Supporting Information

NHC and photoredox co-catalysis 1,4-alkylcarbonylation of 1,3-enynes

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1. General information

All the reactions were conducted in oven-dried Schlenk tubes. All solvents were obtained from commercial suppliers and used without further purification. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

^{1}H NMR (600 Hz), ^{13}C NMR (150 Hz) and ^{19}F NMR (564 Hz) were recorded in $CDCl_3$ using TMS as internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analyses were performed on a GC equipped with a flameionization detector and an Rtx@-65 (30 m × 0.32 mm ID × 0.25 μm df) column. GC-MS analyses were performed on a GC-MS with an EI mode. High-resolution mass spectra were obtained by ESI on a TOF mass analyzer. Blue LED (20 W, λ_{max} = 420 nm, UVA irradiance = 2.3 Mw/mm^2) purchased from CHEM^N KL100 was used for blue light irradiation. All thermal reactions were performed in an oil bath.

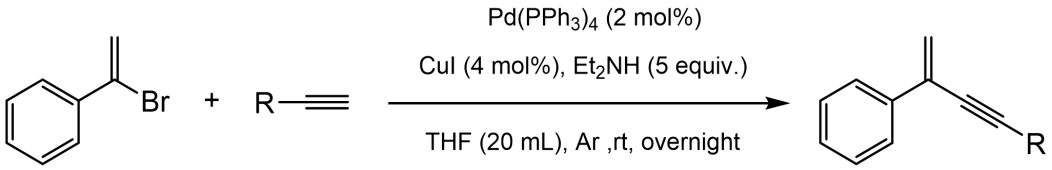
2. Preparation of substrates

Unless otherwise stated, all other purchased chemicals were of the highest purity available from Adamas, Macklin or TCI were used without further purification. Most alkylboronic acids and radical precursors were purchased from commercial sources. 1,3-enynes and acyl imidazole were prepared according to the reported procedures. All the characterization data are consistent with those in the reported literature.

2.1 Preparation of acyl imidazole[1]

To a round-bottomed flask, equipped with a magnetic stirrer, containing a solution of acid (5.0 mmol, 1.0 equiv.) in CH_2Cl_2 (25 mL) was added N,N'-carbonyldiimidazole (1.22 g, 7.5 mmol, 1.5 equiv.). The mixture was stirred at room temperature for 16 hours. Distilled water (25 mL) was added, and the layers were separated. The organic layer was washed with water (2 x 25 mL) and then brine (30 mL). The organic phase was then dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford the title compound.

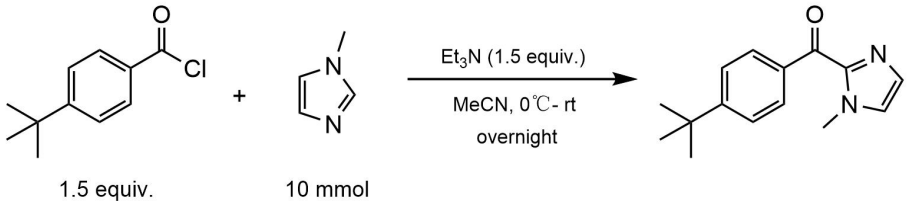
2.2 Preparation of 1,3-enynes[2]



To a Schlenk tube was equipped with magnetic stir bar was added CuI (38 mg, 4 mol%) , $Pd(PPh_3)_4$ (115 mg, 2 mol%), and diethyl amine (3.6 ml, 25 mmol, 5.0 equiv) in THF (20 ml). After that vinyl bromide (1.3 equiv) and alkyne (5.0 mmol, 1.0 equiv) were added into the mixture, which was then stirred at rt overnight under Ar atomsphere. Water was added into the system, followed by extraction with EA. The organic layers were combined, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel to give the titled product.

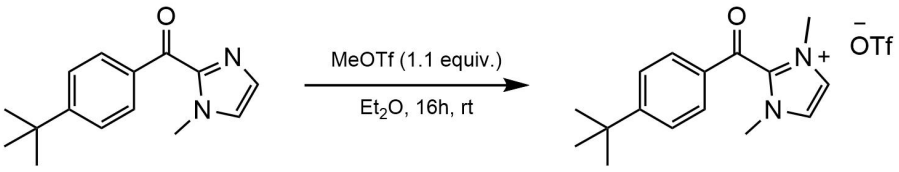
1,3-enyne (1a, 6a-6h) were synthesized using procedure 2.2. Spectral and physical data match literature reported values.

2.3 Preparation of N-methyl-C2-acyl imidazoles[3]



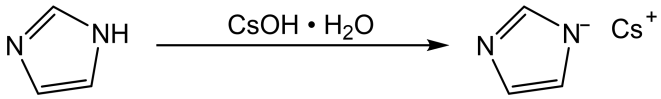
To a solution of 1-methylimidazole (821 mg, 790 μL, 10.0 mmol, 1.0 equiv.) and acid chloride (15.0 mmol, 1.5 equiv.) in anhydrous acetonitrile (30 mL) was added triethylamine (1.52 g, 2.1 mL, 15.0 mmol, 1.5 equiv.) dropwise at 0 °C. The reaction mixture was allowed to slowly warm up to rt and stirred overnight. After addition of water (25 mL), the phases were separated and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic phases were washed with brine (40 mL), dried over sodium sulfate and concentrated under vacuum. Purification by column chromatography on silica gel afforded 2-acyl imidazole.

2.4 Preparation of acyl azolium salt[3]



To a solution of 2-acyl imidazole (2.5 mmol, 1.0 equiv.) in anhydrous diethyl ether (25 mL) was added methyl triflate (451 mg, 311 μL, 2.75 mmol, 1.1 equiv.) at rt and the reaction mixture was stirred overnight. The resulting white precipitate was filtered off and washed with diethyl ether (3×10 mL). Drying under vacuum afforded acyl azolium salt.

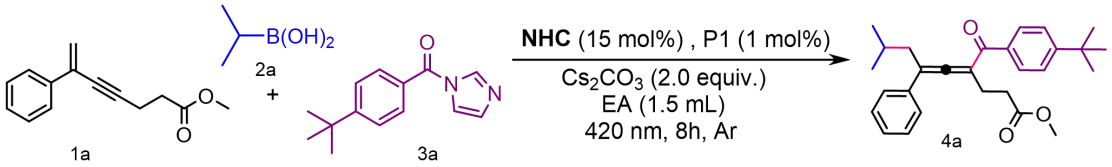
2.5 Preparation of Cs[imidazolide][4]



According to the literature, under a N_2 atmosphere, mixture of 1H-imidazole (1.07 g, 15.8 mmol) and $CsOH·H_2O$ (2.52 g, 15.0 mmol) was stirred at 95 ℃ overnight and then cooled to room temperature. THF (5 mL) was added into the mixture and stirred vigorously for 2 h at room temperature. After stirring, decanted off the THF and concentrated in vacuo. The resultant solid was dried at 100 ºC for 3 h to give cesium imidazolide as an orange brown solid.

3.Complementary Reaction Optimization Data

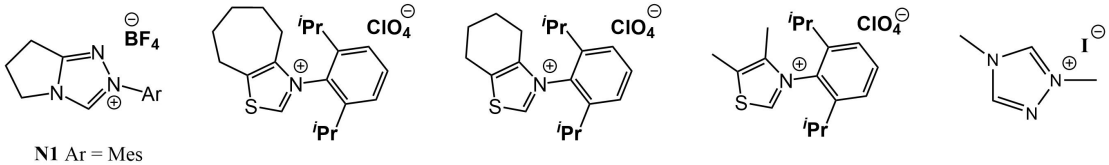
3.1 Table S1. Screening of NHC and Amount [a]



entry	NHC catalyst	amount	yield (%)[b]
1	**NHC1**	**15mol%**	**69**
2	NHC2	15mol%	0
3	NHC3	15mol%	trace
4	NHC4	15mol%	trace
5	NHC5	15mol%	0
6	NHC6	15mol%	12

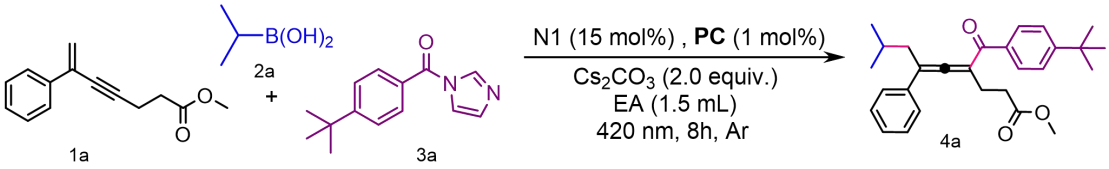
7	NHC1	10mol%	53
8	NHC1	5mol%	22
9	NHC1	2mol%	<10

[a] Reaction conditions: 1a (0.10 mmol), 2a (0.20 mmol), 3a (0.10 mmol), NHC (15.0 mol%), P1 (1.0 mol%), CS_2CO_3 (2.0 equiv), EA (1.5 mL), Ar atmosphere, rt for 8 h. [b] Isolated yield.



N1 Ar = Mes
N2 Ar = C_6H_5 **N3** **N4** **N5** **N6**

3.2 Table S2. Screening of photocatalysts[a]

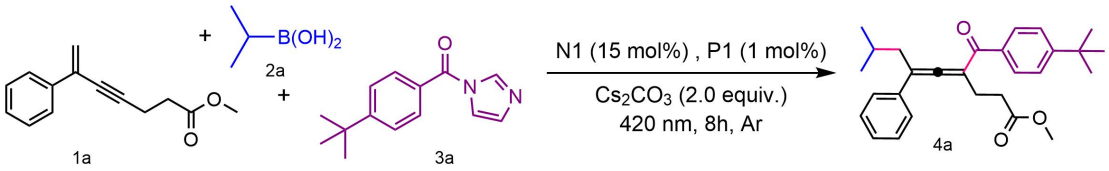


entry	photocatalysts	yield (%)[b]
1	**$[IrdF(CF_3)ppy_2(dtbbpy)]PF_6$**	**69**
2	$[Ir(ppy)_2(dtbbpy)]PF_6$	trace
3	4-CzIPN	35
4	$[Ir(dF(Me)ppy)]_2(dtbbpy)]PF_6$	26
5	$[Ru(bpy)_3](PF_6)_2$	trace
6	$[Ru(Phen)_3]Cl_2$	0
7	4DPAIPN	0

[a] Reaction conditions: 1a (0.10 mmol), 2a (0.20 mmol), 3a (0.10 mmol), N1 (15.0 mol%), PC (1.0 mol%), CS_2CO_3 (2.0 equiv), EA (1.5 mL), Ar atmosphere, rt for 8 h.

[b] Isolated yield.

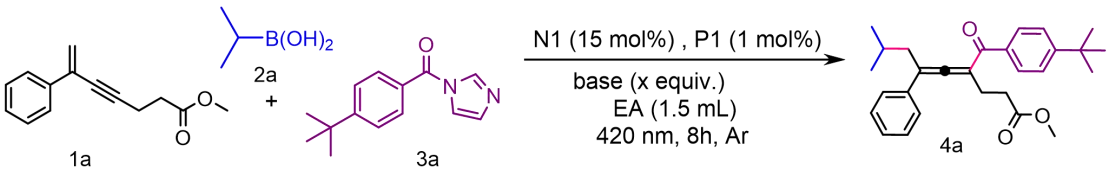
3.3 Table S3. Screening of solvent[a]



entry	solvent	yield (%)[b]
1	DCM	<10
2	Acetone	53
3	CH_3CN	trace
4	$CF_3COOC_2H_5$	<5
5	DMSO	<5
6	DMF	0
7	MA	60
8	EA:MA=2:1	62
9	**EA**	**69**

[a] Reaction conditions: 1a (0.10 mmol), 2a (0.20 mmol), 3a (0.10 mmol), N1 (15.0 mol%), P1 (1.0 mol%), CS_2CO_3 (2.0 equiv), solvent (1.5 mL), Ar atmosphere, rt for 8 h. [b] Isolated yield.

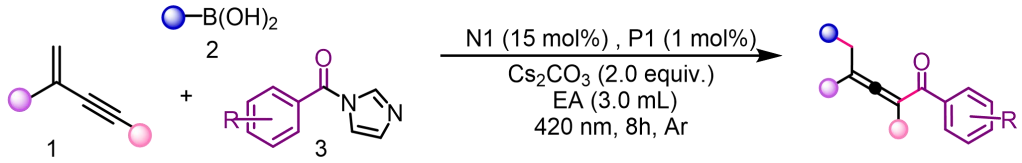
3.4 Table S4. Screening of Base and Amount[a]



entry	Base (x equiv.)	yield (%)[b]
1	**Cs_2CO_3 (2.0 equiv.)**	**69**
2	K_2CO_3 (2.0 equiv.)	<10
3	Na_2CO_3 (2.0 equiv.)	<5
4	K_2HPO_4 (2.0 equiv.)	trace
5	CH_3OLi (2.0 equiv.)	0
6	HCOONa (2.0 equiv.)	trace
7	$CsHCO_3$ (2.0 equiv.)	0
8	Cs_2CO_3 (1.0 equiv.)	47
9	Cs_2CO_3 (0.5 equiv.)	36
10	Cs_2CO_3 (2.5 equiv.)	64

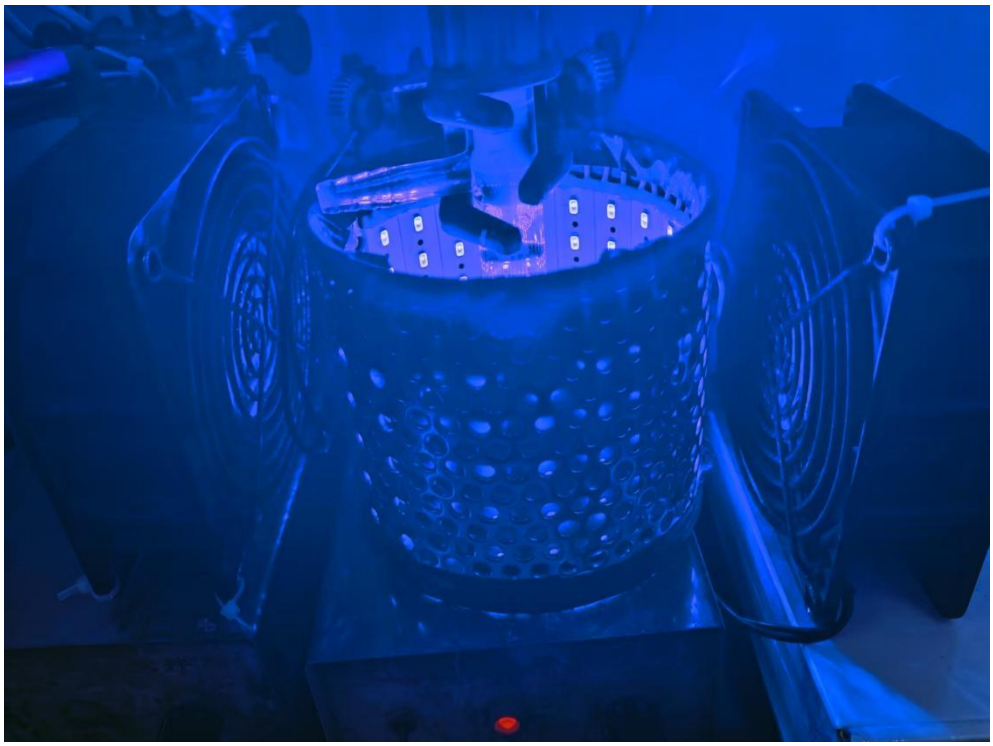
[a] Reaction conditions: 1a (0.10 mmol), 2a (0.20 mmol), 3a (0.10 mmol), N1 (15.0 mol%), P1 (1.0 mol%), base (x equiv), EA (1.5 mL), Ar atmosphere, rt for 8 h. [b] Isolated yield.

4.General procedure for the synthesis of 1,2-alkenyl ketones

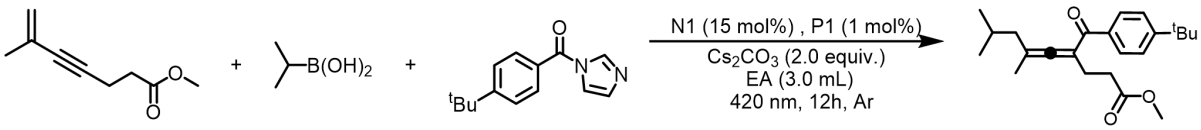


To a 10 mL of Schlenk tube were added carbene catalyst N1 (0.03 mmol, 9.5 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol, 2.2 mg), Cs_2CO_3 (0.4 mmol, 130.3 mg, 2.0 equiv.), alkyl boric acid (0.4 mmol, 2.0 equiv.) and acyl imidazole (0.2 mmol, 1.0 equiv.). The mixture was evacuated and backfilled with Ar (3 times). Subsequently, 1,3-enynes (0.2 mmol, 1.0 equiv.) and ethyl acetate (3.0 mL) were added successively. The mixture was stirred at room temperature for 8 hours while

irradiated by 20W Blue light (420 nm). After that, the residue was purified by silica gel chromatography using the mixture of n-hexane and ethyl acetate as an eluent to afford the product.



5. Elarge experiment

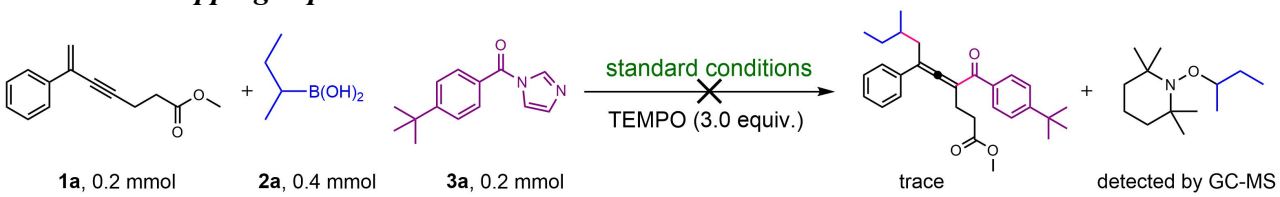


1, 5.0 mmol **2**, 10.0 mmol **3**, 5.0 mmol **6f**, 51%, 909 mg

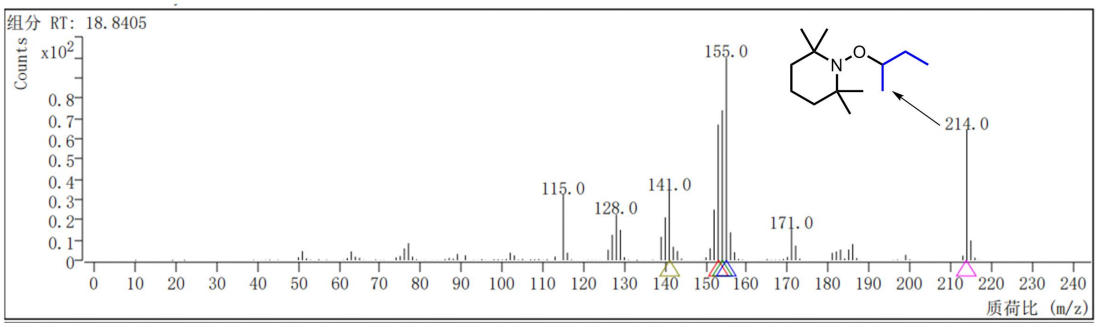
2 (10.0 mmol, 858.9 mg), **3** (5.0 mmol, 1.14 g), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.05 mmol, 56.2 mg) and N1 catalyst (0.75 mmol, 236.4 mg) and Cs_2CO_3 (10.0 mmol, 3.26 g) were placed in a 100 ml round-bottom flask. The mixture was evacuated and backfilled with Ar (3 times), and then adding ethyl acetate (55 mL) and **1** (5.0 mmol, 761.0 mg). The mixture was stirred at room temperature for 12 hours while irradiated by 20 W blue light with fans. After that, the residue was purified by silica gel chromatography using the mixture of n-hexane and ethyl acetate as an eluent to afford the product. Yield = (51%, 909 mg).

6.Mechanistic investigation

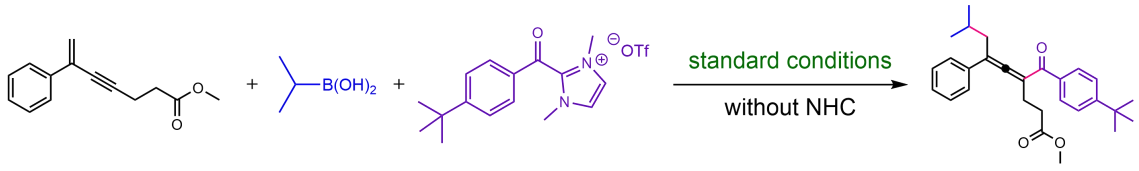
6.1 Radical trapping experiments:



1a, 0.2 mmol **2a**, 0.4 mmol **3a**, 0.2 mmol trace detected by GC-MS



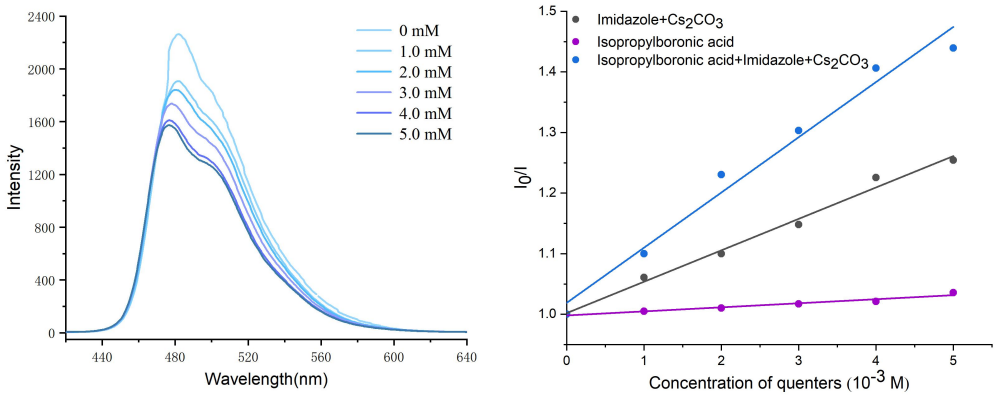
6.2 the acyl salt as substrates:



1a, 0.2 mmol **2a**, 0.4 mmol 1.0 equiv. **4a**, isolated 39%

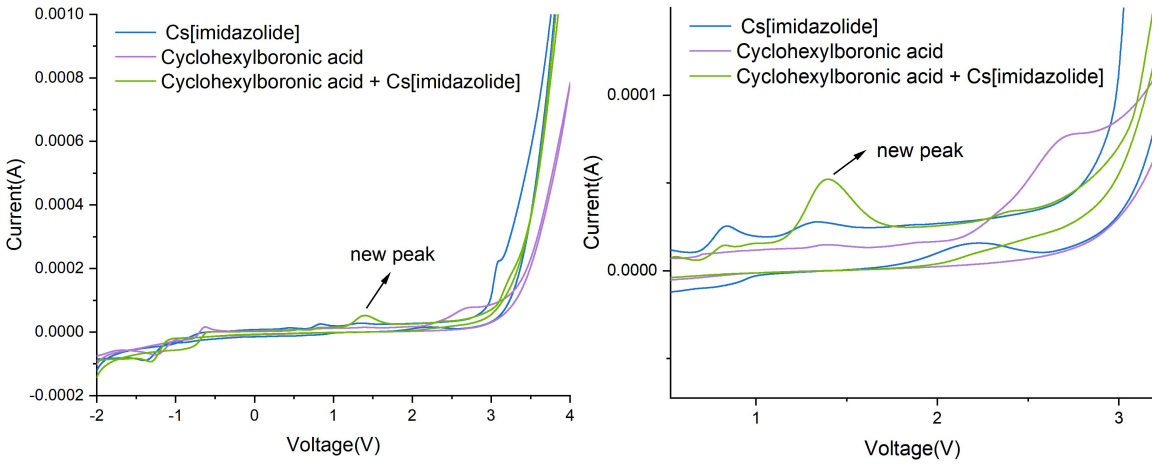
6.3 Stern-volmer quenching studies:

Emission intensities were recorded using a Hitachi-F-4600 Luminescence spectrometer. All $[IrdF(CF_3)ppy_2(dtbbpy)]PF_6$ solutions were excited at 400 nm and the emission intensity at 476 nm was observed. Firstly, the emission spectrum of a 1.0 × 10^{-4} M solution of $[IrdF(CF_3)ppy_2(dtbbpy)]PF_6$ in ethyl acetate was collected. After, an appropriate amount of quencher was added to the measured solution, and the emission spectrum of the sample was collected.

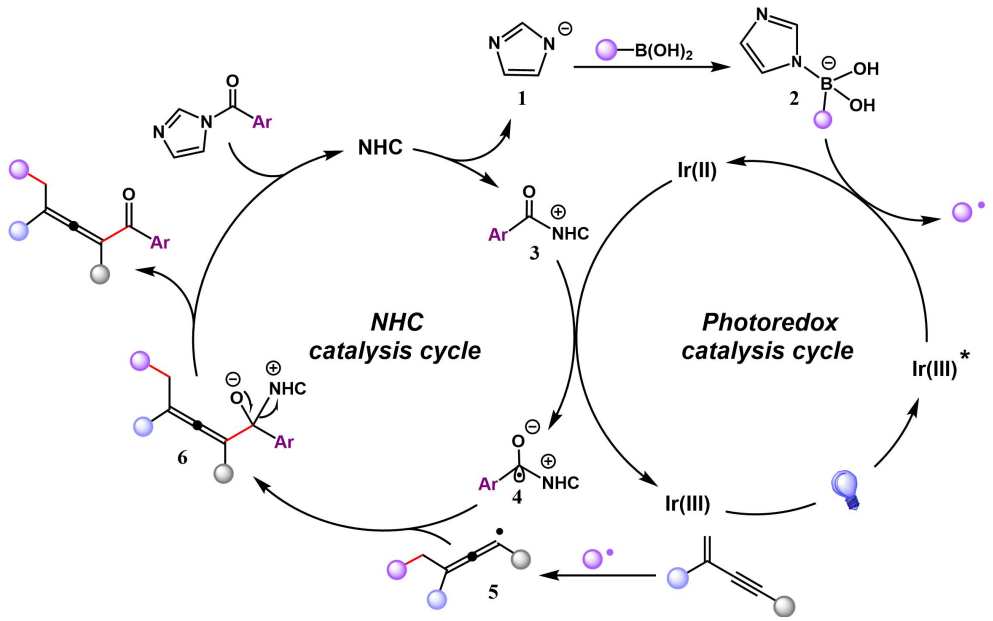


6.4 Cyclic Voltammogram experiments:

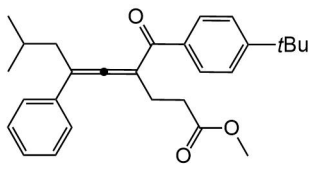
Cyclic voltammetry was conducted on an Electrochemical Workstation (CHI660E) using a three-electrode cell configuration at room temperature (25 ℃). A glassy carbon working electrode (diameter 3 mm) was employed alongside a platinum wire counter electrode and a Ag/AgCl reference electrode. Solvent was degassed by bubbling N_2 prior to measurements. Working electrode was polished on kraft paper with alumina powder with an intermediate particle size of 1.0 μm to 0.3 μm sequentially and washed with deionized water (5 mL), ethanol (5 mL) and MeCN (3 mL). Pt wire auxiliary electrode that washed with deionized water (5 mL), ethanol (5 mL) and MeCN (3 mL), a SCE reference electrode that washed with deionized water (5 mL), and MeCN (3 mL) respectively. In the standard procedure 0.02 mmol substrate were dissolved in 10 mL of a 0.1 M $[N(Bu)_4]PF_6$ electrolyte solution in degassed MeCN and were examined at a scan rate of 0.05 V. s^{-1} . The potential was calibrated versus an aqueous SCE by the addition of ferrocene as an internal standard taking $E_{(Fe/Fe+)}{}^0$ = + 0.424 V vs SCE. $E_{(Ag/Ag+)\ vs\ (Fe/Fe+)}$ = + 0.2 V. The cyclic voltammogram of a mixture of isopropylboronic acid and imidazole + Cs_2CO_3 was measured. In the voltammogram, beside the peaks of the boronic acid, it is possible to observe a new local maximum, which is related to the species formed through the interaction between boronic acid and imidazole ions in the mixture. CV plotting convention is IUPAC.



6.5 plausible mechanism:



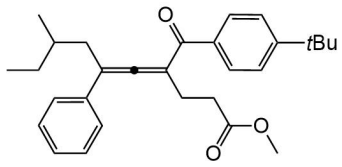
7.Charaterization of product



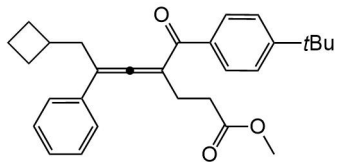
Methyl 8-methyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylnona-4,5-dienoate (4a).

Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (57.7 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.58 (s, 3H), 2.92 – 2.83 (m, 2H), 2.59 (td, *J* = 7.3, 2.5 Hz, 2H), 2.36 – 2.27 (m, 2H), 1.72 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.26 (s, 9H), 0.81 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.0, 194.1, 173.2, 155.5, 135.7, 134.8, 128.6, 128.4, 127.5, 126.5, 124.8, 109.4, 107.8, 51.5, 40.0, 34.8, 32.4, 31.0, 26.9, 24.5, 22.4, 22.4.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{35}O_3^+$: 419.2581; Found: 419.2570.
IR cm^{-1} : 3084, 3057, 3028, 2953, 2867,1925, 1737, 1646, 1603, 1562, 1493, 1435, 1406, 1364, 1311, 1267, 1191, 1165, 1122, 1103, 1015, 990, 870, 847, 762, 694.

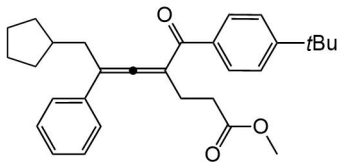


methyl 8-methyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenyldeca-4,5-dienoate (4b).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (55.4 mg, 64%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (t, *J* = 8.0 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.26 – 7.23 (m, 2H), 3.58 (d, *J* = 14.6 Hz, 3H), 2.91 – 2.83 (m, 2H), 2.58 (dq, *J* = 11.6, 4.2 Hz, 2H), 2.45 (dd, *J* = 14.6, 6.4 Hz, 1H), 2.21 (ddd, *J* = 14.6, 7.8, 3.2 Hz, 1H), 1.51 – 1.45 (m, 1H), 1.26 (s, 9H), 1.08 – 0.99 (m, 1H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.75 (d, *J* = 3.8 Hz, 1H), 0.70 (dd, *J* = 36.8, 7.0 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.2, 213.1, 194.3, 194.1, 173.3, 173.2, 155.6, 155.6, 135.8, 135.7, 135.0, 134.9, 128.7, 128.5, 128.5, 127.6, 126.6, 126.6, 124.8, 124.8, 109.5, 109.3, 108.1, 107.7, 51.6, 38.2, 38.0, 34.9, 33.3, 33.2, 32.5, 32.4, 31.1, 29.4, 29.3, 24.6, 24.5, 19.1, 19.1, 11.4, 11.3.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{37}O_3^+$: 433.2738; Found: 433.2724.
IR cm^{-1} : 3084, 3057, 3027, 2957, 2926, 2871, 1925, 1737, 1646, 1604, 1493, 1435, 1406, 1362, 1311, 1268, 1191, 1163, 1122, 1103, 1015, 989, 870, 847, 760, 694.

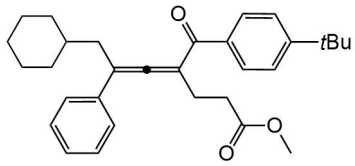


methyl 7-cyclobutyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylhepta-4,5-dienoate (4c).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (37.0 mg, 43%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 3.57 (s, 3H), 2.93 – 2.87 (m, 1H), 2.82 (dt, *J* = 15.2, 7.2 Hz, 1H), 2.57 (dt, *J* = 7.3, 3.5 Hz, 2H), 2.53 (d, *J* = 7.4 Hz, 2H), 2.38 (p, *J* = 7.7 Hz, 1H), 1.87 (ddt, *J* = 20.5, 7.4, 3.8 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.55 – 1.45 (m, 2H), 1.25 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.9, 193.9, 173.3, 155.6, 135.6, 134.8, 128.7, 128.5, 127.6, 126.4, 124.8, 109.1, 108.6, 51.6, 37.6, 34.9, 34.1, 32.3, 31.1, 28.4, 28.2, 24.5, 18.2.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{35}O_3^+$: 431.2581; Found: 431.2576.
IR cm^{-1} : 3084, 3057, 3028, 2963, 2864, 1927, 1737, 1646, 1603, 1560, 1493, 1435, 1406, 1362, 1268, 1191, 1163, 1121, 1102, 1015, 989, 913, 878, 848, 786, 756, 693.

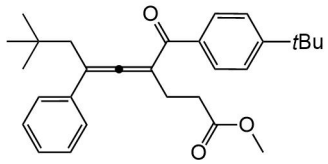


methyl 7-cyclopentyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylhepta-4,5-dienoate (4d).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (56.0 mg, 63%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.37 (dd, *J* = 13.7, 6.6 Hz, 4H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 3H), 2.92 – 2.82 (m, 2H), 2.59 (td, *J* = 7.4, 2.2 Hz, 2H), 2.44 (d, *J* = 7.3 Hz, 2H), 1.92 (p, *J* = 7.6 Hz, 1H), 1.68 – 1.54 (m, 2H), 1.49 (q, *J* = 5.2, 4.5 Hz, 2H), 1.42 – 1.36 (m, 2H), 1.26 (s, 9H), 0.99 (ddd, *J* = 21.0, 12.3, 7.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.2, 194.1, 173.3, 155.6, 135.7, 134.9, 128.7, 128.5, 127.6, 126.5, 124.8, 110.2, 108.2, 51.6, 38.3, 37.2, 34.9, 32.7, 32.6, 32.4, 31.1, 25.2, 25.1, 24.5.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{37}O_3^+$: 445.2738; Found: 445.2744.
IR cm^{-1} : 3084, 3057, 3028, 2950, 2866, 1925, 1736, 1646, 1603, 1562, 1493, 1435, 1405, 1362, 1311, 1268, 1191, 1162, 1122, 1103, 1014, 988, 875, 847, 759, 693.

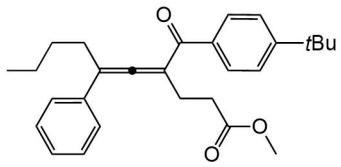


methyl 7-cyclohexyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylhepta-4,5-dienoate (4e).
Following general procedure A, the product was purified by flash chromatography (PE/EA =100:1) colorless oil (66.0 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.26 – 7.23 (m, 2H), 3.57 (s, 3H), 2.86 (td, *J* = 7.3, 5.2 Hz, 2H), 2.58 (td, *J* = 7.4, 3.6 Hz, 2H), 2.30 (h, *J* = 7.2 Hz, 2H), 1.63 – 1.52 (m, 4H), 1.48 (d, *J* = 14.1 Hz, 1H), 1.26 (s, 9H), 1.04 – 0.69 (m, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.3, 194.3, 173.3, 155.6, 135.9, 134.9, 128.7, 128.5, 127.5, 126.6, 124.8, 109.0, 107.8, 51.6, 38.5, 36.5, 34.9, 33.3, 33.2, 32.4, 31.1, 26.3, 26.2, 26.1, 24.5.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{39}O_3^+$: 459.2894; Found: 459.2883.
IR cm^{-1} : 3084, 3057, 3028, 2921, 2850, 1924, 1737, 1646, 1604, 1494, 1448, 1405, 1363, 1311, 1267, 1192, 1164, 1123, 1101, 1012, 986, 877, 847, 760, 694.

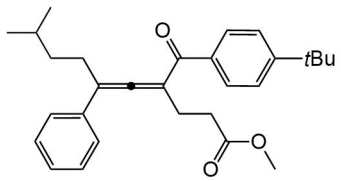


methyl 8,8-dimethyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylnona-4, 5-dienoate (4f).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (36.3 mg, 42%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 6.5 Hz, 4H), 7.28 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.61 (s, 3H), 2.92 (dt, *J* = 15.1, 7.6 Hz, 1H), 2.84 (dt, *J* = 14.9, 7.5 Hz, 1H), 2.62 (td, *J* = 7.6, 2.9 Hz, 2H), 2.39 (d, *J* = 14.1 Hz, 1H), 2.31 (d, *J* = 14.1 Hz, 1H), 1.26 (s, 9H), 0.77 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 214.4, 194.5, 173.3, 155.6, 136.6, 135.8, 128.6, 128.6, 127.4, 126.8, 124.8, 108.4, 106.5, 51.6, 44.2, 34.9, 32.6, 32.2, 31.0, 29.9, 24.8.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{37}O_3^+$: 433.2738; Found: 433.2728.
IR cm^{-1} : 3084, 3057, 3025, 2952, 2866, 1923, 1737, 1646, 1604, 1562, 1494, 1464, 1436, 1406, 1363, 1312, 1268, 1191, 1166, 1121, 1103, 1028, 989, 868, 847, 771, 695.

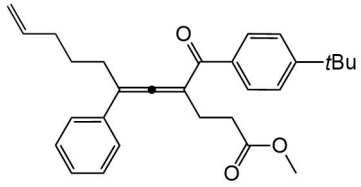


methyl 4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenyldeca-4,5-dienoate (4 g).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (49.4 mg, 59%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 3.56 (s, 2H), 2.87 (tt, *J* = 15.6, 8.0 Hz,

1H), 2.57 (td, *J* = 7.3, 3.2 Hz, 1H), 2.46 (dd, *J* = 9.0, 6.4 Hz, 1H), 1.39 (p, *J* = 7.5 Hz, 2H), 1.26 (s, 5H), 0.84 (t, *J* = 7.2 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.7, 194.0, 173.3, 155.6, 135.7, 134.7, 128.7, 128.6, 127.6, 126.4, 124.8, 110.7, 108.7, 51.8, 51.6, 34.9, 32.3, 31.1, 30.2, 30.0, 24.4, 22.5, 13.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{35}O_3^+$: 419.2581; Found: 419.2584.
IR cm^{-1} : 3085, 3057, 3026, 3026, 2957, 2870, 1928, 1738, 1647, 1604, 1562, 1494, 1436, 1406, 1363, 1312, 1268, 1192, 1164, 1121, 1103, 1016, 990, 912, 874, 848, 782, 756, 693.



methyl 9-methyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenyldeca-4,5-dienoate (4h).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (45.9 mg, 52%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 3H), 3.56 (s, 3H), 2.91 – 2.82 (m, 2H), 2.56 (td, *J* = 7.5, 3.0 Hz, 2H), 2.46 (td, *J* = 7.2, 2.7 Hz, 2H), 1.49 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.33 (dd, *J* = 11.4, 6.0 Hz, 2H), 1.27 (s, 9H), 0.85 (dd, *J* = 6.7, 4.9 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.7, 194.0, 173.3, 155.6, 135.7, 134.6, 128.7, 128.6, 127.6, 126.4, 124.8, 110.7, 108.7, 51.6, 36.8, 34.9, 32.3, 31.1, 28.5, 27.9, 24.3, 22.4.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{34}NaO_3^+$: 455.2557; Found: 455.2549.
IR cm^{-1} : 3084, 3057, 3025, 2953, 2868, 1927, 1738, 1647, 1604, 1562, 1494, 1436, 1406, 1384, 1364, 1312, 1269, 1191, 1164, 1121, 1103, 1015, 991, 875, 848, 785, 761, 694.



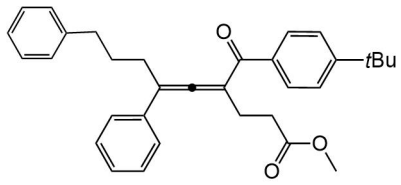
methyl 4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylundeca-4,5,10-trienoate (4i).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (49.1 mg, 57%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.25 (m, 2H), 5.72 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 4.95 – 4.90 (m, 2H), 3.56 (s, 3H), 2.91 – 2.83 (m, 2H), 2.57 (td, *J* =

7.3, 3.5 Hz, 2H), 2.47 (td, *J* = 7.2, 2.1 Hz, 2H), 2.01 (d, *J* = 6.0 Hz, 2H), 1.50 (q, *J* = 7.3 Hz, 2H), 1.26 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 212.6, 193.9, 173.2, 155.7, 138.0, 135.6, 134.6, 128.7, 128.56, 127.7, 126.4, 124.8, 115.1, 110.5, 108.9, 51.6, 34.9, 33.3, 32.3, 31.1, 29.8, 29.7, 24.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{35}O_3^+$: 431.2581; Found: 431.2581.

IR cm^{-1} : 3084, 3061, 3026, 2950, 2925, 2855, 1928, 1738, 1647, 1604, 1562, 1494, 1436, 1406, 1363, 1312, 1269, 1192, 1165, 1121, 1103, 1015, 991, 912, 878, 848, 794, 762, 694.



methyl 4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6,9-diphenylnona-4,5-dienoate (4j).

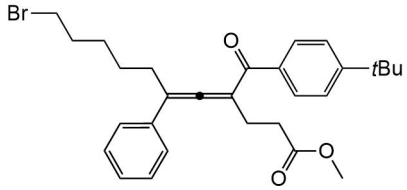
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (45.2 mg, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 7H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 3.54 (s, 3H), 2.88 (tt, *J* = 15.6, 8.1 Hz, 2H), 2.60 – 2.54 (m, 4H), 2.50 – 2.47 (m, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.24 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 212.5, 193.9, 173.2, 155.7, 141.6, 135.6, 134.5, 128.7, 128.6, 128.4, 128.4, 127.7, 126.4, 125.9, 124.9, 110.4, 109.0, 51.6, 35.4, 34.9, 32.3, 31.1, 29.8, 29.3, 24.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{37}O_3^+$: 481.2738; Found: 481.2708.

IR cm^{-1} : 3084, 3057, 3026, 2950, 2865, 1927, 1736, 1644, 1603, 1562, 1494, 1451, 1435, 1406, 1362, 1311, 1268, 1191, 1163, 1121, 1102, 1028, 988, 877, 848, 762, 747, 694.



methy l11-bromo-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylundeca-4,5-dienoate (4k).

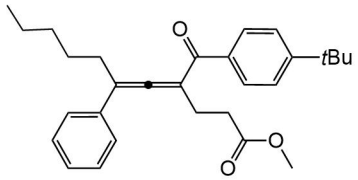
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (52.2 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 5H), 3.56 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.91 – 2.84 (m, 2H), 2.57 (td, *J*

= 7.3, 3.3 Hz, 2H), 2.47 (t, *J* = 7.8 Hz, 2H), 1.79 – 1.74 (m, 2H), 1.40 (dt, *J* = 21.7, 6.9 Hz, 5H), 1.27 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 212.47, 193.75, 173.22, 155.83, 135.64, 134.57, 128.79, 128.60, 127.75, 126.39, 124.90, 110.41, 108.93, 51.61, 34.99, 33.56, 32.51, 32.37, 31.10, 30.34, 29.74, 27.95, 27.00, 24.43, 22.73.

IR cm^{-1} : 3084, 3057, 3026, 2954, 2863, 1928, 1736, 1646, 1605, 1562, 1494, 1450, 1435, 1364, 1311, 1268, 1192, 1163, 1102, 1065, 1028, 877, 848, 782, 754, 694, 647, 559.



methyl 4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylundeca-4,5-dienoate (4l).

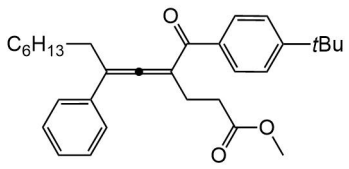
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (41.5 mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.27 – 7.25 (m, 3H), 3.56 (s, 3H), 2.91 – 2.82 (m, 2H), 2.57 (td, *J* = 7.3, 3.9 Hz, 2H), 2.47 – 2.44 (m, 2H), 1.40 (dt, *J* = 14.0, 6.2 Hz, 2H), 1.26 (s, 9H), 1.24 (q, *J* = 3.6 Hz, 4H), 0.82 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 212.6, 193.9, 173.3, 155.6, 135.6, 134.7, 128.7, 128.6, 127.6, 126.4, 126.3, 124.8, 110.7, 108.7, 51.6, 51.5, 34.9, 32.3, 31.6, 31.1, 30.5, 27.51, 24.4, 22.4, 14.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{37}O_3^+$: 433.2738; Found: 433.2721.

IR cm^{-1} : 3084, 3057, 3024, 2955, 2861, 1929, 1739, 1647, 1604, 1562, 1494, 1436, 1363, 1311, 1268, 1192, 1164, 1103, 1026, 877, 848, 781, 756, 693.

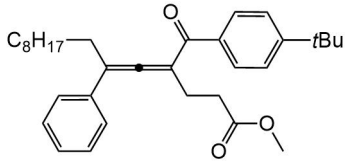


methyl 4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenyltrideca-4,5-dienoate (4m).

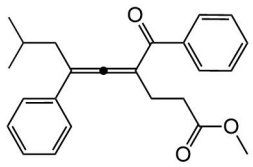
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (49.7 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 3H), 3.56 (s, 3H), 2.91 – 2.82 (m, 2H), 2.56 (dt, *J* = 8.7, 4.8 Hz, 2H), 2.45 (t, *J* = 8.3 Hz, 2H), 1.43 – 1.31 (m, 4H), 1.26 (d, *J* = 1.3 Hz, 9H), 1.22 – 1.10 (m, 6H), 0.86 (td, *J* = 7.2, 1.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 212.6, 193.9, 173.3, 155.6, 135.2, 134.7, 128.7, 128.6, 127.6, 126.4, 124.8, 110.7, 108.7, 51.6, 34.9, 32.3, 31.7, 31.1, 30.5, 29.5, 29.1, 27.8, 23.9, 22.6, 14.1.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{41}O_3^+$: 461.3051; Found: 461.3049.
IR cm^{-1} : 3088, 3063, 3025, 2954, 2926, 2855, 1927, 1739, 1647, 1604, 1494, 1436, 1406, 1363, 1268, 1192, 1164, 1103, 1015, 876, 847, 782, 758, 694.

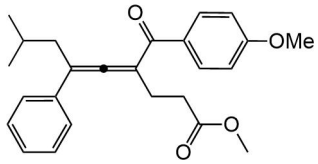


methyl 4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}-6-phenylpentadeca-4,5-dienoate (4n).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (43.9 mg, 45%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.31 (d, *J* = 7.1 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 3H), 3.56 (s, 3H), 2.92 – 2.81 (m, 2H), 2.57 (td, *J* = 7.3, 4.0 Hz, 2H), 2.47 – 2.44 (m, 2H), 1.43 – 1.37 (m, 2H), 1.33 – 1.28 (m, 2H), 1.27 (s, 9H), 1.26 – 1.16 (m, 10H), 0.88 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.6, 193.9, 173.2, 155.6, 135.6, 134.7, 128.7, 128.6, 127.6, 126.4, 124.8, 110.7, 108.7, 51.5, 34.9, 32.3, 31.9, 31.1, 30.5, 29.5, 29.5, 29.4, 29.3, 27.84 24.4, 22.7, 14.1.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{45}O_3^+$: 489.3364; Found: 489.3369.
IR cm^{-1} : 3085, 3059, 3025, 2954, 2925, 2854, 1927, 1737, 1645, 1603, 1577, 1493, 1446, 1363, 1314, 1270, 1171, 1148, 1104, 1012, 942, 876, 846, 768, 723, 694.

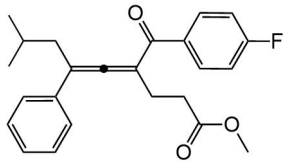


methyl 4-benzoyl-8-methyl-6-phenylnona-4,5-dienoate (5a).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (43.5 mg, 60%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.7 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.23 (t, *J* = 7.7 Hz, 2H), 3.60 (s, 3H), 2.93 – 2.83 (m, 2H), 2.61 (td, *J* = 7.3, 2.7 Hz, 2H), 2.34 – 2.30 (m, 1H), 2.25 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.71 (dt, *J* = 13.5, 6.7 Hz, 1H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.6, 194.8, 173.3, 138.6, 134.8, 131.9, 128.7, 128.5, 127.8, 127.7, 126.6, 109.9, 108.0, 51.6, 40.1, 32.5, 26.9, 24.4, 22.6, 22.4.

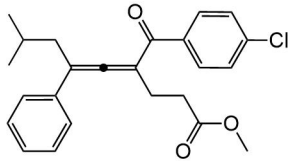
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{26}NaO_3^+$: 385.1775; Found: 385.1769.
IR cm^{-1} : 3087, 3059, 3026, 2953, 2868, 1926, 1738, 1650, 1597, 1578, 1494, 1446, 1436, 1365, 1267, 1198, 1166, 1119, 1025, 991, 781, 755, 711, 693.



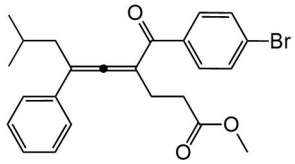
methyl 4-[(4-methoxyphenyl)carbonyl]-8-methyl-6-phenylnona-4,5-dienoate (5b).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (58.1 mg, 74%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 10.2 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.59 (s, 3H), 2.92 – 2.82 (m, 2H), 2.60 (td, *J* = 7.5, 7.0, 2.0 Hz, 2H), 2.36 (dd, *J* = 15.8, 6.6 Hz, 1H), 2.27 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.74 (hept, *J* = 6.7 Hz, 1H), 0.84 – 0.81 (m, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.3, 192.9, 173.3, 162.8, 135.1, 131.1, 131.0, 128.7, 127.6, 126.6, 113.1, 109.4, 107.6, 55.3, 51.6, 40.1, 32.5, 26.9, 24.7, 22.7, 22.4.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}O_4^+$: 393.2061; Found: 393.2048.
IR cm^{-1} : 3054, 3023, 3002, 2953, 2917, 2867, 1926, 1735, 1642, 1597,1573, 1508, 1462, 1436, 1362, 1309, 1251, 1166, 1109, 1027, 989, 869, 841, 763, 695.



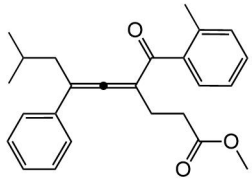
methyl-4-[(4-fluorophenyl)carbonyl]-8-methyl-6-phenylnona-4,5-dienoate (5ca).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (38.0 mg, 50%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.3, 5.8 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.28 (m, 3H), 6.89 (t, *J* = 8.6 Hz, 2H), 3.60 (s, 3H), 2.87 (h, *J* = 8.1, 7.6 Hz, 2H), 2.61 (td, *J* = 7.5, 3.5 Hz, 2H), 2.34 (dd, *J* = 14.5, 6.4 Hz, 1H), 2.24 (dd, *J* = 14.6, 7.6 Hz, 1H), 1.73 – 1.68 (m, 1H), 0.80 (dd, *J* = 11.8, 6.6 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.4, 193.2, 173.2, 165.03 (d, $J_{C\text{-}F}$ = 252.0 Hz), 134.7, 134.6, 131.1 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.8, 127.8, 126.5, 114.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 110.1, 107.8, 77.2, 77.0, 76.8, 51.7, 40.0, 32.4, 26.9, 24.4, 22.6, 22.4.
^{19}F NMR (564 MHz, $CDCl_3$) δ -106.96.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}FO_3^+$: 381.1861; Found: 381.1852.
IR cm^{-1} : 3085, 3059, 3026, 2954, 2926, 2868, 1926, 1736, 1649, 1597, 1504, 1494, 1436, 1365, 1262, 1226, 1154, 1116, 1013, 991, 870, 847, 761, 694.



methyl-4-[(4-chlorophenyl)carbonyl]-8-methyl-6-phenylnona-4,5-dienoate (5cb).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (46.0 mg, 58%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 3H), 7.19 (d, *J* = 8.5 Hz, 2H), 3.60 (s, 3H), 2.90 – 2.83 (m, 2H), 2.60 (td, *J* = 7.4, 3.4 Hz, 2H), 2.35 (dd, *J* = 14.6, 6.5 Hz, 1H), 2.23 (dd, *J* = 14.6, 7.7 Hz, 1H), 1.74 – 1.69 (m, 1H), 0.80 (dd, *J* = 10.4, 6.6 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.6, 193.4, 173.2, 138.2, 136.8, 134.6, 130.0, 128.8, 128.1, 127.9, 126.5, 110.2, 107.9, 77.2, 77.0, 76.8, 51.7, 40.0, 32.4, 26.9, 24.3, 22.6, 22.4.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}ClO_3H^+$: 397.1565; Found: 391.1570.
IR cm^{-1} : 3084, 3057, 3028, 2955, 2868, 1927, 1739, 1651, 1590, 1487, 1436, 1398, 1365, 1261, 1168, 1090, 1014, 867, 841, 780, 752, 693, 519, 471.



methyl 4-[(4-bromophenyl)carbonyl]-8-methyl-6-phenylnona-4,5-dienoate (5cc).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (39.7 mg, 45%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.39 (s, 1H), 7.37 – 7.34 (m, 3H), 7.30 (d, *J* = 7.5 Hz, 3H), 3.60 (s, 3H), 2.90 – 2.83 (m, 2H), 2.60 (td, *J* = 7.4, 3.5 Hz, 2H), 2.35 (dd, *J* = 14.6, 6.5 Hz, 1H), 2.24 (dd, *J* = 14.5, 7.6 Hz, 1H), 1.74 – 1.69 (m, 1H), 0.80 (dd, *J* = 11.3, 6.6 Hz, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.6, 193.5, 173.2, 137.2, 134.5, 131.1, 130.1, 128.8, 127.9, 126.8, 126.5, 110.3, 107.9, 51.6, 40.0, 32.4, 26.9, 24.3, 22.6, 22.4.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}BrO_3^+$: 441.1060; Found: 441.1044.
IR cm^{-1} : 3085, 3060, 3025, 2953, 2926, 2867, 1924, 1737, 1650, 1585, 1493, 1436, 1394, 1365, 1261, 1197, 1166, 1069, 1010, 991, 866, 838, 783, 758, 694, 653, 606.



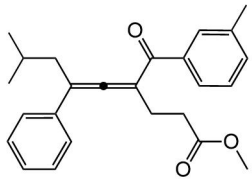
methyl 8-methyl-4-[(2-methylphenyl)carbonyl]-6-phenylnona-4,5-dienoate (5da). Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (44.7 mg, 57%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.17 (dd, *J* = 12.9, 7.3 Hz, 4H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 3.57 (s, 3H), 2.84 (dq, *J* = 23.9, 7.9 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.27 (s, 3H), 2.20 – 2.14 (m, 2H), 1.62 – 1.59 (m, 1H), 0.77 (d, *J* = 6.6 Hz, 3H), 0.67 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 228.2, 199.0, 171.6, 139.2, 138.9, 135.0, 131.5, 129.7, 123.0, 127.0, 126.8, 126.2, 126.00, 125.2, 51.6, 40.1, 32.4, 27.2, 26.7, 22.3, 20.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}O_3^+$: 377.2112; Found: 377.2104.

IR cm^{-1} : 3085, 3060, 3024, 3021, 2954, 2924, 2849, 1926, 1739, 1656, 1598, 1493, 1436, 1365, 1258, 1196, 1168, 1104, 1047, 993, 841, 756, 695.



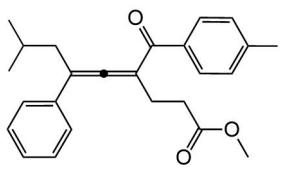
methyl 8-methyl-4-[(3-methylphenyl)carbonyl]-6-phenylnona-4,5-dienoate (5db). Following general procedure A, the product was purified by flash chromatography (PE/EA = 90:1) yellow oil (41.6 mg, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 2.91 – 2.84 (m, 2H), 2.62 (td, *J* = 7.5, 3.7 Hz, 2H), 2.33 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.21 (dd, *J* = 14.5, 7.7 Hz, 1H), 2.07 (s, 3H), 1.69 (dd, *J* = 13.3, 7.0 Hz, 1H), 0.79 (dd, *J* = 9.5, 6.6 Hz, 6H).

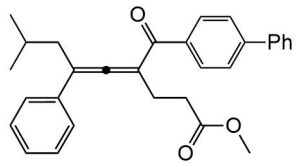
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.7, 194.0, 173.3, 155.6, 135.7, 134.6, 128.7, 128.6, 127.6, 126.4, 124.8, 110.7, 108.7, 51.6, 36.8, 34.9, 32.3, 31.1, 28.5, 27.9, 24.3, 22.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}O_3^+$: 377.2112; Found: 377.2106.

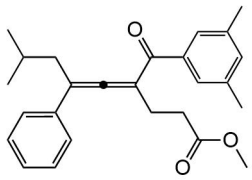
IR cm^{-1} : 3088, 3058, 3025, 2953, 2924, 2867, 1926, 1737, 1649, 1599, 1584, 1493, 1436, 1365, 1274, 1195, 1162, 1114, 1020, 921, 890, 839, 760, 739, 695.



methyl 8-methyl-4-[(4-methylphenyl)carbonyl]-6-phenylnona-4,5-dienoate (5dc).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 90:1) colorless oil (48.7 mg, 62%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 3.59 (s, 3H), 2.92 – 2.82 (m, 2H), 2.60 (td, *J* = 7.5, 2.9 Hz, 2H), 2.35 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.30 (s, 3H), 2.26 (dd, *J* = 14.5, 7.6 Hz, 1H), 1.73 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.81 (dd, *J* = 16.8, 6.6 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.0, 194.2, 173.3, 142.7, 135.8, 134.9, 128.7, 128.7, 128.5, 127.6, 126.6, 109.4, 107.8, 77.2, 77.0, 76.8, 51.6, 40.0, 32.5, 26.9, 24.6, 22.6, 22.4, 21.5.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}O_3^+$: 377.2112; Found: 377.2105.
IR cm^{-1} : 3084, 3057, 3028, 2952, 2920, 2867, 1926, 1736, 1645, 1607, 1568, 1494, 1436, 1365, 1309, 1267, 1208, 1165, 1116, 1018, 991, 869, 832, 792, 759, 695.



methyl 8-methyl-6-phenyl-4-[(4-phenylphenyl)carbonyl]nona-4,5-dienoate (5e).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) colorless oil (33.3 mg, 38%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.29 (t, *J* = 7.2 Hz, 1H), 3.61 (s, 3H), 2.96 – 2.85 (m, 2H), 2.63 (td, *J* = 7.5, 3.0 Hz, 2H), 2.36 (dd, *J* = 14.5, 6.7 Hz, 1H), 2.28 (dd, *J* = 14.6, 7.5 Hz, 1H), 1.75 – 1.70 (m, 1H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.4, 194.2, 173.3, 164.2, 144.6, 140.0, 137.2, 134.8, 129.2, 128.8, 128.7, 128.0, 127.7, 127.2, 126.6, 126.5, 109.9, 108.0, 51.6, 40.1, 32.5, 29.7, 27.0, 24.5, 22.6, 22.4.
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{31}O^+$: 439.2268; Found: 439.2268.
IR cm^{-1} : 3084, 3058, 3030, 2953, 2925, 2867, 1926, 1738, 1648, 1602, 1493, 1448, 1436, 1403, 1365, 1265, 1195, 1167, 1118, 1007, 850, 785, 761, 749, 696.



methyl 4-[(3,5-dimethylphenyl)carbonyl]-8-methyl-6-phenylnona-4,5-dienoate (5f).

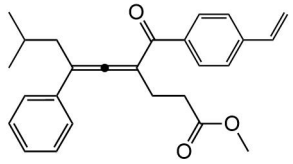
Following general procedure A, the product was purified by flash chromatography (PE/EA = 10:1) yellow oil (35.9 mg, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 (s, 2H), 7.00 (s, 1H), 3.62 (s, 3H), 2.91 – 2.83 (m, 2H), 2.63 (td, *J* = 7.8, 4.2 Hz, 2H), 2.35 – 2.32 (m, 1H), 2.19 (dd, *J* = 14.6, 7.9 Hz, 1H), 2.07 (s, 6H), 1.70 (dt, *J* = 11.8, 5.8 Hz, 1H), 0.80 (d, *J* = 7.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 213.5, 195.3, 173.3, 138.4, 137.3, 135.3, 133.7, 128.7, 127.6, 126.7, 126.5 109.8, 107.9, 53.4, 51.6, 39.9, 32.6, 29.8, 29.7, 29.3, 24.4, 22.6, 22.3, 20.8.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{31}O_4^+$: 391.2268; Found: 391.2260.

IR cm^{-1} : 3085, 3057, 3024, 2952, 2923, 2853, 1928, 1739, 1650, 1602, 1493, 1436, 1365, 1312, 1206, 1165, 1121, 1039, 863, 837, 736, 695.



methyl 8-methyl-6-phenyl-4-[(4-vinylphenyl)carbonyl]nona-4,5-dienoate (5g).

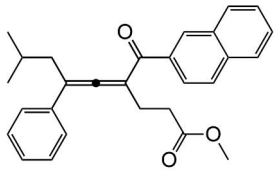
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (37.3 mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 2H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 3.60 (s, 3H), 2.91 – 2.83 (m, 2H), 2.61 (td, *J* = 7.4, 3.0 Hz, 2H), 2.35 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.26 (dd, *J* = 14.6, 7.5 Hz, 1H), 1.72 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.80 (dd, *J* = 16.1, 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 213.2, 194.0, 173.3, 141.0, 137.7, 136.1, 134.8, 129.0, 128.7, 127.7, 126.6, 125.6, 116., 109.8, 107.9, 51.6, 40.0, 32.5, 29.7, 26.9, 25.6, 24.5, 22.6, 22.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{29}O_3^+$: 389.2112; Found: 389.2103.

IR cm^{-1} : 3085, 3058, 3032, 2953, 2923, 2852, 1926, 1736, 1647, 1603, 1558, 1493, 1436, 1365, 1263, 1203, 1164, 1104, 1015, 989, 915, 851, 761, 694.



methyl 8-methyl-6-phenyl-4-[(4-vinylphenyl)carbonyl]nona-4,5-dienoate (5h).

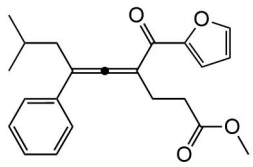
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (37.9 mg, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 – 8.35 (m, 1H), 7.98 – 7.90 (m, 2H), 7.87 – 7.79 (m, 2H), 7.62 – 7.49 (m, 2H), 7.44 – 7.36 (m, 3H), 7.30 – 7.22 (m, 2H), 5.24 (p, J = 0.9 Hz, 1H), 3.62 (s, 3H), 2.85 (tt, J = 8.4, 0.8 Hz, 2H), 2.69 – 2.62 (m, 4H), 2.29 – 2.20 (m, 1H), 1.00 (d, J = 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 228.2, 194.1, 171.6, 136.8, 135.4, 135.0, 132.6, 129.9, 129.6, 129.2, 128.0, 127.3, 127.2, 126.9, 126.8, 126.8, 126.6, 126.2, 126.0, 51.6, 43.9, 32.2, 27.3, 26.6, 22.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{29}O_3^+$: 413.2112; Found: 413.2117.

IR cm^{-1} : 3083, 3058, 3031, 2953, 2924, 2857, 1926, 1738, 1647, 1602, 1493, 1445, 1436, 1403, 1365, 1265, 1195, 1167, 1118, 1007, 858, 833, 771, 761, 749, 696.



methyl 4-(2-furylcarbonyl)-8-methyl-6-phenylnona-4,5-dienoate (5i).

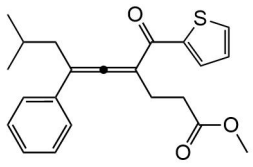
Following general procedure A, the product was purified by flash chromatography (PE/EA = 90:1) yellow oil (30.3 mg, 43%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.05 (d, *J* = 3.6 Hz, 1H), 3.54 (s, 3H), 2.88 – 2.80 (m, 2H), 2.58 – 2.54 (m, 2H), 2.48 – 2.40 (m, 2H), 1.84 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.91 (dd, *J* = 6.6, 3.2 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 212.2, 179.9, 173.1, 151.8, 146.3, 134.4, 128., 127.8, 126.5, 117.9, 111.8, 110.1, 107.2, 51.6, 39.8, 32.4, 29.7, 29.3, 27.2, 26.9, 24.2, 22.7, 22.6, 14.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}O_4^+$: 353.1748; Found: 353.1747.

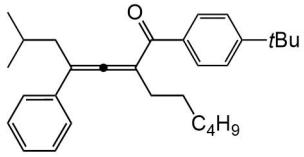
IR cm^{-1} : 3108, 2957, 2925, 2868, 1930, 1737, 1678, 1603, 1561, 1463, 1406, 1364, 1330, 1286, 1260, 1248, 1185, 1159, 1108, 1021, 971, 868, 846, 778, 764, 711, 687, 625.



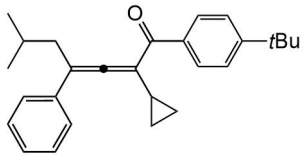
methyl 8-methyl-6-phenyl-4-(thiophen-2-ylcarbonyl)nona-4,5-dienoate (5j).

Following general procedure A, the product was purified by flash chromatography (PE/EA = 90:1) yellow oil (28.7 mg, 39%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 3.6 Hz, 1H), 7.49 (d, *J* = 3.7 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.1 Hz, 1H), 6.96 – 6.94 (m, 1H), 3.57 (s, 3H), 2.92 – 2.83 (m, 2H), 2.60 (dt, *J* = 7.0, 3.4 Hz, 2H), 2.53 – 2.49 (m, 1H), 2.43 – 2.39 (m, 1H), 1.86 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.92 (t, *J* = 6.3 Hz, 7H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.0, 184.0, 173.2, 142.5, 134.4, 133.2, 132.7, 128.8, 127.9, 127.5, 126.6, 111.0, 108.3, 51.6, 40.0, 32.5, 29.7, 27.0, 24.8, 22.9, 22.6.
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{25}O_3S^+$: 369.1519 Found: 369.1513.
IR cm^{-1} : 3726, 3700, 3622, 3600, 2974, 2864, 1938, 1740, 1632, 1509, 1437, 1414, 1355, 1260, 1211, 1167, 1105, 1051, 780, 757, 717, 694.

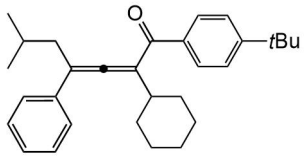


2-(4-methyl-2-phenylpent-1-enylidene)-1-[4-(2-methylprop-2-yl)phenyl]octan-1-one (6a).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (49.2 mg, 59%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.28 – 7.23 (m, 3H), 2.58 – 2.49 (m, 2H), 2.38 (dd, *J* = 14.4, 6.5 Hz, 1H), 2.27 (dd, *J* = 14.4, 7.7 Hz, 1H), 1.76 (dp, *J* = 13.0, 6.6 Hz, 1H), 1.58 (ddt, *J* = 11.3, 7.3, 3.5 Hz, 2H), 1.40 (p, *J* = 7.2, 6.6 Hz, 2H), 1.30 (dt, *J* = 7.4, 3.6 Hz, 4H), 1.26 (s, 9H), 0.89 – 0.86 (m, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 213.6, 194.7, 155.4, 136.0, 135.6, 128.6, 128.6, 127.3, 126.5, 124.7, 109.1, 108.1, 40.1, 34.9, 31.7, 31.1, 29.3, 29.3, 28.5, 27.0, 22.6, 22.6, 22.4, 14.1.
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{41}O^+$: 417.3152; Found: 417.3159.
IR cm^{-1} : 3081, 3057, 3025, 2954, 2925, 2852, 1926, 1710, 1650, 1602, 1561, 1493, 1462, 1406, 1379, 1363, 1293, 1267, 1222, 1189, 1166, 1103, 1074, 1013, 914, 865, 846, 768, 695.

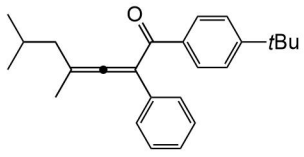


2-cyclopropyl-6-methyl-1-[4-(2-methylprop-2-yl)phenyl]-4-phenylhepta-2,3-dien-1-one (6b).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 90:1) yellow oil (41.7 mg, 56%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.30 – 7.27 (m, 3H), 7.23 (d, *J* = 8.6 Hz, 2H), 2.34 (dd, *J* = 14.5, 6.6 Hz, 1H), 2.24 (dd, *J* = 14.4, 7.5 Hz, 1H), 1.95 (ddd, *J* = 13.3, 8.2, 5.1 Hz, 1H), 1.72 (dt, *J* = 13.7, 6.4 Hz,

1H), 1.26 (s, 9H), 0.89 (dd, *J* = 8.2, 2.2 Hz, 2H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.57 – 0.54 (m, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 211.5, 194.8, 155.5, 135.9, 135.3, 129.1, 128.7, 128.5, 127.5, 126.4, 124.8, 112.9, 110.7, 40.2, 34.9, 31.3, 31.1, 27.0, 22.6, 22.4, 9.2, 7.5, 7.5.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{33}O^+$: 373.2526; Found: 373.2517.
IR cm^{-1} : 3084, 3060, 3024, 3004, 2958, 2921, 2865, 1924, 1713, 1646, 1602, 1561, 1492, 1461, 1404, 1381, 1363, 1311, 1293, 1264, 1191, 1108, 1082, 1019, 934, 848, 816, 772, 725, 696.

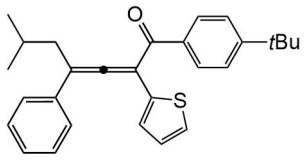


2-cyclohexyl-6-methyl-1-[4-(2-methylprop-2-yl)phenyl]-4-phenylhepta-2,3-dien-1-one (6c).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) yellow oil (49.8 mg, 60%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 5.6 Hz, 4H), 7.27 (dt, *J* = 5.4, 2.7 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.81 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.35 (dd, *J* = 14.4, 6.5 Hz, 1H), 2.25 (dd, *J* = 14.5, 7.8 Hz, 1H), 1.95 (t, *J* = 14.8 Hz, 2H), 1.79 – 1.70 (m, 4H), 1.45 – 1.34 (m, 3H), 1.25 (d, *J* = 0.9 Hz, 9H), 1.21 (td, *J* = 8.6, 4.1 Hz, 2H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 212.5, 194.8, 155.4, 136.3, 135.7, 128.6, 128.6, 127.2, 126.4, 124.7, 114.7, 109.7, 40.3, 37.6, 34.9, 33.0, 32.8, 31.1, 27.1, 26.6, 26.5, 26.2, 22.7, 22.6.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{38}NaO^+$: 437.2815 Found: 437.2800.
IR cm^{-1} : 3085, 3055, 3025, 2958, 2922, 2848, 1916, 1650, 1600, 1495, 1442, 1362, 1268, 1192, 1113, 1075, 1012, 929, 856, 836, 792, 771, 728, 692.

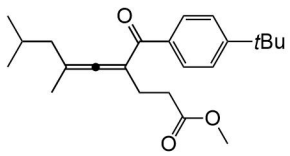


4,6-dimethyl-1-[4-(2-methylprop-2-yl)phenyl]-2-phenylhepta-2,3-dien-1-one (6d).
Following general procedure C, the product was purified by flash chromatography (PE/EA = 50:1) colorless oil (35.3 mg, 51%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.35 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.30 – 7.25 (m, 3H), 2.18 (dd, *J* = 13.7, 7.1 Hz, 1H), 1.99 (td, *J* = 12.8, 6.7 Hz, 1H), 1.69 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.65 (s, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 199.7, 155.9, 133.2, 131.3, 129.7, 128.2, 128.0, 124.9, 123.5, 93.2, 86.0, 48.3, 46.3, 35.0, 31.1, 29.7, 26.9, 25.9, 24.2, 23.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{31}O^+$: 347.2370 Found: 347.2362.
IR cm^{-1} : 3028, 2966, 2933, 2855, 1968, 1682, 1604, 1465, 1365, 1260, 1195, 1109, 967, 779, 754, 689.



6-methyl-1-[4-(2-methylprop-2-yl)phenyl]-4-phenyl-2-(thiophen-2-yl)hepta-2,3-dien-1-one (6e).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 90:1) colorless oil (34.5 mg, 49%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 3.4 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 9.7, 3.6 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.26 (s, 2H), 2.31 – 2.20 (m, 2H), 2.01 (q, *J* = 6.7 Hz, 1H), 1.34 (d, *J* = 4.3 Hz, 9H), 1.21 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 198.6, 154.9, 132.2, 128.7, 128.6, 126.8, 124.1, 123.8, 121.5, 91.6, 80.2, 47.3, 45.3, 34.0, 30.1, 28.7, 25.8, 24.9, 23.2, 22.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}OS$: 271.1151; Found: 271.1142.
IR cm^{-1} : 3083, 3055, 3024, 2953, 2922, 2852, 1929, 1737, 1638, 1597, 1563, 1494, 1464, 1436, 1388, 1365, 1290, 1124, 1103, 1084, 1015, 993, 884, 851, 785, 759, 695, 608, 594, 482.



methyl 6,8-dimethyl-4-{[4-(2-methylprop-2-yl)phenyl]carbonyl}nona-4,5-dienoate (6f).
Following general procedure A, the product was purified by flash chromatography (PE/EA = 100:1) colorless oil (38.5 mg, 54%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.64 (s, 3H), 2.49 (dddd, *J* = 14.8, 9.3, 6.1, 2.7 Hz, 4H), 2.04 (dd, *J* = 13.8, 7.0 Hz, 1H), 1.88 – 1.83 (m, 1H), 1.55 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.50 (s, 3H), 1.34 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 200.0, 172.4, 155.8, 133.1, 129.8, 124.7, 84.5, 84.1, 51.7, 48.2, 45.7, 35.0, 33.3, 31.1, 29.7, 29.1, 27.0, 25.8, 24.2, 23.9, 15.0.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{33}O_3^+$: 357.2425; Found: 357.2416.
IR cm^{-1} : 3026, 2967, 2867, 1968, 1743, 1681, 1604, 1558, 1437, 1364, 1247, 1195, 1166, 1109, 977, 778, 749.

8.Reference:

1 . Dong, Y. X., Zhang, C. L., Gao, Z. H. et al. Iminoacylation of Alkenes via Photoredox N-Heterocyclic Carbene Catalysis. *Org. Lett.* **2023**, 25, 855-860.

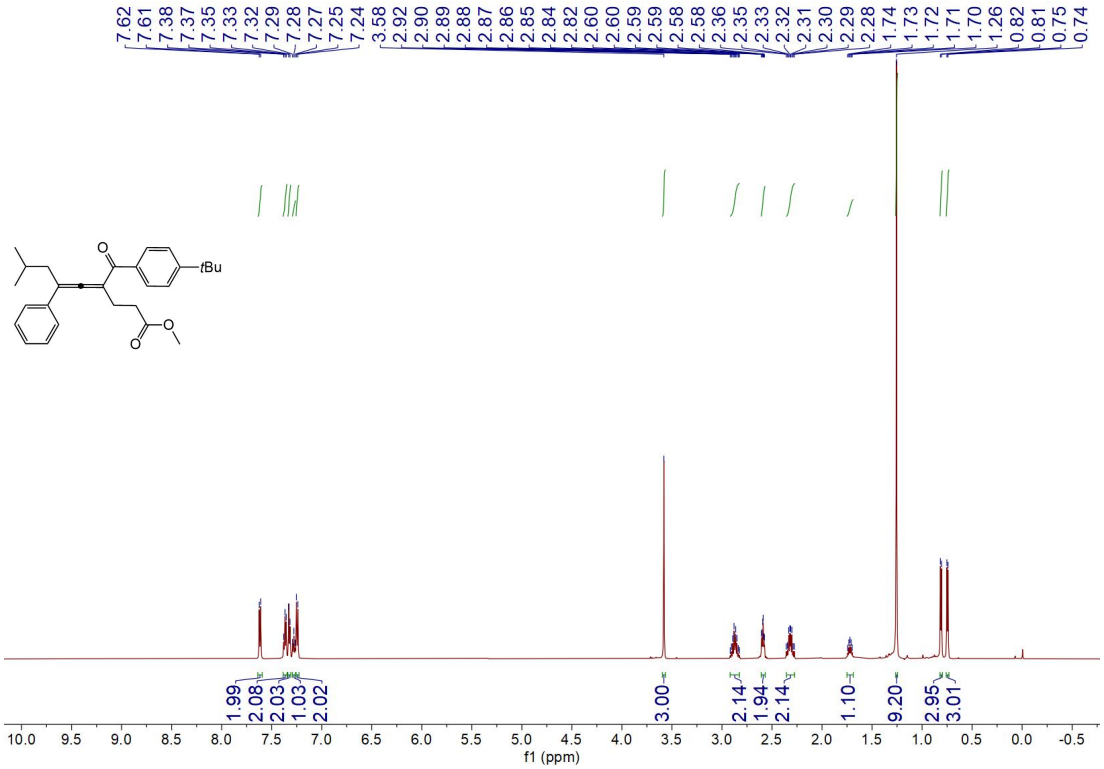
2 . Song, H. Z., Zhang, X. M., Chen, G. et al. Copper-Catalyzed 1,4-Trifluoromethylthio-Arylsulfonylation of 1,3-Enynes via the Insertion of Sulfur Dioxide. *Org. Lett.* 2023, **25**, 5916–5921.

3 . Li, S. H., Zheng, C. L., Wang S. et al. Ketone Synthesis via Irradiation-Induced Generation of a Persistent Ketyl Radical from Acyl Azolium Salts. *Org. Lett.* 2023, **25**, 6522–65274.

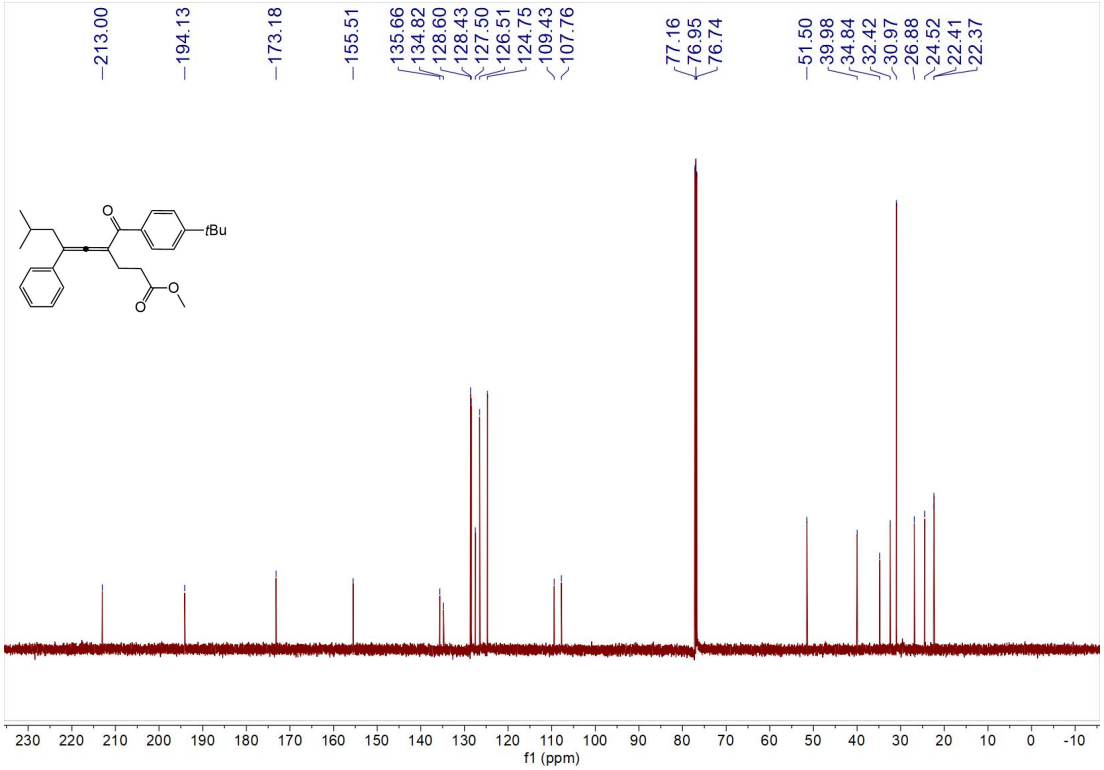
4 . Goto, Y., Sano, M., Sumida, Y. et al. N-heterocyclic carbene- and organic photoredox-catalysed meta-selective acylation of electron-rich arenes. *Nat. Synth.* 2023, **2**, 1037–1045.

9.NMR of Products

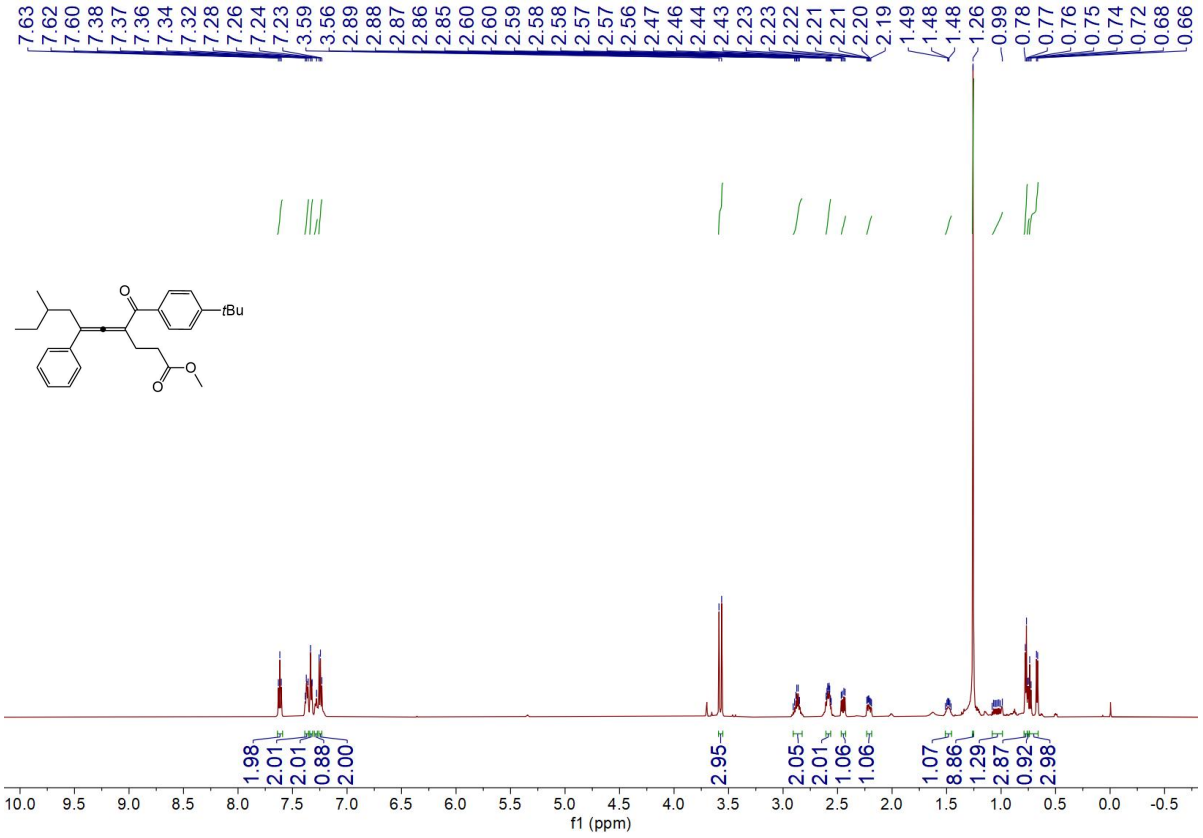
^{1}H NMR (600 MHz, Chloroform-d) of **4a**



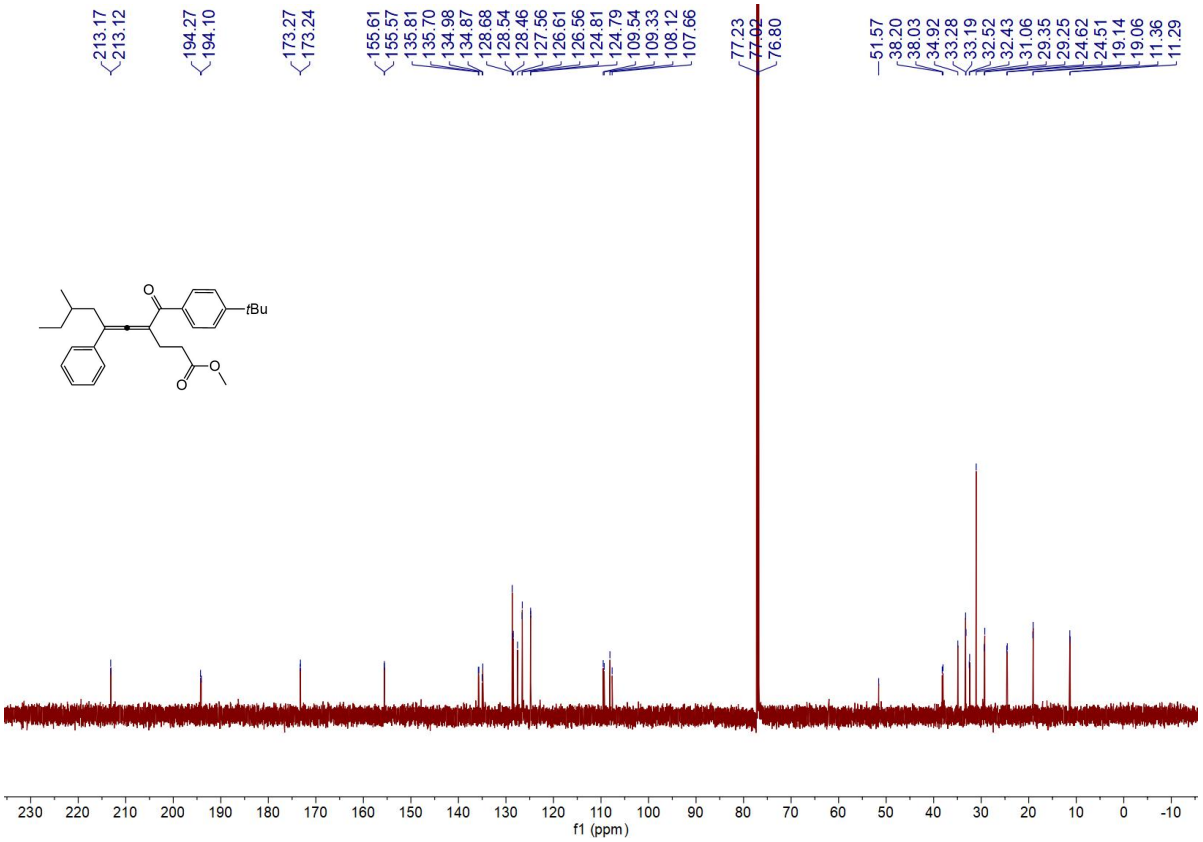
^{13}C NMR (150 MHz, Chloroform-d) of **4a**



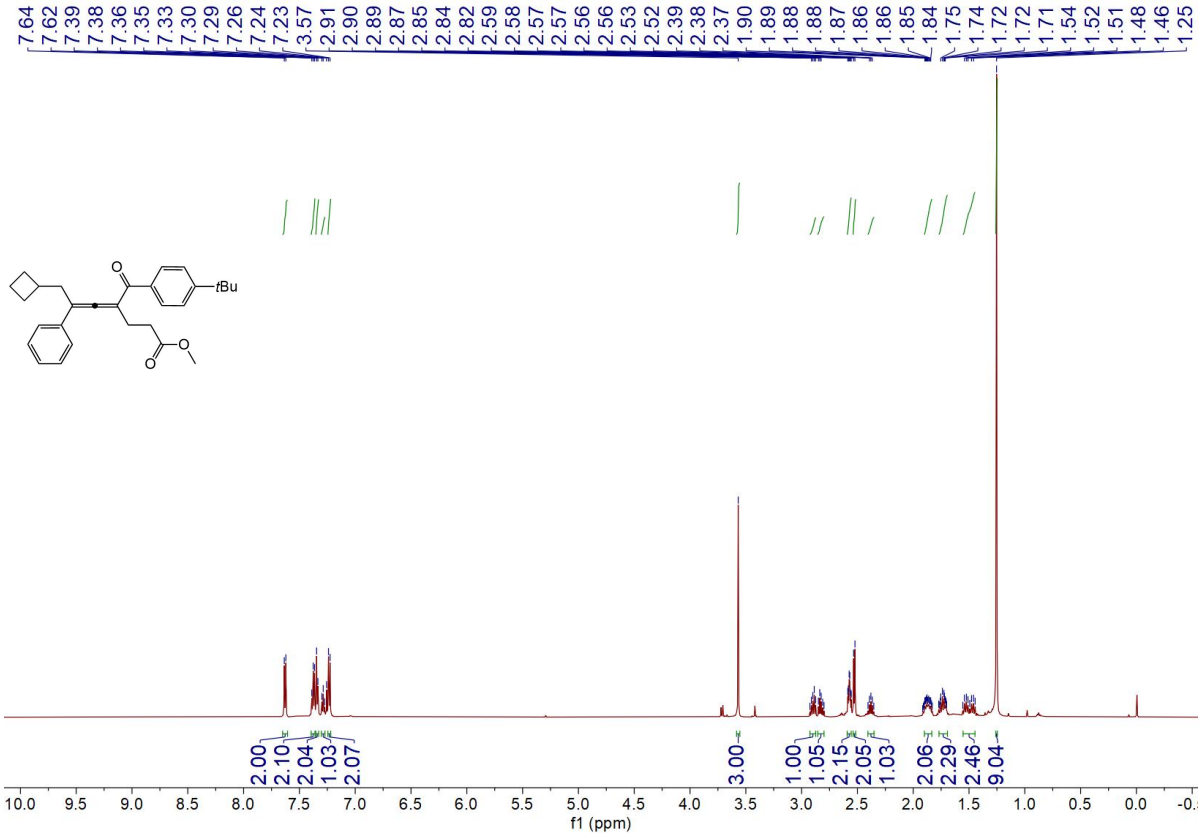
^{1}H NMR (600 MHz, Chloroform-d) of **4b**



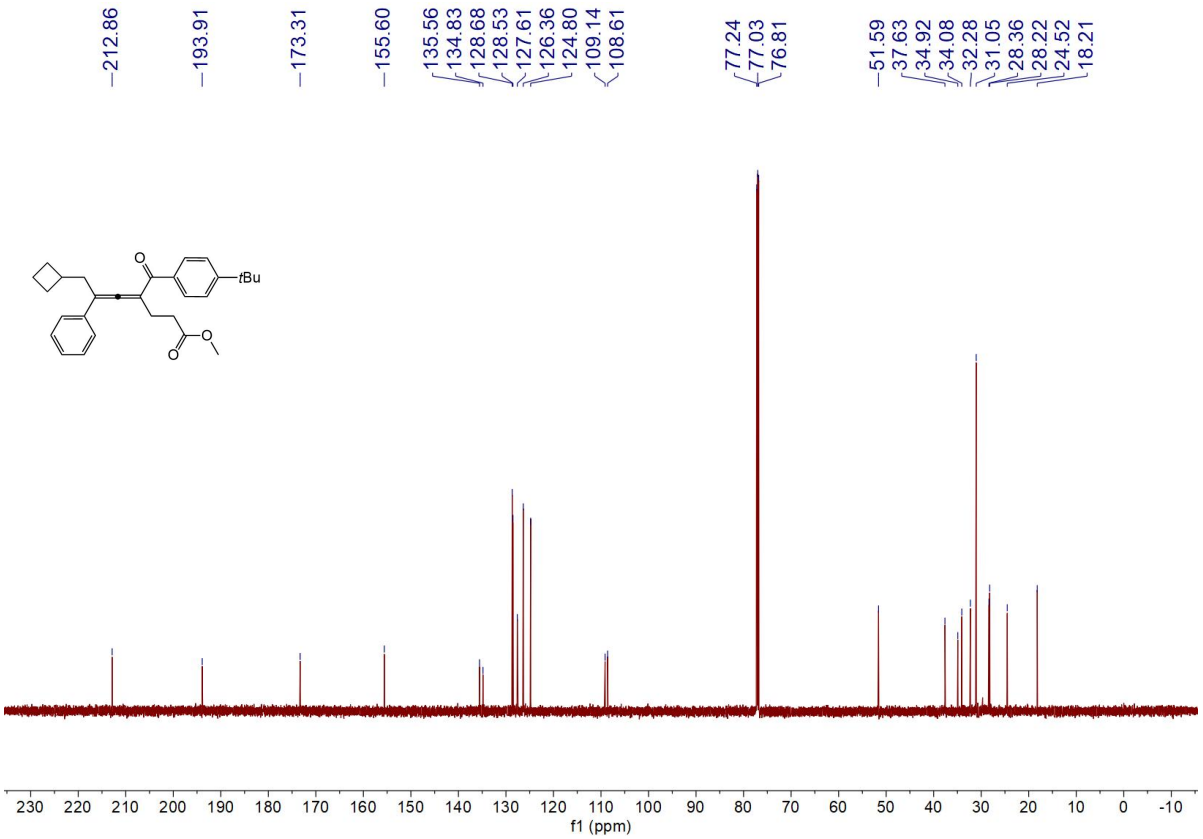
^{13}C NMR (150 MHz, Chloroform-d) of **4b**



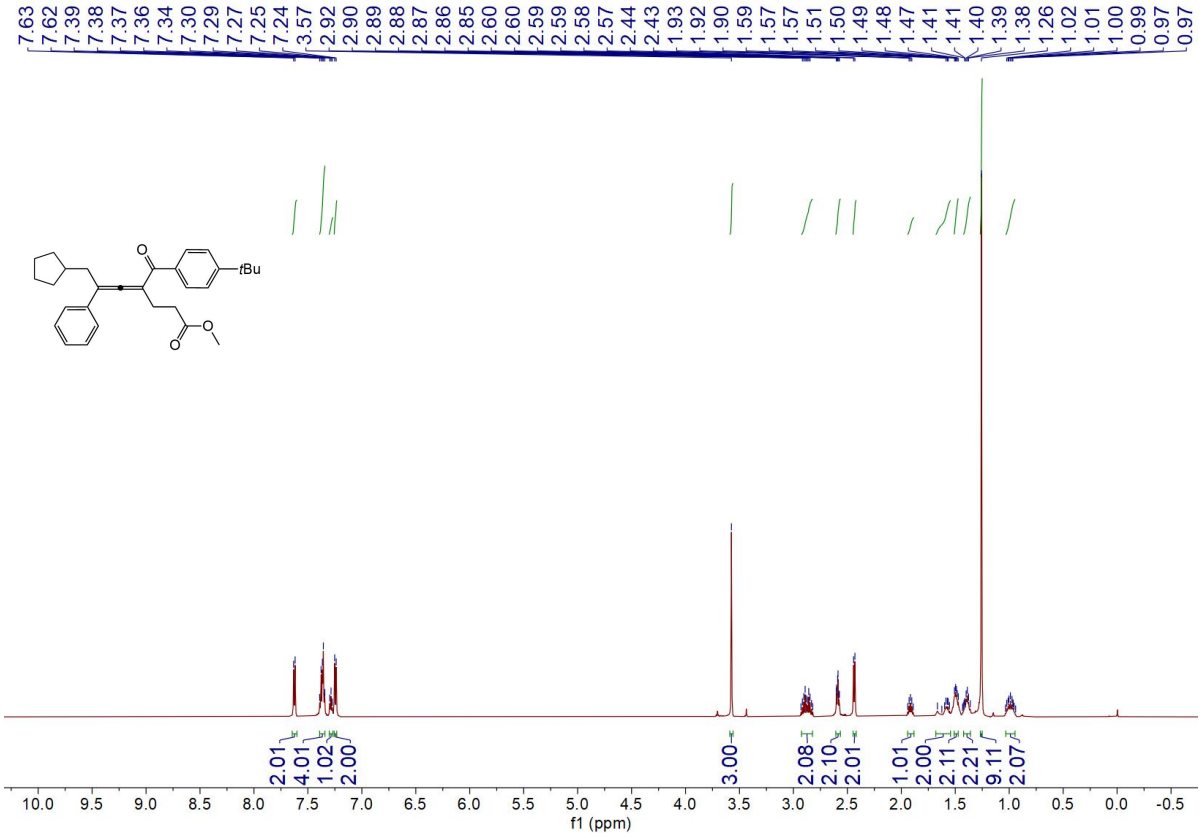
^{1}H NMR (600 MHz, Chloroform-d) of **4c**



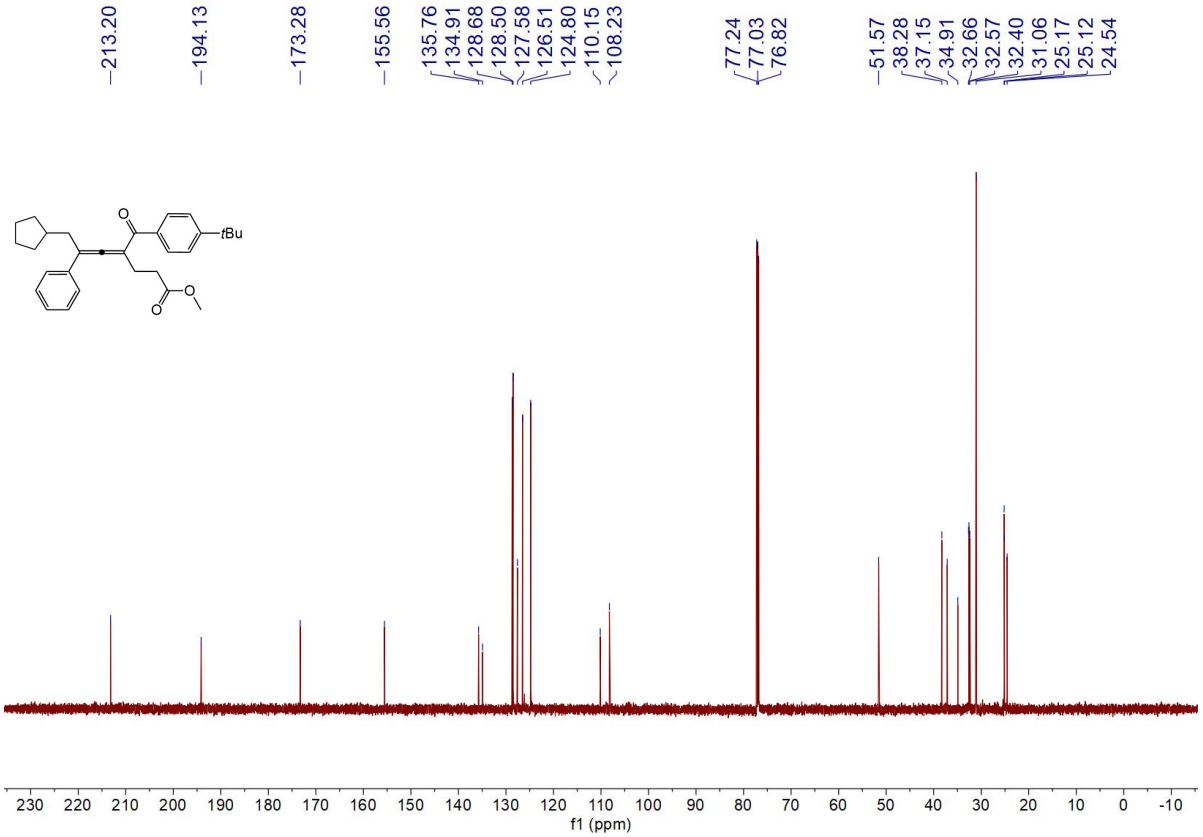
^{13}C NMR (150 MHz, Chloroform-d) of **4c**



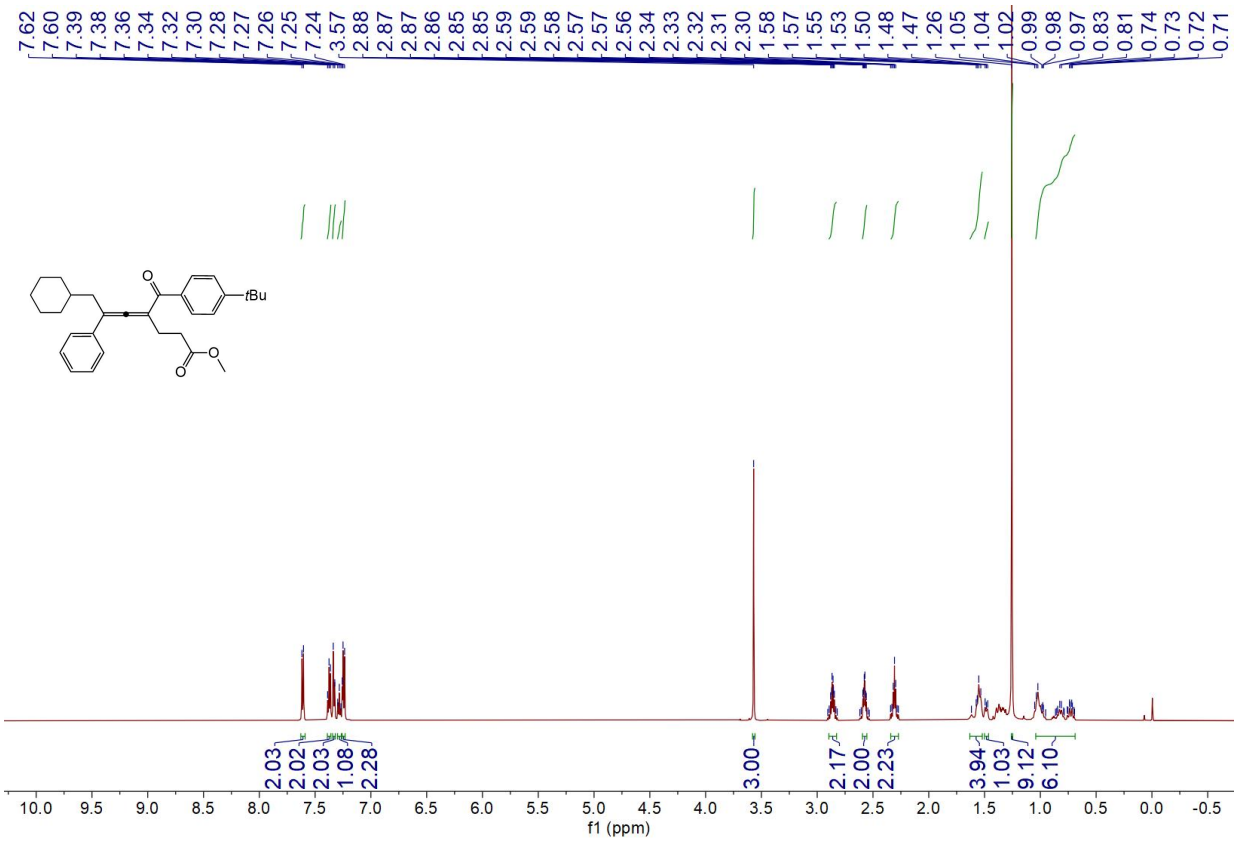
^{1}H NMR (600 MHz, Chloroform-d) of **4d**



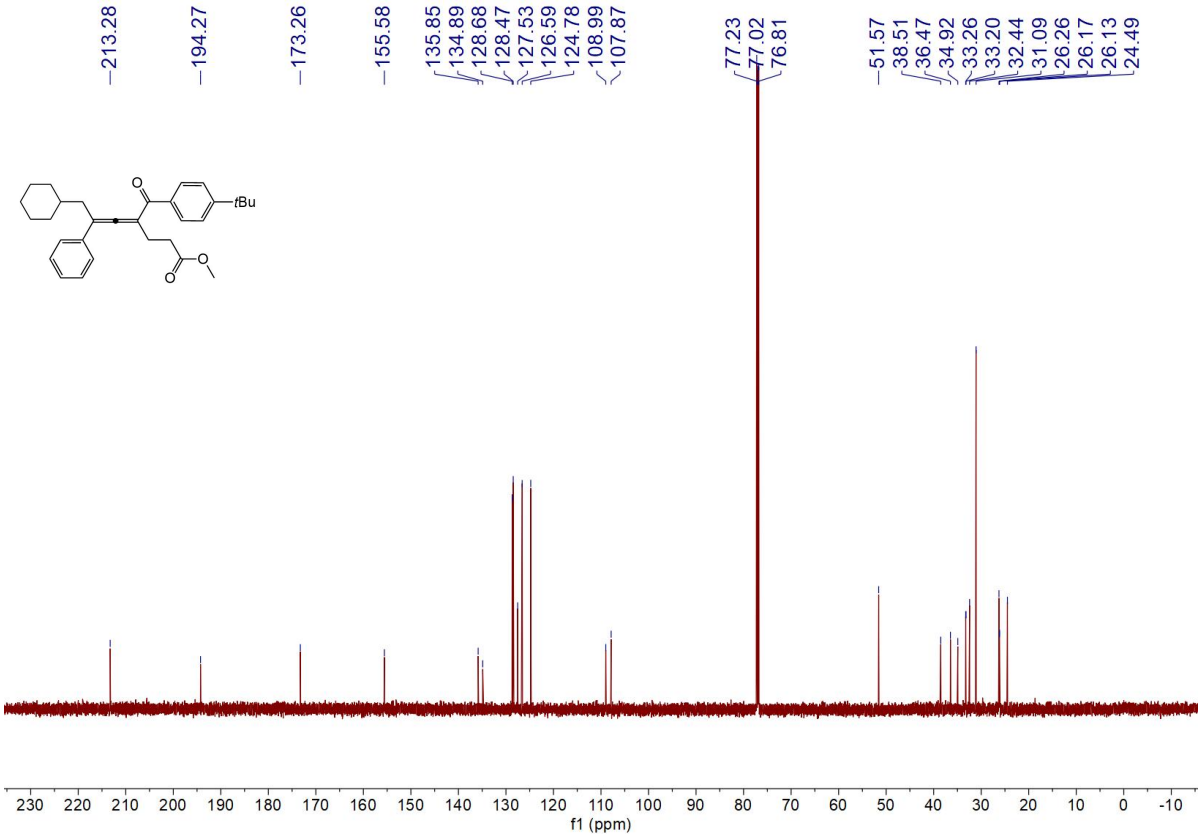
^{13}C NMR (150 MHz, Chloroform-d) of **4d**



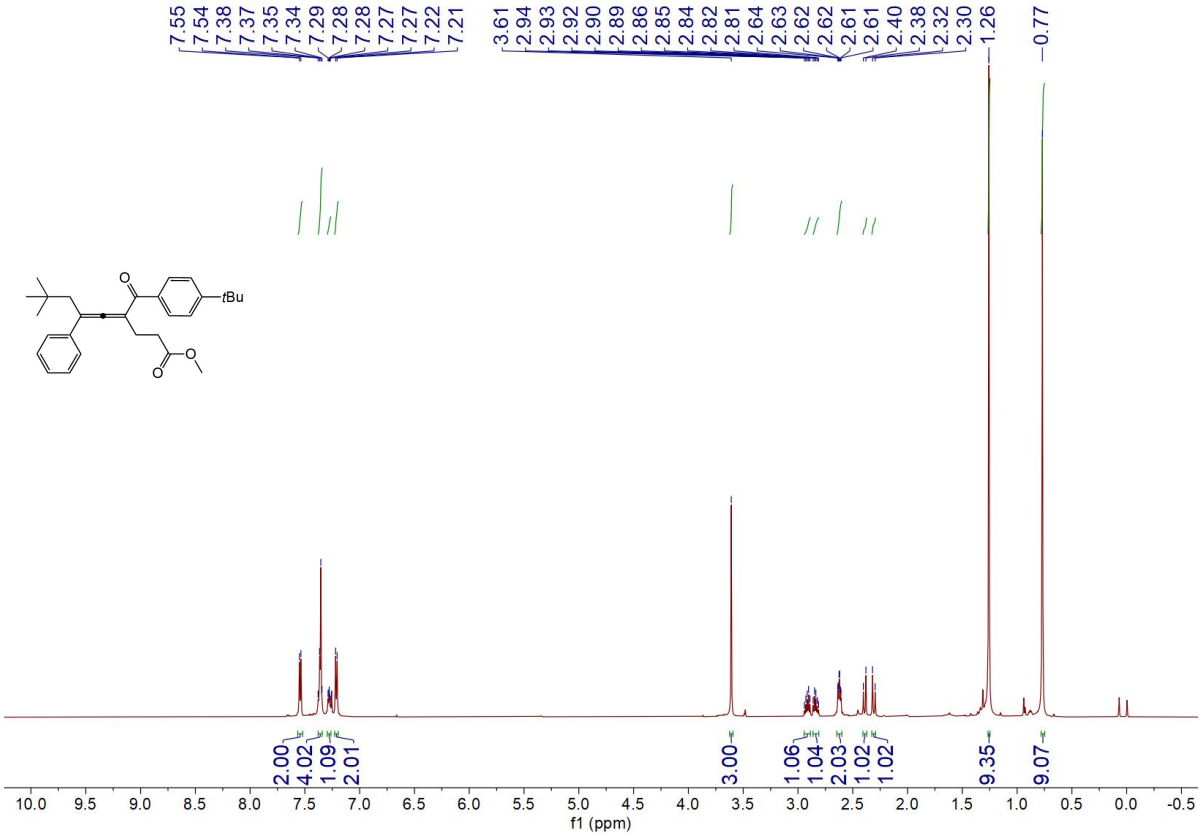
^{1}H NMR (600 MHz, Chloroform-d) of **4e**



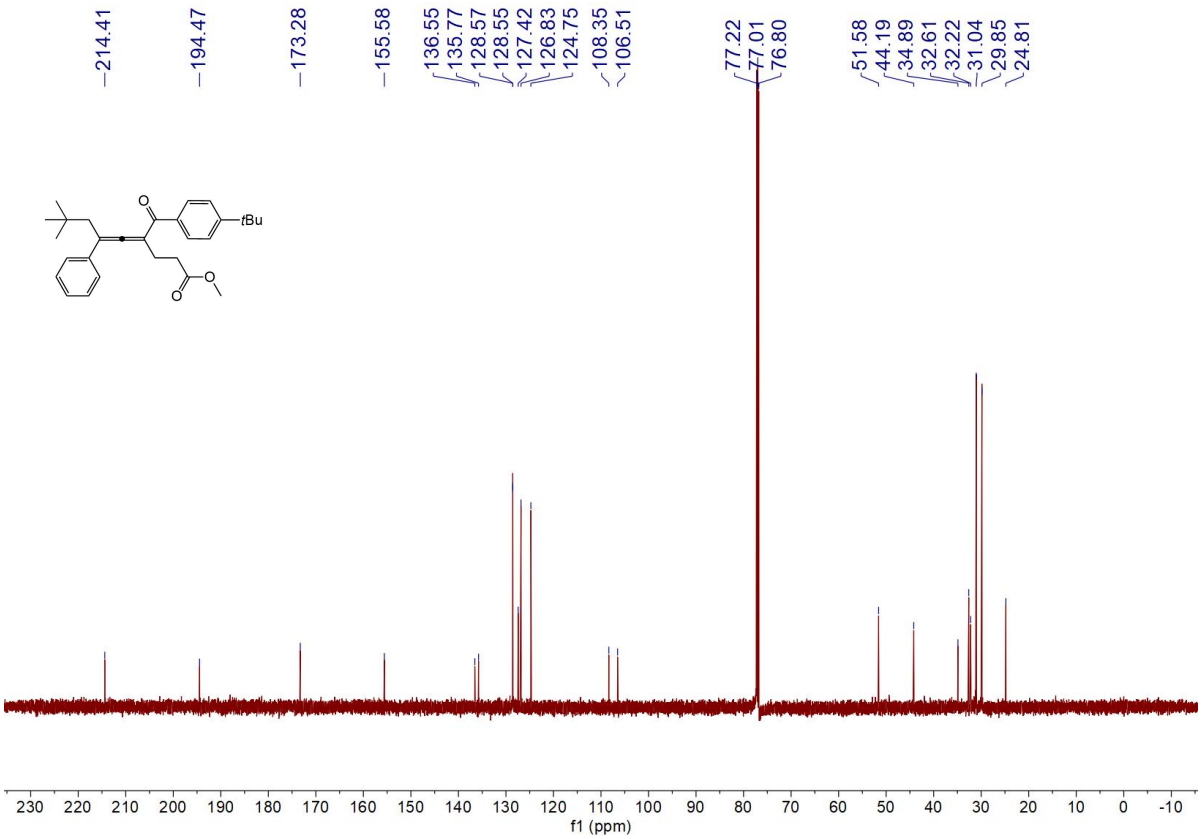
^{13}C NMR (150 MHz, Chloroform-d) of **4e**



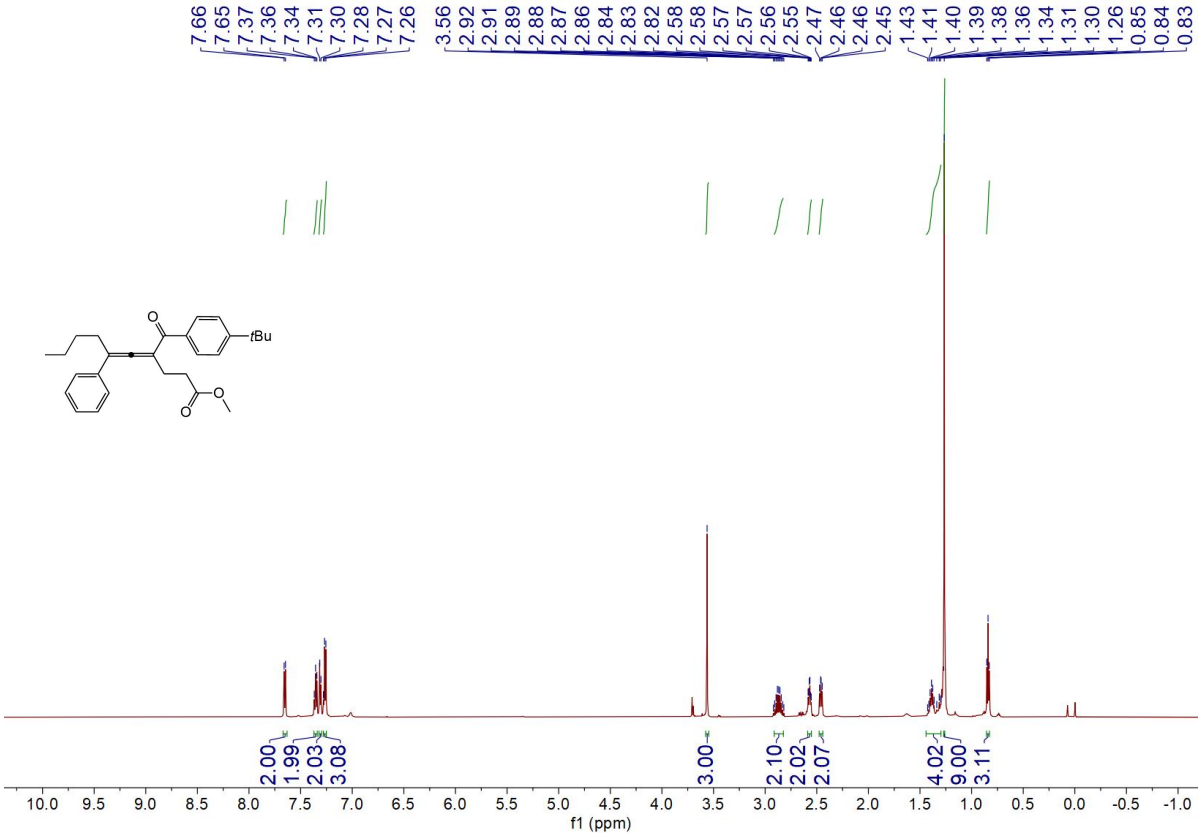
^{1}H NMR (600 MHz, Chloroform-d) of **4f**



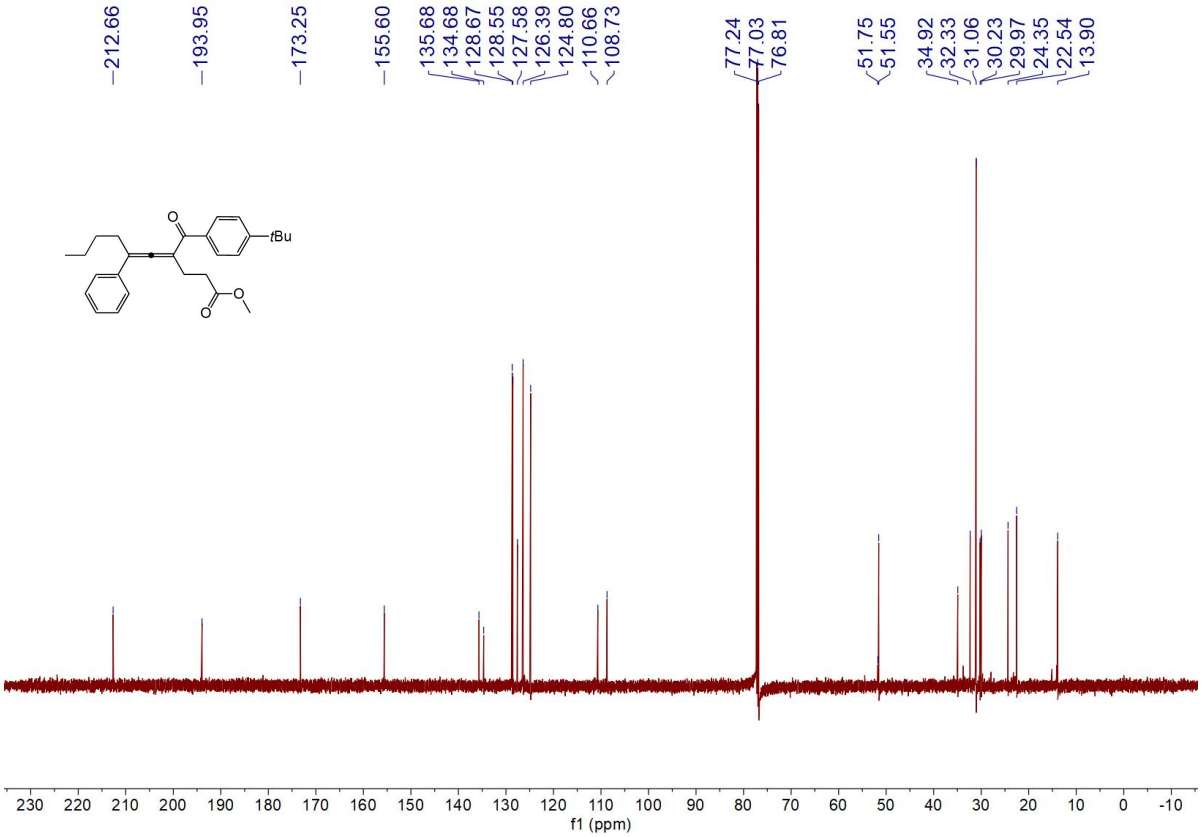
^{13}C NMR (150 MHz, Chloroform-d) of **4f**



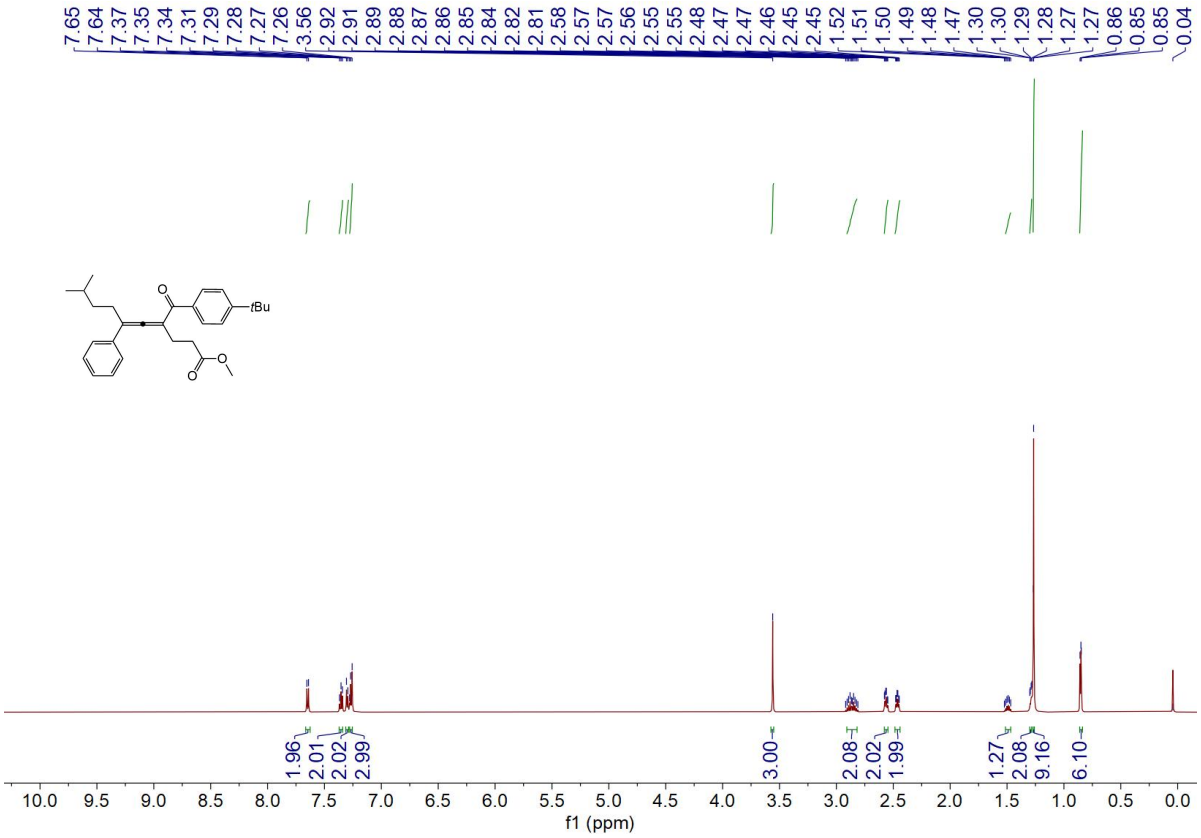
^{1}H NMR (600 MHz, Chloroform-d) of **4g**



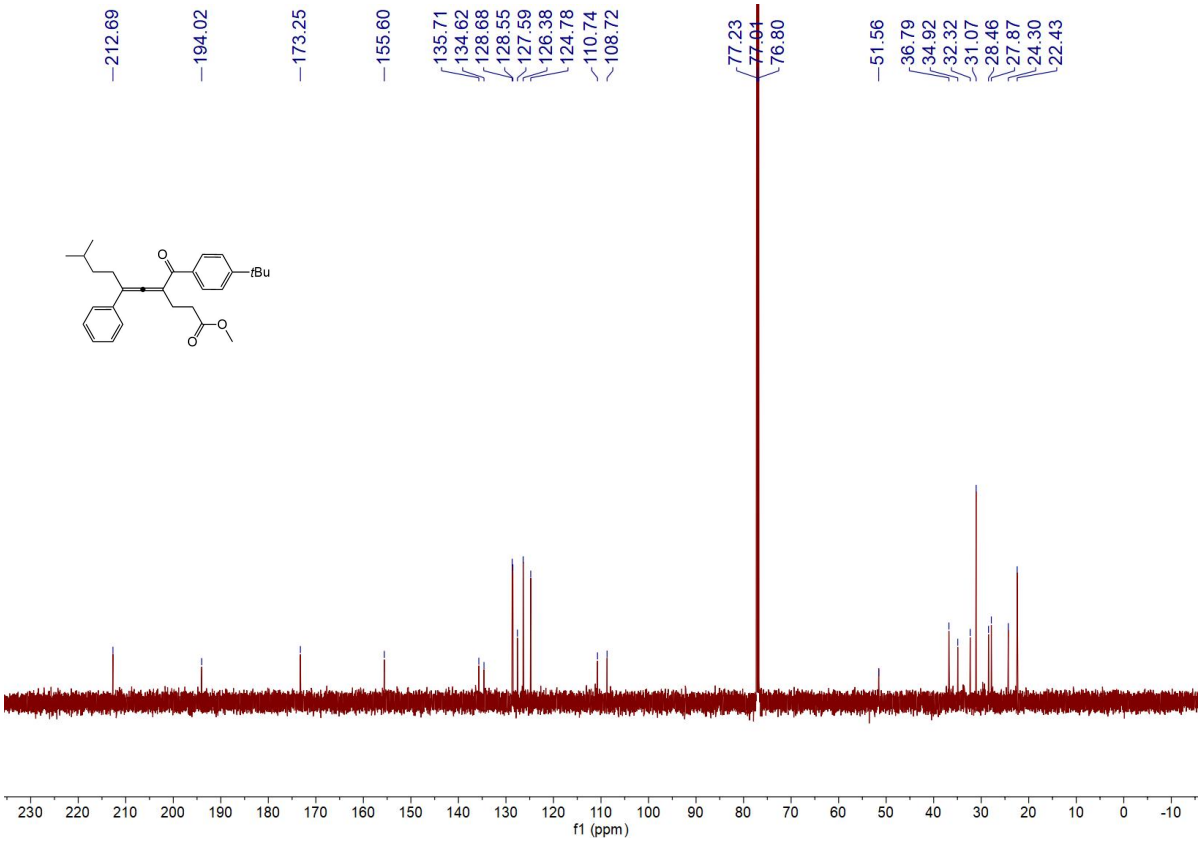
^{13}C NMR (151 MHz, Chloroform-d) of **4g**



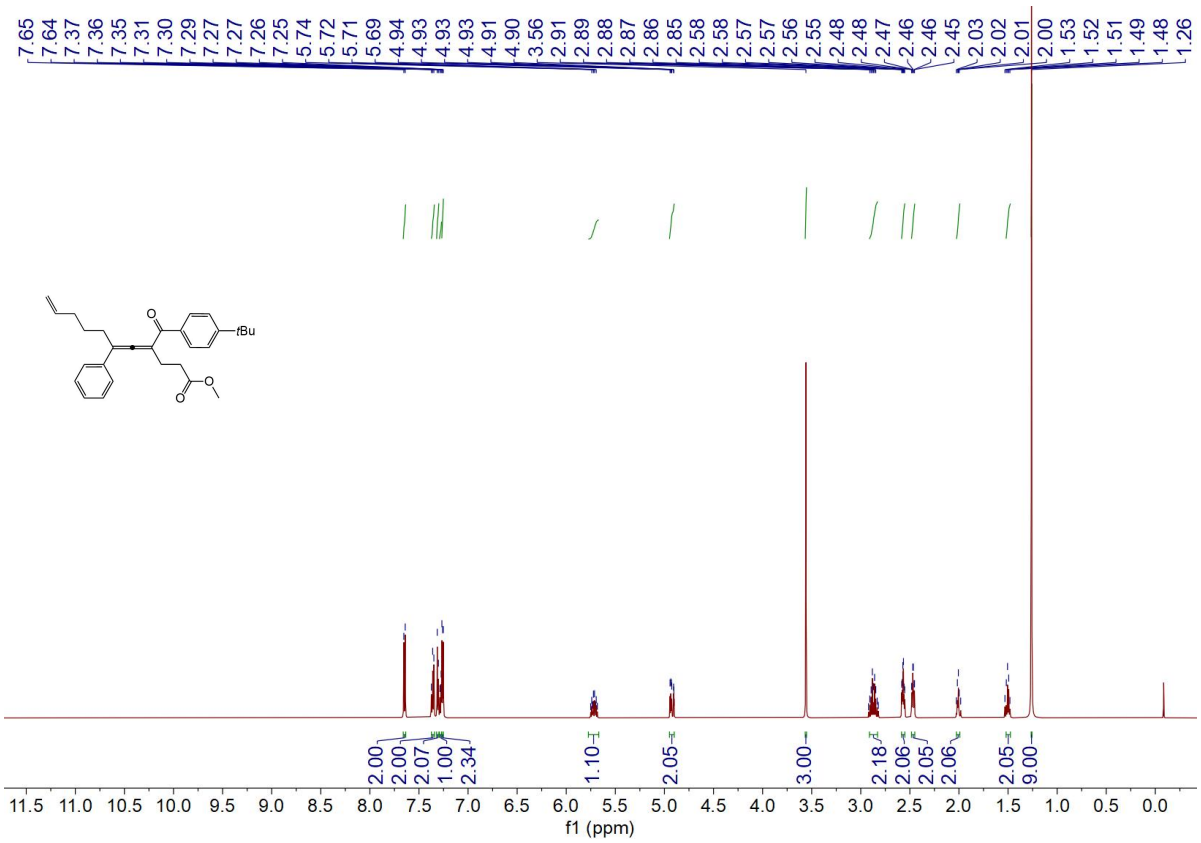
^{1}H NMR (600 MHz, Chloroform-d) of **4h**



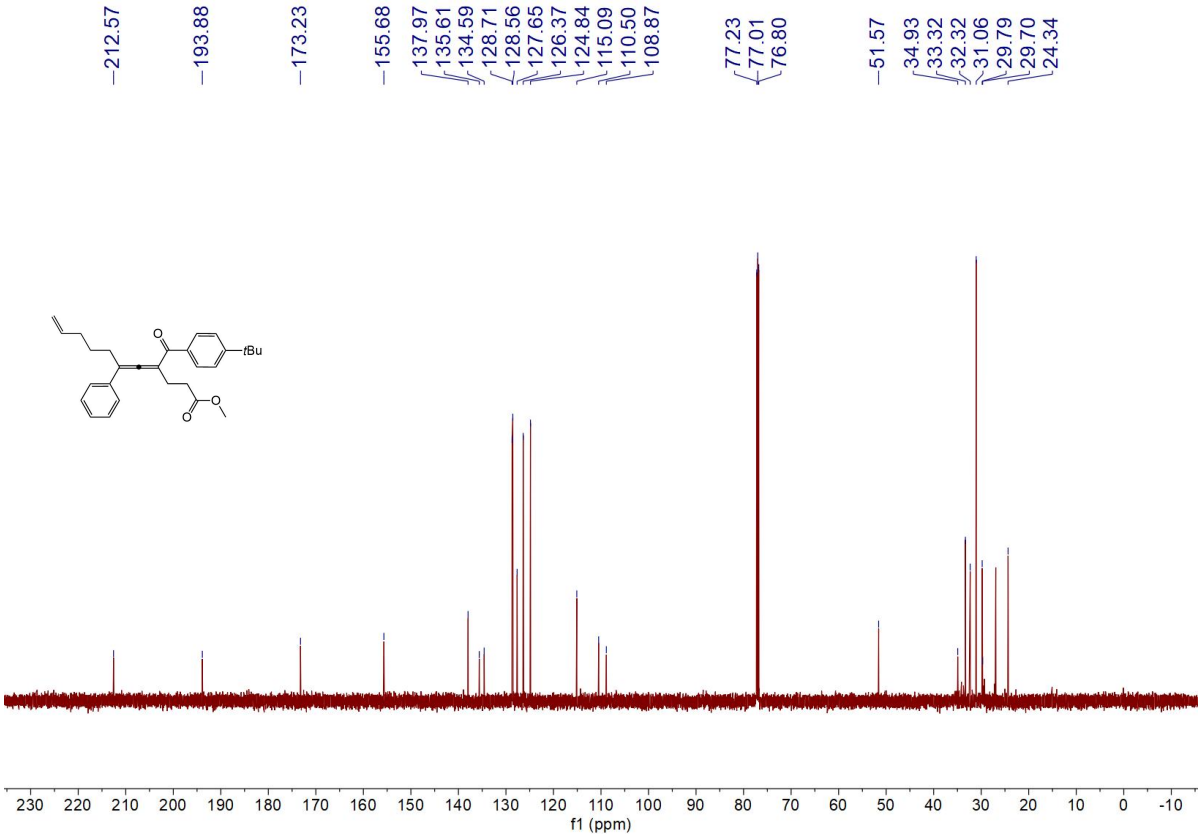
^{13}C NMR (150 MHz, Chloroform-d) of **4h**



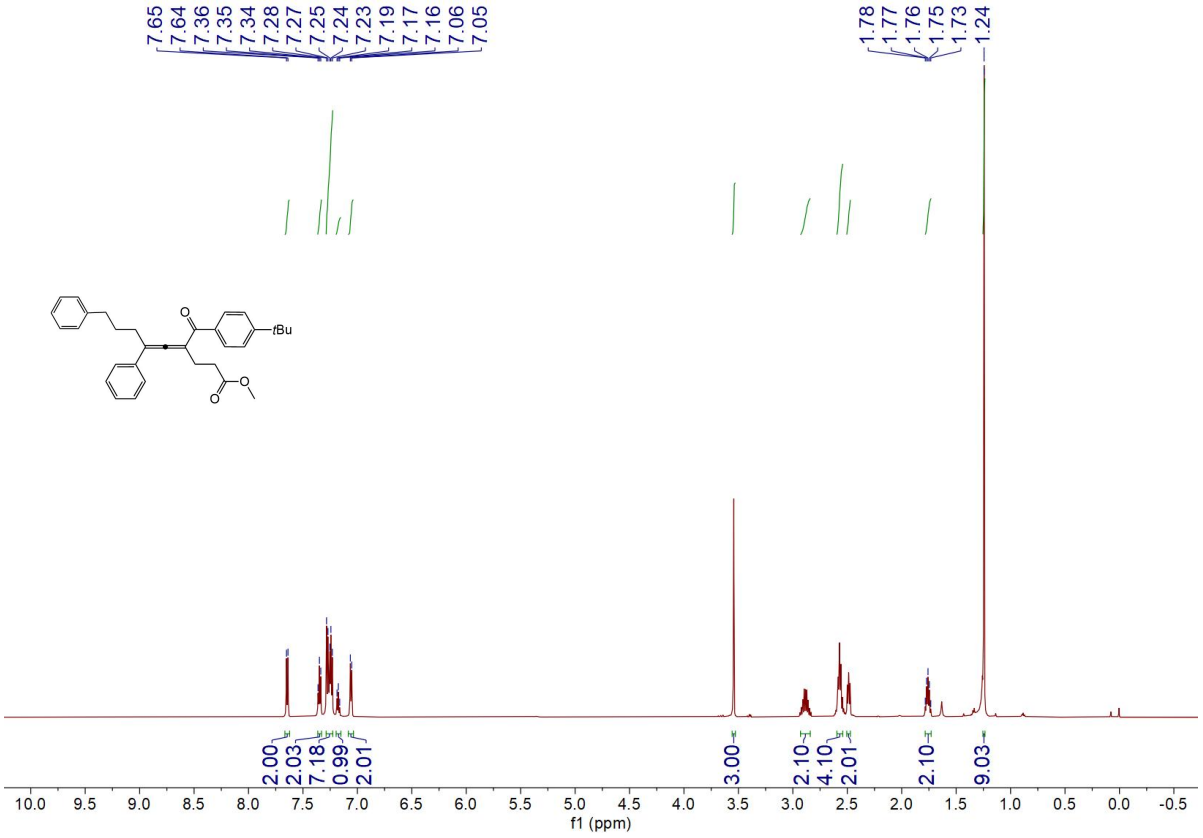
^{1}H NMR (600 MHz, Chloroform-d) of **4i**



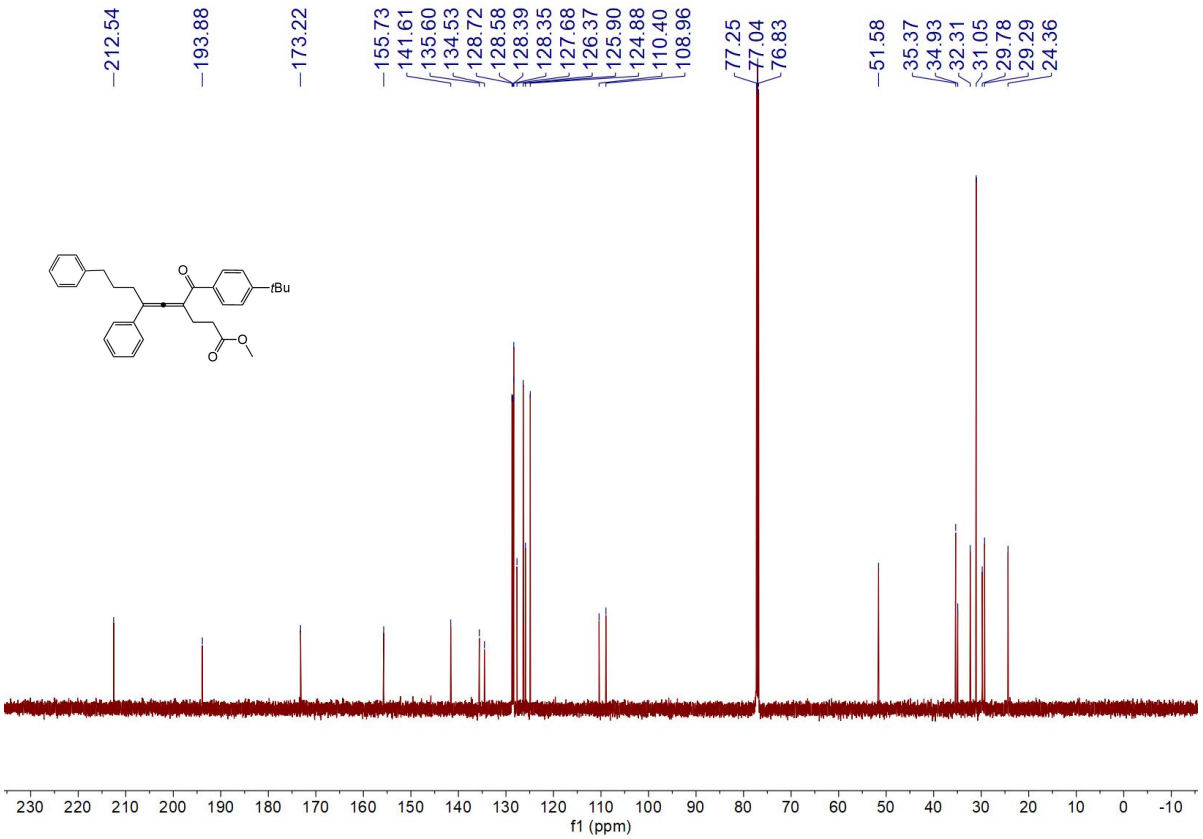
^{13}C NMR (150 MHz, Chloroform-d) of **4i**



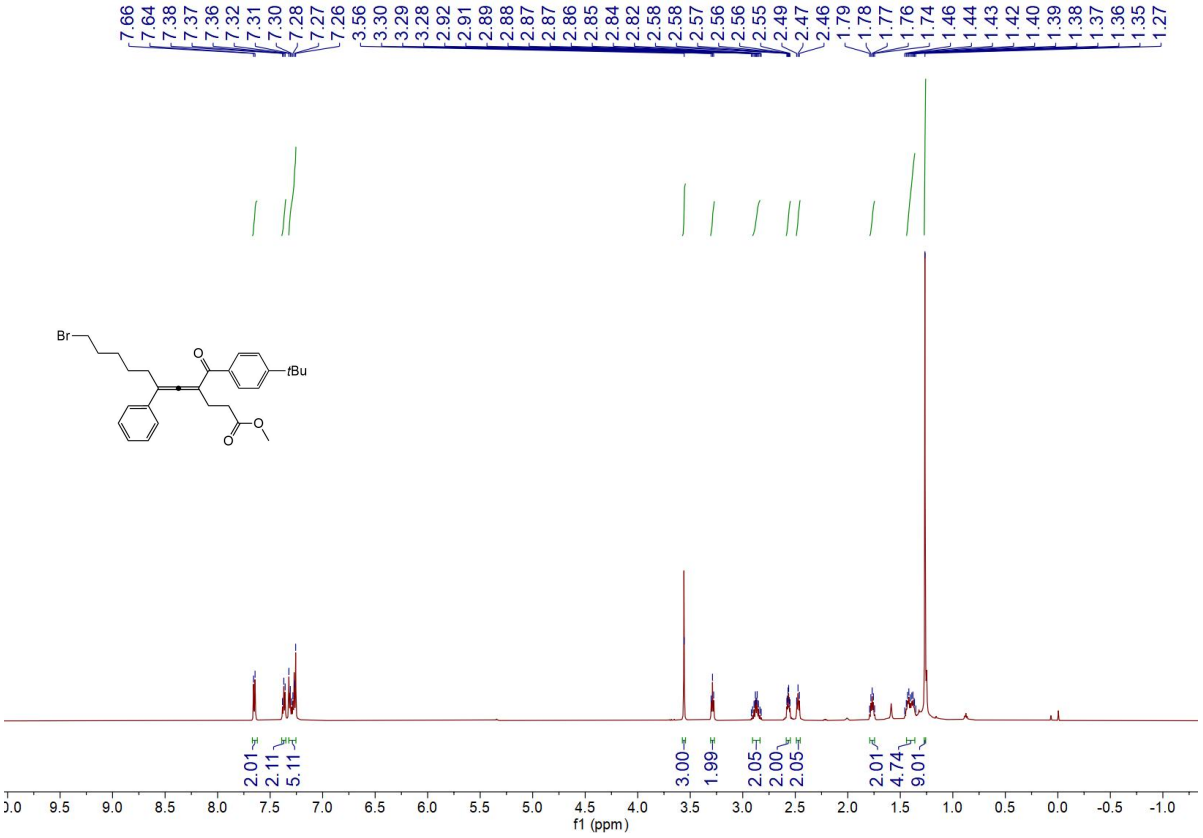
^{1}H NMR (600 MHz, Chloroform-d) of **4j**



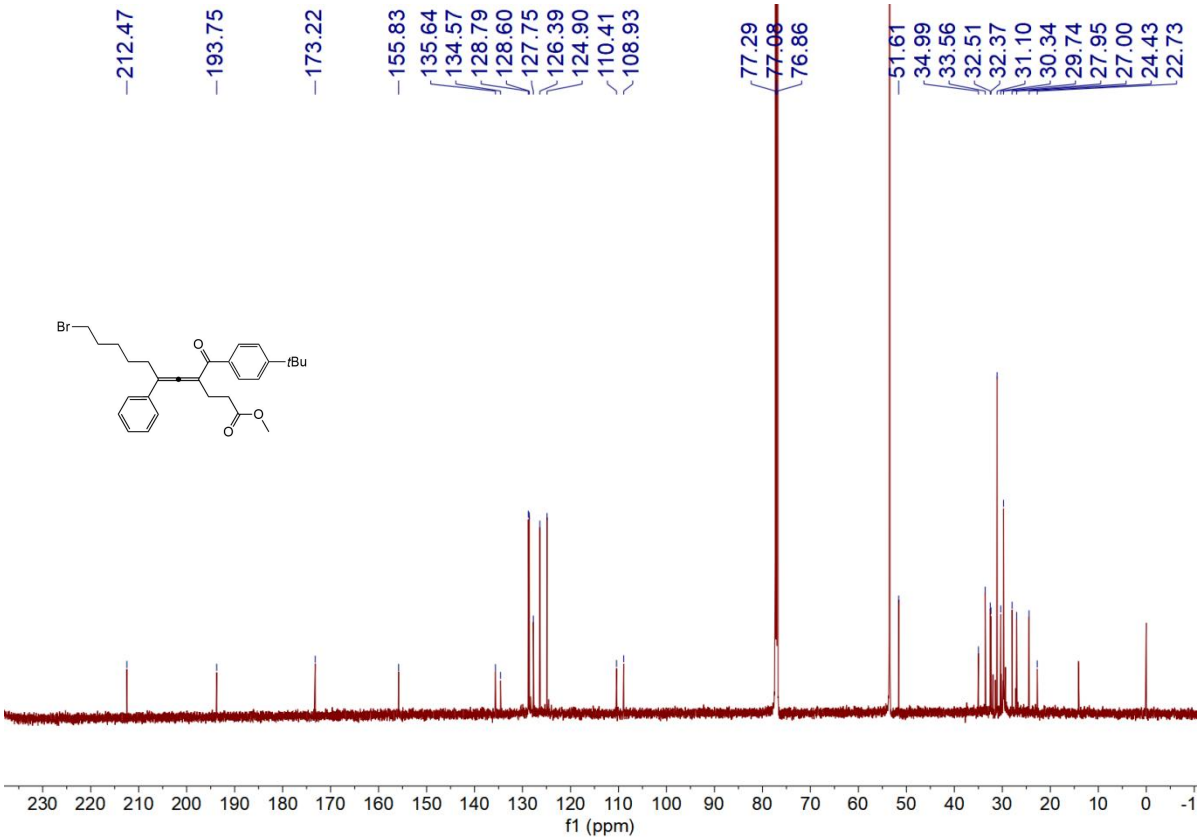
^{13}C NMR (150 MHz, Chloroform-d) of **4j**



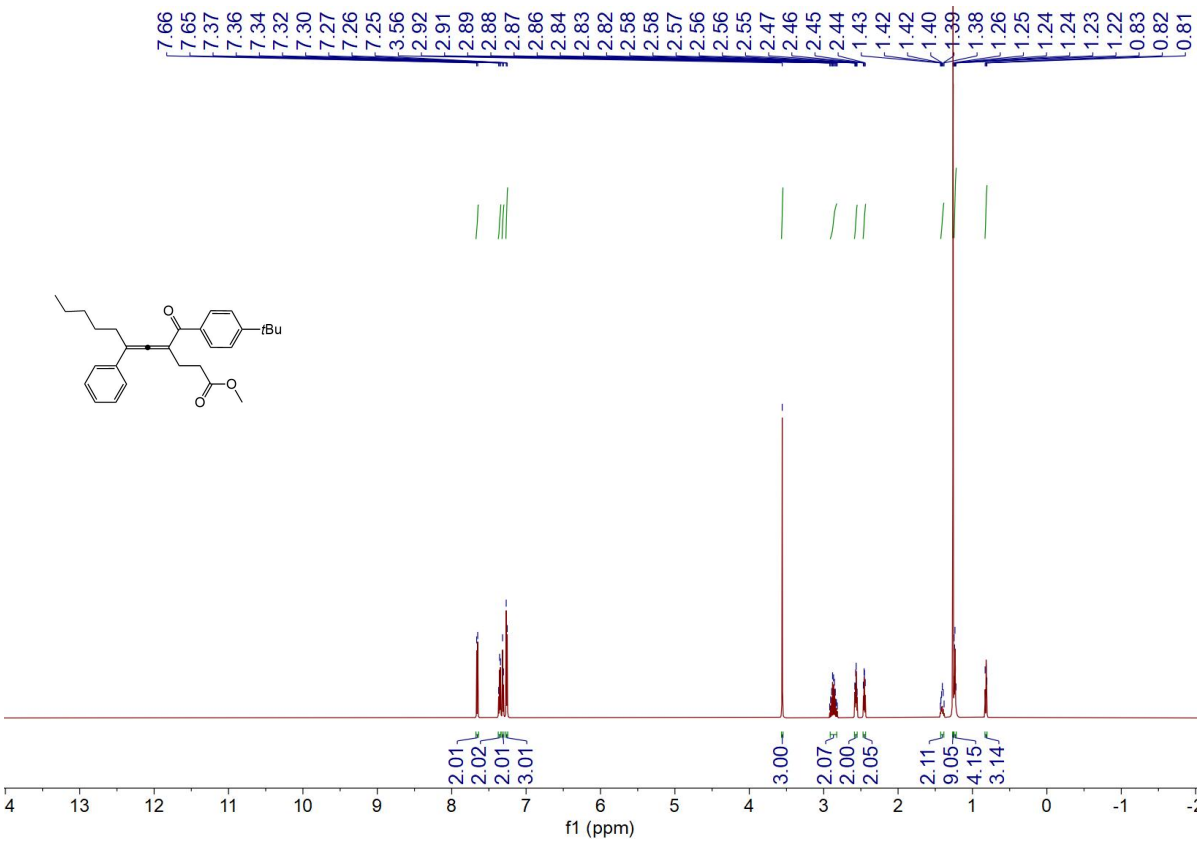
^{1}H NMR (600 MHz, Chloroform-d) of **4k**



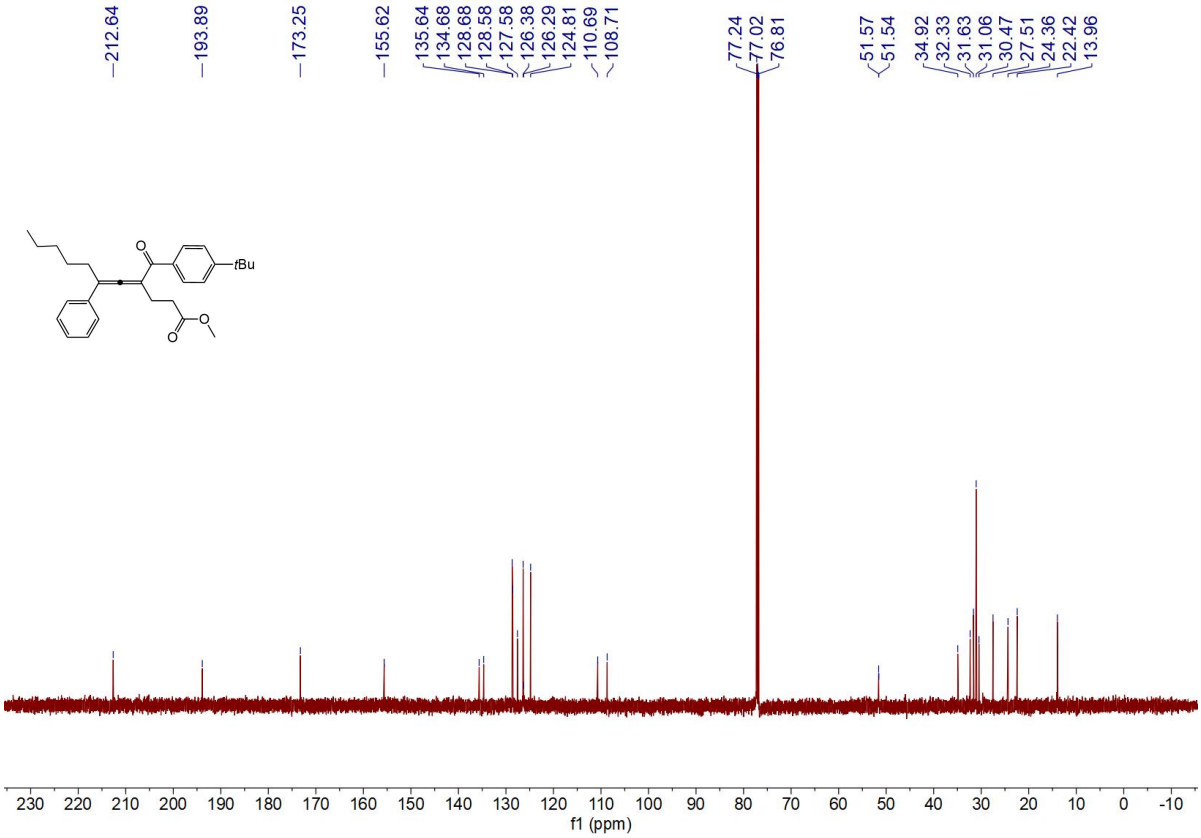
^{13}C NMR (150 MHz, Chloroform-d) of **4k**



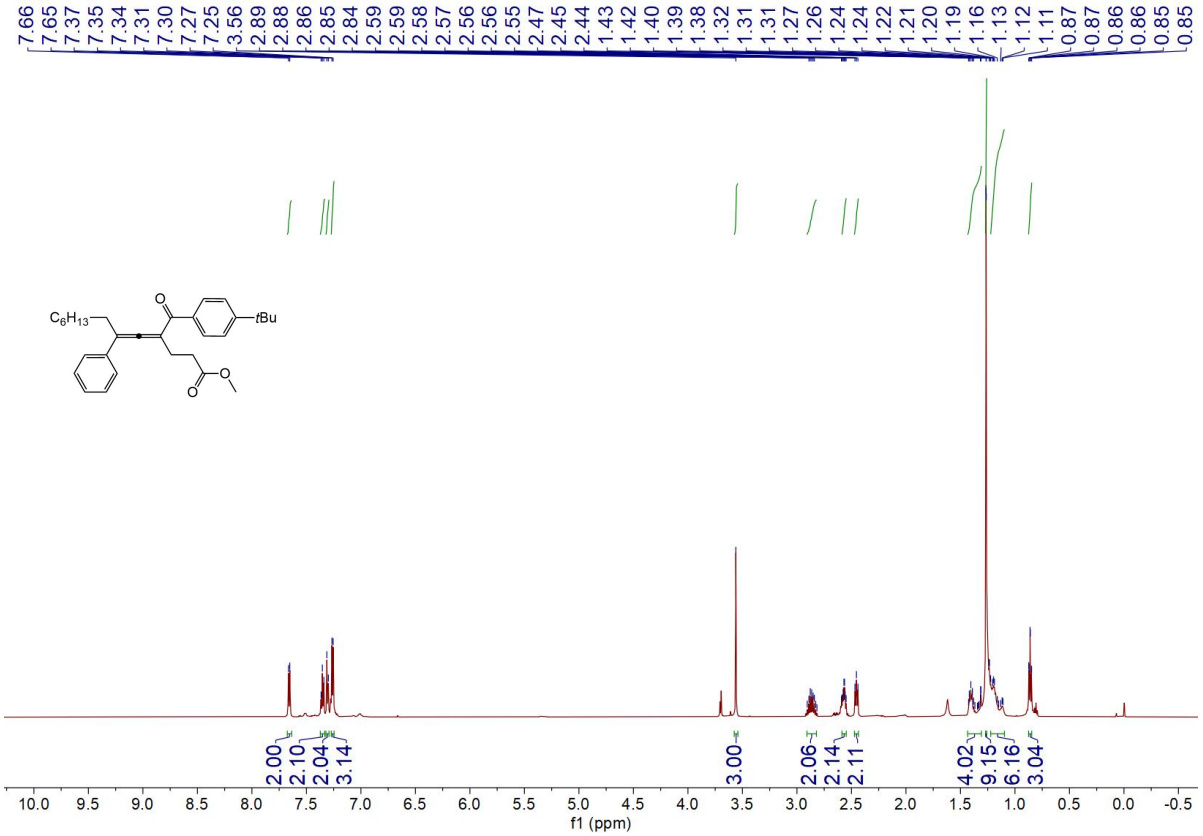
^{1}H NMR (600 MHz, Chloroform-d) of **4l**



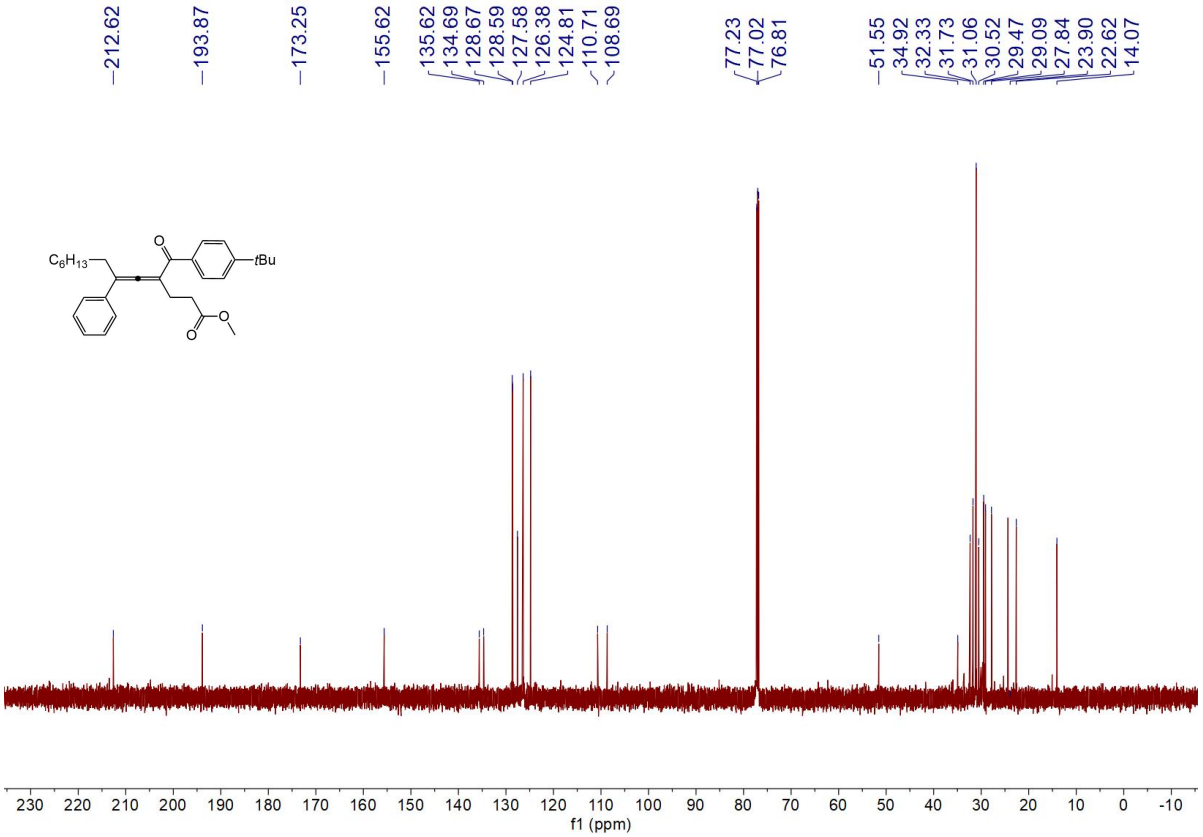
^{13}C NMR (150 MHz, Chloroform-d) of **4l**



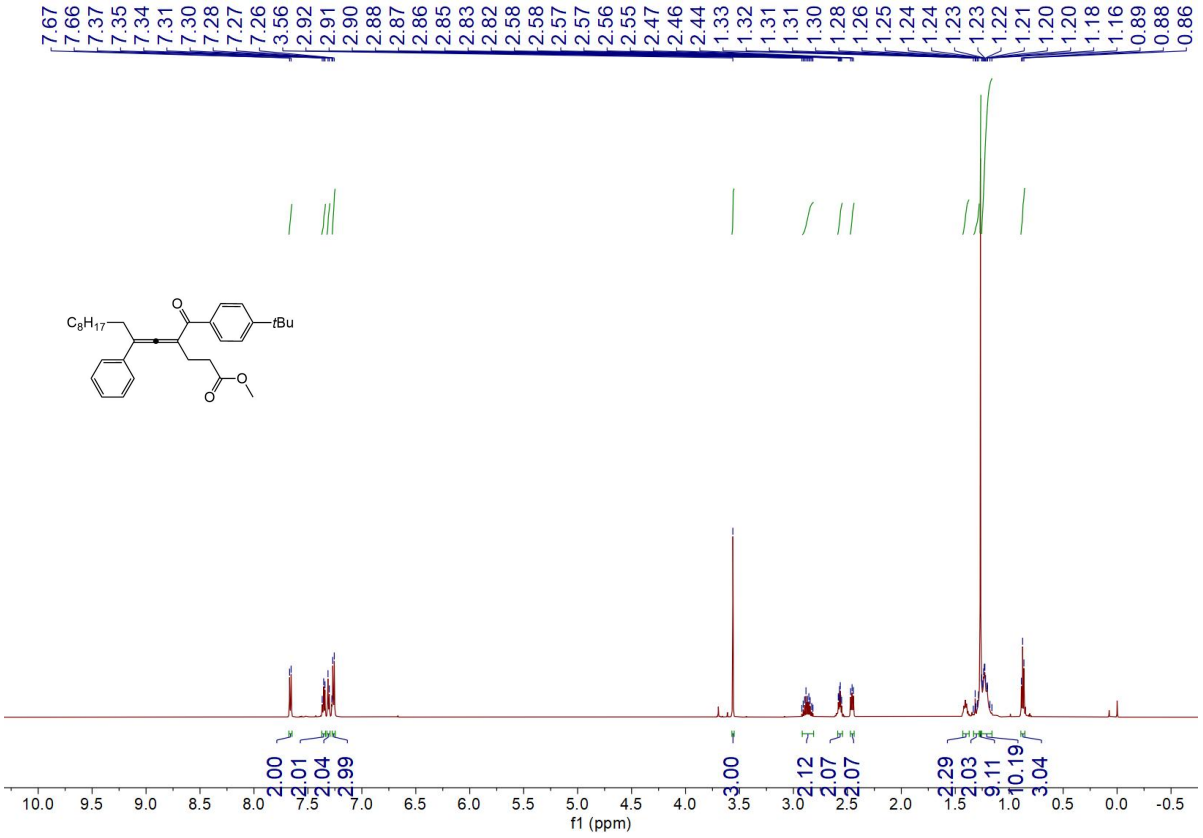
^{1}H NMR (600 MHz, Chloroform-d) of **4m**



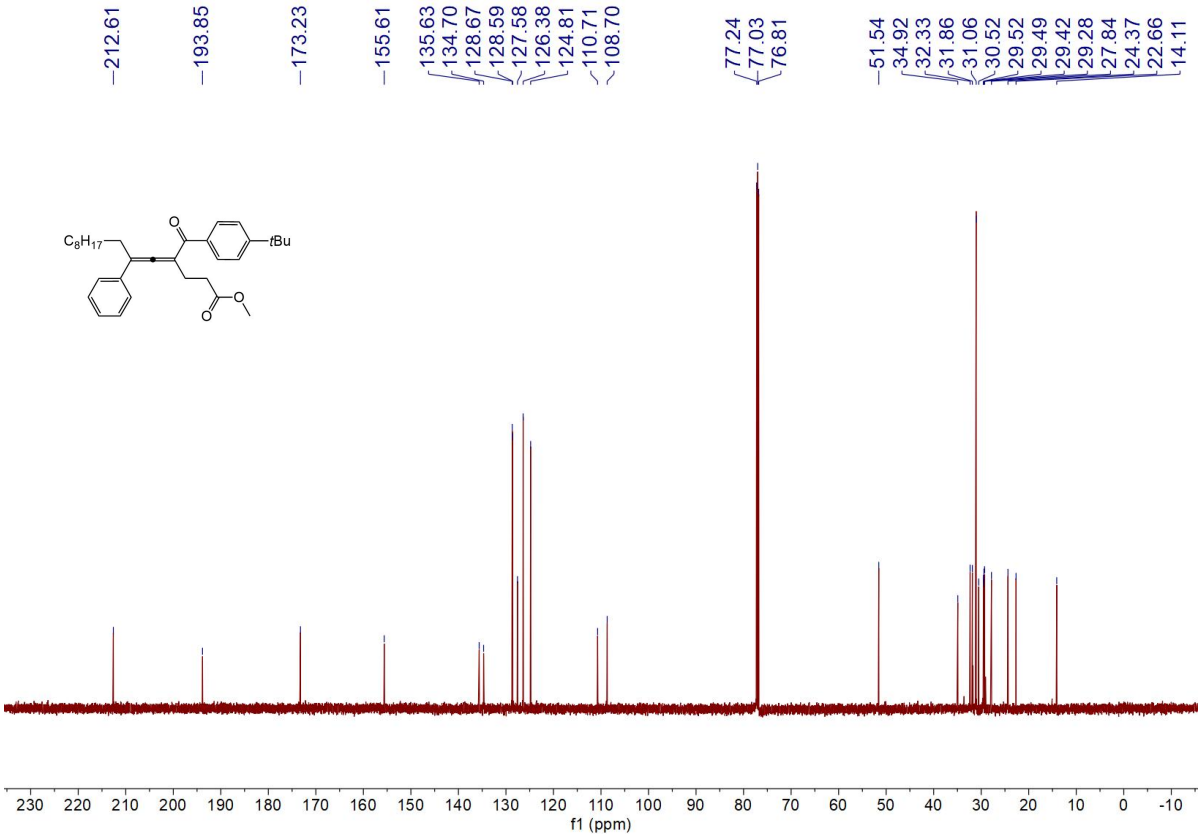
^{13}C NMR (150 MHz, Chloroform-d) of **4m**



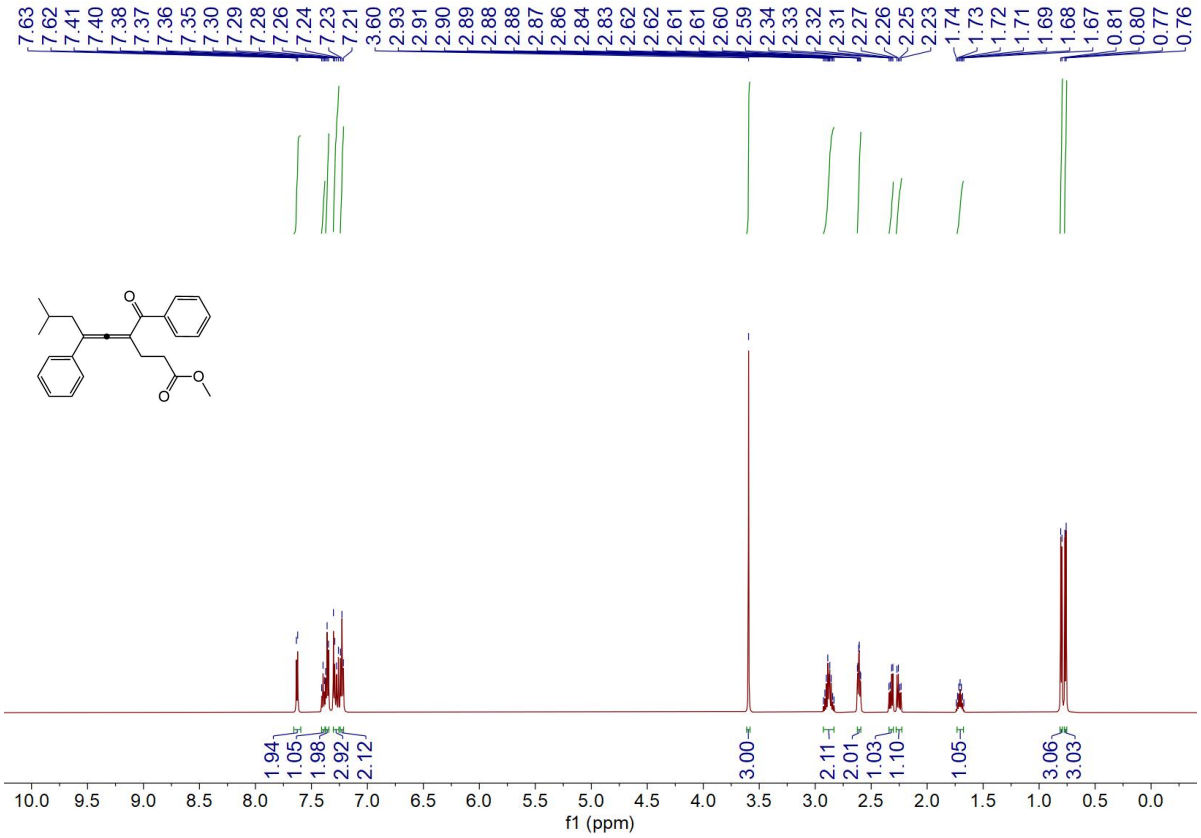
^{1}H NMR (600 MHz, Chloroform-d) of **4n**



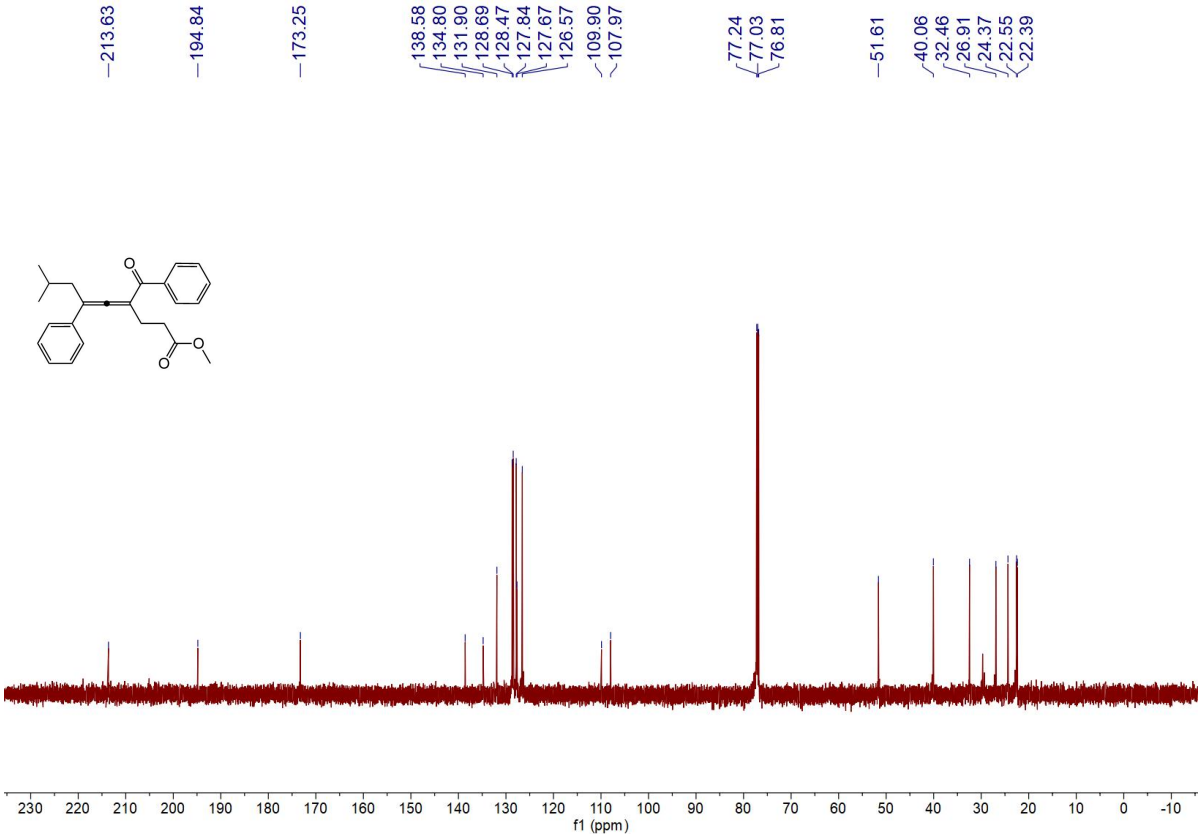
^{13}C NMR (150 MHz, Chloroform-d) of **4n**



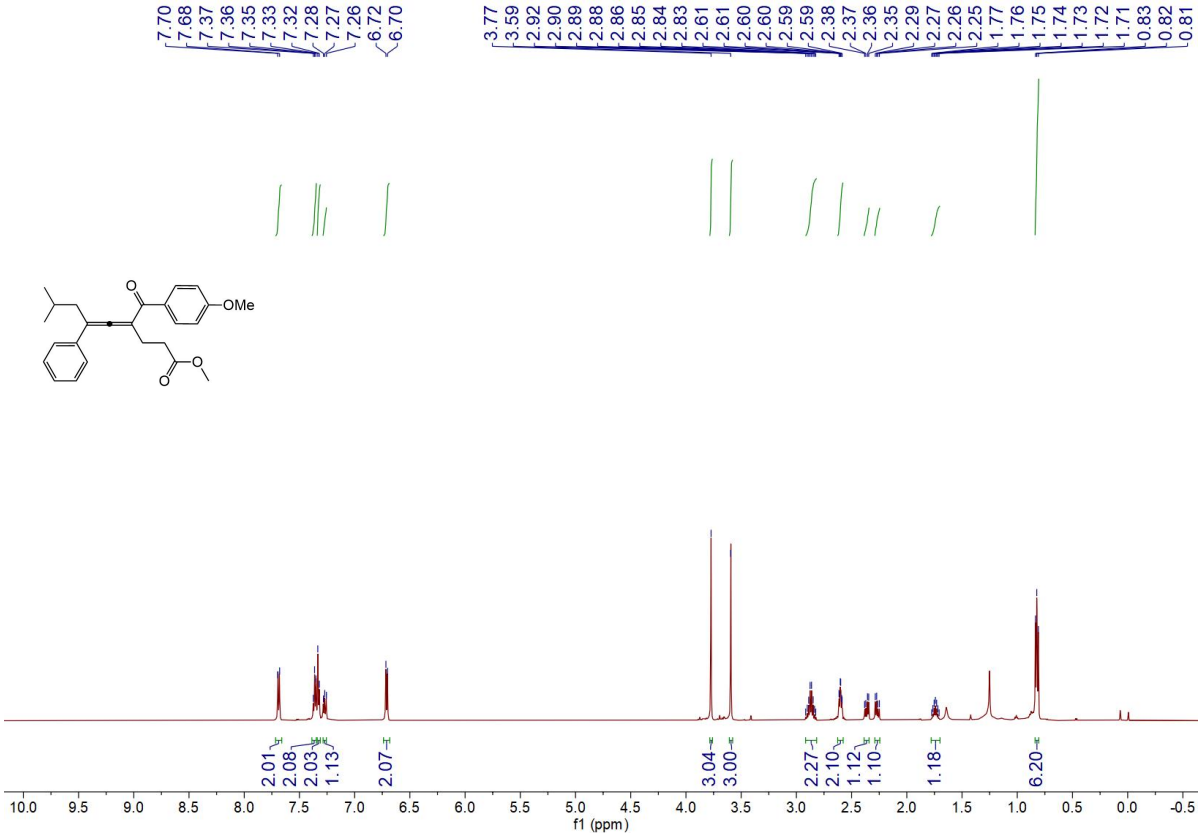
^{1}H NMR (600 MHz, Chloroform-d) of **5a**



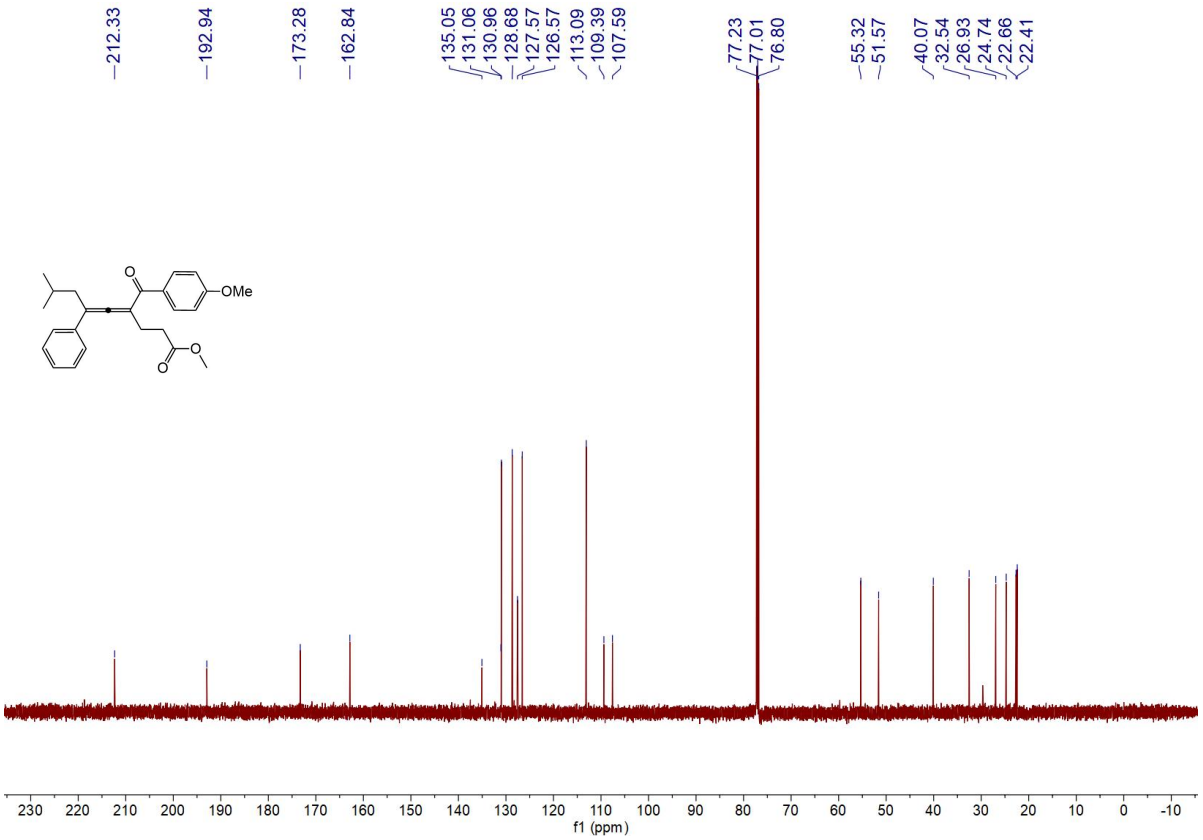
^{13}C NMR (150 MHz, Chloroform-d) of **5a**



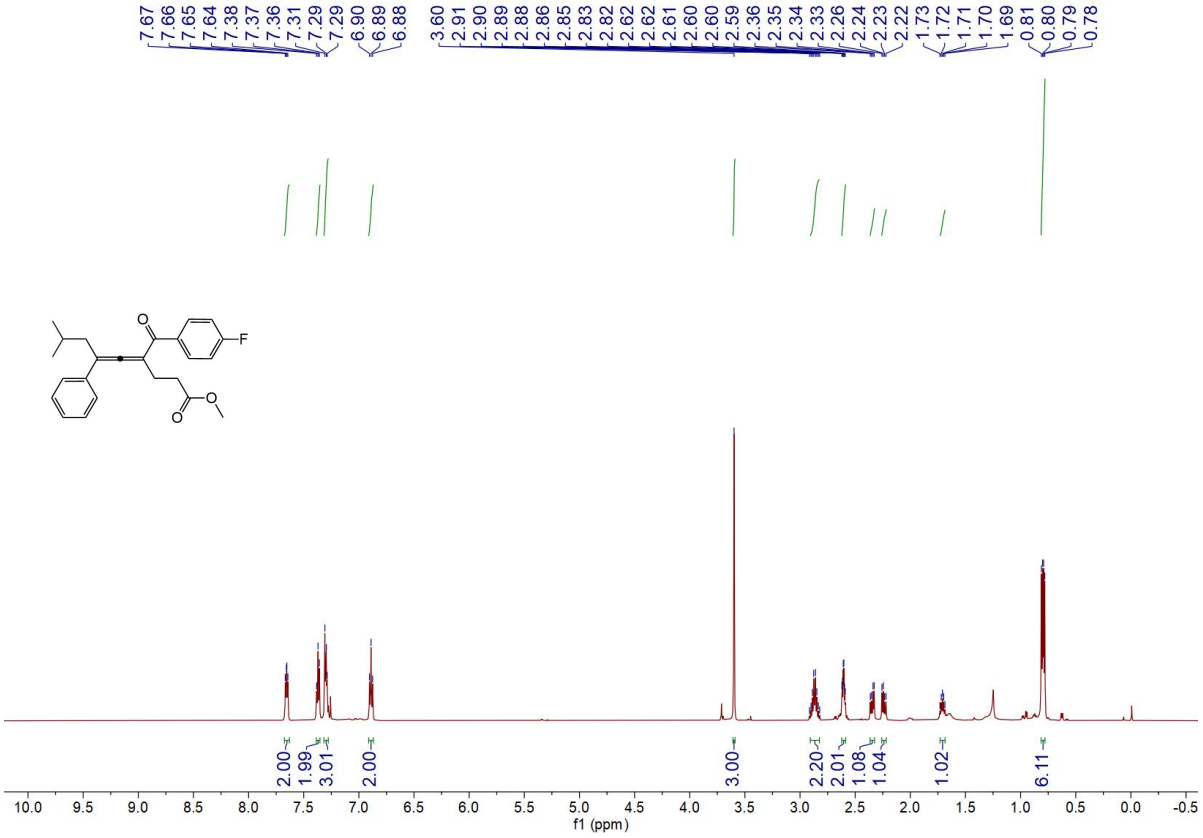
^{1}H NMR (600 MHz, Chloroform-d) of **5b**



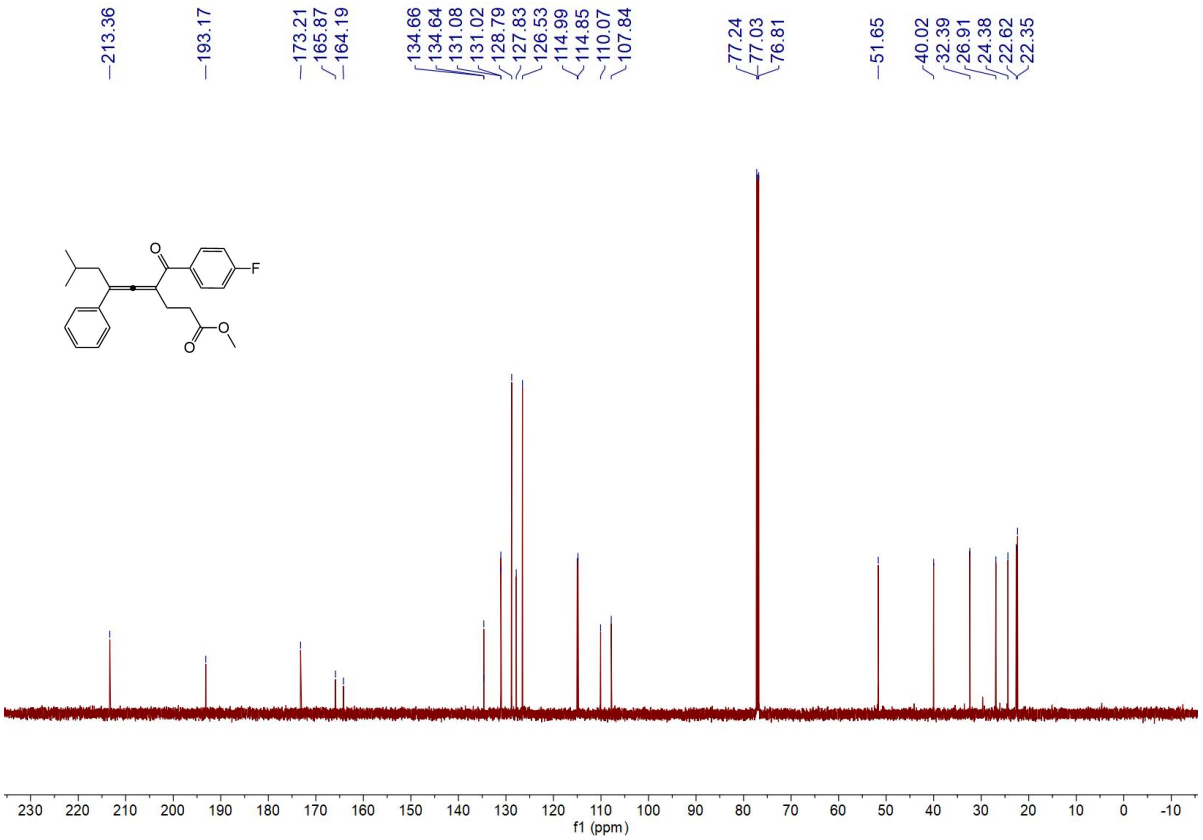
^{13}C NMR (150 MHz, Chloroform-d) of **5b**



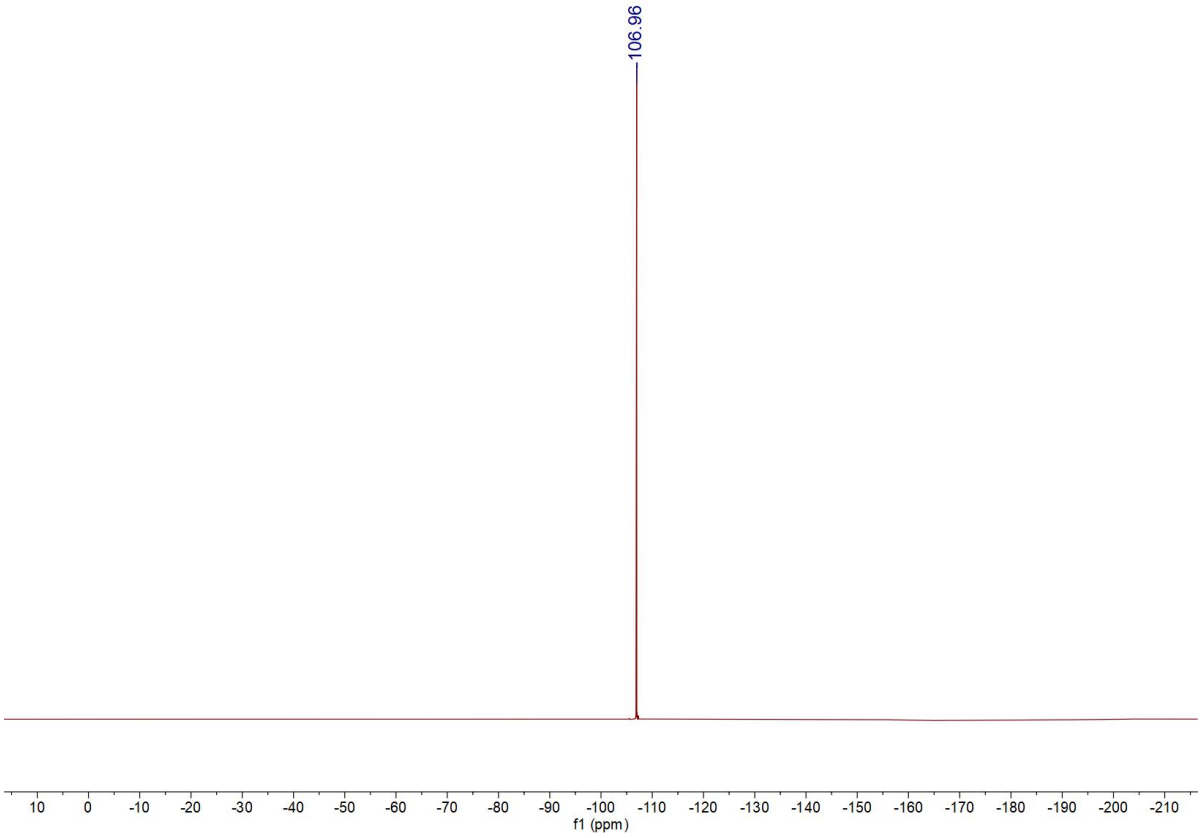
^{1}H NMR (600 MHz, Chloroform-d) of **5ca**



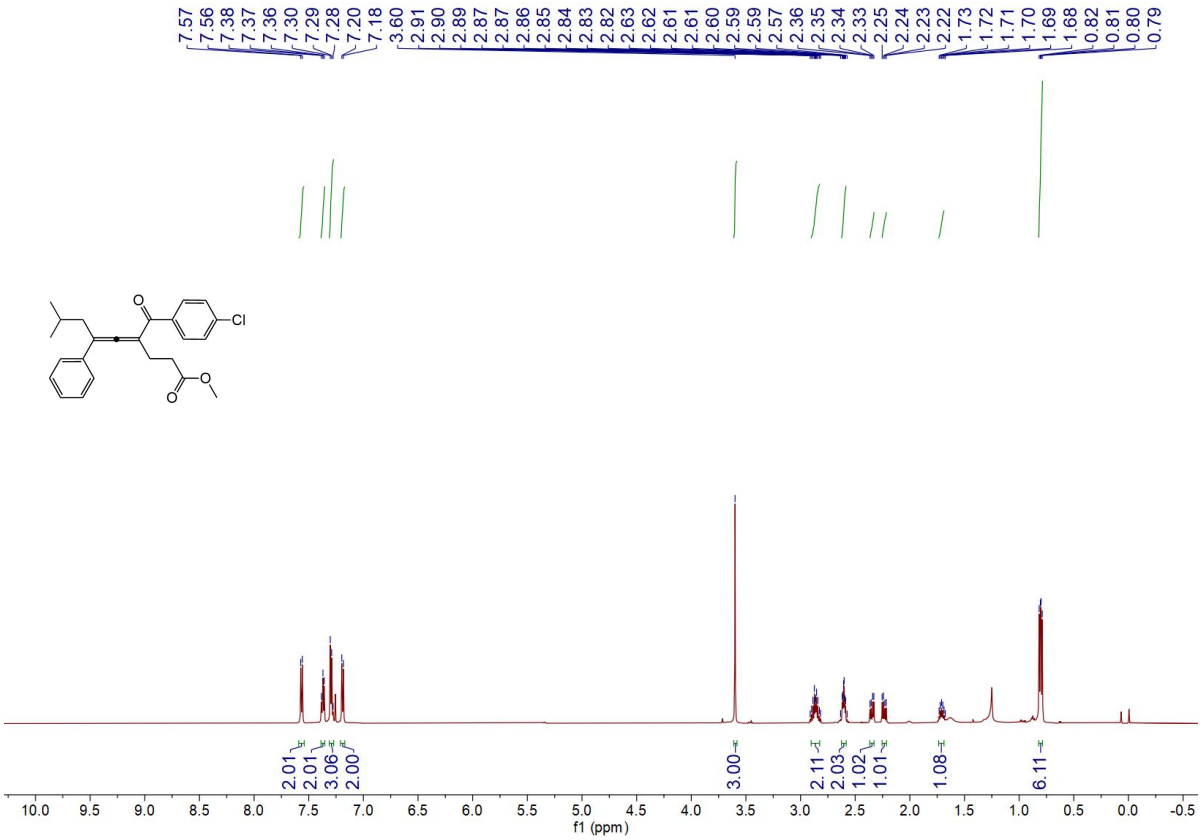
^{13}C NMR (150 MHz, Chloroform-d) of **5ca**



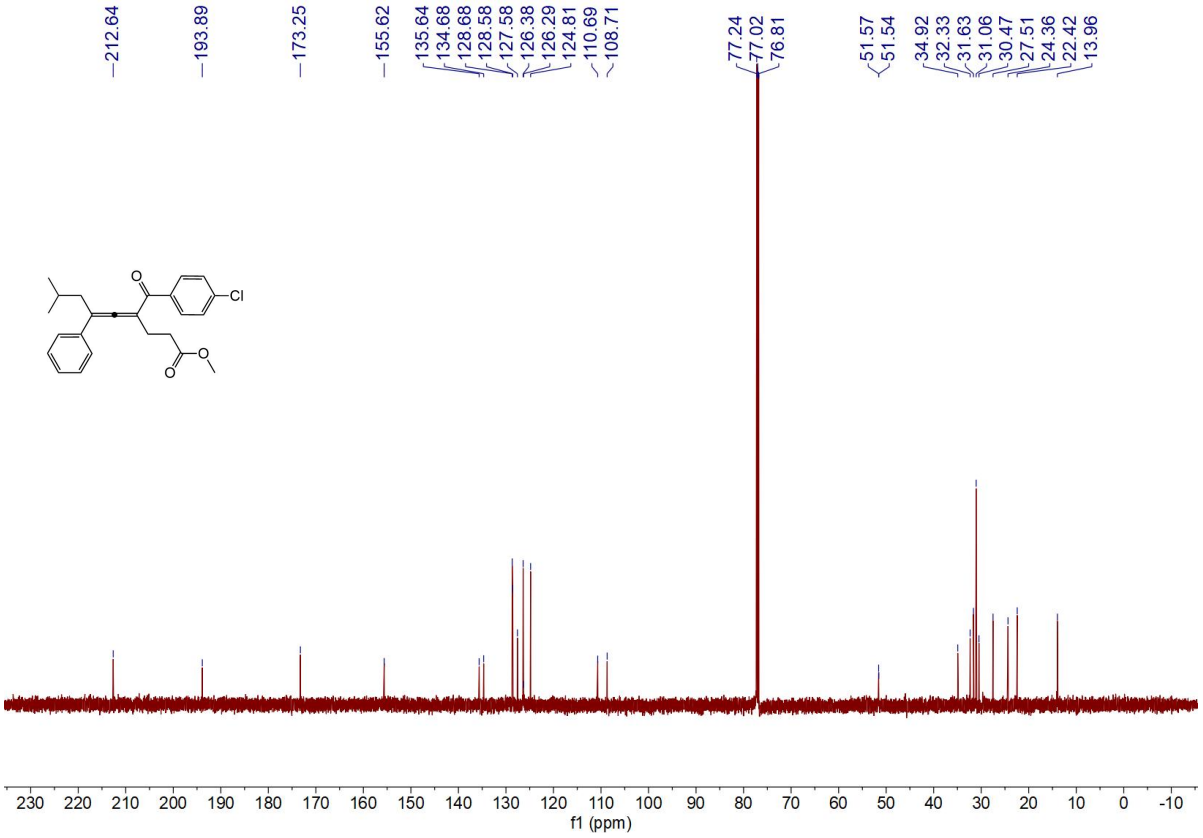
^{19}F NMR (564 MHz, Chloroform-d) of **5ca**



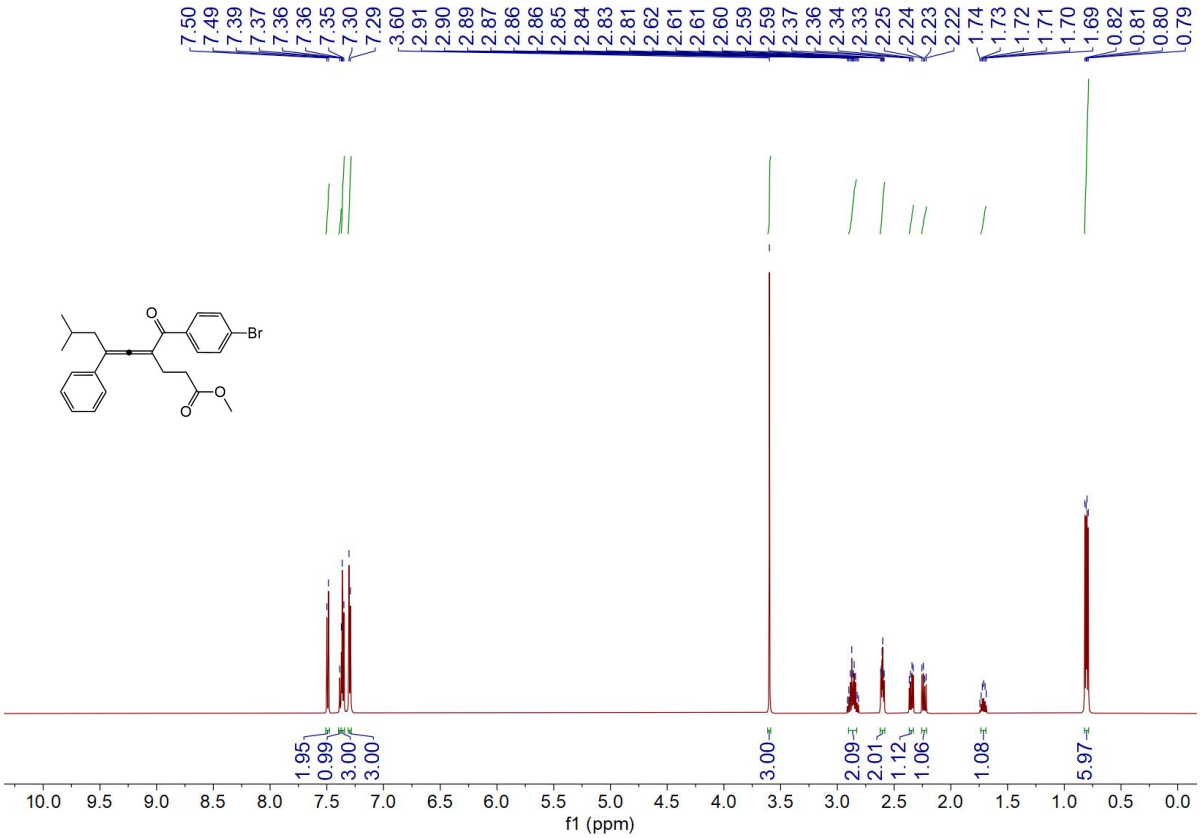
^{1}H NMR (600 MHz, Chloroform-d) of **5cb**



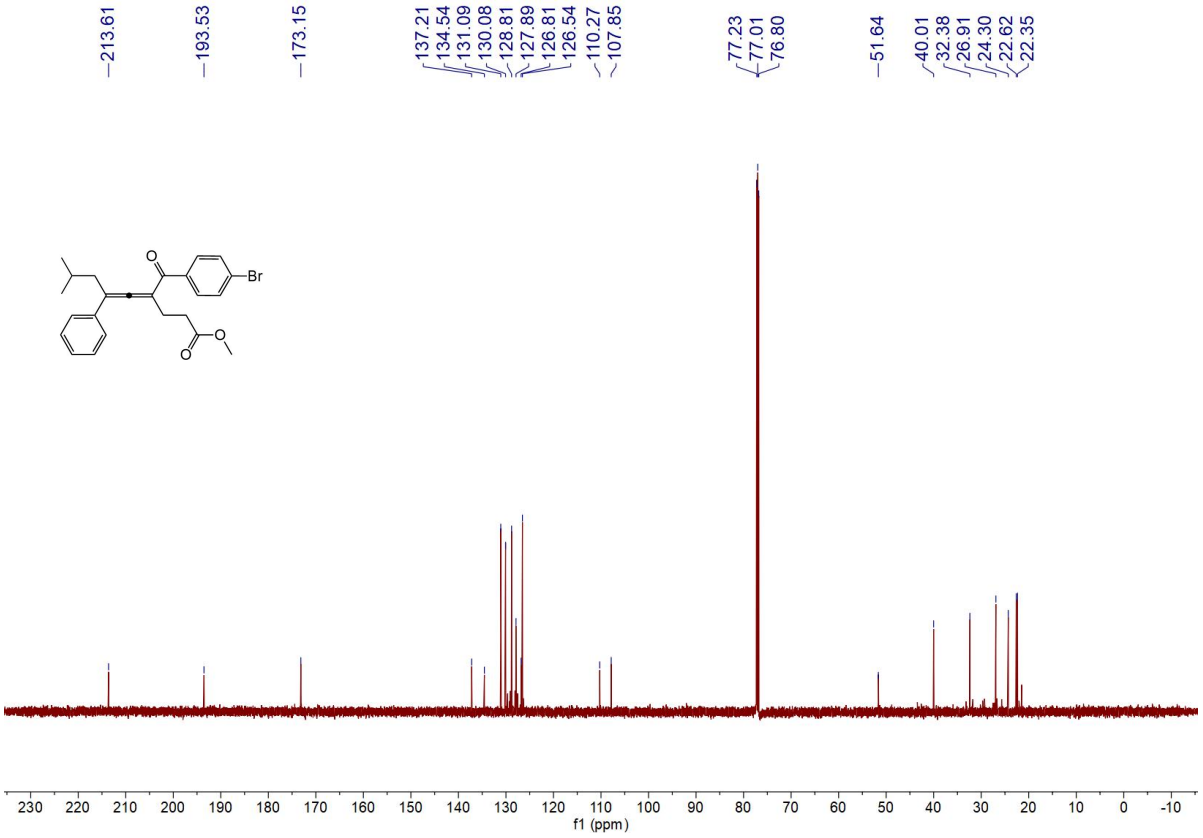
^{13}C NMR (150 MHz, Chloroform-d) of **5cb**



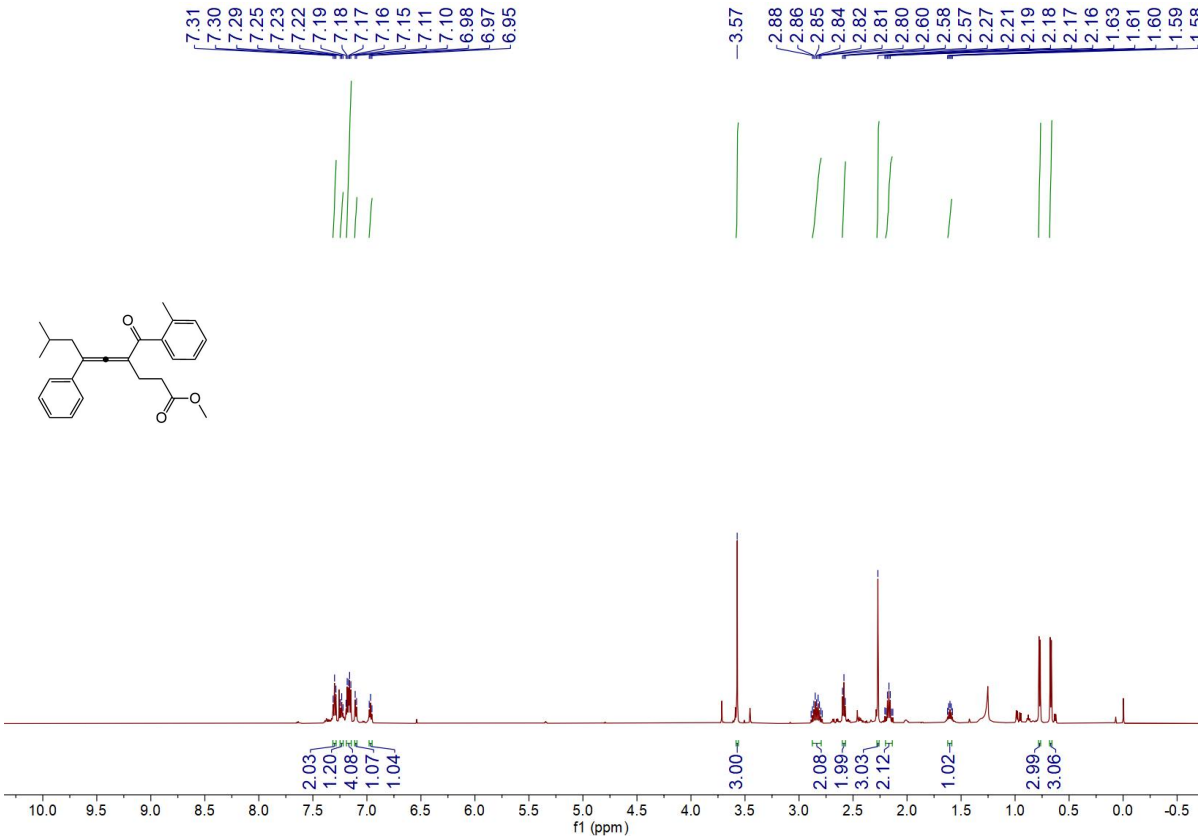
^{1}H NMR (600 MHz, Chloroform-d) of **5cc**



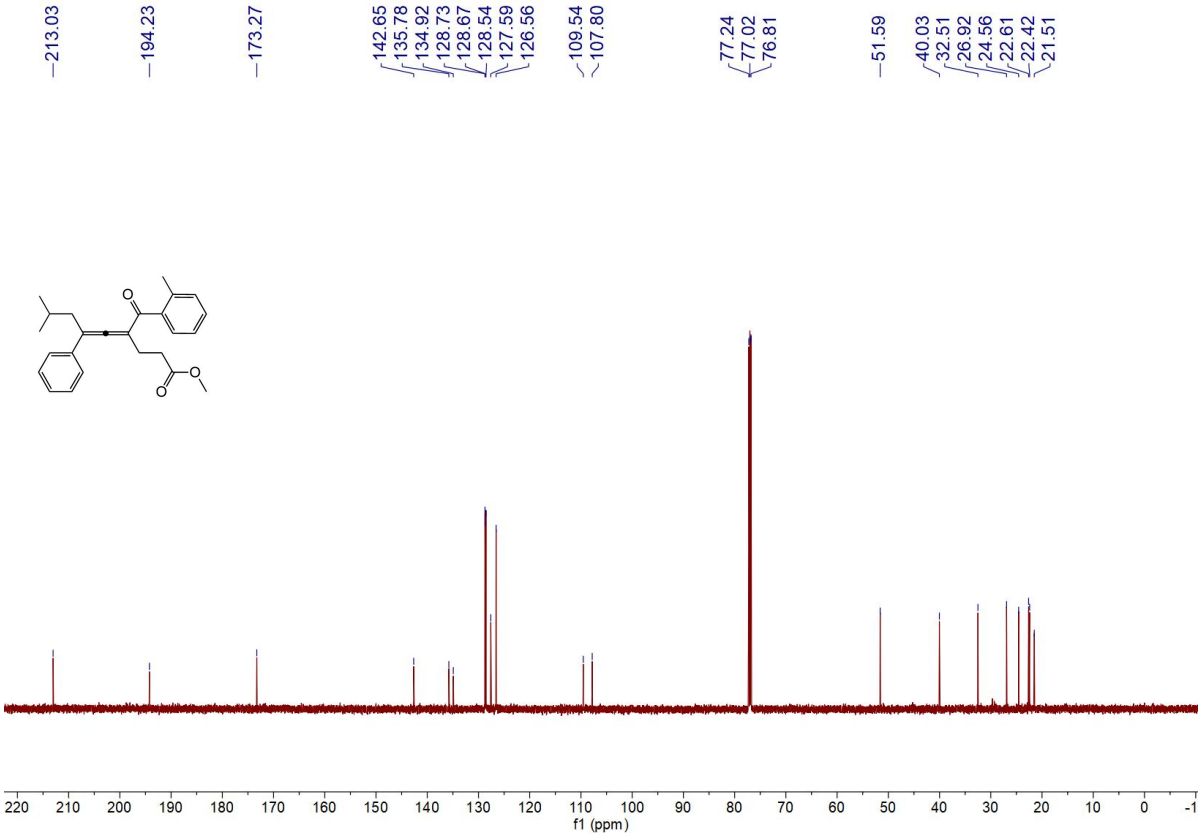
^{13}C NMR (150 MHz, Chloroform-d) of **5cc**



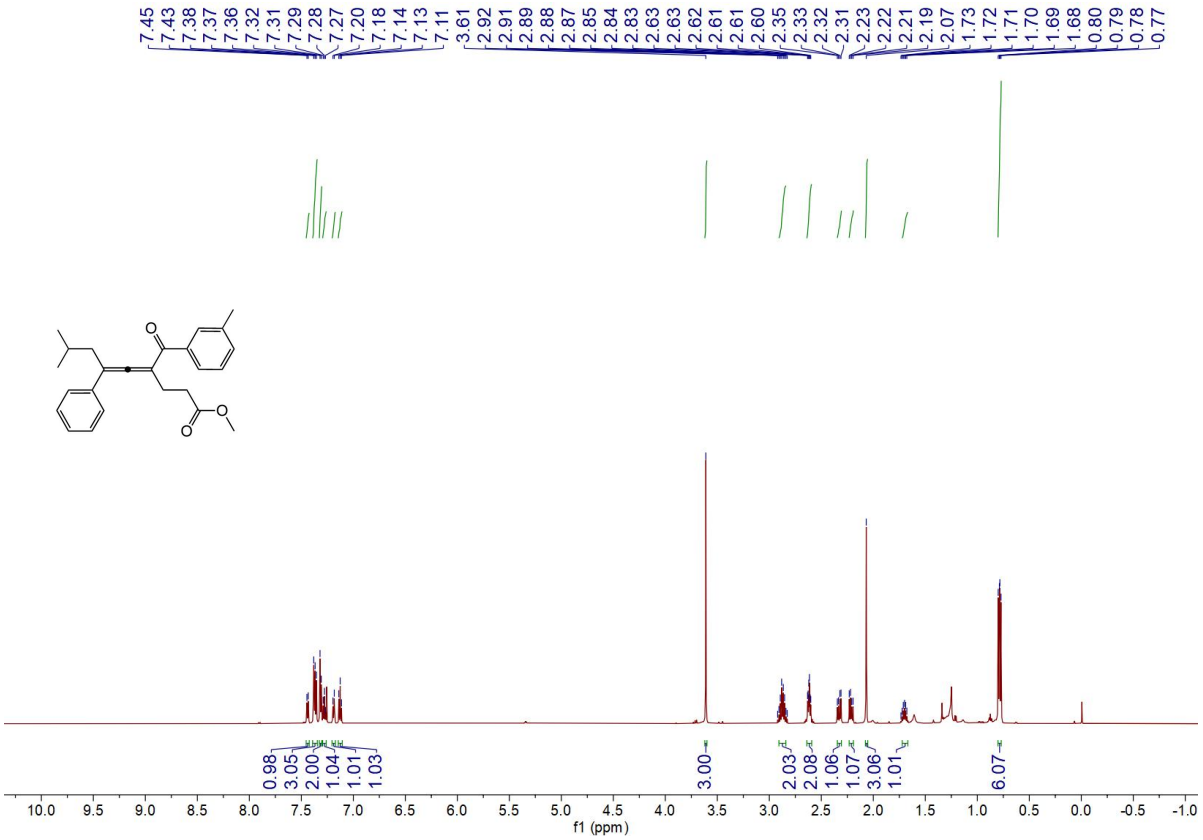
^{1}H NMR (600 MHz, Chloroform-d) of **5da**



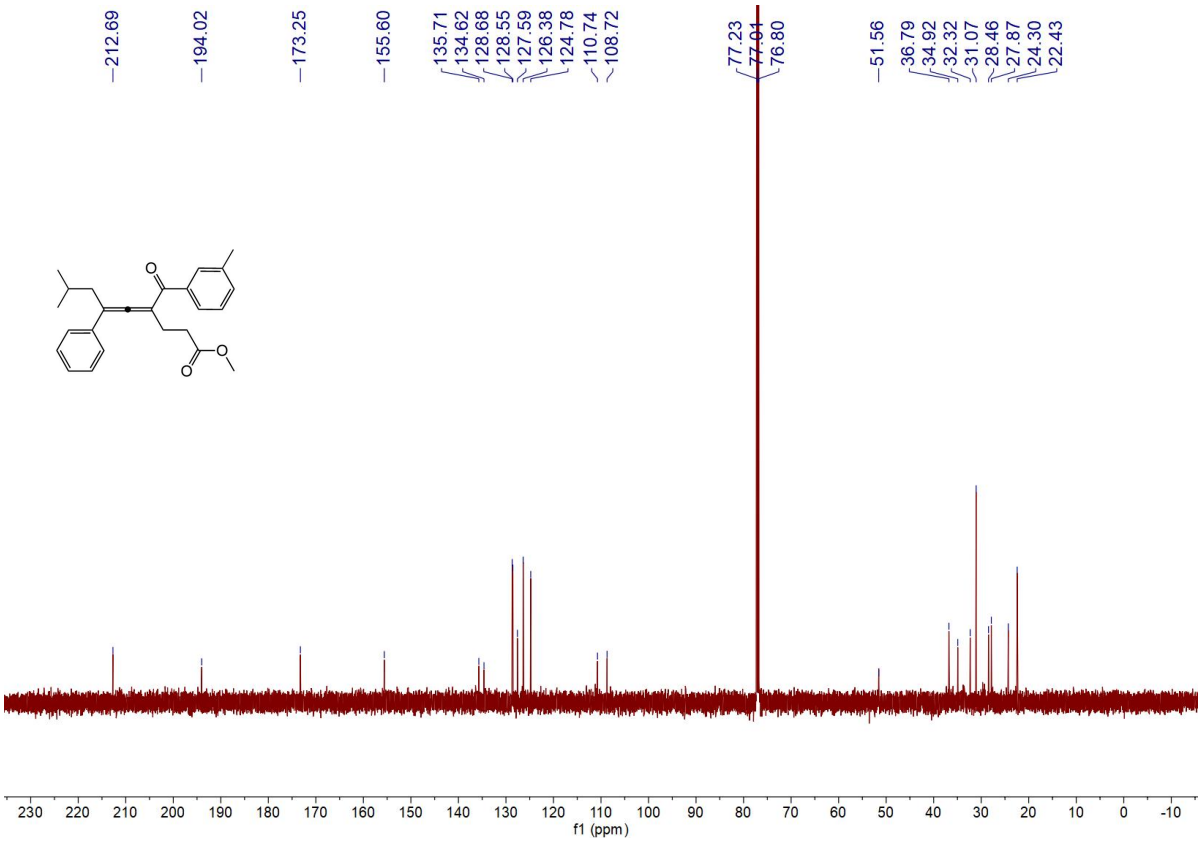
^{13}C NMR (150 MHz, Chloroform-d) of **5da**



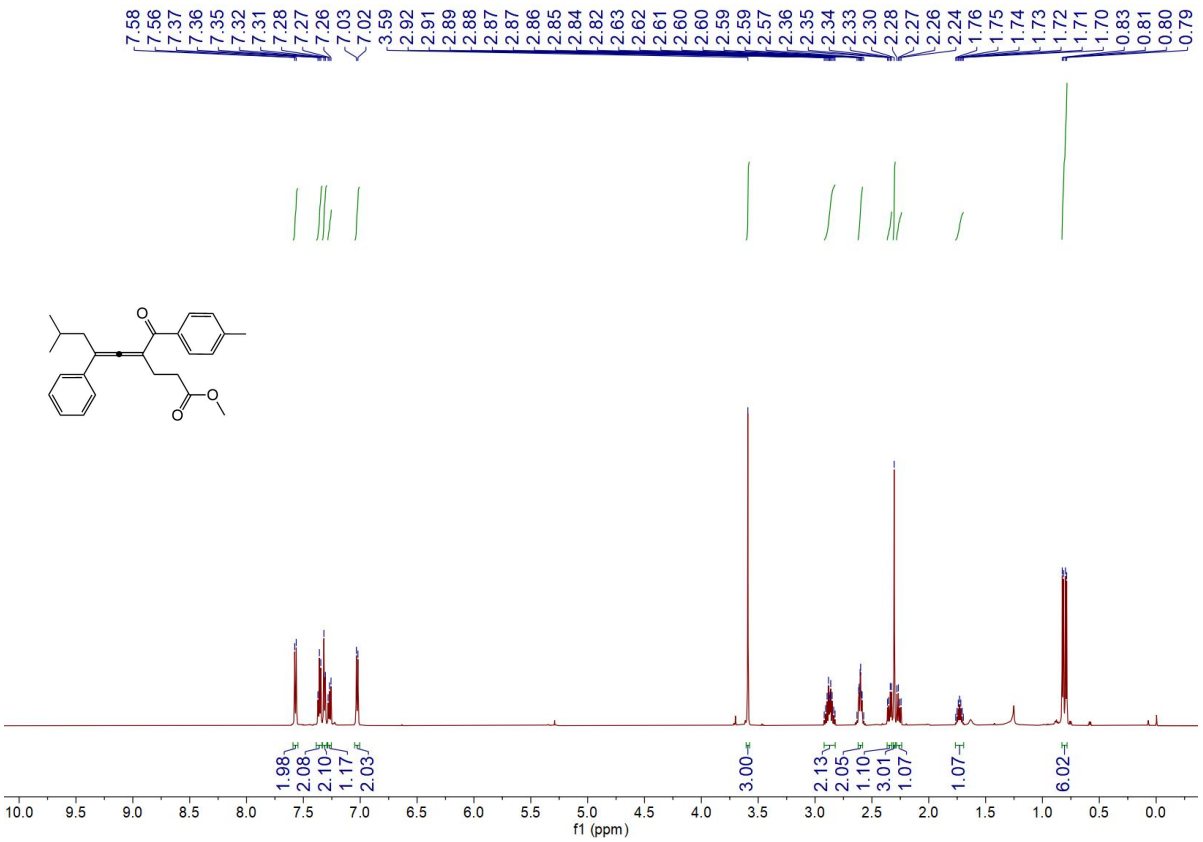
^{1}H NMR (600 MHz, Chloroform-d) of **5db**



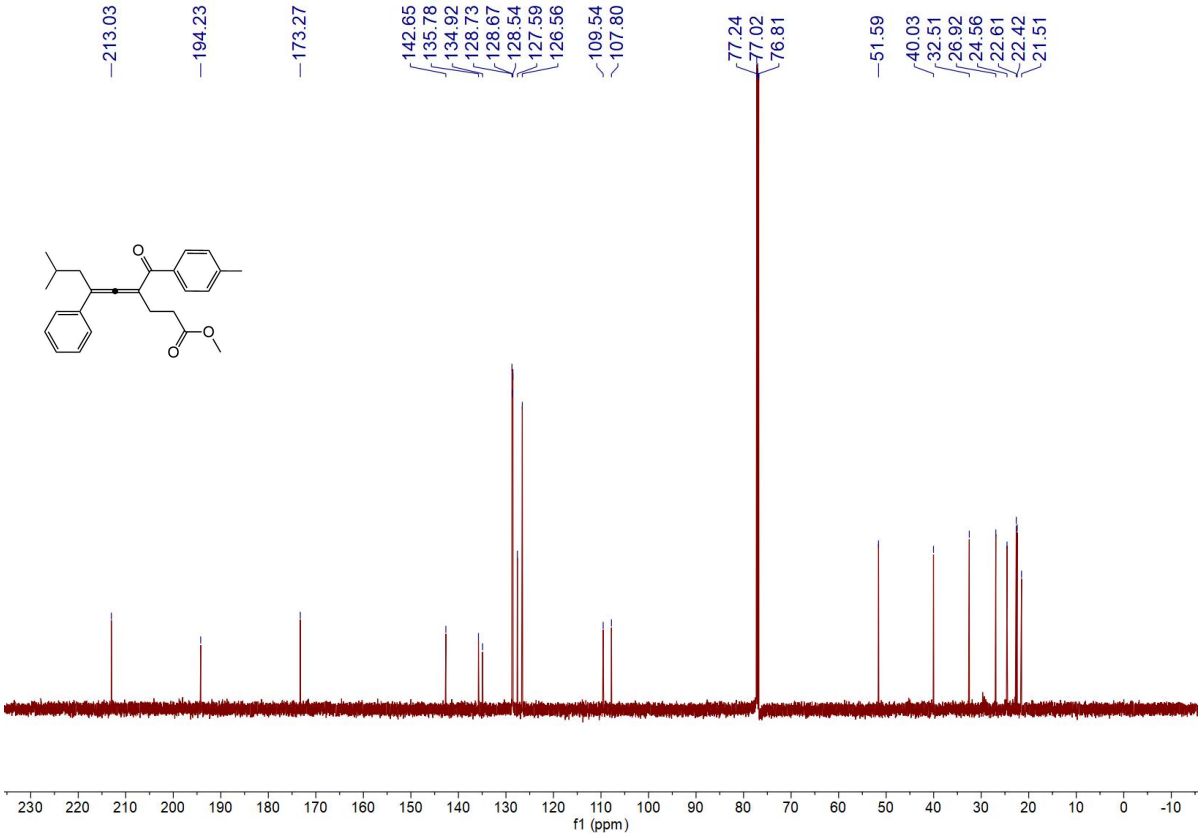
^{13}C NMR (150 MHz, Chloroform-d) of **5db**



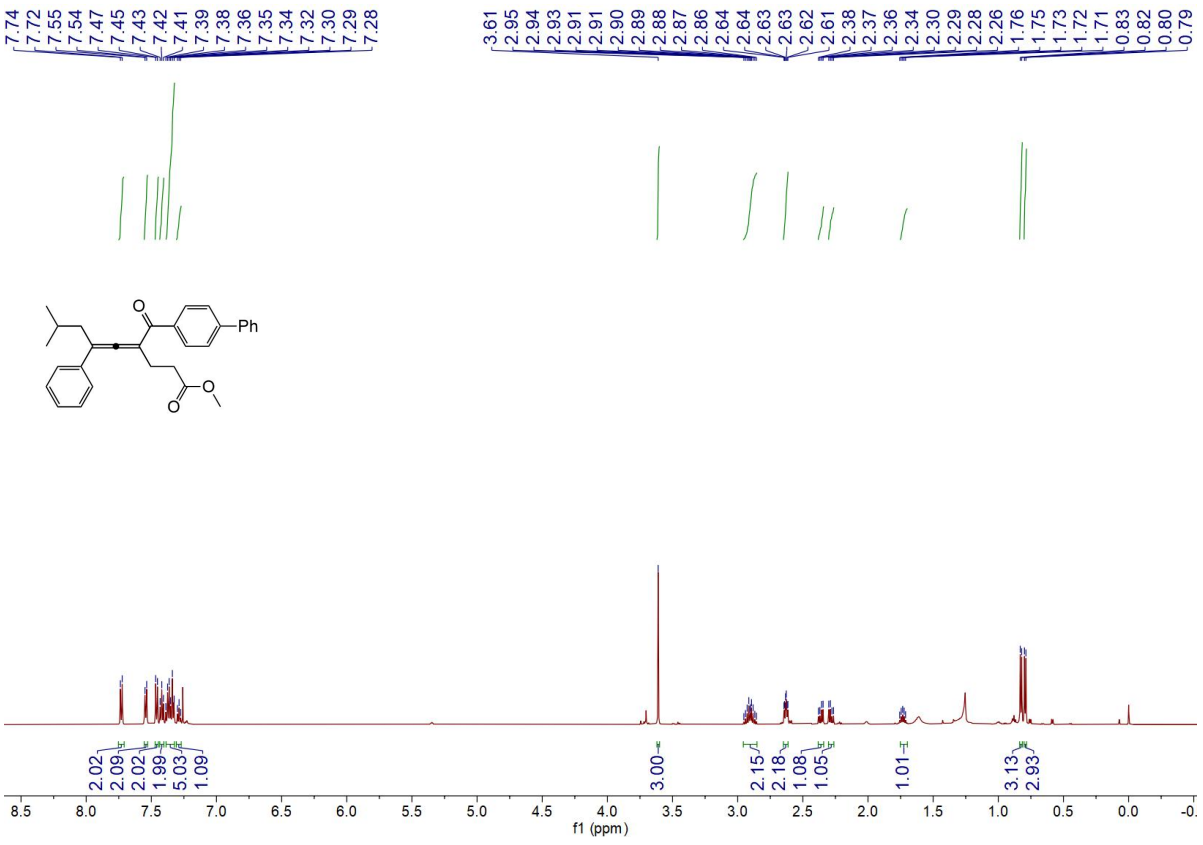
^{1}H NMR (600 MHz, Chloroform-d) of **5dc**



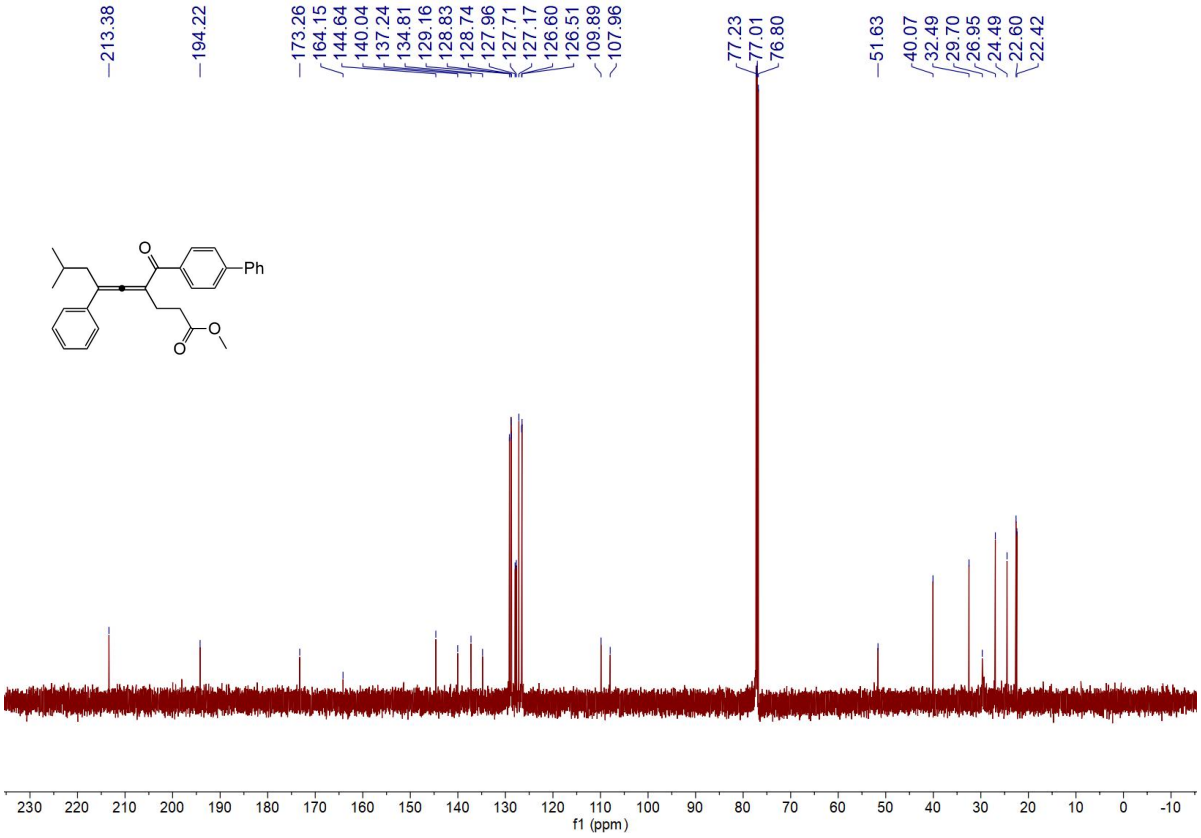
^{13}C NMR (150 MHz, Chloroform-d) of **5dc**



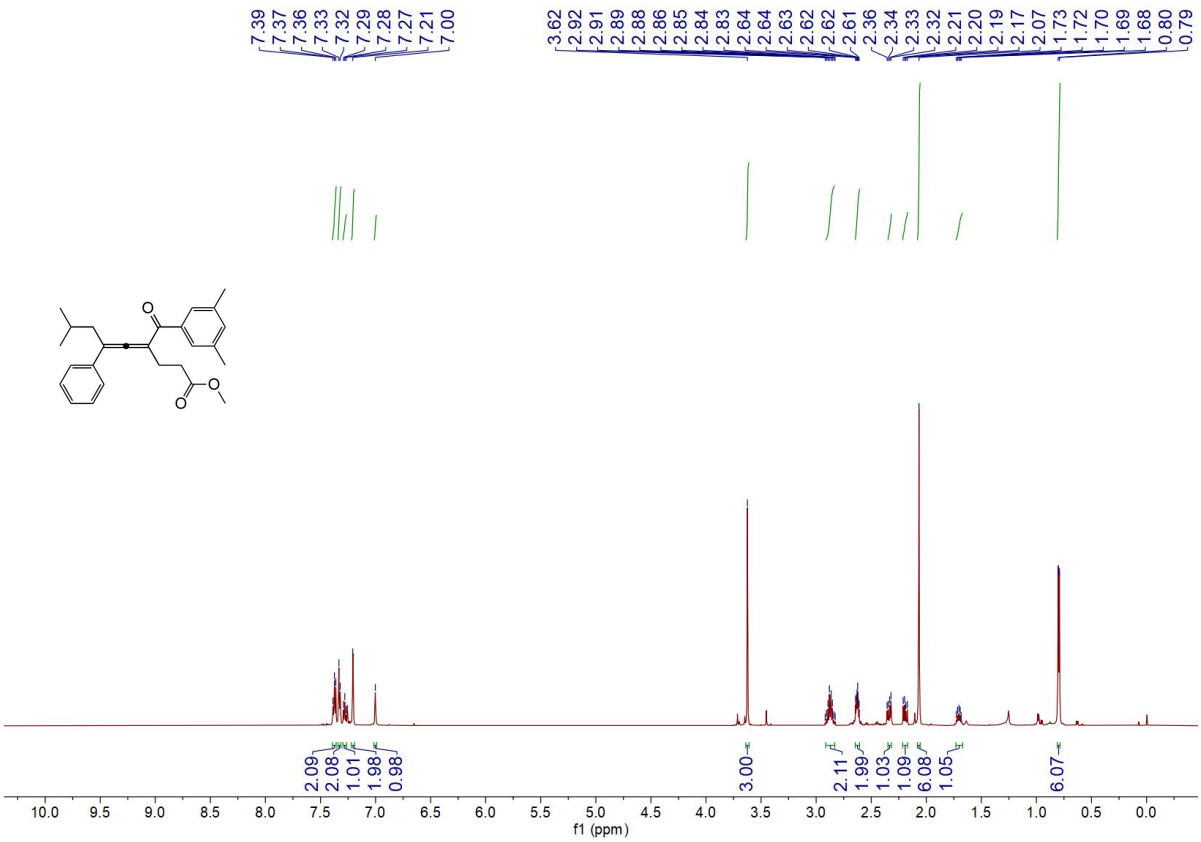
^{1}H NMR (600 MHz, Chloroform-d) of **5e**



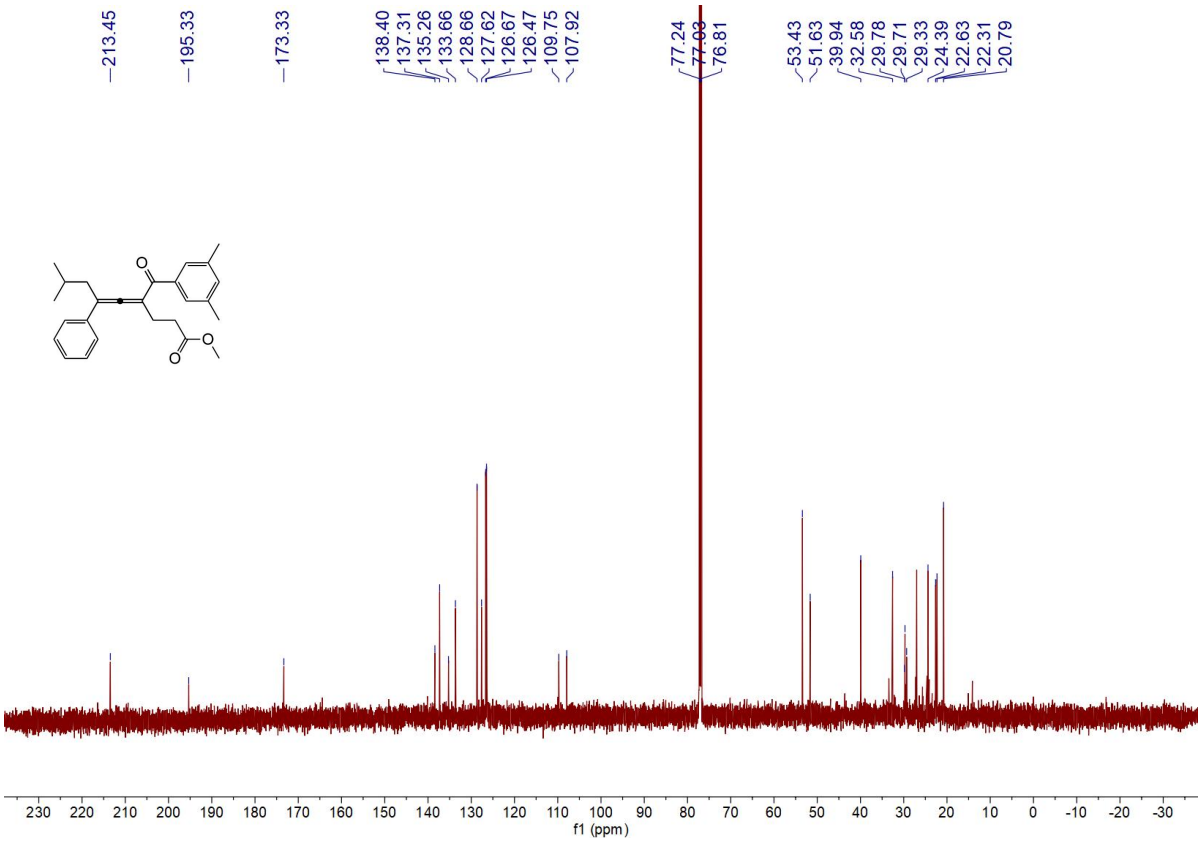
^{13}C NMR (150 MHz, Chloroform-d) of **5e**



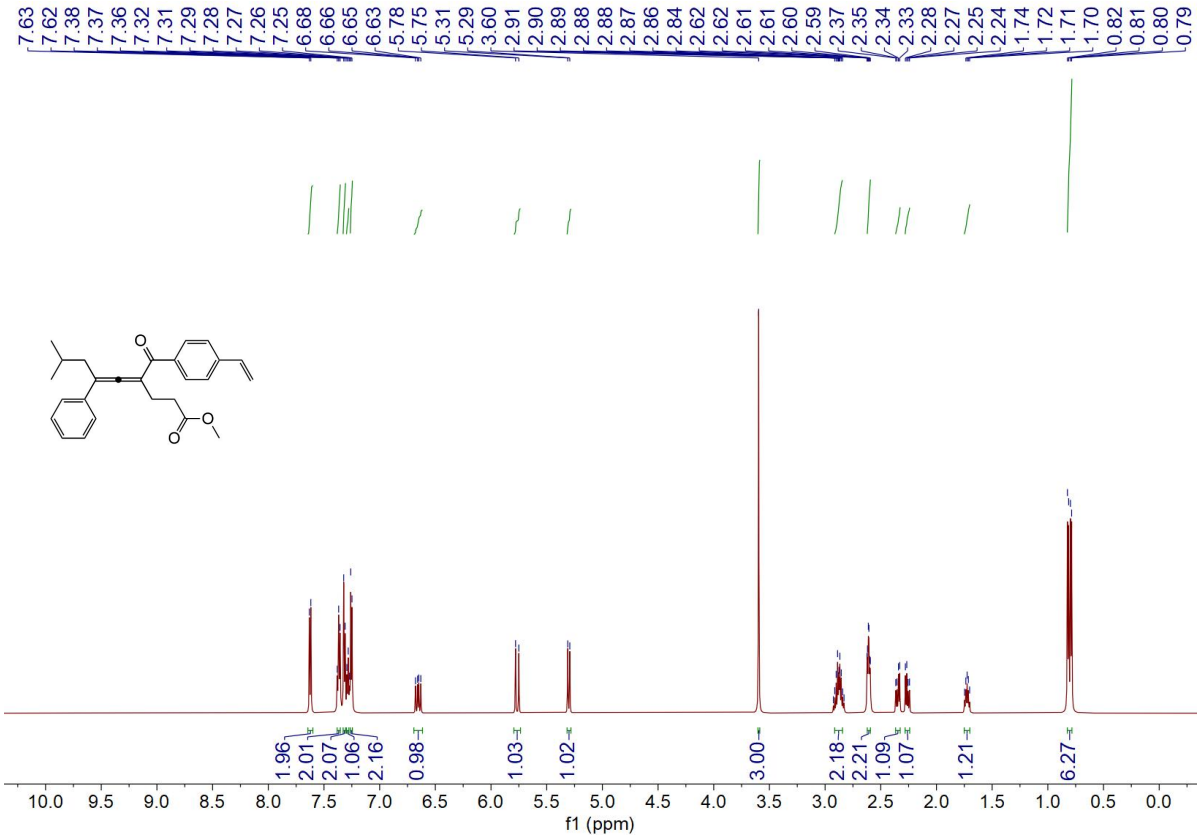
^{1}H NMR (600 MHz, Chloroform-d) of **5f**



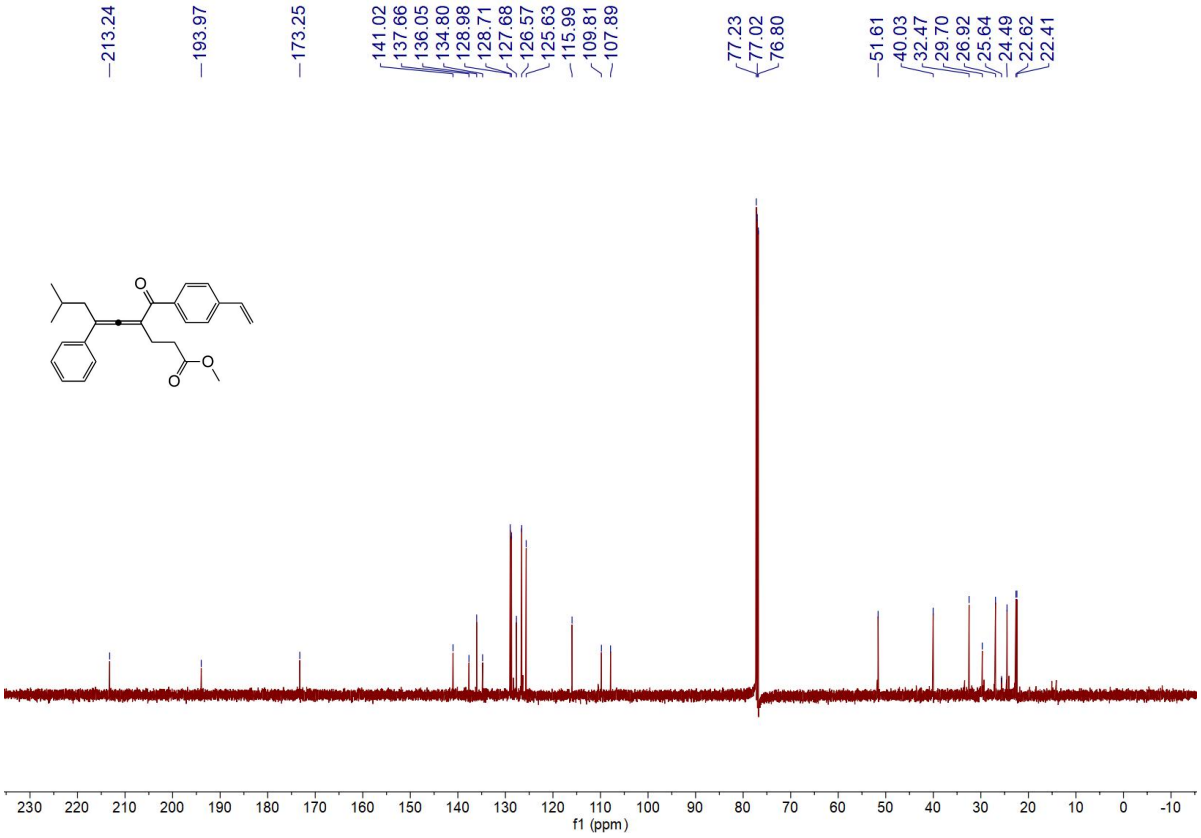
^{13}C NMR (150 MHz, Chloroform-d) of **5f**



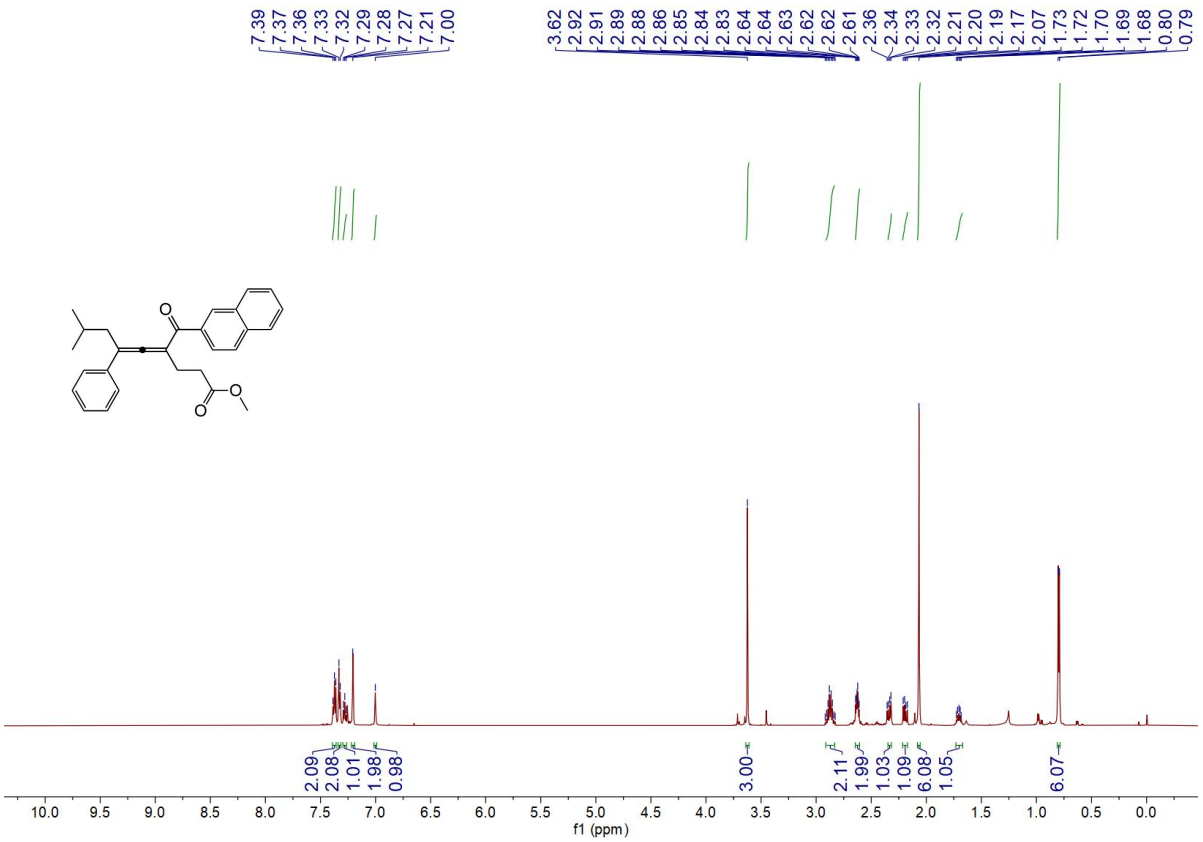
^{1}H NMR (600 MHz, Chloroform-d) of **5g**



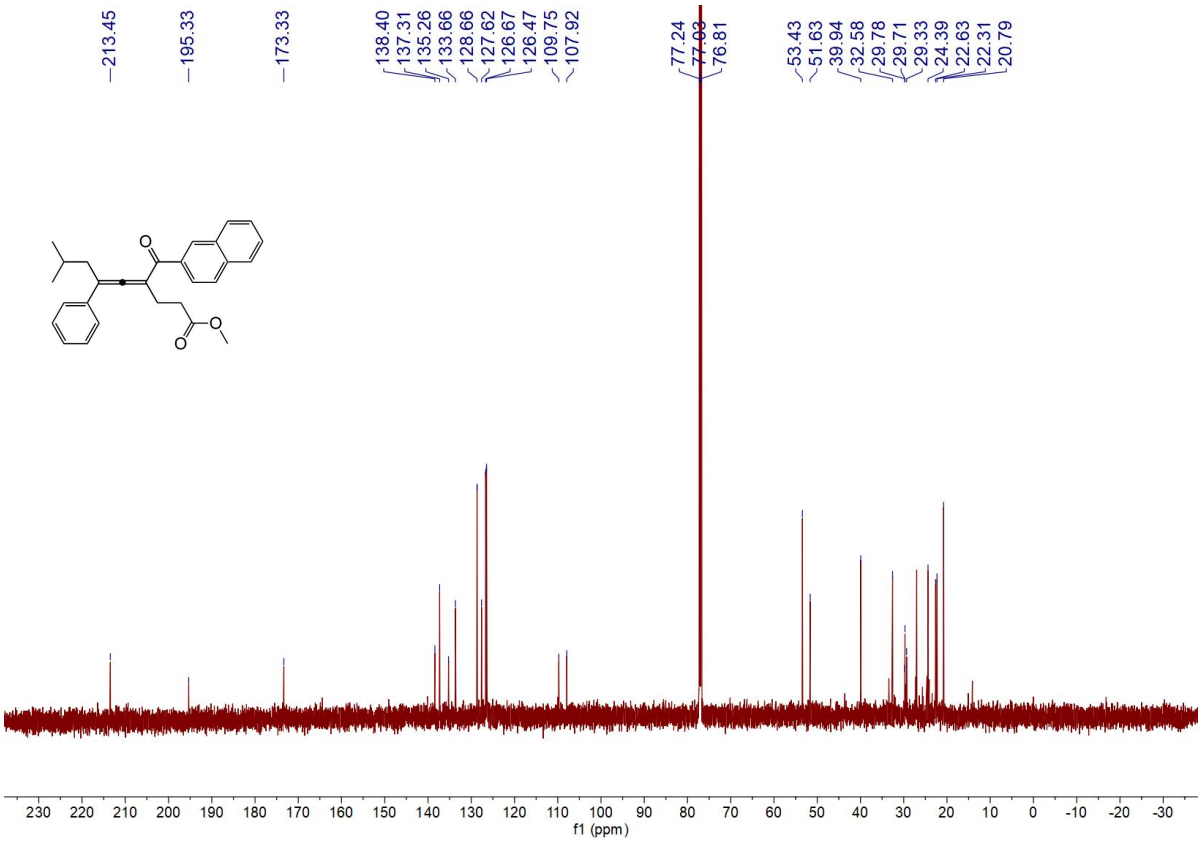
^{13}C NMR (150 MHz, Chloroform-d) of **5g**



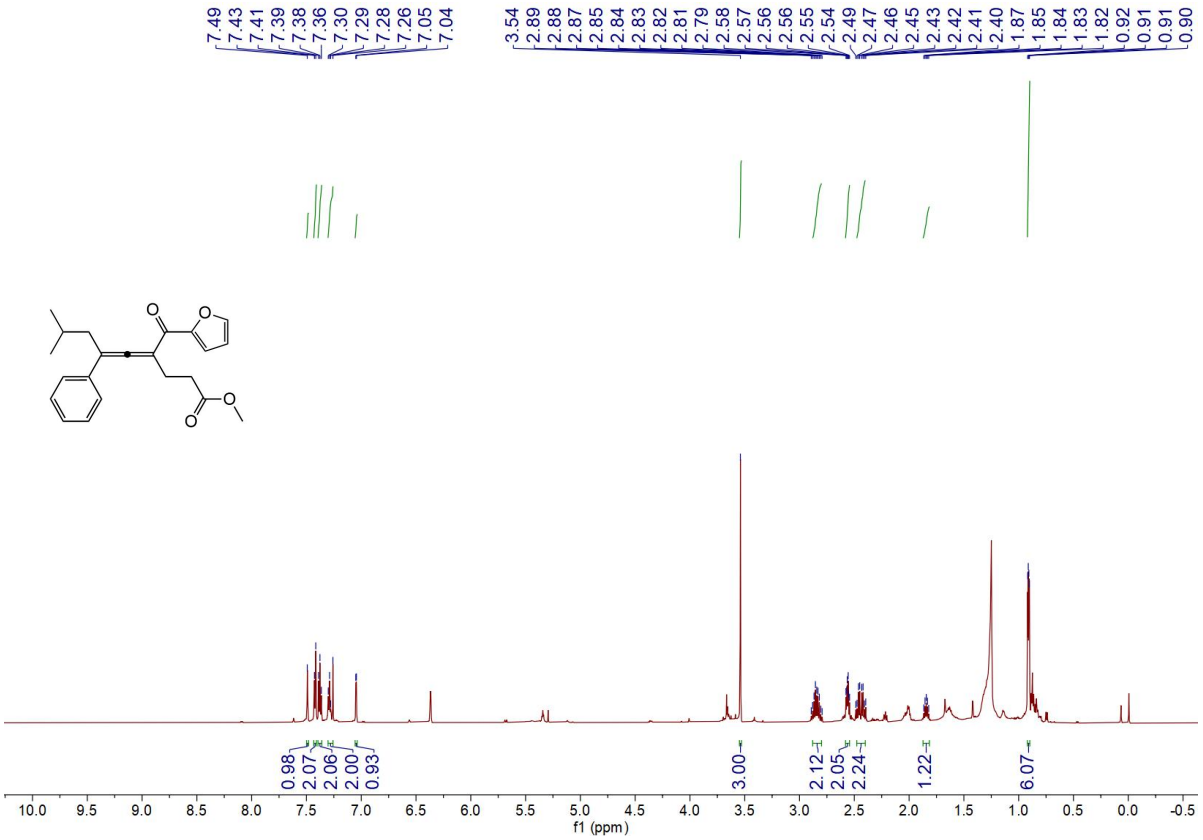
^{1}H NMR (600 MHz, Chloroform-d) of **5h**



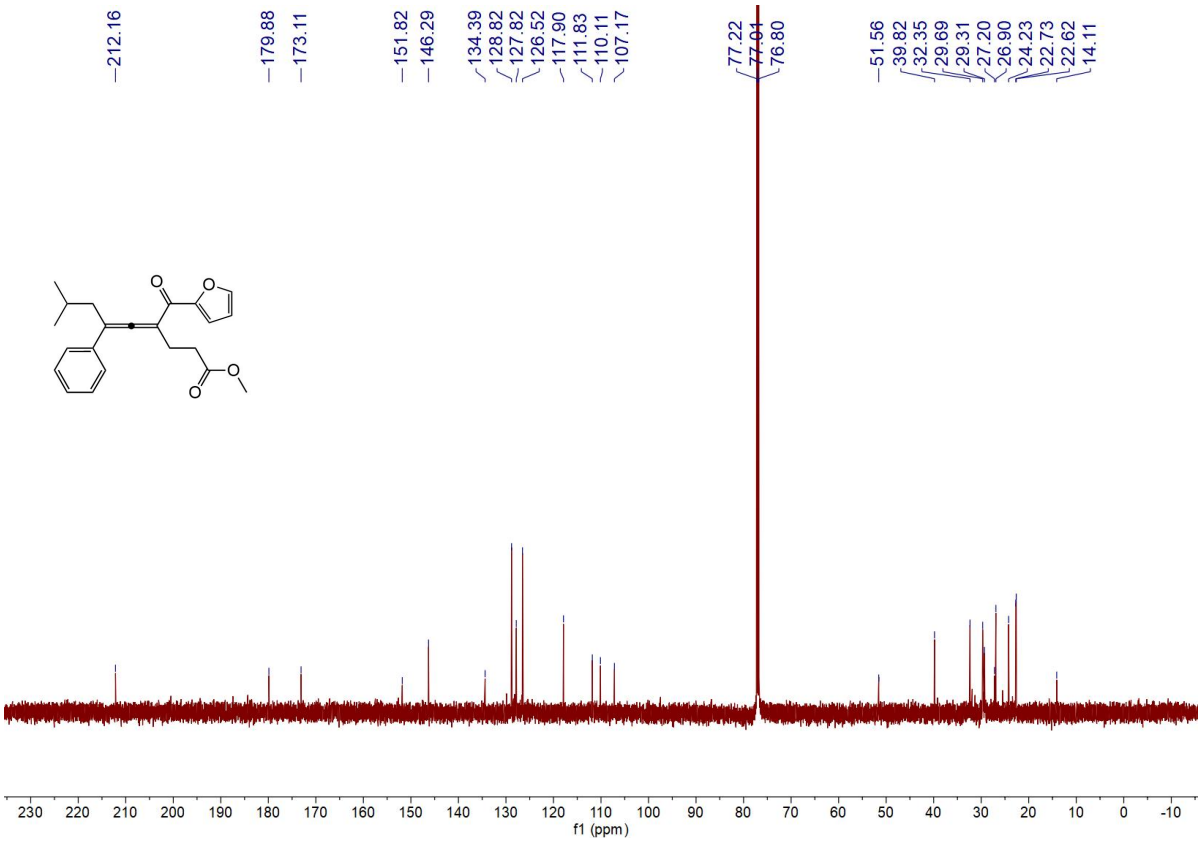
^{13}C NMR (150 MHz, Chloroform-d) of **5h**



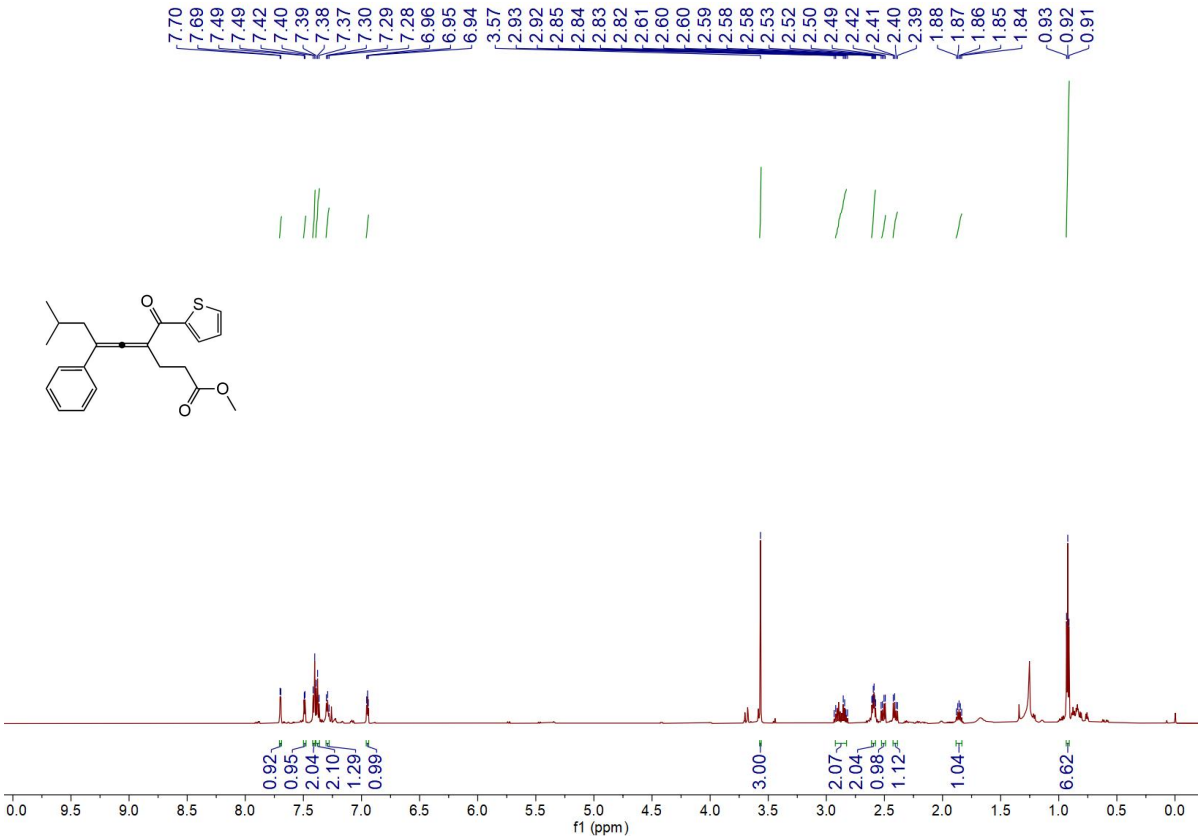
^{1}H NMR (600 MHz, Chloroform-d) of **5i**



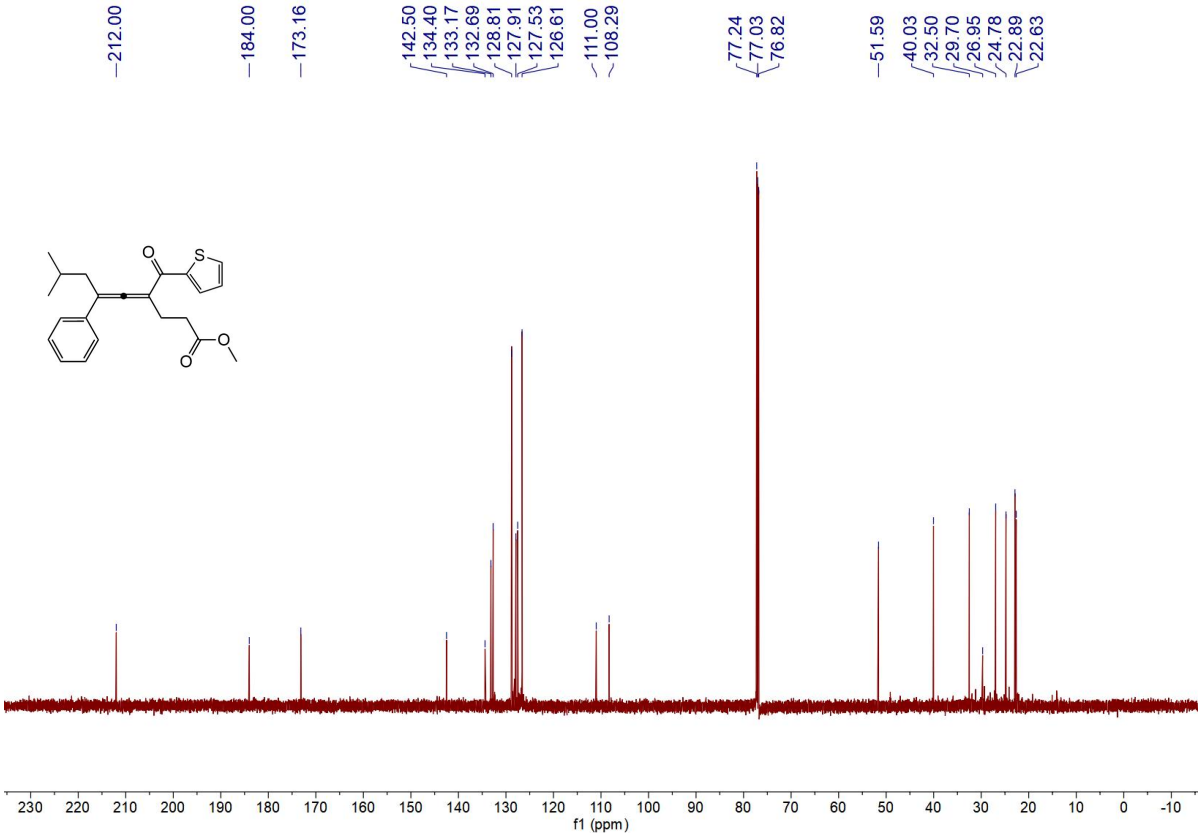
^{13}C NMR (150 MHz, Chloroform-d) of **5i**



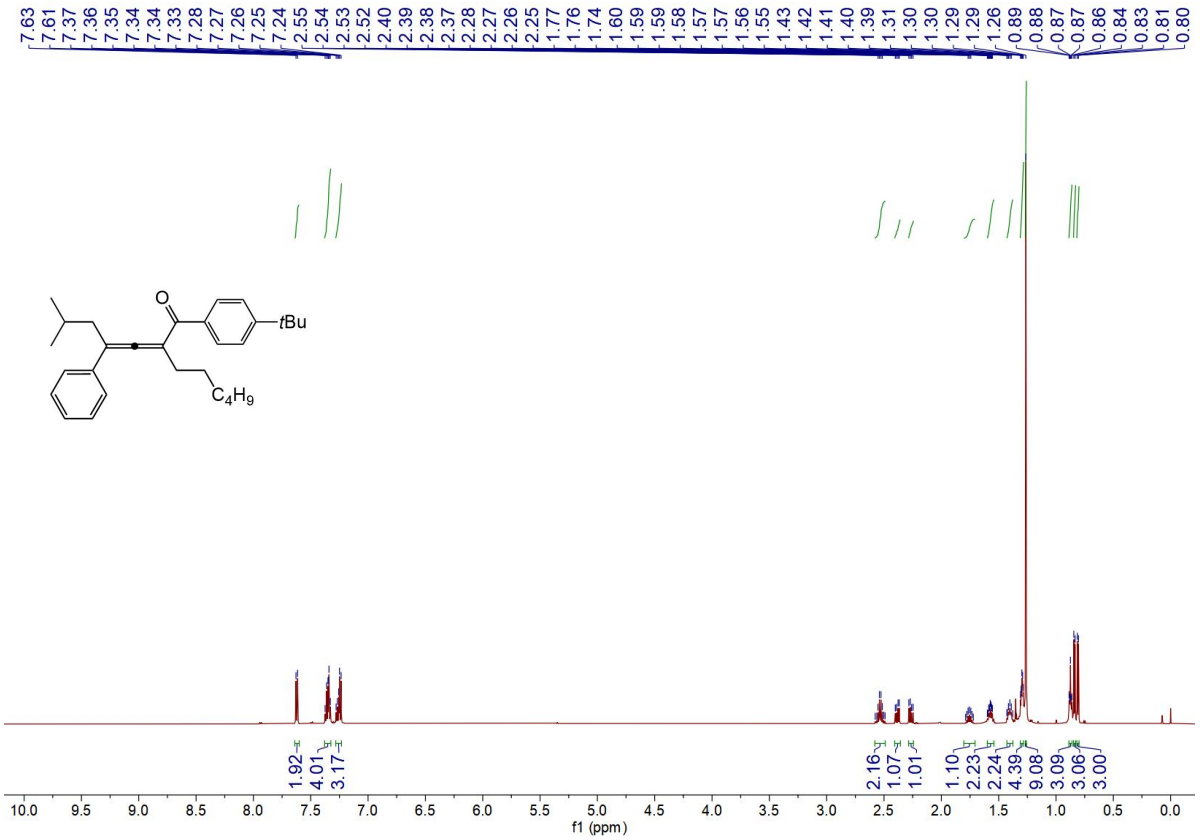
^{1}H NMR (600 MHz, Chloroform-d) of **5j**



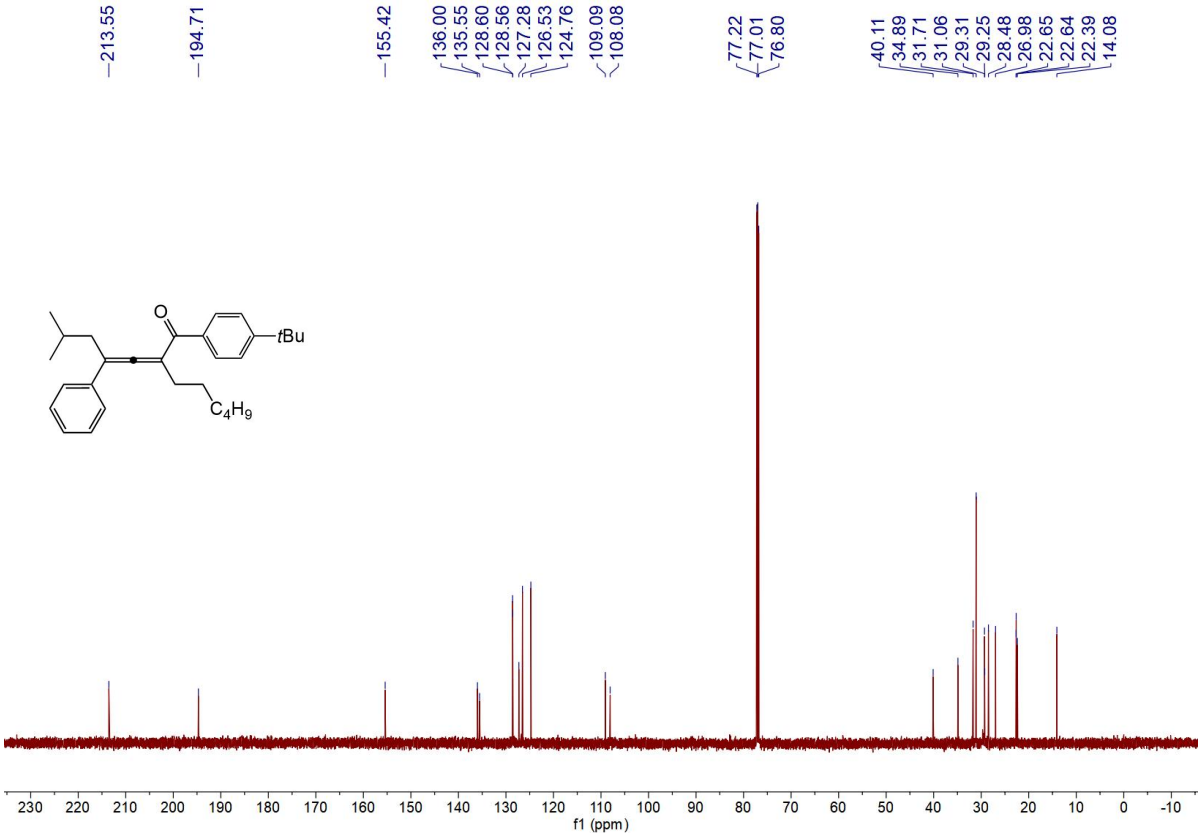
^{13}C NMR (150 MHz, Chloroform-d) of **5j**



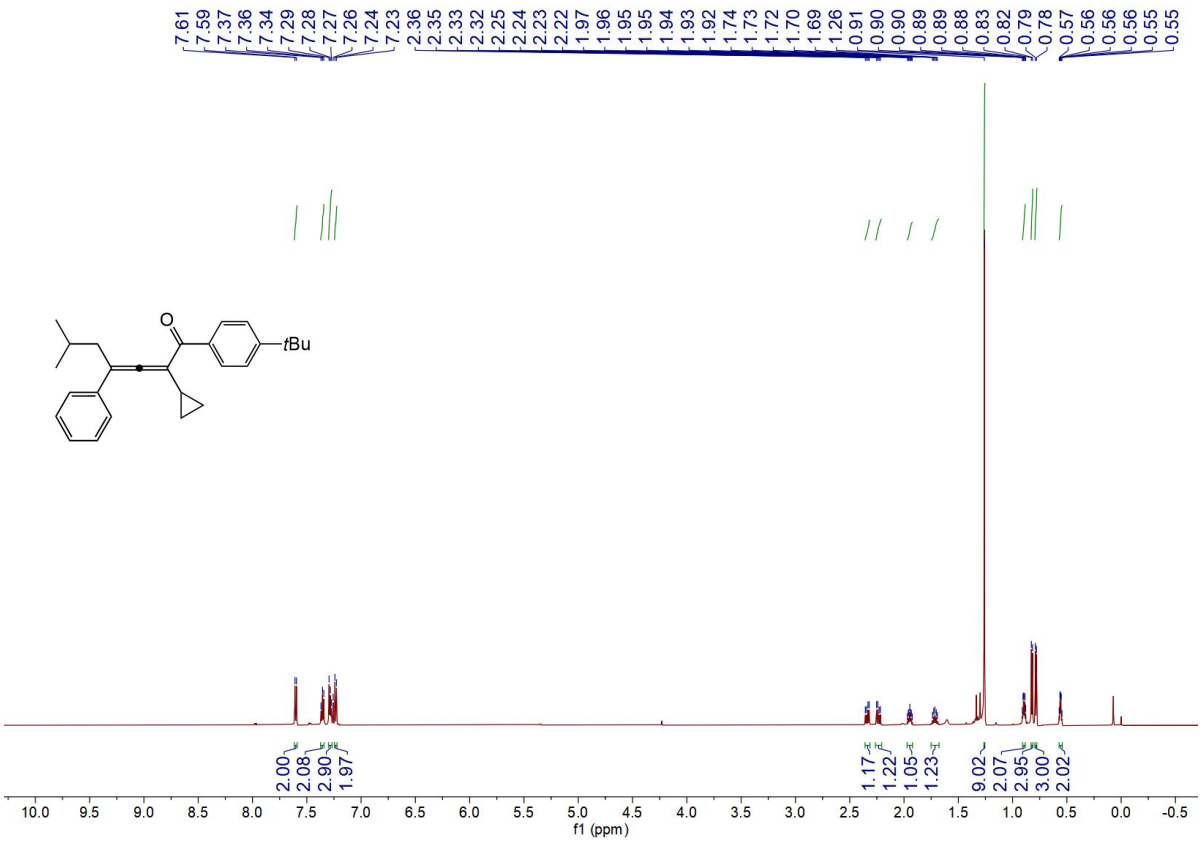
^{1}H NMR (600 MHz, Chloroform-d) of **6a**



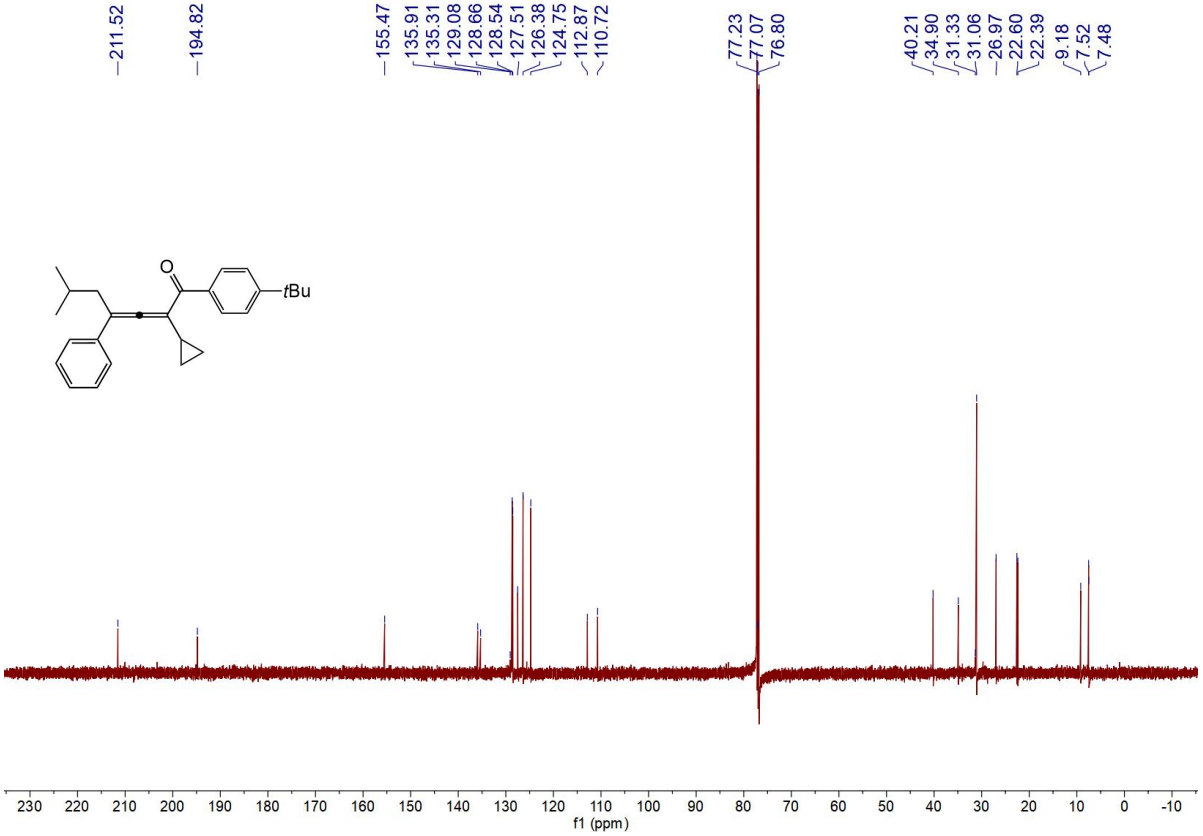
^{13}C NMR (150 MHz, Chloroform-d) of **6a**



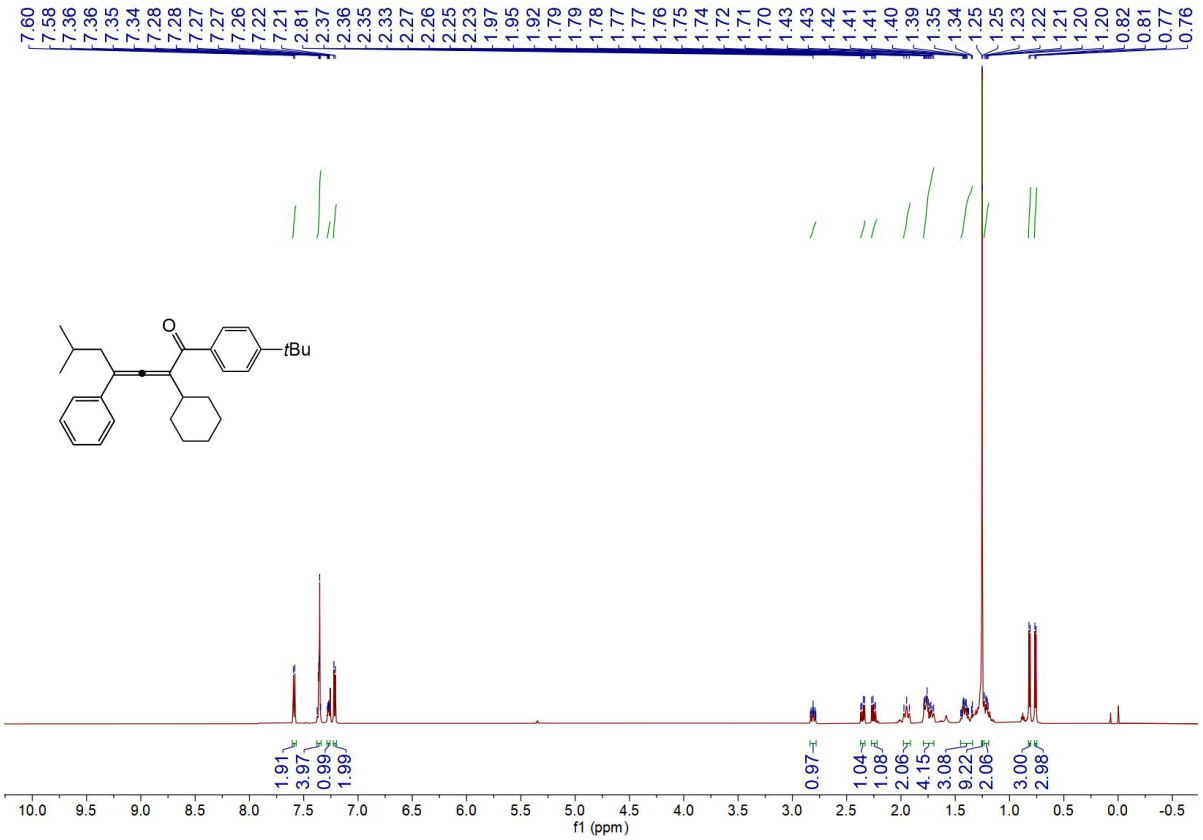
^{1}H NMR (600 MHz, Chloroform-d) of **6b**



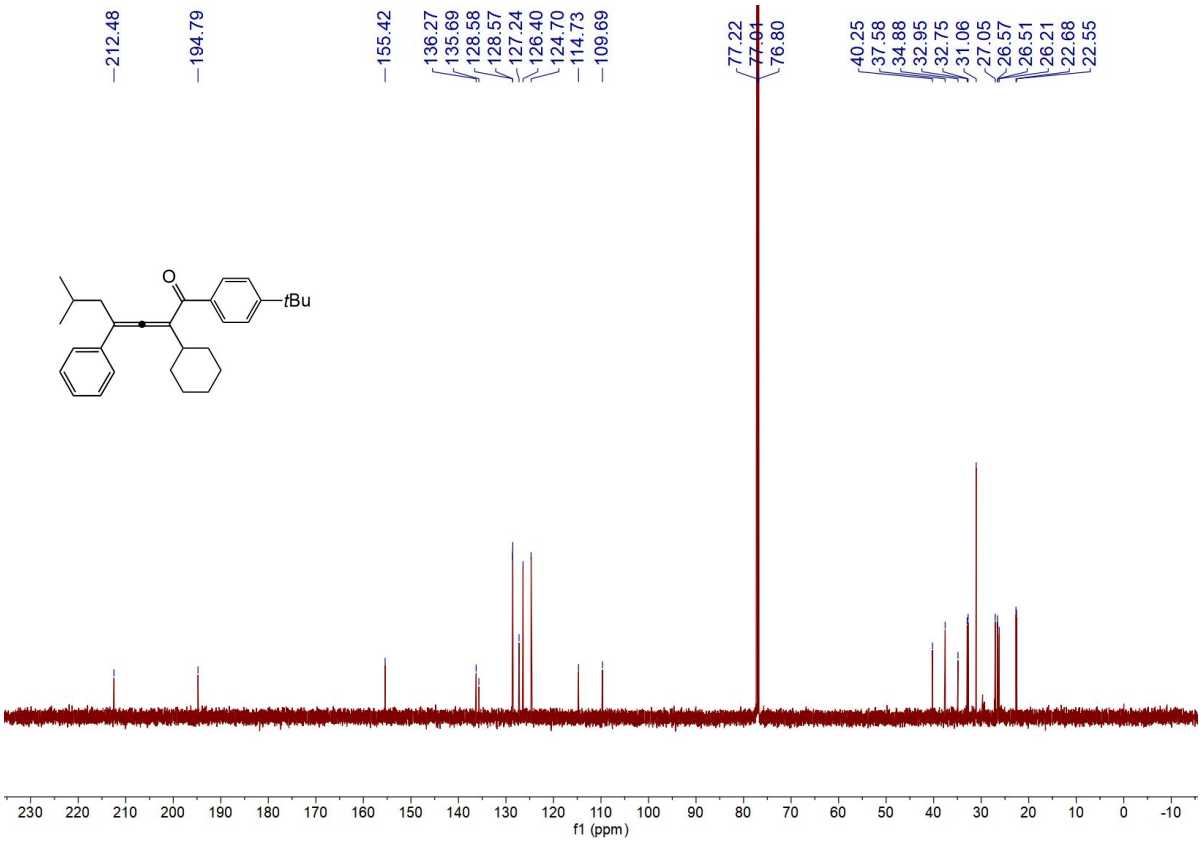
^{13}C NMR (150 MHz, Chloroform-d) of **6b**



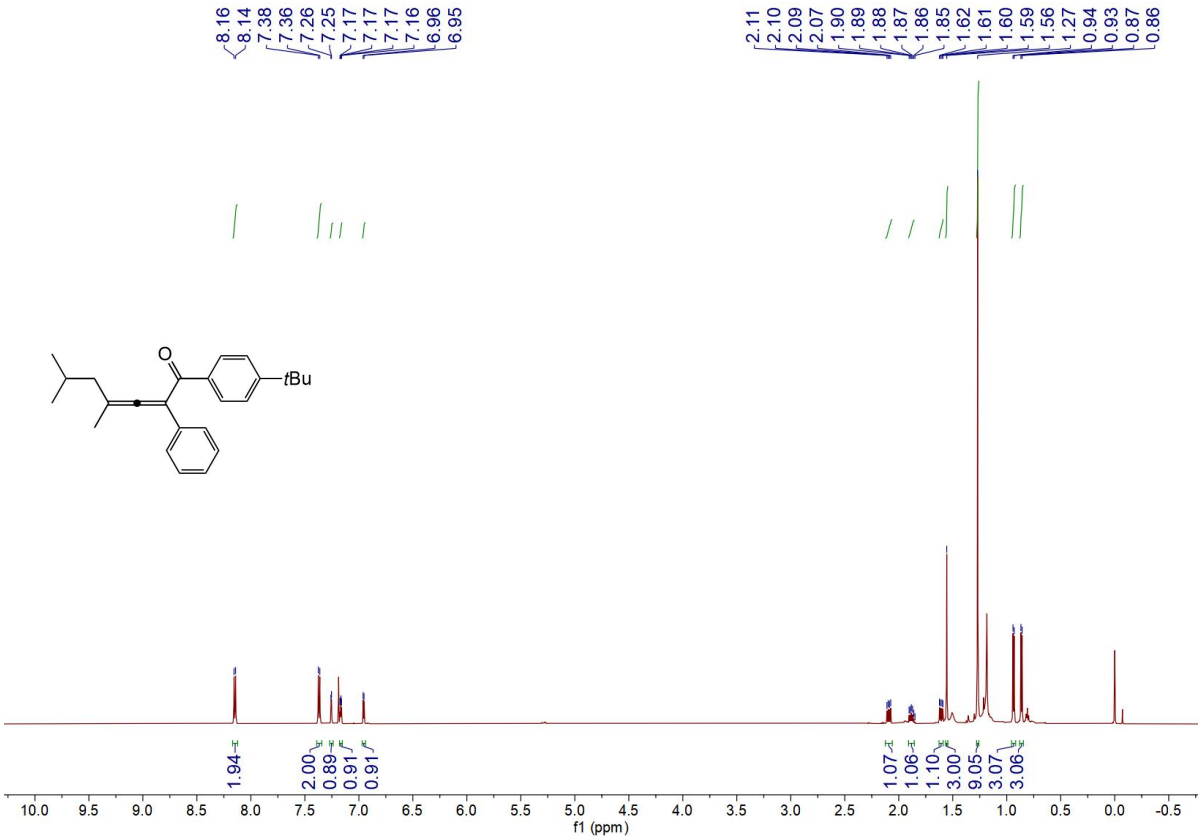
^{1}H NMR (600 MHz, Chloroform-d) of **6c**



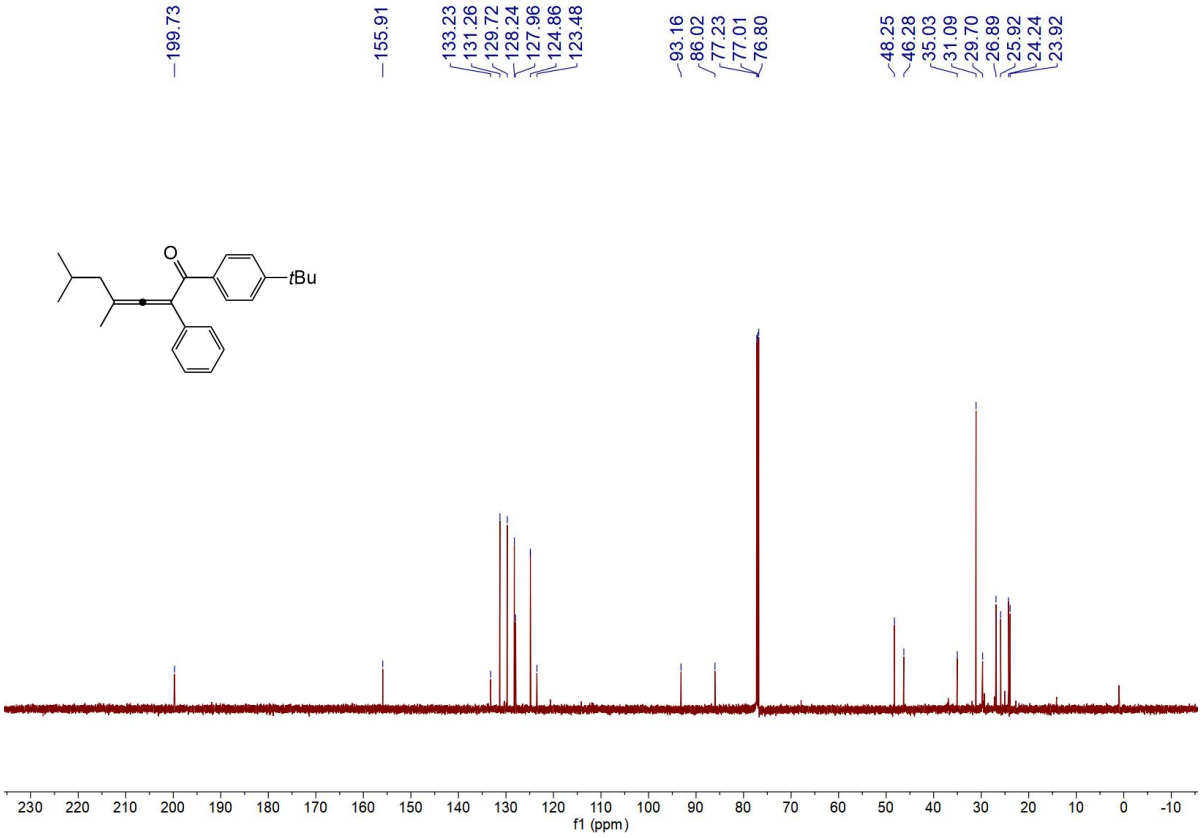
^{13}C NMR (150 MHz, Chloroform-d) of **6c**



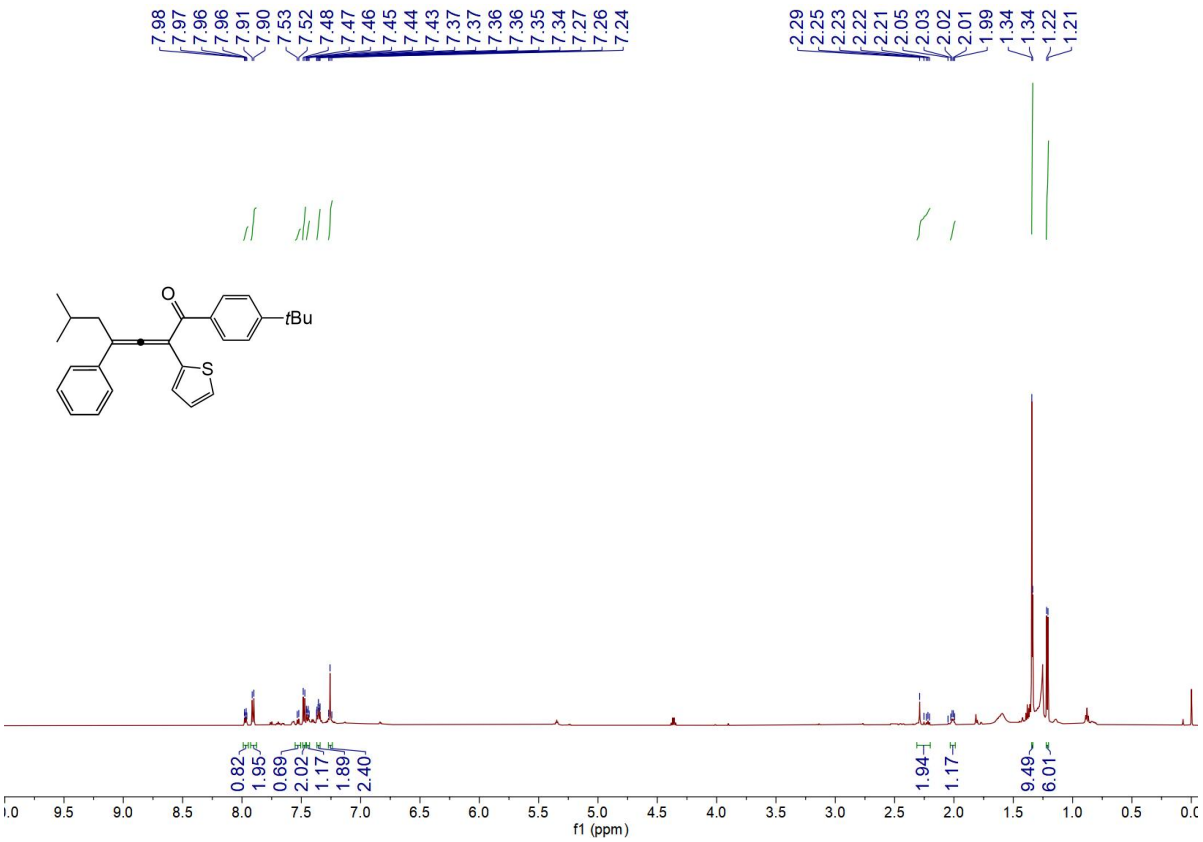
^{1}H NMR (600 MHz, Chloroform-d) of **6d**



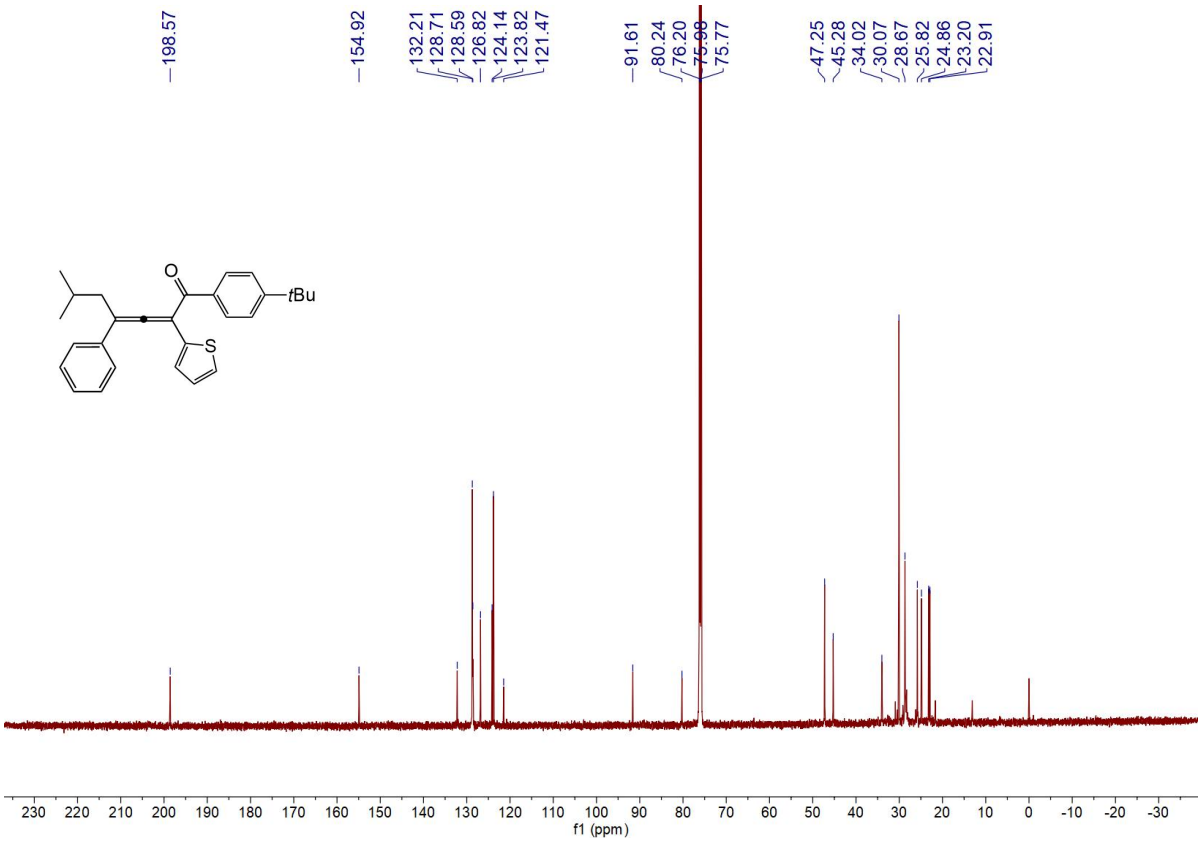
^{13}C NMR (150 MHz, Chloroform-d) of **6d**



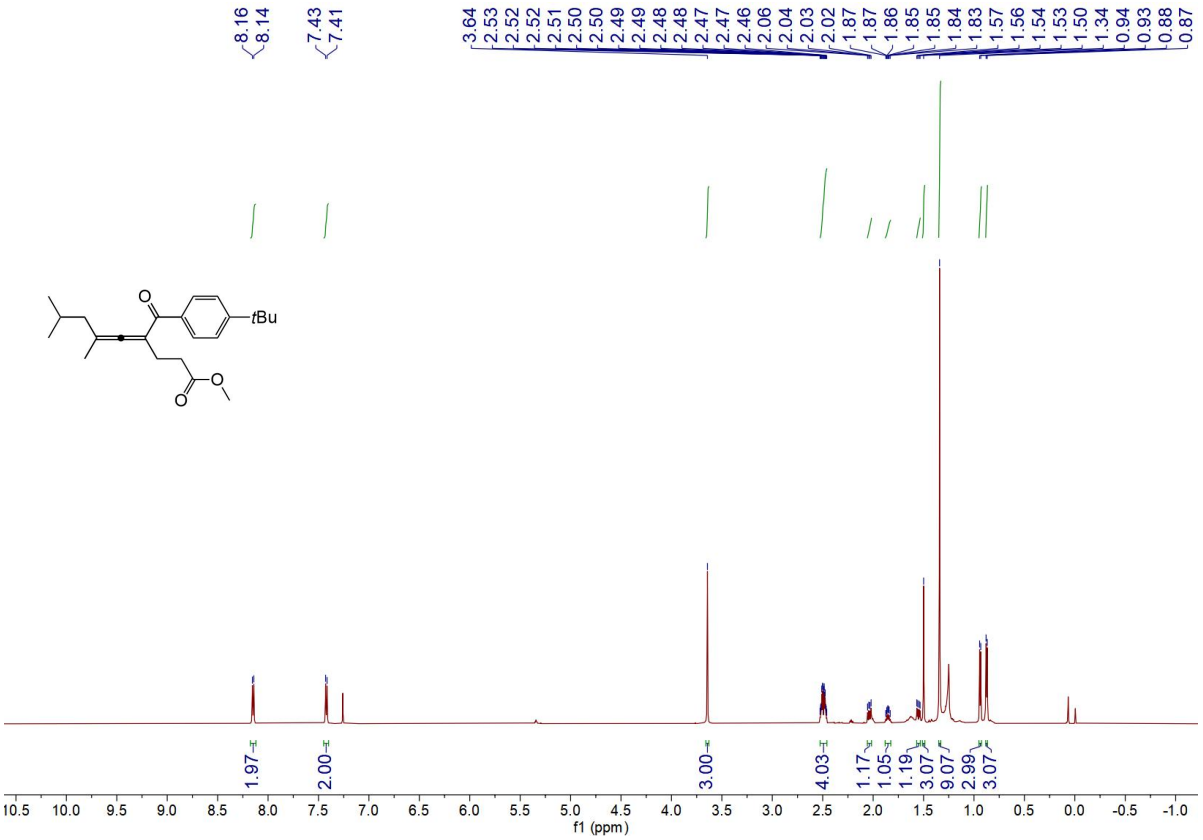
^{1}H NMR (600 MHz, Chloroform-d) of **6e**



^{13}C NMR (150 MHz, Chloroform-d) of **6e**



^{1}H NMR (600 MHz, Chloroform-d) of **6f**



^{13}C NMR (150 MHz, Chloroform-d) of **6f**