Electronic Supplementary Information

Three-Component Regioselective Carboamidation of 1,3-Enynes via Rhodium(III)-Catalyzed C-H Activation

Lingheng Kong,[a,b] Xi Han,[a] Panjie Hu,[a] Fen Wang,*[a] Xingwei Li*[a]

[a]*School of Chemistry and Chemical Engineering, Shaanxi Normal University (SNNU), Xi'an 710062, China*

[b]*College of Chemistry and Chemical Engineering, Taishan University, Tai'an, Shandong, 271000, China.*

Email: lixw@snnu.edu.cn

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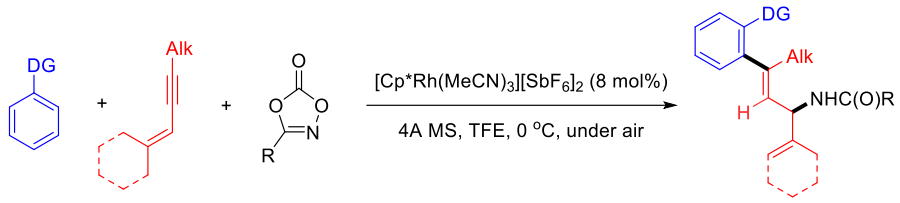
Ⅰ. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. *N*-pyrimidylindole[1], 1,3-enynes[2] and dioxazolones[3] were prepared by following literature reports. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on a 400 or 600 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate (EA)/petroleum ether (PE) or acetone/ petroleum ether.

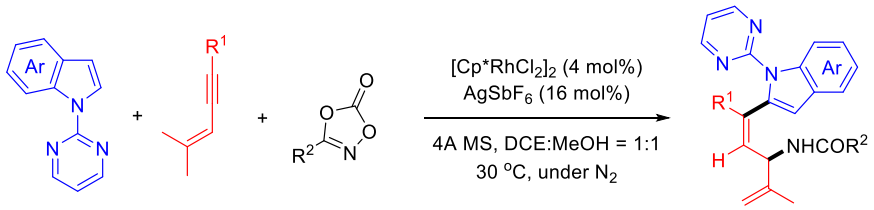
II. Experimental Procedures and Characterizations

(a) General Synthetic Procedure of 4-31



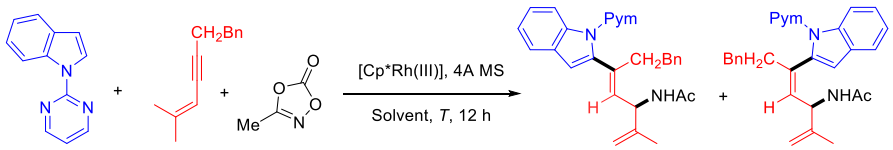
Synthesis of Product 4-31: To a Schlenk tube equipped with a stir bar was charged arene (0.2 mmol), 1,3-enynes (0.3 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8 mol%), 4 Å M.S. (100 mg), and TFE (2.0 mL). Amidating reagents (0.24 mmol) was added in 0 °C and the reaction maintained at 0 °C for 12 h under air atmosphere. Afterwards, the reaction mixture was evaporated under vacuum and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 (v/v)) to give the corresponding products.

(b) General Synthetic Procedure of 32-51



Synthesis of Product 32-51: A mixture of *N*-pyrimidylindoles (0.2 mmol), 1,3-enynes (0.3 mmol), amidating reagents (0.24 mol), $[Cp^*RhCl_2]_2$ (4 mol%), $AgSbF_6$ (16 mol%), 4 Å M.S. (100 mg), and DCE/MeOH = 1:1 (2.0 mL) or DCE/2-Methyl-2-butanol = 1:1 (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 30 °C for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using petroleum ether/ acetone (3:2) to afford the products.

(c) Optimization Studies.[a] (Table S1)

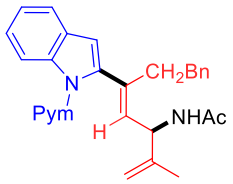


Entry	Catalyst (8 mol%)	Solvent	*T* (°C)	Yield (%)[b]
1	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	HFIP	30	55
2	$[Cp^*RhCl_2]_2$(4)/$AgSbF_6$(16)	HFIP	30	42
3	$[Cp^*Rh(OAc)_2]$	HFIP	30	46
4	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	DCE	30	45 (1:1.4)[c]
5	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	MeCN	30	25
6	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	Ph-Cl	30	47 (1:1.5)[c]

7	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	MeOH	30	30
8	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	TFE	30	65
9	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	TFE	20	71
10	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	TFE	0	88 (85)[d]

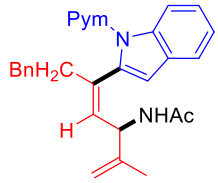
[a]Reaction Conditions: Indole **1a** (0.1 mmol), 1,3-enyne **2a** (0.15 mmol), amidating reagent **3a** (0.12 mmol), [Cp*Rh(III)] catalyst, and 4 Å M.S. (50 mg) in solvent (1 mL) at *T* °C for 12 h without exclusion of air or moisture. [b]Isolated yield; *E*/*Z* ratio >25:1 unless otherwise mentioned. [c]The ratio of *E*/*Z*. [d] 0.2 mmol.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**4**)



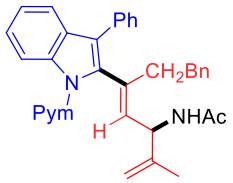
Product **4** was isolated in 85% yield (74.2 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.87 (d, *J* = 4.8 Hz, 2H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 4.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.18 (m, 6H), 7.15 – 7.10 (m, 1H), 6.68 (s, 1H), 5.45 – 5.37 (m, 2H), 4.96 (s, 1H), 4.80 (s, 1H), 2.74 – 2.67 (m, 3H), 2.58 – 2.52 (m, 1H), 1.94 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.9, 159.6, 159.1, 146.5, 143.2, 143.1, 138.6, 136.7, 130.7, 130.2, 129.3, 129.2, 126.7, 124.1, 122.9, 121.3, 119.9, 114.5, 110.9, 108.0, 52.5, 36.0, 35.3, 23.2, 20.4. **HRMS** (ESI) calculated for $C_{28}H_{28}N_4NaO^+$ $[M+Na]^+$: 459.2155, found: 459.2161.

(*Z*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**4'**)



Product **4'** was isolated as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.41 (d, *J* = 8.3, 1H), 7.60 (d, *J* = 7.7, 1H), 7.33 (t, *J* = 4.8, 1H), 7.27 – 7.17 (m, 4H), 7.14 – 7.13 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.67 (s, 1H), 5.51 – 5.50 (m, 1H), 5.04 – 5.02 (m, 1H), 4.71 (s, 1H), 4.60 (s, 1H), 2.73 – 2.70 (m, 2H), 2.60 – 2.52 (m, 2H), 1.75 (s, 3H), 1.57 (s, 3H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.3, 158.3, 157.7, 145.8, 141.9, 137.6, 136.9, 136.3, 129.4, 128.7, 128.3, 128.2, 125.6, 123.0, 121.8, 120.3, 117.6, 114.5, 109.3, 108.3, 53.3, 40.0, 34.3, 22.0, 19.3. **HRMS** (ESI) calculated for $C_{28}H_{28}N_4NaO^+$ $[M+Na]^+$: 459.2155, found: 459.2160.

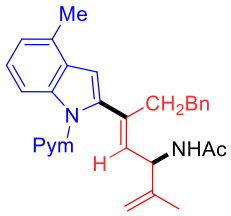
(*E*)-*N*-(2-methyl-7-phenyl-5-(3-phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**5**)



Product **5** was isolated in 72% yield (73.8 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.70 (d, *J* = 4.8 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.40 (m, 2H), 7.35 – 7.31 (m, 2H), 7.23 – 7.21 (m, 1H), 7.13 – 7.15 (m, 2H), 7.11 – 7.07 (m, 2H), 7.05 – 7.00 (m, 2H), 5.31 – 5.25 (m, 2H), 5.21 – 5.19 (m, 1H), 4.80 – 4.73 (m, 2H), 2.68 – 2.53 (m, 3H), 2.37 – 2.25 (m, 1H), 1.91 (s, 3H), 1.64 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.6, 158.2, 158.1, 144.3, 142.0, 137.2, 136.4, 134.8, 134.7, 132.0, 130.7, 129.7, 128.5, 128.4, 128.3, 126.8, 125.8, 124.1, 122.4, 121.3, 119.8, 117.5, 113.6, 110.6, 52.0, 34.9, 34.8, 23.5, 20.0. **HRMS** (ESI) calculated for $C_{34}H_{32}N_4NaO^+$ $[M+Na]^+$: 535.2468, found: 535.2472.

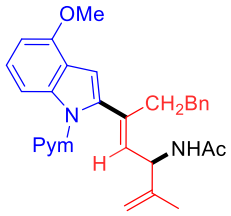
(*E*)-*N*-(2-methyl-5-(4-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)-7-phenylhepta-1,4-dien-3-yl)acetamide (**6**)

Product **6** was isolated in 81% yield (72.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.68 (d, *J* = 4.8 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.13 – 7.01 (m, 5H), 6.60 (s, 1H), 5.62 (d, *J* = 8.2 Hz, 1H), 5.47 (d, *J* = 9.5 Hz, 1H), 5.23



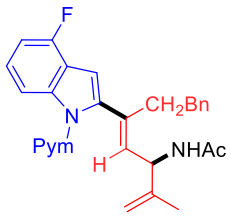
– 5.29 (m, 1H), 4.94 (s, 1H), 4.84 (s, 1H), 2.70 – 2.50 (m, 7H), 2.00 (s, 3H), 1.75 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.8, 158.2, 158.2, 144.6, 141.9, 141.1, 137.8, 137.3, 129.9, 128.8, 128.6, 128.4, 128.3, 125.9, 123.8, 122.6, 117.3, 111.4, 110.9, 106.8, 52.2, 35.0, 34.3, 23.6, 20.1, 18.7. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO^+$ $[M+Na]^+$: 473.2312, found: 473.2314.

(*E*)-*N*-(5-(4-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**7**)



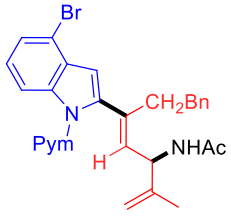
Product **7** was isolated in 66% yield (61.5 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.68 (d, J = 4.8, 2H), 7.88 (d, J = 8.3 Hz, 1H), 7.22 – 7.18 (m, 3H), 7.12 – 7.07 (m, 4H), 6.75 (s, 1H), 6.66 (d, J = 7.9 Hz, 1H), 5.61 (d, J = 8.3 Hz, 1H), 5.47 (d, J = 9.4 Hz, 1H), 5.28 – 5.25 (m, 1H), 4.92 (s, 1H), 4.83 (s, 1H), 3.97 (s, 3H), 2.68 – 2.59 (m, 2H), 2.55 – 2.52 (t, J = 8.2 Hz, 2H), 1.98 (s, 3H), 1.73 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.8, 158.2, 152.9, 144.6, 141.9, 140.2, 138.8, 137.5, 128.6, 128.4, 128.3, 125.8, 124.5, 119.5, 117.4, 110.8, 107.1, 105.3, 102.4, 55.5, 52.2, 34.9, 34.2, 23.5, 20.0. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO_2^+$ $[M+Na]^+$: 489.2261, found: 489.2265.

(*E*)-*N*-(5-(4-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**8**)



Product **8** was isolated in 95% yield (86.3 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.70 (d, J = 4.9 Hz, 2H), 8.05 (d, J = 8.4 Hz, 1H), 7.21 – 7.17 (m, 3H), 7.13 – 7.09 (m, 4H), 6.90 (t, J = 8.8 Hz, 1H), 6.68 (s, 1H), 5.66 (d, J = 8.3 Hz, 1H), 5.50 (d, J = 9.5 Hz, 1H), 5.29 (t, J = 9.0 Hz, 1H), 4.94 (s, 1H), 4.85 (s, 1H), 2.71 – 2.50 (m, 4H), 2.00 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 158.3, 158.0, 155.8 (d, $J_{C\text{-}F}$ = 246.7 Hz), 144.5, 141.8, 141.7, 139.7 (d, $J_{C\text{-}F}$ = 10.0 Hz), 137.1, 129.3, 128.6, 128.4, 125.9, 124.1 (d, $J_{C\text{-}F}$ = 7.4 Hz), 118.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 117.7, 111.0, 109.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 107.3 (d, $J_{C\text{-}F}$ = 18.6 Hz), 103.6, 52.1, 34.9, 34.1, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{28}H_{27}FN_4NaO^+$ $[M+Na]^+$: 477.2061, found: 477.2066.

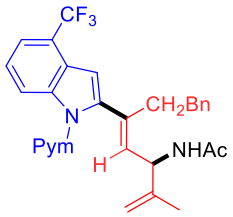
(*E*)-*N*-(5-(4-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**9**)



Product **9** was isolated in 95% yield (97.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.68 (d, J = 4.8 Hz, 2H), 8.22 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 7.7 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.13 – 7.08 (m, 5H), 6.62 (s, 1H), 5.76 (d, J = 8.4 Hz, 1H), 5.50 (d, J = 9.5 Hz, 1H), 5.30 (t, J = 8.9 Hz, 1H), 4.94 (s, 1H), 4.84 (s, 1H), 2.70 – 2.58 (m, 3H), 2.53 – 2.47 (m, 1H), 2.00 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 158.3, 157.8,

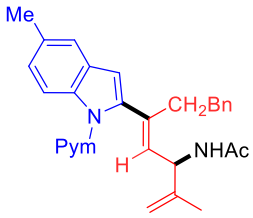
144.4, 142.5, 141.6, 137.6, 137.0, 129.7, 129.4, 128.5, 128.3, 125.9, 125.0, 124.4, 117.8, 114.2, 113.0, 111.0, 107.8, 52.1, 34.9, 34.9, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{28}H_{27}BrN_4NaO^+$ $[M+Na]^+$: 537.1260, found: 537.1269.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-4-(trifluoromethyl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**10**)



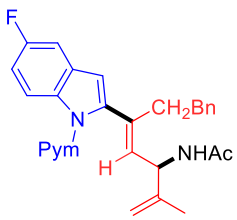
Product **10** was isolated in 84% yield (84.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.72 (d, J = 4.8 Hz, 2H), 8.45 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.19 – 7.15 (m, 3H), 7.11 – 7.06 (m, 3H), 6.73 (s, 1H), 5.74 (d, J = 8.4 Hz, 1H), 5.54 (d, J = 9.5 Hz, 1H), 5.32 (t, J = 9.0 Hz, 1H), 4.95 (s, 1H), 4.85 (s, 1H), 2.68 – 2.60 (m, 3H), 2.51 – 2.44 (m, 1H), 2.02 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.9, 158.4, 157.7, 144.4, 143.6, 141.5, 137.9, 136.9, 129.8, 128.6, 128.3, 126.7 (q, $J_{C\text{-}F}$ = 272.4 Hz), 126.0, 125.7, 122.8, 121.5 (q, $J_{C\text{-}F}$ = 32.5 Hz), 119.5(q, $J_{C\text{-}F}$ = 4.7 Hz), 118.0, 117.4, 111.1, 106.2, 52.1, 34.9, 34.0, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{29}H_{27}F_3N_4NaO^+$ $[M+Na]^+$: 527.2029, found: 527.2035.

(*E*)-*N*-(2-methyl-5-(5-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)-7-phenylhepta-1,4-dien-3-yl)acetamide (**11**)



Product **11** was isolated in 70% yield (63.0 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.68 (d, J = 4.8 Hz, 2H), 8.25 (d, J = 8.5 Hz, 1H), 7.39 (s, 1H), 7.24 – 7.21 (m, 2H), 7.16 – 7.11 (m, 4H), 7.07 (t, J = 4.8 Hz, 1H), 5.69 (d, J = 8.2 Hz, 1H), 5.49 (d, J = 9.5 Hz, 1H), 5.32 (t, J = 8.9 Hz, 1H), 4.96 (s, 1H), 4.86 (s, 1H), 2.70 – 2.56 (m, 4H), 2.48 (s, 3H), 2.01 (s, 3H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.8, 158.2, 158.1, 144.7, 141.9, 141.7, 137.9, 135.9, 131.7, 129.5, 128.6, 128.3, 128.2, 125.9, 125.1, 120.3, 117.0, 113.8, 110.8, 108.3, 52.2, 34.9, 34.3, 23.6, 21.5, 20.1. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO^+$ $[M+Na]^+$: 473.2312, found: 473.2314.

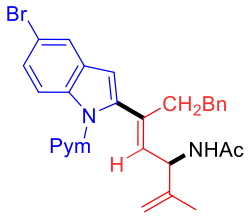
(*E*)-*N*-(5-(5-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**12**)



Product **12** was isolated in 89% yield (80.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.70 (d, J = 4.7 Hz, 2H), 8.28 (dd, J = 8.9, 4.5 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.14 – 7.07 (m, 4H), 7.02 – 6.99 (m, 1H), 6.54 (s, 1H), 5.53 (d, J = 7.9 Hz, 1H), 5.48 (d, J = 9.4 Hz, 1H), 5.30 (t, J = 8.7 Hz, 1H), 4.94 (s, 1H), 4.86 (s, 1H), 2.70 – 2.53 (m, 4H), 2.01 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 168.8 , 159.2 (d, $J_{C\text{-}F}$ = 237.8 Hz), 158.3 , 158.0 , 144.6 , 143.4 , 141.8 , 137.6 , 133.9 , 130.0 (d, $J_{C\text{-}F}$ = 9.9 Hz), 128.9, 128.6, 128.4, 126.0, 117.4, 115.1 (d, $J_{C\text{-}F}$ = 8.9 Hz), 111.4 (d, $J_{C\text{-}F}$ = 25.1 Hz), 111.1, 108.2 (d, $J_{C\text{-}F}$ = 3.9 Hz),

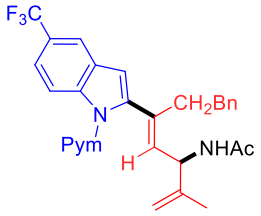
105.7 (d, $J_{C\text{-}F}$ = 23.6 Hz), 52.2, 34.9, 34.2, 23.6, 20.1. **HRMS** (ESI) calculated for $C_{28}H_{27}FN_4NaO^+$ $[M+Na]^+$: 477.2061, found: 477.2063.

(*E*)-*N*-(5-(5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**13**)



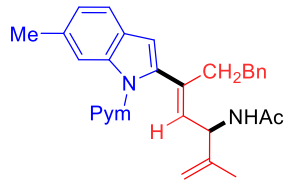
Product **13** was isolated in 86% yield (88.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.70 (d, J = 4.8 Hz, 2H), 8.21 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 2.0 Hz, 1H), 7.36 (dd, J = 8.8, 2.1 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.14 – 7.08 (m, 4H), 6.51 (s, 1H), 5.70 (d, J = 8.3 Hz, 1H), 5.49 (d, J = 9.5 Hz, 1H), 5.31 (t, J = 8.9 Hz, 1H), 4.95 (s, 1H), 4.86 (s, 1H), 2.69 – 2.53 (m, 4H), 2.01 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.9, 158.3, 157.8, 144.5, 142.9, 141.6, 137.2, 136.1, 130.9, 129.1, 128.5, 128.3, 126.3, 125.9, 122.9, 117.6, 115.6, 115.4, 111.0, 107.4, 52.1, 34.8, 34.1, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{28}H_{27}BrN_4NaO^+$ $[M+Na]^+$: 537.1260, found: 537.1266.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-5-(trifluoromethyl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**14**)



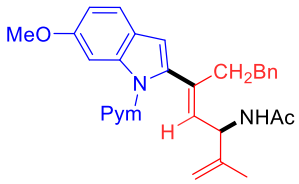
Product **14** was isolated in 90% yield (90.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.71 (d, J = 4.8 Hz, 2H), 8.35 (d, J = 8.7 Hz, 1H), 7.85 (s, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.20 – 7.18 (m, 2H), 7.14 (t, J = 4.8 Hz, 1H), 7.12 – 7.08 (m, 3H), 6.62 (s, 1H), 5.74 (d, J = 8.3 Hz, 1H), 5.49 (d, J = 9.4 Hz, 1H), 5.31 (t, J = 8.9 Hz, 1H), 4.94 (s, 1H), 4.85 (s, 1H), 2.69 – 2.51 (m, 4H), 2.00 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.9, 158.4, 157.8, 144.4, 143.5, 141.6, 138.8, 136.9, 129.6, 128.7, 128.5, 128.4, 126.0, 125.1 (q, $J_{C\text{-}F}$ = 271.6 Hz), 124.4 (q, $J_{C\text{-}F}$ = 31.9 Hz), 120.2 (q, $J_{C\text{-}F}$ = 12.6 Hz), 118.0, 117.9 (q, $J_{C\text{-}F}$ = 4.2 Hz), 114.2, 111.2, 108.1, 52.1, 34.9, 34.1, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{29}H_{27}F_3N_4NaO^+$ $[M+Na]^+$: 527.2029, found: 527.2029.

(*E*)-*N*-(2-methyl-5-(6-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)-7-phenylhepta-1,4-dien-3-yl)acetamide (**15**)



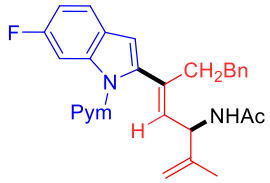
Product **15** was isolated in 66% yield (59.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.69 (d, J = 4.8 Hz, 2H), 8.09 (s, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.20 – 7.18 (m, 2H), 7.12 – 7.05 (m, 5H), 6.56 (s, 1H), 5.62 (d, J = 8.3 Hz, 1H), 5.45 (d, J = 9.4 Hz, 1H), 5.27 (t, J = 8.9 Hz, 1H), 4.92 (s, 1H), 4.84 – 4.81 (m, 1H), 2.68 – 2.52 (m, 4H), 2.49 (s, 3H), 1.98 (s, 3H), 1.73 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.8, 158.3, 158.2, 144.7, 141.9, 141.1, 138.0, 137.6, 133.6, 128.6, 128.3, 128.2, 127.0, 125.8, 123.8, 120.1, 117.2, 113.8, 110.8, 108.3, 52.2, 34.9, 34.2, 23.5, 22.2, 20.0. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO^+$ $[M+Na]^+$: 473.2312, found: 473.2312.

(*E*)-*N*-(5-(6-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**16**)



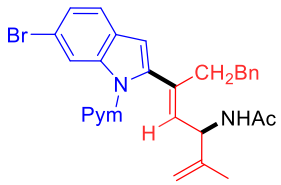
Product **16** was isolated in 56% yield (52.2 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.7 (d, J = 4.8 Hz, 2H), 7.92 (d, J = 2.3 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.12 – 7.07 (m, 4H), 6.88 (dd, J = 8.5, 2.4 Hz, 1H), 6.53 (s, 1H), 5.62 (d, J = 8.2 Hz, 1H), 5.43 (d, J = 9.5 Hz, 1H), 5.27 (t, J = 8.9 Hz, 1H), 4.94 – 4.91 (m, 1H), 4.85 – 4.81 (m, 1H), 3.87 (s, 3H), 2.67 – 2.51 (m, 4H), 1.99 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.8, 158.3, 158.2, 157.5, 144.7, 141.9, 140.7, 138.5, 137.7, 128.6, 128.3, 127.9, 125.9, 123.3, 120.9, 117.2, 111.2, 110.8, 108.4, 98.6, 55.9, 52.2, 34.9, 34.2, 23.6, 20.1. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO_2^+$ $[M+Na]^+$: 489.2261, found: 489.2263.

(*E*)-*N*-(5-(6-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**17**)



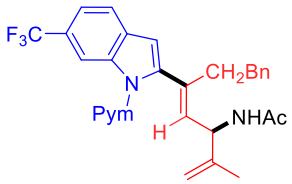
Product **17** was isolated in 82% yield (74.5 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.68 (d, J = 4.8 Hz, 2H), 8.11 – 8.08 (m, 1H), 7.48 – 7.46 (m, 1H), 7.20 – 7.18 (m, 2H), 7.12 – 7.08 (m, 4H), 6.99 – 6.96 (m, 1H), 6.54 (s, 1H), 5.63 (d, J = 8.3 Hz, 1H), 5.45 (d, J = 9.4 Hz, 1H), 5.29 (t, J = 8.9 Hz, 1H), 4.94 (s, 1H), 4.85 (s, 1H), 2.68 – 2.53 (m, 4H), 2.00 (s, 3H), 1.75 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 160.7 (d, J = 238.3 Hz), 158.2, 158.0, 144.6, 142.2 (d, J = 3.9 Hz), 141.8, 137.7 (d, J = 12.6 Hz), 137.5, 128.6, 128.4, 125.9, 125.6, 121.0 (d, J = 9.8 Hz), 117.5, 111.0, 110.6 (d, J = 24.4 Hz), 108.1, 101.4 (d, J = 28.7 Hz), 52.2, 34.9, 34.2, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{28}H_{27}FN_4NaO^+$ $[M+Na]^+$: 477.2061, found: 477.2067.

(*E*)-*N*-(5-(6-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**18**)



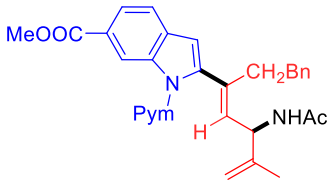
Product **18** was isolated in 84% yield (86.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.69 (d, J = 4.8 Hz, 2H), 8.51 (s, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.20 – 7.18 (m, 2H), 7.12 – 7.07 (m, 4H), 6.53 (s, 1H), 5.72 (d, J = 8.3 Hz, 1H), 5.46 (d, J = 9.5 Hz, 1H), 5.28 (t, J = 8.9 Hz, 1H), 4.93 (s, 1H), 4.84 (s, 1H), 2.67 – 2.50 (m, 4H), 1.99 (s, 3H), 1.73 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 158.3, 157.7, 144.5, 142.3, 141.6, 138.1, 137.1, 128.9, 128.5, 128.3, 128.0, 125.9, 125.4, 121.6, 117.6, 117.1, 117.0, 111.0, 108.0, 52.1, 34.9, 34.1, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{28}H_{27}BrN_4NaO^+$ $[M+Na]^+$: 537.1260, found: 537.1270.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-6-(trifluoromethyl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**19**)



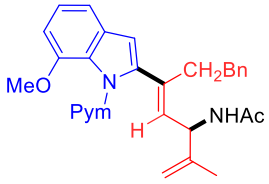
Product **19** was isolated in 92% yield (92.8 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.71 (d, J = 4.8 Hz, 2H), 8.62 (s, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.20 – 7.18 (m, 2H), 7.14 (t, J = 4.8 Hz, 1H), 7.12 – 7.07 (m, 3H), 6.61 (s, 1H), 5.78 (d, J = 8.3 Hz, 1H), 5.50 (d, J = 9.5 Hz, 1H), 5.31 (t, J = 8.9 Hz, 1H), 4.94 (s, 1H), 4.85 (s, 1H), 2.70 – 2.65 (m, 1H), 2.65 – 2.58 (m, 2H), 2.57 – 2.51 (m, 1H), 2.00 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 158.4, 157.7, 144.4, 144.4, 141.6, 137.0, 136.4, 131.7, 129.6, 128.5, 128.4, 126.0,125.4 (q, $J_{C\text{-}F}$ = 31.8 Hz), 125.2 (q, $J_{C\text{-}F}$ = 271.8 Hz), 120.7, 118.9 (q, $J_{C\text{-}F}$ = 3.7 Hz), 117.9, 111.7 (q, $J_{C\text{-}F}$ = 4.4 Hz), 111.2, 107.9, 52.1, 34.9, 34.1, 23.5, 20.0. **HRMS** (ESI) calculated for $C_{29}H_{27}F_3N_4NaO^+$ [M+Na]$^+$: 527.2029, found: 527.2034.

Methyl (*E*)-2-(5-acetamido-6-methyl-1-phenylhepta-3,6-dien-3-yl)-1-(pyrimidin-2-yl)-1H-indole-6-carboxylate (**20**)



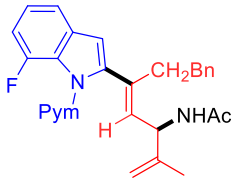
Product **20** was isolated in 90% yield (88.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.94 (s, 1H), 8.73 (d, J = 4.8 Hz, 2H), 7.92 – 7.90 (m, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.20 – 7.18 (m, 2H), 7.14 (t, J = 4.8 Hz, 1H), 7.12 – 7.08 (m, 3H), 6.58 (s, 1H), 5.91 (d, J = 8.3 Hz, 1H), 5.49 (d, J = 9.5 Hz, 1H), 5.31 (t, J = 8.9 Hz, 1H), 4.94 (s, 1H), 4.84 (s, 1H), 3.93 (s, 3H), 2.67 (q, J = 11.0 Hz, 1H), 2.64 – 2.58 (m, 2H), 2.53 (q, J = 10.9 Hz, 1H), 2.01 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 168.1, 158.4, 157.7, 144.9, 144.4, 141.6, 136.8, 136.8, 132.9, 129.7, 128.5, 128.4, 128.3, 125.9, 125.0, 123.3, 120.1, 117.9, 115.8, 111.1, 107.9, 52.1, 34.9, 34.0, 23.5, 20.0. **HRMS** (ESI) calculated for $C_{30}H_{30}N_4NaO_3^+$ [M+Na]$^+$: 517.2210, found: 517.2219.

(*E*)-*N*-(5-(7-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**21**)



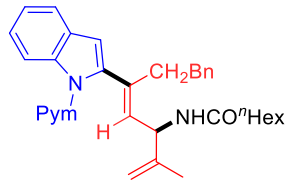
Product **21** was isolated in 52% yield (48.5 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.76 (d, J = 4.8 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.17 – 7.12 (m, 3H), 7.08 (t, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 6.60 (s, 1H), 5.45 (d, J = 8.1 Hz, 1H), 5.41 (d, J = 9.4 Hz, 1H), 5.08 (t, J = 8.8 Hz, 1H), 4.71 (s, 1H), 4.68 (s, 1H), 3.59 (s, 3H), 2.74 – 2.69 (m, 1H), 2.67 – 2.62 (m, 1H), 2.59 – 2.54 (m, 1H), 2.53 – 2.47 (m, 1H), 1.91 (s, 3H), 1.50 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.7, 160.1, 157.8, 147.0, 144.2, 142.3, 141.8, 134.9, 131.0, 130.4, 128.7, 128.3, 125.89, 121.8, 119.5, 113.6, 110.9, 105.0, 104.8, 55.8, 52.2, 34.8, 33.8, 23.4, 19.8. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO_2^+$ [M+Na]$^+$: 489.2261, found: 489.2265.

(*E*)-*N*-(5-(7-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**22**)



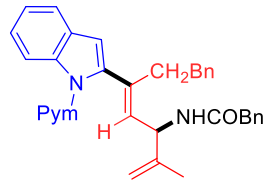
Product **22** was isolated in 94% yield (85.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.75 (d, J = 4.8 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.16 – 7.11 (m, 3H), 7.10 – 7.06 (m, 1H), 6.92 – 6.89 (m, 1H), 6.61 (d, J = 2.2 Hz, 1H), 5.63 (d, J = 8.3 Hz, 1H), 5.36 (d, J = 9.5 Hz, 1H), 5.15 (t, J = 8.9 Hz, 1H), 4.74 (s, 2H), 2.74 – 2.69 (m, 1H), 2.67 – 2.62 (m, 1H), 2.54 – 2.47 (m, 2H), 1.91 (s, 3H), 1.56 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.8, 158.5, 158.4, 149.8 (d, $J_{C\text{-}F}$ = 247.0 Hz), 144.1, 142.8, 141.6, 134.8, 132.2 (d, $J_{C\text{-}F}$ = 4.3 Hz), 131.3, 128.6, 128.4, 125.9, 125.4 (d, $J_{C\text{-}F}$ = 9.3 Hz), 121.7 (d, $J_{C\text{-}F}$ = 6.6 Hz), 119.5, 116.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 111.1, 109.3 (d, $J_{C\text{-}F}$ = 18.5 Hz), 105.8, 52.0, 34.7, 33.8, 23.4, 19.9. **HRMS** (ESI) calculated for $C_{28}H_{27}FN_4NaO^+$ $[M+Na]^+$: 477.2061, found: 477.2066.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)heptanamide (**23**)



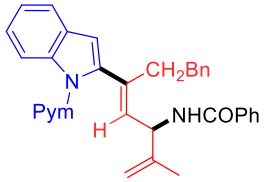
Product **23** was isolated in 74% yield (75.1 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.68 (d, J = 4.8 Hz, 2H), 8.30 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 – 7.17 (m, 4H), 7.12 – 7.08 (m, 3H), 7.07 (t, J = 4.8 Hz, 1H), 6.60 (s, 1H), 5.56 (d, J = 8.2 Hz, 1H), 5.47 (d, J = 9.4 Hz, 1H), 5.31 (t, J = 8.8 Hz, 1H), 4.93 (s, 1H), 4.83 (s, 1H), 2.72 – 2.65 (m, 1H), 2.64 – 2.53 (m, 3H), 2.22 – 2.13 (m, 2H), 1.73 (s, 3H), 1.67 – 1.61 (m, 2H), 1.34 – 1.26 (m, 6H), 0.89 – 0.86 (m, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 172.0, 158.2, 144.8, 141.8, 141.7, 137.6, 137.6, 129.2, 128.7, 128.6, 128.3, 125.9, 123.6, 122.3, 120.5, 117.3, 113.9, 110.8, 108.4, 51.9, 37.1, 35.0, 34.2, 31.7, 29.1, 25.9, 22.6, 20.1, 14.1. **HRMS** (ESI) calculated for $C_{32}H_{36}N_4NaO^+$ $[M+Na]^+$: 529.2938, found: 529.2945.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)-2-phenylacetamide (**24**)



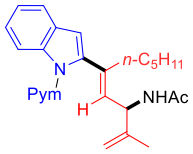
Product **24** was isolated in 83% yield (85.1 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.61 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.29 – 7.25 (m, 4H), 7.23 – 7.18 (m, 3H), 7.13 – 7.08 (m, 3H), 7.03 (t, J = 4.8 Hz, 1H), 6.55 (s, 1H), 5.52 (d, J = 7.9 Hz, 1H), 5.34 – 5.29 (m, 2H), 4.79 (s, 1H), 4.77 (s, 1H), 3.64 – 3.54 (m, 2H), 2.70 – 2.64 (m, 1H), 2.63 – 2.53 (m, 3H), 1.65 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 169.7, 158.2, 158.1, 144.5, 141.8, 141.6, 137.8, 137.5, 135.0, 129.4, 129.2, 129.1, 128.6, 128.4, 128.3, 127.5, 125.9, 123.7, 122.3, 120.5, 117.3, 113.9, 110.9, 108.4, 52.1, 44.1, 35.0, 34.2, 20.0. **HRMS** (ESI) calculated for $C_{34}H_{32}N_4NaO^+$ $[M+Na]^+$: 535.2468, found: 535.2473.

(*E*)-*N*-(2-methyl-7-phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)benzamide (**25**)



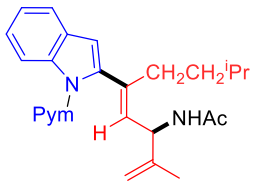
Product **25** was isolated in 61% yield (60.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.62 (d, J = 4.8 Hz, 2H), 8.29 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.44 – 7.42 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 7.13 – 7.12 (m, 2H), 7.09 – 7.06 (m, 1H), 7.00 (t, J = 4.8 Hz, 1H), 6.62 (s, 1H), 6.21 (d, J = 7.9 Hz, 1H), 5.57 (d, J = 9.5 Hz, 1H), 5.49 (t, J = 8.6 Hz, 1H), 5.01 (s, 1H), 4.88 (s, 1H), 2.74 – 2.71 (m, 1H), 2.69 – 2.63 (m, 3H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 166.4, 158.2, 144.6, 141.8, 141.6, 138.0, 137.6, 134.7, 131.6, 129.2, 128.7, 128.6, 128.5, 128.4, 127.0, 125.9, 123.7, 122.3, 120.6, 117.3, 113.9, 111.1, 108.4, 52.6, 35.0, 34.3, 20.2. **HRMS** (ESI) calculated for $C_{33}H_{30}N_4NaO^+$ $[M+Na]^+$: 521.2312, found: 521.2318.

(*E*)-*N*-(2-methyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)deca-1,4-dien-3-yl)acetamide (**26**)



Product **26** was isolated in 73% yield (58.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.71 (d, J = 4.8 Hz, 2H), 8.24 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.21 – 7.19 (m, 1H), 7.11 (t, J = 4.8 Hz, 1H), 6.58 (s, 1H), 5.70 (d, J = 8.3 Hz, 1H), 5.42 (d, J = 9.4 Hz, 1H), 5.27 (t, J = 8.9 Hz, 1H), 4.95 (d, J = 1.6 Hz, 1H), 4.85 (d, J = 1.4 Hz, 1H), 2.25 – 2.21 (m, 2H), 2.00 (s, 3H), 1.77 (s, 3H), 1.36 – 1.29 (m, 2H), 1.20 – 1.16 (m, 4H), 0.79 – 0.76 (m, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.8, 158.2, 144.8, 142.1, 138.6, 137.5, 129.2, 128.0, 123.5, 122.1, 120.4, 117.3, 113.6, 110.8, 108.0, 52.2, 31.9, 31.8, 28.3, 23.5, 22.5, 20.1, 14.1. **HRMS** (ESI) calculated for $C_{25}H_{30}N_4NaO^+$ $[M+Na]^+$: 425.2312, found: 425.2317.

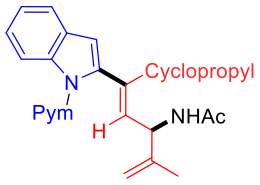
(*E*)-*N*-(2,8-dimethyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)nona-1,4-dien-3-yl)acetamide (**27**)



Product **27** was isolated in 65% yield (52.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.73 (d, J = 4.8 Hz, 2H), 8.23 (d, J = 8.3 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.27 – 7.24 (m, 2H), 7.21 – 7.19 (m, 1H), 7.12 (t, J = 4.8 Hz, 1H), 6.58 (s, 1H), 5.58 (d, J = 8.3 Hz, 1H), 5.42 (d, J = 9.3 Hz, 1H), 5.27 (t, J = 8.8 Hz, 1H), 4.96 (s, 1H), 4.86 (d, J = 1.4 Hz, 1H), 2.29 – 2.20 (m, 2H), 2.01 (s, 3H), 1.78 (s, 3H), 1.45 – 1.41 (m, 1H), 1.26 – 1.18 (m, 2H), 0.76 (d, J = 3.0 Hz, 3H), 0.75 (d, J = 3.0 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.8, 158.3, 144.8, 142.2, 138.8, 137.6, 129.2, 127.9, 123.5, 122.2, 120.5, 117.3, 113.6, 110.9, 108.0, 52.3, 37.7, 29.8, 28.2, 23.6, 22.5, 22.5, 20.1. **HRMS** (ESI) calculated for $C_{25}H_{30}N_4NaO^+$ $[M+Na]^+$: 425.2312, found: 425.2315.

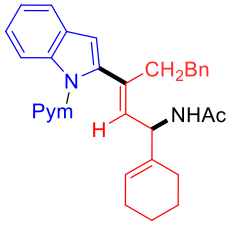
(*E*)-*N*-(1-cyclopropyl-4-methyl-1-(1-(pyrimidin-2-yl)-1H-indol-2-yl)penta-1,4-dien-3-yl)acetamide (**28**)

Product **28** was isolated in 72% yield (53.6 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA



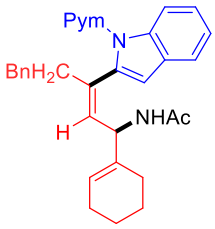
= 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.74 (d, J = 4.8 Hz, 2H), 8.32 – 8.26 (m, 1H), 7.58 – 7.54 (m, 1H), 7.30 – 7.26 (m, 1H), 7.23 – 7.20 (m, 1H), 7.12 (t, J = 4.8 Hz, 1H), 6.49 (s, 1H), 5.81 (d, J = 8.5 Hz, 1H), 5.73 – 5.71 (m, 1H), 5.62 (t, J = 8.8 Hz, 1H), 5.09 – 5.04 (m, 1H), 4.93 – 4.92 (m, 1H), 2.06 (s, 3H), 1.87 (s, 3H), 1.67 – 1.63 (m, 1H), 0.52 – 0.47 (m, 2H), 0.31 – 0.28 (m, 1H), 0.27 – 0.24 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.0, 158.1, 158.0, 144.7, 140.5, 139.3, 136.9, 130.0, 128.9, 123.5, 122.0, 120.4, 117.2, 113.8, 110.8, 108.1, 52.5, 23.6, 20.2, 12.8, 6.5, 6.4. **HRMS** (ESI) calculated for $C_{23}H_{24}N_4NaO^+$ $[M+Na]^+$: 395.1842, found: 395.1849.

(*E*)-*N*-(1-(cyclohex-1-en-1-yl)-5-phenyl-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)pent-2-en-1-yl)acetamide (**29**)



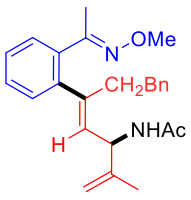
Product **29** was isolated in 62% yield (59.1 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.69 (d, J = 4.8 Hz, 2H), 8.26 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.24 – 7.18 (m, 3H), 7.13 – 7.07 (m, 4H), 6.61 (s, 1H), 5.62 – 5.61 (m, 1H), 5.55 (d, J = 8.5 Hz, 1H), 5.44 (d, J = 9.3 Hz, 1H), 5.24 (t, J = 9.0 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.65 – 2.55 (m, 3H), 1.99 – 1.97 (m, 5H), 1.95 – 1.92 (m, 2H), 1.63 – 1.57 (m, 2H), 1.55 – 1.52 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.8, 158.2, 158.18, 142.0, 141.9, 137.6, 137.0, 136.8, 129.3, 129.2, 128.6, 128.3, 125.8, 123.6, 122.3, 122.2, 120.5, 117.3, 113.7, 108.2, 52.2, 35.0, 34.2, 25.9, 25.2, 23.6, 22.8, 22.4. **HRMS** (ESI) calculated for $C_{31}H_{32}N_4NaO^+$ $[M+Na]^+$: 499.2468, found: 499.2473.

(*Z*)-*N*-(1-(cyclohex-1-en-1-yl)-5-phenyl-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)pent-2-en-1-yl)acetamide (**30**)



Product **30** was isolated in 17% yield (16.2 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-d_6)** δ 8.91 (d, J = 4.8 Hz, 2H), 8.08 (d, J = 8.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.40 (t, J = 4.8 Hz, 1H), 7.24 – 7.13 (m, 8H), 6.82 (s, 1H), 6.57 (d, J = 11.5 Hz, 1H), 6.12 – 6.10 (m, 1H), 4.90 – 4.83 (m, 1H), 2.74 – 2.67 (m, 4H), 2.44 – 2.37 (m, 1H), 2.14 (d, J = 14.2 Hz, 1H), 1.85 (s, 4H), 1.79 (d, J = 12.1 Hz, 1H), 1.70 – 1.65 (m, 1H), 1.56 (d, J = 13.7 Hz, 1H), 1.37 – 1.31 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.0, 158.6, 158.4, 142.7, 142.1, 139.8, 138.2, 134.5, 129.5, 128.6, 128.3, 125.9, 123.9, 123.5, 122.2, 121.6, 120.6, 117.4, 113.4, 108.8, 46.3, 35.3, 34.0, 33.6, 31.8, 27.96, 23.8, 21.4. **HRMS** (ESI) calculated for $C_{31}H_{32}N_4NaO^+$ $[M+Na]^+$: 499.2468, found: 499.2474.

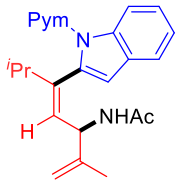
N-((*E*)-5-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2-methyl-7-phenylhepta-1,4-dien-3-yl)acetamide (**31**)



Product **31** was isolated in 55% yield (42.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: PE/EA = 8/1, R_f = 0.3. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 3H), 7.25 – 7.19 (m, 3H), 7.16 – 7.13 (m, 3H), 5.52 (d, J = 7.9 Hz, 1H), 5.35 (d, J = 9.4 Hz, 1H), 5.32 – 5.29 (m, 1H), 4.95 – 4.91 (m, 1H), 4.89 – 4.85 (m, 1H), 3.94 (s,

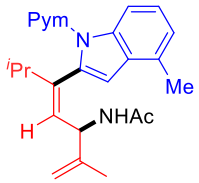
3H), 2.79 – 2.75 (m, 2H), 2.63 – 2.58 (m, 1H), 2.57 – 2.52 (m, 1H), 2.08 (s, 3H), 2.01 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 168.9, 157.7, 144.6, 143.6, 141.8, 141.4, 136.4, 129.7, 129.6, 129.1, 128.7, 128.6, 128.5, 127.5, 126.0, 111.3, 61.8, 52.4, 34.8, 34.2, 23.5, 20.0, 16.6. **HRMS** (ESI) calculated for $C_{25}H_{30}N_2NaO_2^+$ $[M+Na]^+$: 413.2199, found: 413.2203.

(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**32**)



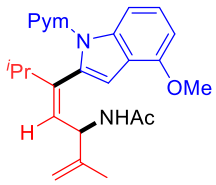
Product **32** was isolated in 97% (25:1) yield (72.6 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.81 (d, *J* = 4.7 Hz, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 4.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 -7.17 (m, 1H), 6.58 – 6.57 (m, 1H), 5.51 (d, *J* = 9.3 Hz, 1H), 5.10 – 4.85 (m, 1H), 4.79 – 4.71 (m, 1H), 4.65 – 4.49 (m, 1H), 2.43 -2.38 (m, 1H), 1.90 – 1.41 (m, 3H), 1.22 – 0.93 (m, 3H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.8, 158.7, 158.2, 146.6, 144.1, 138.5, 137.2, 129.9, 125.9, 123.3, 122.3, 120.7, 118.0, 115.2, 109.7, 108.5(brs), 53.9, 34.9, 22.6, 21.7(brs), 19.9. **HRMS** (ESI) calculated for $C_{23}H_{26}N_4NaO^+$ $[M+Na]^+$: 397.1999, found: 397.2003.

(*Z*)-*N*-(2,6-dimethyl-5-(4-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**33**)



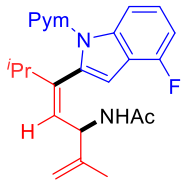
Product **33** was isolated in 84% (20:1) yield (65.3 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.80 (d, *J* = 4.6 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.28 (m, 1H), 7.14 – 7.11 (m, 2H), 7.00 – 6.98 (m, 1H), 6.63 (s, 1H), 5.50 (d, *J* = 9.3 Hz, 1H), 5.13 – 4.92 (m, 1H), 4.82 – 4.73 (m, 1H), 4.62 (s, 1H), 2.53 (s, 3H), 2.42 – 2.32 (m, 1H), 1.89 – 1.50 (m, 6H), 1.15 – 0.92 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.2, 159.2, 158.8, 147.2, 144.8, 138.3, 137.5, 130.2, 129.9, 126.4, 124.0, 123.1, 118.5, 113.3, 110.1, 107.7(brs), 54.4, 35.3, 23.1, 22.4(brs), 20.4, 18.8. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO^+$ $[M+Na]^+$: 411.2155, found: 411.2157.

(*Z*)-*N*-(5-(4-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**34**)



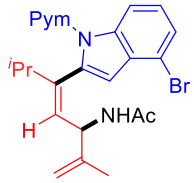
Product **34** was isolated in 84% (>25:1) yield (67.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.30 (t, *J* = 4.8 Hz, 1H), 7.18 – 7.00 (m, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.65 – 6.58 (m, 1H), 5.51 (d, *J* = 10.1 Hz, 1H), 5.00 – 4.90 (m, 1H), 4.79 – 4.68 (m, 1H), 4.66 – 4.48 (m, 1H), 3.94 (s, 3H), 2.42 – 2.37 (m, 1H), 1.85 – 1.49 (m, 6H), 1.16 – 0.96 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.8, 158.7, 158.4, 153.4, 146.8(brs), 144.1, 138.5, 136.9, 126.1, 124.3, 120.2, 118.2, 109.8, 108.5, 105.4(brs), 102.7, 55.4, 54.1, 35.1, 22.6, 22.0(brs), 19.9. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO_2^+$ $[M+Na]^+$: 427.2104, found: 427.2105.

(*Z*)-*N*-(5-(4-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**35**)



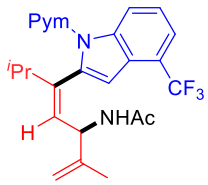
Product **35** was isolated in 54% (25:1) yield (42.3 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.85 (d, J = 4.8 Hz, 2H), 8.22 (d, J = 8.3 Hz, 1H), 7.36 (t, J = 4.8 Hz, 1H), 7.23 – 7.08 (m, 2H), 6.94 – 6.91 (m 1H), 6.68 – 6.61 (m, 1H), 5.55 (d, J = 9.3 Hz, 1H), 4.99 – 4.87 (s, 1H), 4.80 – 4.52 (m, 2H), 2.48 – 2.38 (m, 1H), 1.87 – 1.49 (m, 6H), 1.16 – 0.97 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.3, 158.3, 157.5, 154.5 (d, $J_{C\text{-}F}$ = 244.4 Hz) 146.0 (brs), 143.0, 138.9 (d, $J_{C\text{-}F}$ = 10.3 Hz), 138.4, 126.3, 123.4 (d, $J_{C\text{-}F}$ = 7.6 Hz), 118.1, 117.9 (d, $J_{C\text{-}F}$ = 22.6 Hz), 111.0 (d, $J_{C\text{-}F}$ = 34.6 Hz), 109.4, 106.6(d, $J_{C\text{-}F}$ = 18.6 Hz), 102.7 (brs), 53.4, 34.4, 22.0 (brs), 21.3, 19.3. **HRMS** (ESI) calculated for $C_{23}H_{25}FN_4NaO^+$ $[M+Na]^+$: 415.1905, found: 415.1907.

(*Z*)-*N*-(5-(4-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**36**)



Product **36** was isolated in 71% (25:1) yield (64.2 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.85 (d, J = 4.8 Hz, 2H), 8.40 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 4.8 Hz, 1H), 7.18 – 7.13 (m, 2H), 6.65 – 6.53 (m, 1H), 5.56 (d, J = 10.1 Hz, 1H), 4.96 – 4.86 (m, 1H), 4.72 – 4.60 (m, 2H), 2.48 – 2.40 (m, 1H), 1.85 – 1.49 (m, 6H), 1.20 – 1.06 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.2, 159.4, 158.4, 146.9, 144.0, 140.1, 137.9, 130.6, 127.3, 125.6, 124.9, 119.2, 115.0, 114.4, 110.4, 108.2 (brs), 54.4, 35.4, 23.1, 22.3 (brs), 20.3. **HRMS** (ESI) calculated for $C_{23}H_{25}BrN_4NaO^+$ $[M+Na]^+$: 475.1104, found: 475.1116.

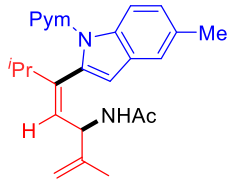
(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-4-(trifluoromethyl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**37**)



Product **37** was isolated in 78% (25:1) yield (68.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.86 (d, J = 4.8 Hz, 2H), 8.65 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.28 – 7.05 (m, 1H), 6.79 – 6.68 (m, 1H), 5.58 (d, J = 9.5 Hz, 1H), 4.92 – 4.80 (m, 1H), 4.75 – 4.52 (m, 2H), 2.51 – 2.40 (m, 1H), 1.85 – 1.45 (m, 6H), 1.19 – 0.95 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.2, 159.4, 158.2, 146.9, 143.8(br), 141.3, 138.1, 127.6, 126.5, 126.1 (q, $J_{C\text{-}F}$ = 271.8 Hz), 123.2, 121.6 (q, $J_{C\text{-}F}$ = 32.2 Hz), 119.9 (q, $J_{C\text{-}F}$ = 5.0 Hz), 119.5, 119.3, 110.4, 106.5 (brs), 54.5, 35.4, 23.0, 22.2 (brs), 20.2. **HRMS** (ESI) calculated for $C_{24}H_{25}F_3N_4NaO^+$ $[M+Na]^+$: 465.1873, found: 465.1882.

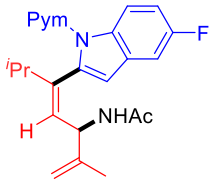
(*Z*)-*N*-(2,6-dimethyl-5-(5-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**38**)

Product **38** was isolated in 91% (25:1) yield (70.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent:

Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.79 (d, J = 4.8 Hz, 2H), 

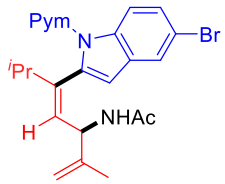
8.34 (d, J = 8.5 Hz, 1H), 7.36 (s, 1H), 7.26 (t, J = 4.8 Hz, 1H), 7.06 (dd, J = 8.5, 1.8 Hz, 1H), 6.52 – 6.45 (m, 1H), 5.49 (d, J = 9.3 Hz, 1H), 5.10 – 4.86 (m, 1H), 4.82 – 4.50 (m, 2H), 2.44 – 2.37 (m, 4H), 1.88 – 1.47 (m, 6H), 1.18 – 0.94 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.1, 158.1, 157.8, 146.2(brs), 143.9, 138.0, 135.0, 130.9, 129.7, 125.1, 124.2, 120.1, 117.2, 114.6, 109.1, 108.1 (brs), 53.3, 34.3, 22.0, 21.3 (brs), 20.5, 19.3. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO^+$ $[M+Na]^+$: 411.2155, found: 411.2160.

(*Z*)-*N*-(5-(5-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**39**)



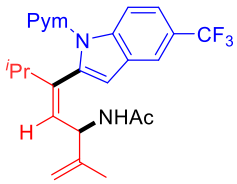
Product **39** was isolated in 80% (>25:1) yield (62.8 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.82 (d, J = 4.8 Hz, 2H), 8.46 (dd, J = 8.7, 4.5 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.04 – 7.00 (m, 2H), 6.57 (s, 1H), 5.52 (dd, J = 9.4, 1.1 Hz, 1H), 4.93 – 4.86 (m, 1H), 4.74 – 4.60 (m, 2H), 2.45 – 2.41 (m, 1H), 1.90 – 1.47 (m, 6H), 1.18 – 0.94 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.3, 158.8 (d, $J_{C\text{-}F}$ = 236.0 Hz), 158.2, 157.5, 146.0 (brs), 143.4, 139.9, 133.1, 130.2 (d, $J_{C\text{-}F}$ = 10.1 Hz), 125.7, 117.6, 116.0 (d, $J_{C\text{-}F}$ = 9.1 Hz), 110.3 (d, $J_{C\text{-}F}$ = 25.2 Hz), 109.3, 107.8 (brs), 105.1 (d, $J_{C\text{-}F}$ = 23.8 Hz), 53.4, 34.3, 22.1, 21.3 (brs), 19.3. **HRMS** (ESI) calculated for $C_{23}H_{25}FN_4NaO^+$ $[M+Na]^+$: 415.1905, found: 415.1908.

(*Z*)-*N*-(5-(5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**40**)



Product **40** was isolated in 70% (25:1) yield (63.3 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.84 (d, J = 4.8 Hz, 2H), 8.38 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 2.1 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.22 – 7.02 (m, 1H), 6.57 (s, 1H), 5.53 (dd, J = 9.4, 1.1 Hz, 1H), 4.97 – 4.84 (m, 1H), 4.71 – 4.59 (m, 2H), 2.49 – 2.38 (m, 1H), 1.85 – 1.49 (m, 6H), 1.18 – 0.94 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.3, 159.3, 158.4, 147.0 (brs), 144.2, 140.6, 136.4, 132.3, 127.0, 126.4, 123.7, 118.9, 117.6, 115.5, 110.4, 108.3 (brs), 54.3, 35.4, 23.1, 22.2 (brs), 20.3. **HRMS** (ESI) calculated for $C_{23}H_{25}BrN_4NaO^+$ $[M+Na]^+$: 475.1104, found: 475.1113.

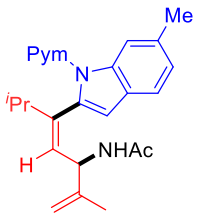
(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-5-(trifluoromethyl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**41**)



Product **41** was isolated in 72% (10:1) yield (63.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.91 (d, J = 4.8 Hz, 0.2H), 8.88 (d, J = 4.8 Hz, 2H), 8.57 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 8.7 Hz, 0.1H), 7.99 (s, 1H), 7.54 (dd, J = 8.8, 1.9 Hz, 1H), 7.47 (t, J = 4.8 Hz, 0.1H), 7.42 – 7.36 (m, 1H), 7.24 – 6.99 (m, 1H), 6.77 – 6.69 (m, 1H), 5.56 (d, J = 9.4 Hz, 1H), 5.18 (d, J = 9.7 Hz, 0.1H), 4.98 – 4.82 (m, 1.13H), 4.71 – 4.60 (m, 2.15H),

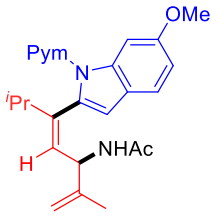
3.22 – 3.18 (m, 0.1H), 2.52 – 2.41 (m, 1H), 1.85 – 1.48 (m, 6.72H), 1.17 – 1.01 (m, 6.66H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.8, 168.3, 159.8, 159.5, 158.3, 146.9, 146.4, 143.9, 143.2, 141.3, 140.7, 139.1, 133.0, 130.0, 129.6, 127.4, 126.4 (q, $J_{C\text{-}F}$ = 270.9 Hz), 124.5 (q, $J_{C\text{-}F}$ = 31.7 Hz), 120.2 (q, $J_{C\text{-}F}$ = 3.9 Hz), 119.3, 118.7 (q, $J_{C\text{-}F}$ = 4.4 Hz), 116.2, 114.7, 111.3, 110.4, 109.1 (brs), 107.5, 54.3, 52.0, 35.4, 30.9, 23.2, 23.1, 22.3 (brs), 20.4, 20.3. **HRMS** (ESI) calculated for $C_{24}H_{25}F_3N_4NaO^+$ $[M+Na]^+$: 465.1873, found: 465.1877.

(*Z*)-*N*-(2,6-dimethyl-5-(6-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**42**)



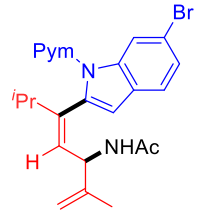
Product **42** was isolated in 97% (25:1) yield (75.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.80 (d, J = 4.8 Hz, 2H), 8.27 (s, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.27 (t, J = 4.7 Hz, 1H), 7.21 – 7.09 (m, 1H), 7.04 – 7.00 (m, 1H), 6.51 (s, 1H), 5.48 (d, J = 9.3 Hz, 1H), 5.10 – 4.89 (m, 1H), 4.81 – 4.69 (m, 1H), 4.66 – 4.39 (m, 1H), 2.44 (s, 3H), 2.41 – 2.33 (m, 1H), 1.84 – 1.51 (m, 6H), 1.14 – 0.95 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.3, 159.1, 158.7, 147.2 (brs), 144.7, 138.4, 138.1, 133.3, 128.2, 126.3, 124.2, 120.9, 118.3, 115.7, 110.1, 108.9 (brs), 54.4, 35.4, 23.1, 22.3, 22.0 (brs), 20.3. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO^+$ $[M+Na]^+$: 411.2155, found: 411.2158.

(*Z*)-*N*-(5-(6-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**43**)



Product **43** was isolated in 95% yield (76.8 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.80 (d, J = 4.8 Hz, 2H), 8.11 (s, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.26 (t, J = 4.8 Hz, 1H), 7.22 – 7.00 (m, 1H), 6.86 (dd, J = 8.6, 2.4 Hz, 1H), 6.53 – 6.48 (m, 1H), 5.47 (d, J = 9.3 Hz, 1H), 5.14 – 4.93 (m, 1H), 4.79 – 4.71 (m, 1H), 4.68 – 4.47 (m, 1H), 3.83 (s, 3H), 2.41 – 2.31 (m, 1H), 1.88 – 1.52 (m, 6H), 1.16 – 0.94 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.3, 159.1, 158.8, 158.2, 147.2, 144.8, 138.6, 137.8, 126.1, 124.4, 121.5, 118.3, 111.8, 110.1, 109.0 (brs), 100.4, 56.0, 54.4, 35.4, 23.1, 22.3 (brs), 20.4. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO_2^+$ $[M+Na]^+$: 427.2104, found: 427.2109.

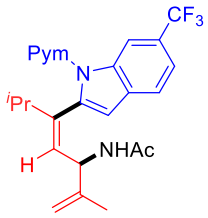
(*Z*)-*N*-(5-(6-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**44**)



Product **44** was isolated in 80% (20:1) yield (72.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.85 (d, J = 4.8 Hz, 2H), 8.68 (s, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.24 – 6.97 (m, 1H), 6.62 – 6.55 (m, 1H), 5.52 (dd, J = 9.3, 1.2 Hz, 1H), 5.04 – 4.84 (m, 1H), 4.77 – 4.51 (m, 2H), 2.48 – 2.39 (m, 1H), 1.88 – 1.52 (m, 6H), 1.19 – 0.98 (d, J=19.3, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.3, 159.3, 158.3, 146.9 (brs), 144.2, 140.0, 138.2, 129.4, 126.9, 125.8, 122.7, 118.9, 118.7, 117.0, 110.4, 108.8 (brs), 54.3, 35.3, 23.1,

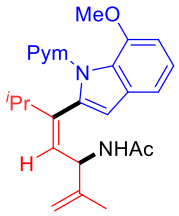
22.4 (brs), 20.3. **HRMS** (ESI) calculated for $C_{23}H_{25}BrN_4NaO^+$ $[M+Na]^+$: 475.1104, found: 475.1118.

(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-6-(trifluoromethyl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**45**)



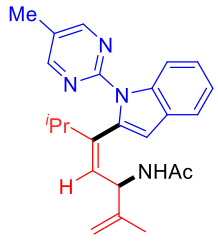
Product **45** was isolated in 91% (9:1) yield (80.4 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.91 (d, J = 4.8 Hz, 0.22H), 8.88 (d, J = 4.8 Hz, 2H), 8.83 (s, 1H), 8.42 (s, 0.11H), 7.82 – 7.79 (m, 1H), 7.51 – 7.49 (m, 1H), 7.45 (t, J = 4.8 Hz, 0.11H), 7.38 (t, J = 4.8, 1H), 7.29 – 6.98 (m, 1H), 6.73 – 6.63 (m, 1H), 5.61 – 5.53 (m, 1H), 5.41 (t, J = 9.2 Hz, 0.11H), 5.19 (d, J = 9.7 Hz, 0.11H), 5.05 – 4.83 (m, 1.13H), 4.80 – 4.52 (m, 2.17H), 2.52 – 2.44 (m, 1H), 1.83 – 1.46 (m, 6.85H), 1.20 – 1.01 (m, 6.75H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.8, 167.3, 158.8, 158.4, 157.3, 145.7 (brs), 145.3, 142.9, 141.3, 139.8, 135.6, 132.1, 126.20, 125.5 (q, $J_{C\text{-}F}$ = 271.0 Hz), 124.1 (q, $J_{C\text{-}F}$ = 31.7 Hz), 120.9, 120.8, 118.8, 118.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 118.1, 112.2 (q, $J_{C\text{-}F}$ = 4.6 Hz) 110.3, 109.4, 107.7 (brs), 106.2, 53.3, 51.0, 34.4, 29.9, 22.2, 22.0, 21.6, 21.2 (brs), 20.9, 19.3. **HRMS** (ESI) calculated for $C_{24}H_{25}F_3N_4NaO^+$ $[M+Na]^+$: 465.1873, found: 465.1882.

(*Z*)-*N*-(5-(7-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-2,6-dimethylhepta-1,4-dien-3-yl)acetamide (**46**)



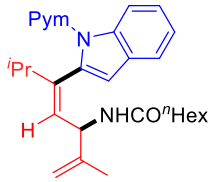
Product **46** was isolated in 72% (20:1) yield (58.2 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.80 (d, J = 4.8 Hz, 2H), 7.48 (t, J = 4.8 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.09 – 6.99 (m, 2H), 6.65 (d, J = 7.8 Hz, 1H), 6.46 (s, 1H), 5.24 (t, J = 9.1 Hz, 1H), 5.19 – 5.13 (m, 1H), 4.69 – 4.64 (m, 2H), 3.54 (s, 3H), 3.10 – 3.04 (m, 1H), 1.84 (s, 3H), 1.51 (s, 3H), 1.12 (d, J = 6.9 Hz, 3H), 1.05 (d, J = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 167.6, 159.3, 157.7, 147.0, 145.2, 139.7, 138.5, 133.0, 130.0, 127.2, 121.0, 119.9, 113.0, 110.0, 103.9, 103.0, 55.1, 50.8, 22.1, 21.4, 20.7, 19.2. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO_2^+$ $[M+Na]^+$: 427.2104, found: 427.2111.

(*Z*)-*N*-(2,6-dimethyl-5-(1-(5-methylpyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)acetamide (**47**)



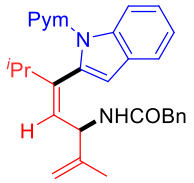
Product **47** was isolated in 90% (25:1) yield (69.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.68 – 8.64 (m, 2H), 8.34 (d, J = 8.4 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.22 – 7.21 (m, 1H), 7.19 – 7.00 (m, 2H), 6.59 – 6.53 (s, 1H), 5.50 (d, J = 9.1 Hz, 1H), 5.09 – 4.88 (m, 1H), 4.79 – 4.71 (m, 1H), 4.58 – 4.55 (m, 1H), 2.39 – 2.33 (m, 4H), 1.83 – 1.49 (m, 6H), 1.16 – 0.96 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.3, 159.1, 156.9, 147.2, 144.5, 138.9, 137.7, 130.2, 128.0, 126.7, 123.6, 122.5, 121.2, 115.3, 110.1, 108.5 (brs), 54.5, 35.4, 23.1, 22.2 (brs), 20.4, 15.1. **HRMS** (ESI) calculated for $C_{24}H_{28}N_4NaO^+$ $[M+Na]^+$: 411.2155, found: 411.2159.

(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)heptanamide (**48**)



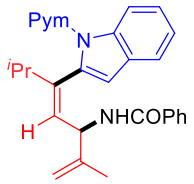
Product **48** was isolated in 84% (>25:1) yield (74.5 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.44 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.29 (t, *J* = 4.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.16(m, 1H), 7.14 – 6.99 (m, 1H), 6.56 (d, *J*=16.0, 1H), 5.57 – 5.48 (m, 1H), 5.11 – 4.95 (m, 1H), 4.83 – 4.55 (m, 2H), 2.39 – 2.35 (m, 1H), 2.02 – 1.86 (m, 1H), 1.77 – 1.38 (m, 6H), 1.31 – 0.96 (m, 13H), 0.88 – 0.81 (m, 3H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 170.5, 158.2, 157.7, 146.3, 143.6, 138.0, 136.8, 129.4, 125.6, 122.8, 121.8, 120.2, 117.5, 114.7, 109.2, 108.2 (brs), 53.3, 35.9, 31.4, 25.6, 22.3, 21.0 (brs), 19.4, 13.5. **HRMS** (ESI) calculated for $C_{28}H_{36}N_4NaO^+$ $[M+Na]^+$: 467.2781, found: 467.2795.

(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)-2-phenylacetamide (**49**)



Product **49** was isolated in 93% (25:1) yield (83.7 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.42 (d, *J* = 8.3, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.12 (m, 9H), 6.48 (s, 1H), 5.51 (d, *J* = 9.1 Hz, 1H), 5.00 – 4.95 (m, 1H), 4.8 0 – 4.69 (m, 1H), 4.67 – 4.44 (m, 1H), 3.60 – 3.09 (m, 2H), 2.37 – 2.30 (m, 1H), 1.64 – 1.47 (m, 3H), 1.13 – 0.89 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.4, 158.2, 157.7, 146.0, 143.9, 137.8, 136.8, 129.4, 129.0, 128.1, 126.3, 125.3, 122.9, 121.8, 120.3, 117.5, 114.7, 109.3, 108.1 (brs), 53.6, 43.0, 34.4, 20.9 (brs), 19.3. **HRMS** (ESI) calculated for $C_{29}H_{30}N_4NaO^+$ $[M+Na]^+$: 473.2312, found: 473.2323.

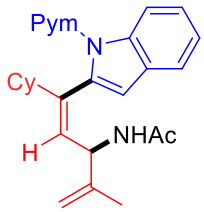
(*Z*)-*N*-(2,6-dimethyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hepta-1,4-dien-3-yl)benzamide (**50**)



Product **50** was isolated in 40% (>25:1) yield (34.9 mg, in 0.2 mmol scale) as light yellow solid. Eluent: Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (600 MHz, Acetone-*d*$_6$)** δ 8.85 – 8.77 (m, 2H), 8.40 (s, 1H), 7.92 – 7.56 (m, 5H), 7.48 – 7.30 (m, 3H), 7.26 – 7.15 (m, 3H), 6.60 (s, 1H), 5.76 -5.71 (m, 1H), 5.34 – 5.17 (m, 1H), 4.93 – 4.80 (m, 1H), 4.76 – 4.57 (m, 1H), 2.46 – 2.39 (m, 1H), 1.73 – 1.68 (m, 3H), 1.30 – 1.28 (m, 1H), 1.20 – 0.96 (m, 6H). **^{13}C NMR (151 MHz, Acetone-*d*$_6$)** δ 168.3, 159.1, 158.8, 158.2, 147.2, 144.8, 138.6, 137.8, 126.1, 124.4, 121.5, 118.3, 111.8, 110.1, 109.0 (brs), 100.4, 56.0, 54.4, 35.4, 23.1, 22.3 (brs), 20.4. **HRMS** (ESI) calculated for $C_{28}H_{28}N_4NaO^+$ $[M+Na]^+$: 459.2155, found: 459.2166.

(*Z*)-*N*-(1-cyclohexyl-4-methyl-1-(1-(pyrimidin-2-yl)-1H-indol-2-yl)penta-1,4-dien-3-yl)acetamide (**51**)

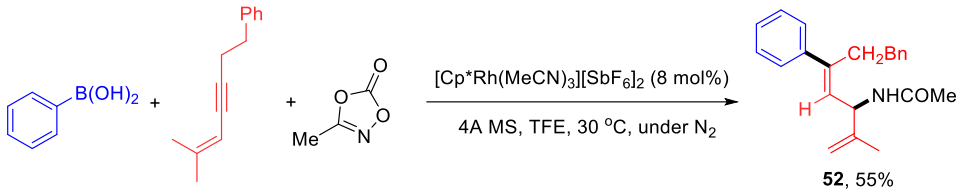
Product **51** was isolated in 79% (>25:1) yield (65.6 mg, in 0.2 mmol scale) as light yellow solid. Eluent:



Petroleum Ether/Acetone = 3/2, R_f = 0.3. **^{1}H NMR (400 MHz, Acetone-*d*$_6$)** δ 8.83 (d, J = 4.8 Hz, 2H), 8.42 (d, J = 8.2 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.33 – 7.31 (m, 1H), 7.27 – 7.00 (m, 3H), 6.55 (s, 1H), 5.48 (d, J = 9.3 Hz, 1H), 4.97 (brs, 1H), 4.74 (brs, 1H), 4.61 (brs, 1H), 2.08 – 2.01 (m, 2H), 1.91 – 1.83 (m, 2H), 1.71 – 1.59 (m, 9H), 1.19 – 1.09 (m, 4H). **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 167.2, 158.2, 157.7, 146.1, 142.7, 138.0, 136.7, 129.4, 126.0, 122.8, 121.7, 120.2, 117.5, 114.7, 109.2, 108.1 (brs), 53.4, 44.8, 32.3 (brs), 26.7, 26.2, 22.1, 19.3. **HRMS** (ESI) calculated for $C_{26}H_{30}N_4NaO^+$ $[M+Na]^+$: 437.2312, found: 437.2333.

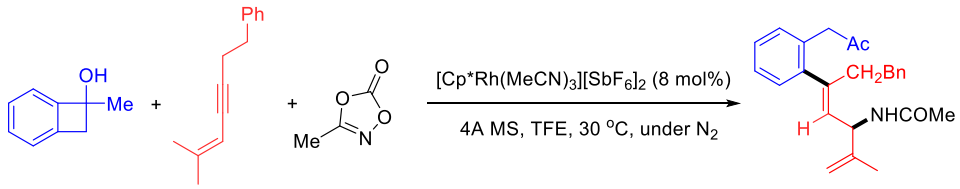
III. Synthetic Applications

(a) Experiments using phenylboronic acid and 7-methylbicyclo[4.2.0]octa-1,3,5-trien-7-ol as Arene



52, 55%

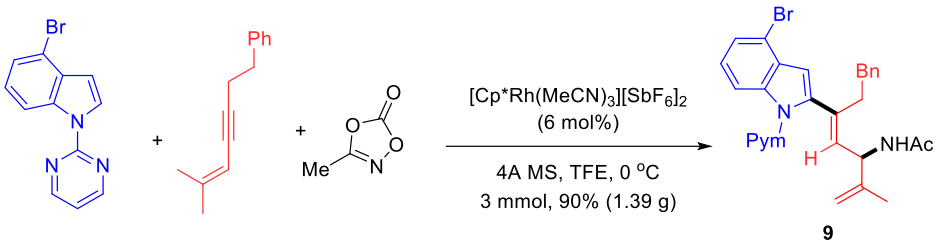
A mixture of phenylboronic acid (0.2 mmol), 1,3-enyne **2a** (0.3 mmol), methyldioxazolone **3a** (0.24 mol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8 mol%), 4 Å M.S. (100 mg), and TFE (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 30 ºC for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate (8:1) to afford the product **52** in 55% yield (35.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.31 – 7.29 (m, 1H), 7.26 – 7.24 (m, 2H), 7.18 – 7.12 (m, 3H), 5.50 – 5.47 (m, 2H), 5.22 (t, J = 8.7 Hz, 1H), 4.89 (d, J = 1.2 Hz, 1H), 4.84 (d, J = 1.3 Hz, 1H), 2.97 – 2.86 (m, 2H), 2.69 – 2.59 (m, 2H), 1.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 144.9, 143.6, 141.9, 141.7, 128.7, 128.6, 128.5, 127.6, 127.4, 126.8, 126.1, 110.9, 52.5, 34.7, 32.5, 23.6, 20.1. **HRMS** (ESI) calculated for $C_{22}H_{25}NNaO^+$ $[M+Na]^+$: 342.1828, found: 342.1832.



53, 50%

A mixture of 7-methylbicyclo[4.2.0]octa-1,3,5-trien-7-ol (0.2 mmol), 1,3-enyne **2a** (0.3 mmol), methyldioxazolone **3a** (0.24 mol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8 mol%), 4 Å M.S. (100 mg), and TFE (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 30 ºC for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate (8:1) to afford the product **53** in 50% yield (37.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.25 – 7.23 (m, 2H), 7.20 – 7.19 (m, 1H), 7.17 – 7.12 (m, 4H), 5.82 (d, J = 7.8 Hz, 1H), 5.25 (t, J = 8.6 Hz, 1H), 5.09 (d, J = 9.3 Hz, 1H), 4.93 (s, 1H), 4.89 – 4.85 (m, 1H), 3.69 – 3.60 (m, 2H), 2.80 – 2.61 (m, 3H), 2.57 – 2.52 (m, 1H), 2.12 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 207.3, 169.2, 144.5, 143.2, 142.6, 141.5, 132.0, 131.0, 129.7, 129.1, 128.51, 128.5, 127.5, 127.1, 126.1, 111.4, 52.5, 49.1, 34.7, 34.1, 29.5, 23.5, 20.1. **HRMS** (ESI) calculated for $C_{25}H_{29}NNaO^+$ $[M+Na]^+$: 398.2091, found: 398.2096.

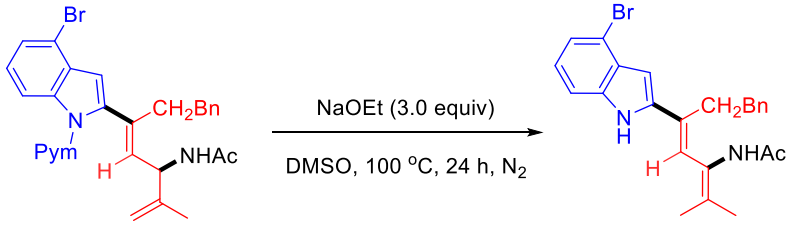
(b) Reaction on a gram scale



9

To a seal-tube equipped with a stir bar was charged 4-bromo-1-(pyrimidin-2-yl)-1H-indole (3.0 mmol), 1,3-enyne **2a** (4.5 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (6 mol%), 4 Å M.S. (1.5 g), and TFE (30.0 mL). Amidating reagent **3a** (3.6 mmol) was added in 0 °C and the reaction maintained at 0 °C for 12 h under air atmosphere. Afterwards, the reaction mixture was evaporated under vacuum and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 (v/v)) to give the corresponding product **9** in 90% yield (1.39 g) as a yellow solid.

(c) Derivatization of 9

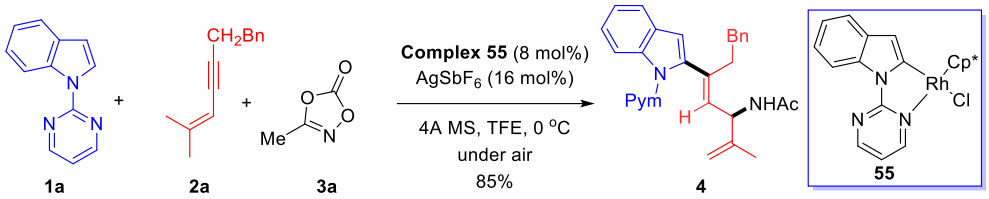


9 **54**, 58%

A pressure tube was charged with **9** (51.5 mg, 0.1 mmol), NaOEt (20.4 mg) and anhydrous DMSO (1 mL). The reaction mixture was stirred at 100 °C for 24 h under N_2. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the corresponding product **54** (25.3 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.29 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.02 – 7.00 (m, 2H), 6.98 (t, J = 7.8 Hz, 1H), 6.62 (d, J = 2.2 Hz, 1H), 6.08 (s, 1H), 4.39 (s, 1H), 2.90 – 2.86 (m, 2H), 2.75 – 2.70 (m, 2H), 1.80 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 142.1, 138.4, 137.6, 132.2, 131.9, 129.8, 129.5, 128.3, 126.0, 123.7, 123.1, 122.4, 122.1, 114.4, 110.6, 101.4, 35.3, 30.8, 23.0, 20.7, 19.7. **HRMS** (ESI) calculated for $C_{24}H_{25}BrN_2NaO^+$ $[M+Na]^+$: 459.1042, found: 459.1046.

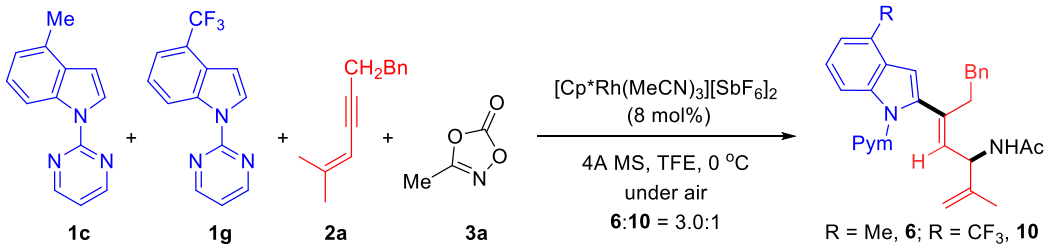
IV. Mechanistic Studies

(a) Catalytic reactivity of rhodacyclic complex 55

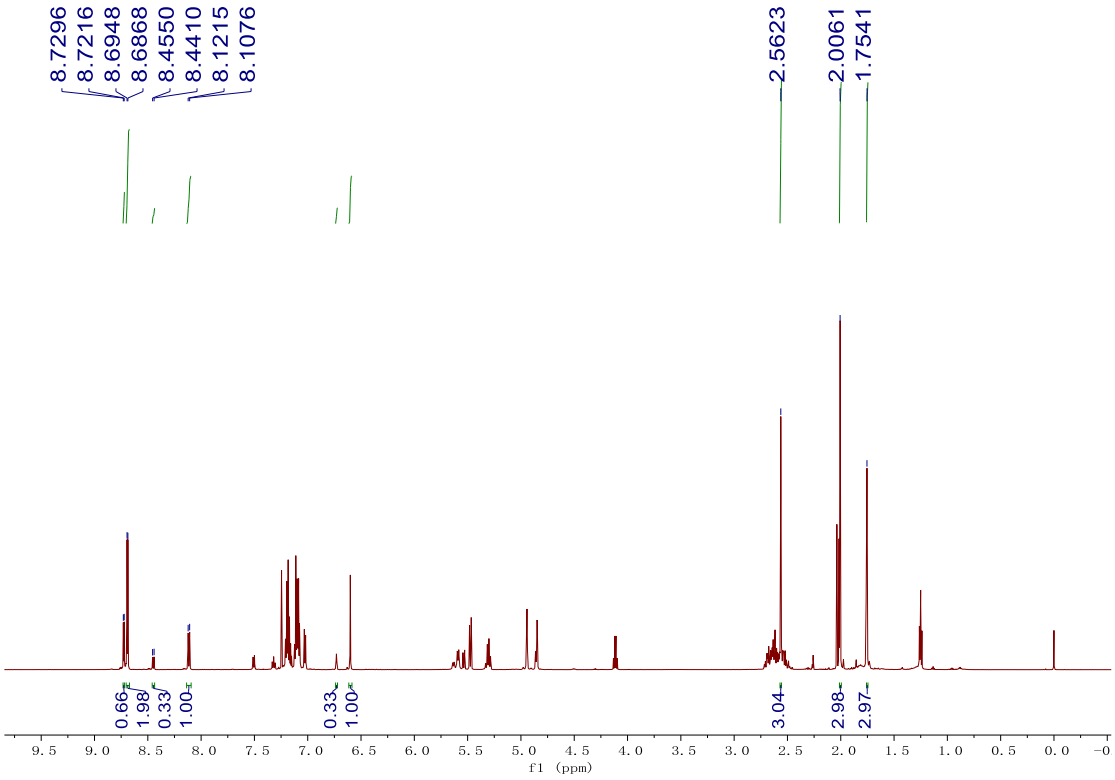


Catalytic reactivity of complex 55: To a seal-tube equipped with a stir bar was charged N-pyrimidylindole **1a** (0.2 mmol), 1,3-enyne **2a** (0.3 mmol), complex **55** (8 mol%), $AgSbF_6$ (16 mol%), 4 Å M.S. (100 mg), and TFE (2.0 mL). Amidating reagent **3a** (0.24 mmol) was added in 0 °C and the reaction maintained at 0 °C for 12 h under air atmosphere. Afterwards, the reaction mixture was evaporated under vacuum and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 (v/v)) to give the corresponding product **4** in 85% yield (74.3 mg) as a yellow solid.

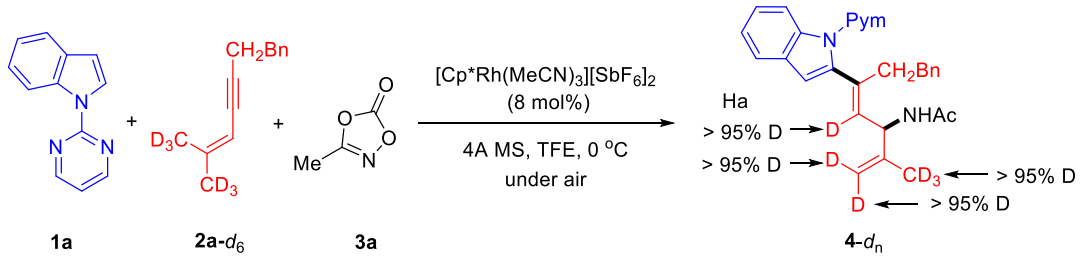
(b) Competition experiment



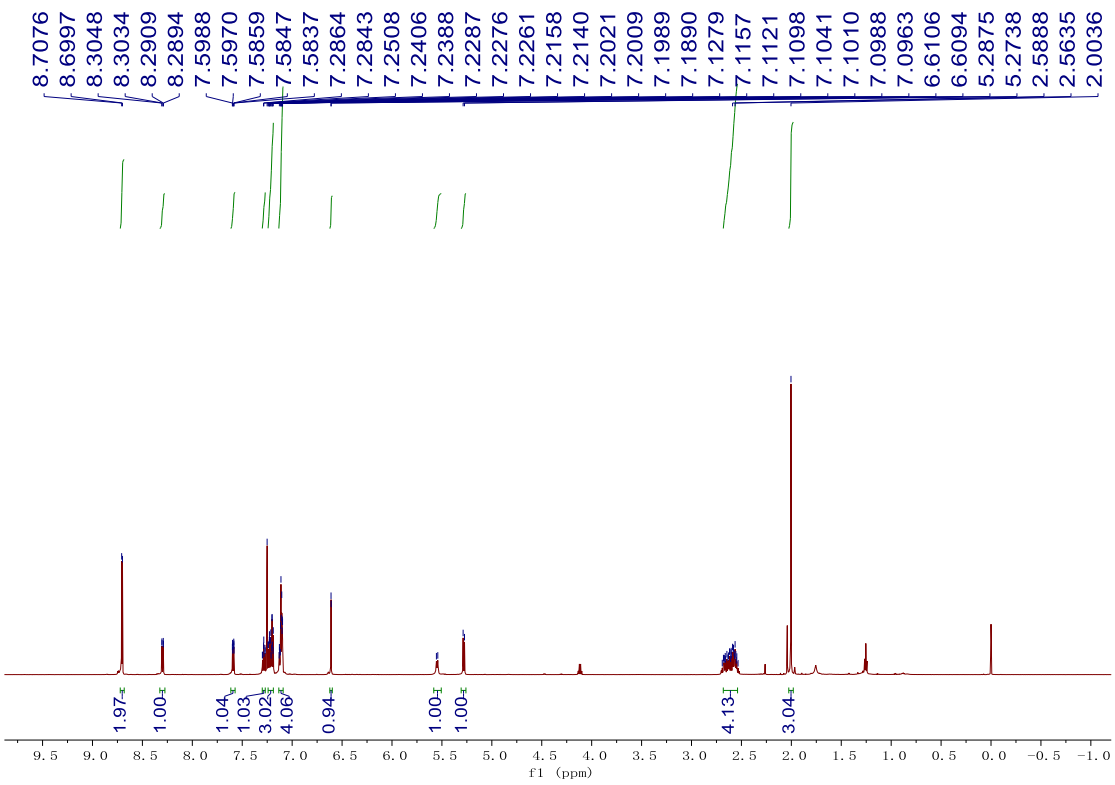
To a seal-tube equipped with a stir bar was charged *N*-pyrimidylindole **1c** (0.2 mmol), **1g** (0.2 mmol), 1,3-enyne **2a** (0.3 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8 mol%), 4 Å M.S. (100 mg), and TFE (2.0 mL). Amidating reagent **3a** (0.24 mmol) was added in 0 °C and the reaction maintained at 0 °C for 12 h under air atmosphere. Afterwards, the reaction mixture was evaporated under vacuum and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 (v/v)) to afford the products **6** and **10**. The ratio of **6**:**10** = 3:1 was determined on the basis of ^1H NMR analysis.



(b) Deuterium labeling experiment



To a seal-tube equipped with a stir bar was charged *N*-pyrimidylindole **1a** (0.1 mmol), 1,3-enyne **2a**-d_6 (0.15 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8 mol%), 4 Å M.S. (100 mg), and TFE (1.0 mL). Amidating reagent **3a** (0.12 mmol) was added in 0 °C and the reaction maintained at 0 °C for 12 h under air atmosphere. Afterwards, the reaction mixture was evaporated under vacuum and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 (v/v)) to afford the product **4**-d_n. The extent of deuteration was obtained by ^{1}H NMR analysis.


8.7076
8.6997
8.3048
8.3034
8.2909
8.2894
7.5988
7.5970
7.5859
7.5847
7.5837
7.2864
7.2843
7.2508
7.2406
7.2388
7.2287
7.2276
7.2261
7.2158
7.2140
7.2021
7.2009
7.1989
7.1890
7.1279
7.1157
7.1121
7.1098
7.1041
7.1010
7.0988
7.0963
6.6106
6.6094
5.2875
5.2738
2.5888
2.5635
2.0036
1.97
1.00
1.04
1.03
3.02
4.06
0.94
1.00
1.00
4.13
3.04
f1 (ppm)

V. X-Ray Crystallographic Data

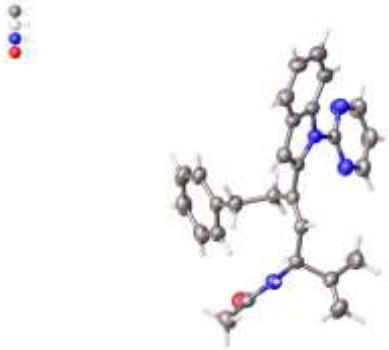


Table S2. Crystal data and structure refinement for **4**

Empirical formula	$C_{28}H_{28}N_4O$
Formula weight	436.54
Temperature/K	211.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.9949(13)
b/Å	8.8643(11)
c/Å	14.6922(19)
α/°	90
β/°	107.946(4)
γ/°	90
Volume/Å^3	1238.4(3)
Z	2
ρcalc g/cm^3	1.171
μ/mm^{-1}	0.570
F(000)	464.0
Radiation	CuKα (λ = 1.54178)
Index ranges	$-11 \le h \le 12$, $-10 \le k \le 9$, $-17 \le l \le 17$
Reflections collected	15593
Independent reflections	4310 [R_{int} = 0.0832 R_{sigma} = 0.0935]
Data/restraints/parameters	4310/1/308
Goodness-of-fit on F2	1.142
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0963
Final R indexes [all data]	R_1 = 0.1052, wR_2 = 0.1299
Largest diff. peak/hole / e Å^{-3}	0.33/-0.41

Table S3. Crystal data and structure refinement for **51**

Empirical formula	$C_{26}H_{30}N_4O$
Formula weight	414.54
Temperature/K	153
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5205(10)
b/Å	21.234(2)
c/Å	10.0310(9)
α/°	90
β/°	90.914(4)
γ/°	90
Volume/Å^3	2240.6(4)
Z	4
ρcalc g/cm^3	1.229
μ/mm^{-1}	0.599
F(000)	888.0
Radiation	CuKα (λ = 1.54178)
Index ranges	$-12 \leq h \leq 12$, $-25 \leq k \leq 25$, $-12 \leq l \leq 12$
Reflections collected	31390
Independent reflections	4090 [R_{int} = 0.0898 R_{sigma} = 0.0482]
Data/restraints/parameters	4098/1/291
Goodness-of-fit on F2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1066
Final R indexes [all data]	R_1 = 0.0752, wR_2 = 0.1259
Largest diff. peak/hole / e Å^{-3}	0.27/-0.27

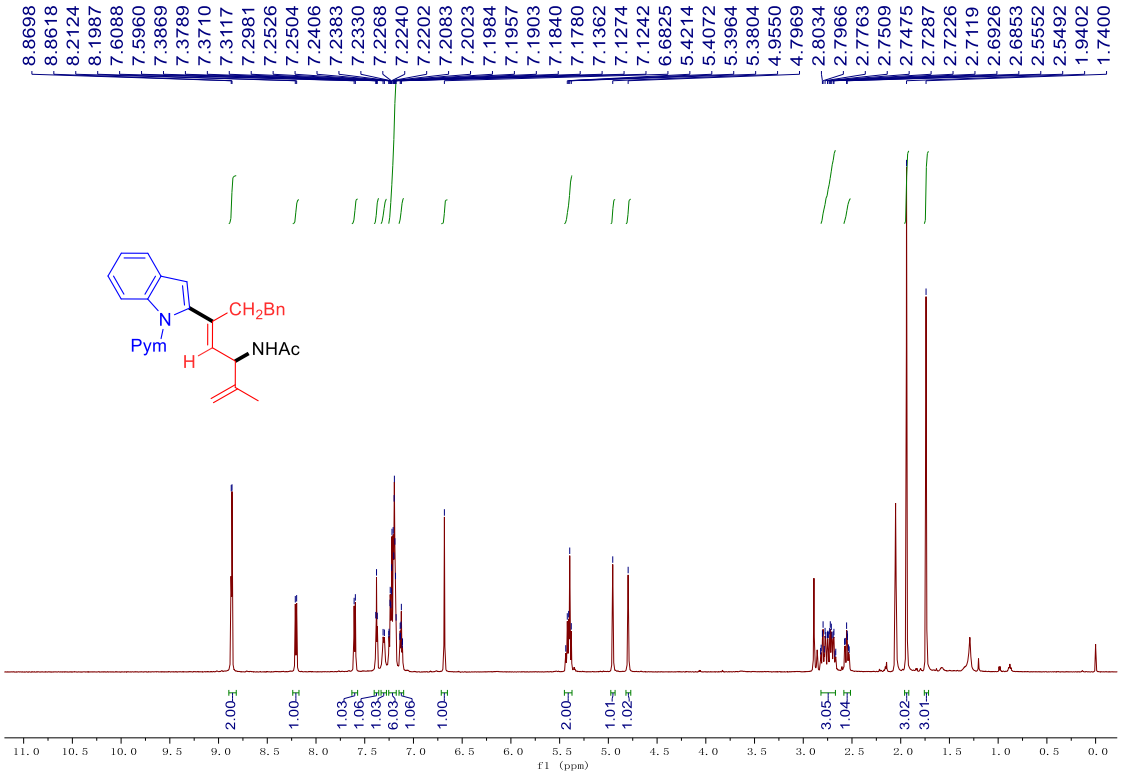
VI. References

(1) L. Ackermann and A. V. Lygin, *Org. Lett.* 2011, **13**, 3332.

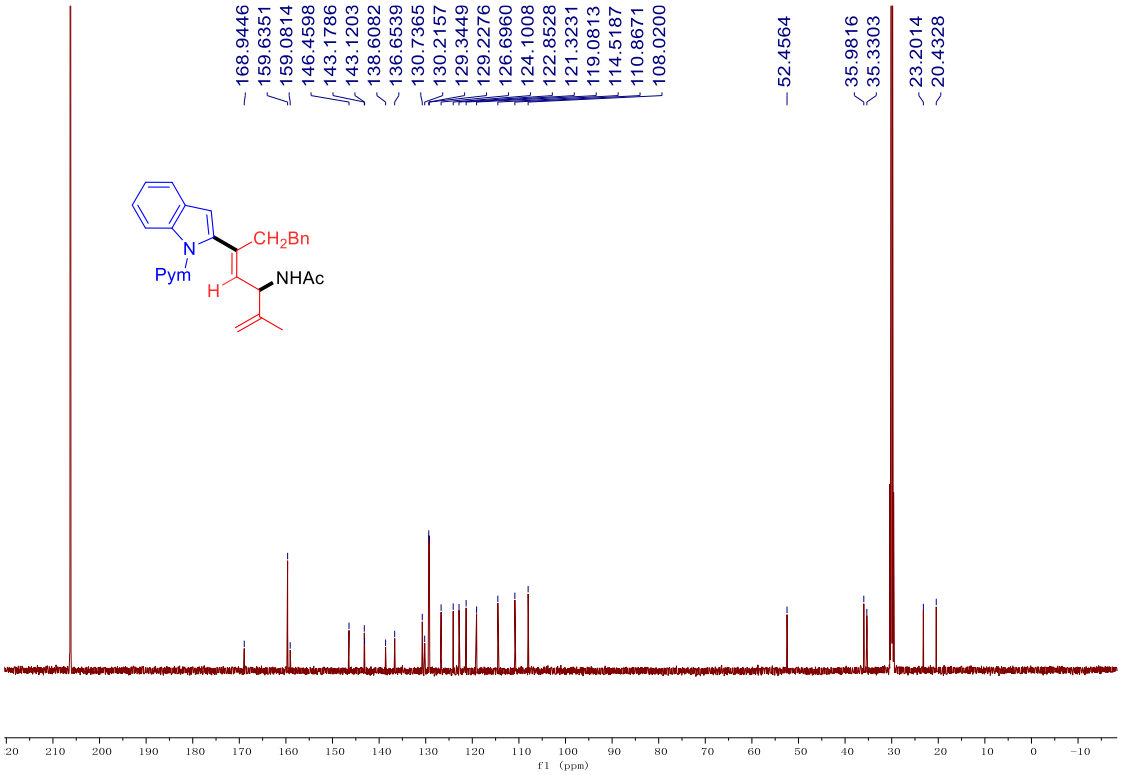
(2) D. J. Burns and H. W. Lam, *Angew. Chem. Int. Ed.* 2014, **53**, 9931.

(3) V. Bizet, L. Buglioni and C. Bolm, *Angew. Chem. Int. Ed.* 2014, **53**, 5639.

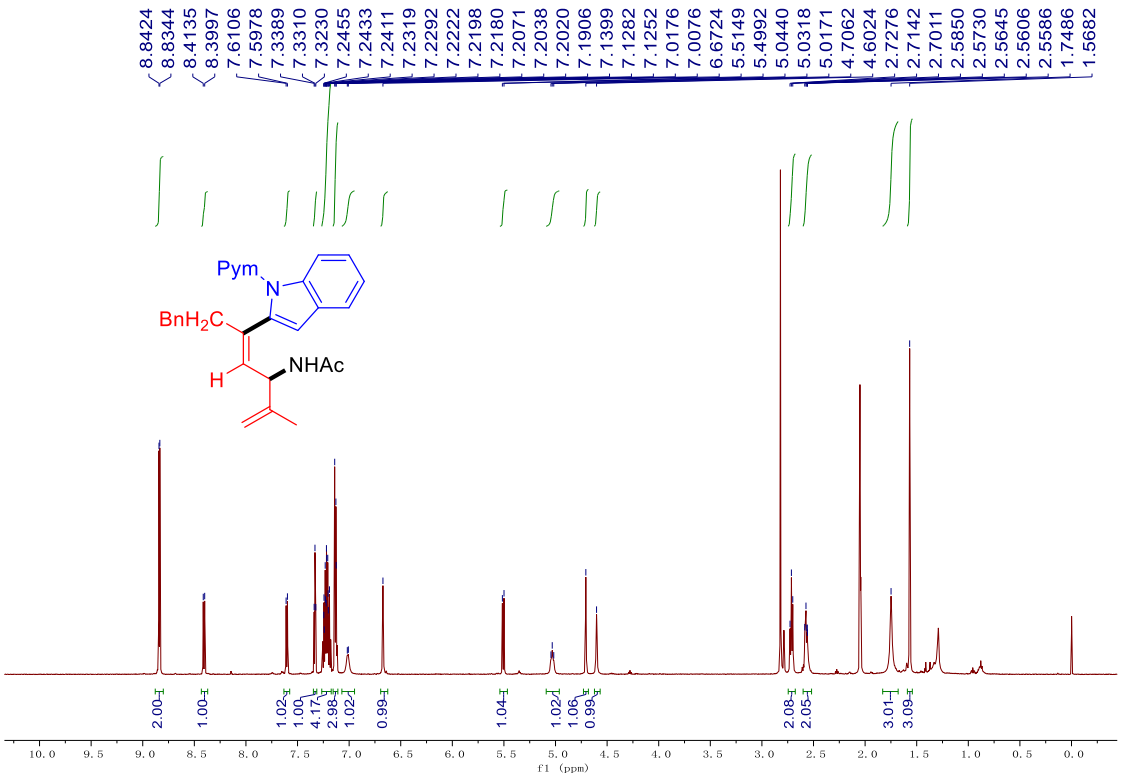
VII. NMR Spectra



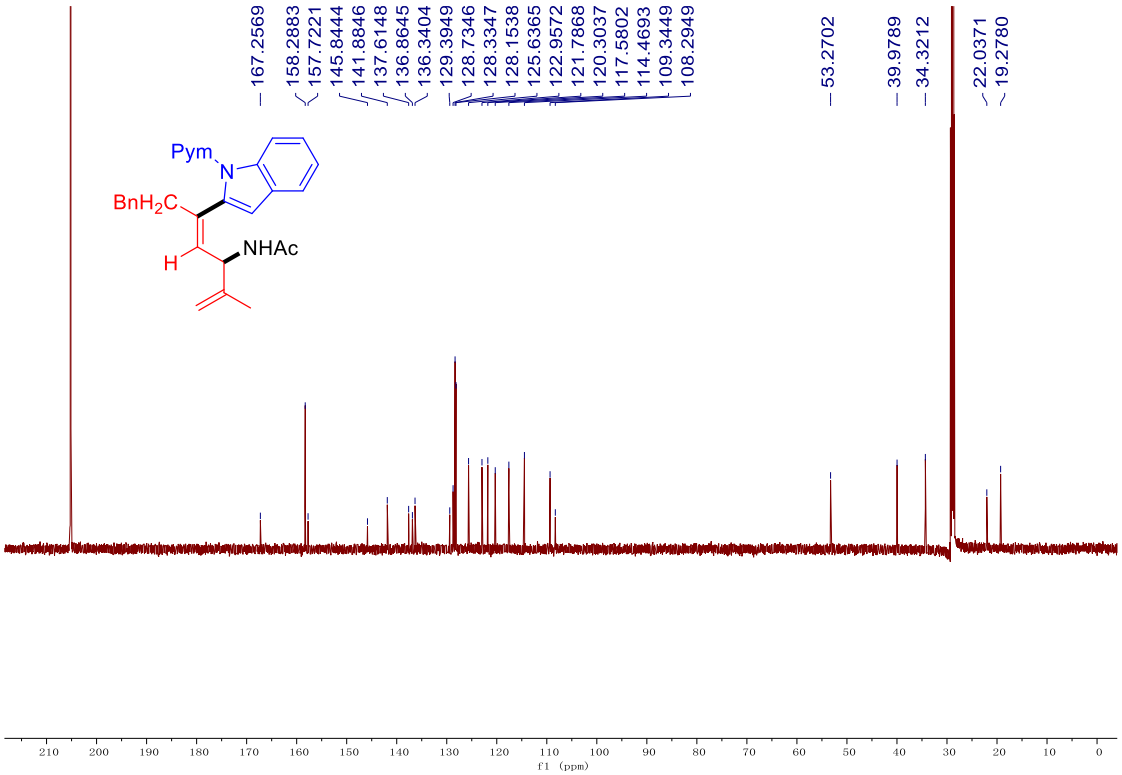
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **4.**



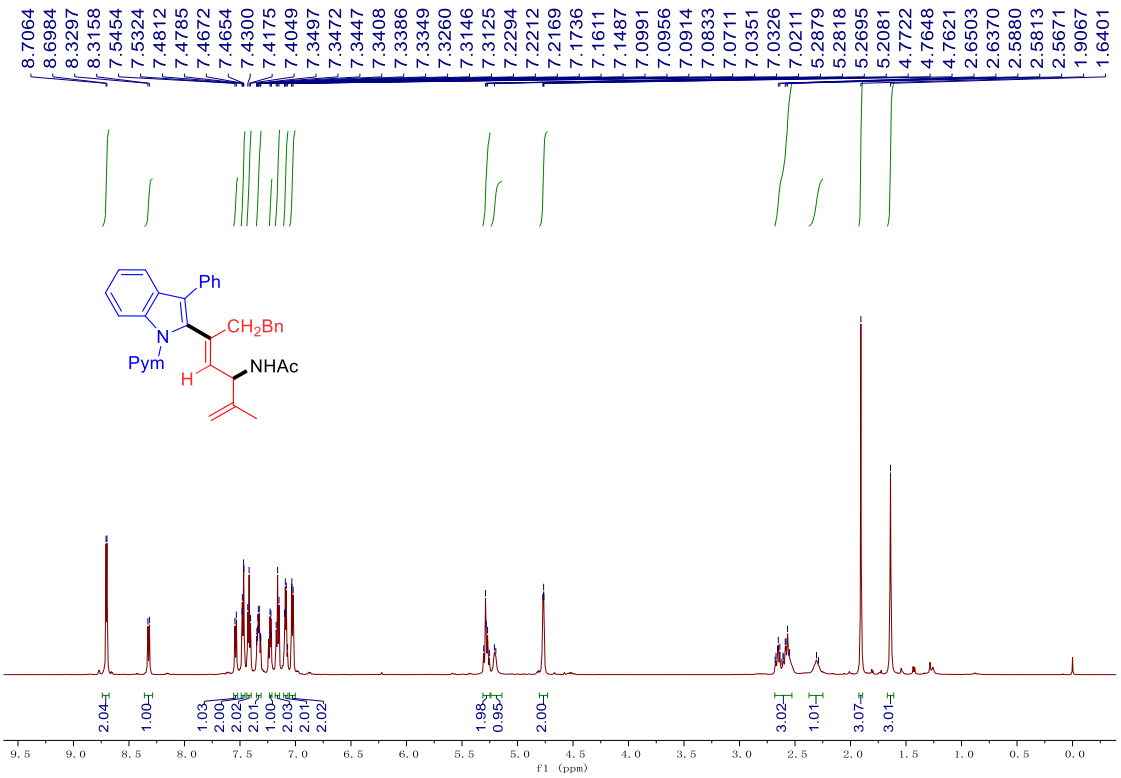
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **4.**



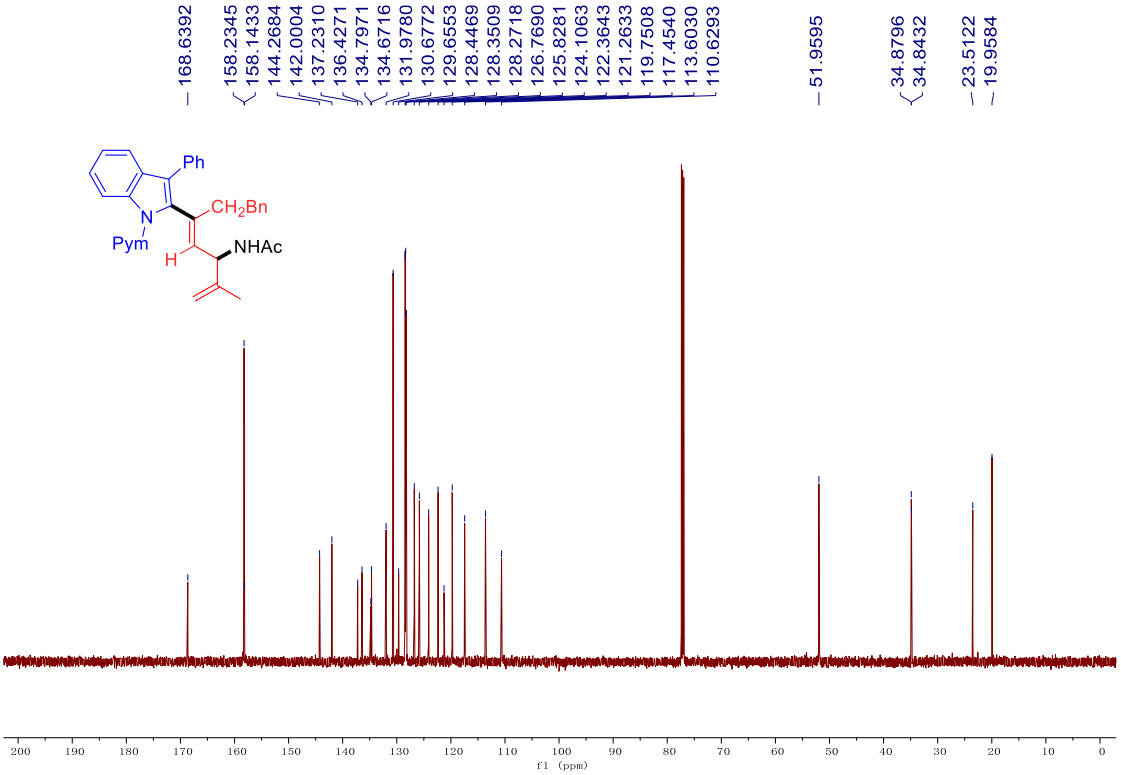
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **4'.**



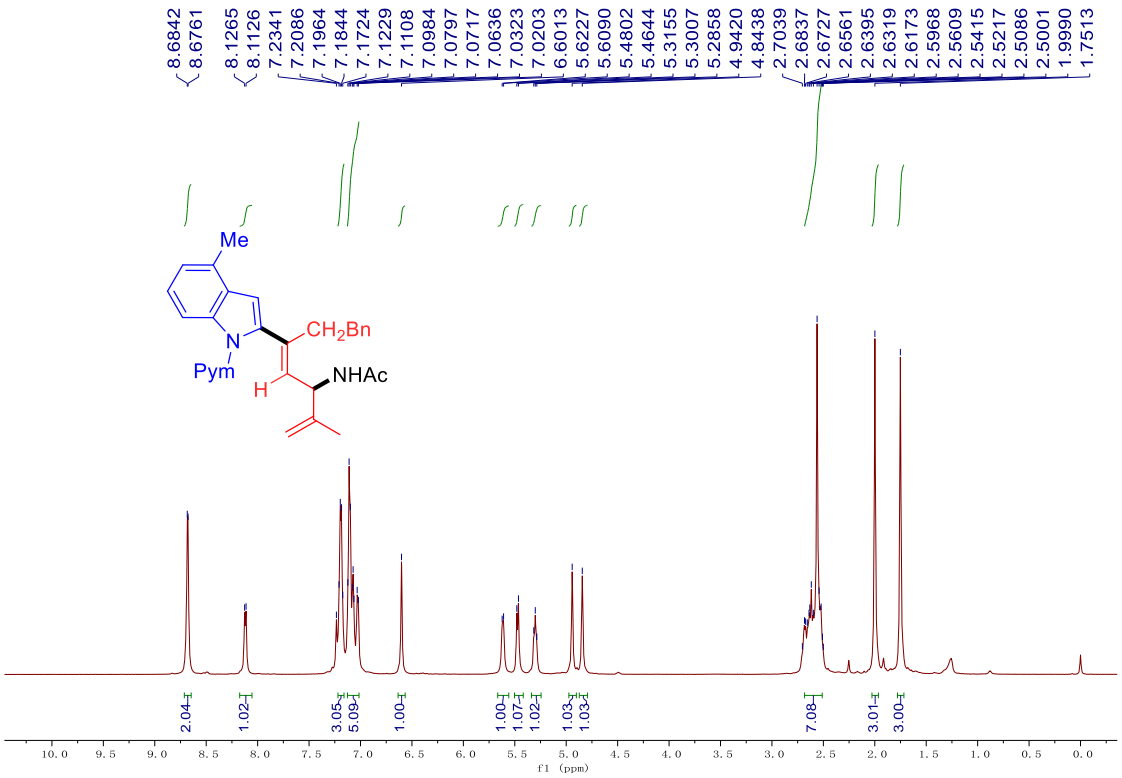
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **4'.**



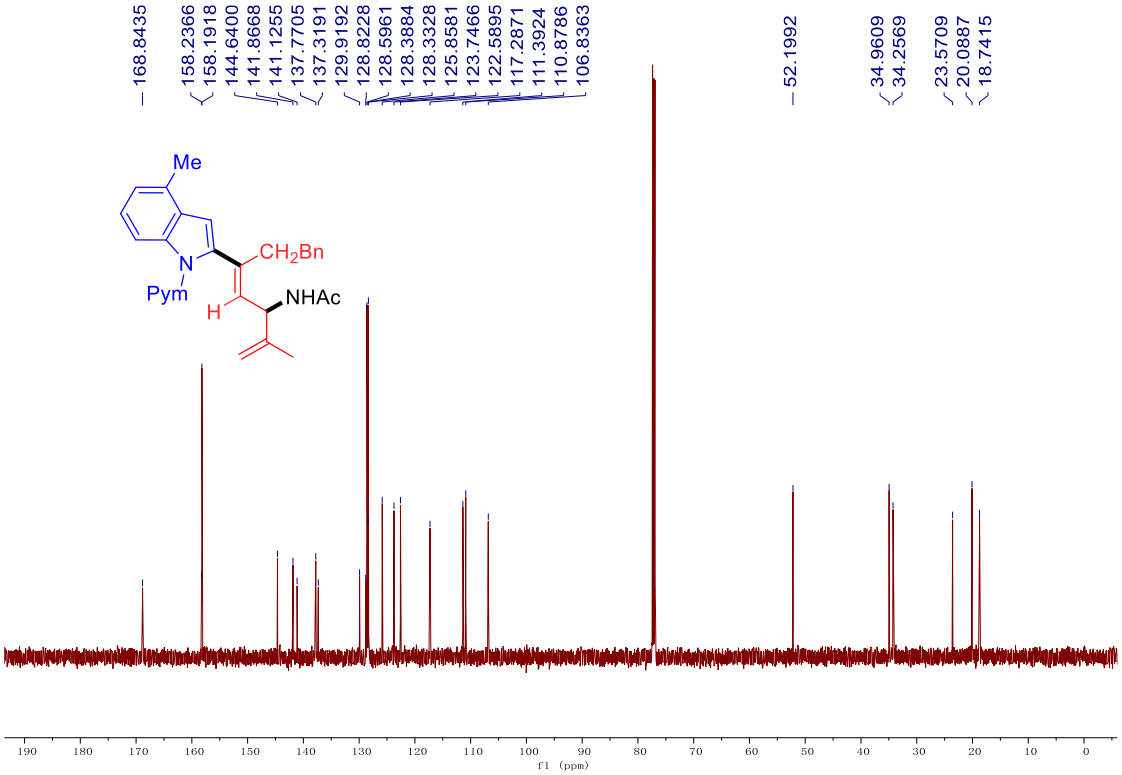
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5.**



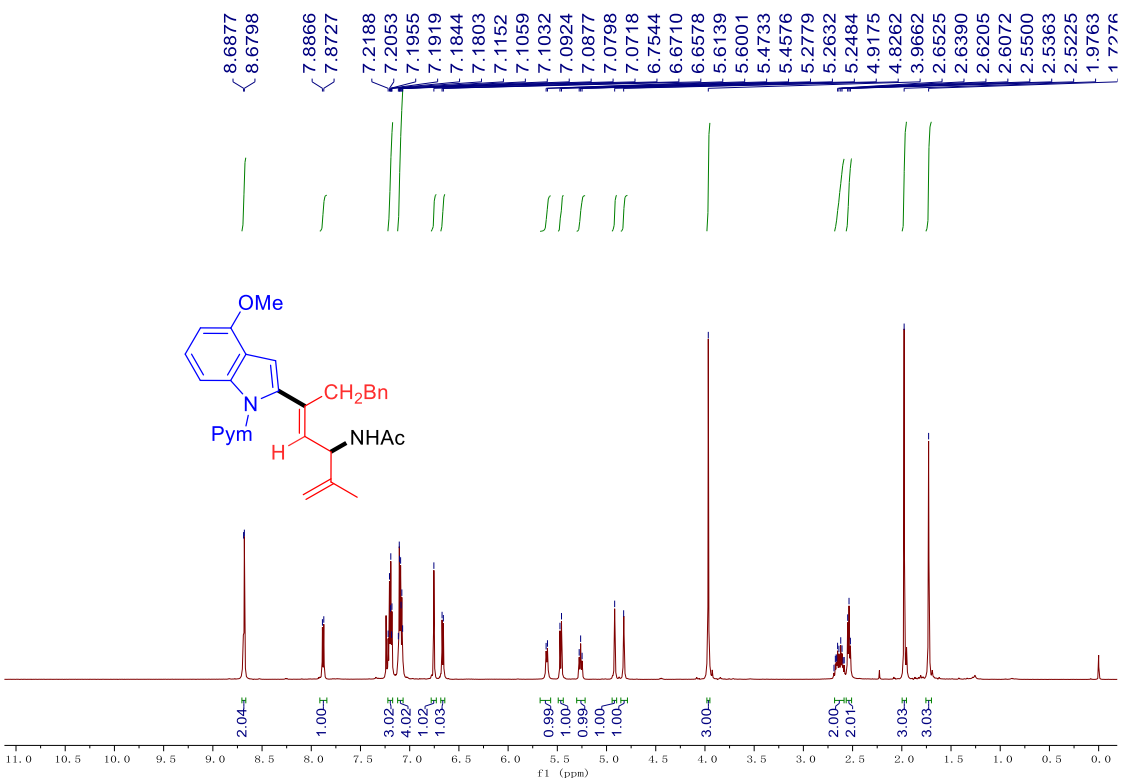
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5.**



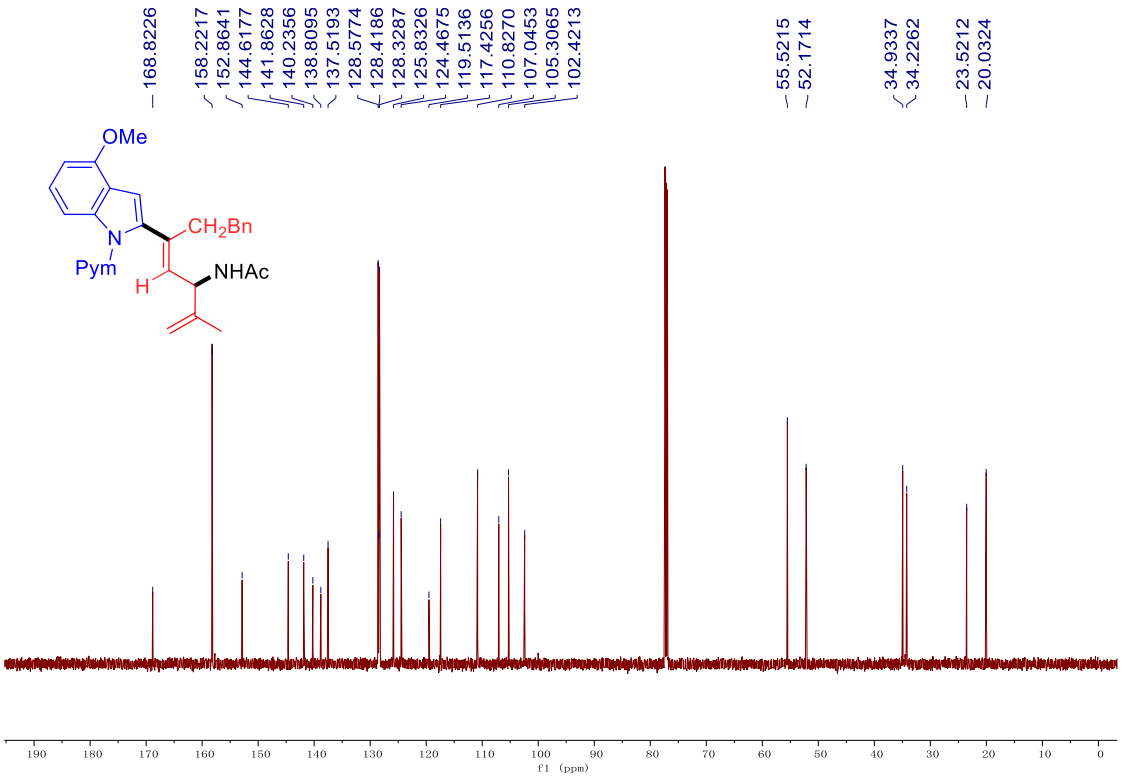
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6.**



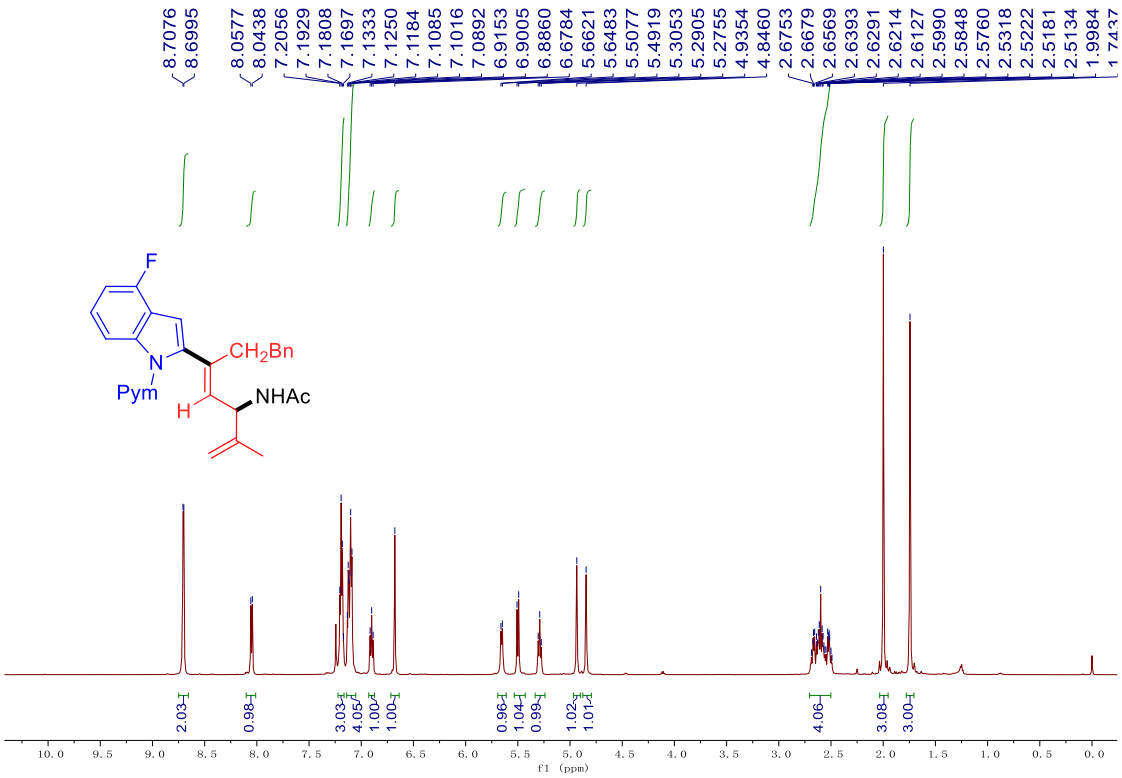
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6.**



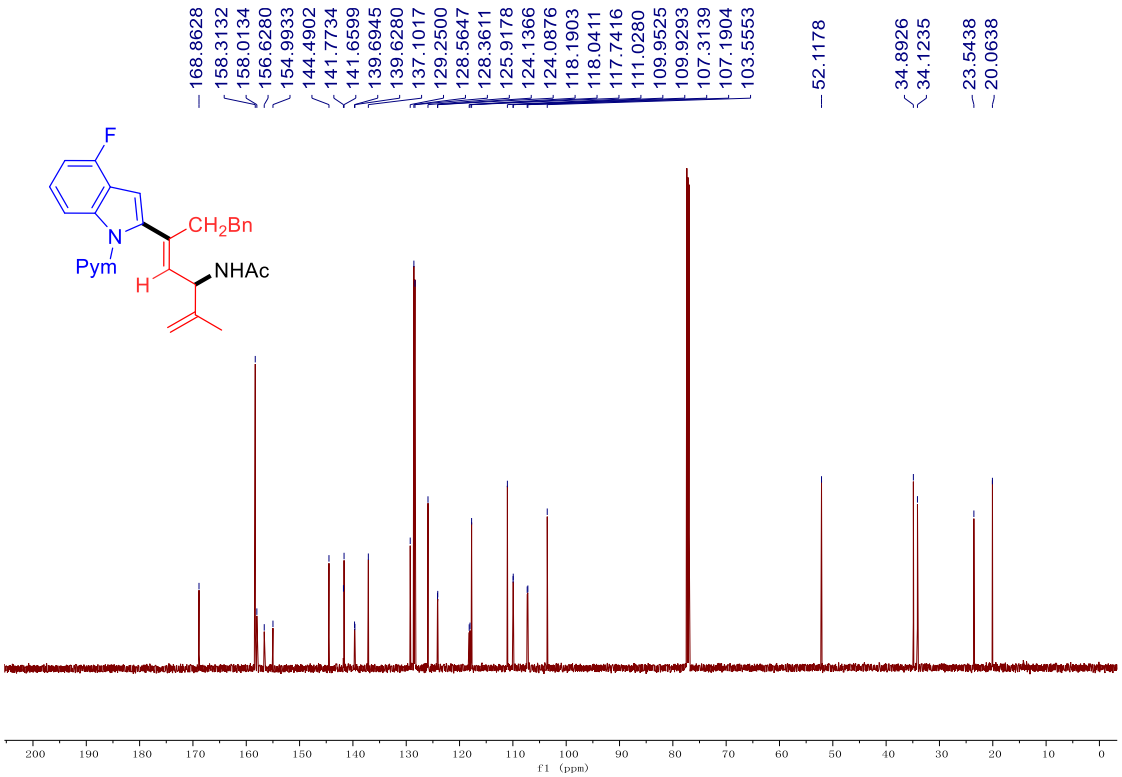
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **7.**



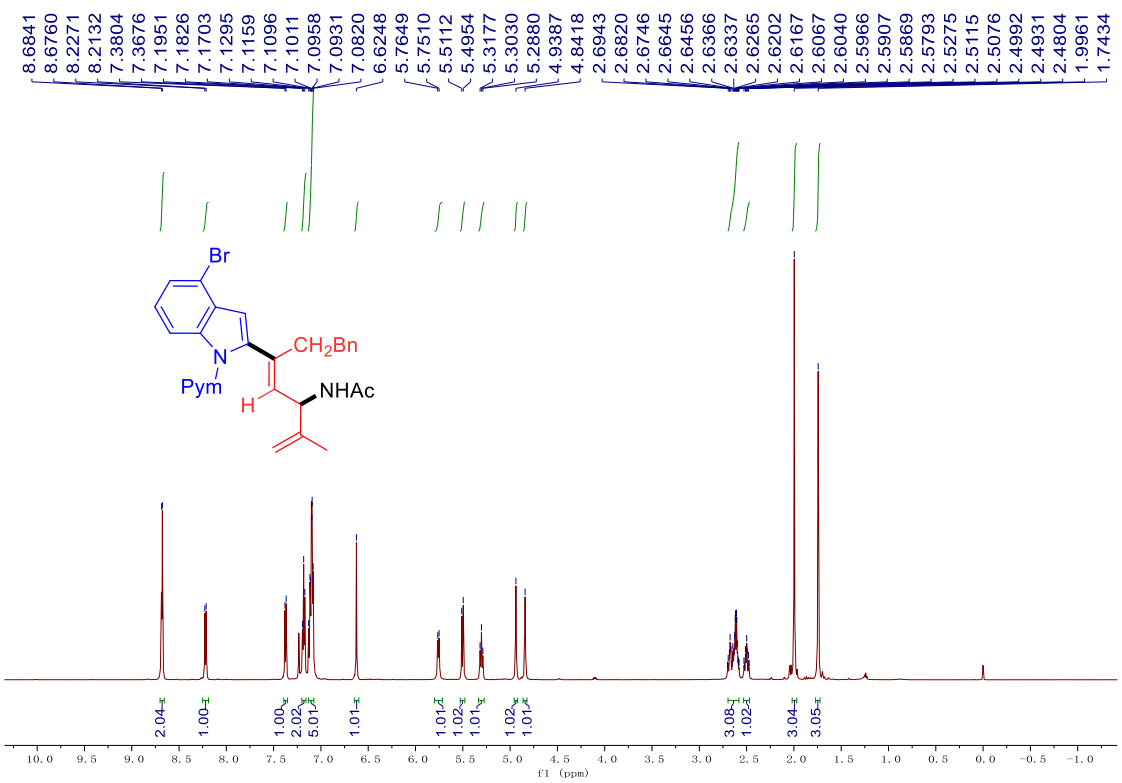
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **7.**



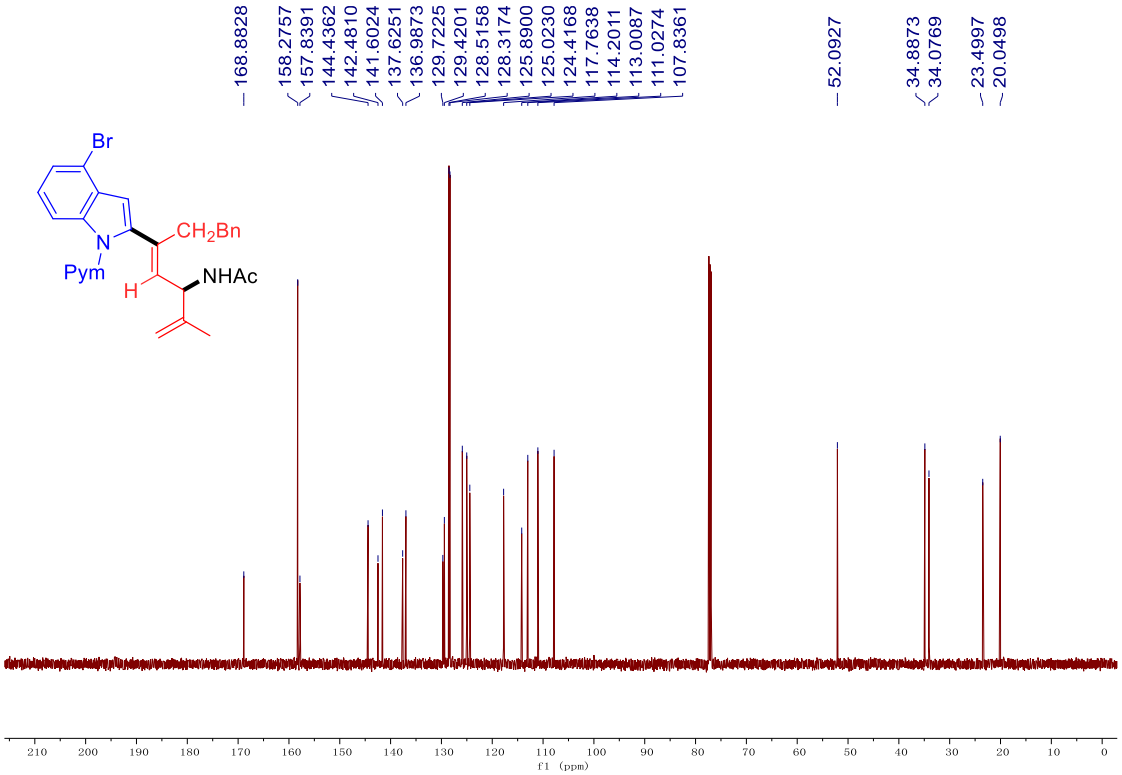
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **8.**



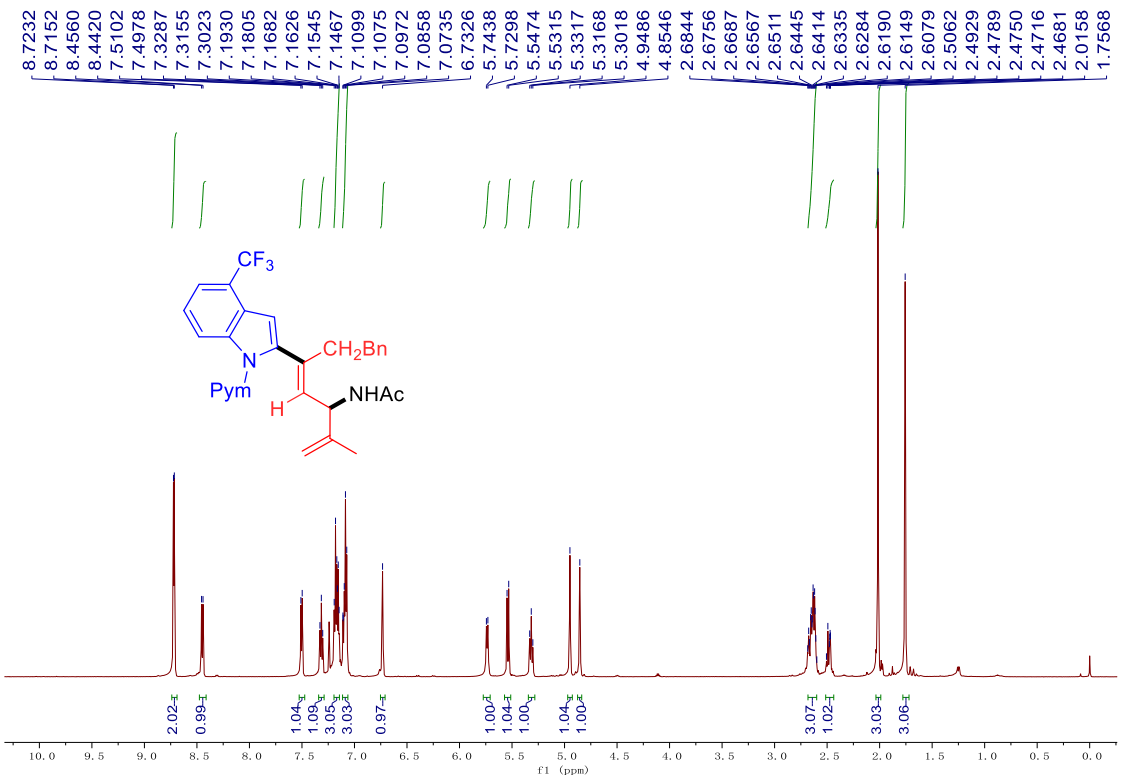
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **8.**



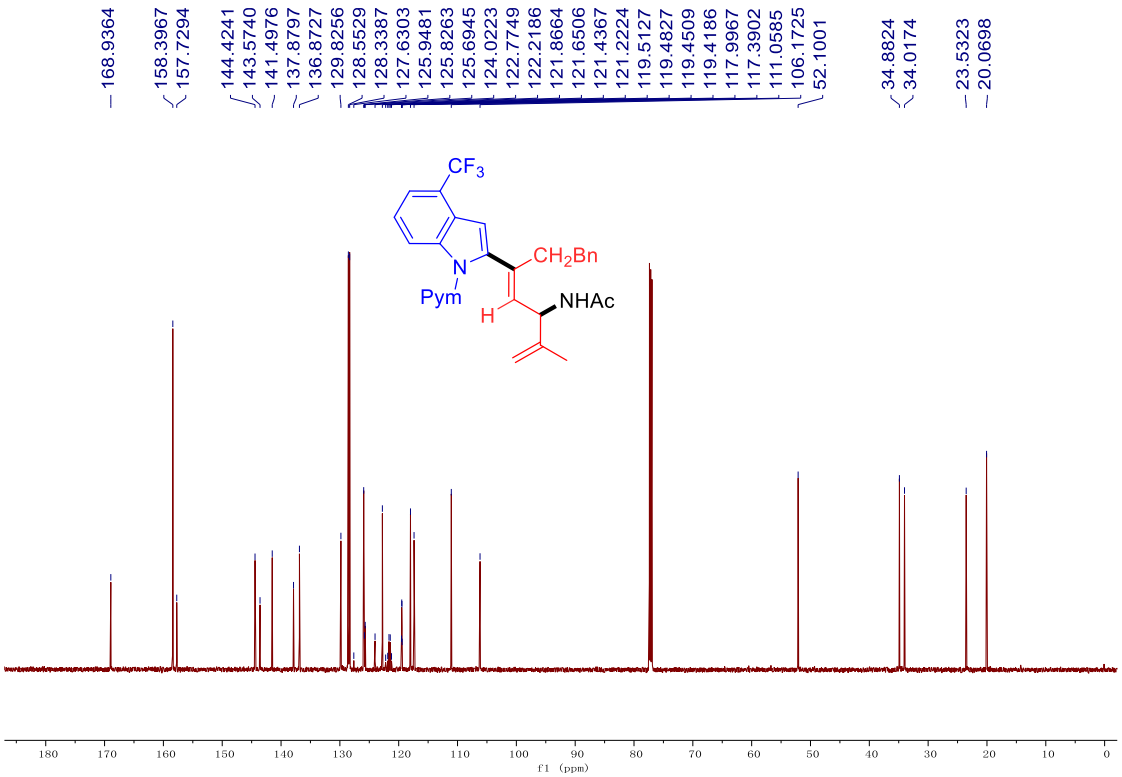
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9.**



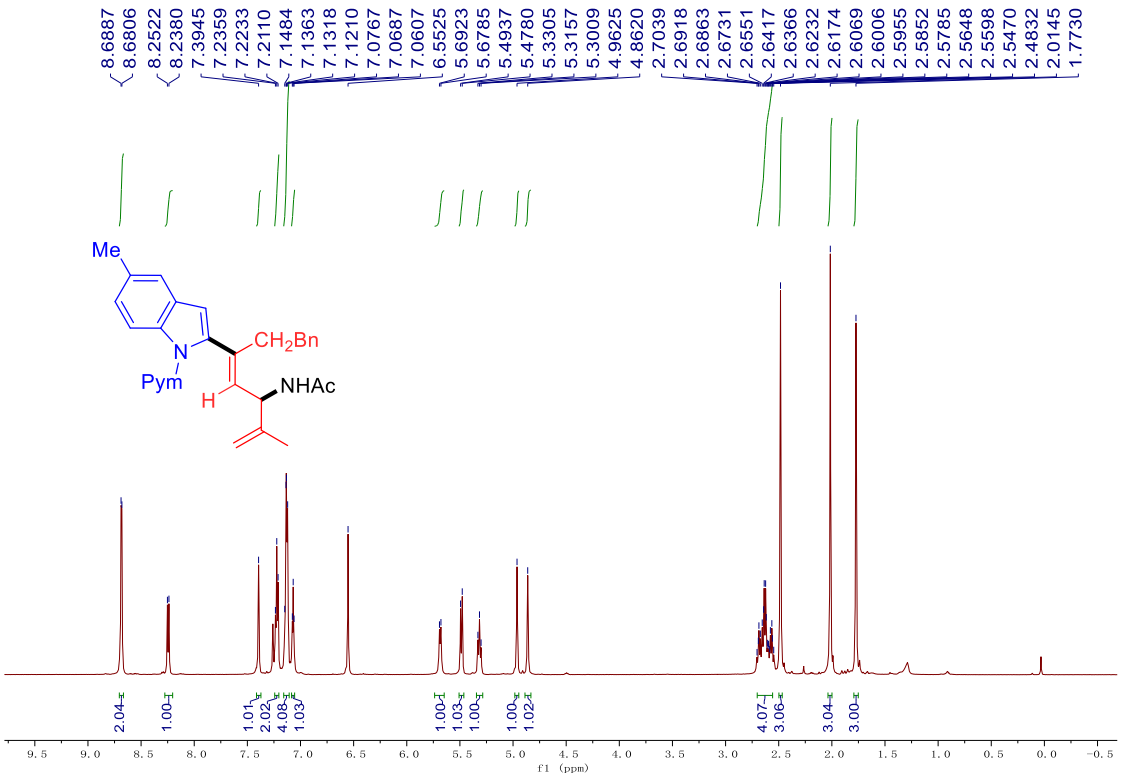
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9.**



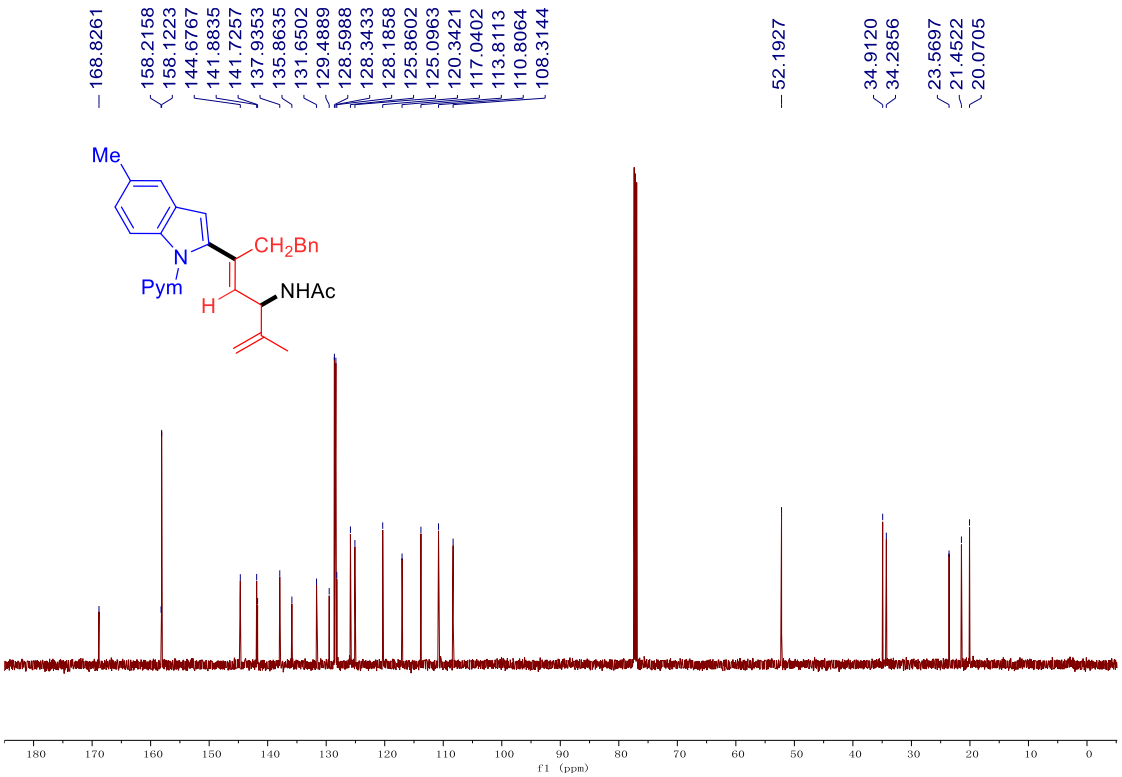
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **10.**



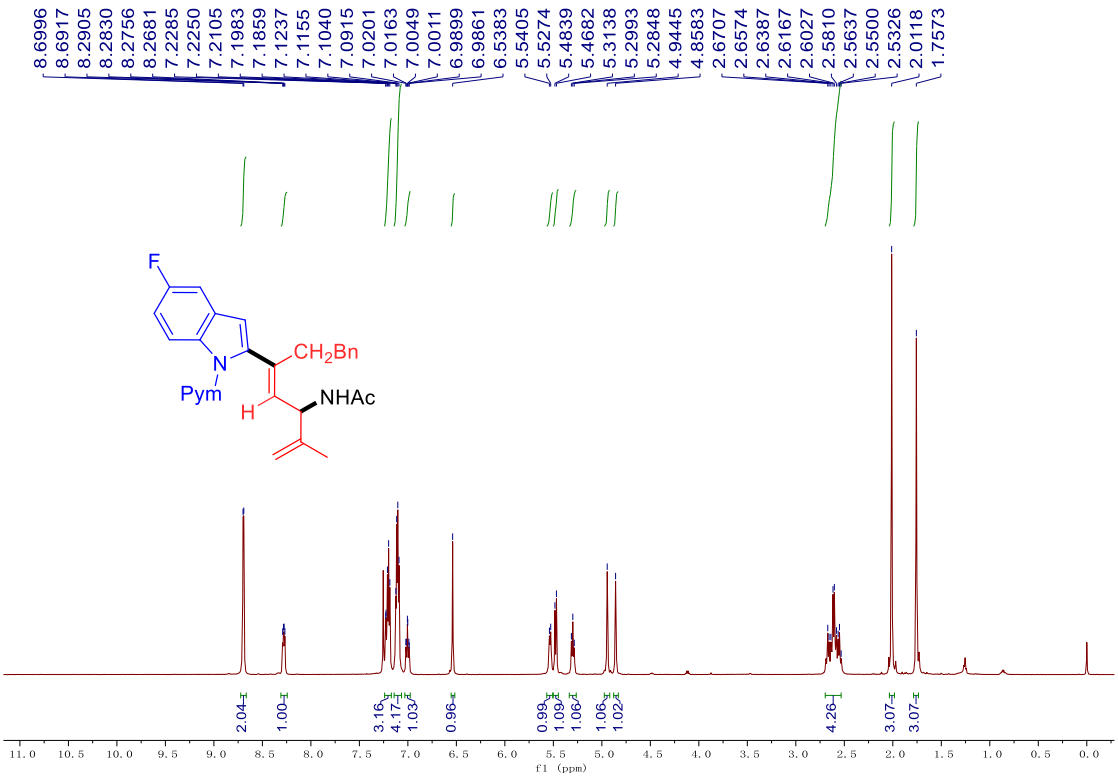
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **10.**



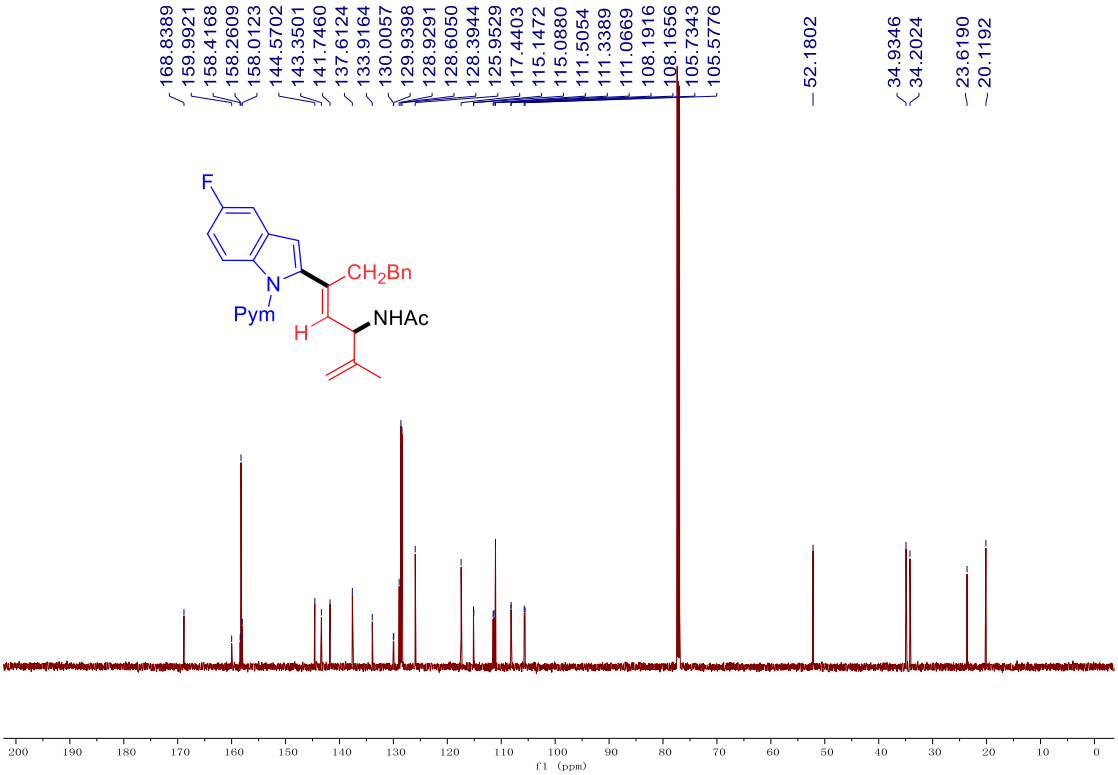
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **11.**



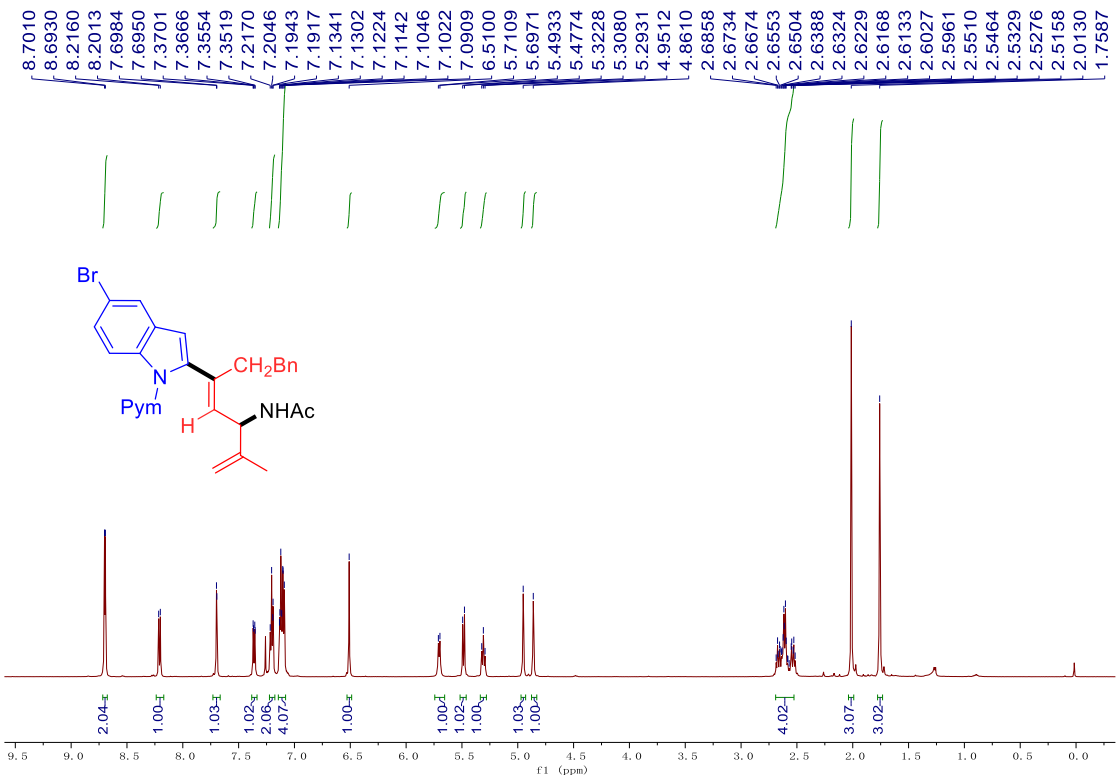
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **11.**



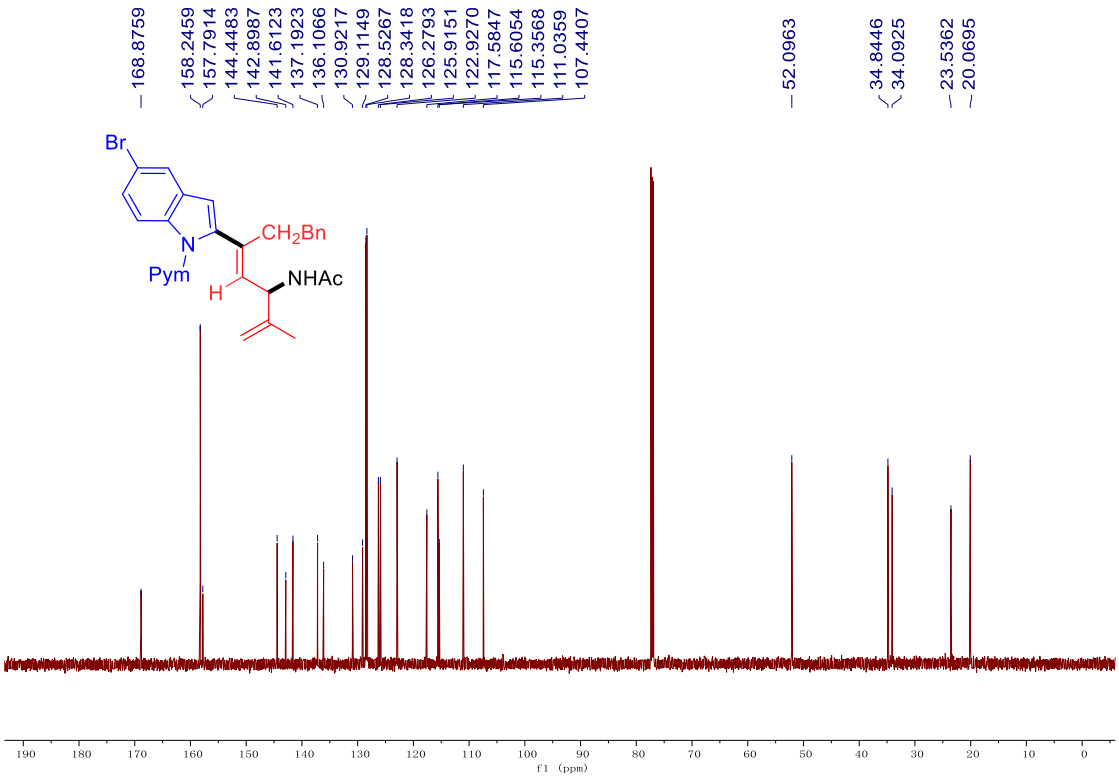
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **12**



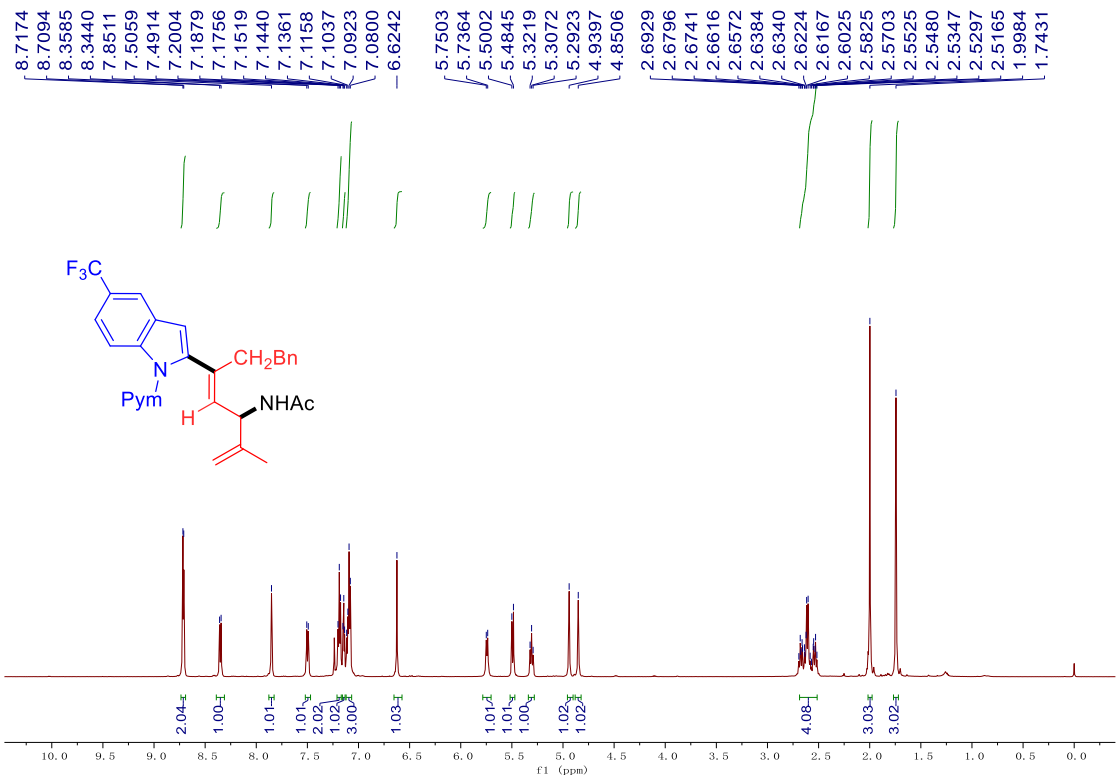
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **12.**



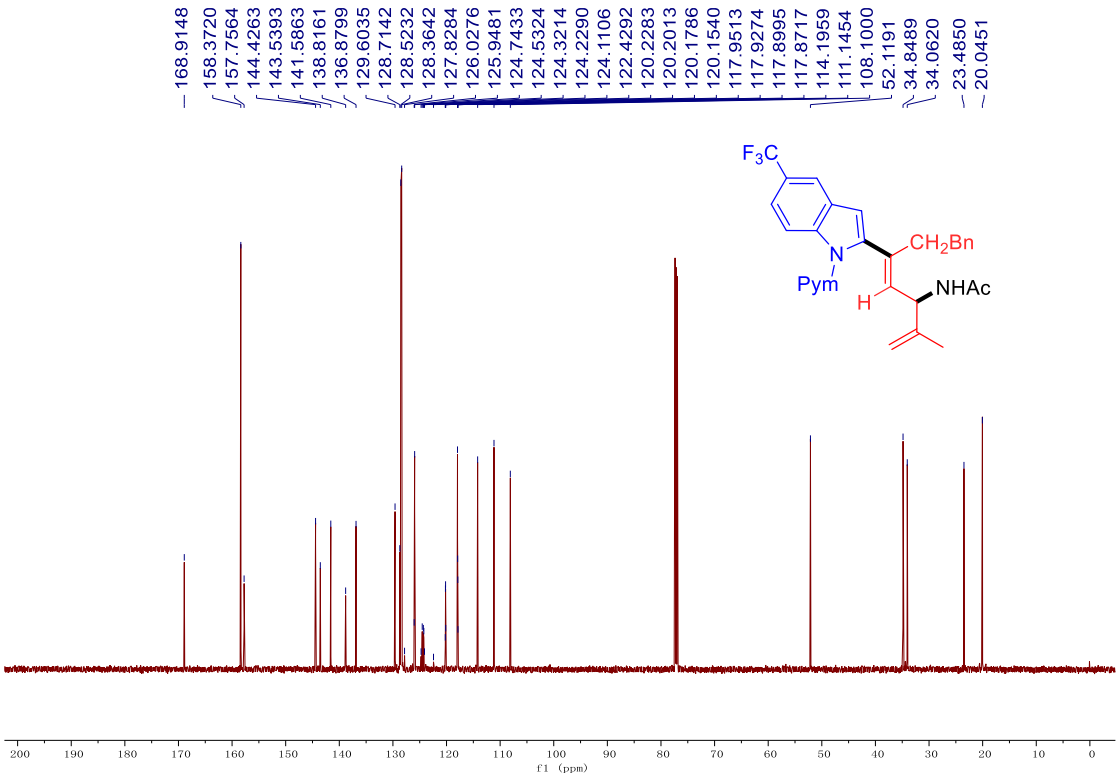
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **13.**



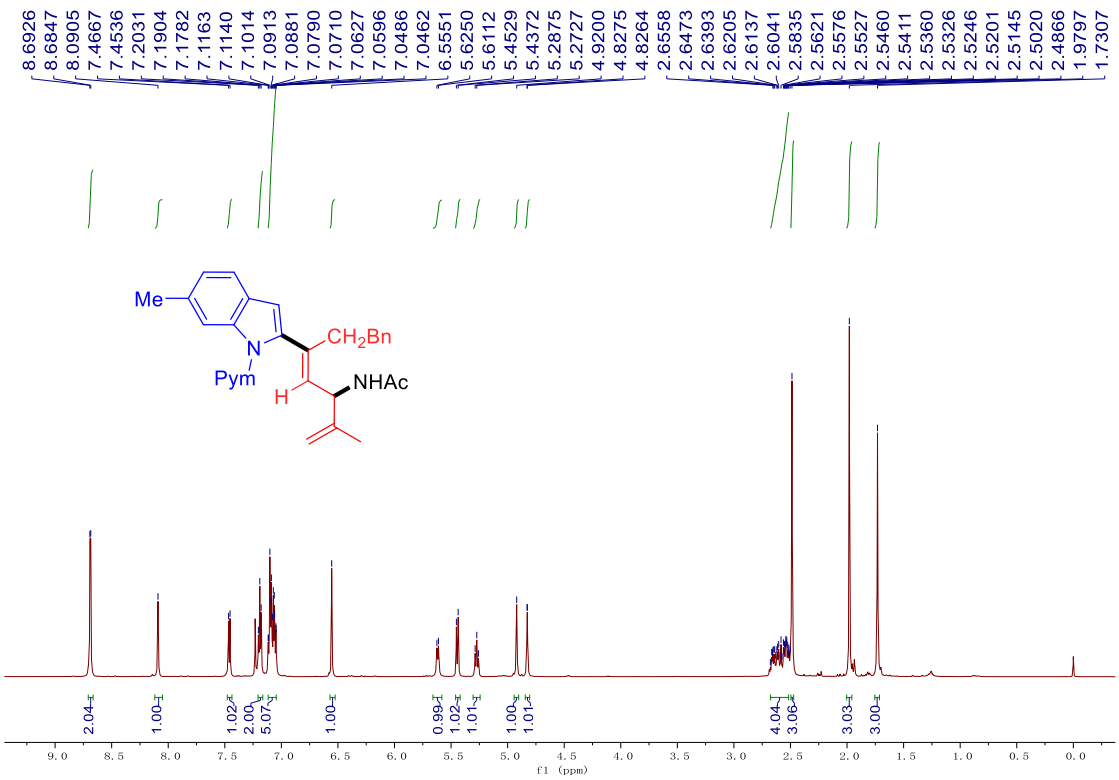
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **13.**



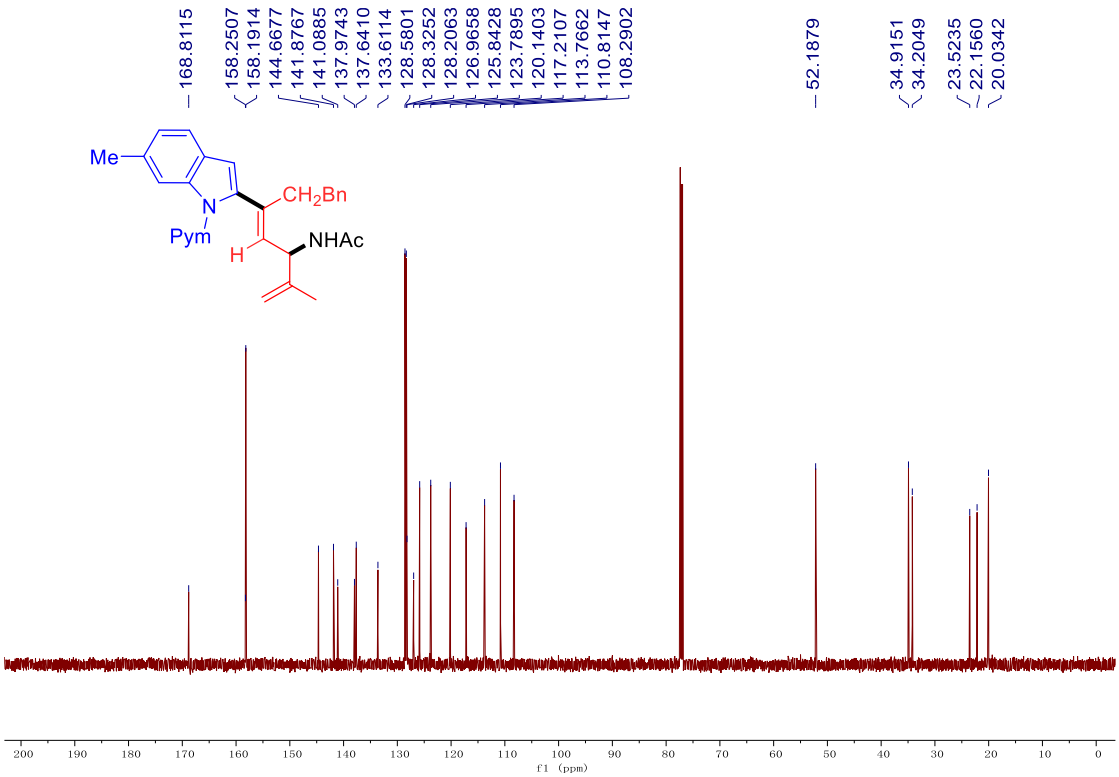
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14.**



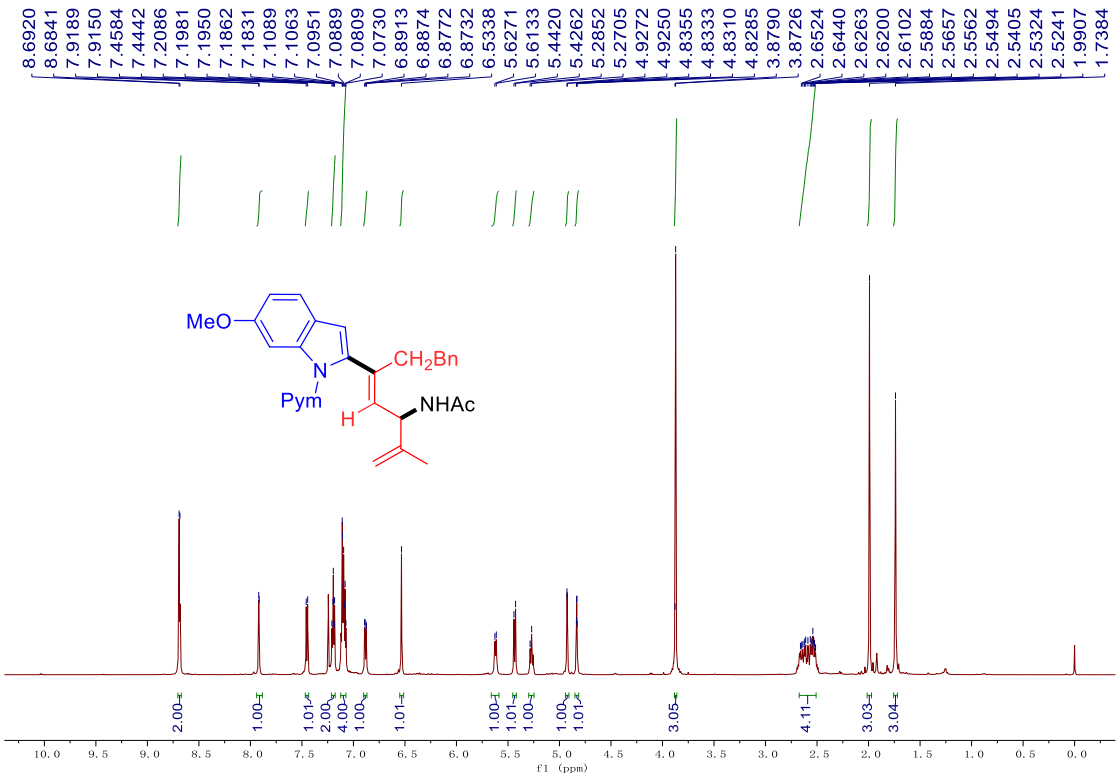
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **14.**



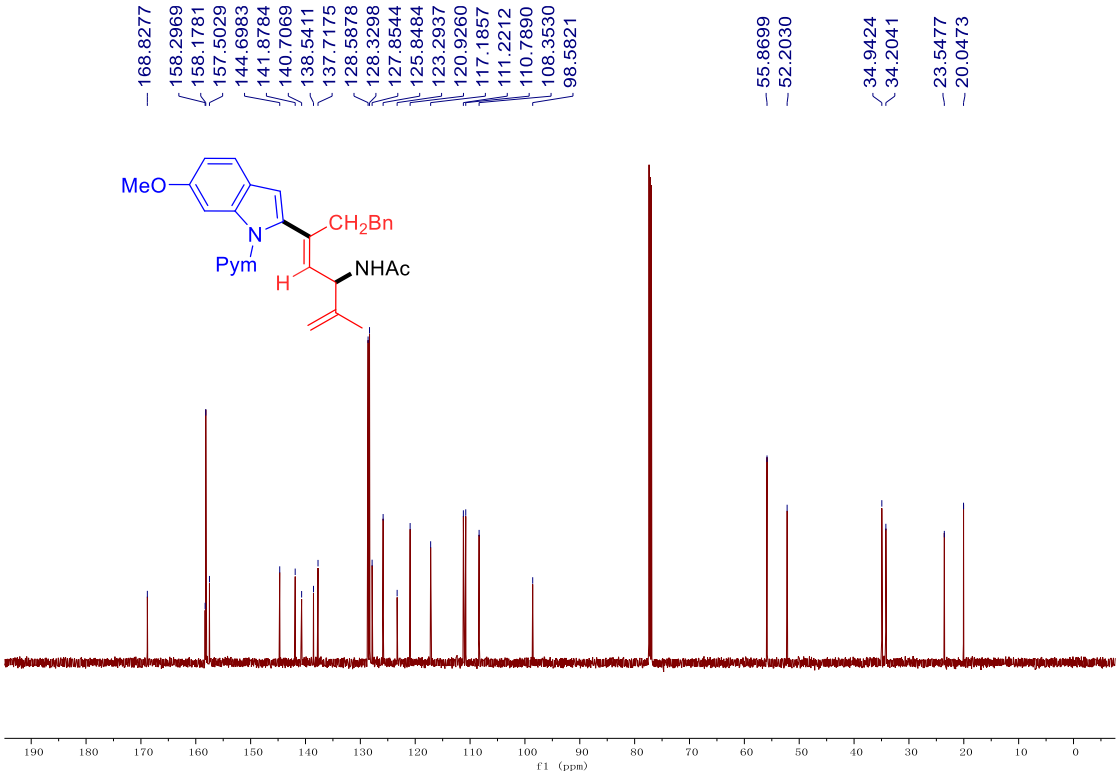
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **15.**



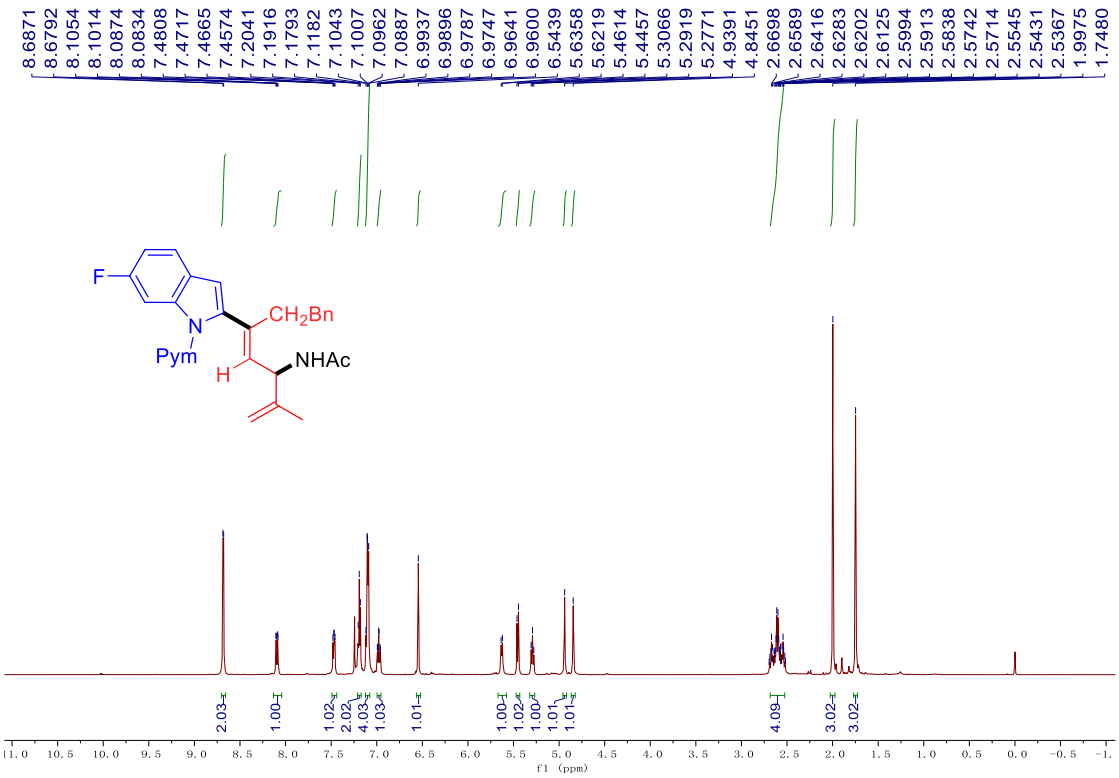
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **15.**



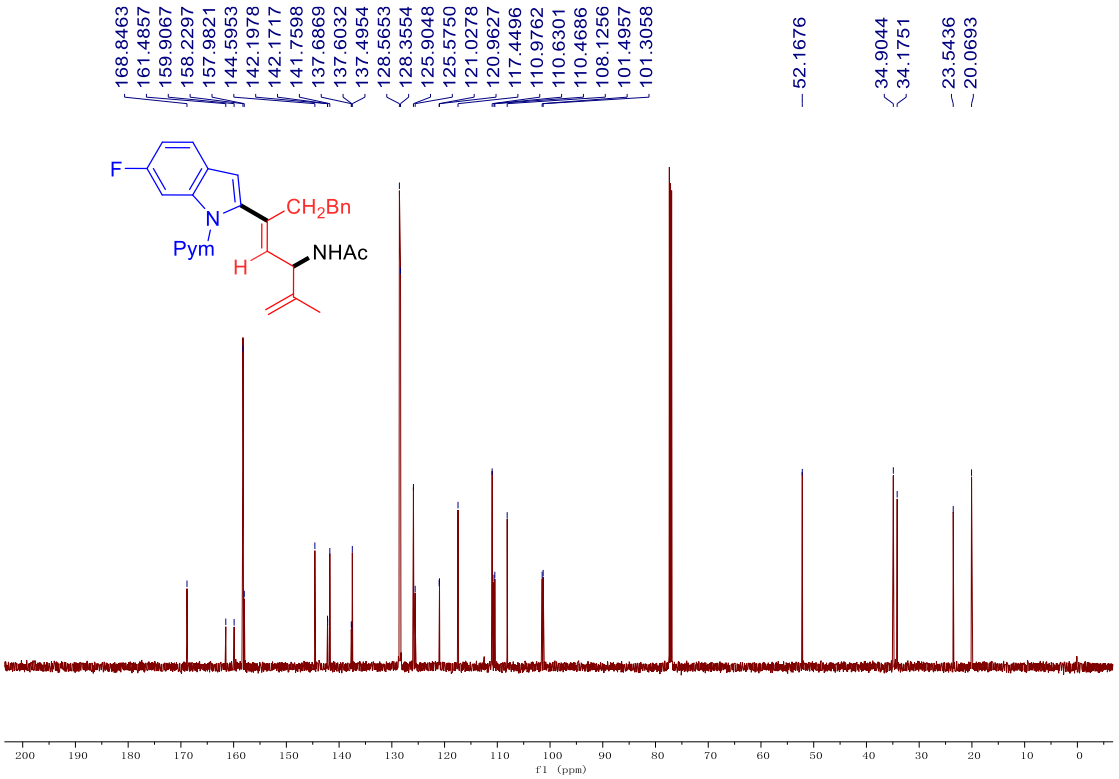
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16.**



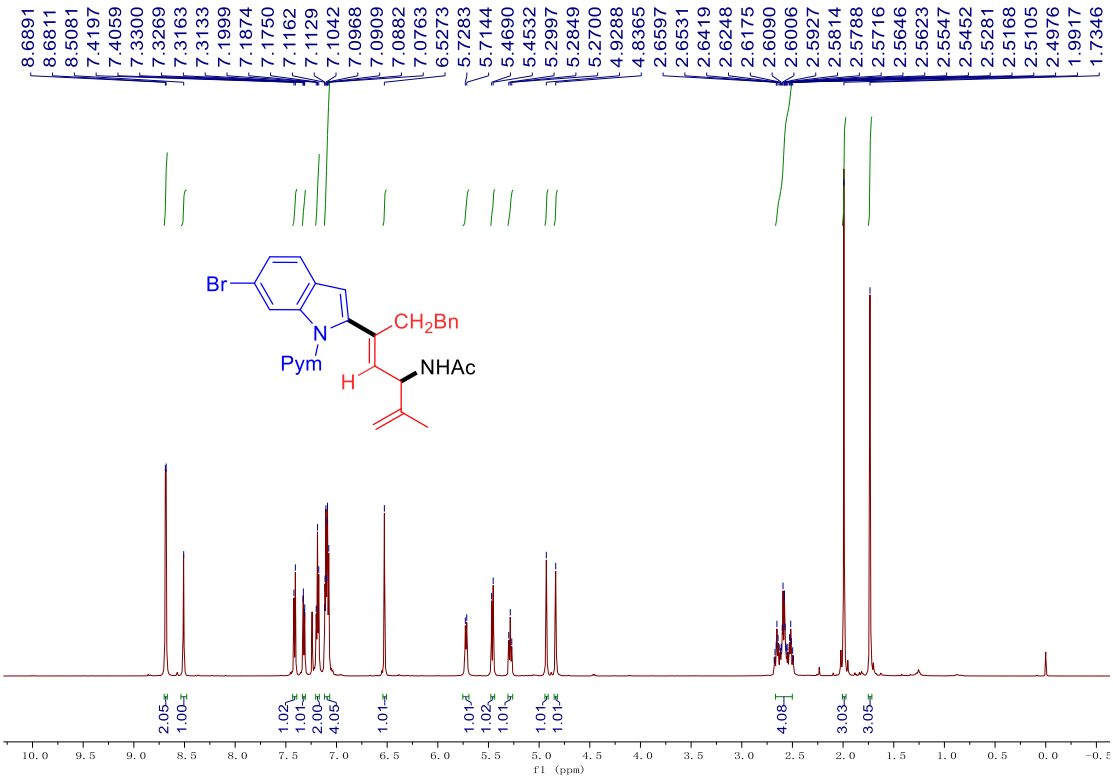
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **16.**



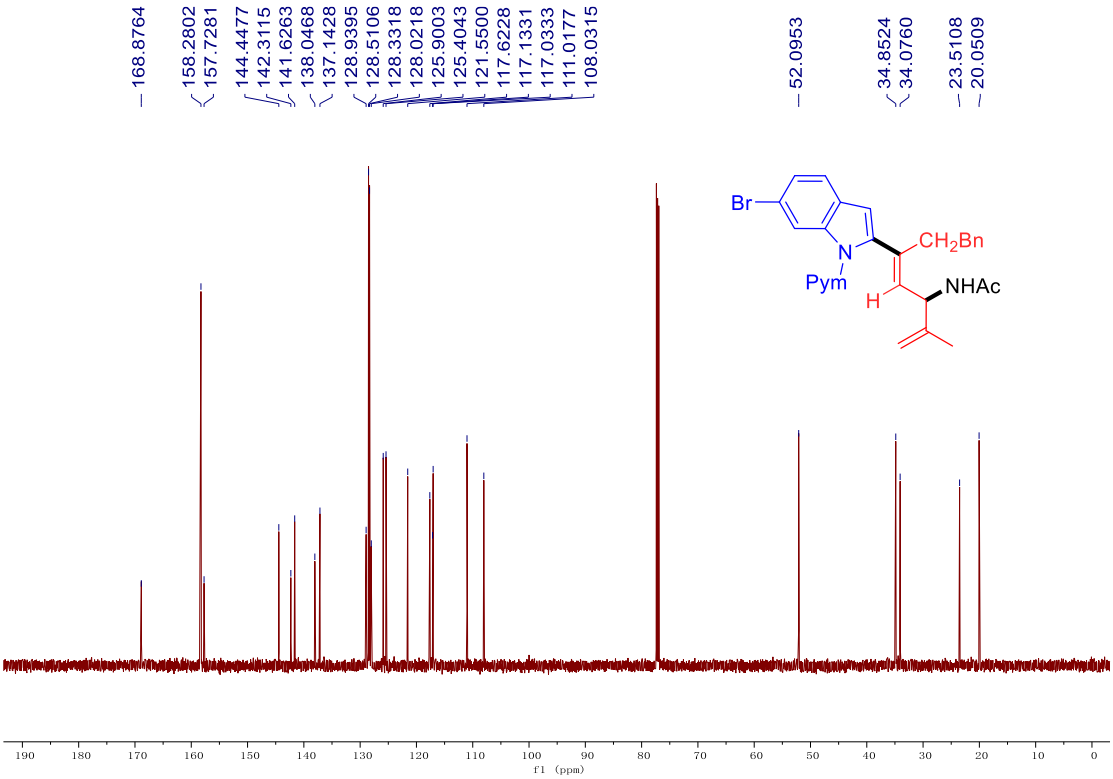
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **17.**



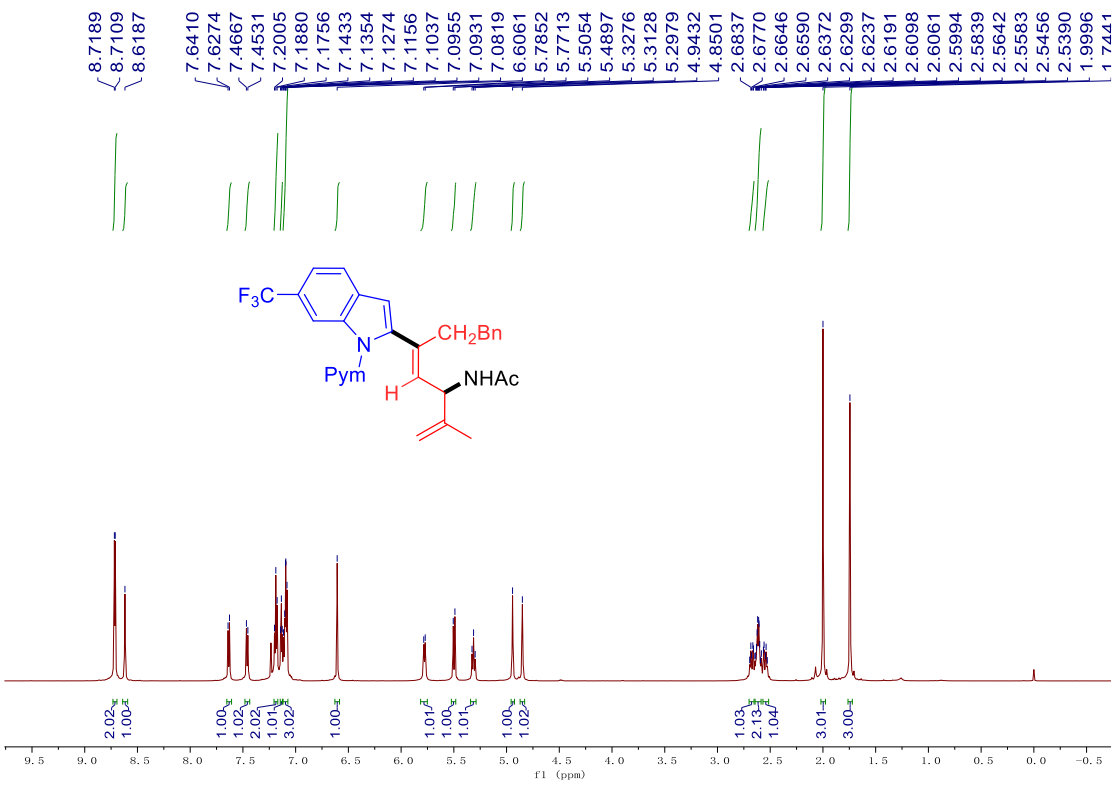
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **17.**



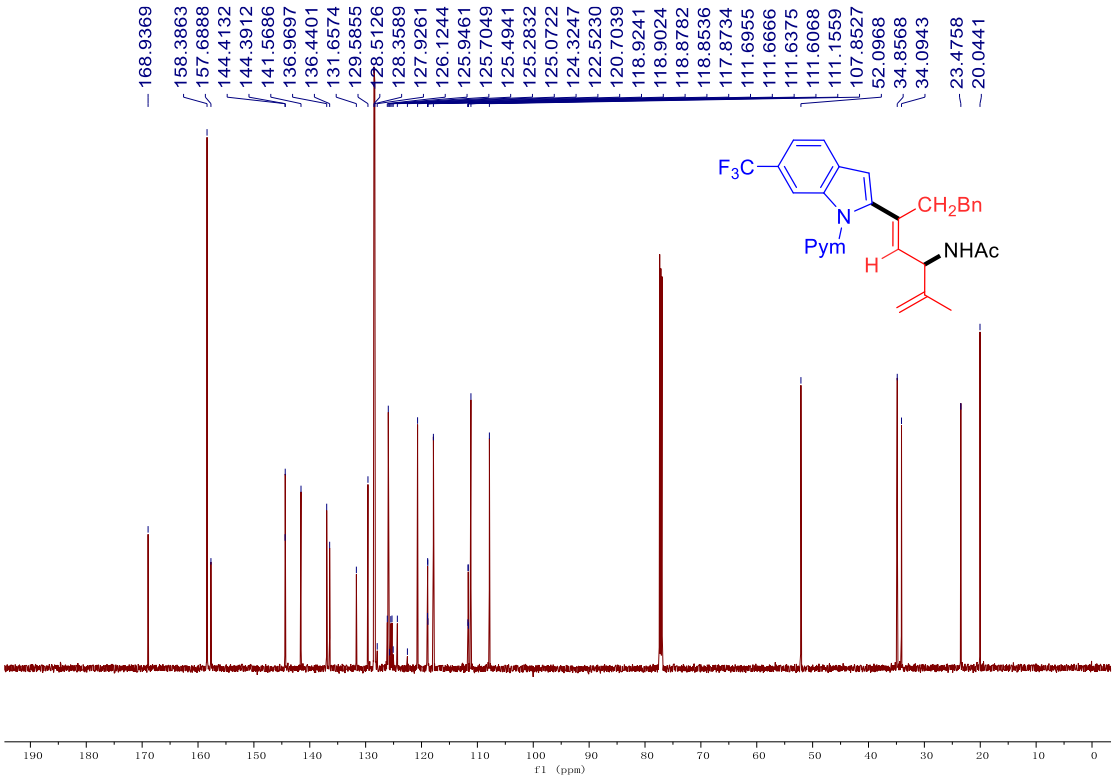
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **18.**



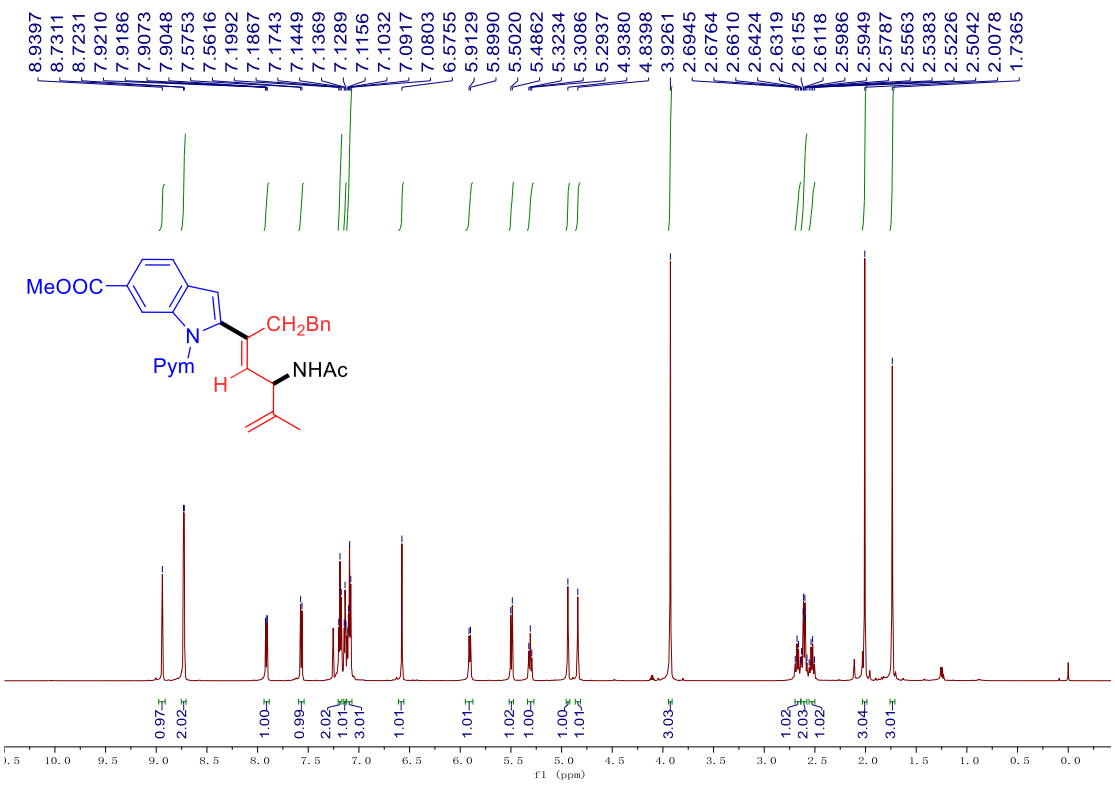
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **18.**



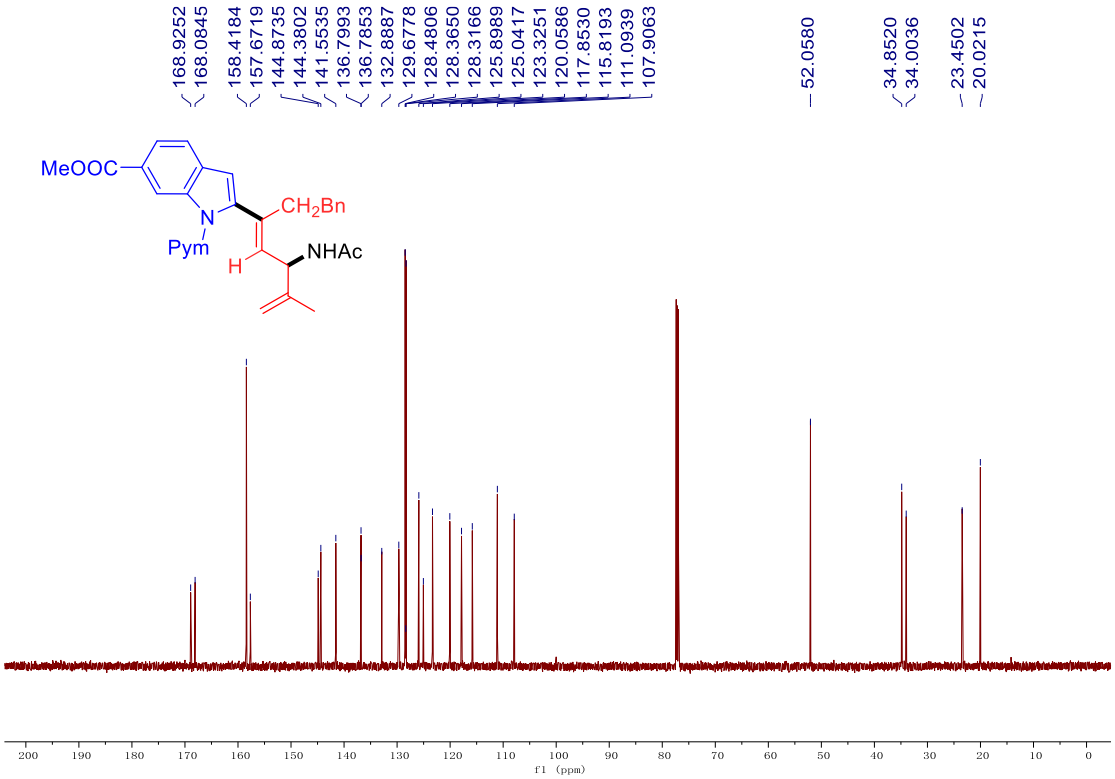
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **19.**



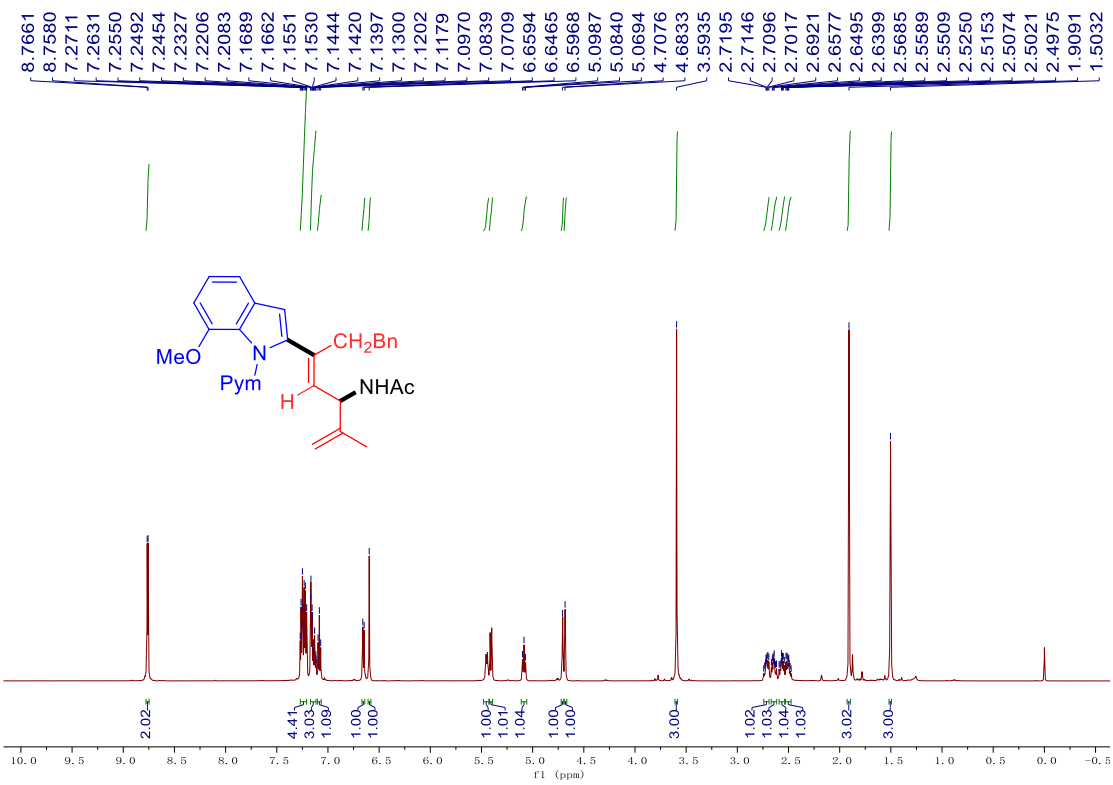
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **19.**



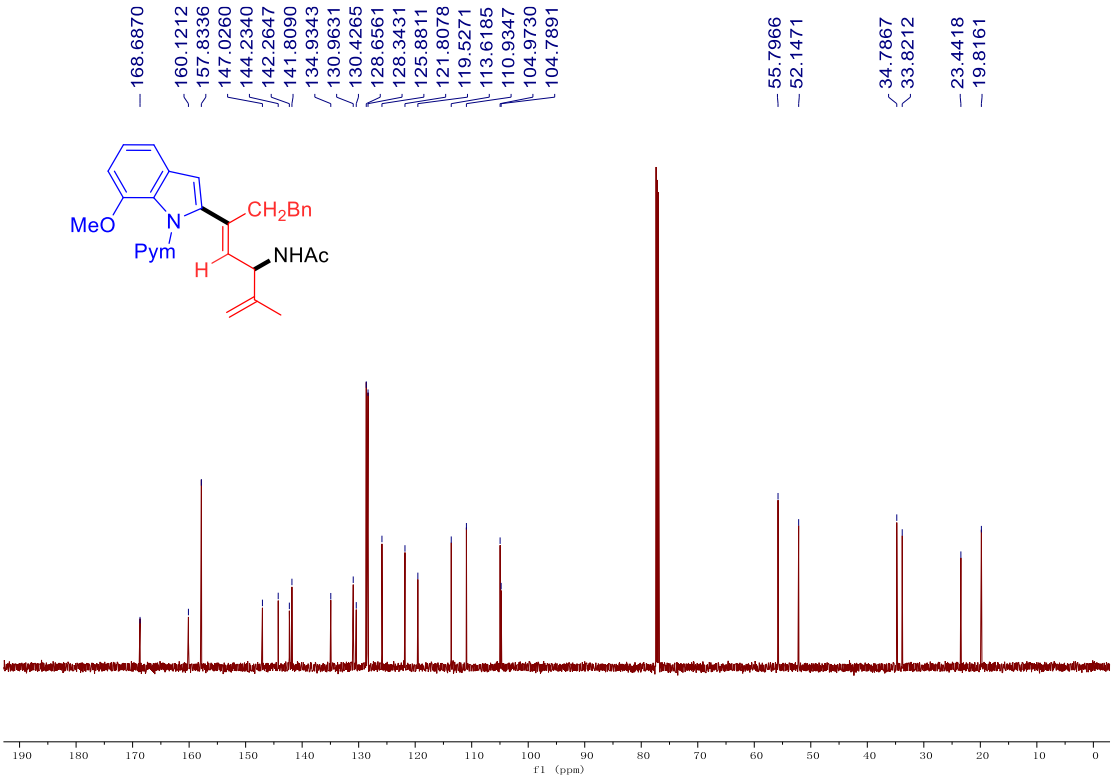
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **20.**



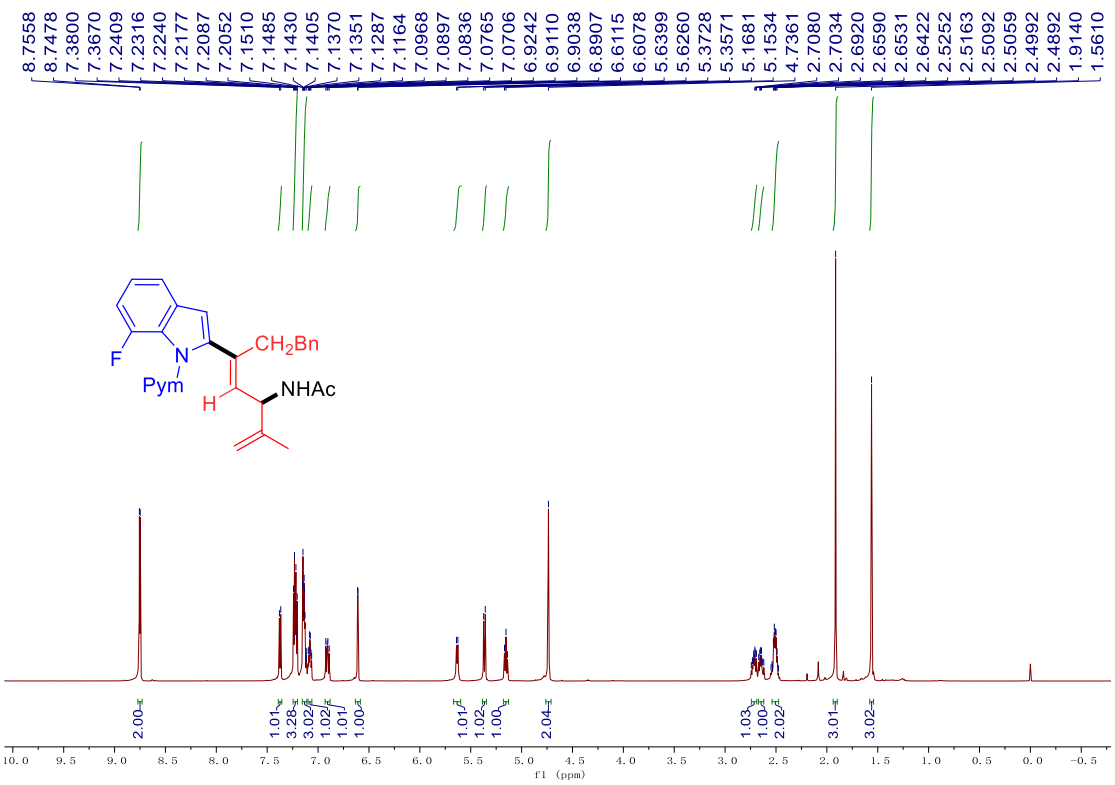
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **20.**



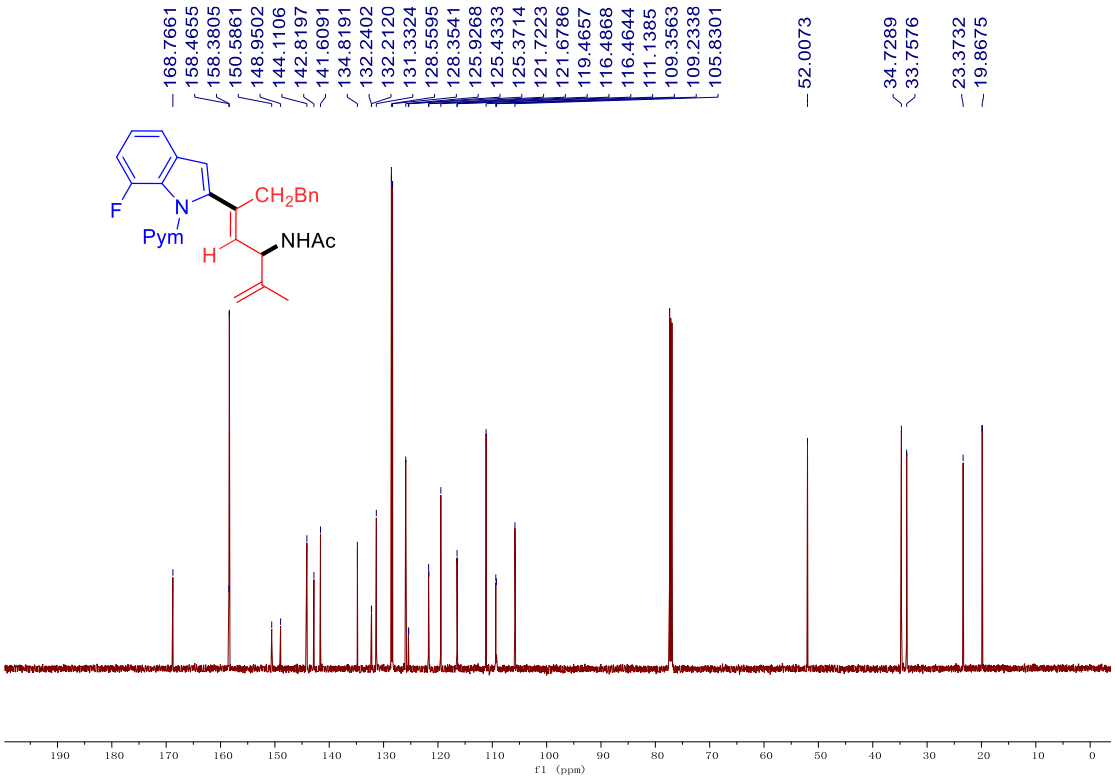
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **21.**



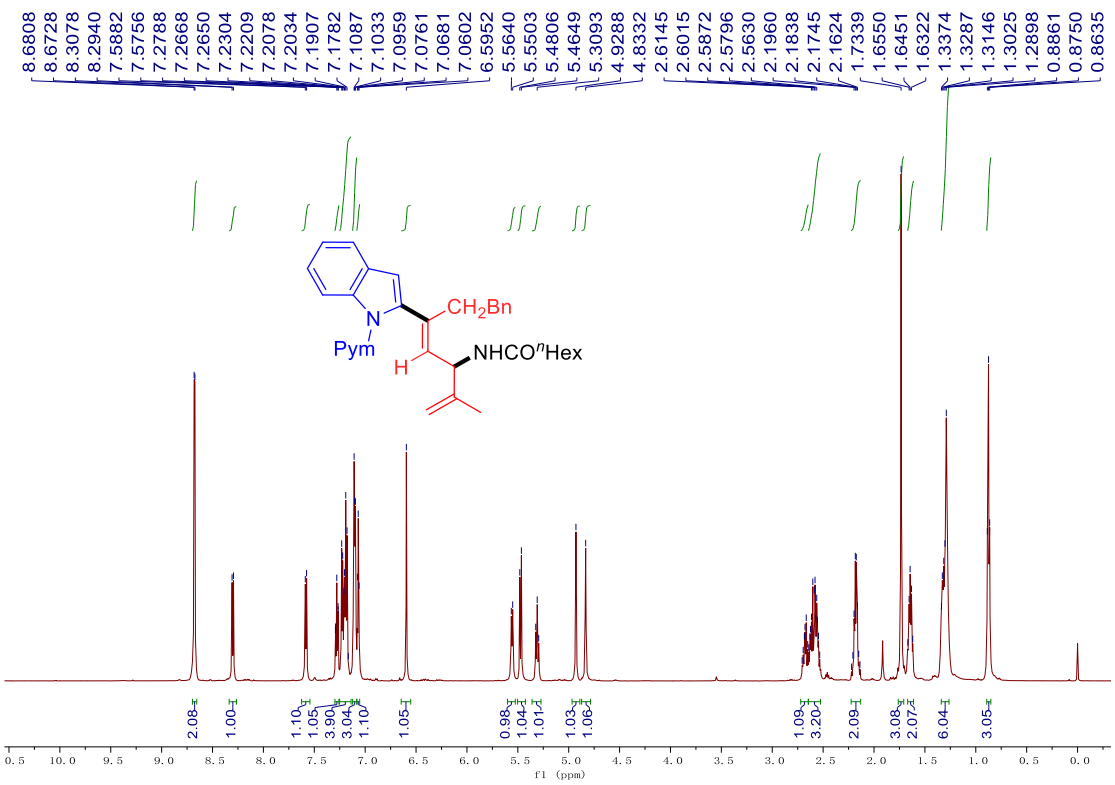
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **21.**



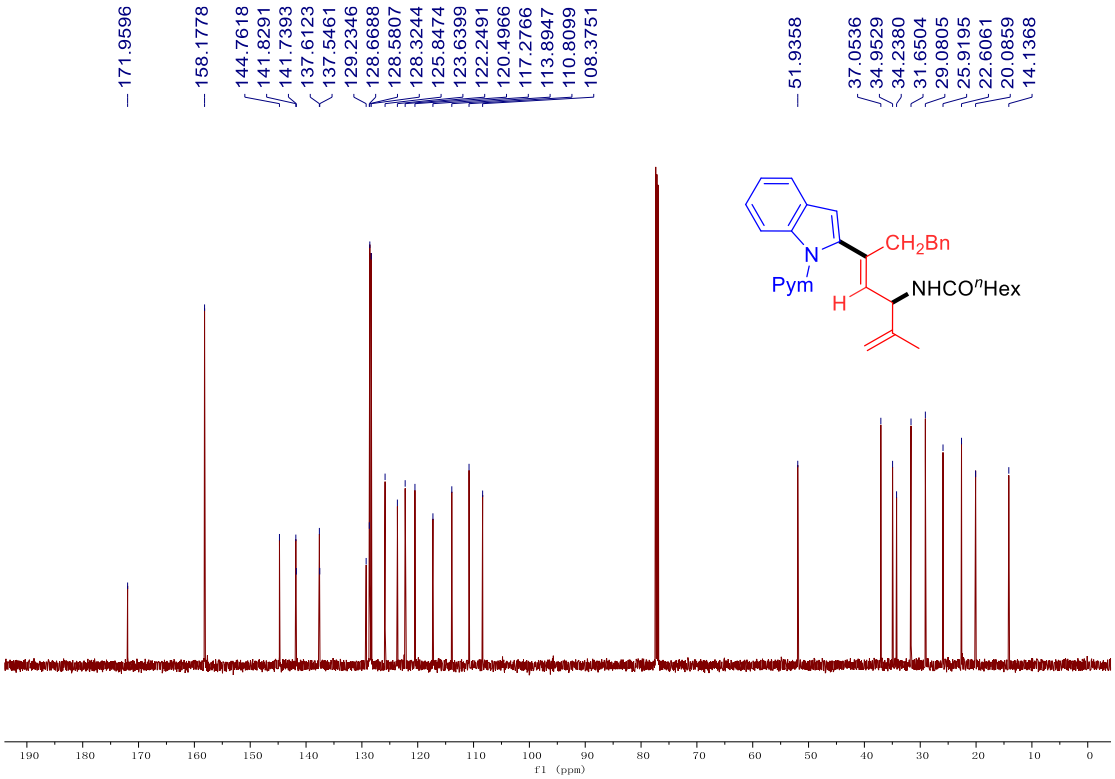
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **22.**



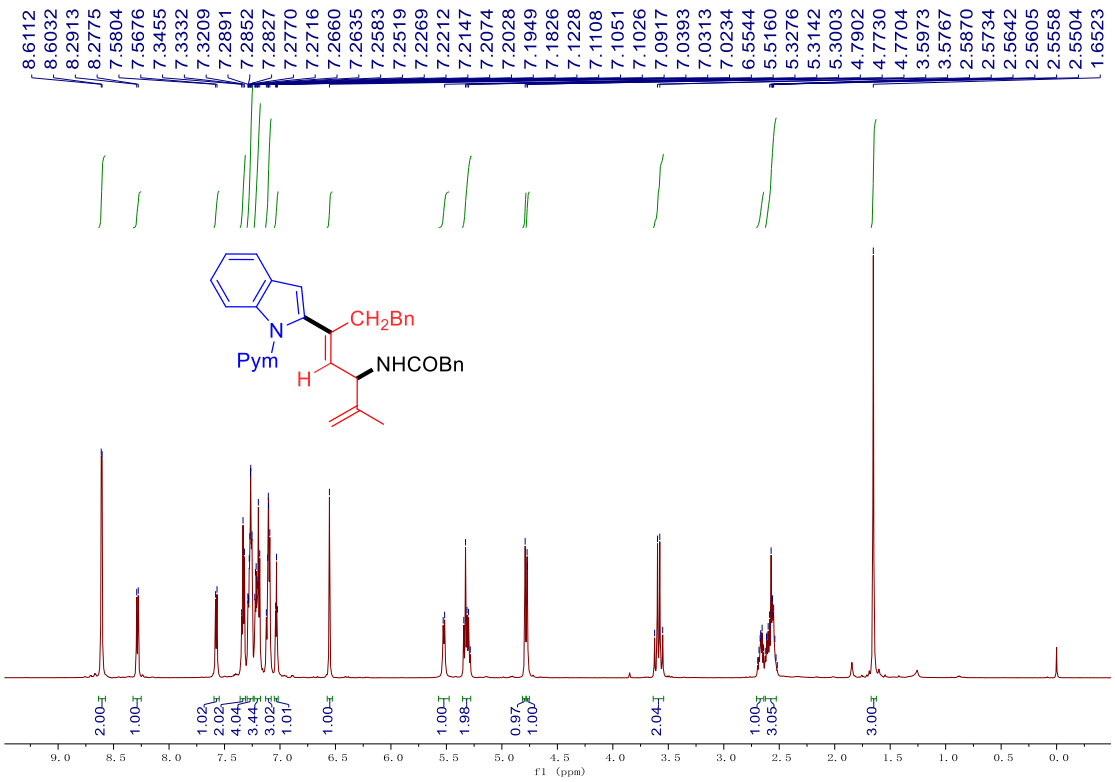
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **22.**



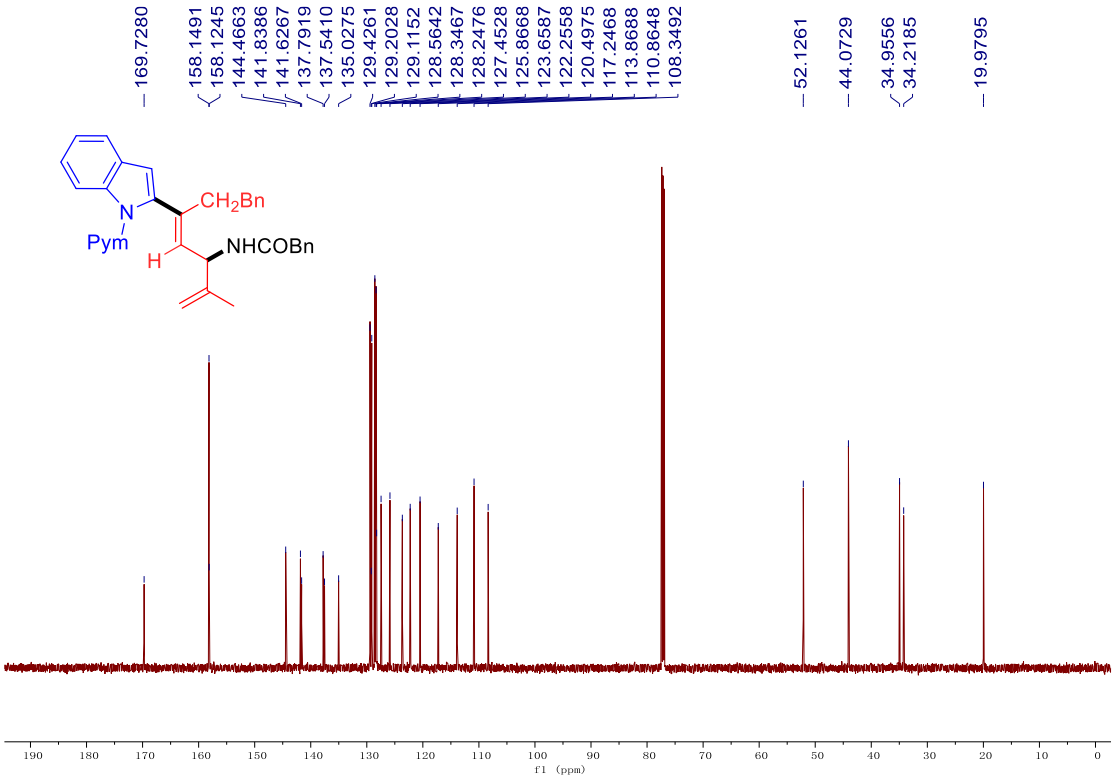
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **23.**



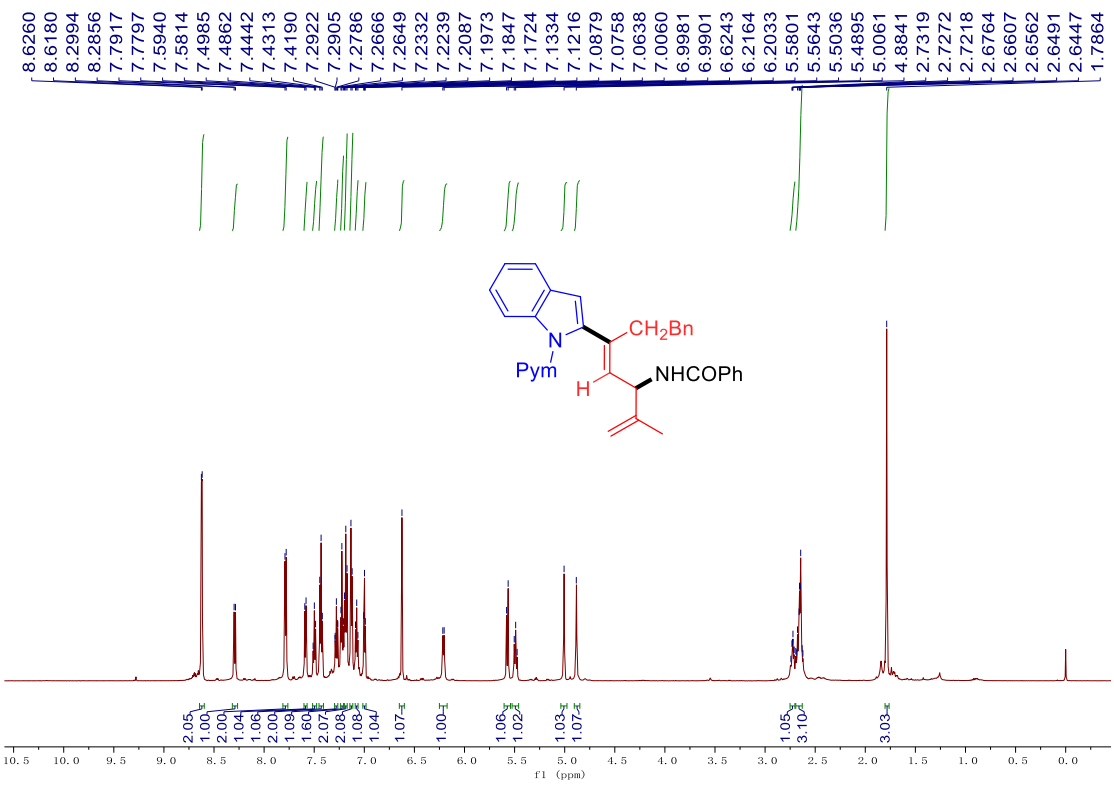
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **23.**



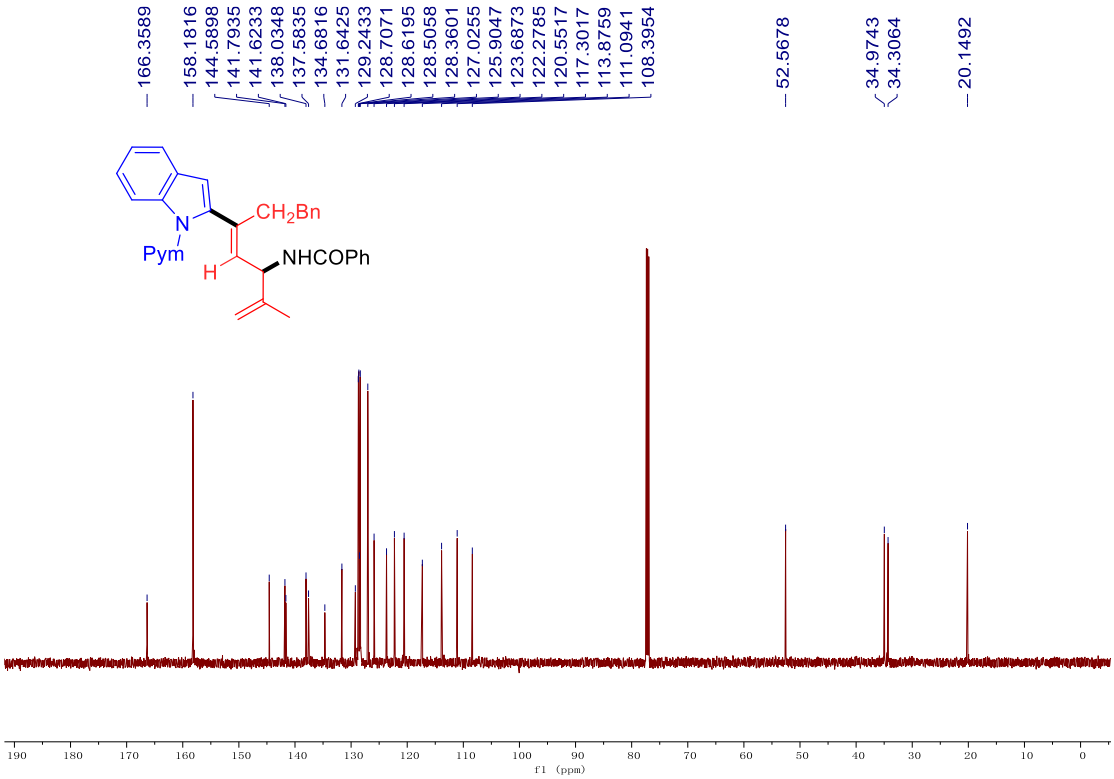
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **24.**



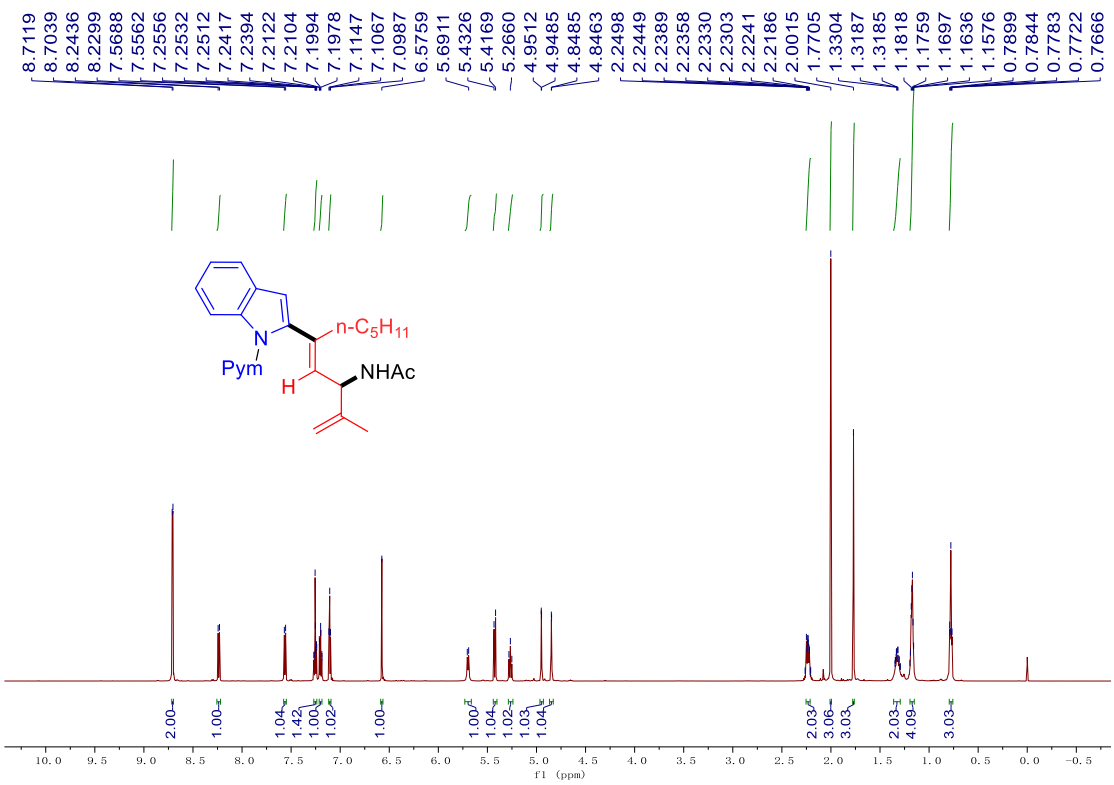
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **24.**



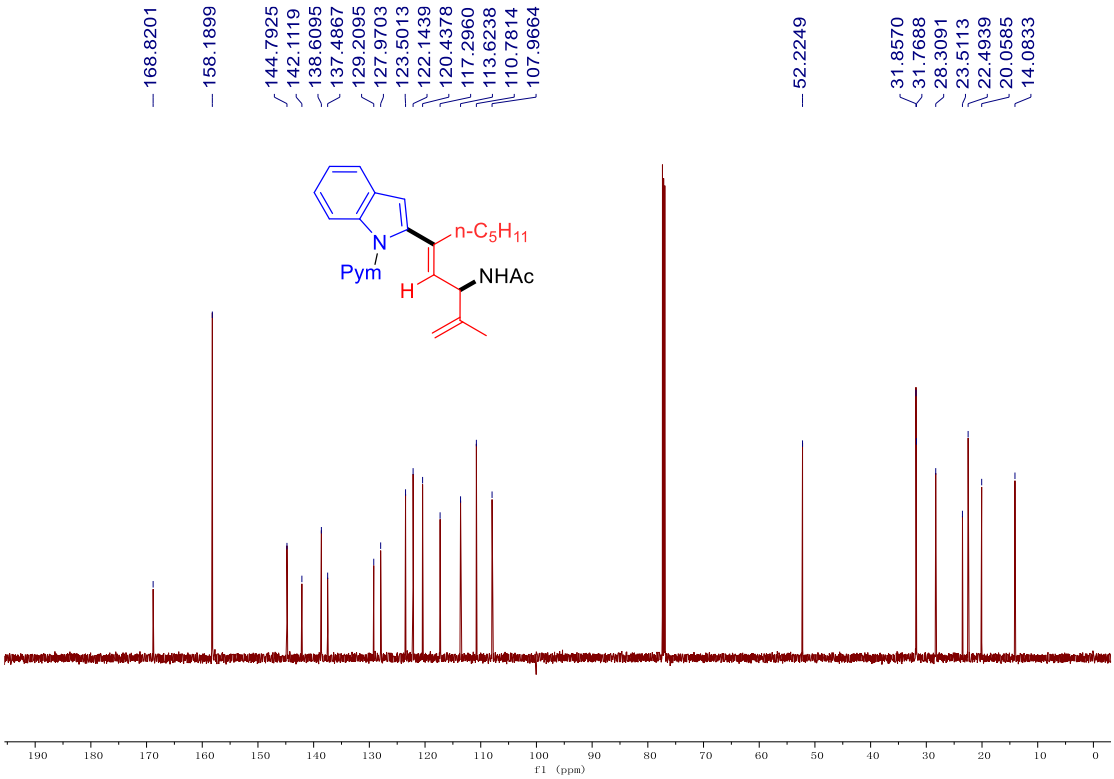
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **25.**



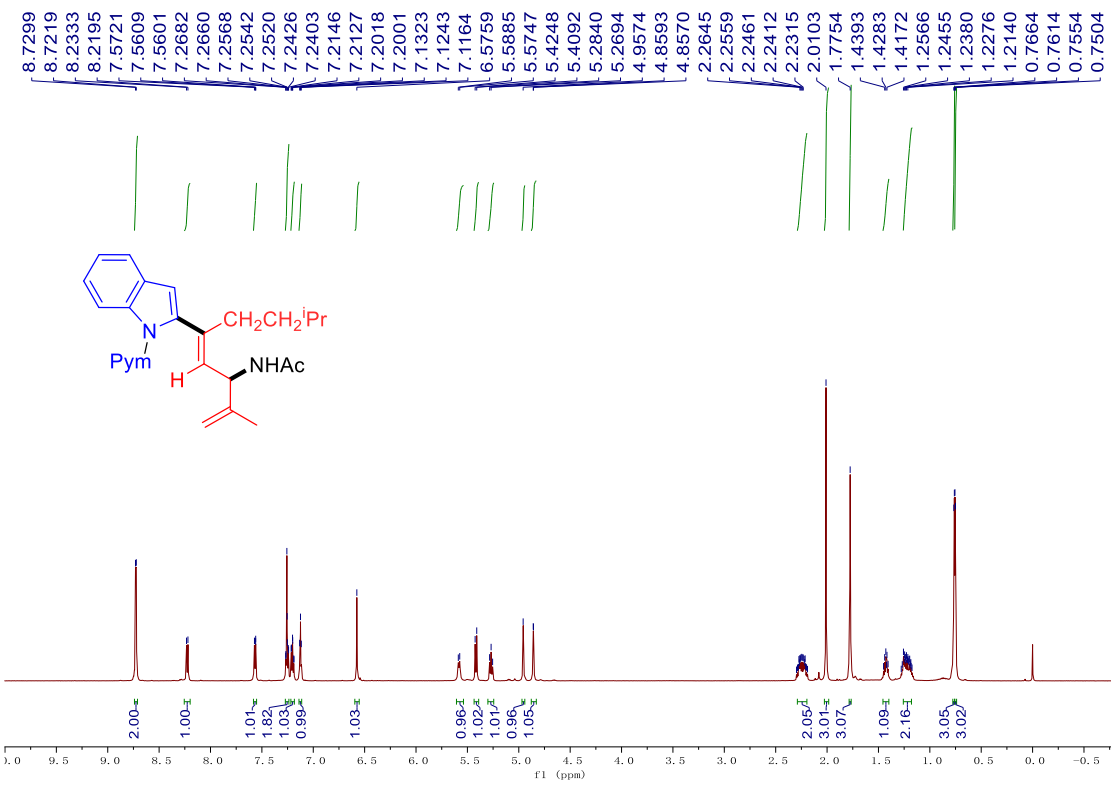
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **25.**



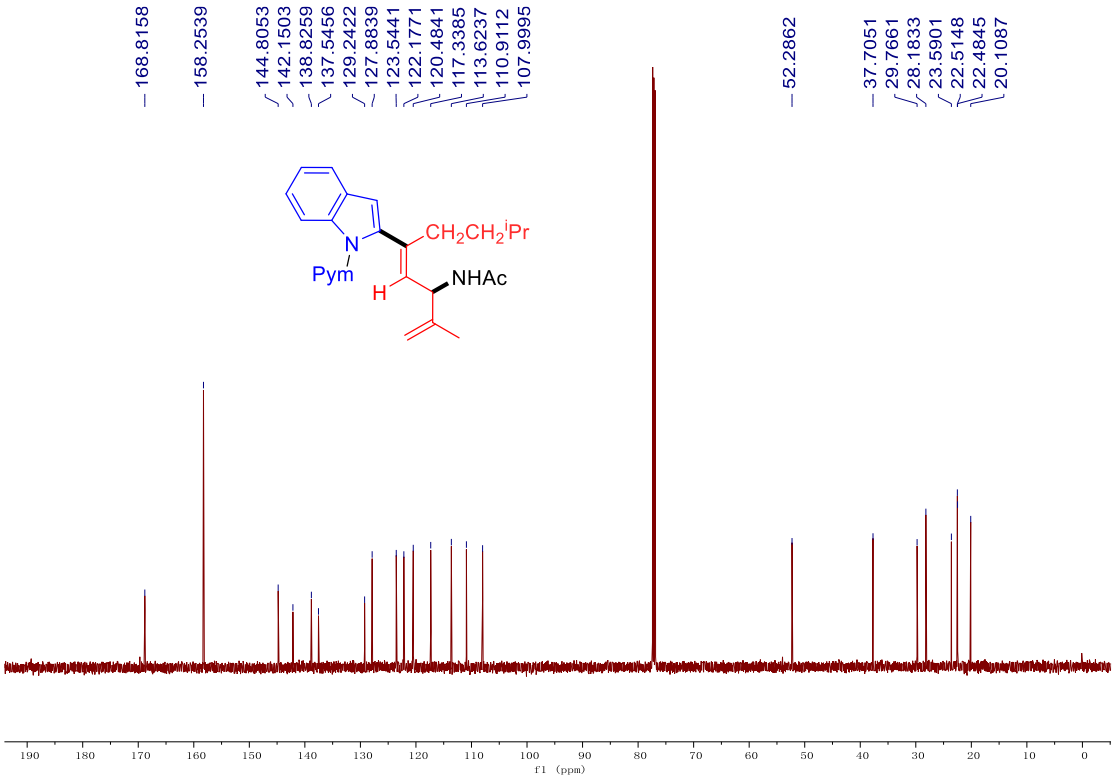
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **26.**



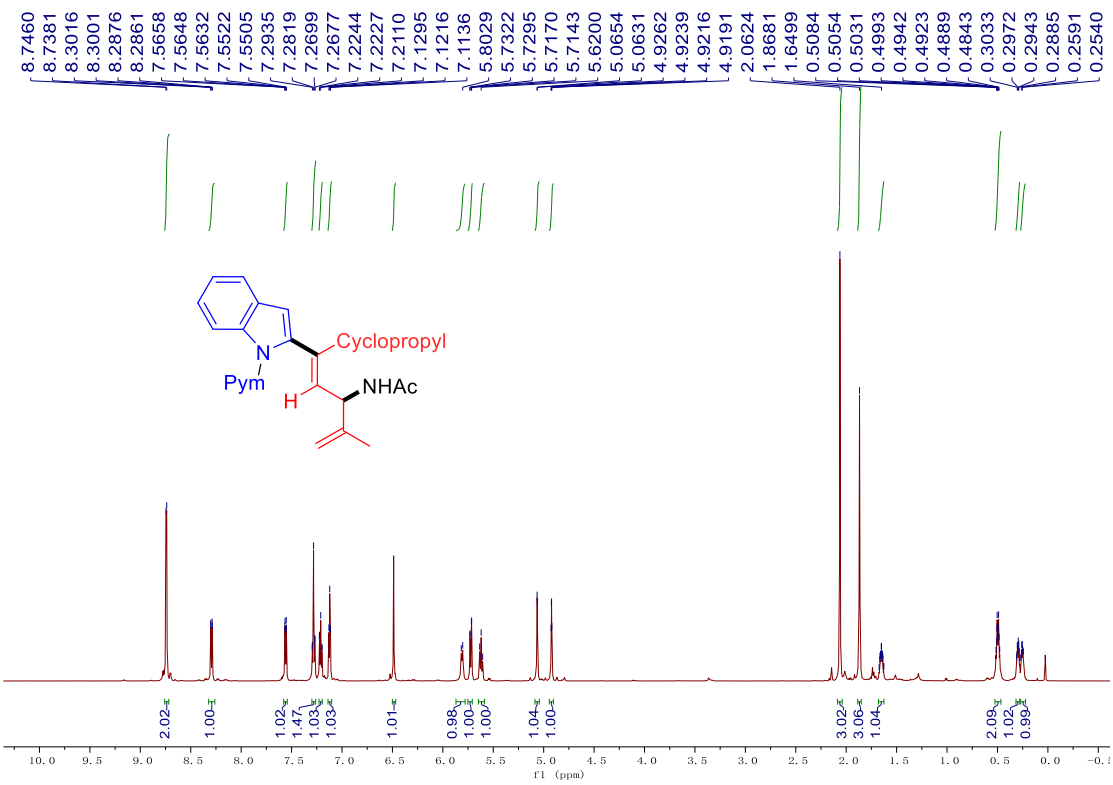
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **26.**



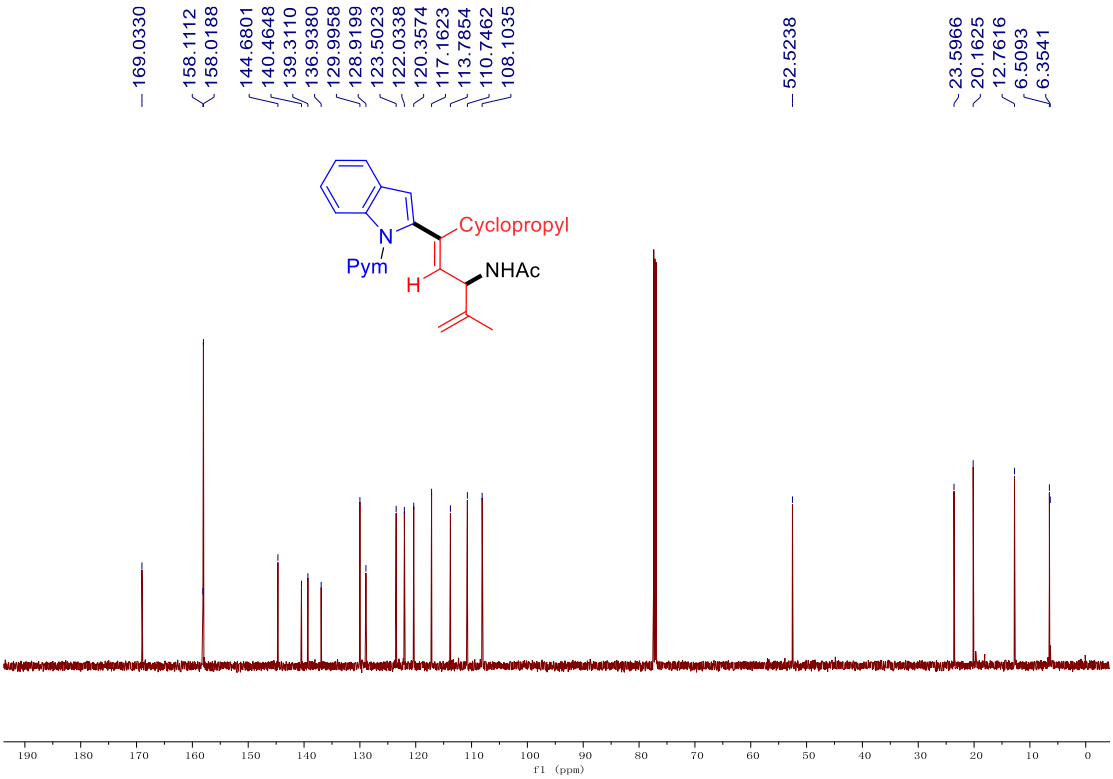
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **27.**



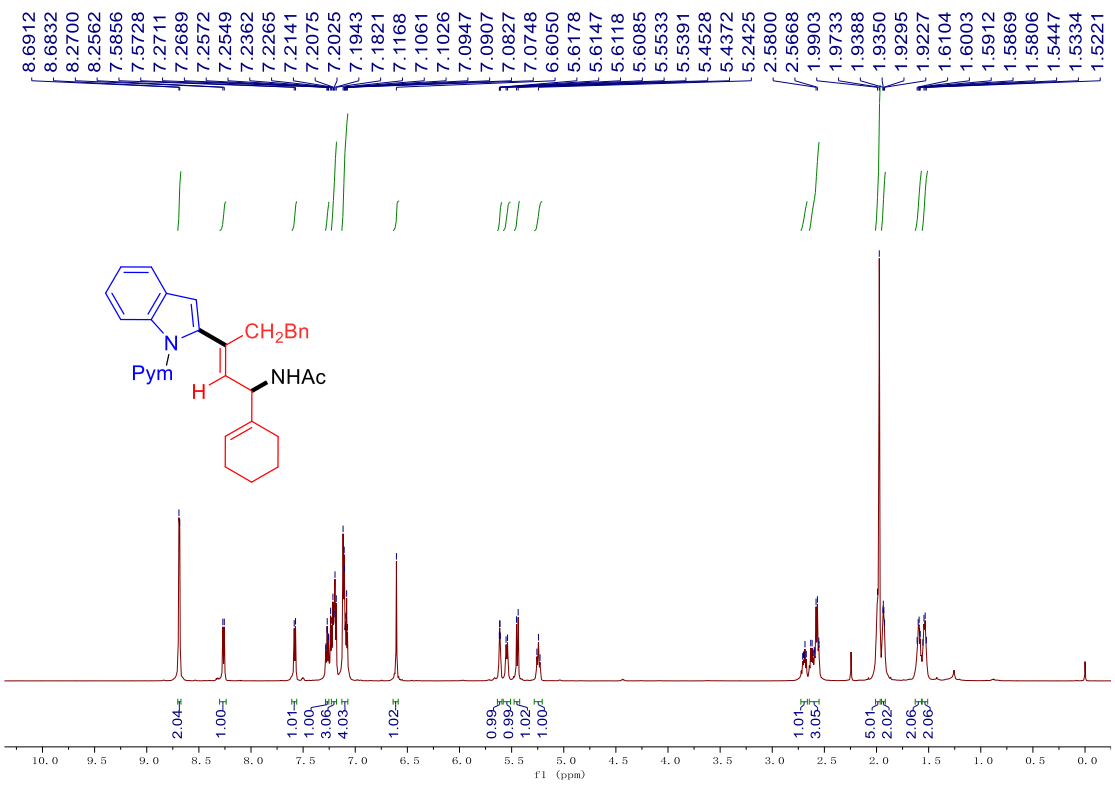
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **27.**



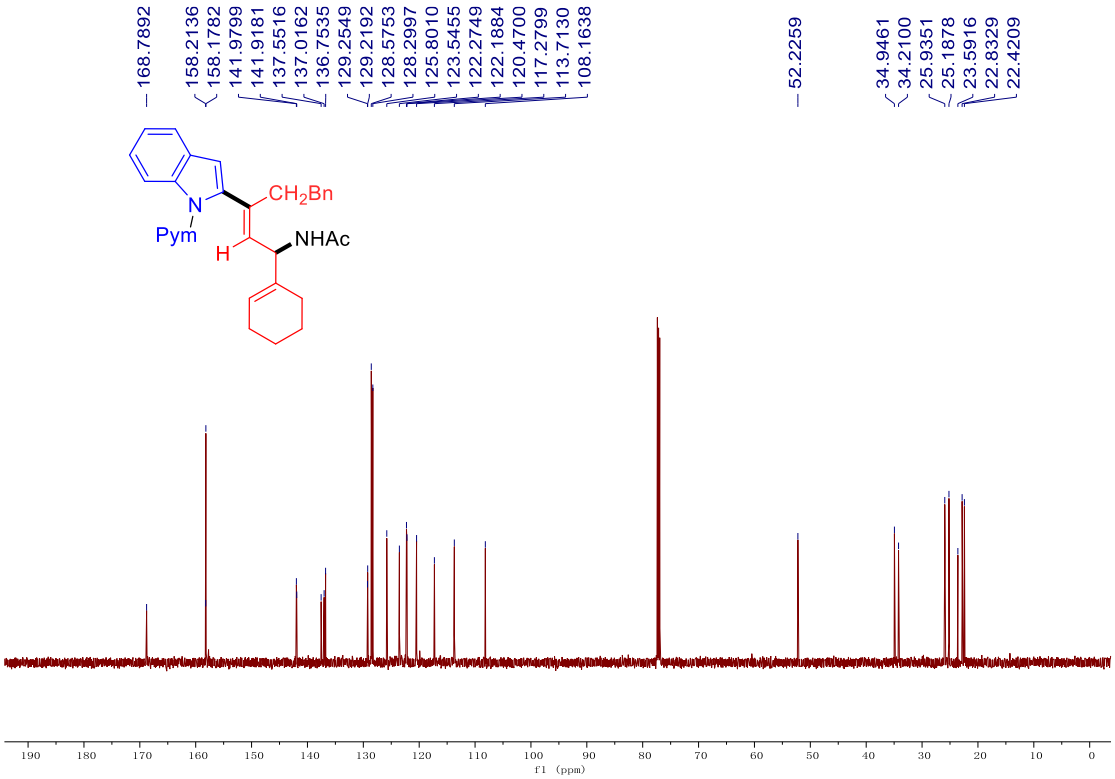
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **28.**



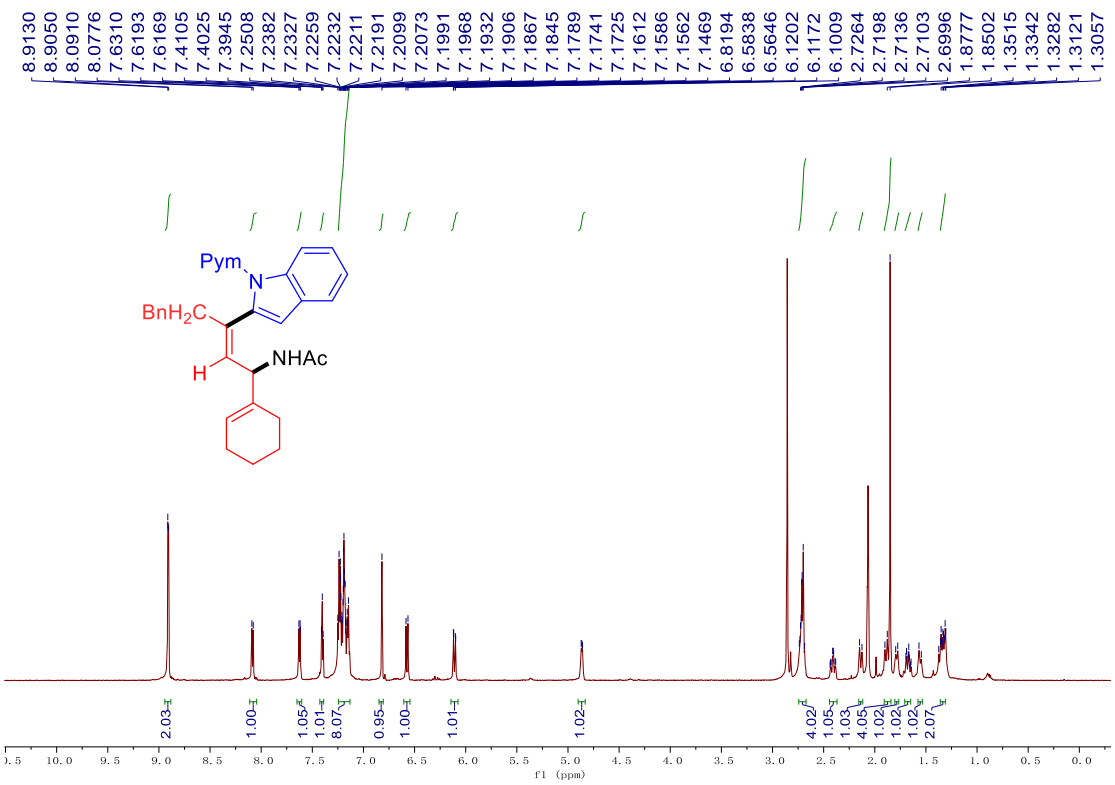
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **28.**



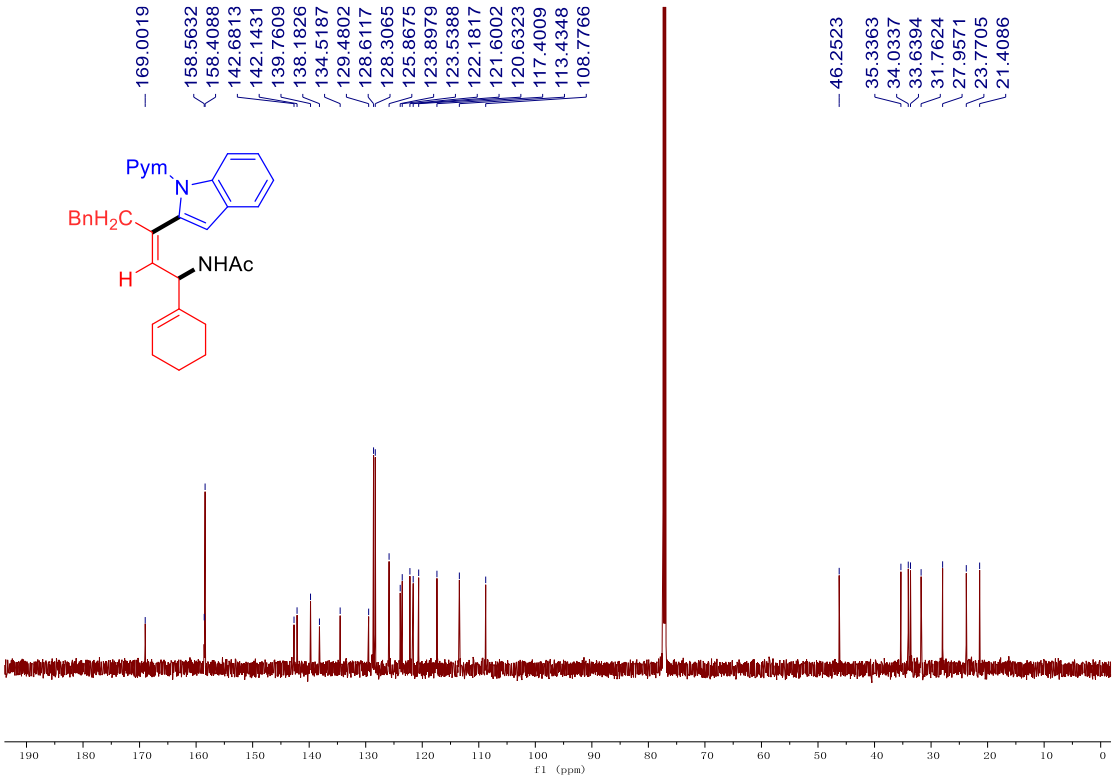
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **29.**



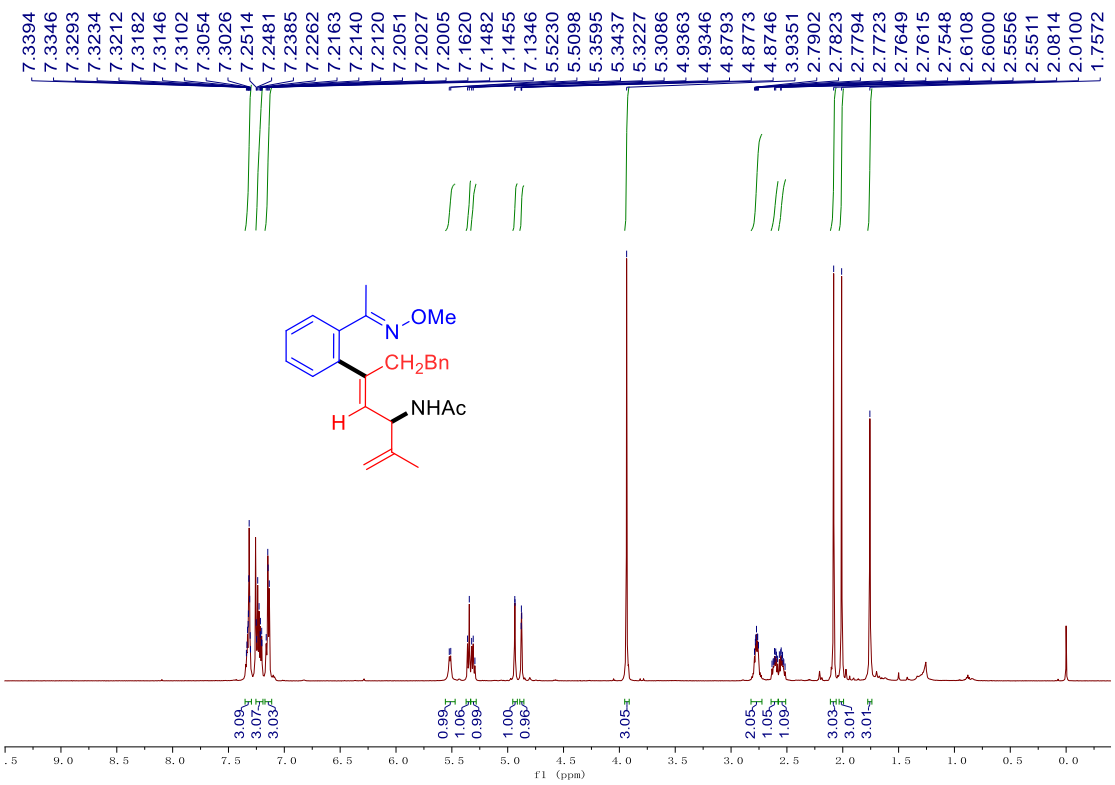
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **29.**



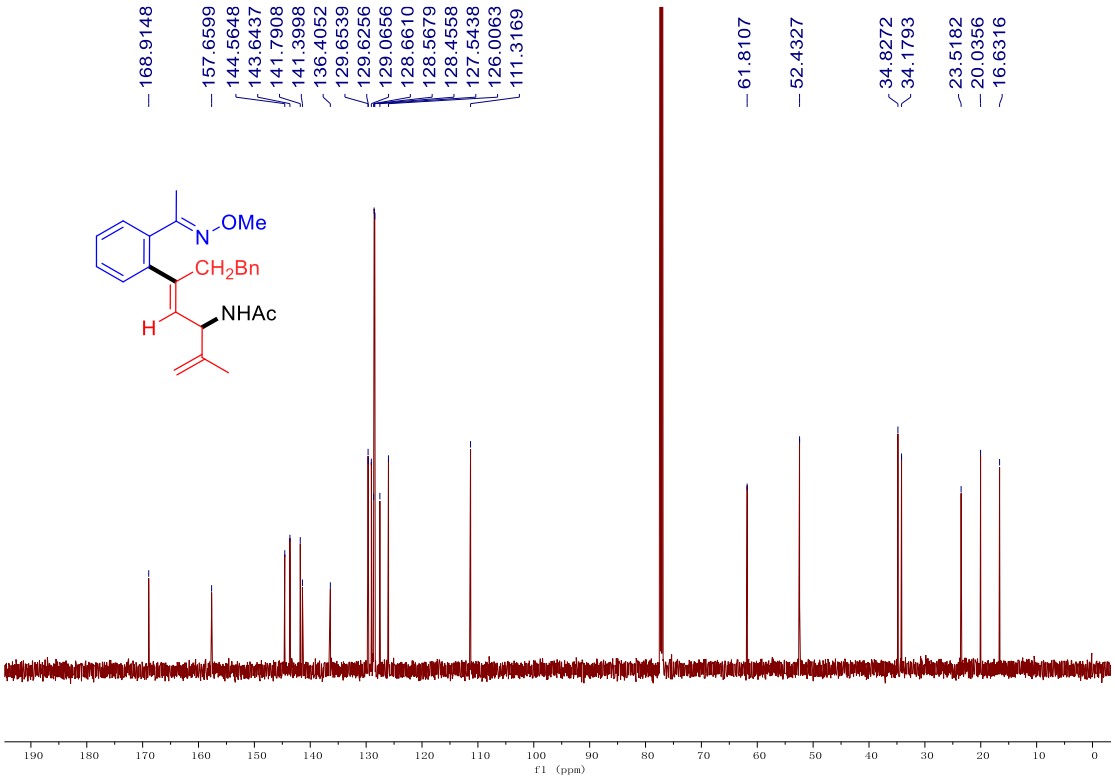
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **30.**



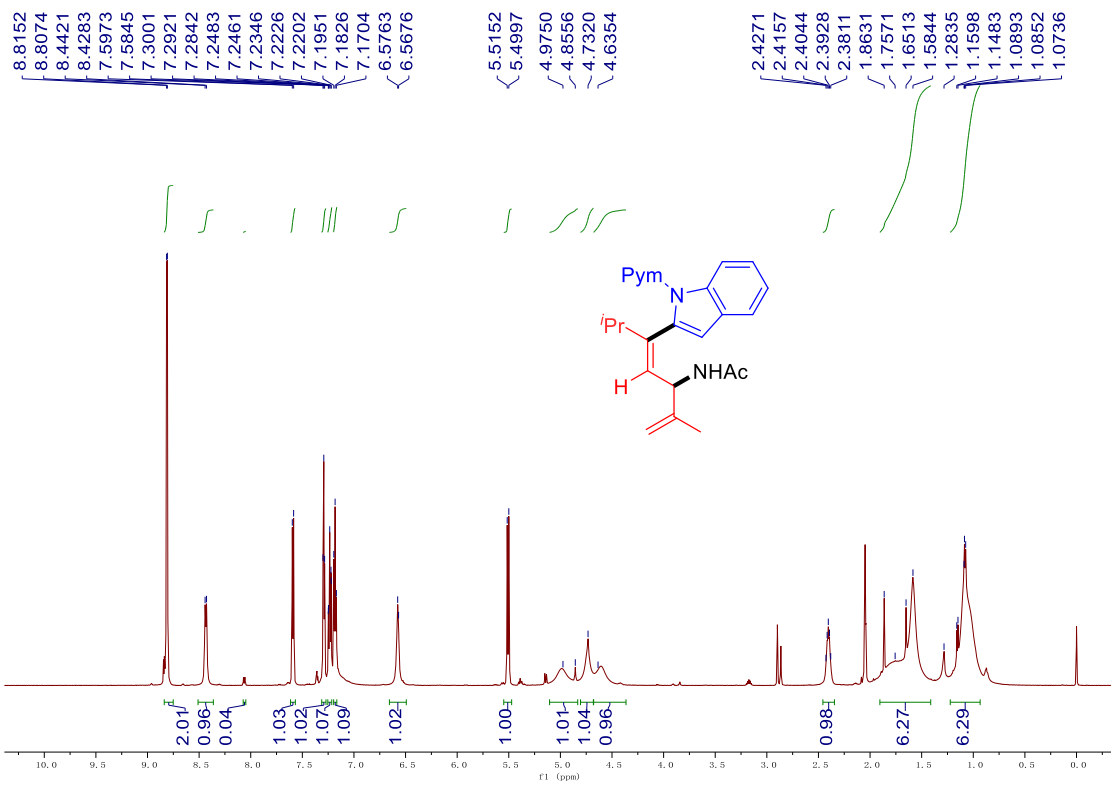
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **30.**



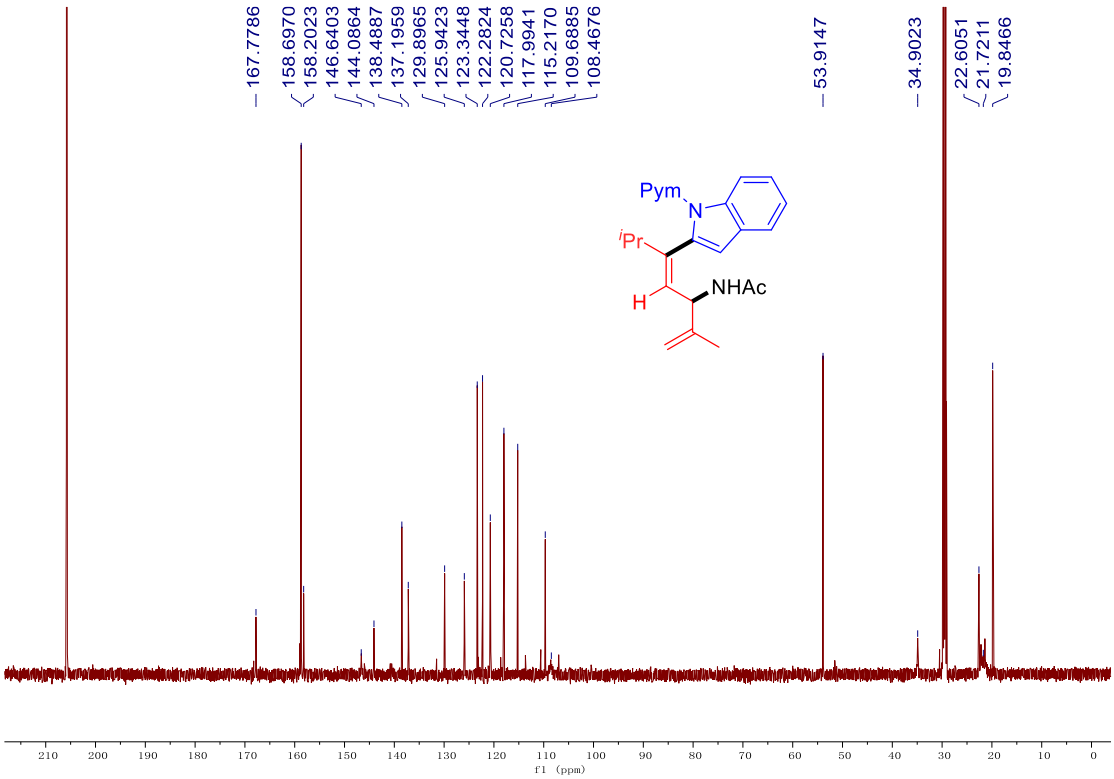
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **31.**



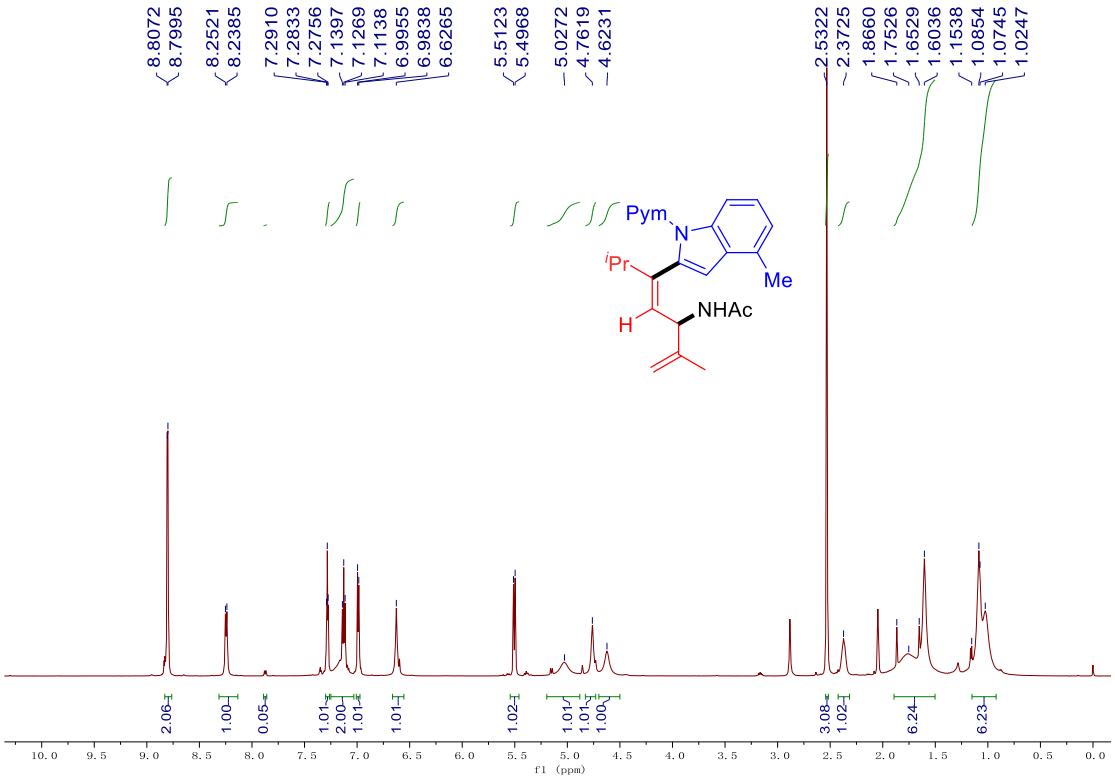
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **31.**



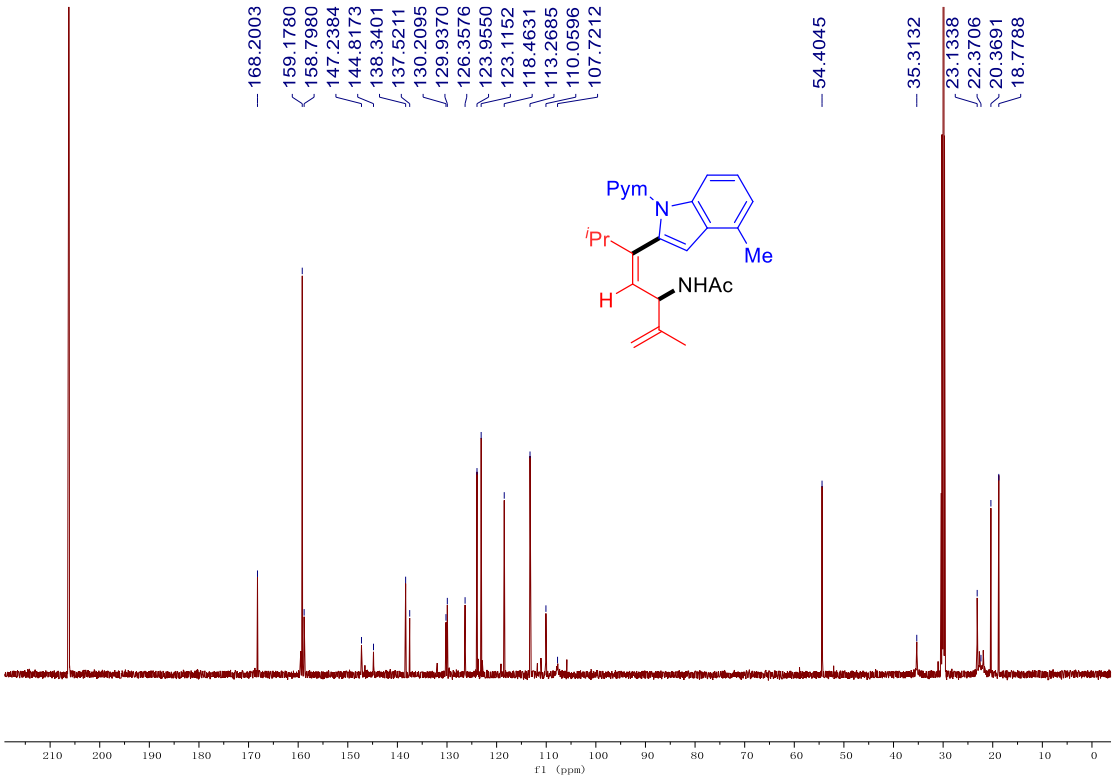
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **32.**



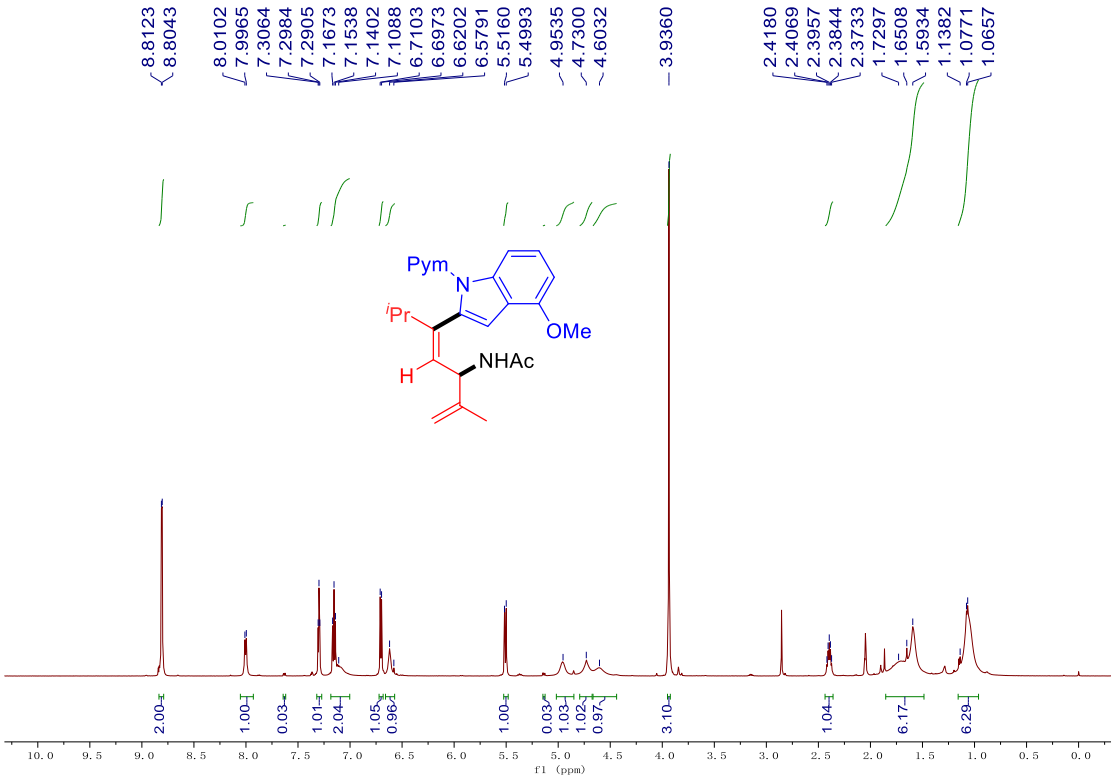
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **32.**



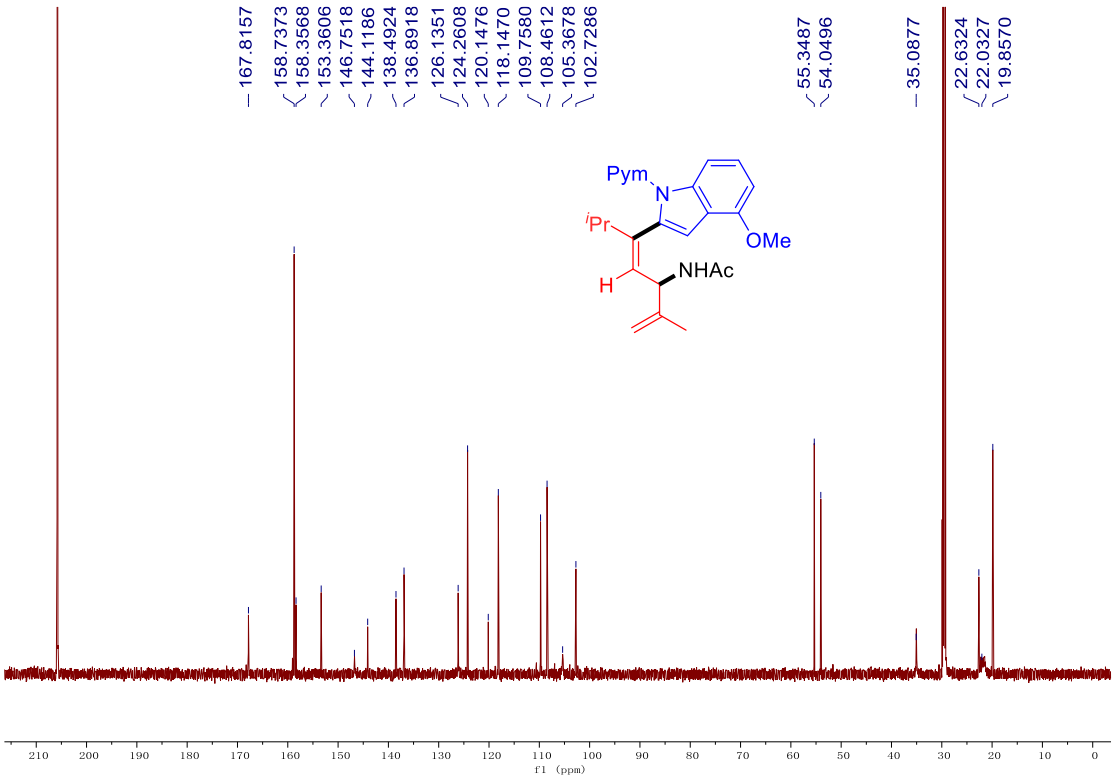
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **33.**



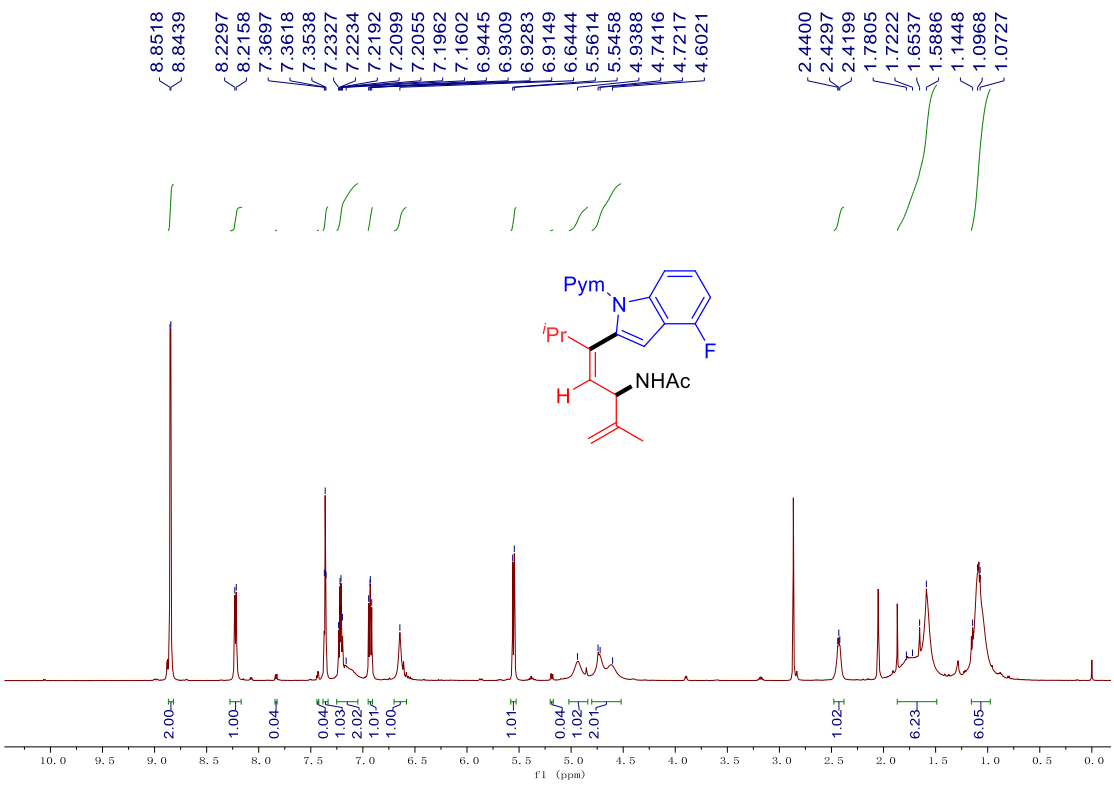
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **33.**



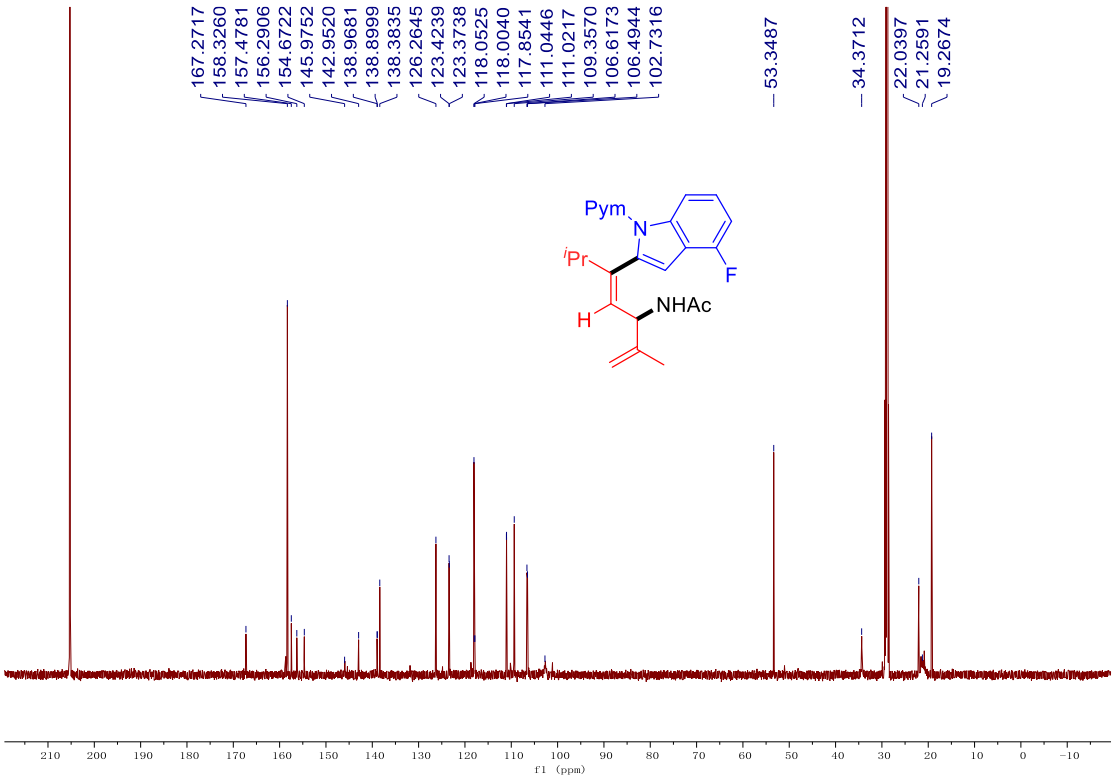
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **34.**



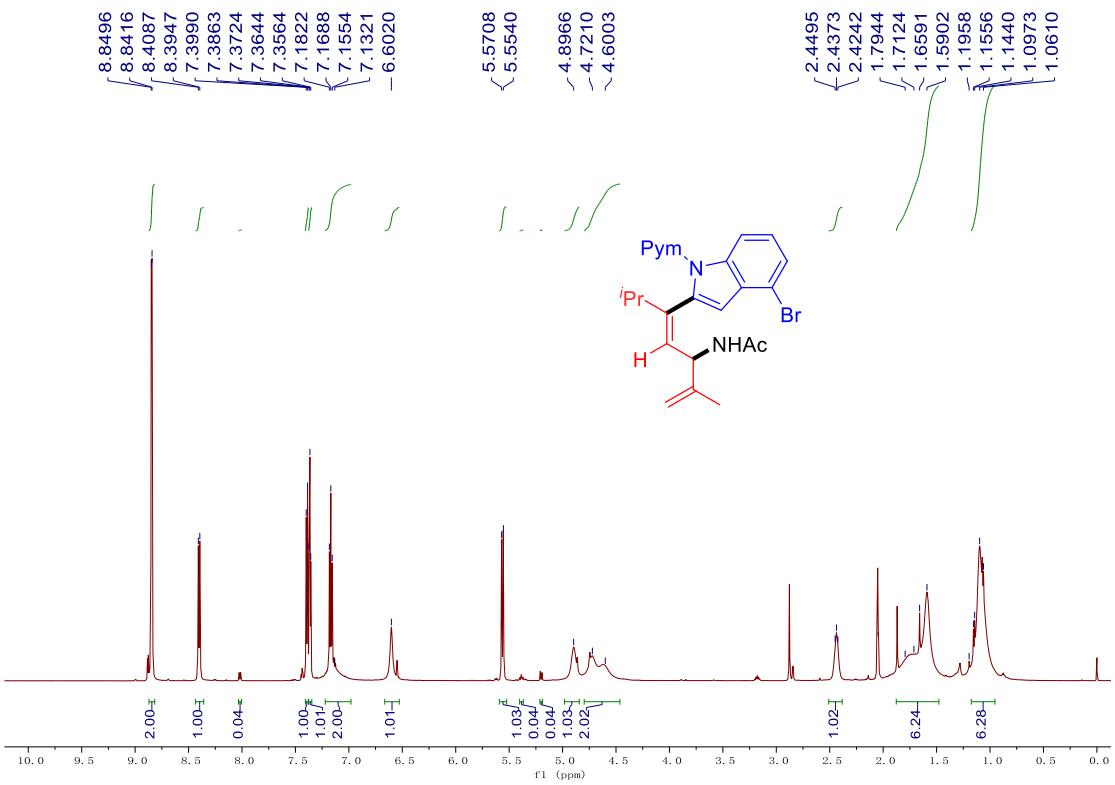
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **34.**



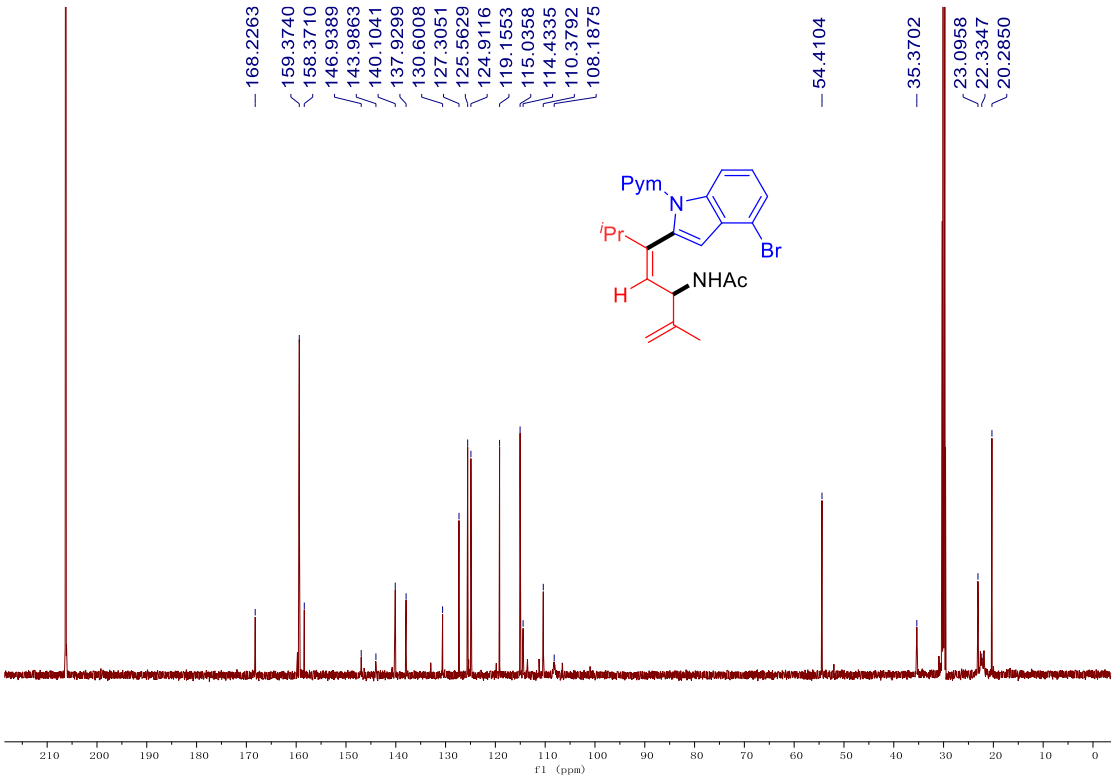
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **35.**



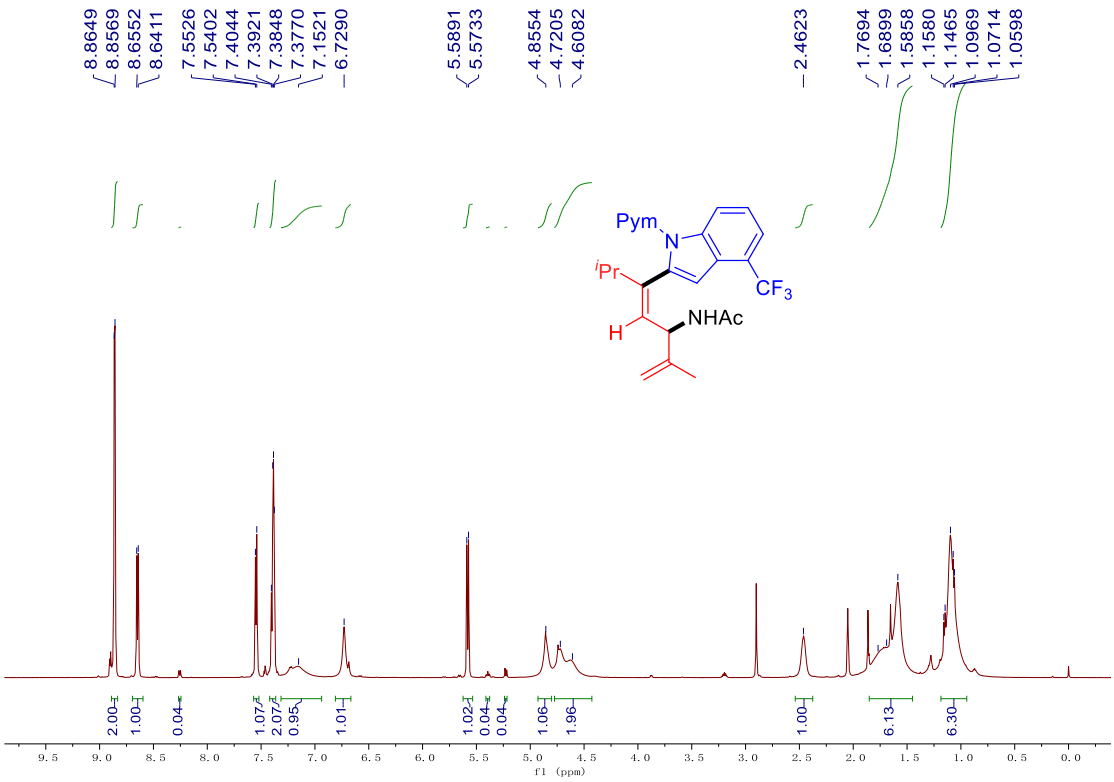
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **35.**



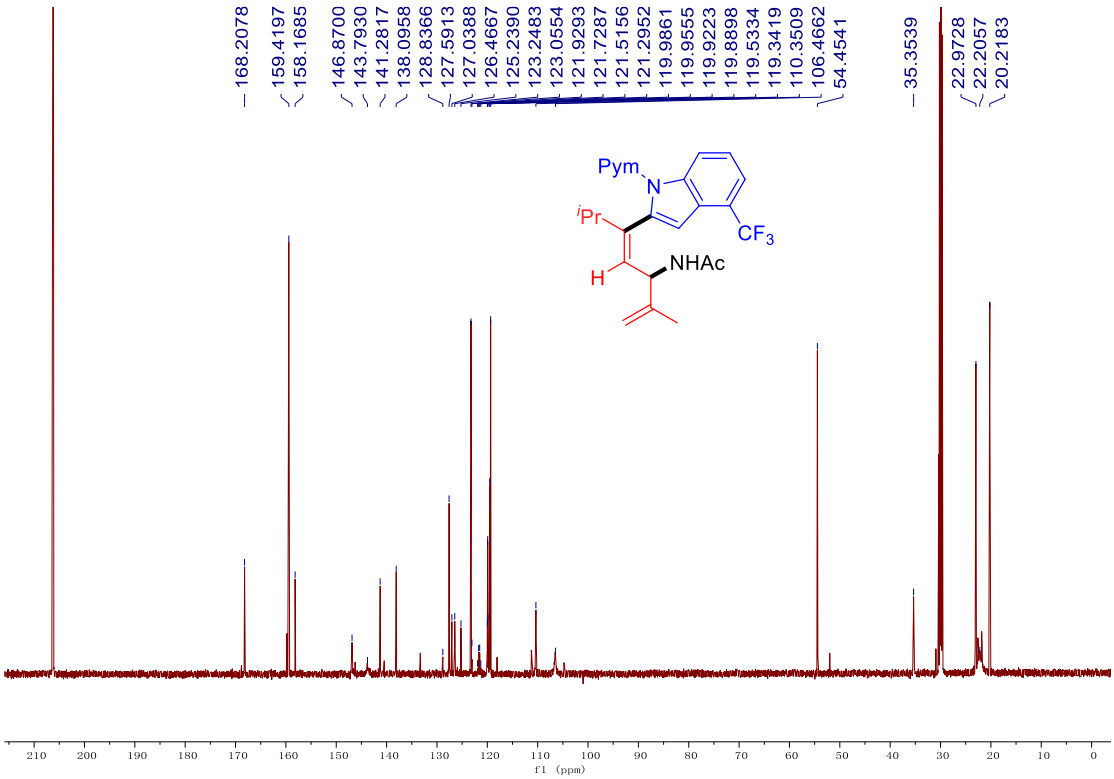
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **36.**



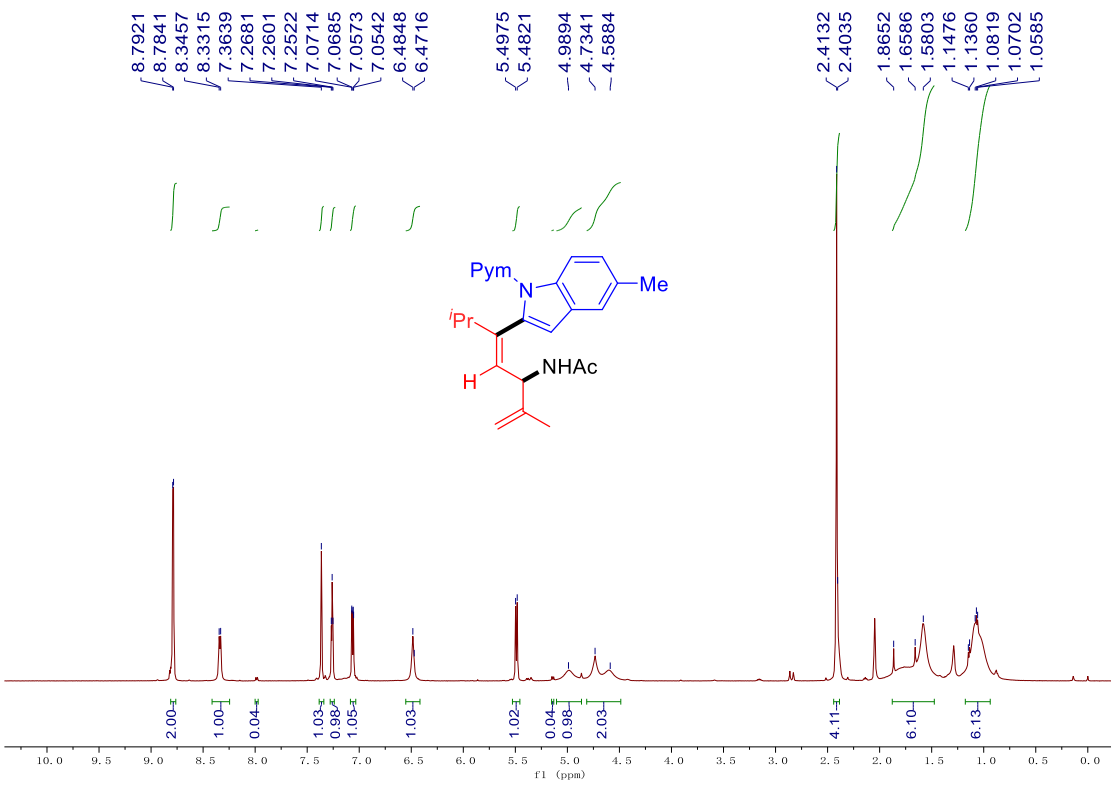
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **36.**



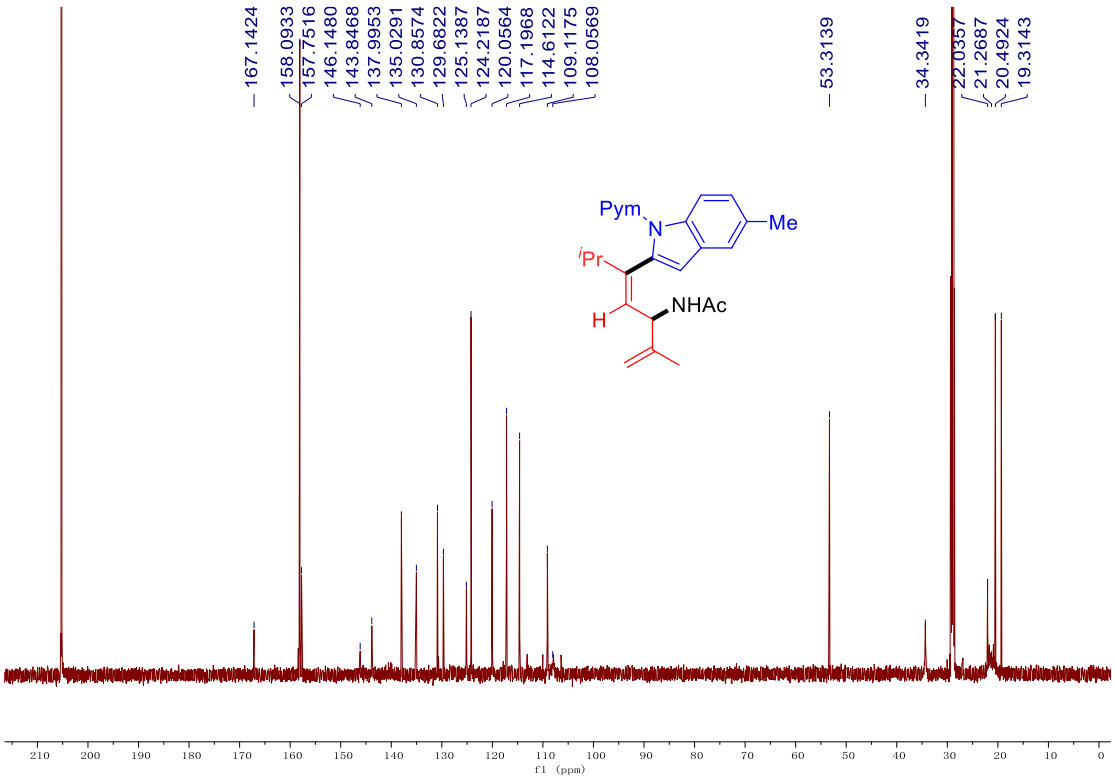
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **37.**



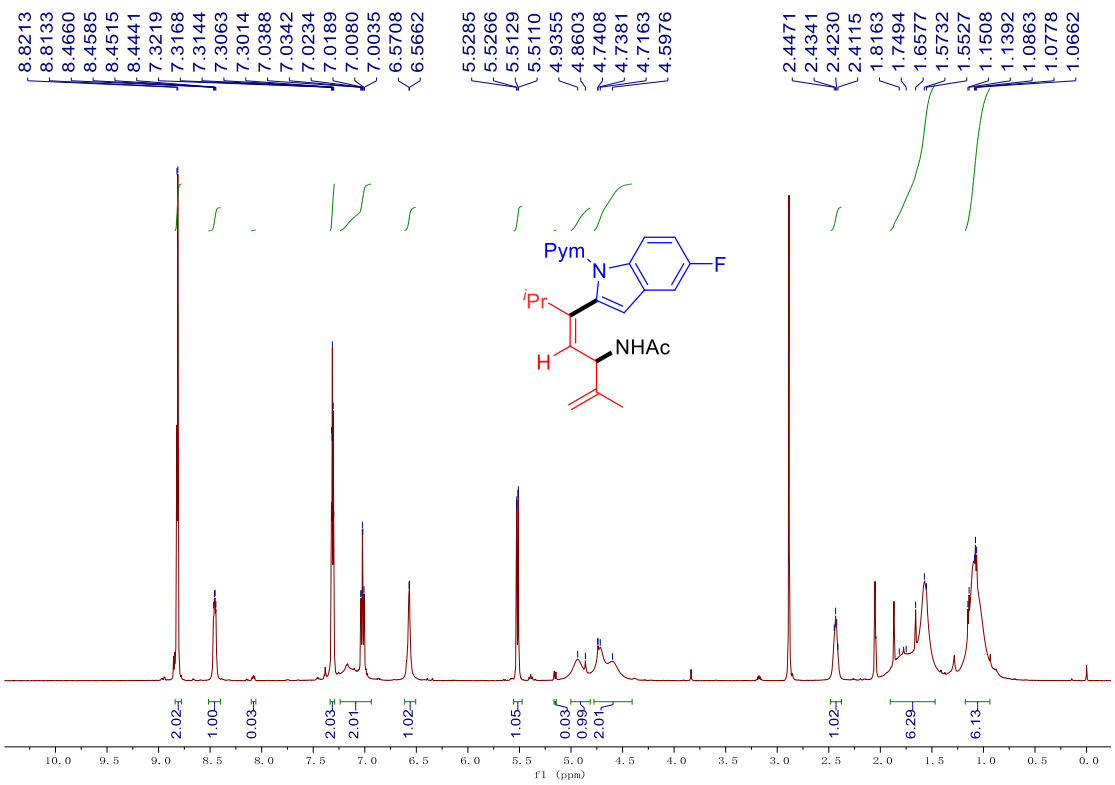
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **37.**



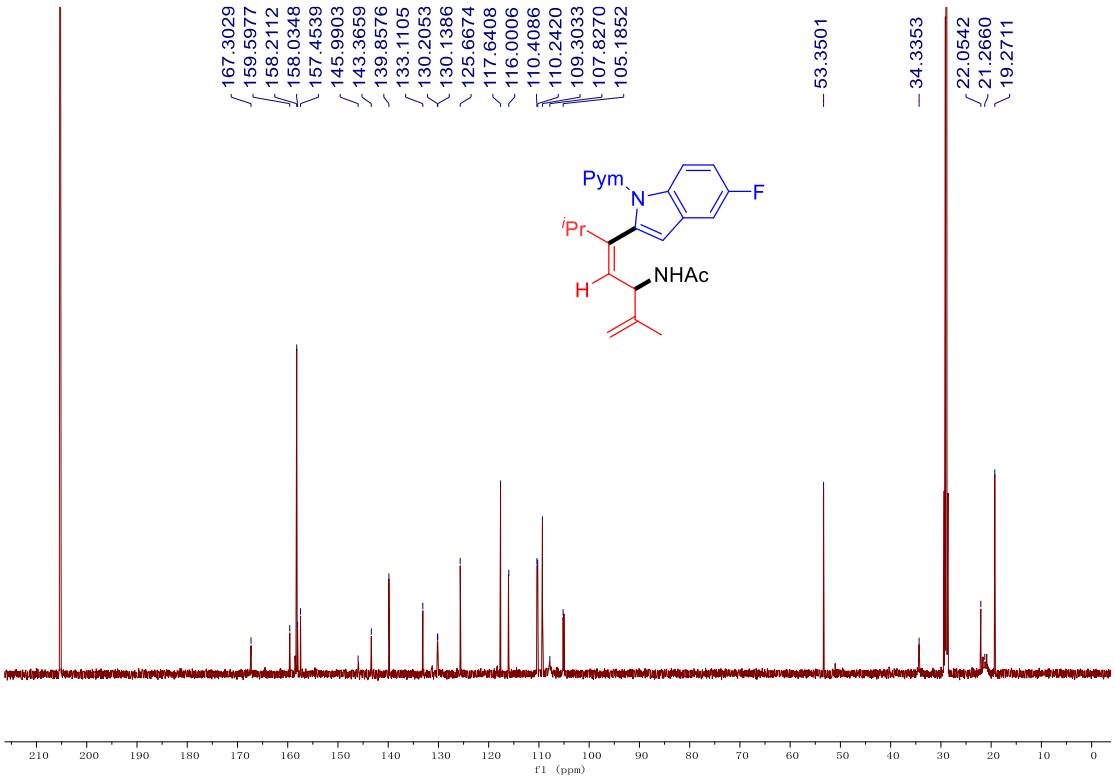
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **38.**



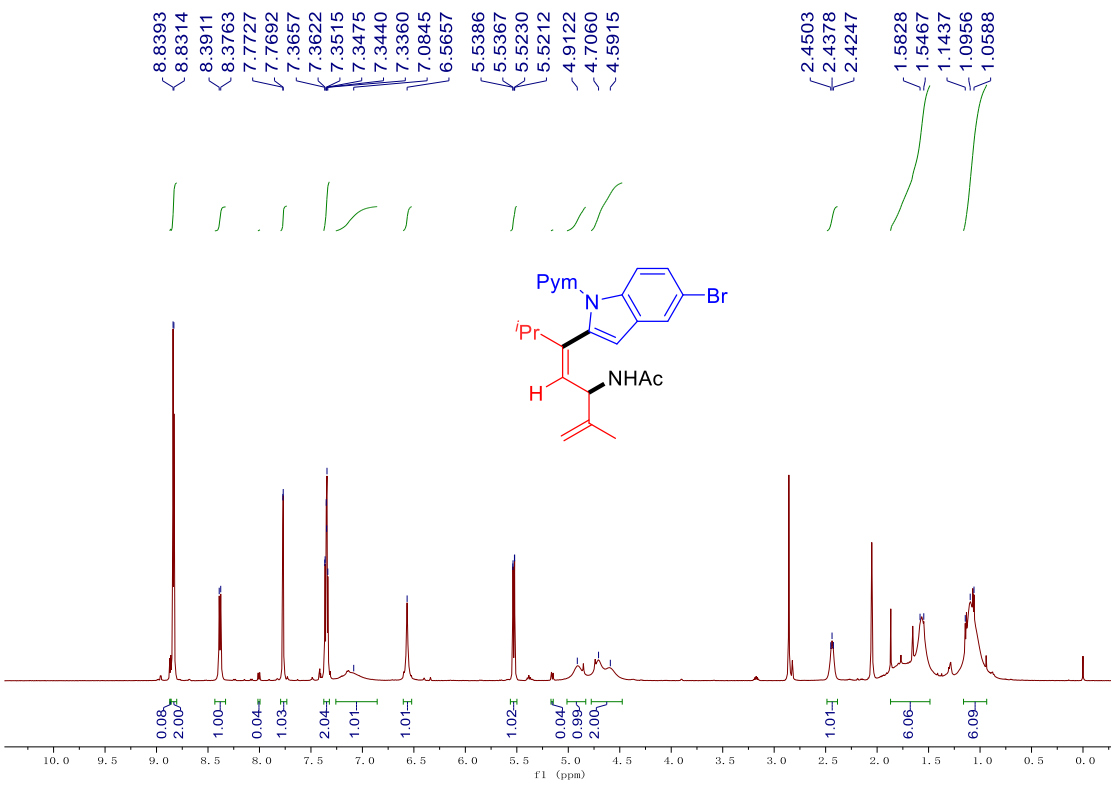
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **38.**



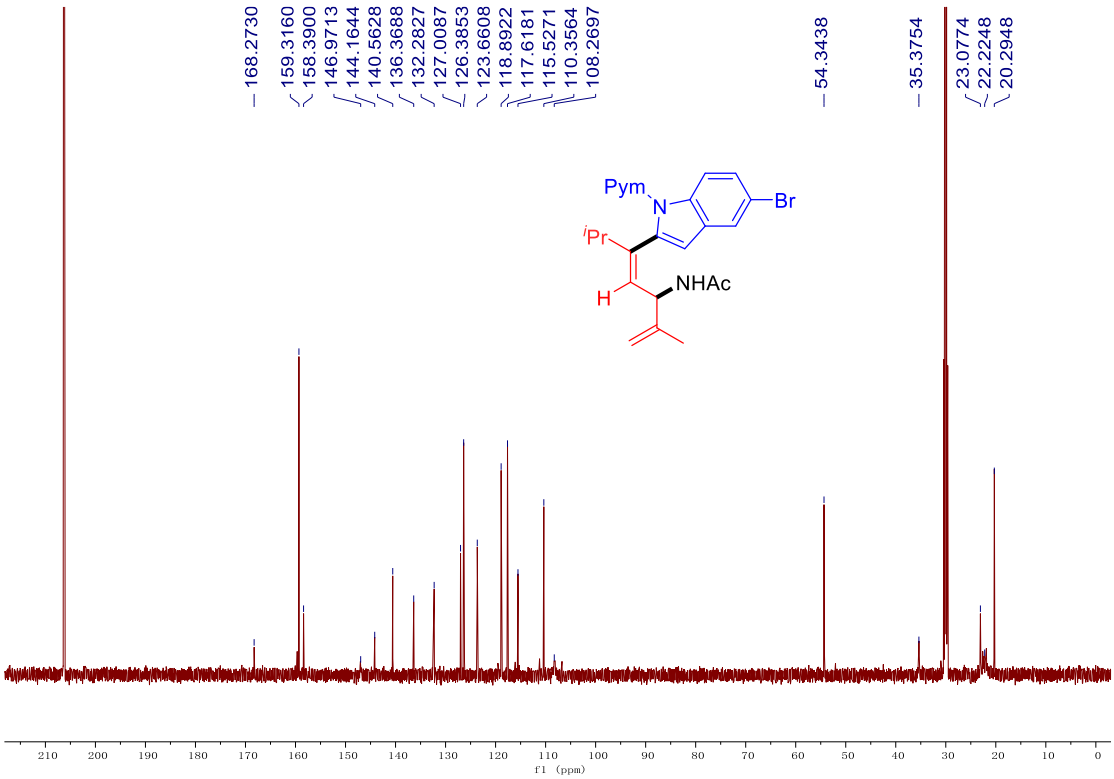
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **39.**



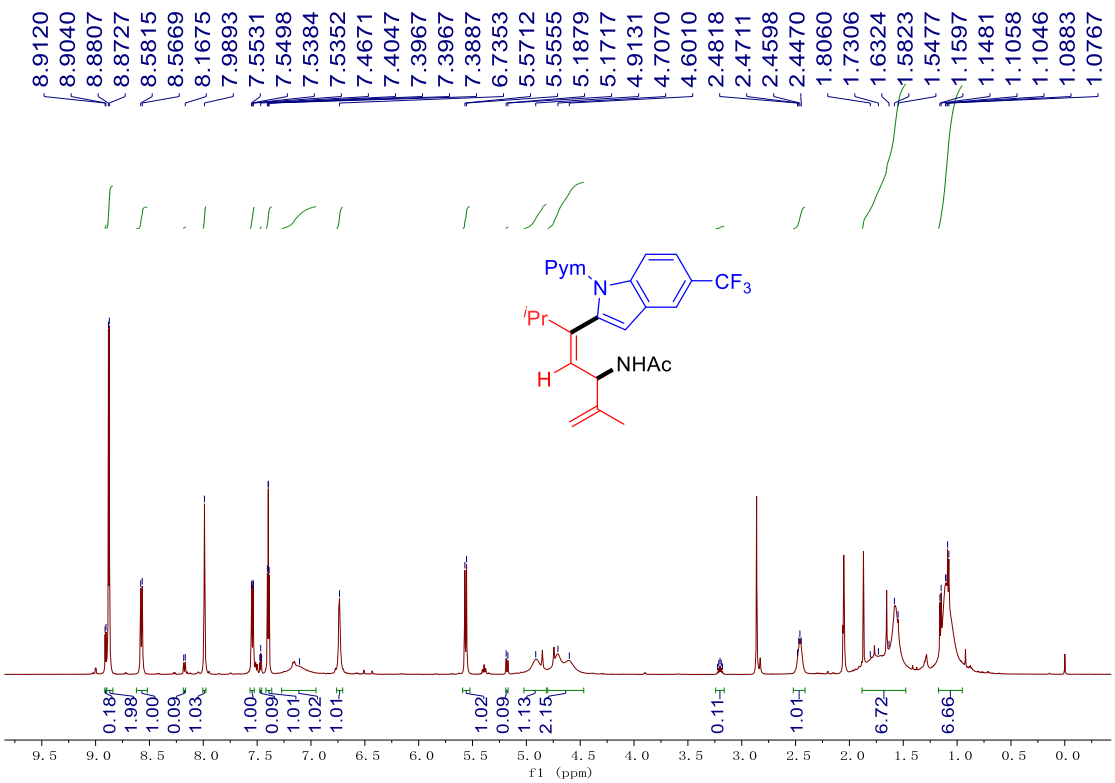
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **39.**



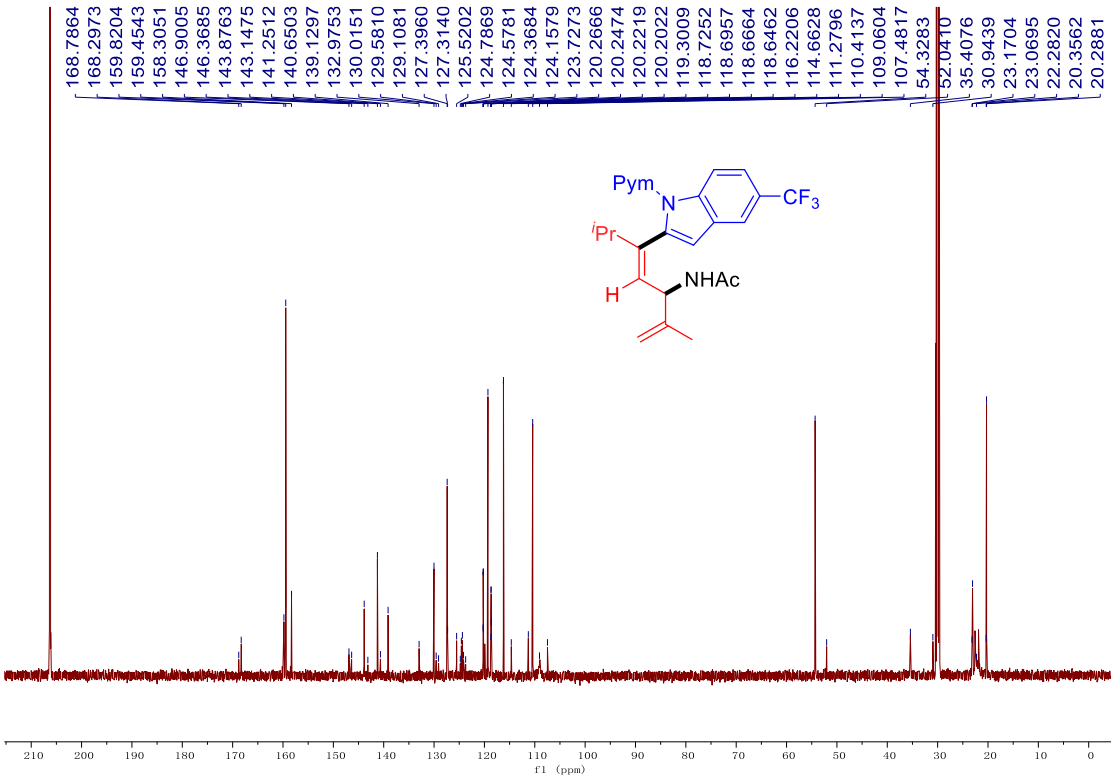
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **40.**



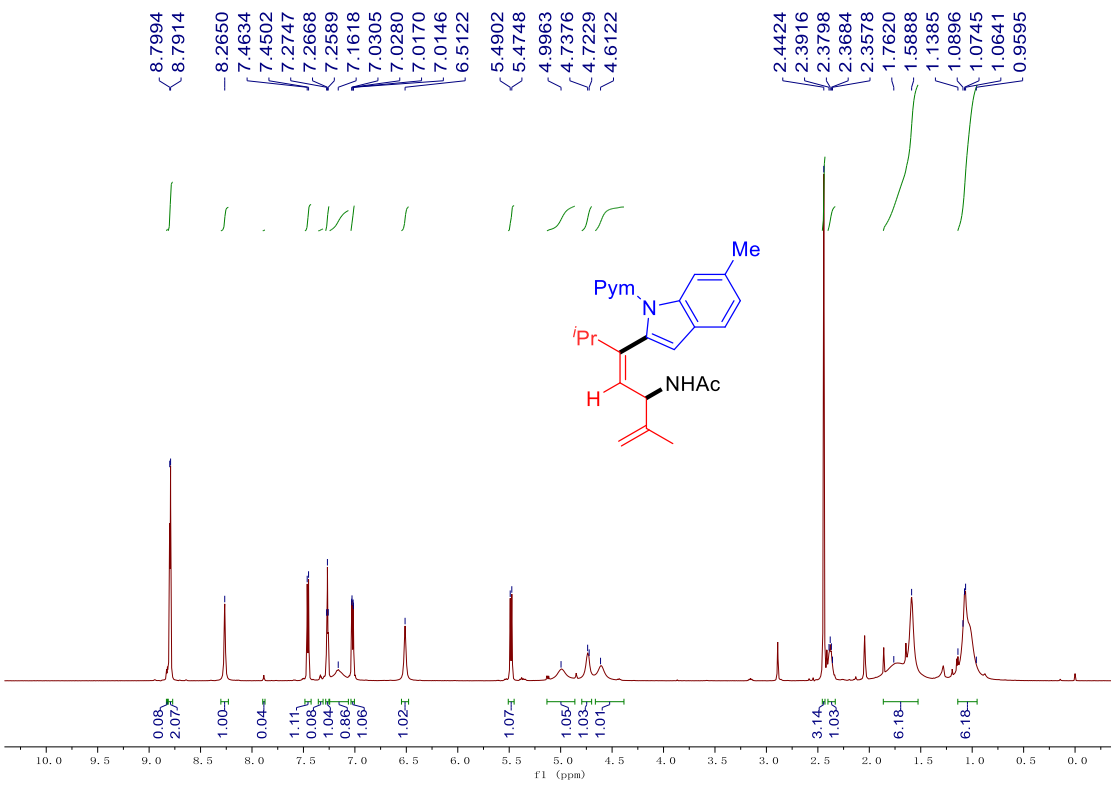
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **40.**



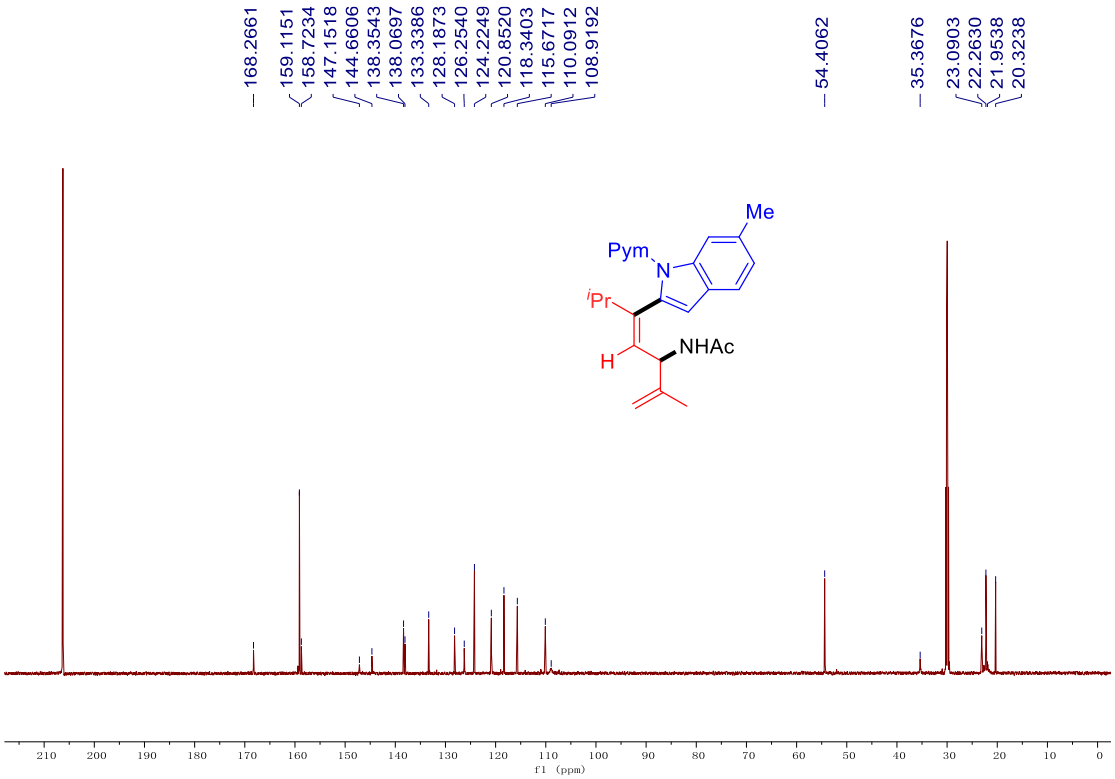
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **41.**



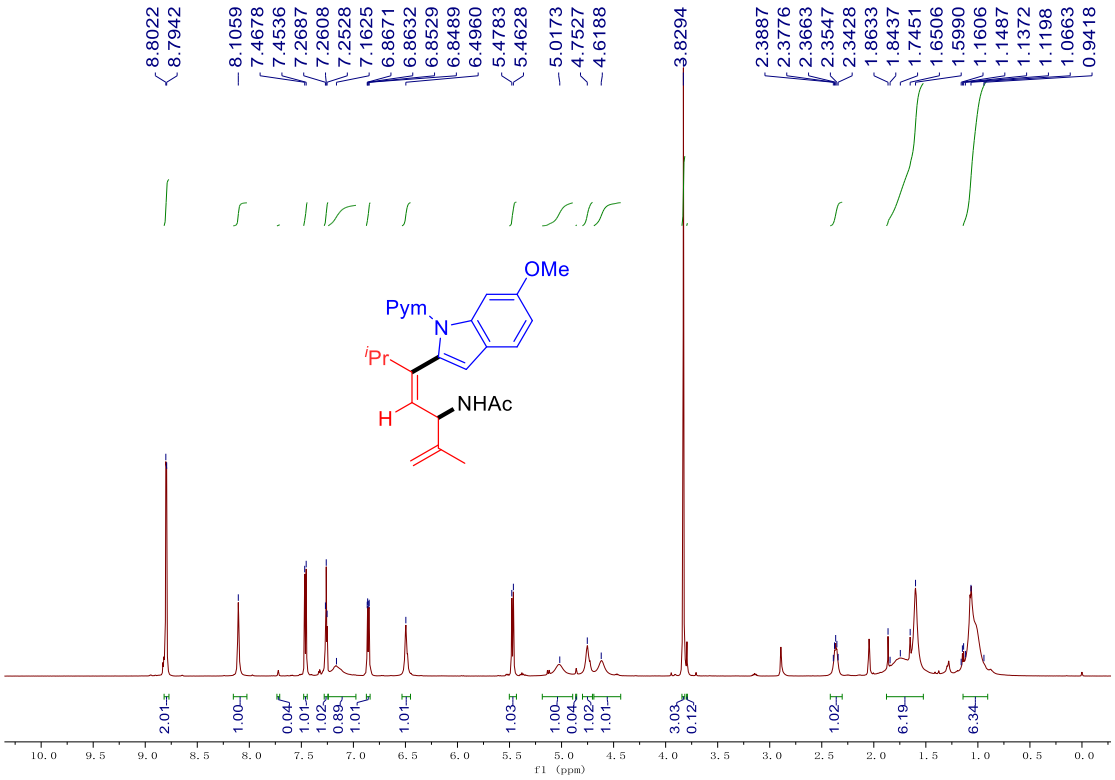
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **41.**



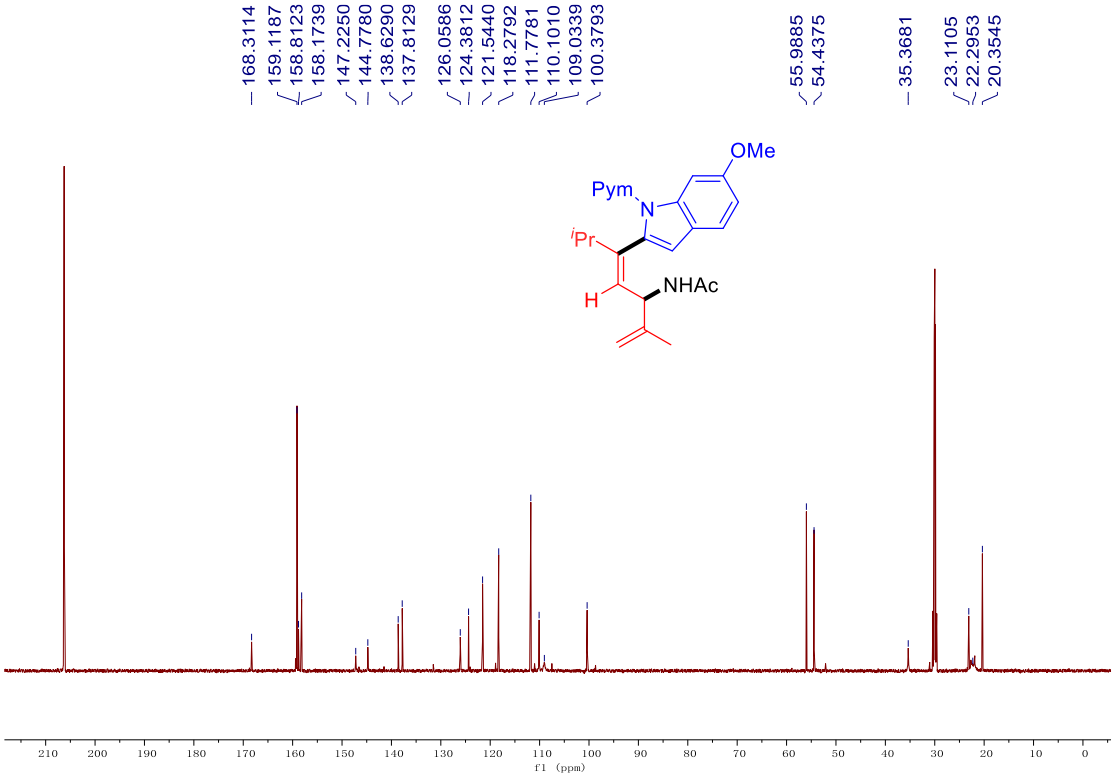
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **42.**



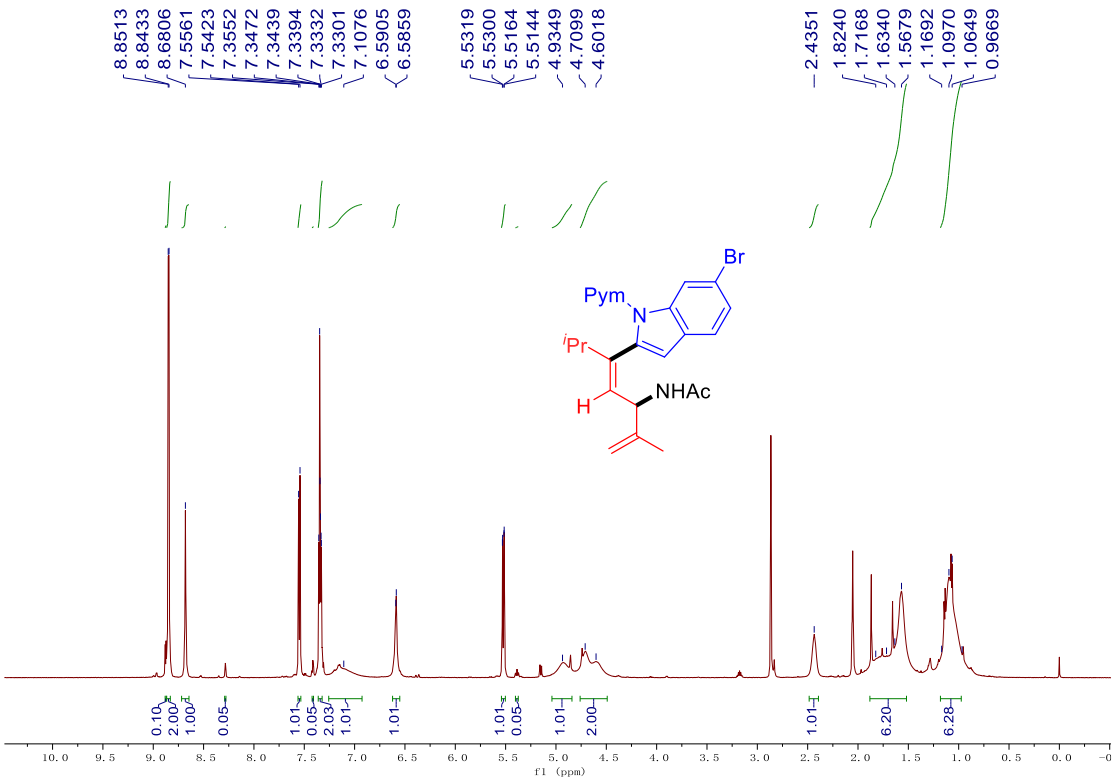
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **42.**



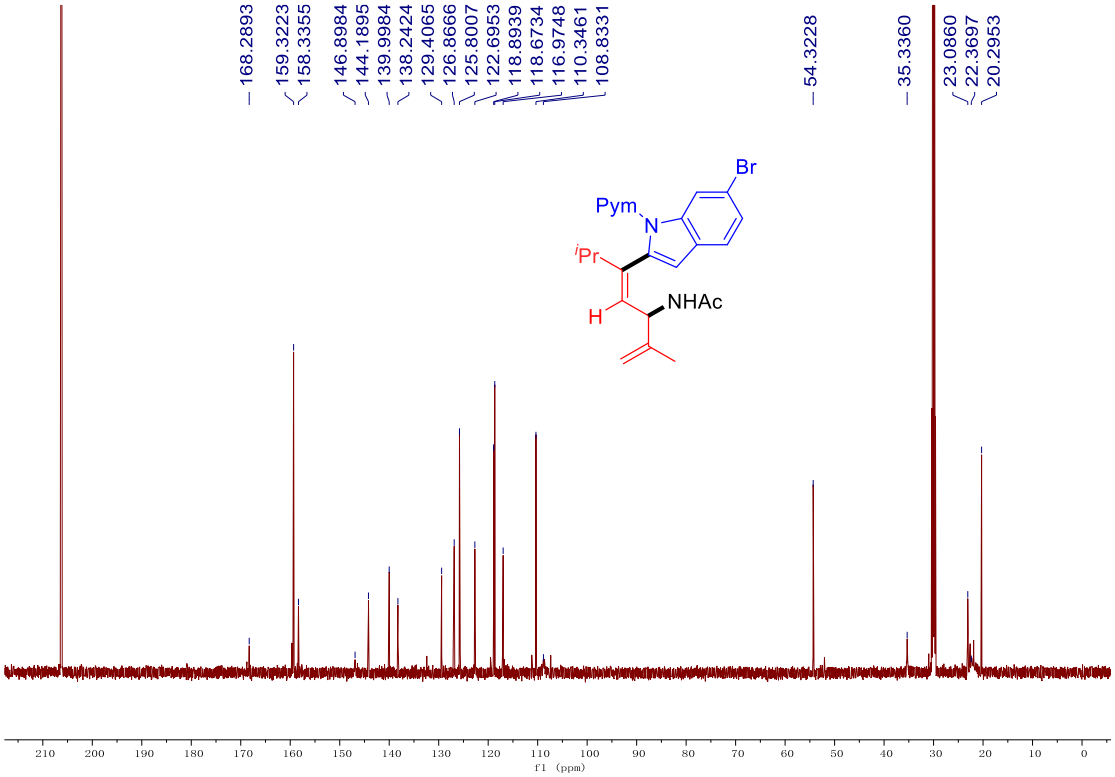
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **43.**



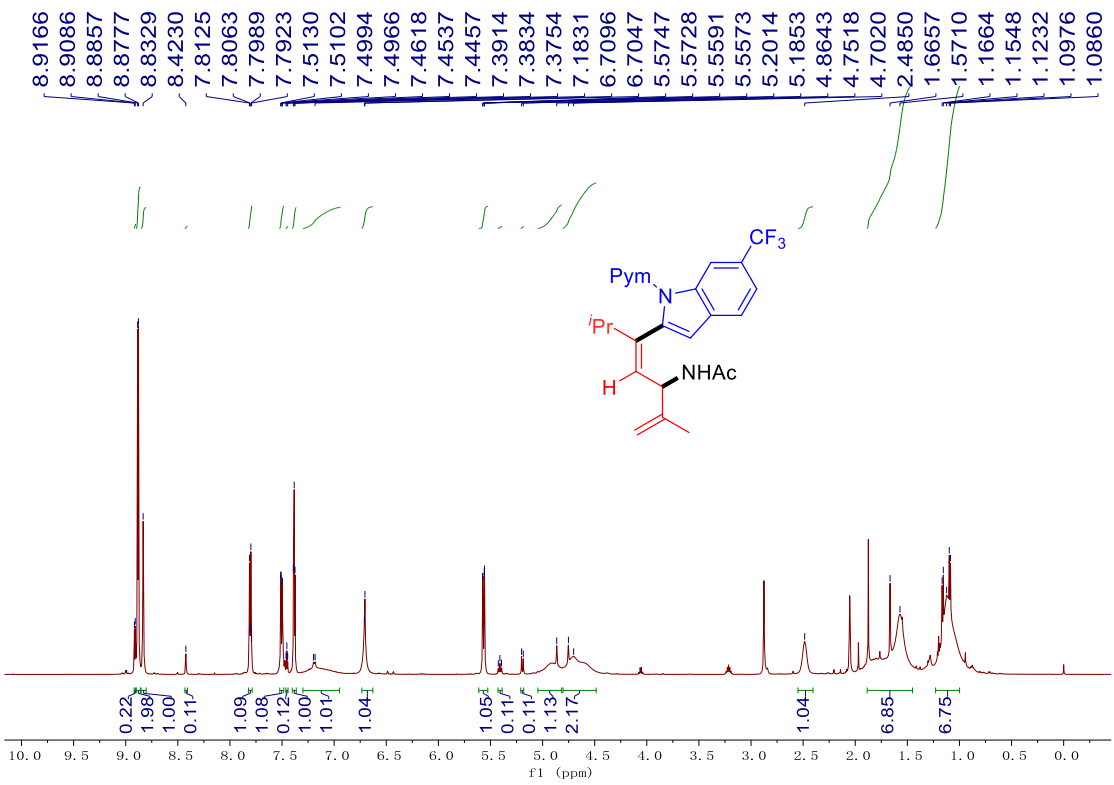
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **43.**



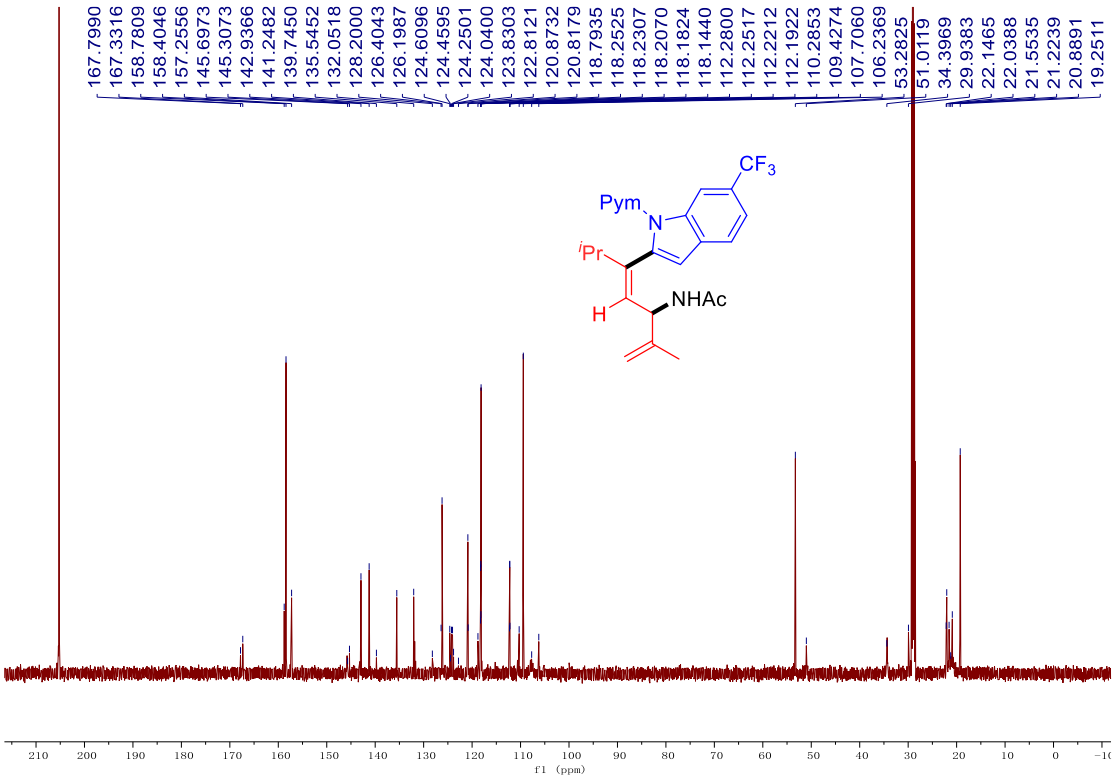
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **44.**



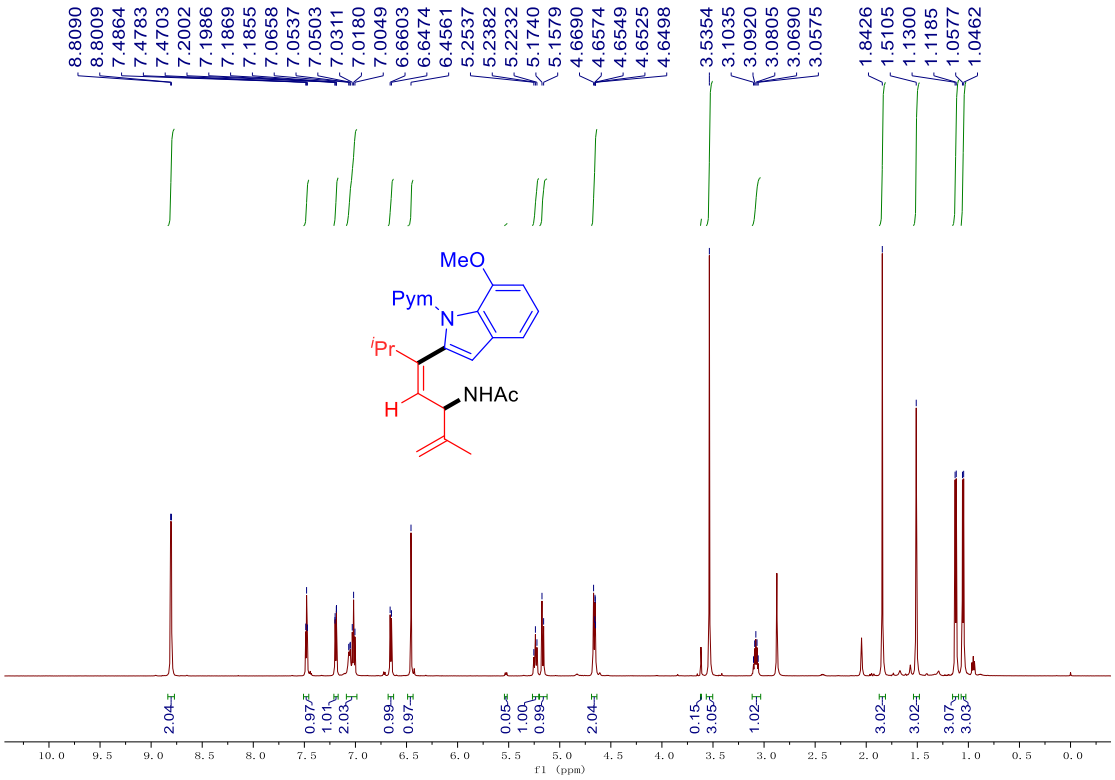
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **44.**



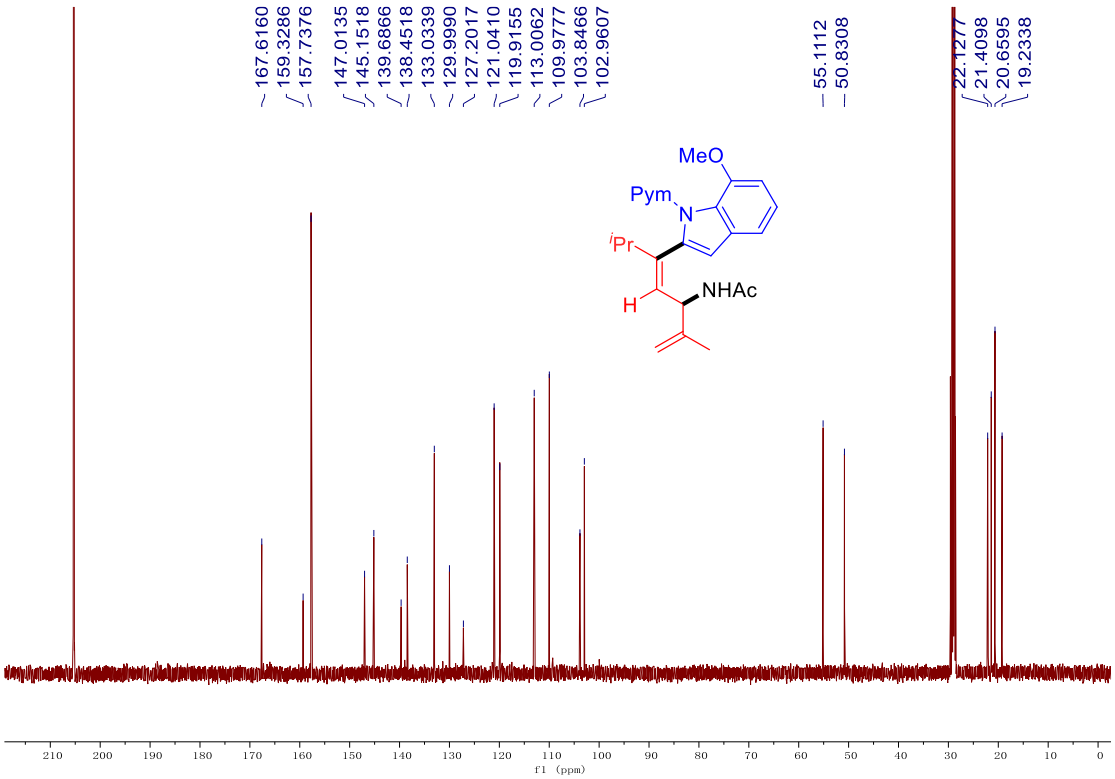
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **45.**



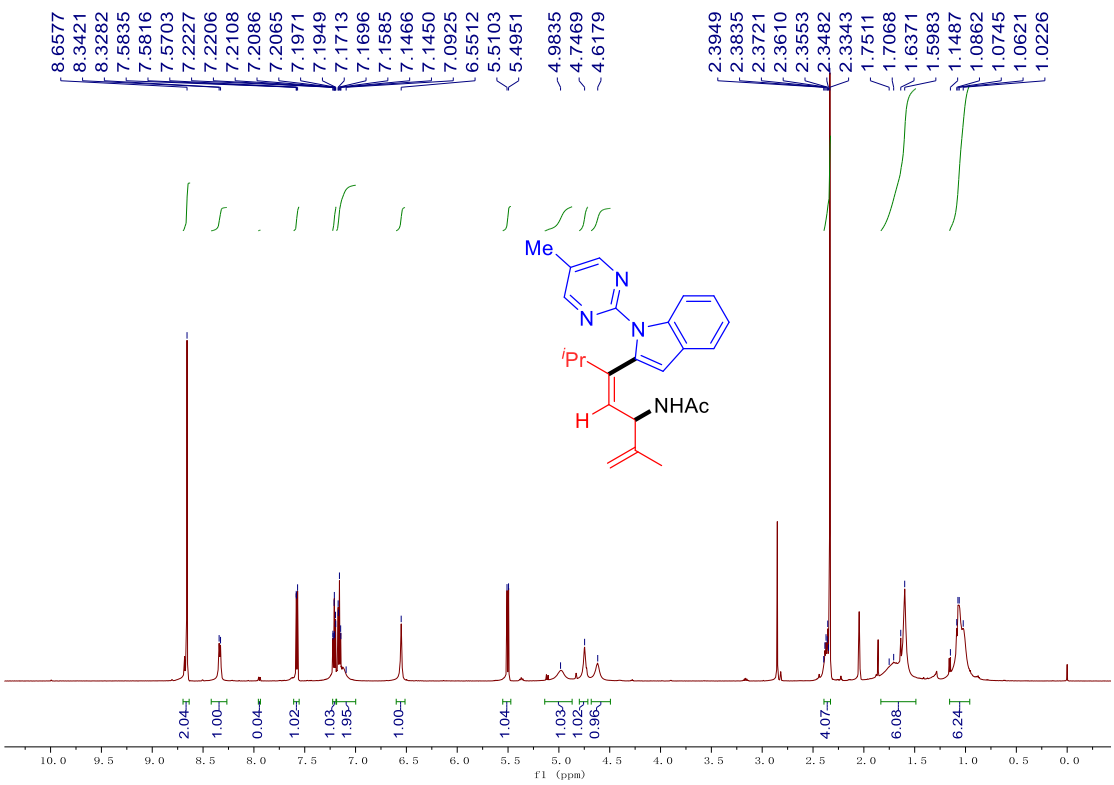
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **45.**



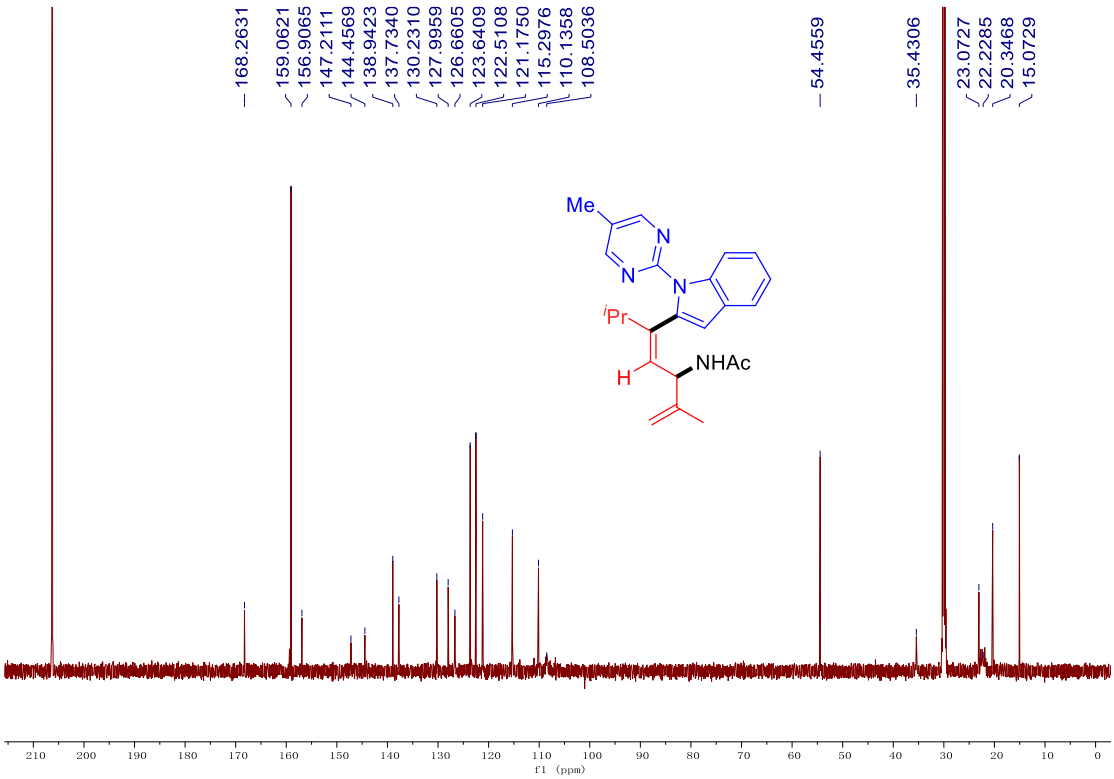
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **46.**



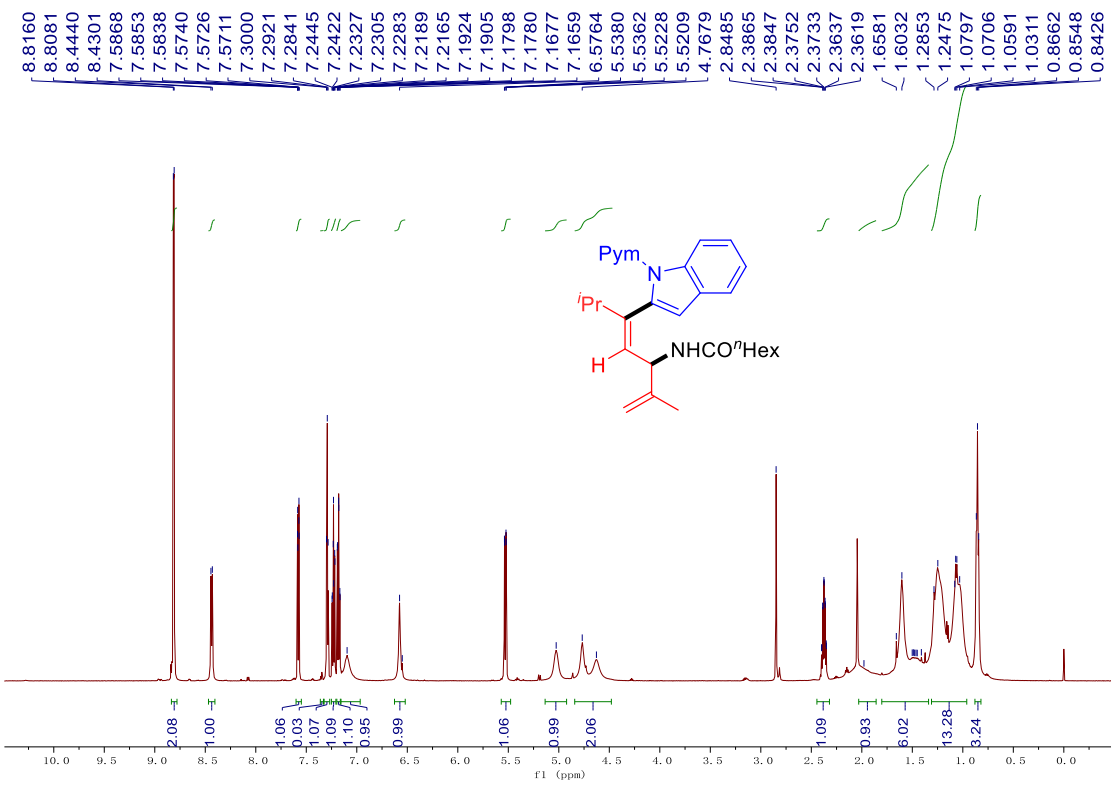
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **46.**



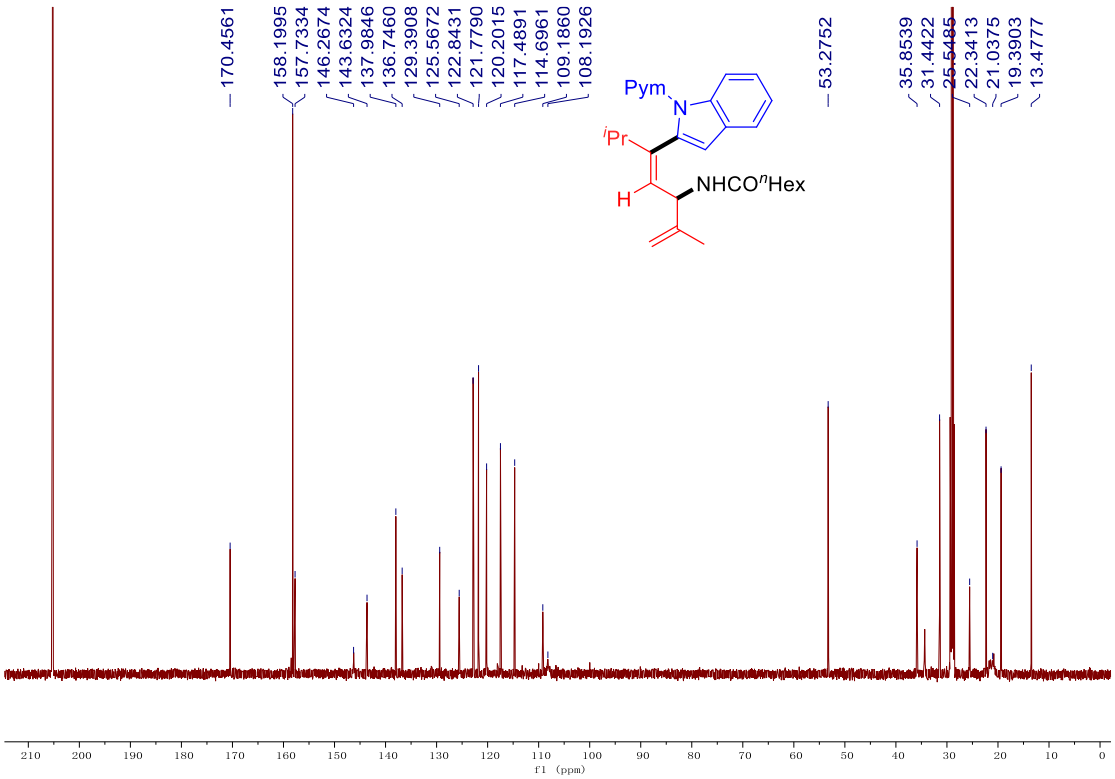
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **47.**



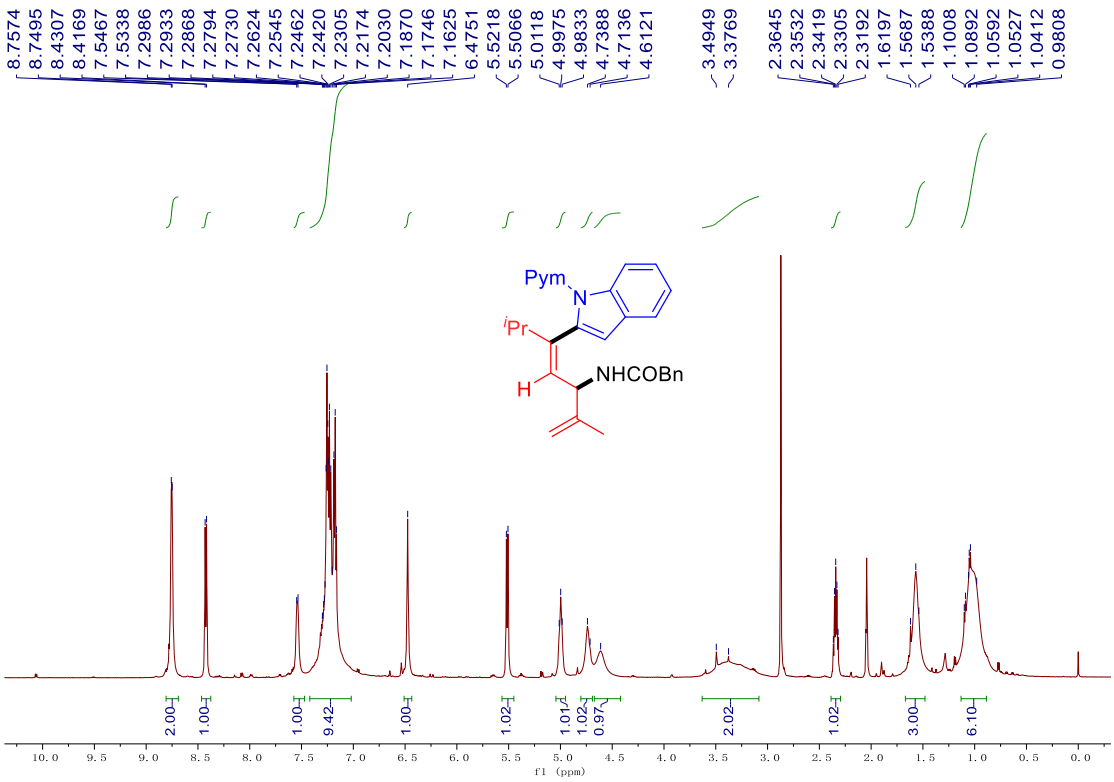
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **47.**



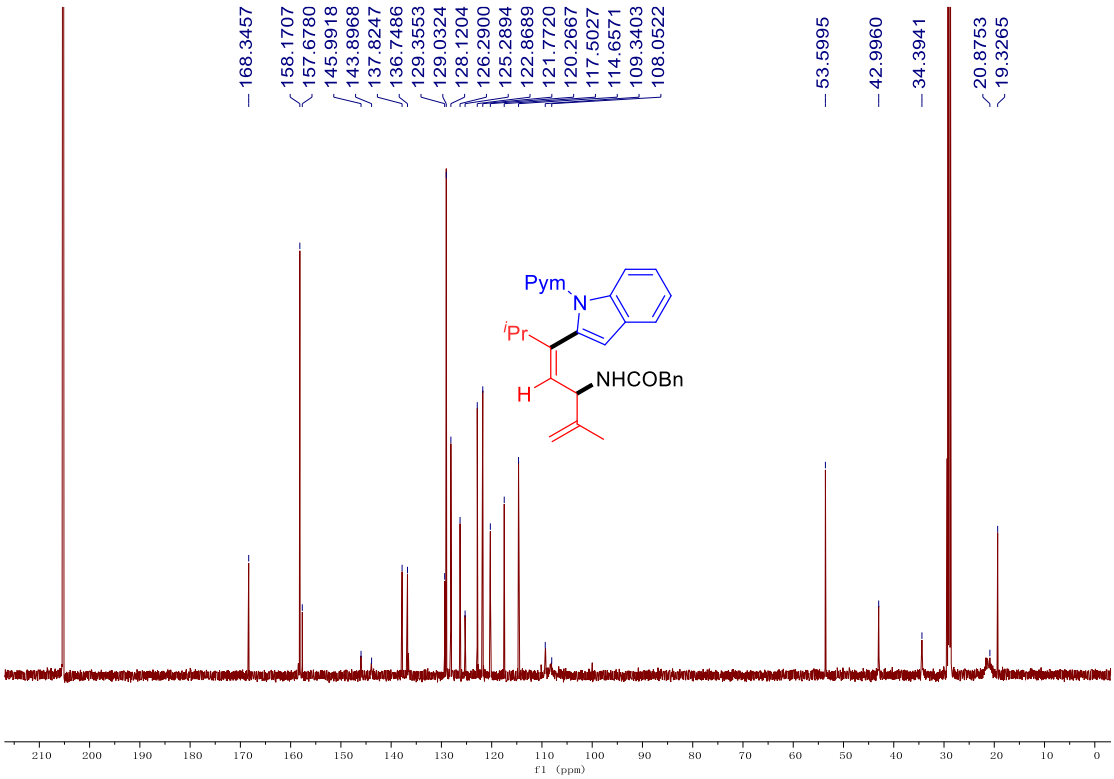
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **48.**



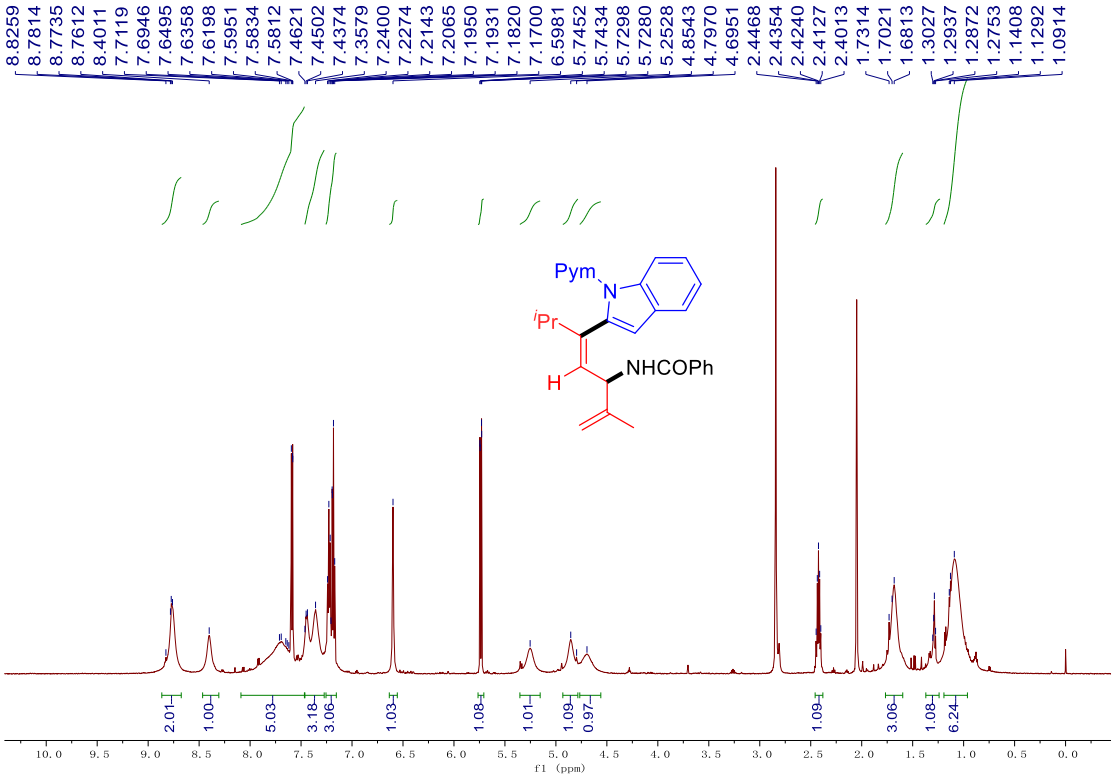
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **48.**



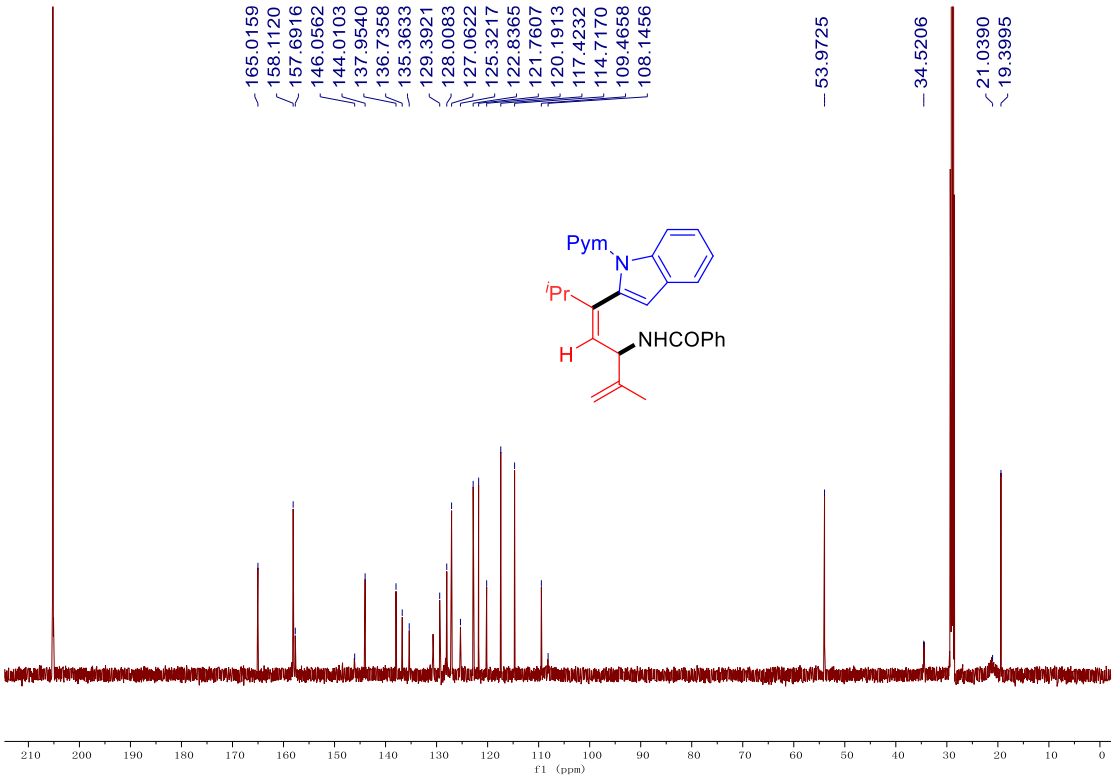
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **49.**



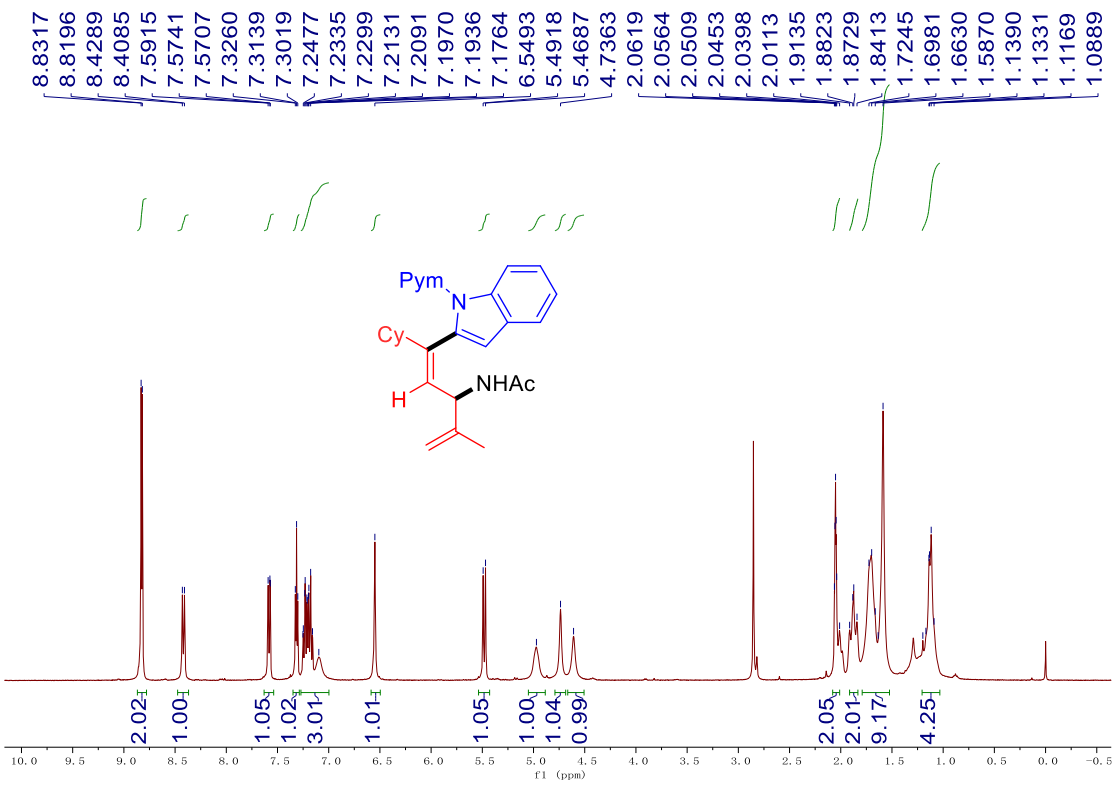
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **49.**



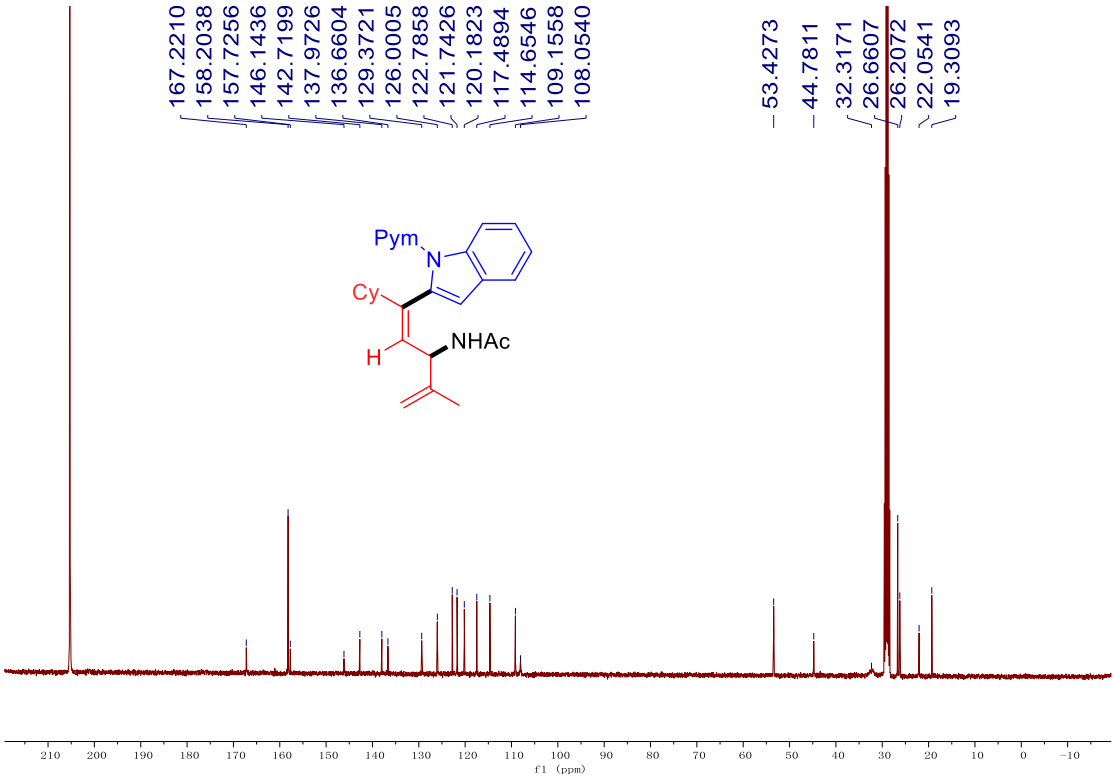
^{1}H NMR (600 MHz, CD_3COCD_3) spectrum of **50.**



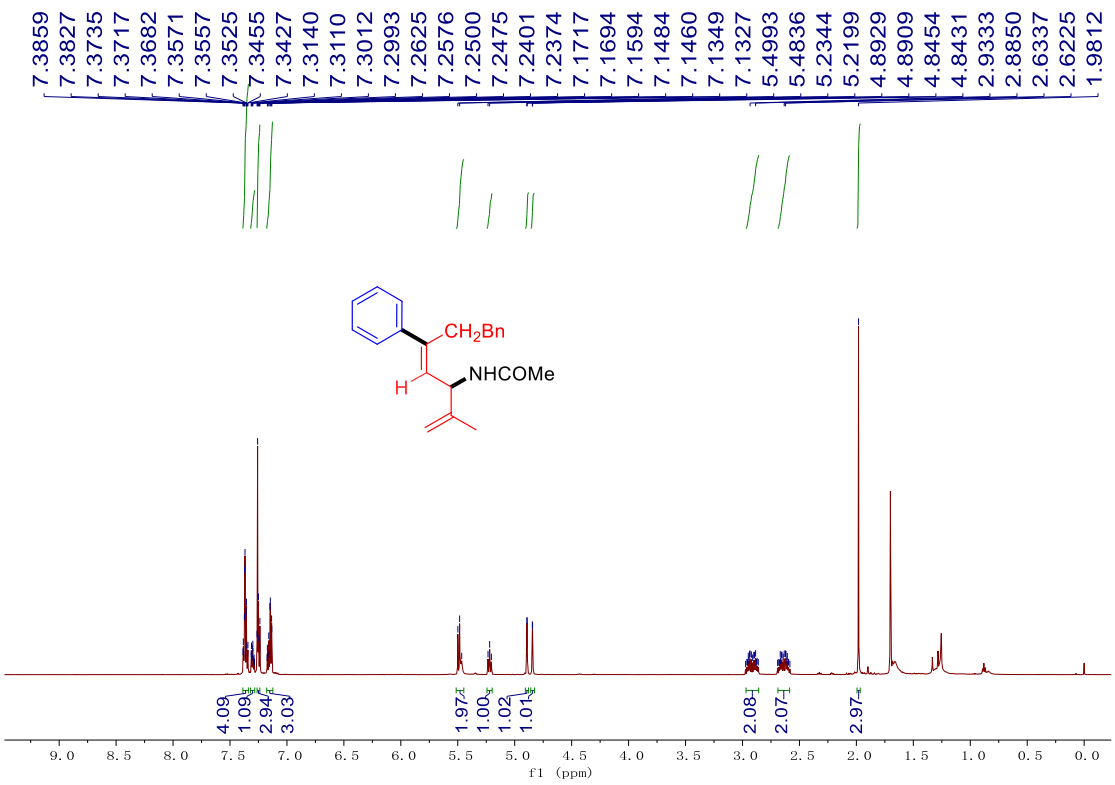
^{13}C NMR (151 MHz, CD_3COCD_3) spectrum of **50.**



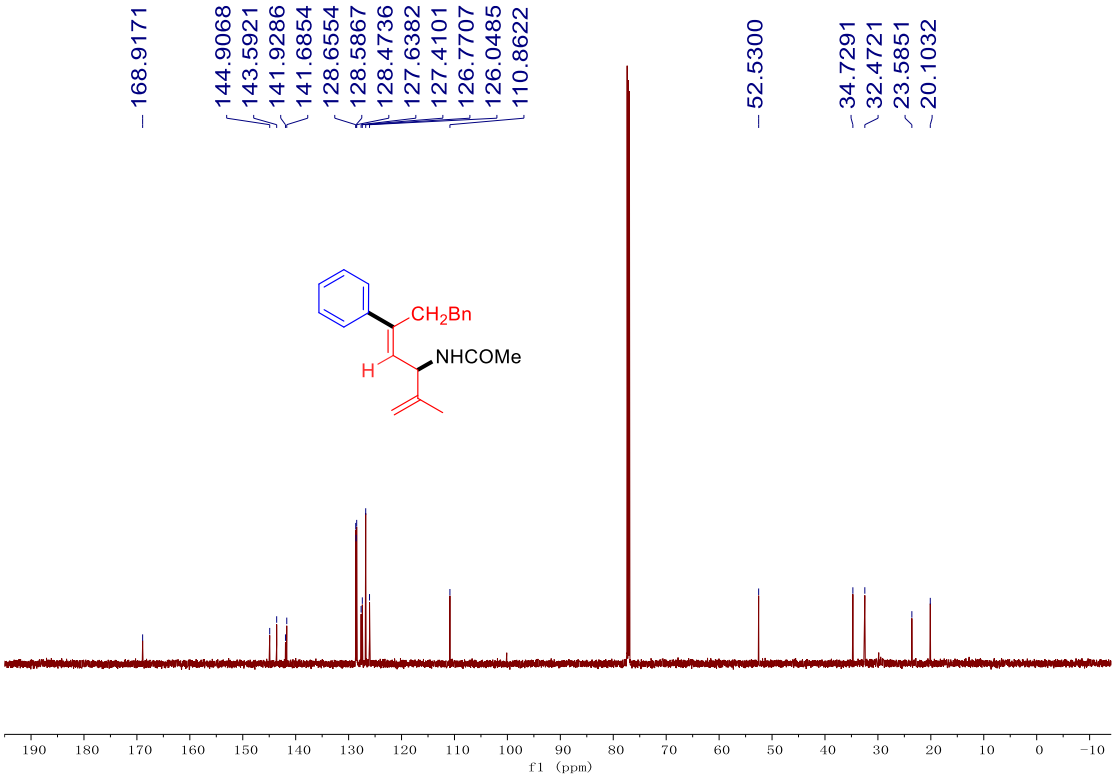
^{1}H NMR (400 MHz, CD_3COCD_3) spectrum of **51.**



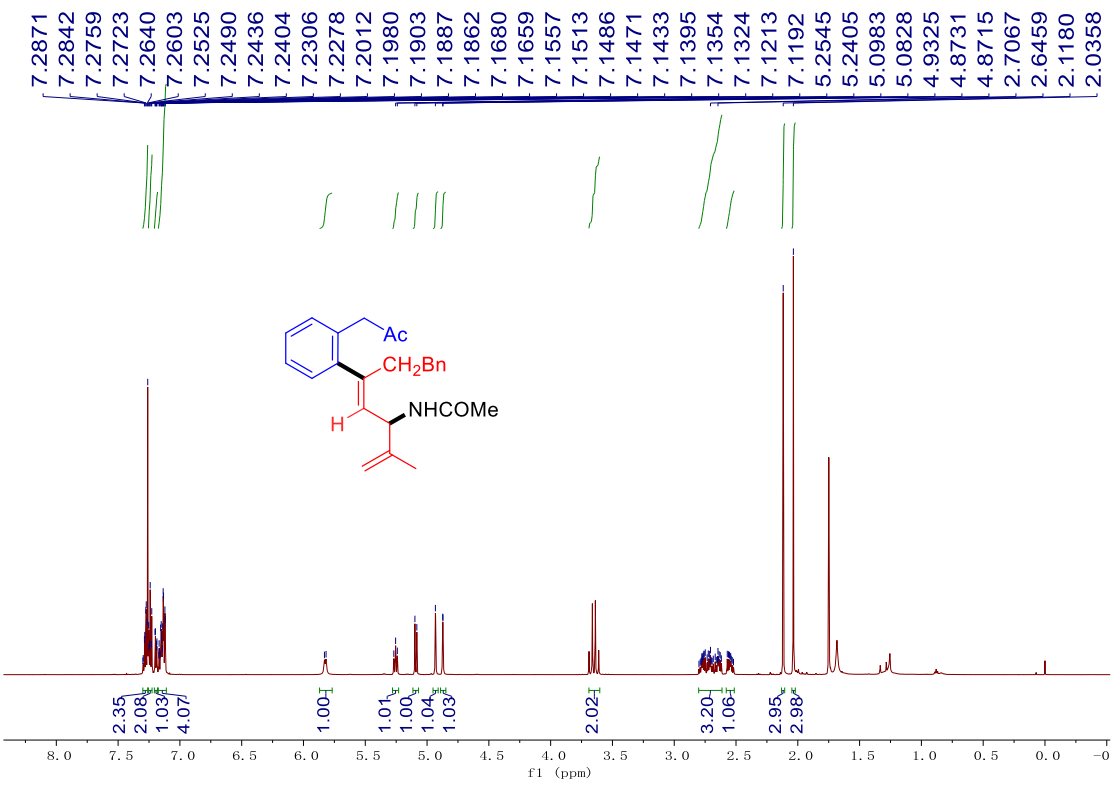
^{13}C NMR (101 MHz, CD_3COCD_3) spectrum of **51.**



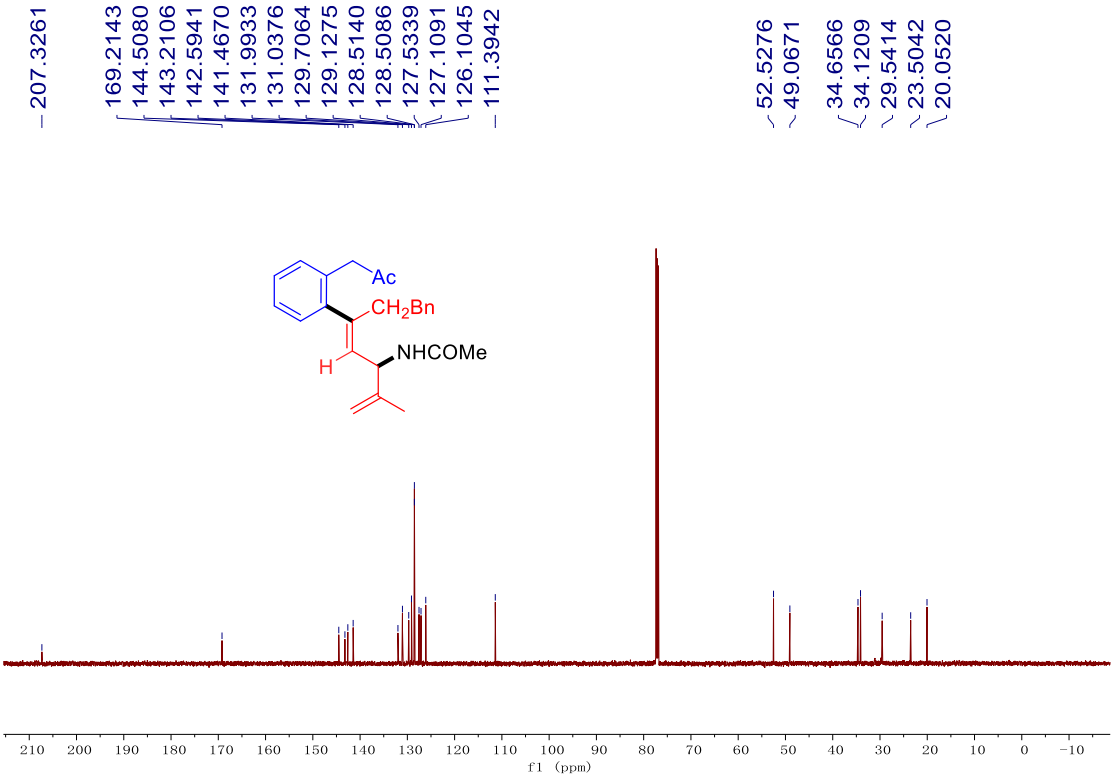
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **52.**



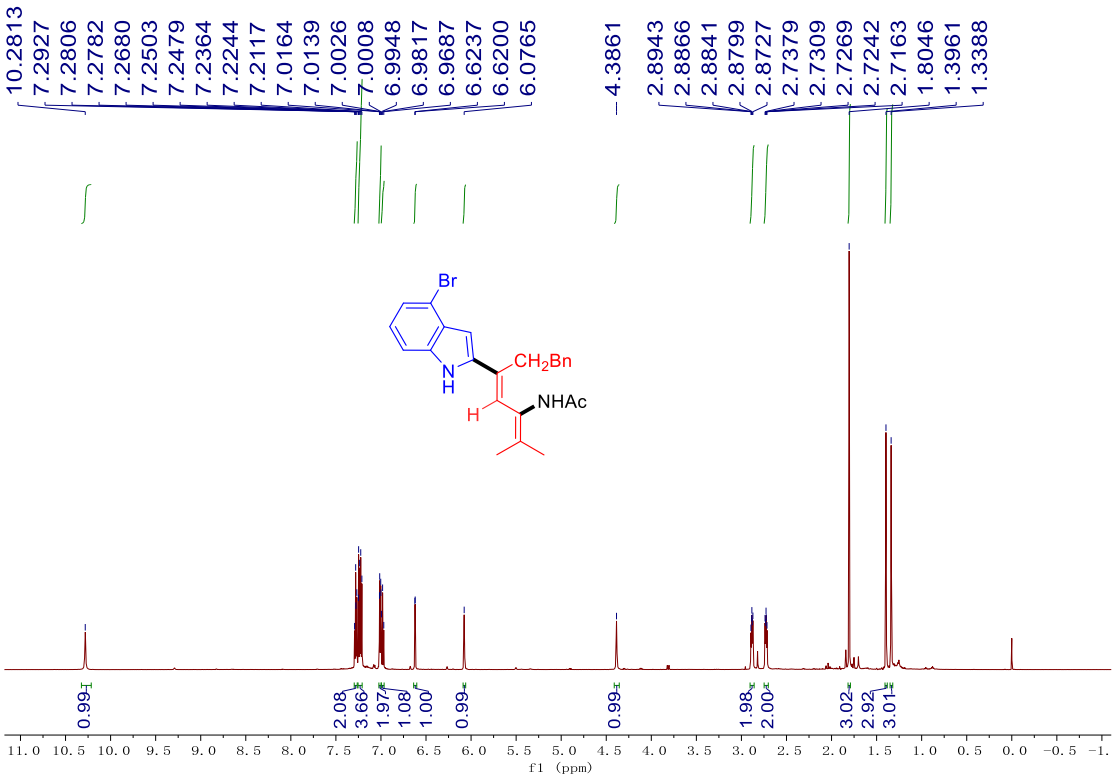
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **52.**



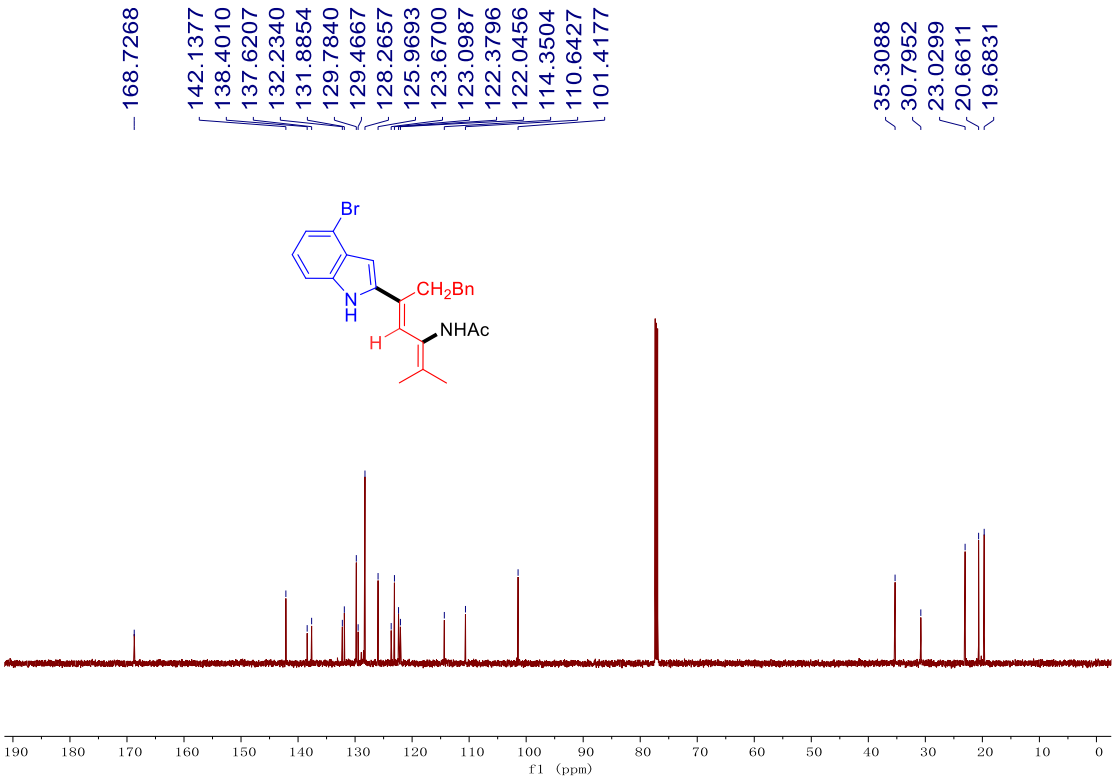
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **53.**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **53.**



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **54.**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **54.**