Supporting information

Photoredox/Nickel Dual Catalyzed Stereospecific Synthesis of Distal Alkenyl Ketones

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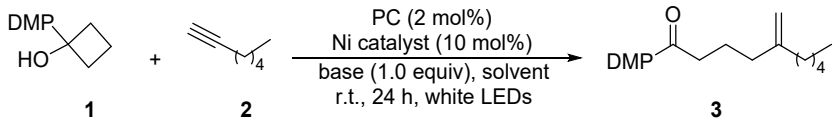
General information:

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography was performed with 0.20 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (200-300 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker AM-40 spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from TMS scale. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants *J* are quoted in Hz. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

1. Optimization of reaction conditions

Table S1 Optimized reaction conditions for 1-(2,4-dimethoxyphenyl) cyclobutan-1-ol **1**



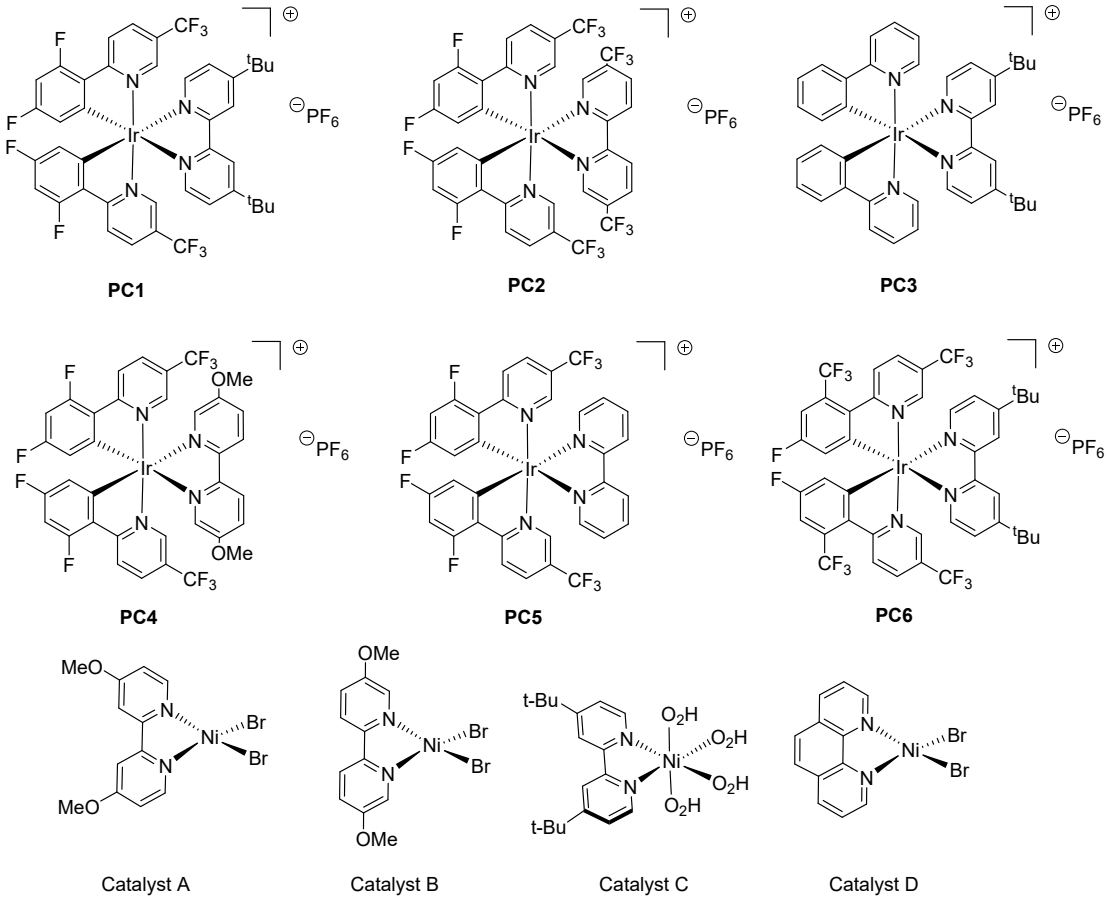
1 **2** **3**

entry	PC	Ni catalyst	base	solvent	yield (%)[a,b]
1	PC1	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	44
2	PC2	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	10
3	PC3	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	trace
4	PC4	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	23
5	PC5	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	40
6	PC6	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	37
7	Acr^+-Mes·ClO_4^-	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	trace
8	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	91
9[c]	4CzIPN	Catalyst A	$PBu_4^+(MeO)_2POO^-$	MeCN	14
10[c]	4CzIPN	Catalyst B	$PBu_4^+(MeO)_2POO^-$	MeCN	16
11[c]	4CzIPN	Catalyst C	$PBu_4^+(MeO)_2POO^-$	MeCN	16
12[c]	4CzIPN	Catalyst D	$PBu_4^+(MeO)_2POO^-$	MeCN	12
13	4CzIPN	$Ni(COD)_2$	$PBu_4^+(MeO)_2POO^-$	MeCN	18
14[d]	4CzIPN	$NiCl_2$·glyme	collidine	MeCN	12
15[d]	Acr^+-Mes·ClO_4^-	$NiCl_2$·glyme	collidine	MeCN	0
16[d]	4CzIPN	$NiCl_2$·glyme	2,6-lutidine	MeCN	trace
17	4CzIPN	$NiCl_2$·glyme	PBu_4^+ CF_3COO^-	MeCN	36
18	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(PhO)_2POO^-$	MeCN	54
19	4CzIPN	$NiCl_2$·glyme	$NBu_4^+(MeO)_2POO^-$	MeCN	66
20	4CzIPN	$NiCl_2$·glyme	K_2CO_3	MeCN	20
21	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	toluene	67
22	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	dixoane	16
23	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	THF	0
24	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	PhCl	35
25	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	DCE	trace
26	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	$MeNO_2$	25
27[e]	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	83
28[f]	4CzIPN	$NiCl_2$·glyme	$PBu_4^+(MeO)_2POO^-$	MeCN	0
29	4CzIPN	-	$PBu_4^+(MeO)_2POO^-$	MeCN	0

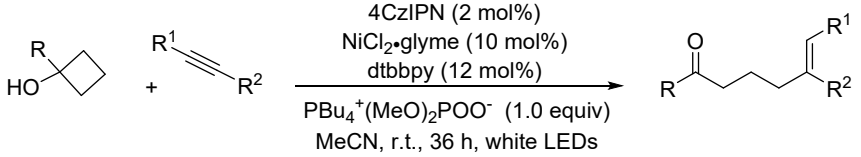
30	4CzIPN	$NiCl_2$·glyme	-	MeCN	trace

[a]Conditions: **1** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv), photocatalyst (0.002 mmol, 2 mol%), Ni catalyst (0.01 mmol, 10 mol%), ligand (0.012 mmol, 12 mol%), base (0.1 mmol, 1.0 equiv), solvent (1.0 mL) at r.t. under the irradiation of 30 W white LEDs. [b]Isolated yields. [c]Without dtbbpy. [d]Base (0.3 mmol, 3.0 equiv). [e]18 W blue LEDs. [f]No light. DMP = 2,4-Dimethoxyphenyl.

Scheme S1. The screen of photocatalysts and Ni catalysts



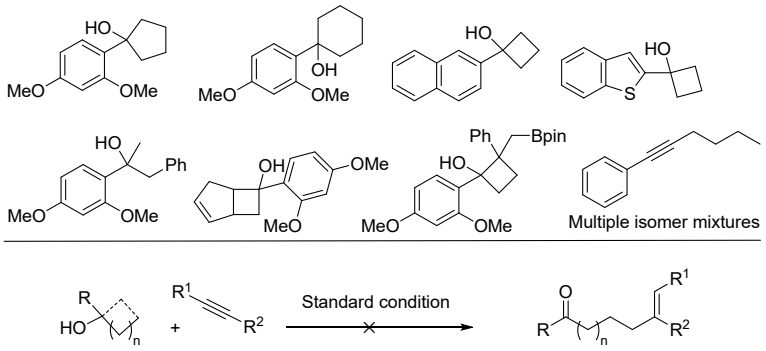
2. General procedure for the synthesis of product



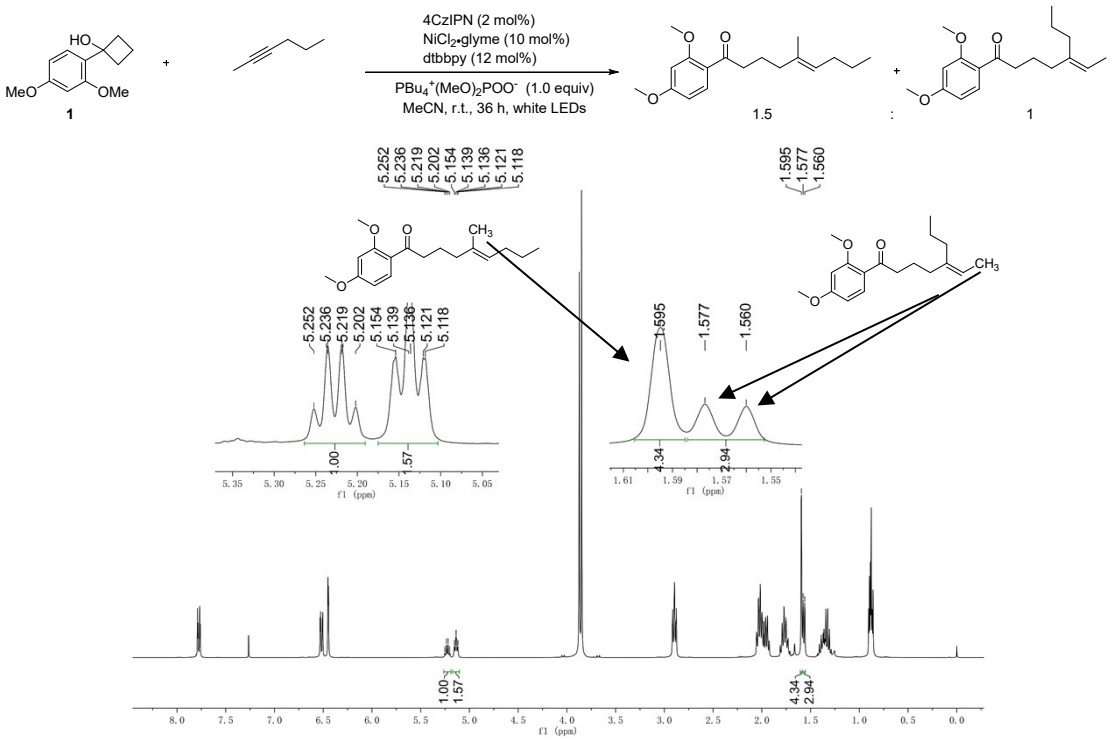
Substrate cycloalkanols (0.2 mmol) and alkynes (0.1 mmol) were added to a mixture of photocatalyst 4CzIPN (2 mol%), $NiCl_2$·glyme (10 mol%), dtbbpy (12 mol%), $PBu_4^+(MeO)_2POO^-$ (1.0 equiv) in dry MeCN (1.0 mL) in a 10 mL glass vial equipped with a magnetic stir bar and a nitrogen inlet. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation

apparatus equipped with 30 W white LEDs. The resulting mixture was stirred at 25 °C until the starting material was completely consumed after 12-36 h. Upon completion of the reaction, the reaction mixture was evaporated under reduced pressure, and the resulting crude mixture was purified by column chromatography (silica gel, EtOAc/petroleum ether = 1:20-1:4) to give the corresponding alkenyl ketones derivatives.

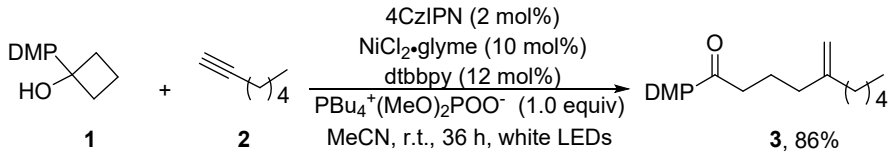
Scheme S2. Unsuccessful examples.



We also tested an unsymmetric internal alkyne, however, the unsymmetric hex-2-yne gave a variety of isomeric products, which were E isomeric products as analyzed from the NMR spectra.



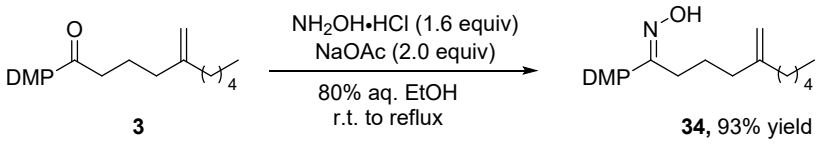
3. Procedure for gram-scale experiment



1 **2** **3**, 86%

A mixture of cycloalkanol **1** (7 mmol), alkyne **2** (3.5 mmol), 4CzIPN (2 mol%), $NiCl_2$·glyme (10 mol%), dtbbpy (12 mol%), $PBu_4^+(MeO)_2POO^-$ (1.0 equiv) and MeCN (35 mL) was degassed by three cycles of freeze-pump-thaw. The mixture was stirred under nitrogen atmosphere at room temperature while irradiated by white LEDs for 72 hours. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the crude mixture was purified by flash column chromatography (silica gel, EtOAc/petroleum ether = 1:20) to furnish the desired product **3** as described.

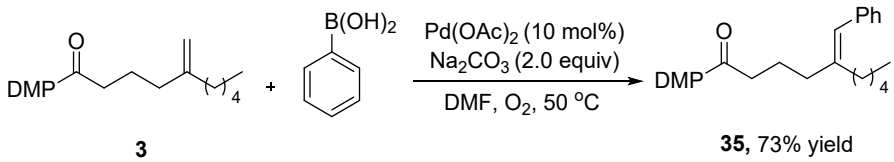
4. The synthesis of δ,ε-unsaturated oximes 34



3 **34,** 93% yield

A suspension of hydroxylamine hydrochloride (1.6 equiv), and NaOAc (2.0 equiv) in 80% aqueous EtOH (20 mL) was stirred at room temperature for 30 min. To this solution, corresponding **3** (1.0 equiv) was added and the reaction mixture was heated gently to reflux for 1 h. After the completion of reaction by TLC, the reaction mass was cooled to r.t. followed by removal of excess ethanol under vacuum. The obtained residue was purified by column chromatography with hexane-ethyl acetate as eluent to obtain crystalline oximes **34** in quantitative yield.[3]

5. The Suzuki-Miyaura reaction between 3 with aryl boride



3 **35,** 73% yield

3 (1 equiv.) was dissolved in DMF (0.2 M solution), and stirred at room temperature. To the clear solution, was added phenylboronic acid (1.2 equiv) followed by a single addition of Na_2CO_3 (2.0 equiv) and $Pd(OAc)_2$ (0.1 equiv). The reaction flask was fitted with an oxygen balloon, heated to 50 °C, and stirred for 3 h. The mixture was then diluted with ethyl acetate (10 mL), and washed with aqueous NaCl solution (3 x 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and flash chromatographed to afforded **35**.[4]

6. Mechanism studies

6.1 Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 3 x 10^{-4} M solution of 4CzIPN in dry MeCN added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 393 nm and fluorescence was measured from 460 nm to 720 nm. After degassing the sample with a stream of N_2 for 10 minutes, the emission of the sample was collected.

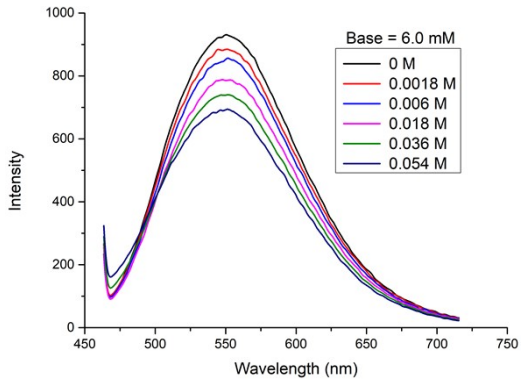


Figure S1. Fluorescence spectra of a 10^{-4} M solution of 4CzIPN in dry MeCN containing 0 M, 0.0018 M, 0.006 M, 0.018M, 0.036M and 0.054 M of alcohol **1** under 6.0 mM base.

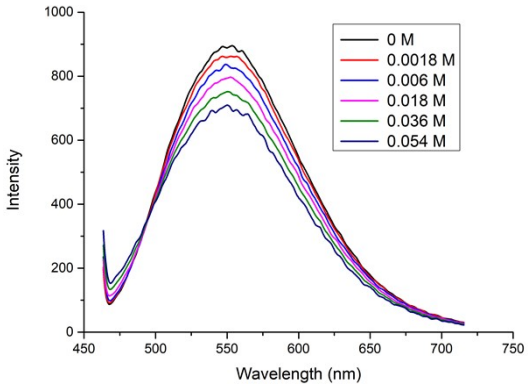


Figure S2. Fluorescence spectra of a 1 × 10^{-4} M solution of 4CzIPN in dry MeCN containing 0 M, 0.0018 M, 0.006 M, 0.018M, 0.036M and 0.054 M of alcohol **1**.

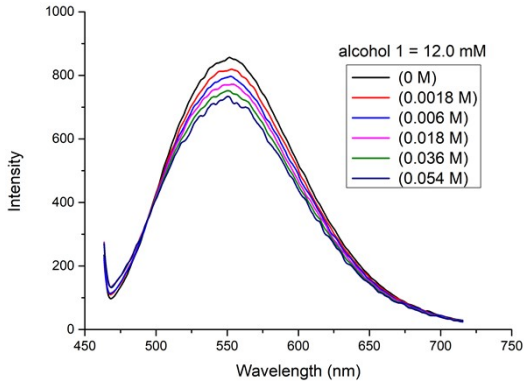


Figure S3. Fluorescence spectra of a 1 × 10^{-4} M solution of 4CzIPN in dry MeCN containing 0 M, 0.0018 M, 0.006 M, 0.018M, 0.036M and 0.054 M of base under 12.0 mM alcohol **1**.

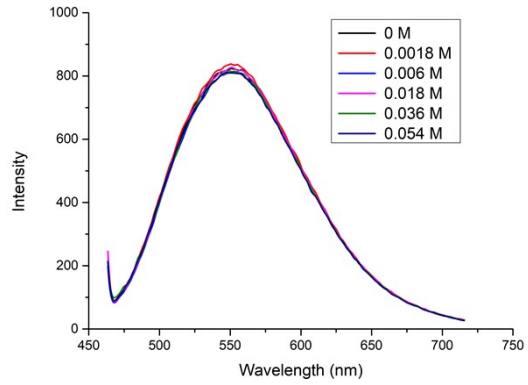


Figure S4. Fluorescence spectra of a 1 × 10^{-4} M solution of 4CzIPN in dry MeCN containing 0 M, 0.0018 M, 0.006 M, 0.018M, 0.036M and 0.054 M of base.

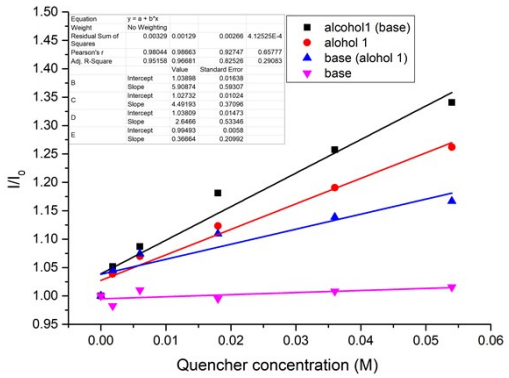
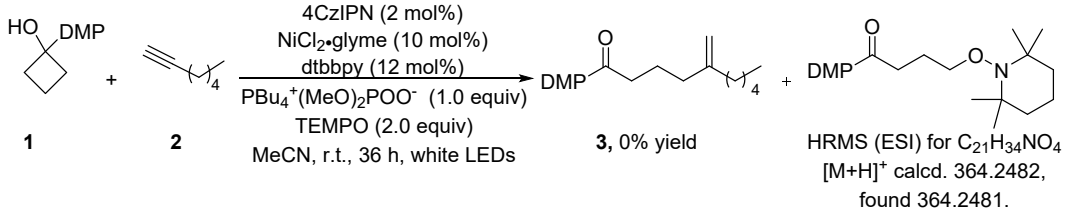


Figure S5. Stern-Volmer plots of quenching of 4CzIPN with base and alcohol **1** in MeCN at 25 °C

6.2 Radical trapping experiment.



1 **2**

Cycloalkanol **1** (0.2 mmol), **2** (0.1 mmol), 4CzIPN (2 mol%), $NiCl_2$·glyme (10 mol%), dtbbpy (12 mol%), $PBu_4^+(MeO)_2POO^-$ (1.0 equiv), TEMPO (0.2 mmol, 2 equiv) and MeCN (1.0 mL) was degassed by three cycles of freeze-pump-thaw. The mixture was stirred under nitrogen atmosphere at room temperature while irradiated by white LEDs for 36 hours. The reaction was completely inhibited and the ring-opened alkyl radical was trapped by TEMPO.

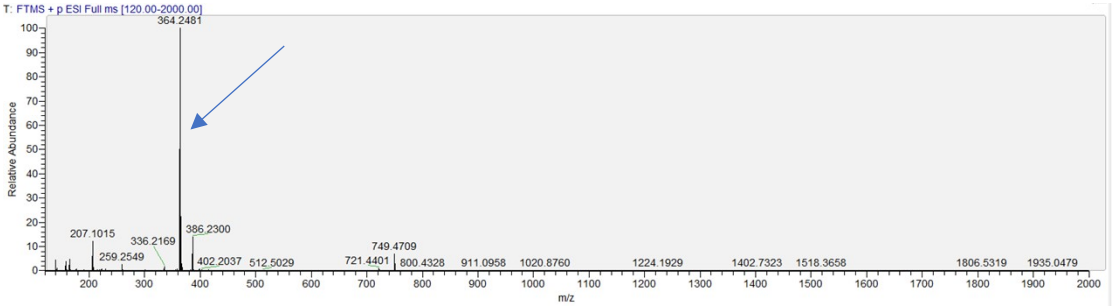


Figure S6. HRMS detection TEMPO trap radical experiment.

6.3 Radical clock experiments.

Substrate cycloalkanols **1** (0.2 mmol) and alkenylcyclopropane **36** (0.1 mmol) or *N*-Boc diallylamine

(Boc, *t*-butyloxycarbonyl) **37** were added to a mixture of photocatalyst 4CzIPN (2 mol%), $NiCl_2$·glyme (10 mol%), dtbbpy (12 mol%), $PBu_4^+(MeO)_2POO^-$ (1.0 equiv) in dry MeCN (1.0 mL) in a 10 mL glass vial equipped with a magnetic stir bar and a nitrogen inlet. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with 30 W white LEDs. The resulting mixture was stirred at 25 °C until the starting material was completely consumed after 12-36 h. The alkyl radical from the substrate **1** were trapped by alkenylcyclopropane **36** and *N*-Boc diallylamine **37**.

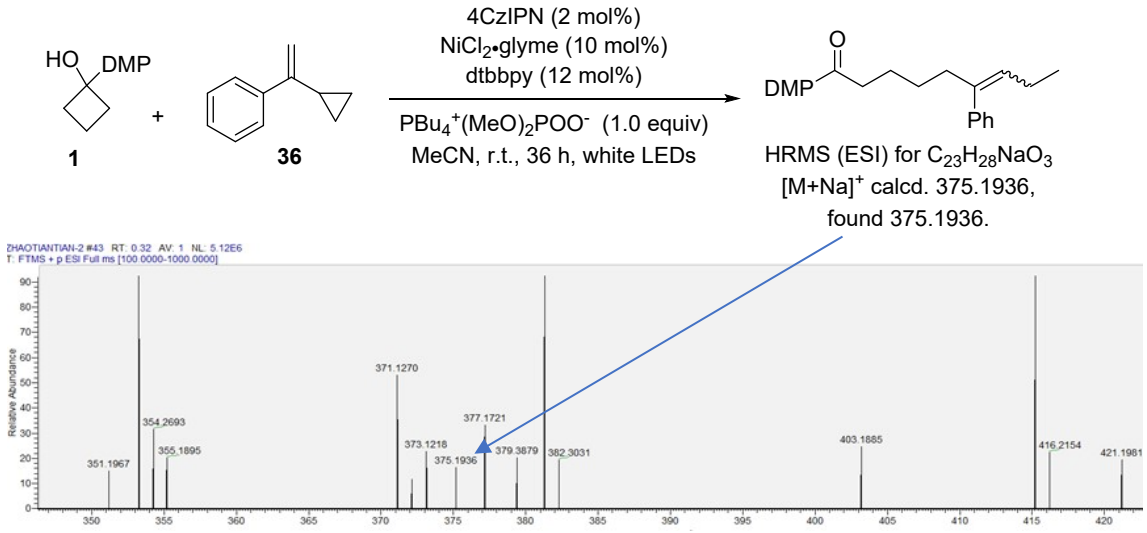


Figure S7. HRMS detection alkenylcyclopropane trap radical experiment.

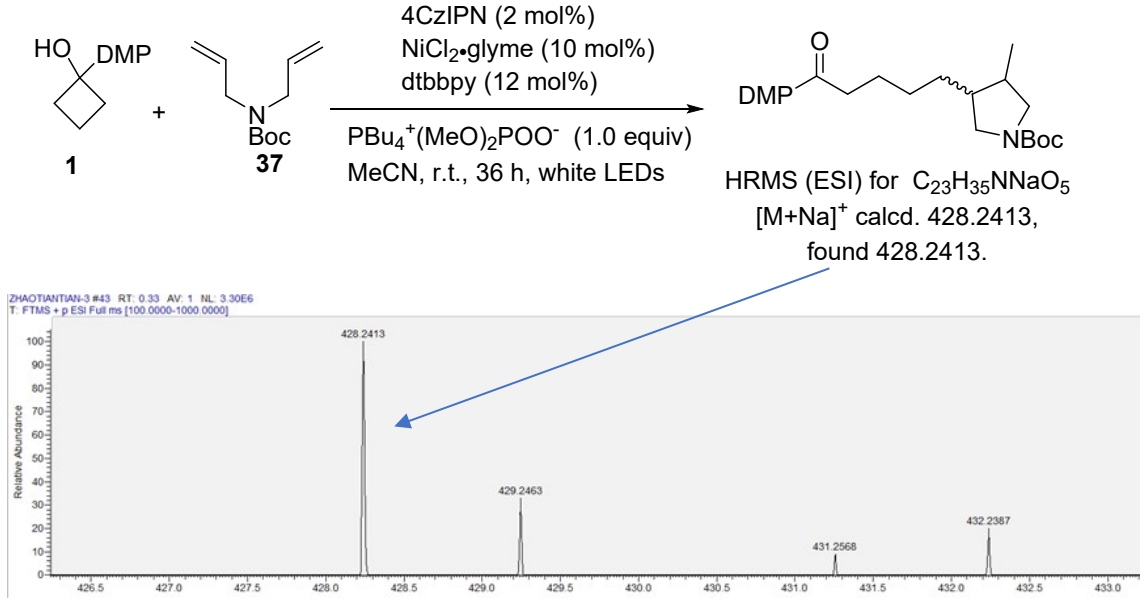
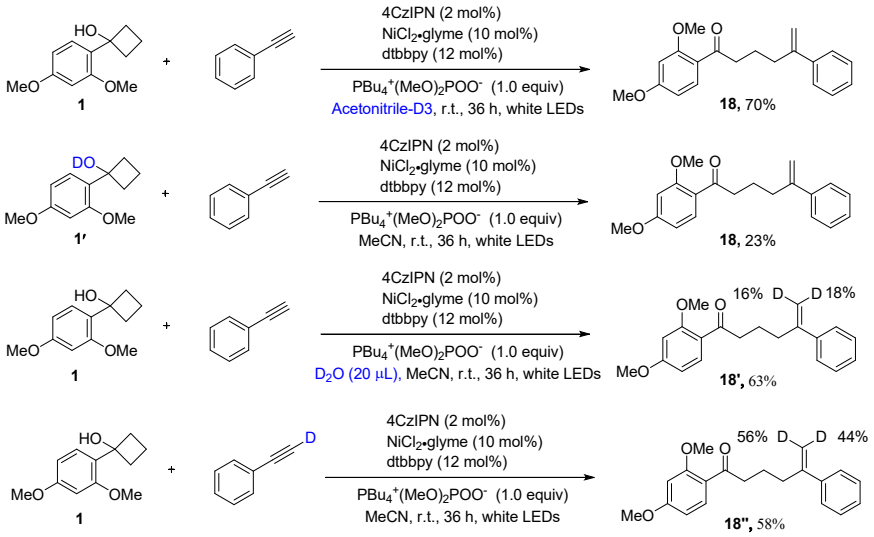


Figure S8. HRMS detection *N*-Boc diallylamine trap radical experiment.

6.4 Deuteration experiments.

Cycloalkanol **1** (0.2 mmol), Phenylacetylene or (ethynyl-d)benzene (0.1 mmol), 4CzIPN (2 mol%), $NiCl_2$·glyme (10 mol%), dtbbpy (12 mol%), $PBu_4^+(MeO)_2POO^-$ (1.0 equiv), solvent (1.0 mL) was degassed by three cycles of freeze-pump-thaw. The mixture was stirred under nitrogen atmosphere at room temperature while irradiated by white LEDs for 36 hours.



We added deuterated acetonitrile as solvent to the reaction system, the product was not deuterated. When the deuterated substrate **1'** was added to the reaction mixture, the tethered alkyl radical was captured to the non-deuterated product in 23% yield. This result demonstrated that the deuterated substrate was detrimental to the PCET process. We then speculated that the hydrogen might come from the water in the system because of the large amount of water present in the preparation of the base. Furthermore, we could obtain a small amount of the deuterium product **18'** by adding 20 μL of deuterium water to the reaction system, and the reaction was inhibited by the addition of 0.1 mL of deuterium water. The experiment results showed that the hydrogen in the product terminal alkenyl ketones came from the trace amount of water in the system.

When deuterated phenylacetylene was tested in the reaction, deuterium product **18''** was obtained, which suggested that the Markovnikov regioselectivity of Ni-alkyl insertion step depends on the space between the alkyl group and the alkyne.

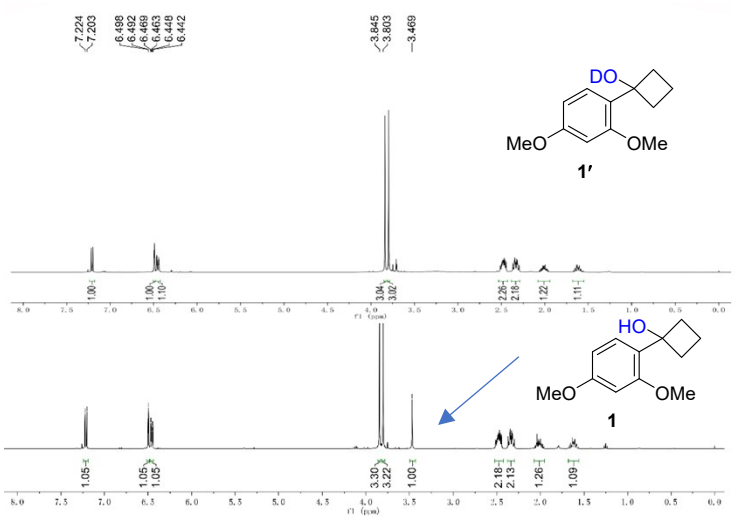


Figure S9. Deuterium spectrum of the substrate **1'**.

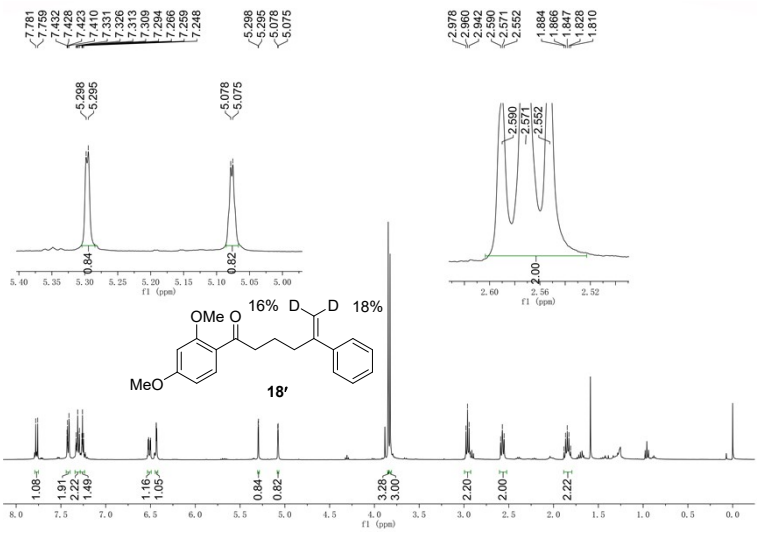


Figure S10. Deuterium spectrum of the substrate **18'**.

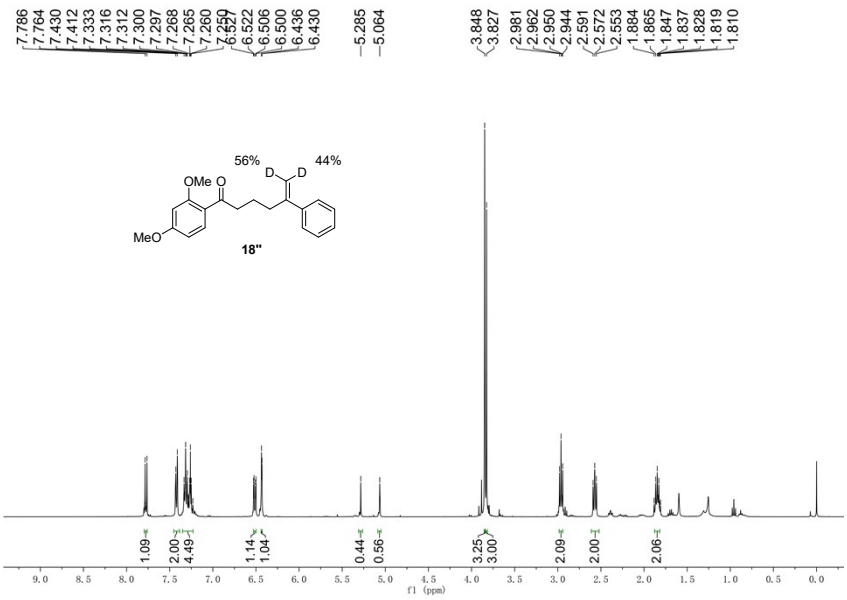


Figure S11. Deuterium spectrum of the substrate **18''**.

6.5 Computational experiment

Quantum mechanical calculations were performed using Gaussian16 C.01 software package.[1] All geometries and frequency analysis were calculated under M06-2X/6-31+G(d,p) level of theory with SMD (acetonitrile) implicit solvation model.[2]

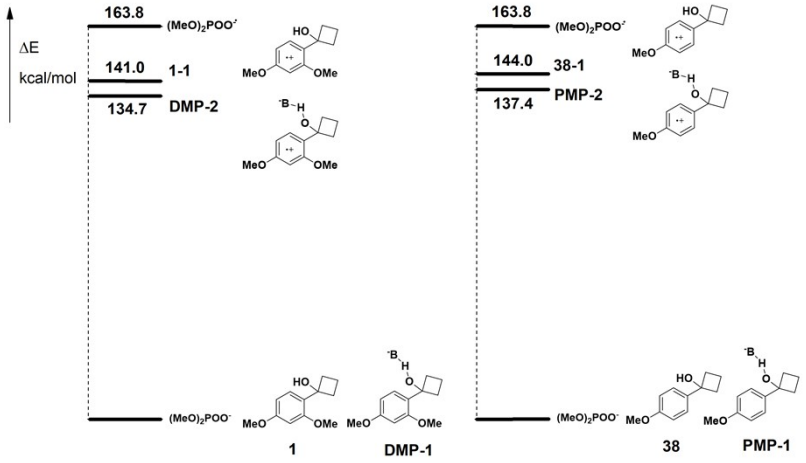


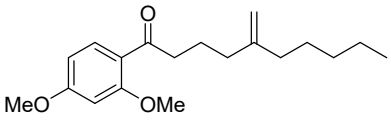
Figure S12. Comparison of the vertical excitation energies (ΔE in kcal/mol) of cycloalkanols and bases.

The calculated results showed that the rich electricity of aromatic cations and weak Brønsted phosphorous salt base are significant to the PCET process. The lowest energy pathway for aromatic radical cation formation required an electron transfer (ET) from the photocatalyst to the substrate

acceptor, where the complex of aromatic cycloalkanols and the phosphoric base (**DMP-2** or **PMP-2**) had a more favorable vertical excitation energy (ΔE = 134.7 or 137.4 kcal/mol) compared to **1** or **38**. Meanwhile, the more electron-rich alkyl-aromatic (**DMP-2**) was expected to present a remarkably lower activation barrier.

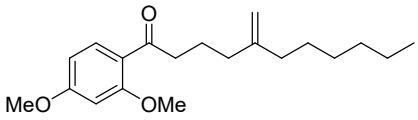
7. Characterization of products

1-(2,4-dimethoxyphenyl)-5-methylenedecan-1-one (3)



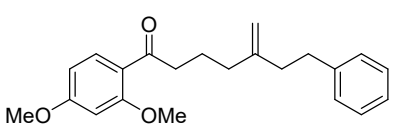
Pale yellow oil; 27 mg, 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.45 (d, *J* = 1.8 Hz, 1H), 4.72 (s, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.04 (dt, *J* = 24.6, 7.6 Hz, 4H), 1.85 – 1.73 (m, 2H), 1.47 – 1.36 (m, 2H), 1.32 – 1.24 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.7, 164.2, 160.6, 149.8, 132.6, 121.3, 108.9, 104.9, 98.4, 55.5, 55.5, 43.3, 35.9, 35.7, 31.7, 27.5, 22.7, 22.6, 14.1. **HRMS (ESI)** m/z calculated for $C_{19}H_{28}NaO_3$ $[M+Na]^+$ 327.1936, found 327.1931.

1-(2,4-dimethoxyphenyl)-5-methyleneundecan-1-one (4)



Pale yellow oil; 28 mg, 89% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 6.52 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.45 (d, *J* = 1.5 Hz, 1H), 4.72 (s, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.04 (dt, *J* = 23.6, 7.5 Hz, 4H), 1.91 – 1.71 (m, 2H), 1.40 (d, *J* = 7.0 Hz, 2H), 1.27 (s, 6H), 0.88 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.7, 164.2, 160.6, 149.8, 132.6, 121.3, 108.9, 105.0, 98.3, 55.5, 55.4, 43.3, 36.0, 35.7, 31.8, 29.2, 27.8, 22.7, 22.7, 14.2. **HRMS (ESI)** m/z calculated for $C_{20}H_{30}NaO_3$ $[M+Na]^+$ 341.2087, found 341.2087.

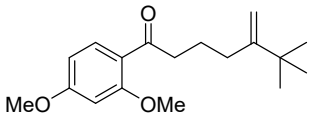
1-(2,4-dimethoxyphenyl)-5-methylene-7-phenylheptan-1-one (5)



Colorless oil; 28 mg, 83% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 3H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 4.78 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.77 – 2.72 (m, 2H), 2.34 (d, *J* = 8.6

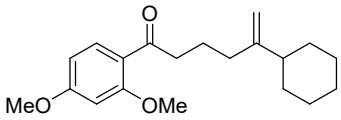
Hz, 2H), 2.15 – 2.09 (m, 2H), 1.88 – 1.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 164.2, 160.6, 148.9, 142.3, 132.6, 128.3, 128.3, 125.7, 121.4, 109.6, 105.0, 98.4, 55.5, 55.4, 43.2, 37.8, 35.9, 34.4, 22.7. **HRMS (ESI)** m/z calculated for $C_{22}H_{26}NaO_3[M+Na]^+$ 361.1774, found 361.1781.

1-(2,4-dimethoxyphenyl)-6,6-dimethyl-5-methyleneheptan-1-one (6)



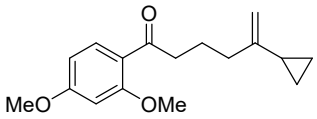
Colorless oil; 18 mg, 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.7 Hz, 1H), 6.50 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 4.85 (s, 1H), 4.71 (d, *J* = 1.0 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.14 – 2.00 (m, 2H), 1.87 – 1.75 (m, 2H), 1.03 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.7, 164.2, 160.6, 157.7, 132.6, 121.4, 106.1, 105.0, 98.4, 55.5, 55.5, 43.6, 36.2, 31.0, 29.2, 24.3. **HRMS (ESI)** m/z calculated for $C_{18}H_{26}NaO_3[M+Na]^+$ 313.1774, found 313.1779.

5-cyclohexyl-1-(2,4-dimethoxyphenyl)hex-5-en-1-one (7)



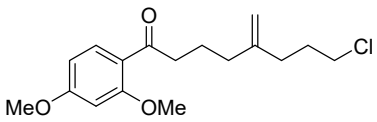
Yellow oil; 22 mg, 70% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.7 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.45 (d, *J* = 2.2 Hz, 1H), 4.71 (d, *J* = 6.8 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.11 – 2.05 (m, 2H), 1.83 – 1.74 (m, 6H), 1.70 – 1.64 (m, 2H), 1.58 (s, 1H), 1.29 – 1.25 (m, 2H), 1.18 – 1.13 (m, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.7, 164.2, 160.6, 155.0, 132.6, 121.4, 107.1, 105.0, 98.4, 55.5, 55.5, 44.0, 43.4, 34.7, 32.5, 26.8, 26.4, 23.2. **HRMS (ESI)** m/z calculated for $C_{20}H_{28}NaO_3$ $[M+Na]^+$ 339.1931, found 339.1938.

5-cyclopropyl-1-(2,4-dimethoxyphenyl)hex-5-en-1-one (8)



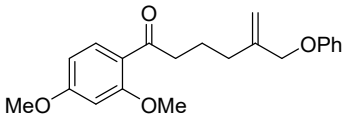
Pale yellow oil, 22 mg, 81% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.45 (d, *J* = 2.2 Hz, 1H), 4.63 (t, *J* = 4.0 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.13 – 2.04 (m, 2H), 1.93 – 1.83 (m, 2H), 1.31 – 1.25 (m, 1H), 0.66 – 0.57 (m, 2H), 0.47 – 0.39 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.6, 164.2, 160.6, 150.7, 132.6, 121.4, 106.3, 105.0, 98.4, 55.5, 55.4, 43.2, 35.6, 23.1, 16.0, 6.1. **HRMS (ESI)** m/z calculated for $C_{17}H_{22}NaO_3$ $[M+Na]^+$ 297.1467, found 297.1462.

8-chloro-1-(2,4-dimethoxyphenyl)-5-methyleneoctan-1-one (9)



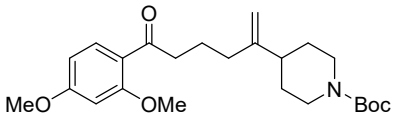
Colorless oil; 24 mg, 79% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 4.79 (s, 1H), 4.77 (s, 1H),3.88 (s, 3H), 3.85 (s, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.96 – 1.86 (m, 2H), 1.86 – 1.77 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 164.3, 160.7, 147.7, 132.6, 121.3, 110.2, 105.1, 98.4, 55.5, 55.5, 44.6, 43.1, 35.6, 33.0, 30.6, 22.6. **HRMS (ESI)** m/z calculated for $C_{17}H_{23}ClNaO_3$ $[M+Na]^+$ 333.1228, found 333.1233.

1-(2,4-dimethoxyphenyl)-5-(phenoxymethyl)hex-5-en-1-one (10)



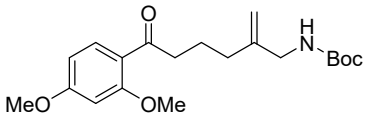
Colorless oil; 25 mg, 73% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 9.6 Hz, 3H), 6.51 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.44 (d, *J* = 1.8 Hz, 1H), 5.16 (s, 1H), 5.02 (s, 1H), 4.47 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.90 (dd, *J* = 15.1, 7.6 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 164.3, 160.7, 158.8, 144.6, 132.6, 129.4, 121.3, 120.8, 114.8, 112.2, 105.1, 98.4, 70.7, 55.5, 55.5, 43.1, 32.8, 22.5. **HRMS (ESI)** m/z calculated for $C_{21}H_{24}NaO_4$ $[M+Na]^+$ 363.1567, found 363.1573.

Tert-butyl 4-(6-(2,4-dimethoxyphenyl)-6-oxohex-1-en-2-yl)piperidine-1-carboxylate (11)



Colorless oil; 32 mg, 76% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 6.53 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.46 (d, *J* = 2.2 Hz, 1H), 4.76 (d, *J* = 10.2 Hz, 2H), 4.15 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 12.7 Hz, 2H), 2.12 – 2.05 (m, 2H), 2.05 – 1.95 (m, 1H), 1.88 – 1.77 (m, 2H), 1.70 (d, *J* = 13.1 Hz, 2H), 1.46 (s, 9H), 1.39 – 1.29 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 164.3, 160.7, 154.8, 152.8, 132.6, 121.3, 108.2, 105.1, 98.4, 79.3, 55.5, 55.4, 44.3, 43.2, 42.0, 34.4, 31.3, 28.5, 23.0. **HRMS (ESI)** m/z calculated for $C_{24}H_{35}NNaO_5$ $[M+Na]^+$ 440.2407, found 440.2414.

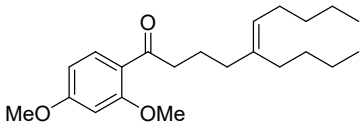
Tert-butyl (6-(2,4-dimethoxyphenyl)-2-methylene-6-oxohexyl)carbamate (12)



Pale yellow oil; 20 mg, 56% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.7 Hz, 1H), 6.52 (d, *J* = 8.7 Hz, 1H), 6.45 (s, 1H),

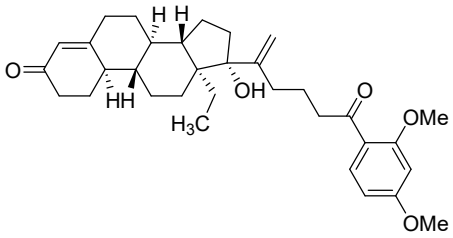
4.87 (d, *J* = 18.4 Hz, 2H), 4.69 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.70 (d, *J* = 5.1 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.08 (t, *J* = 7.6 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.45 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 164.3, 160.7, 155.9, 146.2, 132.6, 121.2, 109.8, 105.1, 98.4, 79.2, 55.5, 55.5, 45.19, 43.0, 33.5, 28.4, 22.4. **HRMS (ESI)** m/z calculated for $C_{20}H_{29}NNaO_5$ $[M+Na]^+$ 386.1938, found 386.1949.

5-butyl-1-(2,4-dimethoxyphenyl)dec-5-en-1-one (13)



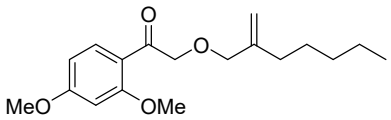
Colorless oil; 22 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.7 Hz, 1H), 6.52 (dd, J = 8.7, 2.3 Hz, 1H), 6.45 (d, J = 2.2 Hz, 1H), 5.11 (t, J = 7.1 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.94 – 2.84 (m, 2H), 2.05 – 1.96 (m, 6H), 1.79 – 1.71 (m, 2H), 1.34 – 1.26 (m, 8H), 0.92 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 164.1, 160.6, 138.9, 132.6, 125.4, 121.5, 105.0, 98.4, 55.5, 55.4, 43.3, 36.6, 32.4, 30.7, 29.6, 27.4, 23.1, 22.9, 22.4, 14.1, 14.1. **HRMS (ESI)** m/z calculated for $C_{22}H_{34}NaO_3$ $[M+Na]^+$ 369.2406, found 369.2402.

(8R,9S,10R,13S,14S,17R)-17-(6-(2,4-dimethoxyphenyl)-6-oxohex-1-en-2-yl)-13-ethyl-17-hydroxy-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (14)



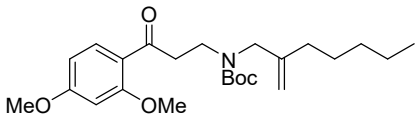
White solid; 35 mg, 67% yield; m.p. 165-167 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, J = 8.7 Hz, 1H), 6.52 (dd, J = 8.7, 2.0 Hz, 1H), 6.45 (d, J = 1.9 Hz, 1H), 5.80 (s, 1H), 4.99 (s, 1H), 4.69 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.00 (t, J = 6.7 Hz, 2H), 2.49 – 2.42 (m, 2H), 2.36 (t, J = 8.8 Hz, 1H), 2.30 – 2.19 (m, 4H), 2.13 – 1.97 (m, 4H), 1.96 – 1.89 (m, 2H), 1.86 – 1.78 (m, 2H), 1.74 (dd, J = 13.3, 3.3 Hz, 1H), 1.60 (dt, J = 14.2, 7.0 Hz, 2H), 1.53 – 1.45 (m, 2H), 1.43 (d, J = 8.1 Hz, 1H), 1.38 (d, J = 8.7 Hz, 2H), 1.08 (t, J = 7.3 Hz, 3H), 1.01 (d, J = 14.4 Hz, 1H), 0.82 – 0.70 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.7, 199.9, 166.9, 164.3, 160.8, 154.3, 132.7, 124.5, 121.2, 111.6, 105.1, 98.3, 89.5, 55.5, 55.4, 48.9, 48.8, 47.9, 43.6, 43.3, 42.5, 41.1, 38.5, 36.5, 35.6, 33.1, 30.8, 29.6, 26.5, 24.8, 23.0, 20.5, 9.9. **HRMS (ESI)** m/z calculated for $C_{33}H_{44}NaO_5$ $[M+Na]^+$ 543.3086, found 543.3086.

1-(2,4-dimethoxyphenyl)-2-((2-methyleneheptyl)oxy)ethan-1-one (15)



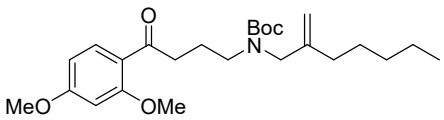
Pale yellow oil; 15 mg, 50% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.7 Hz, 1H), 6.61 – 6.52 (m, 1H), 6.44 (d, *J* = 1.7 Hz, 1H), 5.04 (s, 1H), 4.92 (s, 1H), 4.63 (s, 2H), 4.07 (s, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 2.08 (t, *J* = 7.5 Hz, 2H), 1.62 (d, *J* = 4.2 Hz, 1H), 1.51 – 1.41 (m, 2H), 1.30 (d, *J* = 3.2 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.9, 164.9, 161.1, 146.2, 132.9, 118.8, 111.5, 105.5, 98.1, 76.3, 74.2, 55.6, 55.5, 33.1, 31.6, 27.3, 22.6, 14.1. **HRMS (ESI)** m/z calculated for $C_{18}H_{26}NaO_4$ $[M+Na]^+$ 329.1723, found 329.1723.

***tert*-butyl (3-(2,4-dimethoxyphenyl)-3-oxopropyl)(2-methyleneheptyl)carbamate (16)**



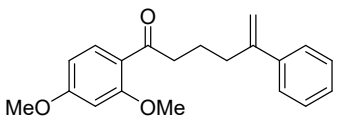
Pale yellow oil; 36 mg, 86% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (t, *J* = 8.7 Hz, 1H), 6.52 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 4.5 Hz, 1H), 4.81 (dd, *J* = 18.2, 9.7 Hz, 2H), 3.85 (m, 8H), 3.52 (dd, *J* = 17.7, 6.9 Hz, 2H), 3.27 – 3.15 (m, 2H), 1.99 – 1.92 (m, 2H), 1.44 (s, 11H), 1.29 (t, *J* = 12.5 Hz, 4H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** 1δ 198.5, 164.6, 160.9, 155.8, 145.6, 132.7, 120.7, 110.3, 105.1, 98.3, 79.3, 55.5, 55.4, 52.3, 51.5, 42.5, 33.5, 31.7, 28.4, 27.3, 22.6, 14.1. **HRMS (ESI)** m/z calculated for $C_{24}H_{37}NNaO_5$ $[M+Na]^+$ 442.2569, found 442.2567.

tert-butyl (4-(2,4-dimethoxyphenyl)-4-oxobutyl)(2-methyleneheptyl)carbamate (17)



Colorless oil; 34 mg, 78% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.6 Hz, 1H), 6.45 (s, 1H), 4.82 (s, 1H), 4.77 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.80 (d, *J* = 21.4 Hz, 2H), 3.28 – 3.14 (m, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 1.98 – 1.92 (m, 2H), 1.87 (dd, *J* = 12.4, 5.4 Hz, 2H), 1.43 (s, 11H), 1.29 (dd, *J* = 15.2, 7.5 Hz, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.5, 164.3, 160.6, 155.9, 145.6, 132.6, 121.0, 110.1, 105.1, 98.3, 79.2, 55.5, 55.4, 51.1, 50.8, 45.6, 40.9, 33.5, 31.6, 28.4, 27.5, 22.5, 14.0. **HRMS (ESI)** m/z calculated for $C_{25}H_{39}NNaO_5$ $[M+Na]^+$ 456.2720, found 456.2727.

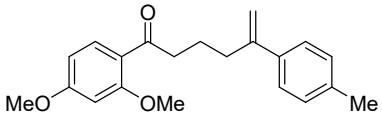
1-(2,4-dimethoxyphenyl)-5-phenylhex-5-en-1-one (18)



Pale yellow oil; 22 mg, 71% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H),

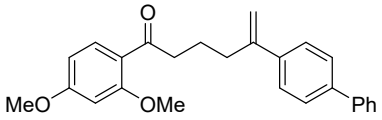
7.26 (dd, *J* = 4.4, 2.8 Hz, 1H), 6.51 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.43 (d, *J* = 2.3 Hz, 1H), 5.29 (s, 1H), 5.08 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.91 – 1.77 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 164.2, 160.6, 148.2, 141.1, 132.6, 128.3, 127.3, 126.1, 121.4, 112.5, 105.0, 98.4, 55.5, 55.4, 43.1, 34.9, 23.3. **HRMS (ESI)** m/z calculated for $C_{20}H_{22}NaO_3$ $[M+Na]^+$ 333.1461, found 333.1469.

1-(2,4-dimethoxyphenyl)-5-(p-tolyl)hex-5-en-1-one (19)



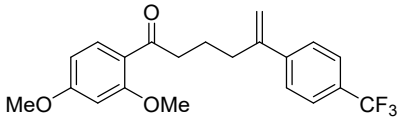
Pale yellow oil; 21 mg, 77% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.51 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.43 (d, *J* = 1.9 Hz, 1H), 5.27 (s, 1H), 5.03 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.83 (dd, *J* = 14.9, 7.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 164.2, 160.6, 147.9, 138.2, 137.0, 132.6, 129.0, 126.0, 121.4, 111.7, 105.0, 98.4, 55.5, 55.4, 43.1, 34.9, 23.3, 21.1. **HRMS (ESI)** m/z calculated for $C_{21}H_{24}NaO_3$ $[M+Na]^+$ 347.1618, found 347.1624.

5-([1,1'-biphenyl]-4-yl)-1-(2,4-dimethoxyphenyl)hex-5-en-1-one (20)



Colorless oil; 25 mg, 65% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.7 Hz, 1H), 7.55 (m, 6H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 6.51 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.43 (d, *J* = 1.7 Hz, 1H), 5.37 (s, 1H), 5.11 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.94 – 1.85 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 164.3, 160.7, 147.6, 140.8, 140.1, 140.0, 132.6, 128.8, 127.3, 127.0, 126.5, 121.3, 112.6, 105.0, 98.4, 55.5, 55.4, 43.1, 34.8, 23.3. **HRMS (ESI)** m/z calculated for $C_{26}H_{26}NaO_3$ $[M+Na]^+$ 409.1774, found 409.1774.

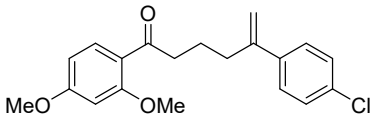
1-(2,4-dimethoxyphenyl)-5-(4-(trifluoromethyl)phenyl)hex-5-en-1-one (21)



Pale yellow oil; 25 mg, 65% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.52 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 5.35 (s, 1H), 5.18 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.62 – 2.54 (m, 2H), 1.89 – 1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.1, 164.3, 160.7, 147.2, 132.6,

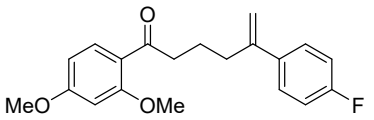
129.4, 128.9, 126.4, 125.2, 125.2, 121.2, 114.4, 105.1, 98.4, 55.5, 55.4, 42.9, 34.7, 23.1. **HRMS (ESI)** m/z calculated for $C_{21}H_{21}F_3NaO_3$ $[M+Na]^+$ 401.1335, found 401.1345.

5-(4-chlorophenyl)-1-(2,4-dimethoxyphenyl)hex-5-en-1-one (22)



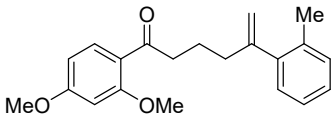
Pale yellow oil; 24 mg, 70% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.26 (s, 2H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 5.28 (d, *J* = 0.9 Hz, 1H), 5.09 (d, *J* = 1.1 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.57 – 2.50 (m, 2H), 1.84 (dd, *J* = 15.0, 7.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 164.3, 160.6, 147.1, 139.6, 133.1, 132.6, 128.4, 127.4, 121.3, 113.0, 105.1, 98.4, 55.5, 55.4, 42.9, 34.8, 23.2. **HRMS (ESI)** m/z calculated for $C_{20}H_{21}ClNaO_3$ $[M+Na]^+$ 367.1071, found 367.1079.

1-(2,4-dimethoxyphenyl)-5-(4-fluorophenyl)hex-5-en-1-one (23)



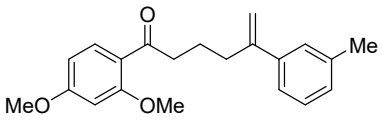
Pale yellow oil; 22 mg, 66% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.41 – 7.35 (m, 2H), 6.99 (t, *J* = 8.8 Hz, 2H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 5.24 (d, *J* = 1.1 Hz, 1H), 5.06 (d, *J* = 1.1 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.53 (dd, *J* = 11.1, 4.1 Hz, 2H), 1.87 – 1.78 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3, 163.9, 160.8, 147.2, 137.2, 132.6, 129.2, 127.7, 121.3, 115.0, 112.4, 105.1, 98.4, 55.5, 55.4, 43.0, 35.0, 23.2. **HRMS (ESI)** m/z calculated for $C_{20}H_{21}FNaO_3$ $[M+Na]^+$ 351.1367, found 351.1376.

1-(2,4-dimethoxyphenyl)-5-(o-tolyl)hex-5-en-1-one (24)



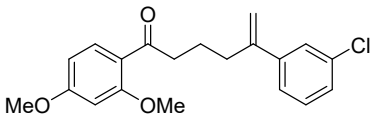
Colorless oil; 22 mg, 69% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.17 – 7.14 (m, 3H), 7.12 – 7.07 (m, 1H), 6.52 – 6.49 (m, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.88 (d, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.41 – 2.36 (m, 2H), 2.29 (s, 3H), 1.80 (dd, *J* = 15.1, 7.6 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 164.2, 160.6, 149.7, 143.1, 134.8, 132.6, 130.1, 128.3, 126.7, 125.4, 121.3, 113.9, 105.0, 98.4, 55.5, 55.4, 43.2, 37.4, 22.7, 19.9. **HRMS (ESI)** m/z calculated for $C_{21}H_{24}NaO_3$ $[M+Na]^+$ 347.1618, found 347.1623.

1-(2,4-dimethoxyphenyl)-5-(m-tolyl)hex-5-en-1-one (25)



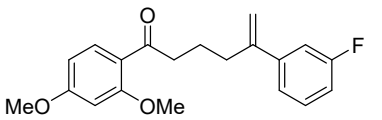
Pale yellow oil; 28 mg, 85% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.7 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.14 – 7.07 (m, 1H), 6.54 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.46 (d, *J* = 2.2 Hz, 1H), 5.30 (d, *J* = 1.3 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.98 (dd, *J* = 9.5, 5.2 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.93 – 1.82 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 164.2, 160.6, 148.3, 141.2, 137.7, 132.6, 128.2, 128.1, 126.9, 123.2, 121.3, 112.3, 105.0, 98.4, 55.5, 55.4, 43.1, 35.0, 23.3, 21.5. **HRMS (ESI)** m/z calculated for $C_{21}H_{24}NaO_3$ $[M+Na]^+$ 347.1618, found 347.1625.

5-(3-chlorophenyl)-1-(2,4-dimethoxyphenyl)hex-5-en-1-one (26)



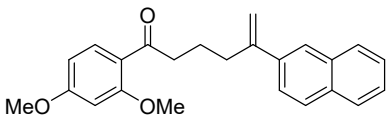
Colorless oil; 23 mg, 68% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.7 Hz, 1H), 7.39 (s, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 6.52 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 5.30 (s, 1H), 5.12 (s, 1H), 3.84 (s, 6H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.89 – 1.76 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 164.3, 160.7, 147.0, 143.1, 134.2, 132.6, 129.5, 127.3, 126.3, 124.3, 121.2, 113.7, 105.1, 98.4, 55.5, 55.4, 43.0, 34.8, 23.1. **HRMS (ESI)** m/z calculated for $C_{20}H_{21}ClNaO_3$ $[M+Na]^+$ 367.1071, found 367.1079.

1-(2,4-dimethoxyphenyl)-5-(3-fluorophenyl)hex-5-en-1-one (27)



Colorless oil; 18 mg, 55% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.22 – 7.17 (m, 1H), 7.13 – 7.07 (m, 1H), 6.94 (m, 1H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 5.32 (d, *J* = 1.0 Hz, 1H), 5.12 (d, *J* = 1.1 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.57 – 2.50 (m, 2H), 1.83 (dd, *J* = 14.9, 7.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.2, 164.2, 161.7, 160.7, 147.1, 143.6, 132.6, 129.7, 121.8, 121.3, 114.1, 113.5, 113.0, 105.1, 98.4, 55.5, 55.4, 43.0, 34.8, 23.2. **HRMS (ESI)** m/z calculated for $C_{20}H_{21}FNaO_3$ $[M+Na]^+$ 351.1367, found 351.1376.

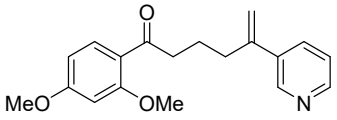
1-(2,4-dimethoxyphenyl)-5-(naphthalen-2-yl)hex-5-en-1-one (28)



Colorless oil; 26 mg, 71% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.75 (m, 5H), 7.59 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.44 (ddd, *J*

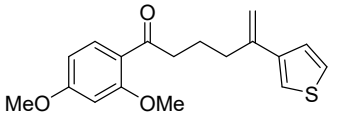
= 6.3, 5.2, 3.5 Hz, 2H), 6.49 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.40 (d, *J* = 1.9 Hz, 1H), 5.45 (s, 1H), 5.19 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.99 (t, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.92 (dd, *J* = 14.9, 7.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 164.2, 160.7, 147.9, 138.3, 133.4, 132.8, 132.6, 128.2, 127.8, 127.5, 126.1, 125.8, 124.7, 124.7, 121.2, 113.2, 105.0, 98.3, 55.5, 55.4, 43.1, 34.9, 23.4. **HRMS (ESI)** m/z calculated for $C_{24}H_{24}NaO_3$ $[M+Na]^+$ 383.1618, found 383.1618.

1-(2,4-dimethoxyphenyl)-5-(pyridin-3-yl)hex-5-en-1-one (29)



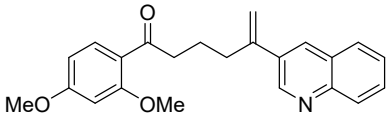
Colorless oil; 19 mg, 60% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, J = 1.9 Hz, 1H), 8.50 (dd, J = 4.8, 1.5 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.28 – 7.21 (m, 1H), 6.52 (dd, J = 8.7, 2.2 Hz, 1H), 6.44 (d, J = 2.2 Hz, 1H), 5.35 (s, 1H), 5.18 (d, J = 1.0 Hz, 1H), 3.85 (s, 6H), 2.98 (t, J = 7.2 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 1.90 – 1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.1, 164.3, 160.7, 148.5, 147.6, 145.3, 136.5, 133.4, 132.6, 123.2, 121.1, 114.2, 105.0, 98.3, 55.6, 55.4, 42.9, 34.6, 22.9. **HRMS (ESI)** m/z calculated for $C_{19}H_{21}NNaO_3$ $[M+Na]^+$ 334.1414, found 334.1414.

1-(2,4-dimethoxyphenyl)-5-(thiophen-3-yl)hex-5-en-1-one (30)



Yellow oil; 24 mg, 76% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, J = 8.7 Hz, 1H), 7.25 (dt, J = 5.5, 2.1 Hz, 3H), 6.51 (dd, J = 8.7, 2.3 Hz, 1H), 6.44 (d, J = 2.2 Hz, 1H), 5.36 (d, J = 1.1 Hz, 1H), 5.02 (d, J = 1.1 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.99 (t, J = 7.2 Hz, 2H), 2.51 (dd, J = 7.9, 7.3 Hz, 2H), 1.99 – 1.87 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 164.3, 160.7, 142.6, 142.4, 132.6, 125.8, 125.4, 121.3, 120.5, 111.2, 105.1, 98.4, 55.5, 55.4, 43.1, 35.1, 23.5. **HRMS (ESI)** m/z calculated for $C_{18}H_{20}NaO_3S$ $[M+Na]^+$ 339.1031, found 339.1024.

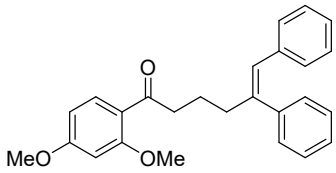
1-(2,4-dimethoxyphenyl)-5-(quinolin-3-yl)hex-5-en-1-one (31)



Colorless oil; 17 mg, 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (s, 1H), 8.50 (d, *J* = 5.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 6.0 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 13.8, 6.9 Hz, 2H), 6.54 – 6.46 (m, 1H), 6.41 (d, *J* = 1.7 Hz, 1H), 5.48 (s, 1H), 5.10 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.86 – 1.77 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.1, 164.3, 160.6,

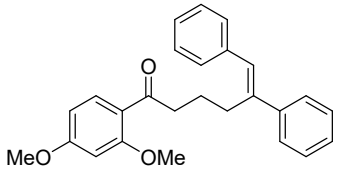
152.9, 146.9, 143.1, 140.2, 133.9, 132.6, 129.1, 128.9, 126.7, 126.7, 121.0, 118.5, 116.5, 105.0, 98.3, 55.6, 55.4, 43.0, 37.9, 22.9. **HRMS (ESI)** m/z calculated for $C_{23}H_{23}NNaO_3$ $[M+Na]^+$ 384.1576, found 384.1570.

(Z)-1-(2,4-dimethoxyphenyl)-5,6-diphenylhex-5-en-1-one (32a)



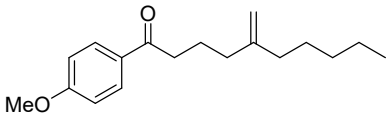
Colorless oil; 25 mg, 63% yield; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.7 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 3H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 6.9 Hz, 3H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.52 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.44 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.82 (dd, *J* = 15.1, 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 164.2, 160.7, 142.9, 141.2, 137.5, 132.6, 129.0, 128.6, 128.5, 127.8, 126.9, 126.6, 126.1, 121.4, 105.0, 98.4, 55.5, 55.4, 42.9, 40.2, 22.9. **HRMS (ESI)** m/z calculated for $C_{26}H_{26}NaO_3$ $[M+Na]^+$ 409.1780, found 409.1780.

(E)-1-(2,4-dimethoxyphenyl)-5,6-diphenylhex-5-en-1-one (32b)



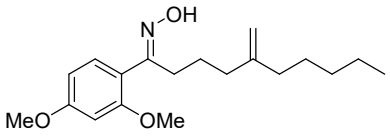
Colorless oil; 3.5 mg, 9% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.7 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.40 – 7.31 (m, 6H), 7.30 – 7.22 (m, 2H), 6.73 (s, 1H), 6.50 (dd, J = 8.7, 2.3 Hz, 1H), 6.41 (d, J = 2.2 Hz, 1H), 3.84 (d, J = 5.3 Hz, 3H), 3.78 (s, 3H), 2.92 (t, J = 7.4 Hz, 2H), 2.77 (dd, J = 9.1, 6.9 Hz, 2H), 1.87 – 1.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 164.3, 160.6, 142.8, 142.8, 138.2, 132.7, 128.8, 128.6, 128.4, 128.3, 127.2, 126.6, 126.5, 121.1, 105.0, 98.3, 55.5, 55.4, 43.6, 29.8, 23.7. **HRMS (ESI)** m/z calculated for $C_{26}H_{26}NaO_3$ $[M+Na]^+$ 409.1780, found 409.1779.

1-(4-methoxyphenyl)-5-phenylhex-5-en-1-one (33)



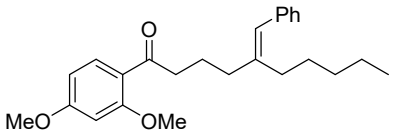
Pale yellow oil; 15 mg, 56% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.74 (d, *J* = 2.4 Hz, 2H), 3.87 (s, 3H), 2.92 (t, *J* = 6.0 Hz, 2H), 2.11 (t, *J* = 7.5 Hz, 2H), 2.02 (t, *J* = 8.0 Hz, 2H), 1.95 – 1.80 (m, 2H), 1.42 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.33 – 1.24 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.0, 163.3, 149.3, 130.3, 130.2, 113.7, 109.3, 55.5, 37.7, 35.9, 35.5, 31.7, 27.4, 22.6, 22.4, 14.1. **HRMS (ESI)** m/z calculated for $C_{18}H_{26}NaO_2$ $[M+Na]^+$ 297.1830, found 297.1824.

1-(2,4-dimethoxyphenyl)-5-methylenedecan-1-one oxime (34)



Colorless oil; 30 mg, 93% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.71 (s, 1H), 7.25 (d, *J* = 9.0 Hz, 1H), 6.52 (dd, *J* = 5.7, 2.3 Hz, 2H), 4.71 (d, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.85 – 2.75 (m, 2H), 2.09 – 2.03 (m, 2H), 2.01 – 1.94 (m, 2H), 1.70 – 1.59 (m, 2H), 1.47 – 1.38 (m, 2H), 1.30 (ddd, *J* = 14.8, 12.6, 5.8 Hz, 4H), 0.93 (dd, *J* = 9.6, 4.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.4, 160.1, 158.6, 149.7, 130.7, 118.7, 108.8, 104.2, 98.8, 55.4, 55.4, 36.1, 35.9, 31.6, 28.1, 27.4, 23.9, 22.6, 14.1. **HRMS (ESI)** m/z calculated for $C_{18}H_{27}NNaO_4$ $[M+Na]^+$ 342.2045, found 342.2038.

5-benzylidene-1-(2,4-dimethoxyphenyl)decan-1-one (35)



Colorless oil; 28 mg, 73% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.6 Hz, 1H), 7.26 (s, 1H), 7.19 – 7.12 (m, 3H), 6.87 (dd, *J* = 14.8, 7.6 Hz, 1H), 6.78 (d, *J* = 15.4 Hz, 1H), 6.51 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.57 (ddd, *J* = 29.9, 13.6, 7.2 Hz, 2H), 2.19 (t, *J* = 6.1 Hz, 2H), 1.33 – 1.17 (m, 10H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.0, 163.9, 160.2, 145.7, 141.0, 132.7, 132.1, 129.2, 128.2, 125.8, 122.1, 104.9, 98.6, 55.6, 55.5, 40.2, 39.6, 36.2, 33.2, 32.1, 26.4, 22.7, 14.1. **HRMS (ESI)** m/z calculated for $C_{25}H_{32}NaO_3$ $[M+Na]^+$ 403.2249, found 403.2244.

8. X-ray data for 14 (CCDC 2084142)

Single crystal of product **14** was obtained through slow evaporation of a solution in dichloromethane-diethyl ether at room temperature.

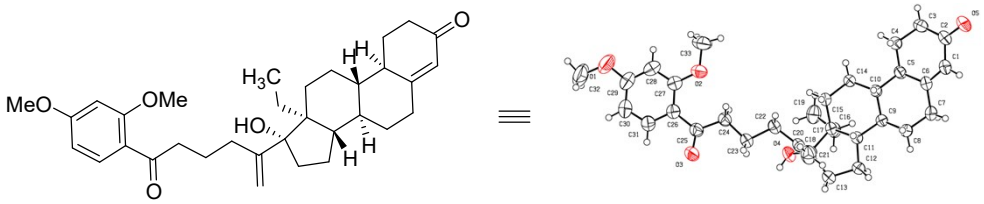


Table S2. Crystal data and structure refinement for **14**

Empirical formula	$C_{33}H_{44}O_5$

Formula weight	520.68
Temperature/K	299.34(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.16900(10)
b/Å	16.3425(3)
c/Å	10.9598(2)
α/°	90
β/°	94.2610(10)
γ/°	90
Volume/Å^3	1459.11(4)
Z	2
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.619
F(000)	564.0
Crystal size/mm^3	0.09 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.09 to 151.782
Index ranges	$-8 \leq h \leq 10$, $-19 \leq k \leq 20$, $-13 \leq l \leq 13$
Reflections collected	9483
Independent reflections	4821 [R_{int} = 0.0300, R_{sigma} = 0.0371]
Data/restraints/parameters	4821/1/355
Goodness-of-fit on F^2	0.945
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.0440, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.14/-0.14
Flack parameter	0.04(13)

9. References

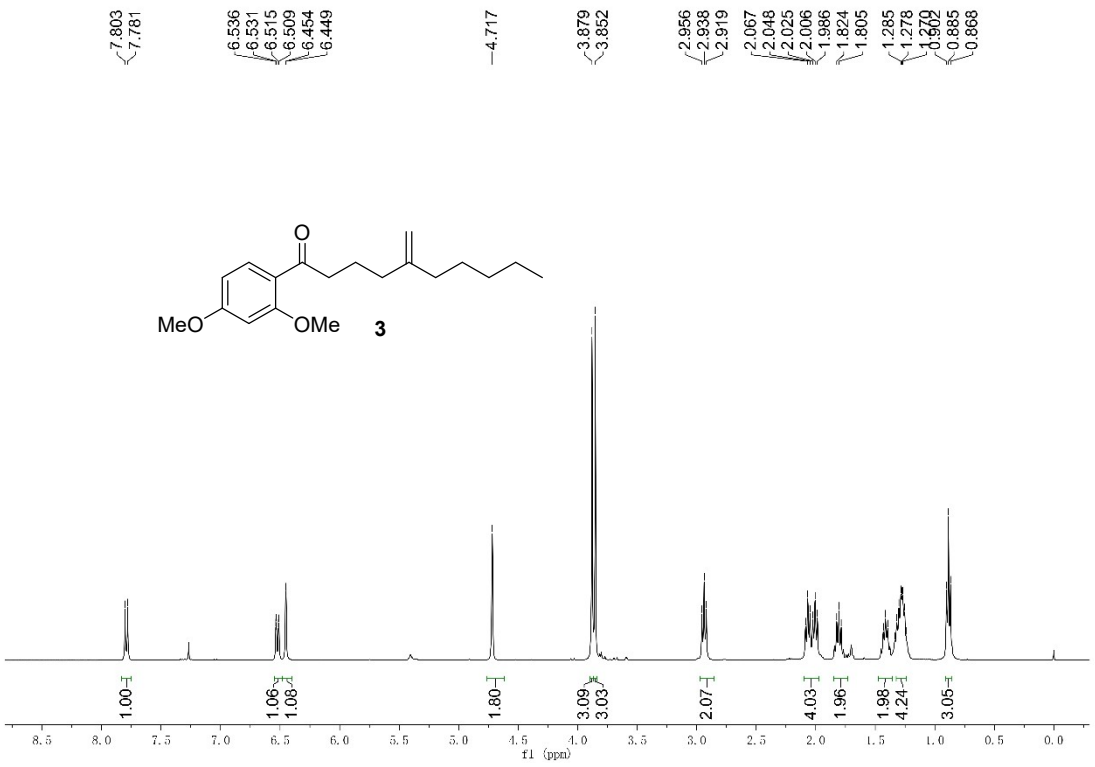
[1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, 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, Inc., Wallingford CT, **2019**.

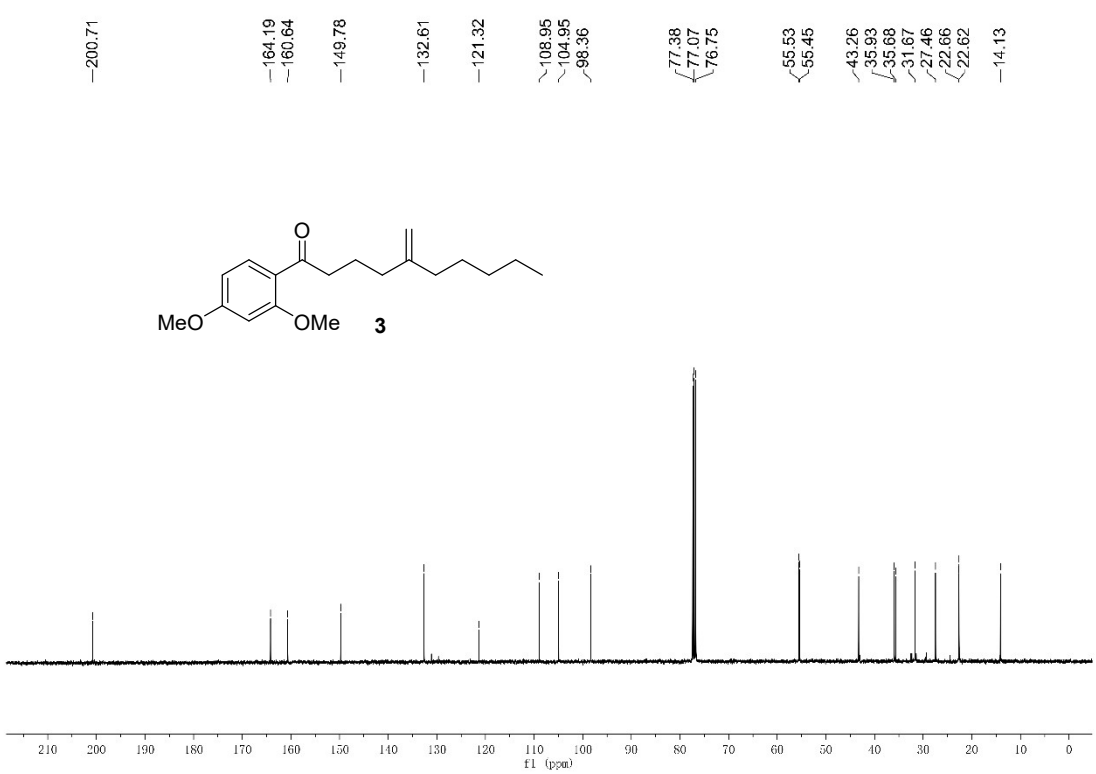
[2] (a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc*., **2008**, *120*, 215-241; (b) A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, **2009**, *113*, 6378-6396.

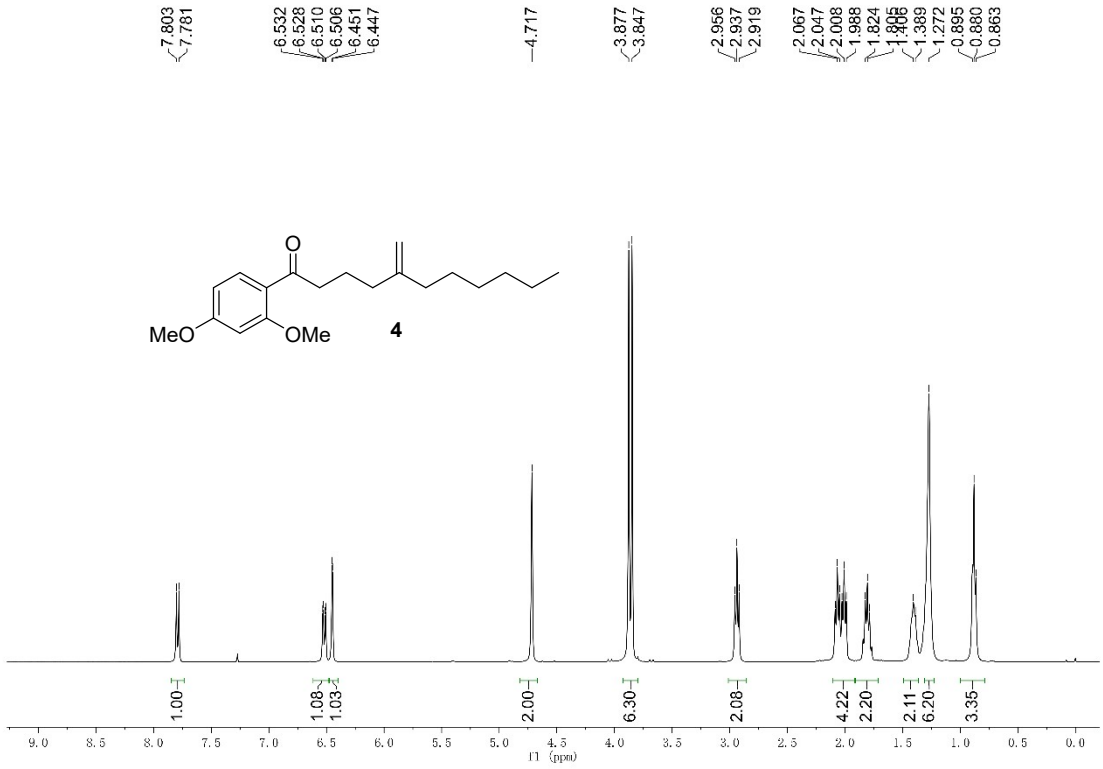
[3] G. C. Senadi, M. R. Mutra, T.-Y. Lua, J.-J. Wang, *Green Chem*., **2017**, *19*, 4272-4277.

[4] Y. C. Jung, R. K. Mishra, C. H. Yoon, K. W. Jung, *Org. Lett*., **2003**, *5*, 2231-2234.

10. NMR spectra of compounds



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0.863
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OMe
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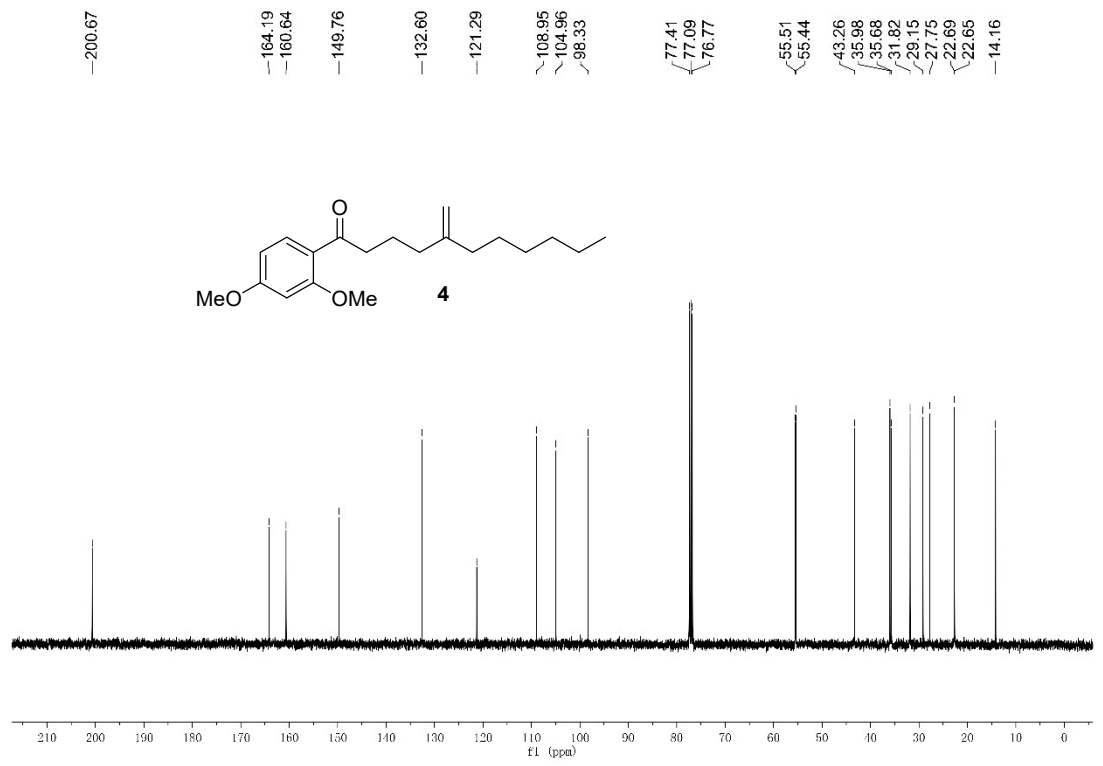
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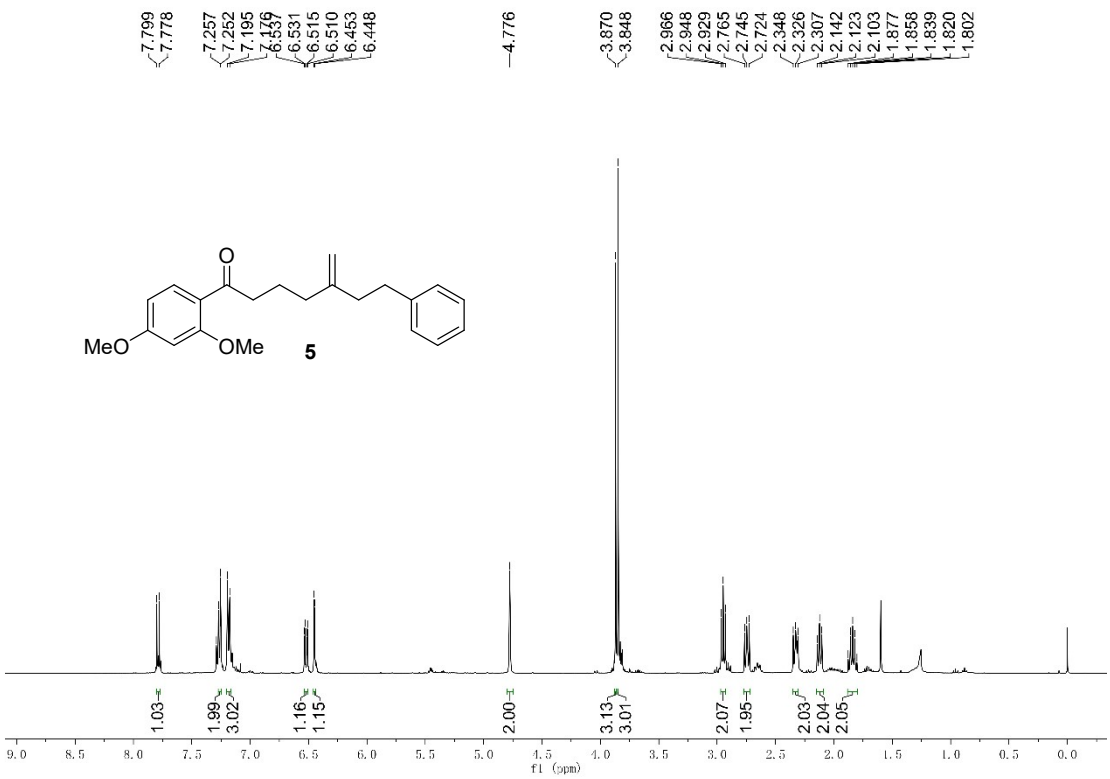
f1 (ppm)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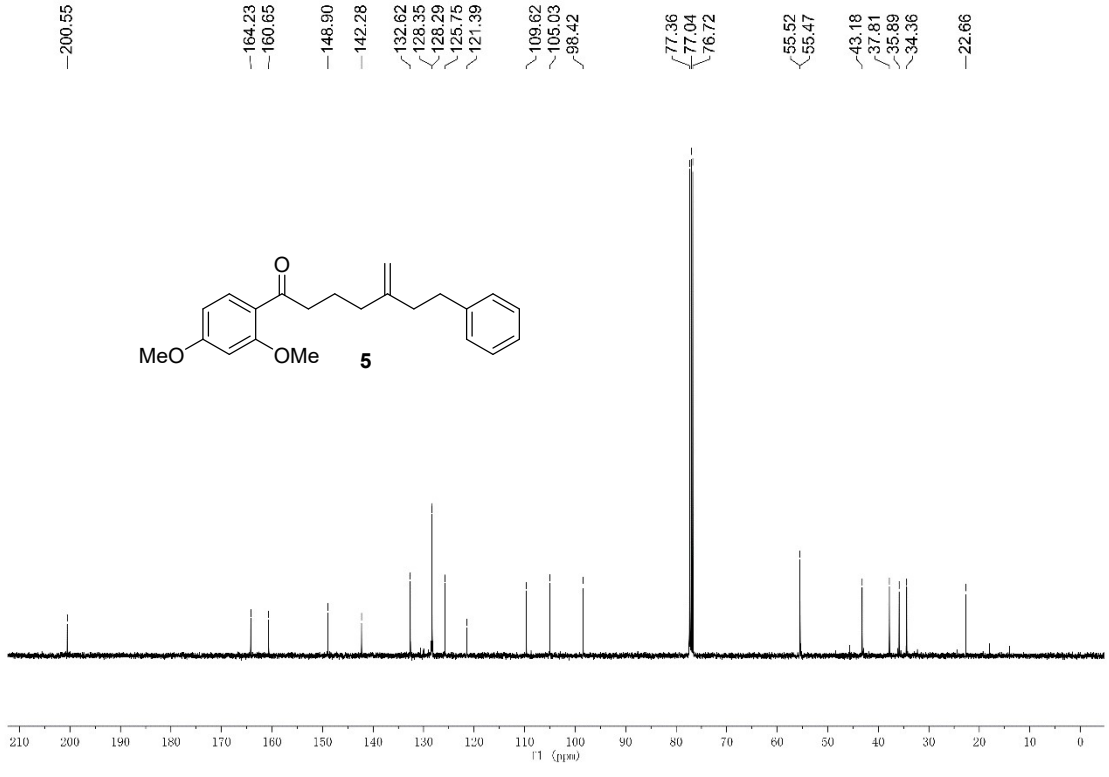
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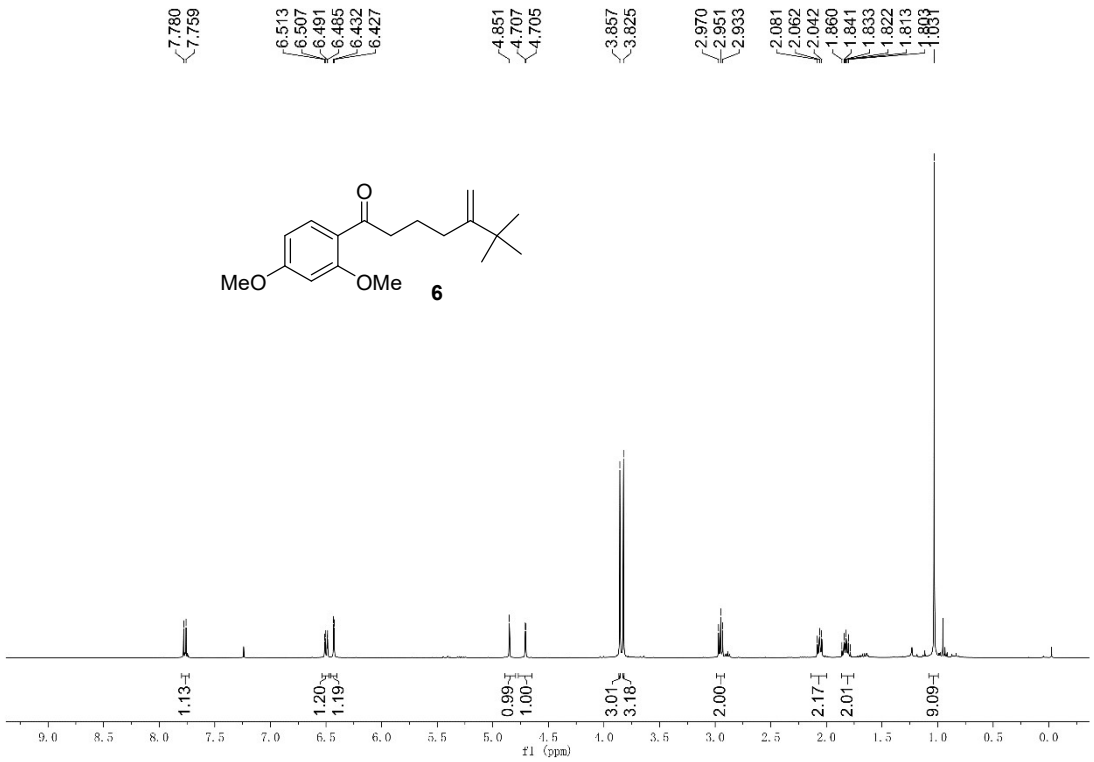
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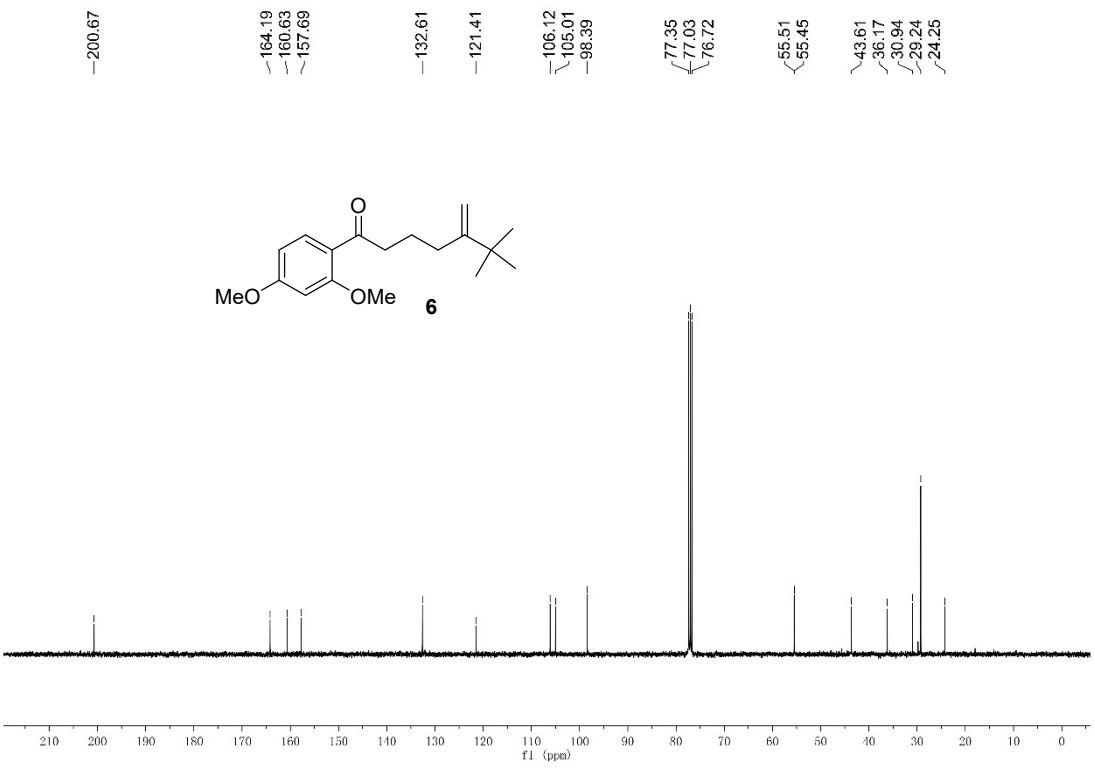
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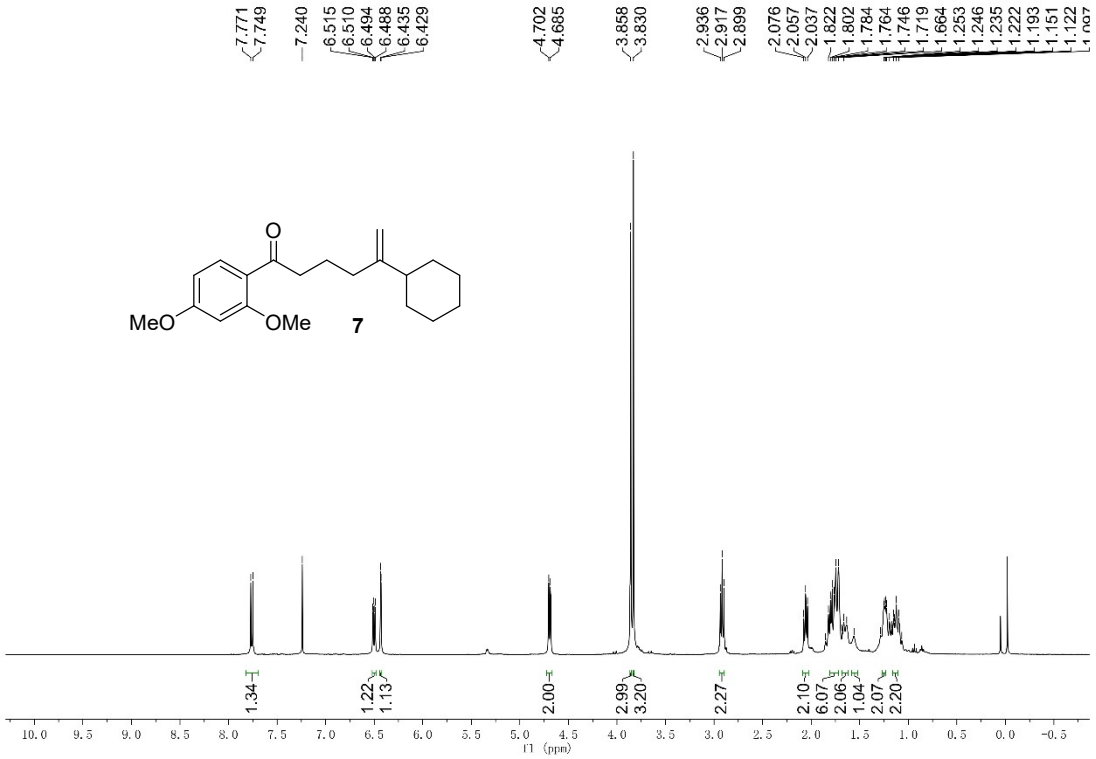
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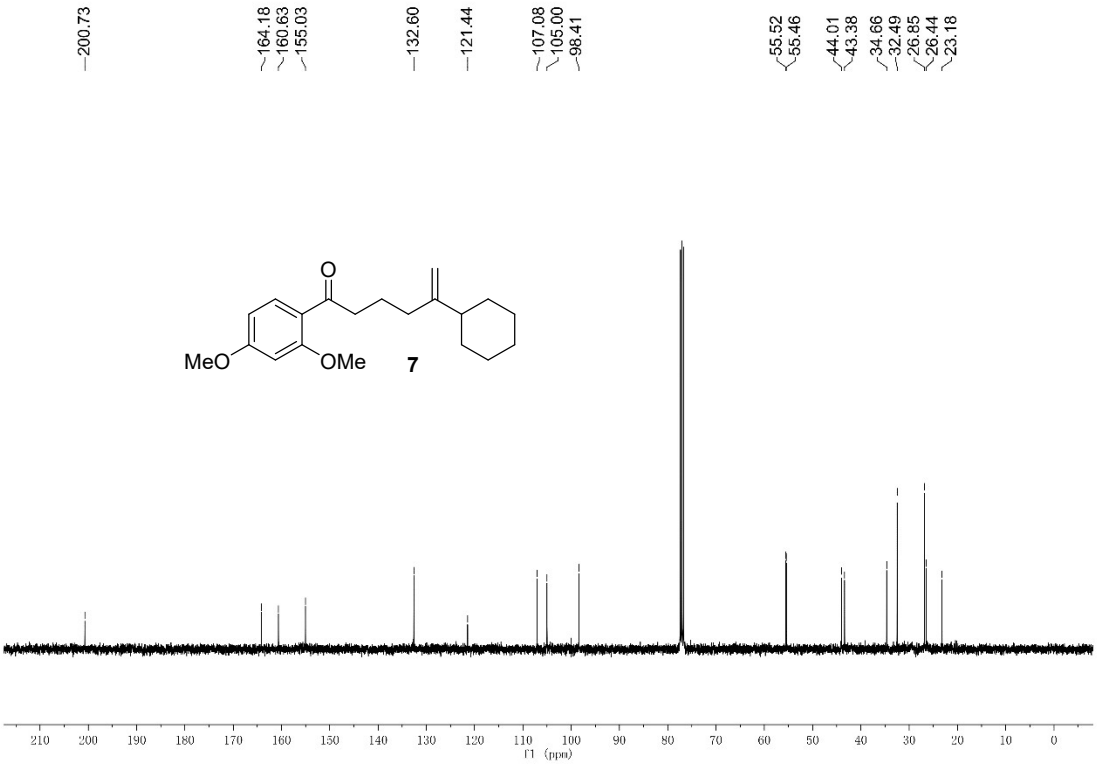
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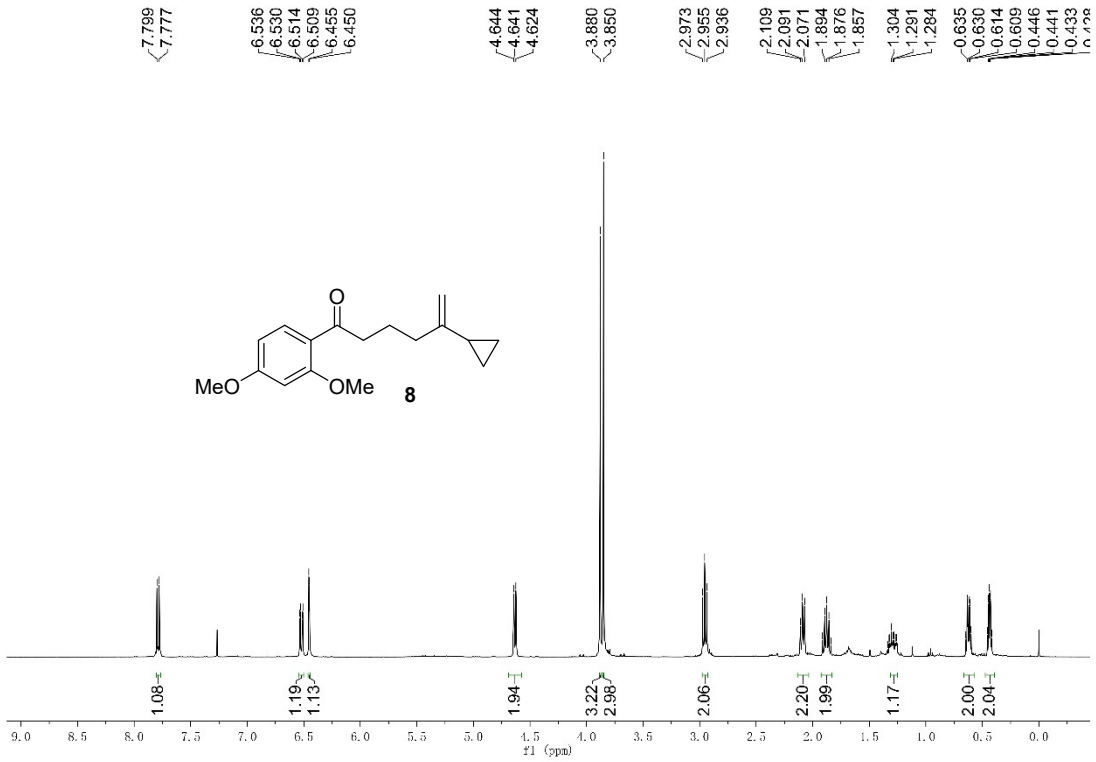
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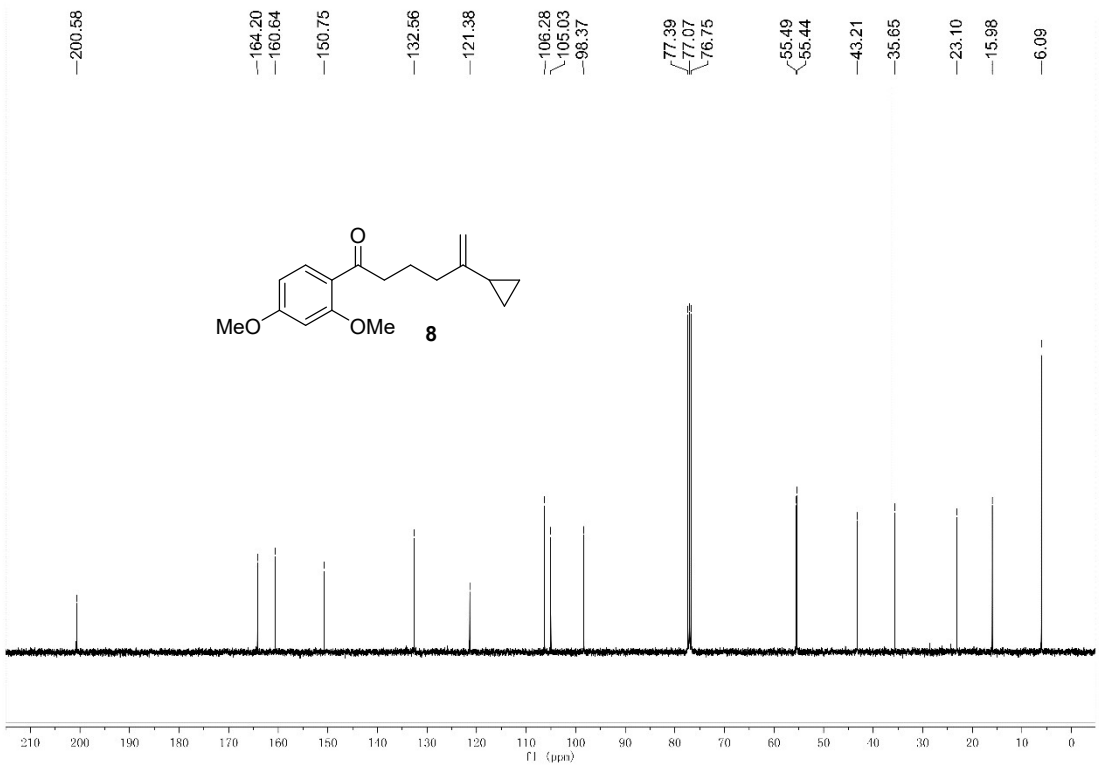
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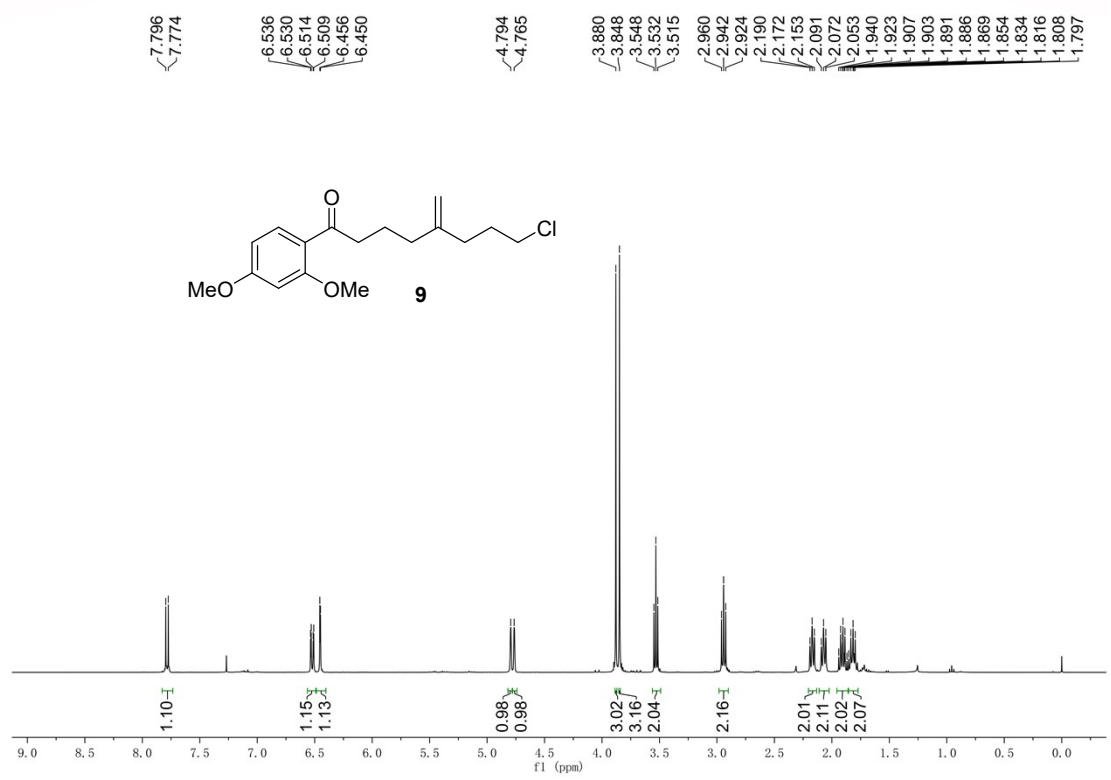
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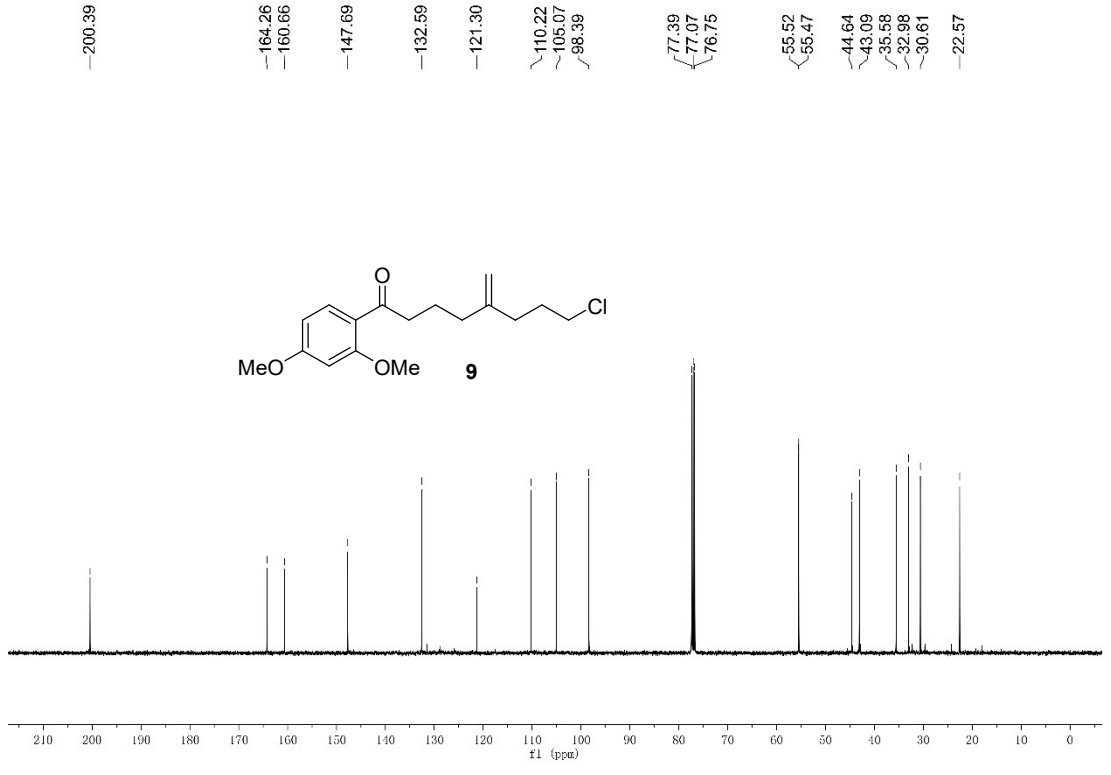
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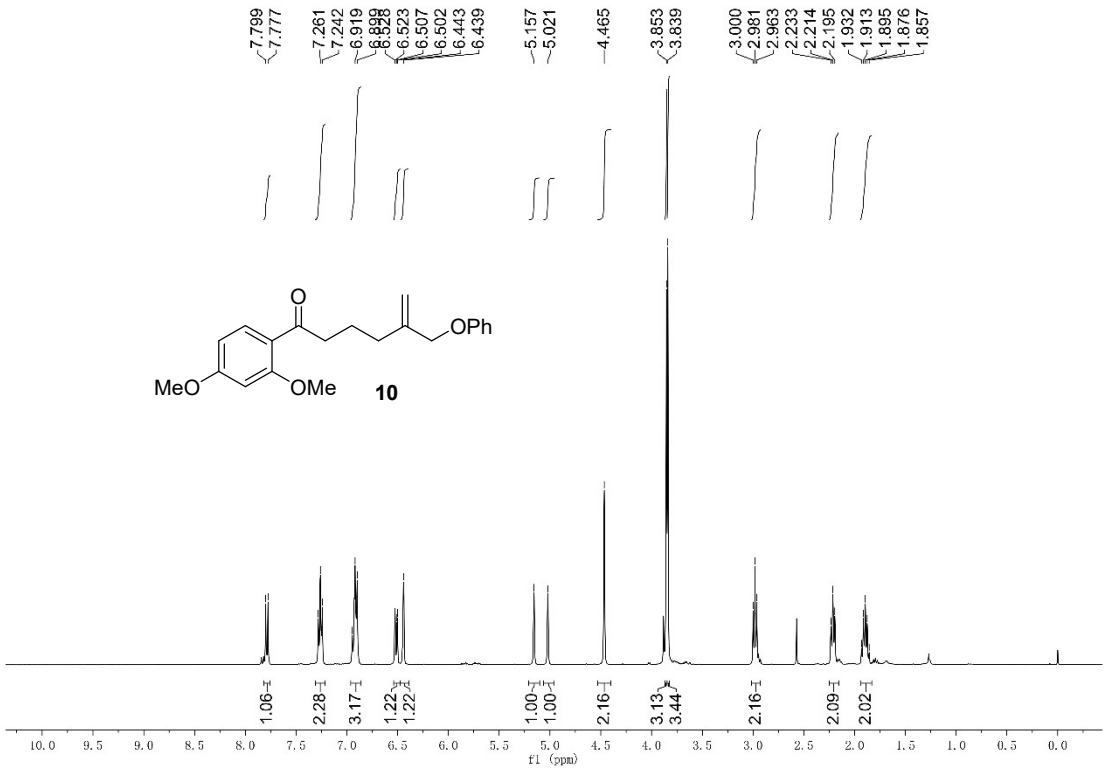
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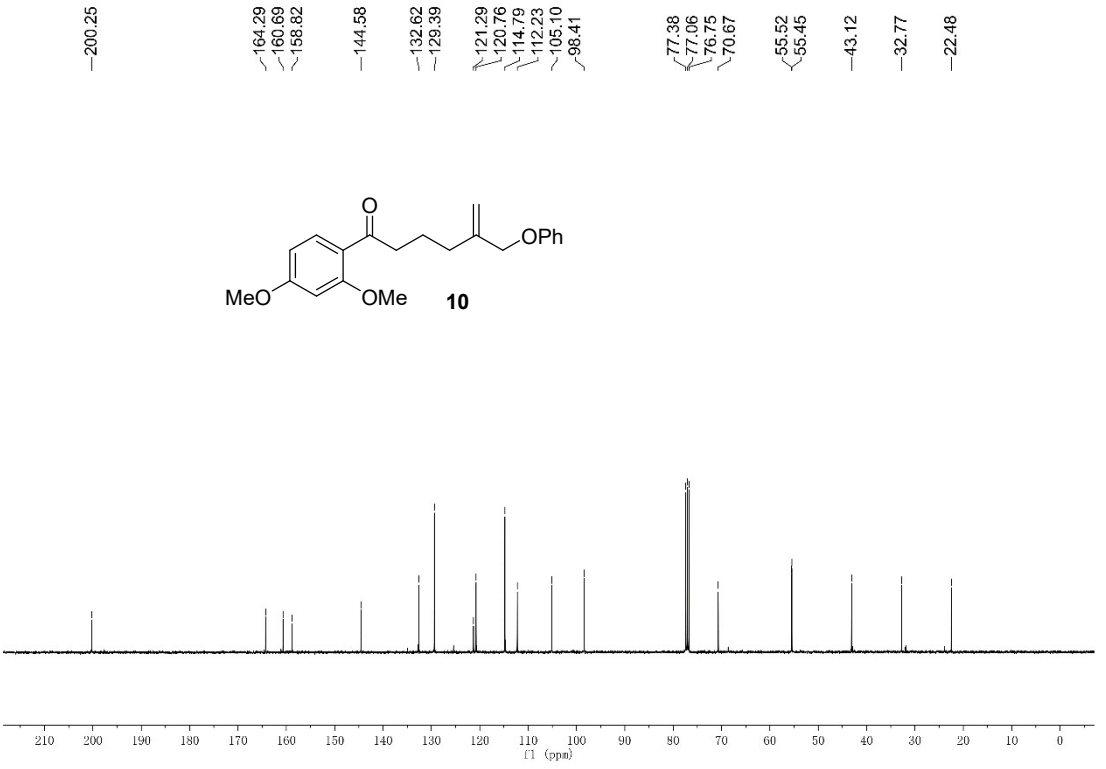
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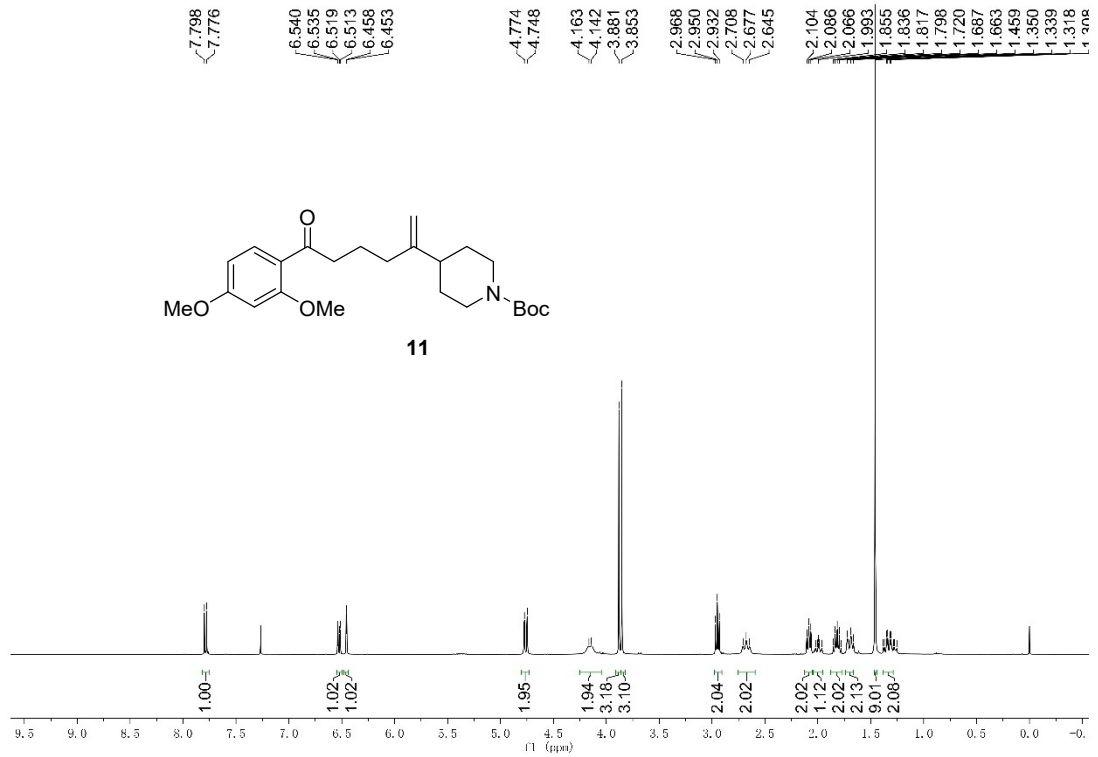
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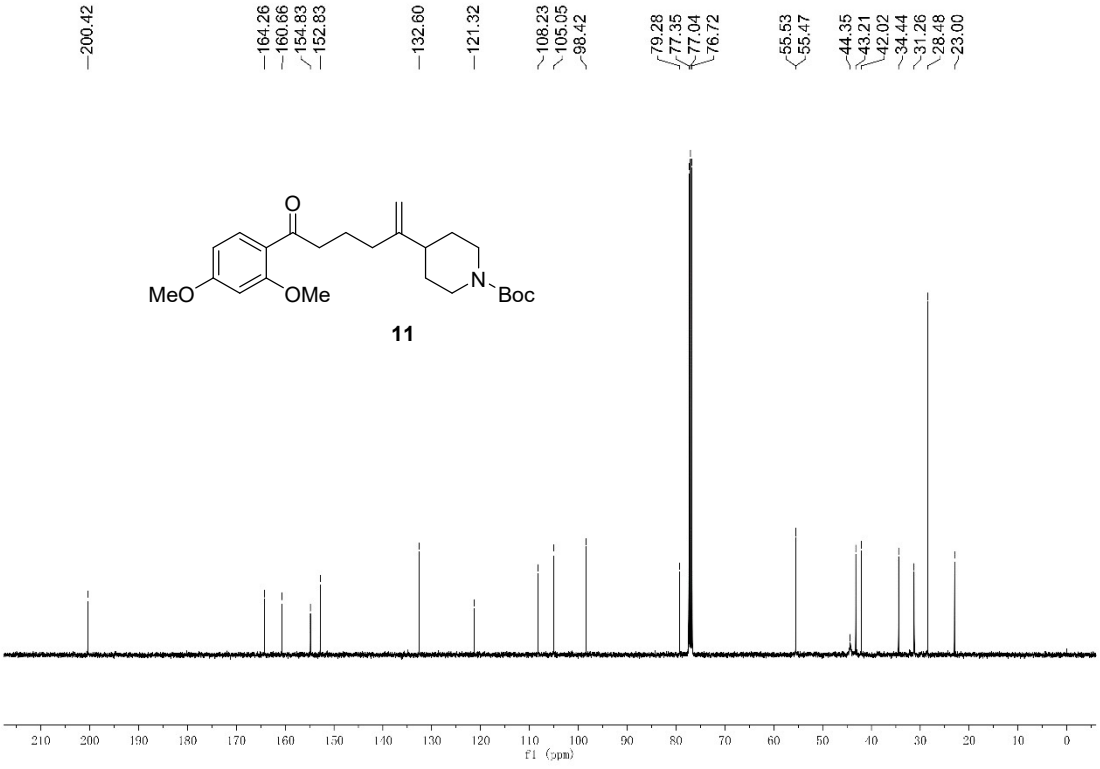
11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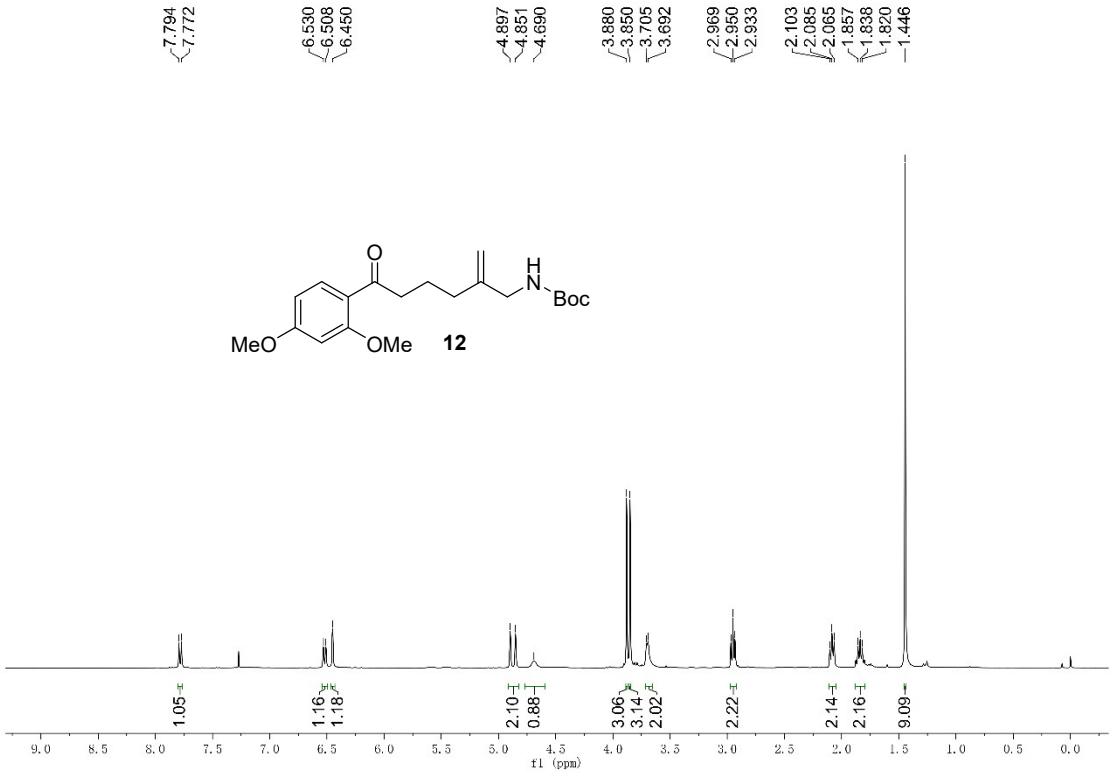
34.44
31.26
28.48
23.00
O
MeO
OMe
N
Boc
f1 (ppm)

11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4.690
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3.850
3.705
3.692
2.969
2.950
2.933
2.103
2.085
2.065
1.857
1.838
1.820
1.446
O
H
N
Boc
MeO
OMe
12
1.05
1.16
1.18
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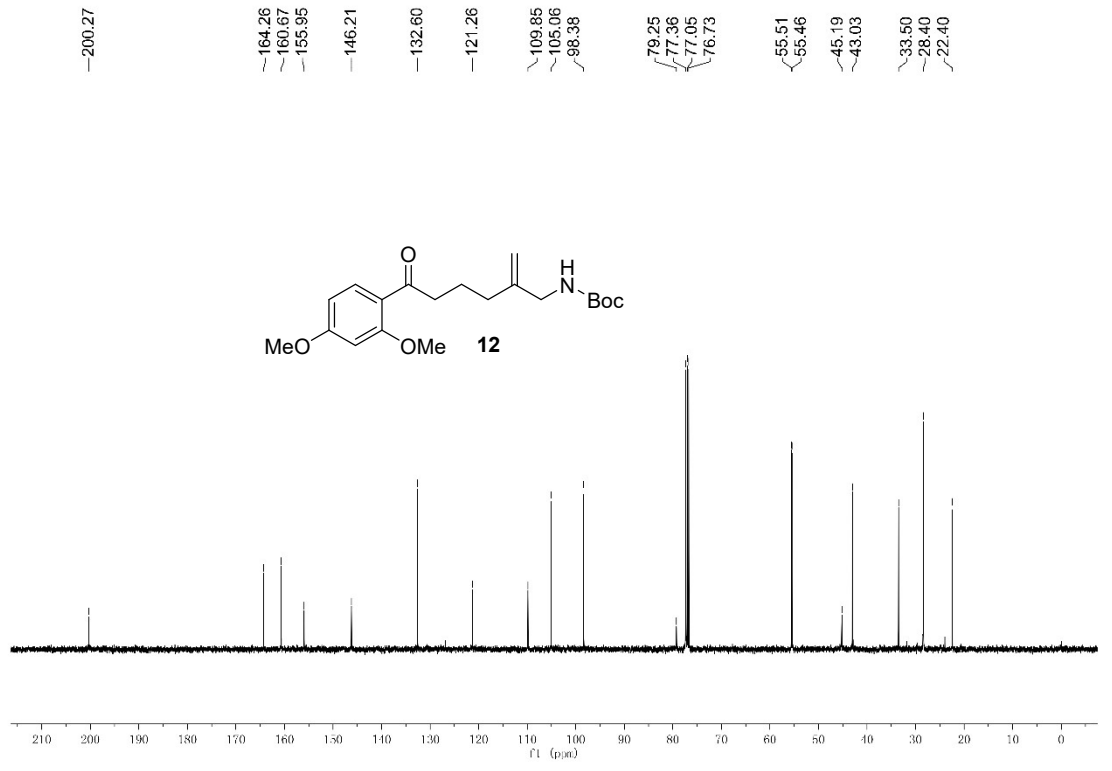
3.14
2.02
2.22
2.14
2.16
9.09
f1 (ppm)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109.85
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98.38
79.25
77.36
77.05
76.73
55.51
55.46
45.19
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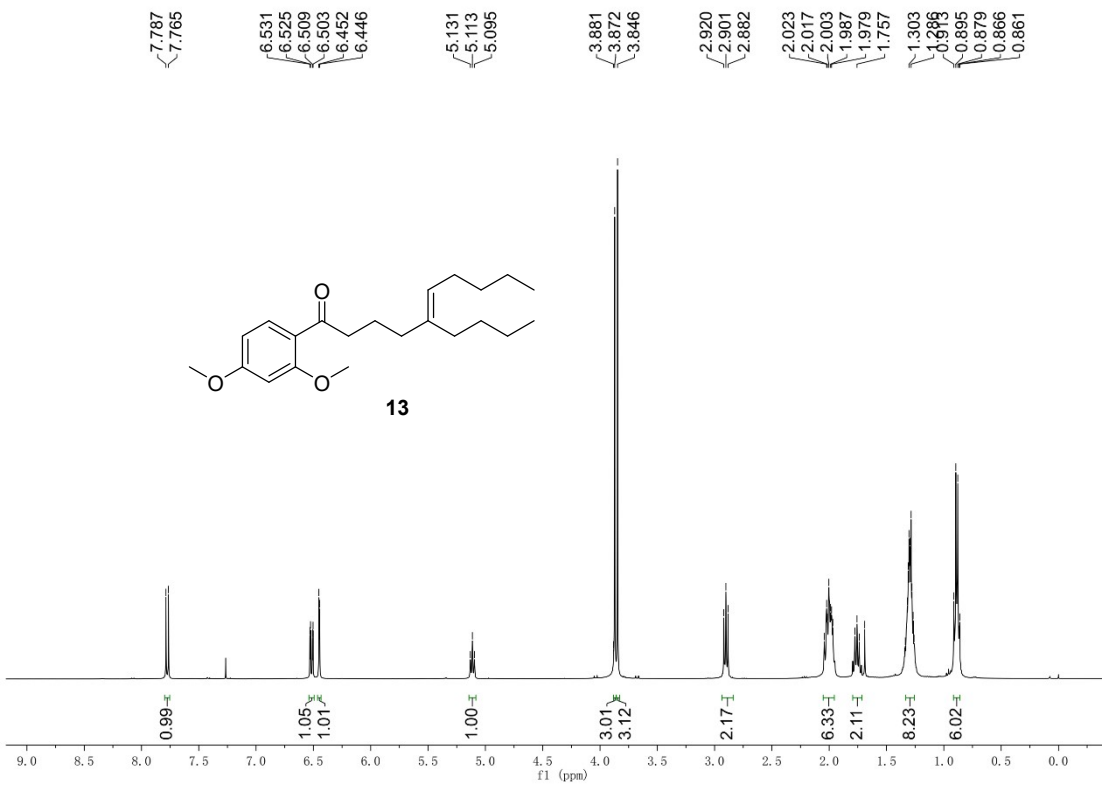
33.50
28.40
22.40
O
H
N
Boc
MeO
OMe
12
f1 (ppm)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6.525
6.509
6.503
6.452
6.446
5.131
5.113
5.095
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3.872
3.846
2.920
2.901
2.882
2.023
2.017
2.003
1.987
1.979
1.757
1.303
0.895
0.879
0.866
0.861
O
O
O
13
0.99
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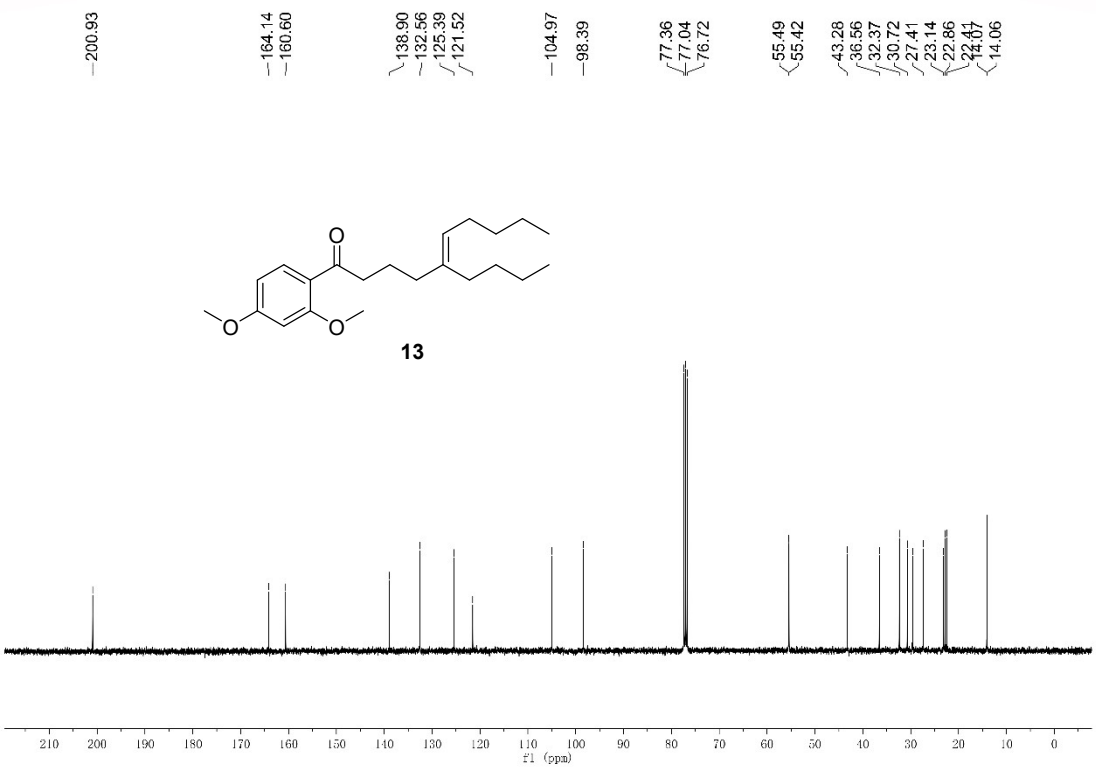
1.01
1.00
3.01
3.12
2.17
6.33
2.11
8.23
6.02
f1 (ppm)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104.97
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77.36
77.04
76.72
55.49
55.42
43.28
36.56
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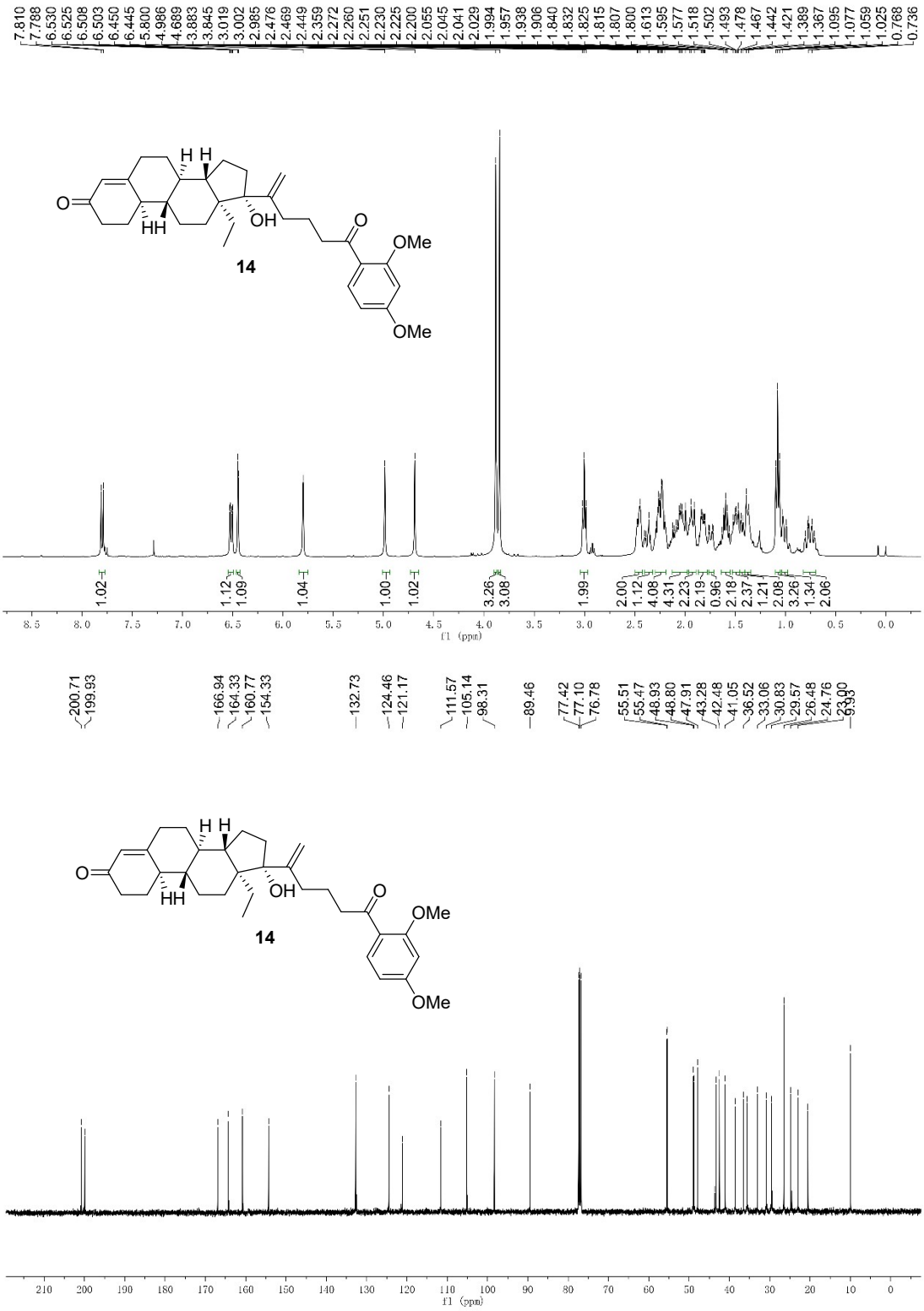
27.41
23.14
22.86
22.41
14.07
14.06
O
O
O
13
f1 (ppm)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6.445
5.800
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4.689
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3.845
3.019
3.002
2.985
2.476
2.469
2.449
2.359
2.272
2.260
2.251
2.230
2.225
2.200
2.055
2.045
2.041
2.029
1.994
1.957
1.938
1.906
1.840
1.832
1.825
1.815
1.807
1.800
1.613
1.595
1.577
1.518
1.502
1.493
1.478
1.467
1.442
1.421
1.389
1.367
1.095
1.077
1.059
1.025
0.768
0.736
H H
O
HH
OH
O
OMe
OMe
14
1.02
1.12
1.09
1.04
1.00
1.02
3.26
3.08
1.99
2.00
1.12
4.08
4.31
2.23
2.19
0.96
2.18
2.37
1.21
2.08
3.26
1.34
2.06
f1 (ppm)
200.71
199.93
166.94
164.33
160.77
154.33
132.73
124.46
121.17
111.57
105.14
98.31
89.46
77.42
77.10
76.78
55.51
55.47
48.93
48.80
47.91
43.28
42.48
41.05
36.52
33.06
30.83
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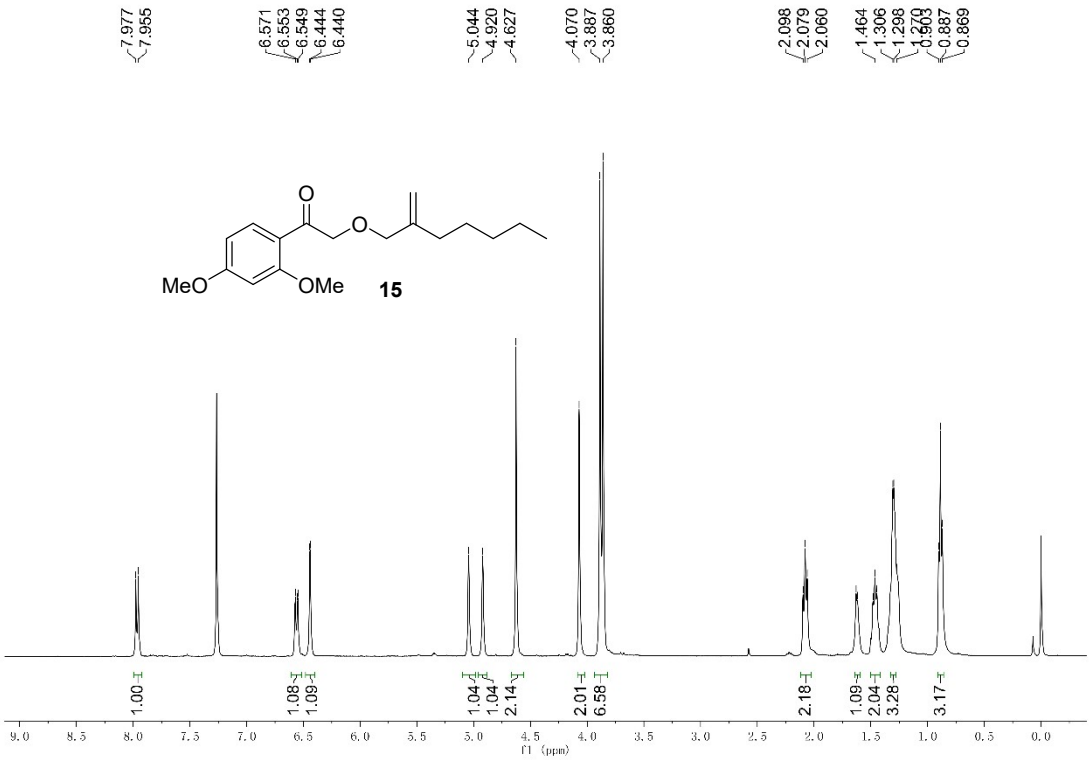
24.76
23.00
13.93
H H
O
HH
OH
O
OMe
OMe
14
f1 (ppm)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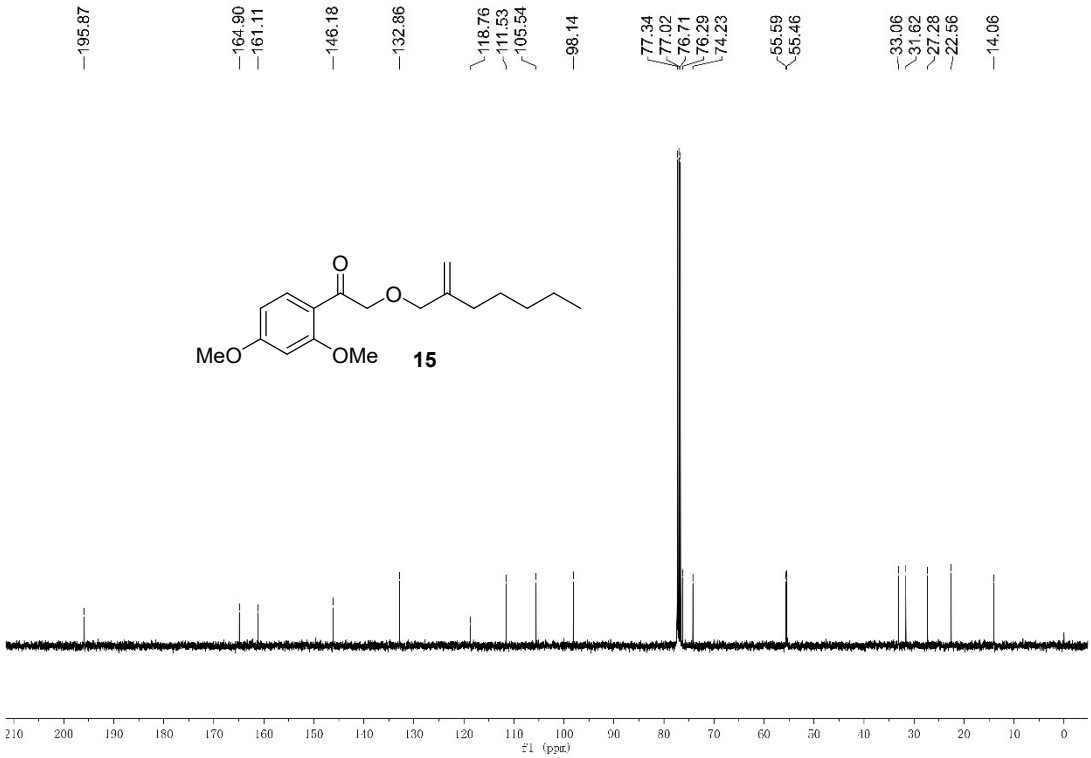
6.571
6.553
6.549
6.444
6.440
5.044
4.920
4.627
4.070
3.887
3.860
2.098
2.079
2.060
1.464
1.306
1.298
1.603
0.887
0.869
MeO
OMe
15
1.00
1.08
1.09
1.04
1.04
2.14
2.01
6.58
2.18
1.09
2.04
3.28
3.17
f1 (ppm)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132.86
118.76
111.53
105.54
98.14
77.34
77.02
76.71
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74.23
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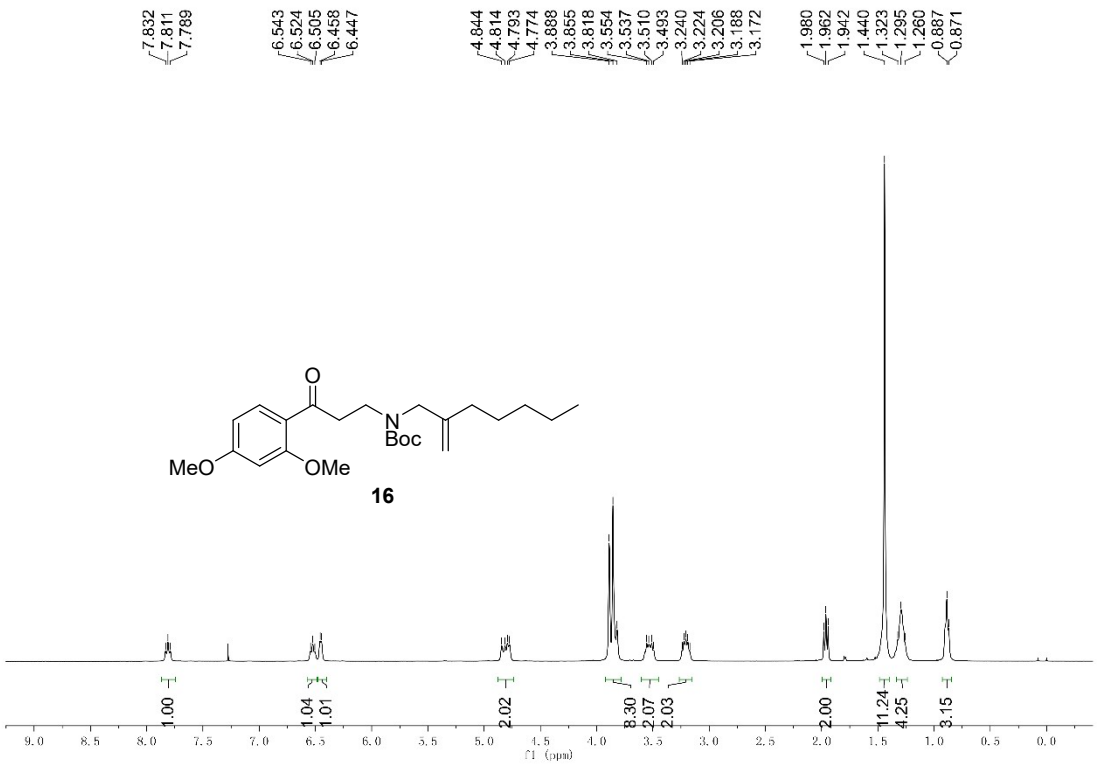
55.46
33.06
31.62
27.28
22.56
14.06
MeO
OMe
15
f1 (ppm)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7.811
7.789
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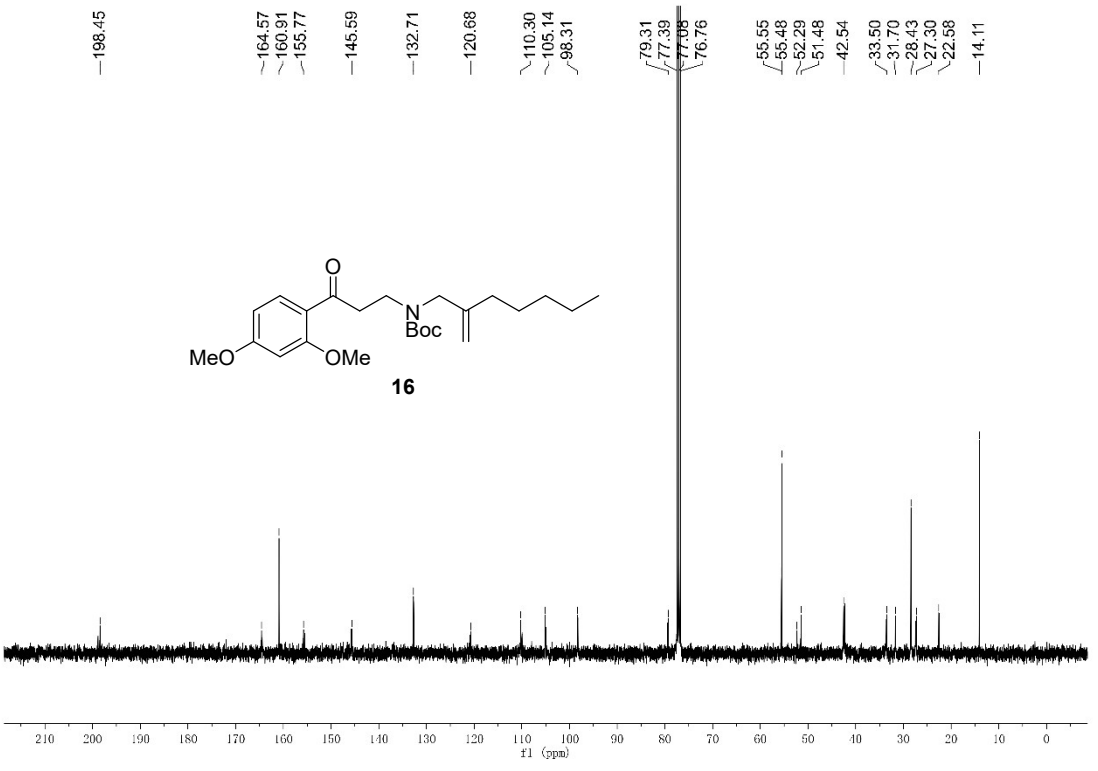
6.524
6.505
6.458
6.447
4.844
4.814
4.793
4.774
3.888
3.855
3.818
3.554
3.537
3.510
3.493
3.240
3.224
3.206
3.188
3.172
1.980
1.962
1.942
1.440
1.323
1.295
1.260
0.887
0.871
O
N
Boc
MeO
OMe
16
1.00
1.04
1.01
2.02
8.30
2.07
2.03
2.00
11.24
4.25
3.15
f1 (ppm)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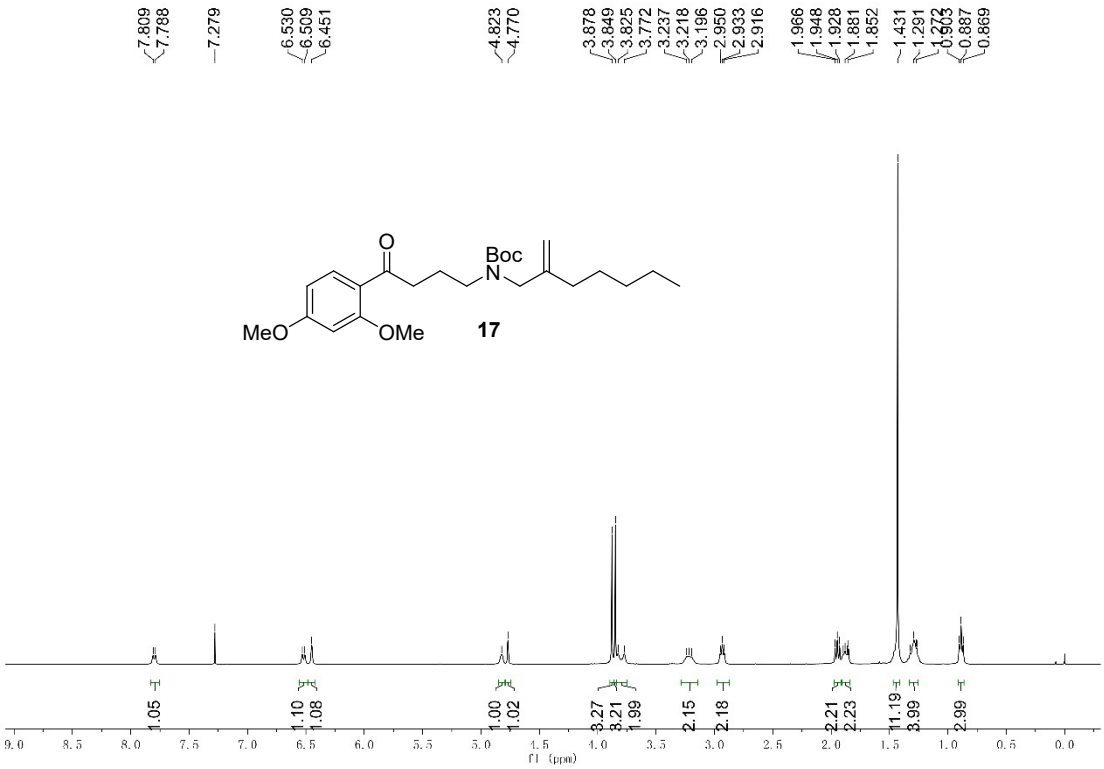
145.59
132.71
120.68
110.30
105.14
98.31
79.31
77.39
77.06
76.76
55.55
55.48
52.29
51.48
42.54
33.50
31.70
28.43
27.30
22.58
14.11
O
N
Boc
MeO
OMe
16
f1 (ppm)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6.530
6.509
6.451
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4.770
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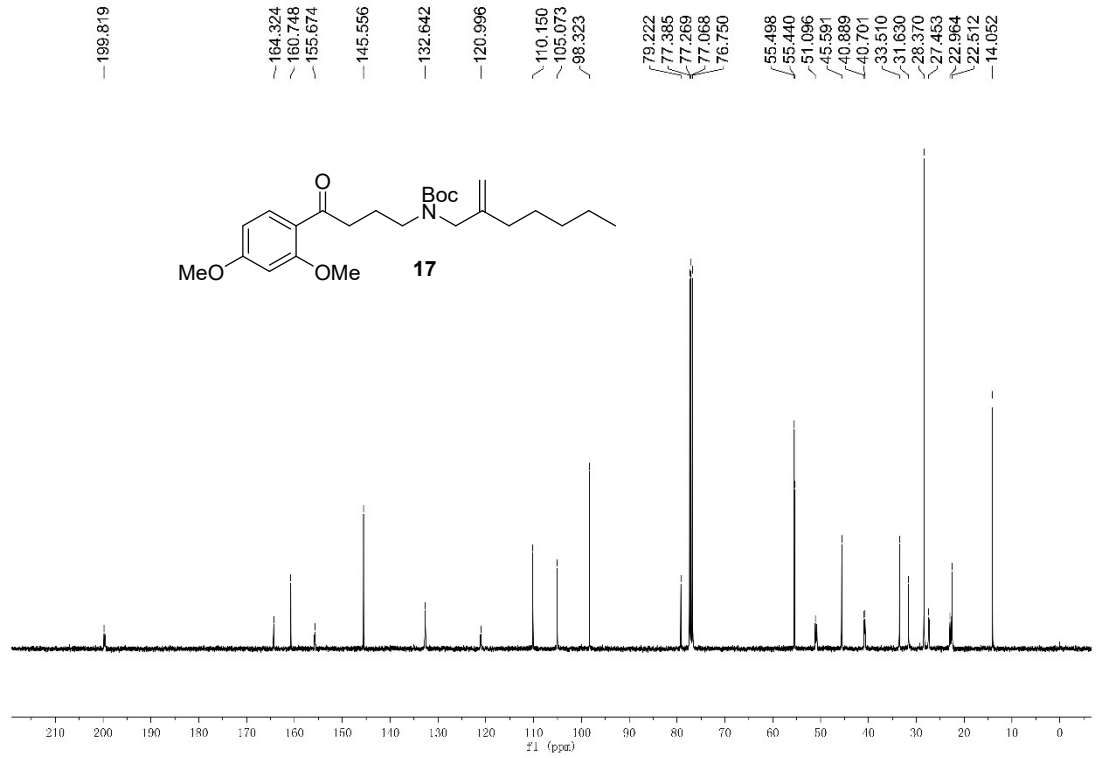
3.825
3.772
3.237
3.218
3.196
2.950
2.933
2.916
1.966
1.948
1.928
1.881
1.852
1.431
1.291
0.903
0.887
0.869
O
Boc
N
MeO
OMe
17
1.05
1.10
1.08
1.00
1.02
3.27
3.21
1.99
2.15
2.18
2.21
2.23
11.19
3.99
2.99
f1 (ppm)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110.150
105.073
98.323
79.222
77.385
77.269
77.068
76.750
55.498
55.440
51.096
45.591
40.889
40.701
33.510
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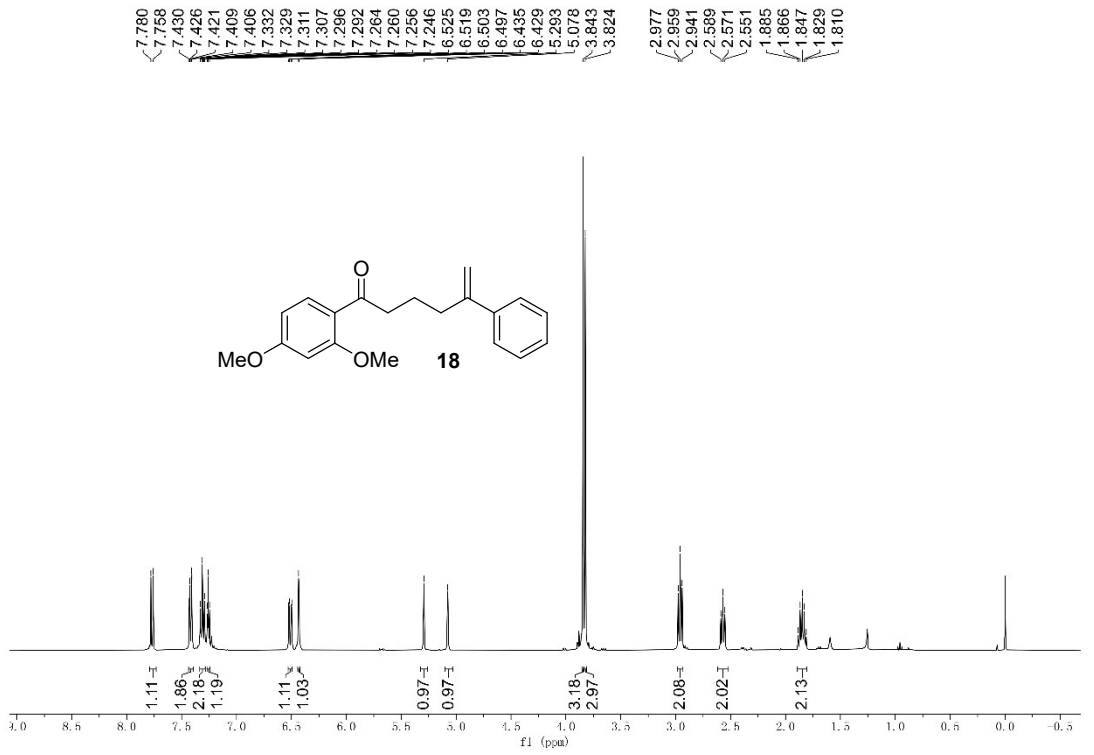
27.453
22.964
22.512
14.052
O
Boc
N
MeO
OMe
17
f1 (ppm)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7.311
7.307
7.296
7.292
7.264
7.260
7.256
7.246
6.525
6.519
6.503
6.497
6.435
6.429
5.293
5.078
3.843
3.824
2.977
2.959
2.941
2.589
2.571
2.551
1.885
1.866
1.847
1.829
1.810
O
MeO
OMe
18
1.11
1.86
2.18
1.19
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1.03
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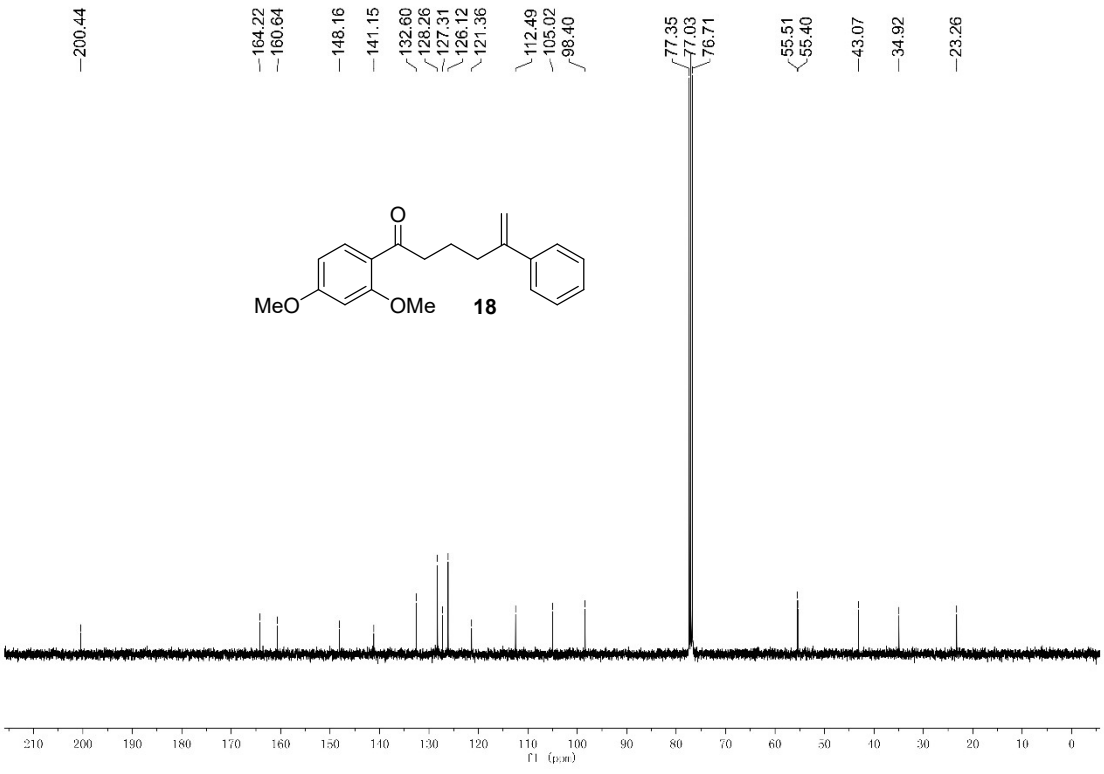
2.08
2.02
2.13
f1 (ppm)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128.26
127.31
126.12
121.36
112.49
105.02
98.40
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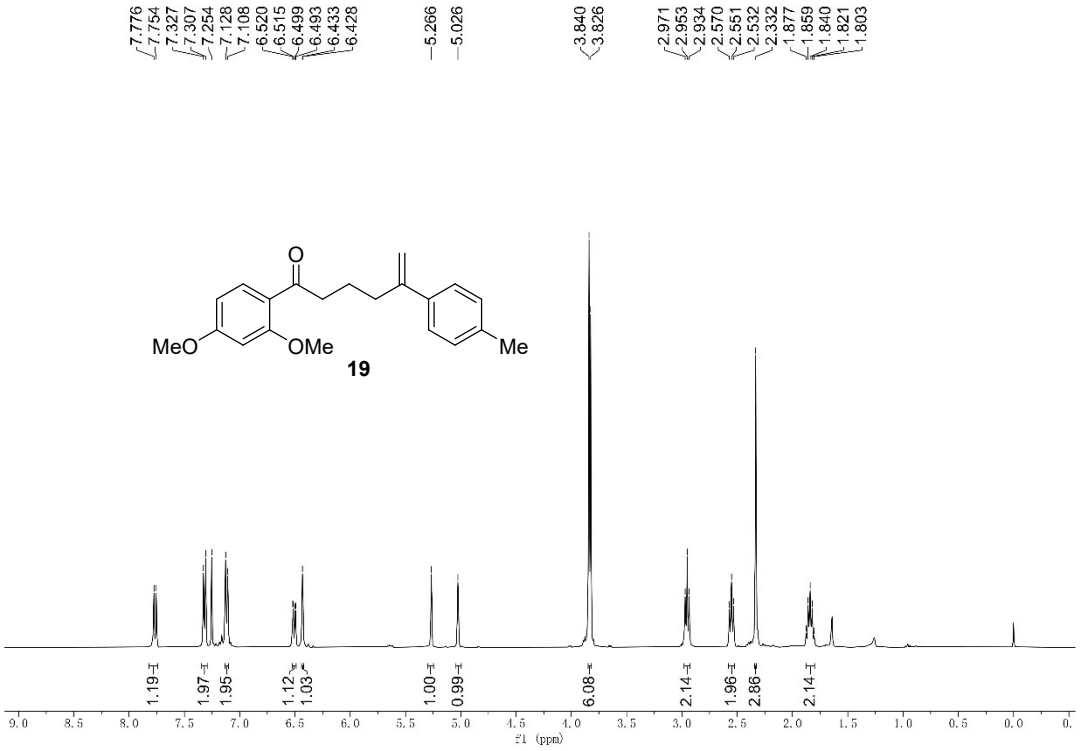
77.03
76.71
55.51
55.40
43.07
34.92
23.26
O
MeO
OMe
18
f1 (ppm)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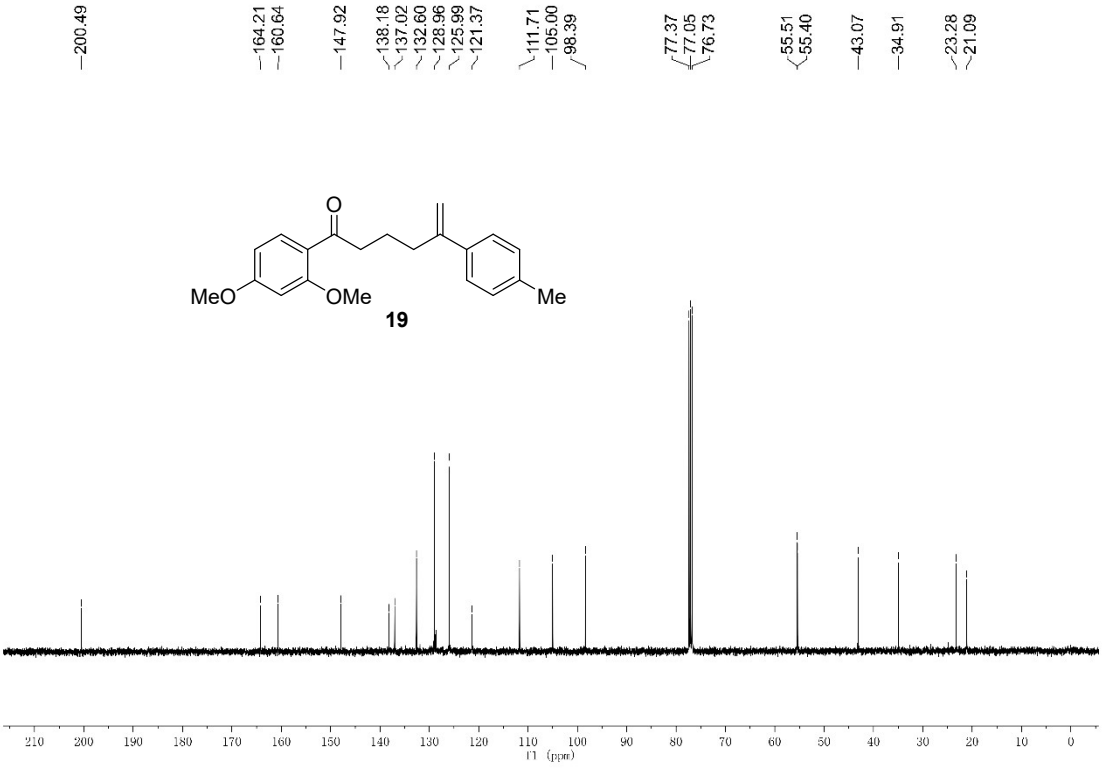
6.499
6.493
6.433
6.428
5.266
5.026
3.840
3.826
2.971
2.953
2.934
2.570
2.551
2.532
2.332
1.877
1.859
1.840
1.821
1.803
O
MeO
OMe
Me
19
1.19
1.97
1.95
1.12
1.03
1.00
0.99
6.08
2.14
1.96
2.86
2.14
f1 (ppm)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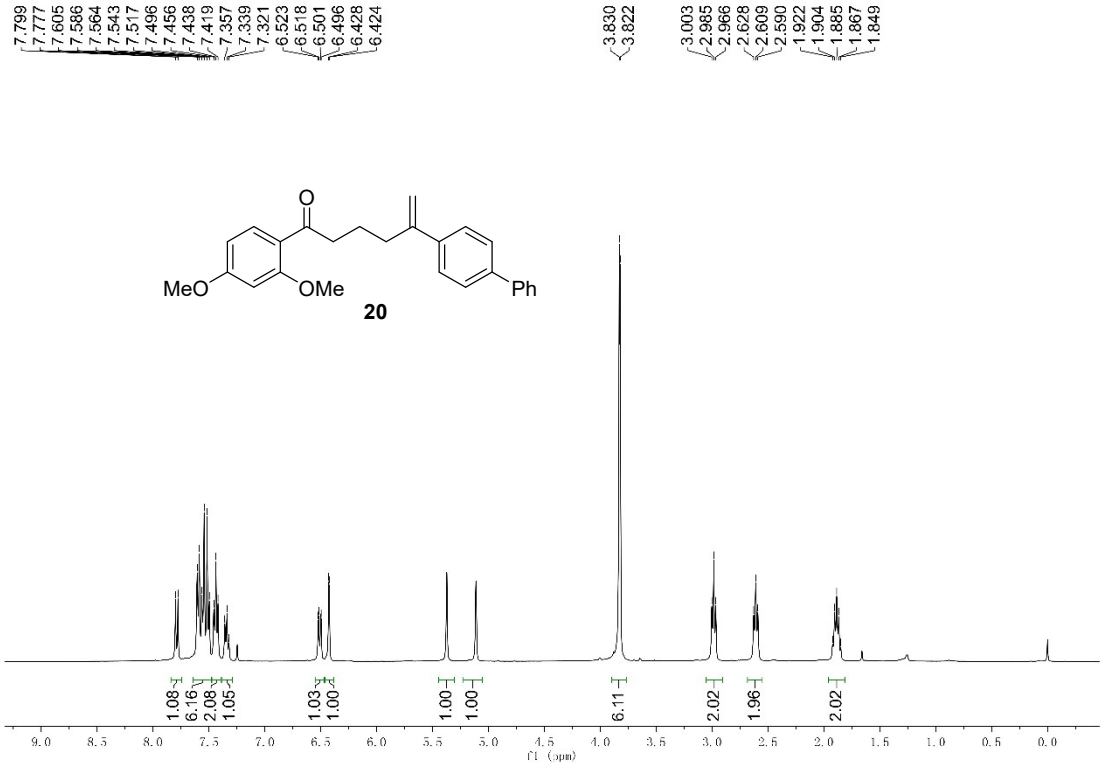
132.60
128.96
125.99
121.37
111.71
105.00
98.39
77.37
77.05
76.73
55.51
55.40
43.07
34.91
23.28
21.09
O
MeO
OMe
Me
19
f1 (ppm)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7.339
7.321
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6.518
6.501
6.496
6.428
6.424
3.830
3.822
3.003
2.985
2.966
2.628
2.609
2.590
1.922
1.904
1.885
1.867
1.849
O
MeO
OMe
Ph
20
1.08
6.16
2.08
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1.03
1.00
1.00
1.00
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2.02
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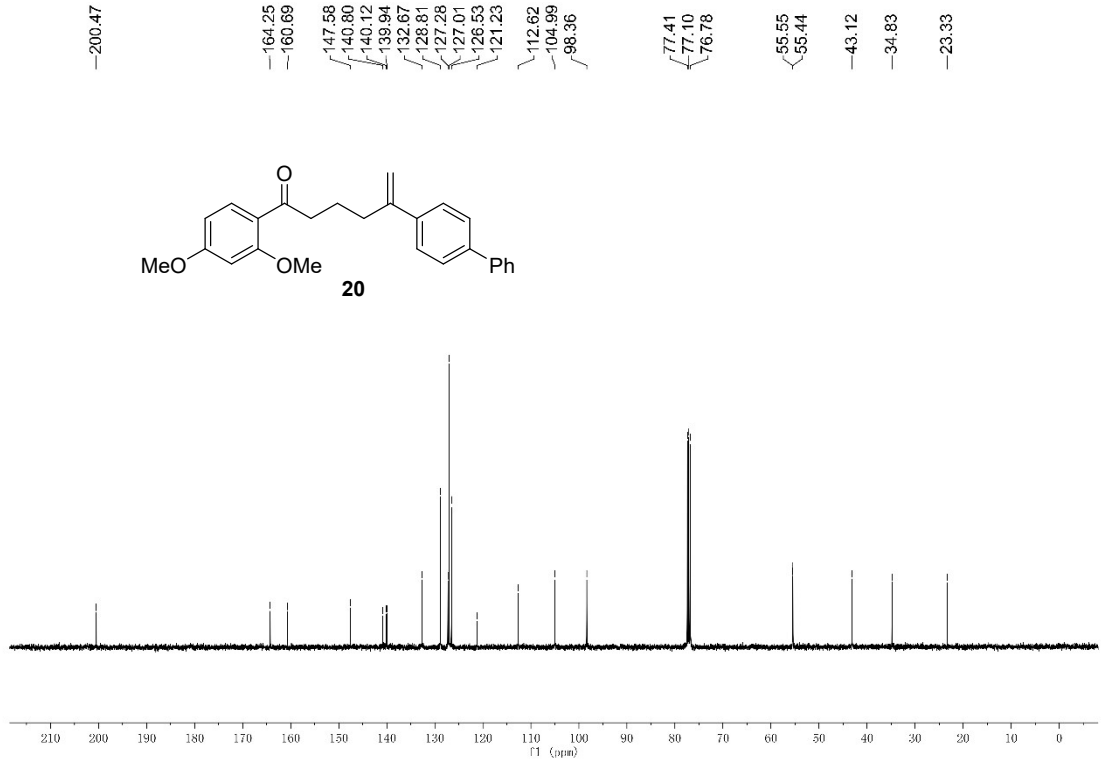
2.02
f1 (ppm)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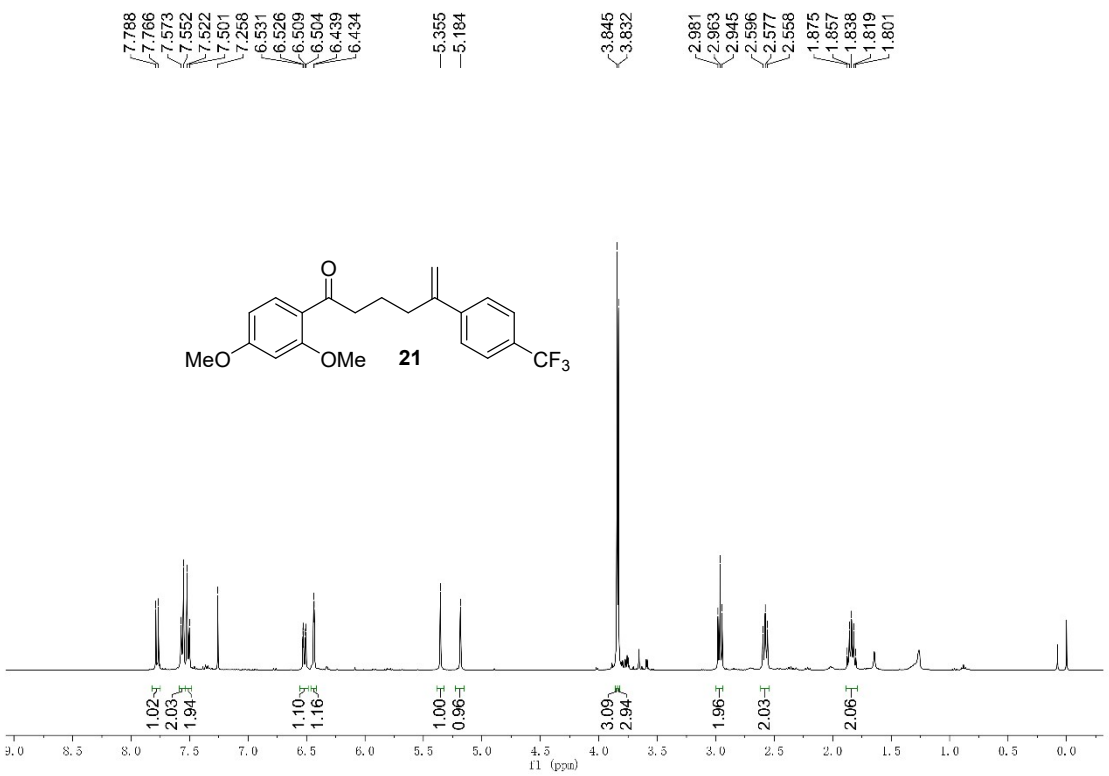
132.67
128.81
127.28
127.01
126.53
121.23
112.62
104.99
98.36
77.41
77.10
76.78
55.55
55.44
43.12
34.83
23.33
O
MeO
OMe
Ph
20
f1 (ppm)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6.526
6.509
6.504
6.439
6.434
5.355
5.184
3.845
3.832
2.981
2.963
2.945
2.596
2.577
2.558
1.875
1.857
1.838
1.819
1.801
O
MeO
OMe
21
CF3
1.02
2.03
1.94
1.10
1.16
1.00
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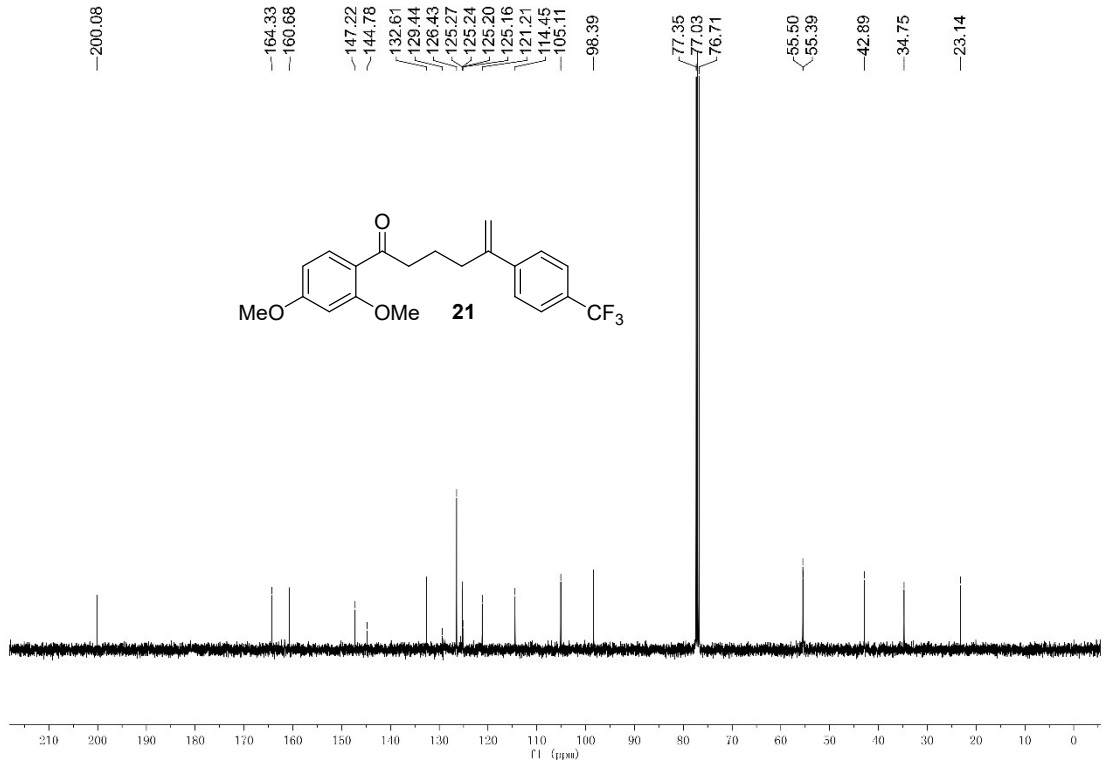
3.09
2.94
1.96
2.03
2.06
f1 (ppm)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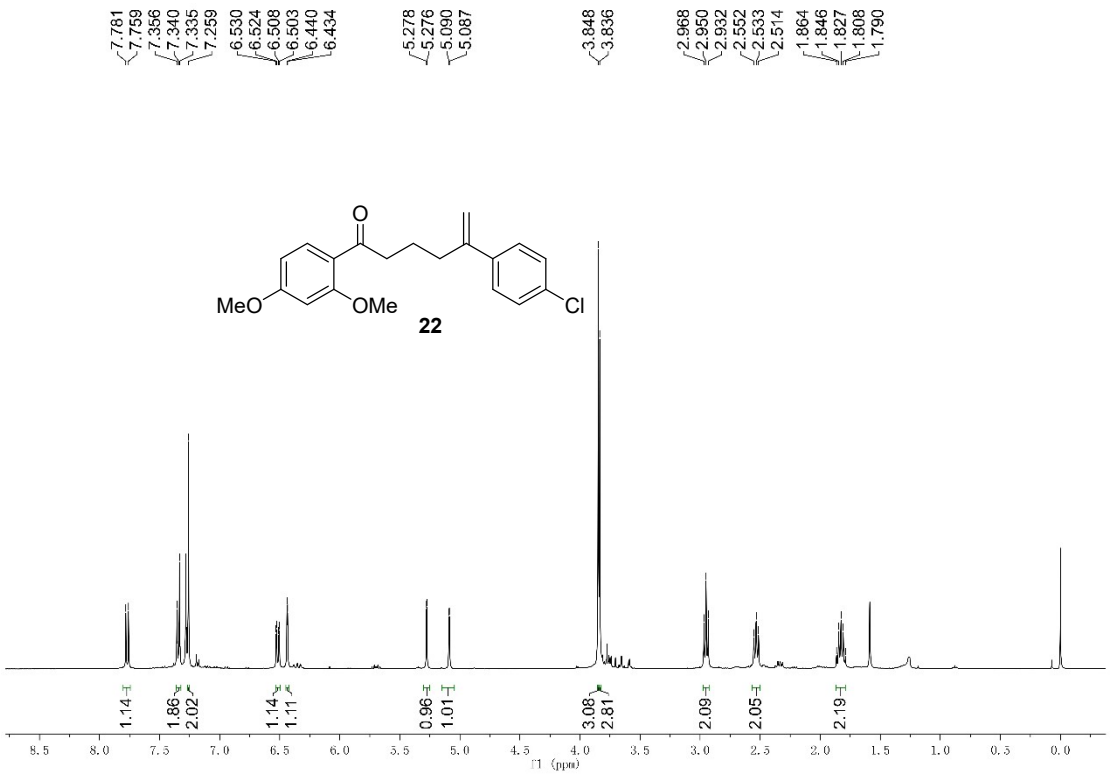
126.43
125.27
125.24
125.20
125.16
121.21
114.45
105.11
98.39
77.35
77.03
76.71
55.50
55.39
42.89
34.75
23.14
O
MeO
OMe
21
CF3
f1 (ppm)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6.508
6.503
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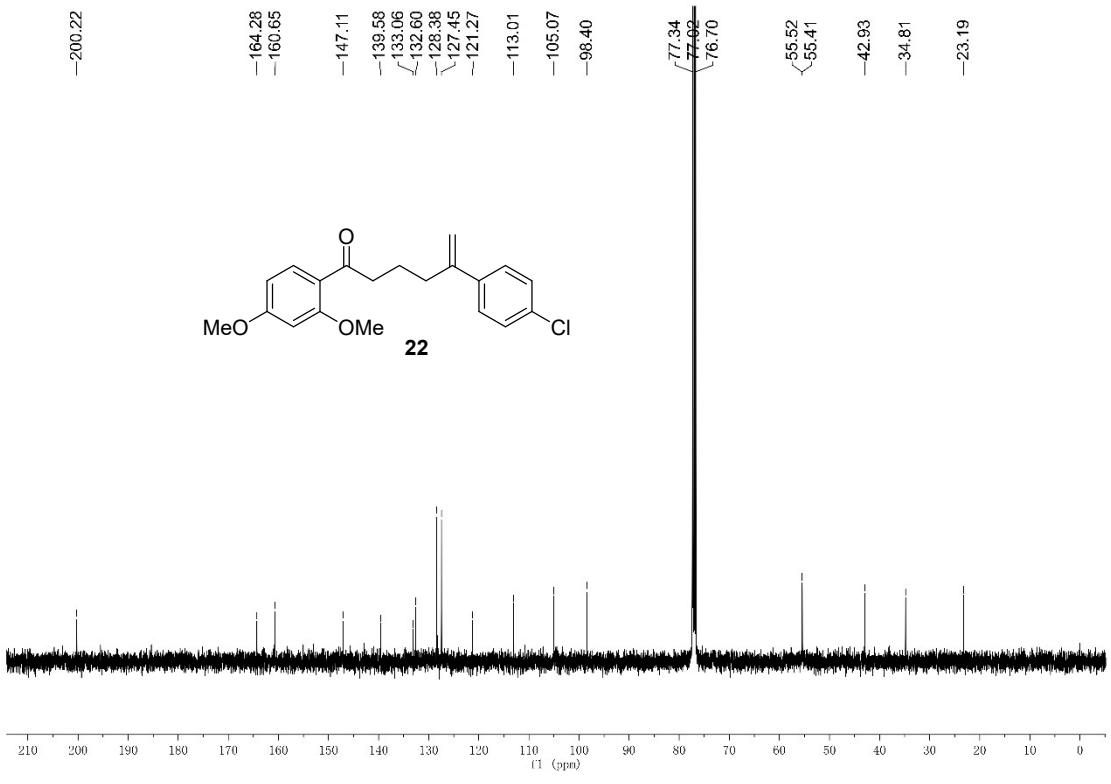
6.434
5.278
5.276
5.090
5.087
3.848
3.836
2.968
2.950
2.932
2.552
2.533
2.514
1.864
1.846
1.827
1.808
1.790
O
MeO
OMe
Cl
22
1.14
1.86
2.02
1.14
1.11
0.96
1.01
3.08
2.81
2.09
2.05
2.19
f1 (ppm)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160.65
147.11
139.58
133.06
132.60
128.38
127.45
121.27
113.01
105.07
98.40
77.34
77.02
76.70
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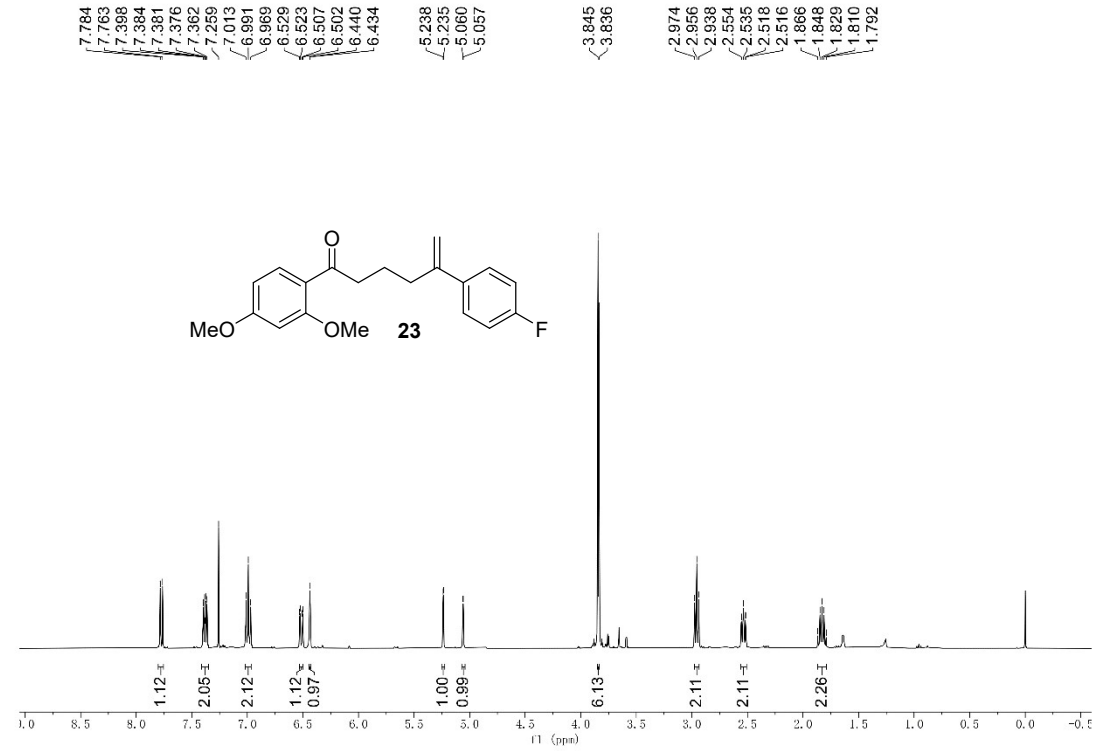
55.41
42.93
34.81
23.19
O
MeO
OMe
Cl
22
f1 (ppm)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6.991
6.969
6.529
6.523
6.507
6.502
6.440
6.434
5.238
5.235
5.060
5.057
3.845
3.836
2.974
2.956
2.938
2.554
2.535
2.518
2.516
1.866
1.848
1.829
1.810
1.792
O
MeO
OMe
23
F
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2.05
2.12
1.12
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1.00
0.99
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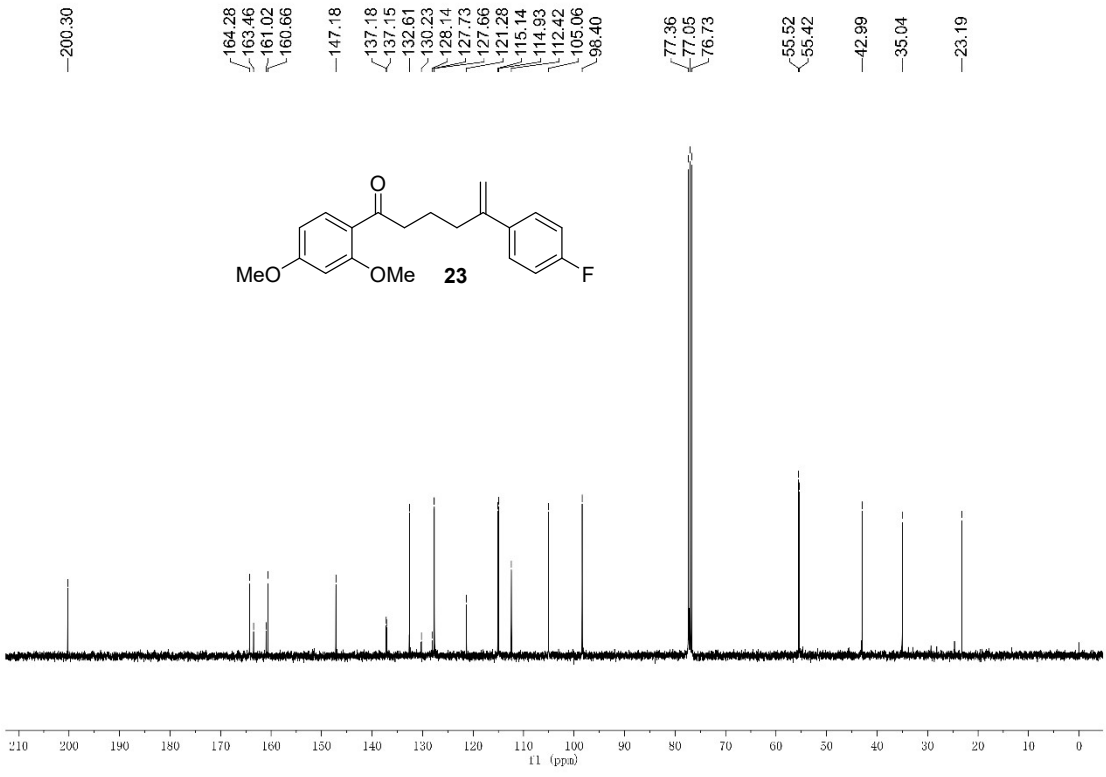
2.11
2.11
2.26
f1 (ppm)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137.18
137.15
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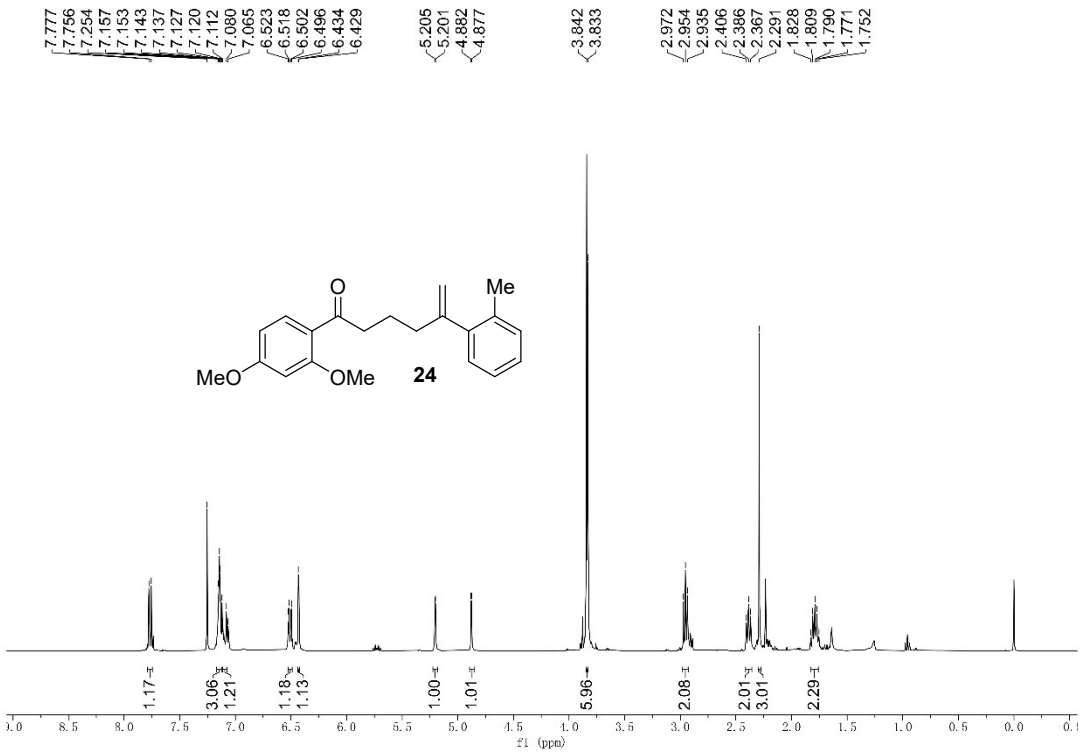
130.23
128.14
127.73
127.66
121.28
115.14
114.93
112.42
105.06
98.40
77.36
77.05
76.73
55.52
55.42
42.99
35.04
23.19
O
MeO
OMe
23
F
f1 (ppm)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7.127
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7.112
7.080
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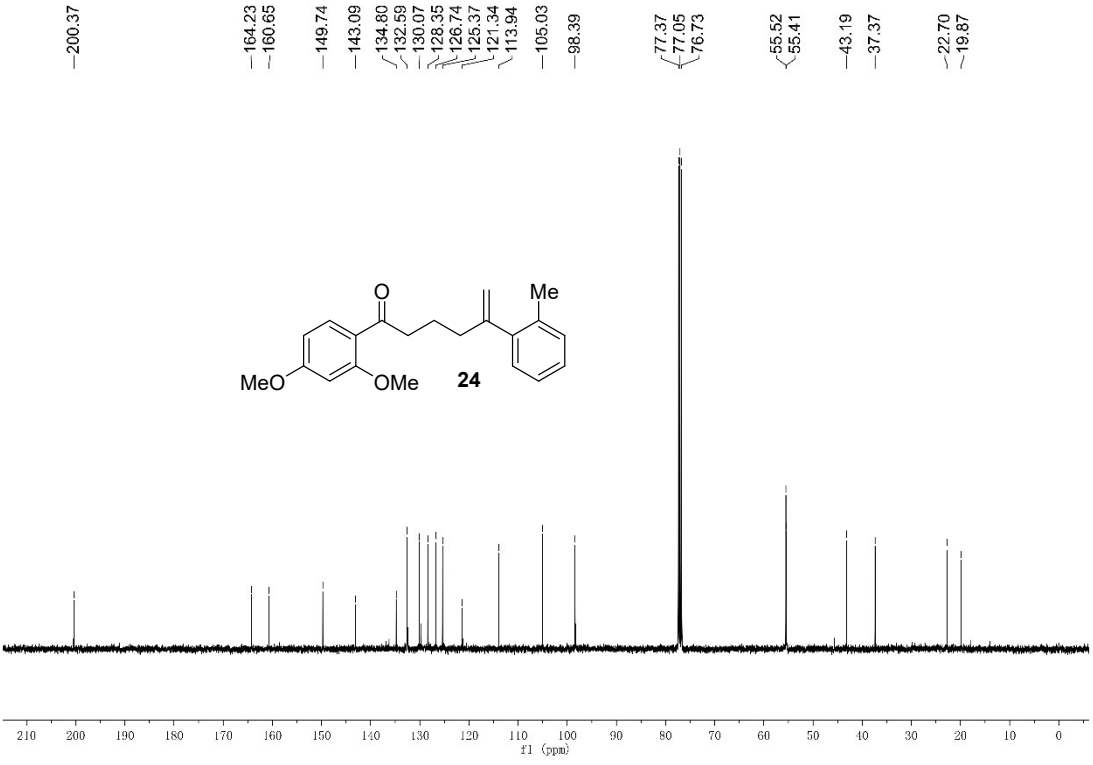
6.523
6.518
6.502
6.496
6.434
6.429
5.205
5.201
4.882
4.877
3.842
3.833
2.972
2.954
2.935
2.406
2.386
2.367
2.291
1.828
1.809
1.790
1.771
1.752
O
Me
MeO
OMe
24
1.17
3.06
1.21
1.18
1.13
1.00
1.01
5.96
2.08
2.01
3.01
2.29
f1 (ppm)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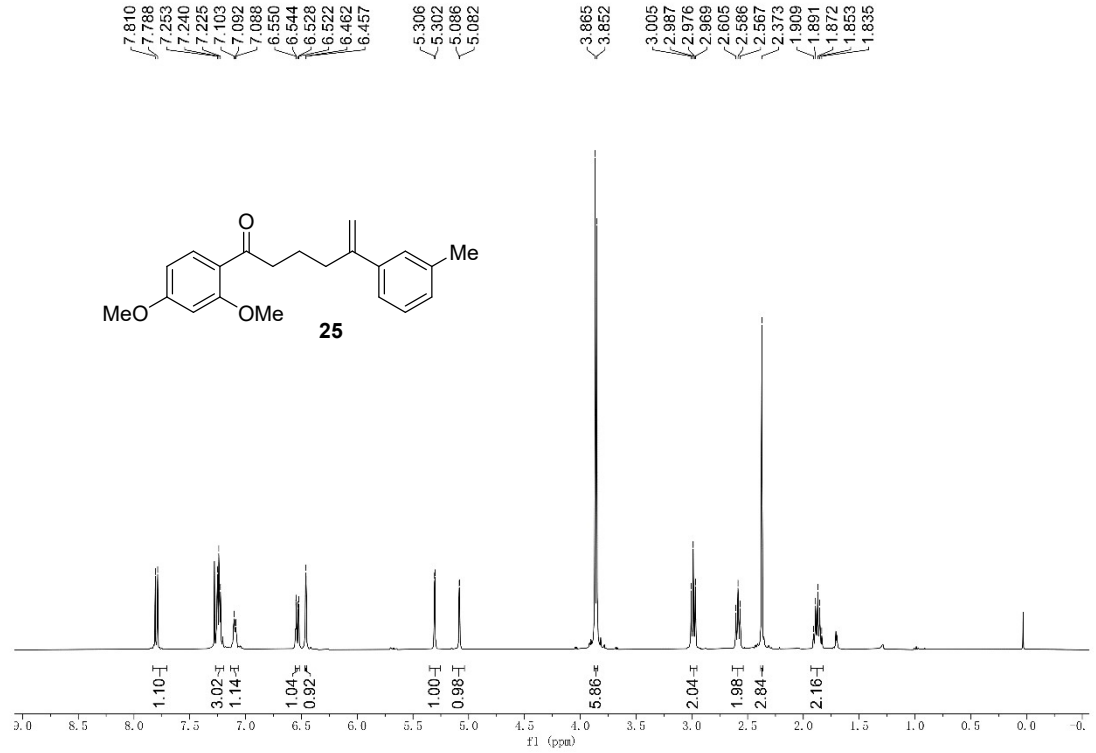
160.65
149.74
143.09
134.80
132.59
130.07
128.35
126.74
125.37
121.34
113.94
105.03
98.39
77.37
77.05
76.73
55.52
55.41
43.19
37.37
22.70
19.87
O
Me
MeO
OMe
24
f1 (ppm)

S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7.788
7.253
7.240
7.225
7.103
7.092
7.088
6.550
6.544
6.528
6.522
6.462
6.457
5.306
5.302
5.086
5.082
3.865
3.852
3.005
2.987
2.976
2.969
2.605
2.586
2.567
2.373
1.909
1.891
1.872
1.853
1.835
O
Me
MeO
OMe
25
1.10
3.02
1.14
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0.92
1.00
0.98
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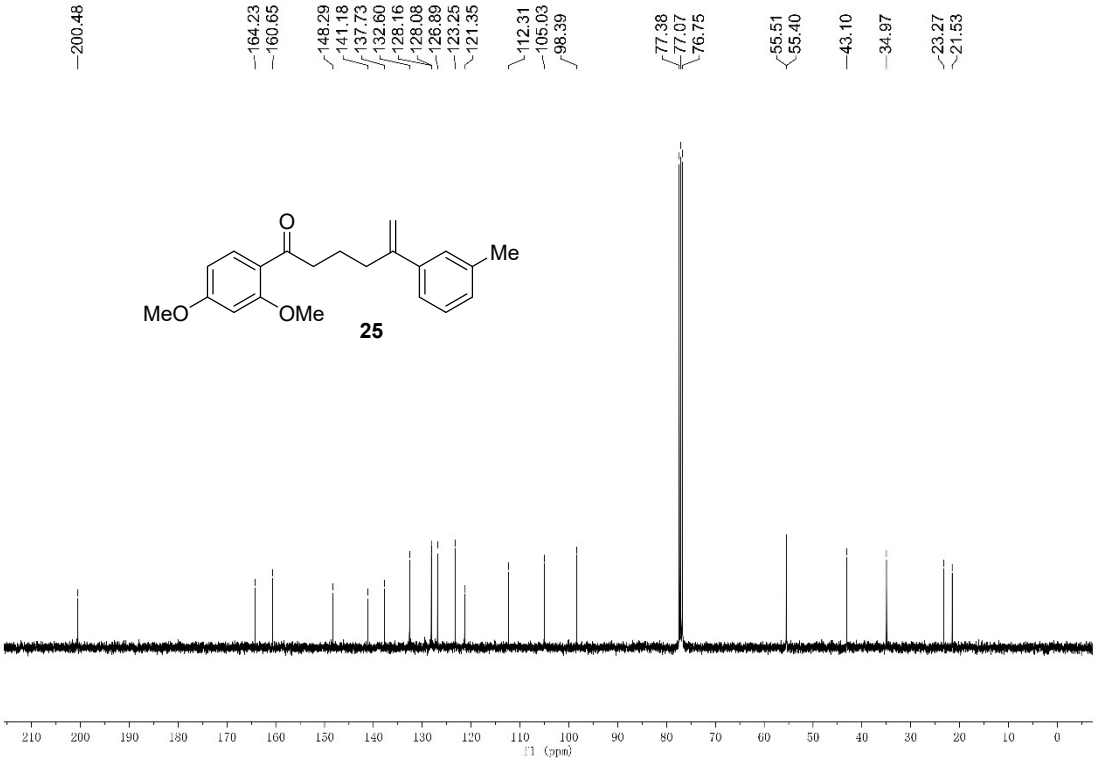
2.04
1.98
2.84
2.16
f1 (ppm)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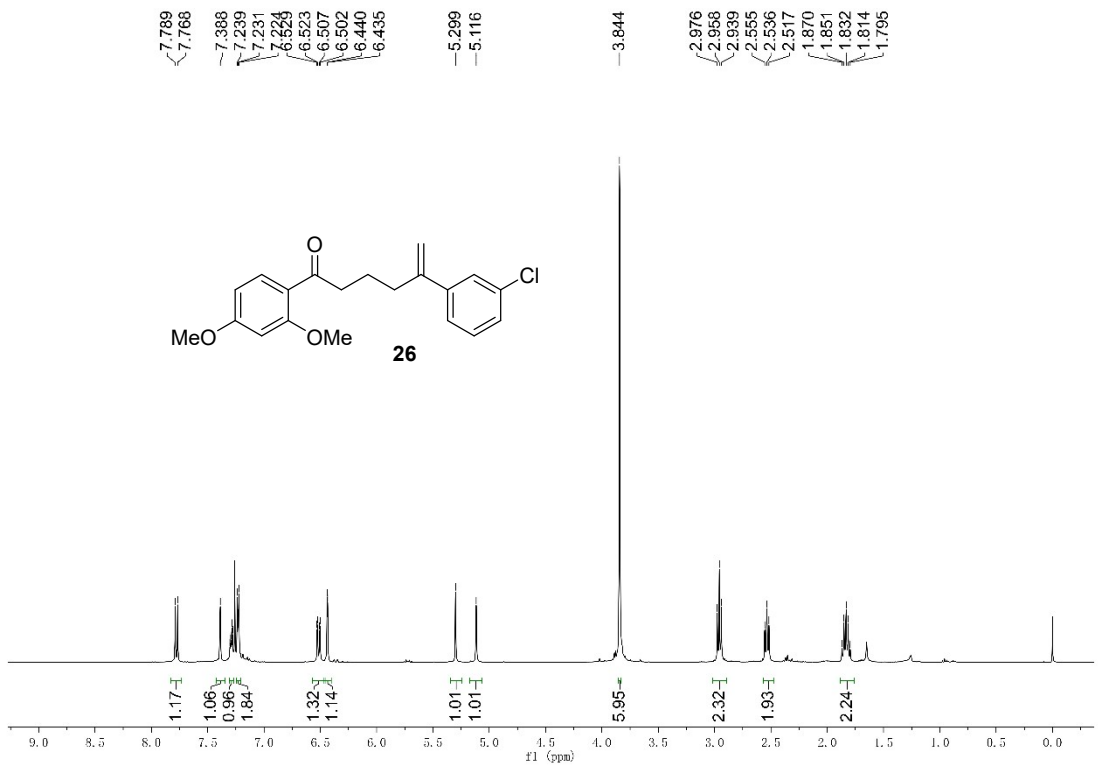
137.73
132.60
128.16
128.08
126.89
123.25
121.35
112.31
105.03
98.39
77.38
77.07
76.75
55.51
55.40
43.10
34.97
23.27
21.53
O
Me
MeO
OMe
25
f1 (ppm)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7.388
7.239
7.231
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6.507
6.502
6.440
6.435
5.299
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3.844
2.976
2.958
2.939
2.555
2.536
2.517
1.870
1.851
1.832
1.814
1.795
O
Cl
MeO
OMe
26
1.17
1.06
0.96
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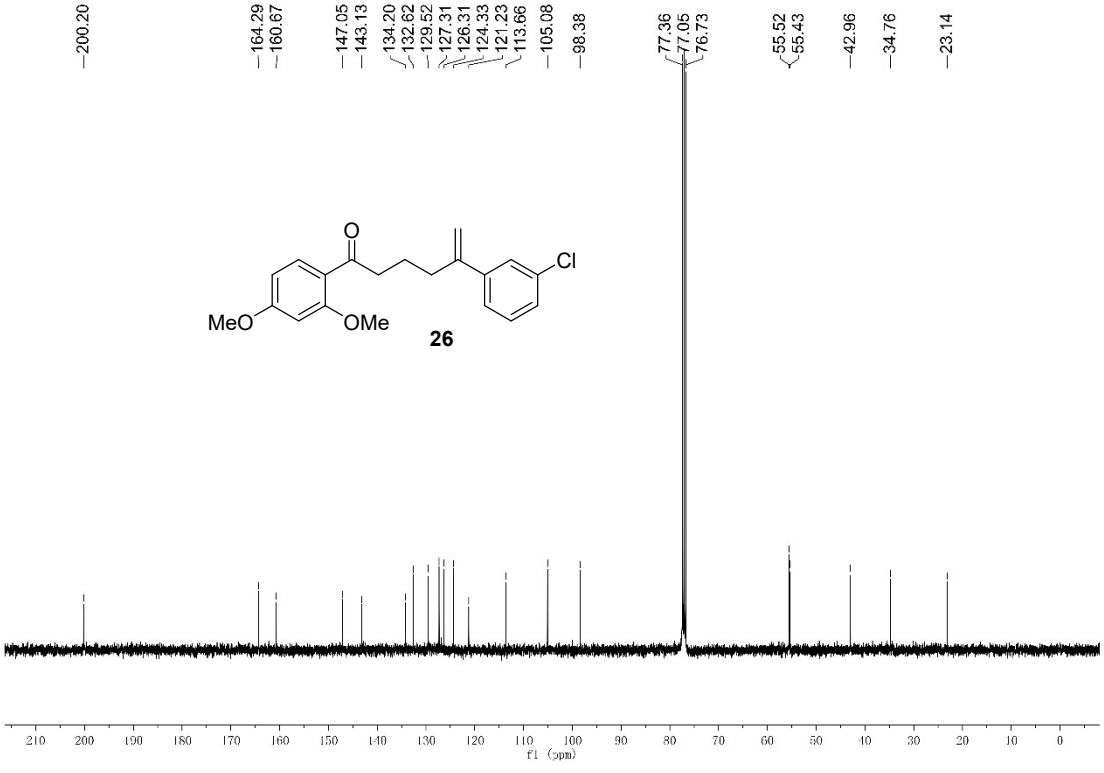
1.32
1.14
1.01
1.01
5.95
2.32
1.93
2.24
f1 (ppm)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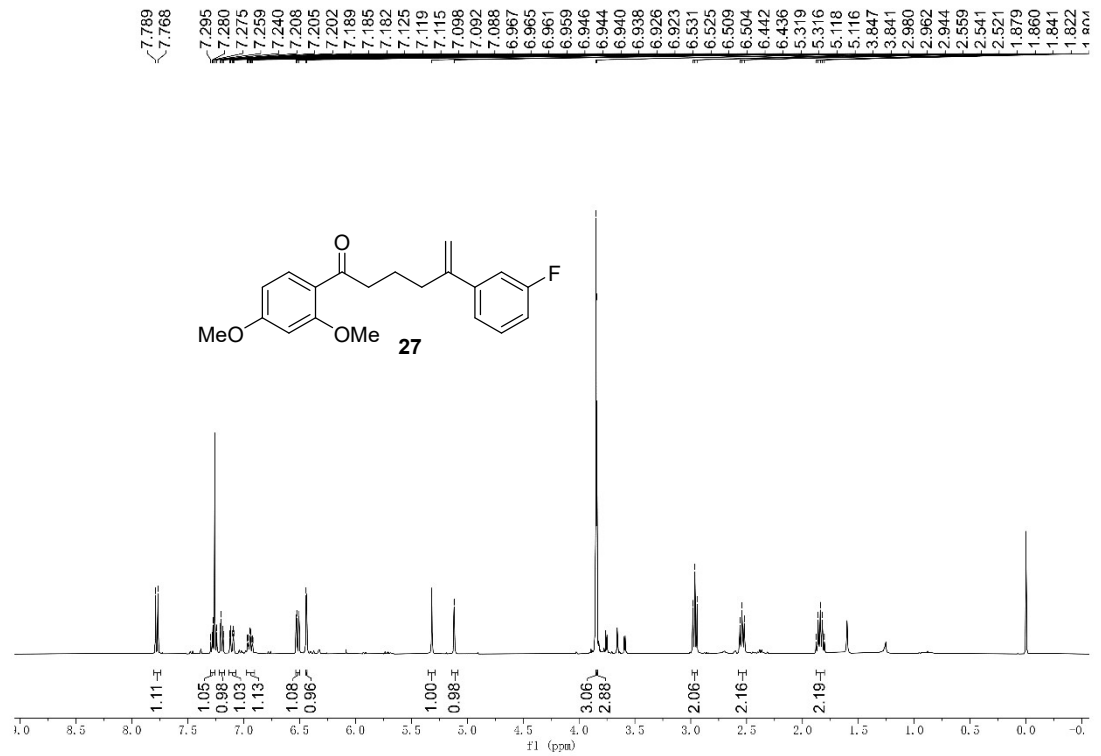
143.13
134.20
132.62
129.52
127.31
126.31
124.33
121.23
113.66
105.08
98.38
77.36
77.05
76.73
55.52
55.43
42.96
34.76
23.14
O
Cl
MeO
OMe
26
f1 (ppm)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7.295
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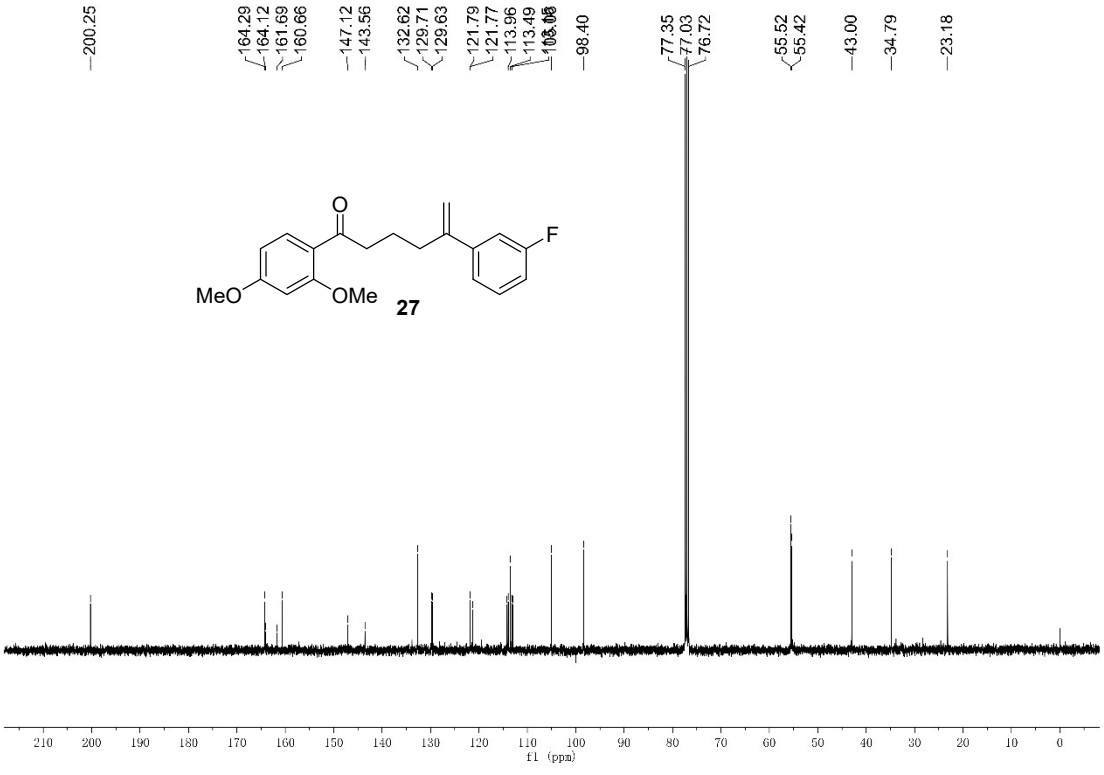
7.275
7.259
7.240
7.208
7.205
7.202
7.189
7.185
7.182
7.125
7.119
7.115
7.098
7.092
7.088
6.967
6.965
6.961
6.959
6.946
6.944
6.940
6.938
6.926
6.923
6.531
6.525
6.509
6.504
6.442
6.436
5.319
5.316
5.118
5.116
3.847
3.841
2.980
2.962
2.944
2.559
2.541
2.521
1.879
1.860
1.841
1.822
O
F
MeO
OMe
27
1.11
1.05
0.98
1.03
1.13
1.08
0.96
1.00
0.98
3.06
2.88
2.06
2.16
2.19
f1 (ppm)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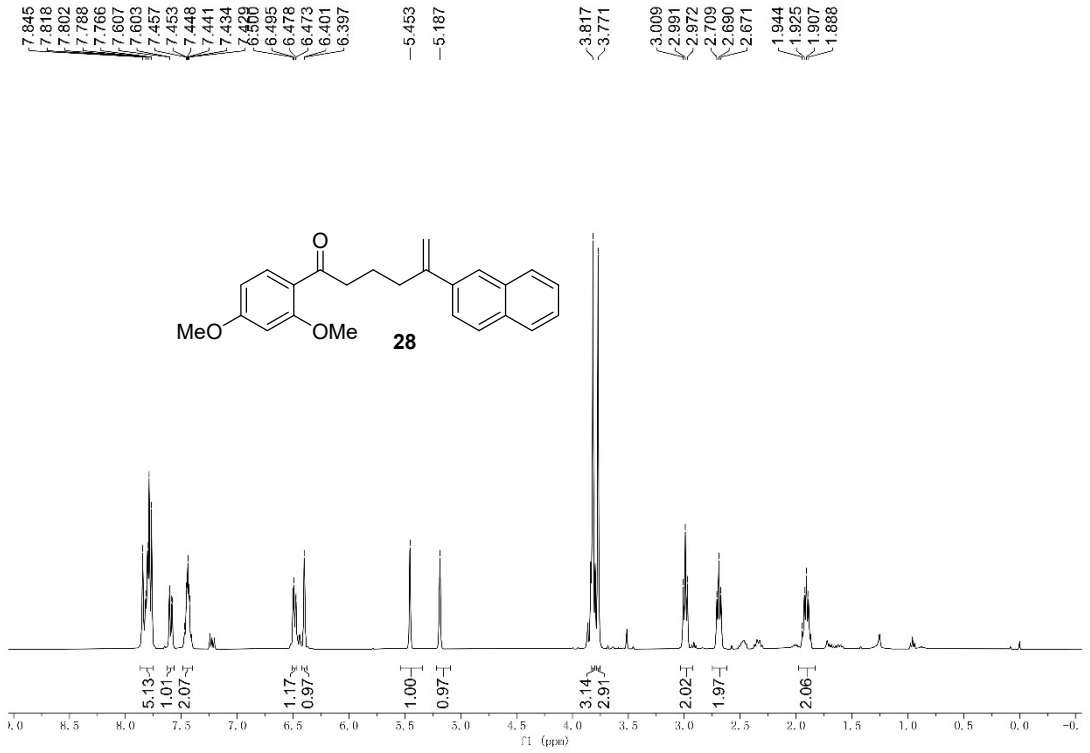
164.12
161.69
160.66
147.12
143.56
132.62
129.71
129.63
121.79
121.77
113.96
113.49
98.40
77.35
77.03
76.72
55.52
55.42
43.00
34.79
23.18
O
F
MeO
OMe
27
f1 (ppm)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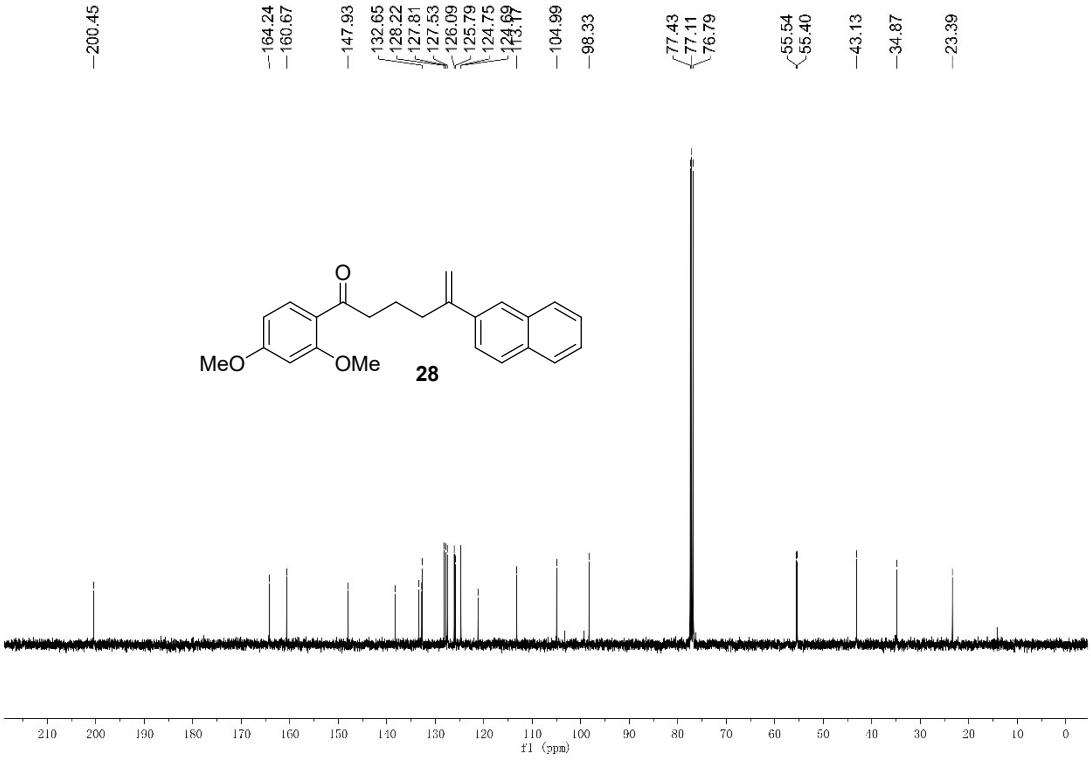
7.818
7.802
7.788
7.766
7.607
7.603
7.457
7.453
7.448
7.441
7.434
6.500
6.495
6.478
6.473
6.401
6.397
5.453
5.187
3.817
3.771
3.009
2.991
2.972
2.709
2.690
2.671
1.944
1.925
1.907
1.888
MeO
OMe
28
5.13
1.01
2.07
1.17
0.97
1.00
0.97
3.14
2.91
2.02
1.97
2.06
f1 (ppm)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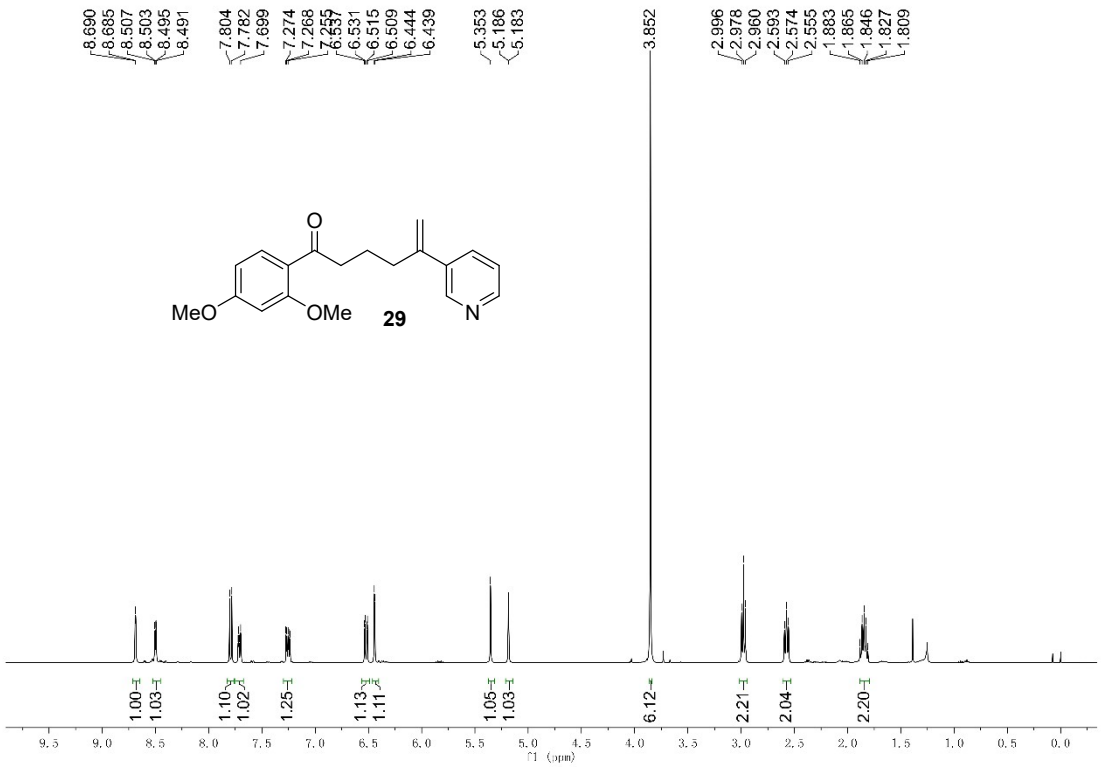
164.24
160.67
147.93
132.65
128.22
127.81
127.53
126.09
125.79
124.75
104.99
98.33
77.43
77.11
76.79
55.54
55.40
43.13
34.87
23.39
MeO
OMe
28
f1 (ppm)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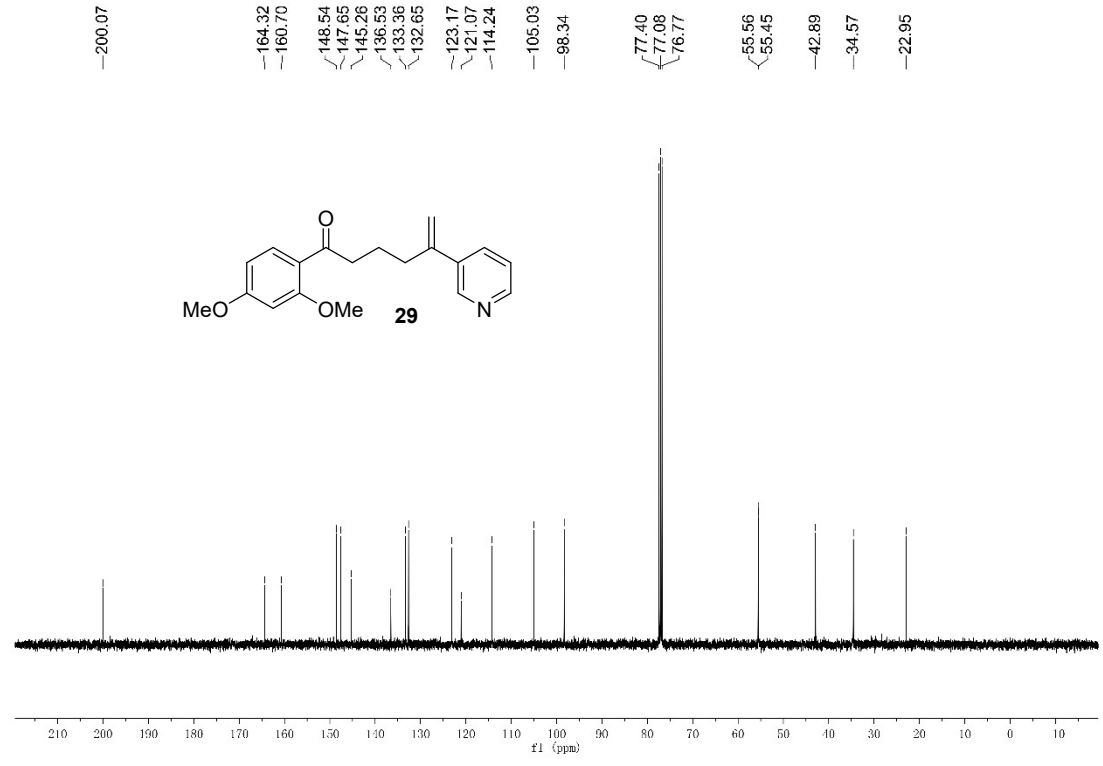
8.685
8.507
8.503
8.495
8.491
7.804
7.782
7.699
7.274
7.268
7.255
6.537
6.531
6.515
6.509
6.444
6.439
5.353
5.186
5.183
3.852
2.996
2.978
2.960
2.593
2.574
2.555
1.883
1.865
1.846
1.827
1.809
O
MeO
OMe
29
N
1.00
1.03
1.10
1.02
1.25
1.13
1.11
1.05
1.03
6.12
2.21
2.04
2.20
f1 (ppm)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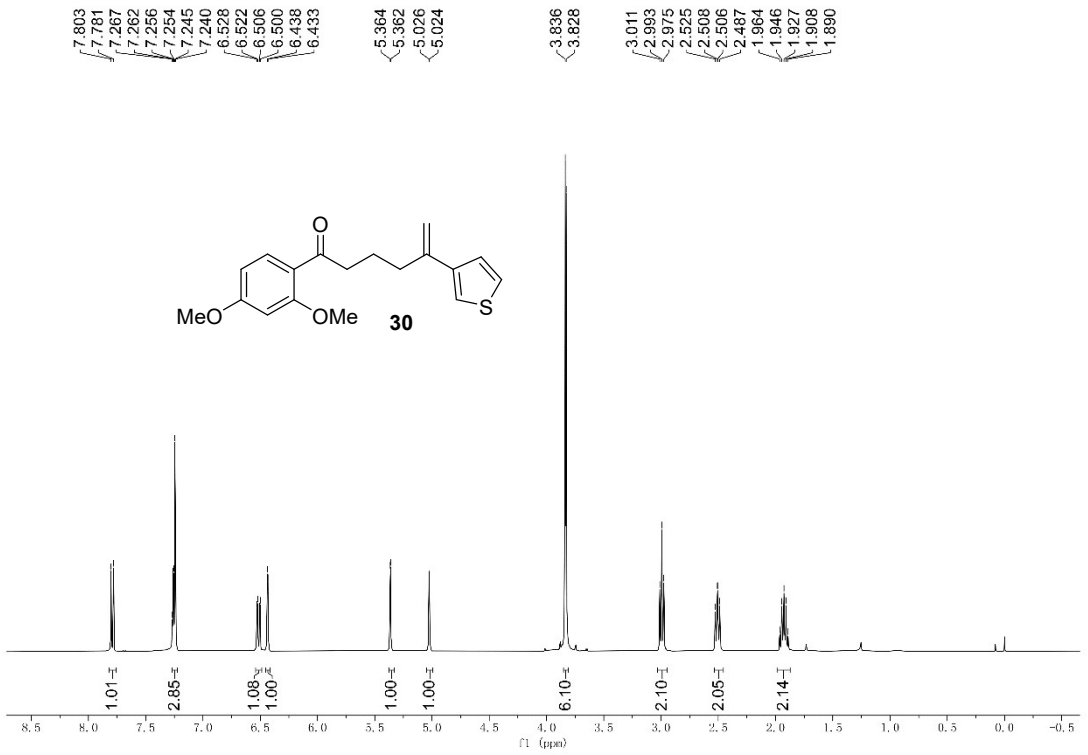
148.54
147.65
145.26
136.53
133.36
132.65
123.17
121.07
114.24
105.03
98.34
77.40
77.08
76.77
55.56
55.45
42.89
34.57
22.95
O
MeO
OMe
29
N
f1 (ppm)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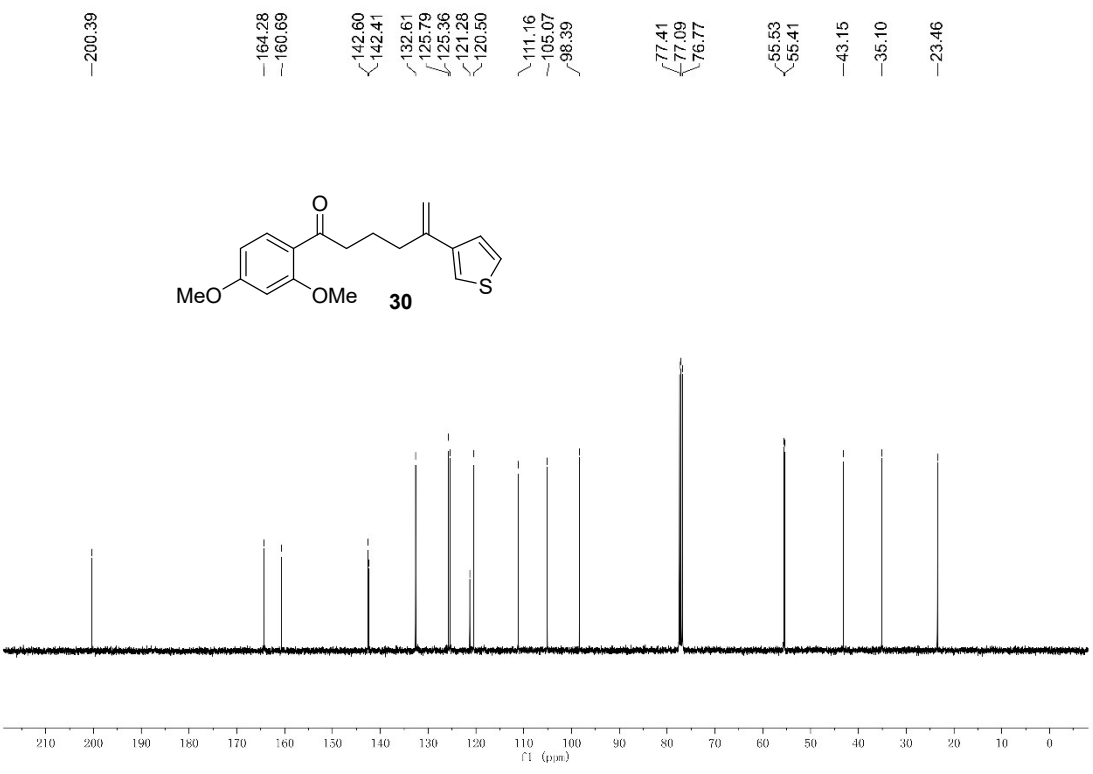
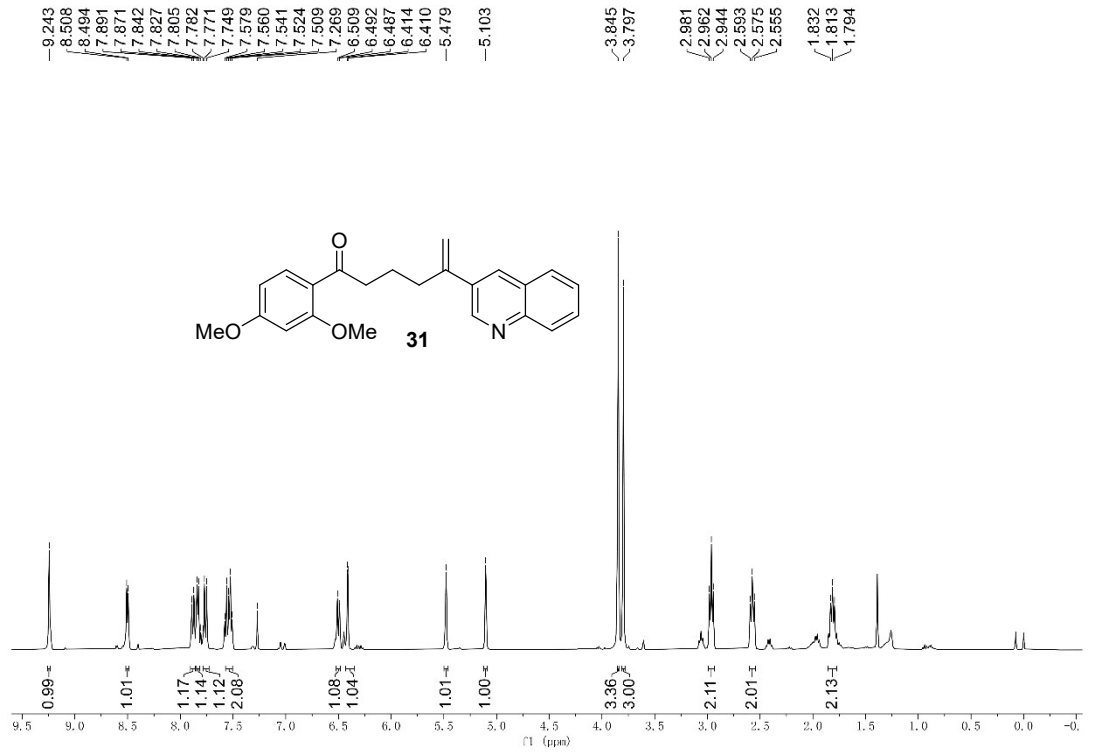
7.267
7.262
7.256
7.254
7.245
7.240
6.528
6.522
6.506
6.500
6.438
6.433
5.364
5.362
5.026
5.024
3.836
3.828
3.011
2.993
2.975
2.525
2.508
2.506
2.487
1.964
1.946
1.927
1.908
1.890
O
MeO
OMe
S
30
1.01
2.85
1.08
1.00
1.00
1.00
6.10
2.10
2.05
2.14
f1 (ppm)


200.39
164.28
160.69
142.60
142.41
132.61
125.79
125.36
121.28
120.50
111.16
105.07
98.39
77.41
77.09
76.77
55.53
55.41
43.15
35.10
23.46
O
MeO
OMe
S
30
f1 (ppm)


9.243
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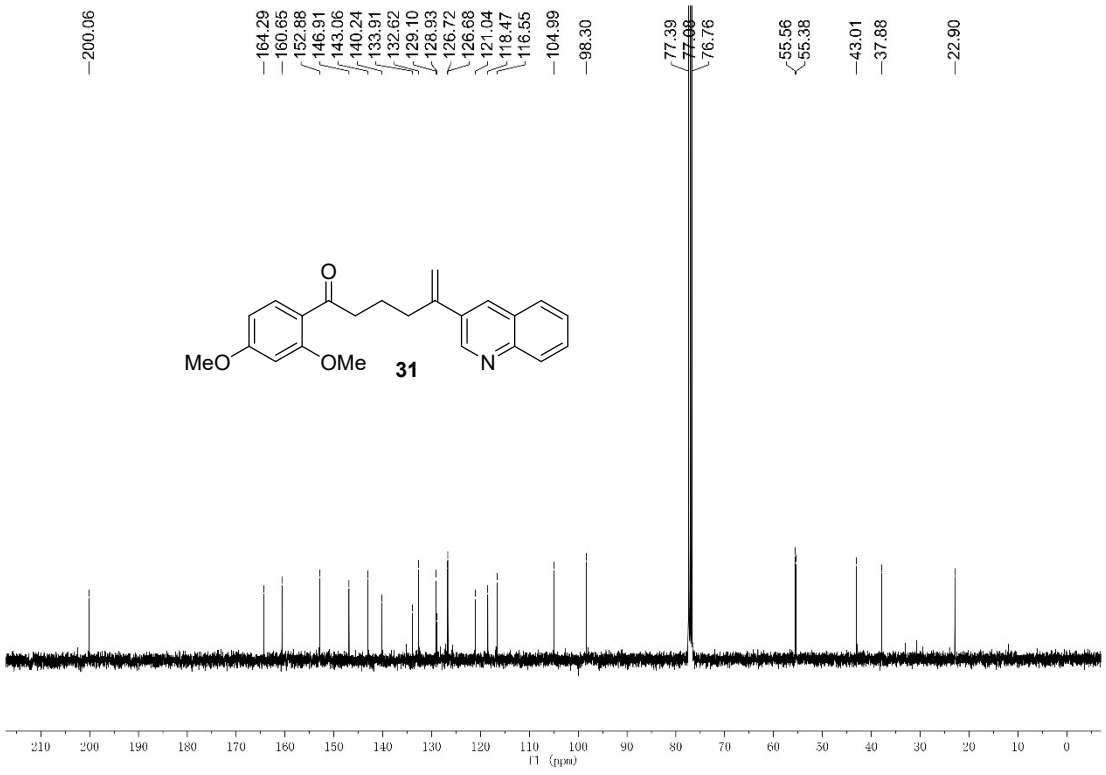
8.494
7.891
7.871
7.842
7.827
7.805
7.782
7.771
7.749
7.579
7.560
7.541
7.524
7.509
7.269
6.509
6.492
6.487
6.414
6.410
5.479
5.103
3.845
3.797
2.981
2.962
2.944
2.593
2.575
2.555
1.832
1.813
1.794
O
MeO
OMe
31
N
0.99
1.01
1.17
1.14
1.12
2.08
1.08
1.04
1.01
1.00
3.36
3.00
2.11
2.01
2.13
f1 (ppm)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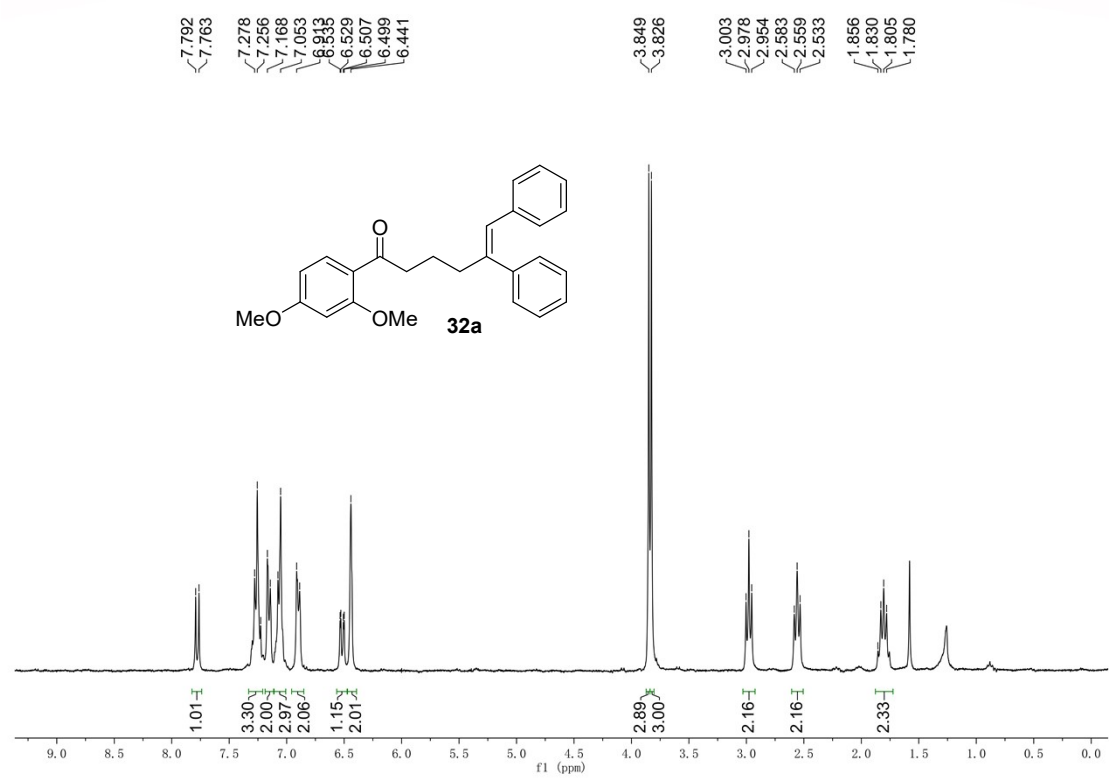
152.88
146.91
143.06
140.24
133.91
132.62
129.10
128.93
126.72
126.68
121.04
118.47
116.55
104.99
98.30
77.39
77.00
76.76
55.56
55.38
43.01
37.88
22.90
O
MeO
OMe
31
N
f1 (ppm)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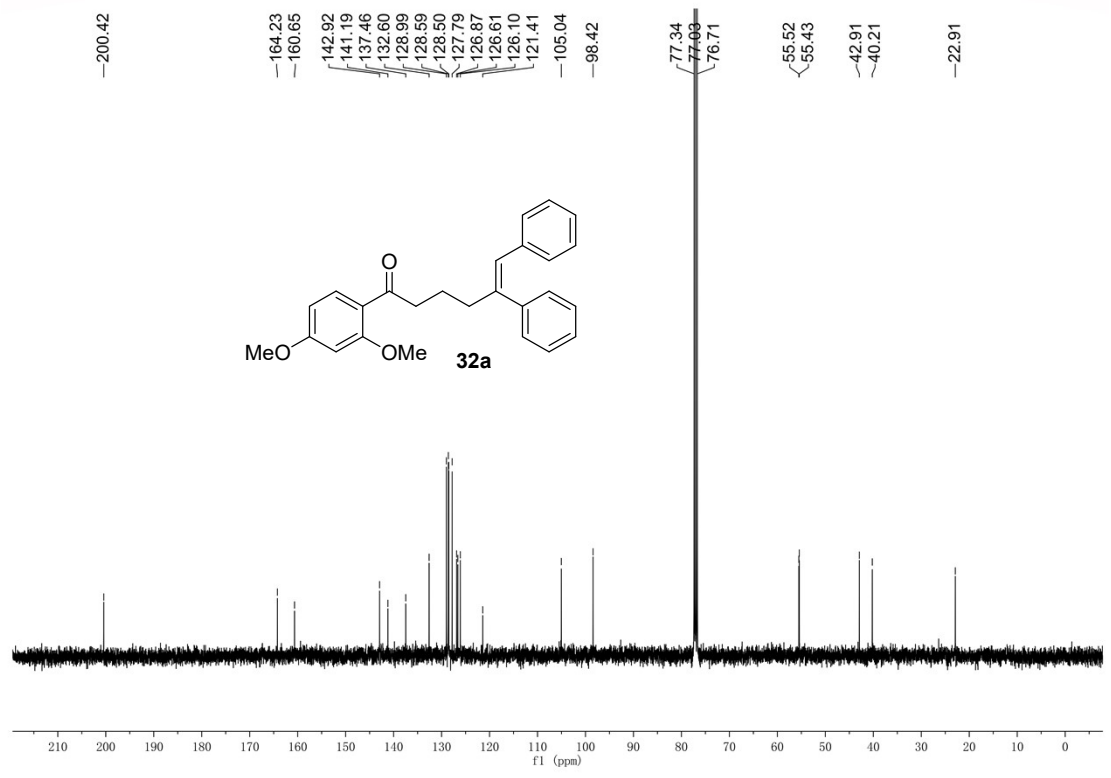
6.533
6.529
6.507
6.499
6.441
3.849
3.826
3.003
2.978
2.954
2.583
2.559
2.533
1.856
1.830
1.805
1.780
O
MeO
OMe
32a
1.01
3.30
2.00
2.97
2.06
1.15
2.01
2.89
3.00
2.16
2.16
2.33
f1 (ppm)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164.23
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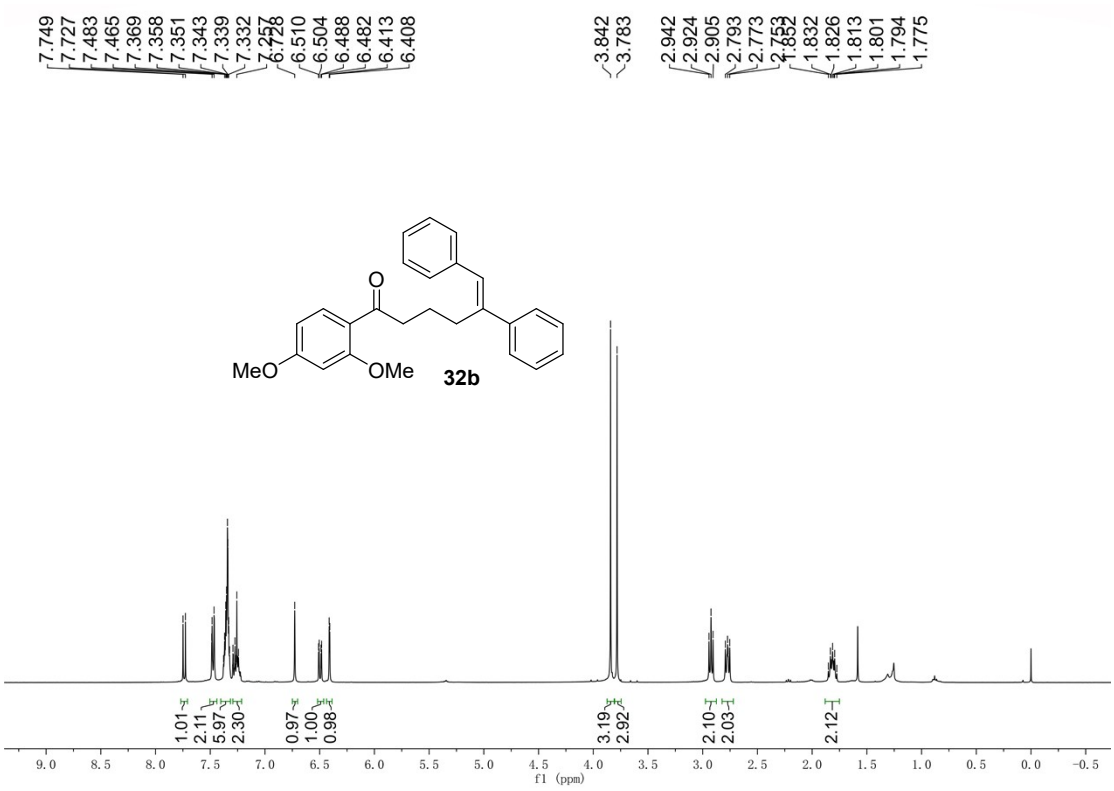
142.92
141.19
137.46
132.60
128.99
128.59
128.50
127.79
126.87
126.61
126.10
121.41
105.04
98.42
77.34
77.03
76.71
55.52
55.43
42.91
40.21
22.91
O
MeO
OMe
32a
f1 (ppm)


7.749
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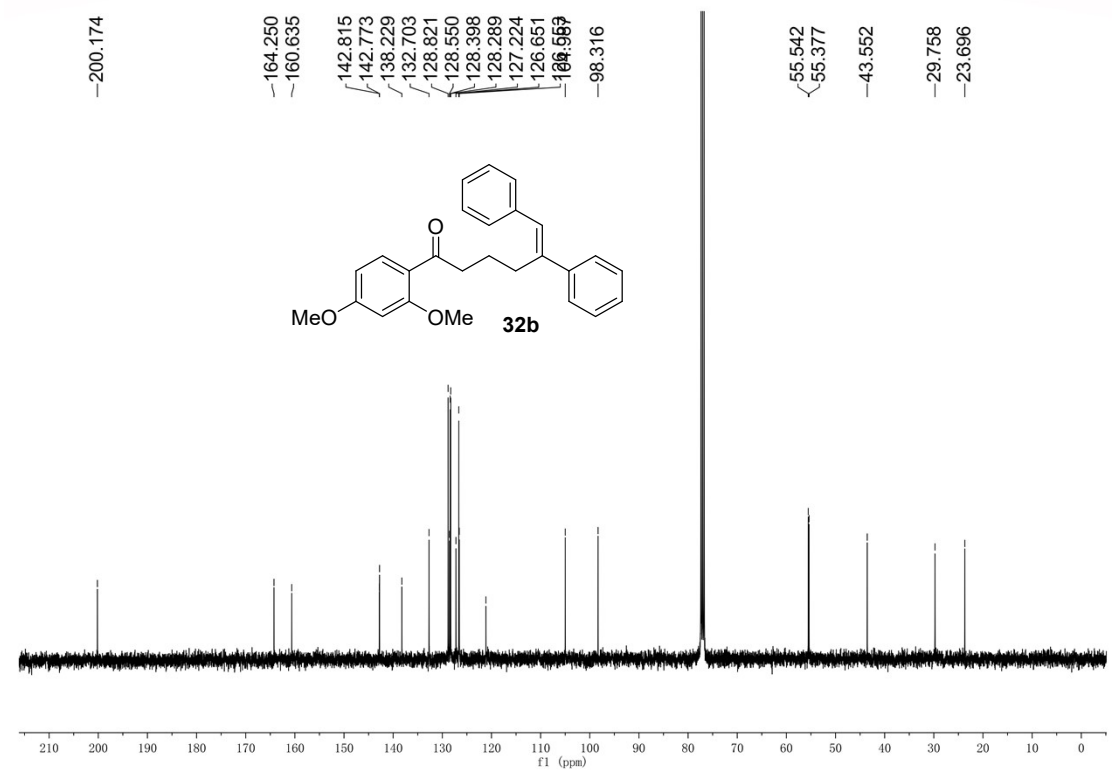
7.483
7.465
7.369
7.358
7.351
7.343
7.339
7.332
6.510
6.504
6.488
6.482
6.413
6.408
3.842
3.783
2.942
2.924
2.905
2.793
2.773
1.832
1.826
1.813
1.801
1.794
1.775
MeO
OMe
32b
1.01
2.11
5.97
2.30
0.97
1.00
0.98
3.19
2.92
2.10
2.03
2.12
f1 (ppm)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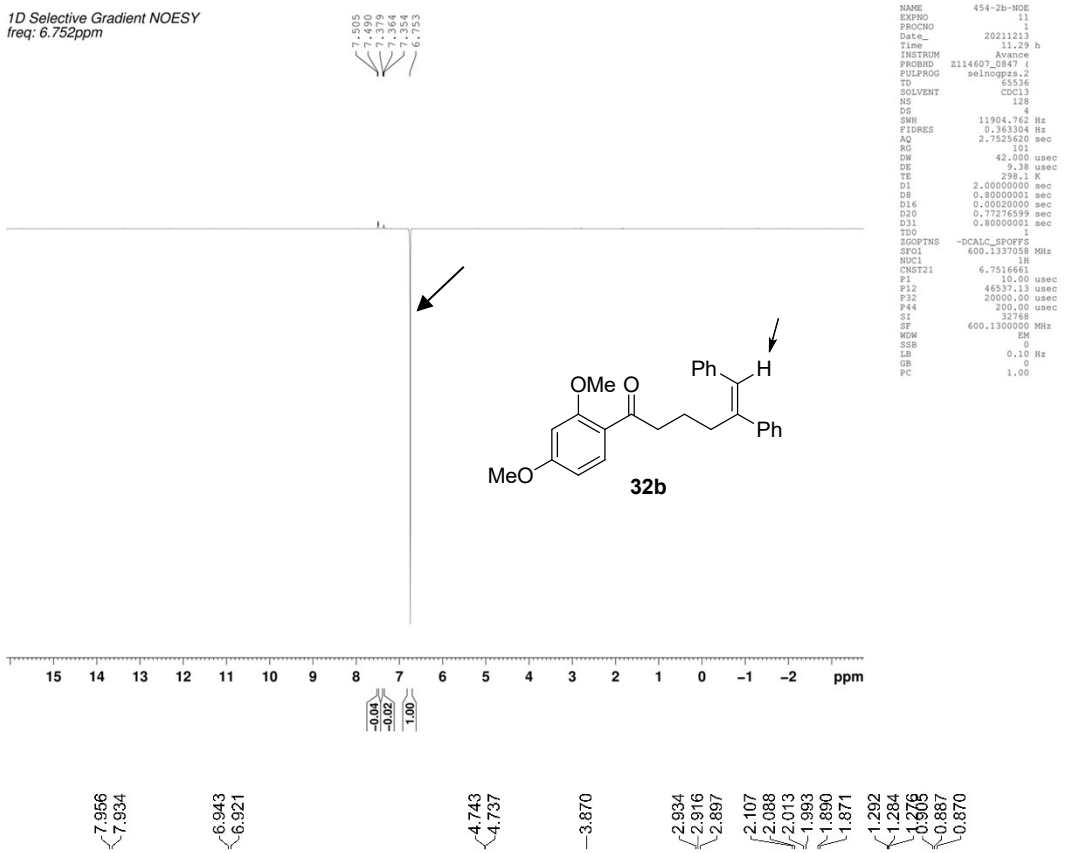
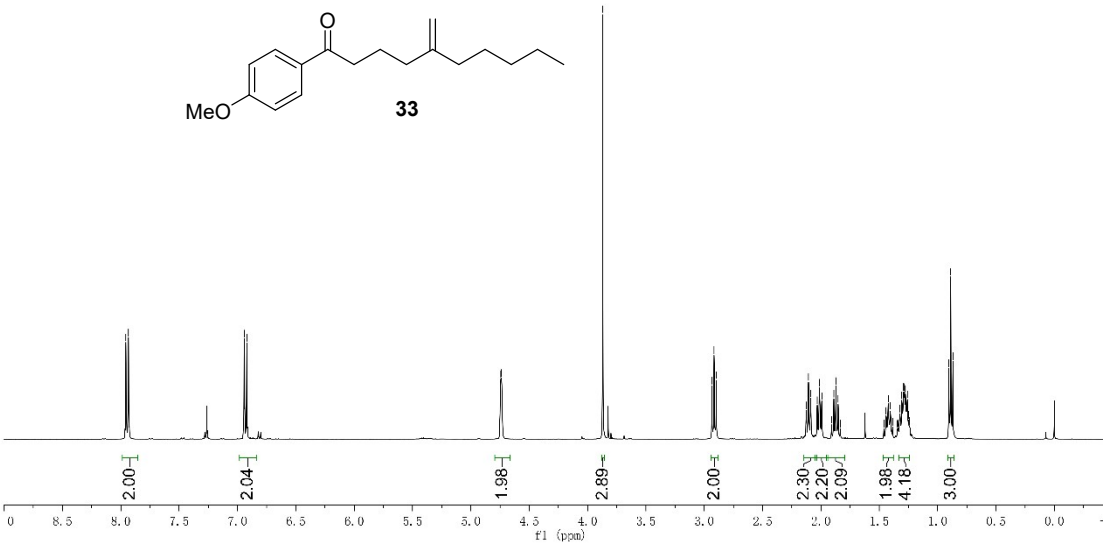
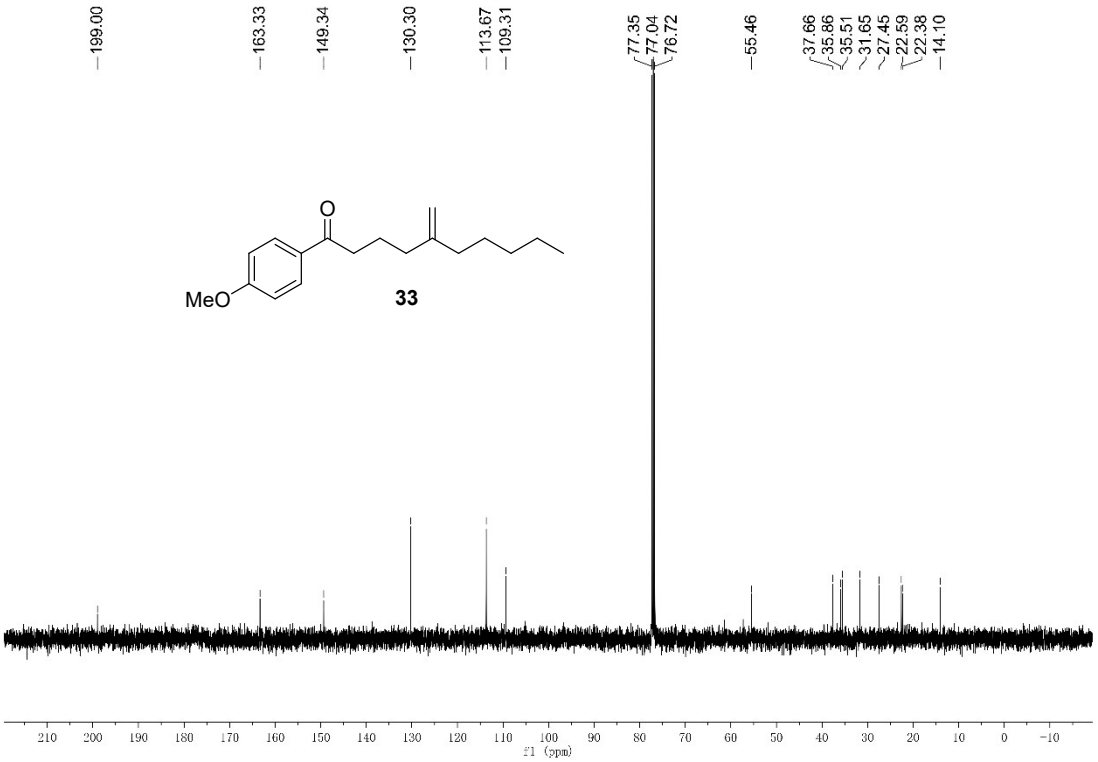
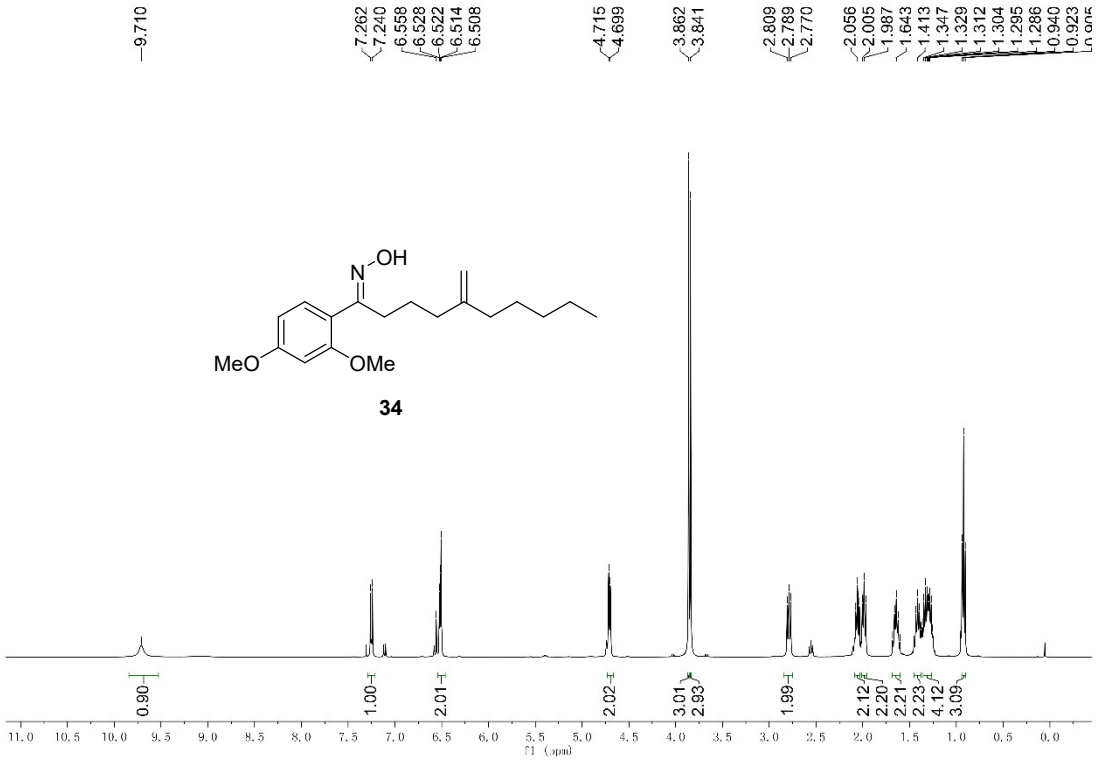
164.250
160.635
142.815
142.773
138.229
132.703
128.821
128.550
128.398
128.289
127.224
126.651
98.316
55.542
55.377
43.552
29.758
23.696
MeO
OMe
32b
f1 (ppm)

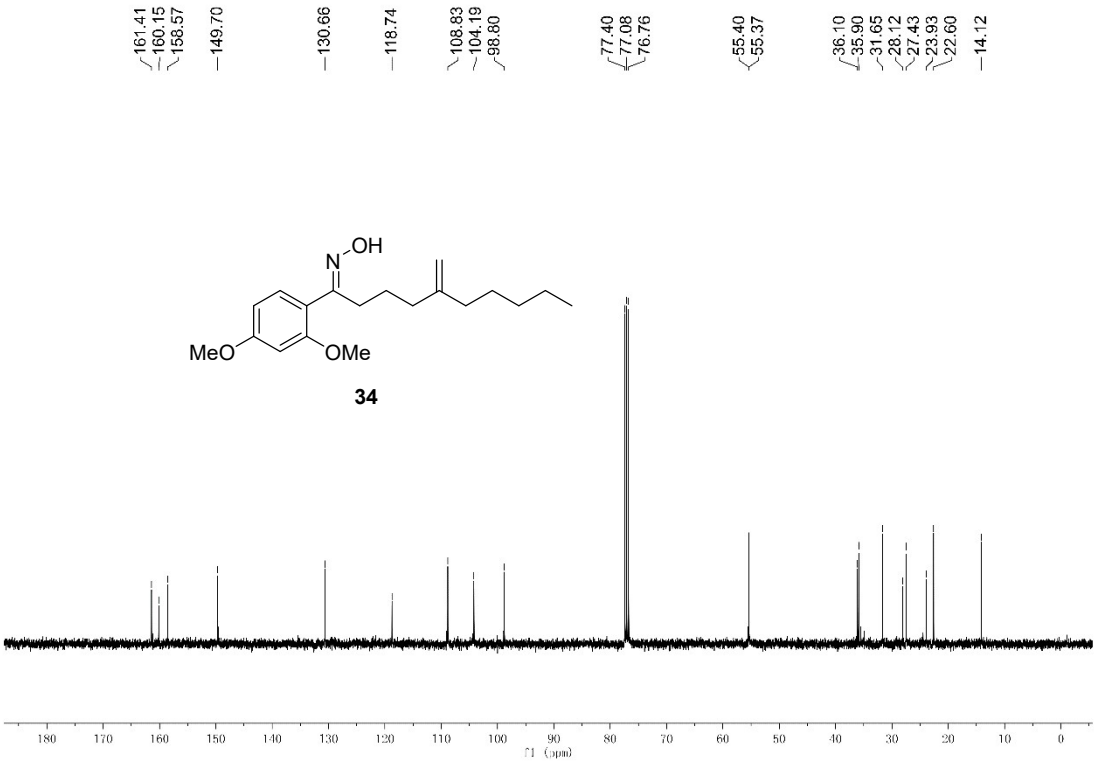

1D Selective Gradient NOESY
freq: 6.752ppm
7.505
7.490
7.379
7.364
7.354
6.753
NAME 454-2b-NOE
EXPNO 11
PROCNO 1
Date_ 20211213
Time 11.29 h
INSTRUM Avance
PROBHD Z114607_0847 (
PULPROG selnogpzs.2
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 11904.762 Hz
FIDRES 0.363304 Hz
AQ 2.7525620 sec
RG 101
DW 42.000 usec
DE 9.38 usec
TE 298.1 K
D1 2.00000000 sec
D8 0.80000001 sec
D16 0.00020000 sec
D20 0.77276599 sec
D31 0.80000001 sec
TD0 1
ZGOPTNS -DCALC_SPOFFS
SFO1 600.1337058 MHz
NUC1 1H
CNST21 6.7516661
P1 10.00 usec
P12 46537.13 usec
P32 20000.00 usec
P44 200.00 usec
SI 32768
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
OMe O
Ph
H
Ph
MeO
32b
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
0.04
0.02
1.00

7.956
7.934
6.943
6.921
4.743
4.737
3.870
2.934
2.916
2.897
2.107
2.088
2.013
1.993
1.890
1.871
1.292
1.284
1.276
0.905
0.887
0.870


O
MeO
33
2.00
2.04
1.98
2.89
2.00
2.30
2.20
2.09
1.98
4.18
3.00
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.00
163.33
149.34
130.30
113.67
109.31
77.35
77.04
76.72
55.46
37.66
35.86
35.51
31.65
27.45
22.59
22.38
14.10
O
MeO
33
f1 (ppm)


9.710
7.262
7.240
6.558
6.528
6.522
6.514
6.508
4.715
4.699
3.862
3.841
2.809
2.789
2.770
2.056
2.005
1.987
1.643
1.413
1.347
1.329
1.312
1.304
1.295
1.286
0.940
0.923
N
OH
MeO
OMe
34
0.90
1.00
2.01
2.02
3.01
2.93
1.99
2.12
2.20
2.21
2.23
4.12
3.09
f1 (ppm)


161.41
160.15
158.57
149.70
130.66
118.74
108.83
104.19
98.80
77.40
77.08
76.76
55.40
55.37
36.10
35.90
31.65
28.12
27.43
23.93
22.60
14.12
N
OH
MeO
OMe
34
f1 (ppm)

7.639
7.617
7.274
7.256
7.240
7.183
7.180
7.164
7.159
7.144
7.127
6.901
6.881
6.862
6.845
6.803
6.765
6.525
6.519
6.504
6.498
6.445
6.440
3.836
3.824
2.632
2.615
2.598
2.581
2.559
2.540
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2.179
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1.278
1.252
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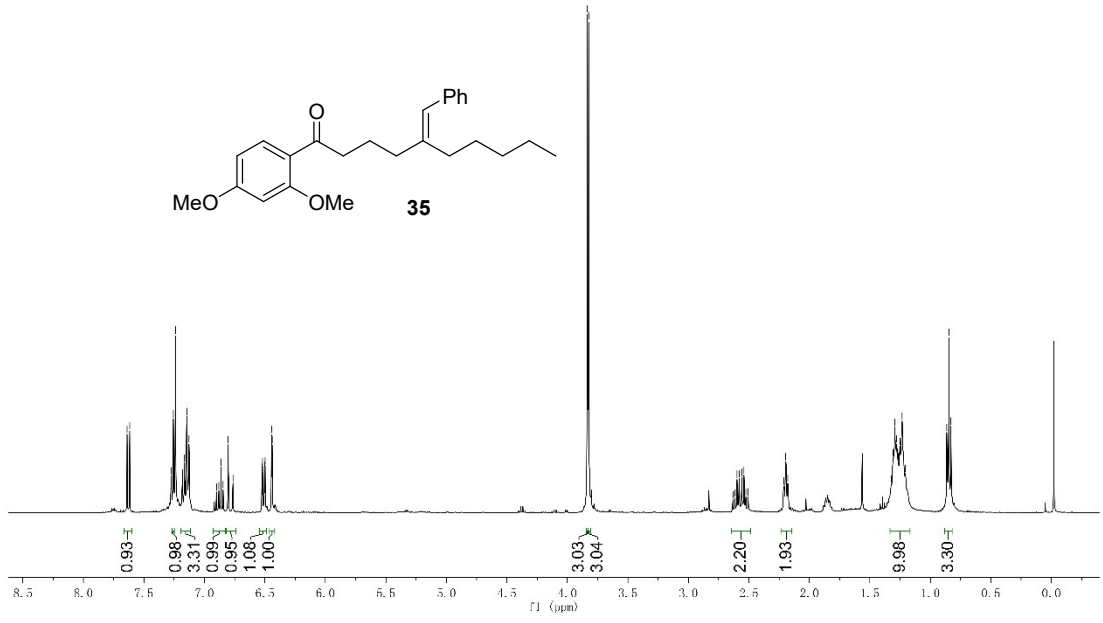
0.829


O
Ph
MeO
OMe
35
0.93
0.98
3.31
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0.95
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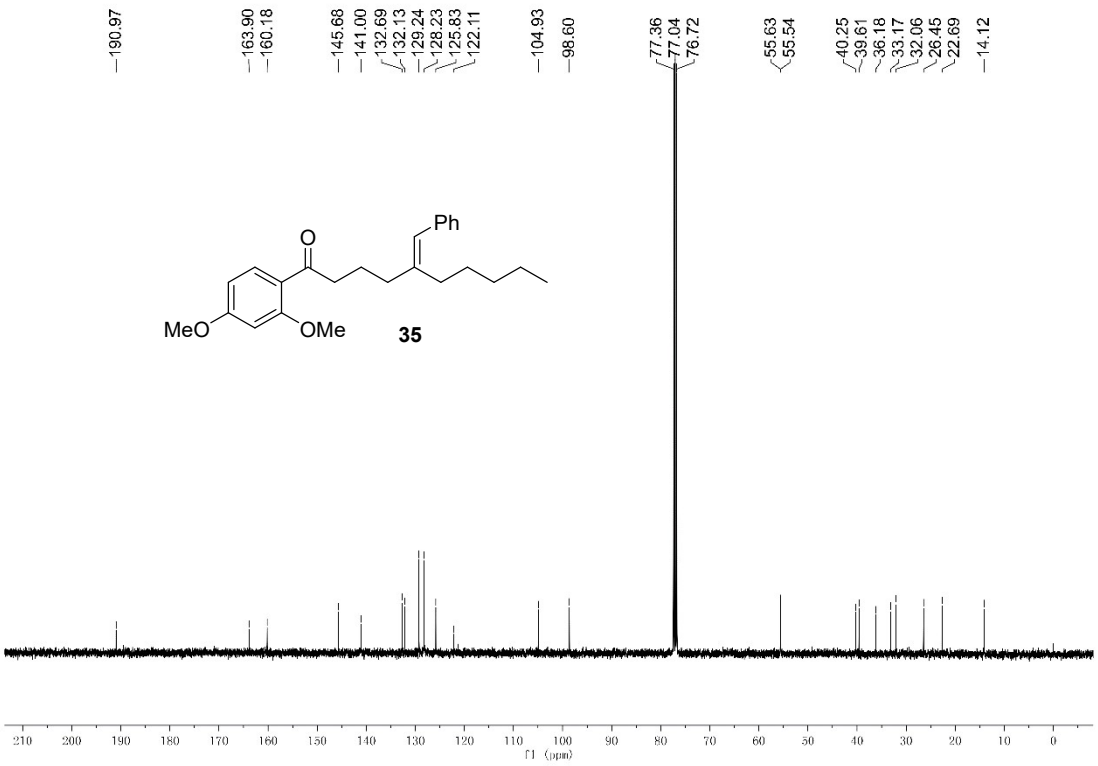
3.03
3.04
2.20
1.93
9.98
3.30
f1 (ppm)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141.00
132.69
132.13
129.24
128.23
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104.93
98.60
77.36
77.04
76.72
55.63
55.54
40.25
39.61
36.18
33.17
32.06
26.45
22.69
14.12
Ph
O
MeO
OMe
35
f1 (ppm)