Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Hydroxyl Group-Directed, Tartaric Acid-Catalyzed Synthesis of *meta*-Functionalized Aryl Ethers and Phenols through Domino Conjugate Addition/Aromatization of *para*-Quinols

Guo-Shu Chen,[a] Jia-Hui Li,[a] Shu-Jie Chen,*[a] Wen-Xia Lin,[a] Hai Ren,[b] Dong-Sheng Deng[c] and Yun-Lin Liu*[a]

[a] School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P.R. China

[b] State Key Laboratory of Functions and Applications of Medicinal Plants, Guizhou Medical University, Guiyang 550014, P.R. China

[c] College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, P.R. China

Email: sjchen@gzhu.edu.cn; ylliu@gzhu.edu.cn

Table of Contents

1. General Information and Materials

All reactions were performed in oven-dried glassware in the air unless otherwise noted. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on an Bruker spectrometer operating at 400 MHz, 100 MHz, and 376 MHz respectively. Chemical shifts (δ) are reported in ppm and the tetramethylsilane peak (TMS: 0.00 ppm) was used as internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectrometry (HRMS) was measured with an ESI-TOF method. Flash chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was carried out using commercial silica gel-precoated glass plates, and compounds were visualized under UV light (254 nm).

p-Quinol[1], *p*-quinol ether **1c**[2] were synthesized from corresponding phenols following the literature method. Alkenyl boronic acids were purchased from Energy Chemical, or prepared according to reported procedures.[3]

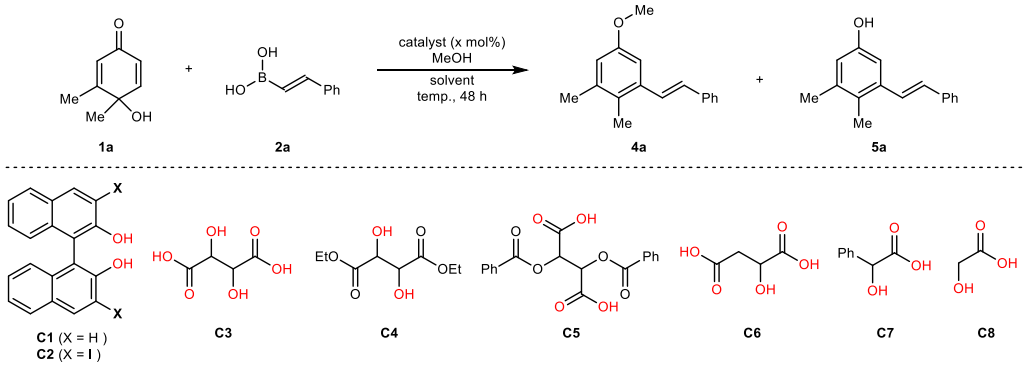
1. (a) M. C. Carreño, M. González-López and A. Urbano, *Angew. Chem. Int. Ed.*, 2006, **45**, 2737; (b) R. M. Moriarty and O. Prakash, *Org. React.*, 2001, **57**, 327; (c) S. Husen, A. Chauhan and R. Kumar, *Green Chem.*, 2020, **22**, 1119.

2. P. Wipf and Y. Kim, *J. Am. Chem. Soc.*, 1994, **116**, 11678.

3. (a) C. Feng and T.-P. Loh, *Org. Lett.*, 2014, **16**, 3444; (b) A. Boelke, L. D. Caspers and B. J. Nachtsheim, *Org. Lett.*, 2017, **19**, 5344.

2. Details for Condition Optimization

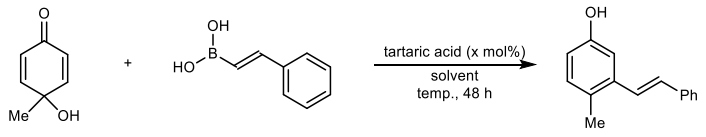
Table S1 Optimization of reaction conditions toward ether products[a]



entry	cat. (x mol%)	1a:2a (mole ratio)	MeOH (equiv)	solvent	temp. (°C)	yield (%)[b]	
						4a	5a
1	C1 (10 mol%)	1:1	4	DCM	50	0	0
2	C2 (10 mol%)	1:1	4	DCM	50	0	0
3	C3 (10 mol%)	1:1	4	DCM	50	53	12
4	C3 (10 mol%)	1:1	4	DCM	RT	12	<5
5	C3 (10 mol%)	1.2:1	4	DCM	50	78	11
6	C3 (20 mol%)	1.2:1	4	DCM	50	92	<5
7	C3 (20 mol%)	1.2:1	2	DCM	50	56	18
8	C3 (20 mol%)	1.2:1	4	THF	50	trace	<5
9	C3 (20 mol%)	1.2:1	4	Toluene	50	8	7
10	C3 (20 mol%)	1.2:1	4	MeCN	50	25	54
11	C3 (20 mol%)	1.2:1	-	MeOH	50	46	14
12	C3 (20 mol%)	1.2:1	0	DCM	50	0	31
13	C4 (20 mol%)	1.2:1	4	DCM	50	0	0
14	C5 (20 mol%)	1.2:1	4	DCM	50	0	0
15	C6 (20 mol%)	1.2:1	4	DCM	50	75	<5
16	C7 (20 mol%)	1.2:1	4	DCM	50	66	15
17	C8 (20 mol%)	1.2:1	4	DCM	50	66	17

[a] Reactions were run on a 0.1 mmol scale in 1 mL solvent. [b] Isolated yields based on **2a**.

Table S2 Optimization of reaction conditions toward phenol products[a]



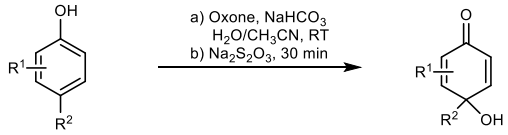
entry	cat. (x mol%)	**1b**:**2a** (mole ratio)	solvent	temp. (°C)	yield of **5b** (%)[b]
1	10	1:1.5	DCM	RT	34%
2	10	1:1.2	DCM	RT	49%
3	10	1:1	DCM	RT	45%
4	20	1:1.2	DCM	RT	52%
5	20	1:1.2	DCM/EtOAc (v/v = 9:1)	RT	38%
6	20	1:1.2	DCM/THF (v/v = 9:1)	RT	23%
7	20	1:1.2	DCM/DMF (v/v = 9:1)	RT	48%
8	20	1:1.2	DCM/MeCN (v/v = 9:1)	RT	65%
9	20	1:1.2	DCM/MeCN (v/v = 9:1)	50	78%
10	20	1.2:1	DCM/MeCN (v/v = 9:1)	50	82%

[a] Reactions were run on a 0.1 mmol scale in 1 mL solvent. [b] Isolated yields.

3. Experimental Procedures and Analytical Data

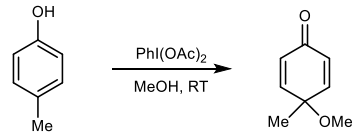
3.1 Preparation of Starting Materials

(a) *p*-Quinol



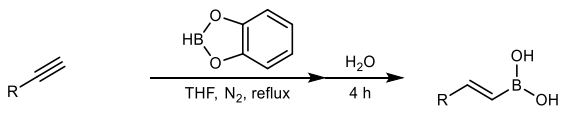
To a flame dried 250 mL round bottom flask equipped with a magnetic stir bar was added *p*-alkyl phenol (5 mmol, 1 equiv), water (85 mL) and CH_3CN (20 mL). Under vigorously stirring, a mixture of Oxone (5 equiv) and $NaHCO_3$ (15 equiv), which have been ground into powder previously, was added in portions. Then an empty balloon was attached immediately to avoid loss of generated singlet oxygen. The mixture was vigorously stirred until total disappearance of the phenol (ca. 1 h, monitored by TLC). Afterwards, the reaction mixture was diluted with water (20 mL) and $Na_2S_2O_3$ (10 equiv) was added portionwise in 5 minutes. The mixture was stirred at rt for 30 min and then extracted three times with EtOAc, dried over Na_2SO_4, filtered, and concentrated. The residue was subjected to column chromatography on silica gel using EtOAc/petroleum ether as eluent to give the *p*-quinols.

(b) *p*-Quinol Ether 1c



To a solution of *p*-cresol (5.0 mmol, 1.0 equiv) in dry MeOH (10 mL) was added $PhI(OAc)_2$ (5.5 mmol, 1.0 equiv) portionwise at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min. Afterwards, the reaction was diluted with EtOAc (15 mL), washed with $NaHCO_{3(sat.)}$ (2 x 5 mL) and brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation under vacuum, the crude residue was purified by column chromatography over silica gel (EtOAc/ petroleum ether) to give the desired **1c**.

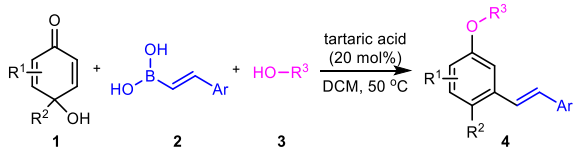
(c) Alkenyl Boronic Acids



The corresponding alkyne (2.0 mmol, 1.0 equiv) was added to catecholborane (1 M in THF, 3 mL, 1.5 equiv) and the mixture was refluxed under nitrogen atmosphere for 16 h. The solvent was evaporated and then H_2O (5 mL) was added. The suspension was vigorously stirred for 4 h at room temperature, then extracted with EtOAc, dried over Na_2SO_4, filtered, and concentrated. The residue was subjected to

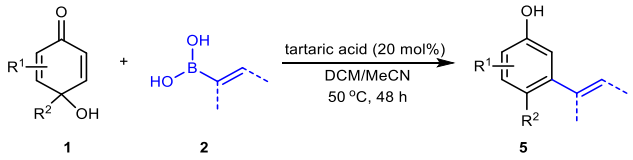
column chromatography on silica gel using EtOAc/petroleum ether as eluent to give the desired alkenyl boronic acids.

3.2 Procedure A: Synthesis of *meta*-Alkenylated Aryl Alkyl Ethers.



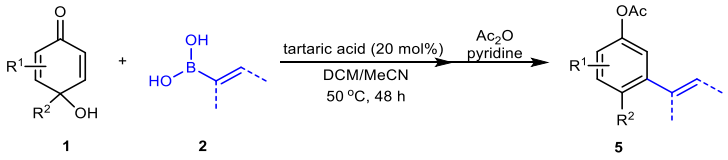
To a flame dried 10 mL reaction tube equipped with a magnetic stir bar was added *p*-quinol **1** (0.12 mmol, 1.2 equiv), alkenyl boronic acid **2** (0.10 mmol, 1.0 equiv), alcohol **3** (0.4 mmol, 4.0 equiv), tartaric acid (0.02 mmol, 0.2 equiv), and DCM (1 mL). After being stirred at 50 °C for 48 h, the mixture was concentrated *in vacuo*, and the residue was directly subjected to column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the corresponding products **4**.

3.3 Procedure B: Synthesis of *meta*-Functionalized Phenols.



To a flame dried 10 mL reaction tube equipped with a magnetic stir bar was added *p*-quinol **1** (0.12 mmol, 1.2 equiv), boronic acid **2** (0.10 mmol, 1.0 equiv), and tartaric acid (0.02 mmol, 0.2 equiv). To the mixture was added 0.9 mL of DCM and 0.1 mL of MeCN. After being stirred at 50 °C for 48 h, the mixture was concentrated *in vacuo*, and the residue was directly subjected to column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the corresponding phenols **5**.

3.4 Procedure C: Synthesis of *meta*-Functionalized Aryl Acetates.

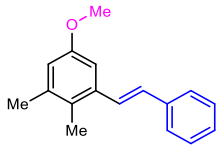


To a flame dried 10 mL reaction tube equipped with a magnetic stir bar was added *p*-quinol **1** (0.12 mmol, 1.2 equiv), boronic acid **2** (0.10 mmol, 1.0 equiv), and tartaric acid (0.02 mmol, 0.2 equiv). To the mixture was added 0.9 mL of DCM and 0.1 mL of MeCN. After being stirred at 50 °C for 48 h, the mixture was cooled to rt. Pyridine (0.5 mmol, 5.0 equiv) and acetic anhydride (0.25 mmol, 2.5 equiv) were added, and the mixture was stirred at 50 °C for 12 h. After being cooled to rt, the mixture was poured into water, and the organic materials were extracted with EtOAc, dried over Na_2SO_4, filtered, and

concentrated. The residue was subjected to column chromatography on silica gel using EtOAc/petroleum ether as eluent to gave aryl acetates **5**.

3.5 Analytical Data

(*E*)-5-Methoxy-1,2-dimethyl-3-styrylbenzene (4a)



Yield: 92%, white solid

TLC (SiO_2) R_f = 0.72 (hexanes/ethyl acetate = 9:1), [UV light]

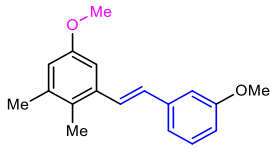
mp 61-62℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.41-7.35 (m, 3H), 7.29-7.23 (m, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 1.9 Hz, 1H), 3.83 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.39, 138.29, 137.76, 137.75, 130.56, 128.78, 127.74, 127.68, 126.90, 126.65, 115.57, 108.64, 55.38, 21.07, 14.85.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{19}O$ 239.1430, found 239.1426.

(*E*)-5-Methoxy-1-(3-methoxystyryl)-2,3-dimethylbenzene (4b)



Yield: 90%, pale yellow oil

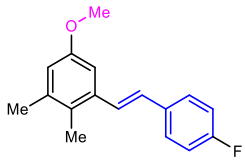
TLC (SiO_2) R_f = 0.50 (hexanes/ethyl acetate = 19:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 16.0 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.07-7.04 (m, 1H), 6.97 (d, *J* = 2.7 Hz, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.83 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.97, 157.38, 139.23, 138.30, 137.63, 130.43, 129.75, 128.08, 126.92, 119.34, 115.63, 113.14, 112.08, 108.64, 55.37, 21.06, 14.85.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{21}O_2$ 269.1536, found 269.1531.

(*E*)-1-(4-Fluorostyryl)-5-methoxy-2,3-dimethylbenzene (4c)



Yield: 81%, white solid

TLC (SiO_2) R_f = 0.62 (hexanes/ethyl acetate = 19:1), [UV light]

mp 64-65℃

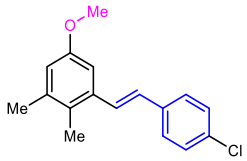
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.29 (d, *J* = 16.0 Hz, 1H), 7.08-7.01 (m, 2H), 6.94 (d, *J* = 2.7 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 2.7 Hz, 1H), 3.82 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.40 (d, *J* = 247.1 Hz), 157.39, 138.32, 137.57, 133.93 (d, *J* = 3.4 Hz), 129.34 (d, *J* = 1.1 Hz), 128.11 (d, *J* = 8.0 Hz), 127.50 (d, *J* = 2.5 Hz), 126.83, 115.79, 115.57 (d, *J* = 2.3 Hz), 108.61, 55.37, 21.06, 14.84.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.37.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{18}FO$ 257.1336, found 257.1330.

(*E*)-1-(4-Chlorostyryl)-5-methoxy-2,3-dimethylbenzene (4d)



Yield: 93%, white solid

TLC (SiO_2) R_f = 0.63 (hexanes/ethyl acetate = 19:1), [UV light]

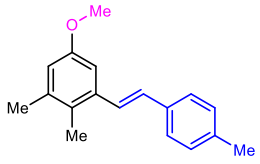
mp 74-76℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.38-7.30 (m, 3H), 6.95 (d, *J* = 2.7 Hz, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.40, 138.37, 137.37, 136.26, 133.20, 129.22, 128.91, 128.31, 127.80, 126.93, 115.75, 108.61, 55.37, 21.06, 14.85.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{18}ClO$ 273.1041, found 273.1035.

(*E*)-5-Methoxy-1,2-dimethyl-3-(4-methylstyryl)benzene (4e)



Yield: 72%, white solid

TLC (SiO_2) R_f = 0.67 (hexanes/ethyl acetate = 19:1), [UV light]

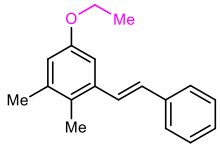
mp 56-58℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 15.7 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.37, 138.23, 137.90, 137.56, 134.98, 130.47, 129.48, 126.78, 126.73, 126.55, 115.40, 108.52, 55.37, 21.35, 21.06, 14.83.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{21}O$ 253.1587, found 253.1581.

(*E*)-5-Ethoxy-1,2-dimethyl-3-styrylbenzene (4f)



Yield: 85%, white solid

TLC (SiO_2) R_f = 0.75 (hexanes/ethyl acetate = 9:1), [UV light]

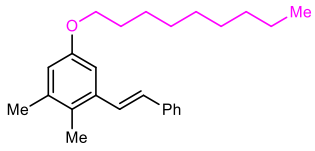
mp 88-90℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.42-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.98 (d, *J* = 2.7 Hz, 1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 2.7 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.72, 138.23, 137.80, 137.71, 130.48, 128.78, 127.75, 127.64, 126.79, 126.63, 116.12, 109.39, 63.50, 21.06, 15.07, 14.84.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{21}O$ 253.1587, found 253.1581.

(*E*)-1,2-Dimethyl-5-(nonyloxy)-3-styrylbenzene (4g)



Yield: 72%, white solid

TLC (SiO_2) R_f = 0.74 (hexanes/ethyl acetate = 19:1), [UV light]

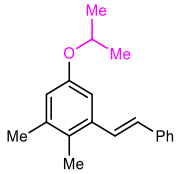
mp 62-63℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.42-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 3.98 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 1.79 (dq, *J* = 13.3, 6.6 Hz, 2H), 1.52-1.42 (m, 2H), 1.36-1.26 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.94, 138.20, 137.81, 137.68, 130.45, 128.77, 127.76, 127.63, 126.69, 126.63, 116.13, 109.36, 68.08, 32.01, 29.68, 29.55, 29.51, 29.40, 26.20, 22.80, 21.06, 14.84, 14.25.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{25}H_{34}NaO$ 373.2502, found 373.2504.

(*E*)-5-Isopropoxy-1,2-dimethyl-3-styrylbenzene (4h)



Yield: 70%, faint yellow solid

TLC (SiO_2) R_f = 0.77 (hexanes/ethyl acetate = 9:1), [UV light]

mp 52-53℃

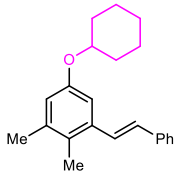
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 5.3, 3.5 Hz, 2H), 7.41-7.34 (m, 3H), 7.28-7.24 (m, 1H), 6.98 (d, *J* = 2.7 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 4.57 (hept, *J* = 6.1 Hz, 1H), 2.28 (s, 3H),

2.25 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.58, 138.24, 137.81, 137.77, 130.46, 128.77, 127.75, 127.63, 126.82, 126.62, 117.52, 111.07, 69.91, 22.28, 21.06, 14.85.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{19}H_{22}NaO$ 289.1563, found 289.1559.

(*E*)-5-(Cyclohexyloxy)-1,2-dimethyl-3-styrylbenzene (4i)



Yield: 79%, white solid

TLC (SiO_2) R_f = 0.77 (hexanes/ethyl acetate = 9:1), [UV light]

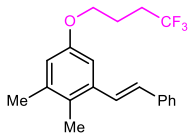
mp 102-104℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.40-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 4.30-4.20 (m, 1H), 2.28 (s, 3H), 2.25 (s, 3H), 2.05-1.97 (m, 2H), 1.83-1.80 (m, 2H), 1.58-1.32 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.46, 138.20, 137.82, 137.77, 130.46, 128.77, 127.77, 127.63, 126.84, 126.63, 117.68, 111.38, 75.53, 32.06, 25.79, 23.94, 21.07, 14.88.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{22}H_{26}NaO$ 329.1876, found 329.1884.

(*E*)-1,2-Dimethyl-3-styryl-5-(4,4,4-trifluorobutoxy)benzene (4j)



Yield: 85%, white solid

TLC (SiO_2) R_f = 0.75 (hexanes/ethyl acetate = 9:1), [UV light]

mp 80-82℃

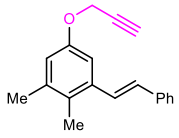
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.41-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 2.1 Hz, 1H), 4.04 (t, *J* = 5.9 Hz, 2H), 2.41-2.29 (m, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 2.09-2.02 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.42, 138.39, 137.83, 137.69, 130.64, 128.79, 127.73, 127.58, 127.31 (q, *J* = 275 Hz), 127.27, 126.64, 116.02, 109.30, 66.11, 30.86 (q, *J* = 29.1 Hz), 22.38 (q, *J* = 3.0 Hz), 21.04, 14.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -66.29.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{22}F_3O$ 335.1617, found 335.1609.

(*E*)-1,2-Dimethyl-5-(prop-2-yn-1-yloxy)-3-styrylbenzene (4k)



Yield: 67%, faint yellow solid

TLC (SiO_2) R_f = 0.63 (hexanes/ethyl acetate = 9:1), [UV light]

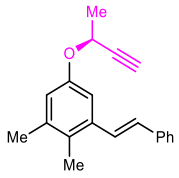
mp 80-82℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.40-7.34 (m, 3H), 7.27 (ddd, *J* = 7.5, 4.0, 1.3 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.76 (d, *J* = 2.7 Hz, 1H), 4.71 (d, *J* = 2.4 Hz, 2H), 2.53 (t, *J* = 2.4 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.33, 138.39, 137.82, 137.68, 130.79, 128.79, 127.87, 127.73, 127.53, 126.67, 116.37, 109.83, 78.94, 75.47, 55.94, 21.08, 14.91.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{19}H_{18}NaO$ 285.1250, found 285.1245.

(*S*,*E*)-5-(But-3-yn-2-yloxy)-1,2-dimethyl-3-styrylbenzene (4l)



Yield: 49%, white solid

TLC (SiO_2) R_f = 0.67 (hexanes/ethyl acetate = 19:1), [UV light]

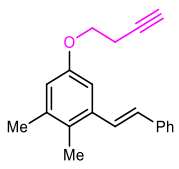
mp 73-74℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.40-7.34 (m, 3H), 7.28-7.24 (m, 1H), 7.09 (d, *J* = 2.7 Hz, 1H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 4.91 (qd, *J* = 6.6, 2.0 Hz, 1H), 2.48 (d, *J* = 2.0 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 1.67 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.03, 138.24, 137.76, 137.71, 130.67, 128.77, 127.77, 127.67, 127.60, 126.65, 117.21, 110.83, 83.28, 73.81, 63.57, 22.30, 21.07, 14.90.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{21}O$ 277.1587, found 277.1581.

(*E*)-5-(But-3-yn-1-yloxy)-1,2-dimethyl-3-styrylbenzene (4m)



Yield: 66%, white solid

TLC (SiO_2) R_f = 0.48 (hexanes/ethyl acetate = 19:1), [UV light]

mp 96-98℃

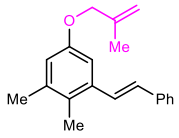
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.39-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.99 (d, *J* = 2.7 Hz,

1H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 4.12 (t, *J* = 7.1 Hz, 2H), 2.69 (td, *J* = 7.1, 2.7 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 2.05 (t, *J* = 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.20, 138.37, 137.80, 137.70, 130.64, 128.79, 127.71, 127.55, 127.37, 126.65, 116.20, 109.55, 80.70, 69.95, 66.11, 21.06, 19.73, 14.88.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{21}O$ 277.1587, found 277.1580.

(*E*)-1,2-Dimethyl-5-((2-methylallyl)oxy)-3-styrylbenzene (4n)



Yield: 44%, colorless oil

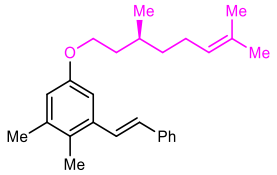
TLC (SiO_2) R_f = 0.79 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.40-7.34 (m, 3H), 7.29-7.24 (m, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 5.12 (s, 1H), 4.99 (s, 1H), 4.45 (s, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.59, 141.30, 138.23, 137.77, 137.68, 130.52, 128.77, 127.71, 127.66, 127.02, 126.64, 116.34, 112.70, 109.63, 71.87, 21.07, 19.61, 14.86.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{23}O$ 279.1743, found 279.1738.

(*S*,*E*)-5-((3,7-Dimethyloct-6-en-1-yl)oxy)-1,2-dimethyl-3-styrylbenzene (4o)



Yield: 89%, colorless oil

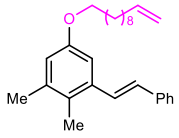
TLC (SiO_2) R_f = 0.83 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.42-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 1.9 Hz, 1H), 5.16-5.07 (m, 1H), 4.07-3.96 (m, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 2.07-1.80 (m, 3H), 1.70 (s, 3H), 1.62 (s, 3H), 1.58-1.20 (m, 4H), 0.98 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.93, 138.20, 137.80, 137.69, 131.38, 130.47, 128.77, 127.76, 127.64, 126.71, 126.63, 124.84, 116.14, 109.37, 66.31, 37.28, 36.39, 29.65, 25.86, 25.59, 21.06, 19.68, 17.80, 14.85.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{26}H_{34}NaO$ 385.2502, found 385.2508.

(*E*)-1,2-Dimethyl-3-styryl-5-(undec-10-en-1-yloxy)benzene (4p)



Yield: 81%, white solid

TLC (SiO_2) R_f = 0.63 (hexanes/ethyl acetate = 19:1), [UV light]

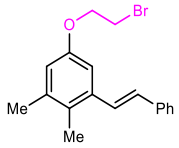
mp 45-47℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.41-7.34 (m, 3H), 7.28-7.24 (m, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.00 (ddt, *J* = 17.1, 2.1, 1.6 Hz, 1H), 4.93 (ddt, *J* = 10.1, 2.3, 1.2 Hz, 1H), 3.97 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 2.08-2.00 (m, 2H), 1.83-1.74 (m, 2H), 1.51-1.29 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.93, 139.35, 138.20, 137.80, 137.67, 130.45, 128.77, 127.75, 127.64, 126.70, 126.63, 116.12, 114.23, 109.35, 68.06, 33.93, 29.65, 29.55, 29.52, 29.50, 29.24, 29.04, 26.19, 21.07, 14.84.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{27}H_{36}NaO$ 399.2658, found 399.2653.

(*E*)-5-(2-Bromoethoxy)-1,2-dimethyl-3-styrylbenzene (4q)



Yield: 67%, white solid

TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 19:1), [UV light]

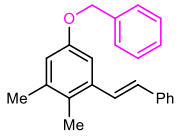
mp 82-84℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.39-7.34 (m, 3H), 7.29-7.24 (m, 1H), 6.98 (d, *J* = 2.7 Hz, 1H), 6.91 (d, *J* = 16.1 Hz, 1H), 6.70 (d, *J* = 2.7 Hz, 1H), 4.31 (t, *J* = 6.3 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.90, 138.49, 137.90, 137.63, 130.76, 128.79, 127.75, 127.73, 127.44, 126.65, 116.28, 109.72, 68.05, 29.50, 21.06, 14.90.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{20}BrO$ 331.0692, found 331.0686.

(*E*)-5-(Benzyloxy)-1,2-dimethyl-3-styrylbenzene (4r)



Yield: 68%, white solid

TLC (SiO_2) R_f = 0.72 (hexanes/ethyl acetate = 9:1), [UV light]

mp 108-110℃

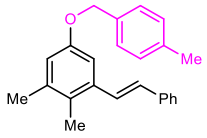
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.49-7.45 (m, 2H), 7.42-7.31 (m, 6H), 7.29-7.25 (m, 1H),

7.07 (d, *J* = 2.7 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 2.7 Hz, 1H), 5.09 (s, 2H), 2.30 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.65, 138.33, 137.78, 137.75, 137.40, 130.63, 128.79, 128.68, 128.00, 127.69, 127.65, 127.19, 126.65, 116.38, 109.75, 70.14, 21.09, 14.88.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{23}H_{22}NaO$ 337.1563, found 337.1563.

(*E*)-1,2-Dimethyl-5-((4-methylbenzyl)oxy)-3-styrylbenzene (4s)



Yield: 78%, white solid

TLC (SiO_2) R_f = 0.57 (hexanes/ethyl acetate = 19:1), [UV light]

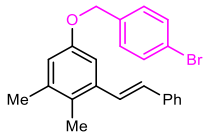
mp 92-94℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.42-7.35 (m, 5H), 7.30-7.25 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 2.6 Hz, 1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 5.05 (s, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.71, 138.29, 137.78, 137.76, 137.73, 134.33, 130.58, 129.37, 128.79, 127.80, 127.68, 127.10, 126.66, 116.40, 109.73, 70.06, 21.34, 21.10, 14.89.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{24}H_{25}O$ 329.1900, found 329.1890.

(*E*)-5-((4-Bromobenzyl)oxy)-1,2-dimethyl-3-styrylbenzene (4t)



Yield: 75%, white solid

TLC (SiO_2) R_f = 0.57 (hexanes/ethyl acetate = 19:1), [UV light]

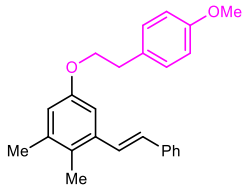
mp 108-110℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 4H), 7.39-7.31 (m, 5H), 7.29-7.24 (m, 1H), 7.02 (d, *J* = 2.7 Hz, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 2.7 Hz, 1H), 5.02 (s, 2H), 2.28 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.34, 138.41, 137.84, 137.67, 136.42, 131.78, 130.70, 129.21, 128.79, 127.73, 127.56, 127.42, 126.65, 121.86, 116.30, 109.70, 69.34, 21.09, 14.89.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{22}BrO$ 393.0849, found 393.0841.

(*E*)-5-(4-Methoxyphenethoxy)-1,2-dimethyl-3-styrylbenzene (4u)



Yield: 57%, white solid

TLC (SiO_2) R_f = 0.46 (hexanes/ethyl acetate = 19:1), [UV light]

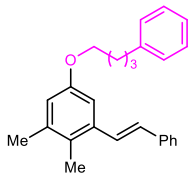
mp 89-91℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.40-7.34 (m, 3H), 7.29-7.21 (m, 3H), 6.97 (d, *J* = 2.7 Hz, 1H), 6.93-6.85 (m, 3H), 6.70 (d, *J* = 2.6 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.35, 156.64, 138.27, 137.76, 137.70, 130.49, 130.46, 130.09, 128.77, 127.66, 126.95, 126.64, 116.23, 114.01, 109.32, 69.08, 55.37, 35.13, 21.06, 14.85.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{25}H_{26}NaO_2$ 381.1825, found 381.1829.

(*E*)-1,2-Dimethyl-5-(4-phenylbutoxy)-3-styrylbenzene (4v)



Yield: 80%, white solid

TLC (SiO_2) R_f = 0.76 (hexanes/ethyl acetate = 9:1), [UV light]

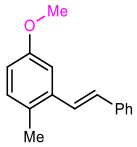
mp 79-81℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.42-7.36 (m, 3H), 7.33-7.19 (m, 6H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 4.01 (t, *J* = 5.8 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 1.85 (dd, *J* = 6.4, 2.8 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.89, 142.40, 138.24, 137.80, 137.71, 130.50, 128.79, 128.57, 128.44, 127.74, 127.66, 126.80, 126.65, 125.89, 116.14, 109.38, 67.84, 35.74, 29.12, 28.03, 21.08, 14.86.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{26}H_{28}NaO$ 379.2032, found 379.2032.

(*E*)-4-Methoxy-1-methyl-2-styrylbenzene (4w)



Yield: 48%, pale yellow oil

TLC (SiO_2) R_f = 0.71 (hexanes/ethyl acetate = 19:1), [UV light]

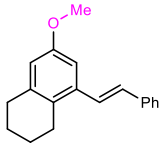
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.36-7.28 (m, 2H), 7.18 (d, *J* = 2.7 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 16.1 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.88 (s, 3H),

2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.04, 137.57, 137.26, 131.26, 130.11, 128.71, 128.19, 127.68, 126.61, 126.60, 113.31, 110.56, 55.39, 19.00.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{17}O$ 255.1274, found 225.1267.

(*E*)-7-Methoxy-5-styryl-1,2,3,4-tetrahydronaphthalene (4x)



Yield: 60%, white solid

TLC (SiO_2) R_f = 0.52 (hexanes/ethyl acetate = 19:1), [UV light]

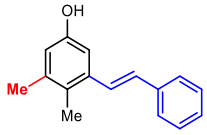
mp 68-70℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.39-7.31 (m, 3H), 7.29-7.25 (m, 1H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.61 (d, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 2.79 (t, *J* = 6.5 Hz, 4H), 1.85-1.76 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.38, 138.89, 137.78, 137.76, 130.42, 128.78, 127.70, 127.42, 126.69, 126.66, 113.88, 109.08, 55.39, 30.61, 26.27, 23.60, 22.90.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{21}O$ 265.1587, found 265.1582.

(*E*)-3,4-Mimethyl-5-styrylphenol (5a)



Yield: 54%, white solid

TLC (SiO_2) R_f = 0.51 (hexanes/ethyl acetate = 8:2), [UV light]

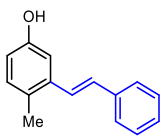
mp 89-91℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.36-7.31 (m, 3H), 7.26-7.22 (m, 1H), 6.89 (s, 1H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 4.72 (s, 1H), 2.24 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.17, 138.55, 137.95, 137.68, 130.63, 128.75, 127.68, 127.32, 126.89, 126.63, 116.58, 110.11, 20.85, 14.76.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{16}NaO$ 247.1093, found 247.1088.

(*E*)-4-Methyl-3-styrylphenol (5b)



Yield: 82%, white solid

TLC (SiO_2) R_f = 0.50 (hexanes/ethyl acetate = 8:2), [UV light].

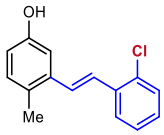
mp 139-141℃

^{1}H NMR (400 MHz, D_6-Acetone) δ 8.17 (s, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.44-7.37 (m, 3H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.08-7.02 (m, 2H), 6.71 (dd, *J* = 8.2, 2.6 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, D_6-Acetone) δ = 155.73, 137.75, 137.07, 131.23, 129.50, 128.63, 127.51, 126.65, 126.55, 126.38, 114.85, 111.60, 18.10.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{14}NaO$ 233.0937, found 233.0940.

(*E*)-3-(2-Chlorostyryl)-4-methylphenol (5c)



Yield: 64%, light orange solid

TLC (SiO_2) R_f = 0.55 (hexanes/ethyl acetate = 8:2), [UV light].

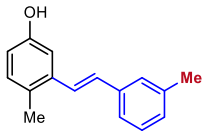
mp 81-83℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.33 (d, *J* = 16.4 Hz, 1H), 7.27-7.14 (m, 4H), 7.10 (d, *J* = 2.7 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.89 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.86, 136.14, 134.58, 132.48, 130.51, 128.81, 127.79, 127.59, 127.38, 125.90, 125.65, 125.26, 114.06, 111.15, 17.96.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{13}NaClO$ 267.0547, found 267.0544.

(*E*)-4-Methyl-3-(3-methylstyryl)phenol (5d)



Yield: 76%, white solid

TLC (SiO_2) R_f = 0.53 (hexanes/ethyl acetate = 8:2), [UV light].

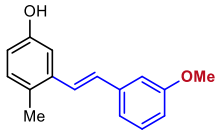
mp 96-98℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 2H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.67 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.84 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.83, 138.29, 137.59, 137.46, 131.45, 130.34, 128.62, 128.57, 128.25, 127.29, 126.04, 123.83, 114.59, 111.82, 21.47, 19.02.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{16}NaO$ 247.1093, found 247.1099.

(*E*)-3-(3-Methoxystyryl)-4-methylphenol (5e)



Yield: 67%, pale yellow oil

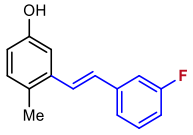
TLC (SiO_2) R_f = 0.40 (hexanes/ethyl acetate = 8:2), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.04-7.00 (m, 3H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.81 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.65 (dd, *J* = 8.2, 2.6 Hz, 1H), 4.96 (s, 1H), 3.83 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.81, 152.80, 137.95, 136.31, 130.43, 129.00, 128.64, 127.22, 125.55, 118.31, 113.69, 112.11, 111.07, 110.83, 54.27, 17.93.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{16}NaO_2$ 263.1043, found 263.1043.

(*E*)-3-(3-Fluorostyryl)-4-methylphenol (5f)



Yield: 74%, faint yellow solid

TLC (SiO_2) R_f = 0.46 (hexanes/ethyl acetate = 8:2), [UV light]

mp 106-107℃

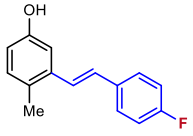
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 1H), 7.22 (dd, *J* = 5.8, 1.9 Hz, 2H), 7.20-7.15 (m, 1H), 7.05-7.00 (m, 2H), 6.93 (td, *J* = 8.0, 2.0 Hz, 1H), 6.87 (d, *J* = 16.1 Hz, 1H), 6.67 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.95 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.15 (d, *J* = 245.2 Hz), 152.81, 138.83 (d, *J* = 7.7 Hz, 1H), 135.94, 130.52, 129.09 (d, *J* = 8.5 Hz), 127.94 (d, *J* = 2.7 Hz), 127.39, 126.48, 121.54 (d, *J* = 2.7 Hz), 114.01, 113.43 (d, *J* = 21.4 Hz), 111.82 (d, *J* = 21.8 Hz), 110.87, 17.92.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.41.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}FNaO$ 251.0843, found 251.0845.

(*E*)-3-(4-Fluorostyryl)-4-methylphenol (5g)



Yield: 61%, white solid

TLC (SiO_2) R_f = 0.43 (hexanes/ethyl acetate = 8:2), [UV light]

Mp 84-86℃

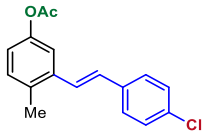
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.18 (d, *J* = 16.1 Hz, 1H), 7.08-7.03 (m, 4H), 6.91 (d, *J* = 16.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.87 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.36 (d, *J* = 247.3 Hz), 152.81, 136.29, 132.65 (d, *J* = 3.3 Hz), 130.45, 127.96, 127.17, 127.06 (d, *J* = 8.0 Hz), 124.97 (d, *J* = 2.3 Hz), 114.60 (d, *J* = 21.6 Hz), 113.66, 110.75, 17.94.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.10.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}FNaO$ 251.0843, found 251.0835.

(*E*)-3-(4-Chlorostyryl)-4-methylphenyl acetate (5h)



Yield: 55%, white solid

TLC (SiO_2) R_f = 0.78 (hexanes/ethyl acetate = 8:2), [UV light]

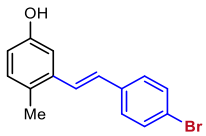
mp 91-92℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.23 (d, *J* = 15.9 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.94-6.87 (m, 2H), 2.39 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.74, 149.13, 137.27, 135.84, 133.47, 131.36, 129.56, 128.90, 127.83, 126.29, 120.72, 118.20, 21.16, 19.37.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{15}ClNaO_2$ 309.0653, found 309.0651.

(*E*)-3-(4-Bromostyryl)-4-methylphenol (5i)



Yield: 67%, white solid

TLC (SiO_2) R_f = 0.47 (hexanes/ethyl acetate = 8:2), [UV light]

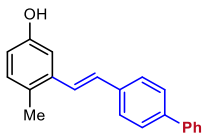
mp 149-151℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.40-7.33 (m, 2H), 7.25 (d, *J* = 16.1 Hz, 1H), 7.07-7.02 (m, 2H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.70 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.83, 137.10, 136.43, 131.80, 131.54, 128.92, 128.33, 128.07, 126.91, 121.43, 114.90, 111.80, 18.98.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}BrNaO$ 311.0042, found 311.0040.

(*E*)-3-(2-([1,1'-Biphenyl]-4-yl)vinyl)-4-methylphenol (5j)



Yield: 58%, white solid

TLC (SiO_2) R_f = 0.46 (hexanes/ethyl acetate = 8:2), [UV light]

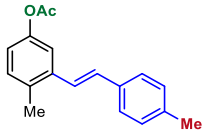
mp 149-150℃

^{1}H NMR (400 MHz, $CDCl_3$) δ7.65-7.58 (m, 6H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 16.1 Hz, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 16.1 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.81 (s, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.82, 139.64, 139.43, 136.44, 135.52, 130.47, 128.68, 127.80, 127.26, 126.36, 126.34, 126.02, 125.92, 125.23, 113.67, 110.77, 17.98.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{18}NaO$ 309.1250, found 309.1250.

(*E*)-4-Methyl-3-(4-methylstyryl)phenyl acetate (5k)



Yield: 50%, white solid

TLC (SiO_2) R_f = 0.78 (hexanes/ethyl acetate = 8:2), [UV light]

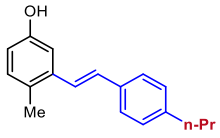
mp 98-100℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.21 (d, *J* = 16.1 Hz, 1H), 7.18-7.15 (m, 3H), 6.94 (d, *J* = 16.1 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.4 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.78, 149.11, 137.82, 134.60, 133.30, 131.25, 130.82, 129.45, 126.60, 124.73, 120.27, 118.06, 21.29, 21.18, 19.40.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{18}NaO_2$ 289.1199, found 289.1206.

(*E*)-4-Methyl-3-(4-propylstyryl)phenol (5l)



Yield: 64%, white solid

TLC (SiO_2) R_f = 0.55 (hexanes/ethyl acetate = 8:2), [UV light]

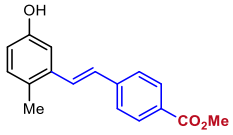
mp 67-69℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 16.1 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 16.1 Hz, 1H), 6.66 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.76 (s, 1H), 2.62-2.56 (m, 2H), 2.34 (s, 3H), 1.70-1.60 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.86, 142.59, 137.76, 135.04, 131.47, 130.24, 128.90, 128.21, 126.58, 125.35, 114.48, 111.79, 37.88, 24.60, 19.05, 13.89.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{18}H_{21}O$ 253.1587, found 253.1582.

Methyl (*E*)-4-(5-hydroxy-2-methylstyryl)benzoate (5m)



Yield: 60%, white solid

TLC (SiO_2) R_f = 0.31 (hexanes/ethyl acetate = 8:2), [UV light]

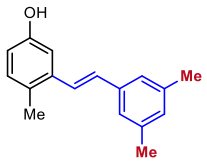
mp 166-168℃

^{1}H NMR (400 MHz, D_6-Acetone) δ 8.15 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.72-7.68 (m, 2H), 7.53 (d, *J* = 16.2 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 16.2 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, D_6-Acetone) δ = 166.17, 155.81, 142.40, 136.64, 131.43, 129.79, 129.13, 128.96, 128.39, 127.18, 126.60, 115.51, 111.82, 51.45, 18.13.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}NaO_3$ 291.0992, found 291.0984.

(*E*)-3-(3,5-Dimethylstyryl)-4-methylphenol (5n)



Yield: 58%, white solid

TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 8:2), [UV light]

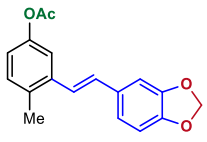
mp 98-99℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 16.1 Hz, 1H), 7.14 (s, 2H), 7.07 (d, *J* = 2.5 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.94 (s, 1H), 6.91 (d, *J* = 16.4 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.78 (s, 1H), 2.37 (s, 3H), 2.36 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.77, 138.18, 137.69, 137.42, 131.43, 130.45, 129.54, 128.24, 125.84, 124.52, 114.51, 111.82, 21.34, 19.05.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{18}NaO$ 261.1250, found 261.1257.

(*E*)-3-(2-(Benzo[d][1,3]dioxol-5-yl)vinyl)-4-methylphenyl acetate (5o)



Yield: 31%, white solid

TLC (SiO_2) R_f = 0.61 (hexanes/ethyl acetate = 8:2), [UV light]

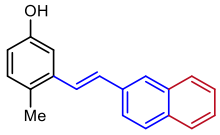
mp 78-80℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 2.3 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H), 7.05 (d, *J* = 1.6 Hz, 1H), 6.93-6.85 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 2.37 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.87, 149.15, 148.24, 147.58, 137.74, 133.30, 131.95, 131.33, 130.55, 124.03, 121.77, 120.29, 118.00, 108.54, 105.73, 101.27, 21.24, 19.47.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{16}NaO_4$ 319.0941, found 319.0933.

(*E*)-4-Methyl-3-(2-(naphthalen-2-yl)vinyl)phenol (5p)



Yield: 56%, white solid

TLC (SiO_2) R_f = 0.44 (hexanes/ethyl acetate = 8:2), [UV light]

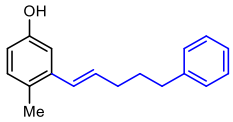
mp 118-120℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 4H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.43 (qd, *J* = 7.1, 3.3 Hz, 2H), 7.37 (d, *J* = 16.1 Hz, 1H), 7.12-7.08 (m, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.67 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.78 (s, 1H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.94, 137.54, 135.04, 133.76, 133.13, 131.57, 130.32, 128.39, 128.37, 128.08, 127.77, 126.78, 126.56, 126.44, 126.02, 123.65, 114.77, 111.84, 19.11.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{19}H_{17}O$ 261.1274, found 261.1284.

(*E*)-4-Methyl-3-(5-phenylpent-1-en-1-yl)phenol (5q)



Yield: 29%, yellow oil

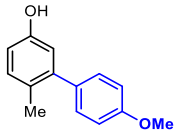
TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 8:2), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.19-7.15 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 2.5 Hz, 1H), 6.58 (dd, *J* = 8.1, 2.5 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.10-6.00 (m, 1H), 4.77 (s, 1H), 2.68-2.62 (m, 2H), 2.27-2.21 (m, 5H), 1.82-1.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.67, 141.33, 137.02, 131.11, 130.16, 127.47, 127.30, 126.82, 126.26, 124.72, 112.78, 110.96, 34.33, 31.72, 30.02, 17.88.

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{20}NaO$ 275.1406, found 275.1413.

4'-Methoxy-6-methyl-[1,1'-biphenyl]-3-ol (5r)



Yield: 57%, pale yellow oil

TLC (SiO_2) R_f = 0.47 (hexanes/ethyl acetate = 8:2), [UV light]

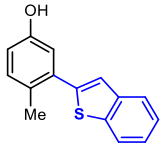
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.4, 6.3 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.96-6.92 (m, 2H), 6.74-

6.69 (m, 2H), 4.76 (s, 1H), 3.85 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.59, 153.46, 142.75, 134.17, 131.45, 130.22, 127.68, 116.76, 113.91, 113.58, 55.40, 19.69.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{14}H_{15}O_2$ 215.1067, found 215.1069.

3-(Benzo[b]thiophen-2-yl)-4-methylphenol (5s)



Yield: 24%, yellow oil

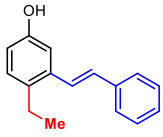
TLC (SiO_2) R_f = 0.51 (hexanes/ethyl acetate = 8:2), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.40-7.30 (m, 2H), 7.24 (s, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 2.7 Hz, 1H), 6.78 (dd, *J* = 8.3, 2.7 Hz, 1H), 4.85 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.44, 143.08, 140.16, 140.01, 135.16, 131.97, 128.57, 124.39, 124.19, 123.55, 123.10, 122.06, 117.31, 115.33, 20.18.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{13}OS$ 241.0682, found 241.0674.

(*E*)-4-Ethyl-3-styrylphenol (5t)



Yield: 45%, white solid

TLC (SiO_2) R_f = 0.51 (hexanes/ethyl acetate = 8:2), [UV light]

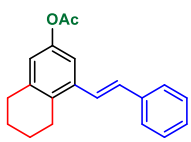
mp 86-88℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.38-7.24 (m, 4H), 7.08 (d, *J* = 2.6 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.77 (s, 1H), 2.71 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.84, 137.63, 136.96, 134.68, 130.38, 130.11, 128.78, 127.75, 126.67, 126.00, 114.93, 112.13, 25.79, 15.86.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{16}NaO$ 247.1093, found 247.1099.

(*E*)-4-Styryl-5,6,7,8-tetrahydronaphthalen-2-yl acetate (5u)



Yield: 35%, white solid

TLC (SiO_2) R_f = 0.84 (hexanes/ethyl acetate = 8:2), [UV light]

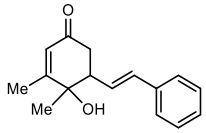
mp 80-82℃

^{1}H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.49-7.45 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.24 (m, 2H), 7.13-6.99 (m, 1H), 6.94-6.72 (m, 2H), 2.82-2.71 (m, 4H), 2.30 (s, 2.4H), 2.19 (s, 0.6H), 1.87-1.73 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) (mixture of rotamers) δ = (170.05), 170.03, 148.43, (146.10), 139.12, 138.04, 137.55, (137.19, 135.32, 134.25), 132.55, 131.06, (129.85, 128.96), 128.77, (127.88), 127.82, 126.71, (126.44), 125.86, (122.53), 121.32, (119.59), 116.10, 30.31, (29.80), (27.93), 26.57, 23.25, (23.10), (22.65), 22.56, 21.25, (21.16).

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{20}H_{20}NaO_2$ 315.1356, found 315.1348.

(*E*)-4-Hydroxy-3,4-dimethyl-5-styrylcyclohex-2-en-1-one (1aa)



Yield: 81%, pale yellow oil

TLC (SiO_2) R_f = 0.21 (hexanes/ethyl acetate = 4:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 4H), 7.25-7.19 (m, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.19 (ddd, *J* = 15.9, 9.4, 1.1 Hz, 1H), 5.83 (s, 1H), 2.93-2.85 (m, 1H), 2.71-2.57 (m, 2H), 2.43 (s, 1H), 1.99 (s, 3H), 1.49 (s, 3H).

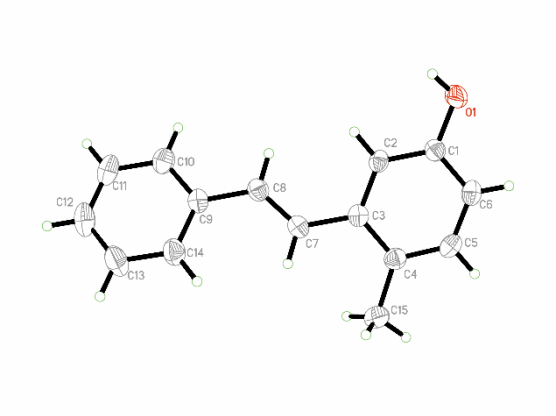
^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.61, 165.32, 136.36, 135.05, 128.73, 128.06, 127.17, 126.53, 126.33, 72.00, 50.84, 41.15, 25.93, 19.38.

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{18}NaO_2$ 265.1199, found 265.1197.

4. Single Crystal Diffraction Data

4.1 Crystal structure and X-ray crystallographic data of 5b

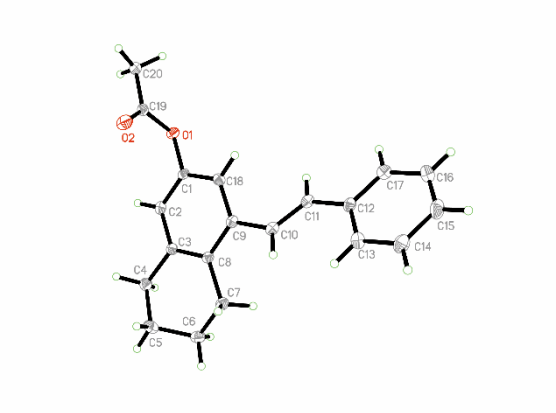
A view of the molecular structure of compound **5b** (thermal ellipsoids are shown with a 30% probability level). CCDC deposition number: 2088626.



Empirical formula	$C_{15}H_{14}O$
Formula weight	210.10
Temperature/K	293(2)
Crystal system	trigonal
Space group	R-3
a/Å	25.237(3)
b/Å	25.237(3)
c/Å	10.3671(11)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5718.0(13)
Z	18
ρ_{calc}g/cm^3	1.153
μ/mm^{-1}	0.071
F(000)	2109.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.348 to 58.852
Index ranges	-32 ≤ h ≤ 15, -25 ≤ k ≤ 32, -10 ≤ l ≤ 14
Reflections collected	5104
Independent reflections	2923 [R_{int} = 0.0295, R_{sigma} = 0.0621]
Data/restraints/parameters	2923/0/147
Goodness-of-fit on F^2	1.727
Final R indexes [I>=2σ (I)]	R_1 = 0.1099, wR_2 = 0.3249
Final R indexes [all data]	R_1 = 0.1604, wR_2 = 0.3453
Largest diff. peak/hole / e Å^{-3}	1.77/-0.24

4.2 Crystal structure and X-ray crystallographic data of 5u

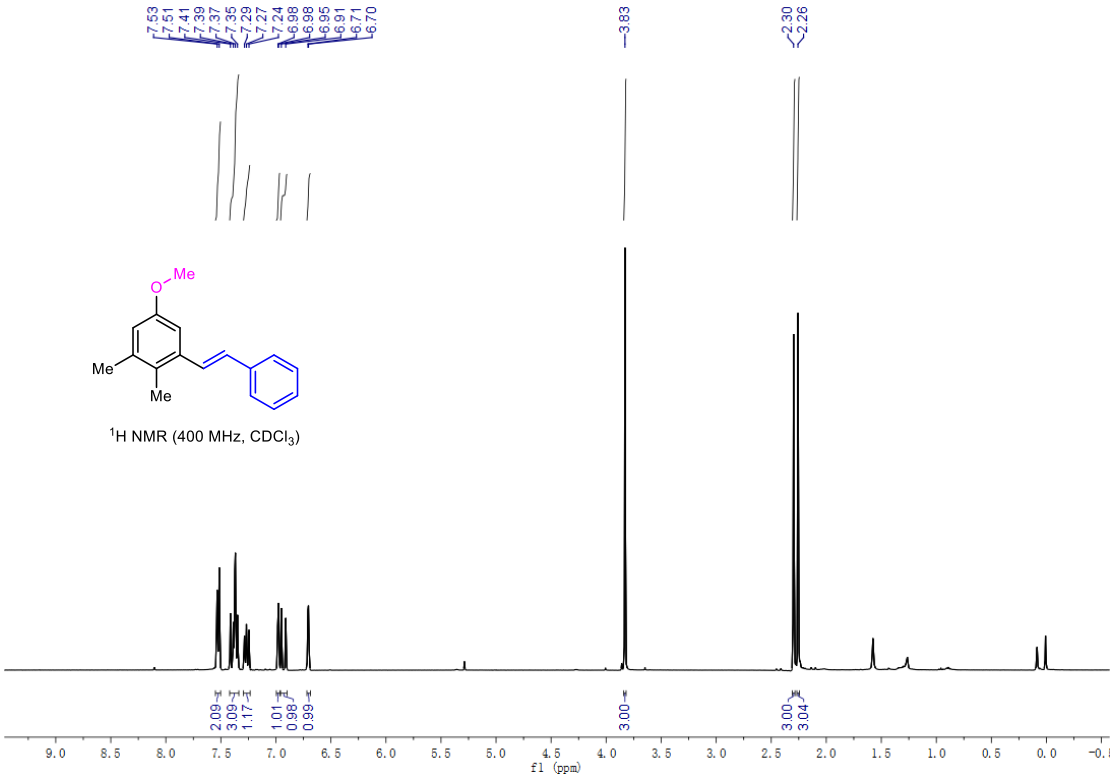
A view of the molecular structure of compound **5u** (thermal ellipsoids are shown with a 30% probability level). CCDC deposition number: 2088627.



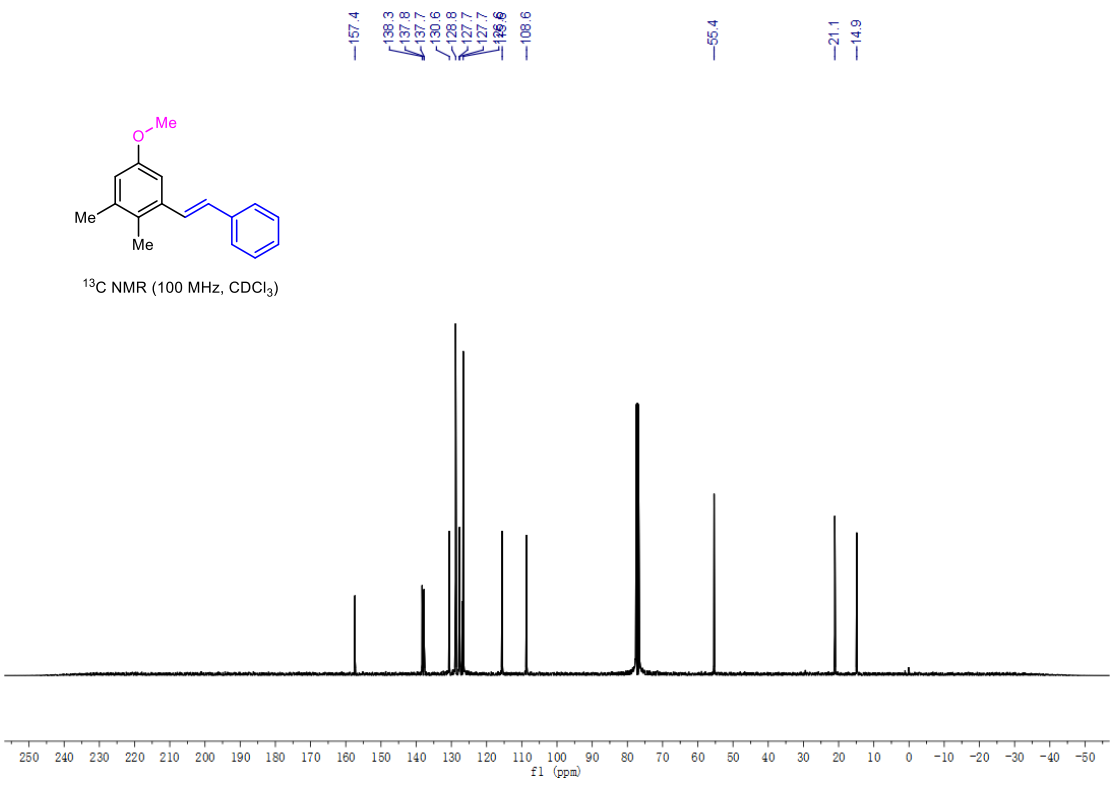
Empirical formula	$C_{20}H_{20}O_2$
Formula weight	292.36
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.0250(17)
b/Å	23.631(3)
c/Å	8.4066(7)
α/°	90
β/°	96.599(9)
γ/°	90
Volume/Å^3	3162.4(6)
Z	14
ρ_{calc}g/cm^3	2.149
μ/mm^{-1}	0.136
F(000)	2184.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.294 to 59.104
Index ranges	-21 ≤ h ≤ 21, -23 ≤ k ≤ 31, -8 ≤ l ≤ 11
Reflections collected	16755
Independent reflections	7444 [R_{int} = 0.0434, R_{sigma} = 0.0731]
Data/restraints/parameters	7444/0/399
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0595, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.1025, wR_2 = 0.1361
Largest diff. peak/hole / e Å^{-3}	0.41/-0.36

5. Copies of NMR Spectra

compound 4a

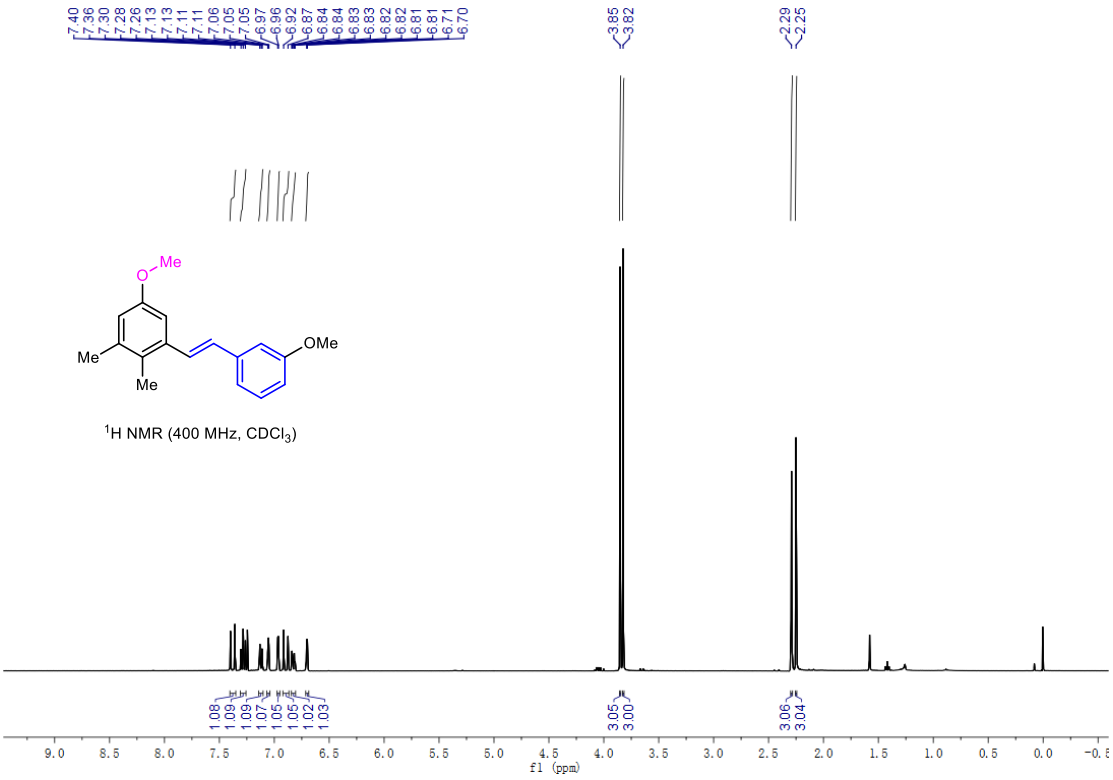


^{1}H NMR (400 MHz, $CDCl_3$)

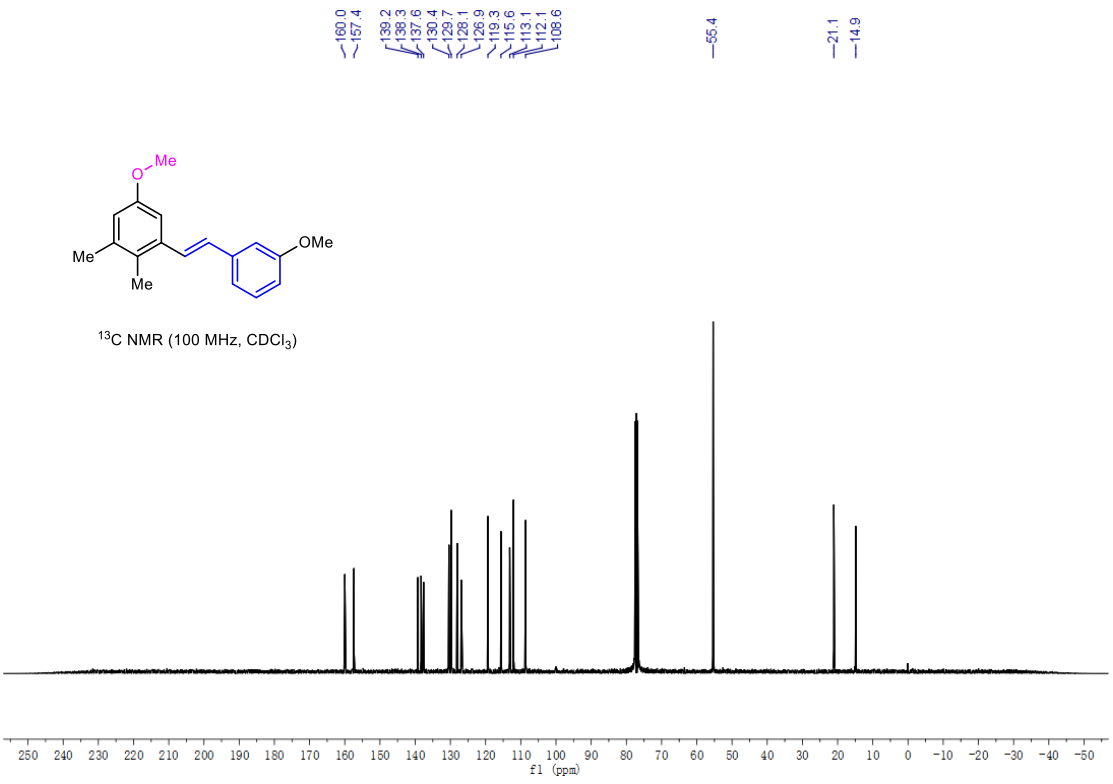


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4b

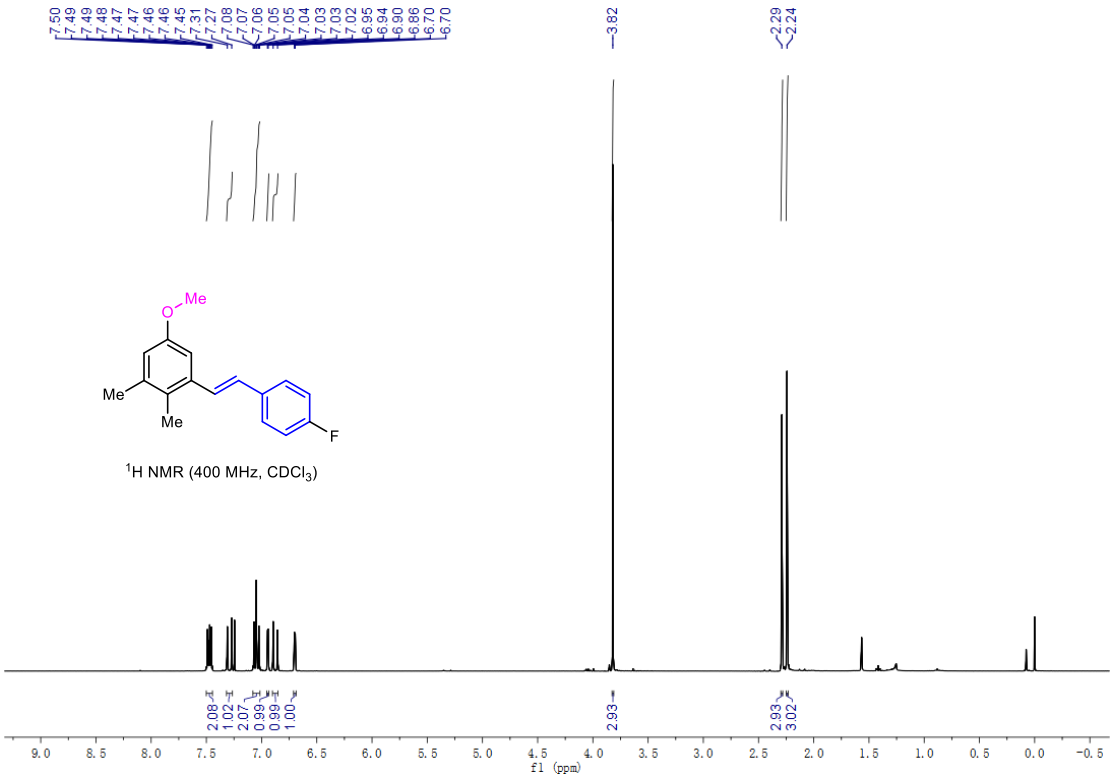


^{1}H NMR (400 MHz, $CDCl_3$)

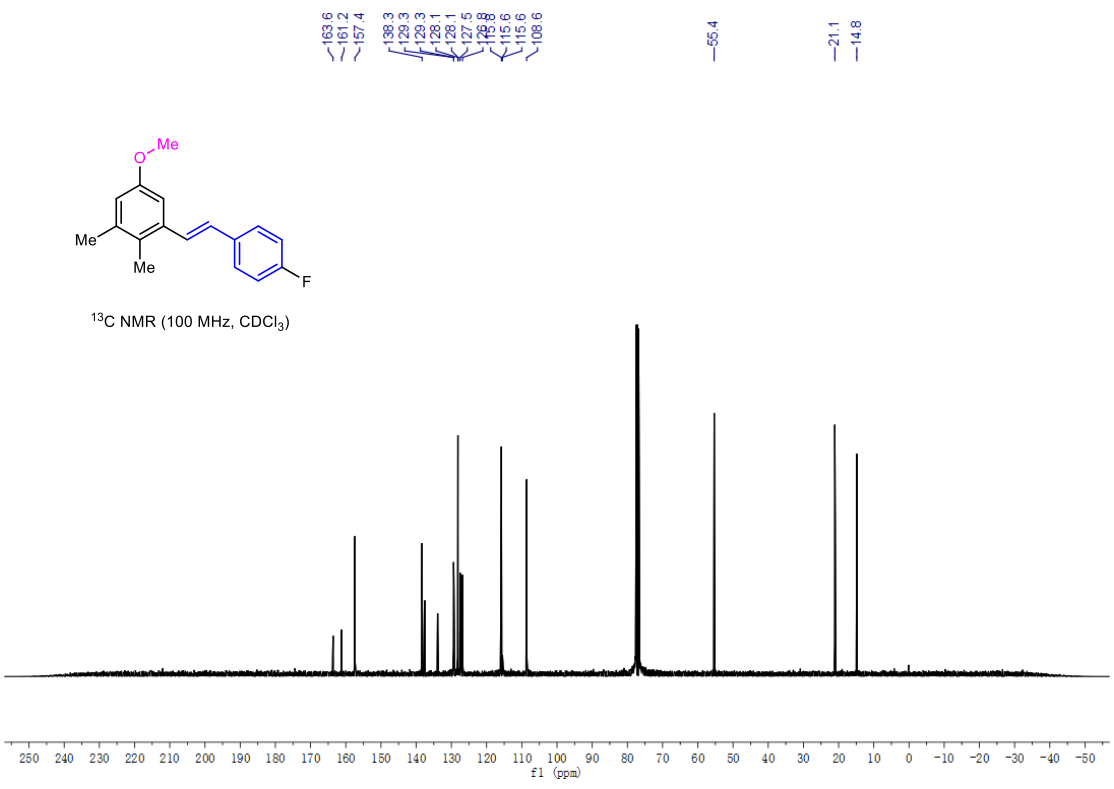


^{13}C NMR (100 MHz, $CDCl_3$)

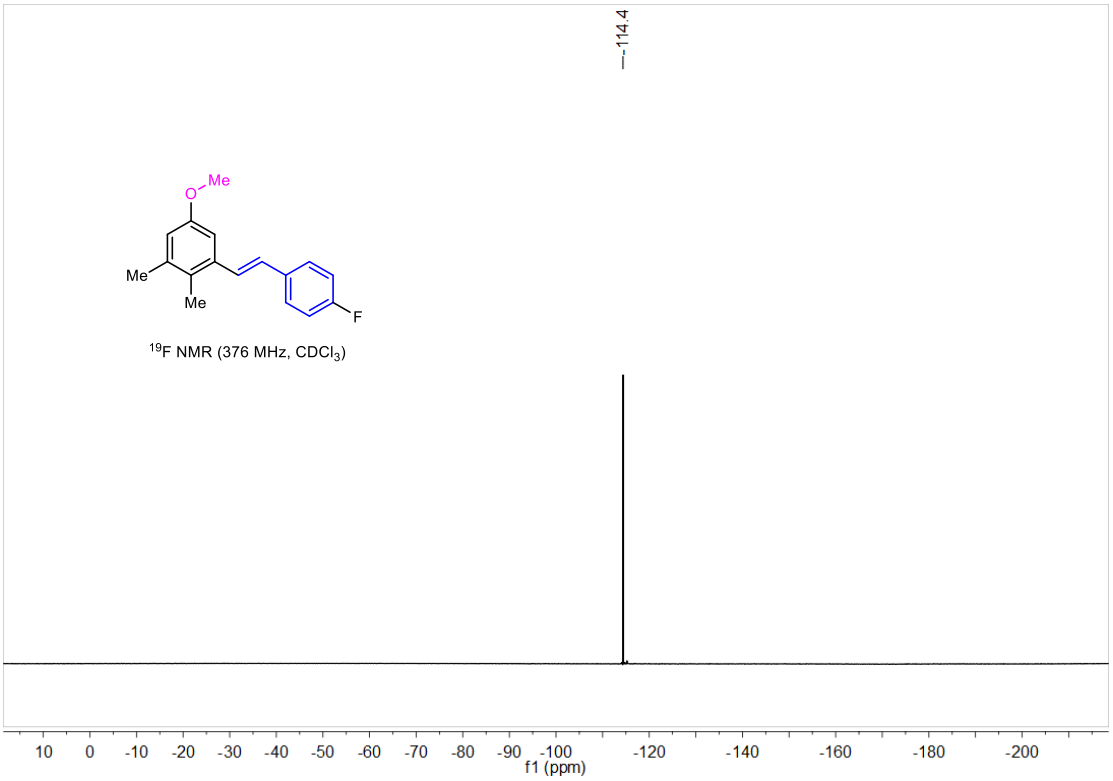
compound 4c



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

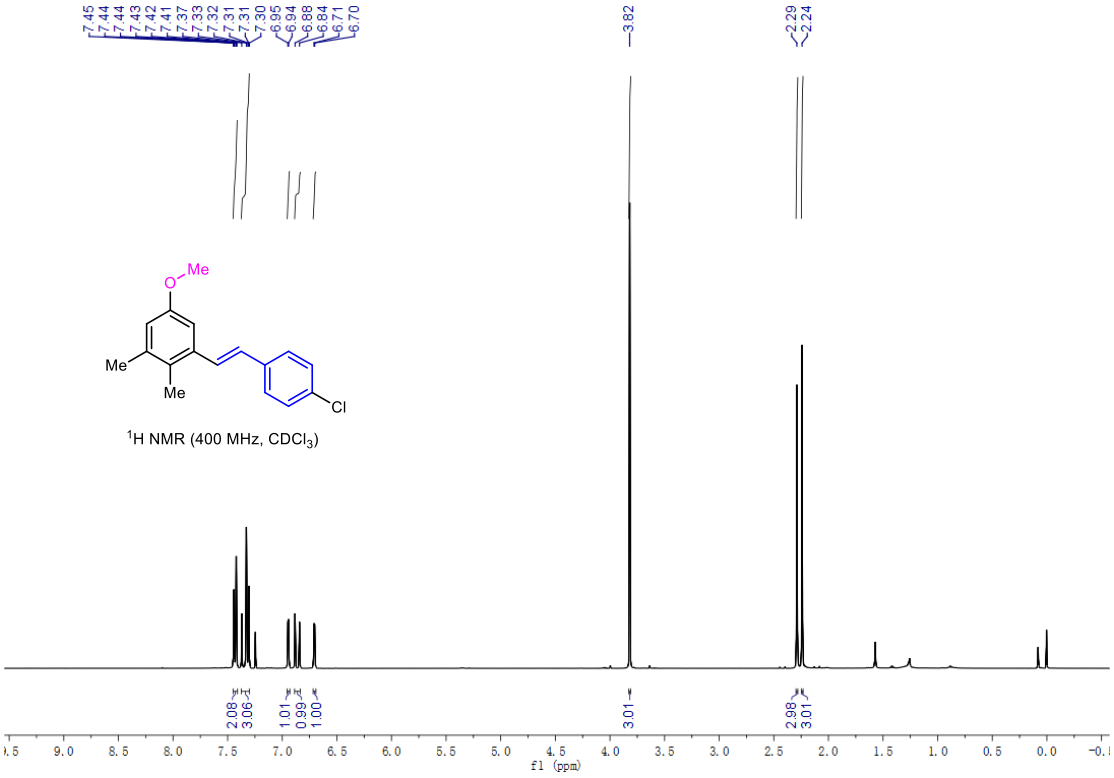


^{13}C NMR (100 MHz, $CDCl_3$)

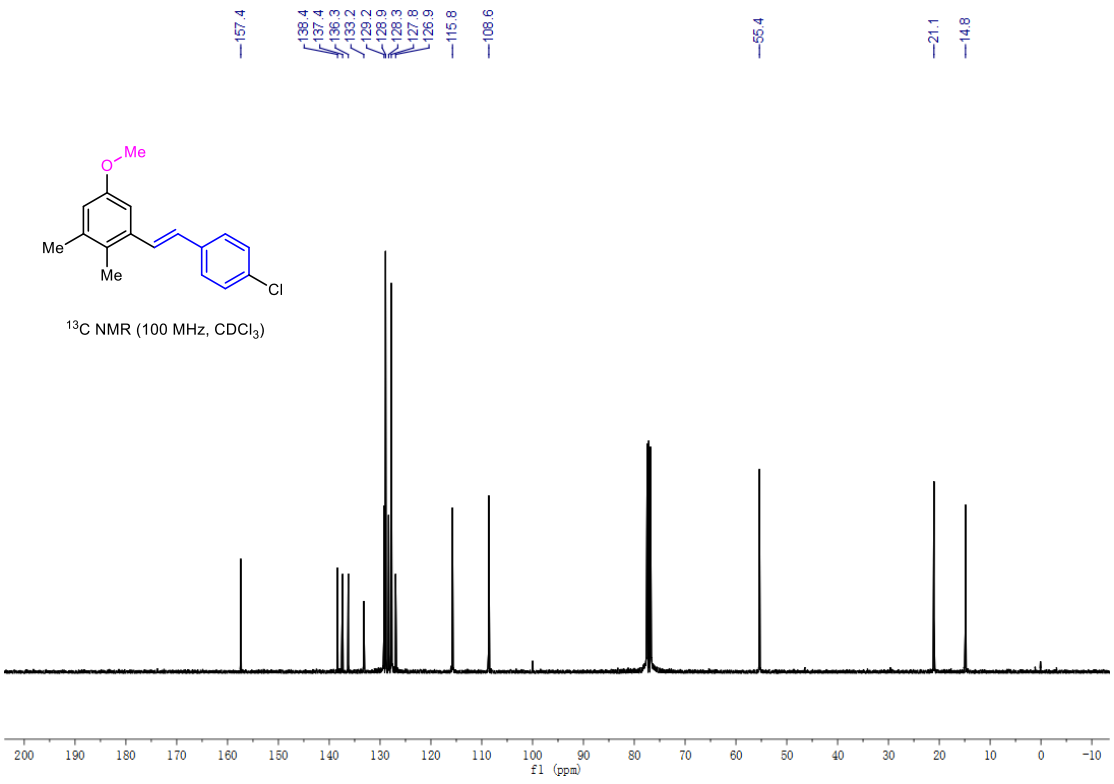


^{19}F NMR (376 MHz, $CDCl_3$)

compound 4d

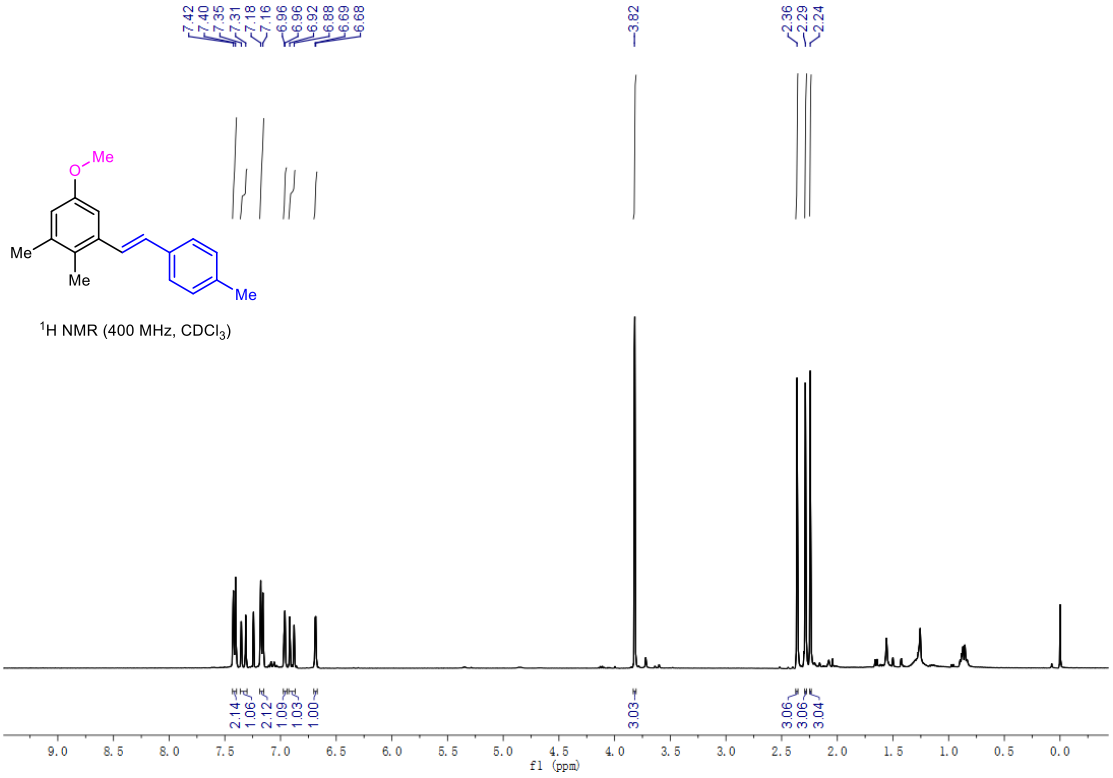


^{1}H NMR (400 MHz, $CDCl_3$)

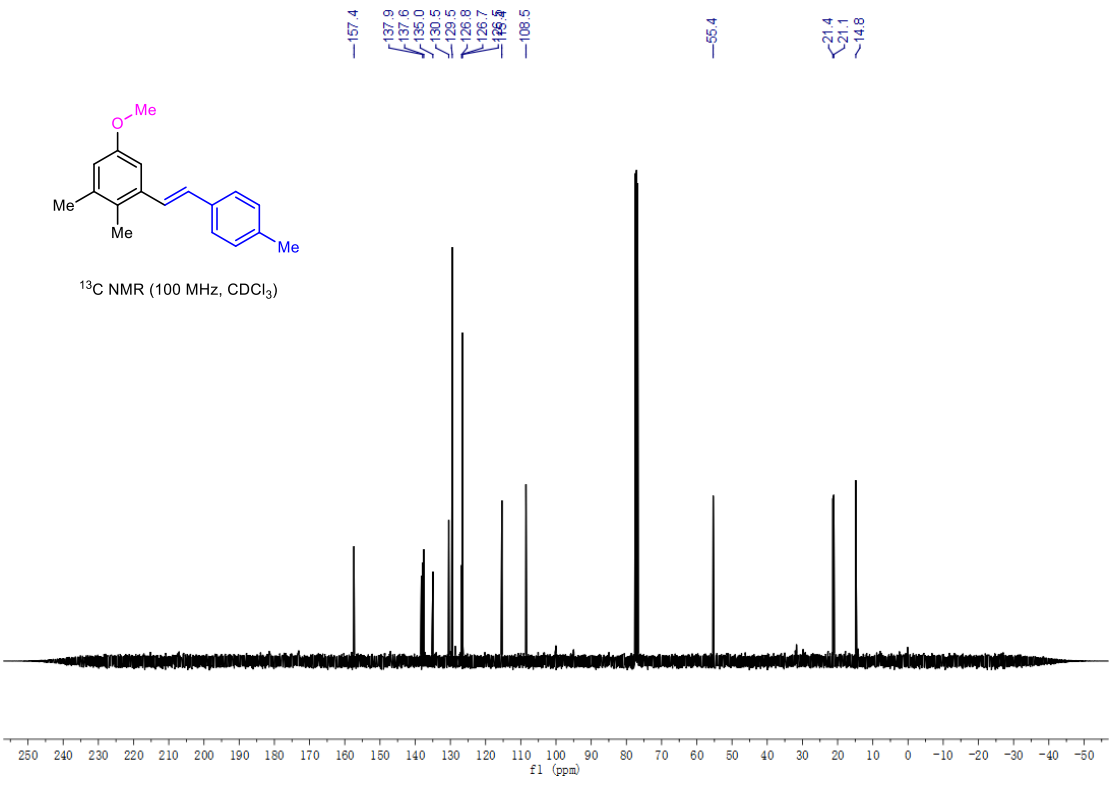


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4e

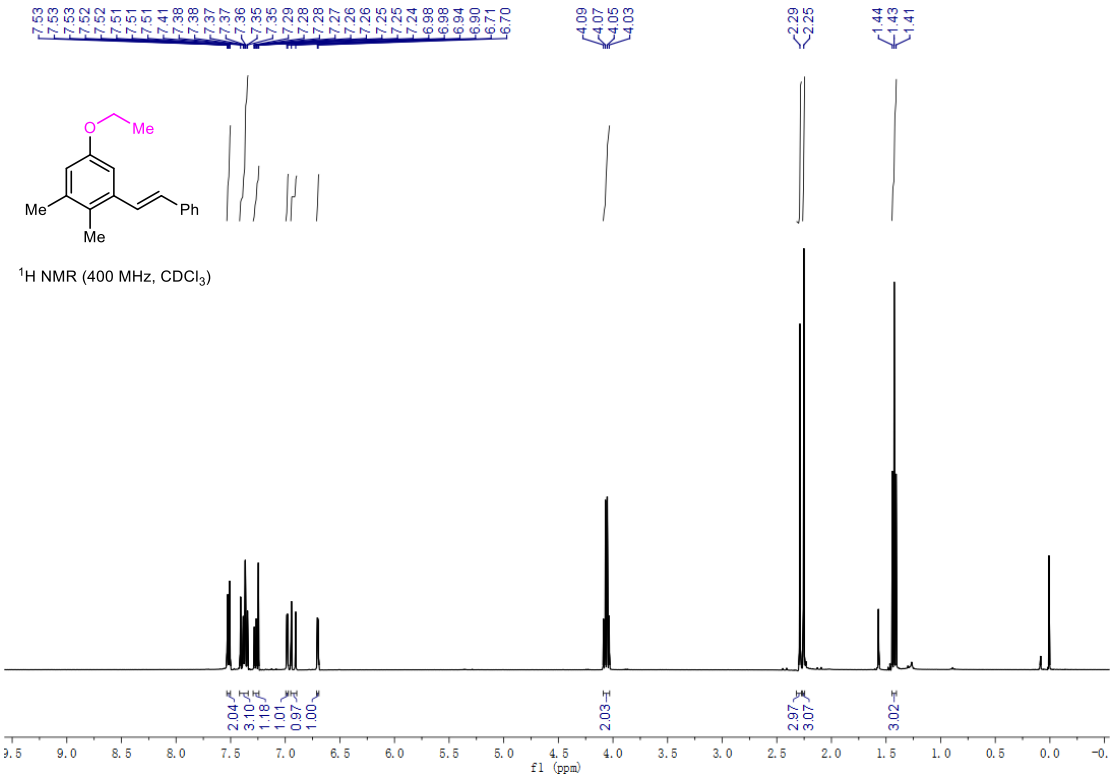


^{1}H NMR (400 MHz, $CDCl_3$)

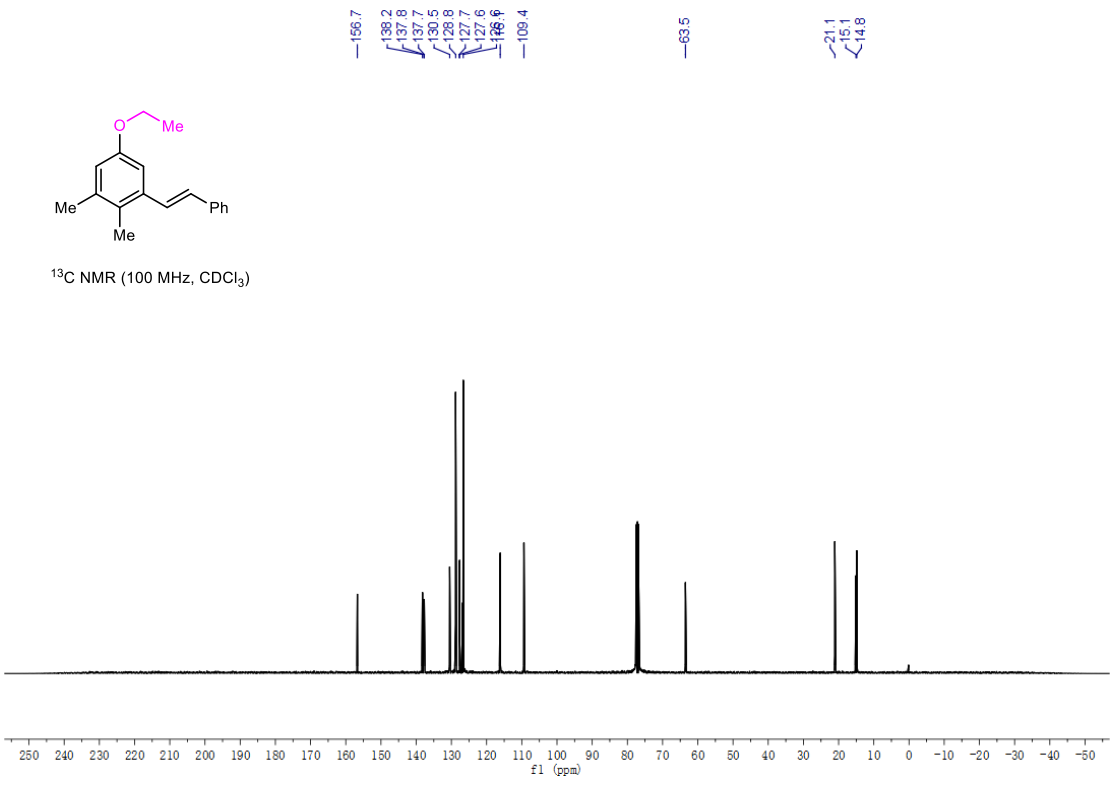


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4f

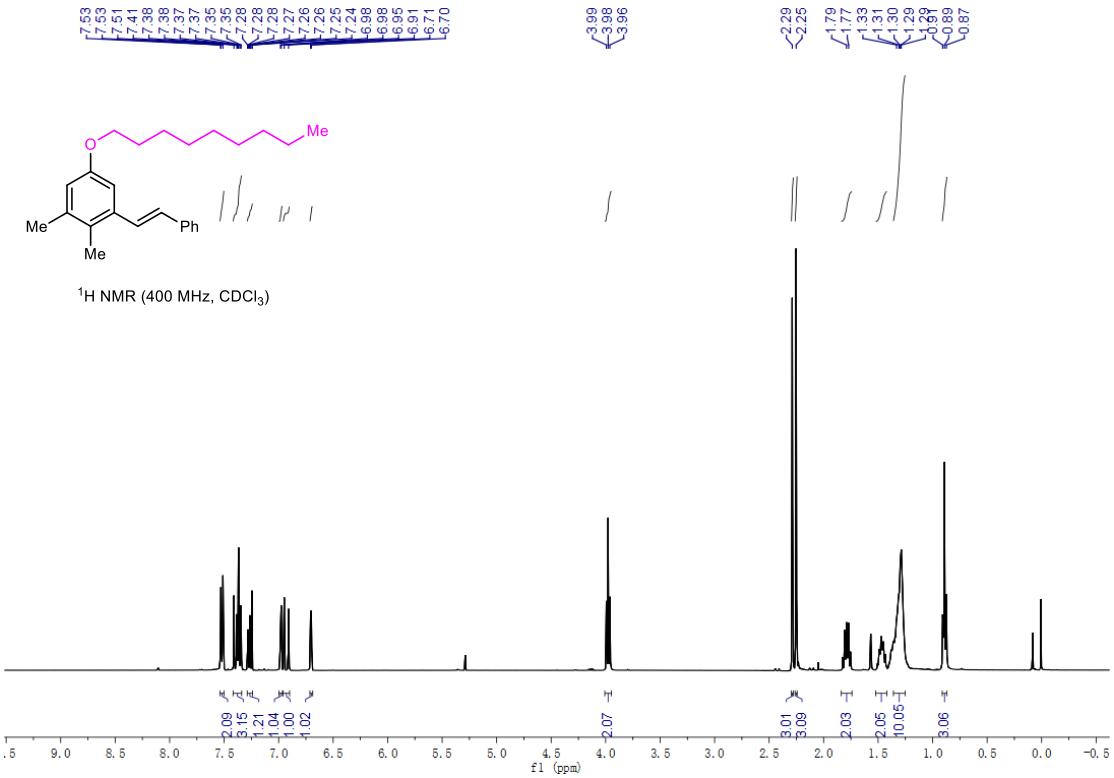


^{1}H NMR (400 MHz, $CDCl_3$)

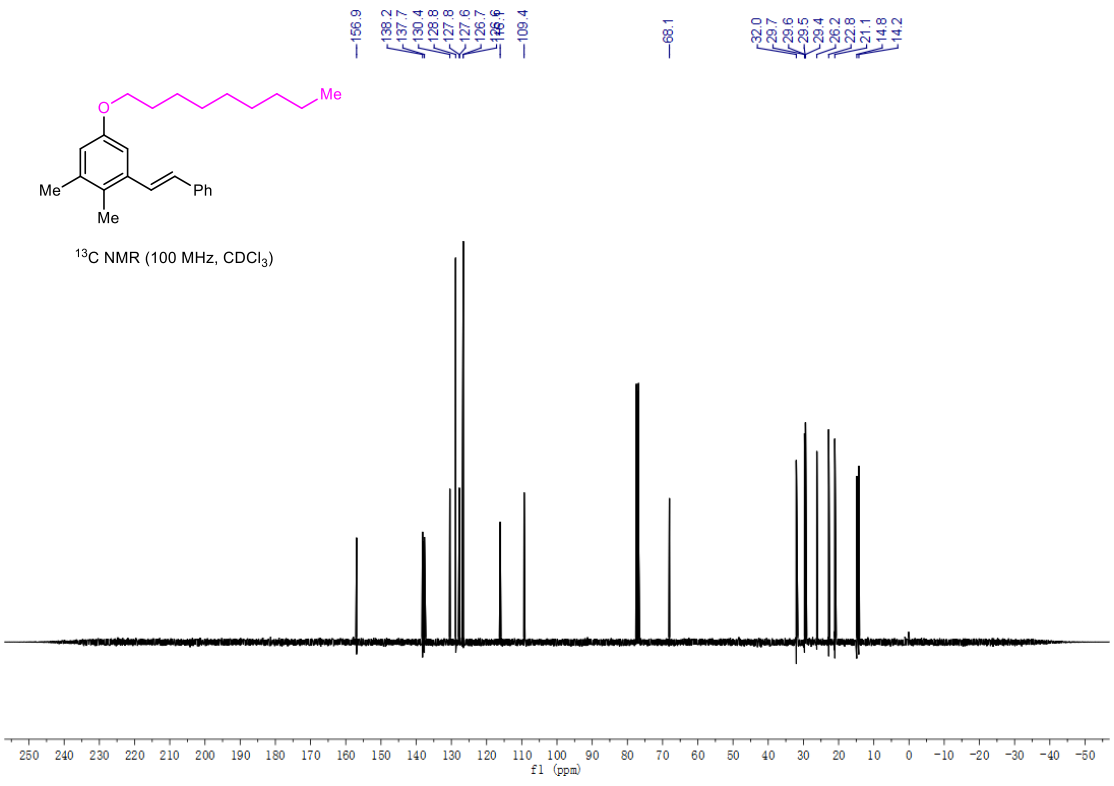


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4g

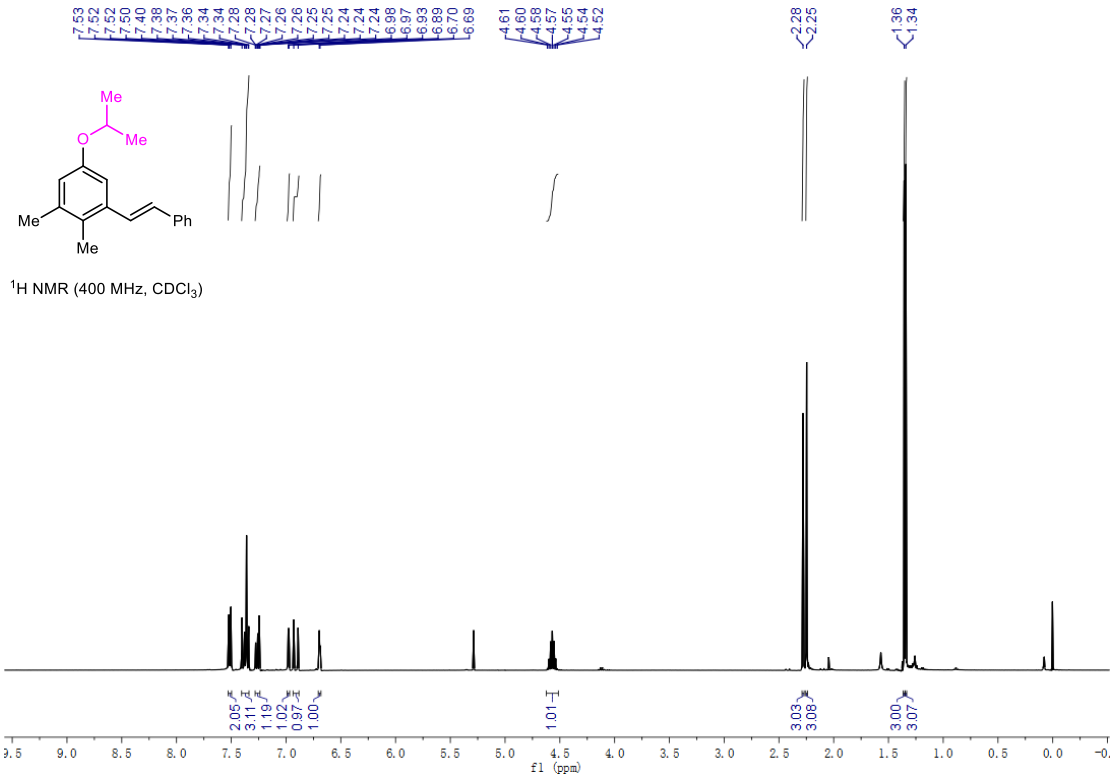


^{1}H NMR (400 MHz, $CDCl_3$)

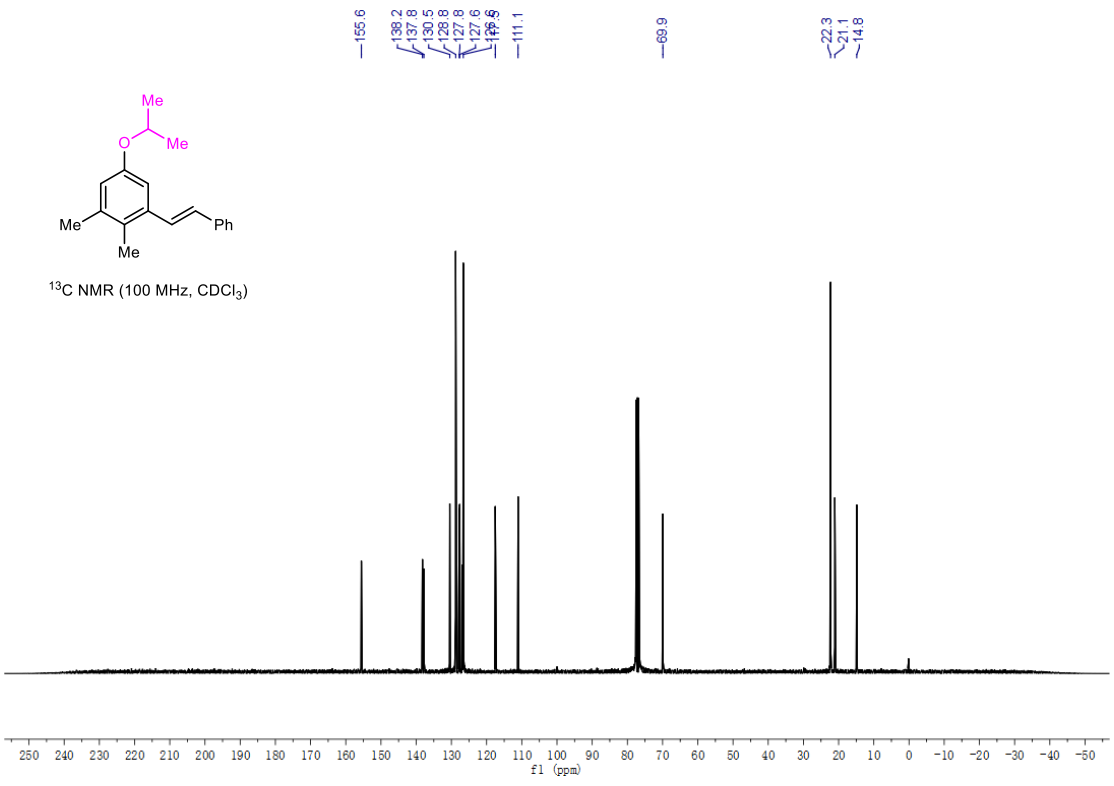


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4h

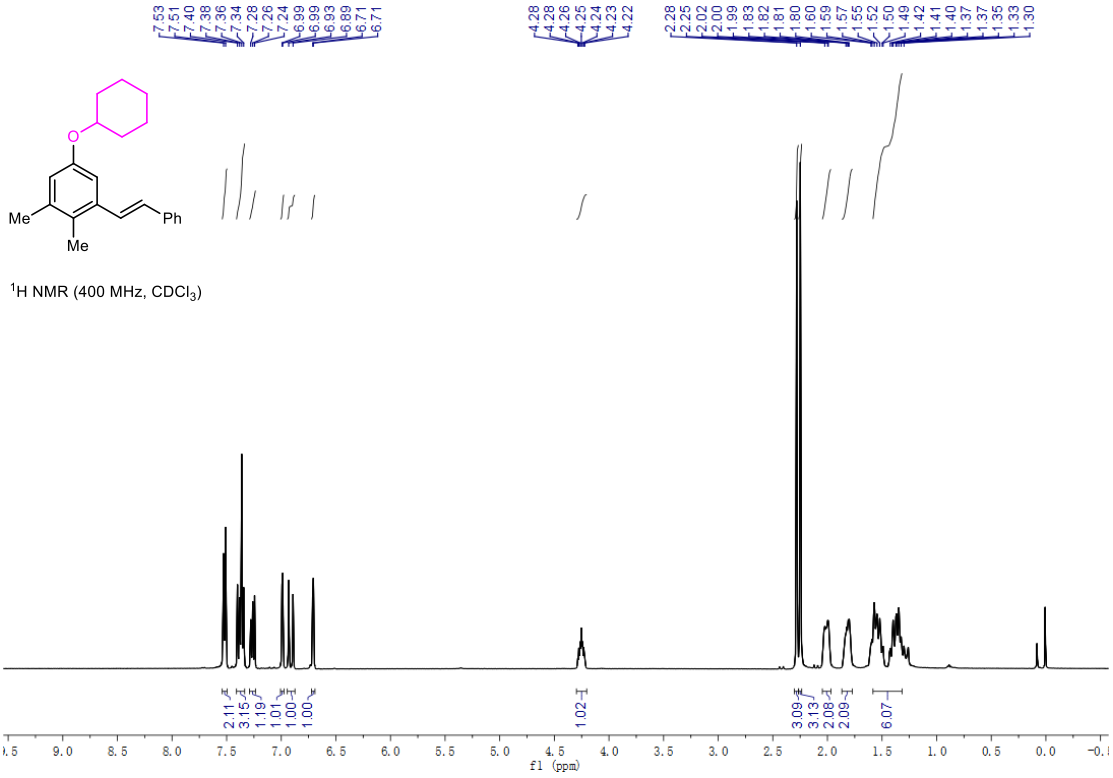


^{1}H NMR (400 MHz, $CDCl_3$)

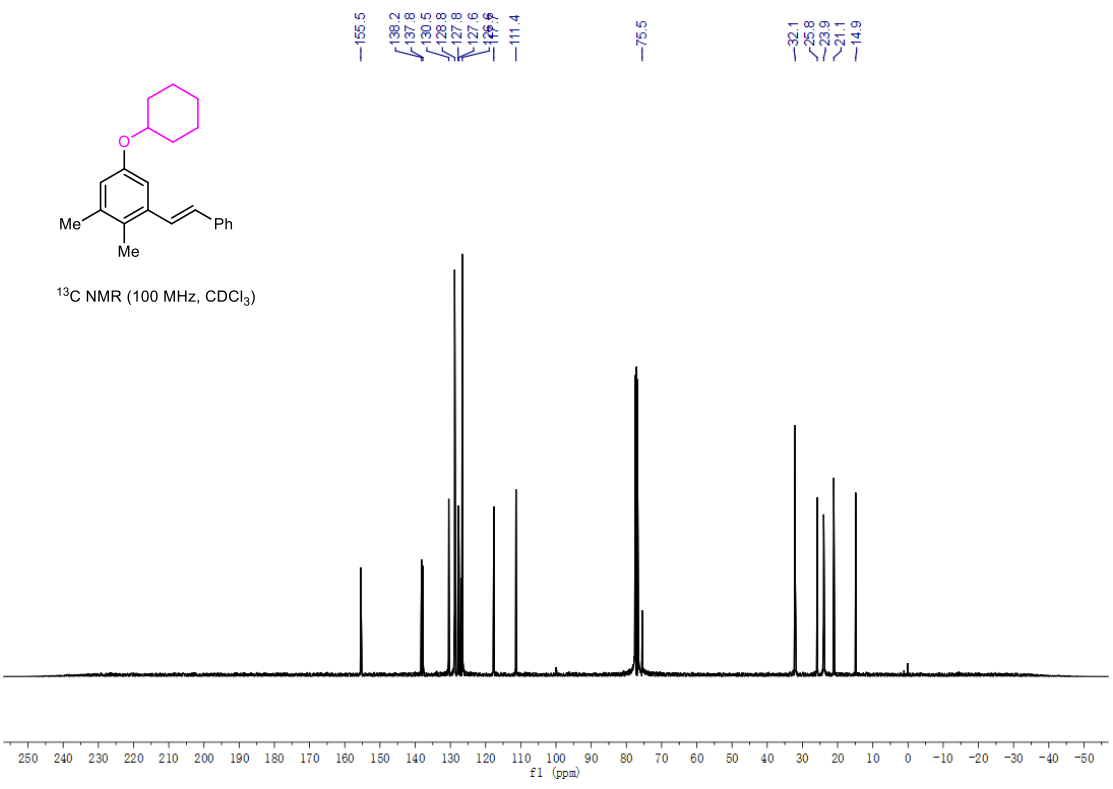


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4i

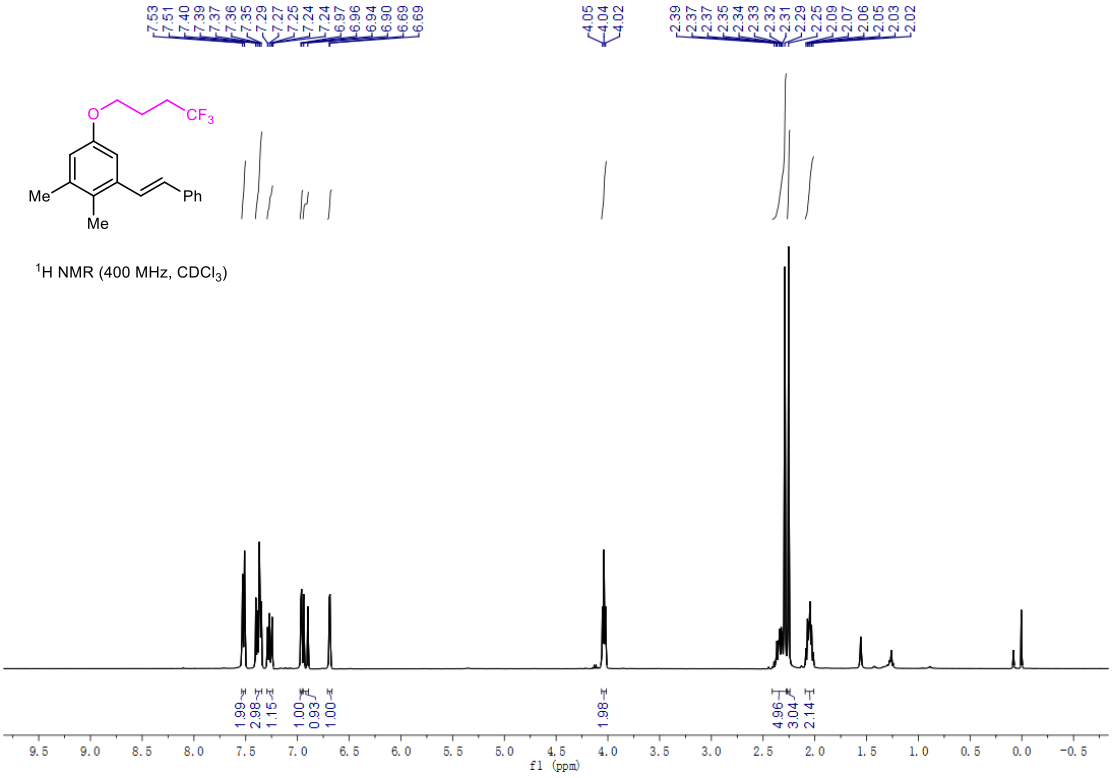


^{1}H NMR (400 MHz, $CDCl_3$)

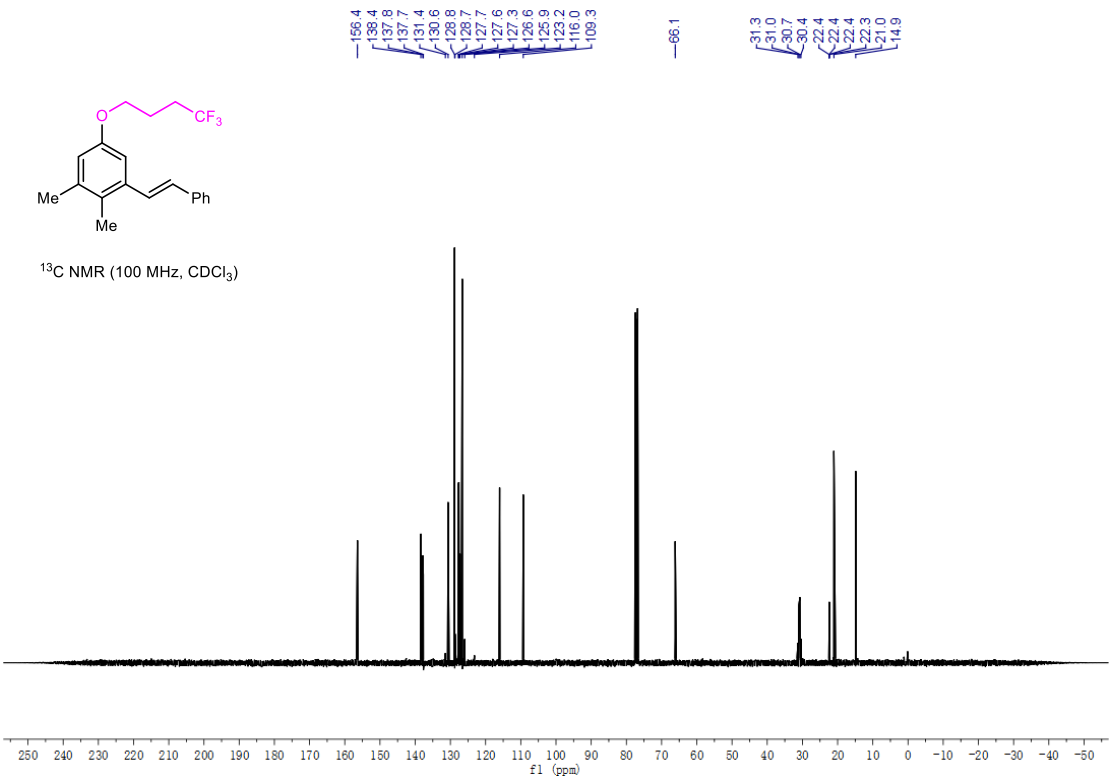


^{13}C NMR (100 MHz, $CDCl_3$)

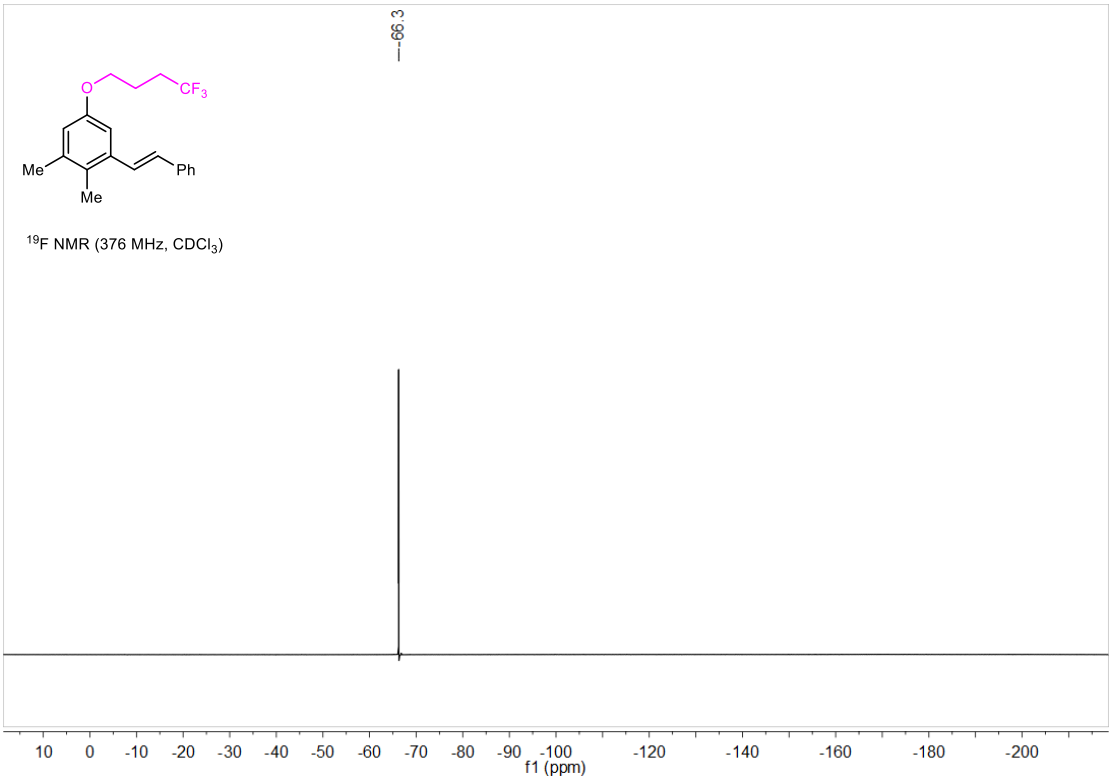
compound 4j



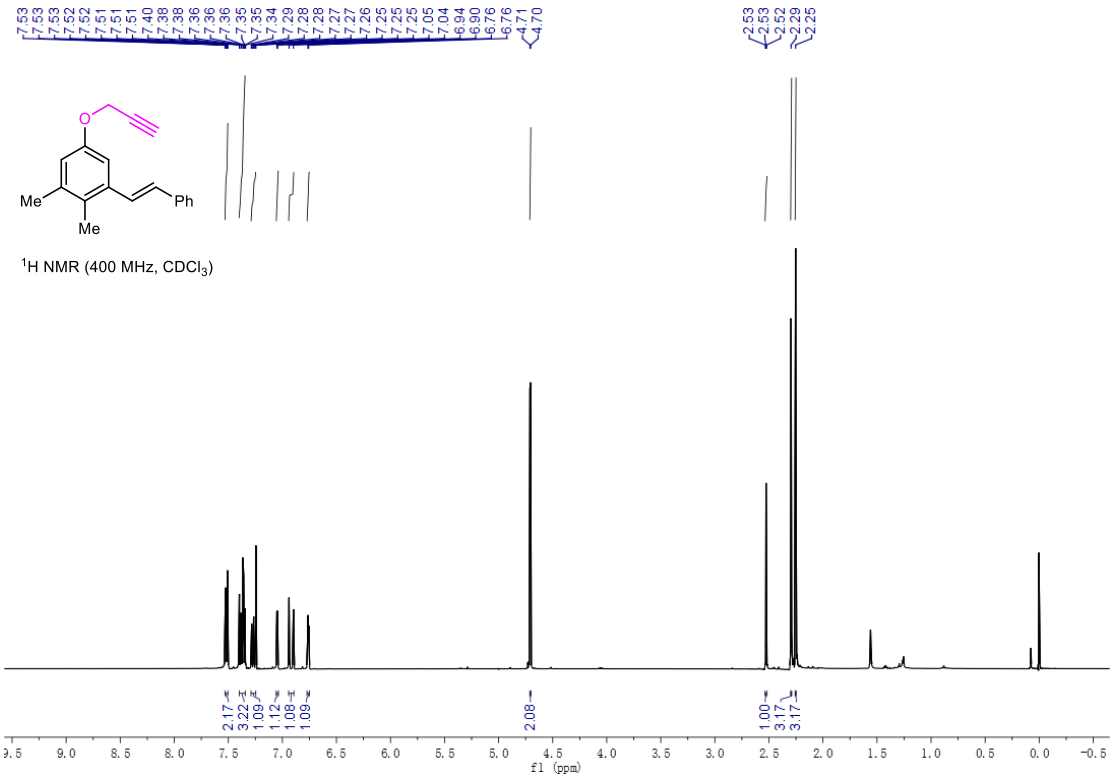
^{1}H NMR (400 MHz, $CDCl_3$)



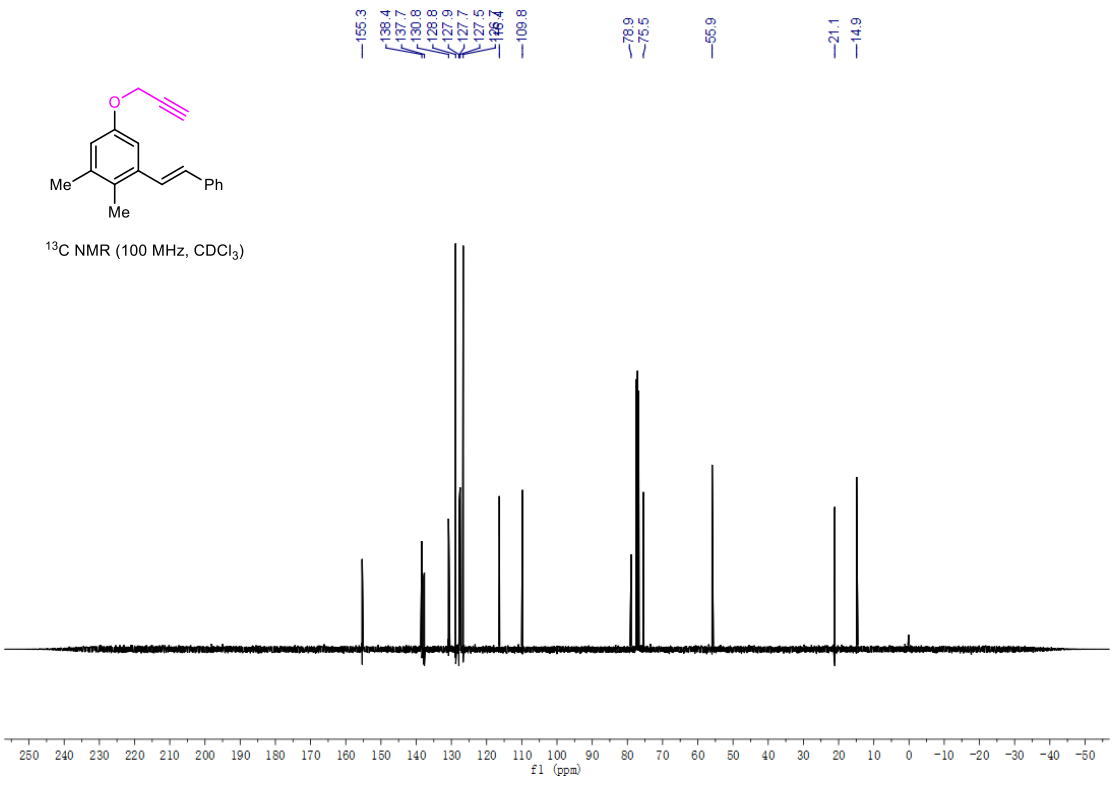
^{13}C NMR (100 MHz, $CDCl_3$)


-66.3
O
CF3
Me
Me
Ph
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

compound 4k

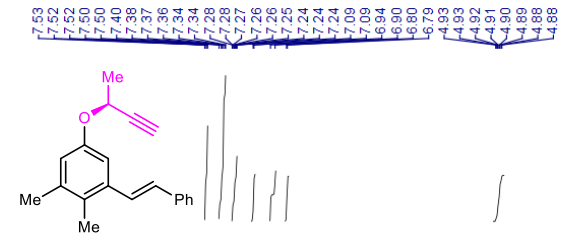


^{1}H NMR (400 MHz, $CDCl_3$)

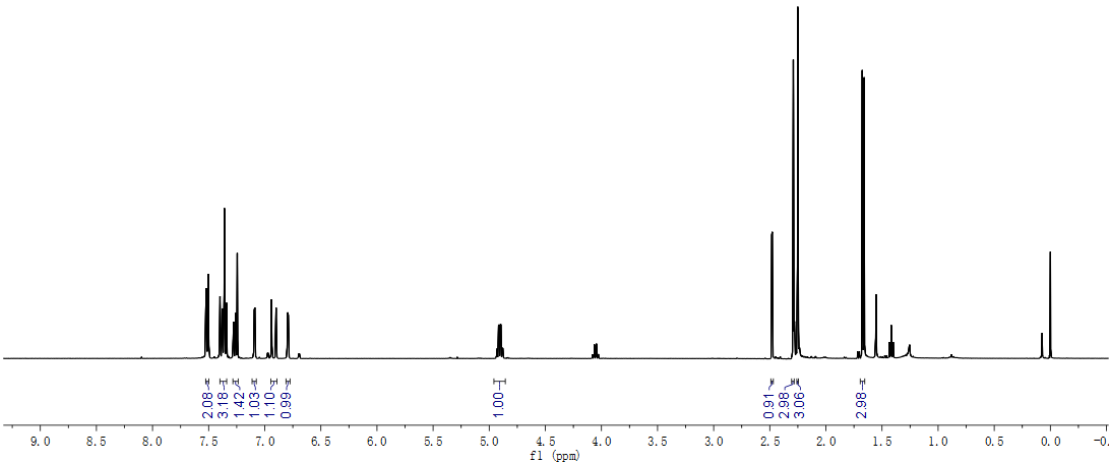


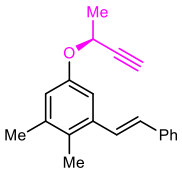
^{13}C NMR (100 MHz, $CDCl_3$)

compound 4l

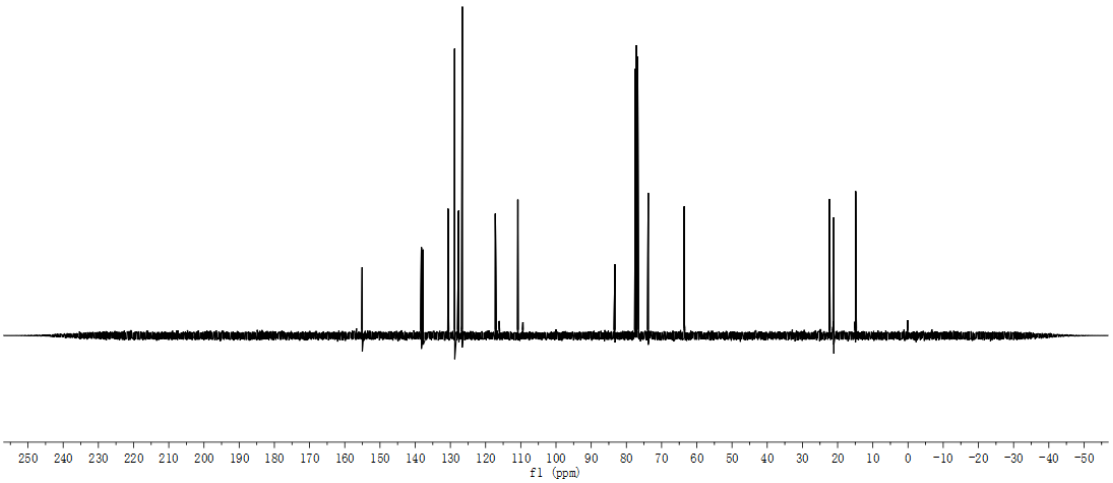


^{1}H NMR (400 MHz, $CDCl_3$)

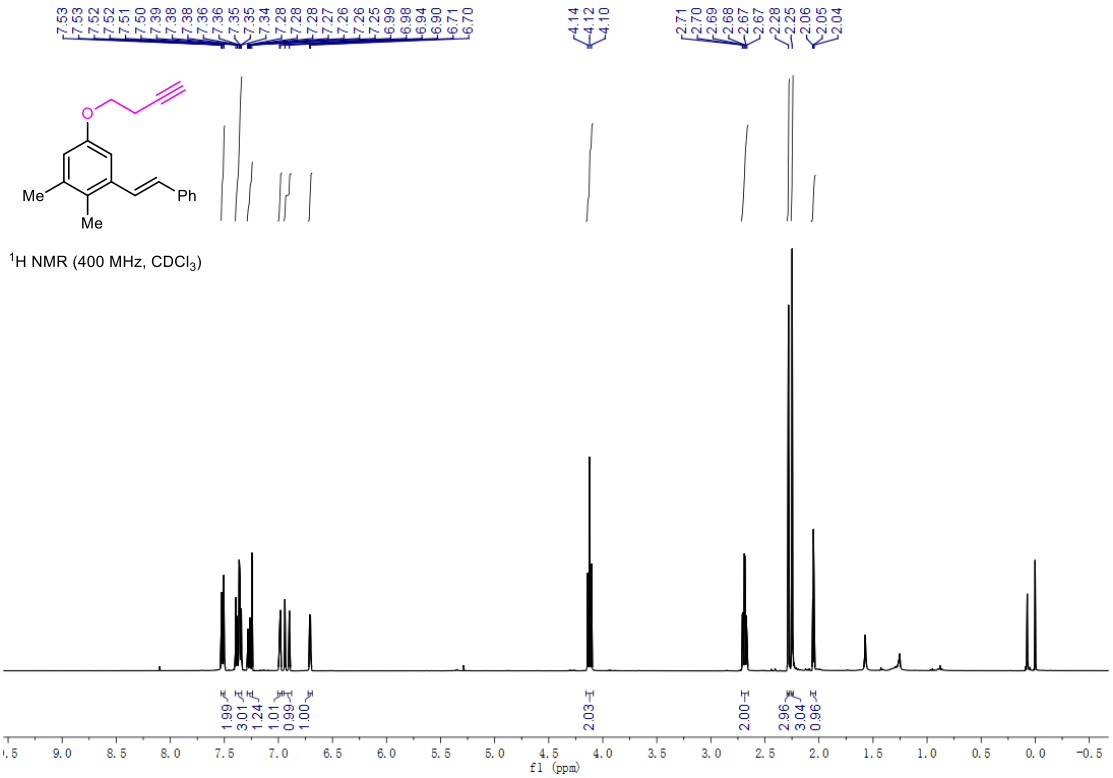




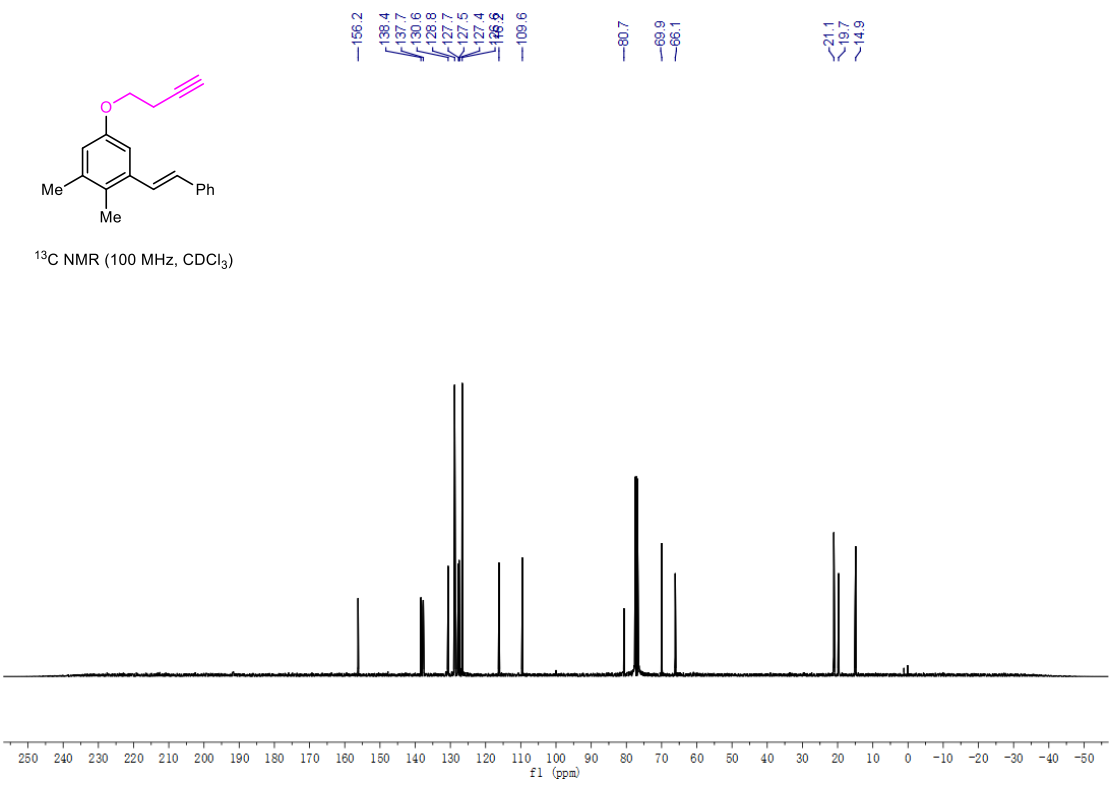
^{13}C NMR (100 MHz, $CDCl_3$)



compound 4m

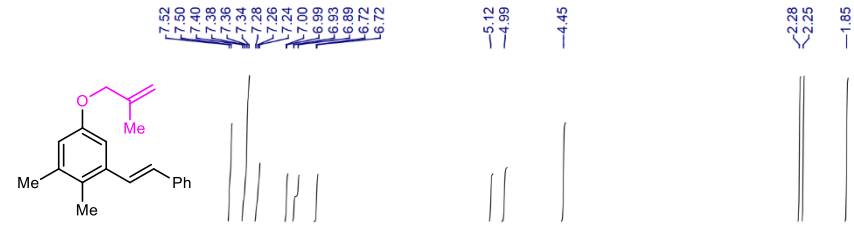


^{1}H NMR (400 MHz, $CDCl_3$)

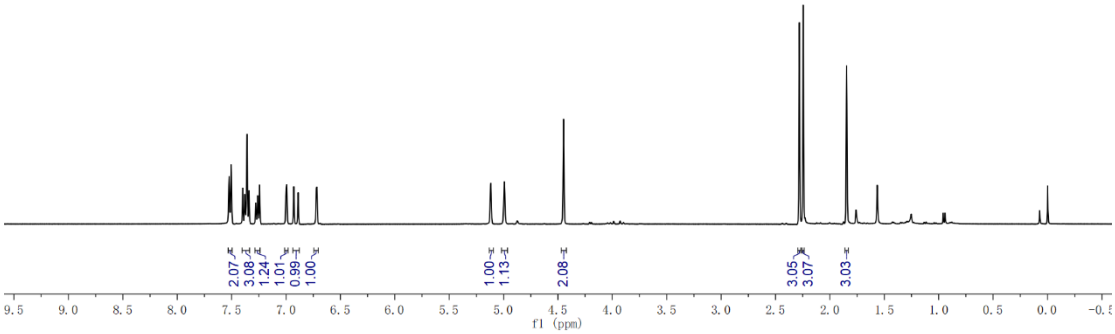


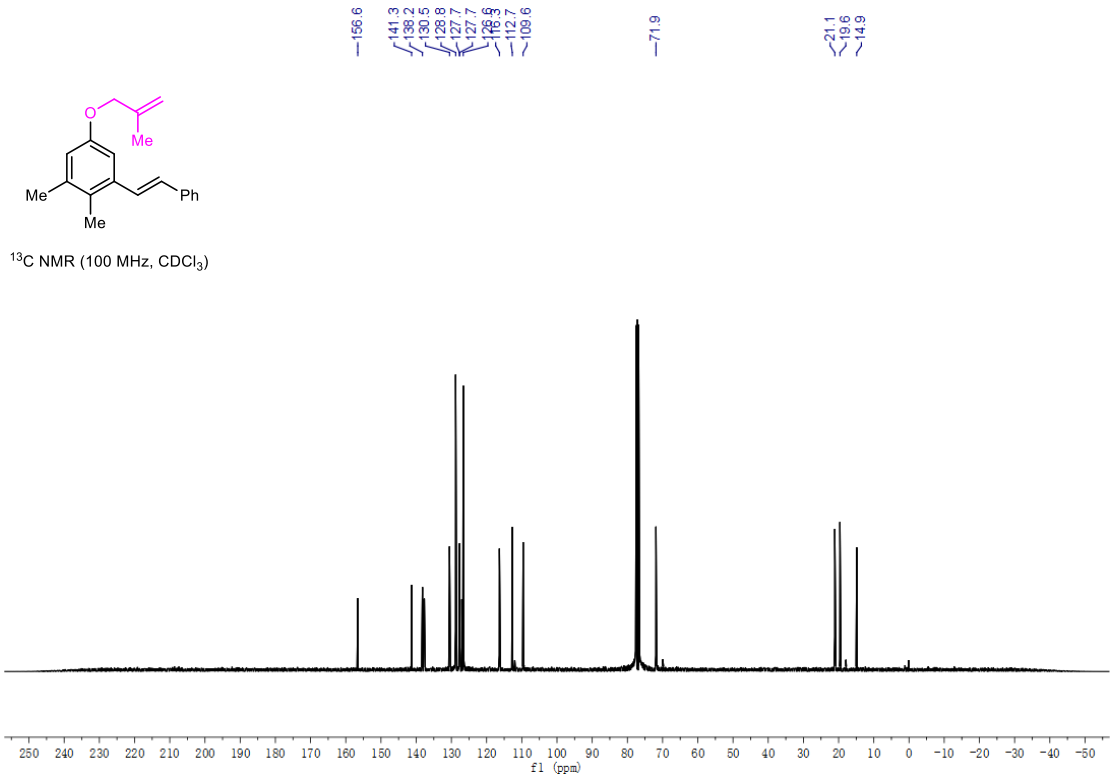
^{13}C NMR (100 MHz, $CDCl_3$)

compound 4n



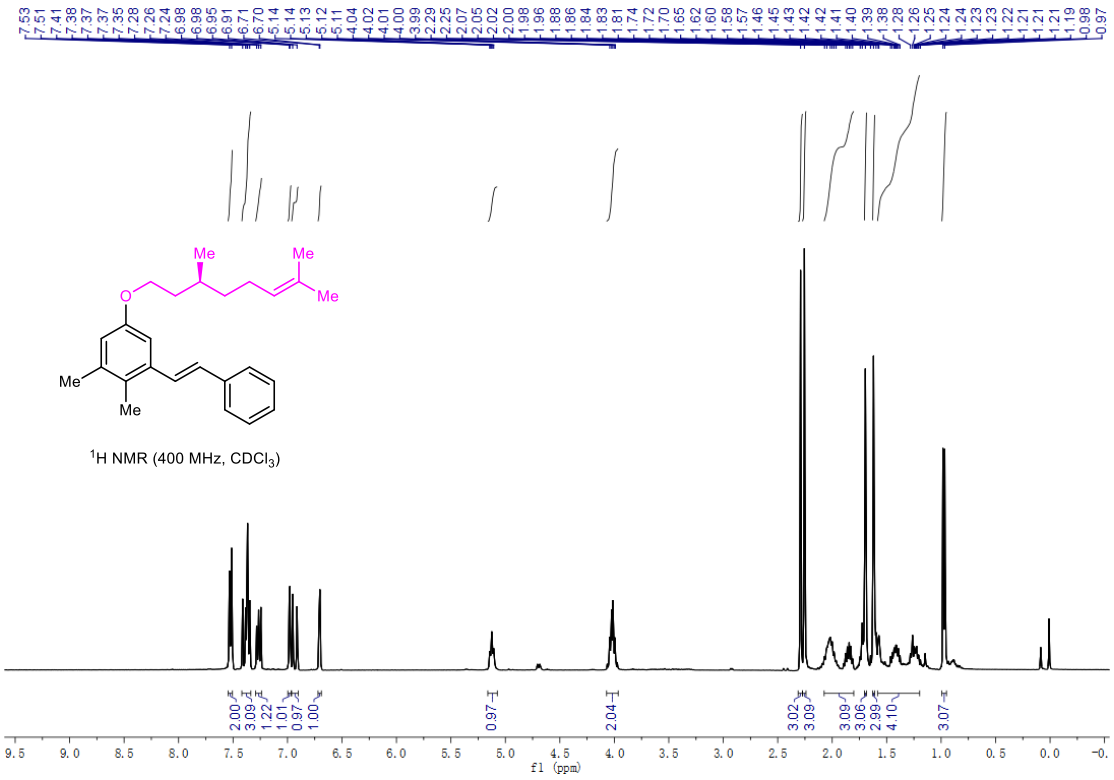
^{1}H NMR (400 MHz, $CDCl_3$)

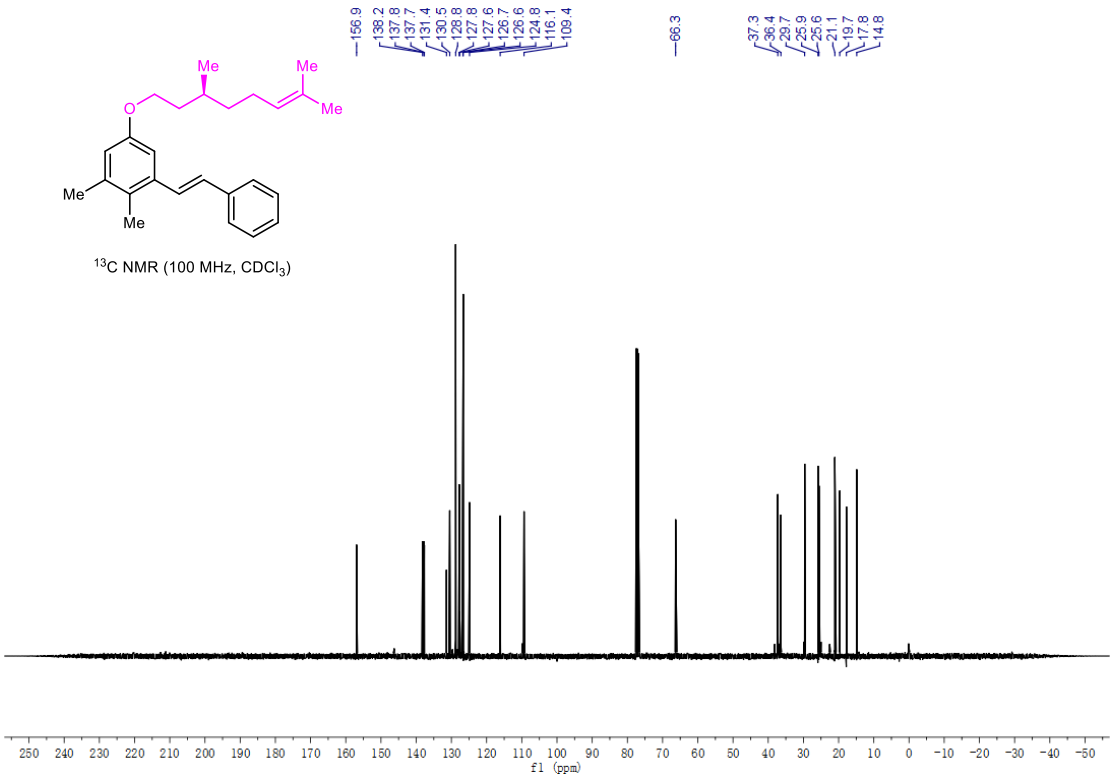




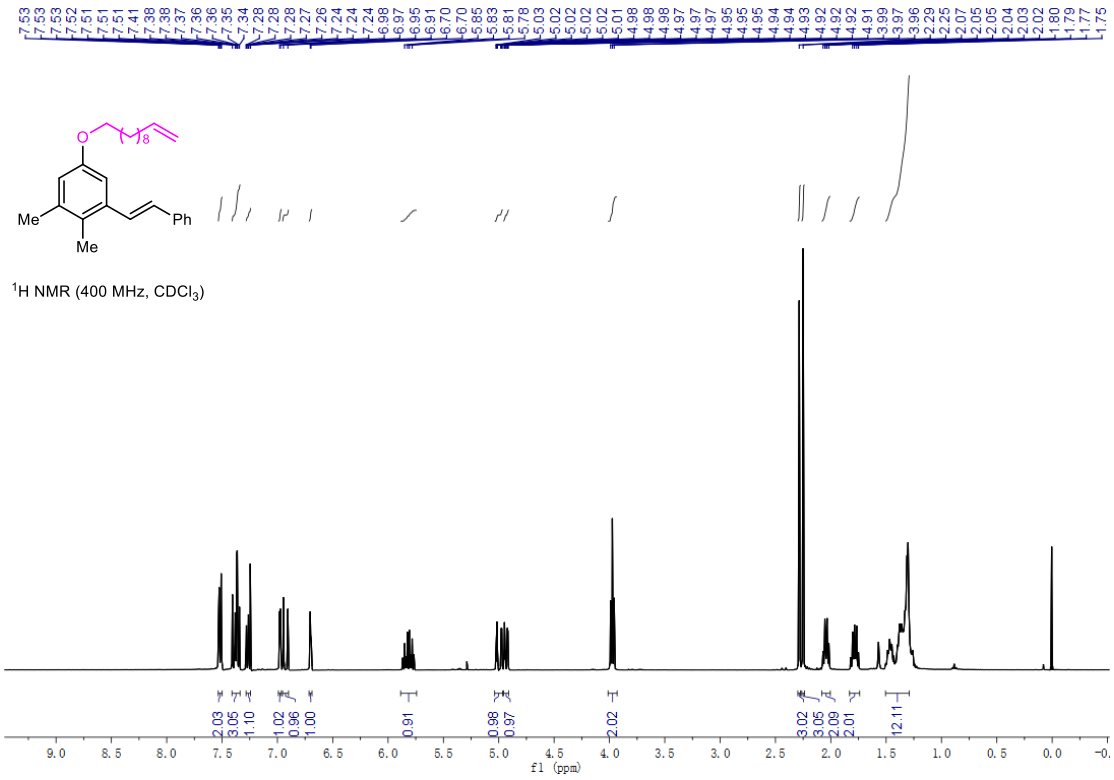
^{13}C NMR (100 MHz, $CDCl_3$)

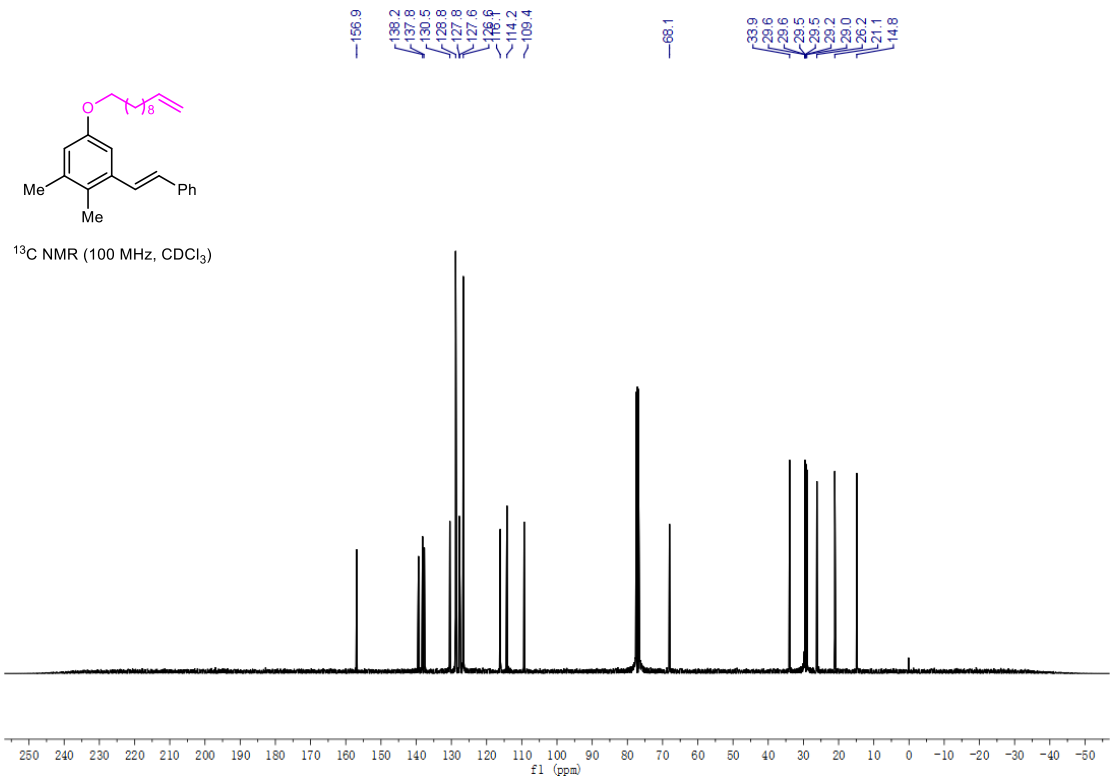
compound 4o


Me
Me
Me
O
Me
Me
1H NMR (400 MHz, CDCl3)
f1 (ppm)

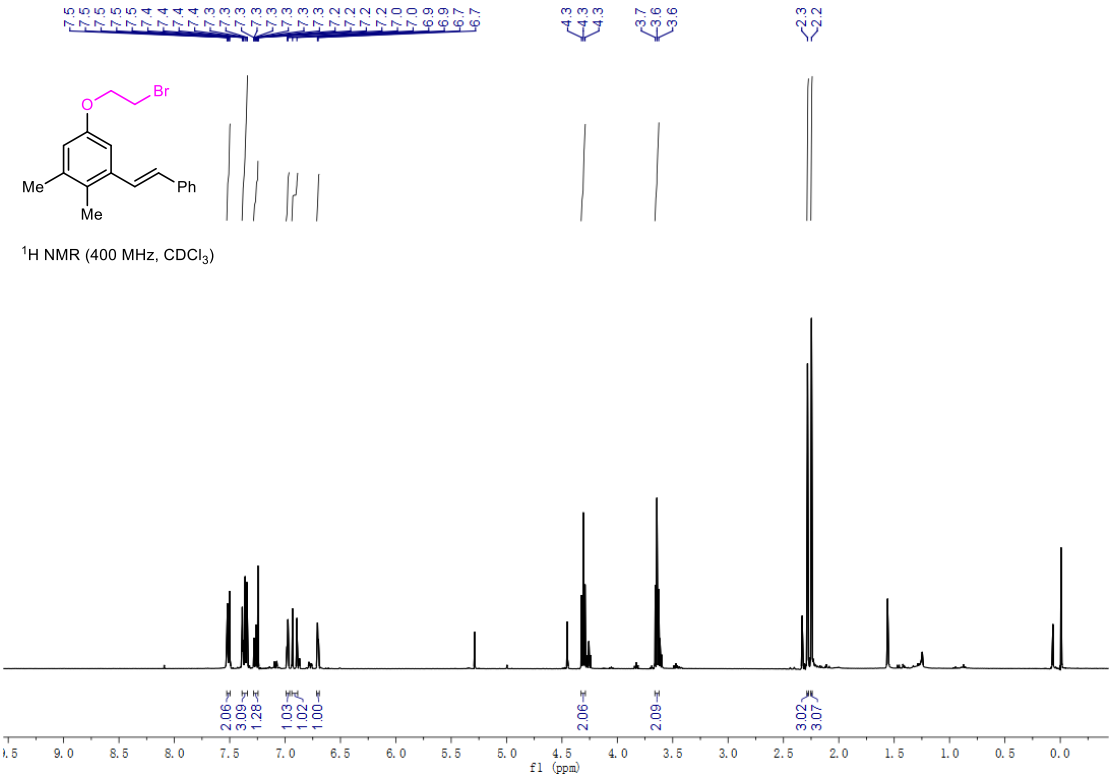

Me
Me
Me
O
Me
Me
13C NMR (100 MHz, CDCl3)
f1 (ppm)

compound 4p

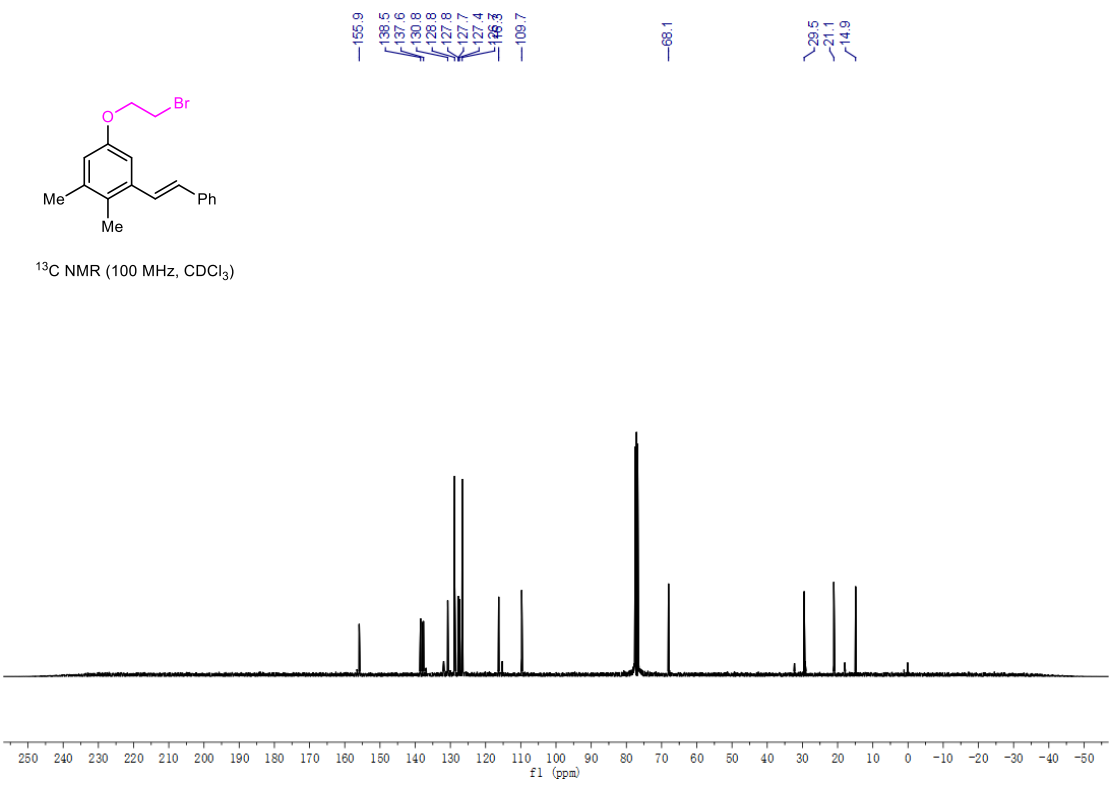

Me
Me
Ph
O
8
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
Me
Ph
O
8
13C NMR (100 MHz, CDCl3)
f1 (ppm)

compound 4q

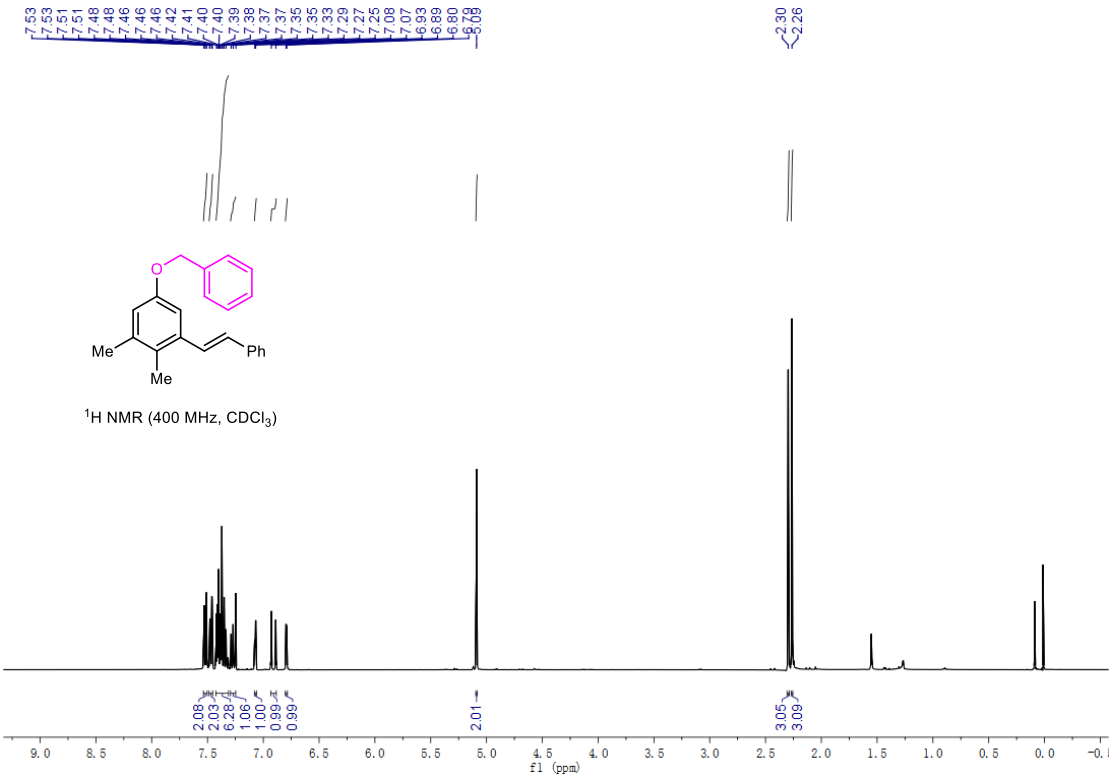


^{1}H NMR (400 MHz, $CDCl_3$)

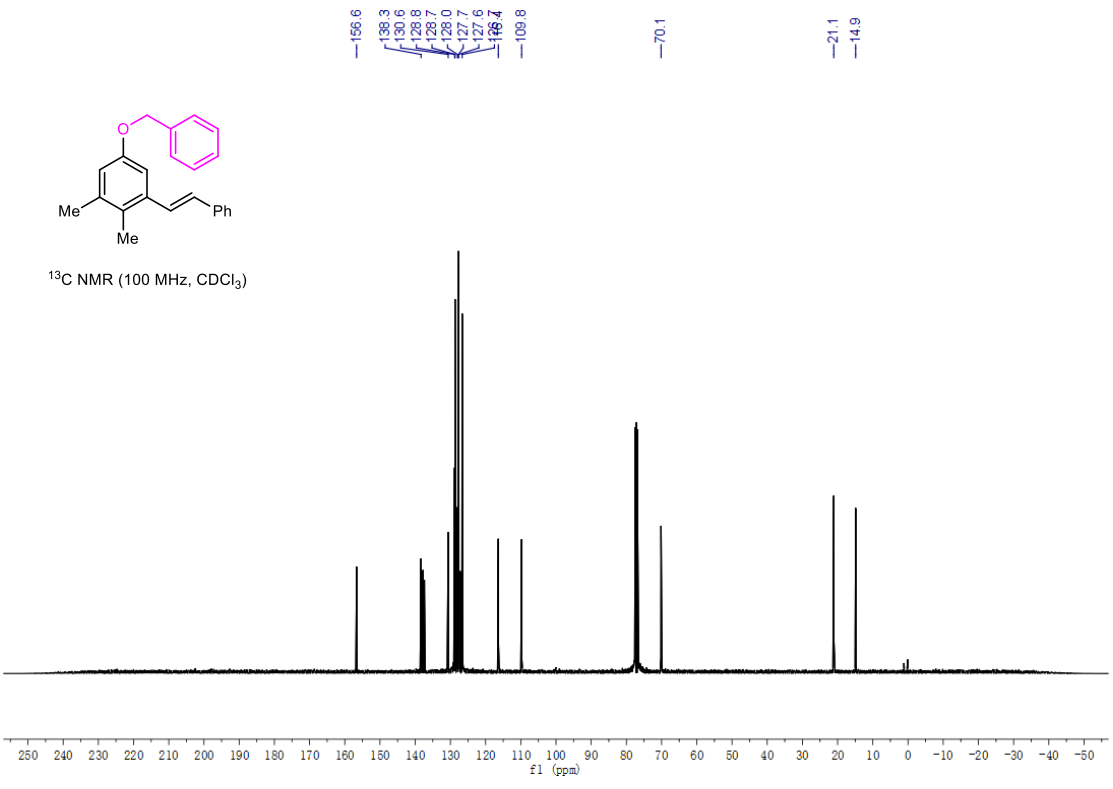


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4r

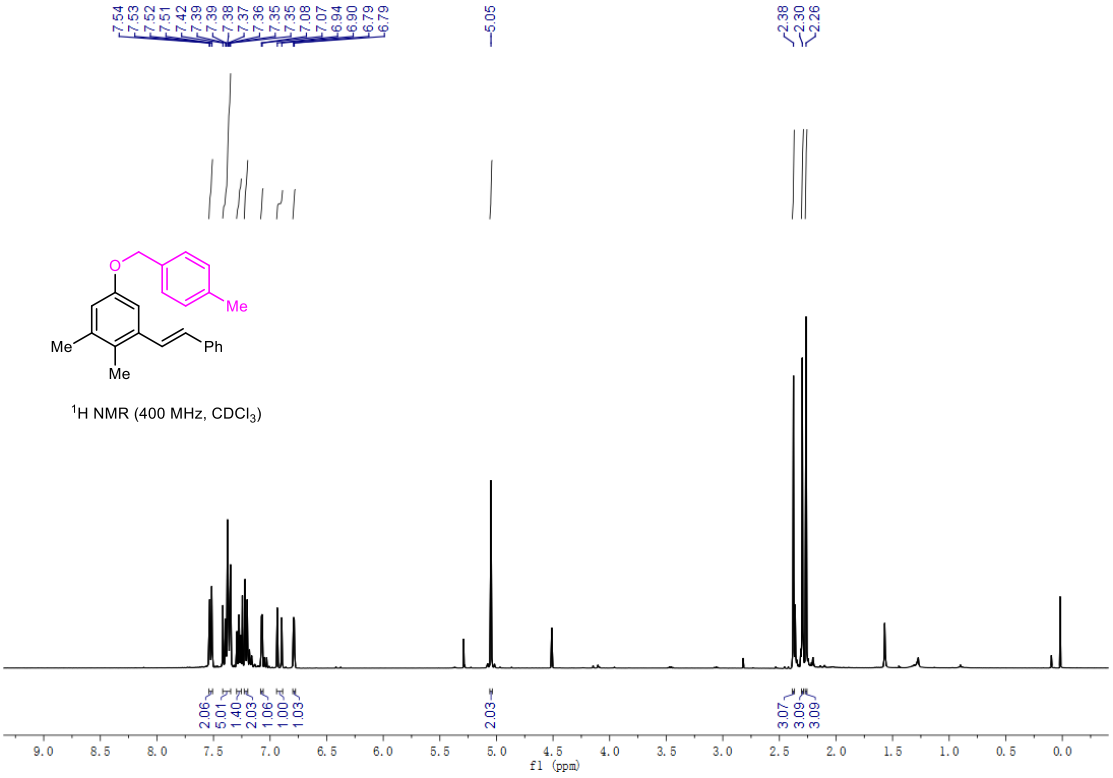


^{1}H NMR (400 MHz, $CDCl_3$)

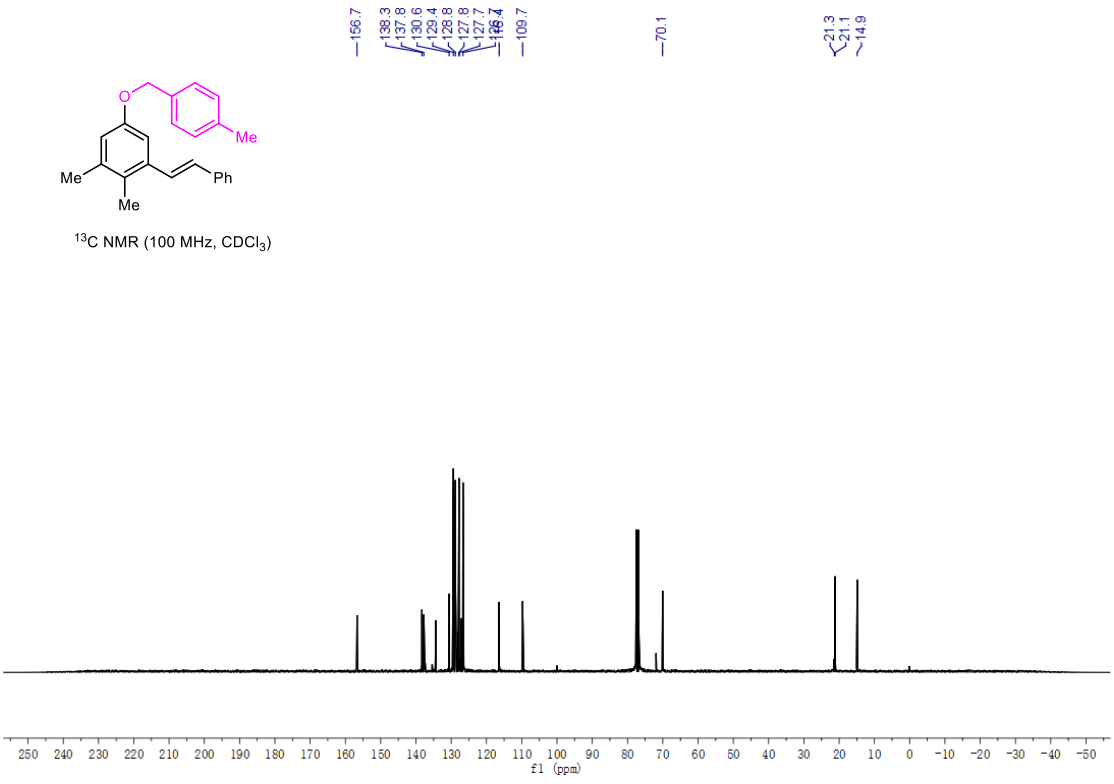


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4s

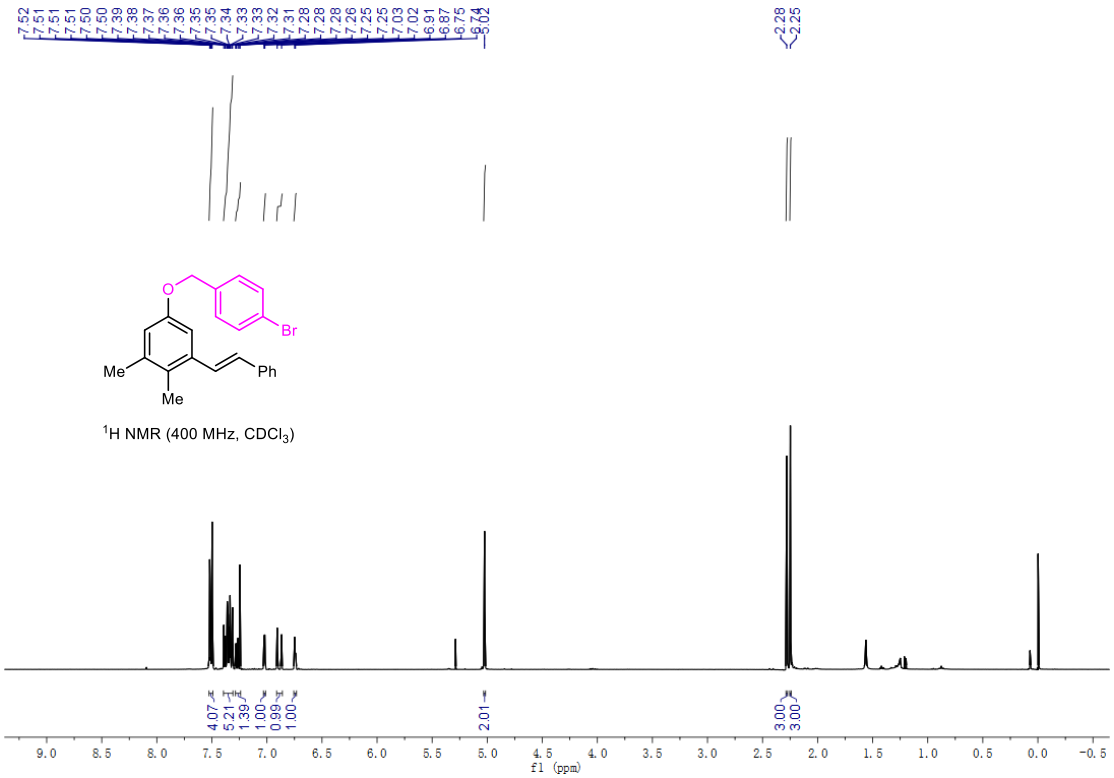


^{1}H NMR (400 MHz, $CDCl_3$)

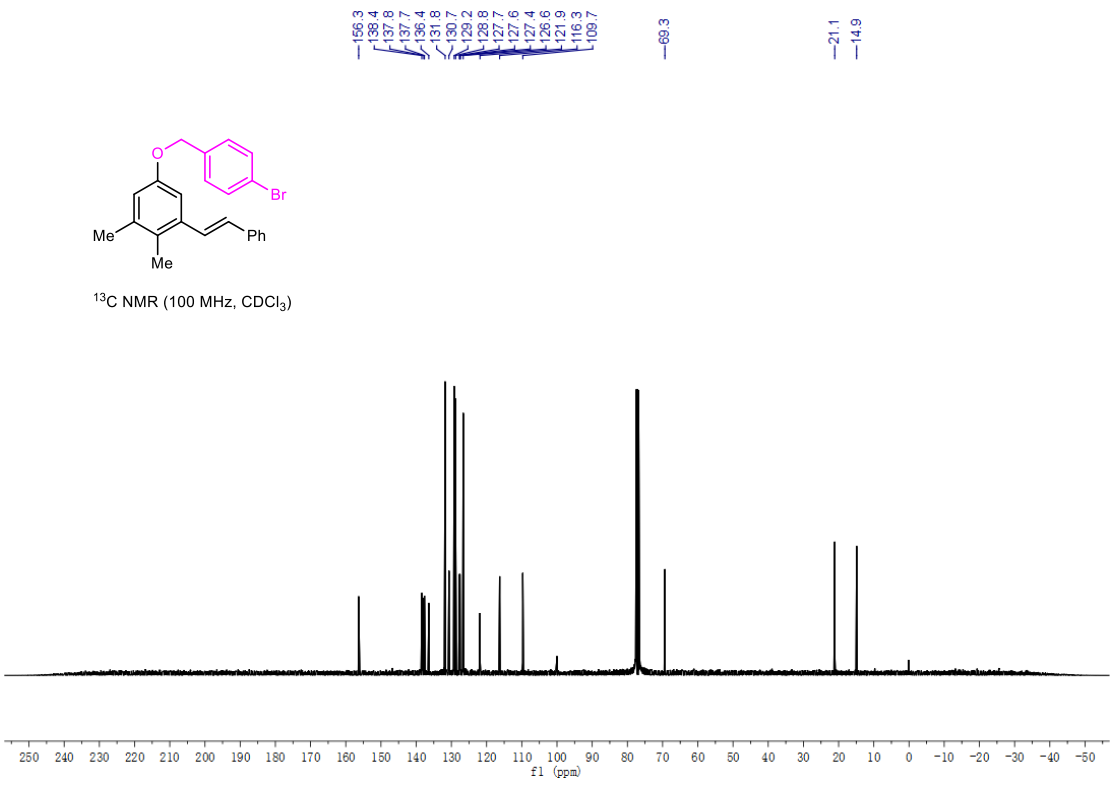


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4t

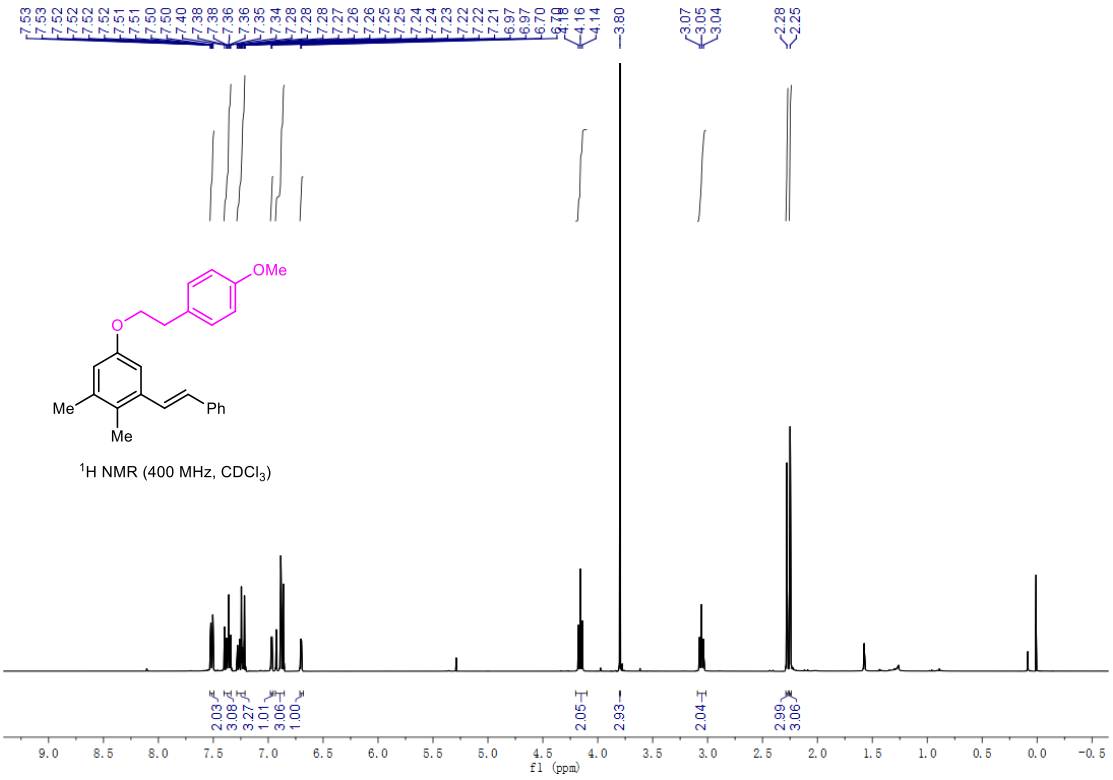


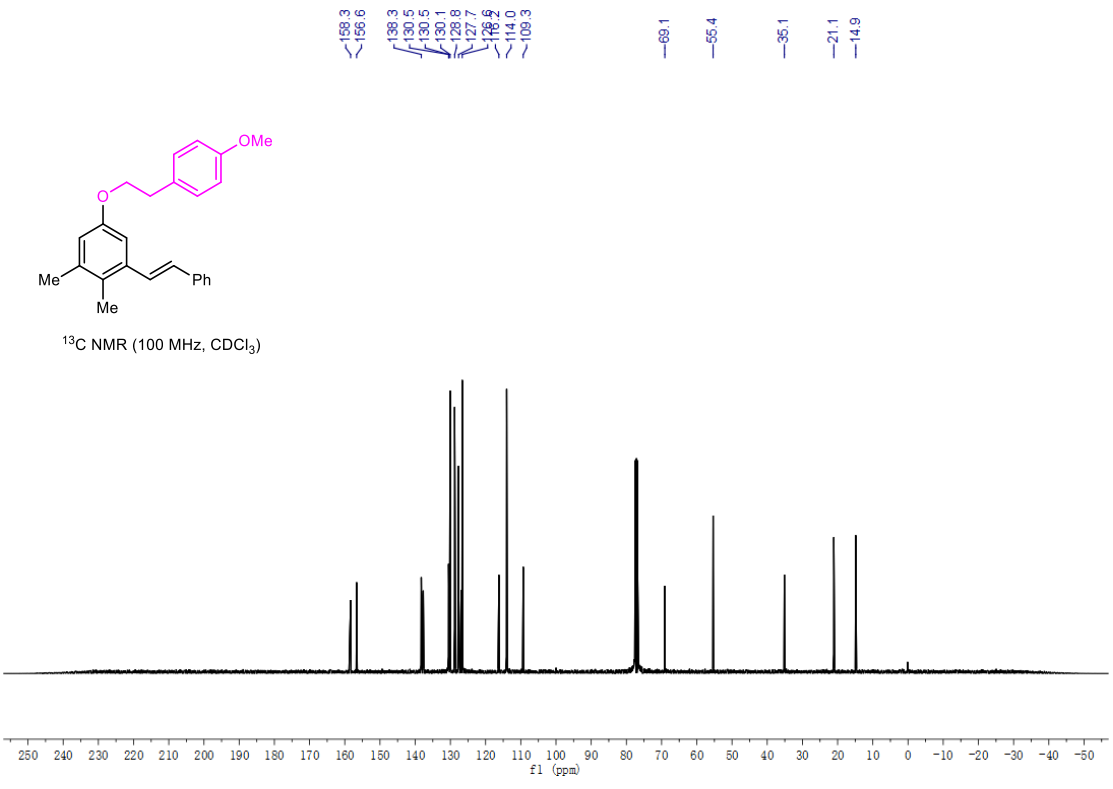
^{1}H NMR (400 MHz, $CDCl_3$)



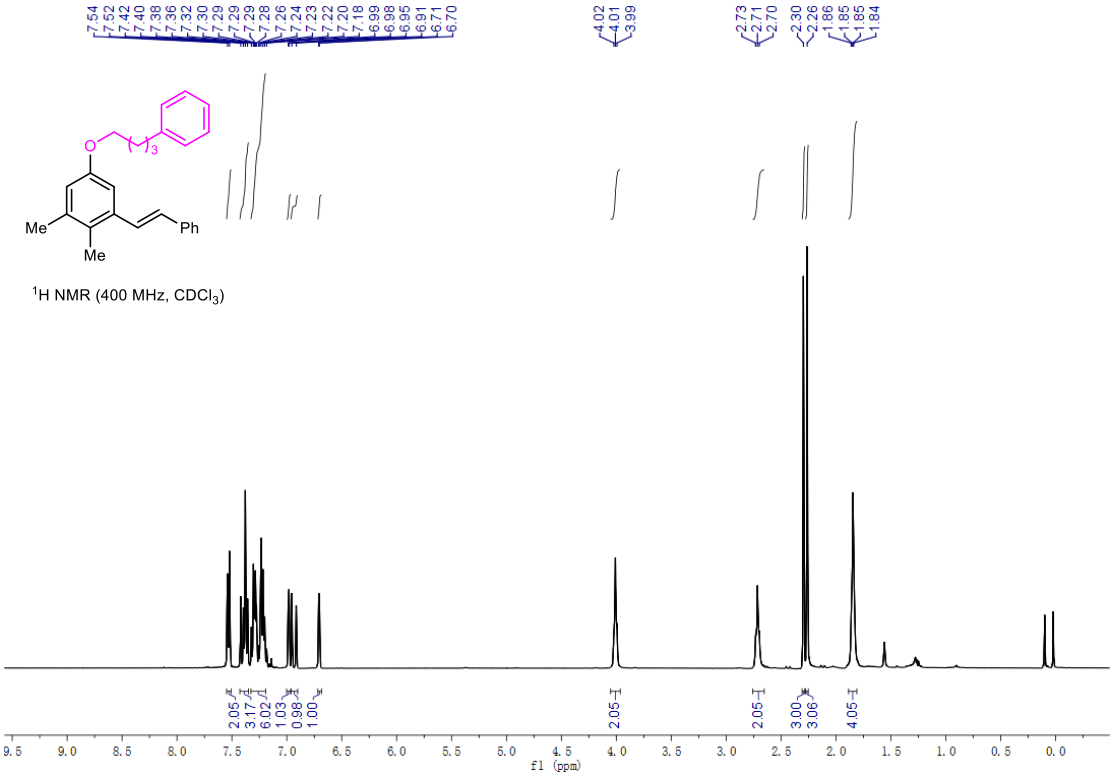
^{13}C NMR (100 MHz, $CDCl_3$)

compound 4u

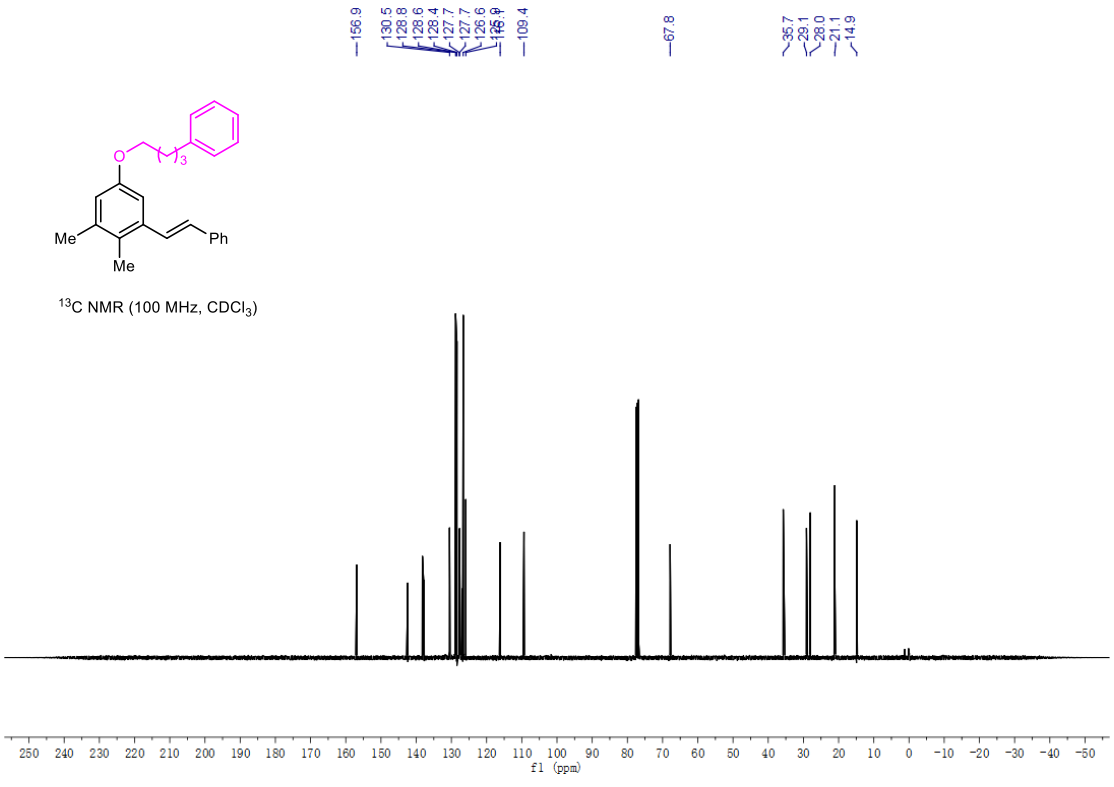

OMe
O
Me
Me
Ph
1H NMR (400 MHz, CDCl3)
f1 (ppm)


OMe
O
Me
Me
Ph
13C NMR (100 MHz, CDCl3)
f1 (ppm)

compound 4v

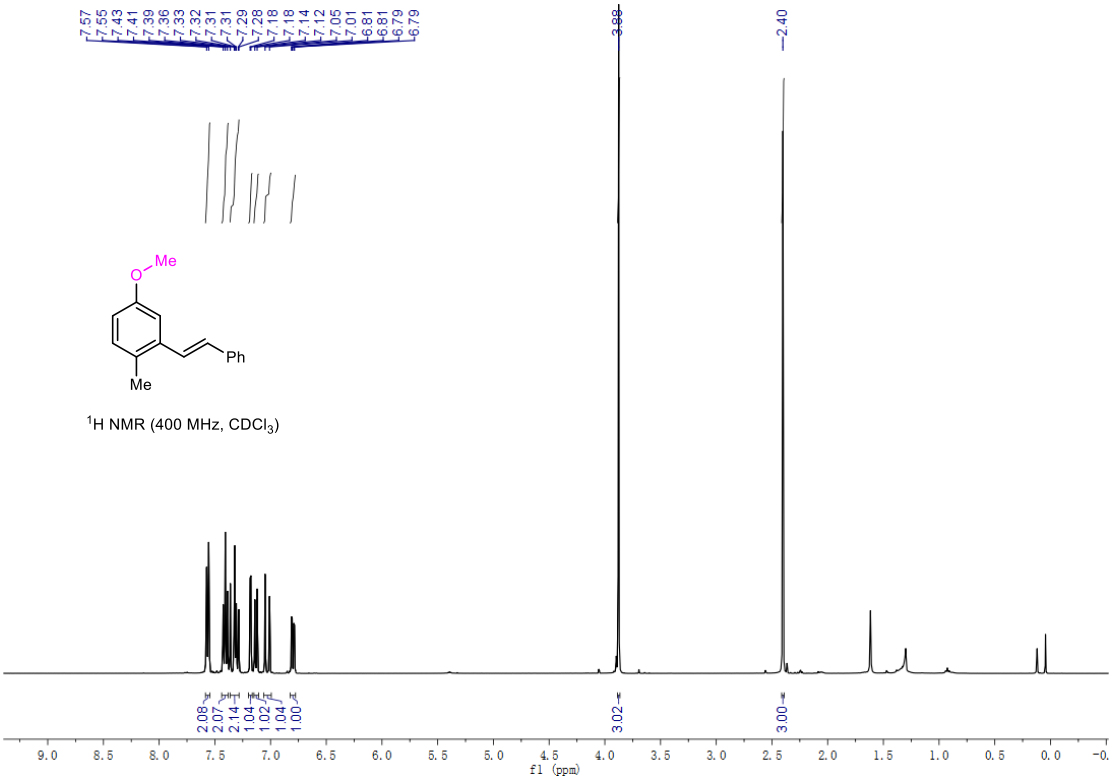


^{1}H NMR (400 MHz, $CDCl_3$)

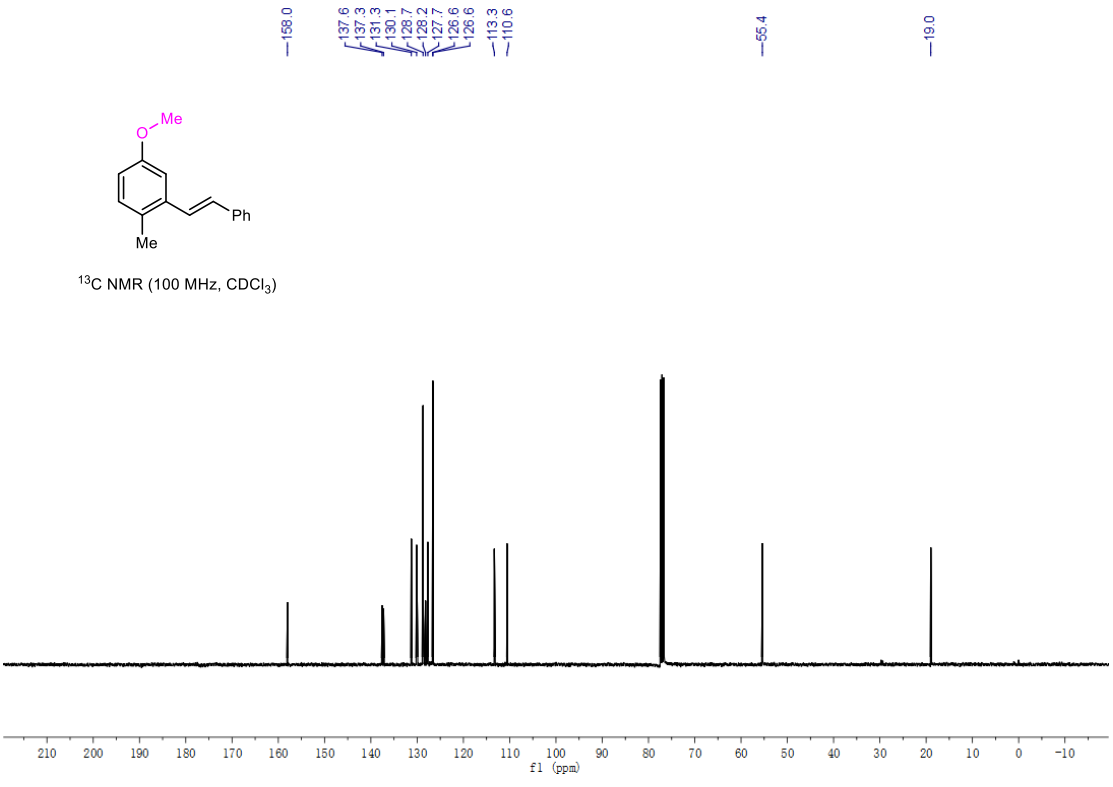


^{13}C NMR (100 MHz, $CDCl_3$)

compound 4w

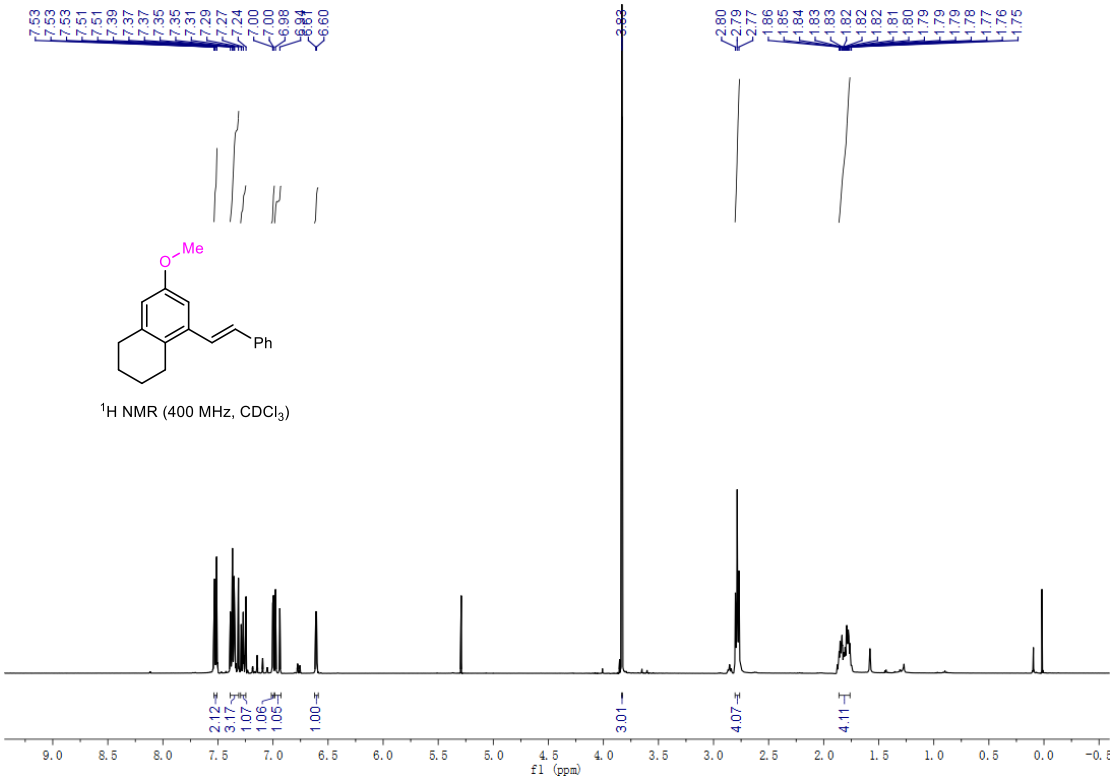


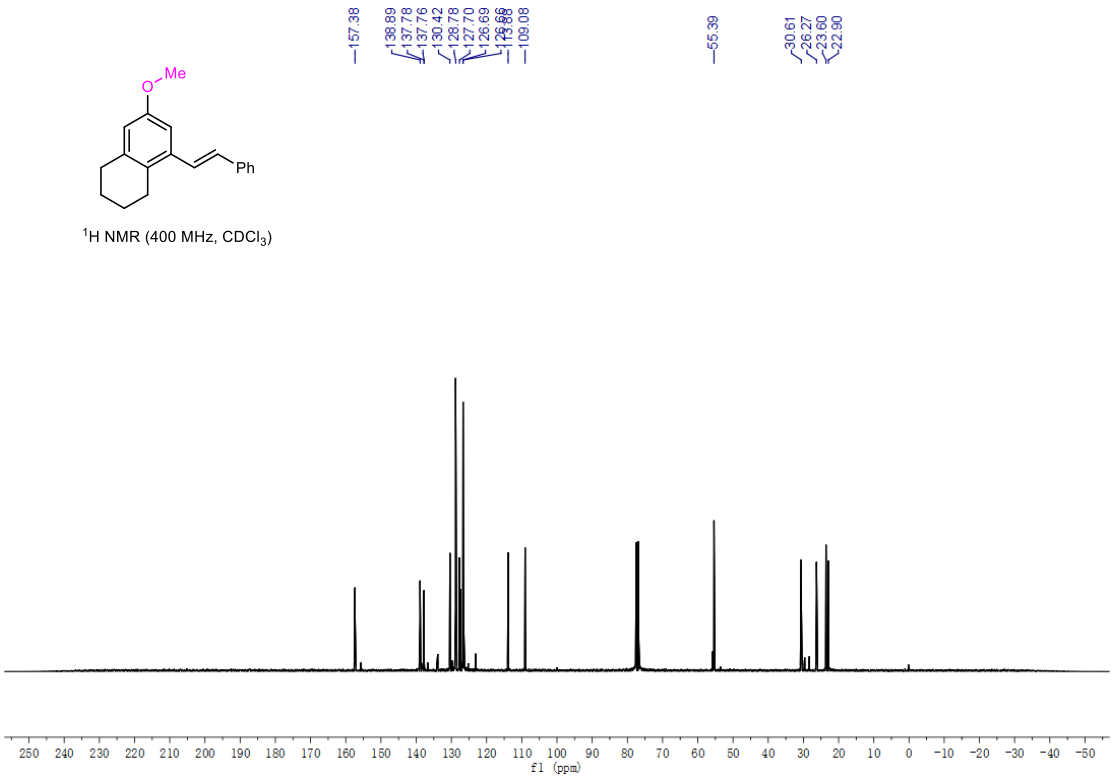
^{1}H NMR (400 MHz, $CDCl_3$)



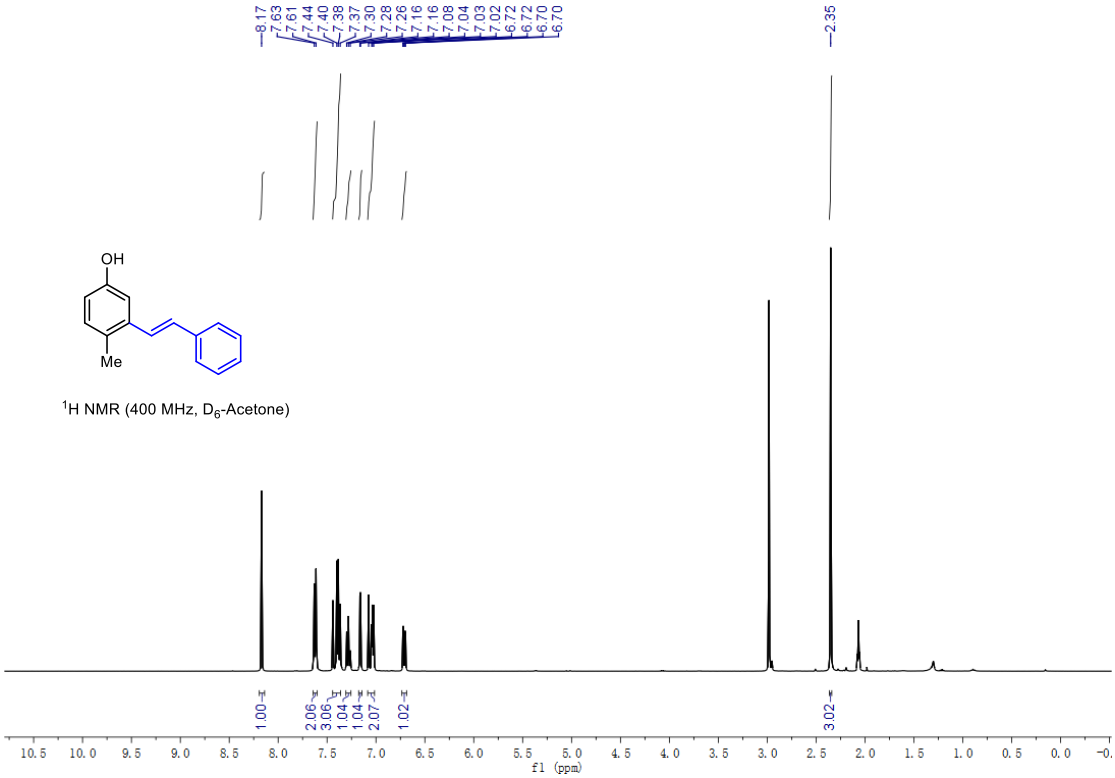
^{13}C NMR (100 MHz, $CDCl_3$)

compound 4x

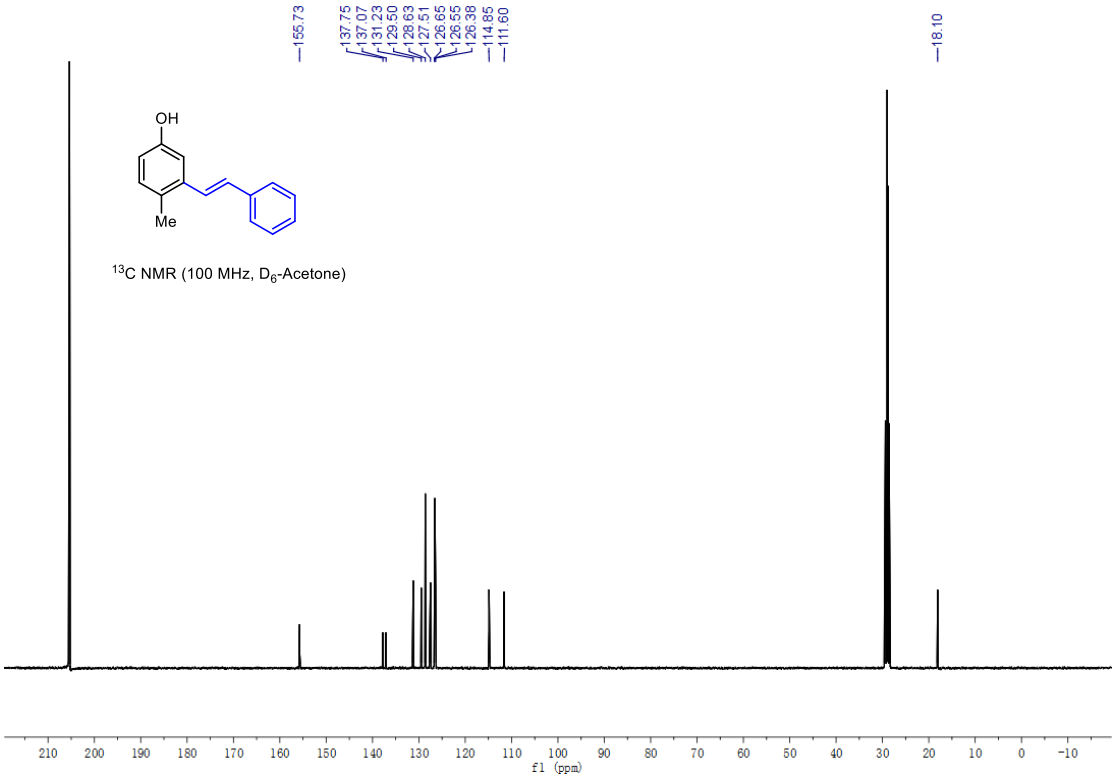

Me
O
Ph
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
O
Ph
1H NMR (400 MHz, CDCl3)
f1 (ppm)

compound 5b

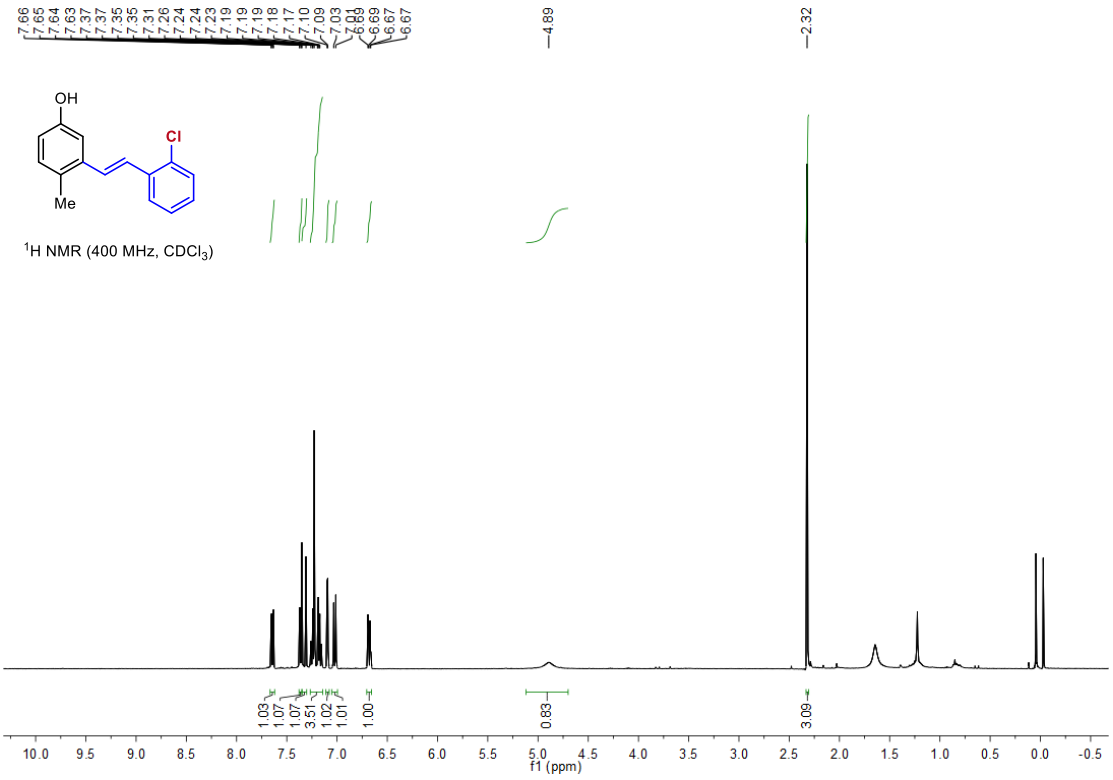


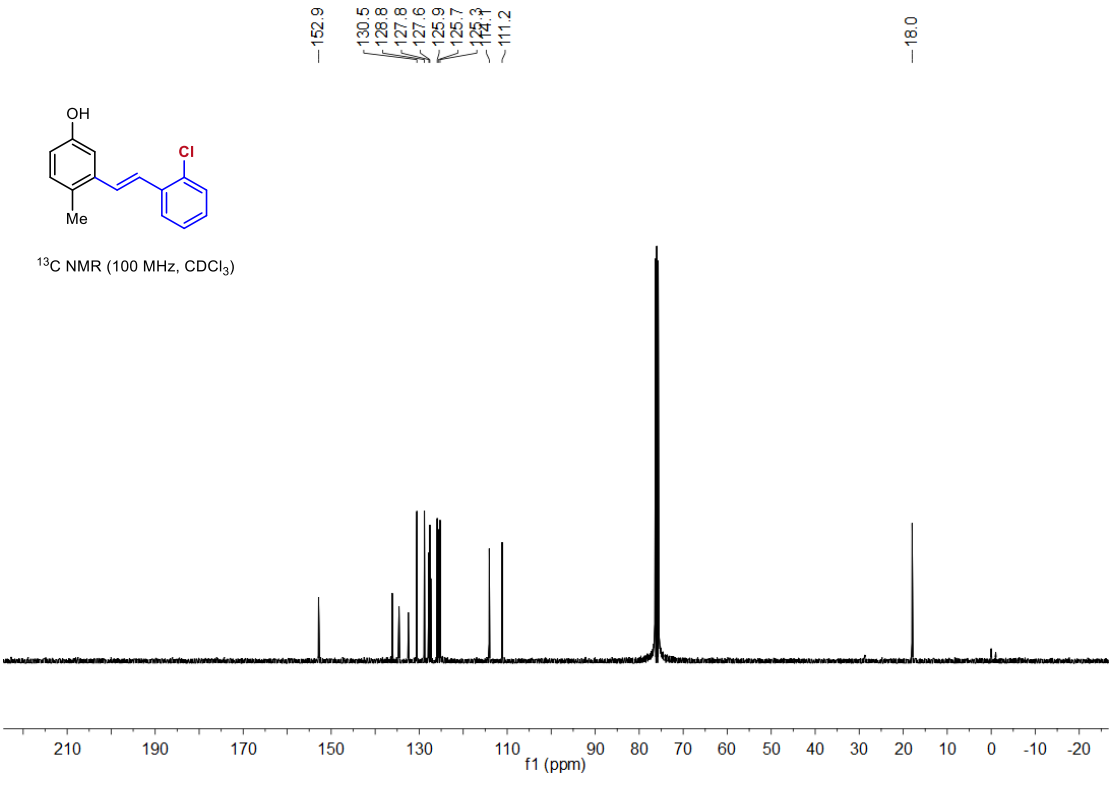
^{1}H NMR (400 MHz, D_6-Acetone)



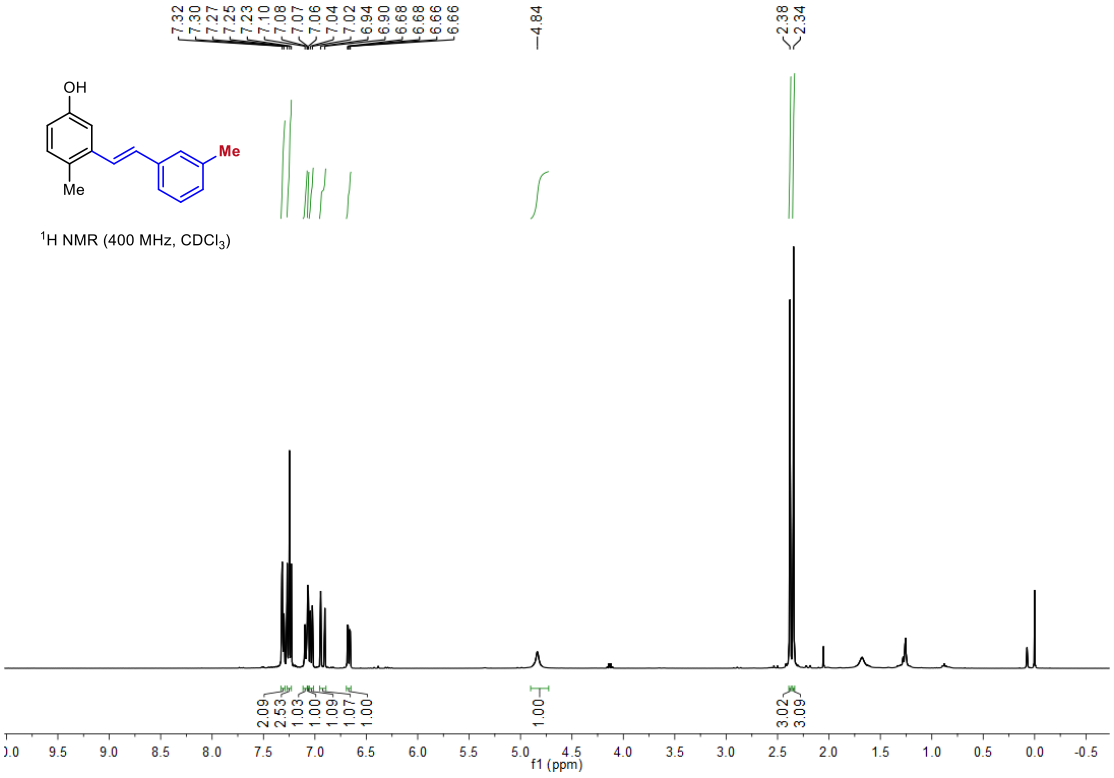
^{13}C NMR (100 MHz, D_6-Acetone)

compound 5c

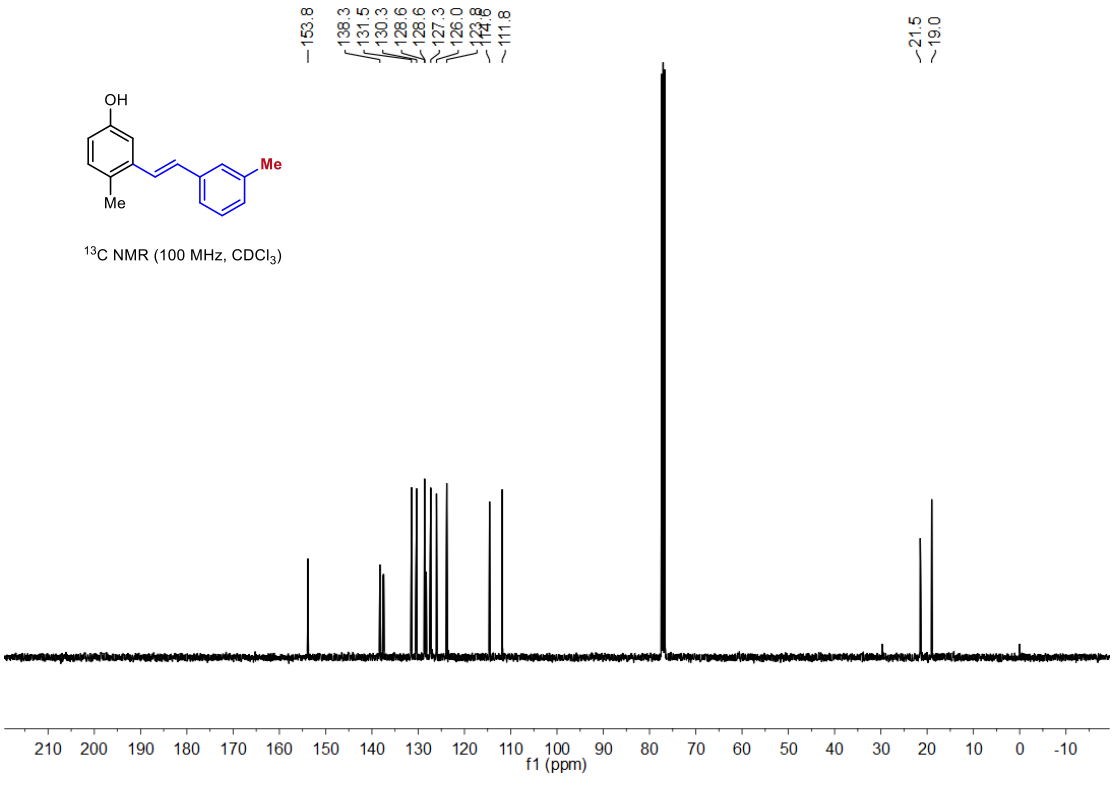

7.66
7.65
7.64
7.63
7.37
7.37
7.35
7.35
7.31
7.26
7.24
7.24
7.23
7.19
7.19
7.19
7.18
7.17
7.10
7.09
7.03
7.01
6.89
6.69
6.67
6.67
4.89
2.32
OH
Cl
Me
1H NMR (400 MHz, CDCl3)
1.03
1.07
1.07
3.51
1.02
1.01
1.00
0.83
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


152.9
130.5
128.8
127.8
127.6
125.9
125.7
125.3
124.1
111.2
18.0
OH
Cl
Me
13C NMR (100 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

compound 5d

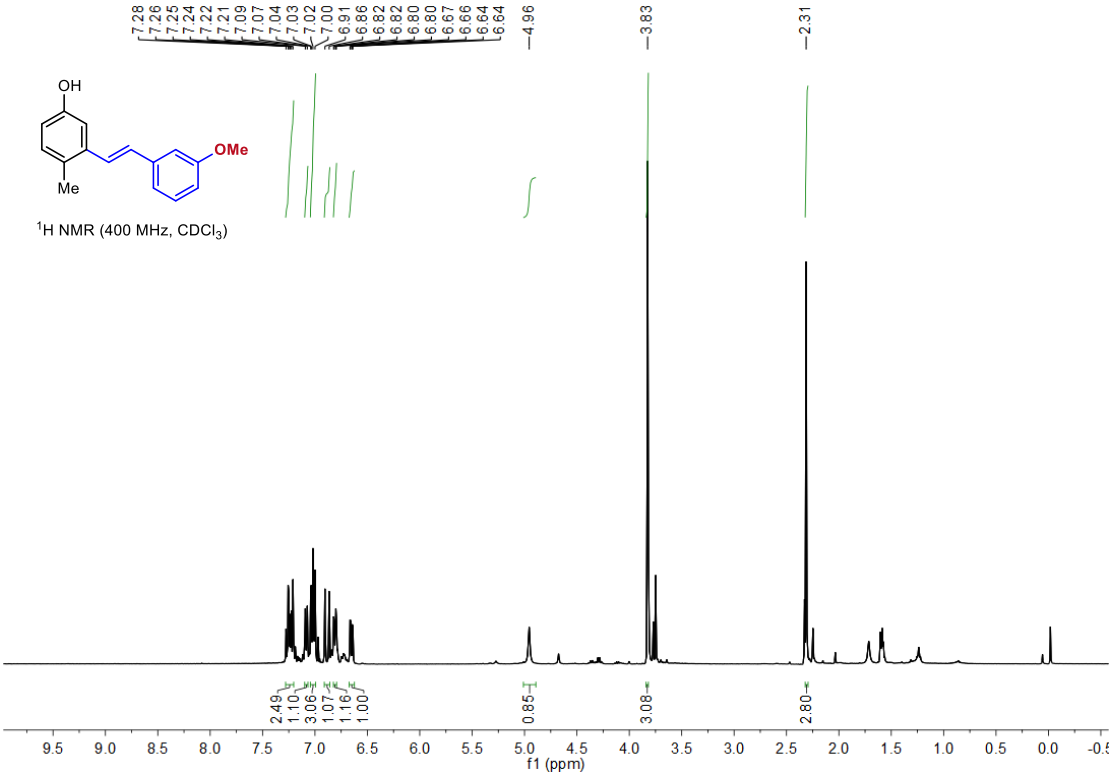


^{1}H NMR (400 MHz, $CDCl_3$)

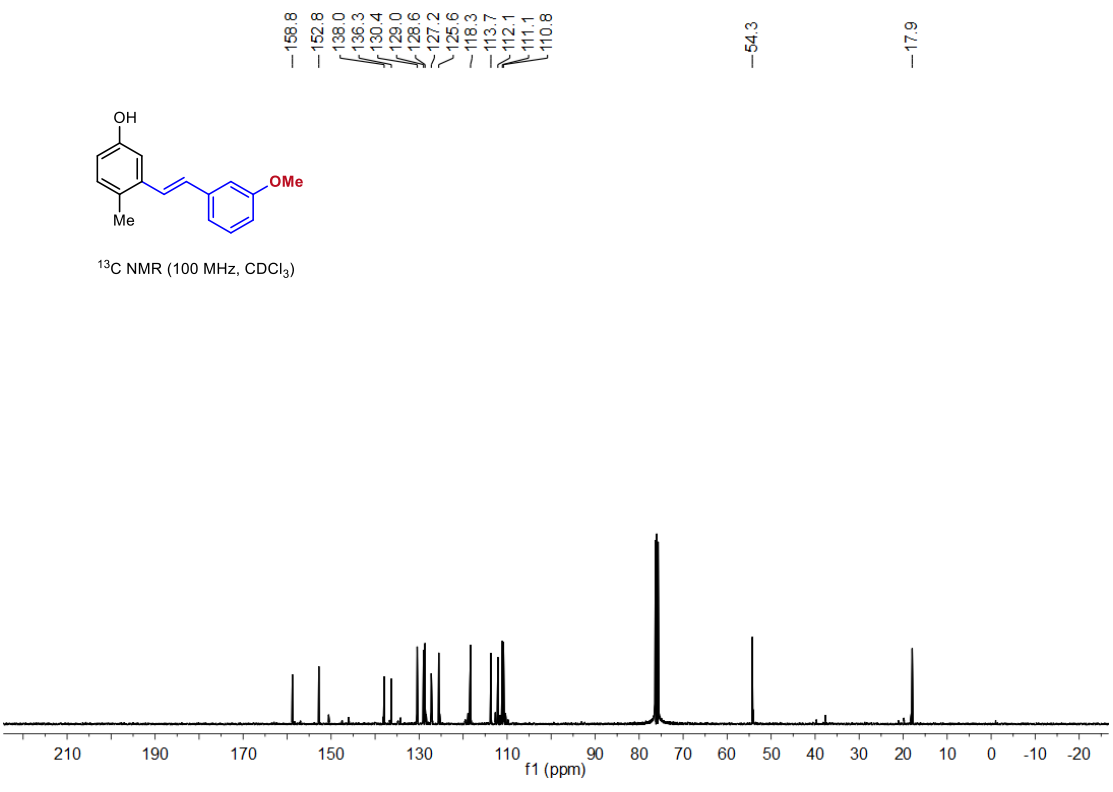


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5e

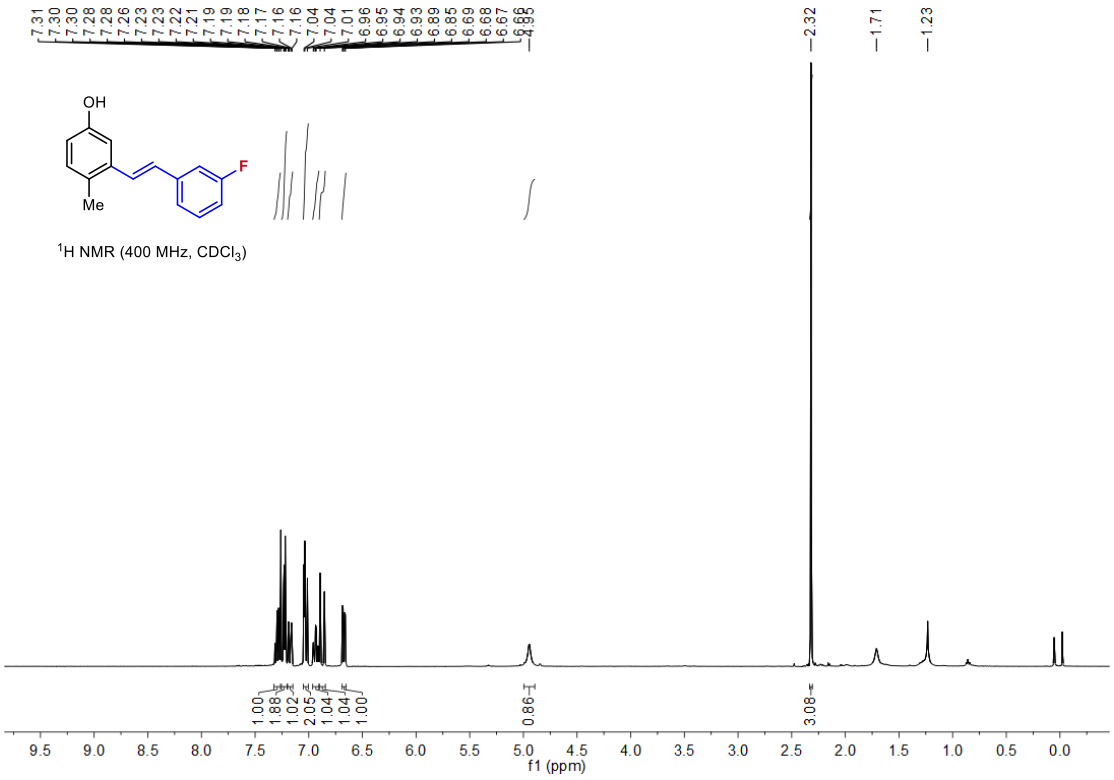


^{1}H NMR (400 MHz, $CDCl_3$)

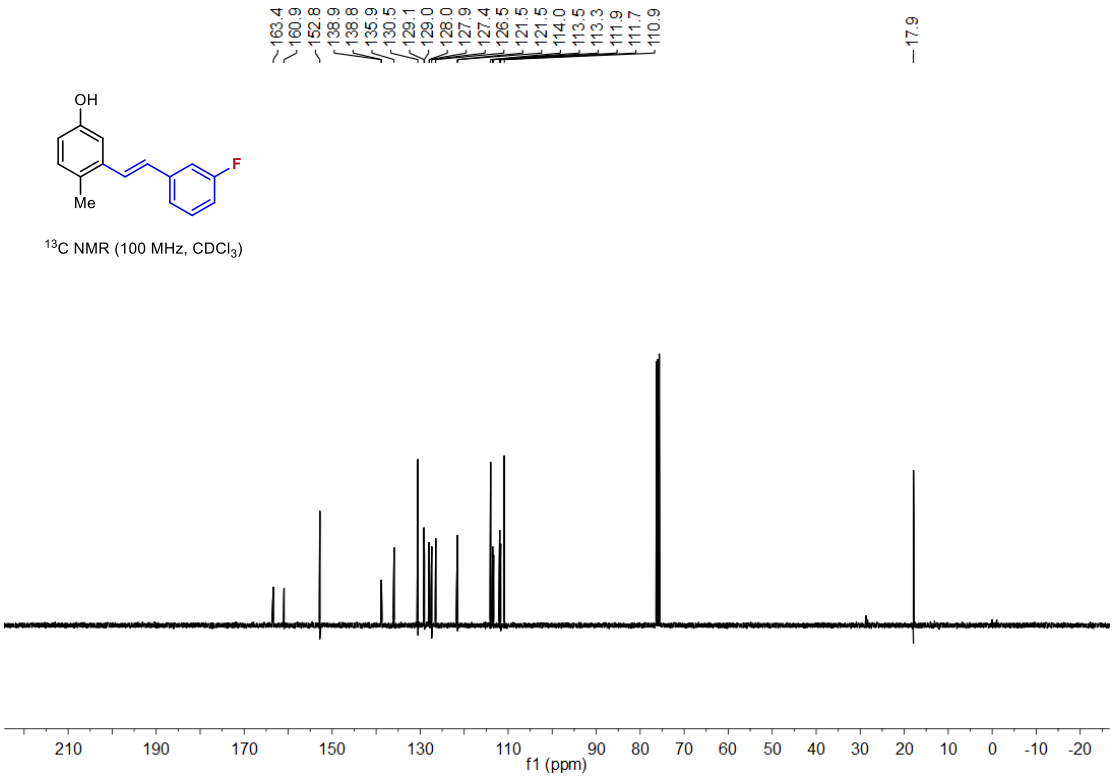


^{13}C NMR (100 MHz, $CDCl_3$)

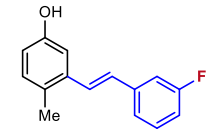
compound 5f



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

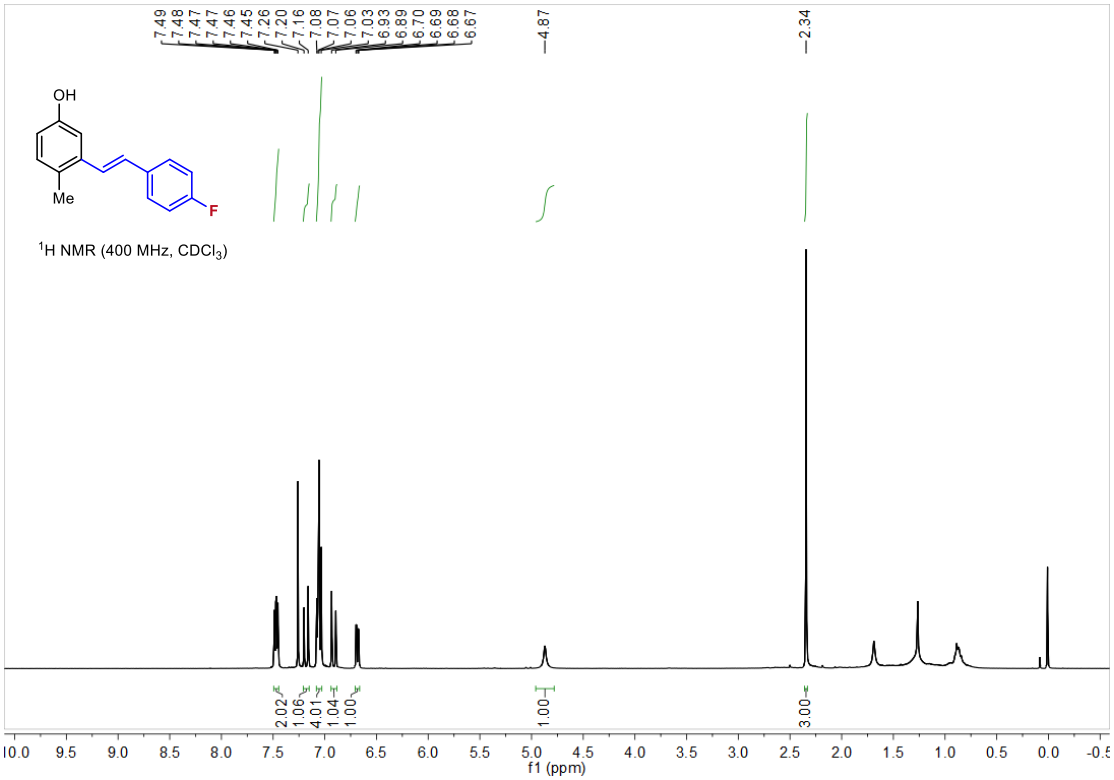


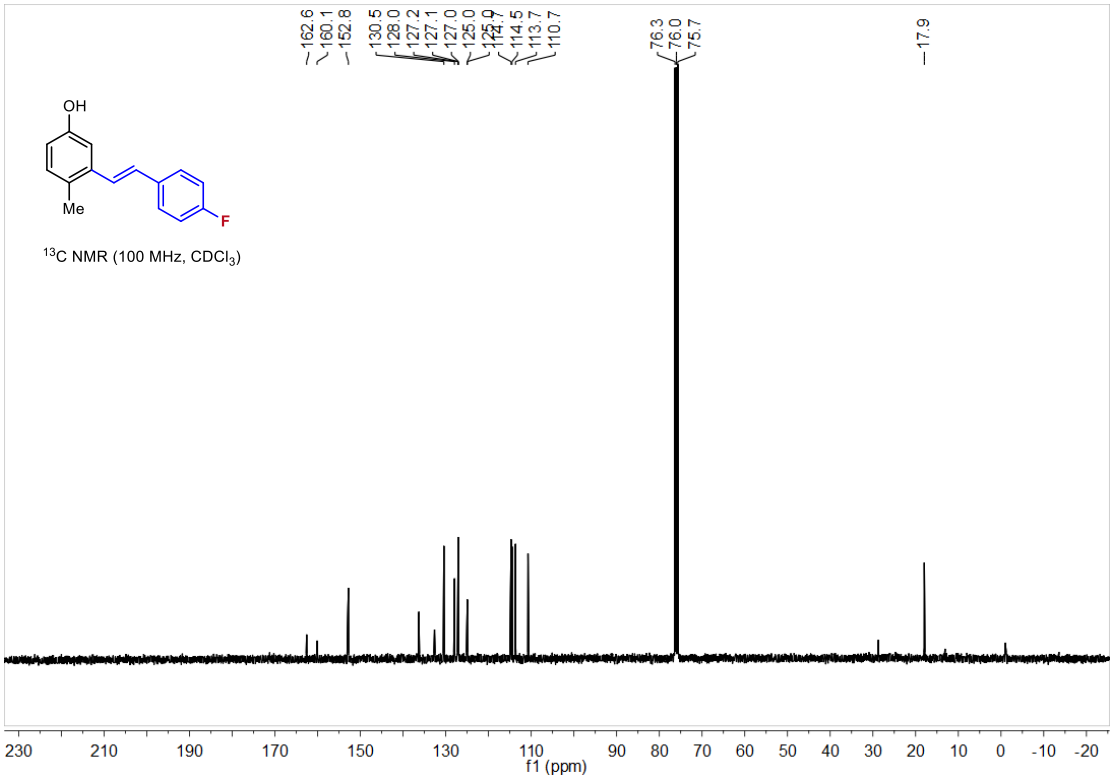
^{13}C NMR (100 MHz, $CDCl_3$)

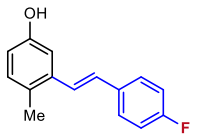


^{19}F NMR (377 MHz, $CDCl_3$)

compound 5g

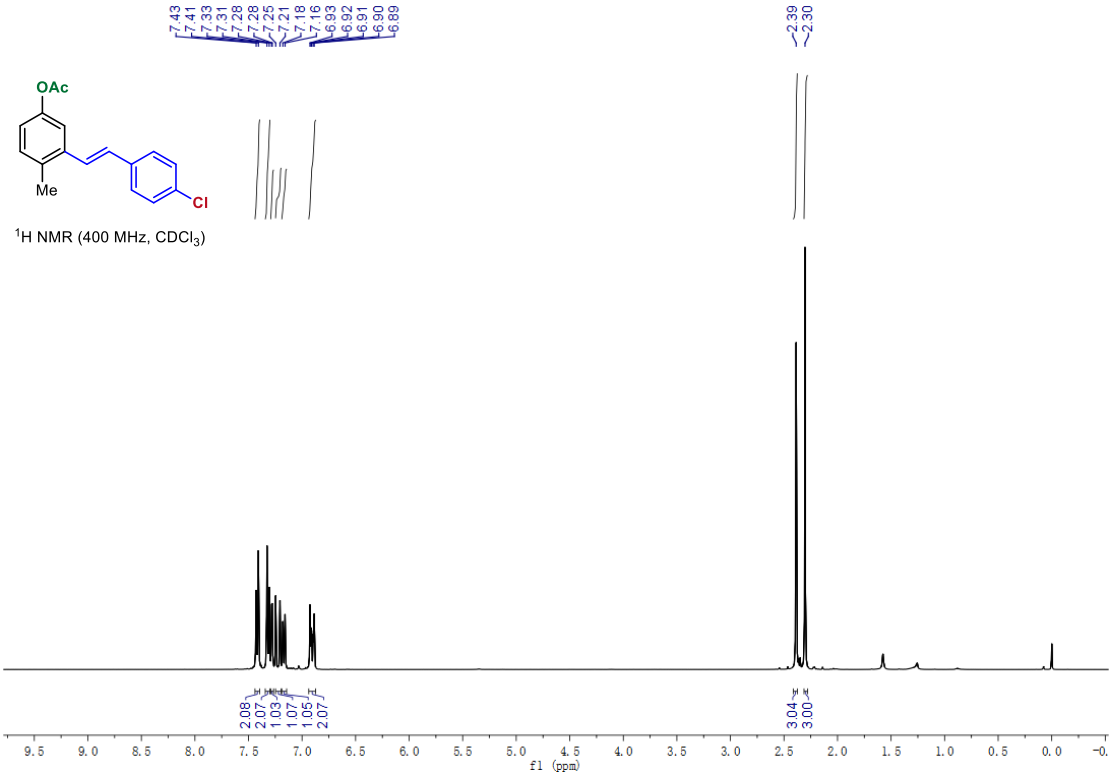

7.49
7.48
7.47
7.47
7.46
7.45
7.26
7.20
7.16
7.08
7.07
7.06
7.03
6.93
6.89
6.70
6.69
6.68
6.67
4.87
2.34
OH
Me
F
^{1}H NMR (400 MHz, CDCl$_3$)
2.02
1.06
4.01
1.04
1.00
1.00
3.00
f1 (ppm)


162.6
160.1
152.8
130.5
128.0
127.2
127.1
127.0
125.0
114.5
113.7
110.7
76.3
76.0
75.7
17.9
OH
Me
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

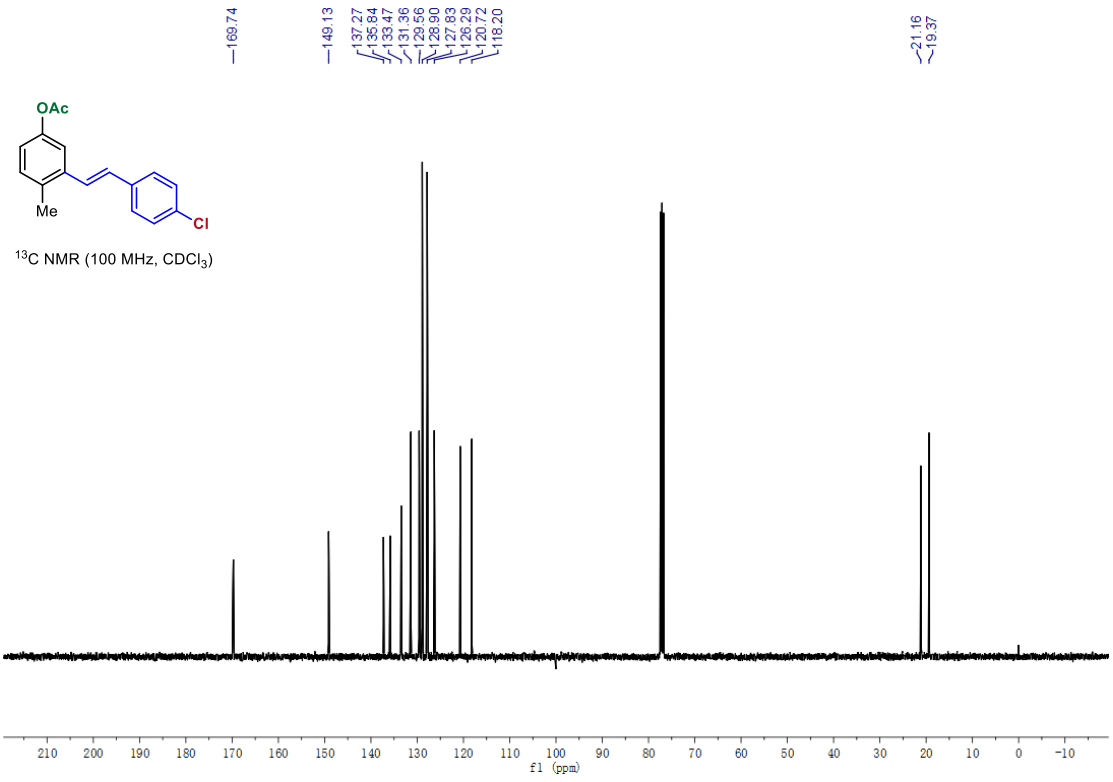


^{19}F NMR (376 MHz, $CDCl_3$)

compound 5h

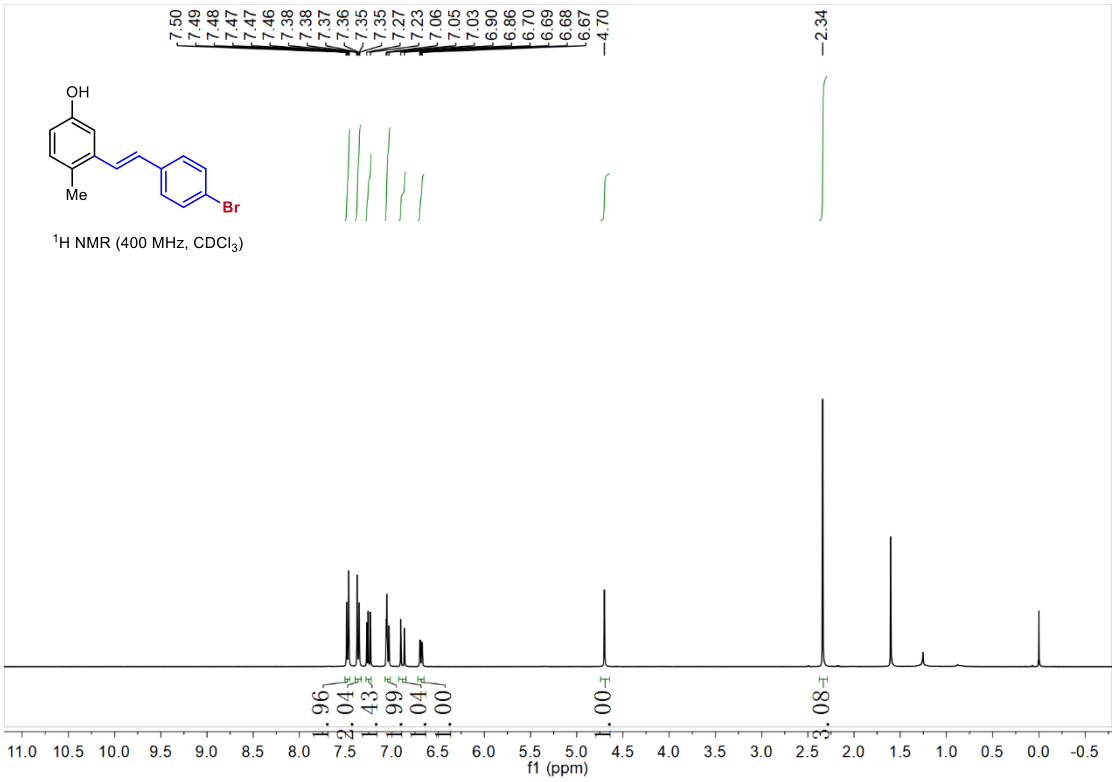


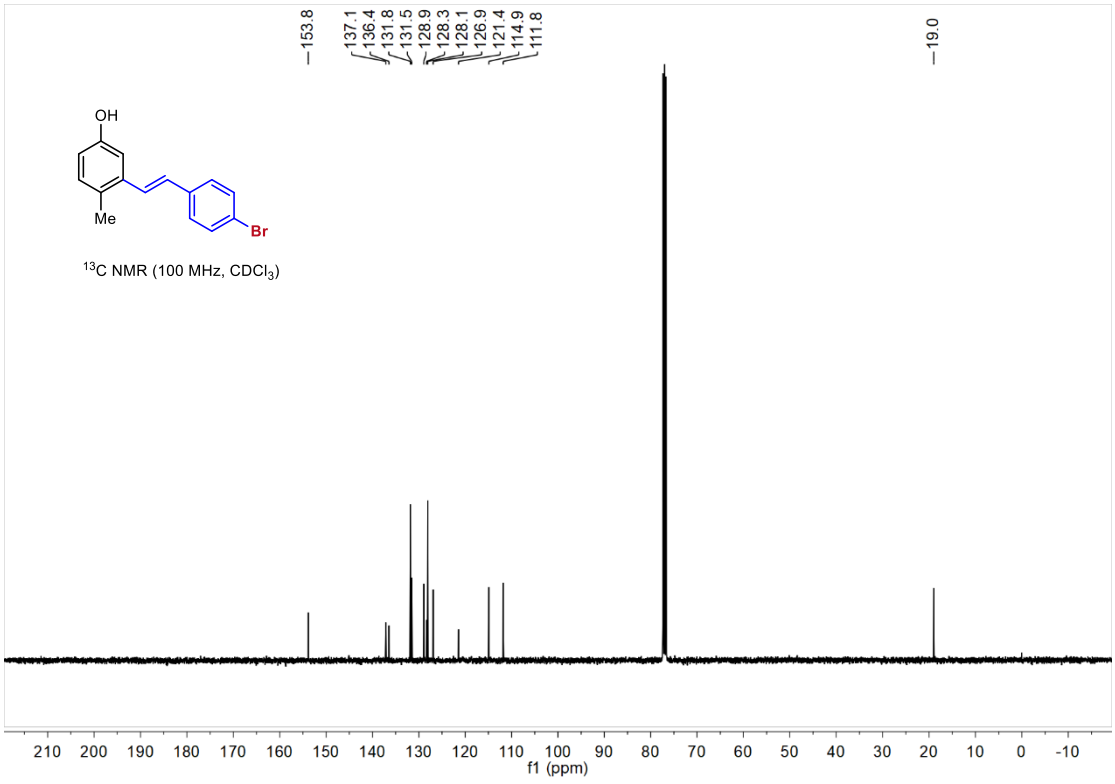
^{1}H NMR (400 MHz, $CDCl_3$)



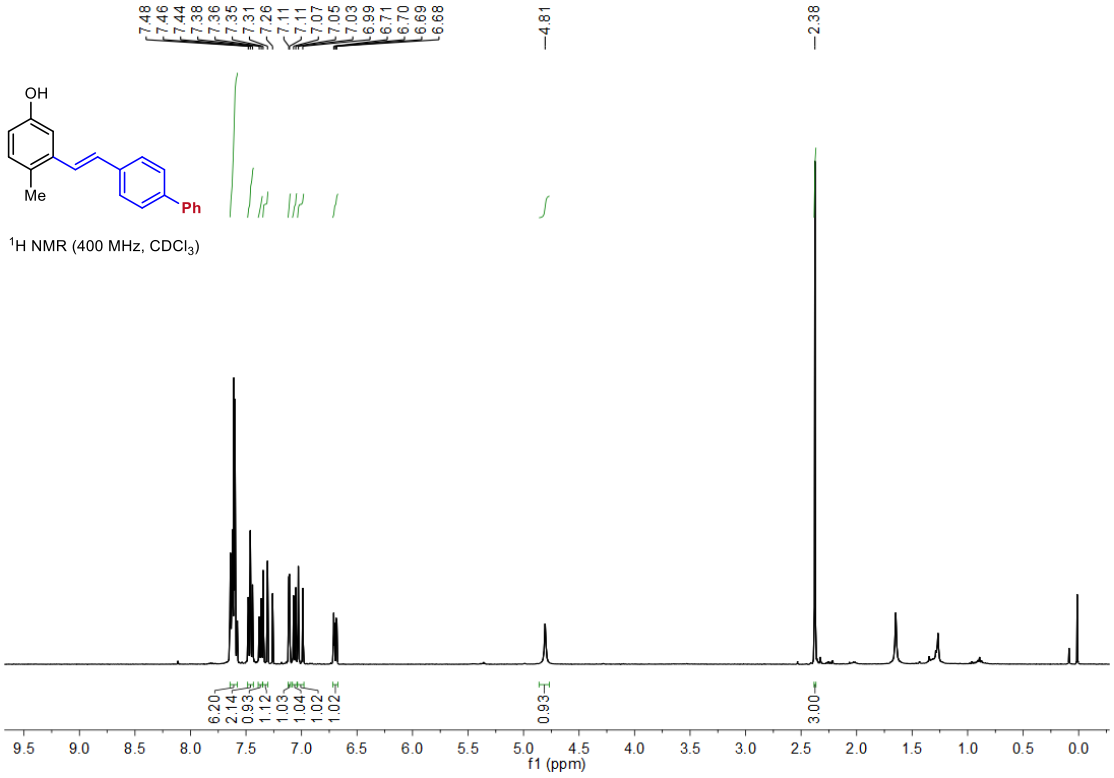
^{13}C NMR (100 MHz, $CDCl_3$)

compound 5i

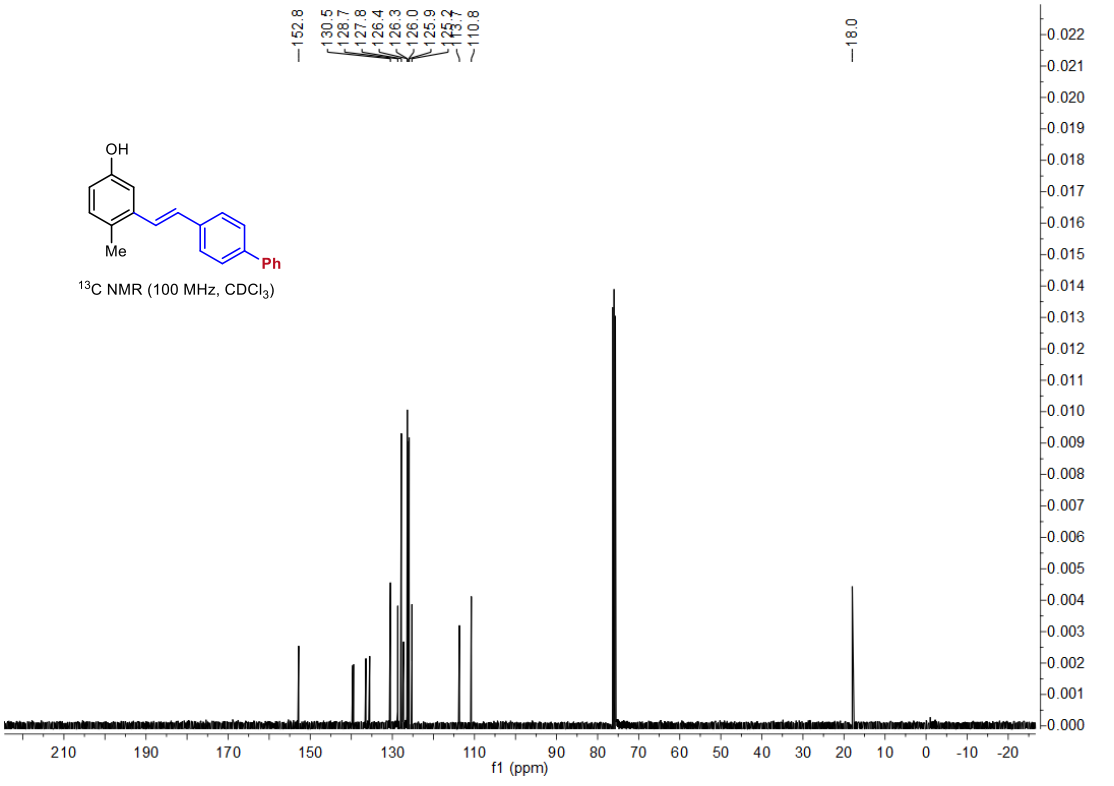

7.50
7.49
7.48
7.47
7.47
7.46
7.38
7.38
7.37
7.36
7.35
7.35
7.27
7.23
7.06
7.05
7.03
6.90
6.86
6.70
6.69
6.68
6.67
4.70
2.34
OH
Me
Br
1H NMR (400 MHz, CDCl3)
1.96
2.04
1.43
1.99
1.04
1.00
1.00
3.08
f1 (ppm)


153.8
137.1
136.4
131.8
131.5
128.9
128.3
128.1
126.9
121.4
114.9
111.8
19.0
OH
Me
Br
13C NMR (100 MHz, CDCl3)
f1 (ppm)

compound 5j

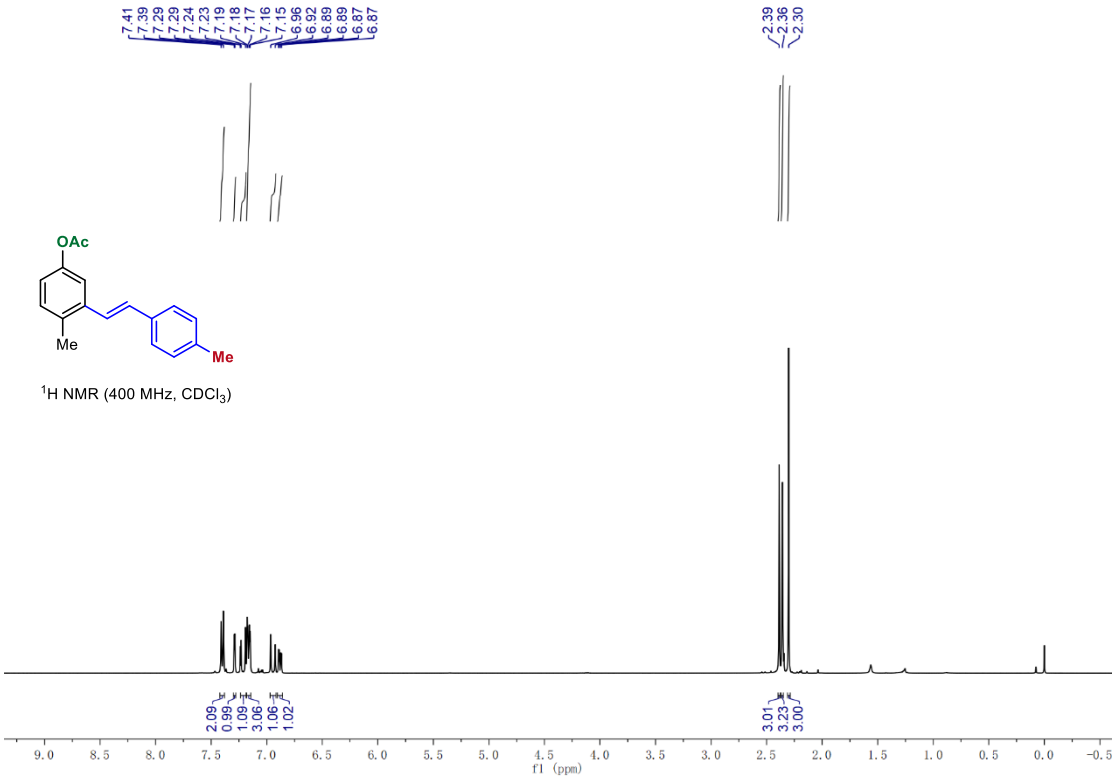


^{1}H NMR (400 MHz, $CDCl_3$)

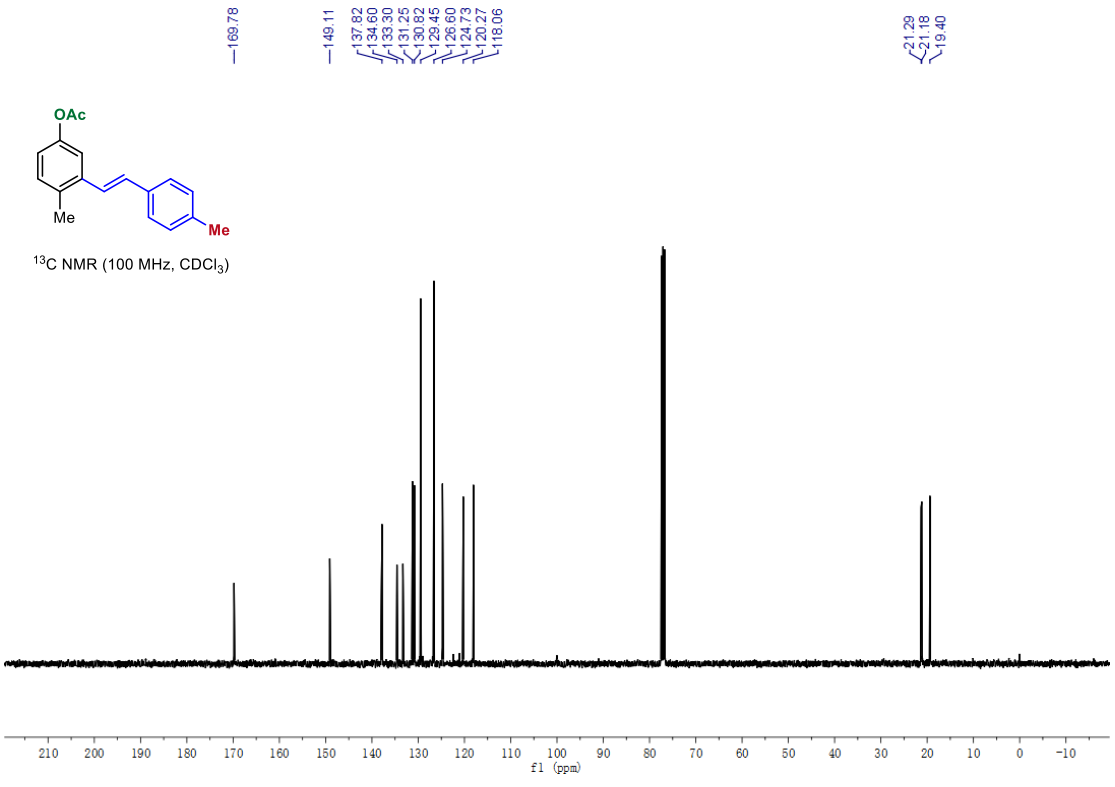


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5k

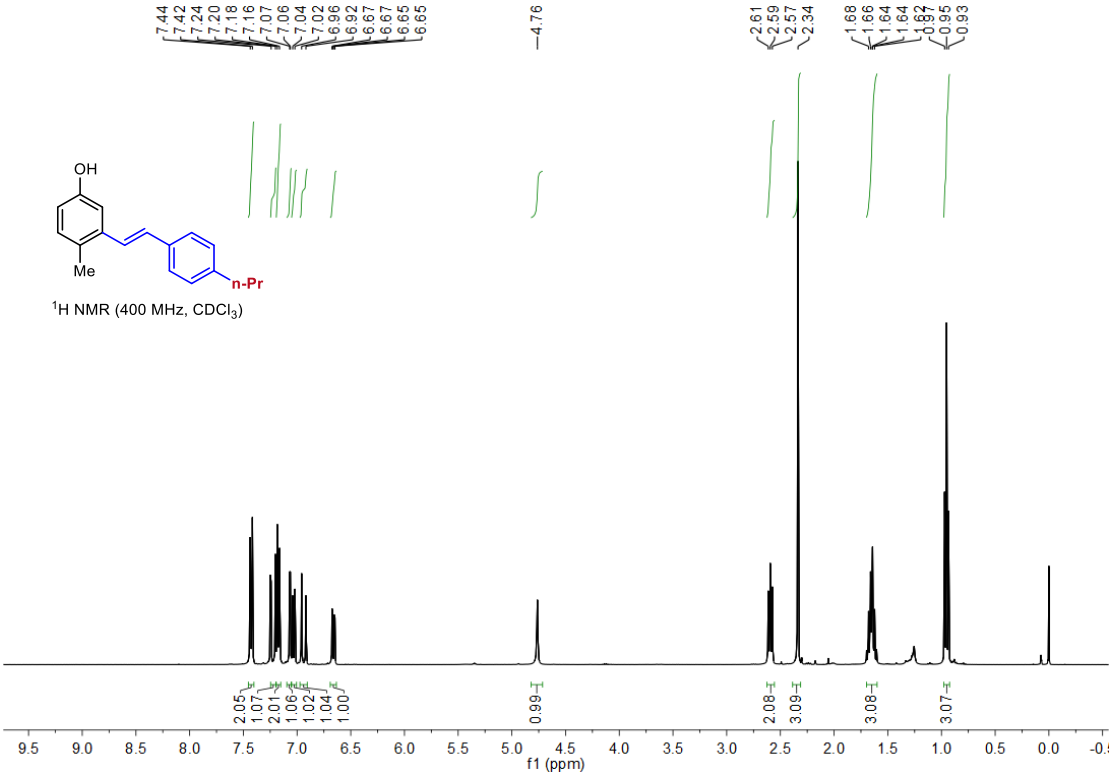


^{1}H NMR (400 MHz, $CDCl_3$)

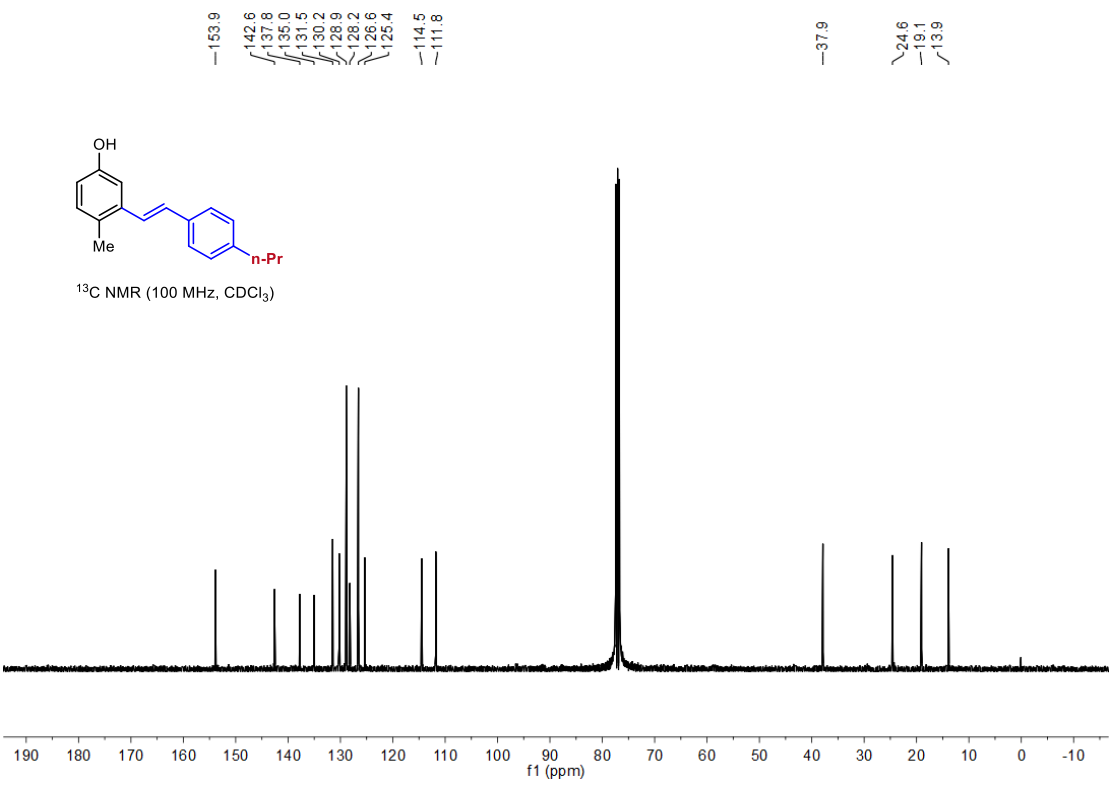


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5l

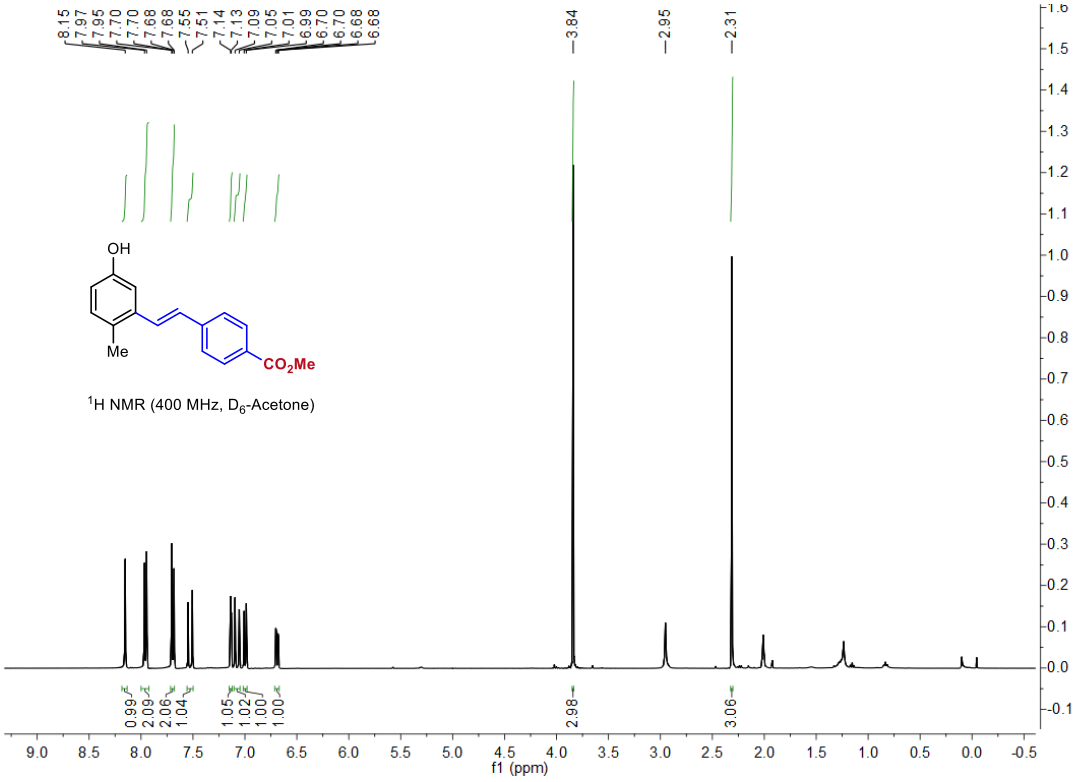


^{1}H NMR (400 MHz, $CDCl_3$)

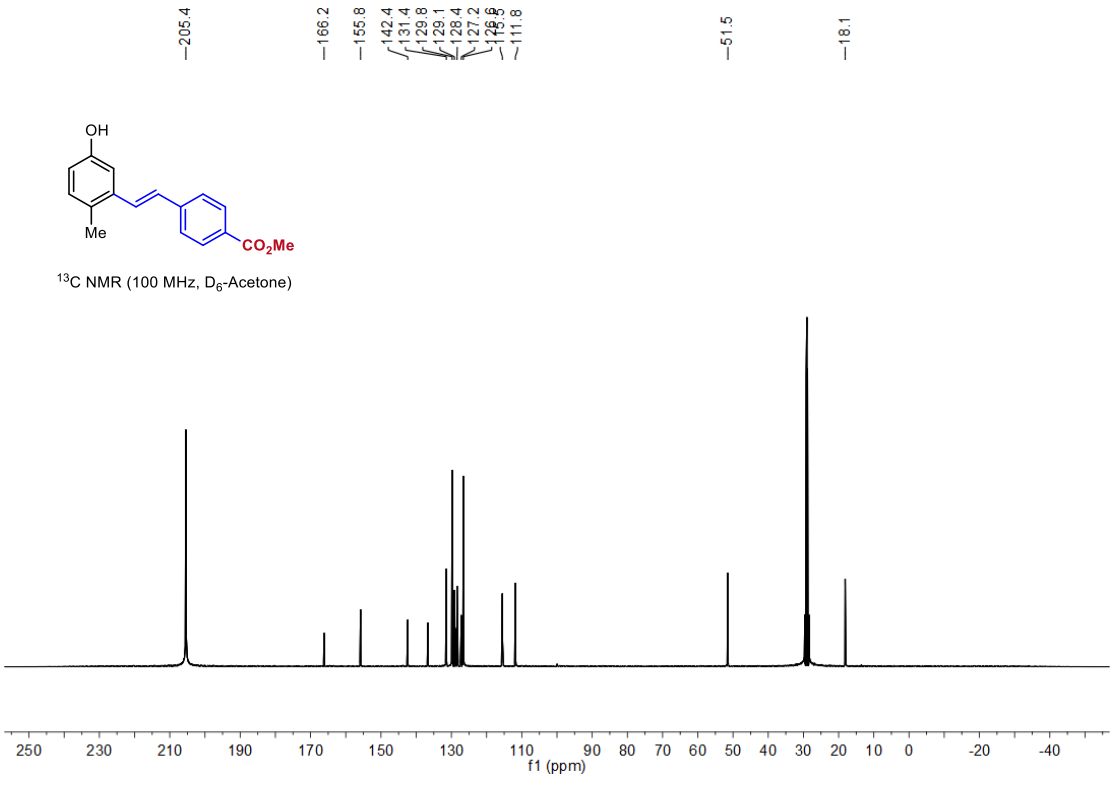


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5m

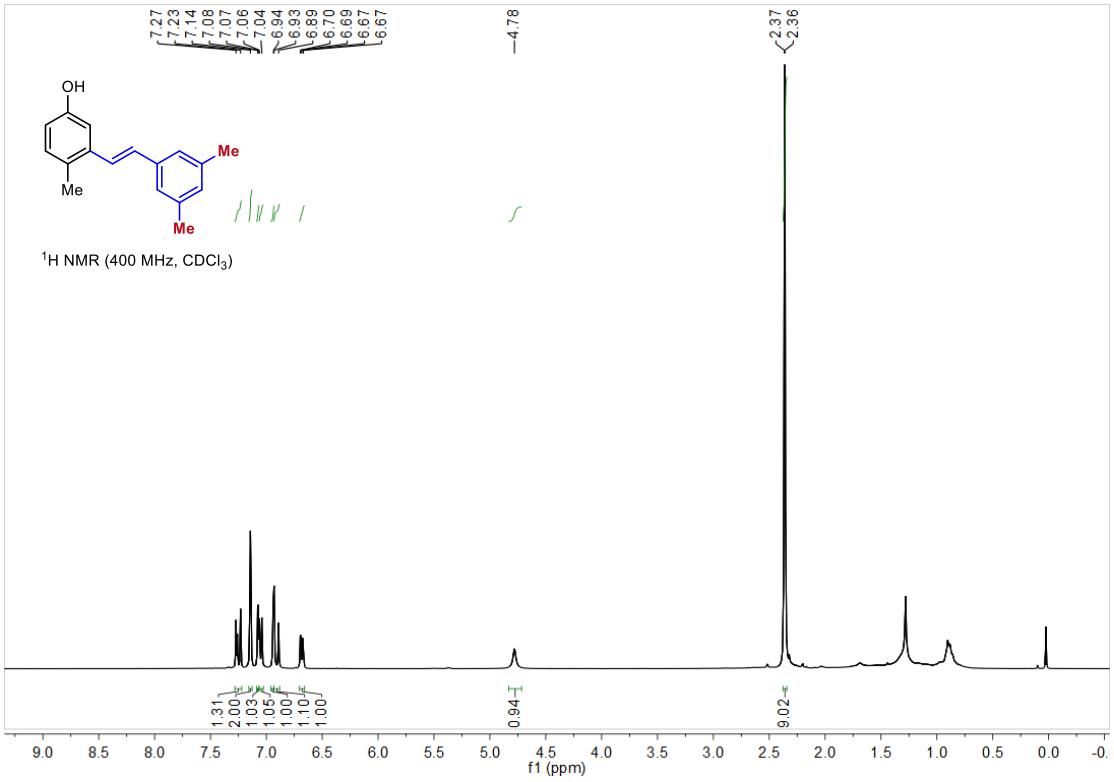


^{1}H NMR (400 MHz, D_6-Acetone)

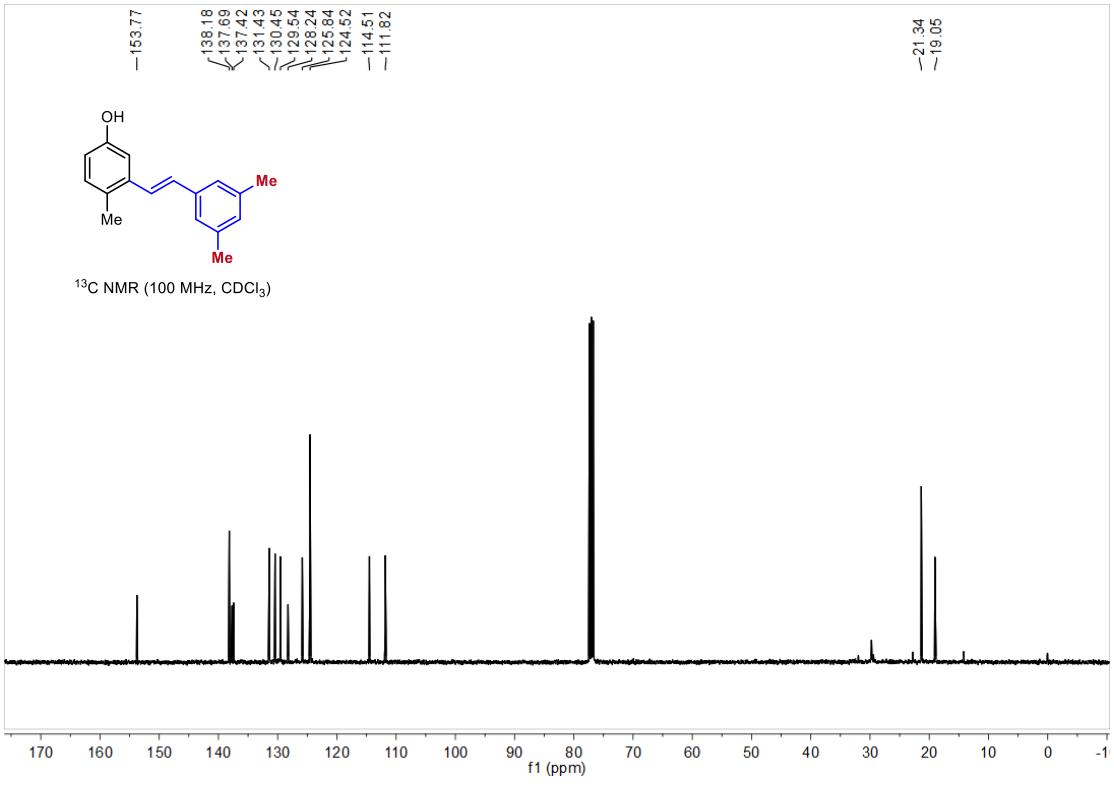


^{13}C NMR (100 MHz, D_6-Acetone)

compound 5n

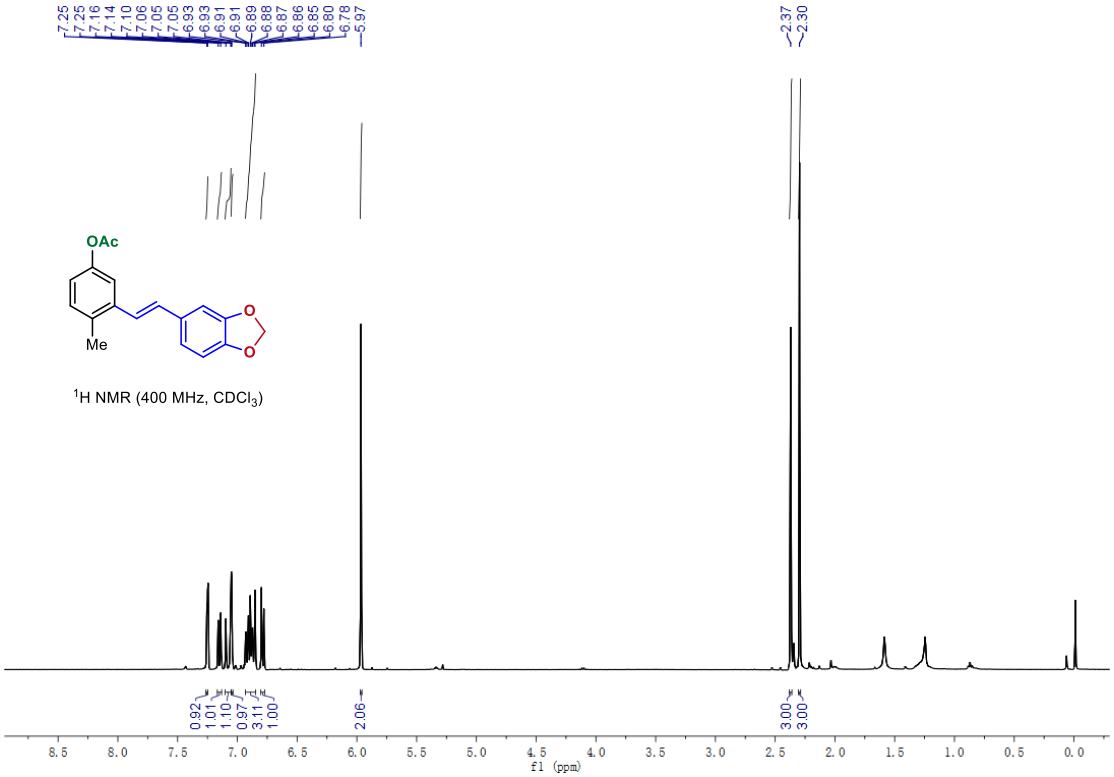


^{1}H NMR (400 MHz, $CDCl_3$)

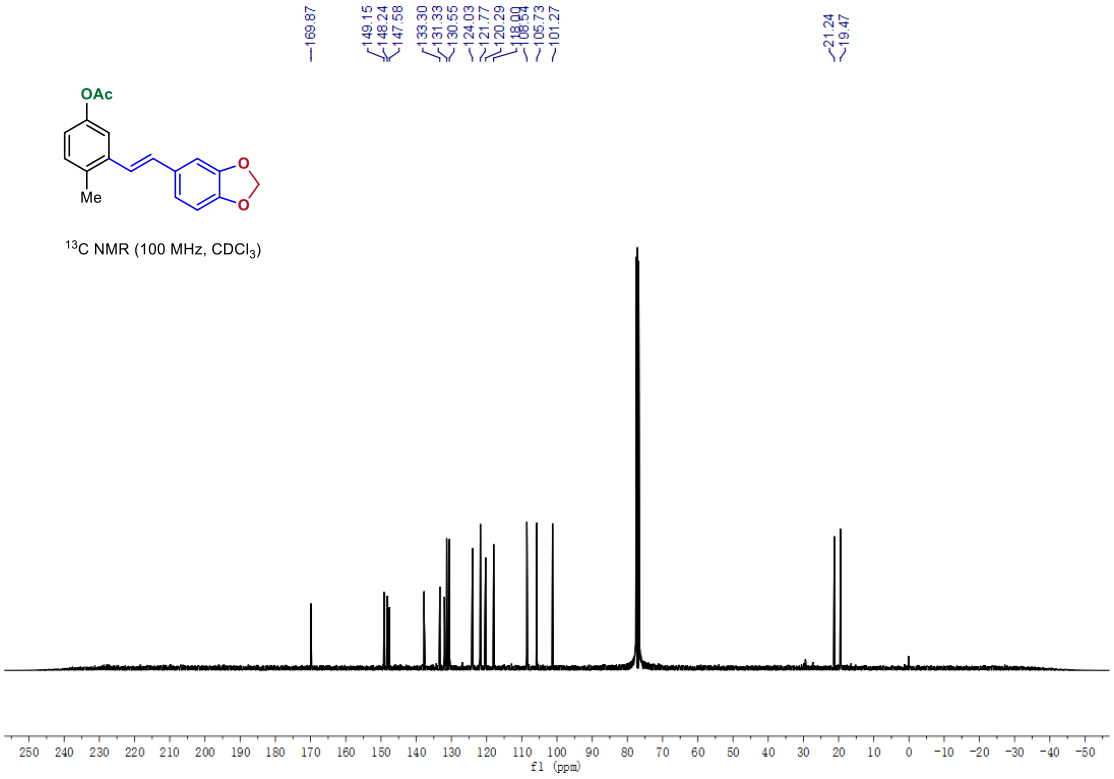


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5o

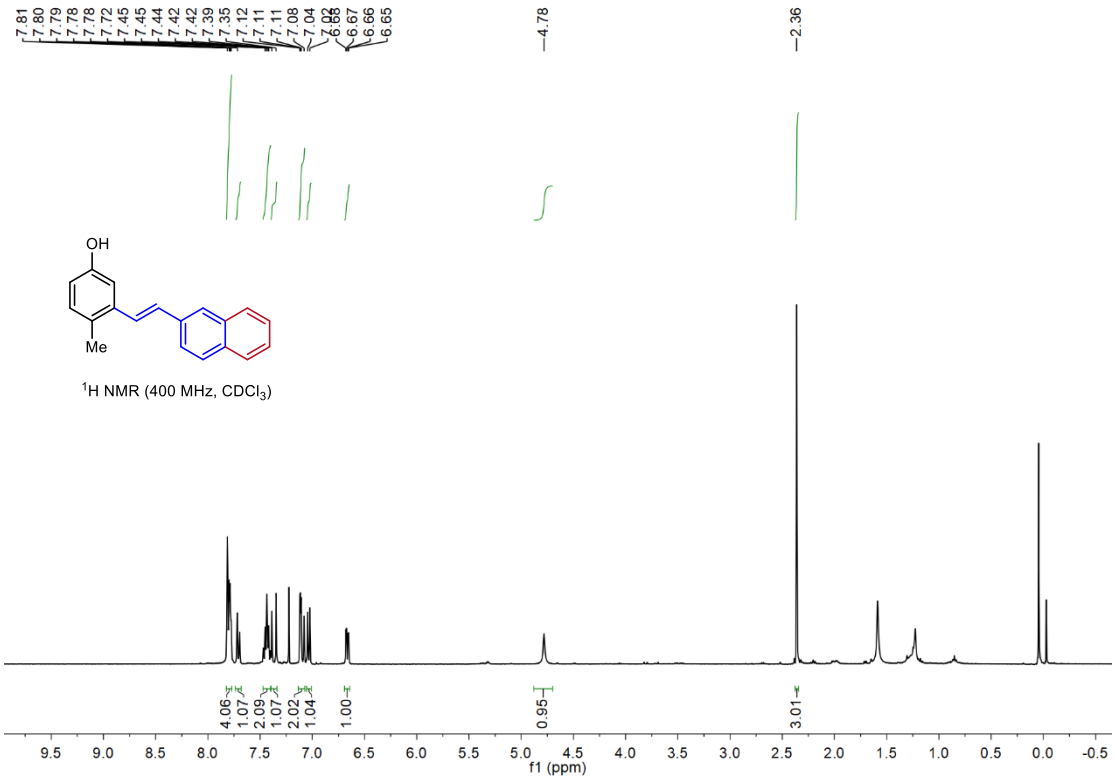


^{1}H NMR (400 MHz, $CDCl_3$)

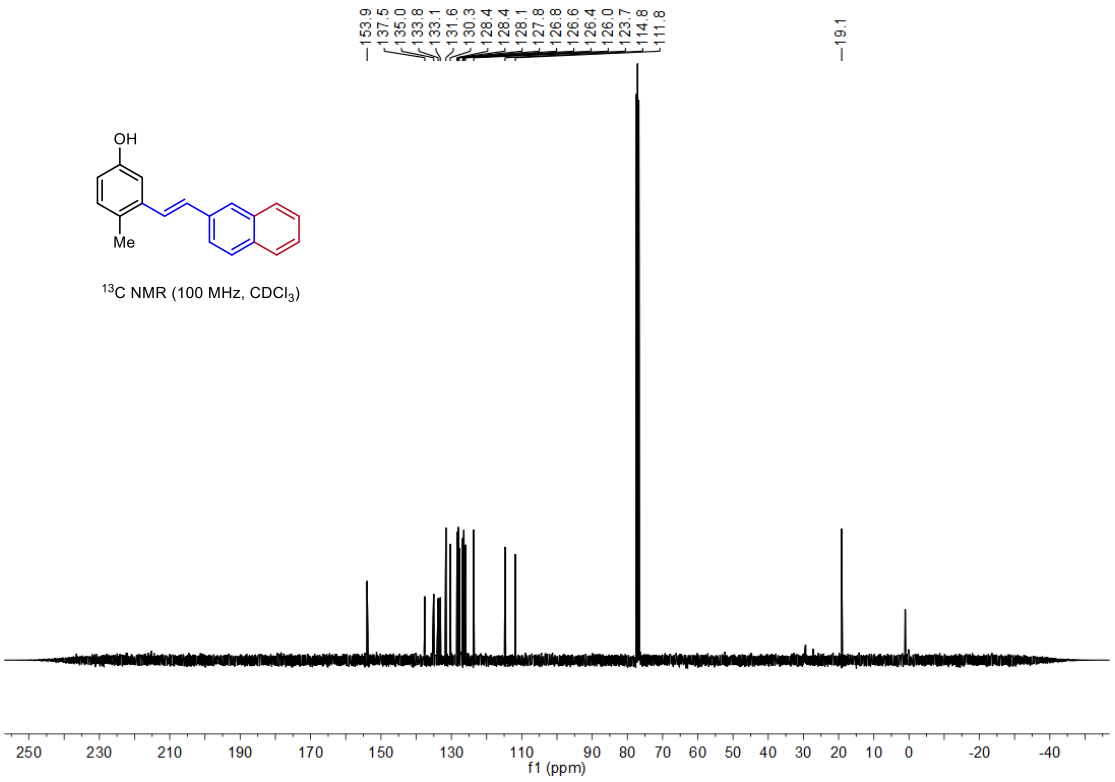


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5p

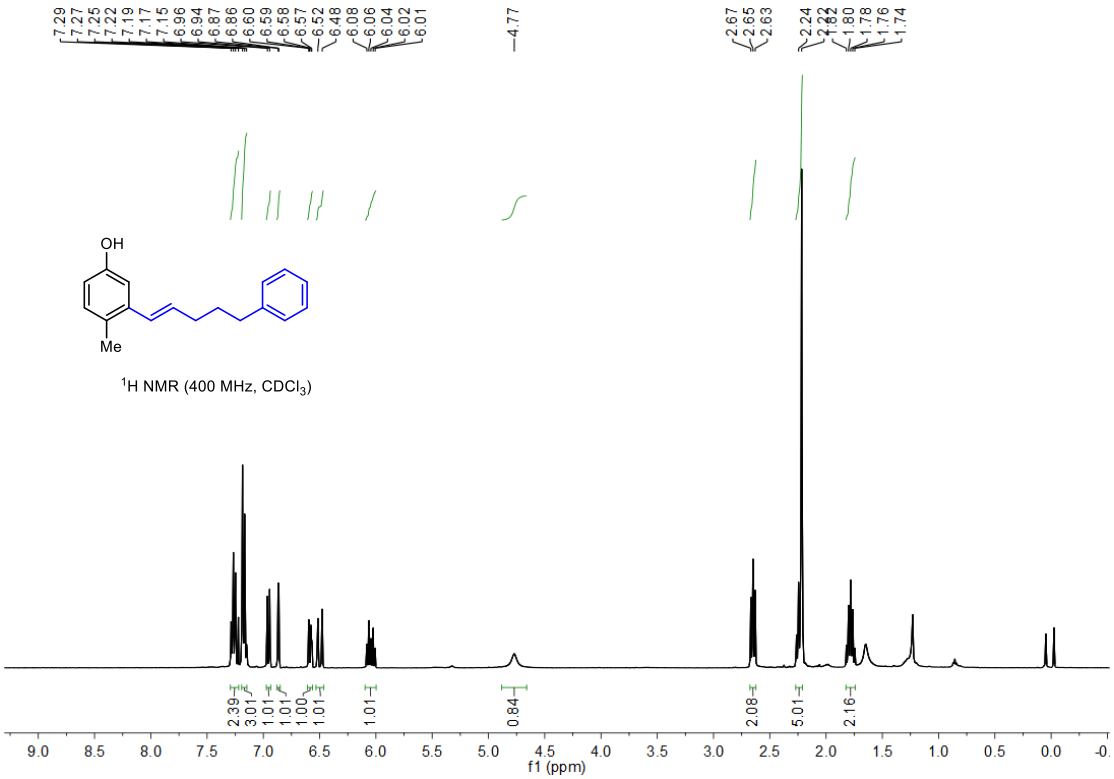


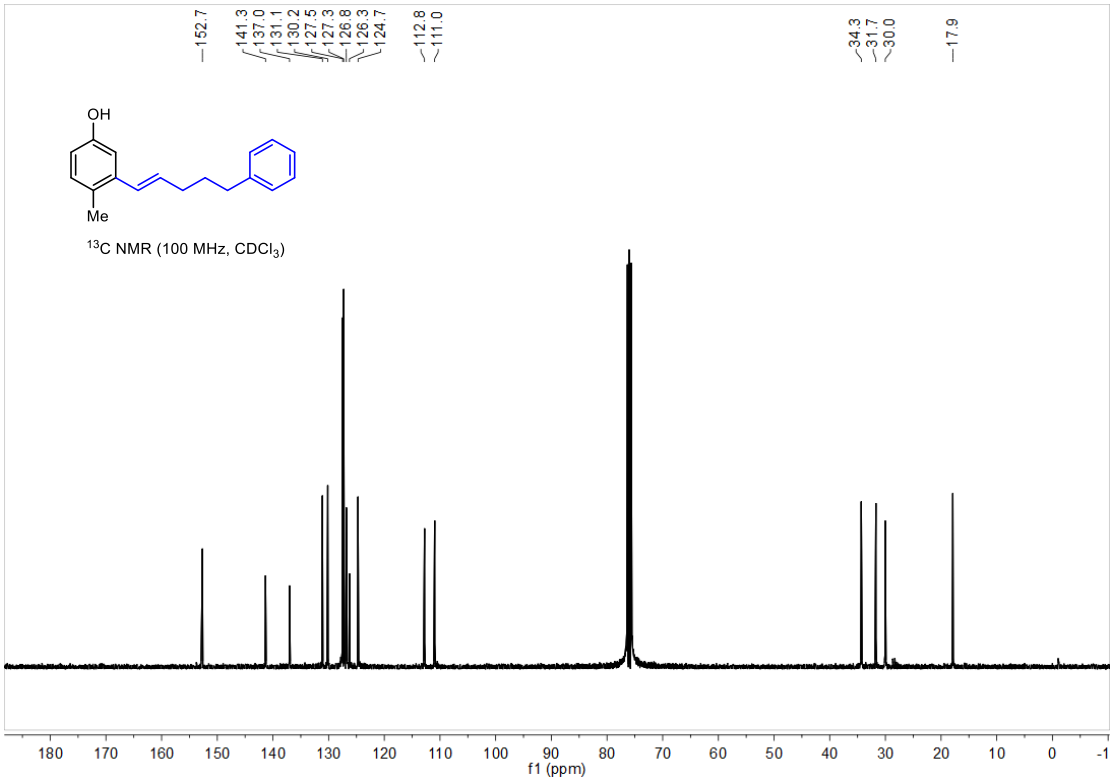
^{1}H NMR (400 MHz, $CDCl_3$)



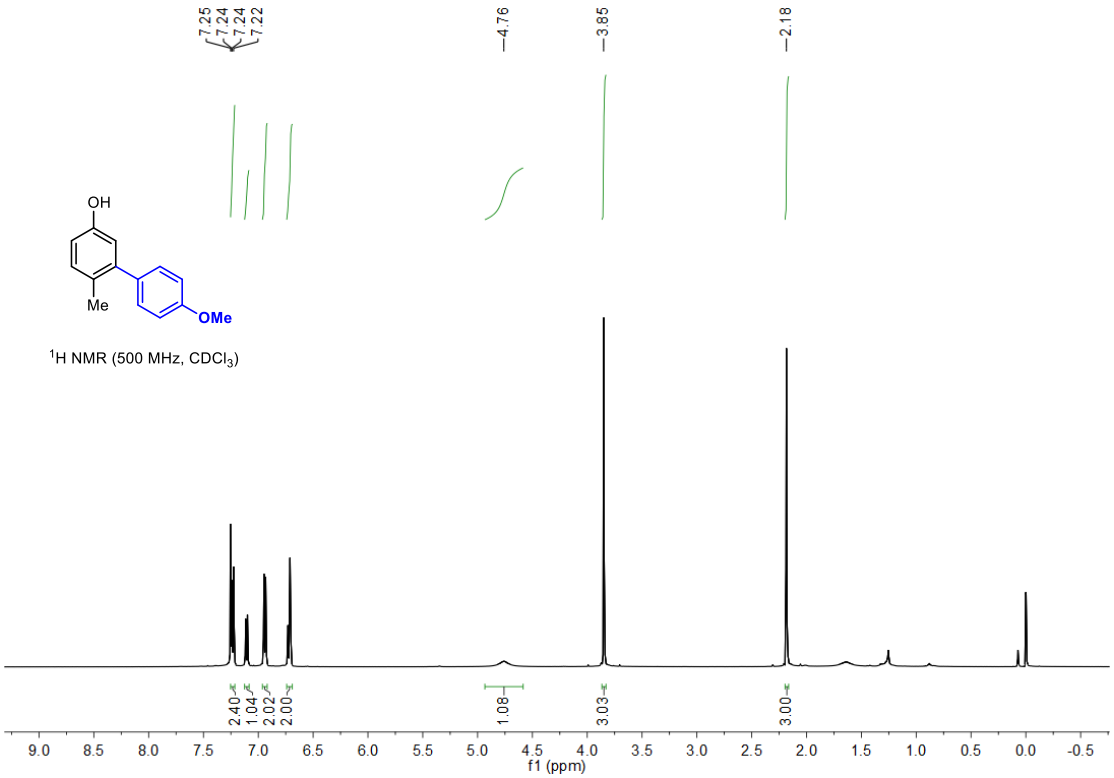
^{13}C NMR (100 MHz, $CDCl_3$)

compound 5q

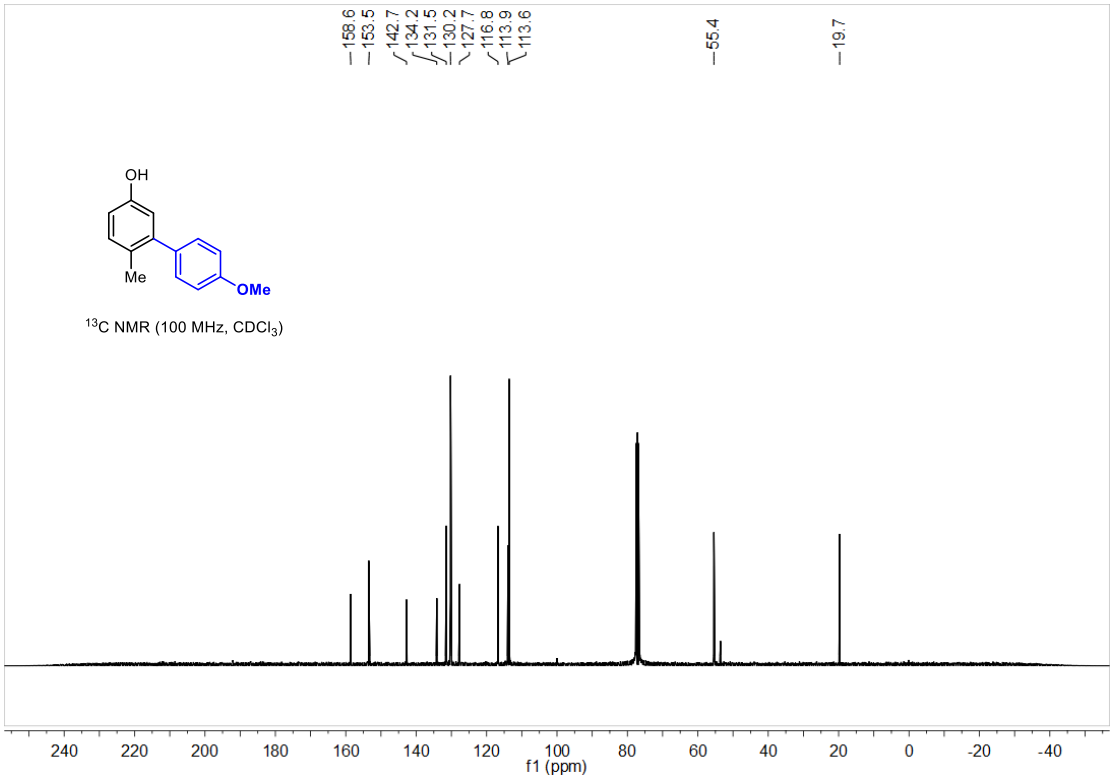

7.29
7.27
7.25
7.22
7.19
7.17
7.15
6.96
6.94
6.87
6.86
6.60
6.59
6.58
6.57
6.52
6.48
6.08
6.06
6.04
6.02
6.01
4.77
2.67
2.65
2.63
2.24
2.22
1.82
1.80
1.78
1.76
1.74
OH
Me
1H NMR (400 MHz, CDCl3)
2.39
3.01
1.01
1.01
1.00
1.01
1.01
0.84
2.08
5.01
2.16
f1 (ppm)


152.7
141.3
137.0
131.1
130.2
127.5
127.3
126.8
126.3
124.7
112.8
111.0
34.3
31.7
30.0
17.9
OH
Me
13C NMR (100 MHz, CDCl3)
f1 (ppm)

compound 5r

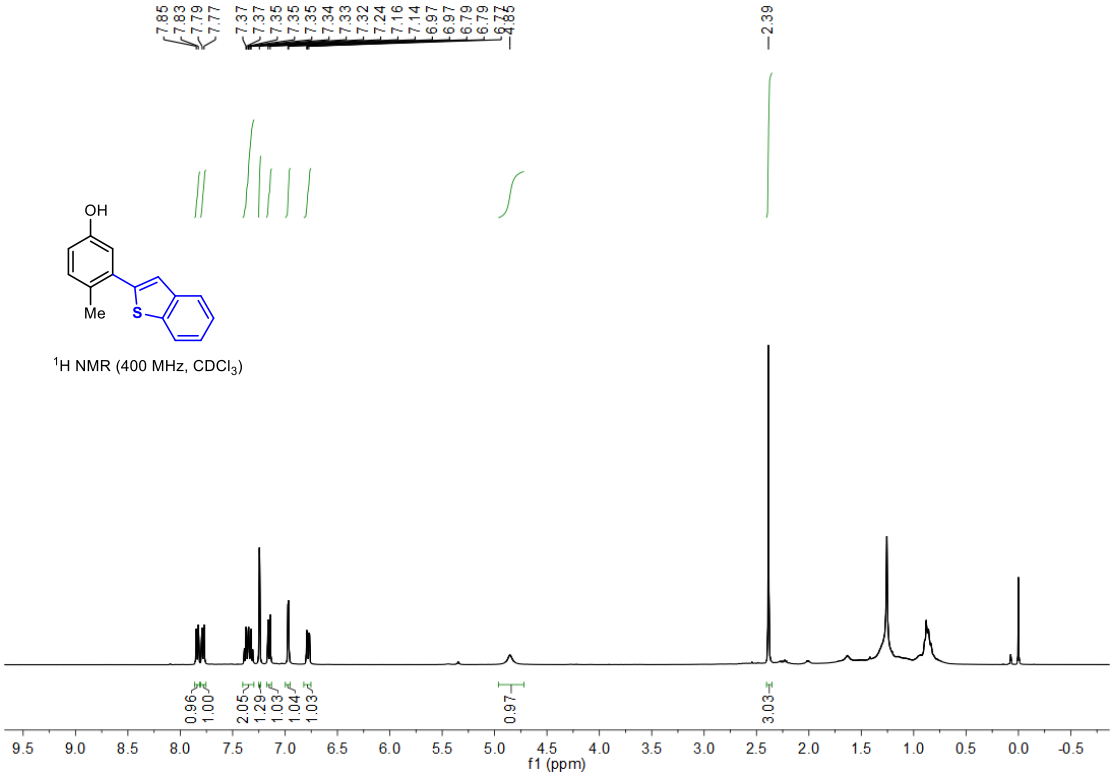


^{1}H NMR (500 MHz, $CDCl_3$)

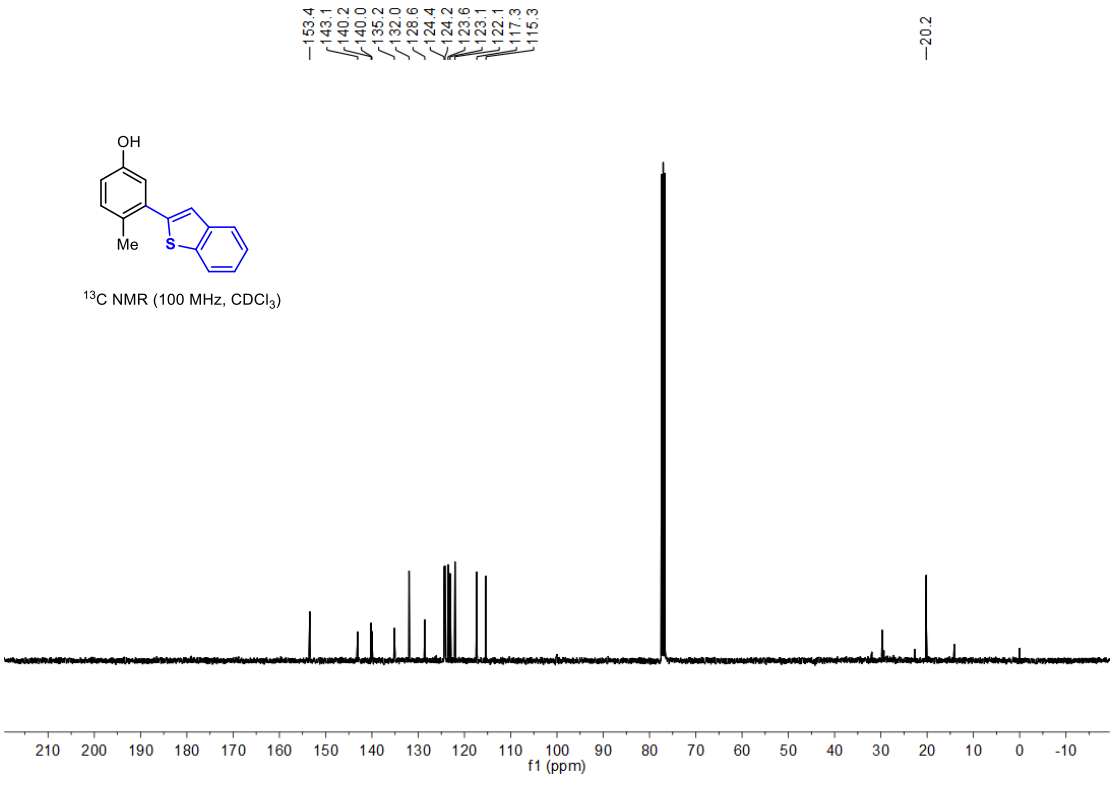


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5s

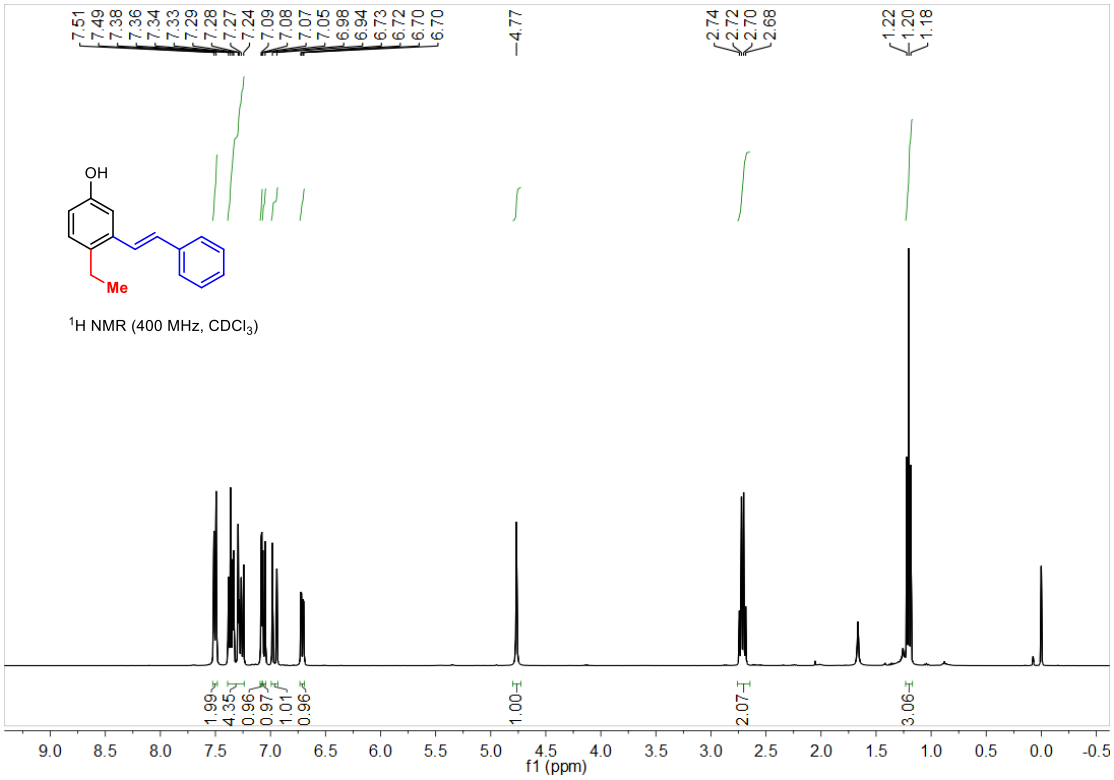


^{1}H NMR (400 MHz, $CDCl_3$)

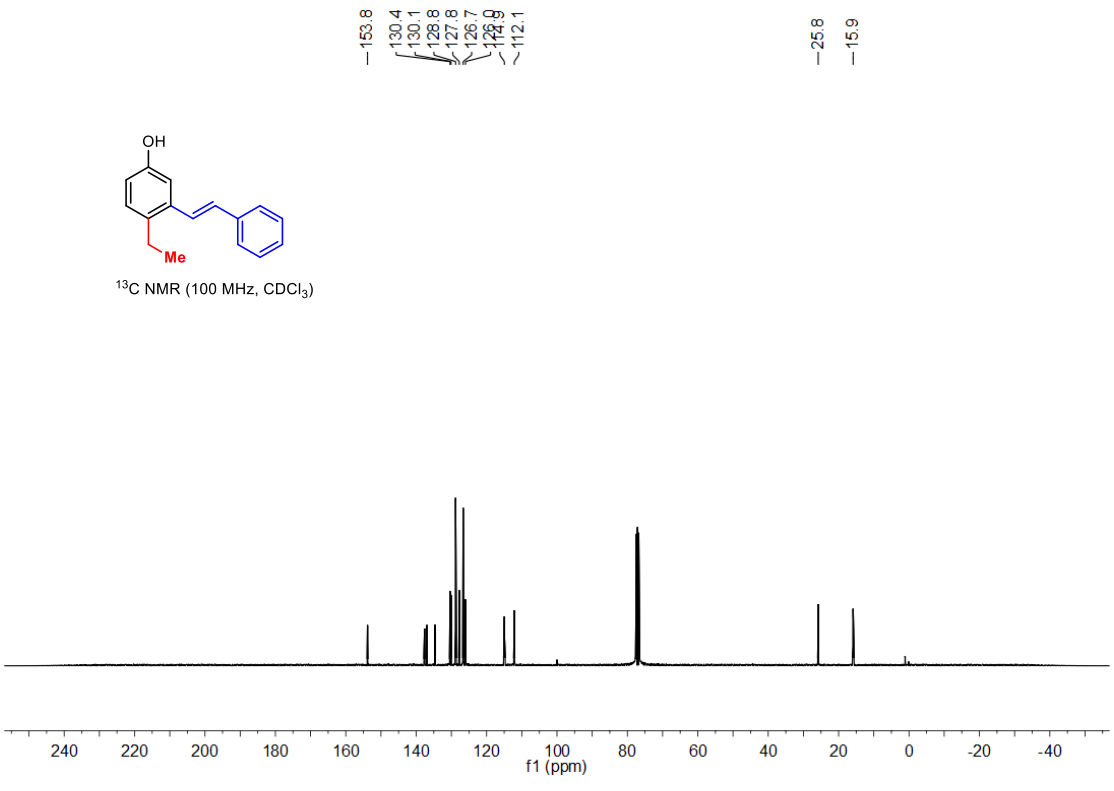


^{13}C NMR (100 MHz, $CDCl_3$)

compound 5t

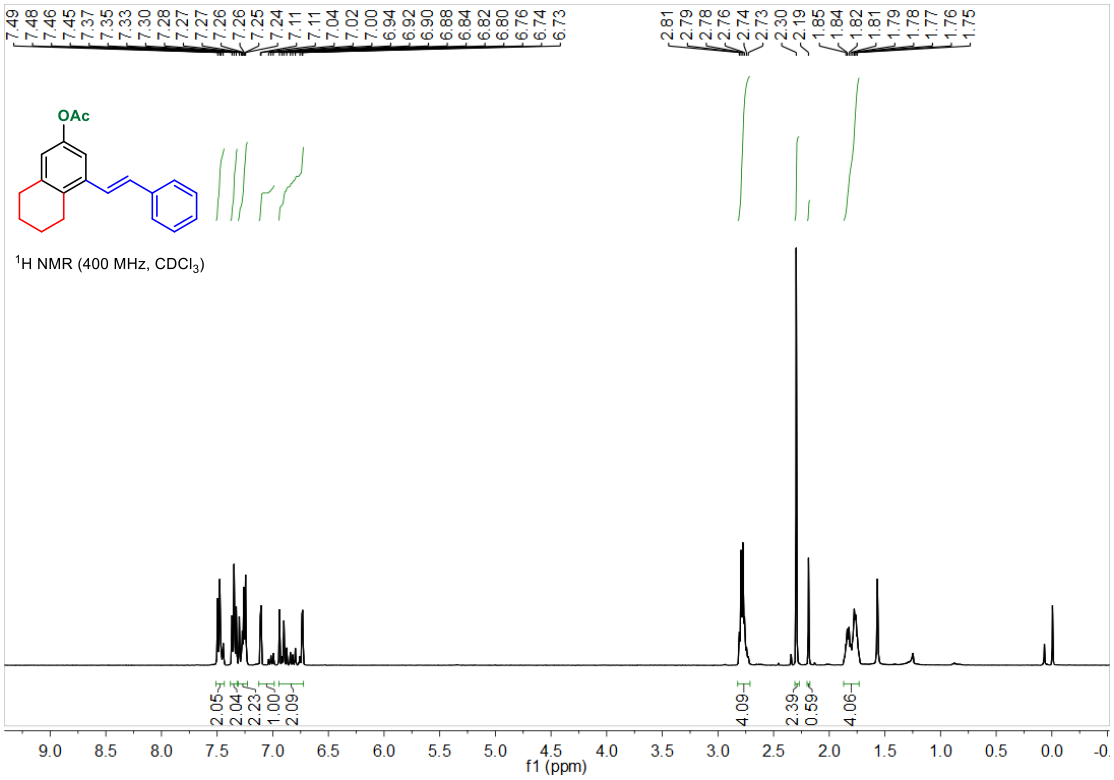


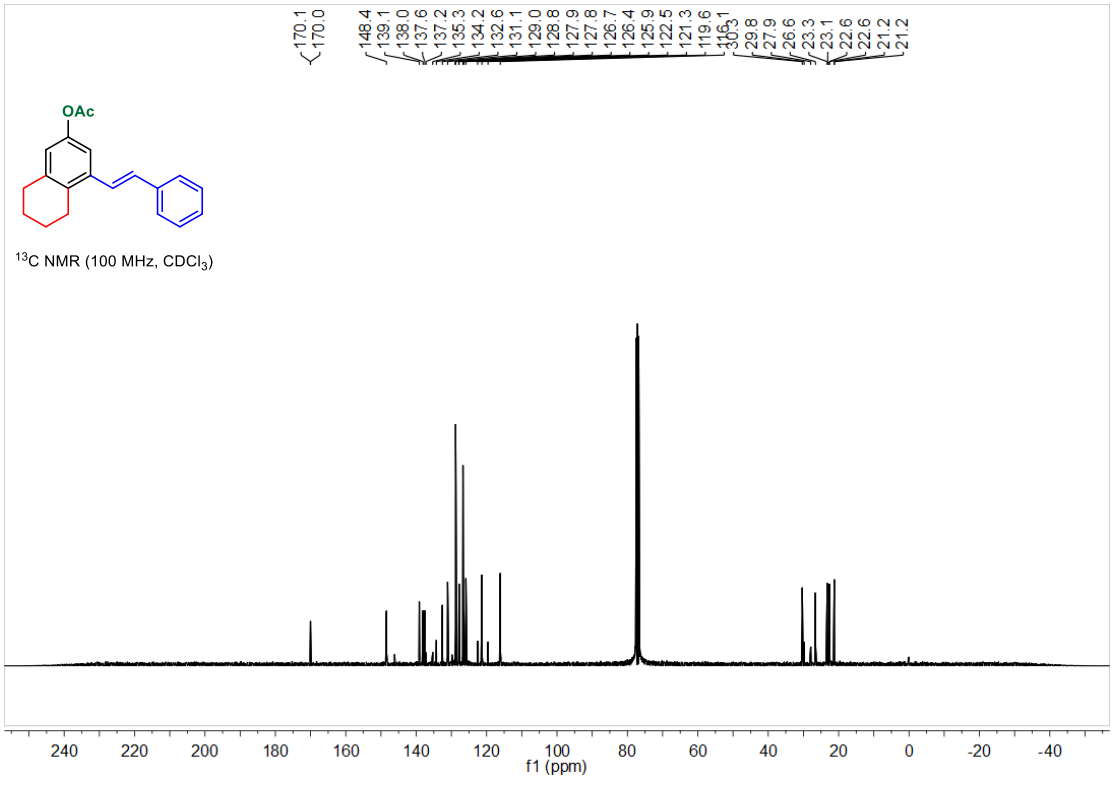
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

compound 5u





compound 1aa