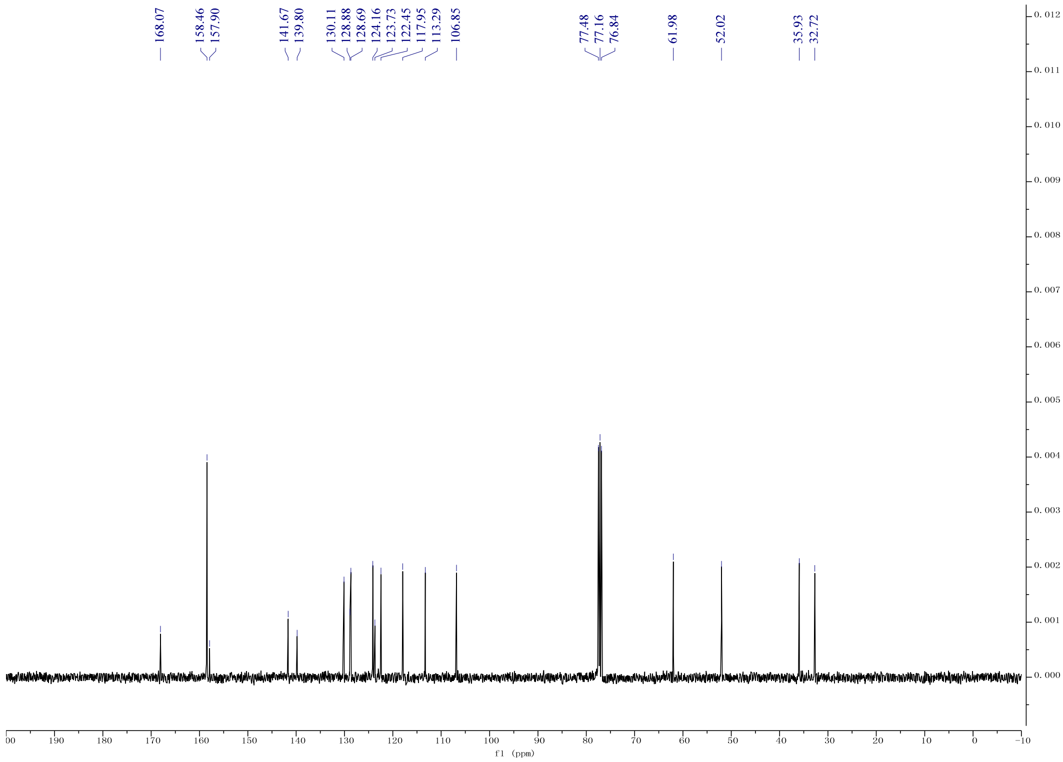
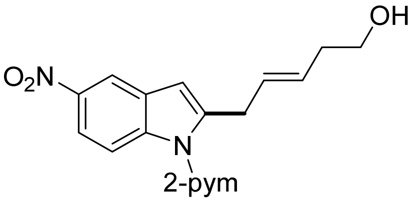
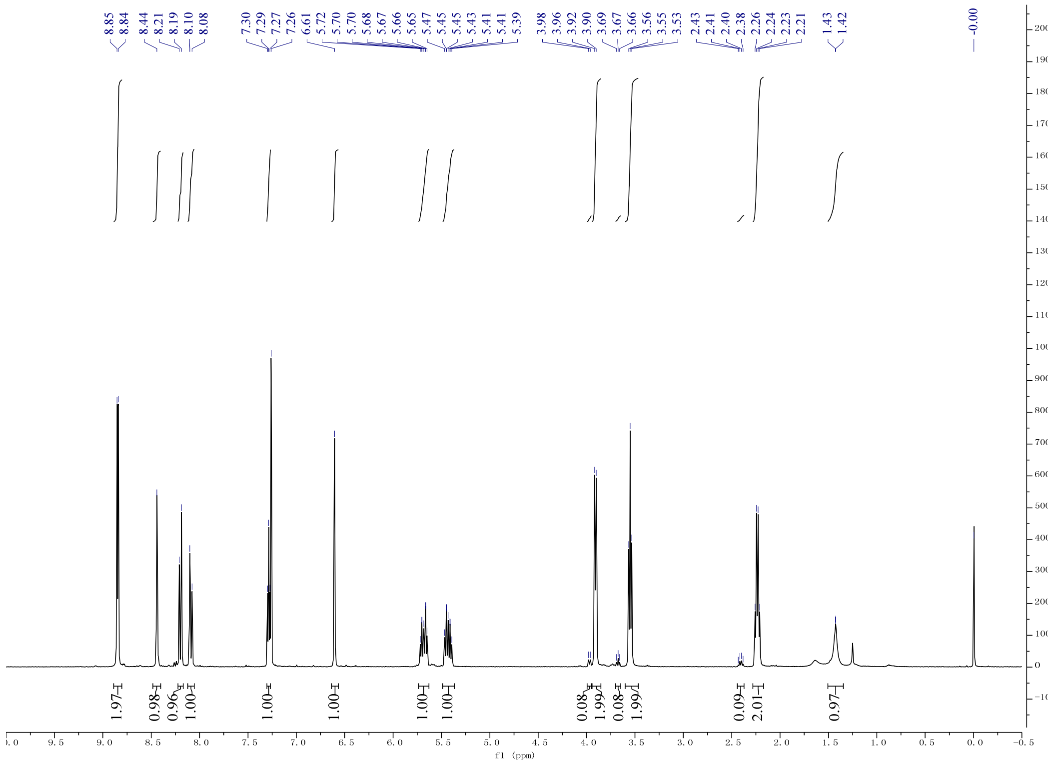
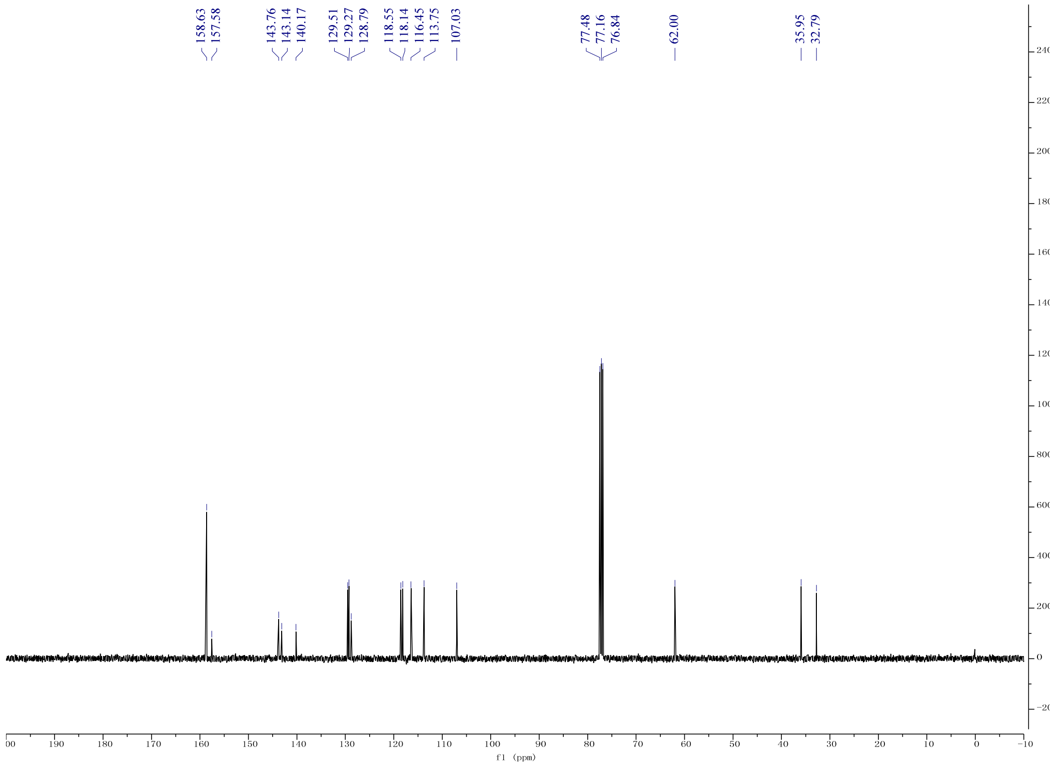


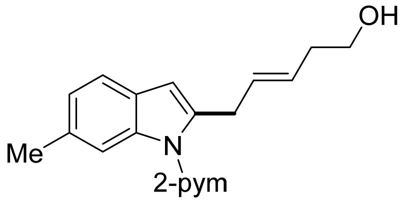


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ka**



^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ka**





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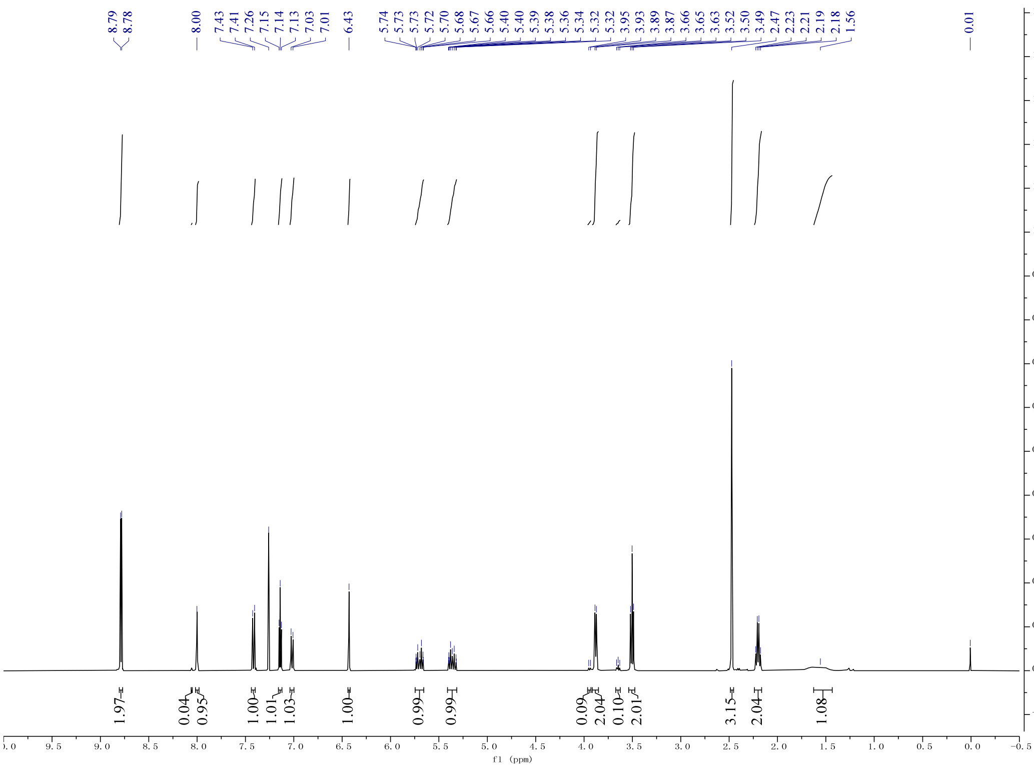
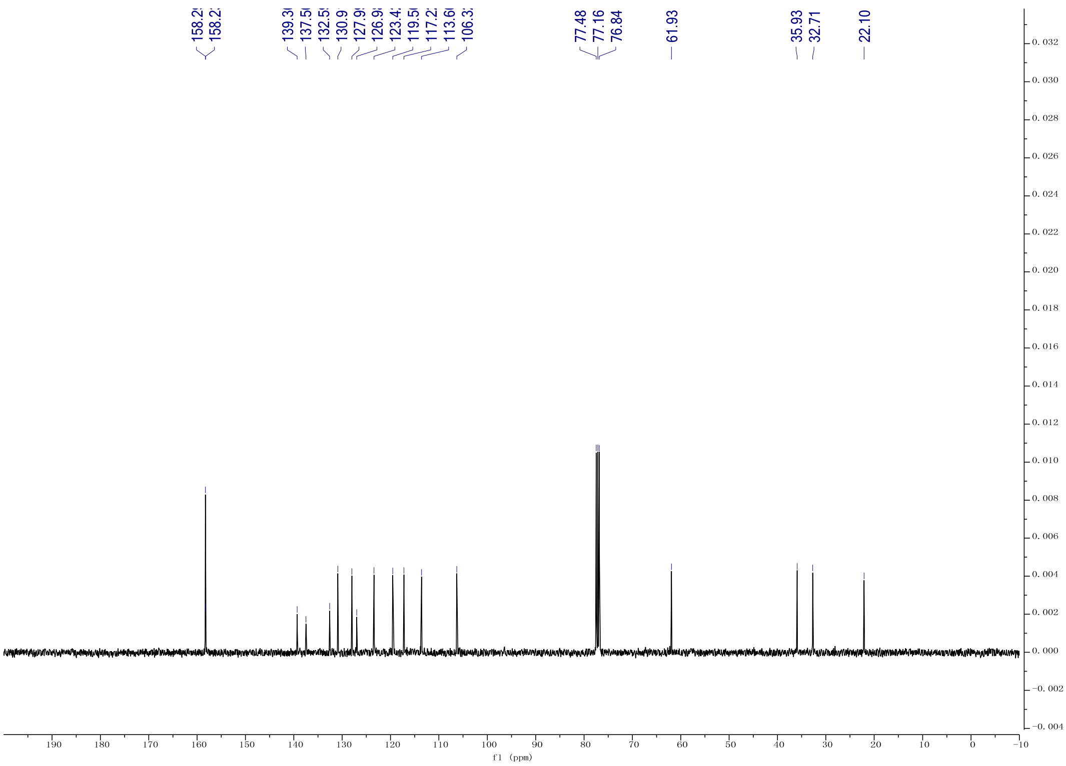
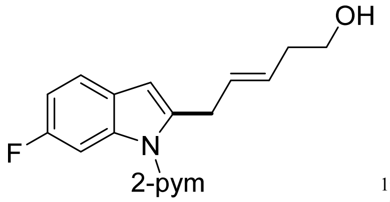
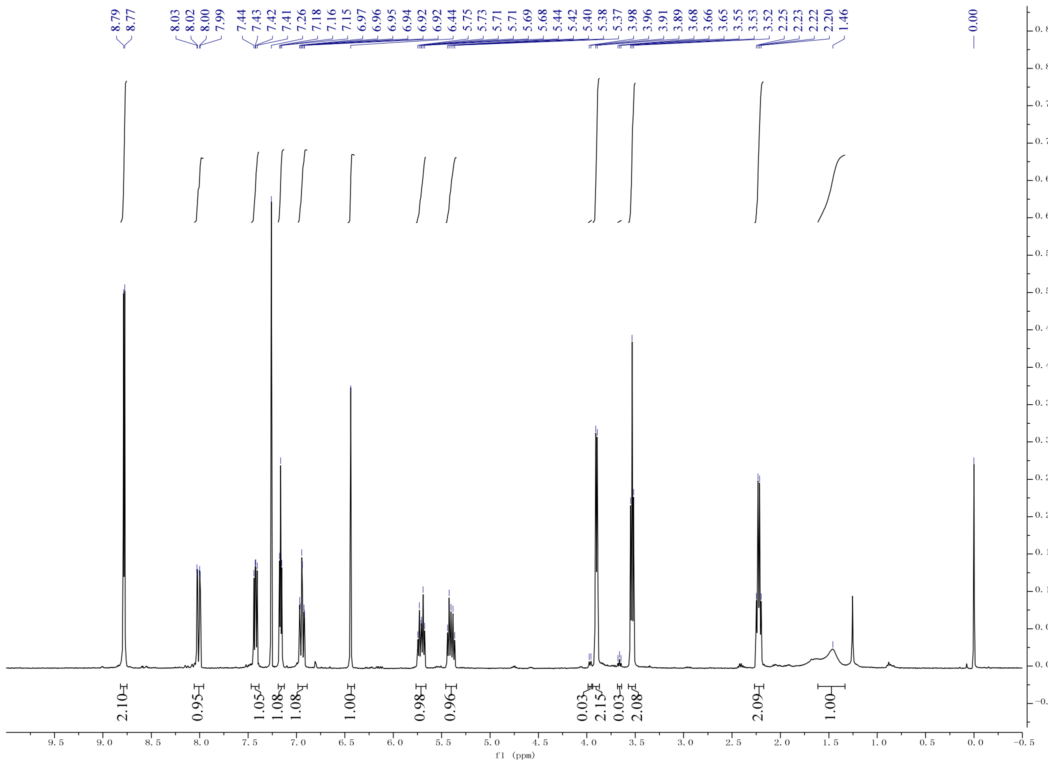


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3la**

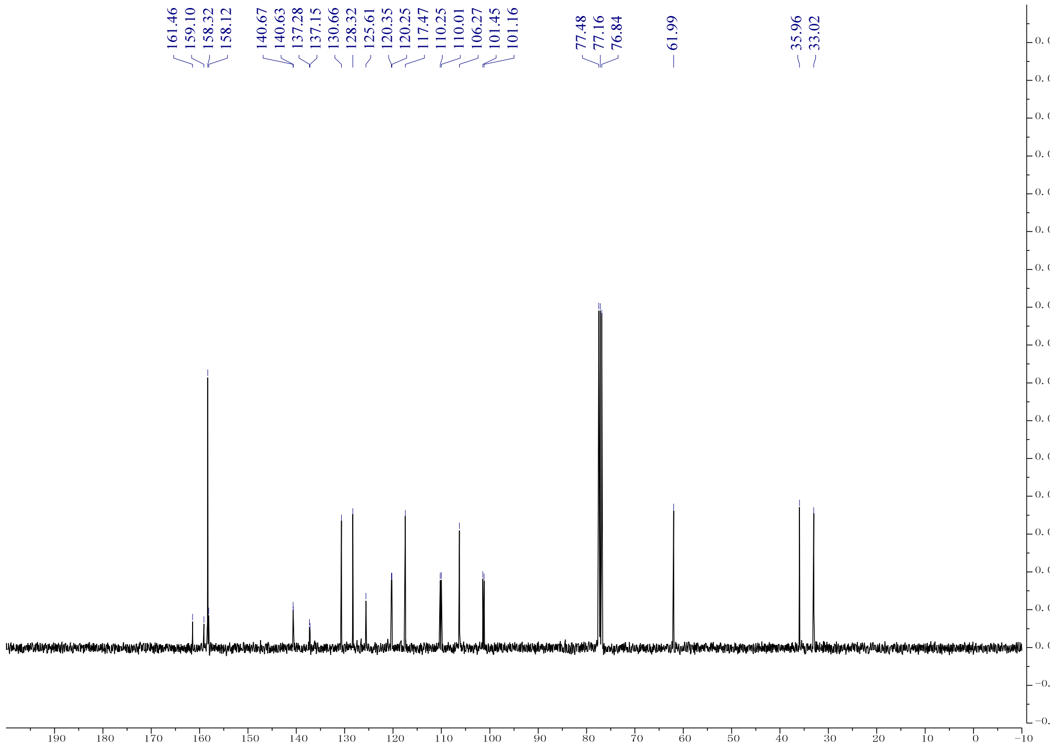


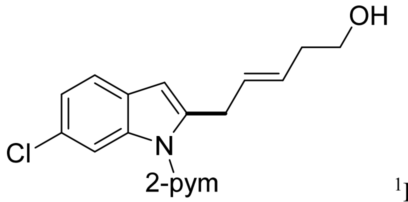


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ma**

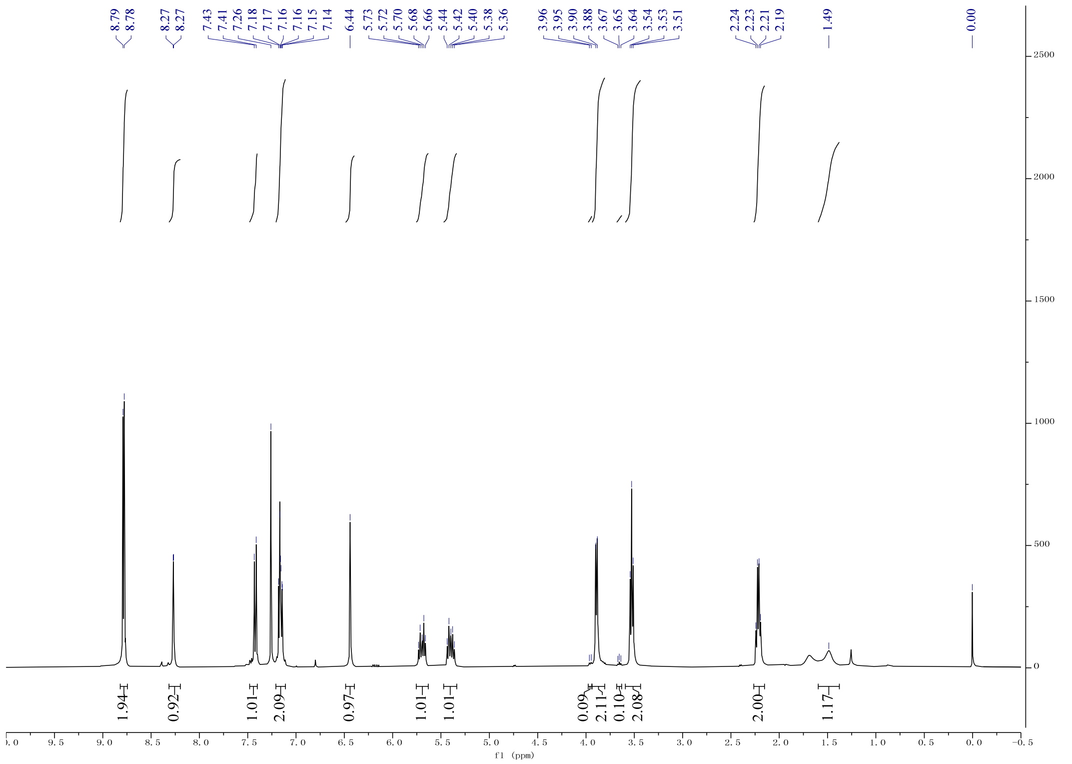


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ma**

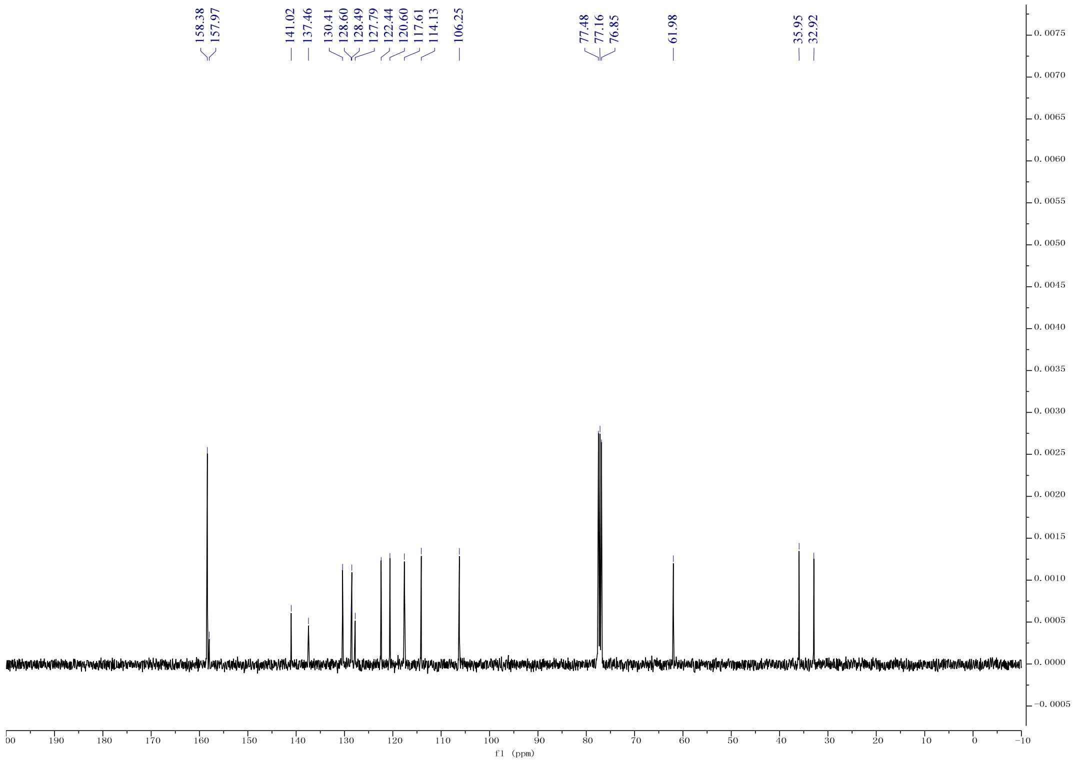


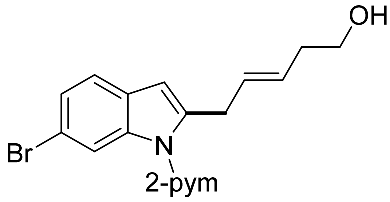


[1]H NMR (400 MHz, $CDCl_3$) Compound **3na**

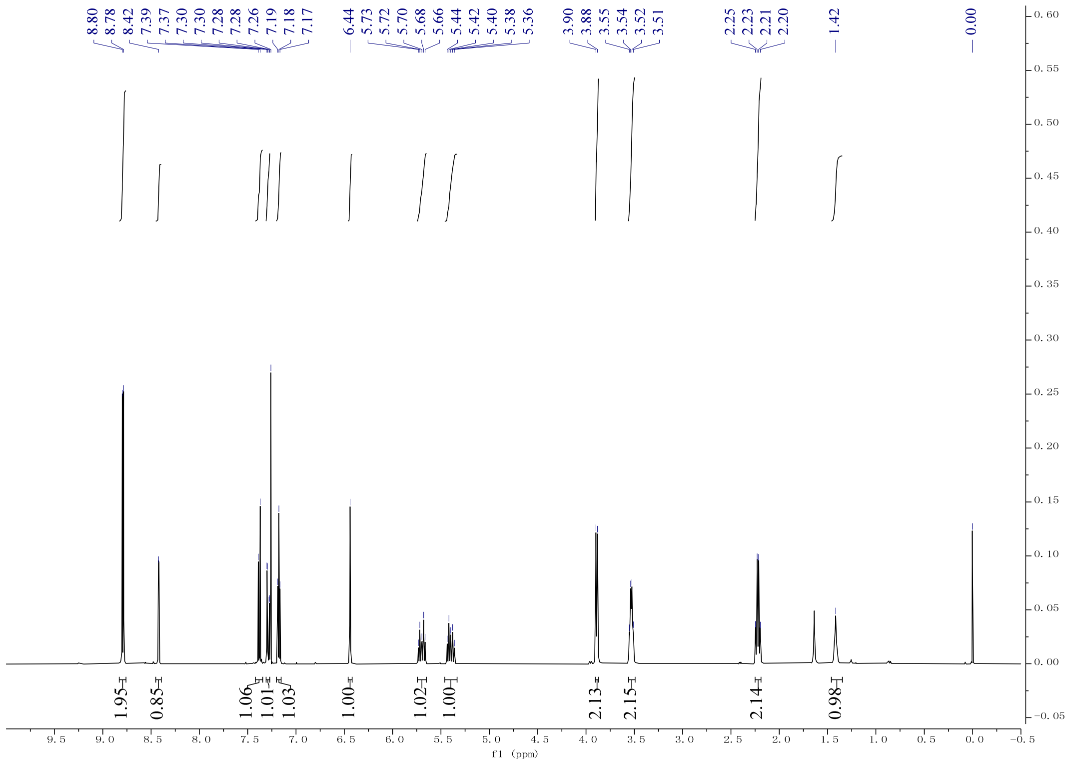


[13]C NMR (101 MHz, $CDCl_3$) Compound **3na**

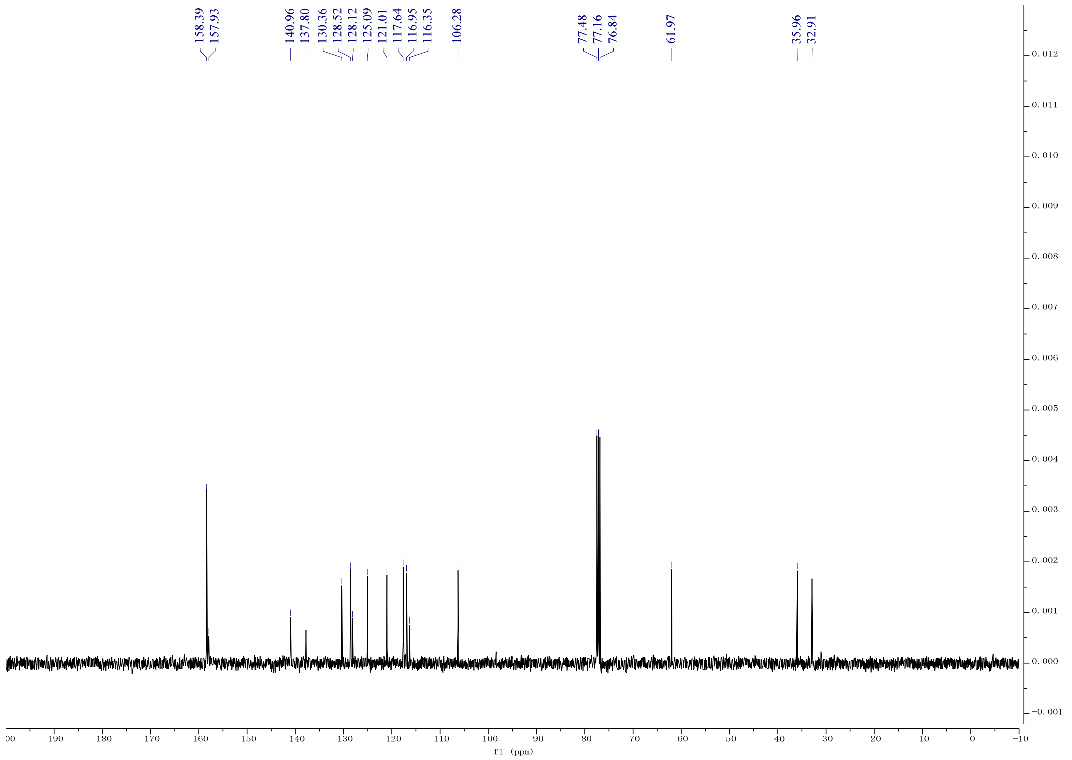


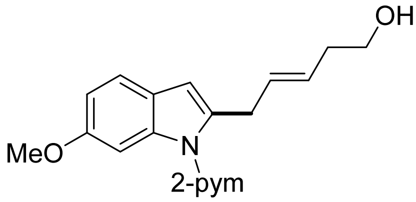


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3oa**

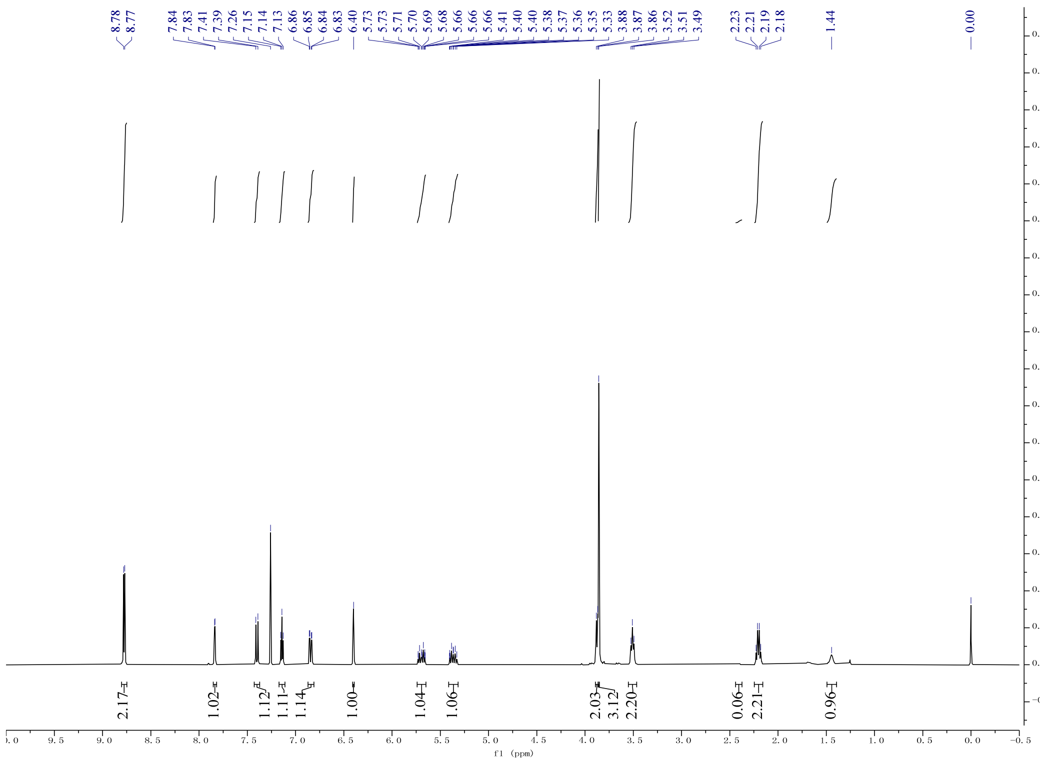


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3oa**

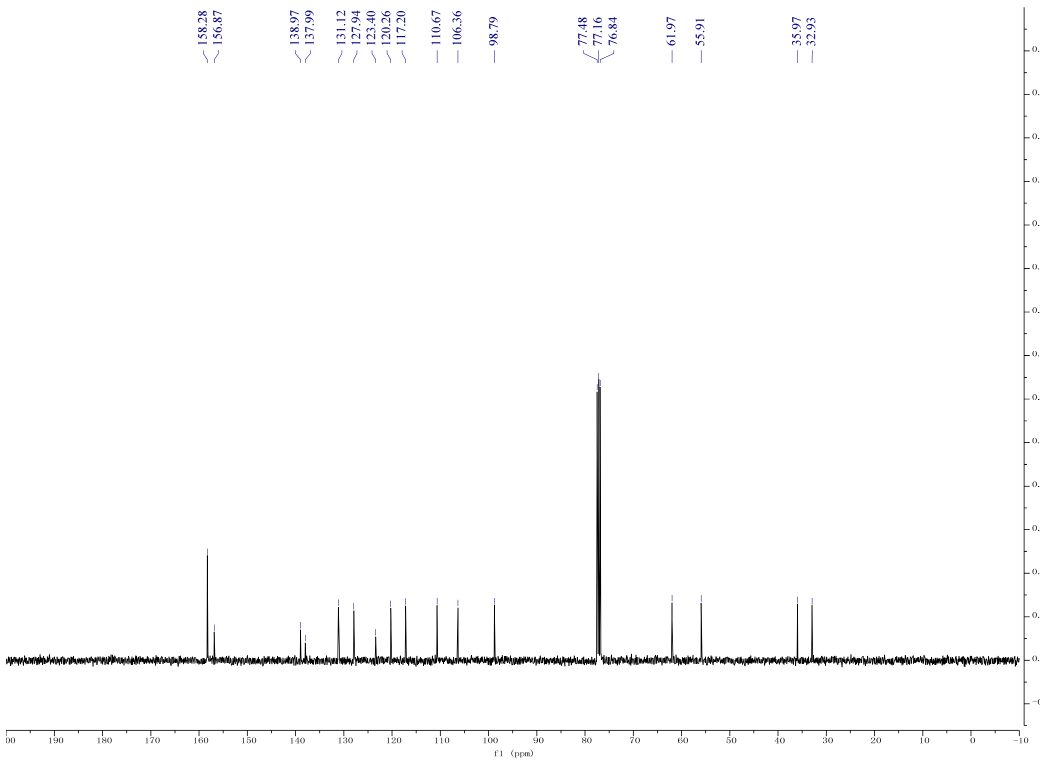


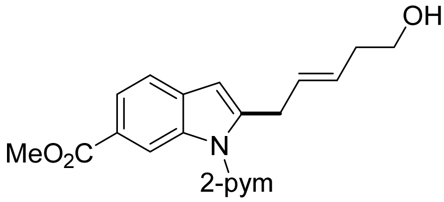


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3pa**



^{13}C NMR (101 MHz, $CDCl_3$) Compound **3pa**





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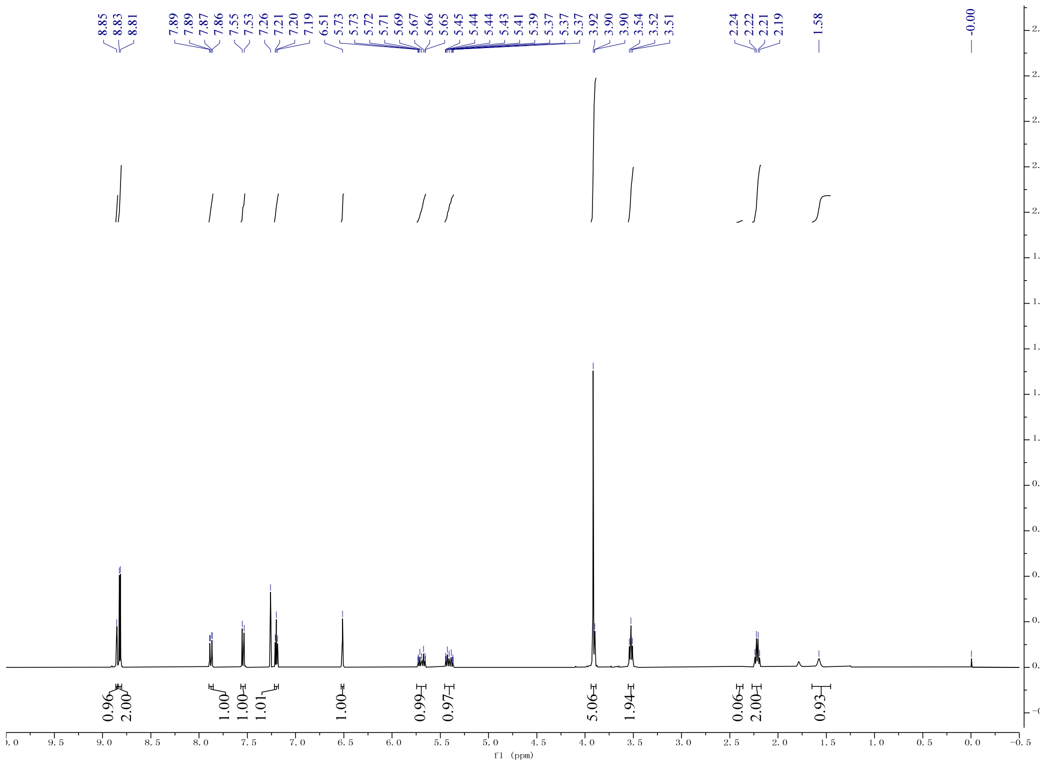
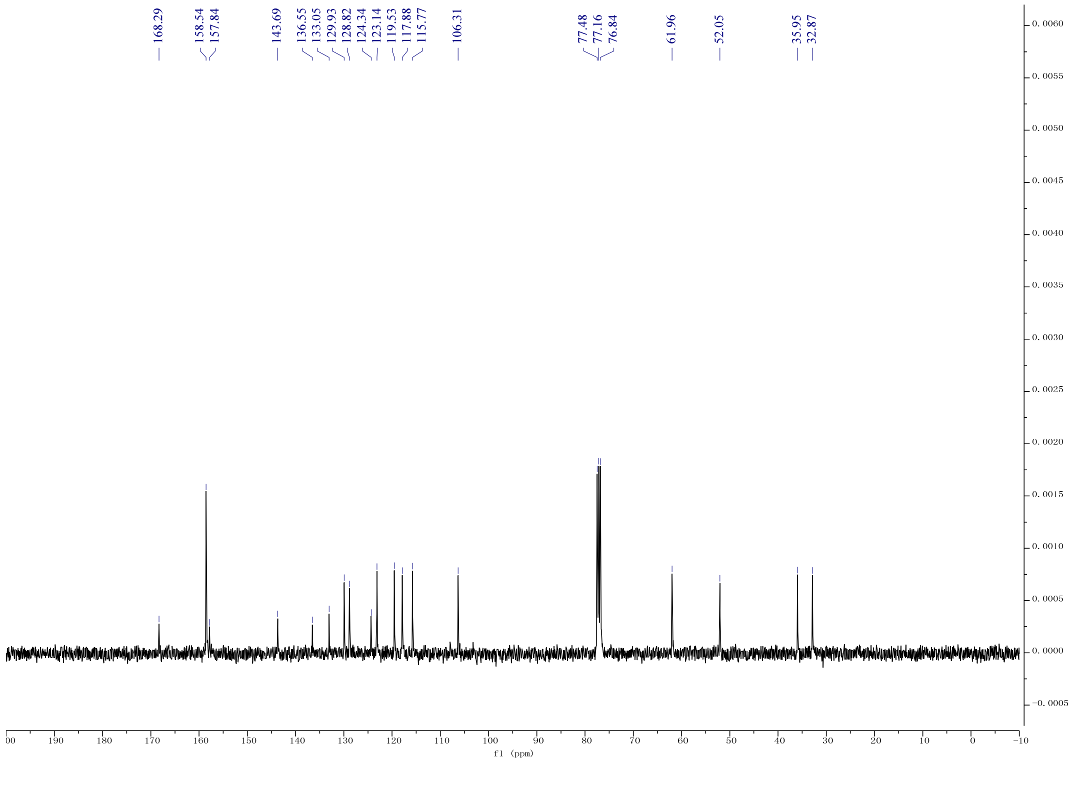
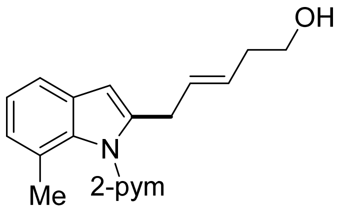


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3qa**





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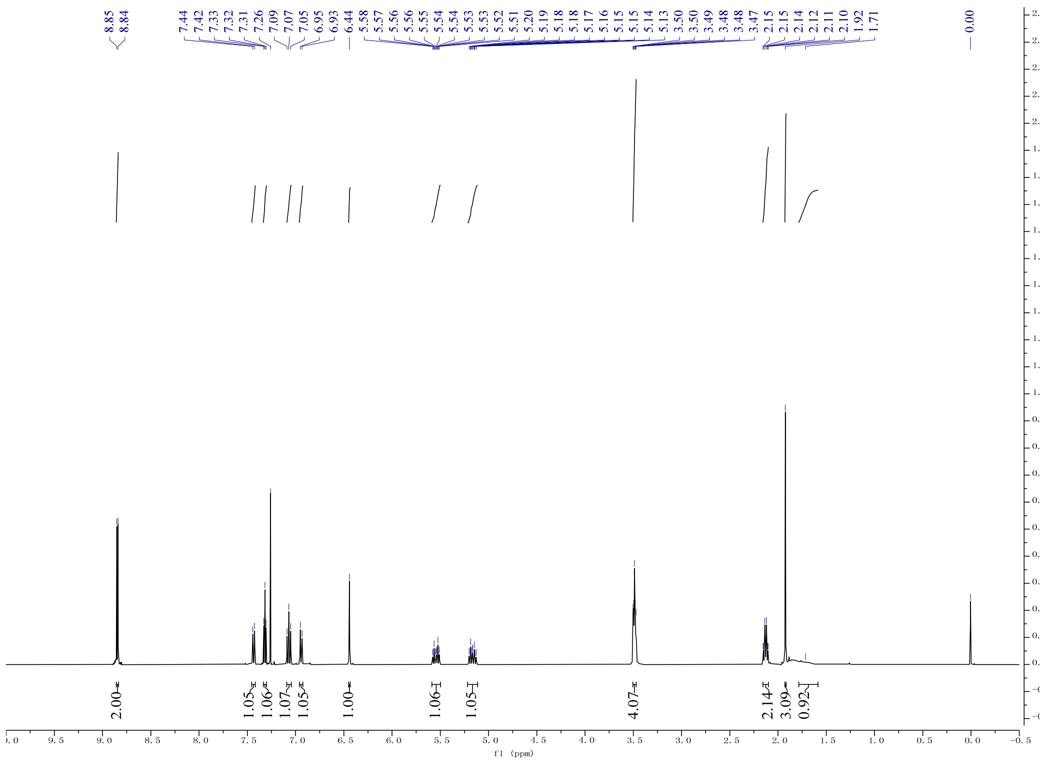

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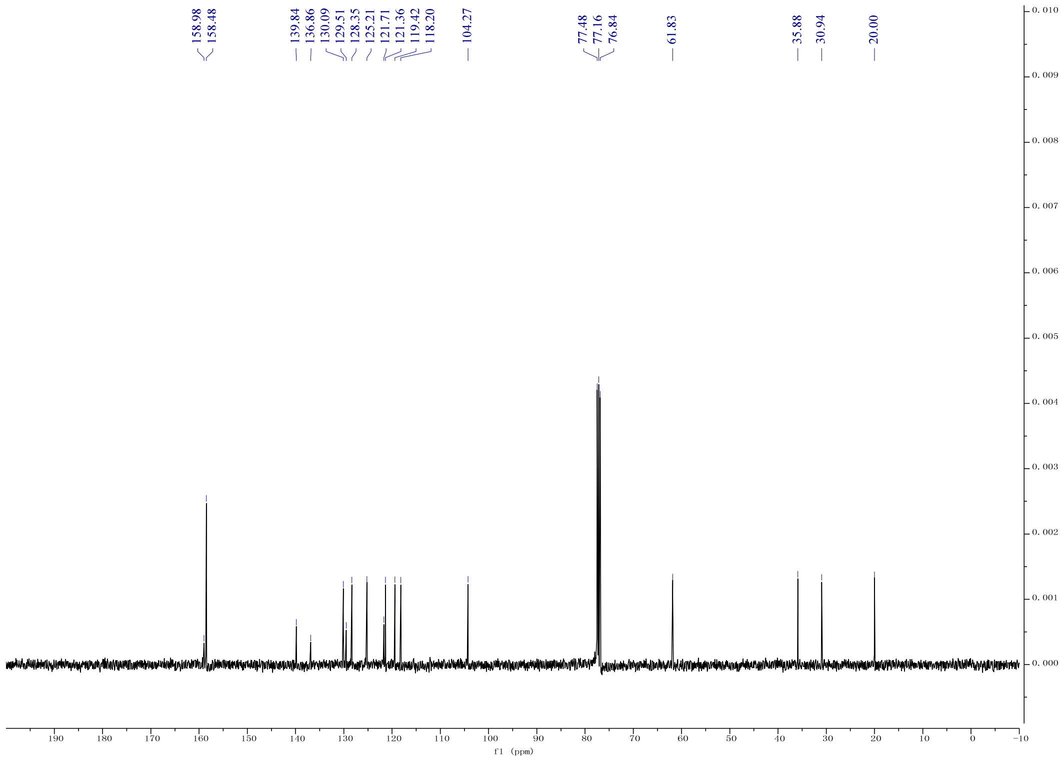

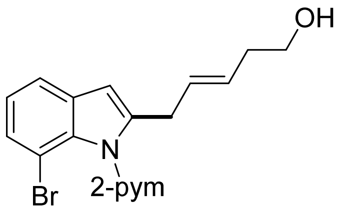

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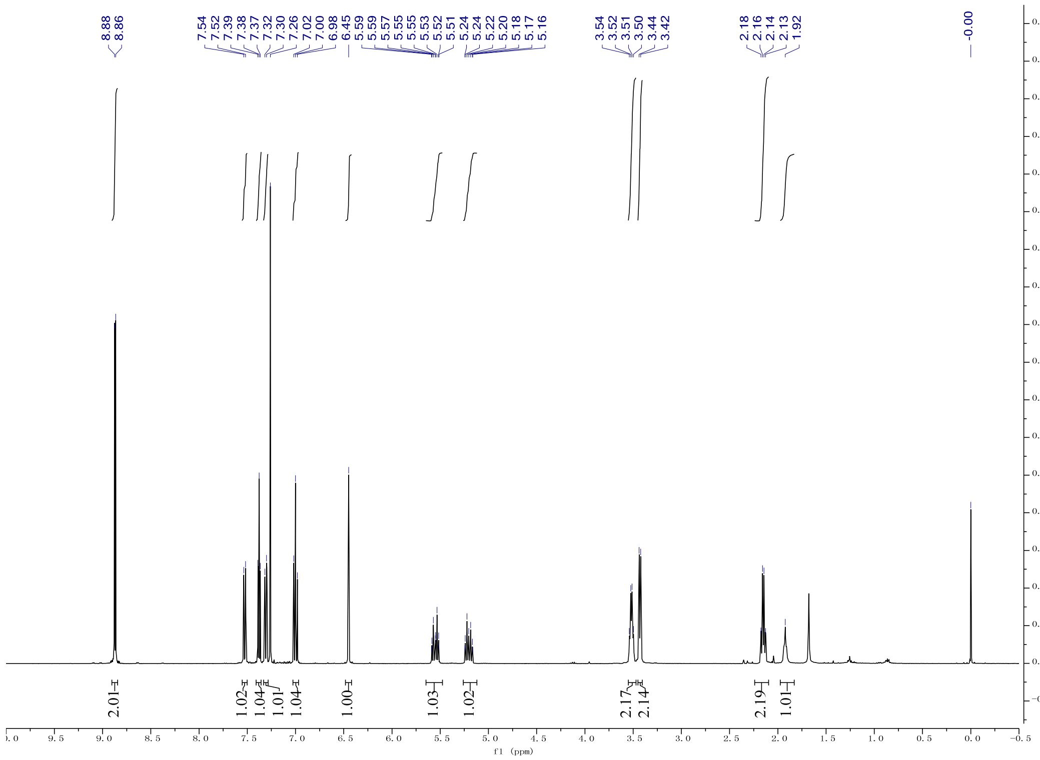

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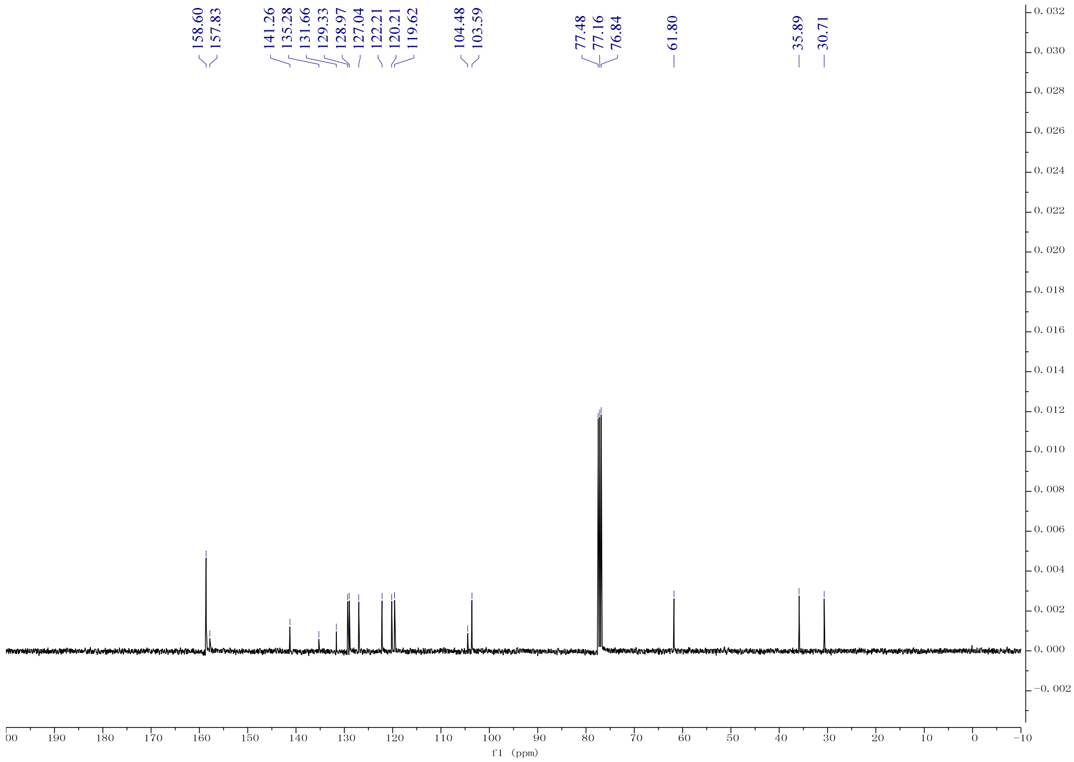

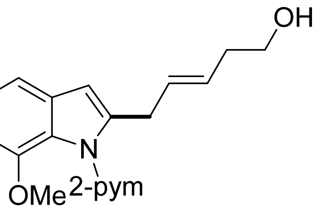

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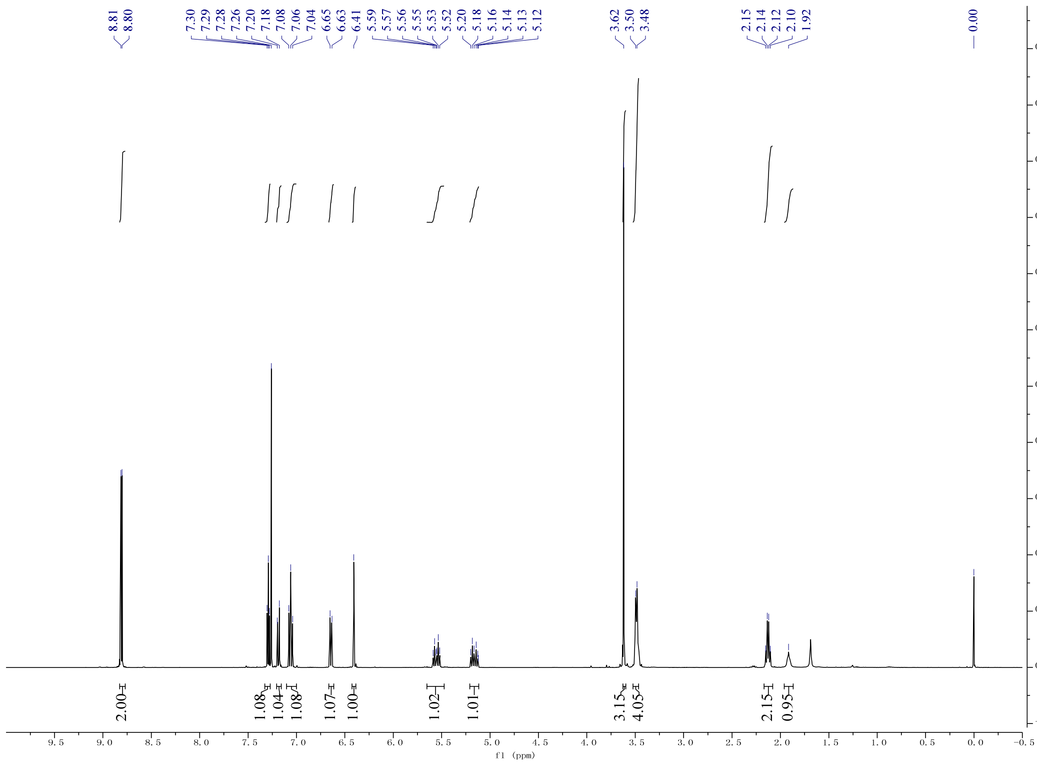
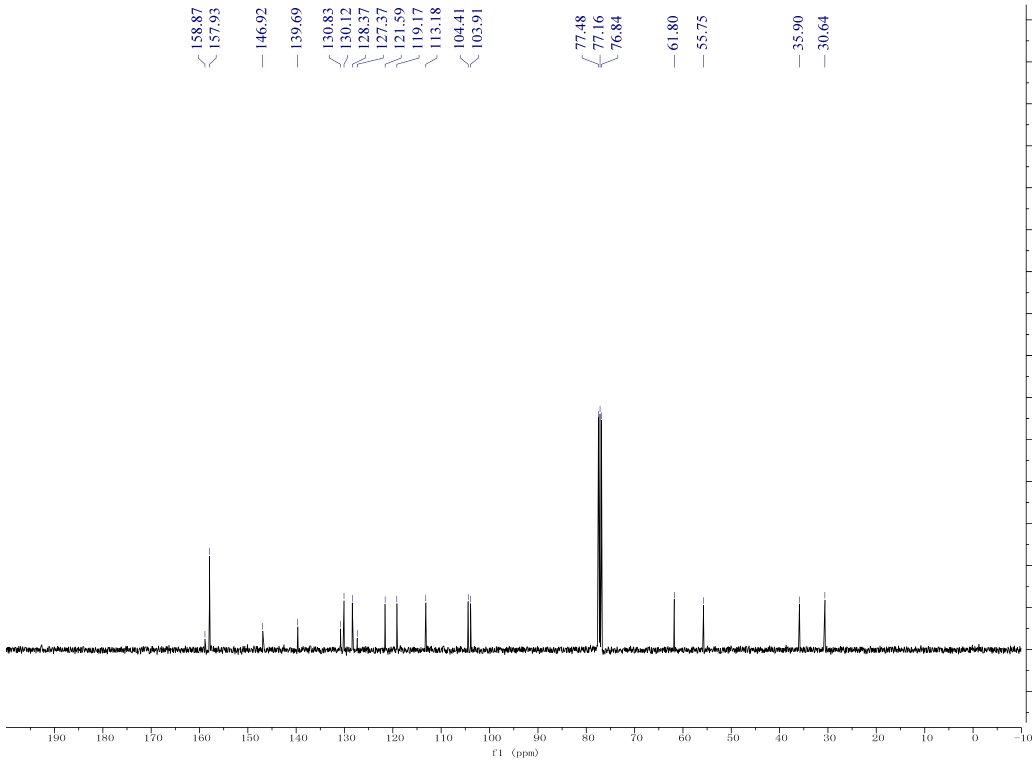
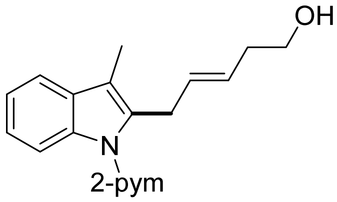


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ta**





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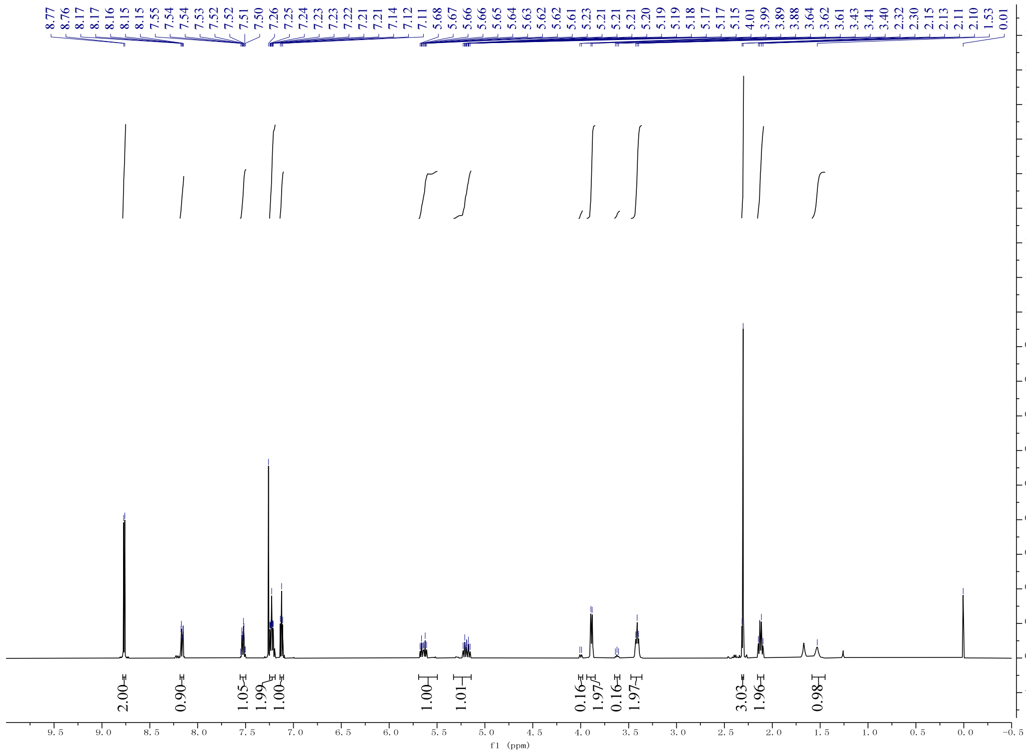

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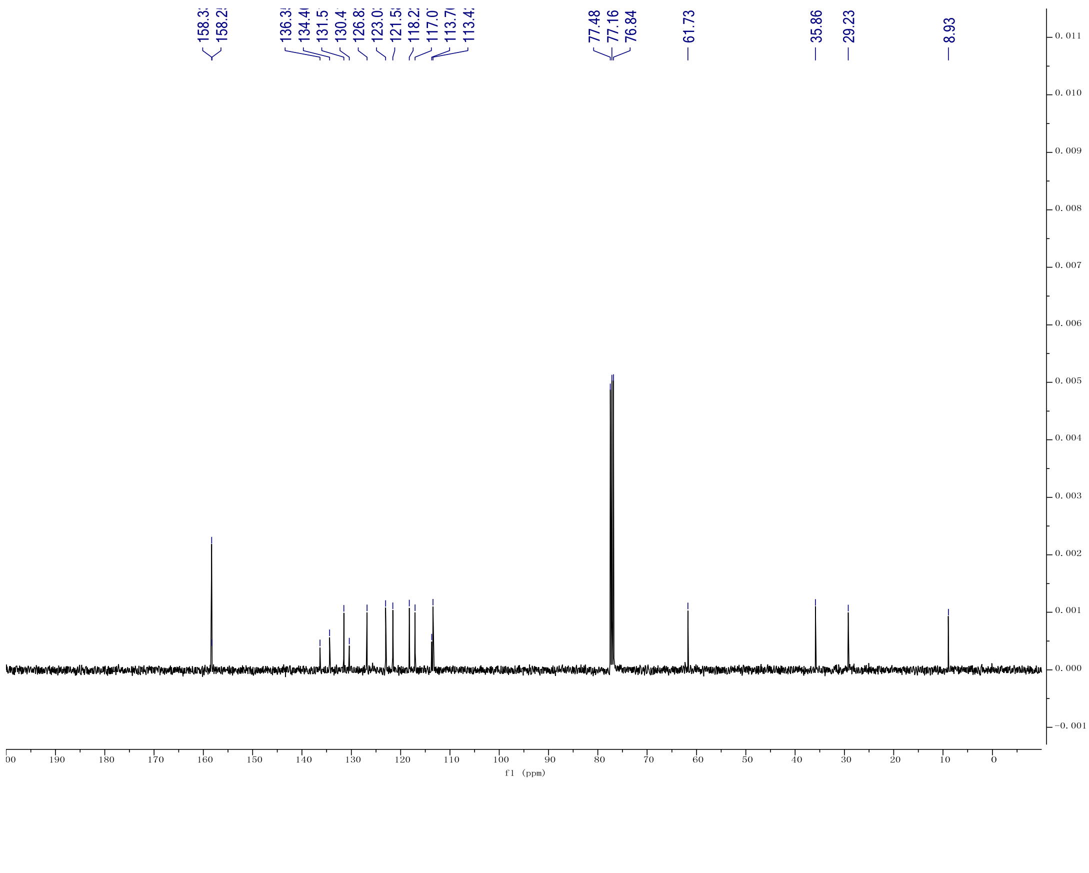
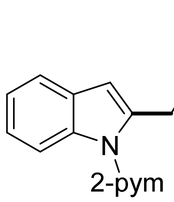
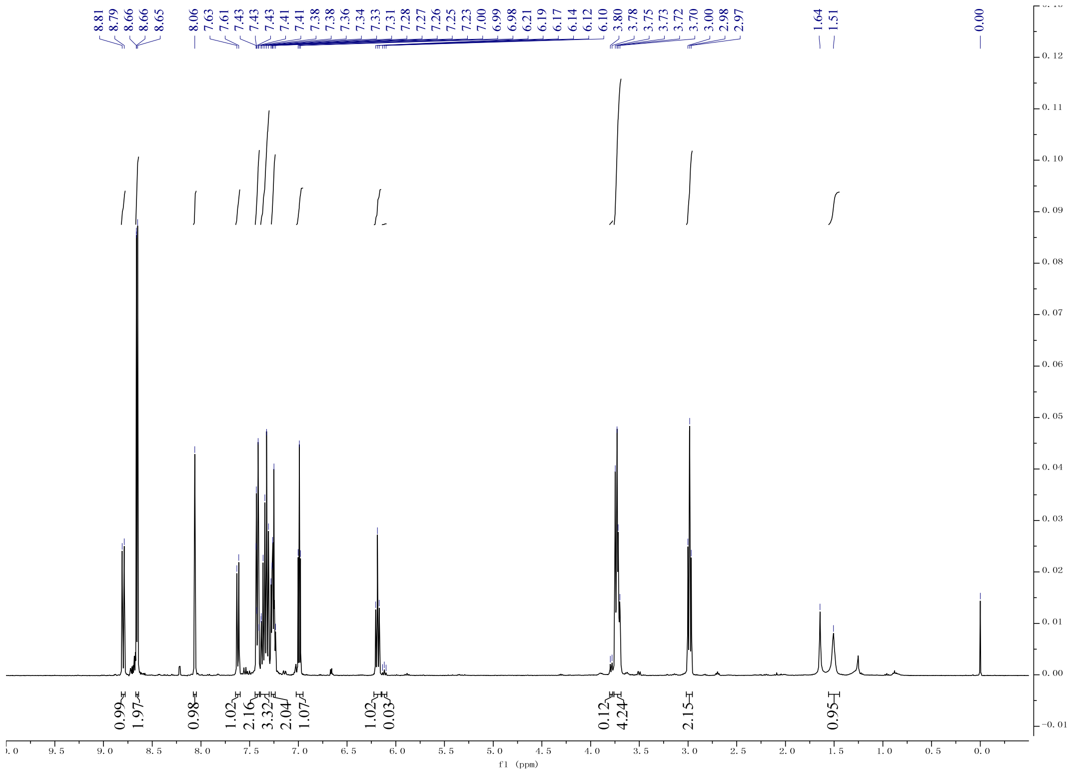
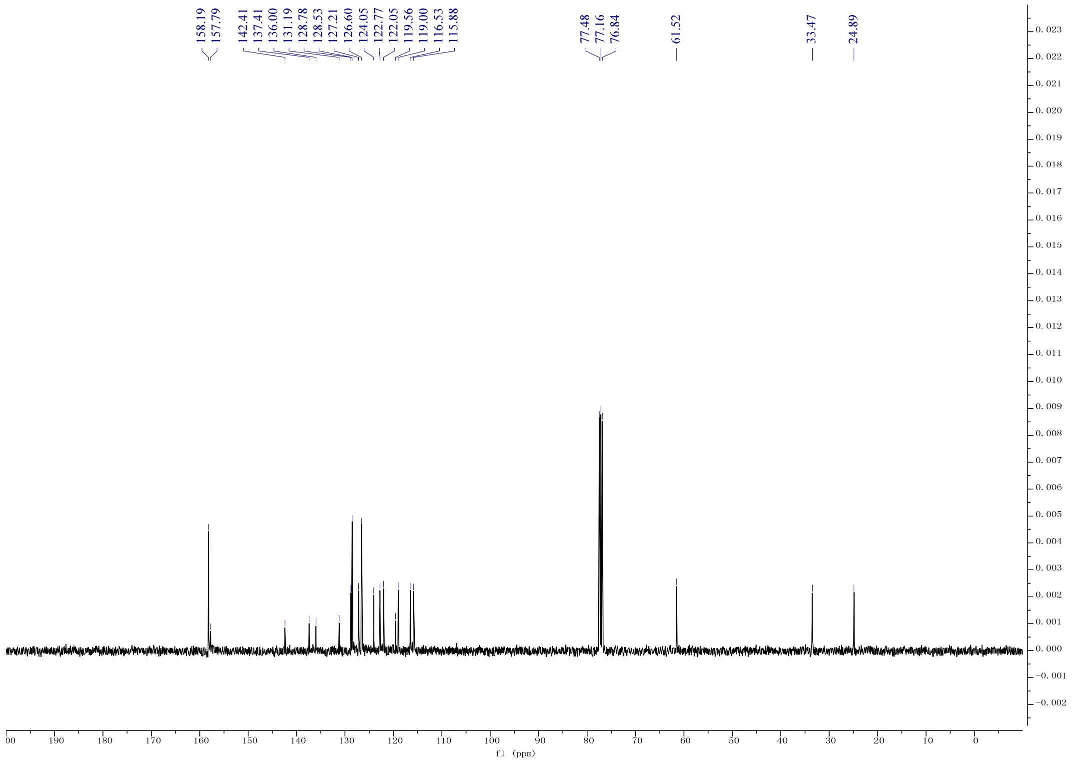


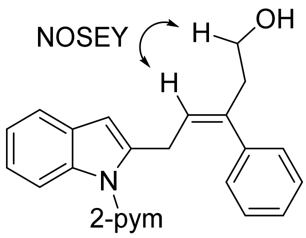


^{1}H NMR (400 MHz, $CDCl_3$) Compounds **3ab**

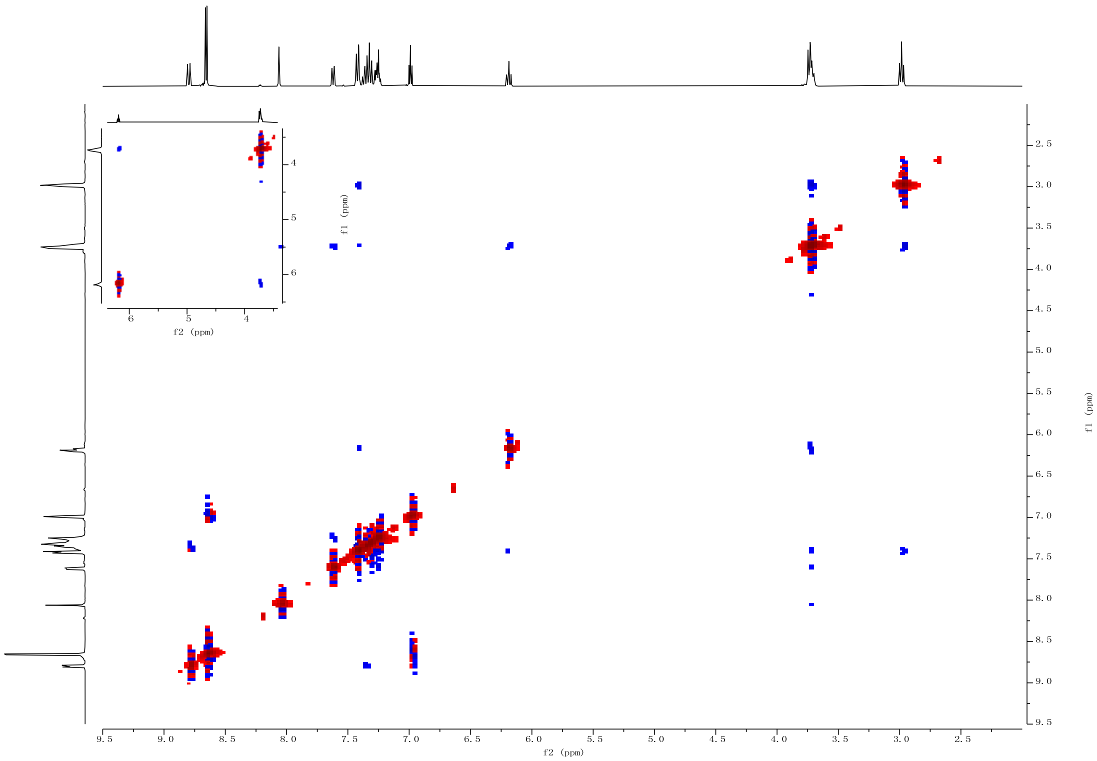


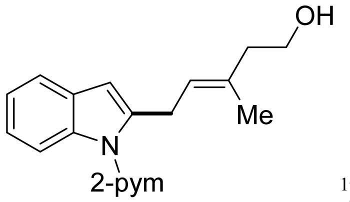
^{13}C NMR (101 MHz, $CDCl_3$) Compounds **3ab**



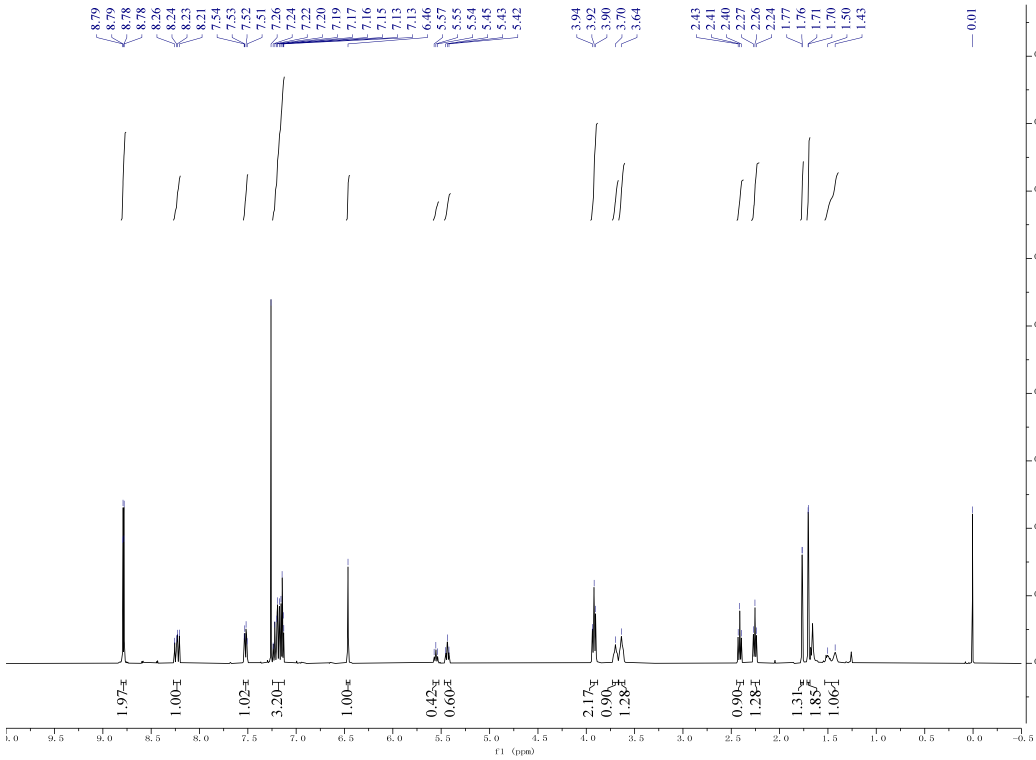


3ab

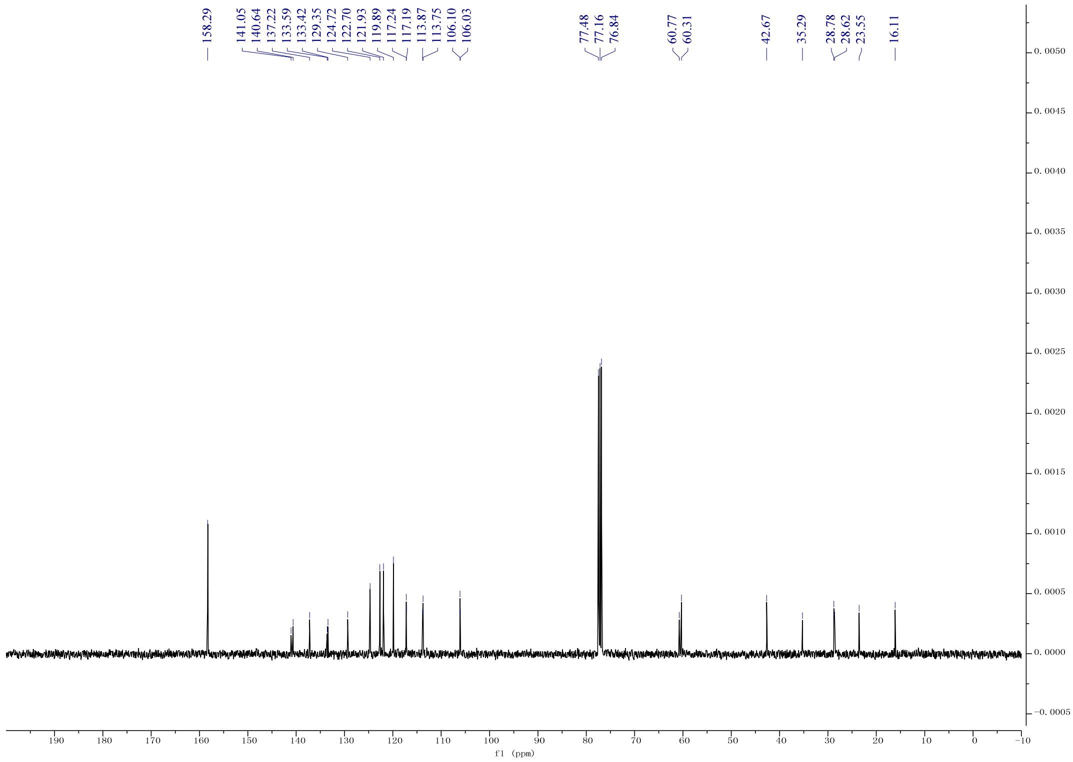


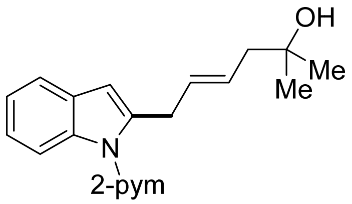


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ac**

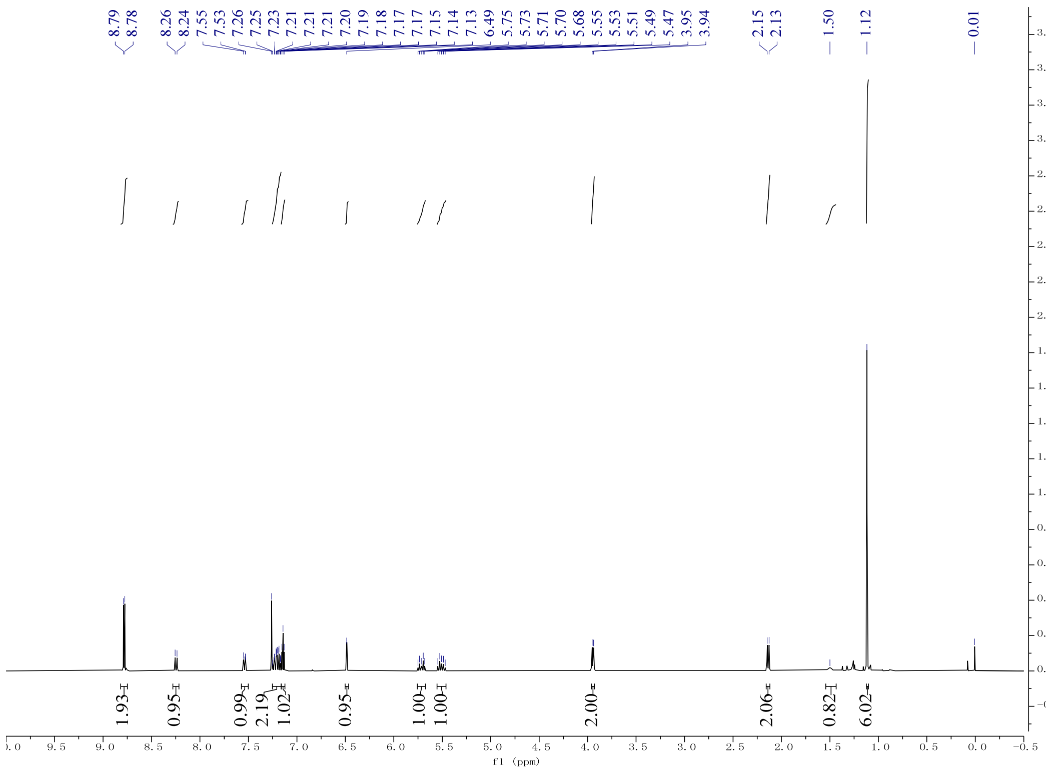


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ac**

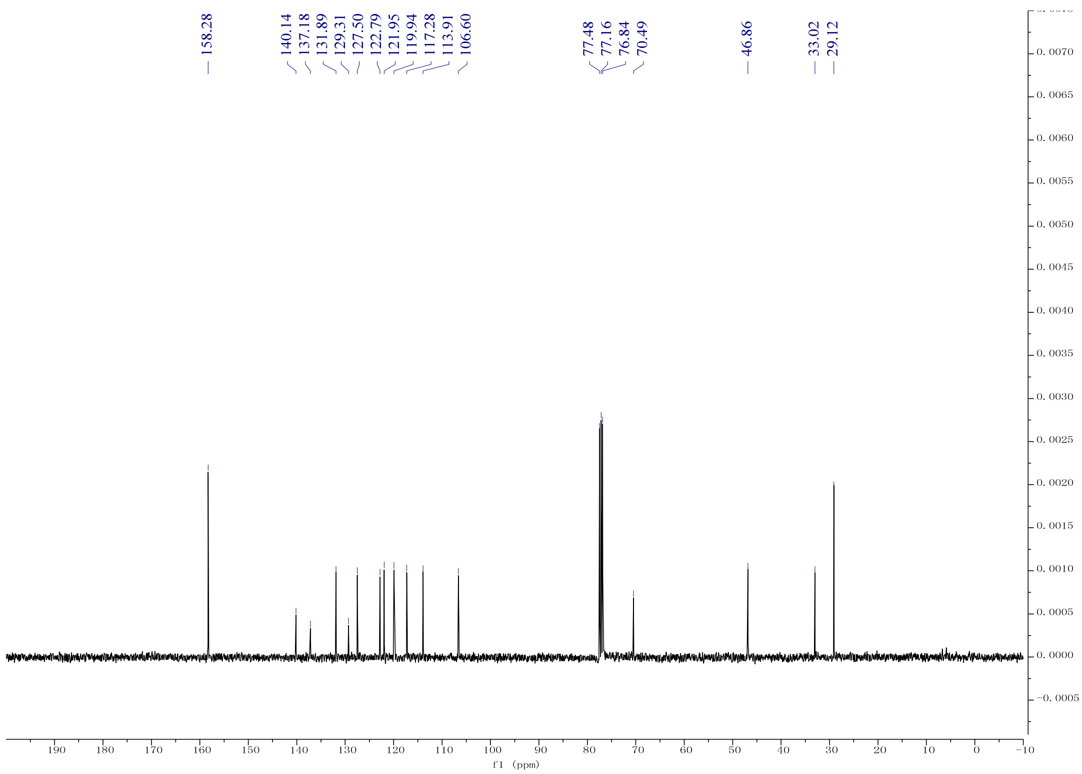


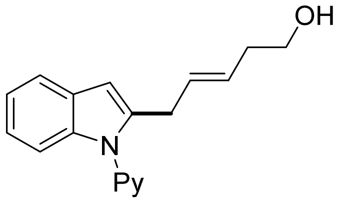


^{1}H NMR (400 MHz, $CDCl_3$) Compound **3ad**

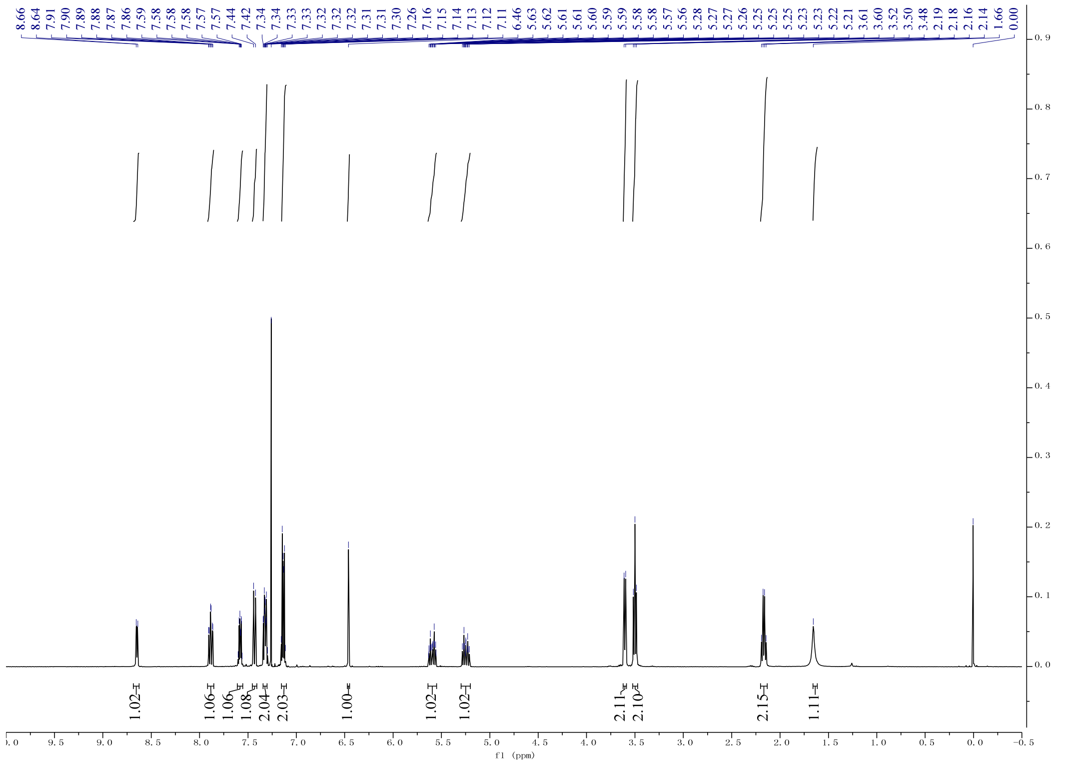


^{13}C NMR (101 MHz, $CDCl_3$) Compound **3ad**

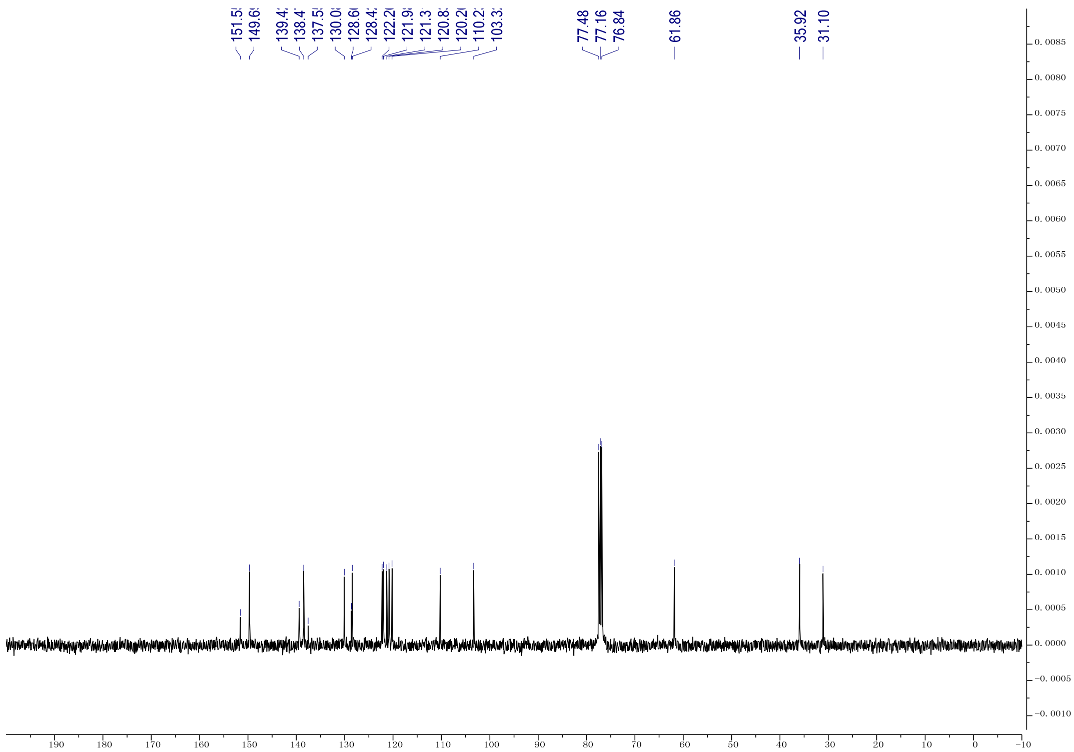


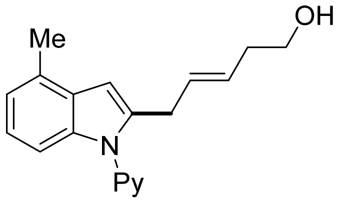


^1H NMR (400 MHz, $CDCl_3$) Compound **5aa**

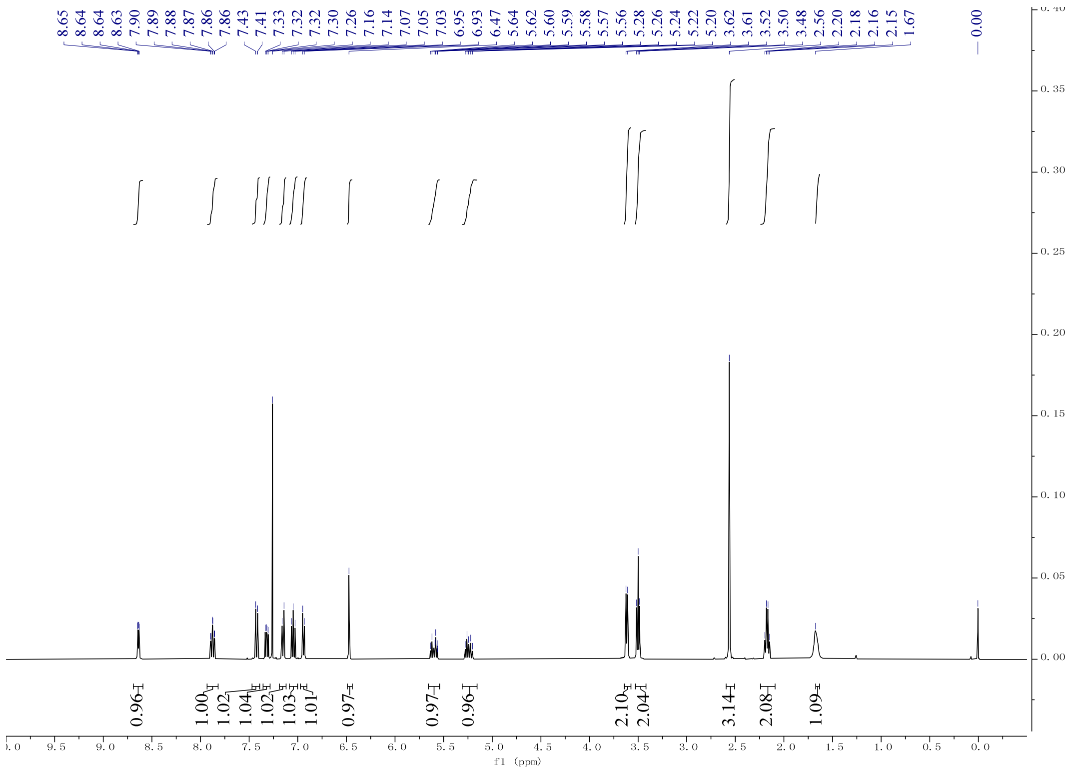


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5aa**

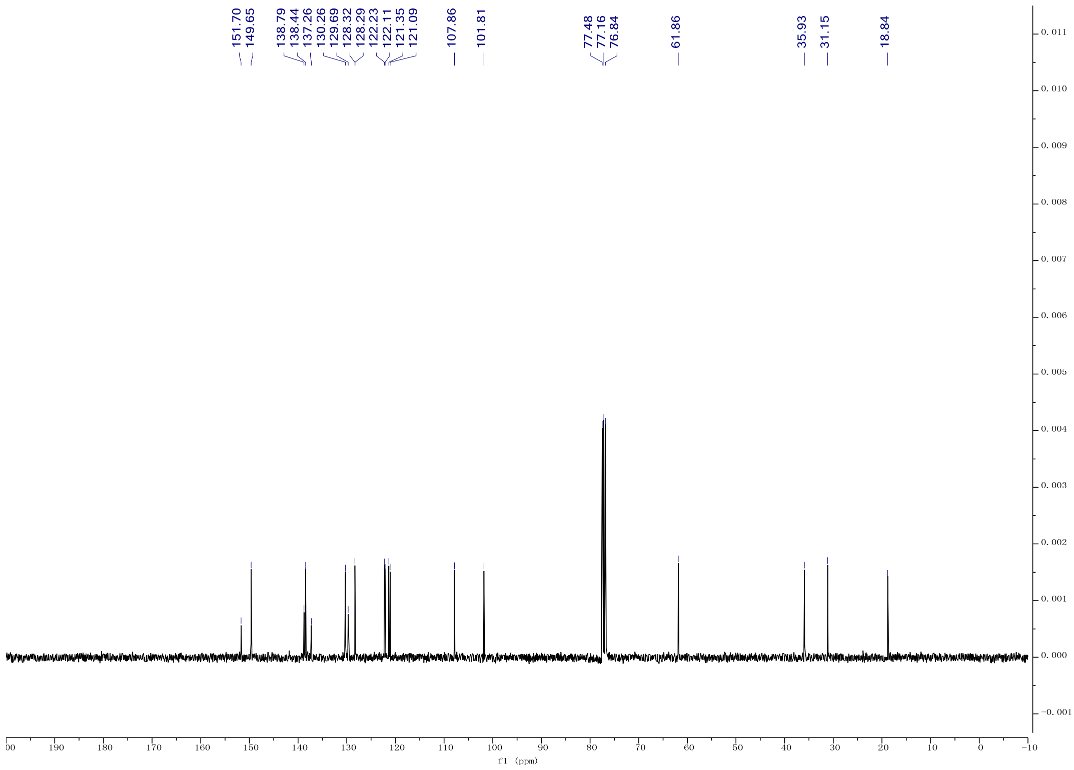


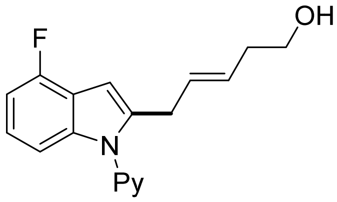


[1]H NMR (400 MHz, $CDCl_3$) Compound **5ba**

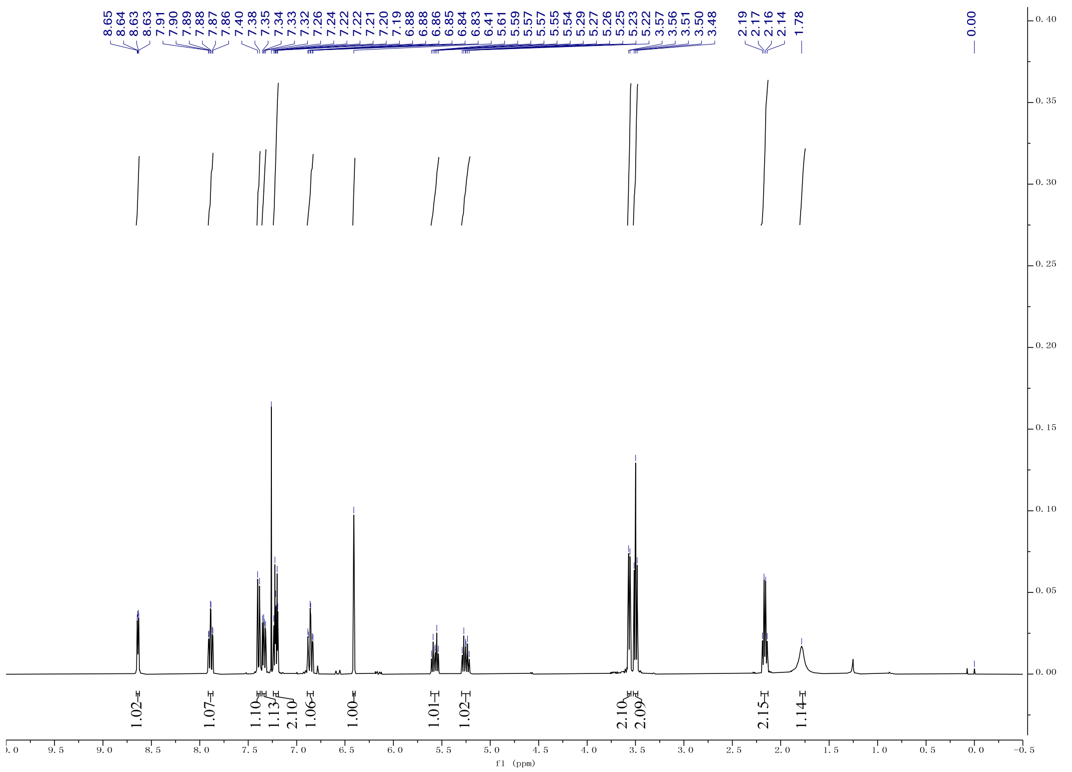


[13]C NMR (101 MHz, $CDCl_3$) Compound **5ba**

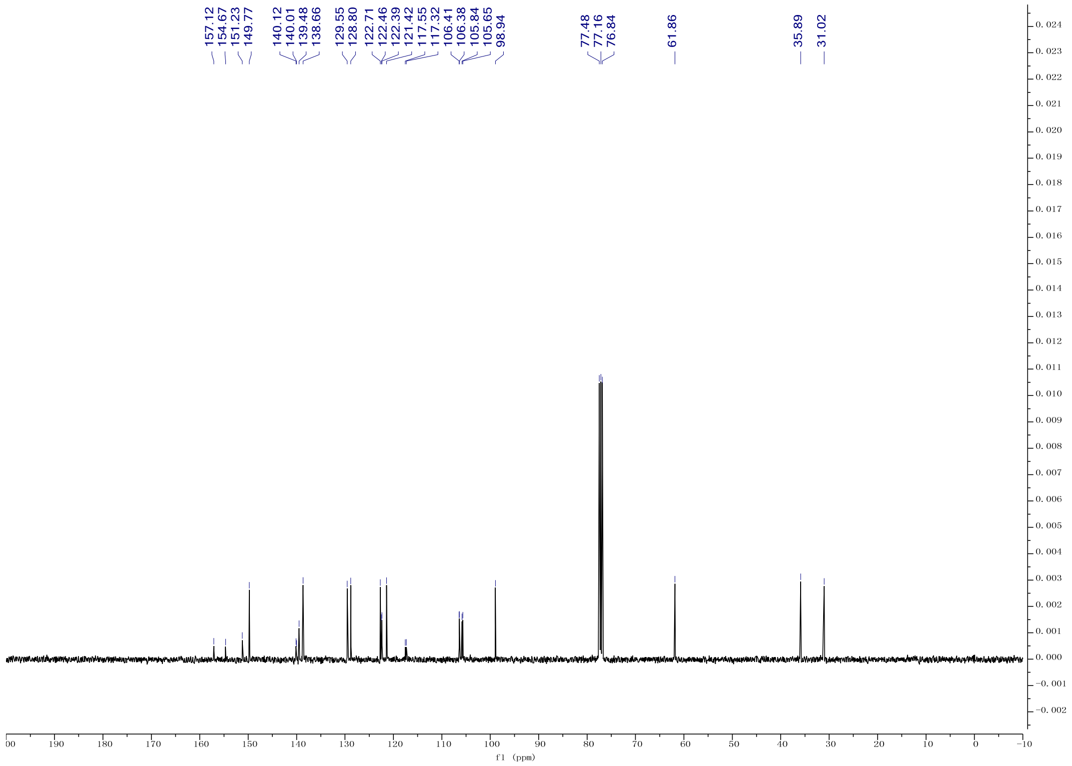


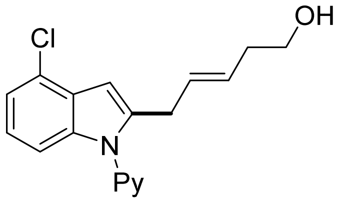


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5ca**



^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ca**





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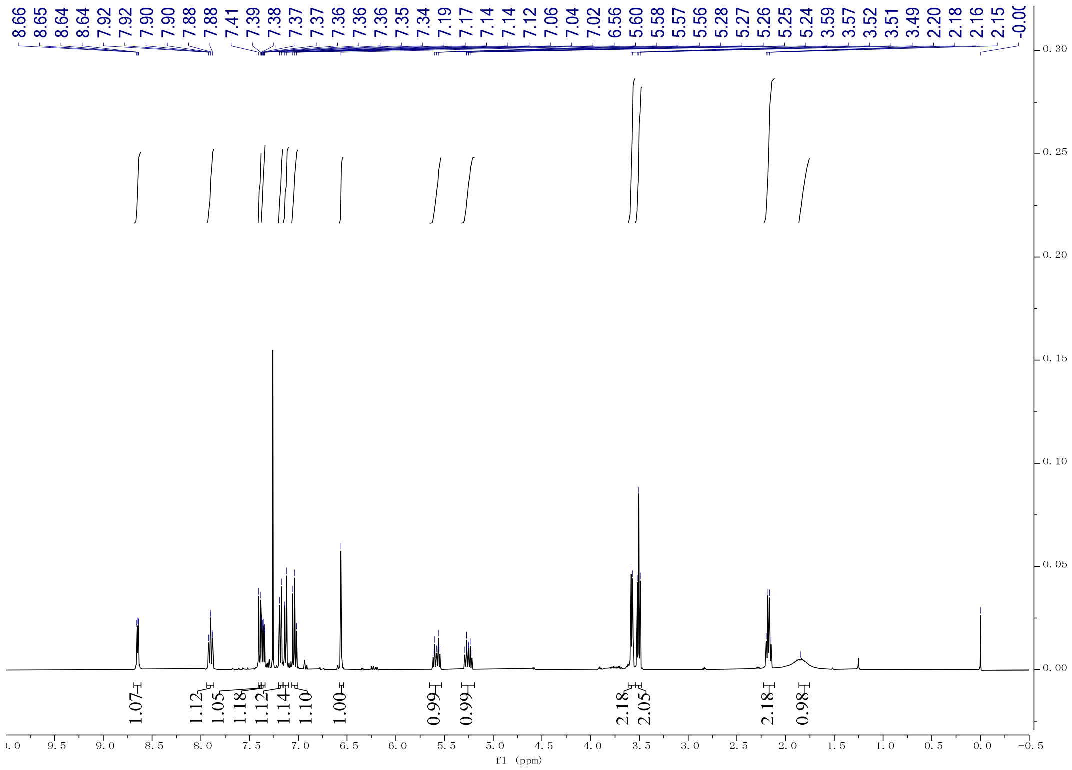
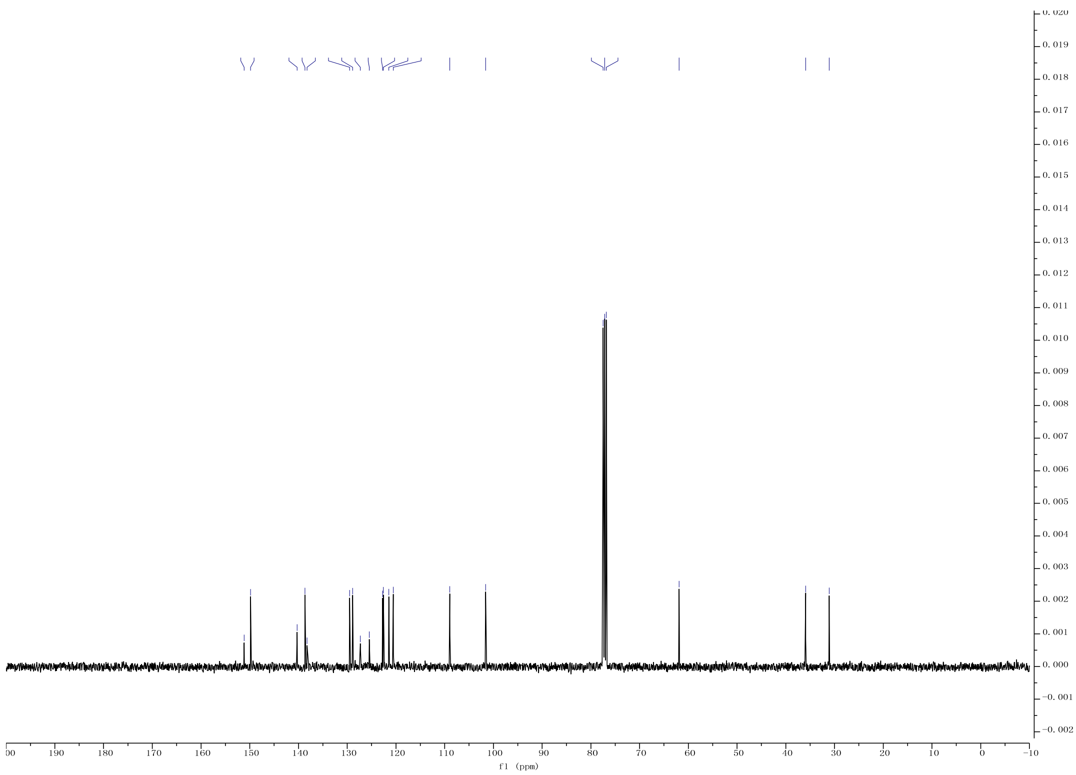
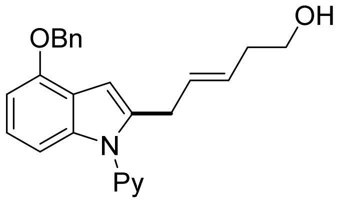
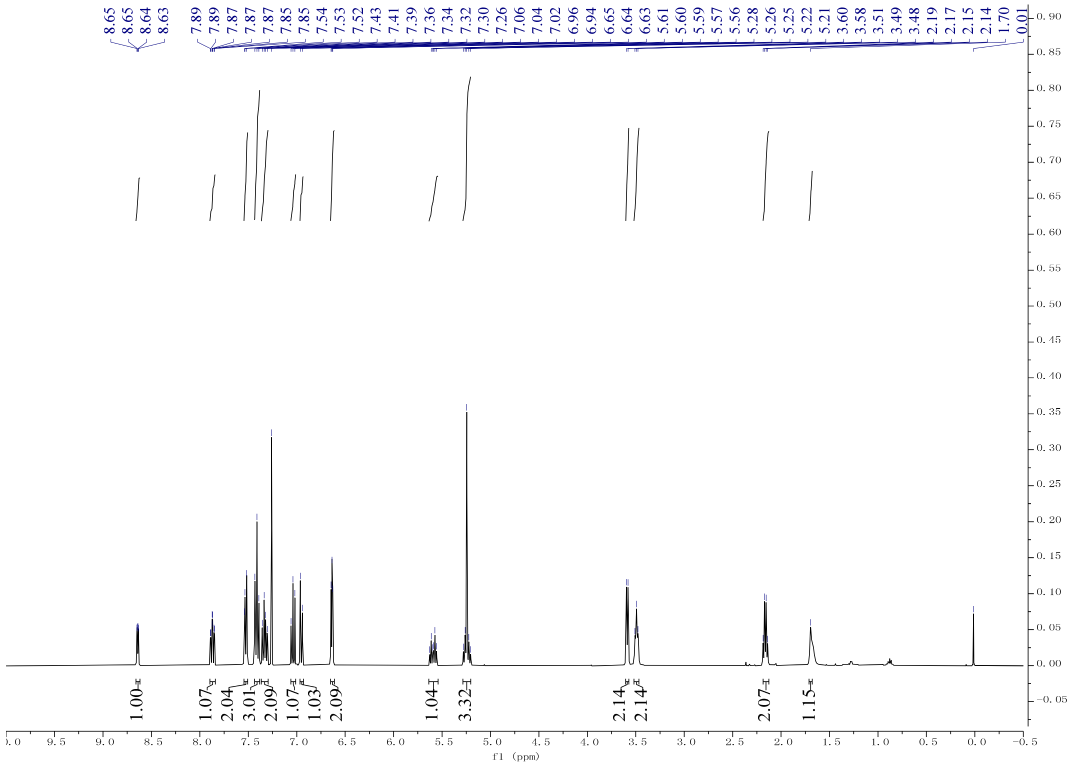


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5da**

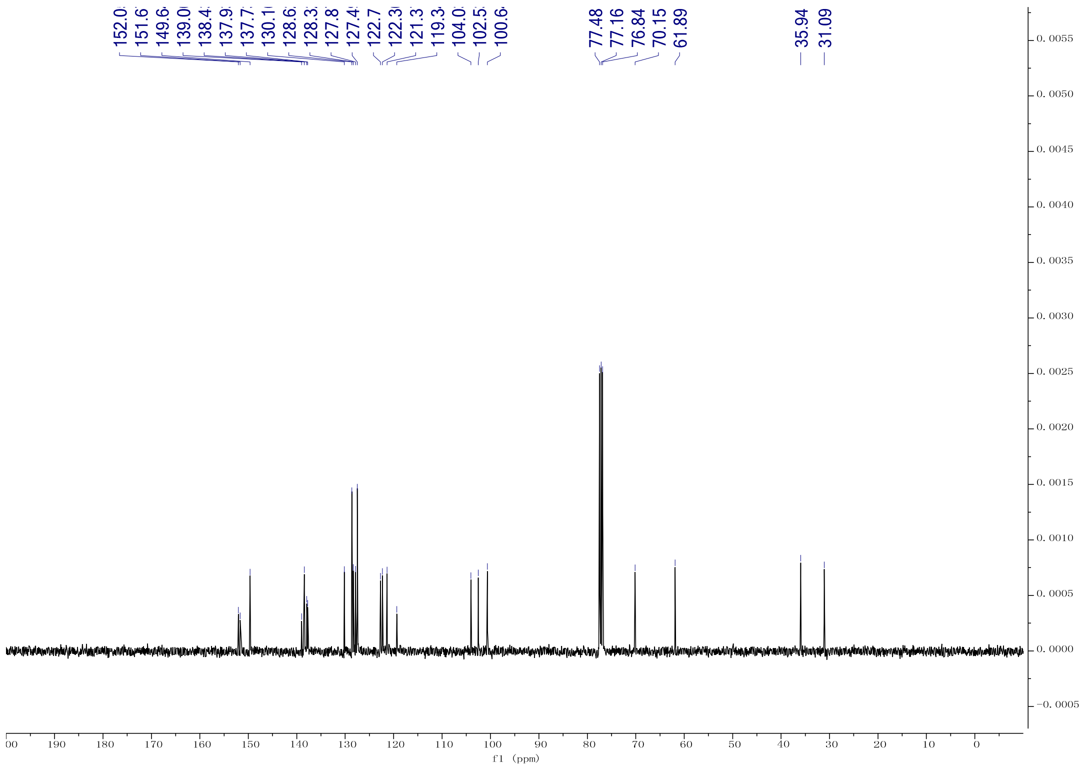


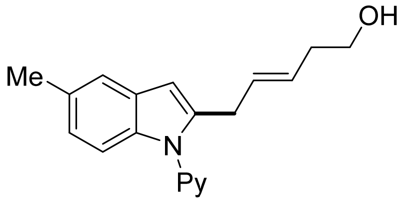


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5ea**

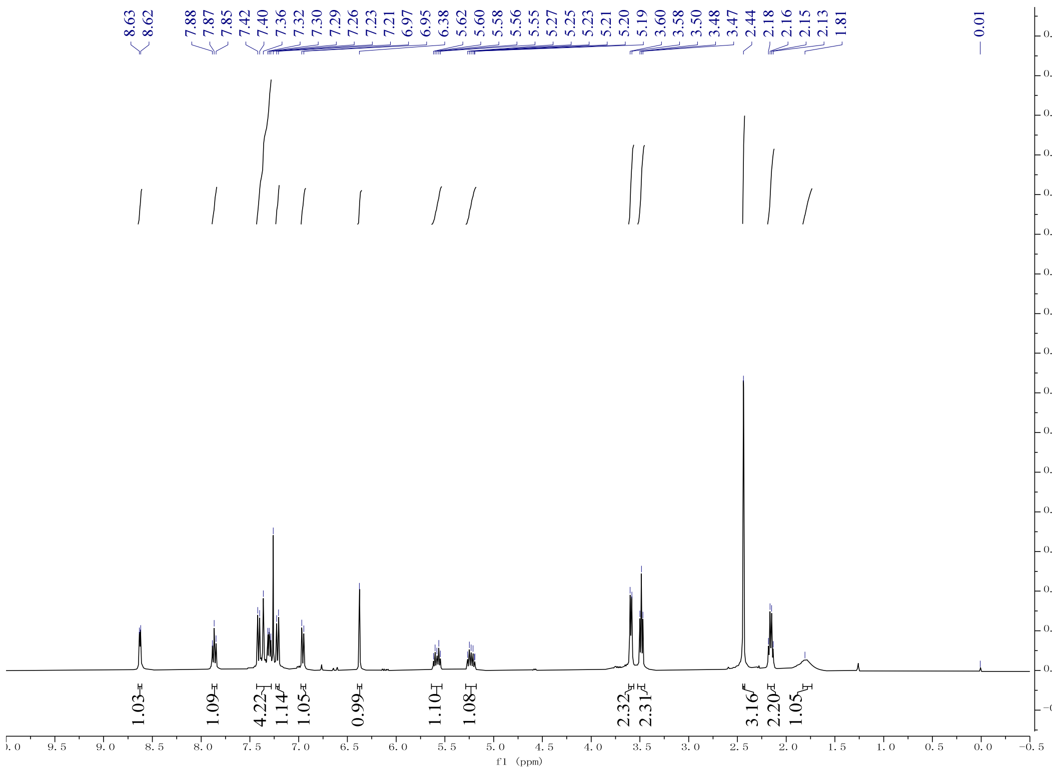


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ea**

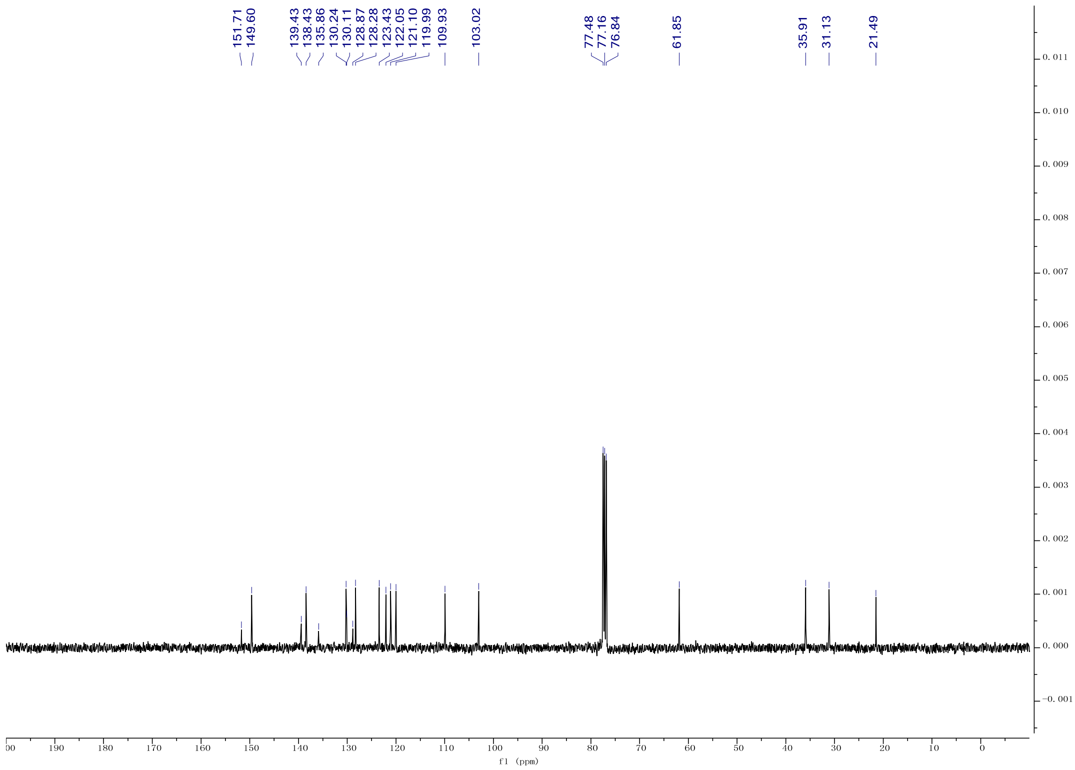


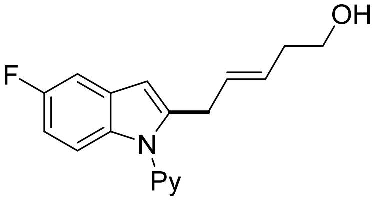


[1]H NMR (400 MHz, $CDCl_3$) Compound **5fa**

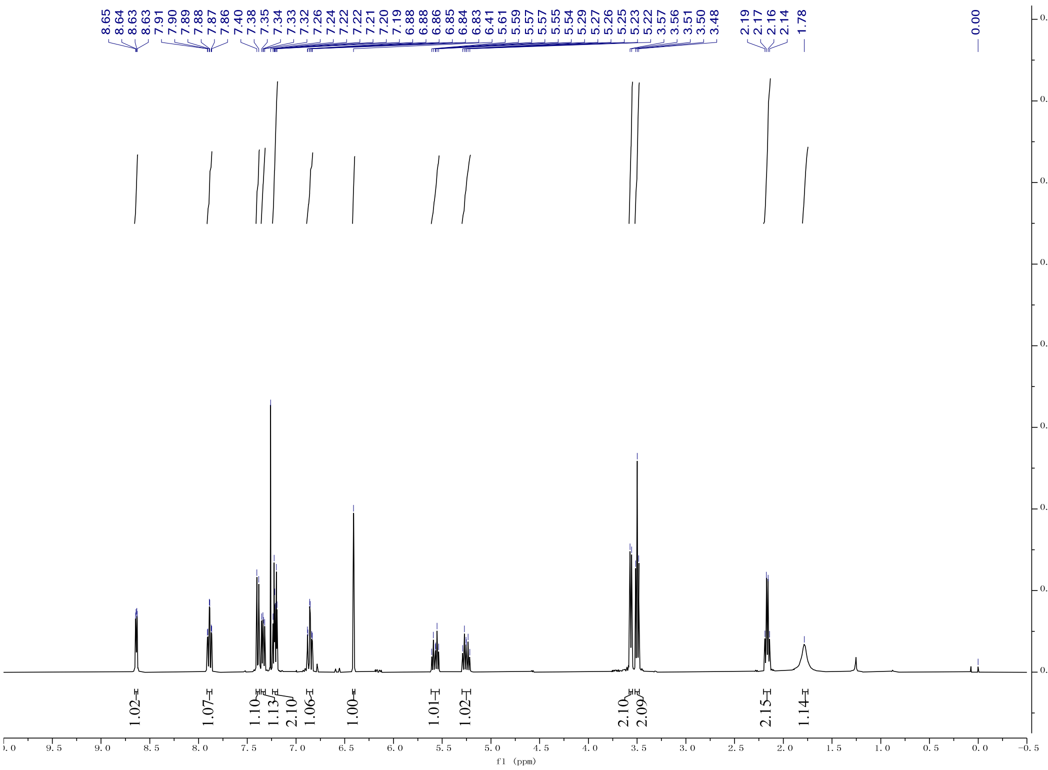


[13]C NMR (101 MHz, $CDCl_3$) Compound **5fa**

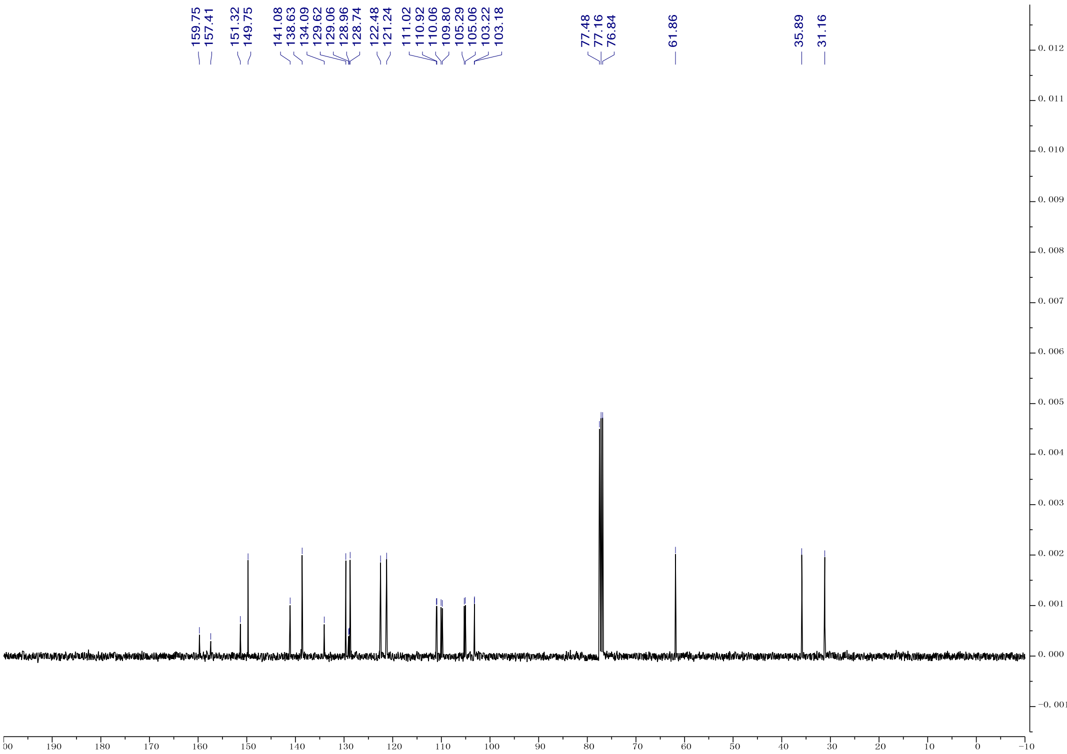


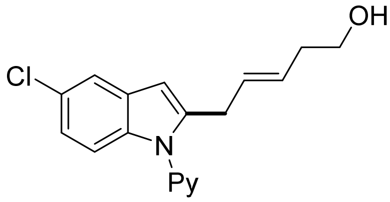


[1]H NMR (400 MHz, CDCl3) Compound **5ga**

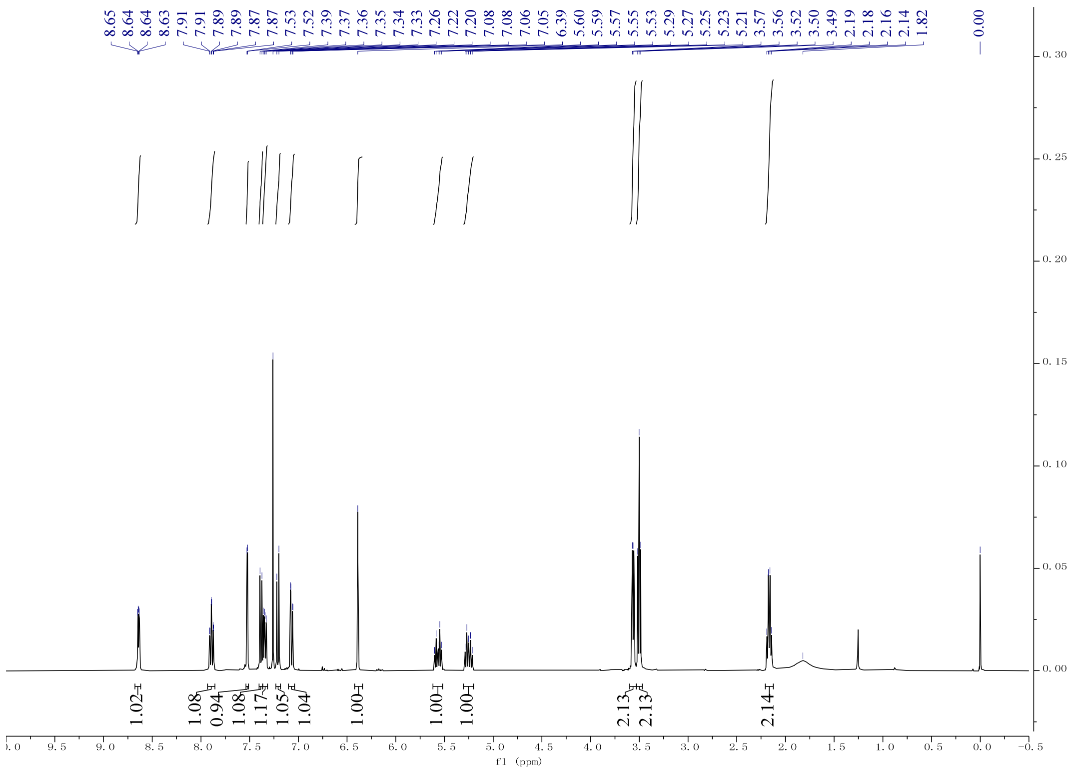


[13]C NMR (101 MHz, CDCl3) Compound **5ga**

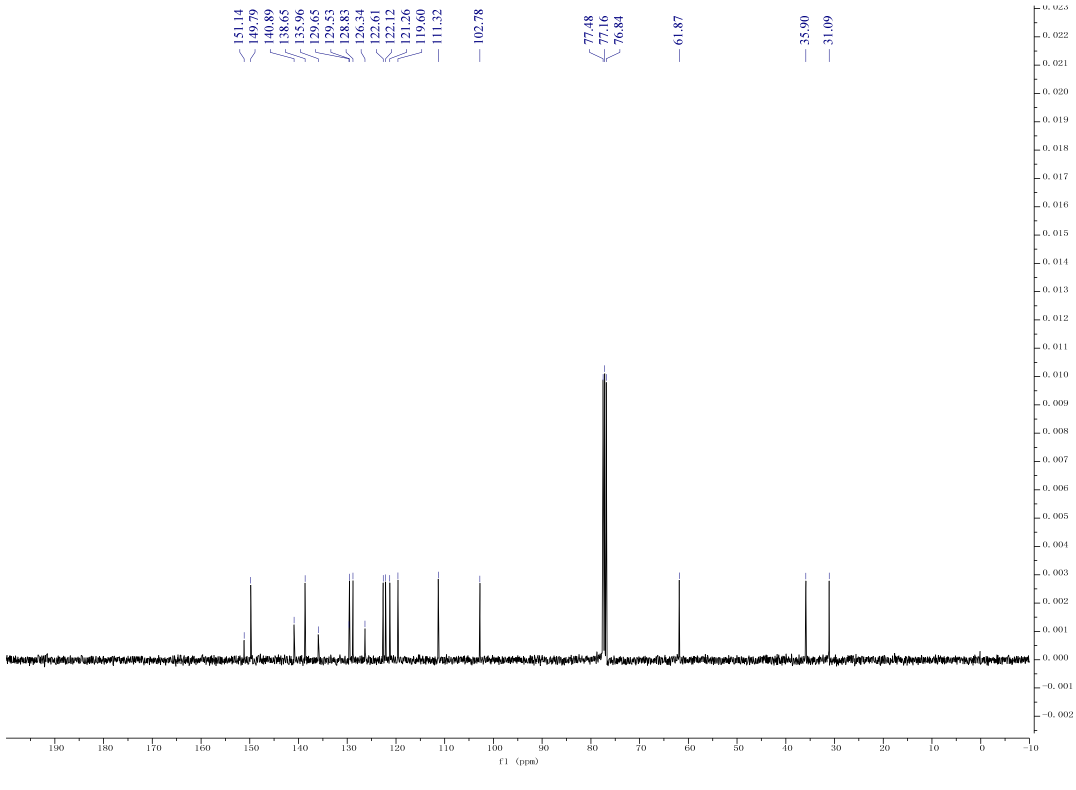


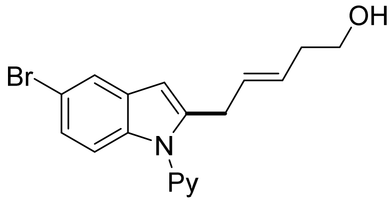


[1]H NMR (400 MHz, $CDCl_3$) Compound **5ha**

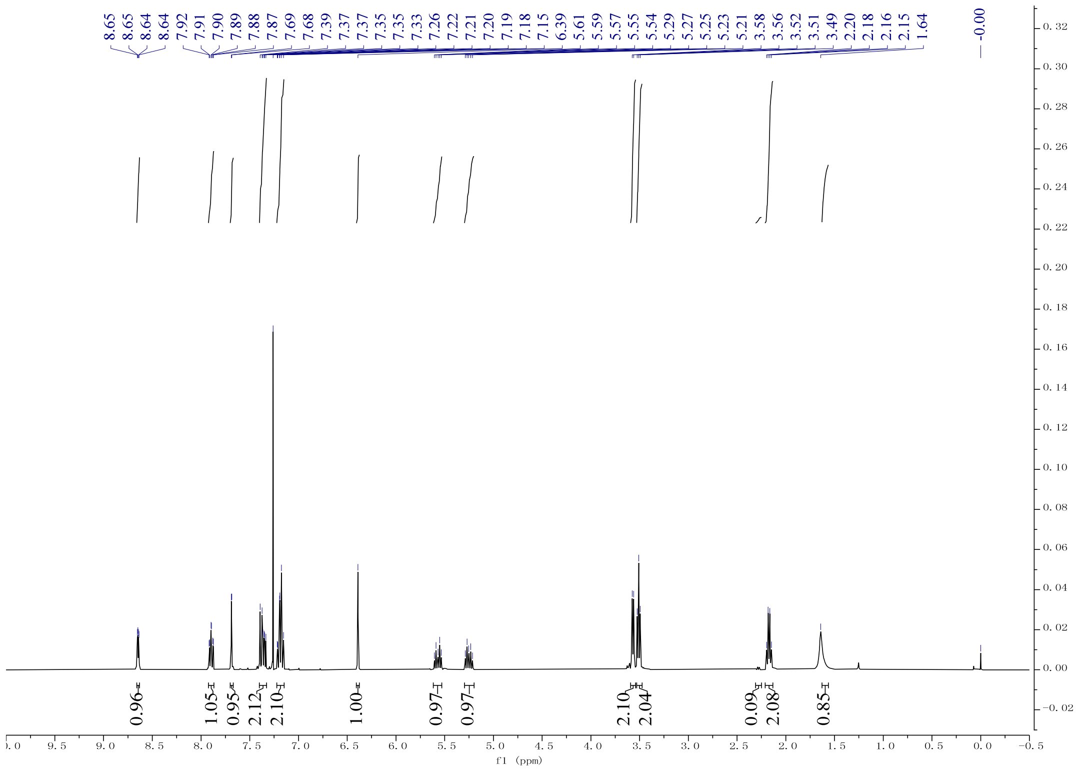


[13]C NMR (101 MHz, $CDCl_3$) Compound **5ha**

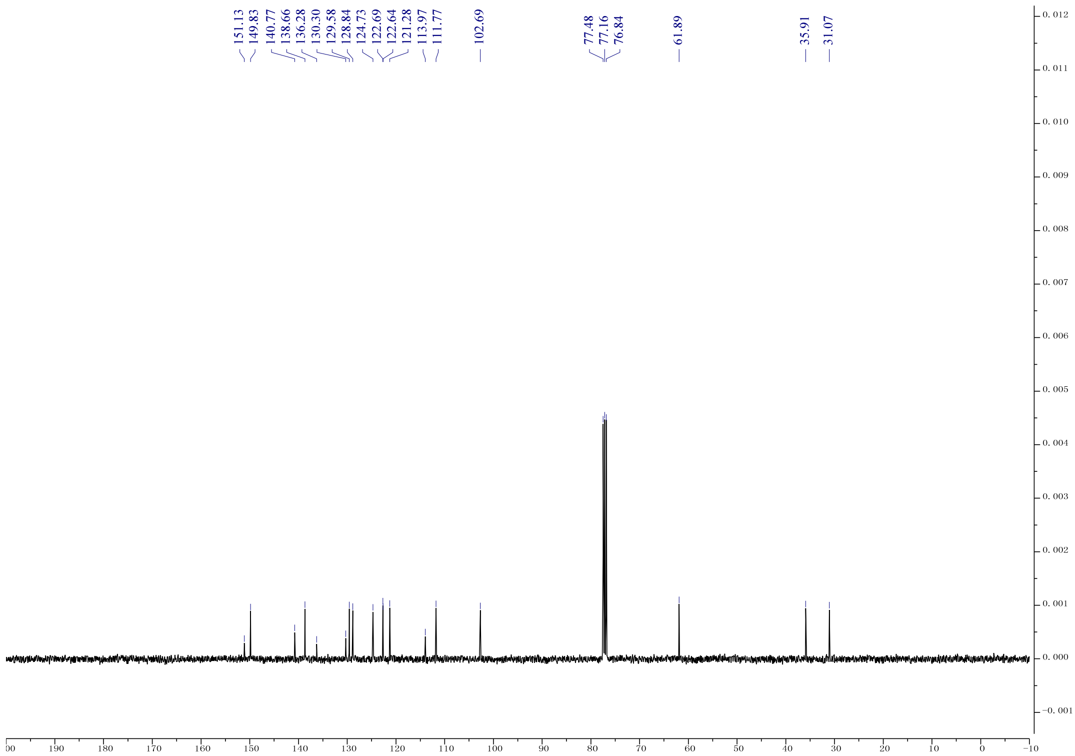


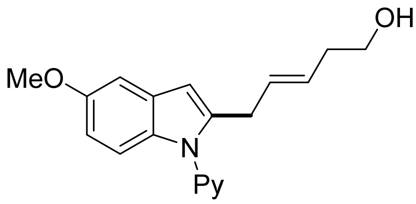


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5ia**

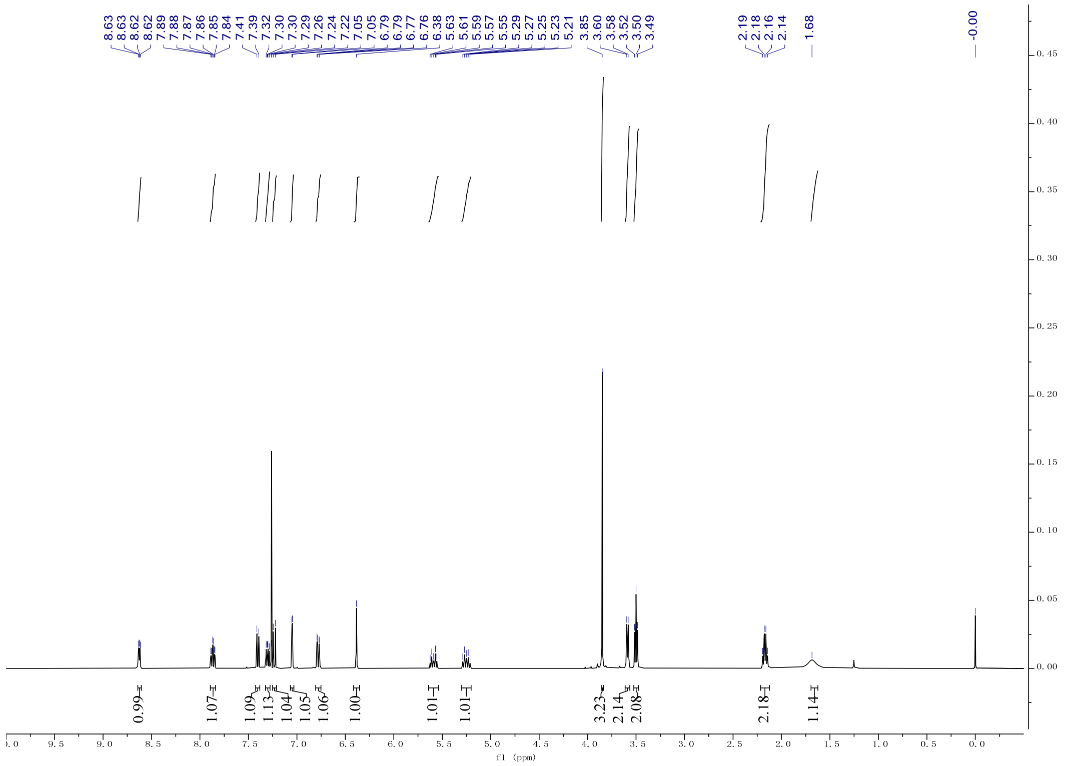


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ia**

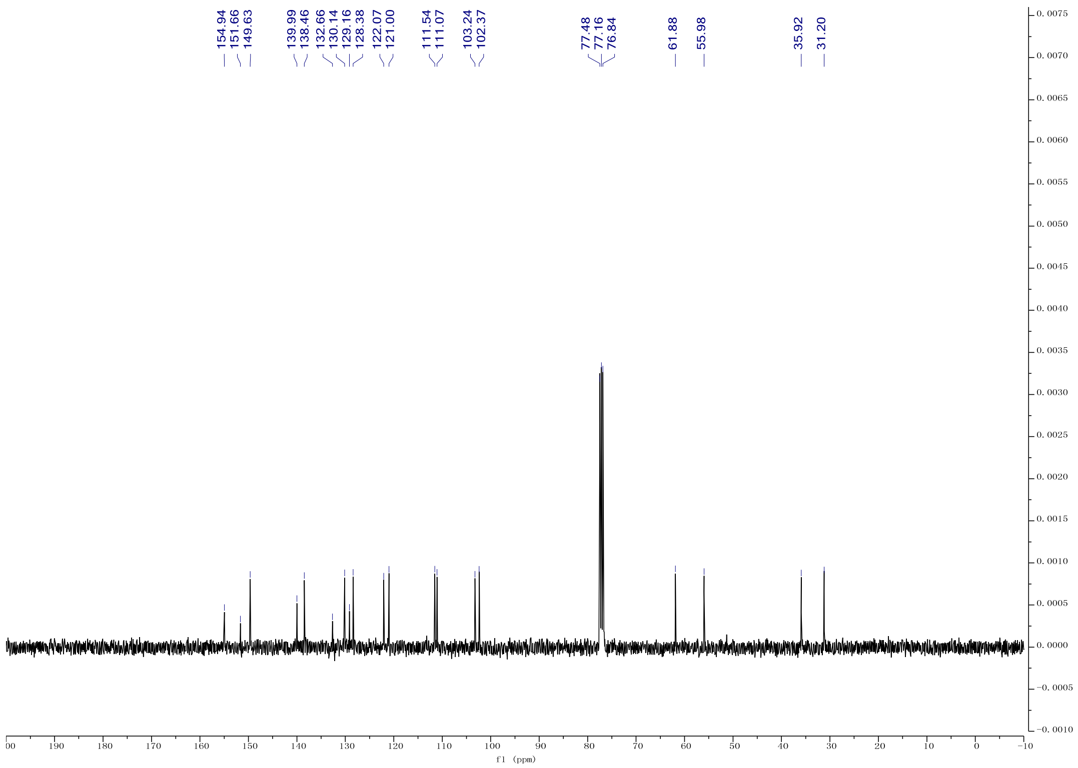


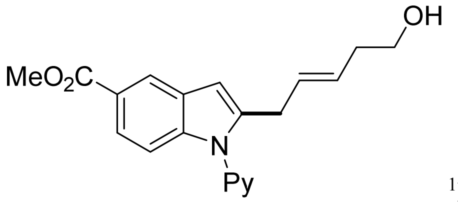


[1]H NMR (400 MHz, $CDCl_3$) Compound **5ja**

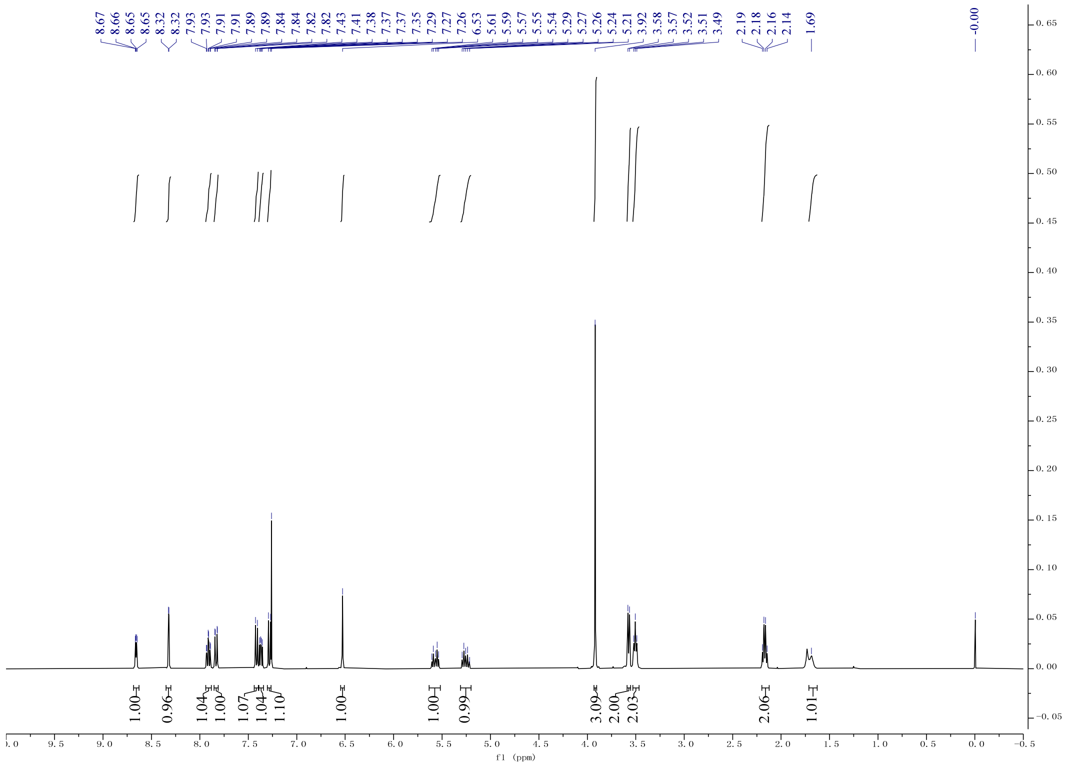


[13]C NMR (101 MHz, $CDCl_3$) Compound **5ja**

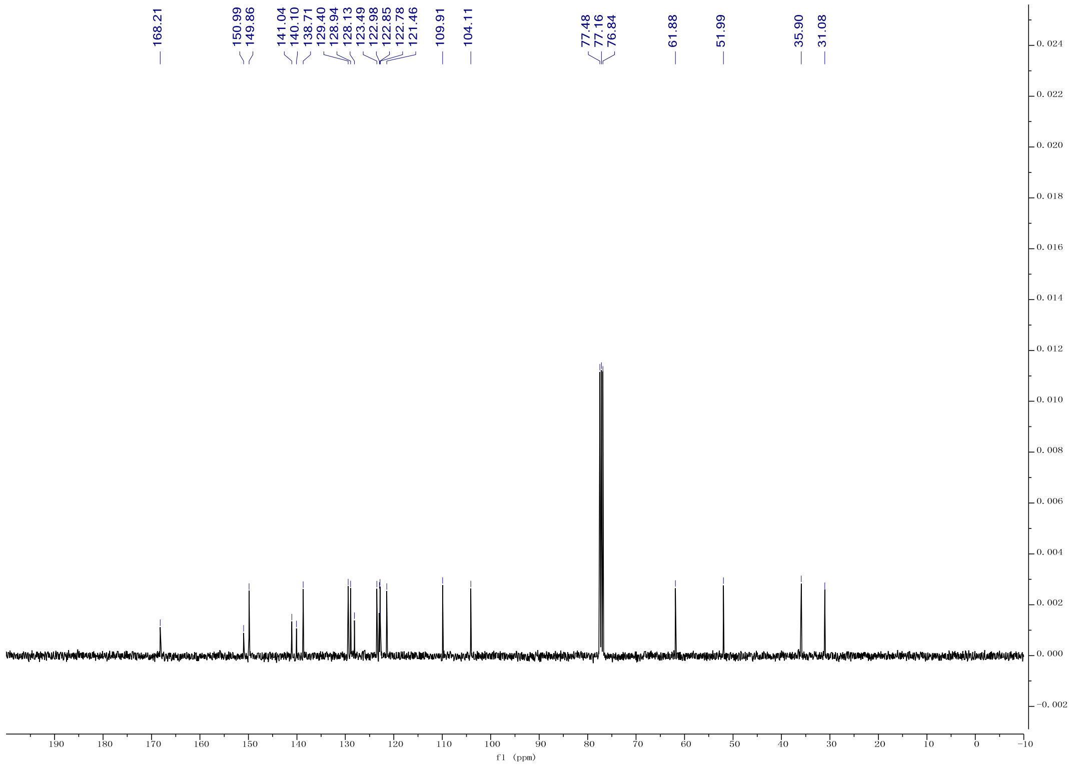


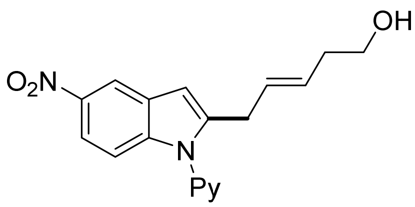


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5ka**

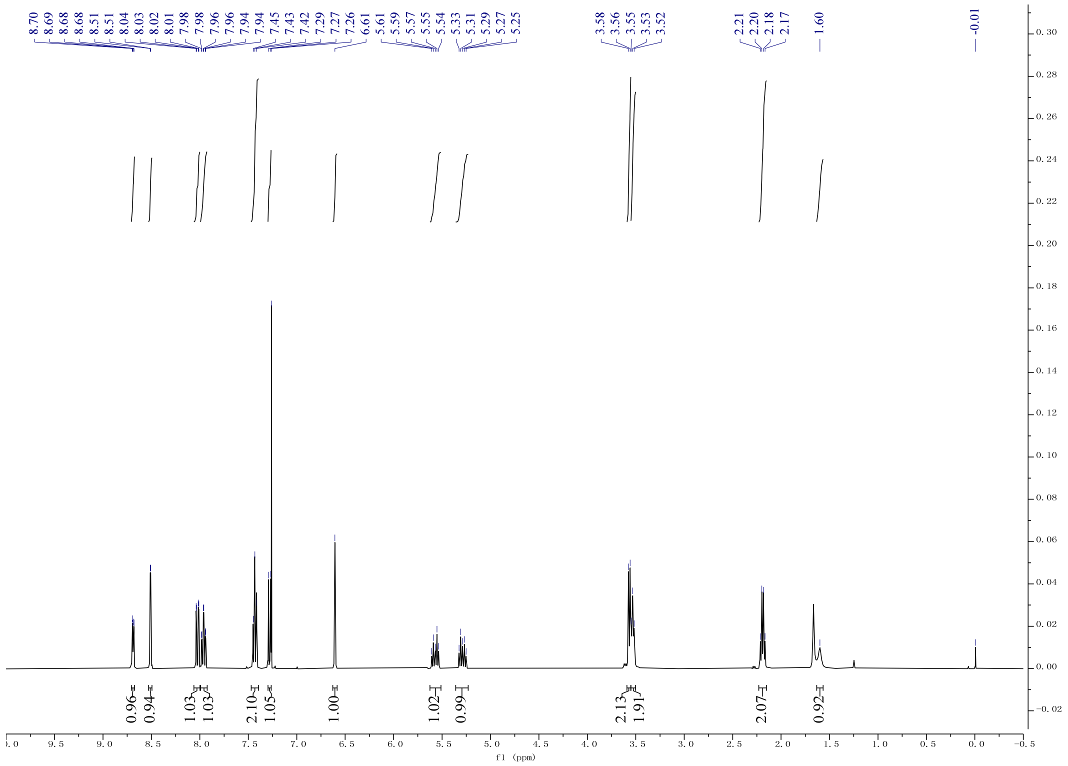


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ka**

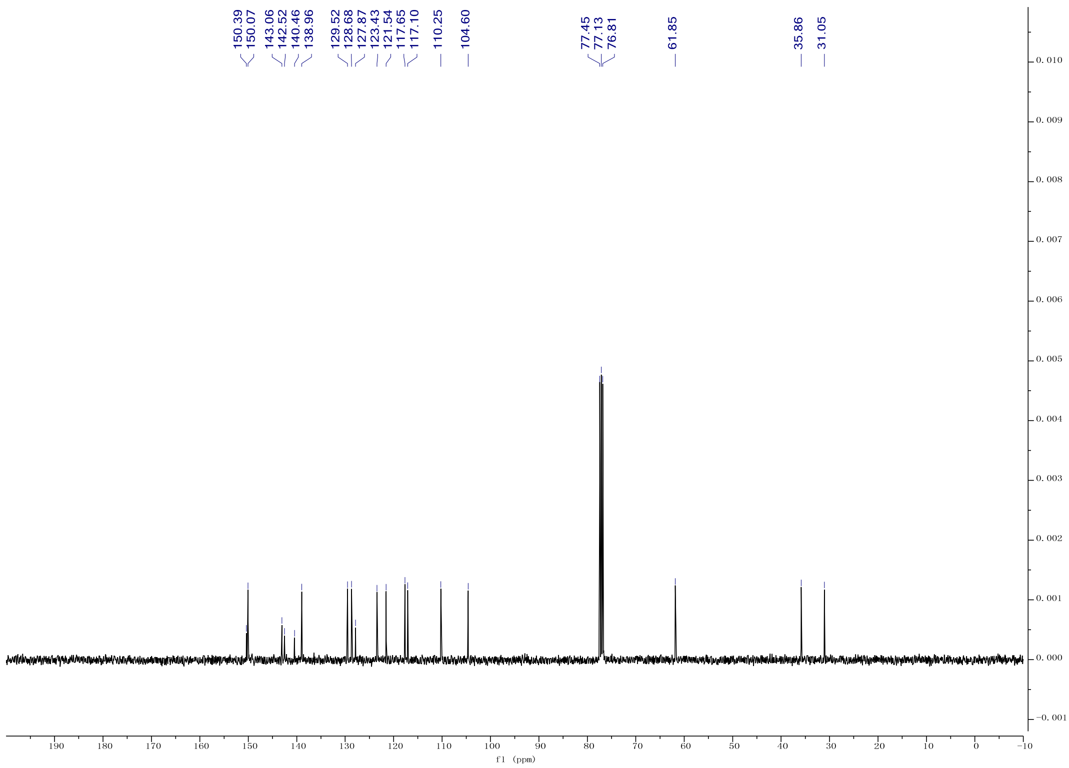


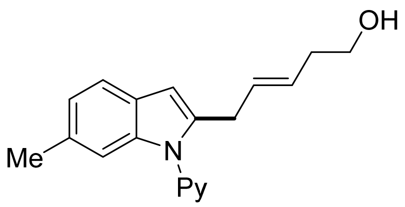


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5la**

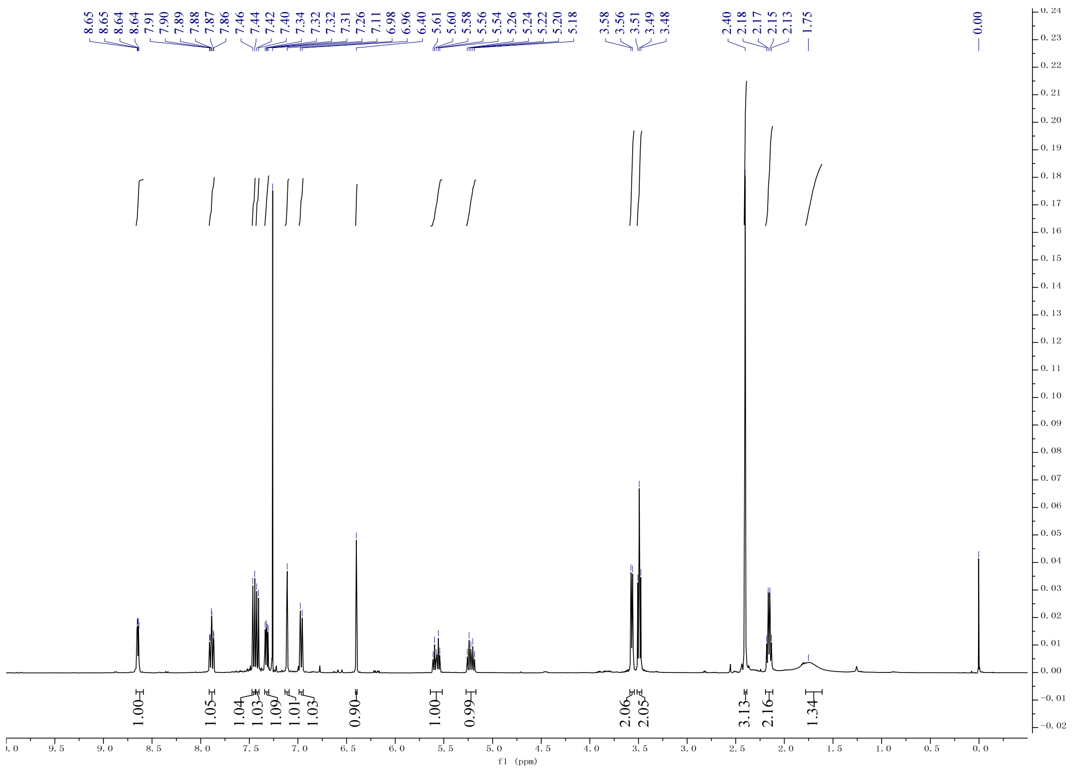


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5la**

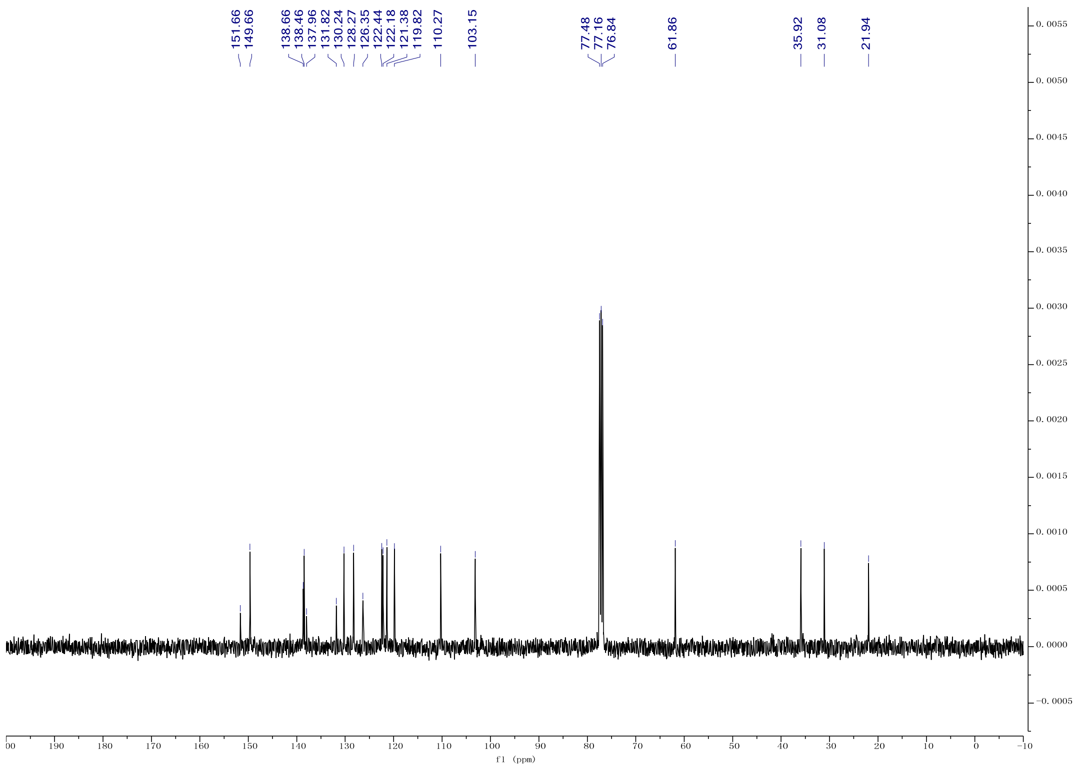


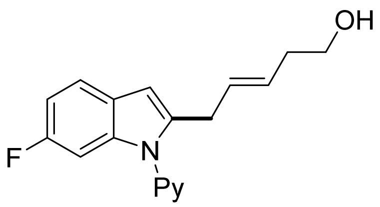


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5ma**

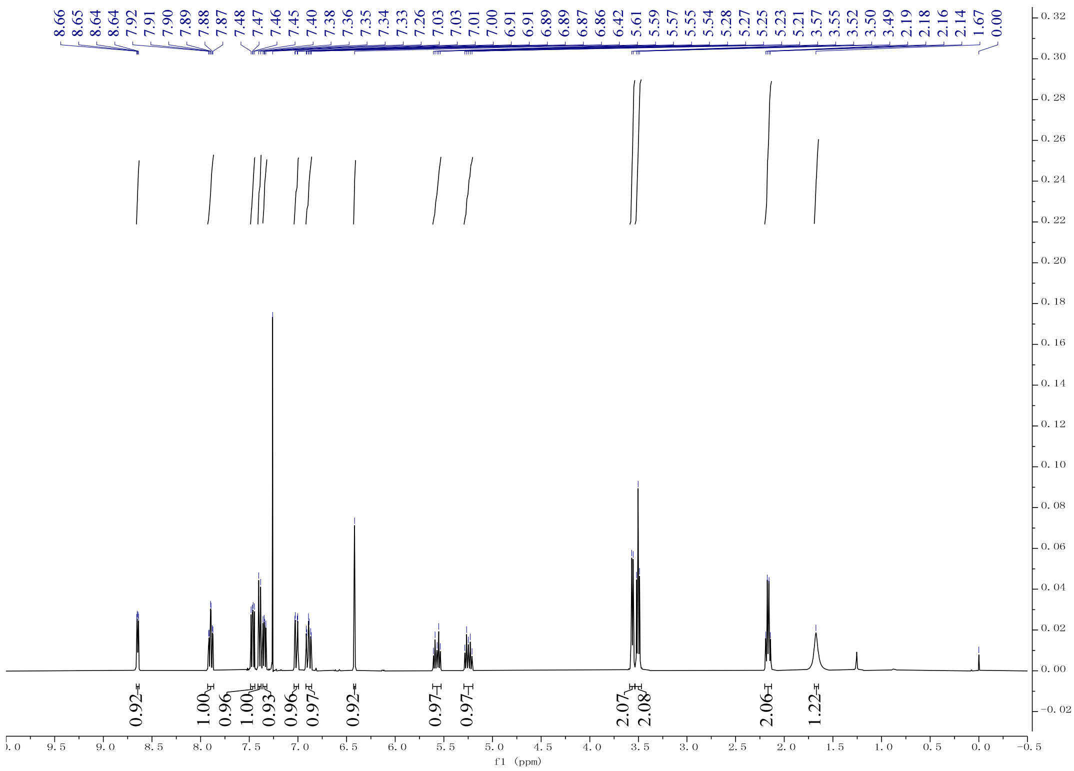


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ma**

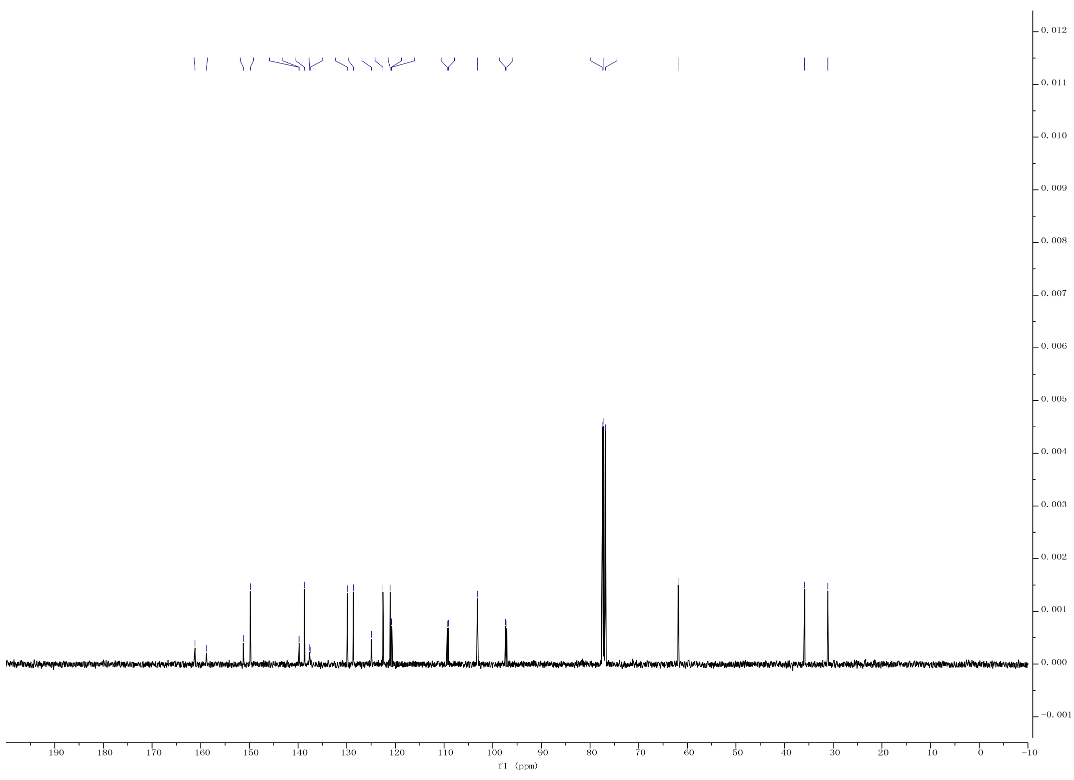


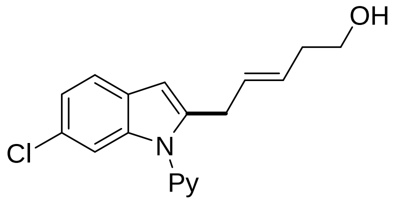


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5na**

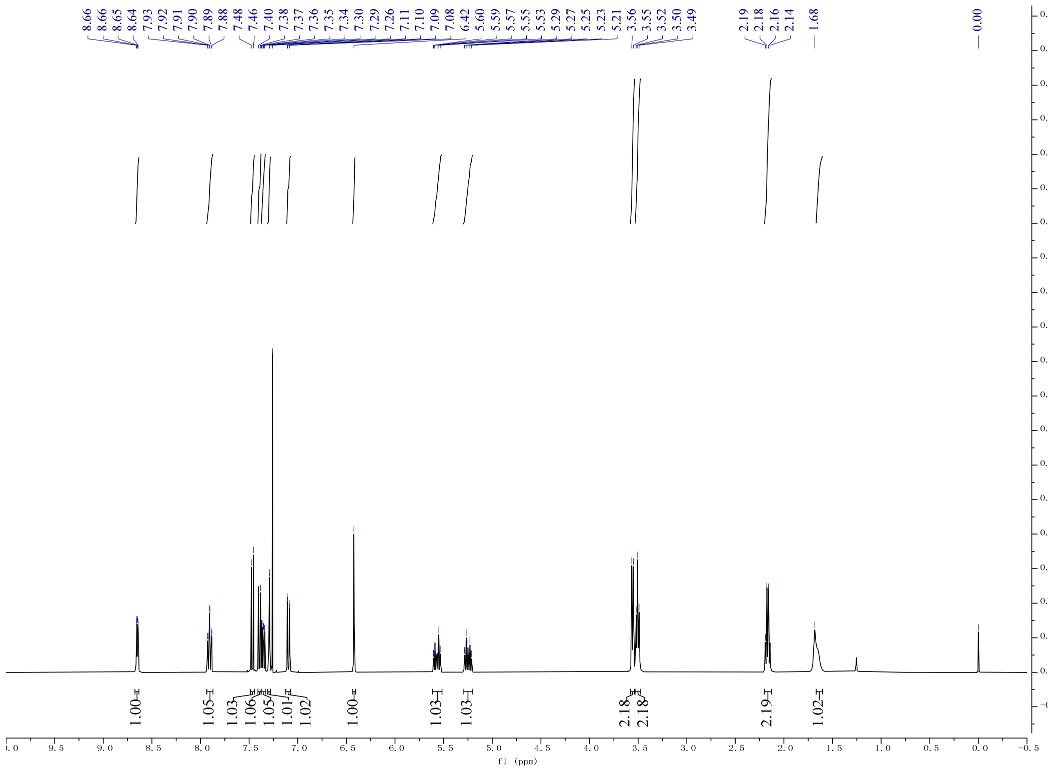


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5na**

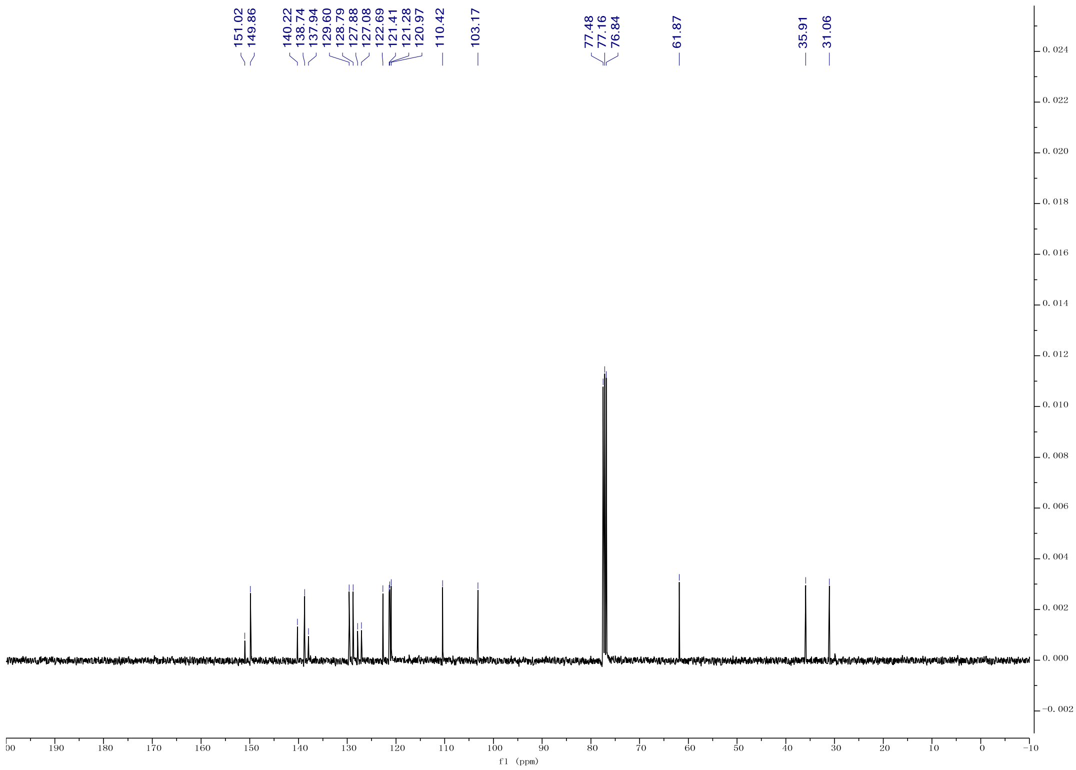


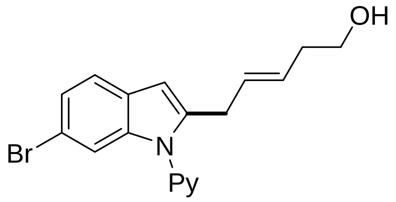


[1]H NMR (400 MHz, $CDCl_3$) Compound **5oa**

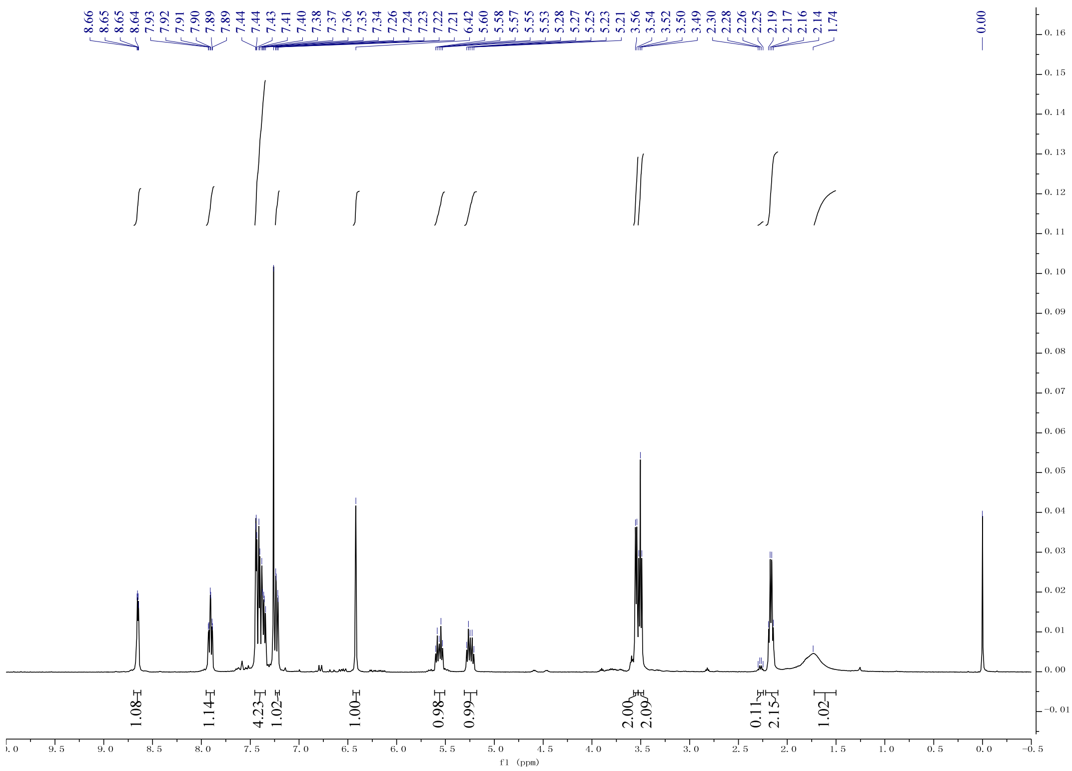


[13]C NMR (101 MHz, $CDCl_3$) Compound **5oa**

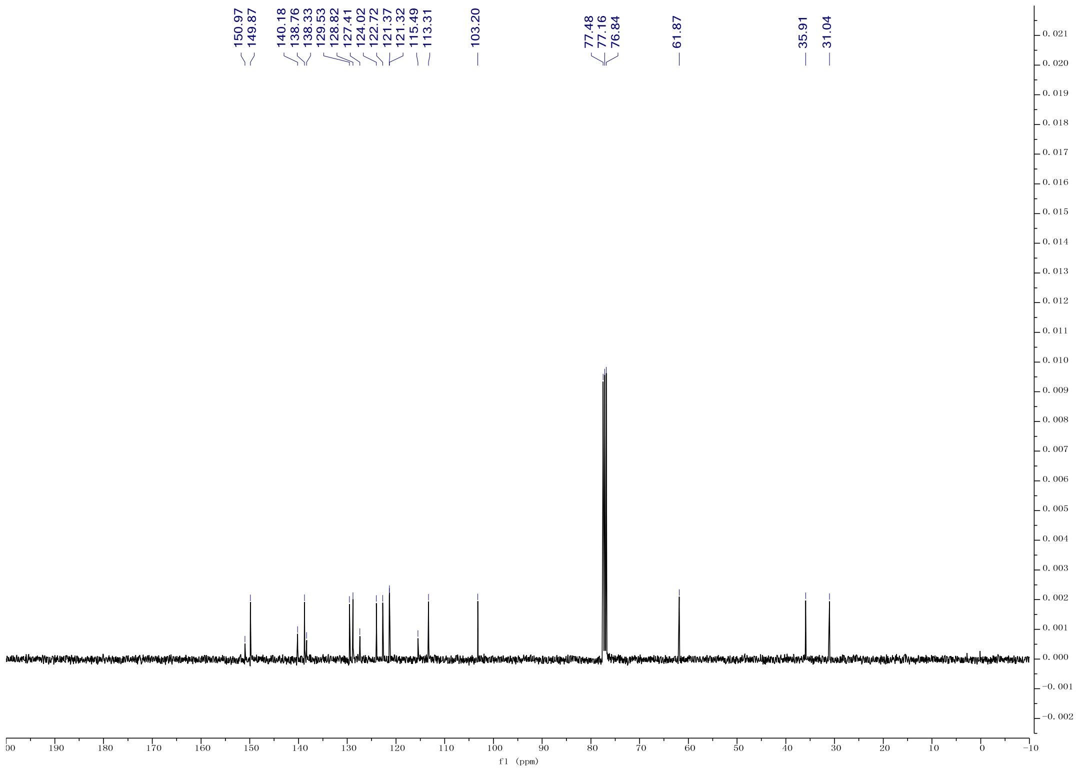


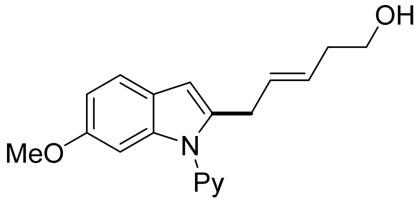


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5pa**



^{13}C NMR (101 MHz, $CDCl_3$) Compound **5pa**





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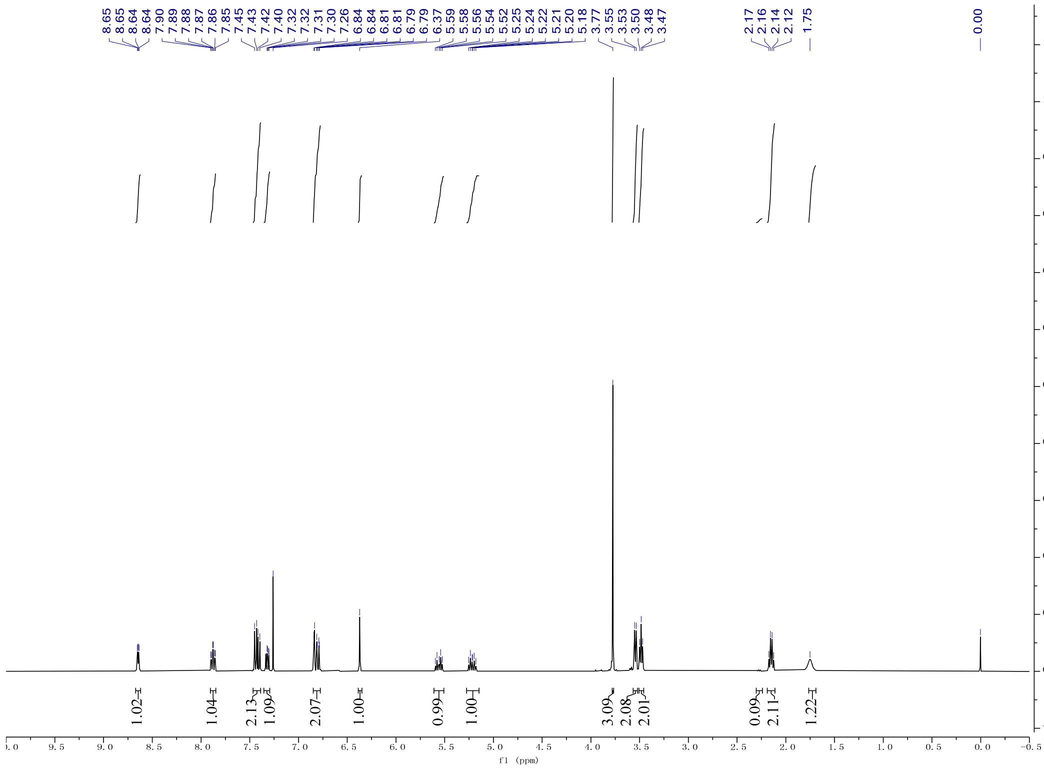

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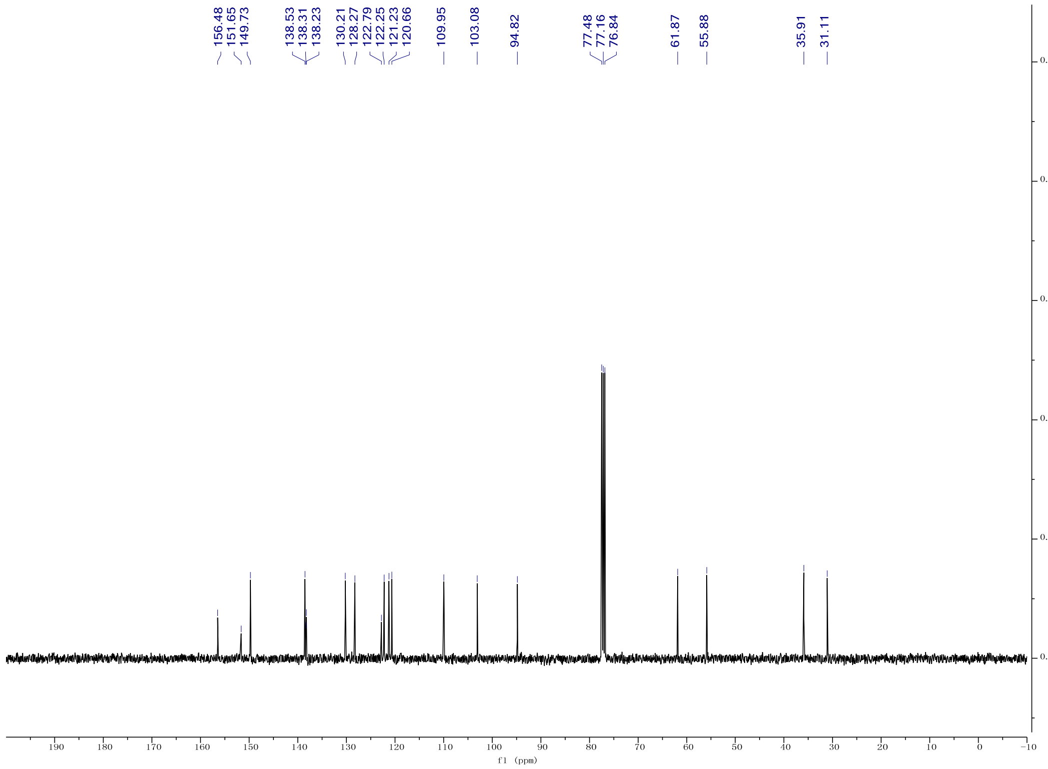

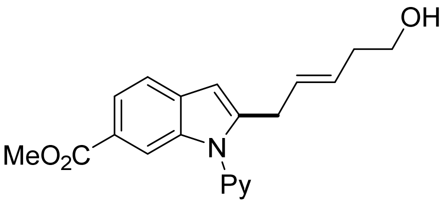

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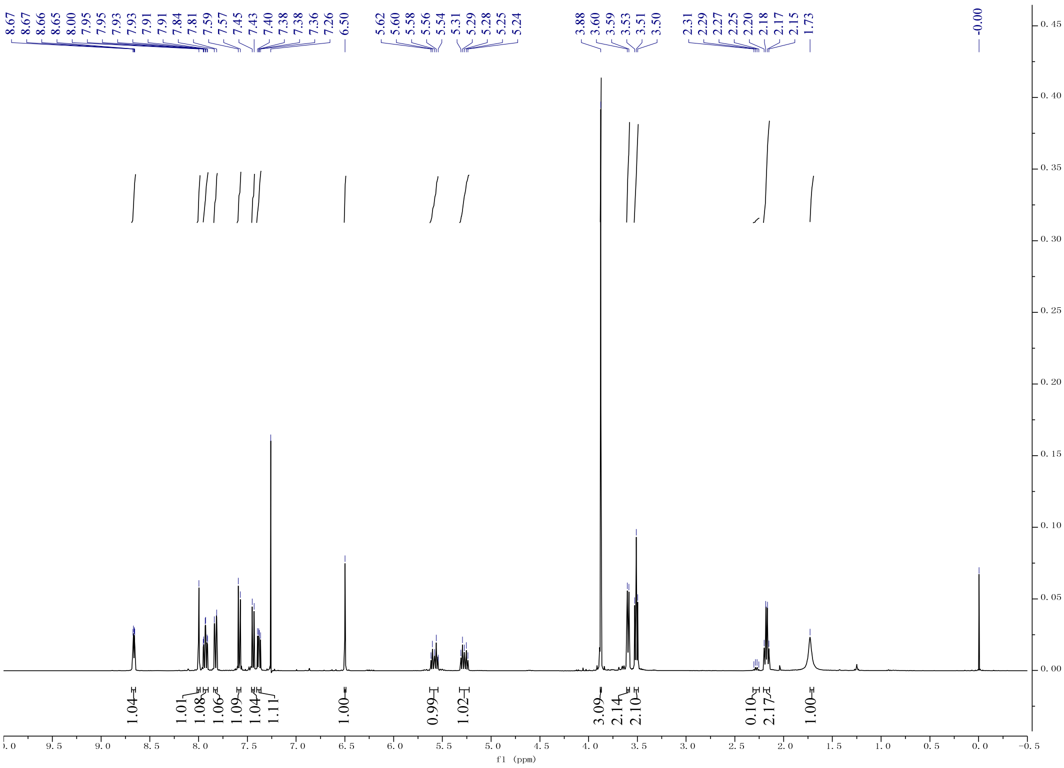
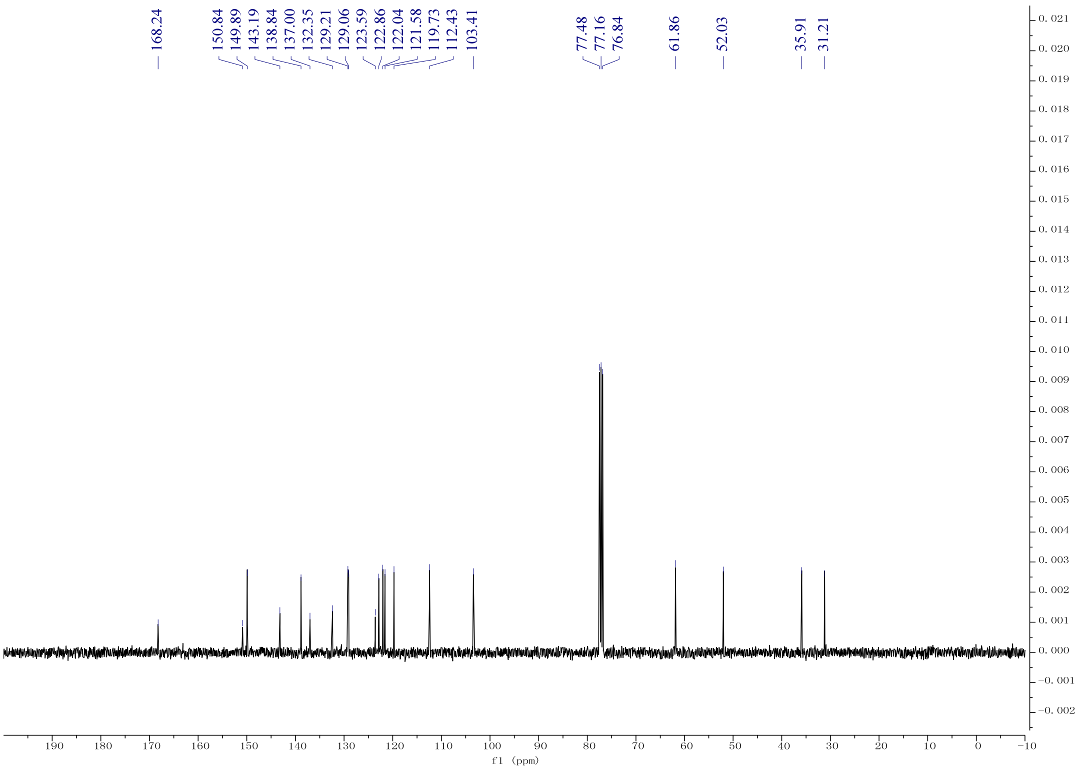
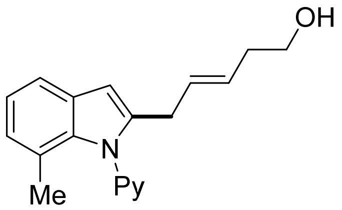
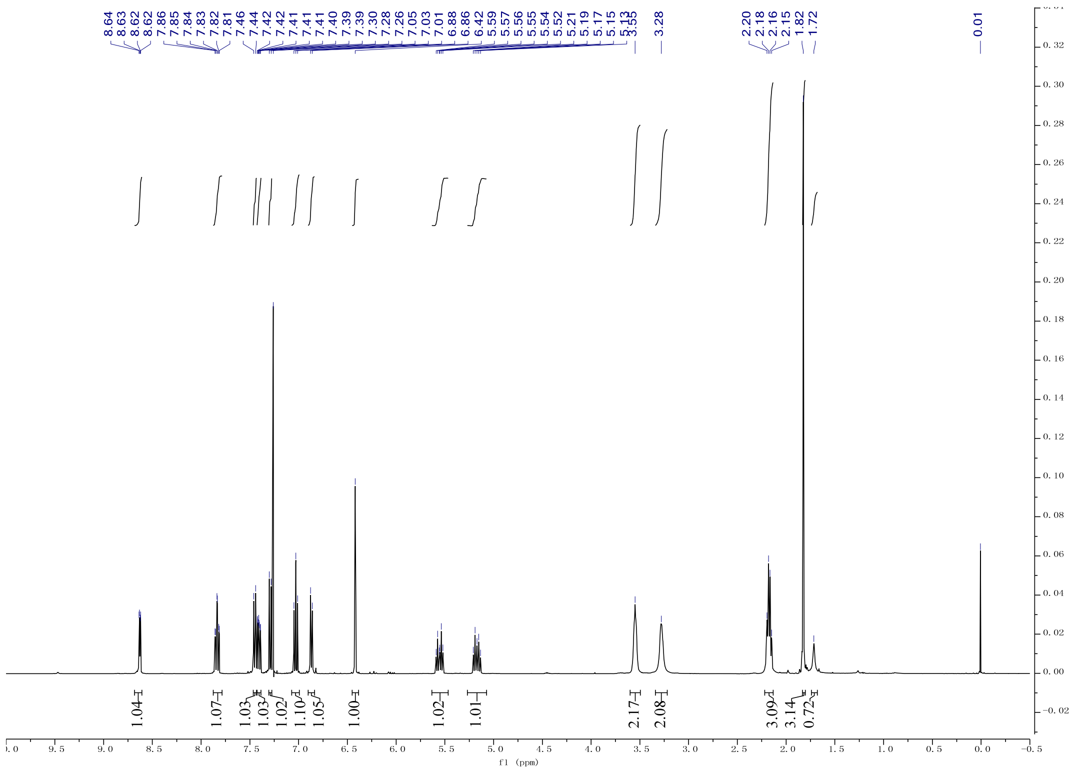


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ra**





^{1}H NMR (400 MHz, $CDCl_3$) Compound **5sa**



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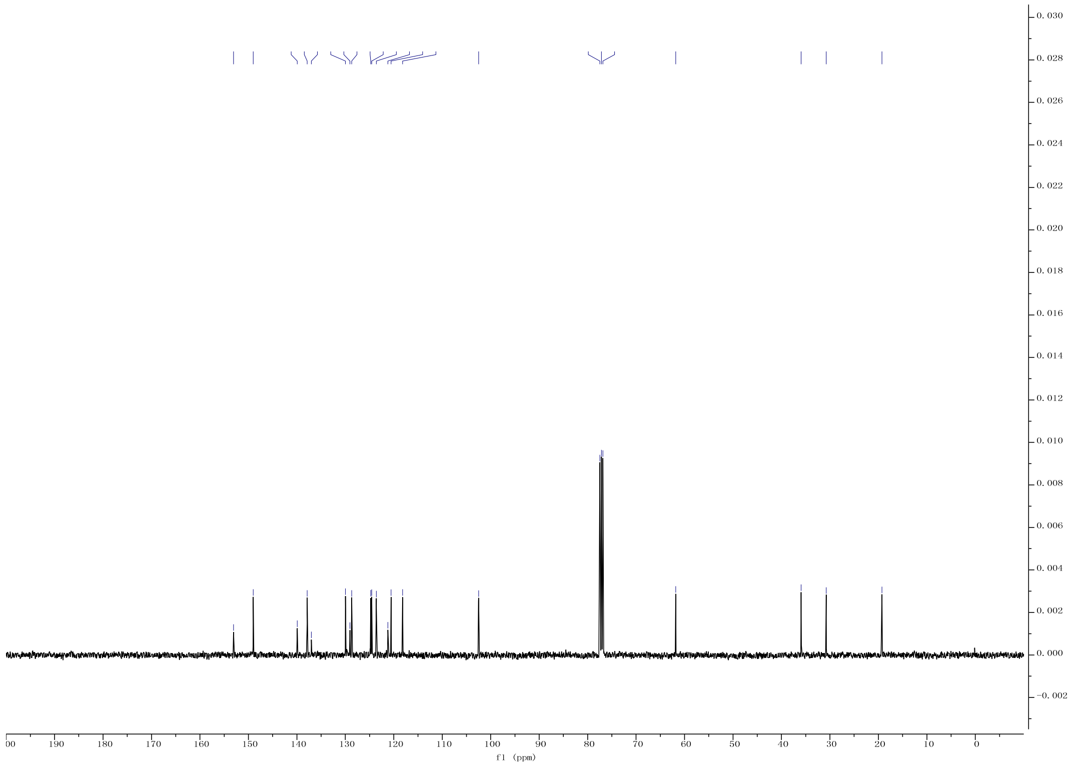
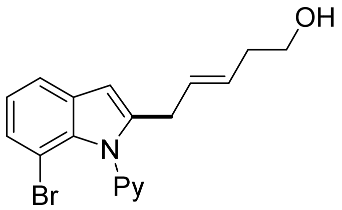
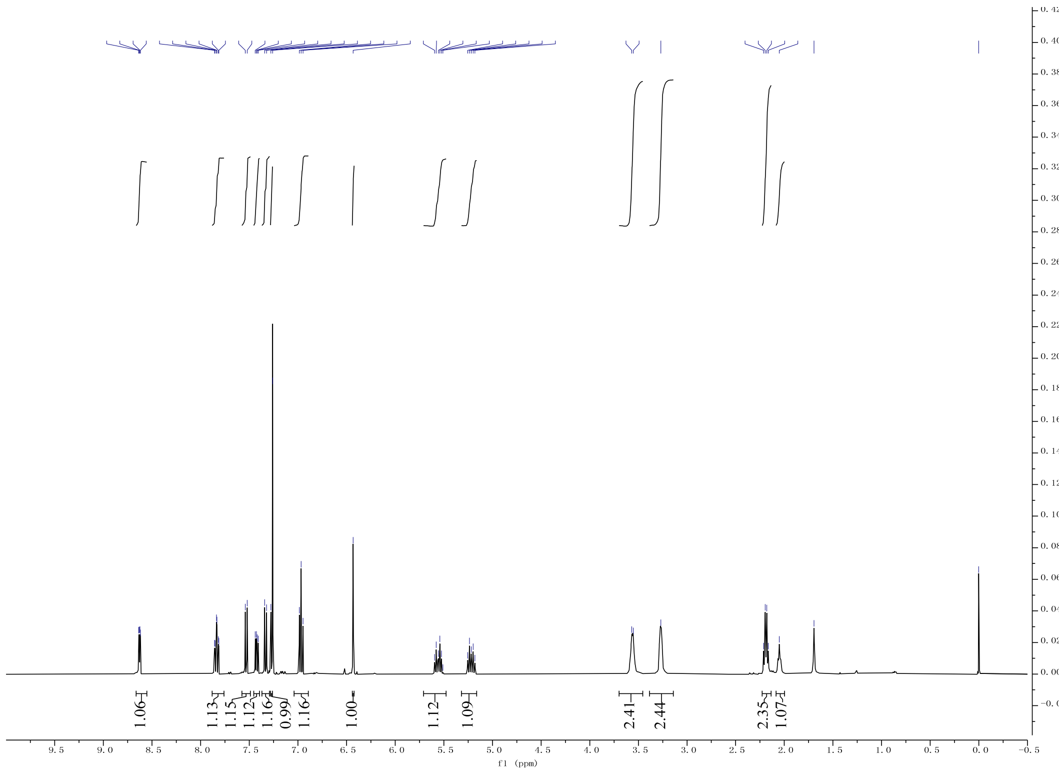
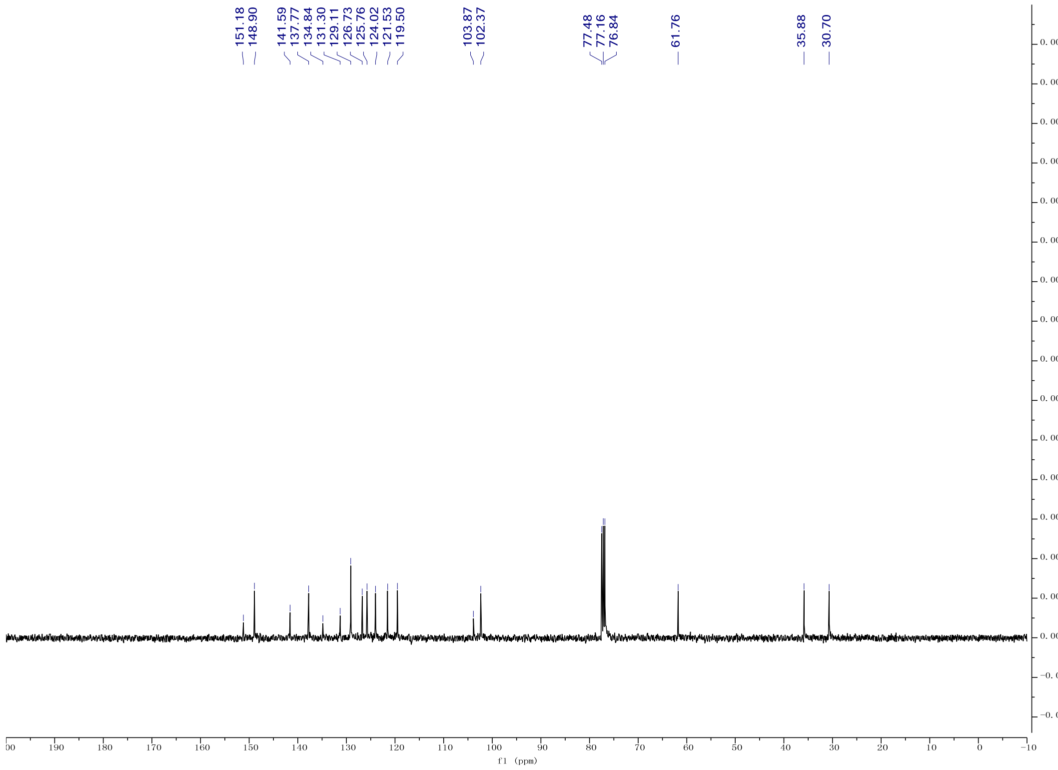


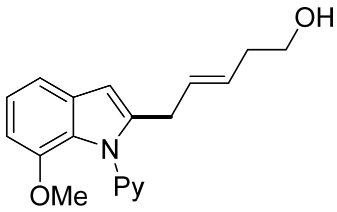


^1H NMR (400 MHz, $CDCl_3$) Compound **5ta**



^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ta**





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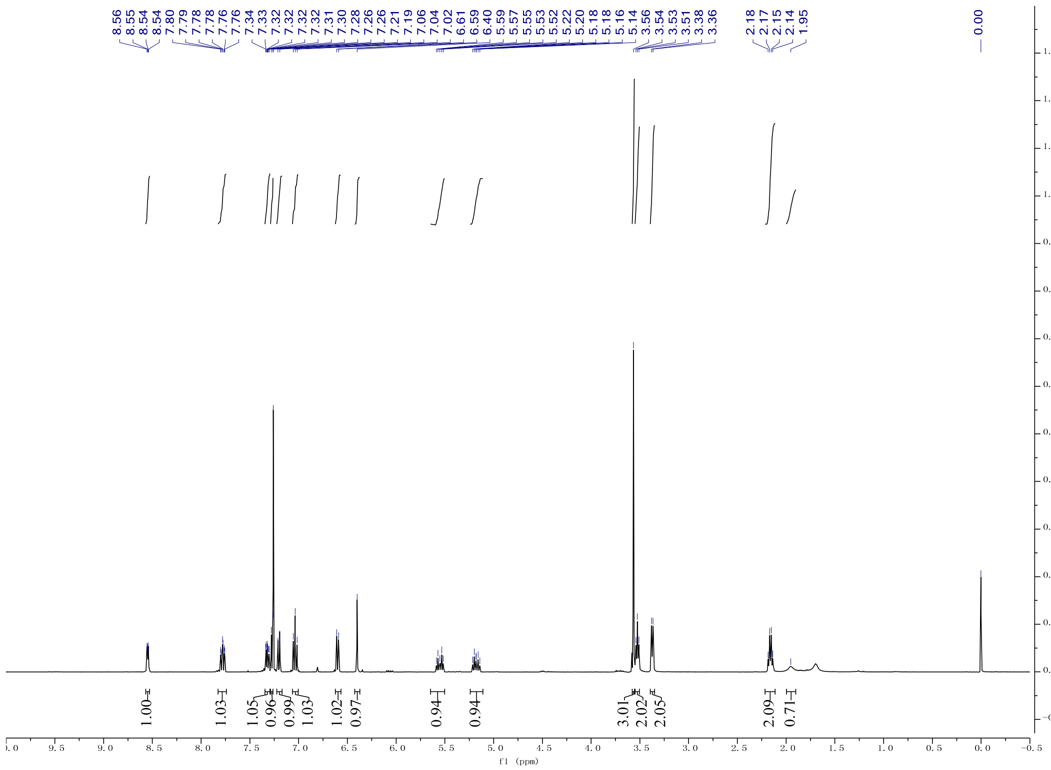

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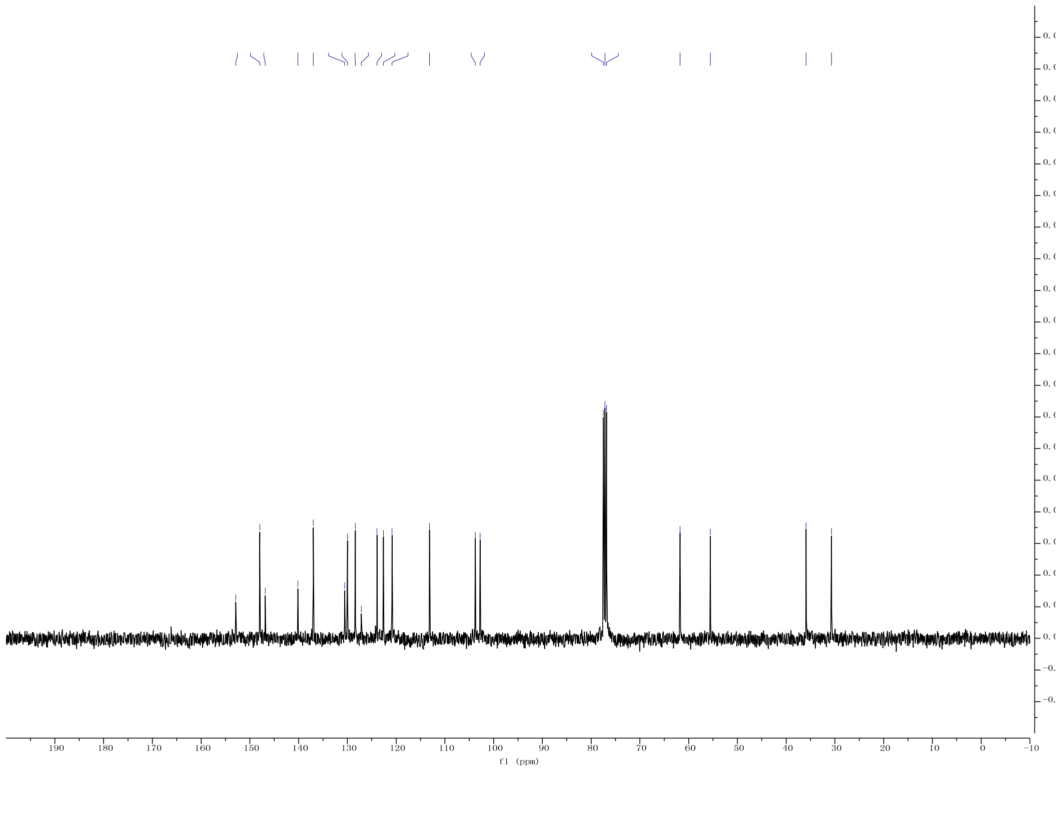

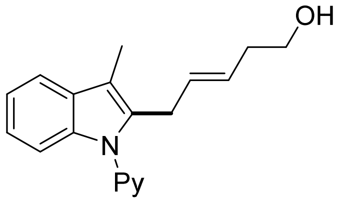

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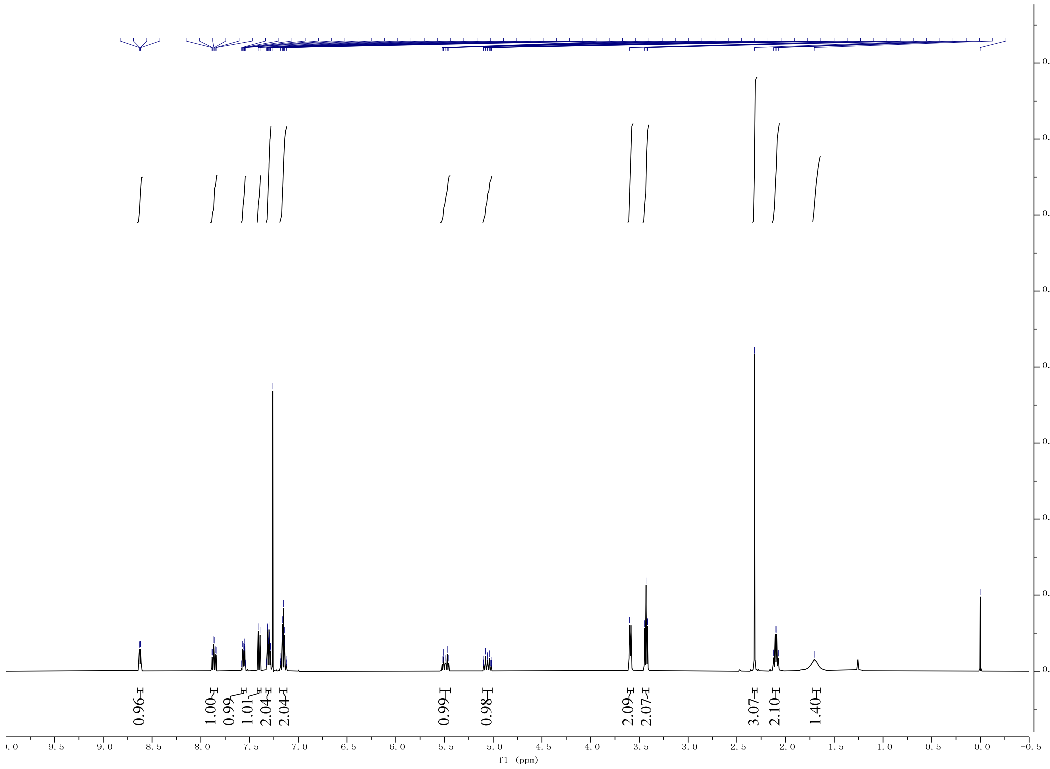

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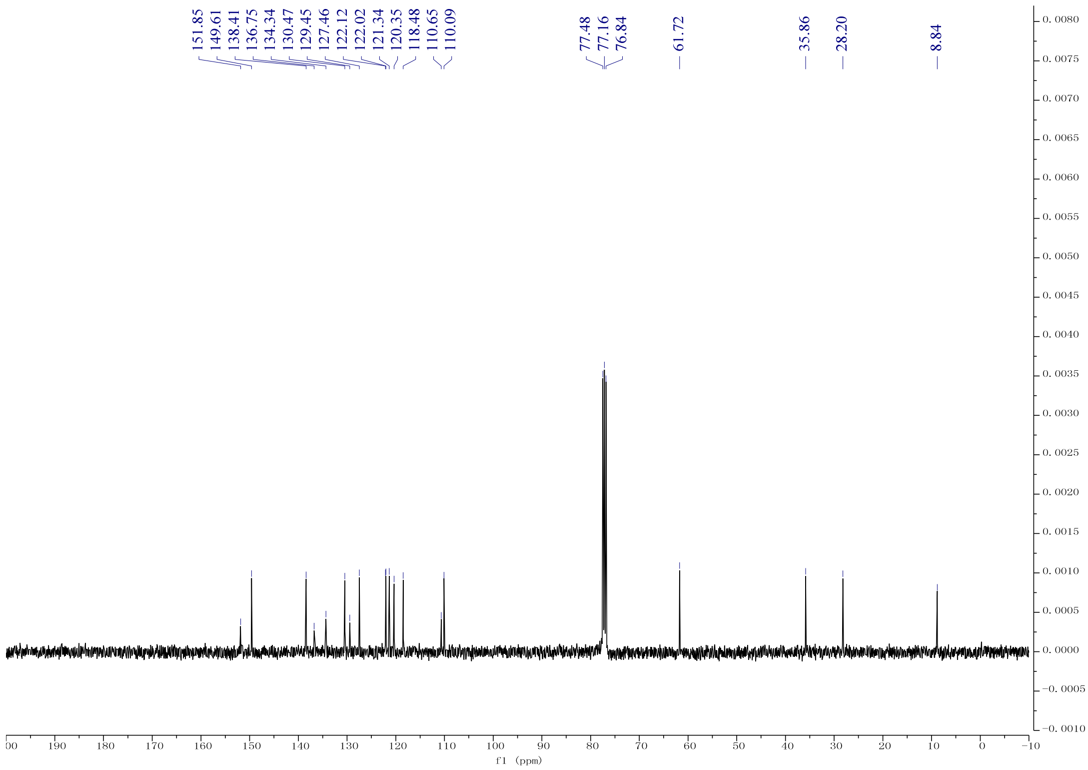
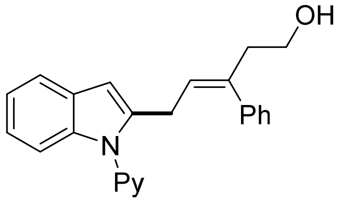
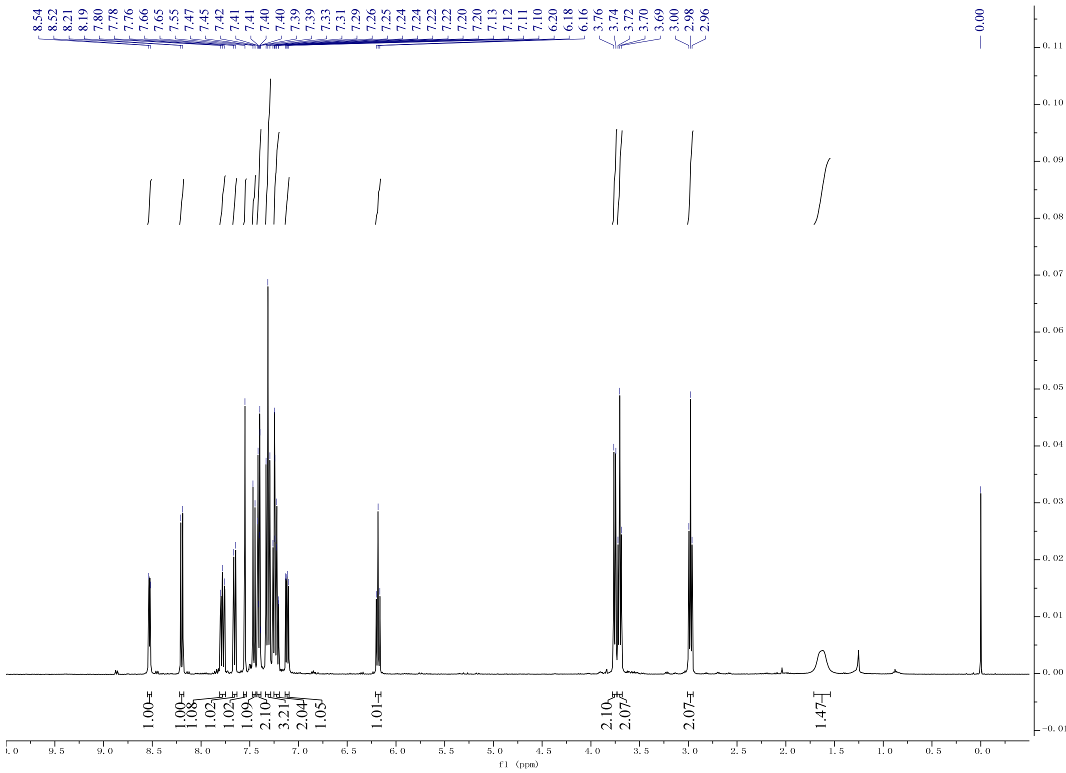
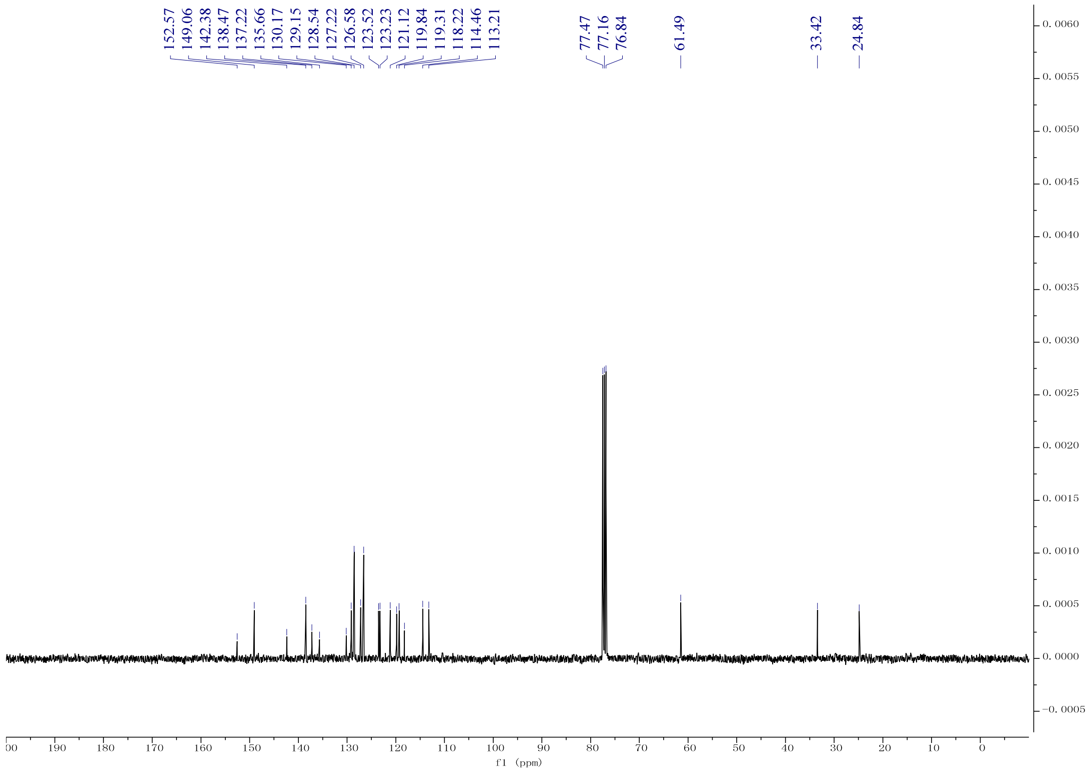


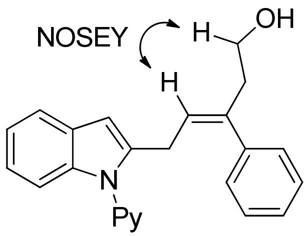


^{1}H NMR (400 MHz, $CDCl_3$) Compound **5ab**

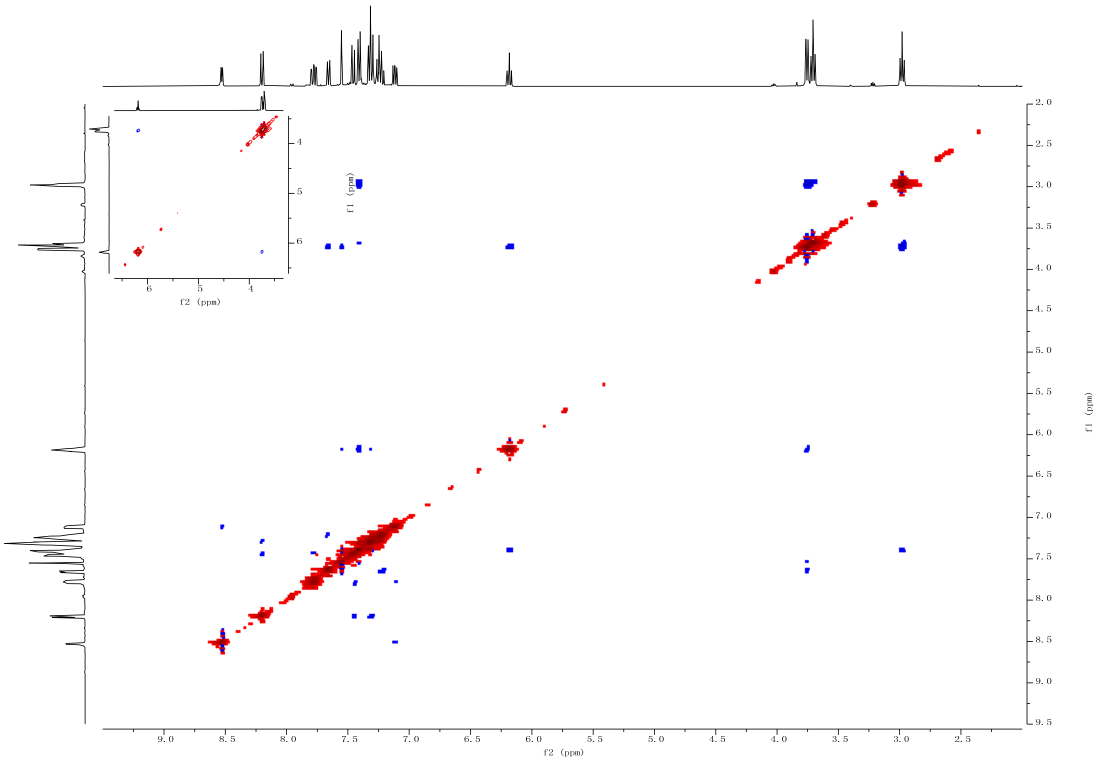


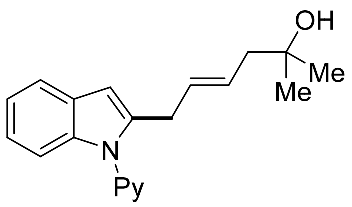
^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ab**





5ab





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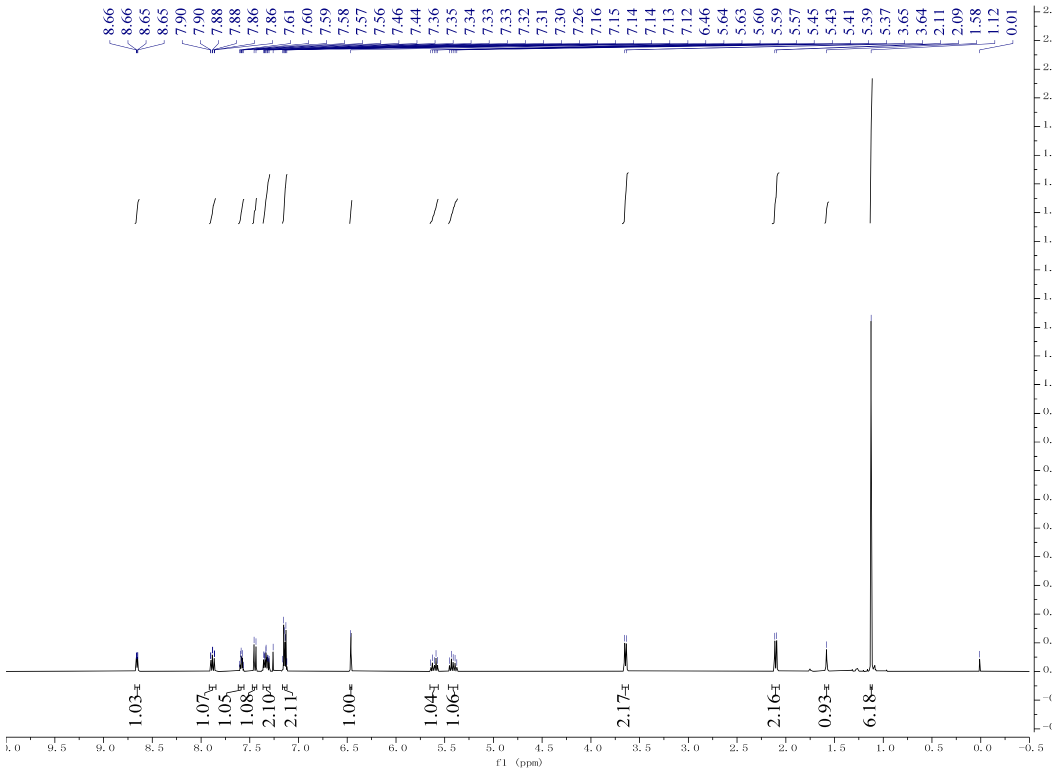
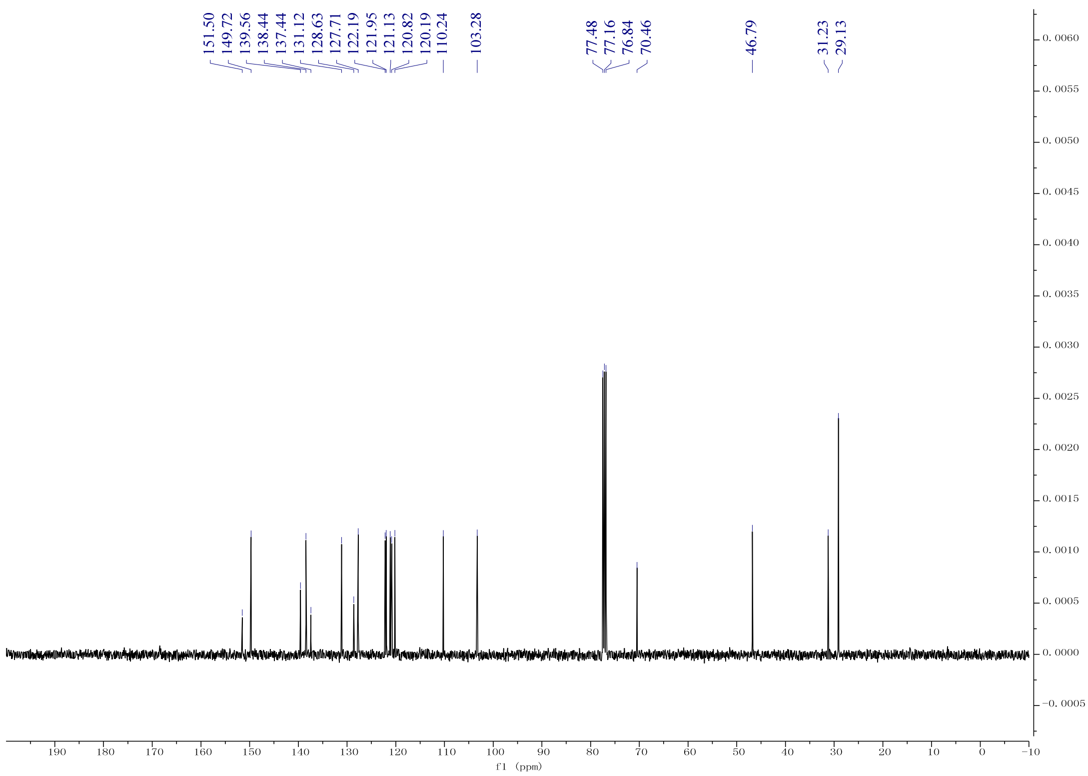
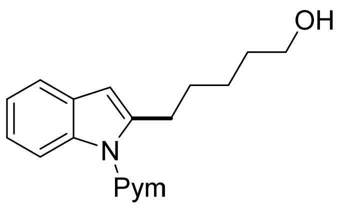
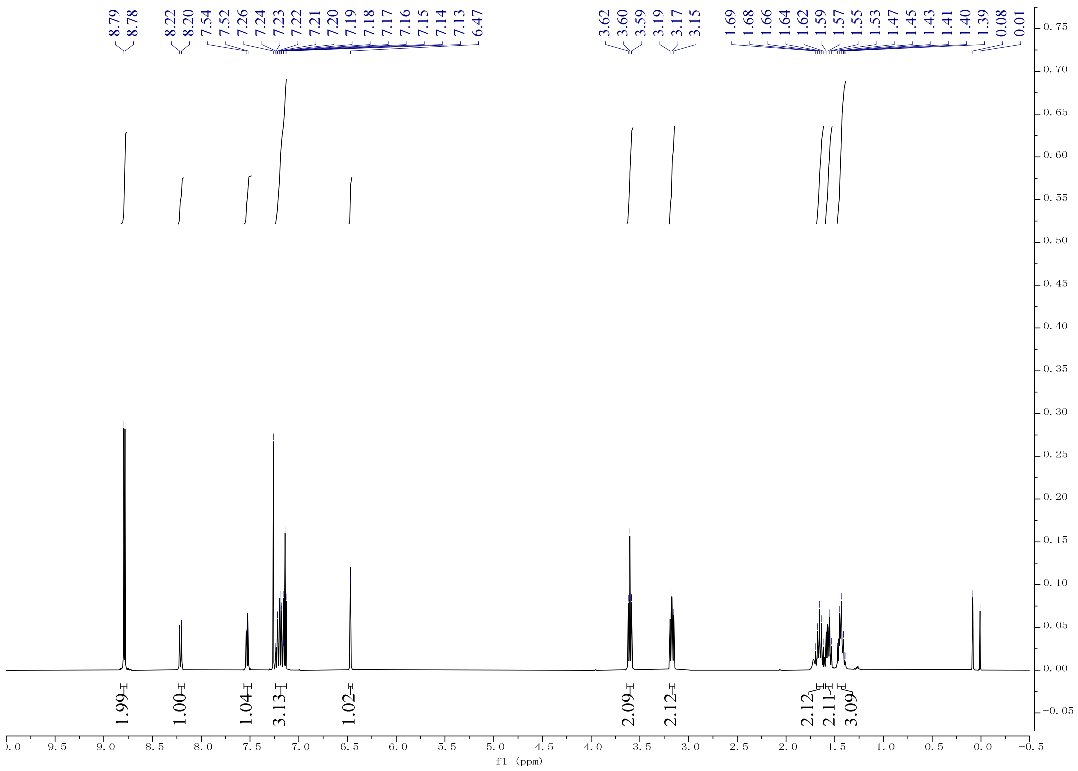


^{13}C NMR (101 MHz, $CDCl_3$) Compound **5ac**

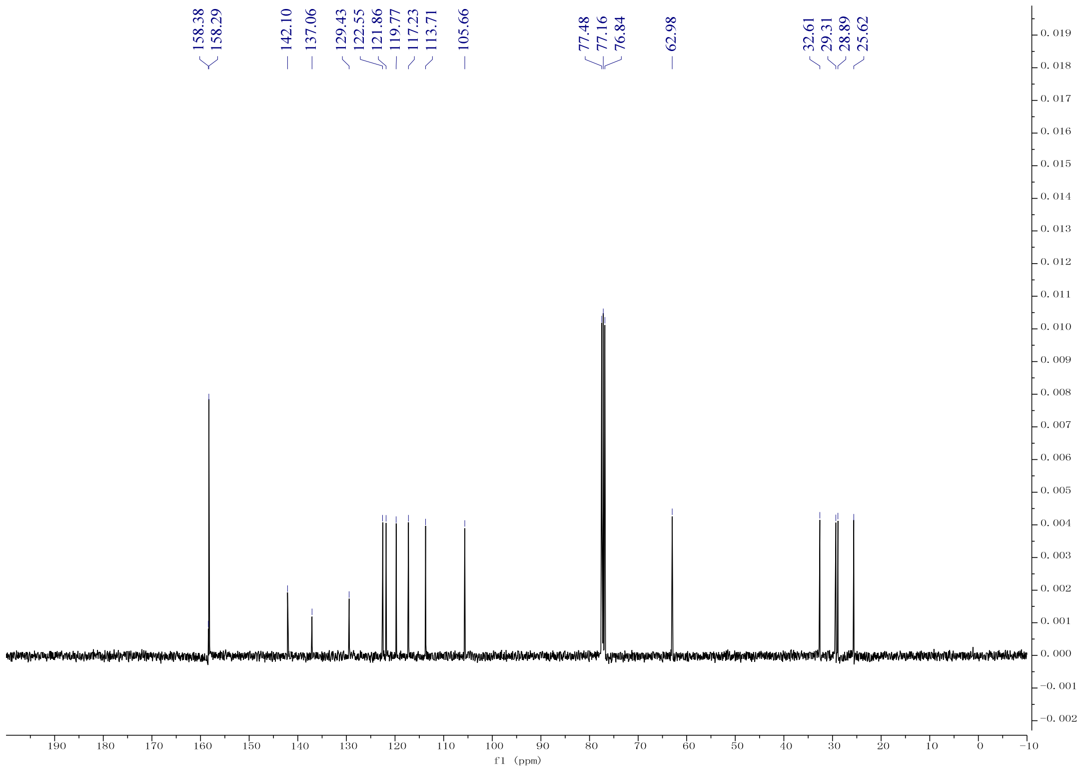


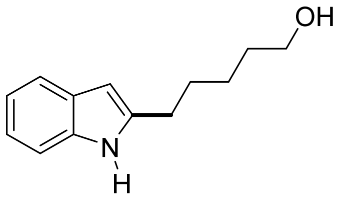


^{1}H NMR (400 MHz, $CDCl_3$) Compound **6**

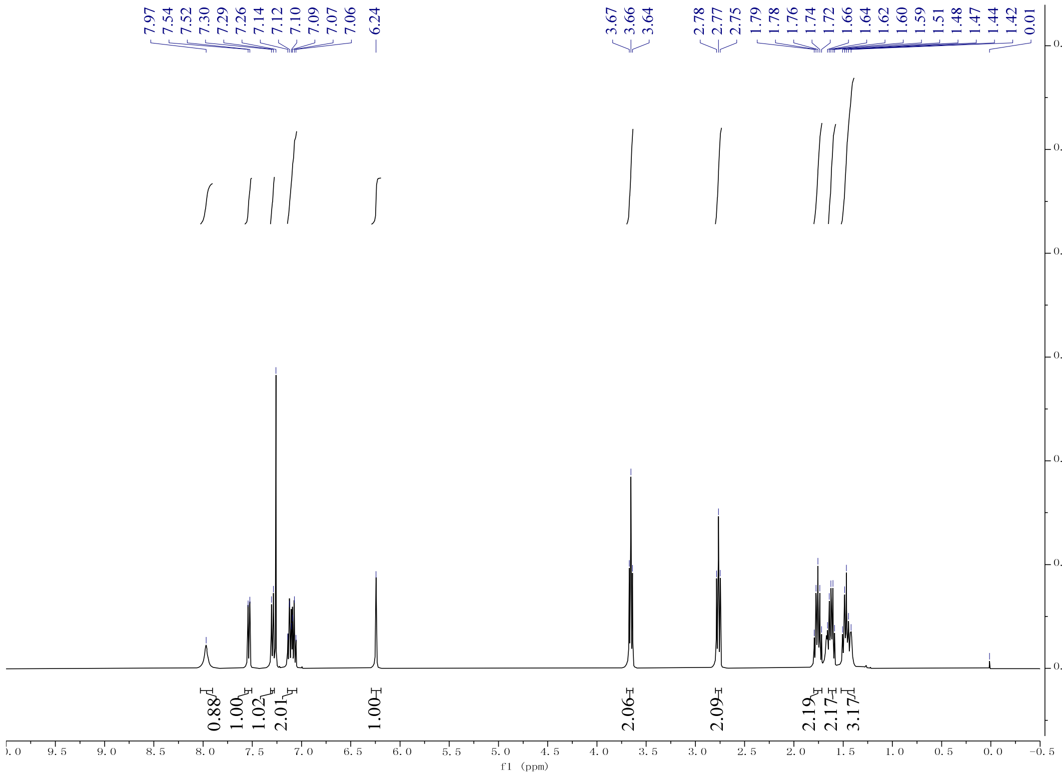


^{13}C NMR (101 MHz, $CDCl_3$) Compound **6**

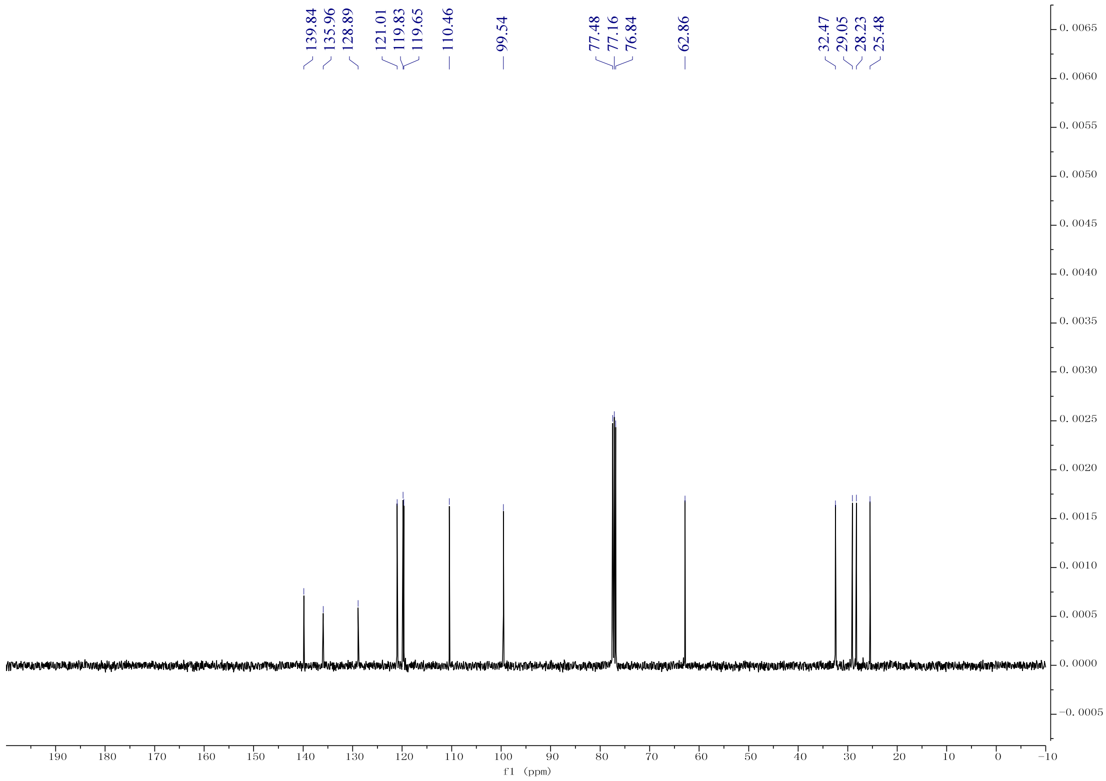


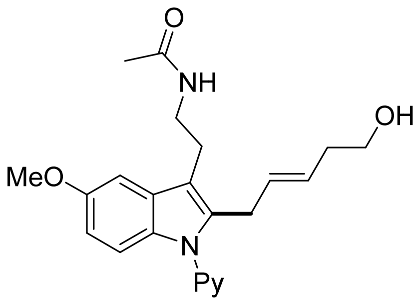


^{1}H NMR (400 MHz, $CDCl_3$) Compound **7**

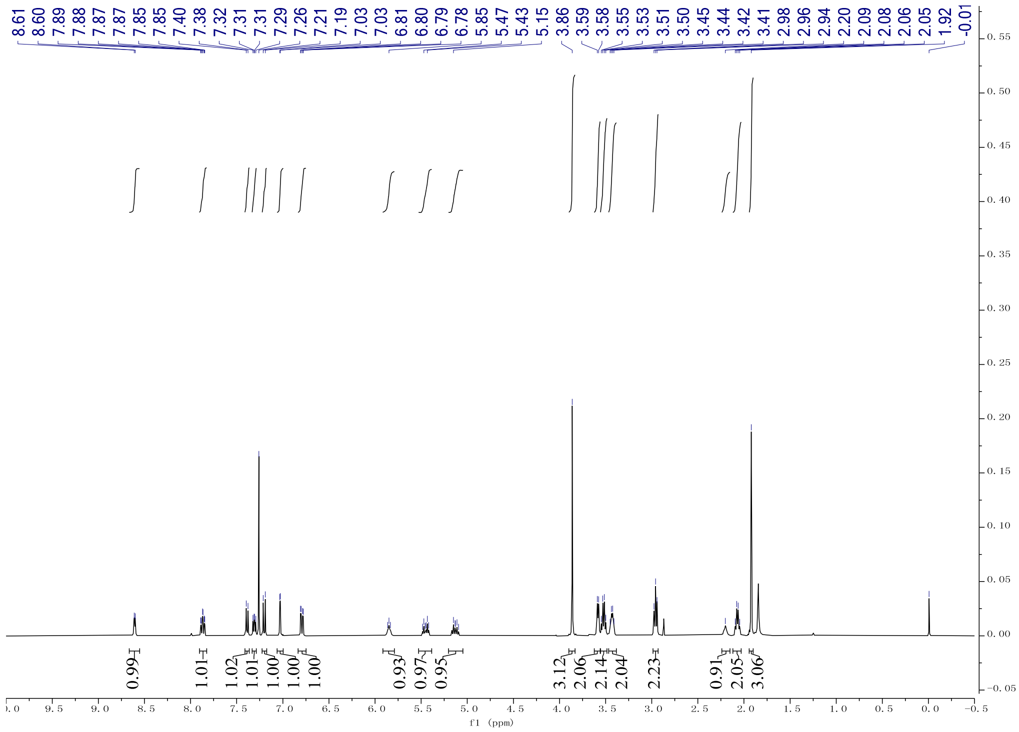


^{13}C NMR (101 MHz, $CDCl_3$) Compound **7**





[1]H NMR (400 MHz, CDCl$_3$) Compound **8**



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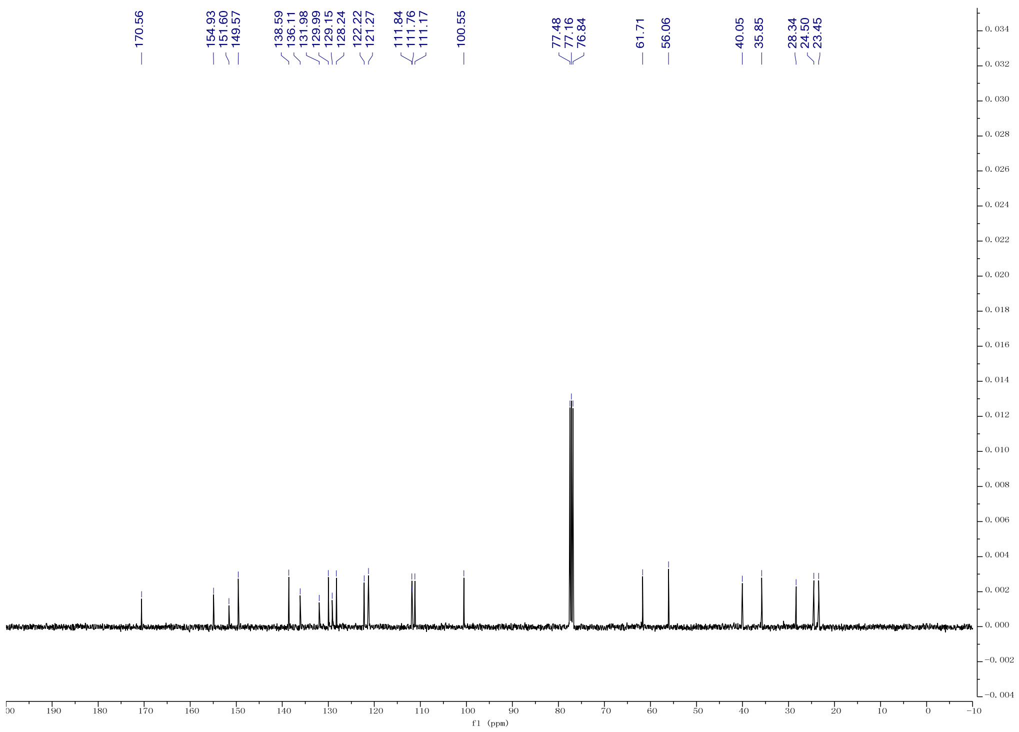
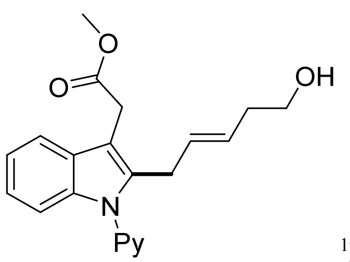
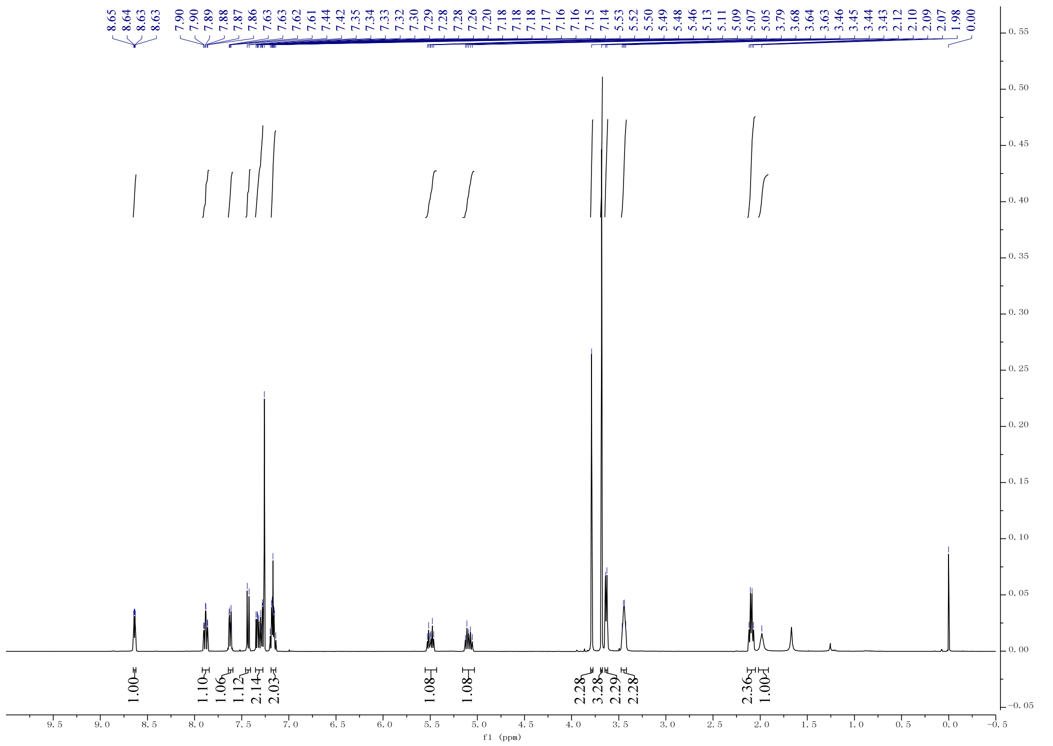
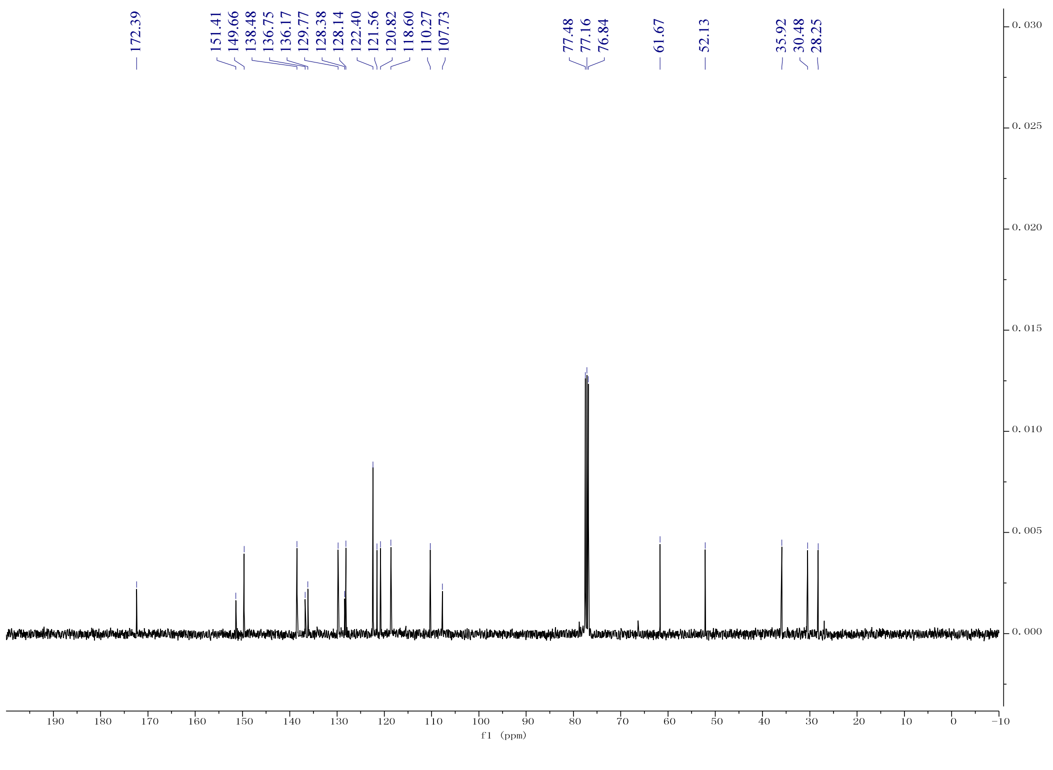


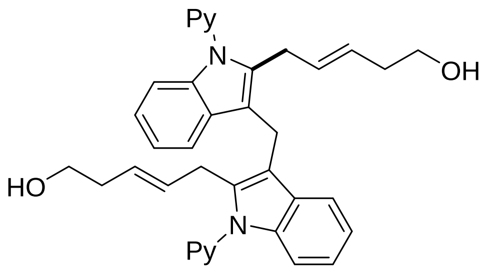


^{1}H NMR (400 MHz, $CDCl_3$) Compound **9**

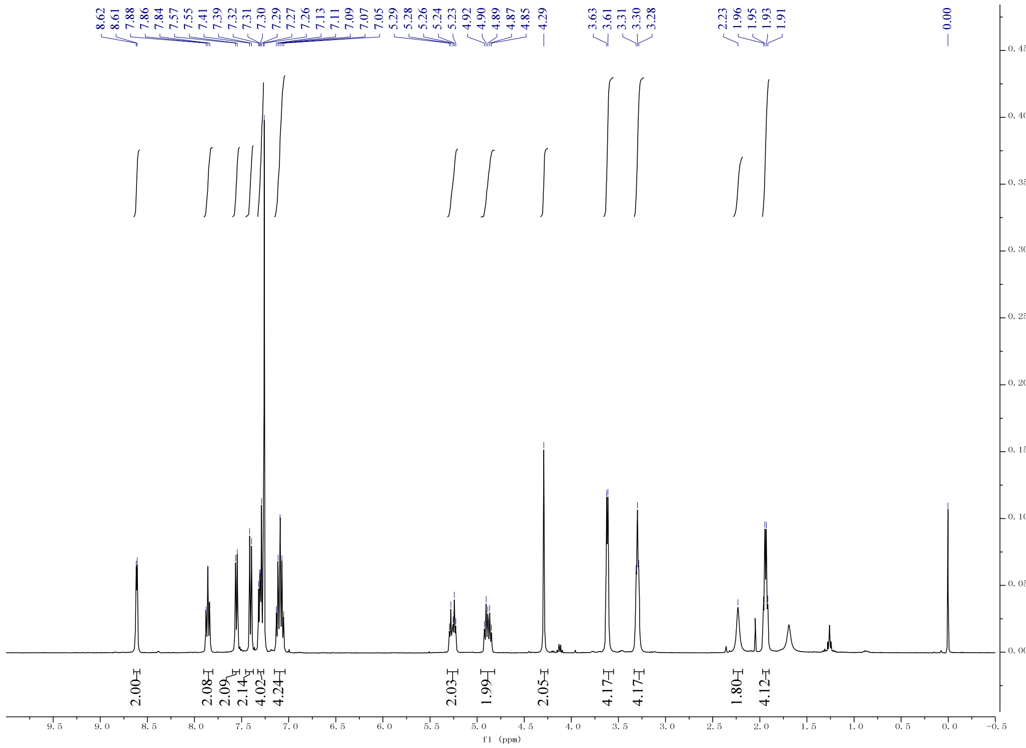


^{13}C NMR (101 MHz, $CDCl_3$) Compound **9**

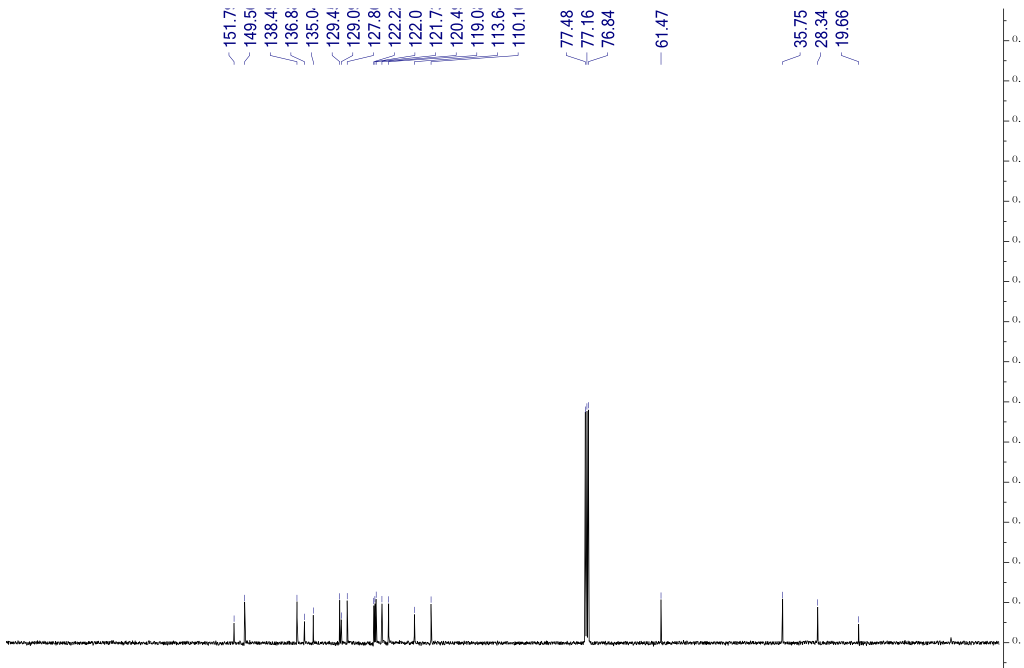


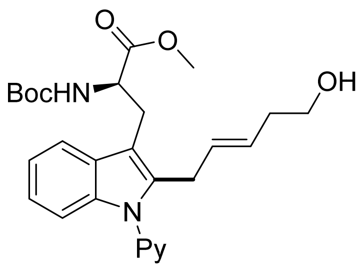


^{1}H NMR (400 MHz, $CDCl_3$) Compound **10**

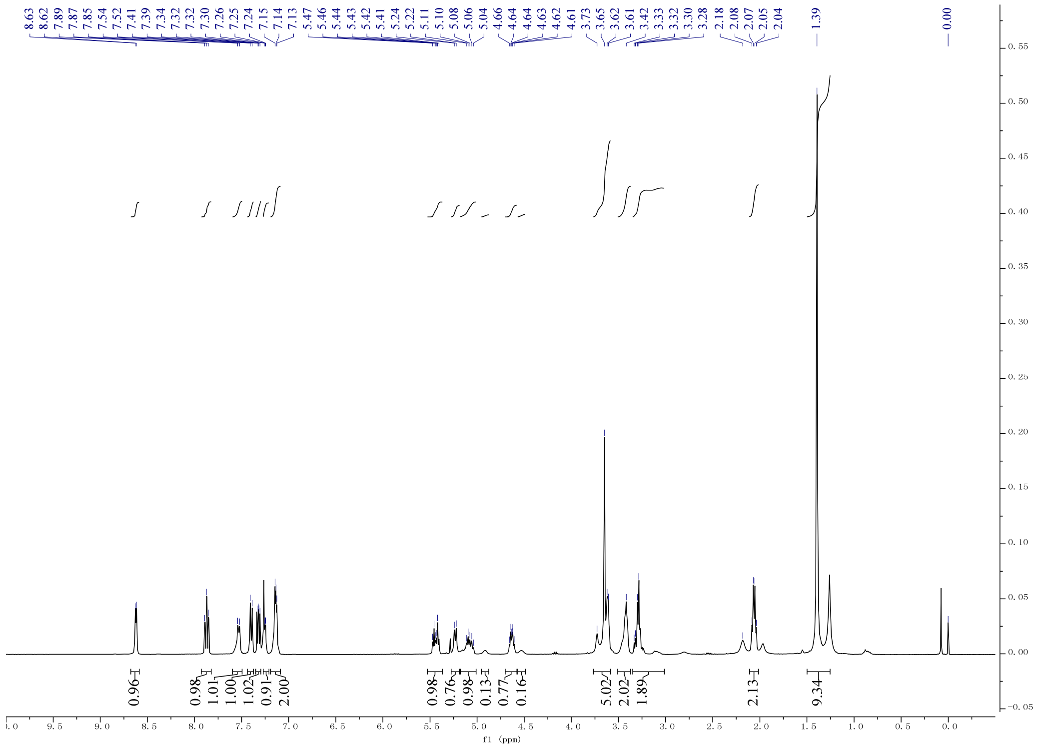


^{13}C NMR (101 MHz, $CDCl_3$) Compound **10**

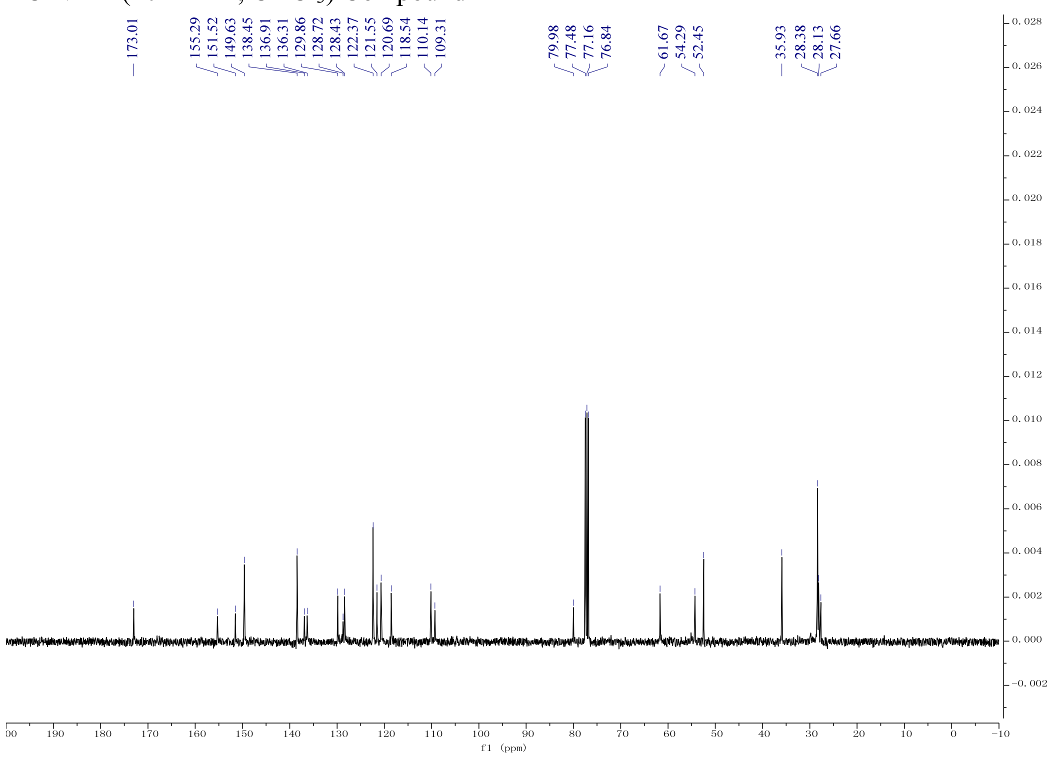


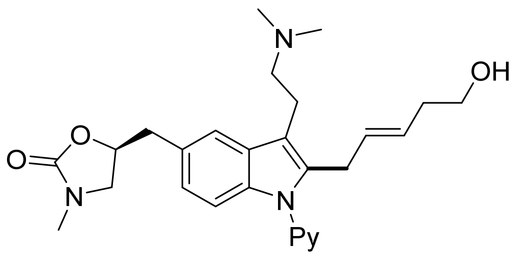


[1]H NMR (400 MHz, $CDCl_3$) Compound **11**



[13]C NMR (101 MHz, $CDCl_3$) Compound **11**





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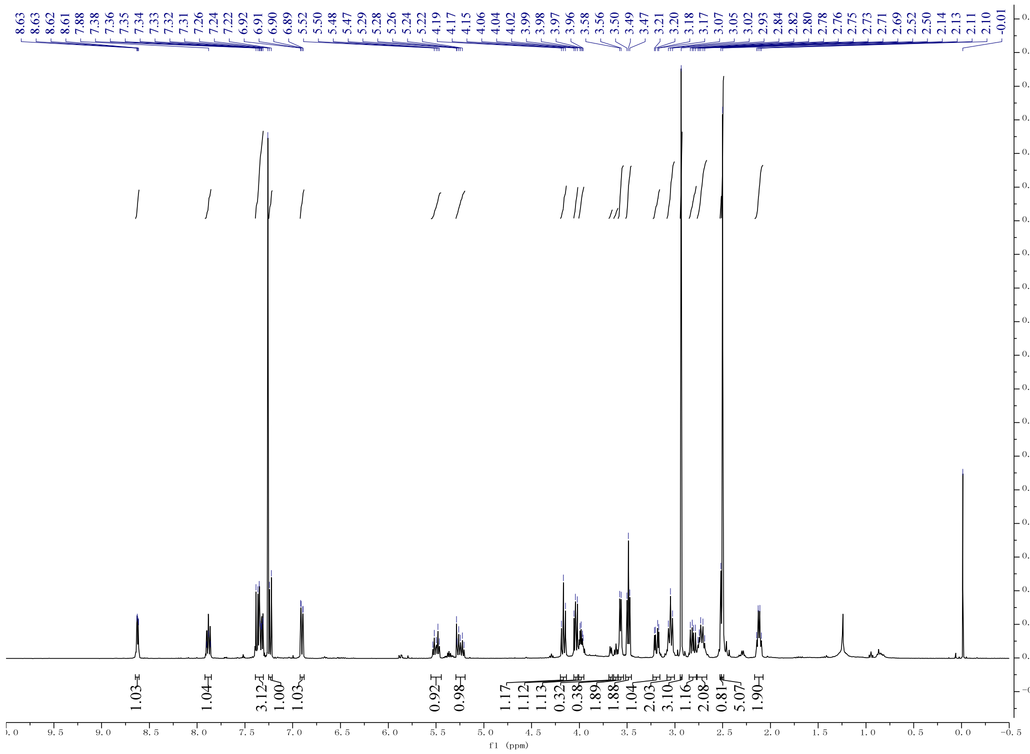
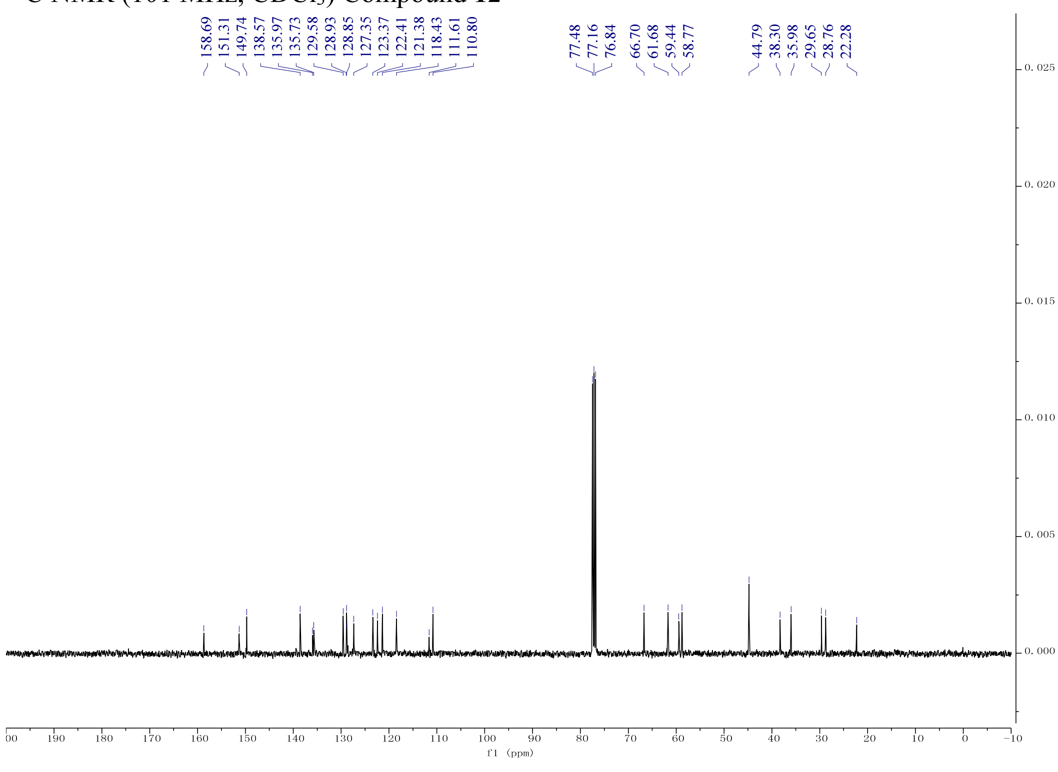


[13]C NMR (101 MHz, $CDCl_3$) Compound **12**



7. References.

[1] Ackermann, L.; Lygin, A. V. Ruthenium-catalyzed direct C–H bond arylations of heteroarenes. *Org. Lett.* **2011**, *13*, 3332−3335.

[2] Leitch, J. A.; McMullin, C. L.; Mahon, M. F.; Bhonoah, Y.; Frost, C. G. Remote C6-selective ruthenium-catalyzed C–H alkylation of indole derivatives via σ-activation. *ACS Catal.* **2017**, *7*, 2616−2623.

[3] Tamaru, Y.; Bando, T.; Hojo, M.; Yoshida, Z.-i. Synthesis of 2-vinyl-γ-butyrolactones by the palladium-catalyzed decarboxylative carbonylation of 3-vinyl-1-oxo-2,6-dioxacyclohexanes. *Tetrahedron Lett.* **1987**, *28*, 3497−3500.

[4] Neelakandan, K.; Manikandan, H.; Santosha, N.; Prabhakaran, B. Convenient and industrially viable process for preparation of zolmitriptan. *J. Heterocyclic Chem.* **2014**, *51*, E332–E334.

[5] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, **1988**, *38*, 3098–3100.

[6] Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **1988**, *37*, 785–789.

[7] Becke, A. D. Density-functional thermochemistry. III. the role of exact exchange. *J. Chem. Phys.*, **1993**, *98*, 5648–5652.

[8] Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.*, **2011**, *32*, 1456–1465.

[9] Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-adjusted *ab initio* pseudopotentials for the first row transition elements. *J. Chem. Phys.*, **1987**, *86*, 866–872.

[10] Pritchard, B. P.; Altarawy, D.; Didier, B.; Gibson, T. D.; Windus, T. L. New basis set exchange: an open, up-to-date resource for the molecular sciences community. *J. Chem. Inf. Model.*, **2019**, *59*, 4814–4820.

[11] Feller, D. The role of databases in support of computational chemistry calculations. *J. Comput. Chem.*, **1996**, *17*, 1571–1586.

[12] Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. Basis set exchange: a community database for computational sciences. *J. Chem. Inf. Model.*, **2007**, *47*, 1045–1052.

[13] Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self—consistent molecular orbital methods. xii. further extensions of gaussian—type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.*, **1972**, *56*, 2257–2261.

[14] Fukui, K. The path of chemical reactions - the IRC approach. *Acc. Chem. Res.*, **1981**, *14*, 363–368.

[15] Becke, A. D. Density-functional thermochemistry. v. systematic optimization of exchange-correlation functionals. *J. Chem. Phys.*, **1997**, *107*, 8554–8560.

[16] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.*, **2010**, *132*, 154104.

[17] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297–3305.

[18] Ehlers, A.W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. A set of f-polarization functions for pseudo-potential

basis sets of the transition metals Sc–Cu, Y–Ag and La–Au. *Chem. Phys. Lett.*, **1993**, *208*, 111–114.
[19] Roy, L. E.; Hay, P. J.; Martin, R. L. Revised basis sets for the LANL effective core potentials. *J. Chem. Theory Comput.*, **2008**, *4*, 1029–1031.
[20] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B*, **2009**, *113*, 6378–6396.
[21] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision E.01. Gaussian, Inc., Wallingford CT, 2013.