Modular Access to Multi-substituted Allenones *via* Environmentally Friendly Organocatalytic C-H Allenylation of Aldehydes

Xinying Hu, Ayisenbati Jialingbieke, Yuzhi Ren, Yifan Yang, Donghui Wei,* Jian Gao, Ding Du*

Supporting Information

Table of contents

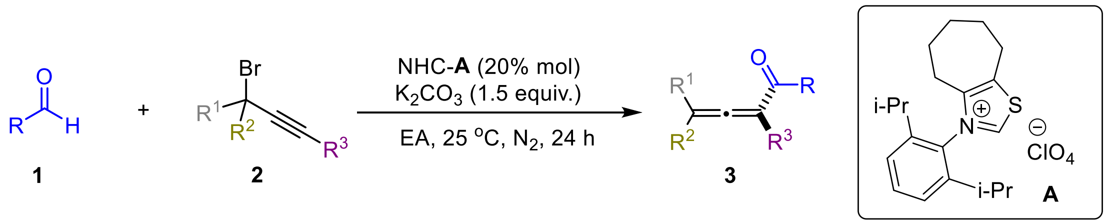
1. General methods

All reactions were carried out in dry glassware and were monitored by analytical thin layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). All NMR spectra were recorded on Bruker spectrometers, running at 300 MHz or 400 MHz for ^{1}H and 75 MHz or 101 MHz for ^{13}C respectively. Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hz respectively. The solvent signals were used as references (residual CHCl3 in CDCl3: δH = 7.26 ppm, δc = 77.16 ppm). The following abbreviations are used to indicate the multiplicity in NMR spectra: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). High resolution mass spectrometry (HRMS) was recorded on TOF perimer for ESI$^+$. The redox potential was obtained on CHI660C electrochemical workstation (Shanghai ChenHua) by cyclic voltammetry.

2. General procedure for the preparation of substrates

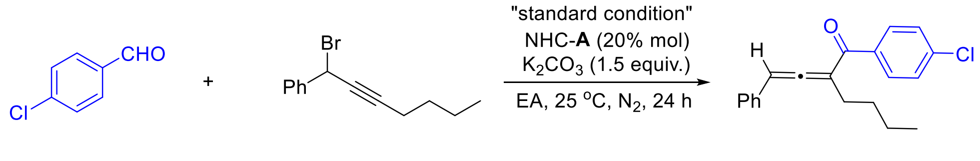
Aldehydes except **1w-1y** are commercially available. Aldehydes **1w-1y** [1-3] and α-brominated alkynes **2**[4-5] were prepared according to the literature procedures.

3. General procedure for the synthesis of products



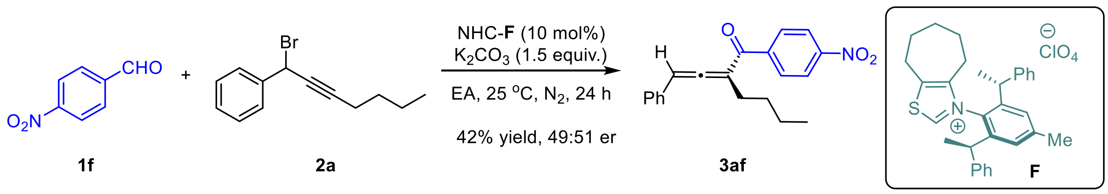
To an oven-dried reaction tube (10 mL) equipped with a magnetic stirrer and fitted with a rubber septum were added NHC precatalyst **A** (16 mg, 0.04 mmol) and K_2CO_3 (42 mg, 0.3 mmol), aldehyde **1** (0.3 mmol), 4Å MS molecular sieve (25 mg), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry EA (3 mL), α-brominated alkyne **2** (0.2 mmol) were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was filtered through diatomite and concentrated under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel (petroleum ether / ethyl acetate from 400/1 to 200/1, v/v) to afford the desired products **3**.

4. Procedure for the scale-up synthesis of 3aa



To an oven-dried reaction tube (50 mL) equipped with a magnetic stirrer and fitted with a rubber septum were added NHC precatalyst **A** (80 mg, 0.2 mmol) and K_2CO_3 (209 mg, 1.5 mmol), 4-chlorobenzaldehyde **2a** (210 mg, 1.5 mmol) , 4Å MS molecular sieve (100mg), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry EA (10 mL) and α-brominated alkyne **1a** (250 mg, 1.0 mmol) were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was filtered through diatomite and concentrated under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel (petroleum ether / ethyl acetate from 400/1 to 200/1, v/v) to afford the desired products **3aa** (238 mg, 77% yield).

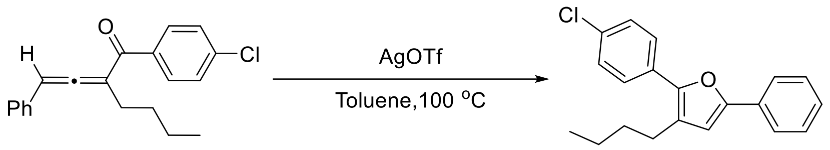
5. General procedure for the asymmetric synthesis of 3af



To an oven-dried reaction tube (10 mL) equipped with a magnetic stirrer and fitted with a rubber septum were added NHC precatalyst **F** (5 mg, 0.01 mmol, 10 mol%) and K_2CO_3 (21 mg, 0.15 mmol, 1.5 equiv.), aldehyde **1f** (23 mg, 0.15 mmol, 1.5 equiv.), 4Å MS molecular sieve (10 mg), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry EA (1.5 mL), α-brominated alkyne **2a** (25 mg, 0.1 mmol, 1.0 equiv.) were added sequentially under the protection of nitrogen.

The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was filtered through diatomite and concentrated under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel (petroleum ether / ethyl acetate from 400/1 to 200/1, v/v) to afford the desired products **3af**. HPLC DAICEL CHIRALCEL IF, n-hexane/ethanol = 99.7/0.3, flow rate = 1.25 mL/min, λ = 254 nm, retention time: 13.00 min (minor), 17.83 min (major).

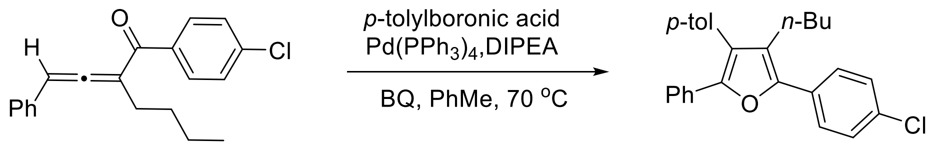
6. General procedure for the synthesis of product 5



3aa **5**

To an oven-dried reaction tube (10ml) with magnetic stirrer and rubber diaphragm wrapped in tin foil was added AgOTf (1.3mg, 0.005mmol, 5% mol), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, dry toluene (2 mL) and **3aa** (31 mg, 0.1mmol, 1.0 equiv.) were added sequentially under the protection of nitrogen. The reaction mixture was stirred at 100 ℃ for 8h. After **3aa** was consumed completely as monitored by TLC, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate from 400/1 to 200/1 , v/v) to afford product **5** (21 mg, 67% yield).

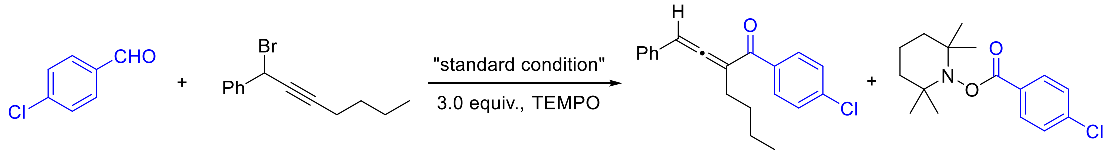
7. General procedure for the synthesis of product 6



3aa **6**, 51% yield

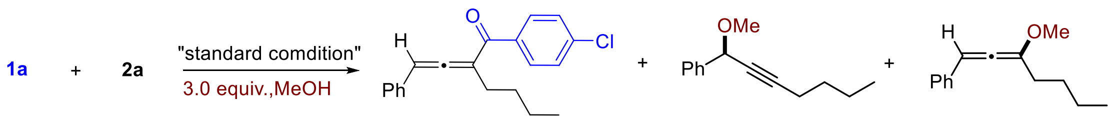
Under an nitrogen atmosphere, Pd $(PPh_3)_4$ (5.8 mg, 0.005 mmol, 2.5 mol%), 1,4-benzoquinone (26 mg, 0.24 mmol) and boronic acid (41 mg, 0.3 mmol) were successively added to a flame-dried 10 mL Schlenk tube. The reaction flask was degassed three times with nitrogen and dry toluene (6.0 mL) was added using a syringe. Then DIPEA (39 mg, 0.3 mmol) was added by syringe successively. After the reaction tube was immersed in 70 ºC bath oil with stirring, a solution of **3aa** (62 mg, 0.2 mmol dissolved in about 0.6 mL of toluene) was added via syringe for 5 min. The reaction was heated with stirring for another 25 min, then cooled to room temperature and filtered through diatomite and concentrated under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel (pure petroleum) to afford product **6** as a colorless liquid (41 mg, 51% yield).

8. Radical trapping experiment



1a **2a** **3aa**, N.D. **7**, 67% yield

To an oven-dried reaction tube (10 mL) equipped with a magnetic stirrer and fitted with a rubber septum were added NHC precatalyst A (16 mg, 0.04 mmol) and K_2CO_3 (42 mg, 0.3 mmol), 4-chlorobenzaldehyde **2a** (43 mg, 0.3 mmol), TEMPO (94 mg, 0.6 mmol) and 4Å MS molecular sieve (25 mg), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, α-brominated alkyne **1a** (0.2 mmol) and dry EA (2 mL) and were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was filtered through diatomite and concentrated under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel (petroleum ether / ethyl acetate from 50/1 to 20/1, v/v) to afford **7** (39 mg, 67%), and no product **3aa** was observed by LC-MS.



3aa, 70% **8,** N.D. **9,** N.D.

To an oven-dried reaction tube (10 mL) equipped with a magnetic stirrer and fitted with a rubber septum were added NHC precatalyst A (16 mg, 0.04 mmol) and K_2CO_3 (42 mg, 0.3 mmol), 4-chlorobenzaldehyde **2a** (43 mg, 0.3 mmol), MeOH (23 mg, 0.6 mmol) and 4Å MS molecular sieve (25 mg), after which the tube was evacuated and back-filled with nitrogen for three times. Subsequently, α-brominated alkyne **1a** (0.2 mmol) and dry EA (2 mL) and were added sequentially under the protection of nitrogen. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was filtered through diatomite and concentrated under reduced pressure, and the main products was purified by column chromatography on silica gel (petroleum ether / ethyl acetate from 400/1 to 200/1, v/v) to afford **3aa** (43 mg, 70%), and no product **8a** and **8b** was observed by LC-MS.

9. Cyclic voltammetry experiment of 1a

Cyclic voltammetry was conducted on a CHI660C electrochemical workstation (Shanghai ChenHua) using a 3-electrode cell configuration. A gold disc working electrode was employed alongside Platinum wire counter electrode and a Silver/Silver chloride pseudo-reference electrode.A mixture solution of 2.5mM $K_3[Fe(CN)_6]$, 2.5mM $K_4[Fe(CN)_6]$ and 0.1M KCl was added as an internal standard to determine the precise potential scale. 0.4M brominated alkyne were freshly prepared in DMSO along with 0.1 M supporting electrolyte (tetrabutylammonium tetrafluoroborate). The REDOX potential curve (**Figure S1.**) was obtained by eight cycles from -1.5V to 1.5V at a scanning speed of 100mV per second. As can be seen from the image, the REDOX potential of the bromine is about -1.1V.

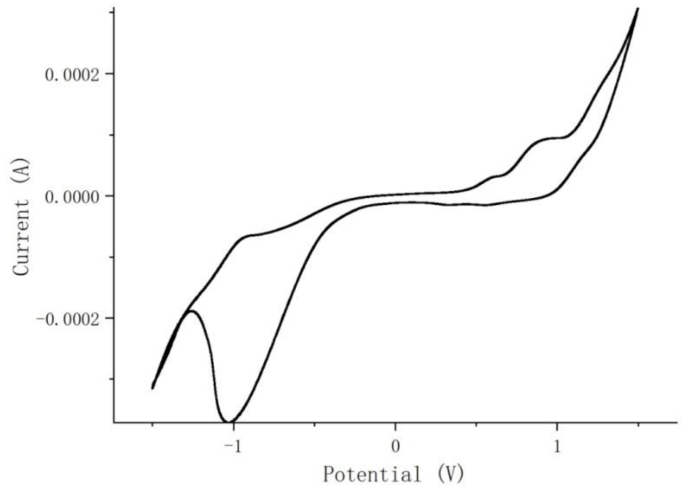
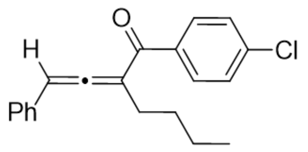


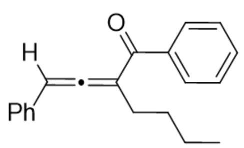
Figure S1. Cyclic voltammetry experiment of **1a**

10. Characterization of the products

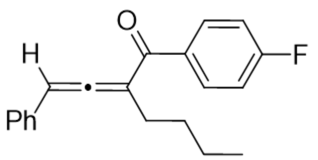
1-(4-chlorophenyl)-2-(2-phenylvinylidene)hexan-1-one (3aa) Yellow liquid, 49 mg, 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.30 – 7.22 (m, 5H), 6.47 (t, *J* = 2.7 Hz, 1H), 2.61 – 2.47 (m, 2H), 1.59 – 1.51 (m, 2H), 1.47 – 1.39 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 193.1, 138.6, 136.6, 132.4, 130.2, 129.1, 128.3, 128.0, 127.3, 111.0, 98.8, 77.6, 76.7, 30.3, 28.4, 22.7, 14.1. HRMS Calcd. For $C_{20}H_{19}ClO$ $[M+H]^+$: 311.1197; found: 311.1195.



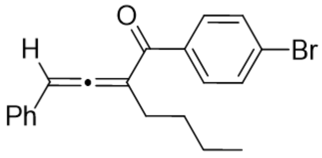
1-phenyl-2-(2-phenylvinylidene)hexan-1-one (3ab) Yellow liquid, 38 mg, 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.32 – 7.24 (m, 5H), 6.46 (t, *J* = 2.7 Hz, 1H), 2.64 – 2.50 (m, 2H), 1.63 – 1.52 (m, 2H), 1.50 – 1.41 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8, 194.3, 138.4, 132.7, 132.2, 129.0, 128.8, 128.0, 127.8, 127.3, 111.0, 98.5, 30.4, 28.6, 22.7, 14.0. HRMS Calcd. For $C_{20}H_{20}O$ $[M+H]^+$:277.1587; found: 277.1587.



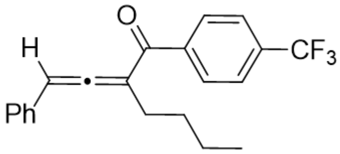
1-(4-fluorophenyl)-2-(2-phenylvinylidene)hexan-1-one (3ac) Yellow liquid, 51 mg, 87 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.48 (t, *J* = 2.6 Hz, 1H), 2.61 – 2.49 (m, 2H), 1.61 – 1.51 (m, 2H), 1.44 (dt, *J* = 14.2, 7.0 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.6, 192.8,165.3 (d, $^1J_{C-F}$ = 254.5 Hz), 134.6 (d, $^4J_{C-F}$ = 3.0 Hz), 132.5, 131.4 (d, $^3J_{C-F}$ = 9.1 Hz), 129.1, 128.0, 127.2, 115.1 (d, $^2J_{C-F}$ = 22.2 Hz), 111.0, 98.6, 30.3, 28.6, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.5. HRMS Calcd. For $C_{20}H_{19}FO$ $[M+H]^+$: 295.1493; found: 295.1494.



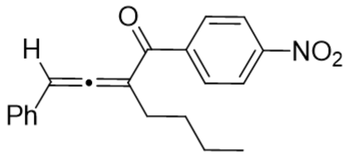
1-(4-bromophenyl)-2-(2-phenylvinylidene)hexan-1-one (3ad) Yellow liquid, 51 mg, 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 7.1 Hz, 2H), 7.30 – 7.25 (m, 3H), 6.48 (t, J = 2.7 Hz, 1H), 2.55 (qd, J = 7.7, 2.7 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.48 – 1.40 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 193.2, 137.1, 132.4, 131.3, 130.4, 129.1, 128.0, 127.3, 127.2, 111.0, 98.8, 30.3, 28.4, 22.7, 14.1. HRMS Calcd. For $C_{20}H_{19}BrO$ $[M+H]^+$:355.0692/357.0762; found: 355.0692/357.0762.



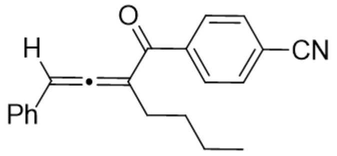
2-(2-phenylvinylidene)-1-(4-(trifluoromethyl)phenyl) hexan-1-one (3ae) Yellow liquid, 30 mg, 43 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.31 – 7.26 (m, 3H), 6.49 (t, J = 2.7 Hz, 1H), 2.63 – 2.50 (m, 2H), 1.60 – 1.53 (m, 2H), 1.49 – 1.41 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7, 193.4, 141.5, 133.5 (q, $^{2}J_{C\text{-}F}$ = 32.32 Hz), 132.18, 129.19, 129.00, 128.19, 127.32, 125.1 (q, $^{4}J_{C\text{-}F}$ = 4.04 Hz), 123.8 (q, $^{1}J_{C\text{-}F}$ = 273.71 Hz), 111.3, 99.2, 30.3, 28.3, 22.7, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.0. HRMS Calcd. For $C_{21}H_{19}F_3O$ $[M+H]^+$: 345.1461; found: 345.1461.



1-(4-nitrophenyl)-2-(2-phenylvinylidene)hexan-1-one (3af) Yellow liquid, 37 mg, 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.22 (m, 3H), 6.50 (t, J = 2.7 Hz, 1H), 2.63 – 2.48 (m, 2H), 1.62 – 1.51 (m, 2H), 1.49 – 1.40 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.2, 192.9, 149.7, 143.7, 131.8, 129.3, 128.4, 127.3, 123.2, 111.7, 99.6, 30.3, 28.0, 22.7, 14.0. HRMS Calcd. For $C_{20}H_{19}NO_3$ $[M+H]^+$: 322.1438; found: 322.1446.

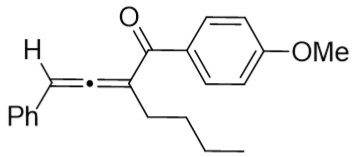


4-(2-(2-phenylvinylidene)hexanoyl)benzonitrile (3ag) Yellow liquid, 25 mg, 41% yield.



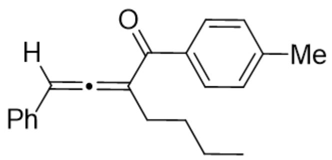
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.4 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.27 – 7.23 (m, 2H), 6.49 (t, *J* = 2.7 Hz, 1H), 2.61-2.48 (m, 2H), 1.59 – 1.50 (m, 2H), 1.47 – 1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0, 193.1, 142.0, 131.9, 131.8, 129.2, 129.0, 128.3, 127.3, 118.1, 115.3, 111.4, 99.4, 30.3, 28.1, 22.6, 14.0. HRMS Calcd. For $C_{21}H_{19}NO$ $[M+Na]^+$: 301.1467; found: 301.1462.

1-(4-methoxyphenyl)-2-(2-phenylvinylidene)hexan-1-one (3ah) Yellow liquid, 31 mg, 50% yield.



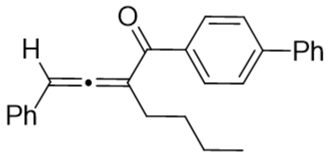
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.38-7.26 (m, 5H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.45 (t, *J* = 2.7 Hz, 1H), 3.79 (s, 3H), 2.61 – 2.49 (m, 2H), 1.59 – 1.50 (m, 2H), 1.48 – 1.40 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 192.7, 163.1, 133.0, 131.3, 131.0, 129.0, 127.7, 127.3, 113.3, 110.7, 98.1, 55.5, 30.4, 28.9, 22.7, 14.1. HRMS Calcd. For $C_{21}H_{22}O_2$ $[M+H]^+$: 307.1693; found: 307.1690.

2-(2-phenylvinylidene)-1-(p-tolyl)hexan-1-one (3ai) Yellow liquid, 47 mg, 81% yield.

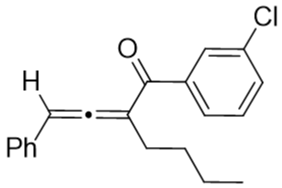


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.29 (d, *J* = 6.9 Hz, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.45 (t, *J* = 2.7 Hz, 1H), 2.63 – 2.49 (m, 2H), 2.32 (s, 3H), 1.60 – 1.51 (m, 2H), 1.49 – 1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.2, 193.9, 143.0, 135.7, 132.9, 129.1, 129.0, 128.7, 127.7, 127.3, 110.9, 98.3, 30.4, 28.7, 22.7, 21.6, 14.1. HRMS Calcd. For $C_{21}H_{22}O$ $[M+H]^+$:291.1743; found: 291.1740.

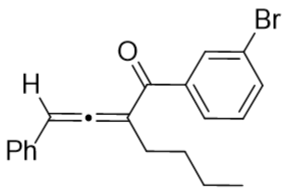
1-([1,1'-biphenyl]-4-yl)-2-(2-phenylvinylidene)hexan-1-one (3aj) White Solid, mp: 80-82°C, 47 mg, 67% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.46 – 7.28 (m, 8H), 6.51 (t, *J* = 2.7 Hz, 1H), 2.69 – 2.53 (m, 2H), 1.65 – 1.55 (m, 2H), 1.53 – 1.44 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 193.8, 145.0, 140.1, 137.0, 132.7, 129.5, 129.1, 128.9, 128.1, 127.8, 127.3, 126.7, 111.0, 98.6, 30.4, 28.7, 22.7, 14.1. HRMS Calcd. For $C_{26}H_{24}O$ $[M+H]^+$:353.1900; found: 353.1898.



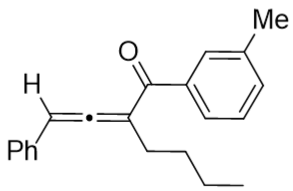
1-(3-chlorophenyl)-2-(2-phenylvinylidene)hexan-1-one (3ak) Yellow liquid, 38 mg, 62 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.29 (t, *J* = 3.1 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.49 (t, *J* = 2.7 Hz, 1H), 2.61 – 2.48 (m, 2H), 1.60 – 1.51 (m, 2H), 1.48 – 1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.3, 193.1, 139.9, 134.2, 132.3, 132.1, 129.3, 129.1, 129.0, 128.1, 127.3, 126.8, 111.1, 99.0, 30.3, 28.3, 22.7, 14.1. HRMS Calcd. For $C_{20}H_{19}ClO$ $[M+H]^+$:311.1197; found: 311.1197.



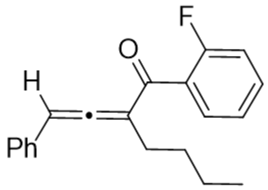
1-(3-bromophenyl)-2-(2-phenylvinylidene)hexan-1-one (3al) Yellow liquid, 33 mg, 47 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (t, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.30 – 7.25 (m, 3H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.49 (t, *J* = 2.7 Hz, 1H), 2.61 – 2.47 (m, 2H), 1.59 – 1.50 (m, 2H), 1.48 – 1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.4, 193.2, 140.1, 135.1, 132.3, 131.9, 129.6, 129.1, 128.1, 127.3, 127.2, 122.2, 111.1, 99.0, 30.3, 28.3, 22.7, 14.1. HRMS Calcd. For $C_{20}H_{19}BrO$ $[M+H]^+$:355.0692/357.0762; found: 355.0685/357.0667.



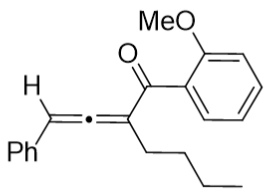
2-(2-phenylvinylidene)-1-(m-tolyl)hexan-1-one (3am) Yellow liquid, 33 mg, 56 % yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 9.2 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.15 (m, 2H), 6.44 (t, *J* = 2.7 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.14 (s, 3H), 1.61 – 1.52 (m, 2H), 1.49 – 1.41 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 194.8, 138.3, 137.7, 133.1, 129.6, 129.0, 127.9, 127.8, 127.3, 125.9, 111.0, 98.4, 30.4, 28.5, 22.7, 21.0, 14.1. HRMS Calcd. For $C_{21}H_{22}O$ $[M+H]^+$:291.1743; found: 291.1739.



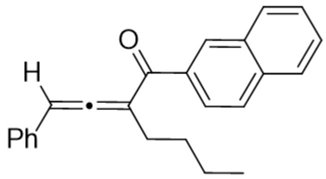
1-(2-fluorophenyl)-2-(2-phenylvinylidene)hexan-1-one (3an) Yellow liquid, 24 mg, 40 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.4, 1.6 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.25 – 7.16 (m, 3H), 7.06 – 7.01 (m, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.44 (t, *J* = 2.7 Hz, 1H), 2.64 – 2.43 (m, 2H), 1.60 – 1.50 (m, 2H), 1.48 – 1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.7, 192.6, 159.6 (d, $^1J_{C-F}$ =252.5Hz), 132.3 (d, $^3J_{C-F}$ = 8.1 Hz) , 132.1, 129.5 (d, $^4J_{C-F}$ = 3.0 Hz), 128.9, 128.4 (d, $^2J_{C-F}$ = 15.2 Hz), 127.9, 127.3, 123.7 (d, $^4J_{C-F}$ = 3.0 Hz), 116.0 (d, $^2J_{C-F}$ = 22.2 Hz), 113.7, 99.2, 30.3, 27.4, 22.6, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.0. HRMS Calcd. For $C_{20}H_{19}FO$ $[M+H]^+$: 295.1493; found: 295.1487.



2-(2-phenylvinylidene)-1-(m-tolyl)hexan-1-one (3ao) Yellow liquid, 33 mg, 56 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 3H), 7.23 – 7.16 (m, 4H), 6.85 – 6.78 (m, 1H), 6.76 (d, J = 8.3 Hz, 1H), 6.29 (t, J = 2.7 Hz, 1H), 3.68 (s, 3H), 2.57 – 2.44 (m, 2H), 1.56 – 1.50 (m, 2H), 1.46 – 1.40 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 216.9, 195.9, 156.5, 132.6, 131.1, 130.5, 128.8, 128.2, 127.6, 127.3, 119.9, 113.9, 110.9, 98.5, 55.6, 30.3, 27.2, 22.6, 14.1. HRMS Calcd. For $C_{21}H_{22}O_2$ $[M+H]^+$: 307.1693; found: 307.1690.

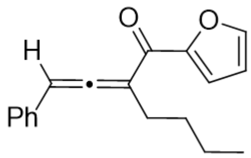


1-(naphthalen-2-yl)-2-(2-phenylvinylidene)hexan-1-one (3ap) Yellow liquid, 52 mg,



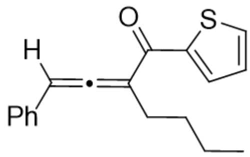
80 % yield. [1]H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.88 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.81 – 7.87 (m, 1H), 7.77 (d, *J* = 3.2 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.45 – 7.38 (m, 3H), 7.37 – 7.32 (m, 3H), 6.48 (t, *J* = 2.7 Hz, 1H), 2.71 – 2.56 (m, 2H), 1.67 – 1.58 (m, 2H), 1.55 – 1.46 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 215.5, 193.1, 138.6, 136.7, 133.7, 133.0, 130.3, 129.8, 128.9, 128.4, 128.0, 127.9, 126.8, 126.6, 126.4, 124.6, 111.3, 99.2, 30.4, 28.5, 22.7, 14.1. HRMS Calcd. For $C_{24}H_{22}O$ $[M+H]^+$: 327.1743; found: 327.1742.

1-(furan-2-yl)-2-(2-phenylvinylidene)hexan-1-one (3aq) Yellow liquid, 37 mg, 70 %



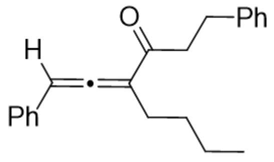
yield. [1]H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42 – 7.33 (m, 4H), 7.32 – 7.26 (m, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.62 (t, *J* = 2.7 Hz, 1H), 6.37 (dd, *J* = 3.5, 1.5 Hz, 1H), 2.63 – 2.42 (m, 2H), 1.58 – 1.46 (m, 2H), 1.45 – 1.35 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 213.3, 179.8, 151.8, 146.6, 132.5, 129.1, 128.0, 127.3, 118.4, 111.9, 110.2, 98.8, 30.2, 28.3, 22.5, 14.0. HRMS Calcd. For $C_{18}H_{18}O_2$ $[M+H]^+$: 267.1380; found: 267.1376.

2-(2-phenylvinylidene)-1-(thiophen-2-yl)hexan-1-one (3ar) Yellow liquid, 38 mg,



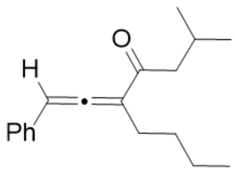
67 % yield. [1]H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 3.7 Hz, 1H), 7.52 (d, *J* = 4.9 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.34 – 7.27 (m, 1H), 7.01 – 6.92 (m, 1H), 6.66 (t, *J* = 2.7 Hz, 1H), 2.63 – 2.48 (m, 2H), 1.61 – 1.50 (m, 2H), 1.48 – 1.38 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 213.1, 184.1, 143.2, 133.3, 132.8, 132.6, 129.1, 128.0, 127.7, 127.5, 111.2, 99.6, 30.3, 28.9, 22.6, 14.0. HRMS Calcd. For $C_{18}H_{18}OS$ $[M+H]^+$: 283.1151; found: 283.1149.

1-phenyl-4-(2-phenylvinylidene)octan-3-one (3as) Yellow liquid, 48 mg, 78 % yield.



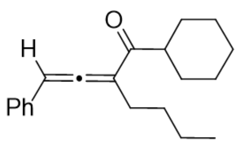
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 – 7.34 (m, 2H), 7.31 – 7.23 (m, 5H), 7.19 (d, *J* = 6.0 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.58 (t, *J* = 2.7 Hz, 1H), 3.07 – 2.91 (m, 4H), 2.43 – 2.27 (m, 2H), 1.48 – 1.34 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 214.4, 199.8, 141.2, 132.3, 129.1, 128.5, 127.9, 127.1, 126.1, 112.9, 99.2, 41.4, 31.0, 30.2, 26.9, 22.6, 14.0. HRMS Calcd. For $C_{22}H_{24}O$ [M+H]$^+$:305.1900; found: 305.1897.

2-methyl-5-(2-phenylvinylidene)nonan-4-one (3at) Yellow liquid, 27 mg, 52 % yield.



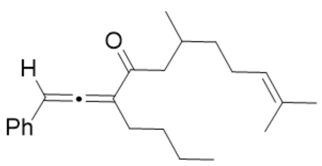
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.41 – 7.28 (m, 5H), 6.58 (t, *J* = 2.7 Hz, 1H), 2.61 – 2.45 (m, 2H), 2.33 (qd, *J* = 7.4, 2.7 Hz, 2H), 2.19 – 2.10 (m, 1H), 1.47 – 1.41 (m, 2H), 1.39 – 1.32 (m, 2H), 0.89 (td, *J* = 7.2, 2.1 Hz, 9H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 214.6, 200.7, 132.5, 129.1, 127.9, 127.1, 113.4, 98.9, 48.5, 30.3, 26.9, 26.0, 22.8, 22.7, 22.6, 14.0. HRMS Calcd. For $C_{18}H_{24}O$ [M+H]$^+$: 257.1900; found: 257.1897.

1-cyclohexyl-2-(2-phenylvinylidene)hexan-1-one (3au) Yellow liquid, 27 mg, 48 % yield.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 3H), 6.58 (t, *J* = 2.7 Hz, 1H), 2.96 (tt, *J* = 11.7, 3.2 Hz, 1H), 2.36 – 2.25 (m, 2H), 1.78 – 1.65 (m, 4H), 1.42 – 1.32 (m, 6H), 1.21 – 1.09 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 213.7, 204.3, 132.7, 129.1, 127.8, 127.1, 111.8, 98.8, 47.5, 30.4, 29.7, 29.6, 27.1, 25.9, 25.8, 25.7, 22.6, 14.0. HRMS Calcd. For $C_{20}H_{26}O$ [M+H]$^+$: 283.2056; found: 283.2050.

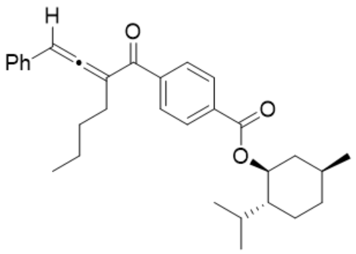
8,12-dimethyl-5-(2-phenylvinylidene)tridec-11-en-6-one (3av) Yellow liquid, 31 mg, 47 % yield, dr = 1:1.



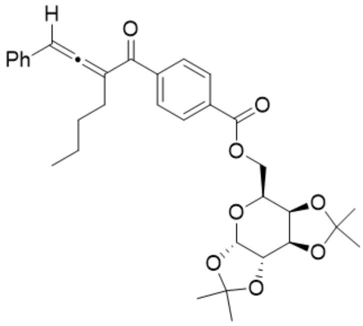
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 6.58 (q, *J* = 2.6 Hz, 1H), 5.12 – 4.93 (m, 1H), 2.71 – 2.57 (m, 1H), 2.51 – 2.40 (m, 1H), 2.38 – 2.24 (m, 2H), 2.04 – 1.83 (m, 3H), 1.67 – 1.62 (m, 3H), 1.54 (d, *J* = 11.5 Hz, 3H), 1.44 – 1.38 (m, 2H), 1.37 – 1.29 (m, 2H), 1.23 – 1.05 (m, 2H), 0.87 (q, *J* = 6.8

Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6 & 214.5 (two isomers), 200.9 (overlap, two isomers), 132.5 & 132.5 (two isomers), 131.5 & 131.4 (two isomers), 129.1 (overlap, two isomers), 127.9 (overlap, two isomers), 127.13 & 127.10 (two isomers), 124.6 & 124.5 (two isomers), 113.5 & 113.4 (two isomers), 99.0 (overlap, two isomers), 47.13 & 47.06 (two isomers), 37.3 & 37.1 (two isomers), 30.5 & 30.4 (two isomers), 30.3 (overlap, two isomers), 27.0 (overlap, two isomers), 25.8 & 25.8 (two isomers), 25.7 (overlap, two isomers), 22.6 (overlap, two isomers), 20.0 & 19.8 (two isomers), 17.8 & 17.7 (two isomers), 14.0 (overlap, two isomers). HRMS Calcd. For $C_{23}H_{32}O$ $[M+H]^+$: 325.2526; found: 325.2544.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(2-((R)-2-phenylvinylidene)hexanoyl)benzoate (3aw) Yellow liquid, 48 mg, 52 % yield, dr = 1:1. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.30 – 7.24 (m, 3H), 6.48 (q, *J* = 2.5 Hz, 1H), 4.91 (tdd, *J* = 10.8, 4.4, 1.8 Hz, 1H), 2.65 – 2.46 (m, 2H), 2.07 (d, *J* = 12.2 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.71 (d, *J* = 10.5 Hz, 2H), 1.59 – 1.40 (m, 6H), 1.24 – 0.99 (m, 2H), 0.98 – 0.87 (m, 10H), 0.76 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 215.58 & 215.52 (two isomers) , 193.91 & 193.87(two isomers), 165.4(overlap, two isomers), 141.97 & 141.96 (two isomers), 133.7(overlap, two isomers), 132.27 & 132.26(two isomers), 129.21 & 129.20(two isomers), 129.13 & 129.08(two isomers), 128.58 & 128.54(two isomers), 128.04 & 128.03(two isomers), 127.29 & 127.28(two isomers), 111.37 & 111.35(two isomers), 99.03 & 98.97(two isomers), 75.34 & 75.32(two isomers), 47.26 & 47.25(two isomers), 40.97 & 40.96(two isomers), 34.35(two isomers), 31.5(overlap, two isomers), 30.3(overlap, two isomers), 28.31 & 28.27(two isomers), 26.53 & 26.49(two isomers), 23.67 & 23.60(two isomers), 22.7(overlap, two isomers), 22.1(overlap, two isomers), 20.88 & 20.85(two isomers), 16.57 & 16.51(two isomers), 14.1(overlap, two isomers). HRMS Calcd. For $C_{20}H_{19}FO$ [M+H]+: 295.1493; found: 295.1494. HRMS Calcd. For $C_{31}H_{38}O_3$ [M+H]+: 459.2894; found: 459.2887.

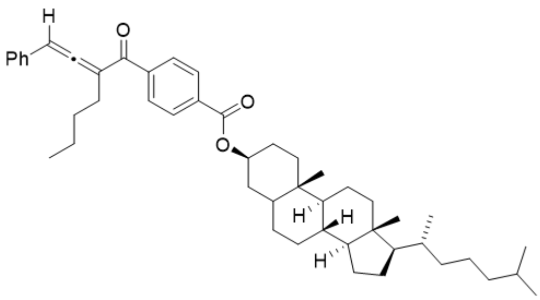


((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(2-(2-phenylvinylidene)hexanoyl)benzoate (3ax)



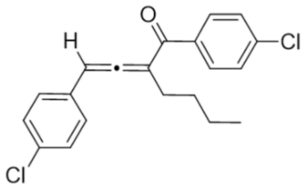
White solid, 58 mg, mp: 153-155 °C, 52% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.31 (m, 2H), 7.29 – 7.23 (m, 3H), 6.46 (t, *J* = 2.7 Hz, 1H), 5.54 (d, *J* = 4.9 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.55 – 4.46 (m, 1H), 4.44 – 4.37 (m, 1H), 4.33 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.29 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.18 – 4.09 (m, 1H), 2.64 – 2.43 (m, 2H), 1.59 – 1.51 (m, 2H), 1.49 – 1.40 (m, 8H), 1.32 (d, *J* = 5.1 Hz, 6H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.7, 194.0, 165.8, 142.3, 132.9, 132.2, 129.4, 129.1, 128.6, 128.1, 127.3, 111.4, 109.8, 108.9, 99.1, 96.4, 71.2, 70.8, 70.6, 66.1, 64.2, 30.3, 28.2, 26.10, 26.07, 25.1, 24.6, 22.7, 14.1. HRMS Calcd. For $C_{33}H_{38}O_8$ $[M+H]^+$: 563.2639; found: 563.2645.

(3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(2-((R)-2-phenylvinylidene)hexanoyl)benzoate (3by)



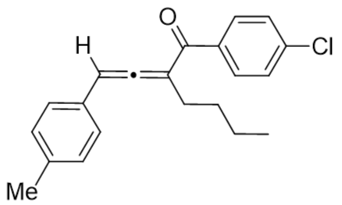
White solid, mp: 114-116 °C, 80 mg, 58 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.30 – 7.24 (m, 3H), 6.47 (t, *J* = 2.7 Hz, 1H), 5.43 – 5.35 (m, 1H), 4.90 – 4.75 (m, 1H), 2.56 (qd, *J* = 7.3, 2.7 Hz, 2H), 2.43 (d, *J* = 7.7 Hz, 2H), 2.09 – 1.90 (m, 4H), 1.90 – 1.74 (m, 2H), 1.74 – 1.62 (m, 2H), 1.62 – 1.46 (m, 8H), 1.46 – 1.42 (m, 2H), 1.42 – 1.31 (m, 4H), 1.30 – 1.21 (m, 3H), 1.20 – 1.07 (m, 6H), 1.05 (s, 4H), 0.97 – 0.91 (m, 6H), 0.87 (dd, *J* = 6.6, 1.1 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.6, 193.9, 165.3, 142.0, 139.6, 133.7, 132.3, 129.2, 129.1, 128.5, 128.1, 127.3, 123.0, 111.4, 99.0, 75.1, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.3, 37.1, 36.7, 36.3, 35.9, 32.04, 31.97, 30.3, 28.4, 28.3, 28.1, 27.9, 24.4, 24.0, 23.0, 22.70, 22.67, 21.2, 19.5, 18.9, 14.1, 12.0. HRMS Calcd. For $C_{48}H_{66}O_3$ $[M+H]^+$:691.5085; found: 691.5108.

1-(4-chlorophenyl)-2-(2-(4-chlorophenyl)vinylidene)hexan-1-one (3ba) White solid,



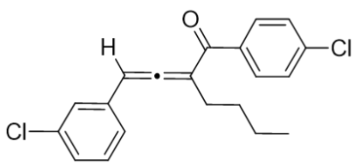
mp: 56-57 °C, 51 mg, 74 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 6.43 (t, *J* = 2.8 Hz, 1H), 2.64-2.41 (m, 2H), 1.57 – 1.47 (m, 2H), 1.47 – 1.37 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.7, 192.8, 138.7, 136.5, 133.7, 131.0, 130.2, 129.3, 128.4, 111.3, 97.9, 30.3, 28.5, 22.6, 14.1. HRMS Calcd. For $C_{20}H_{18}Cl_2O$ $[M+H]^+$:345.0808 ; found: 345.0812.

1-(4-chlorophenyl)-2-(2-(p-tolyl)vinylidene)hexan-1-one (3bb) Yellow liquid, 51



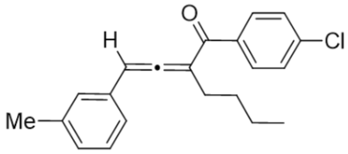
mg, 79 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.17 (s, 4H), 6.45 (t, *J* = 2.7 Hz, 1H), 2.62 – 2.46 (m, 2H), 2.36 (s, 3H), 1.59 – 1.50 (m, 2H), 1.47 – 1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 193.2, 138.5, 138.0, 136.8, 130.3, 129.9, 129.4, 128.3, 127.2, 111.0, 98.6, 30.3, 28.5, 22.7, 21.4, 14.1. HRMS Calcd. For $C_{21}H_{21}ClO$ $[M+H]^+$: 325.1354; found: 325.1353.

1-(4-chlorophenyl)-2-(2-(3-chlorophenyl)vinylidene)hexan-1-one (3bc) Yellow

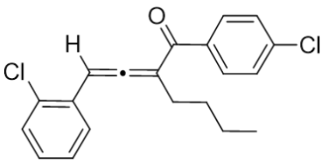


liquid, 50 mg, 72 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.29 – 7.22 (m, 5H), 7.14 (dt, *J* = 7.2, 1.5 Hz, 1H), 6.42 (t, *J* = 2.8 Hz, 1H), 2.60 – 2.50 (m, 2H), 1.57 – 1.49 (m, 2H), 1.47 – 1.39 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 192.7, 138.8, 136.5, 135.1, 134.4, 130.3, 130.2, 128.4, 128.0, 127.1, 125.3, 111.4, 97.9, 30.2, 28.5, 22.6, 14.0. HRMS Calcd. For $C_{20}H_{18}Cl_2O$ $[M+H]^+$: 345.0808; found: 345.0812.

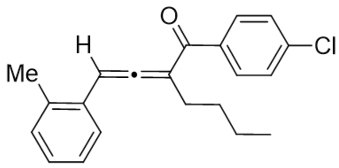
1-(4-chlorophenyl)-2-(2-(m-tolyl)vinylidene)hexan-1- one (3bd) Yellow liquid, 53 mg, 82 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.09 (d, *J* = 8.6 Hz, 3H), 6.45 (t, *J* = 2.7 Hz, 1H), 2.65 – 2.48 (m, 2H), 2.36 (s, 3H), 1.59 – 1.50 (m, 2H), 1.48 – 1.39 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 193.1, 138.8, 138.5, 136.7, 132.3, 130.3, 129.0, 128.9, 128.3, 128.0, 124.4, 110.9, 98.8, 30.3, 28.4, 22.7, 21.5, 14.1. HRMS Calcd. For $C_{21}H_{21}ClO$ $[M+H]^+$: 325.1354; found: 325.1353.



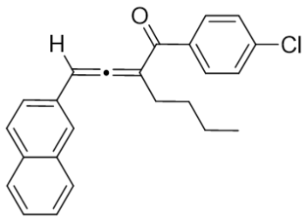
1-(4-chlorophenyl)-2-(2-(2-chlorophenyl)vinylidene)hexan-1-one (3be) Yellow liquid, 46 mg, 67 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.39 – 7.32 (m, 2H), 7.28 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.25 – 7.14 (m, 2H), 6.92 (t, *J* = 2.7 Hz, 1H), 2.55 (td, *J* = 7.7, 2.5 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.48 – 1.39 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.4, 192.7, 138.7, 136.5, 132.6, 130.34, 130.28, 130.2, 129.0, 128.5, 128.4, 127.2, 111.0, 95.3, 30.2, 28.5, 22.6, 14.0. HRMS Calcd. For $C_{20}H_{18}Cl_2O$ $[M+H]^+$: 345.0808; found: 345.0812.



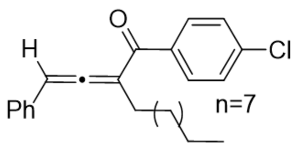
1-(4-chlorophenyl)-2-(2-(o-tolyl)vinylidene)hexan-1-one (3bf) Yellow liquid, 48 mg, 74 % yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.31–7.24 (t, *J* = 8.4 Hz, 3H), 7.22 – 7.14 (m, 3H), 6.67 (t, *J* = 2.7 Hz, 1H), 2.55 (td, *J* = 8.3, 7.9, 2.7 Hz, 2H), 2.29 (s, 3H), 1.61 – 1.51 (m, 2H), 1.49 – 1.40 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.5, 193.1, 138.4, 136.6, 135.4, 130.8, 130.7, 130.2, 128.2, 127.9, 127.5, 126.5, 110.1, 96.1, 30.2, 28.4, 22.6, 19.9, 14.0. HRMS Calcd. For $C_{21}H_{21}ClO$ $[M+H]^+$: 325.1354; found: 325.1353.



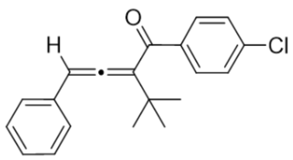
1-(4-chlorophenyl)-2-(2-(naphthalen-2-yl)vinylidene)hexan-1-one (3bg) White solid, mp: 95-97 °C, 54 mg, 75 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.70 (m, 3H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.67 (s, 1H), 7.51 – 7.42 (m, 3H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.65 (t, *J* = 2.7 Hz, 1H), 2.67 – 2.51 (m, 2H), 1.62 – 1.54 (m, 2H), 1.51 – 1.43 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.5, 193.1, 138.6, 136.7, 133.7, 133.0, 130.3, 129.8, 128.9, 128.4, 128.0, 127.9, 126.8, 126.6, 126.4, 124.6, 111.3, 99.2, 30.4, 28.5, 22.7, 14.1. HRMS Calcd. For $C_{24}H_{21}ClO$ [M+H]+: 361.1354; found: 361.1357.



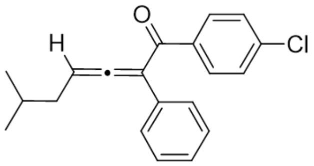
1-(4-chlorophenyl)-2-(2-phenylvinylidene)dodecan-1-one (3bh) White solid, mp: 49-51 °C, 60 mg, 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.30 – 7.22 (m, 5H), 6.47 (t, *J* = 2.6 Hz, 1H), 2.63 – 2.45 (m, 2H), 1.61 – 1.51 (m, 2H), 1.44 – 1.37 (m, 2H), 1.31 – 1.22 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 193.0, 138.6, 136.7, 132.4, 130.2, 129.1, 128.3, 128.0, 127.3, 111.0, 98.8, 32.0, 29.73, 29.70, 29.6, 29.4, 28.7, 28.2, 22.8, 14.3. HRMS Calcd. For $C_{26}H_{31}ClO$ $[M+Na]^+$:417.1946; found: 417.1956.



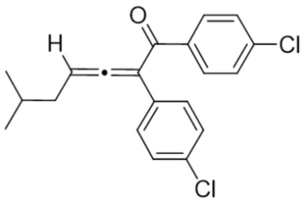
2-(tert-butyl)-1-(4-chlorophenyl)-4-phenylbuta-2,3-dien-1-one (3bi) Yellow liquid, 30 mg, 49 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.40 – 7.33 (m, 3H), 7.33 – 7.27 (d, *J* = 7.1 Hz, 1H), 5.75 (s, 1H), 1.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8, 192.8, 138.8, 136.8, 133.5, 130.8, 128.7, 128.4, 127.8, 127.8, 111.1, 109.3, 33.9, 30.1. HRMS Calcd. For $C_{20}H_{19}ClO$ $[M+H]^+$: 311.1197; found: 311.1200.



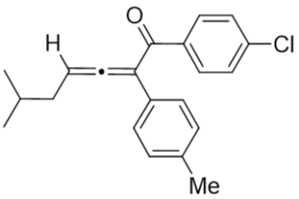
1-(4-chlorophenyl)-6-methyl-2-phenylhepta-2,3-dien-1-one (3bk) Yellow liquid, 54 mg, 55 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 5H), 6.46 (s, 1H), 2.51 – 2.40 (m, 2H), 1.96 – 1.85 (m, 1H), 1.01 (t, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.2, 193.1, 138.6, 136.6, 132.4, 130.3, 129.1, 128.4, 128.0, 127.4, 109.8, 98.2, 38.0, 27.7, 22.9, 22.7. HRMS Calcd. For $C_{20}H_{19}ClO$ $[M+H]^+$: 311.1197; found: 311.1203.



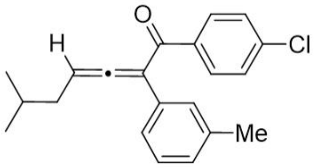
1,2-bis(4-chlorophenyl)-6-methylhepta-2,3-dien-1-one (3bl) Yellow liquid, 31 mg, 45 % yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.29 (dd, *J* = 18.2, 8.4 Hz, 4H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.41 (t, *J* = 2.0 Hz, 1H), 2.46 – 2.42 (m, 2H), 1.93 – 1.81 (m, 1H), 1.00 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 192.8, 138.8, 136.5, 133.7, 130.9, 130.2, 129.3, 128.5, 128.4, 110.0, 97.3, 38.0, 27.6, 22.7. HRMS Calcd. For $C_{20}H_{18}Cl_2O$ $[M+H]^+$:345.0807; found: 345.0812.



1-(4-chlorophenyl)-6-methyl-2-(p-tolyl)hepta-2,3-dien-1-one (3bm) Yellow liquid, 45 mg, 69 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.29 – 7.23 (m, 2H), 7.17 (s, 4H), 6.43 (t, *J* = 2.3 Hz, 1H), 2.46 – 2.42 (m, 2H), 2.36 (s, 3H), 1.95-1.84 (m, 1H), 1.03 – 0.98 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 193.2, 138.5, 138.0, 136.7, 130.3, 129.8, 129.3, 128.3, 127.3, 109.7, 98.0, 55.0, 38.0, 27.6, 22.8, 22.7, 21.4. HRMS Calcd. For $C_{21}H_{21}ClO$ $[M+H]^+$:325.1354; found: 325.1353.

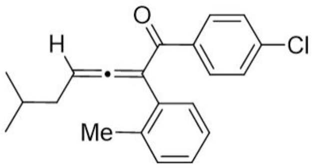


1-(4-chlorophenyl)-6-methyl-2-(m-tolyl)hepta-2,3-dien-1-one (3bn) Yellow liquid, 41 mg, 60 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 3H), 7.12 – 7.06 (m, 3H), 6.44 (s, 1H), 2.51 – 2.42 (m, 2H), 2.36 (s, 3H), 1.96-1.87 (m, 1H), 1.05 – 0.99 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.3, 193.0, 138.7, 138.5,



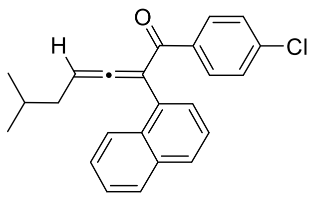
136.5, 132.1, 130.2, 128.9, 128.7, 128.2, 128.0, 124.3, 109.6, 98.1, 37.9, 27.5, 22.8, 21.4. HRMS Calcd. For $C_{20}H_{21}ClO$ $[M+H]^+$: 325.1354; found: 325.1350.

1-(4-chlorophenyl)-6-methyl-2-(o-tolyl)hepta-2,3-dien-1-one (3bo) Yellow liquid,



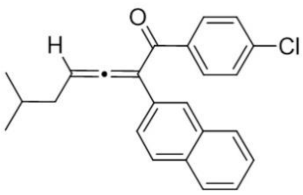
41 mg, 63 % yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.21 – 7.15 (m, 3H), 6.65 (s, 1H), 2.48 – 2.41 (m, 2H), 2.28 (s, 3H), 1.97 – 1.85 (m, 1H), 1.01 (dd, *J* = 6.4, 4.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9, 193.2, 138.5, 136.7, 135.5, 130.9, 130.8, 130.4, 128.3, 127.9, 127.7, 126.5, 109.0, 95.6, 38.0, 27.7, 22.8, 22.7, 20.0. HRMS Calcd. For $C_{21}H_{21}ClO$ $[M+H]^+$:325.1354; found: 325.1350.

1-(4-chlorophenyl)-6-methyl-2-(naphthalen-1-yl)hepta-2,3-dien-1-one (3bp)



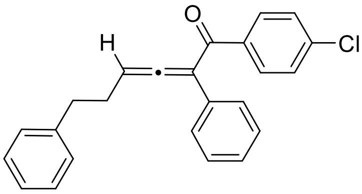
Yellow liquid, 47 mg, 64 % yield. ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 1H), 7.90 – 7.85 (m, 1H), 7.81 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.53 – 7.46 (m, 4H), 7.23 – 7.17 (m, 2H), 7.15 (t, *J* = 2.3 Hz, 1H), 2.52 (dd, *J* = 7.1, 2.3 Hz, 2H), 2.04 – 1.91 (m, 1H), 1.04 (dd, *J* = 6.6, 4.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.5, 193.2, 138.5, 136.7, 134.1, 130.7, 130.3, 128.9, 128.7, 128.6, 128.3, 126.6, 126.2, 126.1, 125.7, 123.5, 108.8, 94.9, 38.0, 27.7, 22.9, 22.8. HRMS Calcd. For $C_{24}H_{21}ClO$ $[M+H]^+$:361.1354; found: 361.1355.

1-(4-chlorophenyl)-6-methyl-2-(naphthalen-2-yl)hepta-2,3-dien-1-one (3bq) White

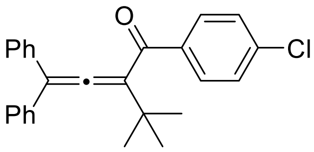


solid, mp: 86-88 ℃ 47 mg, 65 % yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 3H), 7.78 – 7.74 (m, 2H), 7.66 (s, 1H), 7.51 – 7.46 (m, 2H), 7.44 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.26 – 7.22 (m, 2H), 6.63 (t, *J* = 2.3 Hz, 1H), 2.51 (td, *J* = 6.8, 2.4 Hz, 2H), 2.01 – 1.88 (m, 1H), 1.05 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 193.0, 138.6, 136.6, 133.7, 133.0, 130.3, 129.8, 128.9, 128.4, 128.0, 127.9, 126.7, 126.7, 126.4, 124.6, 110.0, 98.6, 38.0, 27.7, 22.9, 22.8. HRMS Calcd. For $C_{24}H_{21}ClO$ $[M+H]^+$:361.1354; found: 361.1355.

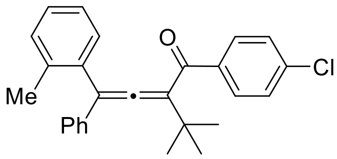
1-(4-chlorophenyl)-2,6-diphenylhexa-2,3-dien-1-one (3br) Yellow liquid, 37 mg, 52 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 2H), 7.34 – 7.22 (m, 10H), 7.06 – 6.97 (m, 2H), 6.38 (t, *J* = 2.4 Hz, 1H), 3.07 – 2.98(m, 1H), 2.97 – 2.91 (m, 2H), 2.87 – 2.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 192.8, 141.3, 138.6, 136.5, 132.1, 130.2, 129.0, 128.8, 128.6, 128.3, 128.0, 127.4, 126.2, 109.7, 98.5, 33.9, 30.7. HRMS Calcd. For $C_{24}H_{19}ClO$ $[M+H]^+$:359.1197; found: 359.1200.



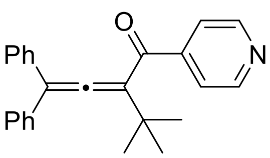
2-(tert-butyl)-1-(4-chlorophenyl)-4,4-diphenylbuta-2,3-dien-1-one (3bs) Yellow liquid, 31 mg, 40 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.40 – 7.29 (m, 6H), 7.21 (d, J = 7.2 Hz, 4H), 7.13 (d, J = 8.5 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 193.7, 138.7, 137.5, 135.5, 130.5, 128.8, 128.3, 128.0, 117.8, 114.0, 36.0, 30.0. HRMS Calcd. For $C_{26}H_{23}ClO$ $[M+H]^+$: 387.1510; found: 387.1509.



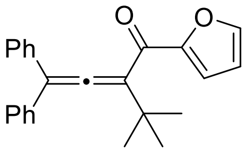
2-(tert-butyl)-1-(4-chlorophenyl)-4-phenyl-4-(o-tolyl)buta-2,3-dien-1-one (3bt) White solid, mp: 70-72 °C, 53 mg, 66 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.30 (q, *J* = 6.7 Hz, 3H), 7.28 – 7.22 (m, 2H), 7.22 – 7.17 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 7.1 Hz, 1H), 1.72 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 193.9, 138.8, 138.1, 137.0, 135.3, 134.6, 130.6, 130.5, 130.1, 128.9, 128.4, 128.4, 127.7, 126.6, 126.2, 77.5, 76.8, 36.0, 30.0, 19.8. HRMS Calcd. For $C_{27}H_{25}ClO$ $[M+H]^+$:401.1667; found: 401.1671.



2-(tert-butyl)-4,4-diphenyl-1-(pyridin-4-yl)buta-2,3-dien-1-one (3bu) Yellow liquid, 48 mg, 68 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.8 Hz, 2H), 7.37 – 7.31 (m, 6H), 7.29 (d, *J* = 5.9 Hz, 2H), 7.11 (dd, *J* = 7.5, 1.7 Hz, 4H), 1.40 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 194.1, 149.9, 146.4, 134.9, 128.9, 128.2, 128.1, 121.8, 118.4, 114.6, 35.7, 29.7. HRMS Calcd. For $C_{25}H_{23}NO$ $[M+H]^+$:354.1853; found: 354.1852.

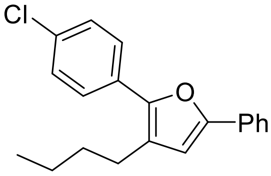


2-(tert-butyl)-1-(furan-2-yl)-4,4-diphenylbuta-2,3-dien-1-one (3bv) Yellow liquid,



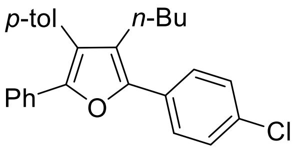
29 mg, 42 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.40 – 7.31 (m, 10H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.28 (d, *J* = 3.1 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 180.9, 152.7, 147.0, 135.6, 128.8, 128.4, 127.9, 119.0, 117.3, 113.9, 111.9, 77.5, 76.8, 36.2, 30.0. HRMS Calcd. For $C_{24}H_{22}O_2$ $[M+H]^+$:343.1693; found: 343.1697.

3-butyl-2-(4-chlorophenyl)-5-phenylfuran (5) Colorless liquid, 21 mg, 67 % yield.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.29 (d, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 2.75 – 2.61 (m, 2H), 1.73 – 1.62 (m, 2H), 1.51 – 1.41 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 147.0, 132.5, 130.8, 130.4, 128.9, 128.8, 127.5, 126.7, 124.7, 123.8, 109.4, 32.2, 25.9, 22.7, 14.1. HRMS Calcd. For $C_{20}H_{19}ClO$ $[M+H]^+$: 311.1197; found: 311.1183.

2-butyl-3-(4-chlorophenyl)-4-phenyl-5-(p-tolyl)furan (6) colorless liquid, 41 mg, 51%



yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 2H), 7.49 – 7.39 (m, 4H), 7.20 – 7.14 (m, 1H), 2.58 – 2.48 (m, 2H), 2.45 (s, 3H), 1.46 – 1.37 (m, 2H), 1.28 – 1.23 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 147.5, 146.4, 137.3, 132.6, 131.1, 130.8, 130.4, 130.1, 129.7, 128.9, 128.4, 127.1, 126.7, 126.0, 125.4, 125.1, 32.0, 23.9, 22.8, 21.5, 13.8. HRMS Calcd. For $C_{27}H_{26}ClO$ $[M+H]^+$: 401.1667; found: 401.1675.

References

1. M. S. Pearson; D. R. Carbery, *J. Org. Chem.*, 2009, 74, 5320.

2. M. S. Liu; W. Shu, *ACS Catal.*, 2020, 10, 12960.

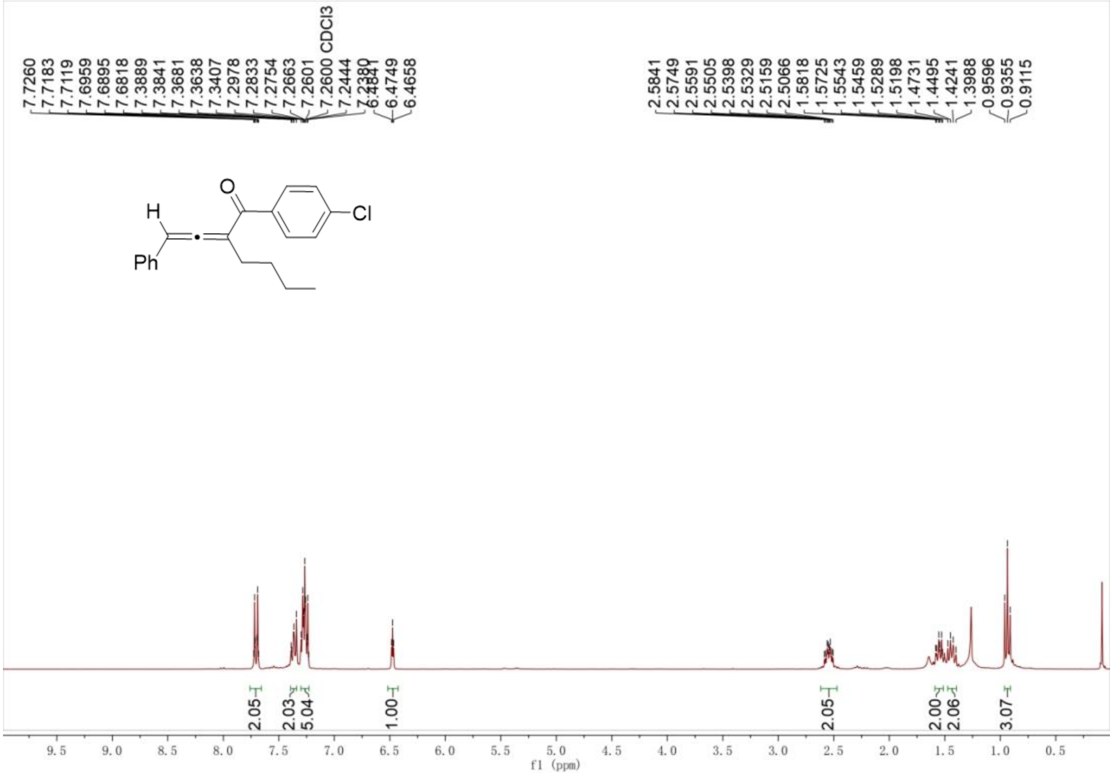
3. L. Guo; W. Srimontree; C. Zhu; B. Maity; X. Liu; L. Cavallo; M. Rueping, *Nat. Commun.*, 2019, 10, 1957.

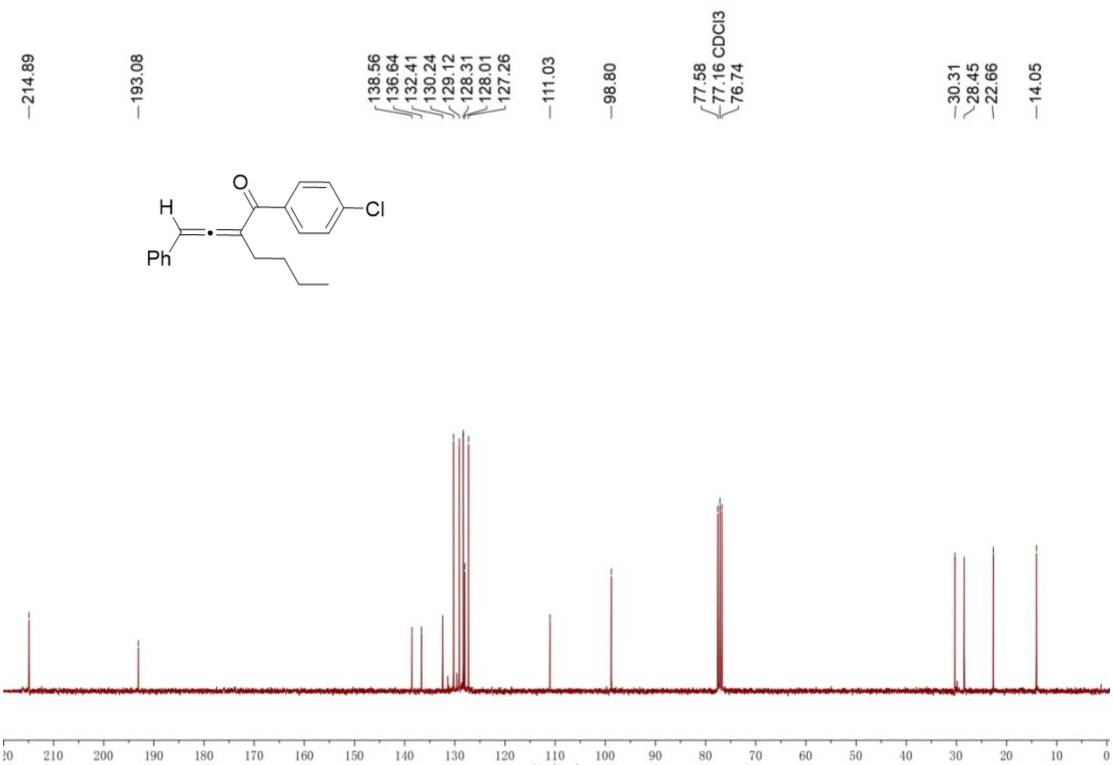
4. M. Ueda; T. Sakaguchi; M. Hayama; T. Nakagawa; Y. Matsuo; A. Munechika; S. Yoshida; H. Yasuda; I. Ryu, *Chem. Commun.*, 2016, 52, 13175-13178.

5. N. Sakai; K. Enomoto; M. Takayanagi; T. Konakahara; Y. Ogiwara, *Tetrahedron Lett.*, 2016, 57, 2175-2178.

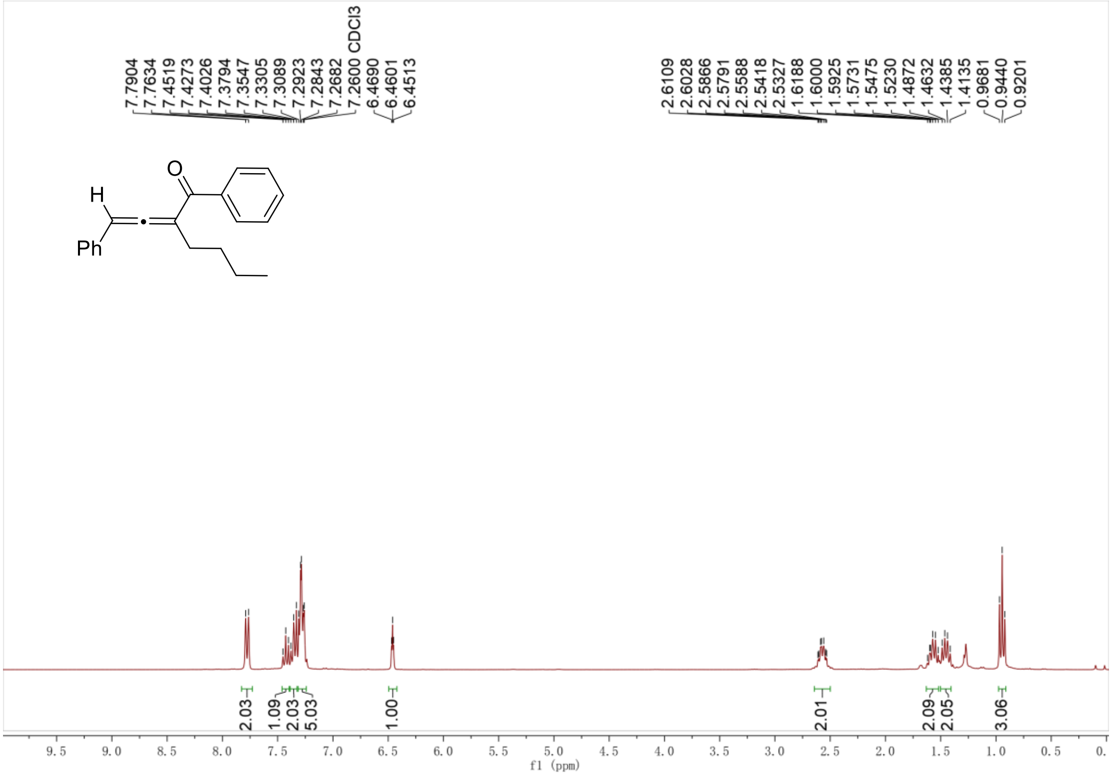
11. Copies of NMR spectra

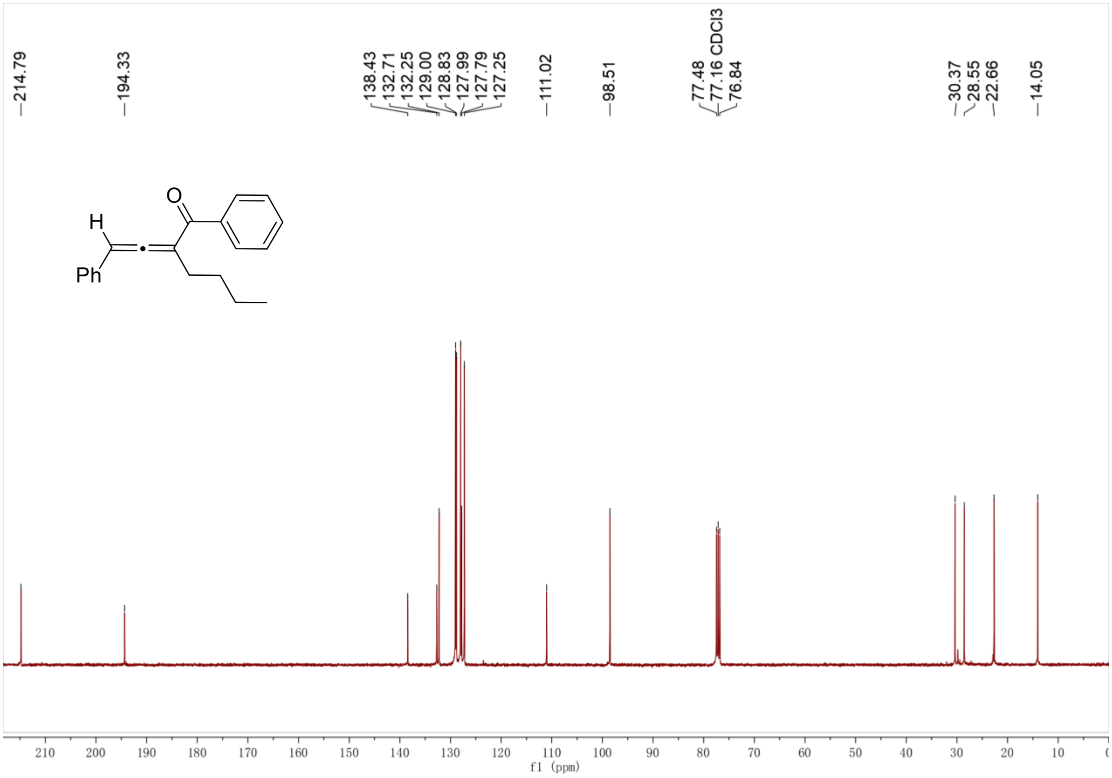
3aa ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



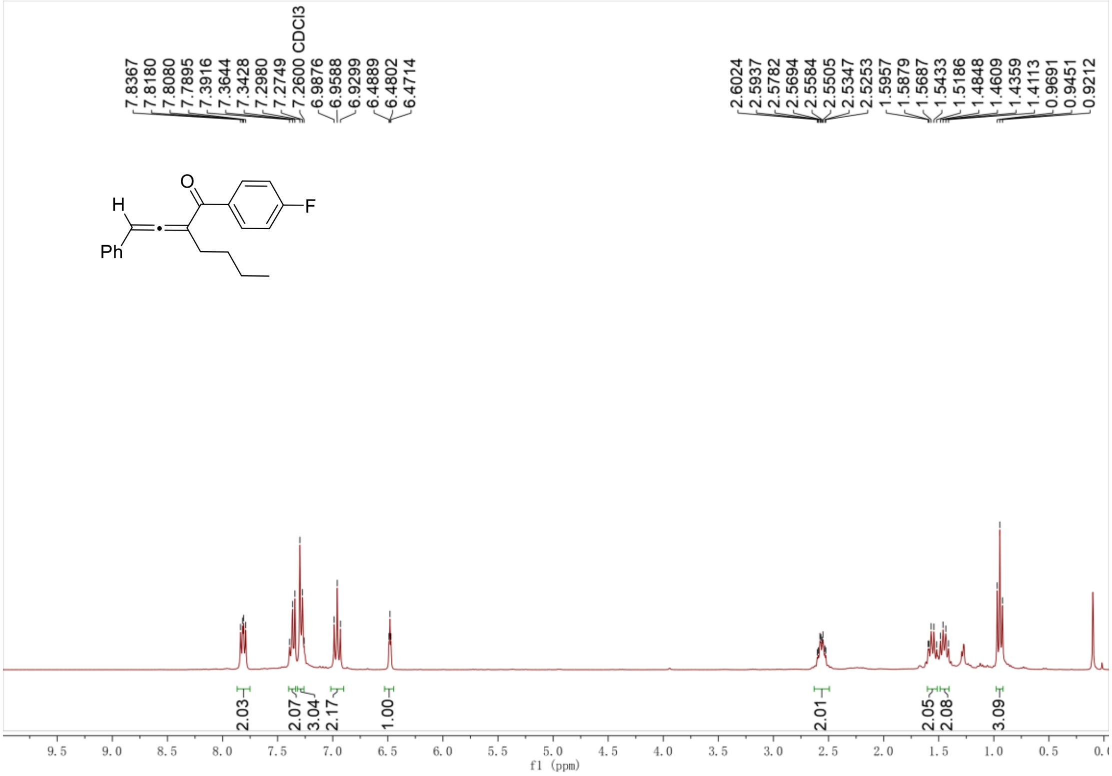


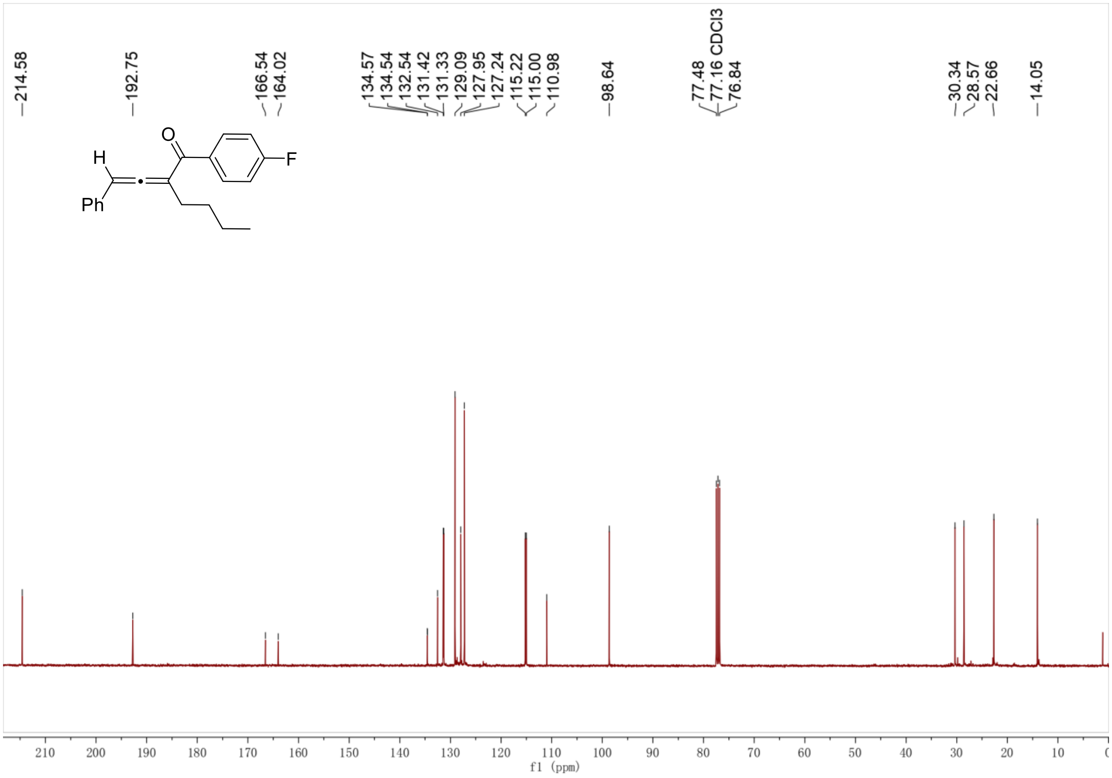
3ab ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



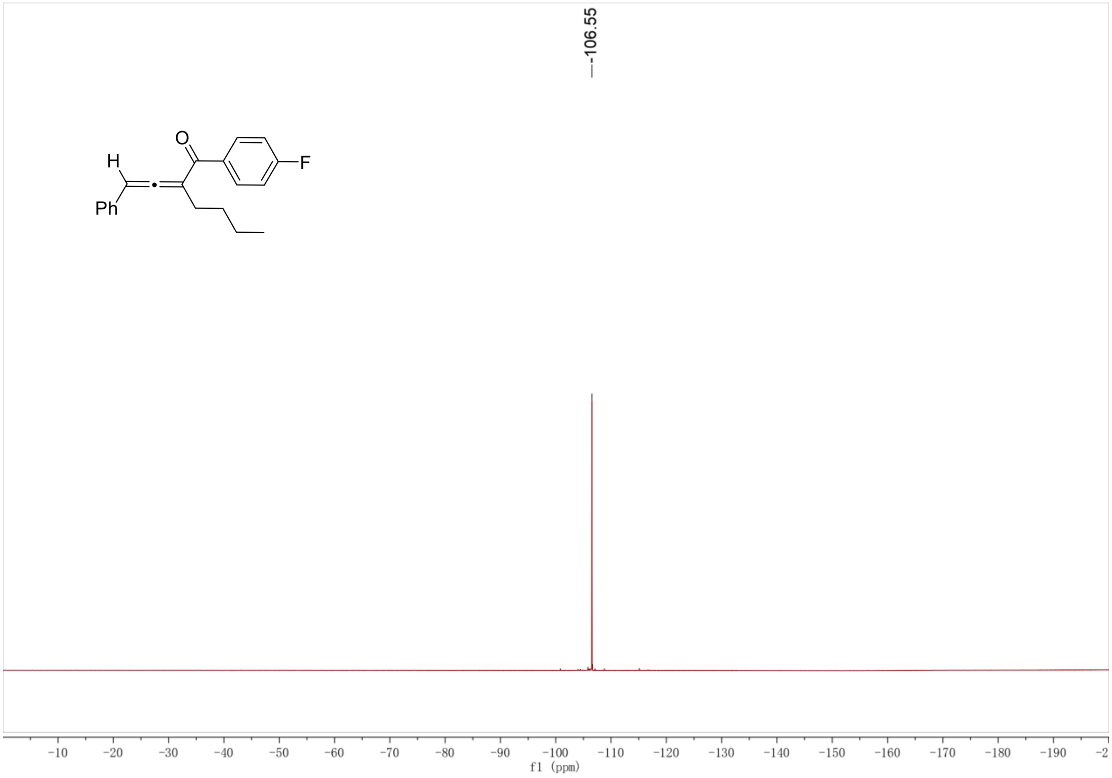


3ac ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)

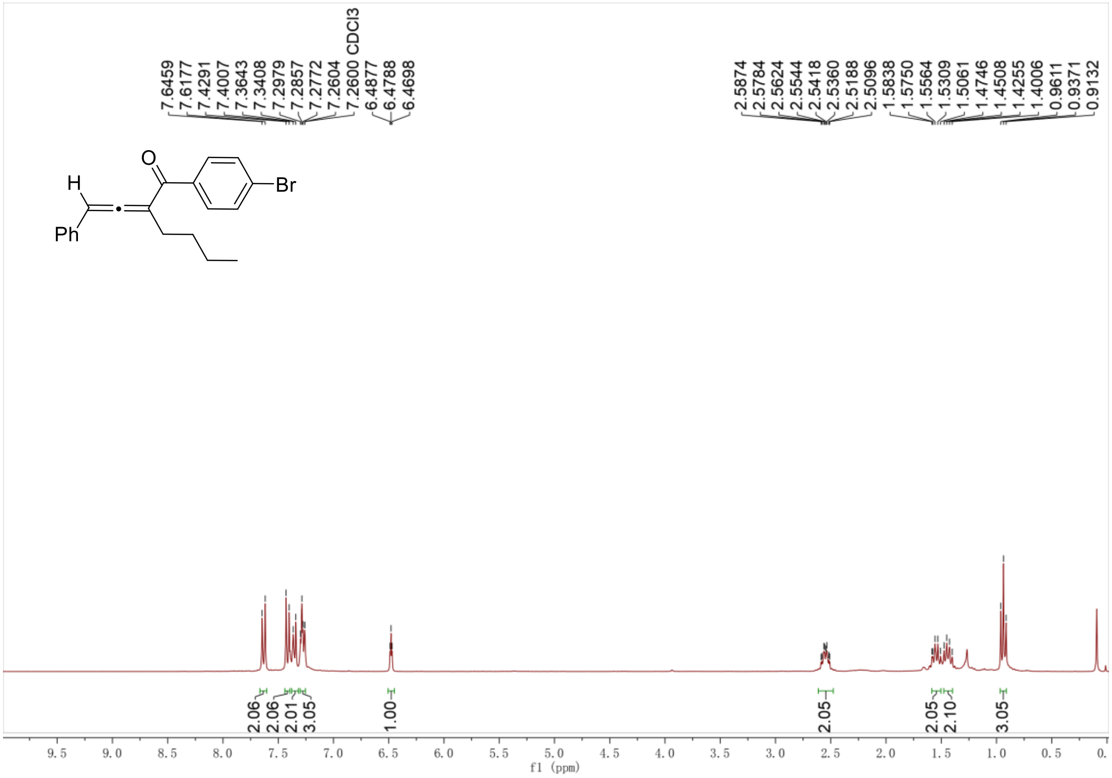


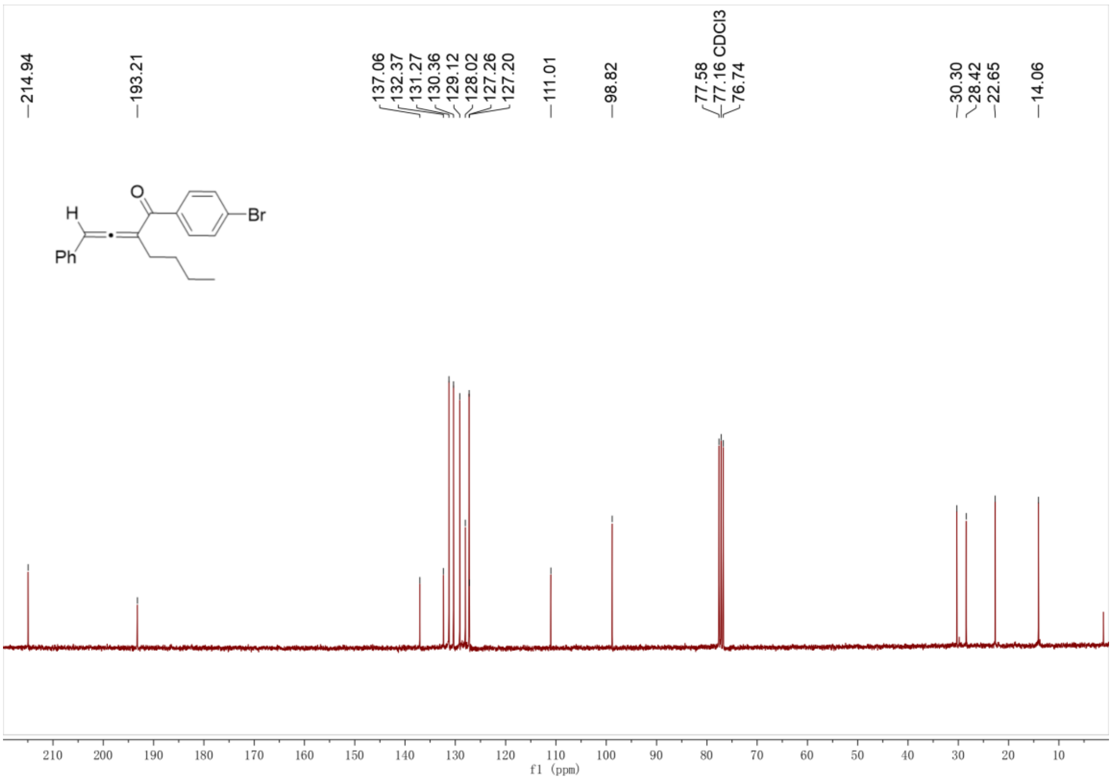


3ac ^{19}F NMR (282 MHz, Chloroform-d)

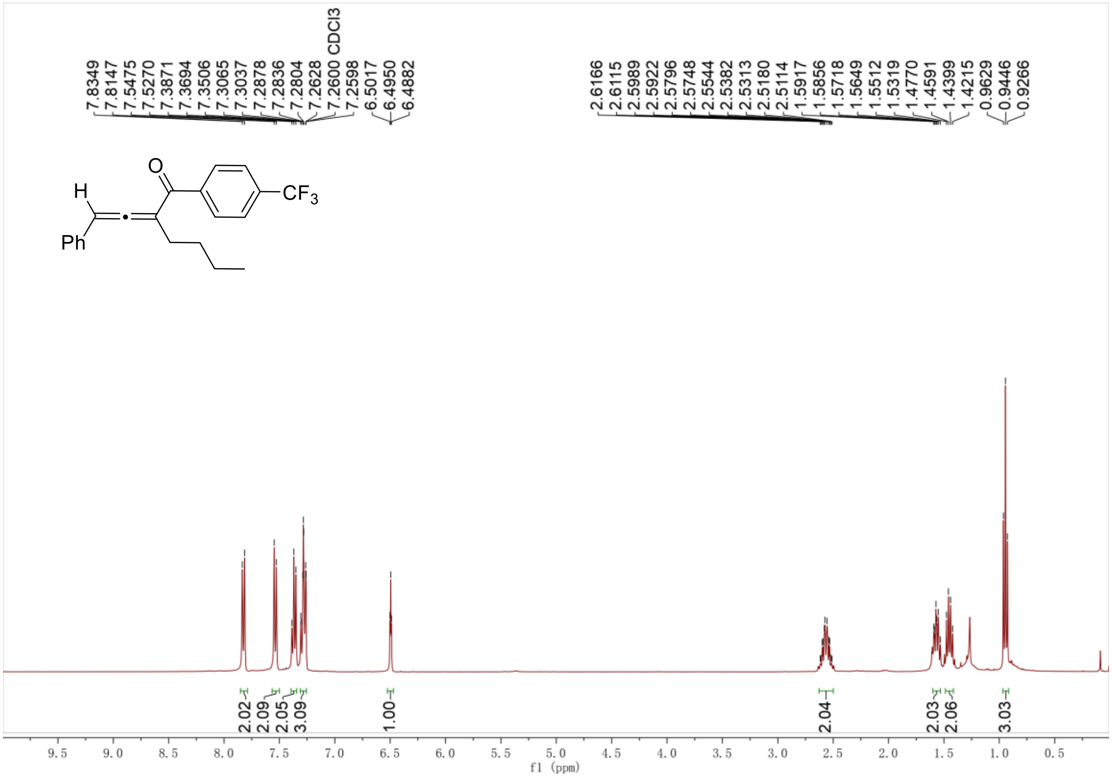


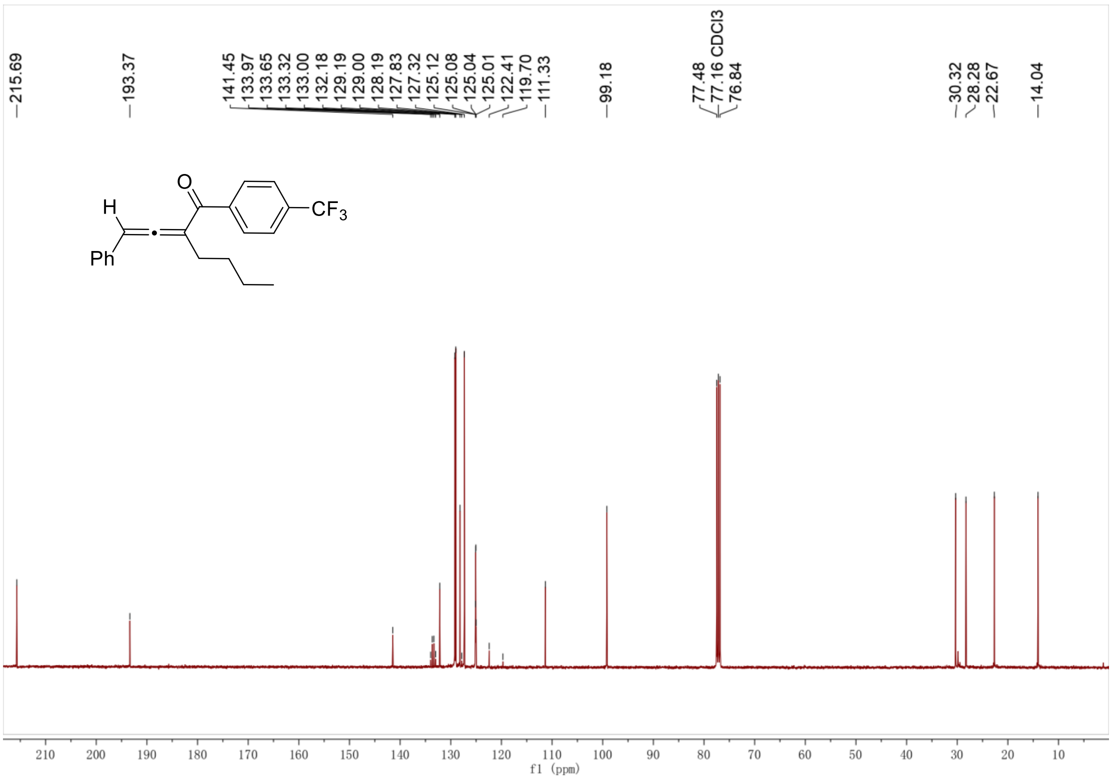
3ad ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



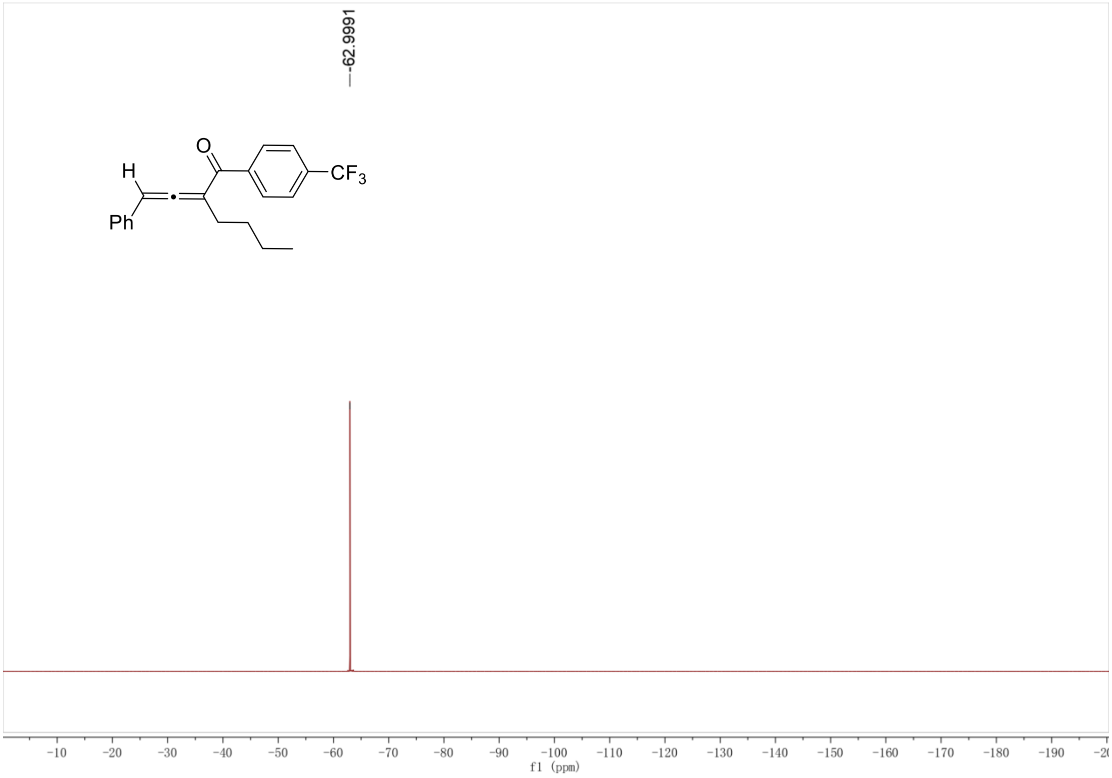


3ae ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)

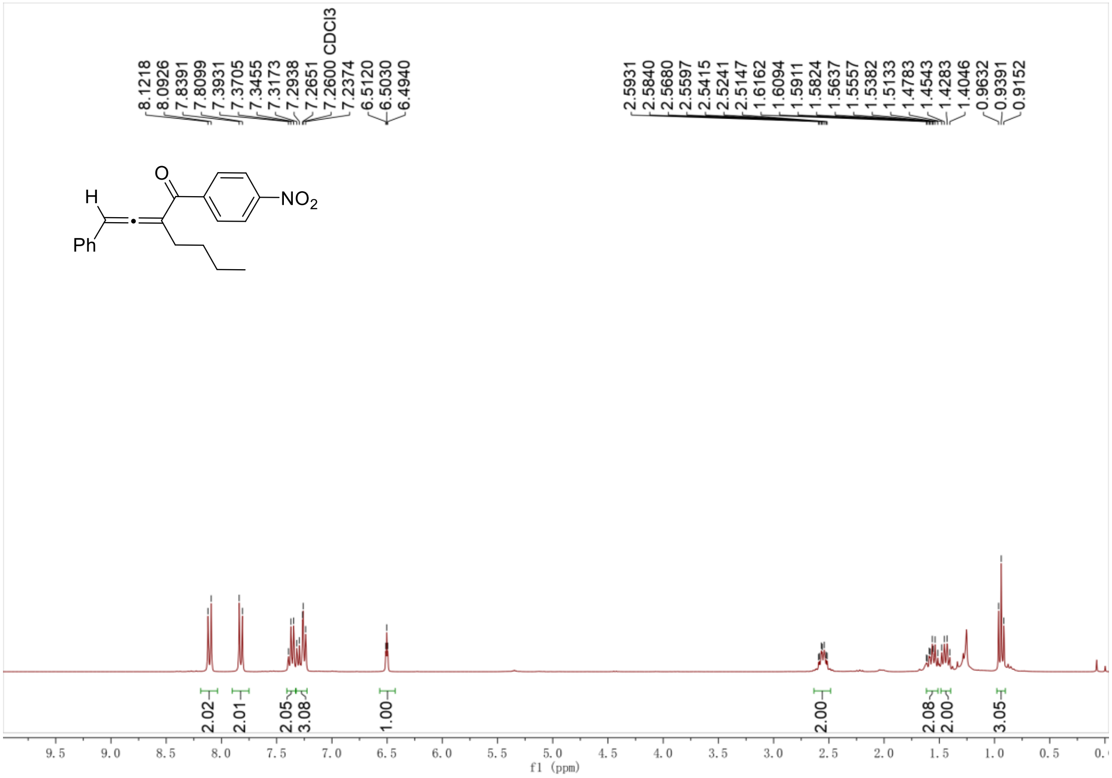


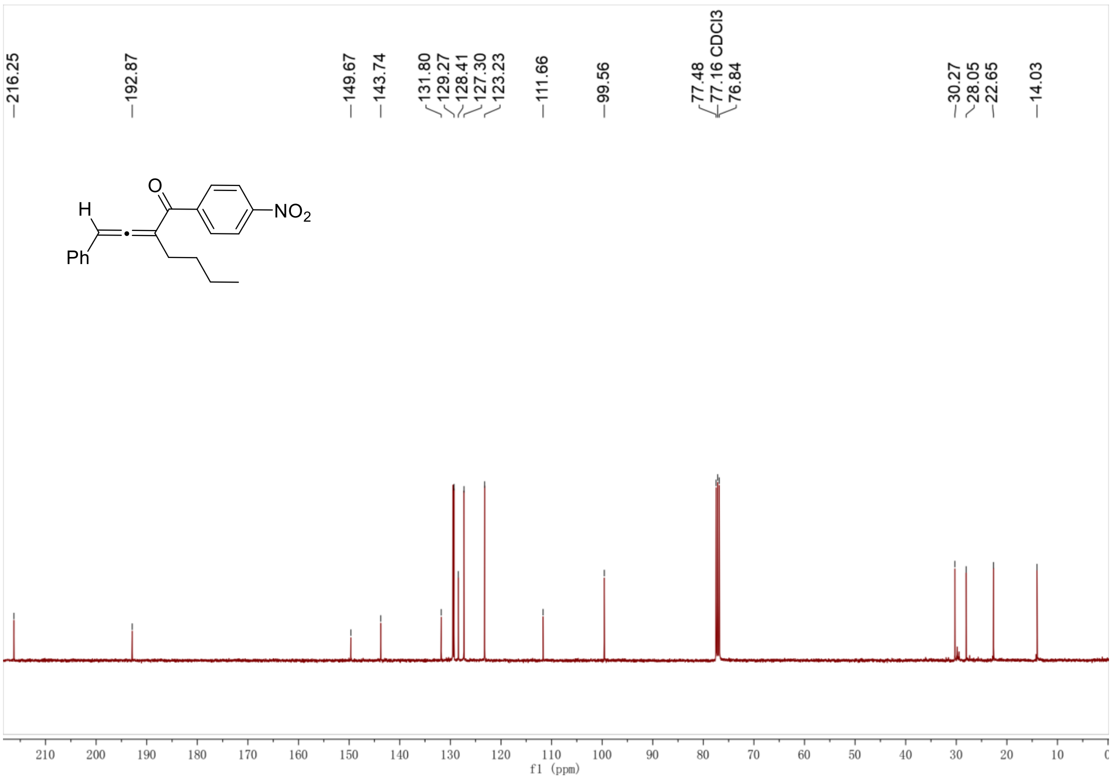


3ae ^{19}F NMR (376 MHz, Chloroform-d)

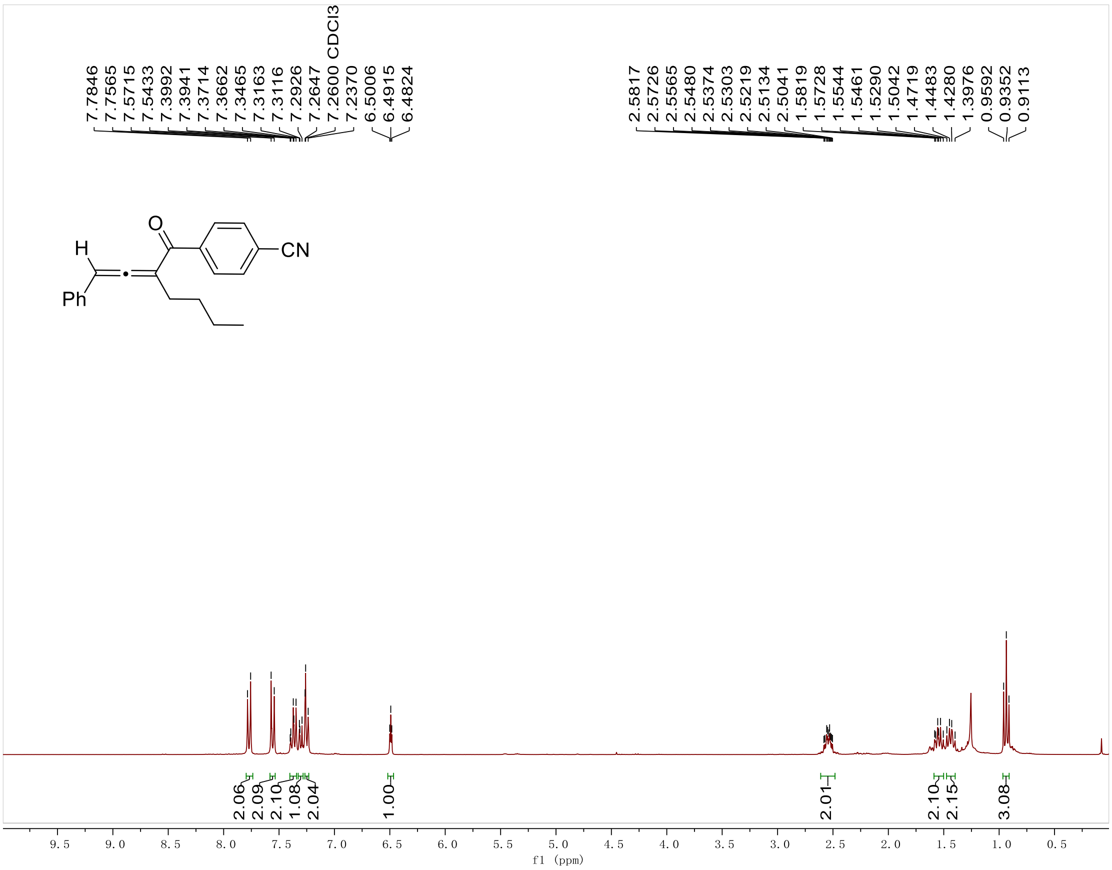


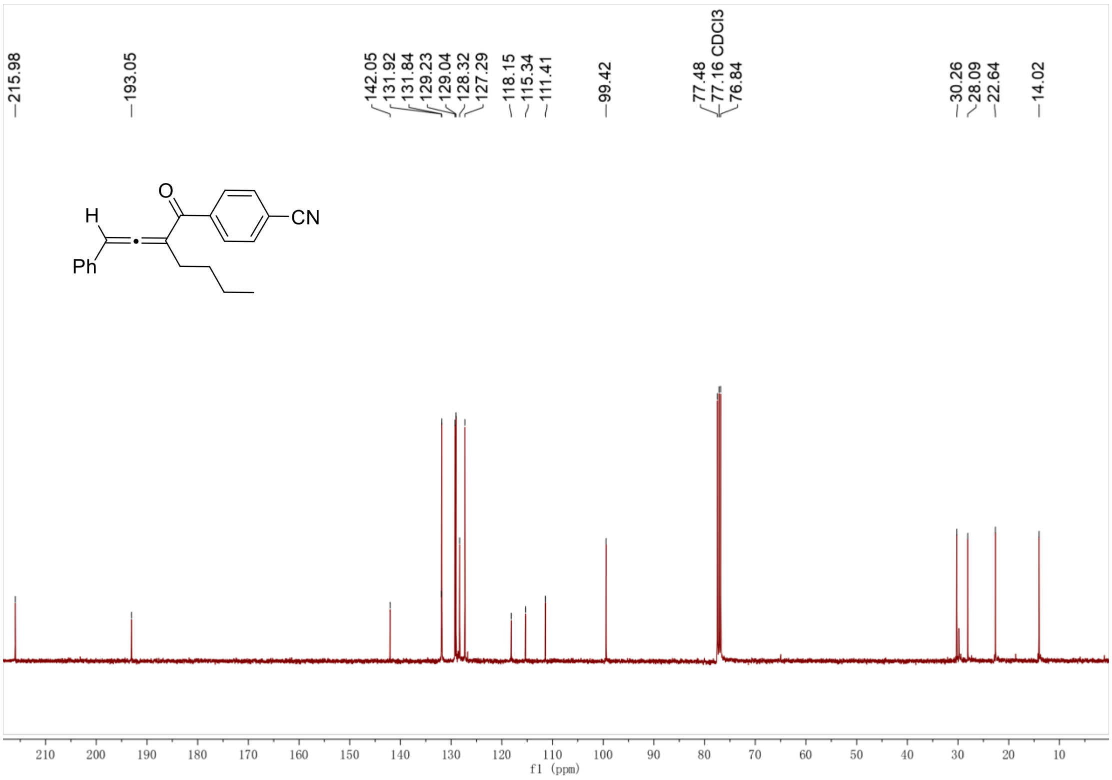
3af ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



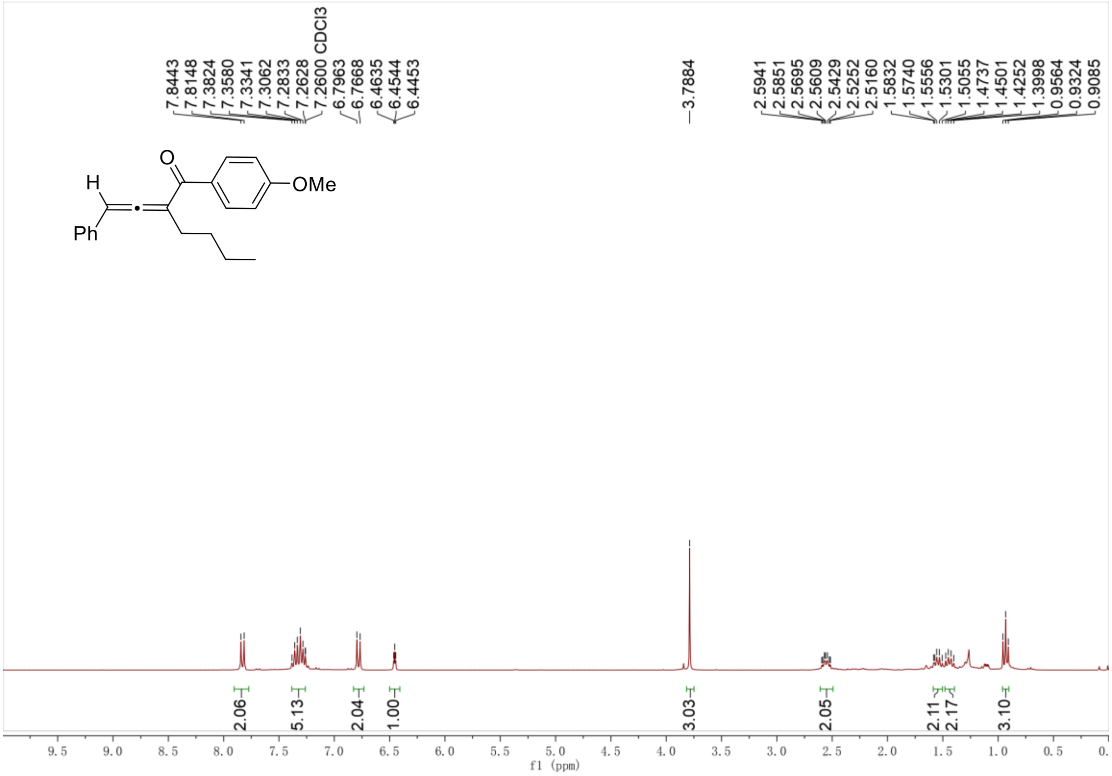


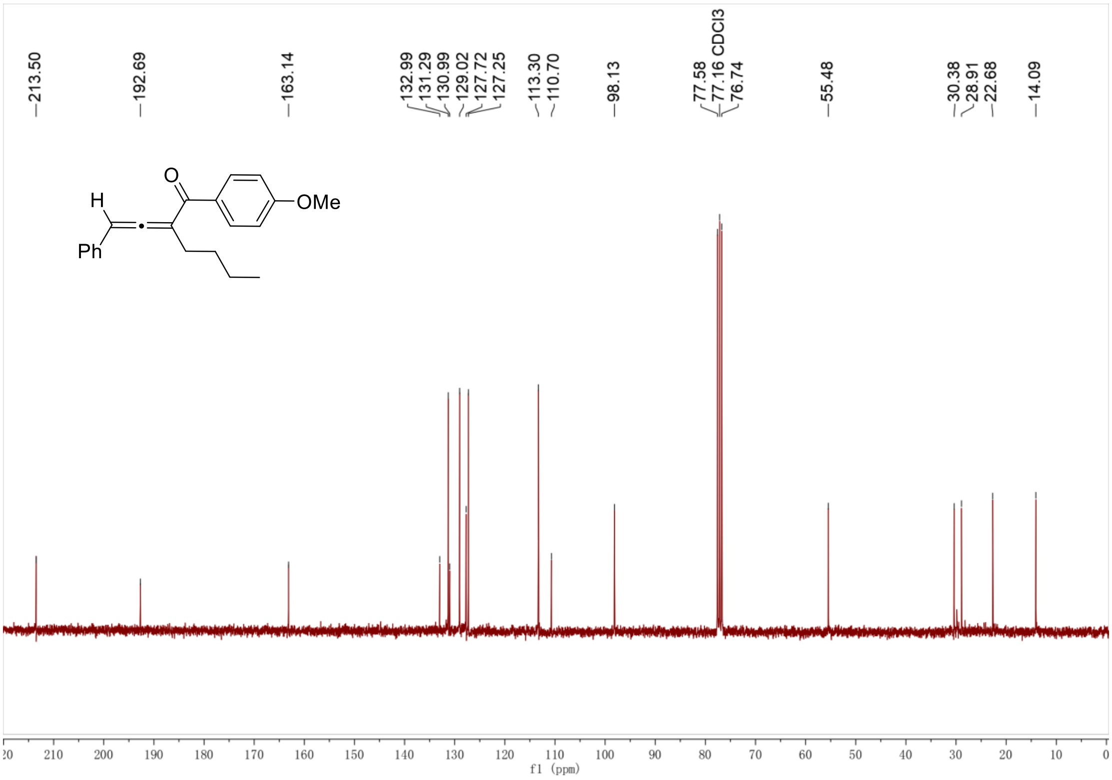
3ag ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



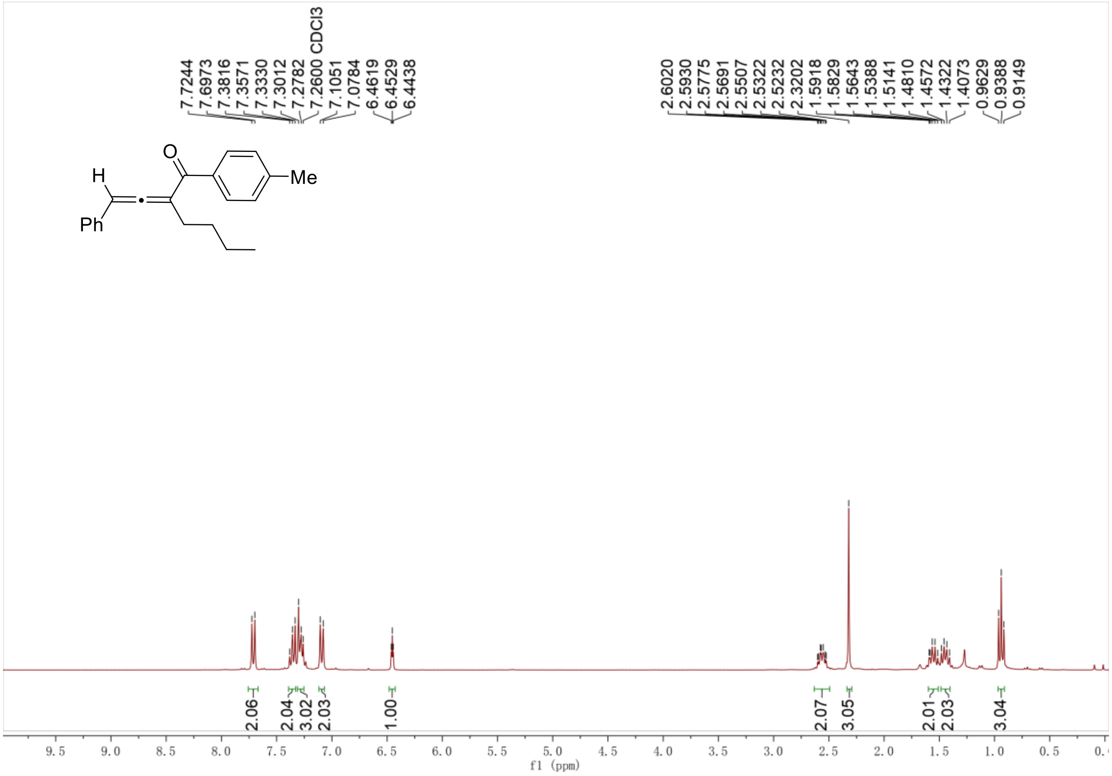


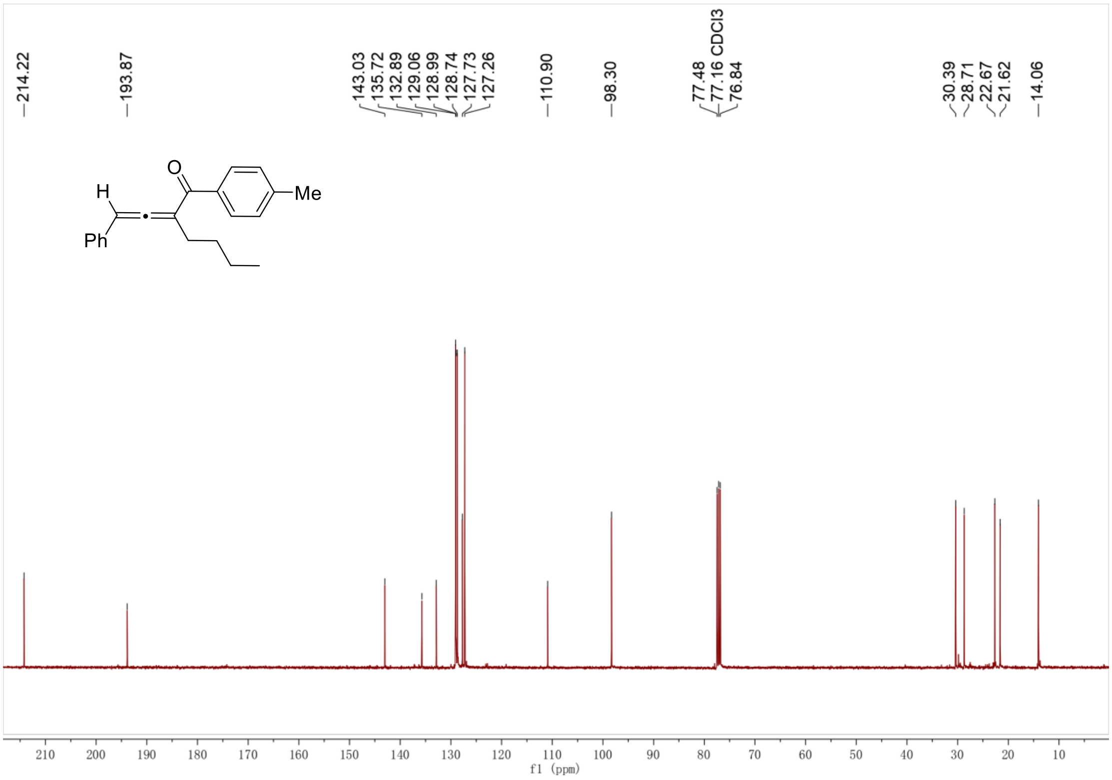
3ah ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



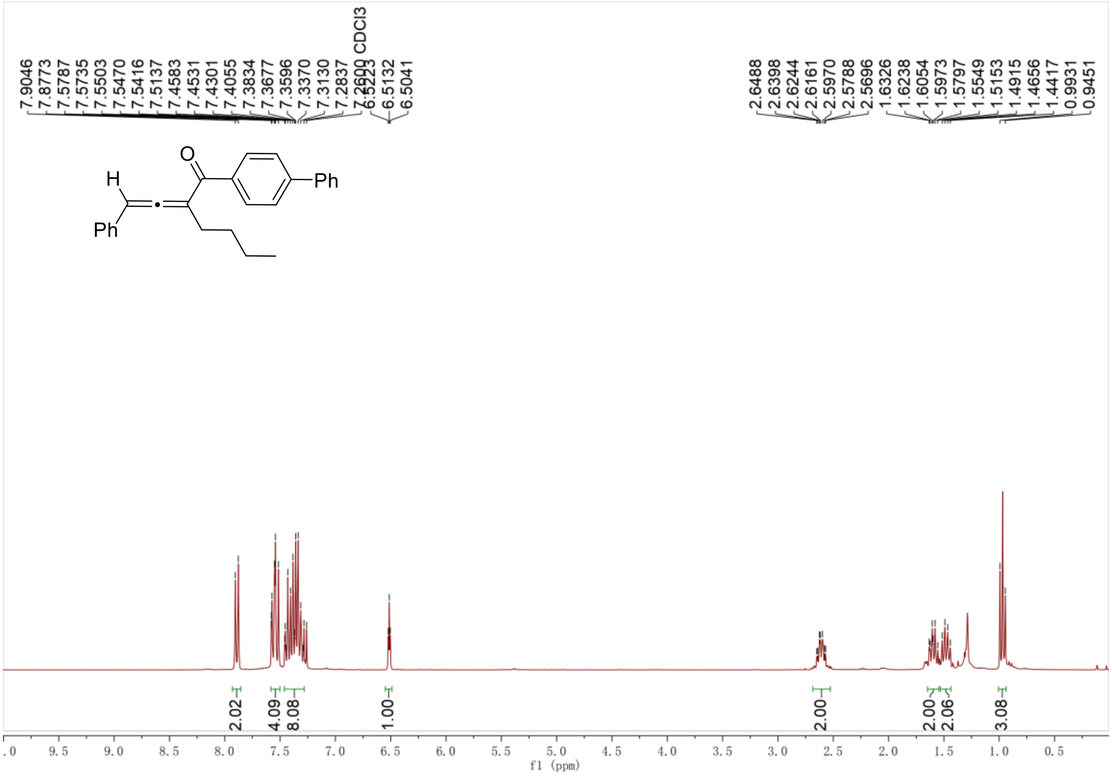


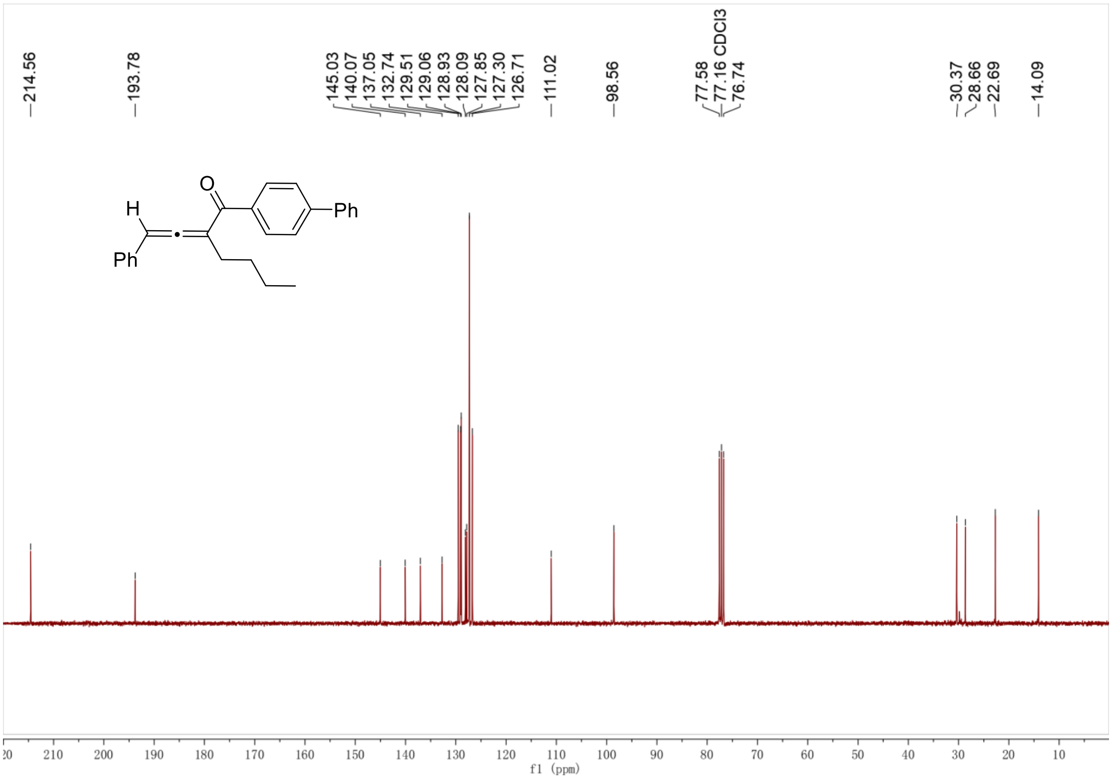
3ai ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



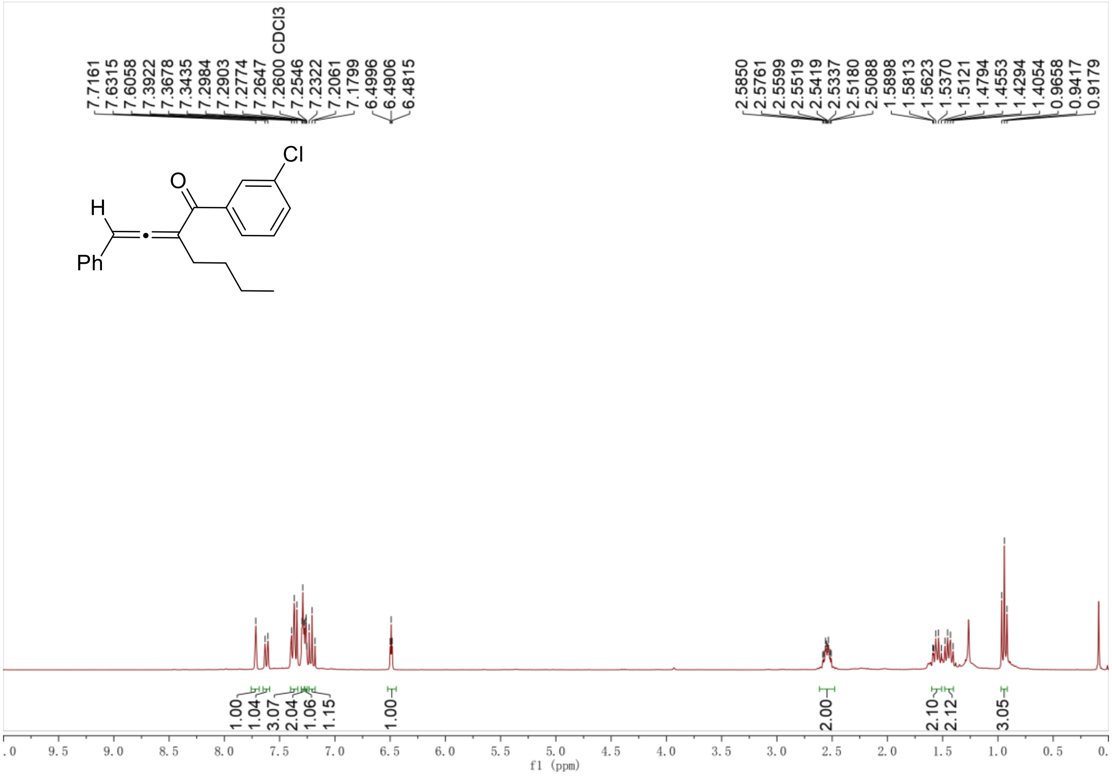


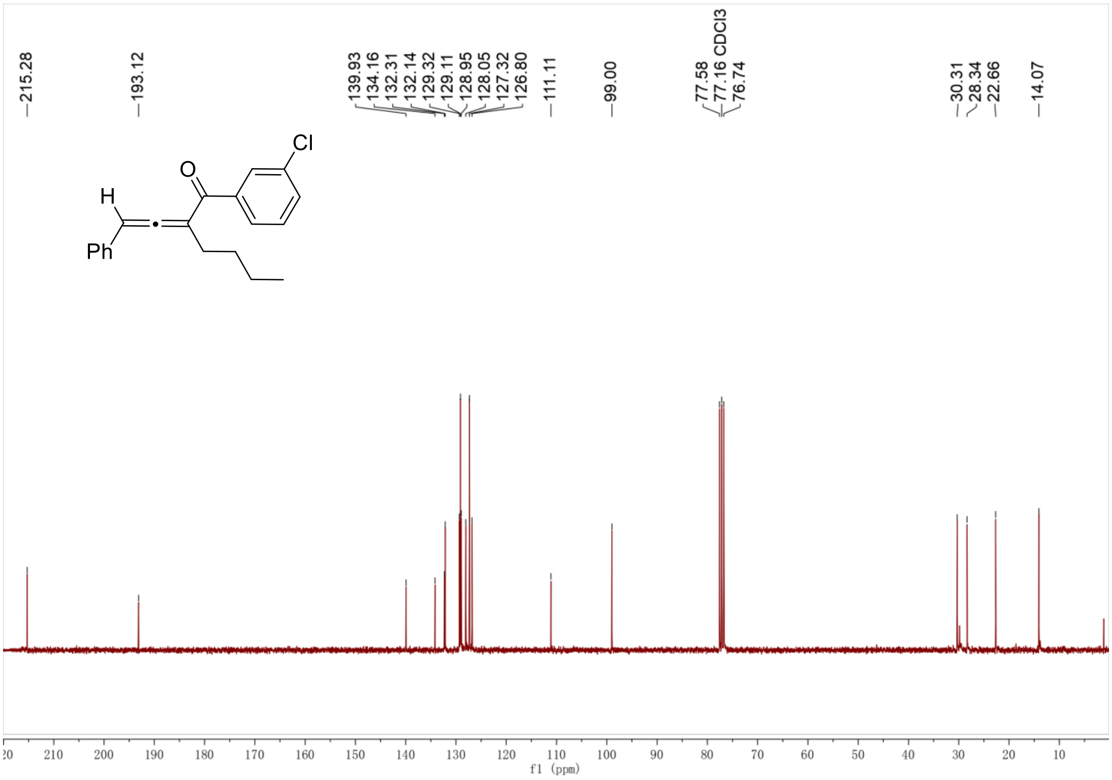
3aj ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



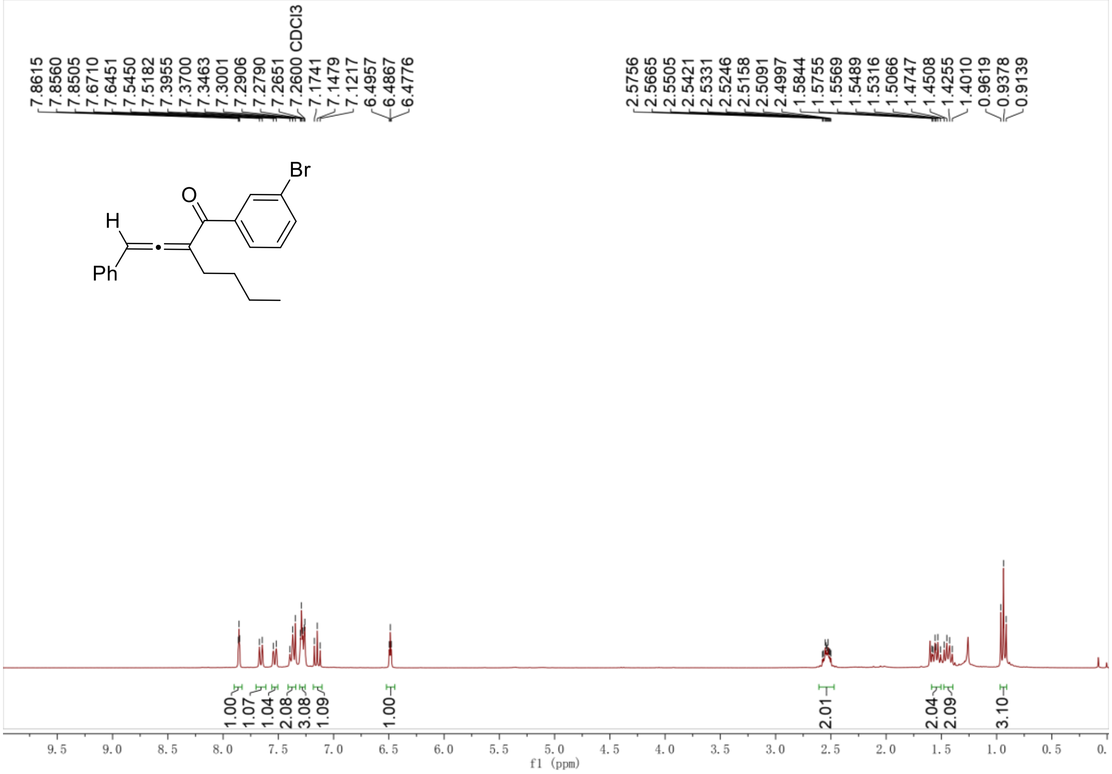


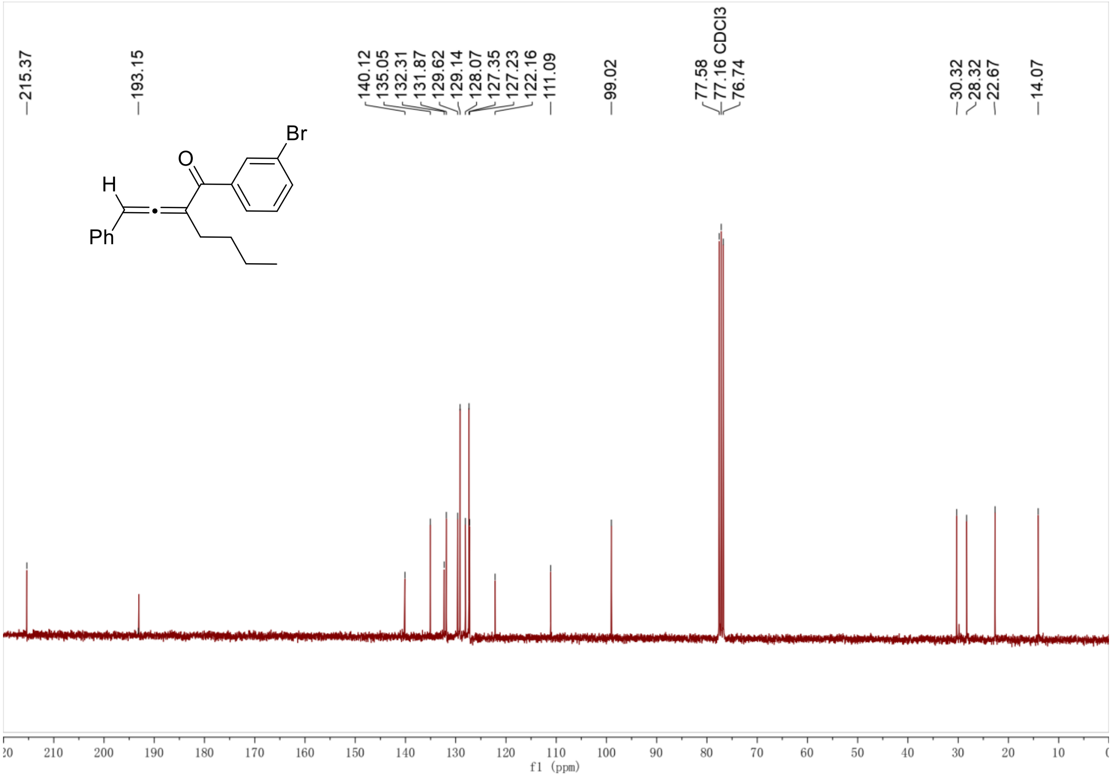
3ak ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



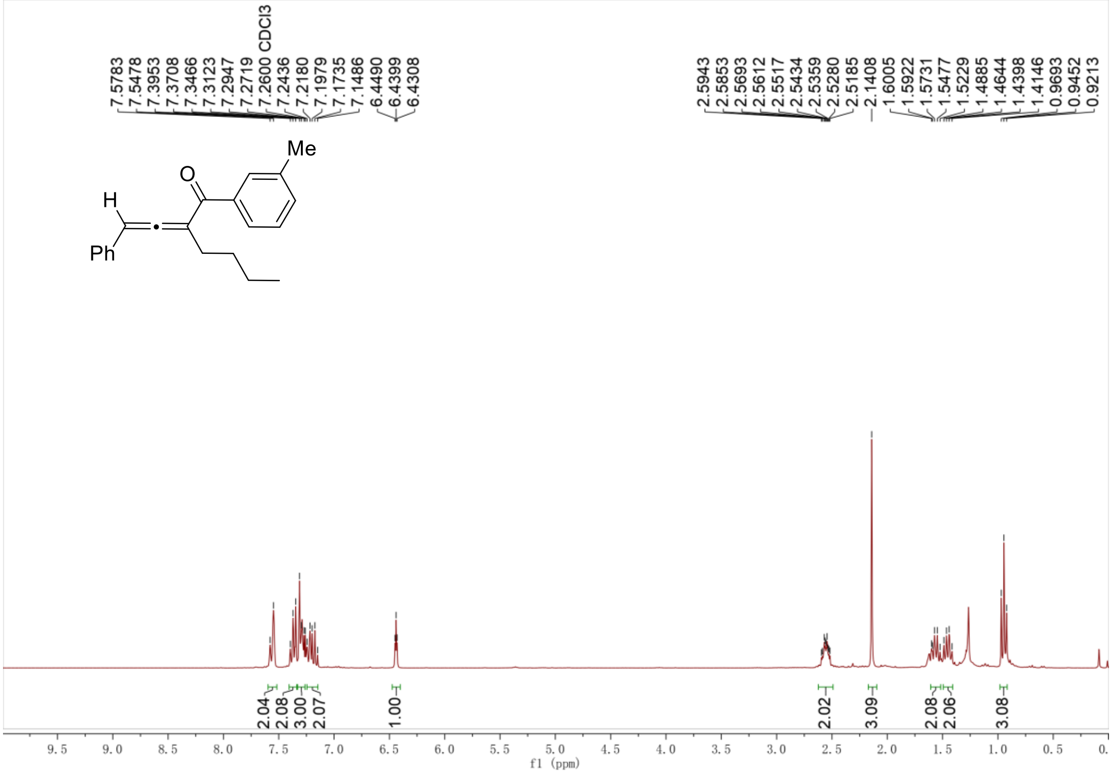


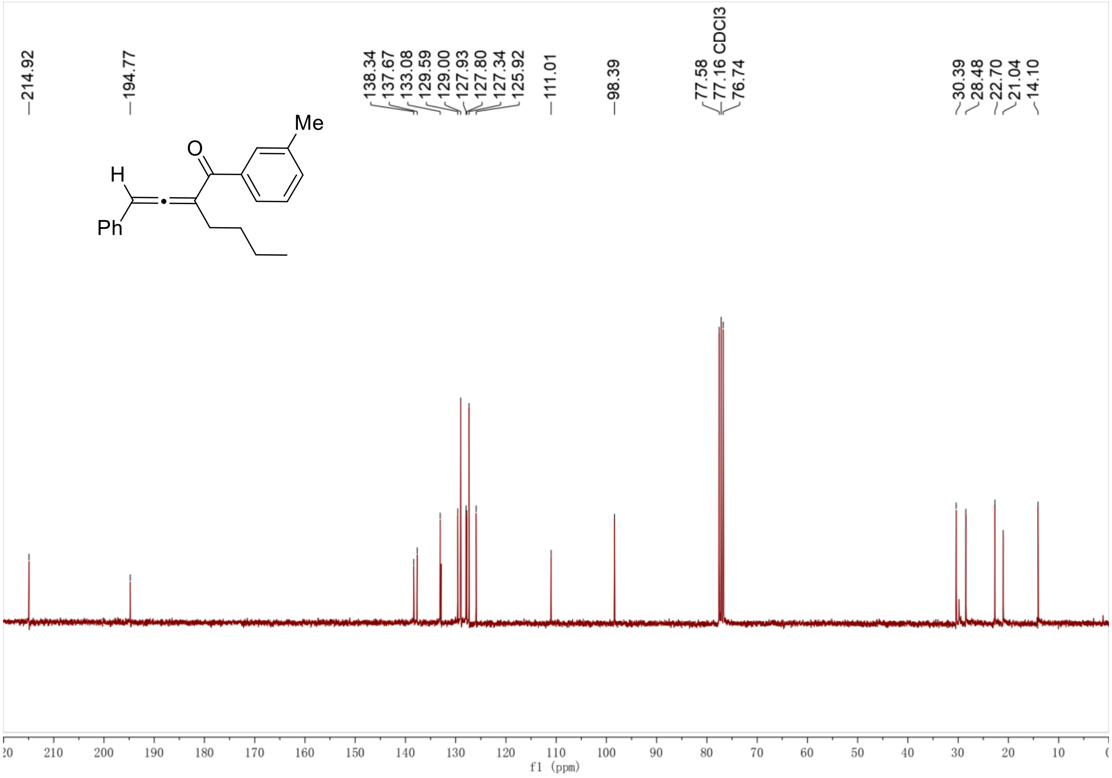
3al ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



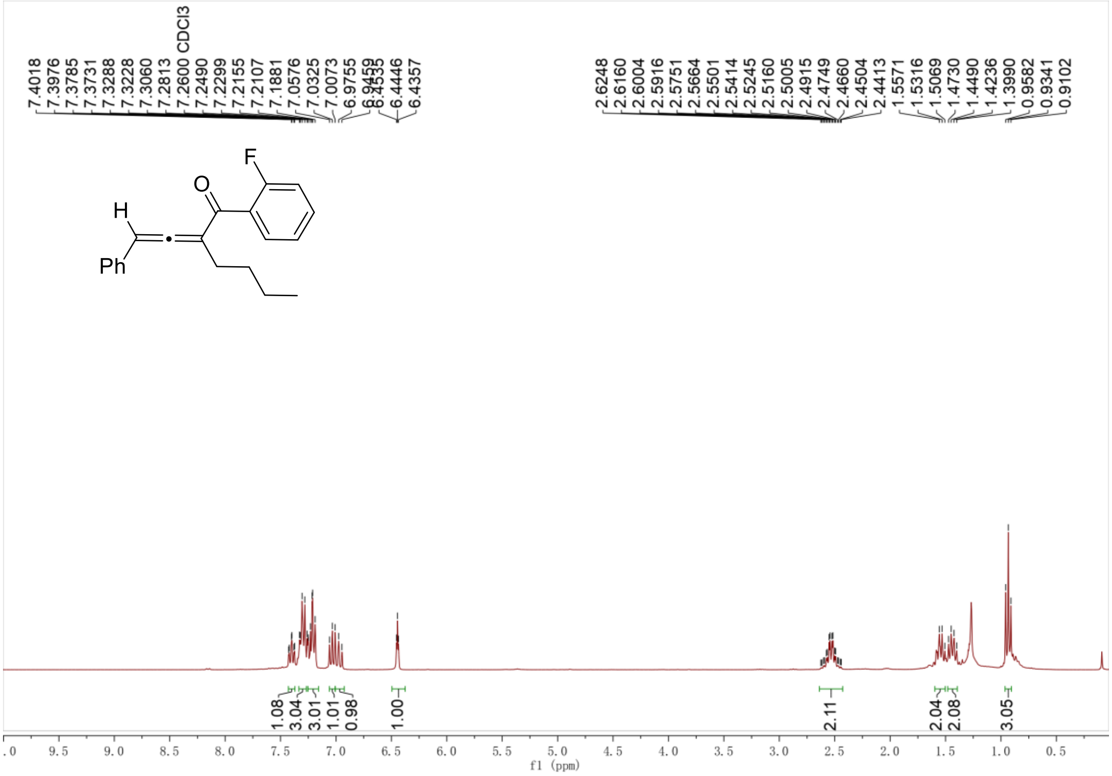


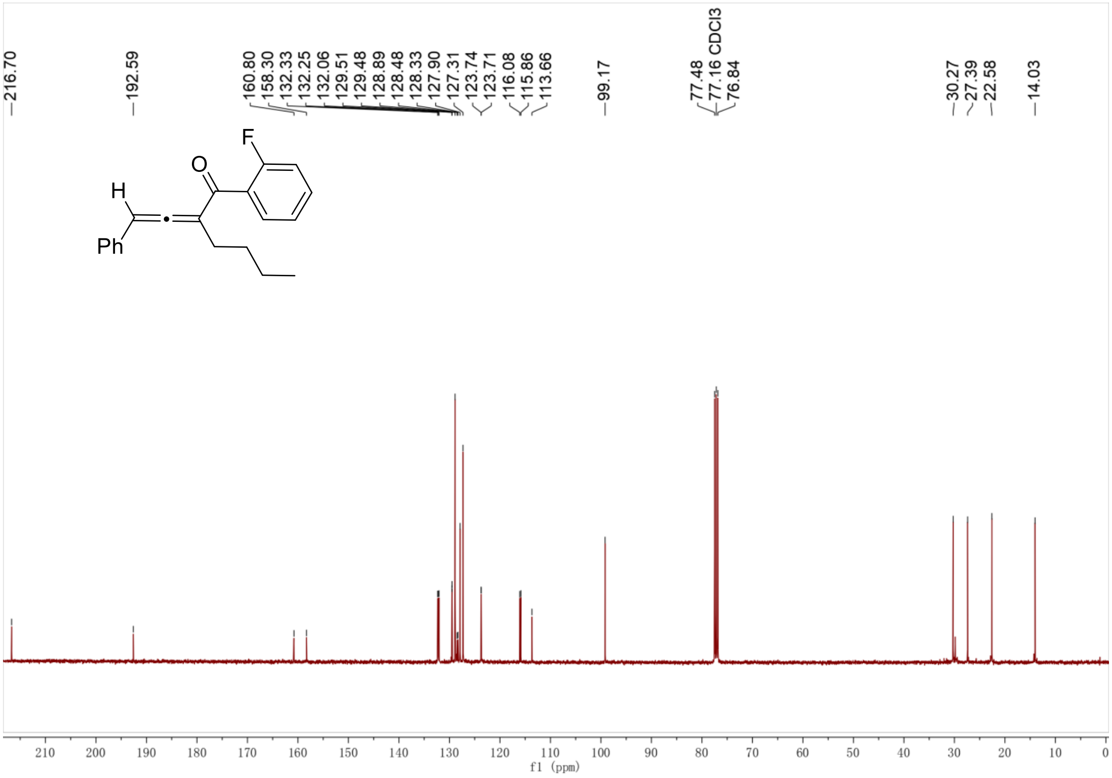
3am ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



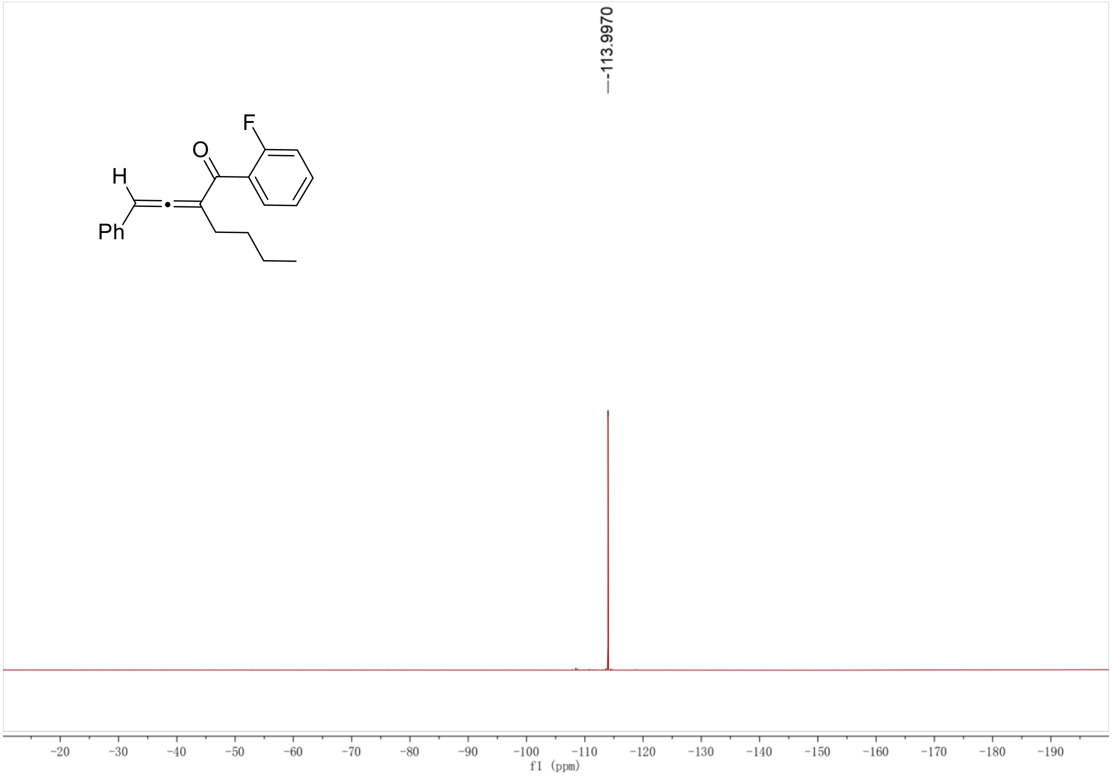


3an ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)

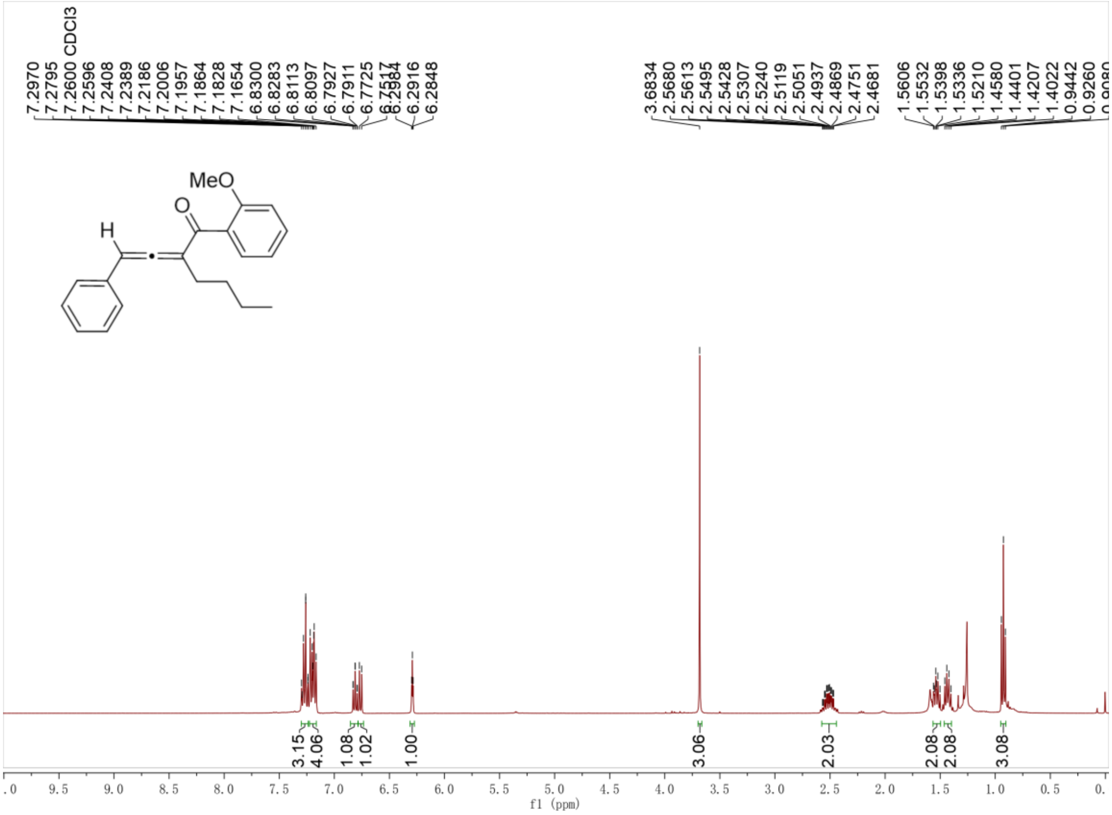


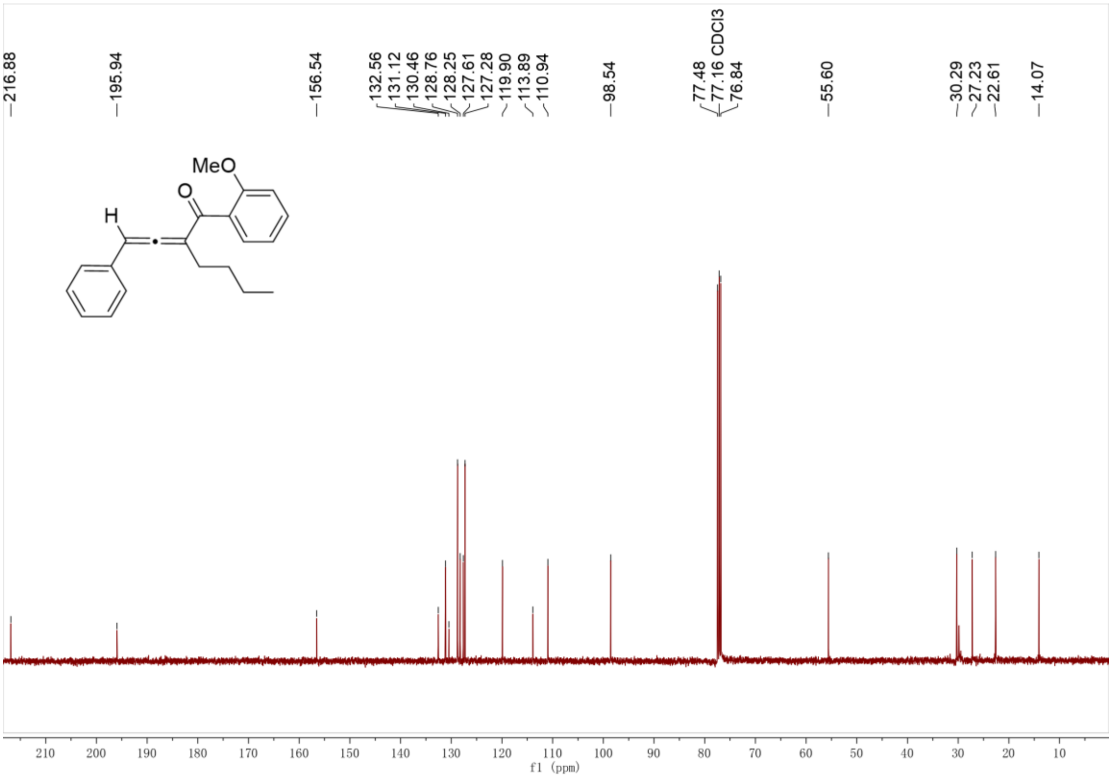


3an ^{19}F NMR (282 MHz, Chloroform-d)

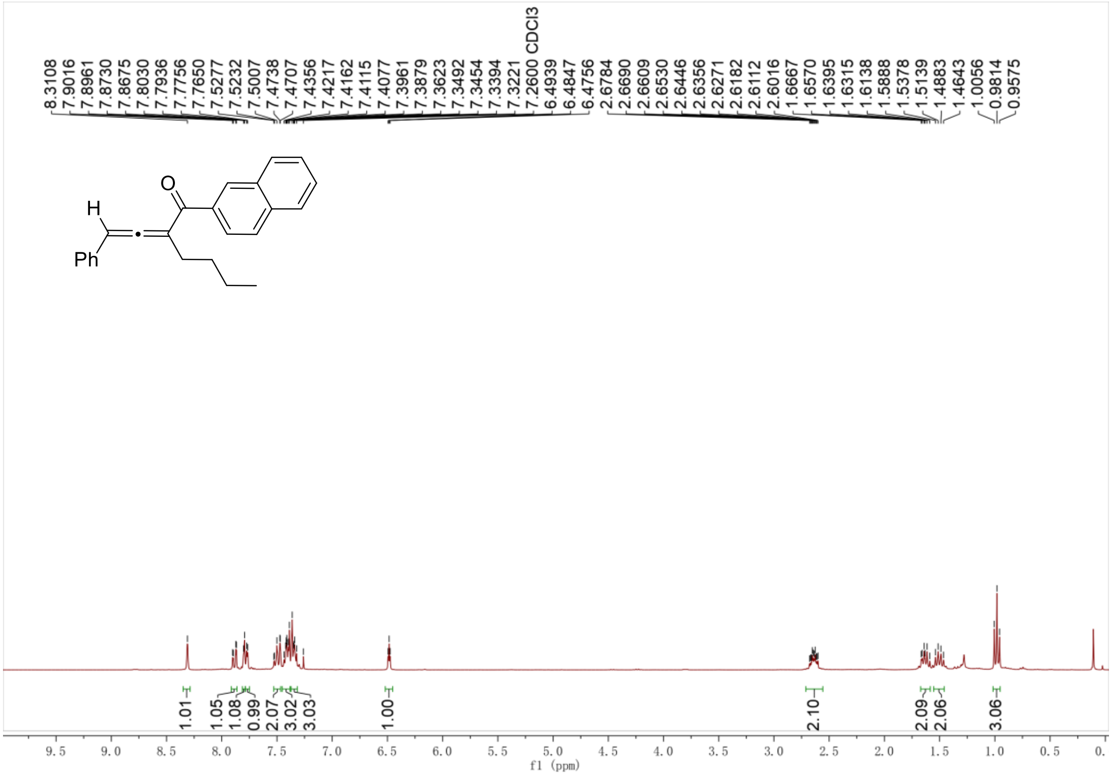


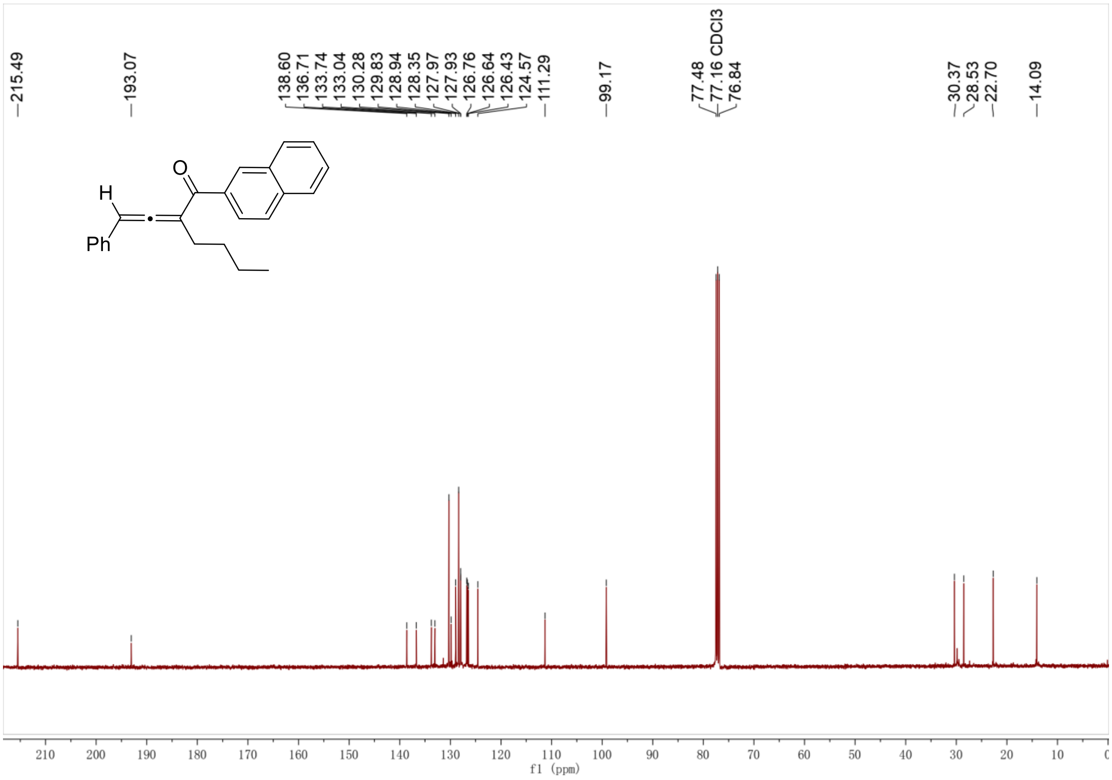
3ao ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



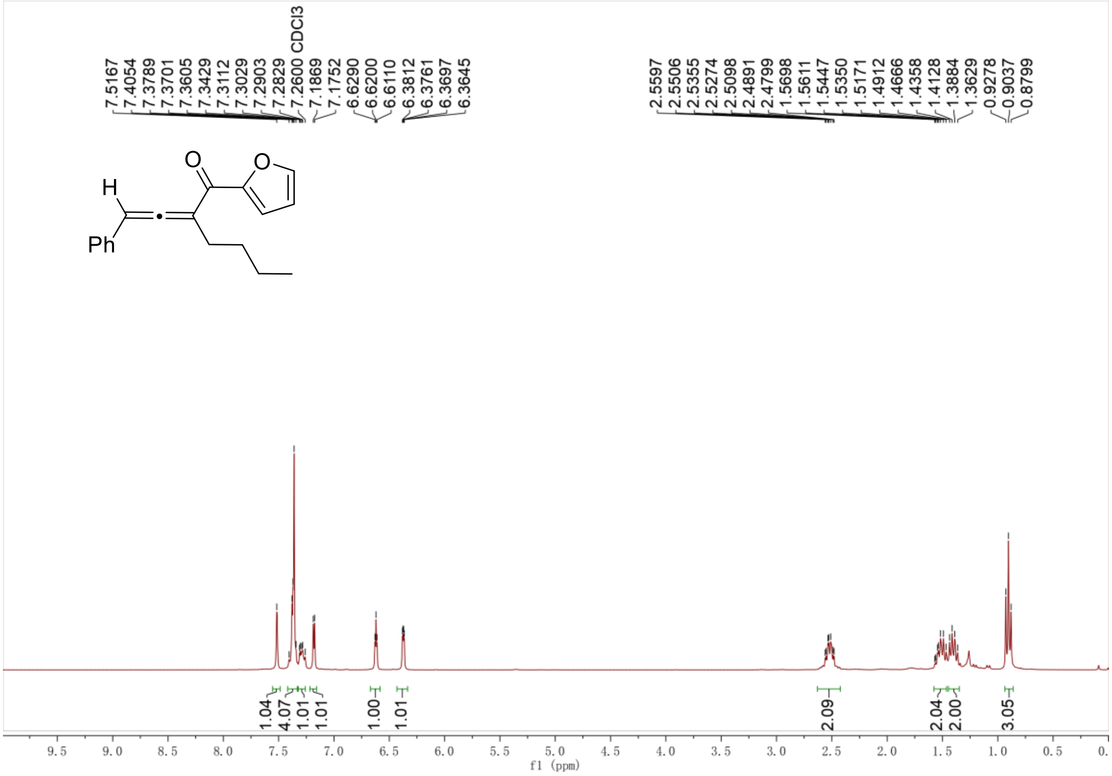


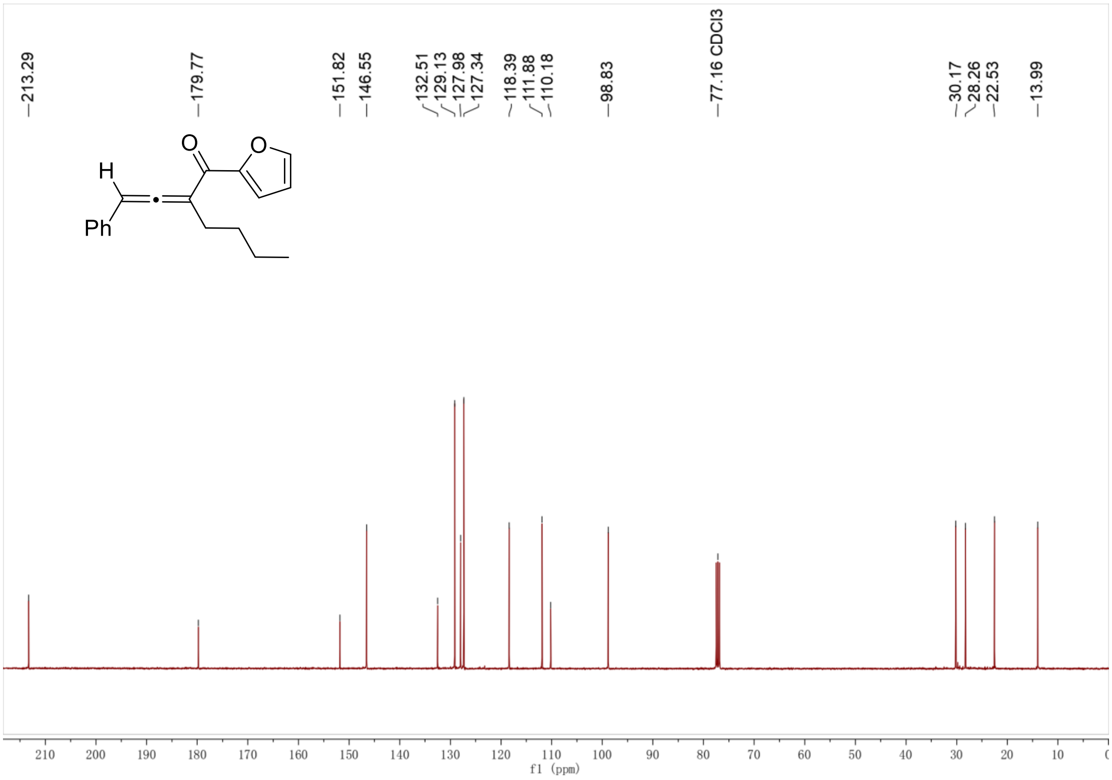
3ap ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



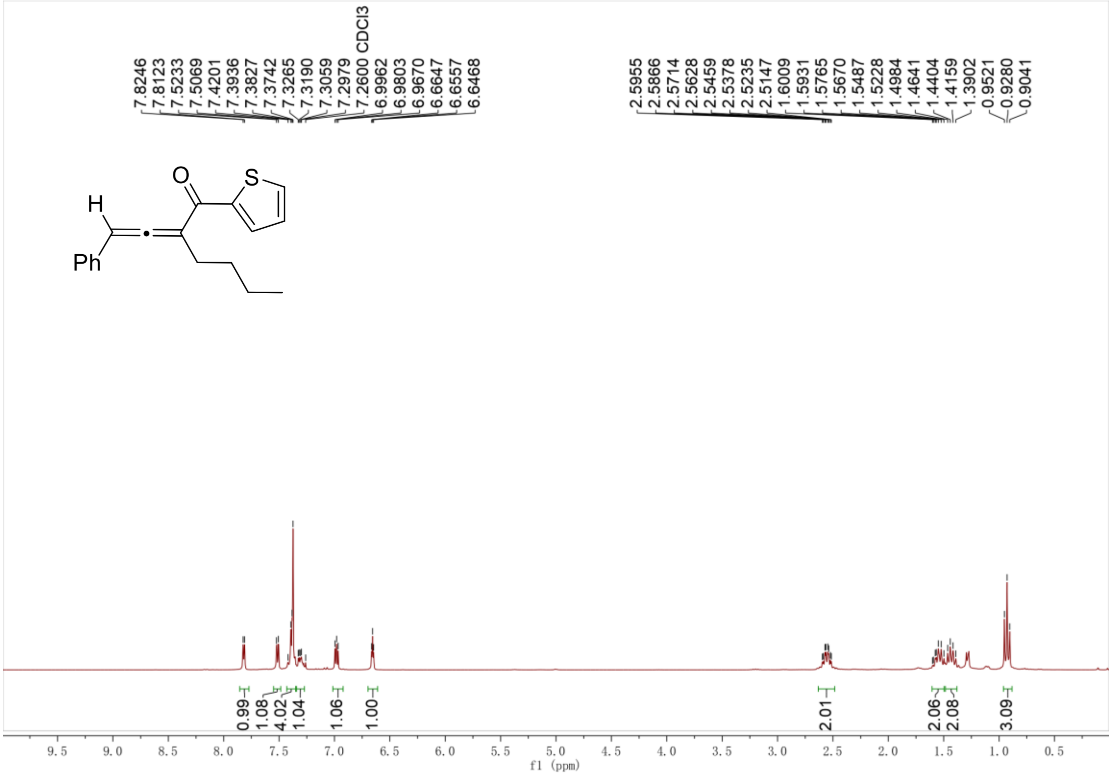


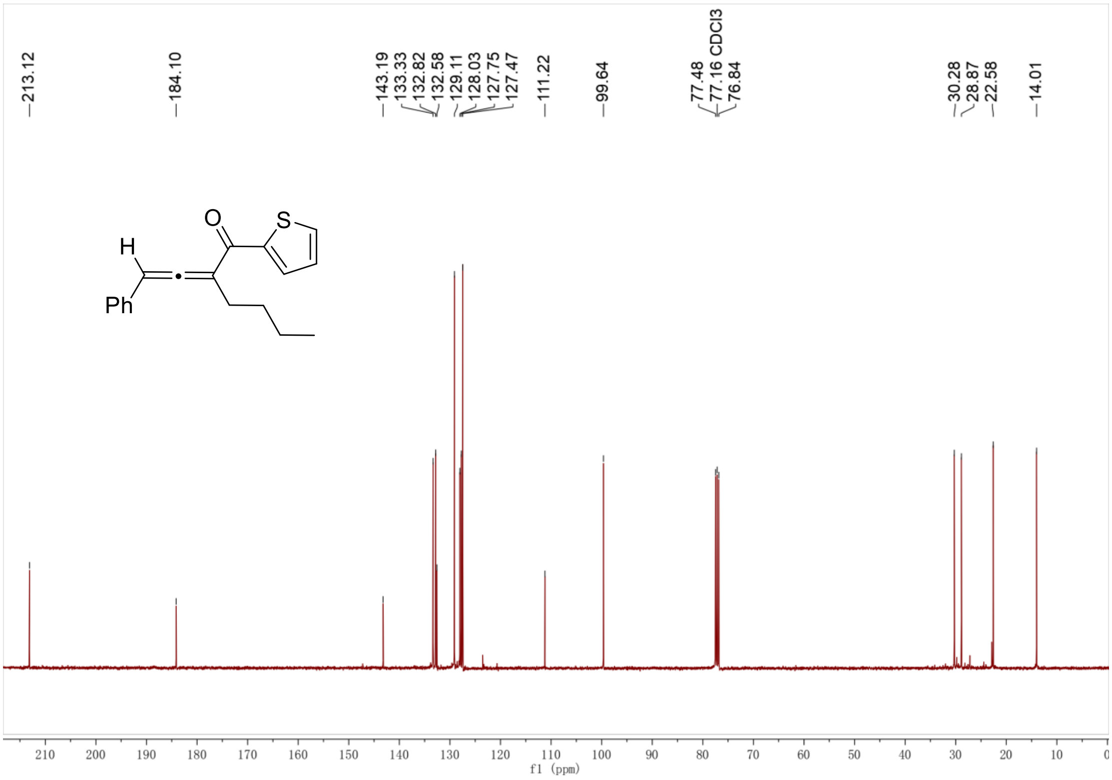
3aq ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



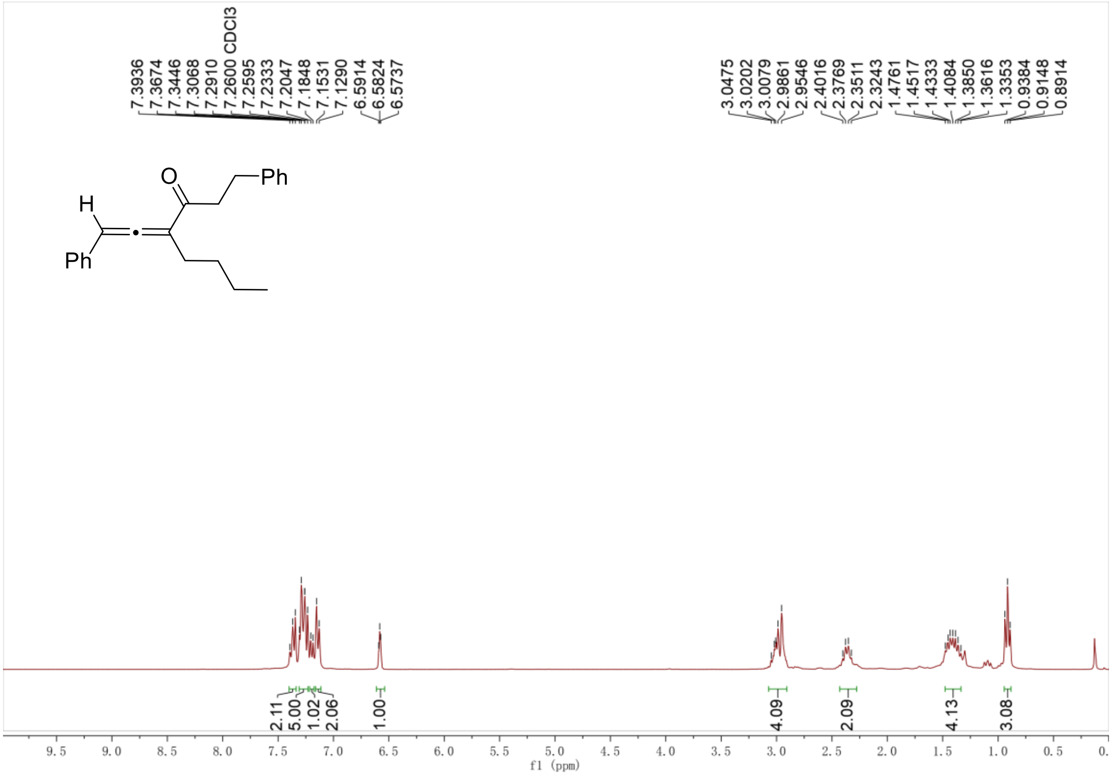


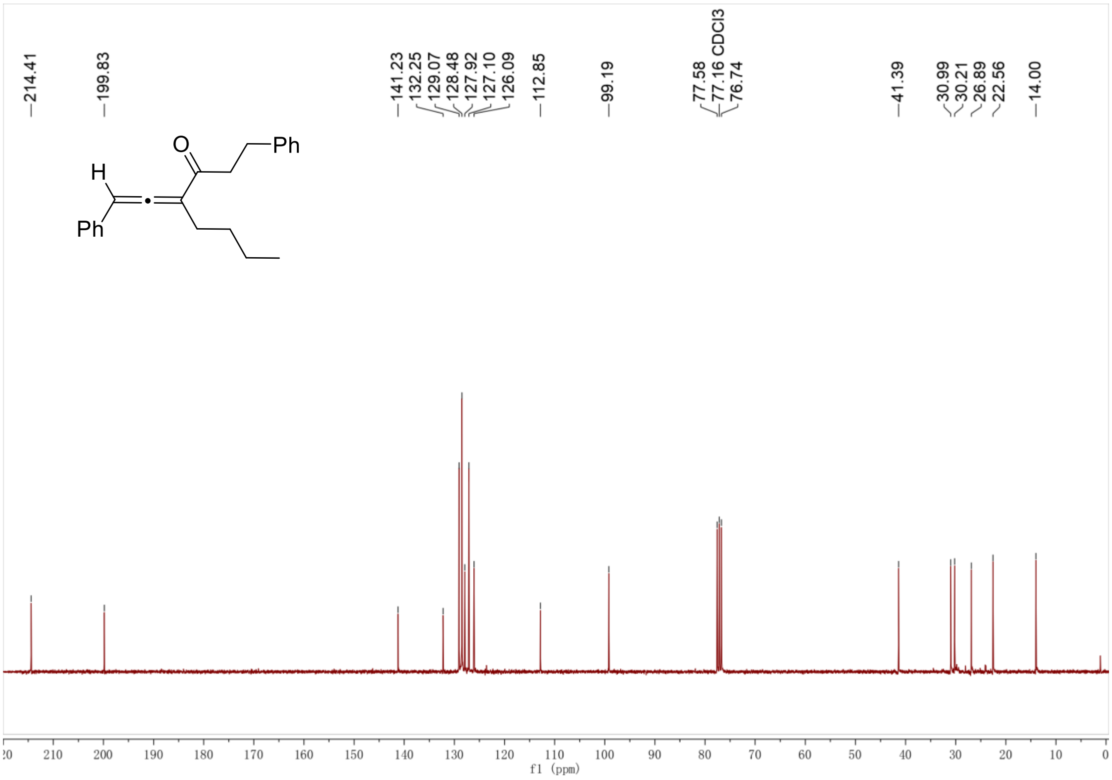
3ar ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



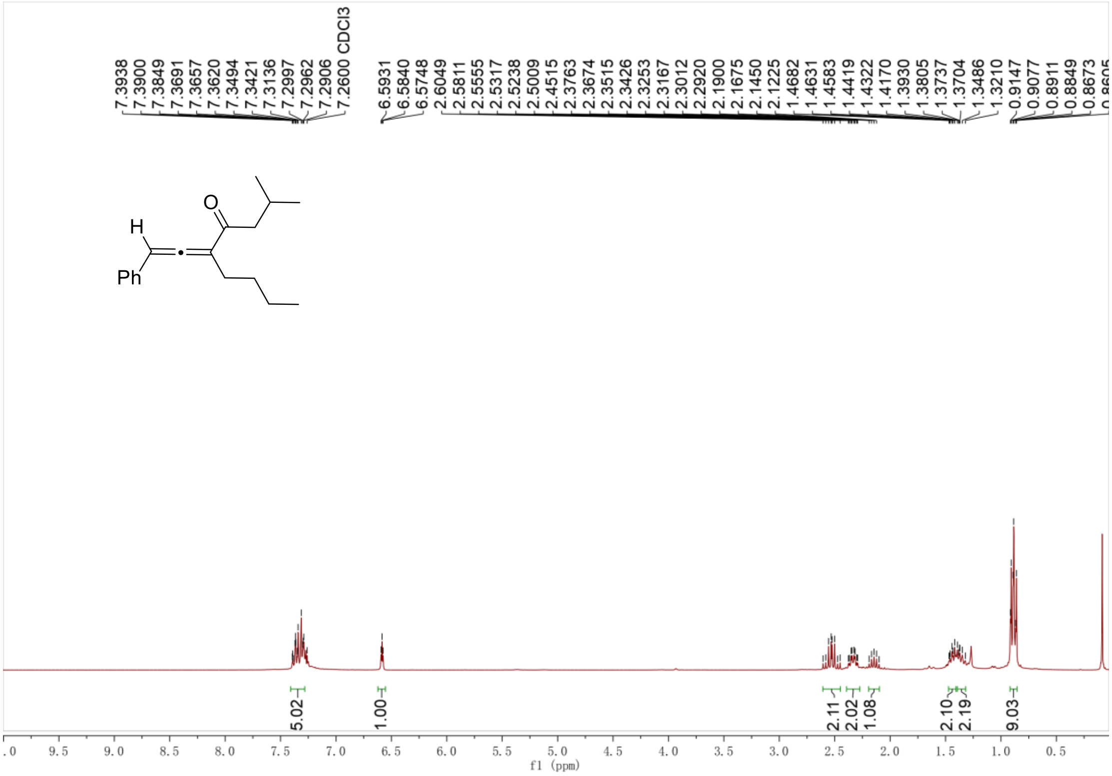


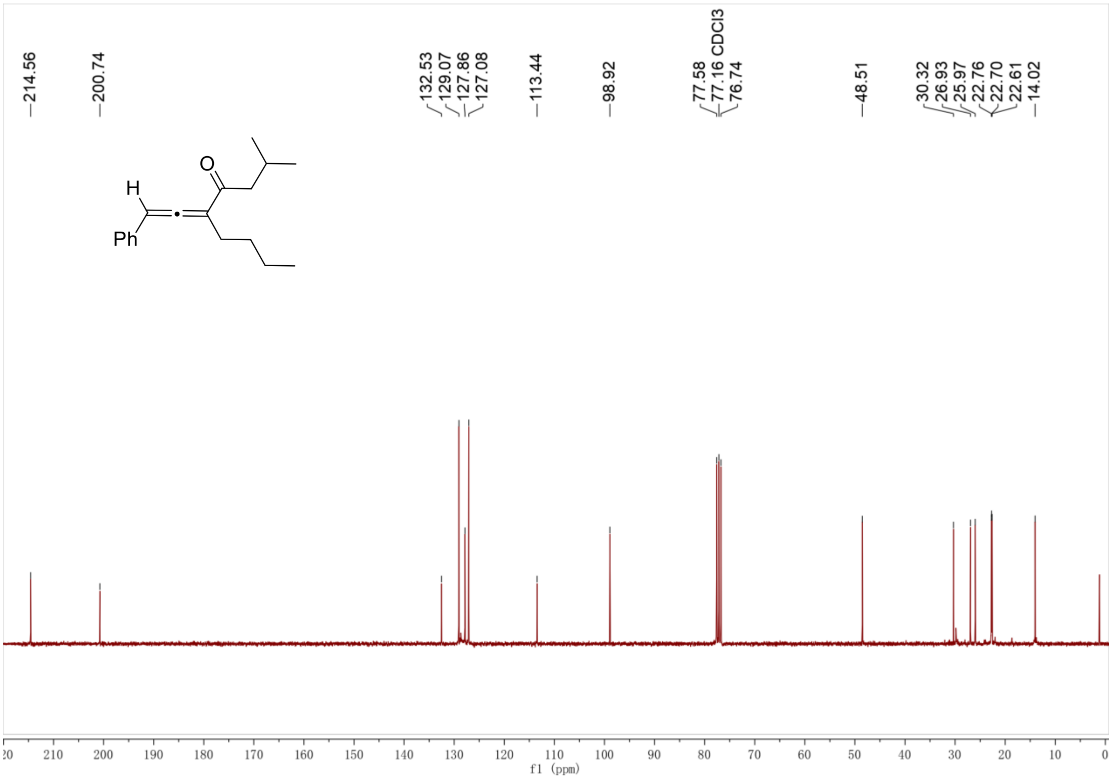
3as ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



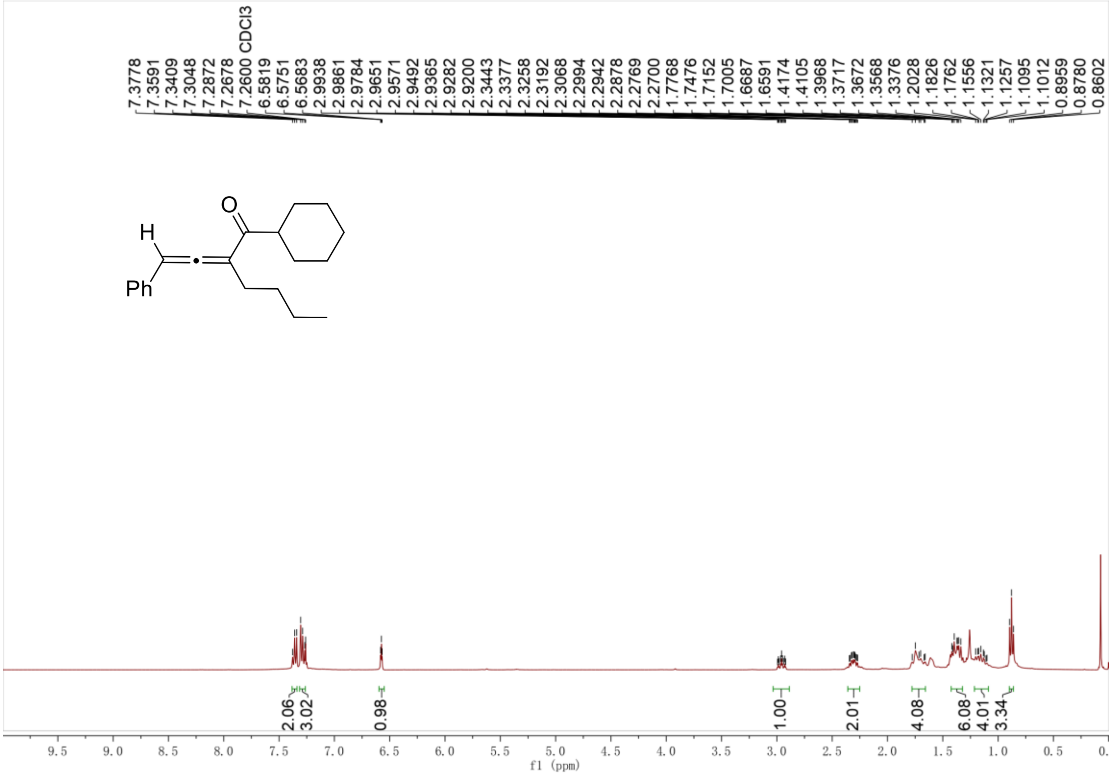


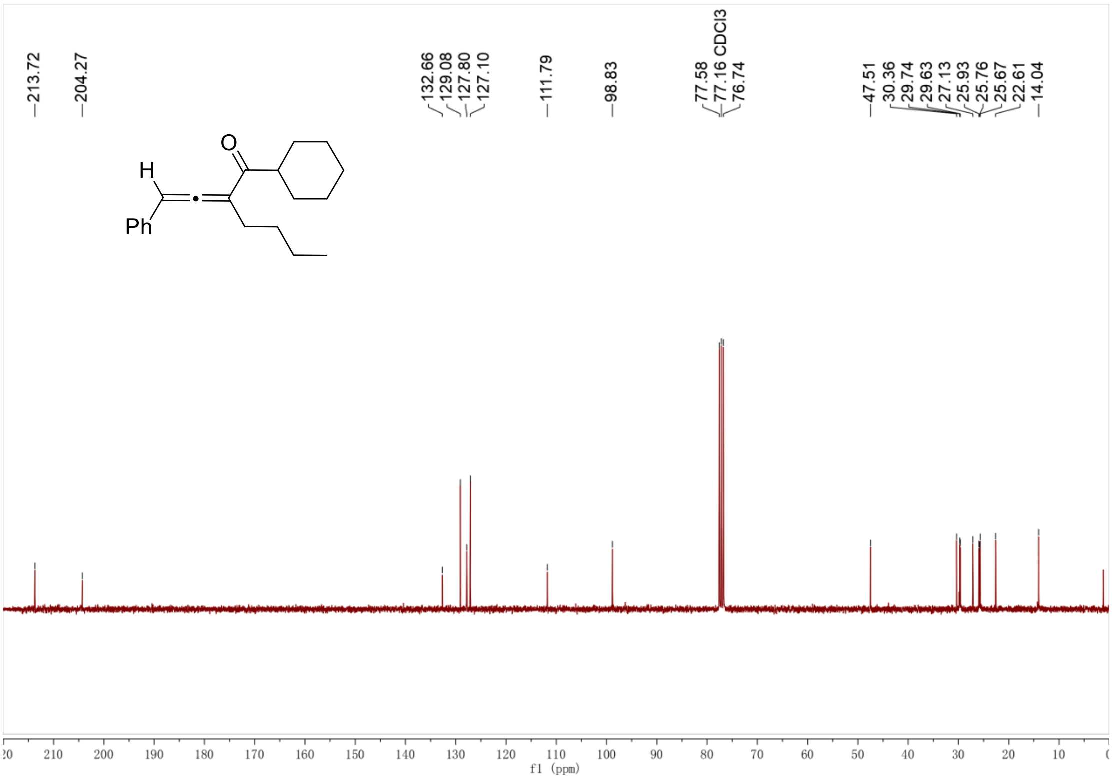
3at ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



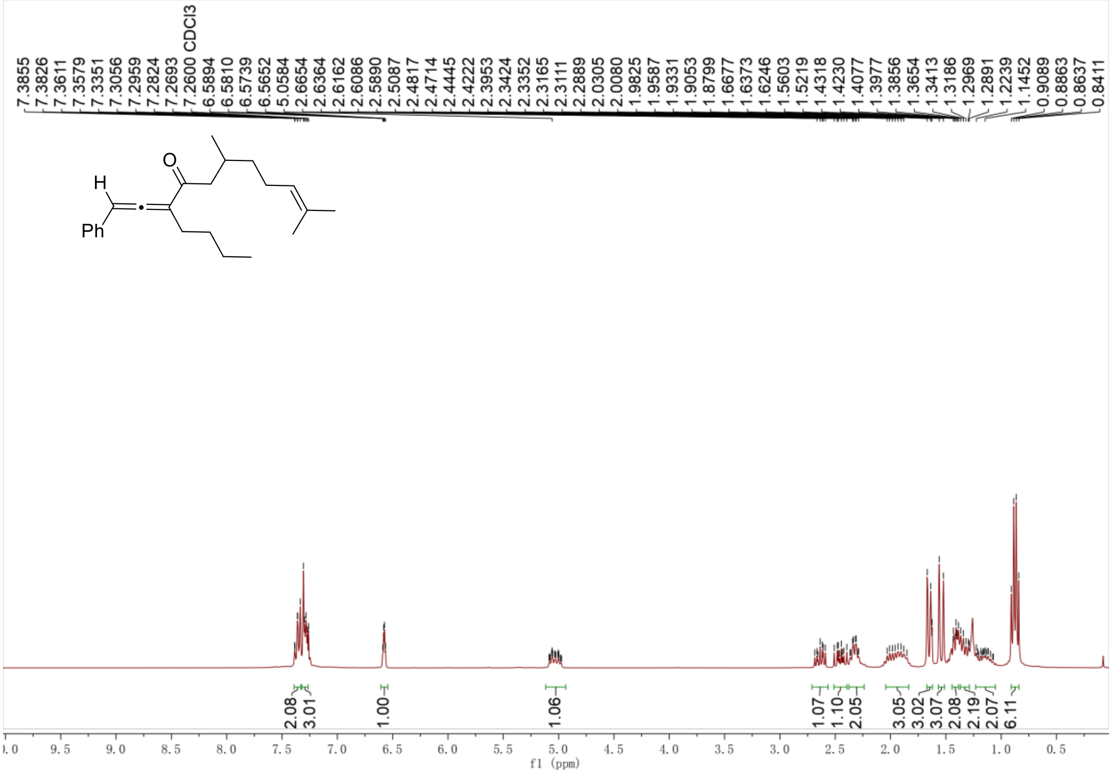


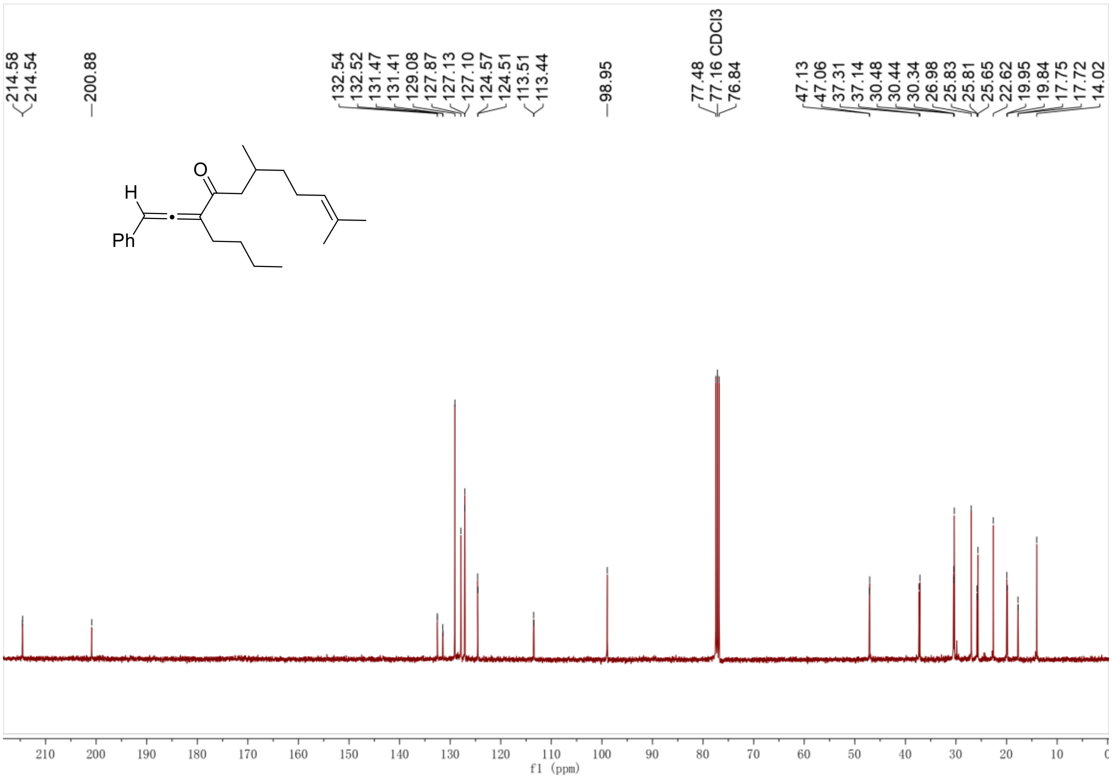
3au ^1H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



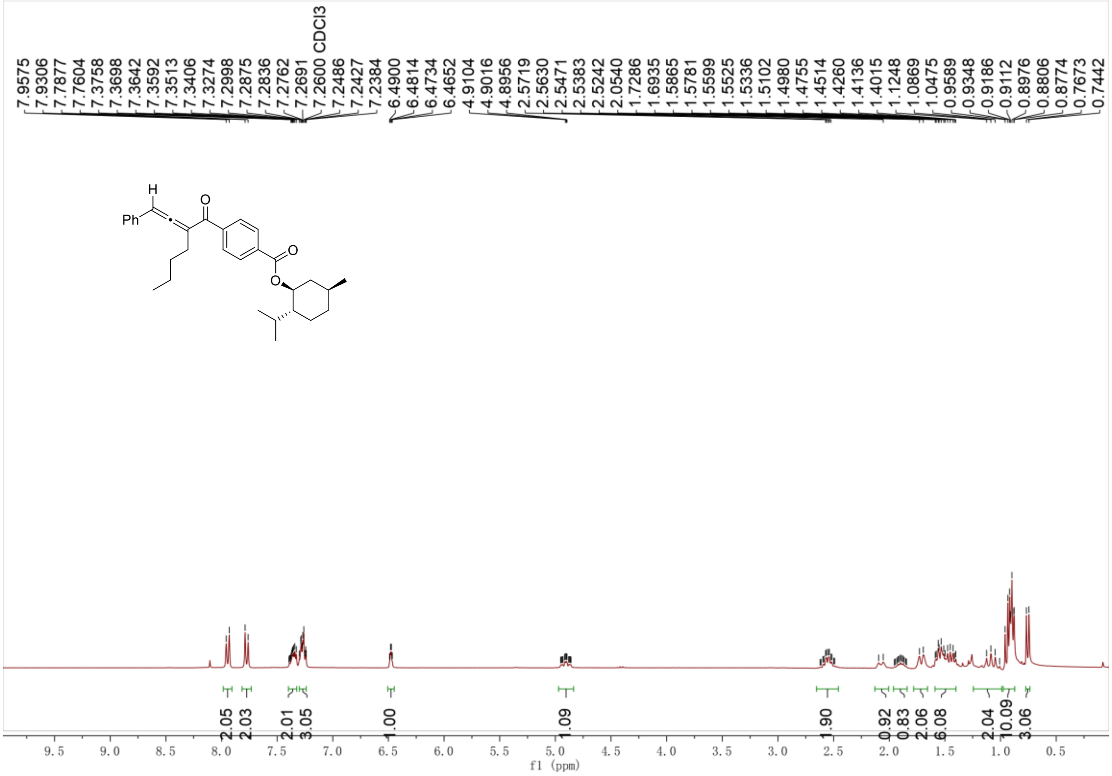


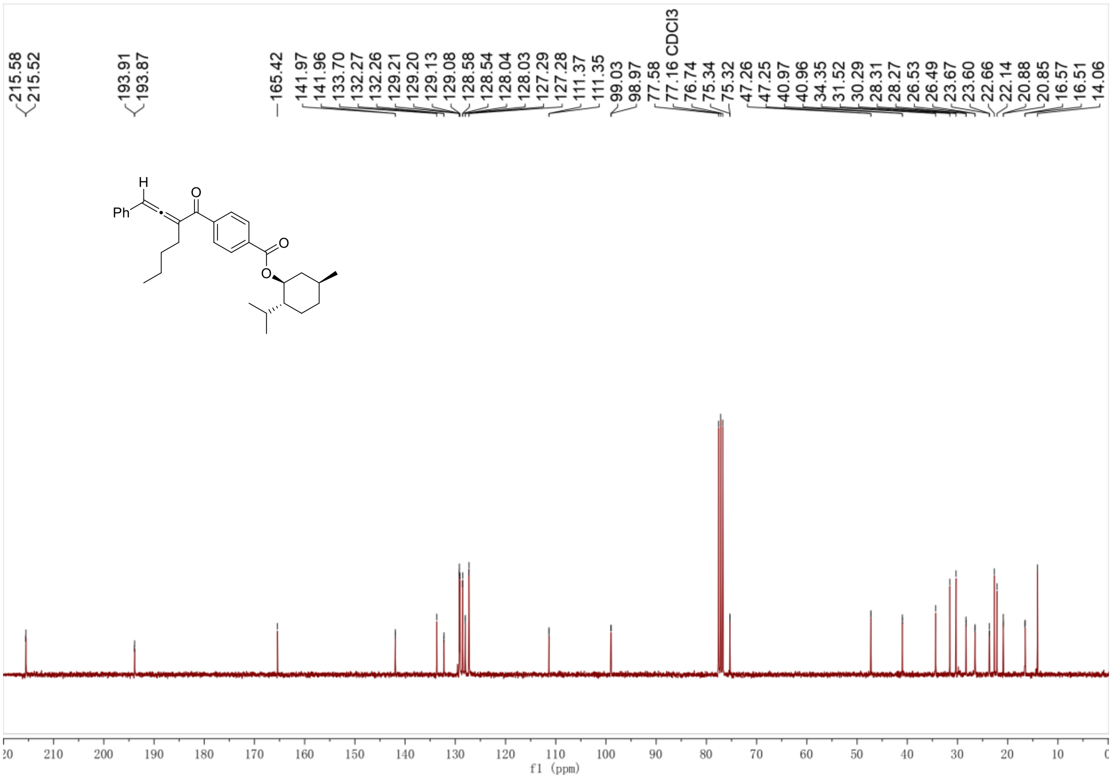
3av ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



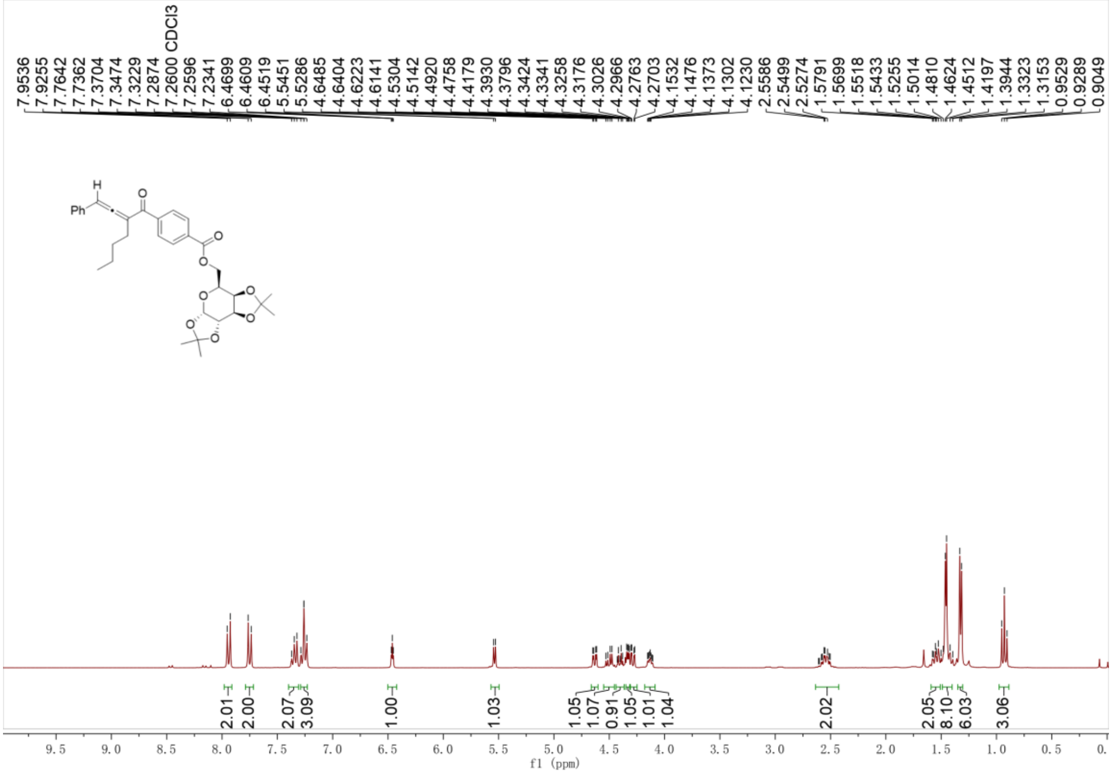


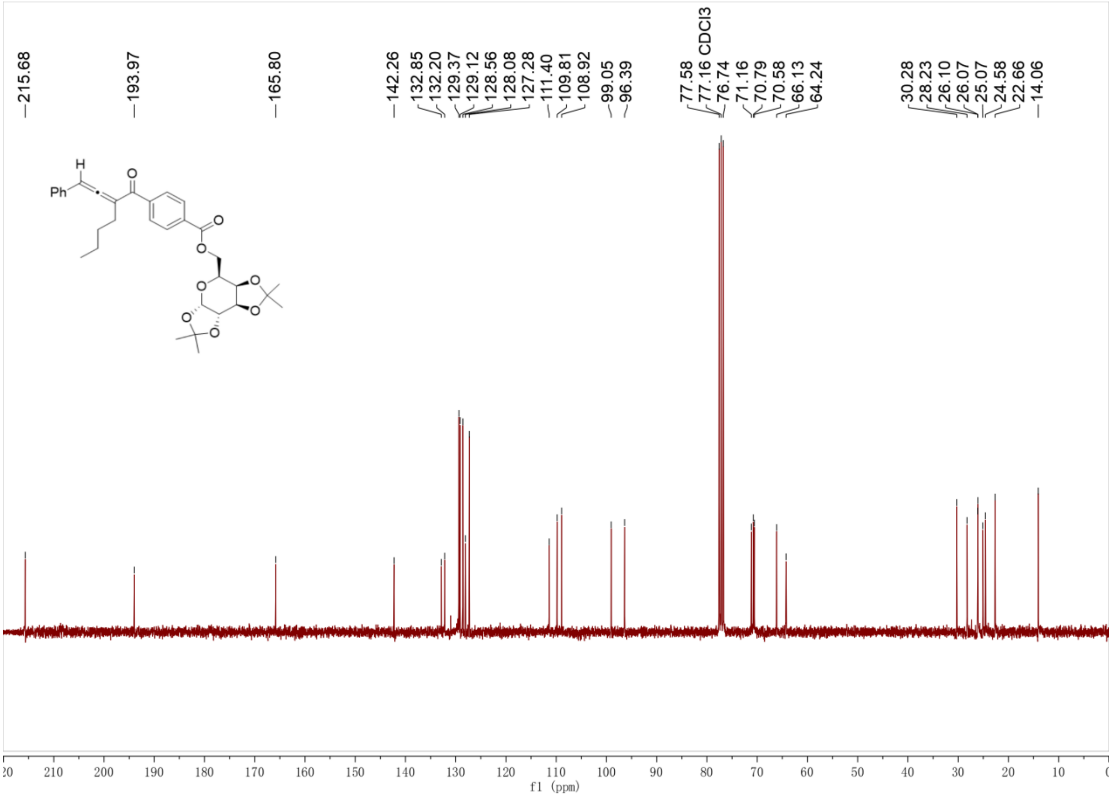
3aw ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



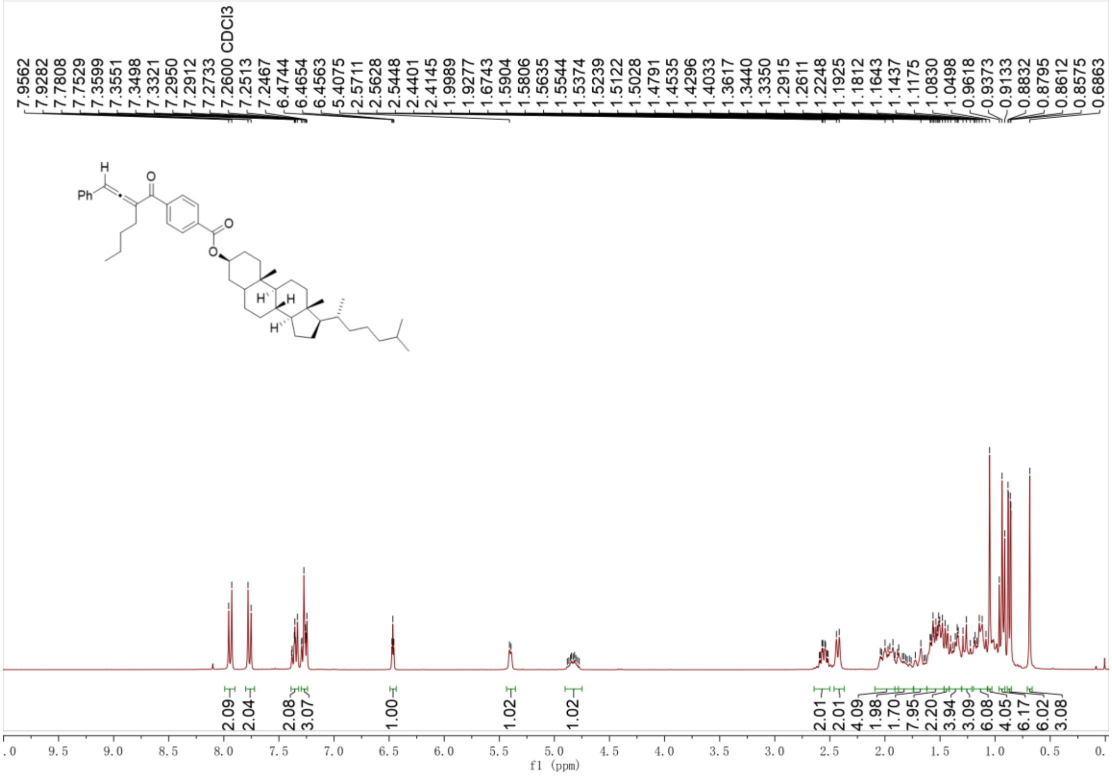


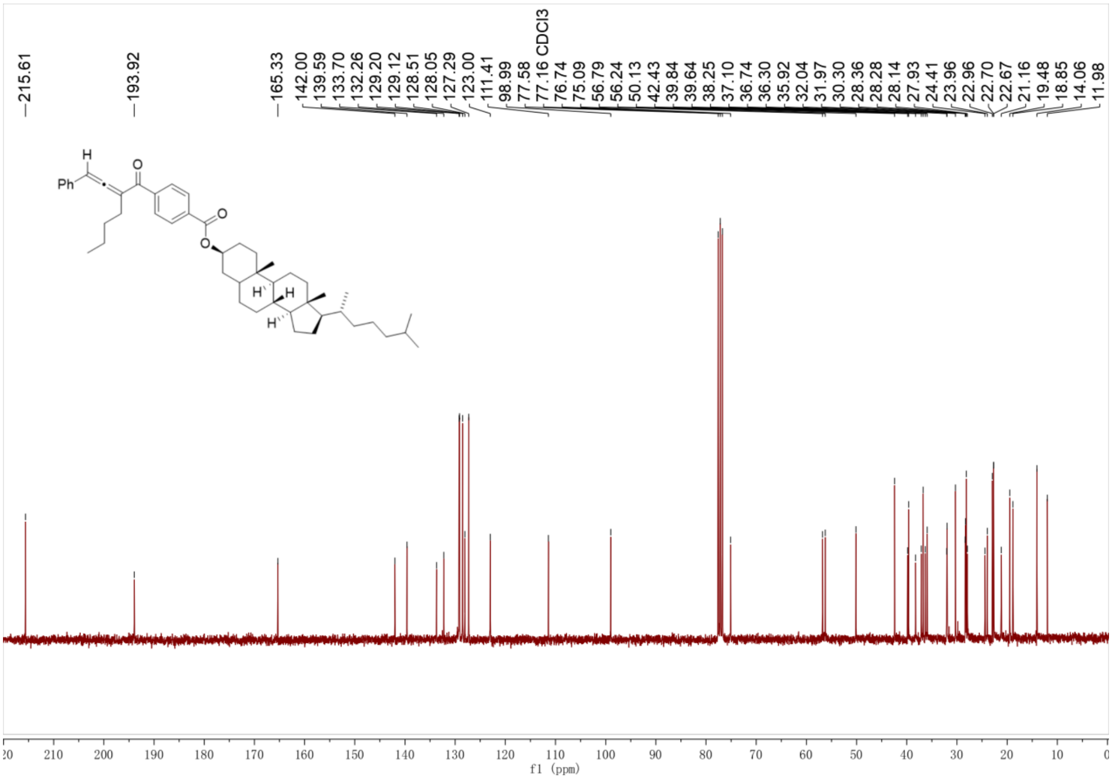
3ax ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



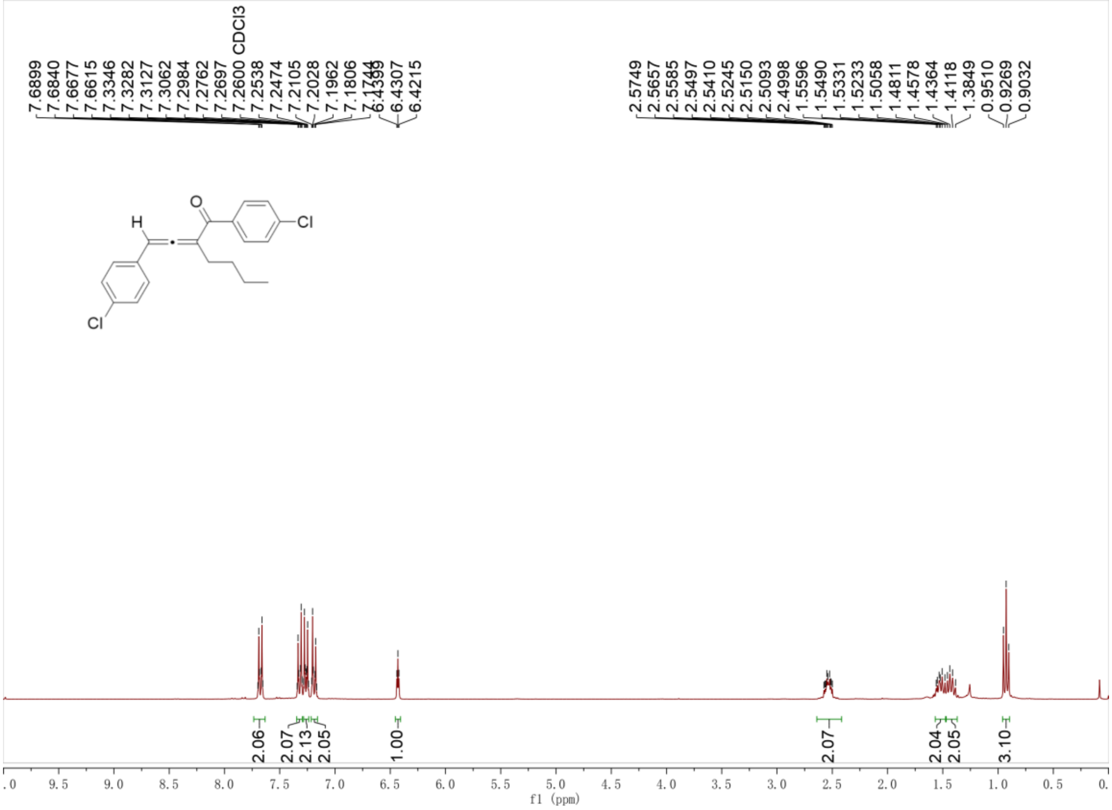


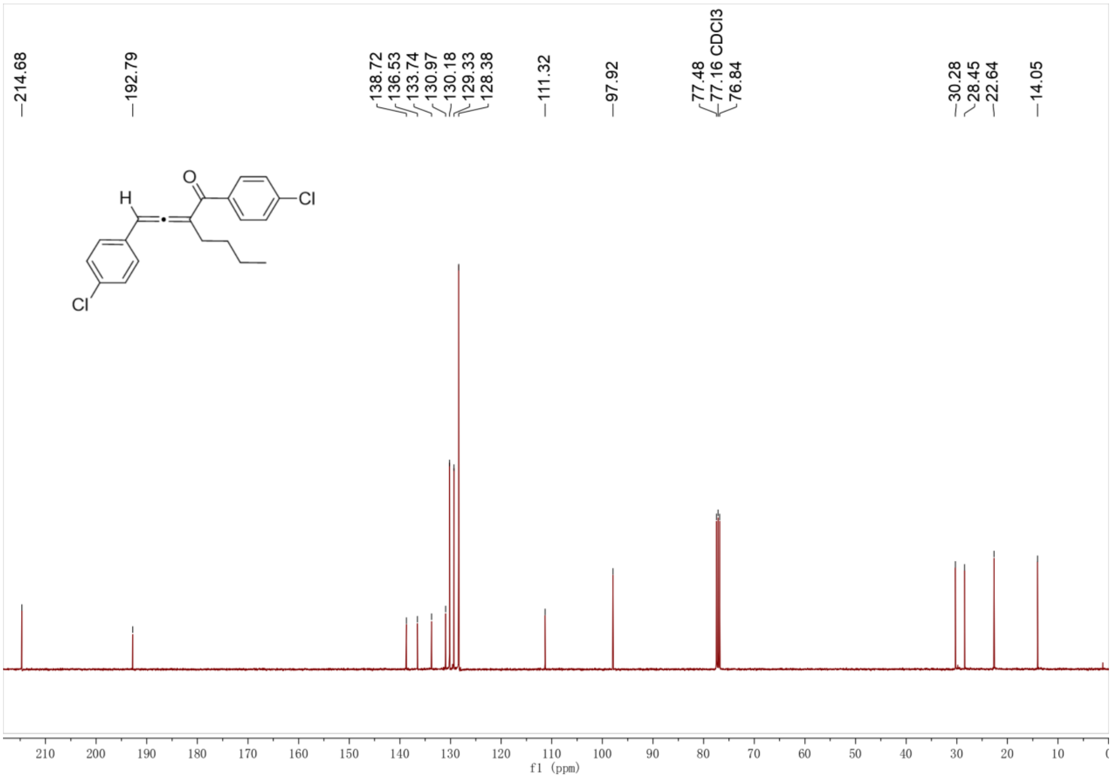
3ay ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



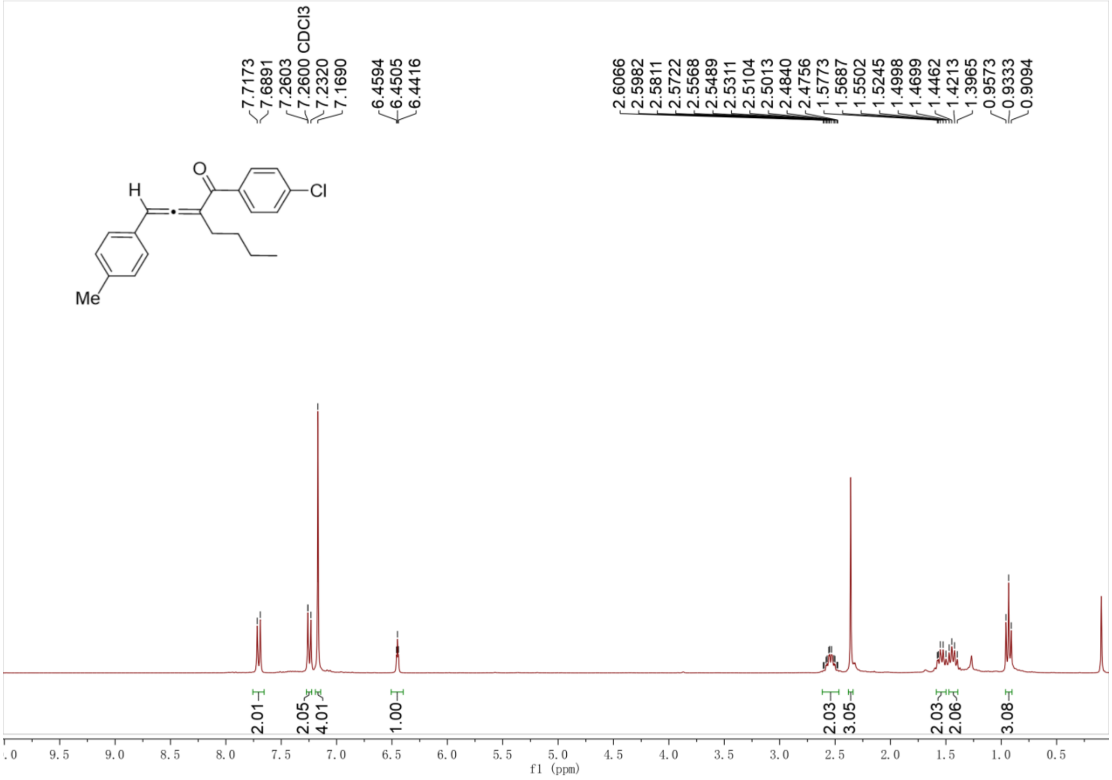


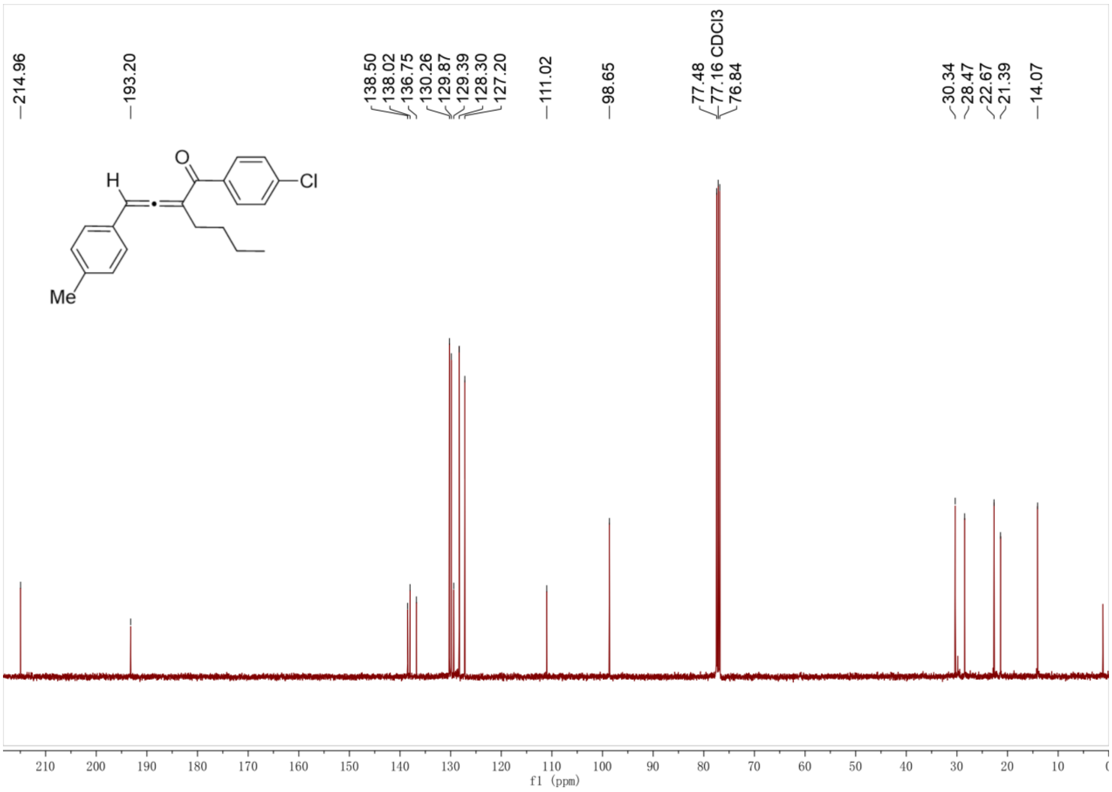
3ba ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



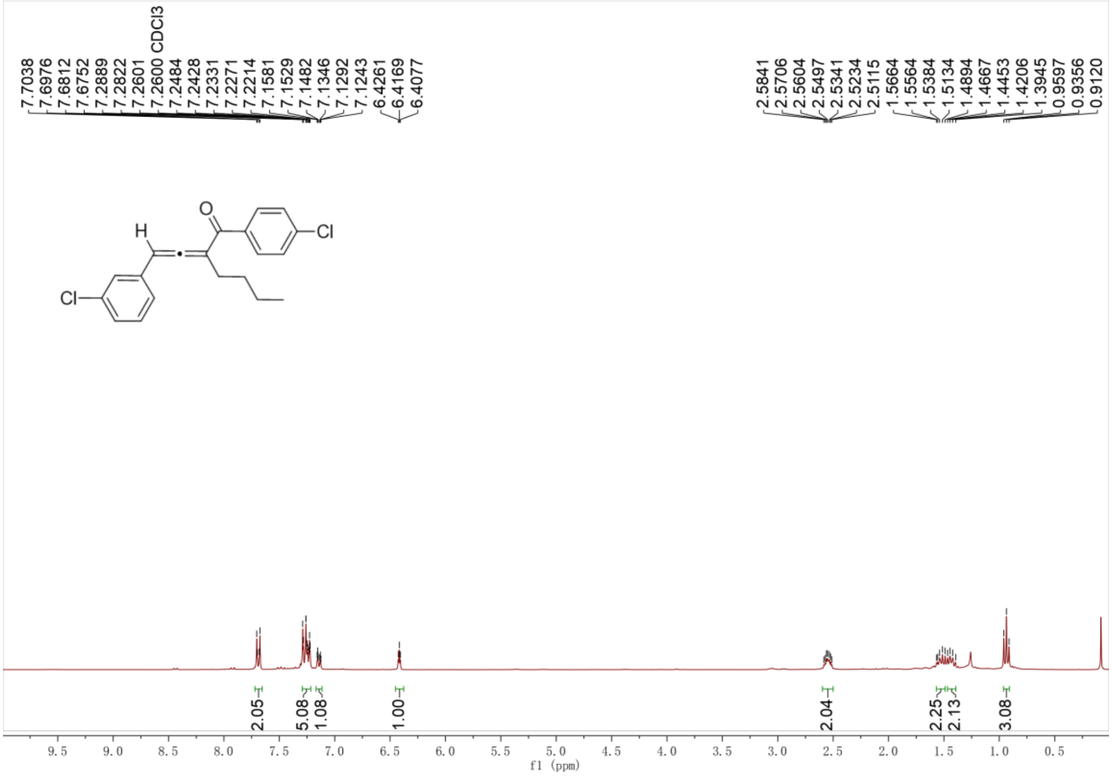


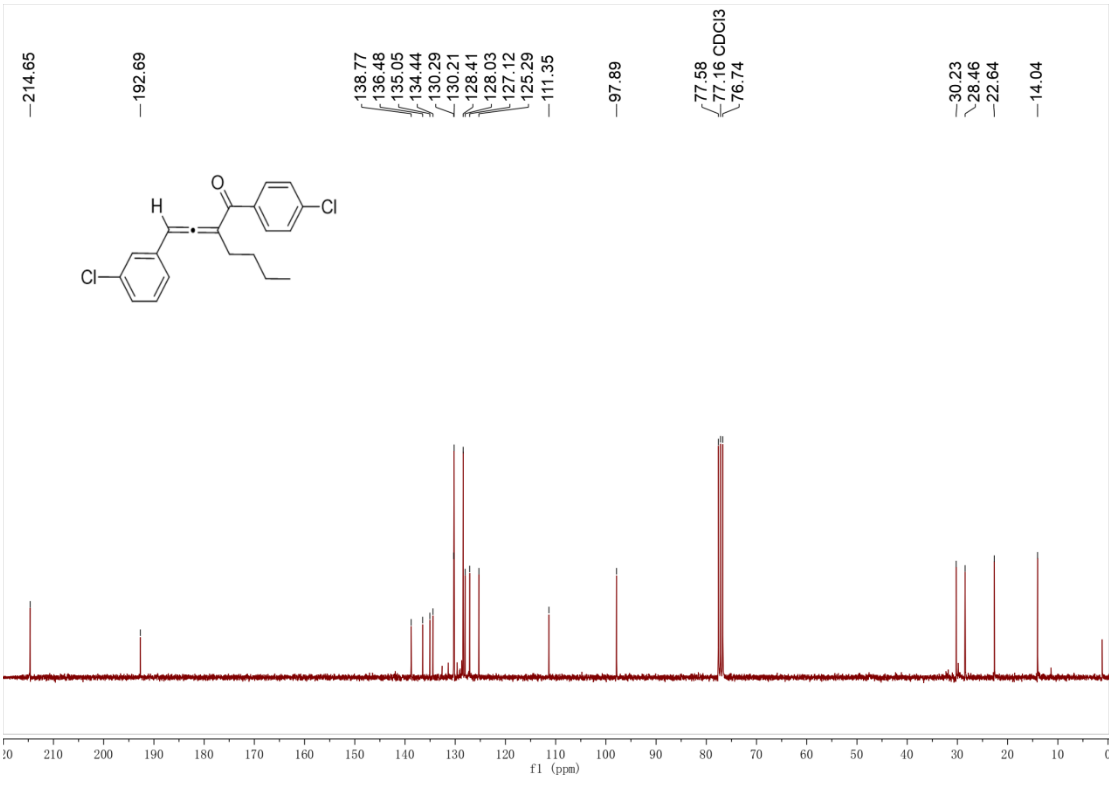
3bb ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



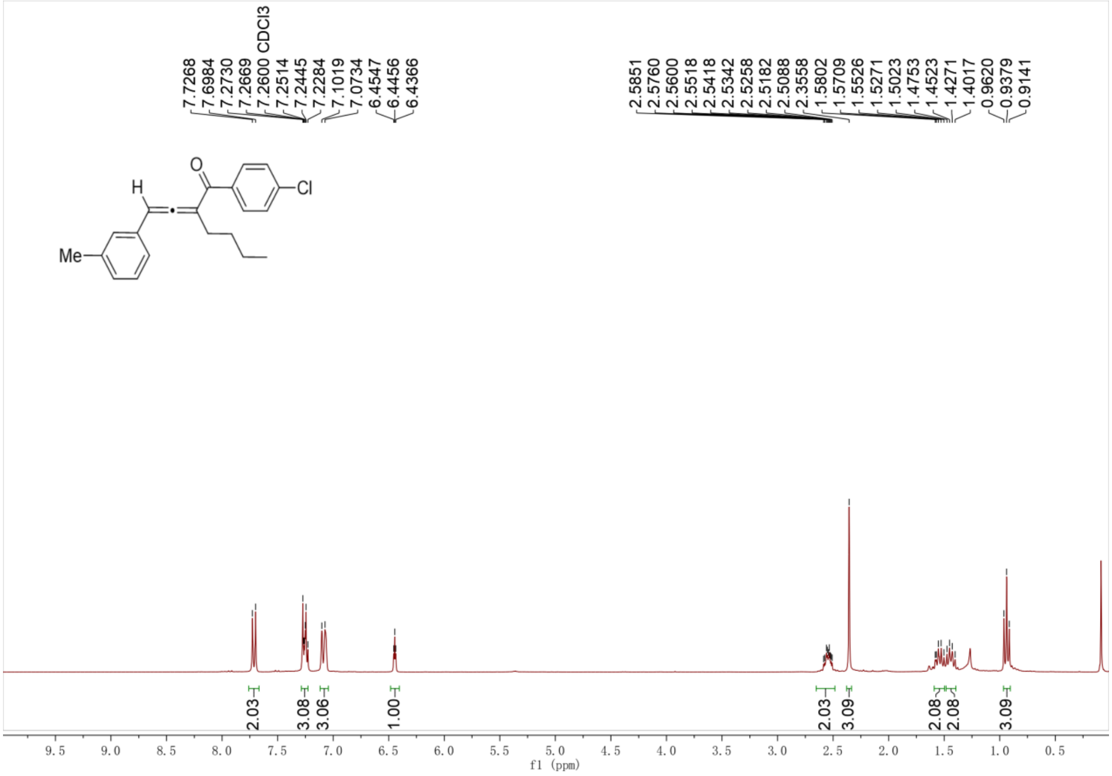


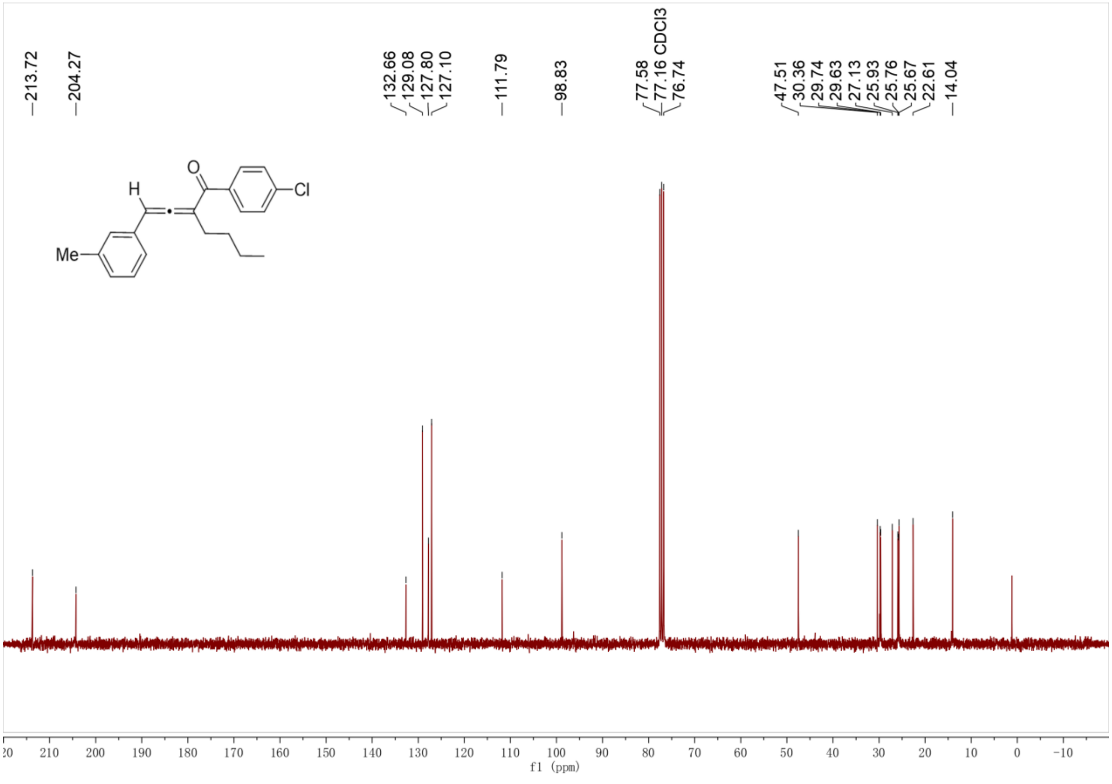
3bc ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



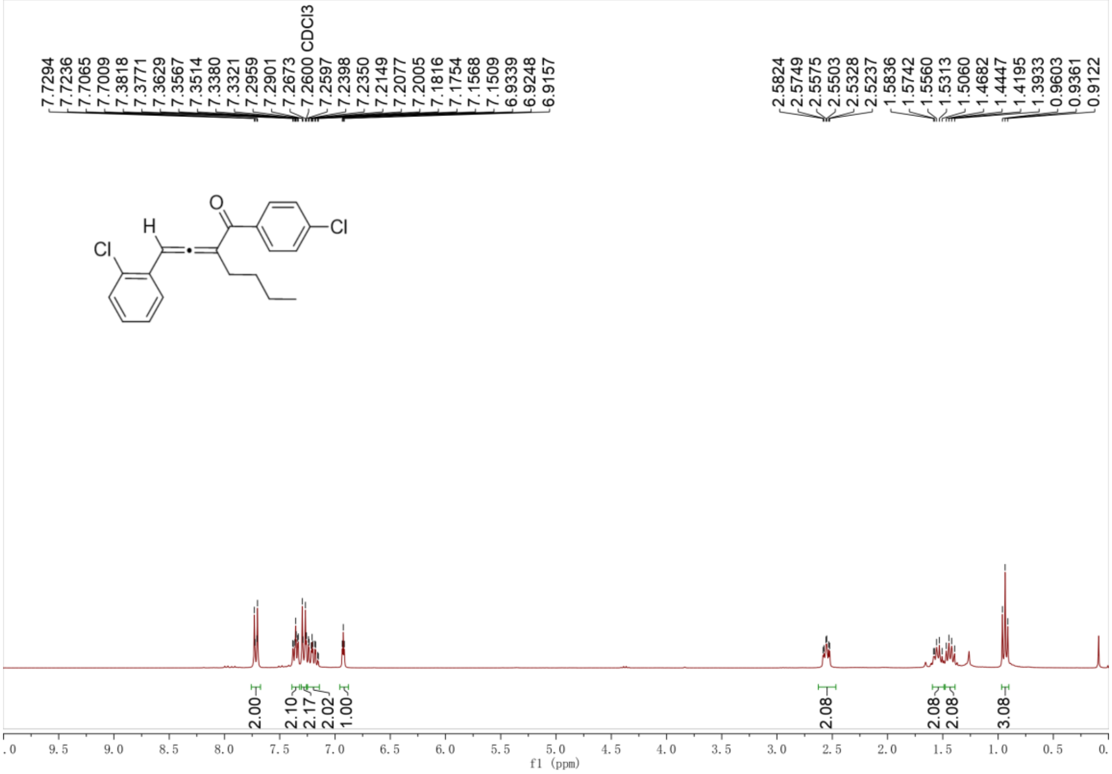


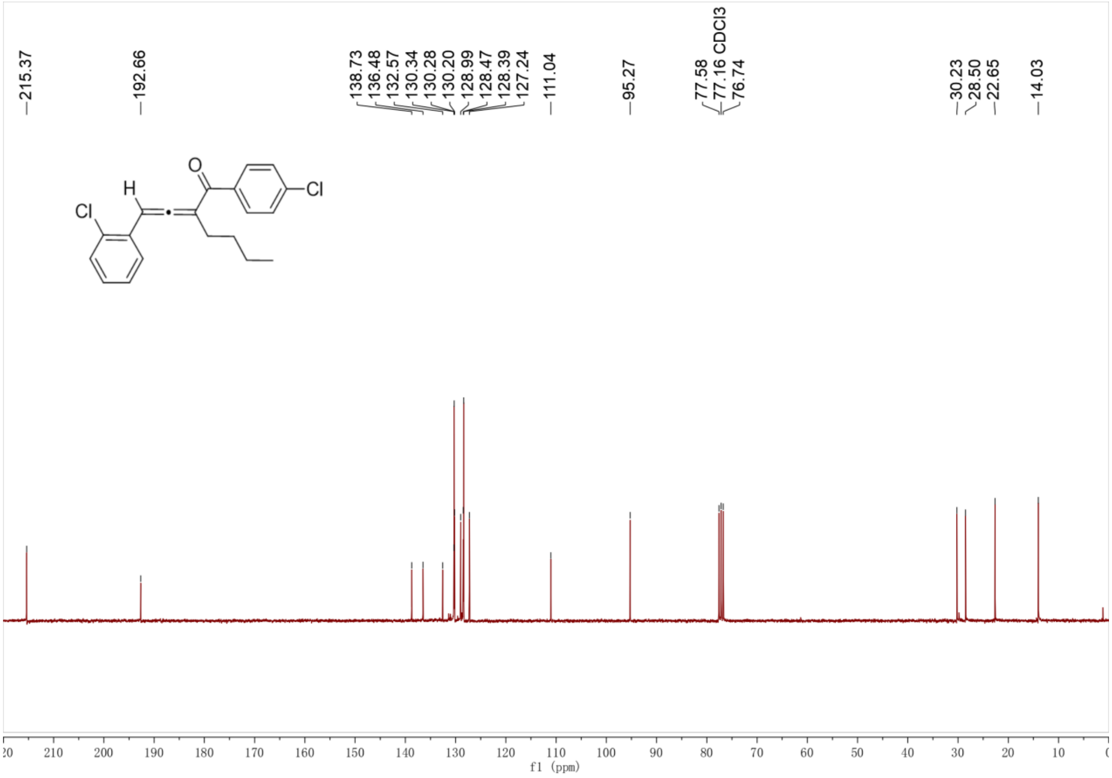
3bd ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



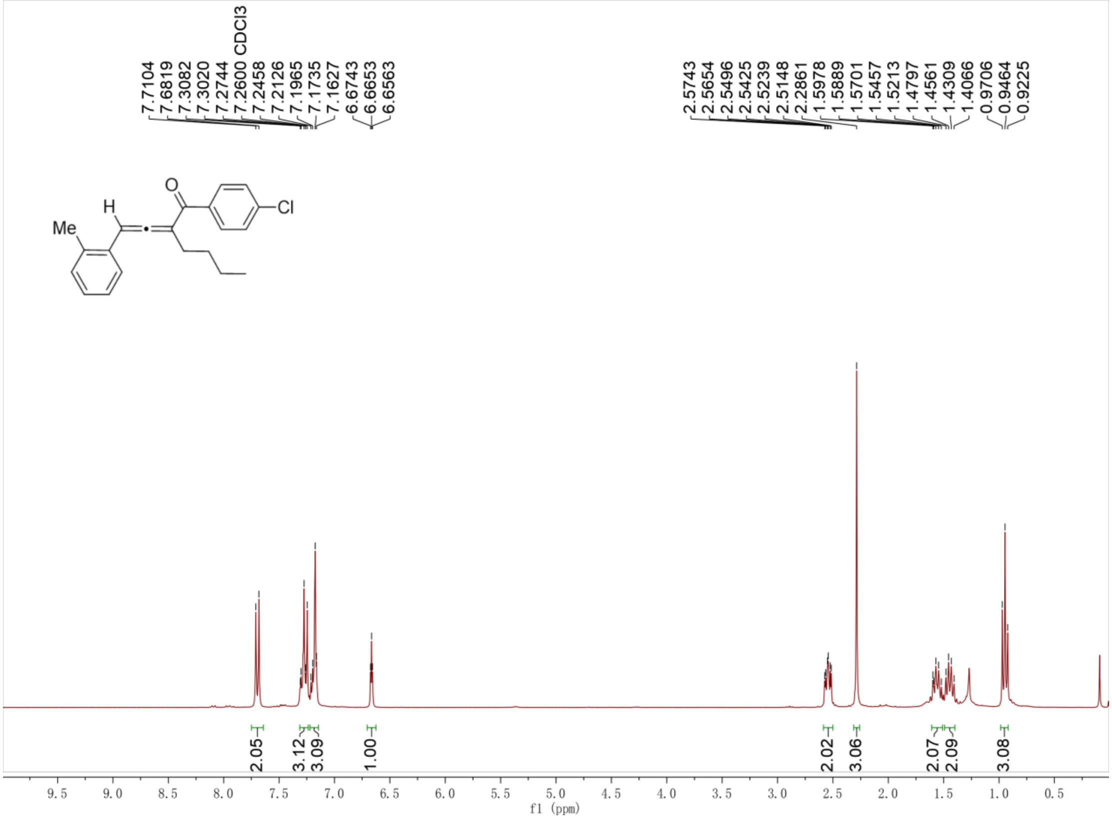


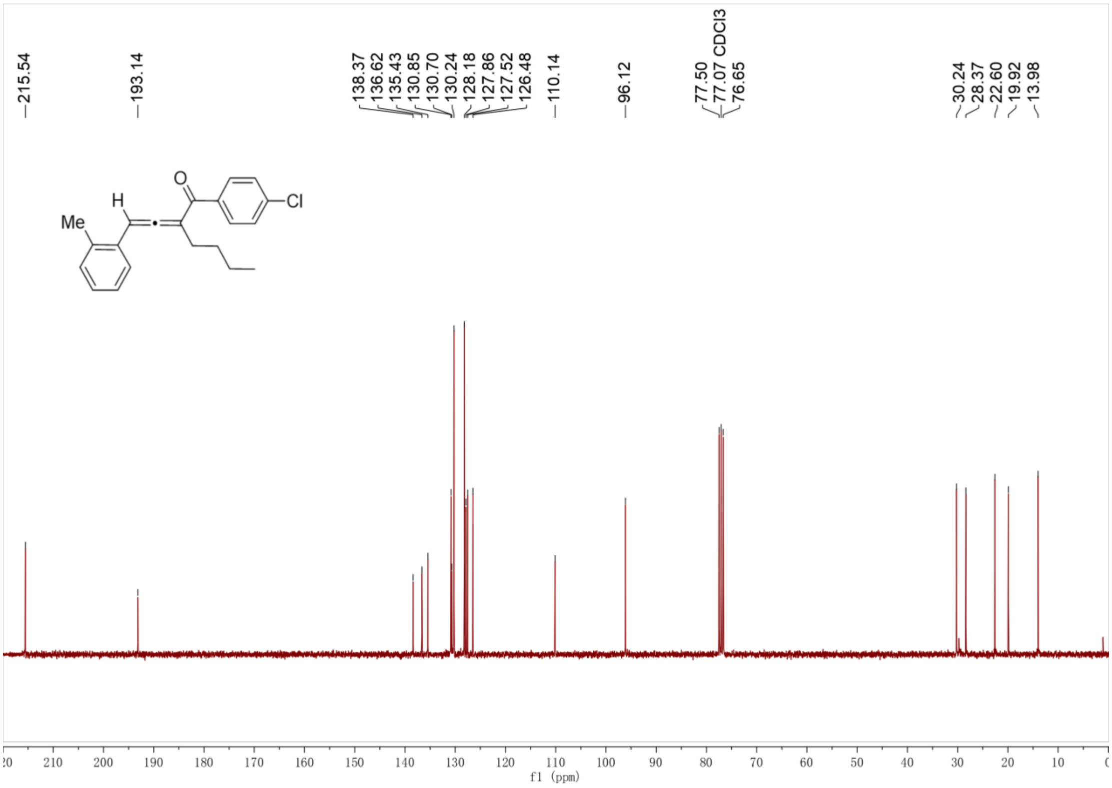
3be ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



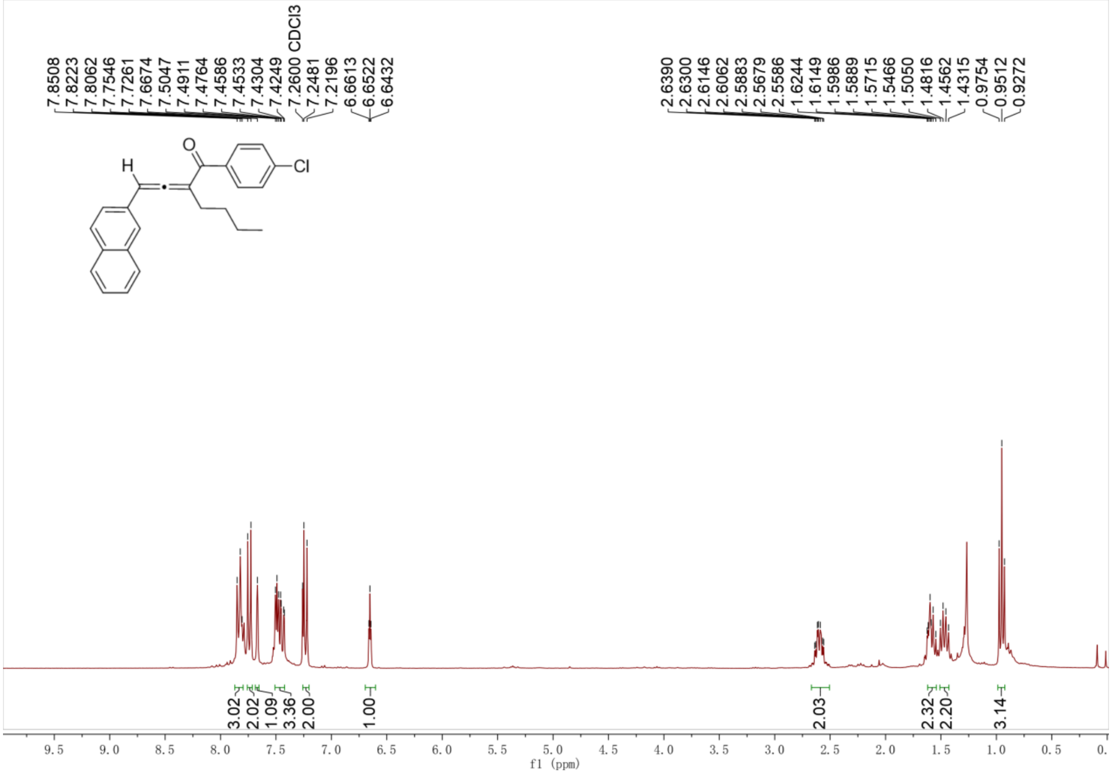


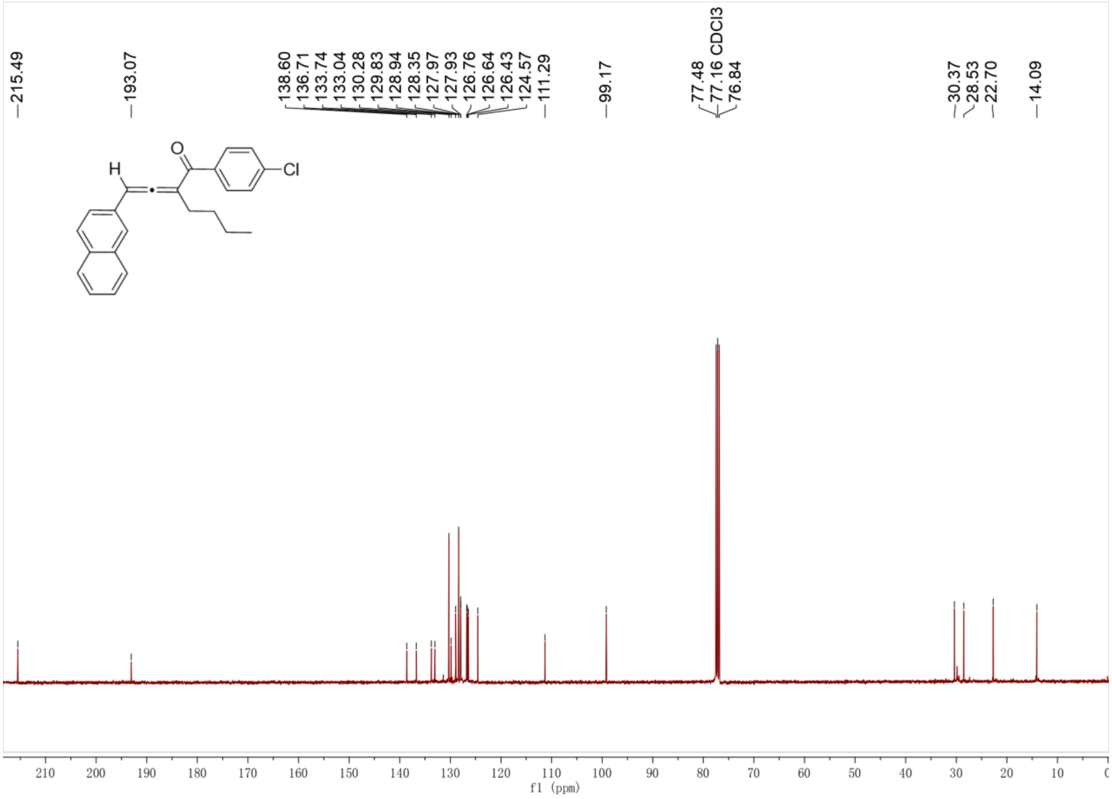
3bf ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



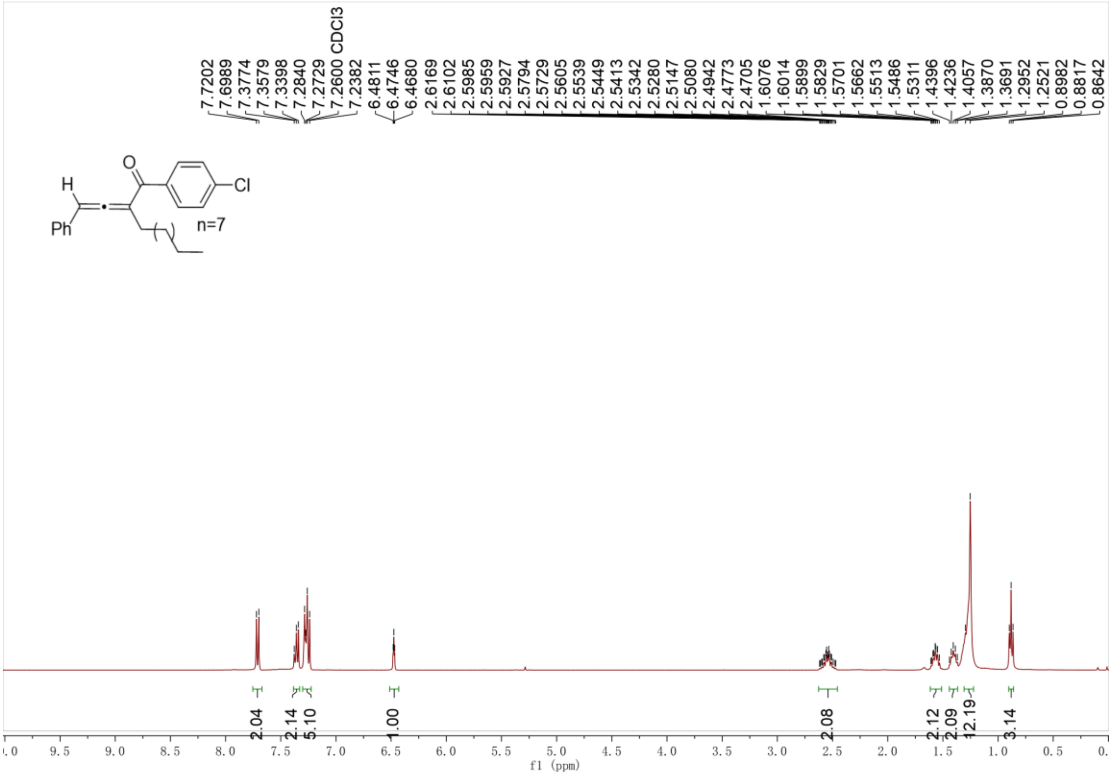


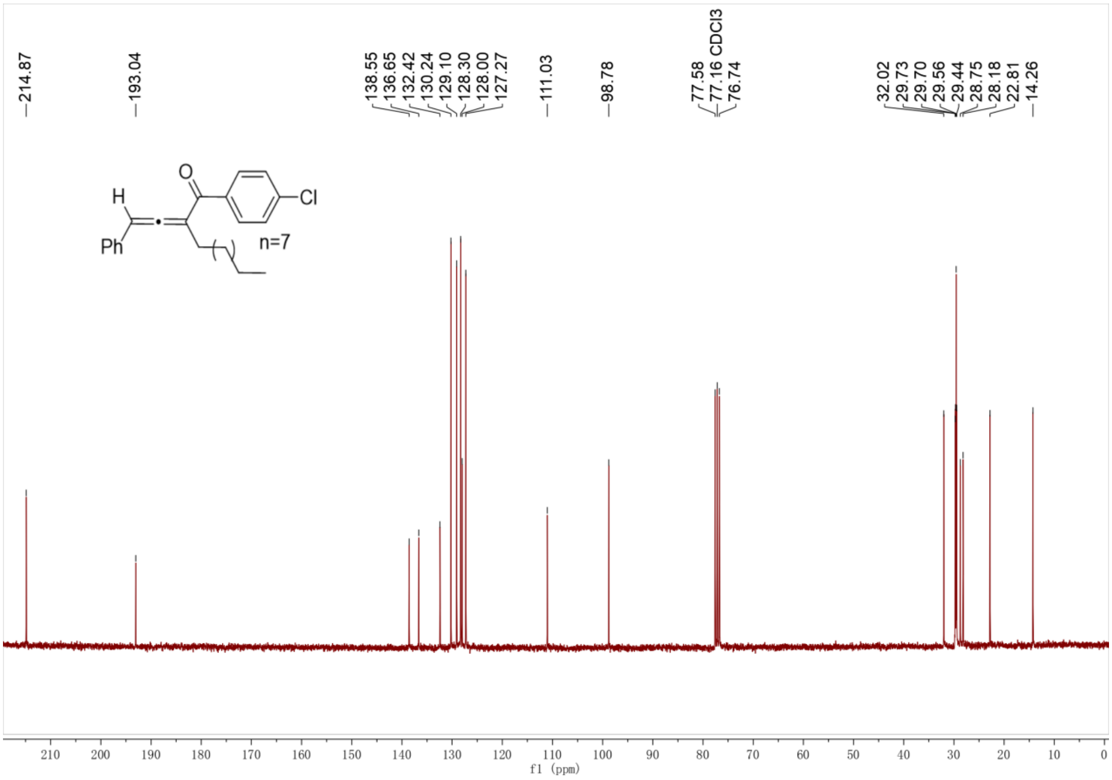
3bg ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



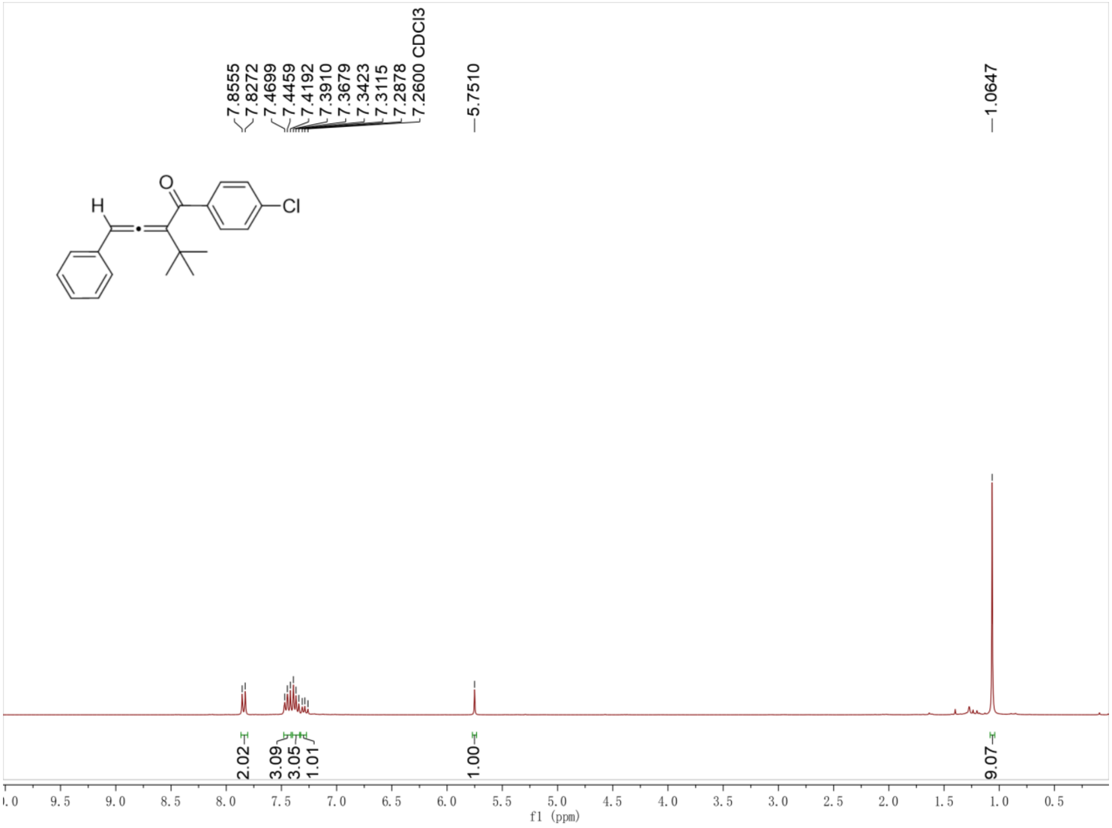


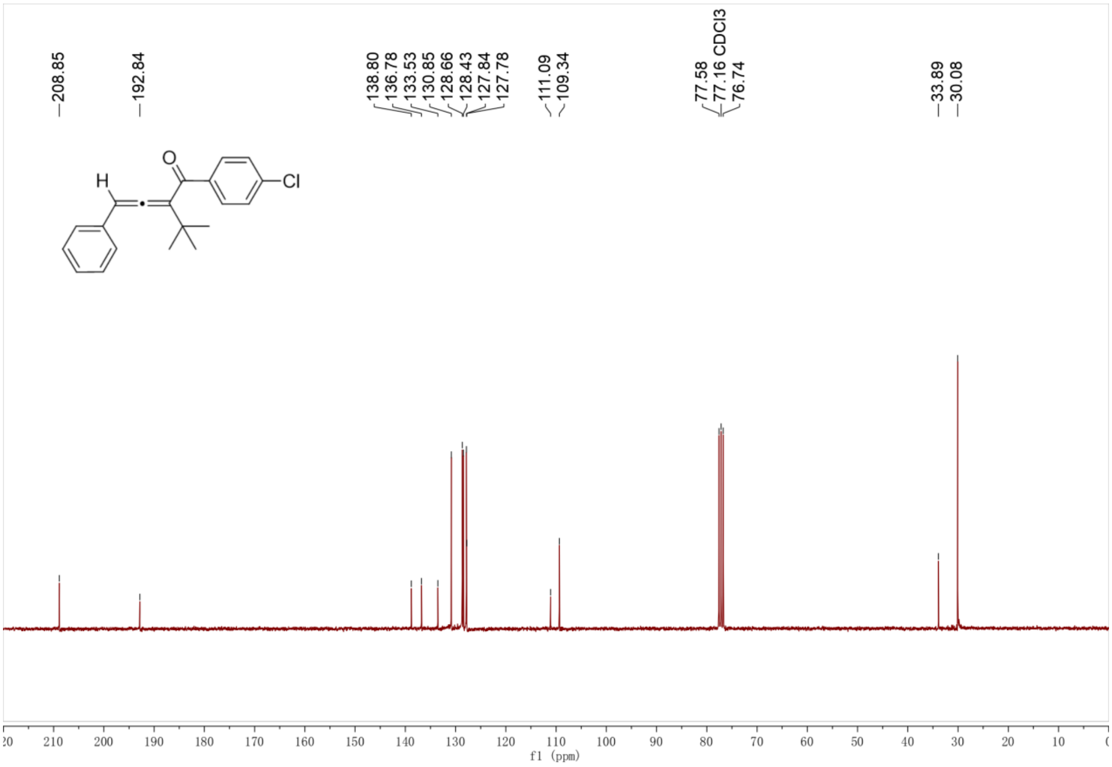
3bh ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



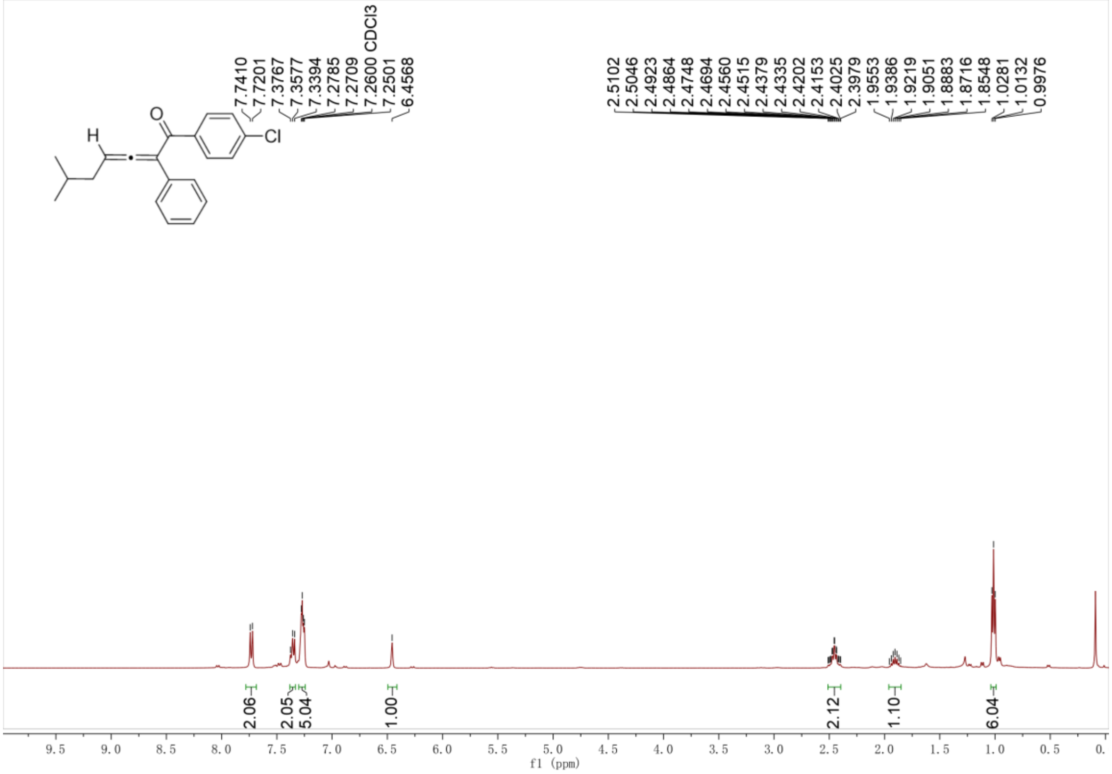


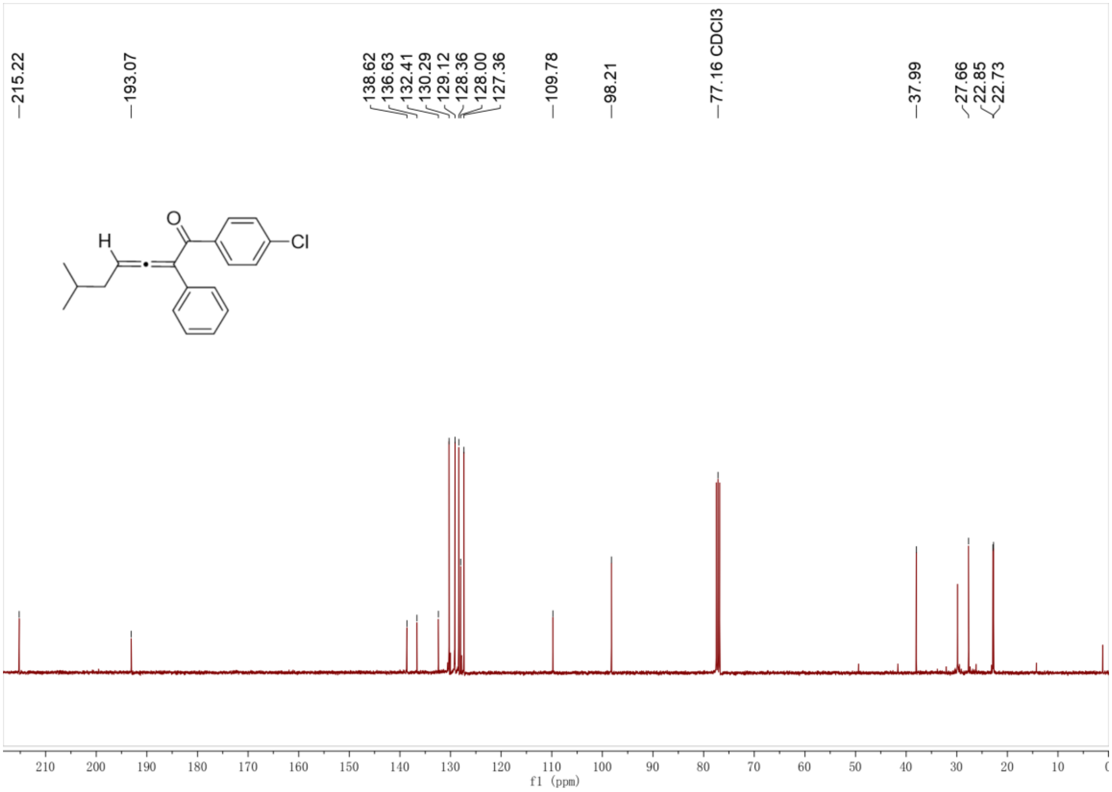
3bi ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



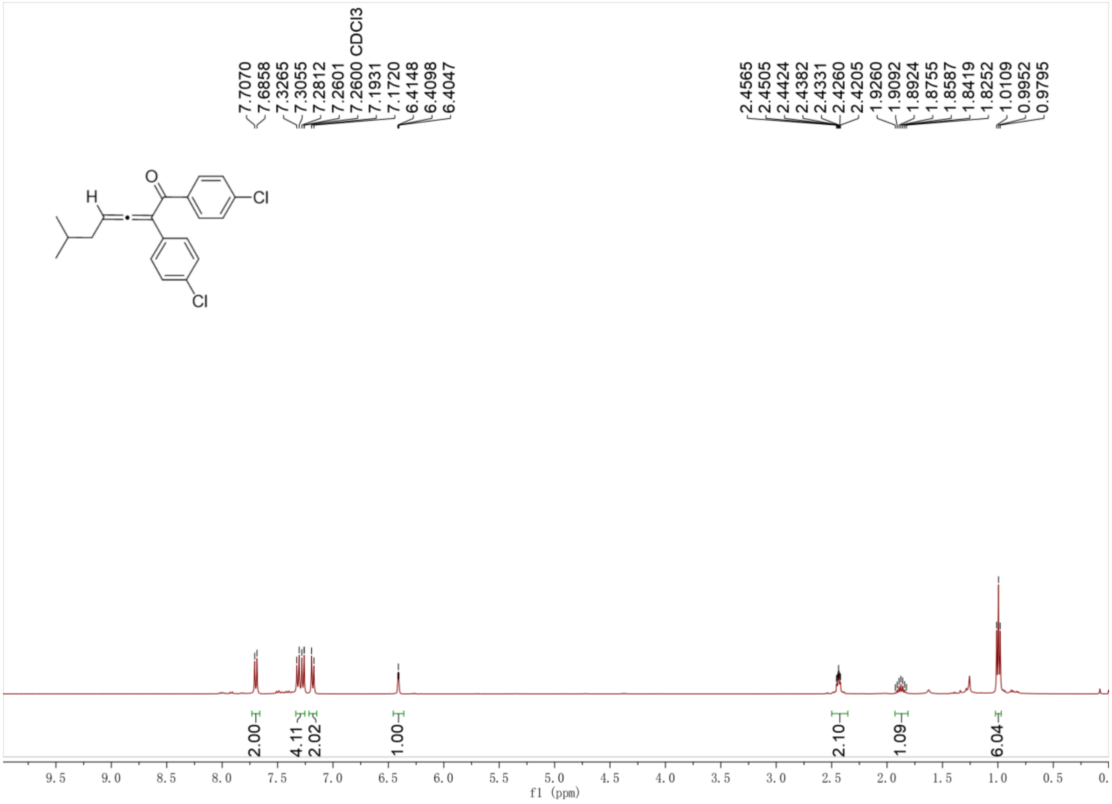


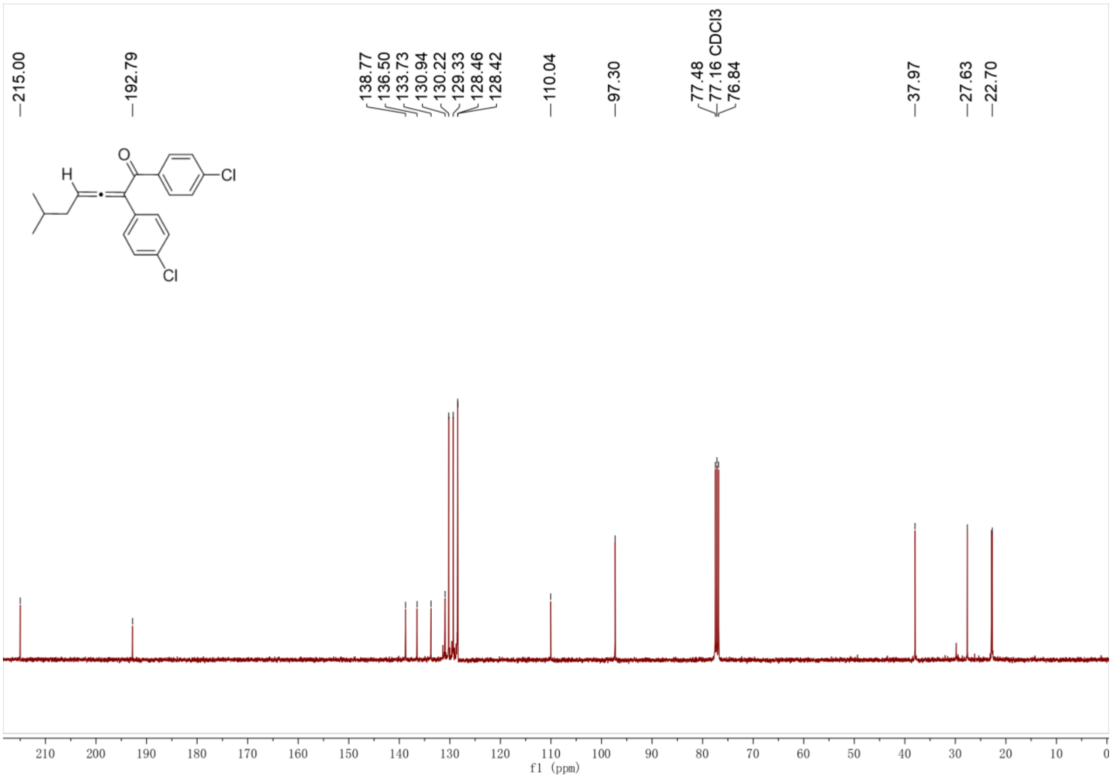
3bk ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



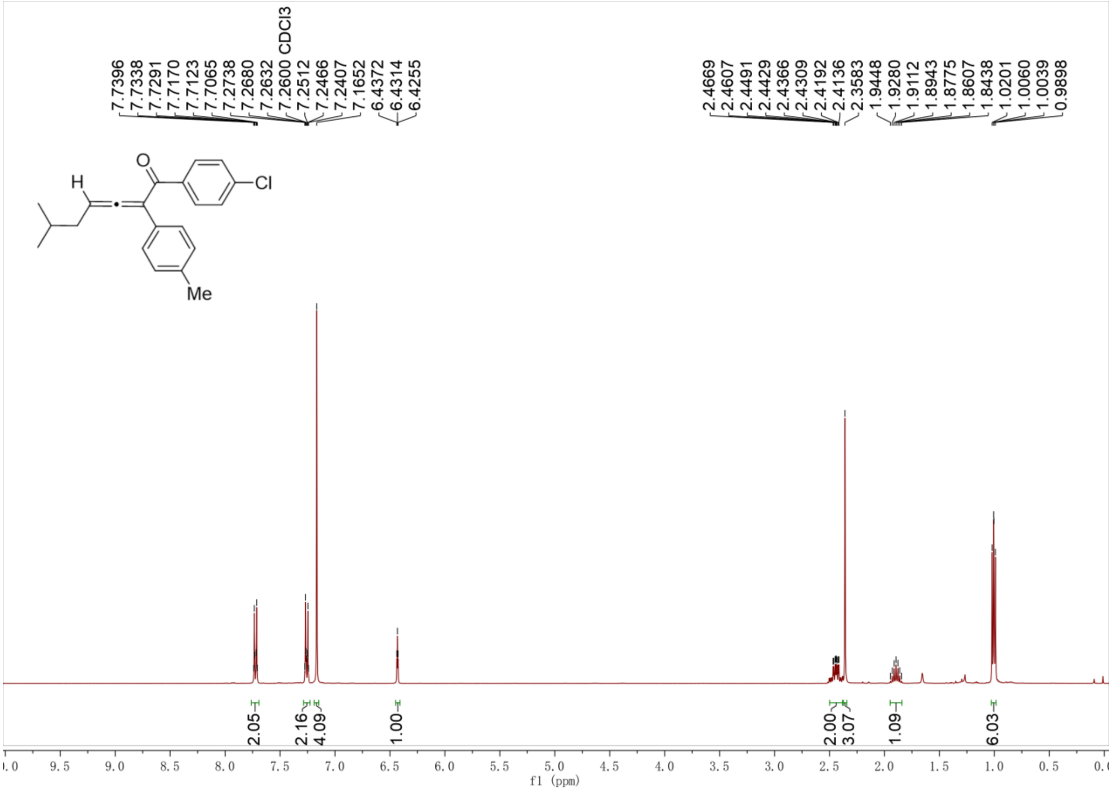


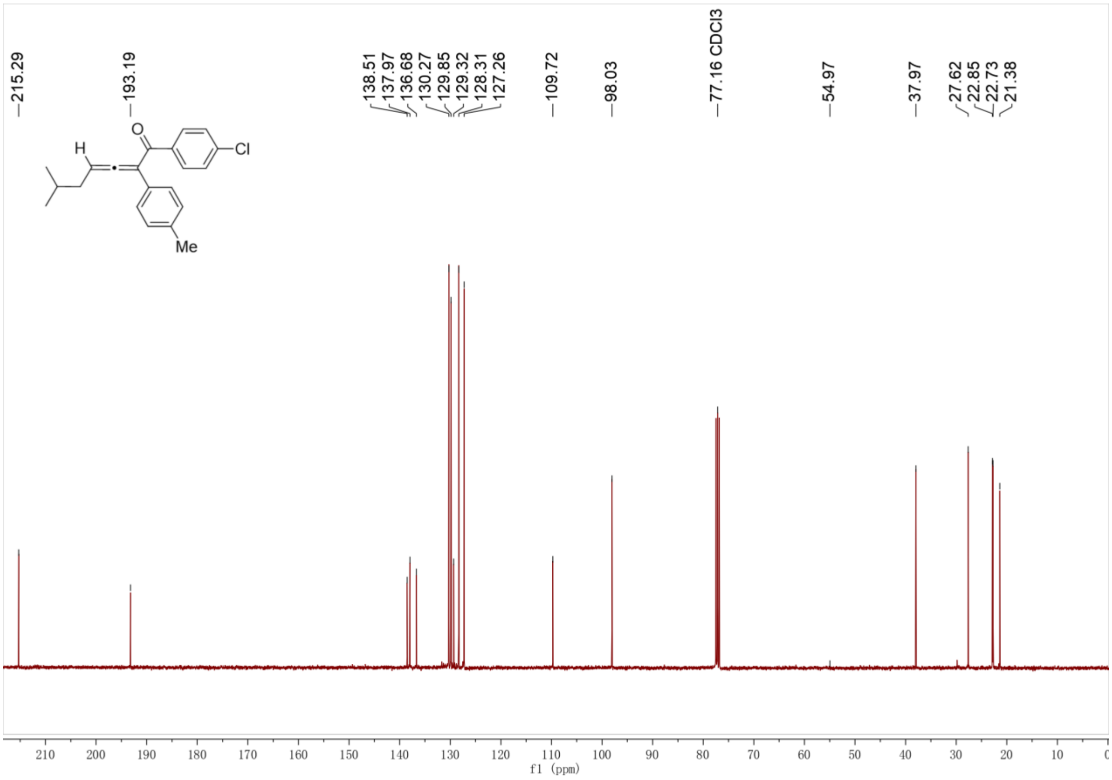
3bl ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



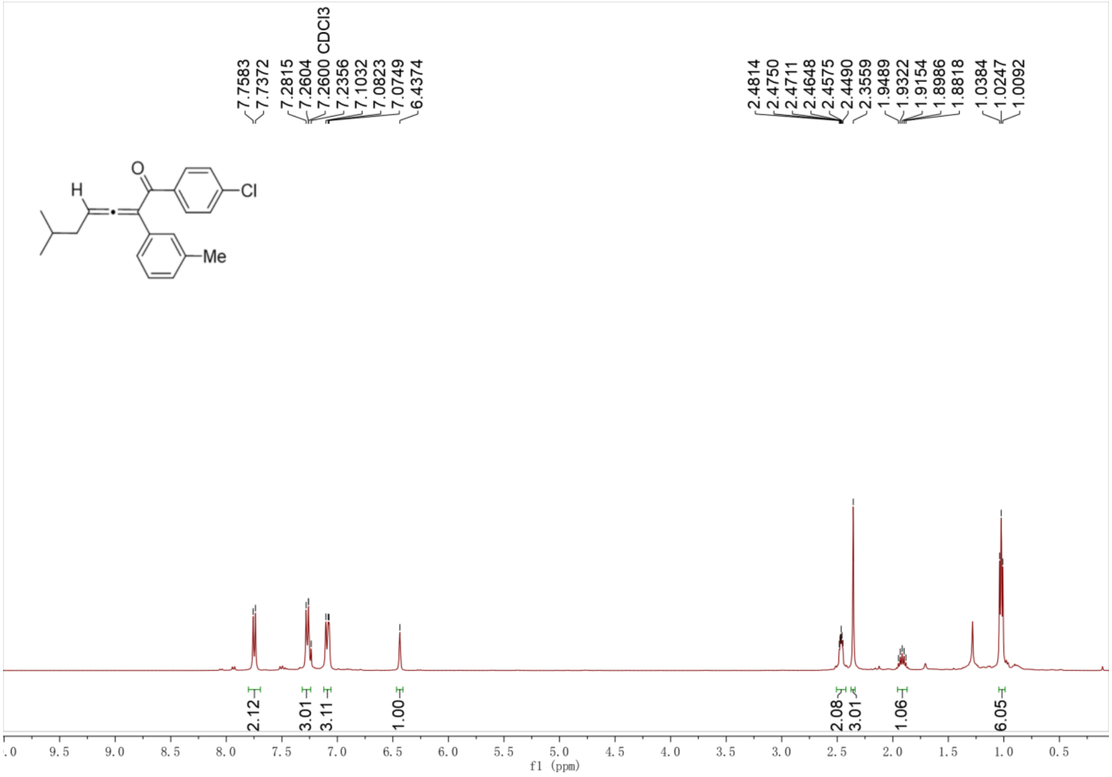


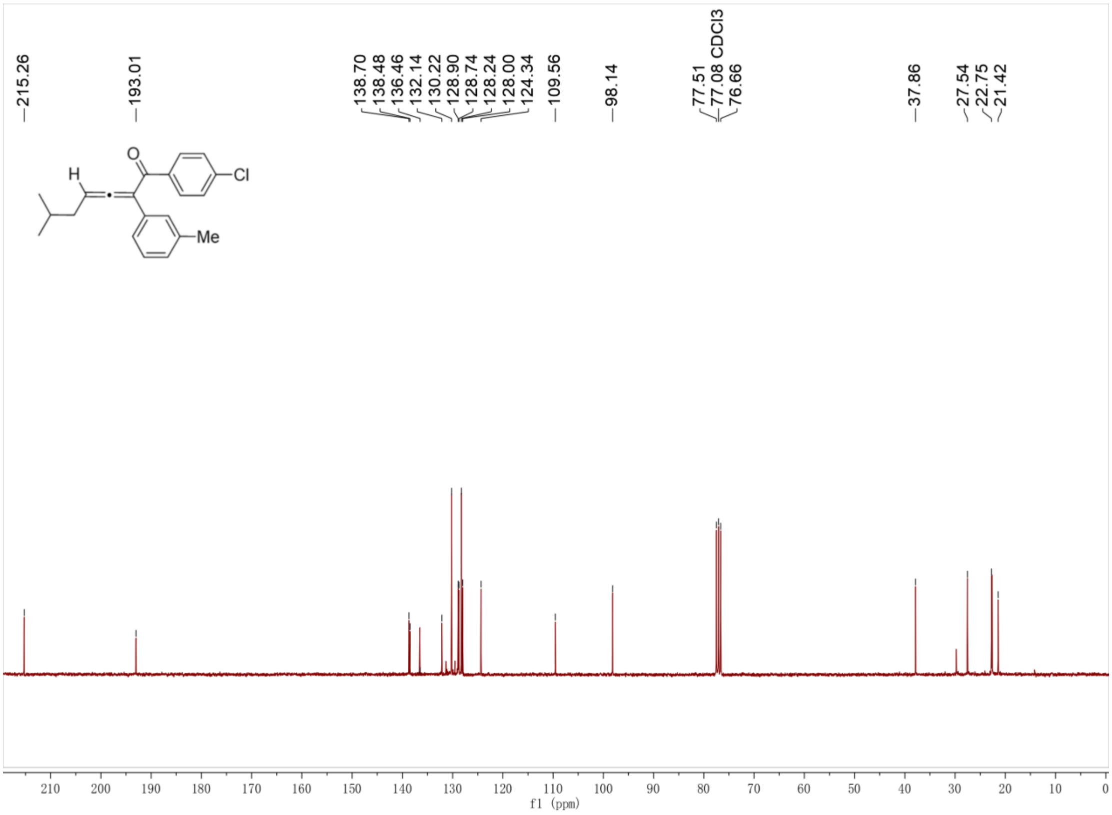
3bm ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



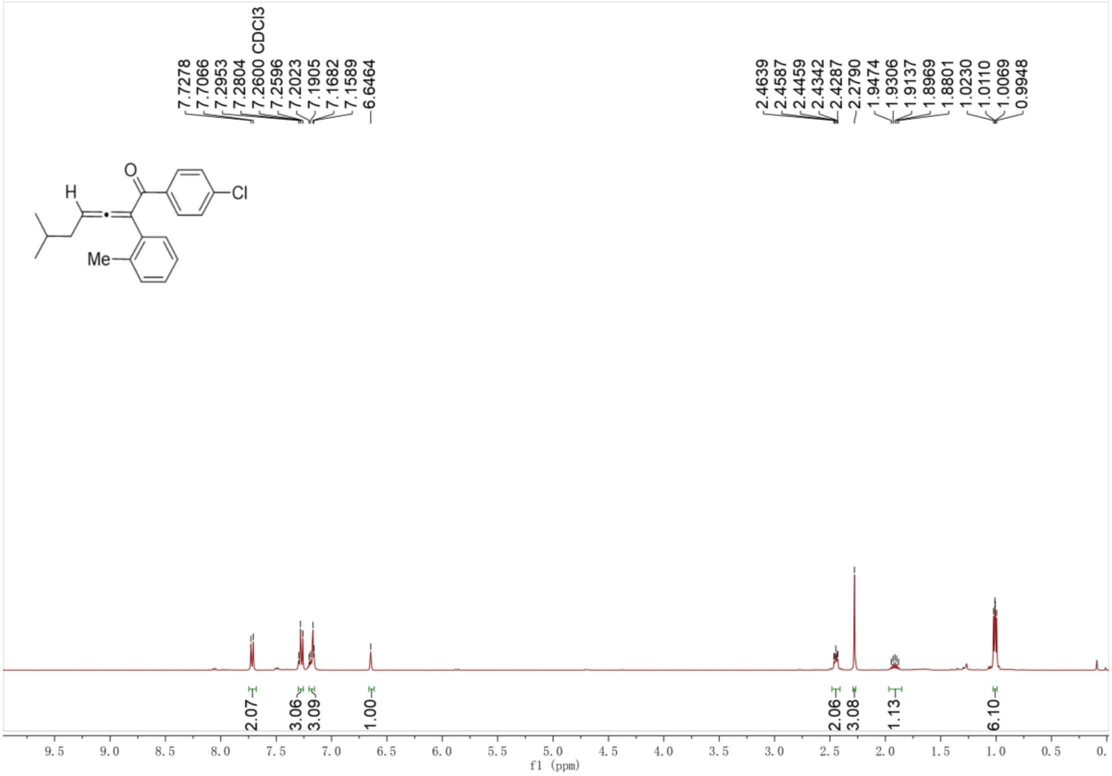


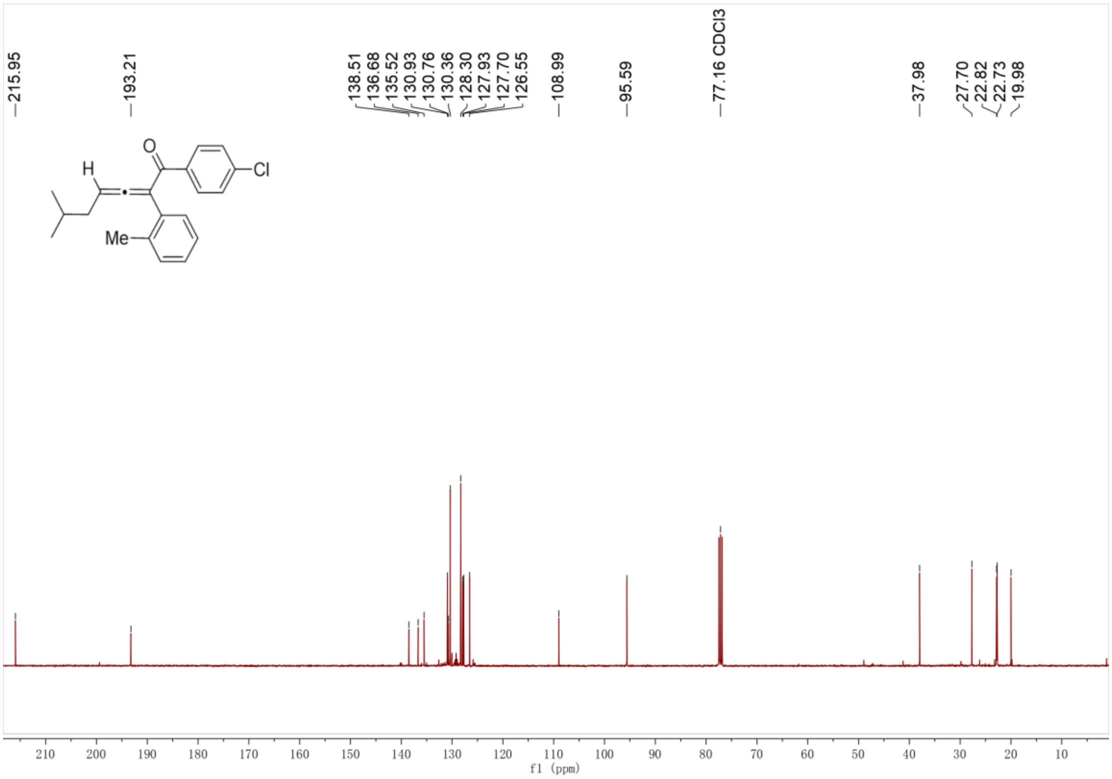
3bn ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



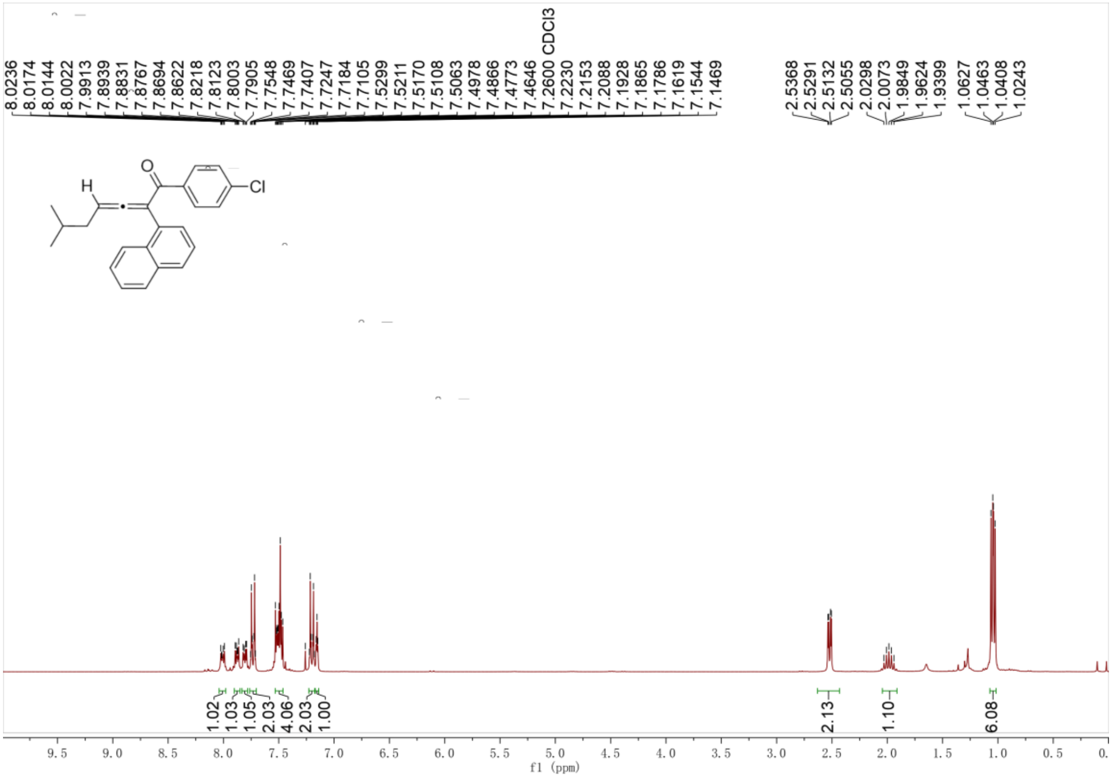


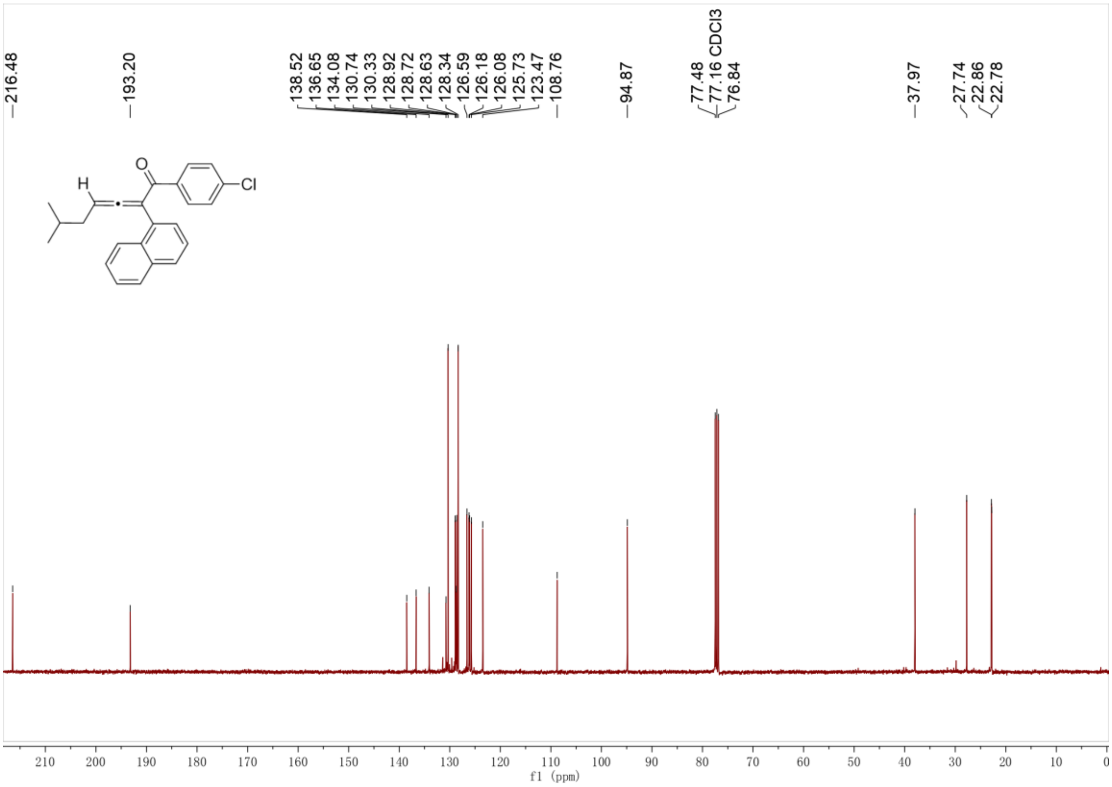
3bo ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



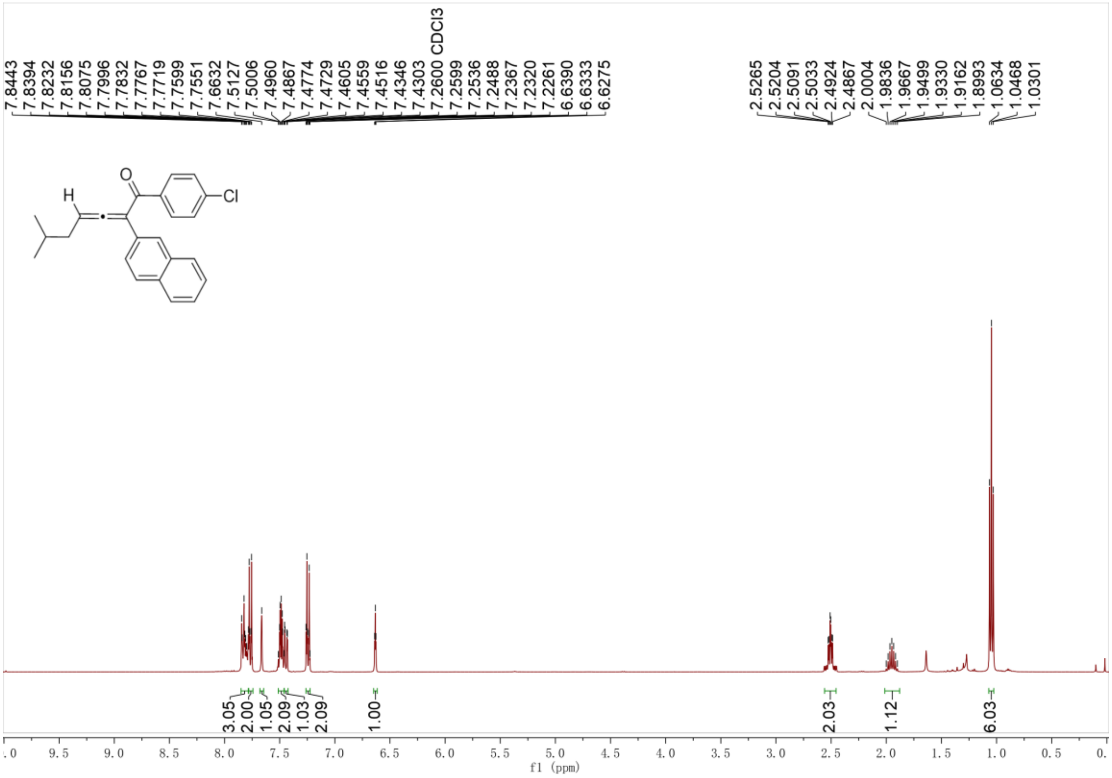


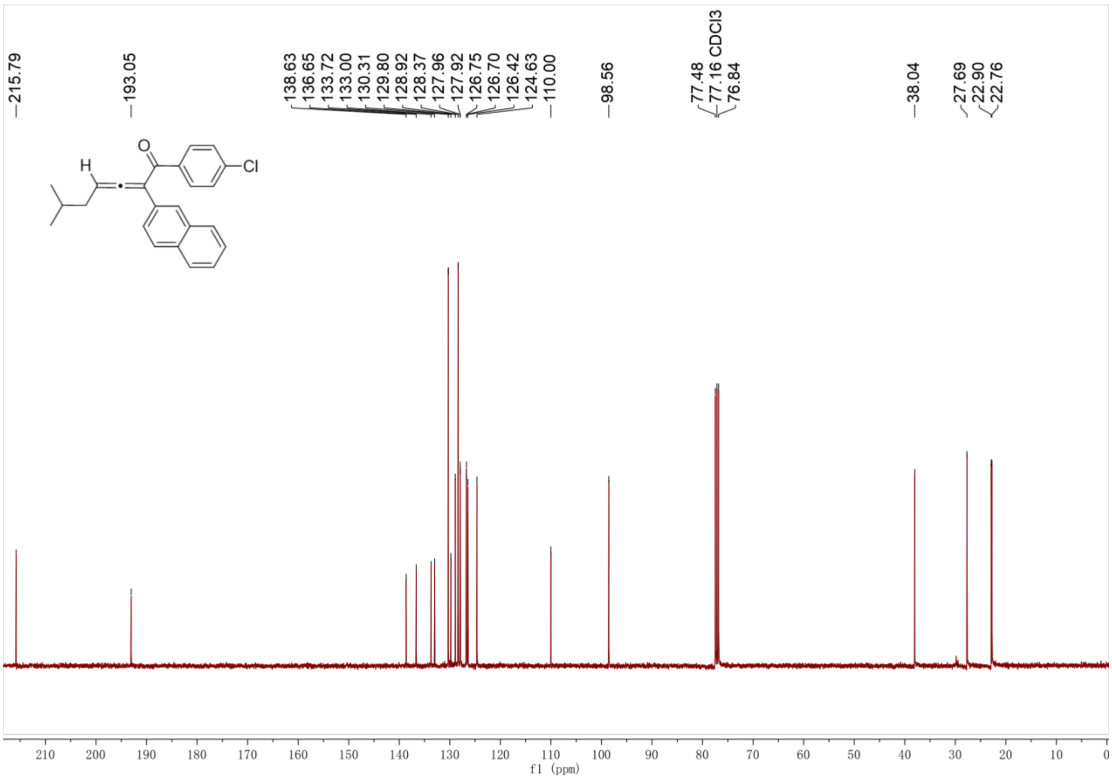
3bp ^{1}H NMR (300 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



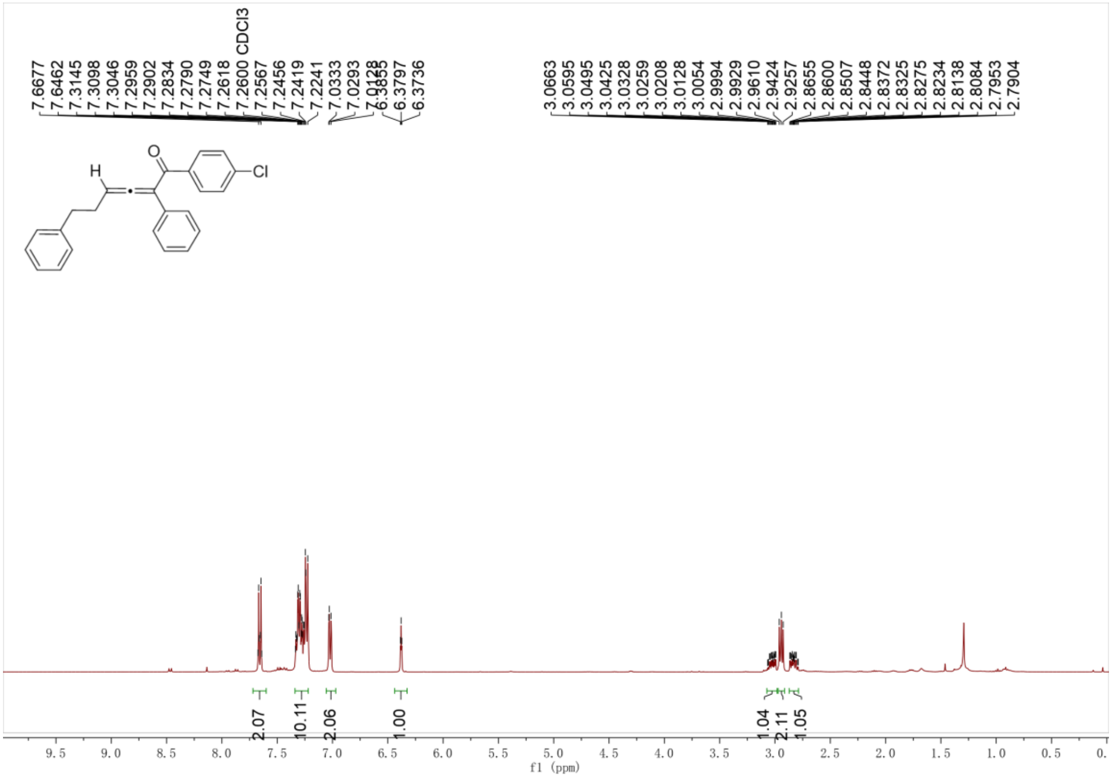


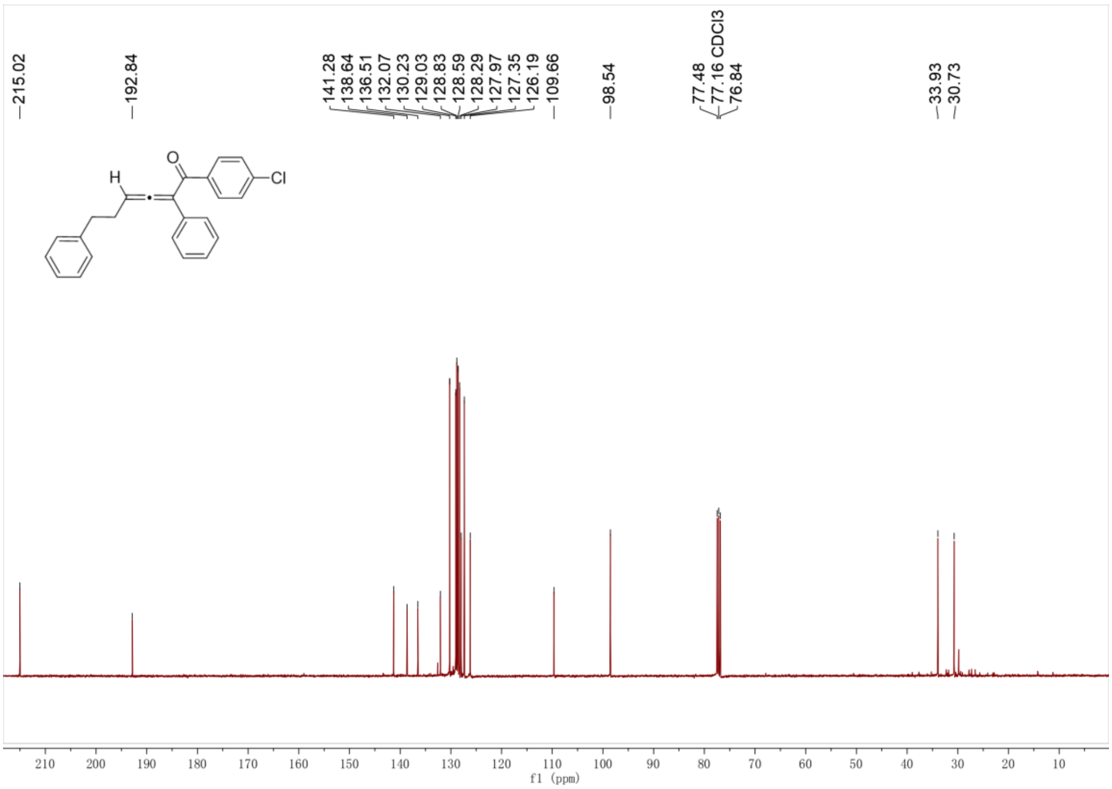
3bq ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



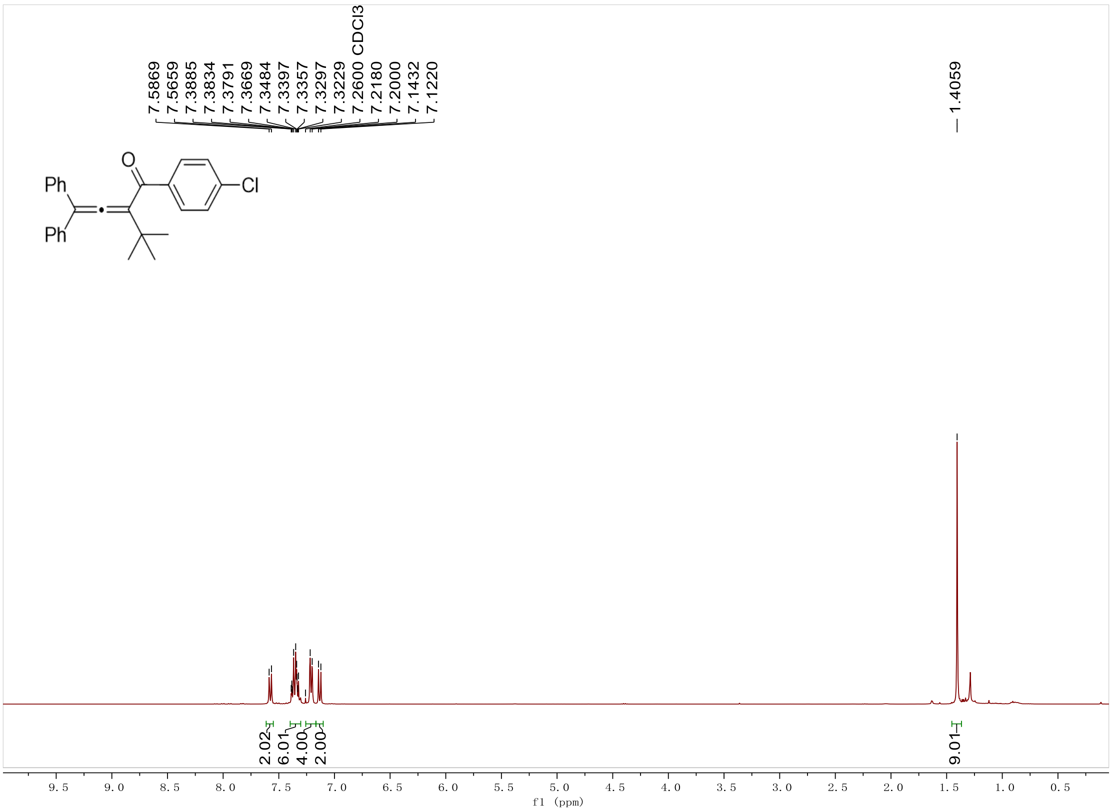


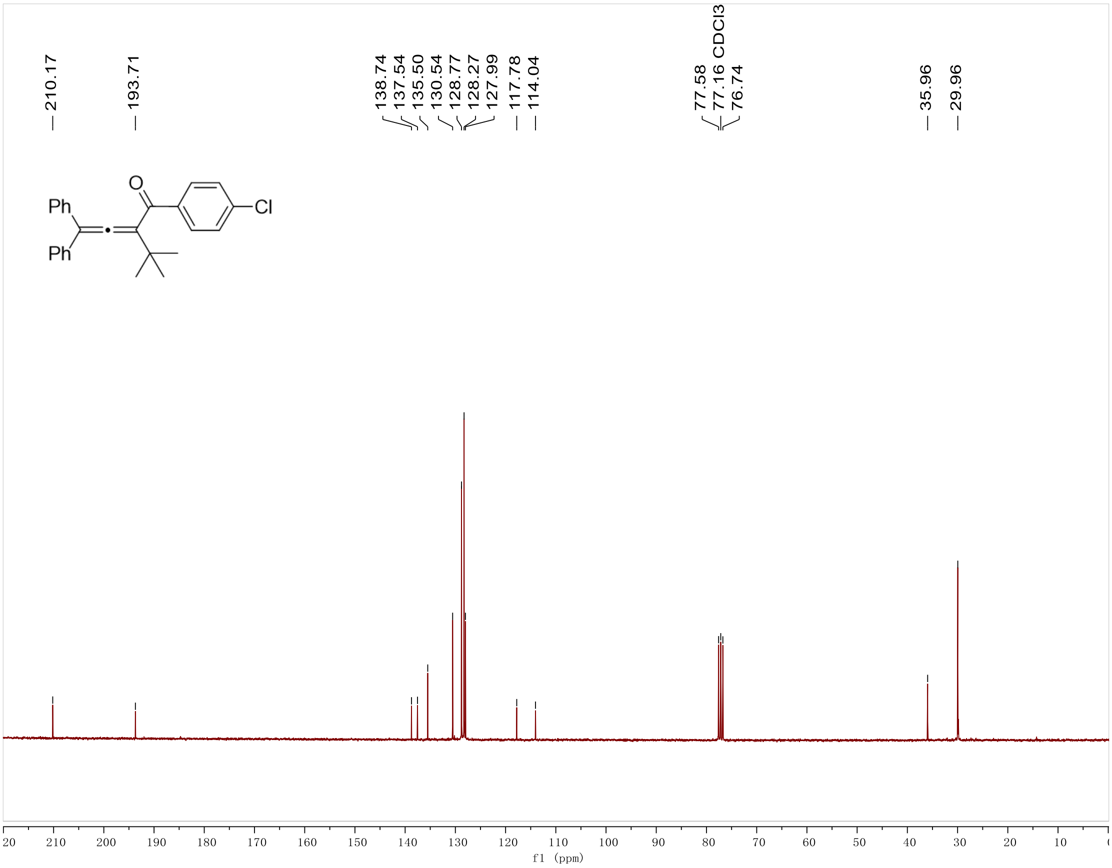
3br ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



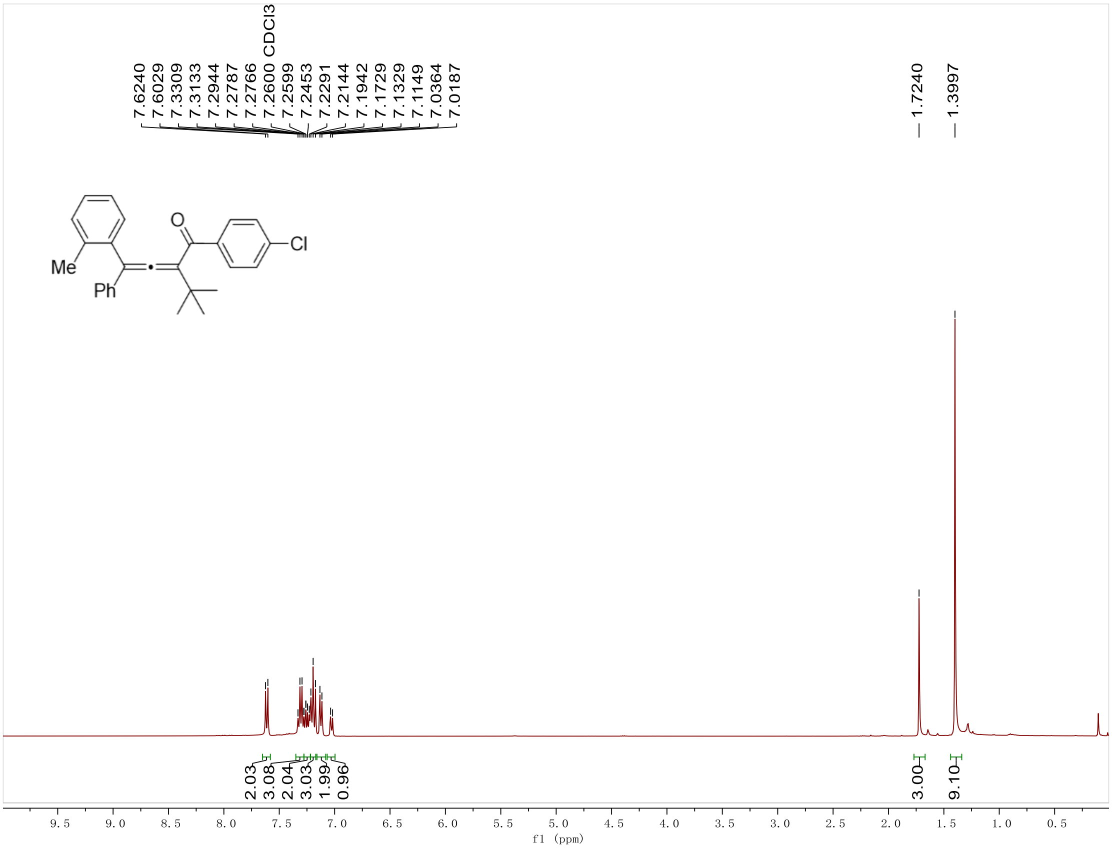


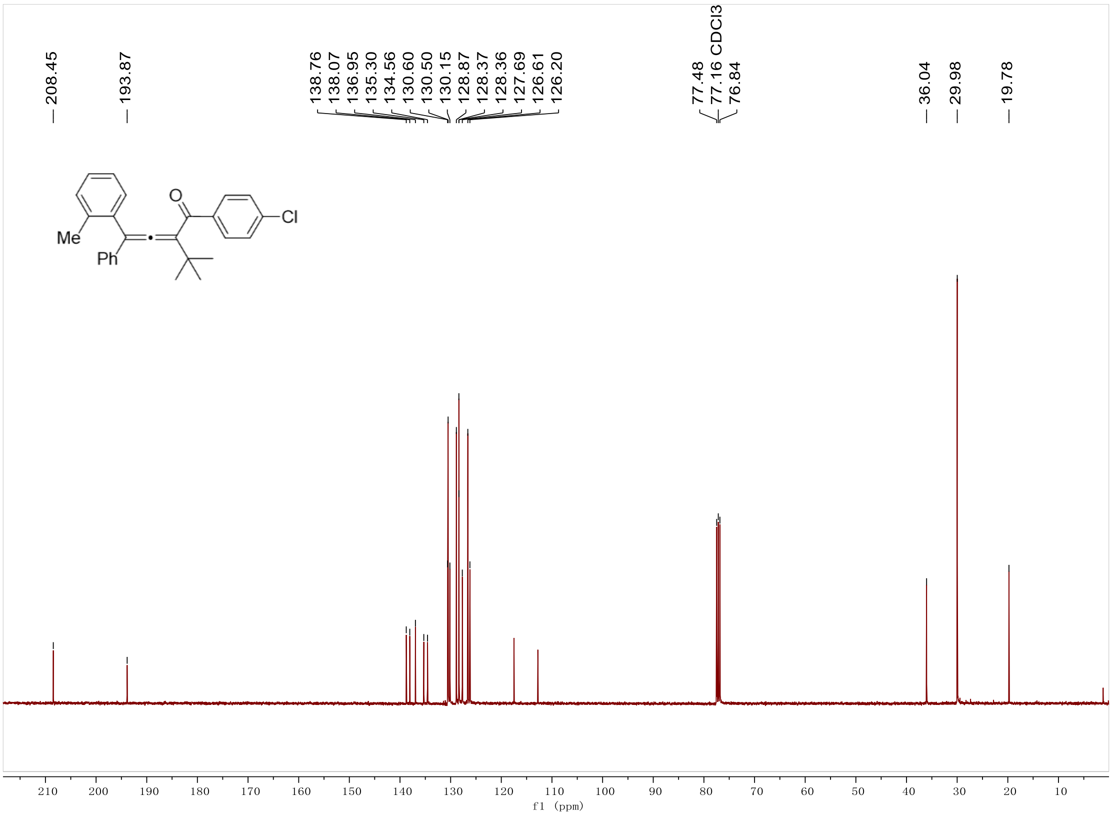
3bs ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



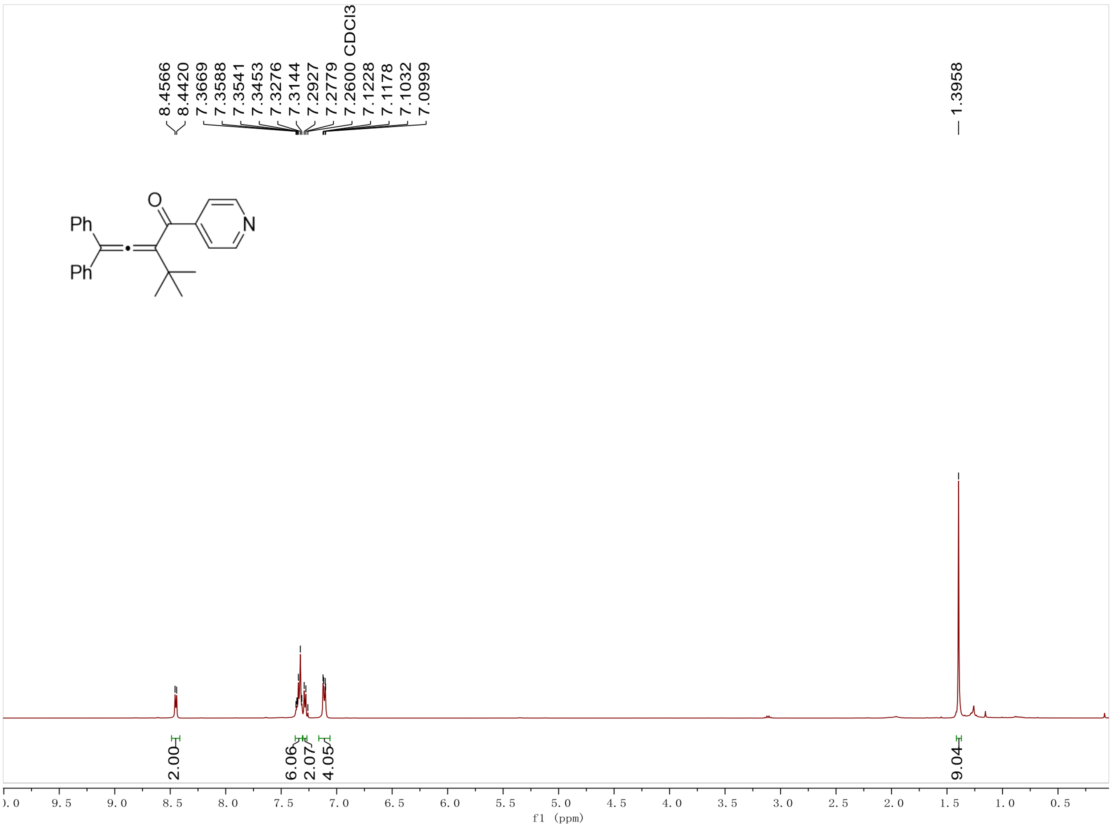


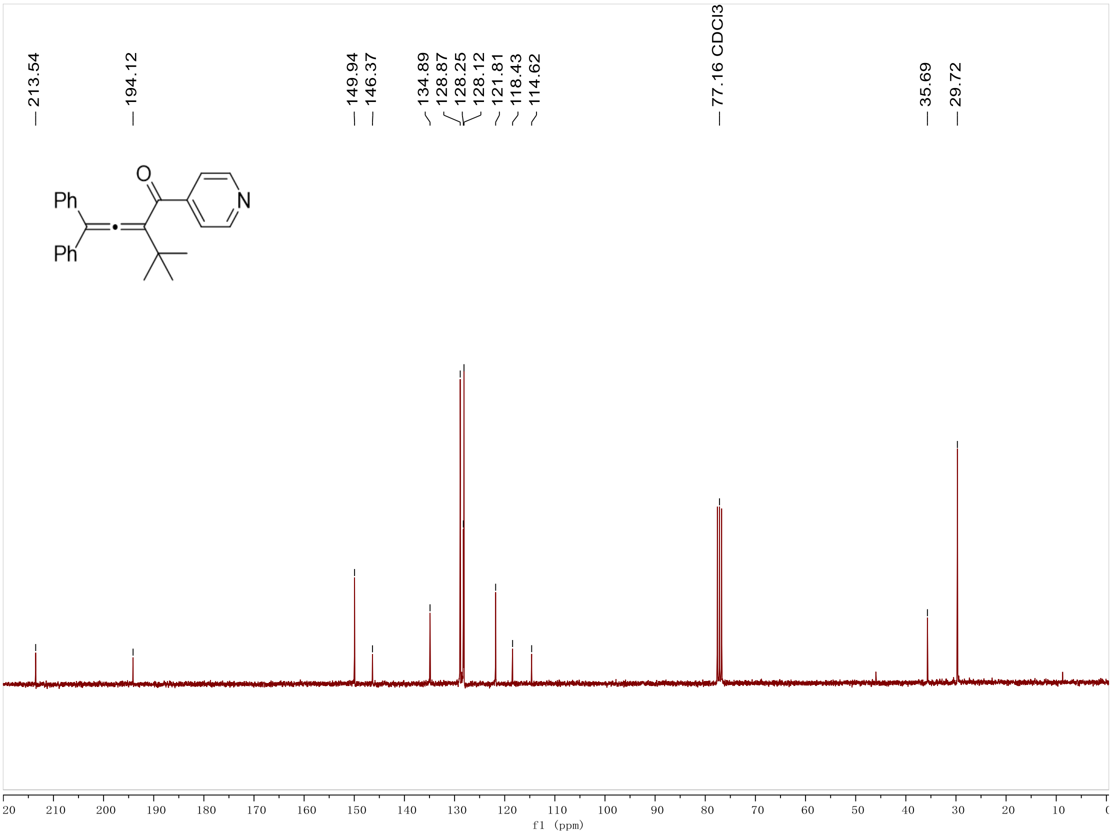
3bt ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



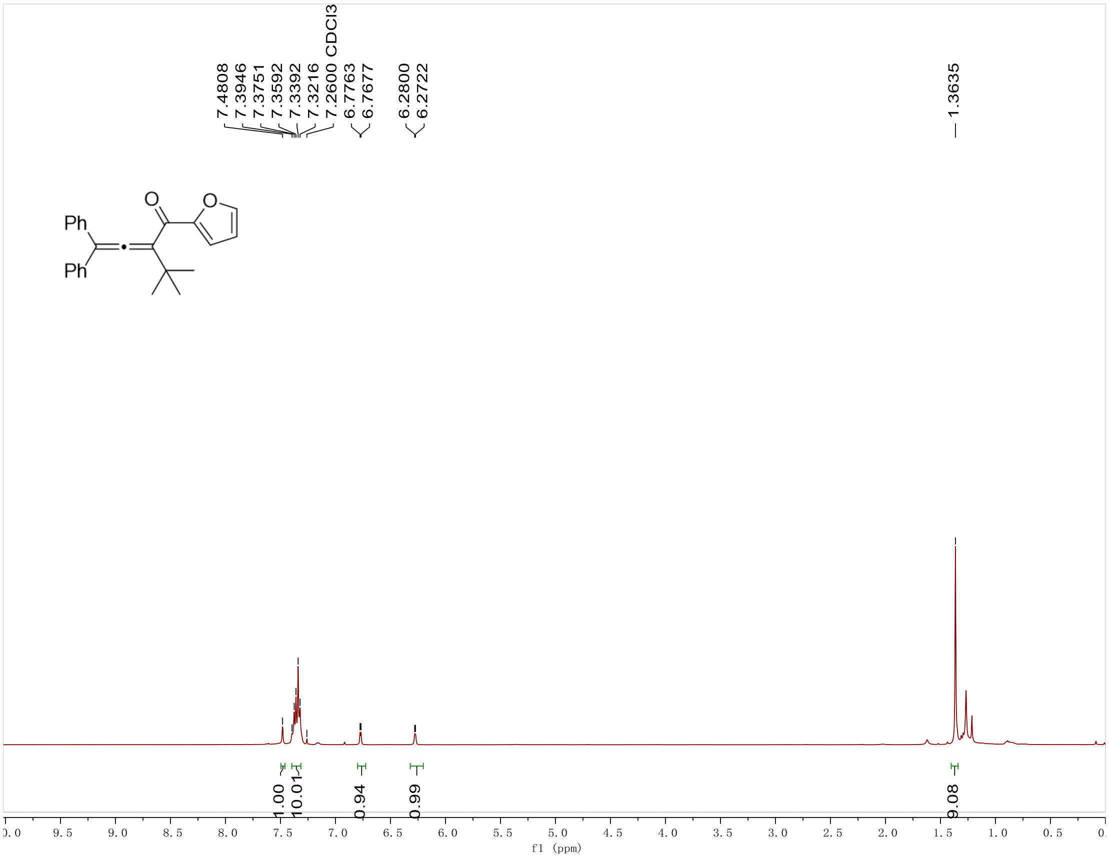


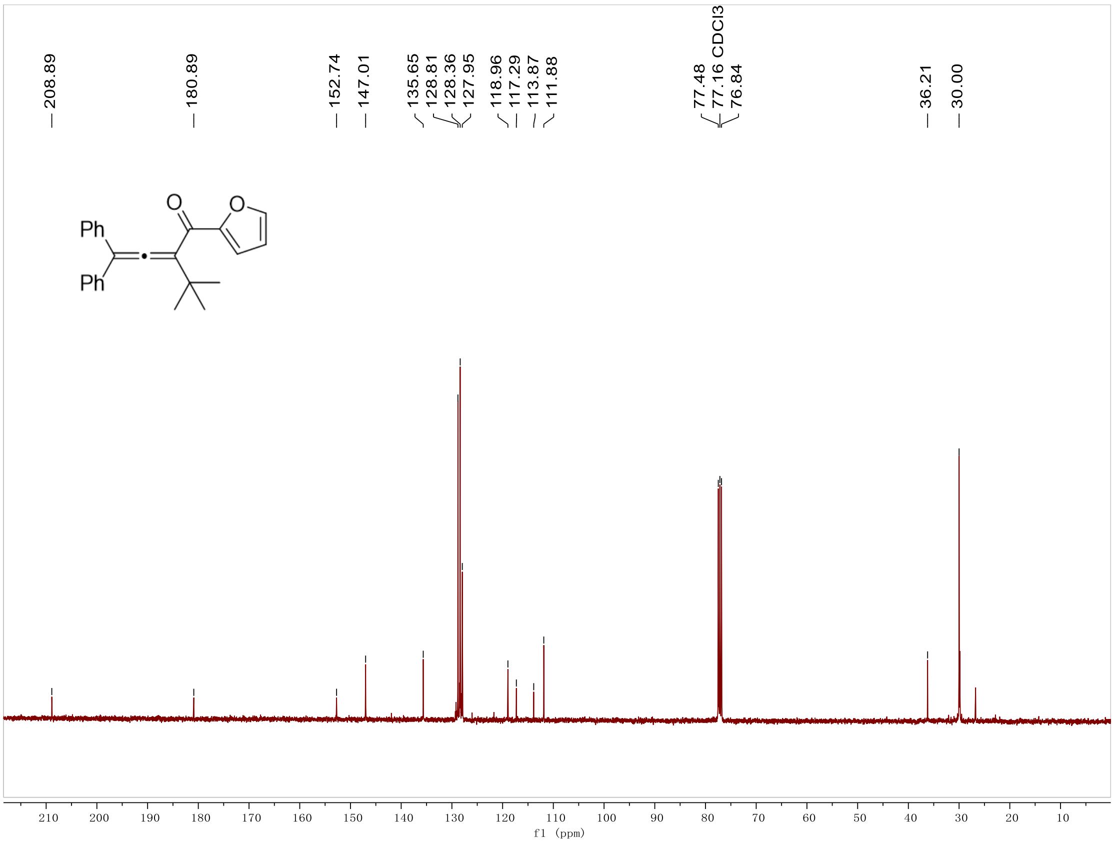
3bu ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (75 MHz, Chloroform-d)



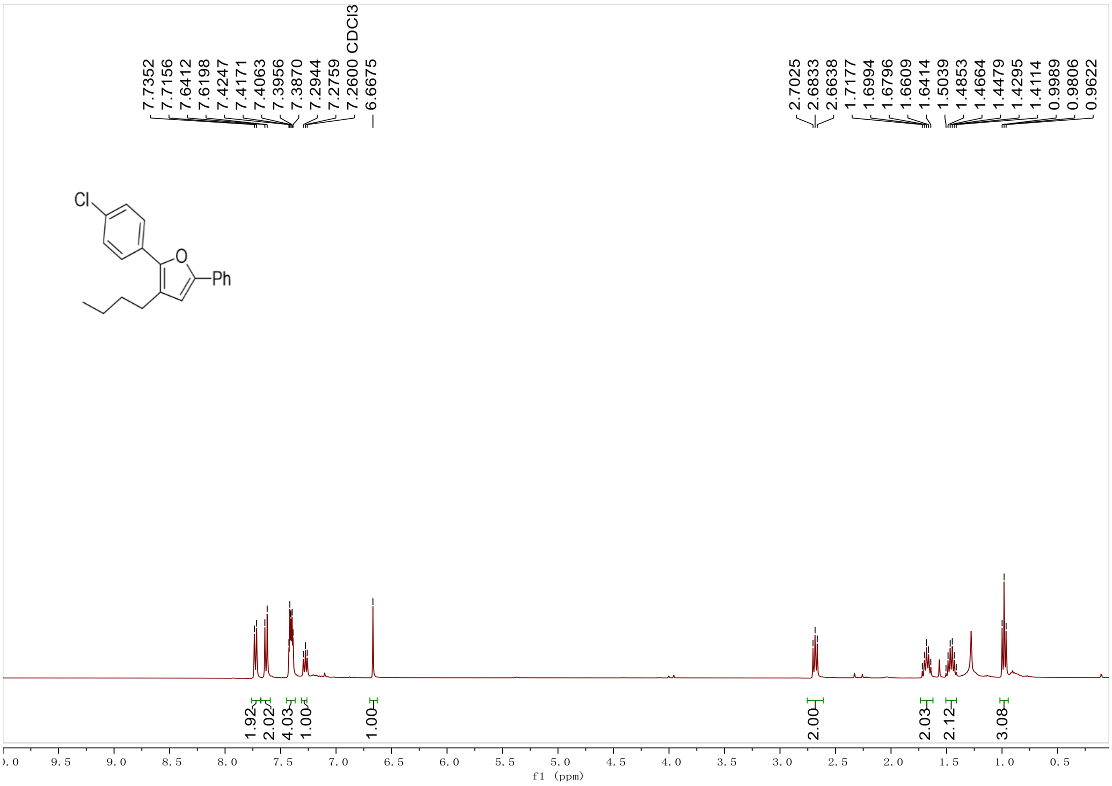


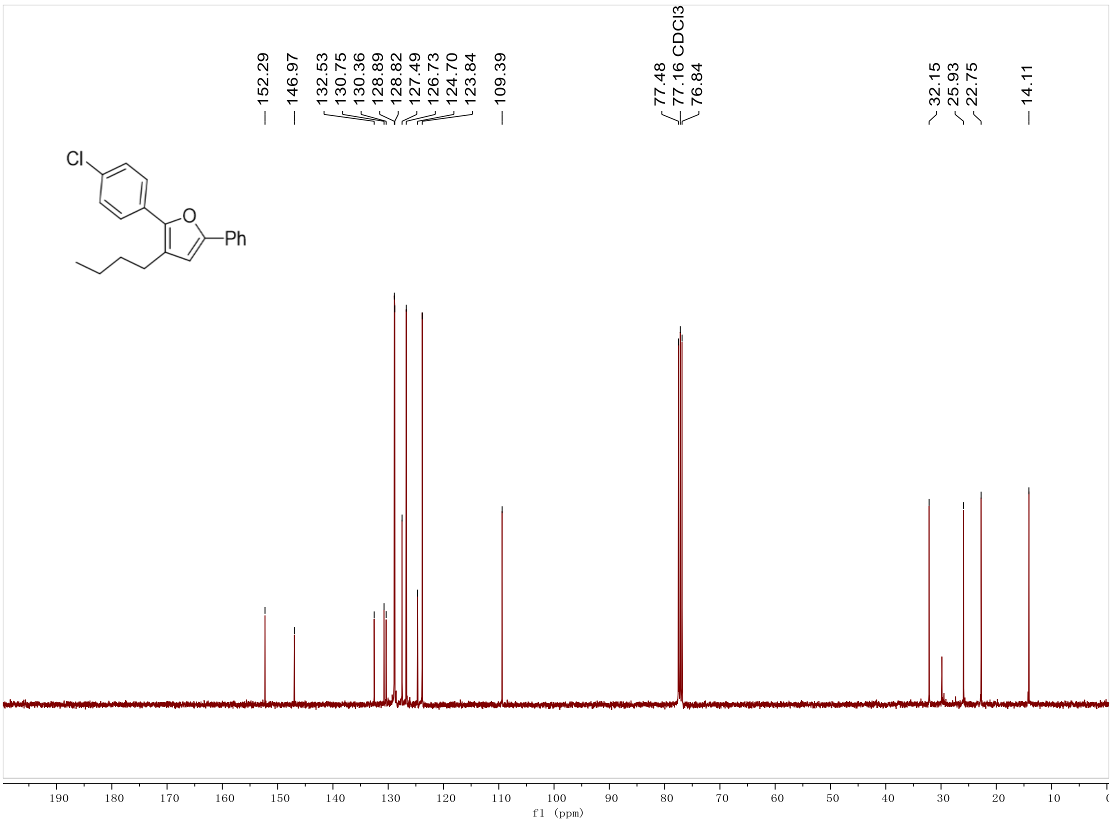
3bv ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



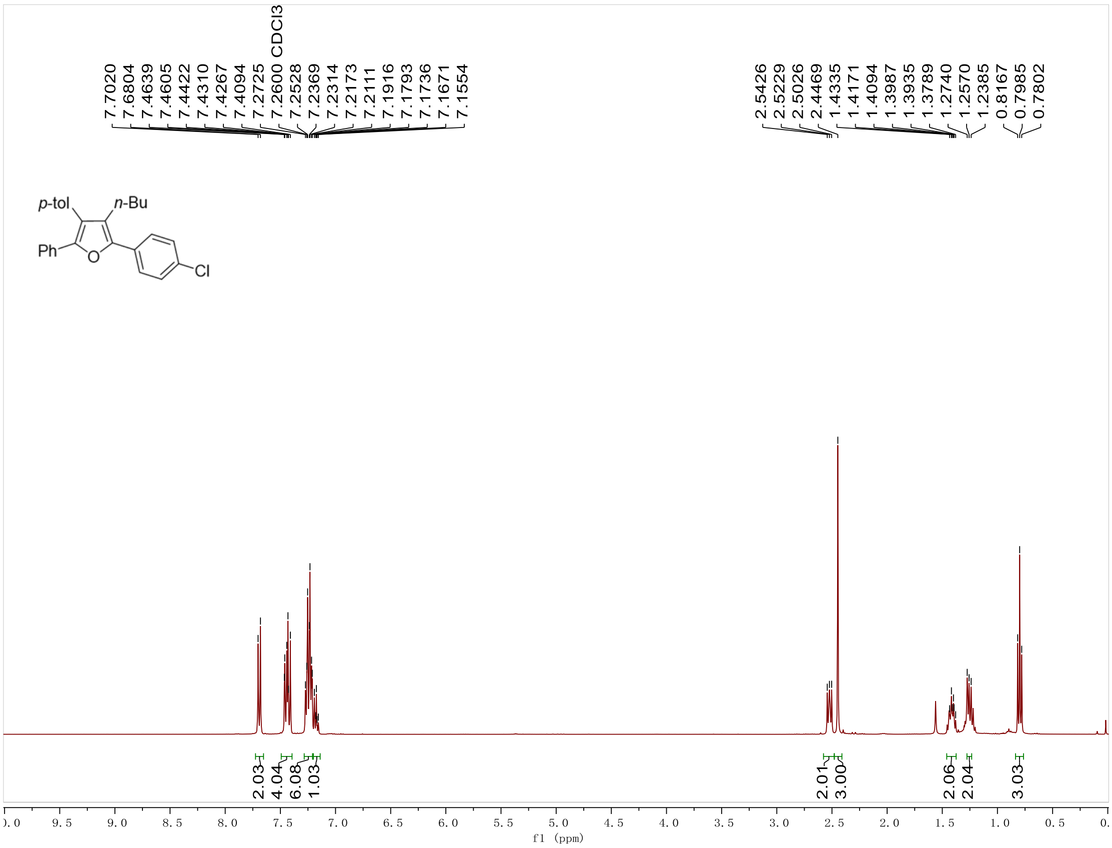


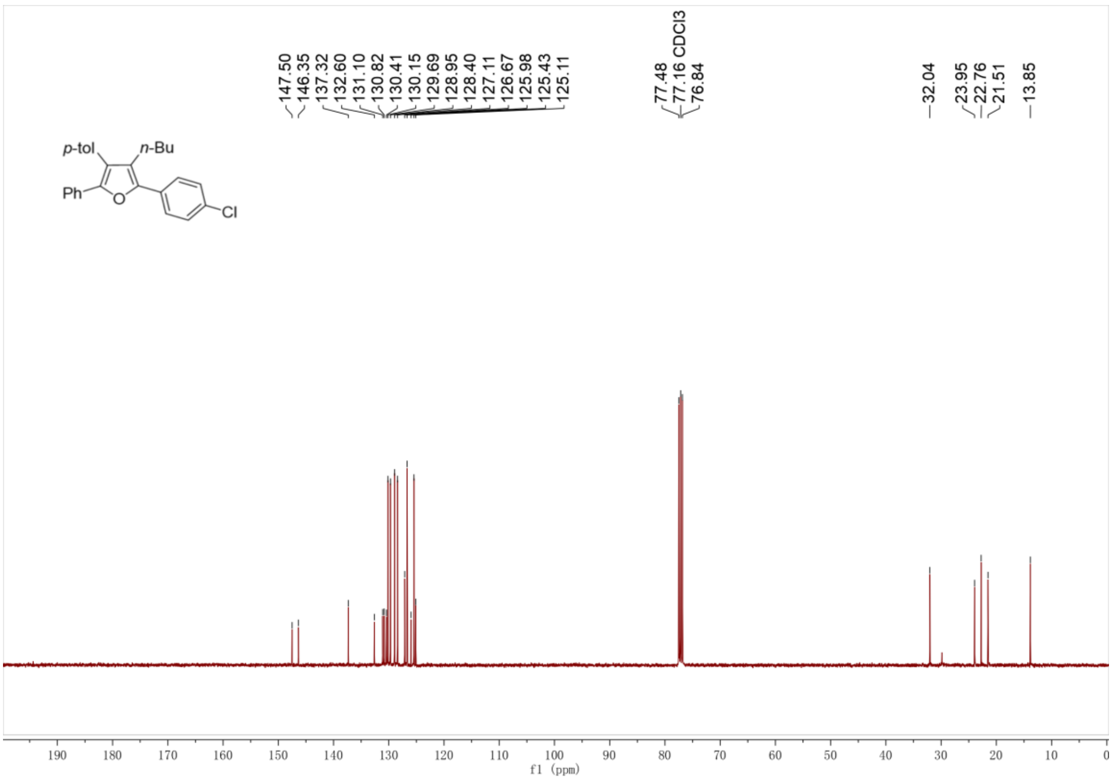
5 ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)





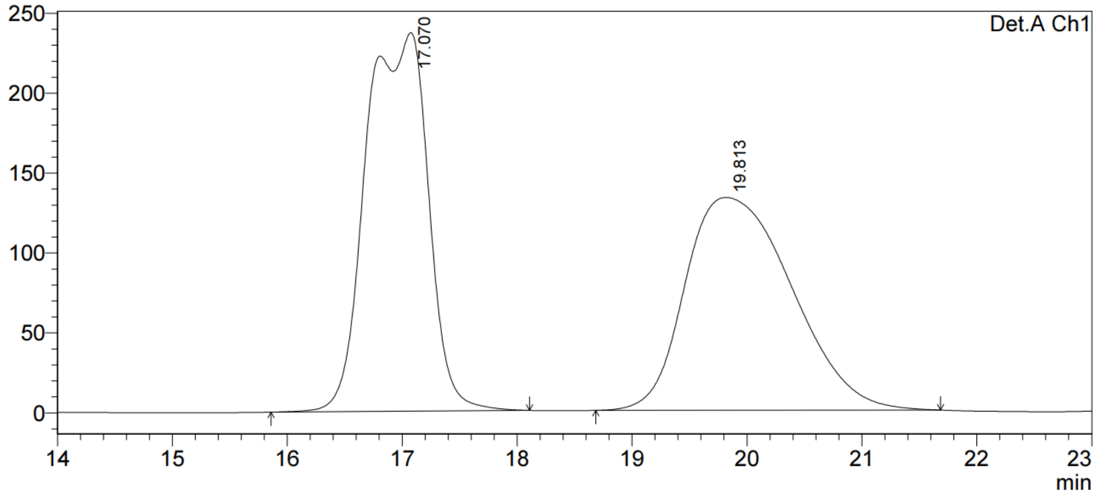
6 ^{1}H NMR (400 MHz, Chloroform-d)/ ^{13}C {1H}NMR (101 MHz, Chloroform-d)



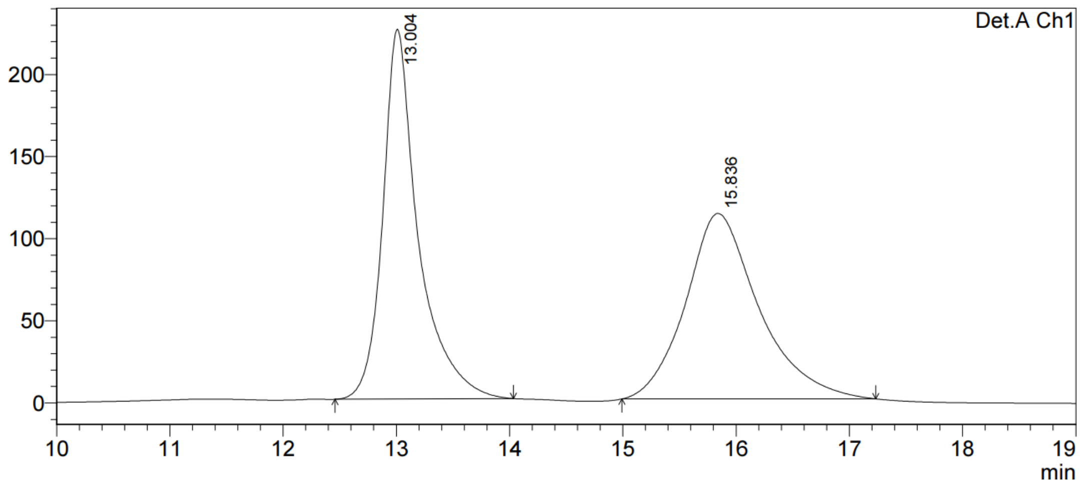


12. HPLC spectra for product 3af

3af (racemic)



Peak#	Ret. Time	Area	Height	Area %
1	17.070	8923211	236923	50.879
2	19.813	8614993	133165	49.121
Total		17538204	370088	100.000



Peak#	Ret. Time	Area	Height	Area %
1	13.004	4896614	225256	49.066
2	15.836	5082965	112926	50.934
Total		9979580	338182	100.000

13. Computational Studies

(1) General Computational Methods

Calculations were performed using Gaussian 16.[1] Due to the reliability of density functional theory in the mechanistic studies of organocatalytic reactions, [2,3] geometry optimizations of all structures were carried out with the (U)M06-2X meta-generalized gradient approximation (GGA) functional in combination with the def2SVP basis set.[4,5] The effect of ethylacetate solvent was evaluated using the IEFPCM implicit solvent model.[6] Harmonic vibrational frequencies at the same level of theory were calculated to characterize stationary points as either minima or transition state (TS) structures and to calculate the zero-point vibrational energy and thermal corrections. Free energies were evaluated at 25 °C and have been corrected to a standard liquid state of 1 mol/L. Single-point energies were evaluated at the (U)M06-2X/def2TZVP/IEFPCM (ethylacetate) level of theory. Molecular graphics were generated with CYLview20.[7]

References:

[1] M. J. Frisch , G. W. Trucks , H. B. Schlegel , G. E. Scuseria , M. A. Robb , J. R. Cheeseman , G. Scalmani , V. Barone , G. A. Petersson , H. Nakatsuji , X. Li , M. Caricato , A. V. Marenich , J. Bloino , B. G. Janesko , R. Gomperts , B. Mennucci , H. P. Hratchian , J. V. Ortiz , A. F. Izmaylov , J. L. Sonnenberg , F. Ding Williams , F. Lipparini , F. Egidi , J. Goings , B. Peng , A. Petrone , T. Henderson , D. Ranasinghe , V. G. Zakrzewski , J. Gao , N. Rega , G. Zheng , W. Liang , M. Hada , M. Ehara , K. Toyota , R. Fukuda , J. Hasegawa , M. Ishida , T. Nakajima , Y. Honda , O. Kitao , H. Nakai , T. Vreven , K. Throssell , J. A. Montgomery Jr. , J. E. Peralta , F. Ogliaro , M. J. Bearpark , J. J. Heyd , E. N. Brothers , K. N. Kudin , V. N. Staroverov , T. A. Keith , R. Kobayashi , J. Normand , K. Raghavachari , A. P. Rendell , J. C. Burant , S. S. Iyengar , J. Tomasi , M. Cossi , J. M. Millam , M. Klene , C. Adamo , R. Cammi , J. W. Ochterski , R. L. Martin , K. Morokuma , O. Farkas , J. B. Foresman and D. J. Fox , Gaussian 16, Revision A.03 , Gaussian, Inc., Wallingford, CT, 2016.

[2] Q. Shi, Z. Pei, J. Song, S.-J. Li, D. Wei, M. L. Coote and Y. Lan, J. Am. Chem. Soc., 2022, 144, 3137 —3145.

[3] S. Zhang, X. Wang, L.-L. Han, J. Li, Z. Liang, D. Wei, D. Du, Angew. Chem. Int., Ed., 2022, 61(52), e202212005.

[4] Y. Zhao, D. Truhlar, Theor. Chem. Acc., 2008, 120, 215-41.

[5] F. Wei, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297.

[6] A. Marenich, C. Cramer, D. Truhlar, J. Phys. Chem. B 2009, 113, 6378–6396.

[7] CYLview20; Legault, C. Y., Unversité de Sherbrooke: Sherbrooke, 2020 (http://www.cylview.org).

(2) Absolute SPE, GFEC, and GFE of the Optimized Structures

Table S1. The Single-Point Energies (SPE) Calculated at M06-2X/def2TZVP/IEF-PCM (ethylacetate) Level, Gibbs Free Energy Corrections (GFEC) Calculated at M06-2X/def2svp/IEF-PCM(DMSO) Level, and Gibbs Free Energies (GFE = SPE + GFEC) of the Stationary Points Involved in the Reaction Models.

Structure	SPE (a.u.)	GFEG (a.u.)	GFE (a.u.)
Int-3	-2035.8312	0.459577	-2035.371623
Int-4	-504.282612	0.197029	-504.085583
^{os}TS1′	-2540.126217	0.687766	-2539.438451
^{os}TS1	-2540.124983	0.685509	-2539.439474
Int-6′	-2540.140319	0.690481	-2539.449838
Int-6	-2540.145249	0.688156	-2539.457093
TS2′	-2540.129743	0.68897	-2539.440773
TS2	-2540.133317	0.688341	-2539.444976
4aa	-1308.894488	0.284182	-1308.610306
3aa	-1308.905704	0.282531	-1308.623173
NHC A’	-1231.2341	0.377954	-1230.856146

(3) Cartesian Coordinates of the Stationary Points

Int-3

C	-4.07890200	3.53760400	0.05369100
C	-2.72805200	4.23940100	-0.09190900
C	-1.63739800	3.73827600	0.86146000
C	-4.12089300	2.05979700	-0.33894700
C	-1.12268000	2.36826300	0.52790800
C	-3.32514100	1.11601500	0.57278600
C	-1.83629100	1.22225000	0.40109300
H	-4.81483300	4.07641400	-0.56235900
H	-2.87592300	5.31322400	0.09793000
H	-2.02800200	3.73880900	1.89420500
H	-3.77275300	1.93809500	-1.37858100
H	-3.57603600	1.33137100	1.62583300
C	0.29520700	0.38819400	-0.04741600
H	-4.42266300	3.63765700	1.09823300
H	-2.36745900	4.14725300	-1.12947100
H	-0.79406000	4.44316800	0.85281700
H	-5.17110800	1.73099300	-0.32119500
H	-3.63557100	0.07939300	0.38967200
N	-1.05036600	0.11403400	0.08664500
C	-1.56785400	-1.22842600	0.13477400
C	-2.29045800	-1.71819400	-0.96442800
C	-1.35911700	-1.98275700	1.29947100
C	-2.80020400	-3.01607400	-0.88183200
C	-1.87941500	-3.28126100	1.33252800
C	-2.59173000	-3.79549800	0.25380100
H	-3.35934500	-3.42841900	-1.72399000
H	-1.72430200	-3.89837900	2.21994900
H	-2.99013400	-4.81028000	0.29826000

C	-2.47222600	-0.89776100	-2.22854200
C	-3.92943600	-0.85619600	-2.69384900
H	-4.03139300	-0.18398700	-3.55849600
H	-4.28024800	-1.85123800	-3.00611000
H	-4.59799600	-0.49479400	-1.89789000
C	-0.57771700	-1.44696100	2.48759500
S	0.58072600	2.08277200	0.26283900
H	-2.16281900	0.13506700	-2.00863000
H	-0.36448600	-0.38306100	2.30765100
C	-1.54492300	-1.42941300	-3.32776800
H	-1.84357900	-2.44867300	-3.61911800
H	-1.59580100	-0.78950700	-4.22115100
H	-0.50882000	-1.46894200	-2.96436100
C	0.76408700	-2.17753100	2.61932700
H	1.37502500	-1.72444300	3.41416300
H	0.60252700	-3.23573700	2.87771300
H	1.32757100	-2.14494100	1.67608300
C	-1.38727000	-1.53472700	3.78447500
H	-0.82265100	-1.08726400	4.61544100
H	-2.34542800	-1.00286100	3.69214200
H	-1.60195200	-2.57990800	4.05314900
C	1.26674200	-0.55718800	-0.50490200
O	0.94192700	-1.65890600	-0.98628500
C	2.72310800	-0.19963800	-0.42744600
C	3.29433900	0.51939200	0.63024100
C	3.56155500	-0.69832100	-1.43415100
C	4.66551300	0.76757900	0.66695800
H	2.67532500	0.87155200	1.45717100
C	4.92926900	-0.45093800	-1.41624100
H	3.11810700	-1.29216100	-2.23423500

C	5.47007500	0.28765100	-0.36337300
H	5.11239300	1.31878500	1.49429800
H	5.58011000	-0.82693900	-2.20571500
Cl	7.18239400	0.59983500	-0.32864000

Int-4

C	1.11277800	-1.32105000	-0.15727500
C	-0.15287900	-0.79538400	-0.43273800
C	2.29965600	-0.52539200	-0.01071000
C	-1.26094800	-0.33773800	-0.67893000
C	-2.59719100	0.19679500	-0.93925800
C	2.27936000	0.88370900	-0.13609200
C	3.44460800	1.62394400	0.01106700
C	4.65971700	0.98689300	0.28609600
C	4.69733400	-0.40534400	0.41325600
C	3.53627700	-1.15311300	0.26752400
C	-3.60051900	-0.10962400	0.18145900
C	-4.98665700	0.45276200	-0.11491400
C	-5.98967800	0.15505400	0.99340600
H	1.33158100	1.38102300	-0.35067400
H	3.41060600	2.71006500	-0.08888000
H	5.57247000	1.57304500	0.40071700
H	5.64174900	-0.90799400	0.62782500
H	3.56779900	-2.24016100	0.36722800
H	-2.52632400	1.28668100	-1.08477400
H	-2.97235200	-0.21901500	-1.88939100
H	-3.66175900	-1.20082200	0.32220000
H	-3.22192000	0.30755800	1.12847100
H	-4.90940100	1.54219500	-0.26642500
H	-5.34892400	0.03556000	-1.06912100

H	-6.10082500	-0.92946600	1.14181800
H	-5.65988000	0.58963100	1.94891000
H	1.20745100	-2.40404600	-0.04579600
H	-6.98141900	0.56666700	0.76054200

^{os}TS1′

C	4.71126700	-0.01745200	-2.96079100
C	3.52185900	-0.65020700	-3.68169300
C	2.61234000	-1.49469700	-2.78351000
C	4.36953700	1.04066300	-1.91085300
C	1.79827500	-0.69345900	-1.80961600
C	3.68599800	0.51047400	-0.64135300
C	2.24205800	0.14928400	-0.84337000
H	5.36549800	0.44562500	-3.71479000
H	3.90487500	-1.30084100	-4.48195900
H	3.22955200	-2.21821300	-2.22088300
H	3.73635100	1.81978800	-2.36497400
H	4.23058200	-0.38544700	-0.29452700
C	-0.04841500	0.33948300	-0.48974200
H	5.30909500	-0.81496600	-2.48482100
H	2.91846900	0.13252100	-4.16963400
H	1.93064900	-2.09078300	-3.40715900
H	5.30310500	1.53323700	-1.60111000
H	3.76771900	1.25609300	0.15955700
N	1.20462700	0.71746400	-0.09509500
C	1.48378100	1.75471600	0.87893700
C	1.42732200	3.09281300	0.45074600
C	1.87869600	1.39263500	2.17831200
C	1.72646400	4.08678600	1.38506000
C	2.17564900	2.42805700	3.07313600

C	2.09102500	3.76107600	2.68854600
H	1.67620000	5.13536900	1.08471800
H	2.48065300	2.17946900	4.09137200
H	2.32031000	4.55137700	3.40483100
C	1.07616100	3.49037400	-0.97388200
C	2.21424900	4.29811600	-1.60965800
H	2.00489600	4.48036000	-2.67386400
H	2.32242800	5.27677600	-1.11829900
H	3.17807000	3.77547600	-1.52926000
C	2.02890400	-0.04896700	2.64098800
S	0.06808800	-0.76638400	-1.80465900
H	0.94417100	2.57388600	-1.56967400
H	1.60787600	-0.70821900	1.86749600
C	-0.23708000	4.27888300	-1.02974500
H	-0.13354200	5.23660200	-0.49641200
H	-0.50268800	4.50229700	-2.07349500
H	-1.05198200	3.71292800	-0.56104500
C	1.27998600	-0.31088600	3.95454200
H	1.23186900	-1.39275500	4.14750400
H	1.80146300	0.15589600	4.80392000
H	0.25317400	0.07900400	3.93535900
C	3.50625600	-0.42453000	2.82008000
H	3.59167500	-1.46812100	3.15776600
H	4.07723800	-0.32052400	1.88859500
H	3.97894300	0.21705200	3.57983500
C	-1.30151600	0.90624700	0.02387200
O	-1.29400700	1.82609000	0.84930100
C	-2.58978500	0.54977200	-0.66290900
C	-2.92511800	-0.72154800	-1.14770900
C	-3.54554500	1.57166500	-0.74532500

C	-4.16278600	-0.95638000	-1.74069500
H	-2.24683900	-1.56547500	-1.01126800
C	-4.78427500	1.35404900	-1.33840900
H	-3.30083800	2.54751700	-0.32511300
C	-5.08029600	0.08674600	-1.83779400
H	-4.42810400	-1.95014700	-2.10140000
H	-5.52199900	2.15318100	-1.41039100
Cl	-6.63018300	-0.20288800	-2.57654300
C	-1.09671400	-1.10161800	1.58628000
C	-0.32395900	-2.14494100	1.05294800
C	-2.49830700	-1.23134600	1.90876700
C	0.39950300	-2.94713900	0.47719300
C	1.39998200	-3.83928600	-0.11240200
C	-3.24534100	-2.38155300	1.57229500
C	-4.61136800	-2.44360500	1.82260800
C	-5.27464100	-1.36194400	2.40936900
C	-4.54691100	-0.21934000	2.75597600
C	-3.17830500	-0.15397300	2.52025700
C	2.81446700	-3.47843000	0.36066300
C	3.89643000	-4.35813500	-0.25515900
C	5.29939000	-3.91604300	0.14379300
H	-2.73261900	-3.22601100	1.10553100
H	-5.16871200	-3.34353500	1.55495500
H	-6.34741600	-1.41155900	2.60124900
H	-5.05497600	0.62937900	3.21808300
H	-2.61343100	0.74535500	2.77433100
H	1.17784600	-4.88894900	0.14117700
H	1.35633200	-3.77356600	-1.21417300
H	3.00605500	-2.41830900	0.11681200
H	2.85413700	-3.54894900	1.46008700

H	3.72913200	-5.40457300	0.04827300
H	3.79859400	-4.34269800	-1.35441900
H	5.49914000	-2.88970700	-0.20248700
H	5.41831200	-3.92600200	1.23771100
H	-0.56298700	-0.27664300	2.05641000
H	6.06967600	-4.57107400	-0.28592600

^{os}TS1

C	-4.87681700	3.21539200	-1.09818100
C	-3.50796200	3.76091500	-1.50679500
C	-2.39239700	3.54947700	-0.47618300
C	-4.98965200	1.69541700	-0.96834500
C	-1.95621000	2.11987400	-0.34229800
C	-4.20423500	1.07990800	0.19860200
C	-2.72188300	1.02862500	-0.03661800
H	-5.61548700	3.55076000	-1.84194600
H	-3.60596100	4.84317200	-1.67937900
H	-2.72501400	3.92495200	0.50779700
H	-4.67769300	1.21392700	-1.91012000
H	-4.38792100	1.67525400	1.10936800
C	-0.66047200	0.00943600	-0.28768100
H	-5.17545600	3.67732000	-0.14089100
H	-3.19831700	3.31398800	-2.46572100
H	-1.51828100	4.15584100	-0.75479800
H	-6.05001100	1.44100900	-0.82338000
H	-4.57592300	0.06857900	0.40385000
N	-2.00153600	-0.14330800	-0.00403100
C	-2.66921500	-1.40994300	0.19122800
C	-3.24773000	-2.03618000	-0.92227800
C	-2.77677700	-1.91170700	1.49385200

C	-3.96366500	-3.21609000	-0.69505700
C	-3.50897000	-3.08836900	1.67345400
C	-4.09812200	-3.73533400	0.59012800
H	-4.42426300	-3.73633600	-1.53640700
H	-3.61412700	-3.50713400	2.67656100
H	-4.66533700	-4.65394600	0.74773300
C	-3.05889200	-1.49669600	-2.33006800
C	-4.33868000	-1.56214000	-3.16594800
H	-4.18933700	-1.04249900	-4.12338100
H	-4.61546900	-2.60125300	-3.39779800
H	-5.18611500	-1.09224700	-2.64548400
C	-2.10745600	-1.22757000	2.67115600
S	-0.30603900	1.65967500	-0.49730800
H	-2.76772800	-0.43695600	-2.25288200
H	-1.50738300	-0.39064500	2.28442700
C	-1.91184400	-2.24191500	-3.02573900
H	-2.17394400	-3.30370400	-3.15338500
H	-1.71781400	-1.81292500	-4.01967000
H	-0.98829200	-2.19611500	-2.43232400
C	-1.13712600	-2.18227800	3.37025700
H	-0.55993800	-1.64351800	4.13691500
H	-1.67409500	-3.00599800	3.86583300
H	-0.43820400	-2.60995200	2.63837100
C	-3.14327600	-0.66112400	3.64666200
H	-2.64409200	-0.14125500	4.47747000
H	-3.81529100	0.05270300	3.14777400
H	-3.76148900	-1.46628000	4.07317400
C	0.27325000	-1.11728000	-0.31976800
O	-0.11960300	-2.23414400	0.02016700
C	1.64028900	-1.01518900	-0.95728100

C	2.38873800	0.14887000	-1.18786300
C	2.22295700	-2.24807800	-1.28479600
C	3.67626900	0.08357700	-1.71079000
H	2.02624200	1.13587500	-0.90842100
C	3.51120100	-2.33148500	-1.80553500
H	1.64651600	-3.15469200	-1.10199900
C	4.23406700	-1.15993300	-2.00688500
H	4.25771600	0.99371700	-1.86049600
H	3.95833200	-3.29708800	-2.04271200
Cl	5.86454100	-1.24955200	-2.60711800
C	0.84601400	2.23936300	1.80792800
C	1.22033500	0.91921300	1.99366000
C	1.73945000	3.25671500	1.27577900
C	1.48002300	-0.28791700	1.96264600
C	2.08904700	-1.60572400	2.15186100
C	1.28732100	4.58582500	1.13555900
C	2.09857600	5.56736100	0.57393100
C	3.38699400	5.25582300	0.13300600
C	3.85375000	3.94550900	0.27318900
C	3.04823800	2.96092800	0.83688300
C	3.58722700	-1.58865500	1.81459900
C	4.20416400	-2.98177800	1.77801900
C	5.66437800	-2.95423200	1.34145600
H	0.28146500	4.84124000	1.47960800
H	1.72243700	6.58808400	0.48075000
H	4.02187500	6.02482900	-0.30854800
H	4.86353800	3.68943000	-0.05466200
H	3.42691900	1.94229200	0.95464100
H	3.72743600	-1.10954100	0.83245000
H	4.11724200	-0.95726300	2.54700400

H	4.11180300	-3.45439600	2.77028500
H	3.62113700	-3.60831500	1.08147600
H	5.76009000	-2.52441100	0.33143800
H	6.26770800	-2.33564900	2.02314400
H	-0.06976400	2.59145800	2.29360500
H	1.93640100	-1.94644600	3.18958700
H	1.57458700	-2.34578100	1.50822900
H	6.10287000	-3.96184700	1.32325100

Int-6′

C	4.71042200	0.67321200	3.22102800
C	3.56168900	1.61594500	3.57878900
C	2.84663900	2.24099100	2.37571700
C	4.31959200	-0.61642600	2.49704500
C	2.01240200	1.26614900	1.59730100
C	3.81784600	-0.42945400	1.05609500
C	2.42316200	0.12126900	0.98805300
H	5.23013200	0.39863000	4.15119900
H	3.96236300	2.43549300	4.19337200
H	3.59133400	2.68876200	1.69563800
H	3.55602500	-1.15354300	3.08269500
H	4.50159100	0.25911700	0.53242100
C	0.16446900	0.02514500	0.50421100
H	5.44810200	1.22012300	2.60830600
H	2.82139000	1.08665600	4.20046700
H	2.20282600	3.06404700	2.71541700
H	5.20311200	-1.27090500	2.45668100
H	3.85818800	-1.38320600	0.51261600
N	1.36227400	-0.54818600	0.35993000
C	1.59762600	-1.74650000	-0.43561400

C	1.55799600	-2.99887100	0.19746900
C	1.92257900	-1.58151500	-1.79156800
C	1.80300800	-4.12214200	-0.59488300
C	2.15763600	-2.74200400	-2.53970100
C	2.08704600	-3.99970300	-1.95268100
H	1.76827200	-5.11312800	-0.13823400
H	2.40647000	-2.65349400	-3.59820200
H	2.26800100	-4.89189500	-2.55394300
C	1.31265600	-3.17206900	1.68523200
C	2.55684600	-3.76663300	2.35920000
H	2.43105000	-3.77995800	3.45207900
H	2.71477100	-4.80428500	2.02766700
H	3.46897600	-3.20016100	2.12362200
C	2.09664600	-0.21793100	-2.44425100
S	0.30550900	1.45325500	1.41786600
H	1.11806700	-2.17885100	2.11890300
H	1.61400100	0.53812100	-1.80767900
C	0.08505700	-4.04334400	1.96547500
H	0.23946800	-5.06715600	1.59056200
H	-0.08572000	-4.11014500	3.05064300
H	-0.79004800	-3.59941700	1.47686900
C	1.45048900	-0.12742300	-3.82955100
H	1.48375600	0.91312800	-4.18497000
H	1.98950800	-0.74452900	-4.56386800
H	0.39847100	-0.44417400	-3.81851100
C	3.58819300	0.12839600	-2.54531700
H	3.72370300	1.12260200	-2.99701400
H	4.07460700	0.13018900	-1.56123800
H	4.10950900	-0.60667100	-3.17765000
C	-1.19982100	-0.60610100	0.02305200

O	-1.16103200	-1.90077800	0.16710100
C	-2.32434100	0.07714000	0.86176400
C	-2.74412300	1.40781800	0.72986000
C	-2.96529300	-0.73121300	1.80249600
C	-3.76783200	1.92073600	1.52641800
H	-2.28016200	2.06532400	-0.00641400
C	-3.98794100	-0.23579500	2.60921500
H	-2.64073700	-1.76990600	1.86945400
C	-4.37897900	1.09264000	2.46422100
H	-4.09610500	2.95473300	1.41835300
H	-4.48585600	-0.87076600	3.34271800
Cl	-5.65948500	1.72818600	3.46534700
C	-1.35862000	-0.19320900	-1.53872400
C	-0.94531000	1.17362700	-1.85639300
C	-2.73856400	-0.57162700	-2.02968200
C	-0.50801800	2.28861700	-2.04959000
C	0.13184300	3.59774100	-2.20635600
C	-3.69221200	0.38714800	-2.38627300
C	-4.96830300	0.00208700	-2.79971000
C	-5.30680100	-1.34910500	-2.86138600
C	-4.35975500	-2.31217900	-2.50784400
C	-3.08434600	-1.92848700	-2.09737200
C	1.63947600	3.52113700	-1.93335800
C	2.33415800	4.87437200	-2.02969700
C	3.83309000	4.77898100	-1.77037500
H	-3.42943200	1.44607000	-2.34187900
H	-5.70013200	0.76323900	-3.07615800
H	-6.30367800	-1.65153700	-3.18667400
H	-4.61634800	-3.37215700	-2.55506500
H	-2.34086100	-2.66458600	-1.79284700

H	-0.04332800	3.98493000	-3.22280800
H	-0.33442300	4.31879100	-1.51474900
H	1.80008600	3.08644600	-0.93059200
H	2.09552900	2.81826300	-2.65032300
H	2.15380000	5.30236000	-3.02961000
H	1.87225300	5.57062700	-1.31028000
H	4.03268200	4.37557700	-0.76585400
H	4.31580200	4.11018300	-2.49900300
H	-0.63328200	-0.88056000	-2.00192900
H	4.31986400	5.76139300	-1.84116700

Int-6

C	-4.59628900	-3.38900800	2.05022700
C	-3.20707100	-3.73834400	2.58425800
C	-2.10084300	-3.76541800	1.52362300
C	-4.77051300	-1.96788100	1.51152200
C	-1.73047400	-2.40688800	1.00464200
C	-4.02116100	-1.66920500	0.20318200
C	-2.54310100	-1.49856200	0.40029700
H	-5.32298200	-3.53761200	2.86295500
H	-3.25250000	-4.73550100	3.04632300
H	-2.42089600	-4.39171100	0.67377400
H	-4.46576500	-1.23970900	2.28062400
H	-4.19604200	-2.50000900	-0.50052200
C	-0.56930600	-0.29988900	0.41205700
H	-4.86989200	-4.10894900	1.25932500
H	-2.92306800	-3.03238700	3.38156000
H	-1.20224000	-4.24206500	1.93880000
H	-5.84151700	-1.79849200	1.32471800
H	-4.42941800	-0.76639800	-0.27105300

N	-1.85446400	-0.32687800	0.05546100
C	-2.50462900	0.74029700	-0.69206200
C	-3.19009300	1.74060900	0.01542200
C	-2.46793900	0.67706300	-2.09276100
C	-3.82591600	2.73111100	-0.73407900
C	-3.11737300	1.70088900	-2.79533300
C	-3.78226000	2.72108000	-2.12640800
H	-4.36008400	3.53012600	-0.21625700
H	-3.10821200	1.68921500	-3.88601400
H	-4.27985400	3.50963100	-2.69289600
C	-3.28947000	1.76988300	1.52963000
C	-4.75154400	1.62193900	1.97143000
H	-4.81343200	1.52377300	3.06547700
H	-5.33334500	2.51040900	1.68206600
H	-5.23625200	0.74539700	1.51846500
C	-1.83506500	-0.47486200	-2.85919100
S	-0.13822800	-1.75753600	1.17318600
H	-2.71443200	0.91978700	1.92900000
H	-1.14111000	-0.99690000	-2.18408100
C	-2.68056500	3.04964300	2.11112700
H	-3.25057300	3.93380600	1.78545000
H	-2.71844400	3.01682000	3.21062600
H	-1.64074700	3.13880700	1.77421700
C	-1.03276000	0.00233500	-4.07219500
H	-0.47553700	-0.83849600	-4.51024200
H	-1.69415700	0.39736900	-4.85762700
H	-0.31483300	0.78524100	-3.79486600
C	-2.91110600	-1.47466800	-3.30142800
H	-2.45252000	-2.31858400	-3.83759500
H	-3.47206100	-1.87508800	-2.44671000

H	-3.63019200	-0.98851600	-3.97848300
C	0.36076300	0.95758000	0.24534000
O	-0.33555900	2.04618900	0.42305600
C	1.51913800	0.78393000	1.28444000
C	2.54794300	-0.15804900	1.18172400
C	1.49630300	1.63159600	2.39328200
C	3.53276000	-0.25925900	2.16392300
H	2.59891600	-0.83110600	0.32424000
C	2.47309000	1.54887500	3.38396800
H	0.69330300	2.36798000	2.44461000
C	3.48536600	0.59957900	3.25938500
H	4.33540000	-0.99239800	2.07682000
H	2.45869400	2.21449300	4.24758300
Cl	4.71594600	0.48848600	4.49126400
C	1.68483200	-1.44596900	-2.28693700
C	1.34797600	-0.27975000	-1.76428300
C	3.01868400	-2.07019400	-2.17093500
C	0.98652700	0.84995000	-1.21326100
C	1.13446400	2.18658600	-1.89381700
C	3.18423700	-3.42241100	-2.50477300
C	4.42786800	-4.04088200	-2.38461600
C	5.53050900	-3.31677500	-1.93154900
C	5.38112300	-1.96561300	-1.60837000
C	4.14051900	-1.34660000	-1.73196100
C	2.18113200	3.07206900	-1.21441800
C	2.32683100	4.43185900	-1.89027900
C	3.36411300	5.31957200	-1.21206200
H	2.32304200	-3.99389300	-2.85831700
H	4.53574200	-5.09478200	-2.64645800
H	6.50432000	-3.79945100	-1.83755600

H	6.24099000	-1.38743900	-1.26581100
H	4.02955400	-0.28545900	-1.49584700
H	1.88521300	3.21091800	-0.16290700
H	3.15568700	2.55215100	-1.21169000
H	2.59607000	4.28650200	-2.95031500
H	1.34633100	4.93654300	-1.88984900
H	3.09841500	5.49599300	-0.15891900
H	4.35723800	4.84542300	-1.22752600
H	0.92905000	-2.01602100	-2.84266500
H	1.39671200	2.04046600	-2.95328700
H	0.15162800	2.68058000	-1.82963300
H	3.44990400	6.29717700	-1.70723100

TS2′

C	-5.14138800	2.65872600	-0.44635200
C	-4.05042300	3.48730100	0.23321600
C	-3.21366400	2.72671300	1.26741700
C	-4.65960100	1.53414100	-1.36509900
C	-2.28839100	1.70750300	0.66892400
C	-3.99059300	0.35078800	-0.65104000
C	-2.61544500	0.66380200	-0.13758400
H	-5.76810800	3.34021900	-1.04129500
H	-4.52845000	4.33598800	0.74492300
H	-3.88670500	2.22130700	1.98161000
H	-3.96763600	1.94320600	-2.11958900
H	-4.63062100	0.04069600	0.19278200
C	-0.29799400	0.34055200	-0.03390800
H	-5.80341100	2.23144000	0.32720500
H	-3.37749900	3.91518600	-0.52786200
H	-2.61962700	3.44017100	1.85539100

H	-5.52871000	1.14276000	-1.91547800
H	-3.93163700	-0.51410000	-1.32708600
N	-1.47475000	-0.07929300	-0.50128800
C	-1.54039200	-1.28205800	-1.30983300
C	-1.59169000	-1.16238400	-2.70599200
C	-1.52757100	-2.52481300	-0.64978200
C	-1.60080900	-2.34397000	-3.45516700
C	-1.53250500	-3.67499900	-1.44423700
C	-1.56189100	-3.58687000	-2.83403000
H	-1.63056200	-2.28517000	-4.54498300
H	-1.51530000	-4.65623300	-0.96888800
H	-1.55992800	-4.49676800	-3.43607800
C	-1.65162700	0.17691900	-3.41991800
C	-2.94743600	0.30305900	-4.23091100
H	-3.03142700	1.31160900	-4.66238100
H	-2.95523700	-0.41804300	-5.06231900
H	-3.83980600	0.11574600	-3.61678400
C	-1.58289700	-2.62724500	0.86650000
S	-0.56612900	1.73127500	0.91106800
H	-1.64275500	0.97349100	-2.65908800
H	-1.10080600	-1.73273800	1.28456800
C	-0.43075200	0.38265000	-4.32345500
H	-0.44531300	-0.33272200	-5.16051200
H	-0.44214000	1.39635400	-4.75119400
H	0.49376800	0.22935000	-3.75265600
C	-0.83779300	-3.84000800	1.42409100
H	-0.78593400	-3.76867400	2.52044300
H	-1.35185300	-4.78201500	1.18050400
H	0.19190800	-3.89990800	1.04229400
C	-3.04351500	-2.63722200	1.33619100

H	-3.09596900	-2.69353300	2.43389400
H	-3.57675700	-1.73103400	1.01715400
H	-3.57465400	-3.50782000	0.92118100
C	1.57183000	-0.29811200	-0.73782400
O	1.41410300	-0.66392100	-1.90812400
C	2.24673400	1.05013900	-0.49812100
C	2.87605600	1.42121600	0.69405800
C	2.22746000	1.96141300	-1.56031800
C	3.45800200	2.68256900	0.83112900
H	2.91902100	0.73270300	1.53666200
C	2.79567400	3.22449000	-1.43761300
H	1.74696000	1.65982800	-2.49196700
C	3.40673900	3.57581000	-0.23405700
H	3.95155100	2.97145500	1.75903800
H	2.77394700	3.93597300	-2.26326100
Cl	4.12478800	5.15521600	-0.06605000
C	1.83451000	-1.44256900	0.30274800
C	1.42480700	-1.15703300	1.67919600
C	3.27576700	-1.92674200	0.16650700
C	1.01102100	-0.89476800	2.78765000
C	0.36986900	-0.51427200	4.04930300
C	4.18786000	-1.86149200	1.22384800
C	5.50125100	-2.30610300	1.05998700
C	5.91875900	-2.82507500	-0.16386600
C	5.01257100	-2.89840000	-1.22364100
C	3.70249400	-2.45421700	-1.06033900
C	-1.15268200	-0.68785000	3.97883800
C	-1.86797100	-0.21699700	5.23944800
C	-3.37817800	-0.40395300	5.15265100
H	3.86410100	-1.46800300	2.18929100

H	6.19895700	-2.24798500	1.89714600
H	6.94447000	-3.17456700	-0.29201000
H	5.32805800	-3.30720200	-2.18512600
H	2.99278100	-2.49742900	-1.88730700
H	0.77712000	-1.11021000	4.88138400
H	0.61228600	0.53848300	4.27103400
H	-1.53533100	-0.13199000	3.10448500
H	-1.38170400	-1.75067900	3.79414000
H	-1.47105600	-0.76553200	6.10964400
H	-1.63143400	0.84601800	5.41258900
H	-3.79210100	0.14899900	4.29523200
H	-3.63561100	-1.46553100	5.01847300
H	1.17725800	-2.24243600	-0.07743000
H	-3.88420200	-0.04713300	6.06032100

TS2

C	-5.12016100	-3.48027900	-0.55243400
C	-3.82161600	-4.23931600	-0.27554800
C	-2.62310500	-3.79736000	-1.12235000
C	-5.13594800	-2.00315900	-0.15447700
C	-2.09180300	-2.44100900	-0.76023800
C	-4.23736600	-1.08976700	-1.00007900
C	-2.77203600	-1.26542200	-0.72521100
H	-5.93463400	-3.98732400	-0.01321600
H	-3.99689500	-5.30757800	-0.47237500
H	-2.90971500	-3.79654700	-2.18814100
H	-4.86194400	-1.90248300	0.90859300
H	-4.43152500	-1.29412600	-2.06710800
C	-0.66302100	-0.49133400	-0.05332600
H	-5.36469200	-3.56555100	-1.62583400

H	-3.55861300	-4.15332500	0.79152500
H	-1.81203600	-4.53194100	-1.02182100
H	-6.16801400	-1.63242300	-0.24825100
H	-4.50857300	-0.03754900	-0.83370400
N	-1.93539000	-0.20139500	-0.33645600
C	-2.39452100	1.17087800	-0.25093000
C	-3.09929900	1.57722200	0.89050600
C	-2.08492900	2.04266000	-1.31020000
C	-3.46806100	2.92397500	0.97650500
C	-2.47008800	3.37949500	-1.17310100
C	-3.14616100	3.81921800	-0.03698800
H	-4.00678400	3.27611700	1.85842900
H	-2.24093000	4.09011300	-1.96751200
H	-3.43149900	4.86854100	0.05246600
C	-3.47055000	0.62167900	2.01182000
C	-4.98549700	0.60682200	2.24551300
H	-5.24815700	-0.16025000	2.98915600
H	-5.33243200	1.57711900	2.63165200
H	-5.54151600	0.39405200	1.32067400
C	-1.44142700	1.54453700	-2.59508000
S	-0.44409800	-2.16405000	-0.27711700
H	-3.16391000	-0.39342600	1.71572100
H	-0.77716700	0.70902100	-2.33218600
C	-2.72245000	0.96855700	3.30320400
H	-3.04168100	1.95347600	3.67885400
H	-2.94061600	0.22295400	4.08214200
H	-1.64193300	1.00810600	3.11570300
C	-0.59513900	2.60669600	-3.29568900
H	-0.03510500	2.15230500	-4.12585400
H	-1.22196300	3.40252600	-3.72556200

H	0.12559700	3.06575400	-2.60465400
C	-2.51831200	1.00891300	-3.54758300
H	-2.05851700	0.62403900	-4.46988400
H	-3.09599300	0.19475800	-3.08907900
H	-3.22078800	1.81118800	-3.82105300
C	0.64803300	0.89413800	0.90063900
O	-0.05518300	1.64581800	1.58122900
C	1.45507000	-0.18686900	1.62035400
C	2.32301000	-1.07474500	0.97515800
C	1.31857600	-0.26946200	3.00858200
C	3.03361300	-2.03190200	1.69540800
H	2.44415600	-1.03887000	-0.10790100
C	2.02216300	-1.22025500	3.74535800
H	0.65056900	0.43445800	3.50601700
C	2.87568300	-2.09612500	3.07866400
H	3.70792900	-2.72361800	1.18993600
H	1.91788000	-1.28335500	4.82875500
Cl	3.76395900	-3.28910000	3.98743200
C	1.97323100	0.19585500	-2.51977700
C	1.65235200	0.85891600	-1.42614300
C	3.25665400	-0.50353000	-2.73491500
C	1.31485000	1.51773000	-0.34608800
C	1.60429700	2.99462000	-0.18688100
C	3.40183400	-1.36003500	-3.83551300
C	4.59448900	-2.04912300	-4.05069000
C	5.66375400	-1.89192500	-3.16914500
C	5.53366500	-1.03429600	-2.07382600
C	4.34461200	-0.34308800	-1.86039700
C	2.66828000	3.27147500	0.87736000
C	2.93221400	4.76126400	1.07331100

C	3.99749100	5.03902000	2.12766000
H	2.56567000	-1.48762300	-4.52653000
H	4.68832800	-2.71283000	-4.91175600
H	6.59760500	-2.43052300	-3.33635400
H	6.36849200	-0.89791100	-1.38443400
H	4.24980400	0.33774600	-1.01091000
H	2.34596400	2.82727600	1.83361900
H	3.60606400	2.76323800	0.59236800
H	3.23550700	5.20542600	0.11029500
H	1.98884400	5.25731100	1.35574900
H	3.70028800	4.62528300	3.10302100
H	4.95606200	4.57568400	1.84915300
H	1.23685000	0.12537600	-3.33040300
H	1.92499300	3.41517400	-1.15182600
H	0.65893000	3.47806300	0.10809400
H	4.16928000	6.11686700	2.25673500

4aa

C	-0.58203500	-0.46902800	1.74927200
O	-0.72970700	-0.54377700	2.94608400
C	-1.14811200	0.68180600	0.97455600
C	-1.09214500	0.77166600	-0.42210000
C	-1.77281300	1.70228400	1.70343900
C	-1.64948100	1.86397500	-1.08084600
H	-0.61503600	-0.01091500	-1.01093700
C	-2.32935600	2.79986800	1.05887800
H	-1.81320600	1.61842600	2.78984900
C	-2.26103500	2.86918800	-0.33321000
H	-1.61300700	1.94057500	-2.16708500
H	-2.81433500	3.59817300	1.62020700

Cl	-2.95254400	4.23563000	-1.15142200
C	0.17379700	-1.59531000	1.01523100
C	1.34182000	-1.07427000	0.29797200
C	-0.79170600	-2.42366800	0.16780300
C	2.30991200	-0.62690600	-0.27613400
C	3.49531800	-0.07921100	-0.94132700
C	-0.52247800	-2.75813600	-1.16072200
C	-1.42776900	-3.53121200	-1.88947600
C	-2.60872400	-3.97601500	-1.29736300
C	-2.88034500	-3.64790200	0.03180200
C	-1.97611100	-2.87800000	0.76017800
C	4.63381300	0.24801200	0.03202300
C	5.85759400	0.81495800	-0.67951000
C	6.99505200	1.14292100	0.28045900
H	0.40185700	-2.41033900	-1.62585700
H	-1.20605200	-3.78631300	-2.92689300
H	-3.31627600	-4.57805800	-1.86913500
H	-3.80006100	-3.99448900	0.50530100
H	-2.18888100	-2.62941900	1.80288000
H	3.84842700	-0.80144900	-1.69486600
H	3.20733600	0.82956000	-1.49396900
H	4.27120900	0.96839200	0.78296300
H	4.91134900	-0.66499000	0.58314600
H	6.20339800	0.09040300	-1.43538200
H	5.56445000	1.72109300	-1.23522500
H	6.67714800	1.88622400	1.02682700
H	7.32153900	0.24393000	0.82438800
H	0.53374600	-2.23670800	1.83474100
H	7.86613600	1.55029200	-0.25099100

3aa

C	-0.76056000	-1.85578600	-0.70235300
O	-1.27269400	-2.95159000	-0.78897000
C	0.68454600	-1.72421300	-0.32496000
C	1.20114700	-0.61288200	0.35106500
C	1.52884200	-2.80301600	-0.61735500
C	2.54522100	-0.56781600	0.71205900
H	0.55575300	0.22246200	0.62266400
C	2.87544900	-2.76521700	-0.27545800
H	1.11238700	-3.67467800	-1.12373800
C	3.37179600	-1.64148200	0.38666700
H	2.95178700	0.29133900	1.24494200
H	3.54126500	-3.59479300	-0.51252000
Cl	5.05257300	-1.58360500	0.82284000
C	-0.43932700	1.62692800	-1.71261400
C	-1.01028000	0.49713100	-1.36162500
C	-0.08113400	2.71204600	-0.77638100
C	-1.58397600	-0.63404500	-1.00793100
C	-3.08428900	-0.82433000	-0.98077800
C	0.72829000	3.76521900	-1.22287100
C	1.10186500	4.78963200	-0.35433500
C	0.66951300	4.77676900	0.97141900
C	-0.14473500	3.73542700	1.42372600
C	-0.52064600	2.71338600	0.55726100
C	-3.62088900	-0.99963400	0.44110900
C	-5.12916700	-1.22665300	0.47623600
C	-5.66674500	-1.39634400	1.89235400
H	1.06995600	3.77560100	-2.25983600
H	1.73430800	5.60173500	-0.71599200
H	0.96101500	5.57850000	1.65126600

H	-0.49460000	3.72436200	2.45703200
H	-1.17426400	1.91055600	0.90822900
H	-3.11156300	-1.85265400	0.91963300
H	-3.36795600	-0.10564700	1.03645500
H	-5.63350600	-0.37853500	-0.01608200
H	-5.37155000	-2.11842100	-0.12505900
H	-5.19474100	-2.25636500	2.39068900
H	-5.45870800	-0.50374800	2.50143600
H	-0.17876300	1.77060600	-2.76713000
H	-3.56891700	0.03588200	-1.46348700
H	-3.32026700	-1.72292100	-1.57164500
H	-6.75334300	-1.55998200	1.89522200

NHC A’

C	-3.66110000	0.30388200	-2.00322300
C	-4.24655500	0.00200400	-0.62238000
C	-3.60054800	-1.17905100	0.11023500
C	-2.22684200	0.83592000	-2.03288800
C	-2.20659100	-0.90352300	0.59312100
C	-1.14732800	-0.16729100	-1.60762300
C	-1.14820800	-0.46989800	-0.13634000
H	-4.31014500	1.04379500	-2.49619100
H	-5.31745000	-0.22055900	-0.74427600
H	-3.58508600	-2.05666700	-0.55948500
H	-2.14971500	1.73754500	-1.40188000
H	-1.28881600	-1.10944000	-2.16600400
C	-0.07567700	-0.60094600	1.98114600
H	-3.71487400	-0.60942000	-2.62177500
H	-4.18079400	0.89917100	0.01511200
H	-4.22314100	-1.46041000	0.97120000

H	-2.00084100	1.15385400	-3.06187300
H	-0.15970800	0.21635100	-1.89626900
N	-0.00101200	-0.31900700	0.66825400
C	1.24267900	0.15206800	0.10845700
C	1.47074800	1.53609800	0.05812900
C	2.15848700	-0.78955300	-0.38565900
C	2.68487000	1.97258600	-0.48180400
C	3.35917400	-0.30630300	-0.91629600
C	3.62191100	1.06047800	-0.96051000
H	2.90067000	3.04095700	-0.53035300
H	4.09916900	-1.00853100	-1.30287100
H	4.56407700	1.41881400	-1.37819000
C	0.45676700	2.52178800	0.61367900
C	0.32628400	3.78429700	-0.23912800
H	-0.50209600	4.40357500	0.13390000
H	1.23774600	4.39890800	-0.19660900
H	0.12687900	3.53970000	-1.29293100
C	1.87746300	-2.28024900	-0.30186400
S	-1.69383500	-1.09366900	2.24854700
H	-0.52560400	2.02423600	0.62014900
H	0.78576100	-2.41088400	-0.24372700
C	0.80869800	2.86513600	2.06648100
H	1.79128200	3.36006900	2.11200800
H	0.05912700	3.54658800	2.49537500
H	0.85052500	1.95420300	2.68022700
C	2.48103800	-2.85198400	0.98719300
H	2.25222500	-3.92418900	1.07828400
H	3.57564700	-2.73236100	0.97898100
H	2.08114400	-2.32913100	1.86734900
C	2.36835500	-3.04851800	-1.52942800

H	2.03133200	-4.09353500	-1.47527700
H	1.98247800	-2.60923400	-2.46091700
H	3.46691700	-3.06329500	-1.58626800