Supporting Information

How to Suppress C(sp^2)–Rh–C(sp^3) Reductive Elimination and Insert CO to Achieve Rhodium-Catalyzed [5 + 2 + 1] Cycloaddition of Yne-vinylcyclopropanes and CO? Answers from Experimental and Computational Investigation

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1. General Information

All chemicals were used as received without further purification. Mesitylene (with molecular sieves) was purchased from Adamas-beta. Reaction tubes (25 mL) were purchased from Synthware. $[Rh(CO)_2Cl]_2$ was purchased from J&K. Ethyl acetate, petroleum ether, dichloromethane, diethyl ether, NaCl, Na_2SO_4, NH_4Cl were purchased from Bei Jing TongGuang Fine Chemicals Company. 1-Hydroxy-1-cyclopropanecarboxylicacid was purchased from leyan, shanghai, China. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Analytical TLCs were performed with 0.25 mm silica gel HSGF254. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) purchased from Yantai Huayang New Material Technology Co. Ltd. and the purified compounds show a single spot by analytical TLC. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III 400 (^1H at 400 MHz, $^{13}C\{^1H\}$ at 101 MHz). Data for ^1H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 ppm), $CHDCl_2$ (5.32 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, dddq = doublet of doublet of doublet of quartets, dtdt = doublet of triplet of doublet of triplets, tq = triplet of quartets, qdd = quartet of doublet of doublets, m = multiplet), coupling constant *J* (Hz), and integration. Data for $^{13}C\{^1H\}$ NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm), or CD_2Cl_2 (53.84 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) with an FT-ICR analyzer. Crystal compound was obtained by adding petroleum ether to their dichloromethane solutions and then stilling for several days.

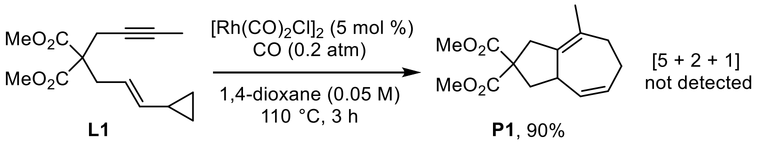
Abbreviations

atm	atmosphere
Bn	benzyl group
Bu	butyl
BRSM	base on recovering starting materials
d	density
DCM	dichloromethane
DCE	1,2-dichloroethane
DFT	density functional theory
DCC	N,N’-dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
d.r.	diastereomeric ratio
EA	ethyl acetate
EI	electron impact ion source
ESI	electron spray ionization
Et	ethyl
HRMS	high-resolution mass spectroscopy
INT	intermediate
Me	methyl
m.p.	melting point
PE	petroleum ether
Ph	phenyl
Pr	propyl
rpm	revolutions per minute
rt	room temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TS	transition state

2. Initial Attempt of [5 + 2 + 1] Reactions

General Procedure A

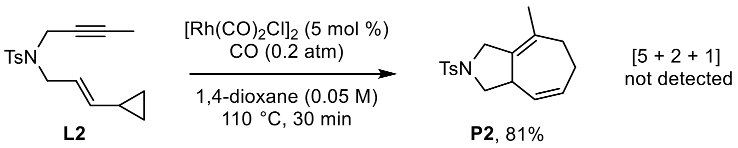
Substrate and $[Rh(CO)_2Cl]_2$ (5 mol % to the substrate) were charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen, and then the dry 1,4-dioxane was added (0.05 M). The solution was bubbled with the mixed gas (CO/N2 = 1: 4) for 3 min. The reaction mixture was stirred at 110 °C under the mixed CO atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to afford the cycloaddition product.



Following the general procedure A: substrate **L1**[1] (28.7 mg, 0.11mmol), $[Rh(CO)_2Cl]_2$ (2.1 mg, 0.0054 mmol), 1,4-dioxane (2.0 mL), reaction time: 3 h, cycloadduct **P1**[1] (25.7 mg, 0.097 mmol), yield: 90%.

^1H NMR (400 MHz, $CDCl_3$, δ): 5.67 – 5.59 (m, 1H), 5.45 (dd, J = 11.1, 2.0 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.62 (brs, 1H), 3.00 (d, J = 16.4 Hz, 1H), 2.86 (d, J = 16.5 Hz, 1H), 2.67 (ddd, J = 12.6, 8.1, 1.8 Hz, 1H), 2.51 (t, J = 12.4 Hz , 1H), 2.31 – 2.19 (m, 1H), 2.13 – 2.02 (m, 1H), 1.96 (dd, J = 12.6, 11.3 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.66 (s, 3H).

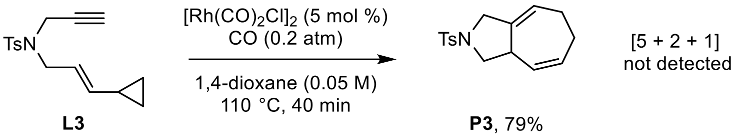
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 172.12, 172.07, 135.3, 131.9, 129.62, 129.57, 58.4, 52.72, 52.65, 41.8, 39.8, 39.2, 32.5, 26.0, 21.2.



Following the general procedure A: substrate **L2**[1] (21.3 mg, 0.070mmol), $[Rh(CO)_2Cl]_2$ (1.4 mg, 0.0036 mmol), 1,4-dioxane (1.4 mL), reaction time: 30 min, cycloadduct **P2**[1] (17.3 mg, 0.057 mmol), yield: 81%.

^1H NMR (400 MHz, $CDCl_3$, δ): 7.71 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.71 – 5.63 (m, 1H), 5.37 – 5.31 (m, 1H), 3.97 (d, J = 13.3 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.51 (d, J = 13.3 Hz, 1H), 2.69 – 2.61 (m, 1H), 2.49 – 2.37 (m, 4H), 2.32 – 2.21 (m, 1H), 2.10 – 2.00 (m, 1H), 1.91 – 1.82 (m, 1H), 1.58 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 143.7, 131.9, 131.8, 131.1, 129.8, 129.6, 129.0, 128.1, 54.8, 51.7, 40.0, 32.1, 25.7, 21.6, 21.2.



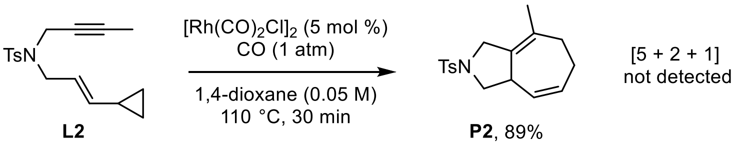
Following the general procedure A: substrate **L3**[1] (19.8 mg, 0.068mmol), $[Rh(CO)_2Cl]_2$ (1.3 mg, 0.0033 mmol), 1,4-dioxane (1.4 mL), reaction time: 40 min, cycloadduct **P3**[1] (15.7 mg, 0.054 mmol), yield: 79%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.79 – 5.71 (m, 1H), 5.61 – 5.54 (m, 1H), 5.39 (dt, J = 10.8, 2.0 Hz, 1H), 3.97 (d, J = 13.2 Hz, 1H), 3.81 – 3.71 (m, 2H), 3.55 (dt, J = 13.3, 2.2 Hz, 1H), 2.76 – 2.65 (m, 1H), 2.44 (s, 3H), 2.41 – 2.22 (m, 2H), 2.10 – 1.98 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ)143.7, 138.2, 132.1, 131.8, 129.7, 128.9, 128.0, 122.4, 54.5, 53.1, 40.3, 26.0, 25.5, 21.6.

General Procedure B

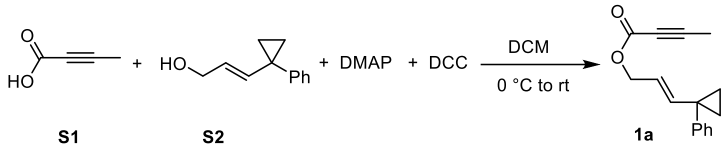
Substrate and $[Rh(CO)_2Cl]_2$ (5 mol % to the substrate) were charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen, and then the dry 1,4-dioxane was added (0.05 M). The solution was bubbled with pure CO gas for 3 min. The reaction mixture was stirred at 110 °C under the CO atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to afford the cycloaddition product.



Following the general procedure B: substrate **L2** (20.8 mg, 0.069mmol), $[Rh(CO)_2Cl]_2$ (1.3 mg, 0.0033 mmol), 1,4-dioxane (1.4 mL), reaction time: 30 min, cycloadduct **P2** (18.5 mg, 0.061 mmol), yield: 89%.

3. Substrates Preparations

The synthesis of all substrates for the present study was not optimized.



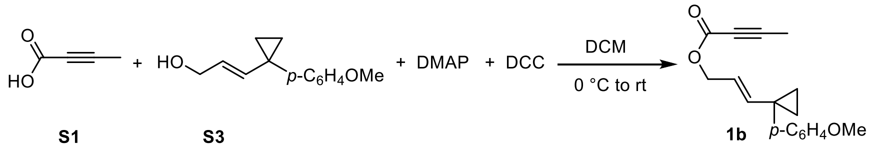
To a 250 mL flask with **S1** (1.86 g, 22.1 mmol) in DCM (50 mL) was added DMAP (244 mg, 2.0 mmol) at 0 °C. Then **S2**[2] (3.49 g, 20.0 mmol) was added dropwise. After 5 min, DCC (4.13 g, 20.0 mmol) was added. The obtained mixture was stirred for 3 h at rt, and then concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) afforded compound **1a** (4.81 g, quantitative) as a colorless oil.

TLC (5:1 PE/EA, R*f*): 0.6.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.33 – 7.26 (m, 4H), 7.25 – 7.19 (m, 1H), 5.66 (dt, *J* = 15.3, 1.2 Hz, 1H), 5.12 (dt, *J* = 15.3, 6.7 Hz, 1H), 4.55 (dd, *J* = 6.7, 1.2 Hz, 2H), 1.96 (s, 3H), 1.15 – 1.09 (m, 2H), 1.03 – 0.97 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.6, 144.5, 142.7, 130.1, 128.4, 126.8, 121.0, 85.7, 72.5, 66.4, 28.0, 15.0, 3.9.

HRMS (ESI) m/z: calcd. for $C_{16}H_{17}O_2$ ([M+H]$^+$): 241.1223, found: 241.1223.



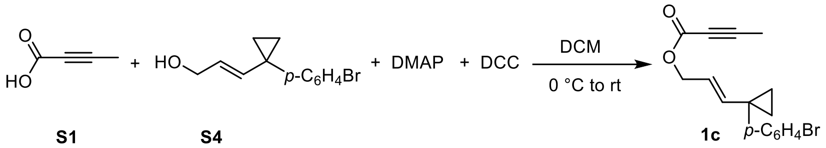
To a flask with **S1** (185 mg, 2.2 mmol) in DCM (10 mL) was added DMAP (22 mg, 0.2 mmol) at 0 °C. Then **S3**[2] (409 mg, 2.0 mmol) was added dropwise. After 5 min, DCC (413 mg, 2.0 mmol) was added. The obtained mixture was stirred for 3 h at rt, and then concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 PE/EA) afforded compound **1b** (470 mg, 79%) as a yellow oil.

TLC (3:1 PE/EA, R*f*): 0.6.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.24 – 7.17 (m, 2H), 6.88 – 6.80 (m, 2H), 5.60 (dt, *J* = 15.3, 1.2 Hz, 1H), 5.10 (dt, *J* = 15.3, 6.7 Hz, 1H), 4.54 (dd, *J* = 6.7, 1.2 Hz, 2H), 3.80 (s, 3H), 1.97 (s, 3H), 1.11 – 1.04 (m, 2H), 0.99 – 0.92 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 158.4, 153.6, 145.1, 134.7, 131.2, 120.8, 113.8, 85.6, 72.5, 66.4, 55.4, 27.3, 15.0, 3.9.

HRMS (ESI) m/z: calcd. for $C_{17}H_{19}O_3$ ([M+H]$^+$): 271.1329, found: 271.1335.



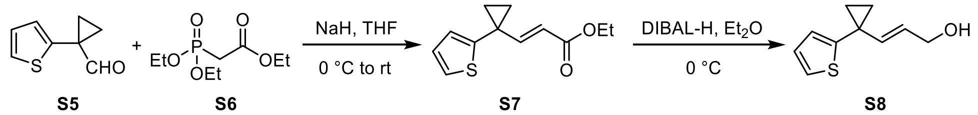
To a flask with **S1** (257 mg, 3.1 mmol) in DCM (7 mL) was added DMAP (34 mg, 0.28 mmol) at 0 °C. Then **S4**[2] (700 mg, 2.78 mmol) was added dropwise. After 5 min, DCC (574 mg, 2.78 mmol) was added. The obtained mixture was stirred for 0.5 h at rt. Purification of the crude product by flash column chromatography (silica gel, 60:1 PE/EA) afforded compound **1c** (760.4 mg, 86%) as a colorless oil.

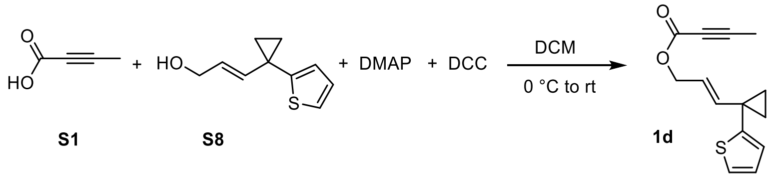
TLC (10:1 PE/EA, R*f*): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.45 – 7.40 (m, 2H), 7.19 – 7.13 (m, 2H), 5.61 (dt, *J* = 15.4, 1.2 Hz, 1H), 5.10 (dt, *J* = 15.3, 6.6 Hz, 1H), 4.55 (dd, *J* = 6.6, 1.2 Hz, 2H), 1.97 (s, 3H), 1.12 – 1.04 (m, 2H), 1.04 – 0.97 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 153.6, 143.8, 141.7, 131.9, 131.6, 121.4, 120.6, 85.8, 72.5, 66.2, 27.5, 15.1, 3.9.

HRMS (ESI) m/z: calcd. for $C_{16}H_{19}BrNO_2$ ($[M+NH_4]^+$): 336.0594, found: 336.0596.





To a flask with NaH (348 mg, 60% dispersion in mineral oil, 8.7 mmol) in THF (15 mL) was added **S6** (1.77 g,7.9 mmol) under an argon atmosphere at 0 °C. After 10 min, **S5** (1.1 g, 7.2 mmol, known compound and commercially available) was added. The obtained mixture was stirred for 40 min at rt. Quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 PE/EA) afforded compound **S7** (1.28 g) as a yellow oil.

To a flask with **S7** (1.28 g, 5.8 mmol) in Et_2O (15 mL) was added DIBAL-H (14.4 mL, 1 M in hexanes, 14.4 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 1.75 h at 0 °C, quenched with saturated aqueous potassium sodium tartrate solution slowly, and kept stirring until the upper organic phase was clear, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. This compound was used for the next step without purification.

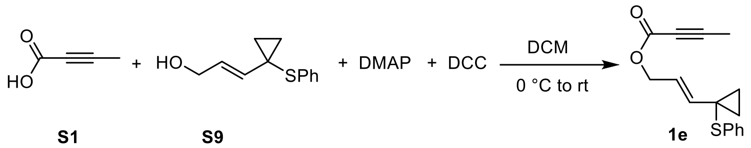
To a flask with **S1** (538 mg, 6.4 mmol) in DCM (30 mL) was added DMAP (65.1 mg, 0.58 mmol) at 0 °C. Then **S8** was added dropwise. After 5 min, DCC (1.2 g, 5.8 mmol) was added. The obtained mixture was stirred for 4 h at rt, and then concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 15:1 PE/EA) afforded compound **1d** (981 mg, 55% over three steps) as a light yellow oil.

TLC (3:1 PE/EA, R*f*): 0.7.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.87 (dd, *J* = 3.5, 1.3 Hz, 1H), 5.71 (dt, *J* = 15.2, 1.3 Hz, 1H), 5.39 (dt, *J* = 15.2, 6.6 Hz, 1H), 4.59 (dd, *J* = 6.7, 1.2 Hz, 2H), 1.97 (s, 3H), 1.26 – 1.19 (m, 2H), 1.13 – 1.07 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.6, 147.3, 142.7, 126.7, 126.1, 124.2, 121.4, 85.8, 72.5, 66.1, 22.7, 17.6, 3.9.

HRMS (ESI) m/z: calcd. for $C_{14}H_{15}O_2S$ ([M+H]$^+$): 247.0787, found: 247.0787.



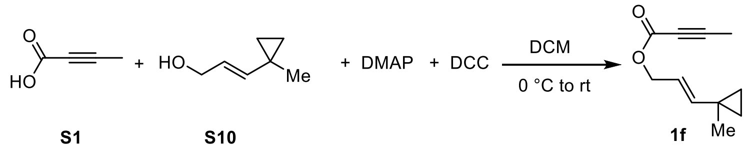
To a flask with **S1** (925 mg, 11 mmol) in DCM (45 mL) was added DMAP (112 mg, 1 mmol) at 0 °C. Then **S9**[2] (10 mmol) was added dropwise. After 5 min, DCC (2.06 g, 10 mmol) was added. The obtained mixture was stirred for 3 h at rt, and then concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 PE/EA) afforded compound **1e** (1.79 g, 66%) as a light yellow oil.

TLC (3:1 PE/EA, R*f*): 0.6.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.29 – 7.22 (m, 4H), 7.17 – 7.08 (m, 1H), 5.85 (dt, *J* = 15.0, 6.4 Hz, 1H), 5.59 (dt, *J* = 15.0, 1.3 Hz, 1H), 4.60 (dd, *J* = 6.4, 1.2 Hz, 2H), 1.97 (s, 3H), 1.30 – 1.24 (m, 2H), 1.23 – 1.17 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.5, 139.1, 137.0, 128.8, 127.3, 125.3, 122.9, 85.8, 72.4, 65.6, 25.7, 18.6, 3.9.

HRMS (ESI) m/z: calcd. for $C_{16}H_{16}NaO_2S$ ([M+Na]$^+$): 295.0763, found: 295.0764.



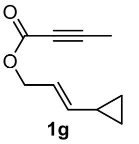
To a flask with **S1** (280 mg, 3.3 mmol) in DCM (5 mL) was added DMAP (37.4 mg, 0.1 mmol) at 0 °C. Then **S10**[2] (343mg, 3 mmol) was added dropwise. After 5 min, DCC (624 g, 3 mmol) was added. The obtained mixture was stirred for 2.75 h at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **1f** (505 mg, 93%) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.5.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 5.52 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.39 (d, *J* = 15.4 Hz, 1H), 4.60 (dd, *J* = 6.8, 0.9 Hz, 2H), 1.98 (s, 3H), 1.17 (s, 3H), 0.60 (s, 4H).

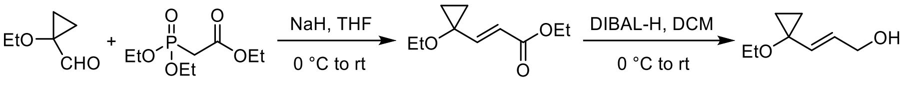
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.7, 145.8, 118.5, 85.5, 72.6, 66.8, 21.1, 17.3, 15.4, 3.9.

HRMS (ESI) m/z: calcd. for $C_{11}H_{15}O_2$ ([M+H]$^+$): 179.1067, found: 179.1067.



1g

1g is a known compound and is synthesized by the reported method.[3]



S11 **S6** **S12** **S13**

To a flask with **S6** (6.78 g, 30.2 mmol) in THF (50 mL) was added NaH (1.5 g, 60% dispersion in mineral oil, 37.5 mmol) slowly at 0 °C. After 10 min, **S11** (25 mmol, known compound and commercially available) was added. The obtained mixture was stirred for 25 min at 0 °C to rt. Quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 to 10:1 to 5:1 PE/EA) afforded compound **S12** (2.24 g).

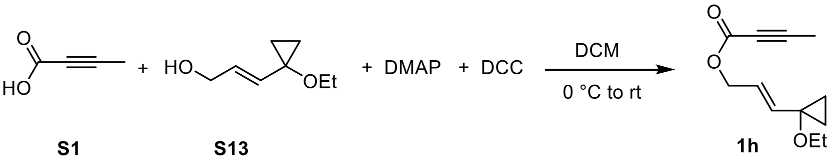
To a flask with **S12** (2.24 g, 12.2 mmol) in DCM (36.5 mL) was added DIBAL-H (40 mL, 1 M in hexanes, 40 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 40 min at 0 °C to rt, Et_2O (40 mL) was added, and quenched with H_2O (1.6 mL), 15% aqueous NaOH solution (1.6 mL), and H_2O (4 mL). After 15 min, $MgSO_4$ (8 g) was added and kept stirring for 1 h, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 25:1 to 20:1 to 17:1 to 10:1 to 5:1 to 2:1 PE/EA) afforded compound **S13** (1.56 g, 44% over two steps). as a colorless oil.

TLC (5:1 PE/EA, R*f*): 0.1.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 5.79 (dt, *J* = 15.6, 5.7 Hz, 1H), 5.50 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.18 (dd, *J* = 5.7, 1.5 Hz, 2H), 3.51 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.07 – 1.01 (m, 2H), 0.73 – 0.67 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 133.6, 126.7, 63.4, 63.1, 60.8, 15.6, 14.7.

HRMS (ESI) m/z: calcd. for $C_8H_{18}NO_2$ ($[M+NH_4]^+$): 160.1332, found: 160.1332.



S1 **S13** **1h**

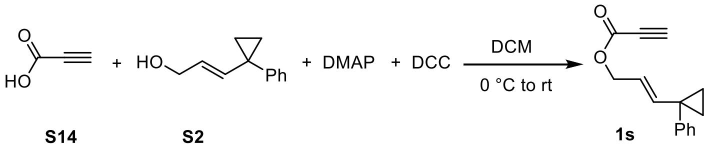
To a flask with **S1** (261 mg, 3.1 mmol) in DCM (15 mL) was added DMAP (78.4 mg, 0.7 mmol) at 0 °C. Then **S13** (2.8 mmol) was added dropwise. After 5 min, DCC (578 mg, 2. 8 mmol) was added. The obtained mixture was stirred for 2.5 h at rt, and then concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 PE/EA) afforded compound **1h** (380 mg, 65%) as a colorless oil.

TLC (3:1 PE/EA, R*f*): 0.6.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 5.72 (dt, *J* = 15.5, 6.4 Hz, 1H), 5.57 (dt, *J* = 15.5, 1.1 Hz, 1H), 4.66 (dd, *J* = 6.4, 1.1 Hz, 2H), 3.50 (q, *J* = 7.1 Hz, 2H), 1.99 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.09 – 1.02 (m, 2H), 0.75 – 0.68 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.6, 138.1, 120.5, 85.8, 72.5, 65.9, 63.3, 60.8, 15.6, 14.9, 3.9.

HRMS (ESI) m/z: calcd. for $C_{12}H_{20}NO_3$ ([M+NH$_4$]$^+$): 226.1438, found: 226.1438.



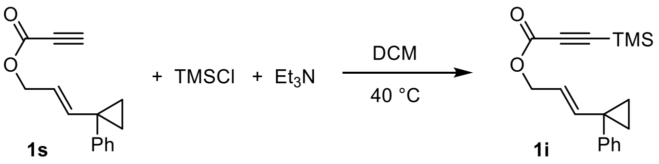
To a flask with **S14** (268 mg, 3.8 mmol) in DCM (10 mL) was added DMAP (38.9 mg, 0.32 mmol) at 0 °C. Then **S2** (523mg, 3 mmol) was added dropwise. After 5 min, DCC (622 g, 3 mmol) was added. The obtained mixture was stirred for 70 min at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1s** (528.2 mg, 78%) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.5.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.34 – 7.27 (m, 4H), 7.26 – 7.19 (m, 1H), 5.67 (dt, *J* = 15.3, 1.2 Hz, 1H), 5.11 (dt, *J* = 15.3, 6.7 Hz, 1H), 4.59 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.84 (s, 1H), 1.17 – 1.10 (m, 2H), 1.04 – 0.96 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 152.6, 145.0, 142.6, 130.1, 128.5, 126.8, 120.6, 74.8, 74.7, 66.8, 28.0, 15.1.

HRMS (ESI) m/z: calcd. for $C_{15}H_{15}O_2$ ([M+H]$^+$): 227.1067, found: 227.1068.



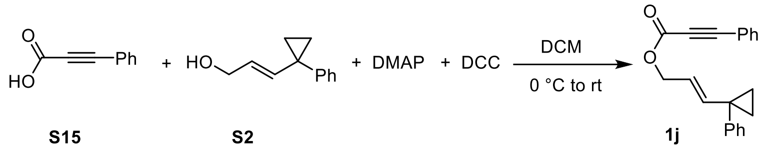
To a tube with **1s** (227.5 mg,1 mmol) in DCM (1 mL) was added TMSCl (169 mg, 1.56 mmol) and Et$_3$N (111 mg, 1.1 mmol, dissolved in 1mL DCM) under an argon atmosphere. The obtained mixture was stirred for 11.7 h at 40 °C. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1i** (141.2 mg, 47%) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.8.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.35 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 5.66 (dt, *J* = 15.4, 1.2 Hz, 1H), 5.12 (dt, *J* = 15.3, 6.8 Hz, 1H), 4.57 (dd, *J* = 6.8, 1.1 Hz, 2H), 1.16 – 1.09 (m, 2H), 1.04 – 0.97 (m, 2H), 0.23 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.0, 144.8, 142.6, 130.1, 128.5, 126.8, 120.9, 94.7, 94.1, 66.6, 28.0, 15.1.

HRMS (ESI) m/z: calcd. for $C_{18}H_{23}O_2Si$ ([M+H]$^+$): 299.1462, found: 299.1465.



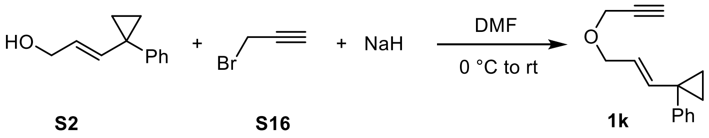
To a flask with **S15** (327 mg, 2.24 mmol) in DCM (5 mL) was added DMAP (32.5 mg, 0.27 mmol) at 0 °C. Then **S2** (341mg, 1.96 mmol) was added dropwise. After 5 min, DCC (425 g, 2.06 mmol) was added. The obtained mixture was stirred for 30 min at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1j** (523.3 mg, 88%) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.4.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.60 – 7.54 (m, 2H), 7.47 – 7.41 (m, 1H), 7.36 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.31 (d, *J* = 4.4 Hz, 4H), 7.27 – 7.20 (m, 1H), 5.70 (d, *J* = 15.3 Hz, 1H), 5.17 (dt, *J* = 15.3, 6.7 Hz, 1H), 4.63 (dd, *J* = 6.8, 1.1 Hz, 2H), 1.17 – 1.11 (m, 2H), 1.04 – 0.99 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 154.0, 144.8, 142.6, 133.1, 130.8, 130.1, 128.7, 128.5, 126.8, 121.0, 119.7, 86.4, 80.7, 66.7, 28.0, 15.1.

HRMS (ESI) m/z: calcd. for $C_{21}H_{19}O_2$ ([M+H]$^+$): 303.1380, found: 303.1379.



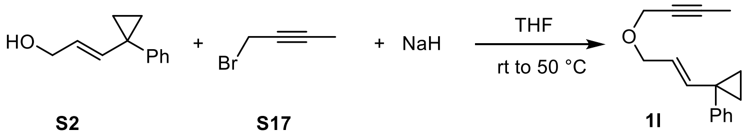
To a flask with NaH (524 mg, 60% dispersion in mineral oil, 13 mmol) in DMF (30 mL) was added **S2** (1.75 g, 10 mmol) under an argon atmosphere at 0 °C. After 20 min, **S16** (1.6 g, 13.4 mmol) was added. The reaction mixture was stirred at rt for 18 h, quenched with saturated aqueous NH$_4$Cl solution, and extracted with Et$_2$O. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1k** (1.6879 g, 79%) as a yellow oil.

TLC (10:1 PE/EA, R*f*): 0.5.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.33 – 7.26 (m, 4H), 7.25 – 7.18 (m, 1H), 5.64 (dt, *J* = 15.3, 1.3 Hz, 1H), 5.13 (dt, *J* = 15.4, 6.4 Hz, 1H), 4.09 (d, *J* = 2.4 Hz, 2H), 3.98 (dd, *J* = 6.4, 1.2 Hz, 2H), 2.39 (t, *J* = 2.4 Hz, 1H), 1.13 – 1.07 (m, 2H), 1.02 – 0.96 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 143.1, 142.5, 130.0, 128.4, 126.6, 123.6, 80.0, 74.4, 70.3, 57.0, 27.9, 15.0.

HRMS (ESI) m/z: calcd. for $C_{15}H_{17}O$ ([M+H]$^+$): 213.1274, found: 213.1273.



To a flask with NaH (99 mg, 60% dispersion in mineral oil, 2.5 mmol) in THF (5 mL) was added **S2**

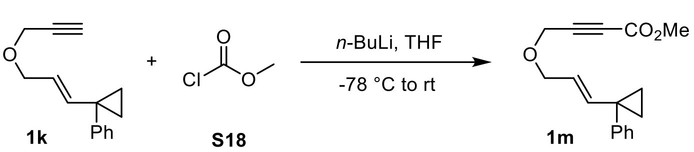
(333 mg, 1.9 mmol) under an argon atmosphere at room temperature. After 15 min, **S17** (0.3 mL, d = 1.483, 3.3 mmol) was added. The reaction mixture was stirred at 50 °C for 10.75 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **1l** (294.9 mg, 68%) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33 – 7.25 (m, 4H), 7.24 – 7.17 (m, 1H), 5.62 (dt, *J* = 15.3, 1.2 Hz, 1H), 5.14 (dt, *J* = 15.4, 6.4 Hz, 1H), 4.04 (q, *J* = 2.3 Hz, 2H), 3.94 (dd, *J* = 6.4, 1.3 Hz, 2H), 1.83 (t, *J* = 2.3 Hz, 3H), 1.12 – 1.06 (m, 2H), 1.01 – 0.96 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.2, 142.0, 130.0, 128.3, 126.5, 124.0, 82.4, 75.3, 70.2, 57.7, 27.9, 14.9, 3.7.

HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O$ ($[M+H]^+$): 227.1430, found: 227.1436.



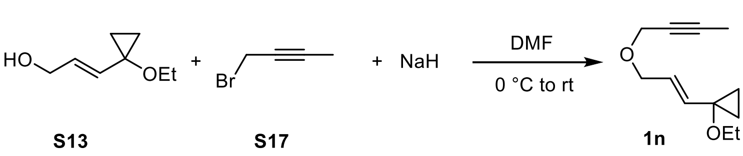
To a flask with **1k** (2.38 mmol) in THF (10 mL) was added *n*-BuLi (1.2 mL, 2.4 M in hexanes, 2.88 mmol) under an argon atmosphere at -78 °C. After 15 min, **S18** (306 mg, 3.24 mmol) was added and stirred at -78 °C for 15 min. The reaction mixture was stirred at rt for 1 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **1m** (309.4 mg, 48%) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 5.64 (dt, *J* = 15.4, 1.2 Hz, 1H), 5.09 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.21 (s, 2H), 3.98 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.77 (s, 3H), 1.15 – 1.07 (m, 2H), 1.03 – 0.96 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.7, 143.3, 143.0, 130.0, 128.4, 126.7, 123.1, 84.0, 77.8, 70.8, 56.6, 52.9, 28.0, 15.0.

HRMS (ESI) m/z: calcd. for $C_{17}H_{22}NO_3$ ($[M+NH_4]^+$): 288.1594, found: 288.1596.



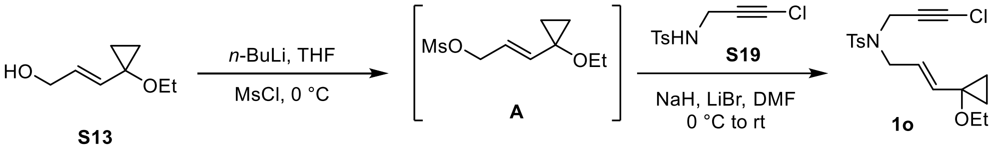
To a flask with NaH (120 mg, 60% dispersion in mineral oil, 3 mmol) in DMF (7.5 mL) was added **S13** (284.2 mg, 2 mmol) under an argon atmosphere at 0 °C. After 10 min, **S17** (398.9 mg, 3 mmol) was added. The reaction mixture was stirred at 0 °C to rt for 4.5 h, quenched with water, and extracted with EA. The combined organic layer was washed with saturated aqueous NH_4Cl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 30:1 PE/EA) afforded compound **1n** (352.4 mg, 91%) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.70 (dt, J = 15.6, 6.1 Hz, 1H), 5.54 (d, J = 15.6 Hz, 1H), 4.10 (q, J = 2.3 Hz, 2H), 4.05 (d, J = 6.2 Hz, 2H), 3.51 (q, J = 7.1 Hz, 2H), 1.86 (t, J = 2.4 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.06 – 0.99 (m, 2H), 0.73 – 0.67 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 135.6, 123.5, 82.6, 75.2, 69.9, 63.2, 60.8, 57.7, 15.6, 14.7, 3.7.

HRMS (ESI) m/z: calcd. for $C_{12}H_{19}O_2$ ($[M+H]^+$): 195.1380, found: 195.1380.



To a solution of **S13** (298 mg, 2.1 mmol) in THF (10 mL) was added *n*-BuLi (2.4 M in hexanes, 1 mL, 2.4 mmol) under argon atmosphere at 0 °C. After 10 min, MsCl (305 mg, 2.66 mmol) was added. The mixture was stirred at 0 °C for 10 min to afford intermediate **A**, which was used for the next step directly.

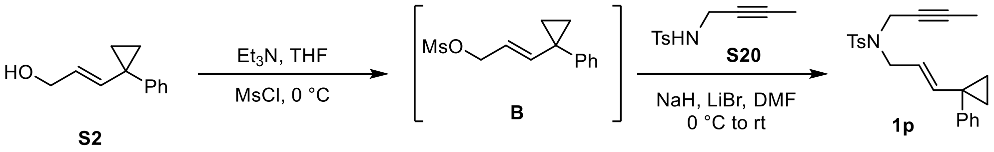
To a flask with NaH (260 mg, 60% dispersion in mineral oil, 6.5 mmol) and LiBr (1.42 g, 16.3 mmol) in DMF (5 mL) was added a solution of **S19**[4] (496 mg, 2 mmol) in DMF (5 mL) under argon atmosphere at 0 °C. After 30 min, the solution of **A** was added and stirred at 0 °C to rt for 12.5 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) afforded compound **1o** (336.2 mg, 45%) as a light yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.52 – 5.41 (m, 2H), 4.07 (s, 2H), 3.84 – 3.77 (m, 2H), 3.43 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.14 (t, J = 7.0 Hz, 3H), 1.07 – 1.00 (m, 2H), 0.70 – 0.62 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.8, 137.9, 135.8, 129.6, 127.8, 120.8, 63.4, 63.3, 62.6, 60.8, 48.5, 36.3, 21.7, 15.6, 14.9.

HRMS (ESI) m/z: calcd. for $C_{18}H_{23}ClNO_3S$ ($[M+H]^+$): 368.1082, found: 368.1081.



To a solution of **S2** (523 mg, 3 mmol) in THF (10 mL) was added Et_3N (364 mg, 3.6 mmol) and MsCl (412 mg, 3.6 mmol) under argon atmosphere at 0 °C. The mixture was stirred at 0 °C for 1 h to afford intermediate **B**, which was used for the next step directly.

To a flask with NaH (360 mg, 60% dispersion in mineral oil, 9 mmol) and LiBr (1.04 g, 12 mmol) in

DMF (10 mL) was added a solution of **S20** (670 mg, 3 mmol) in DMF (5 mL) under argon atmosphere at 0 °C. After 30 min, the solution of **B** was added and stirred at 0 °C to rt for 3.3 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 25:1 PE/EA) afforded compound **1p** (467 mg, 41%) as a white solid.

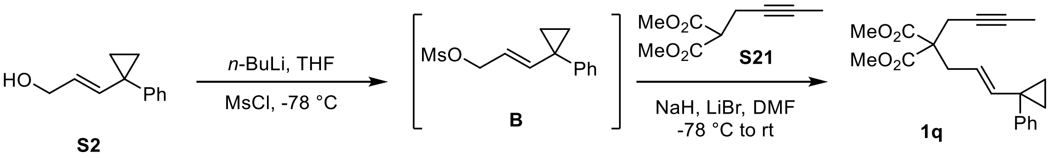
TLC (3:1 PE/EA, R_f): 0.6.

Melting Point: 100.3 – 101.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.68 (d, J = 8.2 Hz, 2H), 7.30 – 7.19 (m, 7H), 5.56 (dt, J = 15.3, 1.3 Hz, 1H), 4.91 (dt, J = 15.2, 6.8 Hz, 1H), 3.95 (q, J = 2.4 Hz, 2H), 3.72 (dd, J = 6.8, 1.2 Hz, 2H), 2.41 (s, 3H), 1.52 (t, J = 2.4 Hz, 3H), 1.11 – 1.05 (m, 2H), 0.97 – 0.89 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.2 (2C), 143.0, 136.5, 129.7, 129.3, 128.4, 128.0, 126.6, 121.7, 81.4, 72.0, 48.4, 36.3, 27.8, 21.6, 15.0, 3.4.

HRMS (ESI) m/z: calcd. for $C_{23}H_{26}NO_2S$ ($[M+H]^+$): 380.1679, found: 380.1678.



To a solution of **S2** (640.9 mg, 3.68 mmol) in THF (10 mL) was added *n*-BuLi (2.4 M in hexanes, 1.8 mL, 4.4 mmol) under argon atmosphere at -78 °C. After 15 min, MsCl (505.7 mg, 4.4 mmol) was added. The mixture was stirred at -78 °C for 30 min to afford intermediate **B**, which was used for the next step directly.

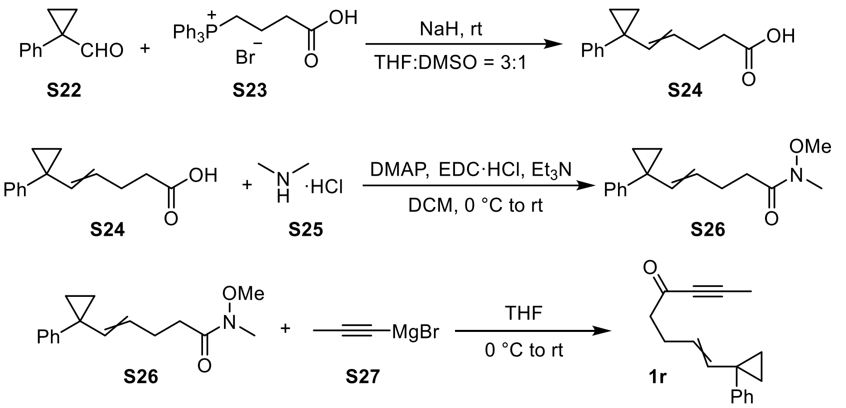
To a flask with NaH (396 mg, 60% dispersion in mineral oil, 9.9 mmol) and LiBr (1.92 g, 22.1 mmol) in DMF (10 mL) was added **S21** (520.9 mg, 2.83 mmol) under argon atmosphere at 0 °C. After 30 min, the mixture was cooled to -78 °C and the solution of **B** was added and stirred at -78 °C for 2 h and then at rt for 10.5 h, quenched with water, and then extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **1q** (645.5 mg, 67%) as a colorless oil.

TLC (3:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 – 7.22 (m, 4H), 7.22 – 7.15 (m, 1H), 5.55 (d, J = 15.0 Hz, 1H), 4.90 (dt, J = 15.2, 7.6 Hz, 1H), 3.67 (s, 6H), 2.72 – 2.62 (m, 4H), 1.73 (t, J = 2.6 Hz, 3H), 1.07 – 1.01 (m, 2H), 0.96 – 0.89 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 170.7, 143.7, 142.0, 129.3, 128.3, 126.4, 121.6, 78.9, 73.5, 57.8, 52.6, 35.2, 27.8, 23.1, 15.0, 3.6.

HRMS (ESI) m/z: calcd. for $C_{21}H_{25}O_4$ ($[M+H]^+$): 341.1747, found: 341.1746.



To a flask with **S23** (2.58 g, 6 mmol) and NaH (486 mg, 60% dispersion in mineral oil, 12 mmol) was added THF/DMSO (10 mL, 3:1) under argon atmosphere at rt. After 1 h, **S22**[2] (737 mg, 5 mmol) in THF/DMSO (2 mL, 3:1) was added and stirred at rt for 13.5 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 to 5:1 PE/EA) afforded compound **S24** (814.5 mg).

To a flask with **S24** (814.5 mg, 3.77 mmol), **S25** (485 mg, 4.97 mmol) and DMAP (55 mg, 0.45 mmol) in DCM (15 mL) were added Et_3N (490 mg, 4.8 mmol) and EDC·HCl (941 mg, 4.9 mmol) at 0 °C. The mixture was stirred for 9.5 h at 0 °C to rt. Eluted with EA (30 mL), then washed with 1 M HCl three times and saturated aqueous $NaHCO_3$ solution three times. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 25:1 to 5:1 PE/EA) afforded compound **S26** (800.9 mg).

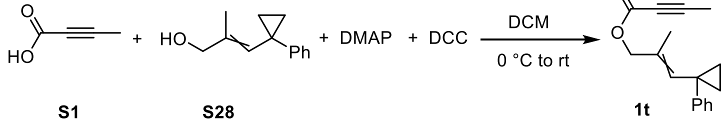
To a solution of **S26** (800.9 mg, 3.09 mmol) in THF (5 mL) was added **S27** (0.5 M in THF, 10 mL, 5 mmol) slowly under argon atmosphere at 0 °C. The mixture was stirred at rt for 4.5 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **1r** (715.7 mg, 59% over three steps, Z/E = 4.3:1) as a light yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR for the major product (400 MHz, $CDCl_3$, δ): 7.30 – 7.19 (m, 4H), 7.18 – 7.10 (m, 1H), 5.73 (dt, J = 11.5, 1.6 Hz, 1H), 5.46 (dt, J = 10.3, 7.0 Hz, 1H), 2.50 – 2.44 (m, 2H), 2.43 – 2.36 (m, 2H), 1.97 (s, 3H), 1.15 – 1.10 (m, 2H), 1.04 – 0.98 (m, 2H).

^{13}C{^{1}H} NMR for the major product (101 MHz, $CDCl_3$, δ): 187.6, 145.2, 134.5, 131.6, 128.4, 126.6, 125.6, 90.3, 80.2, 44.8, 23.3, 23.1, 17.6, 4.1.

HRMS (ESI) m/z: calcd. for $C_{17}H_{19}O$ ($[M+H]^+$): 239.1430, found: 239.1429.



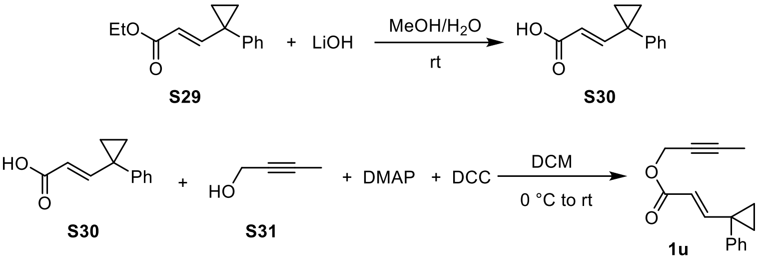
To a flask with **S1** (277 mg, 3.3 mmol) in DCM (5 mL) was added DMAP (37.8 mg, 0.31 mmol) at 0 °C. Then **S28**[5] (564 mg, 3 mmol) was added dropwise. After 5 min, DCC (624 mg, 3 mmol) was added. The obtained mixture was stirred for 1.5 h at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **1t** (671.7 mg, 88%, *Z*: *E* = 1: 3.5) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR for the major product (400 MHz, $CDCl_3$, *δ*): 7.29 – 7.20 (m, 2H), 7.20 – 7.09 (m, 3H), 5.84 (s, 1H), 4.57 (s, 2H), 1.98 (s, 3H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.18 – 1.10 (m, 2H), 1.06 – 0.97 (m, 2H).

^{13}C{^{1}H} NMR for the major product (101 MHz, $CDCl_3$, *δ*): 153.7, 144.8, 134.2, 133.0, 128.4, 126.3, 125.5, 85.8, 72.5, 71.0, 23.0, 17.9, 15.3, 3.9.

HRMS (ESI) m/z: calcd. for $C_{17}H_{22}NO_2$ ($[M+NH_4]^+$): 272.1645, found: 272.1644.



To a flask with LiOH (2.99 g, 125 mmol) in MeOH (30 mL) and H_2O (30 mL) was added **S29**[2] (1.08 g, 5 mmol) at rt. The obtained mixture was stirred for 18 h at rt, quenched with water, and then extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 3:1 PE/EA) afforded compound **S30** for the next step directly.

To a flask with **S30** (5 mmol) in DCM (40 mL) was added DMAP (56.1 mg, 0.5 mmol) at 0 °C. Then **S31** (385 mg, 5.5 mmol) was added dropwise. After 5 min, DCC (1.03 g, 5 mmol) was added. The obtained mixture was stirred for 3 h at rt, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 PE/EA) afforded compound **1u** (521 mg, 43% over two steps) as a white solid.

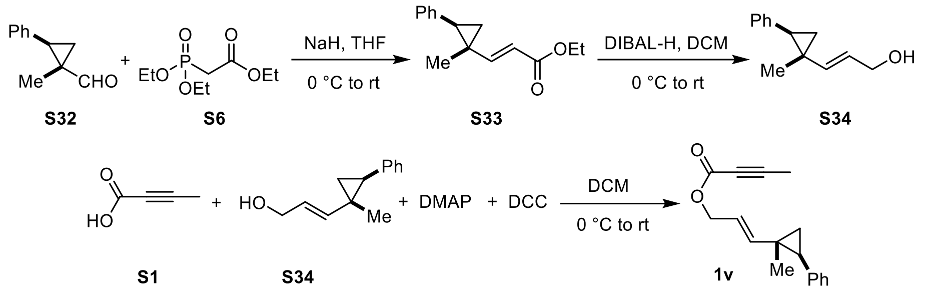
TLC (3:1 PE/EA, R_f): 0.8.

Melting Point: 46 – 48 °C.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.35 – 7.22 (m, 5H), 6.73 (d, *J* = 15.5 Hz, 1H), 5.32 (d, *J* = 15.4 Hz, 1H), 4.64 (q, *J* = 2.4 Hz, 2H), 1.83 (t, *J* = 2.4 Hz, 3H), 1.35 – 1.29 (m, 2H), 1.25 – 1.19 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 166.3, 158.3, 140.9, 130.5, 128.7, 127.4, 118.2, 83.2, 73.4, 52.6, 29.5, 16.6, 3.8.

HRMS (ESI) m/z: calcd. for $C_{16}H_{17}O_2$ ($[M+H]^+$): 241.1223, found: 241.1224.



To a flask with **S6** (850 mg, 3.79 mmol) in THF (10 mL) was added NaH (309 mg, 60% dispersion in mineral oil, 7.7 mmol) slowly at 0 °C. After 5 min, **S32**[6] (3.39 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 30 min at 0 °C to rt. Quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation to afford **S33** which was used for the next step directly.

To a flask with **S33** (3.39 mmol) in DCM (36.5 mL) was added DIBAL-H (10.2 mL, 1 M in hexanes, 10.2 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 40 min at 0 °C to rt, Et_2O (40 mL) was added, and quenched with saturated aqueous potassium sodium tartrate solution slowly and kept stirring until the upper organic phase was clear, extracted with ether. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation to afford **S34** which was used for the next step directly.

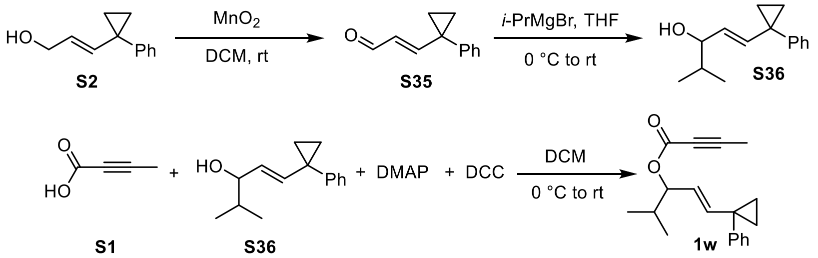
To a flask with **S1** (319 mg, 3.8 mmol) in DCM (5 mL) was added DMAP (43.8 mg, 0.36 mmol) at 0 °C. Then **S34** (3.39 mmol) in DCM (2 mL) was added dropwise. After 5 min, DCC (702 mg, 3.4 mmol) was added. The obtained mixture was stirred for 1 h at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 20:1 PE/EA) afforded compound **1v** (856.7 mg, 99% over three steps) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 5.62 – 5.51 (m, 2H), 4.65 (d, *J* = 5.5 Hz, 2H), 2.20 (dd, *J* = 8.7, 6.7 Hz, 1H), 1.99 (s, 3H), 1.18 – 1.10 (m, 2H), 0.88 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 153.7, 146.0, 138.3, 129.2, 128.2, 126.2, 118.6, 85.7, 72.6, 66.7, 31.1, 24.4, 19.1, 16.4, 3.9.

HRMS (ESI) m/z: calcd. for $C_{17}H_{19}O_2$ ($[M+H]^+$): 255.1380, found: 255.1384.



To a flask with **S2** (513 mg, 2.94 mmol) in DCM (10 mL) was added activated MnO_2 (1.32 g, 15.2 mmol) at rt. The obtained mixture was stirred for 18 h at rt. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 10:1 PE/EA) afforded compound **S35**.

To a flask with **S35** (2.94 mmol) in THF (6 mL) was added *i*-PrMgBr (9 mL, 1 M in THF, 9 mmol) dropwise under an argon atmosphere at 0 °C. The mixture was stirred for 2.7 h at 0 °C to rt. Quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 25:1 to 10:1 PE/EA) afforded compound **S36**.

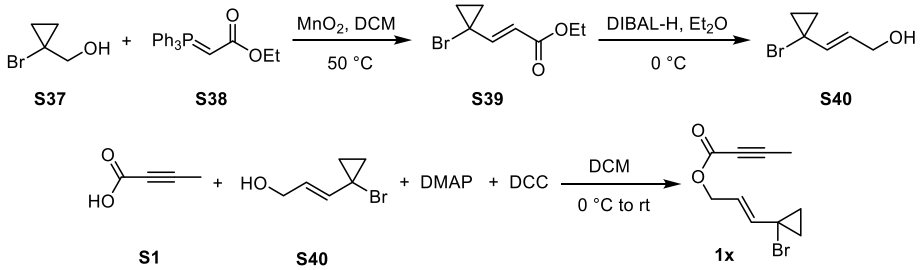
To a flask with **S1** (256 mg, 3 mmol) in DCM (10 mL) was added DMAP (40.8 mg, 0.33 mmol) at 0 °C. Then **S36** (2.94 mmol) was added dropwise. After 5 min, DCC (630 mg, 3.05 mmol) was added. The obtained mixture was stirred for 2 h at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1w** (191.7 mg, 23% over three steps) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.34 – 7.24 (m, 5H), 7.25 – 7.16 (m, 1H), 5.61 (d, *J* = 15.2 Hz, 1H), 5.05 (dd, *J* = 8.1, 6.5 Hz, 1H), 4.94 (dd, *J* = 15.2, 8.0 Hz, 1H), 1.97 (s, 3H), 1.86 – 1.71 (m, 1H), 1.15 – 1.03 (m, 2H), 1.03 – 0.95 (m, 2H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 153.4, 143.0, 143.0, 129.8, 128.4, 126.5, 124.1, 85.2, 81.5, 72.9, 32.2, 27.8, 18.4, 18.2, 15.3, 15.0, 4.0.

HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O_2$ ($[M+H]^+$): 283.1693, found: 283.1699.



To a sealed tube with **S37** (453 mg, 3 mmol, known compound and commercially available) and **S38** (1.32 g, 3.8 mmol) in DCM (15 mL) was added activated MnO_2 (1.3 g, 15 mmol). The obtained mixture was stirred for 46.5 h at 50 °C. Diluted with PE, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 3:1 PE/EA) afforded compound **S39** (426 mg).

To a flask with **S39** (426 mg, 1.9 mmol) in Et_2O (5 mL) was added DIBAL-H (5 mL, 1 M in hexanes, 5 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 2 h at 0 °C and quenched with saturated aqueous potassium sodium tartrate solution slowly and kept stirring until the upper organic phase was clear, extracted with DCM. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation to afford **S40** which was used for the next step directly.

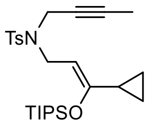
To a flask with **S1** (177 mg, 2.1 mmol) in DCM (10 mL) was added DMAP (21.3 mg, 0.19 mmol) at 0 °C. Then **S40** (1.9 mmol) in DCM (5 mL) was added dropwise. After 5 min, DCC (392 mg, 1.9 mmol) was added. The obtained mixture was stirred for 45 min at rt. Purification of the crude product by flash column chromatography (silica gel, 10:1 PE/EA) afforded compound **1x** (364 mg, 50% over three steps) as a colorless oil.

TLC (3:1 PE/EA, R*f*): 0.7.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 5.85 (dt, *J* = 14.9, 6.3 Hz, 1H), 5.62 (dt, *J* = 14.8, 1.3 Hz, 1H), 4.65 (dd, *J* = 6.3, 1.3 Hz, 2H), 1.99 (s, 3H), 1.40 – 1.34 (m, 2H), 1.13 – 1.07 (m, 2H).

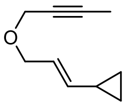
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 153.5, 138.5, 124.1, 86.1, 72.3, 65.0, 30.4, 18.2, 4.0.

HRMS (ESI) m/z: calcd. for $C_{10}H_{12}BrO_2$ ([M+H]$^+$): 243.0015, found: 243.0013.



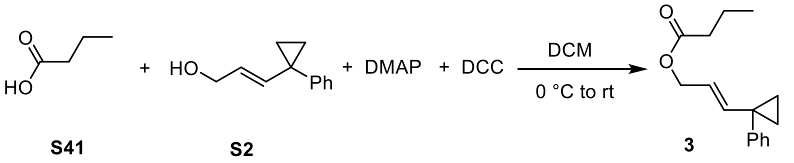
1y

1y is a known compound and synthesized by the reported method.[7a]



1z'

1z' is a known compound and synthesized by the reported method.[7b,c]



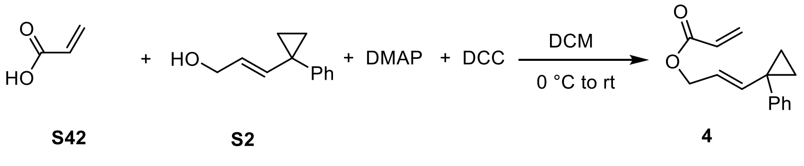
To a flask with **S41** (193.8 mg, 2.2 mmol) and DMAP (24.4 mg, 0.2 mmol) was added the solution of **S2** (345.3 mg, 1.98 mmol) in DCM (5 mL) at 0 °C dropwise. After 5 min, DCC (412.7 mg, 2 mmol) was added. The obtained mixture was stirred for 100 min at rt. Purification of the crude product by flash column chromatography (silica gel, 20:1 PE/EA) afforded compound **3** (455.2 mg, 94%) as a colorless oil.

TLC (10:1 PE/EA, R*f*): 0.6.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.33 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 5.63 (dt, *J* = 15.4, 1.3 Hz, 1H), 5.12 (dt, *J* = 15.3, 6.5 Hz, 1H), 4.48 (dd, *J* = 6.5, 1.3 Hz, 2H), 2.25 (t, *J* = 7.4 Hz, 2H), 1.63 (tq, *J* = 7.4, 7.4 Hz, 2H), 1.14 – 1.08 (m, 2H), 1.02 – 0.96 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 173.6, 143.0, 142.9, 130.0, 128.4, 126.7, 122.2, 64.8, 36.3, 27.9, 18.6, 15.0, 13.8.

HRMS (ESI) m/z: calcd. for $C_{16}H_{21}O_2$ ([M+H]$^+$): 245.1536, found: 245.1540.



To a flask with **S42** (183 mg, 2.5 mmol) and DMAP (26.3 mg, 0.2 mmol) in DCM (5 mL) was added the **S2** (348 mg, 2 mmol) at 0 °C dropwise. After 5 min, DCC (420 mg, 2 mmol) was added. The obtained mixture was stirred for 7 h at rt. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **4** (211 mg, 46%) as a colorless oil.

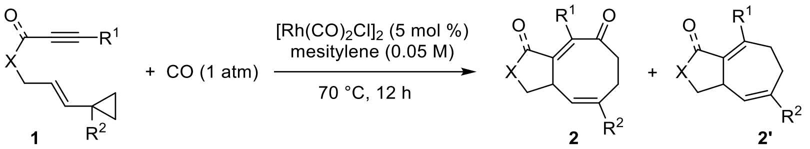
TLC (10:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30 (d, J = 4.4 Hz, 4H), 7.25 – 7.18 (m, 1H), 6.38 (dd, J = 17.4, 1.5 Hz, 1H), 6.09 (dd, J = 17.3, 10.4 Hz, 1H), 5.78 (dd, J = 10.5, 1.5 Hz, 1H), 5.66 (dt, J = 15.3, 1.3 Hz, 1H), 5.15 (dt, J = 15.4, 6.6 Hz, 1H), 4.57 (dd, J = 6.6, 1.3 Hz, 2H), 1.14 – 1.08 (m, 2H), 1.03 – 0.97 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 166.1, 143.3, 142.8, 130.8, 130.0, 128.6, 128.4, 126.7, 121.8, 65.1, 27.9, 15.0.

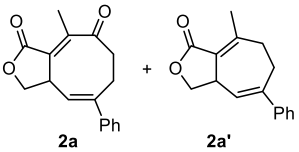
HRMS (ESI) m/z: calcd. for $C_{15}H_{16}NaO_2$ ($[M+Na]^+$): 251.1043, found: 251.1042.

3. General Procedure for [5 + 2 + 1] Cycloadditions



To a reaction tube with **1** and $[Rh(CO)_2Cl]_2$ (5 mol %) was added mesitylene (0.05 M of **1**) under an argon atmosphere. The reaction mixture was charged with CO three times and bubbled with balloon-pressured (slightly higher than 1 atm) gas of CO at room temperature for 5 min and then stirred at 70 °C for 12 h under balloon-pressured gas of CO, 600 rpm for the magnetic stir bars. After cooling, purification of the crude product by flash column chromatography (silica gel, PE/EA) afforded [5 + 2 + 1] cycloadducts **2**.

Note: 1. Only a few [5 + 2] products were isolated and characterized; 2. For some substrates, the oxidation of one methyl group of mesitylene to give alcohol can be observed based on the crude ^{1}H NMR spectrum; 3. This difference of solvent (toluene, xylene, mesitylene) can be attributed to the solubility of CO and/or the dipole moment of the solvent and many others.



run 1: Following general procedure. Substrate: **1a** (48.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); products: **2a** (46.8 mg, 87%), **2a'** (5.0 mg, 10%).

run 2: Following general procedure. Substrate: **1a** (48.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); products: **2a** (47.4 mg, 88%), **2a'** (4.2 mg, 9%).

The average yield of two runs: **2a** (88%) and **2a'** (10%).

run 3: Following general procedure. Substrate: **1a** (48.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 60 °C, 24 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); products: **2a** (47.2 mg, 87%), **2a'** (4.5 mg, 9%).

Gram scale experiments:

run 1: Following general procedure. Substrate: **1a** (1206 mg, 5 mmol), $[Rh(CO)_2Cl]_2$ (19.6 mg, 0.05 mmol), mesitylene (50 mL), 800rpm, 30 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 to 2:1 PE/EA); products: **2a** (998.9 mg, 74%), **2a’** (115.4 mg, 10%).

run 2: Following general procedure. Substrate: **1a** (1203.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (19.5 mg, 0.05 mmol), mesitylene (50 mL), 800rpm, 30 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 to 2:1 PE/EA); products: **2a** (1054.6 mg, 78%), **2a’** (150.7 mg, 12%).

The average yield of two runs: **2a** (76%) and **2a’** (11%).

Note: we also tried 0.1% of $[Rh(CO)_2Cl]_2$, but this led to low efficiency.

Physical Form of 2a: white solid.

Physical Form of 2a’: colorless oil.

Melting Point of 2a: 112 – 114 °C.

TLC (5:1 PE/EA, R_f): **2a** (0.2) and **2a’** (0.4).

^{1}H NMR of **2a** (400 MHz, $CDCl_3$, δ): 7.35 – 7.23 (m, 5H), 5.66 (dd, J = 6.7, 1.5 Hz, 1H), 4.65 (dd, J = 8.6, 8.6 Hz, 1H), 4.40 – 4.31 (m, 1H), 4.20 (dd, J = 8.9, 5.8 Hz, 1H), 3.27 (ddd, J = 13.0, 9.1, 7.3 Hz, 1H), 3.01 – 2.90 (m, 2H), 2.71 (dt, J = 12.6, 6.1 Hz, 1H), 2.35 (d, J = 2.4 Hz, 3H).

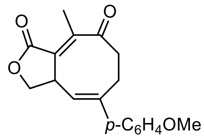
^{13}C{^{1}H} NMR of **2a** (101 MHz, $CDCl_3$, δ): 206.0, 169.9, 150.4, 144.5, 142.6, 128.61, 128.58, 128.0, 127.6, 126.2, 71.6, 41.1, 40.1, 28.4, 14.9.

HRMS of **2a** (ESI) m/z: calcd. for $C_{17}H_{17}O_3$ ($[M+H]^+$): 269.1172, found: 269.1173.

^{1}H NMR of **2a’** (400 MHz, $CDCl_3$, δ): 7.37 – 7.30 (m, 4H), 7.30 – 7.25 (m, 1H), 5.79 (dd, J = 3.2, 1.5 Hz, 1H), 4.60 (dd, J = 9.9, 8.5 Hz, 1H), 4.33 – 4.21 (m, 1H), 4.02 (dd, J = 8.6, 8.6 Hz, 1H), 2.97 – 2.87 (m, 1H), 2.75 – 2.60 (m, 2H), 2.47 – 2.37 (m, 1H), 2.27 (d, J = 2.5 Hz, 3H).

^{13}C{^{1}H} NMR of **2a’** (101 MHz, $CDCl_3$, δ): 170.5, 155.0, 143.0, 142.1, 128.6, 127.6, 127.4, 125.8, 121.8, 70.5, 38.0, 35.3, 28.4, 20.6.

HRMS of **2a’** (ESI) m/z: calcd. for $C_{16}H_{17}O_2$ ($[M+H]^+$): 241.1223, found: 241.1226.



2b

run 1: Following general procedure. Substrate: **1b** (54.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 6:1 to 2:1 PE/EA); product: **2b** (48.3 mg, 80%), byproduct (5.9 mg).

run 2: Following general procedure. Substrate: **1b** (54.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 10:1 to 5:1 to 2:1 PE/EA); product: **2b** (50.2 mg, 84%), byproduct (6.2 mg).

The average yield of two runs: 82%.

Physical Form: white solid.

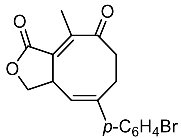
Melting Point: 110.0 – 111.7 °C.

TLC (3:1 PE/EA, R*f*): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.25 – 7.16 (m, 2H), 6.90 – 6.80 (m, 2H), 5.61 (dd, *J* = 6.6, 1.3 Hz, 1H), 4.64 (dd, *J* = 8.6, 8.6 Hz, 1H), 4.38 – 4.28 (m, 1H), 4.19 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.80 (s, 3H), 3.24 (ddd, *J* = 12.9, 8.7, 7.3 Hz, 1H), 2.99 – 2.89 (m, 2H), 2.70 (dt, *J* = 12.7, 6.2 Hz, 1H), 2.35 (d, *J* = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 206.1, 170.0, 159.5, 150.2, 143.9, 134.9, 128.6, 127.4, 126.0, 113.9, 71.6, 55.4, 41.3, 40.2, 28.3, 15.0.

HRMS (ESI) m/z: calcd. for $C_{18}H_{19}O_4$ ([M+H]$^+$): 299.1278, found: 299.1277.



2c

run 1: Following general procedure. Substrate: **1c** (63.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 to 2:1 PE/EA); product: **2c** (57.6 mg, 84%), byproduct (5.6 mg).

run 2: Following general procedure. Substrate: **1c** (64.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 to 2:1 PE/EA); product: **2c** (59.9 mg, 86%), byproduct (8.5 mg).

The average yield of two runs: 85%.

Physical Form: white solid.

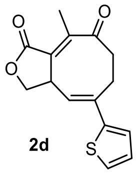
Melting Point: 137.1 – 139.2 °C.

TLC (5:1 PE/EA, R*f*): 0.1.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.47 – 7.40 (m, 2H), 7.17 – 7.08 (m, 2H), 5.66 (dd, *J* = 6.7, 1.2 Hz, 1H), 4.65 (dd, *J* = 8.7, 8.7 Hz, 1H), 4.40 – 4.30 (m, 1H), 4.20 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.27 (ddd, *J* = 13.0, 9.1, 7.4 Hz, 1H), 2.92 (dd, *J* = 8.9, 6.2 Hz, 2H), 2.70 (ddd, *J* = 12.6, 6.1, 6.1 Hz, 1H), 2.35 (d, *J* = 2.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 205.8, 169.8, 150.6, 143.5, 141.5, 131.7, 128.5, 128.2, 127.9, 122.0, 71.5, 41.0, 40.1, 28.3, 14.9.

HRMS (ESI) m/z: calcd. for $C_{17}H_{16}BrO_3$ ([M+H]$^+$): 347.0277, found: 347.0278.



2d

run 1: Following general procedure. Substrate: **1d** (49.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 21 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 to 2:1 PE/EA); product: **2d** (44.2 mg, 80%), byproduct (5.7 mg).

run 2: Following general procedure. Substrate: **1d** (50.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 21 h, flash column chromatography (silica gel, 10:1 to 3:1 PE/EA); product: **2d** (44.4 mg, 80%), byproduct (5.9 mg).

The average yield of two runs: 80%.

Physical Form: white solid.

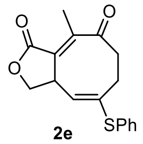
Melting Point: 157.2 – 159.2 °C.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.18 (dd, J = 5.0, 1.2 Hz, 1H), 7.03 (dd, J = 3.7, 1.2 Hz, 1H), 6.98 (dd, J = 5.1, 3.6 Hz, 1H), 5.91 (dd, J = 6.6, 1.6 Hz, 1H), 4.62 (dd, J = 8.5, 8.5 Hz, 1H), 4.37 – 4.28 (m, 1H), 4.20 (dd, J = 8.8, 5.9 Hz, 1H), 3.24 (ddd, J = 13.1, 9.6, 5.7 Hz, 1H), 3.09 – 2.90 (m, 2H), 2.74 (ddd, J = 12.7, 6.2, 6.2 Hz, 1H), 2.34 (d, J = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 205.7, 169.7, 150.1, 145.0, 137.4, 128.0, 127.8, 125.2, 125.1, 123.9, 71.4, 41.1, 40.2, 28.0, 15.1.

HRMS (ESI) m/z: calcd. for $C_{15}H_{15}O_3S$ ($[M+H]^+$): 275.0736, found: 275.0737.



2e

run 1: Following general procedure. Substrate: **1e** (54.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 36 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 to 2:1 PE/EA); product: **2e** (29.9 mg, 50%), byproduct (3.1 mg), S.M. (15 mg), BRSM yield (69%).

run 2: Following general procedure. Substrate: **1e** (54.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.1 mg, 0.01 mmol), mesitylene (4 mL), 36 h, flash column chromatography (silica gel, 20:1 to 5:1 to 2:1 PE/EA); product: **2e** (33.4 mg, 55%), byproduct (4.6 mg) , S.M. (15.8 mg), BRSM yield (77%).

Silica gel: SiliaFlash P60 (Particle size: 40-63um, Pore size 60A) purchased from Innochem.

The average yield of two runs: 52%, BRSM yield (73%).

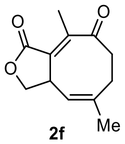
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.39 – 7.28 (m, 5H), 5.61 (dd, J = 6.5, 1.7 Hz, 1H), 4.52 (dd, J = 8.7, 8.7 Hz, 1H), 4.33 – 4.23 (m, 1H), 4.05 (dd, J = 9.0, 5.5 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.74 – 2.64 (m, 1H), 2.64 – 2.52 (m, 2H), 2.30 (d, J = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 205.7, 169.9, 150.0, 140.2, 132.9, 132.8, 129.7, 129.5, 128.5, 128.4, 71.6, 40.6, 40.4, 29.4, 14.8.

HRMS (ESI) m/z: calcd. for $C_{17}H_{17}O_3S$ ($[M+H]^+$): 301.0893, found: 301.0891.



2f

run 1: Following general procedure. Substrate: **1f** (35.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); product: **2f** (25 mg, 60%), byproduct (9.3 mg).

run 2: Following general procedure. Substrate: **1f** (35.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); product: **2f** (24.3 mg, 58%), byproduct (8.2 mg).

The average yield of two runs: 59%.

Physical Form: white solid.

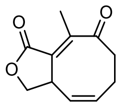
Melting Point: 83.8 – 85.4 °C.

TLC (5:1 PE/EA, R*f*): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.24 (ddd, *J* = 6.1, 1.7, 1.7 Hz, 1H), 4.56 (dd, *J* = 8.7, 8.7 Hz, 1H), 4.30 – 4.19 (m, 1H), 4.08 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.19 (ddd, *J* = 14.6, 11.1, 6.4 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.47 – 2.35 (m, 1H), 2.32 (d, *J* = 2.4 Hz, 3H), 1.74 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.4, 170.2, 149.4, 140.8, 130.1, 124.5, 71.8, 40.2, 39.5, 29.4, 25.9, 14.7.

HRMS (ESI) m/z: calcd. for $C_{12}H_{15}O_3$ ($[M+H]^+$): 207.1016, found: 207.1019.



2g

run 1: Following general procedure. Substrate: **1g** (32.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 100 °C, 24 h, flash column chromatography (silica gel, 50:1 to 20:1 to 5:1 PE/EA); product: **2g** (3.6 mg, 9%), byproducts (9.3 mg).

run 2: Following general procedure. Substrate: **1g** (33.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 100 °C, 24 h, flash column chromatography (silica gel, 50:1 to 20:1 to 5:1 PE/EA); product: **2g** (4.4 mg, 11%), byproducts (8.9 mg).

The average yield of two runs: 10%.

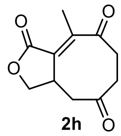
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R*f*): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.74 (dddd, *J* = 11.3, 6.8, 4.7, 1.9 Hz, 1H), 5.46 – 5.37 (m, 1H), 4.52 (dd, *J* = 8.7, 8.7 Hz, 1H), 4.28 – 4.18 (m, 1H), 4.07 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.57 – 2.35 (m, 3H), 2.28 (d, *J* = 2.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.5, 170.1, 149.9, 132.4, 130.5, 129.3, 71.8, 40.0, 39.2, 24.6, 14.7.

HRMS (ESI) m/z: calcd. for $C_{11}H_{13}O_3$ ($[M+H]^+$): 193.0859, found: 193.0861.



2h

run 1: Following general procedure. Substrate: **1h** (41.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 8 h, cooled to rt, 0.1 mL EtOH and 0.2 mL HCl (1M) were added, stirred at rt for 14.7 h vigorously, flash column chromatography (silica gel, 2:1 to 1:1 PE/EA); product: **2h** (36.6 mg, 88%).

run 2: Following general procedure. Substrate: **1h** (41.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 8 h, cooled to rt, 0.1 mL EtOH and 0.2 mL HCl (1M) were added, stirred at rt for 14.7 h vigorously, flash column chromatography (silica gel, 2:1 to 1:1 PE/EA); product: **2h** (34.5 mg, 83%).

The average yield of two runs: 86%.

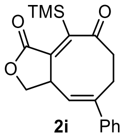
Physical Form: light yellow oil.

TLC (1:1 PE/EA, R*f*): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 4.43 (dd, *J* = 9.1, 7.2 Hz, 1H), 4.03 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.43 – 3.33 (m, 1H), 2.87 – 2.77 (m, 3H), 2.77 – 2.71 (m, 2H), 2.67 (dd, *J* = 13.4, 10.9 Hz, 1H), 2.35 (d, *J* = 1.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 207.3, 206.6, 168.7, 150.3, 124.3, 70.2, 48.0, 38.2, 37.9, 36.0, 14.8.

HRMS (ESI) m/z: calcd. for $C_{11}H_{13}O_4$ ($[M+H]^+$): 209.0808, found: 209.0809.



2i

run 1: Following general procedure. Substrate: **1i** (59.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 50:1 to 25:1 to 20:1 PE/EA); product: **2i** (21.9 mg, 33%).

run 2: Following general procedure. Substrate: **1i** (60.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 50:1 to 25:1 to 20:1 PE/EA); product: **2i** (21.7 mg, 33%).

The average yield of two runs: 33%.

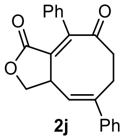
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R*f*): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.39 – 7.27 (m, 5H), 5.82 (d, *J* = 6.9 Hz, 1H), 4.56 (dd, *J* = 8.9, 7.6 Hz, 1H), 4.24 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.00 (ddd, *J* = 14.7, 8.8, 3.8 Hz, 1H), 2.97 – 2.85 (m, 1H), 2.81 (ddd, *J* = 12.2, 8.8, 3.4 Hz, 1H), 2.60 (ddd, *J* = 12.8, 9.5, 3.7 Hz, 1H), 0.26 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 209.5, 169.5, 160.5, 144.0, 142.1, 134.8, 128.7, 128.0, 127.2, 126.2, 71.5, 43.7, 42.0, 28.3, -0.8.

HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O_3Si$ ($[M+H]^+$): 327.1411, found: 327.1412.



2j

run 1: Following general procedure. Substrate: **1j** (61.4 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); product: **2j** (63.0 mg, 94%).

run 2: Following general procedure. Substrate: **1j** (60.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA); product: **2j** (58.4 mg, 89%).

The average yield of two runs: 92%.

Physical Form: white solid.

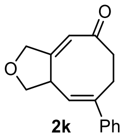
Melting Point: 143 – 145 °C.

TLC (5:1 PE/EA, R_f): 0.1.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.41 – 7.30 (m, 10H), 5.86 (dd, J = 6.7, 1.2 Hz, 1H), 4.61 (dd, J = 8.7, 7.6 Hz, 1H), 4.25 (dd, J = 8.7, 5.5 Hz, 1H), 4.23 – 4.16 (m, 1H), 3.16 – 2.94 (m, 3H), 2.80 – 2.70 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 204.7, 167.9, 151.7, 144.6, 142.1, 132.2, 129.5, 128.72, 128.66, 128.3, 128.1, 126.9, 126.3, 125.4, 70.9, 42.5, 41.2, 28.5.

HRMS (ESI) m/z: calcd. for $C_{22}H_{19}O_3$ ($[M+H]^+$): 331.1329, found: 331.1328.



2k

run 1: Following general procedure. Substrate: **1k** (42.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 7 h, flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2k** (20.6 mg, 42%).

run 2: Following general procedure. Substrate: **1k** (42.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 7 h, flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2k** (20.6 mg, 43%).

The average yield of two runs: 42%.

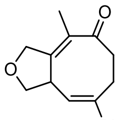
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 – 7.21 (m, 5H), 6.08 (dd, J = 2.0, 2.0 Hz, 1H), 5.71 (dd, J = 5.9, 2.5 Hz, 1H), 4.56 – 4.45 (m, 2H), 4.40 – 4.33 (m, 1H), 4.26 (dd, J = 8.8, 6.9 Hz, 1H), 3.94 (dd, J = 8.8, 4.7 Hz, 1H), 3.54 (ddd, J = 12.4, 12.4, 4.9 Hz, 1H), 3.05 – 2.93 (m, 1H), 2.83 – 2.74 (m, 1H), 2.73 – 2.65 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.3, 162.9, 143.8, 142.4, 128.8, 128.4, 127.5, 126.3, 123.4, 76.3, 72.8, 42.6, 40.6, 29.2.

HRMS (ESI) m/z: calcd. for $C_{16}H_{17}O_2$ ([M+H]$^+$): 241.1223, found: 241.1221.



2l

run 1: Following general procedure. Substrate: **1l** (45.3 mg, 0.2 mmol), [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 21 h, flash column chromatography (silica gel, 50:1 to 20:1 to 10:1 PE/EA); product: **2l** (30.8 mg, 61%), byproduct (8.3 mg).

run 2: Following general procedure. Substrate: **1l** (45.6 mg, 0.2 mmol), [Rh(CO)$_2$Cl]$_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 21 h, flash column chromatography (silica gel, 50:1 to 20:1 to 10:1 PE/EA); product: **2l** (28.8 mg, 56%), byproduct (10.7 mg).

The average yield of two runs: 58%.

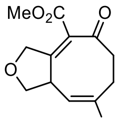
Physical Form: light yellow oil.

TLC (10:1 PE/EA, R*f*): 0.1.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.33 – 7.19 (m, 5H), 5.66 (dd, *J* = 6.2, 2.5 Hz, 1H), 4.53 – 4.47 (m, 2H), 4.35 – 4.24 (m, 2H), 3.89 (dd, *J* = 4.0, 4.0 Hz, 1H), 3.59 (ddd, *J* = 12.7, 12.7, 6.1 Hz, 1H), 2.96 – 2.79 (m, 2H), 2.72 – 2.61 (m, 1H), 1.78 (d, *J* = 1.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 203.8, 155.7, 144.1, 142.0, 130.5, 129.3, 128.4, 127.4, 126.3, 76.7, 72.0, 42.9, 40.3, 29.3, 15.3.

HRMS (ESI) m/z: calcd. for $C_{17}H_{19}O_2$ ([M+H]$^+$): 255.1380, found: 255.1384.



2m

run 1: Following general procedure. Substrate: **1m** (54.1 mg, 0.2 mmol), [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 10:1 to 4:1 PE/EA); product: **2m** (35.6 mg, 60%), byproduct (13.2 mg).

run 2: Following general procedure. Substrate: **1m** (54.2 mg, 0.2 mmol), [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), flash column chromatography (silica gel, 20:1 to 10:1 to 4:1 PE/EA); product: **2m** (35.9 mg, 60%), byproduct (13.9 mg).

The average yield of two runs: 60%.

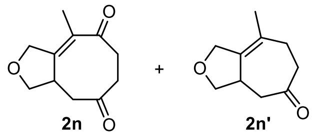
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R*f*): 0.1.

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.35 – 7.24 (m, 5H), 5.78 (dd, *J* = 7.0, 1.3 Hz, 1H), 4.93 – 4.74 (m, 2H), 4.10 (dd, *J* = 8.5, 5.9 Hz, 1H), 3.85 (dd, *J* = 8.5, 5.2 Hz, 1H), 3.83 – 3.77 (m, 1H), 3.74 (s, 3H), 3.07 (ddd, *J* = 11.7, 9.0, 4.2 Hz, 1H), 3.03 – 2.86 (m, 2H), 2.77 (ddd, *J* = 12.0, 8.0, 4.3 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 202.9, 164.3, 161.6, 143.4, 142.6, 128.6, 127.7, 127.3, 127.1, 126.2, 73.5, 72.3, 52.2, 45.5, 43.0, 28.7.

HRMS (ESI) m/z: calcd. for $C_{18}H_{19}O_4$ ($[M+H]^+$): 299.1278, found: 299.1278.



2n **2n'**

run 1: Following general procedure. Substrate: **1n** (38.4 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), cooled to rt, 0.1 mL EtOH and 0.2 mL HCl (1M) were added, stirred at rt for 11 h vigorously, flash column chromatography (silica gel, 5:1 to 3:1 to 1:1 PE/EA); products: **2n** (5.1 mg, 13%), **2n’** (18.3 mg, 56%).

run 2: Following general procedure. Substrate: **1n** (38.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), cooled to rt, 0.1 mL EtOH and 0.2 mL HCl (1M) were added, stirred at rt for 14.7 h vigorously, flash column chromatography (silica gel, 5:1 to 3:1 to 1:1 PE/EA); products: **2n** (4.9 mg, 13%), **2n’** (20.2 mg, 61%).

The average yield of two runs: **2n** (13%) and **2n’** (58%).

Physical Form of 2n: colorless oil.

Physical Form of 2n’: colorless oil.

TLC (1:1 PE/EA, R*f*): **2n** (0.1) and **2n’** (0.5).

^{1}H NMR of **2n** (400 MHz, $CDCl_3$, *δ*): 4.61 (d, *J* = 15.9 Hz, 1H), 4.36 (d, *J* = 15.9 Hz, 1H), 3.95 (dd, *J* = 8.9, 5.4 Hz, 1H), 3.84 (d, *J* = 8.9 Hz, 1H), 3.80 – 3.67 (m, 1H), 3.49 – 3.36 (m, 1H), 2.97 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.85 – 2.72 (m, 2H), 2.65 – 2.50 (m, 2H), 1.73 (s, 3H).

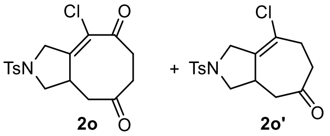
^{13}C{^{1}H} NMR of **2n** (101 MHz, $CDCl_3$, *δ*): 207.6, 200.2, 153.1, 129.7, 75.3, 72.2, 47.3, 40.7, 40.2, 39.5, 15.2.

HRMS of **2n** (ESI) m/z: calcd. for $C_{11}H_{15}O_3$ ($[M+H]^+$): 195.1016, found: 195.1016.

^{1}H NMR of **2n’** (400 MHz, $CDCl_3$, *δ*): 4.48 – 4.30 (m, 2H), 4.16 (dd, *J* = 8.0, 8.0 Hz, 1H), 3.38 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.22 – 3.08 (m, 1H), 2.99 (ddd, *J* = 12.3, 9.1, 5.3 Hz, 1H), 2.55 (dd, *J* = 16.1, 3.5 Hz, 1H), 2.50 – 2.29 (m, 4H), 1.63 (s, 3H).

^{13}C{^{1}H} NMR of **2n’** (101 MHz, $CDCl_3$, *δ*): 211.6, 136.4, 125.9, 74.8, 71.8, 45.7, 41.8, 38.0, 32.0, 21.2.

HRMS of **2n’** (ESI) m/z: calcd. for $C_{10}H_{15}O_2$ ($[M+H]^+$): 167.1067, found: 167.1065.



2o **2o'**

run 1: Following general procedure. Substrate: **1o** (74.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 80 °C, 14 h, cooled to rt, 0.1 mL EtOH and 0.2 mL HCl (1M) were added, stirred at rt for 8 h vigorously, flash column chromatography (silica gel, 5:1 to 2:1 to 1:1 to 1:2 PE/EA); products: **2o** (5.7 mg, 8%), **2o’** (48.0 mg, 70%).

run 2: Following general procedure. Substrate: **1o** (73.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01

mmol), mesitylene (4 mL), 80 °C, 14 h, cooled to rt, 0.1 mL EtOH and 0.2 mL HCl (1M) were added, stirred at rt for 8 h vigorously, flash column chromatography (silica gel, 5:1 to 2:1 to 1:1 to 1:2 PE/EA); products: **2o** (5.2 mg, 7%), **2o'** (50.1 mg, 74%).

The average yield of two runs: **2o** (8%) and **2o'** (72%).

Physical Form of 2o: colorless oil.

Physical Form of 2o': white solid.

Melting Point of 2o': 151 – 153 °C.

TLC (1:1 PE/EA, R*f*): **2o** (0.1) and **2o'** (0.5).

^{1}H NMR of **2o** (400 MHz, $CDCl_3$, *δ*): 7.74 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.34 (dd, *J* = 17.8, 1.7 Hz, 1H), 3.85 (dd, *J* = 12.2, 6.2 Hz, 1H), 3.78 (d, *J* = 17.9 Hz, 1H), 3.49 – 3.43 (m, 1H), 3.32 – 3.21 (m, 2H), 3.03 – 2.89 (m, 2H), 2.87 – 2.78 (m, 1H), 2.73 (ddd, *J* = 13.8, 11.7, 2.0 Hz, 1H), 2.63 (dddd, *J* = 14.8, 13.3, 5.5, 1.9 Hz, 1H), 2.46 (s, 3H).

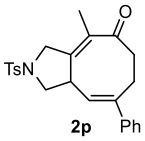
^{13}C{^{1}H} NMR of **2o** (101 MHz, $CDCl_3$, *δ*): 205.2, 191.2, 151.0, 144.8, 131.3, 130.2, 128.8, 128.2, 55.2, 54.5, 47.3, 40.2, 39.5, 38.9, 21.8.

HRMS of **2o** (ESI) m/z: calcd. for $C_{17}H_{19}ClNO_4S$ ($[M+H]^+$): 368.0718, found: 368.0719.

^{1}H NMR of **2o'** (400 MHz, $CDCl_3$, *δ*): 7.72 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.16 (ddd, *J* = 15.1, 2.7, 2.7 Hz, 1H), 3.78 (dd, *J* = 9.5, 7.7 Hz, 1H), 3.70 (ddd, *J* = 15.1, 2.6, 2.6 Hz, 1H), 3.37 – 3.24 (m, 1H), 2.99 (ddd, *J* = 13.8, 10.5, 5.7 Hz, 1H), 2.75 – 2.67 (m, 2H), 2.63 (dd, *J* = 9.5, 9.5 Hz, 1H), 2.57 (dd, *J* = 16.8, 3.4 Hz, 1H), 2.50 – 2.42 (m, 2H), 2.46 (s, 3H).

^{13}C{^{1}H} NMR of **2o'** (101 MHz, $CDCl_3$, *δ*): 208.5, 144.4, 136.0, 131.7, 130.0, 128.2, 126.2, 54.9, 53.7, 45.6, 40.8, 37.4, 33.5, 21.7.

HRMS of **2o'** (ESI) m/z: calcd. for $C_{16}H_{19}ClNO_3S$ ($[M+H]^+$): 340.0769, found: 340.0768.



2p

run 1: Following general procedure. Substrate: **1p** (76.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.1 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 30:1 to 6:1 PE/EA); product: **2p** (14.8 mg, 18%), byproduct (39.0 mg).

run 2: Following general procedure. Substrate: **1p** (75.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), mesitylene (4 mL), 24 h, flash column chromatography (silica gel, 30:1 to 6:1 PE/EA); product: **2p** (15.7 mg, 19%), byproduct (37.8 mg).

The average yield of two runs: 18%.

Physical Form: light yellow solid.

Melting Point: 177.1 – 180.8 °C.

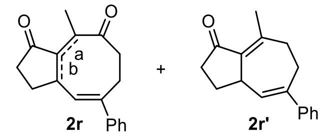
TLC (3:1 PE/EA, R*f*): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.75 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.20 (m, 3H), 7.23 – 7.16 (m, 2H), 5.55 (dd, *J* = 6.6, 2.2 Hz, 1H), 4.31 – 4.19 (m, 1H), 3.98 – 3.85 (m, 2H), 3.61 (dd, *J* = 9.7, 7.3 Hz, 1H), 3.35 (ddd, *J* = 12.5, 12.5 6.2 Hz, 1H), 3.23 (dd, *J* = 9.7, 5.1 Hz, 1H), 2.93 – 2.72

(m, 2H), 2.63 (ddd, *J* = 13.1, 5.1. 5.1 Hz, 1H), 2.44 (s, 3H), 1.75 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 203.9, 150.0, 144.4, 143.5, 142.4, 132.8, 131.7, 130.0, 129.0, 128.4, 128.2, 127.6, 126.3, 55.8, 52.6, 41.7, 40.8, 28.9, 21.7, 15.9.

HRMS (ESI) m/z: calcd. for $C_{24}H_{26}NO_3S$ ([M+H]$^+$): 408.1628, found: 408.1627.



2r **2r'**

run 1: Following general procedure. Substrate: **1r** (47.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 70 °C for 12 h then 90 °C for 10 h, flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); products: **2r** (28.1 mg, 52%, a/b = 2.6:1), **2r'** (8.2 mg, 17%).

run 2: Following general procedure. Substrate: **1r** (48.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 70 °C for 12 h then 90 °C for 10 h, flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); products: **2r** (28.3 mg, 53%, a/b = 2.6:1), **2r'** (5.6 mg, 12%).

The average yield of two runs: **2r** (52%) and **2r'** (14%).

Physical Form of 2r: light yellow oil.

Physical Form of 2r': colorless oil.

TLC (5:1 PE/EA, R*f*): **2r** (0.3) and **2r'** (0.5).

^{1}H NMR for the major product of **2r** (400 MHz, $CDCl_3$, *δ*): 7.40 – 7.34 (m, 1H), 7.34 – 7.23 (m, 4H), 5.75 (dd, *J* = 6.5, 1.2 Hz, 1H), 3.96 (qd, *J* = 6.7, 2.5 Hz, 1H), 3.18 (ddd, *J* = 13.1, 8.6, 6.3 Hz, 1H), 2.97 – 2.86 (m, 2H), 2.72 – 2.63 (m, 1H), 2.52 (ddd, *J* = 17.6, 8.3, 5.8 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.39 – 2.30 (m, 1H), 2.29 (d, *J* = 2.3 Hz, 3H), 2.00 – 1.78 (m, 1H).

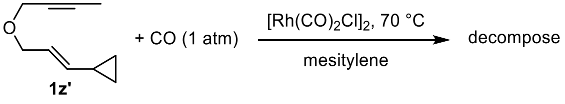
^{13}C{^{1}H} NMR of **2r** (101 MHz, $CDCl_3$, *δ*): 214.1, 209.1, 208.2, 208.0, 162.1, 154.3, 146.4, 144.9, 143.9, 143.0, 142.8, 136.6, 131.4, 128.6, 128.5, 128.3, 127.5, 126.4, 126.2, 123.7, 41.8, 41.8, 38.5, 34.5, 31.3, 30.3, 29.5, 28.1, 27.8, 19.6, 15.2.

HRMS of **2r** (ESI) m/z: calcd. for $C_{18}H_{19}O_2$ ([M+H]$^+$): 267.1380, found: 267.1380.

^{1}H NMR of **2r'** (400 MHz, $CDCl_3$, *δ*): 7.39 – 7.29 (m, 4H), 7.28 – 7.21 (m, 1H), 5.89 (dd, *J* = 3.0, 1.4 Hz, 1H), 3.92 (ddq, *J* = 10.9, 5.5, 2.5 Hz, 1H), 2.95 – 2.80 (m, 1H), 2.74 – 2.62 (m, 1H), 2.62 – 2.52 (m, 1H), 2.45 – 2.34 (m, 2H), 2.34 – 2.27 (m, 2H), 2.24 (d, *J* = 2.4 Hz, 3H), 1.78 – 1.60 (m, 1H).

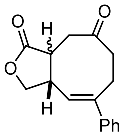
^{13}C{^{1}H} NMR of **2r'** (101 MHz, $CDCl_3$, *δ*): 207.1, 152.7, 142.9, 141.2, 133.5, 132.3, 128.5, 127.1, 125.7, 39.8, 39.5, 36.1, 28.3, 28.1, 21.2.

HRMS of **2r'** (ESI) m/z: calcd. for $C_{17}H_{19}O$ ([M+H]$^+$): 239.1430, found: 239.1430.



1z'

Following general procedure. Substrate: **1z'** (30.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 70 °C for 24 h, flash column chromatography (silica gel, 50:1 to 20:1 to 10:1 PE/EA); decompose.



5

run 1: Following general procedure. Substrate: **4** (45.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 150 °C, 48 h, flash column chromatography (silica gel, 20:1 to 10:1 to 2:1 PE/EA); product: **5** (9.0 mg, 18%, d.r. = 4:1).

run 2: Following general procedure. Substrate: **4** (45.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), mesitylene (4 mL), 150 °C, 48 h, flash column chromatography (silica gel, 5:1 to 2:1 PE/EA); product: **5** (10.3 mg, 20%, d.r. = 4:1).

The average yield of two runs: 19%.

Physical Form: yellow oil.

TLC (5:1 PE/EA, R_f): 0.1.

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 7.46 – 7.28 (m, 5H), 5.81 (d, J = 8.5 Hz, 1H), 4.45 (dd, J = 9.3, 4.8 Hz, 1H), 4.36 (d, J = 9.3 Hz, 1H), 3.39 – 3.31 (m, 1H), 2.97 (ddd, J = 12.3, 8.0, 4.3 Hz, 1H), 2.93 – 2.85 (m, 1H), 2.75 – 2.65 (m, 3H), 2.62 (d, J = 12.0 Hz, 1H), 2.59 – 2.48 (m, 1H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 211.0, 176.4, 144.2, 140.9, 128.9, 128.3, 126.1, 124.8, 71.9, 46.1, 40.3, 39.0, 38.9, 27.6.

HRMS (ESI) m/z: calcd. for $C_{16}H_{17}O_3$ ($[M+H]^+$): 257.1172, found: 257.1174.

4. DFT Studies

Computed at the DLPNO-CCSD(T)/def2-TZVPP:SMD(mesitylene)//BMK/def2-SVP level. For key intermediates **TS7**, **TS10**, **TS11**, **1f-TS2**, **1f-TS4** in the main text, DLPNO-CCSD(T1)/def2-QZVPP:SMD(mesitylene)//BMK/def2-TZVPP level was used to improve the accuracy, which is more consistent with the experiments. For example, **1f-TS2** (24.8 kcal/mol) is lower than **1f-TS4** (26.3 kcal/mol) in DLPNO-CCSD(T)/def2-TZVPP:SMD(mesitylene)//BMK/def2-SVP level, implying that [5 + 2] product should be generated, which is inconsistent with the experiments.

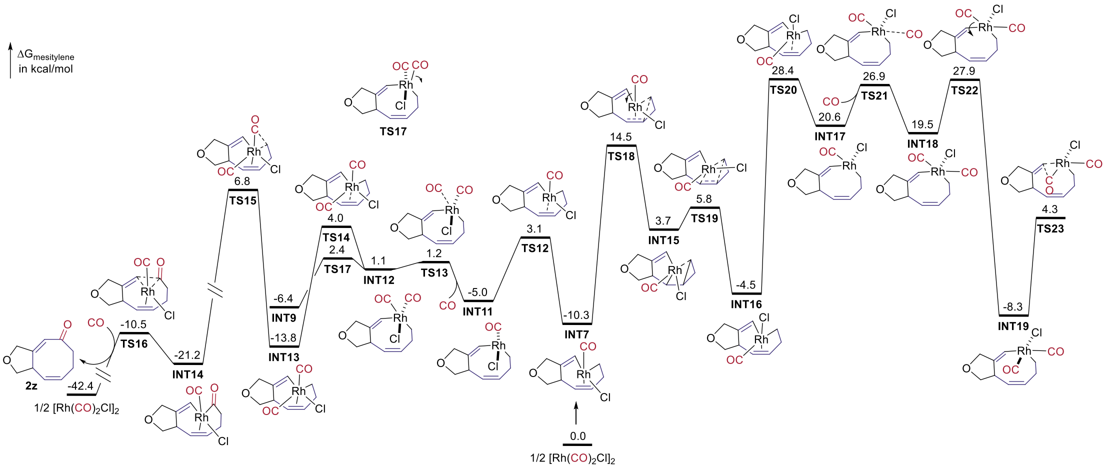


Figure S1

In **Figure S1**, we also discuss other possible CO insertion pathways. First, **INT7** can dissociate the alkene group via **TS12** to generate **INT11**, followed by the coordination of CO to give **INT12**, which can also be generated from **INT9** via **TS17**. Then, re-coordination of the alkene occurs to convert **INT12** into **INT13**. Then CO insertion and reductive elimination give the final product. We found that CO inserted into C(sp^2)–Rh bond (**TS10**, from **INT9**, 12.0 kcal/mol, in **Figure 1**) is more favored than C(sp^3)–Rh bond (**TS15**, from **INT13**, 20.6 kcal/mol), and reductive elimination to form C(sp^2)–C(sp^2) (via **TS16**, from **INT14**, 10.7 kcal/mol) bond is faster than forming C(sp^2)–C(sp^3) (via **TS11**, from **INT10**, 18.9 kcal/mol, in **Figure 1**). **TS15** is higher than **TS11**, suggesting that this CO insertion pathway is unlikely. Even though **TS23** is lower than **TS11**, this transition state cannot be accessed because its previous steps (via **TS18**, **TS20**, **TS21**, and **TS22**) are difficult to occur. Therefore, this pathway is impossible.

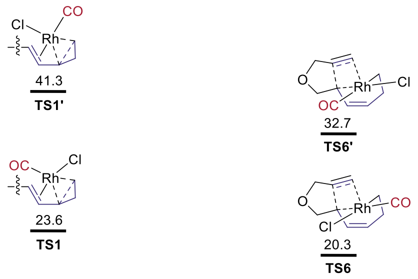
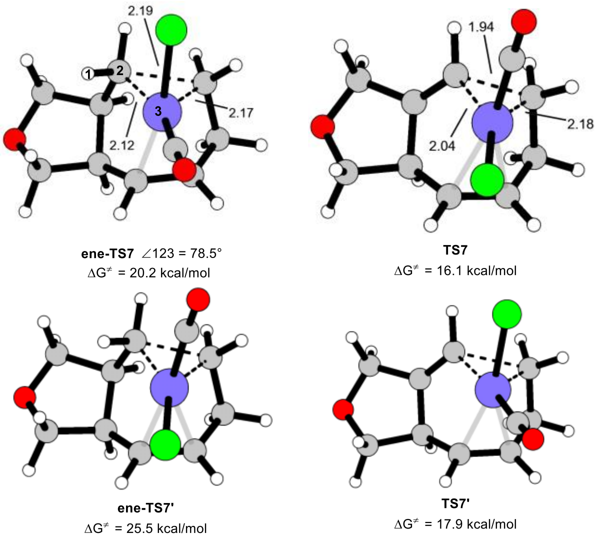


Figure S2

In **Figure S2**, we changed the position of CO and Cl in **TS1** and **TS6**, finding that the activation free energies are prohibitive (>30 kcal/mol) for the corresponding **TS1’** and **TS6’**. Therefore, configuration changes between CO and Cl are necessary: via **TS2**, **TS3**, **TS4**, **TS5**, and then to **TS6**.



ene-TS7 ∠123 = 78.5°
ΔG$^{\neq}$ = 20.2 kcal/mol

TS7
ΔG$^{\neq}$ = 16.1 kcal/mol

ene-TS7'
ΔG$^{\neq}$ = 25.5 kcal/mol

TS7'
ΔG$^{\neq}$ = 17.9 kcal/mol

Figure S3

As shown in **Figure S3**, the direct reductive elimination for ene-VCP via **ene-TS7** (20.2 kcal/mol) is more favored than **ene-TS7’** (25.5 kcal/mol). However, the activation free energy of **TS7** (16.1 kcal/mol) is lower than **TS7’** (17.9 kcal/mol) for yne-VCP. All activation free energies are calculated from **ene-INT7** or **INT7**.

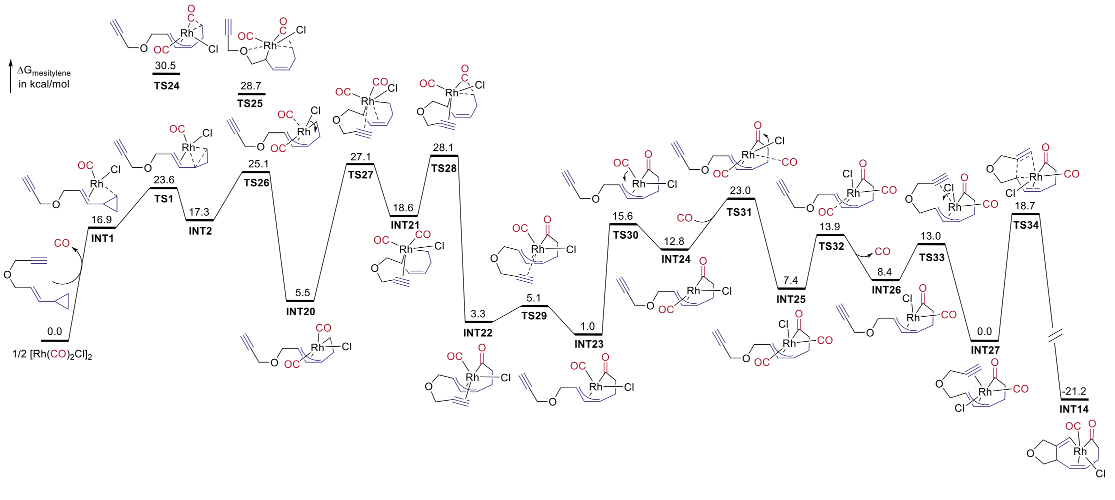


Figure S4 [5 + 1 + 2] pathway

In **Figure S4**, we calculated the [5 + 1 + 2] pathway. After oxidative addition (**TS1**), the total activation free energy of direct CO insertion is 30.5 kcal/mol (**TS24**), which is impossible. Coordination of the oxygen atom of the tether can decrease the activation free energy (**TS25**, 28.7 kcal/mol). Also, **INT2** can coordinate with another CO via **TS26** to generate **INT20**, followed by replacing the 2π component (alkene was replaced by alkyne) via **TS27** to give **INT21**. After that, CO insertion occurs via **TS28** to form **INT22**, followed by dissociation of the alkyne group to generate

INT23. Then rotation of CO (**TS30**), coordination of another CO (**TS31**), dissociation of CO (**TS32**), and coordination of alkyne (**TS33**) take place consequently giving **INT27**. Finally, alkyne insertion (**TS34**) generates **INT14**. The total activation free energy of this pathway is 28.1 kcal/mol, which is higher than **TS2** (27.4 kcal/mol) and is disfavored.

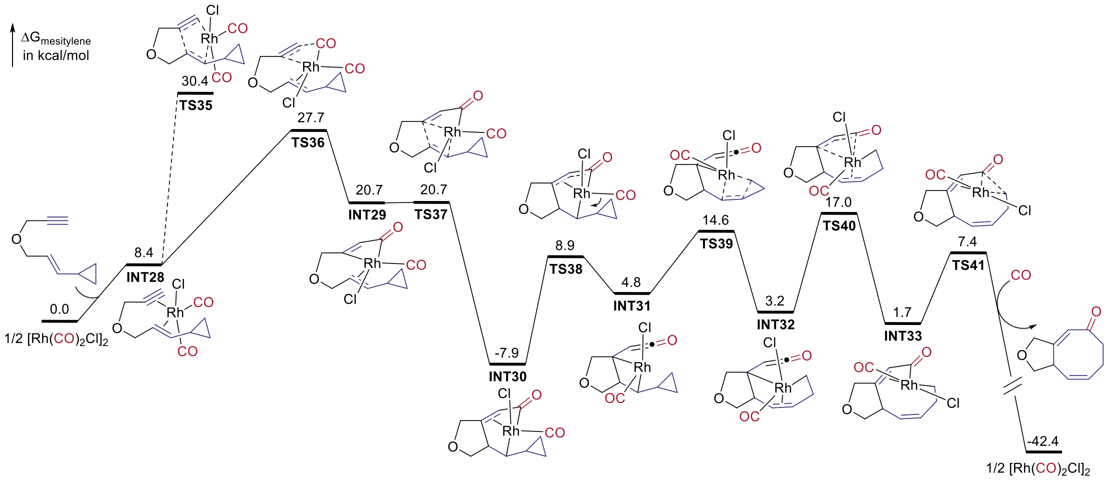


Figure S5 [1 + 2 + 5] pathway

In **Figure S5**, we calculated the [1 + 2 + 5] pathway. First, the activation free energy of oxidative cyclization is 30.4 kcal/mol, implying that this pathway is impossible. **INT28** can also undergo CO insertion into the alkyne group via **TS36** to generate **INT29**, which is followed by a barrierless alkene insertion (**TS37**) to give **INT30**. After that, rotation of CO occurs, generating ketene **INT31** via **TS38**, β-C elimination (**TS39**) happens in a sequence, generating **INT32**, which then undergoes isomerization (**TS40**) and reductive elimination (**TS41**) to give the final product. The total activation free energy of this pathway is 27.7 kcal/mol, which is higher than **TS2** (27.4 kcal/mol). This pathway could also be possible.

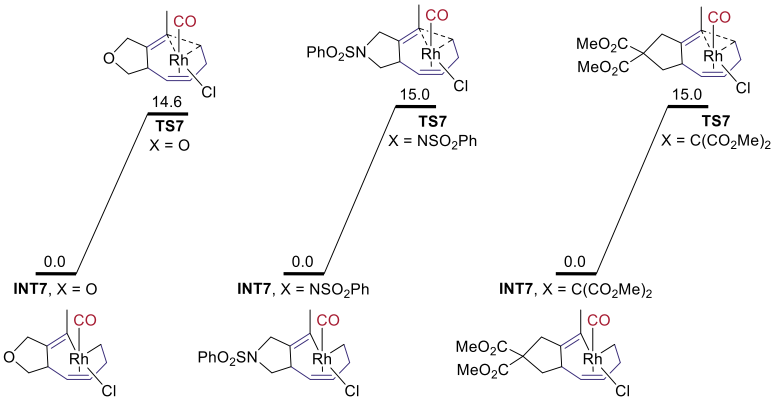


Figure S6

As shown in **Figure S6**, Similar activation free energies of **TS7** (ca. 15 kcal/mol) were observed with different tethers.

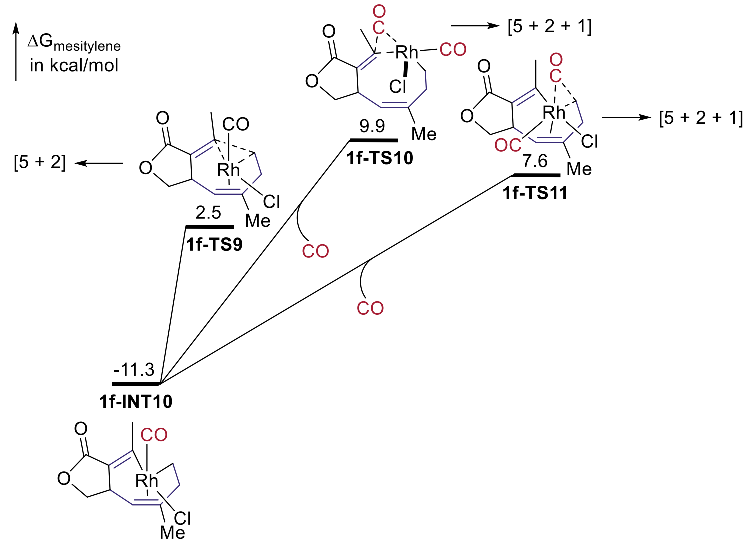


Figure S7

In **Figure S7**, we discuss the chemoselectivity of **1f** which has an ester tether. If this substrate undergoes [5 + 2 + 1] pathway, the calculation results are inconsistent with the experiments because **1f-TS9** is lower than **1f-TS10** and **1f-TS11**. Therefore, [5 + 1 + 2] pathway is most possible for ester-tethered substrates.

Computed Energies for the Stationary Points:

Table S1. Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase and solvent

	Imaginary Frequencies (cm-1)	SPE^a (a. u.)	TCG^{a,b} (a. u.)	SPE^c (a. u.)	SPE^d (a. u.)
CO	none	-113.172745	-0.01386	-113.168202	-113.158173
$[Rh(CO)_2Cl]_2$	none	-1592.916752	-0.008309	-1592.91757	-1593.122141
1z	none	-424.639257	0.147781	-424.649673	-424.5166015
INT1	none	-1107.883499	0.152458	-1107.90095	-1107.882207
TS1	-265.94	-1107.873382	0.151652	-1107.888903	-1107.872675
TS1’	-247.68	-1107.854259	0.153186	-1107.869786	-1107.845865
INT2	none	-1107.883757	0.152225	-1107.899061	-1107.883392
TS2	-144.19	-1107.866018	0.151604	-1107.880841	-1107.867166
INT3	none	-1107.893654	0.152331	-1107.909151	-1107.892378
TS3	-65.14	-1221.060174	0.153641	-1221.072457	-1221.044663
INT4	none	-1221.095272	0.161600	-1221.106525	-1221.081552
TS4	-99.35	-1221.061499	0.153505	-1221.071734	-1221.047103
INT5	none	-1107.885289	0.153985	-1107.899818	-1107.887547
TS5	-29.77	-1107.884018	0.155667	-1107.897065	-1107.884784
INT6	none	-1107.912054	0.158885	-1107.924915	-1107.91229
TS6	-240.94	-1107.889659	0.15892	-1107.903593	-1107.886713
TS6’	-246.78	-1107.871037	0.157417	-1107.885153	-1107.865338
INT7	none	-1107.945005	0.159008	-1107.961273	-1107.933278
TS7	-405.16	-1107.918584	0.160682	-1107.933256	-1107.910938
TS7’	-382.68	-1107.913616	0.159486	-1107.927521	-1107.907521
TS8	-41.73	-1221.117893	0.1602	-1221.128822	-1221.094224
INT8	none	-1221.136713	0.165276	-1221.15001	-1221.112555
TS9	-57.54	-1221.114015	0.165539	-1221.127361	-1221.092193
INT9	none	-1221.122305	0.163399	-1221.137897	-1221.101383
TS10	-251.77	-1221.110322	0.165304	-1221.127231	-1221.082815
INT10	none	-1221.144315	0.167245	-1221.163046	-1221.111986
TS11	-185.03	-1221.120941	0.167291	-1221.138763	-1221.082784
2z	none	-537.931888	0.167496	-537.945317	-537.7701779
TS12	-73.00	-1107.921797	0.160511	-1107.93853	-1107.912896
INT11	none	-1107.931859	0.160614	-1107.950568	-1107.924032
TS13	-24.43	-1221.104987	0.156037	-1221.118791	-1221.083729

INT12	none	-1221.115193	0.164494	-1221.128898	-1221.092382
TS14	-50.56	-1221.112997	0.165049	-1221.125411	-1221.089556
INT13	none	-1221.142728	0.165394	-1221.155018	-1221.118392
TS15	-210.21	-1221.11325	0.167756	-1221.1286	-1221.084956
INT14	none	-1221.161102	0.168645	-1221.179686	-1221.127197
TS16	-203.17	-1221.147447	0.170625	-1221.164949	-1221.113172
TS17	-39.67	-1221.107713	0.16036	-1221.122203	-1221.085345
TS18	-154.31	-1107.904445	0.157034	-1107.918862	-1107.893602
INT15	none	-1107.924981	0.159706	-1107.941526	-1107.911392
TS19	-137.63	-1107.922343	0.159487	-1107.93959	-1107.90705
INT16	none	-1107.934477	0.158108	-1107.950753	-1107.923054
TS20	-54.22	-1107.884595	0.15807	-1107.9056	-1107.865912
INT17	none	-1107.897852	0.157116	-1107.917196	-1107.879088
TS21	-10.68	-1221.071051	0.152482	-1221.085806	-1221.038286
INT18	none	-1221.087772	0.162596	-1221.103479	-1221.059122
TS22	-115.70	-1221.073483	0.157845	-1221.088671	-1221.041622
INT19	none	-1221.128341	0.164605	-1221.143302	-1221.106206
TS23	-228.43	-1221.112214	0.164672	-1221.130139	-1221.083187
TS24	-225.00	-1221.057071	0.159086	-1221.073815	-1221.037117
TS25	-318.40	-1221.065287	0.160882	-1221.07959	-1221.044284
TS26	-45.56	-1221.057347	0.153254	-1221.069082	-1221.044927
INT20	none	-1221.094567	0.158966	-1221.107679	-1221.080447
TS27	-35.51	-1221.064574	0.16399	-1221.080419	-1221.048296
INT21	none	-1221.079789	0.163143	-1221.092503	-1221.06413
TS28	-317.42	-1221.066682	0.163352	-1221.081055	-1221.047518
INT22	none	-1221.110926	0.165037	-1221.126757	-1221.087327
TS29	-42.69	-1221.101584	0.162312	-1221.120341	-1221.078723
INT23	none	-1221.106822	0.161222	-1221.125004	-1221.084772
TS30	-96.20	-1221.083027	0.161052	-1221.100705	-1221.061925
INT24	none	-1221.087239	0.160829	-1221.106074	-1221.065038
TS31	-86.17	-1334.256854	0.161163	-1334.272711	-1334.221213
INT25	none	-1334.292328	0.16968	-1334.307921	-1334.254896
TS32	-114.04	-1334.272775	0.162805	-1334.287821	-1334.238191
INT26	none	-1221.096209	0.162826	-1221.113629	-1221.075458
TS33	-68.22	-1221.089288	0.163067	-1221.107311	-1221.06766
INT27	none	-1221.117936	0.167046	-1221.133364	-1221.094945

TS34	-235.73	-1221.089494	0.167615	-1221.107148	-1221.063498
INT28	none	-1221.096243	0.161249	-1221.108607	-1221.0788
TS35	-248.23	-1221.06077	0.160617	-1221.075481	-1221.040841
TS36	-317.25	-1221.070923	0.162279	-1221.086213	-1221.046174
INT29	none	-1221.082475	0.164231	-1221.101261	-1221.055841
TS37	-103.96	-1221.082422	0.164266	-1221.101227	-1221.055763
INT30	none	-1221.131669	0.164875	-1221.151106	-1221.101314
TS38	-71.62	-1221.103475	0.164085	-1221.1208	-1221.075878
INT31	none	-1221.112712	0.163163	-1221.131759	-1221.079836
TS39	-161.20	-1221.109437	0.167499	-1221.127597	-1221.069436
INT32	none	-1221.12116	0.166884	-1221.138513	-1221.08786
TS40	-42.03	-1221.099654	0.167862	-1221.116768	-1221.067054
INT33	none	-1221.118457	0.168465	-1221.134964	-1221.09266
TS41	-213.91	-1221.114737	0.168603	-1221.131279	-1221.083631
ene-INT7	none	-1109.169181	0.184049	-1109.185049	-1109.162781
ene-TS7	-389.44	-1109.132149	0.183689	-1109.146525	-1109.13176
ene-TS7'	-462.36	-1109.125949	0.184133	-1109.141326	-1109.122728
ene-TS10	-227.35	-1222.337797	0.190957	-1222.353922	-1222.314193
ene-TS11	-300.31	-1222.354321	0.191889	-1222.371383	-1222.32131
INT7$_{X = O}$	none	-1147.200161	0.185869	-1147.21729	-1147.177343
TS7$_{X = O}$	-391.08	-1147.174891	0.186355	-1147.190686	-1147.155902
TS10$_{X = O}$	-252.58	-1260.3662	0.189572	-1260.383441	-1260.32757
INT7$_{X = NSO2Ph}$	none	-1906.234033	0.279358	-1906.261177	-1905.929121
TS7$_{X = NSO2Ph}$	-372.41	-1906.208726	0.280746	-1906.234521	-1905.908029
TS10$_{X = NSO2Ph}$	-222.49	-2019.397704	0.28387	-2019.425149	-2019.076997
INT7$_{X = C(CO2Me)2}$	none	-1566.52511	0.284007	-1566.546732	-1566.40387
TS7$_{X = C(CO2Me)2}$	-399.37	-1566.499965	0.285054	-1566.520262	-1566.382351
TS10$_{X = C(CO2Me)2}$	-204.85	-1679.688266	0.288962	-1679.711179	-1679.551266
1f	none	-577.124412	0.179829	-577.138712	-576.9589736
1f-INT1	none	-1260.368126	0.18574	-1260.38869	-1260.325321
1f-TS1	-196.57	-1260.361361	0.183887	-1260.380615	-1260.319212
1f-INT2	none	-1260.370319	0.183973	-1260.389248	-1260.329289

1f-TS2	-134.99	-1260.352451	0.182363	-1260.370424	-1260.313112
1f-TS3	-29.71	-1373.544481	0.18516	-1373.55975	-1373.491749
1f-INT3	none	-1373.581413	0.187379	-1373.598067	-1373.527078
1f-INT4	none	-1373.557501	0.189557	-1373.575997	-1373.504007
1f-INT5	none	-1373.576058	0.192568	-1373.593204	-1373.512917
1f-TS4	-302.67	-1373.557864	0.194081	-1373.576338	-1373.491273
1f-INT6	none	-1373.56765	0.194217	-1373.588884	-1373.498032
1f-TS5	-131.37	-1373.536417	0.197429	-1373.558922	-1373.46273
1f-INT7	none	-1373.576967	0.197294	-1373.598214	-1373.518997
1f-TS6	-36.52	-1373.573425	0.198887	-1373.594541	-1373.513361
1f-INT8	none	-1373.589821	0.201925	-1373.609567	-1373.530254
1f-TS7	-180.53	-1373.576783	0.20132	-1373.596519	-1373.51265
1f-INT9	none	-1373.640215	0.204504	-1373.661018	-1373.566868
1f-TS8	-205.20	-1373.622299	0.205144	-1373.642204	-1373.548089
2f	none	-690.412853	0.200891	-690.42826	-690.2106928
1f-INT10	none	-1260.431147	0.193462	-1260.449867	-1260.381092
1f-TS9	-346.99	-1260.408365	0.195241	-1260.426567	-1260.361423
1f-TS10	-222.05	-1373.589166	0.200163	-1373.608706	-1373.522443
1f-TS11	-205.00	-1373.595126	0.201535	-1373.614284	-1373.527889

[a] Computed at the BMK/def2-SVP level

[b] Computed at 1 atm and 298 K

[c] Computed at the SMD(mesitylene)/BMK/def2-SVP//BMK/def2-SVP level

[d] Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level

Table S2. Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase and solvent (high level)

	Imaginary Frequencies (cm-1)	SPE[a] (a. u.)	TCG[a,b] (a. u.)	SPE[c] (a. u.)	SPE[d] (a. u.)
CO	none	-113.30961	-0.0139	-113.304998	-113.1879188
$[Rh(CO)_2Cl]_2$	none	-1593.840961	-0.008843	-1593.842094	-1593.489302
1z	none	-425.129101	0.148878	-425.139669	-424.6375249
INT7	none	-1108.756898	0.160037	-1108.774382	-1108.201546
TS7	-408.93	-1108.729058	0.160945	-1108.744603	-1108.182365
TS10	-208.76	-1222.053033	0.165063	-1222.070967	-1221.382223
TS11	-168.01	-1222.059432	0.167845	-1222.078262	-1221.38487
INT7$_{R = Ph}$	none	-1339.727103	0.235596	-1339.74919	-1338.888432

TS7$_{R = Ph}$	-411.34	-1339.699621	0.236218	-1339.720209	-1338.869062
TS10$_{R = Ph}$	-226.75	-1453.027431	0.23941	-1453.049904	-1452.072488
TS11$_{R = Ph}$	-186.37	-1453.031085	0.243677	-1453.054865	-1452.073811
1f	none	-577.785097	0.180708	-577.799782	-577.1232445
1f-TS2	-131.58	-1261.340694	0.183653	-1261.359794	-1260.623267
1f-TS4	-293.99	-1374.672408	0.194672	-1374.691712	-1373.834194

[a] Computed at the BMK/def2-TZVPP level

[b] Computed at 1 atm and 298 K

[c] Computed at the SMD(mesitylene)/BMK/def2-TZVPP//BMK/def2-TZVPP level

[d] Computed at the DLPNO-CCSD(T1)/def2-QZVPP//BMK/def2-TZVPP level

The concentration of CO and 1.0 M for other species

$$\Delta G_{std} = -RTln\left(\frac{V_1}{V_2}\right) = -RTln\left(\frac{\frac{1}{24.46}}{1}\right) = 1.89\ kcal/mol$$

In 295.3 K, the Mol fraction of CO[8] in 1,2,4-trimethylbenzene is 8.63×10^{-4}

The concentration of CO in mesitylene is *ca.* $8.63 \times 10^{-4} \times \frac{0.867\times1000}{120.19} = 6.2\ mM$

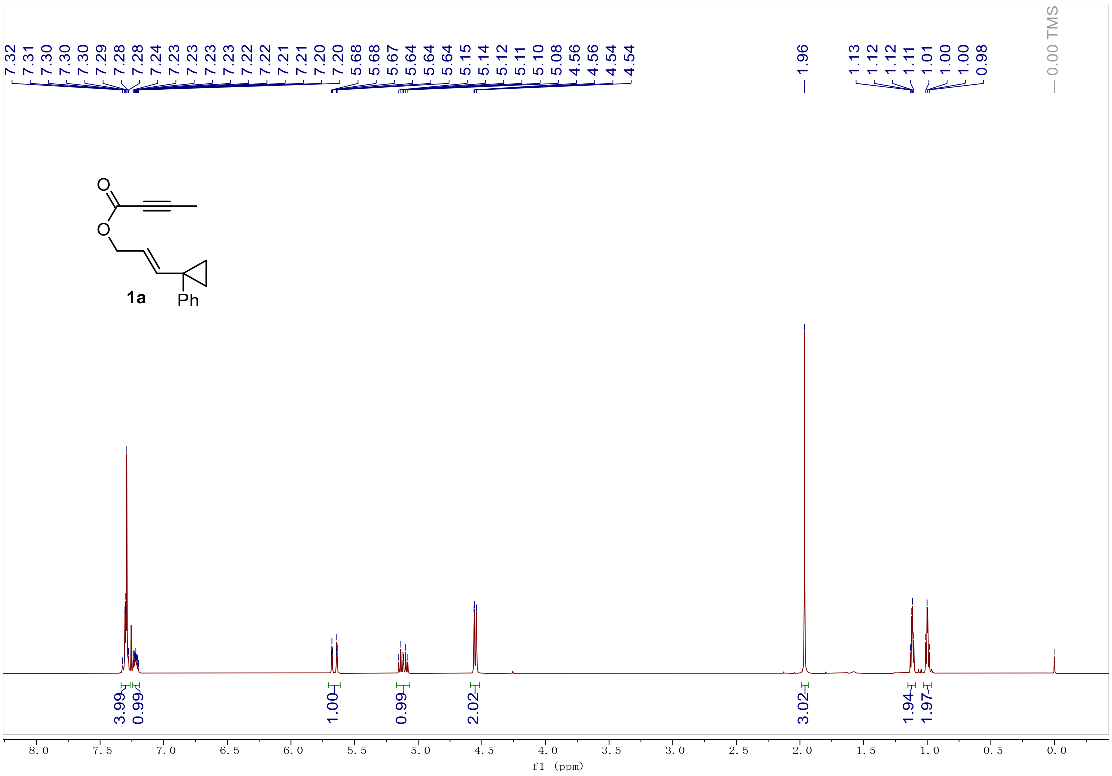
$$\Delta G_{co} = -RTln\left(\frac{V_1}{V_2}\right) - RTln\left(\frac{c_1}{c_2}\right) = -RTln\left(\frac{\frac{1}{24.46}}{1}\right) - RTln\left(\frac{1}{0.0062}\right) = -1.117\ kcal/mol$$

5. References

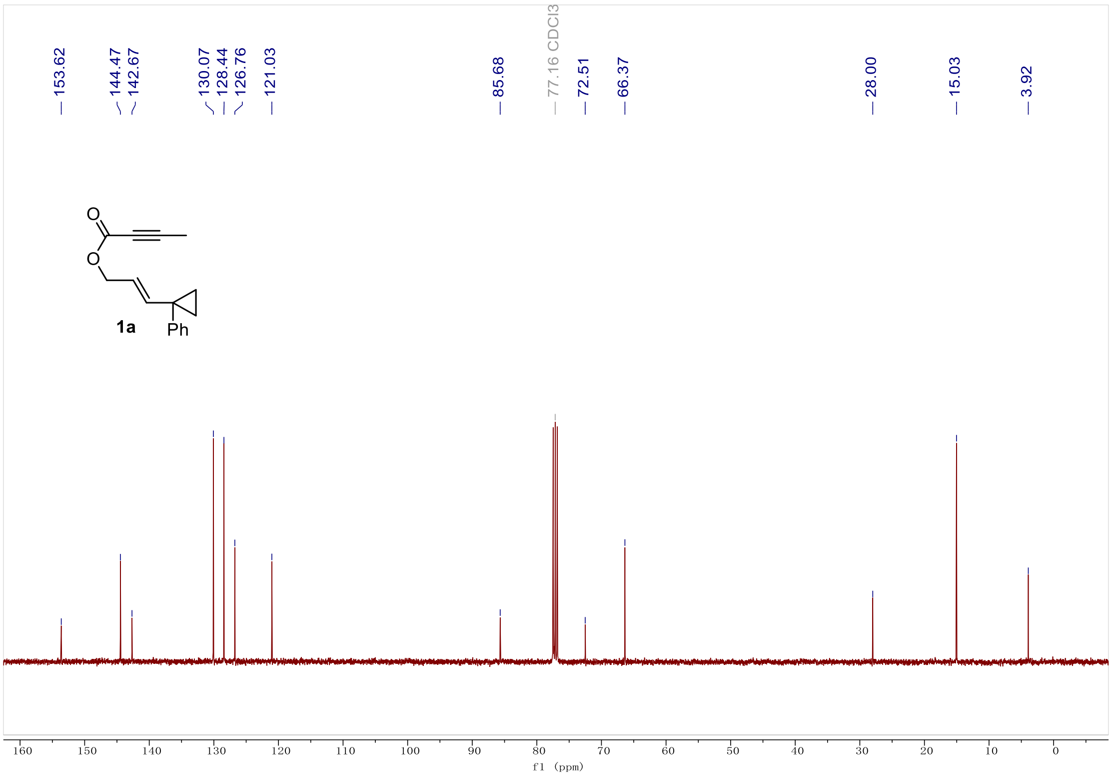
1. Wender, P. A.; Williams, T. J.; *Angew. Chem., Int. Ed.* **2002**, *41*, 4550.
2. Liu, J.; Zhou, Y.; Zhu, J.; Yu, Z.-X. *Org. Lett.* **2021**, *23*, 7566.
3. Saito, A.; Ono, T.; Hanzawa, Y. *J. Org. Chem.* **2006**, *71*, 6437.
4. Ylagan, R. M. P.; Lee, E. J.; Negru, D. E.; Ricci, P.; Park, B.; Ryu, H.; Baik, M.-H.; Evans, P. A. *Angew. Chem., Int. Ed.* **2023**, *62*, e202300211.
5. Wang, L.-N.; Huang, Z.; Yu, Z.-X. *Org. Lett.* **2023**, *25*, 1732.
6. Liu, R.; Zhang, M.; Winston-McPherson, G.; Tang, W. *Chem. Commun.* **2013**, *49*, 4376.
7. (a) Zhong, L.-P.; Feng, R.; Wang, J.-J.; Li, C.-C. *J. Am. Chem. Soc.* **2023**, *145*, 2098; (b) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720; (c) Wu, C.; Yoshikai, N. *Angew. Chem., Int. Ed.* **2018**, *57*, 6558.
8. Krauss, V. W.; Gestrich, W., *Khemie – Technik*, **1977**, *6*, 513–516.

6. NMR Spectra of New Compounds

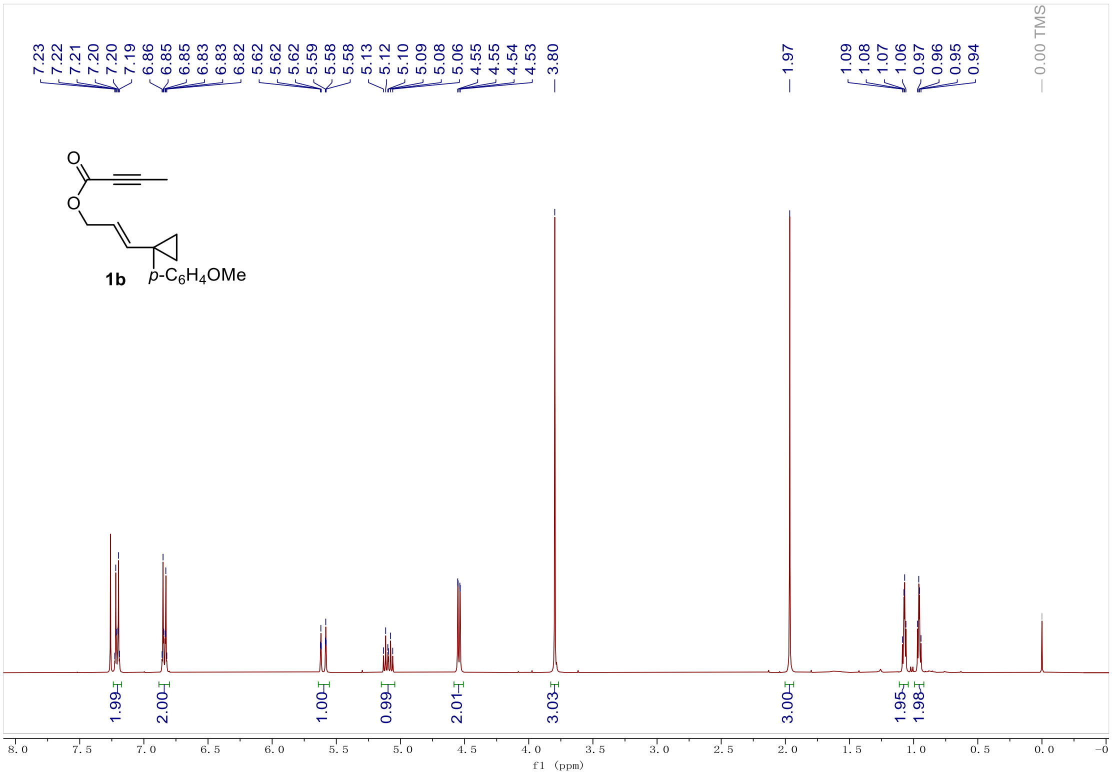
^{1}H NMR in CDCl$_3$, 400 MHz



^{13}C NMR in CDCl$_3$, 101 MHz



^{1}H NMR in $CDCl_3$, 400 MHz



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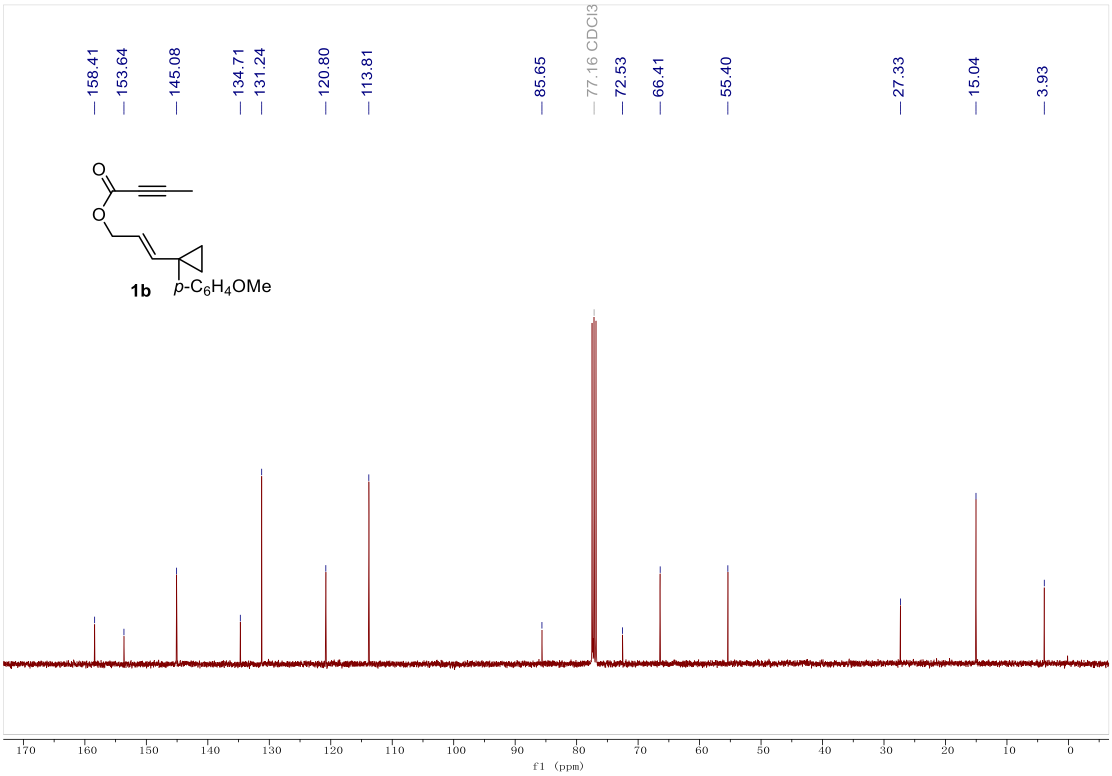

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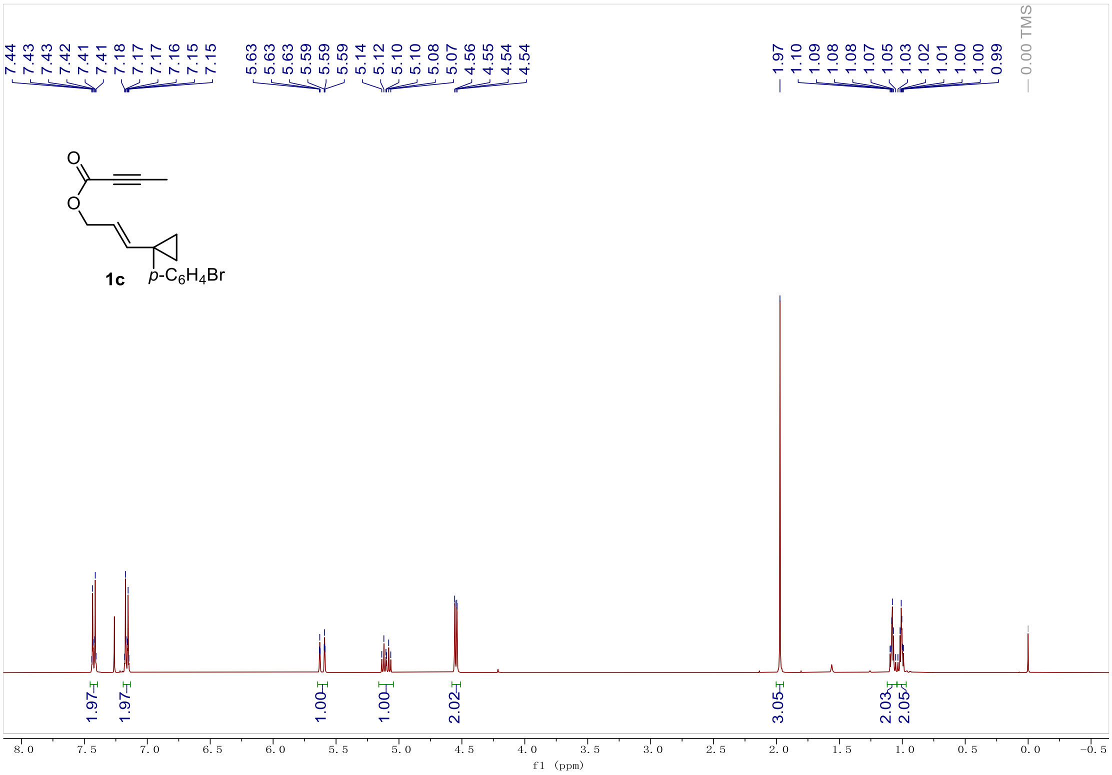

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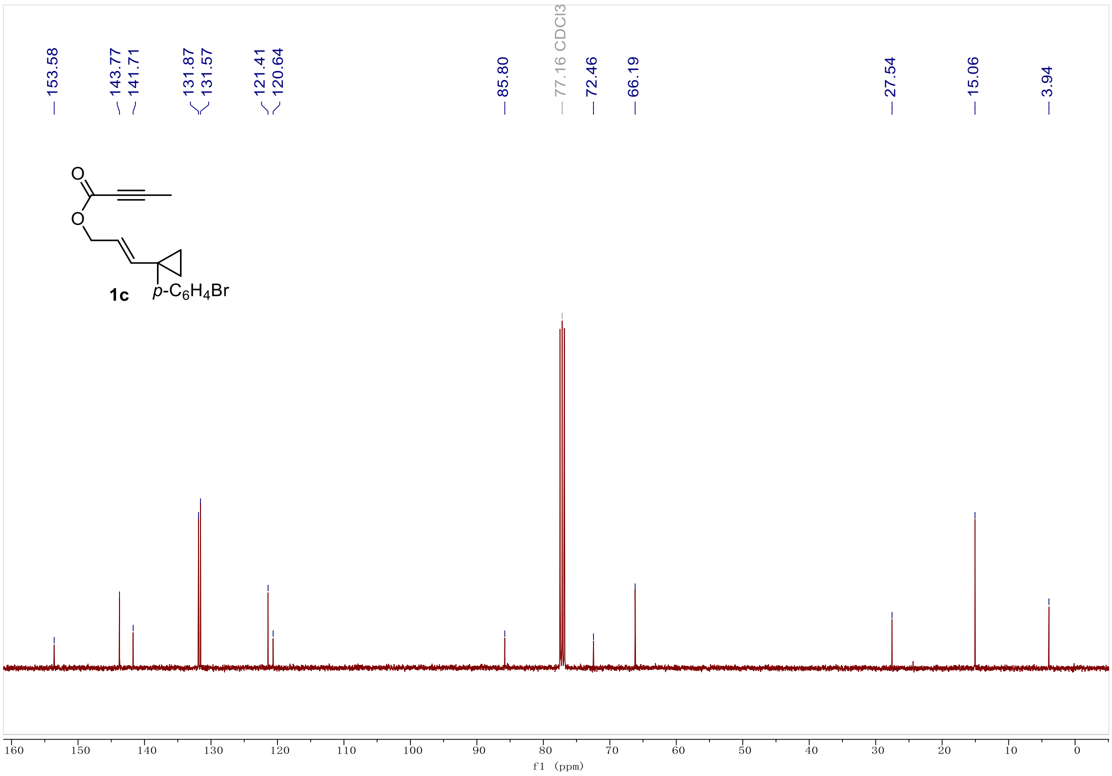

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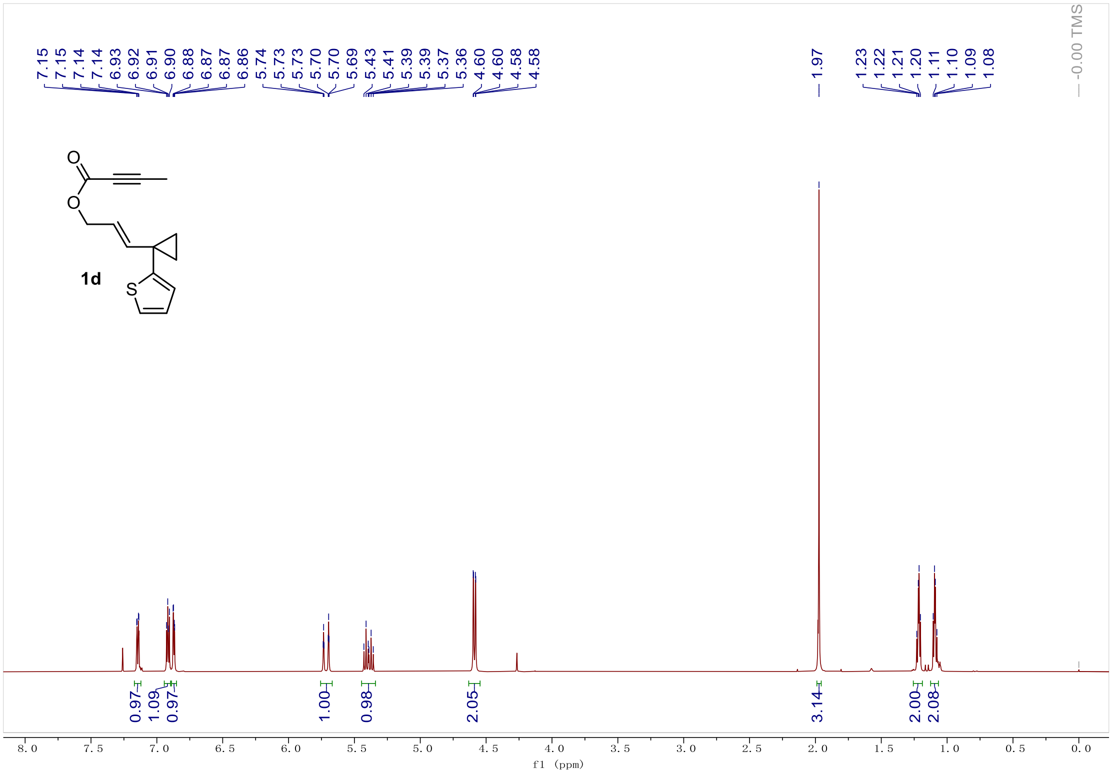

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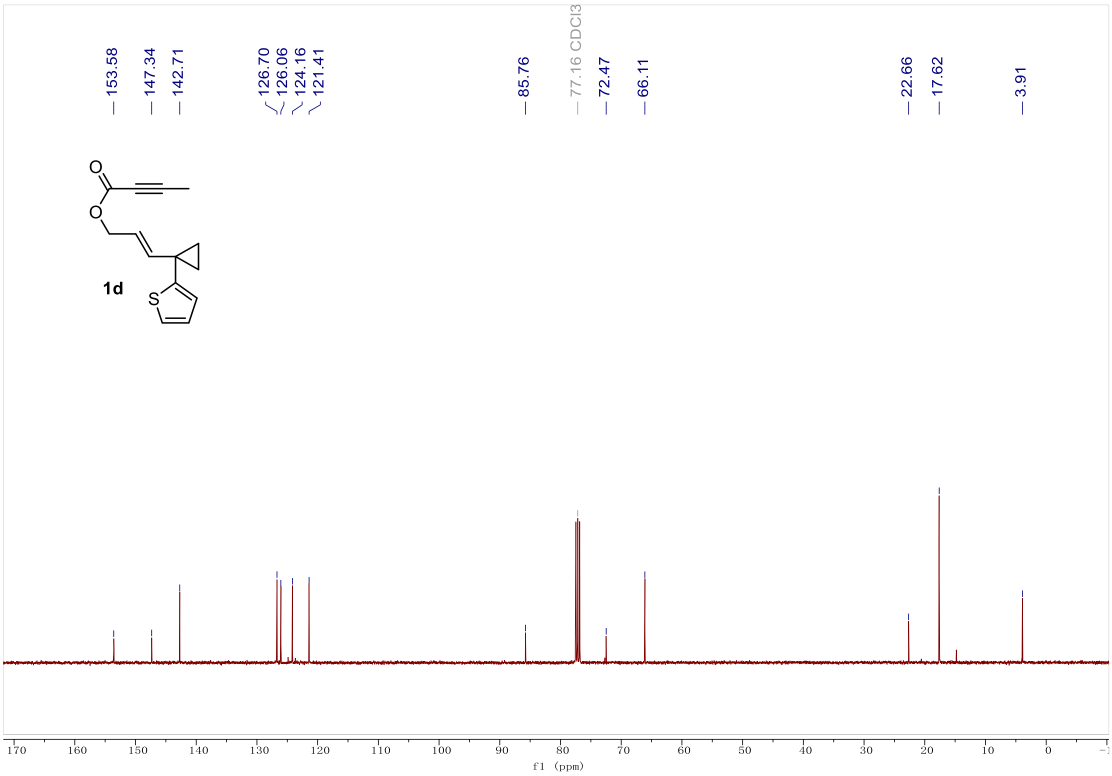

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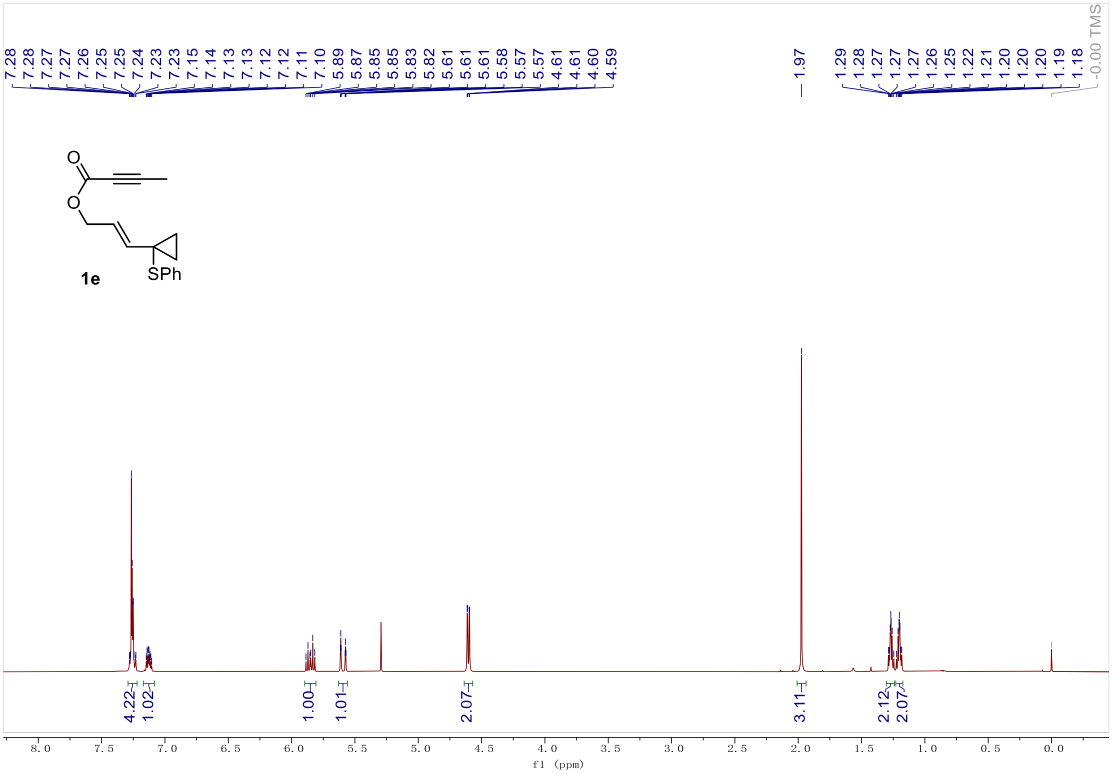

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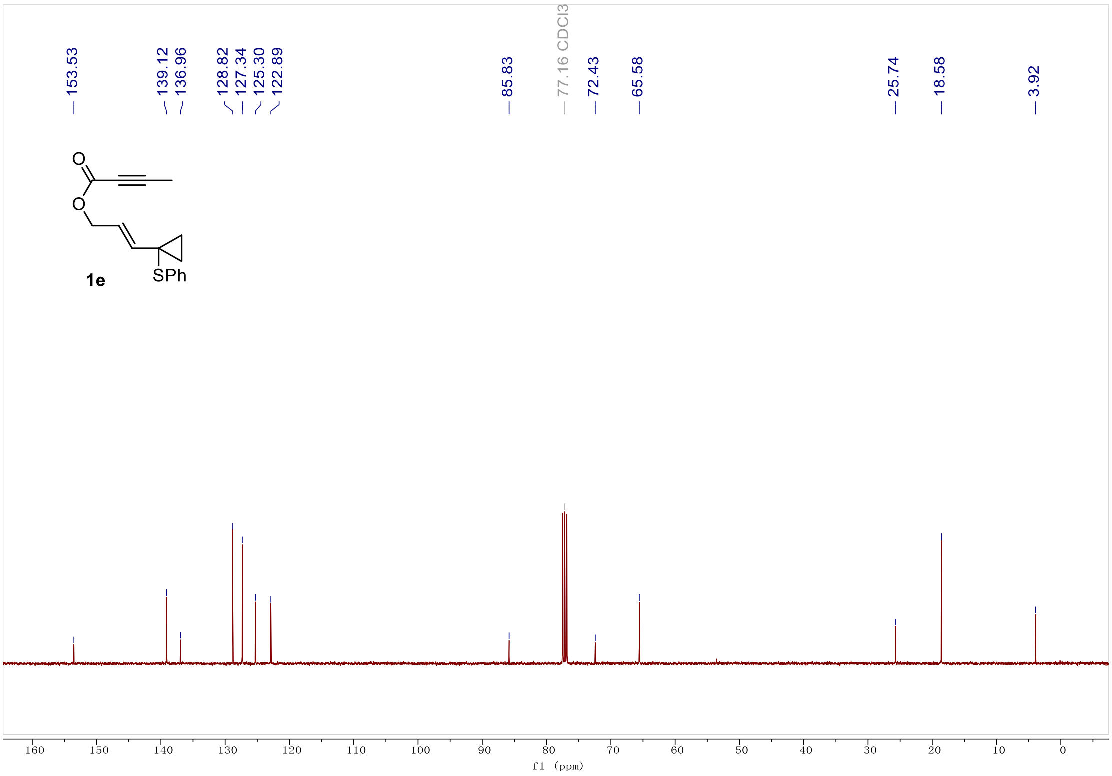

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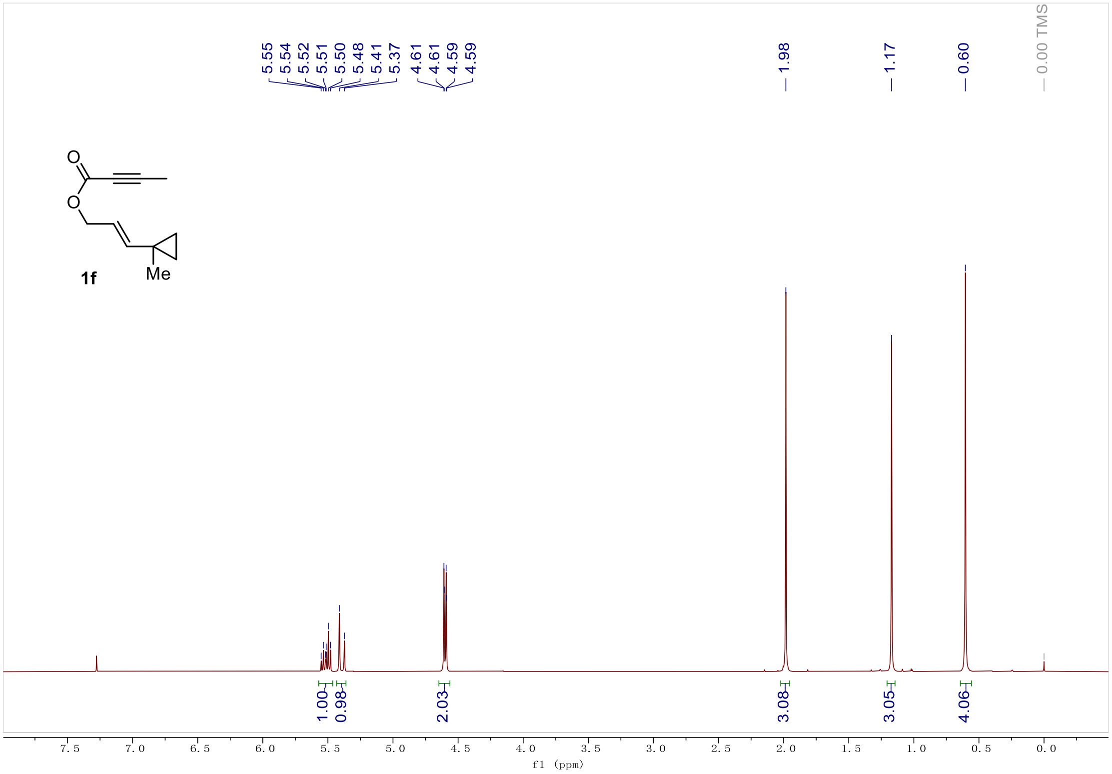

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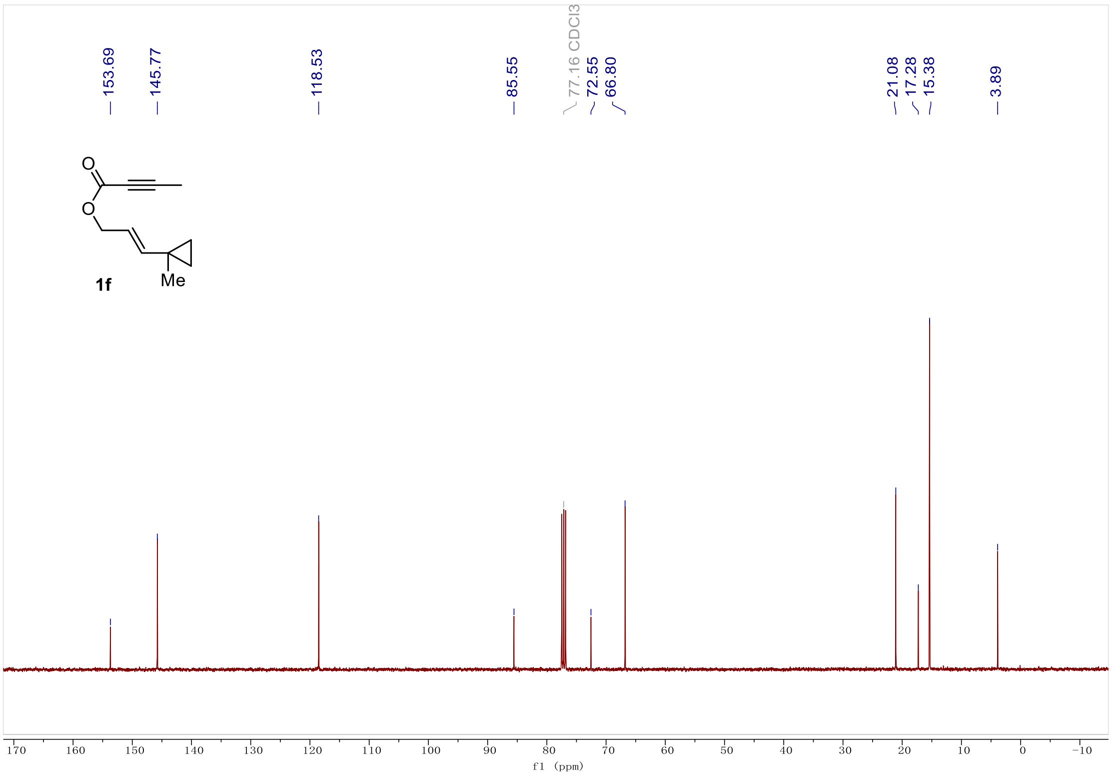

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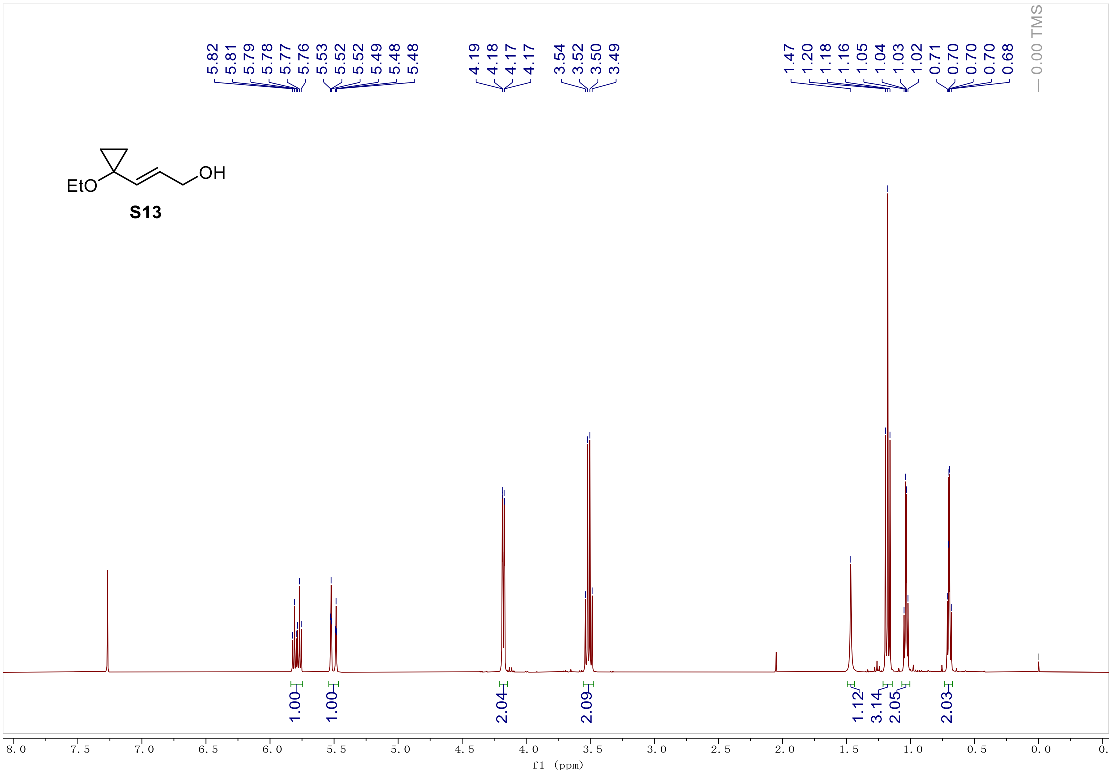

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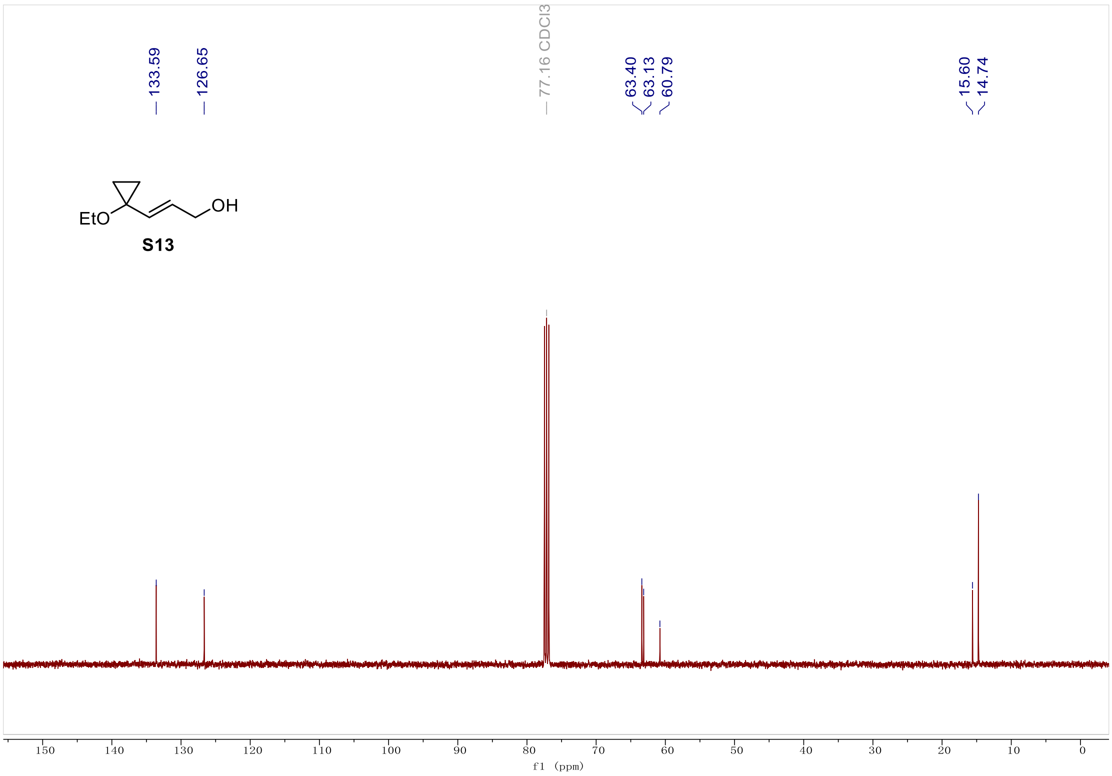

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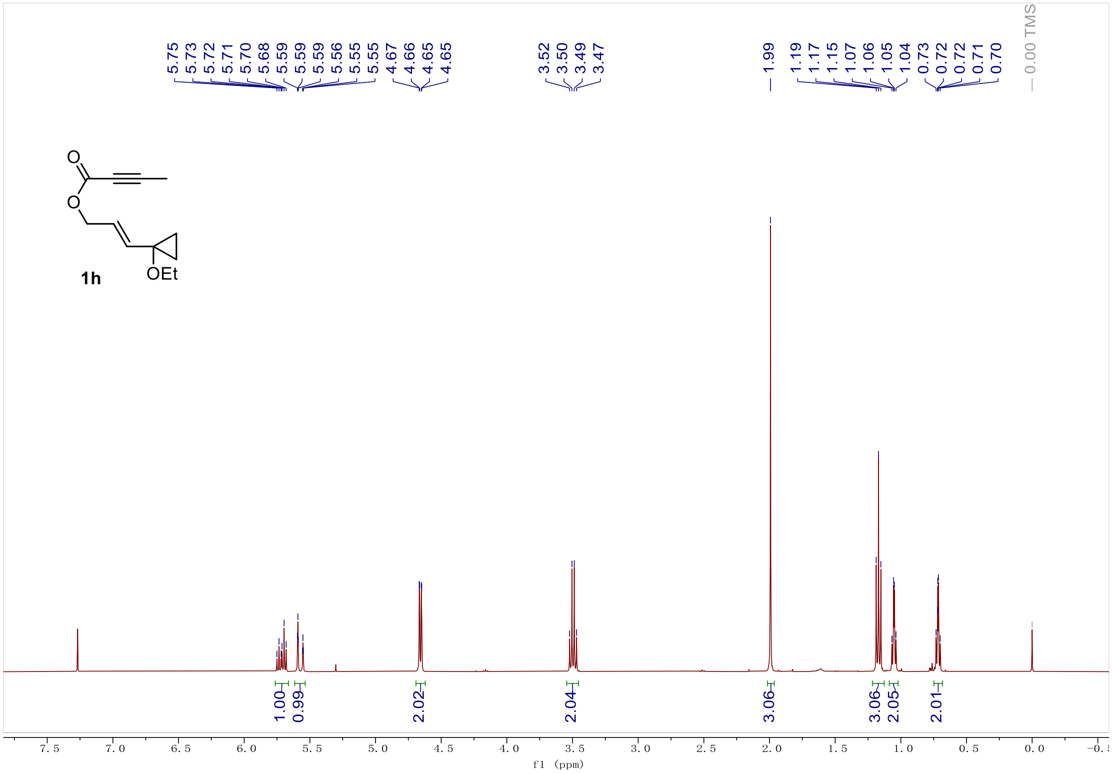

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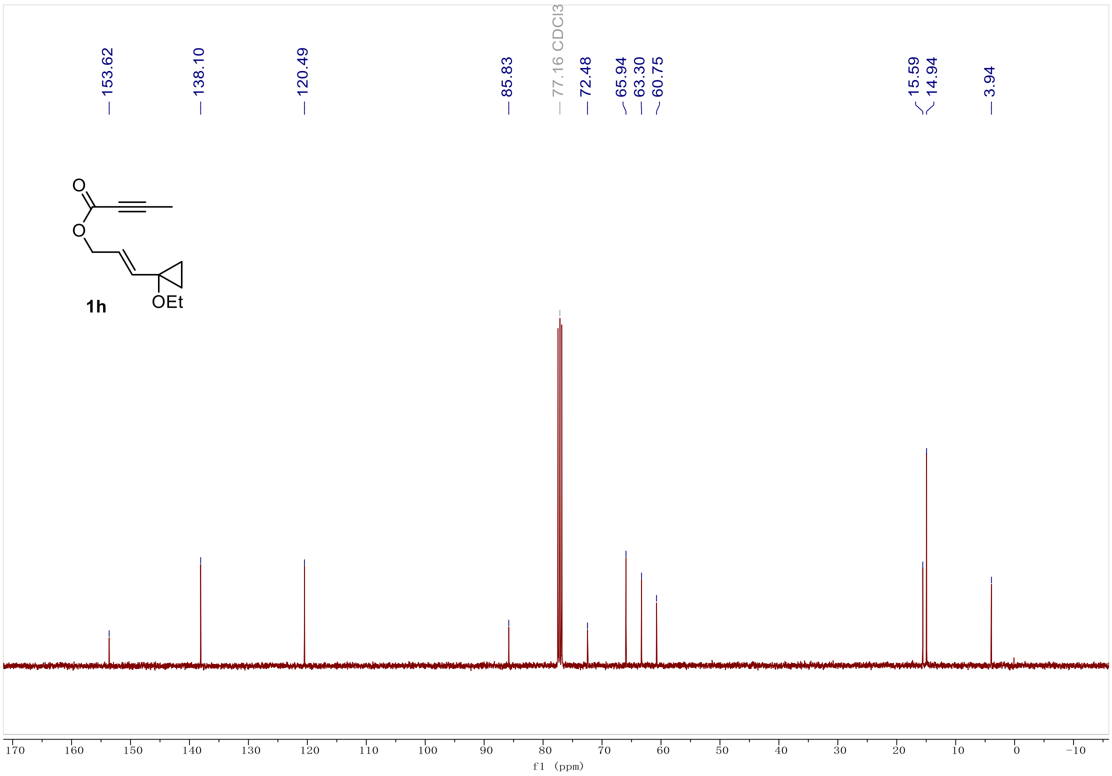

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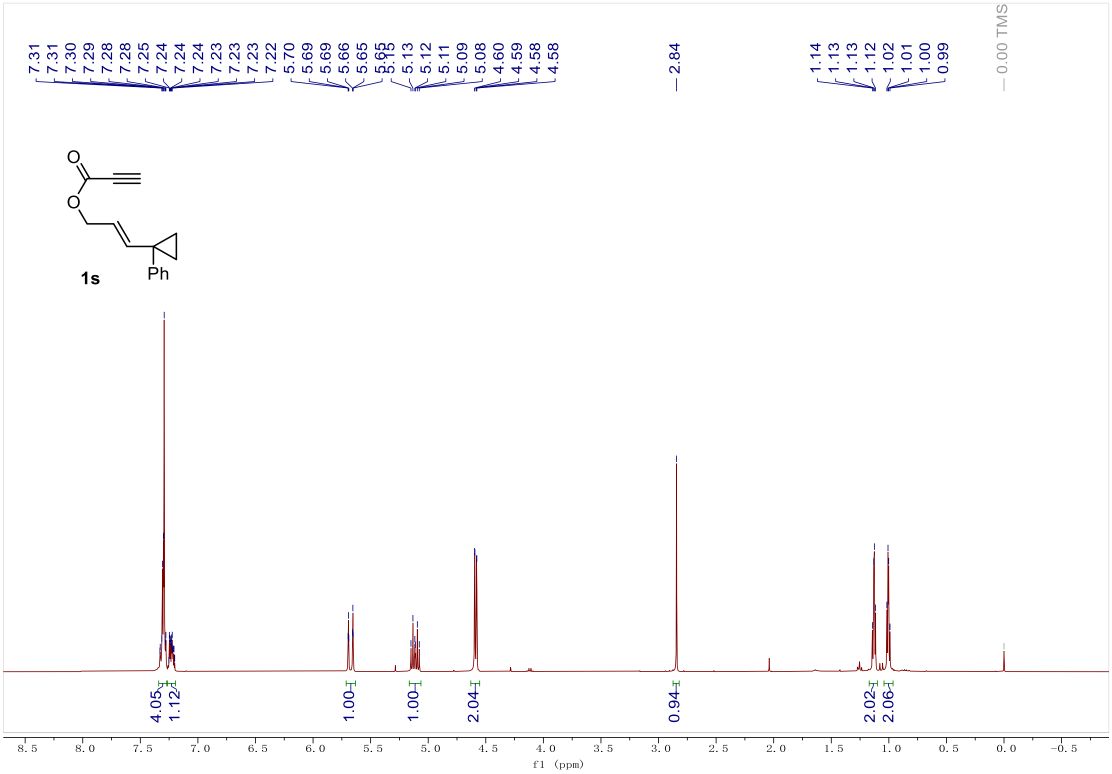

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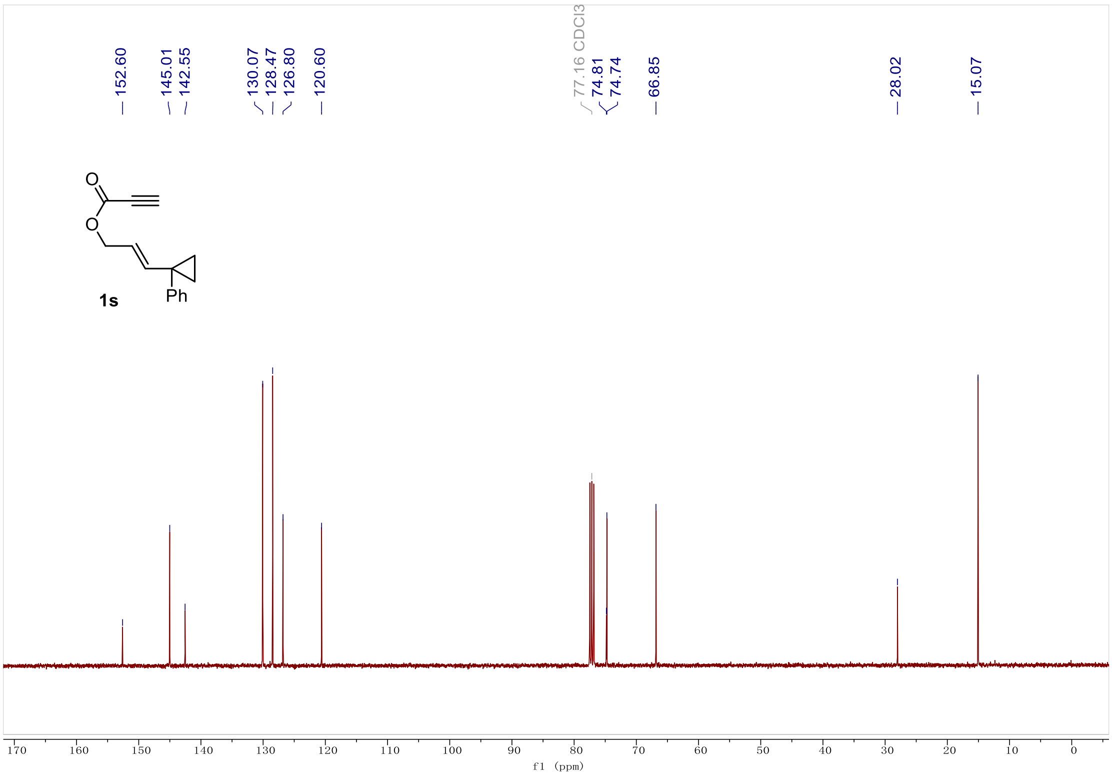

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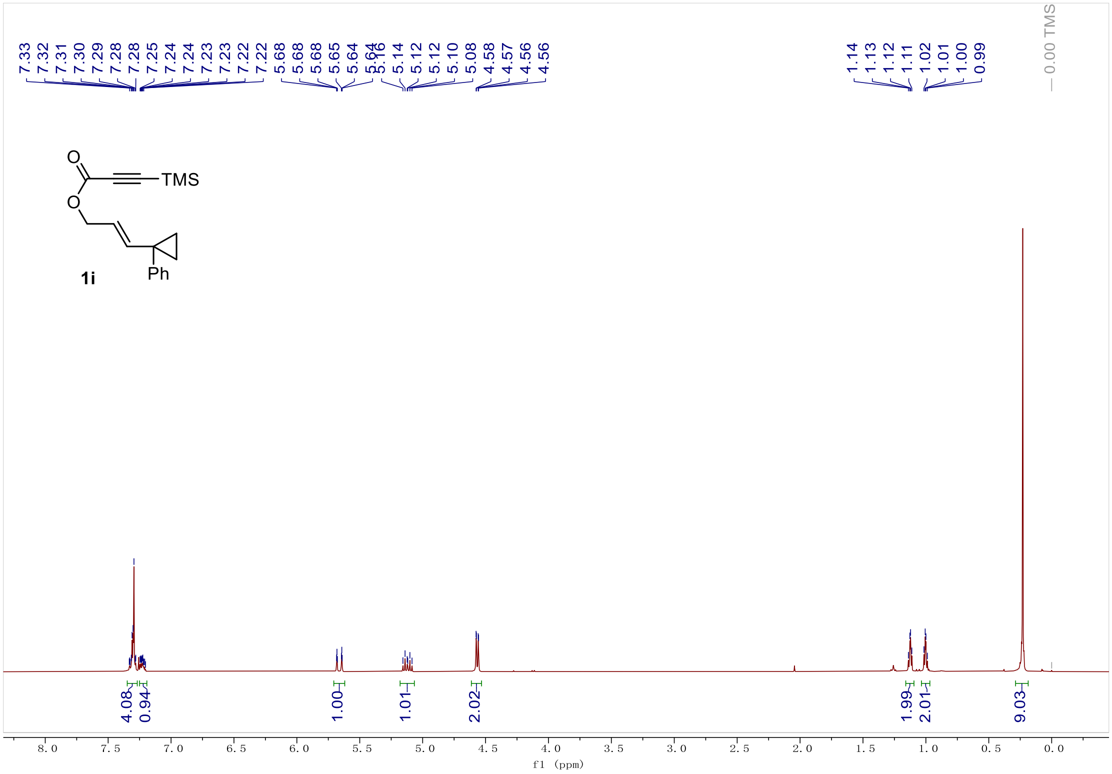

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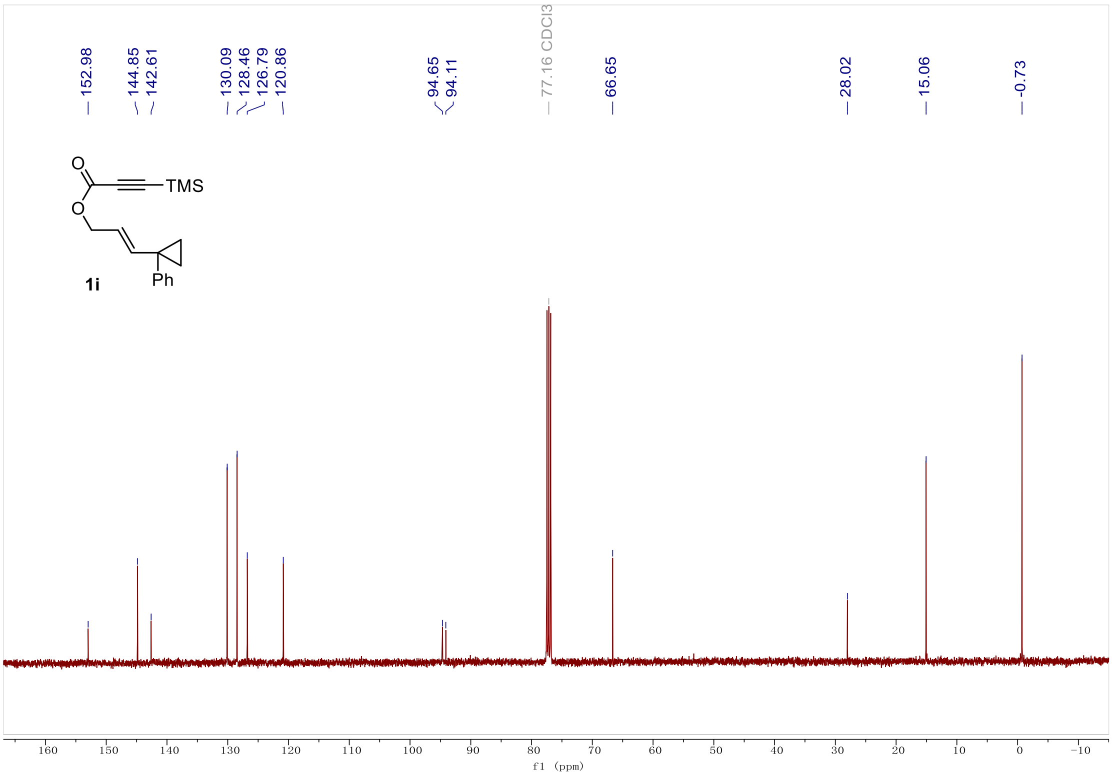

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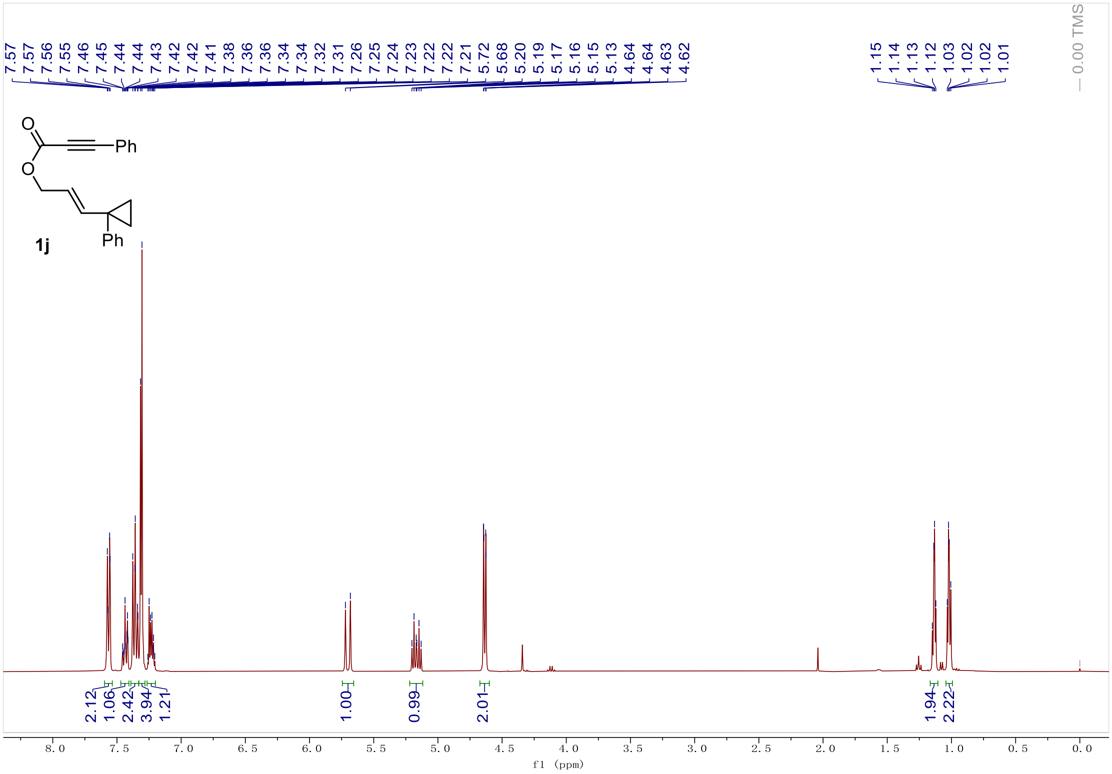

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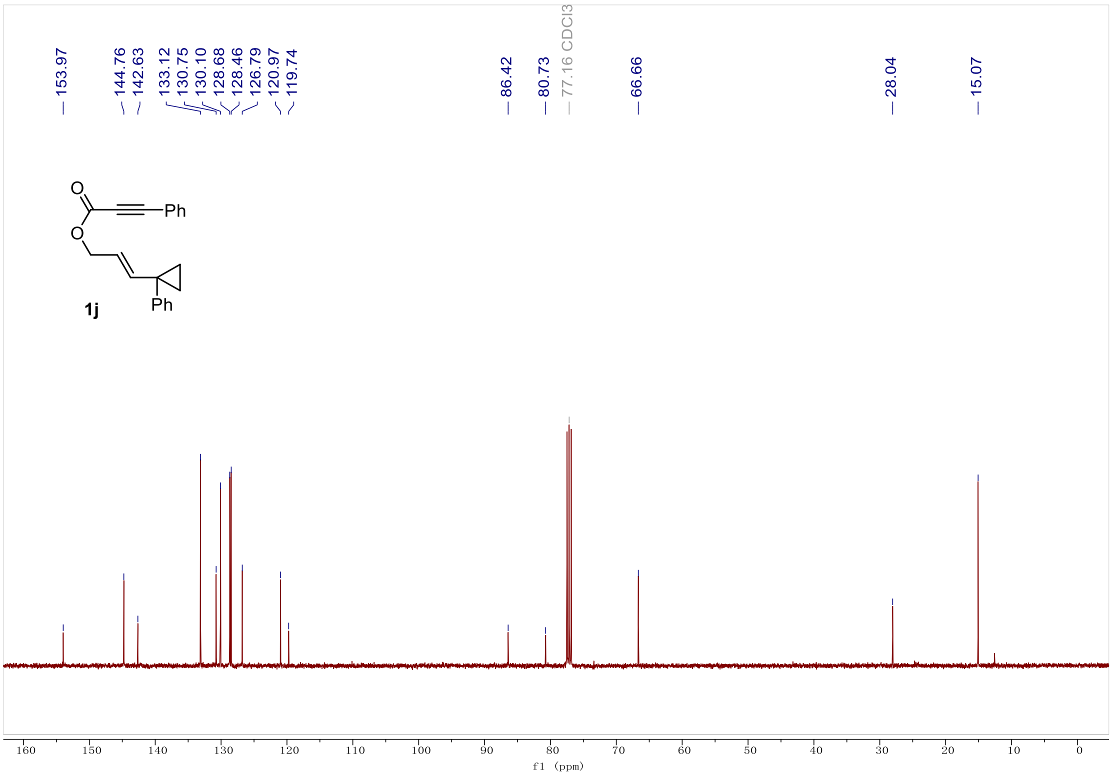

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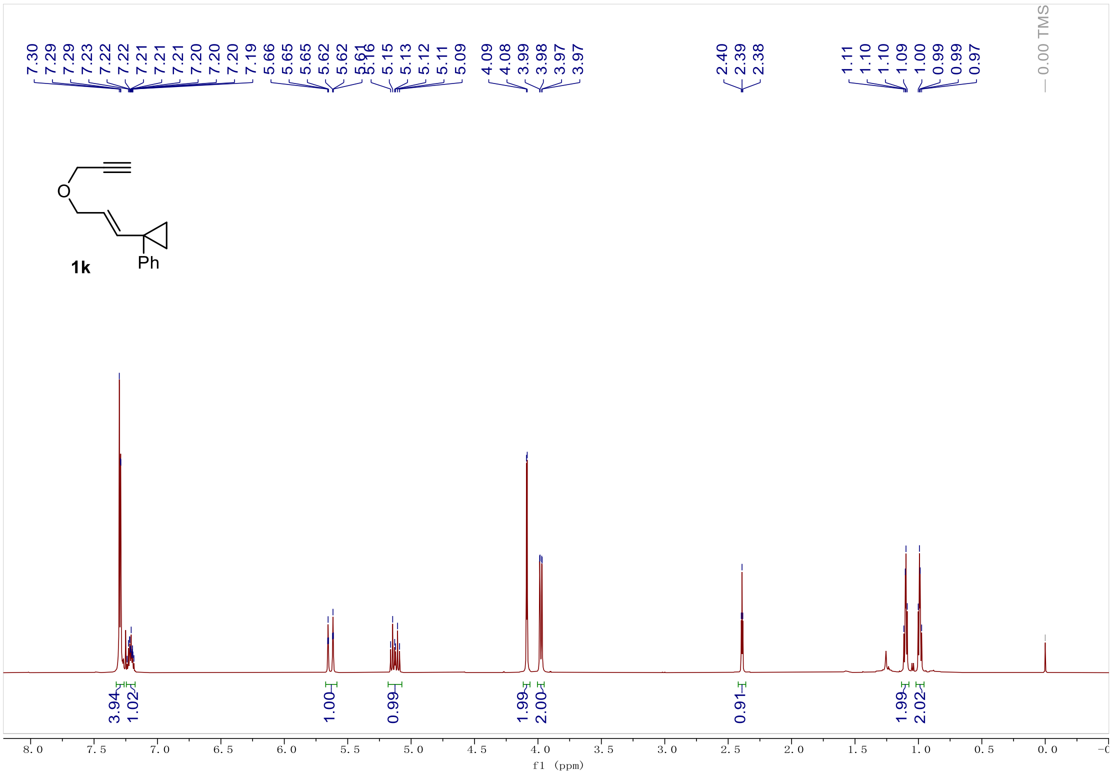

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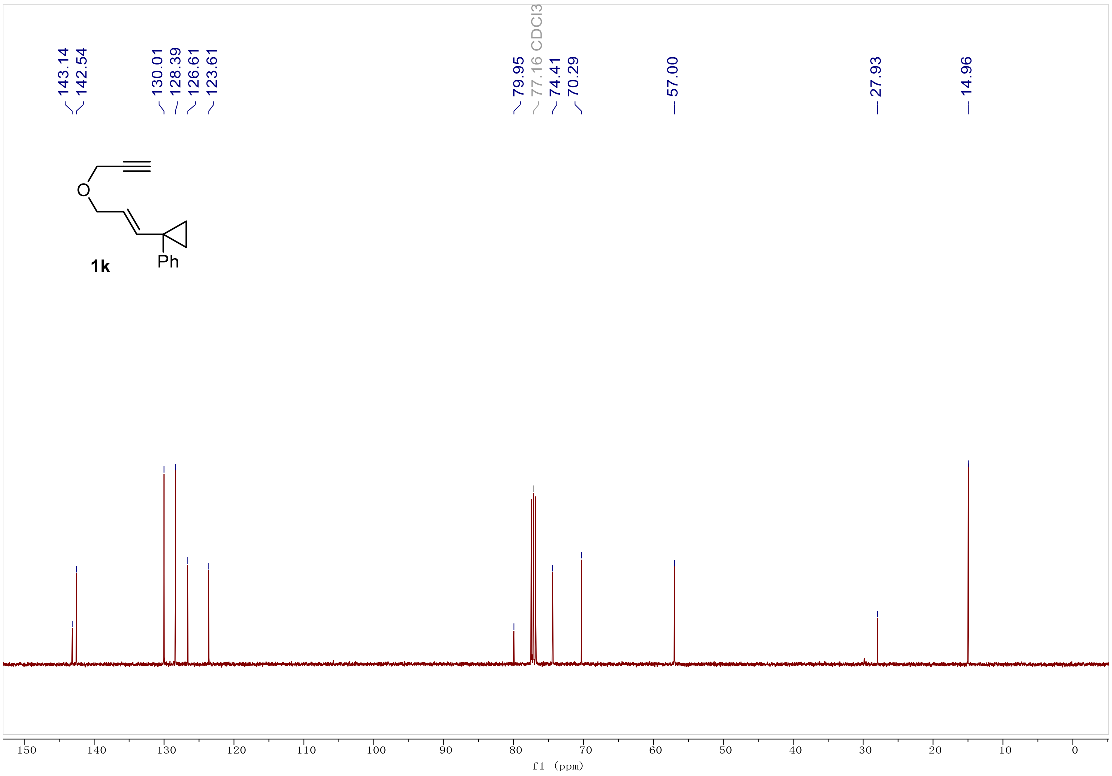

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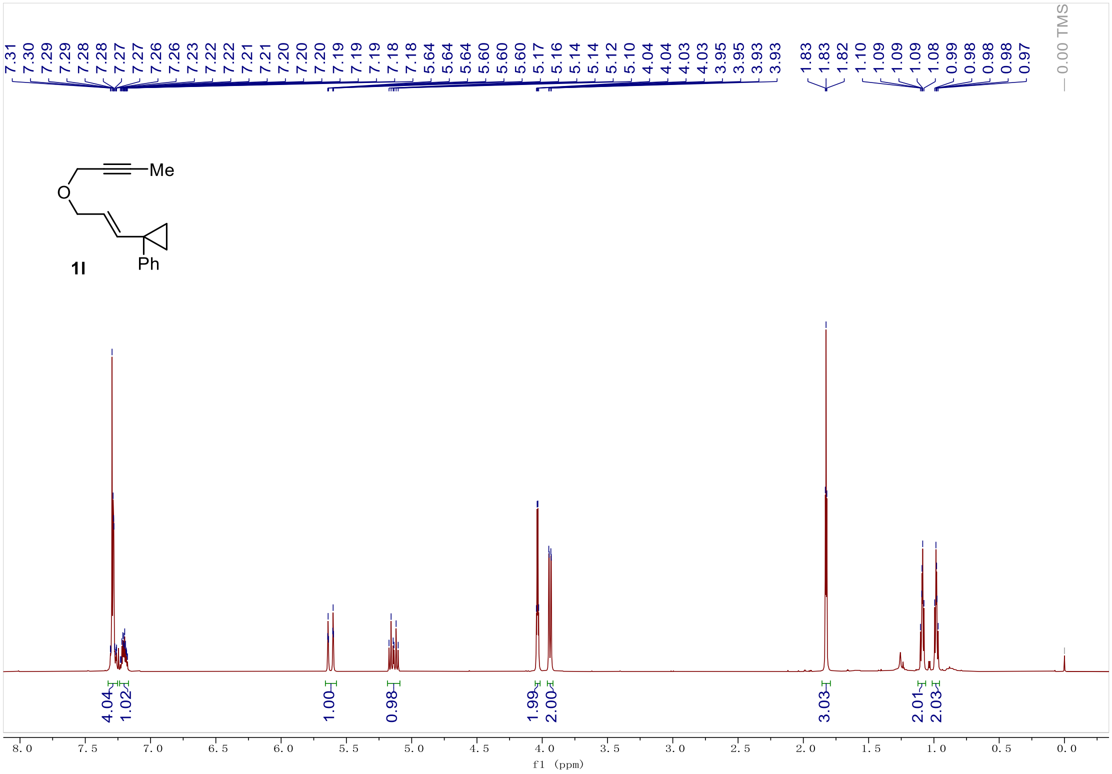

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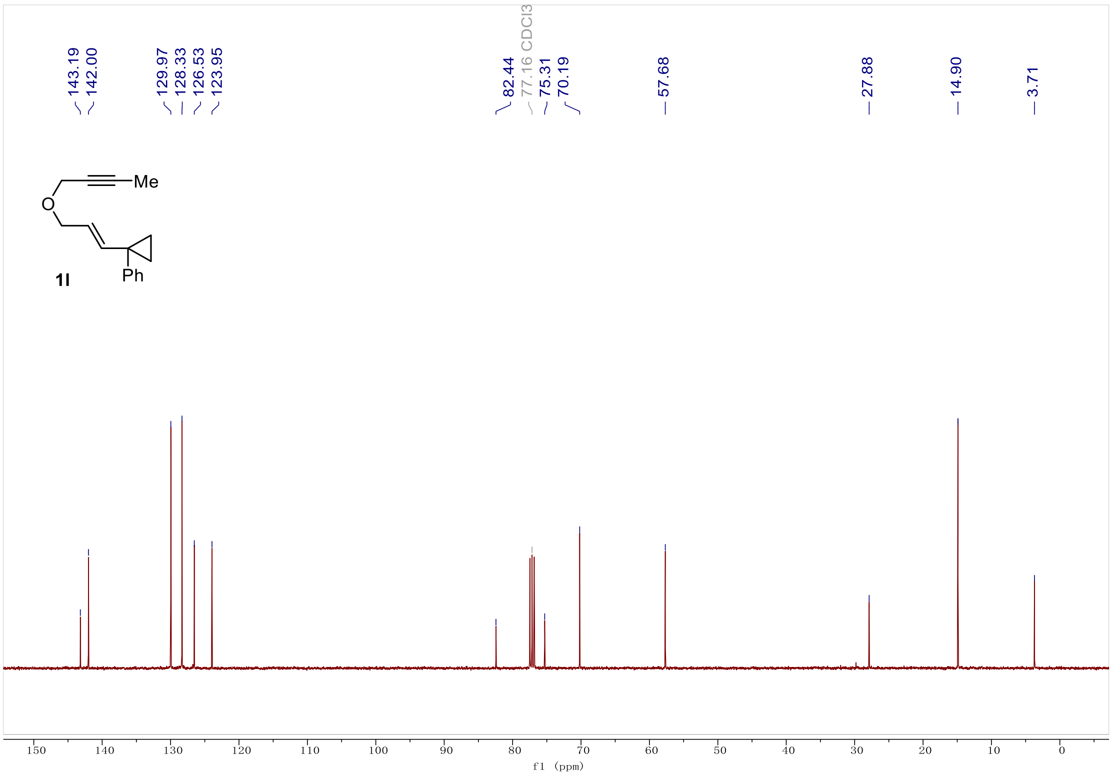

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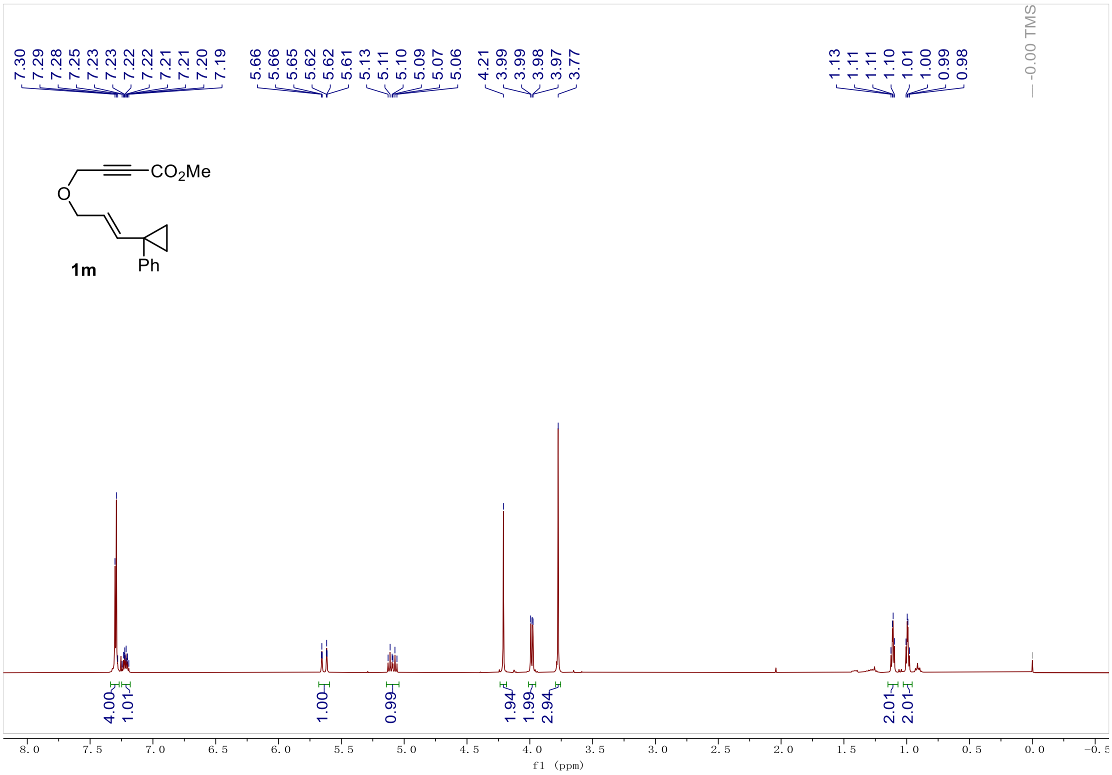

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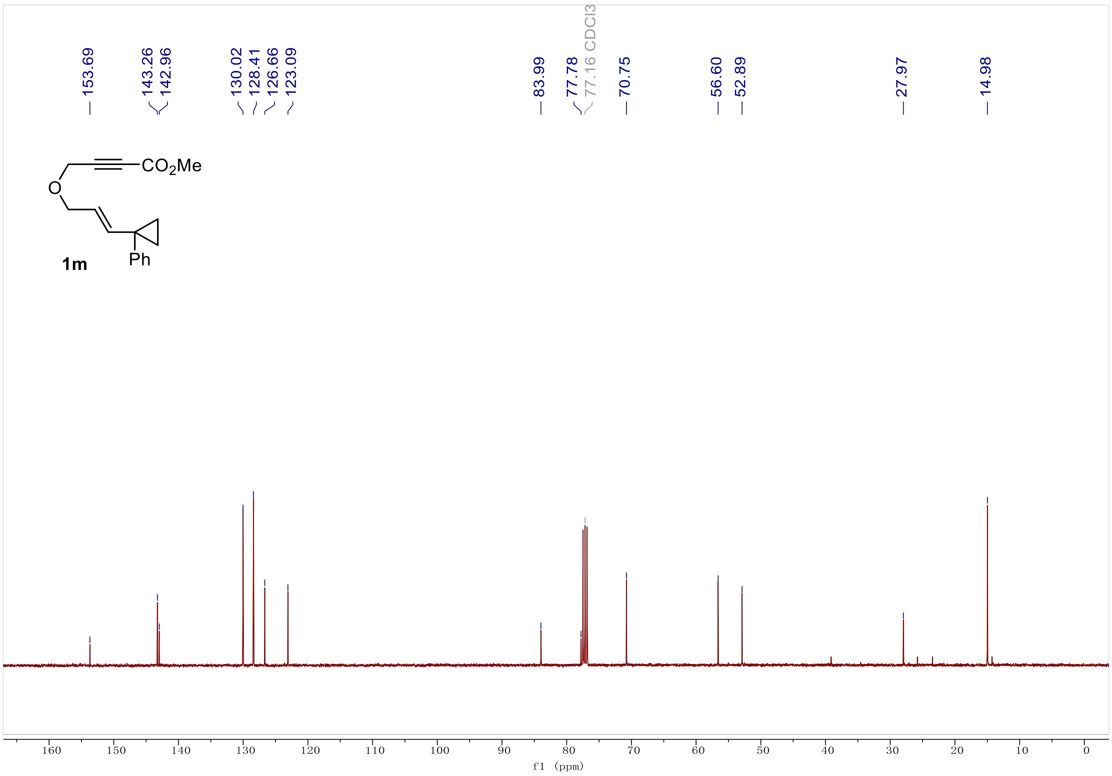

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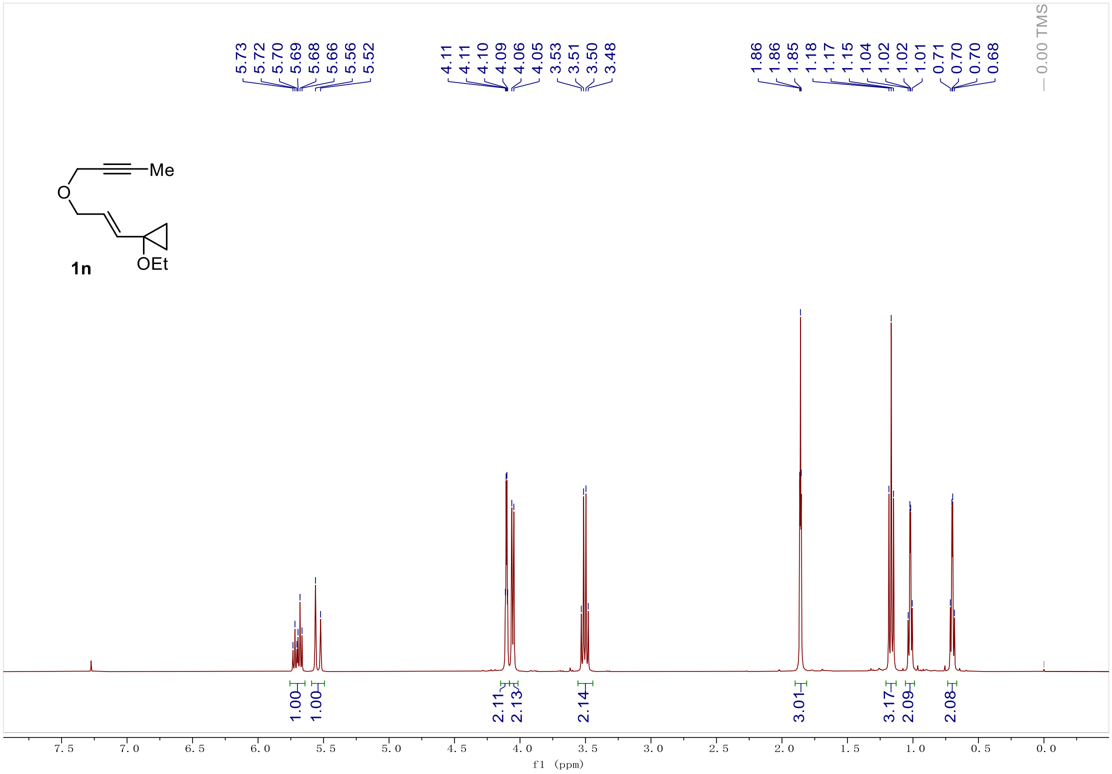

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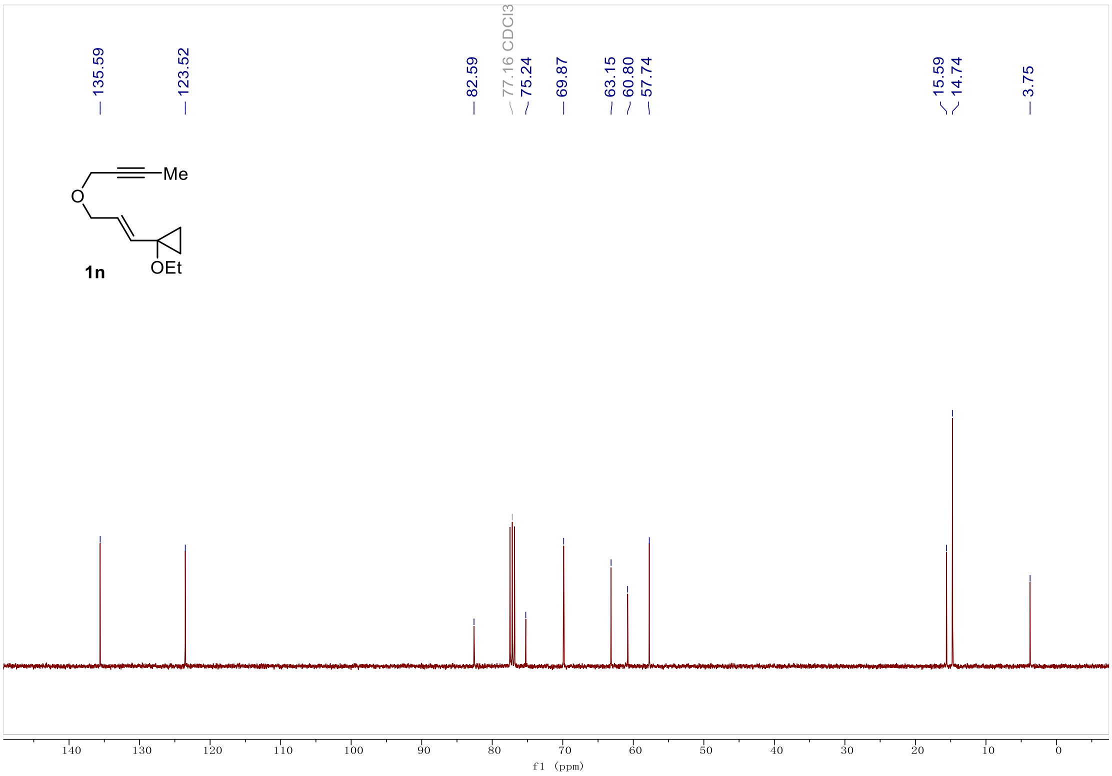

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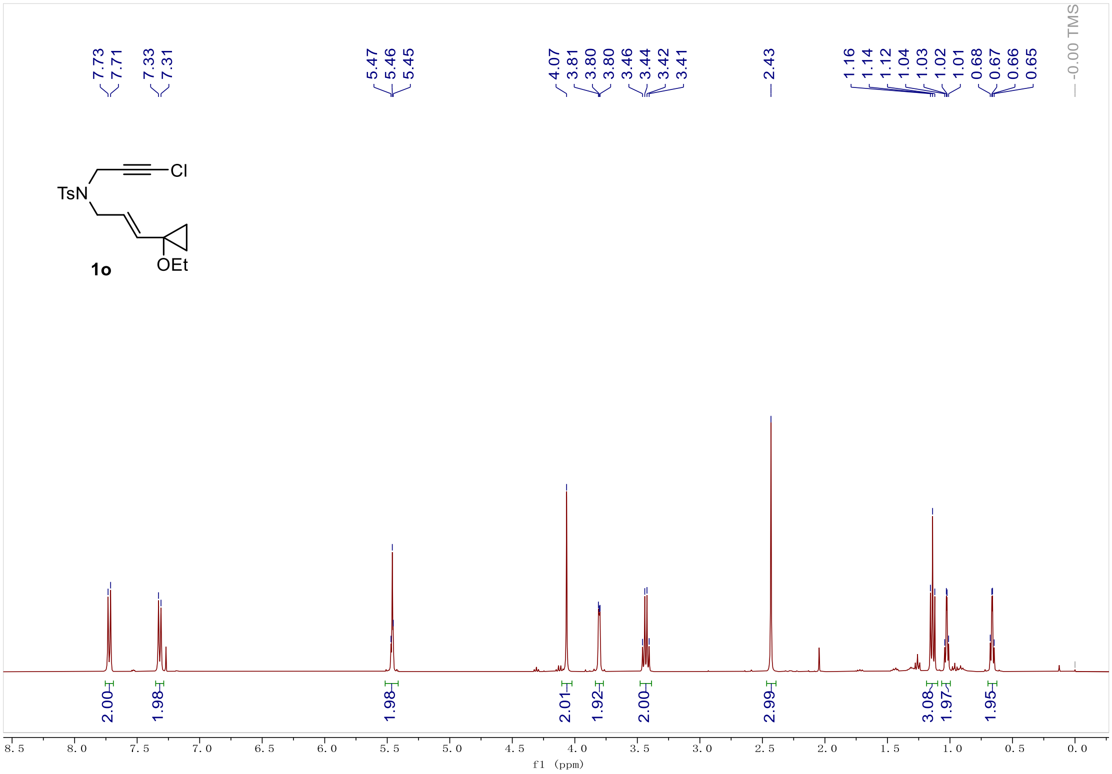

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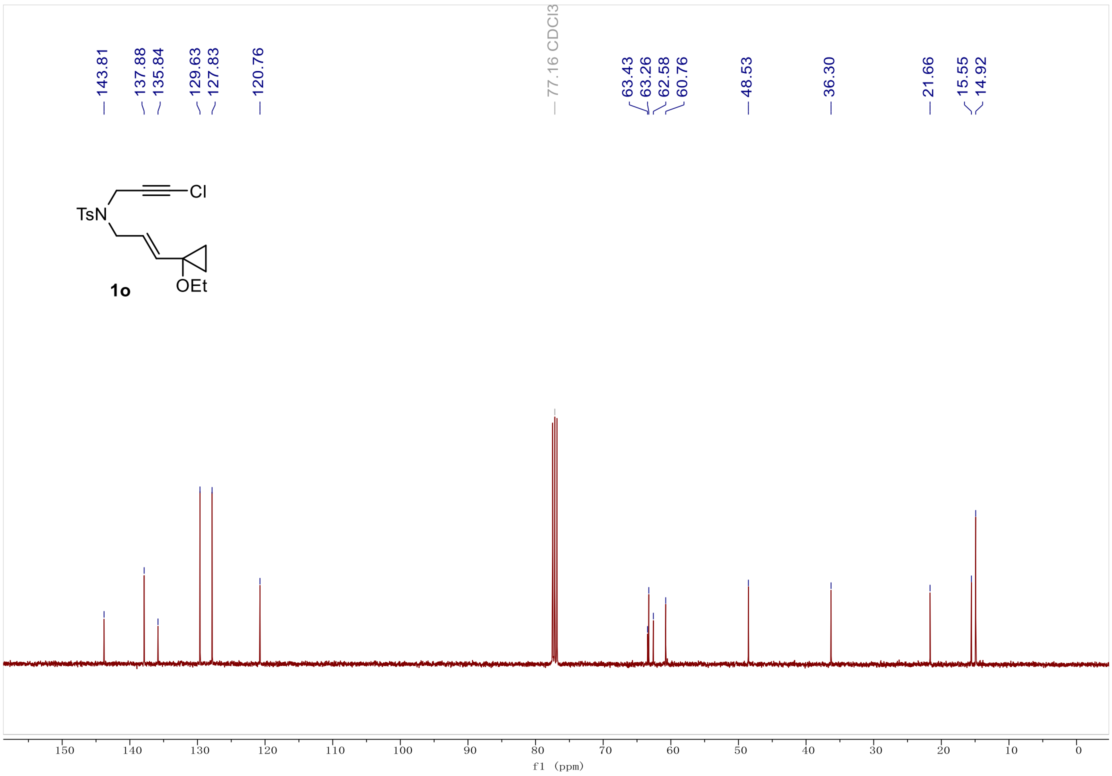

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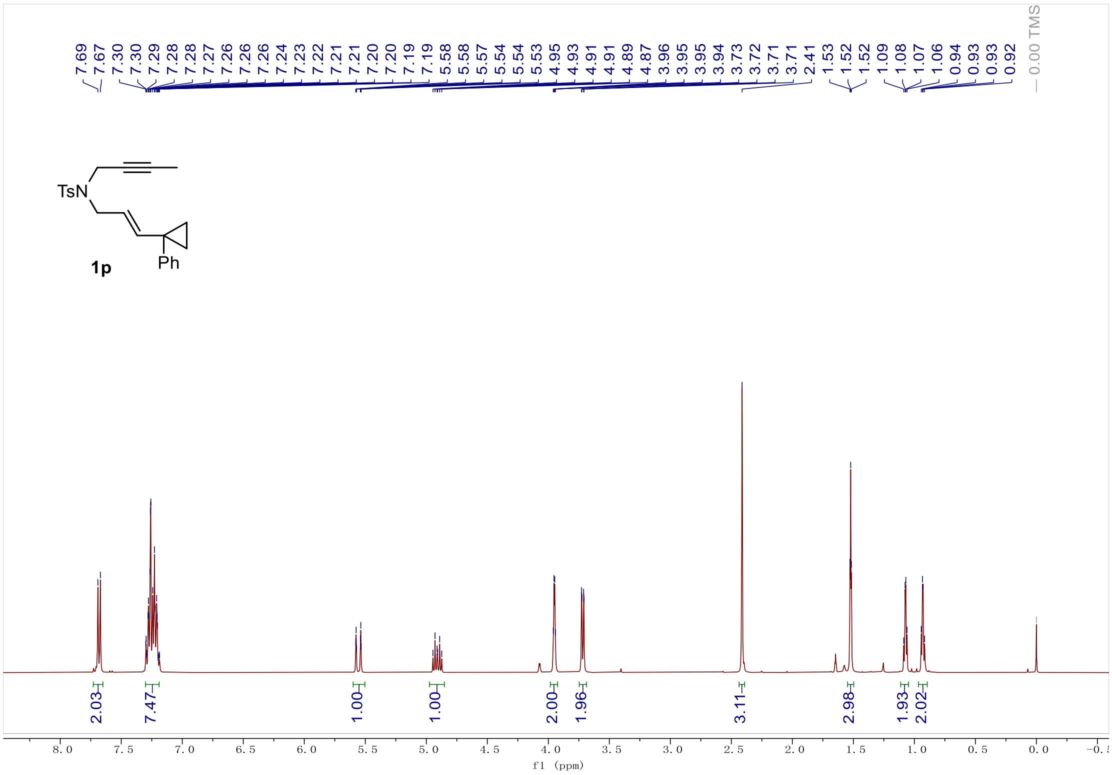

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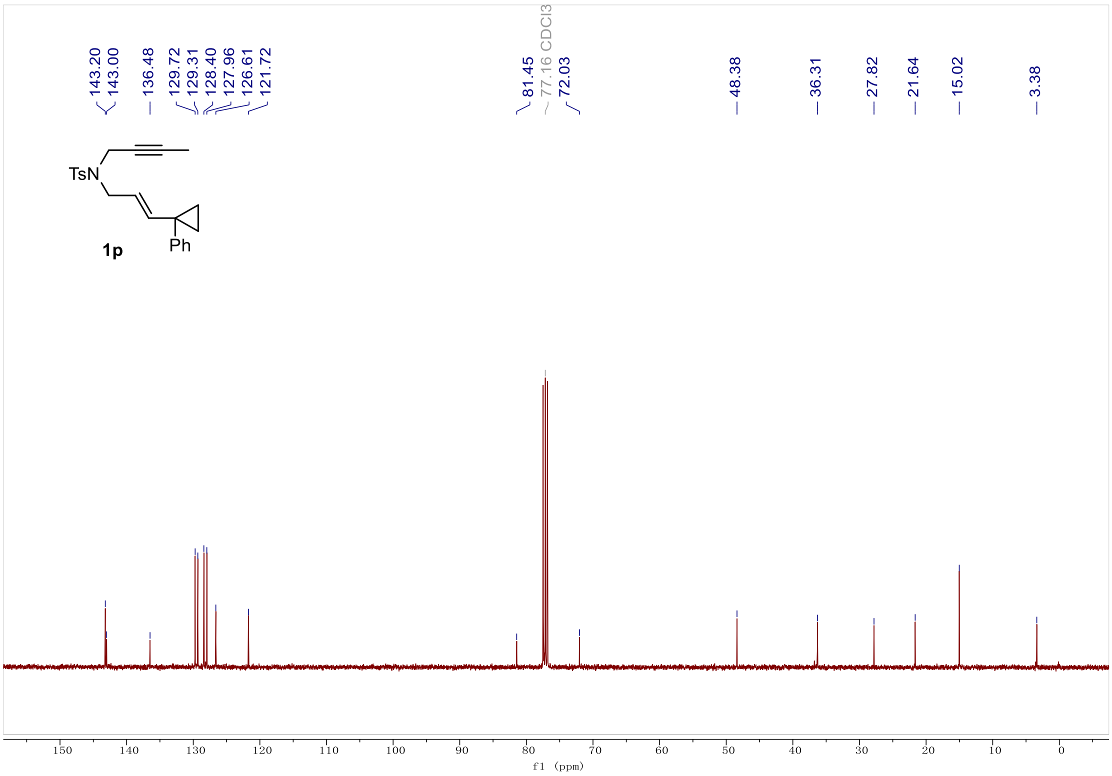

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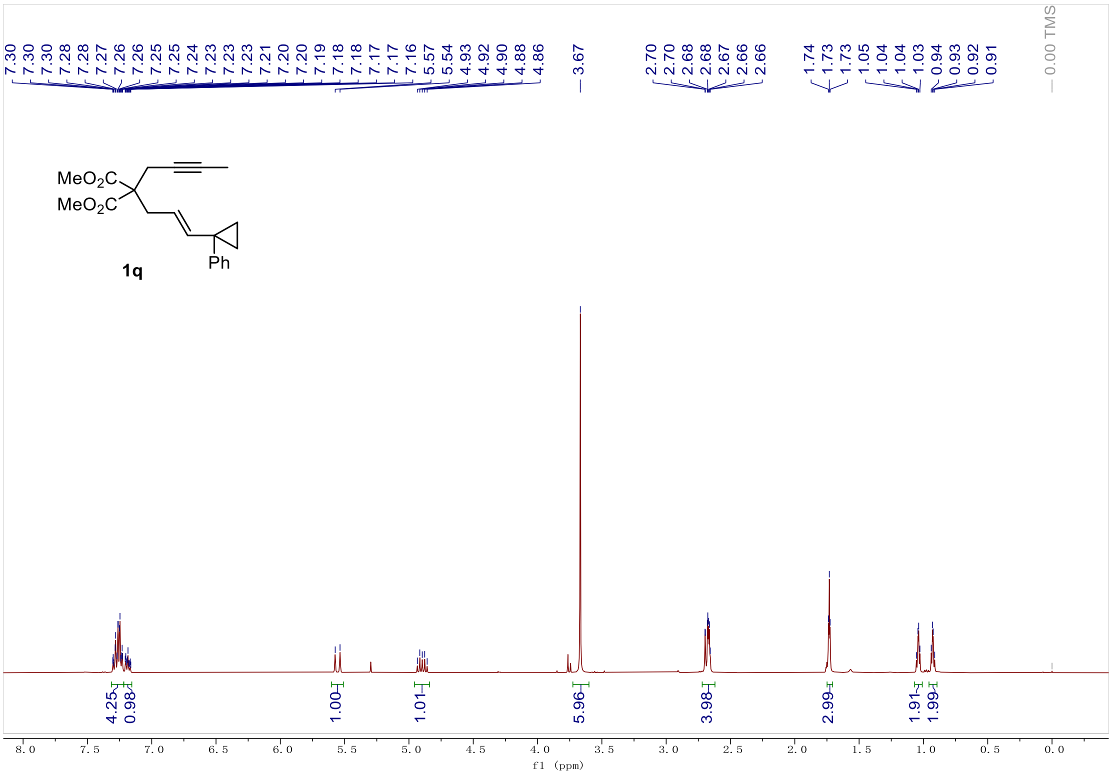
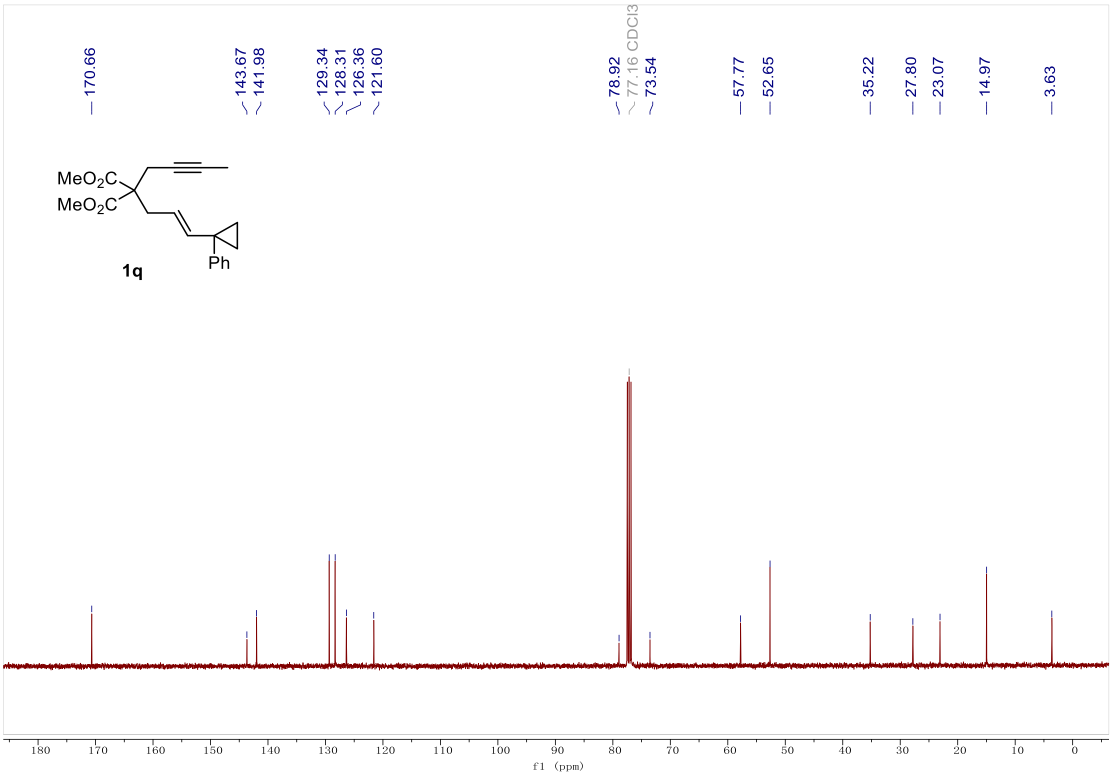
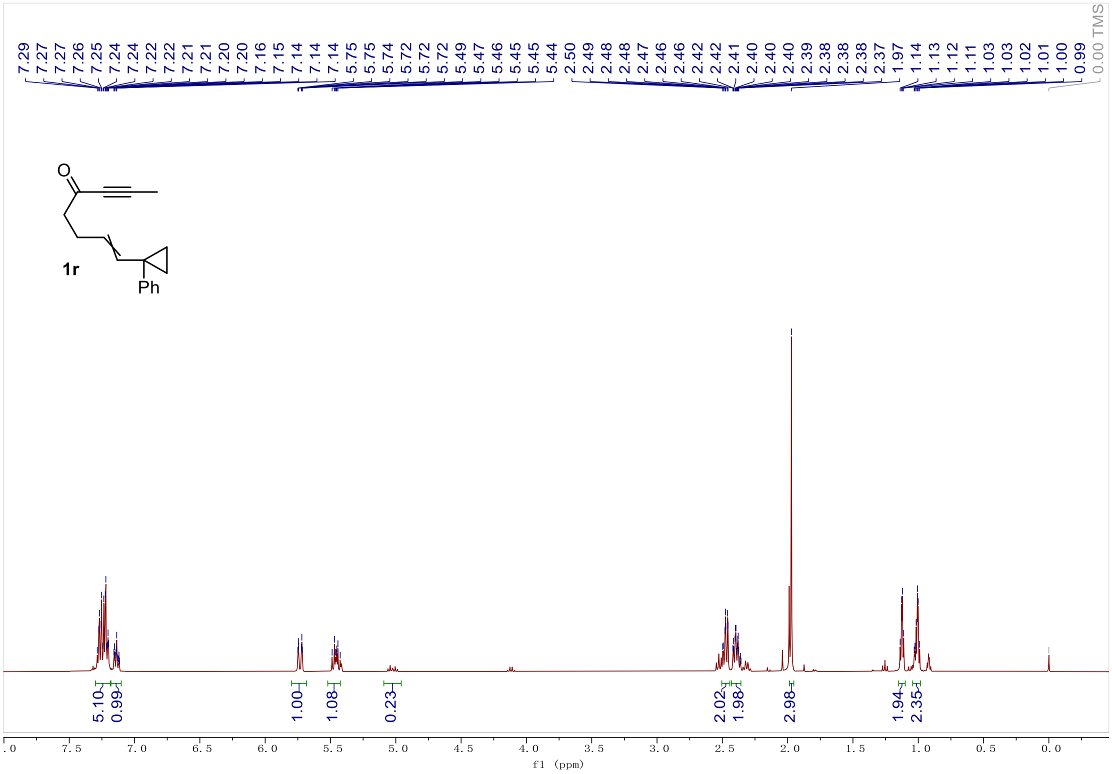


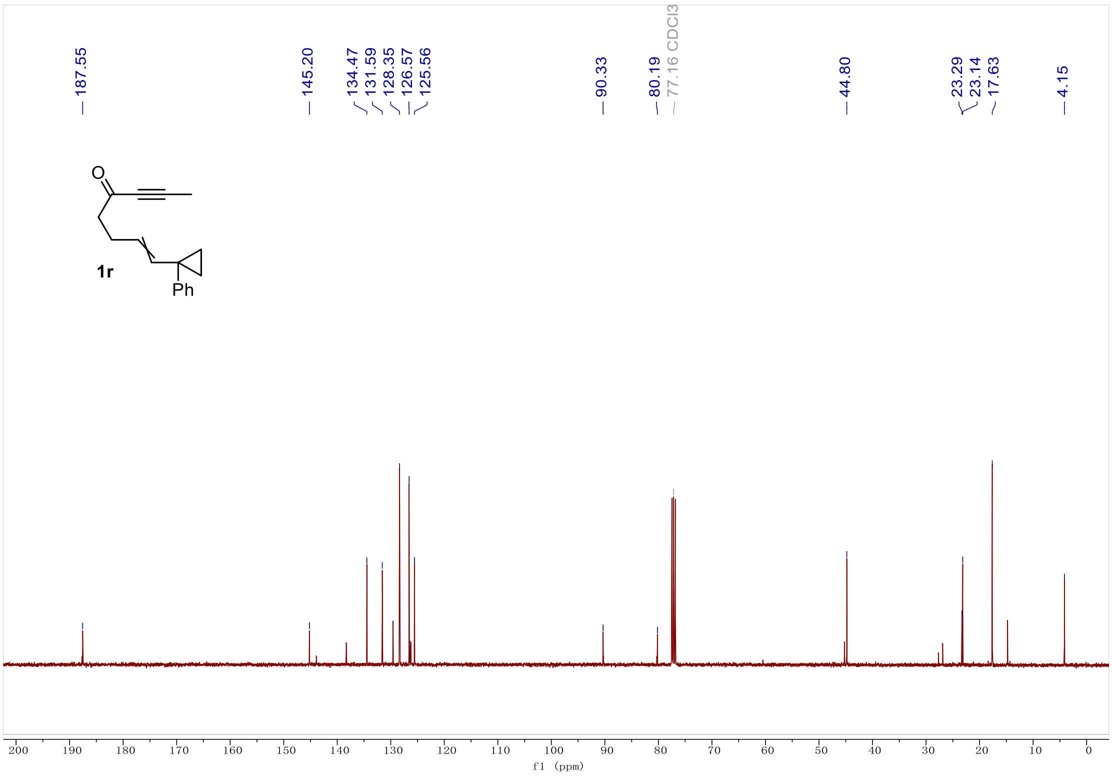
^{13}C NMR in $CDCl_3$, 101 MHz



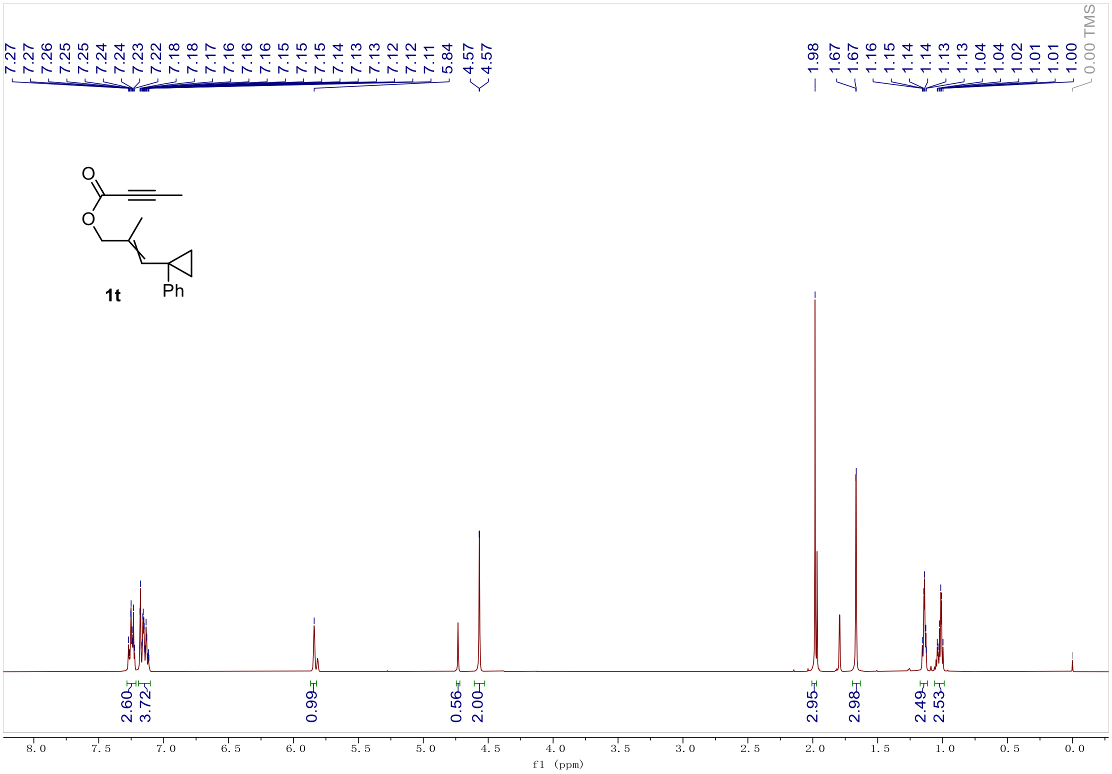
^{1}H NMR in CDCl$_3$, 400 MHz



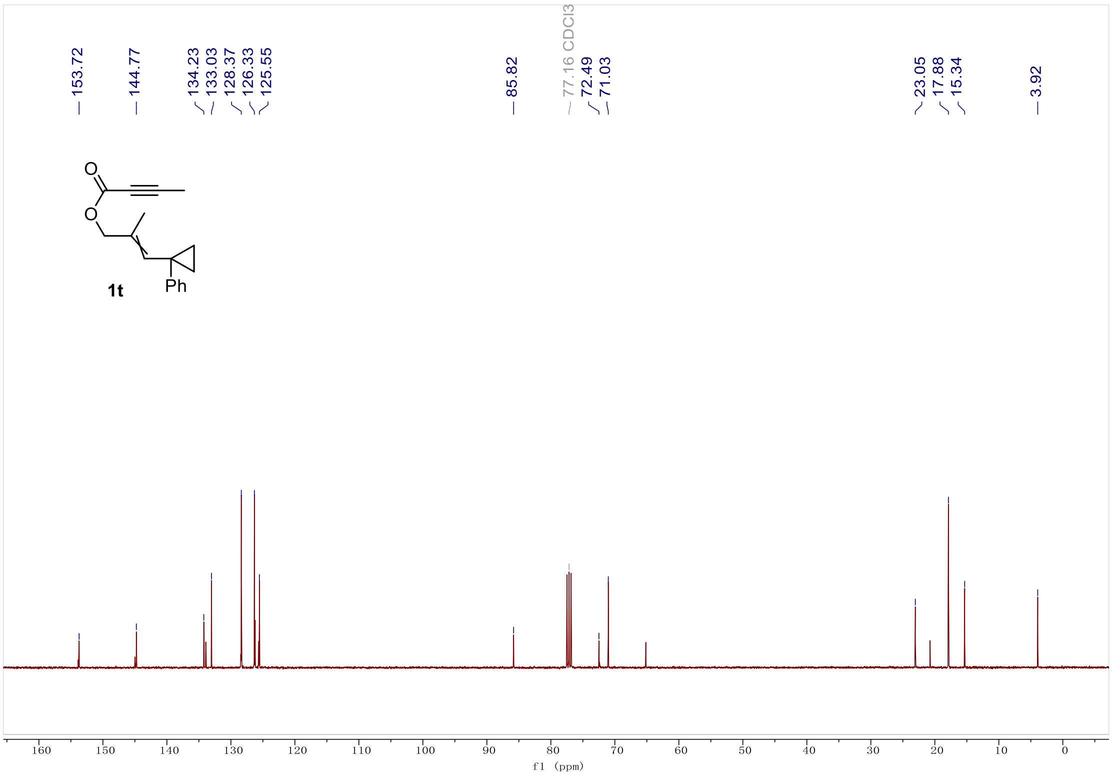
^{13}C NMR in CDCl$_3$, 101 MHz



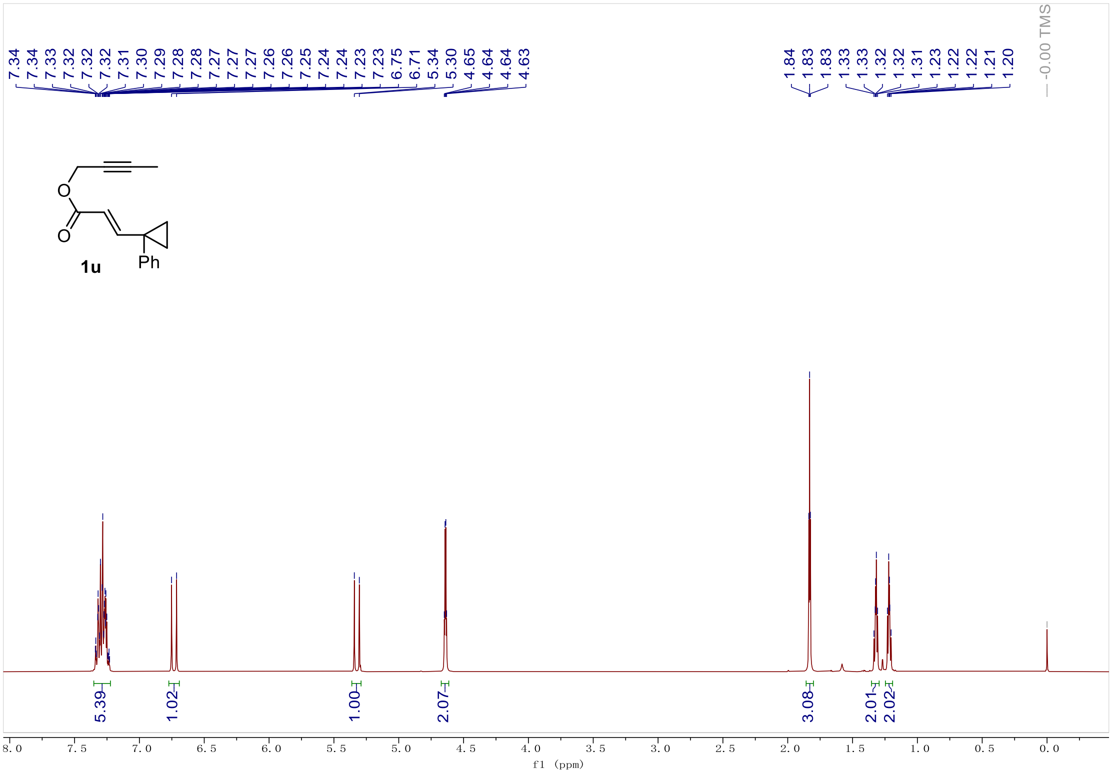
^{1}H NMR in CDCl$_3$, 400 MHz



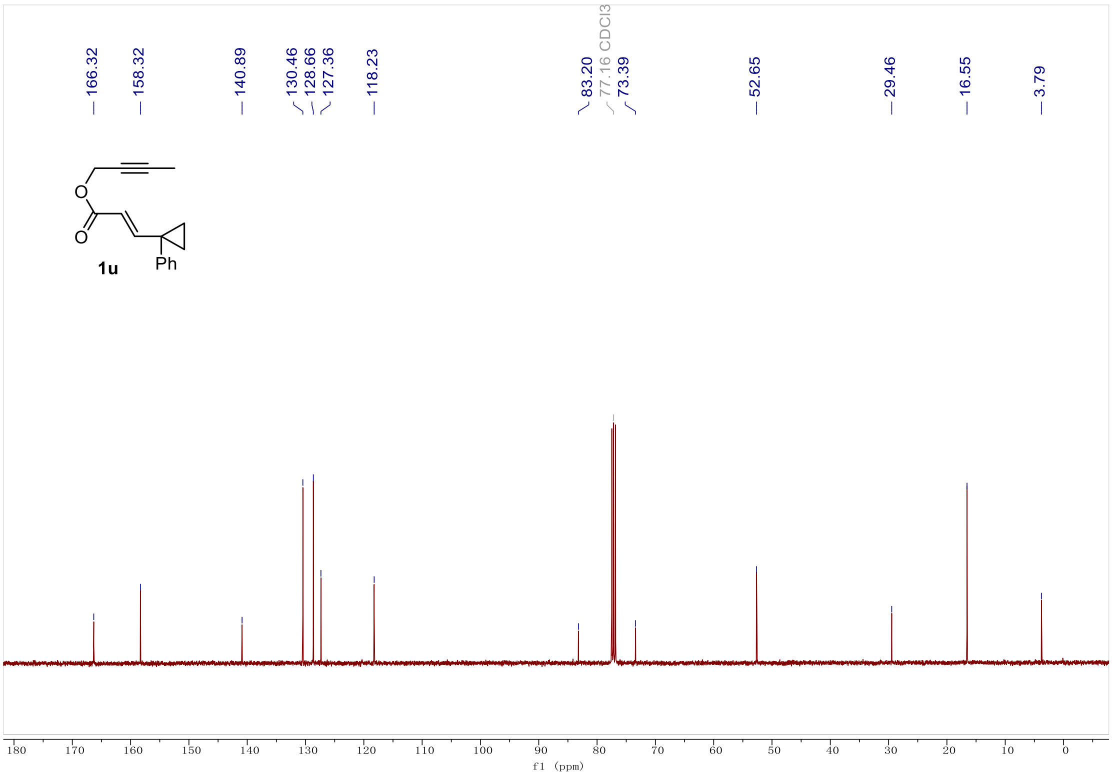
^{13}C NMR in CDCl$_3$, 101 MHz



^1H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz



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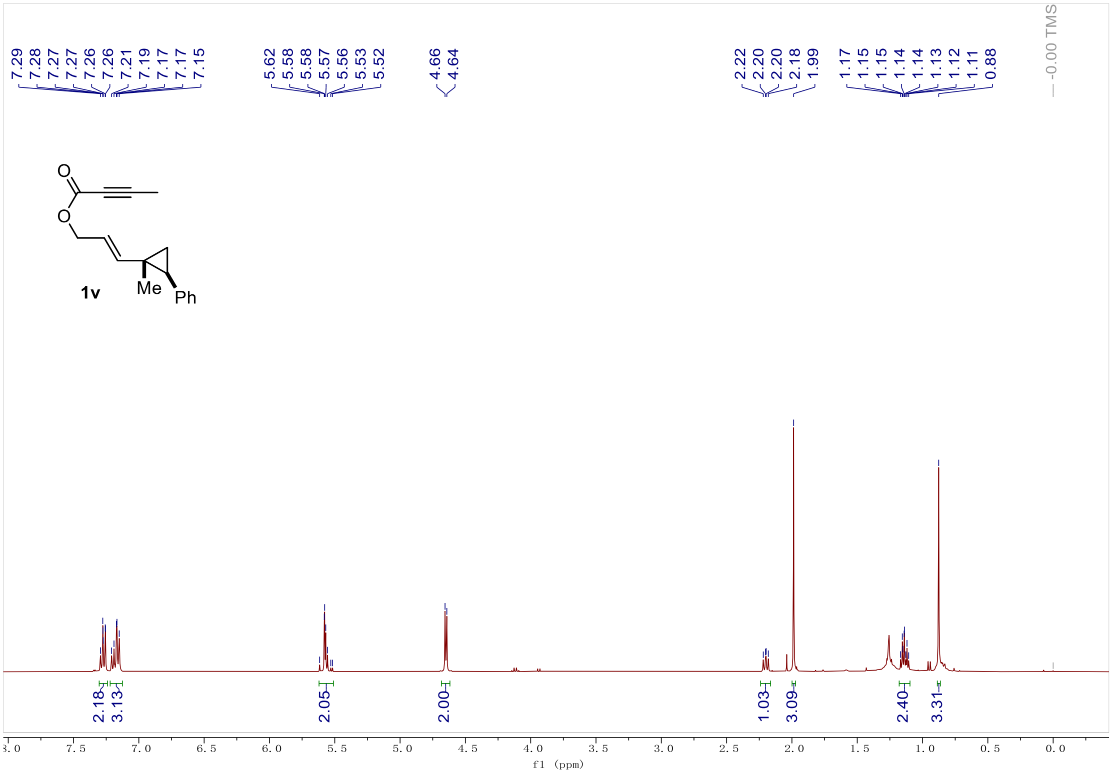
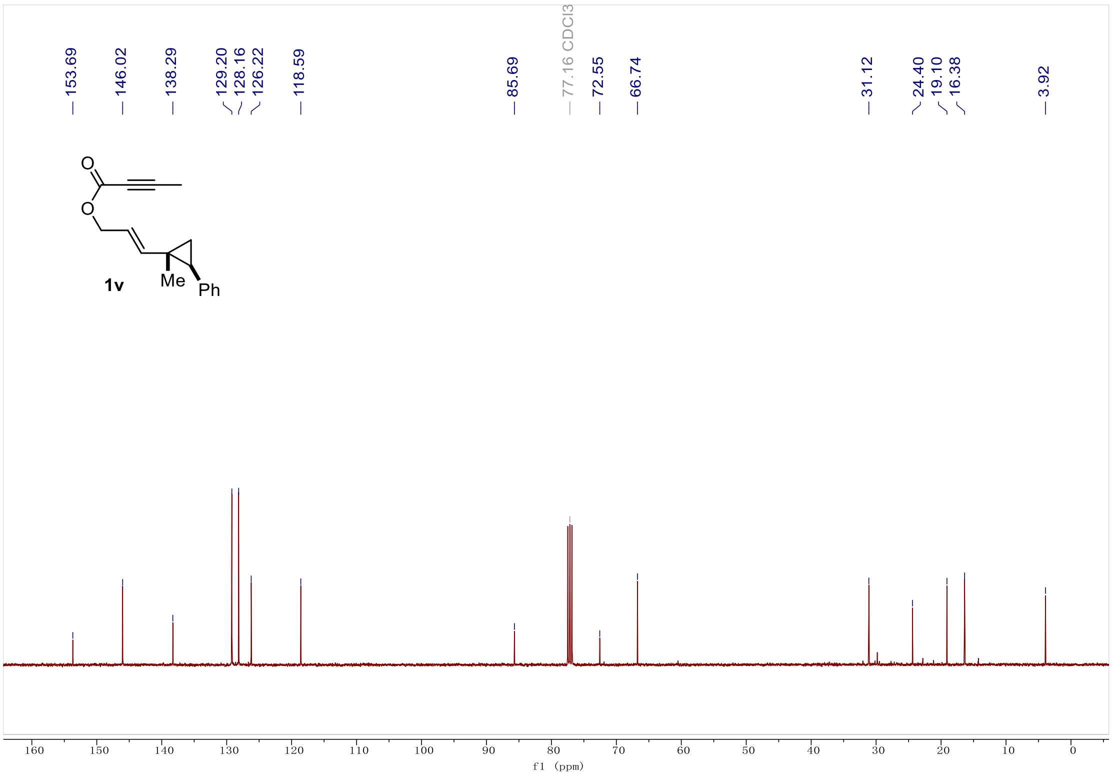


^{13}C NMR in CDCl$_3$, 101 MHz



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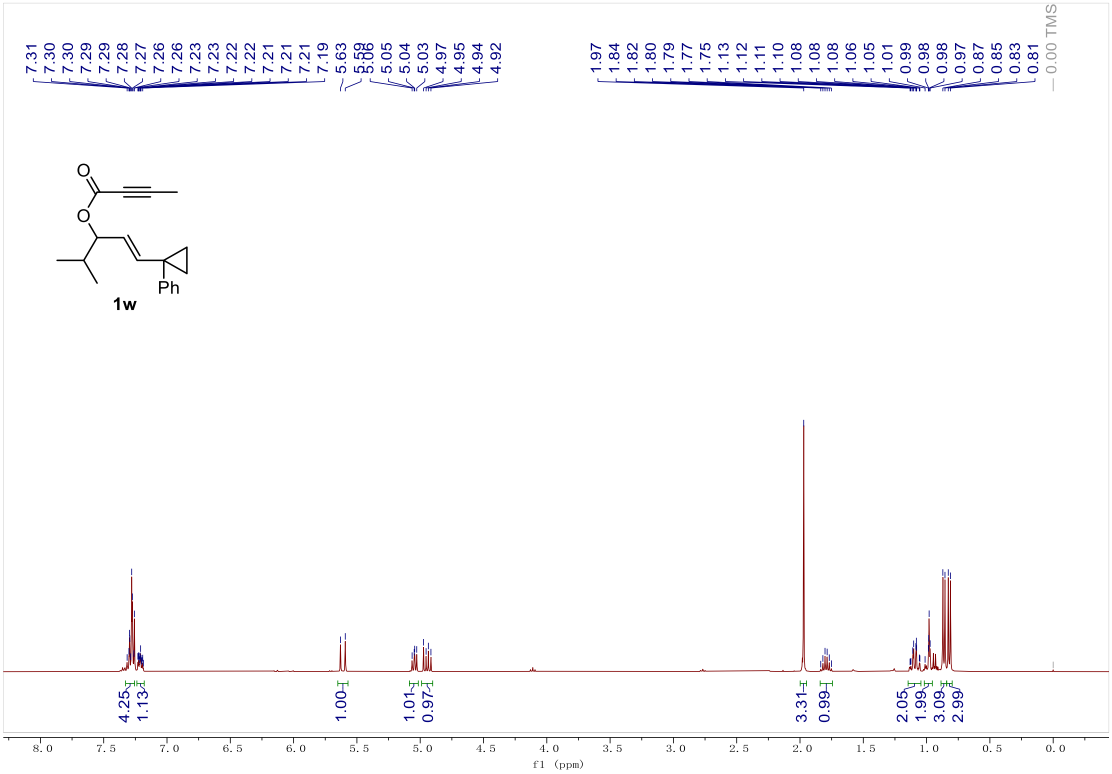
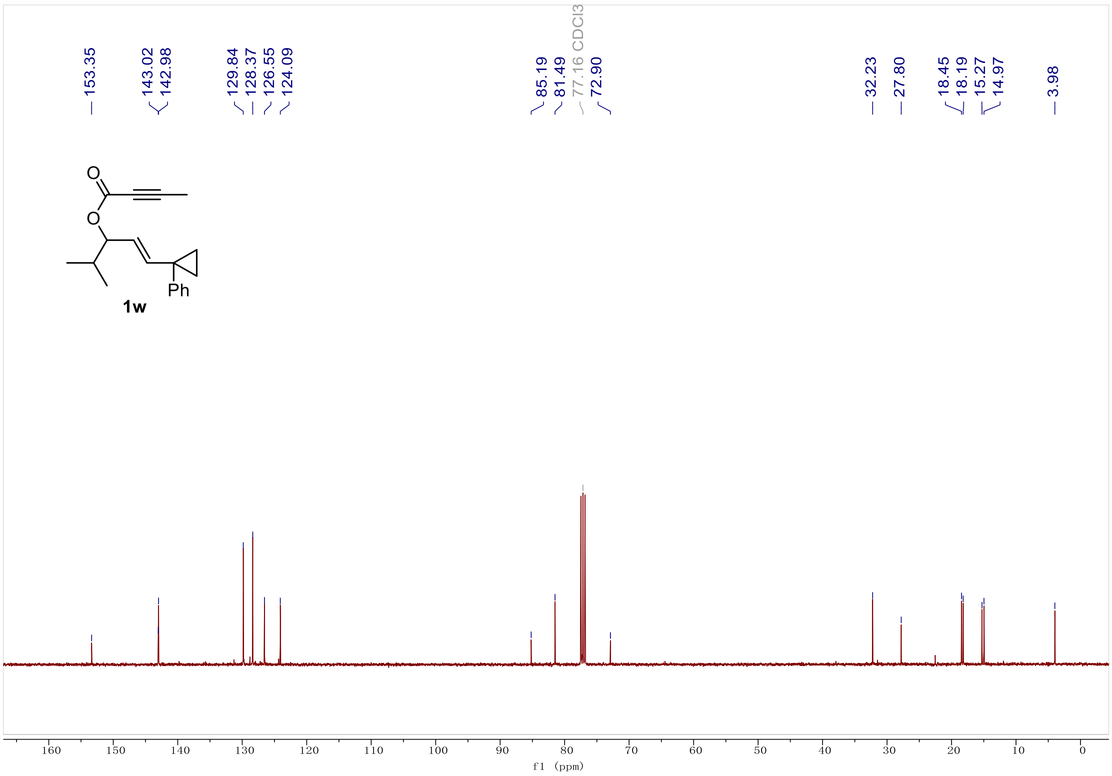
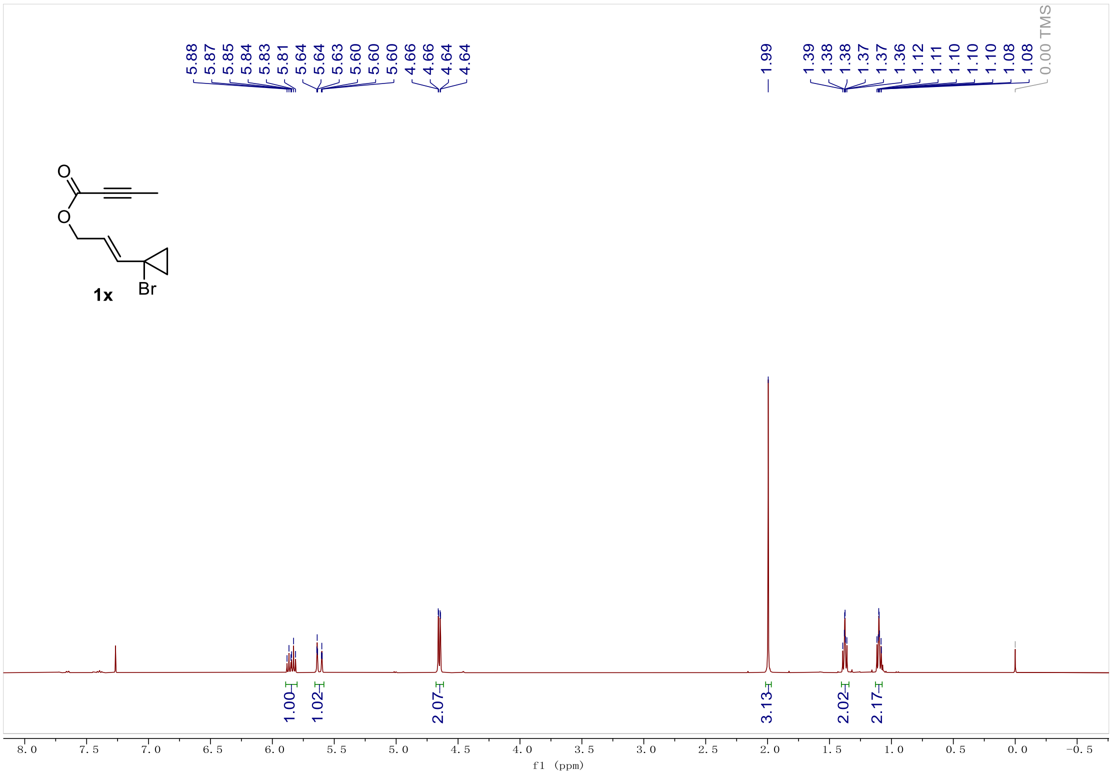


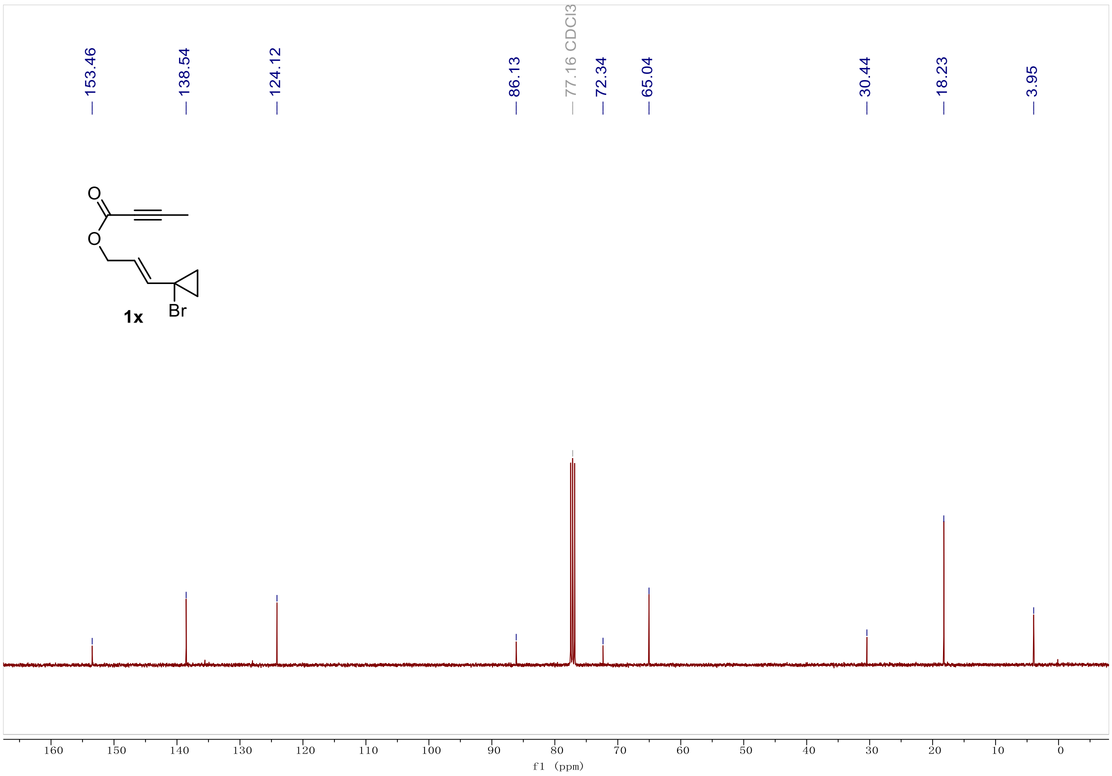
^{13}C NMR in $CDCl_3$, 101 MHz



^1H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz



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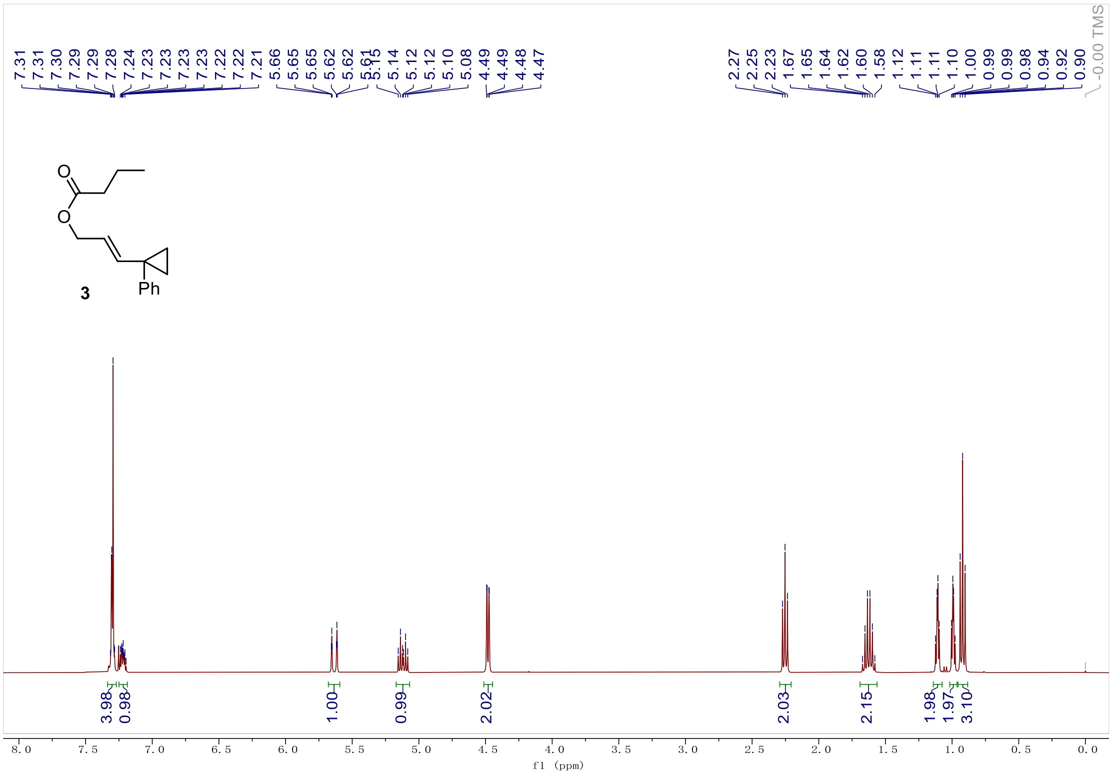

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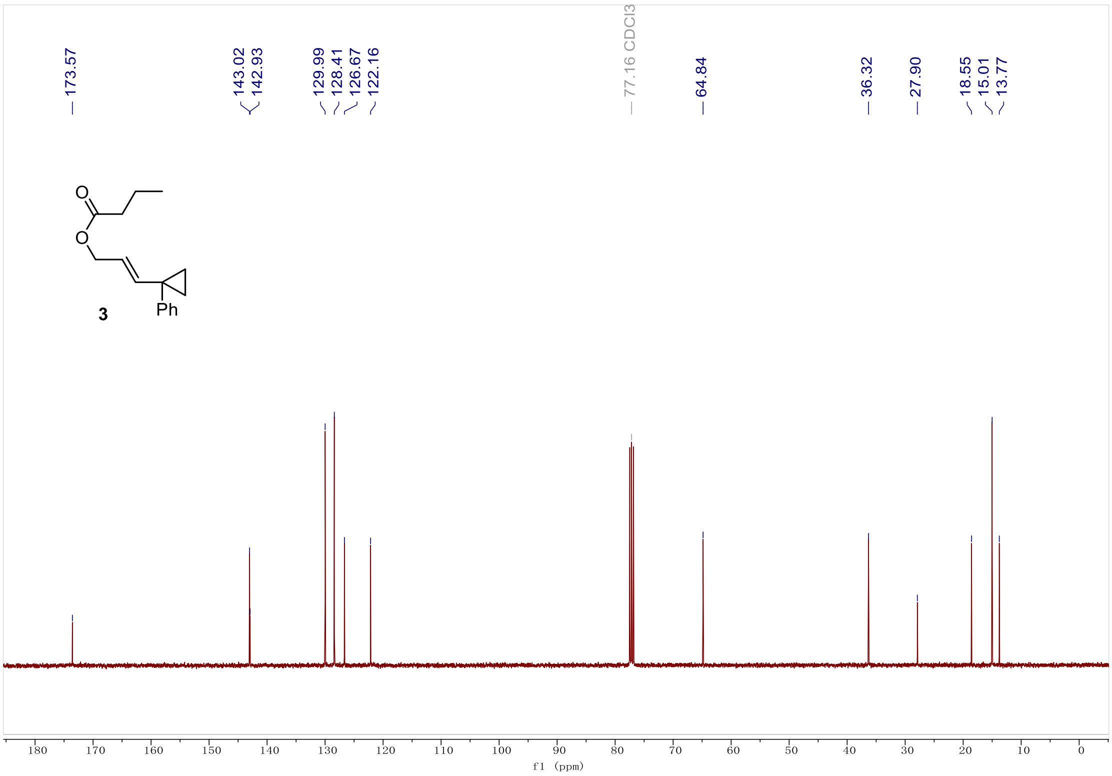

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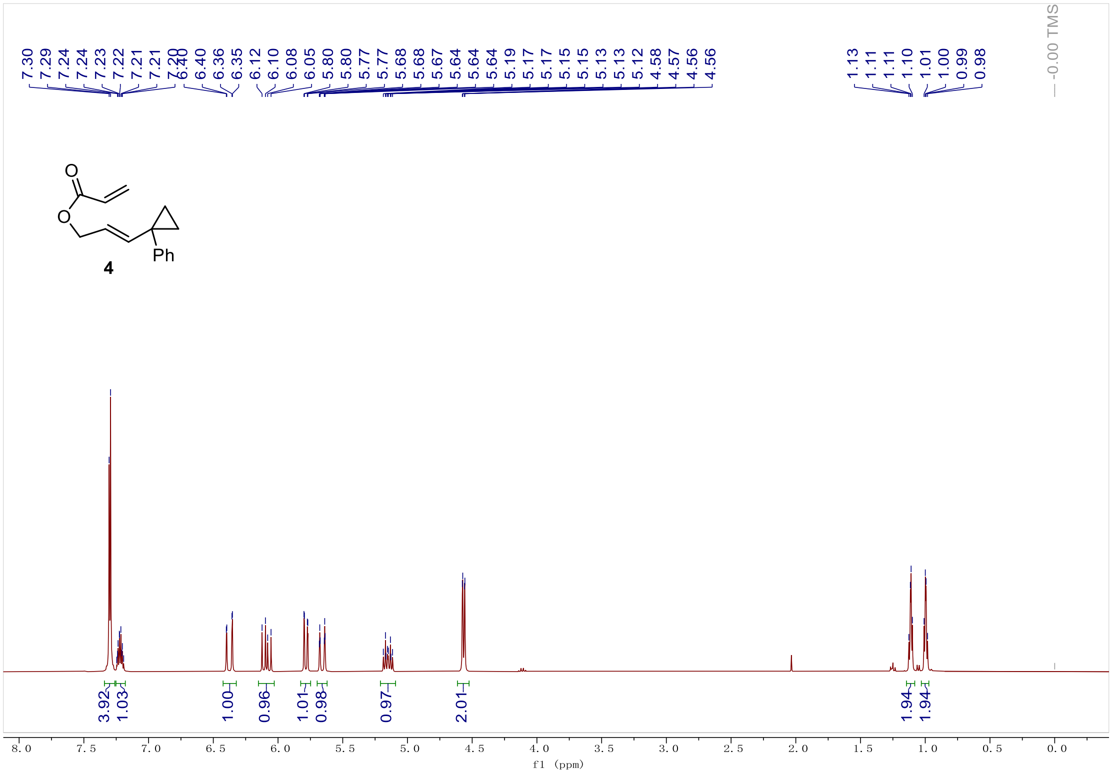

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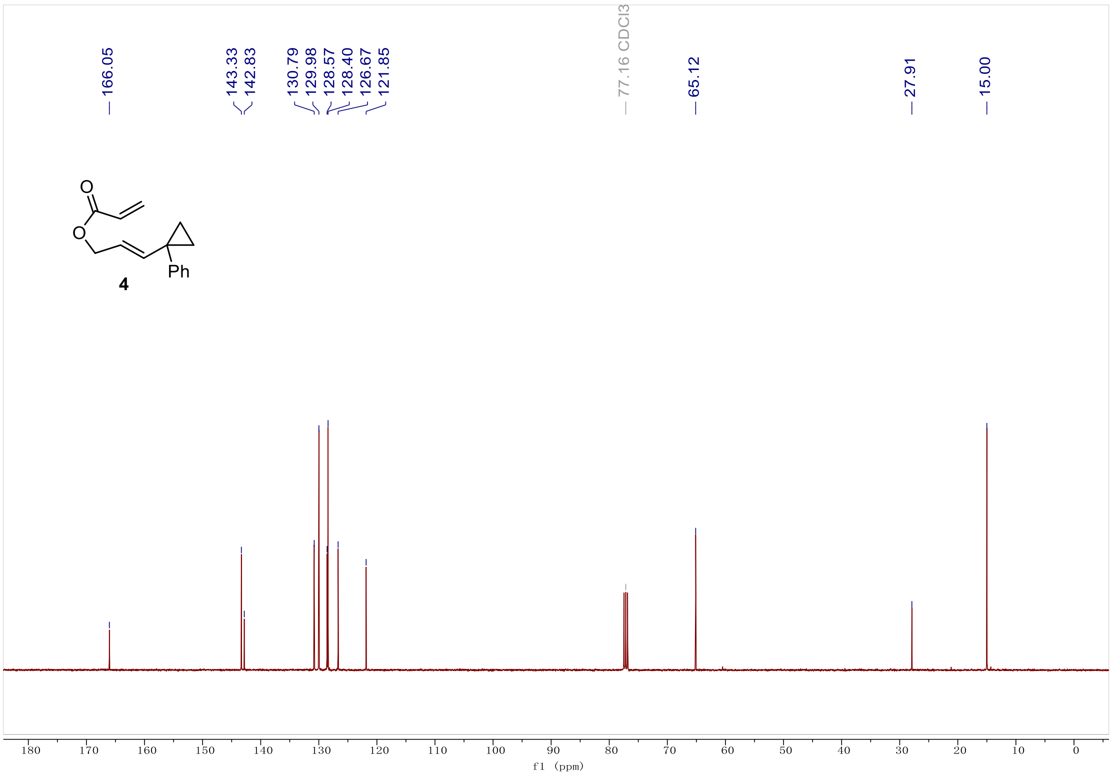

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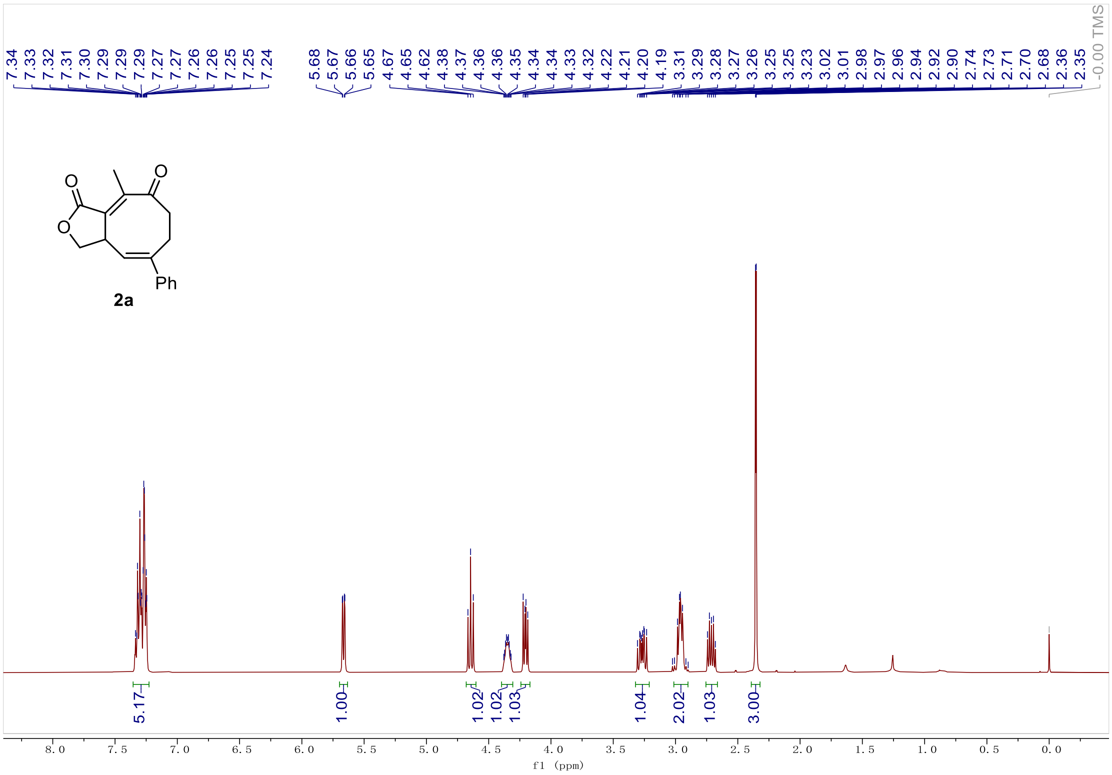
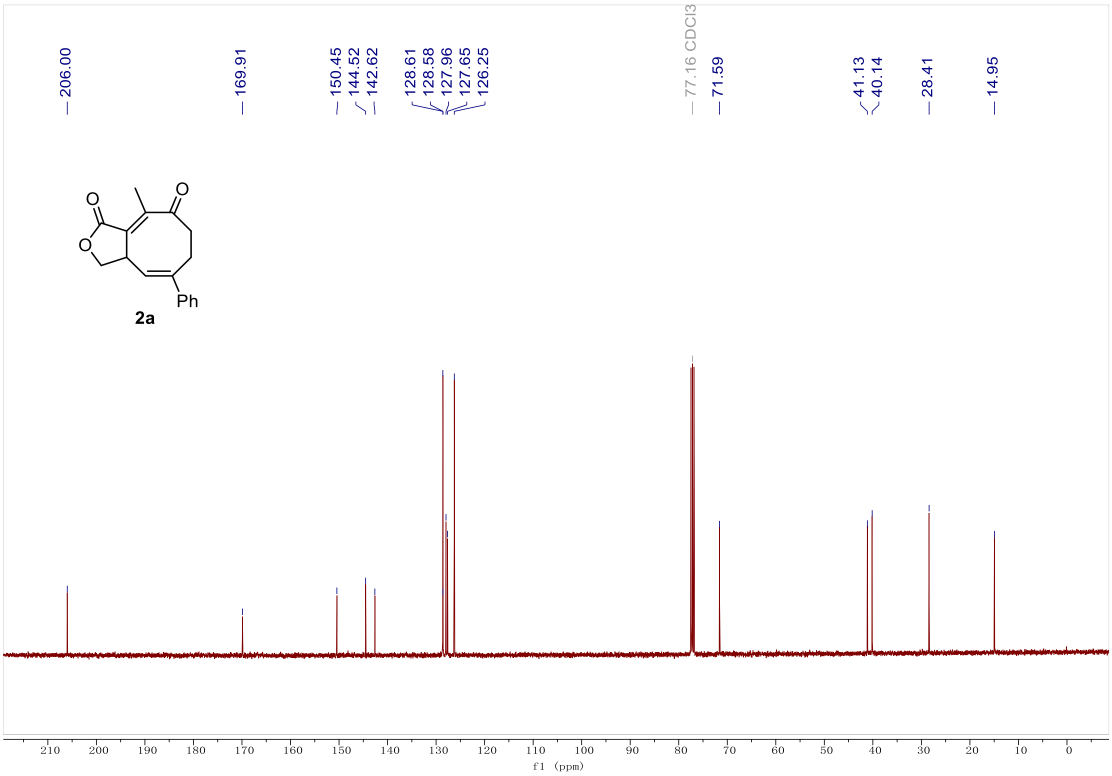


^{13}C NMR in $CDCl_3$, 101 MHz



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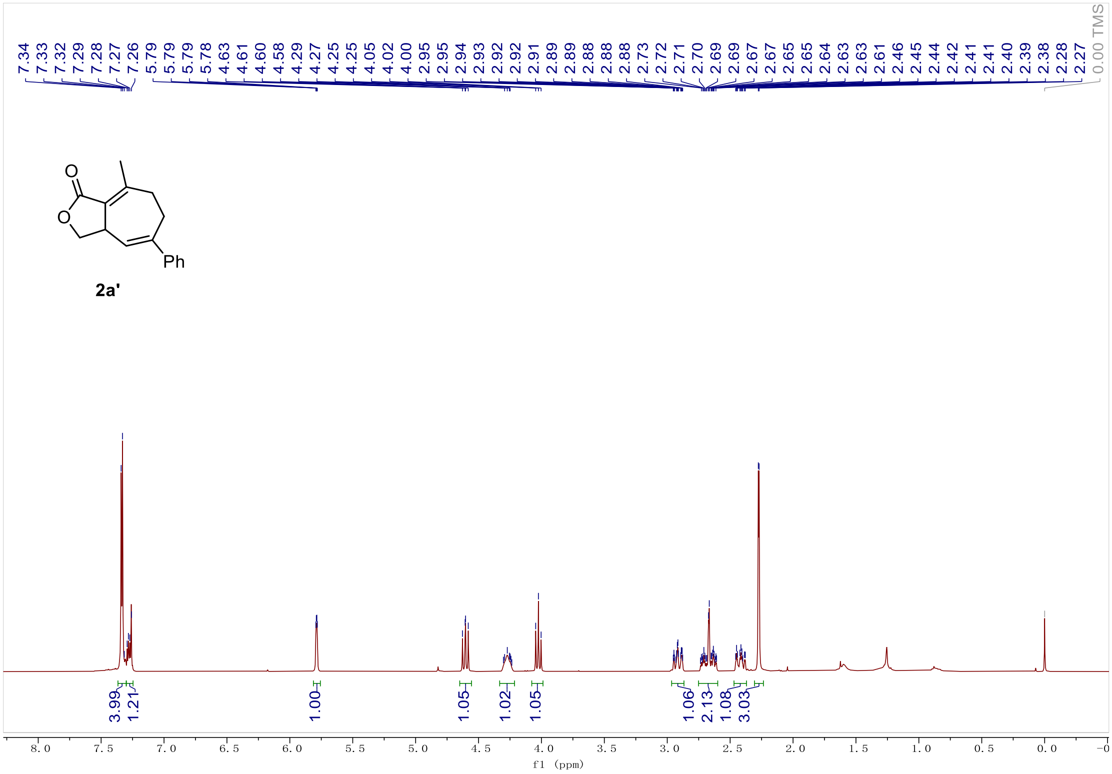

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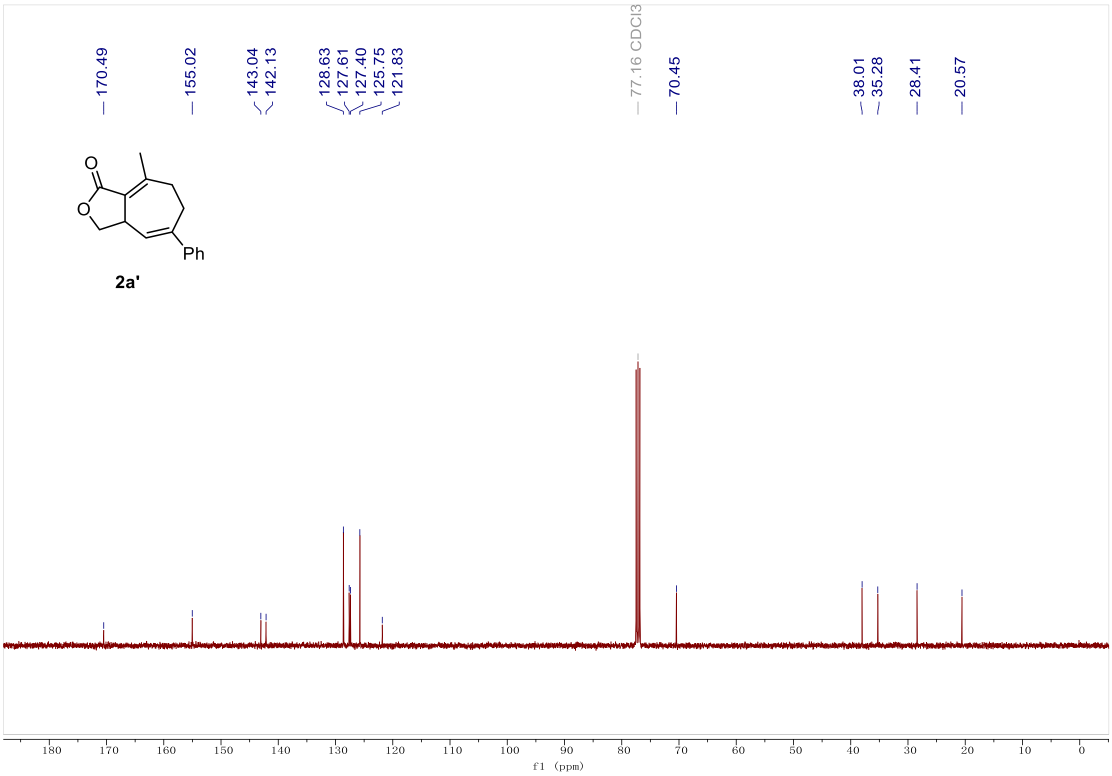

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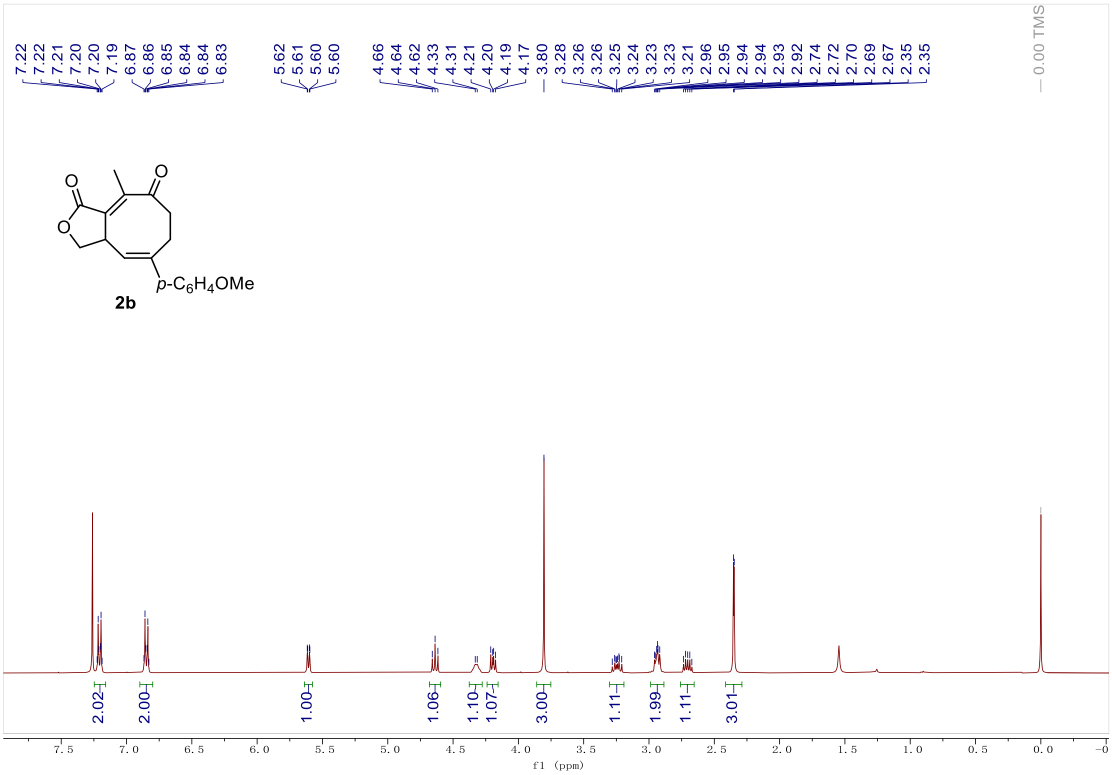

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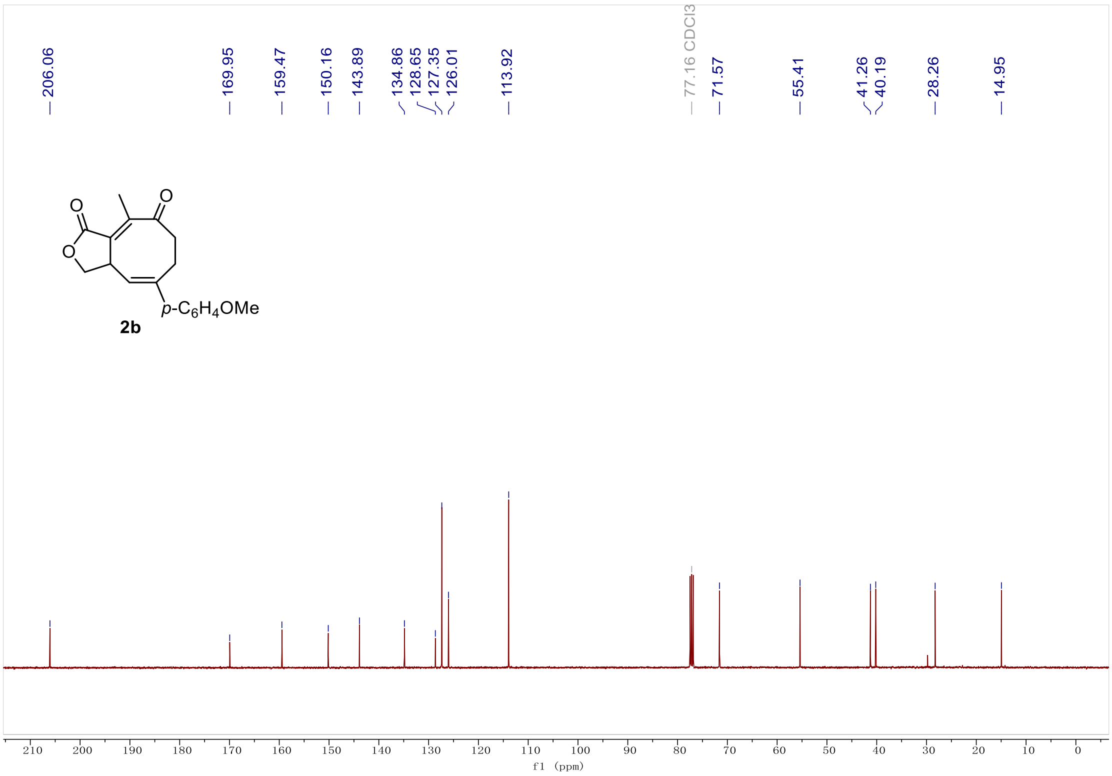

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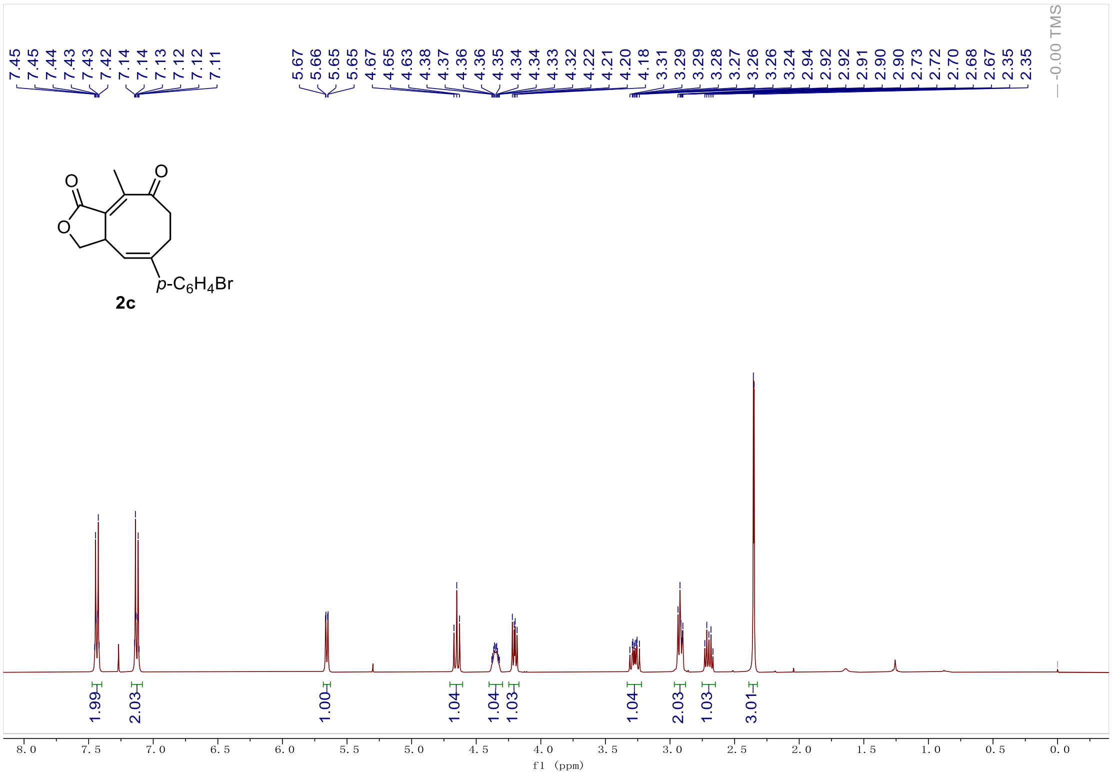

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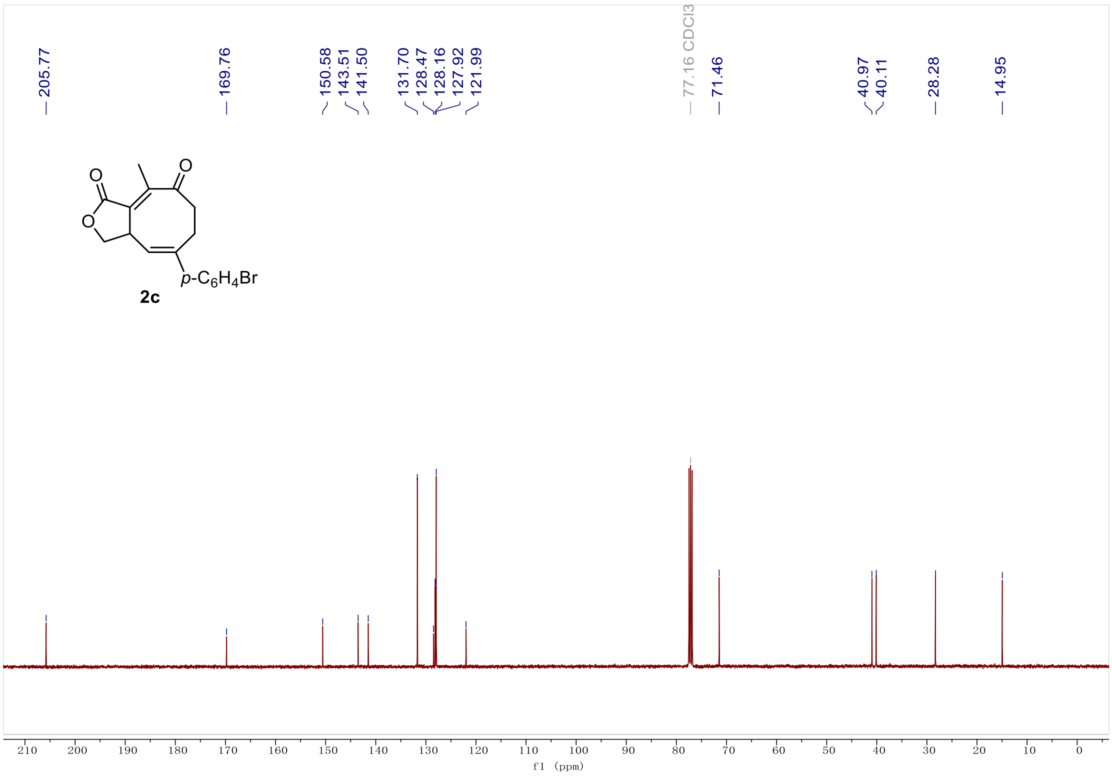

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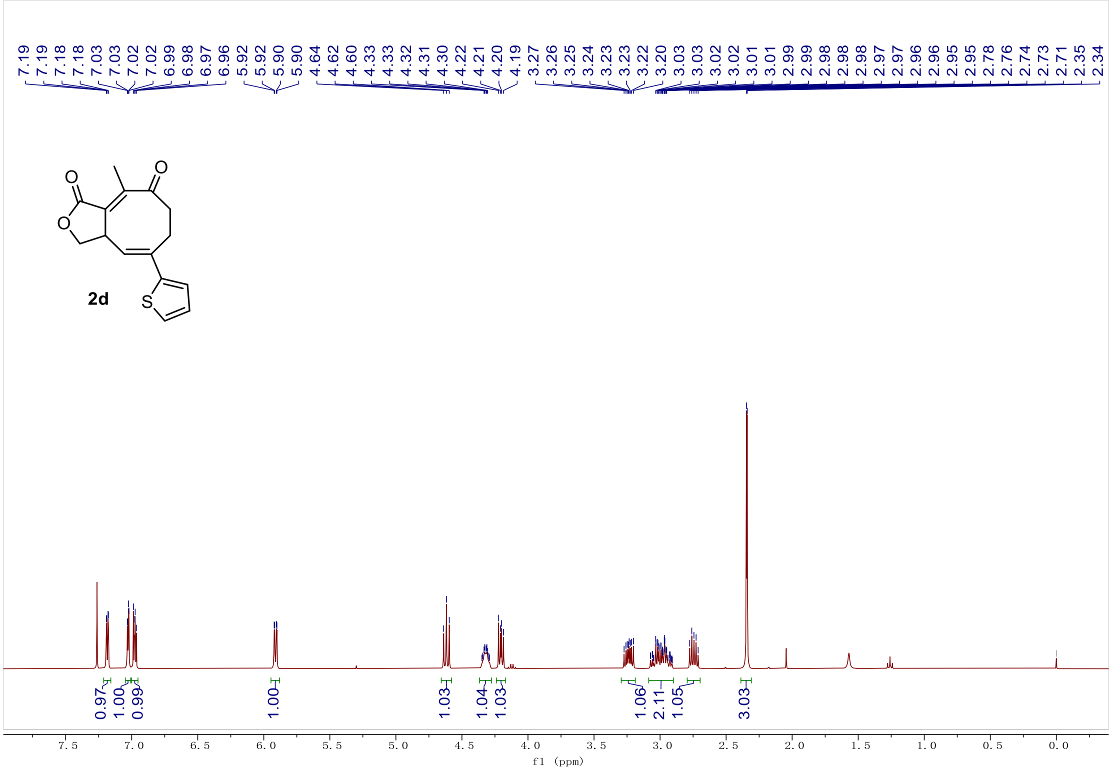

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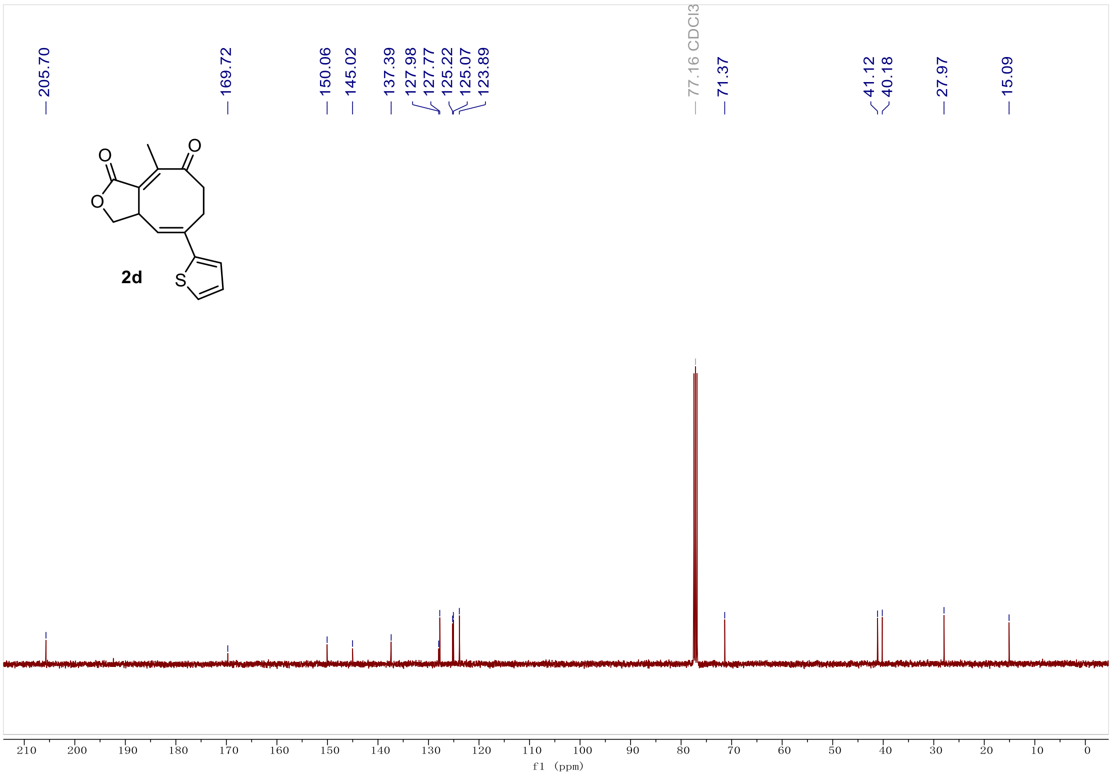
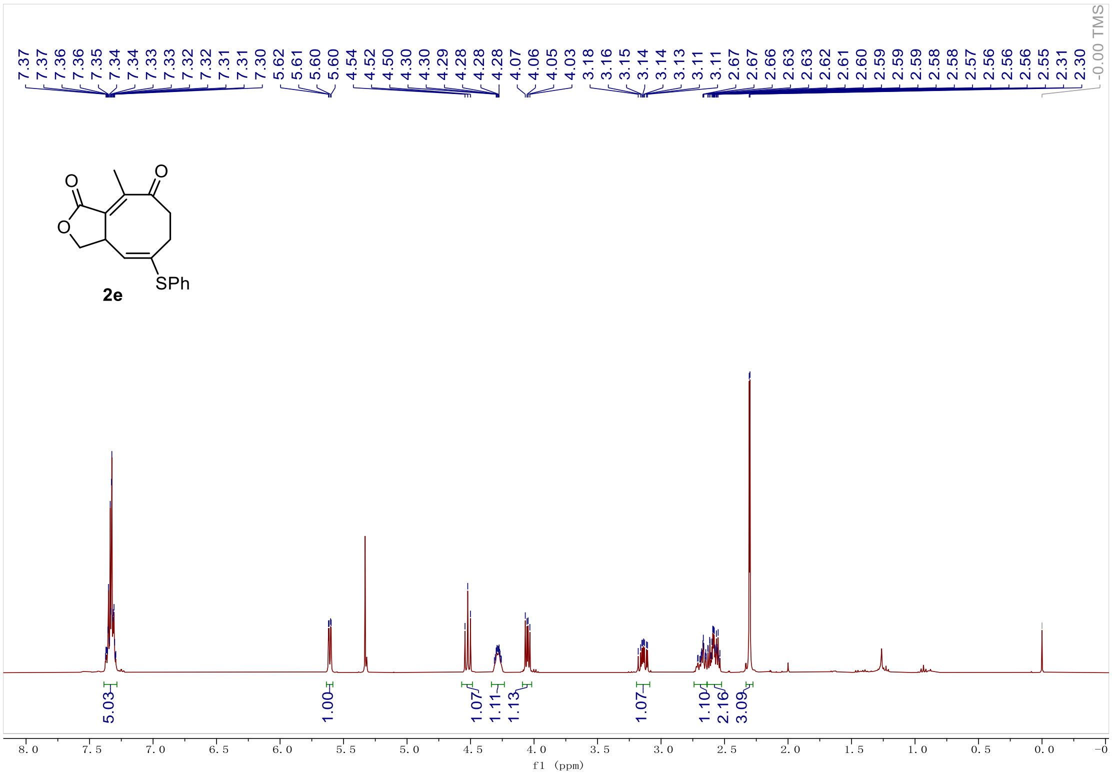
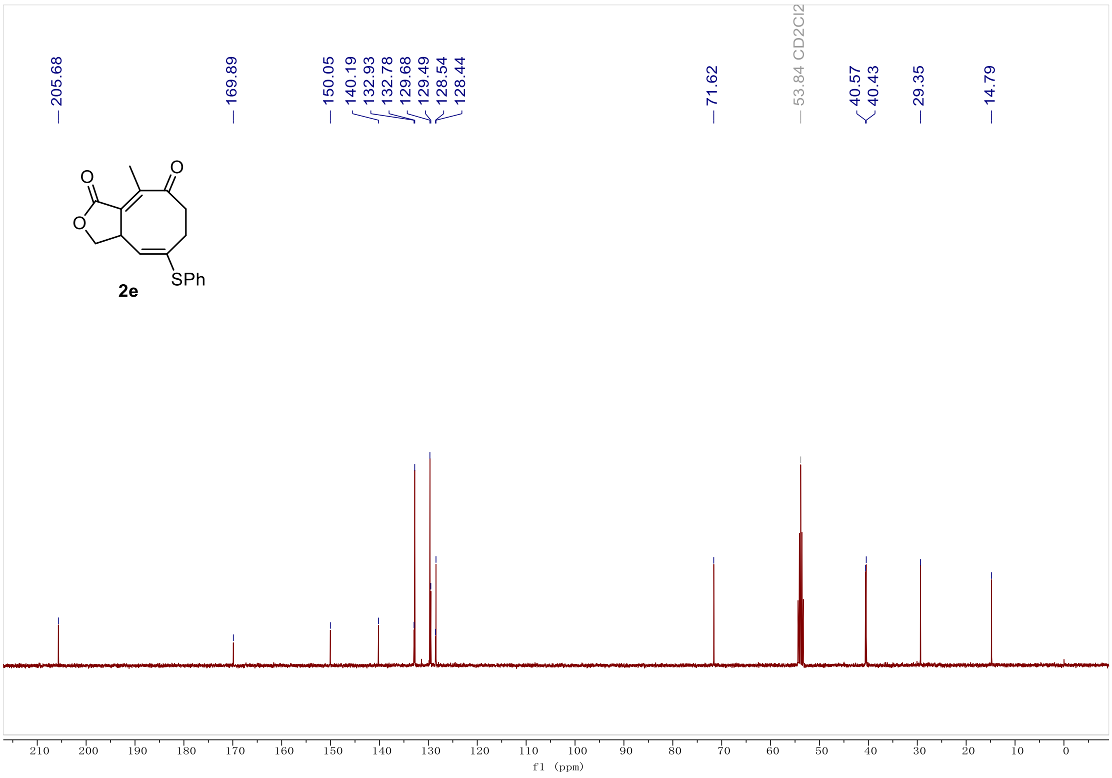


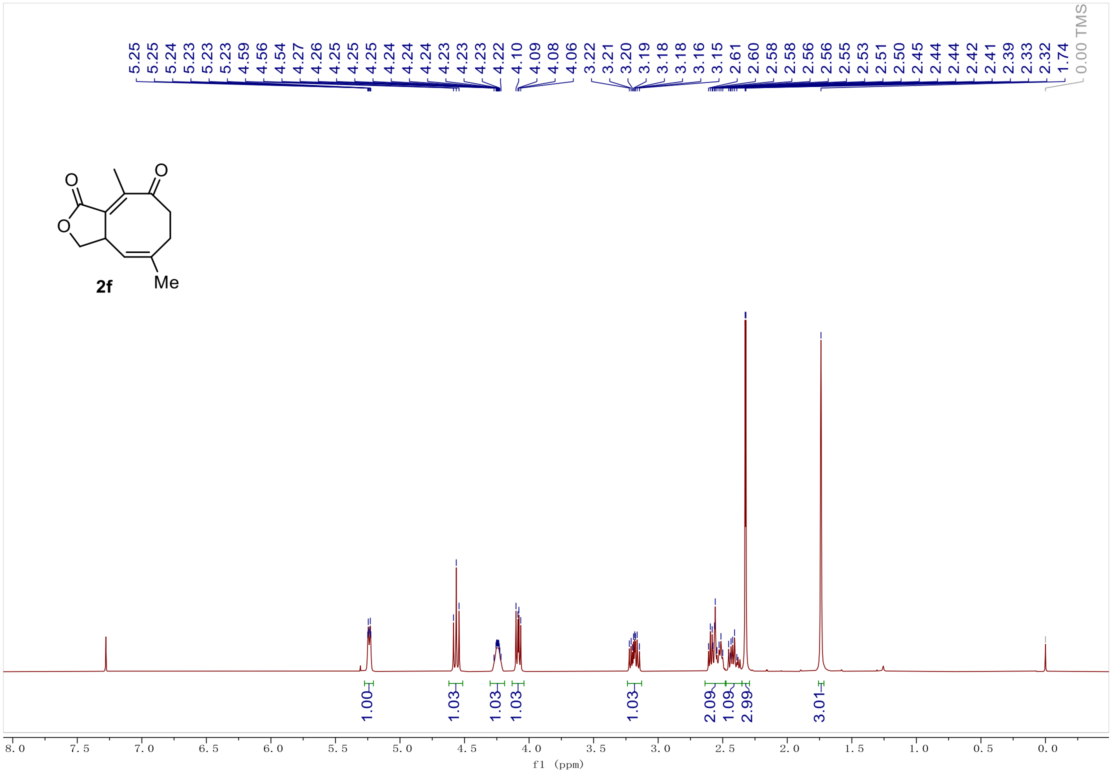
^1H NMR in CD_2Cl_2, 400 MHz



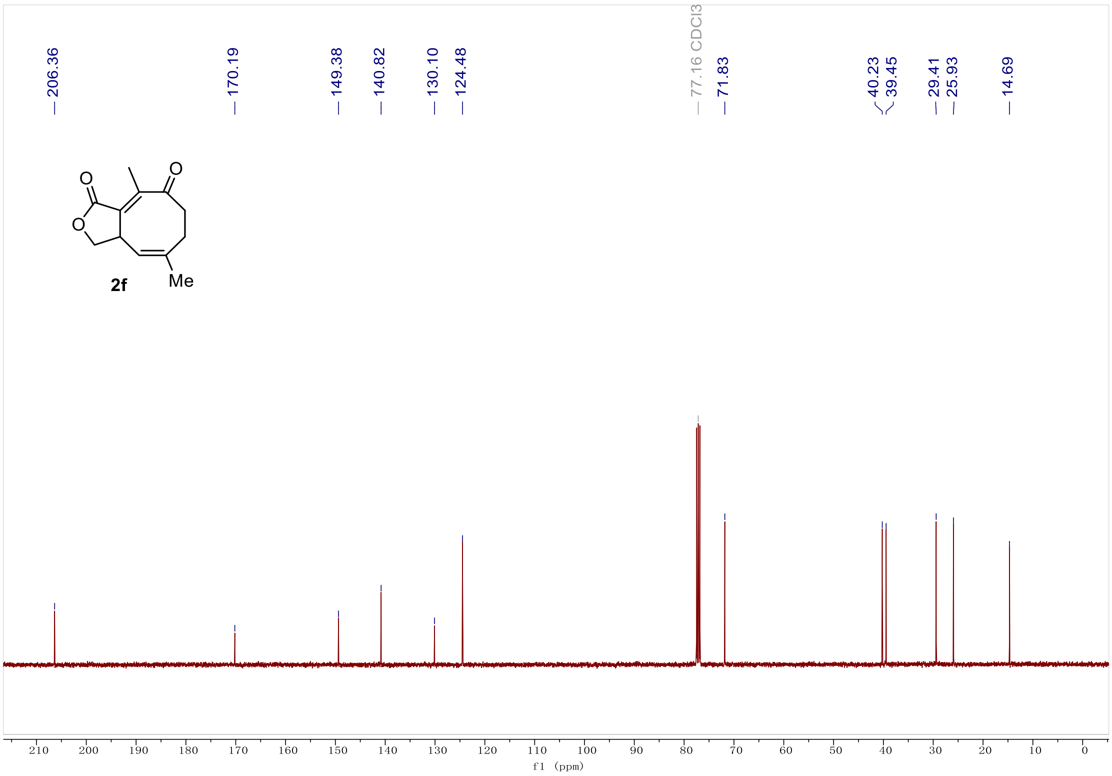
^{13}C NMR in CD_2Cl_2, 101 MHz



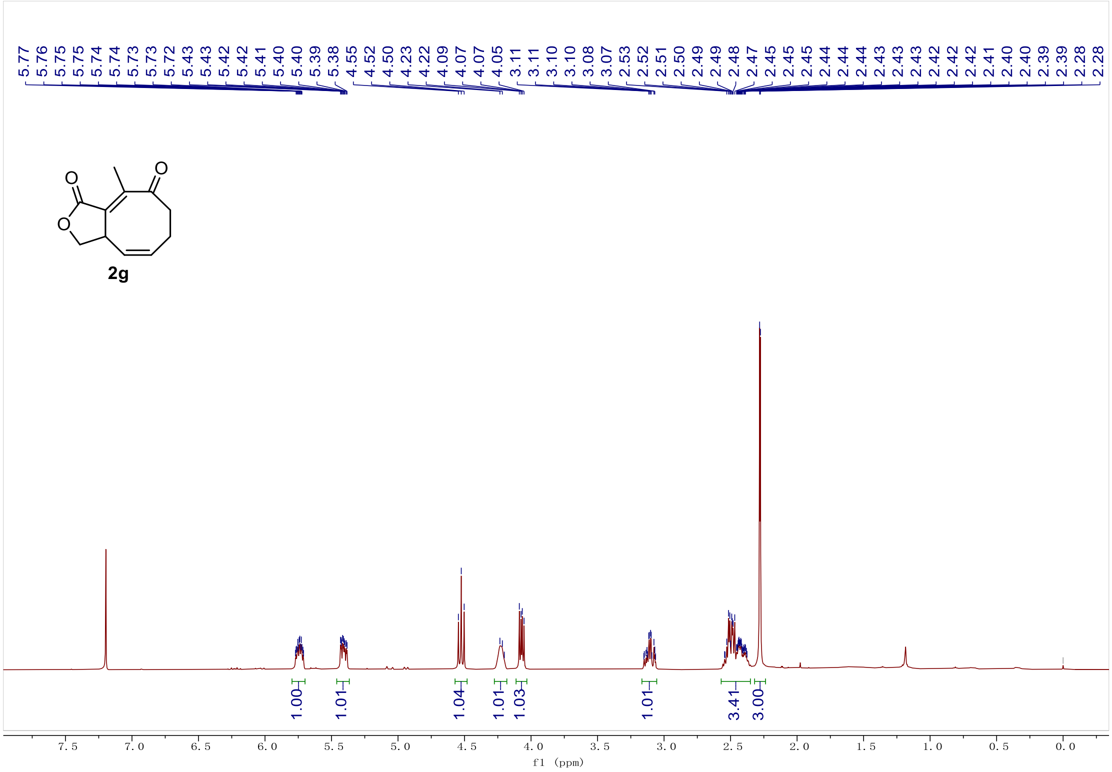
^{1}H NMR in CDCl$_3$, 400 MHz



^{13}C NMR in CDCl$_3$, 101 MHz



^{1}H NMR in $CDCl_3$, 400 MHz



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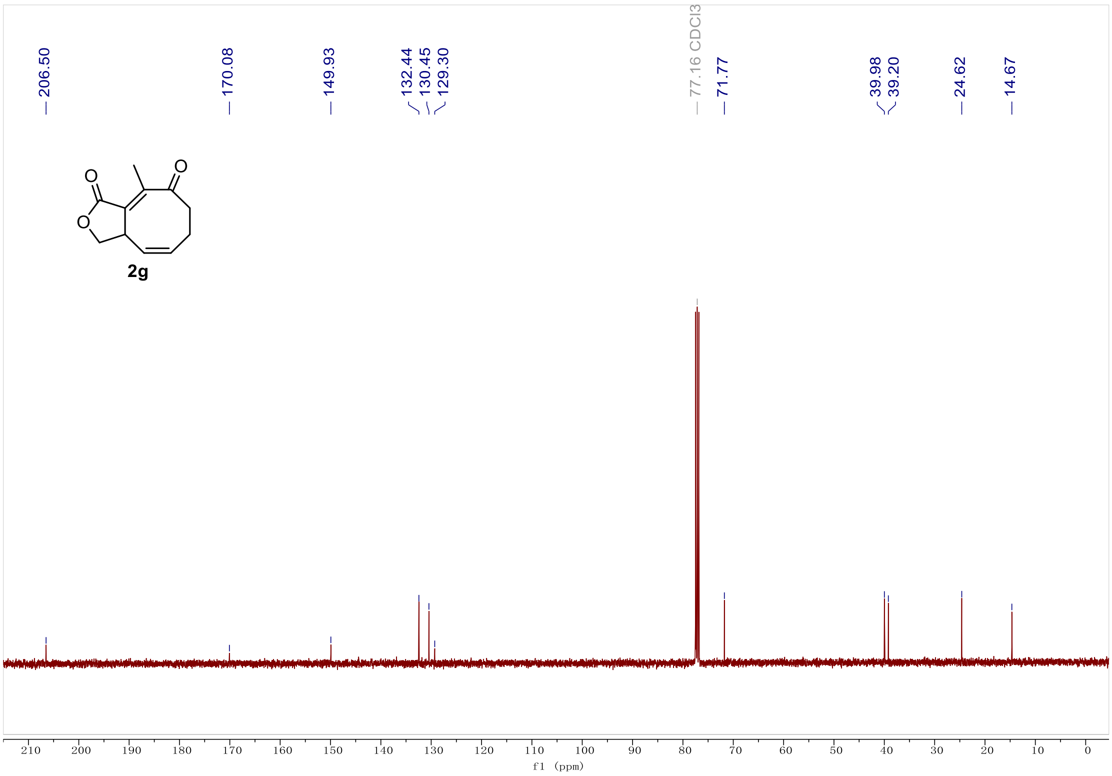

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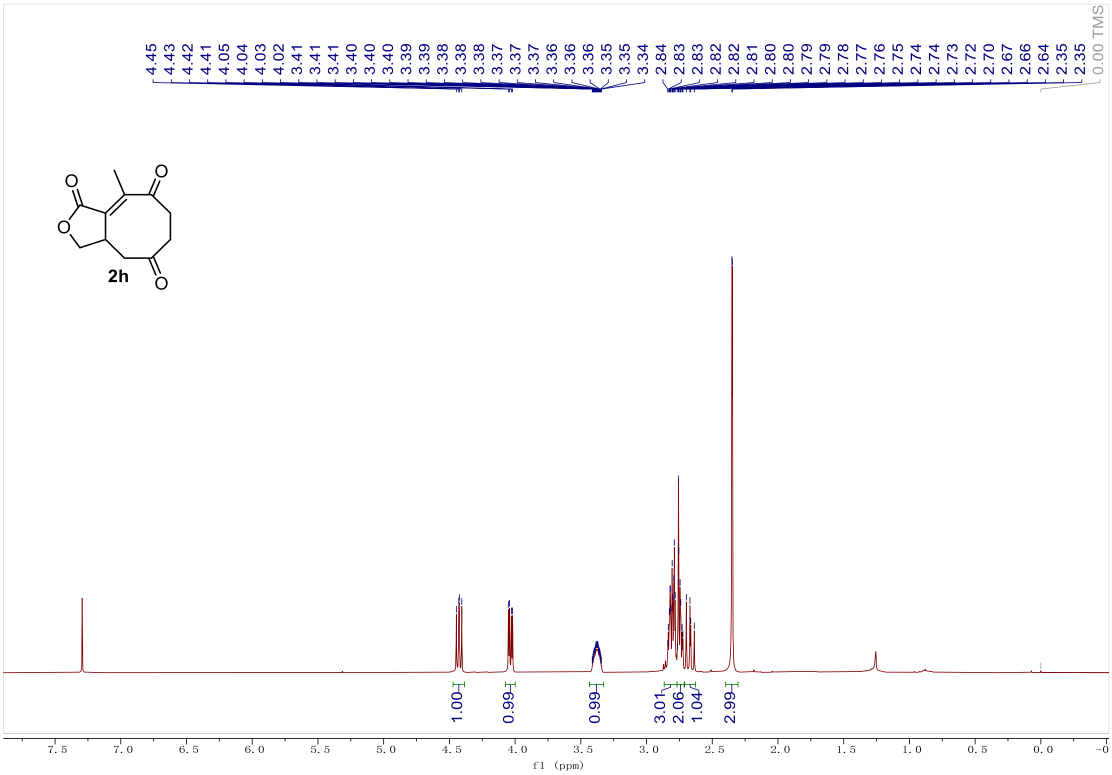

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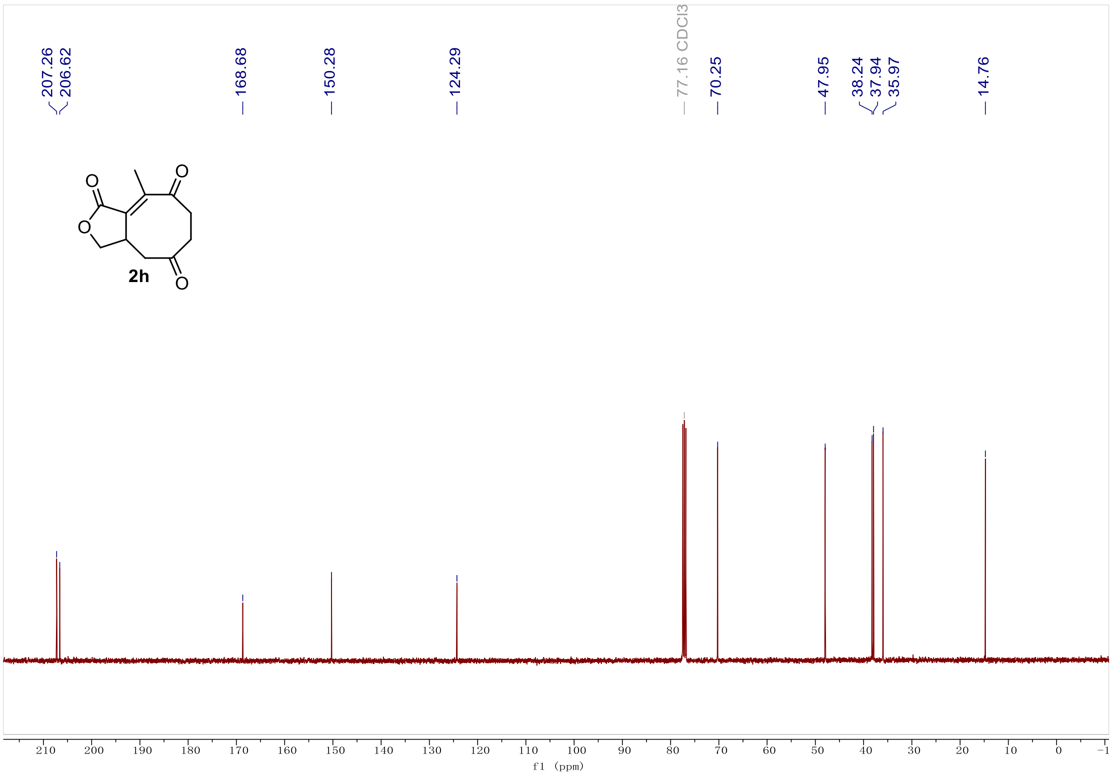

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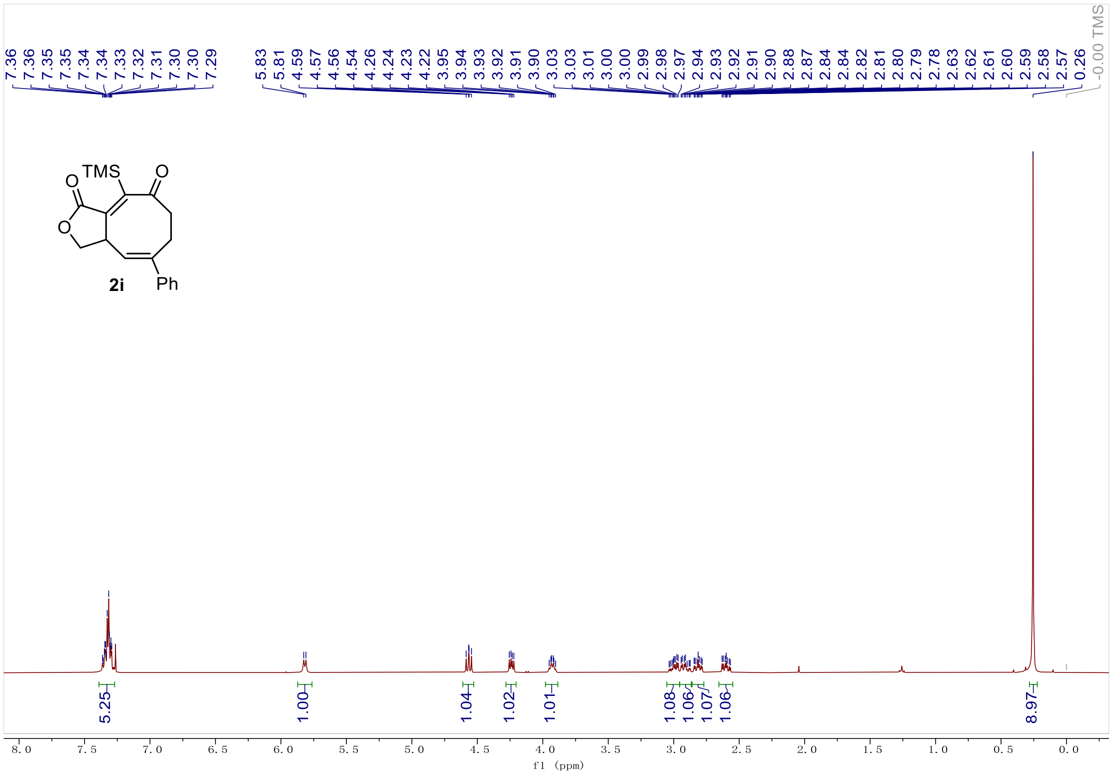

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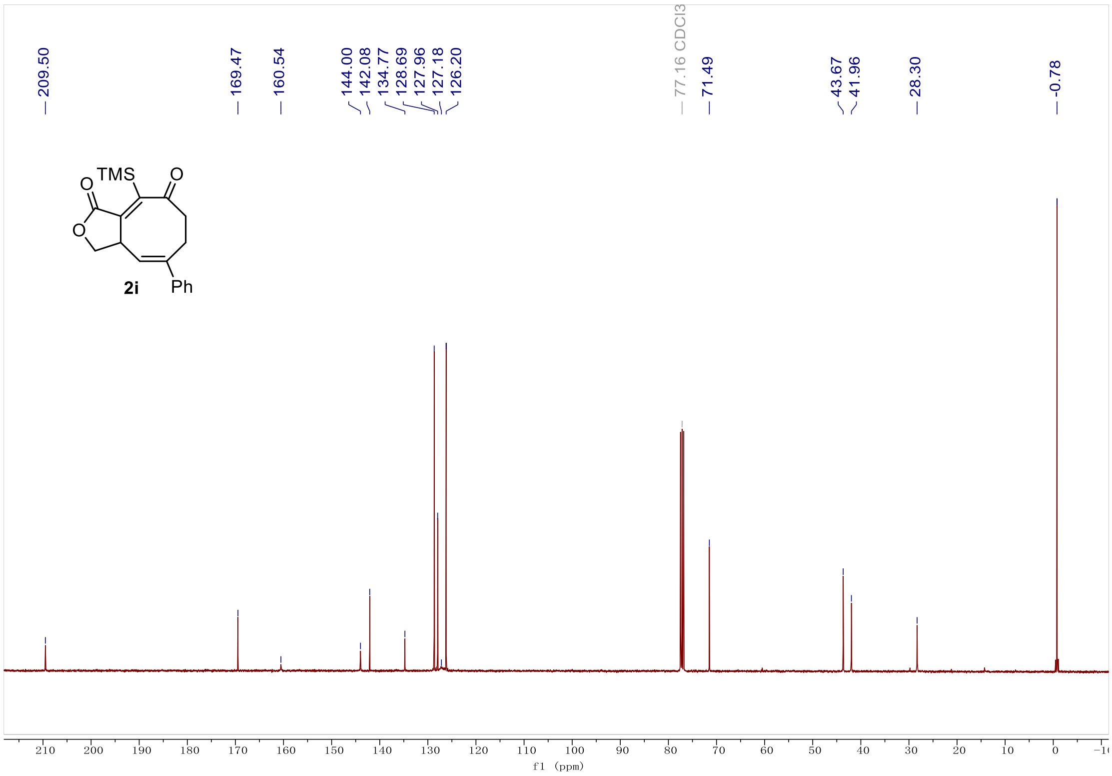

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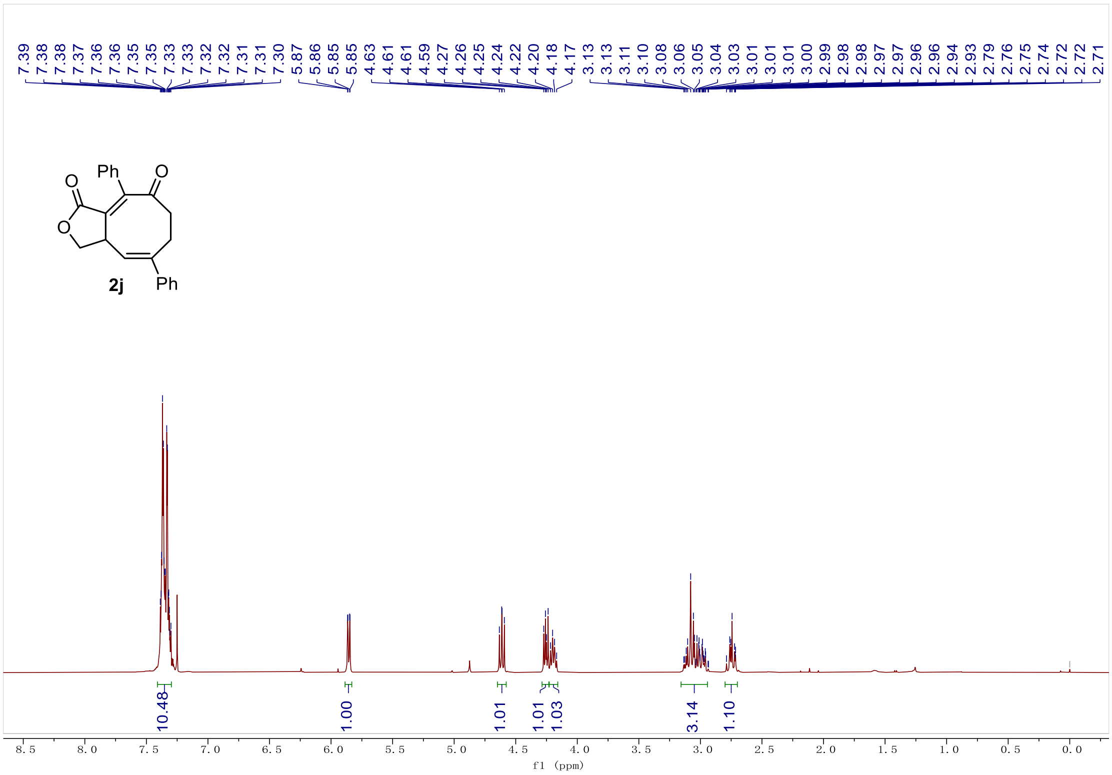

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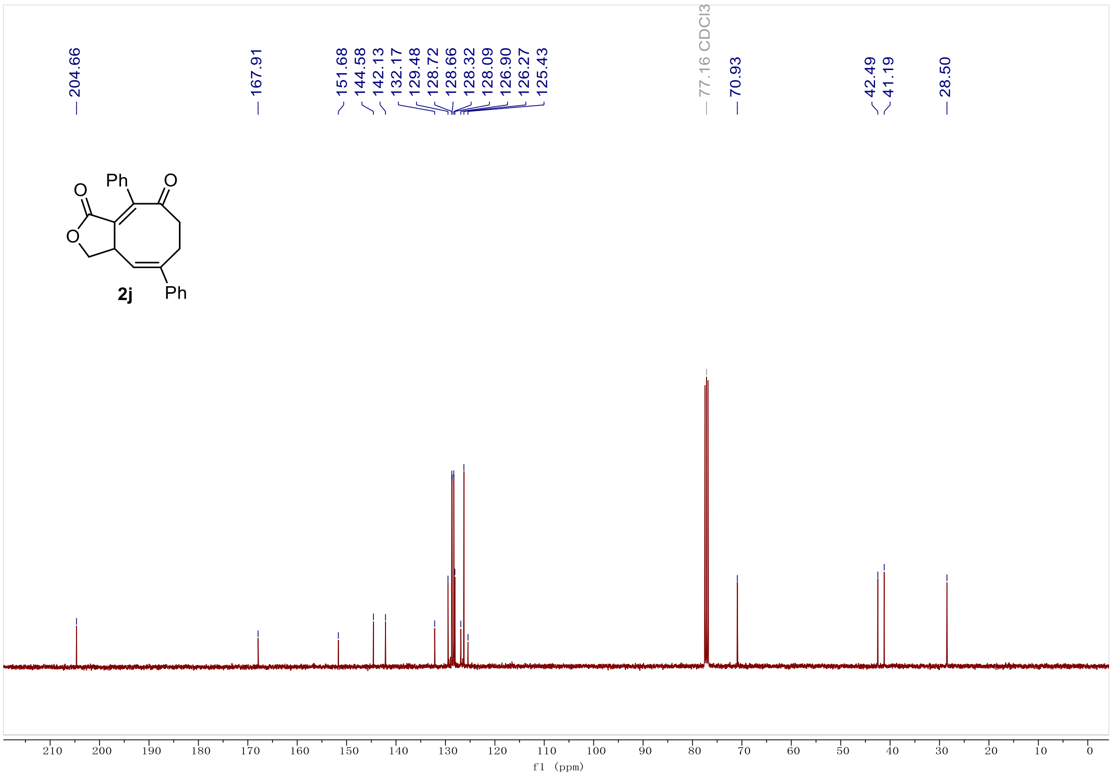

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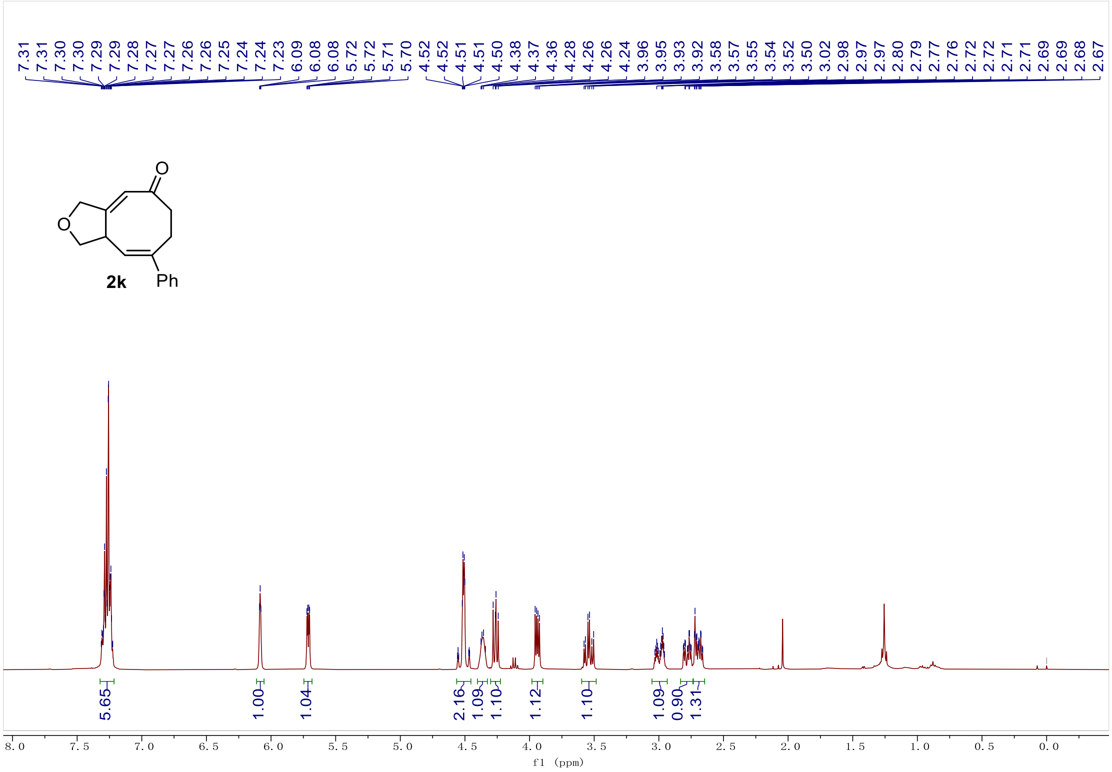

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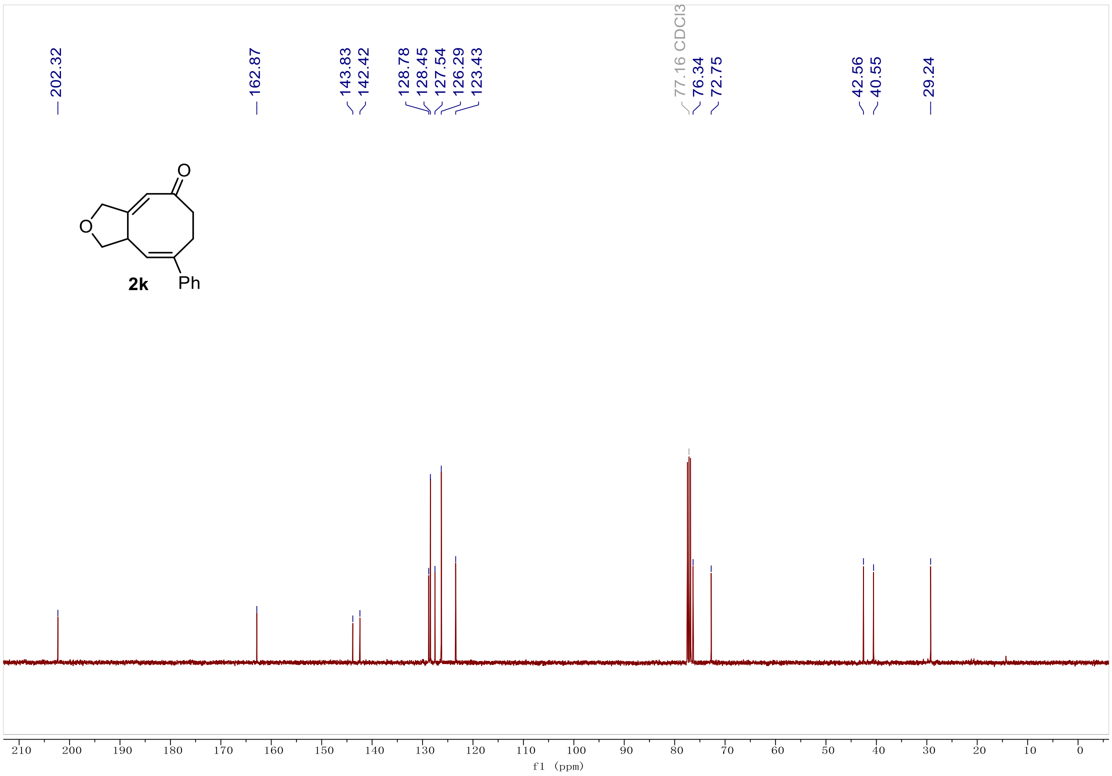

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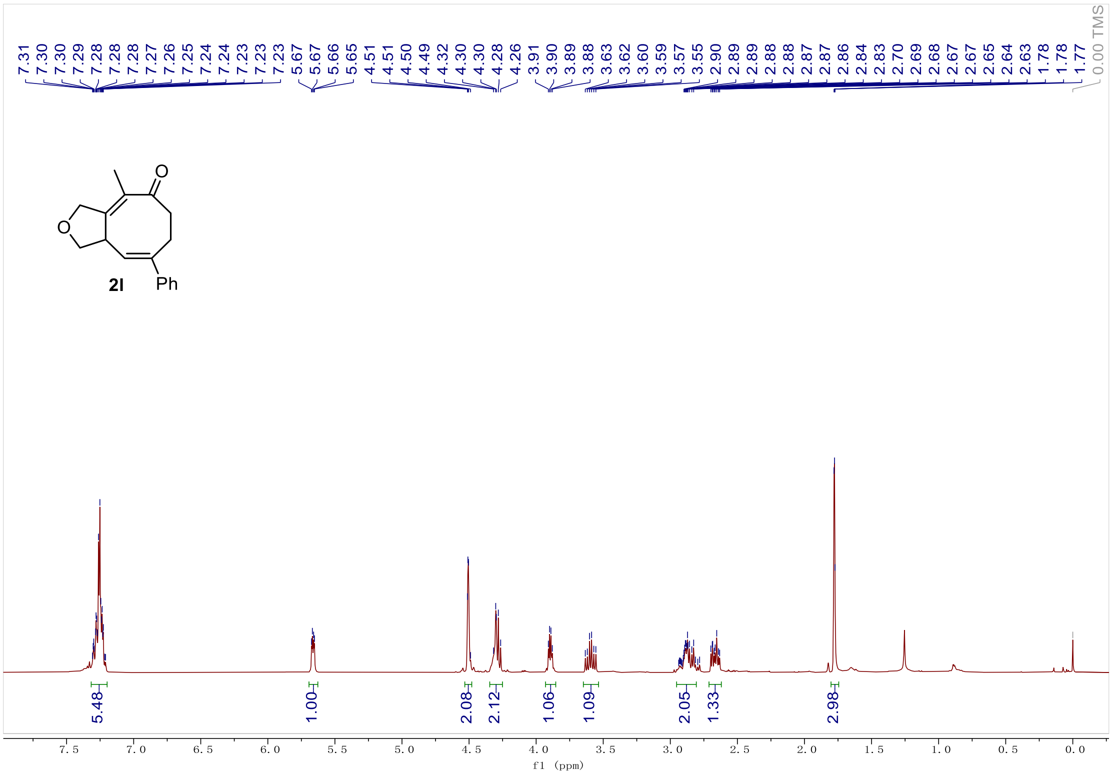

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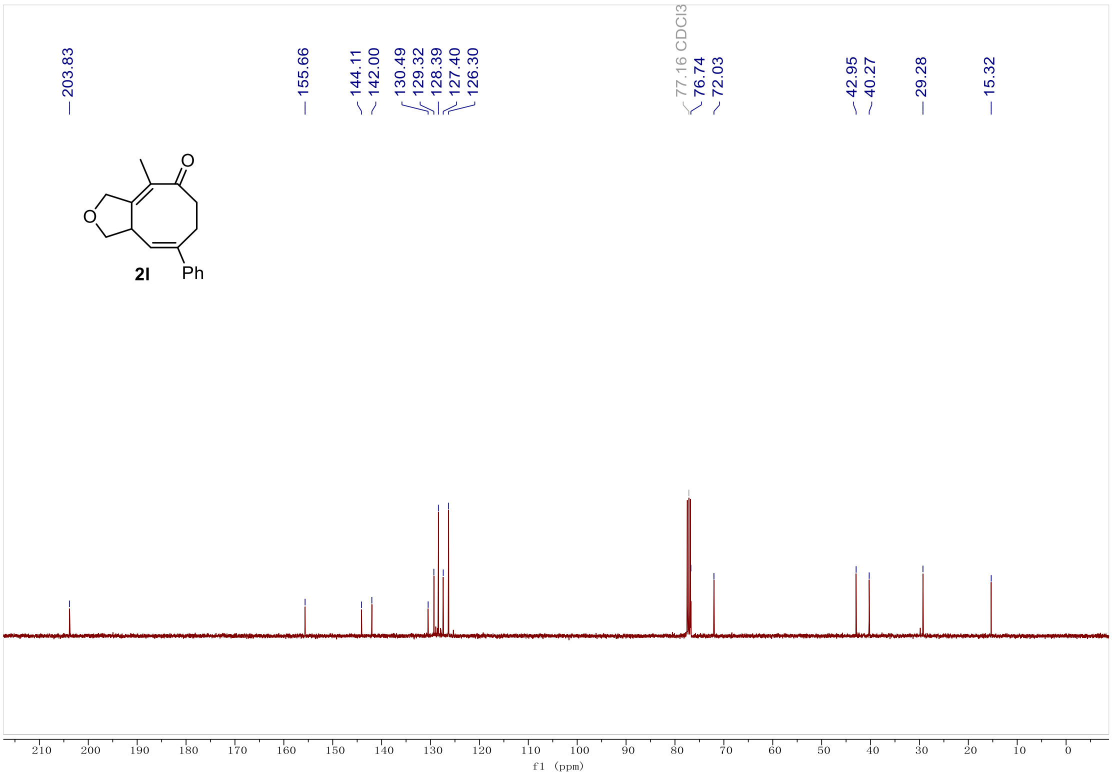

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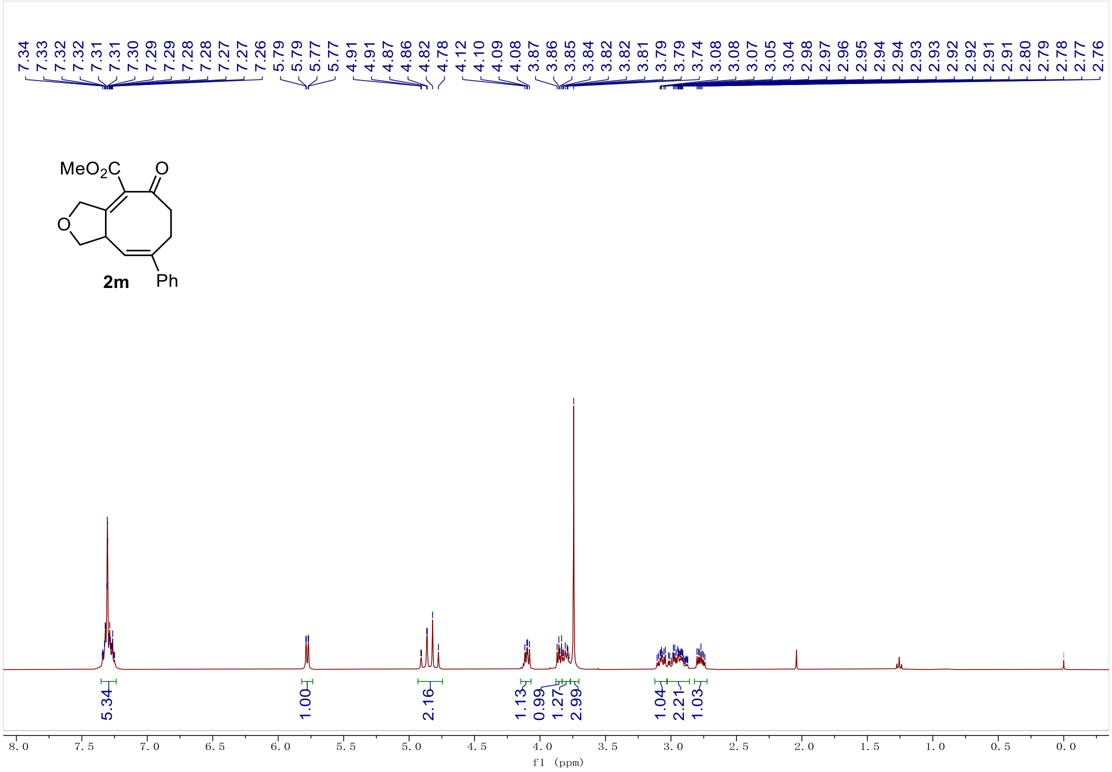
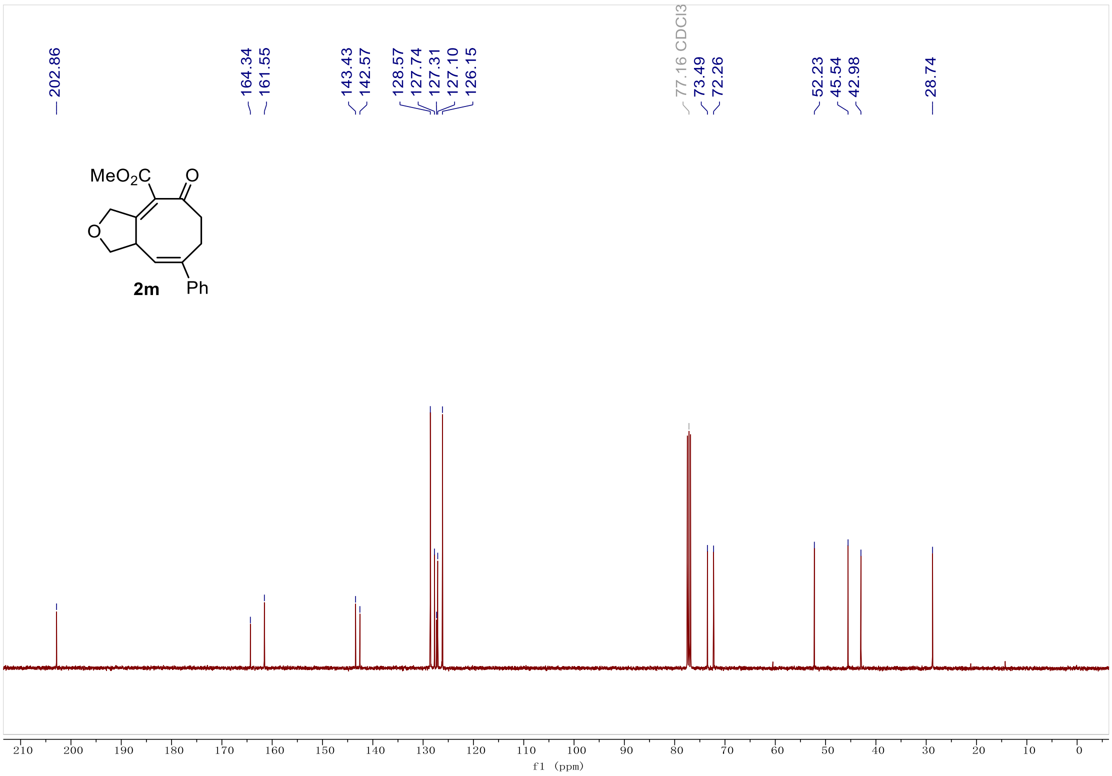


^{13}C NMR in $CDCl_3$, 101 MHz



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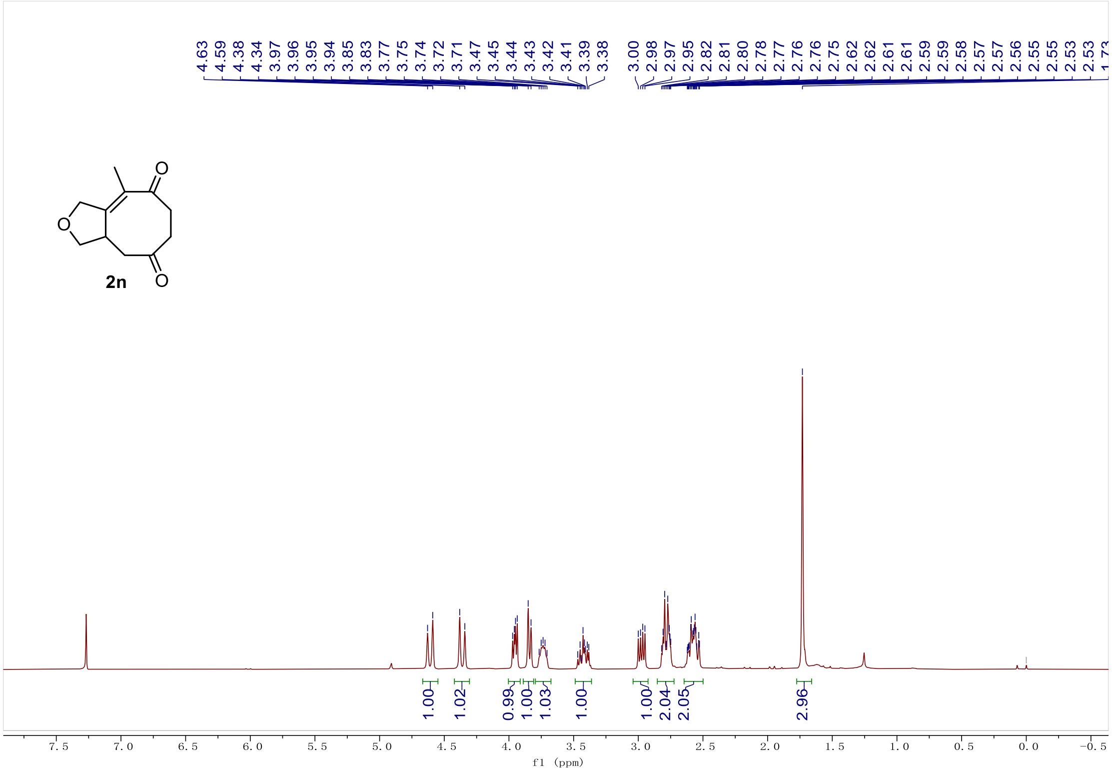

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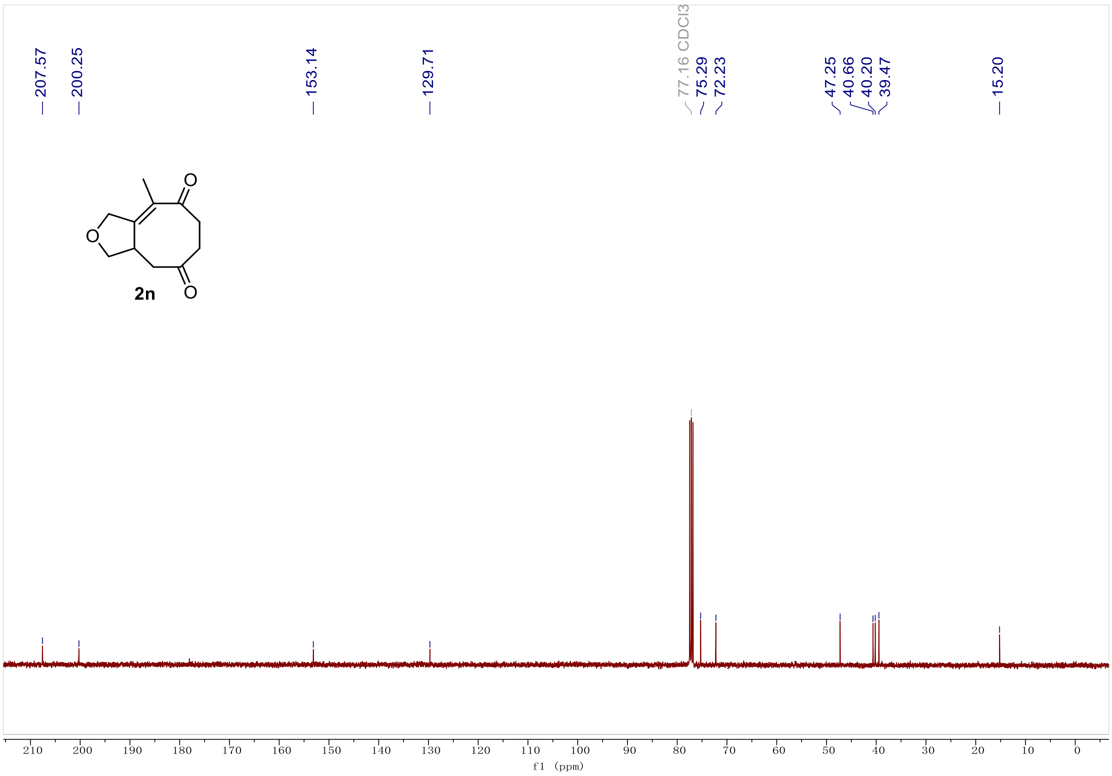
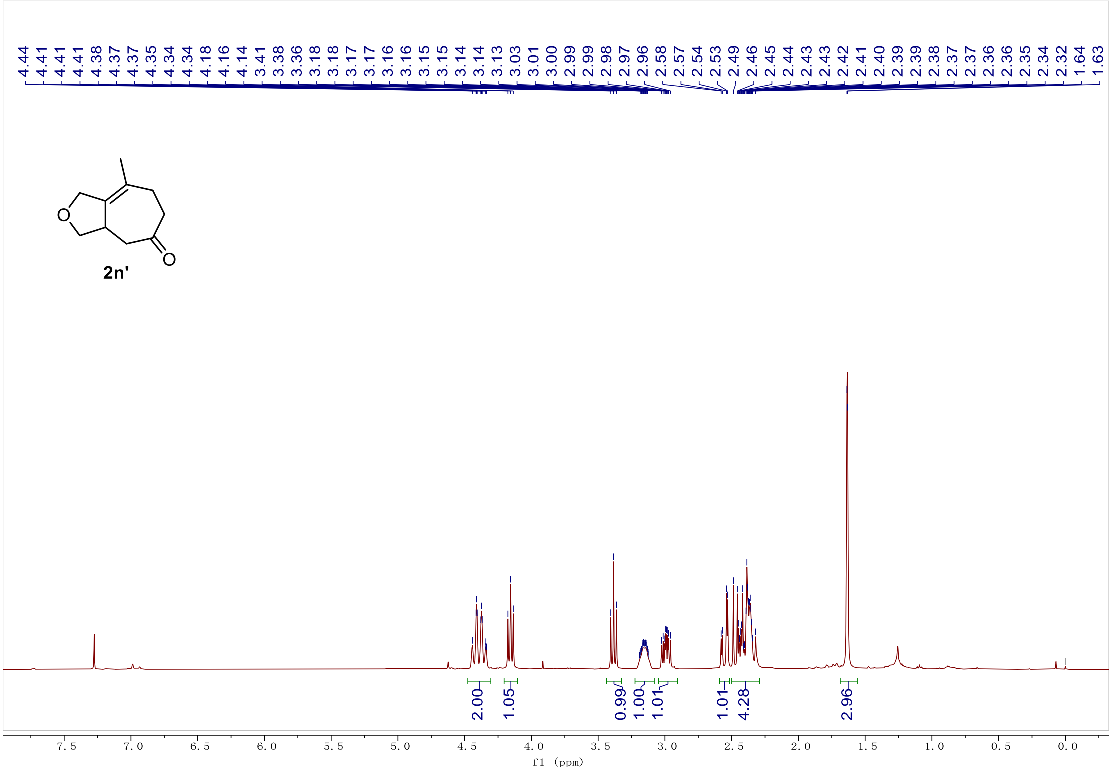
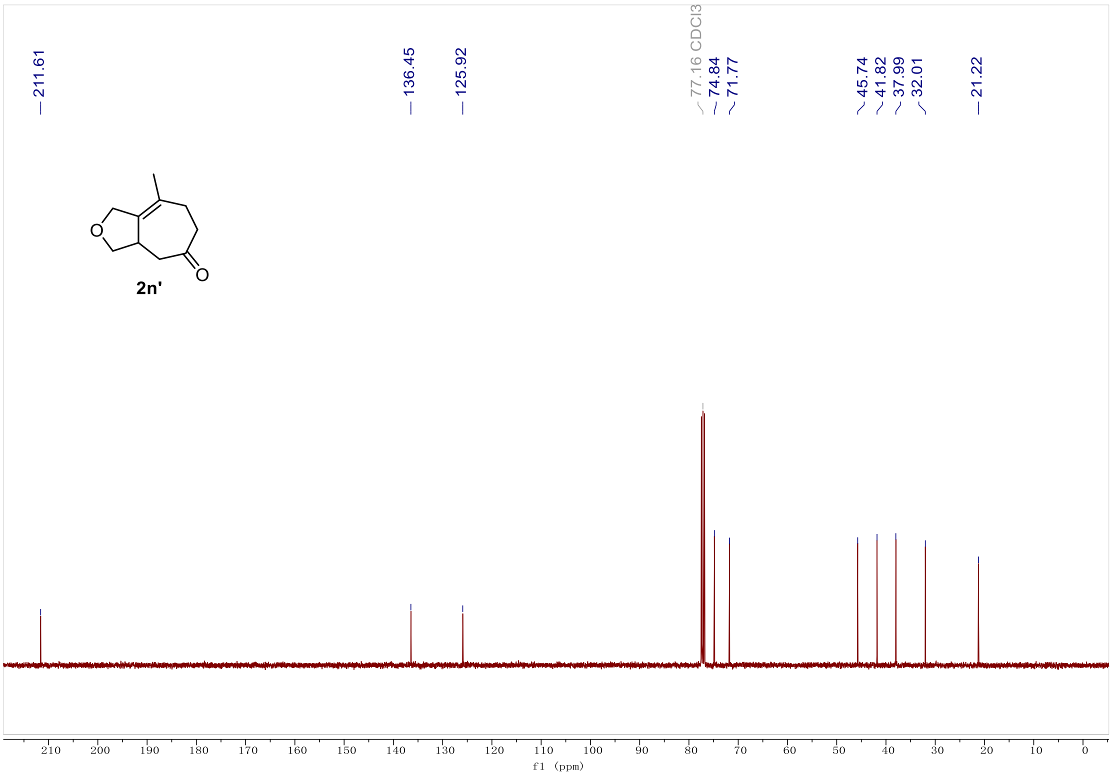


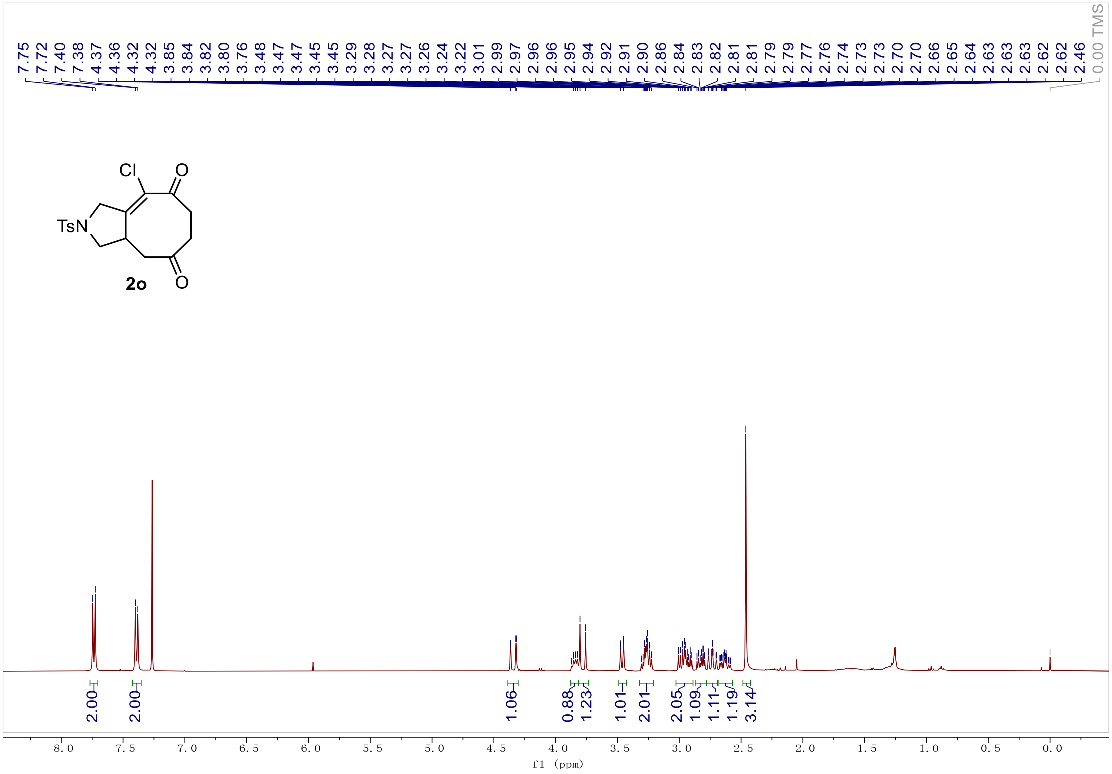
^{1}H NMR in CDCl$_3$, 400 MHz



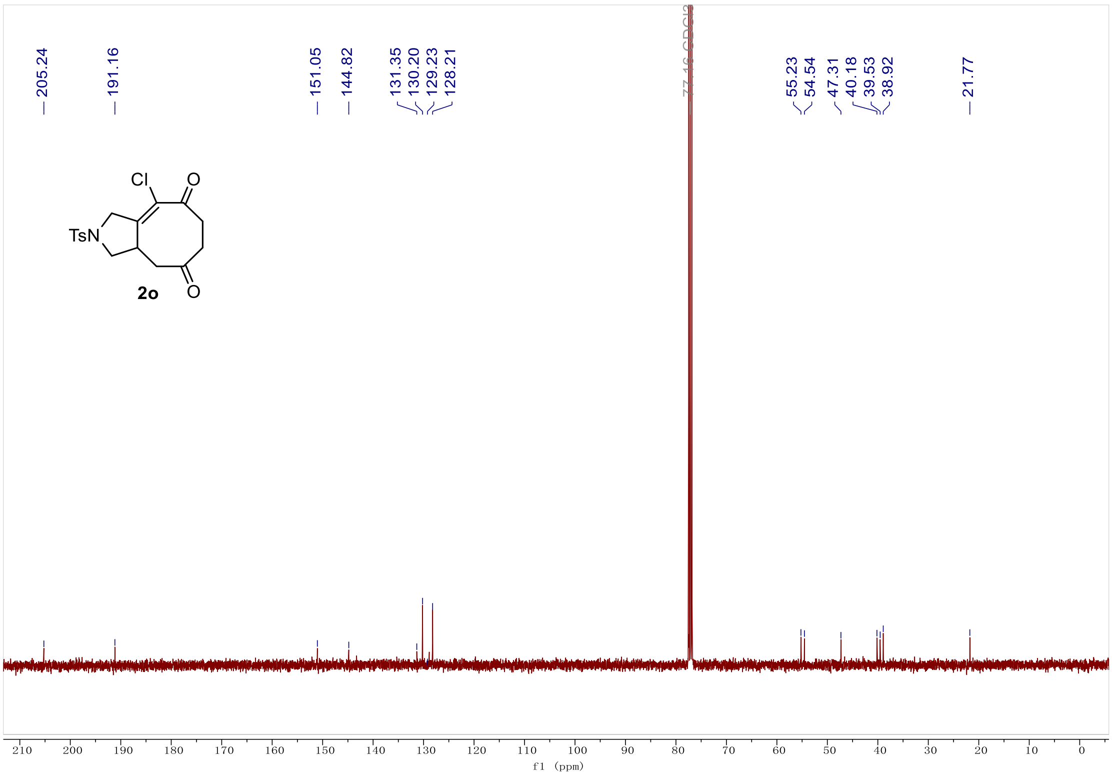
^{13}C NMR in CDCl$_3$, 101 MHz



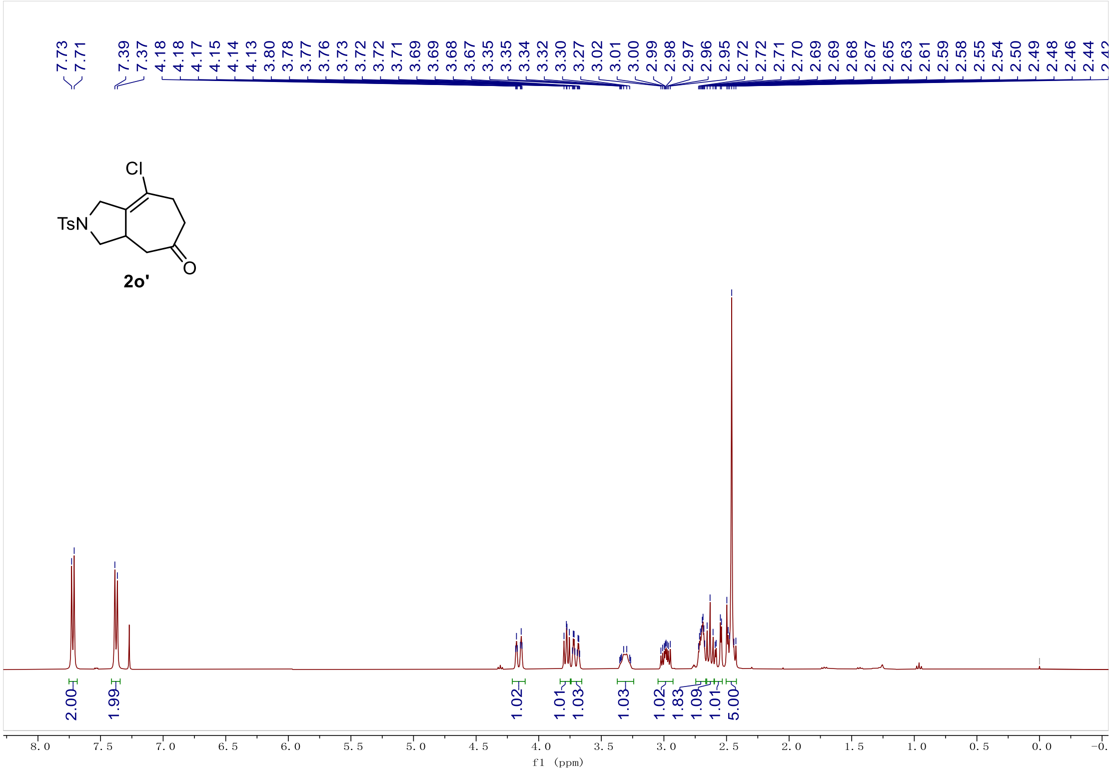
^{1}H NMR in $CDCl_3$, 400 MHz



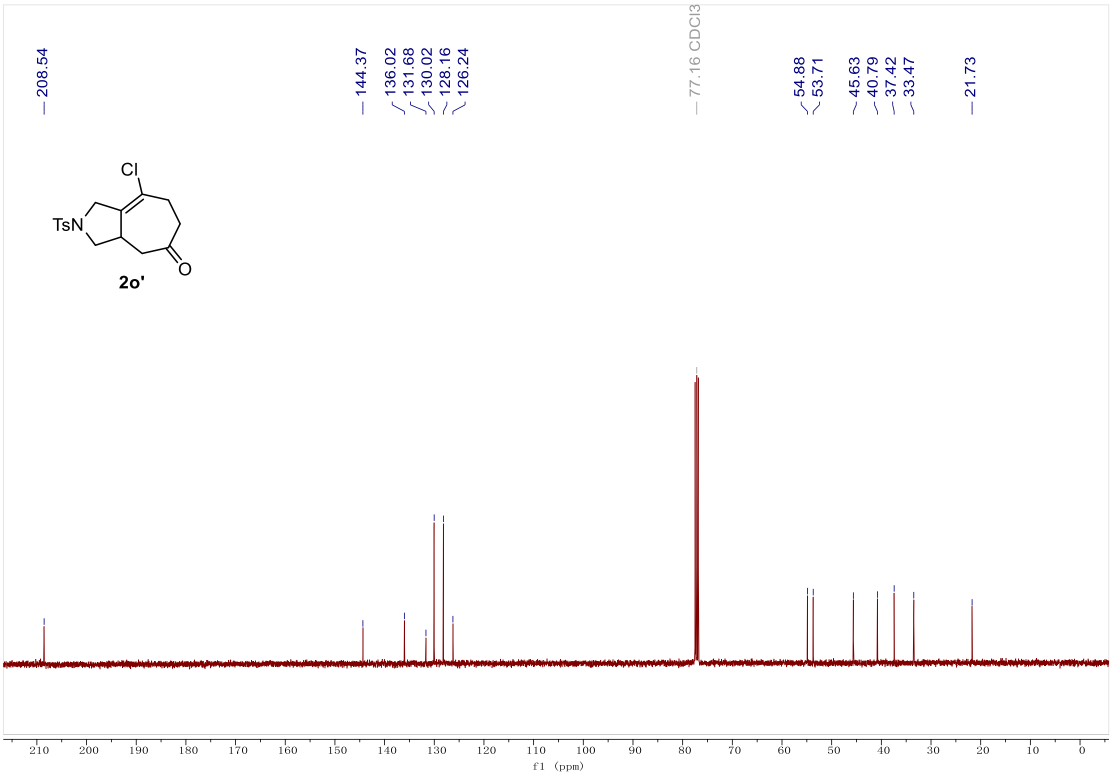
^{13}C NMR in $CDCl_3$, 101 MHz



^1H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz



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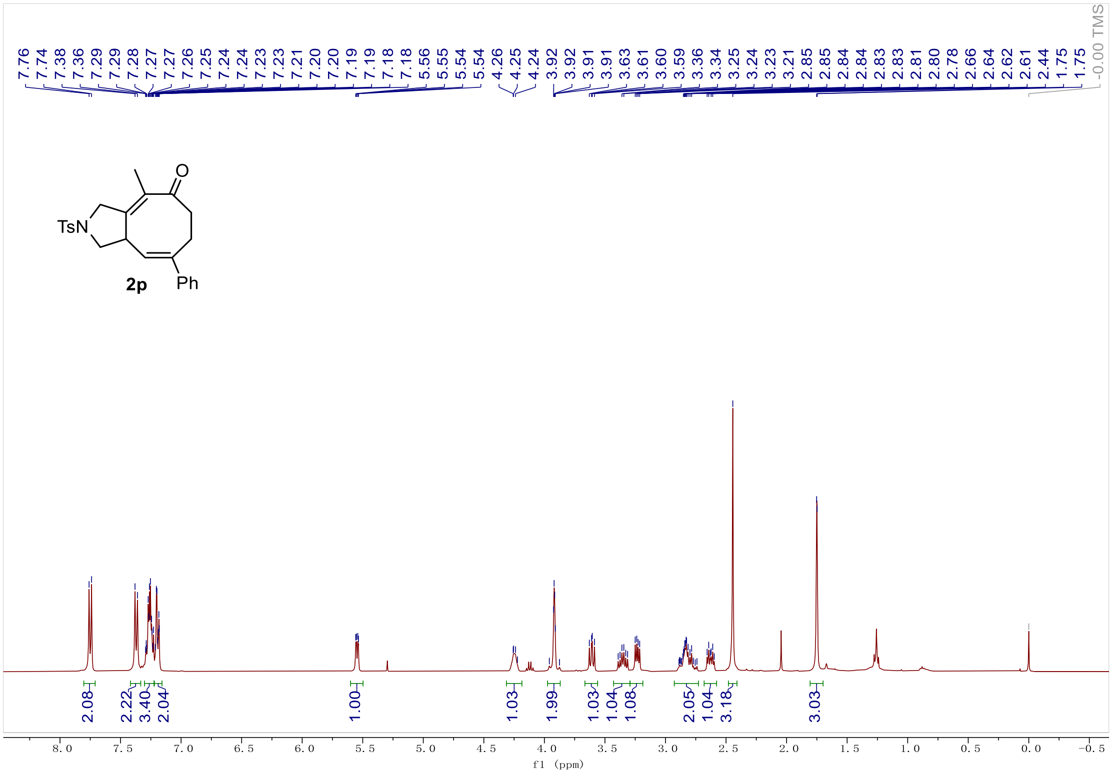

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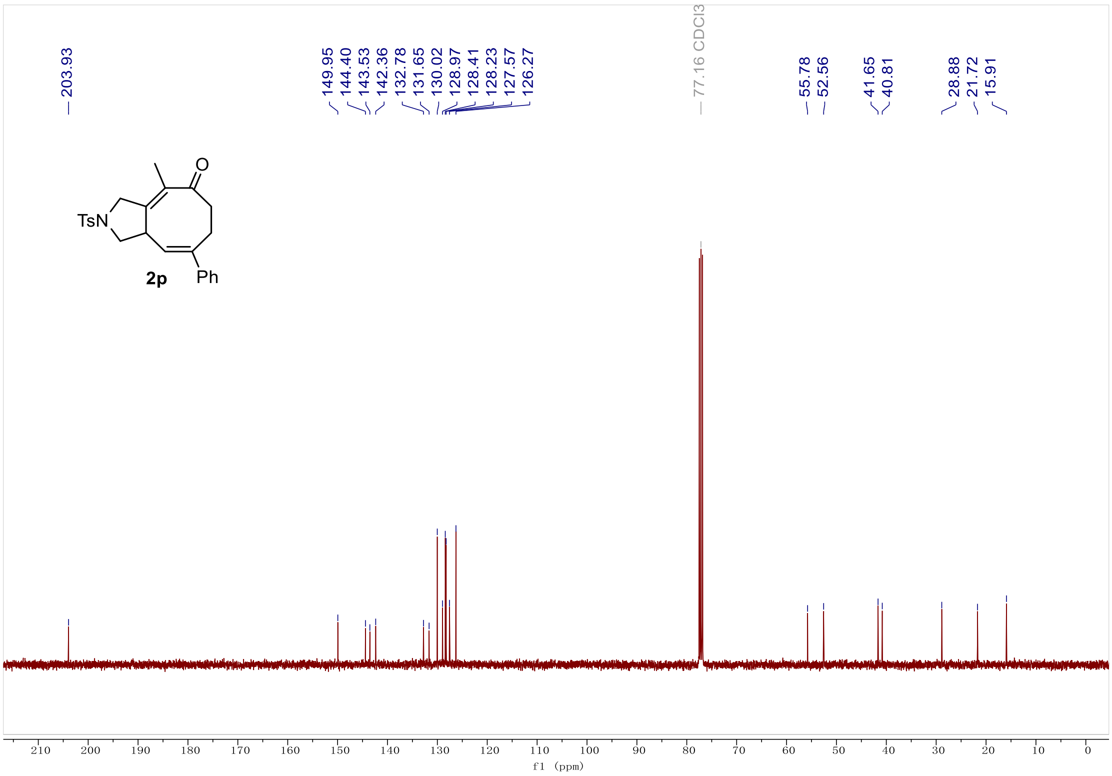

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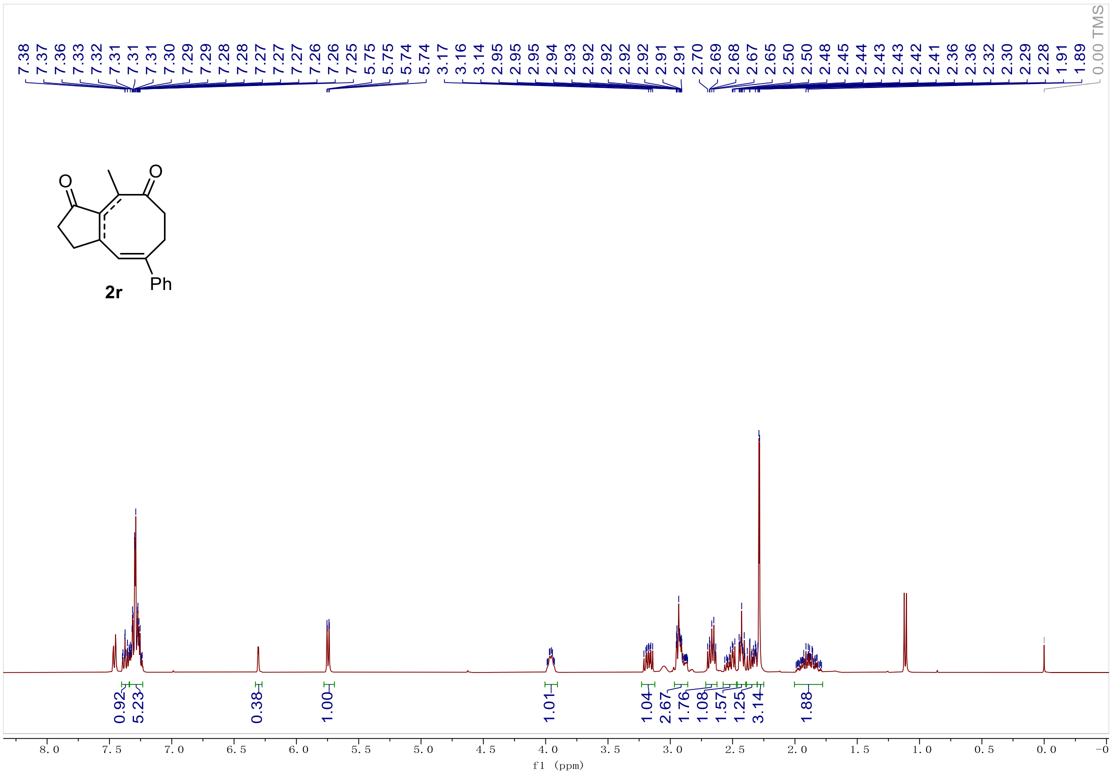

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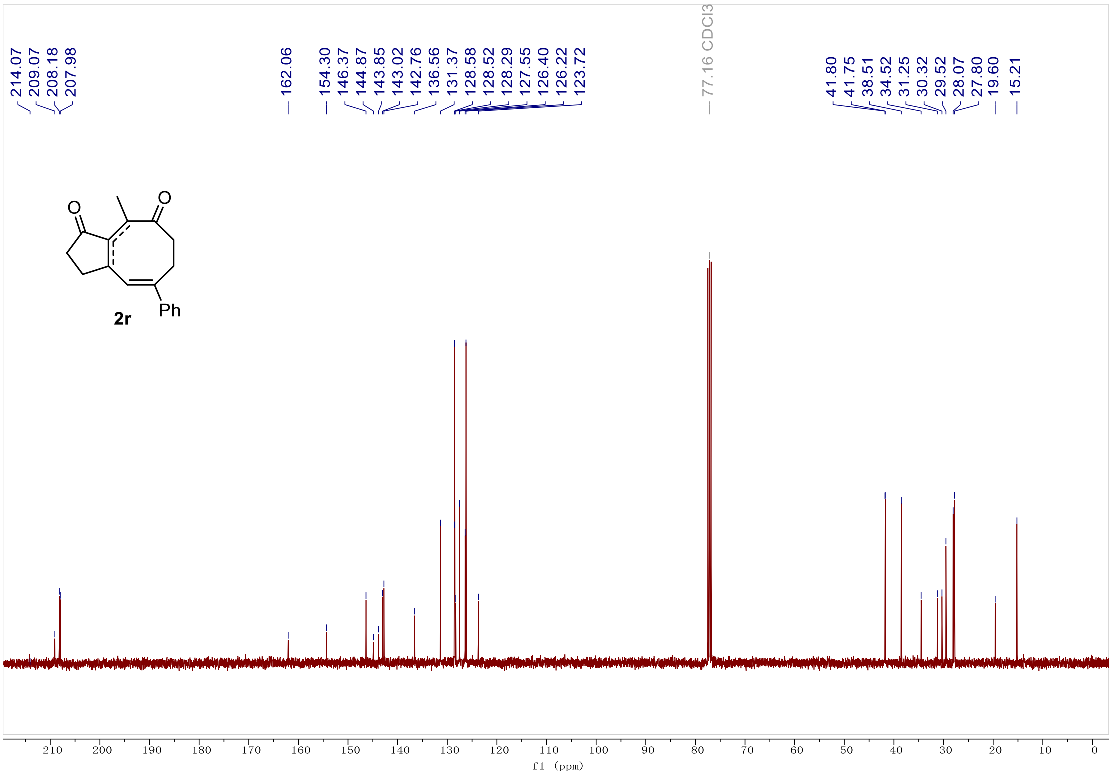

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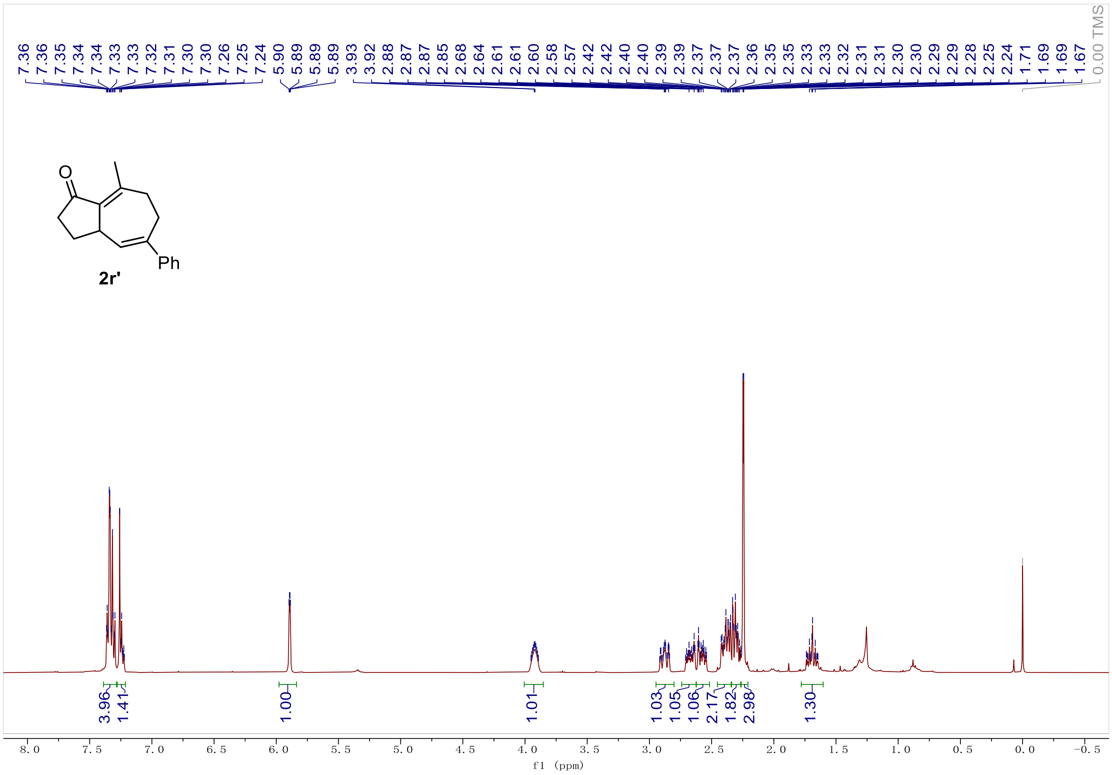
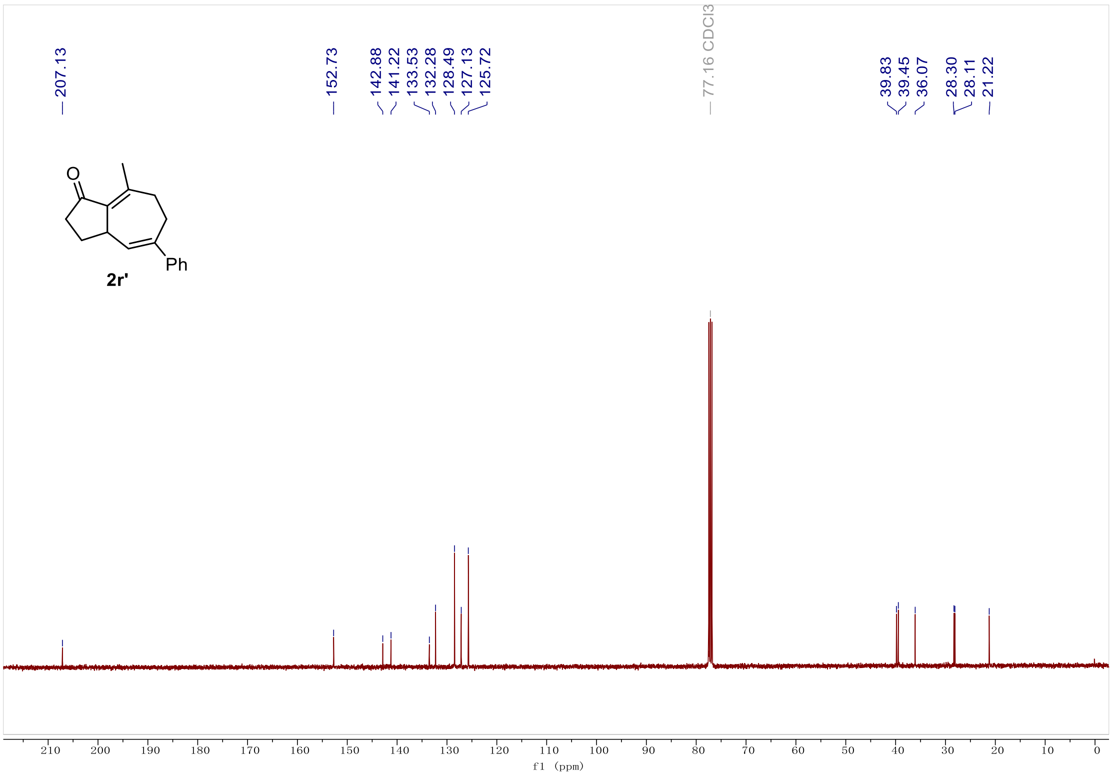
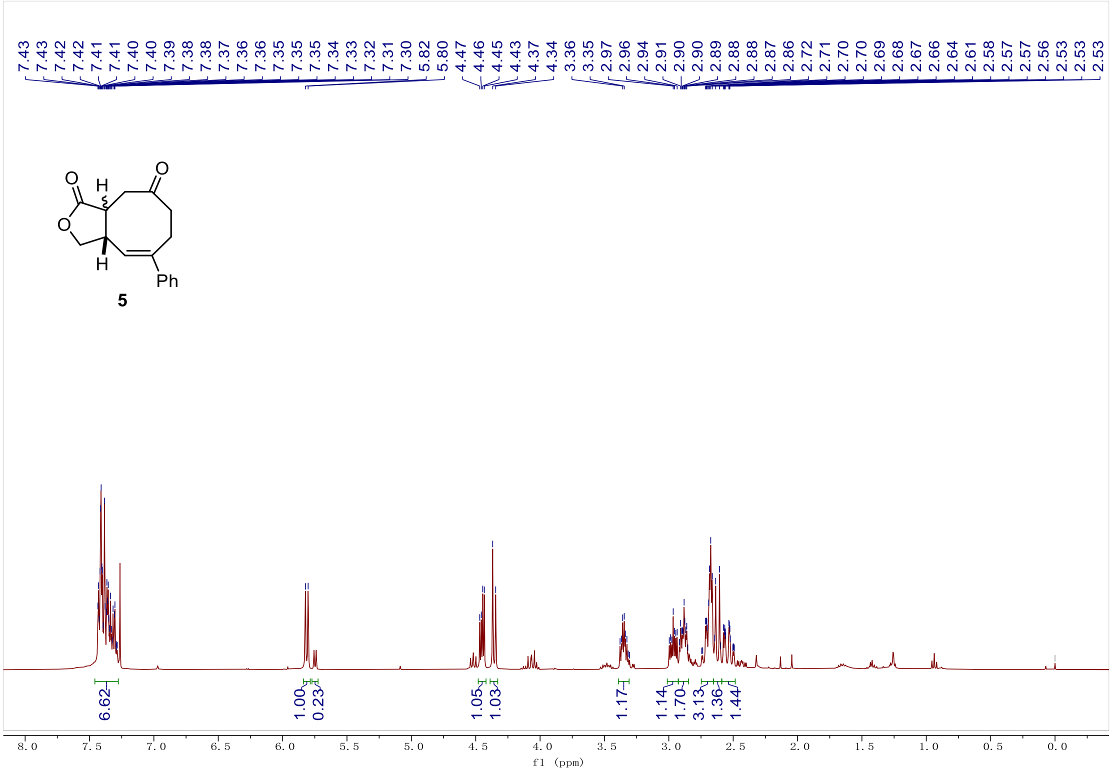


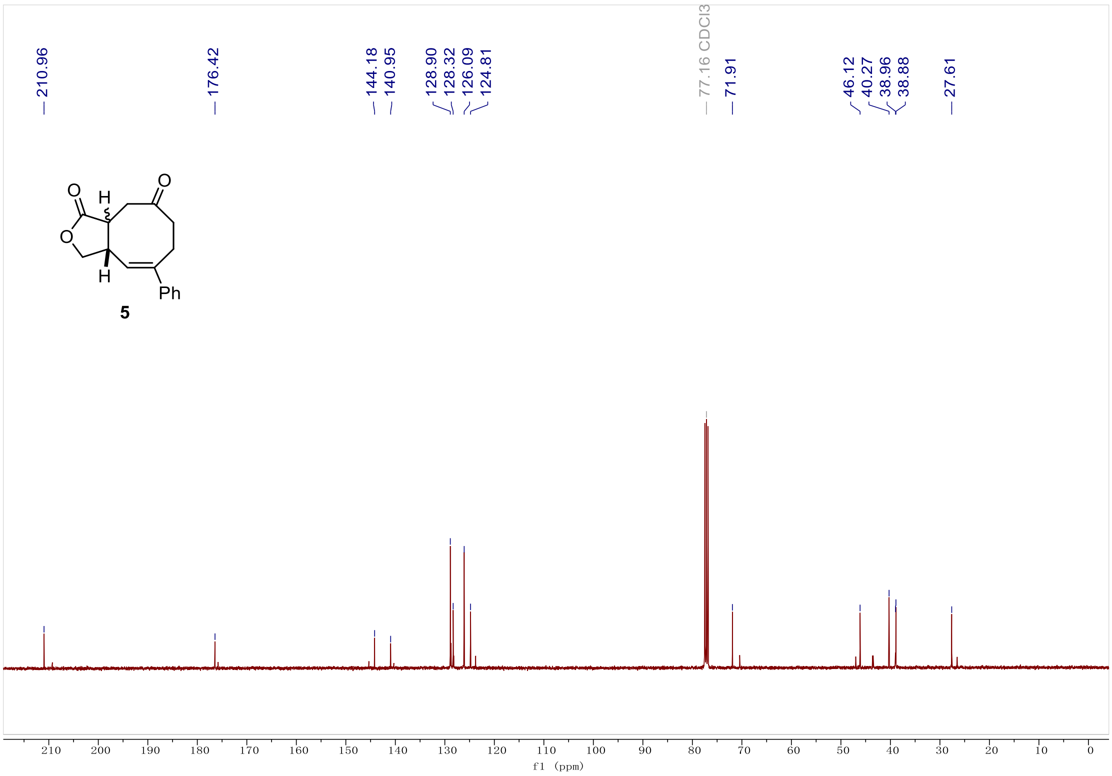
^{13}C NMR in $CDCl_3$, 101 MHz



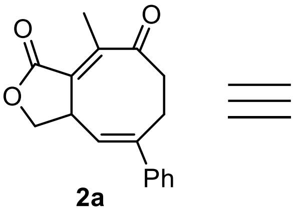
^{1}H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz

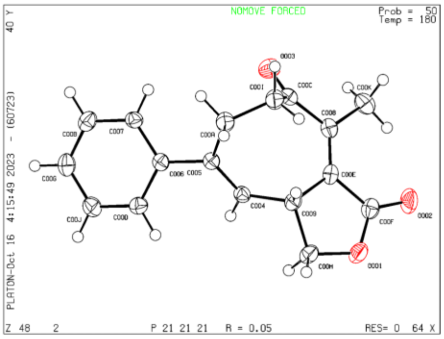


7. X-Ray Crystal Structure of 2a



2a

CCDC 2324922



Ellipsoids are drawn at 50% probability

Crystallographic Data of Compound **2a**

Crystal data	
Chemical formula	$C_{17}H_{16}O_3$
Mr	268.32
Crystal system, space group	Orthorhombic, P212121
Temperature (K)	180
a, b, c (Å)	5.7865 (3), 14.0028 (9), 16.4213 (11)
V (Å3)	1330.57 (14)
Z	4
Radiation type	Mo Kα
μ (mm−1)	0.09
Crystal size (mm)	0.5 × 0.05 × 0.05
Refinement	
R[F2 > 2σ(F2)], wR(F2), S	0.047, 0.112, 1.03
No. of reflections	3451
No. of parameters	182
H-atom treatment	H-atom parameters constrained
Δρmax, Δρmin (e Å−3)	0.30, −0.31