Supplementary Information for

Divergent 1,2-Carboallylation of Terminal Alkynes Enabled by Metallaphotoredox Catalysis with Switchable Triplet Energy Transfer

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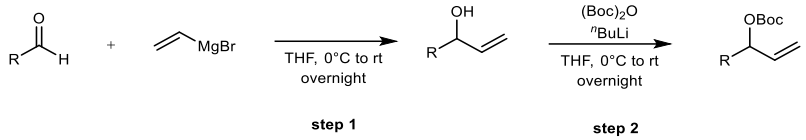
1. General Information

Commercial reagents were purchased from Aldrich, TCI, Energy Chemical, Bide, Leyan.com, and J&K Chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates.^{1}H, ^{19}F NMR, and ^{13}C NMR spectra were recorded on Bruker 400 (400, 376, and 100 MHz) and Bruker 600 (600, 564, and 150 MHz), and are internally referenced to residual solvent signals (for $CDCl_3$, 7.26 and 77.0 ppm). Data for ^{1}H NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry and Shanghai Jiao Tong University mass spectrometry facilities. All allylic carbonates and alkyl trifluoroborates were prepared according to literature procedures or synthetic procedures described in this Supporting Information. Photochemical experiments have been performed using a blue LED light (λ_{max} = 467 nm, 393 mW/cm^2, Kessil A360W E-SERIES TUNA Blue LED).

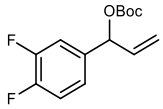
2. Preparation of substrates

2.1. preparation of Allylic Carbonates



Step 1. Based on a reported literature procedure,[1] aldehyde (1 equiv.) was dissolved in dry THF (0.5 M) at 0°C. Vinylmagnesium bromide (1.2 equiv. 1 M in THF) was added slowly into above solution, the mixture was moved to room temperature after the addition of vinylmagnesium bromide and stirred overnight. Then saturated NH_4Cl was added and extracted with EtOAc, dried over $MgSO_4$, filtered, evaporated and the residue was purified by chromatography on silica gel to afford the corresponding substitutive allylic alcohol.

Step 2. Based on a slightly modified literature procedure,[1] to a flame-dried round-bottomed flask with stir bar was added allylic alcohol and dried THF (0.5 M), then ^{n}BuLi (1.6 M in hexane, 1.0 equiv.) was added dropwise at 0℃. After stirring for 20 mins at this temperature, the $(Boc)_2O$ (1.2 equiv.) was added and the reaction mixture was stirred overnight. The reaction mixture was quenched by water and stirred vigorously, then extrated with ethyl acetate (3 times), washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.



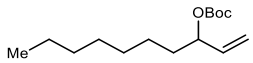
***tert*-butyl (1-(3,4-difluorophenyl)allyl) carbonate (S1):** According to the step 1 and step 2, compound **S1** was prepared from 3,4-difluorobenzaldehyde (1.42 g, 10 mmol), affording **S1** as a pale yellow oil in 36% (0.95 g) isolated yield (2 steps total yield) after column chromatography.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.06 (m, 3H), 6.02 – 5.91 (m, 2H), 5.35 – 5.25 (m, 2H), 1.47 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.01 – -137.53 (m, 1F), -137.99 – -138.48 (m, 1F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.47, 151.41 (dd, *J* = 18.7, 12.7 Hz), 148.94 (dd, *J* = 18.8, 12.7 Hz), 135.80 (dd, *J* = 5.4, 3.8 Hz), 135.43, 123.14 (dd, *J* = 6.5, 3.7 Hz), 117.76, 117.27 (d, *J* = 17.4 Hz), 116.12 (d, *J* = 18.1 Hz), 82.66, 77.76 (d, *J* = 1.6 Hz), 27.67.

HRMS (ESI): $C_{14}H_{17}F_2O_3^+$ ($M+H^+$): 271.1141, found: 271.1145.



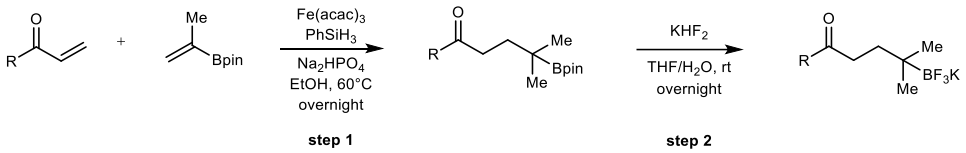
***tert*-butyl dec-1-en-3-yl carbonate (S2)**: According to the step 1 and step 2, compound **S2** was prepared from octanal (385.6 mg, 3 mmol), affording **S2** as a colorless oil in 36% (0.27 g) isolated yield (2 steps total yield) after column chromatography.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.84 – 5.73 (m, 1H), 5.26 (m, 1H), 5.17 (m, 1.2 Hz, 1H), 4.97 (q, *J* = 6.6 Hz, 1H), 1.72 – 1.64 (m, 1H), 1.59 – 1.52 (m, 1H), 1.48 (s, 9H), 1.33 – 1.21 (m, 10H), 0.91 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.06, 136.50, 116.89, 81.85, 78.09, 34.27, 31.73, 29.28, 29.14, 27.81, 25.06, 22.60, 14.06.

HRMS (ESI): $C_{15}H_{29}O_3^+$ ($M+H^+$): 257.2112, found: 257.2110.

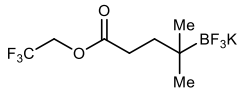
2.2 preparation of alkyl trifluoroborates



Step 1. Based on a slightly modified literature procedure,[2] to a solution of 4,4,5,5-tetramethyl-2-(prop-1-en-2-yl)-1,3,2- dioxaborolane (1.0 equiv.) in EtOH (0.25 M)

was added anhydrous Na_2HPO_4 (2.0 equiv.), $Fe(acac)_3$ (10 mol%), acceptor olefin (3.0 equiv.), and $PhSiH_3$ (3.0 equiv.). The resulting mixture was heated in an oil bath preheated to 60 °C with stirring overnight. The reaction mixture was then cooled to room temperature and diluted with brine and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 times). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude product was then purified by silica gel flash column chromatography. The pinacol boronic esters were obtained after column chromatography.

Step 2. Alkyl trifluoroborates were prepared according to a previously reported procedure.[3] To a stirred solution of boronic ester (1.0 equiv.) in tetrahydrofuran (0.43 M) was added aqueous solution of KHF_2 (6.0 equiv.) in H_2O (0.87 M) dropwise at ambient temperature and the reaction mixture was stirred overnight. Then, all volatile materials were removed on a rotary evaporator including H_2O, the residue was redissolved in acetone and heated to 50℃, stirred for another 1h. The suspension was filtered while it was hot to filter KHF_2 and obtain a transparent solution. The combined washings were collected and concentrated in vacuo to give the desired trifluoroborate as a colorless crystalline or amorphous solid. Wash the white solid with ice ether (-18℃) to obtain the final potassium salt. All alkyl trifluoroborates were prepared through this method.



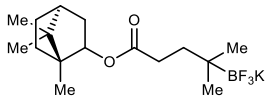
2,2,2-trifluoroethyl 4-methyl-4-(trifluoro-λ^4-boraneyl)pentanoate, potassium salt (S3): According to the step 1 and 2, compound **S3** was prepared from 2,2,2-trifluoroethyl acrylate (2.31 g, 15 mmol), affording **S3** as a white powder in 40% (0.6 g) isolated yield (2 steps total yield).

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 4.60 (q, *J* = 9.0 Hz, 2H), 2.48 – 2.41 (m, 2H), 1.49 – 1.41 (m, 2H), 0.70 (s, 6H).

^{19}F NMR (376 MHz, Acetone-d_6) δ -74.55 (t, *J* = 9.0 Hz, 3F), -150.71 (d, *J* = 92.6 Hz, 3F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.97, 129.01 (q, *J* = 276.5 Hz), 64.44 (q, *J* = 35.4 Hz), 41.48, 35.43, 29.65.

^{11}B NMR (193 MHz, Acetone-d_6) δ 6.04.



(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-methyl-4-(trifluoro-l4-boraneyl)pentanoate, potassium salt (S4): According to the step 1 and 2, compound **S4** was prepared from (1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl acrylate (3.12 g, 15 mmol), affording **S4** as a white powder in 45% (0.79 g) isolated yield (2 steps total yield).

^{1}H NMR (400 MHz, Acetone-d_6) δ 4.61 (dd, *J* = 7.2, 3.9 Hz, 1H), 2.33 – 2.26 (m, 2H), 1.76 – 1.66 (m, 4H), 1.61 – 1.52 (m, 1H), 1.46 – 1.39 (m, 2H), 1.18 – 1.07 (m, 2H), 1.02 (s, 3H), 0.85 (s, 3H), 0.83 (s, 3H), 0.69 (s, 6H).

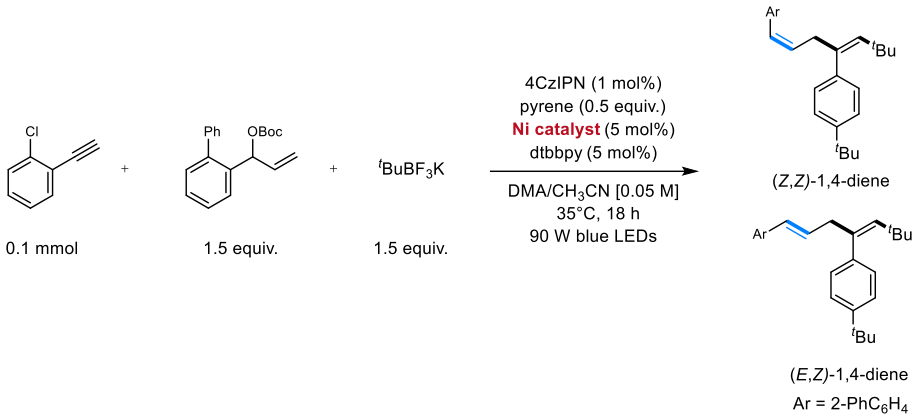
^{19}F NMR (376 MHz, Acetone-d_6) δ -150.81 (d, *J* = 98.2 Hz, 3F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.89, 84.57, 53.52, 51.81, 50.23, 43.82, 41.67, 38.84, 36.33, 31.98, 29.69, 29.63, 24.81, 24.74, 16.14.

^{11}B NMR (193 MHz, Acetone-d_6) δ 5.4.

3. Reaction optimization studies

Table S1. Nickel catalyst effect

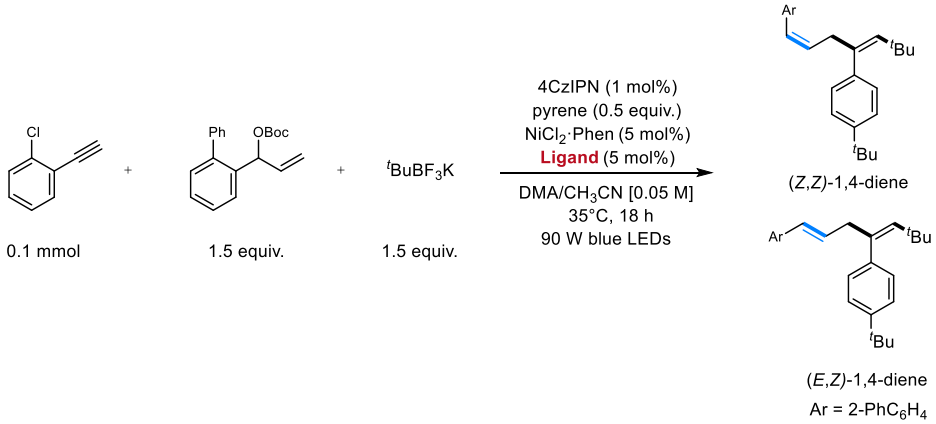


0.1 mmol | 1.5 equiv. | 1.5 equiv.

Entry	Ni catalyst	Yield	(*Z*,*Z*)/(*E*,*Z*)
1	$NiCl_2$·DME	59%	7/93
2	$NiBr_2$·Phen	60%	3/97
3	$NiCl_2$·Phen	87%	8/92
4	$Ni(OTf)_2$	75%	10/90
5	$NiCl_2$·$(PPh_3)_2$	70%	16/84
6	$Ni(COD)_2$	63%	14/86
7	$NiCl_2$	73%	10/90
8	$Ni(acac)_2$	40%	77/23

Reaction conditions: Alkyne (0.1 mmol), allylic carbonate (0.15 mmol) *tert*-butyl trifluoroborate (0.15 mmol), 4CzIPN (1 mol%), Ni-catalyst (5 mol%), dtbbpy (5 mol%), pyrene (0.5 equiv.), DMA/MeCN = 3:1 (0.05 M), 35 °C, 18 h.

Table S2. Ligand effect

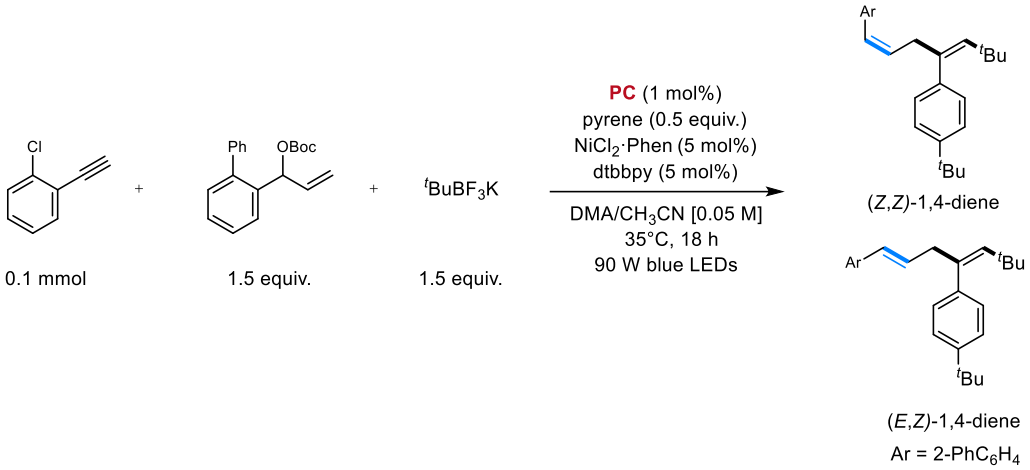


0.1 mmol | 1.5 equiv. | 1.5 equiv.

Entry	Ligand	Yield	(*Z*,*Z*)/(*E*,*Z*)
1	2,2'-bpy	84%	12/88
2	4,4'-di^{t}Bu-bpy	87%	8/92
3	4,4'-diMe-bpy	78%	10/90
4	4,4'-diOMe-bpy	78%	9/91
5	4,7-diOMe-1,10-Phen	77%	7/93
6	1,10-Phen	85%	10/90
7	PPh_3	-	-

Reaction conditions: Alkyne (0.1 mmol), allylic carbonate (0.15 mmol) *tert*-butyl trifluoroborate (0.15 mmol), 4CzIPN (1 mol%), $NiCl_2$·Phen (5 mol%), ligand (5 mol%), pyrene (0.5 equiv.), DMA/MeCN = 3:1 (0.05 M), 35 °C, 18 h.

Table S3. Photocatalyst catalyst effect



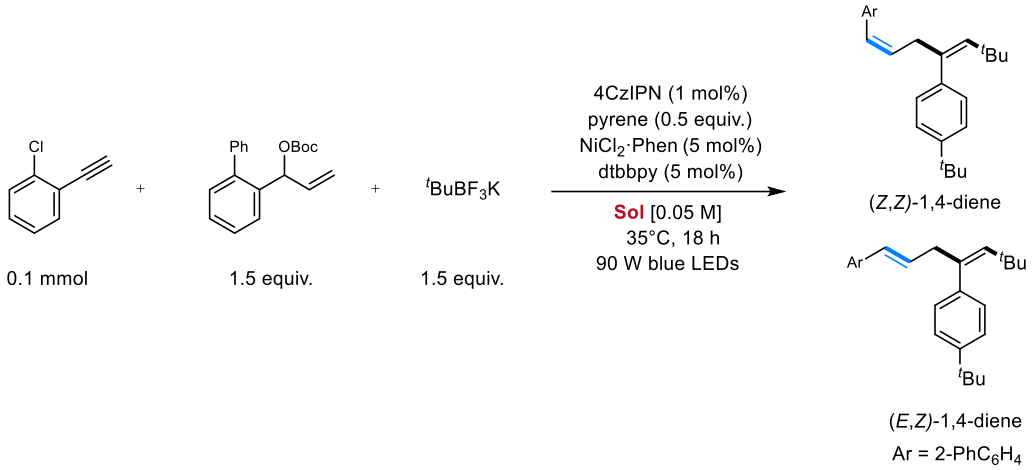
Entry	Photosensister	Yield	E_T / Kcal·mol^{-1}	(*Z*,*Z*)/(*E*,*Z*)
1	$Ru(bpy)_3Cl_3$	-	46	-
2	Fluorescein	7%	47.2	E only
3	$Ir(ppy)_3$	8%	55.2	37/63
4	4CzIPN	87%	56.4	8/92
5	$Ir[(dFCF_3ppy)_2(dtbbpy)]PF_6$	37%	60.1	83/17
6	$Ir[(dFCF_3ppy)_2(bpy)]PF_6$	65%	62	85/15
7	Pyrene	23%	48.4; 50.9 (cal.)*	3/97
	4a		~ 52.6 (cal.)*	

Reaction conditions: Alkyne (0.1 mmol), allylic carbonate (0.15 mmol) *tert*-butyl

trifluoroborate (0.15 mmol), PC (1 mol%), $NiCl_2$·Phen (5 mol%), dtbbpy (5 mol%), pyrene (0.5 equiv.), DMA/MeCN = 3:1 (0.05 M), 35 °C, 18 h.

*Kindly calculated by Prof. Jin Wen at Donghua University.

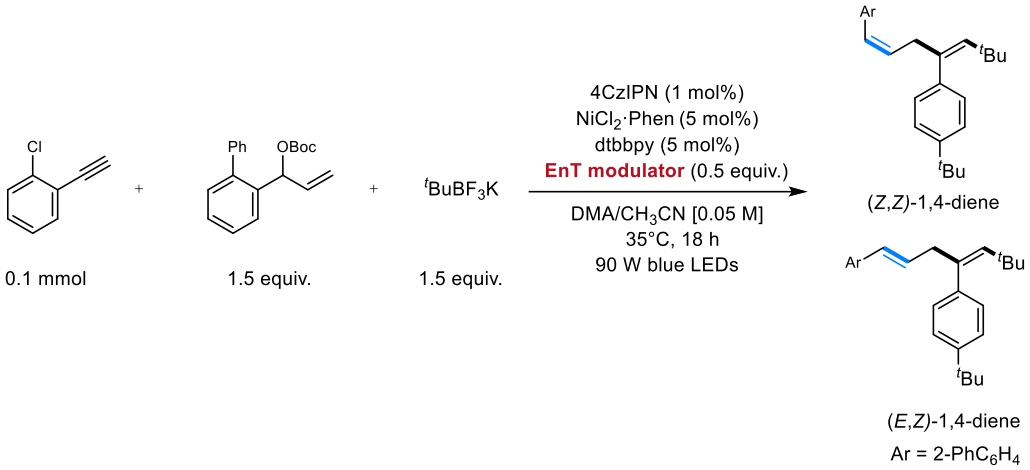
Table S4. Solvent effect



Entry	Solvents	Yield	(*Z*,*Z*)/(*E*,*Z*)
1	DMSO	12%	6/94
2	DMA	66%	9/91
3	DMF	78%	9/91
4	Acetone	76%	9/91
5	CH_3CN	76%	11/89
6	THF	48%	23/77

Reaction conditions: Alkyne (0.1 mmol), allylic carbonate (0.15 mmol) *tert*-butyl trifluoroborate (0.15 mmol), 4CzIPN (1 mol%), $NiCl_2$·Phen (5 mol%), dtbbpy (5 mol%), pyrene (0.5 equiv.), solvent (0.05 M), 35 °C, 18 h.

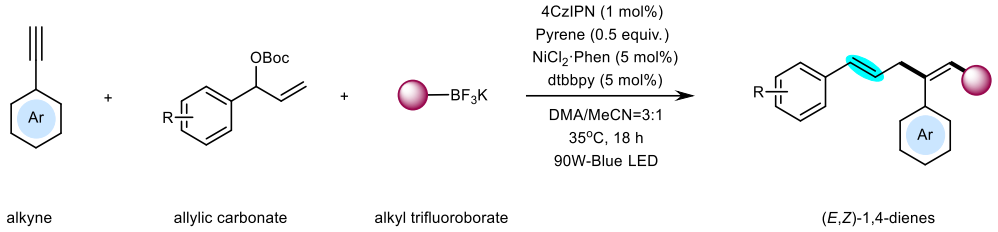
Table S5. Energy transfer modulator effect



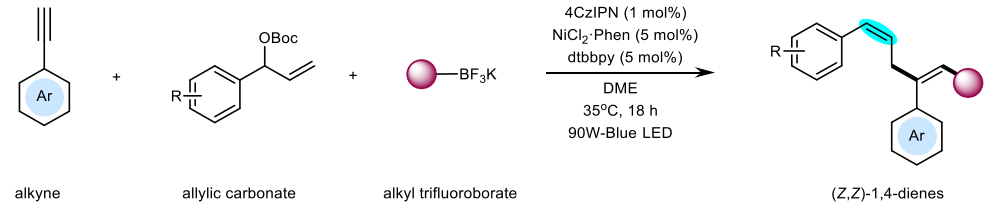
Entry	E_nT modulator	Yield	(*Z*,*Z*)/(*E*,*Z*)
1	Naphthalene	85%	88/12
2	Pyrene	84%	8/92
3	Solvent Red 43	2%	-
4	Anthracene	72%	67/33
5	*trans*-Stilbene	81%	81/19
6	9,10-Diphenylanthracene	86%	12/88

Reaction conditions: Alkyne (0.1 mmol), allylic carbonate (0.15 mmol) *tert*-butyl trifluoroborate (0.15 mmol), 4CzIPN (1 mol%), $NiCl_2$·Phen (5 mol%), dtbbpy (5 mol%), E_nT modulator (0.5 equiv.), DMA/CH_3CN = 3:1 (0.05 M), 35 ^oC, 18 h.

4. General procedures for divergent carboallylation of alkynes



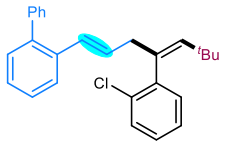
General procedures for the preparation of (*E*, *Z*)-1,4-dienes (General Procedure A). To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.7 mg, 0.01 mmol, 5 mol%), Pyrene (20.2 mg, 0.1 mmol, 50 mol%), alkyl trifluoroborate **3** (1.5 equiv.), alkyne **1** (1.0 equiv. if solid) and allylic carbonate **2** (1.5 equiv. if solid). After DMA (3 mL) and MeCN (1 mL) were added as a solution, the reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of alkyne **1** (1.0 equiv. if liquid) and allylic carbonate **2** (1.5 equiv. if liquid). The reaction mixture was then irradiated with 90 W blue LEDs for 18 h at 35°C. The reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the (*E*, *Z*)-1,4-dienes.



General procedures for the preparation of (*Z*, *Z*)-1,4-dienes. (General Procedure B). To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.7 mg, 0.01 mmol, 5 mol%), alkyl trifluoroborate **3** (1.5 equiv.), alkyne **1** (1.0 equiv. if solid) and allylic carbonate **2** (1.5 equiv. if solid). After

DME (4 mL) was added as a solution, the reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of alkyne **1** (1.0 equiv. if liquid) and allylic carbonate **2** (1.5 equiv. if liquid). The reaction mixture was then irradiated with a 90 W blue LEDs for 18 h at 35 °C. The reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the (*Z, Z*)-1,4-dienes.

5. Characterization Data of Products

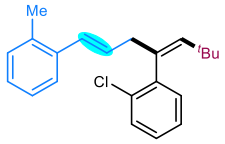


2-((1*E*,4*Z*)-4-(2-chlorophenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (4a). The title compound **4a** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (65 mg, 84% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 1H), 7.37 – 7.23 (m, 7H), 7.23 – 7.13 (m, 4H), 7.04 (dd, *J* = 7.1, 2.2 Hz, 1H), 6.23 (d, *J* = 15.7 Hz, 1H), 6.17 – 6.05 (m, 1H), 5.52 (s, 1H), 3.09 – 2.92 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.88, 140.68, 140.22, 139.20, 135.81, 133.75, 132.91, 131.48, 130.55, 130.01, 129.75, 129.15, 129.11, 127.88, 127.35, 126.92, 126.78, 126.16, 125.78, 44.01, 33.62, 30.51.

HRMS (ESI): $C_{27}H_{27}ClNa^+$ ($M+Na^+$): 409.1694, found: 409.1697.

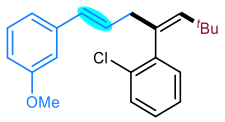


1-chloro-2-((1*E*,4*Z*)-6,6-dimethyl-1-(o-tolyl) hepta-1,4-dien-4-yl) benzene (4b). The title compound **4b** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (48.7 mg, 75% yield, *E*/*Z* >20:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 2H), 7.19 – 7.06 (m, 6H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.03 (dt, *J* = 15.1, 7.2 Hz, 1H), 5.55 (s, 1H), 3.18 – 3.02 (m, 2H), 2.23 (s, 3H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.73, 139.16, 136.99, 135.10, 133.92, 132.93, 131.61, 130.09, 129.48, 129.19, 127.97, 126.91, 126.00, 125.79, 125.71, 124.98, 43.95, 33.68, 30.58, 19.78

HRMS (ESI): $C_{22}H_{25}ClNa^+$ ($M+Na^+$): 347.1537, found: 347.1541

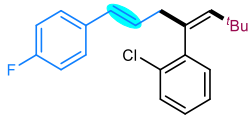


1-chloro-2-((1*E*,4*Z*)-1-(3-methoxyphenyl)-6,6-dimethylhepta-1,4-dien-4-yl) benzene (4c). The title compound **4c** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (51.8 mg, 76% yield, *E*/*Z*=93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 1H), 7.23 – 7.12 (m, 3H), 7.10 – 7.06 (m, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.78 – 6.72 (m, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.21 – 6.13 (m, 1H), 5.53 (s, 1H), 3.79 (s, 3H), 3.15 – 3.00 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.72, 140.70, 139.24, 139.05, 133.77, 132.89, 131.43, 131.25, 129.38, 129.17, 128.42, 127.96, 125.82, 118.77, 112.43, 111.56, 55.15, 43.59, 33.65, 30.54.

HRMS (ESI): $C_{22}H_{25}ClNaO^+$ ($M+Na^+$): 363.1487, found: 363.1489.



1-chloro-2-((1*E*,4*Z*)-1-(4-fluorophenyl)-6,6-dimethylhepta-1,4-dien-4-yl) benzene (4d). The title compound **4d** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (56 mg, 85% yield, *E*/*Z* > 20:1).

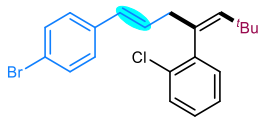
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 1H), 7.29 – 7.23 (m, 2H), 7.20 – 7.13 (m, 2H), 7.10 – 7.06 (m, 1H), 6.96 (t, *J* = 8.5 Hz, 2H), 6.21 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.3, 7.1 Hz, 1H), 5.52 (s, 1H), 3.15 – 2.99 (m, 2H), 0.87 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.46 – -115.61 (m, 1F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.93 (d, *J* = 245.8 Hz), 140.66, 139.07, 133.87 (d, *J* = 3.2 Hz), 133.74, 132.91, 131.40, 130.15, 129.19, 127.99, 127.79 (d, *J* =

2.2 Hz), 127.47 (d, *J* = 7.9 Hz), 125.82, 115.27 (d, *J* = 21.5 Hz), 43.61, 33.66, 30.54.

HRMS (FI): $C_{21}H_{22}ClF$: 328.1394, found: 328.1390.

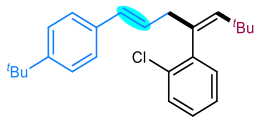


1-((1*E*,4*Z*)-1-(4-bromophenyl)-6,6-dimethylhepta-1,4-dien-4-yl)-2-chlorobenzene (4e). The title compound **4e** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow solid (42.9 mg, 55% yield, *E*/*Z* = 94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.20 – 7.13 (m, 4H), 7.09 – 7.04 (m, 1H), 6.20 – 6.14 (m, 2H), 5.52 (s, 1H), 3.13 – 3.00 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.56, 139.24, 136.65, 133.54, 132.91, 131.50, 131.39, 130.19, 129.20, 128.96, 128.02, 127.61, 125.83, 120.58, 43.67, 33.67, 30.52.

HRMS (ESI): $C_{21}H_{22}BrClNa^+$ ($M+Na^+$): 411.0486, found: 411.0488.

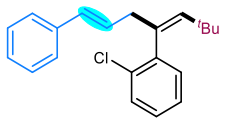


1-((1*E*,4*Z*)-1-(4-(tert-butyl)phenyl)-6,6-dimethylhepta-1,4-dien-4-yl)-2-chlorobenzene (4f). The title compound **4f** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil (62.4 mg, 85% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 3H), 7.28 – 7.22 (m, 2H), 7.19 – 7.11 (m, 2H), 7.10 – 7.06 (m, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.52 (s, 1H), 3.15 – 2.98 (m, 2H), 1.31 (s, 9H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.93, 140.85, 138.87, 135.02, 134.00, 132.89, 131.45, 131.11, 129.15, 127.91, 127.24, 125.81, 125.35, 43.61, 34.49, 33.64, 31.31, 30.56.

HRMS (ESI): $C_{25}H_{31}ClNa^+$ ($M+Na^+$): 389.2007, found: 389.1995.

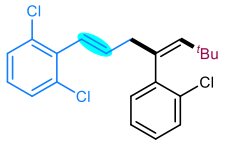


1-chloro-2-((1*E*,4*Z*)-6,6-dimethyl-1-phenylhepta-1,4-dien-4-yl) benzene (4g). The title compound **4g** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (52.3 mg, 84% yield, *E*/*Z* > 20:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.24 (m, 5H), 7.22 – 7.13 (m, 3H), 7.11 – 7.07 (m, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 6.23 – 6.14 (m, 1H), 5.53 (s, 1H), 3.16 – 2.99 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.78, 139.05, 137.79, 133.87, 132.93, 131.48, 131.39, 129.21, 128.48, 128.10, 128.00, 126.96, 126.13, 125.86, 43.66, 33.69, 30.59.

HRMS (ESI): $C_{21}H_{23}ClNa^+$ ($M+Na^+$): 333.1381, found: 333.1381.

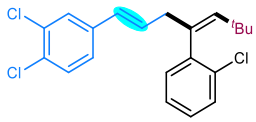


1,3-dichloro-2-((1*E*,4*Z*)-4-(2-chlorophenyl)-6,6-dimethylhepta-1,4-dien-1-yl) benzene (4h). The title compound **4h** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (53.2 mg, 70% yield, *E*/*Z* > 20:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 (q, *J* = 3.0 Hz, 3H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 6.25 – 6.13 (m, 1H), 5.65 (s, 1H), 3.26 – 3.02 (m, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.73, 139.66, 136.80, 135.09, 134.39, 133.31, 132.89, 131.64, 129.19, 128.32, 128.03, 127.70, 125.89, 125.30, 43.81, 33.70, 30.57.

HRMS (ESI): $C_{21}H_{21}Cl_3Na^+$ ($M+Na^+$): 401.0602, found: 401.0611.

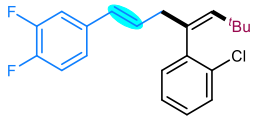


1,2-dichloro-4-((1*E*,4*Z*)-4-(2-chlorophenyl)-6,6-dimethylhepta-1,4-dien-1-yl) benzene (4i). The title compound **4i** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (47.9 mg, 63% yield, *E*/*Z*=89:11).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 3H), 7.20 – 7.15 (m, 2H), 7.11 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.23 – 6.09 (m, 2H), 5.52 (s, 1H), 3.14 – 3.01 (m, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.42, 139.49, 137.83, 133.29, 132.91, 132.48, 131.36, 130.48, 130.30, 130.28, 129.23, 129.10, 128.09, 127.75, 125.88, 125.28, 43.66, 33.70, 30.51.

HRMS (ESI): $C_{21}H_{21}Cl_3Na^+$ ($M+Na^+$): 401.0602, found: 401.0604.



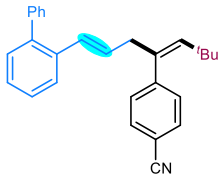
4-((1*E*,4*Z*)-4-(2-chlorophenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,2-difluorobenzene (4j). The title compound **4j** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (52.1 mg, 75% yield, *E*/*Z*=94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 7.02 (m, 3H), 7.00 – 6.94 (m, 1H), 6.19 – 6.04 (m, 2H), 5.52 (s, 1H), 3.15 – 3.00 (m, 2H), 0.87 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.23 – -138.44 (m, 1F), -140.15 – -140.35 (m, 1F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.41 (dd, *J* = 247.9, 13.2 Hz), 149.5 (dd, *J* = 248.7, 12.9 Hz)140.50, 139.36, 134.98 (dd, *J* = 5.8, 3.9 Hz), 133.43, 132.93, 131.37, 129.34, 129.27 (dd, *J* = 2.5 Hz), 129.23, 128.07, 125.87, 122.14 (dd, *J* = 5.9, 3.4 Hz), 117.09 (d, *J* = 17.5 Hz), 114.31 (d, *J* = 17.5 Hz), 43.57, 33.69, 30.51.

HRMS (ESI): $C_{21}H_{21}ClF_2Na^+$ ($M+Na^+$): 369.1193, found: 369.1196.

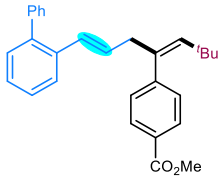


4-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl)benzonitrile (4k). The title compound **4k** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (56.6 mg, 75% yield, E/Z = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.49 (m, 3H), 7.37 – 7.28 (m, 4H), 7.29 – 7.21 (m, 3H), 7.20 – 7.12 (m, 3H), 6.21 (d, *J* = 15.7 Hz, 1H), 6.08 – 5.95 (m, 1H), 5.53 (d, *J* = 1.3 Hz, 1H), 2.97 (d, *J* = 7.1 Hz, 2H), 0.83 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.60, 140.86, 140.42, 139.63, 135.35, 135.21, 131.39, 130.95, 130.15, 129.91, 129.63, 128.23, 127.93, 127.41, 127.14, 126.92, 125.92, 118.99, 110.20, 45.57, 33.56, 31.31.

HRMS (ESI): $C_{28}H_{27}NNa^+$ ($M+Na^+$): 400.2036, found: 400.2036.



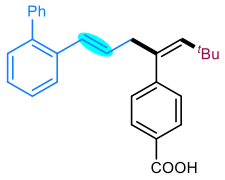
methyl 4-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) benzoate (4l). The title compound **4l** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (69.8 mg, 85% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.21 (m, 6H), 7.19 – 7.11 (m, 4H), 6.21 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.50 (s, 1H), 3.90 (s, 3H), 2.99 (d, *J* = 7.0 Hz, 1H), 0.84 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.07, 147.54, 140.86, 140.33, 138.86, 136.11, 135.55, 130.65, 130.06, 129.68, 129.15, 128.89, 128.73, 128.13, 127.88,

127.35, 126.99, 126.82, 125.97, 51.97, 45.78, 33.47, 31.32.

HRMS (ESI): $C_{29}H_{30}NaO_2^+$ ($M+Na^+$): 433.5462, found: 433.5465.

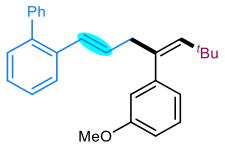


4-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) benzoic acid (4m). The title compound **4m** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (61.9 mg, 78% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.35 – 7.21 (m, 6H), 7.20 – 7.14 (m, 4H), 6.22 (d, *J* = 15.7 Hz, 1H), 6.06 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.52 (s, 1H), 3.00 (d, *J* = 7.0 Hz, 2H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.05, 148.60, 140.89, 140.40, 139.04, 136.01, 135.56, 130.73, 130.11, 129.69, 129.56, 129.32, 128.68, 127.91, 127.39, 127.03, 126.88, 125.99, 45.76, 33.53, 31.35.

HRMS (ESI): $C_{28}H_{28}NaO_2^+$ ($M+Na^+$): 419.1982, found: 419.1984.

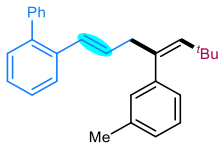


2-((1*E*,4*Z*)-4-(3-methoxyphenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (4n). The title compound **4n** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (46 mg, 60% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 6.9 Hz, 1H), 7.36 – 7.15 (m, 9H), 6.78 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.69 – 6.61 (m, 2H), 6.25 (d, *J* = 15.7 Hz, 1H), 6.09 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.44 (s, 1H), 3.77 (s, 3H), 2.98 (d, *J* = 7.0 Hz, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.89, 143.73, 140.93, 140.26, 138.03, 137.01, 135.86, 130.29, 130.04, 129.79, 129.44, 128.48, 127.89, 127.34, 126.88, 126.77, 126.10, 121.74, 114.69, 111.60, 55.12, 46.00, 33.42, 31.33.

HRMS (ESI): $C_{28}H_{30}NaO^+$ ($M+Na^+$): 405.5362, found: 405.5366.

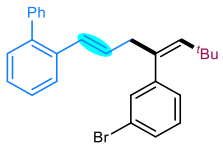


2-((1*E*,4*Z*)-6,6-dimethyl-4-(m-tolyl)hepta-1,4-dien-1-yl)-1,1'-biphenyl (4o). The title compound **4o** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (46.2 mg, 63% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 6.9 Hz, 1H), 7.35 – 7.19 (m, 8H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.88 (m, 2H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.09 (m, 1H), 5.43 (s, 1H), 2.97 (d, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.25, 140.96, 140.25, 137.88, 137.31, 136.89, 135.94, 130.20, 130.04, 129.79, 129.64, 129.62, 127.89, 127.36, 127.34, 126.89, 126.86, 126.75, 126.17, 126.14, 46.13, 33.39, 31.41, 21.48.

HRMS (ESI): $C_{28}H_{30}Na^+$ ($M+Na^+$): 389.2240, found: 389.2245.

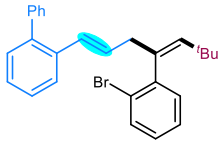


2-((1*E*,4*Z*)-4-(3-bromophenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (4p). The title compound **4p** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (44 mg, 51% yield, *E*/*Z* = 96:4).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.18 (m, 10H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.98 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 6.05 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.47 (s, 1H), 2.96 (d, *J* = 7.1 Hz, 2H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.45, 140.90, 140.38, 139.07, 135.65, 135.58, 131.78, 130.69, 130.07, 129.72, 129.34, 129.09, 128.82, 127.94, 127.88, 127.37, 127.00, 126.83, 126.08, 121.64, 45.85, 33.51, 31.36.

HRMS (ESI): $C_{27}H_{27}BrNa^+$ ($M+Na^+$): 453.1189, found: 453.1193.

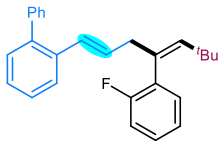


2-((1*E*,4*Z*)-4-(2-bromophenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (4q). The title compound **4q** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (60.4 mg, 70% yield, *E*/*Z* = 95:5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (t, *J* = 8.7 Hz, 2H), 7.36 – 7.16 (m, 9H), 7.13 – 7.01 (m, 2H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.18 – 6.06 (m, 1H), 5.48 (s, 1H), 3.09 – 2.92 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.68, 140.90, 140.25, 138.88, 135.82, 135.25, 132.31, 131.50, 130.63, 130.03, 129.76, 129.14, 128.03, 127.90, 127.36, 126.94, 126.80, 126.36, 126.17, 123.40, 43.86, 33.71, 30.54.

HRMS (ESI): $C_{27}H_{27}BrNa^+$ ($M+Na^+$): 453.1189, found: 453.1196.



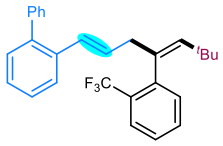
2-((1*E*,4*Z*)-4-(2-fluorophenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (4r). The title compound **4r** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (60 mg, 81% yield, *E*/*Z* = 91:9).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 9.0 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.27 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.07 – 6.97 (m, 3H), 6.21 (d, *J* = 15.6 Hz, 1H), 6.15 – 6.03 (m, 1H), 5.60 (s, 1H), 3.00 (d, *J* = 6.9 Hz, 2H), 0.87 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.22 – -114.31 (m, 1F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.47 (d, *J* = 243.3 Hz), 140.92, 140.27, 140.25, 135.82, 131.56 (d, *J* = 4.3 Hz), 130.53, 130.49, 130.00, 129.75, 129.09, 128.33 (d, *J* = 7.9 Hz), 127.89, 127.36, 126.92, 126.75, 126.18, 123.22 (d, *J* = 3.6 Hz), 115.14 (d, *J* = 22.6 Hz), 45.11, 33.46, 30.73.

HRMS (ESI): $C_{27}H_{27}FNa^+$ ($M+Na^+$): 393.1989, found:393.1981.



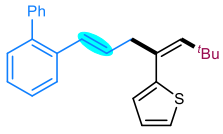
2-((1*E*,4*Z*)-6,6-dimethyl-4-(2-(trifluoromethyl)phenyl)hepta-1,4-dien-1-yl)-1,1'-biphenyl (4s). The title compound **4s** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (68.2 mg, 81% yield, *E*/*Z* = 94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 6.1 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.41 – 7.19 (m, 9H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.25 (d, *J* = 15.7 Hz, 1H), 6.14 – 6.04 (m, 1H), 5.45 (s, 1H), 3.14 – 2.88 (m, 2H), 0.80 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.51(s, 3F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.88, 140.31, 139.09, 135.80, 132.91, 132.11, 130.82, 130.53, 130.06, 129.73, 129.24, 128.21 (q, *J* = 29.5 Hz), 127.90, 127.39, 127.00, 126.85, 126.79, 126.27 (q, *J* = 5.1 Hz), 126.19, 124.37 (q, *J* = 274.3 Hz), 44.93 (d, *J* = 2.3 Hz), 34.06, 30.49.

HRMS (ESI): $C_{28}H_{27}F_3Na^+$ ($M+Na^+$): 443.1958, found: 443.1960.



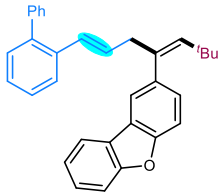
2-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) thiophene (4t). The title compound **4t** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (52.4 mg, 73% yield, *E*/*Z* =

93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 1H), 7.39 – 7.20 (m, 9H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.70 (dd, *J* = 3.5, 1.2 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 6.10 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.62 (s, 1H), 3.01 (d, *J* = 6.9 Hz, 2H), 0.93 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.73, 142.48, 140.97, 140.36, 135.79, 130.47, 130.05, 129.80, 129.65, 129.28, 127.94, 127.36, 126.94, 126.79, 126.23, 126.18, 126.11, 124.39, 46.44, 33.58, 30.93.

HRMS (ESI): $C_{25}H_{26}NaS^+$ ($M+Na^+$): 381.1648, found: 381.1642.

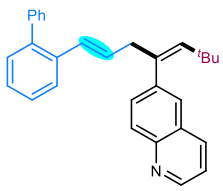


2-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) dibenzo[b,d]furan (4u). The title compound **4u** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (53.2 mg, 60% yield, *E*/*Z* = 92:8).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.50 – 7.40 (m, 2H), 7.35 – 7.11 (m, 10H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.13 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.56 (s, 1H), 3.07 (d, *J* = 6.9 Hz, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.43, 154.98, 140.89, 140.33, 138.84, 136.91, 136.82, 135.80, 130.45, 130.08, 129.68, 129.33, 128.46, 127.78, 127.35, 127.03, 126.91, 126.75, 126.07, 124.31, 123.58, 122.61, 120.72, 120.65, 111.66, 110.65, 46.59, 33.52, 31.48.

HRMS (ESI): $C_{33}H_{30}NaO^+$ ($M+Na^+$): 465.2189, found: 465.2192.



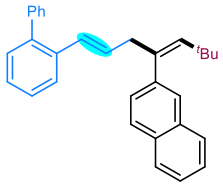
6-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) quinoline

(4v). The title compound **4v** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (58.1 mg, 72% yield, *E*/*Z* = 92:8).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 – 8.07 (m, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.37 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.32 – 7.16 (m, 4H), 7.12 – 7.04 (m, 4H), 6.20 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.7, 6.8 Hz, 1H), 5.60 (s, 1H), 3.07 (d, *J* = 6.9 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.99, 147.12, 140.76, 140.70, 140.32, 139.27, 136.24, 135.94, 135.60, 131.61, 130.66, 130.05, 129.57, 128.92, 128.52, 127.74, 127.68, 127.33, 127.12, 126.97, 126.74, 126.02, 121.14, 46.17, 33.53, 31.42.

HRMS (ESI): $C_{30}H_{29}NNa^+$ ($M+Na^+$): 426.2193, found: 426.2191.

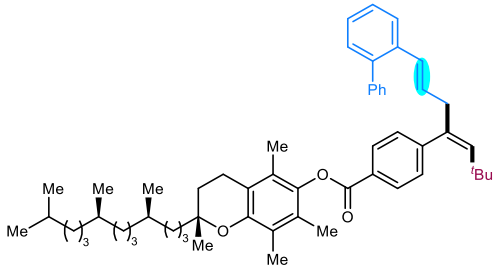


2-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) naphthalene (4w). The title compound **4w** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (48.3 mg, 60% yield, *E*/*Z* = 89:11).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.42 (m, 2H), 7.31 – 7.14 (m, 5H), 7.10 – 6.98 (m, 4H), 6.20 (d, *J* = 15.8 Hz, 1H), 6.16 – 6.08 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.57 (s, 1H), 3.06 (d, *J* = 7.0 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.80, 140.30, 139.83, 138.70, 137.09, 135.78, 133.01, 132.12, 130.45, 130.04, 129.67, 129.34, 128.06, 127.86, 127.75, 127.63, 127.32, 127.27, 126.97, 126.90, 126.69, 126.10, 125.86, 125.46, 46.40, 33.50, 31.46.

HRMS (ESI): $C_{31}H_{30}Na^+$ ($M+Na^+$): 425.2240, found: 425.2239.

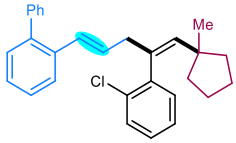


2,2,2,5,6,8-hexamethyl-2-(2,2,2,4,8-pentamethyl-2l5-nonyl)-2l6-chroman-7-yl 4-((1*E*,4*Z*)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) benzoate (4x). The title compound **4x** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (110 mg, 68% yield, *E*/*Z* = 91:9).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.12 (m, 10H), 6.24 (d, *J* = 15.6 Hz, 1H), 6.08 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.55 (s, 1H), 3.02 (d, *J* = 7.0 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.12 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.88 – 1.73 (m, 2H), 1.63 – 1.34 (m, 8H), 1.32 – 1.21 (m, 9H), 1.18 – 1.02 (m, 7H), 0.92 – 0.82 (m, 21H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.22, 149.43, 148.09, 140.84, 140.64, 140.36, 139.09, 136.11, 135.59, 130.77, 130.07, 129.68, 129.47, 129.38, 128.78, 127.93, 127.61, 127.38, 127.04, 126.95, 126.81, 126.06, 125.17, 123.08, 117.41, 75.04, 45.96, 39.36, 37.53, 37.44, 37.39, 37.28, 33.52, 32.77, 32.70, 31.42, 27.96, 24.81, 24.79, 24.43, 22.72, 22.62, 21.04, 20.62, 19.75, 19.68, 19.60, 13.14, 12.29, 11.85.

HRMS (ESI): $C_{57}H_{76}F_3NaO_3^+$ ($M+Na^+$): 831.5687, found: 831.5689.



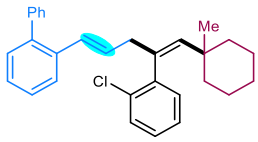
2-((1*E*,4*Z*)-4-(2-chlorophenyl)-5-(1-methylcyclopentyl)penta-1,4-dien-1-yl)-1,1'-biphenyl (4y). The title compound **4y** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (71.9 mg,

87% yield, *E*/*Z*=94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.39 – 7.12 (m, 11H), 7.05 (dd, *J* = 7.2, 2.1 Hz, 1H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.17 – 6.05 (m, 1H), 5.69 (s, 1H), 3.10 – 2.95 (m, 2H), 1.58 – 1.46 (m, 5H), 1.45 – 1.35 (m, 1H), 1.31 – 1.22 (m, 1H), 1.15 – 1.05 (m, 1H), 0.84 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.90, 140.82, 140.23, 138.90, 135.84, 134.46, 132.99, 131.55, 130.47, 130.02, 129.76, 129.29, 129.15, 127.90, 127.90, 127.36, 126.92, 126.79, 126.15, 125.82, 44.64, 43.52, 40.90, 39.36, 25.90, 23.63, 23.19.

HRMS (ESI): $C_{29}H_{29}ClNa^+$ ($M+Na^+$): 435.1850, found: 435.1856.

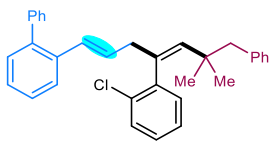


2-((1*E*,4*Z*)-4-(2-chlorophenyl)-5-(1-methylcyclohexyl)penta-1,4-dien-1-yl)-1,1'-biphenyl (4z). The title compound **4z** was prepared according to the General Procedure A and isolated by flash chromatography as a white solid (70 mg, 82% yield, *E*/*Z*=95:5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 1H), 7.37 – 7.11 (m, 11H), 7.05 (dd, *J* = 7.3, 2.1 Hz, 1H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.16 – 6.06 (m, 1H), 5.54 (s, 1H), 3.11 – 2.97 (m, 2H), 1.50 – 1.29 (m, 8H), 1.14 – 1.02 (m, 2H), 0.83 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.89, 140.67, 140.23, 139.00, 135.85, 134.95, 132.77, 131.53, 130.51, 130.01, 129.75, 129.35, 129.24, 127.88, 127.36, 126.92, 126.79, 126.18, 125.70, 44.11, 39.59, 38.59, 36.31, 26.64, 26.14, 22.60, 22.43.

HRMS (ESI): $C_{30}H_{31}ClNa^+$ ($M+Na^+$): 449.2007, found: 449.2004.



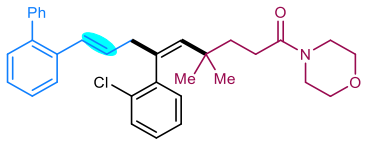
2-((1*E*,4*Z*)-4-(2-chlorophenyl)-6,6-dimethyl-7-phenylhepta-1,4-dien-1-yl)-1,1'-

biphenyl (4aa). The title compound **4aa** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (74.1 mg, 80% yield, *E*/*Z*=94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.34 – 7.18 (m, 12H), 7.13 – 7.06 (m, 3H), 6.98 (td, *J* = 7.5, 1.3 Hz, 1H), 6.42 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.22 (d, *J* = 15.7 Hz, 1H), 6.17 – 6.05 (m, 1H), 5.47 (s, 1H), 3.08 – 2.89 (m, 2H), 2.64 – 2.44 (m, 2H), 0.91 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.88, 140.55, 140.26, 139.00, 137.28, 135.75, 134.49, 132.77, 131.04, 130.74, 130.56, 130.05, 129.74, 128.94, 128.89, 127.91, 127.75, 127.53, 127.37, 126.96, 126.80, 126.12, 125.87, 125.60, 50.26, 44.19, 38.25, 29.30, 26.04.

HRMS (ESI): $C_{31}H_{31}ClNa^{+}$ ($M+Na^{+}$): 485.2007, found: 485.2010.

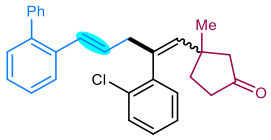


(5*Z*,8*E*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethyl-1-morpholinonona-5,8-dien-1-one (4ab). The title compound **4ab** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (59.6 mg, 58% yield, *E*/*Z*=87:13).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 6.5 Hz, 1H), 7.37 – 7.16 (m, 11H), 7.03 (dd, *J* = 7.1, 2.1 Hz, 1H), 6.23 (d, *J* = 15.7 Hz, 1H), 6.14 – 6.04 (m, 1H), 5.41 (s, 1H), 3.67 – 3.56 (m, 6H), 3.40 (t, *J* = 4.8 Hz, 2H), 3.10 – 2.96 (m, 2H), 2.35 – 2.22 (m, 2H), 1.67 – 1.50 (m, 2H), 0.85 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.15, 140.80, 140.27, 140.24, 137.20, 135.78, 135.57, 132.63, 131.30, 130.74, 130.06, 129.69, 129.16, 128.72, 128.11, 127.89, 127.38, 127.05, 126.81, 126.03, 125.94, 66.86, 66.55, 45.93, 44.05, 41.85, 39.79, 36.61, 29.12, 28.59, 26.69.

HRMS (ESI): $C_{33}H_{37}ClNO_2^{+}$ ($M+H^{+}$): 514.2507, found: 514.2515.

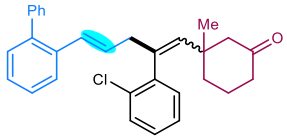


(*R*)-3-((1*Z*,4*E*)-5-([1,1'-biphenyl]-2-yl)-2-(2-chlorophenyl)penta-1,4-dien-1-yl)-3-methylcyclopentan-1-one (4ac). The title compound **4ac** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (40.1 mg, 47% yield, 4*E*/4*Z* = 95:5, 1*E*/1*Z* = 1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 6.5 Hz, 1H), 7.33 – 7.06 (m, 11H), 6.95 (d, *J* = 6.7 Hz, 1H), 6.20 (d, *J* = 15.8 Hz, 0.5H), 6.19 (d, *J* = 15.8 Hz, 0.5H), 6.08 – 5.96 (m, 1H), 5.59 (s, 1H), 3.05 – 2.90 (m, 2H), 2.10 – 1.64 (m, 4H), 1.58 – 1.46 (m, 2H), 0.95 (s, 1.40H), 0.94 (s, 1.56H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 219.18, 218.91, 140.86, 140.31, 139.79, 139.72, 136.49, 135.99, 135.77, 135.54, 135.52, 132.76, 132.60, 131.16, 131.03, 130.99, 130.92, 130.07, 129.71, 129.55, 129.47, 128.59, 128.48, 128.33, 128.24, 127.91, 127.39, 127.07, 126.84, 126.25, 126.21, 126.06, 52.61, 51.11, 43.57, 43.06, 41.56, 41.39, 36.68, 36.30, 35.77, 35.76, 26.41, 25.95.

HRMS (FI): $C_{29}H_{27}ClO$: 426.1750, found: 426.1747.

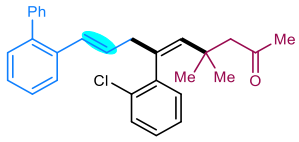


4-((1*Z*,4*E*)-5-([1,1'-biphenyl]-2-yl)-2-(2-chlorophenyl)penta-1,4-dien-1-yl)-4-methylcyclohexan-1-one (4ad). The title compound **4ad** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (72.3 mg, 80% yield, 4*E*/4*Z*=95:5, 1*E*/1*Z*=1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.3 Hz, 1H), 7.31 – 7.05 (m, 11H), 7.00 – 6.90 (m, 1H), 6.15 (d, *J* = 15.7 Hz, 1H), 6.04 – 5.94 (m, 1H), 5.40 (s, 1H), 3.02 – 2.85 (m, 2H), 2.20 – 2.07 (m, 3H), 1.96 – 1.74 (m, 2H), 1.70 – 1.54 (m, 2H), 1.44 – 1.34 (m, 1H), 0.80 (s, 1.48H), 0.78 (s, 1.45H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.33, 211.31, 140.83, 140.27, 139.81, 139.76, 136.45, 136.39, 136.14, 136.05, 135.55, 132.60, 132.55, 131.30, 130.98, 130.94, 130.01, 129.69, 129.44, 129.40, 128.38, 128.35, 127.87, 127.37, 127.03, 126.80, 126.09, 126.06, 53.91, 53.54, 44.09, 43.99, 41.33, 41.22, 40.79, 40.72, 37.34, 36.76, 25.79, 25.24, 22.15, 21.99.

HRMS (ESI): $C_{30}H_{29}ClNaO^+$ ($M+Na^+$): 463.1800, found: 463.1805.

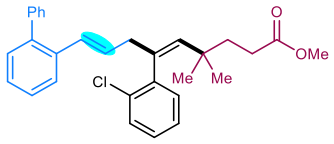


(5*Z*,8*E*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dien-2-one (4ae). The title compound **4ae** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (53.2 mg, 62% yield, *E*/*Z*=90:10).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.38 – 7.14 (m, 11H), 7.07 – 7.02 (m, 1H), 6.22 (d, *J* = 15.7 Hz, 1H), 6.16 – 6.04 (m, 1H), 5.61 (s, 1H), 3.12 – 2.92 (m, 2H), 2.44 – 2.27 (m, 2H), 2.07 (s, 3H), 0.92 (d, *J* = 10.2 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.99, 140.85, 140.26, 140.21, 136.97, 135.66, 134.92, 132.78, 131.33, 130.81, 130.03, 129.74, 129.26, 128.66, 128.13, 127.89, 127.39, 127.00, 126.80, 126.16, 125.96, 56.28, 44.20, 36.21, 31.92, 28.56, 28.03.

HRMS (ESI): $C_{29}H_{29}ClNaO^+$ ($M+Na^+$): 451.1800, found: 451.1801.

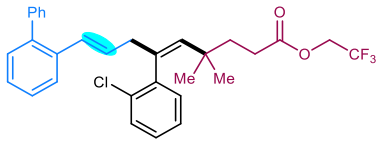


methyl (5*Z*,8*E*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dienoate (4af). The title compound **4af** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (71.6 mg, 78% yield, *E*/*Z*=94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 1H), 7.36 – 7.15 (m, 11H), 7.03 (dd, *J* = 7.1, 2.2 Hz, 1H), 6.22 (d, *J* = 15.7 Hz, 1H), 6.09 (dt, *J* = 15.2, 7.1 Hz, 1H), 5.40 (s, 1H), 3.65 (s, 3H), 3.09 – 2.94 (m, 2H), 2.35 – 2.26 (m, 2H), 1.63 – 1.55 (m, 2H), 0.79 (s, 3H), 0.76 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.59, 140.84, 140.28, 140.25, 136.87, 135.90, 135.67, 132.80, 131.21, 130.76, 130.00, 129.70, 129.17, 128.76, 128.03, 127.87, 127.36, 126.98, 126.79, 126.16, 125.87, 51.48, 44.17, 39.38, 36.43, 30.21, 27.60, 27.45.

HRMS (ESI): $C_{30}H_{31}ClNaO_2^+$ ($M+Na^+$): 481.1905, found: 481.1907



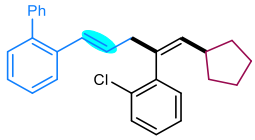
2,2,2-trifluoroethyl (5Z,8E)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dienoate (4ag). The title compound **4ag** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (47.4 mg, 45% yield, *E*/*Z*=89:11).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.30 – 7.08 (m, 11H), 6.96 (dd, *J* = 7.2, 2.1 Hz, 1H), 6.16 (d, *J* = 15.7 Hz, 1H), 6.06 – 5.96 (m, 1H), 5.32 (s, 1H), 4.37 (q, *J* = 8.5 Hz, 2H), 3.03 – 2.88 (m, 2H), 2.38 – 2.28 (m, 2H), 1.57 – 1.49 (m, 2H), 0.73 (d, *J* = 5.0 Hz, 6H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.72 (t, *J* = 8.6 Hz, 3F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.51, 140.87, 140.30, 140.17, 136.57, 136.36, 135.65, 132.77, 131.16, 130.87, 130.04, 129.72, 129.25, 128.64, 128.14, 127.89, 127.39, 127.03, 126.82, 126.15, 125.94, 123.00 (d, *J* = 277.1 Hz), 60.21 (q, *J* = 36.5 Hz), 44.15, 38.91, 36.41, 29.82, 27.78, 27.44.

HRMS (ESI): $C_{31}H_{30}ClF_3NaO_2^+$ ($M+Na^+$): 549.1779, found: 549.1780.

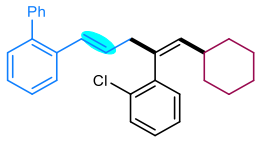


2-((1*E*,4*Z*)-4-(2-chlorophenyl)-5-cyclopentylpenta-1,4-dien-1-yl)-1,1'-biphenyl (4ah). The title compound **4ah** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (44.7 mg, 56% yield, *E*/*Z*=88:12).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.53 (m, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.16 (m, 10H), 7.05 – 7.01 (m, 1H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.13 (dt, *J* = 15.2, 7.1 Hz, 1H), 5.48 (d, *J* = 9.8 Hz, 1H), 3.08 (d, *J* = 7.1 Hz, 2H), 2.14 – 2.02 (m, 1H), 1.77 – 1.67 (m, 1H), 1.64 – 1.56 (m, 1H), 1.45 – 1.36 (m, 2H), 1.25-1.18 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.90, 140.20, 135.80, 135.70, 135.10, 132.93, 131.03, 130.47, 130.01, 129.76, 129.31, 128.99, 127.89, 127.88, 127.36, 126.91, 126.78, 126.32, 126.14, 41.65, 40.18, 33.68, 33.13, 25.33, 25.28.

HRMS (ESI): $C_{28}H_{27}ClNa^+$ ($M+Na^+$): 421.1694, found: 421.1699.

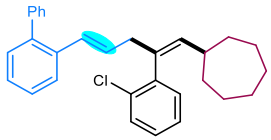


2-((1*E*,4*Z*)-4-(2-chlorophenyl)-5-cyclohexylpenta-1,4-dien-1-yl)-1,1'-biphenyl (4ai). The title compound **4ai** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (44.7 mg, 52% yield, *E*/*Z*=91:9).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.07 (m, 10H), 6.97 – 6.89 (m, 1H), 6.19 (d, *J* = 15.7 Hz, 1H), 6.04 (dt, *J* = 15.0, 7.0 Hz, 1H), 5.32 (d, *J* = 9.8 Hz, 1H), 2.98 (d, *J* = 7.1 Hz, 2H), 1.66 – 1.37 (m, 6H), 1.07 – 0.90 (m, 5H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.91, 140.22, 140.14, 135.82, 135.72, 135.34, 132.80, 130.85, 130.51, 130.01, 129.76, 129.35, 128.99, 127.89 (d, *J* = 1.3 Hz), 127.35, 126.91, 126.77, 126.34, 126.15, 41.71, 38.13, 33.22, 32.51, 25.96, 25.63.

HRMS (FI): $C_{29}H_{29}Cl$: 412.1958, found: 412.1951.

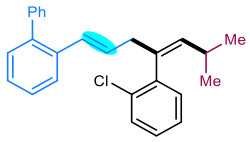


2-((1*E*,4*Z*)-4-(2-chlorophenyl)-5-cycloheptylpenta-1,4-dien-1-yl)-1,1'-biphenyl (4aj). The title compound **4aj** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (46.1 mg, 54% yield, *E*/*Z*=85:15).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.16 (m, 10H), 7.03 – 6.98 (m, 1H), 6.26 (d, *J* = 15.7 Hz, 1H), 6.12 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.50 (d, *J* = 10.2 Hz, 1H), 3.06 (d, *J* = 7.0 Hz, 2H), 1.91 – 1.82 (m, 1H), 1.70 – 1.51 (m, 4H), 1.51 – 1.38 (m, 4H), 1.33 – 1.21 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.90, 140.19, 140.10, 136.34, 135.82, 133.81, 132.84, 130.86, 130.43, 130.00, 129.75, 129.31, 129.05, 127.89, 127.86, 127.35, 126.89, 126.77, 126.31, 126.14, 41.61, 39.57, 34.97, 34.11, 30.91, 28.63, 28.54, 26.11.

HRMS (ESI): $C_{30}H_{31}ClNa^+$ ($M+Na^+$): 449.2007, found: 449.2015.

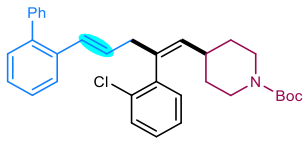


2-((1*E*,4*Z*)-4-(2-chlorophenyl)-6-methylhepta-1,4-dien-1-yl)-1,1'-biphenyl (4ak). The title compound **4ak** was prepared according to the General Procedure A and isolated by flash chromatography as a colorless oil liquid (36.6 mg, 49% yield, *E*/*Z*=90:10).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.53 (m, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.17 (m, 10H), 7.04 – 7.00 (m, 1H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.12 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.38 (d, *J* = 10.0 Hz, 1H), 3.06 (d, *J* = 7.1 Hz, 2H), 2.06 – 1.96 (m, 1H), 0.89 (dd, *J* = 18.1, 6.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.91, 140.23, 140.11, 137.03, 135.80, 134.90, 132.84, 130.81, 130.56, 130.02, 129.76, 129.35, 128.90, 127.90, 127.36, 126.93, 126.79, 126.35, 126.15, 41.61, 28.63, 23.10, 22.47.

HRMS (ESI): $C_{26}H_{25}ClNa^+$ ($M+Na^+$): 395.1537, found: 395.1537.

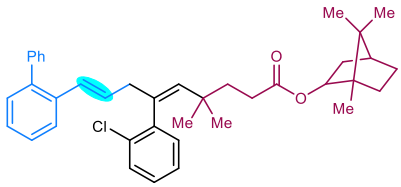


***tert*-butyl 4-((1*Z*,4*E*)-5-([1,1'-biphenyl]-2-yl)-2-(2-chlorophenyl)penta-1,4-dien-1-yl)piperidine-1-carboxylate (4al).** The title compound **4al** was prepared according to the General Procedure A and isolated by flash chromatography as a pale-yellow oil liquid (58.6 mg, 57% yield, *E*/*Z*=89:11).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.15 (m, 10H), 7.04 – 6.98 (m, 1H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.10 (dt, *J* = 15.1, 7.1 Hz, 1H), 5.37 (d, *J* = 9.8 Hz, 1H), 4.08 – 3.87 (m, 2H), 3.07 (d, *J* = 7.1 Hz, 2H), 2.60 – 2.46 (m, 2H), 1.89 – 1.78 (m, 1H), 1.72 – 1.55 (m, 2H), 1.44 (s, 9H), 1.29 – 1.20 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.79, 140.87, 140.25, 139.68, 136.92, 135.63, 133.48, 132.65, 130.79, 130.56, 130.02, 129.72, 129.48, 128.40, 128.16, 127.89, 127.36, 126.99, 126.79, 126.50, 126.09, 79.20, 41.71, 36.38, 31.94, 31.32, 28.42.

HRMS (ESI): $C_{33}H_{36}ClNNaO_2^+$ ($M+Na^+$): 536.2327, found: 536.2325.



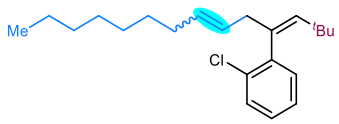
(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (5*Z*,8*E*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dienoate (4am). The title compound **4am** was prepared according to the General Procedure A and isolated by flash

chromatography as a pale-yellow oil liquid (87.2 mg, 75% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.37 – 7.12 (m, 11H), 7.03 (dd, *J* = 7.1, 2.1 Hz, 1H), 6.22 (d, *J* = 15.7 Hz, 1H), 6.15 – 6.03 (m, 1H), 5.41 (s, 1H), 4.66 (dd, *J* = 7.7, 3.7 Hz, 1H), 3.10 – 2.93 (m, 2H), 2.27 (dd, *J* = 9.9, 6.7 Hz, 2H), 1.83 – 1.64 (m, 4H), 1.62 – 1.48 (m, 3H), 1.19 – 1.02 (m, 2H), 0.97 (s, 3H), 0.83 (s, 6H), 0.78 (d, *J* = 9.5 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.65, 140.84, 140.28, 140.23, 137.05, 135.89, 135.67, 132.79, 131.23, 130.75, 129.99, 129.71, 129.18, 128.80, 128.02, 127.87, 127.36, 126.97, 126.78, 126.14, 125.85, 80.71, 48.62, 46.87, 44.99, 44.18, 39.42, 38.75, 36.38, 33.70, 30.86, 27.70 (d, *J* = 3.7 Hz), 27.49 (d, *J* = 3.1 Hz), 27.00, 20.10, 19.91, 11.46.

HRMS (ESI): $C_{39}H_{45}ClNaO_2^+$ ($M+Na^+$): 603.3001, found: 603.3002.

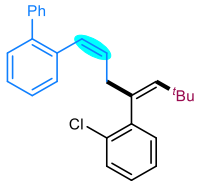


1-chloro-2-((3*Z*,6*E*)-2,2-dimethyltetradeca-3,6-dien-4-yl)benzene (S4an). The title compound **S4an** was prepared according to the General Procedure A and isolated by flash chromatography as a pale yellow oil (37 mg, 56% yield, the *Z*/*E* ratio cannot be determined through NMR analysis).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 1H), 7.19 – 7.12 (m, 2H), 7.09 – 7.02 (m, 1H), 5.47 (s, 0.27H), 5.46 (s, 0.74H), 5.42 – 5.25 (m, 2H), 2.95 – 2.78 (m, 2H), 1.99 – 1.80 (m, 2H), 1.33 – 1.18 (m, 10H), 0.91 – 0.87 (m, 3H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.01, 138.19, 138.07, 134.54, 133.94, 132.87, 132.59, 131.88, 131.58, 131.56, 129.03, 127.78, 127.72, 127.35, 126.40, 125.67, 125.59, 43.21, 37.58, 33.50, 32.47, 31.88, 31.83, 30.57, 29.51, 29.43, 29.22, 29.19, 29.04, 27.02, 22.68, 14.11.

HRMS (ESI): $C_{22}H_{33}ClNa^+$ ($M+Na^+$): 355.2163, found: 355.2165.

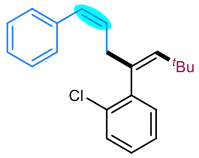


2-((1*Z*,4*Z*)-4-(2-chlorophenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (5a). The title compound **5a** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (55 mg, 71% yield, *Z*/*E* = 94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 10H), 7.20 – 7.15 (m, 2H), 7.15 – 7.10 (m, 1H), 6.29 (d, *J* = 11.4 Hz, 1H), 5.67 (dt, *J* = 11.4, 7.6 Hz, 1H), 5.53 (s, 1H), 3.18 (d, *J* = 7.6 Hz, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.15, 141.05, 141.04, 138.60, 135.10, 133.81, 132.96, 131.26, 130.70, 129.69, 129.64, 129.61, 129.19, 129.14, 127.97, 127.80, 127.06, 126.82, 126.73, 125.91, 38.72, 33.68, 30.55.

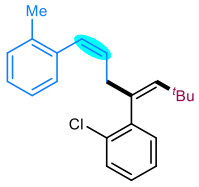
HRMS (ESI): $C_{27}H_{27}ClNa^+$ ($M+Na^+$): 409.1694, found: 409.1698.



1-chloro-2-((1*Z*,4*Z*)-6,6-dimethyl-1-phenylhepta-1,4-dien-4-yl) benzene (5b). The title compound **5b** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (49 mg, 79% yield, *Z*/*E* = 86:14). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.35 – 7.25 (m, 3H), 7.22 – 7.11 (m, 6H), 6.52 (d, *J* = 11.6 Hz, 1H), 5.72 (dt, *J* = 11.5, 7.7 Hz, 1H), 5.54 (t, *J* = 1.5 Hz, 1H), 3.22 – 3.10 (m, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.04, 138.67, 137.28, 133.51, 132.97, 131.28, 130.55, 129.41, 129.20, 128.54, 128.04, 128.00, 126.60, 125.94, 38.63, 33.68, 30.54.

HRMS (ESI): $C_{21}H_{23}ClNa^+$ ($M+Na^+$): 333.1381, found: 333.1385.

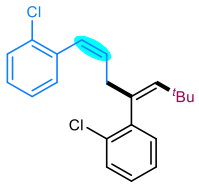


1-chloro-2-((1*Z*,4*Z*)-6,6-dimethyl-1-(o-tolyl)hepta-1,4-dien-4-yl)benzene (5c). The title compound **5c** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (48 mg, 74% yield, *Z*/*E* > 20:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 1H), 7.08 – 6.97 (m, 6H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 11.4 Hz, 1H), 5.68 (dt, *J* = 11.4, 7.6 Hz, 1H), 5.41 (s, 1H), 2.92 (dq, *J* = 7.9, 1.6 Hz, 2H), 2.09 (s, 3H), 0.79 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.02, 138.48, 136.35, 136.17, 133.83, 132.98, 131.27, 129.65, 129.58, 129.39, 129.13, 128.75, 127.90, 126.85, 125.84, 125.22, 38.51, 33.64, 30.54, 19.79.

HRMS (ESI): $C_{22}H_{25}ClNa^+$ (M+Na^+): 347.1537, found: 347.1539.

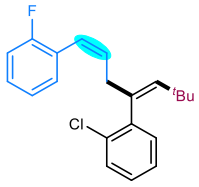


2,2'-((1*Z*,4*Z*)-6,6-dimethylhepta-1,4-diene-1,4-diyl)bis(chlorobenzene) (5d). The title compound **5d** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (51.1 mg, 74% yield, *Z*/*E* = 94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 2H), 7.20 – 7.08 (m, 6H), 6.60 (d, *J* = 12.9 Hz, 1H), 5.85 (dt, *J* = 11.5, 7.8 Hz, 1H), 5.51 (s, 1H), 3.11 – 2.96 (m, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.81, 138.76, 135.32, 133.54, 133.32, 132.88, 131.25, 130.72, 130.21, 129.18, 129.15, 128.10, 128.03, 127.91, 126.12, 125.97, 38.46, 33.68, 30.50.

HRMS (ESI): $C_{21}H_{22}Cl_2Na^+$ (M+Na^+): 367.0991, found: 367.0994.



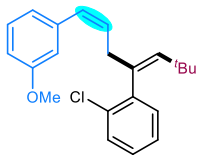
2,2'-((1*Z*,4*Z*)-6,6-dimethylhepta-1,4-diene-1,4-diyl) bis(chlorobenzene) (5e). The title compound **5e** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (47 mg, 68% yield, *Z*/*E* = 88:12).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 1H), 7.22 – 7.08 (m, 5H), 7.06 – 6.96 (m, 2H), 6.53 (d, *J* = 11.5 Hz, 1H), 5.85 (dt, *J* = 11.5, 7.7 Hz, 1H), 5.51 (s, 1H), 3.17 – 3.02 (m, 2H), 0.87 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.48 – -115.67 (m, 1F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.13 (d, *J* = 246.9 Hz), 140.81, 138.80, 133.29, 132.90, 131.42, 131.28, 130.24 (d, *J* = 3.6 Hz), 129.17, 128.46 (d, *J* = 8.1 Hz), 128.03, 125.95, 124.81 (d, *J* = 14.6 Hz), 123.44 (d, *J* = 3.6 Hz), 123.21 (d, *J* = 3.6 Hz), 115.16 (d, *J* = 22.0 Hz), 38.71, 33.68, 30.51.

HRMS (ESI): $C_{21}H_{22}ClFNa^{+}$ ($M+Na^{+}$): 351.1287, found: 351.1289.

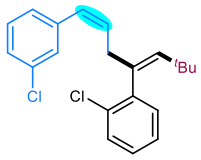


1-chloro-2-((1*Z*,4*Z*)-1-(3-methoxyphenyl)-6,6-dimethylhepta-1,4-dien-4-yl) benzene (5f). The title compound **5f** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (51.8 mg, 76% yield, *Z*/*E* = 88:12).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 1H), 7.23 – 7.10 (m, 4H), 6.83 – 6.71 (m, 3H), 6.48 (d, *J* = 11.6 Hz, 1H), 5.71 (dt, *J* = 11.6, 7.7 Hz, 1H), 5.55 (s, 1H), 3.77 (s, 3H), 3.17 (d, *J* = 7.7 Hz, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.41, 140.98, 138.72, 138.66, 133.55, 132.95, 131.25, 130.38, 129.73, 129.19, 129.00, 127.99, 125.92, 121.10, 113.94, 112.35, 55.17, 38.68, 33.66, 30.54.

HRMS (ESI): $C_{22}H_{25}ClNaO^+$ ($M+Na^+$): 363.1487, found: 363.1488.

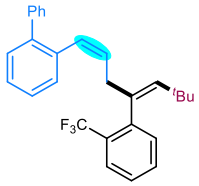


1-chloro-2-((1Z,4Z)-1-(3-chlorophenyl)-6,6-dimethylhepta-1,4-dien-4-yl) benzene (5g). The title compound **5g** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (58 mg, 84% yield, *Z*/*E* = 88:12).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.32 (m, 1H), 7.21 – 7.13 (m, 6H), 7.05 – 7.01 (m, 1H), 6.46 (d, *J* = 11.5 Hz, 1H), 5.76 (dt, *J* = 11.5, 7.9 Hz, 1H), 5.54 (t, *J* = 1.5 Hz, 1H), 3.19 – 3.07 (m, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.76, 138.98, 138.89, 133.96, 133.16, 132.98, 131.22, 130.62, 129.52, 129.26, 129.25, 128.34, 128.09, 126.69, 126.00, 38.60, 33.72, 30.52.

HRMS (FI): $C_{21}H_{22}Cl_2$: 344.1099, found: 344.1096.



2-((1*Z*,4*Z*)-6,6-dimethyl-4-(2-(trifluoromethyl)phenyl)hepta-1,4-dien-1-yl)-1,1'-biphenyl (5h). The title compound **5h** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (51.3 mg, 61% yield, *Z*/*E* = 95:5).

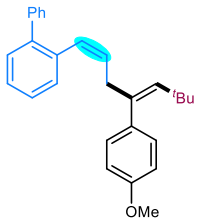
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.22 (m, 9H), 7.18 (d, *J* = 7.0 Hz, 2H), 6.31 (d, *J* = 11.4 Hz, 1H), 5.65 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.48 (s, 1H), 3.25 – 3.10 (m, 2H), 0.83 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.53 (s, 3F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.16, 141.06, 140.90 (q, *J* = 2.1 Hz),

138.53, 135.03, 133.03, 131.92, 130.80, 130.66, 129.67, 129.42, 129.27, 128.21 (q, *J* = 29.7 Hz), 127.81, 127.11, 126.90, 126.84, 126.73, 126.32 (q, *J* = 5.0 Hz), 124.33 (q, *J* = 274.2 Hz), 39.85 (d, *J* = 2.2 Hz), 34.10, 30.51.

HRMS (ESI): $C_{28}H_{27}F_3Na^+$ ($M+Na^+$): 443.1958, found: 443.1957.

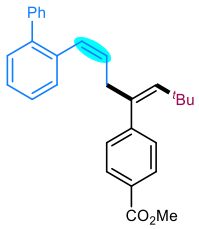


2-((1*Z*,4*Z*)-4-(4-methoxyphenyl)-6,6-dimethylhepta-1,4-dien-1-yl)-1,1'-biphenyl (5i). The title compound **5i** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (62 mg, 81% yield, *Z*/*E* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 6H), 7.23 – 7.17 (m, 3H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.23 (d, *J* = 11.5 Hz, 1H), 5.62 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.47 (s, 1H), 3.78 (s, 3H), 3.15 (d, *J* = 7.5 Hz, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.12, 141.10, 141.08, 137.88, 137.05, 135.26, 134.59, 130.19, 129.90, 129.87, 129.70, 129.63, 127.76, 126.97, 126.81, 126.63, 55.12, 41.23, 33.38, 31.45.

HRMS (ESI): $C_{28}H_{30}NaO^+$ ($M+Na^+$): 405.2189, found: 405.2193.

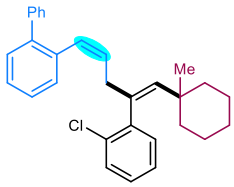


methyl 4-((1Z,4Z)-1-([1,1'-biphenyl]-2-yl)-6,6-dimethylhepta-1,4-dien-4-yl) benzoate (5j). The title compound **5j** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (43.5 mg, 53% yield, *E*/*Z* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.23 (m, 6H), 7.21 – 7.13 (m, 5H), 6.25 (d, *J* = 11.5 Hz, 1H), 5.59 (dt, *J* = 11.4, 7.5 Hz, 1H), 5.51 (s, 1H), 3.90 (s, 3H), 3.16 (d, *J* = 7.5 Hz, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.04, 147.76, 141.14, 141.00, 138.34, 136.41, 135.00, 130.74, 129.69, 129.59, 129.52, 129.12, 129.03, 128.97, 128.25, 127.77, 127.10, 126.86, 126.64, 51.99, 40.71, 33.50, 31.35.

HRMS (ESI): $C_{29}H_{30}NaO_2^+$ ($M+Na^+$): 433.2138, found: 433.2137.

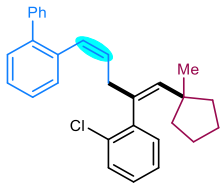


2-((1*Z*,4*Z*)-4-(2-chlorophenyl)-5-(1-methylcyclohexyl)penta-1,4-dien-1-yl)-1,1'-biphenyl (5k). The title compound **5k** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (53 mg, 62% yield, *Z*/*E* =95:5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 10H), 7.21 – 7.13 (m, 3H), 6.29 (d, *J* = 11.5 Hz, 1H), 5.67 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.56 (s, 1H), 3.21 (d, *J* = 7.6 Hz, 2H), 1.50 – 1.31 (m, 8H), 1.17 – 1.04 (m, 2H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.18, 141.08, 141.06, 138.31, 135.14, 132.85, 131.30, 130.65, 129.70, 129.65, 129.34, 129.31, 127.98, 127.80, 127.07, 126.82, 126.73, 125.84, 39.62, 38.86, 38.74, 36.37, 26.77, 26.16, 22.64, 22.48.

HRMS (ESI): $C_{30}H_{31}ClNa^+$ ($M+Na^+$): 450.2007, found: 450.2008.



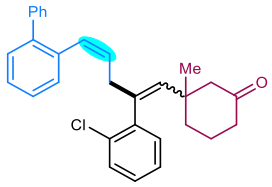
2-((1*Z*,4*Z*)-4-(2-chlorophenyl)-5-(1-methylcyclopentyl)penta-1,4-dien-1-yl)-1,1'-biphenyl (5l). The title compound **5l** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (57 mg, 69%

yield, *Z*/*E* =91:9).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 10H), 7.21 – 7.17 (m, 2H), 7.16 – 7.13 (m, 1H), 6.28 (d, *J* = 11.5 Hz, 1H), 5.72 – 5.61 (m, 2H), 3.20 (d, *J* = 7.5 Hz, 2H), 1.56 – 1.26 (m, 7H), 1.16 – 1.08 (m, 1H), 0.87 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.17, 141.14, 141.07, 138.24, 135.12, 134.58, 133.05, 131.32, 130.62, 129.68, 129.63, 129.61, 129.23, 127.99, 127.79, 127.05, 126.80, 126.73, 125.93, 44.69, 40.92, 39.44, 38.31, 25.93, 23.64, 23.22.

HRMS (ESI): $C_{29}H_{29}ClNa^+$ ($M+Na^+$): 435.1850, found: 435.1856.

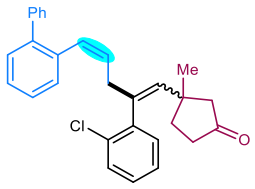


3-((1*Z*,4*Z*)-5-([1,1'-biphenyl]-2-yl)-2-(2-chlorophenyl)penta-1,4-dien-1-yl)-3-methylcyclohexan-1-one (5m). The title compound **5m** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (46.7 mg, 53% yield, 4*Z*/4*E* = 92:8, 1*Z*/1*E* = 1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.01 (m, 13H), 6.23 (d, *J* = 11.6 Hz, 1H), 5.58 – 5.50 (m, 1H), 5.41 (s, 1H), 3.13 – 3.06 (m, 2H), 2.22 – 2.08 (m, 3H), 1.96 – 1.57 (m, 5H), 1.46 – 1.37 (m, 1H), 0.82 (s, 1.5H), 0.80 (s, 1.5H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.36, 141.02, 140.13, 140.08, 136.67, 136.16, 135.79, 135.42, 134.85, 132.62, 132.56, 131.18, 131.14, 131.08, 130.74, 129.67, 129.60, 129.50, 129.46, 129.41, 128.45, 128.44, 128.42, 128.38, 127.79, 127.15, 126.83, 126.72, 126.19, 53.85, 53.52, 41.33, 41.26, 40.76, 40.69, 38.90, 38.80, 37.33, 36.93, 25.82, 25.27, 22.14, 21.98.

HRMS (ESI): $C_{30}H_{29}ClNaO^+$ ($M+Na^+$): 463.1800, found: 463.1804.

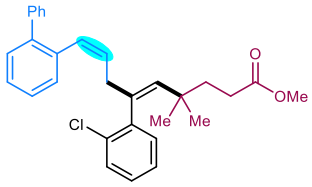


(*R*)-3-((1*Z*,4*Z*)-5-([1,1'-biphenyl]-2-yl)-2-(2-chlorophenyl)penta-1,4-dien-1-yl)-3-methylcyclopentan-1-one (5n). The title compound **5n** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (55.5 mg, 65% yield, 4*Z*/4*E* =94:6, 1*Z*/1*E* =1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 6.97 (m, 13H), 6.26 (d, *J* = 11.4 Hz, 1H), 5.68 – 5.48 (m, 2H), 3.14 (d, *J* = 7.4 Hz, 2H), 2.16 – 1.51 (m, 6H), 0.98 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 219.18, 218.93, 141.08, 141.06, 141.04, 140.08, 140.01, 136.61, 136.59, 135.36, 135.13, 134.87, 132.78, 132.62, 131.22, 131.15, 130.95, 130.70, 129.72, 129.61, 129.53, 129.40, 128.66, 128.55, 128.39, 128.32, 127.81, 127.19, 126.86, 126.75, 126.36, 126.33, 52.58, 51.13, 41.59, 41.41, 38.44, 37.94, 36.69, 36.29, 35.85, 35.75, 26.43, 25.95.

HRMS (ESI): $C_{29}H_{27}ClNaO^+$ ($M+Na^+$): 449.1643, found: 449.1644.

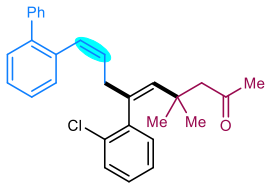


methyl (5*Z*,8*Z*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dienoate (5o). The title compound **5o** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (71.6 mg, 78% yield, *Z*/*E* = 94:6).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 6H), 7.25 – 7.15 (m, 6H), 7.14 – 7.09 (m, 1H), 6.30 (d, *J* = 11.4 Hz, 1H), 5.64 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.41 (s, 1H), 3.65 (s, 3H), 3.19 (d, *J* = 7.5 Hz, 2H), 2.36 – 2.27 (m, 2H), 1.64 – 1.56 (m, 2H), 0.82 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.58, 141.10, 141.09, 140.65, 136.34, 136.00, 134.99, 132.86, 131.00, 130.90, 129.66, 129.64, 129.52, 129.26, 128.81, 128.13, 127.80, 127.11, 126.82, 126.73, 126.00, 51.48, 39.43, 38.92, 36.48, 30.23, 27.61, 27.52.

HRMS (ESI): $C_{30}H_{31}ClNaO_2^+$ ($M+Na^+$): 481.1905, found: 481.1908.

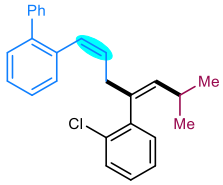


(5*Z*,8*Z*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dien-2-one (5p). The title compound **5p** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (60 mg, 72% yield, *Z*/*E* = 93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 6H), 7.26 – 7.17 (m, 6H), 7.16 – 7.12 (m, 1H), 6.31 (d, *J* = 11.5 Hz, 1H), 5.70 – 5.63 (m, 1H), 5.62 (s, 1H), 3.20 (dt, *J* = 7.6, 1.5 Hz, 2H), 2.43 – 2.32 (m, 2H), 2.07 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.88, 141.05, 141.01, 140.53, 136.33, 134.93, 134.90, 132.76, 131.09, 130.97, 129.63, 129.55, 129.27, 128.65, 128.18, 127.78, 127.10, 126.80, 126.74, 126.05, 56.24, 38.91, 36.20, 31.88, 28.66, 27.95.

HRMS (ESI): $C_{29}H_{29}ClNaO^+$ ($M+Na^+$): 451.1800, found: 451.1803.



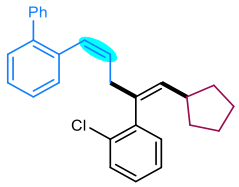
2-((1*Z*,4*Z*)-4-(2-chlorophenyl)-6-methylhepta-1,4-dien-1-yl)-1,1'-biphenyl (5q). The title compound **5q** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (50 mg, 67% yield, *Z*/*E* =93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 1H), 7.35 – 7.17 (m, 11H), 7.13 – 7.04 (m, 1H), 6.29 (d, *J* = 11.4 Hz, 1H), 5.68 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.41 (d, *J* = 10.0 Hz, 1H), 3.29 – 3.17 (m, 2H), 2.11 – 1.99 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.14, 141.07, 140.36, 136.54, 135.10, 134.91, 132.87, 130.67, 130.63, 129.69, 129.66, 129.64, 129.41, 128.87, 127.99,

127.80, 127.07, 126.82, 126.74, 126.45, 36.54, 28.61, 23.12, 22.47.

HRMS (ESI): $C_{26}H_{25}ClNa^+$ ($M+Na^+$): 395.1537, found: 395.1539.

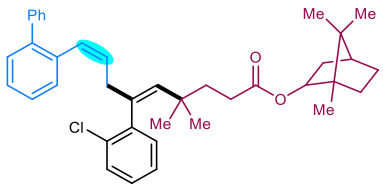


2-((1*Z*,4*Z*)-4-(2-chlorophenyl)-5-cyclopentylpenta-1,4-dien-1-yl)-1,1'-biphenyl (5r). The title compound **5r** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (46.3 mg, 58% yield, *Z*/*E* =95:5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.07 (m, 12H), 7.01 (d, *J* = 7.0 Hz, 1H), 6.21 (d, *J* = 11.5 Hz, 1H), 5.60 (q, *J* = 8.1 Hz, 1H), 5.42 (d, *J* = 9.8 Hz, 1H), 3.23 – 3.09 (m, 2H), 2.13 – 1.99 (m, 1H), 1.71 – 1.61 (m, 1H), 1.60 – 1.45 (m, 3H), 1.38 – 1.30 (m, 2H), 1.23 – 1.13 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.15, 141.07, 140.46, 135.70, 135.11, 134.63, 132.99, 130.83, 130.60, 129.67, 129.65, 129.37, 128.95, 127.94, 127.79, 127.05, 126.80, 126.74, 126.40, 40.12, 36.60, 33.69, 33.11, 25.34, 25.30.

HRMS (ESI): $C_{28}H_{27}ClNa^+$ ($M+Na^+$): 421.1694, found: 421.1695.



(1*R*, 4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (5*Z*, 8*Z*)-9-([1,1'-biphenyl]-2-yl)-6-(2-chlorophenyl)-4,4-dimethylnona-5,8-dienoate (5s). The title compound **5s** was prepared according to the General Procedure B and isolated by flash chromatography as a colorless oil liquid (77.9 mg, 67% yield, *Z*/*E* =93:7).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 8H), 7.24 – 7.16 (m, 4H), 7.14 – 7.09 (m, 1H), 6.30 (d, *J* = 11.5 Hz, 1H), 5.64 (dt, *J* = 11.3, 7.7 Hz, 1H), 5.42 (s, 1H), 4.69 – 4.61 (m, 1H), 3.19 (d, *J* = 7.6 Hz, 2H), 2.32 – 2.25 (m, 2H), 1.78 – 1.51 (m,

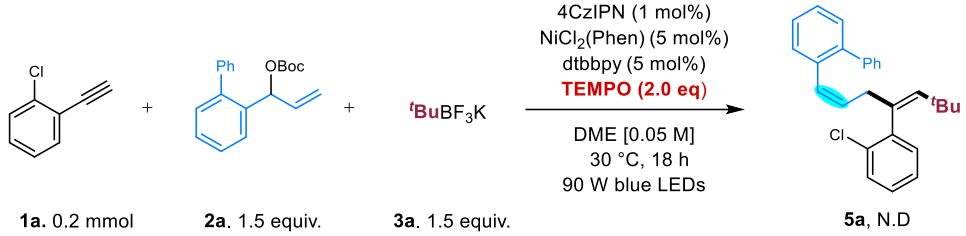
7H), 1.18 – 1.05 (m, 2H), 0.97 (s, 3H), 0.84 – 0.81 (m, 9H), 0.80 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.65, 141.09, 141.06, 140.64, 136.50, 135.96, 134.98, 132.84, 131.02, 130.90, 129.63, 129.50, 129.26, 128.83, 128.11, 127.80, 127.10, 126.82, 126.72, 125.99, 80.72, 48.62, 46.87, 45.00, 39.46, 38.91, 38.75, 36.43, 33.71, 30.86, 27.71 (d, *J* = 4.2 Hz), 27.54 (d, *J* = 2.8 Hz), 27.01, 20.10, 19.92, 11.45.

HRMS (ESI): $C_{39}H_{45}ClNaO_2^+$ ($M+Na^+$): 603.3001, found: 603.3004.

6. Mechanistic studies

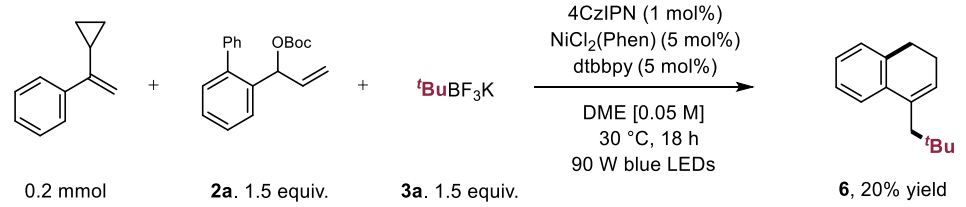
6.1 Radical inhibition reaction



1a. 0.2 mmol **2a**. 1.5 equiv. **3a**. 1.5 equiv. **5a**, N.D

To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (0.8 mg, 0.001 mmol, 1 mol%), $NiCl_2$·Phen (1.6 mg, 0.005 mmol, 5 mol%), dtbbpy (1.4 mg, 0.005 mmol, 5 mol%), $^tBuBF_3K$ (24.6 mg, 0.15 mmol, 1.5 equiv.), and TEMPO (15.6 mg, 0.2 mmol, 2 equiv.). After DME were added as a solution (2 mL). The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-chloro-2-ethynylbenzene (12.2 μL, 0.1 mmol, 1.0 equiv.), and 1-([1,1'-biphenyl]-2-yl) allyl *tert*-butyl carbonate (45 μL, 0.15 mmol, 1.5 equiv.). The reaction mixture was then irradiated with a 90 W blue LEDs for 18 h at 35 °C. Dodecane (22.7 μL, 0.1 mmol, 1.0 equiv.) was added and the mixture was analyzed by GC. The GC analysis of the reaction mixture indicated that no products were generated with the addition of 2.0 equiv. TEMPO.

6.2 Radical probe reaction



0.2 mmol **2a**. 1.5 equiv. **3a**. 1.5 equiv. **6**, 20% yield

To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.8 mg, 0.01 mmol, 5 mol%), and $^tBuBF_3K$ (49.2 mg, 0.3 mmol, 1.5 equiv.). After DME were added as a solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of (1-

cyclopropylvinyl)benzene (29 μL, 0.2 mmol, 1.0 equiv.), and 1-([1,1'-biphenyl]-2-yl)allyl *tert*-butyl carbonate (90 μL, 0.3 mmol, 1.5 equiv.). The reaction mixture was then irradiated with a 90 W blue LED for 18 h at 35°C. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the alkene **6**.

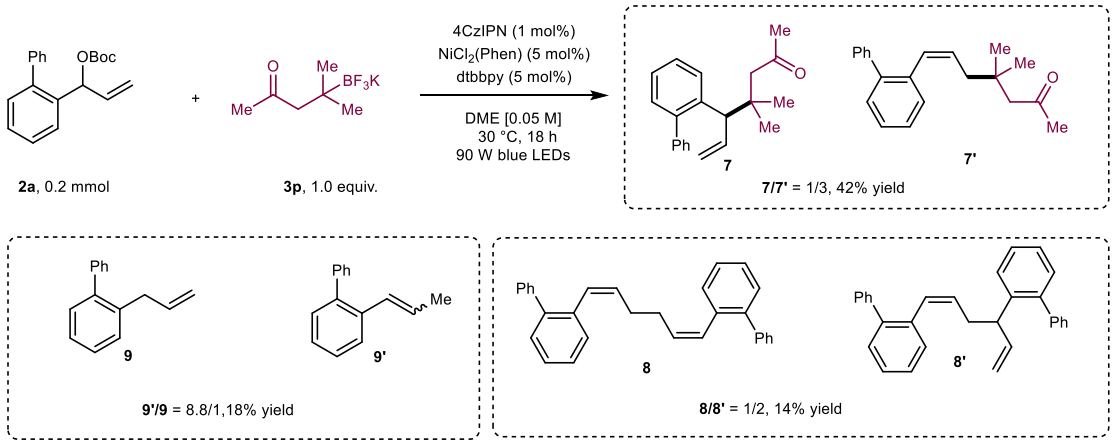
4-neopentyl-1,2-dihydronaphthalene (6)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.07 (m, 3H), 5.82 (t, *J* = 4.7 Hz, 1H), 2.72 (t, *J* = 7.9 Hz, 2H), 2.40 (s, 2H), 2.27 – 2.17 (m, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.57, 136.26, 134.74, 128.64, 127.41, 126.17, 125.86, 123.55, 44.91, 31.77, 30.25, 29.00, 23.32.

6.3 Control experiments

a) control experiments between carbonates and trifluoroborates



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.8 mg, 0.01 mmol, 5 mol%), and 4-methyl-4-(trifluoro-l4-boraneyl)pentan-2-one, potassium salt (41.2 mg, 0.2 mmol, 1.0 equiv.). After DME were added as a solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-([1,1'-biphenyl]-2-yl)allyl tert-

butyl carbonate (90 μL, 0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs for 18 h at 35°C. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the correspond product **7**, **7'**, **8**, **8'**, **9** and **9'**. The ratios were determined by ^{1}H-NMR analysis.

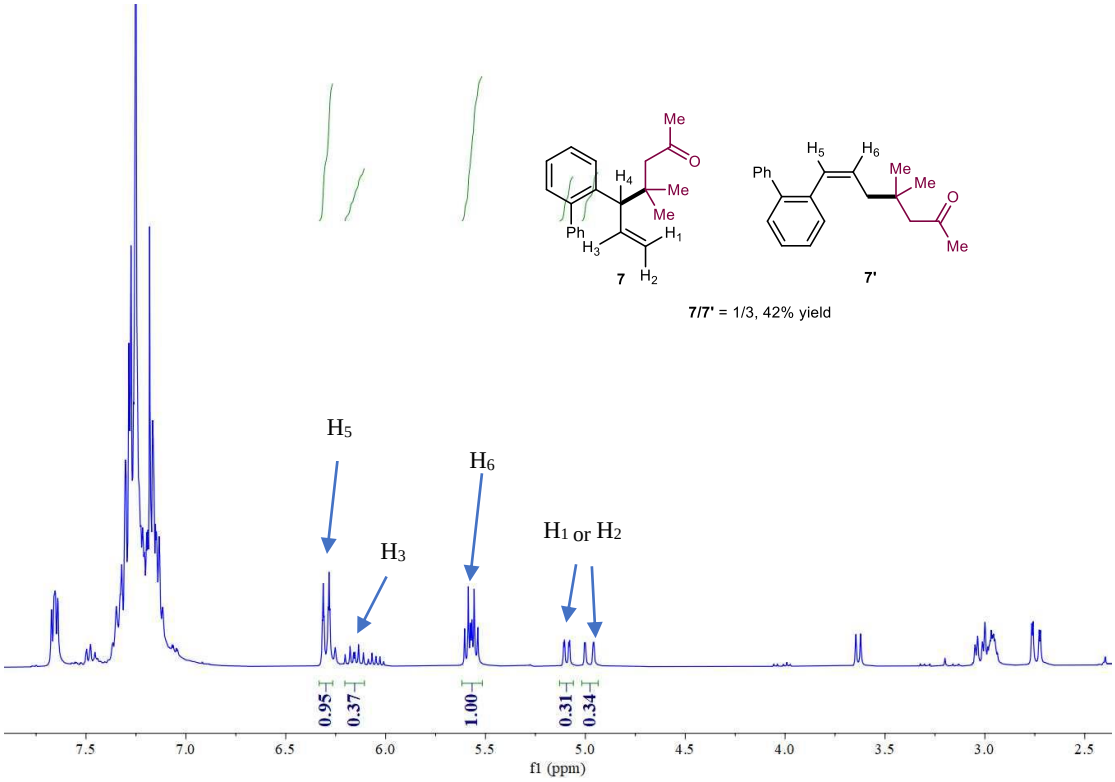


Figure S1. ^{1}H-NMR spectrum of **7**/**7'**

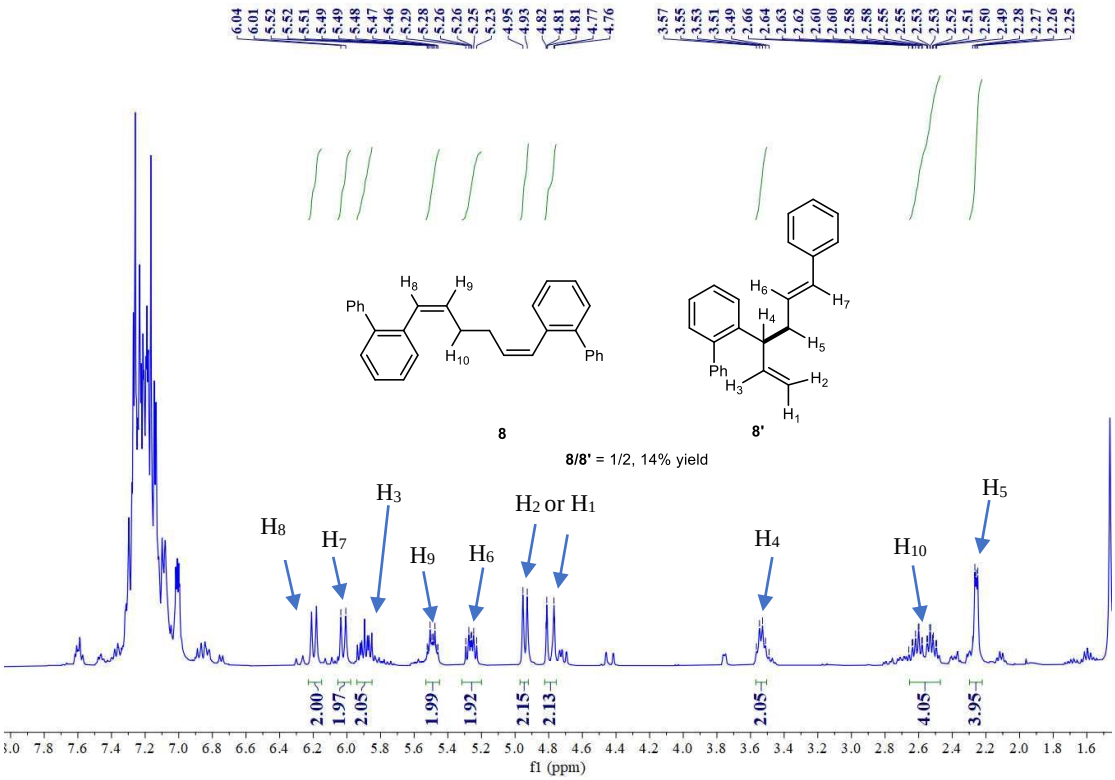


Figure S2. ^{1}H-NMR spectrum of **8**/**8'**

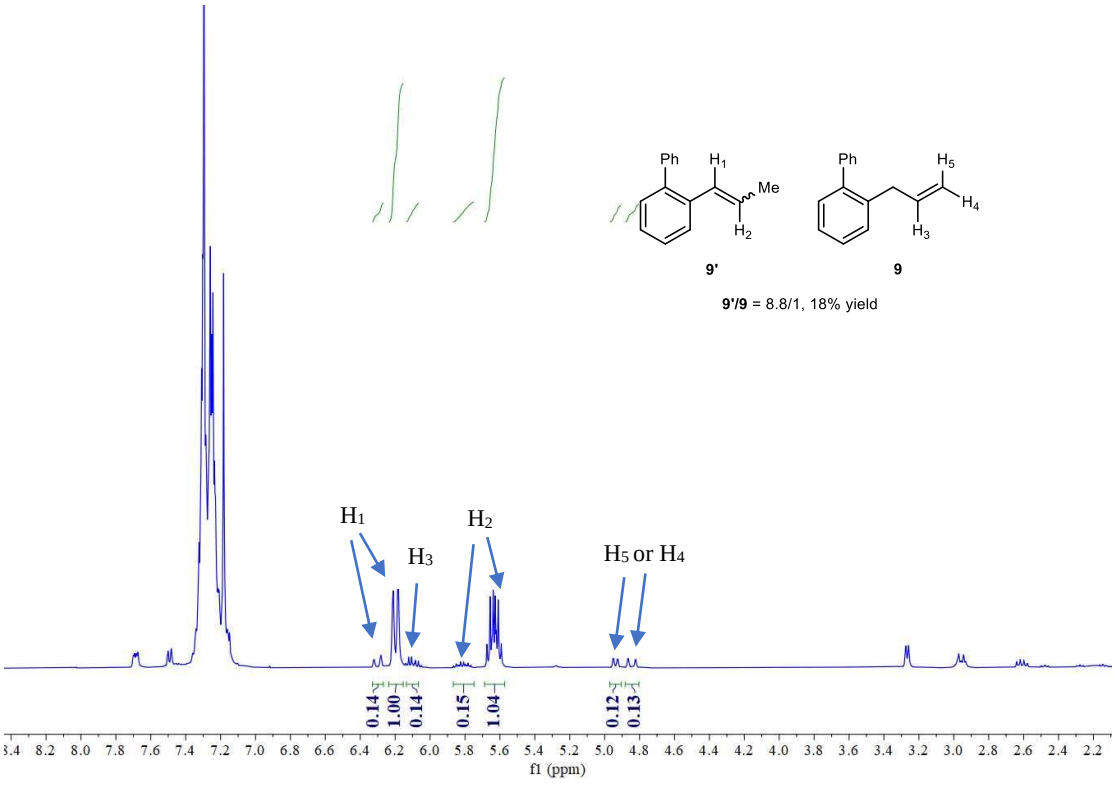
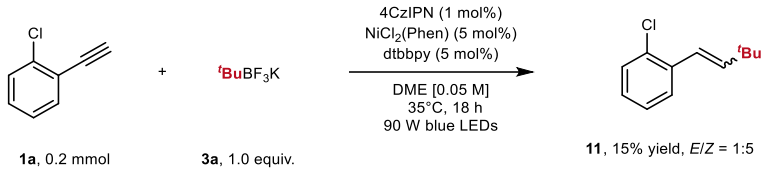


Figure S3. ^{1}H-NMR spectrum of **9**/**9'**

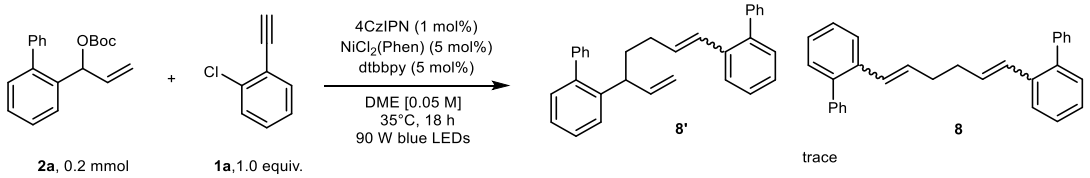
b) control experiments between alkynes and trifluoroborates



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.8 mg, 0.01 mmol, 5 mol%), and $^tBuBF_3K$ (32.8 mg, 0.2 mmol, 1.0 equiv.). After DME were added as a solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-chloro-2-ethynylbenzene (24.5 μL, 0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs for 18 h at 35°C. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the alkene **11** (*E*/*Z* = 1:5) in 15% yield. The NMR data was in accordance with previous reports.[4]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.09 (m, 4.8H), 6.69 (d, *J* = 16.0 Hz, 0.2H), 6.23 (d, *J* = 12.4 Hz, 1.2H), 5.69 (d, *J* = 12.6 Hz, 1H), 1.14 (s, 1.8H), 0.96 (s, 9H).

c) control experiments between carbonates and alkynes

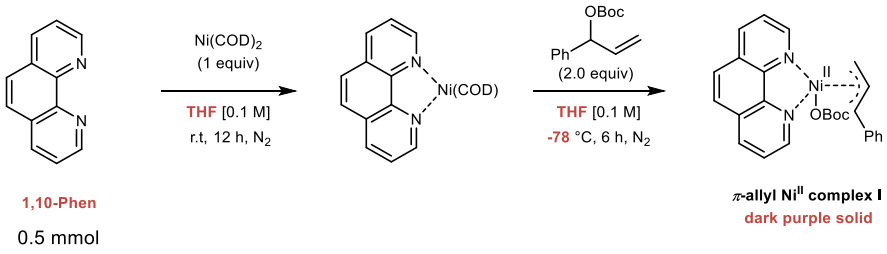


To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), and dtbbpy (2.8 mg, 0.01 mmol, 5 mol%). After DME were added as a

solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-chloro-2-ethynylbenzene (24.5 μL, 0.2 mmol, 1.0 equiv.) and 1-([1,1'-biphenyl]-2-yl)allyl *tert*-butyl carbonate (90 μL, 0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs for 18 h at 35°C. The reaction mixture was quenched with water, extracted with ethyl acetate. The crude mixture was analyzed by GCMS and the **8**/**8'** were not detected in the reaction mixture.

6.4 Reactions with prepared allylnickel complex

a). Preparation of (allyl)Ni^{II} complex



Allylic nickel complex was synthesized according to a reported procedure[5] with a slight modification. In a nitrogen filled glove box, a 50 mL round bottom flask containing a stirring bar was charged with Ni(COD)$_2$ (138 mg, 0.5 mmol, 1.0 equiv.), 1,10-phenanthroline (90 mg, 0.5 mmol, 1.0 equiv.), and dry THF (5 mL). The dark purple mixture was stirred overnight at room temperature. After cooling to -78 °C, *tert*-butyl (1-phenylallyl) carbonate (234.3 mg, 1.0 mmol, 2.0 equiv.) was added and the solution became blackish green. Then the mixture was transferred into the glove box, slowly warmed to room temperature and stirred for an additional 6 hours. THF was removed under vacuum. The resulting solid was washed with dry pentane (3 × 10 mL) and dried under vacuum to obtain the Ni$^{(II)}$ complex as a purple solid. The product turned out to be highly insoluble in the vast majority of solvents used for NMR spectroscopy, obtaining in all cases broad signals. **Caution**: This complex is extremely sensitive to air and water, and all operations, except for the addition of carbonates at -78 °C, are performed in the glove box. **^{1}H-NMR (400 MHz, CD$_2$Cl$_2$)** δ (ppm) 8.16– 6.62 (m, 13H), 6.44 – 6.16 (m, 2H), 4.24 – 3.93 (m, 2H). 1.68 – 1.06 (s,

9H).

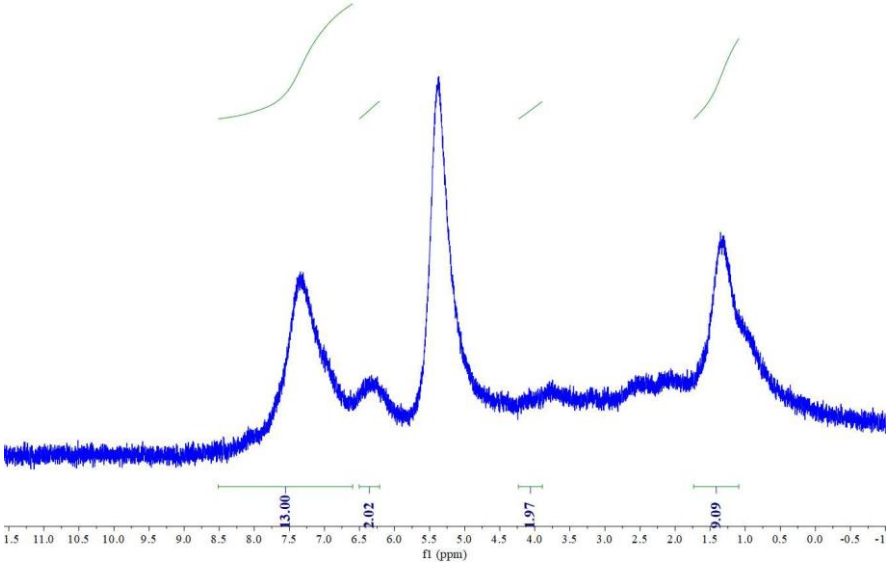


Figure S4. ^{1}H-NMR spectrum of **(allyl)Ni^{II} complex**

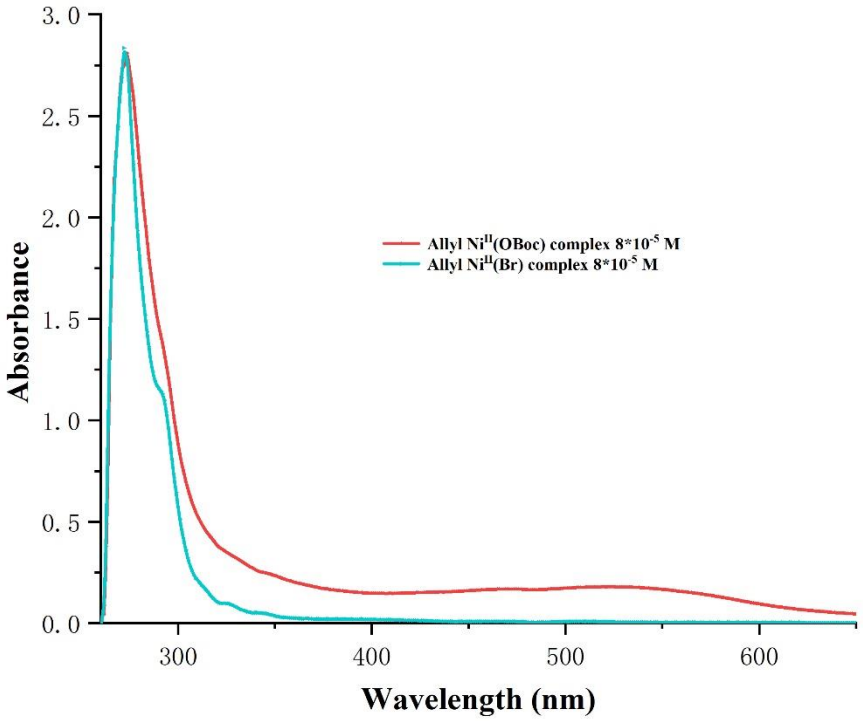
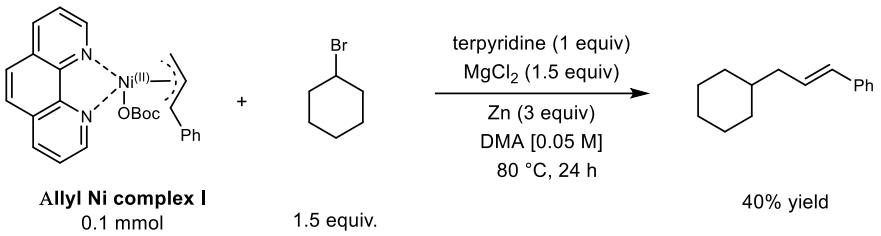


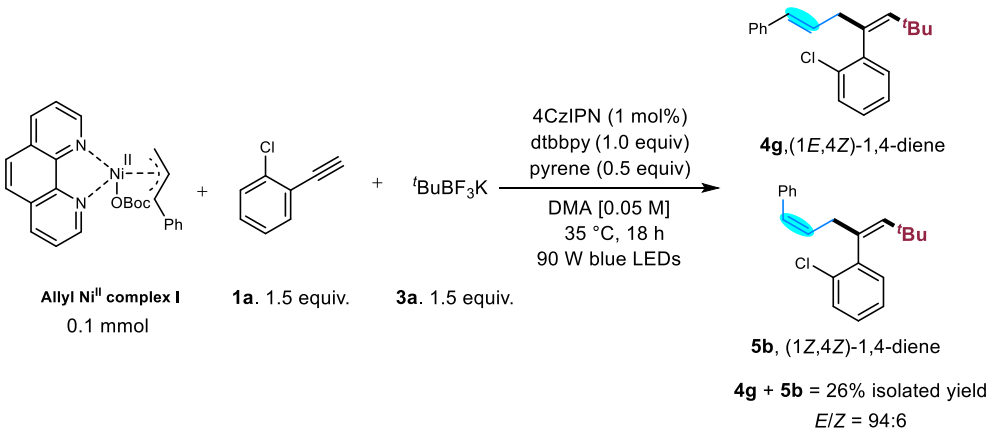
Figure S5. UV-Vis absorption spectrum of (allyl)Ni^{II} complex **I**

Comment: The UV-Vis spectrum of complex **I** also matches the one prepared from allylic bromide, previously reported by Studer.[5]



Comment: To further validate the structure of the prepared allylnickel complex, we have carried it for the stoichiometric reductive reaction with cyclohexyl bromide in the presence of Zn (slightly modified conditions, based on Gong's report[6]), delivering a 40% yield of the allyl-alkyl coupling product which have been reported by Wu and co-workers[7].

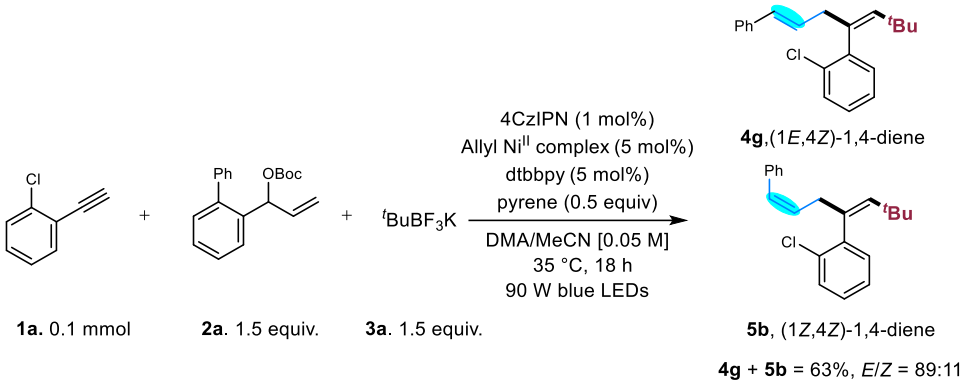
b). Stoichiometric experiment with (allyl)Ni^{II} complex



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (0.8 mg, 0.001 mmol, 1.0 mol%), dtbbpy (26.8 mg, 0.1 mmol, 1.0 equiv.), pyrene (10.1 mg, 0.05 mmol, 0.5 equiv.), and ^{t}BuBF$_3$K (24.6 mg, 0.15 mmol, 1.5 equiv.). The reaction vial was transferred into the glove box and Ni^{II} complex (47.3 mg, 0.10 mmol, 1.0 equiv.) was added, followed by the addition of DMA (2.0 mL) and 1-chloro-2-ethynylbenzene (20.6 mg, 0.15 mmol, 1.5 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs for 18 h at 35 °C. The reaction was

quenched with water, extracted with ethyl acetate, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography to afford the desired alkenes in 26% yield with *E*/*Z* = 94:6.

c). Catalytic experiment with (allyl)Ni^{II} complex



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (0.8 mg, 0.001 mmol, 1.0 mol%), dtbbpy (1.4 mg, 0.005 mmol, 5 mol%), pyrene (10.1 mg, 0.05 mmol, 0.5 equiv.) and ^{t}BuBF$_3$K (24.6 mg, 0.15 mmol, 1.5 equiv.). The reaction vial was transferred into glove box and Ni^{II} complex (2.4 mg, 0.005 mmol, 5 mol%) was added. Removed the vial from glove box and added DMA/CH_3CN = 1.5 mL/0.5 mL, followed by the addition of 1-chloro-2-ethynylbenzene (13.7 mg, 0.10 mmol, 1.0 equiv.) and allylic carbonate (46.6 mg, 0.15 mmol, 1.5 equiv.) via microsyringe respectively under nitrogen. The reaction mixture was then irradiated with 90 W blue LEDs for 18 h at 35 °C. The reaction mixture was quenched with water, extracted with ethyl acetate and added 1,3-benzodioxole (12.2 mg, 0.10 mmol, 1.0 equiv.) used as ^{1}H-NMR internal standard. The yield and *E*/*Z* ratio were determined by the ^{1}H-NMR analysis.

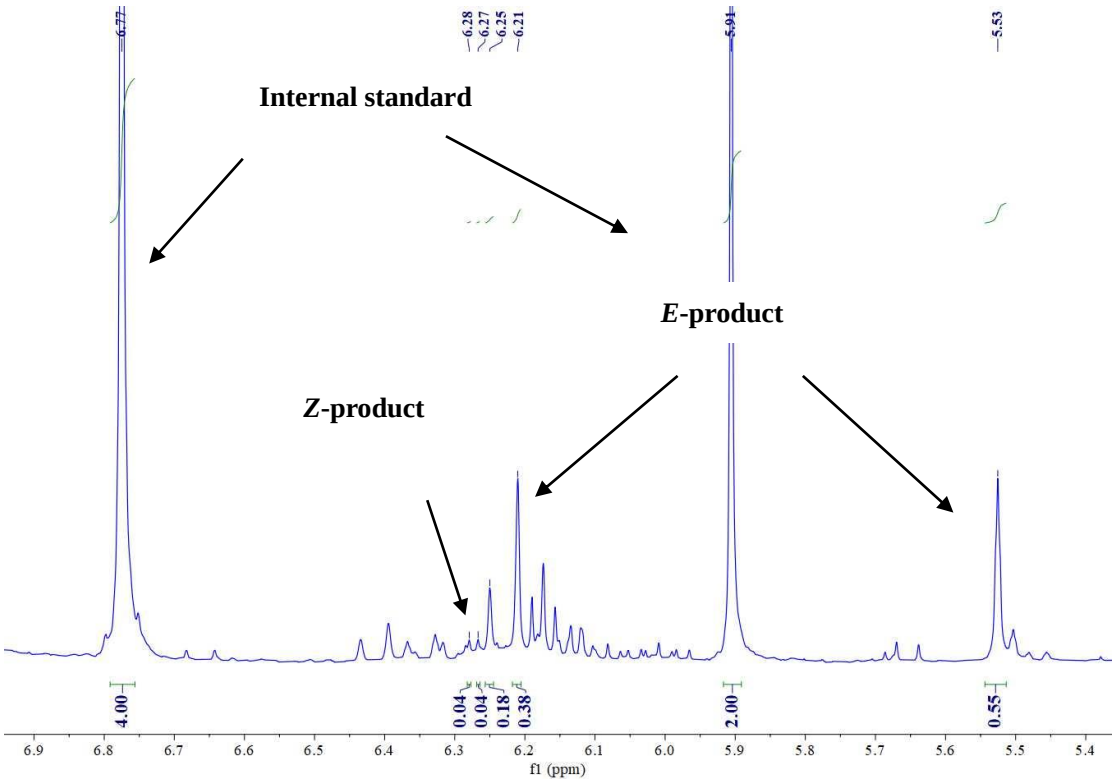


Figure S6. ^{1}H-NMR spectrum of reaction mixture

6.5 Stern-Volmer quenching experiments

Stern-Volmer quenching experiments were carried by Shimadzu RF-5301pc spectrofluorophotometer, using a 0.0025 mM solution of 4CzIPN with variable concentrations (0.5, 1.0, 1.5, 2.0, 2.5 mM) of ^{t}BuBF$_3$K, 1-(*tert*-butyl)-4-ethynylbenzene and allylic carbonate in DMA. The samples were prepared in 3 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box. The intensity of the emission peak at 528 nm (λex = 365 nm) expressed as the ratio I_0 /I, where I_0 is the emission intensity of photocatalyst at 528 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Stern-Volmer plots for each component are given below.

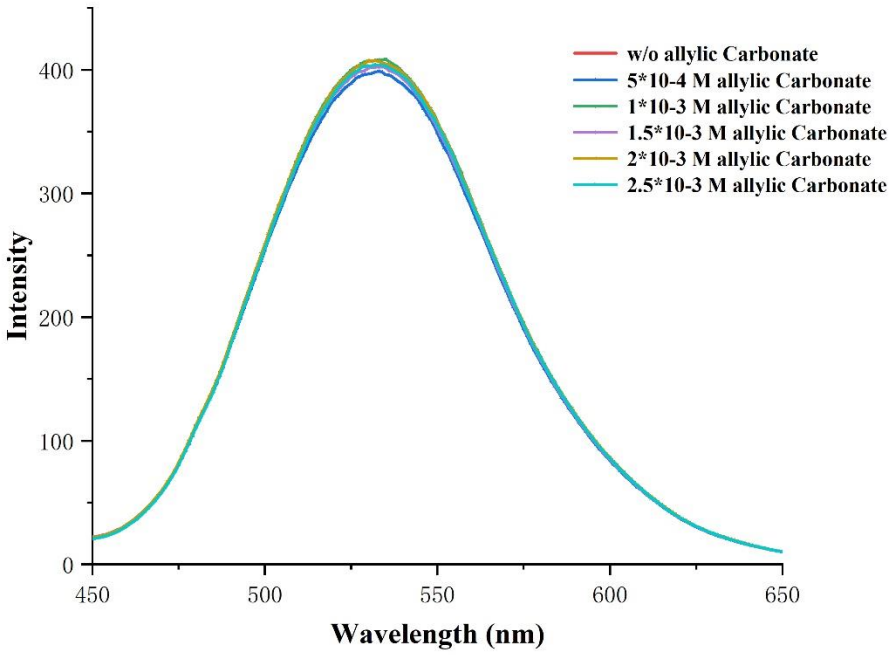


**Figure S7. ***4CzIPN emission quenching with allylic carbonate

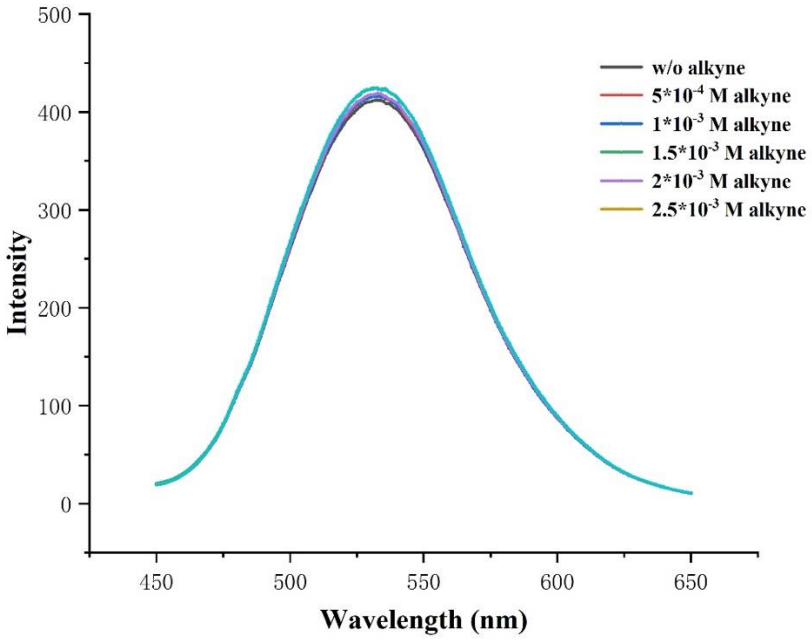


**Figure S8. ***4CzIPN emission quenching with alkyne

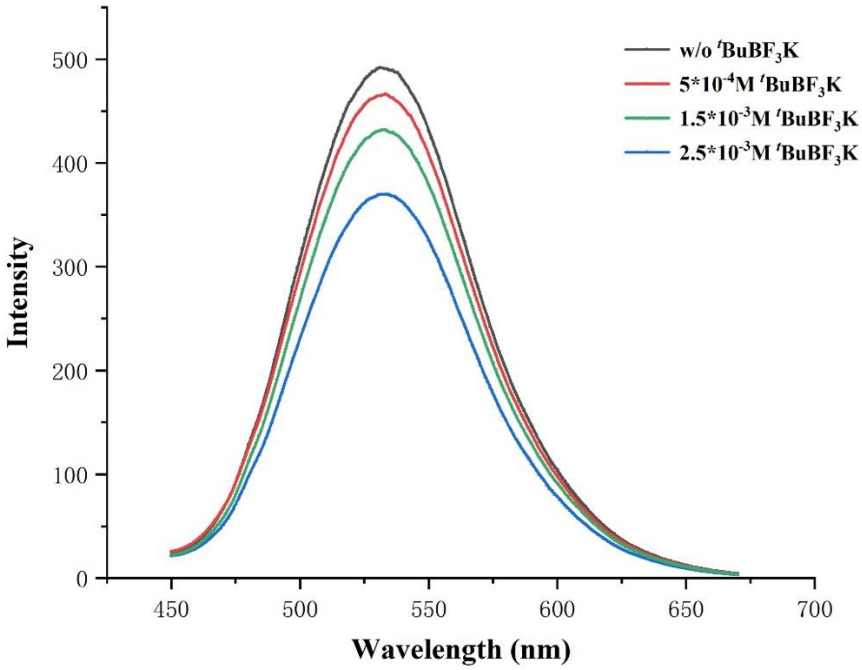


**Figure S9. ***4CzIPN emission quenching with $^{t}BuBF_3K$

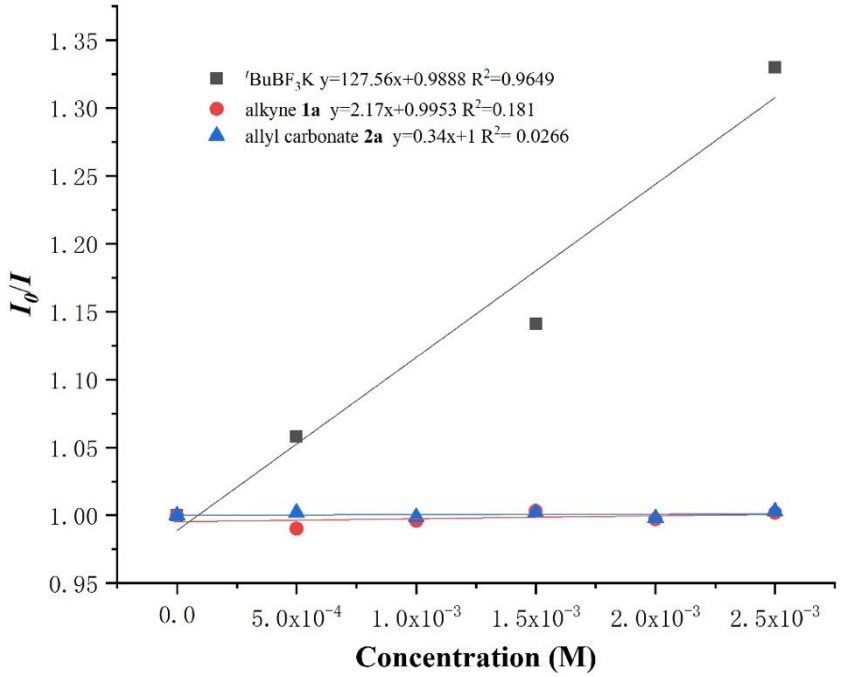


Figure S10. Stern-Volmer plot of *4CzIPN with $^{t}BuBF_3K$, carbonate and alkyne

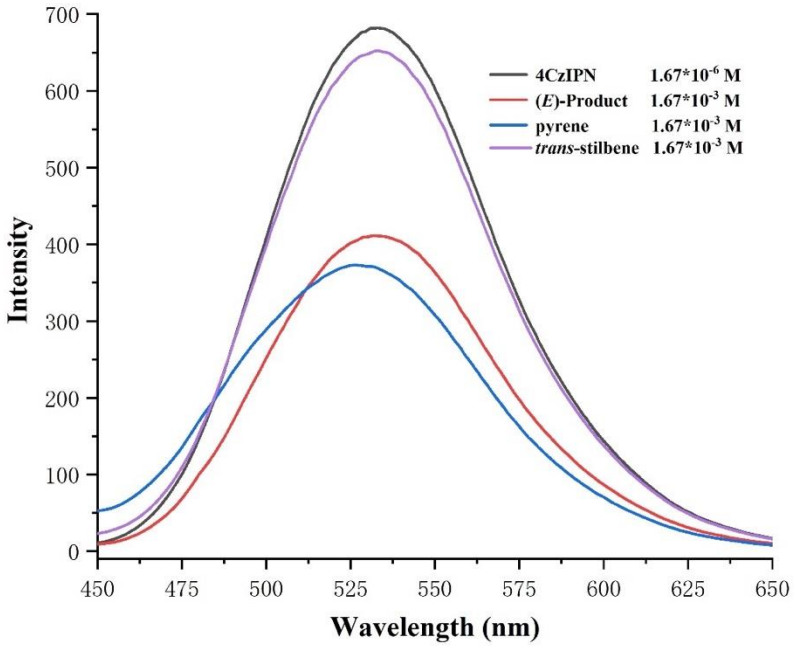


Figure S11. 4CzIPN emission quenching with **4a**, pyrene and *trans*-stilbene

Comment: Both (*E*)-product and pyrene showed an obvious quenching effect to 4CzIPN* while *trans*-stilbene did not give apparent effect.

6.6 Light on/off experiments

For (*E,Z)*-1,4-diene 4a: To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.8 mg, 0.01 mmol, 5 mol%), Pyrene (20.2 mg, 0. 1 mmol, 0.5 equiv.) and $^{t}BuBF_3K$ (49.2 mg, 0.3 mmol, 1.5 equiv.). After DMA (3 mL) and MeCN (1 mL) were added as a solution. The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-chloro-2-ethynylbenzene (24.5 μL, 0.2 mmol, 1.0 equiv.), tert-butyl (1-(o-tolyl)allyl) carbonate (70 μL, 0.3 mmol, 1.5 equiv.) and dodecane (45.5 μL, 0.2 mmol). The reaction mixture was then irradiated with 90 W blue LEDs at 35°C. **Note: (a)**. Dodecane (45.5 μL, 0.2 mmol) was added as GC internal standard. The lights were turned on and off per one hour, and samples were taken for analysis. **(b)**. The *E*/*Z* ratio

of the product was determined by GC analysis. **(c)**. During the monitoring of the reaction, we found that the yield did not increase after 7 hours of the light-on-off experiment, thus we no longer monitored the subsequent yield. **(d)**. As for the monitoring of the *E*/*Z* ratio of the product, we extended the reaction time from 8 h/9h to 19 h since *E*/*Z* ratio and yield of the product displayed different trend over time. In both 2 cases, the *E*/*Z* ratio will significantly increase as the reaction be in progress after 8 h and 9 h respectively.

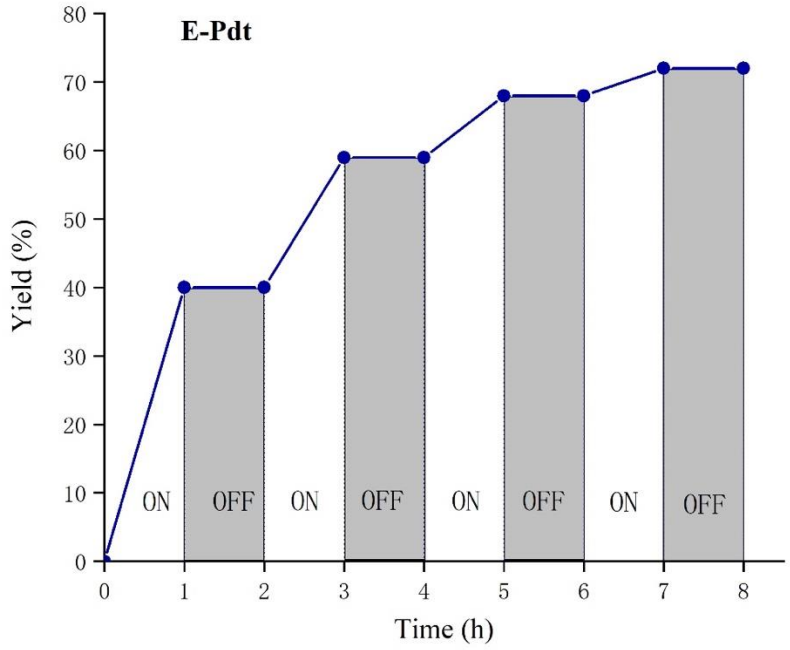


Figure S12. Light-on/off experiments of *E*-pdt **4a** regard to yield

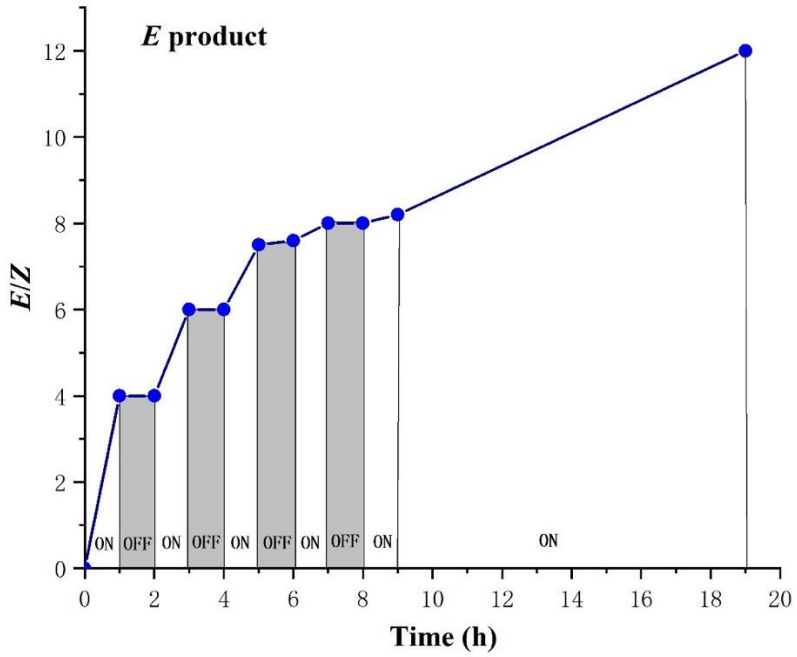


Figure S13. Light-on/off experiments of *E*-pdt **4a** regard to *E*/*Z* ratio.

For *(Z,Z)*-1,4-diene 5a: To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (1.6 mg, 0.002 mmol, 1 mol%), $NiCl_2$·Phen (3.2 mg, 0.01 mmol, 5 mol%), dtbbpy (2.8 mg, 0.01 mmol, 5 mol%) and $^tBuBF_3K$ (49.2 mg, 0.3 mmol, 1.5 equiv.). After DME (4 mL) was added as a solution. The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-chloro-2-ethynylbenzene (24.5 μL, 0.2 mmol, 1.0 equiv.), *tert*-butyl (1-(o-tolyl)allyl) carbonate (70 μL, 0.3 mmol, 1.5 equiv.) and dodecane (45.5 μL, 0.2 mmol). The reaction mixture was then irradiated with 90 W blue LEDs at 35°C. **Note: (a)**. Dodecane (45.5 μL, 0.2 mmol) was added as GC internal standard. The lights were turned on and off per one hour, and samples were taken for analysis. **(b)**. The *E*/*Z* ratio of the product was determined by GC analysis. **(c)**. During the monitoring of the reaction, we found that the yield did not increase after 7 hours of the light-on-off experiment, so we no longer monitored the subsequent yield. (**d**). As for the monitoring of the *E*/*Z* ratio of the product, we extended the reaction time from 8 h/9h to 19 h since *E*/*Z* ratio and yield of the product displayed different trend over time. In

both 2 cases, the *E*/*Z* ratio will significantly increase as the reaction be in progress after 8 h and 9 h respectively.

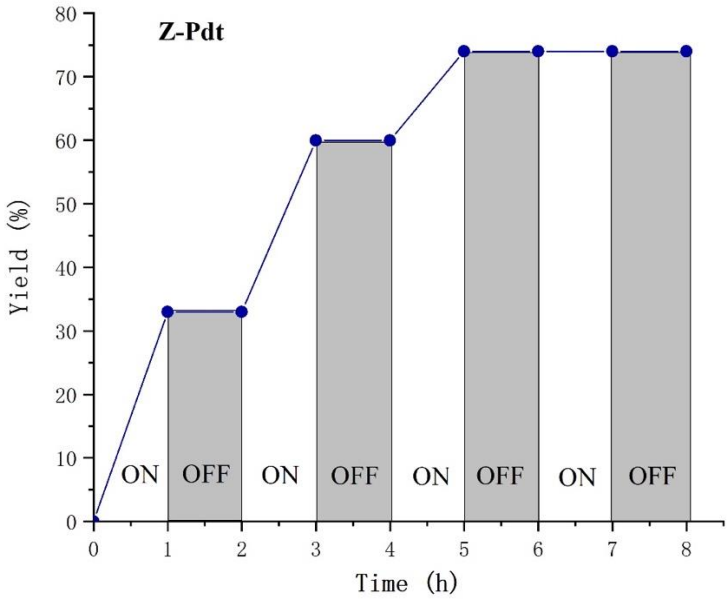


Figure S14. Light-on/off experiments of *Z*-pdt **5a** regard to yield

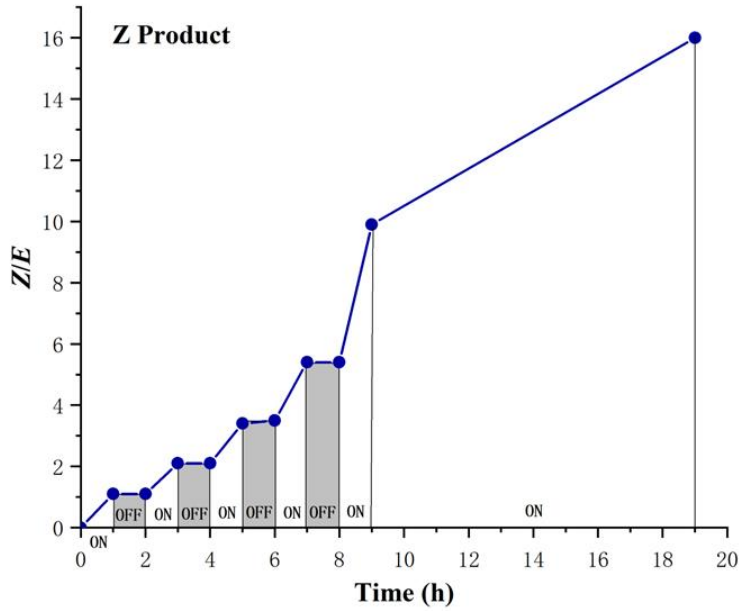
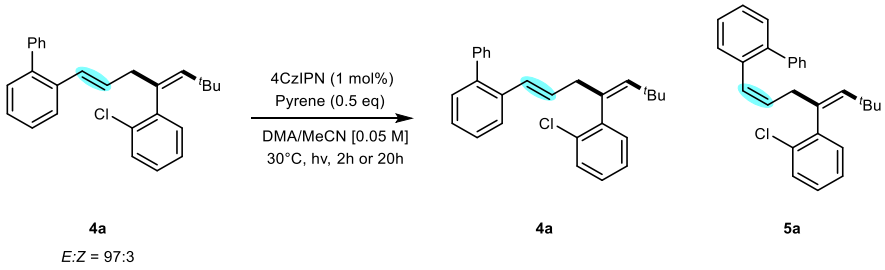


Figure S15. Light-on/off experiments of *Z*-pdt **5a** regard to *E*/*Z* ratio.

6.7 *E*/*Z* isomerization studies

Table S6. *E*/*Z* isomerization studies of (*E*,*Z*)-1,4-diene **4a**



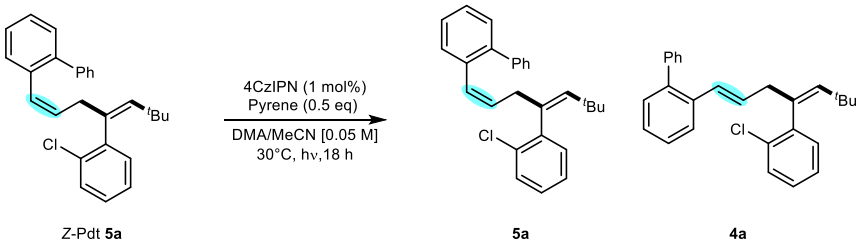
4a *E*:*Z* = 97:3 **4a** **5a**

Entry	*E* : *Z*
Standard conditions	93:7
w/o Pyrene	17:83
w/o 4CzIPN	96:4
w/o 4CzIPN and Pyrene	96:4
w/o 4CzIPN and Pyrene [a]	74:26

[a] prolong the reaction time to 20 h

For (*E*,*Z*)-1,4-diene 4a: To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (0.4 mg, 0.0005 mmol, 1 mol%) and pyrene (5 mg, 0.025 mmol, 0.5 equiv.). After DMA (0.75 mL) and MeCN (0.25 mL) was added as a solution. The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of **1** (19.4 mg, 0.05 mmol, 1.0 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs at 35°C for 2 h. The reaction mixtures were analyzed by GC analysis.

Table S7. *E*/*Z* isomerization studies of (*Z*,*Z*)-1,4-diene **5a**



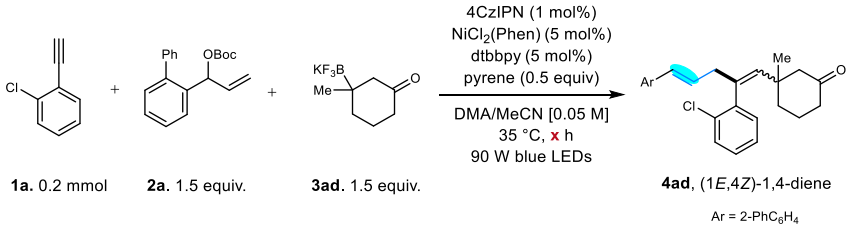
Z-Pdt **5a** *Z*:*E* = 94:6 **5a** **4a**

Entry	*Z* : *E*
Starting material	94:6
Standard conditions	75:25
w/o Pyrene	86:14

w/o 4CzIPN	87:13
w/o 4CzIPN and Pyrene	72:28

For (*Z,Z*)-1,4-diene 5a: To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with 4CzIPN (0.4 mg, 0.0005 mmol, 1 mol%) and Pyrene (5 mg, 0.025 mmol, 0.5 equiv.). After DMA (0.75 mL) and MeCN (0.25 mL) was added as a solution. The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of **5a** (19.4 mg, 0.05 mmol, 1.0 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs at 35°C for 18 h. The reaction mixtures were analyzed by GC analysis.

Table S8. Time course studies of (*E,Z)*-1,4-diene **4ad**



Entry	Time	Yield (%)[a]	*Z*/*E* of bond 4[b]
1	0.5 h	20	1:1
2	1 h	34	1:1
3	2.5 h	61	1:1
4	4 h	68	1:1
5	18 h	80	1:1

[a] Isolated yield. [b] *Z*/*E* ratio was determined by ^{1}H-NMR analysis.

6.8 Cyclic Voltammetry of pyrene

Cyclic voltammetry was conducted on an Electrochemical Workstation (CHI730E) using a 3-electrode cell configuration. A glassy carbon working electrode was employed alongside a platinum wire counter electrode and a Ag/AgCl reference electrode. DMAc was degassed by bubbling N_2 prior to measurements. 0.01 M solutions of pyrene in DMAc were freshly prepared along with 0.1 M of

tetrabutylammonium hexafluorophosphate as supporting electrolyte and were examined at a scan rate of 0.05 $V.S^{-1}$ or 0.1 $V.S^{-1}$.

Comment: Based on the redox potentials of pyrene, we reason that SET between pyrene [$E(py^{\cdot+}/py)$ = 1.54 V; $E(py/py^{\cdot-})$ = -1.82 V] and 4CzIPN* [$E_{1/2}(P^*/P^{\cdot-})$ = -1.04 V; $E_{1/2}(P^{\cdot+}/P^*)$ = 1.35 V] could be thermodynamically unfavorable.

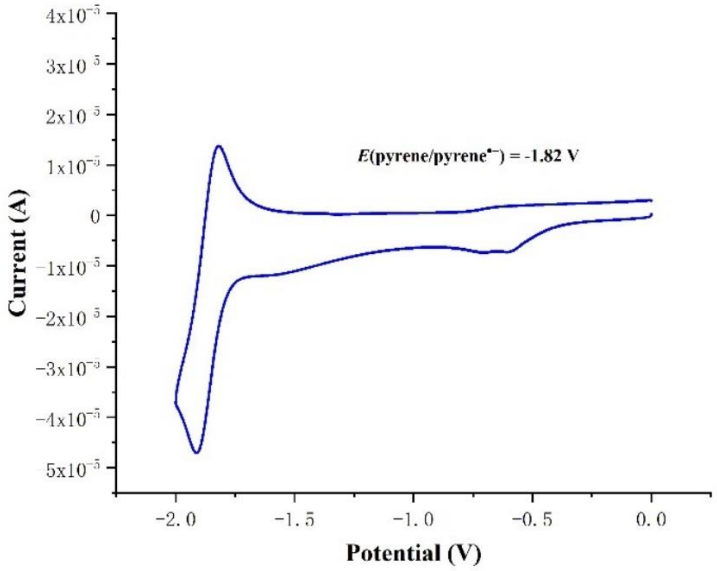


Figure S16. The reductive potential of pyrene

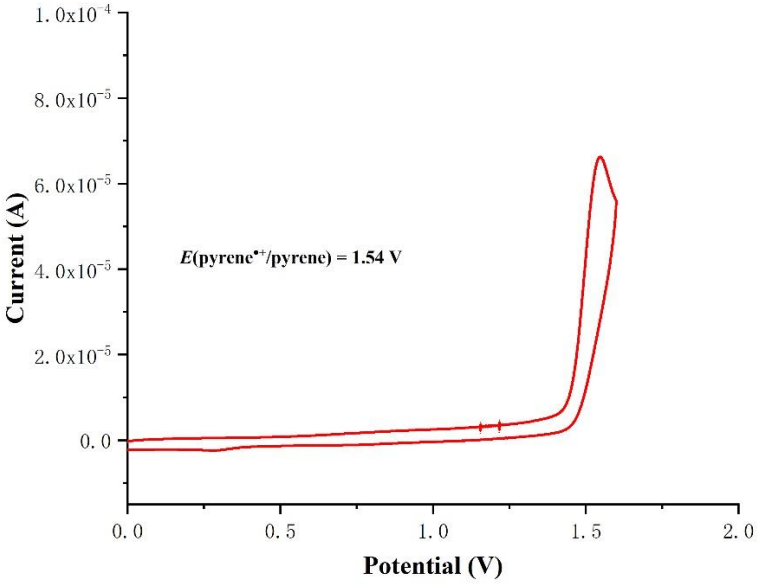


Figure S17. The oxidative potential of pyrene

6.9 Relevant photophysical experiments

a) The UV-Vis and fluorescence spectrum of pyrene and 4CzIPN

UV-vis spectra were collected on a PerkinElmer UV/VIS/NIR Spectrometer Lambda 950. Emission spectra was collected on Horiba fluoro-max+ wide spectral fluorescence spectrometer and Shimadzu RF-5301pc spectrofluorophotometer. All samples were degassed with a stream of nitrogen for 10 minutes. The samples of 4CzIPN and pyrene were excited at 365 nm and 340 nm respectively.

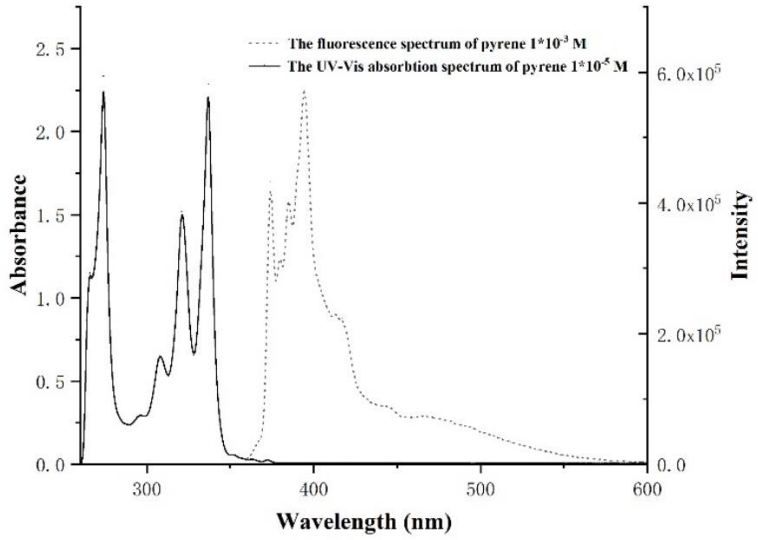


Figure S18. The UV-Vis absorption and fluorescence emission spectrum of pyrene

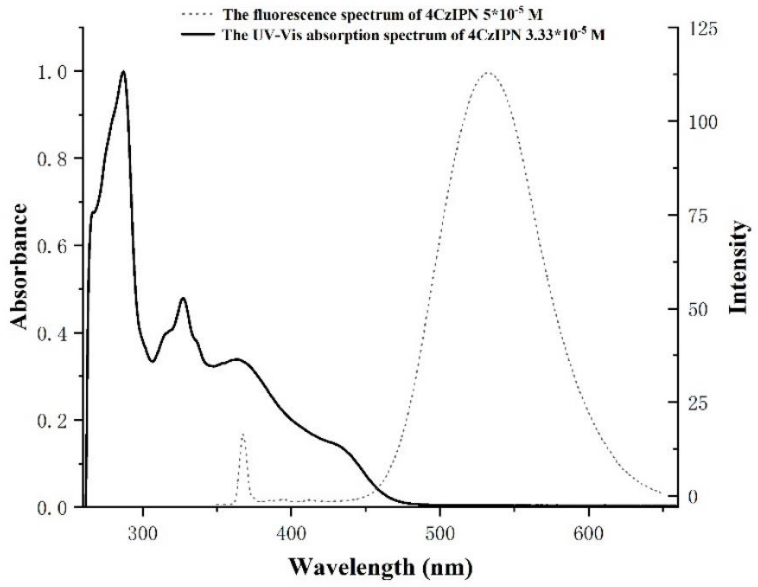


Figure S19. The UV-Vis absorption and fluorescence emission spectrum of 4CzIPN

b) The delayed fluorescence spectrum of 4CzIPN with pyrene

The delayed fluorescence spectrums were carried by Horiba fluoro max+ wide spectral fluorescence spectrometer and a photoluminescence system composed of fluorescence spectrometer (KYMERA-328I-B2; Andor Technology), Si-EMCCD camera (DU970P-BVF; Andor Technology), super-continuous white laser (Super K EXU-6, NKT photonics) and narrowband filters (LLTF Contrast SR-VIS-HP8, LLTF Contrast SR-SWIR-HP8, NKT photonics) which are used to acquire the tunable excitation wavelength. After excited by the laser, the measurement processes of the emission spectra are the same as electroluminescence spectra. The DMAc solvent was deaerated with nitrogen gas for at least 20 mins prior to be used and all samples were prepared in a nitrogen glove box.

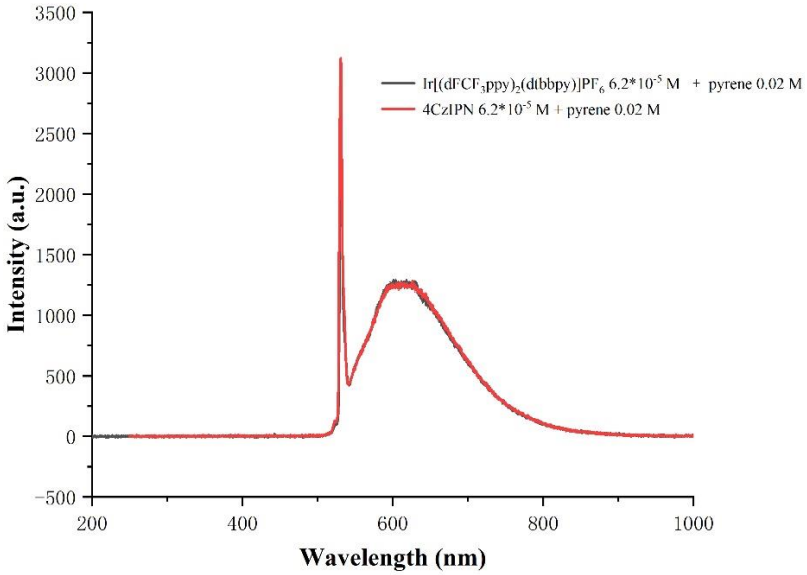


Figure S20. The delayed fluorescence spectrum measured in a DMAc solution containing pyrene (0.02 M) and 4CzIPN ($6.2*10^{-5}$ M) measured 50 μs, excited at 532 nm.

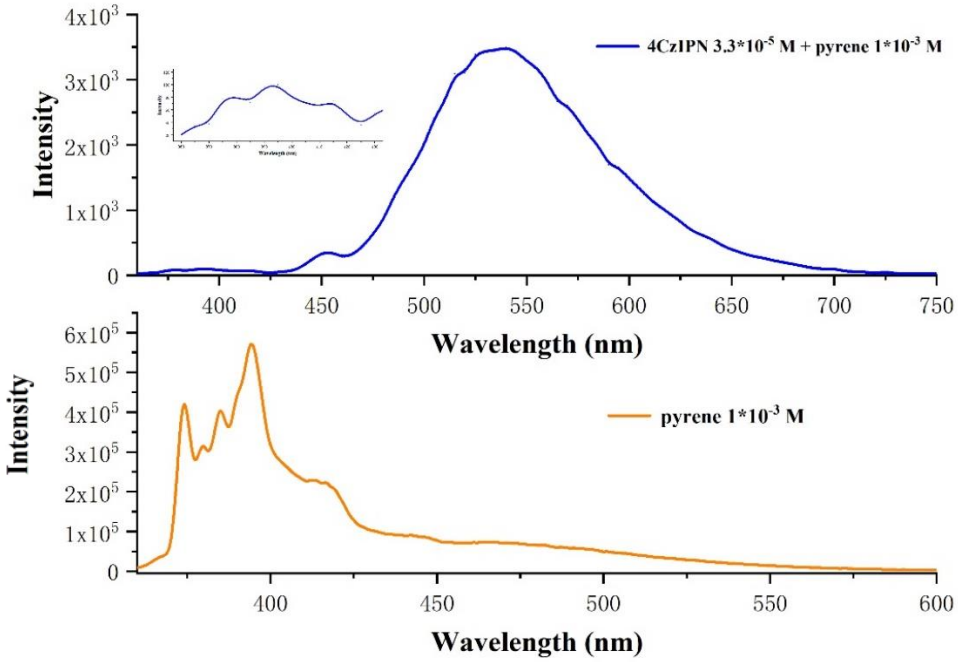


Figure S21. (A) The delayed fluorescence spectrum measured in a DMAc solution containing pyrene ($1*10^{-3}$ M) and 4CzIPN ($3.33*10^{-5}$ M) measured 50 μs, excited at

450 nm. (B) The fluorescence emission spectrum of pyrene ($1*10^{-3}$ M) in DMAc, excited at 340 nm.

Comment: Selective excitation of 4CzIPN at 532 nm in the presence of 0.01M pyrene in DMAc caused no appearance of delayed fluorescence of pyrene, and selective excitation of 4CzIPN at 450 nm in the presence of 0.01M pyrene also caused no significant appearance of delayed fluorescence of pyrene (should be around 400 nm). However, a slight difference is that the latter shows a weak appearance around 400 nm, which, we are not sure, is sufficient for determining the involvement of triplet–triplet annihilation (TTA).

Overall, we reason that the quenching of *4CzIPN by pyrene could proceed via a selective triplet energy transfer (EnT) or TTA process. Due to the complicated nature of this photoinduced catalytic system, we cannot provide an unambiguous conclusion for this specific quenching phenomenon at the current stage.

7. Gram-scale experiment

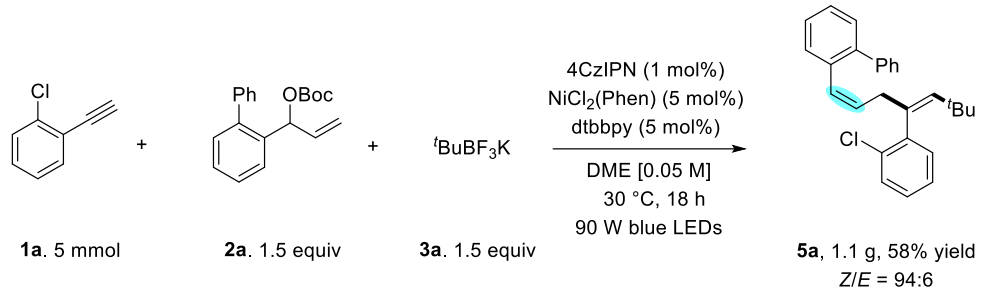


Figure S22. The set-up of scale-up experiment

To a flame-dried 250 mL reaction flask equipped with a magnetic stir bar was charged with 4CzIPN (39.5 mg, 0.05 mmol, 1 mol%) and $NiCl_2$·Phen (78 mg, 0.25 mmol, 5 mol%), dtbbpy (70 mg, 0.25 mmol, 5 mol%) and $^tBuBF_3K$ (1.23 g, 7.5 mmol, 1.5 equiv.). After DME (100 mL) was added as a solution. The reaction mixture was degassed by nitrogen sparging for 15 mins, followed by the addition of 1-chloro-2-ethynylbenzene (610 μL, 5 mmol, 1.0 equiv.) and 1-([1,1'-biphenyl]-2-yl) allyl tert-butyl carbonate (2.33 g, 7.5 mmol, 1.5 equiv.). The reaction mixture was then irradiated with 90 W blue LEDs at 30°C for 18 h. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the (*Z,Z)*-1,4-diene **5a** in 58% yield (*Z*/*E* = 94:6)

8. NMR spectra

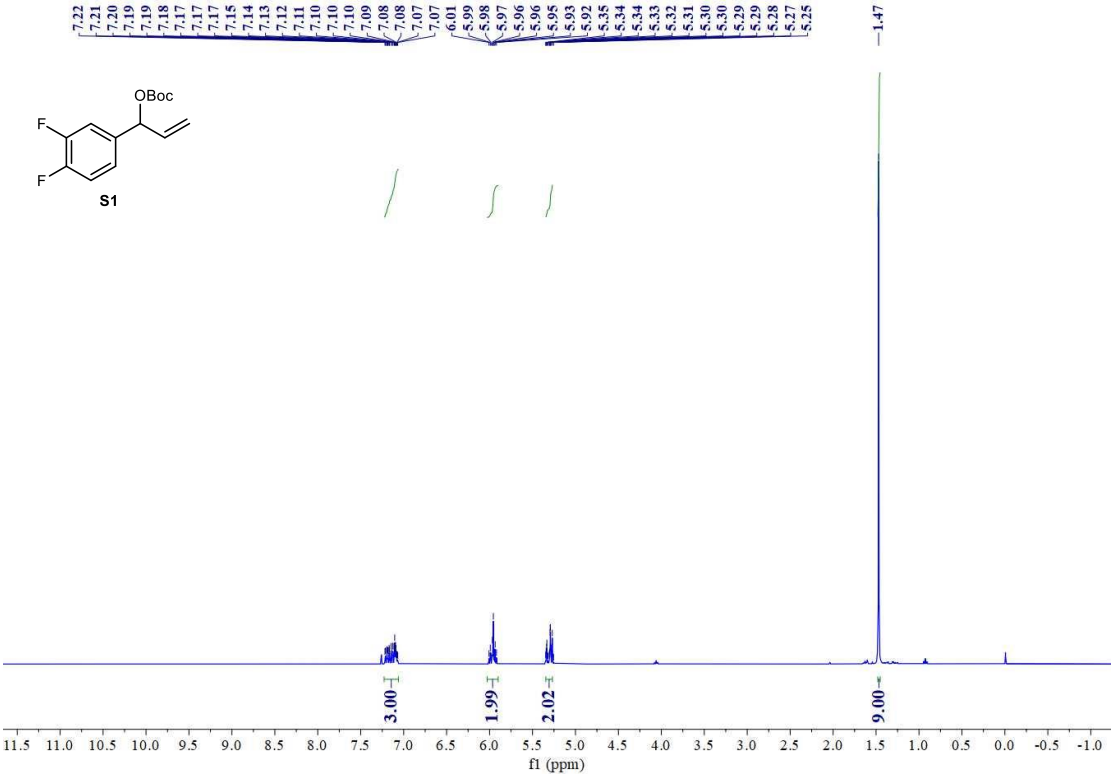


Figure S23. ^{1}H-NMR spectrum of **S1**

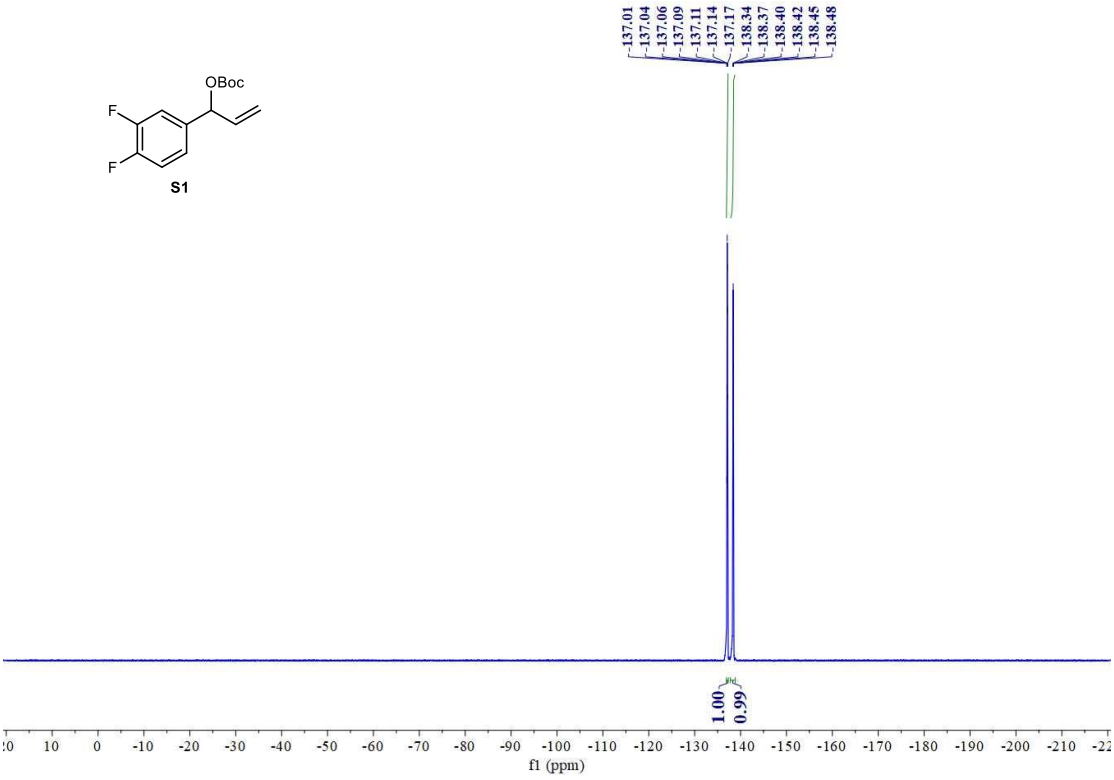


Figure S24. ^{19}F-NMR spectrum of **S1**

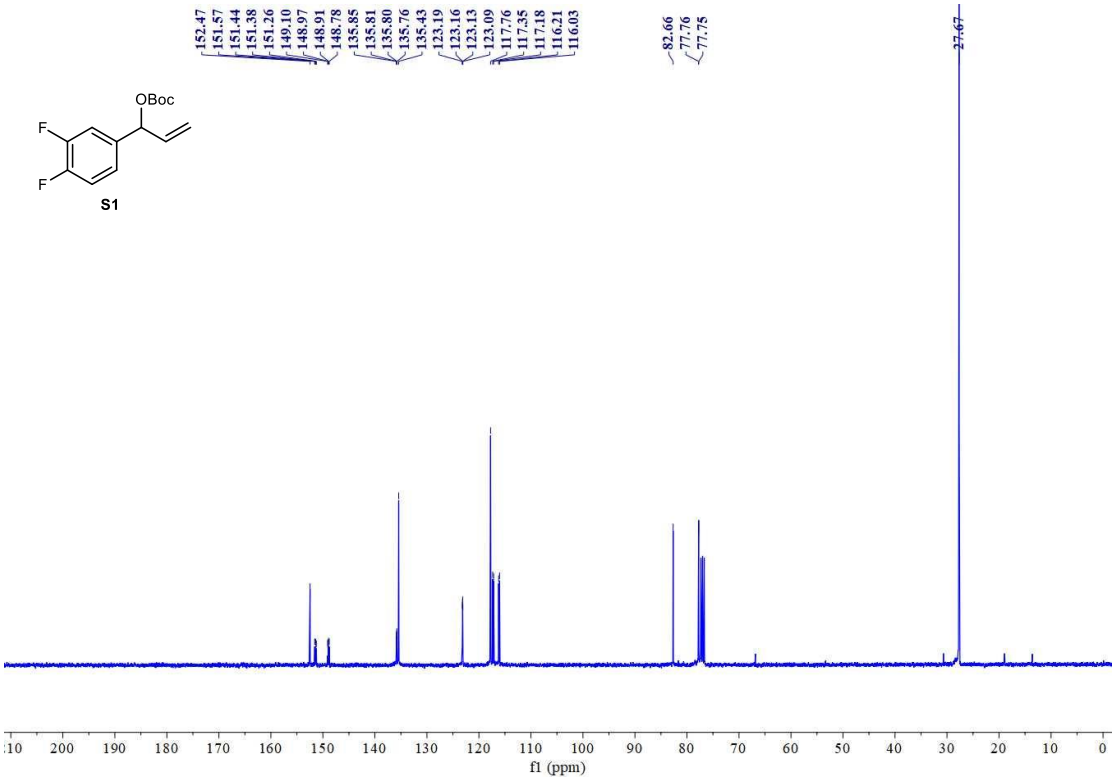


Figure S25. ^{13}C-NMR spectrum of **S1**

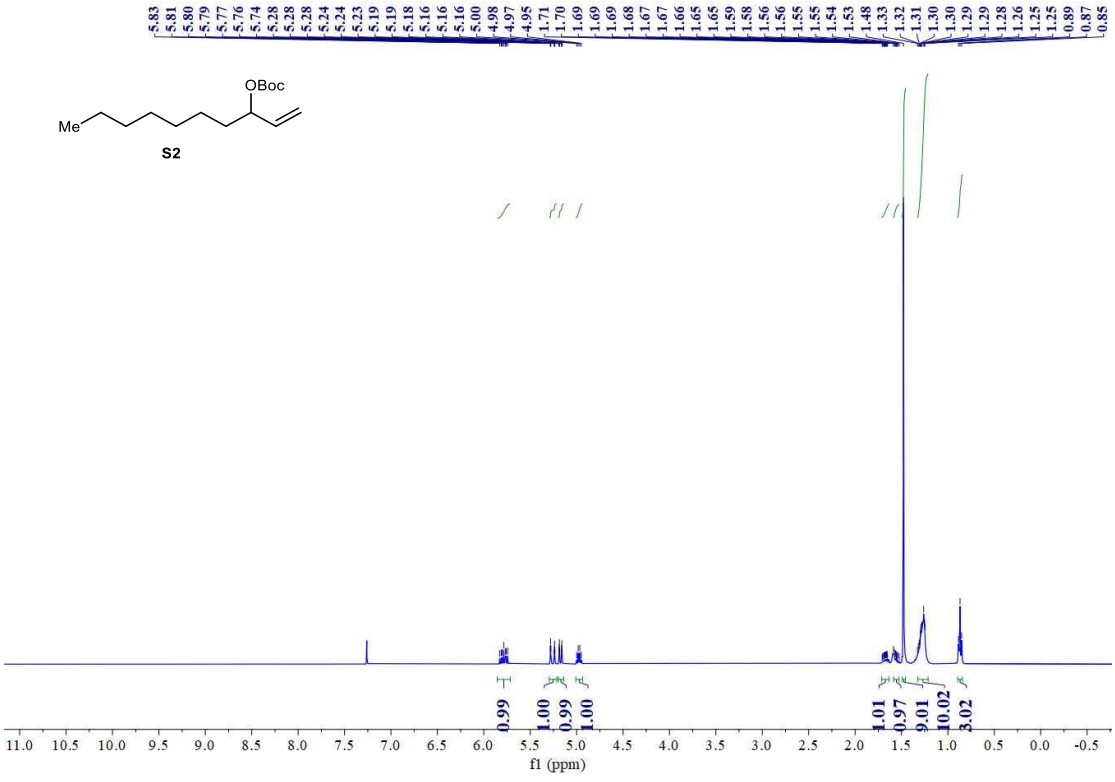


Figure S26. ^{1}H-NMR spectrum of **S2**

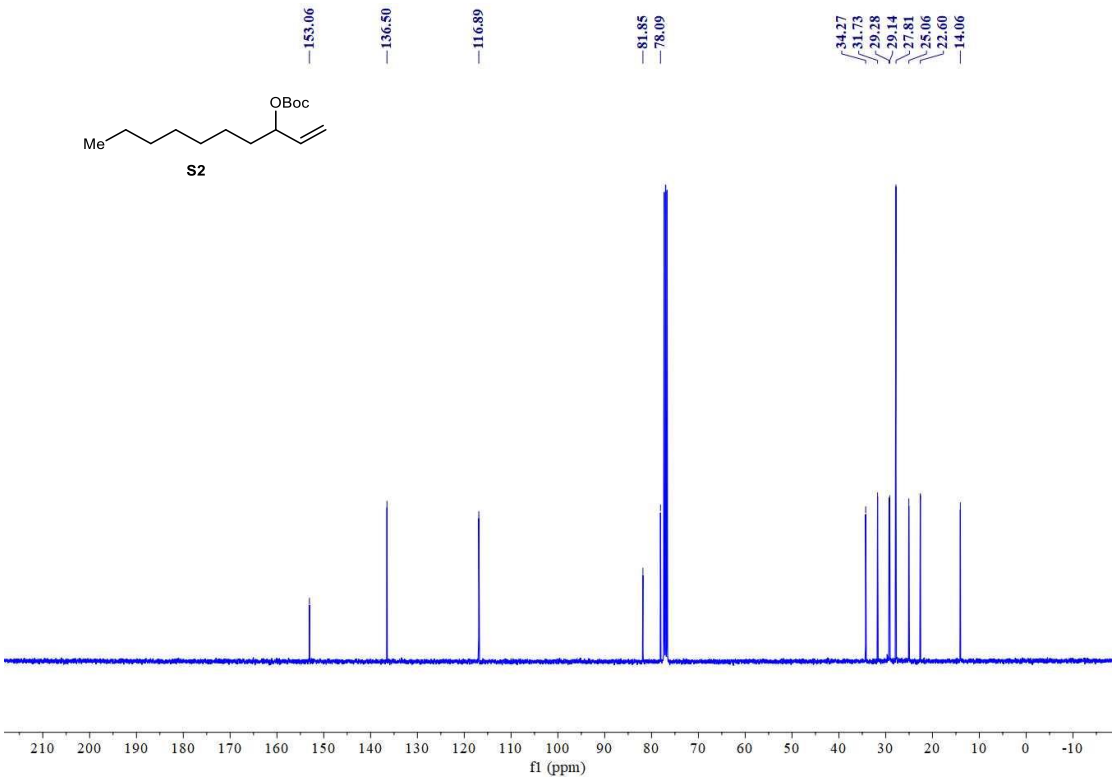


Figure S27. ^{13}C-NMR spectrum of **S2**

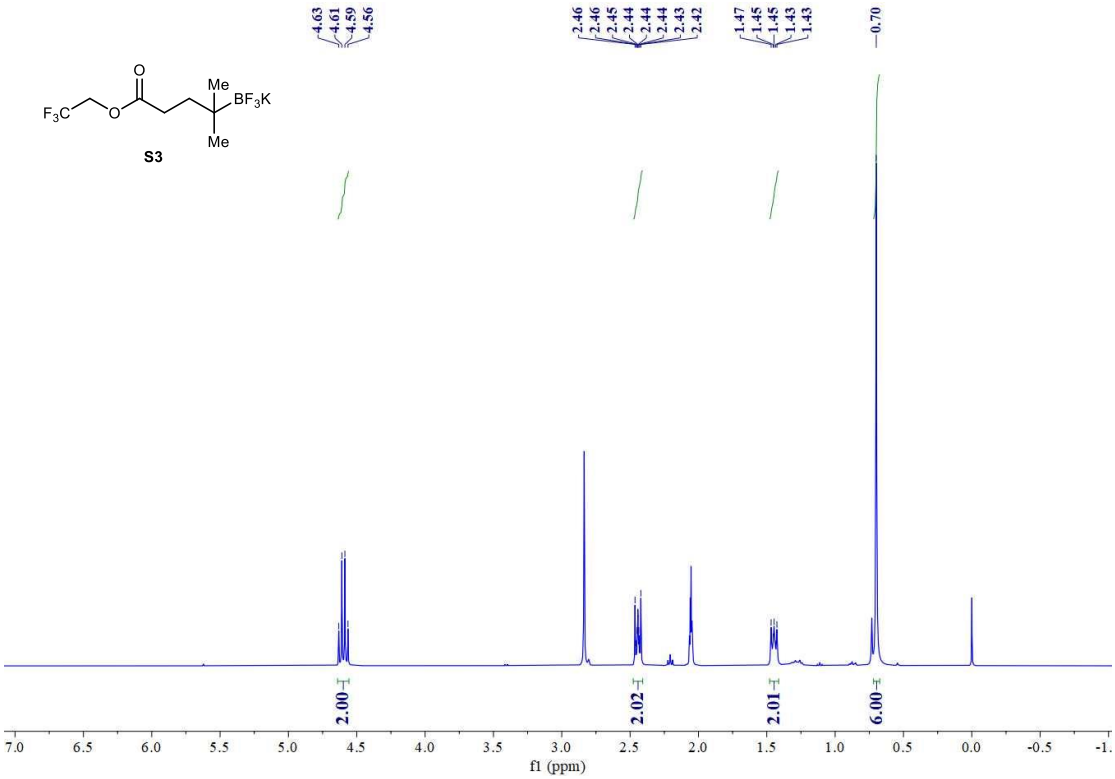


Figure S28. ^{1}H-NMR spectrum of **S3**

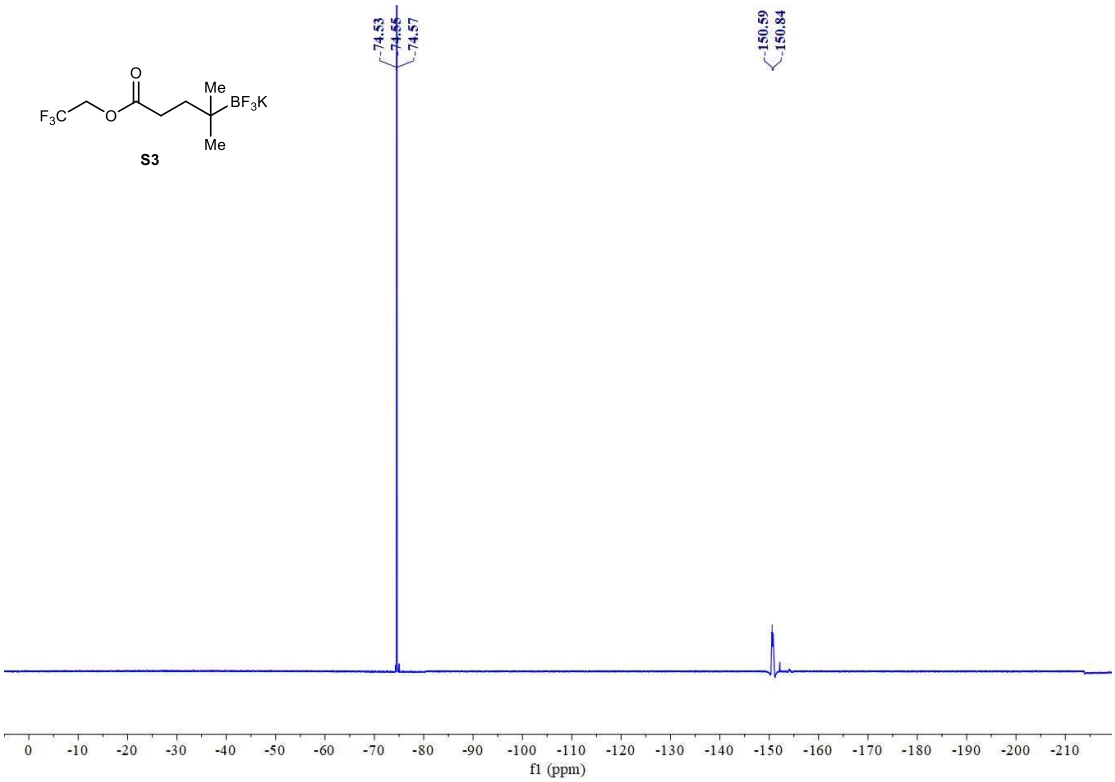


Figure S29. ^{19}F-NMR spectrum of **S3**

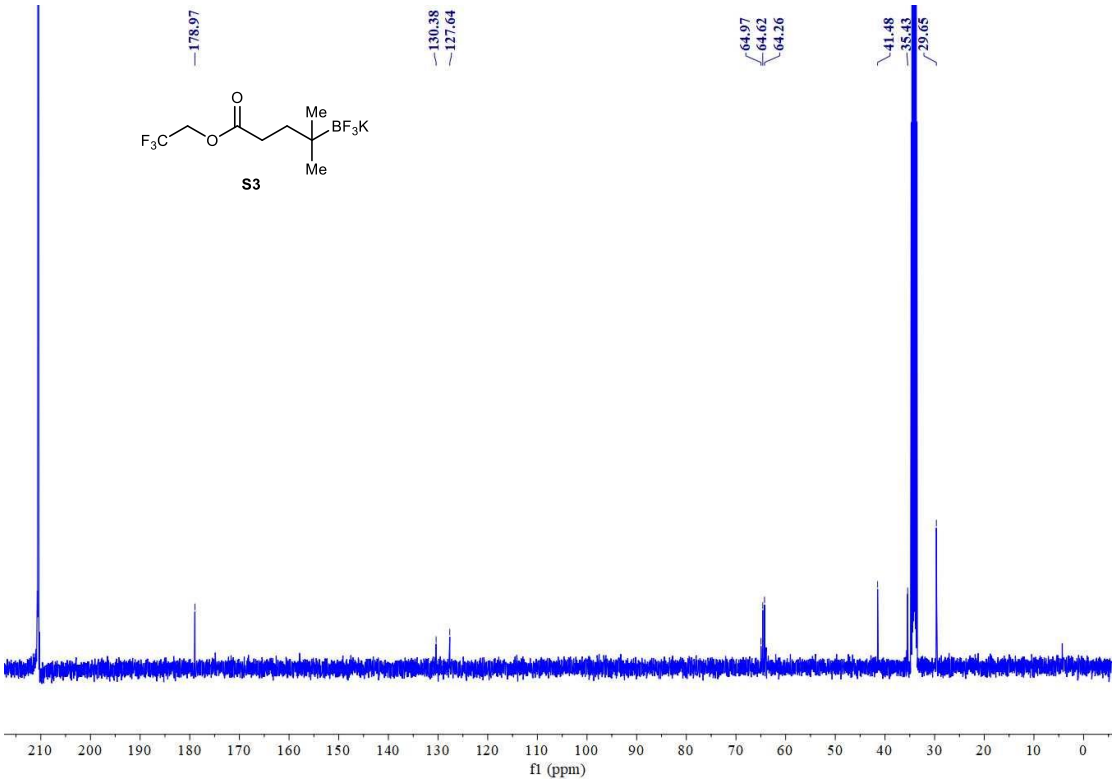


Figure S30. ^{13}C-NMR spectrum of **S3**

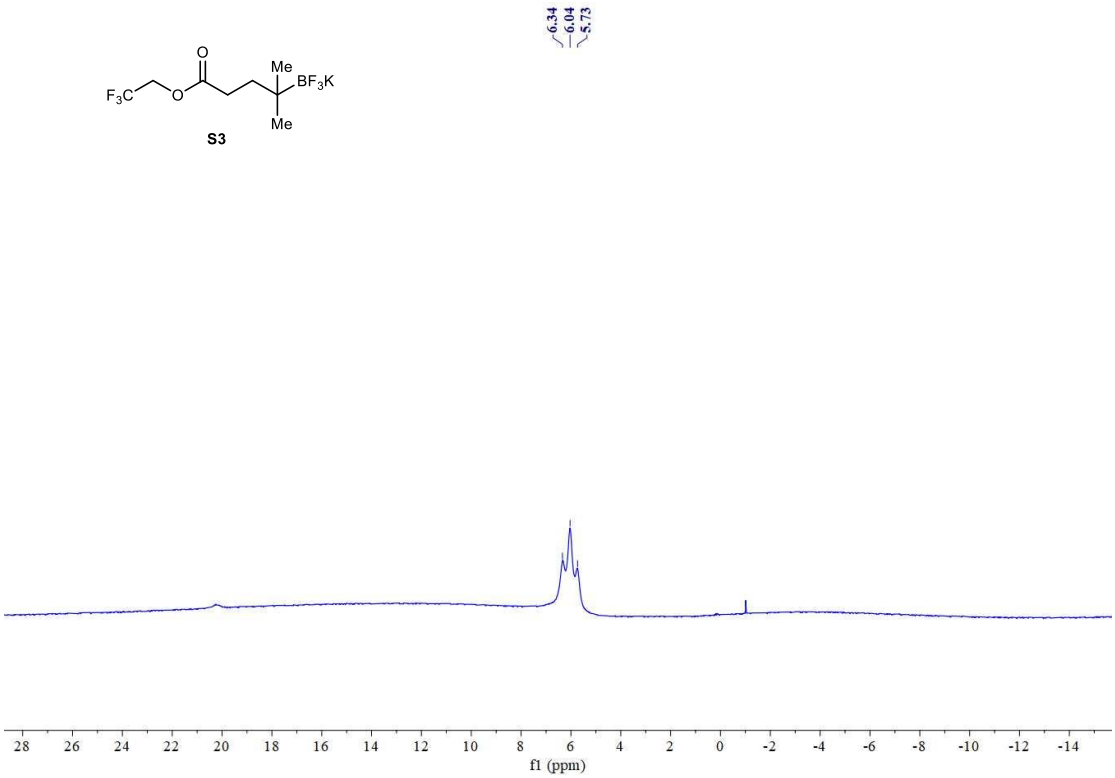


Figure S31. ^{11}B-NMR spectrum of **S3**

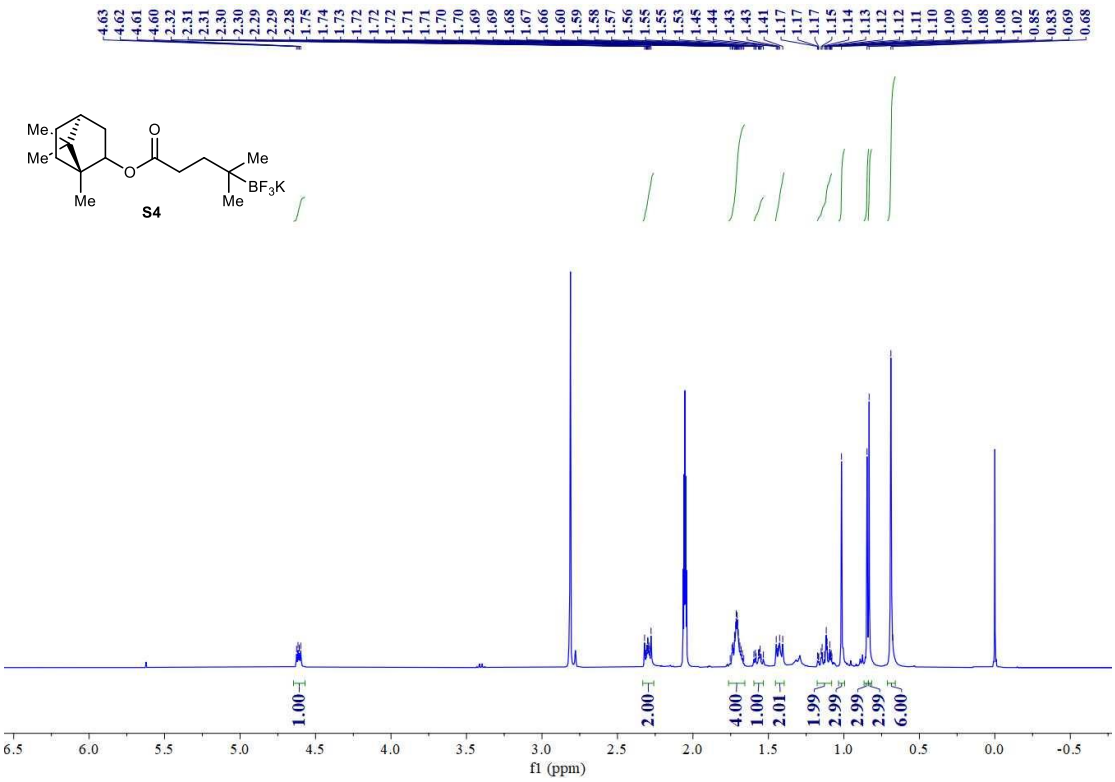


Figure S32. ^{1}H-NMR spectrum of **S4**

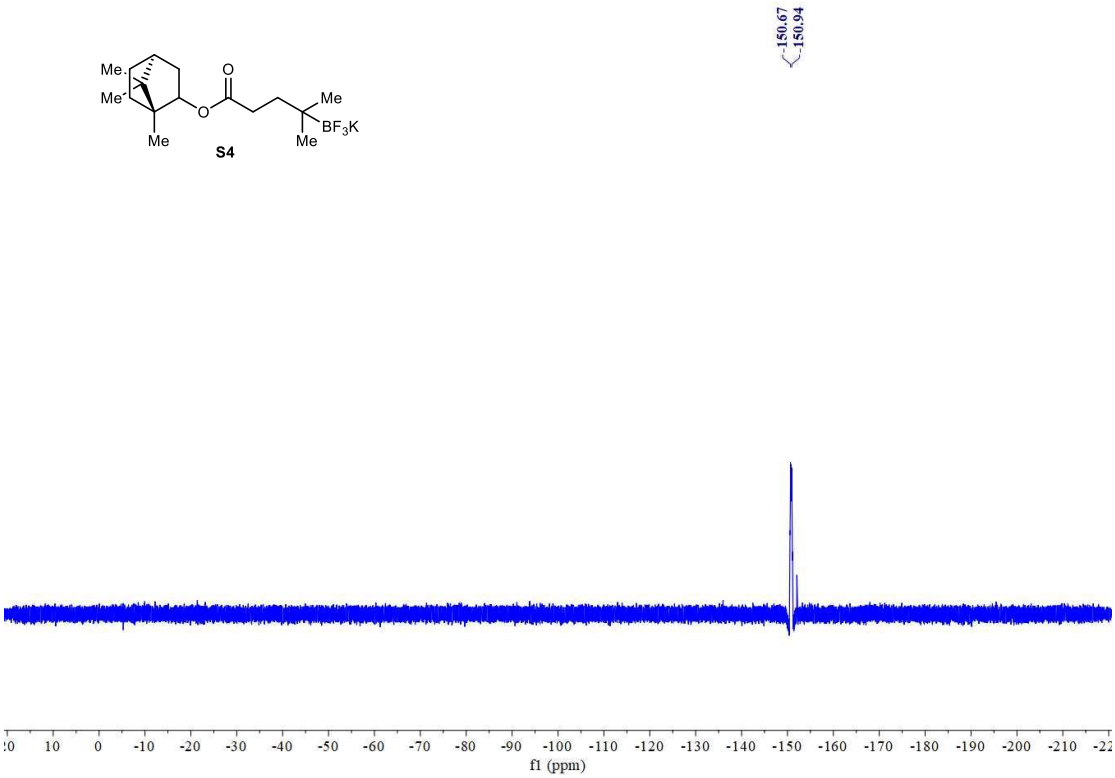


Figure S33. ^{19}F-NMR spectrum of **S4**

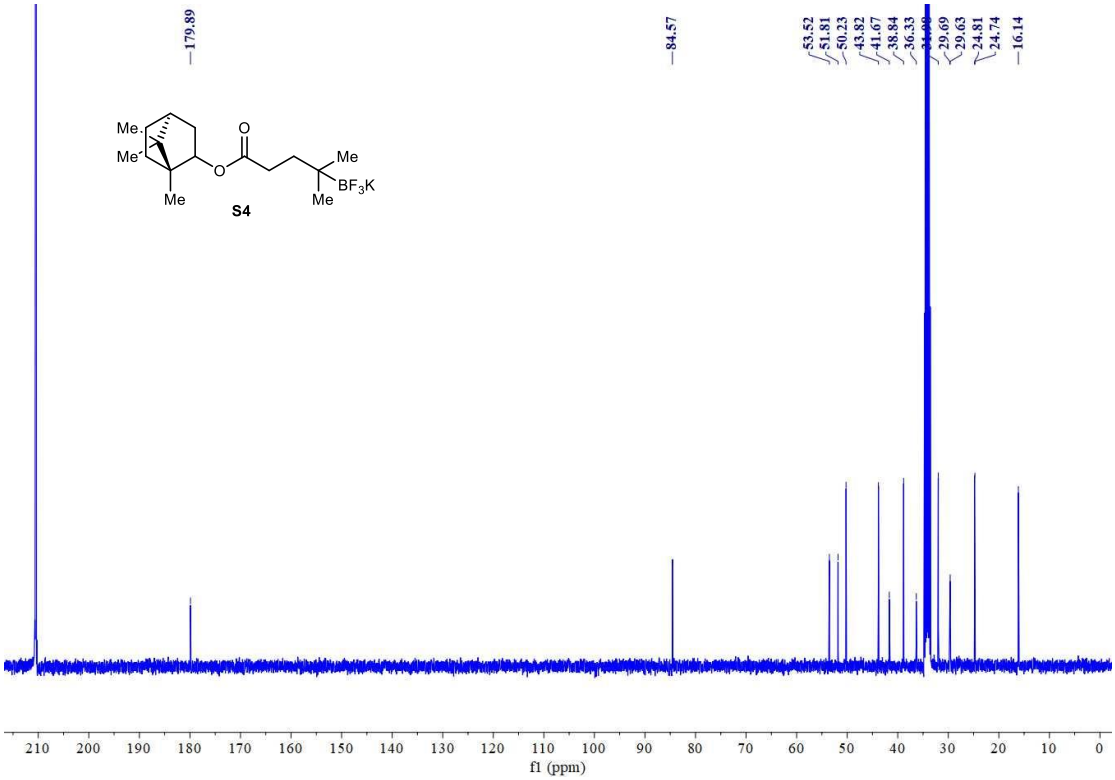


Figure S34. ^{13}C-NMR spectrum of **S4**

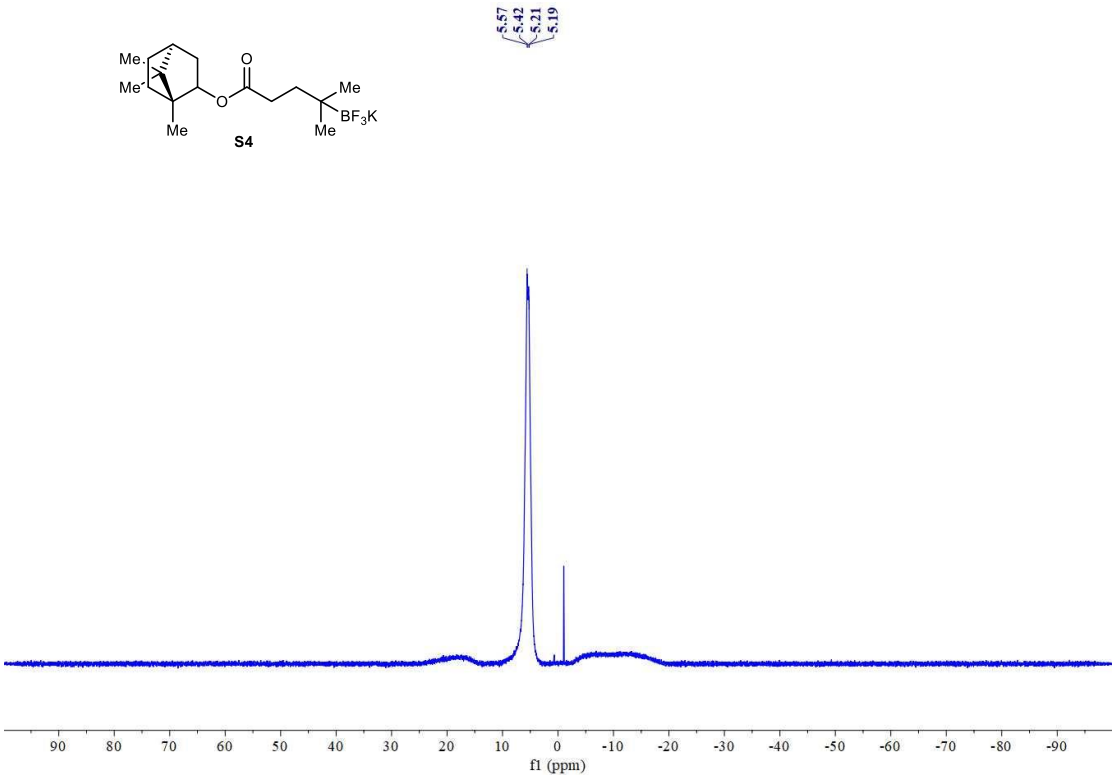


Figure S35. ^{11}B-NMR spectrum of **S4**

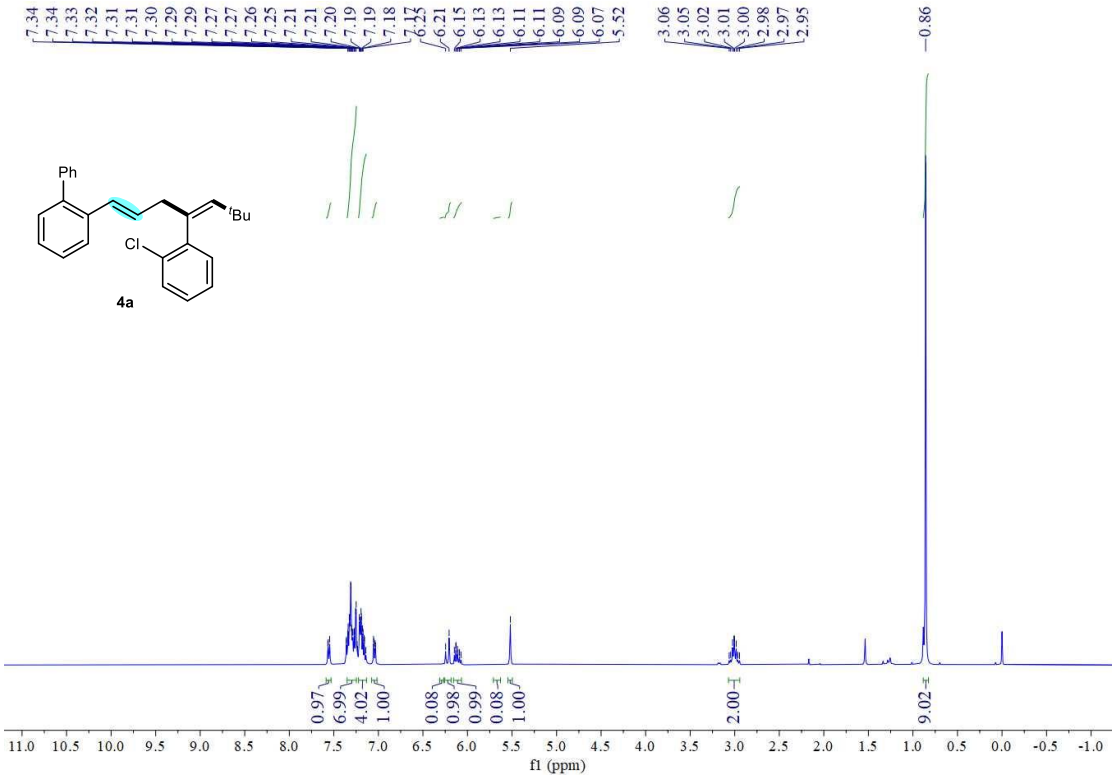


Figure S36. ^{1}H-NMR spectrum of **4a**

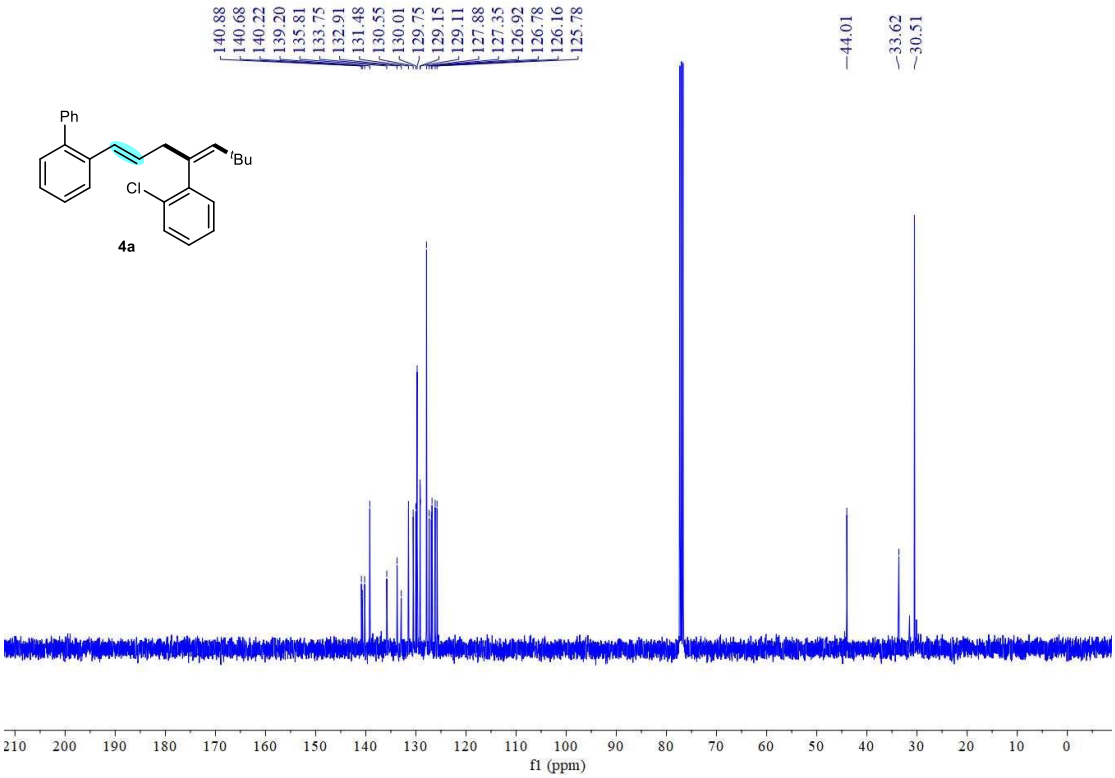


Figure S37. ^{13}C-NMR spectrum of **4a**

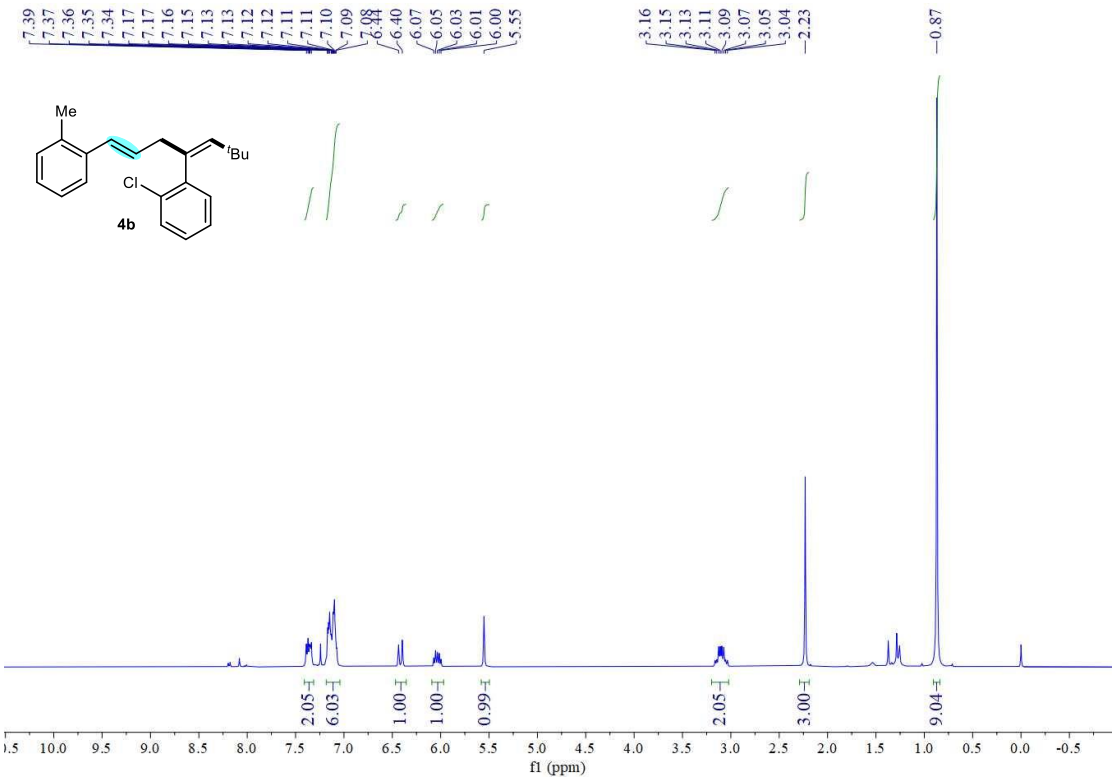


Figure S38. ^{1}H-NMR spectrum of **4b**

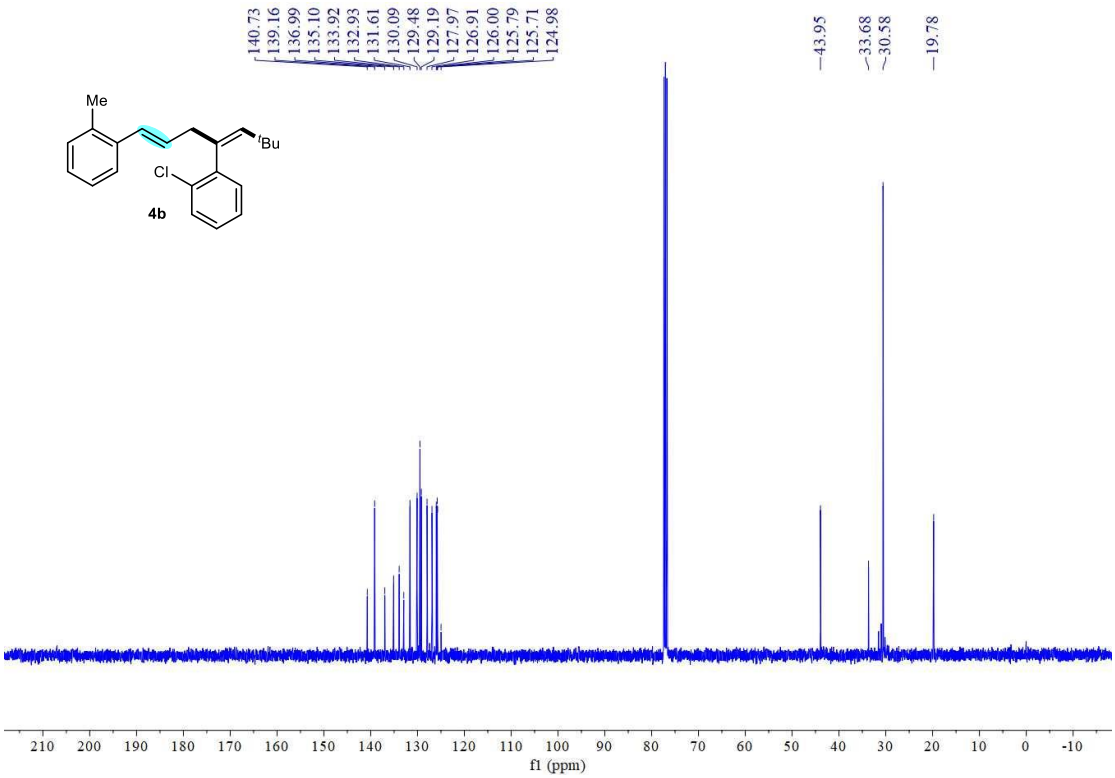


Figure S39. ^{13}C-NMR spectrum of **4b**

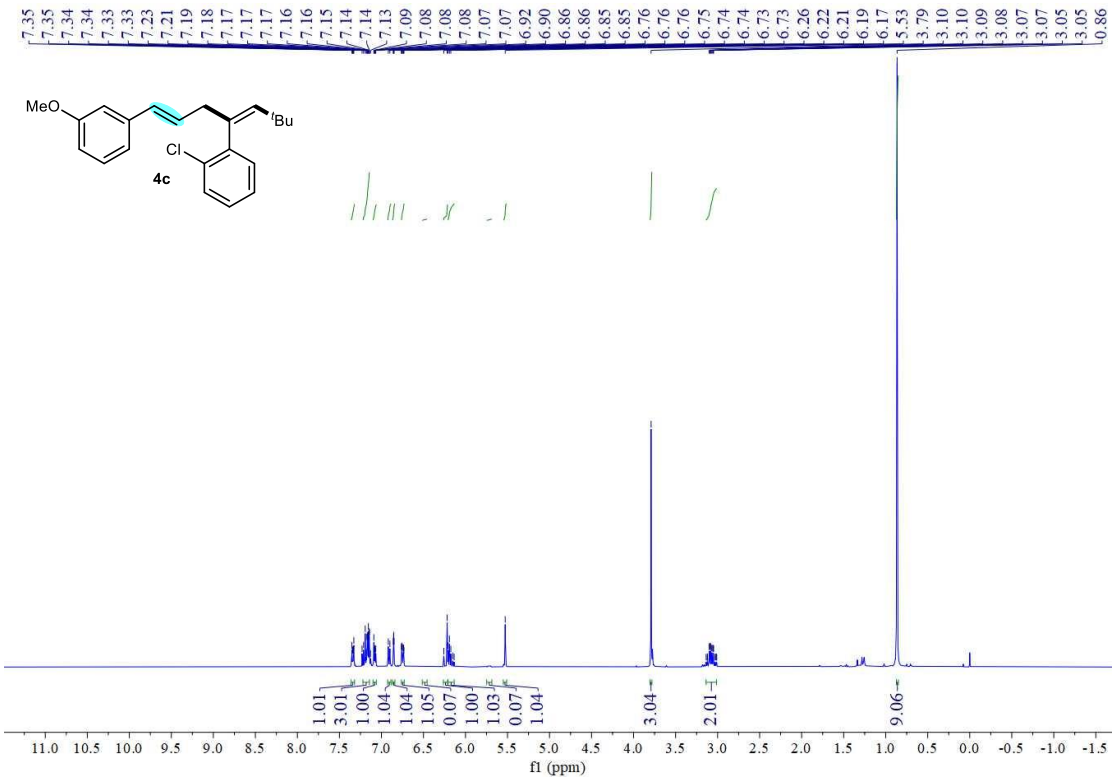


Figure S40. ^{1}H-NMR spectrum of **4c**

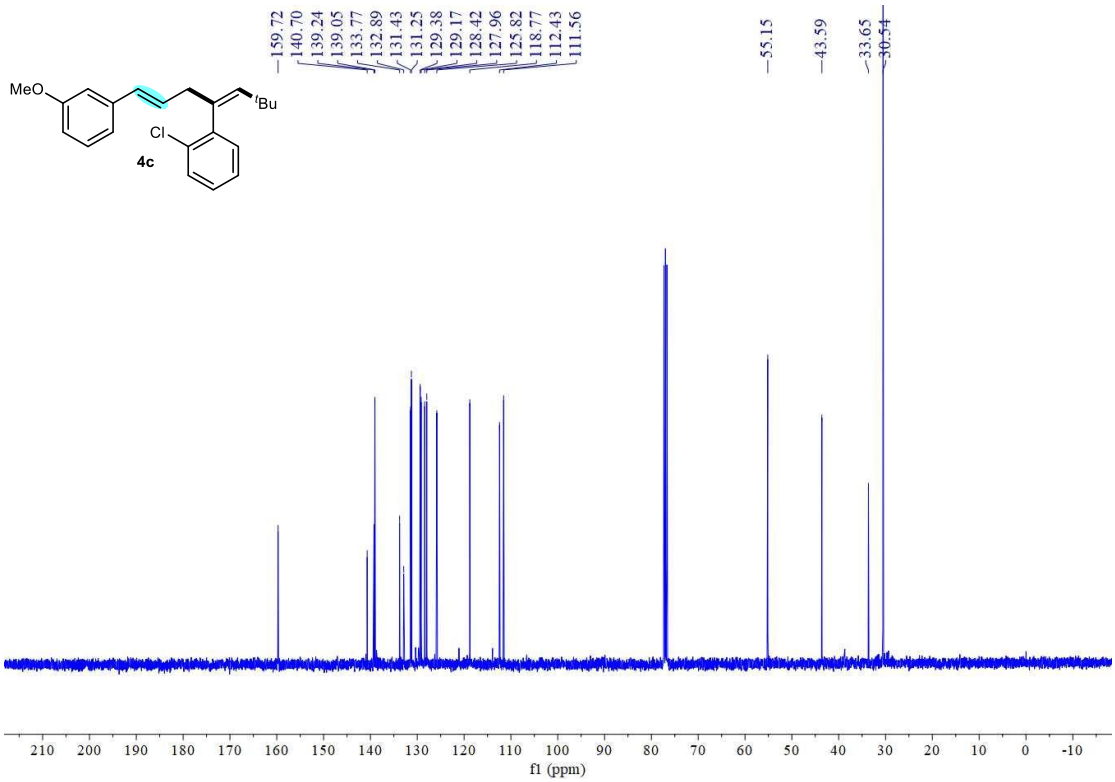


Figure S41. ^{13}C-NMR spectrum of **4c**

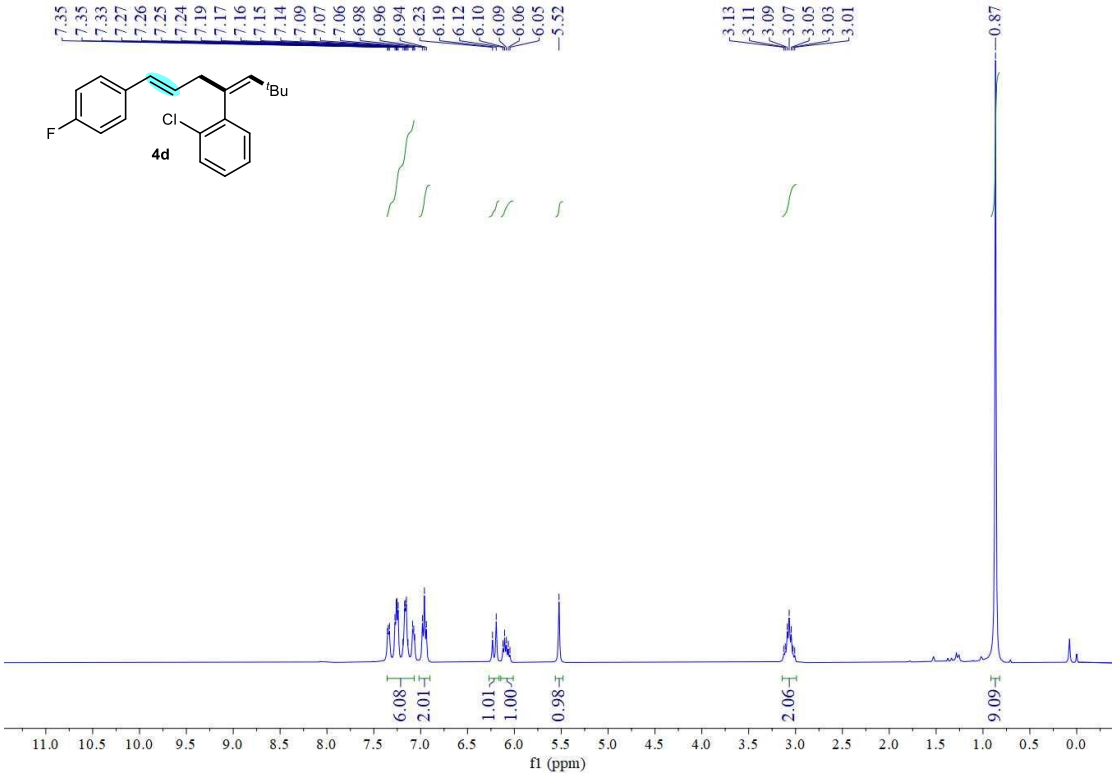


Figure S42. ^{1}H-NMR spectrum of **4d**

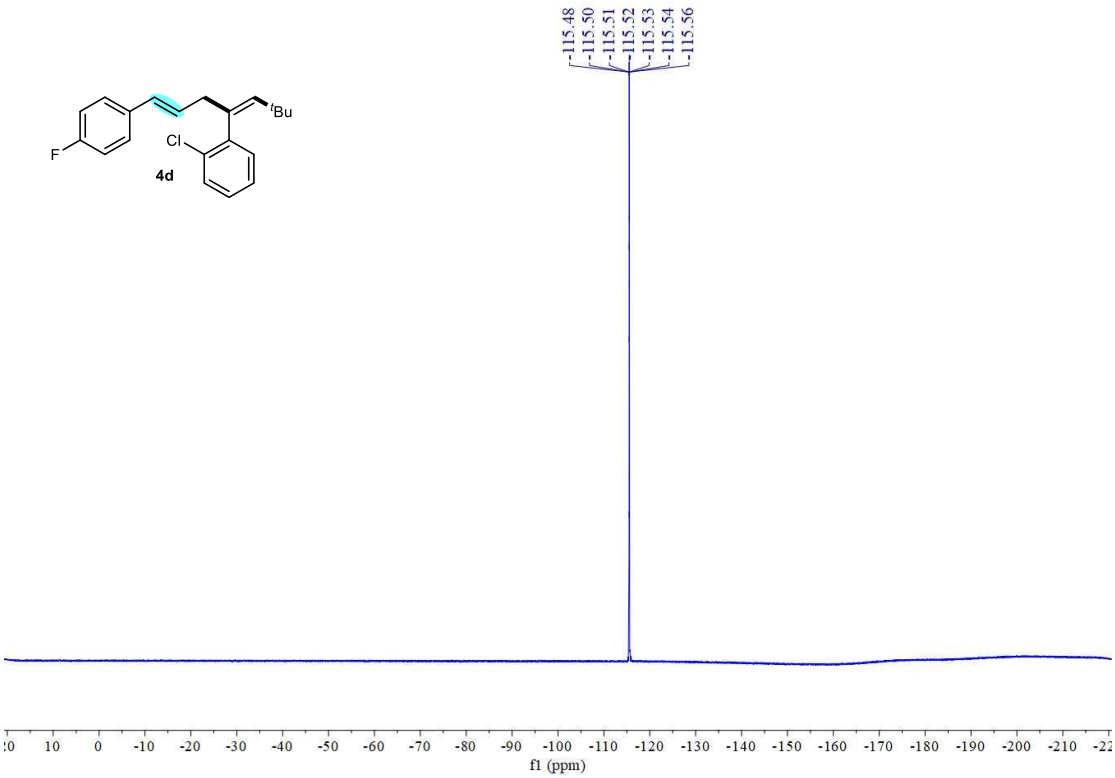


Figure S43. ^{19}F-NMR spectrum of **4d**

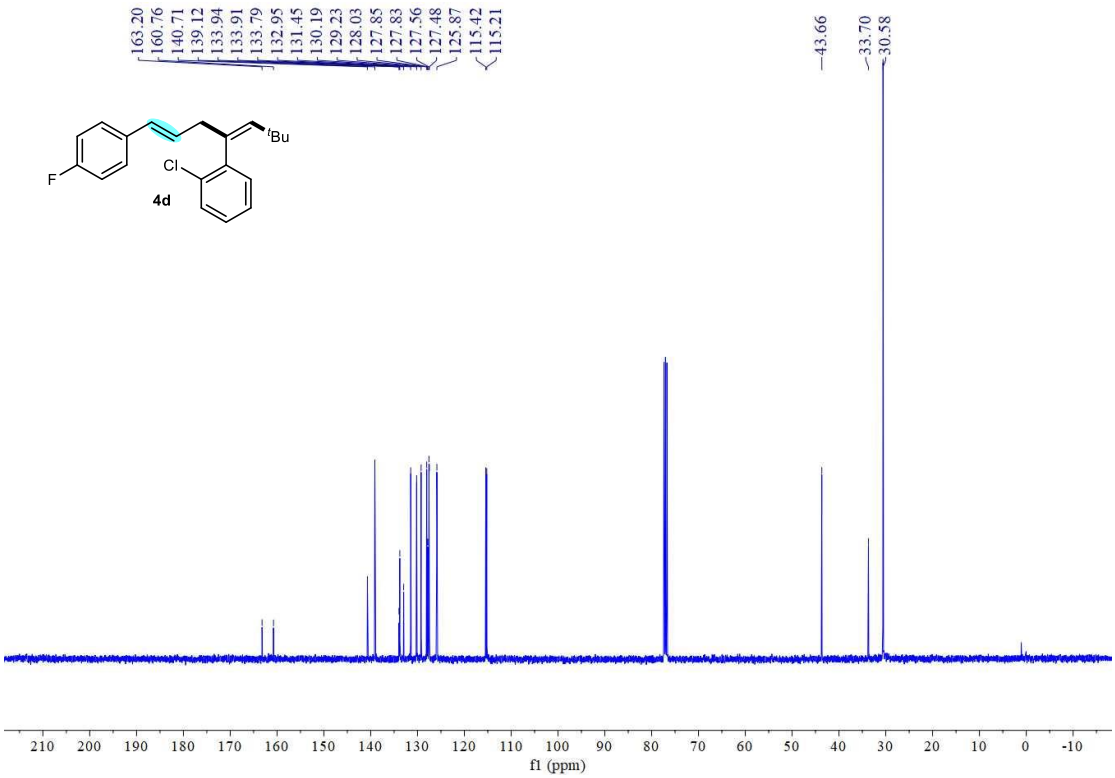


Figure S44. ^{13}C-NMR spectrum of **4d**

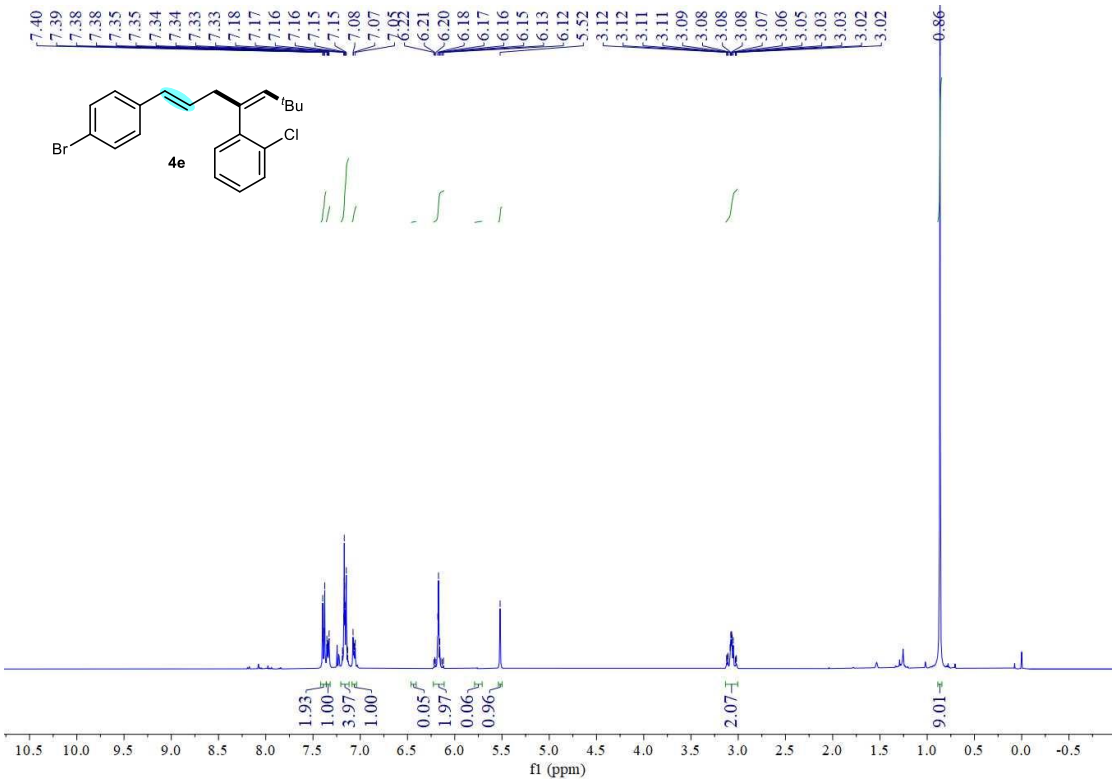


Figure S45. ^{1}H-NMR spectrum of **4e**

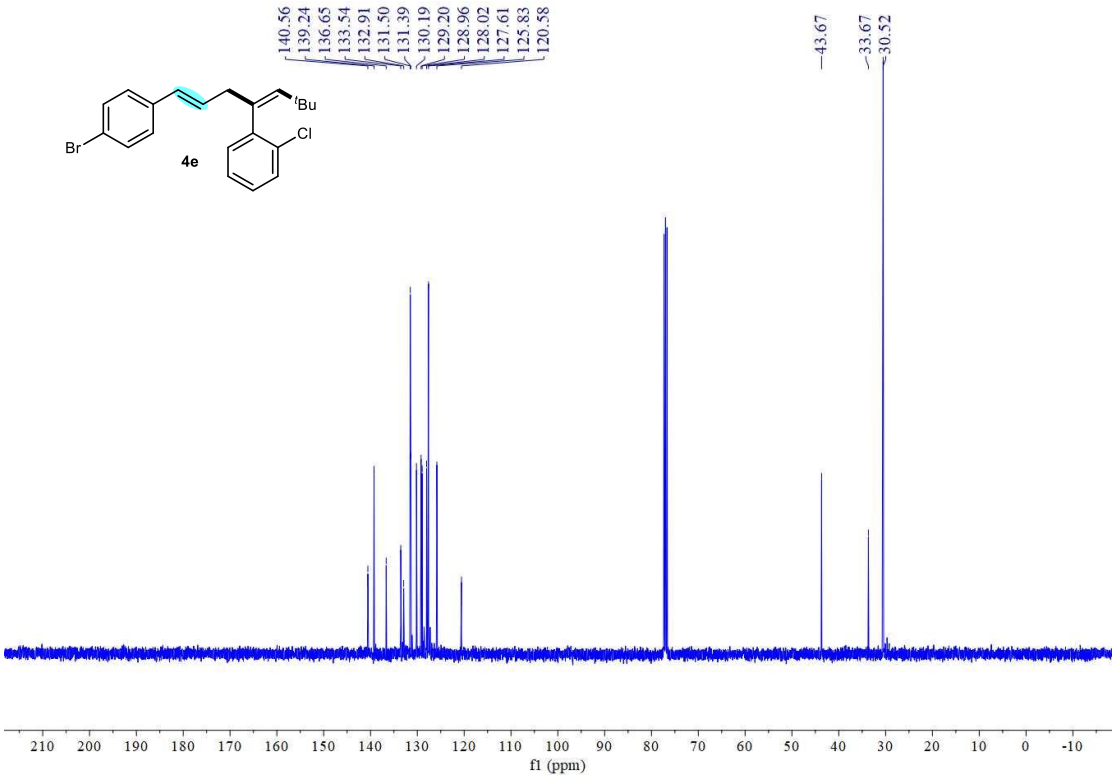


Figure S46. ^{13}C-NMR spectrum of **4e**

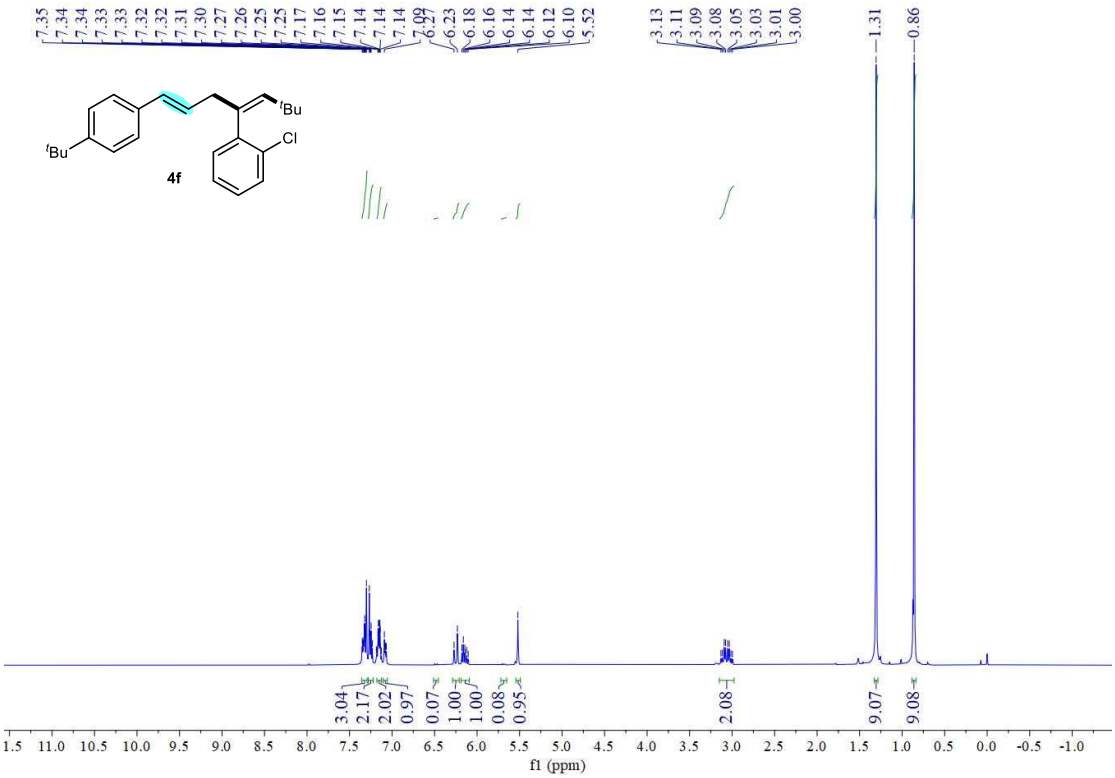


Figure S47. ^{1}H-NMR spectrum of **4f**

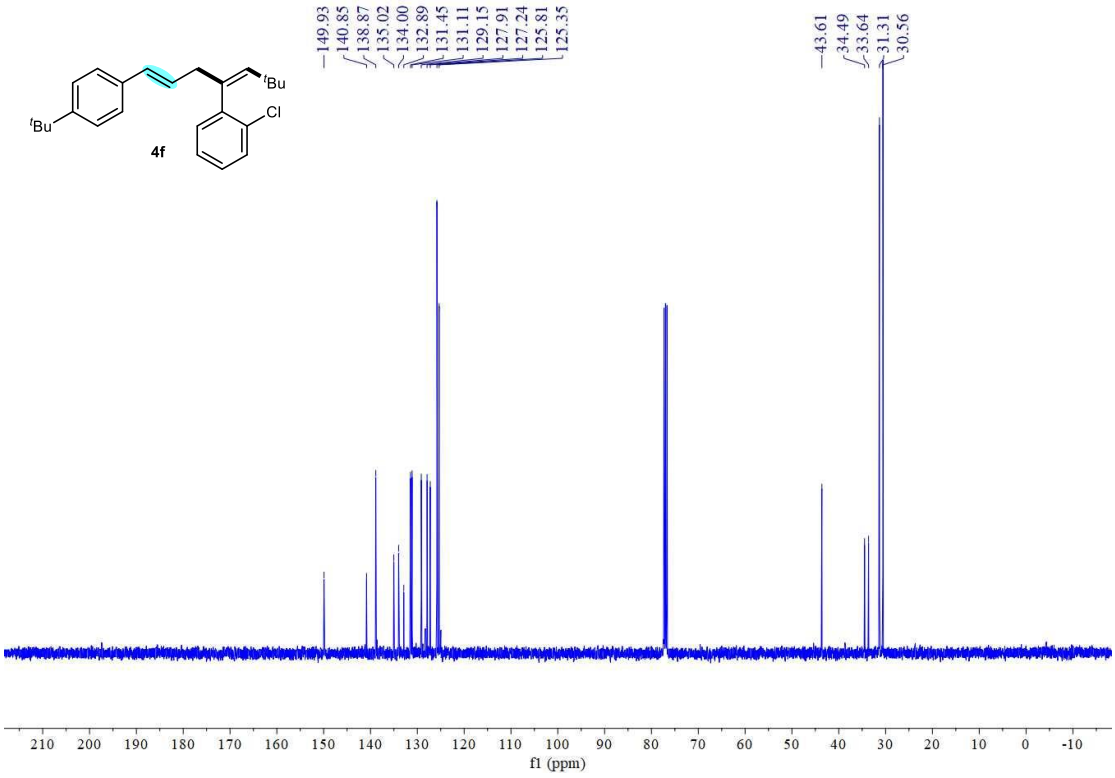


Figure S48. ^{13}C-NMR spectrum of **4f**

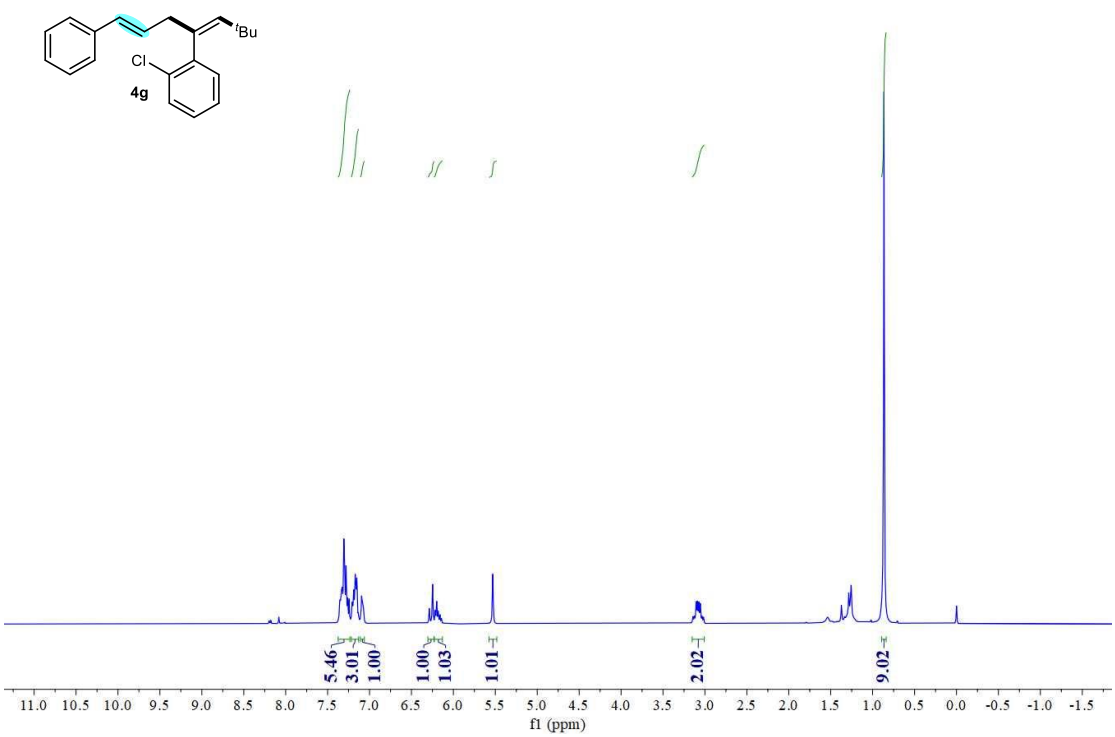


Figure S49. ^{1}H-NMR spectrum of **4g**

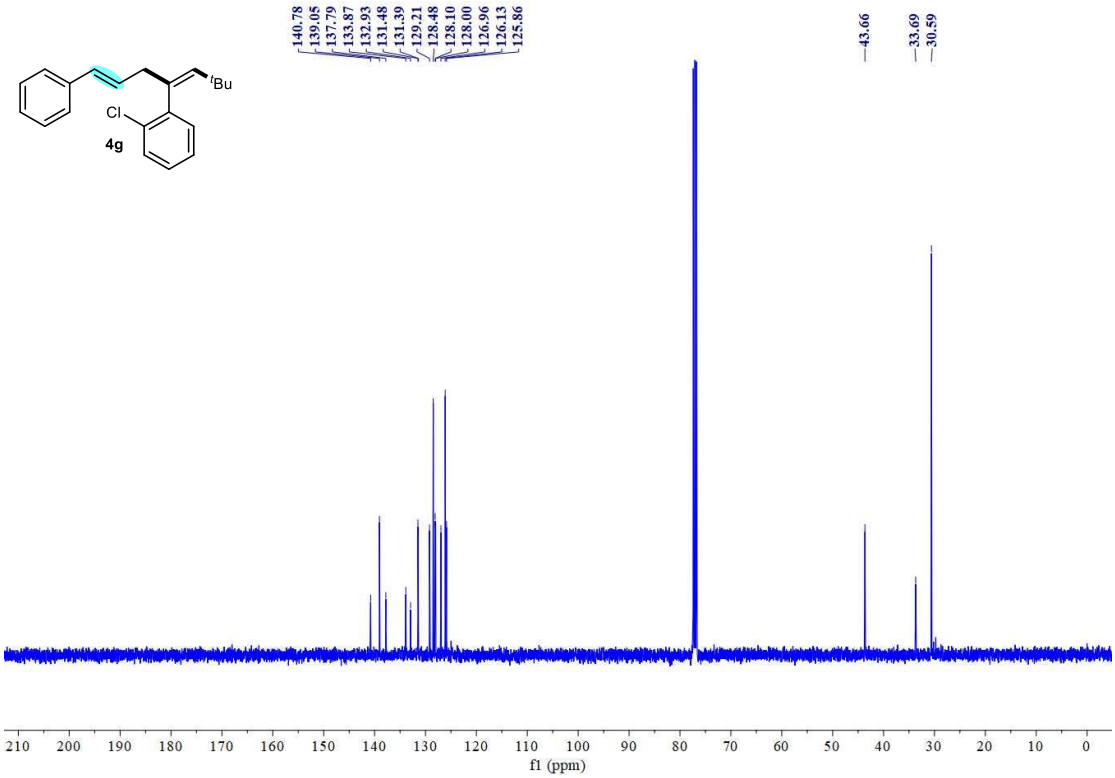


Figure S50. ^{13}C-NMR spectrum of **4g**

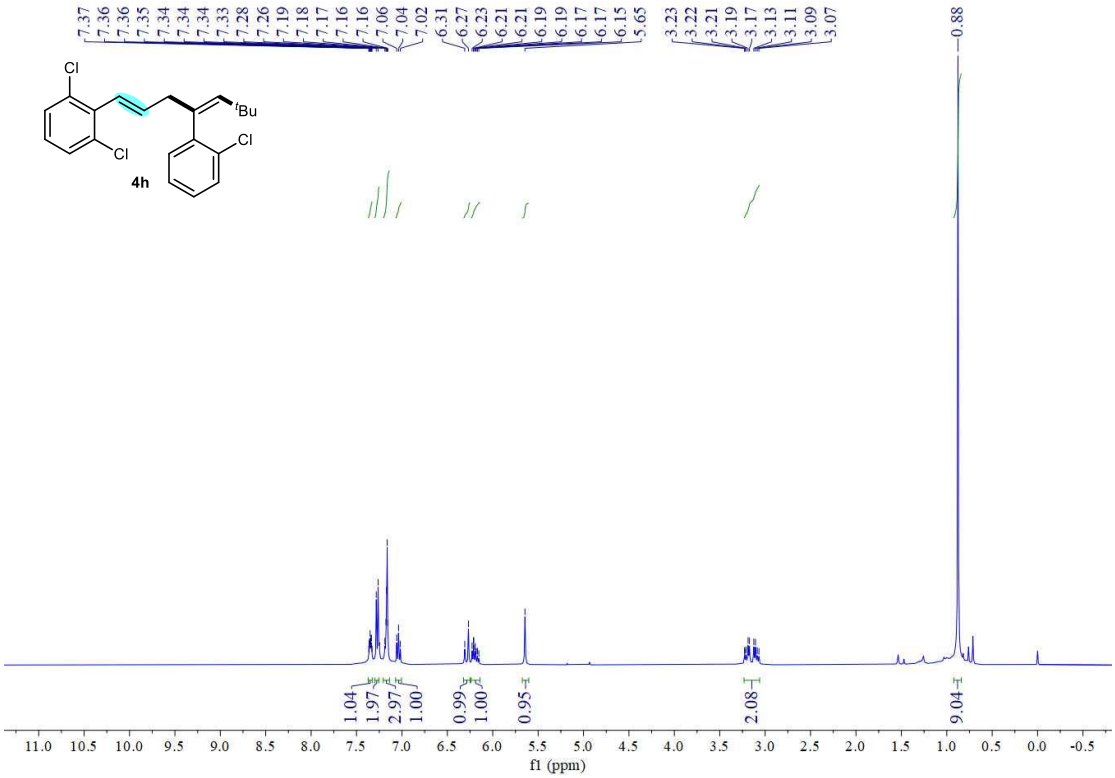


Figure S51. ^{1}H-NMR spectrum of **4h**

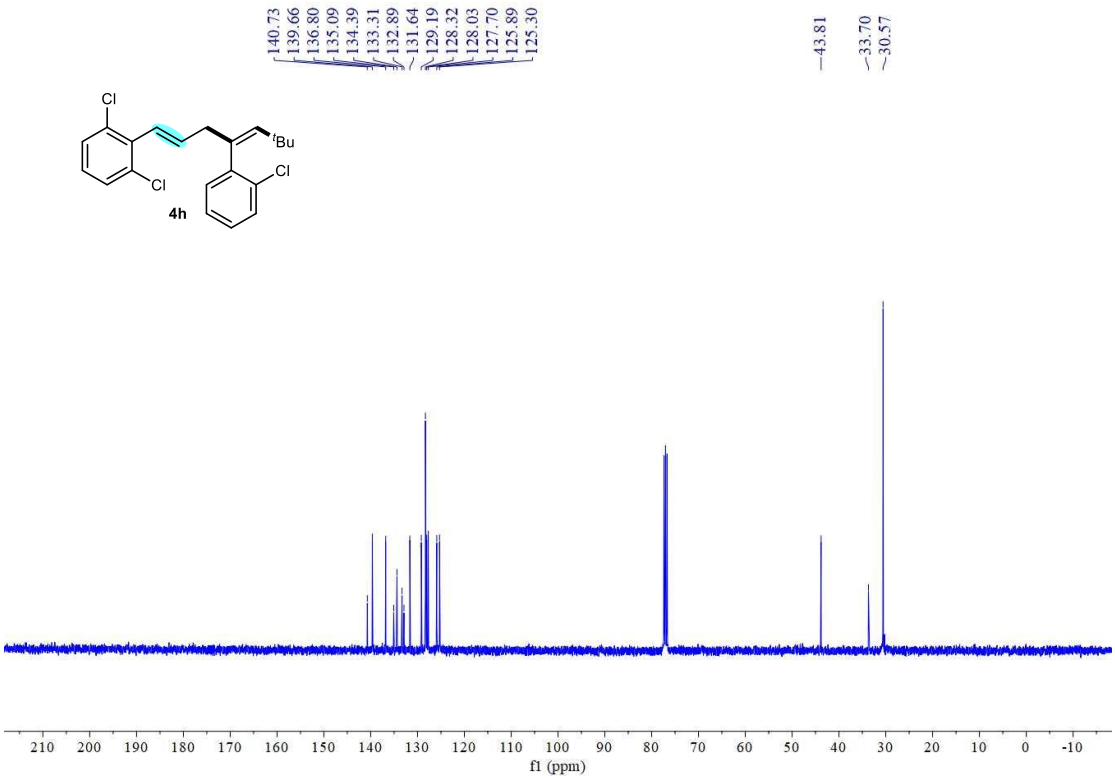


Figure S52. ^{13}C-NMR spectrum of **4h**

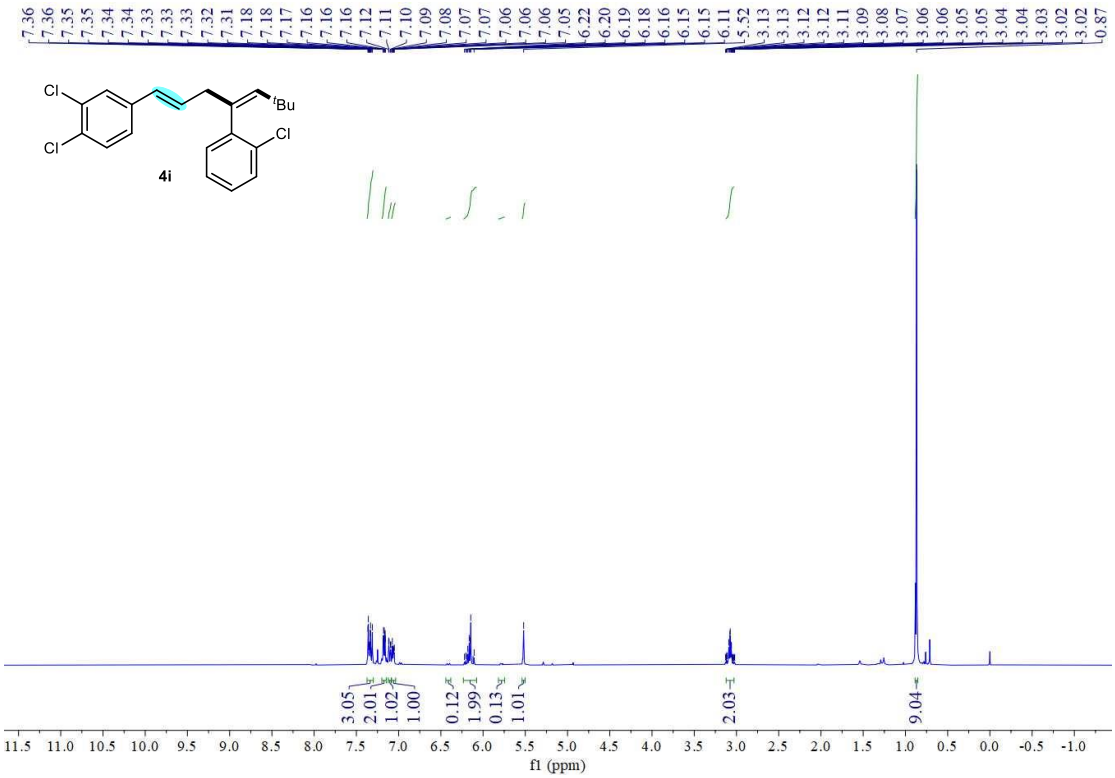


Figure S53. ^{1}H-NMR spectrum of **4i**

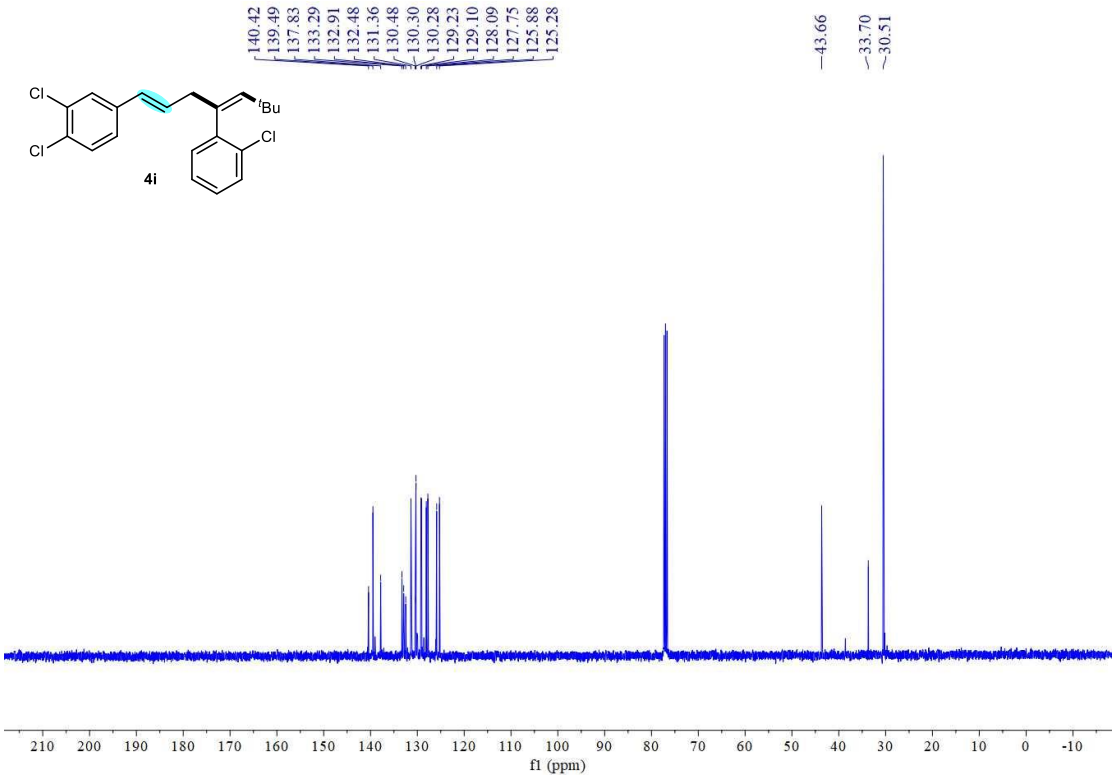


Figure S54. ^{13}C-NMR spectrum of **4i**

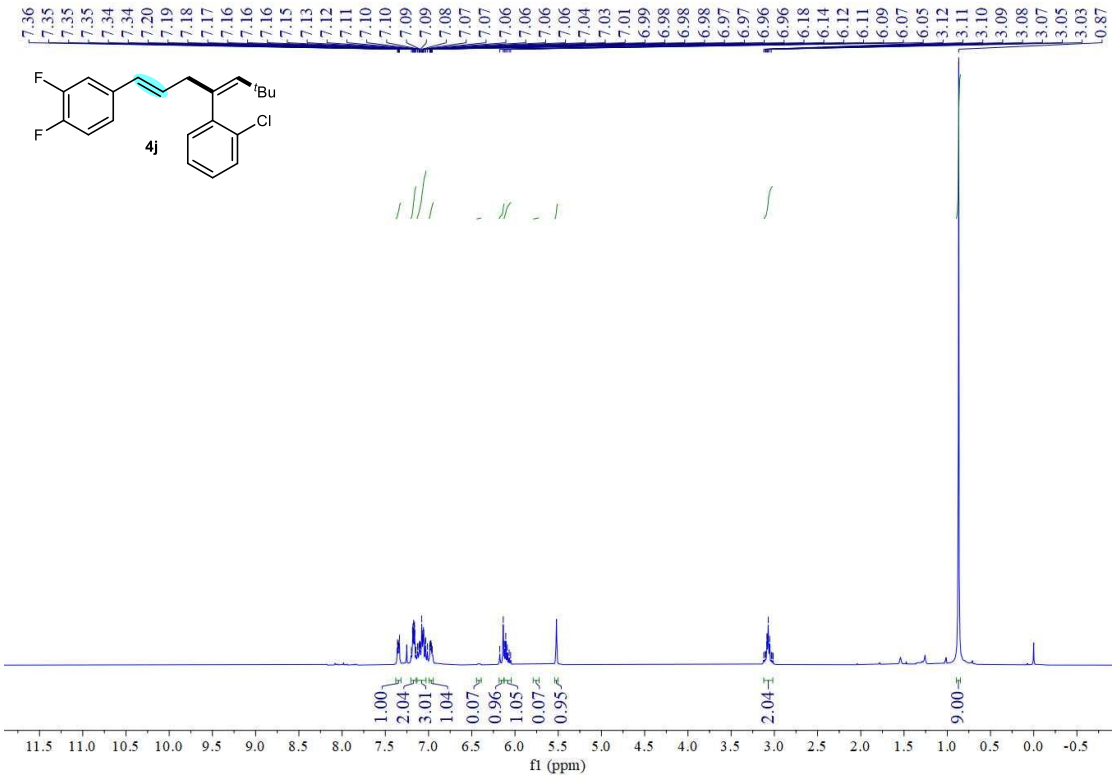


Figure S55. ^{1}H-NMR spectrum of **4j**

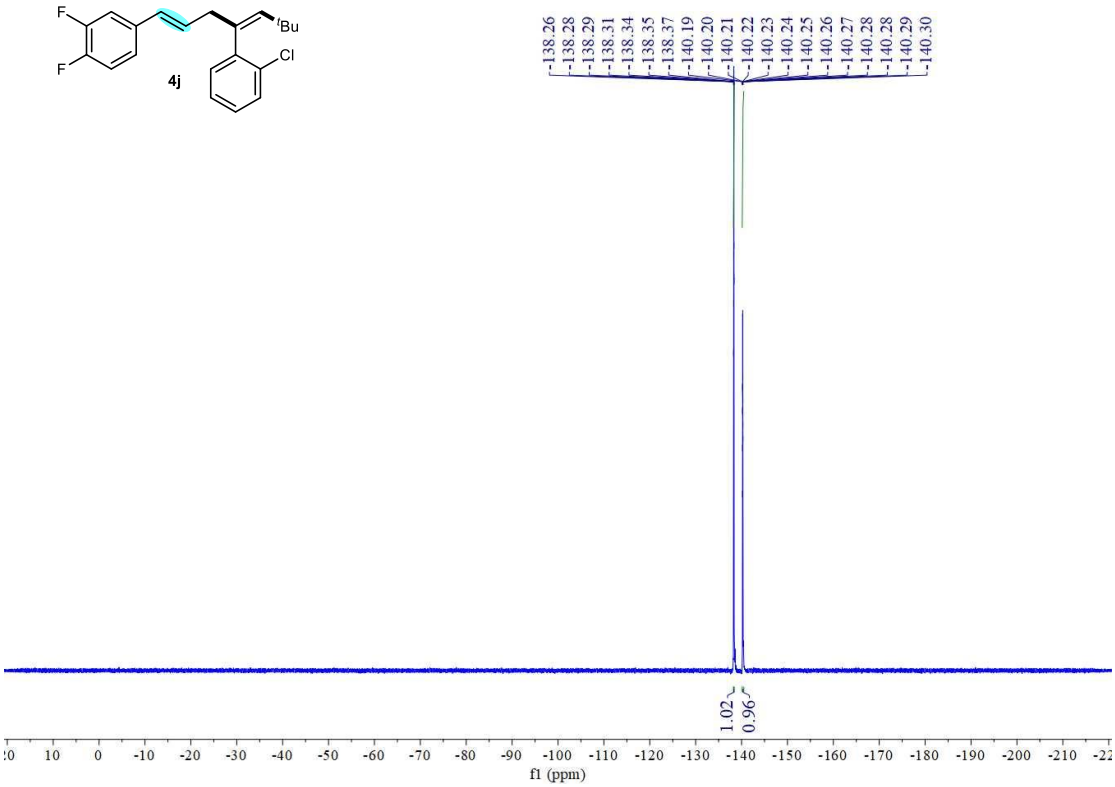


Figure S56. ^{19}F-NMR spectrum of **4j**

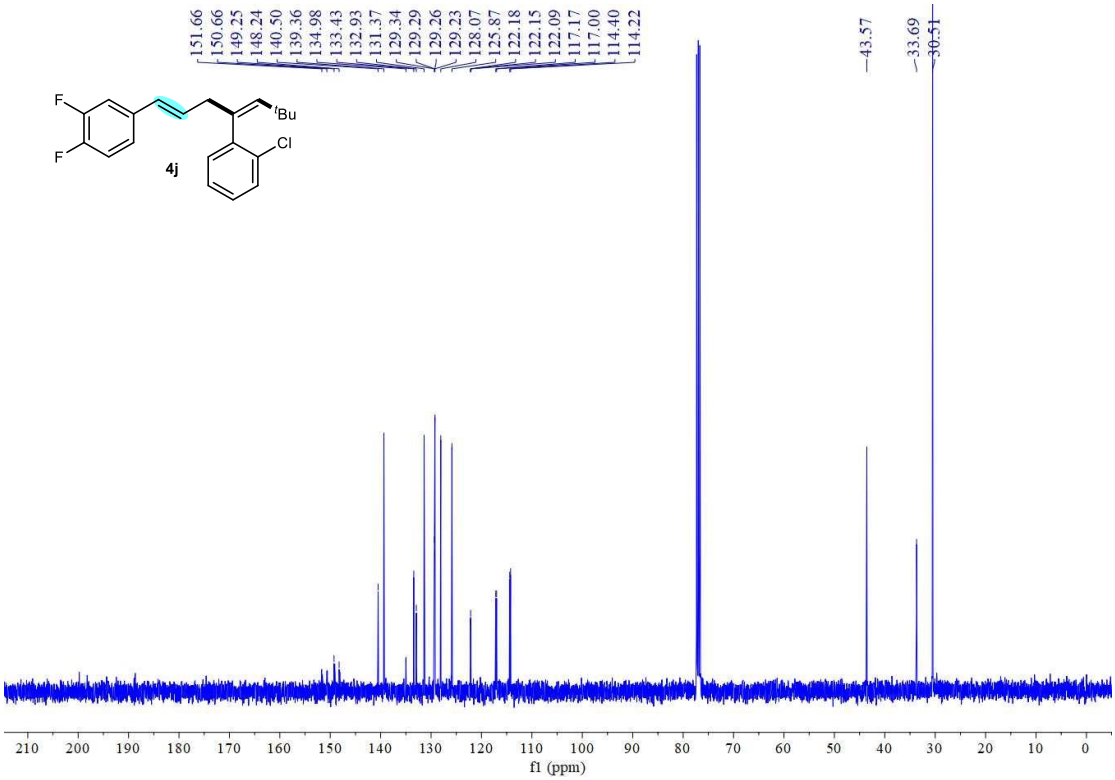


Figure S57. ^{13}C-NMR spectrum of **4j**

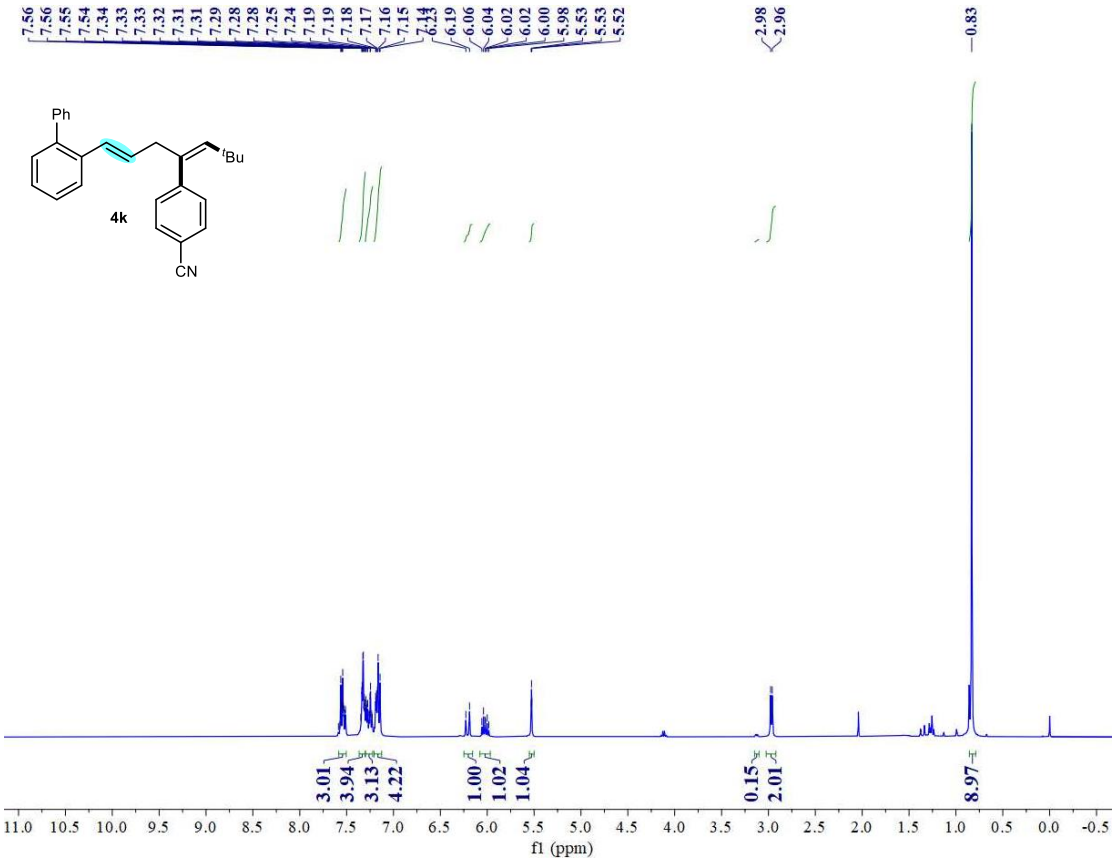


Figure S58. ^{1}H-NMR spectrum of **4k**

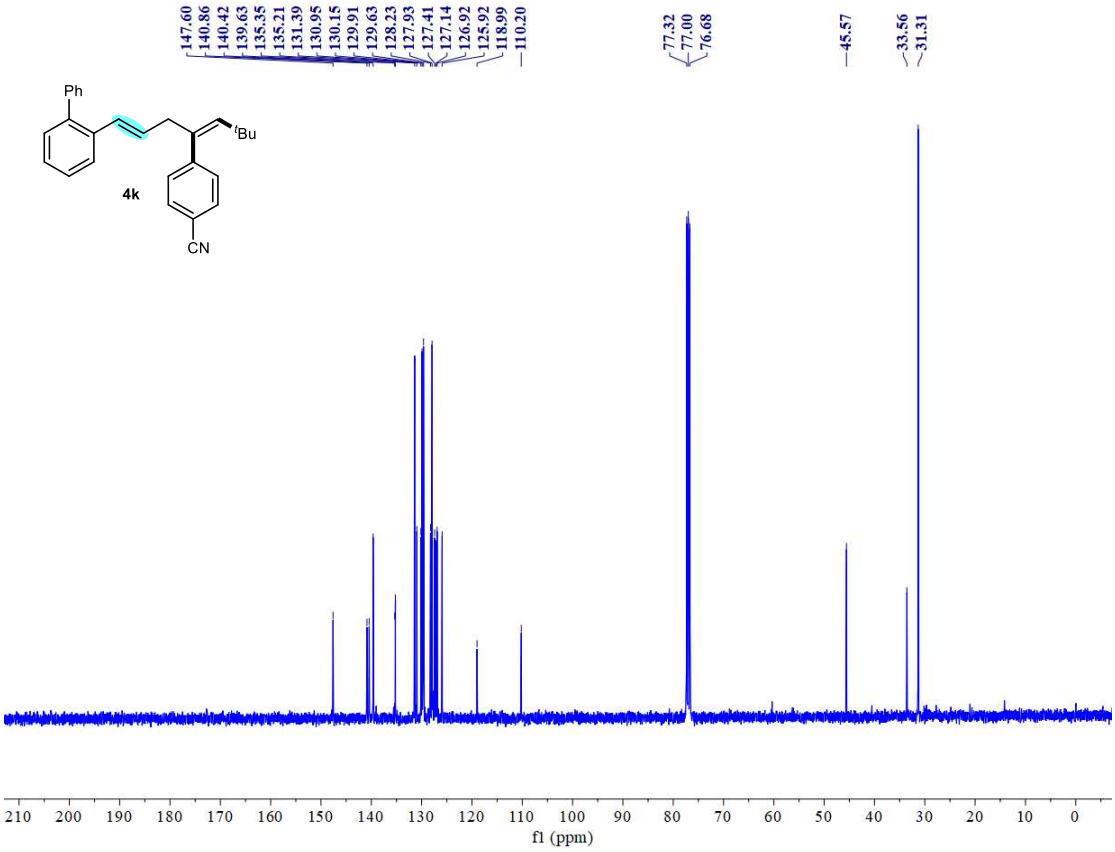


Figure S59. ^{13}C-NMR spectrum of **4k**

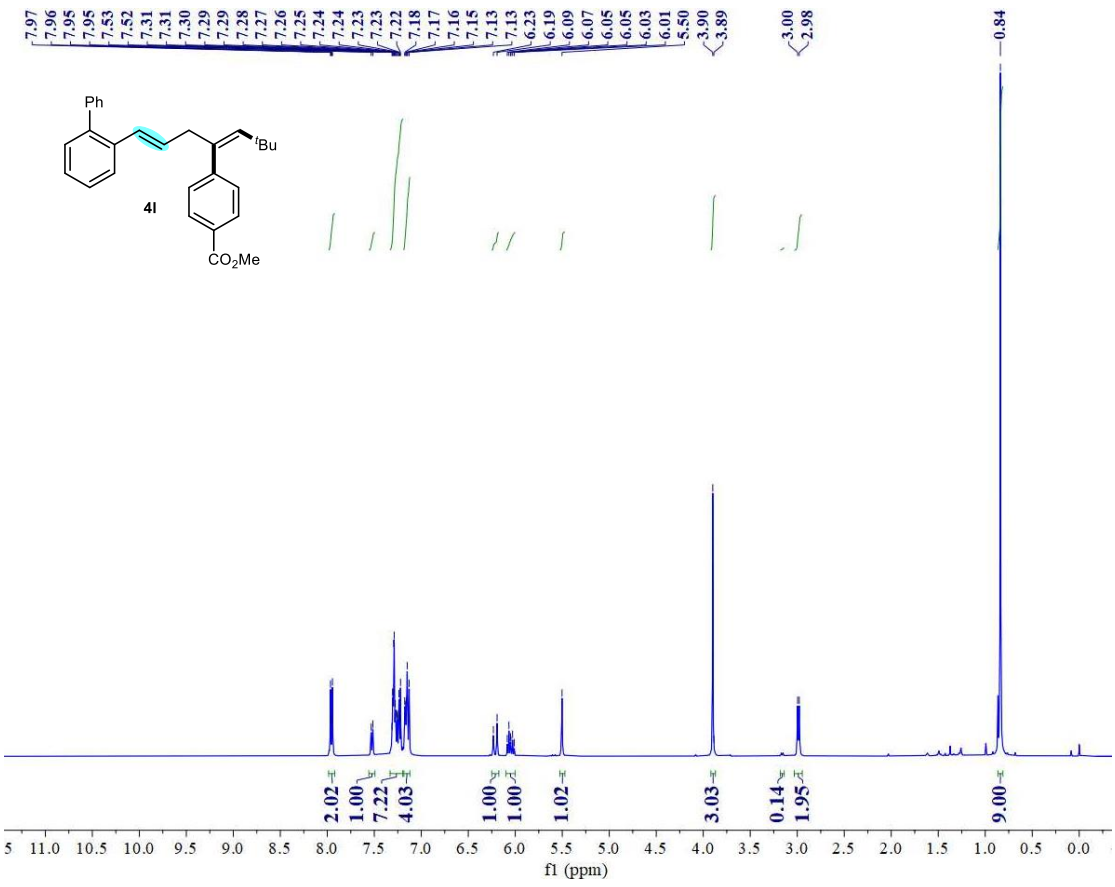


Figure S60. ^{1}H-NMR spectrum of **4l**

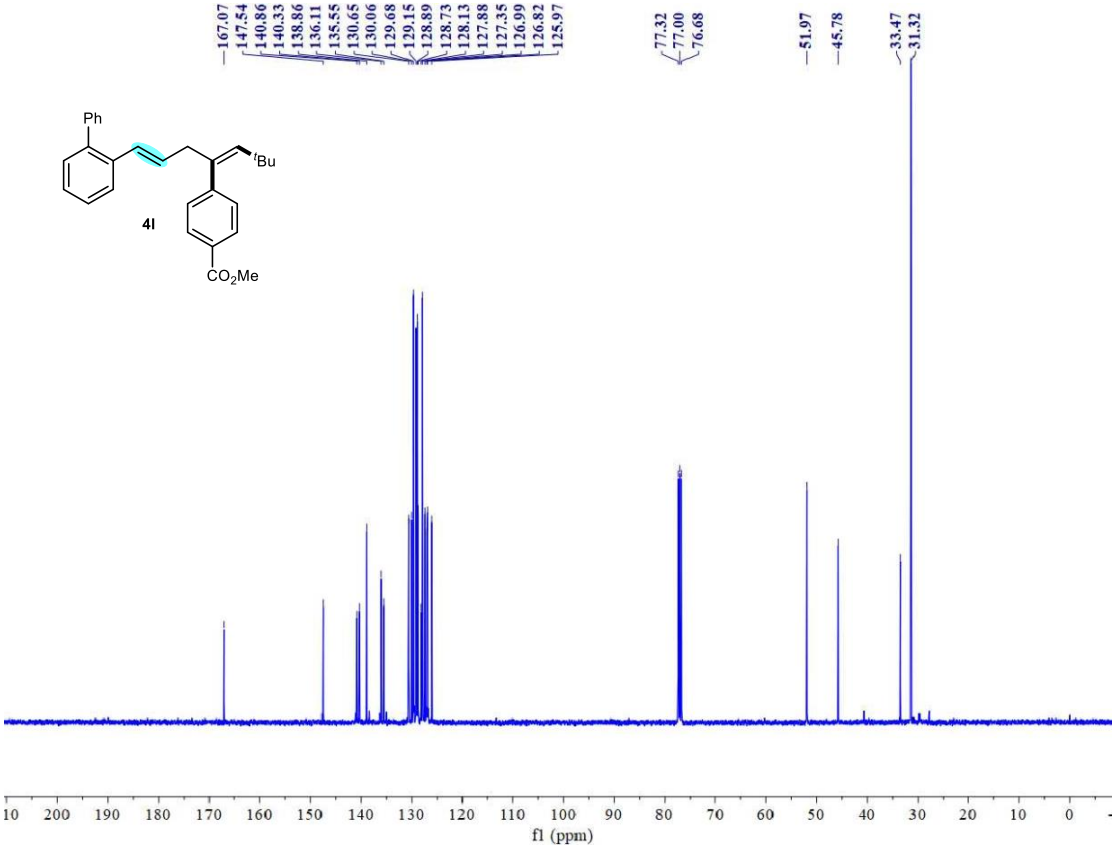


Figure S61. ^{13}C-NMR spectrum of **4l**

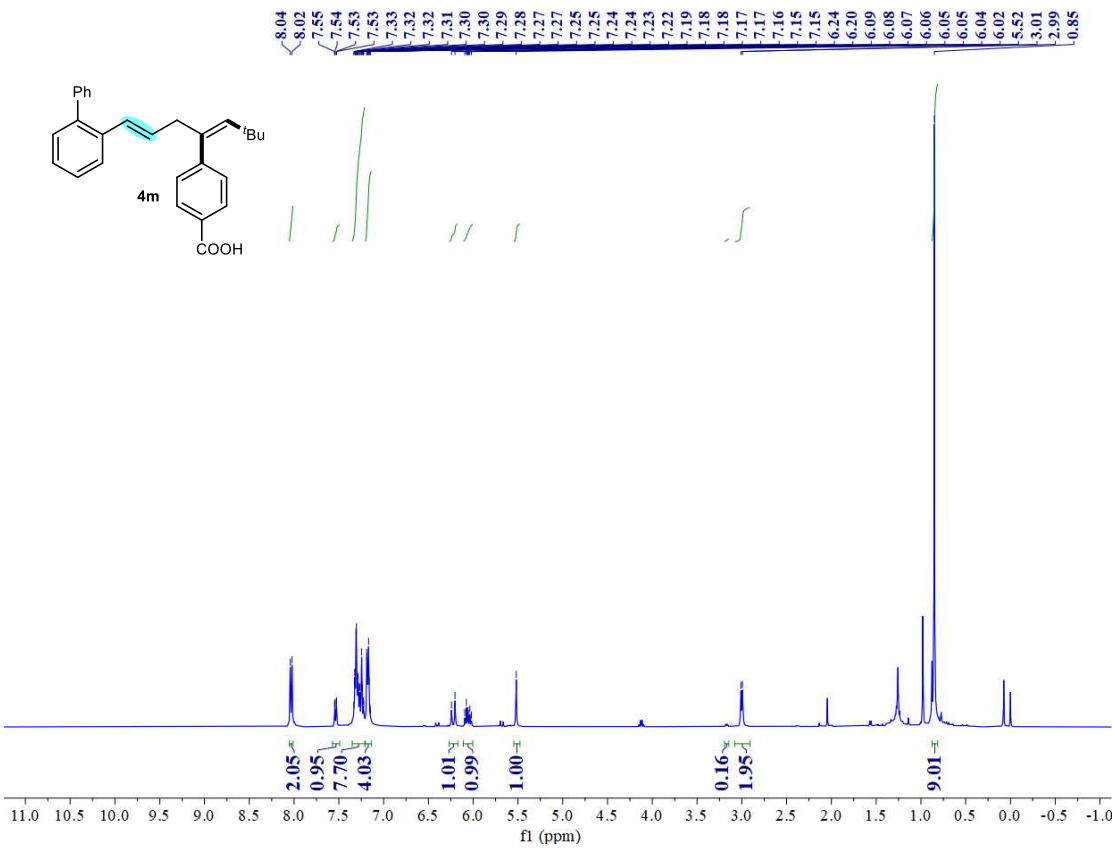


Figure S62. ^{1}H-NMR spectrum of **4m**

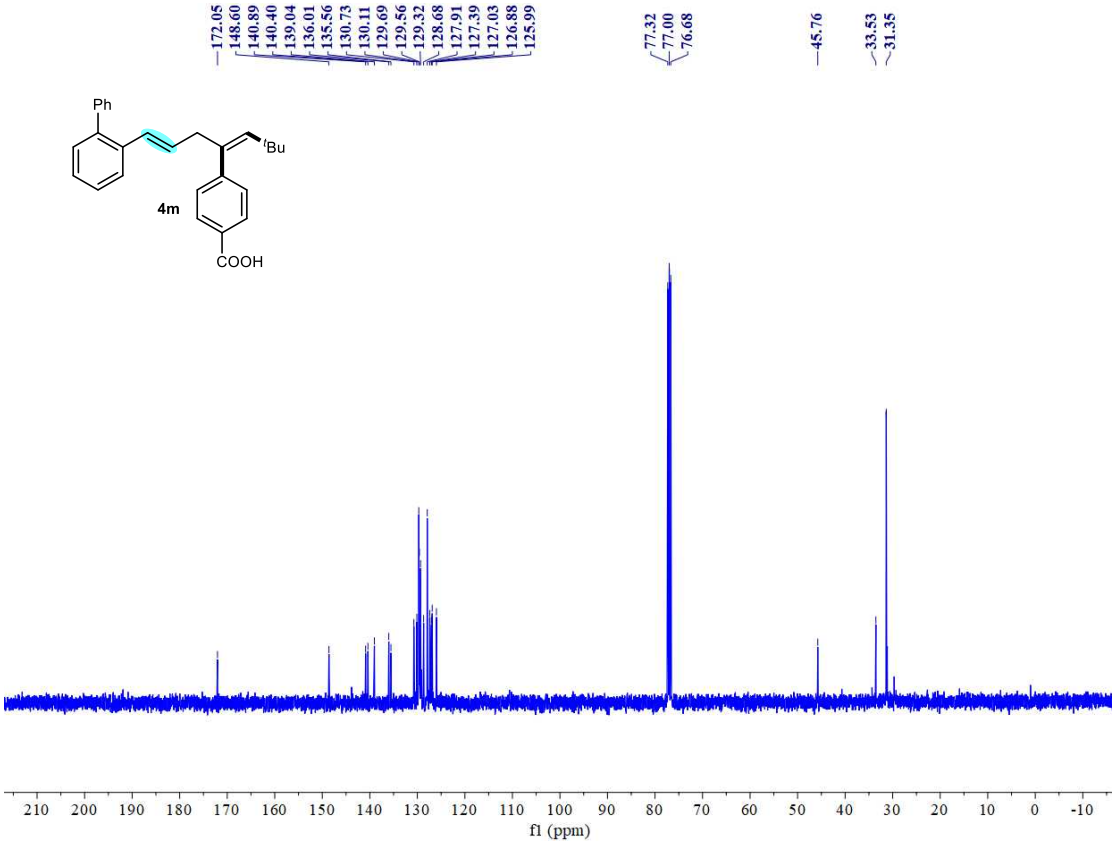


Figure S63. ^{13}C-NMR spectrum of **4m**

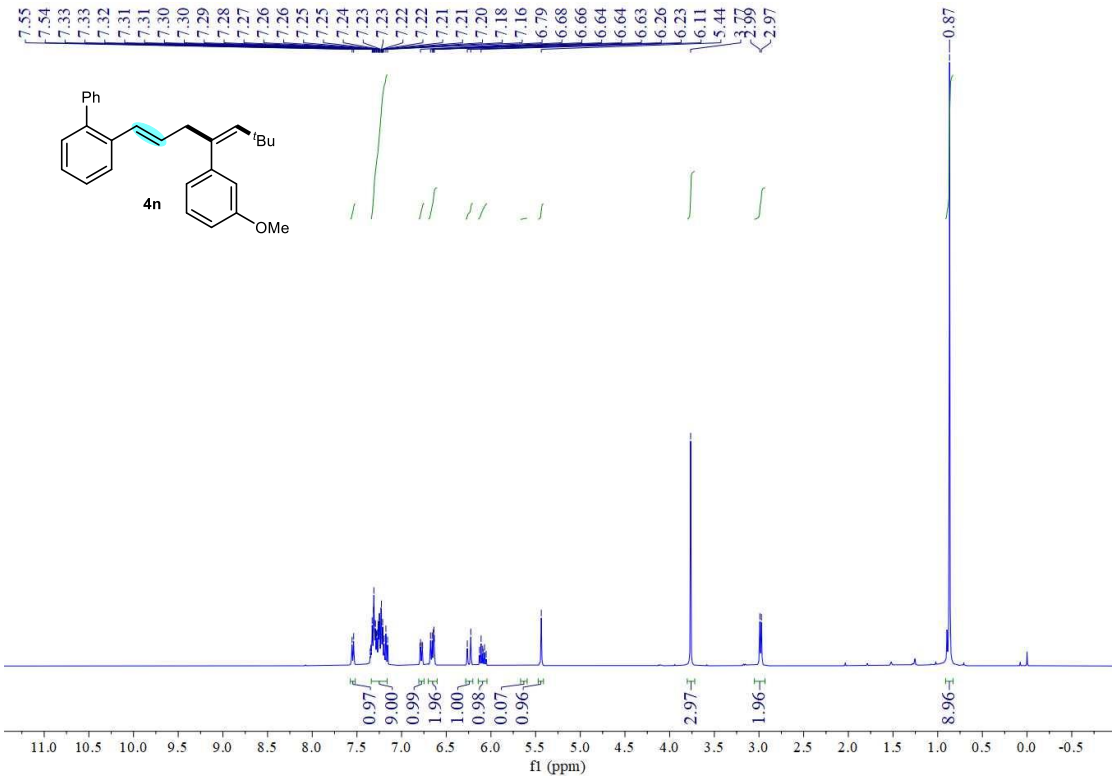


Figure S64. ^{1}H-NMR spectrum of **4n**

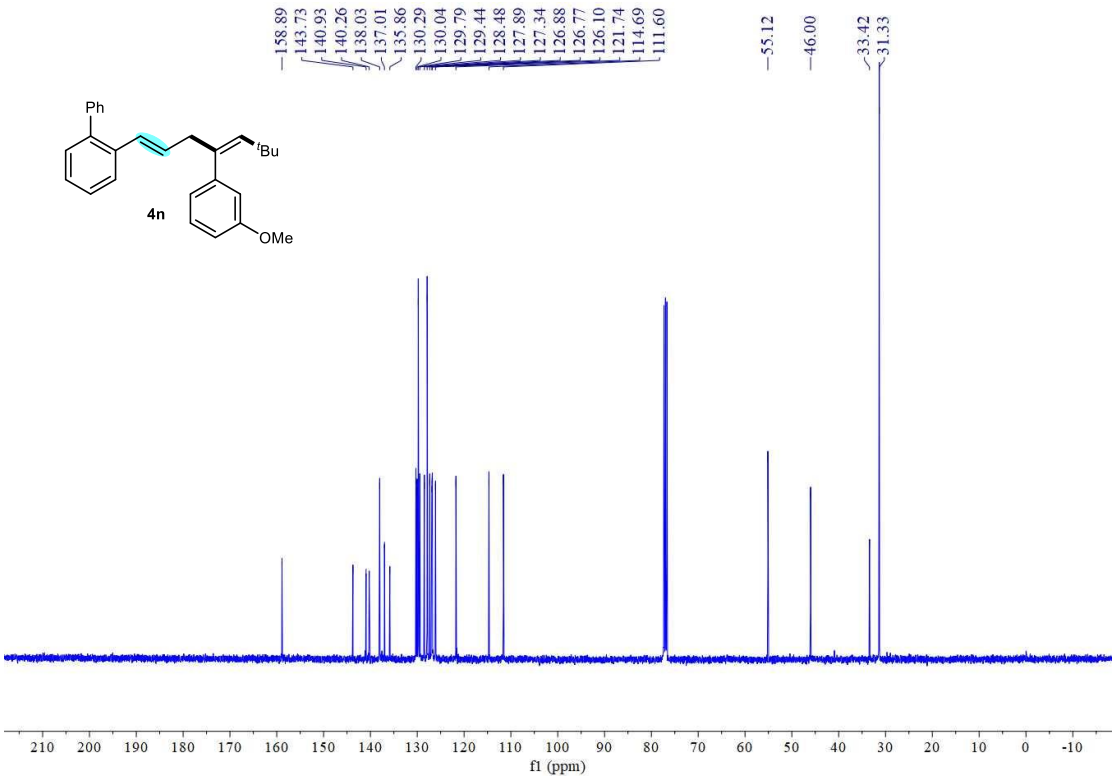


Figure S65. ^{13}C-NMR spectrum of **4n**

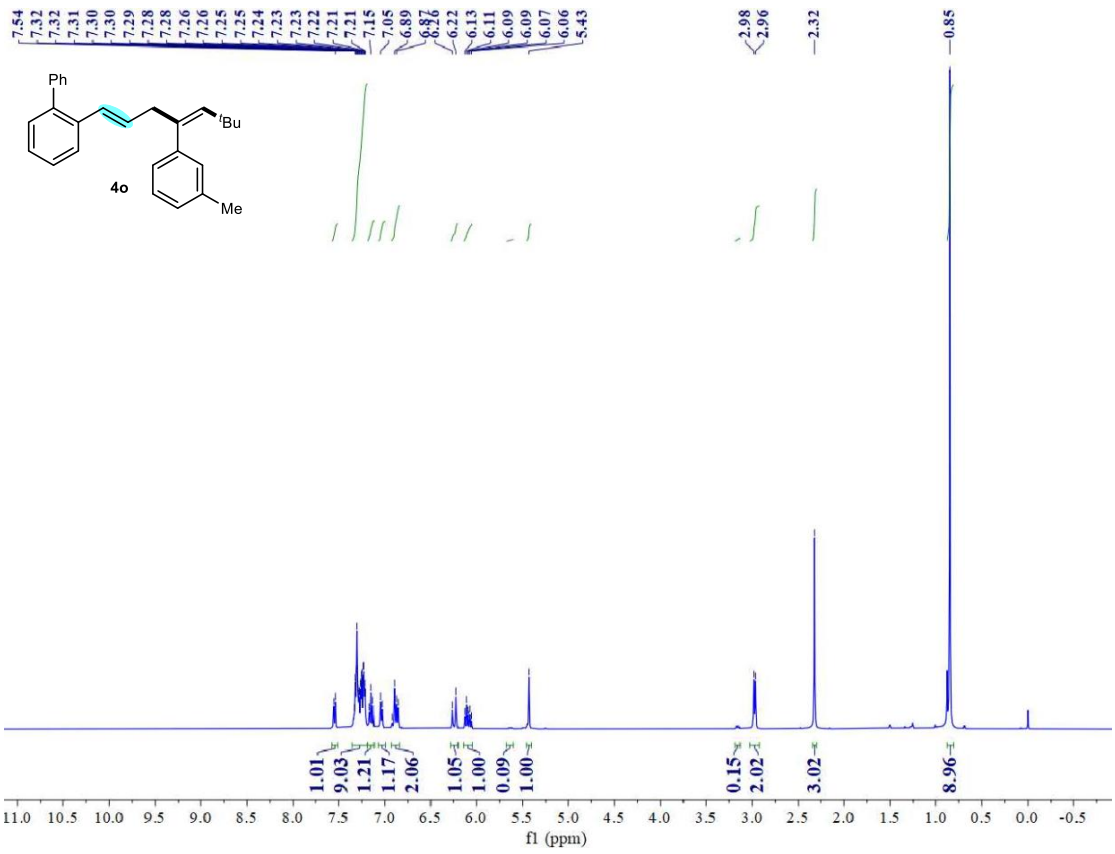


Figure S66. ^{1}H-NMR spectrum of **4o**

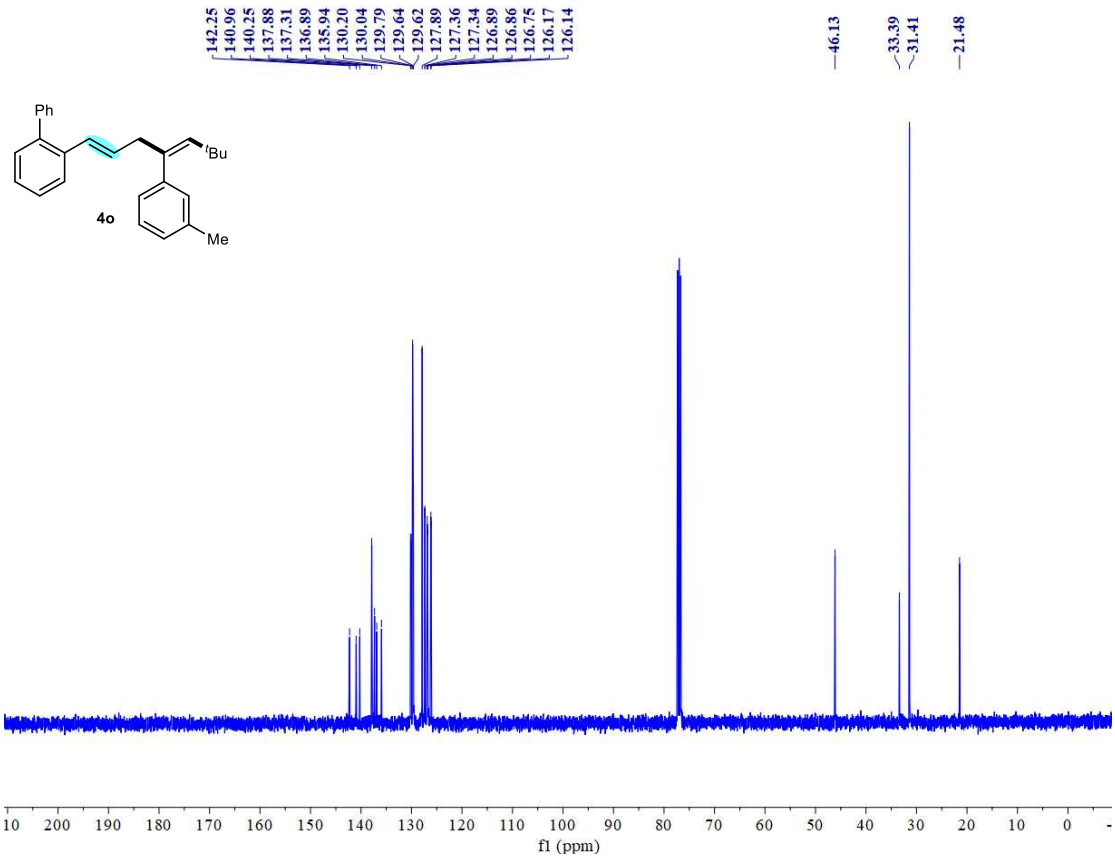


Figure S67. ^{13}C-NMR spectrum of **4o**

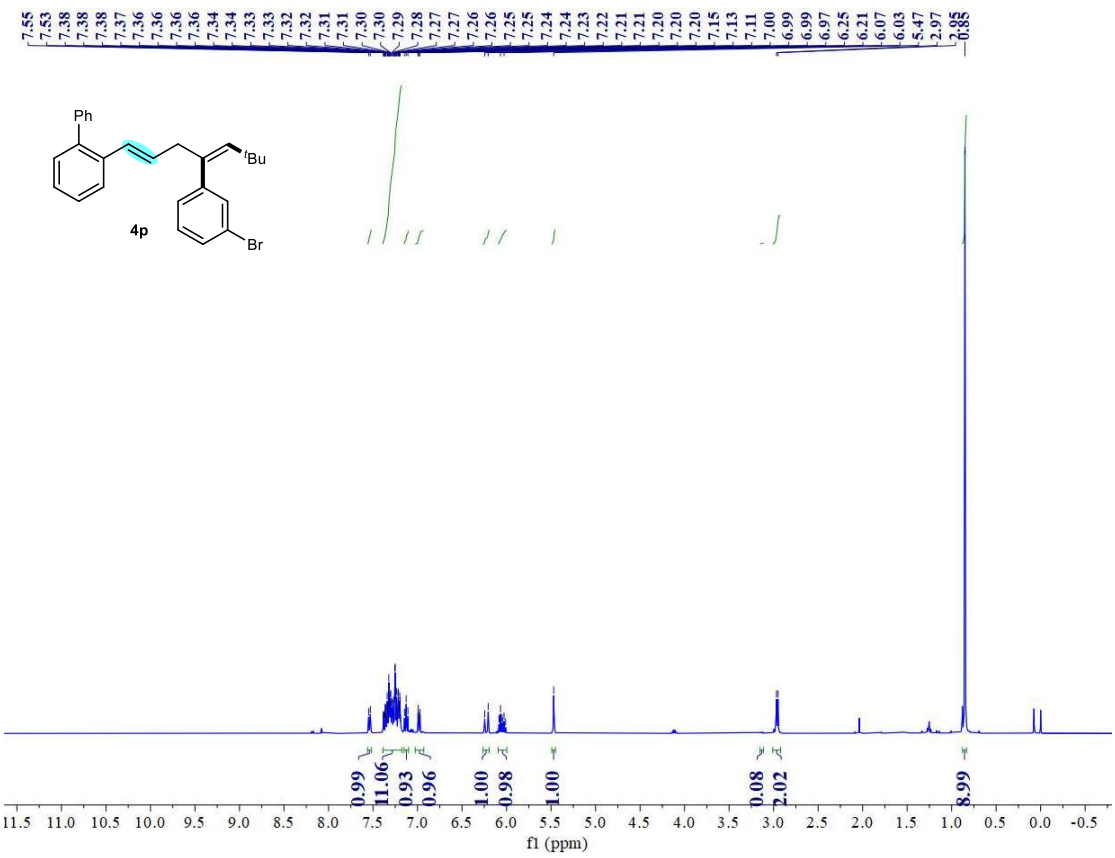


Figure S68. ^{1}H-NMR spectrum of **4p**

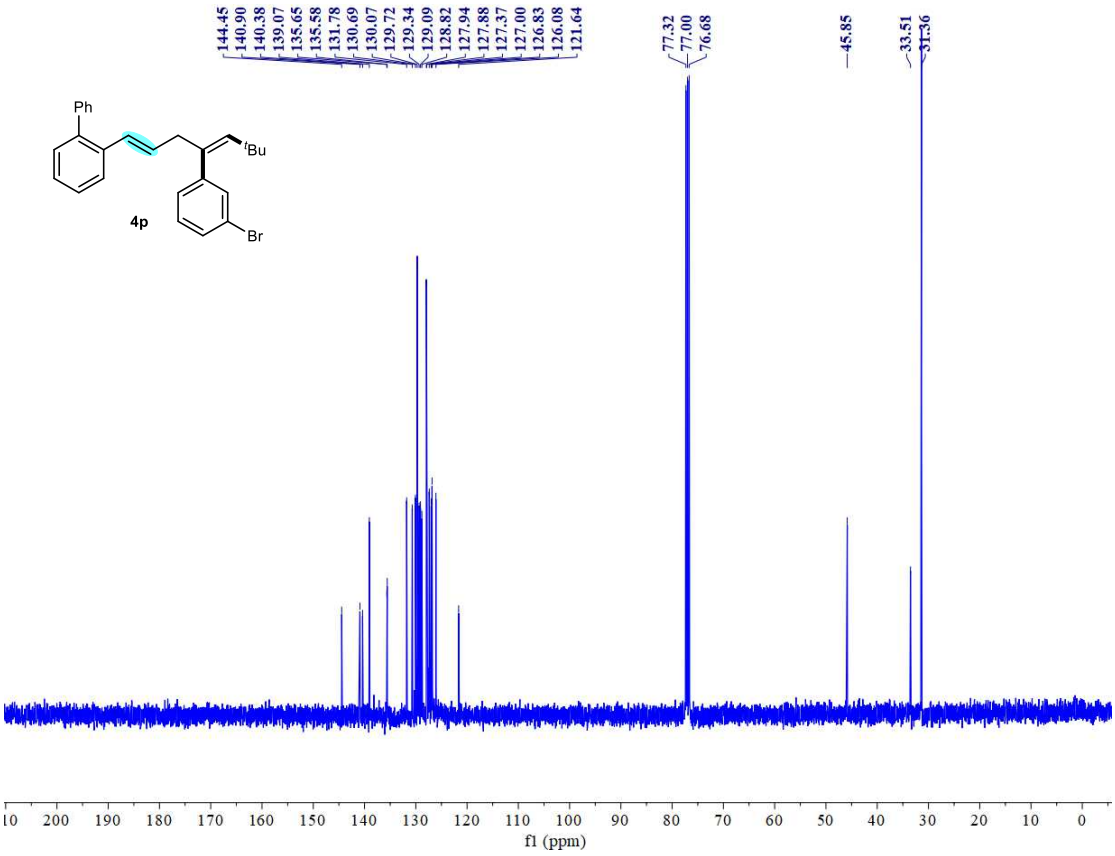


Figure S69. ^{13}C-NMR spectrum of **4p**

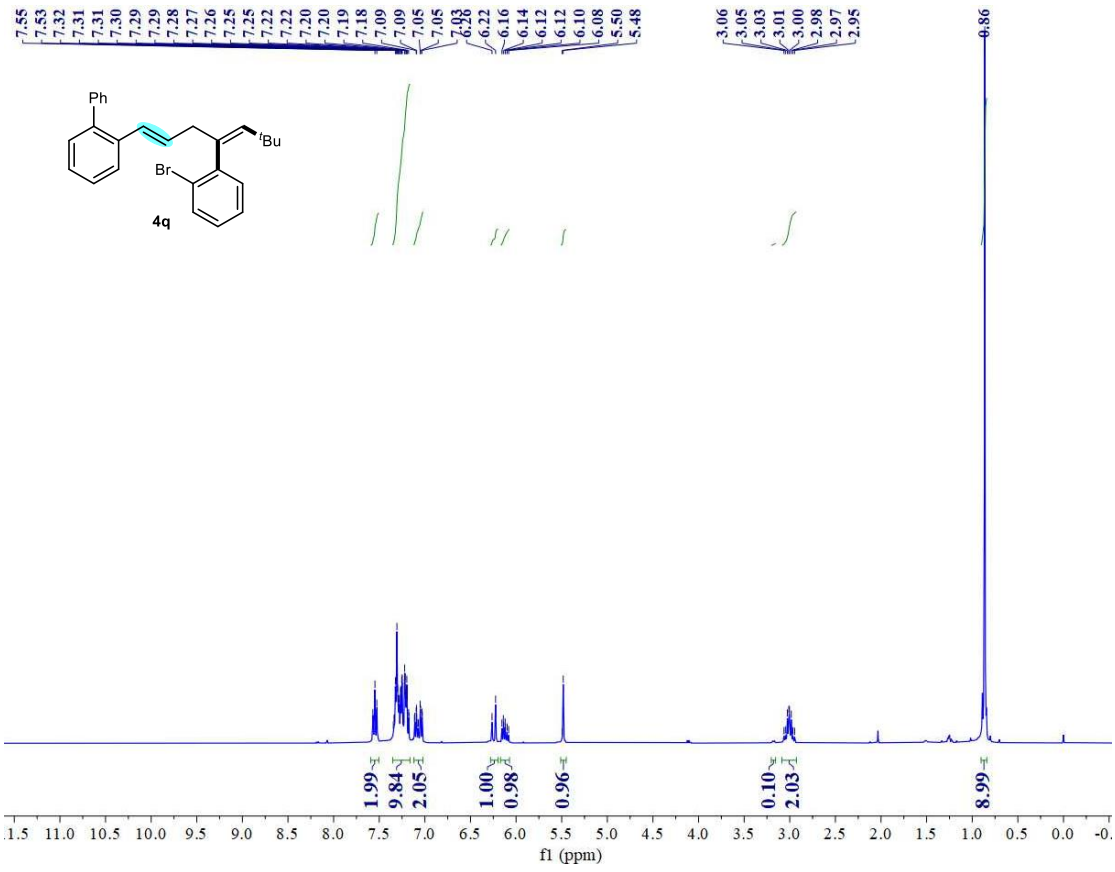


Figure S70. ^{1}H-NMR spectrum of **4q**

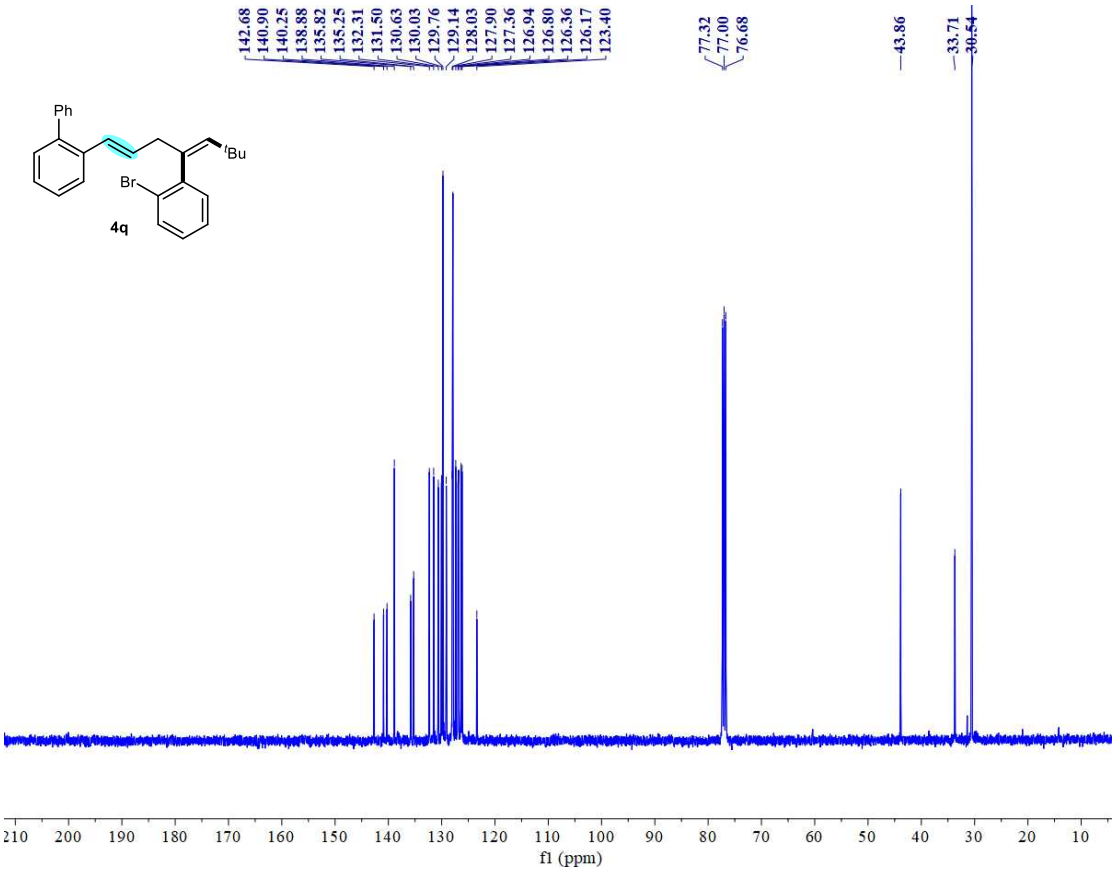


Figure S71. ^{13}C-NMR spectrum of **4q**

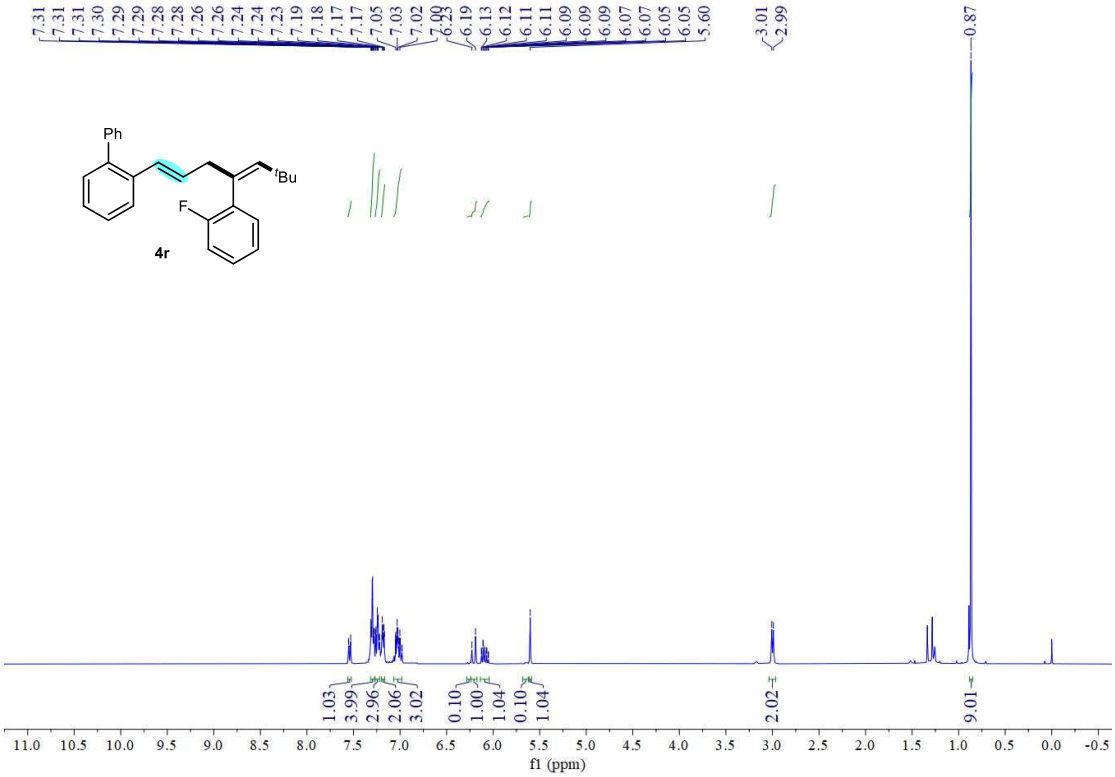


Figure S72. ^{1}H-NMR spectrum of **4r**

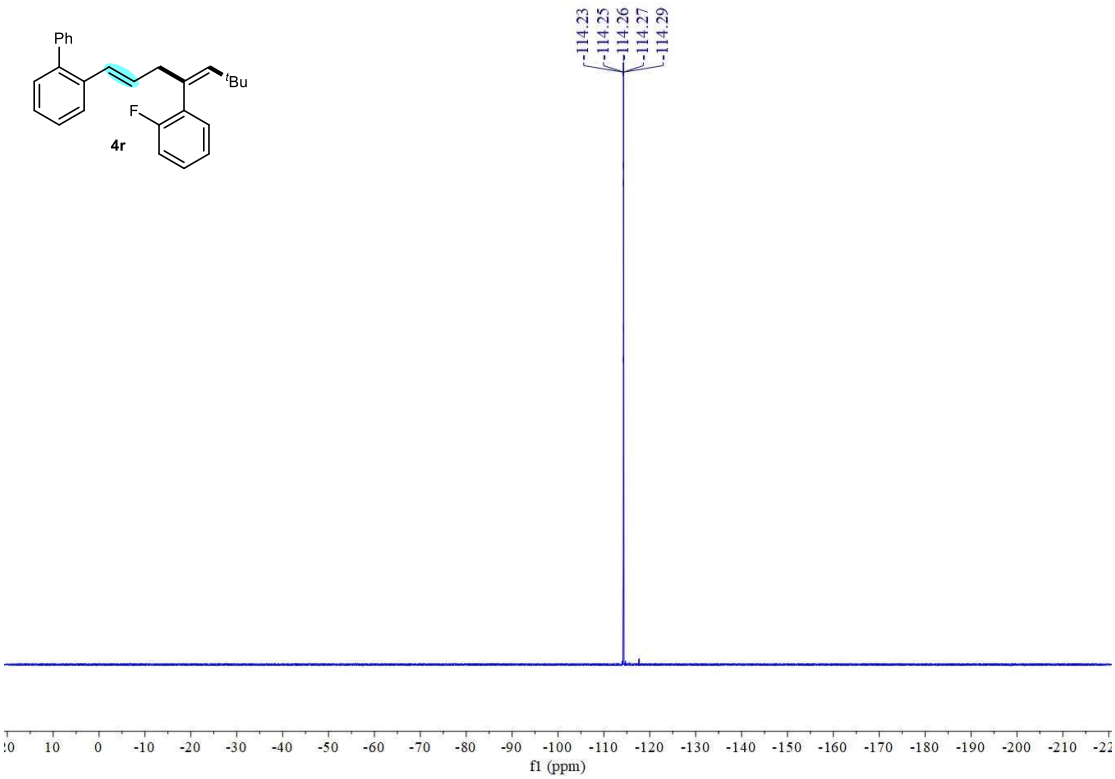


Figure S73. ^{19}F-NMR spectrum of **4r**

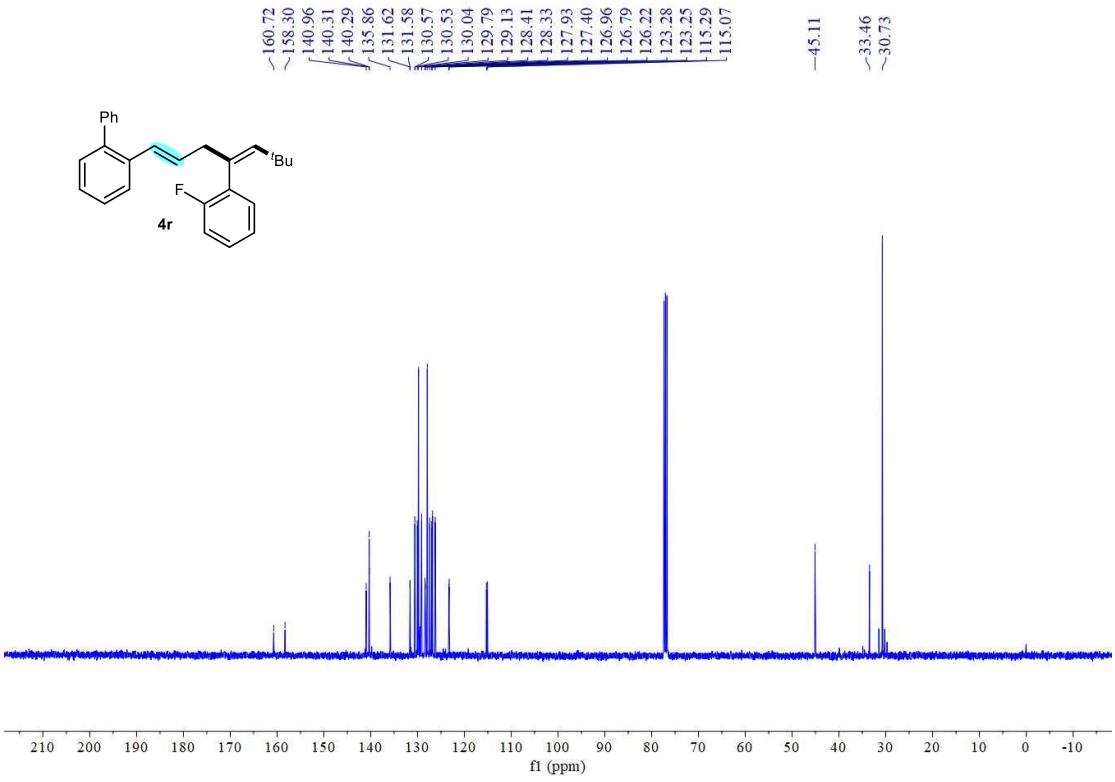


Figure S74. ^{13}C-NMR spectrum of **4r**

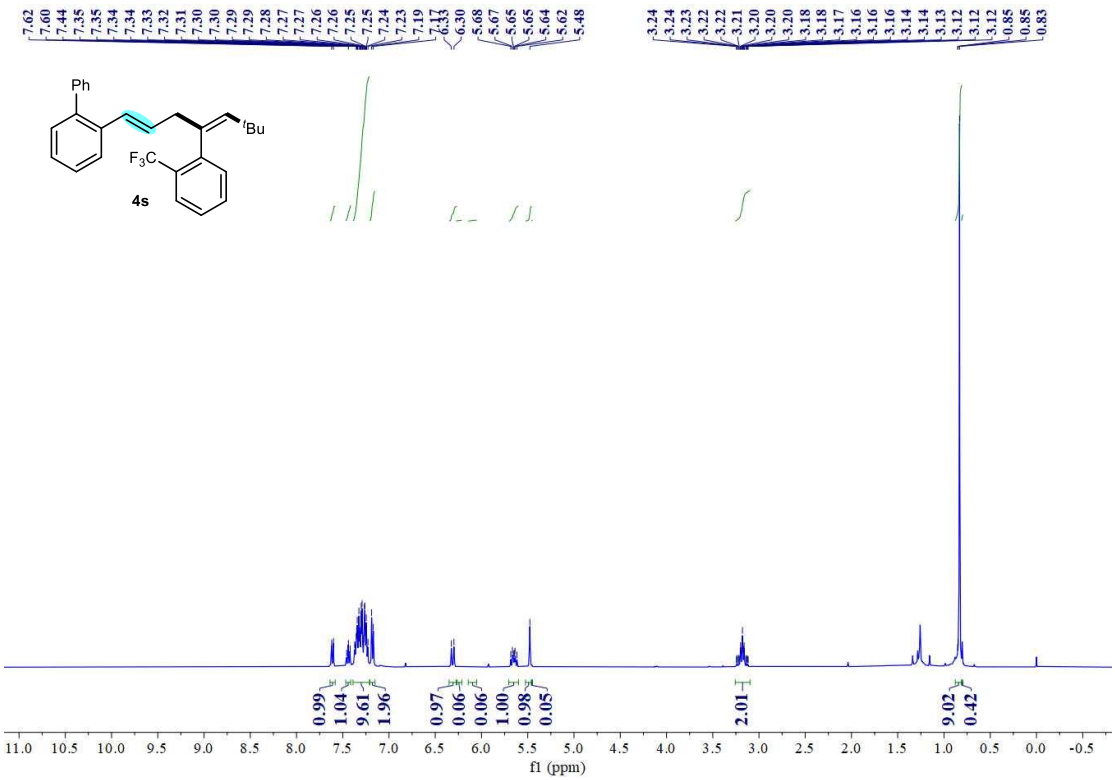


Figure S75. ^{1}H-NMR spectrum of **4s**

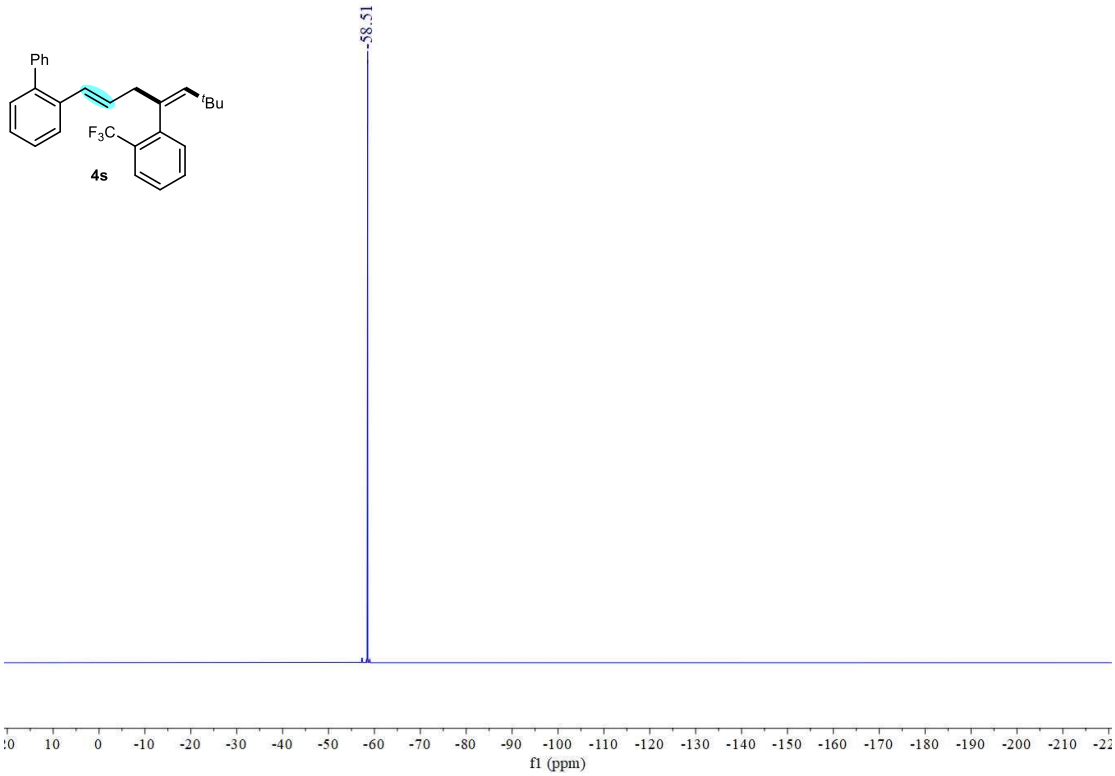


Figure S76. ^{19}F-NMR spectrum of **4s**

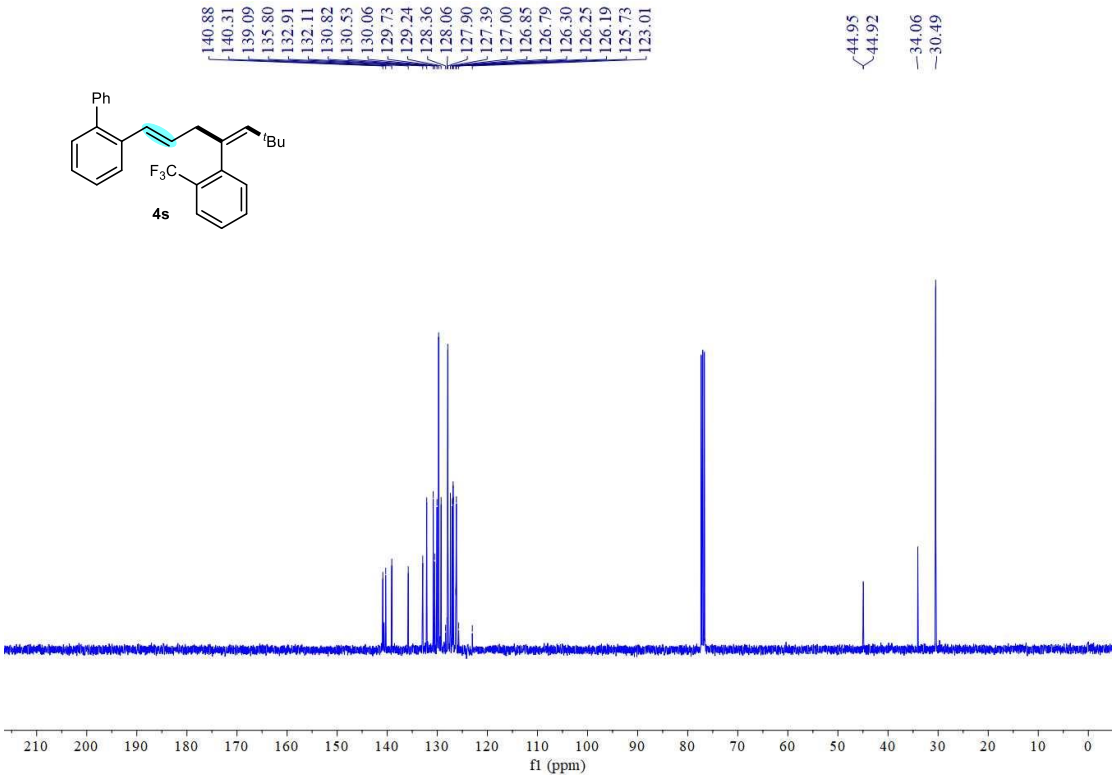


Figure S77. ^{13}C-NMR spectrum of **4s**

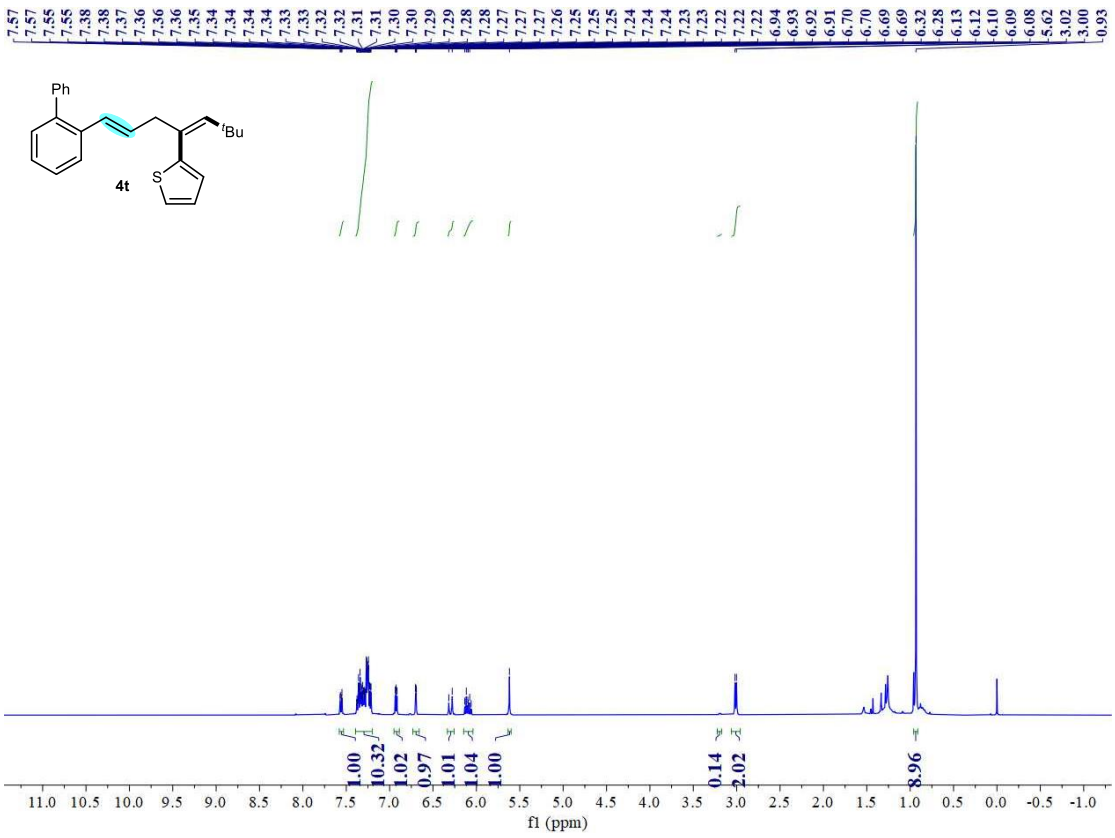


Figure S78. ^{1}H-NMR spectrum of **4t**

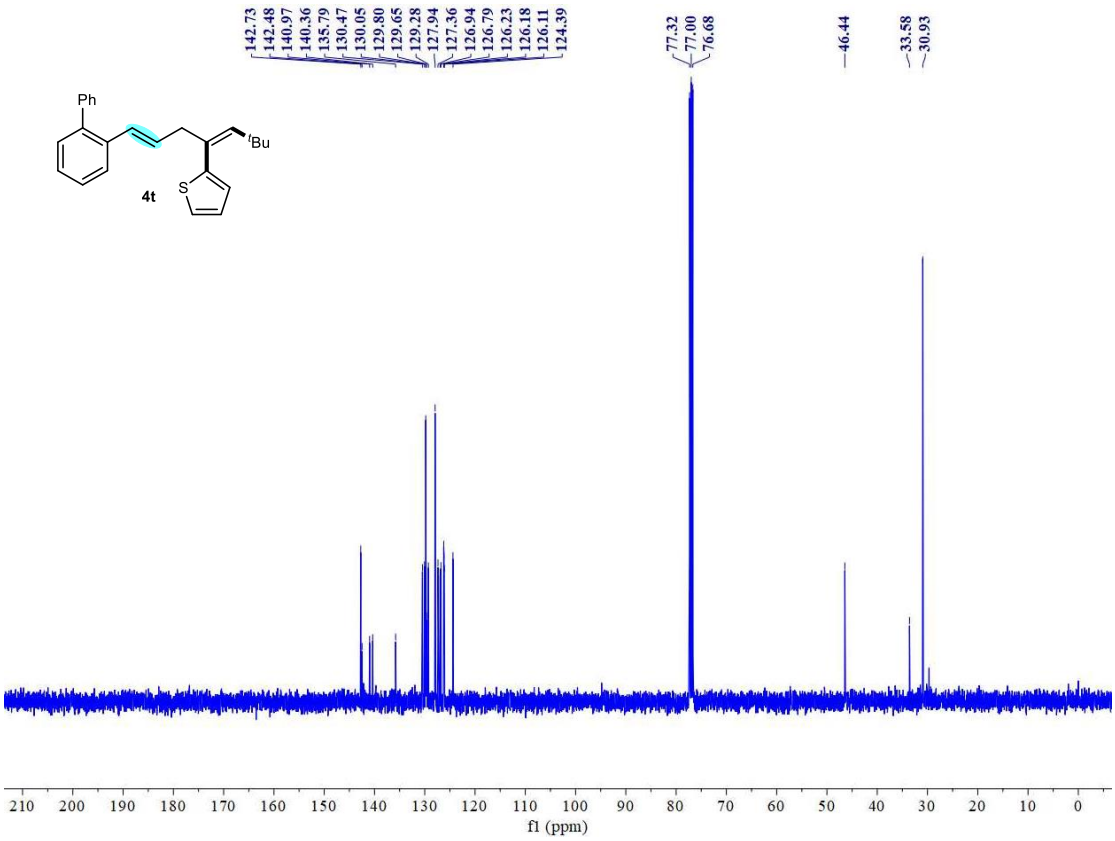


Figure S79. ^{13}C-NMR spectrum of **4t**

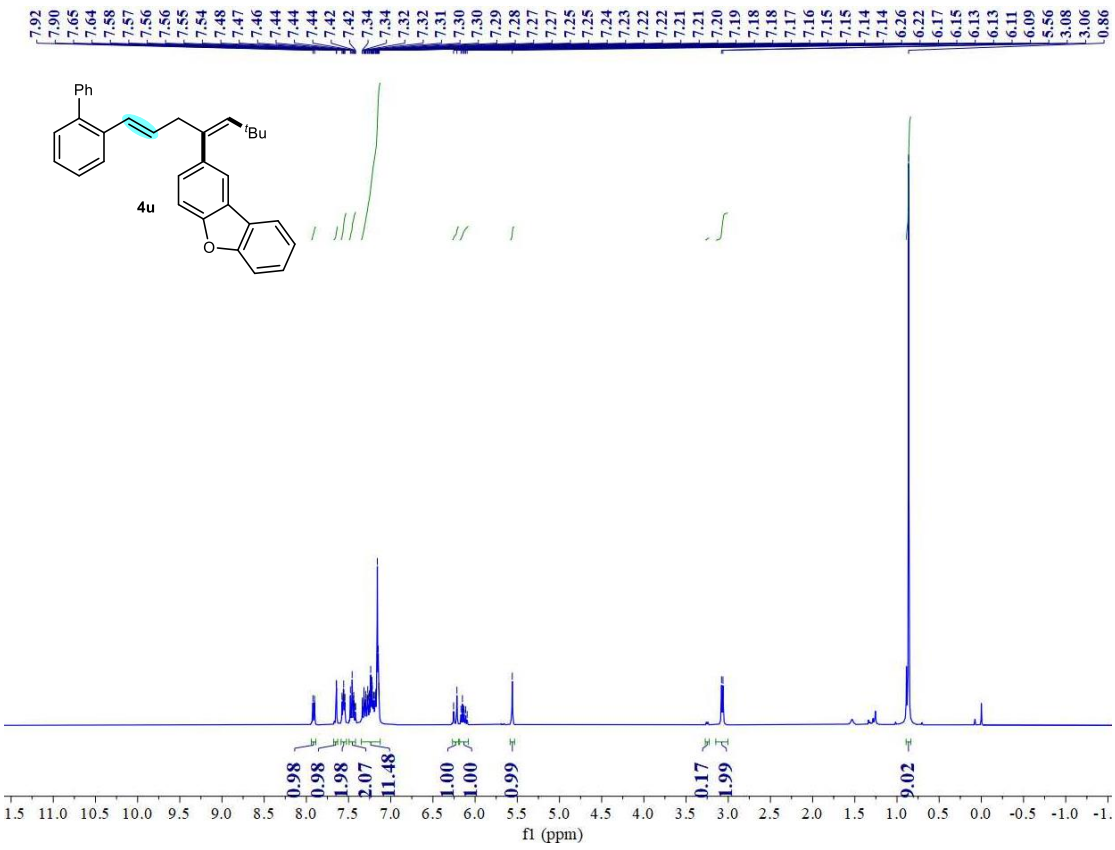


Figure S80. ^{1}H-NMR spectrum of **4u**

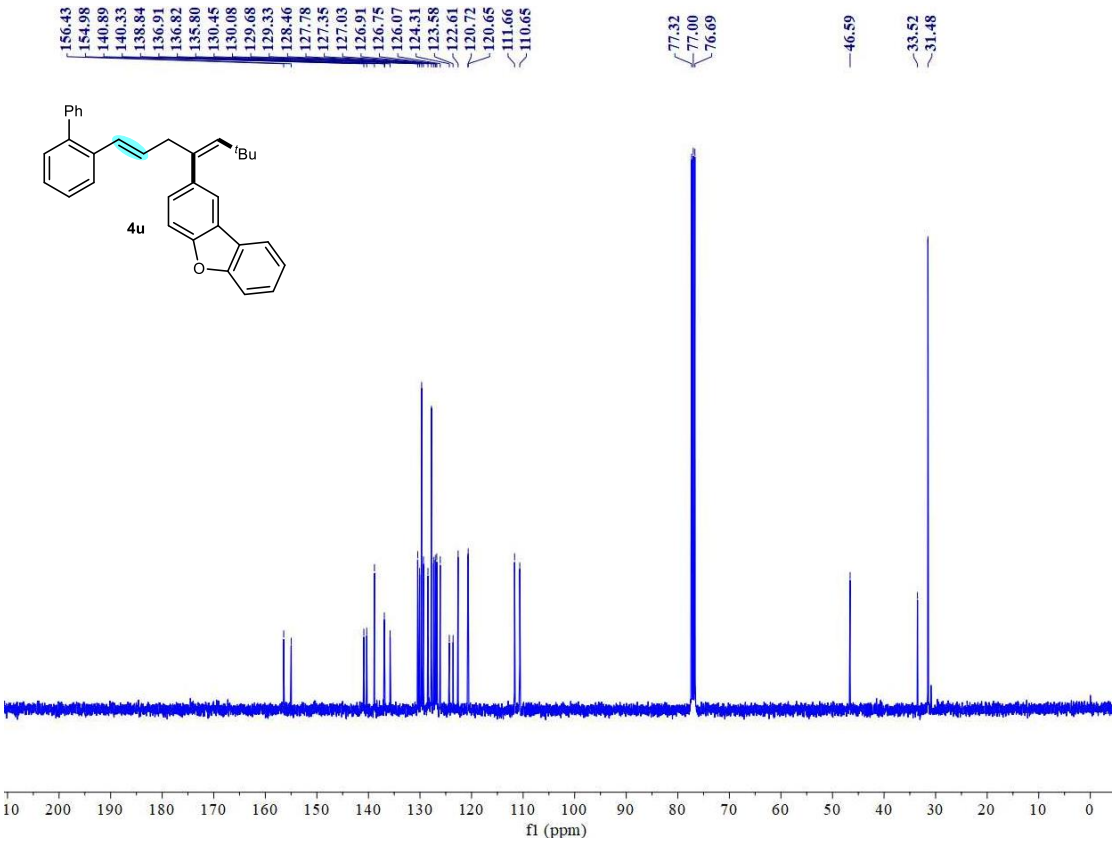


Figure S81. ^{13}C-NMR spectrum of **4u**

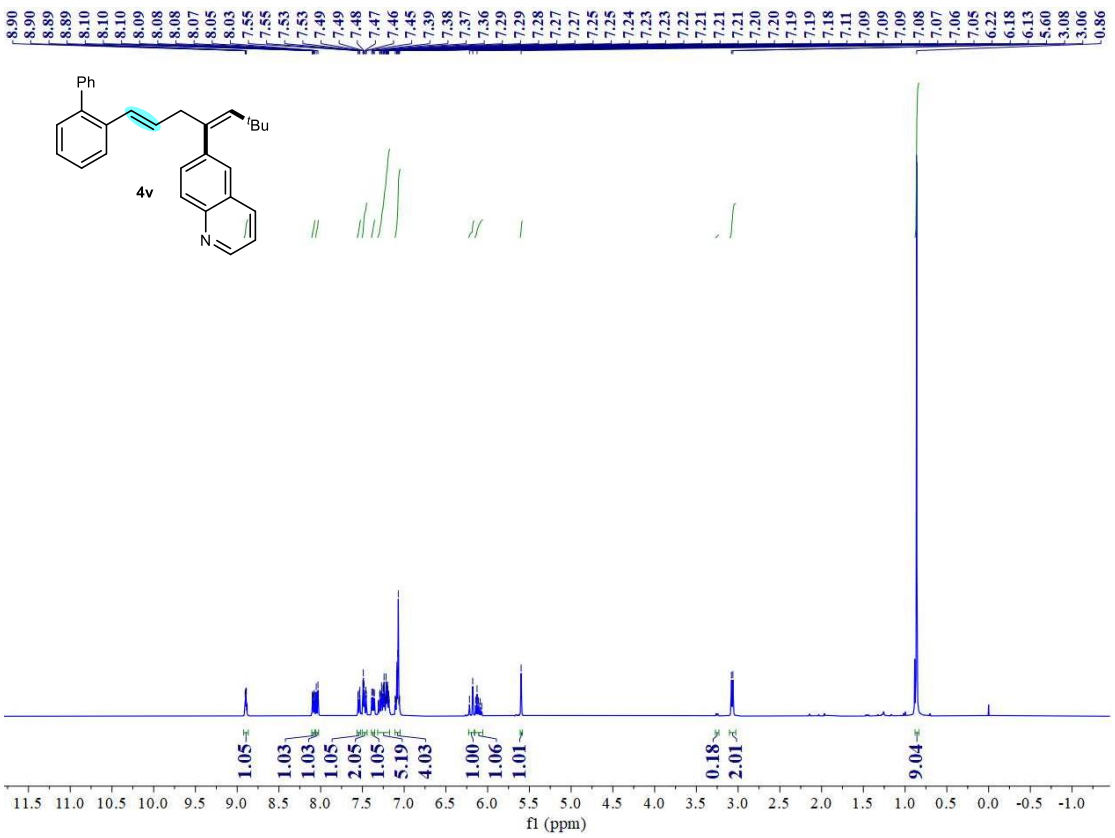


Figure S82. ^{1}H-NMR spectrum of **4v**

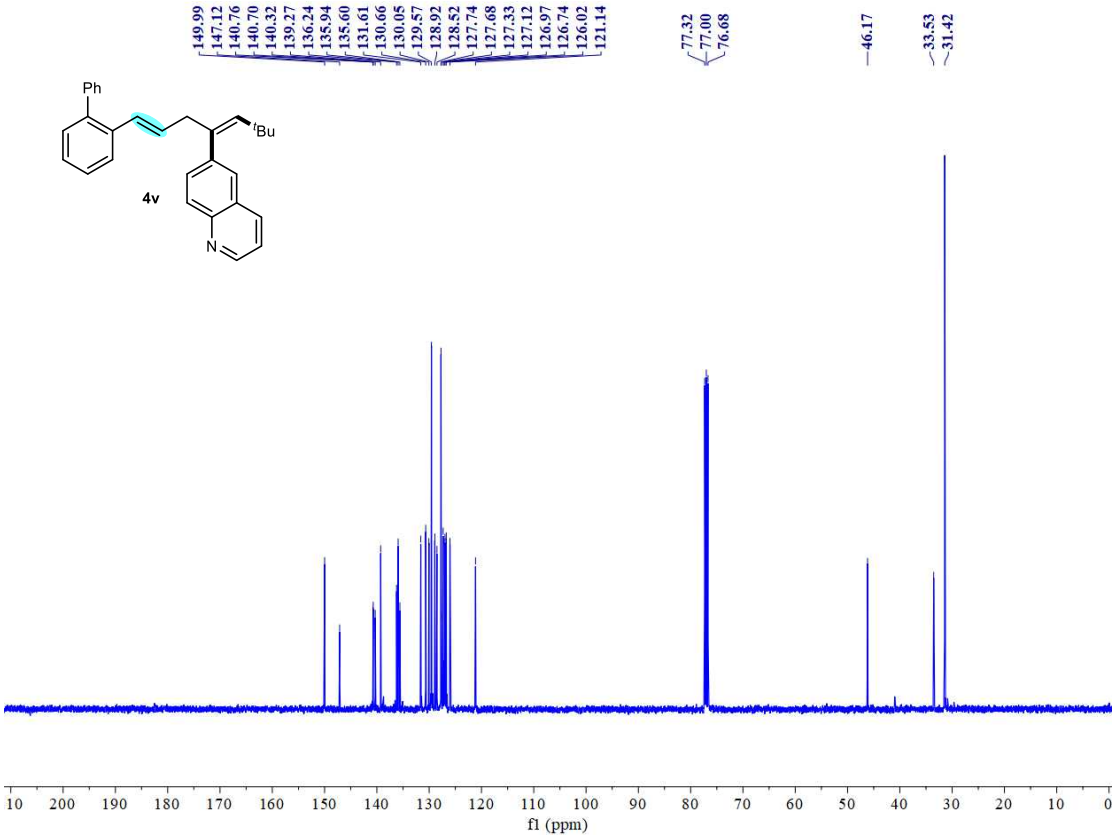


Figure S83. ^{13}C-NMR spectrum of **4v**

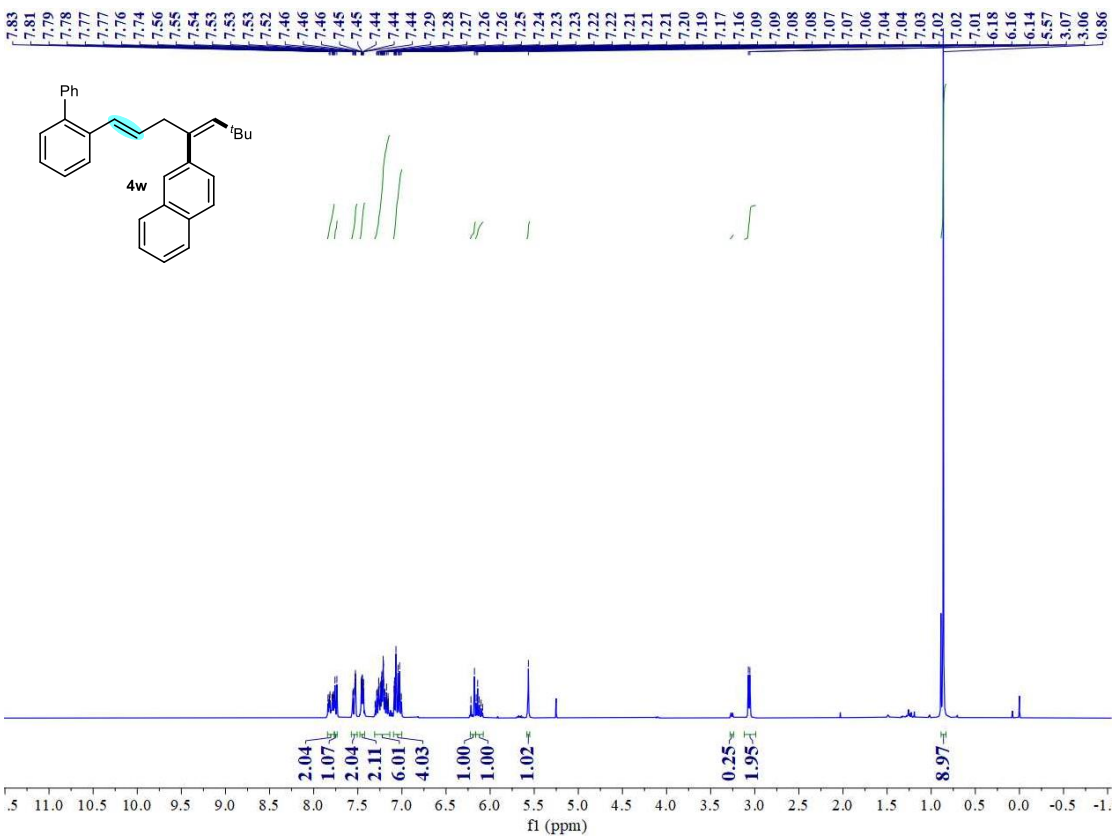


Figure S84. ^{1}H-NMR spectrum of **4w**

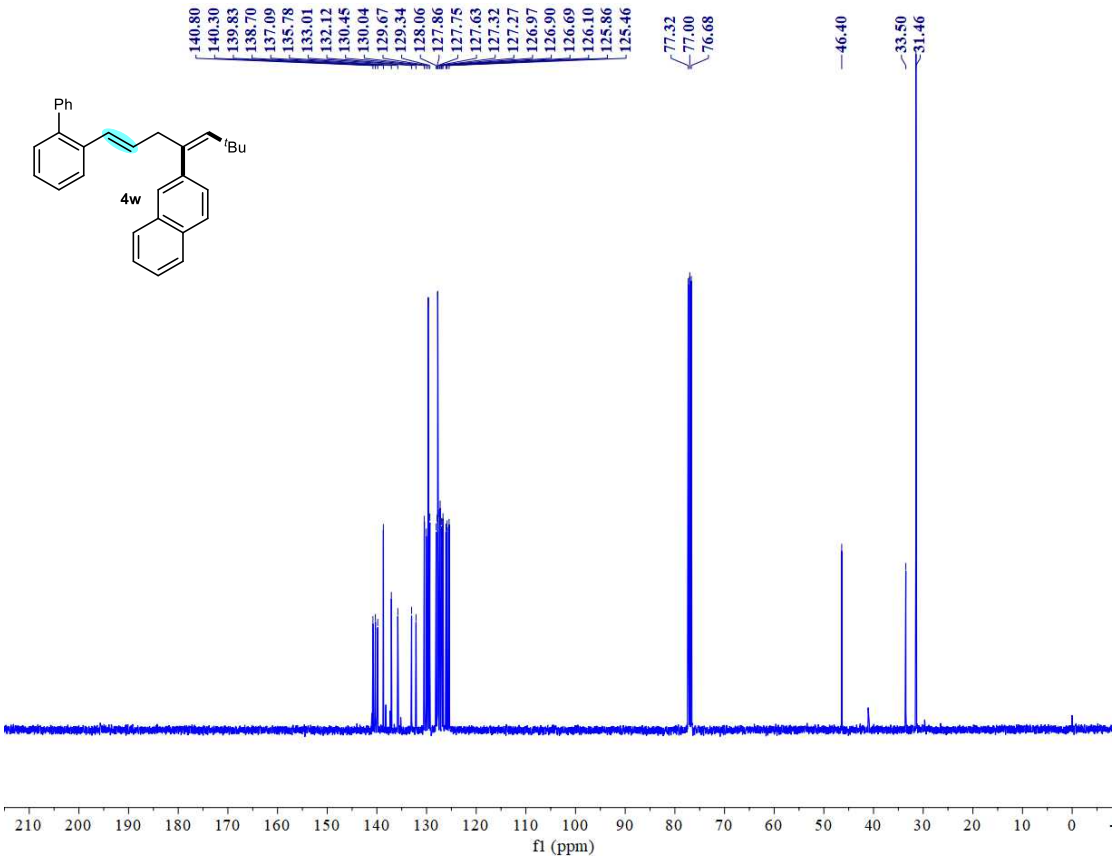


Figure S85. ^{13}C-NMR spectrum of **4w**

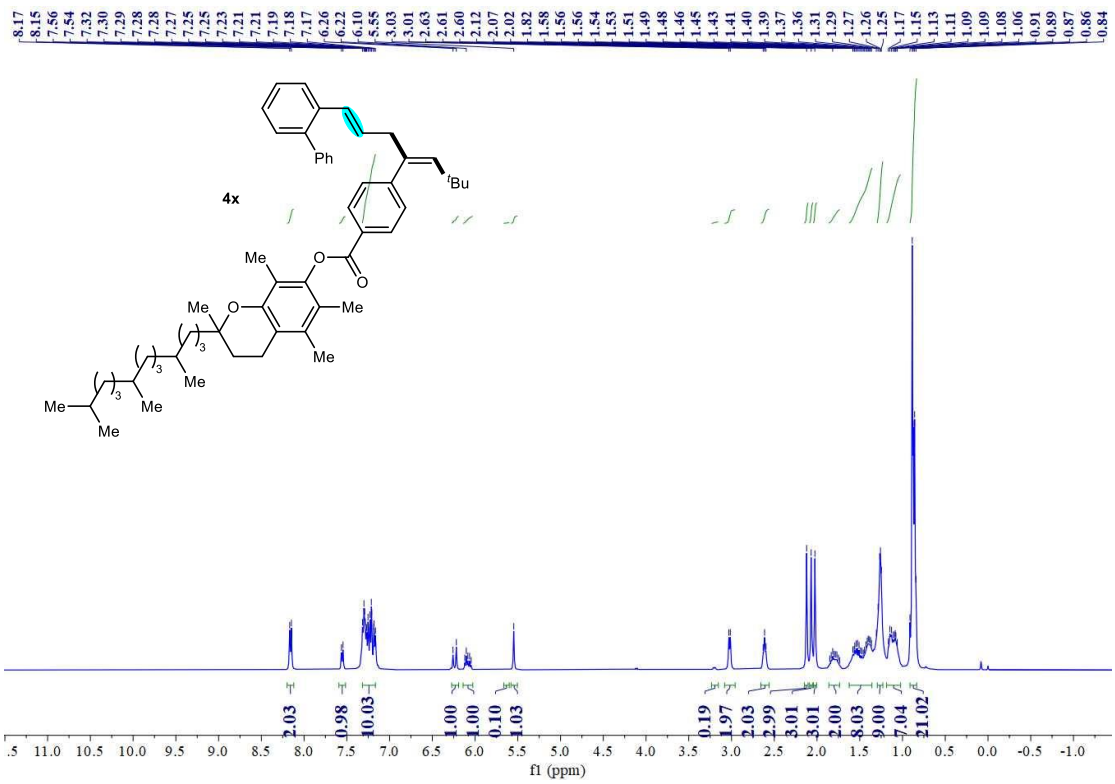


Figure S86. ^{1}H-NMR spectrum of **4x**

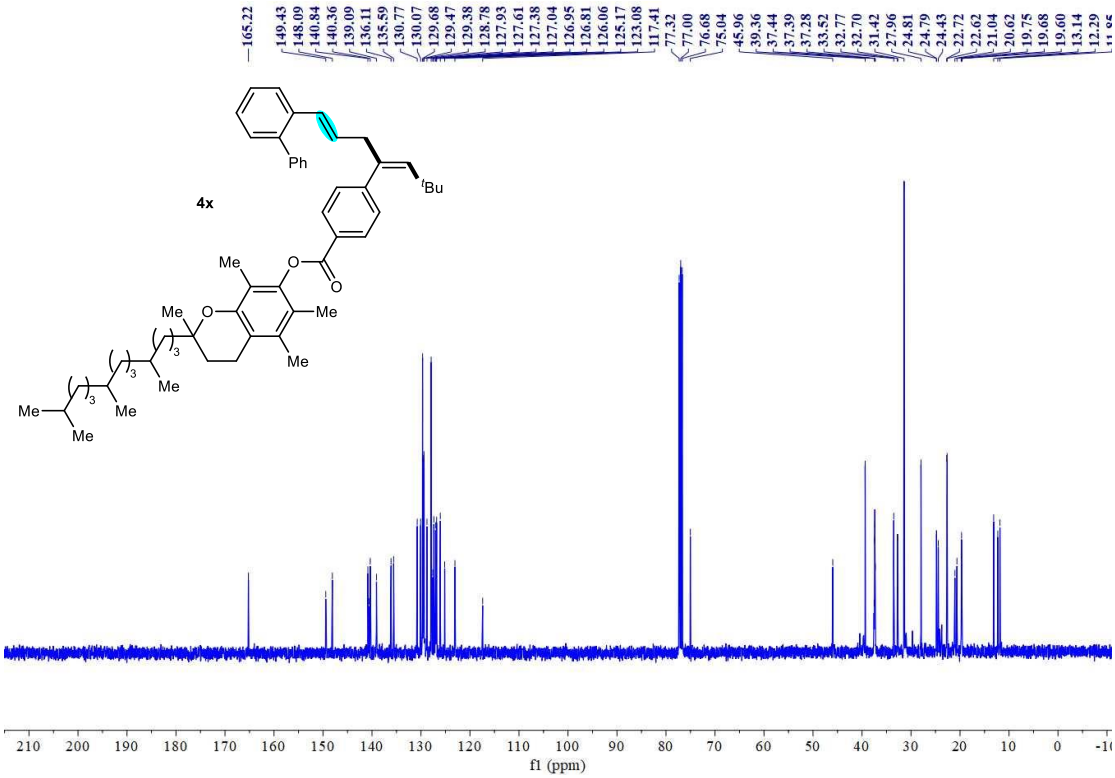


Figure S87. ^{13}C-NMR spectrum of **4x**

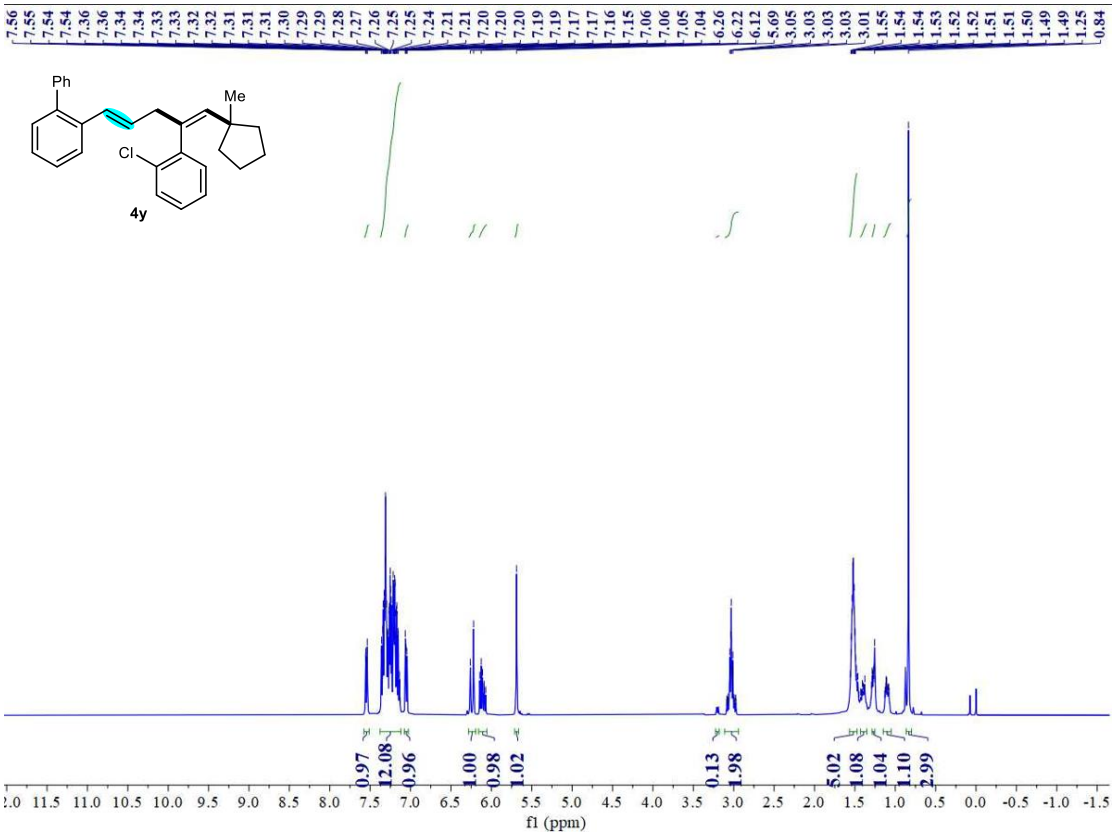


Figure S88. ^{1}H-NMR spectrum of **4y**

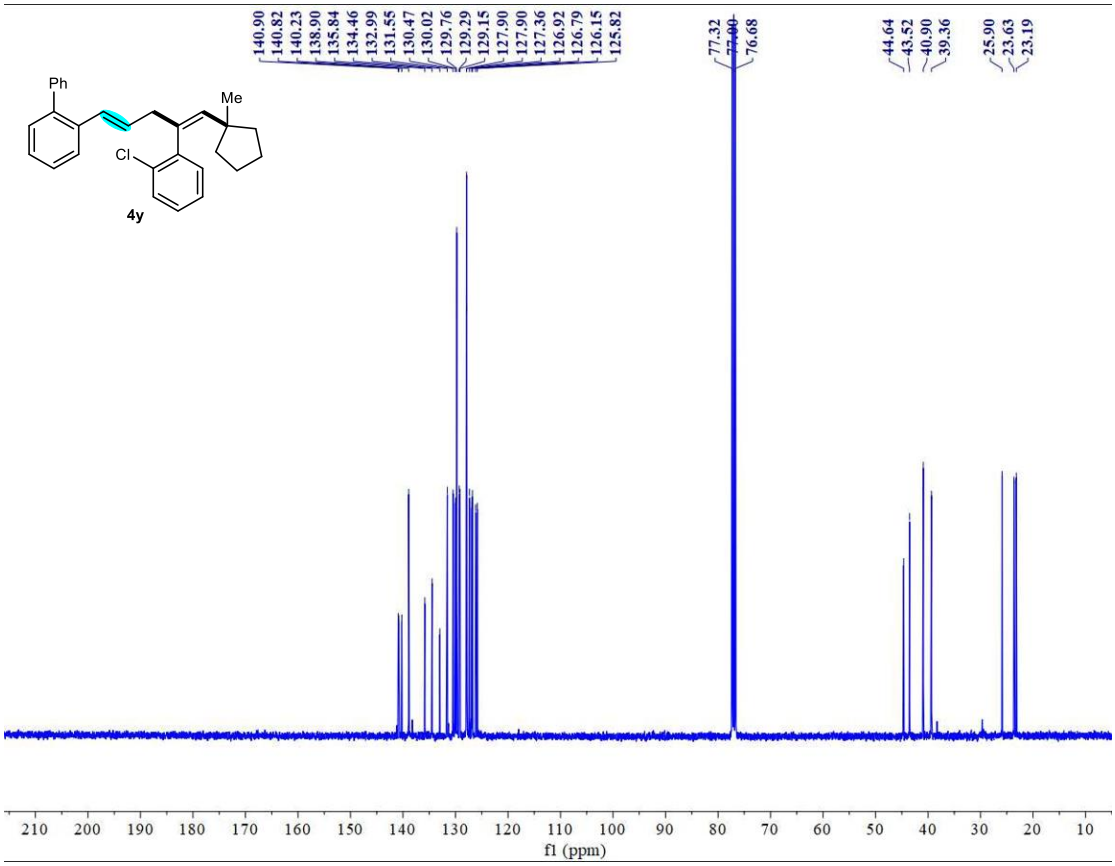


Figure S89. ^{13}C-NMR spectrum of **4y**

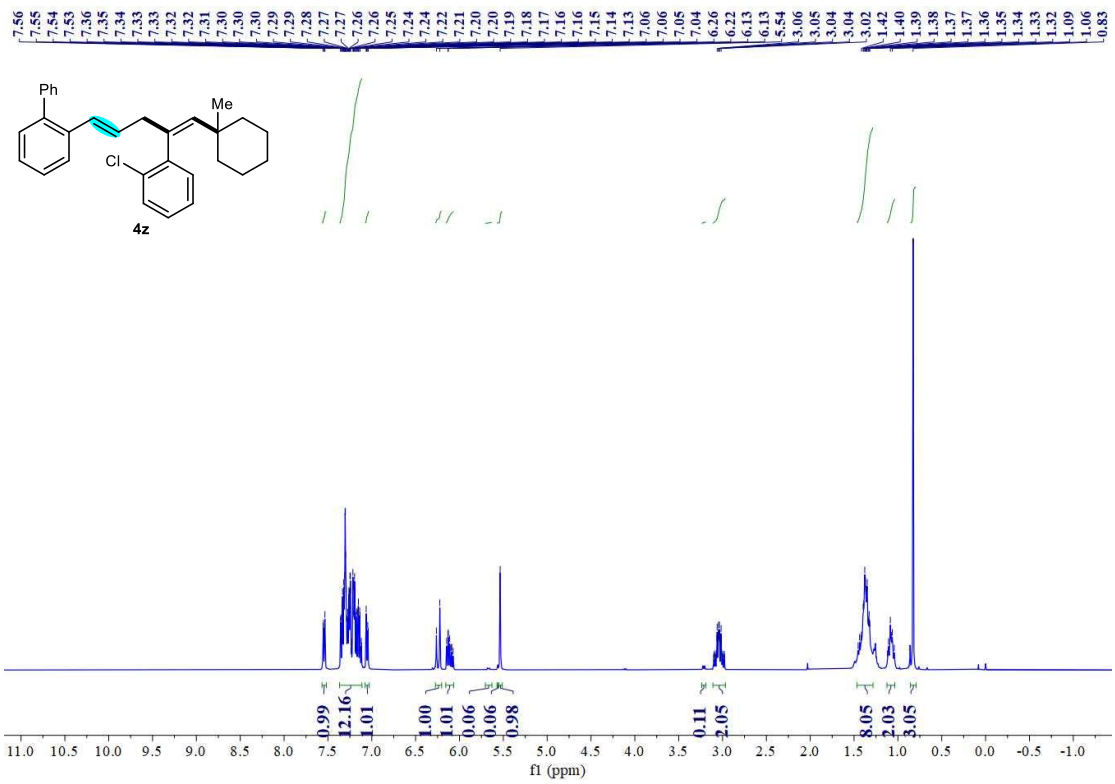


Figure S90. ^{1}H-NMR spectrum of **4z**

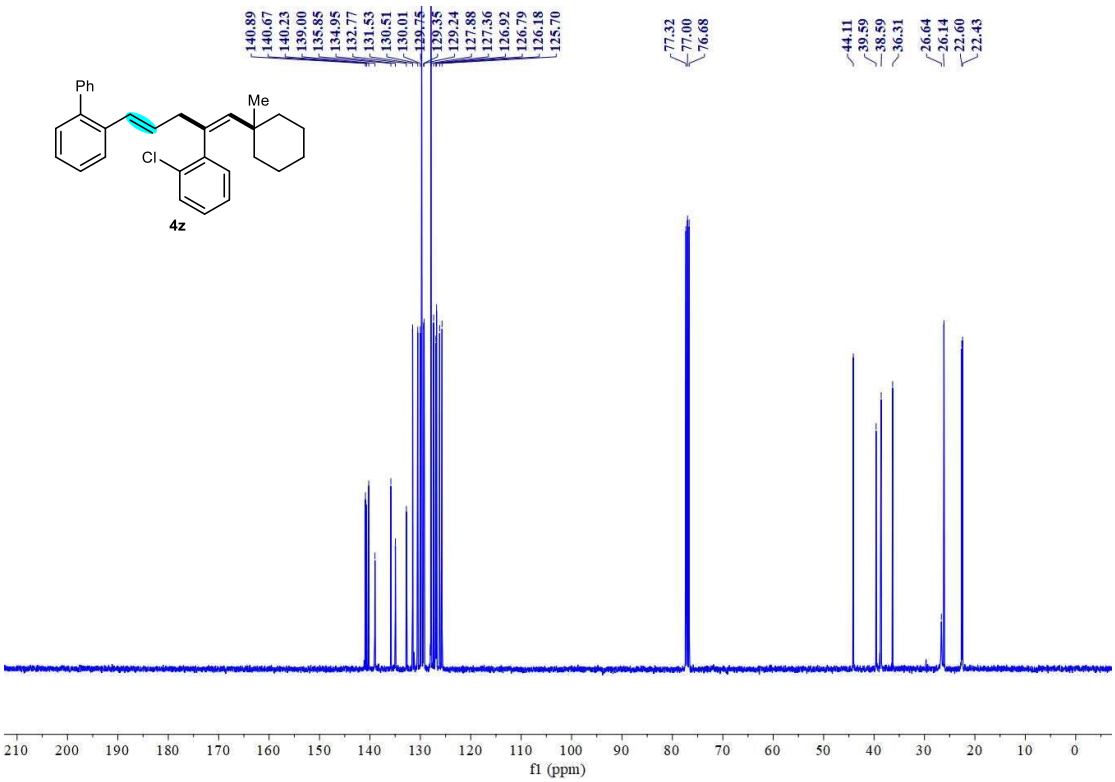


Figure S91. ^{13}C-NMR spectrum of **4z**

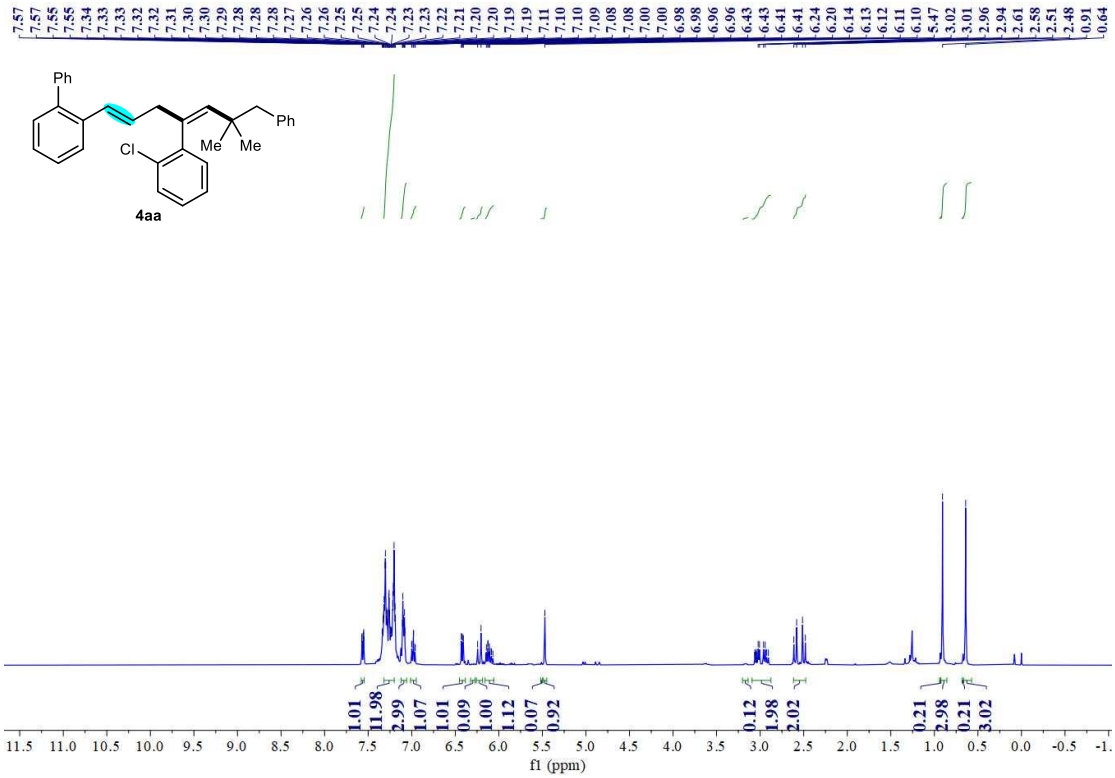


Figure S92. ^{1}H-NMR spectrum of **4aa**

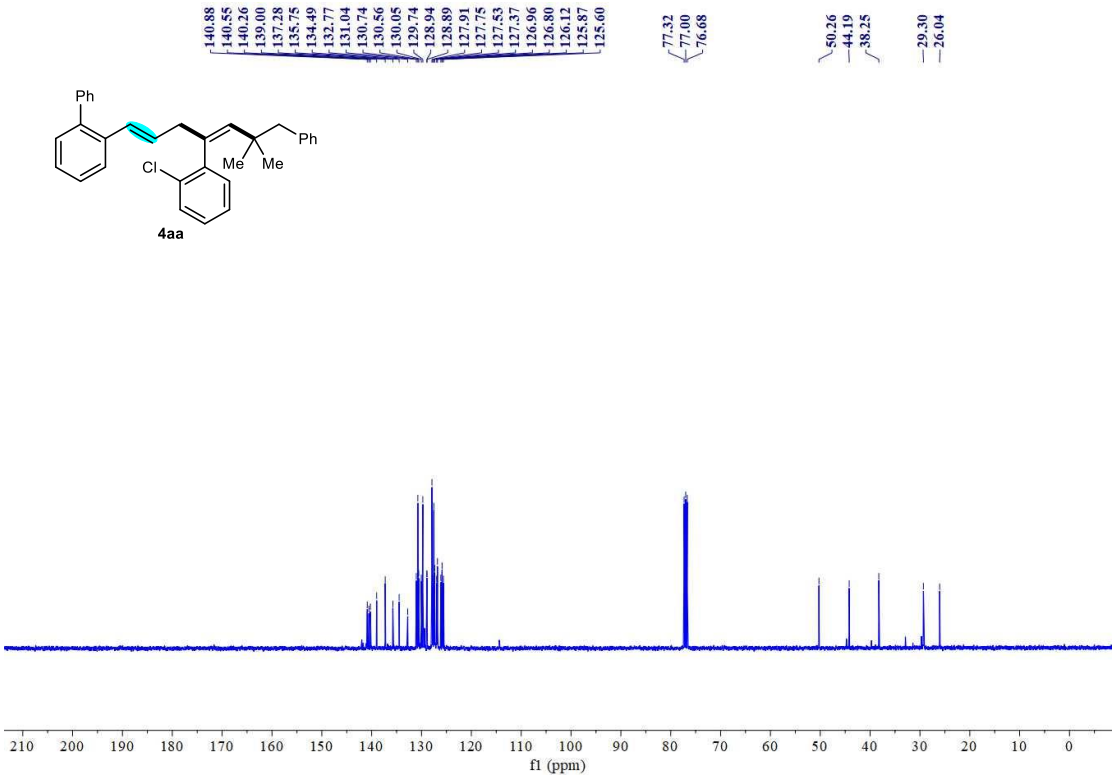


Figure S93. ^{13}C-NMR spectrum of **4aa**

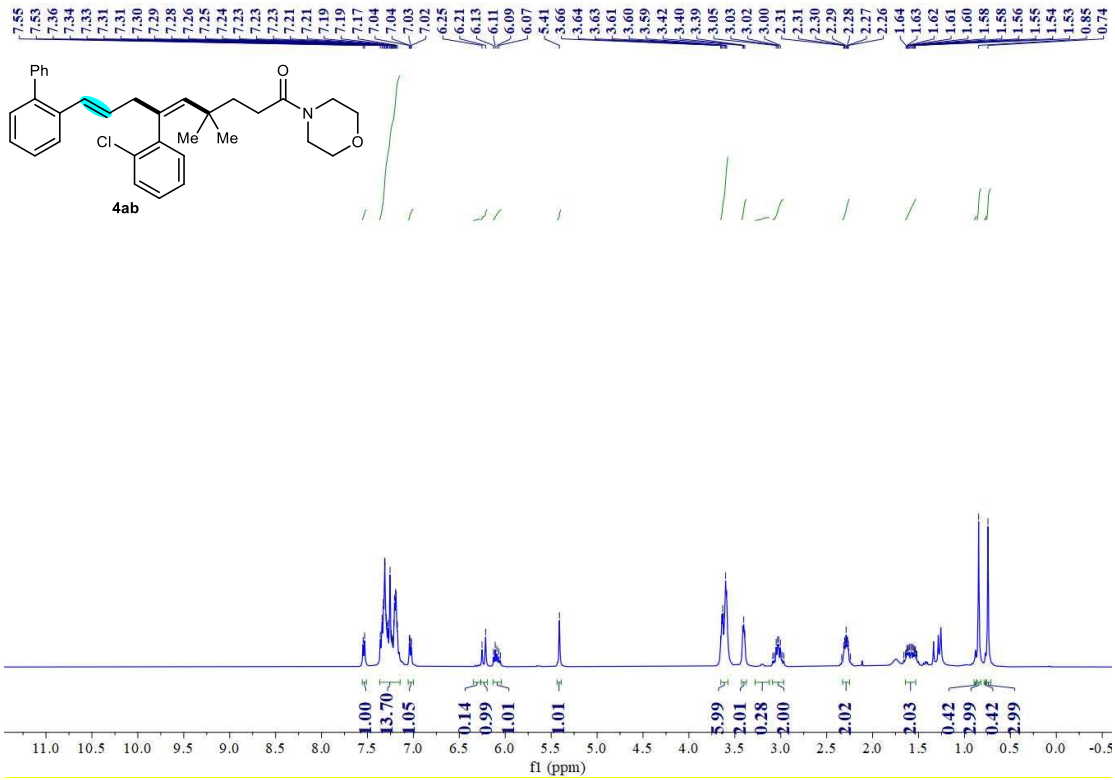


Figure S94. ^{1}H-NMR spectrum of **4ab**

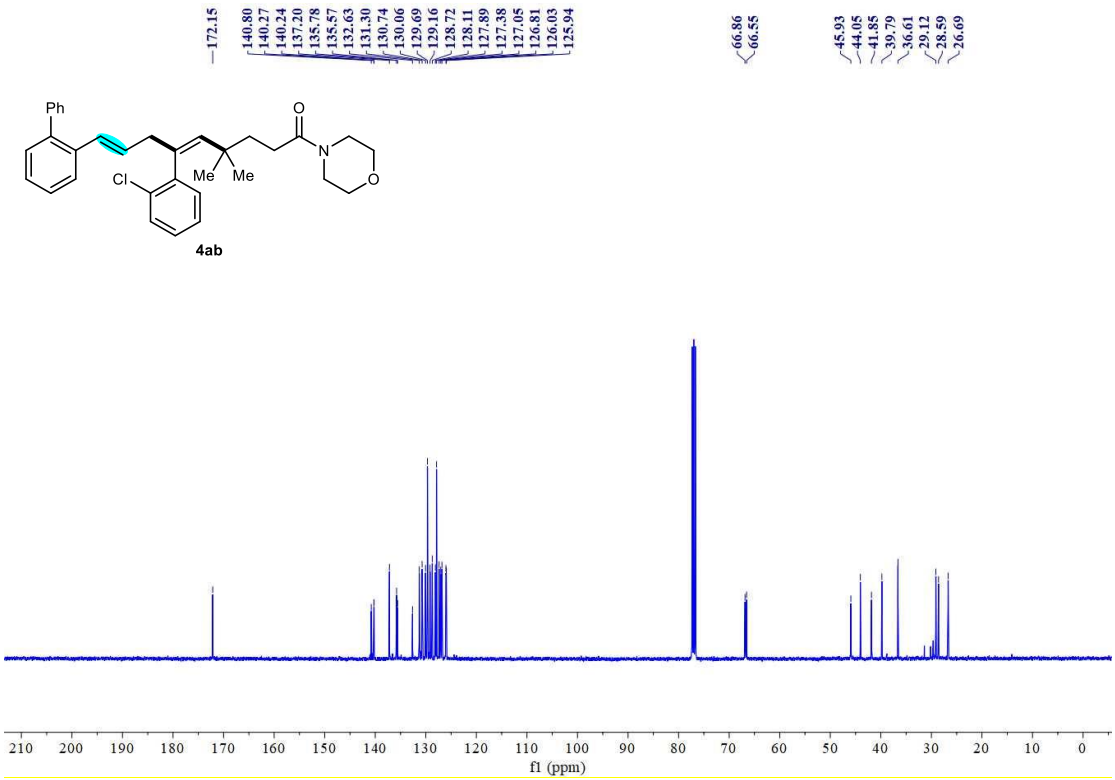


Figure S95. ^{13}C-NMR spectrum of **4ab**

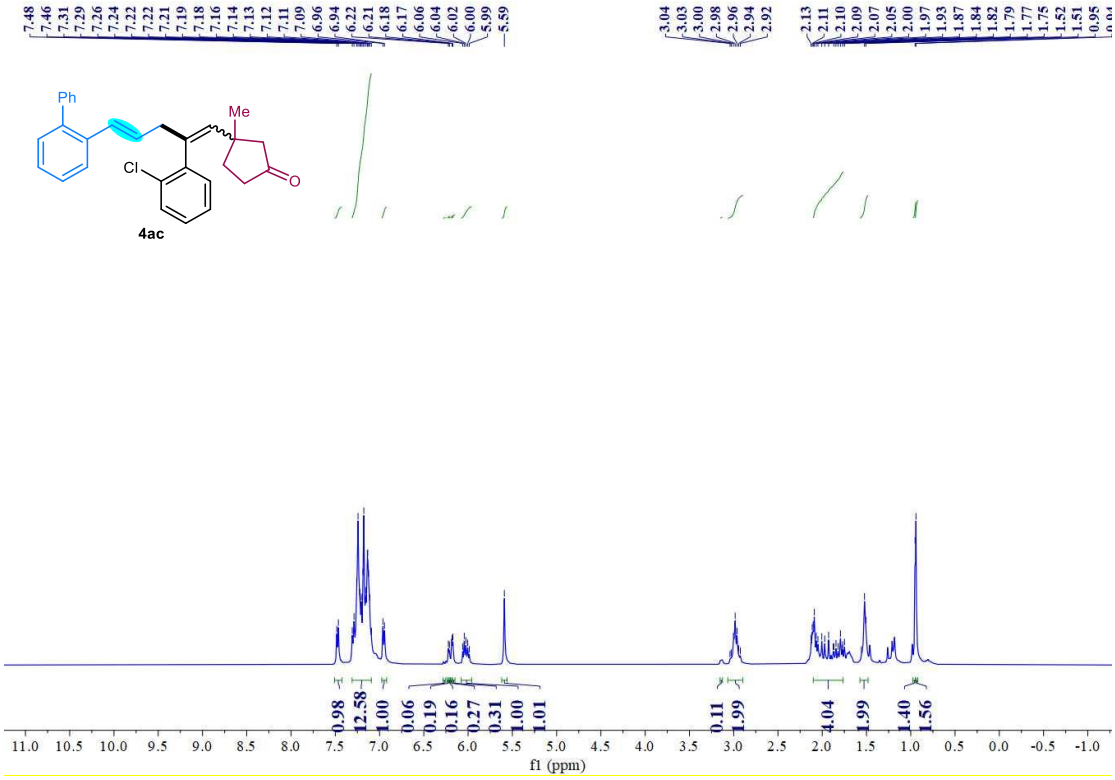


Figure S96. ^{1}H-NMR spectrum of **4ac**

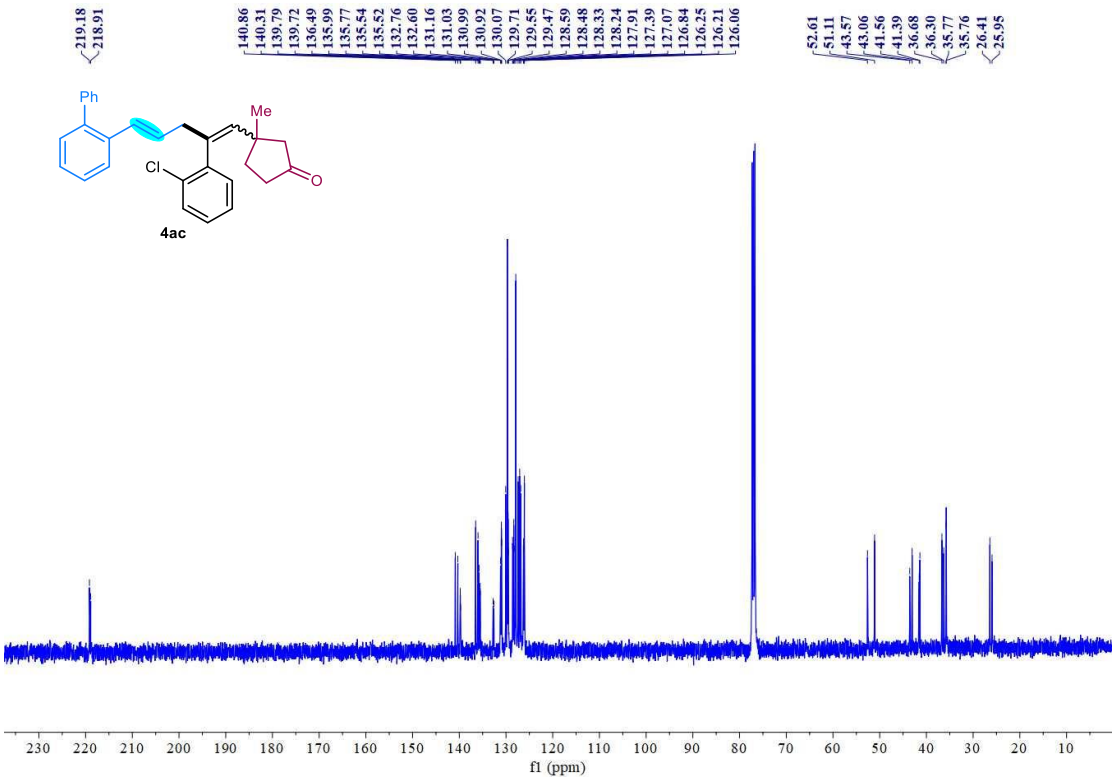


Figure S97. ^{13}C-NMR spectrum of **4ac**

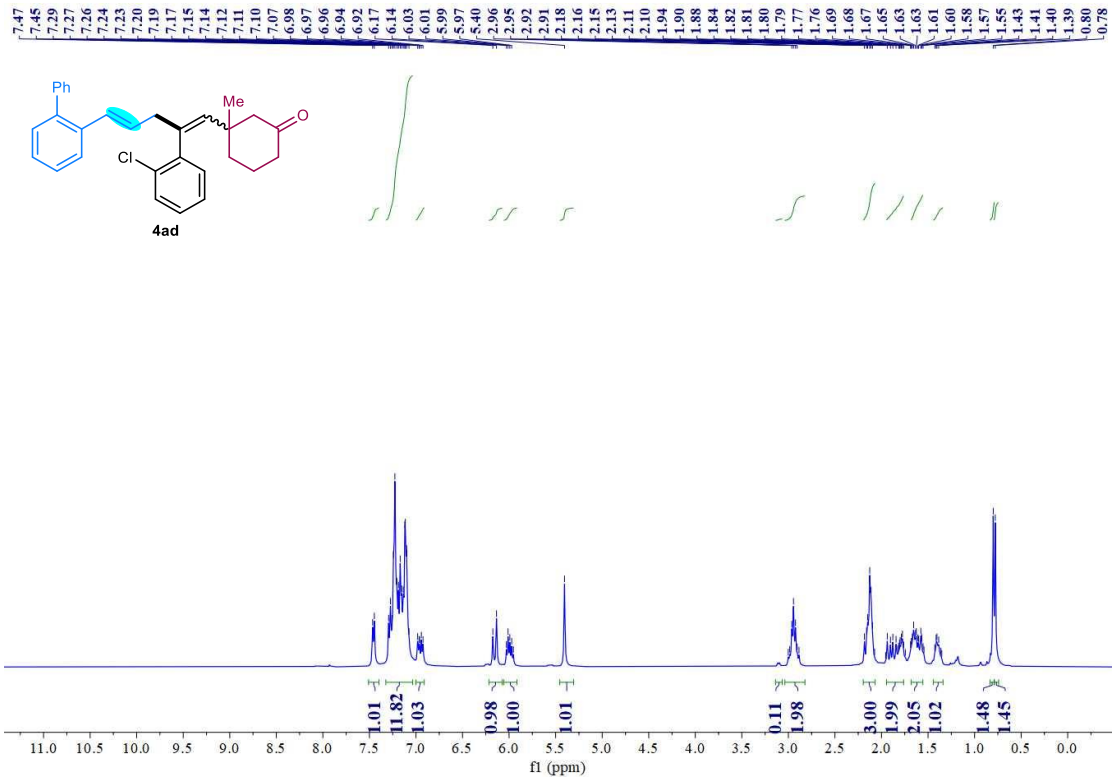


Figure S98. ^{1}H-NMR spectrum of **4ad**

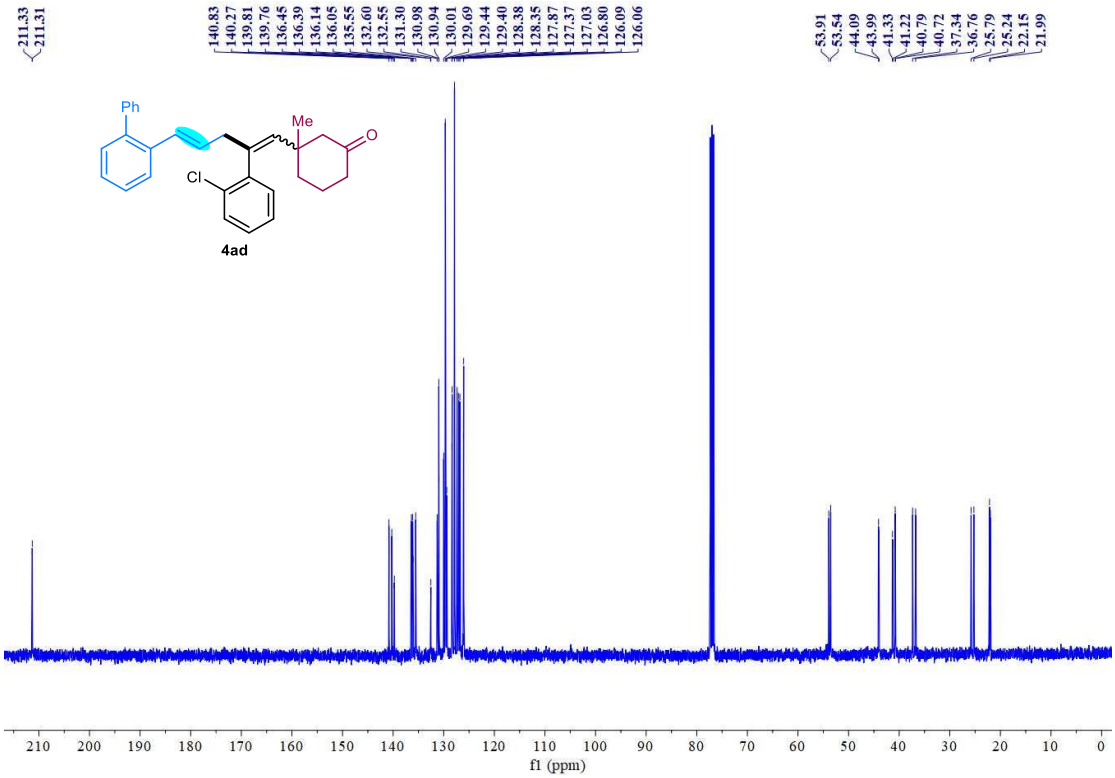


Figure S99. ^{13}C-NMR spectrum of **4ad**

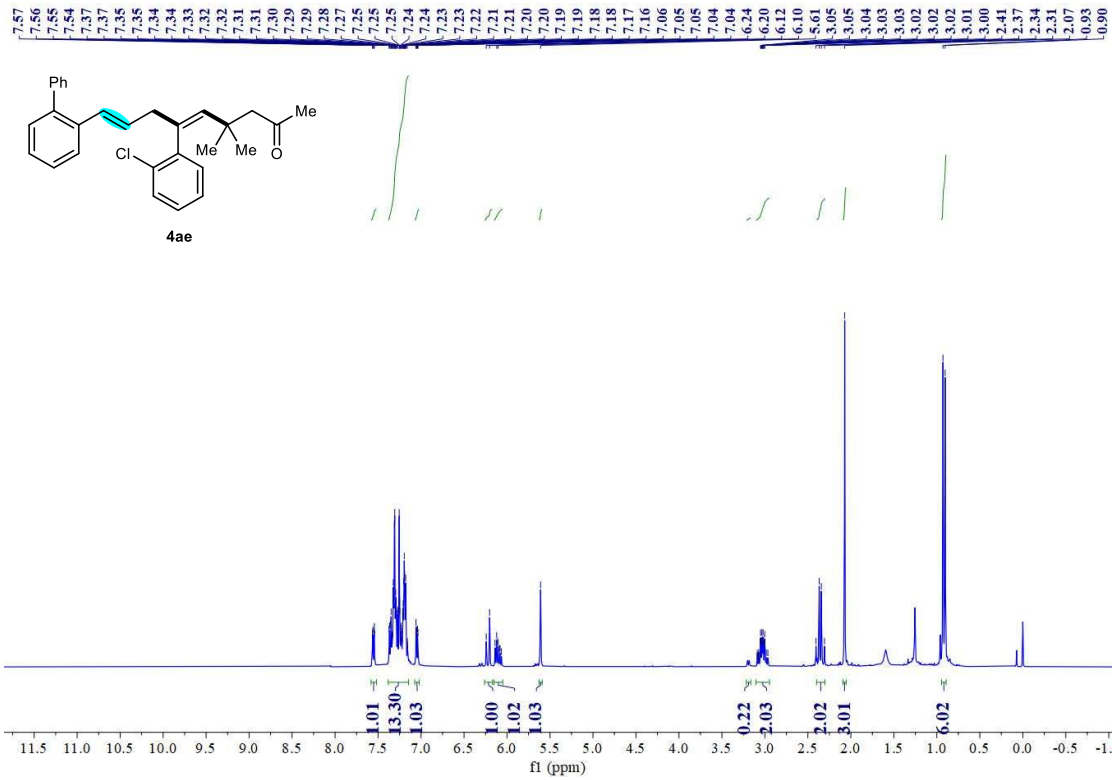


Figure S100. ^{1}H-NMR spectrum of **4ae**

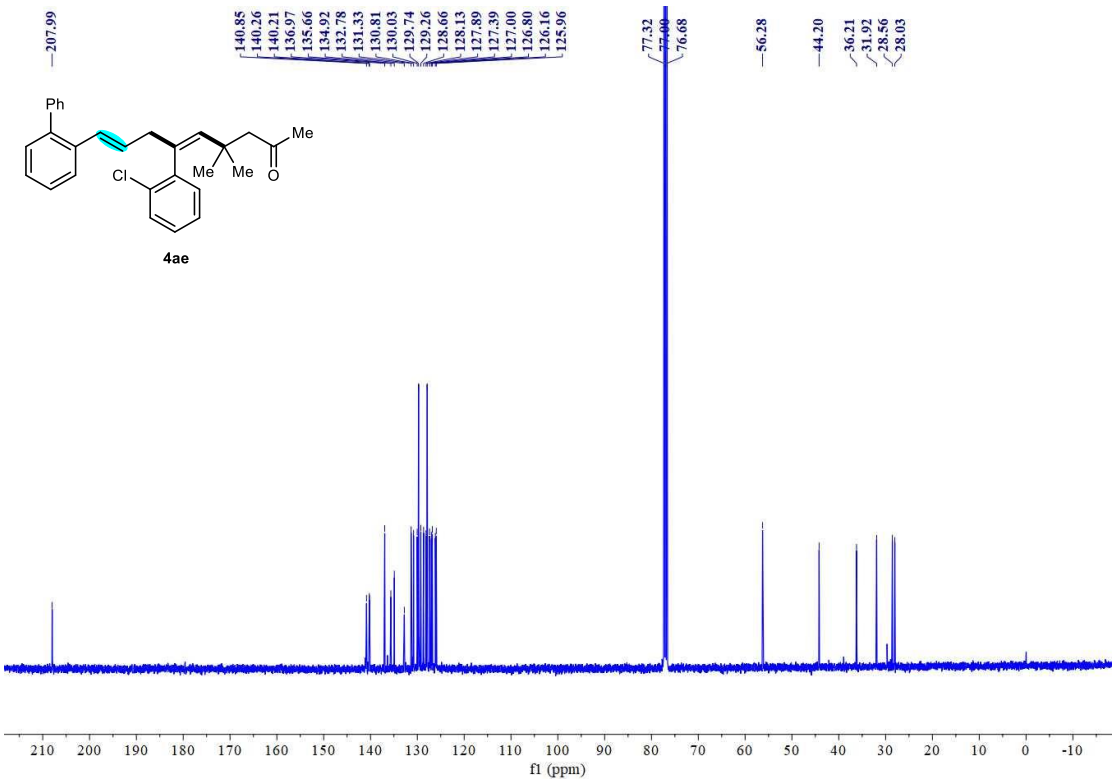


Figure S101. ^{13}C-NMR spectrum of **4ae**

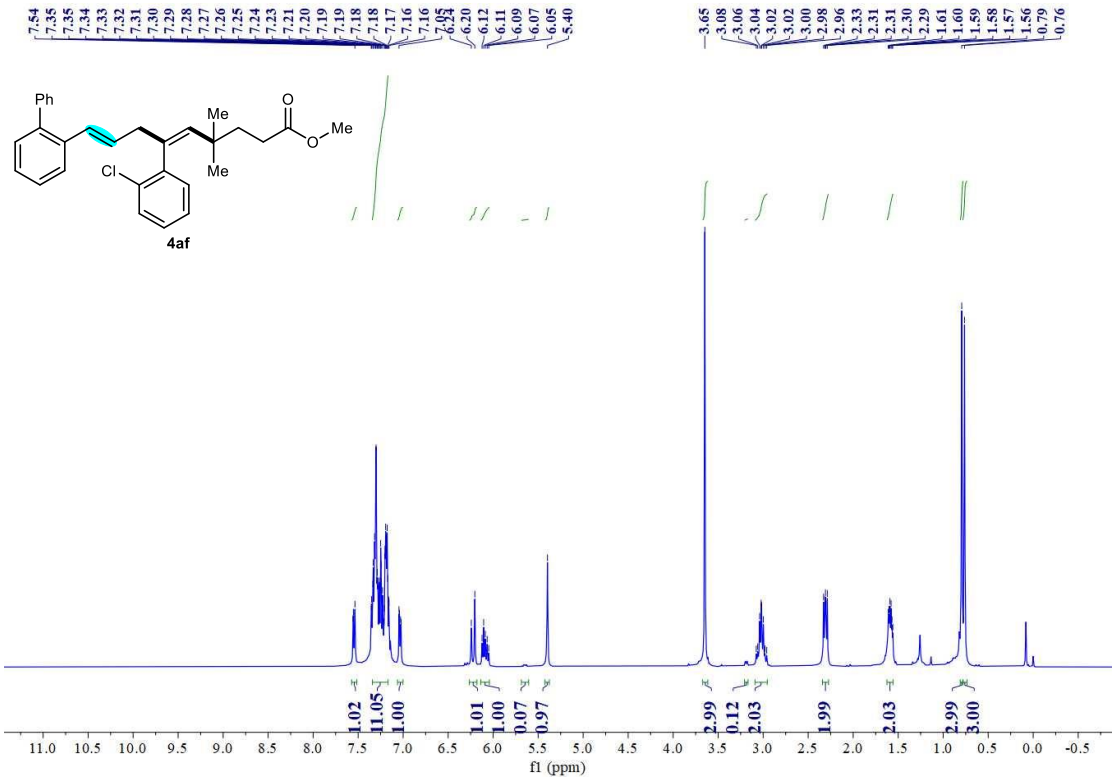


Figure S102. ^{1}H-NMR spectrum of **4af**

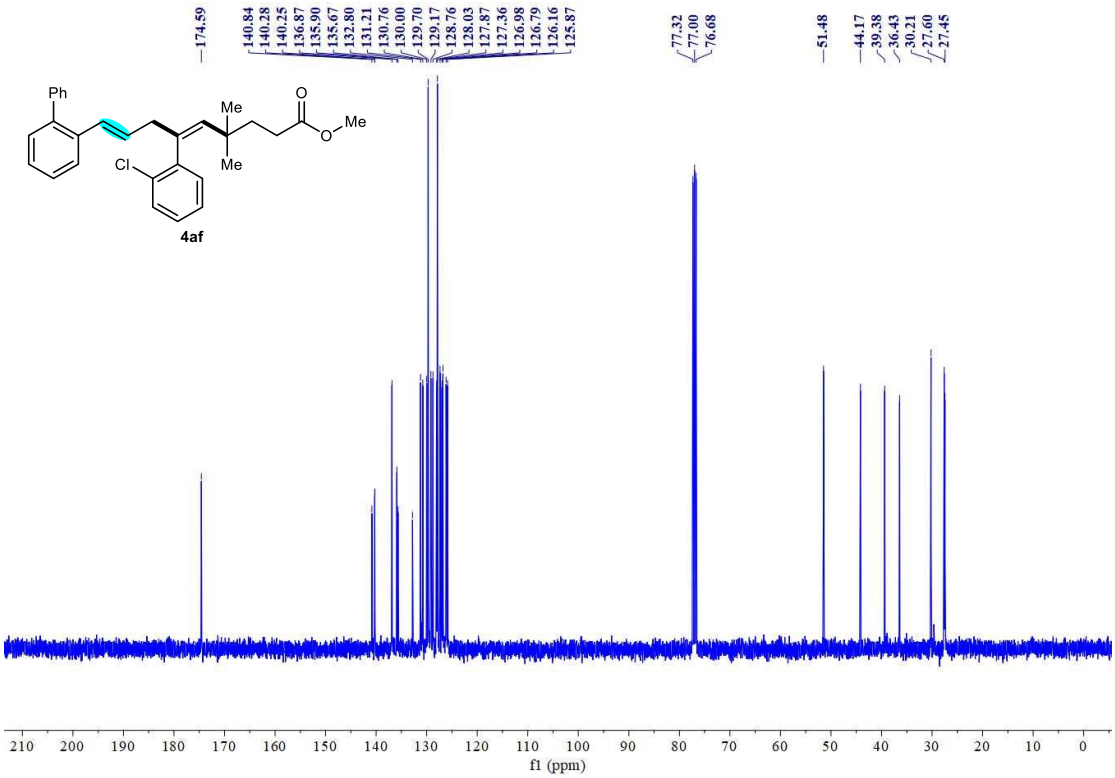


Figure S103. ^{13}C-NMR spectrum of **4af**

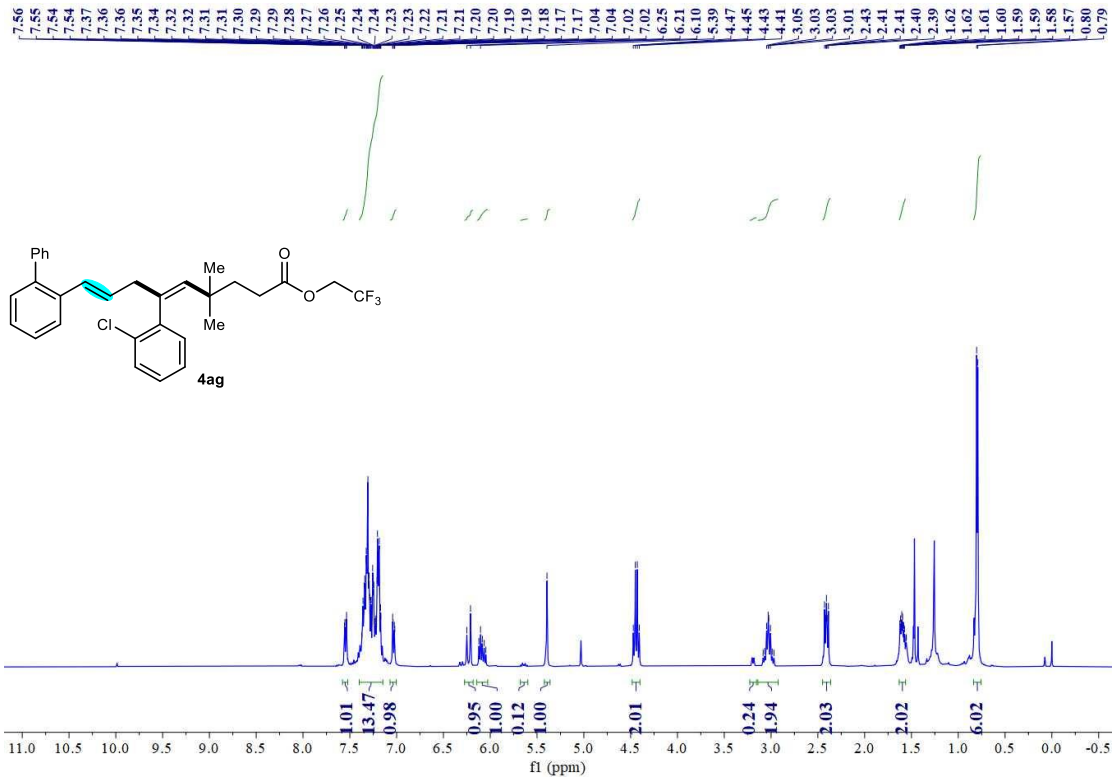


Figure S104. ^{1}H-NMR spectrum of **4ag**

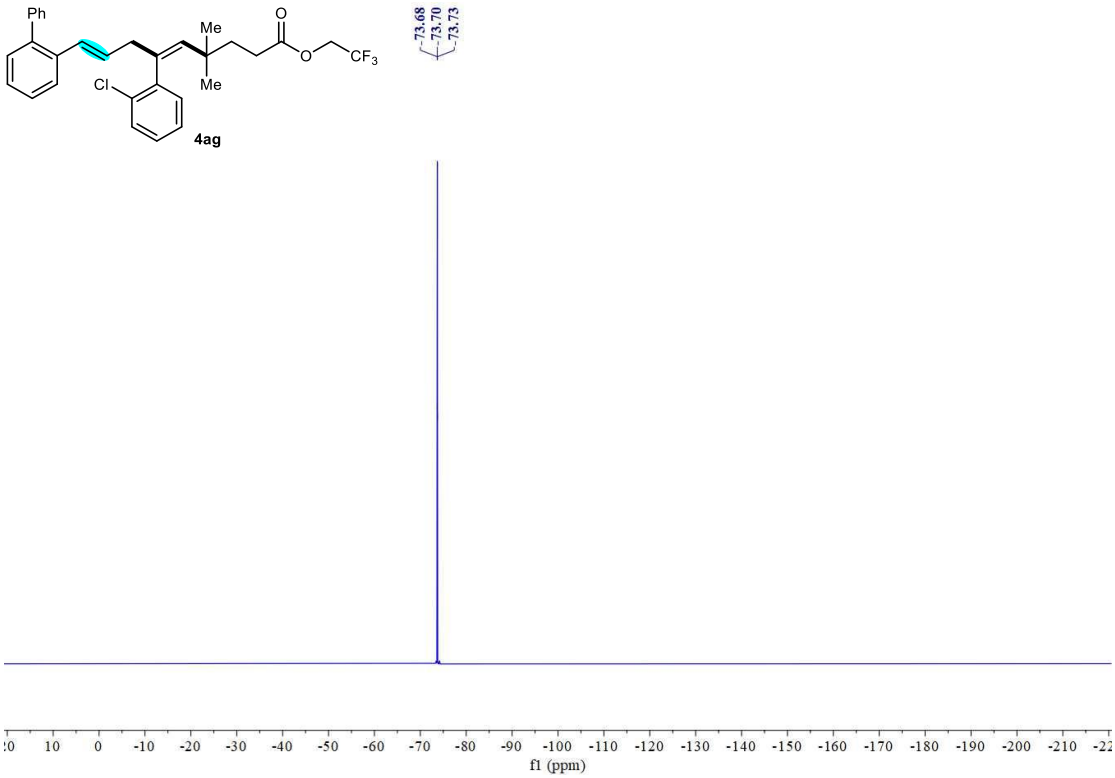


Figure S105. ^{19}F-NMR spectrum of **4ag**

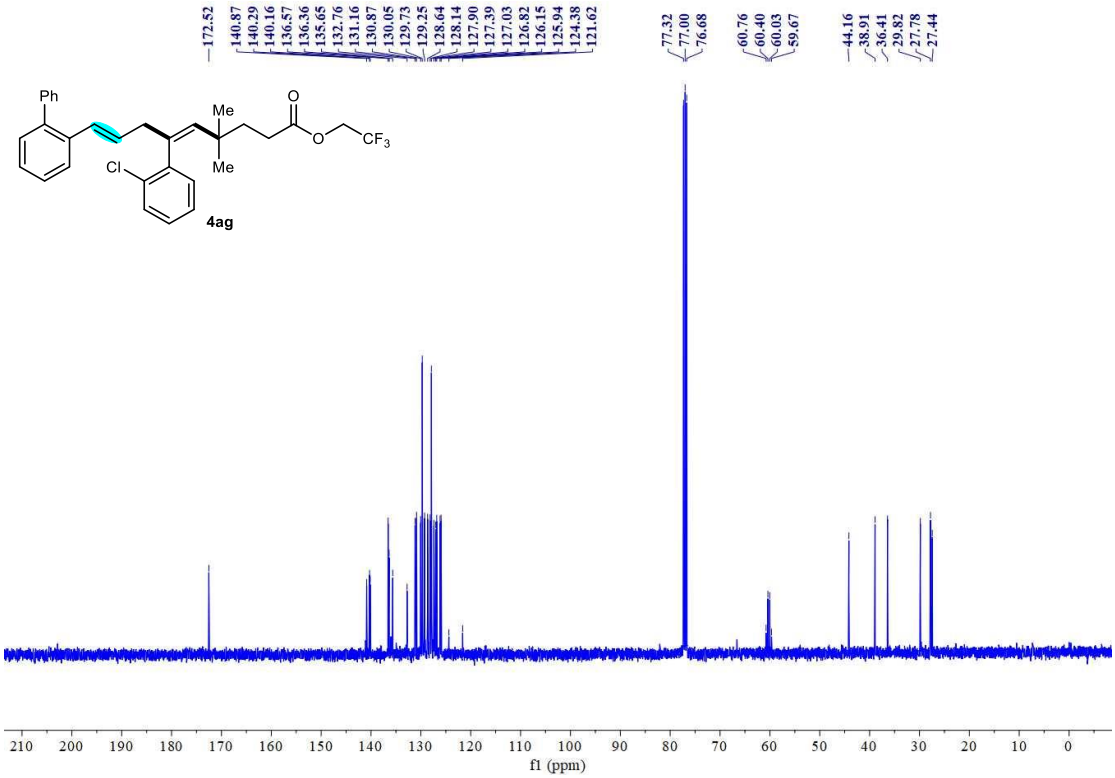


Figure S106. ^{13}C-NMR spectrum of **4ag**

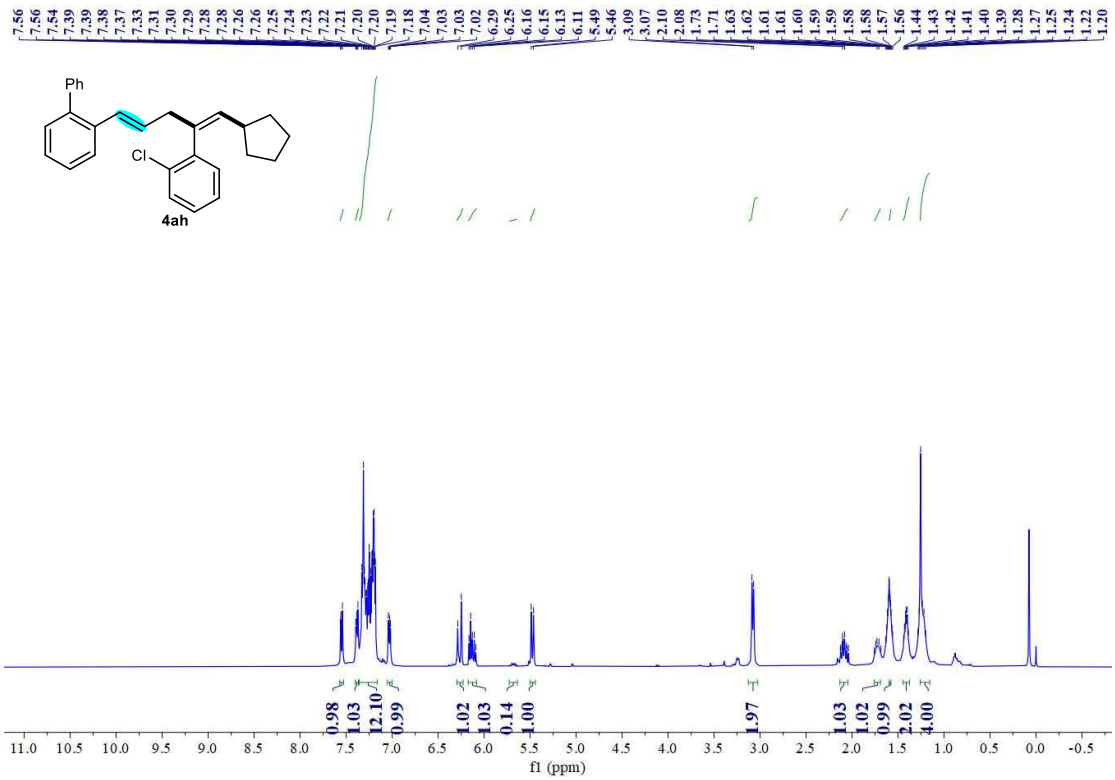


Figure S107. ^{1}H-NMR spectrum of **4ah**

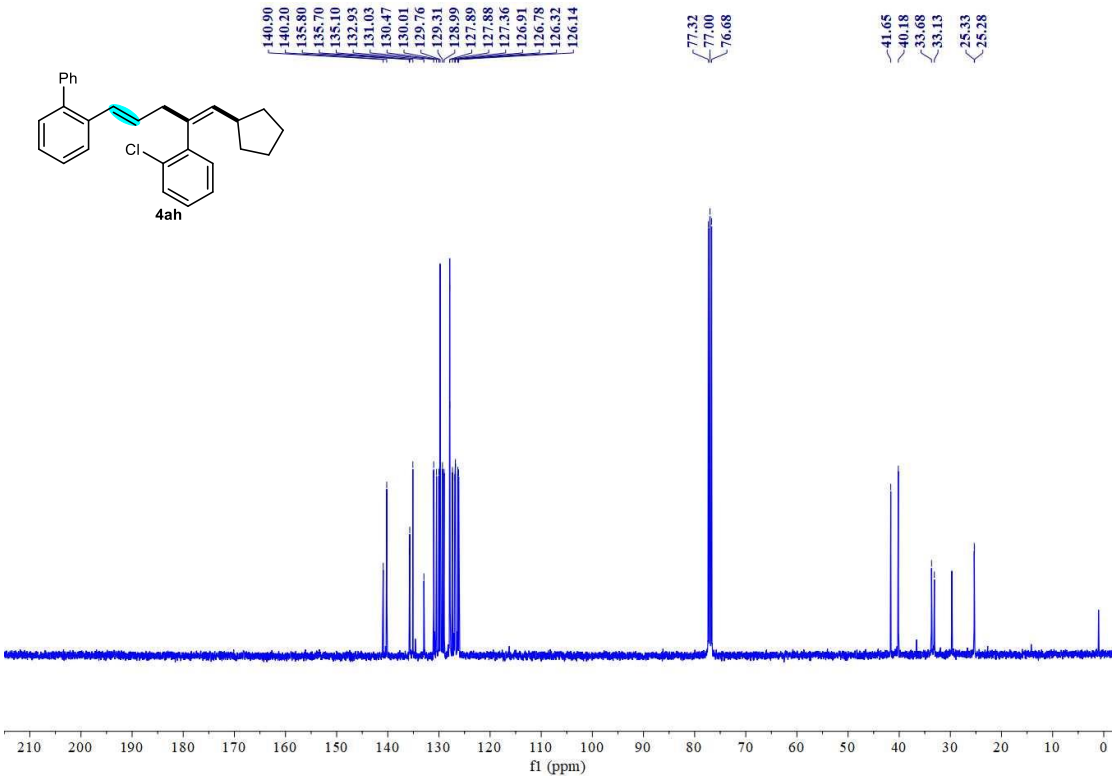


Figure S108. ^{13}C-NMR spectrum of **4ah**

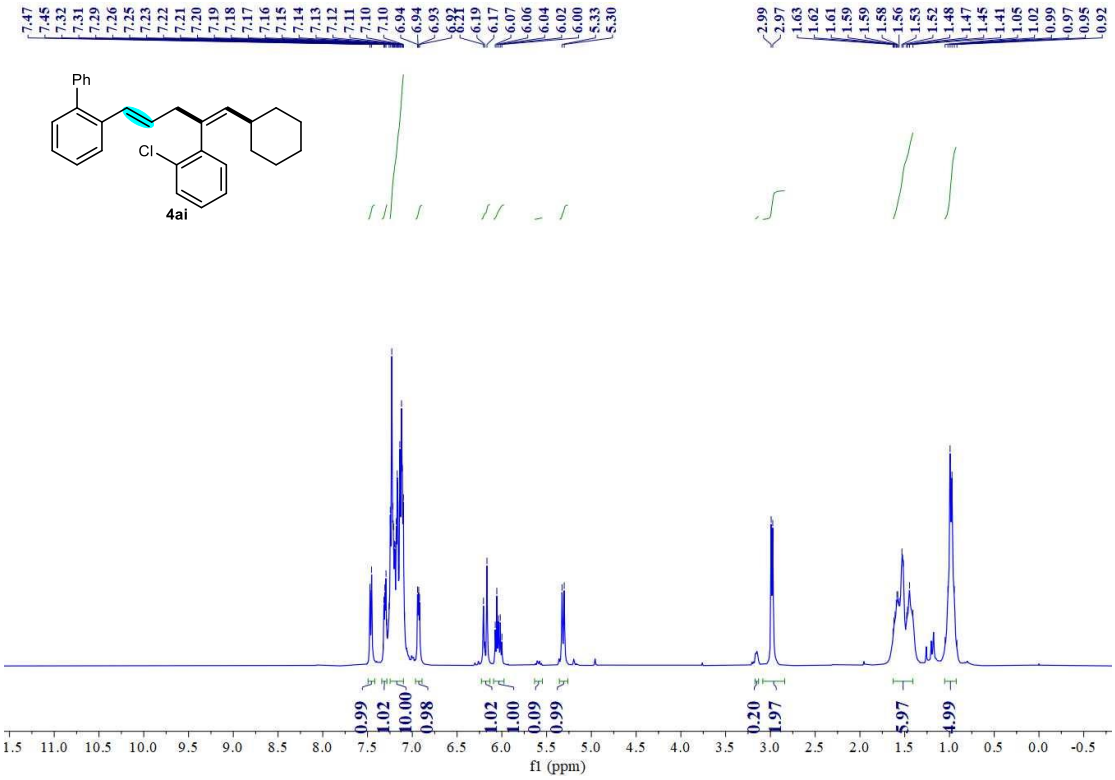


Figure S109. ^{1}H-NMR spectrum of **4ai**

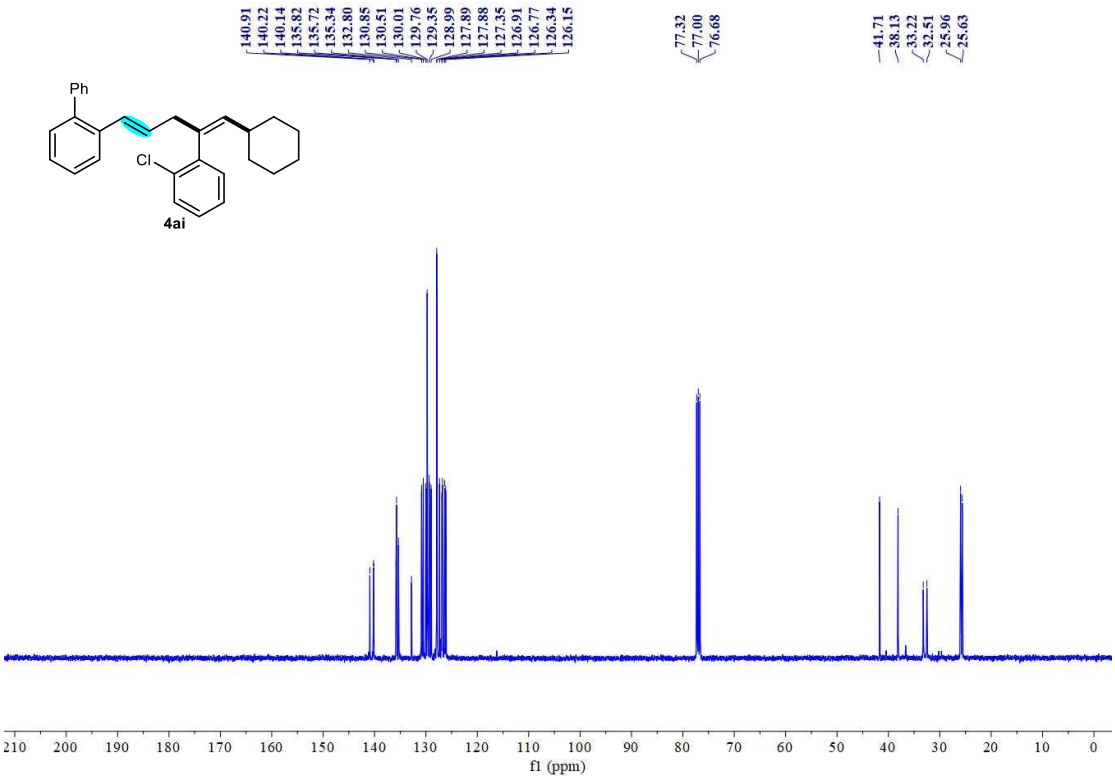


Figure S110. ^{13}C-NMR spectrum of **4ai**

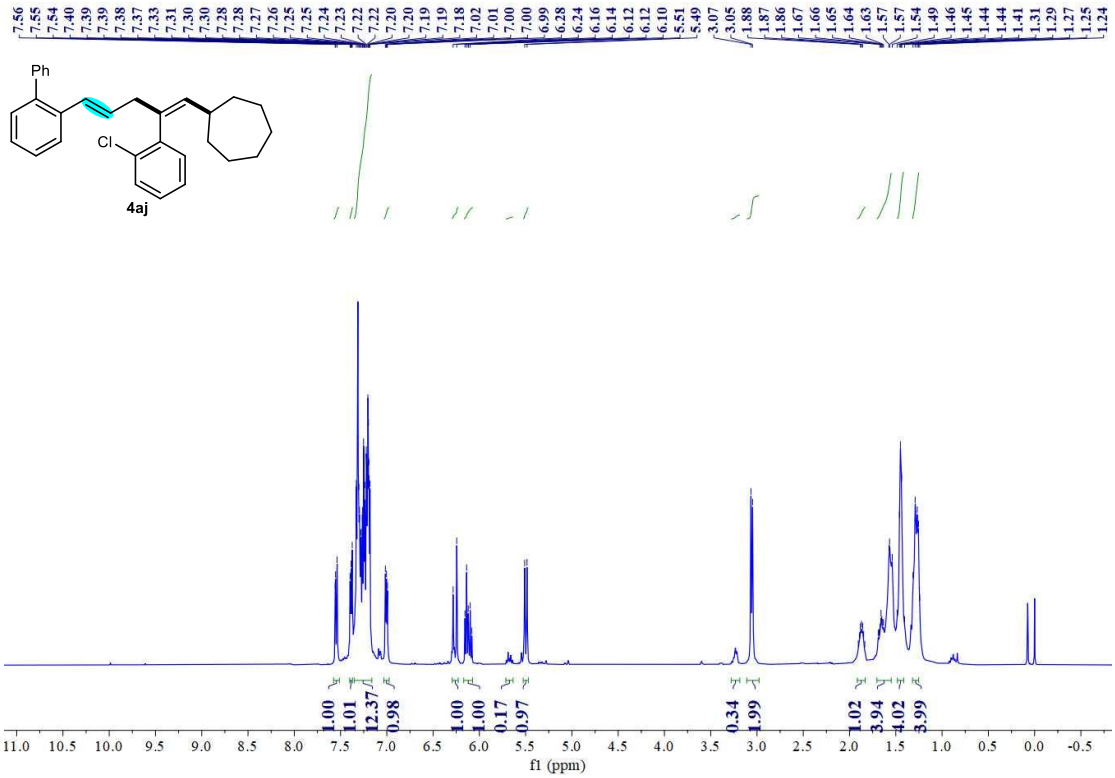


Figure S111. ^{1}H-NMR spectrum of **4aj**

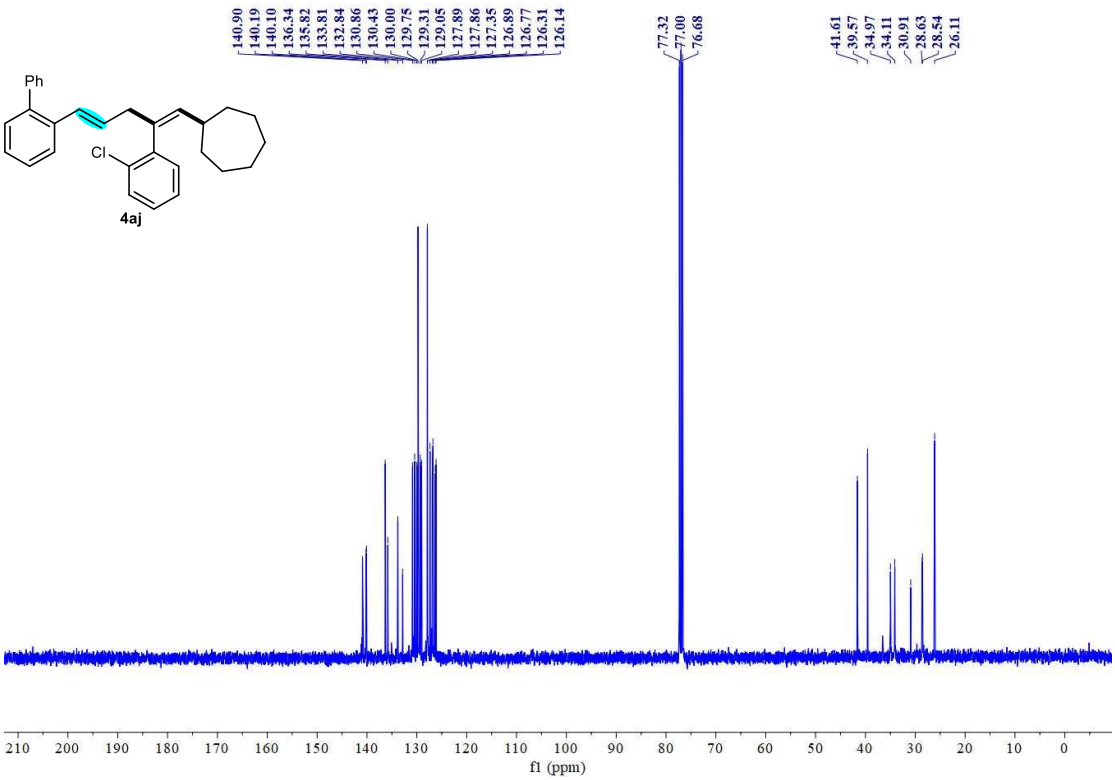


Figure S112. ^{13}C-NMR spectrum of **4aj**

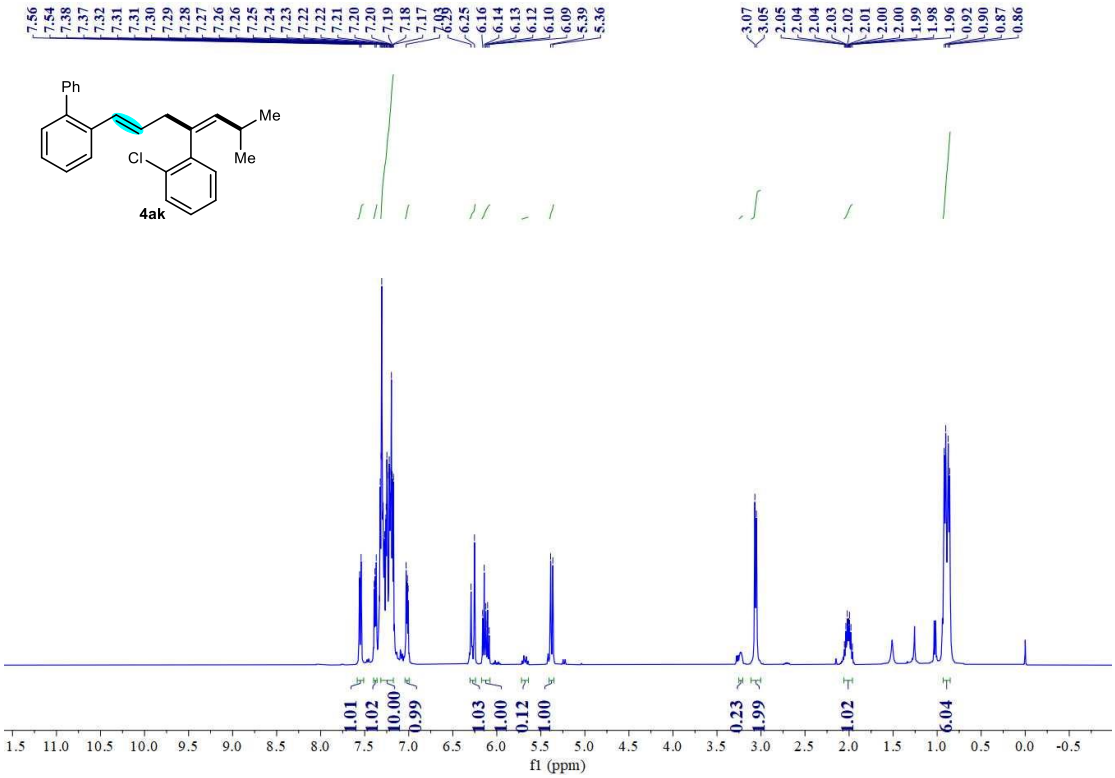


Figure S113. ^{1}H-NMR spectrum of **4ak**

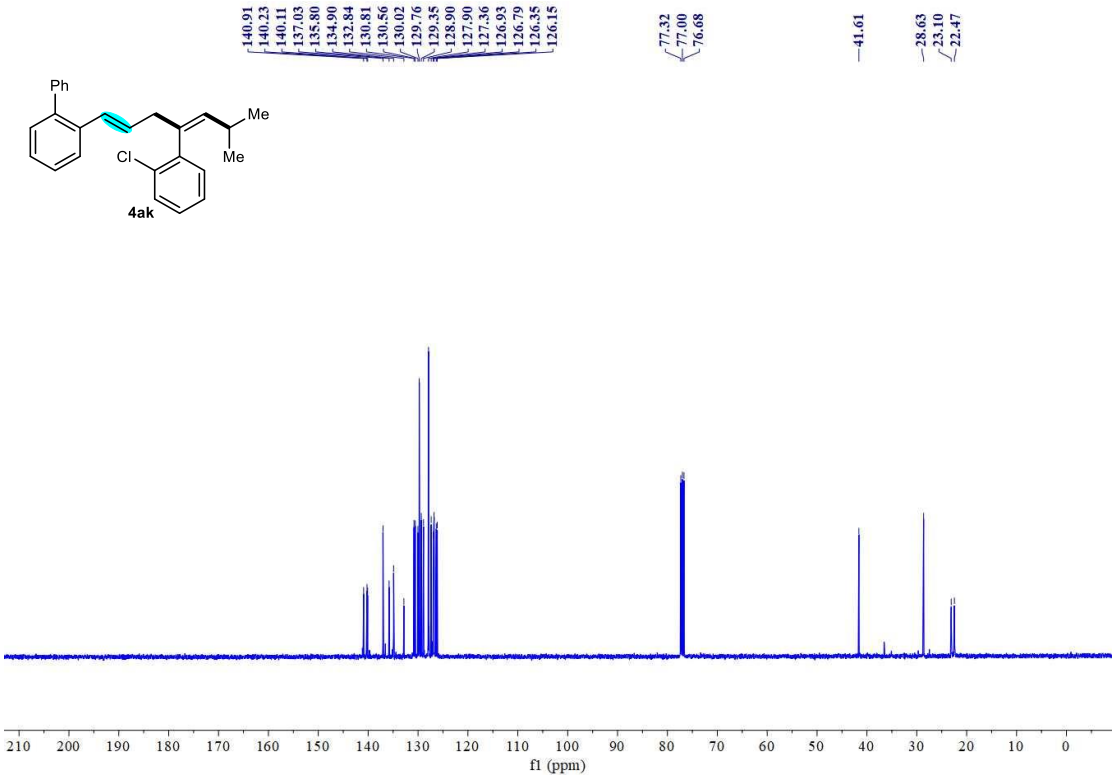


Figure S114. ^{13}C-NMR spectrum of **4ak**

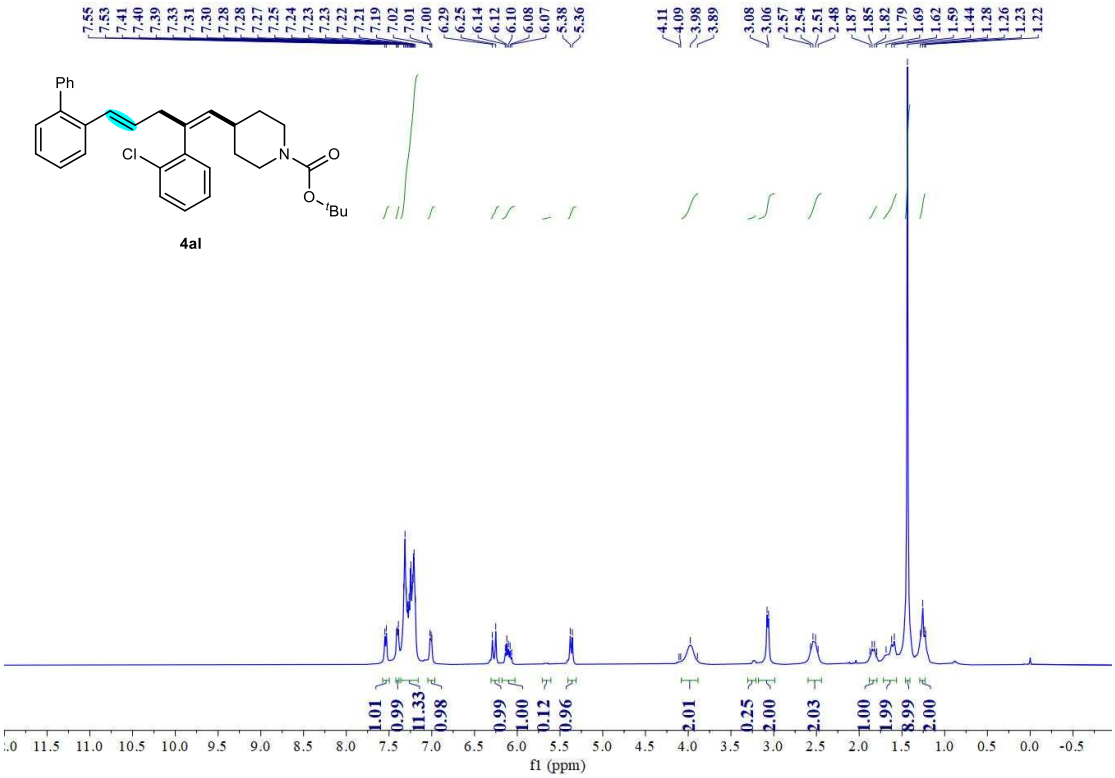


Figure S115. ^{1}H-NMR spectrum of **4al**

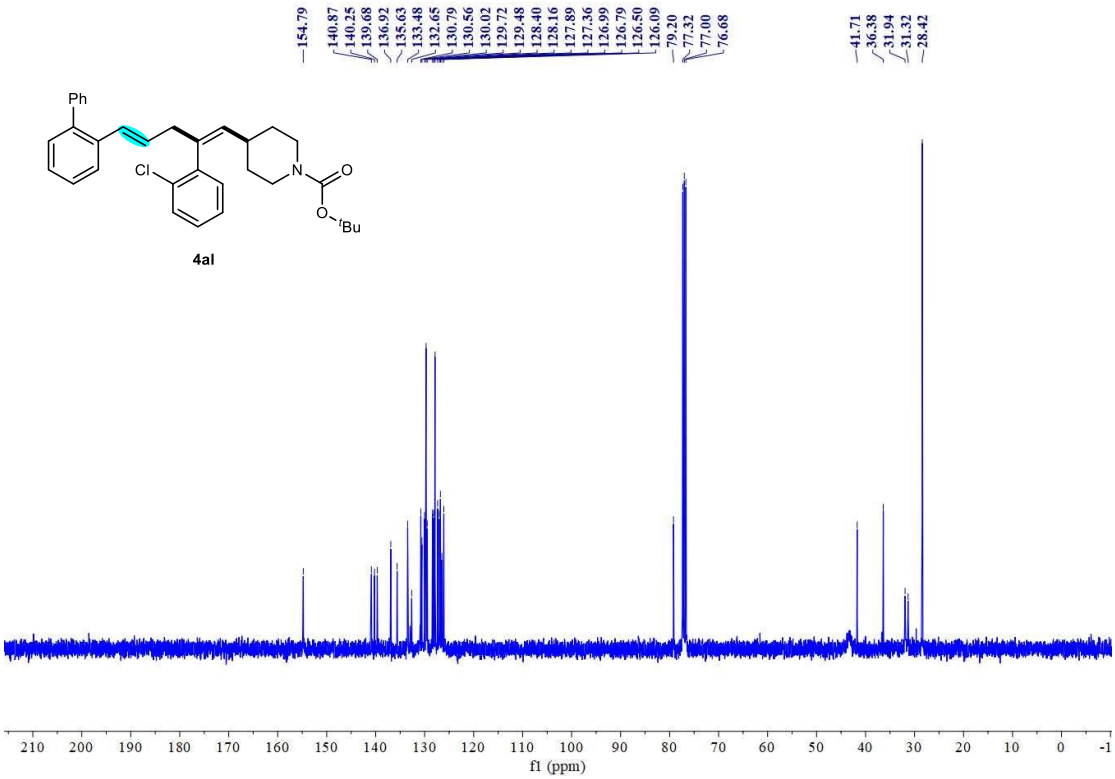


Figure S116. ^{13}C-NMR spectrum of **4al**

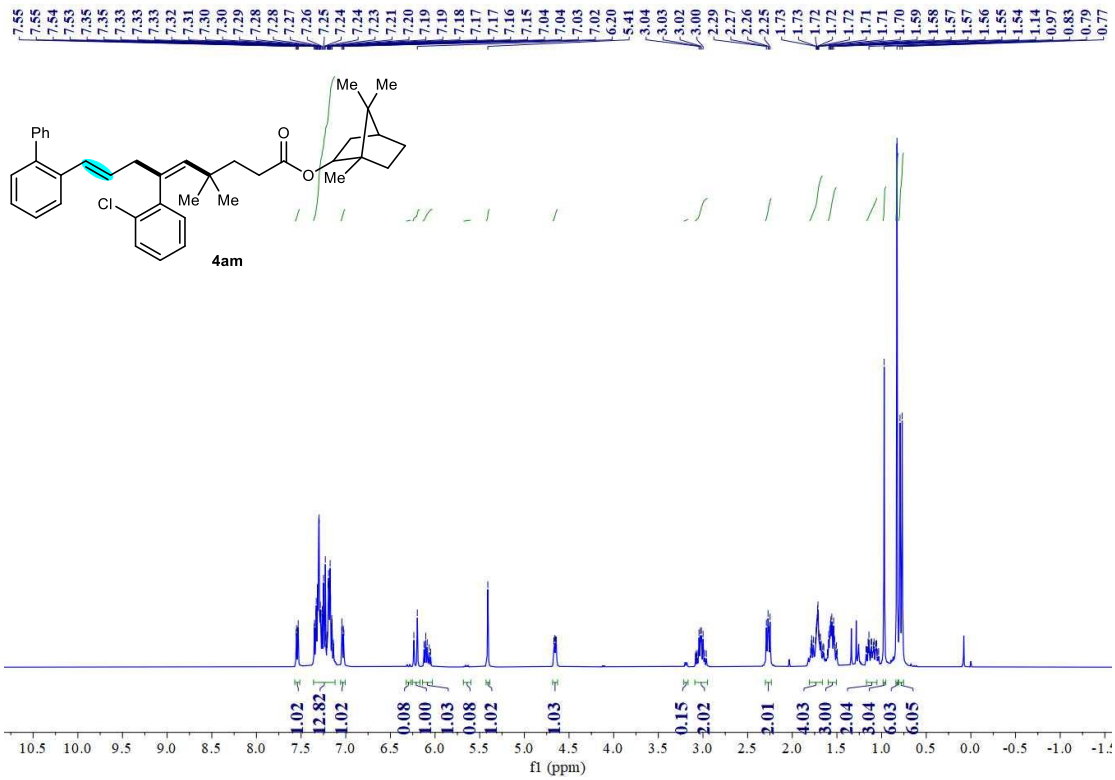


Figure S117. ^{1}H-NMR spectrum of **4am**

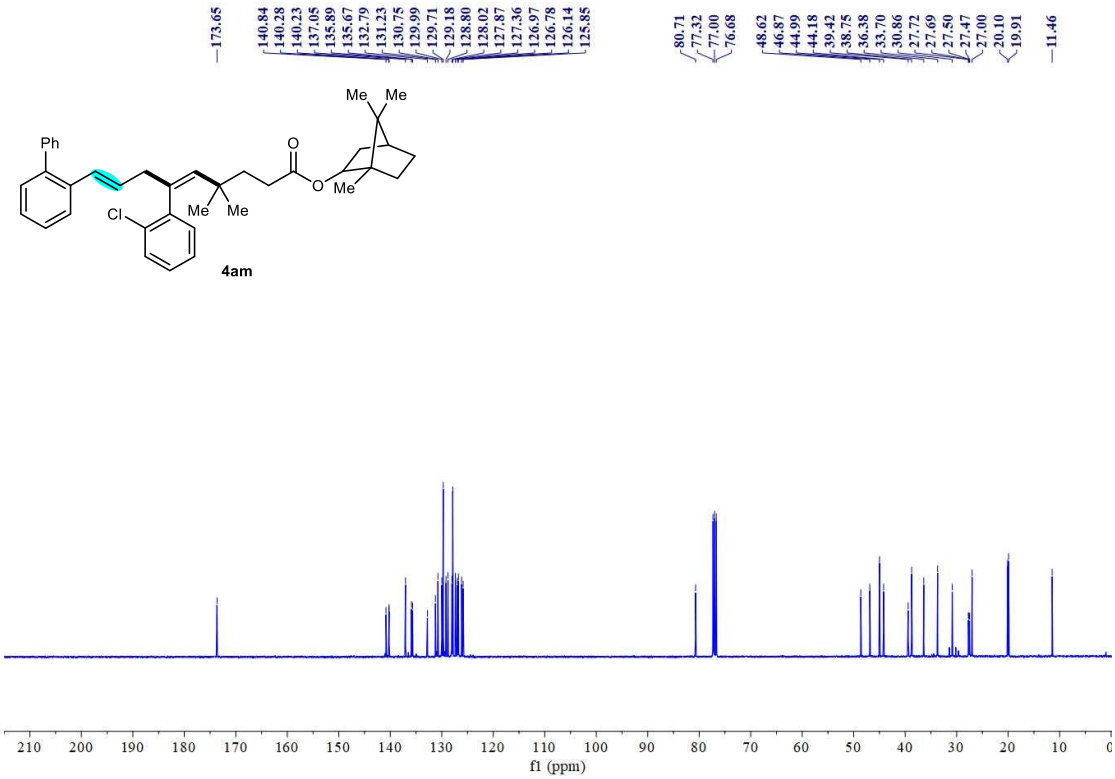


Figure S118. ^{13}C-NMR spectrum of **4am**

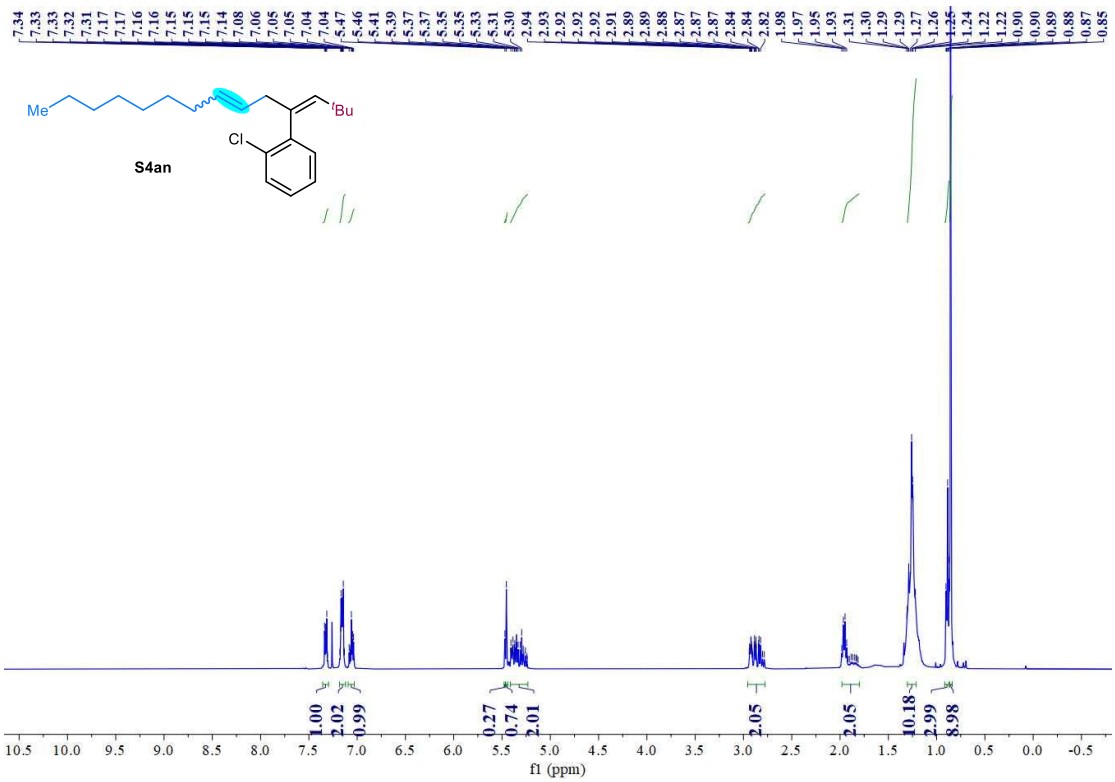


Figure S119. ^{11}H-NMR spectrum of **S4an**

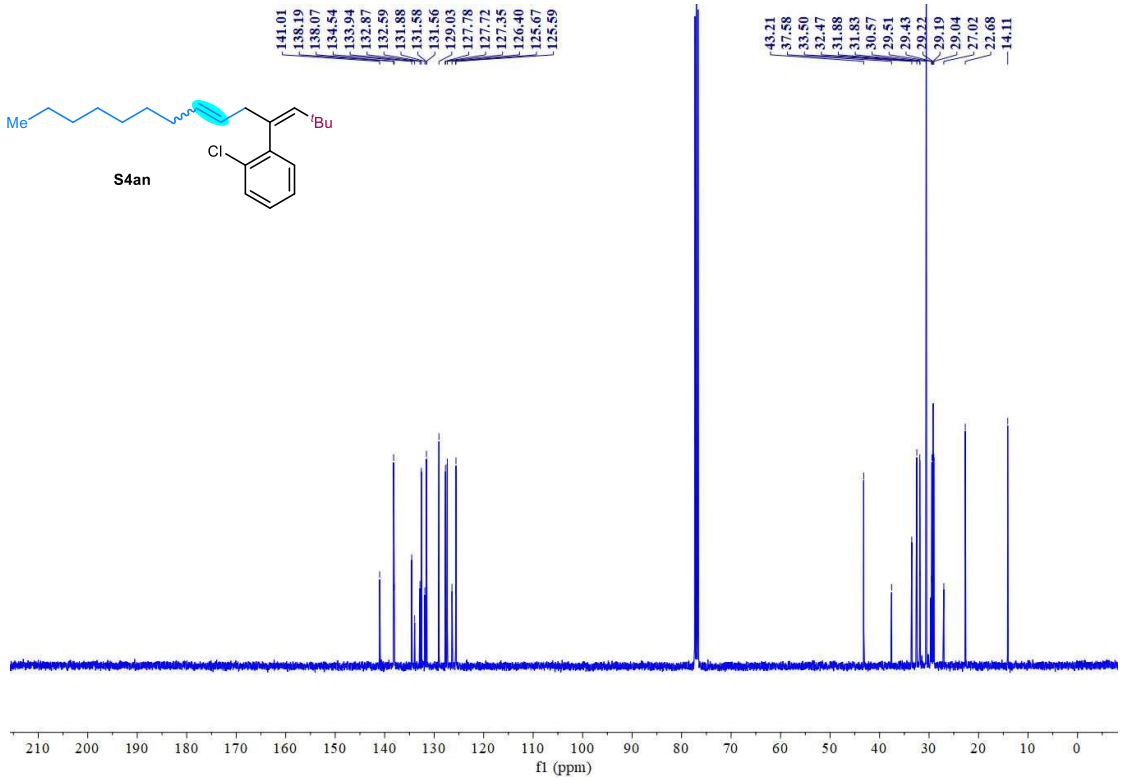


Figure S120. ^{13}C-NMR spectrum of **S4an**

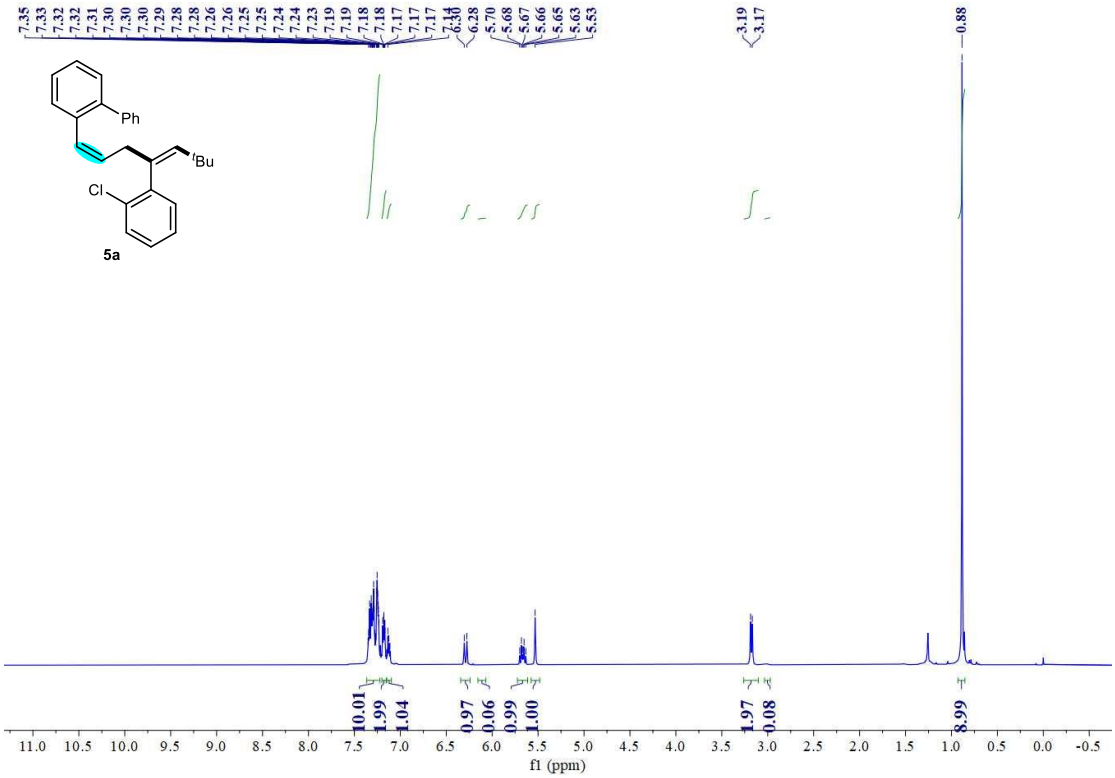


Figure S121. ^{1}H-NMR spectrum of **5a**

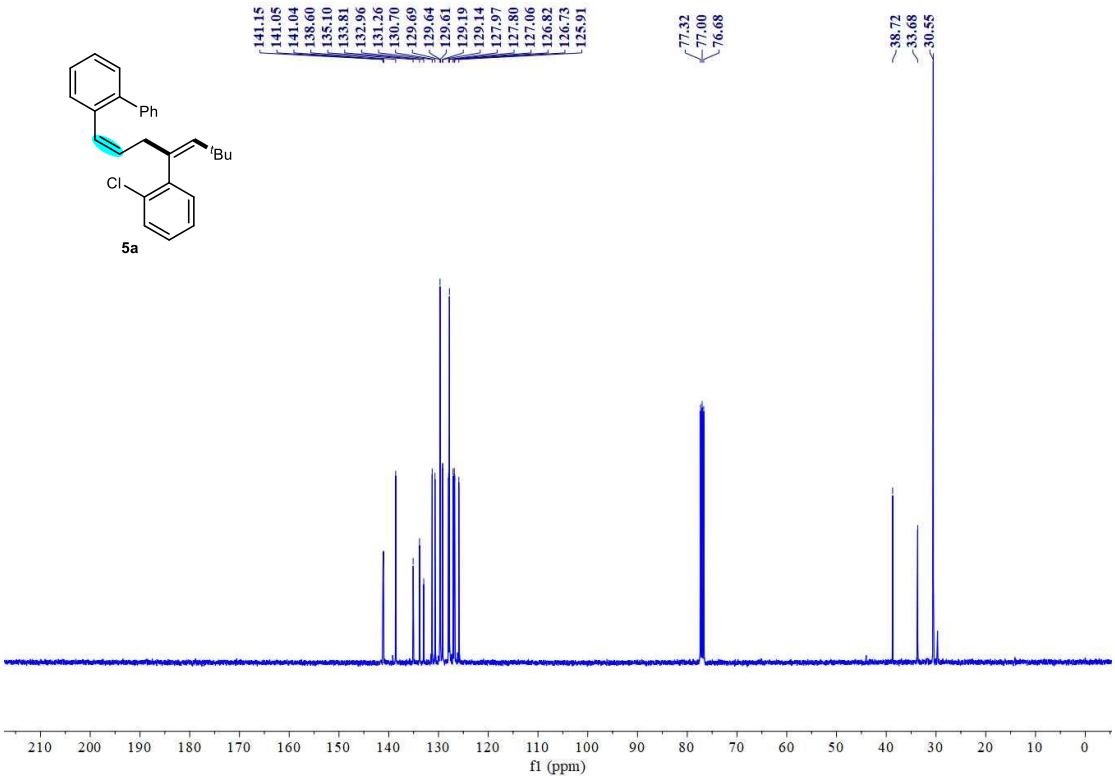


Figure S122. ^{13}C-NMR spectrum of **5a**

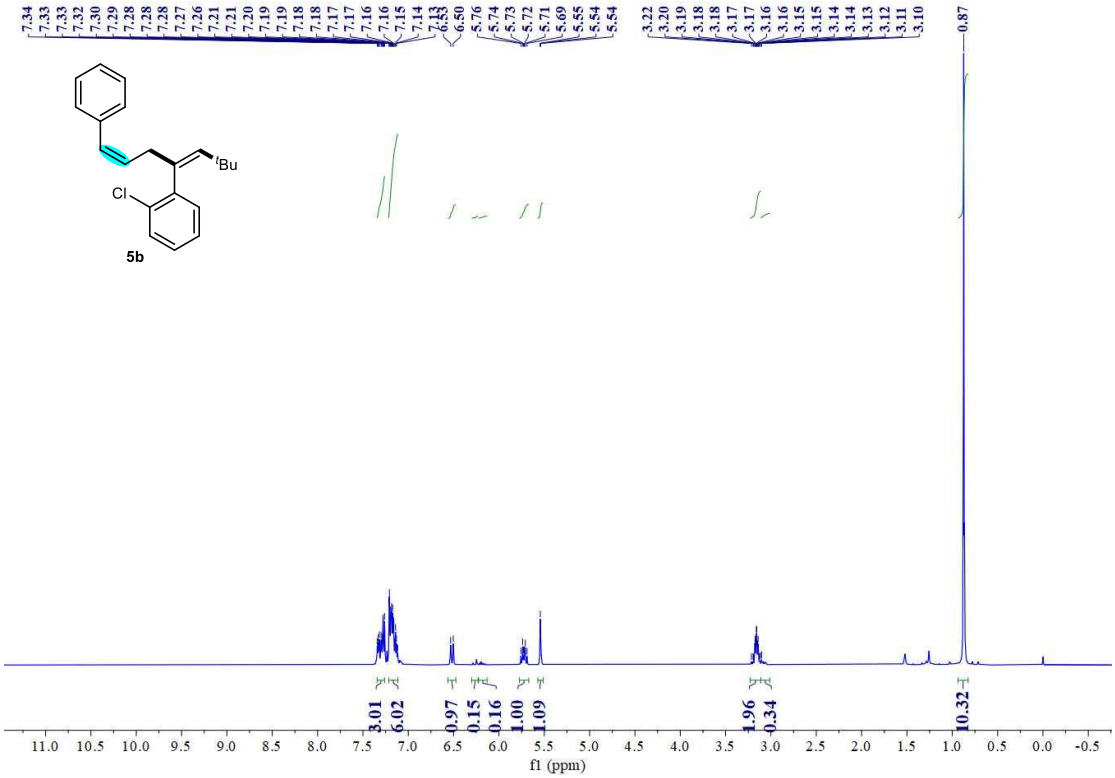


Figure S123. ^{1}H-NMR spectrum of **5b**

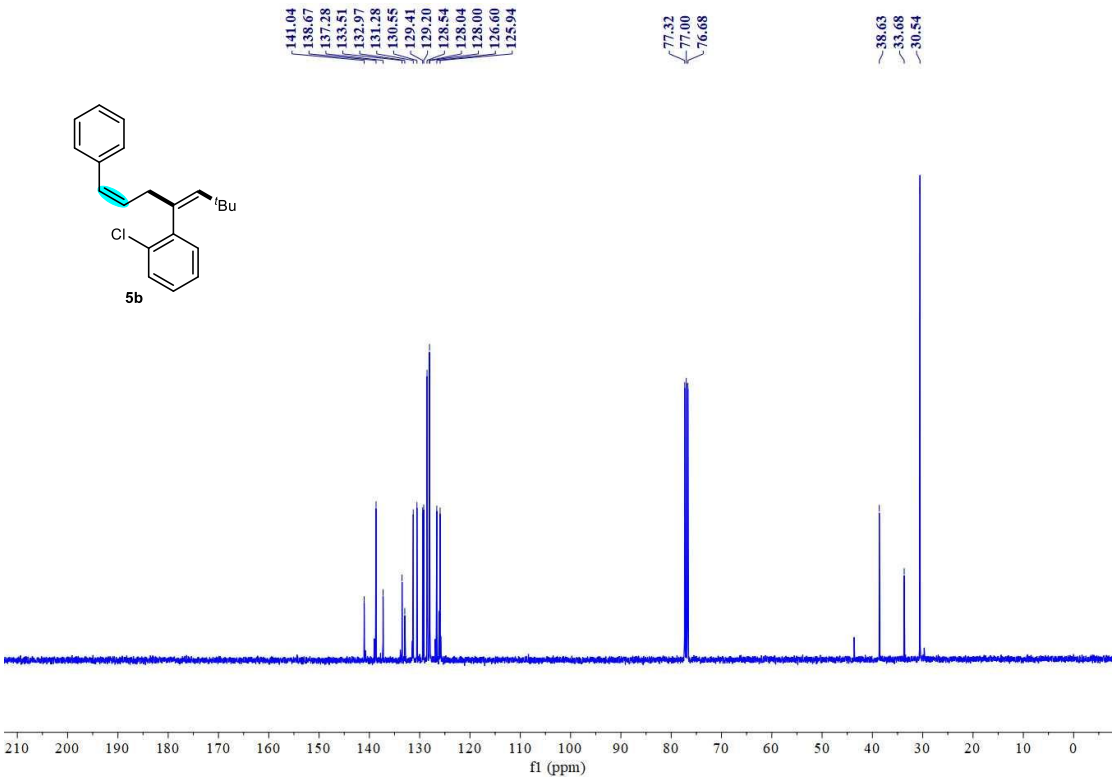


Figure S124. ^{13}C-NMR spectrum of **5b**

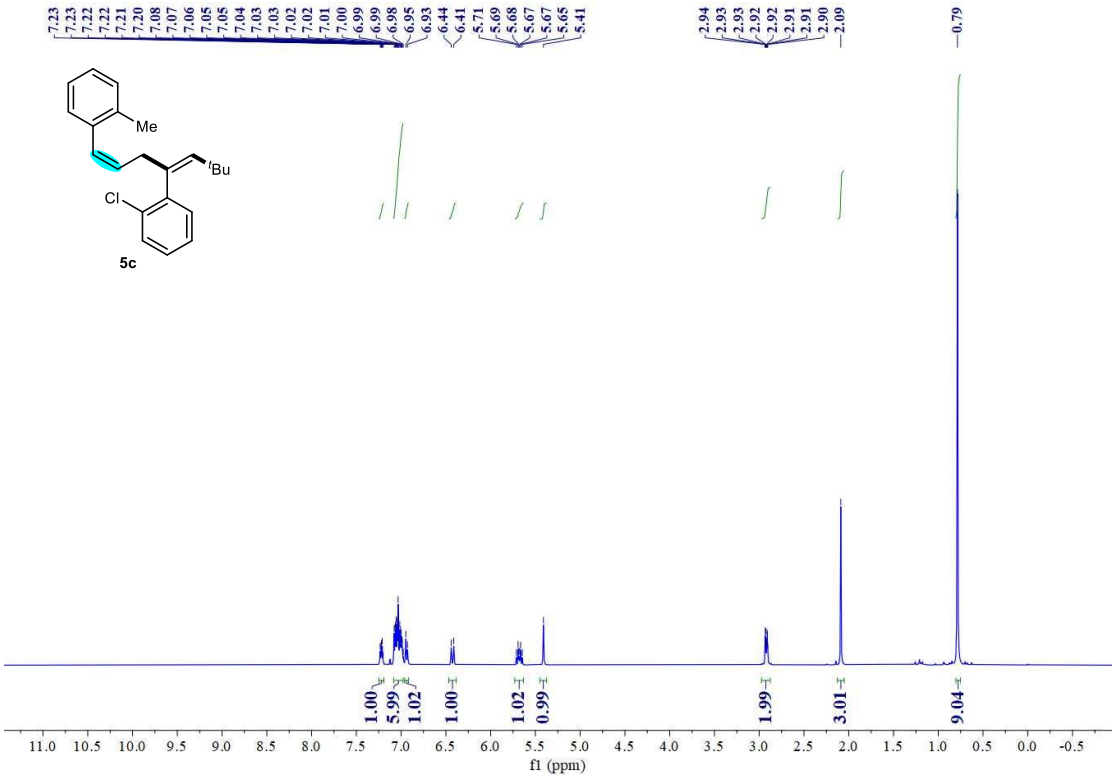


Figure S125. ^{1}H-NMR spectrum of **5c**

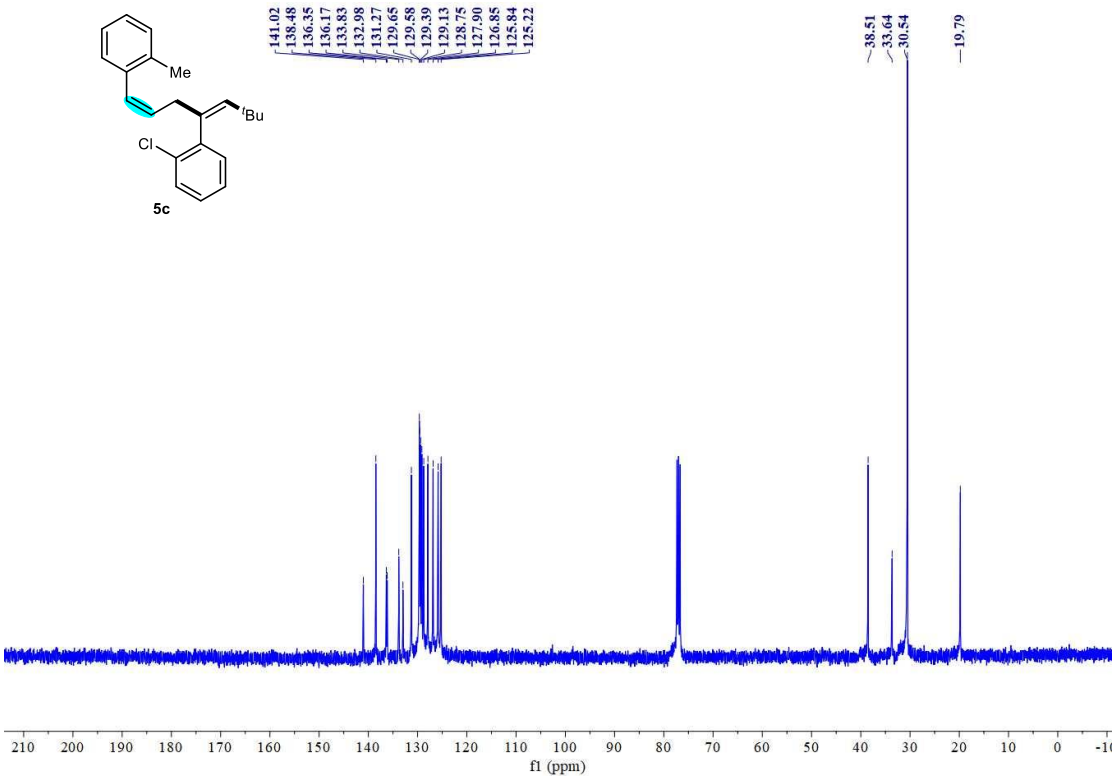


Figure S126. ^{13}C-NMR spectrum of **5c**

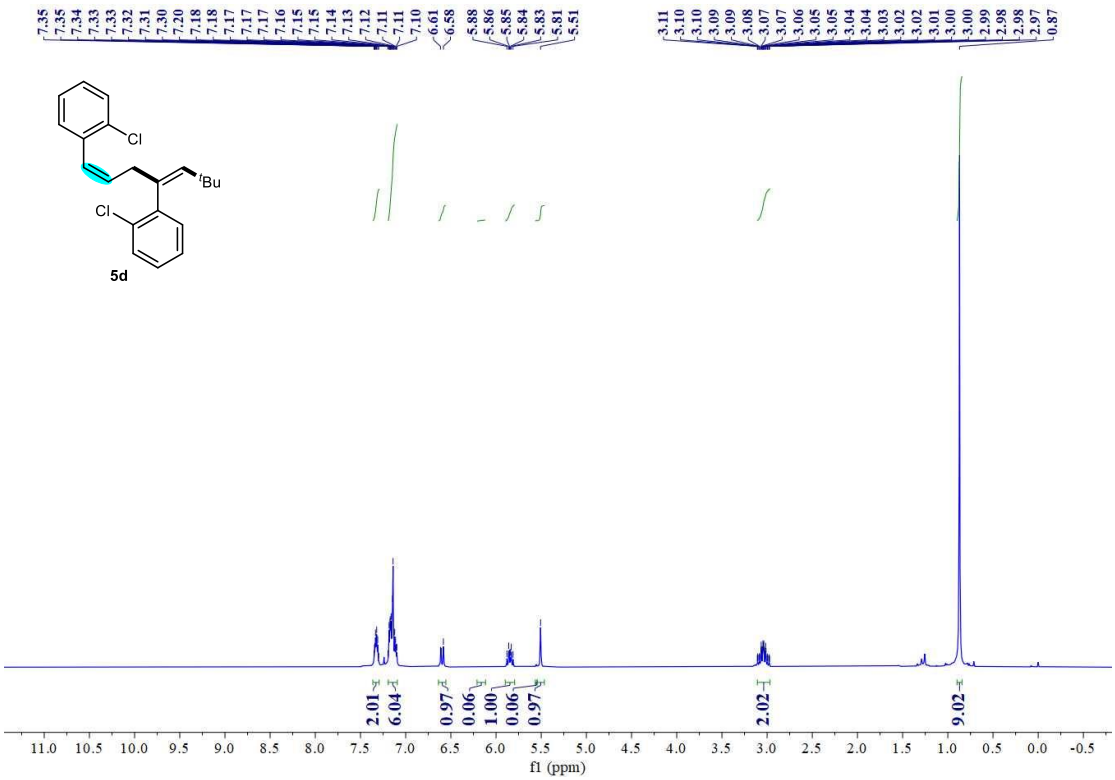


Figure S127. ^{1}H-NMR spectrum of **5d**

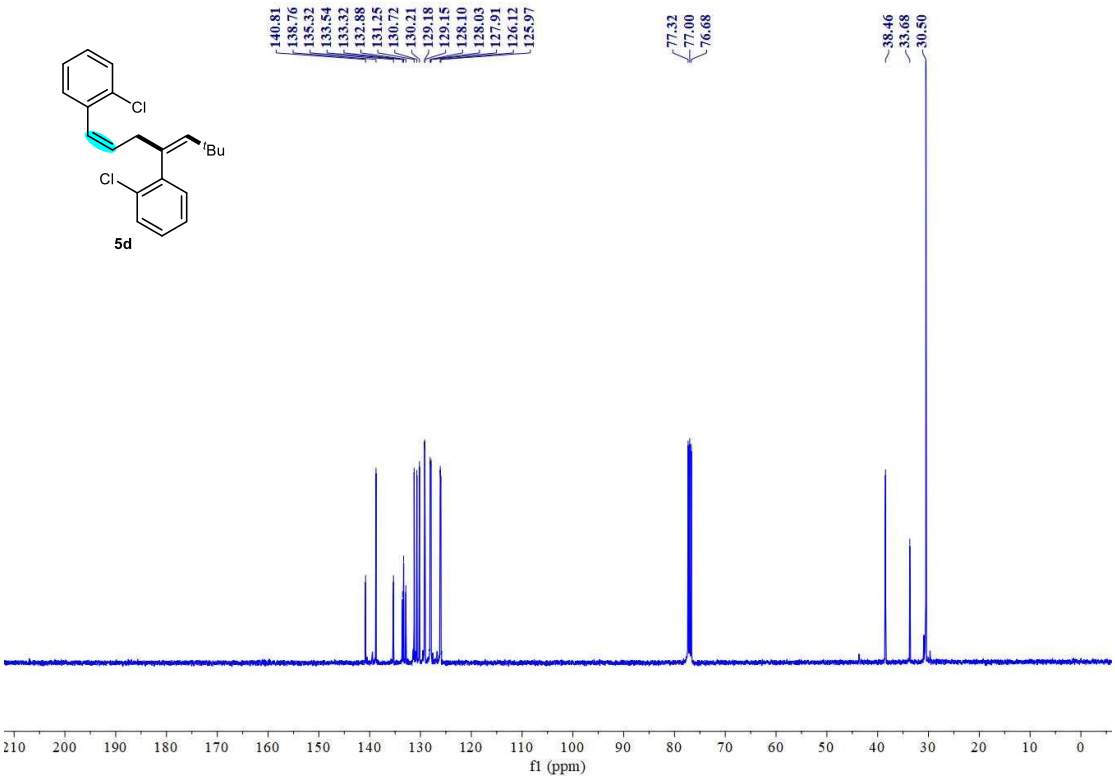


Figure S128. ^{13}C-NMR spectrum of **5d**

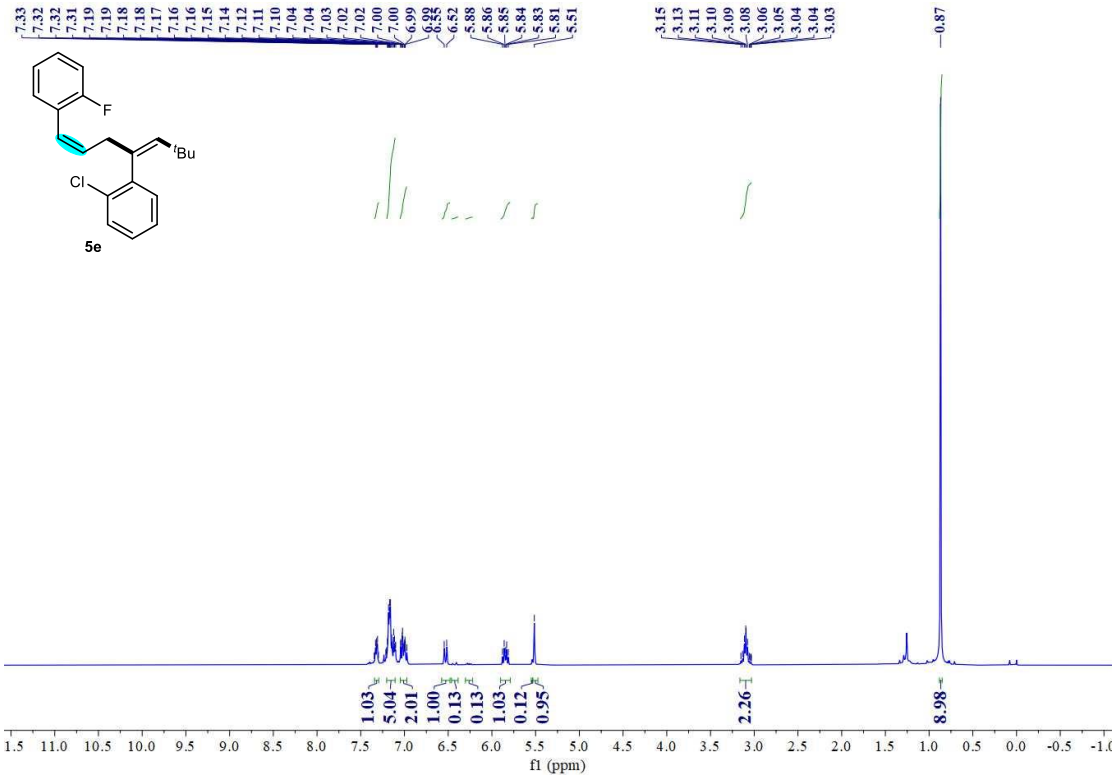


Figure S129. ^{1}H-NMR spectrum of **5e**

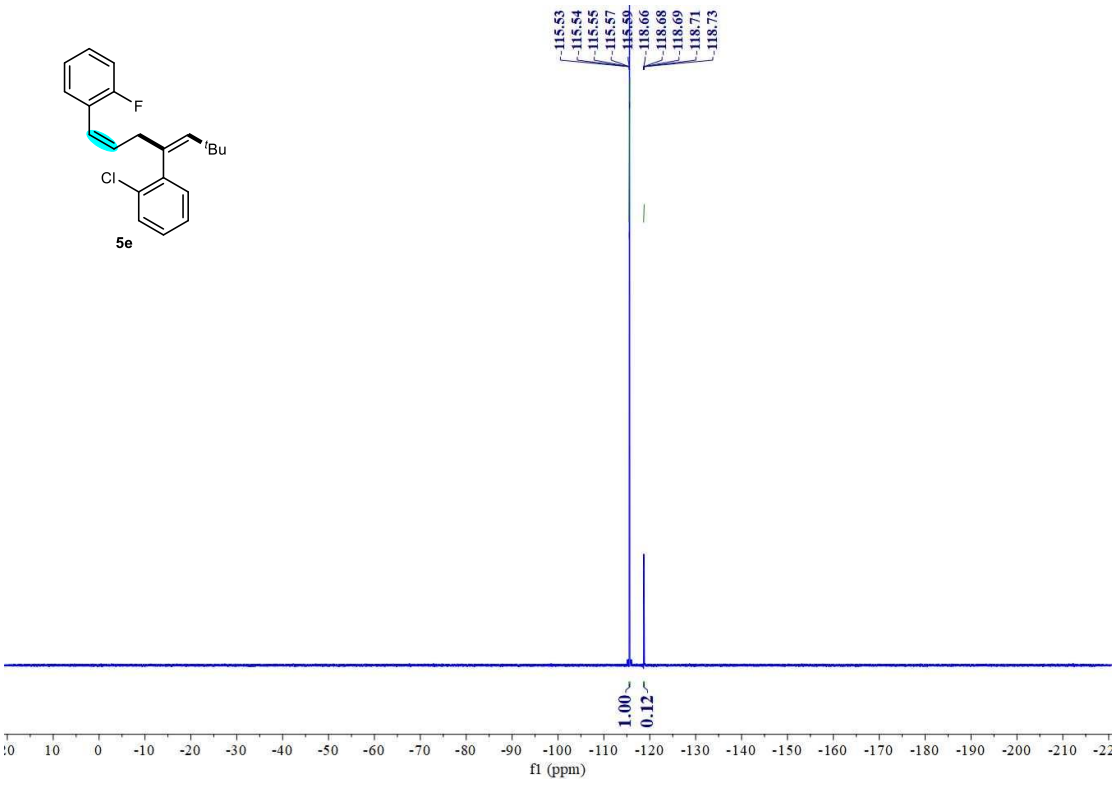


Figure S130. ^{19}F-NMR spectrum of **5e**

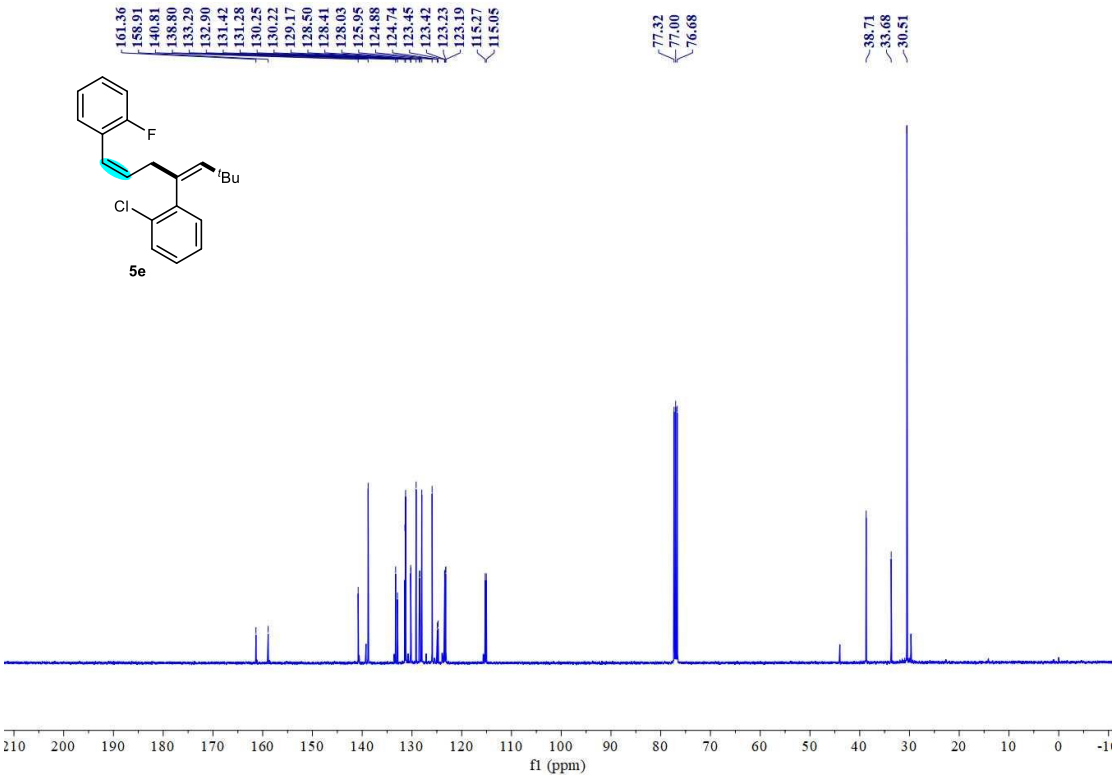


Figure S131. ^{13}C-NMR spectrum of **5e**

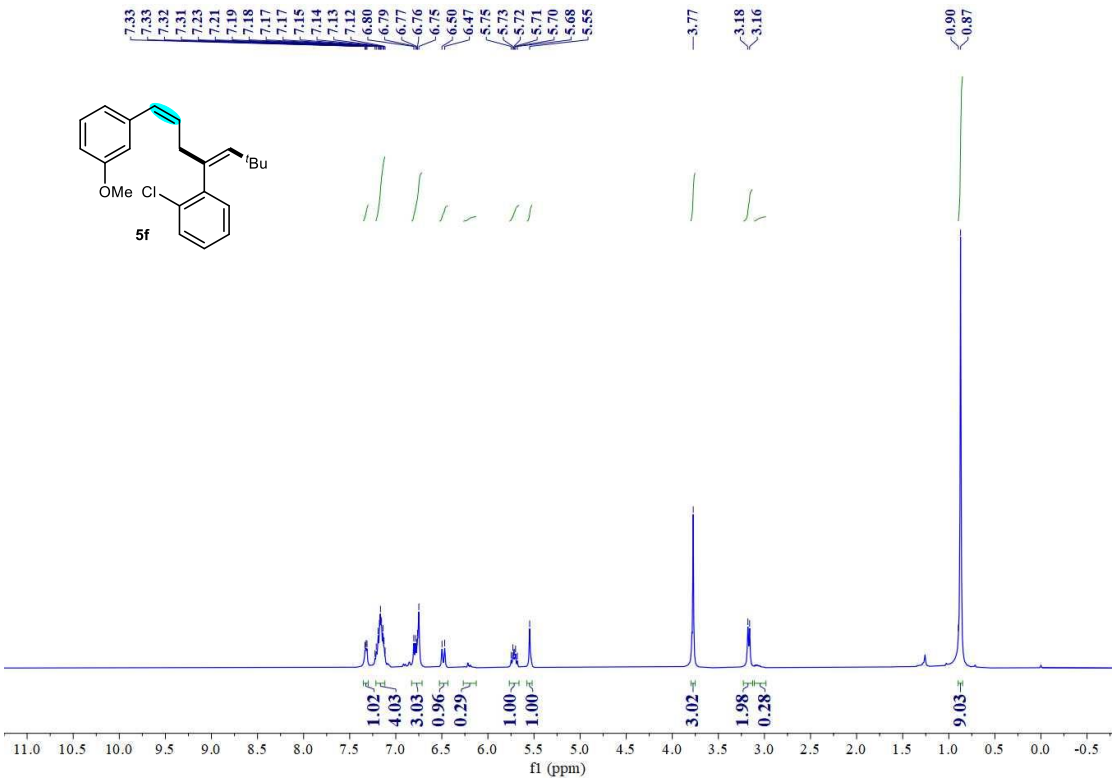


Figure S132. ^{1}H-NMR spectrum of **5f**

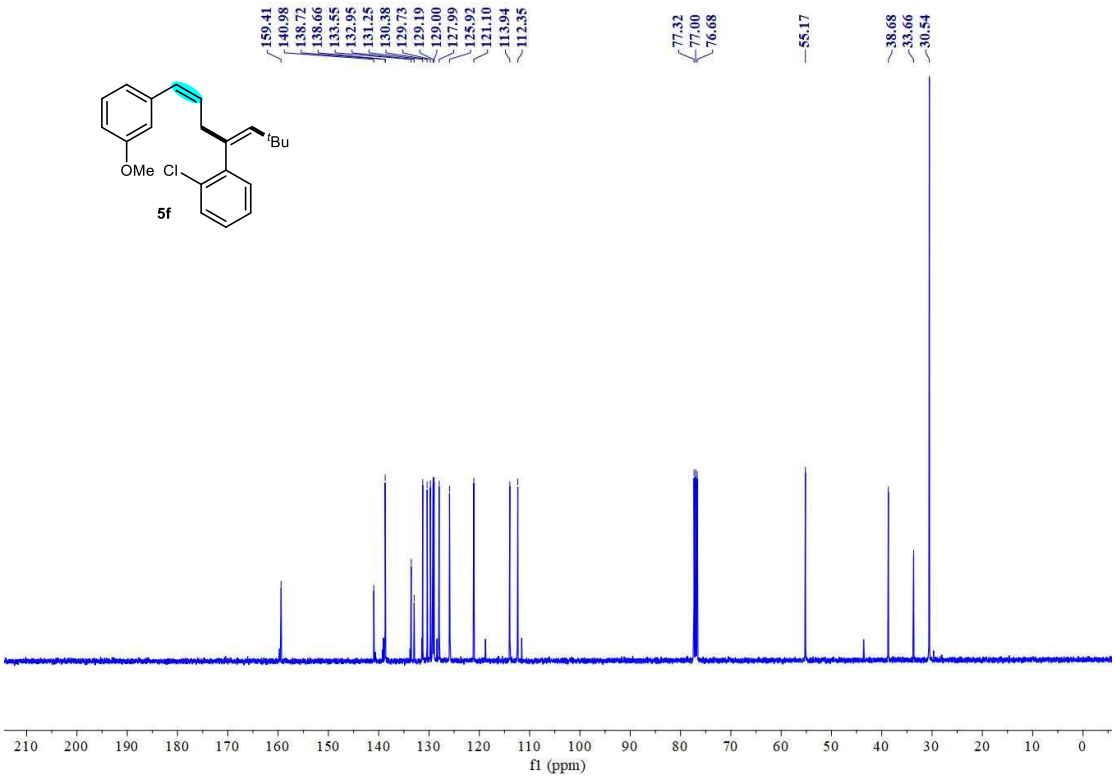


Figure S133. ^{13}C-NMR spectrum of **5f**

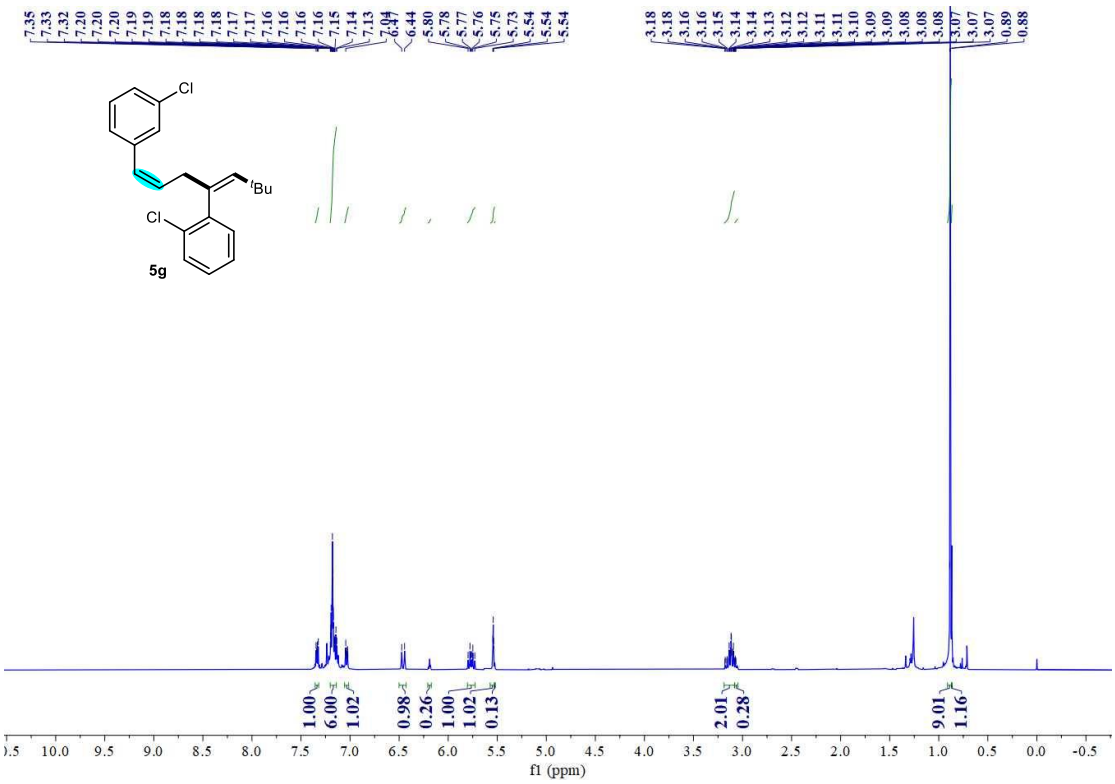


Figure S134. ^{1}H-NMR spectrum of **5g**

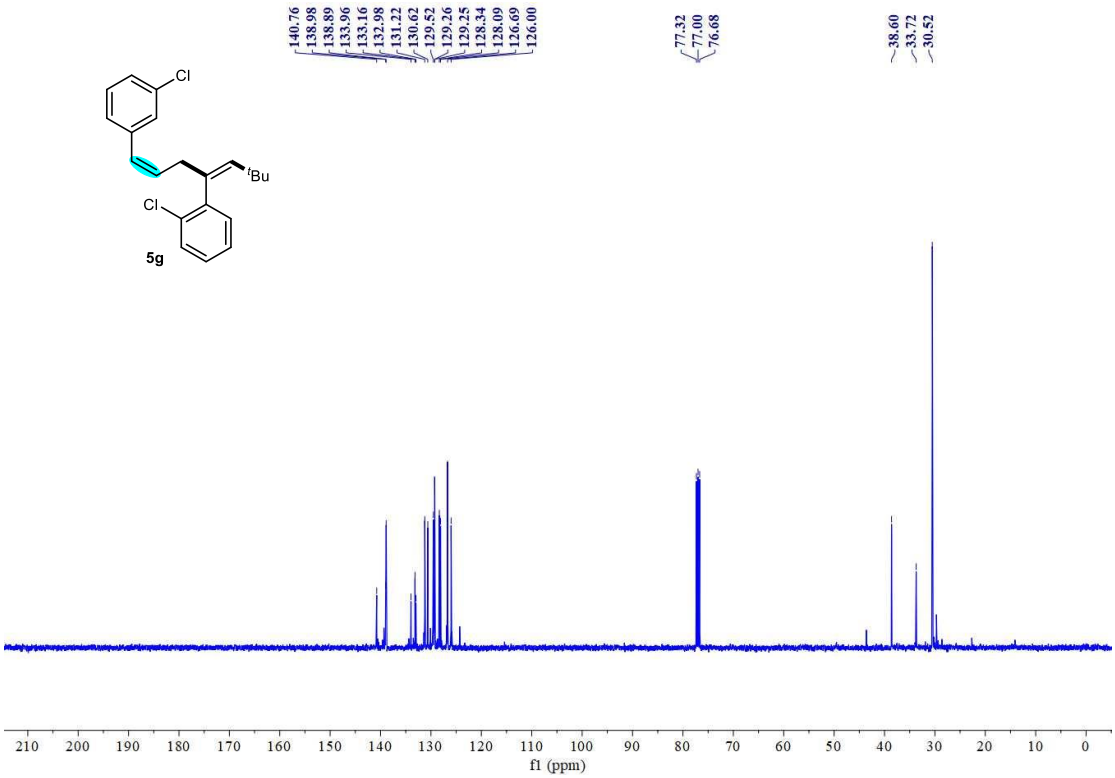


Figure S135. ^{13}C-NMR spectrum of **5g**

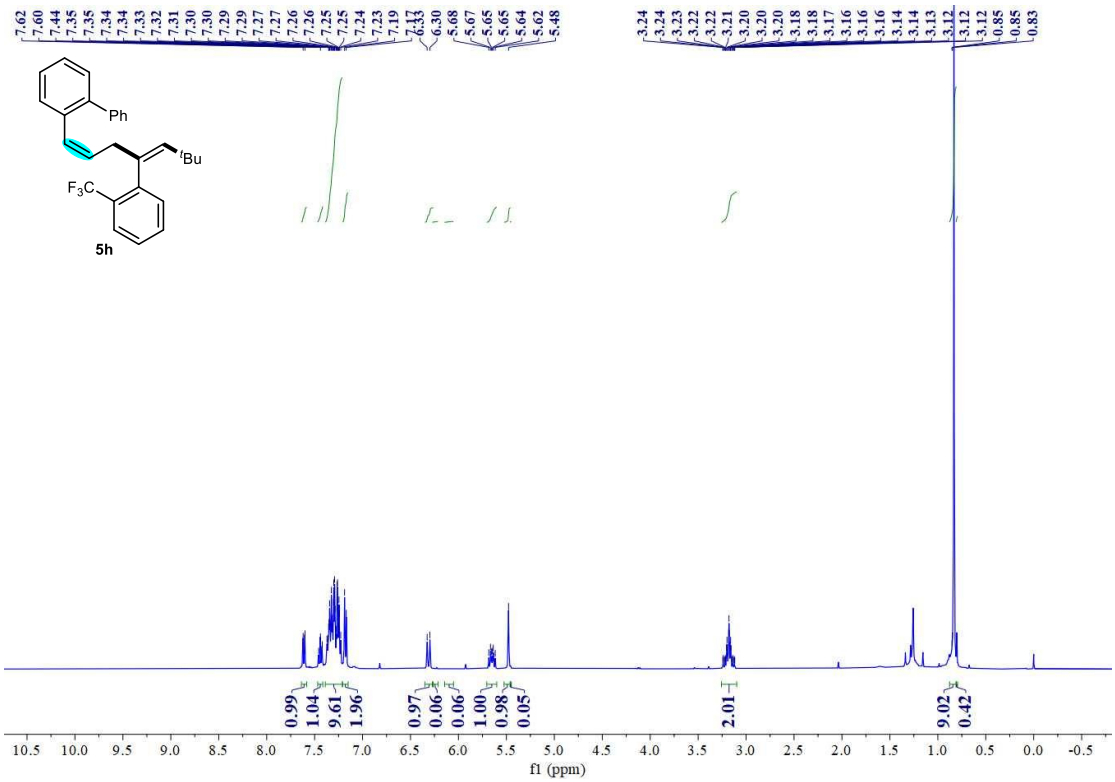


Figure S136. ^{1}H-NMR spectrum of **5h**

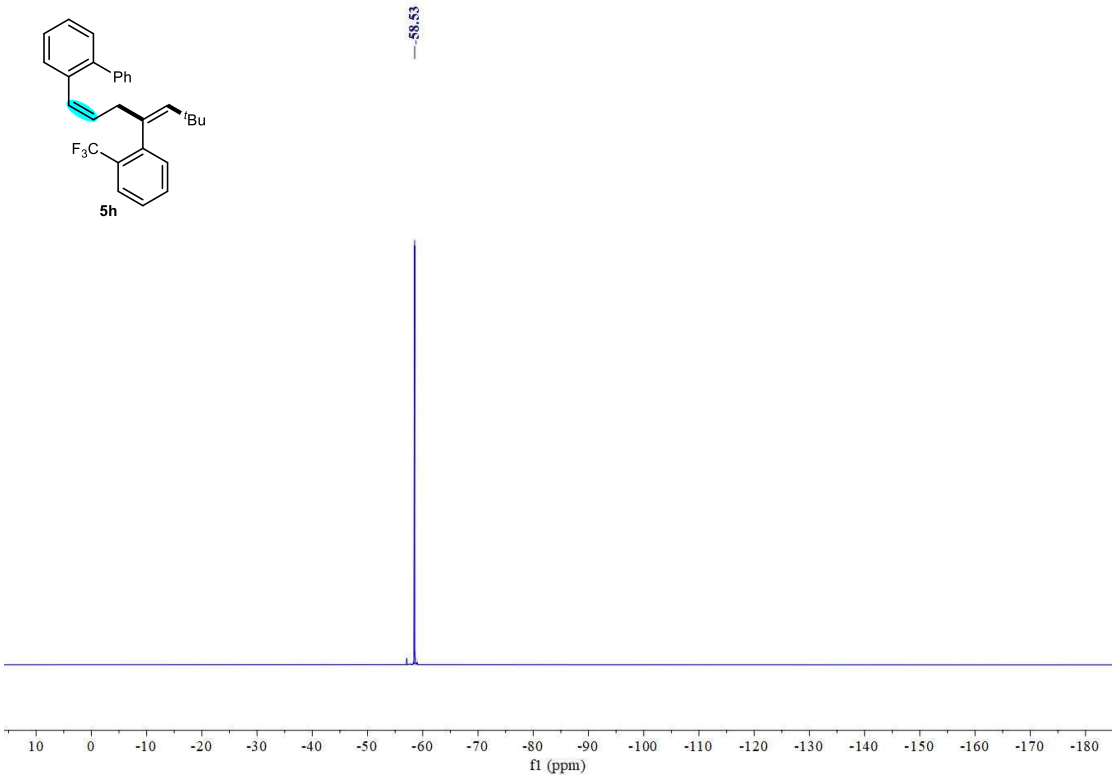


Figure S137. ^{19}F-NMR spectrum of **5h**

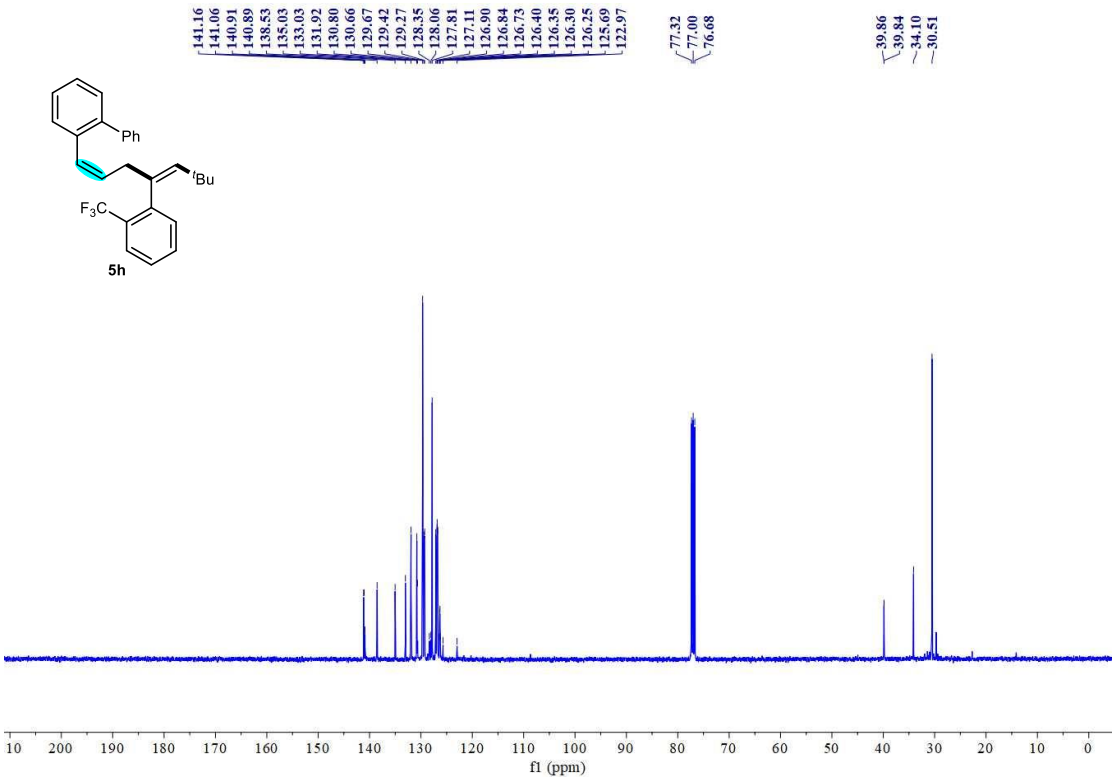


Figure S138. ^{13}C-NMR spectrum of **5h**

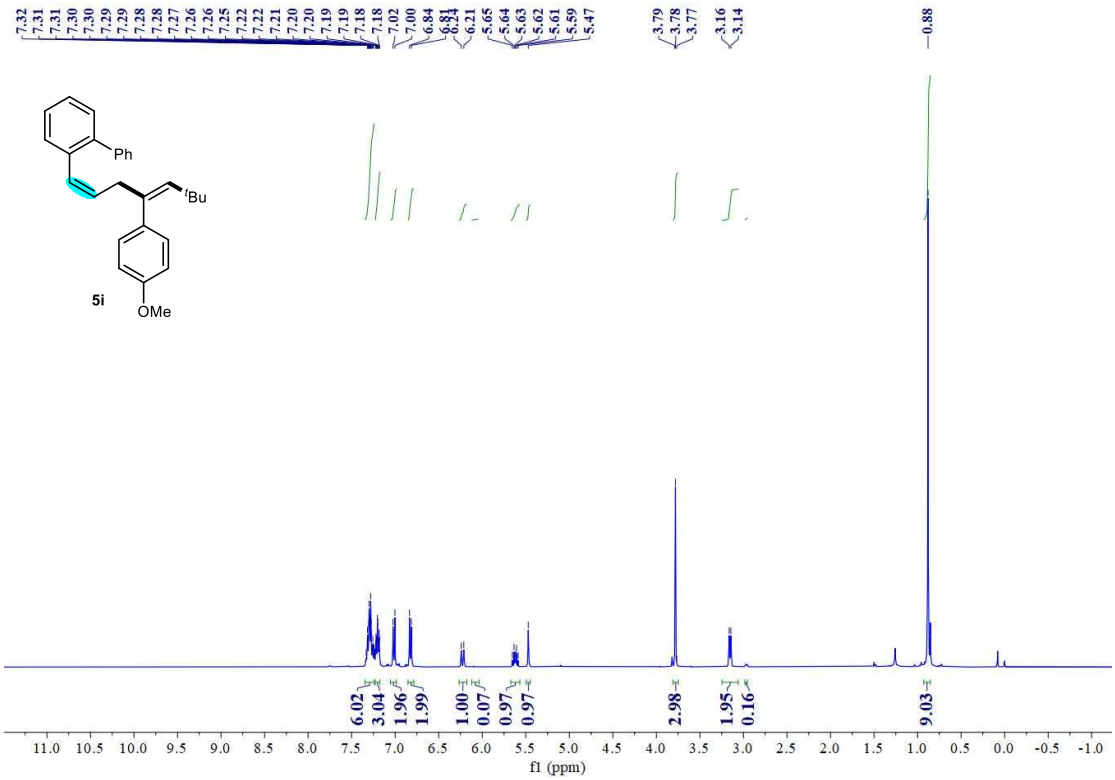


Figure S139. ^{1}H-NMR spectrum of **5i**

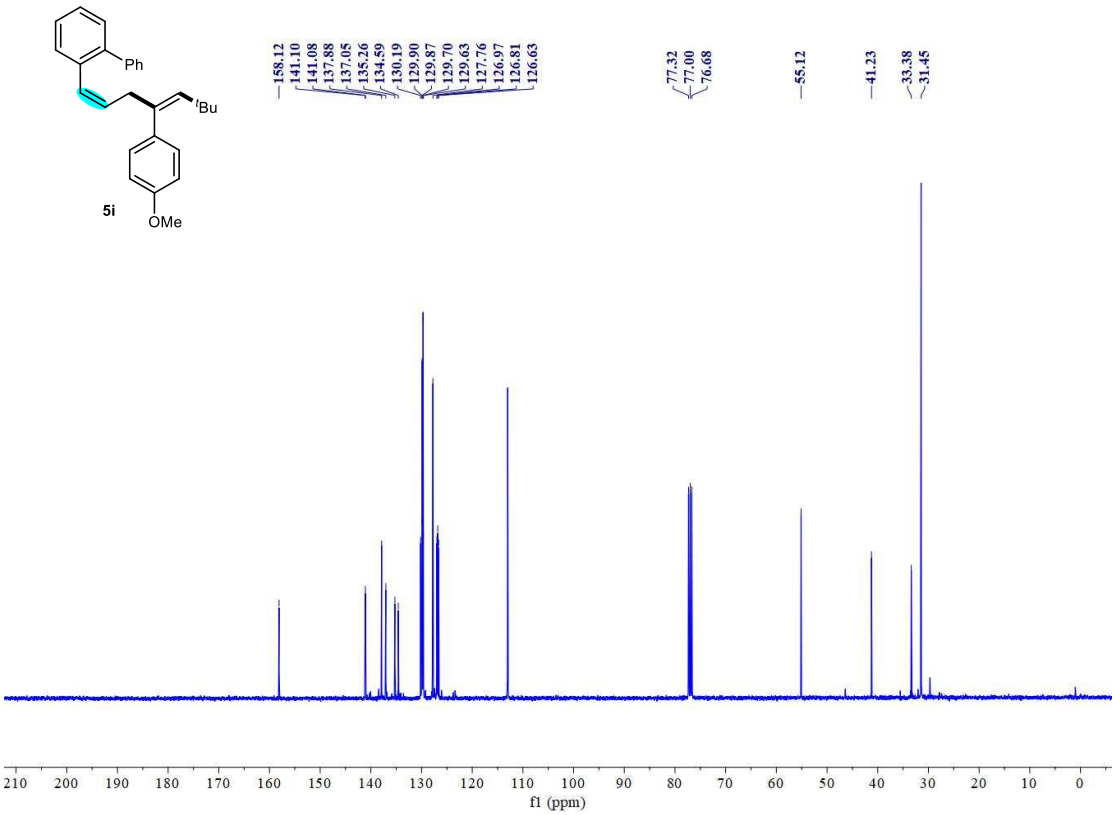


Figure S140. ^{13}C-NMR spectrum of **5i**

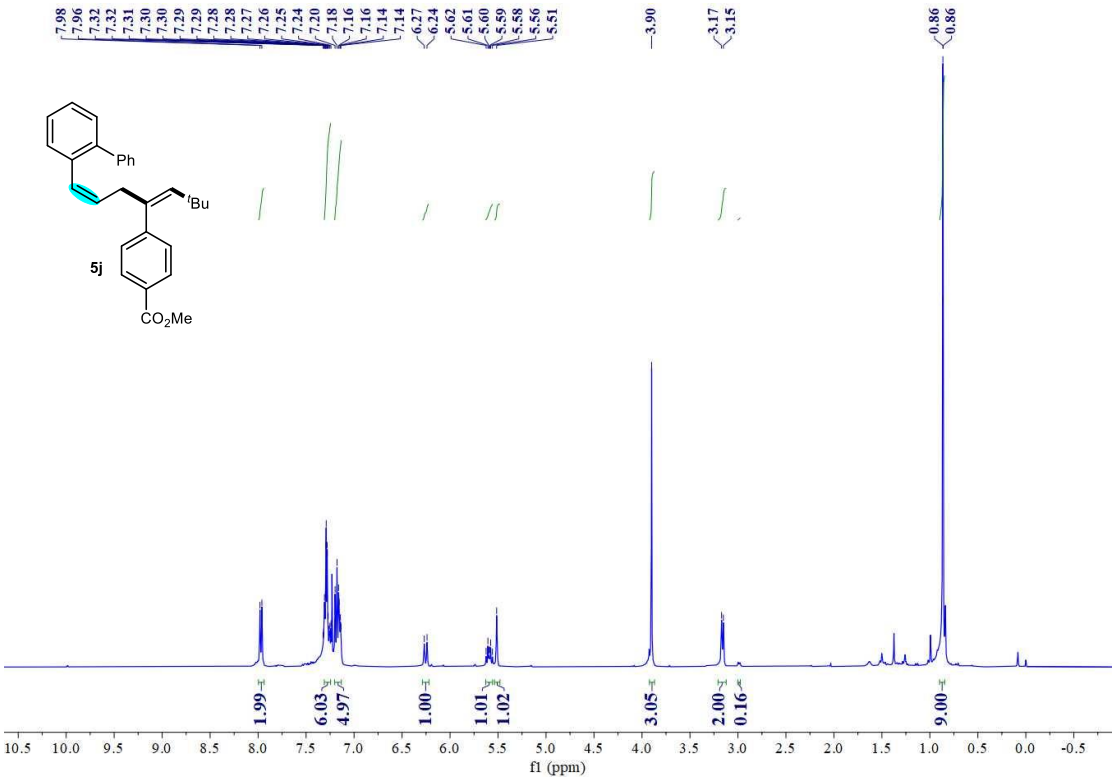


Figure S141. ^{1}H-NMR spectrum of **5j**

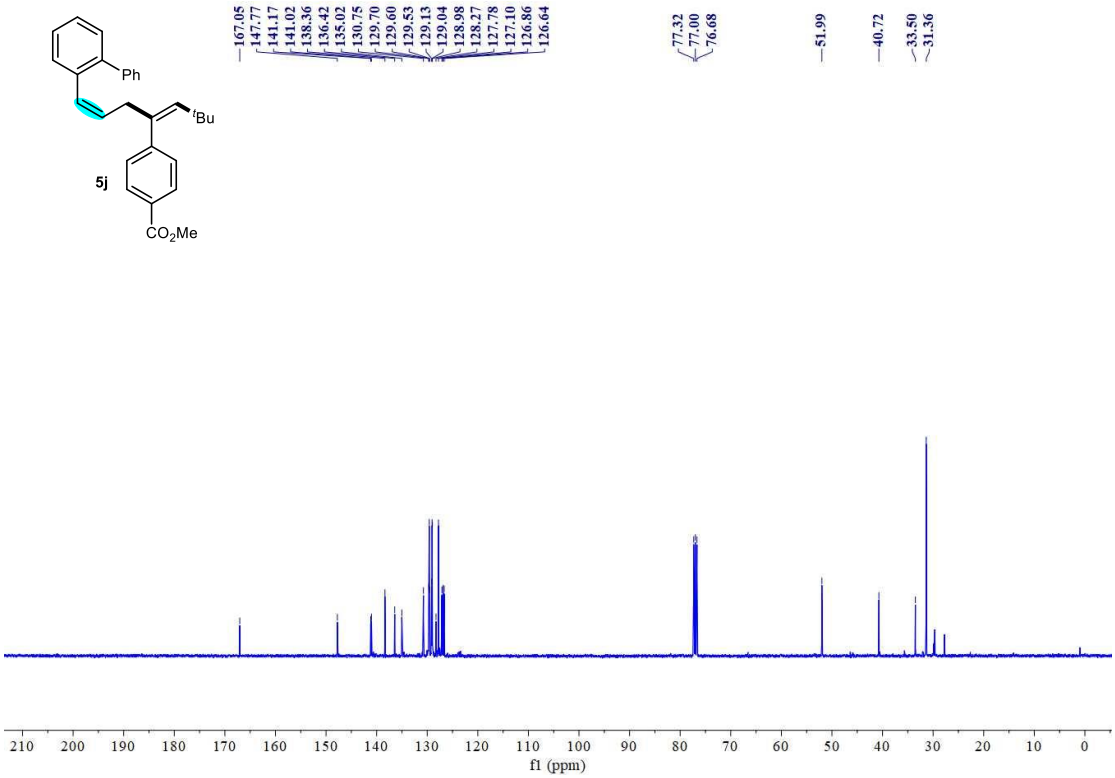


Figure S142. ^{13}C-NMR spectrum of **5j**

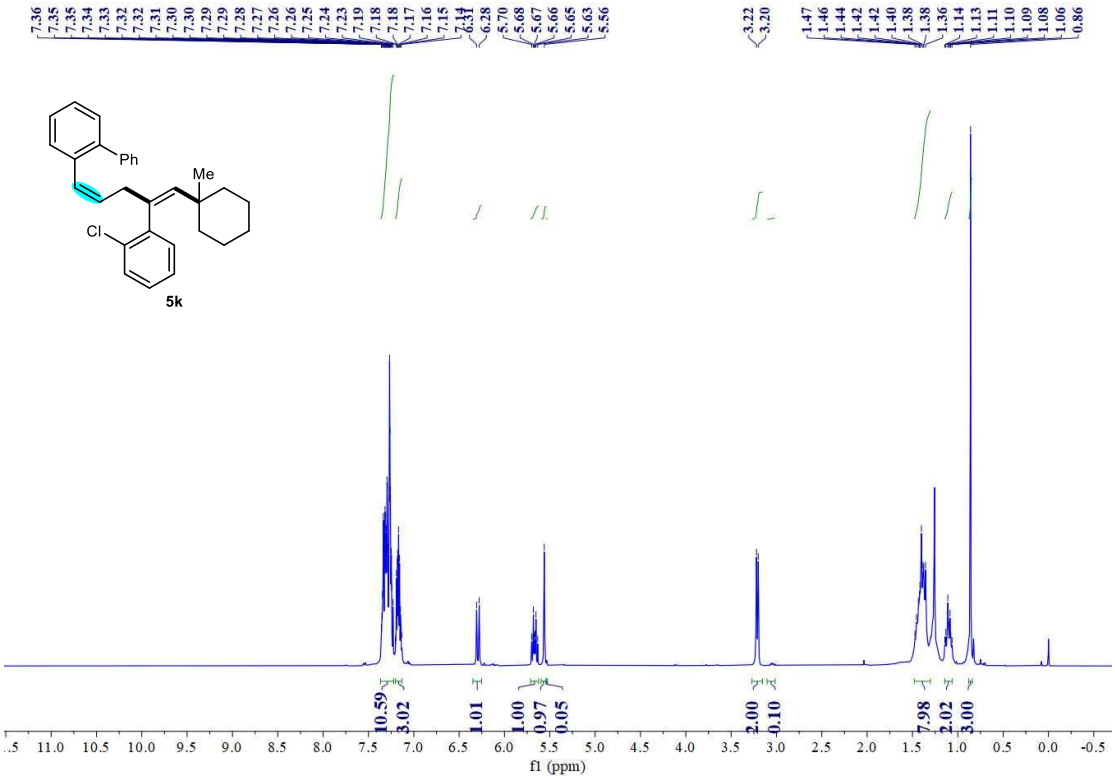


Figure S143. ^{1}H-NMR spectrum of **5k**

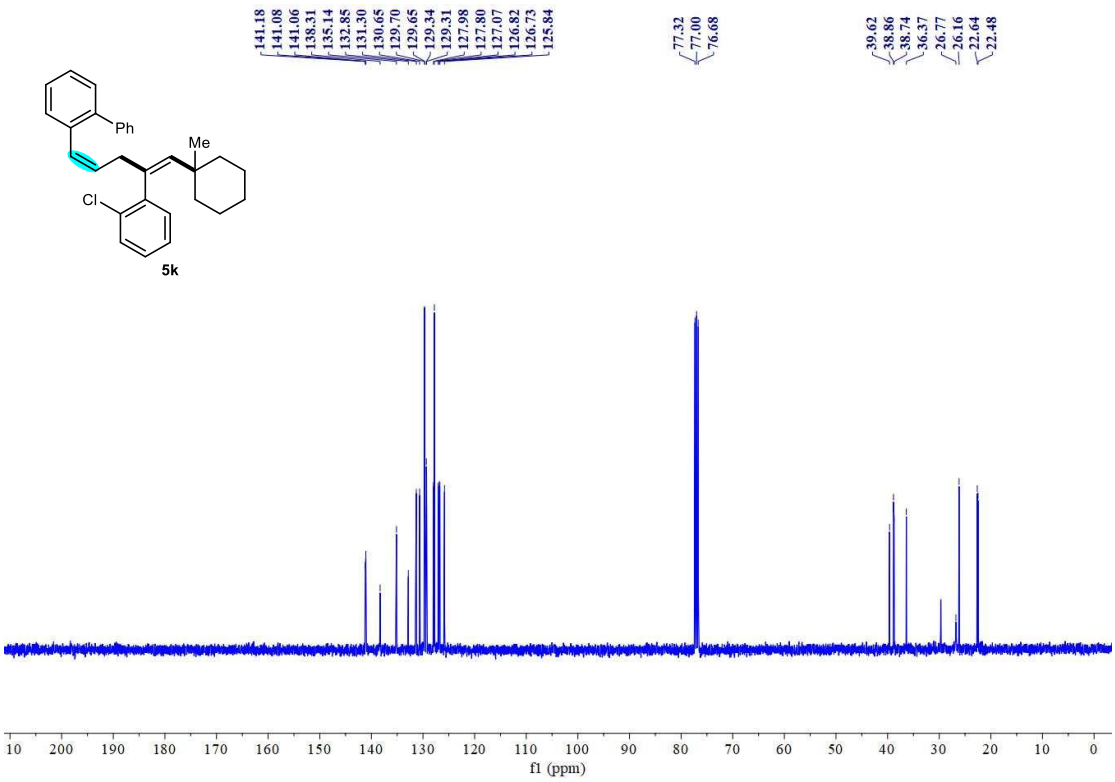


Figure S144. ^{13}C-NMR spectrum of **5k**

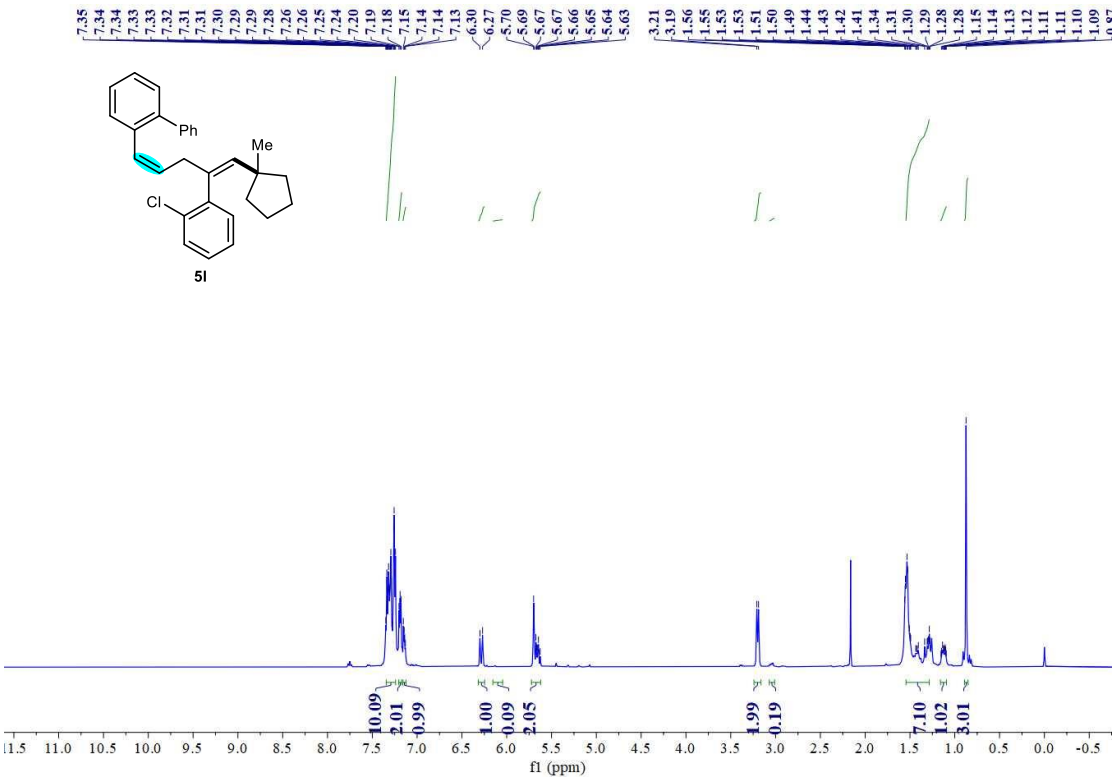


Figure S145. ^{1}H-NMR spectrum of **5l**

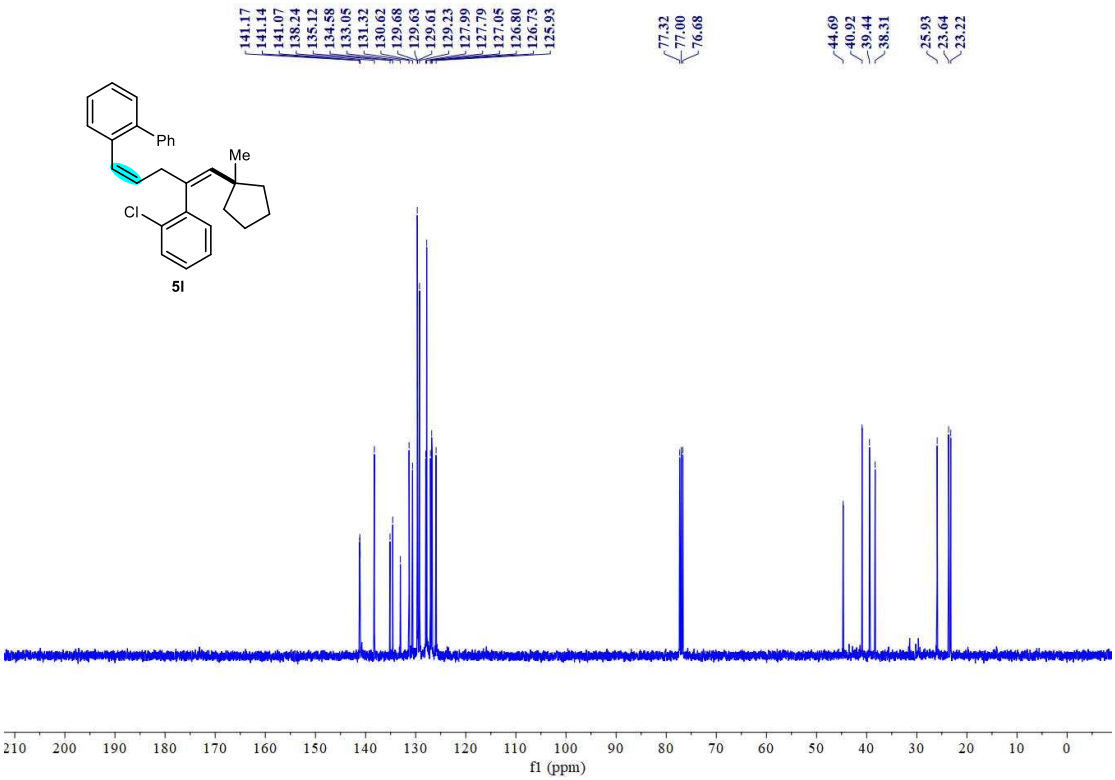


Figure S146. ^{13}C-NMR spectrum of **5l**

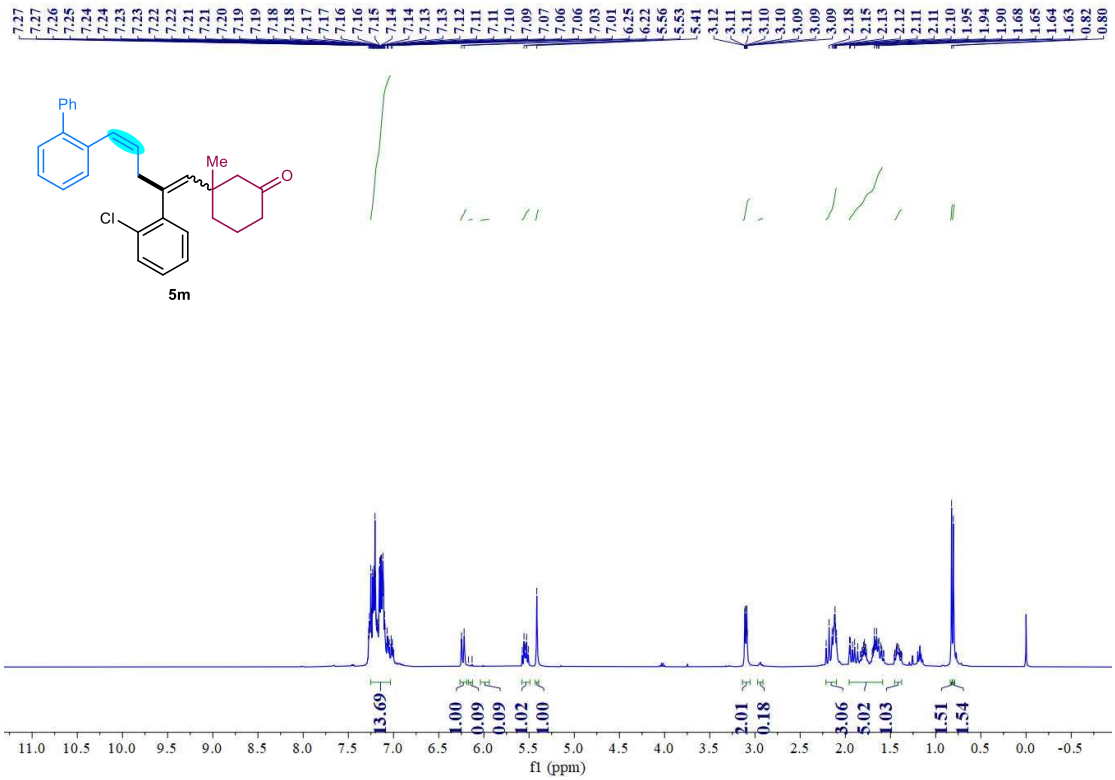


Figure S147. ^{1}H-NMR spectrum of **5m**

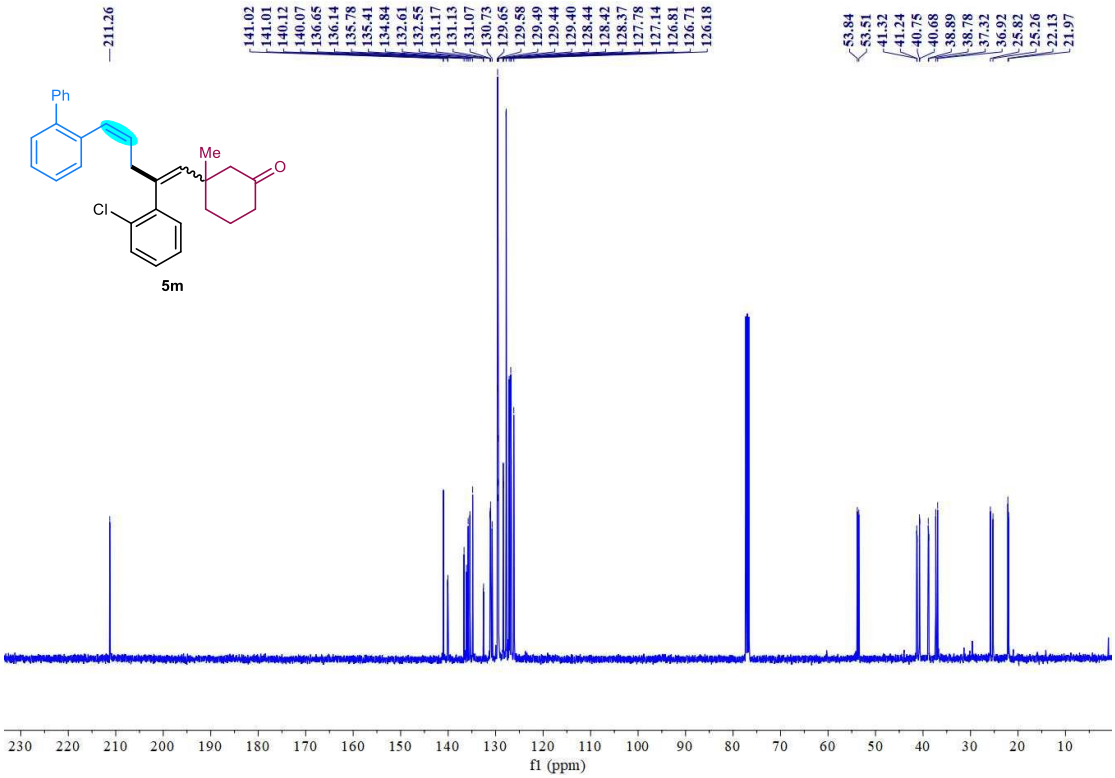


Figure S148. ^{13}C-NMR spectrum of **5m**

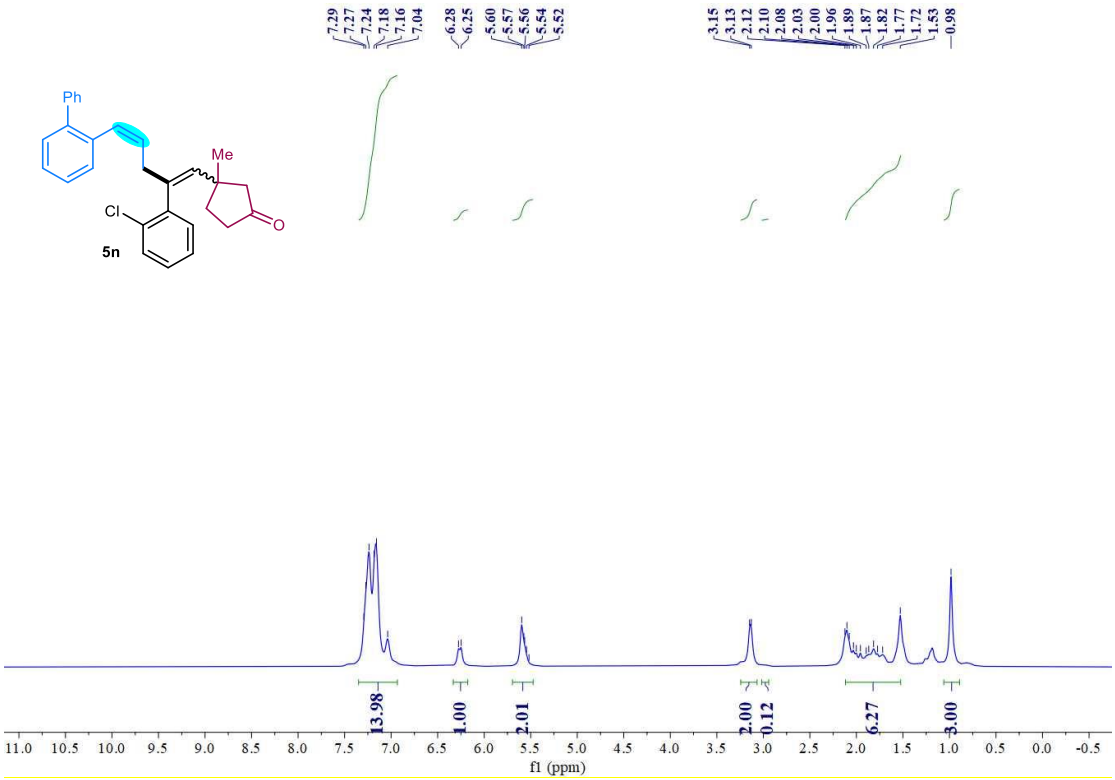


Figure S149. ^{1}H-NMR spectrum of **5n**

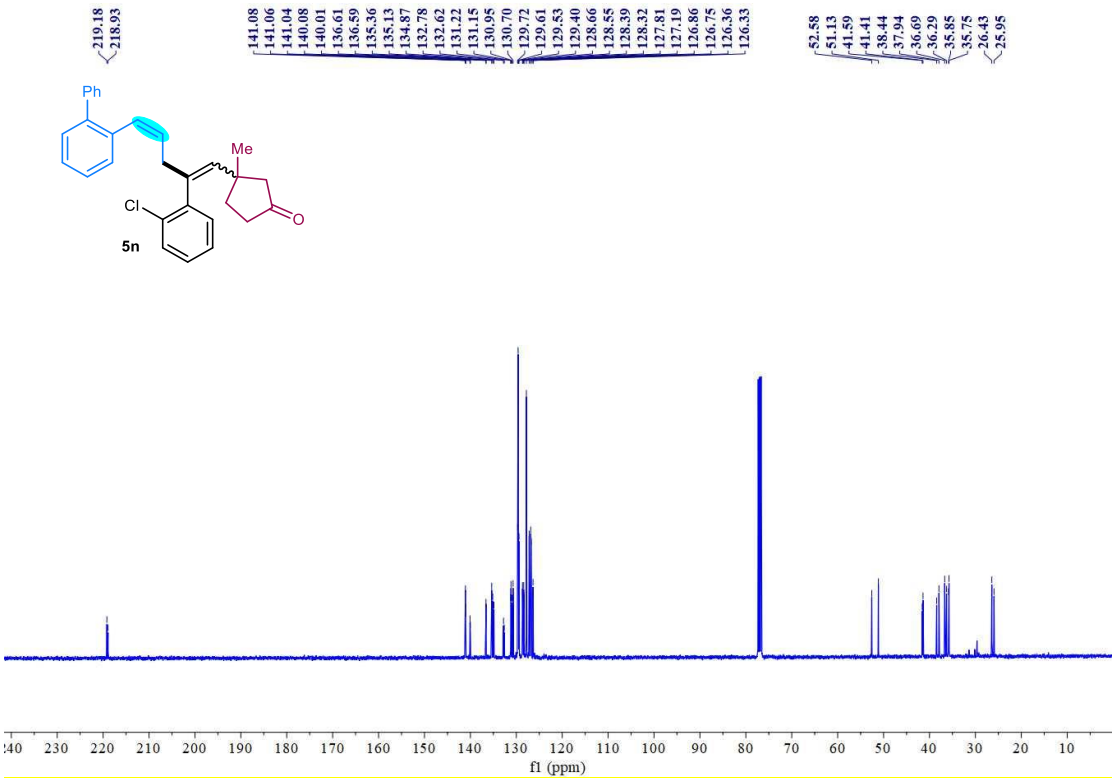


Figure S150. ^{13}C-NMR spectrum of **5n**

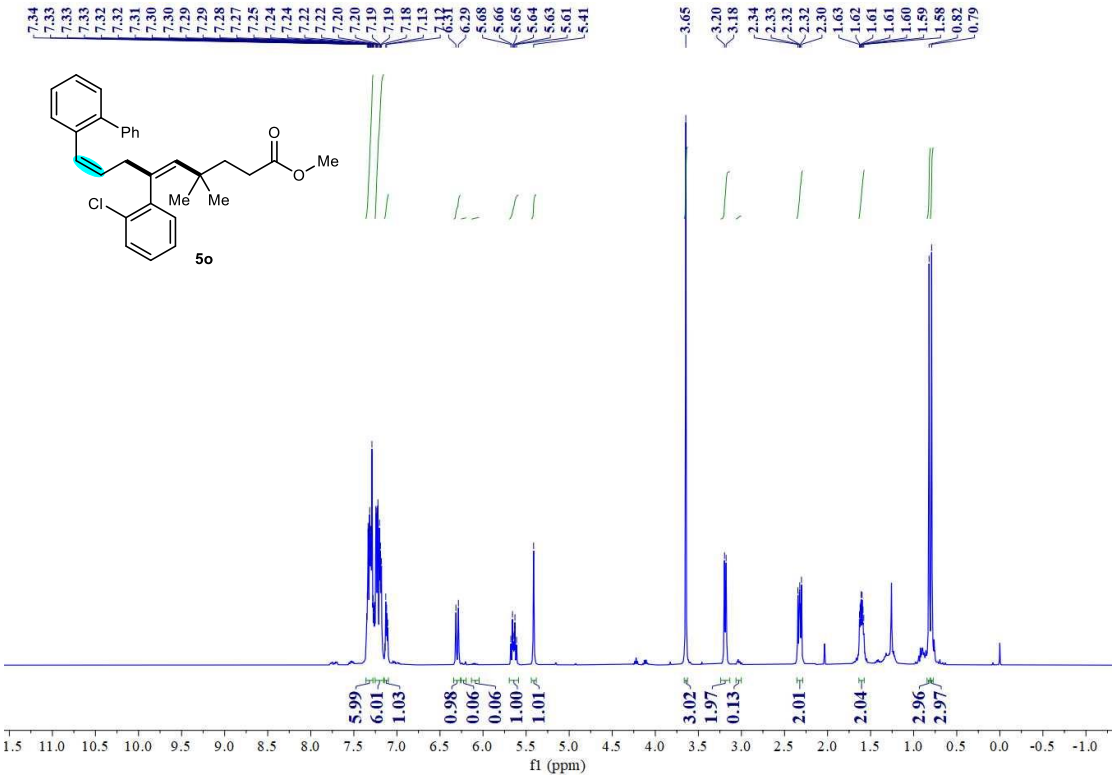


Figure S151. ^{1}H-NMR spectrum of **5o**

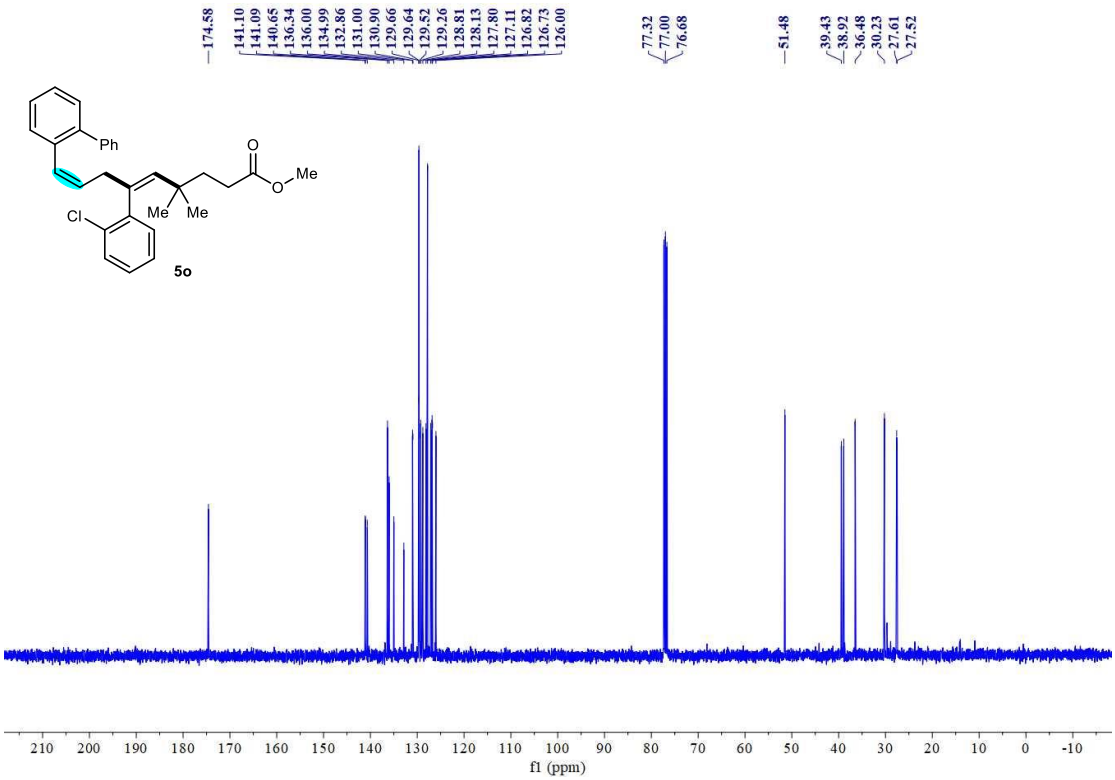


Figure S152. ^{13}C-NMR spectrum of **5o**

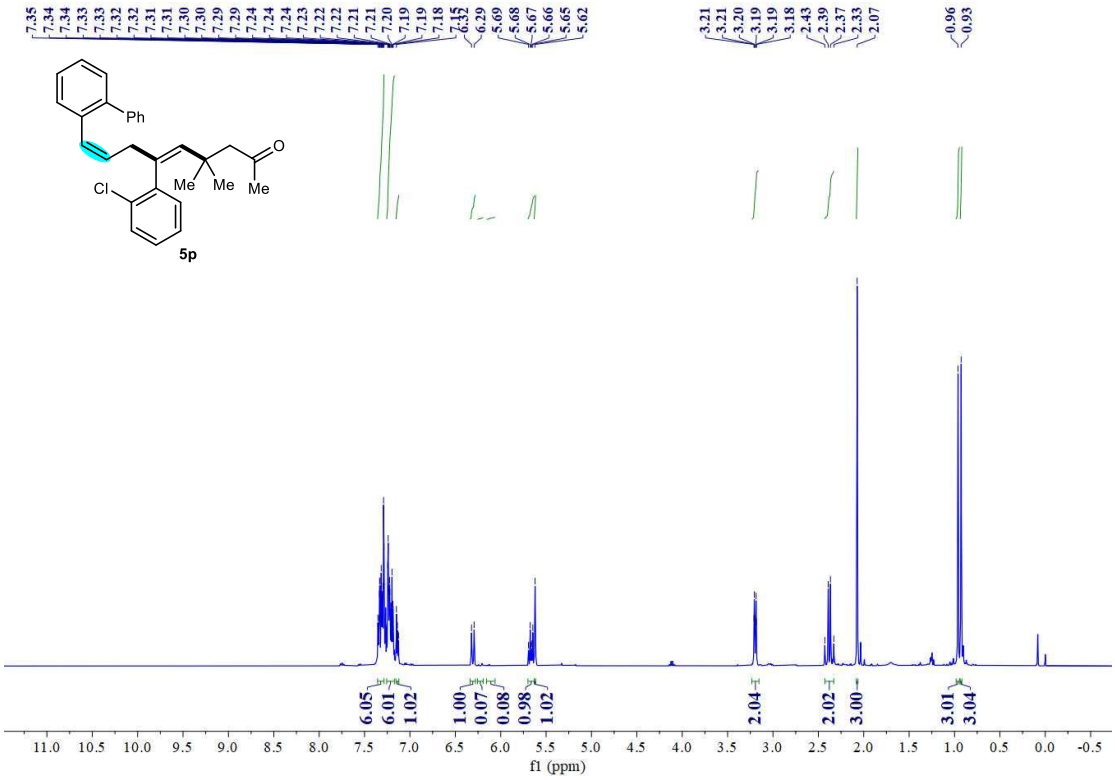


Figure S153. ^{1}H-NMR spectrum of **5p**

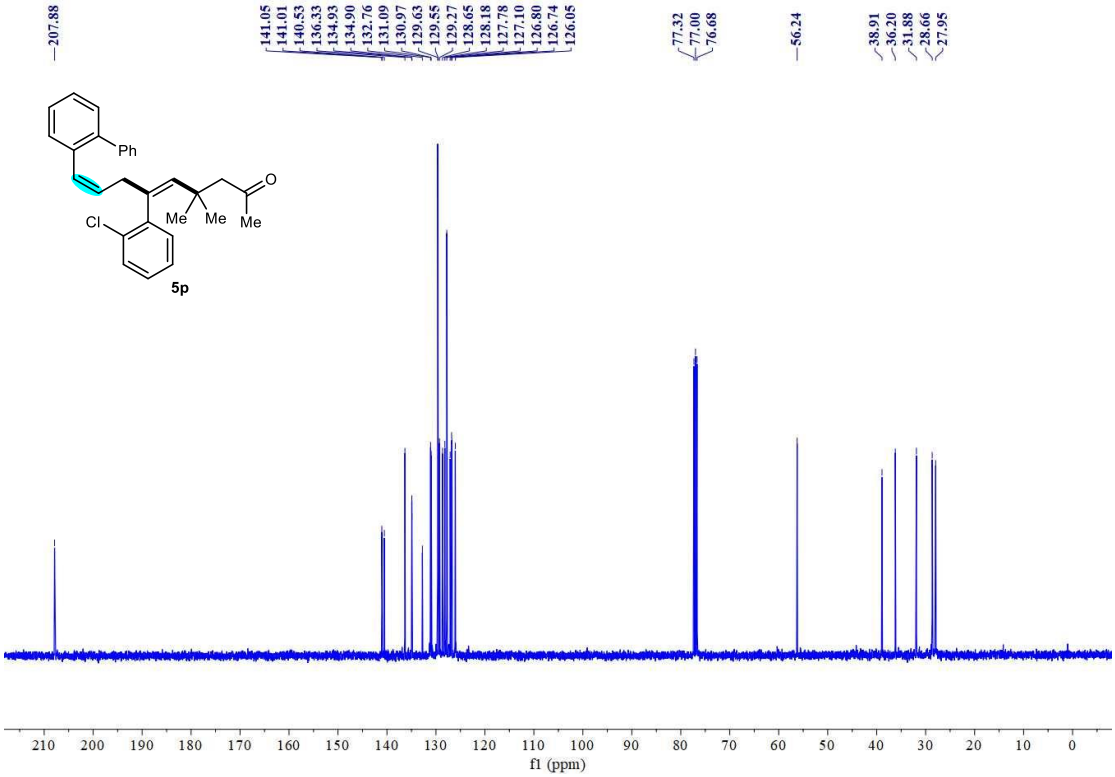


Figure S154. ^{13}C-NMR spectrum of **5p**

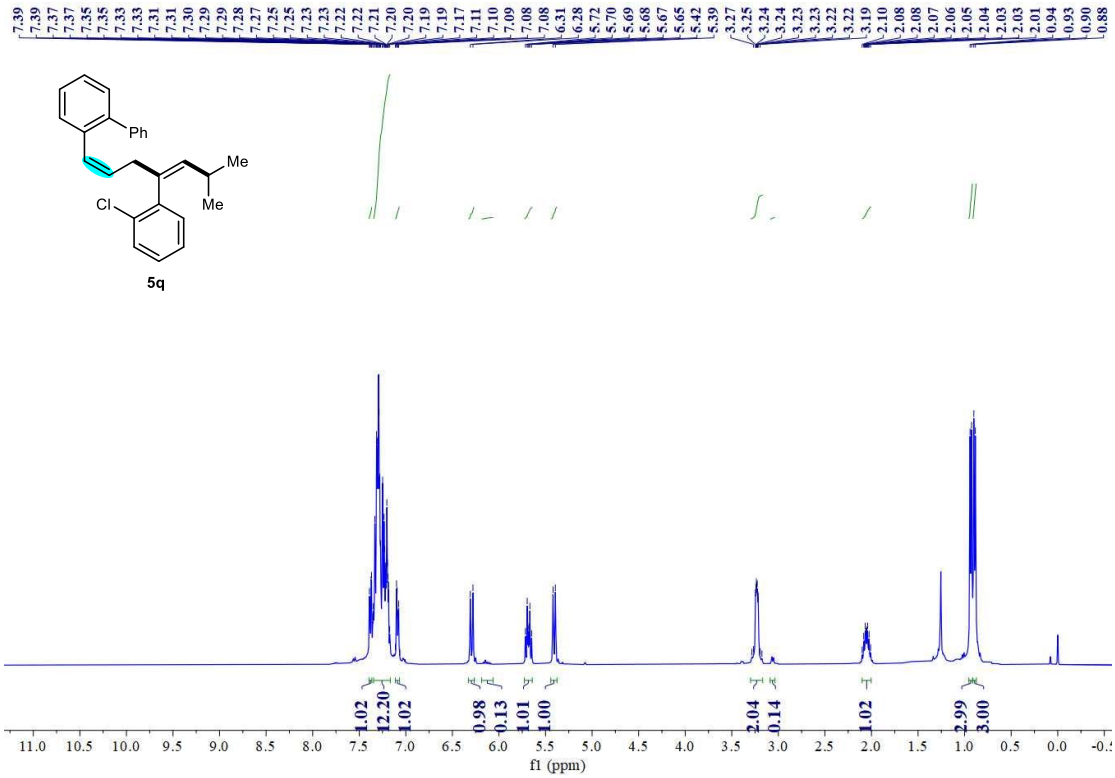


Figure S155. ^{1}H-NMR spectrum of **5q**

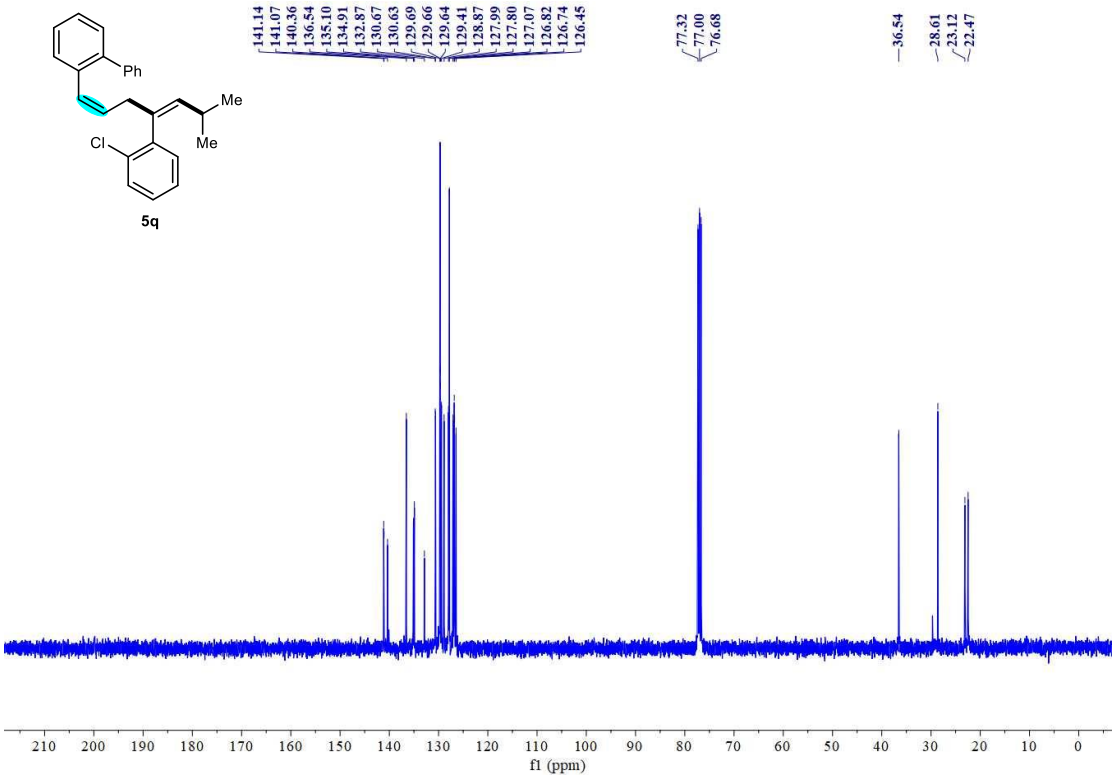


Figure S156. ^{13}C-NMR spectrum of **5q**

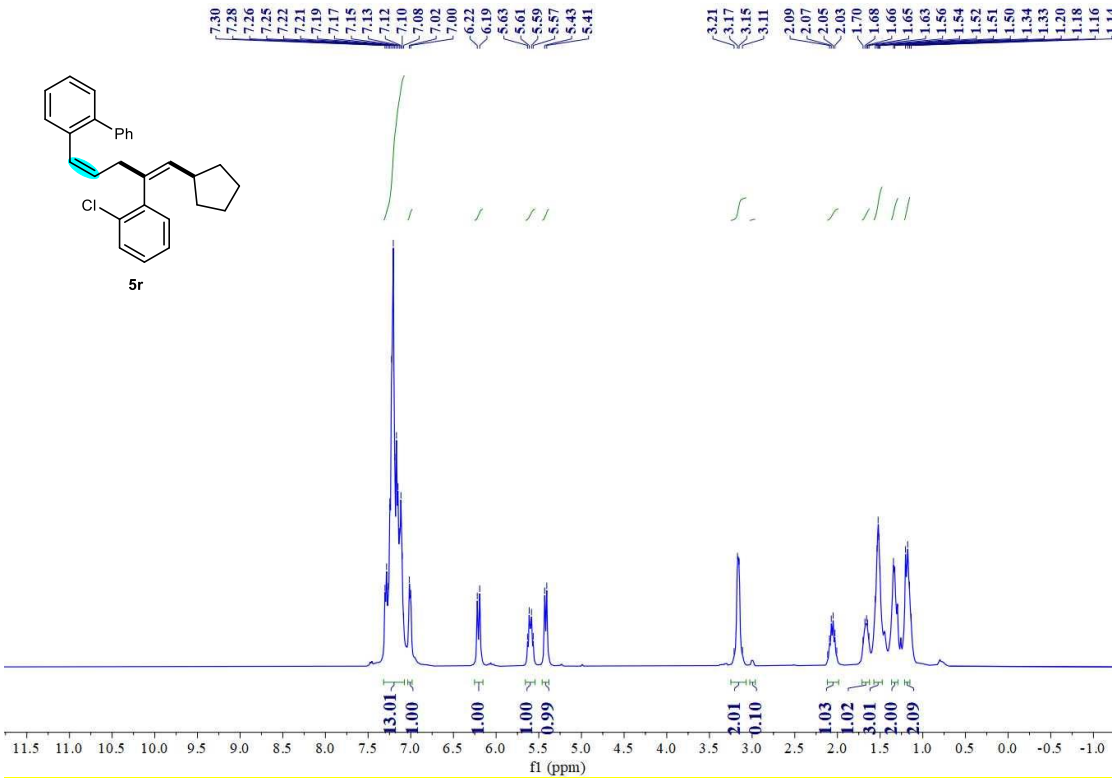


Figure S157. ^{1}H-NMR spectrum of **5r**

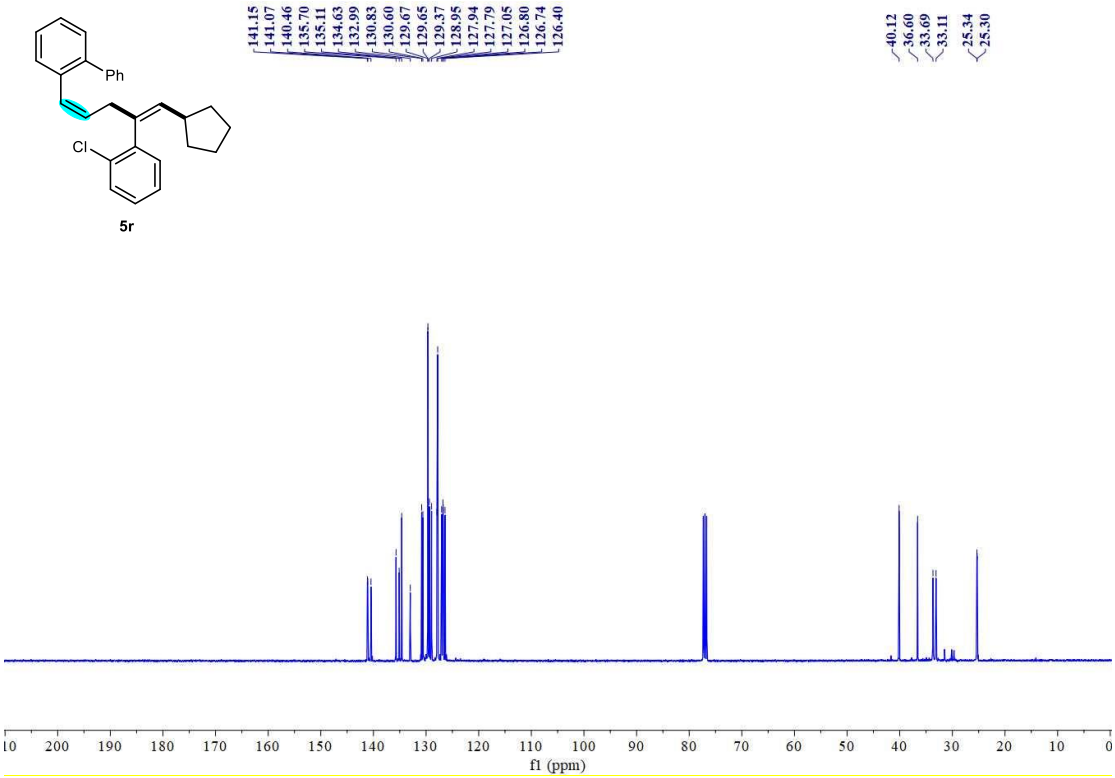


Figure S158. ^{13}C-NMR spectrum of **5r**

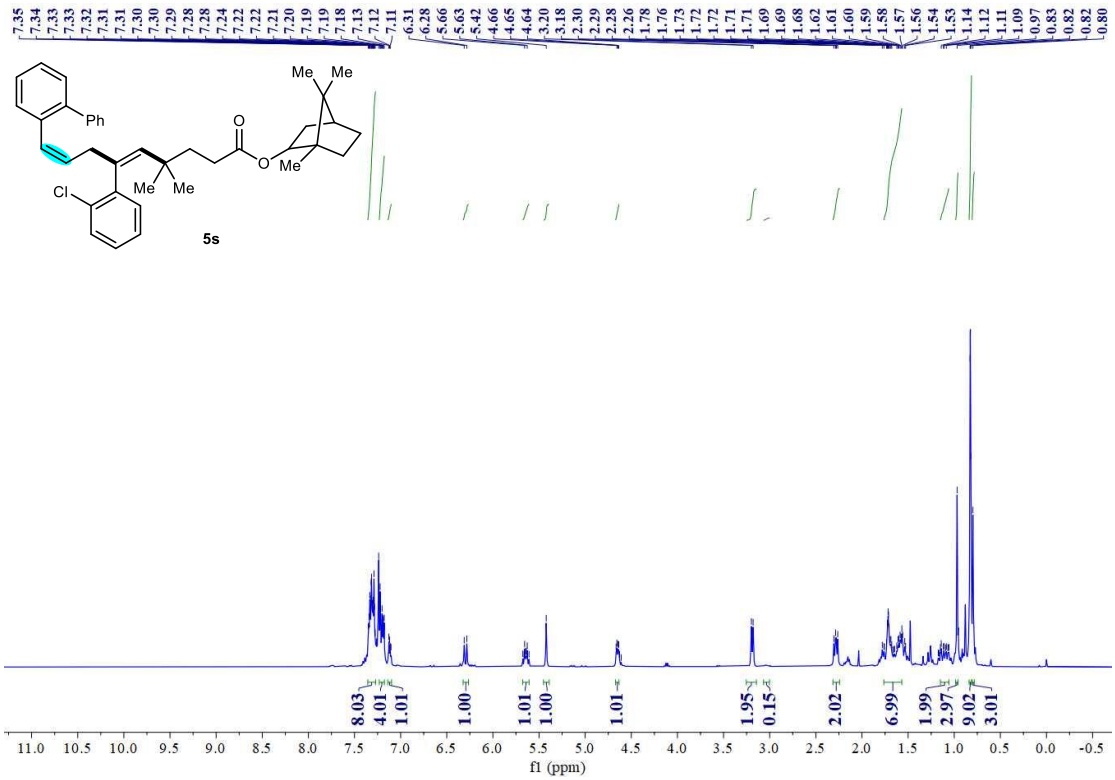


Figure S159. ^{1}H-NMR spectrum of **5s**

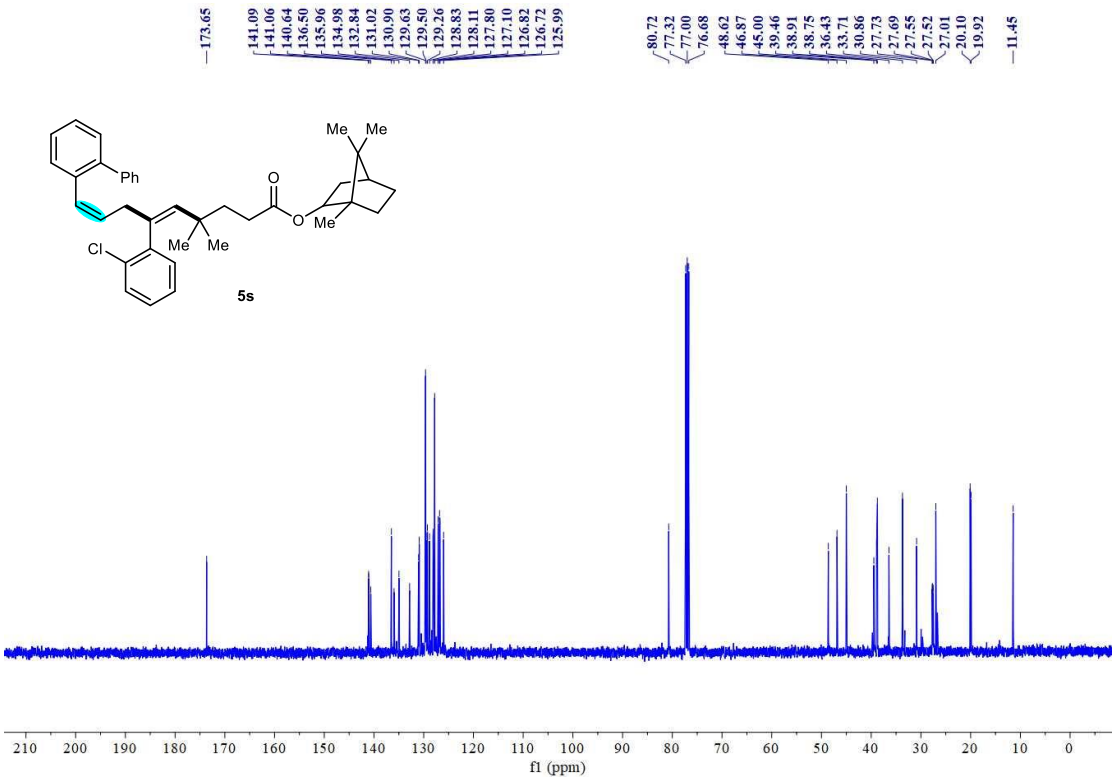


Figure S160. ^{13}C-NMR spectrum of **5s**

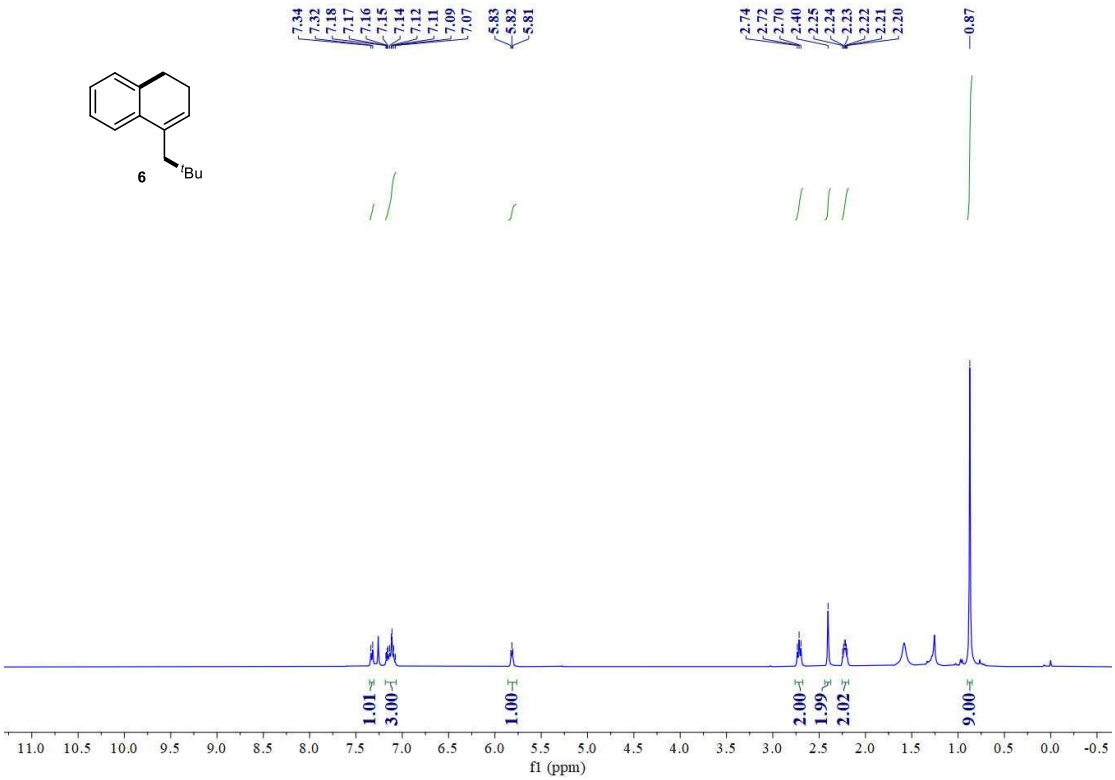


Figure S161. ^{1}H-NMR spectrum of **6**

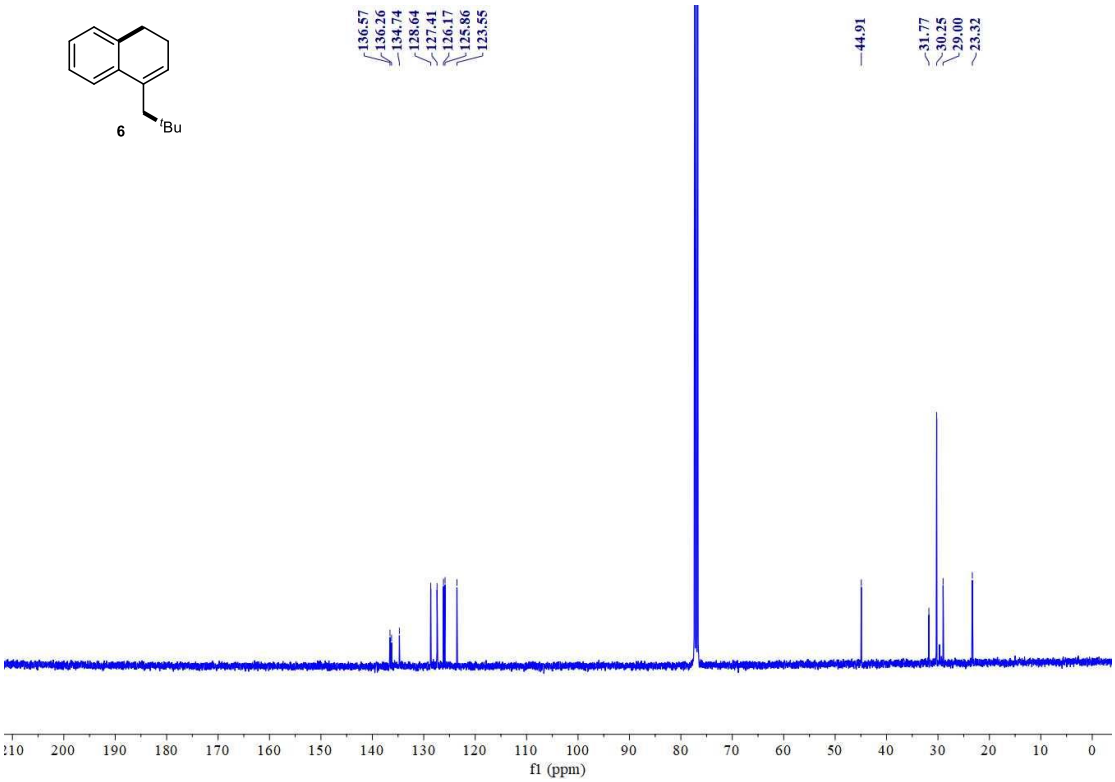


Figure S162. ^{13}C-NMR spectrum of **6**

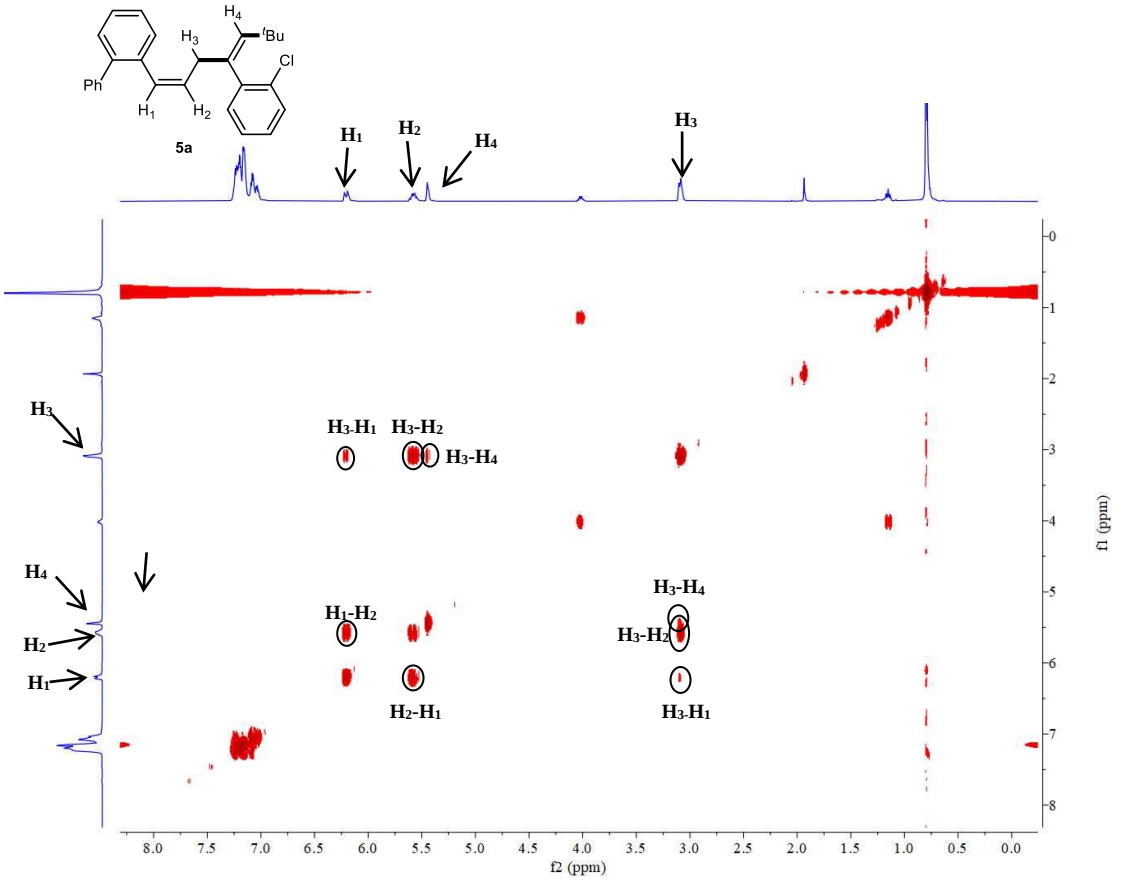


Figure S163. COSY spectrum of **5a**

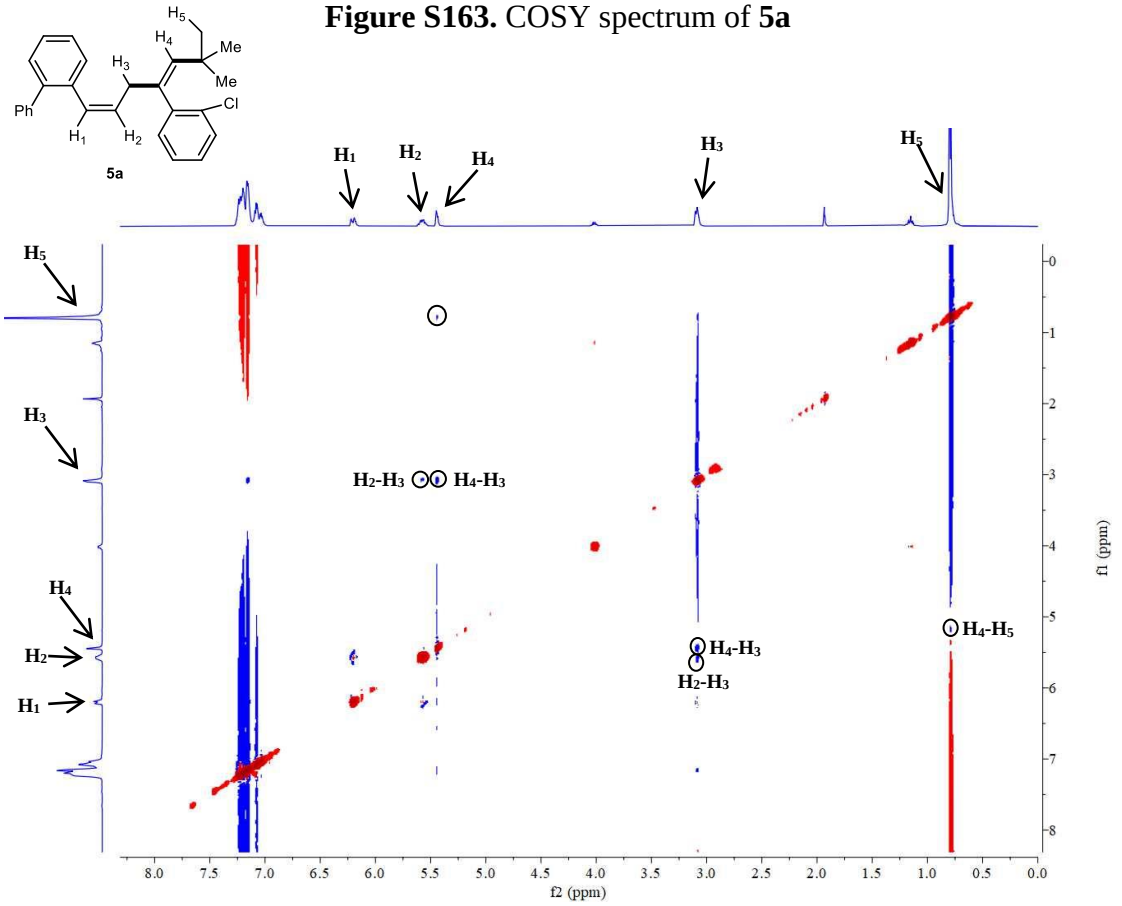


Figure S164. NOESY spectrum of **5a**

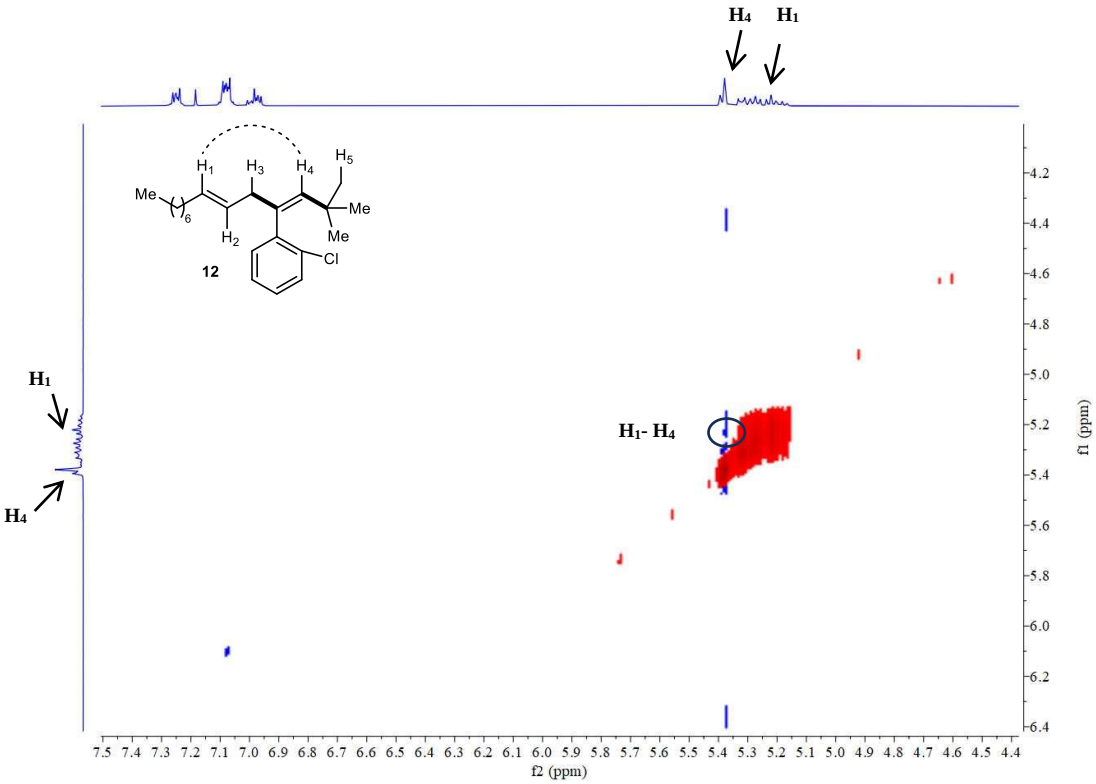


Figure S165. NOESY spectrum of **12**

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