Electronic Supplementary Material (ESI) for ChemComm.

Dual Nickel- and Photoredox-Catalyzed Reductive Cross-coupling of Aryl Vinyl Halides and Unactivated Tertiary Alkyl Bromides

Weijie Yu[a], Long Chen[a], Jiasi Tao[a], Tao Wang,*[a] and Junkai Fu*[b,c]

[a] National Research Center for Carbohydrate Synthesis and Key Laboratory of Chemical Biology, Jiangxi Normal University, Nanchang 330022, Jiangxi, P. R. China

[b] Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Department of Chemistry, Northeast Normal University, Changchun 130024, China

[c] Key Laboratory of Chemical Genomics, School of Chemical Biology and Biotechnology, Peking University Shenzhen Graduate School, Shenzhen 518055, China

Content

Part 1: General information

Unless otherwise noted, all reagents were purchased from commercial suppliers without further purification. Bis(2,2,6,6-tetramethyl-3,5-heptanedio)nickel(II) [$Ni(TMHD)_2$] was purchased from Alfa Aesar. *N*,*N*-dimethylaniline, 1,3-dimethylimidazol-1-ium iodide, magnesium chloride ($MgCl_2$) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were purchased from *J&K* or Aladdin. $[Ir(dF(CF_3)ppy]_2(dtbbpy)PF_6$ was synthesized according to the previous literature (*Chem. Mater*. **2005**, *17*, 5712-5719).

All the reactions were monitored by thin-layer chromatography (TLC).

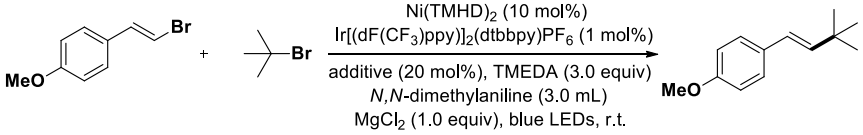
NMR spectra were recorded on a Brüker Advance 400 (^1H: 400 MHz, ^{13}C:100 MHz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and chloroform at δ 77.16 (77.84, 77.16, 76.48) ppm, respectively.

Unless otherwise indicated, mass spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry.

Melting points were determined on an X-4 digital display microscope apparatus.

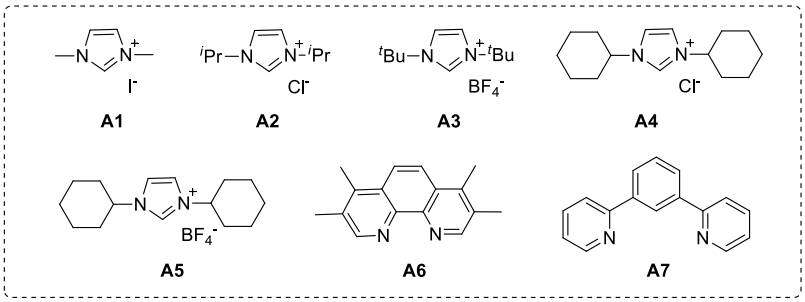
Part 2. Supplementary Data

Table S1. Investigation of different additives



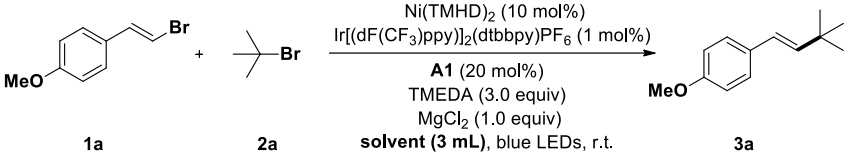
1a **2a** **3a**

Entry	additive (mol%)	Yield/% (E/Z)
1	**A1** (20)	73 (>20:1)
2	**A2** (20)	23 (>20:1)
3	**A3** (20)	11 (>20:1)
4	**A4** (20)	24 (>20:1)
5	**A5** (20)	17 (>20:1)
6	**A6** (20)	30 (>20:1)
7	**A7** (20)	43 (>20:1)
8	dtbbpy (20)	25 (>20:1)
9	1,10-phen (20)	12 (>20:1)



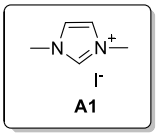
A1 **A2** **A3** **A4** **A5** **A6** **A7**

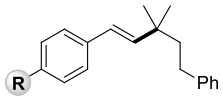
Table S2. Investigation of different solvents



1a 2a 3a

Entry	Solvent	Yield/% (E/Z)
1	*N,N*-Dimethylaniline	73 (>20:1)
2	CH_3CN	55 (>20:1)
3	DME	40 (>20:1)
4	DCE	15 (1:2)
5	THF	24 (>20:1)
6	DMF	trace
7	DMSO	trace

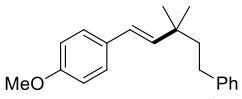




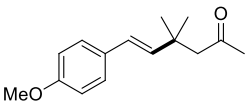
R= H, **3b**, 73%[a] (62%)[b]

R= CF_3, **3i,** 60%[a] (51%)[b]

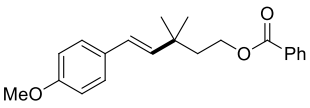
R= COOMe, **3j,** 60%[a] (51%)[b]



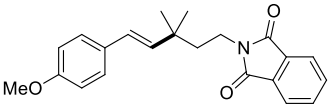
4c, 68%[a] (52%)[b]



4d, 67%[a] (60%)[b]



4e, 61%[b]

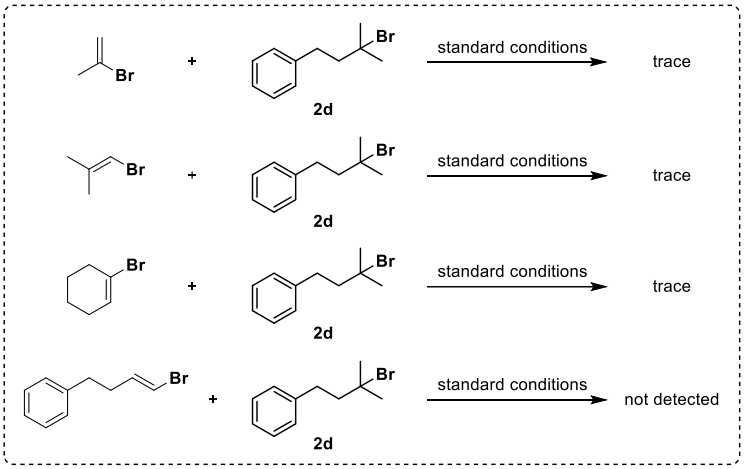


4f, 56%[b]

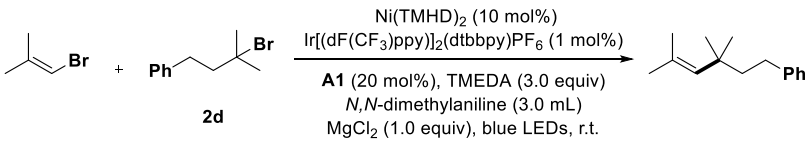
[a]*N,N*-Dimethylaniline as solvent, [b]CH_3CN as solvent.

Table S3. Several unsuccessful examples with non-conjugated vinyl bromides and the details for the related reaction conditions screening.

A series of non-conjugated vinyl bromides, such as 2-bromoprop-1-ene, 1-bromo-2-methylprop-1-ene, 1-bromocyclohex-1-ene and (*E*)-(4-bromobut-3-en-1-yl)benzene were tested under the standard conditions. However, the desired products were either obtained in only trace amount or not detected at all.



What's more, by using 1-bromo-2-methylprop-1-ene as the model compound, we have tried several different reaction conditions (see below).



Entry	variation of standard conditions	Yield/%
1	none	trace
2	$NiBr_2$ instead of $Ni(TMHD)_2$	trace
3	$Ni(cod)_2$ instead of $Ni(TMHD)_2$	n.d.
4	CH_3CN instead of *N,N*-dimethylaniline	trace
5	40 °C instead of room temperature	n.d.

The light off/on experiments has been done (Figure 1). It was observed that the transformation progressed smoothly under irradiation with visible-light, but no further conversion was observed when the light source was removed. This result showed that the continuous irradiation of visible light is indispensable and also indicated that the reaction proceeds through a photoredox catalytic pathway rather than radical chain propagation.

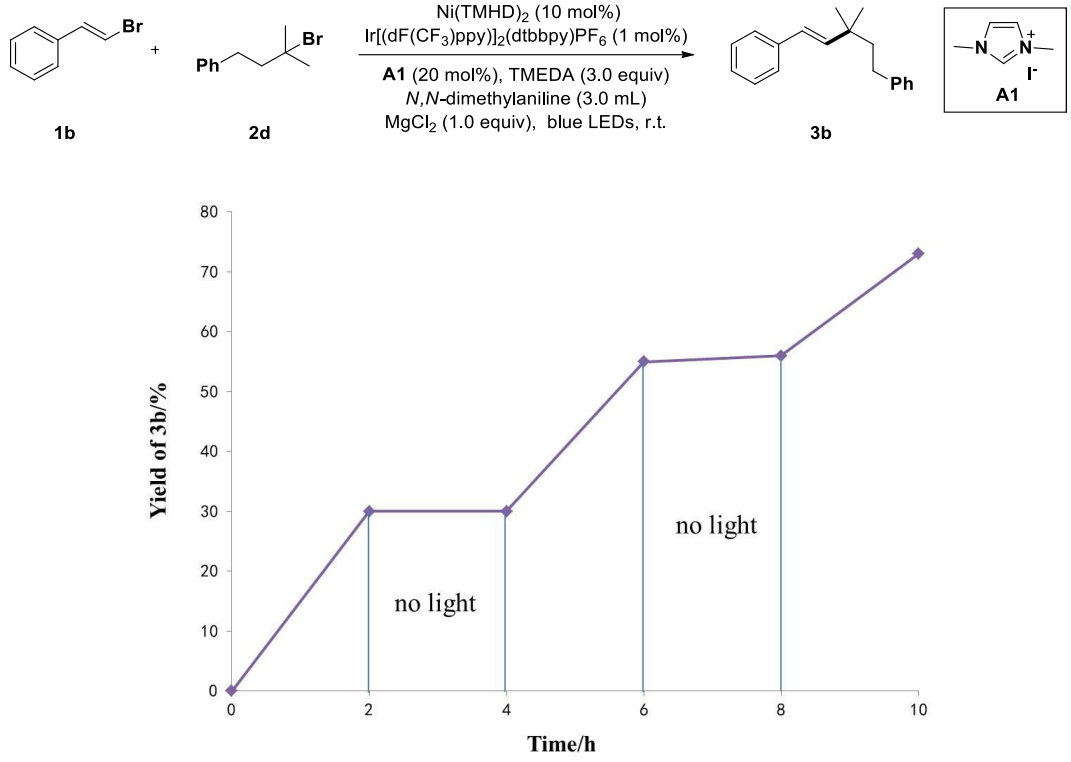


Figure 1. Profile of the reaction with the light off/on over time (the yield of **3b** was determined by GC analysis)

In addition, emission quenching experiments were recorded using a HITACHI F-4500 Fluorescence Spectrometer. $Ir[(dF(CF_3)ppy)]_2(dtbbpy)PF_6$ solutions were excited at 380 nm and the emission intensity at 470 nm was observed. All experiments were performed under argon atmosphere with a gas-tight quartz cuvette containing 2.0 mL of iridium catalyst solution at room temperature, a 5×10^{-5} M solution of $Ir[(dF(CF_3)ppy)]_2(dtbbpy)PF_6$ in CH_3CN was collected. Then appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. As shown in Figure 2 and 3, the experiments revealed that both $Ni(TMHD)_2$ and TMEDA could quench the excited state of $Ir[(dF(CF_3)ppy)]_2(dtbbpy)PF_6$.

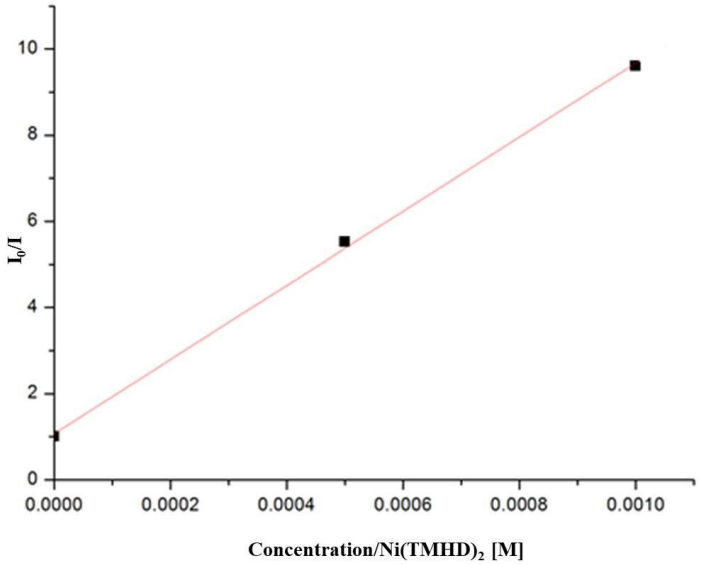


Figure 2. $Ir[(dF(CF_3)ppy)]_2(dtbbpy)PF_6$ emission quenching by $Ni(TMHD)_2$

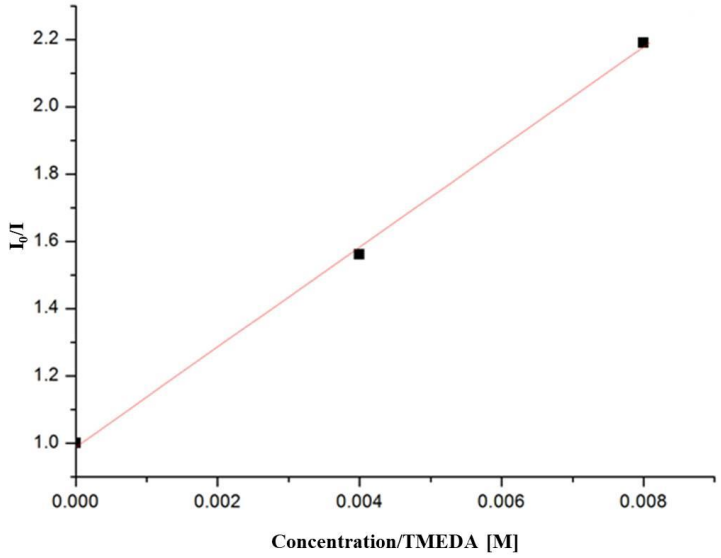
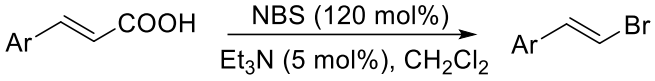


Figure 3. $Ir[(dF(CF_3)ppy)]_2(dtbbpy)PF_6$ emission quenching by TMEDA

Part 3. Preparation of substrates

3.1 Preparation of vinyl bromides

General procedure A for the preparation of vinyl bromides

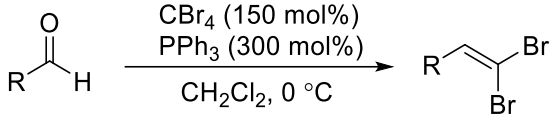


To a solution of cinnamic acid (20 mmol, 1.0 equiv) in CH_2Cl_2 (80 mL) was added NEt_3 (0.5 mmol, 5 mol %). The mixture was stirred for 5 min at room temperature, then NBS (24 mmol, 1.2 equiv) was added in small portions. Reactions were monitored by thin-layer chromatography indicating the completion. Solvent was evaporated under reduced pressure and the remaining slush was purified by flash chromatography on silica gel (petroleum ether:ethyl acetate = 100:1).

Compounds **1a** and **1e** were synthesized following the general procedure A, and analytical data were in agreement with ref. 1 and 2, respectively.

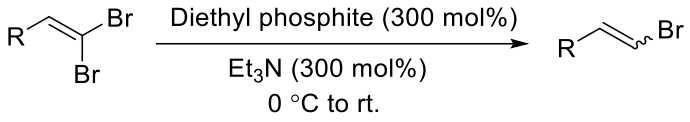
General procedure B for the preparation of vinyl bromides

Step 1: The Ramirez protocol for the Wittig-type dibromoolefination.[3]



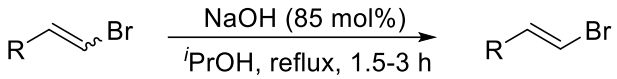
To a dry flask was added aldehyde (20 mmol, 1.0 equiv), CBr_4 (30 mmol, 1.5 equiv) and CH_2Cl_2 (80 mL). The mixture was cooled to 0 °C, and then a solution of PPh_3 (60 mmol, 3.0 equiv) in CH_2Cl_2 (70 mL) was added dropwise *via* dropping funnel over 30 min under N_2 atmosphere. The reaction mixture was stirred at 0 °C for 1.0 h, and then the solvent was evaporated under reduced pressure. When half of the volume of CH_2Cl_2 was removed, pentane (100 mL) was added, and triphenylphosphine oxide (TPPO) was precipitated out. The solution was filtrated, and the filtrate was concentrated *in vacuo*. Pentane (50 mL) was added to the residue, and TPPO was precipitated out again. Filtration and evaporation of the solvent afforded the crude dibromide, which was directly used for the next step.

Step 2: Hayes protocol of the Hirao reaction.[4]



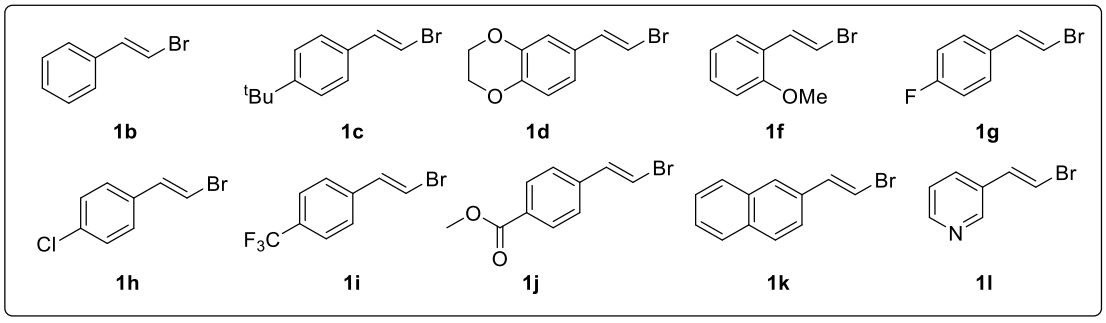
To a dry flask was added the crude dibromide (~ 20 mmol, 1.0 equiv), NEt_3 (60 mmol, 3.0 equiv) and DMF (20 mL). The mixture was cooled down to 0 °C, and diethylphosphonate (60 mmol, 3.0 equiv) was added slowly *via* a syringe. The mixture was stirred overnight at room temperature. Water (60 mL) was added into the reaction, and the mixture was extracted with pentane (2 × 100 mL). The combined organic phases were washed with an aqueous solution of HCl (1.0 M, 55 mL), dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography (petroleum ether:ethyl acetate = 100:1).

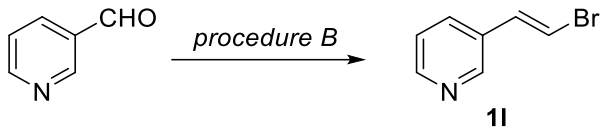
Step 3: Selective destruction of the (*Z*)-isomer as reported by Dolby.[5]



The crude product (~ 20 mmol, 1.0 equiv) from step 2 was dissolved in *i*-PrOH (30 mL), then NaOH (17 mmol, 0.85 equiv) was added. The reaction mixture was heated to reflux for 1.5~3 h, and then cooled to room temperature, diluted with pentane (100 mL), and partitioned with distillated H_2O (2 × 100 mL). The organic phase was collected, and washed with an aqueous solution of HCl (1.0 M, 75 mL), dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (petroleum ether:ethyl acetate = 100:1).

Compounds **1b**, **1c**, **1d**, **1f**, **1g**, **1h**, **1i**, and **1k** were synthesized from aldehyde according to the general procedure B. **1b** is a known compound according to ref. 1; **1c** is a known compound according to ref. 6; **1d** is a known compound according to ref. 7; **1f** is a known compound according to ref. 8; **1g** is a known compound according to ref. 9; **1h, 1i**, **1j** and **1k** are known compounds according to ref. 10.

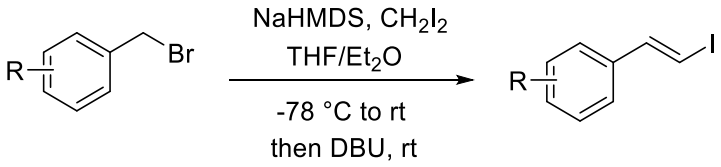




1l

(*E*)-3-(2-bromovinyl)pyridine (**1l**) was synthesized from aldehyde according to the general procedure B as yellow oil in 28% yield (512 mg, 2.8 mmol, prepared from 10 mmol scale of 3-pyridinecarboxaldehyde). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.53 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 7.2, 4.4 Hz, 1H), 7.10 (d, *J* = 14.0 Hz, 1H), 6.88 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 147.8, 133.9, 132.7, 131.8, 123.7, 108.9. FTIR (thin film): 3062, 2941, 1611, 1563, 1491, 1302, 1285, 1260, 1237, 1025, 947, 838 cm^{-1}. HRMS (ESI) m/z calcd for C_7H_7BrN $[M+H]^+$: 183.9762; found: 183.9756.

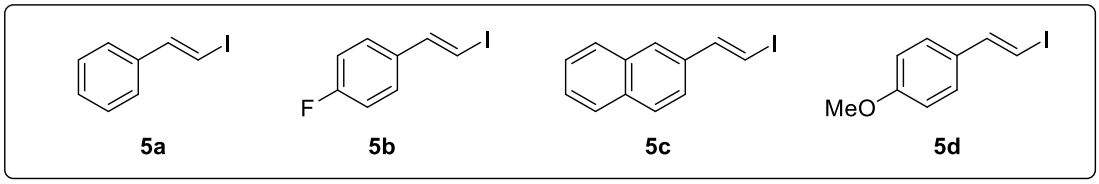
3.2 Preparation of vinyl iodides



General procedure C

A solution of CH_2I_2 (0.48 mL, 6.0 mmol, 1.5 equiv) in THF (1.5 mL) was added dropwise into the solution of NaHMDS (6.0 mL, 12.0 mmol, 3.0 equiv, 2.0 M in THF) in THF/ether (8.0 mL/8.0 mL) at –78 °C in dark. The mixture was stirred for 20 min, then a solution of benzyl bromide substrate (4.0 mmol, 1.0 equiv) in THF (3.0 mL) was added dropwise. The reaction was stirred at –78 °C for 90 min and then warmed up to room temperature. The mixture was stirred for another 30 min, and DBU (597 μL, 4.0 mmol, 1.0 equiv) was added dropwise. After being stirred for 1 h, ether (50 mL) was added, and the reaction mixture was filtered through a pad of celite. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography (petroleum ether:ethyl acetate = 100:1) to provide the pure vinyl iodide.

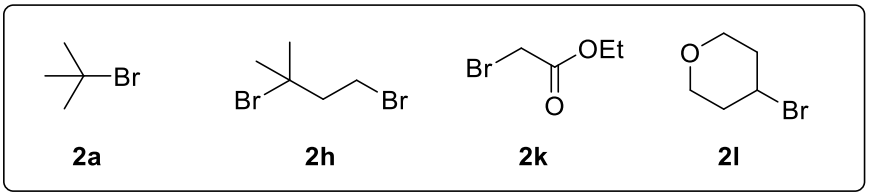
Products **5a**, **5b**, **5c** and **5d** were synthesized according to the general procedure C, and analytical data were in agreement with previous literature[11].



5a **5b** **5c** **5d**

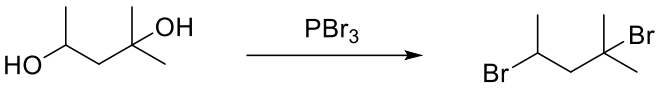
3.3 Preparation of tertiary alkyl bromides

Tertiary alkyl bromides **2a**, **2h**, **2k** and **2l** were purchased from commercial suppliers.



2a **2h** **2k** **2l**

Synthesis of dibromide 2i[12]



2i

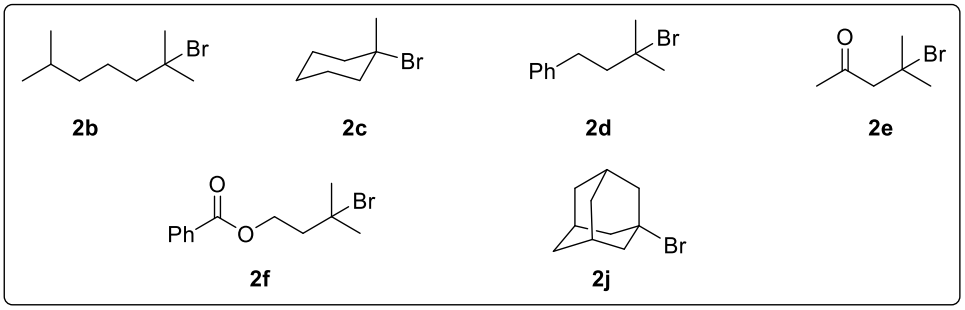
To the dry flask was added 2-methyl-2,4-pentanediol (2.36 g, 20.0 mmol, 1.0 equiv) and the mixture was cooled to -24 °C. Phosphorus tribromide (5.90 g, 22.0 mmol, 1.1 equiv) was added dropwise with efficient stirring over 4 h, during which the temperature was kept below -15 °C. The reaction mixture changed gradually from a viscous emulsion to a homogeneous amber liquid. The stirring was stopped and the flask was left in a dry ice-bath and the contents allowed to warm to room temperature over a period of about two days. After standing at room temperature for 1~3 days, two liquid layers separated. The lower layer consisted of phosphorus acid. The upper layer represented an almost quantitative yield of 2-methyl-2,4-dibromopentane **2i**. It was washed rapidly with 50 mL ice water and dried over anhydrous sodium sulfate. It was purified by distillation under diminished pressure. The product **2i** was collected at 61-62°C and obtained in 80% yield (3.88g, 16.0 mmol) as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (qt, *J* = 8.4, 5.4 Hz, 1H), 2.51 (dd, *J* = 16.0, 6.4 Hz, 1H), 2.43 (dd, *J* = 16.0, 4.4 Hz, 1H), 1.87 (s, 3H), 1.83 (s, 3H), 1.81 (dd, *J* = 6.8, 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.1, 57.8, 46.5, 36.0, 33.8, 28.8. HRMS (ESI) m/z calcd for $C_6H_{12}Br_2Na$ $[M+Na]^+$: 264.9203; found: 264.9201.

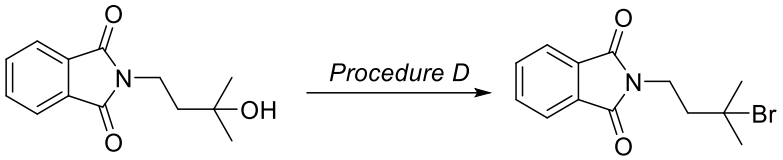
General procedure D

To a solution of alcohol (10 mmol, 1.0 equiv) in CH_2Cl_2 was added LiBr (1.80 g, 20 mmol) in 48 wt% aqueous HBr at 0 ^{o}C. The reaction mixture was allowed to warm to r.t. and stirred for overnight. The reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, brine, dried over $MgCl_2$, and concentrated. The residue was purified by column chromatograph to afford the product.

Products **2b**, **2c**, **2d**, **2e**, **2f**, **2j** was synthesized according to the general procedure D. **2c**, **2d**, **2j** analytical data were in agreement with ref. 13; **2b** analytical data were in

agreement with ref. 14; **2e**, **2f** analytical data were in agreement with ref. 15.





2g

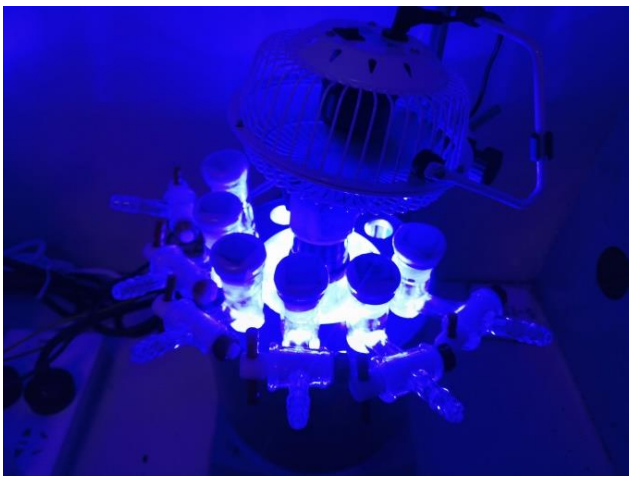
Product **2g** was synthesized according to the general procedure D in 65% yield as yellow solid. Mp: 70 – 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.72 (dd, *J* = 5.6, 3.2 Hz, 2H), 3.98 – 3.91 (m, 2H), 2.22 – 2.14 (m, 2H), 1.85 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 134.1, 132.3, 123.4, 63.7, 44.9, 35.8, 34.4. FTIR (thin film): 2940, 1772, 1611, 1438, 1402, 1343, 1250, 1206, 1151, 1104, 940, 820 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{15}BrNO_2$ $[M+H]^+$: 296.0286; found: 296.0281.

Part 4. Reductive cross-coupling of vinyl halides and tertiary alkyl bromides

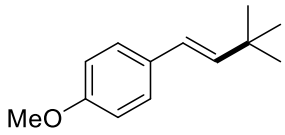
General procedure E

To a dry Schlenk tube were added Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1 mol%), $MgCl_2$ (19.0 mg, 0.20 mmol, 1.0 equiv), Ni(TMHD)$_2$ (8.5 mg, 0.02 mmol, 10 mol%) and 1,3-dimethyl-1H-imidazolium iodide (9.0 mg, 0.04 mmol, 20 mol%). The mixture was degassed three times with argon, then TMEDA (90 μL, 0.60 mmol, 3.0 equiv), vinyl halides (0.20 mmol, 1.0 equiv) and tertiary alkyl bromide (0.40 mmol, 2.0 equiv) in *N*,*N*-Dimethylaniline (3.0 mL) was added *via* a syringe. The mixture was stirred at room temperature under the irradiation of 20W blue LEDs for 24 h. Then 20 mL aqueous HCl (4.0 M) was added and the mixture was stirred for another 15 min for neutralizing *N*,*N*-Dimethylaniline. The reaction mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. The residue was further purified

by flash column chromatography. The ratio of *E*/*Z* was monitored by ^{1}H NMR of the product mixture.

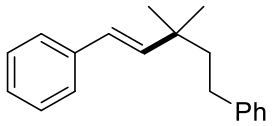


(*E*)-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene (3a)[16]



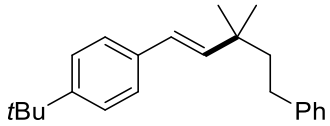
Product **3a** was synthesized according to the general procedure E in 73% yield (27.6 mg) as white solid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.2 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.25 (d, *J* = 16.0 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 140.0, 131.1, 127.2, 124.1, 114.1, 55.5, 33.4, 29.9. HRMS (ESI) m/z calcd for $C_{13}H_{18}NaO$ $[M+Na]^+$: 213.1255; found: 213.1250.

(*E*)-(3,3-dimethylpent-1-ene-1,5-diyl)dibenzene (3b)



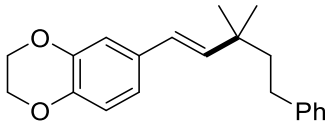
Product **3b** was synthesized according to the general procedure E in 73% yield (36.6 mg) as colourless liquid (petroleum ether: ethyl acetate= 100:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.19 (m, 5H), 7.16 (d, *J* = 7.2 Hz, 3H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 2.63 – 2.53 (m, 2H), 1.74 – 1.66 (m, 2H), 1.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.3, 138.1, 128.7, 128.46, 128.45, 127.0, 126.4, 126.2, 125.7, 45.4, 36.6, 31.5, 27.4. FTIR (thin film): 3061, 3025, 2960, 2862, 1601, 1494, 1454, 1384, 1363, 1702, 969, 742, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{23}$ $[M+H]^+$: 251.1800; found: 251.1794.

(*E*)-1-(tert-butyl)-4-(3,3-dimethyl-5-phenylpent-1-en-1-yl)benzene (3c)



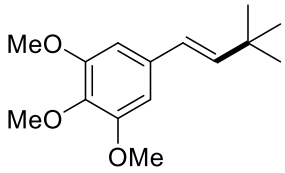
Product **3c** was synthesized according to the general procedure E in 66% yield (40.6 mg) as white solid (petroleum ether: ethyl acetate= 100:1), *E:Z* > 20:1, Mp: 43 – 45 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.4 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 6.8 Hz, 3H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 2.61 – 2.50 (m, 2H), 1.74 – 1.64 (m, 2H), 1.31 (s, 9H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.4, 139.6, 135.3, 128.4, 126.1, 125.9, 125.7, 125.6, 45.5, 36.6, 34.6, 31.5, 31.5, 27.5. FTIR (thin film): 3026, 2961, 2866, 1604, 1496, 1364, 971, 813, 743, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{30}Na$ $[M+Na]^+$: 329.2245; found: 329.2240.

(*E*)-6-(3,3-dimethyl-5-phenylpent-1-en-1-yl)-2,3-dihydrobenzo[b][1,4]dioxine (3d)



Product **3d** was synthesized according to the general procedure E in 67% yield (41.4 mg) as colourless liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7. 16 (d, *J* = 7.6 Hz, 3H), 6.91 (s, 1H), 6.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.80 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 6.07 (d, *J* = 16.0 Hz, 1H), 4.23 (s, 4H), 2.57 – 2.50 (m, 2H), 1.76 – 1.62 (m, 2H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.4, 142.8, 138.9, 132.0, 128.4, 125.7, 125.6, 119.6, 117.3, 114.6, 100.1, 64.6, 64.5, 45.5, 36.5, 31.5, 27.4. FTIR (thin film): 3025, 2960, 2861, 1583, 1509, 1458, 1430, 1070, 970, 887, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}NaO_2$ $[M+Na]^+$: 331.1674; found: 331.1672.

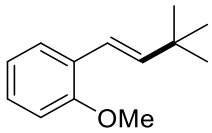
(*E*)-5-(3,3-dimethylbut-1-en-1-yl)-1,2,3-trimethoxybenzene (3e)



Product **3e** was synthesized according to the general procedure E in 85% yield (42.4

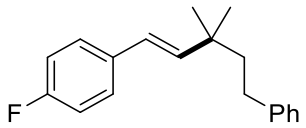
mg) as white solid (petroleum ether: ethyl acetate= 30:1), *E:Z* > 20:1, Mp: 48 – 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (s, 2H), 6.24 (d, *J* = 16.0 Hz, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 6H), 3.83 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 141.5, 137.4, 133.9, 124.7, 103.3, 61.0, 56.2, 33.5, 29.8. FTIR (thin film): 3023, 2957, 2837, 1582, 1506, 1417, 1338, 1238, 1125, 1010, 967, 858, 813, 773 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{22}NaO_3$ $[M+Na]^+$: 273.1467; found: 273.1461.

(*E*)-1-(3,3-dimethylbut-1-en-1-yl)-2-methoxybenzene (3f)



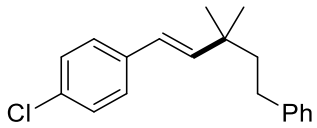
Product **3f** was synthesized according to the general procedure E in 50% yield (19.1 mg) as colourless liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (td, *J* = 8.4, 2.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 142.5, 127.9, 127.3, 126.3, 120.8, 119.1, 111.0, 55.6, 33.8, 29.8. FTIR (thin film): 3025, 2958, 2864, 1598, 1489, 1463, 1437, 1242, 1107, 1031, 976, 749 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}NaO$ $[M+Na]^+$: 213.1255; found: 213.1250.

(*E*)-1-(3,3-dimethyl-5-phenylpent-1-en-1-yl)-4-fluorobenzene (3g)



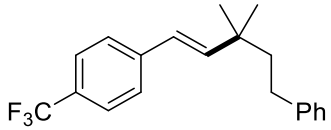
Product **3g** was synthesized according to the general procedure E in 71% yield (38.0 mg) as colourless liquid (petroleum ether: ethyl acetate= 100:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.4 Hz, 1H), 7.31 (d, *J* = 6.4 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 6.8 Hz, 3H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.30 (d, *J* = 16.4 Hz, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 2.61 – 2.52 (m, 2H), 1.74 – 1.65 (m, 2H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.6 Hz), 143.2, 140.2, 134.2, 128.5, 128.4, 127.6 (d, *J* = 7.9 Hz), 125.8, 125.3, 115.5 (d, *J* = 21.5 Hz), 45.4, 36.6, 31.5, 27.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.8 (s). FTIR (thin film): 3026, 2960, 2925, 1598, 1506, 1220, 1157, 973, 860, 812, 742, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{21}NaF$ $[M+Na]^+$: 291.1525; found: 291.1519.

(*E*)-1-chloro-4-(3,3-dimethyl-5-phenylpent-1-en-1-yl)benzene (3h)



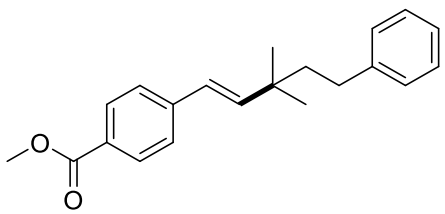
Product **3h** was synthesized according to the general procedure E in 63% yield (35.8 mg) as colourless liquid (petroleum ether: ethyl acetate= 100:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 6H), 7.16 (d, *J* = 6.0 Hz, 3H), 6.28 (d, *J* = 16.4 Hz, 1H), 6.19 (d, *J* = 16.4 Hz, 1H), 2.59 – 2.52 (m, 2H), 1.73 – 1.66 (m, 2H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 141.1, 136.6, 132.5, 128.7, 128.5, 128.4, 127.4, 125.8, 125.3, 45.3, 36.7, 31.5, 27.3. FTIR (thin film): 3025, 2960, 2861, 1487, 1460, 1437, 1100, 1028, 976, 744, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{21}NaCl$ $[M+Na]^+$: 307.1229; found: 307.1226.

(*E*)-1-(3,3-dimethyl-5-phenylpent-1-en-1-yl)-4-(trifluoromethyl)benzene (3i)



Product **3i** was synthesized according to the general procedure E in 60% yield (38.1 mg) as white solid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1, Mp: 42 – 44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 6.0 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 3H), 6.37 (d, *J* = 16.4 Hz, 1H), 6.32 (d, *J* = 16.4 Hz, 1H), 2.60 – 2.53 (m, 2H), 1.76 – 1.68 (m, 2H), 1.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 143.1, 141.6, 128.9 (d, *J* = 128.4 Hz), 128.5, 128.4, 126.3, 125.8, 125.6 (q, *J* = 3.8 Hz), 125.3, 123.1, 45.2, 36.9, 31.5, 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ - 62.3 (s). FTIR (thin film): 3027, 2961, 2860, 1616, 1326, 1164, 1124, 1068, 743, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{22}F_3$ $[M+H]^+$: 319.1674; found: 319.1681.

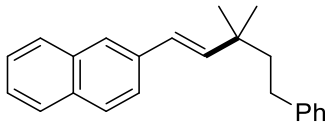
methyl (*E*)-4-(3,3-dimethyl-5-phenylpent-1-en-1-yl)benzoate (3j)



Product **3j** was synthesized according to the general procedure E in 70% yield (43.2

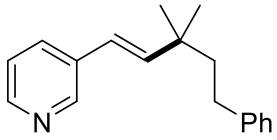
mg) as colourless liquid (petroleum ether: ethyl acetate= 30:1), *E:Z* > 20:1, the reaction mixture was directly purified through a silica column after spin away solvent without any work-up. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 7.6, 5.6 Hz, 2H), 7.16 (d, *J* = 6.8 Hz,, 3H), 6.36 (s, 2H), 3.90 (s, 3H), 2.60 – 2.54 (m, 2H), 1.75 – 1.69 (m, 2H). 1.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 143.2, 143.1, 142.6, 130.0, 128.5, 128.4, 126.1, 125.8, 125.7, 52.1, 45.2, 36.9, 31.5, 27.2. FTIR (thin film): 3049, 2955, 2922, 2862, 1710, 1605, 1594, 1490, 1363, 972, 813, 741, 712 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}O_2Na$ $[M+Na]^+$: 331.1674; found: 331.1670.

(*E*)-2-(3,3-dimethyl-5-phenylpent-1-en-1-yl)naphthalene (3k)



Product **3k** was synthesized according to the general procedure E in 62% yield (37.2 mg) as white solid (petroleum ether: ethyl acetate= 100:1), *E:Z* > 20:1, Mp: 71 – 73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.4, 6.4 Hz, 3H), 7.71 (s, 1H), 7.59 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.42 (ddt, J = 16.0, 6.8, 6.0 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 3H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 2.63 – 2.57 (m, 2H), 1.77 – 1.70 (m, 2H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.8, 135.5, 133.9, 132.8, 128.5, 128.2, 128.0, 127.8, 126.5, 126.3, 125.7, 125.6, 125.5, 123.8, 45.5, 36.7, 31.5, 27.4. FTIR (thin film): 3048, 2954, 2920, 2863, 1594, 1491, 1361, 972, 817, 742, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{24}Na$ $[M+Na]^+$: 323.1776; found: 323.1778.

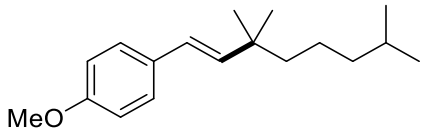
(*E*)-3-(3,3-dimethyl-5-phenylpent-1-en-1-yl)pyridine (3l)



Product **3l** was synthesized according to the general procedure E in 70% yield (35.2 mg) as yellow liquid, *E:Z* > 20:1, except that the reaction mixture was directly purified through a silica column without any work-up (petroleum ether: ethyl acetate = 4:1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 7.22 (dd, *J* = 8.0, 4.8 Hz, 3H), 7.17 (d, *J* = 6.0 Hz, 1H) 6.33 (d, *J* = 16.4 Hz, 1H), 6.28 (d, *J* = 16.4 Hz, 1H), 2.61 – 2.52 (m, 2H), 1.78 – 1.67 (m, 2H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 148.1, 143.0, 142.8, 133.6, 132.6, 128.5, 128.4, 125.8, 123.5, 123.0, 45.2, 36.9, 31.4, 27.2. FTIR (thin film): 3026, 2960, 2863, 1568, 1455, 1414,

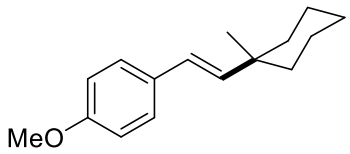
1384, 971, 744, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{22}N$ $[M+H]^+$: 252.1752; found: 252.1747.

(*E*)-1-methoxy-4-(3,3,7-trimethyloct-1-en-1-yl)benzene (4a)



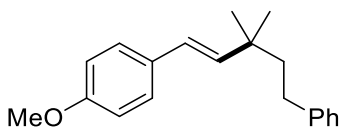
Product **4a** was synthesized according to the general procedure E in 63% yield (32.9 mg) as colourless liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 6.04 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 1.51 (dt, *J* = 12.8, 6.4 Hz, 1H), 1.33 (t, *J* = 9.6 Hz, 2H), 1.29 – 1.20 (m, 2H), 1.13 (t, *J* = 6.4 Hz, 2H), 1.07 (s, 6H), 0.85 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 139.1, 131.2, 127.2, 125.0, 114.1, 55.5, 43.8, 40.0, 36.3, 28.0, 27.5, 22.8, 22.6. FTIR (thin film): 3026, 2955, 2931, 1609, 1511, 1464, 1247, 1174, 1039, 969, 815 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{29}O$ $[M+H]^+$: 261.2218; found: 261.2213.

(*E*)-1-methoxy-4-(2-(1-methylcyclohexyl)vinyl)benzene (4b)



Product **4b** was synthesized according to the general procedure E in 71% yield (32.7 mg) as colourless liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.26 (d, *J* = 16.4 Hz, 1H), 6.07 (d, *J* = 16.4 Hz, 1H), 3.80 (s, 3H), 1.63 – 1.55 (m, 2H), 1.50 (dt, *J* = 11.2, 8.4 Hz, 4H), 1.44 – 1.32 (m, 4H), 1.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 139.1, 131.2, 127.1, 125.4, 114.0, 55.5, 38.6, 38.2, 36.2, 26.5, 22.6. FTIR (thin film): 3015, 2926, 2852, 1609, 1511, 1463, 1247, 1175, 1038, 967, 812 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{23}O$ $[M+H]^+$: 231.1749; found: 231.1743.

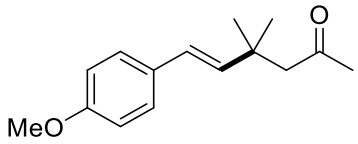
(*E*)-1-(3,3-dimethyl-5-phenylpent-1-en-1-yl)-4-methoxybenzene (4c)



Product **4c** was synthesized according to the general procedure E in 68% yield (41.9 mg) as colourless liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR

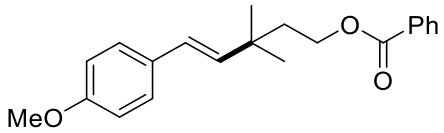
(400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 3H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 2.55 – 2.45 (m, 2H), 1.65 – 1.57 (m, 2H), 1.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.4, 138.3, 131.0, 128.4, 127.3, 125.72, 125.68, 114.1, 55.4, 45.5, 36.5, 31.5, 27.5. FTIR (thin film): 3026, 2958, 2861, 1608, 1511, 1302, 1247, 1175, 1037, 970, 814, 740, 749 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{25}O$ $[M+H]^+$: 281.1905; found: 281.1903.

(*E*)-6-(4-methoxyphenyl)-4,4-dimethylhex-5-en-2-one (4d)



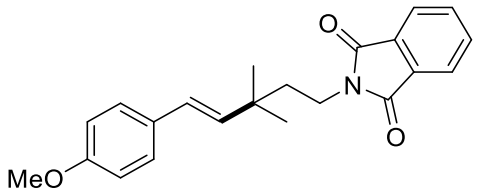
Product **4d** was synthesized according to the general procedure E in 67% yield (25.3 mg) as yellow liquid (petroleum ether: ethyl acetate= 30:1), *E:Z* > 20:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.50 (s, 2H), 2.10 (s, 3H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 159.0, 137.0, 130.4, 127.4, 125.8, 114.1, 55.9, 55.4, 36.1, 32.3, 27.7. FTIR (thin film): 3026, 2959, 2837, 1701, 1608, 1511, 1463, 1359, 1246, 1175, 1034, 971, 853, 818 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1542; found: 233.1536.

(*E*)-5-(4-methoxyphenyl)-3,3-dimethylpent-4-en-1-yl benzoate (4e)



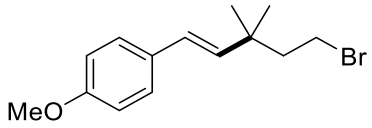
Product **4e** was synthesized according to the general procedure E in 61% yield (39.8 mg) as colourless liquid (petroleum ether: ethyl acetate= 20:1), *E:Z* > 20:1, except that the reaction mixture was directly purified through a silica column after spin away solvent without any work-up; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 0.8 Hz, 2H), 7.54 (t, *J* = 0.8, 1H), 7.41 (t, *J* = 0.8 Hz, 2H), 7.09 (d, *J* = 0.8 Hz, 2H), 6.79 (d, *J* = 0.8 Hz, 2H), 6.47 (d, *J* = 1.2 Hz, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 4.34 (t, *J* = 1.2 Hz, 2H), 3.76 (d, *J* = 0.8 Hz, 3H), 1.79 (t, *J* = 0.8 Hz, 2H), 1.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.3, 140.3, 132.9, 131.3, 130.7, 129.9, 129.6, 128.5, 128.4, 113.2, 62.9, 55.2, 42.0, 36.4, 29.6. FTIR (thin film): 3062, 2960, 2835, 1716, 1606, 1510, 1453, 1274, 1175, 1114, 1028, 813, 712 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}NaO_3$ $[M+Na]^+$: 347.1623; found: 347.1618.

(*E*)-2-(5-(4-methoxyphenyl)-3,3-dimethylpent-4-en-1-yl)isoindoline-1,3-dione (4f)



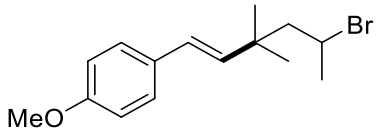
Product **4f** was synthesized according to the general procedure E in 56% yield (39.0 mg) as colourless liquid (petroleum ether: ethyl acetate= 20:1), *E:Z* > 20:1, except that the reaction mixture was directly purified through a silica column after spin away solvent without any work-up; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.62 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 16.4 Hz, 1H), 6.03 (d, *J* = 16.4 Hz, 1H), 3.78 (s, 3H), 3.73 – 3.65 (m, 2H), 1.84 – 1.76 (m, 2H), 1.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 158.8, 136.7, 133.8, 132.3, 130.6, 127.2, 126.0, 123.1, 114.0, 55.4, 40.6, 35.7, 34.9, 27.5. FTIR (thin film): 3465, 3061, 2926, 1771, 1713, 1608, 1512, 1398, 1368, 1247, 1175, 1085, 816, 719 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}NO_3$ $[M+H]^+$: 350.1756; found: 350.1751.

(*E*)-1-(5-bromo-3,3-dimethylpent-1-en-1-yl)-4-methoxybenzene (4g)



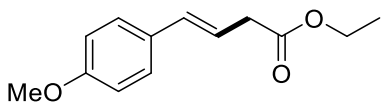
Product **4g** was synthesized according to the general procedure E in 53% yield (29.6 mg) as yellow liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.85 (t, *J* = 8.8 Hz, 2H), 6.25 (d, *J* = 16.4 Hz, 1H), 5.99 (d, *J* = 16.4 Hz, 1H), 3.81 (s, 3H), 3.38 – 3.30 (m, 2H), 2.05 – 1.97 (m, 2H), 1.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 136.4, 130.3, 127.3, 126.5, 114.1, 55.5, 46.7, 37.6, 29.6, 27.4. FTIR (thin film): 3062, 2959, 2867, 2836, 1607, 1512, 1463, 1247, 1175, 1036, 971, 854, 817 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{20}BrO$ $[M+H]^+$: 283.0698; found: 283.0692.

(*E*)-1-(5-bromo-3,3-dimethylhex-1-en-1-yl)-4-methoxybenzene (4h)



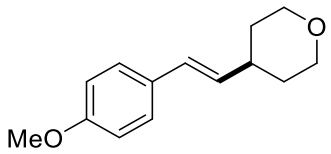
Product **4h** was synthesized according to the general procedure E in 64% yield (37.8 mg) as yellow liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.25 (d, *J* = 16.0 Hz, 1H), 6.05 (d, *J* = 16.4 Hz, 1H), 4.24 – 4.13 (m, 1H), 3.80 (s, 3H), 2.24 (dd, *J* = 14.8, 6.0 Hz, 1H), 1.94 (dd, *J* = 14.8, 6.0 Hz, 1H), 1.70 (d, *J* = 6.8 Hz, 3H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 137.3, 130.6, 127.3, 125.9, 114.1, 77.5, 77.2, 76.8, 55.5, 54.6, 47.5, 37.2, 28.9, 28.8, 27.1. FTIR (thin film): 3061, 2961, 2835, 1608, 1510, 1464, 1248, 1175, 1036, 917, 849, 815 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{22}BrO$ $[M+H]^+$: 297.0854; found: 297.0850.

Ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate (4j)



Product **4j** was synthesized according to the general procedure E in 23% yield (15.3 mg) as colorless liquid (petroleum ether: ethyl acetate= 30:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 11.6 Hz, 1H), 5.81 (dd, *J* = 18.8, 7.6 Hz, 1H), 4.17 (dd, *J* = 14.0, 6.8 Hz, 2H), 3.82 (s, 3H), 3.33 (d, *J* = 5.6 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 158.8, 131.6, 130.1, 129.4, 121.9, 113.9, 60.9, 55.4, 34.4, 14.4. FTIR (thin film): 3060, 2961, 2834, 1721, 1610, 1510, 1455, 1175, 1029, 850, 813 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1178; found: 221.1175.

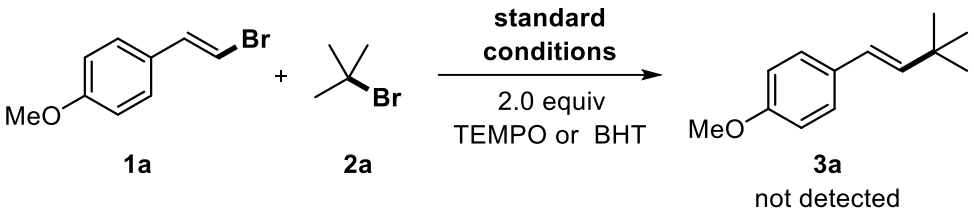
(*E*)-4-(4-methoxystyryl)tetrahydro-2H-pyran (4k)



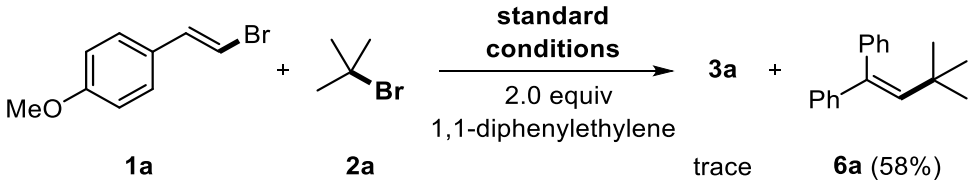
Product **4k** was synthesized according to the general procedure E in 40% yield (4.0 equiv 4-bromotetrahydro-2H-pyran was used, 17.6 mg) as colorless liquid (petroleum ether: ethyl acetate= 50:1), *E:Z* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.01 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.00 (d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H), 3.46 (t, *J* = 10.8 Hz, 2H), 2.43 – 2.28 (m, 1H), 1.69 (d, *J* = 11.6 Hz, 2H), 1.64 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 132.7, 130.5, 127.7, 127.3, 114.1, 67.9, 55.4, 38.5, 32.9. FTIR (thin film): 3058, 2947, 2840, 1609, 1510, 1464, 1246, 1175, 1037, 957, 813 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1385; found: 219.1380.

Part 5. Mechanistic experiments

Radical trap experiment



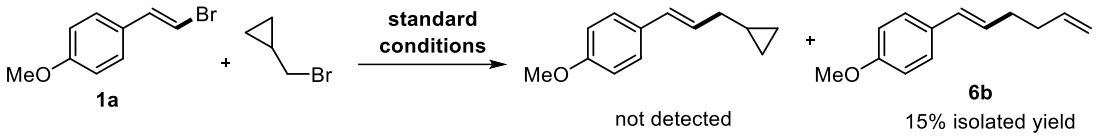
To a dry Schlenk tube were added Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1 mol%), $MgCl_2$ (19.0 mg, 0.20 mmol, 1.0 equiv), Ni(TMHD)$_2$ (8.5 mg, 0.02 mmol, 10 mol%) and 1,3-dimethyl-1H-imidazolium iodide (9.0 mg, 0.04 mmol, 20 mol%), 2.0 equiv 2,2,6,6-tetramethylpiperidinooxy (TEMPO) or butylated hydroxytoluene (BHT) extra added respectively. The mixture was degassed three times with argon, then **1a** (42.2 mg, 0.20 mmol, 1.0 equiv), TMEDA (90 μL, 0.60 mmol, 3.0 equiv) and 2-bromo-2-methylpropane (54.8 mg, 0.40 mmol, 2.0 equiv) in *N*,*N*-Dimethylaniline (3.0 mL) was added *via* a syringe. The mixture was stirred at room temperature under the irradiation of 20W blue LEDs for 24 h. Then 20 mL aqueous HCl (4.0 M) was added and the mixture was stirred for another 15 min for neutralizing *N*,*N*-Dimethylaniline, the reaction mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. The desired product **3a** all were not detected by GC-MS(EI).



To a dry Schlenk tube were added Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1 mol%), $MgCl_2$ (19.0 mg, 0.20 mmol, 1.0 equiv), Ni(TMHD)$_2$ (8.5 mg, 0.02 mmol, 10 mol%), 1,3-dimethyl-1H-imidazolium iodide (9.0 mg, 0.04 mmol, 20 mol%) and 1,1-diphenylethylene (72.0 mg, 0.40 mmol, 2.0 equiv). The mixture was degassed three times with argon, then TMEDA (90 μL, 0.60 mmol, 3.0 equiv) and 2-bromo-2-methylpropane (54.8 mg, 0.40 mmol, 2.0 equiv) in *N*,*N*-Dimethylaniline (3.0 mL) was added *via* a syringe. The mixture was stirred at room temperature under the irradiation of 20W blue LEDs for 24 h. Then 20 mL aqueous HCl (4.0 M) was added and the mixture was stirred for another 15 min for neutralizing *N*,*N*-Dimethylaniline. The reaction mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. The crude ^{1}H-NMR spectrum of the residue showed a 58% yield

of the known Heck-type coupling product **6a** by using mesitylene as the internal standard.

Radical clock experiment



To a dry Schlenk tube were added **1a** (42.2 mg, 0.20 mmol, 1.0 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1 mol%), $MgCl_2$ (19.0 mg, 0.20 mmol, 1.0 equiv), Ni(TMHD)$_2$ (8.5 mg, 0.02 mmol, 10 mol%) and 1,3-dimethyl-1H-imidazolium iodide (9.0 mg, 0.04 mmol, 20 mol%). The mixture was degassed three times with argon, then TMEDA (90 μL, 0.60 mmol, 3.0 equiv) and (bromomethyl)cyclopropane (53.6 mg, 0.40 mmol, 2.0 equiv) in *N*,*N*-Dimethylaniline (3.0 mL) was added *via* a syringe. The mixture was stirred at room temperature under the irradiation of 20W blue LEDs for 24 h. Then 20 mL aqueous HCl (4.0 M) was added and the mixture was stirred for another 15 min for neutralizing *N*,*N*-Dimethylaniline. The reaction mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. The residue was purified by flash column chromatography to afford the coupling product (*E*)-1-(hexa-1,5-dien-1-yl)-4-methoxybenzene **6b**[17] in 15% yield as colourless liquid (petroleum ether: ethyl acetate= 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 10.0 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.08 (dt, 16.0, 8.4 Hz, 1H), 5.92 – 5.80 (m, 1H), 5.06 (dd, 17.2, 1.6 Hz, 1H), 4.99 (dd, 10.4, 0.8 Hz, 1H), 3.80 (s, 3H), 2.29 (dt, 14.4, 6.4 Hz, 2H), 2.23 (dt, 13.6, 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 138.4, 130.8, 129.7, 128.1, 127.2, 115.0, 114.1, 55.4, 33.9, 32.6. HRMS (ESI) m/z calcd for $C_{13}H_{17}O$ $[M+H]^+$: 189.1279; found: 189.1279.

Part 6. References

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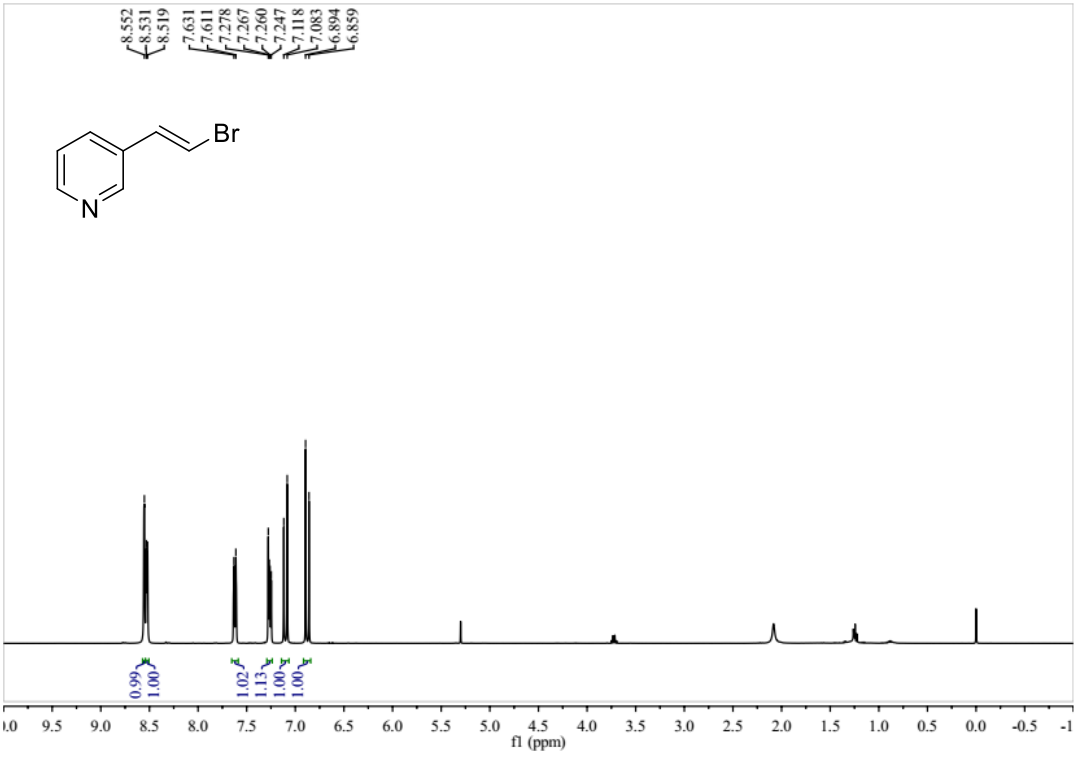
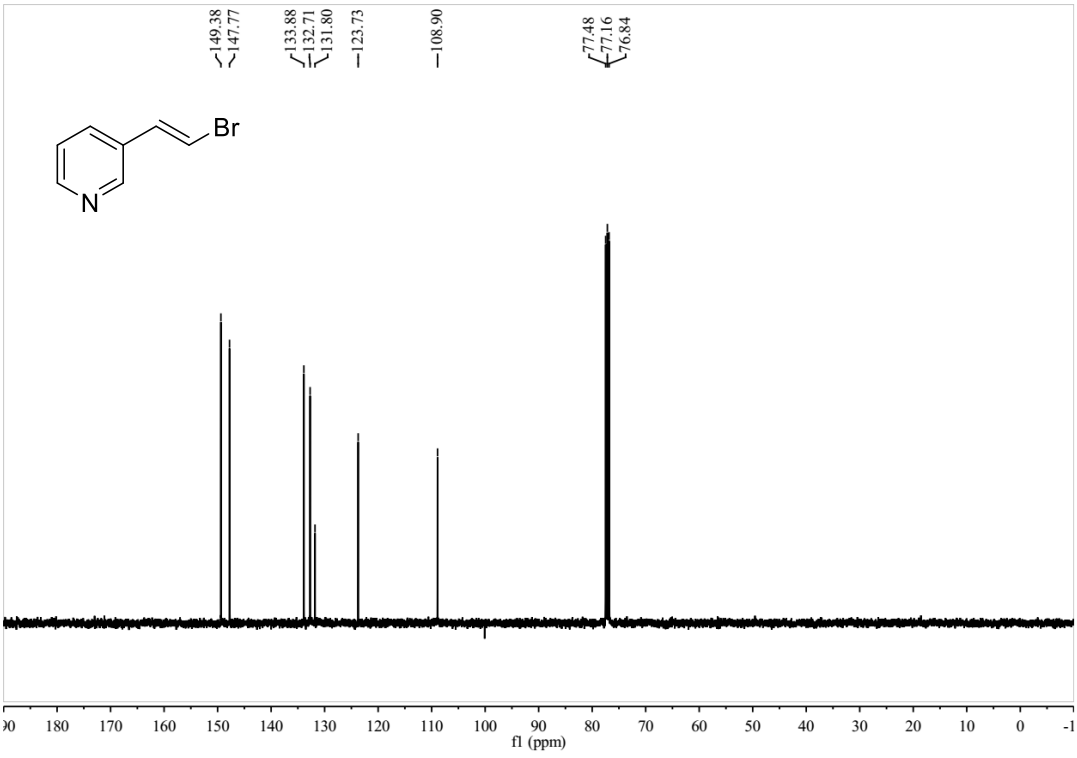
Part 7. ^{1}H NMR and ^{13}C NMR spectra

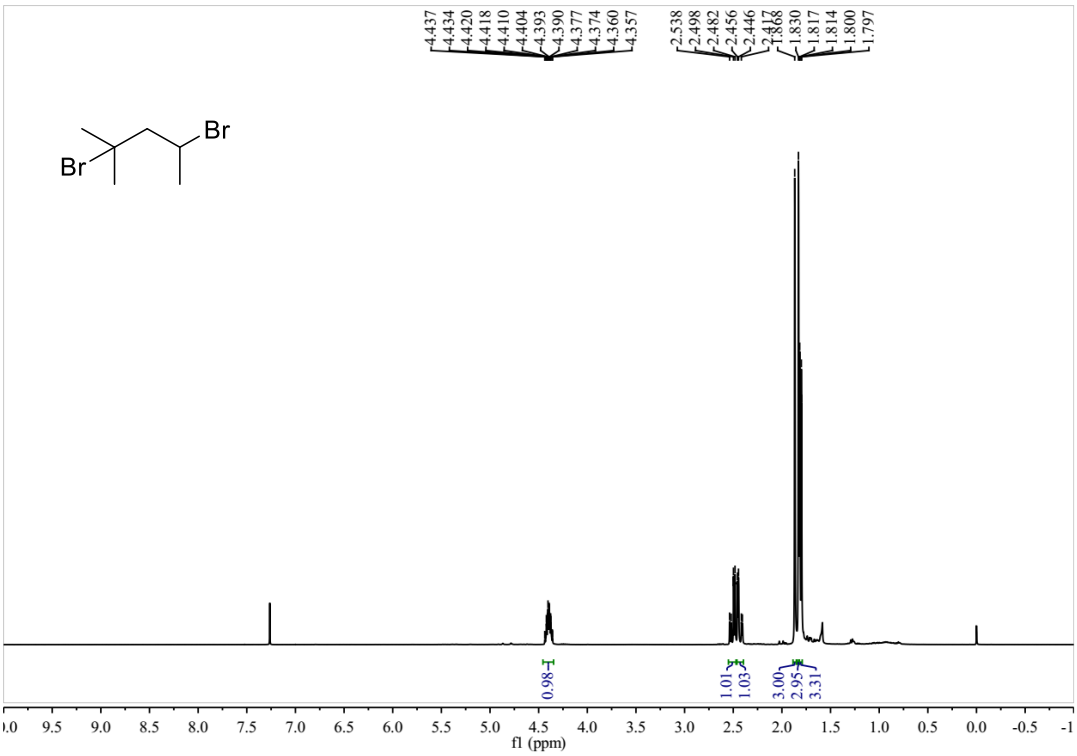
^{1}H NMR Spectra of **1l**



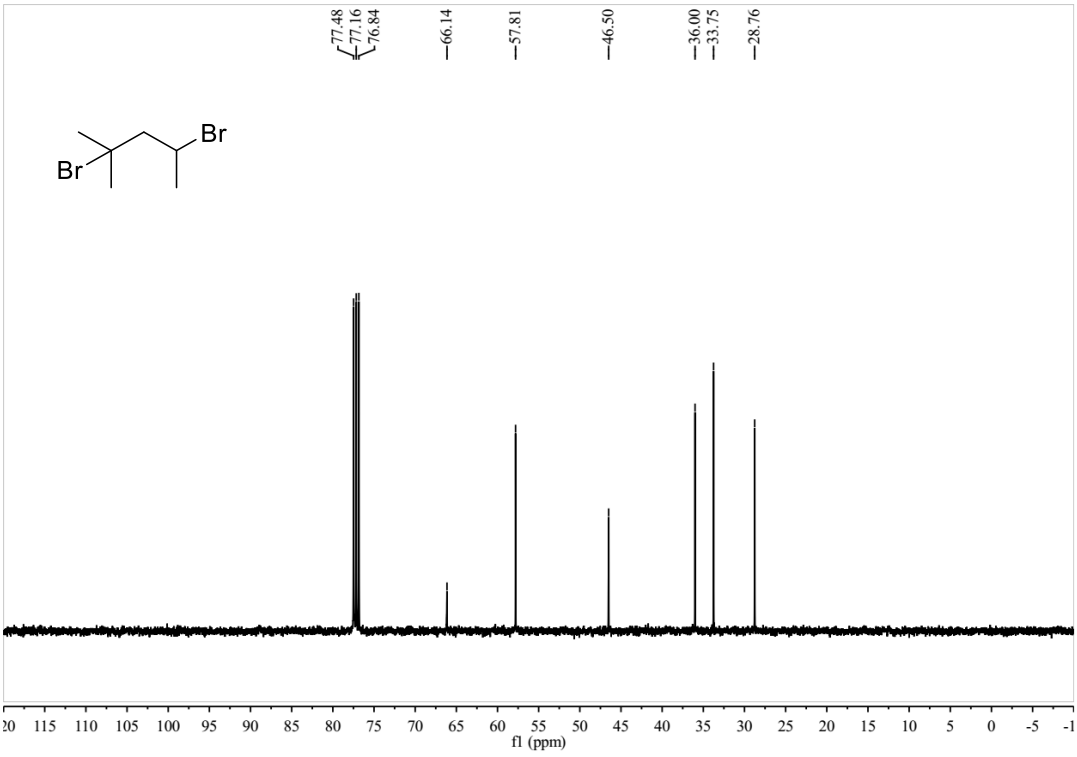
^{13}C NMR Spectra of **1l**



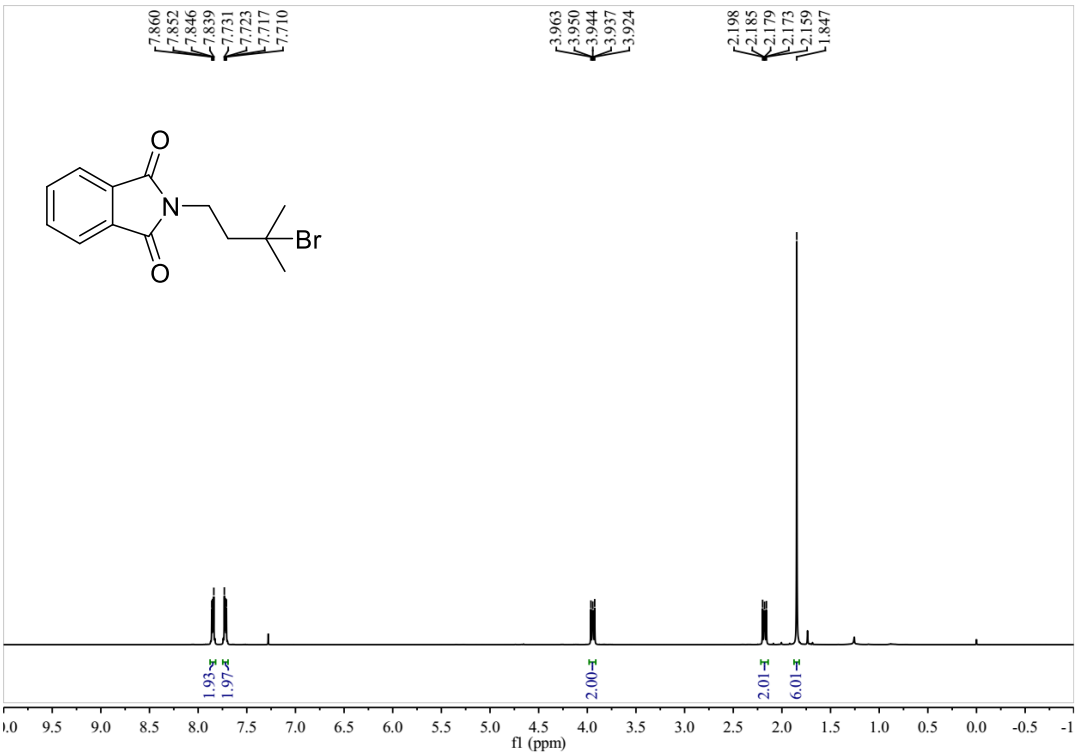
^{1}H NMR Spectra of **2i**



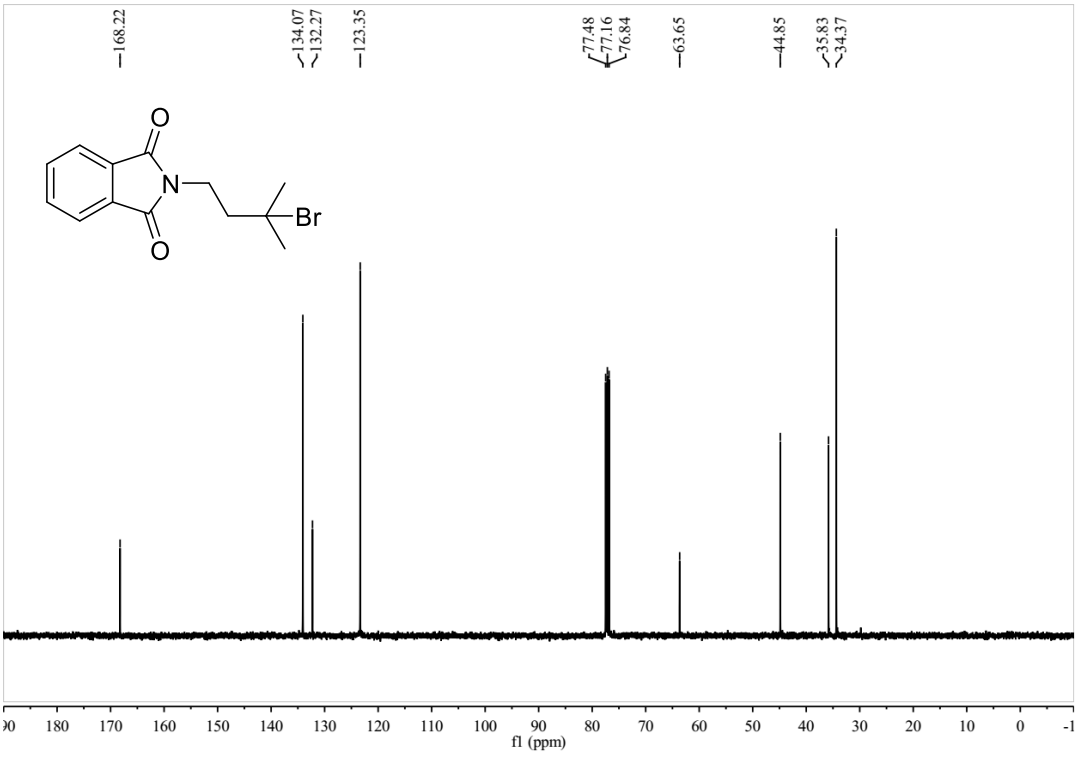
^{13}C NMR Spectra of **2i**



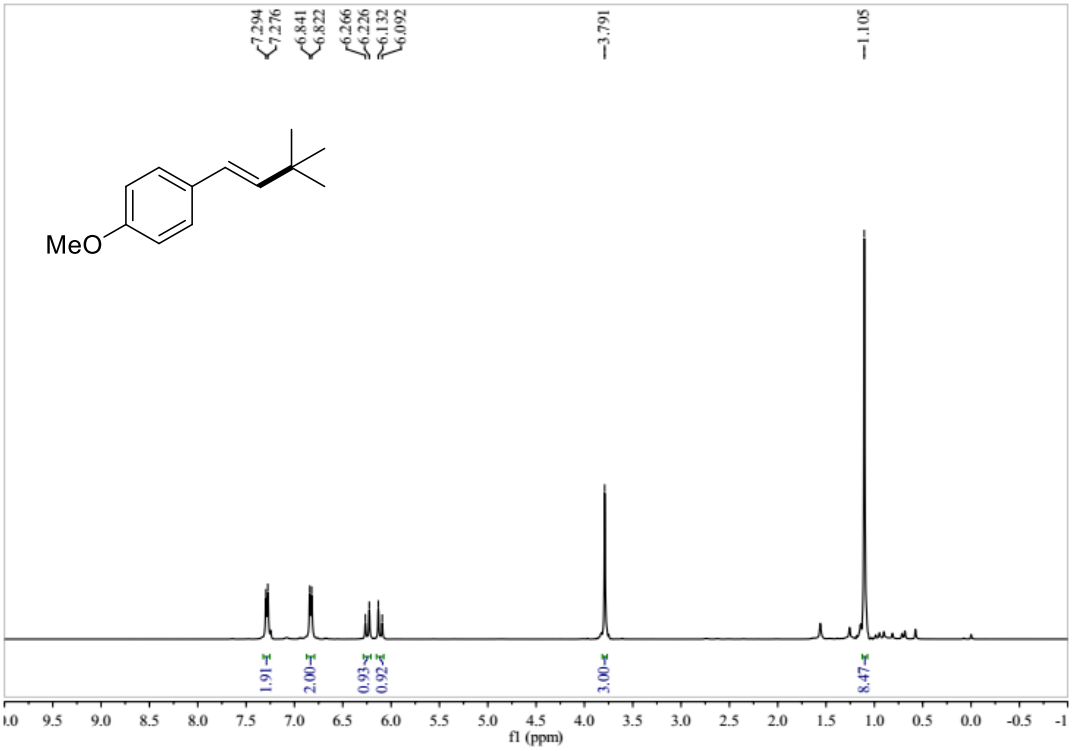
^{1}H NMR Spectra of **2g**



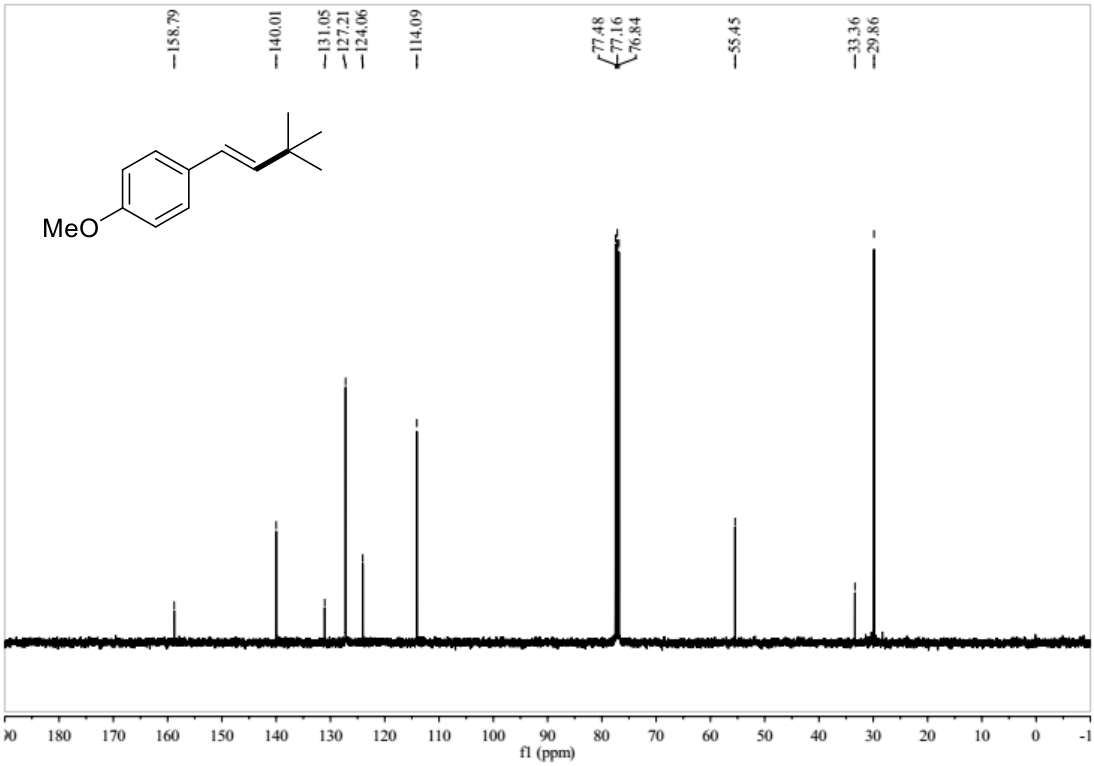
^{13}C NMR Spectra of **2g**



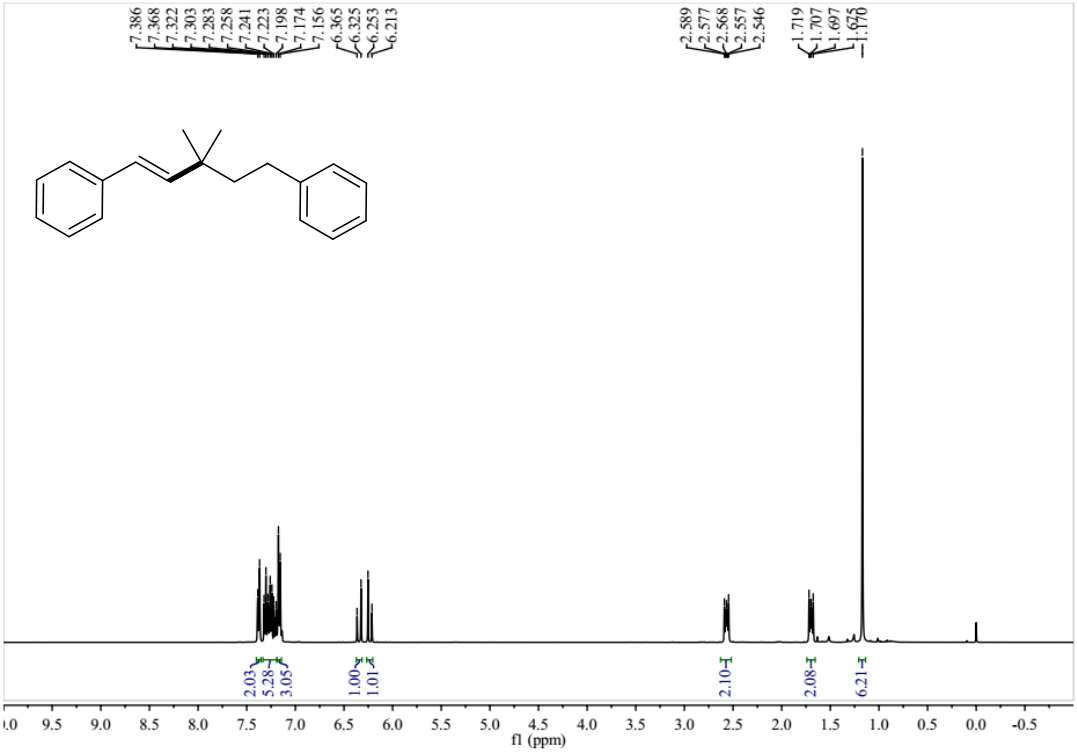
^{1}H NMR Spectra of **3a**



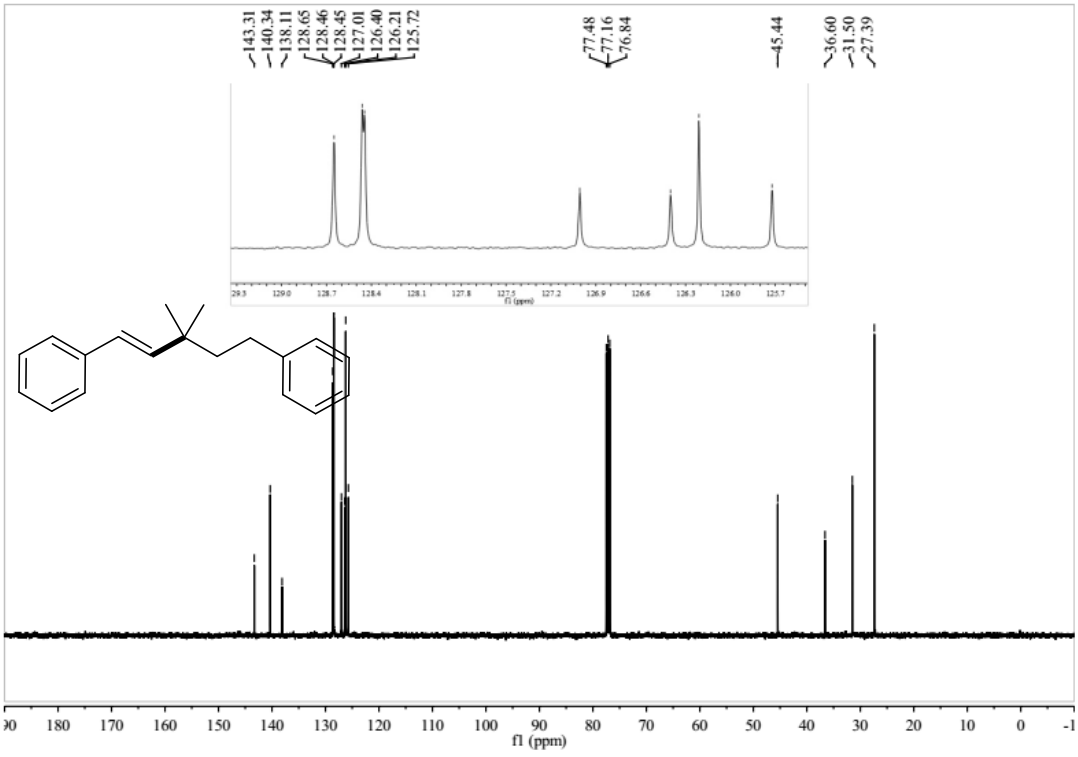
^{13}C NMR Spectra of **3a**



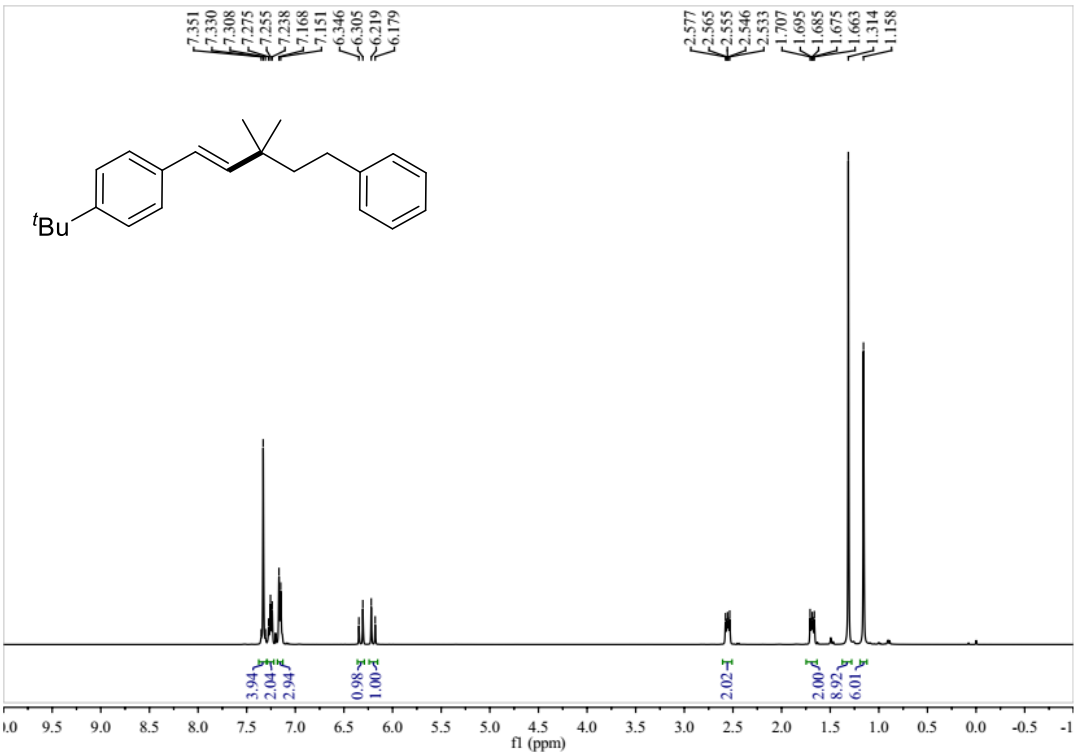
^{1}H NMR Spectra of **3b**



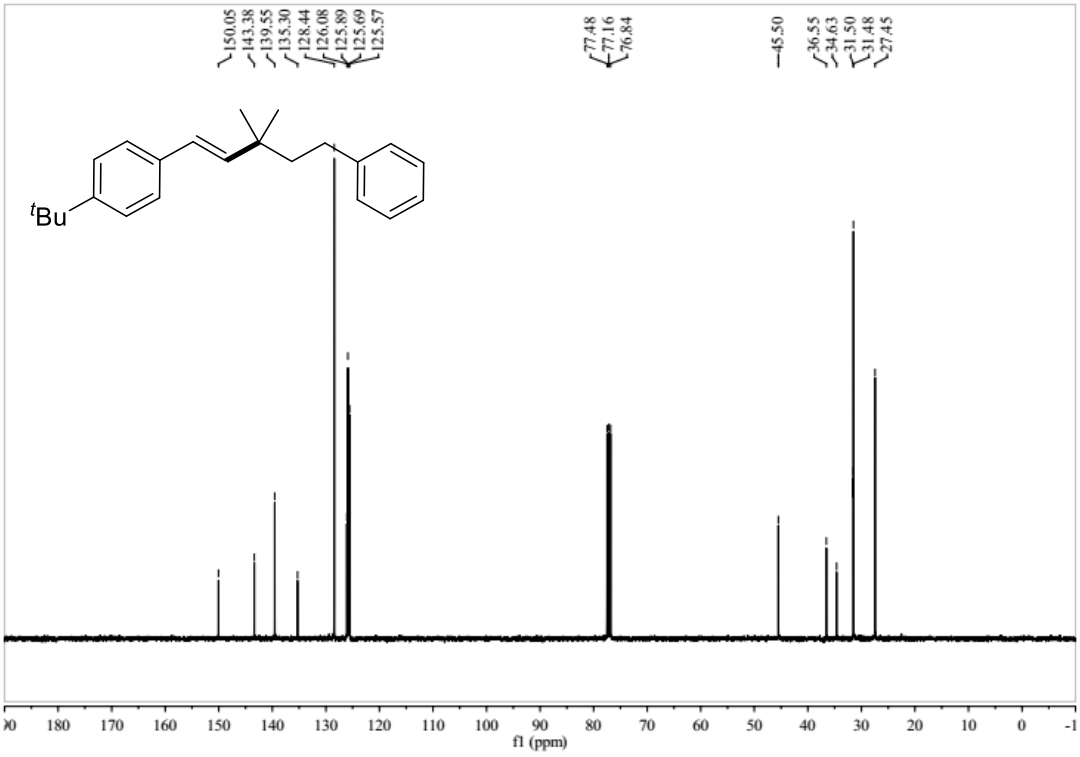
^{13}C NMR Spectra of **3b**



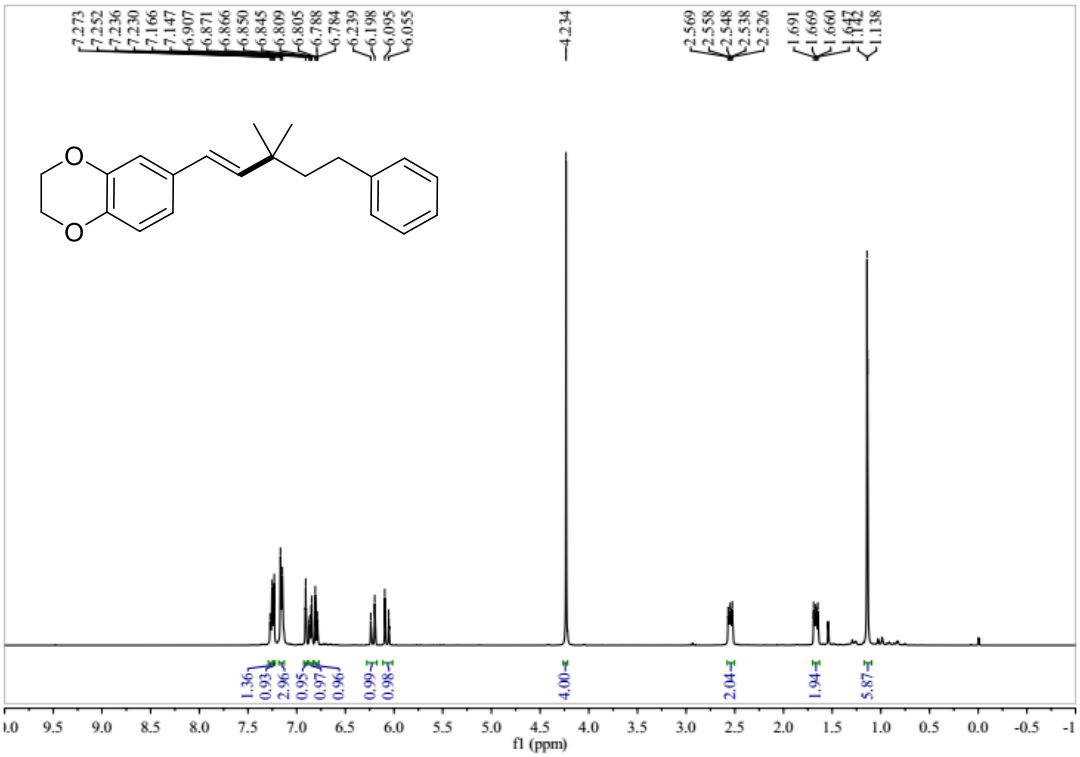
^{1}H NMR Spectra of **3c**



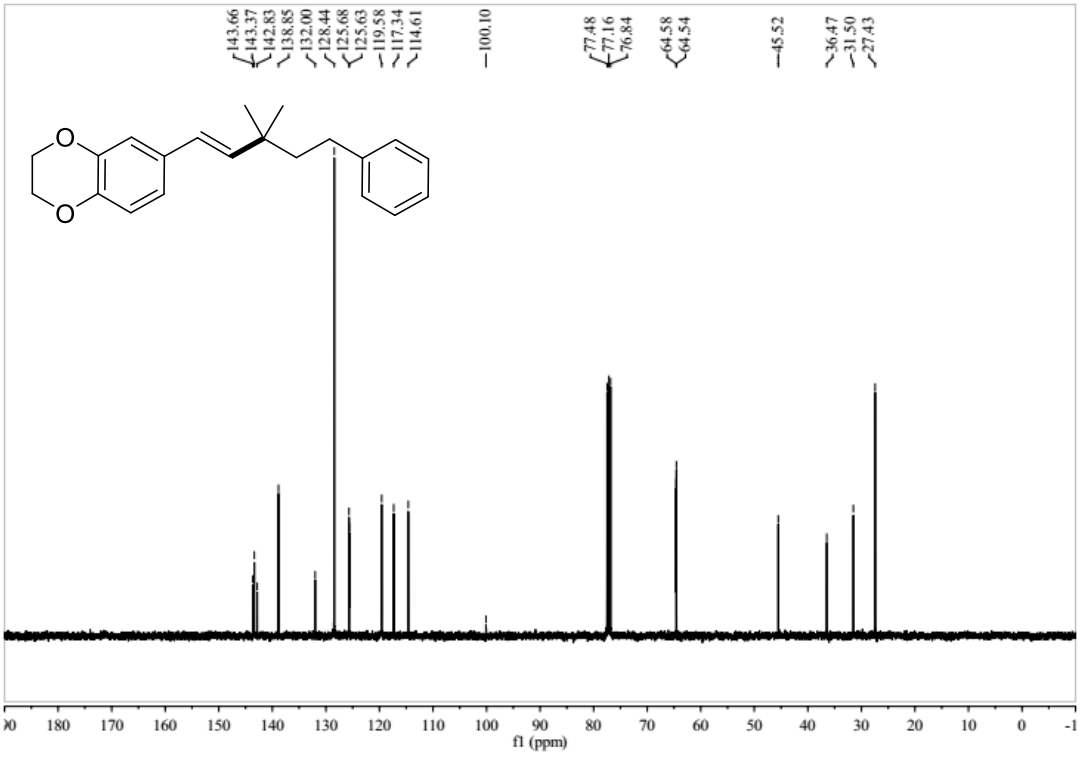
^{13}C NMR Spectra of **3c**



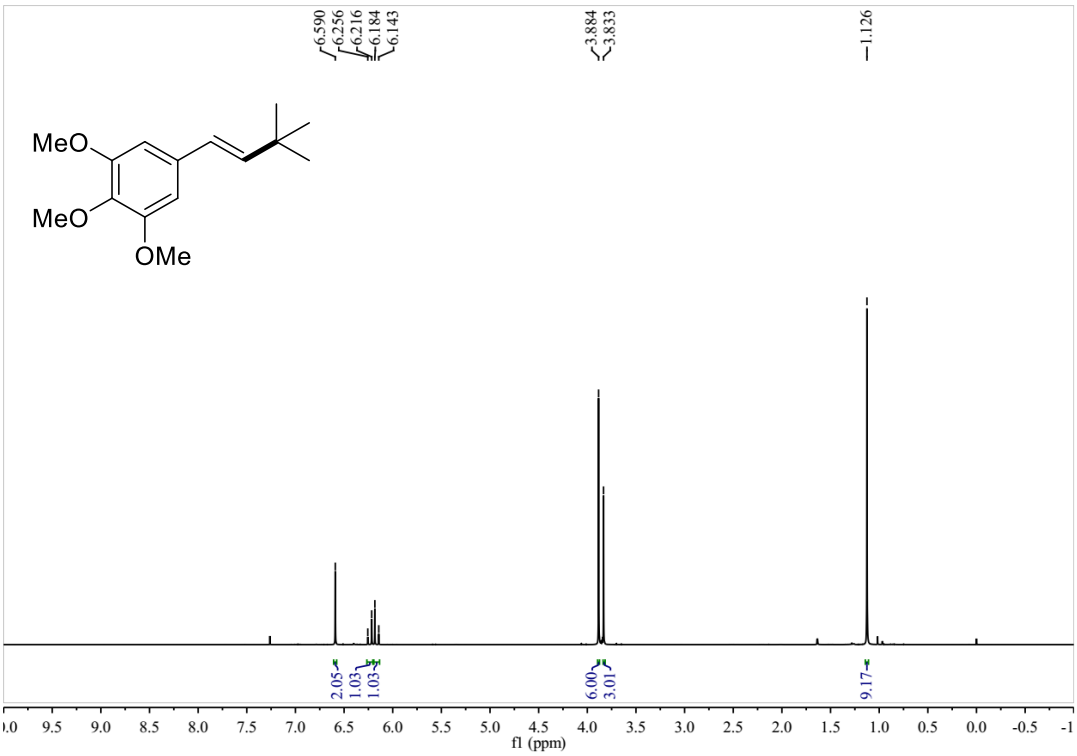
^{1}H NMR Spectra of **3d**



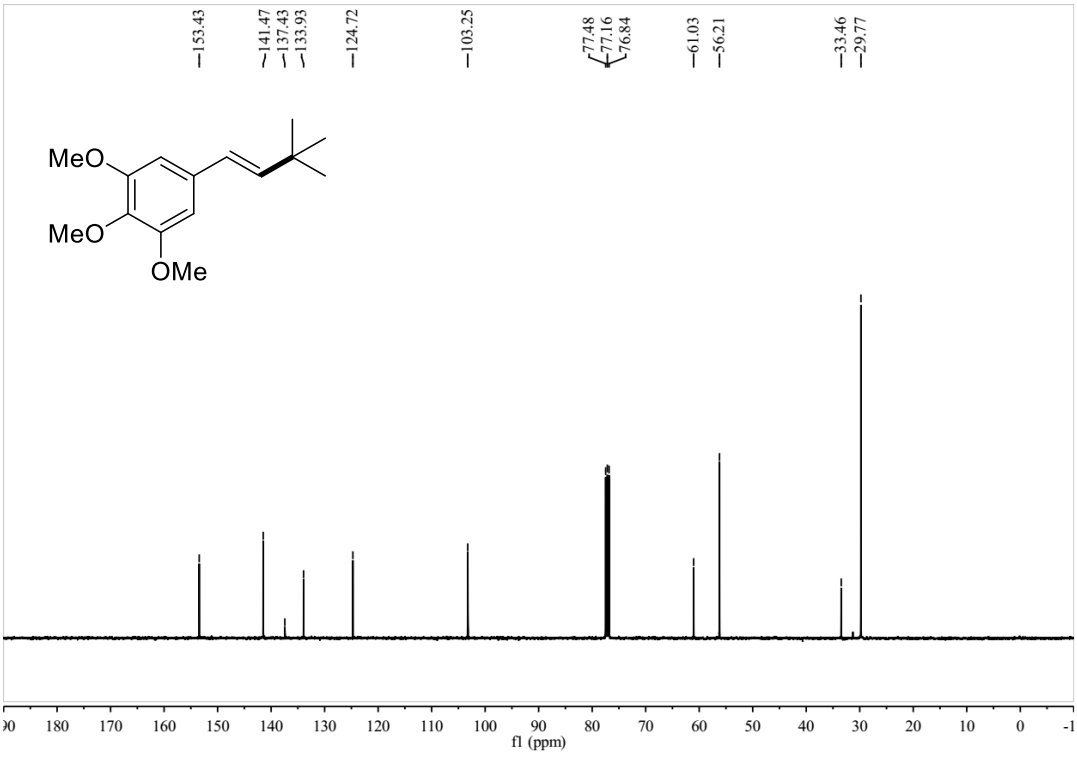
^{13}C NMR Spectra of **3d**



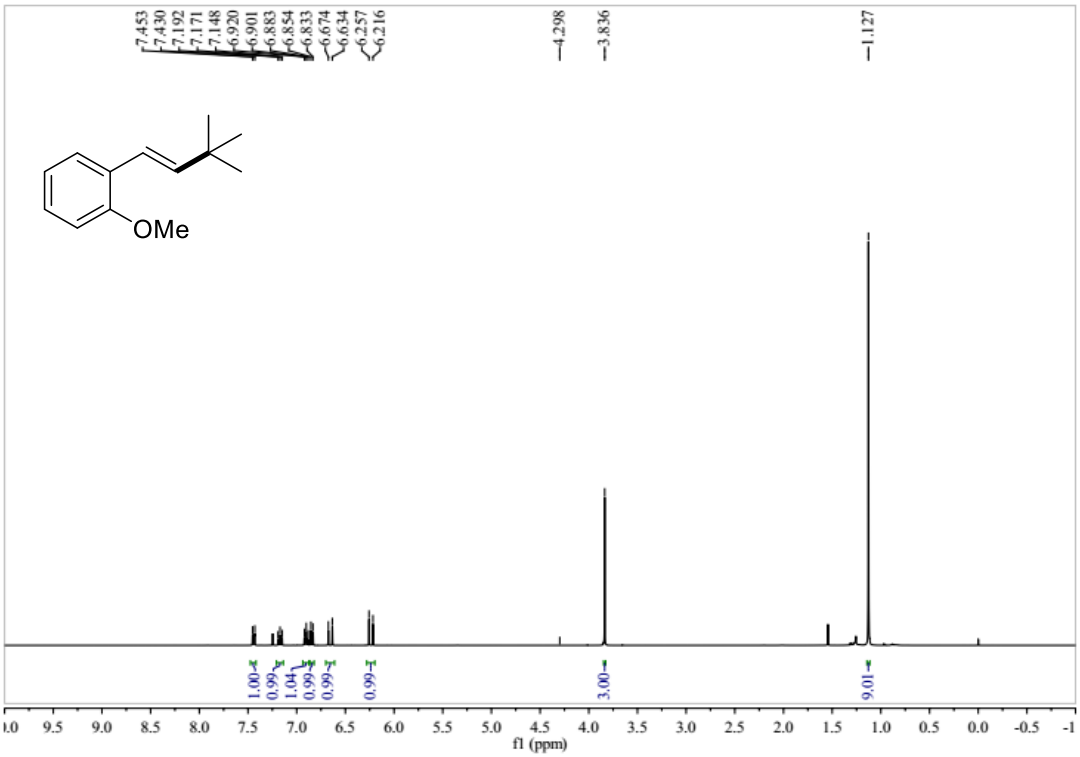
^{1}H NMR Spectra of **3e**



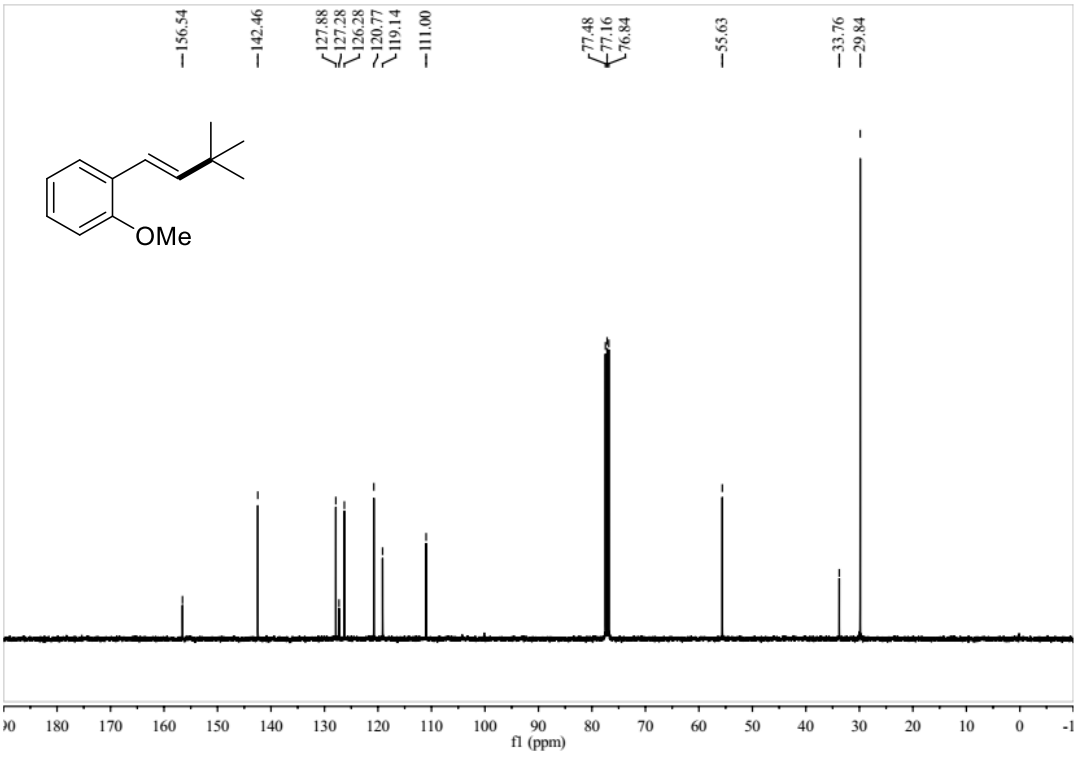
^{13}C NMR Spectra of **3e**



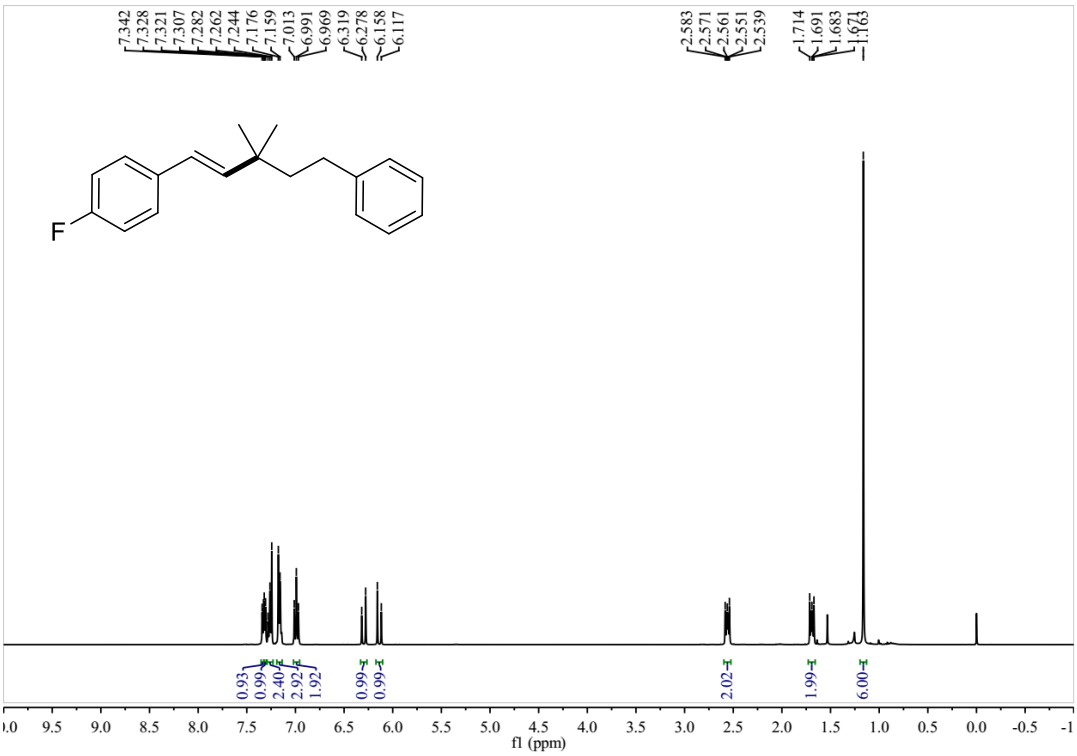
^{1}H NMR Spectra of **3f**



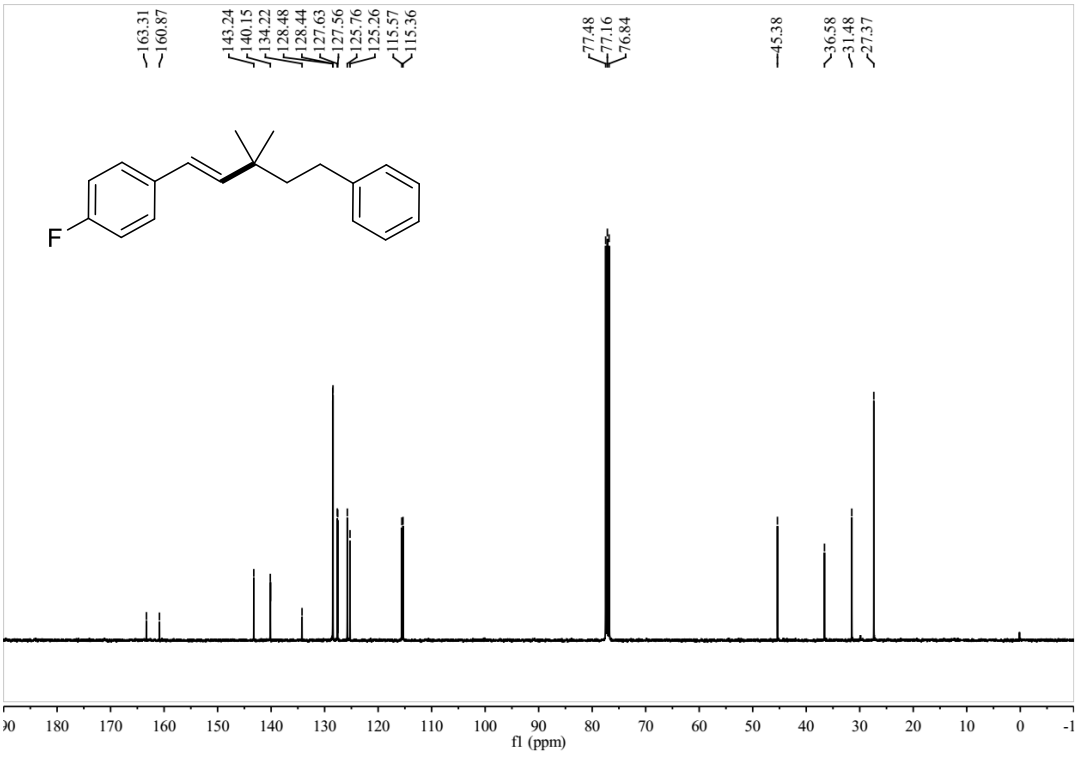
^{13}C NMR Spectra of **3f**



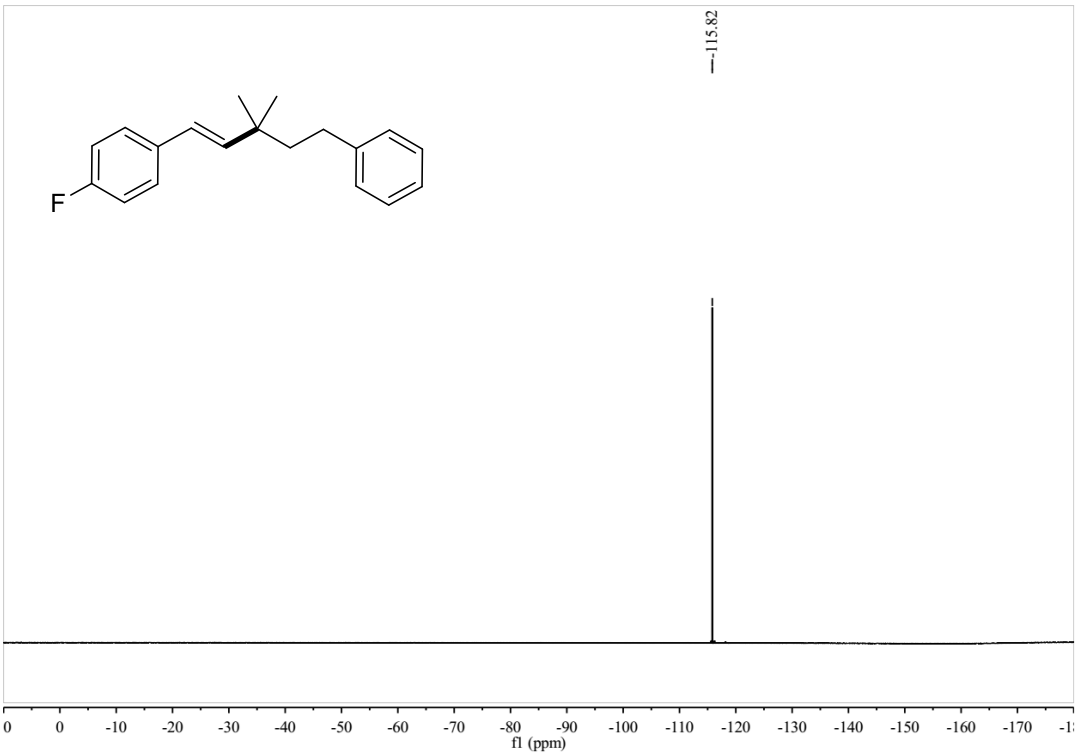
^{1}H NMR Spectra of **3g**



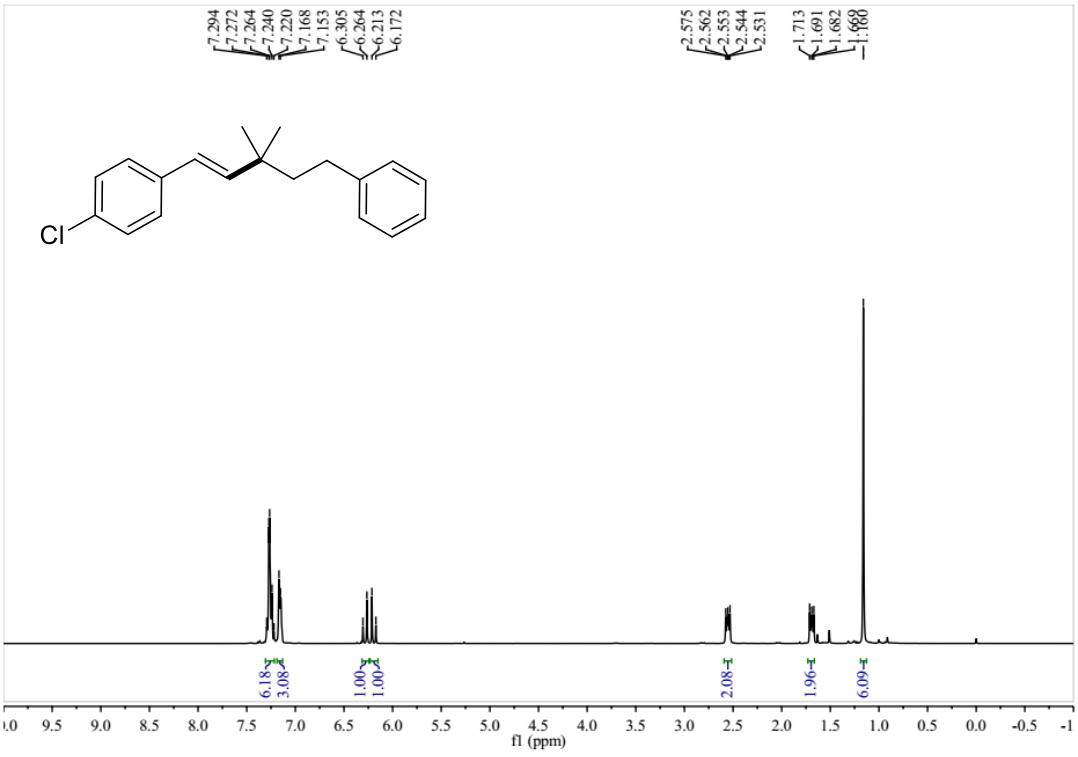
^{13}C NMR Spectra of **3g**



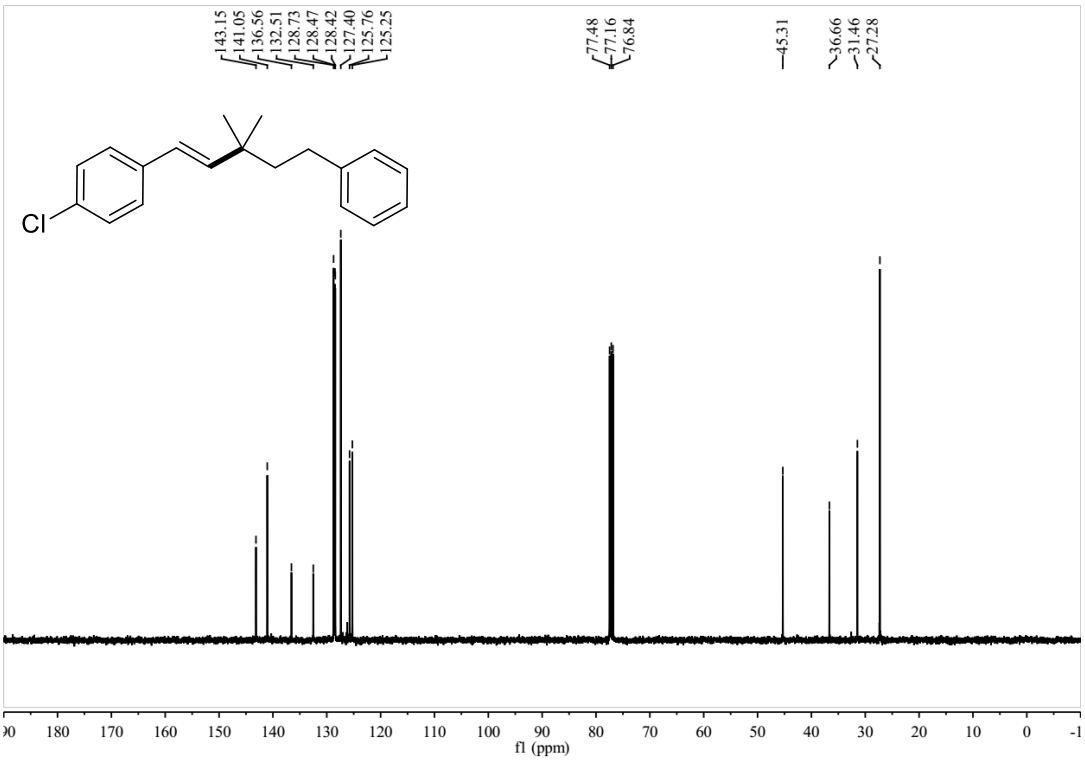
^{19}F NMR Spectra of **3g**



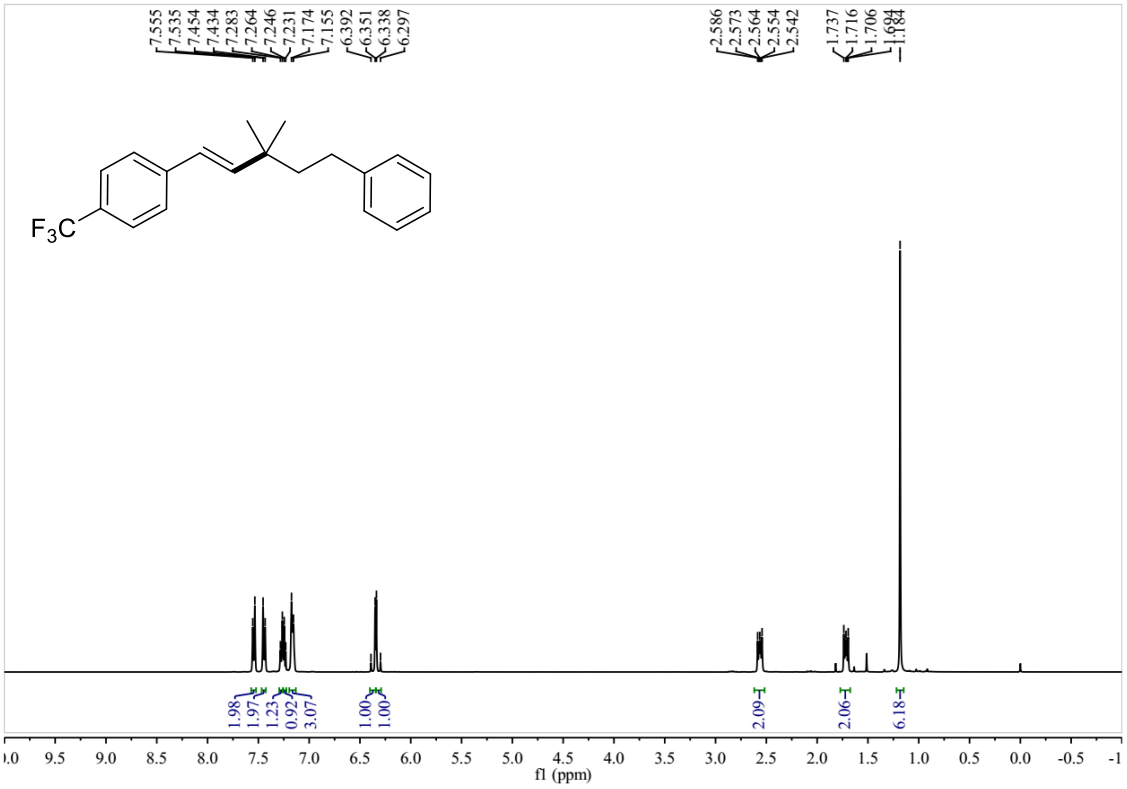
^{1}H NMR Spectra of **3h**



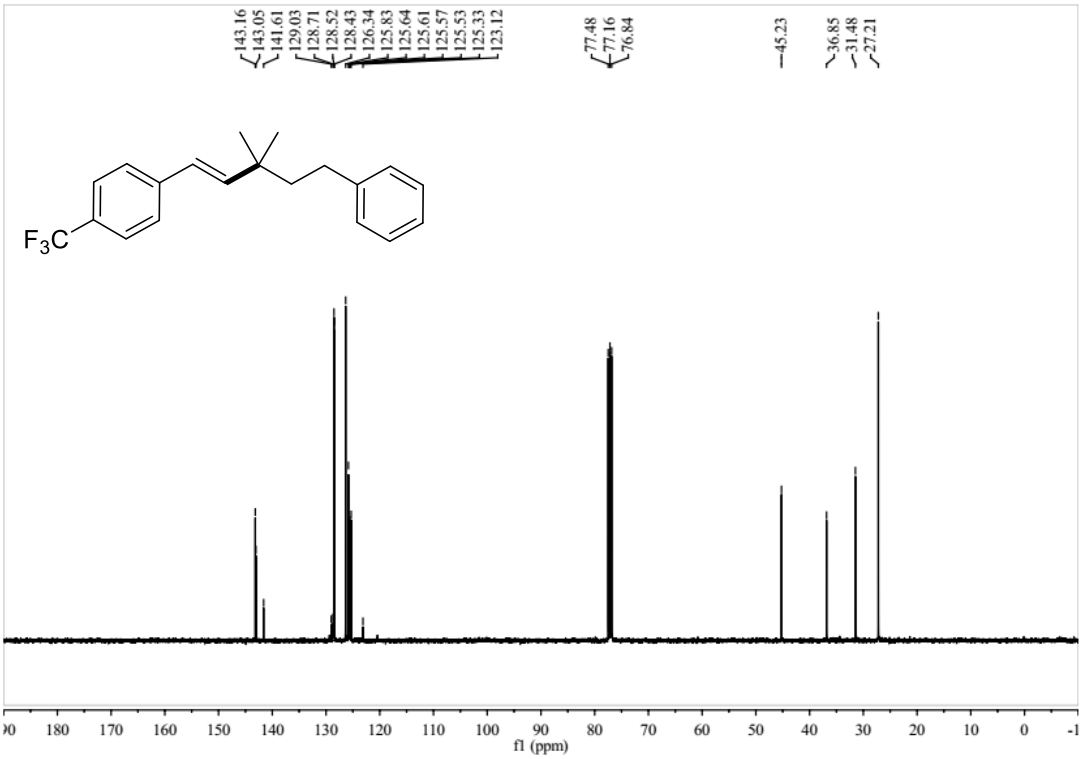
^{13}C NMR Spectra of **3h**



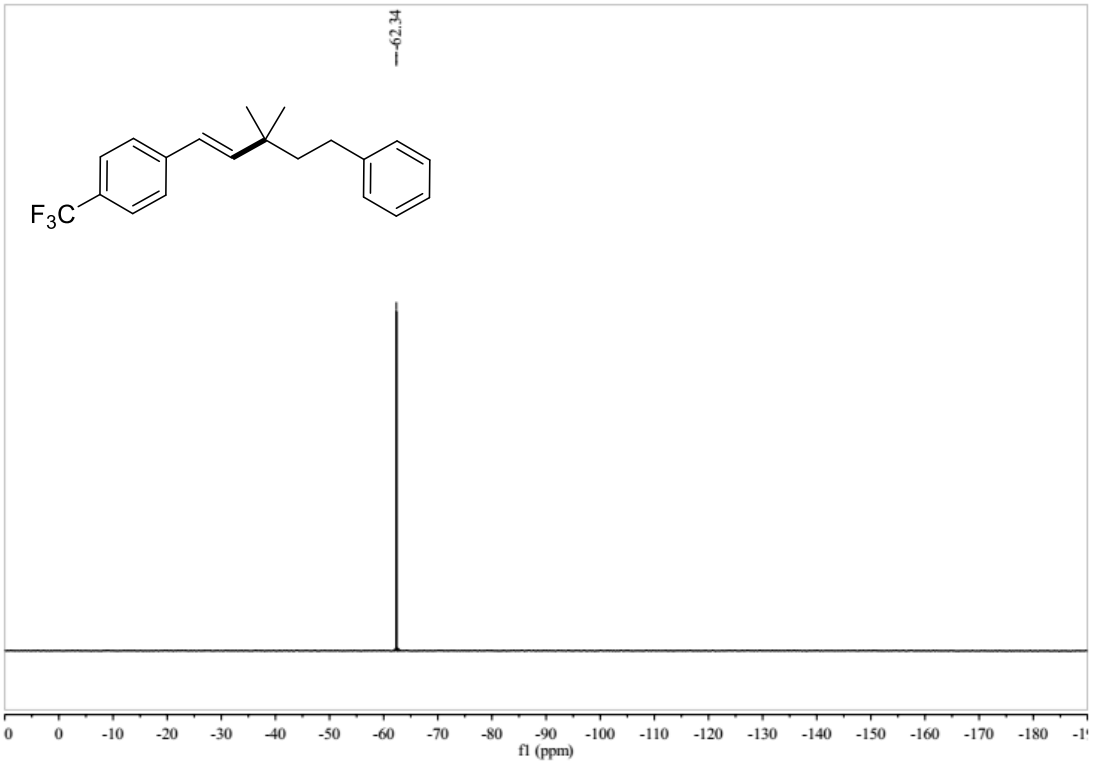
^{1}H NMR Spectra of **3i**



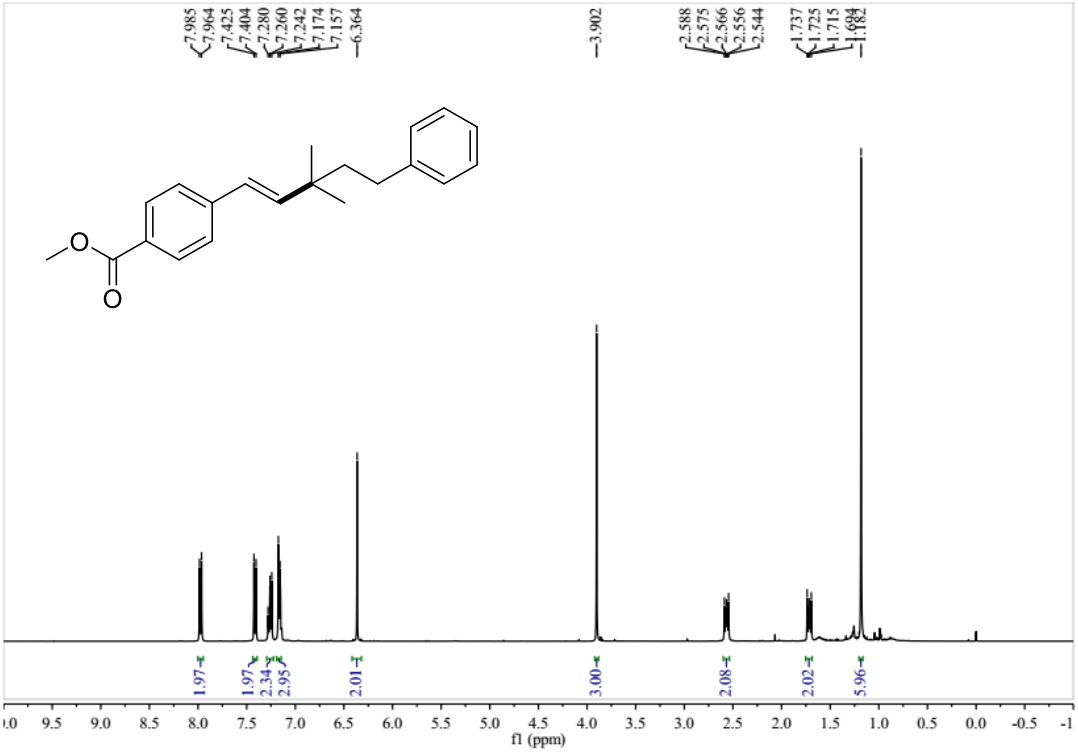
^{13}C NMR Spectra of **3i**



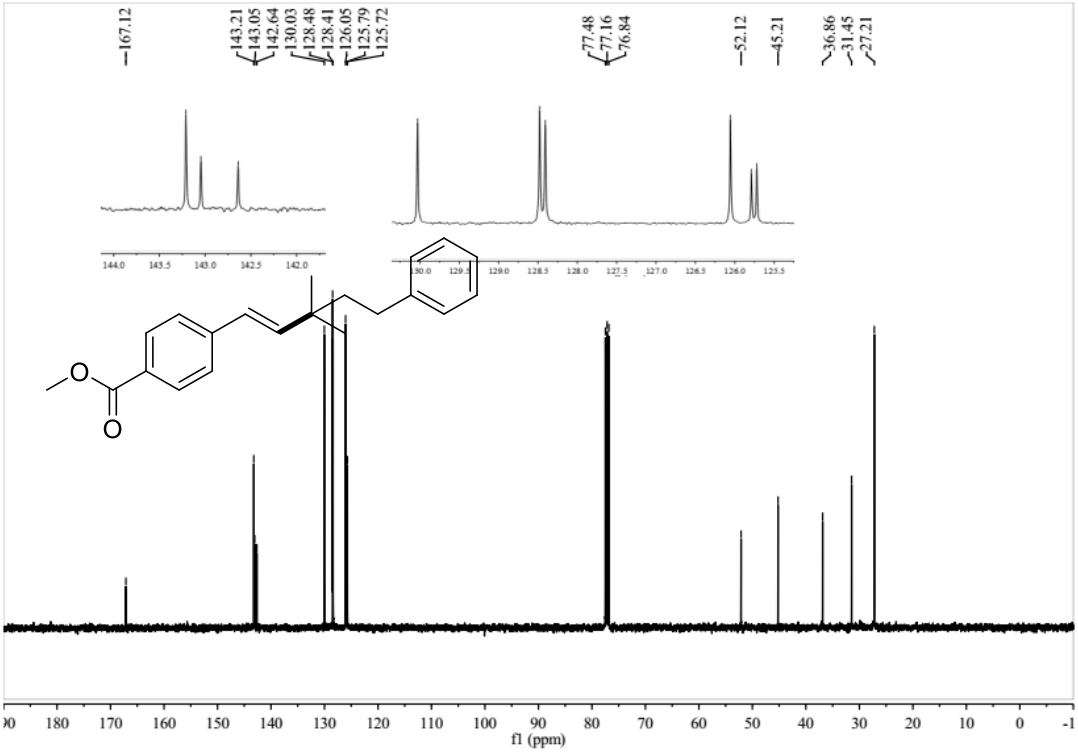
^{19}F NMR Spectra of **3i**



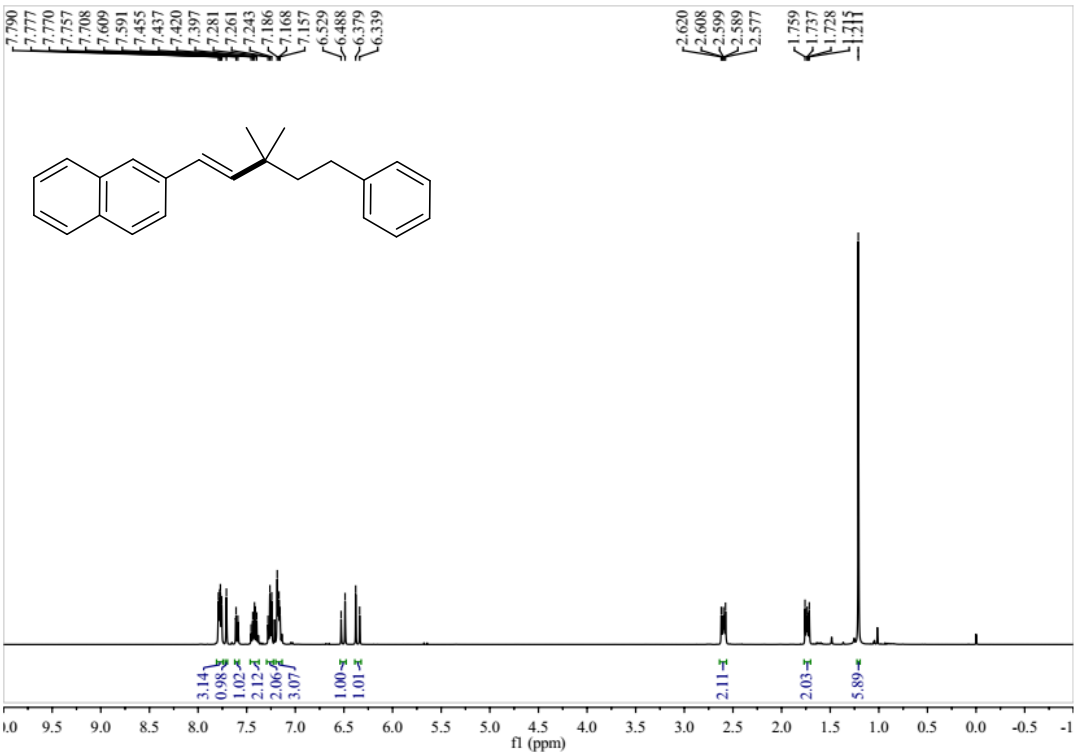
^{1}H NMR Spectra of **3j**



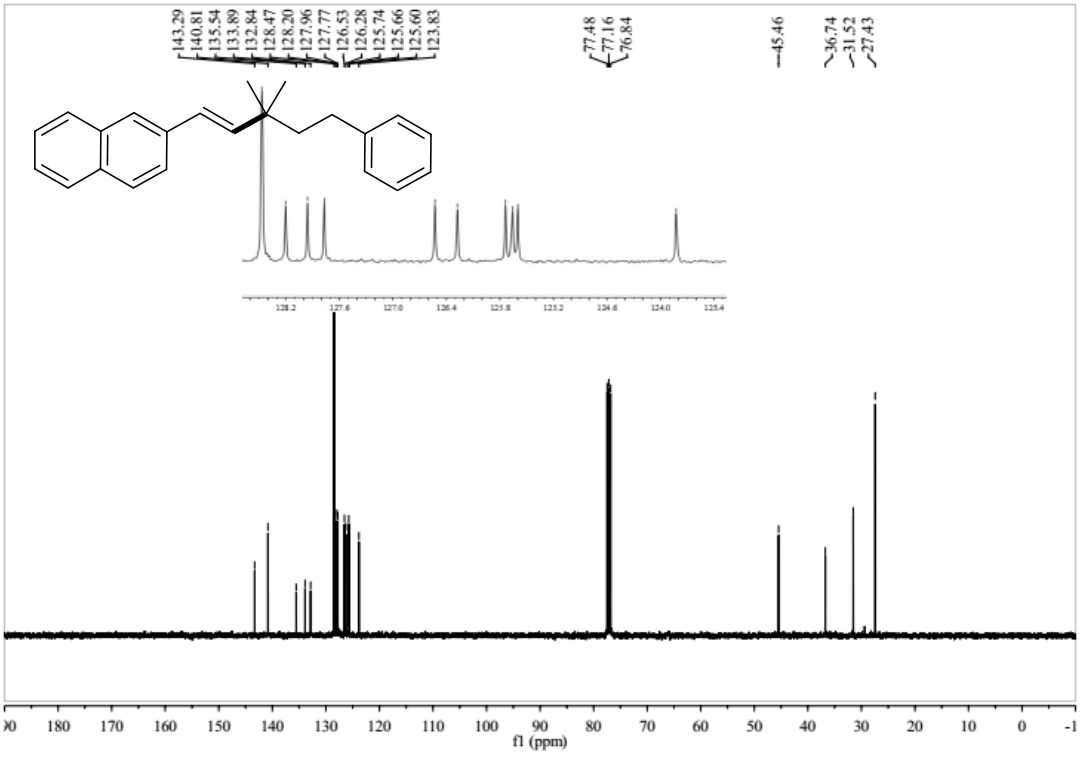
^{13}C NMR Spectra of **3j**



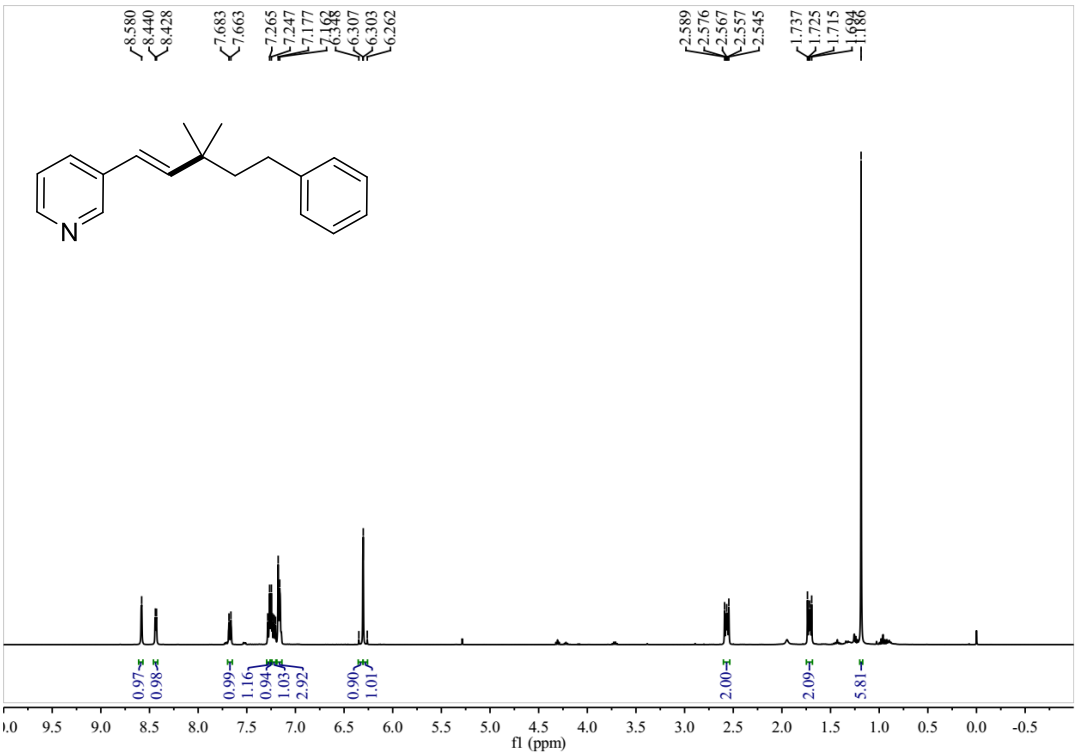
^{1}H NMR Spectra of **3k**



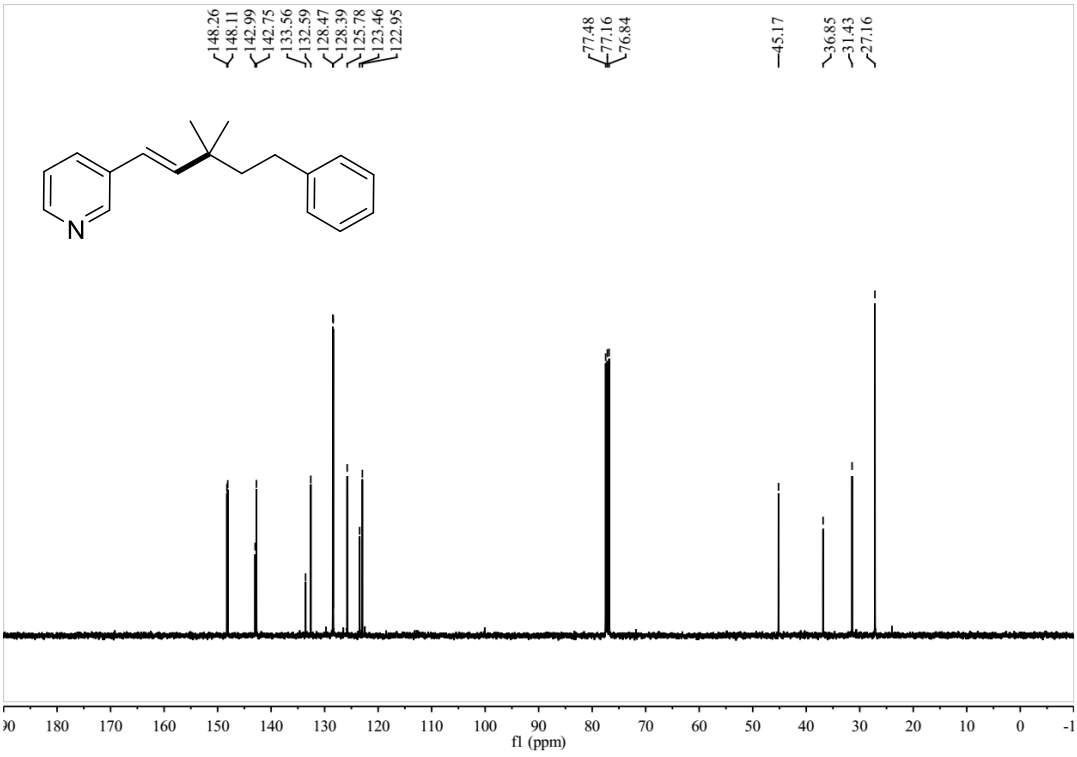
^{13}C NMR Spectra of **3k**



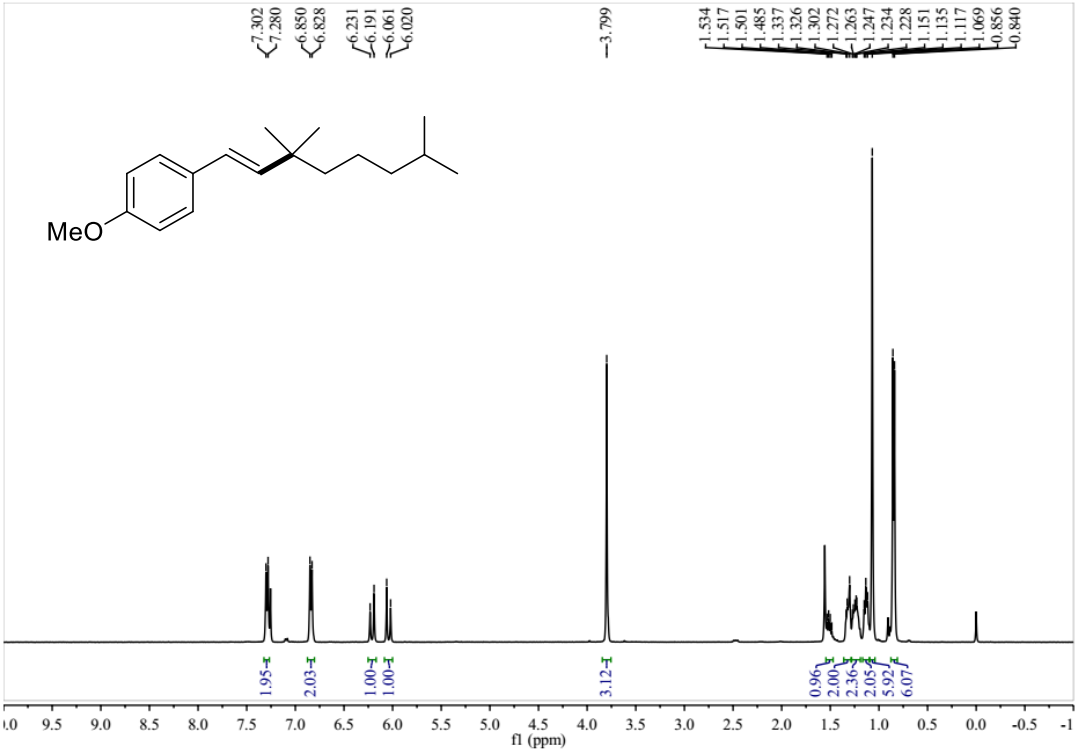
^{1}H NMR Spectra of **3l**



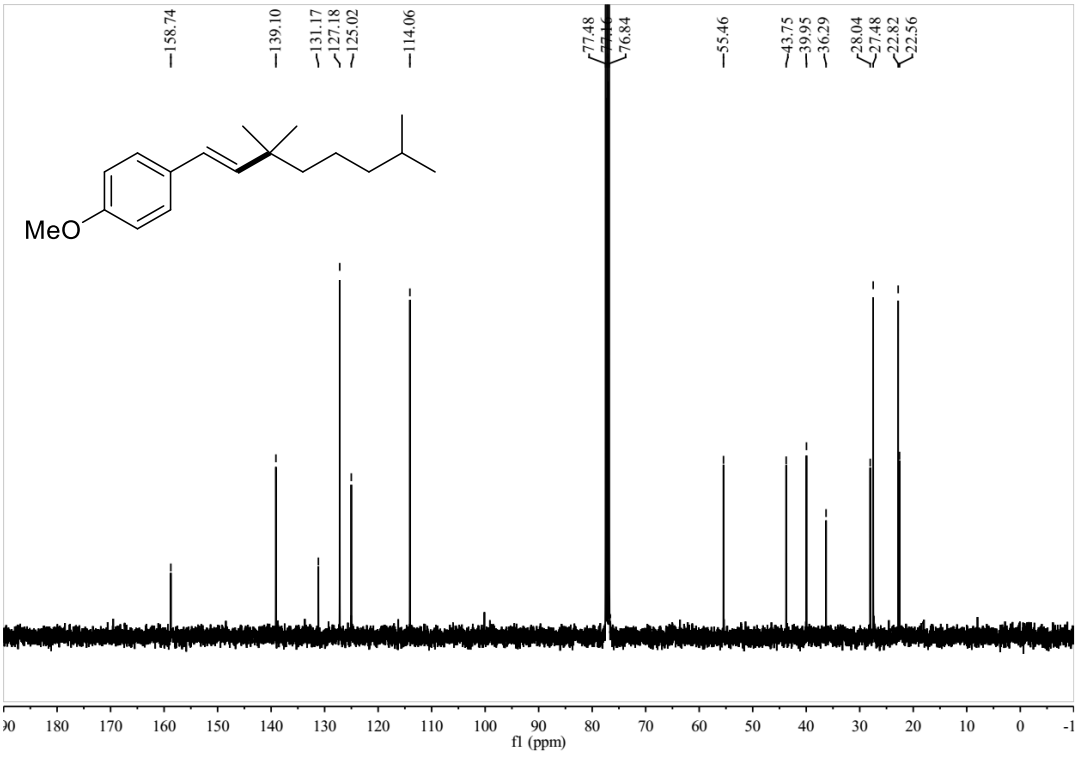
^{13}C NMR Spectra of **3l**



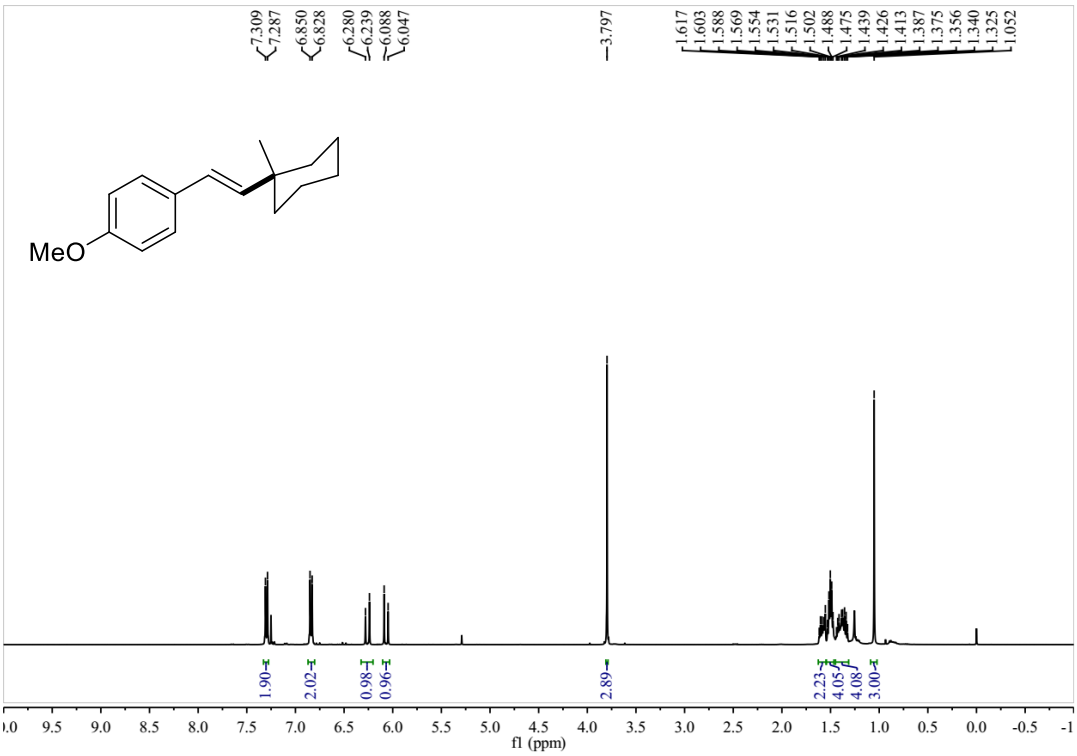
^{1}H NMR Spectra of **4a**



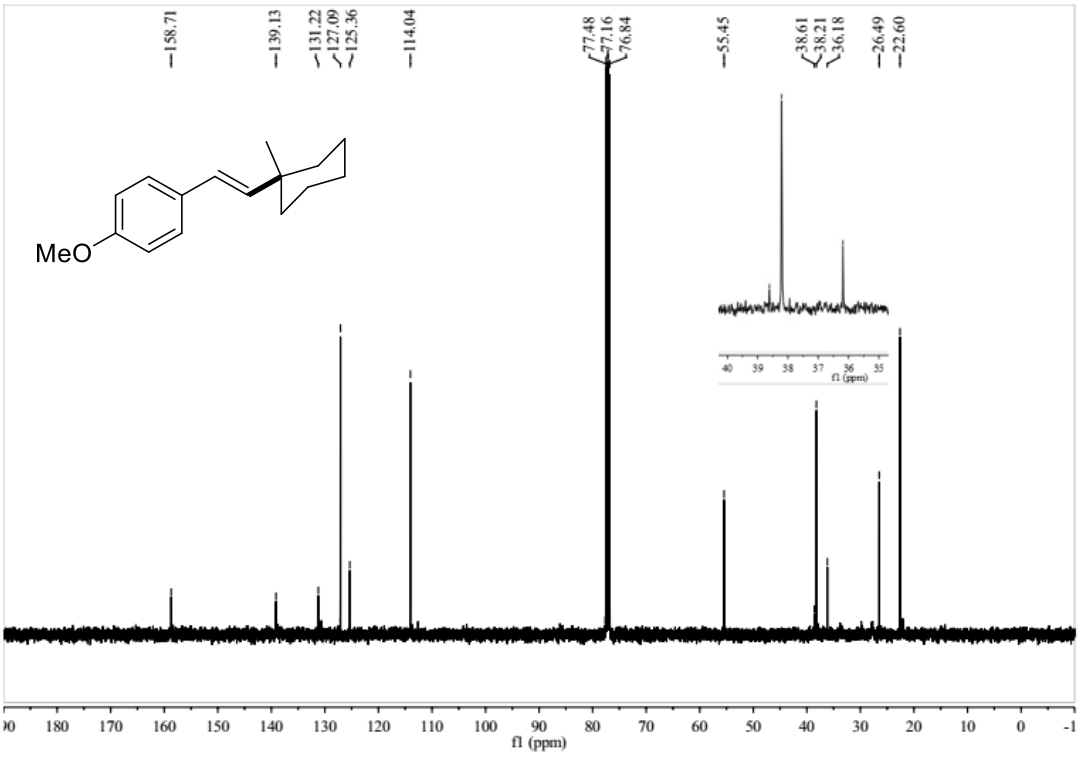
^{13}C NMR Spectra of **4a**



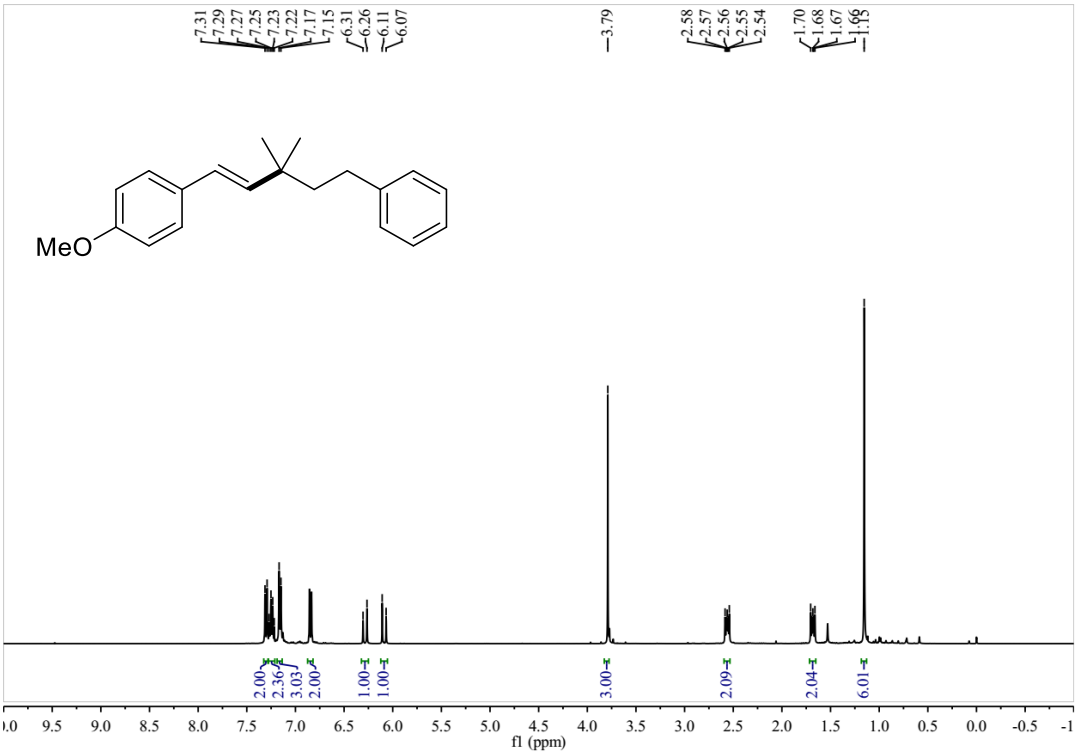
^{1}H NMR Spectra of **4b**



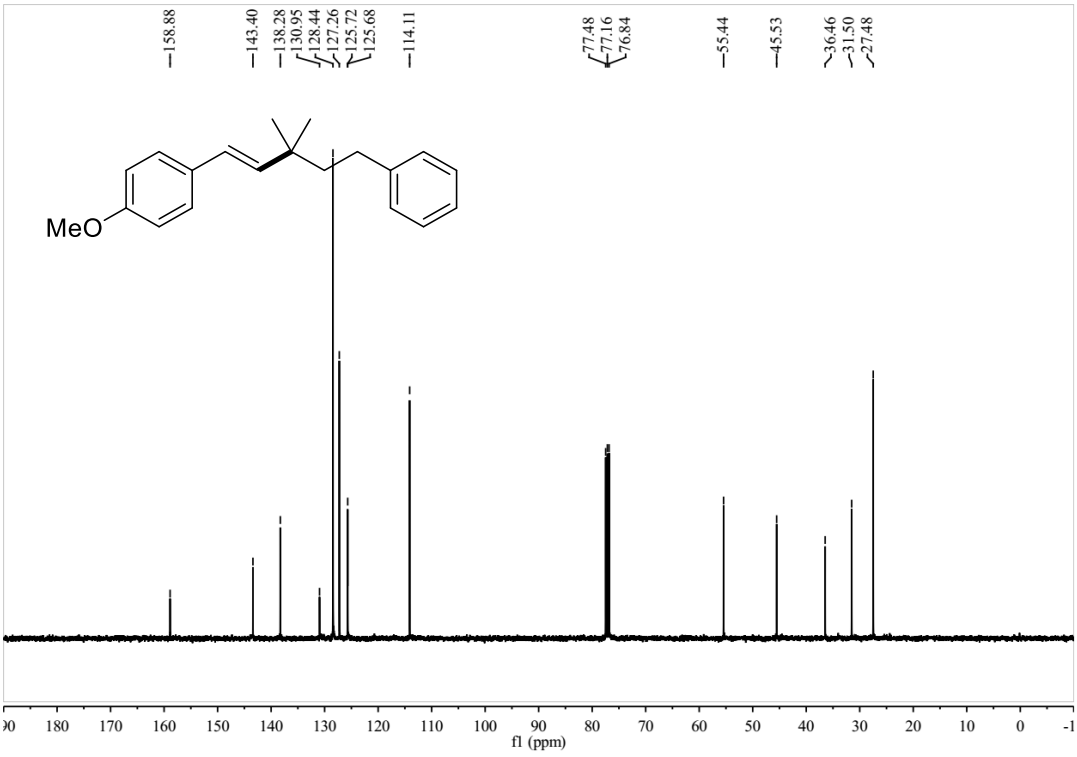
^{13}C NMR Spectra of **4b**



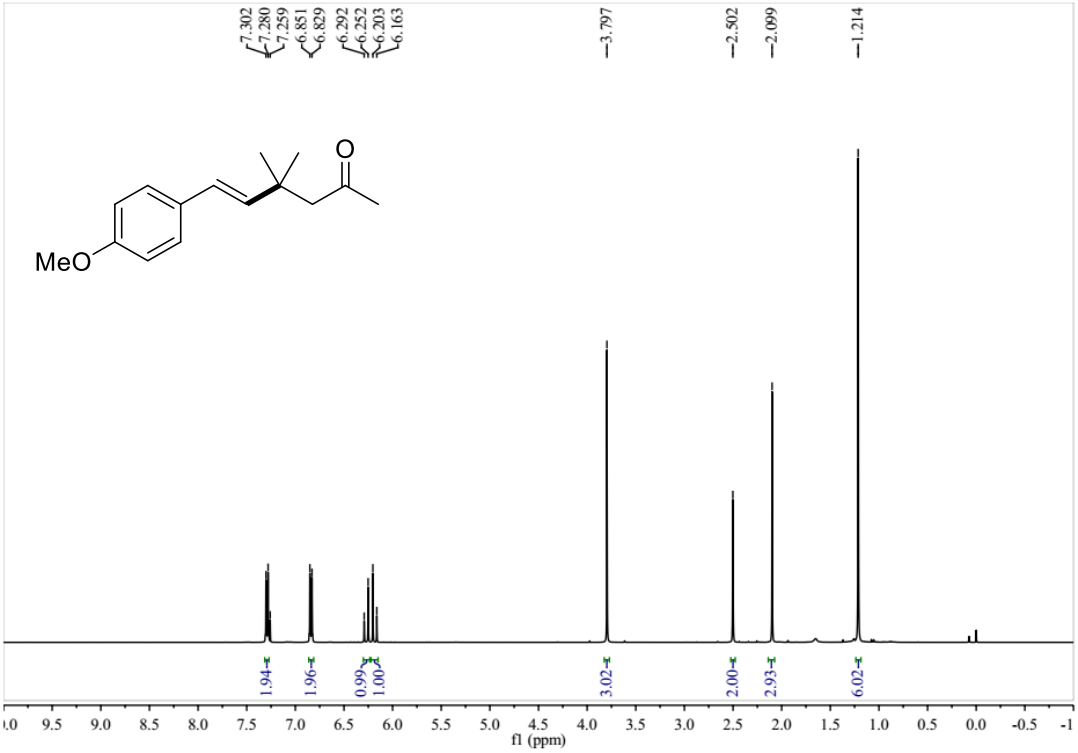
^{1}H NMR Spectra of **4c**



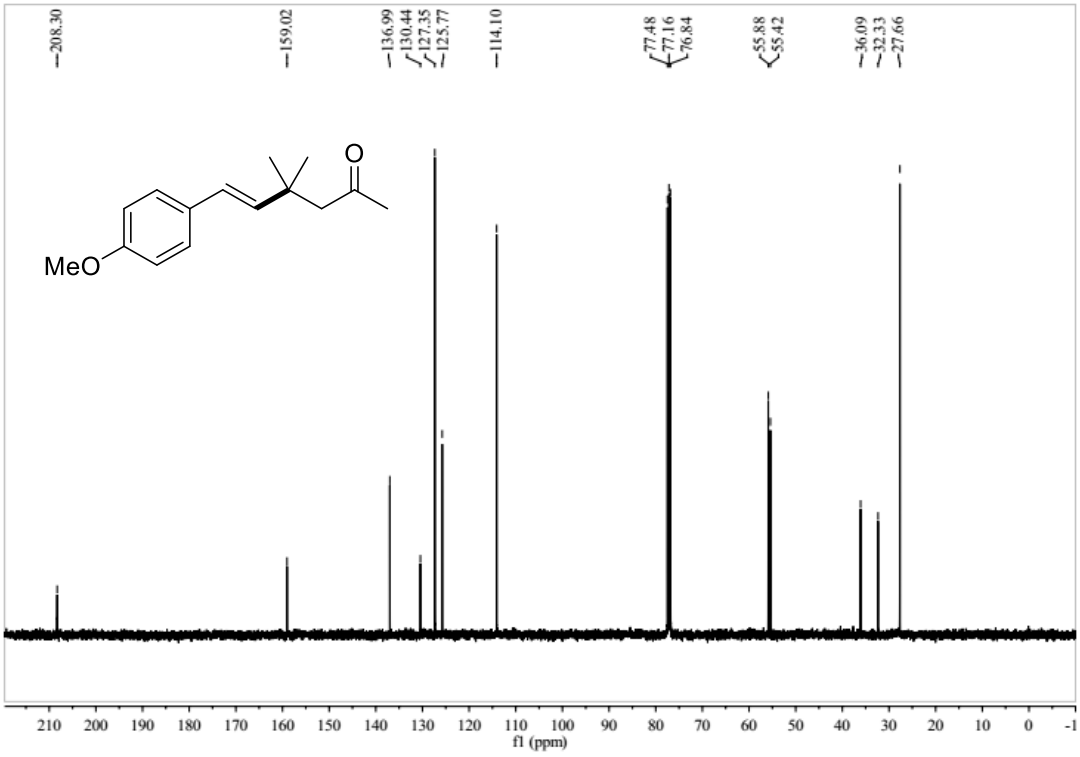
^{13}C NMR Spectra of **4c**



^{1}H NMR Spectra of **4d**



^{13}C NMR Spectra of **4d**



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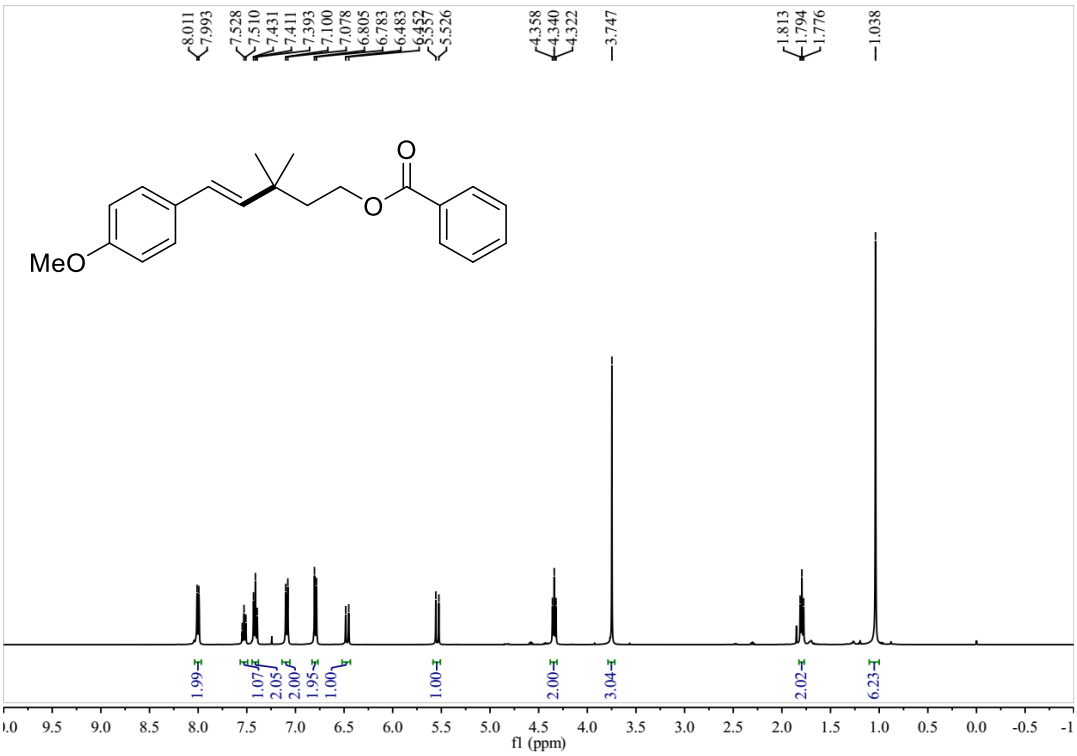

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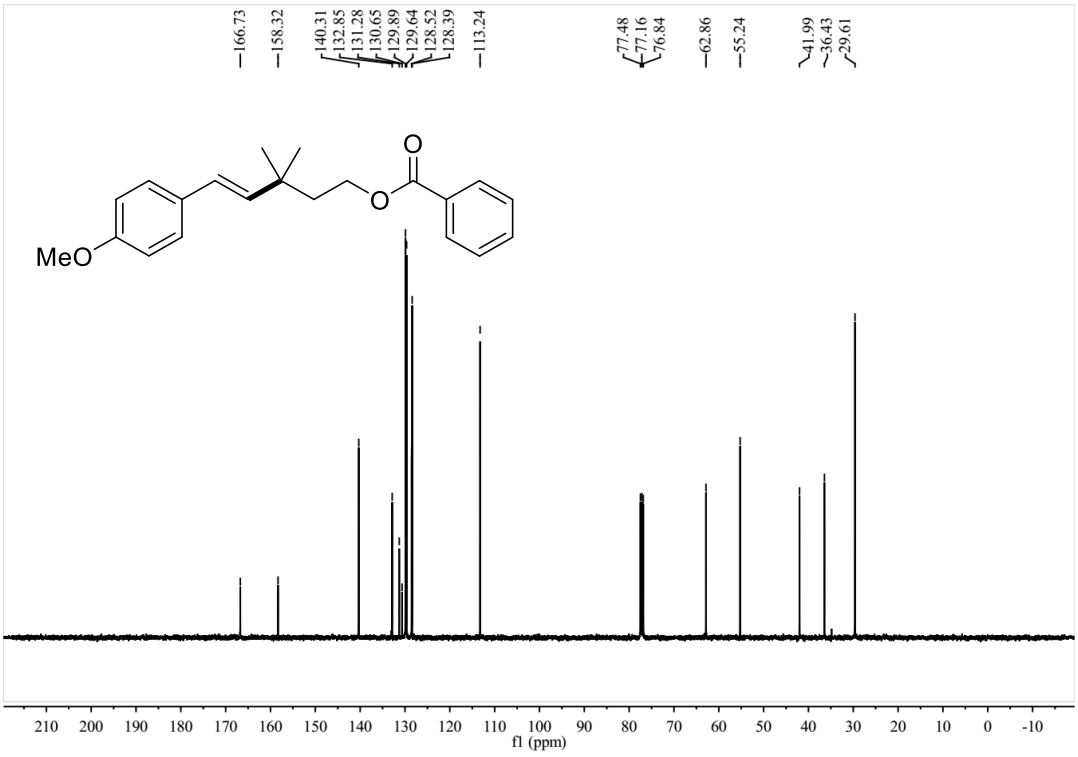
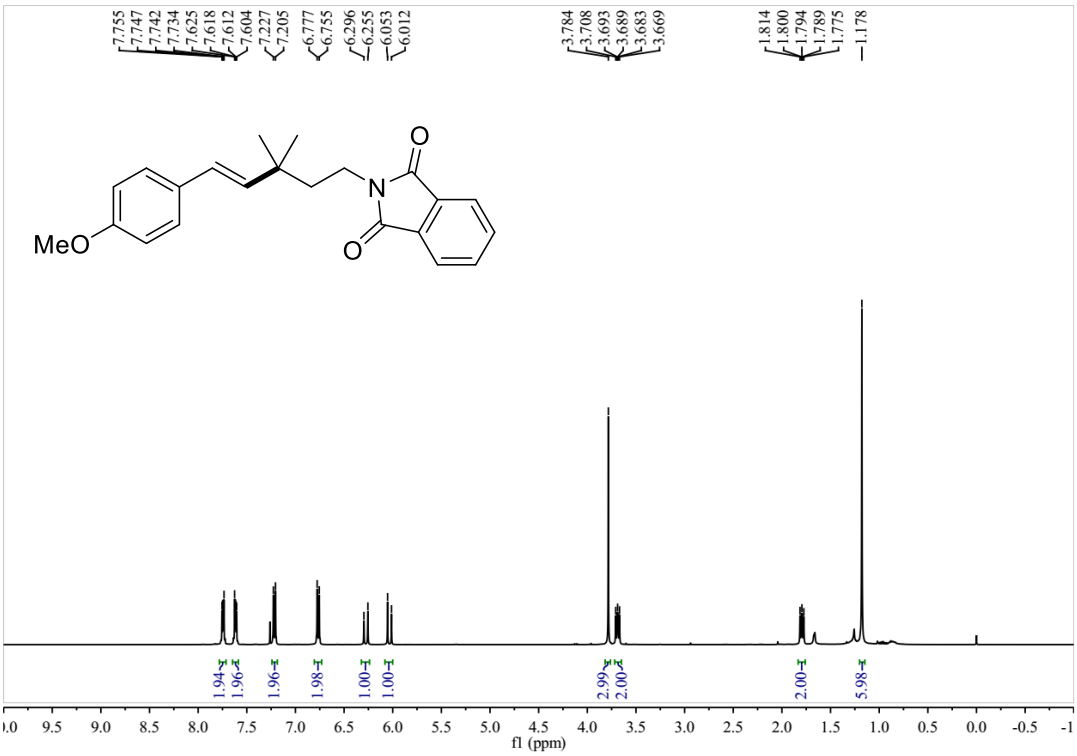
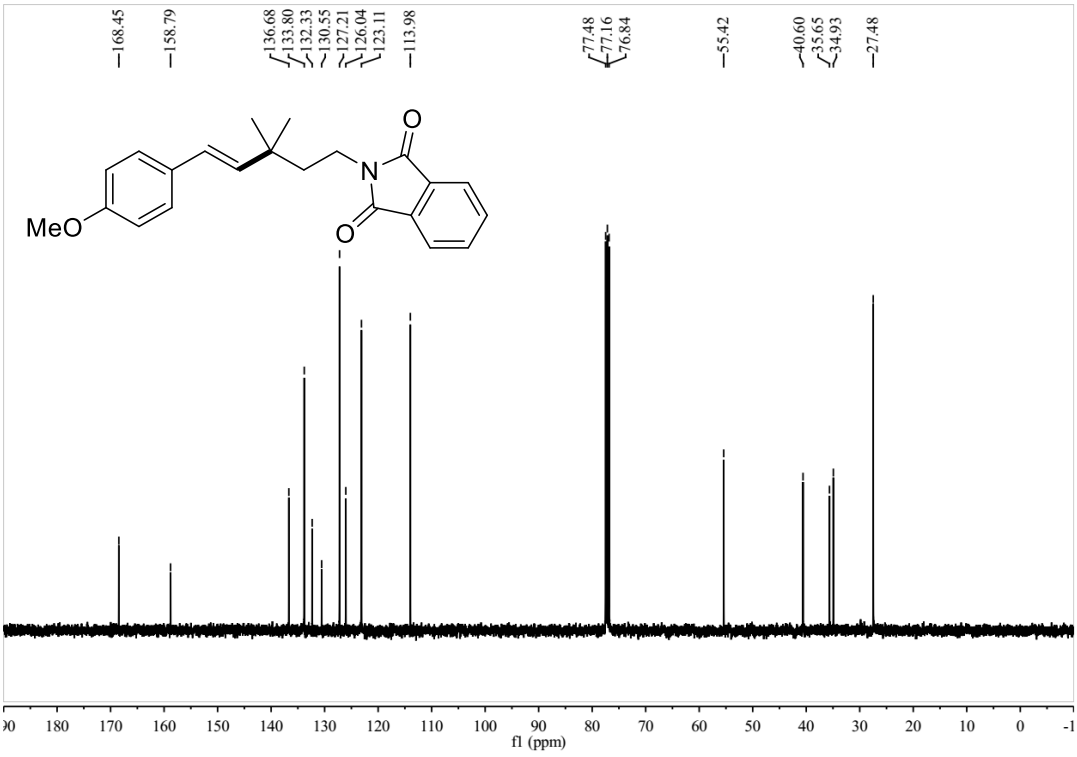


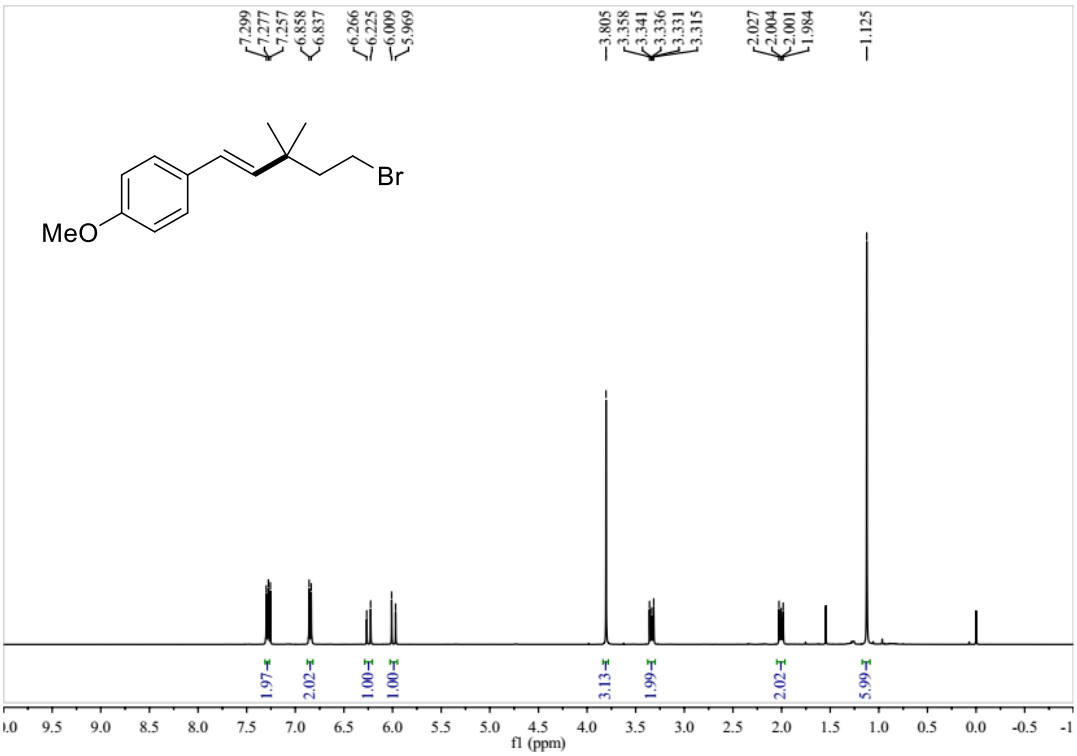
^{1}H NMR Spectra of **4f**



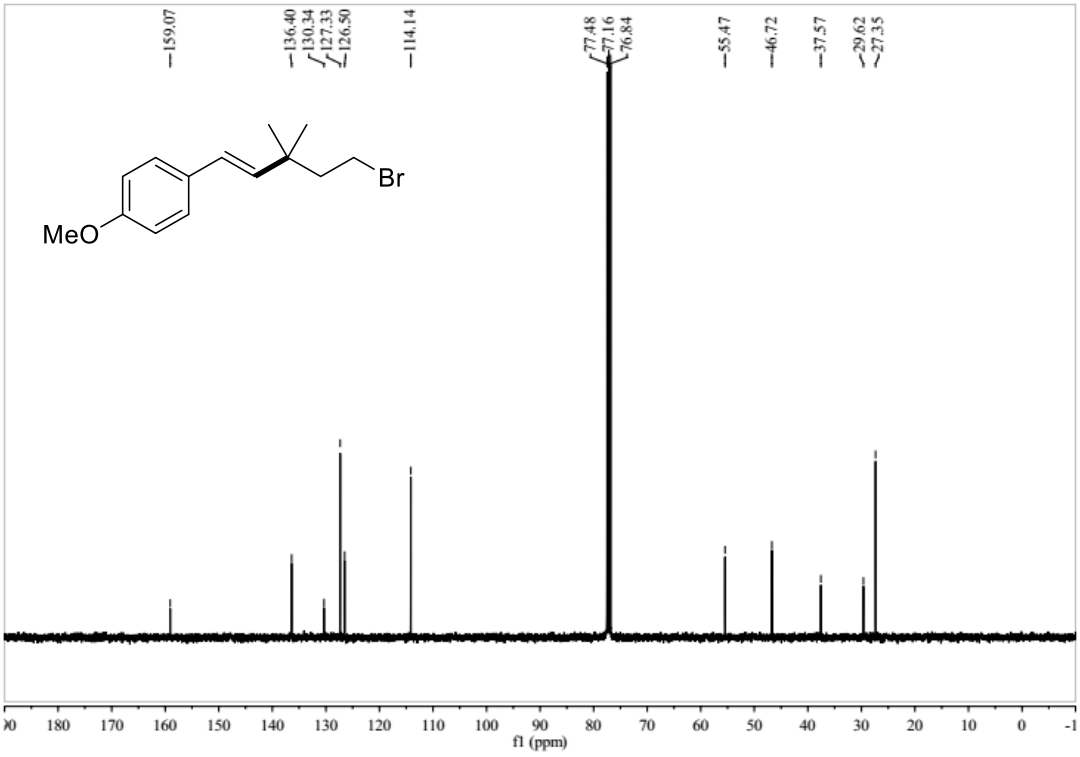
^{13}C NMR Spectra of **4f**



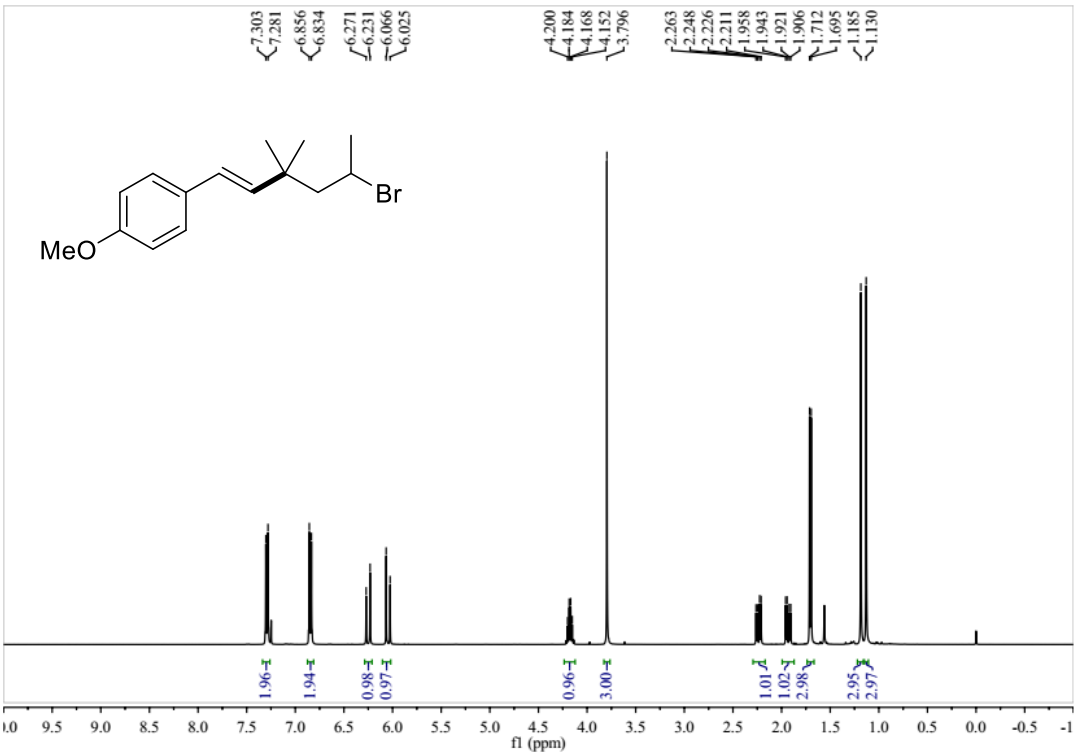
^{1}H NMR Spectra of **4g**



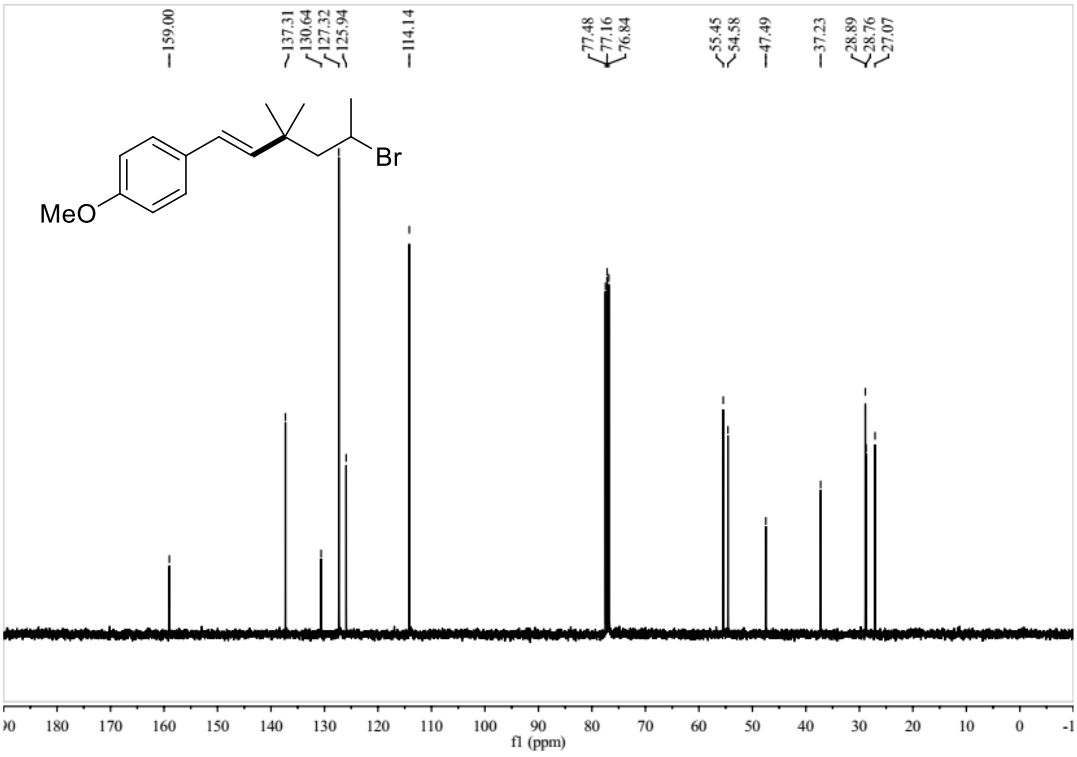
^{13}C NMR Spectra of **4g**



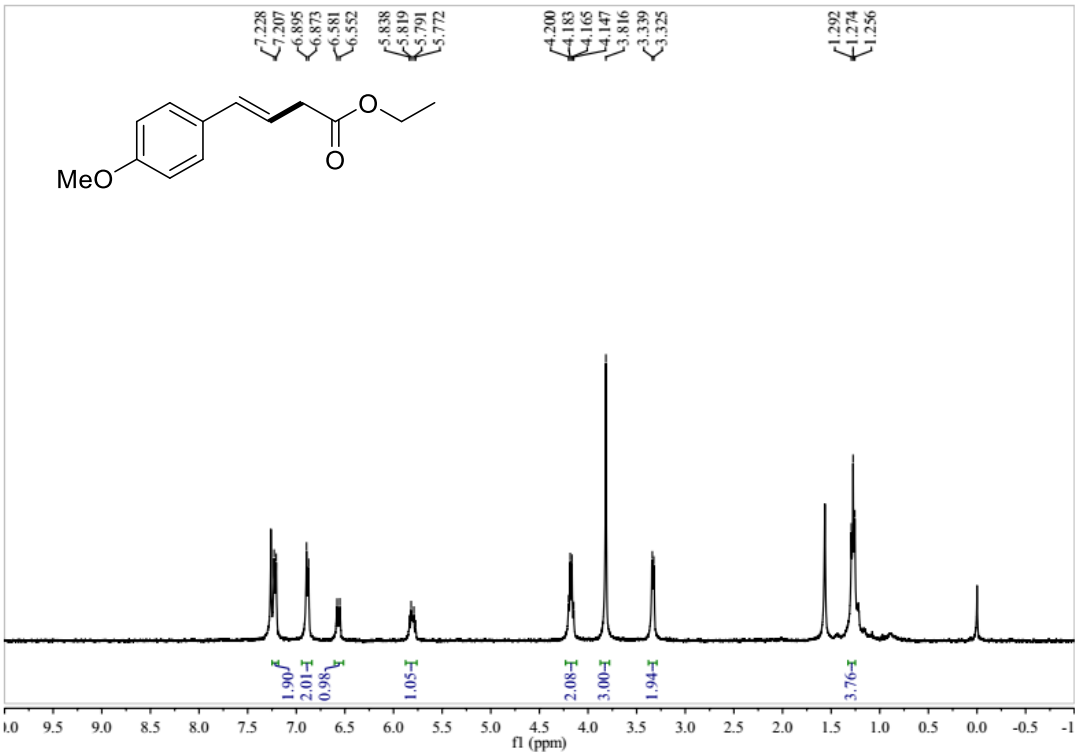
^{1}H NMR Spectra of **4h**



^{13}C NMR Spectra of **4h**



^{1}H NMR Spectra of **4j**



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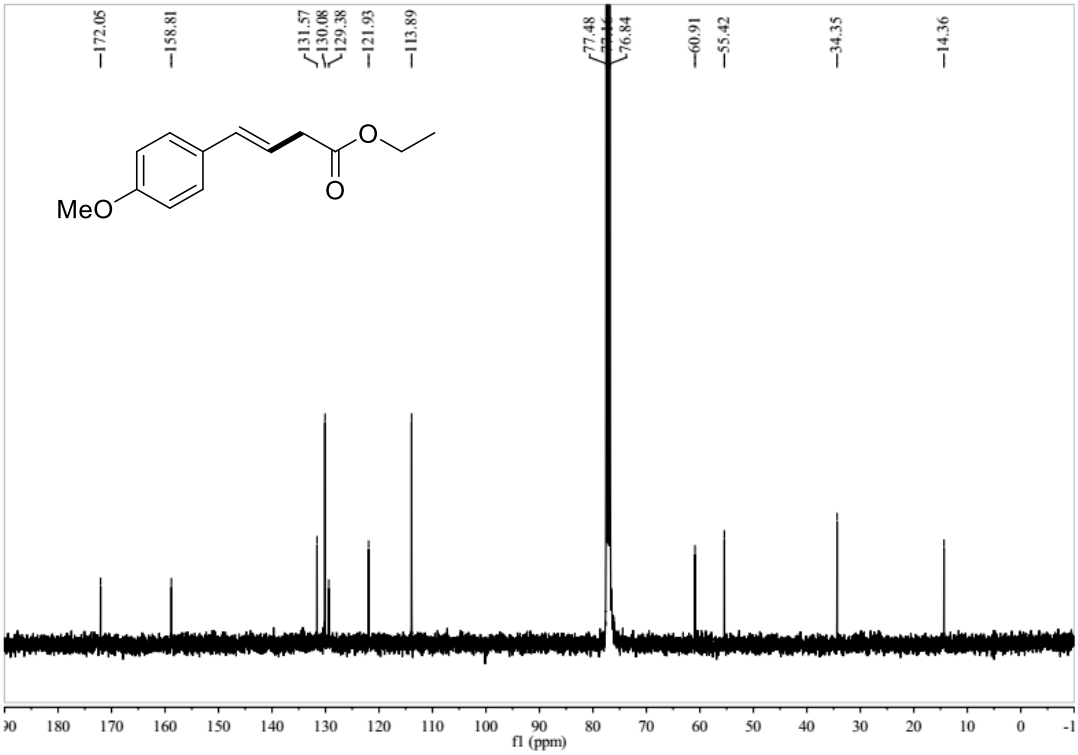

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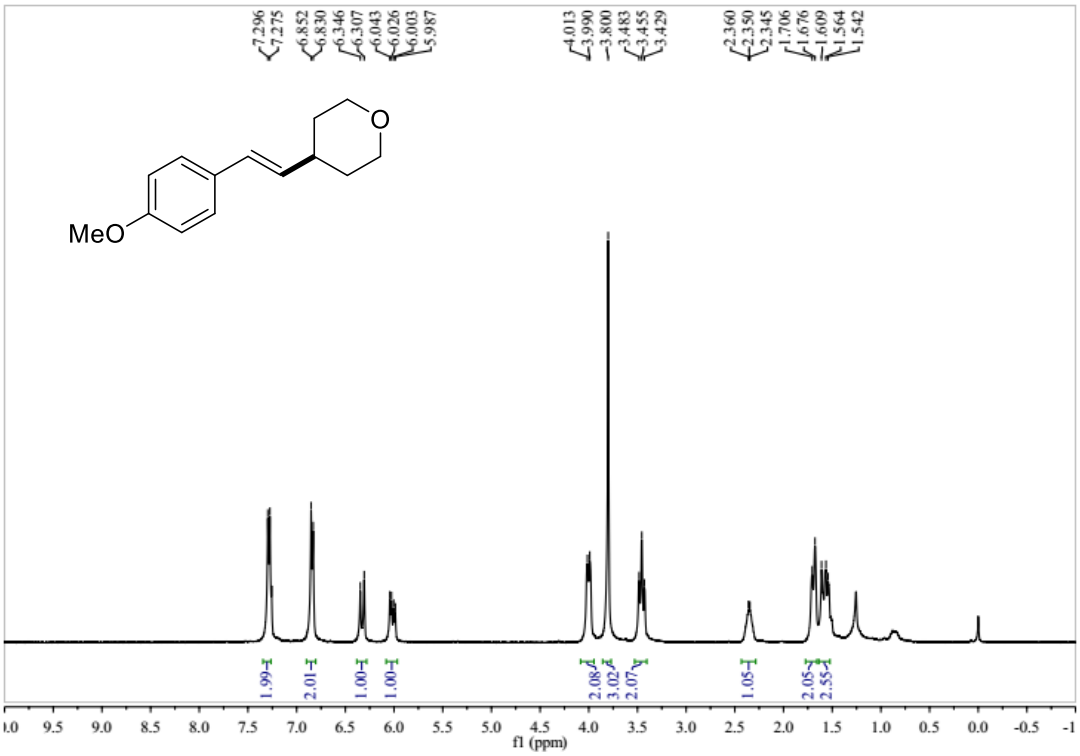

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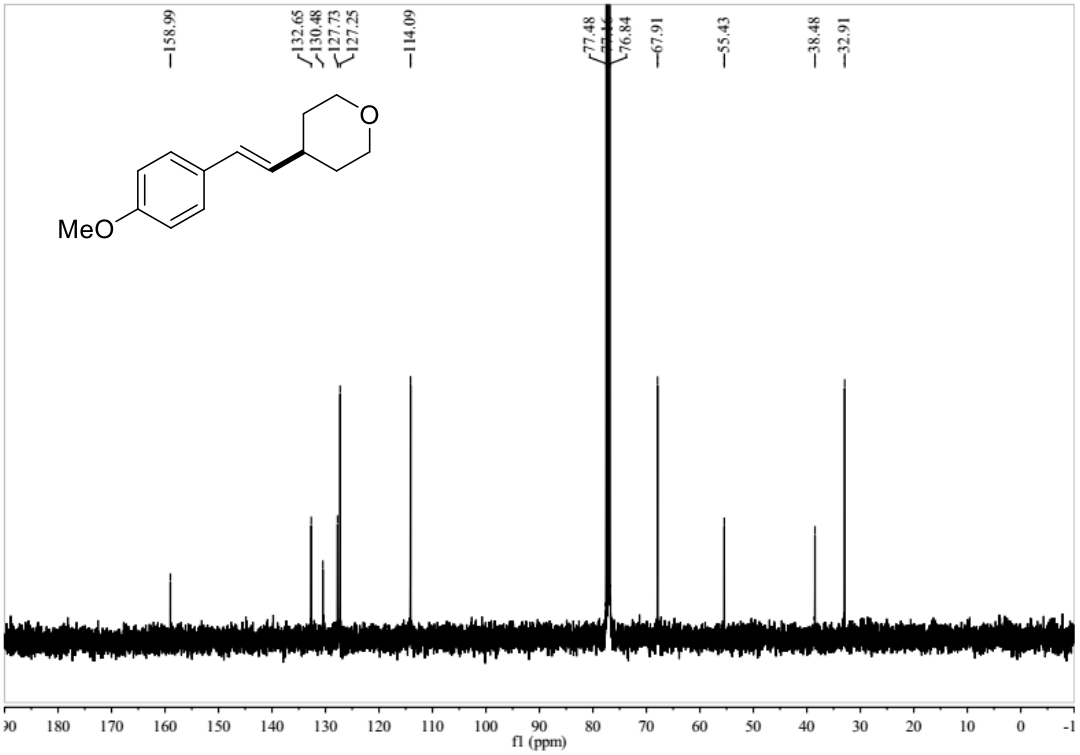
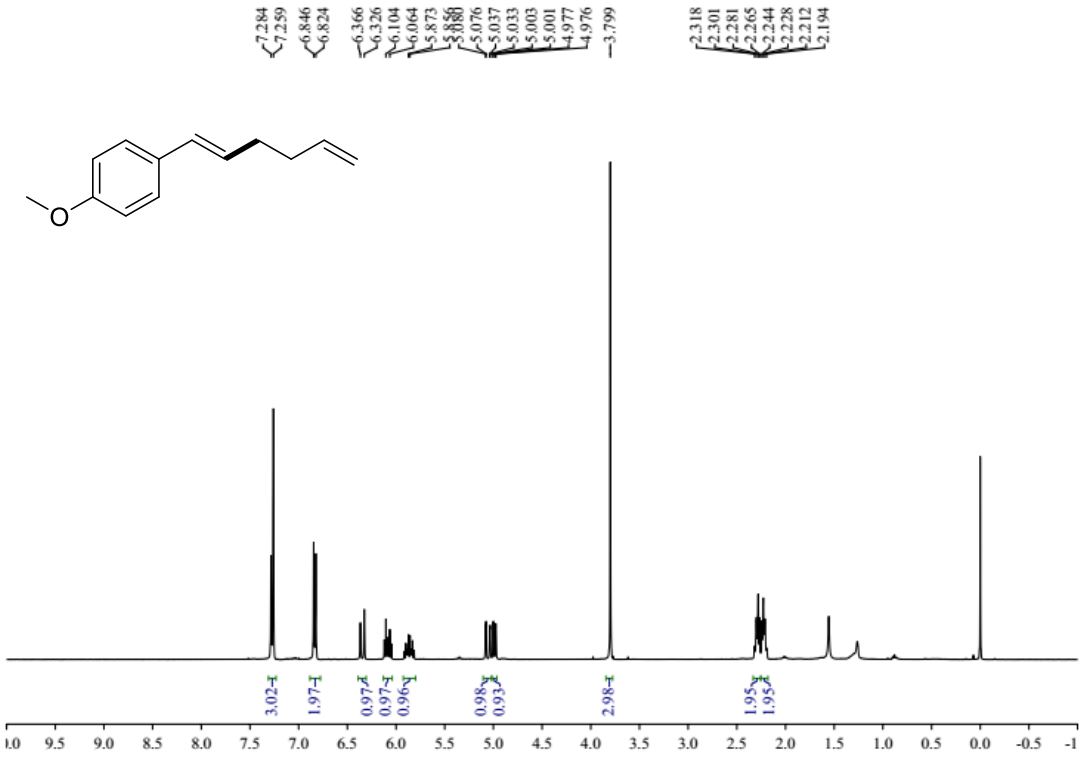


^{1}H NMR Spectra of **6b**



^{13}C NMR Spectra of **6b**