Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Visible-light-induced iodine anion catalyzed decarboxylative/deaminative C-H alkylation of enamides

Jia-Xin Wang,† Ya-Ting Wang,† Hao Zhang and Ming-Chen Fu*

Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Urban Pollutant Conversion, Anhui Province Key Laboratory of Biomass Clean Energy, iChEM, University of Science and Technology of China, Hefei 230026, China

† Jia-Xin Wang and Ya-Ting Wang contributed equally to this work.

Email: fumingchen@ustc.edu.cn

Table of Contents

1. General Information

A. Materials:

All reactions were conducted in oven-dried Schlenk tubes under argon atmosphere (purity ≥ 99.99%) unless otherwise mentioned. Commercial reagents were purchased from Energy Chemical, Adamas-beta, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. The LED lamps were purchased from Kessil (PR160-390 nm, 427 nm, 440 nm, 456 nm, 467 nm, 520 nm). The Photo Reaction Setup was purchased from Anhui kemi machinery technology Co., Ltd.

The starting materials of enamides[1-3], redox-active esters (NHPI-esters)[4,5] and Katritzky salts[6]) were readily prepared according to the related literatures.

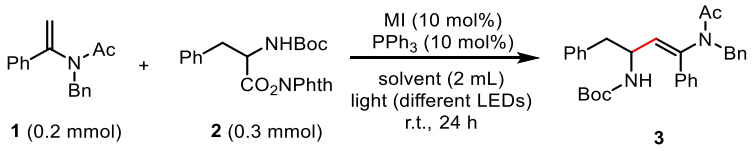
Figure S1. The Photo Reaction Setup and Blue LED lamps

B. Analytical Methods:

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. ^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. UV-Vis spectra was measured by UV-3600. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Investigation of the Key Reaction Parameters

Table S1: Key reaction parameters for decarboxylative C-H alkylation of enamides

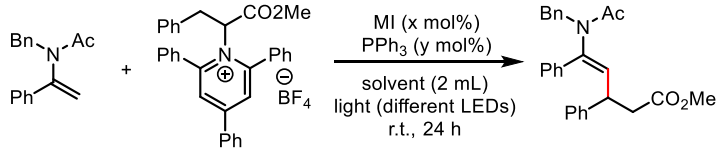


entry	MI	solvent	light (nm)	**3** (%)
1	NaI	acetone	456	88
2	NaI	DMF	456	42
3	NaI	ACETONE	456	78
4	NaI	CH_3CN	456	16
5	NaI	THF	456	78
6	NaI	dioxane	456	0
7	NaI	$PhCF_3$	456	0
8	NaI	EtOAc	456	72
9	NaI	CH_2Cl_2	456	0
10	$^nBu_4NI$	acetone	456	84
11	LiI	acetone	456	82
12	KI	acetone	456	84
13	RbI	acetone	456	80
14	CaI_2	acetone	456	0
15	THAI	acetone	456	74
16	ZnI_2	acetone	456	0
17	CuI	acetone	456	0
18	NaCl	acetone	456	0
19	NaBr	acetone	456	0
20[a]	NaI	acetone	456	78
21[b]	NaI	acetone	456	83
22[c]	NaI	acetone	456	0
23[d]	NaI	acetone	456	0
24[e]	NaI	acetone	456	0
25[f]	NaI	acetone	456	0
26	NaI	acetone	520	0
27	NaI	acetone	467	80
28	NaI	acetone	440	78
29	NaI	acetone	427	76
30	NaI	acetone	390	76

Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.3 mmol), MI (10 mol%), PPh_3 (10 mol%), solvent (2 mL), 24 h, r.t., blue LEDs. Isolated yield.

[a]reaction time: 15h. [b]reaction time: 20h. [c]no NaI. [d]no PPh_3. [e]no NaI, no PPh_3. [f]no light, 50 °C.

Table S2: Key reaction parameters for deaminative C-H alkylation of enamides



1 (0.2 mmol) **35a** (0.3 mmol) **35**

entry	MI	PPh_3	solvent	light (nm)	**35** (%)[a]
1	LiI (20 mol%)	PPh_3 (20 mol%)	acetone	456	36
2	LiI (20 mol%)	PPh_3 (20 mol%)	acetone	427	46
3	NaI (20 mol%)	PPh_3 (20 mol%)	DMF	427	66
4	LiI (20 mol%)	PPh_3 (20 mol%)	DMF	427	72
5	LiI (20 mol%)	0	DMF	427	76
6	LiI (10 mol%)	0	DMF	427	80 (76[b])
7	LiI(10 mol%)	0	DMA	427	68
8	NaI(10 mol%)	0	DMF	427	72
9	--	0	DMF	427	25

Reaction conditions: **1** (0.2 mmol, 1 equiv), **35a** (0.3 mmol), MI (x mol%), PPh_3 (y mol%), solvent (2.0 mL), 24 h, r.t., light (different LEDs). [a]The yield was determined by ^{1}H-NMR using diphenylmethane as the internal standard. [b]Isolated yield.

3. Experimental Procedures and Characterization Datas

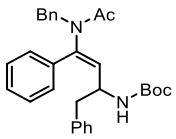
3.1 General Procedure A: Decarboxylative C-H alkylation of enamides

Enamides (1.0 eq., 0.2 mmol) (if solid), redox-active esters (1.5 eq., 0.3 mmol) (if solid), NaI (10 mol%), PPh_3 (10 mol%) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three cycles). To these solids, enamides (1.0 eq., 0.2 mmol) (if liquid), redox-active esters (1.5 eq., 0.3 mmol) (if liquid), acetone (2.0 mL) were added under argon atmosphere. The reaction mixture was stirred under irradiation with blue LEDs (Kessil, PR160-456 nm), maintained at approximately room temperature (28 ± 2 °C). After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The product was purified *via* flash column chromatography on silica gel. (Eluent: petroleum ether/ethyl acetate).

General Procedure B: Deaminative C-H alkylation of enamides

Enamides (1.0 eq., 0.2 mmol) (if solid), Katritzky salts (1.5 eq., 0.3 mmol), LiI (10 mol%) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three cycles). To these solids, enamides (1.0 eq., 0.2 mmol) (if liquid) and DMF (2.0 mL) were added under argon atmosphere. The reaction mixture was stirred under irradiation with blue LEDs (Kessil, PR160-427 nm), maintained at approximately room temperature (28 ± 2 °C). After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The product was purified *via* flash column chromatography on silica gel. (Eluent: petroleum ether/ethyl acetate).

3.2 Characterization data for the products

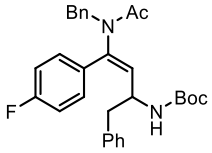


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-1,4-diphenylbut-3-en-2-yl)carbamate (3)**: Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 88% yield (82.7 mg) as viscous liquid. (Eluent: petroleum

ether/ethyl acetate = 10/1 to 2/1). The compound data was in agreement with the literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 6H), 7.21 – 7.16 (m, 5H), 7.10 (dd, *J* = 6.4, 2.9 Hz, 2H), 6.85 – 6.79 (m, 2H), 5.08 (d, *J* = 10.1 Hz, 1H), 4.80 (d, *J* = 14.5 Hz, 1H), 4.43 (br, 2H), 4.05 (br, 1H), 2.90 – 2.69 (m, 2H), 2.09 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 154.6, 140.3, 137.6, 136.4, 134.3, 131.3, 129.6, 129.1, 129.0, 128.7, 128.6, 128.4, 127.3, 126.8, 79.4, 49.7, 48.7, 41.4, 28.3, 22.1. (one carbon signal was overlapped)



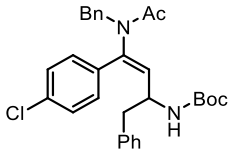
***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(4-fluorophenyl)-1-phenylbut-3-en-2-yl)carbamate (4):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 81% yield (79.1 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.22 – 7.12 (m, 5H), 7.04 – 6.97 (m, 4H), 6.84 – 6.79 (m, J = 5.8 Hz, 2H), 5.08 (d, J = 10.0 Hz, 1H), 4.78 (d, J = 14.4 Hz, 1H), 4.60 – 4.35 (m, 2H), 4.02 (d, J = 13.5 Hz, 1H), 2.85 (dd, J = 13.3, 4.6 Hz, 1H), 2.68 (dd, J = 13.4, 7.6 Hz, 3H), 2.07 (s, 1H), 1.36 (s, 9H).

13C NMR (126 MHz, CDCl3) δ 170.68, 162.97 (d, J = 249.4 Hz), 154.54, 139.47, 137.40, 136.27, 131.33, 130.48 (d, J = 8.3 Hz), 130.32 (d, J = 2.8 Hz), 129.56, 128.93, 128.61, 128.42, 127.39, 126.85, 115.75 (d, J = 21.6 Hz), 79.52, 49.84, 48.66, 41.38, 28.27, 22.06.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.71 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{34}FN_2O_3^+$ 489.2548; Found 489.2552.



***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(4-chlorophenyl)-1-phenylbut-3-en-2-yl)carbamate (5):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 82% yield (82.7 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 7.22 – 7.13 (m, 5H), 6.93 (d, J =

8.3 Hz, 2H), 6.81 (d, J = 6.1 Hz, 2H), 5.09 (d, J = 9.5 Hz, 1H), 4.80 (d, J = 13.2 Hz, 1H), 4.42 (s, 2H), 4.00 (d, J = 13.7 Hz, 1H), 2.85 (d, J = 10.1 Hz, 1H), 2.68 (dd, J = 13.4, 7.3 Hz, 1H), 2.07 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 154.5, 139.4, 137.3, 136.2, 135.1, 132.8, 131.8, 129.9, 129.6, 128.9, 128.6, 128.4, 127.4, 126.9, 99.3, 79.6, 49.8, 48.7, 41.4, 28.3, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{34}ClN_2O_3^+$ 505.2252; Found 505.2256.

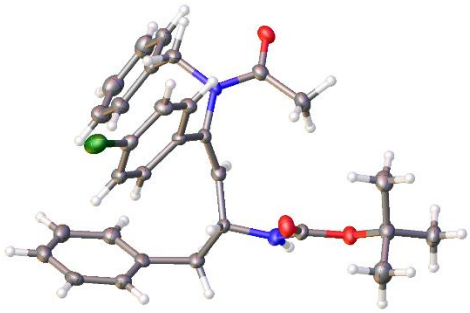
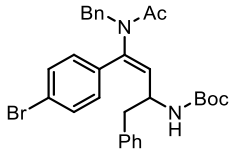


Table S3 Crystal data and structure refinement for *tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(4-chlorophenyl)-1-phenylbut-3-en-2-yl)carbamate (5)

Empirical formula	$C_{30}H_{33}ClN_2O_3$
Formula weight	505.03
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.6509(13)
b/Å	9.1864(5)
c/Å	25.8961(16)
α/°	90
β/°	101.701(4)
γ/°	90
Volume/Å^3	5509.4(6)
Z	8
ρ_{calc}g/cm^3	1.218
μ/mm^{-1}	0.965
F(000)	2144.0
Crystal size/mm^3	0.08 × 0.06 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.908 to 109.766
Index ranges	$-28 \le h \le 23$, $-11 \le k \le 11$, $-31 \le l \le 31$
Reflections collected	39841
Independent reflections	10209 [R_{int} = 0.1093, R_{sigma} = 0.0948]

Data/restraints/parameters	10209/1/657
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0986, wR_2 = 0.2558
Final R indexes [all data]	R_1 = 0.1557, wR_2 = 0.3150
Largest diff. peak/hole / e $Å^{-3}$	0.56/-0.57

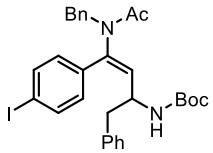


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(4-bromophenyl)-1-phenylbut-3-en-2-yl)carbamate (6):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 79% yield (86.6 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.23 – 7.10 (m, 5H), 6.91 – 6.74 (m, 4H), 5.10 (d, J = 10.0 Hz, 1H), 4.81 (d, J = 14.4 Hz, 1H), 4.64 – 4.27 (m, 2H), 3.98 (d, J = 13.9 Hz, 1H), 2.84 (dd, J = 13.3, 4.9 Hz, 1H), 2.67 (dd, J = 13.4, 7.7 Hz, 1H), 2.07 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 154.5, 139.4, 137.3, 136.2, 133.3, 131.9, 131.9, 130.2, 129.6, 128.9, 128.7, 128.4, 127.4, 126.9, 123.4, 79.6, 49.9, 48.7, 41.3, 28.3, 22.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}BrN_2NaO_3^+$ 571.1567; Found 571.1567.

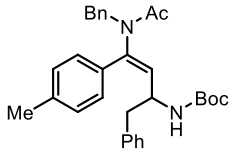


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(4-iodophenyl)-1-phenylbut-3-en-2-yl)carbamate (7):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL ACETONE, obtained in 65% yield (77.5 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.22 – 7.11 (m, 5H), 6.85 – 6.77 (m, 2H), 6.71 (d, J = 8.3 Hz, 2H), 5.10 (d, J = 10.0 Hz, 1H), 4.82 (d, J = 14.5 Hz, 1H), 4.58 – 4.34 (m, 2H), 3.98 (d, J = 14.1 Hz, 1H), 2.84 (dd, J = 13.4, 4.8 Hz, 1H), 2.67 (dd, J = 13.4, 7.7 Hz, 1H), 2.06 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 154.5, 139.5, 137.8, 137.3, 136.2, 133.8, 131.9, 130.3, 129.6, 128.9, 128.7, 128.5, 127.4, 126.9, 95.3, 79.6, 49.8, 48.7, 41.3, 28.3, 22.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}IN_2NaO_3^+$ 619.1428; Found 619.1435.

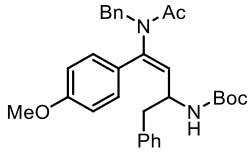


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-1-phenyl-4-(*p*-tolyl)but-3-en-2-yl)carbamate (8):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 80% yield (77.5 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.22 – 7.13 (m, 7H), 6.97 (d, J = 8.0 Hz, 2H), 6.86 – 6.78 (m, 2H), 5.03 (d, J = 9.9 Hz, 1H), 4.80 (d, J = 14.2 Hz, 1H), 4.57 – 4.36 (m, 2H), 4.05 (d, J = 13.8 Hz, 1H), 2.84 (d, J = 9.1 Hz, 1H), 2.72 (dd, J = 13.4, 6.9 Hz, 1H), 2.37 (s, 3H), 2.06 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 154.5, 140.6, 138.3, 137.6, 136.5, 134.1, 131.0, 130.0, 129.6, 129.0, 128.6, 128.5, 128.4, 127.3, 126.7, 79.4, 49.8, 48.7, 41.5, 28.3, 22.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{36}N_2NaO_3^+$ 507.2618; Found 507.2619.

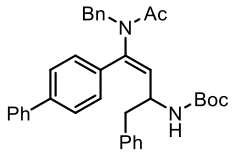


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(4-methoxyphenyl)-1-phenylbut-3-en-2-yl)carbamate (9):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 75% yield (75.1 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dt, J = 14.0, 4.7 Hz, 3H), 7.21 – 7.14 (m, 5H), 7.01 (d, J = 8.7 Hz, 2H), 6.90 – 6.81 (m, 4H), 5.00 (d, J = 9.9 Hz, 1H), 4.77 (d, J = 14.1 Hz, 1H), 4.58 – 4.37 (m, 2H), 4.16 – 4.03 (m, 1H), 3.83 (s, 3H), 2.93 – 2.78 (m, 1H), 2.71 (dd, J = 13.4, 7.0 Hz, 1H), 2.04 (d, J = 3.7 Hz, 3H), 1.36 (d, J = 3.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 160.1, 154.6, 140.1, 137.6, 136.4, 130.1, 129.9, 129.6, 129.0, 128.5, 128.3, 127.3, 126.7, 126.5, 114.1, 79.4, 55.3, 49.7, 48.7, 41.5, 28.3, 22.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{36}N_2NaO_4^+$ 523.2567; Found 523.2568.

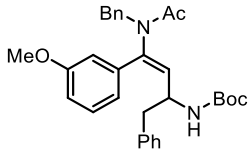


***tert*-butyl (*E*)-(4-([1,1'-biphenyl]-4-yl)-4-(*N*-benzylacetamido)-1-phenylbut-3-en-2-yl)carbamate (10):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 73% yield (79.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 14.9, 7.8 Hz, 4H), 7.47 (t, J = 7.6 Hz, 2H), 7.35 (dt, J = 20.9, 7.3 Hz, 4H), 7.24 – 7.12 (m, 7H), 6.87 – 6.80 (m, 2H), 5.10 (d, J = 10.0 Hz, 1H), 4.87 (d, J = 14.4 Hz, 1H), 4.51 (d, J = 43.3 Hz, 2H), 4.08 (d, J = 13.4 Hz, 1H), 3.00 – 2.65 (m, 2H), 2.11 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 154.6, 141.9, 140.3, 140.0, 137.6, 137.3, 136.3, 133.1, 131.4, 129.6, 129.1, 129.0, 128.9, 128.6, 128.4, 127.7, 127.4, 127.1, 126.8, 79.5, 48.8, 41.4, 29.4, 28.3, 22.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{38}N_2NaO_3^+$ 569.2775; Found 569.2966.

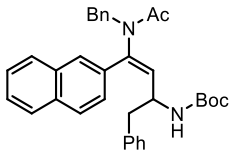


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(3-methoxyphenyl)-1-phenylbut-3-en-2-yl)carbamate (11):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 88% yield (88.0 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.23 – 7.14 (m, 5H), 6.96 – 6.89 (m, 1H), 6.85 – 6.80 (m, 2H), 6.70 (d, J = 7.4 Hz, 2H), 5.09 (d, J = 10.0 Hz, 1H), 4.74 (d, J = 13.7 Hz, 1H), 4.61 – 4.43 (m, 2H), 4.15 (d, J = 14.4 Hz, 1H), 3.77 (s, 3H), 2.98 – 2.56 (m, 2H), 2.05 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 159.7, 154.5, 140.2, 137.6, 136.3, 135.7, 131.3, 129.7, 129.5, 129.0, 128.5, 128.4, 127.3, 126.7, 121.0, 114.6, 114.2, 79.4, 55.3, 49.6, 48.8, 41.4, 28.2, 22.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{36}N_2NaO_4^+$ 523.2567; Found 523.2568.

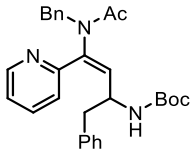


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-4-(naphthalen-2-yl)-1-phenylbut-3-en-2-yl)carbamate (12):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 80% yield (83.3 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.1 Hz, 2H), 7.70 (s, 1H), 7.52 (s, 2H), 7.37 – 7.10 (m, 10H), 6.85 (d, J = 6.3 Hz, 2H), 5.20 (d, J = 9.2 Hz, 1H), 4.87 (d, J = 14.5 Hz, 1H), 4.53 (s, 2H), 4.03 (d, J = 13.3 Hz, 1H), 2.92 (d, J = 12.4 Hz, 1H), 2.75 (dd, J = 12.5, 6.9 Hz, 1H), 2.16 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 154.5, 140.6, 137.6, 136.5, 133.5, 133.0, 131.6, 131.5, 129.7, 129.0, 128.7, 128.6, 128.4, 127.7, 127.4, 126.8, 126.5, 125.4, 76.8, 50.1, 48.8, 41.6, 28.3, 22.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{37}N_2O_3^+$ 521.2779; Found 521.2809.

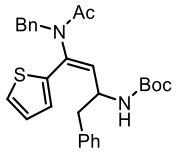


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-1-phenyl-4-(pyridin-2-yl)but-3-en-2-yl)carbamate (13):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 82% yield (77.2 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 4.0 Hz, 1H), 7.69 (td, J = 7.8, 1.8 Hz, 1H), 7.34 – 7.13 (m, 10H), 7.01 (d, J = 6.1 Hz, 2H), 5.33 (d, J = 9.3 Hz, 1H), 5.23 – 5.02 (m, 2H), 4.61 (s, 1H), 4.07 (d, J = 14.2 Hz, 1H), 3.05 (s, 1H), 2.81 (dd, J = 12.4, 7.1 Hz, 1H), 2.07 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 155.1, 153.7, 149.7, 138.2, 137.6, 137.4, 137.3, 136.8, 129.5, 129.4, 128.5, 128.4, 127.5, 126.6, 123.0, 122.2, 79.3, 49.8, 40.2, 29.3, 28.2, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{34}N_3O_3^+$ 472.2595; Found 472.2599.



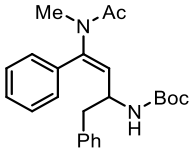
***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-1-phenyl-4-(thiophen-2-yl)but-3-en-2-yl)carbamate (14):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10

mol%), 2.0 mL acetone, obtained in 89% yield (84.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 4H), 7.20 (s, 5H), 7.07 – 6.87 (m, 4H), 5.01 (d, J = 9.9 Hz, 1H), 4.86 (d, J = 14.5 Hz, 2H), 4.41 – 4.18 (m, 2H), 2.91 – 2.66 (m, 2H), 1.99 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 167.9, 154.7, 137.5, 137.5, 136.2, 134.1, 132.4, 129.5, 129.3, 128.6, 128.4, 128.2, 127.6, 127.5, 126.8, 79.6, 49.3,41.2, 39.0, 28.3, 21.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{33}N_2O_3S^+$ 477.2206; Found 477.2209.

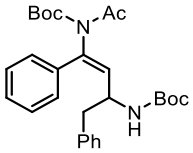


***tert*-butyl (*E*)-(4-(*N*-methylacetamido)-1,4-diphenylbut-3-en-2-yl)carbamate (15):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 88% yield (69.4 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.25 – 7.19 (m, 2H), 7.16 – 7.04 (m, 4H), 5.47 (d, J = 9.6 Hz, 1H), 4.68 – 4.54 (m, 2H), 3.06 – 3.30 (m, 1H), 2.95 – 2.71 (m, 4H), 1.96 (s, 3H), 1.41 (d, J = 12.5 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 154.6, 143.3, 136.7, 134.6, 133.3, 129.5, 129.0, 128.6, 128.6, 128.3, 126.8, 79.8, 50.1, 41.7, 35.1, 28.3, 22.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{30}N_2NaO_3^+$ 417.2149; Found 417.2130.

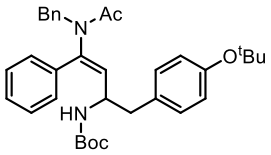


***tert*-butyl (*E*)-acetyl(3-((*tert*-butoxycarbonyl)amino)-1,4-diphenylbut-1-en-1-yl)carbamate（16）：** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 74% yield (71.1 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 6H), 7.24 – 7.12 (m, 4H), 5.48 (d, J = 9.8 Hz, 1H), 4.73 – 4.42 (m, 2H), 2.89 (dd, J = 12.8, 5.8 Hz, 1H), 2.50 (s, 3H), 1.35 (d, J = 24.8 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 154.7, 152.5, 137.2, 137.0, 136.1, 131.0, 130.0, 128.7, 128.4, 128.3, 128.2, 126.5, 83.2, 49.9, 41.2, 28.3, 28.3, 27.8, 26.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{37}N_2O_5^+$ 481.2697; Found 481.2705.

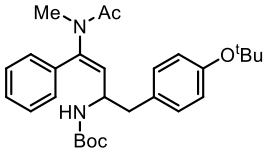


***tert*-butyl (*E*)-(4-(N-benzylacetamido)-1-(4-(*tert*-butoxy)phenyl)-4-phenylbut-3-en-2-yl)carbamate (17)：** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 85% yield (92.3 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 14.2, 6.9 Hz, 6H), 7.17 (d, J = 6.5 Hz, 2H), 7.02 (d, J = 6.8 Hz, 2H), 6.80 (d, J = 8.3 Hz, 2H), 6.70 (d, J = 8.3 Hz, 2H), 5.09 (d, J = 10.0 Hz, 1H), 4.78 (d, J = 14.4 Hz, 1H), 4.50 (d, J = 47.0 Hz, 2H), 4.04 (d, J = 14.4 Hz, 1H), 2.90 – 2.72 (m, 1H), 2.64 (dd, J = 13.4, 7.9 Hz, 1H), 2.09 (s, 3H), 1.35 (d, J = 17.5 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 154.5, 154.1, 140.4, 137.5, 134.2, 131.4, 130.0, 129.5, 129.1, 128.9, 128.7, 128.5, 128.4, 127.4, 127.3, 124.3, 121.1, 79.3, 78.4, 50.0, 48.6, 40.8, 28.8, 28.3, 22.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{43}N_2O_4^+$ 543.3217; Found 543.3221.

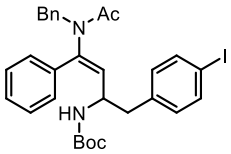


***tert*-butyl (*E*)-(1-(4-(tert-butoxy)phenyl)-4-(*N*-methylacetamido)-4-phenylbut-3-en-2-yl)carbamate (18)：** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 78% yield (72.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 3H), 7.14 – 7.05 (m, 2H), 6.97 (d, J = 7.9 Hz, 2H), 6.88 (d, J = 7.8 Hz, 2H), 5.46 (d, J = 9.3 Hz, 1H), 4.62 (d, J = 27.5 Hz, 2H), 2.98 (d, J = 8.9 Hz, 1H), 2.88 (s, 3H), 2.77 (dd, J = 12.9, 7.7 Hz, 1H), 1.95 (s, 3H), 1.35 (d, J = 29.3 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 154.7, 154.2, 143.3, 134.6, 131.7, 129.9, 129.0, 128.8, 128.6, 128.3, 124.3, 78.4, 77.3, 50.2, 41.2, 35.1, 28.8, 28.3, 22.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{38}N_2NaO_4^+$ 489.2724; Found 489.2724.

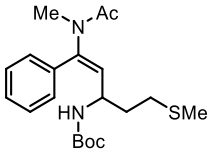


***tert*-butyl (*E*)-(4-(N-benzylacetamido)-1-(4-iodophenyl)-4-phenylbut-3-en-2-yl)carbamate (19)：** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 86% yield (102.6 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2H), 7.33 (m, 6H), 7.21 – 7.04 (m, 4H), 6.54 (d, J = 7.9 Hz, 2H), 5.06 (d, J = 6.4 Hz, 1H), 4.82 (d, J = 14.4 Hz, 1H), 4.40 (d, J = 54.4 Hz, 2H), 4.04 (d, J = 14.0 Hz, 1H), 2.85 – 2.60 (m, 2H), 2.10 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 154.5, 140.6, 137.6, 136.1, 136.0, 134.2, 131.5, 130.7, 129.3, 129.0, 128.8, 128.5, 128.4, 127.4, 92.1, 79.7, 49.5, 48.6, 40.9, 28.3, 22.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}IN_2NaO_3^+$ 619.1428; Found 619.1435.

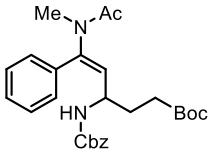


***tert*-butyl (*E*)-(1-(*N*-methylacetamido)-5-(methylthio)-1-phenylpent-1-en-3-yl)carbamate (20):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 73% yield (55.2 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 7.39 (dd, J = 16.3, 6.4 Hz, 1H), 5.50 (d, J = 9.8 Hz, 1H), 4.79 (d, J = 7.6 Hz, 1H), 2.94 (s, 3H), 2.50 (s, 2H), 2.15 (s, 3H), 2.05 (s, 3H), 1.87 (dt, J = 15.8, 7.9 Hz, 2H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 154.9, 142.7, 134.5, 129.9, 129.2, 128.8, 128.4, 79.6, 48.6, 35.1, 35.0, 30.3, 28.3, 22.2, 15.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{31}N_2O_3S^+$ 379.2050; Found 379.2052.



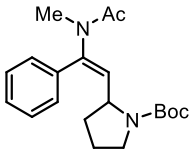
***tert*-butyl (*E*)-4-(((benzyloxy)carbonyl)amino)-6-(*N*-methylacetamido)-6-phenylhex-5-enoate (21)：** Following the general procedure A, using NaI (10 mol%),

PPh_3 (10 mol%), 2.0 mL acetone, obtained in 82% yield (76.5 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 24.7 Hz, 9H), 5.44 (d, J = 9.8 Hz, 1H), 5.24 (s, 1H), 5.16 – 4.98 (m, 2H), 4.50 – 4.34 (m, 1H), 2.91 (s, 3H), 2.35 – 2.20 (m, 2H), 2.06 (d, J = 28.0 Hz, 4H), 1.88 (m, 2H), 1.38 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 170.9, 155.5, 143.0, 136.4, 134.4, 129.1, 128.8, 128.5, 128.2, 128.1, 80.9, 66.7, 49.7, 35.0, 31.8, 30.2, 28.0, 22.1. (one carbon signal was overlapped)

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{35}N_2O_5^+$ 467.2540; Found 467.2542.

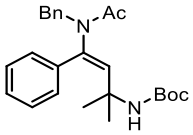


***tert*-butyl (*E*)-2-(2-(*N*-methylacetamido)-2-phenylvinyl)pyrrolidine-1-carboxylate (22)：** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 81% yield (55.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 6.8 Hz, 5H), 5.54 (d, J = 8.4 Hz, 1H), 4.57 (s, 1H), 3.43 (s, 2H), 2.95 (s, 3H), 2.16 (s, 3H), 1.92 (d, J = 9.3 Hz, 4H), 1.33 (d, J = 53.7 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 154.5, 140.6, 134.8, 130.8, 128.8, 128.6, 79.6, 54.9, 46.6, 35.2, 33.6, 28.4, 23.6, 22.1. (one carbon signal was overlapped)

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{28}N_2NaO_3^+$ 367.1992; Found 367.1995.

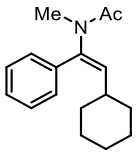


***tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-2-methyl-4-phenylbut-3-en-2-yl)carbamate (23)：** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 51% yield (41.7mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 7.30 – 7.19 (m, 7H), 5.30 (s, 1H), 4.40 (s, 2H), 4.30 (s, 1H), 2.44 (s, 3H), 1.23 (s, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 153.3, 138.3, 137.6, 136.8, 135.5, 129.6, 129.1, 128.6, 128.2, 127.1, 123.5, 78.6, 51.6, 48.0, 29.3, 28.2, 22.5.

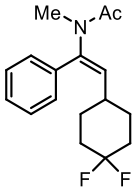
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}N_2O_3^+$ 409.2486; Found 409.2493.



(*E*)-*N*-(2-cyclohexyl-1-phenylvinyl)-*N*-methylacetamide (24): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 74% yield (38.0 mg) as colorless oil. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1). The compound data was in agreement with the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 3H), 7.29 – 7.25 (m, 2H).5.45 (d, J = 10.7 Hz, 1H), 2.91 (s, 3H), 2.41 (dd, J = 13.8, 6.6 Hz, 1H), 2.15 (s, 3H), 1.81 – 1.61 (m, 5H), 1.32 – 1.09 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 139.4, 135.7, 135.4, 128.6, 128.5, 128.2, 37.1, 34.9, 32.8, 25.8, 25.4, 22.1.

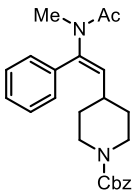


(*E*)-*N*-(2-(4,4-difluorocyclohexyl)-1-phenylvinyl)-*N*-methylacetamide (25): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 68% yield (39.9 mg) as colorless oil. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 3H), 7.30 – 7.15 (m, 2H), 5.45 (d, J = 10.5 Hz, 1H), 2.91 (s, 3H), 2.47 (dd, J = 21.3, 10.6 Hz, 1H), 2.18 – 2.06 (m, 5H), 1.67 (m,6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 141.2, 135.1, 132.8, 128.9, 128.8, 128.2, 35.2, 34.9, 33.2, 32.9, 32.9, 32.7, 29.0, 28.9, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}F_2NO^+$ 294.1664; Found 294.1674.

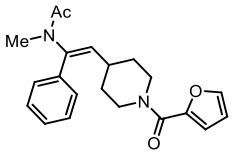


benzyl (*E*)-4-(2-(*N*-methylacetamido)-2-phenylvinyl)piperidine-1-carboxylate (26): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 70% yield (55.0 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 9H),7.26 – 7.24,(m,1H), 5.41 (d, J = 10.5 Hz, 1H), 5.14 (d, J = 7.8 Hz, 2H), 4.18 (s, 2H), 2.91 (s, 3H), 2.67 – 2.49 (m, 1H), 2.14 (s, 3H), 1.70 (s, 2H), 1.48 – 1.19 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 155.2, 141.0, 136.8, 135.1, 133.0, 129.1, 128.9, 128.8, 128.5, 128.2, 128.0, 127.9, 125.0, 67.1, 43.4, 35.4, 34.9, 31.7, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}N_2O_3^+$ 393.2173; Found 393.2181.

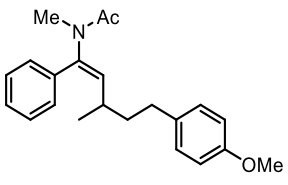


(*E*)-*N*-(2-(1-(furan-2-carbonyl)piperidin-4-yl)-1-phenylvinyl)-*N*-methylacetamide (27): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 69% yield (48.6 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.35 (m, 5H), 7.34 – 7.18 (m, 1H), 7.05 – 6.92 (m, 1H), 6.48 (d, J = 1.7 Hz, 1H), 5.44 (dd, J = 10.5, 2.6 Hz, 1H), 3.14 (s, 1H), 2.92 (s, 3H), 2.71 (d, J = 10.7 Hz, 1H), 2.16 (d, J = 2.9 Hz, 3H), 1.97 (s, 1H), 1.82 (d, J = 13.2 Hz, 2H), 1.53 (dd, J = 24.7, 12.4 Hz, 3H), 1.26 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 159.2, 148.0, 143.6, 141.2, 135.1, 132.7, 128.9, 128.2, 125.0, 116.1, 111.3, 35.7, 34.9, 32.1, 22.1, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}N_2O_3^+$ 353.1860; Found 353.1862.

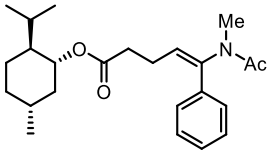


(*E*)-*N*-(5-(4-methoxyphenyl)-3-methyl-1-phenylpent-1-en-1-yl)-*N*-methylacetamide (28): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 72% yield (48.6 mg) as colorless liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.24 – 7.20 (m, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 5.47 (d, J = 10.8 Hz, 1H), 3.77 (s, 3H), 2.96 (s, 3H), 2.70 – 2.57 (m, 1H), 2.56 – 2.48 (m, 2H), 2.16 (s, 3H), 1.65 (dd, J = 14.4, 7.3 Hz, 2H), 1.09 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 157.8, 140.2, 135.9, 135.5, 133.9, 129.2, 128.6, 128.4, 128.2, 113.8, 55.3, 39.3, 35.3, 32.7, 31.8, 22.3, 20.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{28}NO_2^+$ 338.2115; Found 338.2121.

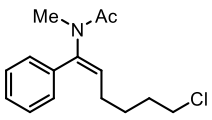


(*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl (*E*)-5-(*N*-methylacetamido)-5-phenylpent-4-enoate (29): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 59% yield (45.5 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.32 – 7.28 (m, 2H), 5.62 (t, J = 7.5 Hz, 1H), 4.68 (td, J = 10.9, 4.4 Hz, 1H), 2.95 (s, 3H), 2.69 – 2.58 (m, 2H), 2.42 (t, J = 7.3 Hz, 2H), 2.12 (s, 3H), 1.98 – 1.91 (m, 1H), 1.86 – 1.75 (m, 1H), 1.69 – 1.61 (m, 2H), 1.52 – 1.43 (m, 1H), 1.37 – 1.30 (m, 1H), 1.10 – 0.89 (m, 9H), 0.73 (d, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 171.0, 142.1, 134.9, 128.7, 128.7, 128.4, 127.9, 74.5, 47.0, 40.9, 35.1, 34.2, 34.1, 31.4, 26.3, 24.0, 23.4, 22.1, 22.0, 20.7, 16.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{36}NO_3^+$ 386.2690; Found 386.2694.

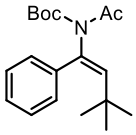


(*E*)-*N*-(6-chloro-1-phenylhex-1-en-1-yl)-*N*-methylacetamide (30): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 1.0 mL acetone, obtained in 58% yield (30.8 mg) as colorless liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.29 – 7.27 (m, 2H), 5.65 (t, J = 7.5 Hz, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.96 (s, 3H), 2.32 (q, J = 7.3 Hz, 2H), 2.12 (s, 3H), 1.87 – 1.71 (m, 2H), 1.70 – 1.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 141.6, 135.1, 129.4, 128.6, 128.6, 128.4, 44.6, 35.3, 32.1, 27.8, 26.8, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}ClNO^+$ 266.1306; Found 266.1314.

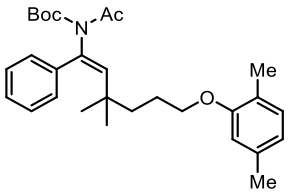


***tert*-butyl (*E*)-acetyl(3,3-dimethyl-1-phenylbut-1-en-1-yl)carbamate (31):** Following the general procedure A, using NaI (20 mol%), PPh_3 (20 mol%), 2.0 mL acetone, obtained in 80% yield (50.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.35 – 7.24 (m, 3H), 5.61 – 5.52 (m, 1H), 2.43 (s, 3H), 1.52 (s, 9H), 0.95 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.2, 142.5, 137.7, 133.5, 130.6, 128.5, 128.2, 127.9, 127.3, 82.8, 32.7, 30.7, 28.1, 26.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{27}NNaO_3^+$ 340.1883; Found 340.1887.

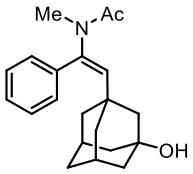


***tert*-butyl (*E*)-acetyl(6-(2,5-dimethylphenoxy)-3,3-dimethyl-1-phenylhex-1-en-1-yl)carbamate (32):** Following the general procedure A, using NaI (20 mol%), PPh_3 (20 mol%), 2.0 mL acetone, obtained in 77% yield (71.7 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.34 (m, 2H), 7.31 – 7.23 (m, 3H), 6.99 (d, J = 7.5 Hz, 1H), 6.69 – 6.52 (m, 2H), 5.53 (s, 1H), 3.81 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.30 (s, 3H), 2.17 (s, 3H), 1.94 – 1.75 (m, 2H), 1.51 (s, 9H), 1.47 – 1.39 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 157.1, 153.1, 141.5, 137.8, 136.5, 134.2, 130.5, 130.3, 128.1, 127.5, 123.5, 120.6, 112.0, 83.0, 68.3, 40.6, 35.7, 28.7, 28.1, 26.7, 25.2, 21.5, 15.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{39}NNaO_4^+$ 488.2771; Found 488.2775.

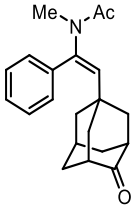


***N*-((*E*)-2-((*1r,3s,5R,7S*)-3-hydroxyadamantan-1-yl)-1-phenylvinyl)-*N*-methylacetamide (33):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 63% yield (40.9 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H), 7.25 (dd, J = 6.2, 2.7 Hz, 2H), 5.44 (s, 1H), 2.82 (s, 3H), 2.29 (s, 3H), 2.11 (s, 2H), 1.70 – 1.37 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 139.4, 138.8, 136.3, 129.6, 128.7, 128.0, 68.3, 50.2, 44.2, 41.4, 38.4, 34.9, 33.8, 30.4, 22.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{28}NO_2^+$ 326.2115; Found 326.2132.

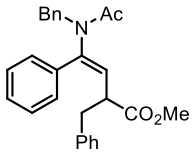


***N*-methyl-*N*-((*E*)-2-((*1s,3R,5S,7s*)-4-oxoadamantan-1-yl)-1-phenylvinyl)acetamide (34):** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 78% yield (50.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.24 (d, J = 3.6 Hz, 2H), 5.45 (s, 1H), 2.82 (s, 3H), 2.45 (s, 2H), 2.26 (d, J = 18.6 Hz, 3H), 2.06 (t, J = 5.2 Hz, 1H), 2.03 – 1.72 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.1, 170.1, 140.4, 137.0, 136.0, 129.5, 129.0, 128.2, 46.2, 43.7, 41.8, 38.2, 34.8, 33.7, 27.5, 22.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}NNaO_2^+$ 346.1778; Found 346.1778.

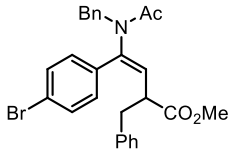


methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-phenylbut-3-enoate (35): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 75% yield (62.0 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 6H), 7.21 – 7.12 (m, 5H), 6.95 (dd, J = 7.7, 1.7 Hz, 2H), 6.81 (dd, J = 6.5, 2.9 Hz, 2H), 5.31 (d, J = 11.1 Hz, 1H), 4.57 (d, J = 14.5 Hz, 1H), 4.21 (d, J = 14.5 Hz, 1H), 3.78 – 3.52 (m, 4H), 3.02 (dd, J = 13.7, 5.6 Hz, 1H), 2.77 (dd, J = 13.7, 8.7 Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 170.6, 141.4, 137.6, 137.4, 134.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 127.3, 126.7, 52.0, 48.7, 46.3, 38.5, 22.0. (one carbon signal was overlapped)

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_3^+$ 414.2064; Found 414.2070.

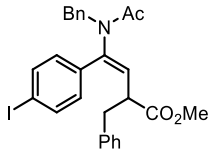


methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-(4-bromophenyl)but-3-enoate (36): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 66% yield (65.0 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.35 – 7.27 (m, 3H), 7.21 – 7.15 (m, 3H), 7.11 (dd, J = 7.4, 1.7 Hz, 2H), 6.81 (dd, J = 7.2, 2.1 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 5.34 (d, J = 11.2 Hz, 1H), 4.58 (d, J = 14.5 Hz, 1H), 4.17 (d, J = 14.6 Hz, 1H), 3.61 (s, 3H), 3.55 – 3.41 (m, 1H), 3.04 (dd, J = 13.7, 5.2 Hz, 1H), 2.75 (dd, J = 13.7, 9.2 Hz, 1H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 170.5, 140.6, 137.5, 137.1, 133.1, 131.9, 130.2, 129.0, 128.8, 128.6, 128.4, 127.4, 126.8, 123.3, 52.1, 48.7, 46.5, 38.4, 22.0. (one carbon signal was overlapped)

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}BrNO_4^+$ 492.1169; Found 492.1182.

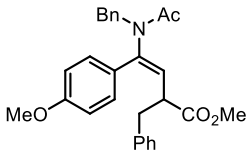


methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-(4-iodophenyl)but-3-enoate (37): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 69% yield (74.4 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.23 – 7.06 (m, 5H), 6.81 (dd, J = 7.2, 2.1 Hz, 2H), 6.58 (d, J = 8.3 Hz, 2H), 5.34 (d, J = 11.1 Hz, 1H), 4.59 (d, J = 14.6 Hz, 1H), 4.16 (d, J = 14.6 Hz, 1H), 3.61 (s, 3H), 3.50 (ddd, J = 11.1, 9.3, 5.1 Hz, 1H), 3.04 (dd, J = 13.7, 5.1 Hz, 1H), 2.75 (dd, J = 13.7, 9.2 Hz, 1H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 170.6, 140.7, 137.9, 137.5, 137.1, 133.7, 130.3, 129.0, 128.9, 128.8, 128.6, 128.4, 127.4, 126.8, 95.2, 52.1, 48.7, 46.5, 38.4, 22.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}INO_4^+$ 540.1030; Found 540.1041.

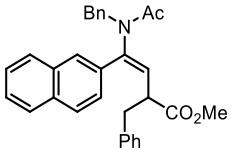


methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-(4-methoxyphenyl)but-3-enoate (38): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 70% yield (62.1 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 3H), 7.22– 7.06 (m, J = 12.2, 7.9, 3.2 Hz, 5H), 6.92 – 6.78 (m, 6H), 5.20 (dd, J = 24.5, 12.4 Hz, 1H), 4.54 (d, J = 14.4 Hz, 1H), 4.24 (d, J = 14.5 Hz, 1H), 3.83 (s, 3H), 3.69 – 3.52 (m, 4H), 3.08 – 2.96 (m, 1H), 2.77 (dd, J = 13.8, 8.7 Hz, 1H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 170.6, 160.1, 141.2, 137.7, 137.4, 130.0, 129.0, 128.9, 128.5, 128.3, 127.3, 127.2, 126.7, 126.4, 114.1, 55.3, 52.0, 48.6, 46.4, 38.5, 22.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_4^+$ 444.2169; Found 444.2179.

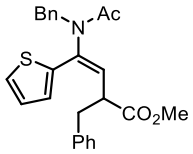


methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-(naphthalen-2-yl)but-3-enoate (39): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 62% yield (57.5 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 2H), 7.71 – 7.64 (m, 1H), 7.55 – 7.49 (m, 2H), 7.37 – 7.29 (m, 3H), 7.24 – 7.14 (m, 6H), 7.08 (dd, J = 8.5, 1.5 Hz, 1H), 6.88 – 6.78 (m, 2H), 5.44 (d, J = 11.1 Hz, 1H), 4.73 (d, J = 14.6 Hz, 1H), 4.11 (d, J = 14.4 Hz, 1H), 3.74 – 3.56 (m, 4H), 3.07 (dd, J = 13.7, 5.0 Hz, 1H), 2.81 (dd, J = 13.6, 9.2 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 170.8, 141.7, 137.8, 137.4, 133.3, 132.9, 131.4, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 127.7, 127.3, 126.9, 126.8, 126.6, 125.4, 52.0, 48.8, 46.7, 38.5, 22.2. (two carbon signals were overlapped)

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}NO_3^+$ 464.2220; Found 464.2227.

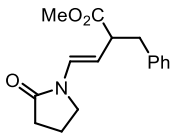


methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-(thiophen-2-yl)but-3-enoate (40): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 52% yield (43.6 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 5.1, 0.9 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.21 – 7.16 (m, 5H), 6.94 – 6.85 (m, 3H), 5.25 (d, J = 10.9 Hz, 1H), 4.54 (dd, J = 45.3, 14.1 Hz, 2H), 3.93 (ddd, J = 10.9, 8.4, 6.1 Hz, 1H), 3.61 (s, 3H), 3.03 (dd, J = 13.8, 6.1 Hz, 1H), 2.79 (dd, J = 13.8, 8.4 Hz, 1H), 1.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 170.5, 137.5, 137.5, 137.3, 135.3, 129.4, 129.2, 128.9, 128.6, 128.5, 128.3, 127.5, 127.4, 127.3, 126.8, 52.1, 49.4, 46.5, 38.4, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_3S^+$ 420.1628; Found 420.1636.

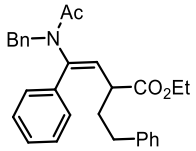


methyl (*E*)-2-benzyl-4-(2-oxopyrrolidin-1-yl)but-3-enoate (41): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 60% yield (32.8 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.25 – 7.24 (m, 1H), 7.22 – 7.16 (m, 1H), 7.14 – 7.12 (m, 2H), 6.94 (d, J = 14.4 Hz, 1H), 4.95 (dd, J = 14.4, 9.3 Hz, 1H), 3.61 (s, 3H), 3.57 – 3.39 (m, 2H), 3.39 – 3.23 (m, 1H), 3.09 (dd, J = 13.6, 8.0 Hz, 1H), 2.93 – 2.78 (m, 1H), 2.46 (t, J = 8.1 Hz, 2H), 2.08 (dt, J = 16.5, 8.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.2, 138.4, 129.0, 128.4, 126.5, 126.0, 108.8, 51.9, 48.8, 45.1, 39.5, 31.1, 17.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{19}NNaO_3^+$ 296.1257; Found 296.1259.

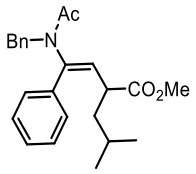


ethyl (*E*)-4-(*N*-benzylacetamido)-2-phenethyl-4-phenylbut-3-enoate (42): Following the general procedure B, using LiI (10 mol%),2.0 mL DMF, obtained in 76% yield (67.0 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3H), 7.31 – 7.26 (m, 2H), 7.25 – 7.26 (m, 8H), 7.02 – 6.96 (m, 2H), 5.33 (d, J = 11.0 Hz, 1H), 4.68 (d, J = 14.4 Hz, 1H), 4.29 (d, J = 14.5 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.37 (dt, J = 11.1, 6.9 Hz, 1H), 2.41 (t, J = 7.9 Hz, 2H), 2.29 (s, 3H), 2.07 – 1.90 (m, 1H), 1.73 (td, J = 15.2, 7.6 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 170.5, 140.9, 140.7, 137.3, 134.2, 129.4, 129.1, 128.9, 128.6, 128.4, 128.4, 128.3, 127.4, 126.1, 60.9, 48.6, 44.1, 34.4, 33.0, 22.4, 14.2. (one carbon signal was overlapped)

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{32}NO_3^+$ 442.2377; Found 442.2379.

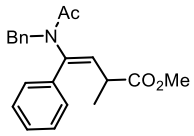


methyl (*E*)-2-(2-(*N*-benzylacetamido)-2-phenylvinyl)-4-methylpentanoate (43): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 76% yield (57.7 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 3H), 7.30 – 7.15 (m, 7H), 5.24 (d, J = 10.9 Hz, 1H), 4.48 (dd, J = 42.9, 14.3 Hz, 2H), 3.59 (s, 3H), 3.39 (dt, J = 10.8, 7.2 Hz, 1H), 2.24 (s, 3H), 1.76 – 1.44 (m, 1H), 1.31 (tt, J = 19.7, 6.7 Hz, 2H), 0.78 (d, J = 6.4 Hz, 3H), 0.67 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 170.4, 140.3, 137.3, 134.4, 130.0, 129.1, 128.8, 128.6, 128.2, 127.3, 51.9, 48.8, 43.1, 41.6, 25.8, 22.5, 22.4, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_3^+$ 380.2220; Found 380.2225.

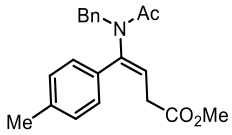


methyl (*E*)-4-(*N*-benzylacetamido)-2-methyl-4-phenylbut-3-enoate (44): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 73% yield (49.3 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 3H), 7.30 – 7.22 (m, 5H), 7.21 – 7.15 (m, 2H), 5.27 (d, J = 10.9 Hz, 1H), 4.47 (dd, J = 56.2, 14.3 Hz, 2H), 3.62 (s, 3H), 3.43 (dq, J = 11.0, 7.0 Hz, 1H), 2.25 (s, 3H), 1.17 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 170.6, 139.7, 137.2, 134.3, 130.6, 129.2, 129.1, 128.9, 128.6, 128.2, 127.3, 52.0, 48.7, 39.0, 22.3, 17.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_3^+$ 338.1751; Found 338.1768.

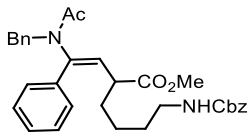


methyl (*E*)-4-(*N*-benzylacetamido)-2-methyl-4-phenylbut-3-enoate (45): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 73% yield (49.3 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 8H), 7.15 – 7.08 (m, 2H), 5.47 (t, J = 7.6 Hz, 1H), 4.48 (s, 2H), 3.63 (s, 3H), 3.21 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 170.9, 141.5, 139.2, 137.4, 131.1, 129.5, 128.9, 128.7, 128.3, 127.2, 122.5, 52.0, 48.9, 33.8, 22.4, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_3^+$ 338.1751; Found 338.1754.

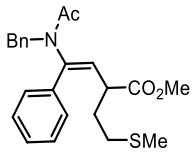


methyl (*E*)-2-(2-(*N*-benzylacetamido)-2-phenylvinyl)-6-(((benzyloxy)carbonyl)amino)hexanoate (46): Following the general procedure B, using LiI (10 mol%), PPh_3 (10 mol%), 2.0 mL DMF, obtained in 65% yield (68.7 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 8H), 7.25 (m, 5H), 7.15 (d, J = 6.4 Hz, 2H), 5.24 (d, J = 11.0 Hz, 1H), 5.09 (s, 2H), 4.63 (d, J = 14.6 Hz, 2H), 4.31 (d, J = 14.2 Hz, 1H), 3.59 (s, 3H), 3.46 – 3.23 (m, 1H), 3.09 (d, J = 5.9 Hz, 2H), 2.25 (s, 3H), 1.73 – 1.54 (m, 1H), 1.34 – 1.26 (m, 3H), 1.22 – 1.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 170.4, 156.3, 140.5, 137.3, 136.5, 134.2, 129.4, 129.2, 129.1, 128.9, 128.6, 128.6, 128.3, 128.2, 127.3, 66.7, 52.0, 48.5, 44.4, 40.7, 32.2, 29.7, 24.0, 22.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{36}N_2NaO_5^+$ 551.2516; Found 551.2531.

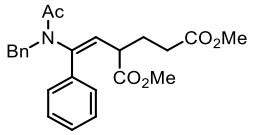


methyl (*E*)-4-(*N*-benzylacetamido)-2-(2-(methylthio)ethyl)-4-phenylbut-3-enoate (47): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 69% yield (54.2 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.32 – 7.27 (m, 4H), 7.26 – 7.24 (m, 2H) 7.20 – 7.15 (m, 2H), 5.21 (d, J = 11.0 Hz, 1H), 4.71 (d, J = 14.4 Hz, 1H), 4.25 (d, J = 14.4 Hz, 1H), 3.61 (s, 3H), 3.50 (dt, J = 11.1, 6.9 Hz, 1H), 2.31 – 2.11 (m, 5H), 2.03 – 1.90 (m, 4H), 1.70 (dt, J = 21.9, 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 170.3, 141.1, 137.2, 134.1, 129.2, 129.1, 128.9, 128.7, 128.7, 128.3, 127.4, 52.1, 48.5, 43.5, 31.7, 31.1, 22.3, 15.3.

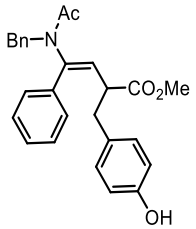
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{27}N_2NaO_3S^+$ 420.1604; Found 420.1607.



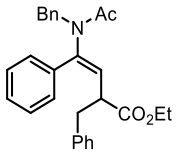
dimethyl (E)-2-(2-(N-benzylacetamido)-2-phenylvinyl)succinate (48): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 80% yield (63.3 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (q, J = 5.1 Hz, 3H), 7.31 – 7.22 (m, 5H), 7.20 – 7.15 (m, 2H), 5.21 (d, J = 11.1 Hz, 1H), 4.65 (d, J = 14.3 Hz, 1H), 4.32 (d, J = 14.3 Hz, 1H), 3.60 (d, J = 7.9 Hz, 6H), 3.39 (dt, J = 11.1, 7.1 Hz, 1H), 2.25 (s, 3H), 2.11 (q, J = 7.8 Hz, 2H), 1.98 (dq, J = 15.1, 7.4 Hz, 1H), 1.76 (dq, J = 14.7, 7.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.8, 170.3, 141.3, 137.2, 134.1, 129.2, 129.1, 128.9, 128.7, 128.5, 128.3, 127.3, 52.1, 51.7, 48.6, 43.6, 31.0, 27.3, 22.4.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}NO_5^+$ 410.1962; Found 410.1965.



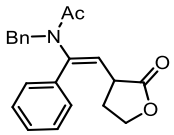
methyl (*E*)-4-(*N*-benzylacetamido)-2-(4-hydroxybenzyl)-4-phenylbut-3-enoate (49): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 78% yield (67.0 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.23 (m, 7H), 7.15 (d, J = 6.4 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.65 (q, J = 8.6 Hz, 4H), 5.39 – 4.99 (m, 1H), 4.41 (dd, J = 31.5, 14.4 Hz, 2H), 3.67 – 3.50 (m, 4H), 2.96 (dd, J = 14.0, 5.2 Hz, 1H), 2.71 (dd, J = 13.9, 9.3 Hz, 1H), 1.94 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 171.5, 155.4, 141.0, 137.0, 133.9, 130.0, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 128.3, 127.4, 115.5, 52.1, 48.9, 46.3, 37.6, 21.6.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{27}NNaO_4^+$ 452.1832; Found 452.1840.



ethyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-phenylbut-3-enoate (50): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 82% yield (70.1 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 6H), 7.20 – 7.12 (m, 5H), 6.98 (dd, J = 7.8, 1.6 Hz, 2H), 6.83 (dd, J = 6.5, 2.9 Hz, 2H), 5.34 (d, J = 11.1 Hz, 1H), 4.58 (d, J = 14.6 Hz, 1H), 4.19 (d, J = 14.5 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.59 (ddd, J = 11.1, 8.6, 5.7 Hz, 1H), 3.01 (dd, J = 13.7, 5.7 Hz, 1H), 2.79 (dd, J = 13.7, 8.6 Hz, 1H), 2.05 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 170.7, 141.3, 137.6, 137.4, 134.2, 129.1, 128.9, 128.7, 128.6, 128.5, 128.5, 128.3, 127.3, 126.7, 61.0, 48.7, 46.5, 38.6, 22.1, 14.2. (one carbon signal was overlapped)

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{29}NNaO_3^+$ 450.2040; Found 450.2050.



(*E*)-*N*-benzyl-*N*-(2-(2-oxotetrahydrofuran-3-yl)-1-phenylvinyl)acetamide (51): Following the general procedure B, using LiI (10 mol%), 2.0 mL DMF, obtained in 68% yield (45.6 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

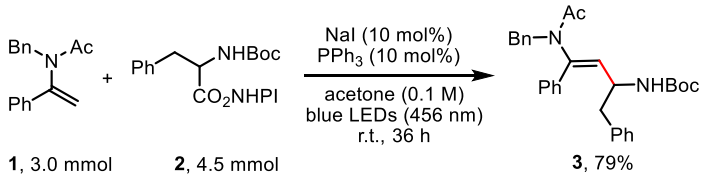
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 5H), 7.31 – 7.20 (m, 5H), 5.15 (d, J = 10.1 Hz, 1H), 4.75 – 4.61 (m, 1H), 4.45 – 4.24 (m, 2H), 4.14 (td, J = 9.7, 6.5 Hz, 1H), 3.49 (dd, J = 19.3, 10.3 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.26 (s, 3H), 2.04 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 170.6, 143.8, 137.2, 134.2, 129.6, 129.2, 129.0, 128.7, 128.3, 127.4, 125.8, 66.5, 49.3, 39.8, 30.3, 22.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{21}NNaO_3^+$ 358.1414; Found 358.1425.

4. Gram-scale Reactions

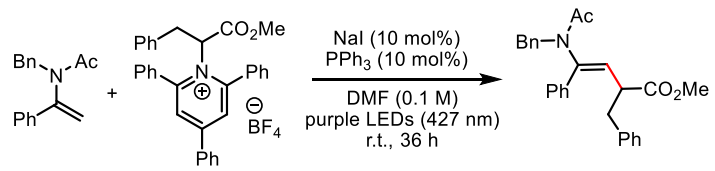
A. Synthesis of *tert*-butyl (*E*)-(4-(*N*-benzylacetamido)-1,4-diphenylbut-3-en-2-yl)carbamate (3):



1, 3.0 mmol **2**, 4.5 mmol **3**, 79%

NHPI-esters of Boc-protected phenylalanine (**2**, 1.5 equiv., 4.5 mmol), NaI (10 mol%), PPh_3 (10 mol%) were placed in a 100 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, *N*-benzyl-*N*-(1-phenylvinyl)acetamide (**1**, 1.0 equiv., 3.0 mmol) and acetone (30 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with blue LEDs (Kessil, PR160-456 nm), maintained at approximately room temperature by a desk fan in the air-conditioned room of 25 °C. After 36 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The product was purified *via* flash column chromatography on silica gel. (obtained in 79% yield, 1.1 g, viscous solid. Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

B. Synthesis of methyl (*E*)-2-benzyl-4-(*N*-benzylacetamido)-4-phenylbut-3-enoate (35):



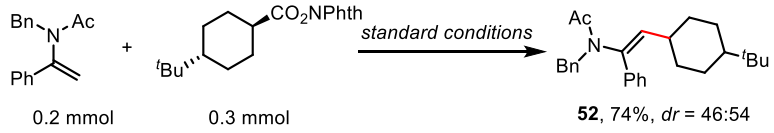
1, 3.0 mmol **35a**, 4.5 mmol **35**, 70%

Katritzky salts of methyl phenylalaninate (**35a**, 1.5 equiv., 4.5 mmol), NaI (10 mol%), PPh_3 (10 mol%) were placed in a 100 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, *N*-benzyl-*N*-(1-phenylvinyl)acetamide (**1**, 1.0 equiv., 3.0 mmol) and acetone (30 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with purple LEDs (Kessil, PR160-427 nm), maintained at

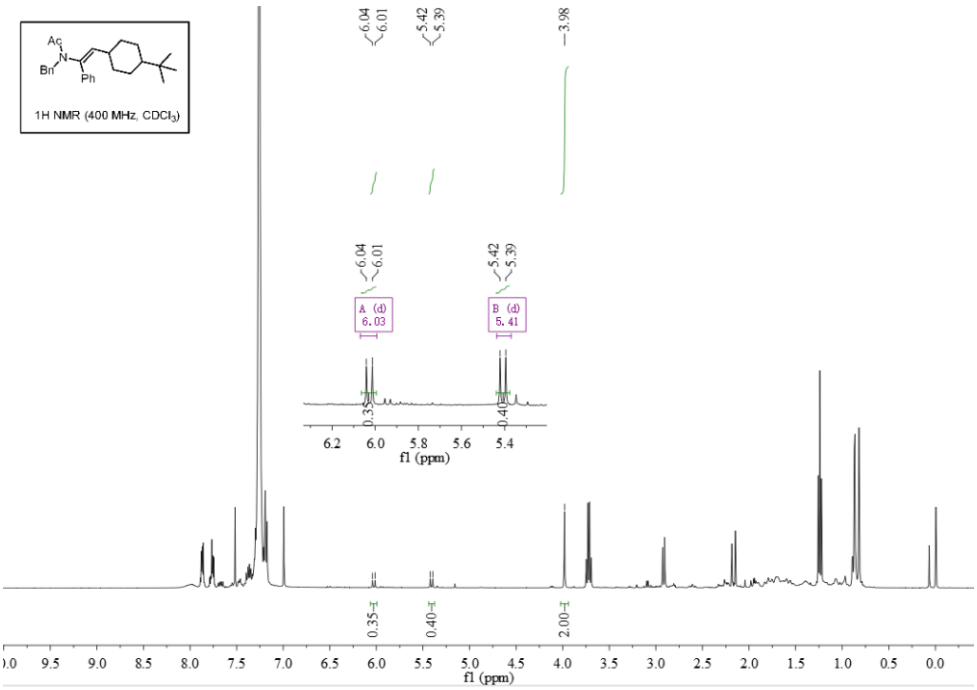
approximately room temperature by a desk fan in the air-conditioned room of 25 ºC. After 36 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The product was purified *via* flash column chromatography on silica gel. (obtained in 70% yield, 0.86 g, viscous liquid. Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

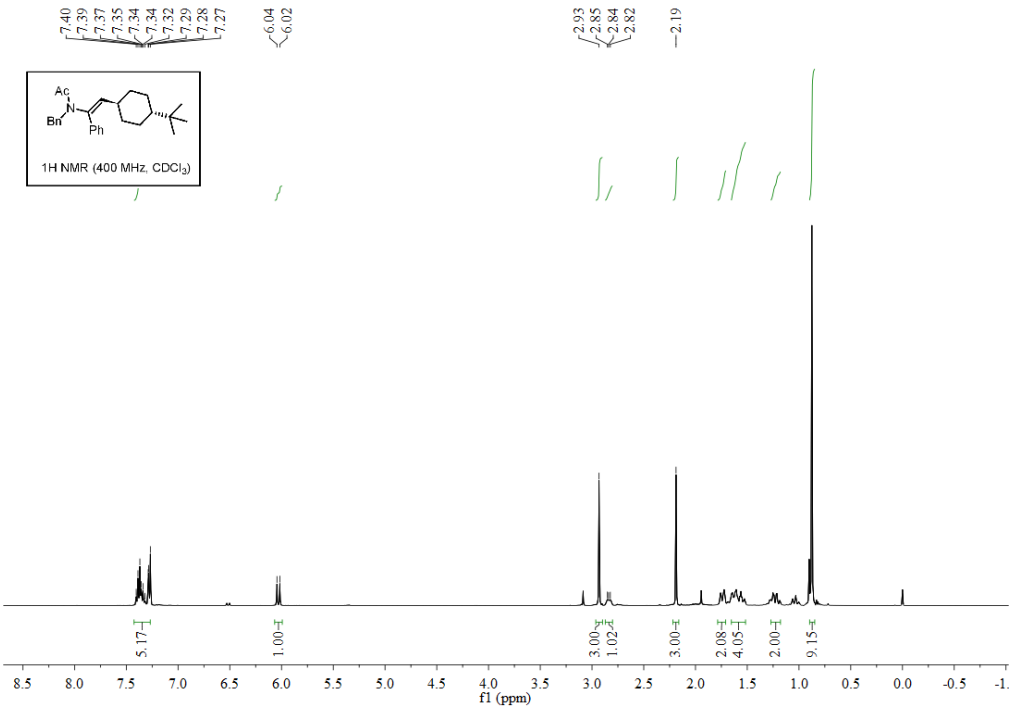
5. Experimental Studies on Mechanism

5.1 Diastereoselectivity experiment

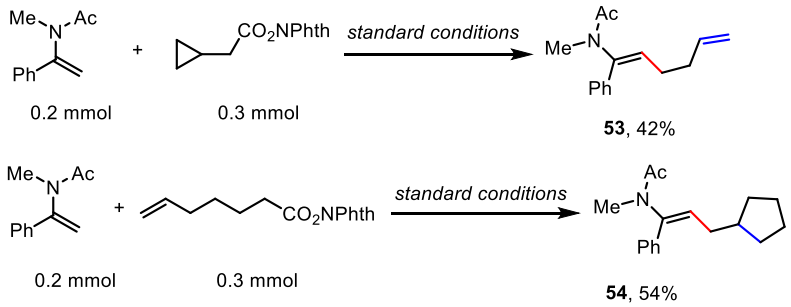


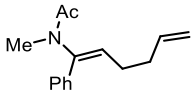
The yield of the trans/cis-product of **52** was determined by ^{1}H-NMR used diphenylmethane as an internal standard. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{36}NO^+$ 390.2791; Found 390.2760.





5.2 Radical clock experiments



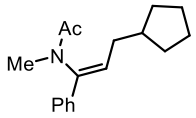


(*E*)-*N*-(3-cyclopentyl-1-phenylprop-1-en-1-yl)-*N*-methylacetamide (53): Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 42% yield (19.2 mg) as viscous liquid. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 3H), 7.20 (d, J = 7.4 Hz, 2H), 5.83 – 5.50 (m, 2H), 5.09 – 4.72 (m, 2H), 2.87 (s, 3H), 2.52 – 2.29 (m, 2H), 2.26 – 2.08 (m, 2H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 141.3, 137.4, 135.2, 129.5, 128.6, 128.5, 128.4, 115.7, 35.2, 33.5, 27.7, 22.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO^+$ 230.1539; Found 230.1548.



***N*-(3-cyclopentyl-1-phenylprop-1-en-1-yl)-*N*-methylacetamide (54) :** Following the general procedure A, using NaI (10 mol%), PPh_3 (10 mol%), 2.0 mL acetone, obtained in 54% yield (27.8 mg) as viscous liquid. 7% yield of *Z*-*N*-(3-cyclopentyl-1-phenylprop-1-en-1-yl)-*N*-methylacetamide was determined by ^{1}H-NMR. (Eluent: petroleum ether/ethyl acetate = 10/1 to 2/1)

(*E*)-N-(3-cyclopentyl-1-phenylprop-1-en-1-yl)-N-methylacetamide:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.22 (m, 5H), 5.69 (t, *J* = 7.5 Hz, 1H), 2.96 (s, 3H), 2.31 (t, *J* = 7.3 Hz, 2H), 2.14 (s, 3H), 1.91 (dt, *J* = 15.3, 7.8 Hz, 1H), 1.78 (dt, *J* = 10.6, 5.8 Hz, 2H), 1.63 – 1.44 (m, 4H), 1.17 – 1.05 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 171.2, 140.9, 135.3, 130.1, 128.5, 128.5, 128.3, 40.4, 35.2, 34.7, 32.5, 25.1, 22.1.

(*Z*)-*N*-(3-cyclopentyl-1-phenylprop-1-en-1-yl)-*N*-methylacetamide:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 6.19 – 6.07 (m, 1H), 3.05 (s, 3H), 2.26 – 2.14 (m, 2H), 1.98 – 1.95 (m, 4H), 1.83 (dd, J = 11.7, 7.0 Hz, 2H), 1.71 – 1.51 (m, 4H), 1.28 – 1.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 140.9, 136.2, 129.0, 128.3, 128.0, 125.0, 39.7, 34.8, 34.0, 32.7, 32.6, 25.1, 25.1, 21.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}NO^+$ 258.1852; Found 258.1866.

6. References

[1] Pankajakshan, S.; Xu, Y.-H; Cheng, J. K.; Low, M. T.; Loh, T.-P. Palladium-Catalyzed Direct C-H Arylation of Enamides with Simple Arenes. *Angew. Chem. Int. Ed.* **2012**, *51*, 5701–5705.

[2] Guo, J.-Y.; Zhang, Z.-Y.; Guan, T.; Mao, L.-W.; Ban, Q.; Zhao, K.; Loh, T.-P. Photoredox-catalyzed stereoselective alkylation of enamides with N-hydroxyphthalimide esters via decarboxylative cross-coupling reactions. *Chem. Sci.* **2019**, *10*, 8792–8798.

[3] Chang, X.-H.; Wang, Z.-L.; Zhao, M.; Yang, C.; Li, J.-J.; Ma, W.-W.; Xu, Y.-H. Synthesis of Functionalized Vinylsilanes via Metal-Free Dehydrogenative Silylation of Enamides. *Org. Lett.* **2020**, *22*, 1326–1330.

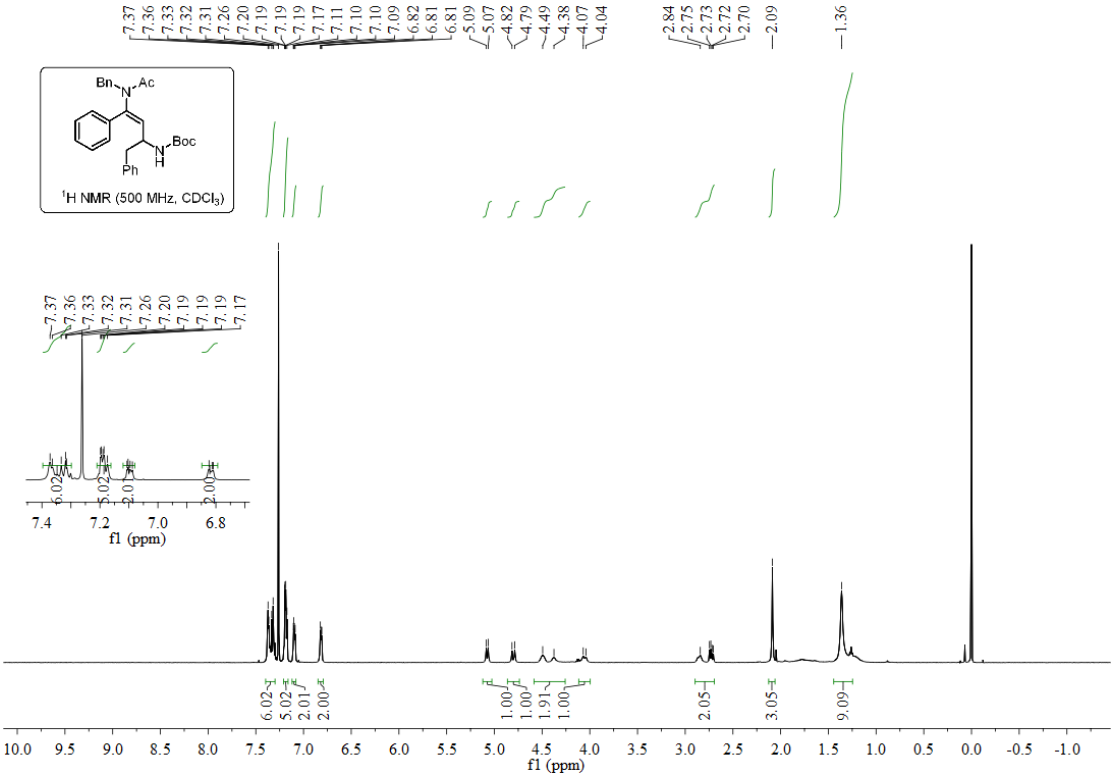
[4] Cornella, J.; Edwards, J. T.; Qin, T.; Kawamura, S.; Wang, J.; Pan, C.-M; Gianatassio, R.; Schmidt, M.; Eastgate, M. D.; Baran, P. S. Practical Ni-Catalyzed Aryl–Alkyl Cross-Coupling of Secondary Redox-Active Esters. *J. Am. Chem. Soc.* **2016**, *138*, 2174–2177.

[5] Lu, X.; Xiao, B.; Liu, L; Fu, Y. Formation of $C(sp^3)$-$C(sp^3)$ bonds through nickel-catalyzed decarboxylative olefin hydroalkylation reactions. *Chem. Eur. J.* **2016**, *22*, 11161–11164.

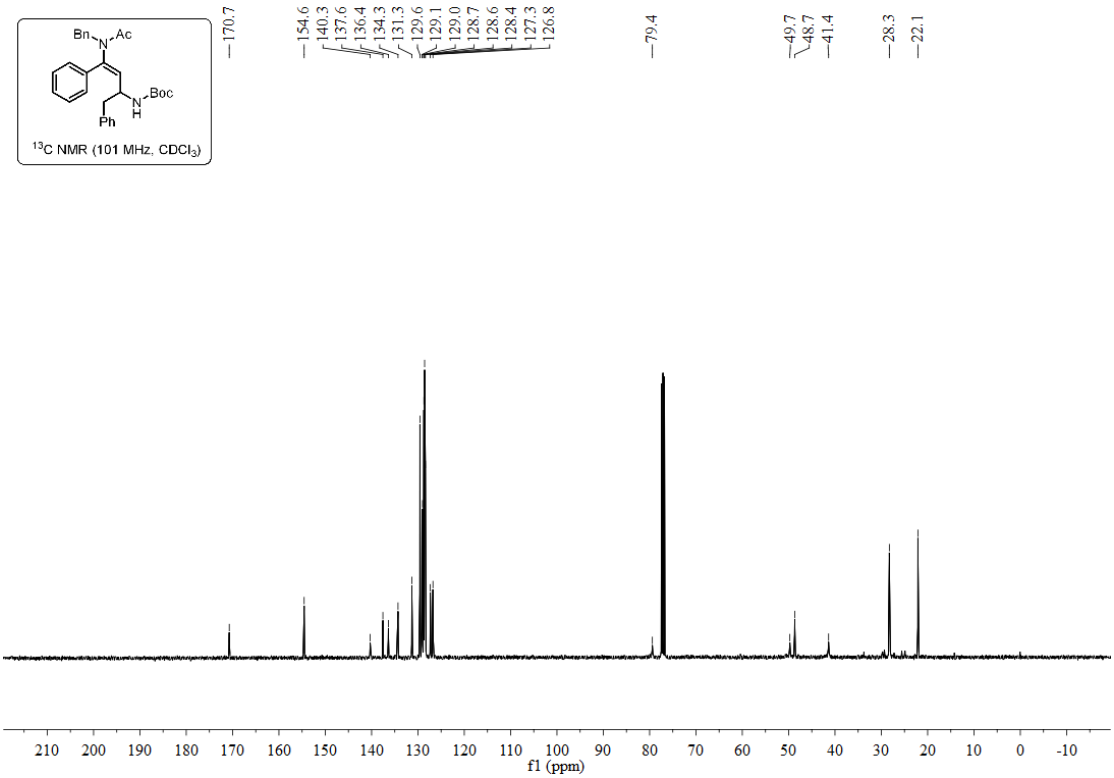
[6] Wu, J.; He, L.; Noble, A.; Aggarwal, V. K. Photoinduced Deaminative Borylation of Alkylamines. *J. Am. Chem. Soc.* **2018**, *140*, 10700–10704.

7. NMR Spectra

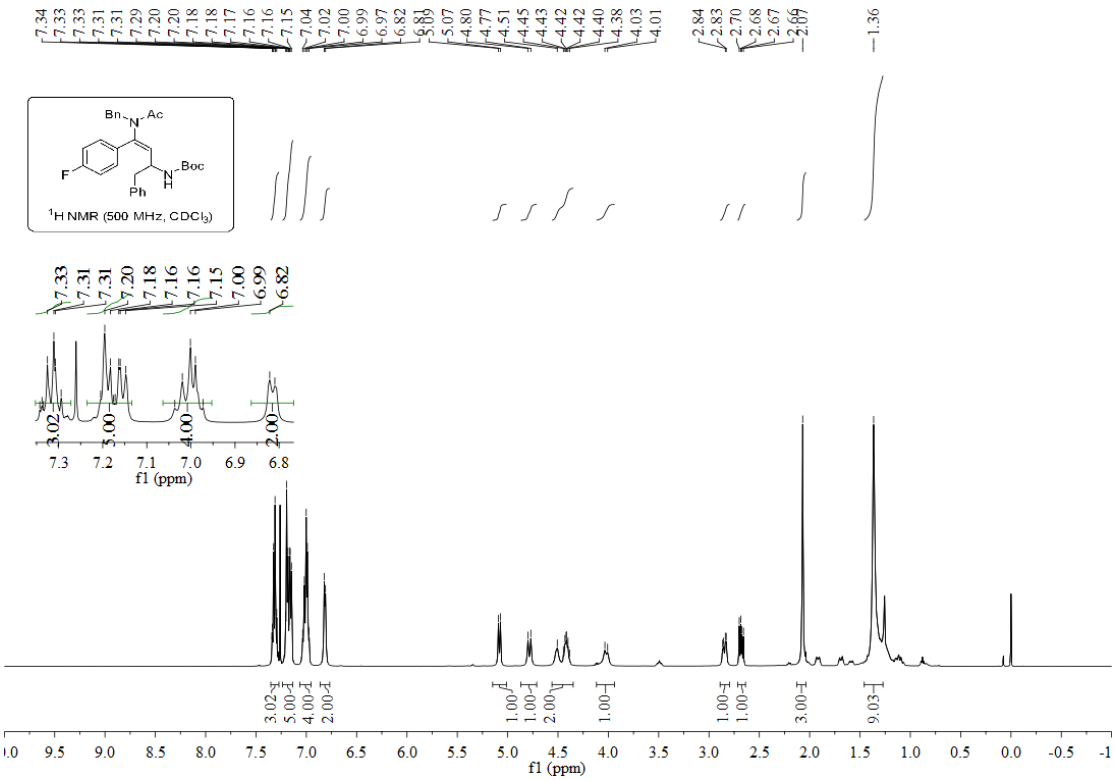
^{1}H NMR spectrum of compound **3**



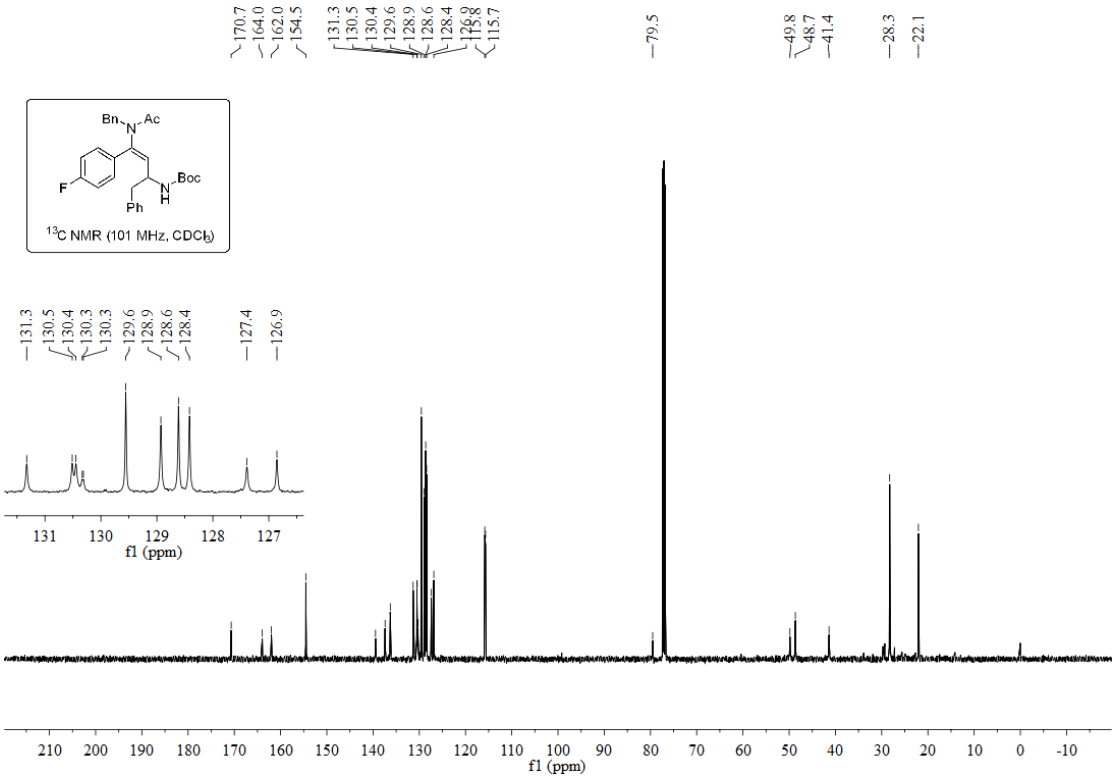
^{13}C NMR spectrum of compound **3**



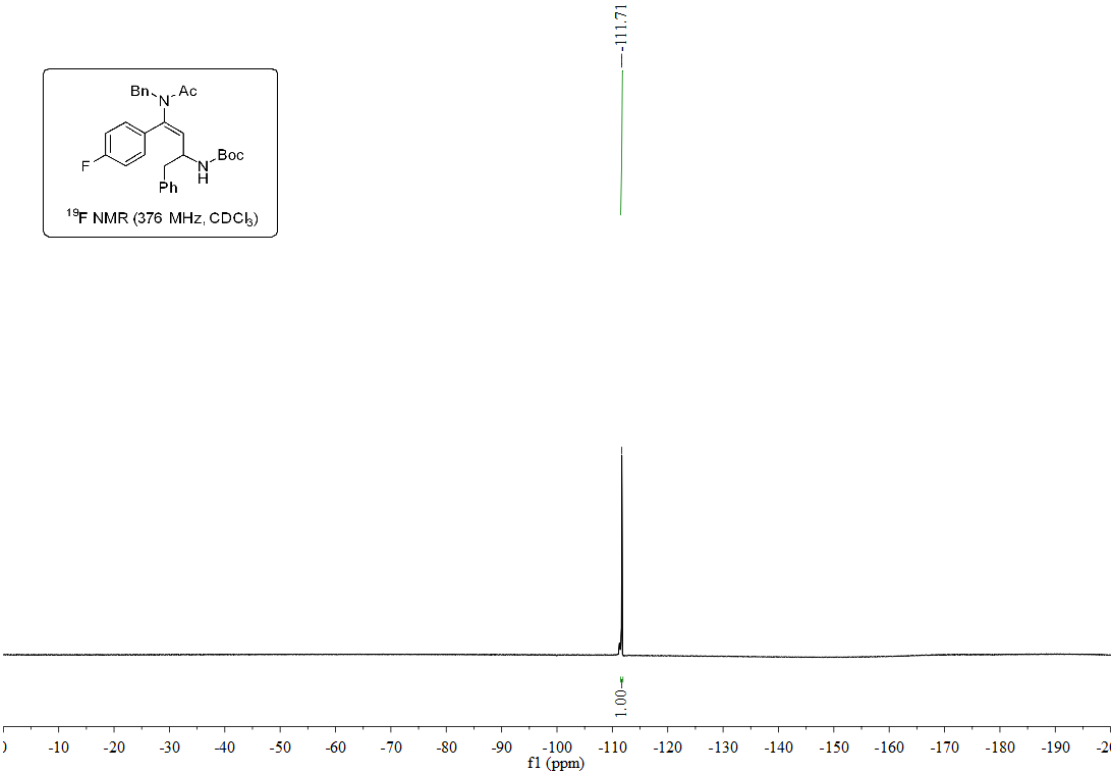
^{1}H NMR spectrum of compound **4**



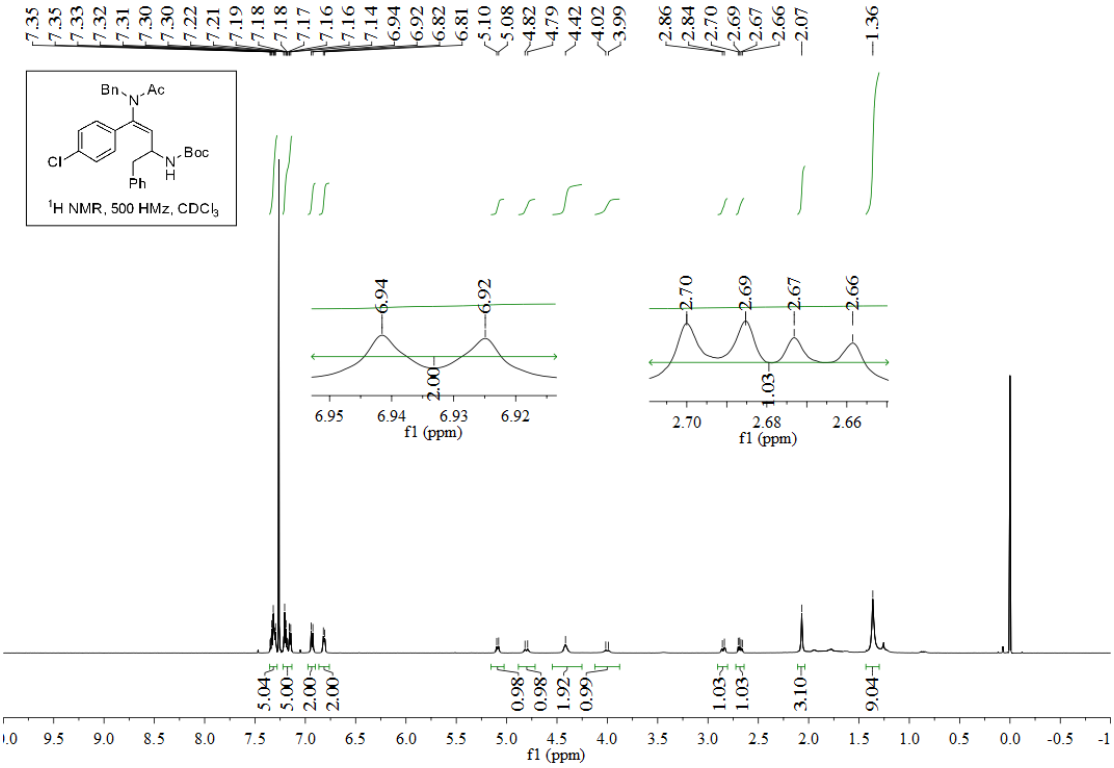
^{13}C NMR spectrum of compound **4**



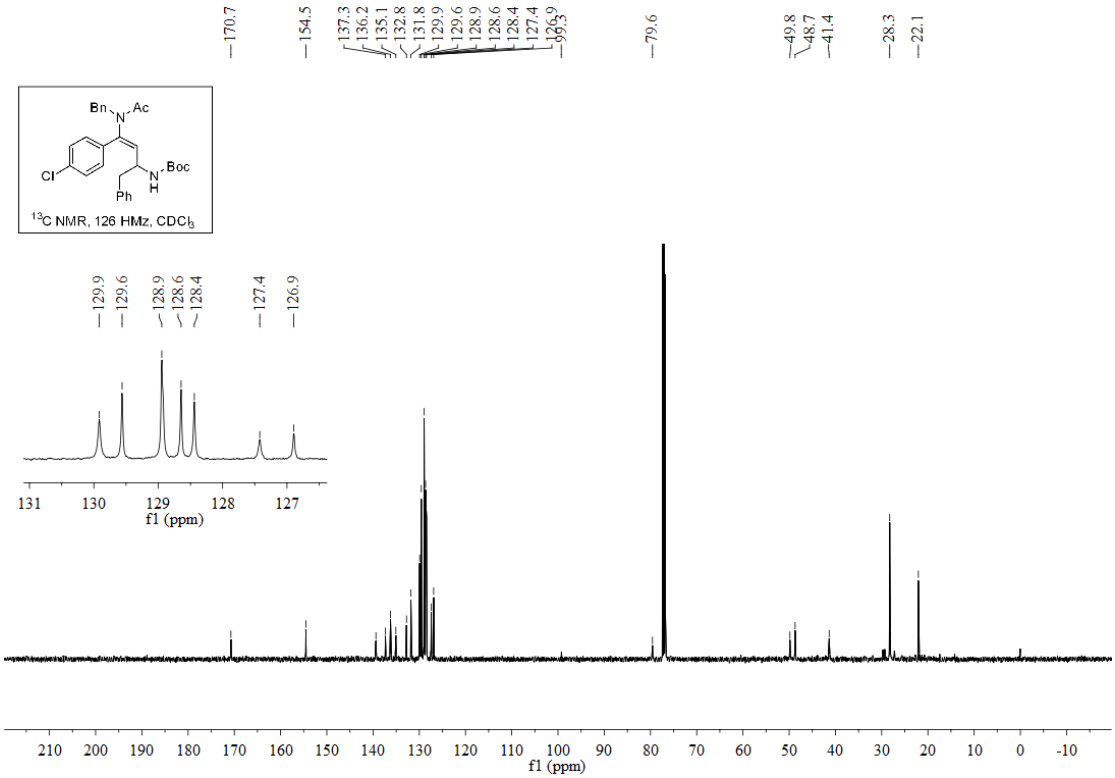
^{19}F NMR spectrum of compound **4**



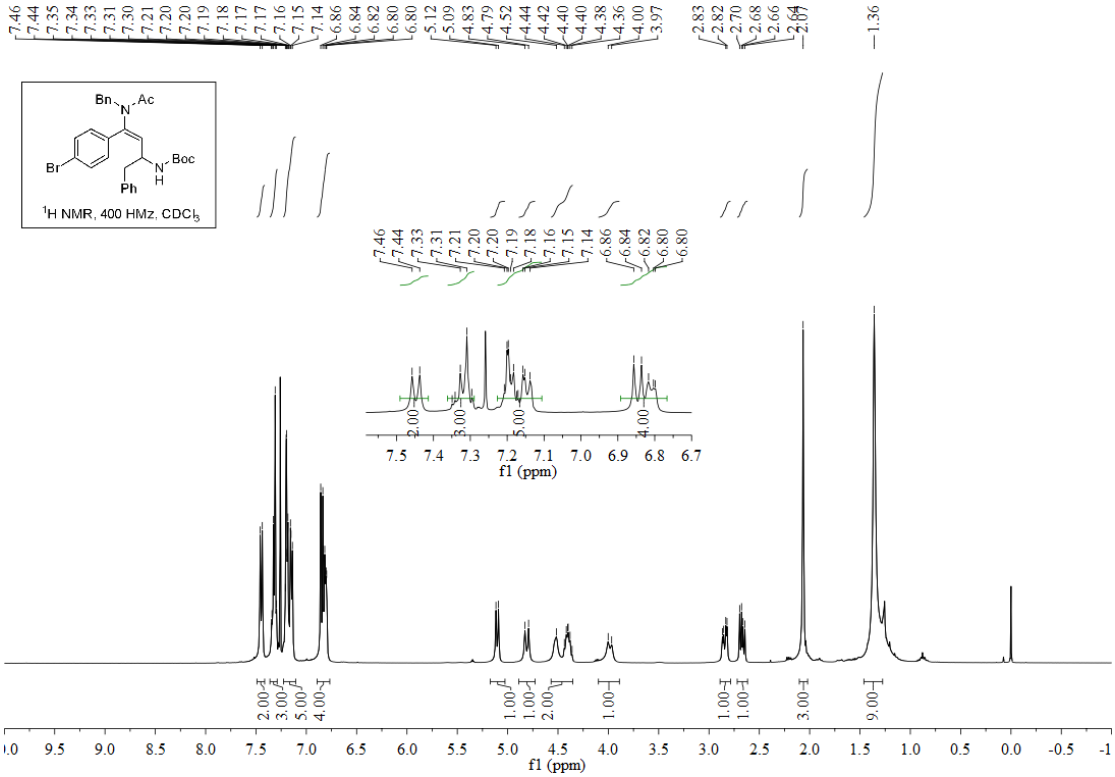
^{1}H NMR spectrum of compound **5**



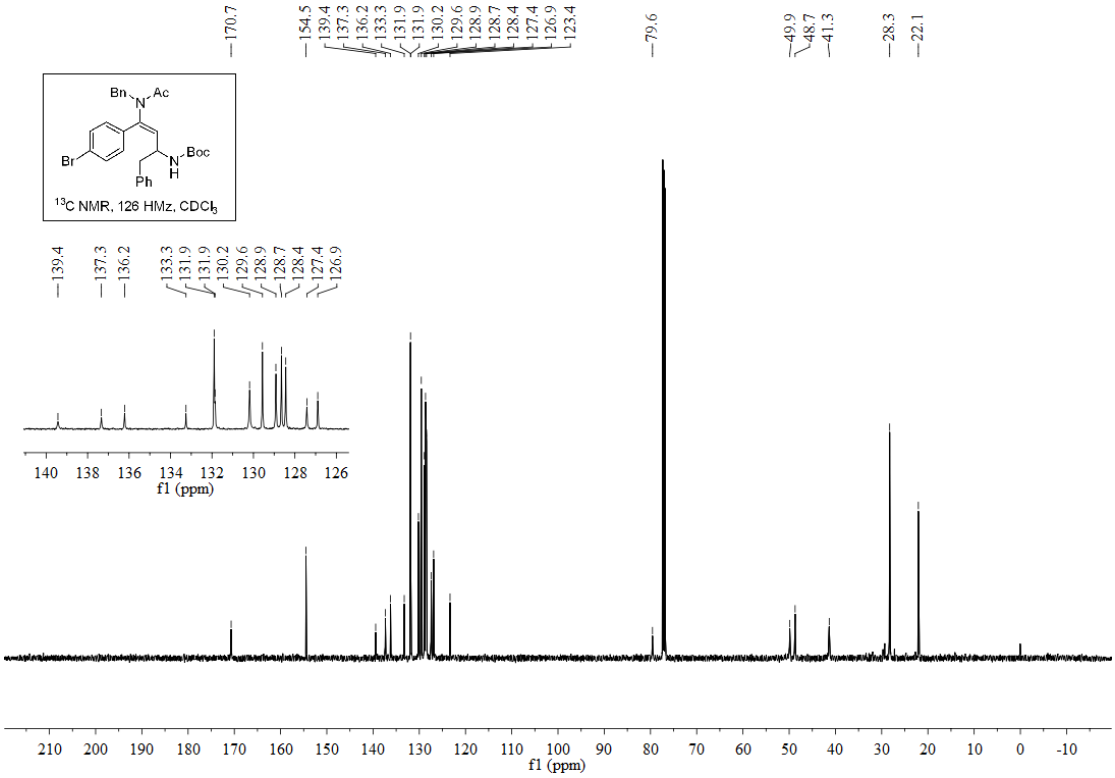
^{13}C NMR spectrum of compound **5**



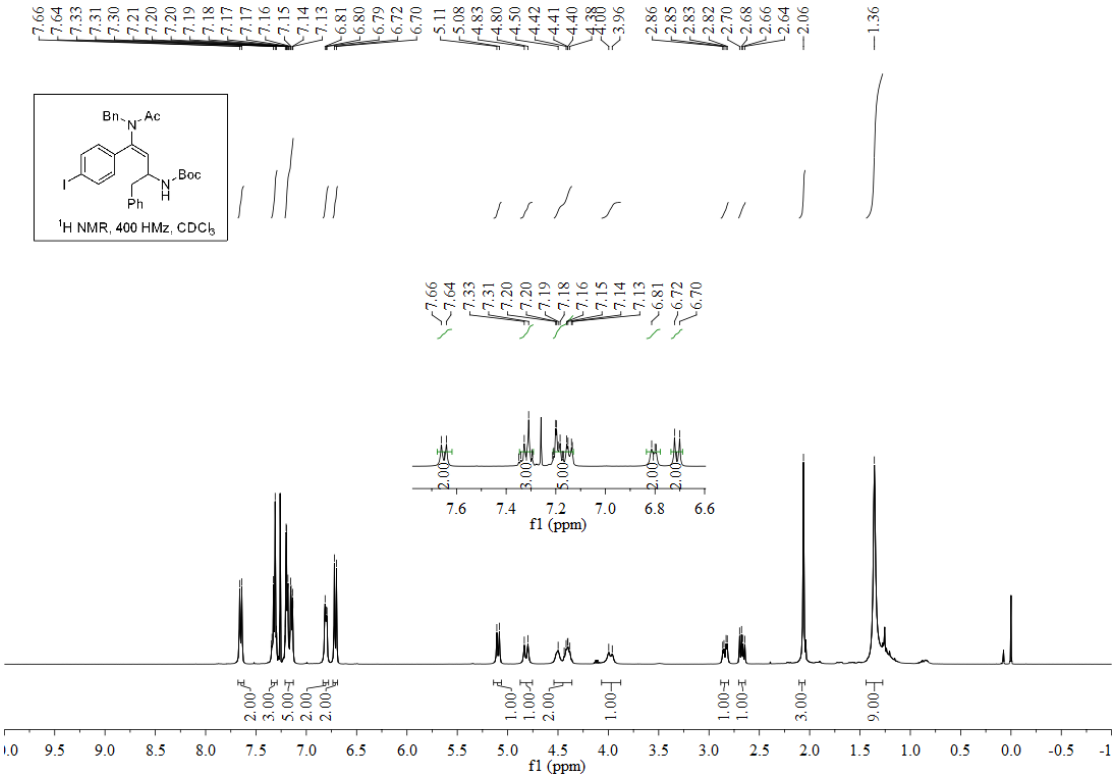
^{1}H NMR spectrum of compound **6**



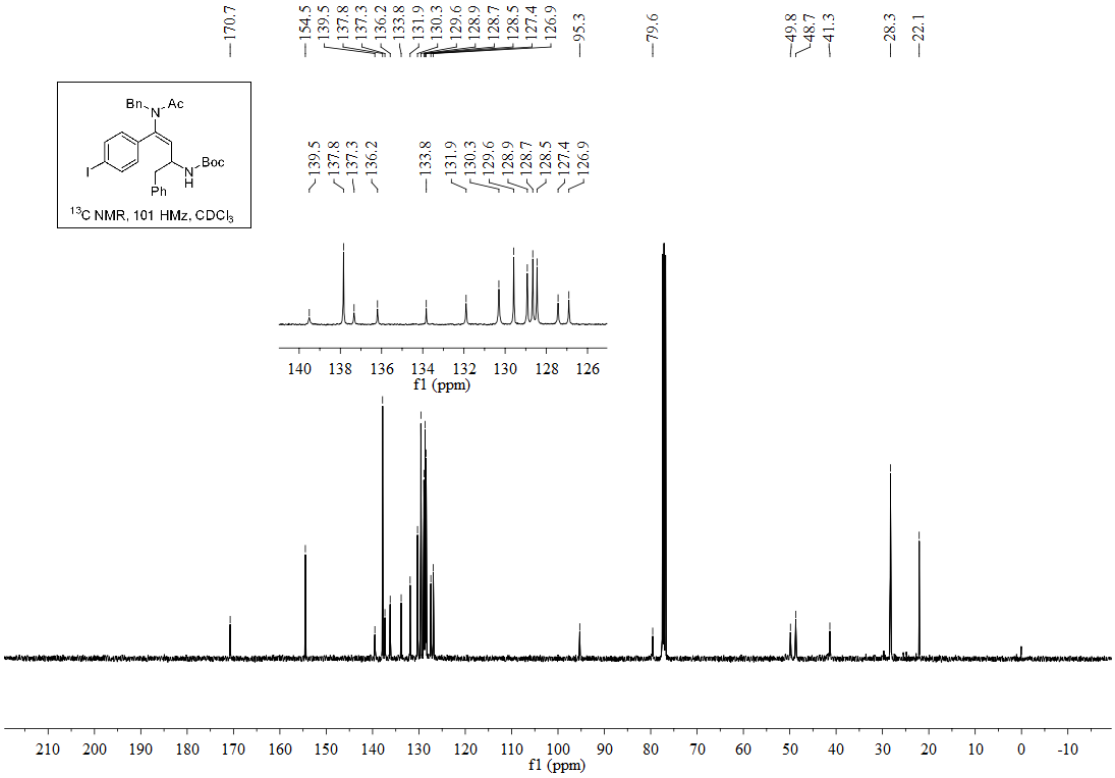
^{13}C NMR spectrum of compound **6**



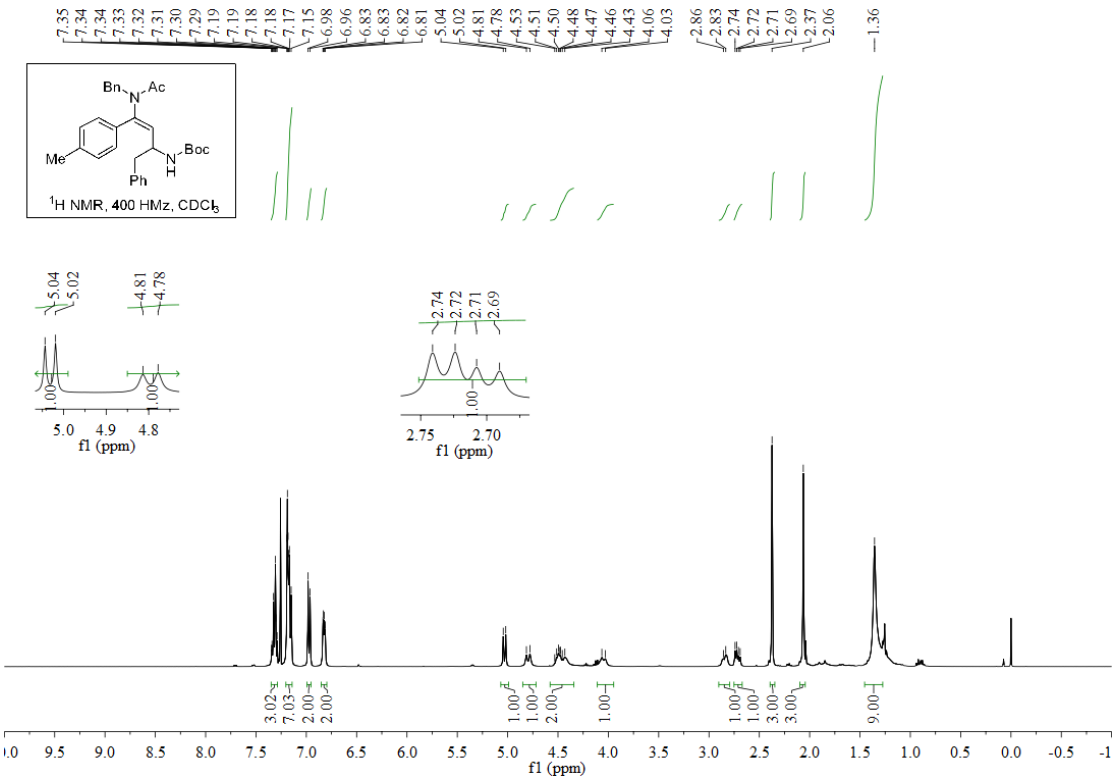
^{1}H NMR spectrum of compound **7**



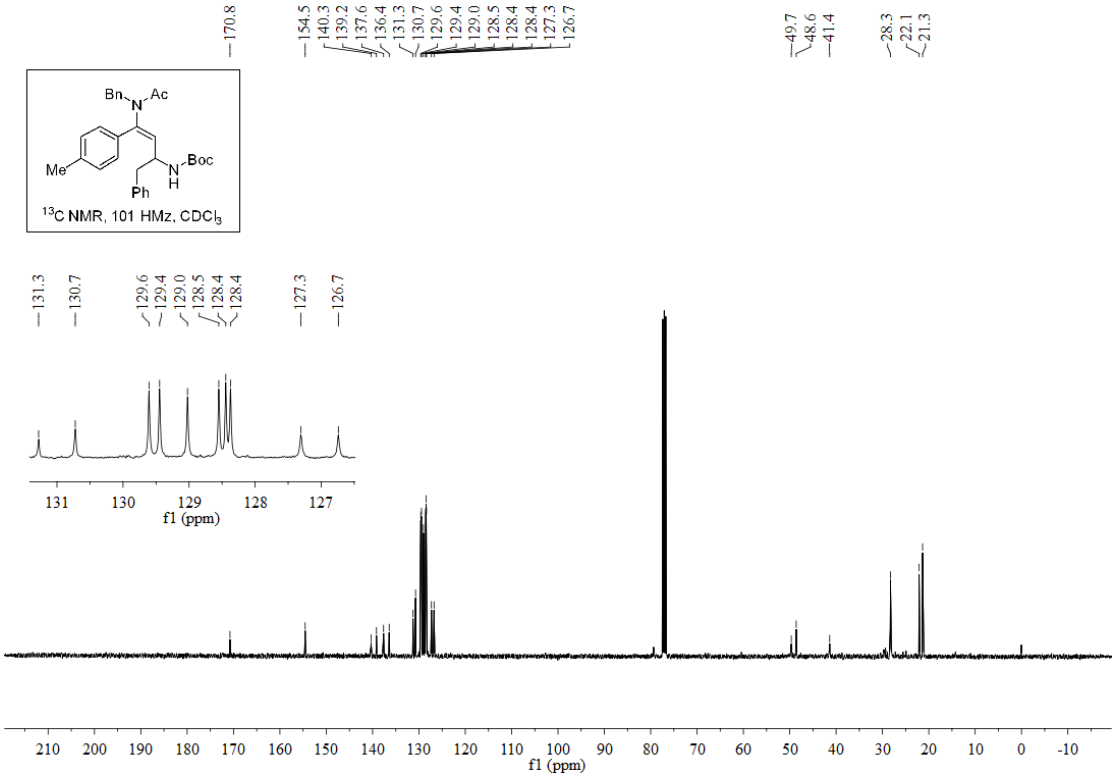
^{13}C NMR spectrum of compound **7**



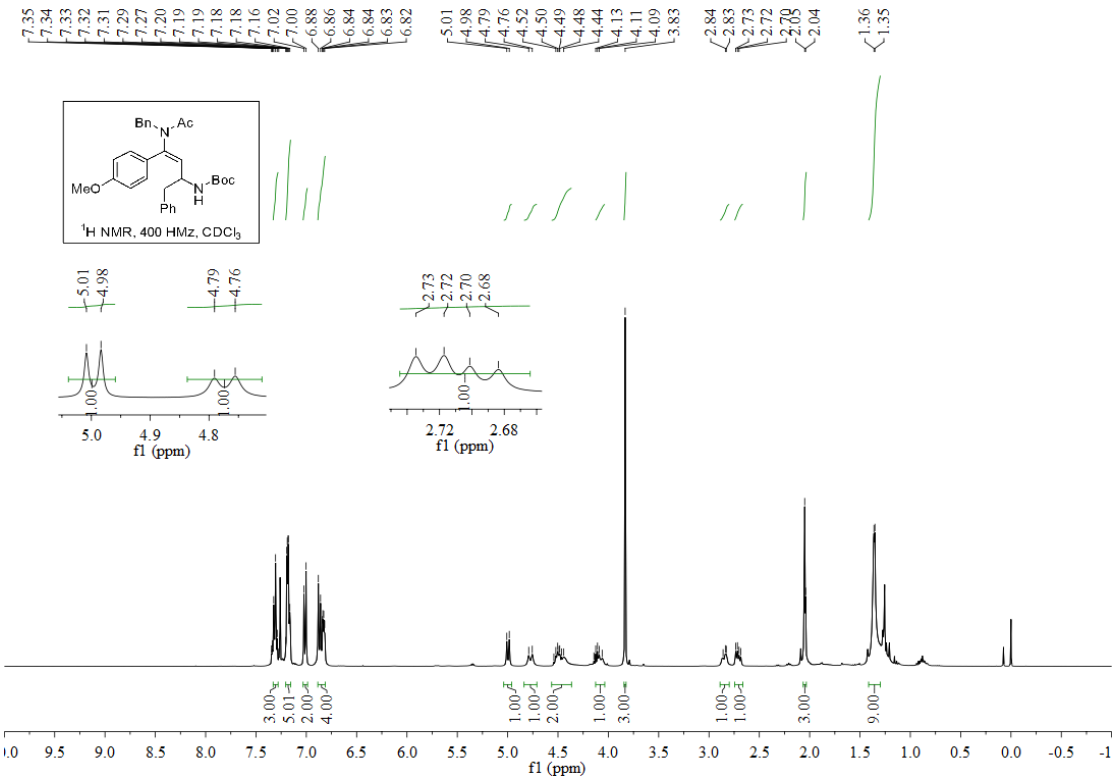
^{1}H NMR spectrum of compound **8**



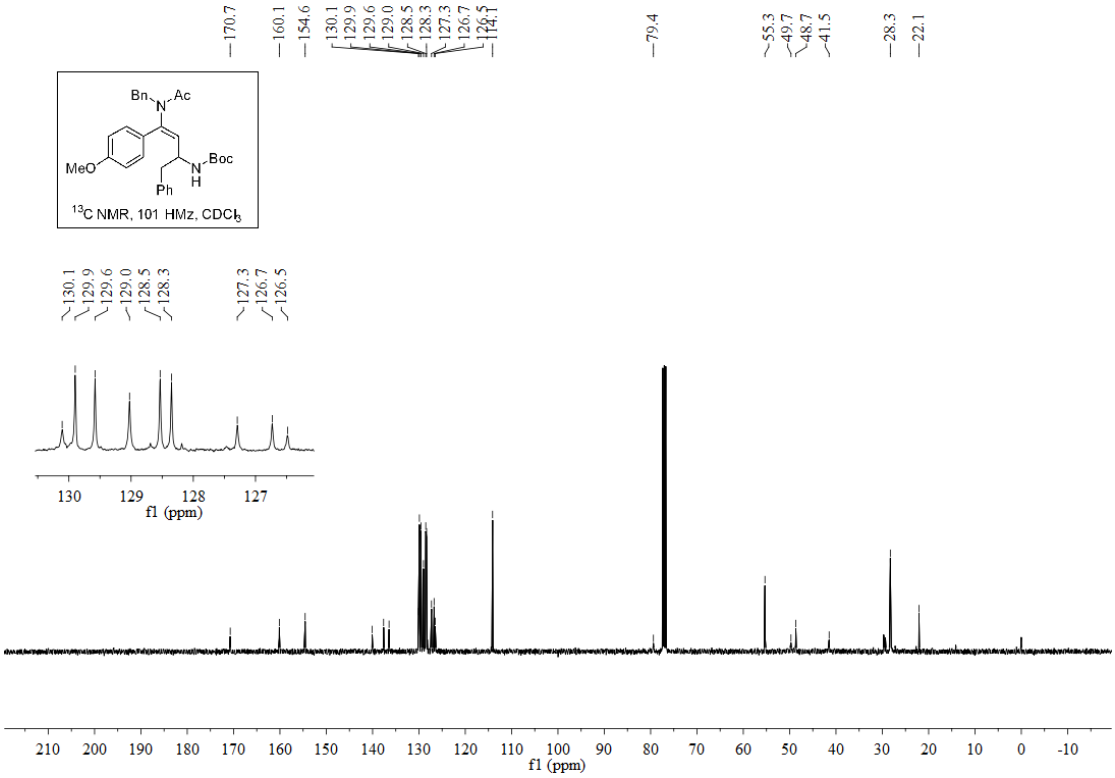
^{13}C NMR spectrum of compound **8**



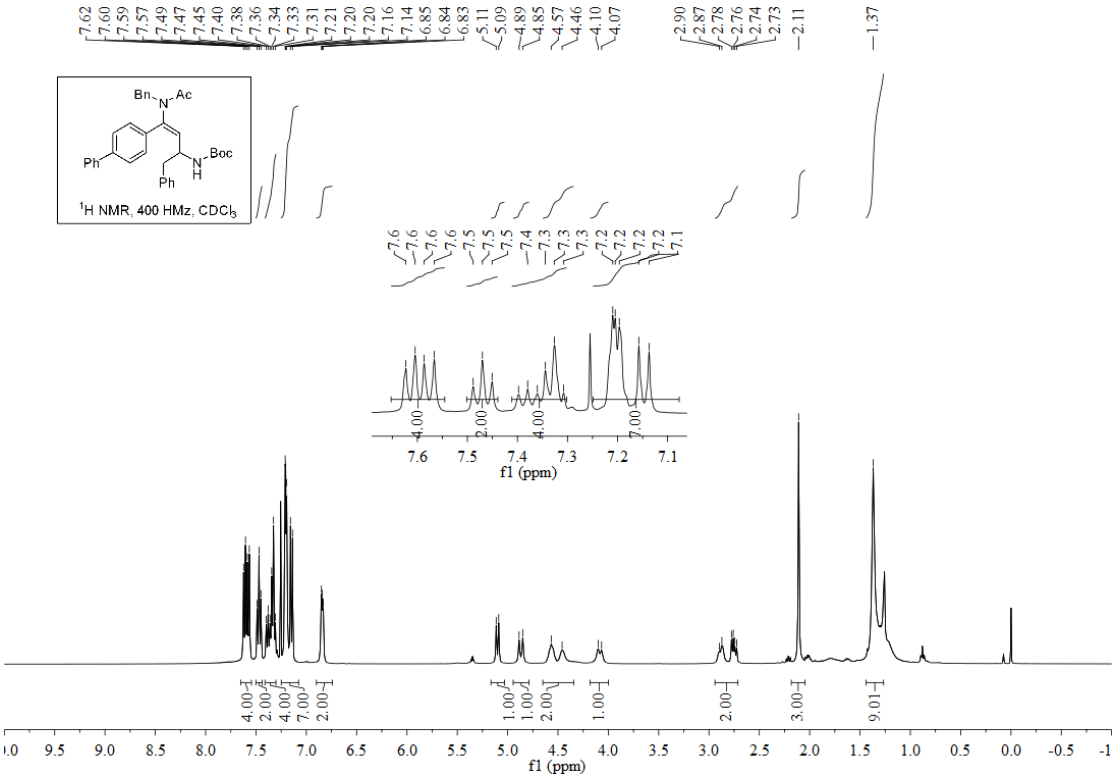
^{1}H NMR spectrum of compound **9**



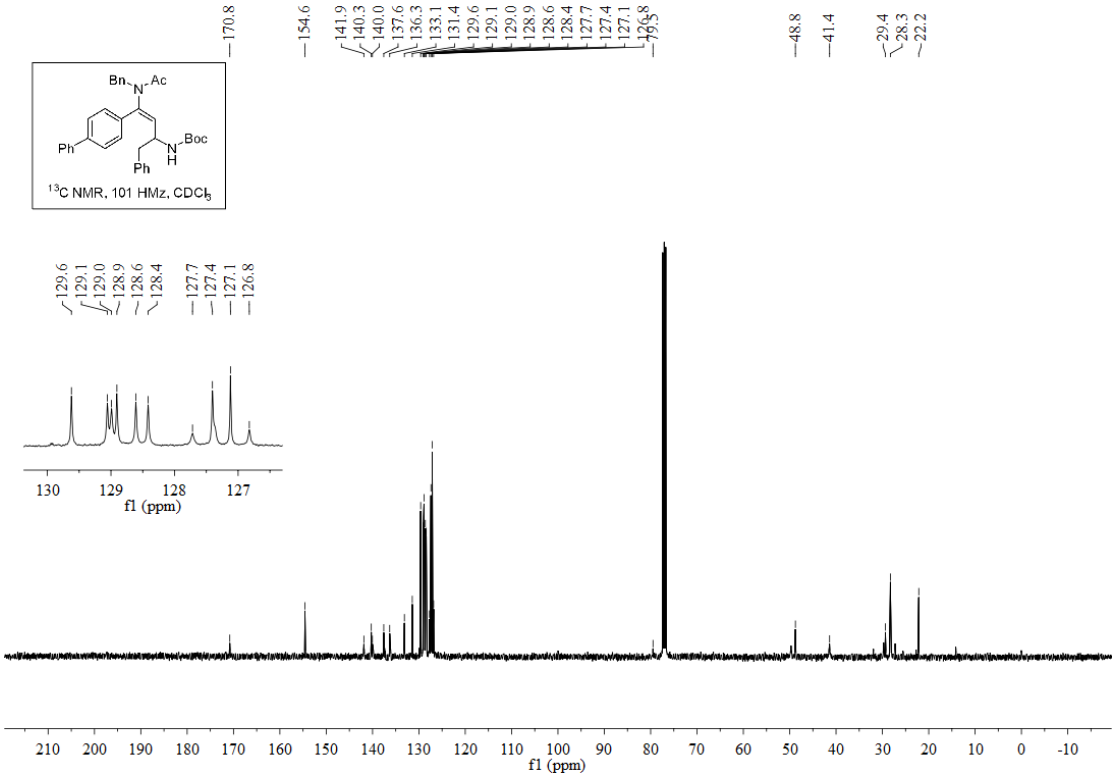
^{13}C NMR spectrum of compound **9**



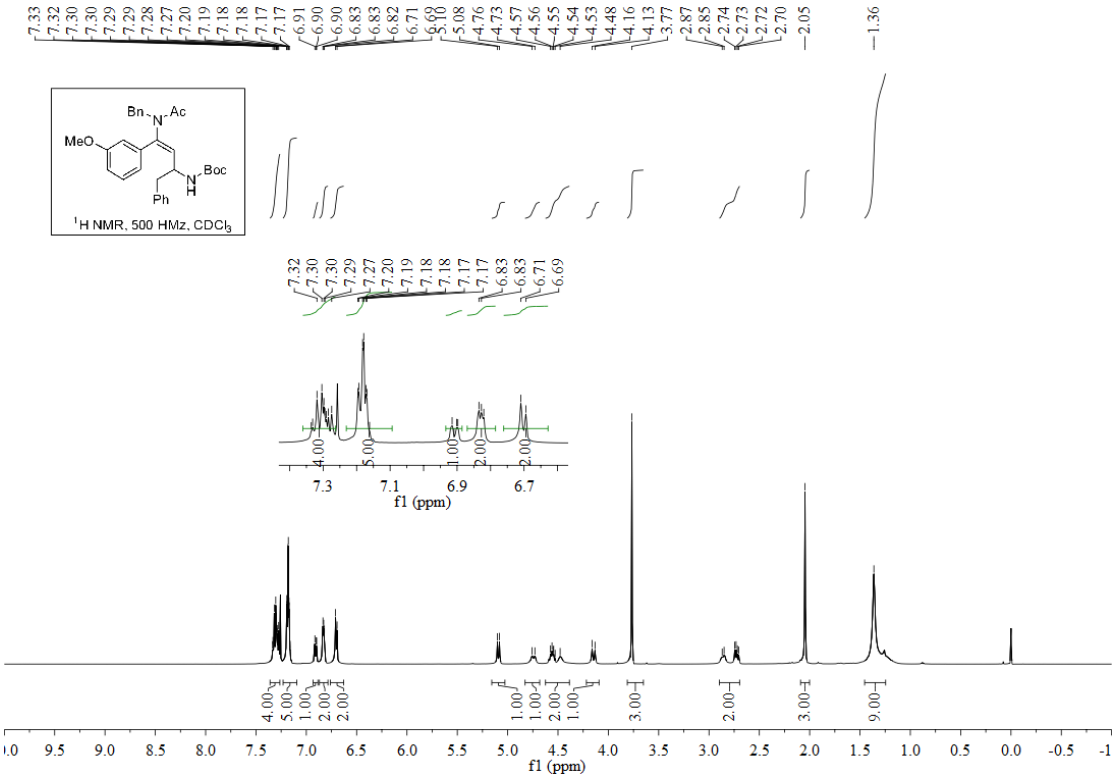
^{1}H NMR spectrum of compound **10**



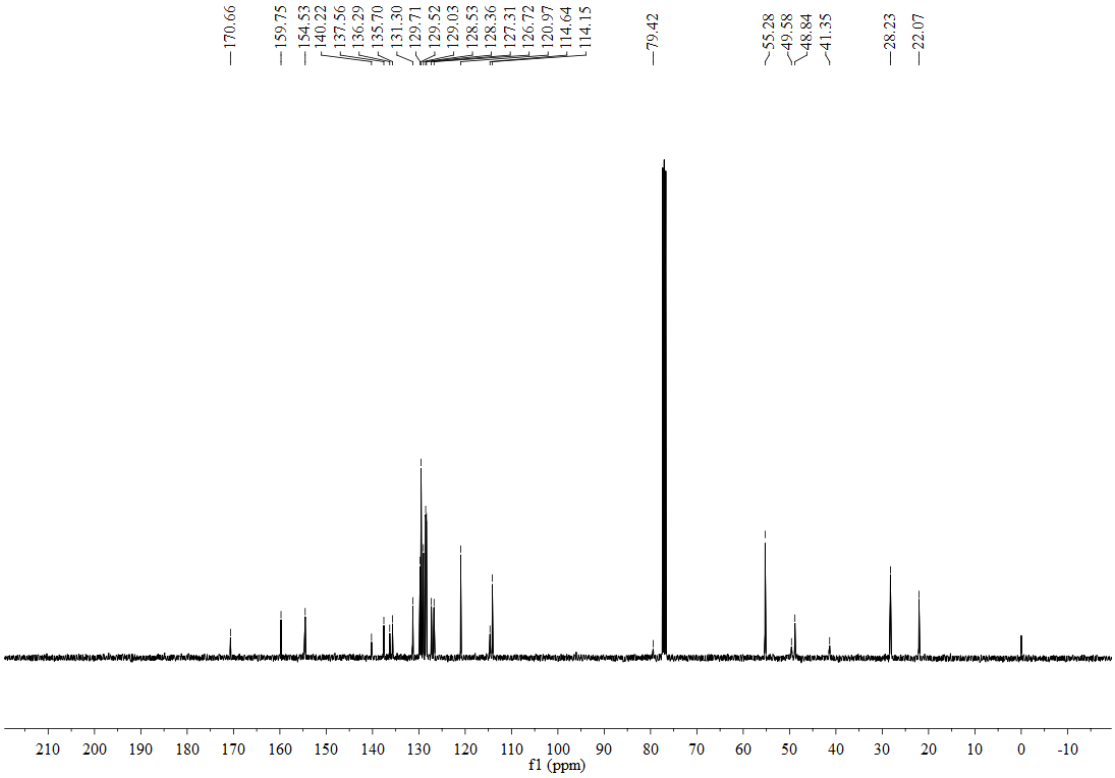
^{13}C NMR spectrum of compound **10**



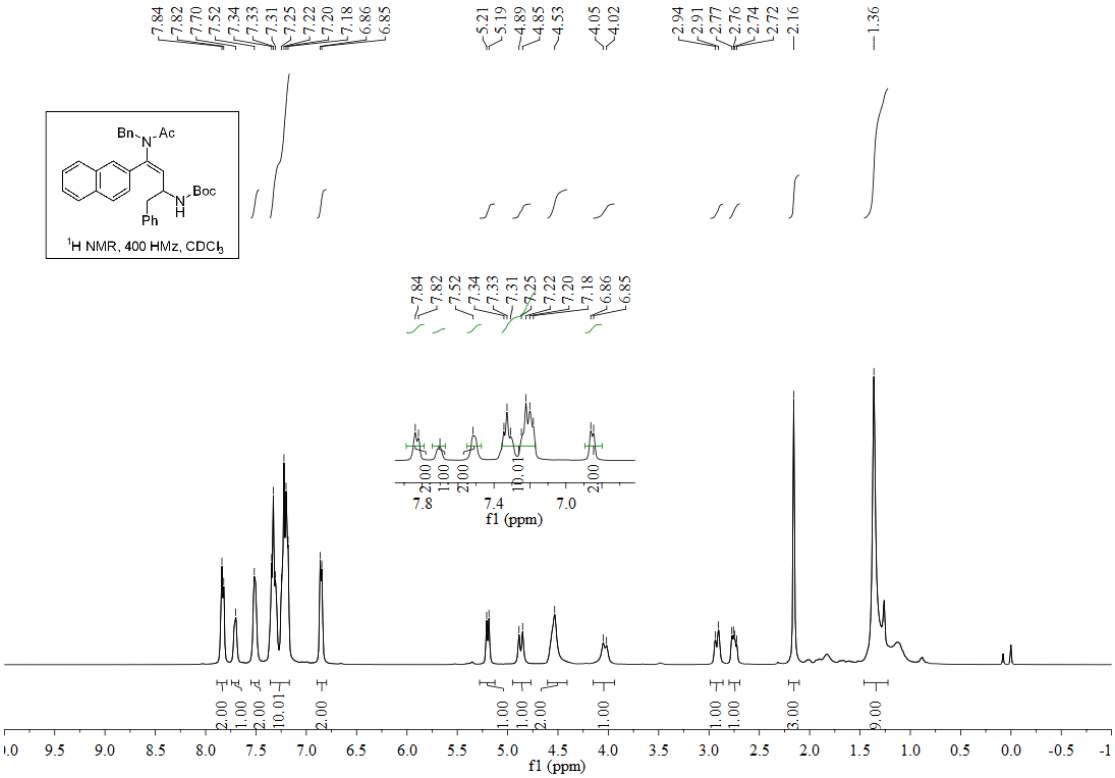
^{1}H NMR spectrum of compound **11**



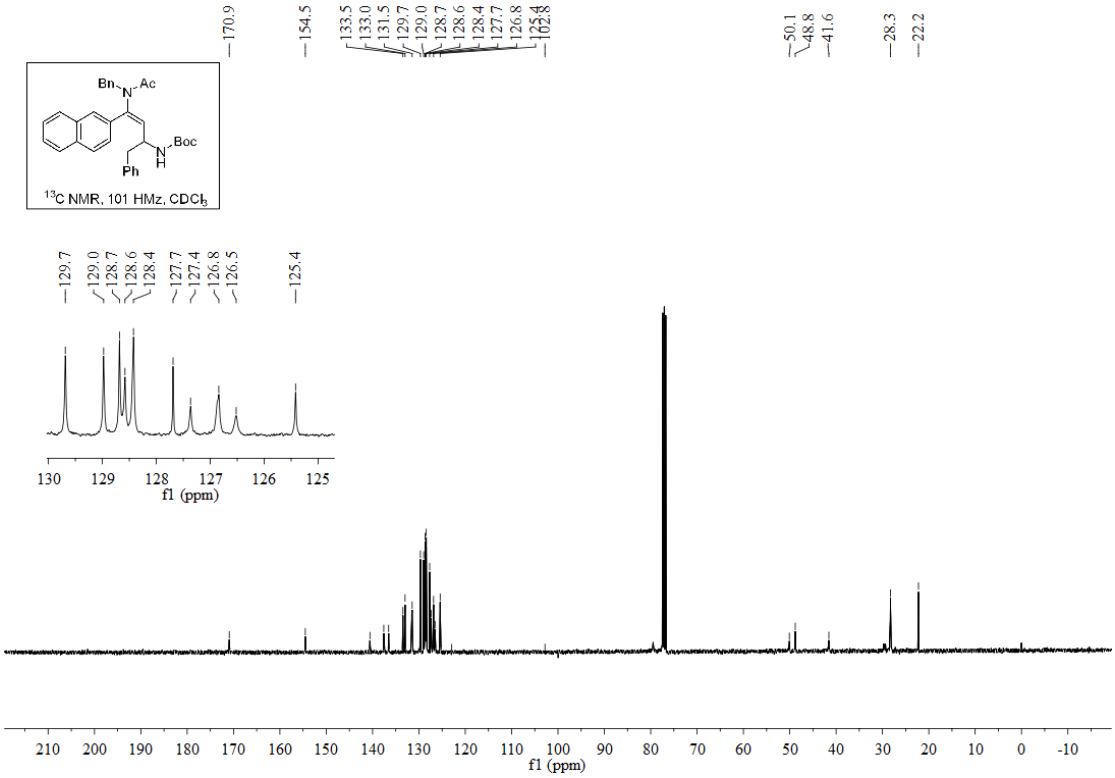
^{13}C NMR spectrum of compound **11**



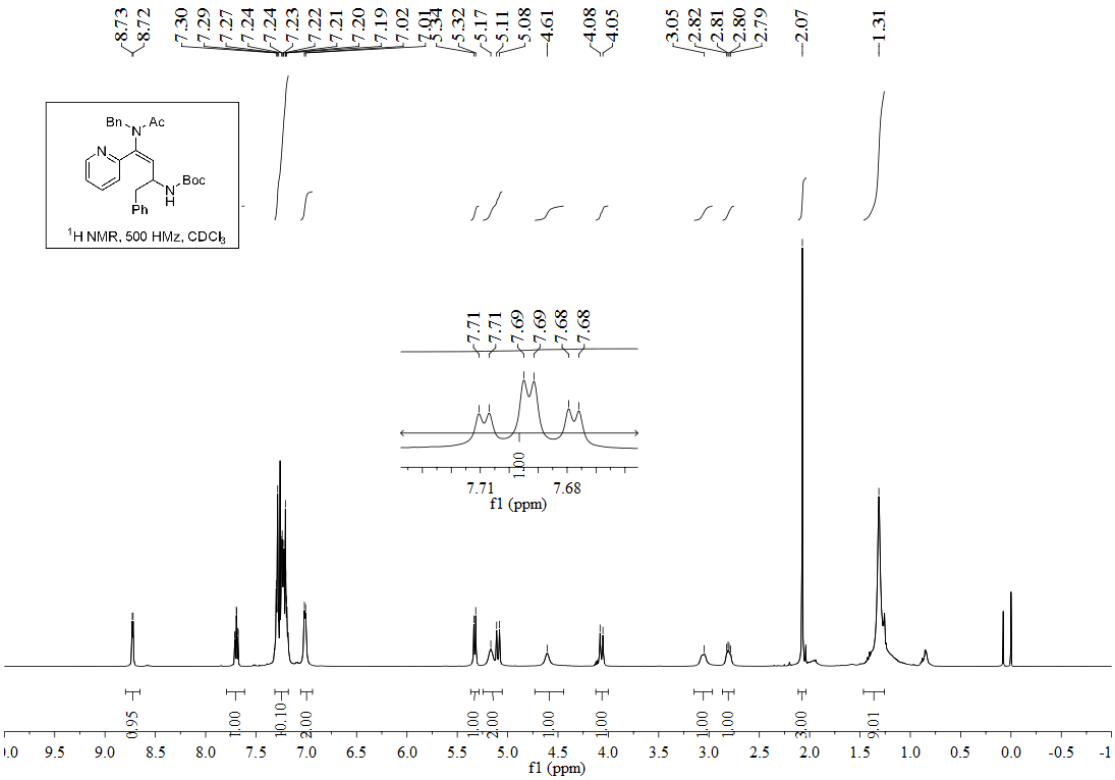
^{1}H NMR spectrum of compound **12**



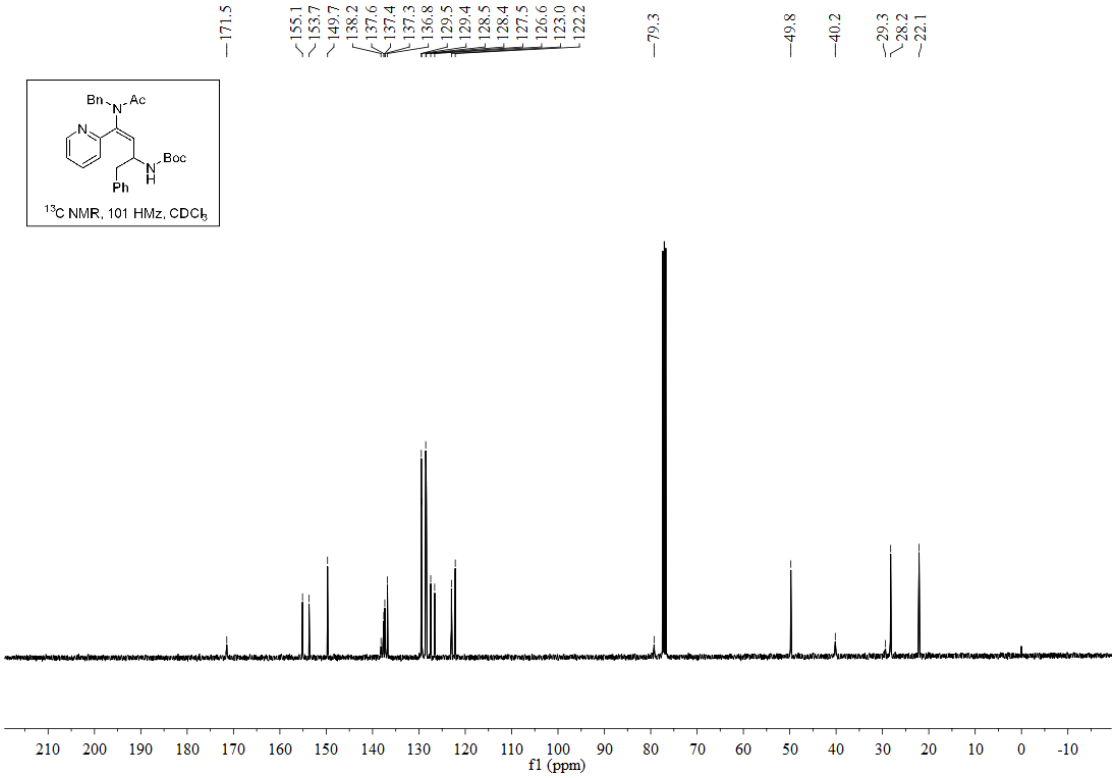
^{13}C NMR spectrum of compound **12**



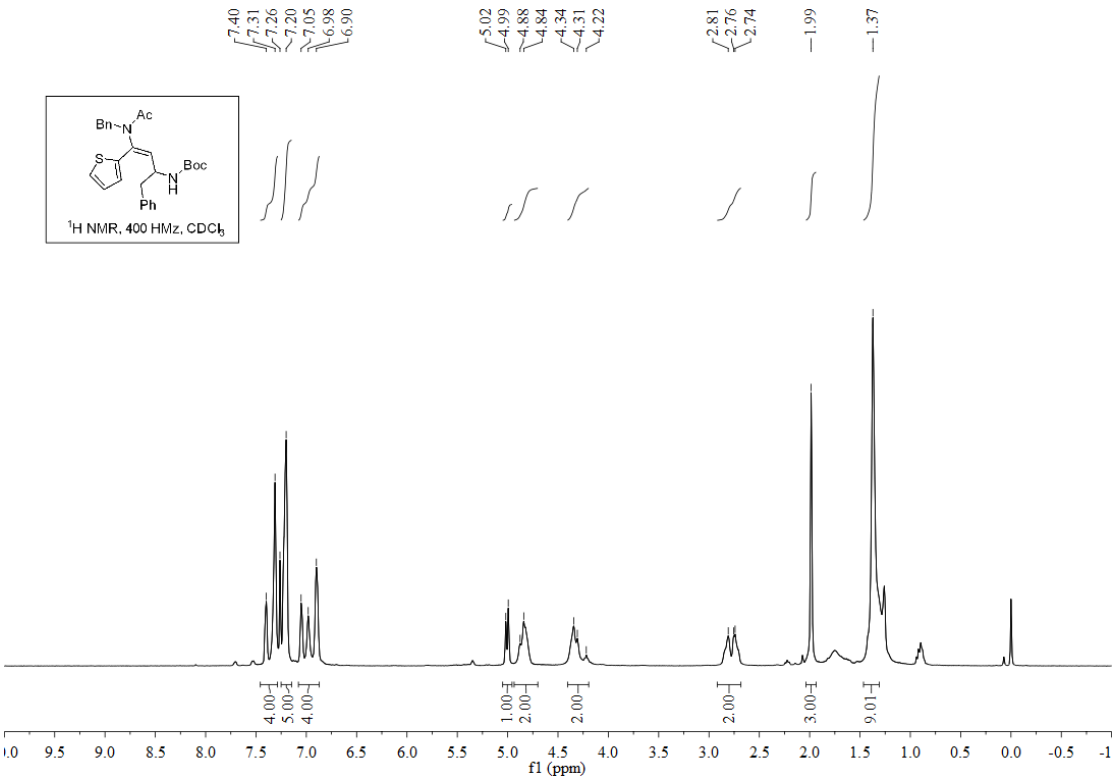
^{1}H NMR spectrum of compound **13**



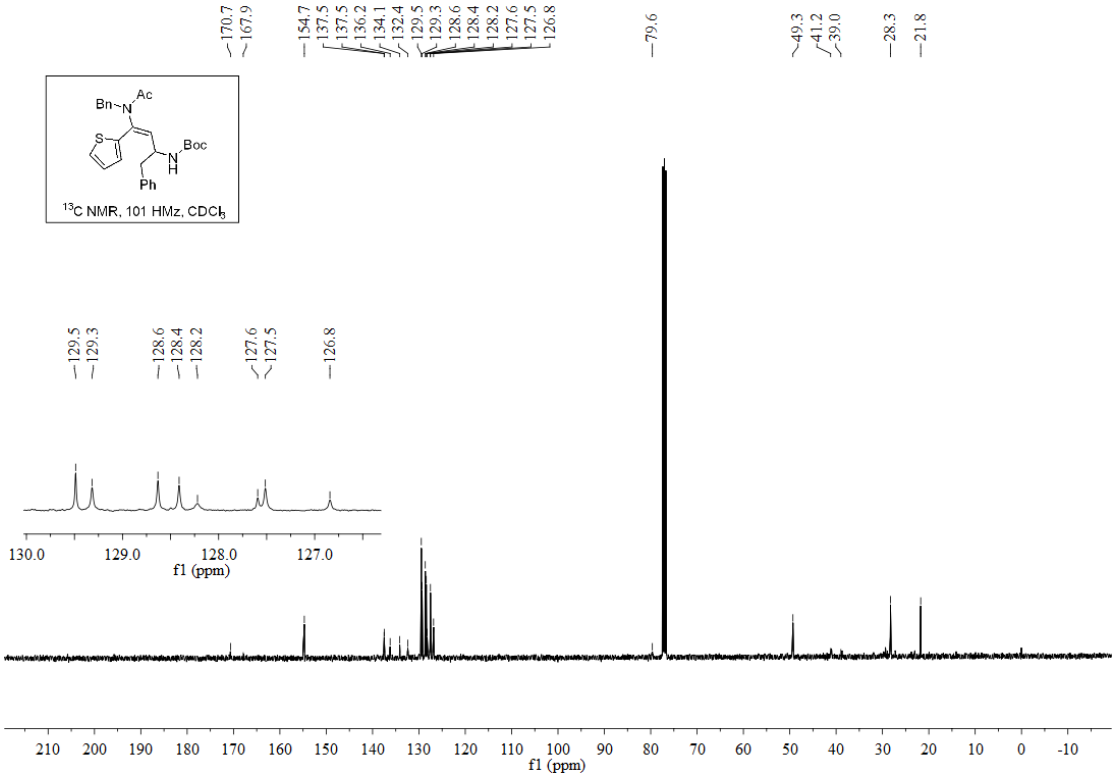
^{13}C NMR spectrum of compound **13**



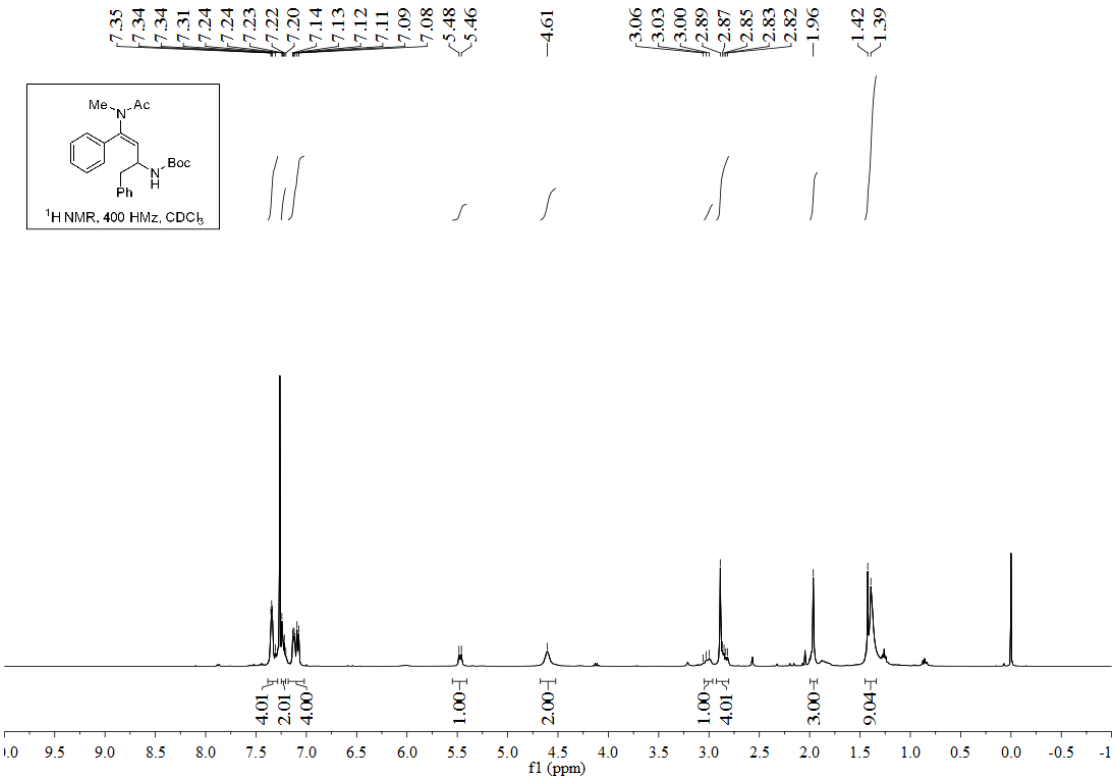
^{1}H NMR spectrum of compound **14**



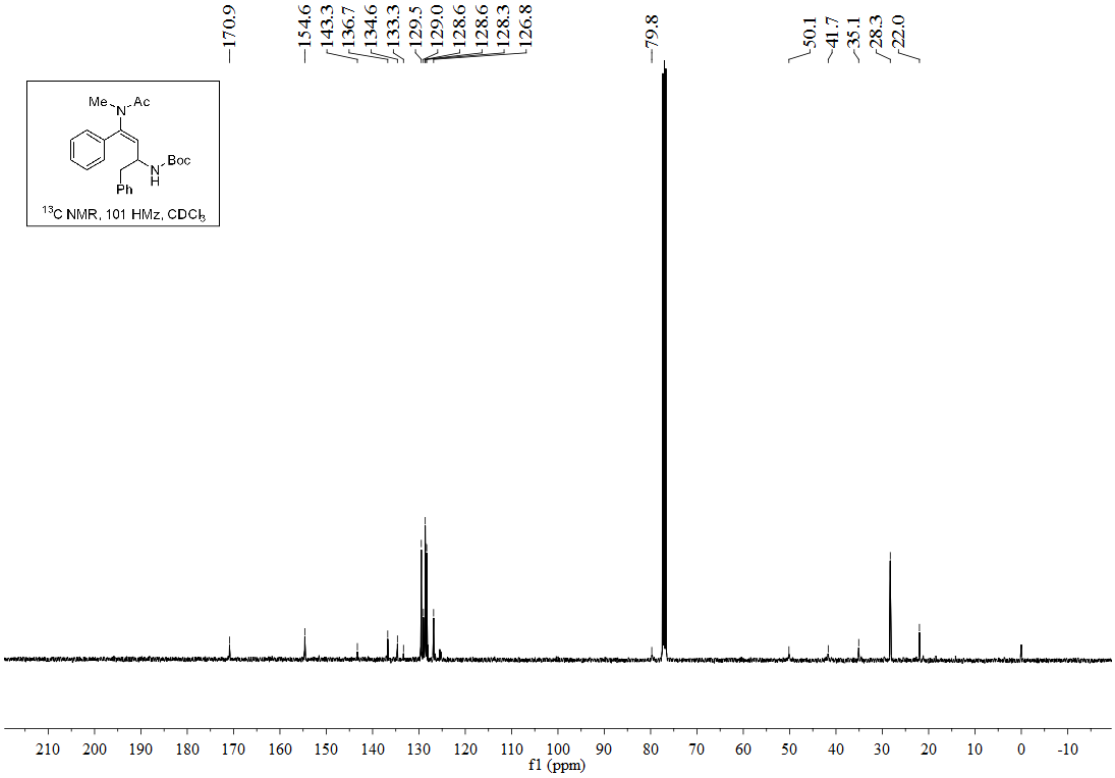
^{13}C NMR spectrum of compound **14**



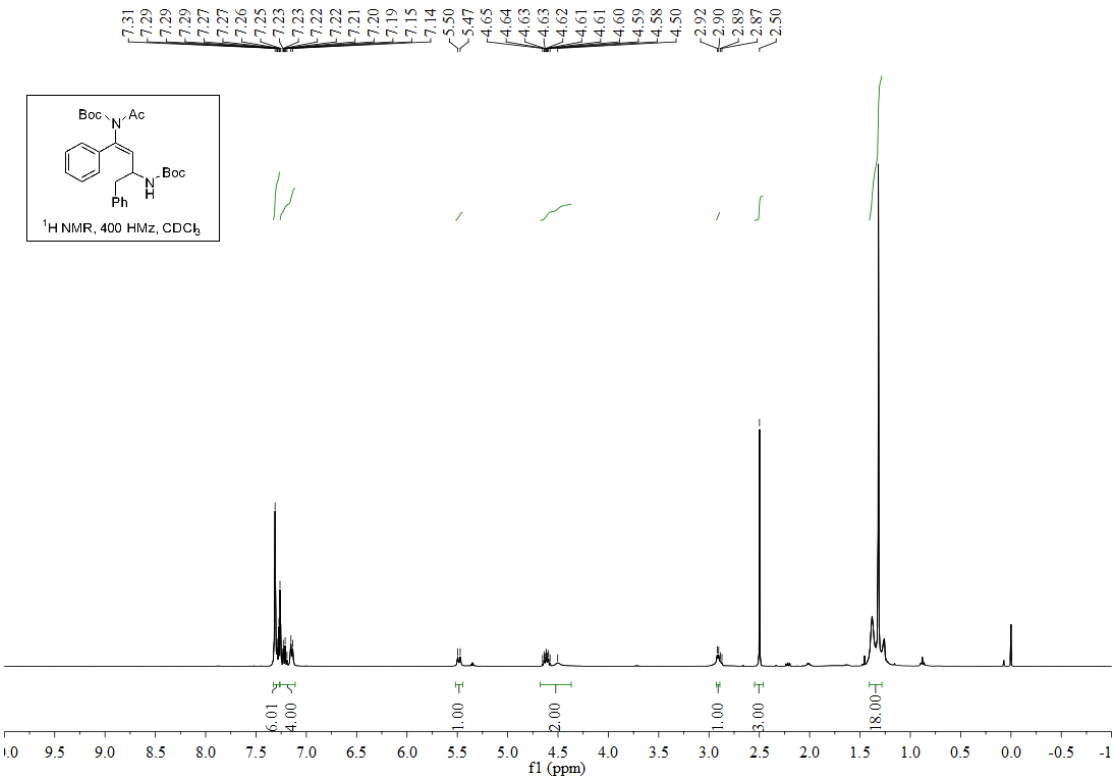
^{1}H NMR spectrum of compound **15**



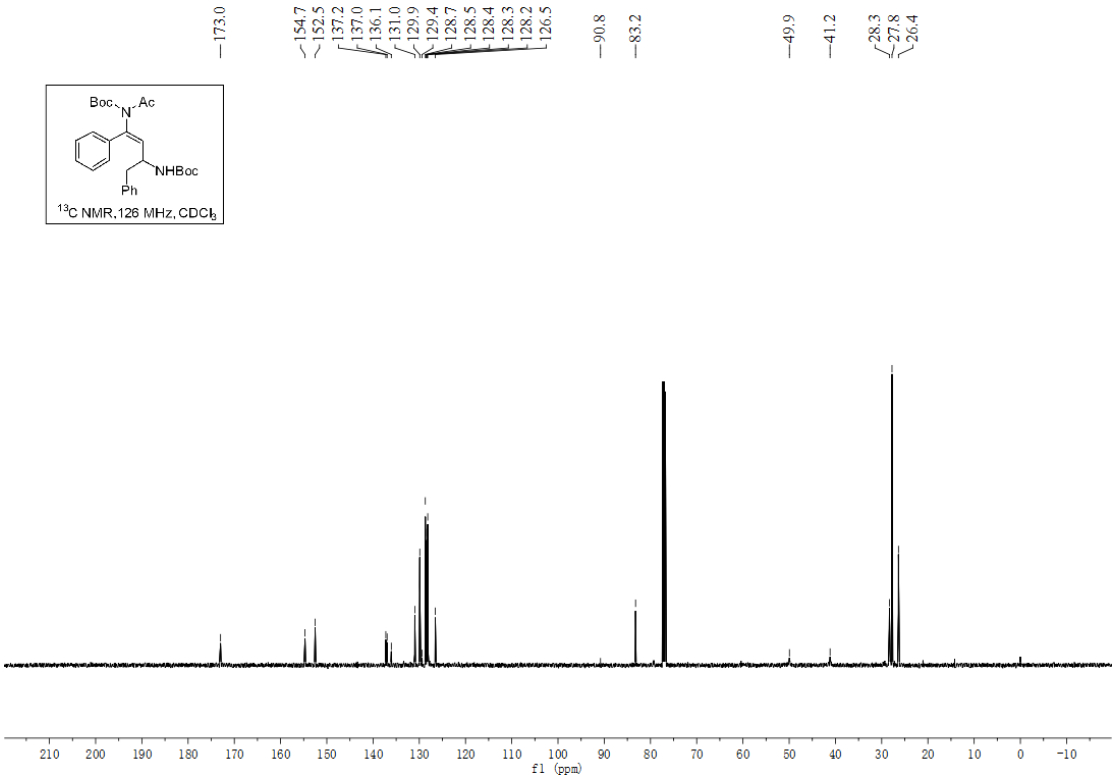
^{13}C NMR spectrum of compound **15**



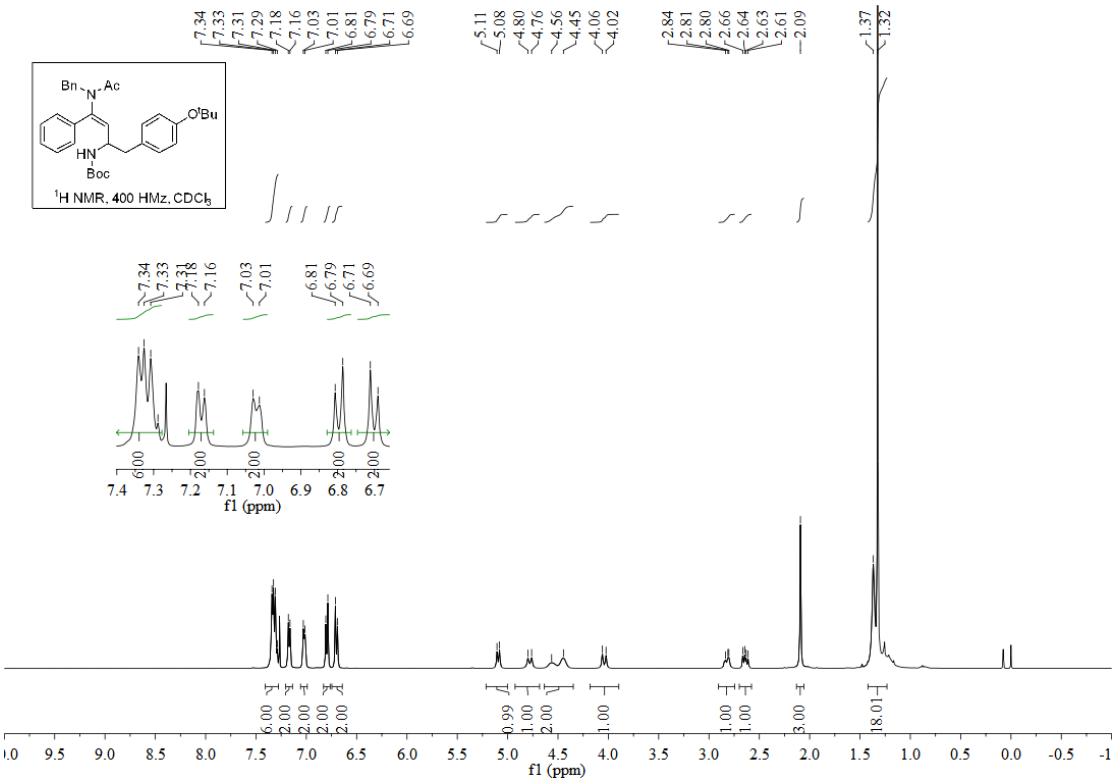
^{1}H NMR spectrum of compound **16**



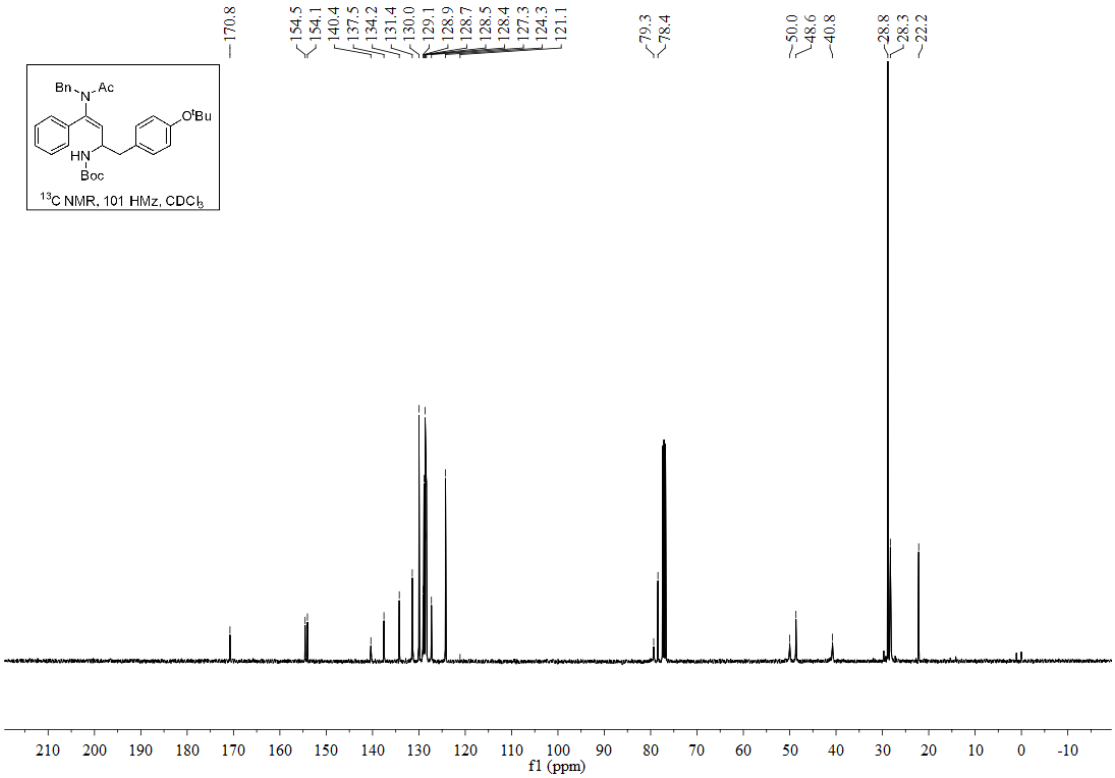
^{13}C NMR spectrum of compound **16**



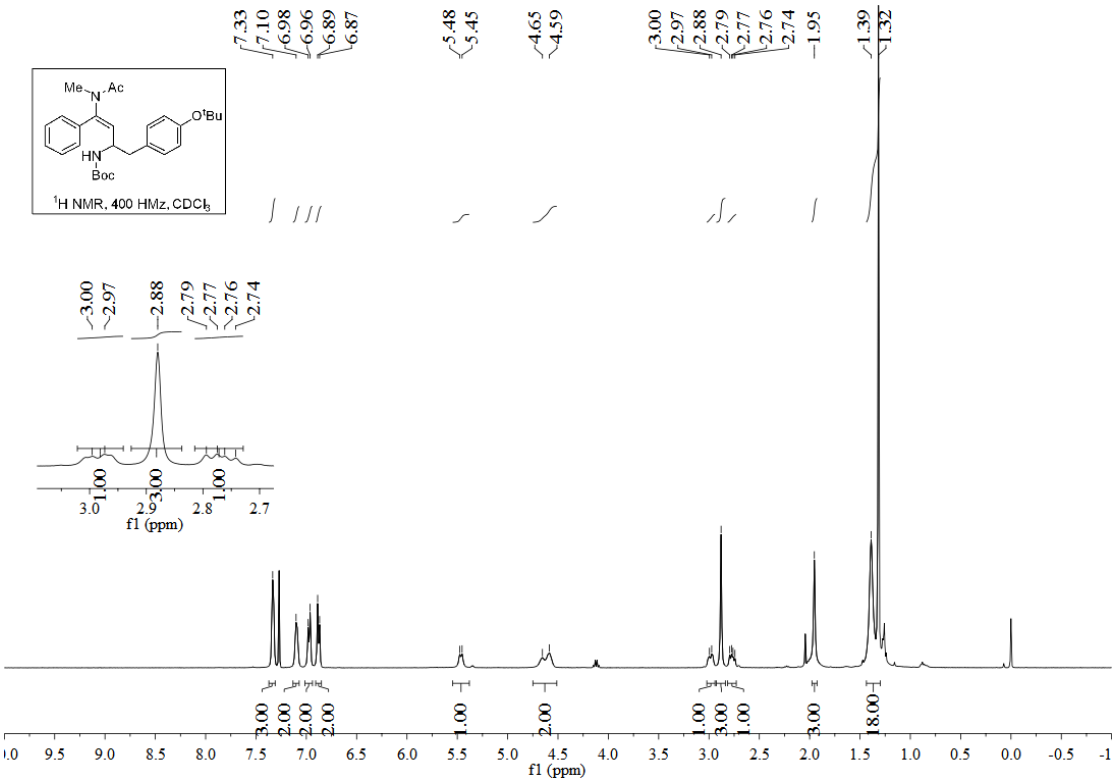
^{1}H NMR spectrum of compound **17**



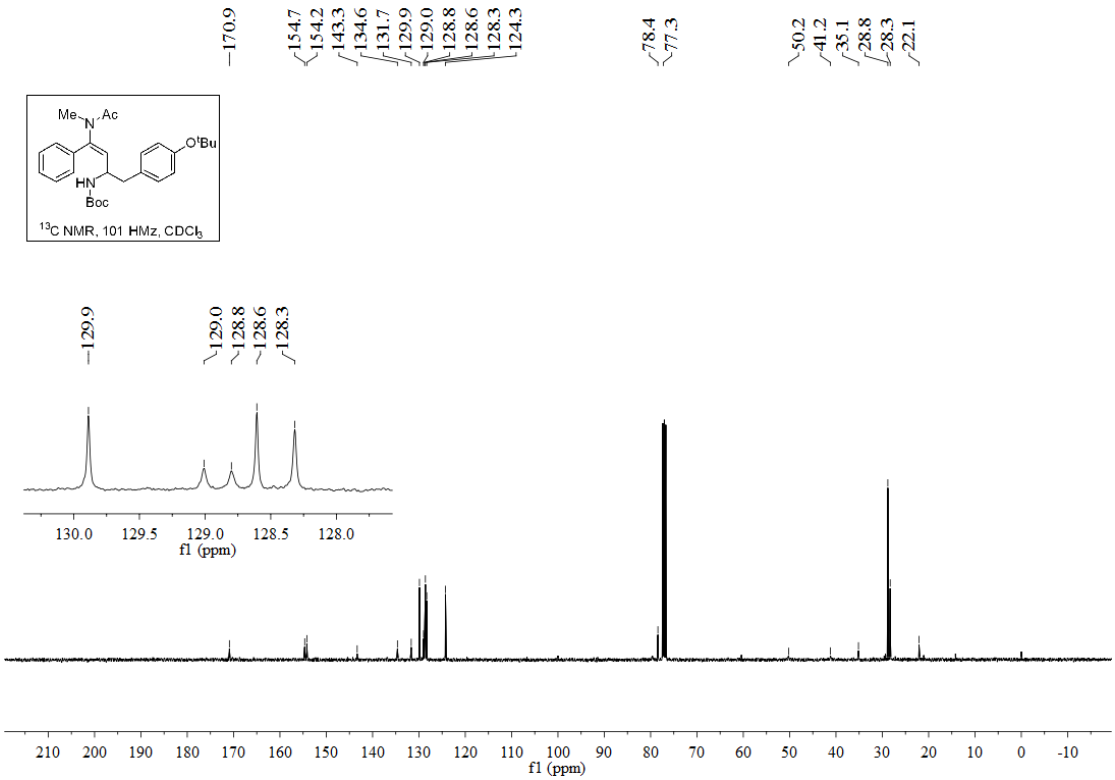
^{13}C NMR spectrum of compound **17**



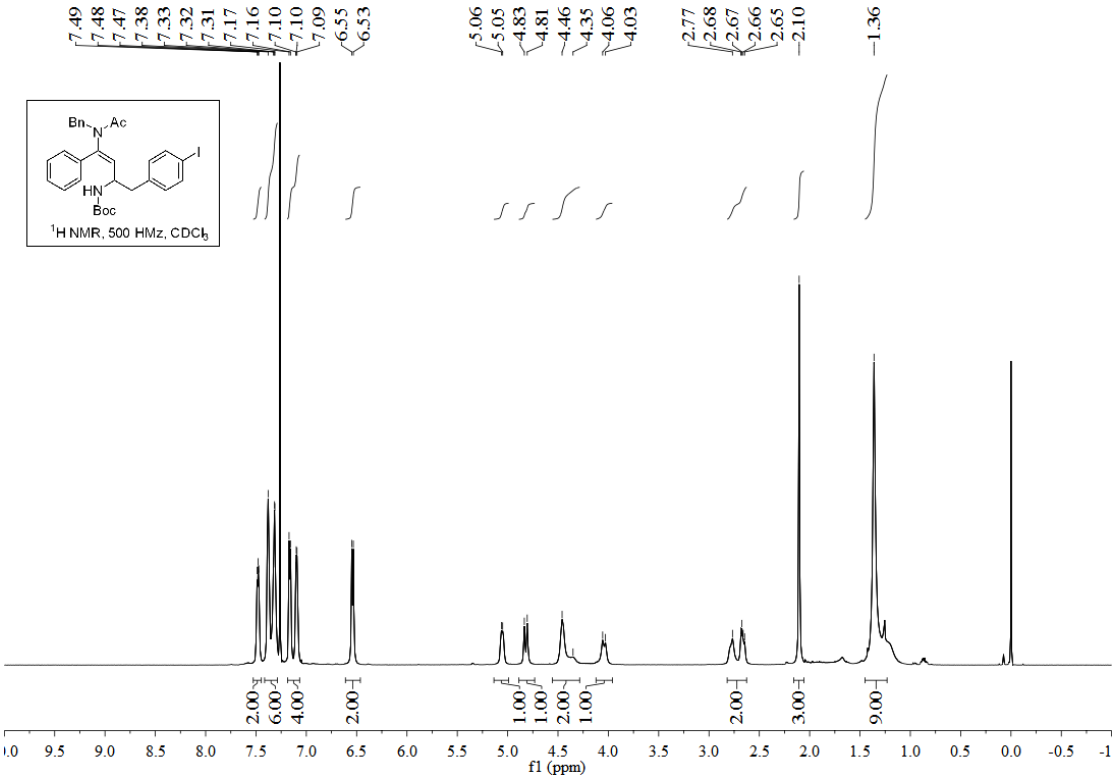
^{1}H NMR spectrum of compound **18**



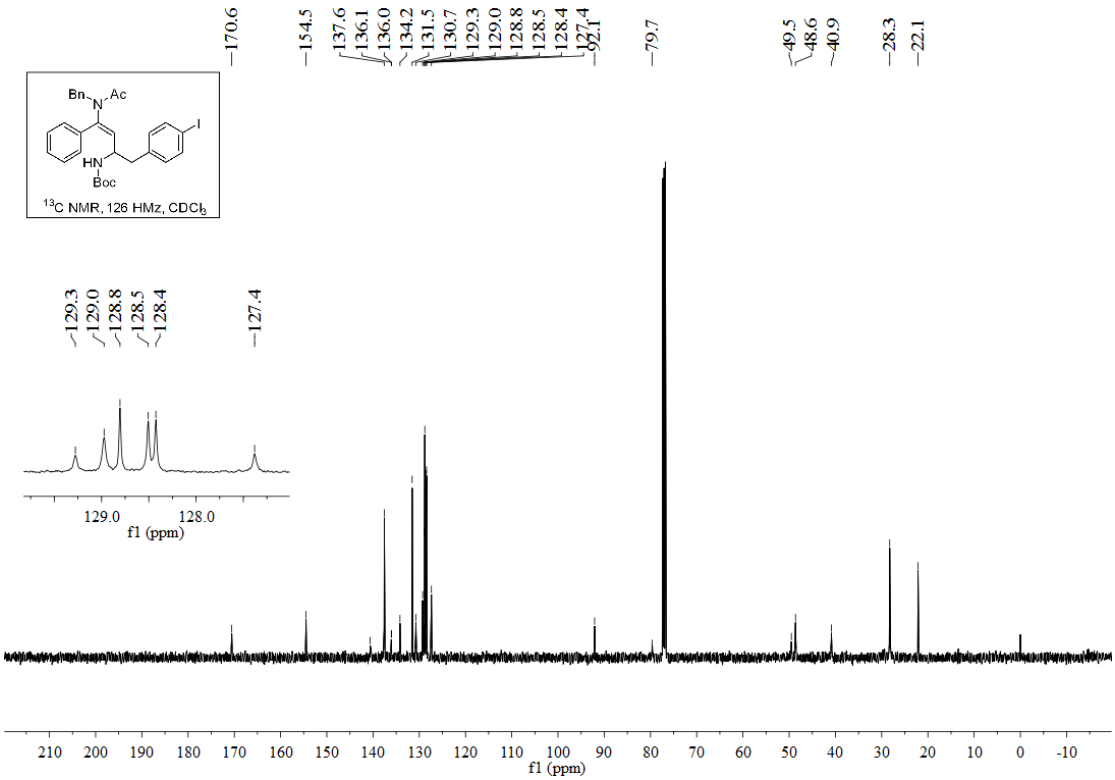
^{13}C NMR spectrum of compound **18**



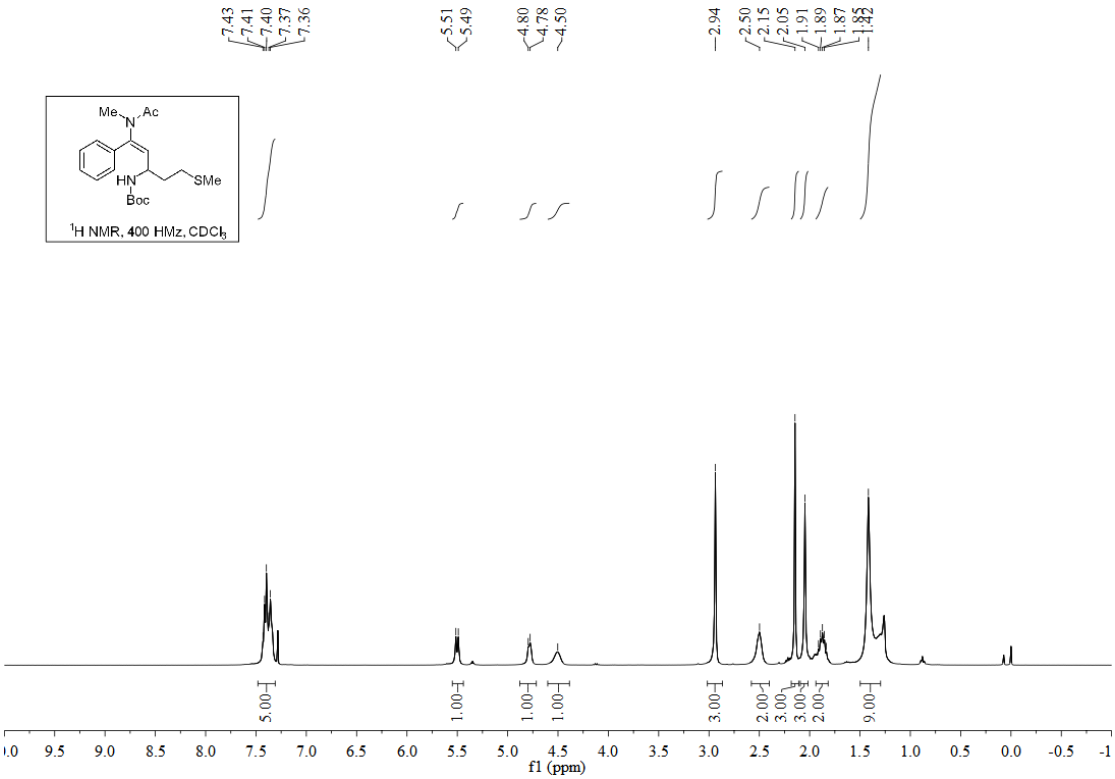
^{1}H NMR spectrum of compound **19**



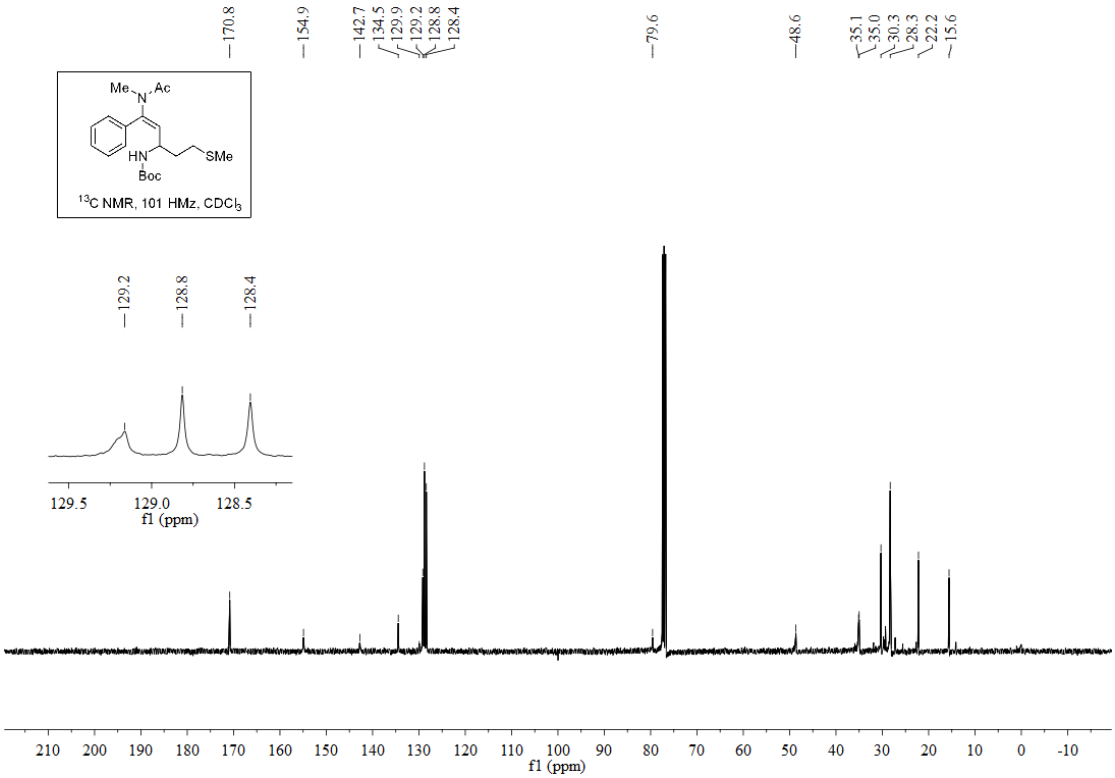
^{13}C NMR spectrum of compound **19**



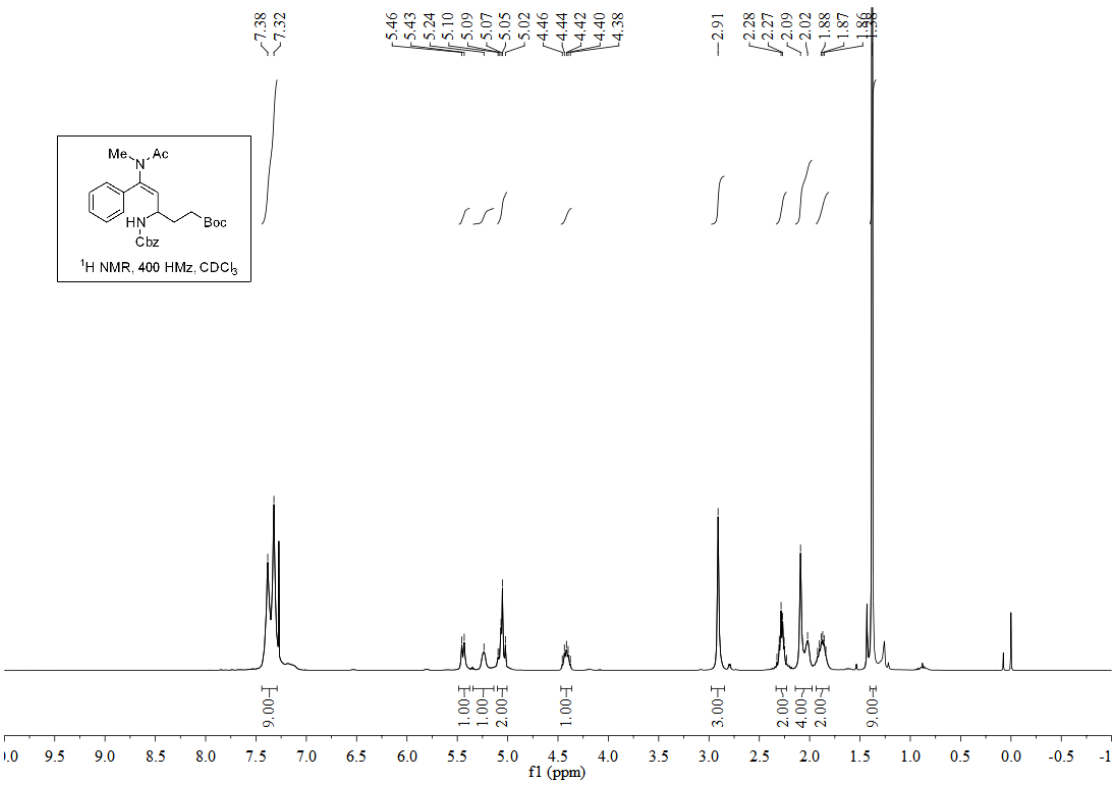
^{1}H NMR spectrum of compound **20**



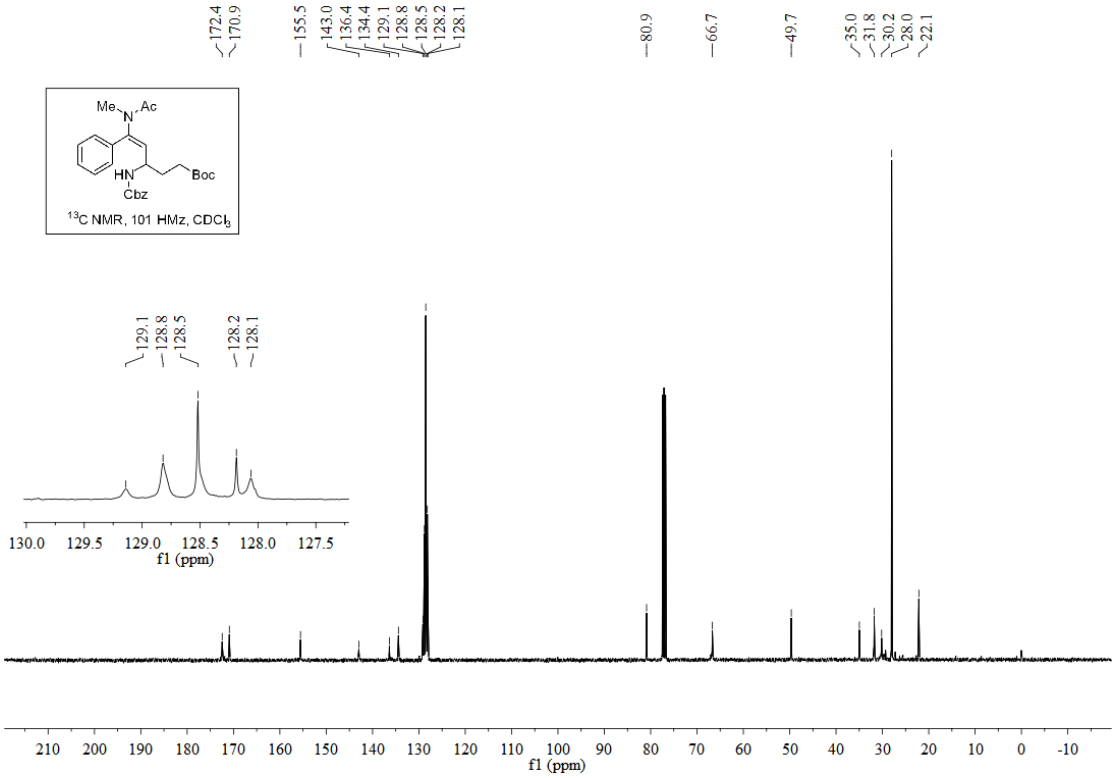
^{13}C NMR spectrum of compound **20**



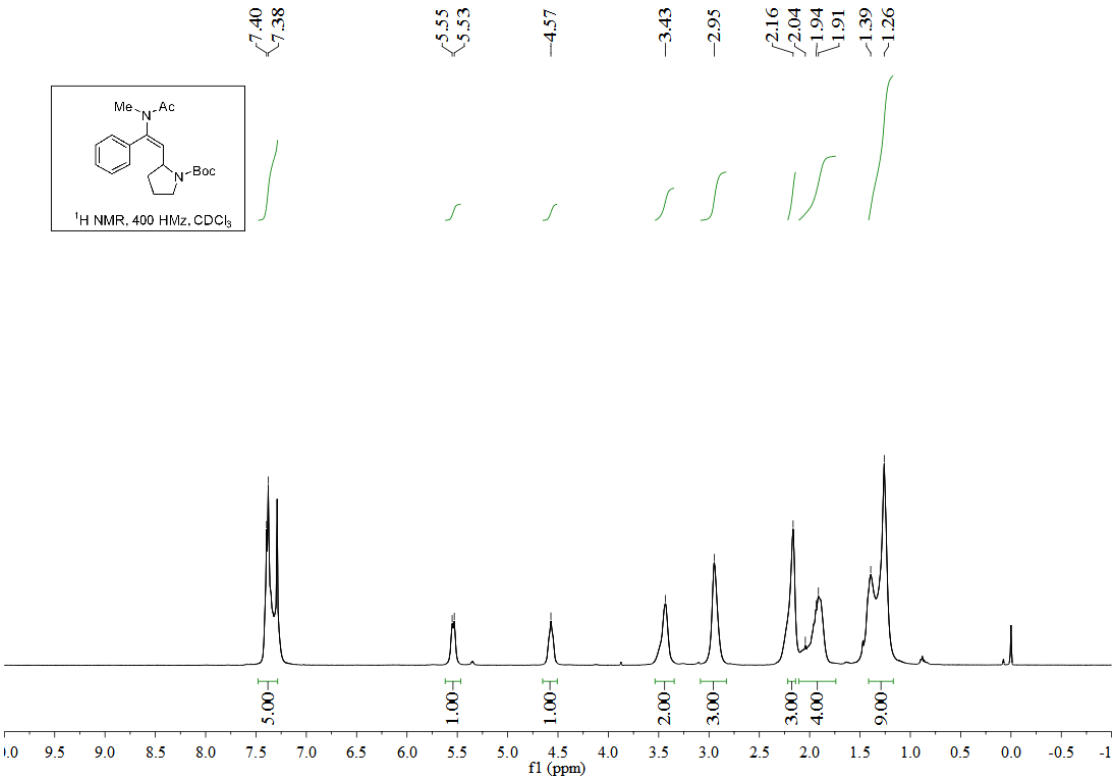
^{1}H NMR spectrum of compound **21**



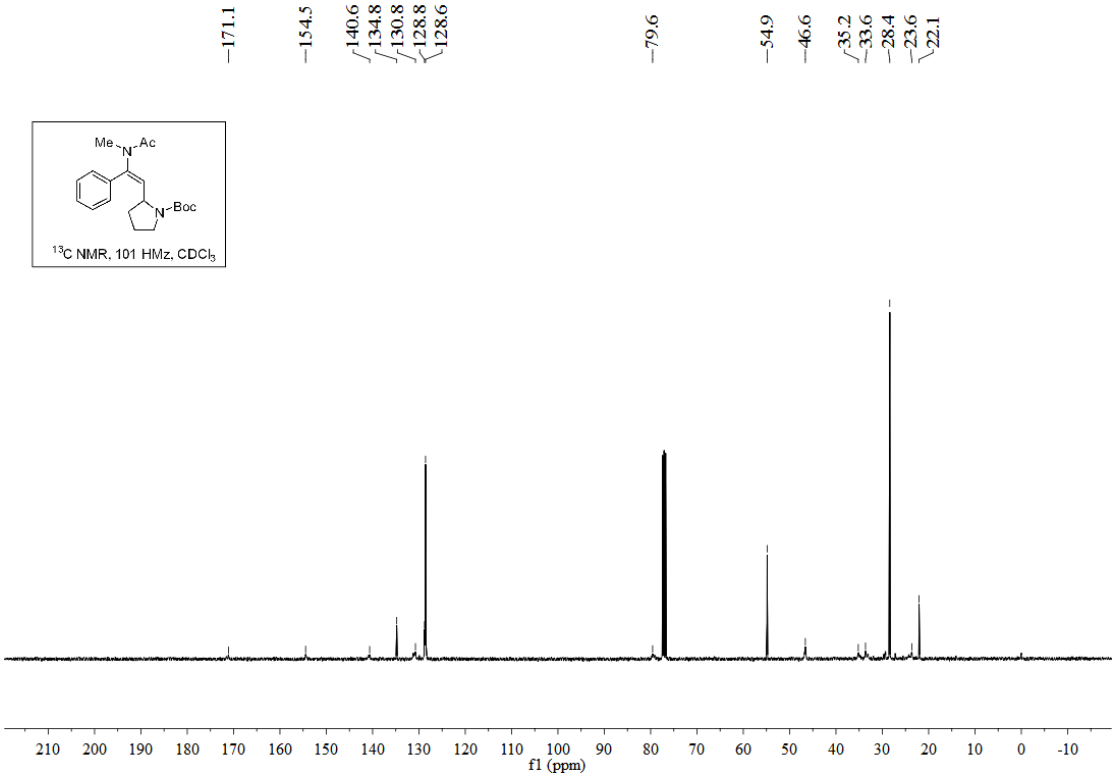
^{13}C NMR spectrum of compound **21**



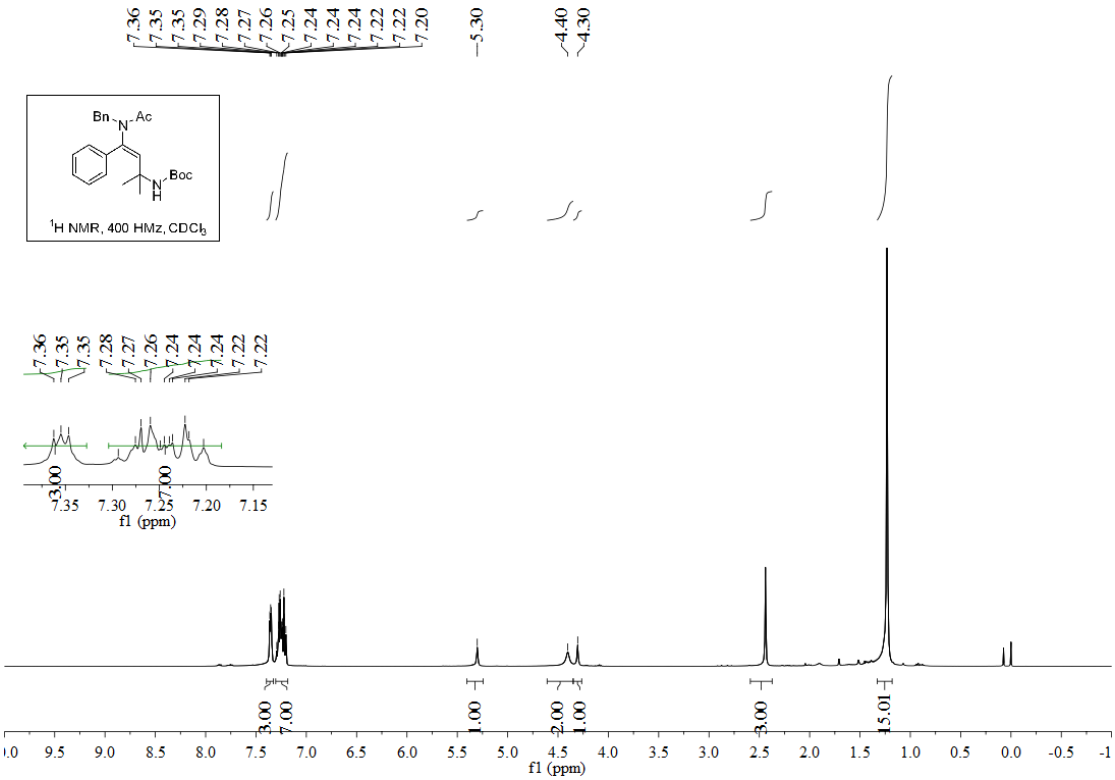
^{1}H NMR spectrum of compound **22**



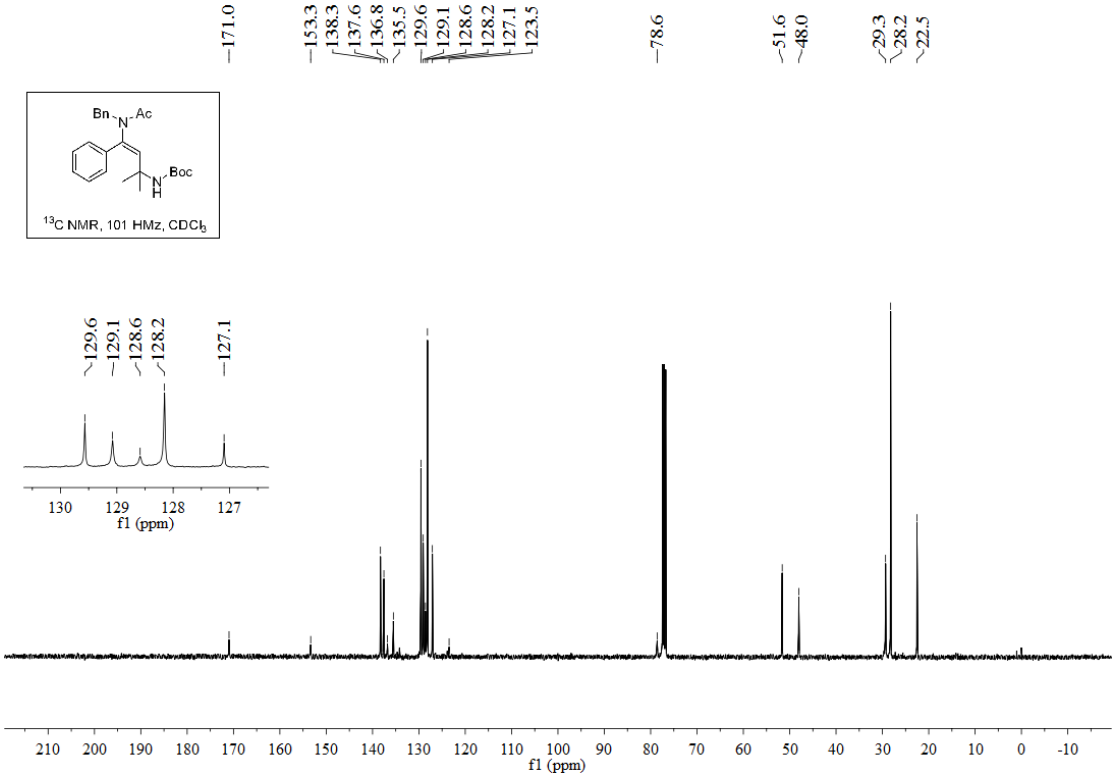
^{13}C NMR spectrum of compound **22**



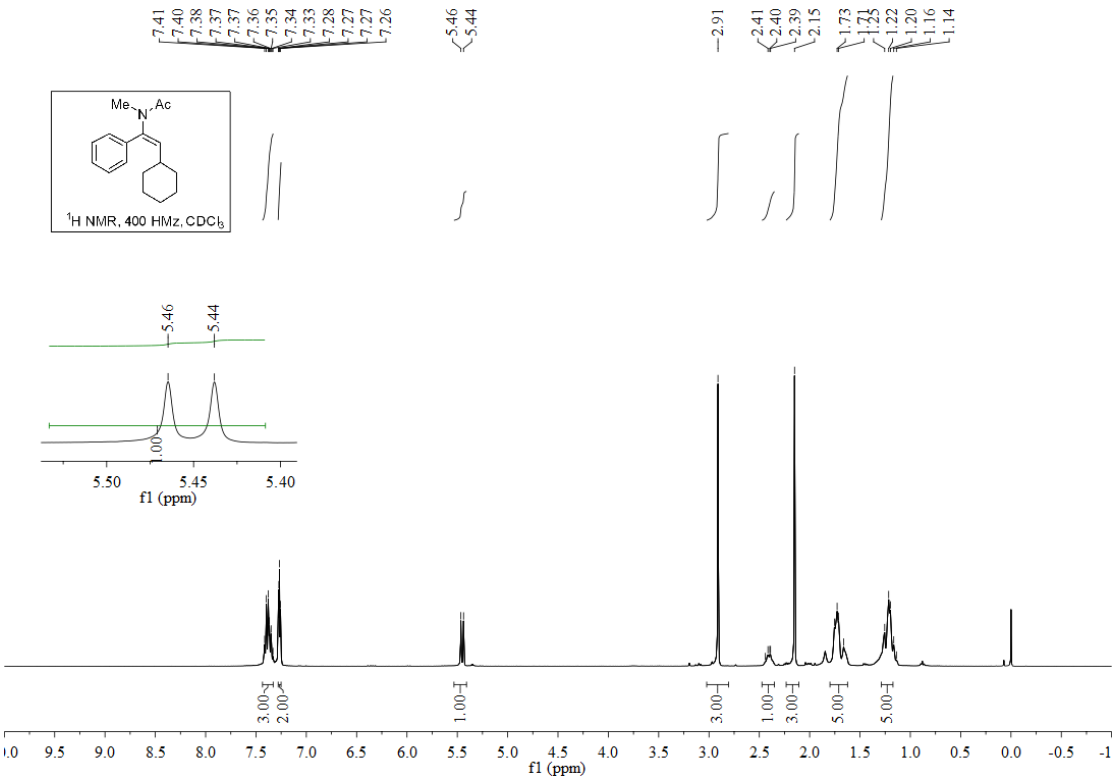
^{1}H NMR spectrum of compound **23**



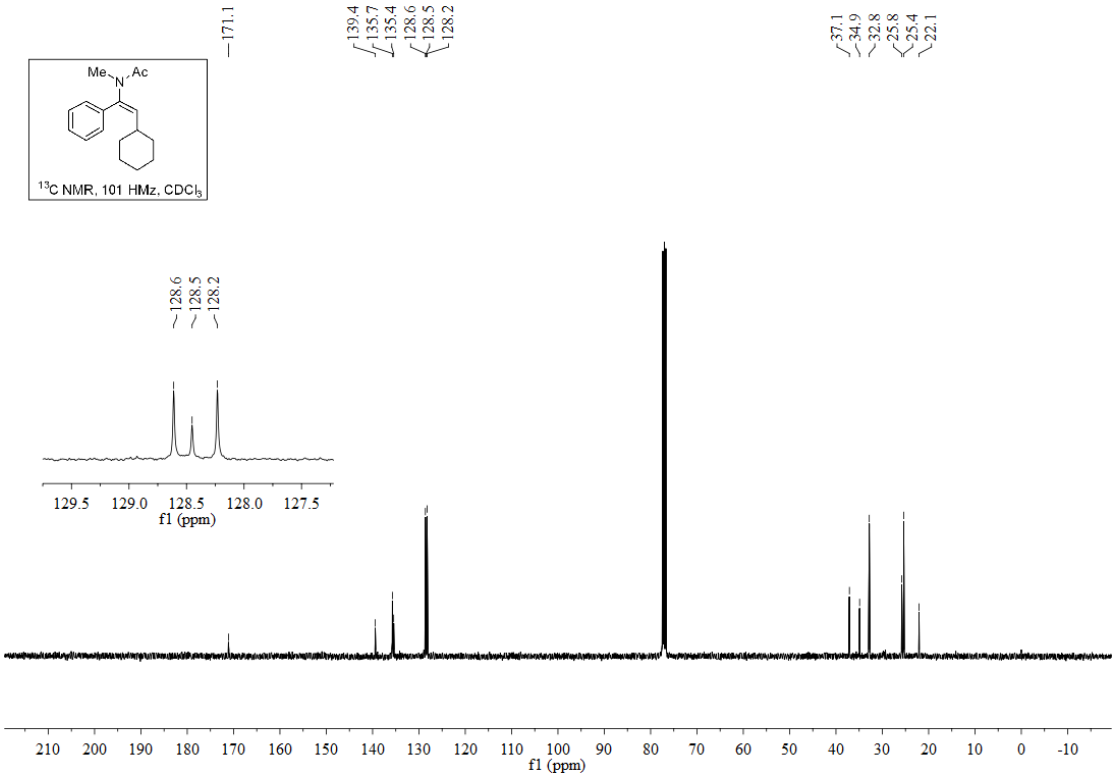
^{13}C NMR spectrum of compound **23**



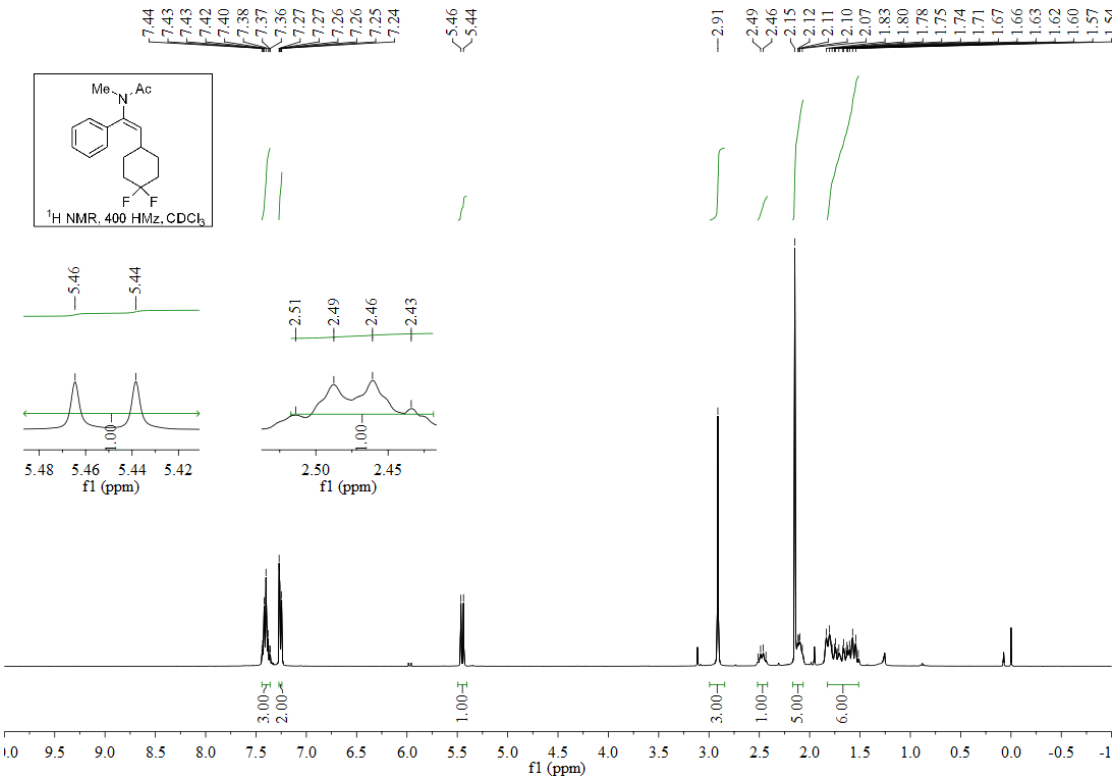
^{1}H NMR spectrum of compound **24**



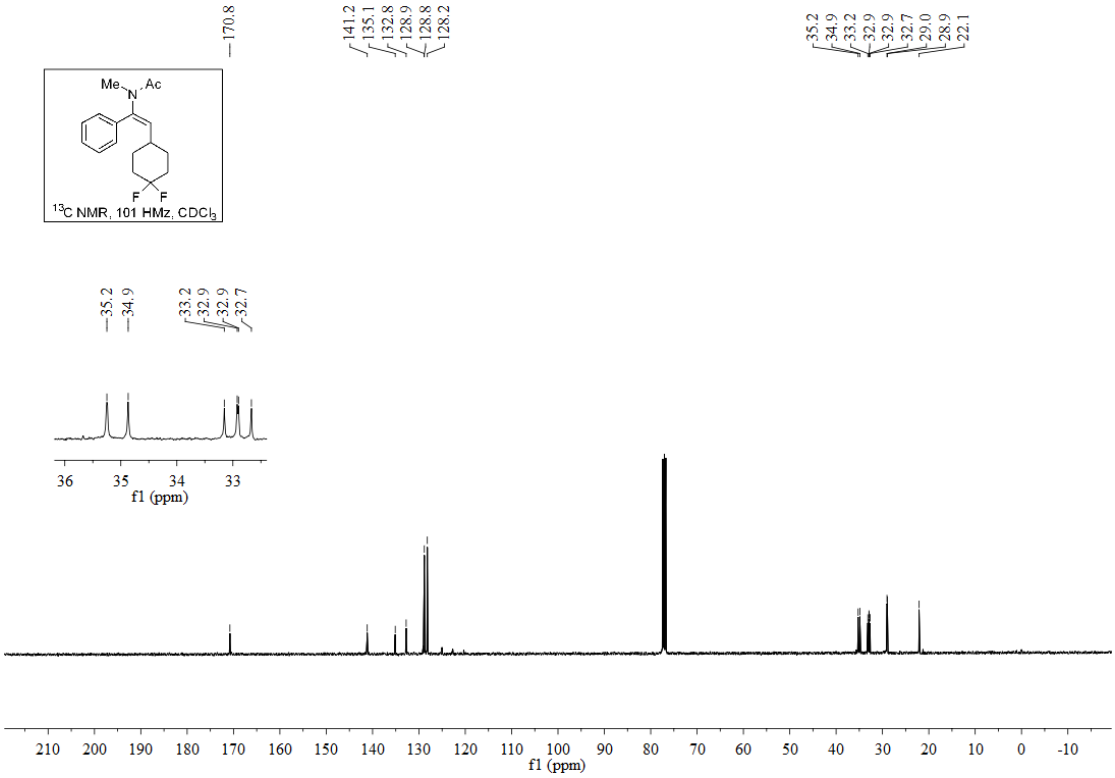
^{13}C NMR spectrum of compound **24**



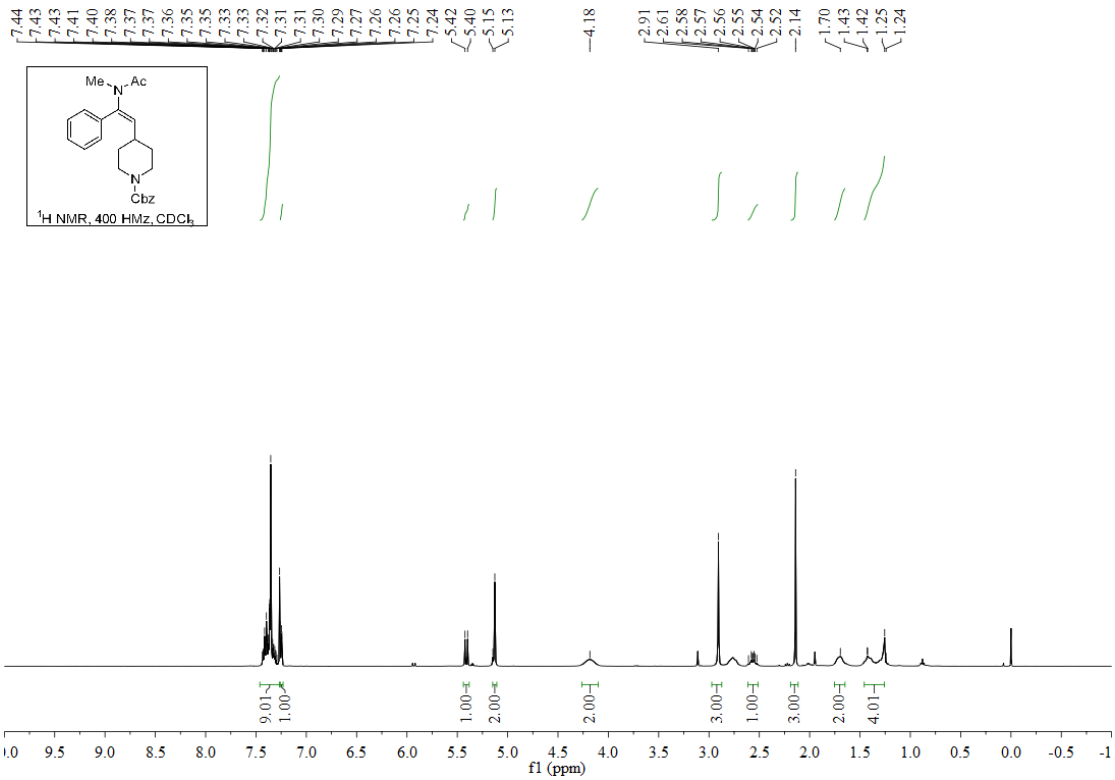
^{1}H NMR spectrum of compound **25**



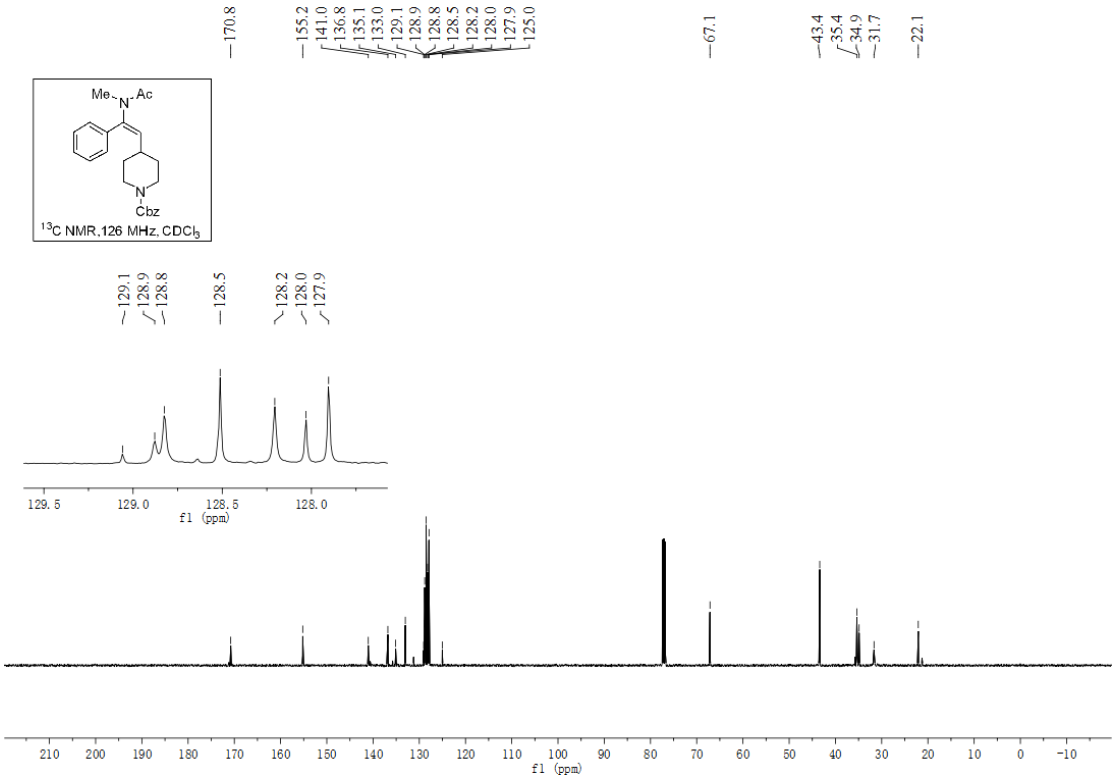
^{13}C NMR spectrum of compound **25**



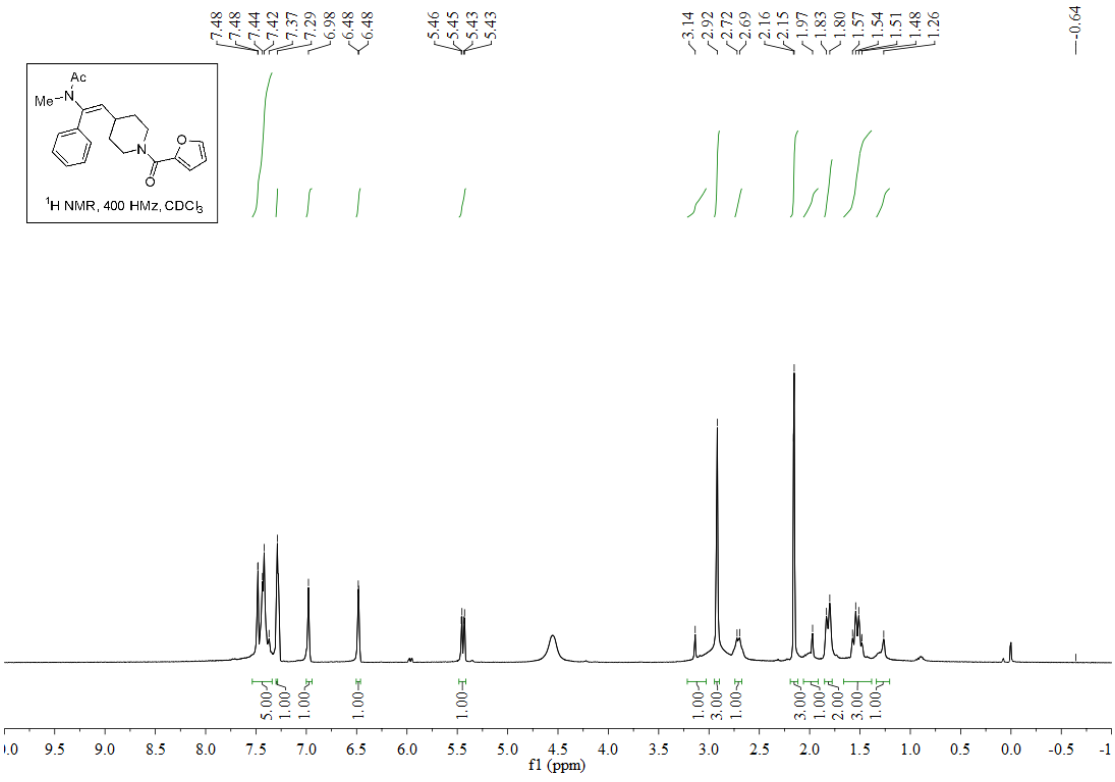
^{1}H NMR spectrum of compound **26**



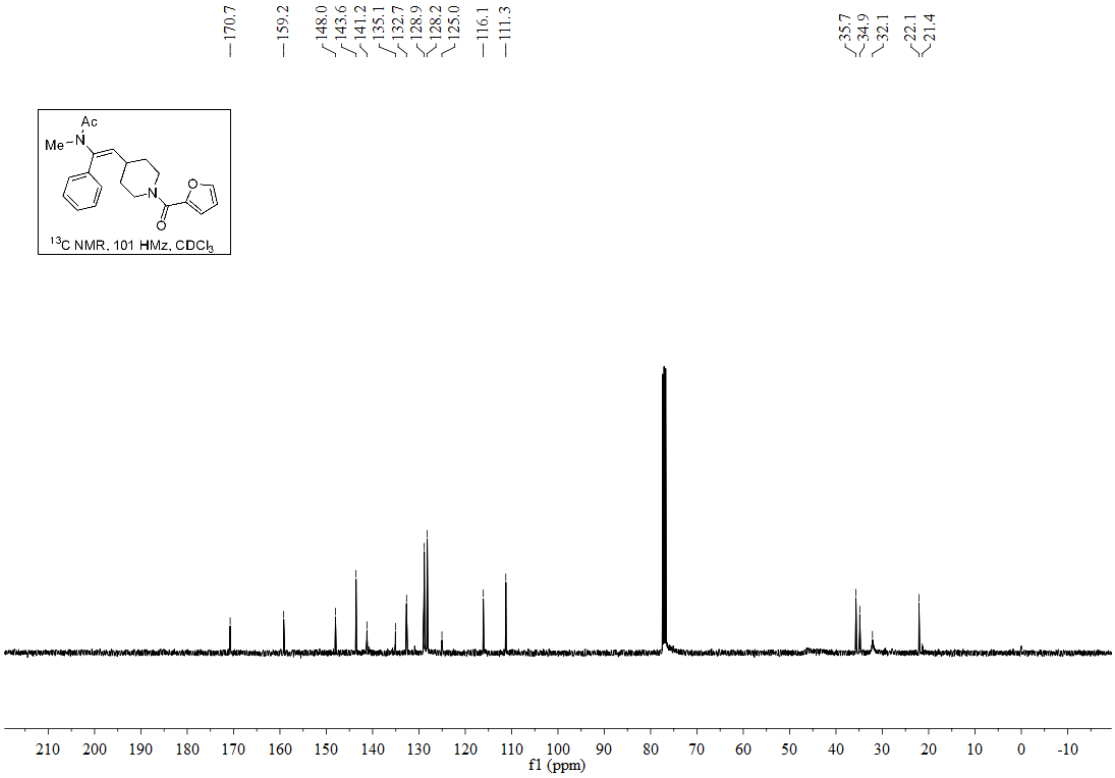
^{13}C NMR spectrum of compound **26**



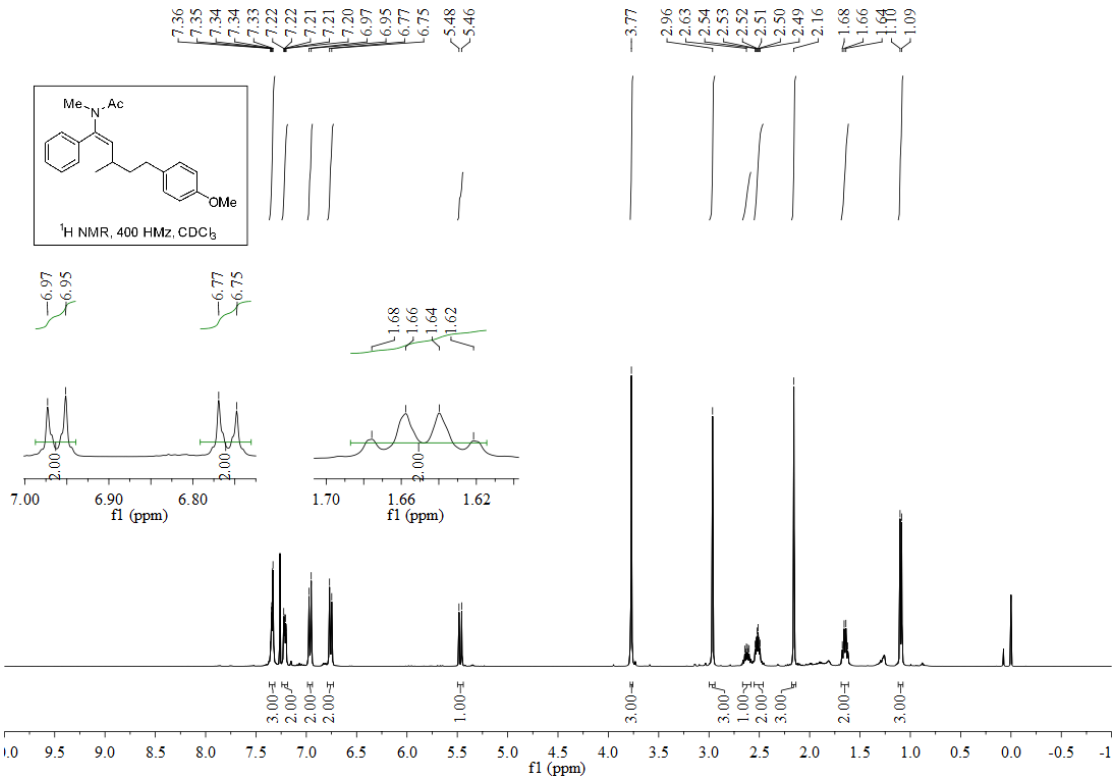
^{1}H NMR spectrum of compound **27**



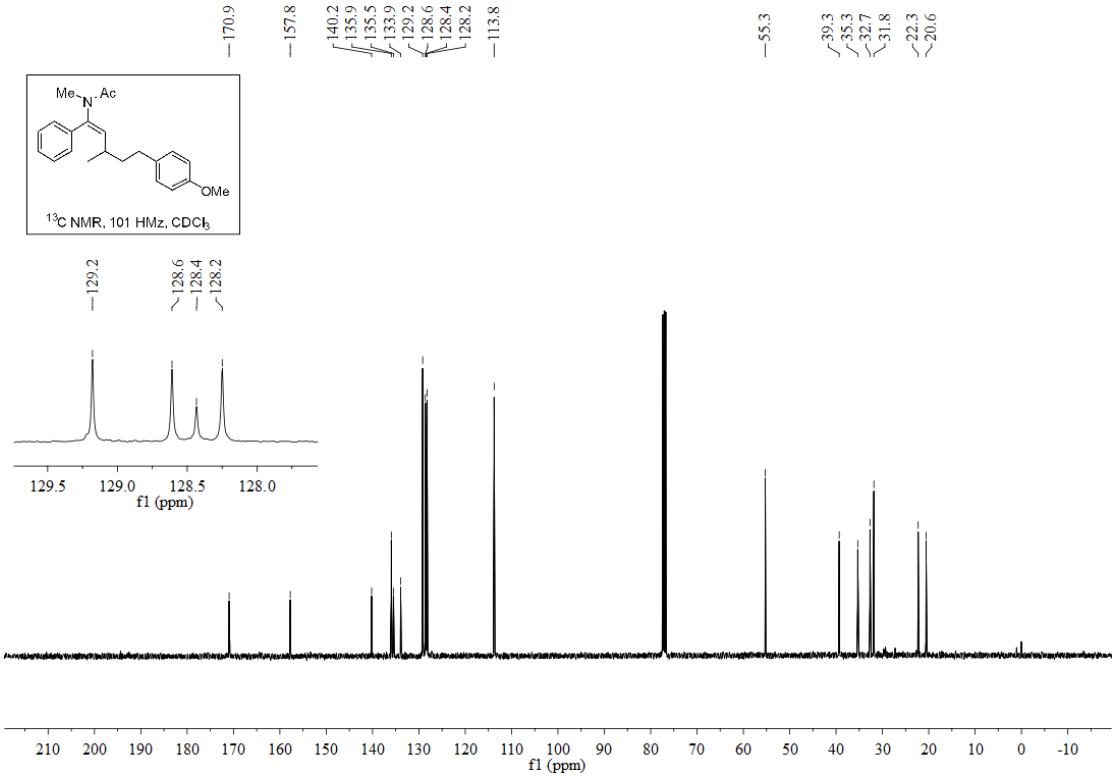
^{13}C NMR spectrum of compound **27**



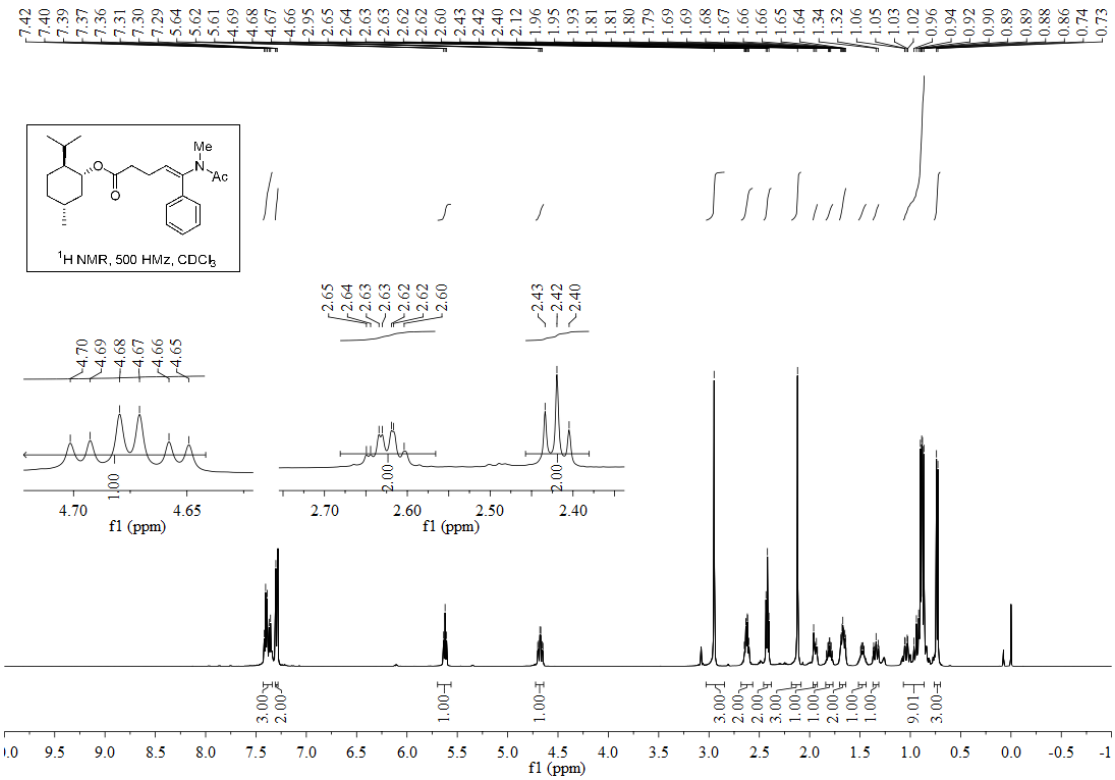
^{1}H NMR spectrum of compound **28**



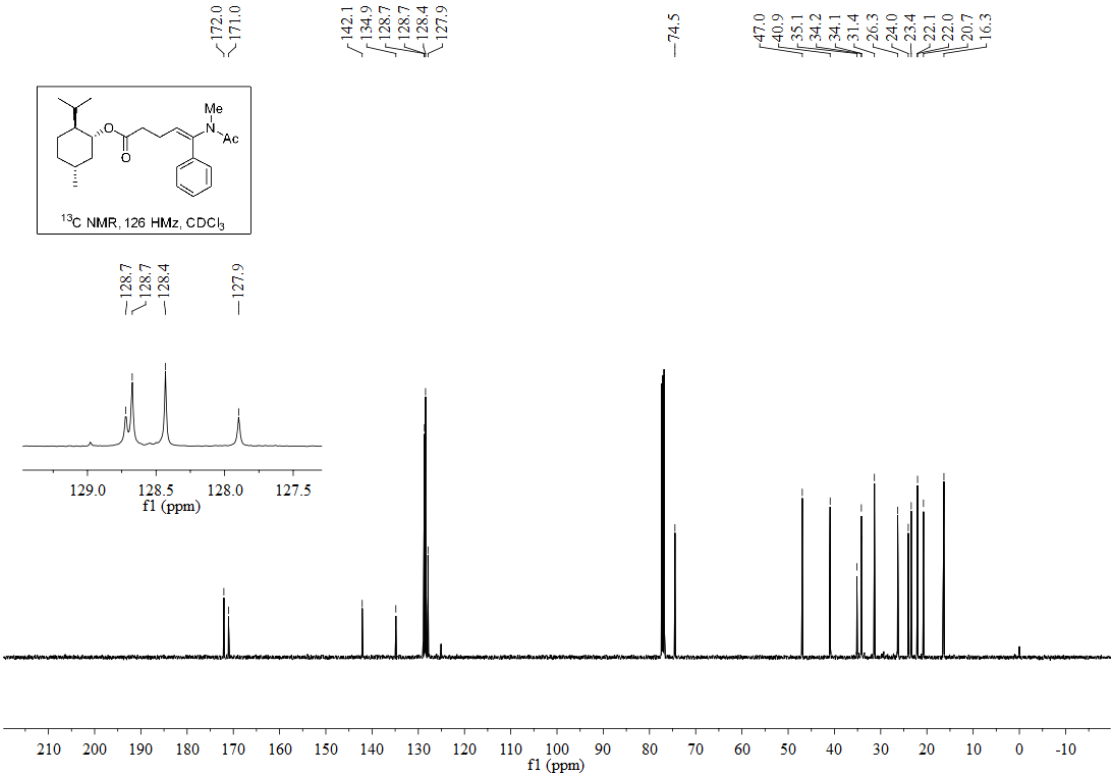
^{13}C NMR spectrum of compound **28**



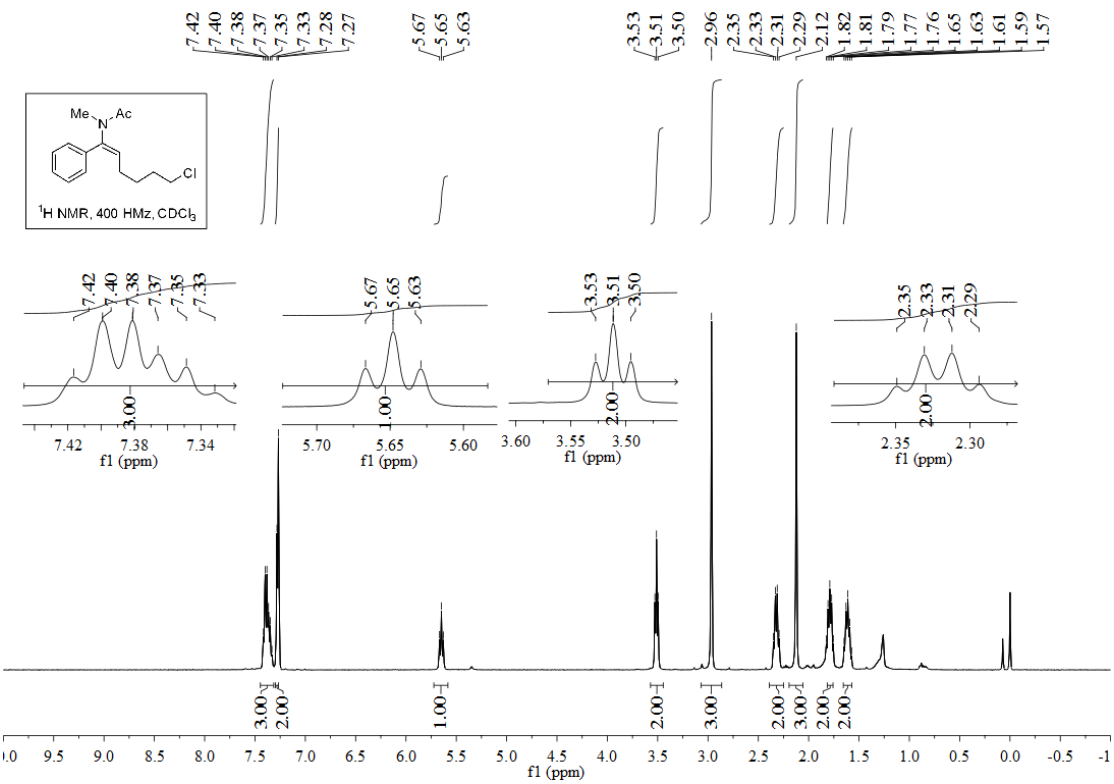
^{1}H NMR spectrum of compound **29**



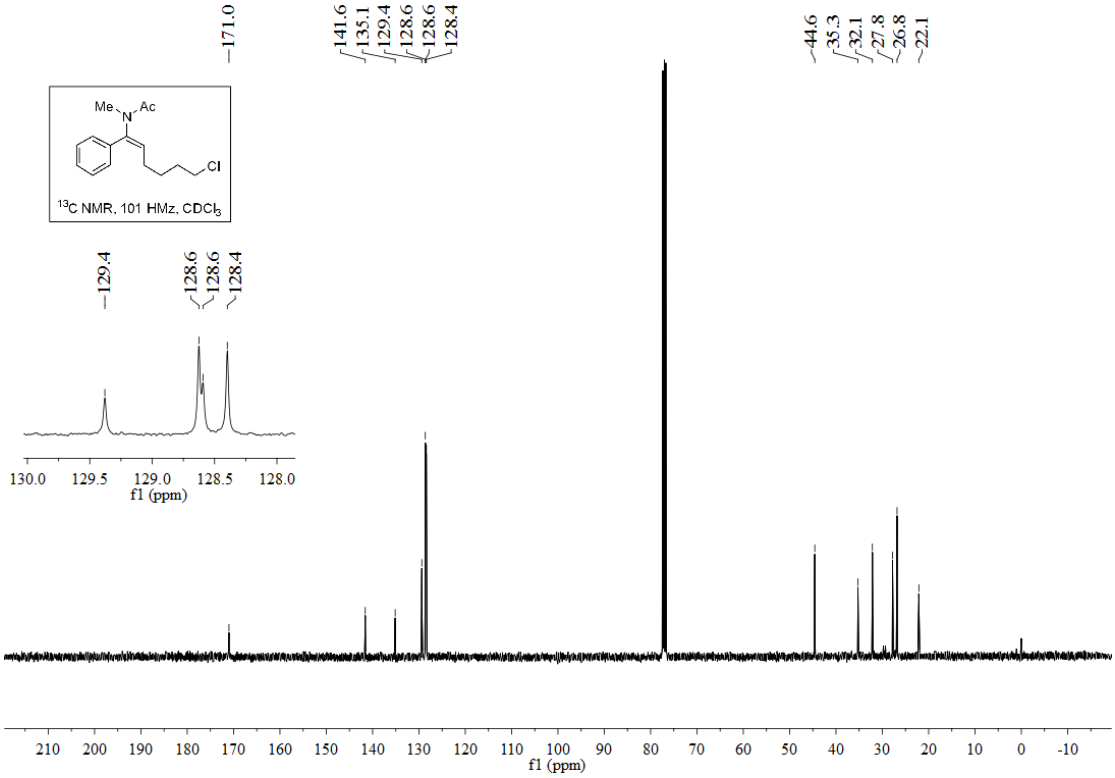
^{13}C NMR spectrum of compound **29**



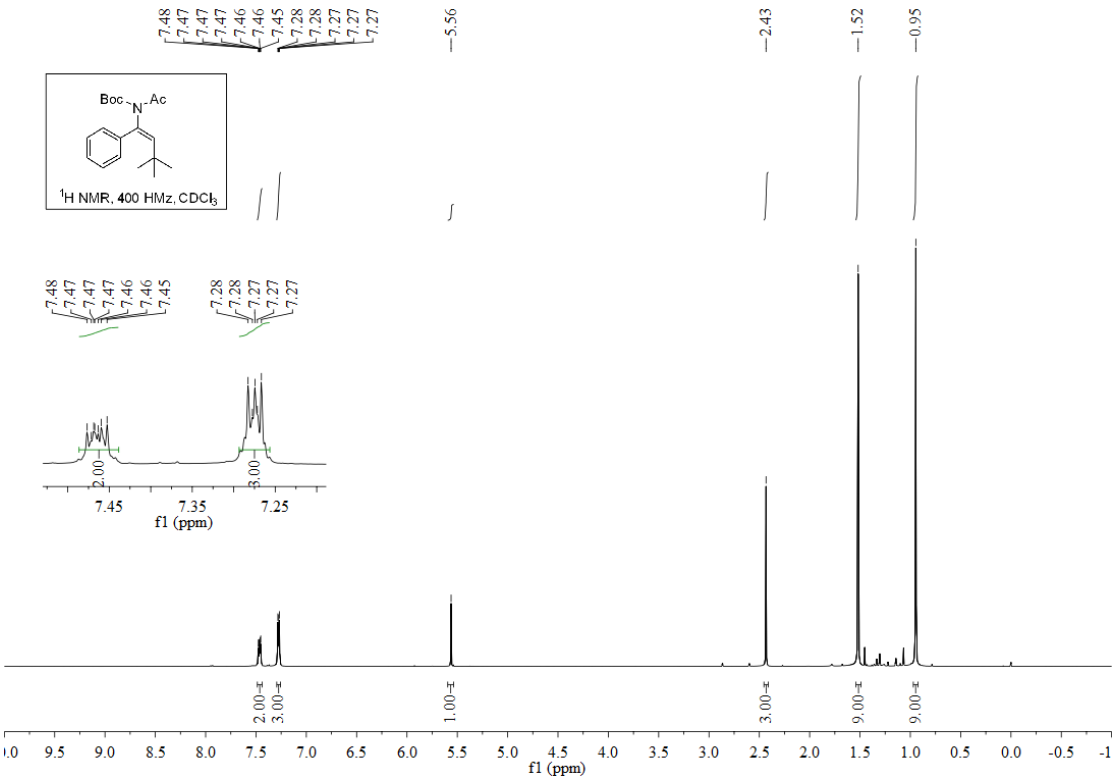
^{1}H NMR spectrum of compound **30**



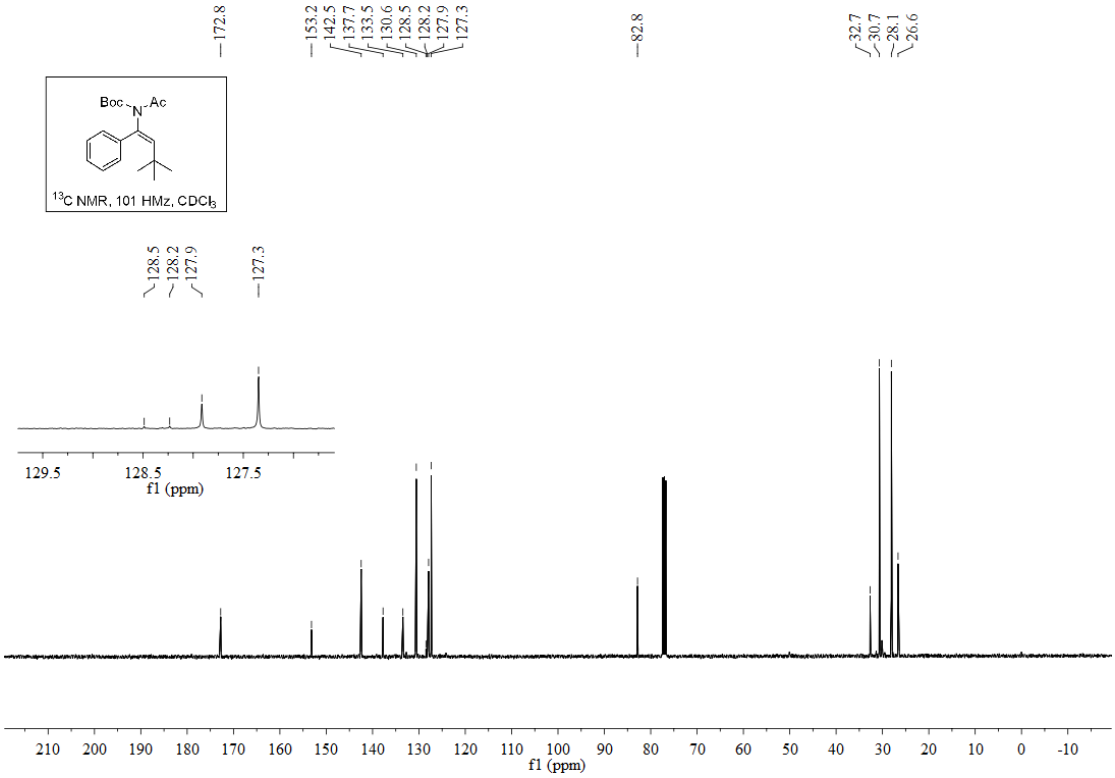
^{13}C NMR spectrum of compound **30**



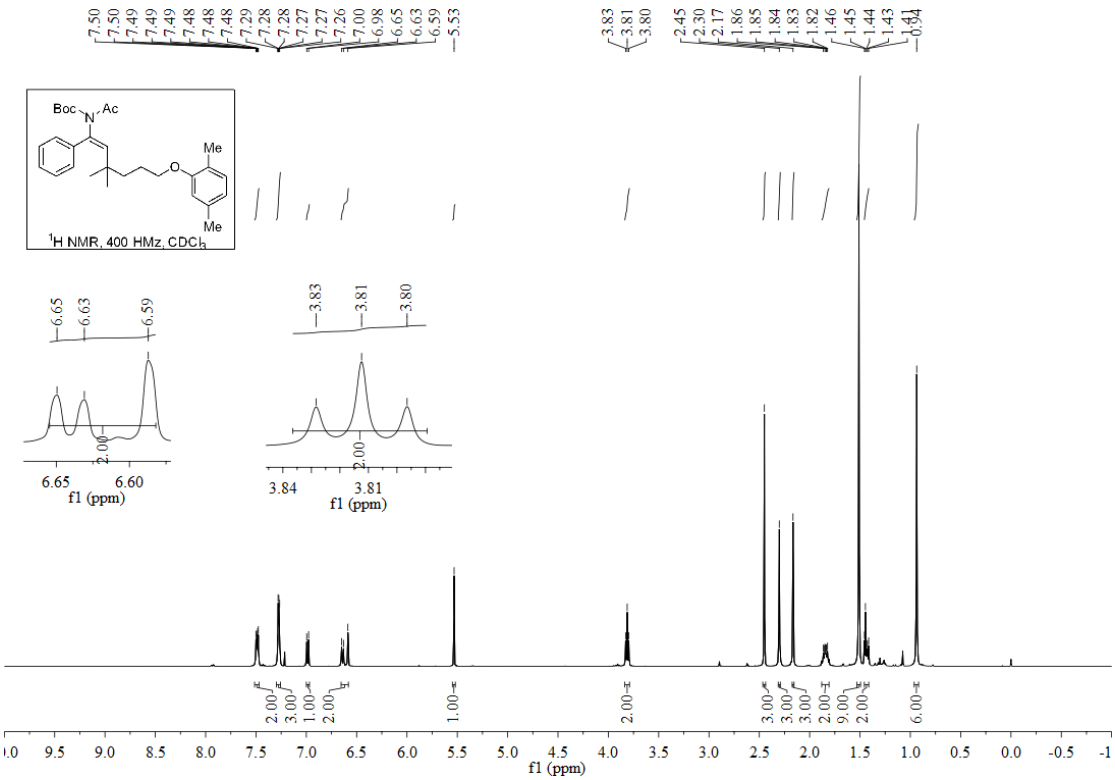
^{1}H NMR spectrum of compound **31**



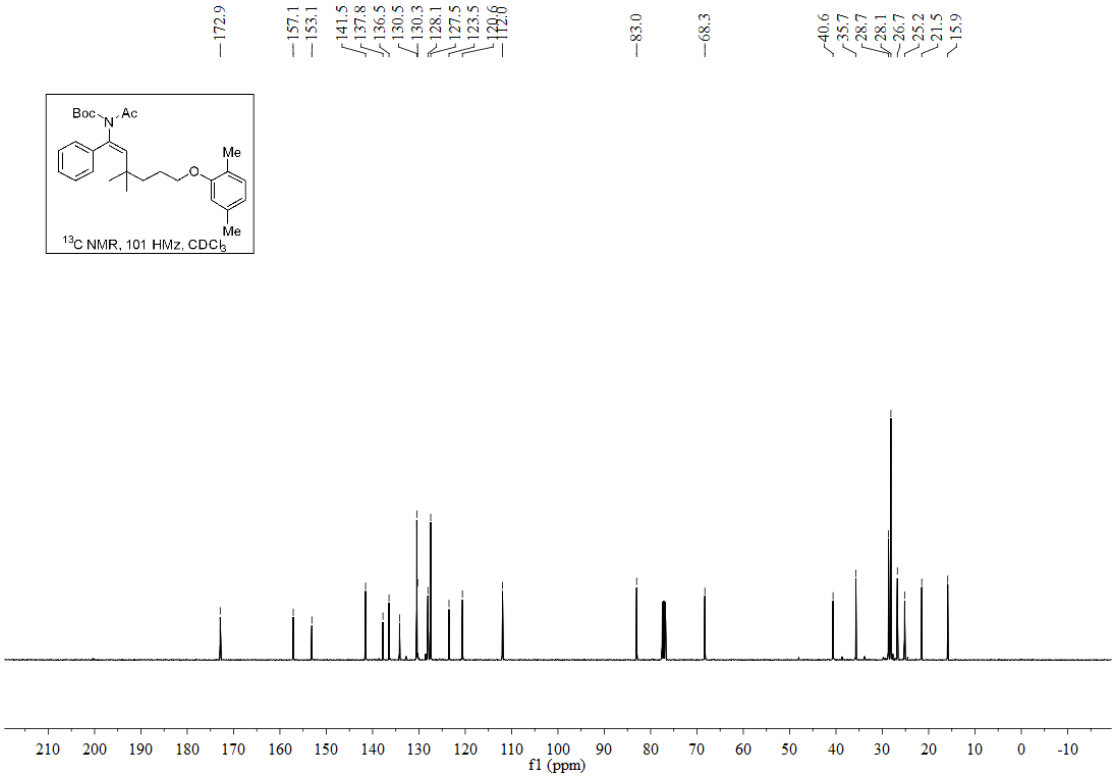
^{13}C NMR spectrum of compound **31**



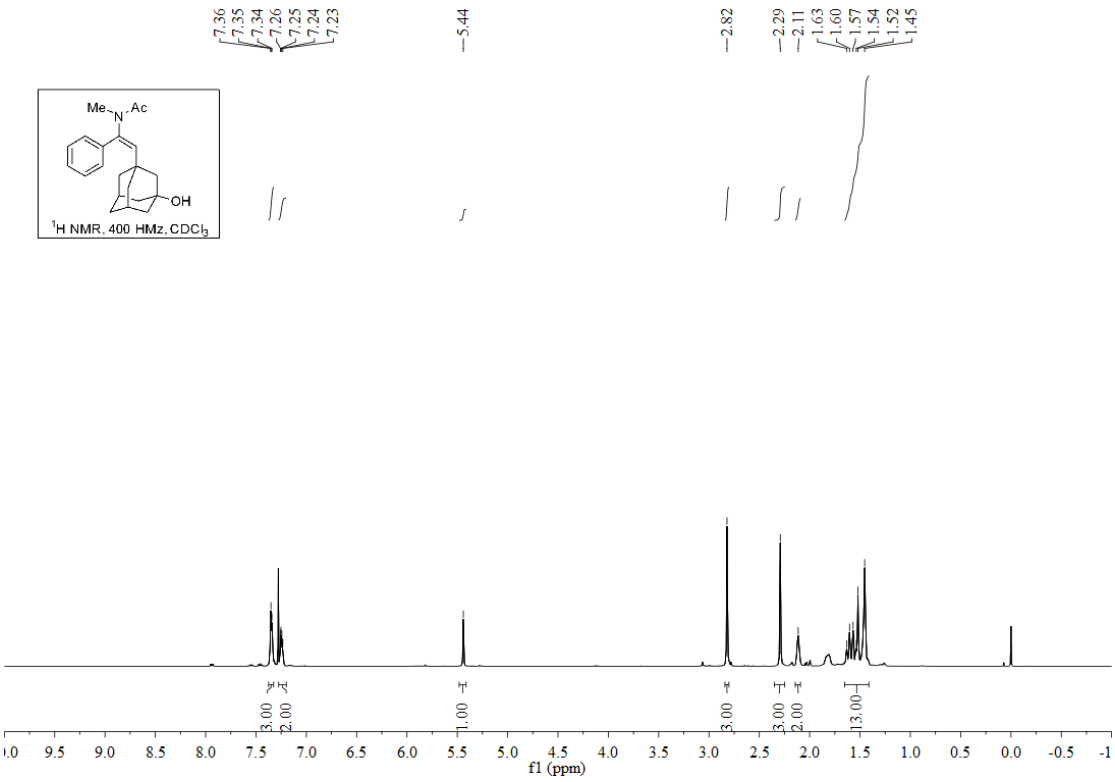
^{1}H NMR spectrum of compound **32**



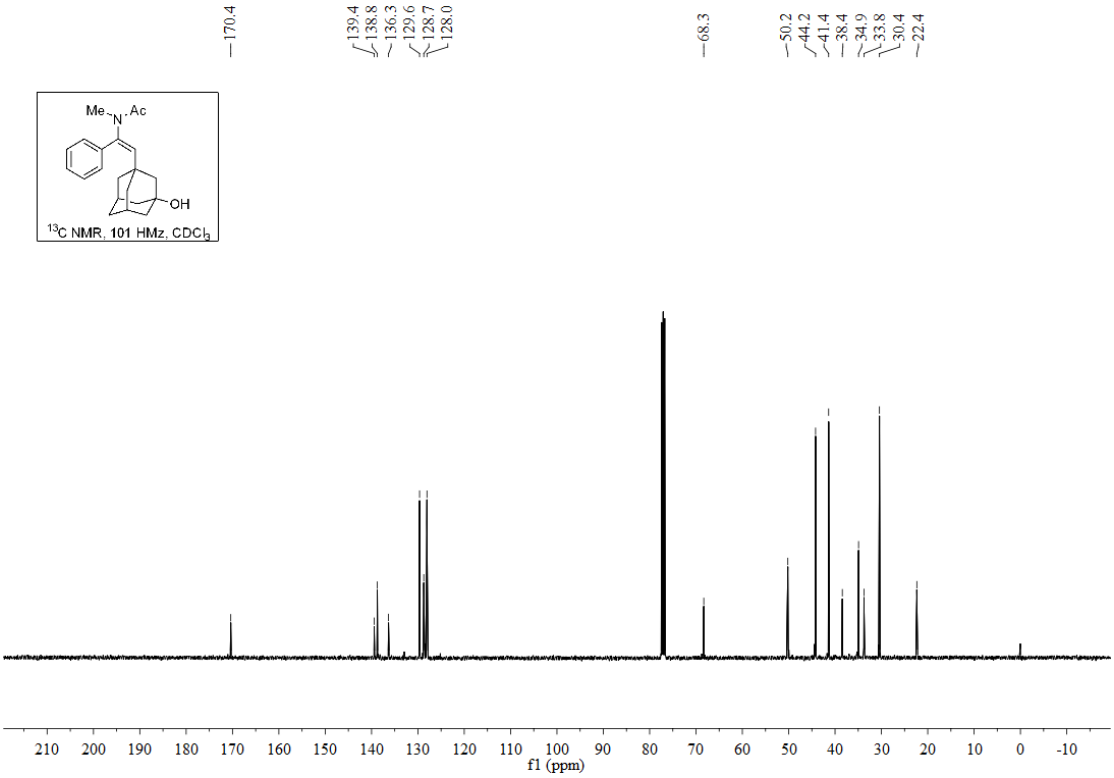
^{13}C NMR spectrum of compound **32**



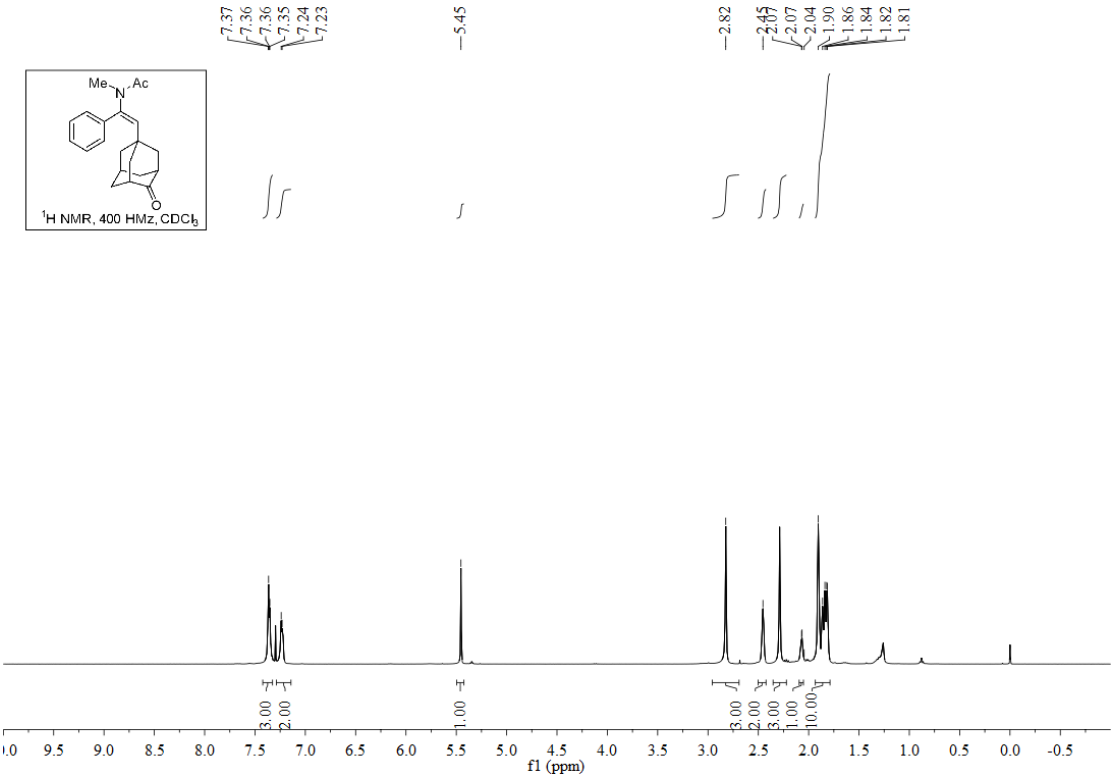
^{1}H NMR spectrum of compound **33**



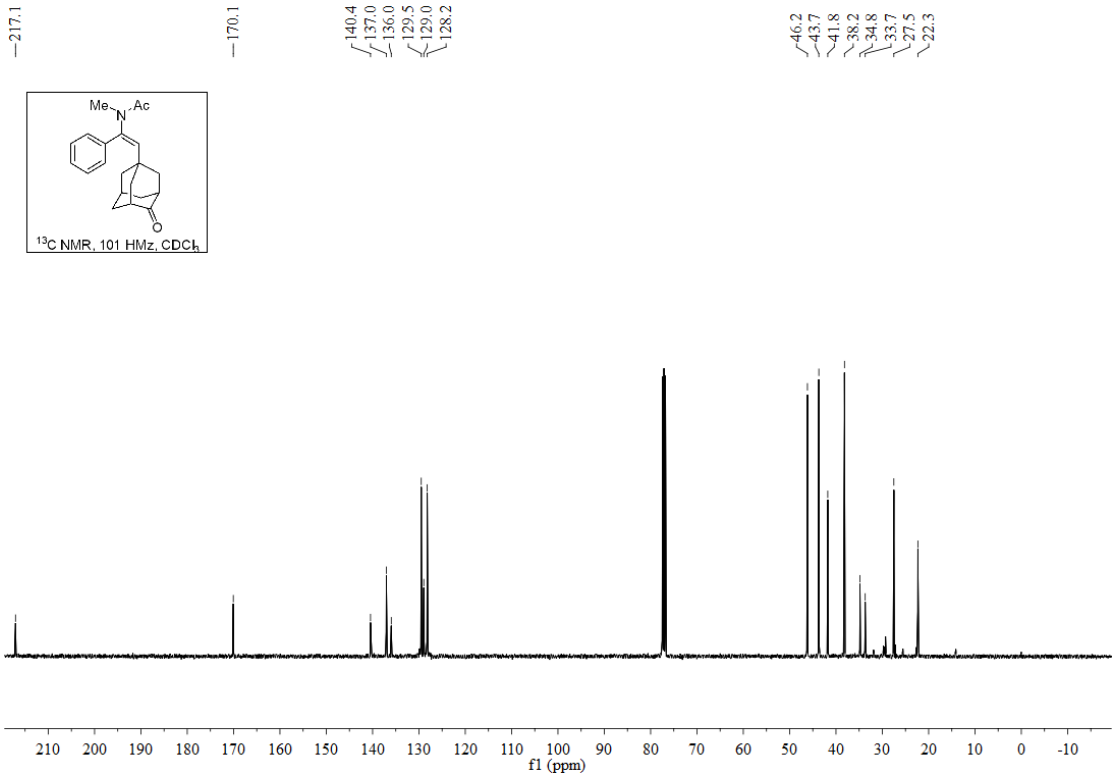
^{13}C NMR spectrum of compound **33**



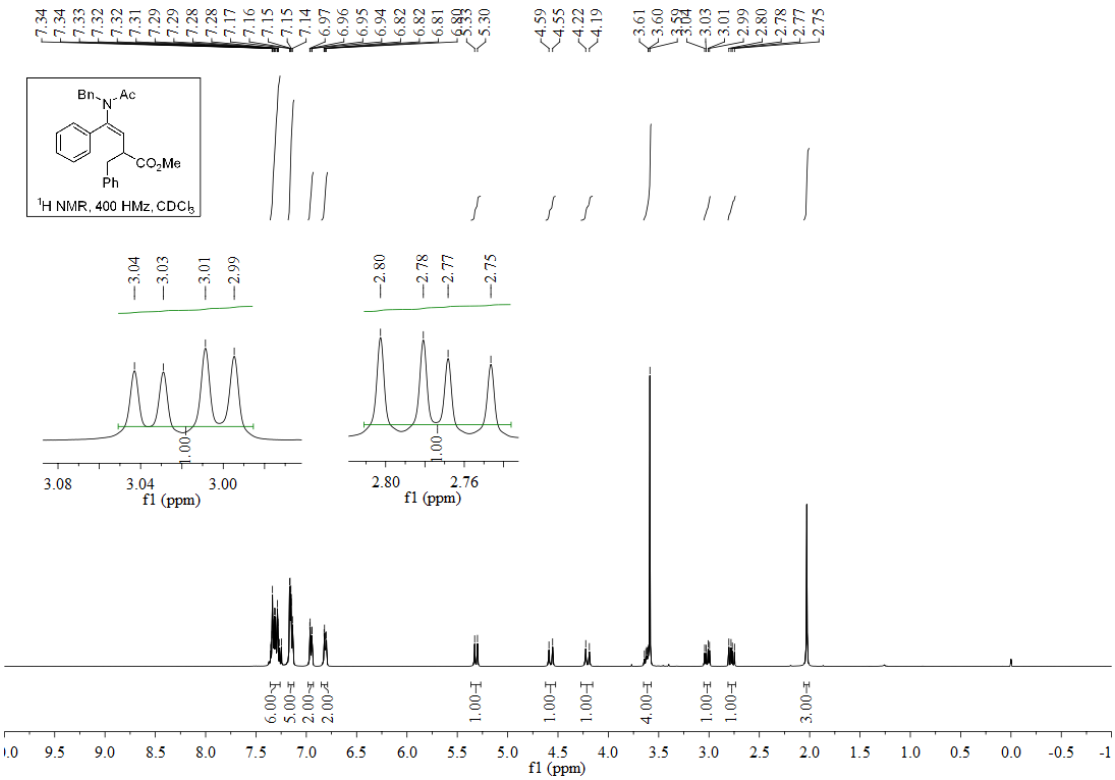
^{1}H NMR spectrum of compound **34**



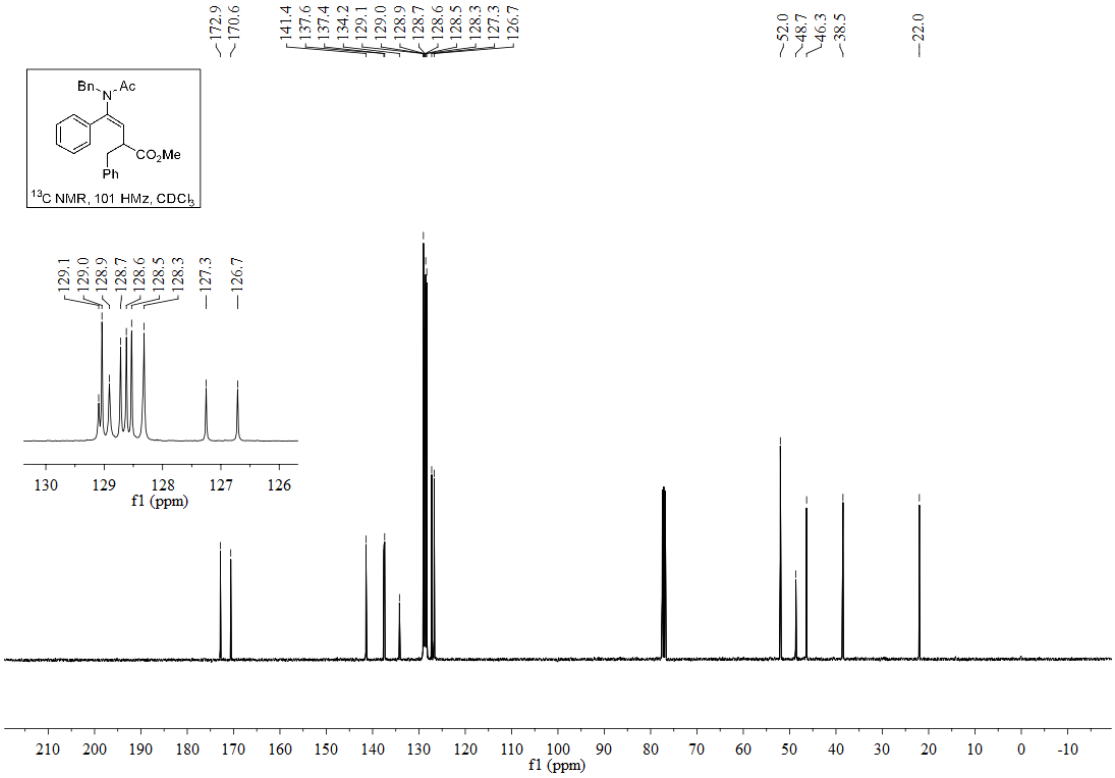
^{13}C NMR spectrum of compound **34**



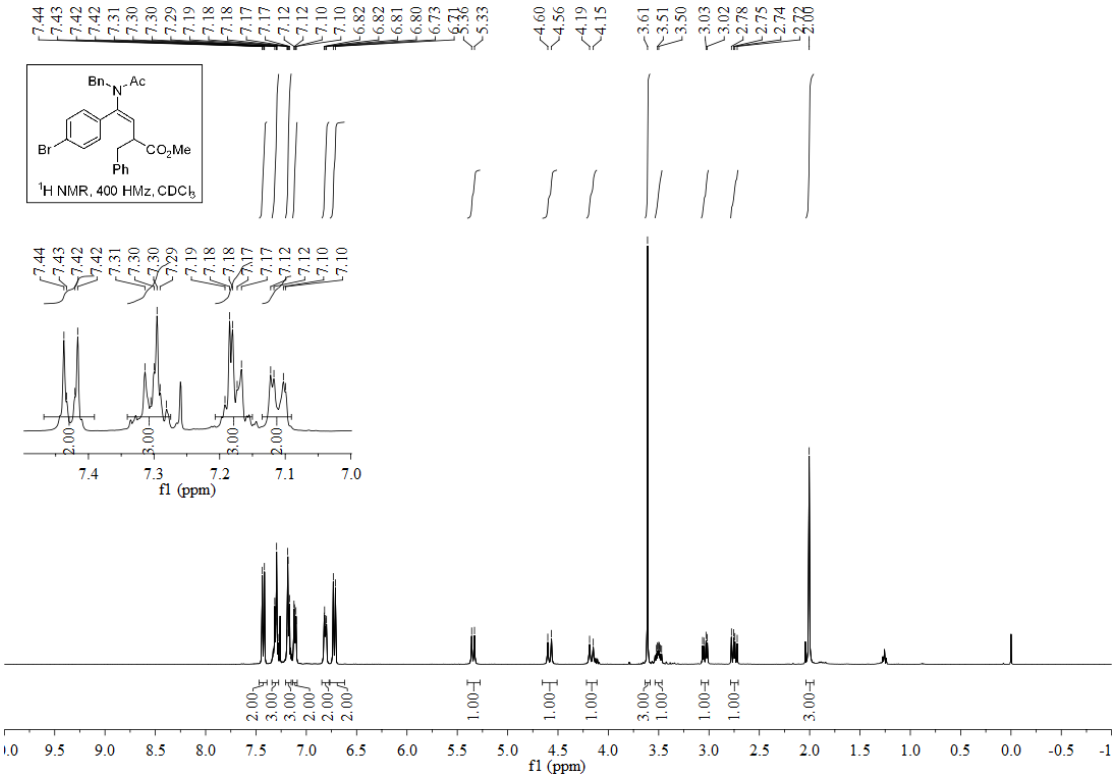
^{1}H NMR spectrum of compound **35**



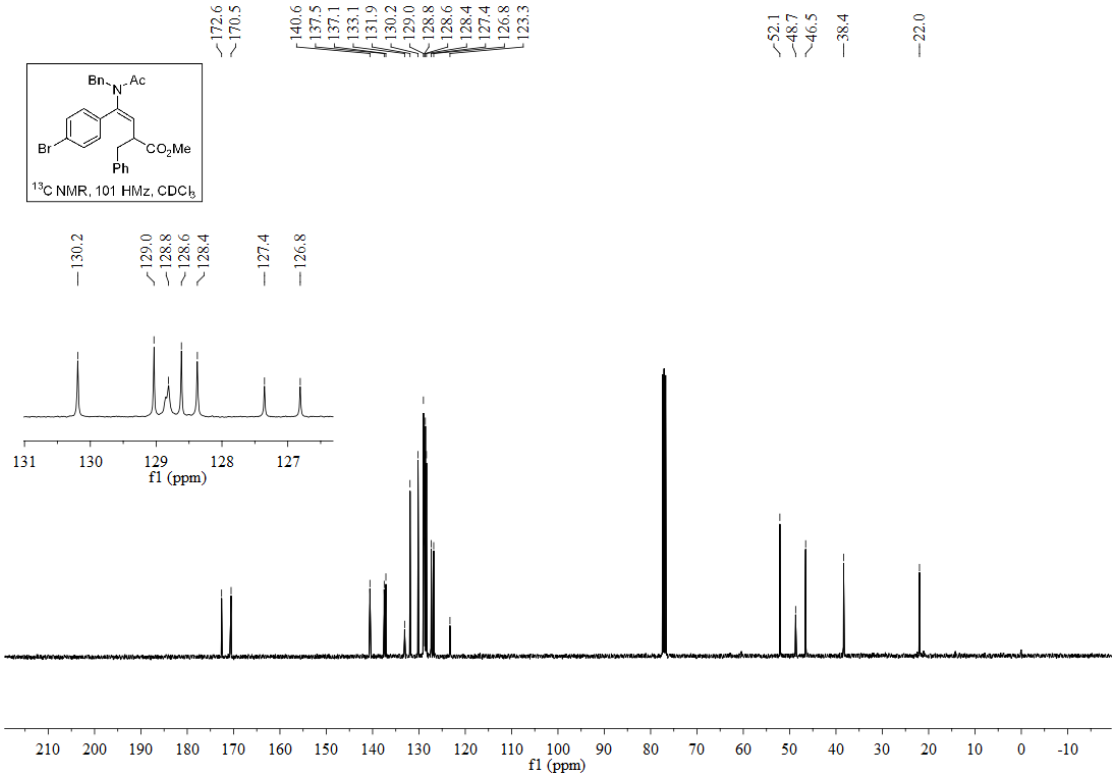
^{13}C NMR spectrum of compound **35**



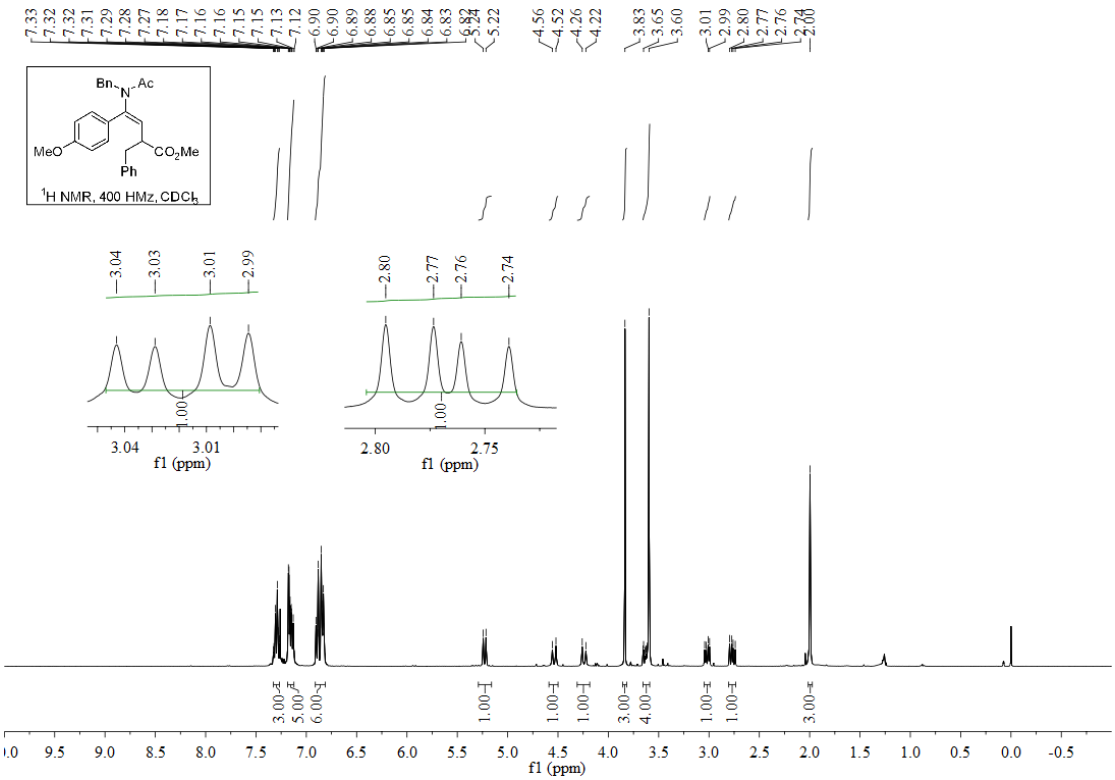
^{1}H NMR spectrum of compound **36**



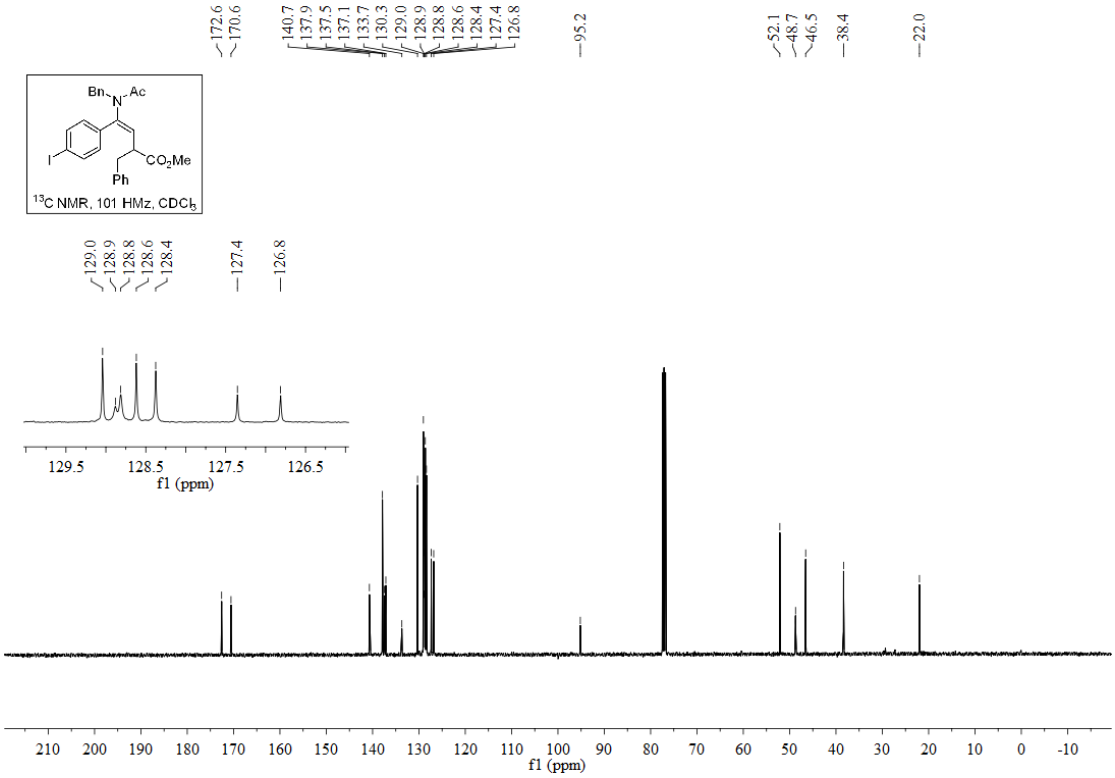
^{13}C NMR spectrum of compound **36**



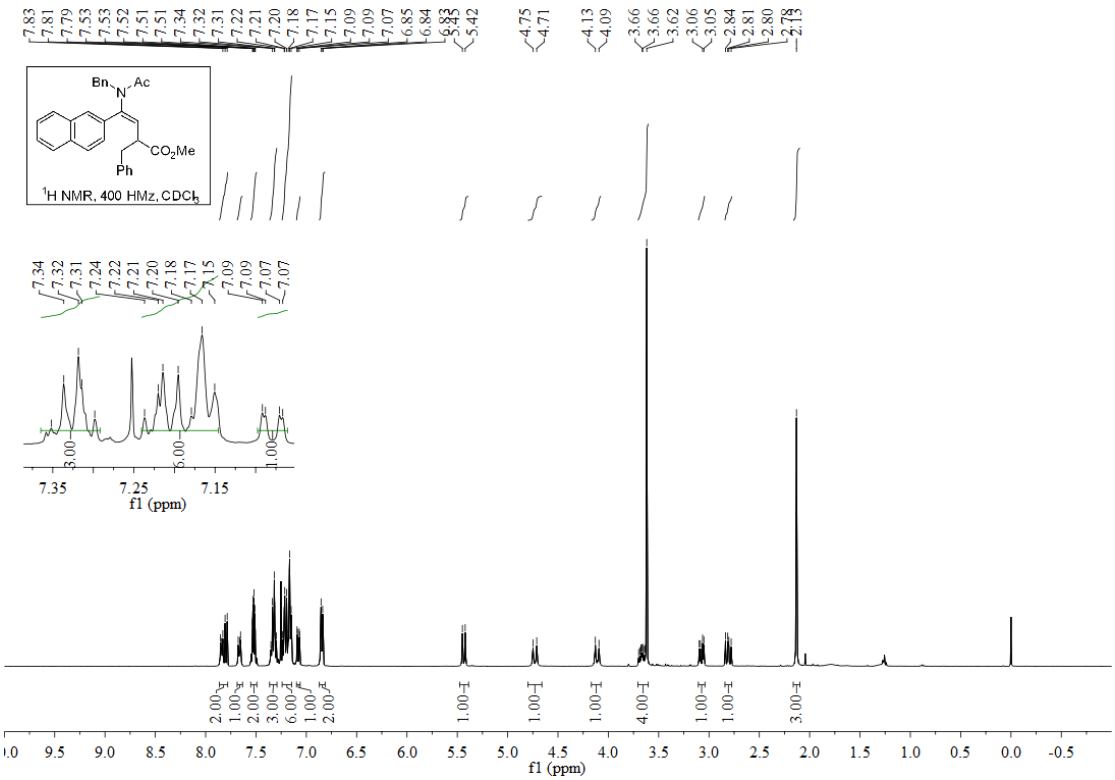
^{1}H NMR spectrum of compound **37**



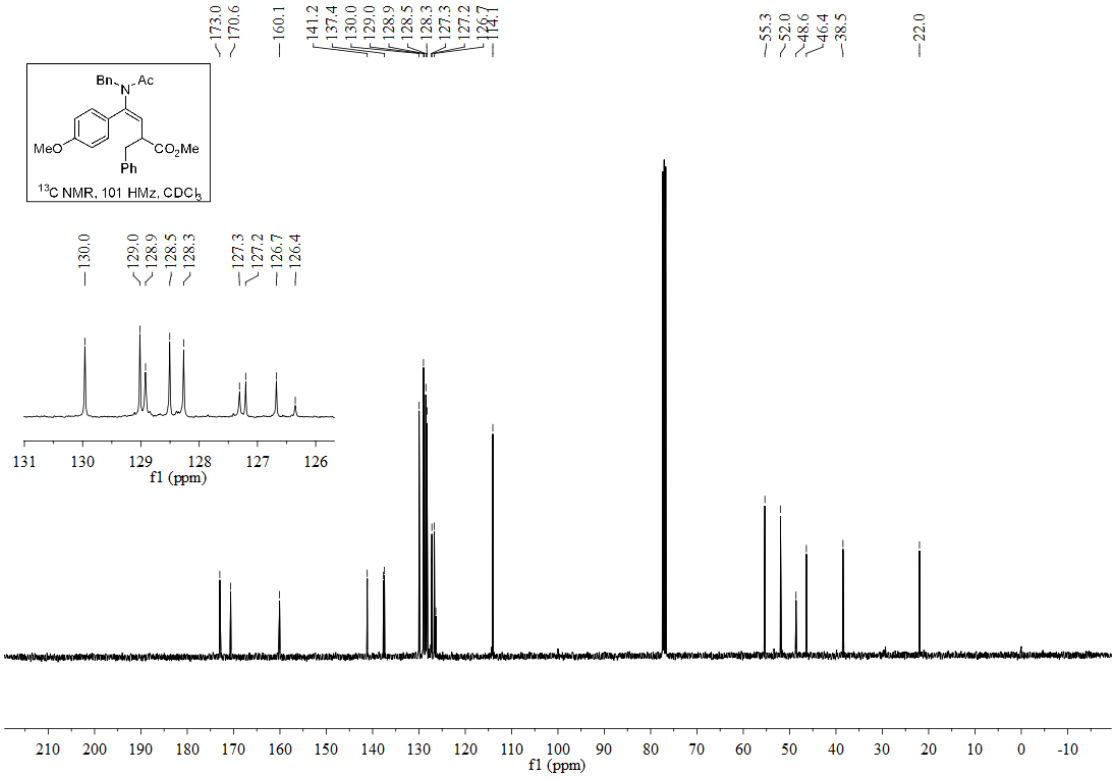
^{13}C NMR spectrum of compound **37**



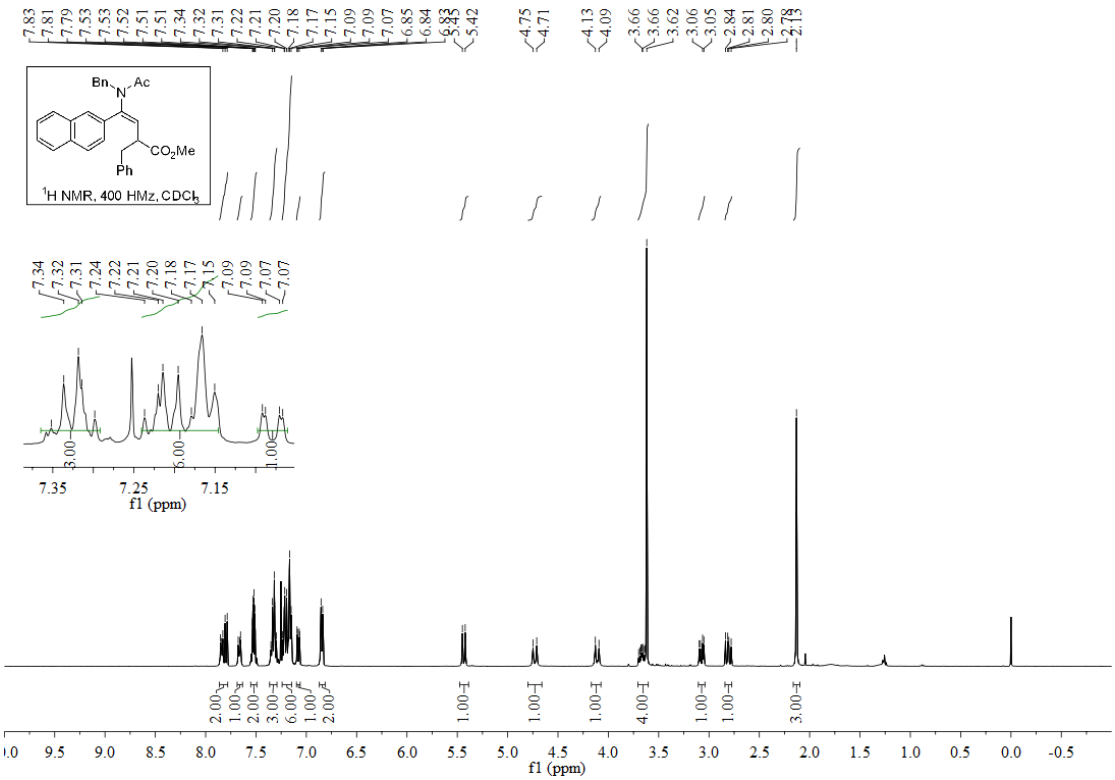
^{1}H NMR spectrum of compound **38**



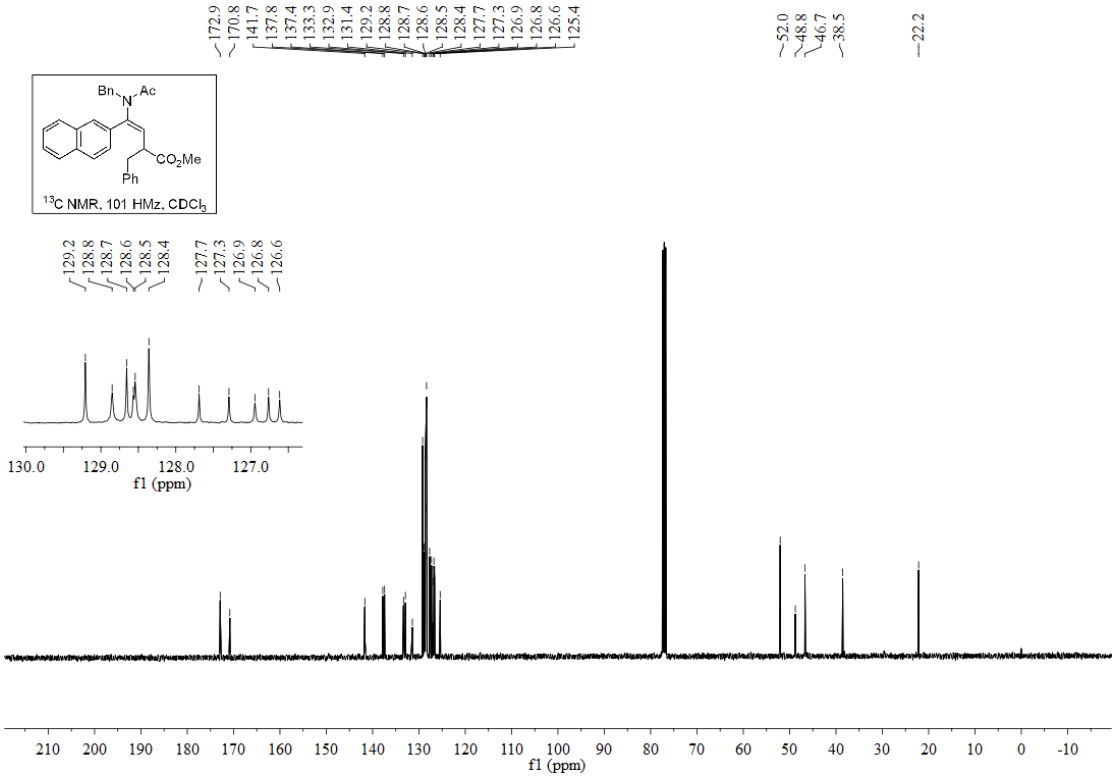
^{13}C NMR spectrum of compound **38**



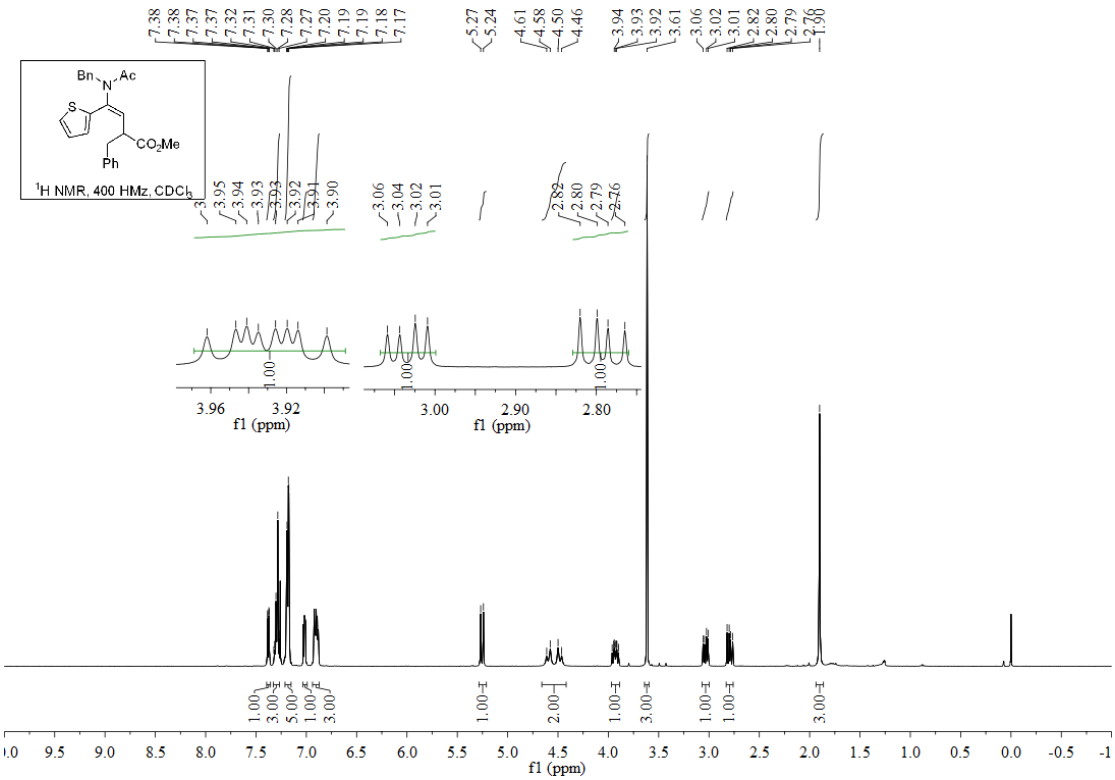
^{1}H NMR spectrum of compound **39**



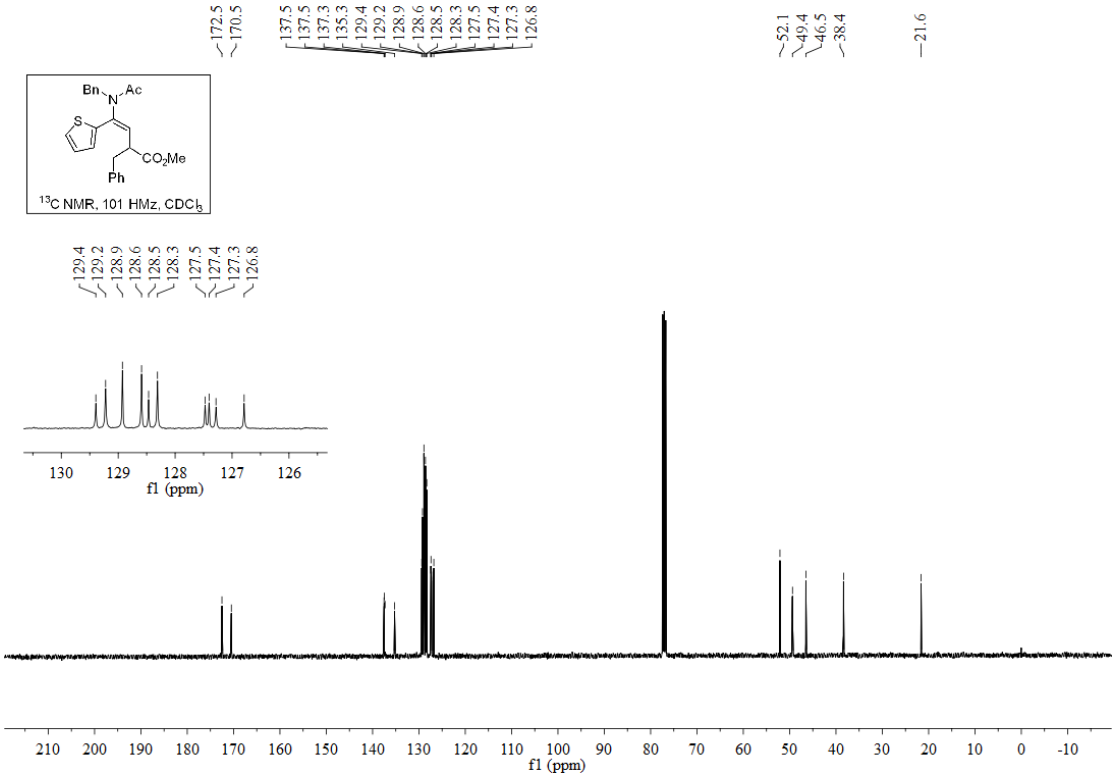
^{13}C NMR spectrum of compound **39**



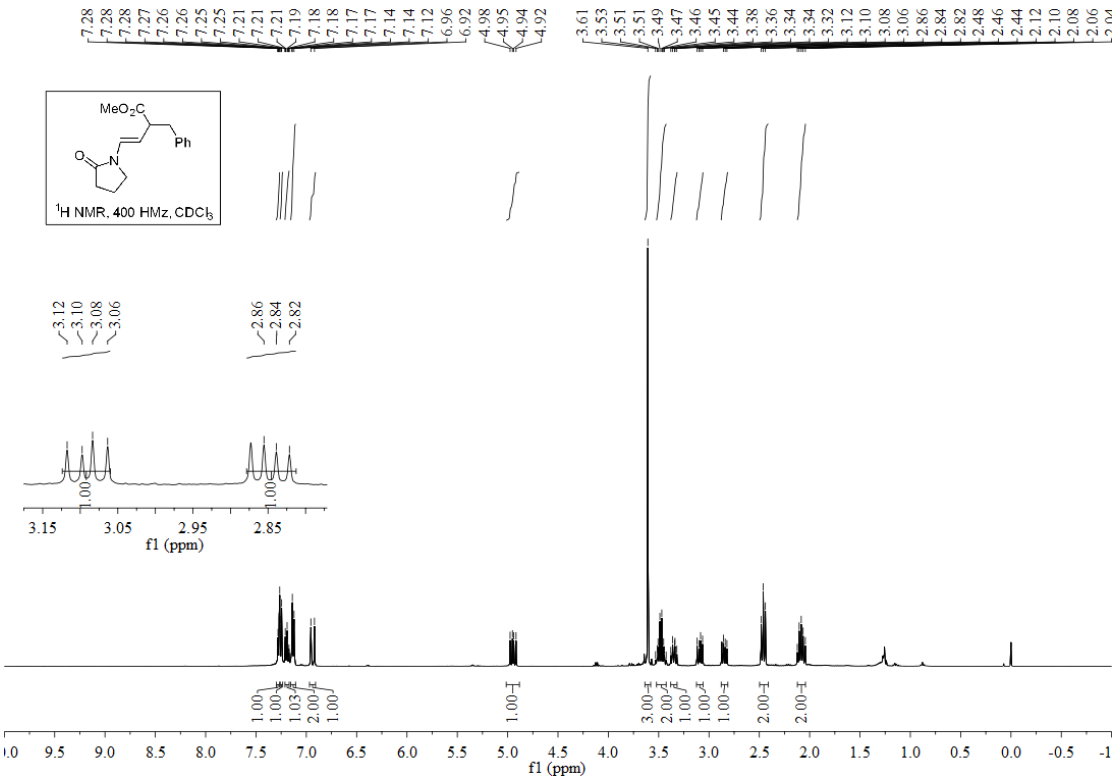
^{1}H NMR spectrum of compound **40**



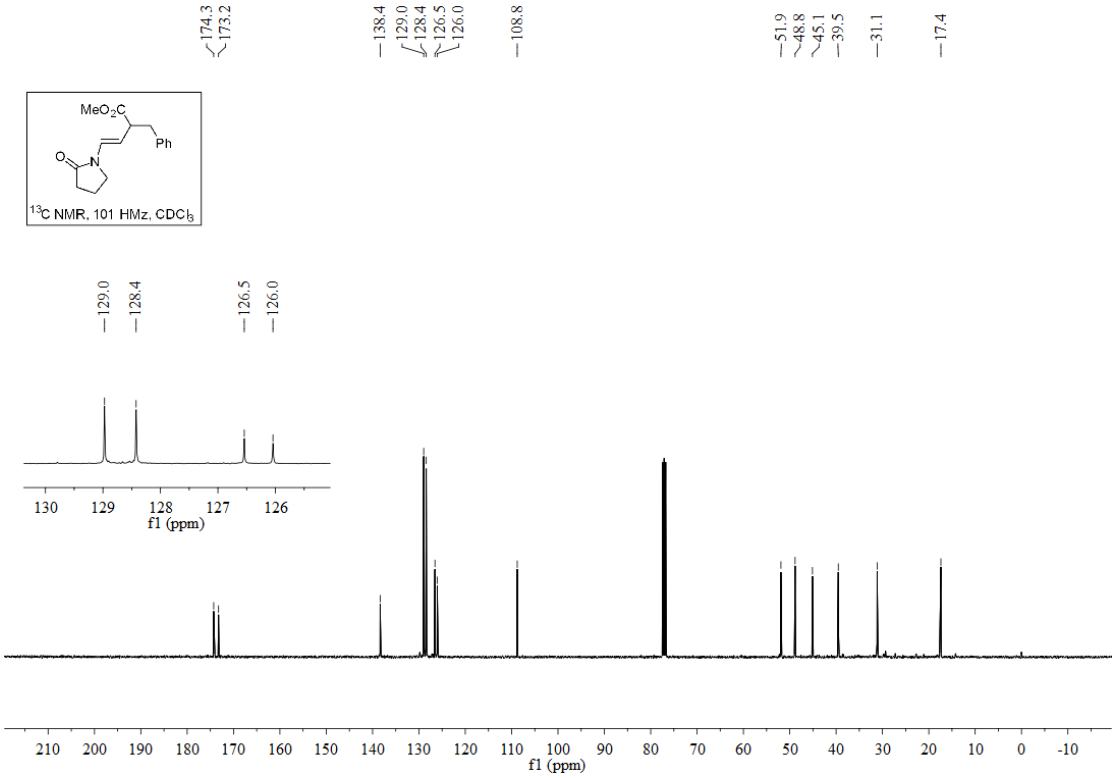
^{13}C NMR spectrum of compound **40**



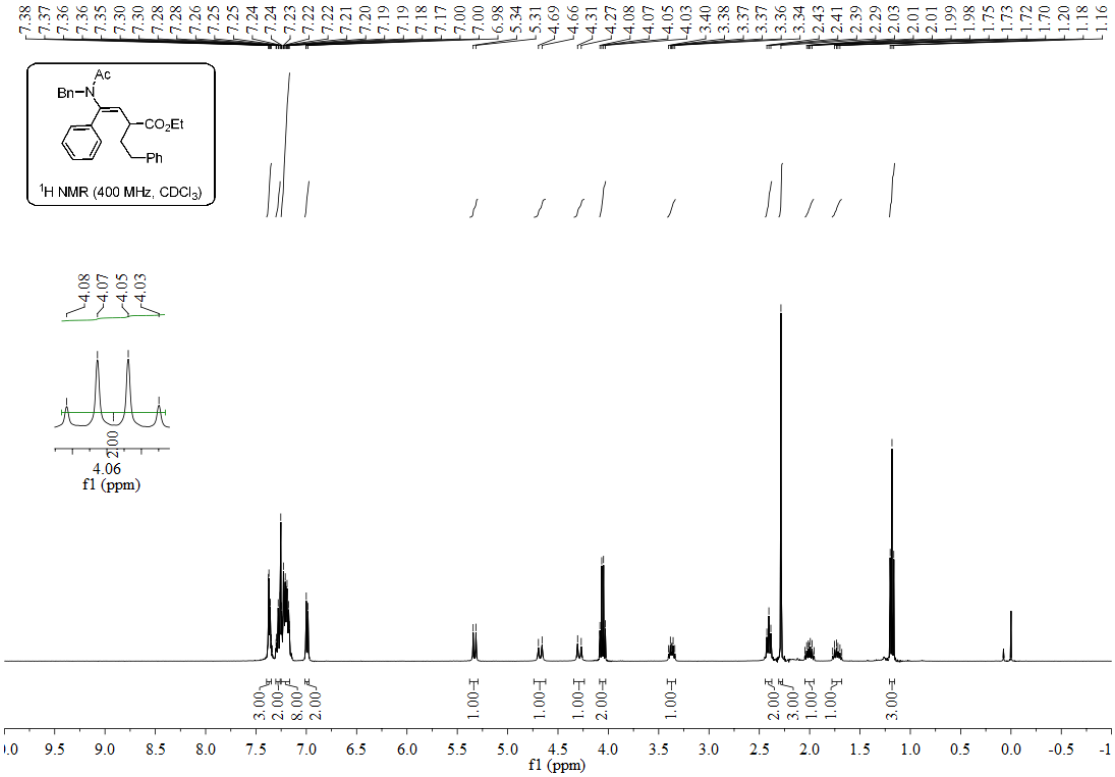
^{1}H NMR spectrum of compound **41**



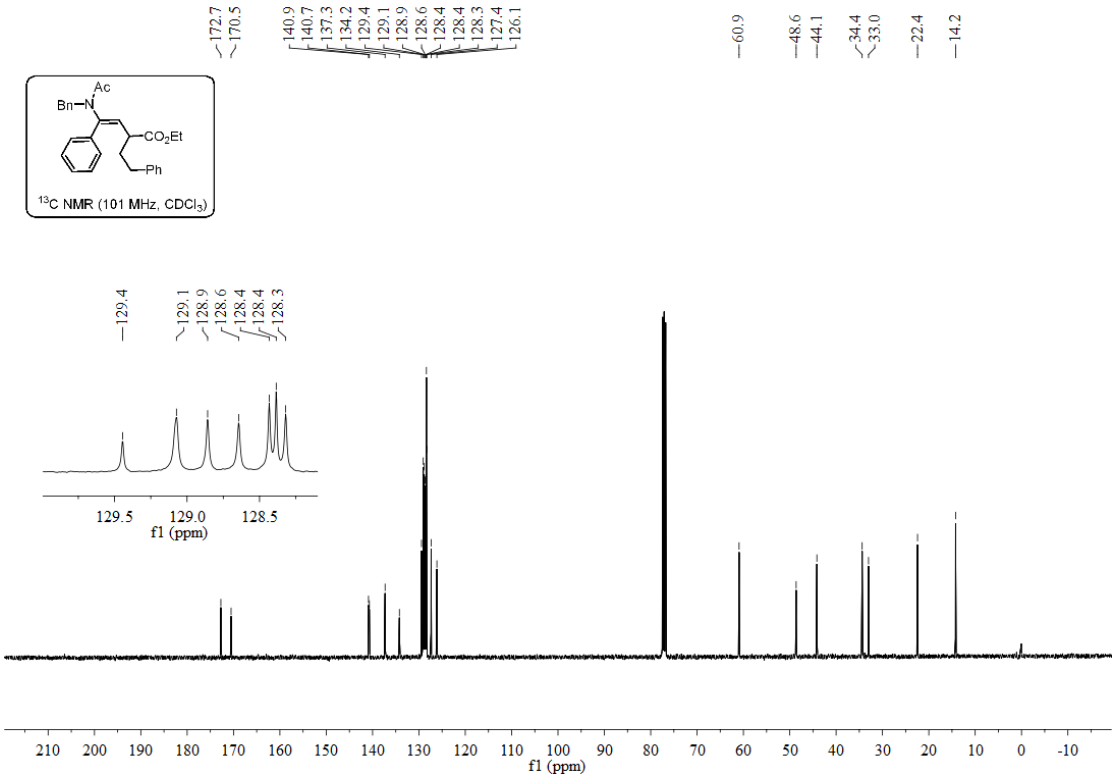
^{13}C NMR spectrum of compound **41**



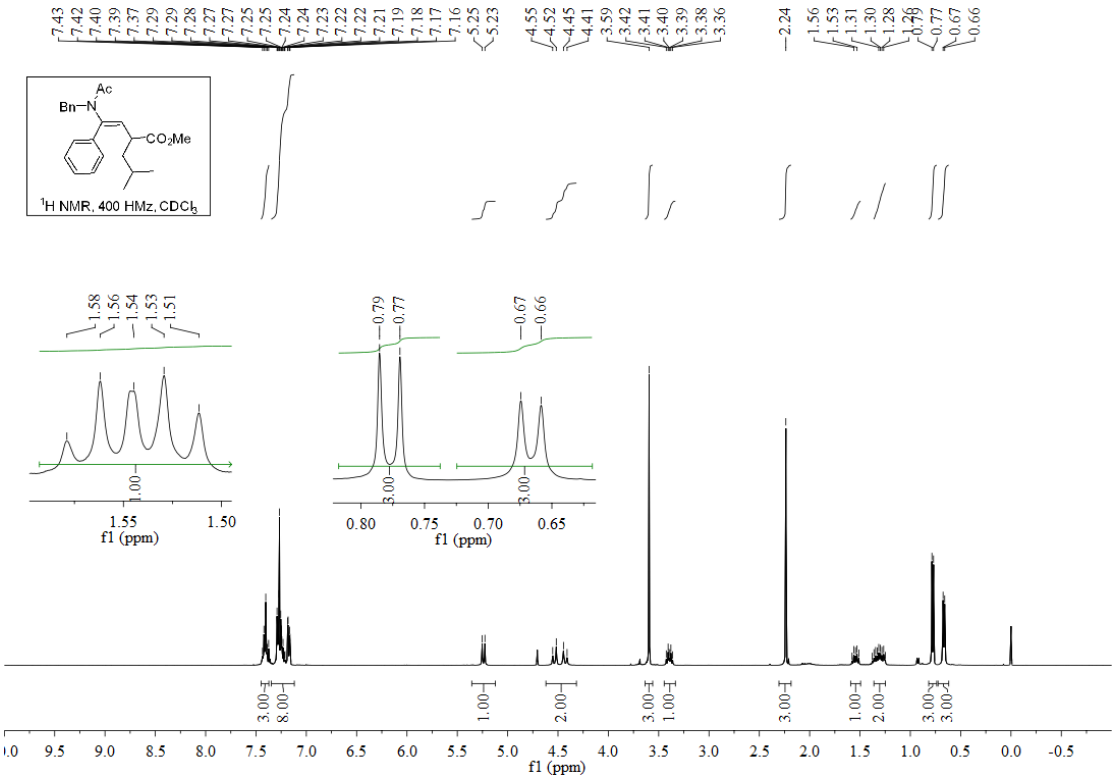
^{1}H NMR spectrum of compound **42**



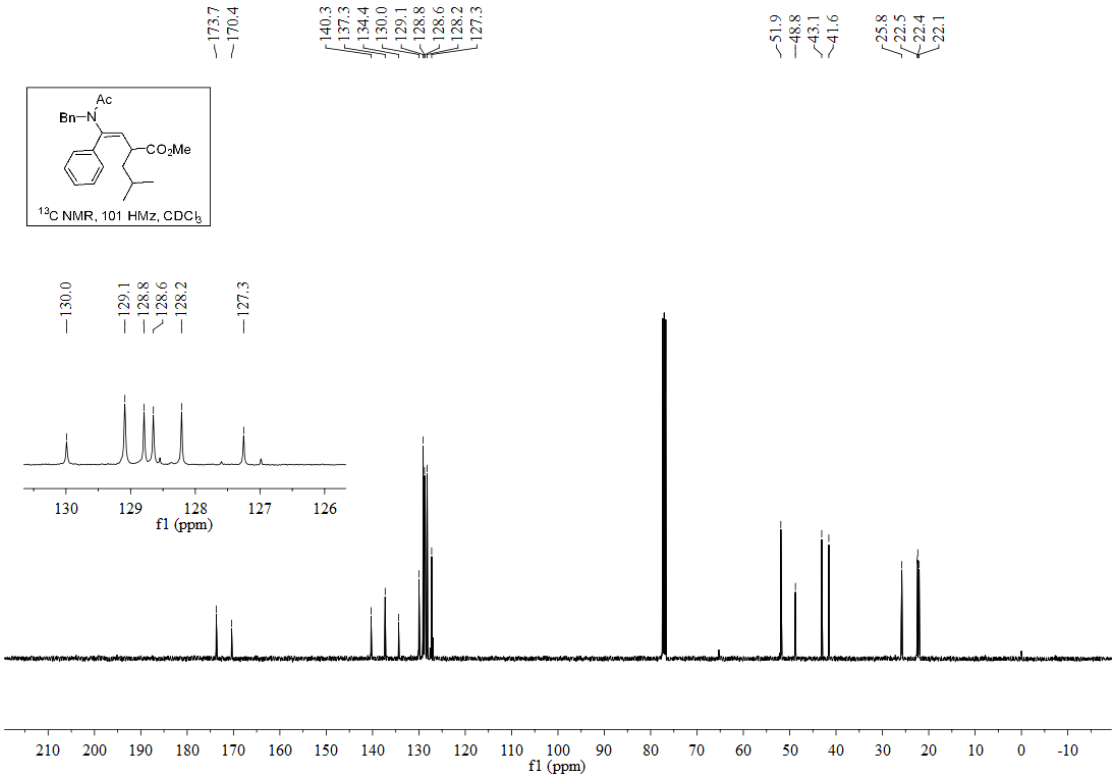
^{13}C NMR spectrum of compound **42**



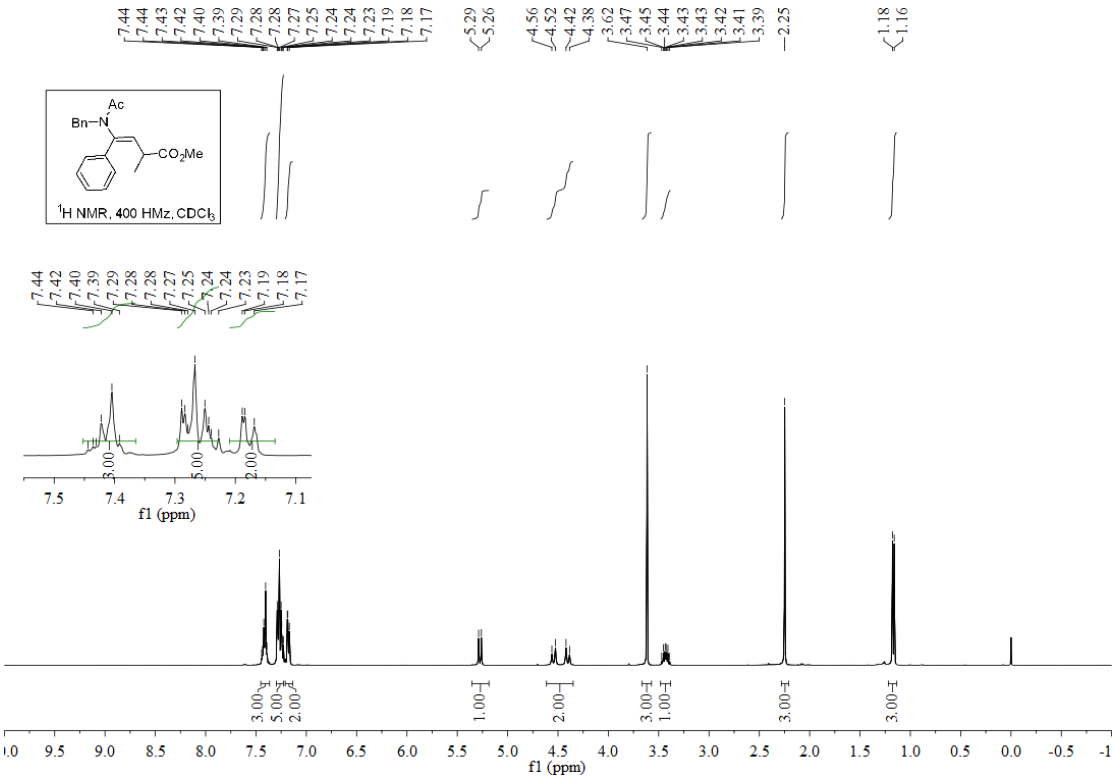
^{1}H NMR spectrum of compound **43**



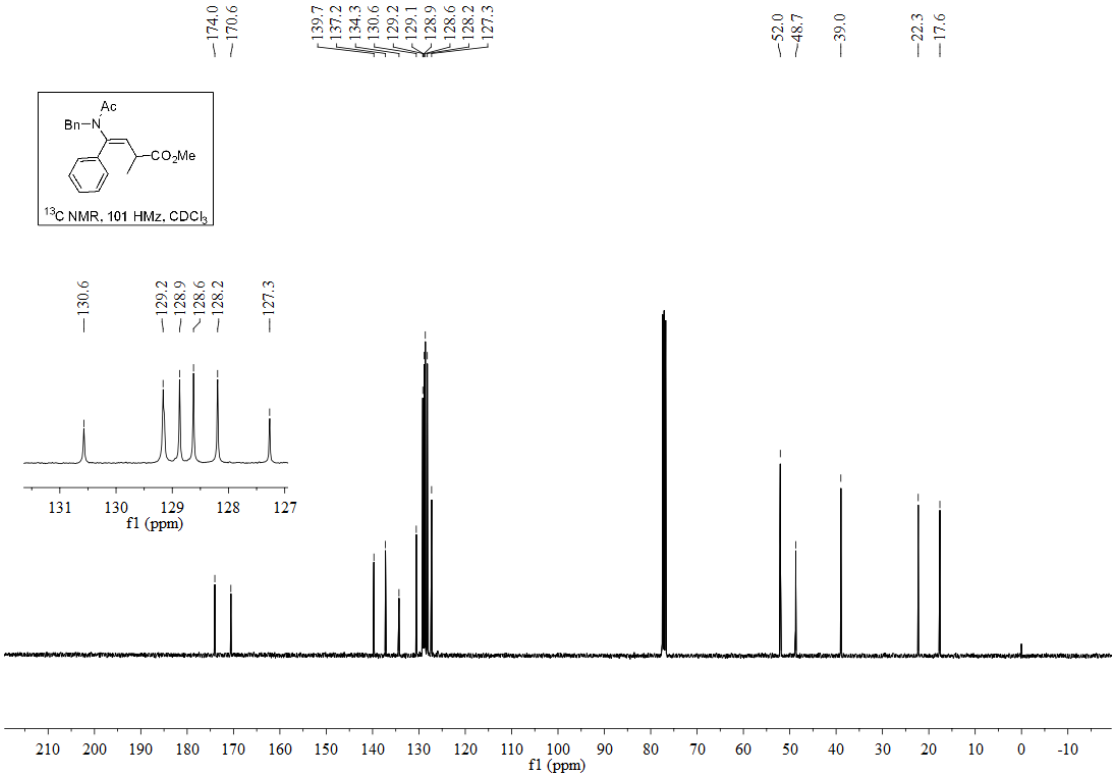
^{13}C NMR spectrum of compound **43**



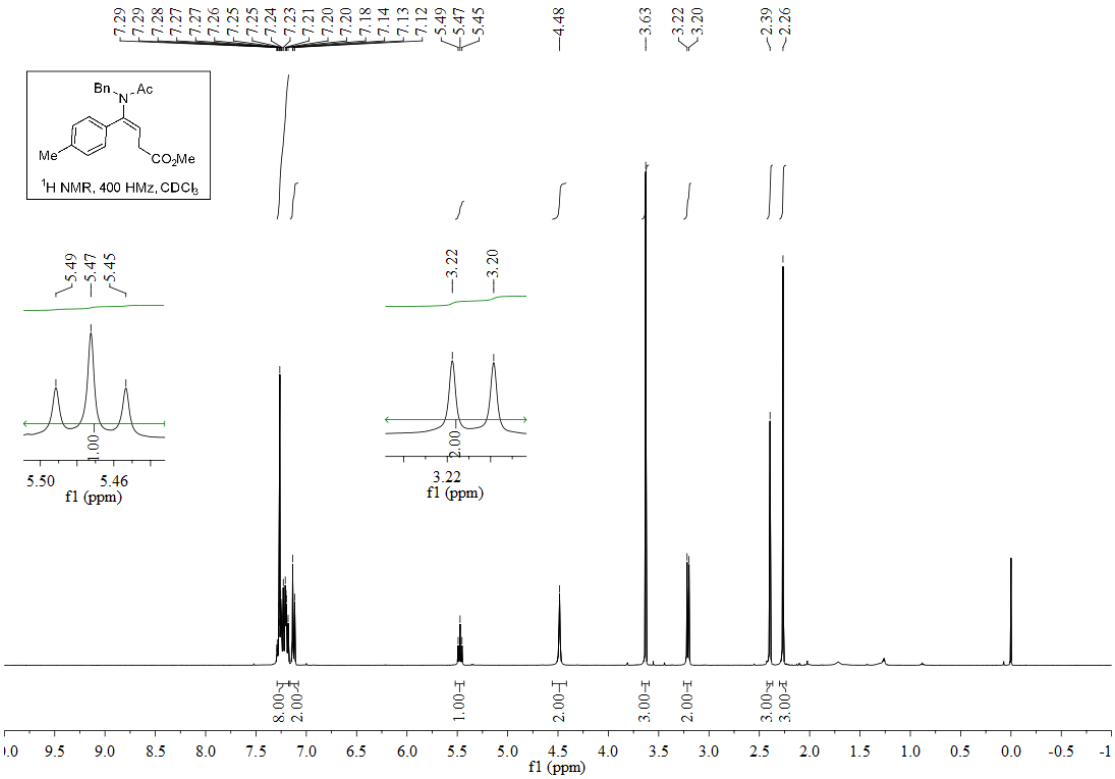
^{1}H NMR spectrum of compound **44**



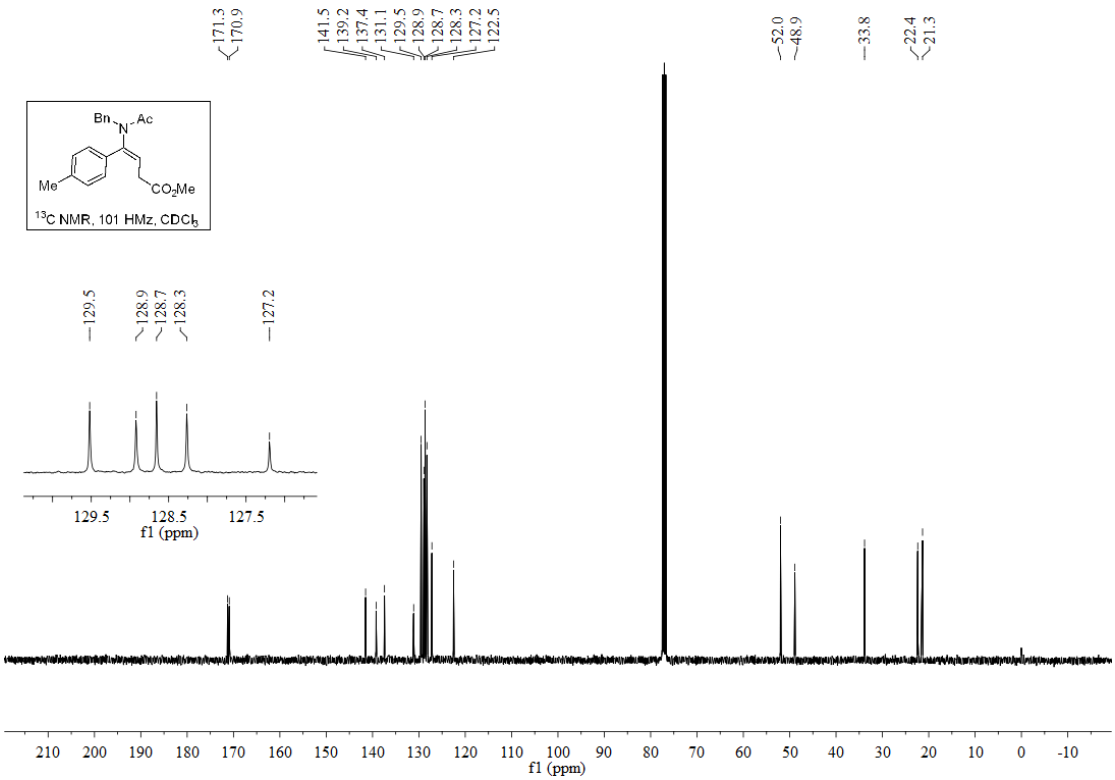
^{13}C NMR spectrum of compound **44**



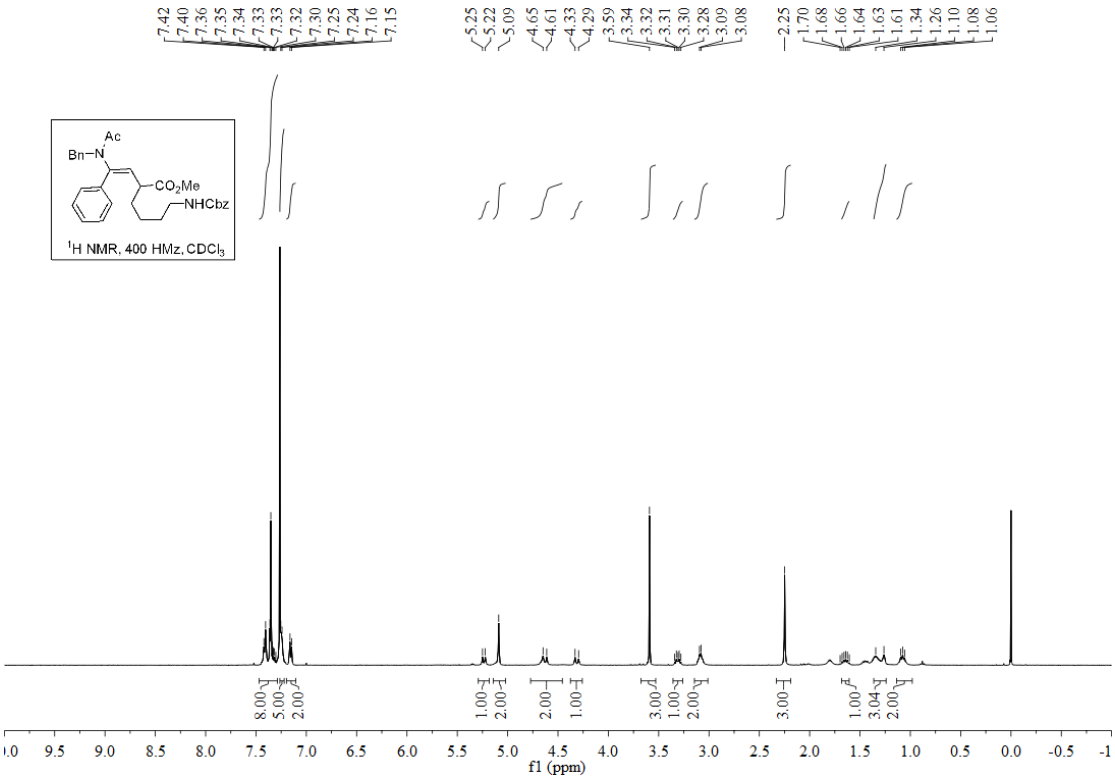
^{1}H NMR spectrum of compound **45**



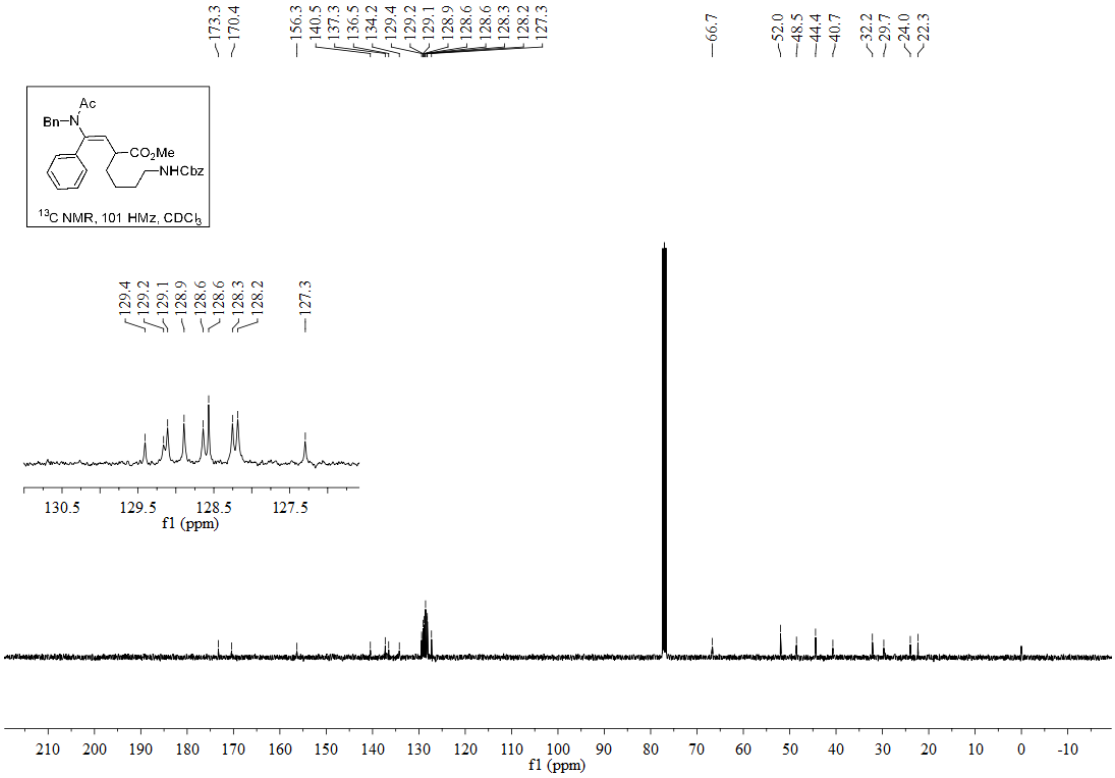
^{13}C NMR spectrum of compound **45**



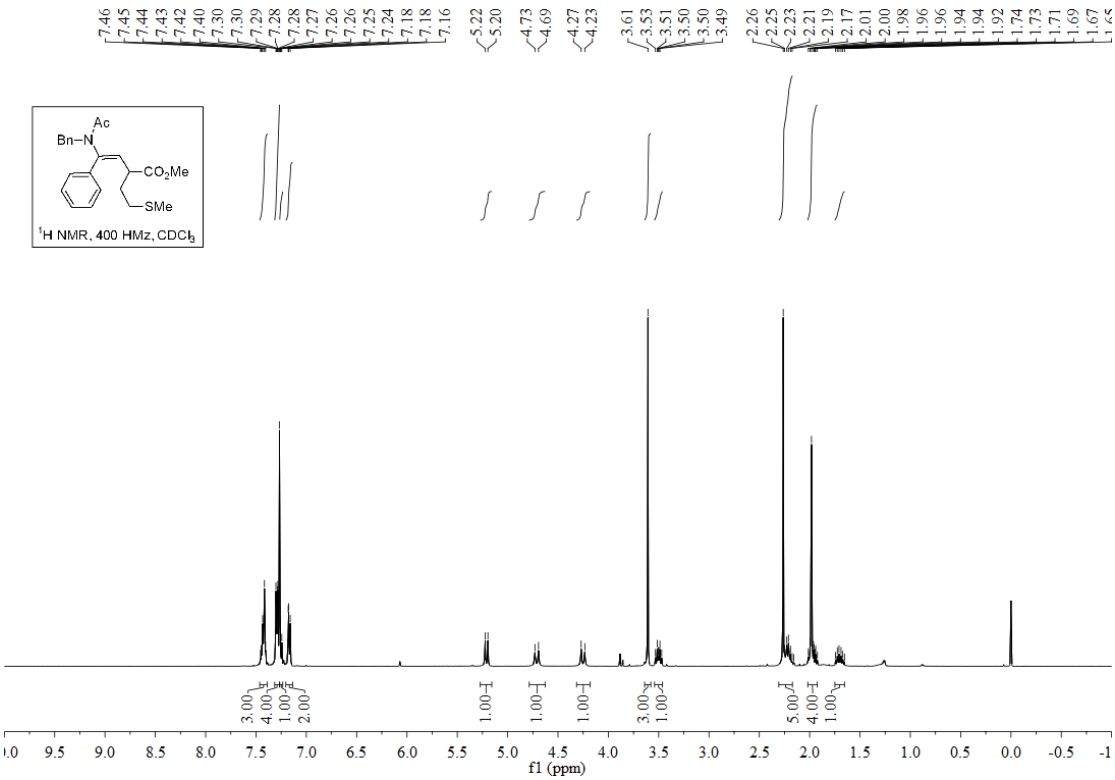
^{1}H NMR spectrum of compound **46**



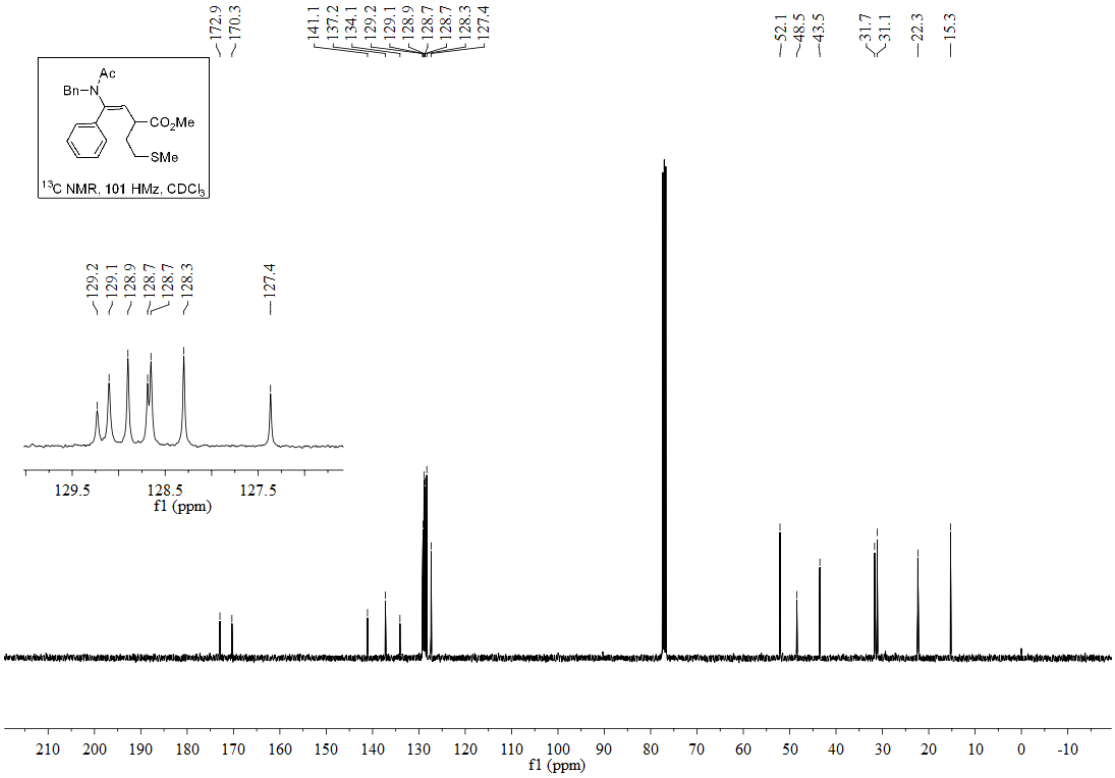
^{13}C NMR spectrum of compound **46**



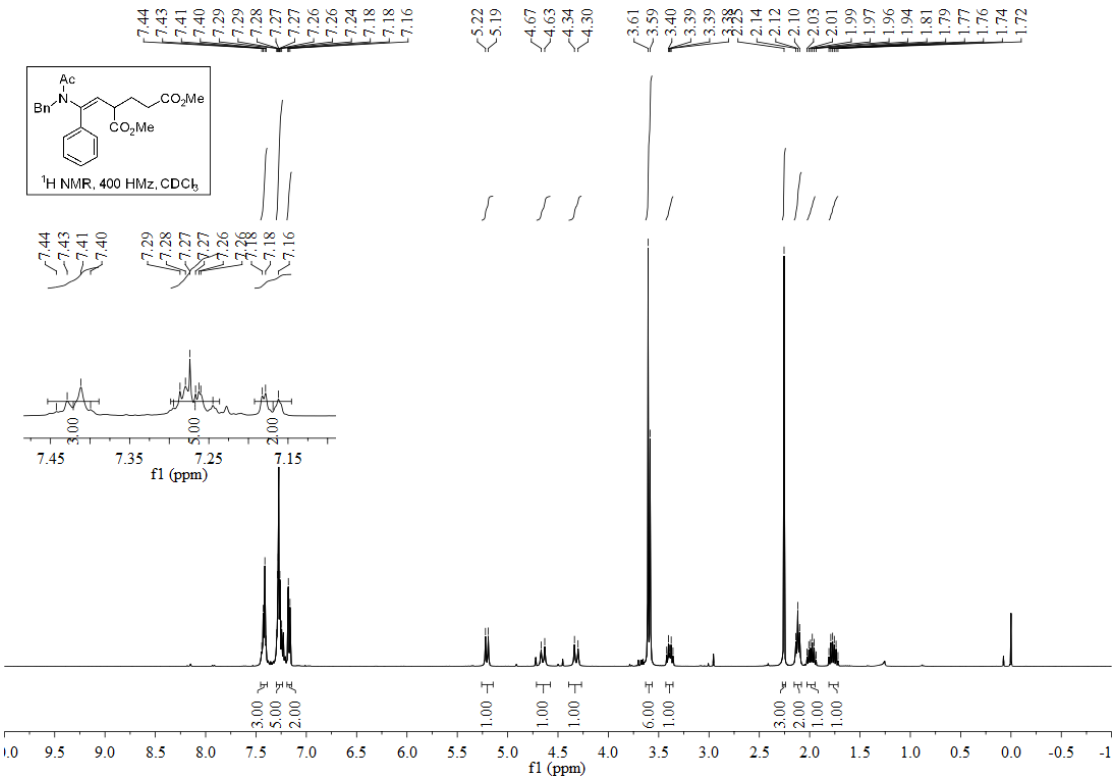
^{1}H NMR spectrum of compound **47**



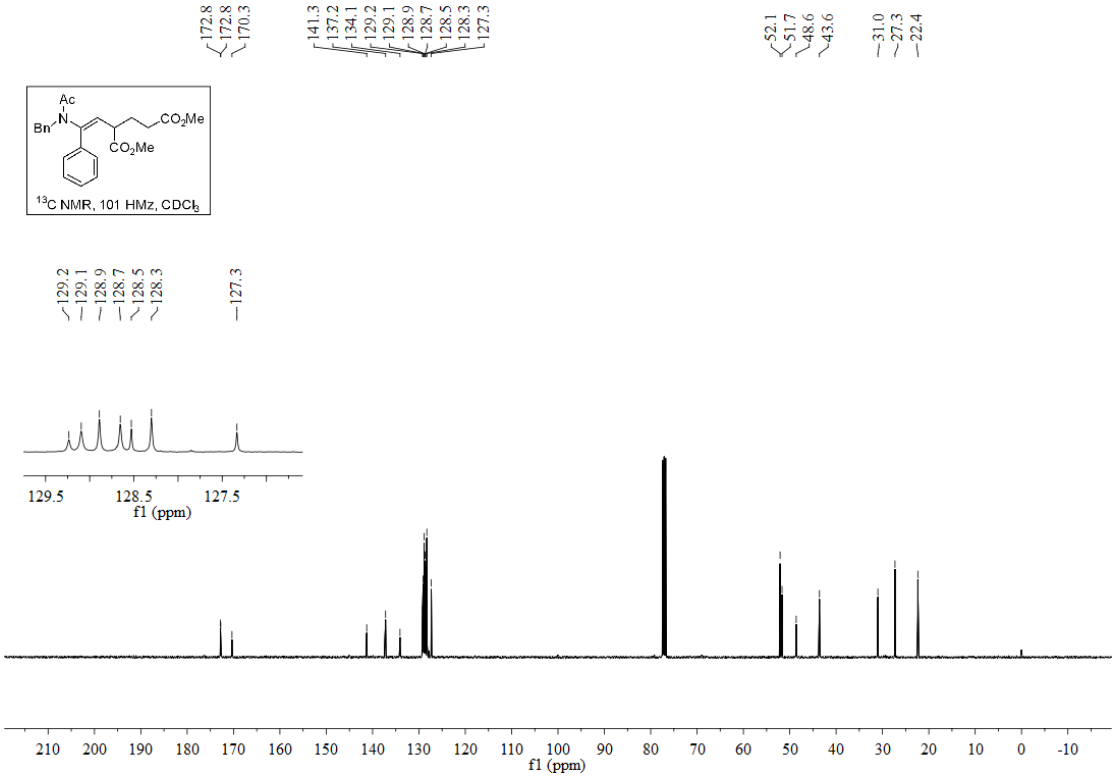
^{13}C NMR spectrum of compound **47**



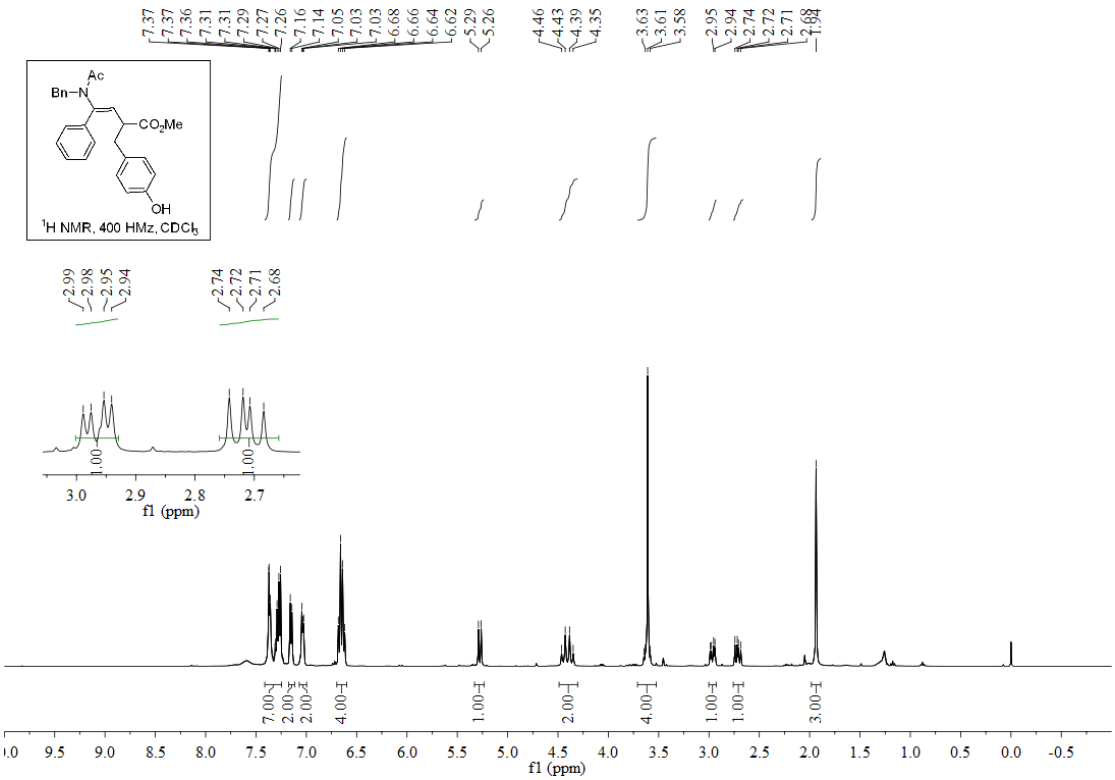
^{1}H NMR spectrum of compound **48**



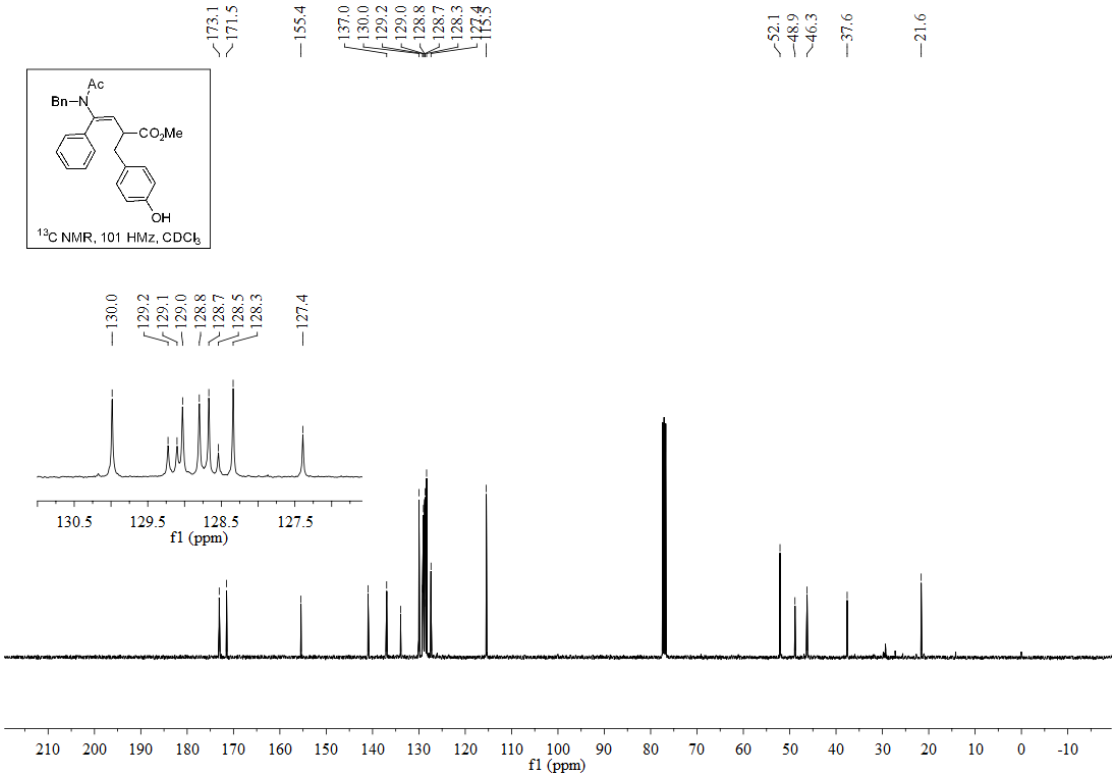
^{13}C NMR spectrum of compound **48**



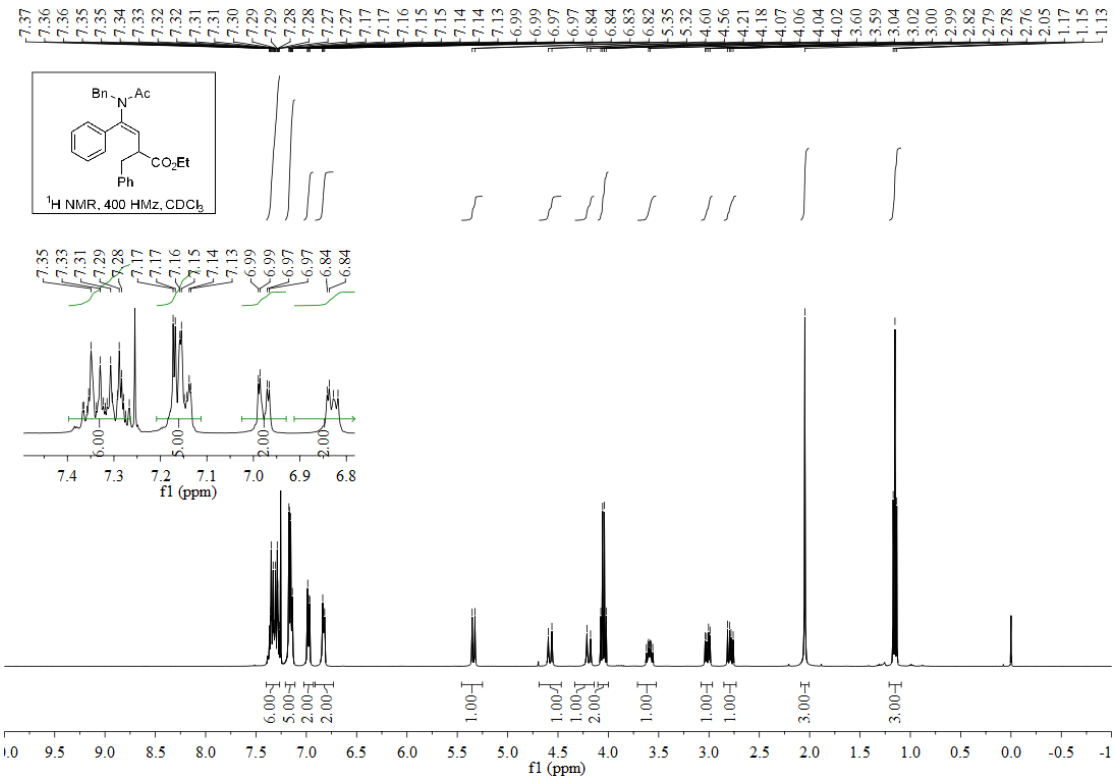
^{1}H NMR spectrum of compound **49**



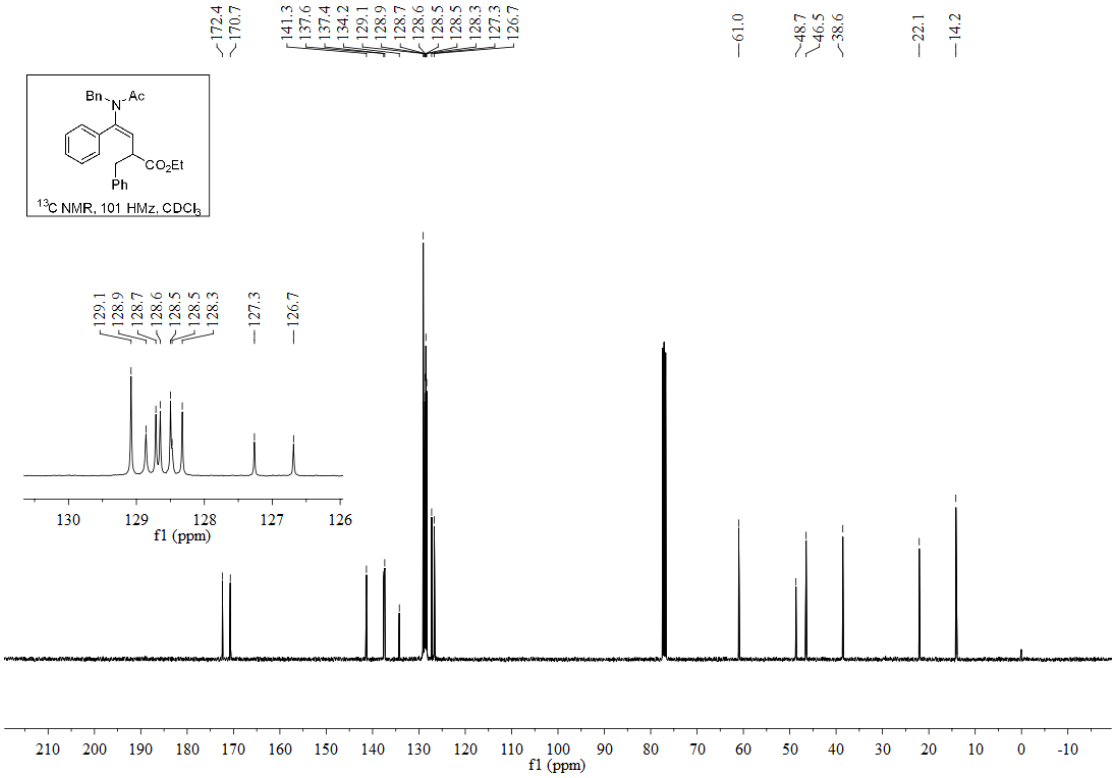
^{13}C NMR spectrum of compound **49**



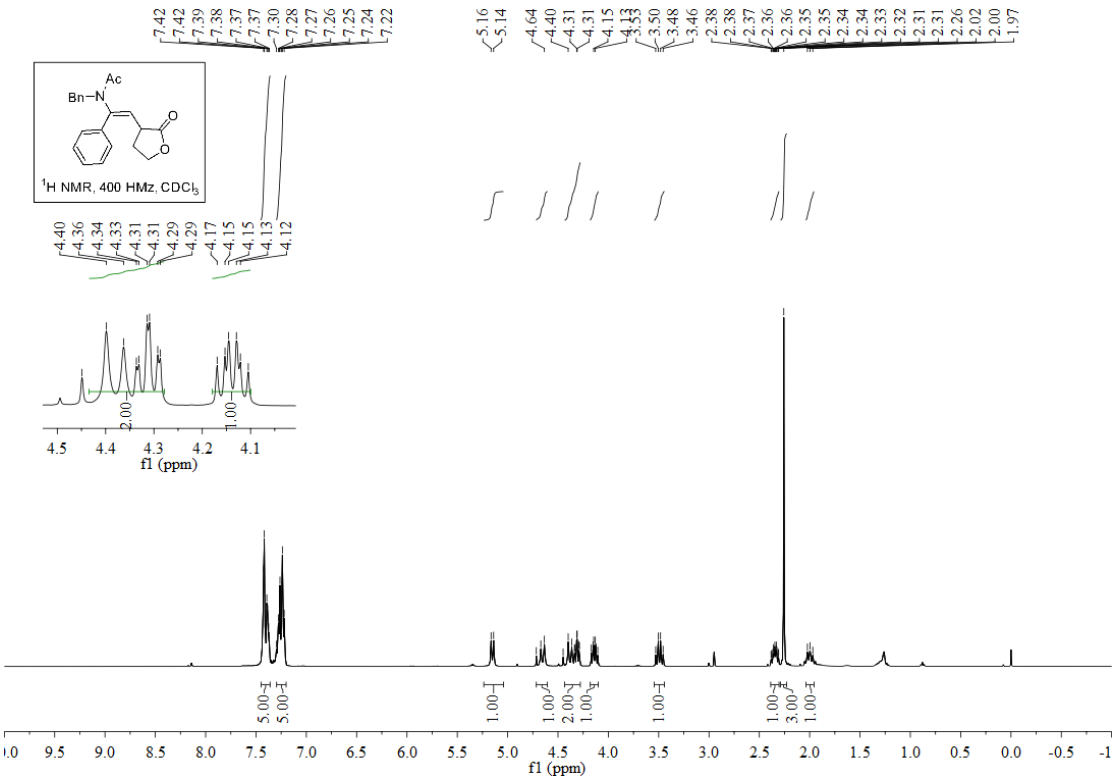
^{1}H NMR spectrum of compound **50**



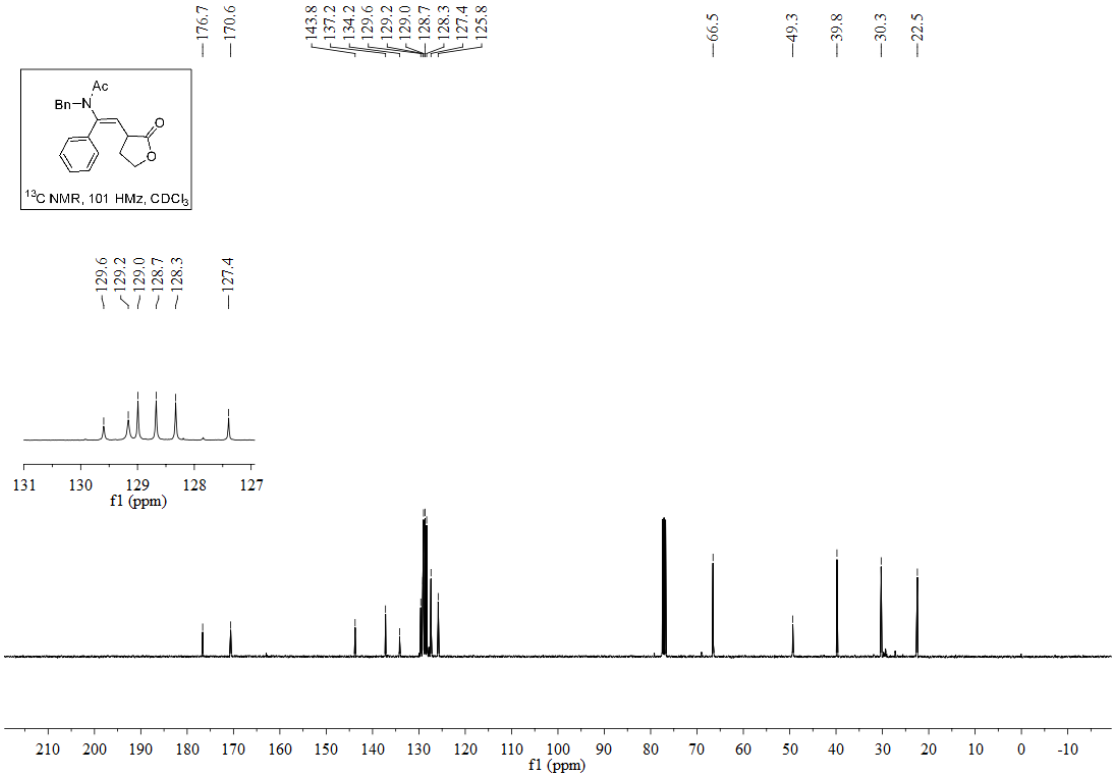
^{13}C NMR spectrum of compound **50**



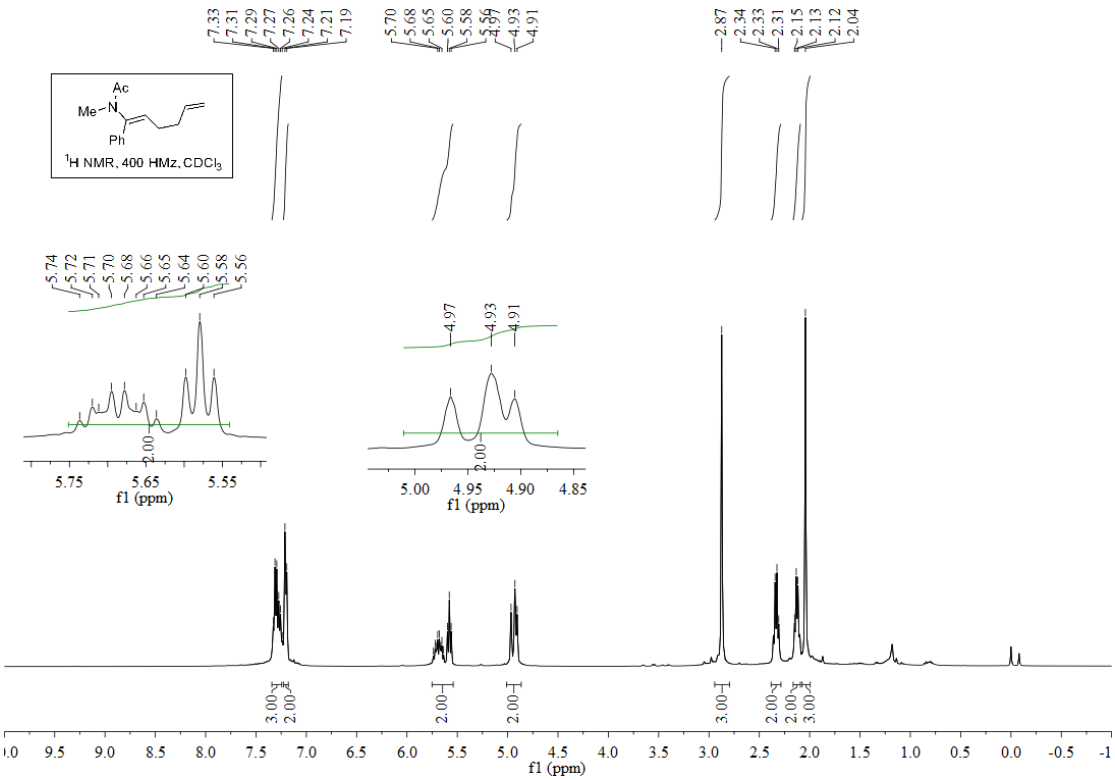
^{1}H NMR spectrum of compound **51**



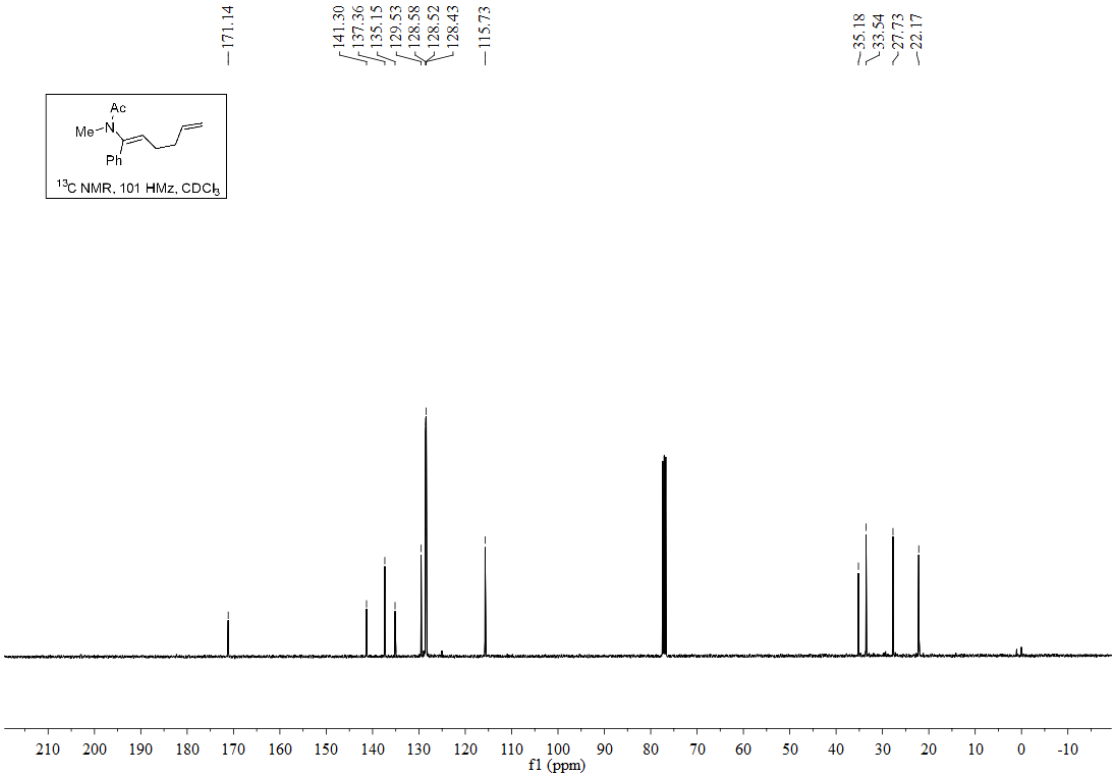
^{13}C NMR spectrum of compound **51**



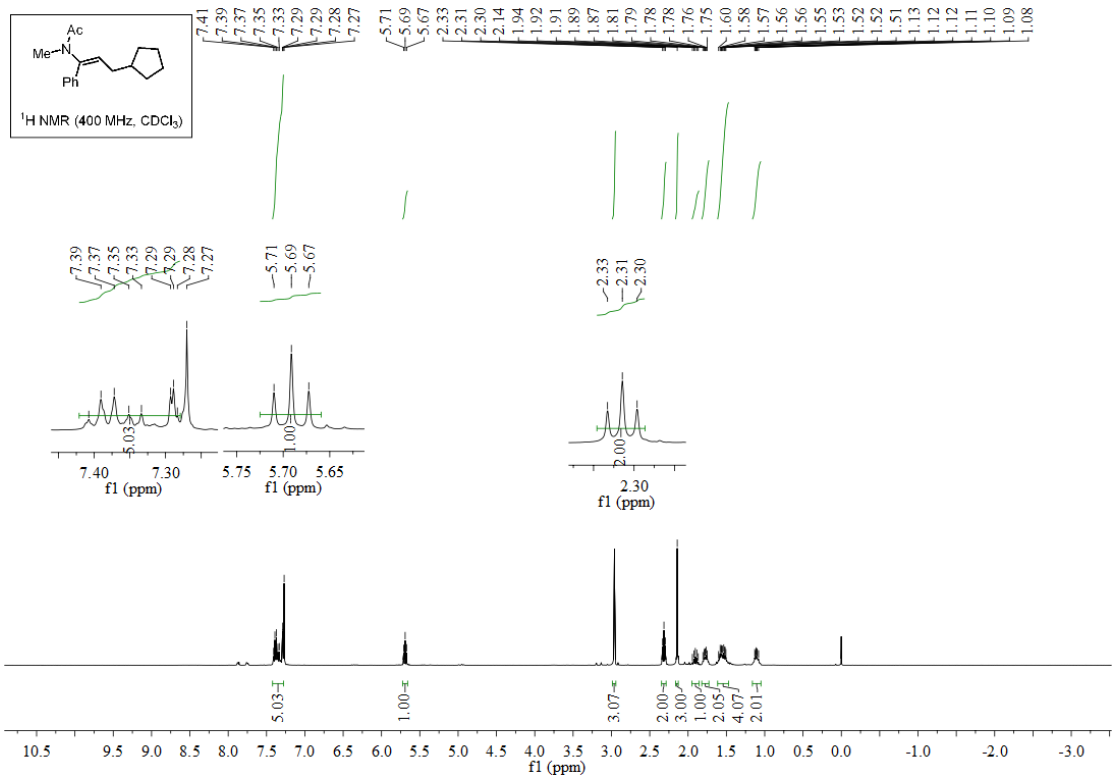
^{1}H NMR spectrum of compound **53**



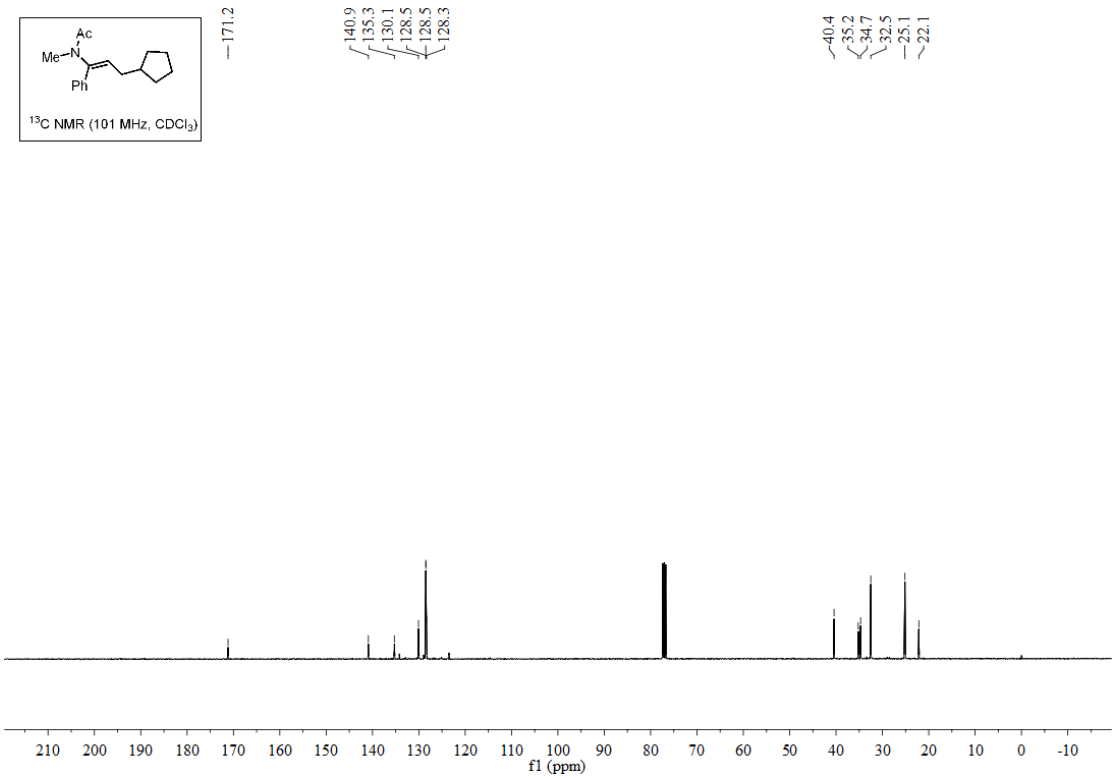
^{13}C NMR spectrum of compound **53**



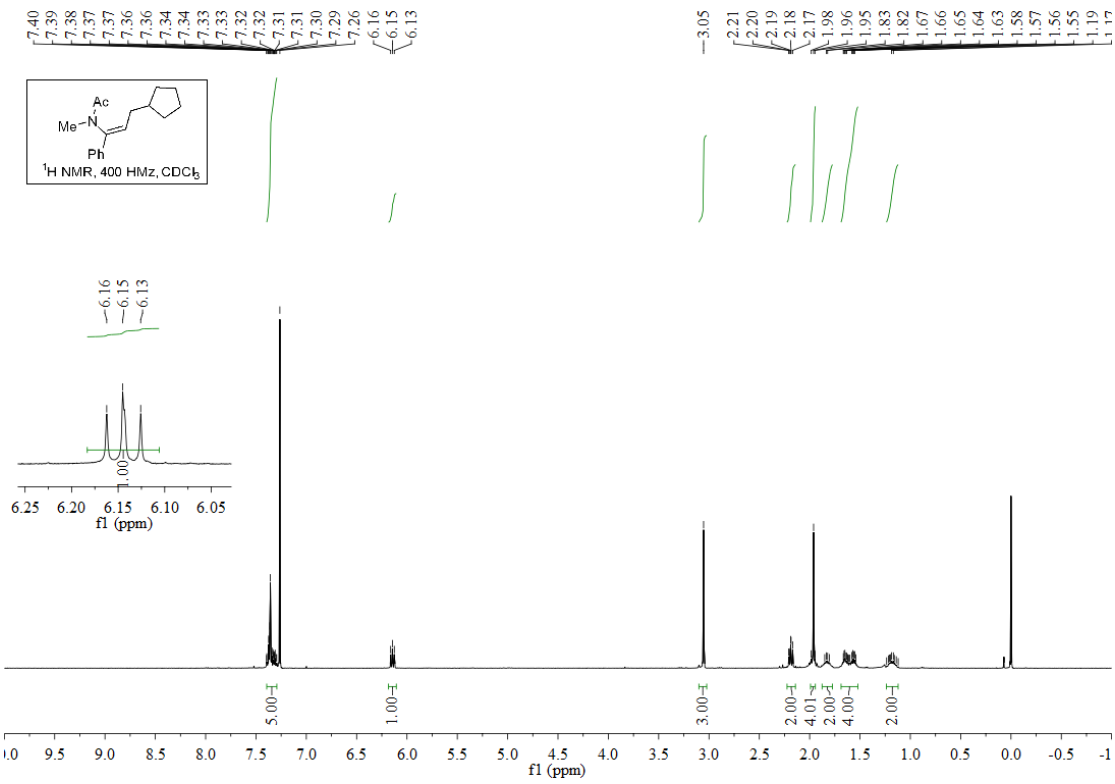
^{1}H NMR spectrum of compound **54** (*E-type*)



^{13}C NMR spectrum of compound **54** (*E-type*)



^{1}H NMR spectrum of compound **54** (*Z-type*)



^{13}C NMR spectrum of compound **54** (*Z-type*)