Supporting Information

Ni(0)-Catalyzed Rearrangement of Vinylcyclobutanones (VCBOs) to Synthesize Six-Membered Non-Conjugated Enones

Jiguo Ma, Jicheng Duan and Zhi-Xiang Yu*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

*E-mail: yuzx@pku.edu.cn

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1. General Information

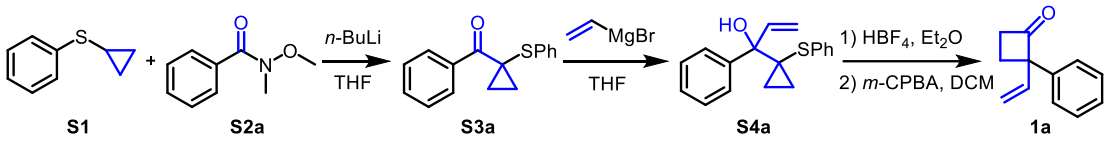
All commercially available reagents were used without further purification unless otherwise stated. $Ni(cod)_2$ was purchased from J&K. dppBz was purchased from Heowns. Ethyl acetate, petroleum ether, dichloromethane, diethyl ether, NaCl, Na_2SO_4, NH_4Cl were purchased from Bei Jing TongGuang Fine Chemicals Company. Grignard reagents were purchased from Energy Chemical. Strat material to synthesize the substrates was purchased from leyan-chem and bidepharm. Dry toluene and THF were obtained by fresh distillation from sodium benzophenone under argon atmosphere. DCM was freshly distilled from CaH_2. ^1H NMR spectra were recorded on a 400 MHz NMR spectrometer, ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer and ^{19}F NMR spectra were recorded on a 471 MHz NMR spectormeter. ^1H shifts were referenced to $CDCl_3$ at 7.26 ppm and ^{13}C shifts were referenced to $CDCl_3$ at 77.16 ppm. ^1H shifts were referenced to CD_3OD at 3.31 ppm and ^{13}C shifts were referenced to CD_3OD at 49.00 ppm. ^1H shifts were referenced to d_6-DMSO at 2.50 ppm and ^{13}C shifts were referenced to d_6-DMSO at 39.52 ppm. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) with an FT-ICR analyzer. Melting points were uncorrected.

Abbreviations

Bu	Butyl
DCM	Dichloromethane
DFT	density functional theory
EA	ethyl acetate
ESI	electron spray ionization
Et	Ethyl
HRMS	high-resolution mass spectroscopy
INT	intermediate
Me	methyl
m.p.	melting point
PE	petroleum ether
Ph	phenyl
r.t.	room temperature
THF	Tetrahydrofuran
TLC	thin layer chromatography
TS	transition state
m-CPBA	3-chloroperbenzoic acid
$Ni(cod)_2$	Bis(1,5-cyclooctadiene) nick
(±)-BINAP	(±)-2,2'-bis(diphenylphosphino)-1,1'-binaphtyl
dppm	Bis(diphenylphosphino)methane
dppp	1,3-Bis(diphenylphosphino)propane
dppb	1,4-Bis(diphenylphosphino)butane
dppBz	1,2-Bis(Diphenylphosphino)benzene
DMP	Dess-Martin periodinane
ZnI_2	Zinc iodide
$LiAlH_4$	Lithium Aluminum Hydride

2. Substrate preparations

2.1 Synthesis of 1a-k with Compound 1a as the Representative Example[1]



To a solution of cyclopropyl phenyl sulfide (**S1**) (5.0 g, 33.28 mmol) in dry THF (20 mL) was added *n*-BuLi (2.4 M in hexane) (16.60 mL, 39.94 mmol) at 0 °C under N_2 atmosphere. After the reaction mixture was stirred at room temperature for 3 h, a solution of compound **S2a** (5.5 g, 33.28 mmol) in THF (40 mL) was added via a syringe at -10 °C, and stirred in that temperature for another 1 h. The reaction was quenched by addition of 1 M HCl (50 mL), and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 80:1) to give compound **S3a** (5.67 g, 67%).

To a solution of compound **S3a** (5.67 g, 22.29 mmol) in THF (50 mL) was added vinyl magnesium bromide (1.0 M in THF) (26.70 mL, 26.75 mmol) at 0 °C under N_2 atmosphere. The mixture was allowed to warm up to room temperature and stirred for 4 h. The reaction mixture was quenched with saturated ammonium chloride solution (50 mL), and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 80:1) to give compound **S4a** (5.85 g, 93%) as a yellow oil.

To a solution of compound **S4a** (5.85 g, 20.7 mmol) in Et_2O (120 mL) was added tetrafluoroboric acid (50 mL of a 48% aqueous solution) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 0.5 h. The reaction was quenched by addition of 15% NaOH aqueous solution till pH 7~8, and extracted with Et_2O (100 mL × 3). The organic layers were combined, dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **1a**.

Importantly, we found that there were some inseparable impurities in the above product that interfered the key Ni catalyzed reaction here. We hypothesized that these impurities could be sulfur compounds and tried to remove them by oxidation. To our delight, such an additional step was helpful to get pure compound. This procedure is

described below (this has also been applied for all substrates if similar rearrangement was used).

To a solution of crude **1a** in DCM (120 mL) was added 3-chloroperbenzoic acid (*m*-CPBA) (4.28 g, 24.89 mmol) at room temperature for 5 mins. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (80 mL) and extracted with DCM (100 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate : dichloromethane = 100:1 ~ 50:1) to give compound **1a** (1.90 g, 53%) as a colorless liquid.

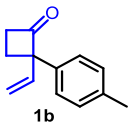
TLC (50:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.30 (m, 4H), 7.27 – 7.16 (m, 1H), 6.04 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 5.11 (d, *J* = 17.2 Hz, 1H), 3.26 – 3.10 (m, 1H), 3.10 – 2.94 (m, 1H), 2.62 – 2.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 140.1, 139.1, 128.8, 127.2, 126.5, 114.6, 75.5, 43.1, 23.6.

Compounds **1b-k** were prepared, respectively, in 22%; 37%; 19%; 27%; 13%; 18%; 3%; 31%; 29% and 17% yields in three steps by following a similar procedure.

Compound 1b (Table 2)[2]



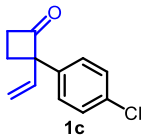
TLC (50:1 PE/EA, R_f): 0.6.

Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.05 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 3.26 – 3.12 (m, 1H), 3.09 – 2.96 (m, 1H), 2.61 – 2.43 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.8, 139.2, 137.2, 136.8, 129.5, 126.4, 114.5, 75.2, 43.0, 23.6, 21.1.

Compound 1c (Table 2)



1c

TLC (50:1 PE/EA, R_f): 0.4.

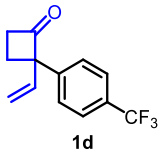
Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.17 (m, 4H), 5.94 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.23 – 3.09 (m, 1H), 3.04 – 2.90 (m, 1H), 2.48 – 2.38 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 138.7, 138.6, 133.1, 128.9, 127.9, 115.0, 74.8, 43.1, 23.6.

HRMS (ESI) m/z: calcd. for $C_{12}H_{12}ClO$ ($[M+H]^+$): 207.0571, found: 207.0571

Compound 1d (Table 2)[2]



1d

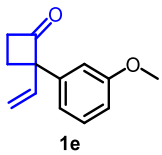
TLC (50:1 PE/EA, R_f): 0.4.

Physical Form: Pale yellow liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.03 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 3.35 – 3.18 (m, 1H), 3.13 – 2.95 (m, 1H), 2.63 – 2.46 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 144.0, 138.4, 129.4 (q, *J* = 32.4 Hz), 126.9, 125.7 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 207.3 Hz), 115.3, 75.2, 43.2, 23.5.

Compound 1e (Table 2)



1e

TLC (50:1 PE/EA, R_f): 0.6.

Physical Form: colorless liquid

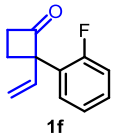
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.82 – 6.75 (m, 1H), 6.03 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 5.13

(d, J = 17.2 Hz, 1H), 3.80 (s, 3H), 3.23 – 3.12 (m, 1H), 3.09 – 2.94 (m, 1H), 2.58 – 2.42 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 159.9, 141.7, 138.9, 129.7, 118.7, 114.6, 112.5, 112.3, 75.4, 55.3, 43.0, 23.7.

HRMS (ESI) m/z: calcd. for $C_{13}H_{15}O_2$ ($[M+H]^+$): 203.1067, found: 203.1064.

Compound 1f (Table 2)



1f

TLC (50:1 PE/EA, R_f): 0.6.

Physical Form: colorless liquid

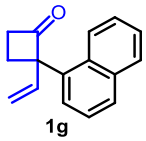
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.43 (m, 1H), 7.29 – 7.20 (m, 1H), 7.13 – 6.99 (m, 2H), 6.10 (dd, J = 17.2, 10.4 Hz, 1H), 5.24 (d, J = 10.4 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 3.28 – 3.16 (m, 1H), 3.16 – 3.03 (m, 1H), 2.65 – 2.53 (m, 1H), 2.53 – 2.41 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 160.4 (d, J = 245.8 Hz), 136.6, 129.0 (d, J = 8.3 Hz), 127.954 (d, J = 13.5 Hz), 127.951 (d, J = 4.4 Hz), 124.1 (d, J = 3.5 Hz), 116.2 (d, J = 21.5 Hz), 115.8, 71.5, 43.3 (d, J = 1.5 Hz), 24.5 (d, J = 3.4 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.86.

HRMS (ESI) m/z: calcd. for $C_{12}H_{12}FO$ ($[M+H]^+$): 191.0867, found: 191.0865.

Compound 1g (Table 2)



1g

TLC (5:1 PE/EA, R_f): 0.4.

Physical Form: white solid

Melting Point: 38 – 40 °C

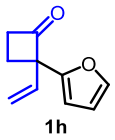
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.81 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 7.2, 0.8 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.38 (m, 1H), 6.25 (dd, J = 17.2, 10.4 Hz, 1H), 5.22 (d, J = 10.4 Hz, 1H), 5.08 (d, J = 17.2 Hz, 1H), 3.33 – 3.07 (m, 2H), 2.94

– 2.79 (m, 1H), 2.70 – 2.52 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.5, 138.2, 136.1, 135.0, 130.3, 129.2, 128.3, 125.7, 125.7, 125.5, 125.3, 123.8, 116.4, 75.3, 43.7, 26.1.

HRMS (ESI) m/z: calcd. for $C_{16}H_{15}O$ ($[M+H]^+$): 223.1117, found: 223.1117.

Compound 1h (Table 2)



1h

TLC (50:1 PE/EA, R_f): 0.5.

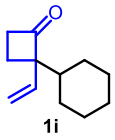
Physical Form: Pale yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.34 (m, 1H), 6.32 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 6.09 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.293 (d, *J* = 11.2 Hz, 1H), 5.286 (d, *J* = 16.8 Hz, 1H), 3.19 (dd, *J* = 8.8, 8.8 Hz, 2H), 2.68 – 2.51 (m, 1H), 2.44 – 2.32 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 205.6, 152.3, 142.6, 134. 6, 116.5, 110.5, 106.6, 70.9, 43.9, 22.6.

HRMS (ESI) m/z: calcd. for $C_{10}H_{11}O_2$ ($[M+H]^+$): 163.0754, found: 163.0751.

Compound 1i (Table 2)[2]



1i

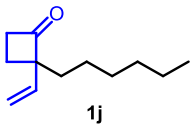
TLC (50:1 PE/EA, R_f): 0.6.

Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 5.12 (d, *J* = 17.6 Hz, 1H), 3.02 – 2.72 (m, 2H), 2.12 – 1.90 (m, 2H), 1.83 – 1.67 (m, 3H), 1.67 – 1.51 (m, 3H), 1.28 – 0.88 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.5, 136.3, 115.2, 75.9, 43.2, 42.4, 27.9, 27.8, 26.52, 26.47, 26.4, 19.7.

Compound 1j (Table 2)[2]



1j

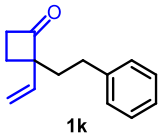
TLC (50:1 PE/EA, R_f): 0.6.

Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 3.05 – 2.85 (m, 2H), 2.17 – 2.05 (m, 1H), 1.96 – 1.83 (m, 1H), 1.70 – 1.52 (m, 2H), 1.40 – 1.10 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.1, 137.4, 114.5, 71.8, 42.4, 35.7, 31.8, 29.6, 24.4, 22. 7, 21.6, 14.1.

Compound 1k (Table 2)[2]



1k

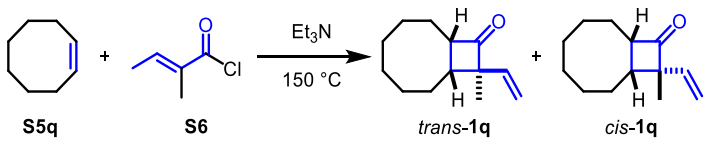
TLC (50:1 PE/EA, R_f): 0.6.

Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 2H), 7.21 – 7.09 (m, 3H), 5.90 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.24 (d, *J* = 18.4 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 3.11 – 2.91 (m, 2H), 2.74 – 2.61 (m, 1H), 2.61 – 2.49 (m, 1H), 2.25 – 2.11 (m, 1H), 2.05 – 1.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 141.8, 136.9, 128.5, 128.4, 126.1, 115.3, 71.5, 42.5, 37.5, 30.9, 21.9.

2.2 Synthesis of 1l-r via [2+2] Cycloaddition Reaction with Compound 1q as the Representative Example [3]



S5q S6 *trans*-1q *cis*-1q

To a 25 mL sealed tube with (*Z*)-cyclooctene (**S5q**) (7.80 mL, 60.00 mmol) and **S6** (1.18 g, 10.00 mmol) was added Et_3N (1.46 mL, 10.50 mmol) under N_2 atmosphere. The reaction mixture was stirred at 150 °C for 4 h, after which time the initially clear mixture contained a brown cake of $Et_3N{\cdot}HCl$. The cooled tube was opened, its contents

diluted with H_2O (20 mL) and extracted with pentane (20 mL × 3). The combined organic layers were successively washed with HCl aqueous solution (2M, 20 mL) and saturated aqueous $NaHCO_3$ (20 mL), dried over Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 500:1 ~ 300:1) to give compound *trans*-**1q** and *cis*-**1q** (807 mg, 42%) as a colorless liquid.

TLC (50:1 PE/EA, R_f): 0.5; *trans*:*cis* = 9:5

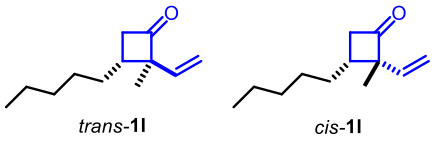
The configurations of *trans*-**1q** and *cis*-**1q** were determined according to literature 3

Major isomer (*trans*-**1q**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.91 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.15 – 4.99 (m, 2H), 3.33 – 3.19 (m, 1H), 2.41 – 2.32 (m, 1H), 1.92 – 1.36 (m, 9H), 1.33 – 1.19 (m, 3H), 1.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 215.3, 140.7, 113.0, 67.5, 59.9, 40.3, 30.4, 28.8, 26.2, 25.65, 23.9, 22.2, 15.4.

Minor isomer (*cis*-**1q**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.73 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.15 – 4.99 (m, 2H), 3.33 – 3.19 (m, 1H), 2.20 – 2.12 (m, 1H), 1.92 – 1.36 (m, 9H), 1.34 (s, 3H), 1.33 – 1.19 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 216.5, 135.4, 115.7, 66.5, 59.6, 43.4, 30.3, 29.2, 26.2, 25.56, 24.8, 22.67, 22.66.

Compounds **1l-p** and **1r** were prepared, respectively, in 34%; 45%; 19%; 13%; 33% and 46% yields by following a similar procedure.

Compound 1l (Table 2)[3]



TLC (50:1 PE/EA, R_f): 0.5; *trans*:*cis* = 7:3

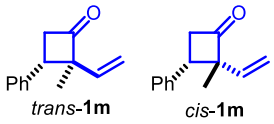
Physical Form: colorless liquid

The configurations of *trans*-**1l** and *cis*-**1l** were determined according to literature 3

Major isomer (*trans*-**1l**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.89 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.19 – 4.98 (m, 2H), 3.11 (dd, *J* = 17.6, 10.0 Hz, 1H), 2.67 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.39 – 2.28 (m, 1H), 1.70 – 1.29 (m, 8H), 1.20 (s, 3H), 0.96 – 0.82 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 211.8, 139.6, 113.8, 67.5, 48.8, 34.8, 32.01, 30.7, 28.2, 22.7, 15.6, 14.2.

Minor isomer (*cis*-**1l**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.84 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.19 – 4.98 (m, 2H), 3.20 – 2.99 (m, 1H), 2.78 – 2.61 (m, 1H), 2.15 – 2.00 (m, 1H), 1.70 – 1.29 (m, 8H), 1.28 (s, 3H), 0.96 – 0.82 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 211.5, 135.3, 115.7, 67.9, 49.2, 38.0, 31.96, 31.8, 28.1, 21.6, 15.6, 14.2.

Compound 1m (Table 2)[4]



TLC (50:1 PE/EA, R_f): 0.5; *trans*:*cis* = 3:2

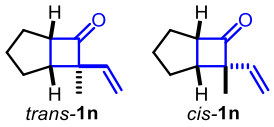
Physical Form: colorless liquid

The configurations of *trans*-**1m** and *cis*-**1m**were determined according to literature 4

Major isomer (*trans*-**1m**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.07 (m, 5 H), 6.07 (dd, *J* = 17.2, 10.8 Hz, 1 H), 5.27 (d, *J* = 17.6 Hz, 1 H), 5.23 (d, *J* = 10.8 Hz, 1H), 3.77 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.56 – 3.45 (m, 2 H), 0.93 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.3, 139.0, 138.4, 128.6, 127.9, 126.90, 114.7, 70.0, 46.1, 39.7, 17.1.

Minor isomer (*cis*-**1m**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.07 (m, 5 H), 5.35 (dd, *J* = 17.2, 10.4 Hz, 1 H), 5.08 (d, *J* = 17.2 Hz, 1 H), 4.97 (d, *J* = 10.8 Hz, H), 3.39 – 3.24 (m, 3 H), 1.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.6, 138.6, 135.8, 128.6, 128.0, 126.92, 115.5, 70.8, 47.3, 42.5, 21.9.

Compound 1n (Table 2)[3]



TLC (50:1 PE/EA, R_f): 0.5; *trans*:*cis* = 7:3

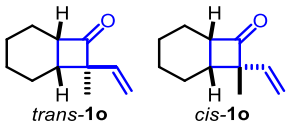
Physical Form: pale yellow liquid

The configurations of *trans*-**1n** and *cis*-**1n** were determined according to literature 3

Major isomer (*trans*-**1n**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.89 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.11 – 5.02 (m, 2H), 3.70 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.78 (dd, *J* = 8.4, 8.4 Hz, 1H), 2.08 – 1.38 (m, 6H), 1.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 217.5, 140.2, 113.2, 67.0, 62.0, 40.5, 28.6, 27.5, 26.9, 14.3.

Minor isomer (*cis*-**1n**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.68 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.22 (dd, *J* = 17.6, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.65 (dd, *J* = 8.0, 8.0 Hz, 1H), 2.58 (dd, *J* = 7.6, 8.0 Hz, 1H), 2.08 – 1.38 (m, 6H), 1.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 218.5, 134.3, 115.7, 65.2, 61.0, 43.6, 29.1, 28.3, 26.2, 23.8.

Compound 1o (Table 2)[5]



TLC (50:1 PE/EA, R_f): 0.4; *trans*:*cis* = 7:3

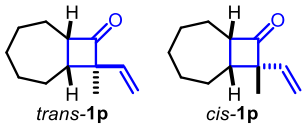
Physical Form: pale yellow liquid

The configurations of *trans*-**1o** and *cis*-**1o** were determined according to literature 5

Major isomer (*trans*-**1o**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.95 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 10.4 Hz, 1H), 3.60 – 3.45 (m, 1H), 2.41 – 2.31 (m, 1H), 2.04 – 1.79 (m, 3H), 1.65 – 1.36 (m, 3H), 1.28 – 1.06 (m, 2H); 1.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 211.5, 141.7, 113.5, 68.7, 53.4, 32.8, 24.5, 22.5, 22.4, 20.6, 15.4.

Minor isomer (*cis*-**1o**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.79 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.31 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.14 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.60 – 3.45 (m, 1H), 2.26 – 2.17 (m, 1H), 2.04 – 1.79 (m, 3H), 1.65 – 1.36 (m, 3H), 1.42 (s, 3H); 1.28 – 1.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.8, 136.4, 116.2, 66.8, 52.4, 35.3, 25.5, 24.8, 22.332, 22.325, 20.7.

Compound 1p (Table 2)[5]



TLC (50:1 PE/EA, R_f): 0.4; *trans*:*cis* = 7:3

Physical Form: pale yellow liquid

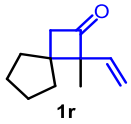
The configurations of *trans*-**1p** and *cis*-**1p** were determined according to literature 5

Major isomer (*trans*-**1p**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.90 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.07 (d, *J* = 17.6 Hz, 1H), 5.04 (d, *J* = 10.4 Hz, 1H), 3.63 – 3.53 (m, 1H), 2.56 –

2.40 (m, 1H), 2.06 – 1.02 (m, 10H), 1.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.8, 140.9, 113.0, 65.6, 60.5, 40.6, 32.0, 29.9, 28.5, 27.1, 25.8, 15.6.

Minor isomer (*cis*-**1p**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.72 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.17 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.10 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.53 – 3.45 (m, 1H), 2.35 – 2.23 (m, 1H), 2.06 – 1.02 (m, 10H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 216.0, 135.8, 115.6, 64.5, 59.8, 43.7, 31.8, 29.7, 28.9, 28.3, 25.6, 23.4.

Compound 1r (Table 2)[3]



1r

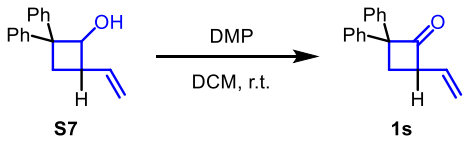
TLC (100:1 PE/EA, R_f): 0.5.

Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.14 – 5.03 (m, 2H), 2.91 – 2.77 (m, 2H), 1.80 – 1.53 (m, 8H), 1.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 136.9, 114.7, 67.6, 56.6, 45.4, 35.2, 34.1, 23.5, 23.4, 17.0.

2.3 Preparation of Substrate 1s



S7 **1s**

To a solution of compound **S7**[6] (450.0 mg, 1.80 mmol) in dry THF (10 mL) was added DMP (915 mg, 2.16 mmol) at room temperature. The reaction mixture was then stirred at the same temperature for 4 h before quenched with a saturated aqueous solution of $Na_2S_2O_3$ (10 mL) and $NaHCO_3$ (10 mL) and extracted with DCM (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether) to give compound **1s** (382 mg, 86%) as a pale yellow oil.

TLC (20:1 PE/EA, R_f): 0.8.

Physical Form: pale yellow oil

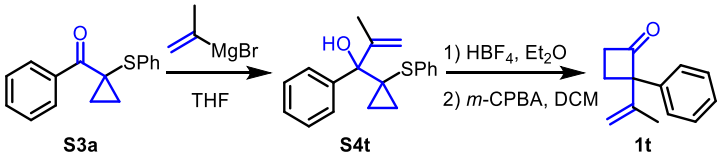
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 2H), 7.35 – 7.15 (m, 8H), 5.94 – 5.80 (m, 1H), 5.23 – 5.11 (m, 2H), 4.14 – 4.00 (m, 1H), 3.16 (dd, *J* = 10.8, 10.8 Hz, 1H),

2.72 (dd, J = 11.2, 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 142.3, 141.8, 132.3, 129.1, 128.7, 127.3, 126.9, 126.7, 126.7, 117.8, 74.0, 59.5, 32.1.

HRMS (ESI) m/z: calcd. for $C_{18}H_{17}O$ ($[M+H]^+$): 249.1274, found: 249.1272.

2.4 Preparation of Substrate 1t-u and 1w



To a solution of compound **S3a** (2.5 g, 9.84 mmol) in THF (25 mL) was added prop-1-en-2-ylmagnesium bromide (1.0 M in THF) (11.80 mL, 11.81 mmol) at 0 ℃ under N_2 atmosphere. The mixture was allowed to warm up to room temperature and stirred for 4 h. The reaction mixture was quenched with saturated ammonium chloride solution (30 mL), and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 50:1) to give compound **S4t** (1.98 g, 68%) as a colorless oil.

To a solution of compound **S4t** (1.98 g, 6.69 mmol) in Et_2O (30 mL) was added tetrafluoroboric acid (30 mL of a 48% aqueous solution) at 0 ℃. The mixture was allowed to warm up to room temperature and stirred for 0.5 h. The reaction was quenched by addition of 15% NaOH aqueous solution till pH 7~8, and extracted with Et_2O (30 mL × 3). The organic layers were combined, dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **1t**.

To a solution of crude **1t** in DCM (30 mL) was added 3-chloroperbenzoic acid (*m*-CPBA) (0.86 g, 5.01 mmol) at room temperature for 5 mins. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (30 mL) and extracted with DCM (30 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate : dichloromethane = 300:1 ~ 100:1) to give compound **1t** (0.57 g, 46%) as a colorless liquid.

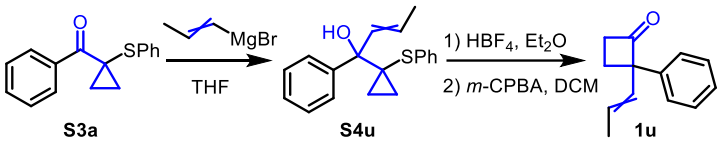
TLC (50:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 5.08 (s, 1H), 4.88 (s, 1H), 3.20 – 3.06 (m, 1H), 3.03 – 2.89 (m, 1H), 2.60 – 2.42 (m, 2H), 1.63 (s,

3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.8, 144.8, 139.7, 128.6, 127.1, 126.5, 111.0, 78.2, 42.6, 22.8, 19.5.

HRMS (EI) m/z: calcd. for $C_{13}H_{14}O^{\bullet+}$ ($[M]^{\bullet+}$): 186.1039, found: 186.1036.



To a solution of compound **S3a** (2.2 g, 8.65 mmol) in THF (20 mL) was added 1-Propenylmagnesium bromide (0.5 M in THF) (20.7 mL, 10.38 mmol) at 0 ℃ under N_2 atmosphere. The mixture was allowed to warm up to room temperature and stirred for 5 h. The reaction mixture was quenched with saturated ammonium chloride solution (30 mL), and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 50:1) to give compound **S4u** (2.6 g, 99%) as a colorless oil.

To a solution of compound **S4u** (2.6 g, 8.78 mmol) in Et_2O (45 mL) was added tetrafluoroboric acid (20 mL of a 48% aqueous solution) at 0 ℃. The mixture was allowed to warm up to room temperature and stirred for 0.5 h. The reaction was quenched by addition of 15% NaOH aqueous solution till pH 7~8, and extracted with Et_2O (40 mL × 3). The organic layers were combined, dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **1u**.

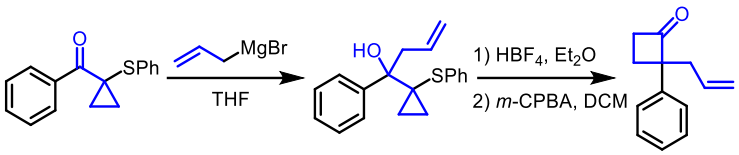
To a solution of crude **1u** in DCM (50 mL) was added 3-chloroperbenzoic acid (*m*-CPBA) (1.27 g, 7.38 mmol) at room temperature for 5 mins. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (50 mL) and extracted with DCM (50 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate : dichloromethane = 300:1 ~ 100:1) to give compound **1u** (*Z:E* = 1:1, 0.57 g, 35%) as a colorless liquid.

TLC (50:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 7H), 7.27 – 7.18 (m, 3H), 5.80 (dd, *J* = 10.8, 1.6 Hz, 1H), 5.72 – 5.58 (m, 2H), 5.56 – 5.43 (m, 1H), 3.25 – 2.91 (m, 4H), 2.68 – 2.37 (m, 4H), 1.67 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.57 (dd, *J* = 6.8, 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.5, 208.8, 141.3, 141.0, 132.5, 131.6, 128.92, 128.90, 128.8, 127.1, 127.0, 126.6, 126.5, 125.9, 74.8, 73.5, 44.2, 43.0, 27.5, 24.3, 18.1, 15.1.

HRMS (EI) m/z: calcd. for $C_{13}H_{14}O^{\bullet+}$ ($[M]^{\bullet+}$): 186.1039, found: 186.1036.



S3a **S4w** **1w**

To a solution of compound **S3a** (2.0 g, 7.86 mmol) in THF (20 mL) was added 1-Propenylmagnesium bromide (1.0 M in THF) (9.4 mL, 9.43 mmol) at 0 ℃ under N_2 atmosphere. The mixture was allowed to warm up to room temperature and stirred for 3 h. The reaction mixture was quenched with saturated ammonium chloride solution (30 mL), and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **S4w**.

Tetrafluoroboric acid (15 mL of a 48% aqueous solution) was added to a solution of compound **S4w** in Et_2O (30 mL) at 0 ^oC. The mixture was allowed to warm up to room temperature and stirred for 0.5 h. The reaction was quenched by addition of 15% NaOH aqueous solution till pH 7~8, and extracted with Et_2O (40 mL × 3). The organic layers were combined, dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **1w**.

To a solution of crude **1w** in DCM (40 mL) was added 3-chloroperbenzoic acid (*m*-CPBA) (1.0 g, 5.90 mmol) at room temperature for 5 mins. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (40 mL) and extracted with DCM (40 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 300:1 ~ 100:1) to give compound **1w** (1.18 g, 81%) as a colorless liquid.

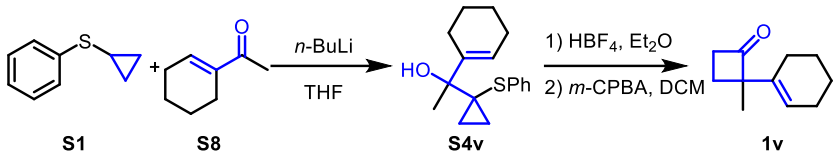
TLC (50:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 4H), 7.26 – 7.20 (m, 1H), 5.70 – 5.54 (m, 1H), 5.11 – 4.99 (m, 2H), 3.14 – 2.92 (m, 2H), 2.64 – 2.49 (m, 2H), 2.44 (ddd, J = 11.6, 10.0, 7.2 Hz, 1H), 2.28 (ddd, J = 11.6, 10.0, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 140.6, 132.9, 128.5, 126.9, 126.4, 118.9, 71.8, 44.0, 42.7, 22.2.

HRMS (ESI) m/z: calcd. for $C_{13}H_{15}O$ ($[M+H]^+$): 187.1117, found: 187.1118.

2.5 Preparation of Substrate 1v[1] and 1x



To a solution of cyclopropyl phenyl sulfide (**S1**) (2.0 g, 13.31 mmol) in dry THF (30 mL) was added *n*-BuLi (2.4 M in hexane) (5.5 mL, 13.31 mmol) at 0 °C under N_2 atmosphere. After the reaction mixture was stirred for 2.5 h, compound **S8** (1.65 g, 13.31 mmol) was added via a syringe at 0 °C, and stirred in that temperature for another 1.5 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (30 mL), and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 50:1) to give compound **S4v** (2.38 g, 65%) as a colorless oil.

To a solution of compound **S4v** (2.38 g, 8.68 mmol) in Et_2O (20 mL) was added tetrafluoroboric acid (2.3 mL of a 48% aqueous solution) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 0.5 h. The reaction was quenched by addition of 15% NaOH aqueous solution till pH 7~8, and extracted with Et_2O (30 mL × 3). The organic layers were combined, dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **1v**.

To a solution of crude **1v** in DCM (30 mL) was added 3-chloroperbenzoic acid (*m*-CPBA) (1.12 g, 6.51 mmol) at room temperature for 5 mins. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (30 mL) and extracted with DCM (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, concentrated via rotary evaporation, and purified by column chromatography on silica gel (pentane: ethyl ether = 100:1 ~ 50:1) to give compound **1v** (475 mg, 33%) as a colorless liquid.

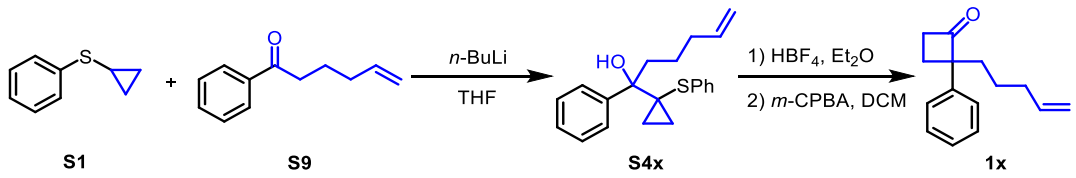
TLC (50:1 PE/EA, R_f): 0.5.

Physical Form: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.57 (s, 1H), 3.07 – 2.87 (m, 2H), 2.26 – 2.12 (m, 1H),

2.08 – 1.88 (m, 4H), 1.79 – 1.68 (m, 1H), 1.68 – 1.50 (m, 4H), 1.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.6, 136.9, 121.0, 69.8, 42.3, 25.3, 25.0, 23.9, 23.0, 22.4, 21.8.



To a solution of cyclopropyl phenyl sulfide (**S1**) (1.38 g, 9.19 mmol) in dry THF (10 mL) was added *n*-BuLi (2.4 M in hexane) (4.6 mL, 11.03 mmol) at 0 °C under N_2 atmosphere. After the reaction mixture was stirred for 1 h, compound **S9** (1.60 g, 9.19 mmol) was added via a syringe at 0 °C, and stirred in that temperature for another 1.5 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (30 mL), and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 80:1) to give compound **S4x** (2.17 g, 73%) as a colorless oil.

To a solution of compound **S4x** (2.17 g, 6.69 mmol) in Et_2O (20 mL) was added tetrafluoroboric acid (10 mL of a 48% aqueous solution) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 0.5 h. The reaction was quenched by addition of 15% NaOH aqueous solution till pH 7~8, and extracted with Et_2O (30 mL × 3). The organic layers were combined, dried over Na_2SO_4, filtered, evaporated in vacuo to give the crude product **1x**.

To a solution of crude **1x** in DCM (25 mL) was added 3-chloroperbenzoic acid (*m*-CPBA) (1.38 g, 8.03 mmol) at room temperature for 5 mins. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (30 mL) and extracted with DCM (30 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, concentrated via rotary evaporation, and purified by column chromatography on silica gel (pentane: ethyl ether = 100:1 ~ 50:1) to give compound **1x** (901 mg, 63%) as a colorless liquid.

TLC (50:1 PE/EA, R_f): 0.5.

Physical Form: colorless liquid

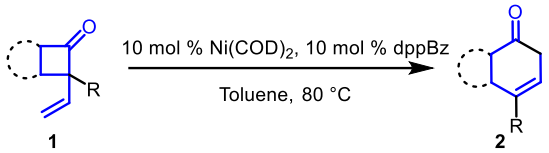
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.30 (m, 4H), 7.26 – 7.19 (m, 1H), 5.76 – 5.62

(m, 1H), 4.98 – 4.85 (m, 2H), 3.16 – 3.04 (m, 1H), 3.04 – 2.93 (m, 1H), 2.52 – 2.40 (m, 1H), 2.28 – 2.16 (m, 1H), 2.02 – 1.91 (m, 2H), 1.90 – 1.78 (m, 2H), 1.38 – 1.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 140.8, 138.3, 128.5, 126.8, 126.4, 115.0, 72.4, 42.6, 39.1, 33.8, 23.9, 23.5.

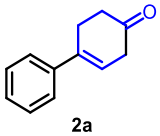
HRMS (ESI) m/z: calcd. for $C_{15}H_{19}O^+$ ($[M+H]^+$): 215.1430, found: 215.1430.

3. General Procedure for Rearrangement of VCBOs



To a 10 mL Schlenk tube, Ni(cod)2 (5.6 mg, 0.020 mmol), dppBz (8.9 mg, 0.020 mmol), toluene (2.0 mL), and compound **1** (0.20 mmol) were added in the glove box atmosphere. The resulting mixture was then stirred at indicated temperature and time (4 hours at 80 ℃ for **1a-b** and **1d**; 20 hours at room temperature **1a-b** and **1d**; for 24 hours at 80 ℃ for **1c** and **1e-s**; and 48 hours at 110 ℃ for **1t-u**). After cooling, the crude product was submitted to purification by column chromatography on silica gel (petroleum ether: ethyl acetate) to give rearrangement product **2**.

Compound 2a (Table 2)[7]



run 1: The reaction was stirred at 80 °C for 4 h. Substrate: **1a** (34.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2a** (31.0 mg, 90%).

run 2: The reaction was stirred at 80 °C for 4 h. Substrate: **1a** (34.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2a** (30.5 mg, 89%).

The average yield of two runs: 90%.

This reaction can also be carried out **at room temperature** for 20 h**,** with similar yield: Substrate: **1a** (34.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2a** (29.8 mg, 86%).

The average yield of two runs: 86%.

Physical Form: white solid.

Melting Point: 51 – 53 °C.

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

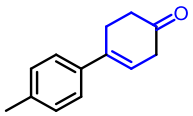
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.23 (m, 4H), 7.23 – 7.16 (m, 1H), 6.04 – 5.97 (m, 1H), 3.03 – 2.95 (m, 2H), 2.86 – 2.77 (m, 2H), 2.56 (t, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 140.9, 137.9, 128.7, 127.6, 125.4, 121.2, 40.1, 38.9, 28.1.

Gram scale experiments:

Following general procedure. Substrate: **1a** (1.0 g, 5.81 mmol), $Ni(cod)_2$ (80.0 mg, 0.29 mmol), dppBz (129.0 mg, 0.29 mmol), toluene (29 mL), 4 h, flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); products: **2a** (869 mg, 87%).

Compound 2b (Table 2)[8]



2b

run 1: The reaction was stirred at 80 °C for 4 h. Substrate: **1b** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2b** (34 mg, 91%).

run 2: The reaction was stirred at 80 °C for 4 h. Substrate: **1b** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2b** (34.7 mg, 93%).
The average yield of two runs: 92%.

This reaction can also be carried out **at room temperature** for 20 h**,** with similar yield: Substrate: **1b** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2b** (33.4 mg, 90%).

Physical Form: white solid.

Melting Point: 75 – 77 °C.

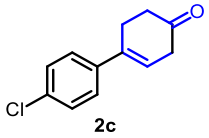
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.97 (t, J = 4.0 Hz, 1H), 3.02 – 2.92 (m, 2H), 2.85 – 2.75 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.3, 137.9, 137.6, 137.3, 129.2, 125.2, 120.2, 40.0,

38.8, 28.0, 21.2.

Compound 2c (Table 2)[7]



2c

run 1: Following general procedure. Substrate: **1c** (41.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2c** (35.1 mg, 85%).

run 2: Following general procedure. Substrate: **1c** (41.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2c** (35.3 mg, 86%).

The average yield of two runs: 86%.

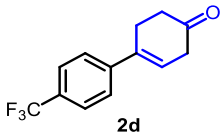
Physical Form: pale yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.24 (m, 4H), 6.12 – 6.04 (m, 1H), 3.09 – 3.00 (m, 2H), 2.91 – 2.80 (m, 2H), 2.63 (t, J = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6, 139.3, 136.8, 133.3, 128.7, 126.6, 121.7, 40.0, 38.7, 27.9.

Compound 2d (Table 2)[7]



2d

run 1: The reaction was stirred at 80 °C for 4 h. Substrate: **1d** (48.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2d** (44.7 mg, 93%).

run 2: The reaction was stirred at 80 °C for 4 h. Substrate: **1d** (48.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2d** (45.5 mg, 95%).

The average yield of two runs: 94%.

This reaction was carried out **at room temperature** for 20 h, with similar yield: Substrate: **1d** (48.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02

mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2d** (42.9 mg, 89%).

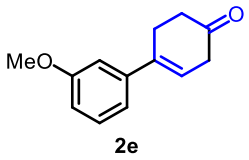
Physical Form: pale yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.18 (t, *J* = 4.0 Hz, 1H), 3.14 – 3.05 (m, 2H), 2.96 – 2.85 (m, 2H), 2.66 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 144.3, 136.9, 129.5 (q, *J* = 32.3 Hz), 125.63, 125.56 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.2 Hz), 123.4, 40.0, 38.6, 27.9.

Compound 2e (Table 2)



2e

run 1: Following general procedure. Substrate: **1e** (40.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2e** (40.3 mg, 99%).

run 2: Following general procedure. Substrate: **1e** (40.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2e** (39.2 mg, 97%).
The average yield of two runs: 98%.

Physical Form: white solid.

Melting Point: 57 – 59 °C.

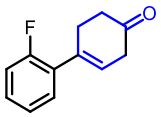
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 6.83 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.09 (t, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 3.11 – 3.02 (m, 2H), 2.94 – 2.83 (m, 2H), 2.64 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 159.8, 142.4, 137.8, 129.6, 121.3, 117.9, 112.7, 111.4, 55.4, 40.0, 38.8, 28.1.

HRMS (ESI) m/z: calcd. for $C_{13}H_{15}O_2$ ($[M+H]^+$): 203.1067, found: 203.1065.

Compound 2f (Table 2)



2f

run 1: Following general procedure. Substrate: **1f** (38.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2f** (35.3 mg, 93%).

run 2: Following general procedure. Substrate: **1f** (38.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2f** (36.0 mg, 95%).

The average yield of two runs: 94%.

Physical Form: colorless oil.

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

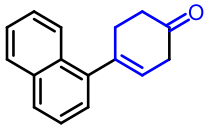
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.13 (m, 2H), 7.07 – 7.01 (m, 1H), 7.01 – 6.94 (m, 1H), 5.91 (t, J = 4.0 Hz, 1H), 3.03 – 2.96 (m, 2H), 2.83 – 2.74 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 159.9 (d, J = 245.9 Hz), 134.9, 129.5 (d, J = 13.7 Hz), 129.2 (d, J = 20.1 Hz), 129.1 (d, J = 24.2 Hz), 124.6 (d, J = 2.8 Hz), 124.3 (d, J = 3.5 Hz), 116.0 (d, J = 22.5 Hz), 40.2, 38.9, 28.9 (d, J = 3.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.98.

HRMS (ESI) m/z: calcd. for $C_{12}H_{12}FO$ ($[M+H]^+$): 191.0867, found: 191.0868.

Compound 2g (Table 2)



2g

run 1: Following general procedure. Substrate: **1g** (44.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2g** (40.4 mg, 91%).

run 2: Following general procedure. Substrate: **1g** (44.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2g** (41.9 mg, 94%).

The average yield of two runs: 93%.

Physical Form: white solid.

Melting Point: 122 – 123 °C.

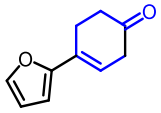
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.92 (m, 1H), 7.92 – 7.85 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.48 – 7.42 (m, 1H), 7.35 – 7.29 (m, 1H), 5.88 (t, *J* = 3.6 Hz, 1H), 3.22 – 3.10 (m, 2H), 2.95 – 2.84 (m, 2H), 2.75 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 140.7, 138.9, 133.9, 131.1, 128.6, 127.7, 126.1, 125.9, 125.5, 125.4, 125.2, 124.1, 40.1, 39.1, 31.2.

HRMS (ESI) m/z: calcd. for $C_{16}H_{15}O$ ($[M+H]^+$): 223.1117, found: 223.1114.

Compound 2h (Table 2)



2h

run 1: Following general procedure. Substrate: **1h** (16.2 mg, 0.1 mmol), $Ni(cod)_2$ (2.8 mg, 0.01 mmol), dppBz (4.5 mg, 0.01 mmol), toluene (1 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2h** (12.7 mg, 78%).

run 2: Following general procedure. Substrate: **1h** (16.2 mg, 0.1 mmol), $Ni(cod)_2$ (2.8 mg, 0.01 mmol), dppBz (4.5 mg, 0.01 mmol), toluene (1 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2h** (12.4 mg, 77%).

The average yield of two runs: 78%.

Physical Form: pale yellow solid.

Melting Point: 34 – 36 °C.

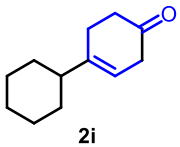
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H), 6.43 – 6.35 (m, 1H), 6.31 – 6.23 (m, 2H), 3.11 – 3.01 (m, 2H), 2.77 (t, *J* = 6.8 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.7, 153.7, 142.1, 127.8, 118.2, 111.3, 105.5, 39.5, 38.3, 25.5.

HRMS (ESI) m/z: calcd. for $C_{10}H_{11}O_2$ ($[M+H]^+$): 163.0754, found: 163.0752.

Compound 2i (Table 2)



2i

run 1: Following general procedure. Substrate: **1i** (35.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2i** (34.1 mg, 96%).

run 2: Following general procedure. Substrate: **1i** (35.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2i** (33.6 mg, 94%).

The average yield of two runs: 95%.

This reaction was carried out **at room temperature** for 24 h: Substrate: **1i** (35.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2i** (21.1 mg, 59%).

Physical Form: colorless oil.

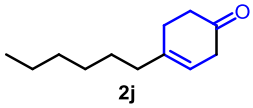
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 – 5.34 (m, 1H), 2.90 – 2.75 (m, 2H), 2.50 – 2.42 (m, 2H), 2.42 – 2.34 (m, 2H), 1.90 (t, J = 11.6 Hz, 1H), 1.81 – 1.62 (m, 5H), 1.33 – 1.20 (m, 2H), 1.20 – 1.06 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 144.2, 115.8, 45.2, 39.8, 39.1, 31.7, 27.2, 26.7, 26.4.

HRMS (ESI) m/z: calcd. for $C_{12}H_{19}O$ ($[M+H]^+$): 179.1430, found: 179.1431.

Compound 2j (Table 2)



2j

run 1: Following general procedure. Substrate: **1j** (36.03 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2j** (34.5 mg, 96%).

run 2: Following general procedure. Substrate: **1j** (36.03 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2j** (34.6 mg, 96%).

The average yield of two runs: 96%.

Physical Form: colorless oil.

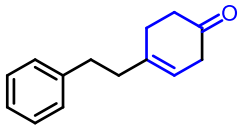
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.50 – 5.32 (m, 1H), 2.88 – 2.79 (m, 2H), 2.52 – 2.43 (m, 2H), 2.42 – 2.33 (m, 2H), 2.04 (t, *J* = 7.2 Hz, 2H), 1.46 – 1.34 (m, 2H), 1.28 (d, *J* = 10.7 Hz, 6H), 0.87 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 139.1, 117.7, 39.8, 38.9, 37.2, 31.8, 29.1, 28.7, 27.7, 22.7, 14.2.

HRMS (ESI) m/z: calcd. for $C_{12}H_{21}O$ ($[M+H]^+$): 181.1587, found: 181.1586.

Compound 2k (Table 2)



2k

run 1: Following general procedure. Substrate: **1k** (40.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2k** (34.6 mg, 87%).

run 2: Following general procedure. Substrate: **1k** (40.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2k** (34.2 mg, 86%).

The average yield of two runs: 87%.

Physical Form: colorless oil

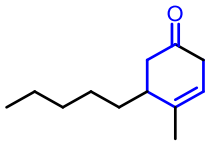
TLC (10:1 PE/EA, R_f): 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.16 (m, 2H), 7.15 – 7.05 (m, 3H), 5.38 (t, *J* = 3.6 Hz, 1H), 2.81 – 2.73 (m, 2H), 2.72 – 2.62 (m, 2H), 2.46 – 2.38 (m, 2H), 2.36 (d, *J* = 6.0 Hz, 2H), 2.30 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 141.8, 138.2, 128.5, 128.4, 126.0, 118.5, 39.7, 39.0, 38.7, 34.4, 28.8.

HRMS (ESI) m/z: calcd. for $C_{14}H_{17}O$ ($[M+H]^+$): 201.1274, found: 201.1273.

Compound 2l (Table 2)



2l

run 1: Following general procedure. Substrate: **1l** (36.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 10:1 PE/EA); product: **2l** (34.3 mg, 95%).

run 2: Following general procedure. Substrate: **1l** (36.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 10:1 PE/EA); product: **2l** (33.2 mg, 92%).

The average yield of two runs: 94%.

Physical Form: colorless oil.

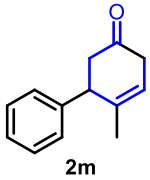
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 – 5.30 (m, 1H), 2.89 – 2.68 (m, 2H), 2.56 (dd, J = 14.4, 6.4 Hz, 1H), 2.46 – 2.34 (m, 2H), 1.77 (d, J = 1.6 Hz, 3H), 1.55 – 1.42 (m, 1H), 1.39 – 1.11 (m, 7H), 0.85 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.2, 139.0, 118.3, 43.8, 41.2, 39.7, 33.4, 32.0, 26.5, 22.6, 22.1, 14.1.

HRMS (EI) m/z: calcd. for $C_{12}H_{20}O^{\bullet+}$ ($[M]^{\bullet+}$): 180.1509, found: 180.1506.

Compound 2m (Table 2)



2m

run 1: Following general procedure. Substrate: **1m** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 30:1 to 10:1 PE/EA); product: **2m** (29.3 mg, 79%).

run 2: Following general procedure. Substrate: **1m** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 30:1 to 10:1 PE/EA); product: **2m** (29.9 mg, 80%).

The average yield of two runs: 80%.

This reaction was carried out **at 50 °C** for 24 h, with similar yield: Substrate: **1m** (37.2

mg, 0.2 mmol), Ni(cod)2 (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2m** (29.4 mg, 79%).

Physical Form: colorless oil.

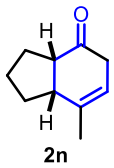
TLC (20:1 PE/EA, R_f): 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.25 (m, 2H), 7.24 -7.16 (m, 1H), 7.13 – 7.03 (m, 2H), 5.70 – 5.62 (m, 1H), 3.72 (t, *J* = 5.6 Hz, 1H), 2.96 (s, 2H), 2.91 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.57 (dd, *J* = 14.4, 4.0 Hz, 1H), 1.68 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 142.4, 136.8, 128.9, 127.5, 127.0, 120.2, 48.4, 47.4, 40.1, 22.2.

HRMS (ESI) m/z: calcd. for $C_{13}H_{15}O$ ($[M+H]^+$): 187.1117, found: 187.1119.

Compound 2n (Table 2)



2n

run 1: Following general procedure. Substrate: **1n** (30.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 40:1 to 20:1 PE/EA); product: **2n** (22.8 mg, 76%).

run 2: Following general procedure. Substrate: **1n** (30.0 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 40:1 to 20:1 PE/EA); product: **2n** (22.4 mg, 75%).

The average yield of two runs: 76%.

Physical Form: white solid.

Melting Point: 50 – 52 °C.

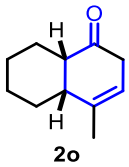
TLC (20:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (t, *J* = 4.0 Hz, 1H), 2.98 – 2.71 (m, 4H), 2.24 – 2.08 (m, 1H), 2.06 – 1.92 (m, 1H), 1.82 – 1.65 (m, 5H), 1.62 – 1.45 (m, 1H), 1.30 – 1.14 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 136.9, 117.1, 50.6, 49.1, 39.0, 32.3, 26.1, 24.3, 22.1.

HRMS (ESI) m/z: calcd. for $C_{10}H_{15}O$ ($[M+H]^+$): 151.1117, found: 151.1116.

Compound 2o (Table 2)



2o

run 1: Following general procedure. Substrate: **1o** (32.8 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2o** (24.8 mg, 76%).

run 2: Following general procedure. Substrate: **1o** (32.8 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2o** (26.1 mg, 80%).

The average yield of two runs: 78%.

Physical Form: colorless oil.

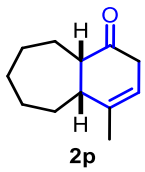
TLC (50:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45 – 5.25 (m, 1H), 2.94 – 2.64 (m, 3H), 2.36 – 2.20 (m, 2H), 1.90 – 1.79 (m, 1H), 1.77 (d, J = 2.0 Hz, 3H), 1.72 – 1.64 (m, 1H), 1.55 – 1.37 (m, 2H), 1.31 – 1.12 (m, 2H), 1.02 – 0.86 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.0, 139.5, 117.4, 48.2, 44.5, 39.7, 29.7, 26.2, 24.6, 22.4, 21.7.

HRMS (ESI) m/z: calcd. for $C_{11}H_{17}O$ ($[M+H]^+$): 165.1274, found: 165.1273.

Compound 2p (Table 2)



2p

run 1: Following general procedure. Substrate: **1p** (35.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2p** (30.0 mg, 84%).

run 2: Following general procedure. Substrate: **1p** (35.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6

mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2p** (29.3 mg, 82%).
The average yield of two runs: 83%.

Physical Form: colorless oil.

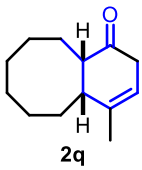
TLC (50:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (s, 1H), 2.91 – 2.70 (m, 3H), 2.44 (t, J = 8.4 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.77 (s, 3H), 1.74 – 1.53 (m, 4H), 1.45 – 1.04 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 139.8, 117.3, 50.8, 47.1, 40.1, 30.4, 29.9, 29.4, 26.0, 24.1, 22.0.

HRMS (ESI) m/z: calcd. for $C_{12}H_{19}O$ ($[M+H]^+$): 179.1430, found: 179.1430.

Compound 2q (Table 2)



2q

run 1: Following general procedure. Substrate: **1q** (38.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 150:1 to 100:1 PE/EA); product: **2q** (35.0 mg, 91%).

run 2: Following general procedure. Substrate: **1q** (38.4 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 150:1 to 100:1 PE/EA); product: **2q** (34.1 mg, 89%).
The average yield of two runs: 90%.

This reaction was carried out **at 50 °C** for 24 h, with similar yield: Substrate: **1q** (38.4 mg, 0.2 mmol), Ni(cod)2 (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 10:1 to 5:1 PE/EA); product: **2q** (33.8 mg, 88%).

Physical Form: colorless oil.

TLC (50:1 PE/EA, R_f): 0.4

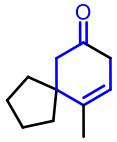
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 – 5.22 (m, 1H), 2.90 – 2.59 (m, 4H), 1.89 – 1.79 (m, 1H), 1.77 (d, J = 1.6 Hz, 3H), 1.76 – 1.70 (m, 1H), 1.70 – 1.20 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 140.9, 117.2, 52.3, 42.5, 40.4, 29.4, 28.9, 28.2,

25.1, 24.2, 22.7, 22.1.

HRMS (ESI) m/z: calcd. for $C_{13}H_{21}O$ ($[M+H]^+$): 193.1587, found: 193.1586.

Compound 2r (Table 2)



2r

run 1: Following general procedure. Substrate: **1r** (32.8 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 30:1 PE/EA); product: **2r** (29.0 mg, 88%).

run 2: Following general procedure. Substrate: **1r** (32.8 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 30:1 PE/EA); product: **2r** (28.6 mg, 87%).

The average yield of two runs: 88%.

Physical Form: white solid.

Melting Point: 45 – 47 °C.

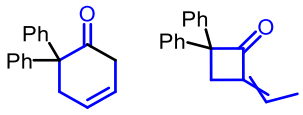
TLC (10:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.43 – 5.31 (m, 1H), 2.87 – 2.72 (m, 2H), 2.39 (s, 2H), 1.73 (d, J = 1.6 Hz, 3H) 1.72 – 1.61 (m, 6H), 1.46 – 1.29 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 141.3, 118.6, 51.3, 49.7, 40.5, 36.8, 24.8, 19.0.

HRMS (ESI) m/z: calcd. for $C_{11}H_{17}O$ ($[M+H]^+$): 165.1274, found: 165.1275.

Compound 2s (Table 2)



2s **1s'**

run 1: Following general procedure. Substrate: **1s** (49.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6 mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 30:1 PE/EA); product: **2s** (22.6 mg, 46%) and byproduct: **1s′** (*Z*:*E* = 1:4, 21.1 mg, 43%).

run 2: Following general procedure. Substrate: **1s** (49.6 mg, 0.2 mmol), $Ni(cod)_2$ (5.6

mg, 0.02 mmol), dppBz (8.9 mg, 0.02 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 30:1 PE/EA); product: **2s** (24.3 mg, 49%) and byproduct: **1s′** (*Z*:*E* = 1:4, 21.2 mg, 43%).

The configurations of *Z*-**1s′** and *E*-**1s′** were proposed according to literature 9

The average yield of two runs: 48%.

Physical Form: white solid.

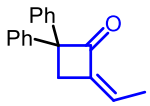
Melting Point: 131 – 133 °C.

TLC (50:1 PE/EA, R_f): 0.4

2s: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 – 7.20 (m, 6H), 7.16 – 7.05 (m, 4H), 6.02 – 5.92 (m, 1H), 5.66 – 5.55 (m, 1H), 3.12 (dt, *J* = 3.2, 1.6 Hz, 2H), 2.93 (dt, *J* = 3.6, 1.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.3, 141.5, 128.9, 128.3, 127.2, 126.1, 124.6, 62.6, 40.1, 39.0.

HRMS (ESI) m/z: calcd. for $C_{18}H_{17}O$ ($[M+H]^+$): 249.1274, found: 249.1275.

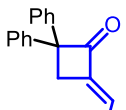


Z-**1s'**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 4H), 7.33 – 7.27 (m, 4H), 7.23 – 7.16 (m, 2H), 5.83 (qt, *J* = 7.6, 2.4 Hz, 1H), 3.38 (p, *J* = 2.4 Hz, 2H), 2.11 (dt, *J* = 7.2, 2.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 143.4, 142.6, 134.0, 128.7, 127.0, 126.9, 71.4, 38.1, 16.5.

HRMS (ESI) m/z: calcd. for $C_{18}H_{17}O$ ($[M+H]^+$): 249.1274, found: 249.1270.



E-**1s'**

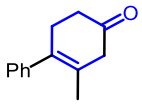
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 4H), 7.34 – 7.27 (m, 4H), 7.25 – 7.16 (m, 2H), 6.55 (qt, *J* = 7.2, 3.2 Hz, 1H), 3.41 (p, *J* = 2.0 Hz, 2H), 1.82 (dt, *J* = 7.2, 2.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 145.2, 142.5, 129.3, 128.7, 127.0, 126.9, 71.6,

36.9, 14.8.

HRMS (ESI) m/z: calcd. for $C_{18}H_{17}O$ ($[M+H]^+$): 249.1274, found: 249.1270.

Compound 2t (Table 2)



2t

run 1: Following general procedure. Substrate: **1t** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (11.0 mg, 0.04 mmol), dppBz (17.8 mg, 0.04 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2t** (6.8 mg, 18%).

run 2: Following general procedure. Substrate: **1t** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (11.0 mg, 0.04 mmol), dppBz (17.8 mg, 0.04 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2t** (5.9 mg, 16%).

The average yield of two runs: 17%.

Physical Form: colorless oil.

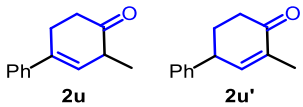
TLC (20:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, J = 7.2, 7.2 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 – 7.07 (m, 2H), 2.97 (s, 2H), 2.78 – 2.68 (m, 2H), 2.61 (t, J = 6.8 Hz, 2H), 1.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 142.3, 132.9, 128.38, 128.35, 127.1, 126.8, 45.7, 39.4, 31.9, 20.4.

HRMS (EI) m/z: calcd. for $C_{13}H_{14}O^{\bullet+}$ ($[M]^{\bullet+}$): 186.1039, found: 186.1036.

Compound 2u and 2u' (Table 2)



2u **2u'**

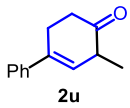
run 1: Following general procedure. Substrate: **1u** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (11.0 mg, 0.04 mmol), dppBz (17.8 mg, 0.04 mmol), toluene (2 mL), flash column chromatography (silica gel, 80:1 to 50:1 PE/EA); product: **2u** (4.5 mg, 12%) and **2u'** (5.3 mg, 14%).

run 2: Following general procedure. Substrate: **1u** (37.2 mg, 0.2 mmol), $Ni(cod)_2$ (11.0

mg, 0.04 mmol), dppBz (17.8 mg, 0.04 mmol), toluene (2 mL), flash column chromatography (silica gel, 80:1 to 50:1 PE/EA); product: **2u** (4.4 mg, 12%) and **2u'** (6.3 mg, 17%).

The average yield of two runs: 28%.

Compound 2u (Table 2)



2u

Physical Form: colorless oil.

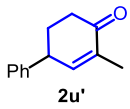
TLC (20:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.26 (m, 5H), 5.98 (d, *J* = 3.2 Hz, 1H), 3.17 – 2.98 (m, 1H), 2.96 – 2.82 (m, 2H), 2.75 – 2.55 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.5, 140.7, 137.0, 128.6, 128.0, 127.6, 125.4, 43.4, 37.6, 28.7, 16.7.

HRMS (EI) m/z: calcd. for $C_{13}H_{14}O^{\bullet+}$ ($[M]^{\bullet+}$): 186.1039, found: 186.1035.

Compound 2u' (Table 2)



2u'

Physical Form: colorless oil.

TLC (20:1 PE/EA, R_f): 0.4

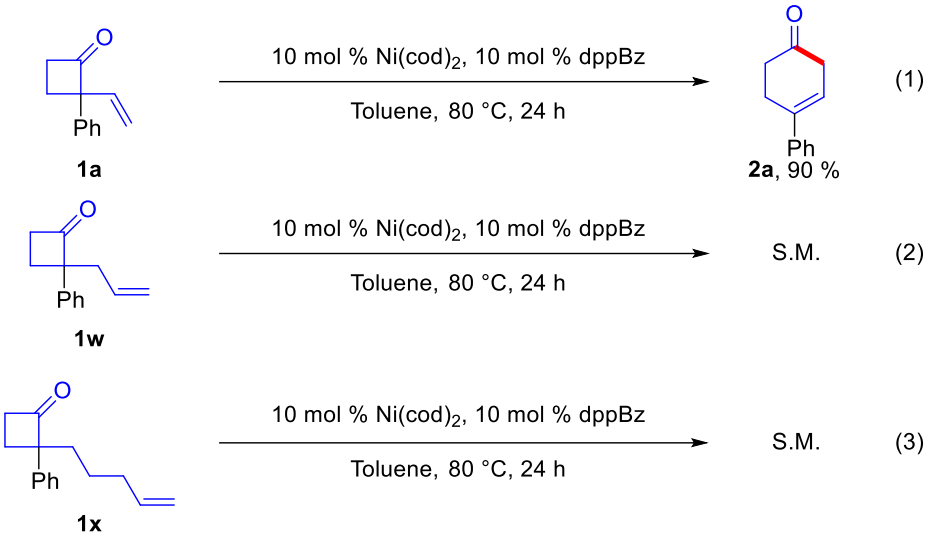
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 7.24 – 7.19 (m, 2H), 6.78 – 6.72 (m, 1H), 3.75 – 3.65 (m, 1H), 2.57 (dt, *J* = 16.6, 4.9 Hz, 1H), 2.46 (ddd, *J* = 16.6, 12.0, 4.7 Hz, 1H), 2.38 – 2.27 (m, 1H), 2.10 – 1.95 (m, 1H), 1.87 (dd, *J* = 2.0, 2.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 148.3, 143.7, 136.1, 128.9, 127.7, 127.1, 43.2, 37.3, 33.0, 16.2.

HRMS (EI) m/z: calcd. for $C_{13}H_{14}O^{\bullet+}$ ($[M]^{\bullet+}$): 186.1039, found: 186.1034.

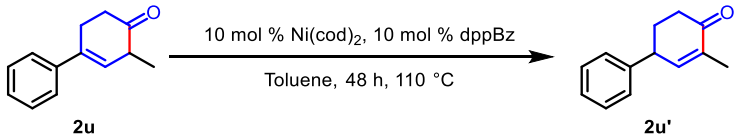
4. Controlled Experiment

4.1 Experimental Comparison of C-C Cleavage Assisted by Vinyl Group (1a), Allyl Group (1w), and Alkyl Group (1x) in Substrates



To a 10 mL Schlenk tube, $Ni(cod)_2$ (5.6 mg, 0.020 mmol), dppBz (8.9 mg, 0.020 mmol), toluene (2.0 mL), and compound **1a** (34.4 mg, 0.20 mmol) or **1w** (37.2 mg, 0.2 mmol) or **1x** (42.8 mg, 0.2 mmol) were added in the glove box atmosphere. The resulting mixture was then stirred at 80 °C for 24 hours. After cooling, the crude product was concentrated via rotary evaporator to remove most of the solvent. The residue was submitted to ^1H NMR analysis in $CDCl_3$ to determine the yield, using dimethyl terephthalate (δ = 8.10) as the internal standard (for **1a**: 90% yield; for **1w**: 100% recycled materials; for **1x**: 100% recycled materials). The above experimental results show that vinyl can effectively assist C-C cleavage.

4.2 The Experimental Process from 2u to 2u′

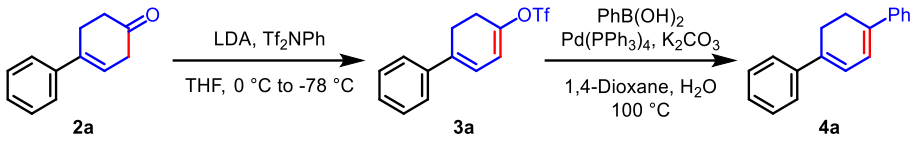


To a 10 mL Schlenk tube, $Ni(cod)_2$ (1.0 mg, 0.0036 mmol), dppBz (1.6 mg, 0.0036 mmol), toluene (0.4 mL), and compound **2u** (6.7 mg, 0.036 mmol) were added in the glove box atmosphere. The resulting mixture was then stirred at 110 °C for 48 hours. After cooling, the crude product was concentrated via rotary evaporator to remove most of the solvent. The residue was submitted to ^1H NMR analysis in $CDCl_3$ to determine

the yield, using dimethyl terephthalate (δ = 8.10) as the internal standard (for **2u′**: 100% yield). The above experimental results show that non-conjugated enone **2u** can be converted to the conjugated enone **2u′** under standard conditions.

5. Procedures for Synthetic Transformations

5.1 Procedure for the Synthesis of 4a



To a solution of $^{i}Pr_2NH$ (0.23 mL, 1.65 mmol) in anhydrous THF (2 mL) was added *n*-BuLi (0.69 mL, 1.65 mmol) at 0 ℃ under N_2 atmosphere for 30 min. The reaction solution was cooled to -78 ℃. Compound **2a** (258 mg, 1.5 mmol) in THF (2 mL) was added dropwise, and the reaction mixture was stirred for 30 min at -78 ℃. A solution of Tf_2NPh (619 mg, 1.65 mmol) dissolved in THF (2 mL) was then added. After complete addition, the reaction mixture was allowed to warm up to 0 ℃ and stirred for 2 h. The reaction mixture was quenched with saturated ammonium chloride solution (10 mL), and extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 ~ 50:1) to give compound **3a** (417 mg, 91%) as a yellow oil.

Run 2: **2a** (86.0 mg, 0.50 mmol) was converted to the title compound **3a** (137 mg, 90%) using the same procedure as above.

The average yield of two runs was 91%.

TLC (20:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.23 (m, 5H), 6.21 (d, J = 6.0 Hz, 1H), 6.07 (d, J = 6.4 Hz, 1H), 2.90 (d, J = 10.0 Hz, 2H), 2.70 (d, J = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 139.6, 136.9, 128.7, 128.1, 125.4, 118.8 (q, J = 318.7 Hz), 117.7, 115.7, 27.3, 26.4.

HRMS (ESI) m/z: calcd. for $C_{13}H_{12}F_3O_3S$ ($[M+H]^+$): 305.0454, found: 305.0457.

To a 25 mL Schlenk tube were added compound **3a** (304 mg, 1.0 mmol), $PhB(OH)_2$ (244 mg, 2.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and K_2CO_3 (414 mg, 3.0 mmol). The sealed flask was evacuated and refilled with N_2 three times, followed by addition of 1,4-dioxane (5 mL) and H_2O (0.5 mL) via a syringe. The reaction mixture was stirred at room temperature for 10 min and then in an oil bath at 100 °C for 12 h. After being cooled down to room temperature, the reaction mixture was filtered,

concentrated, and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 400:1 ~ 200:1) to give compound **4a**[10] (123 mg, 53%) as a pale yellow solid.

Run 2: **3a** (60.8 mg, 0.20 mmol) was converted to the title compound **4a** (26.6 mg, 57%) using the same procedure as above.

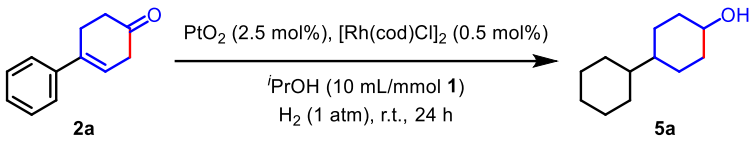
The average yield of two runs was 55%.

TLC (50:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 4H), 7.38 – 7.30 (m, 4H), 7.27 – 7.21 (m, 2H), 6.52 (s, 2H), 2.77 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 136.0, 128.6, 127.2, 125.0, 121.8, 26.2.

5.2 Procedure for the Synthesis of 5a[11]



To a reaction vessel were added with compound **2a** (86 mg, 0.50 mmol), PtO_2 (5.7 mg, 0.025 mmol) and $[Rh(cod)Cl]_2$ (2.5 mg, 0.005 mol). Isopropanol (5 mL) was added to dissolve the Rh catalyst, and the vessel was sealed with a rubber septum. An H_2 balloon (~1 L) was attached to the reaction vessel, which was then evacuated and refilled with H_2 for three times. The H_2 balloon was kept, and the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was filtered and concentrated via rotary evaporator to remove most of solvent. The residue was submitted to ^{1}H NMR analysis in $CDCl_3$ to determine the ratio of *trans*-**5a** and *cis*-**5a.** The sample in $CDCl_3$ was concentrated. The residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 ~ 10:1) to give compound *trans*-5**a** and *cis*-**5a** (90.1 mg, 99%)

The *trans*/*cis* = 1:1 ratios of product **5a** was determined by ^{1}H NMR analysis of the crude reaction mixture.

The configurations of *trans*-**5a** and *cis*-**5a** were determined according to literature 12

Run 2: **2a** (86.0 mg, 0.5 mmol) was converted to the title compound **5a** (90.3 mg, 99%) using the same procedure as above.

The average yield of two runs was 99%.

TLC (10:1 PE/EA, R_f): 0.3.

trans-**5a: ^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.57 – 3.44 (m, 1H), 2.03 – 1.93 (m, 2H),

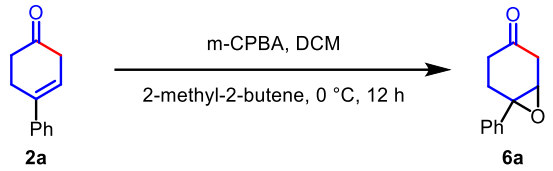
1.80 – 1.52 (m, 9H), 1.26 – 0.88 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 71.4, 42.9, 42.5, 36.1, 30.5, 28.2, 26.93, 26.91.

cis-**5a: ^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.03 – 3.90 (m, 1H), 1.79 – 0.84 (m, 20H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 67.2, 42.6, 42.4, 33.0, 30.5, 27.03, 27.02, 24.0.

5.3 Procedure for the Synthesis of 6a



To a solution of compound **2a** (172 mg, 1.0 mmol) in DCM (5 mL) was added m-CPBA (241 mg, 1.4 mmol) at 0 ℃. The reaction mixture was stirred at the same temperature for further 12 h before quenched with 2-methyl-2-butene (0.13 mL, 1.2 mmol) for 5 min. The reaction mixture was added a saturated aqueous Na_2SO_3 solution (10), saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with DCM (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 ~ 10:1) to give compound **6a** (120 mg, 64%) as a colorless oil.

Run 2: **2a** (51.6 mg, 0.30 mmol) was converted to the title compound **6a** (35.1 mg, 62%) using the same procedure as above.

The average yield of two runs was 63%.

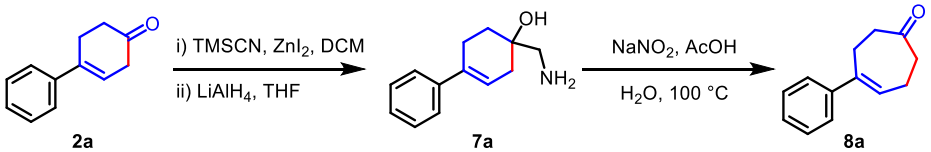
TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 3.29 (dd, J = 3.2, 1.6 Hz, 1H), 2.97 (dd, J = 19.6, 2.0 Hz, 1H), 2.82 – 2.57 (m, 3H), 2.55 – 2.47 (m, 1H), 2.41 – 2.32 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8, 139.8, 128.6, 128.1, 125.2, 59.6, 59.3, 39.0, 36.1, 25.6.

HRMS (ESI) m/z: calcd. for $C_{12}H_{13}O_2$ ($[M+H]^+$): 189.0910, found: 189.0910.

5.4 Procedure for the Synthesis of 8a



To solution of compound **2a** (172 mg, 1.0 mmol), ZnI_2 (12.8 mg, 0.04 mmol) in DCM (3 mL) was added TMSCN (0.19 mL, 1.5 mmol) at 0 ℃ under N_2 atmosphere. The reaction mixture was stirred 10 h at room temperature and added a saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with DCM (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo to give the crude product.

$LiAlH_4$ (76 mg, 2.0 mmol) was added to a solution of crude in anhydrous THF (5 mL) at 0 ºC. The reaction mixture was allowed to warm up to room temperature and stirred for 4 h. The reaction was quenched by the sequential addition of H_2O (0.076 mL), 15% NaOH aqueous solution (0.076 mL) and H_2O (0.23 mL). The reaction mixture was filtered, concentrated, and purified by column chromatography on silica gel (dichloromethane : methanol : triethylamine = 10:1:1) to give compound **7a** (180 mg, 89%) as a white solid.

Run 2: **2a** (172 mg, 1.0 mmol) was converted to the title compound **7a** (184 mg, 91%) using the same procedure as above.

The average yield of two runs was 90%.

TLC (10:1:1 DCM/MeOH/Et_3N, R_f): 0.4.

Melting Point: 68-70 °C.

^{1}H NMR (400 MHz, CD_3OD): δ 7.43 – 7.36 (m, 2H), 7.32 – 7.24 (m, 2H), 7.24 – 7.14 (m, 1H), 6.03 – 5.97 (m, 1H), 2.74 – 2.58 (m, 3H), 2.50 – 2.39 (m, 1H), 2.36 – 2.21 (m, 2H), 1.92 – 1.72 (m, 2H).

^{13}C NMR (100 MHz, CD_3OD): δ 143.1, 137.4, 129.2, 127.8, 126.1, 122.3, 70.6, 51.0, 37.1, 32.4, 25.9.

HRMS (ESI) m/z: calcd. for $C_{13}H_{18}NO$ ($[M+H]^+$): 204.1383, found: 204.1382.

To solution of compound **7a** (61 mg, 0.3 mmol) in H_2O (0.49 mL) was added AcOH (0.03 mL, 0.53 mmol) at room temperature under N_2 atmosphere. The reaction mixture was cooled to 0 ℃, and a solution of $NaNO_2$ (31 mg, 0.45 mmol) in H_2O (0.49 mL) was added dropwise over 5 min. The mixture was stirred for 1 h at 0 ℃ and was heated to reflux 2 h. After being cooled down to room temperature, the reaction mixture was added saturated aqueous $NaHCO_3$ solution (15 mL) and extracted with DCM (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 ~ 16:1) to give compound **8a**[13] (13 mg, 23%) as a pale yellow oil.

Run 2: **7a** (61.0 mg, 0.3 mmol) was converted to the title compound **8a** (13.8 mg, 25%) using the same procedure as above.

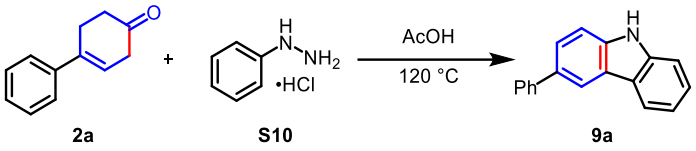
The average yield of two runs was 24%.

TLC (10:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 4H), 7.28 – 7.21 (m, 1H), 6.10 (t, *J* = 6.0 Hz, 1H), 2.82 – 2.72 (m, 4H), 2.72 – 2.65 (m, 2H), 2.57 – 2.47 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.9, 144.0, 142.3, 128.5, 127.7, 127.2, 125.9, 42.8, 42.5, 27.8, 24.4.

5.5 Procedure for the Synthesis of 9a



2a **S10** **9a**

To solution of compound **2a** (86 mg, 0.5 mmol) in AcOH (0.8 mL) was added **S10** (109 mg, 0.75 mmol). The reaction mixture was heated to reflux 12 h at 120 ℃, and then added H_2O (10 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, evaporated in vacuo and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 ~ 10:1) to give compound **9a**[14] (61 mg, 50%) as a pale yellow solid.

Run 2: **2a** (51.6 mg, 0.3 mmol) was converted to the title compound **9a** (39.0 mg, 53%) using the same procedure as above.

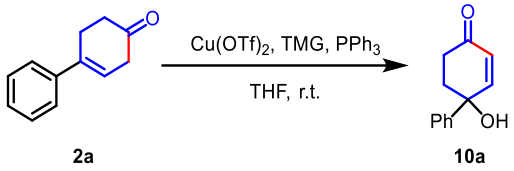
The average yield of two runs was 52%.

TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.31 (s, 1H), 8.44 (d, *J* = 1.6 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.70 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.40 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.18 (ddd, *J* = 7.6, 7.2, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 141.3, 140.2, 139.3, 130.9, 128.8, 126.7, 126.3, 125.7, 124.6, 123.1, 122.6, 120.4, 118.6, 118.3, 111.3, 111.1.

5.6 Procedure for the Synthesis of 10a[15]



2a **10a**

To solution of compound **2a** (34.4 mg, 0.20 mmol), $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), PPh_3 (68.2 mg, 0.26 mmol) in THF (1.0 mL) was added TMG (0.010 mL, 0.08 mmol) at room temperature for 5 h under air balloon. The reaction mixture was submitted to purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1 ~ 4:1) to give compound **10a** (26 mg, 69%) as a colorless oil.

Run 2: **2a** (34.4 mg, 0.2 mmol) was converted to the title compound **10a** (25.2 mg, 67%) using the same procedure as above.

The average yield of two runs was 68%.

TLC (3:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 6.89 (d, J = 10.4 Hz, 1H), 6.14 (d, J = 10.4 Hz, 1H), 2.66 – 2.54 (m, 1H), 2.42 – 2.32 (m, 2H), 2.31 – 2.22 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 152.5, 143.7, 129.6, 128.8, 128.2, 125.5, 72.7, 38.9, 34.6.

6. Computed Energies for the Stationary Points:

6.1 Computational Method

DFT calculations were performed with the Gaussian 09 software package.[16] Geometric optimizations of intermediates and transition states were calculated at the PBE0[17]-D3[18](BJ)[19]/def2-SVP[20] level. Unscaled harmonic frequency calculations were also performed at the same level to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. Standard state concentration of 1.0 mol/L was used for all species. Based on the optimized structures, Gibbs energies of solvation in Toluene were computed at the SMD[21]/ PBE0-D3(BJ)/def2-SVP level, and single point energies were calculated at the PBE0-D3(BJ)/def2-TZVPP level.

6.2 Comparison of transition state free energies for C-C cleavage assisted by vinyl (1a), allyl (1w), and alkyl (1x) groups (Figure S1).

In Figure S1, we discuss the free energy of vinyl (**1a**), allyl (**1w**), and alkyl (**1x** for a vinyl group at terminal position of alkyl group) substrates on the cleavage of the C-C bond of cyclobutanone under the catalysis of Ni through DFT calculations. The results show that the free energy of transition states **1w-TS1** (28.2 kcal/mol) and **1x-TS1** (27.1 kcal/mol) is significantly higher than that of **TS1** (18.1 kcal/mol), indicating that the oxidative addition process of cyclobutanone C-C bond assisted by vinyl is more favored than that with allyl and alkyl substrates.

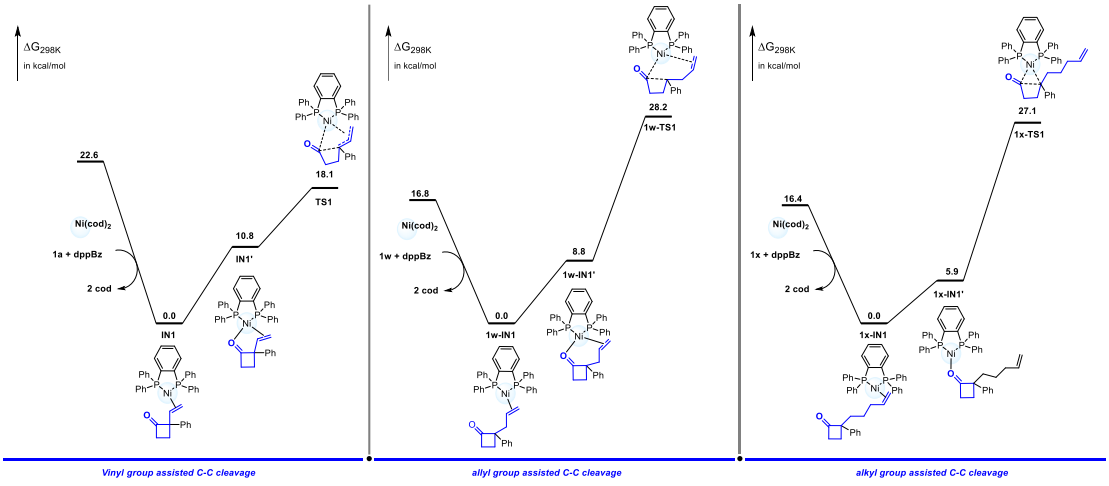


Figure S1 Computed at the PBE0-D3(BJ)/def2-TZVPP:SMD(toluene)//PBE0-D3(BJ)/def2-SVP level

6.3 Comparison of Transition State Free Energies of Oxidative Addition of 2-Aryl (1a) and 2-Alkyl (1i) Vinyl Cyclobutanones (Figure S2).

In Figure S2, we discuss the effect of substituent changes (**1a** represents 2-aryl vinylcyclobutanone and **1i** represents 2- alkyl vinylcyclobutanone) on the free energy of the oxidative addition process. We found that there is almost no difference in the free energy between the two types of substrates (18.1 kcal/mol for **1a**; 19.0 kcal/mol for **1i**), which is consistent with experimental observations that showed yields of 86% for **1a** and 59% for **1i** at room temperature.

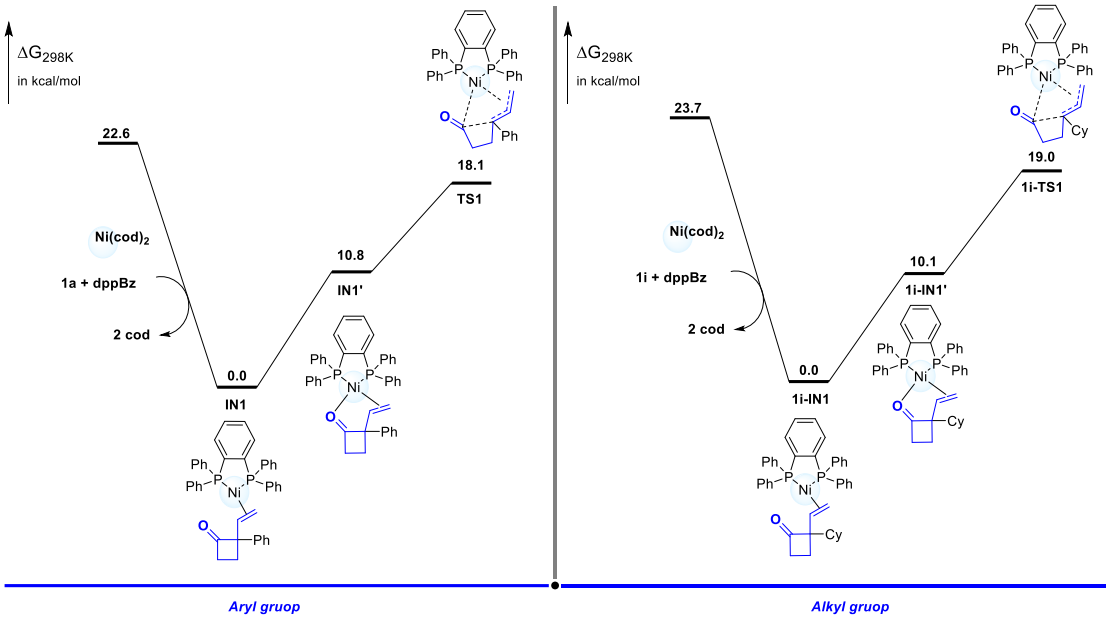


Figure S2 Computed at the PBE0-D3(BJ)/def2-TZVPP:SMD(toluene)//PBE0-D3(BJ)/def2-SVP level

6.4 Comparison of the Thermodynamic Stabilities of Products 2u and 2u' (Figure S3).

In Figure S4, we compared the thermodynamic stabilities of products **2u** and **2u'** and found that the latter is lower than the former by 2 kcal/mol in terms of free energy, indicating that it is more thermodynamically stable.

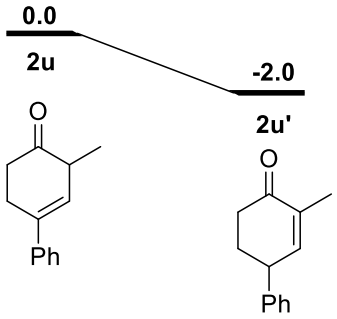


Figure S3 Computed at the PBE0-D3(BJ)/def2-TZVPP:SMD(toluene)//PBE0-D3(BJ)/def2-SVP level

6.5 Thermal Corrections to Gibbs Energies (TCGs), Single-point Energies (SPEs)

	Imaginary Frequencies (cm^{-1})	TCG[a,b] (a. u.)	SPE[a,b] (a. u.)	SPE[c,b] (a. u.)	SPE[d,b] (a. u.)
$Ni(cod)_2$	none	0.324835	-2130.877311	-2130.890525	-2131.732148
cod	none	0.149581	-311.4468	-311.456142	-311.774761
1a	none	0.168071	-538.681919	-538.695467	-539.257198
dppBz	none	0.387329	-1837.779184	-1837.808196	-1839.221647
IN1	none	0.583482	-3884.468789	-3884.506832	-3886.698914
IN1′	none	0.584678	-3884.461332	-3884.499071	-3886.683246
TS1	-248.39	0.583987	-3884.447925	-3884.485367	-3886.671227
IN2	none	0.587166	-3884.477215	-3884.513721	-3886.699512
TS2	-287.14	0.586741	-3884.466939	-3884.503912	-3886.689012
IN3	none	0.582461	-3884.457807	-3884.497349	-3886.69702
2a	none	0.171852	-538.726768	-538.743007	-539.301832
1w	none	0.193474	-577.923672	-577.938398	-578.539708
1w-IN1	none	0.61113	-3923.702521	-3923.741181	-3925.975092
1w-IN1′	none	0.615786	-3923.707627	-3923.744191	-3925.967765
1w-TS1	-218.12	0.615257	-3923.676516	-3923.712234	-3925.937145
1x	none	0.24802	-656.406125	-656.422238	-657.103936
1x-IN1	none	0.667538	-4002.191104	-4002.229325	-4004.542306
1x-IN1′	none	0.663966	-4002.172946	-4002.213824	-4004.526618
1x-TS1	-185.72	0.66145	-4002.139868	-4002.180525	-4004.490524
1i	none	0.237428	-542.291046	-542.303816	-542.869232
1i-IN1	none	0.653011	-3888.079152	-3888.117158	-3890.312133
1i-IN1′	none	0.653489	-3888.074642	-3888.110424	-3890.298783
1i-TS1	-248.76	0.653576	-3888.059688	-3888.09502	-3890.285024
2o	none	-577.969226	0.198362	-577.985389	-578.584566
2o′	none	-577.973652	0.198523	-577.989145	-578.588588

[a]Computed at the PBE0-D3(BJ)/def2-SVP level.

[b]A standard state at 1 atm and 298 K was used.

[c]Computed at the SMD (toluene)/PBE0-D3(BJ)/def2-SVP level.

[d]Computed at the PBE0-D3(BJ)/def2-TZVPP level.

6.6 Cartesian Coordinates of the Stationary Points

Ni(cod)$_2$

C	2.571538	-0.617028	-1.384115
C	2.184191	-1.845531	-0.553842
C	1.308683	-1.507047	0.623625
C	1.458197	-0.408169	1.457267
C	2.573338	0.615818	1.383026
C	2.186684	1.844764	0.553088
C	1.309910	1.507294	-0.623659
C	1.457367	0.408132	-1.457441
H	2.831934	-0.935947	-2.405371
H	3.483825	-0.150371	-0.984091
H	1.629253	-2.550709	-1.194524
H	3.088406	-2.394104	-0.225097
H	0.717010	-2.340860	1.016610
H	0.943538	-0.465497	2.420086
H	3.484884	0.148216	0.982395
H	2.834804	0.934463	2.404101
H	1.633099	2.550576	1.194258
H	3.091298	2.392321	0.223711
H	0.718668	2.341724	-1.016014
H	0.942389	0.466298	-2.420038
C	-2.571423	-0.617026	1.384122
C	-2.184198	-1.845551	0.553775
C	-1.308684	-1.507058	-0.623687
C	-1.458175	-0.408101	-1.457356
C	-2.573273	0.615936	-1.383018
C	-2.186540	1.844833	-0.553077
C	-1.309705	1.507310	0.623623
C	-1.457199	0.408109	1.457423
H	-2.831747	-0.936001	2.405376
H	-3.483742	-0.150346	0.984174
H	-1.629393	-2.550853	1.194430
H	-3.088510	-2.393944	0.224994
H	-0.716975	-2.340782	-1.016812
H	-0.943550	-0.465476	-2.420195
H	-3.484819	0.148361	-0.982314
H	-2.834820	0.934647	-2.404051
H	-1.632969	2.550625	-1.194288
H	-3.091139	2.392410	-0.223682
H	-0.718640	2.341830	1.016062
H	-0.942397	0.466470	2.420108
Ni	-0.000167	0.000958	0.000059

cod

C	1.082981	-1.087164	0.666382
C	1.913737	0.002527	-0.017325
C	1.200293	1.229598	-0.500150
C	-0.026556	1.688125	-0.221256
C	-1.082979	1.087163	0.666385
C	-1.913737	-0.002525	-0.017325
C	-1.200294	-1.229597	-0.500149
C	0.026556	-1.688125	-0.221257
H	0.651126	-0.701858	1.599693
H	1.773413	-1.887910	0.974627
H	2.727529	0.316061	0.664072
H	2.433084	-0.442274	-0.885103

H	1.796334	1.840285	-1.189509
H	-0.320459	2.614211	-0.729698
H	-1.773409	1.887908	0.974634
H	-0.651122	0.701852	1.599692
H	-2.727531	-0.316059	0.664069
H	-2.433081	0.442278	-0.885104
H	-1.796337	-1.840286	-1.189506
H	0.320455	-2.614213	-0.729696

IN1

C	4.567482	1.370584	-2.220706
C	3.765539	0.926301	-0.977750
C	2.580741	1.853199	-1.382430
C	3.531035	2.467260	-2.431173
H	5.598096	1.728472	-2.076407
H	4.567771	0.639631	-3.045097
H	4.239712	1.241473	-0.037794
H	3.505932	-0.139175	-0.917017
O	3.494219	3.451259	-3.111817
C	1.496469	1.071982	-2.118864
H	1.915594	0.359362	-2.845248
C	0.204628	1.590919	-2.382014
H	-0.329407	1.271387	-3.284802
H	-0.079525	2.587833	-2.026208
Ni	0.139712	0.229428	-0.973034
C	-3.218614	-2.546678	0.134509
C	-3.218862	-3.880440	0.535224
C	-2.020501	-4.502605	0.887865
C	-0.821019	-3.796928	0.827729
C	-0.808529	-2.458759	0.424624
C	-2.020472	-1.825979	0.089488
H	-4.152421	-2.061634	-0.163152
H	-4.156492	-4.440829	0.564213
H	-2.018194	-5.550966	1.195895
H	0.115899	-4.300644	1.074754
P	-1.890258	-0.056428	-0.406638
P	0.728110	-1.437527	0.233418
C	1.201234	-1.072669	1.964505
C	2.544595	-0.873629	2.313366
C	0.207591	-0.793427	2.910929
C	2.883500	-0.409421	3.582289
H	3.333667	-1.070608	1.583248
C	0.548515	-0.319477	4.175408
H	-0.845016	-0.933638	2.657079
C	1.886559	-0.124996	4.515497
H	3.934743	-0.259101	3.839445
H	-0.242090	-0.096850	4.895963
H	2.153778	0.247869	5.507064
C	1.964260	-2.678502	-0.306887
C	2.269993	-2.709307	-1.672573
C	2.590748	-3.590913	0.552314
C	3.170457	-3.645690	-2.176211
H	1.797324	-1.977706	-2.333677
C	3.496652	-4.522442	0.049238
H	2.379360	-3.564255	1.624347
C	3.785260	-4.553454	-1.315244
H	3.399752	-3.660346	-3.244397
H	3.983015	-5.227580	0.727759
H	4.497790	-5.283505	-1.706797

C	-3.296992	0.130062	-1.559030	H	1.239753	2.834842	2.978787
C	-3.189756	-0.494927	-2.809763	H	0.836280	5.961101	0.034614
C	-4.433143	0.892071	-1.271158	H	0.582858	5.175993	2.384816
C	-4.211681	-0.376985	-3.745853				
H	-2.293992	-1.076943	-3.046845	**IN1′**			
C	-5.452240	1.017218	-2.216102				
H	-4.521634	1.392150	-0.303897	C	0.196688	-3.711840	0.338157
C	-5.346234	0.381518	-3.450858	C	1.107615	-3.711197	1.593830
H	-4.120292	-0.872036	-4.715670	C	1.846906	-2.423953	1.130486
H	-6.335334	1.617011	-1.982591	C	0.902934	-2.442454	-0.104238
H	-6.145621	0.480605	-4.189080	H	0.383557	-4.548735	-0.354987
C	-2.422613	0.857808	1.087225	H	-0.888447	-3.640158	0.504848
C	-3.294268	0.334099	2.050342	H	1.759213	-4.592045	1.651986
C	-1.876617	2.133154	1.275716	H	0.582131	-3.600996	2.551929
C	-3.617206	1.077816	3.183247	O	1.031210	-1.835774	-1.194945
H	-3.713380	-0.666412	1.921190	C	1.436384	-1.119255	1.800203
C	-2.210724	2.879149	2.404064	H	2.221982	-0.386327	2.008355
H	-1.172601	2.534720	0.541953	C	0.146608	-0.919919	2.285194
C	-3.077233	2.352457	3.360086	H	-0.071337	-0.015737	2.862004
H	-4.293215	0.659300	3.932996	H	-0.539232	-1.753203	2.464872
H	-1.773458	3.870561	2.538728	Ni	0.206144	-0.632018	0.282610
H	-3.329973	2.934374	4.249904	C	-1.075923	3.290343	-1.758306
C	2.033156	2.788340	-0.339492	C	-2.266451	3.674774	-2.367282
C	1.875407	2.353779	0.981071	C	-3.377302	2.829415	-2.325767
C	1.647501	4.092984	-0.670105	C	-3.294542	1.601061	-1.677357
C	1.356341	3.201802	1.956112	C	-2.102611	1.206771	-1.058915
H	2.158981	1.337025	1.252464	C	-0.986027	2.059507	-1.097711
C	1.125318	4.942399	0.305495	H	-0.202648	3.945817	-1.805837
H	1.782115	4.440451	-1.696281	H	-2.327421	4.634425	-2.886217
C	0.981517	4.502887	1.621126	H	-4.309877	3.126342	-2.811625

H	-4.159738	0.933936	-1.660270
P	0.552321	1.457955	-0.284283
P	-1.903769	-0.417252	-0.201441
C	1.870801	1.931613	-1.458995
C	2.269274	0.957144	-2.384684
C	2.488595	3.188758	-1.467988
C	3.263059	1.248206	-3.317476
H	1.815937	-0.037691	-2.344843
C	3.484608	3.471508	-2.400398
H	2.199233	3.944154	-0.732635
C	3.870654	2.503409	-3.327644
H	3.572641	0.482289	-4.032567
H	3.965178	4.453020	-2.400527
H	4.654976	2.726475	-4.055182
C	0.787914	2.605109	1.114879
C	-0.237416	3.415761	1.613707
C	2.011916	2.558053	1.800327
C	-0.041175	4.169978	2.770325
H	-1.195272	3.463166	1.090889
C	2.207676	3.318239	2.949083
H	2.820752	1.924968	1.424001
C	1.179767	4.125109	3.439626
H	-0.850304	4.799720	3.148287
H	3.167906	3.275897	3.468686
H	1.331934	4.717330	4.344977
C	-3.025565	-0.262779	1.233725
C	-3.362400	-1.425772	1.942783
C	-3.443644	0.975579	1.731874
C	-4.112257	-1.350673	3.112257
H	-3.037459	-2.401439	1.569821
C	-4.186460	1.049862	2.909887
H	-3.188445	1.891310	1.194617
C	-4.524956	-0.110481	3.602014
H	-4.371938	-2.266345	3.649014
H	-4.504720	2.025051	3.286533
H	-5.108578	-0.050660	4.523590
C	-2.793023	-1.570073	-1.310511
C	-4.176520	-1.786766	-1.262206
C	-2.019730	-2.250265	-2.261619
C	-4.780520	-2.659839	-2.164393
H	-4.783302	-1.277975	-0.508685
C	-2.631336	-3.118155	-3.164702
H	-0.933851	-2.108202	-2.270428
C	-4.009661	-3.323116	-3.119309
H	-5.860049	-2.824352	-2.120524
H	-2.022721	-3.645496	-3.903306
H	-4.485502	-4.008651	-3.824929
C	3.316944	-2.470026	0.833573
C	4.175775	-3.452923	1.331847
C	3.857658	-1.460465	0.021520
C	5.537064	-3.433822	1.025131
H	3.784678	-4.242624	1.977410
C	5.212973	-1.443768	-0.290124
H	3.192780	-0.691524	-0.376079
C	6.061013	-2.432187	0.211441
H	6.192394	-4.209748	1.429193
H	5.607136	-0.652166	-0.932877
H	7.126575	-2.420520	-0.030640

IN2

				C	0.997481	-3.003454	-1.629643
C	0.315138	3.480911	-0.337559	C	-0.675504	-4.852544	-0.399323
C	0.613470	3.205861	-1.812242	H	-0.779266	-3.456492	1.240052
C	1.394496	1.908778	-1.925096	C	0.691918	-4.198145	-2.274714
C	0.392798	2.133215	0.391493	H	1.632993	-2.265679	-2.127516
H	1.024226	4.171719	0.147833	C	-0.152802	-5.125424	-1.661605
H	-0.693385	3.900929	-0.182042	H	-1.343939	-5.569735	0.083153
H	1.162228	4.043892	-2.276048	H	1.103930	-4.401308	-3.266176
H	-0.321213	3.113774	-2.382367	H	-0.405811	-6.058122	-2.171416
O	0.629783	2.079794	1.575384	C	2.507312	-1.234810	1.063391
C	0.917282	0.811855	-2.699732	C	2.995383	-0.144816	1.801289
H	1.642189	0.041309	-2.979230	C	3.334864	-2.341119	0.842115
C	-0.436690	0.522689	-2.896870	C	4.288927	-0.172218	2.311187
H	-0.694994	-0.402183	-3.418384	H	2.353553	0.725275	1.963477
H	-1.193296	1.310620	-2.958381	C	4.635536	-2.355628	1.346864
Ni	0.080494	0.710984	-0.865893	H	2.963696	-3.198008	0.275231
C	-2.385639	-0.353595	2.755845	C	5.115097	-1.273393	2.081968
C	-2.049779	-0.972072	3.957061	H	4.660375	0.683757	2.879296
C	-0.811222	-1.600046	4.097280	H	5.274184	-3.224499	1.168520
C	0.082879	-1.625378	3.030443	H	6.134503	-1.286484	2.475348
C	-0.248622	-1.013116	1.817781	C	-2.809852	1.927581	0.436545
C	-1.483395	-0.354151	1.688288	C	-2.580408	2.678934	1.596966
H	-3.352347	0.145247	2.653334	C	-3.666885	2.438041	-0.549331
H	-2.755236	-0.958193	4.791270	C	-3.217110	3.905630	1.774358
H	-0.542731	-2.076174	5.043386	H	-1.876102	2.317863	2.348979
H	1.051336	-2.121059	3.134500	C	-4.298848	3.665399	-0.367933
P	-1.827551	0.434681	0.065646	H	-3.841648	1.867946	-1.465896
P	0.838133	-1.064882	0.337889	C	-4.078133	4.401448	0.796427
C	0.486267	-2.724979	-0.352085	H	-3.029736	4.481913	2.683480
C	-0.355397	-3.663580	0.255428	H	-4.967130	4.049918	-1.142181

H	-4.573629	5.364775	0.938289
C	-3.052873	-0.731095	-0.649246
C	-2.595536	-1.714471	-1.530923
C	-4.396785	-0.738350	-0.251857
C	-3.463966	-2.694055	-2.008419
H	-1.548018	-1.706143	-1.834244
C	-5.266029	-1.710892	-0.739276
H	-4.768627	0.023995	0.437194
C	-4.800742	-2.692078	-1.616095
H	-3.087338	-3.461528	-2.688508
H	-6.313869	-1.705226	-0.429279
H	-5.484676	-3.456328	-1.993342
C	2.827088	1.923568	-1.530290
C	3.583004	0.738493	-1.450666
C	3.483286	3.118159	-1.190919
C	4.915895	0.745711	-1.063169
H	3.110061	-0.222114	-1.657266
C	4.820202	3.128862	-0.797817
H	2.943910	4.065368	-1.231524
C	5.548038	1.944140	-0.730909
H	5.456387	-0.201075	-0.992140
H	5.294564	4.079139	-0.539555
H	6.593135	1.950797	-0.412996

IN3

C	2.347968	-2.235151	0.119195
C	3.545292	-1.292566	0.247464
C	4.604415	-1.569862	-0.790381
C	1.891081	-2.224149	-1.301133
H	2.653533	-3.257435	0.404827
H	1.509477	-1.915514	0.756715
H	3.973247	-1.371765	1.258222
H	3.191047	-0.250669	0.156900
O	0.776745	-1.809256	-1.622607
C	4.292668	-2.183311	-1.947695
H	5.070702	-2.338893	-2.700980
C	2.906958	-2.616963	-2.328496
H	2.876444	-3.717236	-2.464989
H	2.604719	-2.189440	-3.298653
Ni	-0.502030	-0.904108	-0.565629
C	-3.553378	0.011752	2.560424
C	-3.487526	0.815280	3.697457
C	-2.408264	1.680265	3.881221
C	-1.392934	1.742605	2.927727
C	-1.446883	0.938664	1.784976
C	-2.537942	0.064496	1.601797
H	-4.396386	-0.668763	2.416999
H	-4.281015	0.763294	4.447211
H	-2.353965	2.306634	4.775202
H	-0.540978	2.410032	3.083365
P	-2.489327	-0.939741	0.051820
P	-0.198281	0.906844	0.421506
C	-3.393883	0.114142	-1.149939
C	-3.911821	1.374415	-0.831342
C	-3.445360	-0.322641	-2.481890
C	-4.467752	2.180759	-1.823534
H	-3.863684	1.738013	0.197239
C	-4.014196	0.477222	-3.468695
H	-3.024148	-1.298055	-2.742282

C	-4.523000	1.735197	-3.142315	H	-0.485056	1.181477	-2.385248
H	-4.852092	3.169464	-1.561903	C	-1.451867	4.632223	-0.904337
H	-4.050577	0.121633	-4.501572	H	-0.990185	3.766210	1.014631
H	-4.956253	2.370455	-3.918728	C	-1.519041	4.428294	-2.283404
C	-3.721412	-2.251126	0.438331	H	-1.225079	3.023618	-3.899074
C	-5.080359	-2.166681	0.113060	H	-1.735359	5.598605	-0.479653
C	-3.248674	-3.399695	1.085564	H	-1.857471	5.234544	-2.938996
C	-5.949071	-3.208065	0.438993	C	5.978202	-1.101294	-0.503765
H	-5.459849	-1.278814	-0.399439	C	6.183463	0.023772	0.310789
C	-4.117755	-4.433371	1.423615	C	7.106770	-1.752025	-1.026725
H	-2.180856	-3.477082	1.314237	C	7.468253	0.494782	0.569523
C	-5.471746	-4.340094	1.098246	H	5.326656	0.551002	0.735085
H	-7.007878	-3.132942	0.177955	C	8.390194	-1.283492	-0.764677
H	-3.736764	-5.321945	1.933419	H	6.975502	-2.654248	-1.628461
H	-6.154199	-5.154683	1.352988	C	8.578127	-0.154364	0.032699
C	1.317348	1.483234	1.276529	H	7.600989	1.379344	1.197628
C	2.182411	2.422379	0.697036	H	9.253175	-1.811828	-1.177418
C	1.726835	0.832821	2.452811	H	9.586290	0.211538	0.240855
C	3.414064	2.711654	1.283356				
H	1.884877	2.934792	-0.221480	**dppBz**			
C	2.952497	1.128810	3.041784				
H	1.071803	0.086507	2.912277	C	1.374041	-0.223437	2.296358
C	3.803480	2.070346	2.459189	C	0.686066	-0.115550	3.505346
H	4.072906	3.449448	0.818238	C	-0.686417	0.115985	3.505292
H	3.248483	0.619938	3.962749	C	-1.374313	0.223789	2.296252
H	4.765982	2.302301	2.921408	C	-0.698498	0.103248	1.078767
C	-0.671475	2.360363	-0.598252	C	0.698306	-0.102989	1.078821
C	-0.743497	2.164592	-1.981548	H	2.452890	-0.394678	2.299206
C	-1.029665	3.603740	-0.065243	H	1.229881	-0.205919	4.448889
C	-1.162032	3.193541	-2.821866	H	-1.230295	0.206413	4.448794

H	-2.453162	0.395030	2.299014	C	2.554797	3.196690	-2.566186
P	1.539979	-0.219770	-0.562258	H	2.441634	1.075756	-2.944835
P	-1.540051	0.219899	-0.562387	C	2.348943	4.220450	-1.641207
C	-1.852740	-1.555097	-0.921844	H	1.725395	4.711370	0.367198
C	-2.296356	-1.875094	-2.212173	H	2.906009	3.430674	-3.574203
C	-1.648981	-2.588217	0.000079	H	2.540360	5.259175	-1.921281
C	-2.552685	-3.196998	-2.566663	C	3.207023	-0.806854	-0.057428
H	-2.438545	-1.076192	-2.945811	C	3.373388	-2.192414	0.082117
C	-1.892649	-3.913121	-0.360260	C	4.302622	0.033720	0.172571
H	-1.297398	-2.354272	1.007547	C	4.600664	-2.724318	0.468437
C	-2.348295	-4.220501	-1.641085	H	2.526955	-2.857294	-0.115790
H	-2.902578	-3.431228	-3.575082	C	5.535485	-0.501750	0.544969
H	-1.727524	-4.710938	0.368303	H	4.189556	1.114697	0.060883
H	-2.539558	-5.259275	-1.921085	C	5.686550	-1.878819	0.698719
C	-3.207200	0.806778	-0.057687	H	4.714125	-3.805559	0.579465
C	-3.373638	2.192298	0.082238	H	6.383861	0.164755	0.719697
C	-4.302852	-0.033880	0.171711	H	6.653167	-2.295340	0.992242
C	-4.601032	2.724053	0.468367				
H	-2.527168	2.857266	-0.115216	**2a**			
C	-5.535840	0.501451	0.543910				
H	-4.189736	-1.114819	0.059722	C	-2.427211	-0.989302	0.808474
C	-5.686977	1.878462	0.698057	C	-1.021726	-1.225075	0.261416
H	-4.714545	3.805257	0.579704	C	-0.284689	0.065503	-0.003134
H	-6.384254	-0.165130	0.718164	C	-3.194358	0.007024	-0.023273
H	-6.653689	2.294876	0.991422	H	-3.012598	-1.916372	0.875842
C	1.852993	1.555153	-0.921788	H	-2.344735	-0.562459	1.824850
C	1.647796	2.588519	-0.000470	H	-1.080436	-1.815806	-0.671043
C	2.298264	1.874849	-2.211631	H	-0.449058	-1.843134	0.970135
C	1.891655	3.913367	-0.360902	O	-4.318049	-0.186647	-0.416902
H	1.294971	2.354811	1.006614	C	-0.965751	1.197893	-0.257122

H	-0.411208	2.112520	-0.488466
C	-2.456838	1.298751	-0.310660
H	-2.804874	1.673842	-1.287919
H	-2.819247	2.045652	0.422670
C	1.194701	0.032046	-0.008425
C	1.955148	1.152148	0.364332
C	1.882663	-1.131609	-0.387029
C	3.345400	1.118161	0.336630
H	1.445374	2.055939	0.705393
C	3.274721	-1.165784	-0.418038
H	1.322988	-2.021834	-0.681817
C	4.013542	-0.040904	-0.058069
H	3.913493	2.001576	0.638337
H	3.785605	-2.080898	-0.727242
H	5.105474	-0.068963	-0.076127

1a

C	2.286894	-1.380827	-0.856092
C	1.681388	-0.146484	-1.556556
C	0.986828	0.310819	-0.230395
C	1.834954	-0.789783	0.466003
H	1.750484	-2.319458	-1.070553
H	3.366832	-1.568077	-0.951600
H	1.006935	-0.353374	-2.396095
H	2.443069	0.573692	-1.886122
O	2.090909	-1.011353	1.611266
C	1.323074	1.702635	0.223419
H	2.389767	1.954802	0.170107
C	0.463798	2.615218	0.677338
H	0.810981	3.603061	0.989925
H	-0.607110	2.408269	0.754088
C	-0.493071	0.001456	-0.139794
C	-1.039274	-0.463492	1.062450
C	-1.347728	0.234345	-1.222244
C	-2.407110	-0.705770	1.172396
H	-0.379543	-0.631421	1.916797
C	-2.716109	-0.004424	-1.111423
H	-0.942395	0.618533	-2.161356
C	-3.249967	-0.479327	0.085558
H	-2.816384	-1.074478	2.116097
H	-3.369716	0.183544	-1.966758
H	-4.322261	-0.670469	0.171393

TS1

C	0.474785	-3.576932	-0.431037
C	-0.496786	-3.638816	-1.614746
C	-1.303766	-2.346068	-1.324988
C	-0.343273	-2.463214	0.207666
H	0.538350	-4.477373	0.197799
H	1.489049	-3.254151	-0.704960
H	-1.146827	-4.519619	-1.541023
H	-0.026735	-3.630235	-2.607629
O	-0.793516	-2.454337	1.334256
C	-1.031440	-1.172700	-2.199338
H	-1.872184	-0.522391	-2.460046
C	0.242304	-0.917832	-2.680623
H	0.420931	-0.037533	-3.303430
H	1.006738	-1.696896	-2.734396

Ni	-0.030308	-0.663433	-0.590894	H	-3.154648	1.338972	-1.370597
C	0.401455	3.109491	2.000348	C	-2.070865	4.105466	-3.034632
C	1.488363	3.637089	2.690309	H	-0.240829	5.169919	-2.612824
C	2.732589	3.005416	2.625001	H	-3.817775	2.844317	-3.219395
C	2.887284	1.848749	1.867780	H	-2.359674	4.764944	-3.856381
C	1.800218	1.318581	1.163446	C	3.036528	0.296622	-1.220342
C	0.550005	1.951402	1.227535	C	3.616572	-0.695961	-2.024229
H	-0.576887	3.591524	2.069634	C	3.215268	1.638694	-1.570534
H	1.363607	4.539547	3.293592	C	4.368754	-0.352068	-3.142582
H	3.583151	3.412378	3.177118	H	3.480041	-1.750567	-1.768823
H	3.856172	1.344644	1.829663	C	3.960658	1.981516	-2.698458
P	-0.848774	1.163365	0.321584	H	2.767695	2.424751	-0.958846
P	1.922806	-0.210033	0.142356	C	4.540815	0.990085	-3.485768
C	-2.178245	1.304861	1.580742	H	4.819162	-1.136954	-3.754962
C	-2.262276	0.273222	2.526436	H	4.088965	3.034553	-2.960543
C	-3.081377	2.372489	1.644094	H	5.126080	1.260404	-4.367769
C	-3.228538	0.321303	3.528219	C	2.993708	-1.272986	1.188129
H	-1.594547	-0.590246	2.443730	C	4.391121	-1.295455	1.087276
C	-4.050209	2.412456	2.645997	C	2.365113	-2.067770	2.156766
H	-3.033187	3.173576	0.902511	C	5.146000	-2.098456	1.940548
C	-4.123270	1.389819	3.590925	H	4.894567	-0.684411	0.334575
H	-3.291352	-0.491513	4.255631	C	3.124727	-2.865801	3.009413
H	-4.753068	3.248364	2.686899	H	1.274790	-2.076395	2.234573
H	-4.885652	1.421178	4.373247	C	4.514782	-2.884537	2.903378
C	-1.327650	2.413758	-0.922674	H	6.235159	-2.108435	1.851467
C	-0.515091	3.492208	-1.287383	H	2.622367	-3.483147	3.757993
C	-2.514789	2.185738	-1.637449	H	5.107752	-3.515580	3.569932
C	-0.885366	4.330945	-2.338945	C	-2.763965	-2.500032	-1.024615
H	0.412894	3.682115	-0.743358	C	-3.547617	-3.495754	-1.619077
C	-2.887075	3.030406	-2.677979	C	-3.388410	-1.590261	-0.166600

C	-4.916128	-3.571866	-1.362737
H	-3.092567	-4.212566	-2.306654
C	-4.753199	-1.663347	0.094448
H	-2.776834	-0.830209	0.314816
C	-5.525557	-2.657459	-0.504844
H	-5.511506	-4.352925	-1.842471
H	-5.206689	-0.943742	0.781123
H	-6.597171	-2.723462	-0.301567

TS2

C	-1.954246	-1.297131	-2.937164
C	-2.947492	-0.153756	-2.685320
C	-2.443602	0.953427	-1.777321
C	-0.482819	-0.942608	-2.780831
H	-2.120572	-2.094083	-2.193502
H	-2.107480	-1.759401	-3.927710
H	-3.869632	-0.581011	-2.266255
H	-3.235168	0.291389	-3.656571
O	0.400909	-1.640955	-3.244834
C	-1.290407	1.636557	-2.135676
H	-1.052831	2.602169	-1.678465
C	-0.390618	1.029989	-3.112617
H	0.555980	1.541024	-3.318883
H	-0.855068	0.698974	-4.052331
Ni	-0.217903	0.161537	-1.250966
C	-0.452845	-0.810860	3.081513
C	-0.236077	-0.015941	4.207010
C	0.463601	1.185067	4.091601
C	0.948282	1.600094	2.850866
C	0.723225	0.817296	1.716670
C	0.019353	-0.397814	1.835167
H	-1.005062	-1.750176	3.167031
H	-0.621370	-0.333537	5.178789
H	0.629677	1.807516	4.974257
H	1.487201	2.546780	2.760606
P	-0.215328	-1.342846	0.273906
P	1.229905	1.232016	-0.002000
C	1.176774	-2.529569	0.289859
C	2.095242	-2.593109	1.344035
C	1.367391	-3.339770	-0.838747
C	3.183328	-3.460393	1.275565
H	1.970713	-1.951553	2.218656
C	2.447280	-4.217122	-0.892747
H	0.697244	-3.252258	-1.696721
C	3.358393	-4.278407	0.161115
H	3.900834	-3.491755	2.098819
H	2.586534	-4.843043	-1.777456
H	4.212861	-4.957633	0.108904
C	-1.682434	-2.379601	0.619453
C	-2.930425	-1.741635	0.661404
C	-1.610512	-3.761169	0.826095
C	-4.085799	-2.474412	0.913706
H	-2.996935	-0.664397	0.495186
C	-2.773146	-4.493405	1.068326
H	-0.643451	-4.267562	0.795469
C	-4.010307	-3.853843	1.113274
H	-5.049803	-1.961126	0.946521
H	-2.707955	-5.573003	1.224006
H	-4.918580	-4.431199	1.302285

C	2.885943	0.466051	-0.136451	H	-3.090558	2.791938	2.442903
C	3.126789	-0.396092	-1.212129	H	-6.606021	1.980596	0.086721
C	3.875288	0.658670	0.835995	H	-5.578885	2.836062	2.190306
C	4.354636	-1.048964	-1.315809				
H	2.340189	-0.585411	-1.951027	**2u'**			
C	5.097446	0.002109	0.729192				
H	3.684641	1.319748	1.685749	C	-1.289914	-1.226644	1.133870
C	5.337167	-0.852908	-0.348379	C	-0.581008	-1.856345	-0.052018
H	4.530833	-1.730507	-2.150733	C	-0.002382	-0.787272	-0.990128
H	5.864807	0.151487	1.492787	C	-2.358027	-0.243341	0.710704
H	6.293791	-1.375406	-0.427006	H	-1.759205	-1.971927	1.791687
C	1.566983	3.025211	0.021319	H	-0.568340	-0.666884	1.756474
C	0.565936	3.910298	0.452122	H	-1.300452	-2.466483	-0.623769
C	2.749620	3.551069	-0.514756	H	0.219453	-2.532753	0.284059
C	0.756342	5.286754	0.371934	O	-3.343720	-0.034538	1.386208
H	-0.371393	3.521734	0.856890	C	-1.033002	0.256945	-1.302128
C	2.933212	4.930226	-0.600717	H	-0.855830	0.866060	-2.196610
H	3.533160	2.875062	-0.864475	C	-2.126759	0.507577	-0.555795
C	1.941250	5.801352	-0.154867	C	1.284860	-0.186256	-0.446669
H	-0.030412	5.961411	0.717752	C	1.295025	0.977051	0.329799
H	3.862224	5.325287	-1.018886	C	2.501327	-0.837961	-0.685155
H	2.088481	6.881849	-0.221234	C	2.486615	1.469829	0.861668
C	-3.317259	1.477312	-0.711459	H	0.358756	1.509693	0.513373
C	-2.761593	1.955759	0.489647	C	3.692504	-0.348386	-0.156812
C	-4.717955	1.488417	-0.824448	H	2.512043	-1.744733	-1.297498
C	-3.557979	2.447496	1.516592	C	3.688786	0.809115	0.621646
H	-1.681813	1.867639	0.623889	H	2.472930	2.380356	1.465693
C	-5.519446	1.976615	0.206348	H	4.631101	-0.870750	-0.357615
H	-5.188402	1.126452	-1.741418	H	4.622658	1.196799	1.035351
C	-4.947256	2.462577	1.381007	C	-3.150916	1.539518	-0.900886

H	-4.144440	1.076421	-1.002871	C	-2.944186	1.881912	-0.812893
H	-3.245278	2.278958	-0.090654	H	-2.656812	1.573553	-1.829323
H	-2.900888	2.059485	-1.835660	H	-4.039619	1.845757	-0.748788
H	0.264604	-1.280917	-1.940211	H	-2.610959	2.919248	-0.661611
				H	-2.623037	1.320133	1.229709

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C	-2.043096	-1.516689	0.781516				
C	-0.641331	-1.520255	0.176701	C	-4.584329	0.017674	-2.469450
C	-0.034536	-0.138963	0.143921	C	-3.759492	0.128822	-1.165998
C	-2.896742	-0.450831	0.143923	C	-2.784718	-0.983237	-1.655146
H	-2.546906	-2.486305	0.670054	C	-3.762768	-1.217946	-2.820626
H	-1.964926	-1.285413	1.858475	H	-5.666716	-0.164046	-2.381662
H	-0.680151	-1.933514	-0.847569	H	-4.431719	0.844365	-3.181658
H	0.009593	-2.200155	0.748486	H	-4.329214	-0.153555	-0.269579
O	-3.954533	-0.686384	-0.387076	H	-3.273782	1.098580	-0.988745
C	-0.818889	0.953956	0.173337	O	-3.870757	-2.080252	-3.644295
H	-0.352592	1.942696	0.108348	C	-1.516103	-0.373582	-2.239598
C	-2.321729	0.955265	0.224345	H	-1.727726	0.524255	-2.839333
C	1.438745	-0.033045	0.049760	C	-0.370393	-1.126955	-2.593740
C	2.132173	1.060313	0.593736	H	0.242005	-0.811521	-3.446596
C	2.188944	-1.034084	-0.587371	H	-0.335155	-2.207281	-2.410294
C	3.514910	1.161545	0.482972	Ni	-0.014423	-0.014091	-1.004481
H	1.577723	1.830959	1.133828	C	3.791764	1.511215	0.923141
C	3.573406	-0.932349	-0.701432	C	4.073452	2.673315	1.635983
H	1.683065	-1.900056	-1.019400	C	3.036841	3.530802	2.008969
C	4.243631	0.166649	-0.168801	C	1.722490	3.233002	1.658956
H	4.030574	2.019686	0.920936	C	1.428028	2.070842	0.939621
H	4.132407	-1.720149	-1.212246	C	2.471446	1.197624	0.582151
H	5.330097	0.244080	-0.252568	H	4.602328	0.843927	0.618121

H	5.106348	2.916388	1.896820	C	4.418610	-0.100782	-3.597046
H	3.256711	4.445538	2.564735	H	2.496543	0.659549	-2.961490
H	0.921094	3.921526	1.934661	C	5.538773	-1.565501	-2.038240
P	1.976986	-0.319369	-0.338534	H	4.511570	-1.934031	-0.174410
P	-0.276029	1.602649	0.369677	C	5.507682	-0.908384	-3.267150
C	-1.135170	1.250920	1.946456	H	4.385467	0.406519	-4.564191
C	-2.513651	1.464105	2.080702	H	6.385944	-2.206090	-1.781029
C	-0.457072	0.553344	2.953647	H	6.330778	-1.032816	-3.974928
C	-3.194336	0.995999	3.202382	C	2.150646	-1.661689	0.897504
H	-3.063770	1.987415	1.295451	C	2.632389	-1.475586	2.197275
C	-1.140740	0.079986	4.070433	C	1.689223	-2.930725	0.516666
H	0.613130	0.360094	2.855559	C	2.648467	-2.538700	3.101478
C	-2.511562	0.299130	4.198944	H	2.995161	-0.493401	2.509248
H	-4.269231	1.170343	3.293262	C	1.718547	-3.991967	1.415257
H	-0.597089	-0.470618	4.841843	H	1.290400	-3.076048	-0.491369
H	-3.048620	-0.075316	5.073497	C	2.193343	-3.796676	2.713498
C	-0.976464	3.205697	-0.174721	H	3.021222	-2.379628	4.116360
C	-1.033105	3.423396	-1.556288	H	1.352920	-4.974122	1.106553
C	-1.437305	4.205319	0.692406	H	2.203812	-4.626989	3.423482
C	-1.519207	4.625978	-2.064818	C	-2.556605	-2.197173	-0.751344
H	-0.698679	2.625932	-2.225763	C	-1.790133	-1.825963	0.522002
C	-1.930593	5.404564	0.183122	C	-3.828811	-2.948808	-0.358274
H	-1.427591	4.039471	1.772801	C	-1.899707	-2.883039	1.628984
C	-1.968417	5.618287	-1.195028	H	-0.725542	-1.657064	0.271730
H	-1.556391	4.784577	-3.145202	C	-3.481488	-4.302006	0.282558
H	-2.291289	6.176977	0.866815	H	-4.402392	-2.333201	0.356474
H	-2.357573	6.559206	-1.591571	C	-2.146258	-4.264091	1.039456
C	3.397204	-0.596825	-1.456597	H	-0.988987	-2.871457	2.247789
C	3.364709	0.047385	-2.700009	H	-4.292026	-4.597850	0.968844
C	4.488379	-1.411196	-1.134039	H	-1.317613	-4.505399	0.351292

H	-2.168480	-0.866140	0.898731
H	-1.952566	-2.902540	-1.348438
H	-4.480804	-3.107725	-1.230240
H	-3.441556	-5.081880	-0.495289
H	-2.125416	-5.040128	1.821316
H	-2.731362	-2.627915	2.308220

1i-IN1'

C	-0.418920	-3.571893	-0.804576
C	-1.201077	-3.340199	-2.124375
C	-1.878171	-2.053898	-1.562364
C	-1.039924	-2.284394	-0.288090
H	-0.758226	-4.447434	-0.225284
H	0.678942	-3.609164	-0.870069
H	-1.913439	-4.139115	-2.371488
H	-0.571082	-3.156468	-3.004765
O	-1.199762	-1.783236	0.856319
C	-1.327855	-0.736327	-2.083394
H	-2.018544	0.092507	-2.259917
C	0.004753	-0.599970	-2.463245
H	0.336636	0.336230	-2.922490
H	0.636873	-1.464613	-2.685106
Ni	-0.172975	-0.514826	-0.445566
C	1.244456	3.026971	2.131158
C	2.391233	3.219597	2.895182
C	3.414475	2.269371	2.870293
C	3.290775	1.130898	2.079565
C	2.143911	0.931522	1.302464
C	1.113100	1.886371	1.330967
H	0.435311	3.760728	2.164289
H	2.484708	4.108968	3.523066
H	4.310175	2.413626	3.479328
H	4.086738	0.382331	2.072229
P	-0.386416	1.527609	0.323425
P	1.894446	-0.552794	0.232069
C	-1.761628	1.989149	1.437502
C	-2.317523	0.957631	2.207093
C	-2.275208	3.287563	1.546494
C	-3.364083	1.231111	3.085447
H	-1.942571	-0.062778	2.084051
C	-3.325146	3.553087	2.423408
H	-1.862334	4.091888	0.932073
C	-3.868863	2.526394	3.195436
H	-3.797111	0.421594	3.678003
H	-3.723733	4.567678	2.501523
H	-4.695502	2.736114	3.878756
C	-0.393954	2.838342	-0.944511
C	0.751158	3.565082	-1.287831
C	-1.561060	3.009710	-1.705117
C	0.727624	4.452733	-2.363077
H	1.668136	3.439238	-0.708008
C	-1.584063	3.902237	-2.772251
H	-2.461217	2.443311	-1.449463
C	-0.438013	4.625559	-3.106238
H	1.629078	5.014758	-2.619261
H	-2.501806	4.030756	-3.351189
H	-0.454799	5.322330	-3.947535
C	3.154736	-0.328699	-1.074122
C	3.421742	-1.412912	-1.923951

C	3.770847	0.899816	-1.333804	H	-6.354206	-1.614009	-1.451626
C	4.296783	-1.273862	-2.996207	H	-3.844373	-2.140035	-2.389323
H	2.942370	-2.378090	-1.735822	H	-4.141514	-0.023013	-1.493369
C	4.638963	1.040682	-2.416408	H	-5.621692	0.000082	0.353977
H	3.576551	1.754059	-0.681833	H	-7.017031	-2.038087	0.123366
C	4.907023	-0.043811	-3.248087	H	-5.722810	-3.991451	0.298879
H	4.500245	-2.129819	-3.644230	H	-3.496540	-3.171179	0.457769
H	5.112228	2.007170	-2.606511				
H	5.589518	0.067240	-4.093898	**1w-IN1**			
C	2.587153	-1.907054	1.250259				
C	3.944281	-2.254702	1.264642	C	-4.744004	-4.142876	0.054676
C	1.684029	-2.613401	2.057080	C	-4.762294	-2.860103	-0.806014
C	4.394781	-3.284789	2.087799	C	-3.848184	-2.137531	0.229306
H	4.650349	-1.723987	0.620829	C	-4.125437	-3.311998	1.172074
C	2.142454	-3.639379	2.881572	H	-5.704874	-4.617753	0.302474
H	0.618199	-2.365253	2.011488	H	-4.054750	-4.921861	-0.308154
C	3.495514	-3.975460	2.900198	H	-5.761683	-2.406679	-0.862617
H	5.454791	-3.550792	2.093483	H	-4.347515	-2.941447	-1.820530
H	1.433189	-4.186960	3.507074	O	-3.994607	-3.481830	2.350232
H	3.850803	-4.784262	3.543581	C	-2.373145	-2.151899	-0.239436
C	-3.397310	-2.066290	-1.378506	H	-2.126647	-3.149041	-0.644321
C	-3.884730	-3.268982	-0.569398	Ni	0.314293	-1.071391	0.169978
C	-3.895816	-0.760196	-0.711010	C	3.884509	0.623503	-2.041669
C	-5.413514	-3.358336	-0.548942	C	3.962099	1.533568	-3.095318
H	-3.468367	-4.208365	-0.964654	C	2.835074	2.260802	-3.480029
C	-5.121995	-0.965731	0.178769	C	1.623774	2.074243	-2.815901
H	-3.080380	-0.323680	-0.116380	C	1.536713	1.160606	-1.762778
C	-6.076047	-1.974400	-0.445694	C	2.675422	0.432422	-1.367764
H	-5.769125	-3.873313	-1.456797	H	4.765363	0.045032	-1.750382
H	-4.806841	-1.324776	1.173363	H	4.908194	1.671830	-3.624562

H	2.897986	2.969385	-4.309465	H	3.085030	-2.580245	-1.995513
H	0.734313	2.629837	-3.124988	C	5.804978	-2.977888	0.739526
P	2.415954	-0.703498	0.070399	H	4.776588	-1.397089	1.789545
P	-0.006671	0.772033	-0.836787	C	5.844267	-3.778591	-0.399578
C	-0.163905	2.124302	0.381266	H	4.887321	-4.258366	-2.277975
C	-1.286512	2.109134	1.222638	H	6.564351	-3.093485	1.516842
C	0.842930	3.070397	0.596869	H	6.634214	-4.523795	-0.519717
C	-1.403893	3.039707	2.250154	C	2.877670	0.393857	1.469632
H	-2.074653	1.365816	1.073586	C	3.969335	1.269367	1.424939
C	0.728549	3.989957	1.638579	C	2.025835	0.419350	2.579653
H	1.729217	3.079415	-0.041026	C	4.206185	2.150693	2.476985
C	-0.393357	3.978653	2.464778	H	4.630959	1.273597	0.555155
H	-2.288722	3.019671	2.890722	C	2.261810	1.302869	3.630468
H	1.528013	4.715218	1.807003	H	1.162997	-0.251079	2.599831
H	-0.479738	4.699858	3.281209	C	3.350735	2.170490	3.579548
C	-1.312636	1.116733	-2.070370	H	5.058811	2.832869	2.432482
C	-1.566891	0.119462	-3.022913	H	1.581443	1.322733	4.484702
C	-2.076562	2.287664	-2.089741	H	3.531545	2.870679	4.398833
C	-2.564953	0.290984	-3.977837	C	-4.251999	-0.754754	0.668561
H	-0.975234	-0.800872	-3.005636	C	-4.514165	0.225057	-0.298124
C	-3.078161	2.457296	-3.045497	C	-4.336055	-0.405763	2.021774
H	-1.892987	3.066510	-1.346124	C	-4.866769	1.518610	0.077900
C	-3.326963	1.460655	-3.987579	H	-4.430492	-0.022974	-1.360258
H	-2.754622	-0.493519	-4.714474	C	-4.689683	0.890978	2.396466
H	-3.669548	3.376409	-3.052239	H	-4.125807	-1.165466	2.777078
H	-4.115770	1.594194	-4.731781	C	-4.958590	1.856658	1.428185
C	3.820066	-1.863782	-0.090814	H	-5.062828	2.268486	-0.691780
C	3.856953	-2.685394	-1.227067	H	-4.756183	1.145446	3.457421
C	4.799439	-2.023248	0.894611	H	-5.234677	2.871937	1.723072
C	4.866224	-3.629378	-1.384627	H	-2.342032	-1.455875	-1.094321

C	-1.384151	-1.776611	0.833644
H	-1.774678	-1.071637	1.579844
C	-0.308498	-2.608917	1.228406
H	-0.150686	-3.575420	0.731211
H	0.050642	-2.582456	2.263925

1w-IN1'

C	-0.866615	-3.518604	-0.899040
C	-2.250792	-3.674555	-1.573944
C	-2.485722	-2.134628	-1.547399
C	-1.255111	-2.071397	-0.588128
H	-0.671823	-4.142254	-0.015038
H	-0.015311	-3.618318	-1.587234
H	-2.967354	-4.213377	-0.938954
H	-2.262480	-4.127331	-2.576650
O	-1.219667	-1.468961	0.531790
C	-2.026432	-1.444810	-2.828043
H	-2.845111	-1.319476	-3.558274
Ni	-0.254349	-0.401714	-0.837938
C	0.778806	1.966050	2.941937
C	1.596416	1.655201	4.024262
C	2.477491	0.574814	3.945923
C	2.533496	-0.197786	2.789569
C	1.708345	0.098839	1.699514
C	0.832645	1.196136	1.775168
H	0.083450	2.807252	3.001291
H	1.545221	2.255715	4.935689
H	3.119326	0.328878	4.795391
H	3.212680	-1.052252	2.739555
P	-0.190041	1.541173	0.292317
P	1.715809	-0.863544	0.120626
C	-1.719929	2.282314	0.952354
C	-2.774919	1.399875	1.224135
C	-1.884293	3.655084	1.177989
C	-3.975577	1.890738	1.732538
H	-2.646203	0.330636	1.028119
C	-3.090374	4.138886	1.681250
H	-1.069370	4.347126	0.950517
C	-4.134978	3.257361	1.960579
H	-4.793660	1.195843	1.932380
H	-3.215647	5.210800	1.853918
H	-5.081404	3.640034	2.350972
C	0.673203	2.937289	-0.504472
C	1.960022	3.346769	-0.137521
C	0.065583	3.526289	-1.624945
C	2.623478	4.329138	-0.872116
H	2.452052	2.889683	0.723648
C	0.726302	4.512948	-2.350200
H	-0.937064	3.209117	-1.926426
C	2.010186	4.915371	-1.977012
H	3.629711	4.635136	-0.575925
H	0.239077	4.966720	-3.216616
H	2.531110	5.685901	-2.550357
C	3.337307	-0.361471	-0.571304
C	3.326929	0.598856	-1.588162
C	4.566435	-0.824642	-0.081594
C	4.522626	1.099899	-2.100744
H	2.368448	0.956412	-1.967031
C	5.759743	-0.333078	-0.603172

H	4.591217	-1.578881	0.708734	C	0.026859	0.040628	-2.772222
C	5.740145	0.633063	-1.611118	H	0.583692	-0.743036	-3.298469
H	4.497320	1.857360	-2.887625	H	0.438273	1.050339	-2.880033
H	6.713160	-0.702680	-0.217638				
H	6.678859	1.019570	-2.015649	**1x-IN1**			
C	1.960445	-2.581126	0.674814				
C	2.665370	-3.490350	-0.125809	C	5.659341	2.163961	-1.669204
C	1.280264	-3.054228	1.805414	C	6.005640	0.916017	-0.830029
C	2.710356	-4.840835	0.211220	C	4.490190	0.548081	-0.723187
H	3.180497	-3.139138	-1.023730	C	4.219183	1.976780	-1.229593
C	1.331445	-4.405089	2.140988	H	6.118879	3.128632	-1.409648
H	0.689165	-2.363857	2.409785	H	5.764238	2.003886	-2.754328
C	2.046085	-5.302016	1.347630	H	6.431988	1.180702	0.147224
H	3.267065	-5.537907	-0.419809	H	6.641904	0.160331	-1.310572
H	0.799713	-4.760845	3.026899	O	3.284411	2.725060	-1.158272
H	2.082214	-6.361480	1.612228	C	4.138565	-0.555825	-1.751324
C	-3.770727	-1.626698	-0.951813	H	4.655953	-0.334738	-2.702382
C	-4.179496	-2.092096	0.308708	C	2.655824	-0.784977	-2.006728
C	-4.576840	-0.672850	-1.582546	H	2.495758	-1.831164	-2.315846
C	-5.355914	-1.642428	0.899148	Ni	-0.400007	0.228419	-1.411039
H	-3.554460	-2.808745	0.845556	C	-0.510470	-1.616294	2.725973
C	-5.755813	-0.215515	-0.993642	C	-0.683862	-1.029120	3.978255
H	-4.286853	-0.273231	-2.555375	C	-1.106187	0.297016	4.079502
C	-6.155827	-0.702651	0.247084	C	-1.361702	1.037022	2.925477
H	-5.649097	-2.025882	1.879857	C	-1.189191	0.456899	1.666349
H	-6.364636	0.528799	-1.512840	C	-0.753788	-0.879171	1.564259
H	-7.081315	-0.348879	0.708153	H	-0.158434	-2.648249	2.651402
H	-1.285816	-2.097222	-3.317038	H	-0.479186	-1.608400	4.882120
C	-1.334838	-0.136676	-2.502162	H	-1.231335	0.759230	5.061677
H	-1.976770	0.742604	-2.366890	H	-1.682090	2.078990	3.003212

P	-0.566243	-1.505988	-0.167593	H	-0.750882	-4.307291	-1.113353
P	-1.476072	1.316434	0.058415	C	2.343767	-5.097158	0.069770
C	-3.296602	1.270602	-0.110147	H	3.616207	-3.756565	1.198383
C	-4.116280	0.483823	0.705547	H	0.863058	-6.185979	-1.065029
C	-3.862825	1.940116	-1.204862	H	3.054551	-5.926831	0.090832
C	-5.479095	0.371113	0.433047	C	-2.231784	-2.231433	-0.453453
H	-3.686594	-0.060209	1.549045	C	-2.855964	-3.073999	0.474054
C	-5.225355	1.836479	-1.465933	C	-2.931712	-1.837643	-1.599055
H	-3.223470	2.539061	-1.859892	C	-4.159238	-3.513649	0.257710
C	-6.037276	1.047075	-0.649173	H	-2.321551	-3.379877	1.377034
H	-6.105458	-0.256568	1.071265	C	-4.236402	-2.276609	-1.814682
H	-5.656064	2.367344	-2.318559	H	-2.447819	-1.164592	-2.312504
H	-7.105361	0.956848	-0.861331	C	-4.852222	-3.112311	-0.885732
C	-1.096750	3.065603	0.419104	H	-4.640601	-4.168239	0.988570
C	-1.987385	3.942328	1.050871	H	-4.777835	-1.950425	-2.705495
C	0.168693	3.525539	0.035410	H	-5.878609	-3.450076	-1.049034
C	-1.602060	5.254841	1.318159	C	3.969455	0.215225	0.652110
H	-2.988817	3.597471	1.323257	C	2.775996	0.755549	1.144988
C	0.555389	4.834435	0.313516	C	4.690522	-0.670169	1.463740
H	0.850611	2.860280	-0.500674	C	2.326564	0.432360	2.424942
C	-0.329088	5.699276	0.957102	H	2.202518	1.444304	0.525309
H	-2.300780	5.936852	1.809191	C	4.236071	-1.002848	2.737839
H	1.549442	5.172035	0.011306	H	5.623549	-1.103498	1.092270
H	-0.031099	6.729173	1.169105	C	3.051963	-0.448058	3.224380
C	0.516351	-2.968413	0.016585	H	1.394974	0.866533	2.792572
C	1.756193	-2.827773	0.657739	H	4.812133	-1.695980	3.356168
C	0.208170	-4.185295	-0.603932	H	2.690731	-0.705012	4.222743
C	2.658454	-3.886869	0.688772	H	4.600057	-1.477171	-1.357856
H	2.022615	-1.882661	1.135401	C	2.032595	0.152890	-3.034792
C	1.117566	-5.241724	-0.577209	H	2.279116	1.193057	-2.774610

H	2.098148	-0.683071	-1.062963
H	2.502881	-0.032322	-4.020371
C	0.528631	0.057284	-3.156086
H	0.150569	-0.810965	-3.713798
C	-0.262326	1.229523	-3.094101
H	0.221810	2.210502	-3.002151
H	-1.241429	1.258752	-3.590647

1x-IN1'

C	-1.629177	0.205722	3.252370
C	-3.033924	0.816441	3.063390
C	-2.758604	1.029519	1.549495
C	-1.252950	0.844477	1.910964
H	-1.037538	0.560687	4.108838
H	-1.627399	-0.894568	3.238423
H	-3.121226	1.773941	3.596021
H	-3.897039	0.182618	3.320222
O	-0.381169	1.803849	1.811541
C	-3.292781	-0.133421	0.708374
H	-2.939561	-1.085102	1.142962
C	-4.806460	-0.159353	0.568875
H	-5.271122	-0.204827	1.570218
Ni	0.160556	0.444278	0.673180
C	2.715909	0.213599	-3.044379
C	2.672259	-0.661509	-4.127962
C	1.913681	-1.829410	-4.051331
C	1.180898	-2.114729	-2.900422
C	1.201125	-1.234091	-1.814900
C	1.991883	-0.068840	-1.884002
H	3.310117	1.128073	-3.104826
H	3.233139	-0.430779	-5.036769
H	1.882316	-2.518558	-4.898713
H	0.568632	-3.018800	-2.855974
P	1.998566	0.946483	-0.355730
P	0.258730	-1.468736	-0.236213
C	3.506325	0.385260	0.511218
C	3.801166	1.001660	1.735826
C	4.280843	-0.697363	0.083107
C	4.865548	0.550148	2.509153
H	3.180743	1.831703	2.086854
C	5.339376	-1.153974	0.867516
H	4.048224	-1.197059	-0.859727
C	5.635486	-0.531800	2.078003
H	5.090202	1.039161	3.460183
H	5.931980	-2.007101	0.529097
H	6.464641	-0.892749	2.691270
C	2.365003	2.661792	-0.839356
C	1.325880	3.588413	-0.690265
C	3.616286	3.086676	-1.305157
C	1.524398	4.920767	-1.049073
H	0.377431	3.262190	-0.253540
C	3.809200	4.418780	-1.661856
H	4.445330	2.376280	-1.368747
C	2.760875	5.333561	-1.542481
H	0.709786	5.638519	-0.926287
H	4.784978	4.749056	-2.026464
H	2.917308	6.378962	-1.819978
C	-1.085313	-2.601717	-0.739926
C	-1.859482	-2.294349	-1.867699

C	-1.424757	-3.717312	0.033301	H	-3.846321	5.720874	-0.909853
C	-2.929301	-3.105648	-2.231645	H	-2.824657	-0.079719	-0.288740
H	-1.619494	-1.412773	-2.468575	C	-5.304346	-1.332390	-0.271573
C	-2.508806	-4.518845	-0.323980	H	-4.884372	-1.264012	-1.288072
H	-0.833296	-3.964456	0.918353	H	-4.905227	-2.270560	0.156731
C	-3.258577	-4.220379	-1.459700	C	-6.794017	-1.419393	-0.345893
H	-3.518760	-2.860767	-3.118403	H	-7.315931	-1.525449	0.615192
H	-2.763860	-5.386925	0.288697	C	-7.519163	-1.363714	-1.464082
H	-4.105723	-4.850216	-1.740636	H	-7.043770	-1.249480	-2.444261
C	1.393238	-2.528187	0.740401	H	-8.610447	-1.427441	-1.445549
C	1.726310	-2.093388	2.027600	H	-5.156016	0.784651	0.118656
C	1.999114	-3.678751	0.222874				
C	2.656273	-2.797610	2.789186	**1i**			
H	1.260394	-1.182609	2.415111				
C	2.927274	-4.382506	0.985365	C	-2.571010	-1.065114	1.095377
H	1.750866	-4.020771	-0.785084	C	-1.858494	0.236290	1.521066
C	3.258818	-3.940310	2.267503	C	-1.103081	0.317716	0.148865
H	2.919541	-2.442837	3.787988	C	-2.002895	-0.859850	-0.300353
H	3.400749	-5.278086	0.575613	H	-2.189939	-1.982977	1.571137
H	3.994868	-4.489061	2.860127	H	-3.670226	-1.089675	1.144828
C	-3.081872	2.347156	0.908150	H	-1.203984	0.164074	2.399552
C	-2.407455	2.700450	-0.269631	H	-2.549563	1.076962	1.672359
C	-4.037973	3.231398	1.412769	O	-2.204652	-1.371402	-1.361606
C	-2.674238	3.901858	-0.917880	C	-1.371234	1.579182	-0.614476
H	-1.646676	2.020803	-0.664125	H	-2.442027	1.801187	-0.716778
C	-4.314094	4.435335	0.762634	C	-0.516827	2.449242	-1.156665
H	-4.579818	2.975640	2.326805	H	-0.889595	3.334589	-1.678354
C	-3.632355	4.776745	-0.402862	H	0.567029	2.330232	-1.110343
H	-2.128364	4.159232	-1.829737	C	0.350371	-0.176973	0.257808
H	-5.069405	5.110936	1.172358	C	1.002800	-0.505313	-1.086941

C	1.244521	0.748304	1.115005	C	-1.050391	-1.054037	0.909347
C	2.312322	-1.271256	-0.875637	C	-1.330439	0.177216	-1.140978
H	0.308128	-1.086501	-1.711144	C	-2.414626	-1.336173	0.925706
C	2.712725	0.677896	0.688796	H	-0.402382	-1.428075	1.705852
H	0.884605	1.786951	1.067861	C	-2.695338	-0.102795	-1.123631
C	3.104130	-0.752867	0.339585	H	-0.916132	0.784356	-1.948980
H	2.098084	-2.344901	-0.745894	C	-3.242110	-0.862771	-0.091376
H	2.884242	1.326336	-0.188118	H	-2.833018	-1.933782	1.739294
H	4.186926	-0.827210	0.154024	H	-3.336156	0.279037	-1.922165
H	0.287746	-1.144110	0.794048	H	-4.311765	-1.085120	-0.079266
H	1.161909	0.449231	2.172816	H	2.328380	1.425246	0.879311
H	3.355680	1.077358	1.488841	C	0.634547	2.537616	0.199876
H	2.906274	-1.390016	1.219345	H	1.080621	2.907326	-0.732347
H	2.923351	-1.194144	-1.789181	C	-0.402316	3.193768	0.721500
H	1.198603	0.420285	-1.646730	H	-0.808975	4.090728	0.247248
				H	-0.884927	2.853239	1.643057

1w

1x

C	2.461641	-1.283365	-1.068892				
C	1.723703	0.013361	-1.469970	C	-0.401516	2.964226	-0.258024
C	0.981513	0.048113	-0.098505	C	0.182923	2.030265	-1.340503
C	1.866062	-1.140252	0.320593	C	0.158997	0.828141	-0.346772
H	2.088970	-2.189370	-1.573316	C	-0.198793	1.843743	0.749629
H	3.561315	-1.293471	-1.110929	H	0.144629	3.892185	-0.031270
H	1.079452	-0.071207	-2.353543	H	-1.466411	3.215779	-0.386808
H	2.398373	0.869815	-1.609356	H	1.204102	2.308710	-1.633793
O	2.056724	-1.679345	1.371375	H	-0.426465	1.899208	-2.245101
C	1.236446	1.295665	0.772458	O	-0.266042	1.781292	1.944063
H	0.836648	1.098332	1.778957	C	-1.047474	-0.095818	-0.604679
C	-0.491057	-0.298396	-0.128597	H	-1.947077	0.526331	-0.757776

C	-1.313377	-1.108899	0.496341	H	-0.083670	-4.435388	-0.272067
H	-1.382938	-0.585766	1.465649	H	1.232591	-3.346155	-0.800492
C	1.437164	0.046771	-0.180070	H	-1.240039	-4.047806	-2.391753
C	1.924467	-0.300836	1.084889	H	0.102057	-3.029259	-2.943728
C	2.140271	-0.377977	-1.313941	O	-1.114949	-2.334744	0.990175
C	3.090119	-1.055990	1.208808	C	-1.012070	-0.706054	-2.393563
H	1.384856	0.033131	1.973249	H	-1.796238	0.035542	-2.572216
C	3.302923	-1.134421	-1.189325	C	0.284041	-0.439199	-2.805209
H	1.771159	-0.111377	-2.308460	H	0.510224	0.519634	-3.279402
C	3.781878	-1.476977	0.074884	H	1.025654	-1.225564	-2.960234
H	3.460564	-1.316208	2.203452	Ni	-0.031335	-0.506725	-0.705287
H	3.839595	-1.457073	-2.084979	C	0.636802	2.840976	2.378585
H	4.694689	-2.069018	0.174899	C	1.717276	3.129596	3.206459
H	-0.869812	-0.615928	-1.563233	C	2.878197	2.355784	3.138510
C	-2.589170	-1.920715	0.260131	C	2.957810	1.297831	2.238410
H	-2.649884	-2.706498	1.033618	C	1.878649	1.009491	1.394670
H	-2.531356	-2.441277	-0.711177	C	0.709492	1.781751	1.466586
C	-3.833420	-1.091348	0.315547	H	-0.278694	3.433457	2.448085
H	-4.010151	-0.564972	1.263562	H	1.650901	3.955241	3.919164
C	-4.710958	-0.935950	-0.677165	H	3.721208	2.573575	3.798698
H	-5.600606	-0.310838	-0.563157	H	3.859715	0.681837	2.193991
H	-4.574972	-1.437379	-1.641422	P	-0.690293	1.297501	0.367174
H	-0.455790	-1.794635	0.581735	P	1.905500	-0.374643	0.179159
				C	-2.119134	1.498273	1.499741
1i-TS1				C	-2.489851	0.369156	2.242831
				C	-2.829274	2.693958	1.662684
C	0.141631	-3.478582	-0.767985	C	-3.546670	0.445080	3.147265
C	-0.572242	-3.226389	-2.100759	H	-1.965871	-0.578144	2.076769
C	-1.371903	-1.965407	-1.692369	C	-3.891550	2.761388	2.562930
C	-0.586372	-2.315021	-0.107608	H	-2.556596	3.575400	1.076906

C	-4.249453	1.638886	3.308882	H	4.754488	-1.358262	0.370577
H	-3.831774	-0.441115	3.719575	C	2.573066	-3.408996	2.836487
H	-4.443050	3.697458	2.681828	H	0.904474	-2.256226	2.106421
H	-5.084258	1.693125	4.012042	C	3.942182	-3.658269	2.743977
C	-0.845173	2.721404	-0.769229	H	5.794303	-3.108260	1.777622
C	0.218052	3.594055	-1.026794	H	1.954831	-3.987110	3.527510
C	-2.014915	2.835887	-1.536752	H	4.402611	-4.431493	3.363841
C	0.111064	4.565859	-2.020913	C	-2.891776	-2.148505	-1.539300
H	1.138478	3.513484	-0.444598	C	-3.349393	-3.408485	-0.800796
C	-2.122984	3.812517	-2.521989	C	-3.554978	-0.905672	-0.911882
H	-2.850718	2.155102	-1.352697	C	-4.861856	-3.605060	-0.937872
C	-1.058340	4.680581	-2.769507	H	-2.834609	-4.303360	-1.182582
H	0.950388	5.239903	-2.209244	C	-4.799231	-1.230912	-0.090095
H	-3.043578	3.893747	-3.105167	H	-2.812905	-0.399923	-0.277345
H	-1.141094	5.443791	-3.546833	C	-5.642803	-2.285511	-0.793067
C	3.186742	0.150645	-1.020156	H	-5.090311	-4.066567	-1.913132
C	3.624061	-0.781452	-1.973323	H	-4.502464	-1.596913	0.906426
C	3.661258	1.463788	-1.094102	H	-5.921672	-1.900656	-1.789610
C	4.526543	-0.412082	-2.964811	H	-3.259614	-2.252304	-2.579813
H	3.254157	-1.809987	-1.933770	H	-3.826906	-0.190520	-1.705765
C	4.556061	1.836646	-2.097484	H	-5.378034	-0.311379	0.089809
H	3.332194	2.203025	-0.360893	H	-6.590993	-2.453831	-0.258546
C	4.993365	0.902038	-3.032372	H	-5.193080	-4.328935	-0.175808
H	4.862874	-1.152134	-3.694965	H	-3.070862	-3.328340	0.259609
H	4.915542	2.867548	-2.143827				
H	5.696300	1.195084	-3.815655	**1w-TS1**			
C	2.760108	-1.680368	1.148567				
C	4.134785	-1.933833	1.061659	C	0.611484	-3.478842	-0.764477
C	1.981937	-2.428724	2.043550	C	-0.705119	-3.794172	-1.477905
C	4.720666	-2.919395	1.854965	C	-1.247767	-2.354542	-1.625527

C	-0.069189	-2.266882	-0.143463	H	-5.504337	2.582655	1.506839
H	0.985694	-4.220205	-0.044433	H	-6.004839	0.619932	2.957913
H	1.404706	-3.197818	-1.471158	C	-0.895594	2.565833	-0.420447
H	-1.339797	-4.409713	-0.829305	C	-0.146048	3.599990	0.151637
H	-0.606234	-4.303121	-2.450520	C	-1.563101	2.807899	-1.631645
O	-0.507735	-2.277228	0.993585	C	-0.060314	4.842574	-0.476203
C	-0.902361	-1.827441	-3.041552	H	0.389224	3.431369	1.087901
H	-1.797175	-1.912700	-3.682800	C	-1.489498	4.052707	-2.249500
Ni	0.167700	-0.567331	-1.062168	H	-2.151682	2.008247	-2.089252
C	-0.374433	1.585460	2.953114	C	-0.729863	5.073861	-1.675777
C	0.461682	1.674051	4.061619	H	0.537816	5.635335	-0.020217
C	1.763290	1.171817	4.000275	H	-2.021196	4.224914	-3.188476
C	2.224023	0.580697	2.828744	H	-0.661751	6.048406	-2.165086
C	1.383663	0.477557	1.714895	C	3.115760	1.078366	-0.407941
C	0.078889	0.989373	1.769587	C	2.612061	2.151586	-1.152085
H	-1.393796	1.975515	3.002625	C	4.453776	1.105967	0.004805
H	0.096358	2.137502	4.981251	C	3.427361	3.231885	-1.480557
H	2.420197	1.241357	4.870649	H	1.565714	2.141572	-1.461636
H	3.242794	0.188263	2.779087	C	5.272092	2.181144	-0.336116
P	-0.965571	0.859853	0.253395	H	4.861997	0.283206	0.596151
P	1.927982	-0.225133	0.107796	C	4.761866	3.246063	-1.078383
C	-2.627675	0.815556	1.033014	H	3.012405	4.064316	-2.053824
C	-2.919754	-0.296123	1.834917	H	6.316169	2.188938	-0.013559
C	-3.566273	1.846433	0.918092	H	5.405858	4.088902	-1.340843
C	-4.124692	-0.356110	2.528130	C	2.982462	-1.647069	0.545241
H	-2.191801	-1.109256	1.900153	C	3.971127	-2.075515	-0.353015
C	-4.778934	1.770719	1.602358	C	2.690298	-2.437256	1.664136
H	-3.347489	2.722354	0.304188	C	4.675514	-3.253344	-0.118297
C	-5.057716	0.674169	2.415412	H	4.190579	-1.481211	-1.244289
H	-4.341757	-1.226102	3.152540	C	3.397991	-3.615103	1.894941

H	1.881204	-2.147558	2.337321
C	4.393501	-4.024624	1.009635
H	5.447365	-3.572561	-0.822817
H	3.160751	-4.222142	2.771921
H	4.945768	-4.949269	1.193338
C	-2.650886	-2.082906	-1.204566
C	-3.304418	-2.874792	-0.246847
C	-3.374593	-1.004863	-1.742874
C	-4.623108	-2.626475	0.122096
H	-2.772462	-3.695714	0.234353
C	-4.684921	-0.739898	-1.358594
H	-2.900126	-0.348929	-2.473805
C	-5.324042	-1.556885	-0.429026
H	-5.101547	-3.268491	0.866130
H	-5.211301	0.115155	-1.789709
H	-6.352291	-1.350472	-0.124568
H	-0.148085	-2.500204	-3.480033
C	-0.326981	-0.438214	-3.031102
H	-0.956106	0.425039	-3.269818
C	1.045264	-0.297026	-2.938432
H	1.703574	-1.158765	-3.097058
H	1.516796	0.679783	-3.064876

1x-TS1

C	-0.521714	2.484217	-2.645808
C	-2.036504	2.346891	-2.493666
C	-2.086475	1.100069	-1.569034
C	-0.355063	1.020851	-2.310297
H	-0.149074	2.763050	-3.641908
H	-0.073405	3.131104	-1.877645
H	-2.482280	2.116094	-3.470267
H	-2.545458	3.230723	-2.077306
O	-0.029243	0.127771	-3.089108
C	-2.313366	1.542591	-0.107277
H	-1.625109	2.374503	0.120023
C	-3.740206	1.986181	0.205432
H	-4.062753	2.759535	-0.513522
Ni	-0.161345	0.216671	-0.671251
C	1.066602	-1.390407	3.356727
C	1.691622	-0.742008	4.421340
C	2.288908	0.503860	4.229771
C	2.267135	1.104493	2.971538
C	1.645507	0.463304	1.897196
C	1.036577	-0.793365	2.093958
H	0.585587	-2.360390	3.507469
H	1.705004	-1.209018	5.409094
H	2.769138	1.015194	5.067549
H	2.718859	2.089594	2.827712
P	0.198676	-1.507908	0.624139
P	1.543831	1.123930	0.181095
C	1.508050	-2.466684	-0.220053
C	1.299737	-2.797436	-1.566303
C	2.719264	-2.802408	0.393571
C	2.283060	-3.479219	-2.277160
H	0.381706	-2.483221	-2.070539
C	3.708880	-3.466993	-0.328901
H	2.898161	-2.524802	1.435040
C	3.489673	-3.812103	-1.661173
H	2.113078	-3.730705	-3.326637

H	4.659524	-3.709717	0.151674	H	4.370876	1.173088	1.170089
H	4.268055	-4.330452	-2.226436	C	5.545036	-0.206373	-1.710693
C	-0.899568	-2.784412	1.340832	H	4.336875	-0.740092	-3.420071
C	-2.128812	-2.356936	1.862407	H	6.489841	0.414338	0.132453
C	-0.600164	-4.151070	1.329045	H	6.478609	-0.550096	-2.163147
C	-3.033837	-3.277131	2.381853	C	-3.036658	0.019514	-1.994859
H	-2.381045	-1.292647	1.847002	C	-2.834965	-1.311550	-1.608377
C	-1.512370	-5.072767	1.842546	C	-4.193829	0.304526	-2.735799
H	0.348935	-4.494120	0.909948	C	-3.744889	-2.314380	-1.928420
C	-2.726884	-4.638646	2.371072	H	-1.931789	-1.547883	-1.041960
H	-3.989733	-2.932348	2.783065	C	-5.106372	-0.695312	-3.068139
H	-1.271872	-6.138644	1.827031	H	-4.399668	1.330894	-3.048195
H	-3.441480	-5.363486	2.768361	C	-4.888512	-2.011558	-2.665590
C	1.655614	2.931309	0.406060	H	-3.550571	-3.339588	-1.602916
C	0.750811	3.563597	1.273072	H	-5.999832	-0.439661	-3.643793
C	2.510141	3.716945	-0.376091	H	-5.603044	-2.795400	-2.928367
C	0.715993	4.951528	1.366488	H	-2.052186	0.727885	0.592390
H	0.071410	2.960217	1.881943	C	-3.870091	2.528144	1.627764
C	2.465960	5.107896	-0.286561	H	-3.532818	1.763981	2.349551
H	3.213693	3.235455	-1.059565	H	-3.181184	3.386513	1.742146
C	1.572190	5.728504	0.583813	C	-5.259196	2.962776	1.967690
H	0.012277	5.431187	2.051295	H	-5.679634	3.756403	1.335267
H	3.138495	5.710147	-0.902235	C	-6.012450	2.453781	2.943434
H	1.540246	6.818328	0.653016	H	-5.637360	1.657104	3.594779
C	3.157189	0.656102	-0.546841	H	-7.028451	2.811420	3.130192
C	3.152670	0.115079	-1.837616	H	-4.430968	1.138591	0.068894
C	4.362858	0.762757	0.157511				
C	4.348097	-0.311403	-2.415460				
H	2.210822	0.019976	-2.385746				
C	5.552437	0.333519	-0.423395				

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8. NMR Spectra of New Compounds

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

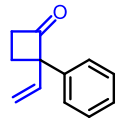
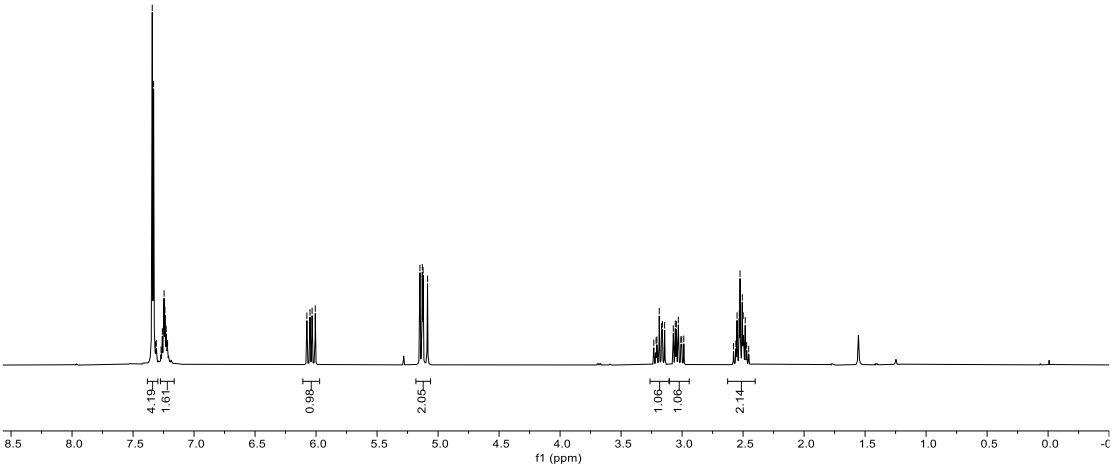


Table 2, 1a



^{13}C NMR in $CDCl_3$, 100 MHz

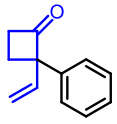
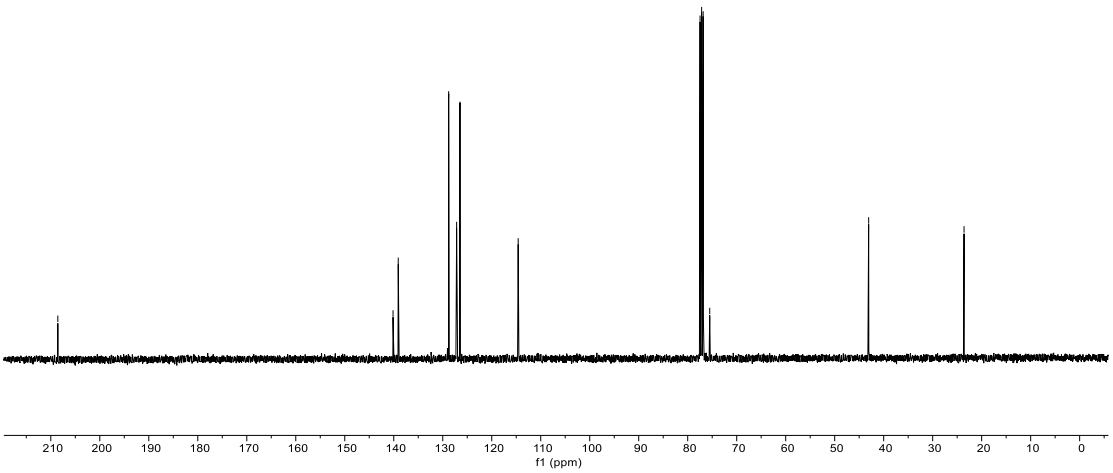


Table 2, 1a



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

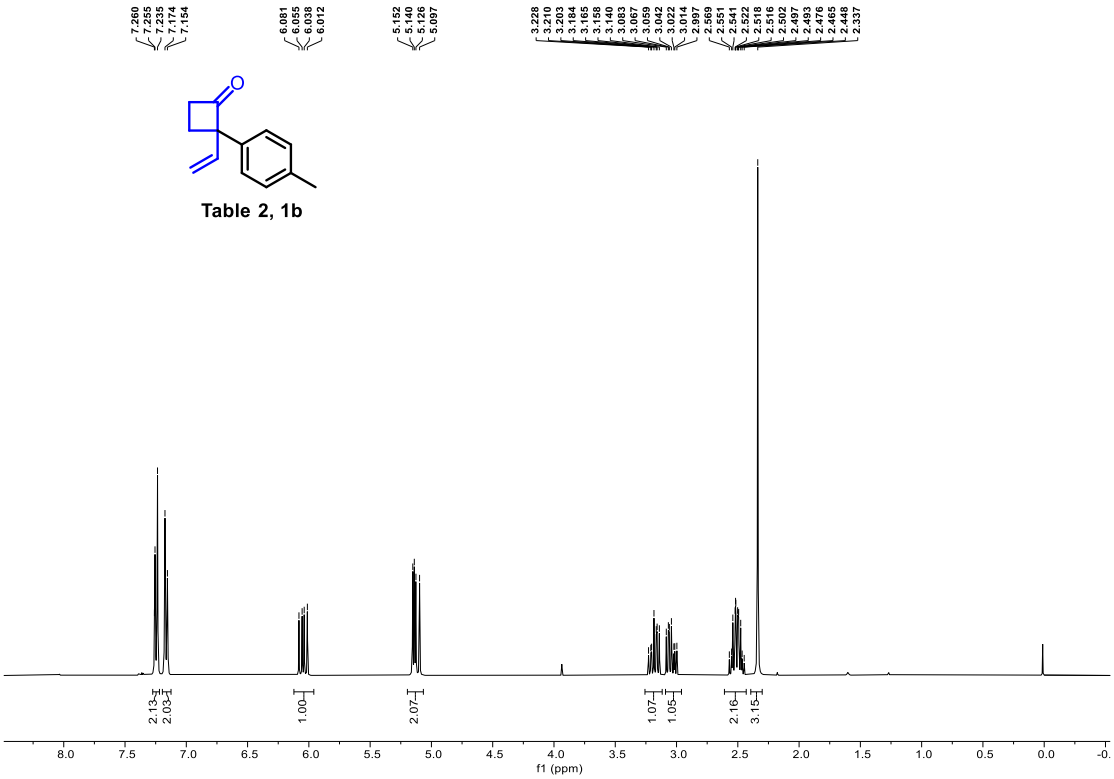


Table 2, 1b

^{13}C NMR in $CDCl_3$, 100 MHz

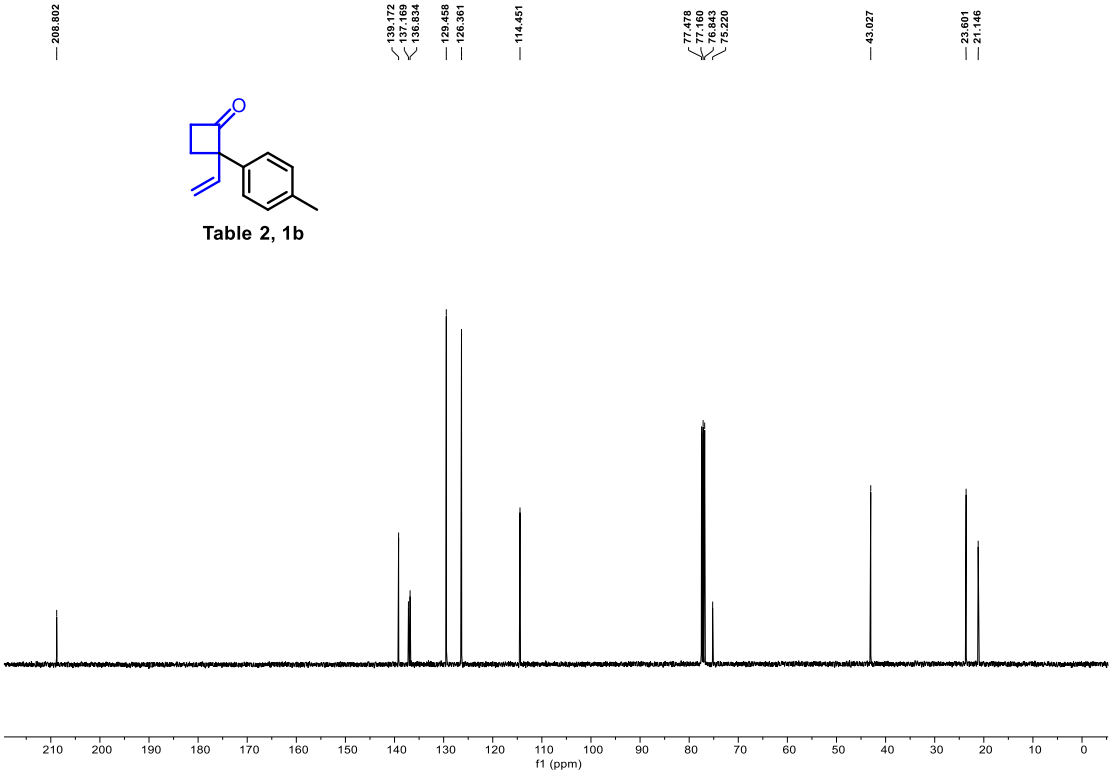


Table 2, 1b

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

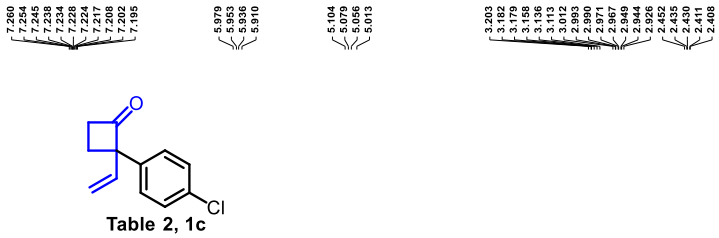
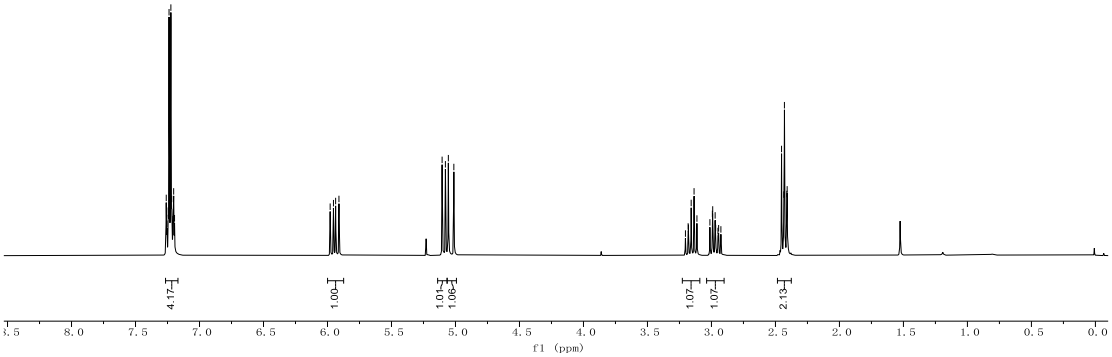


Table 2, 1c



^{13}C NMR in $CDCl_3$, 100 MHz

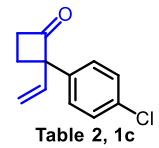
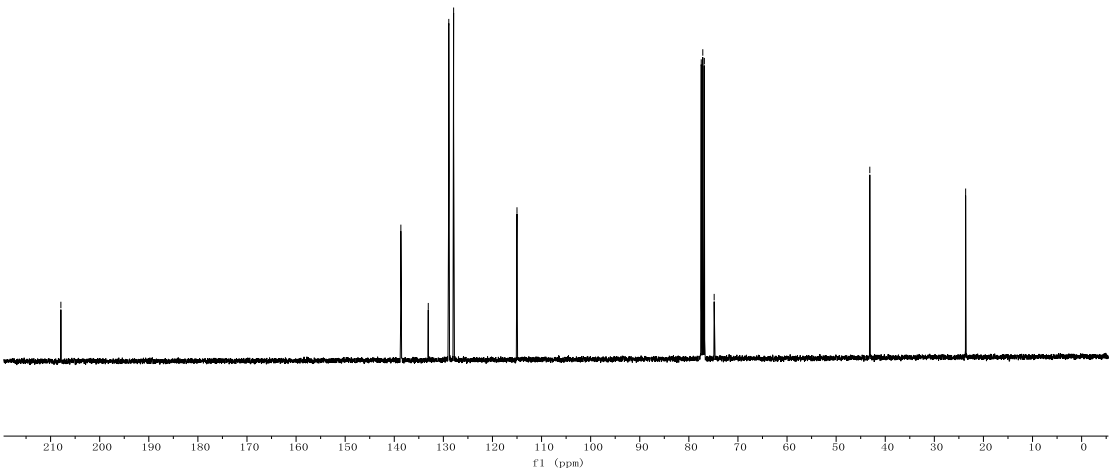
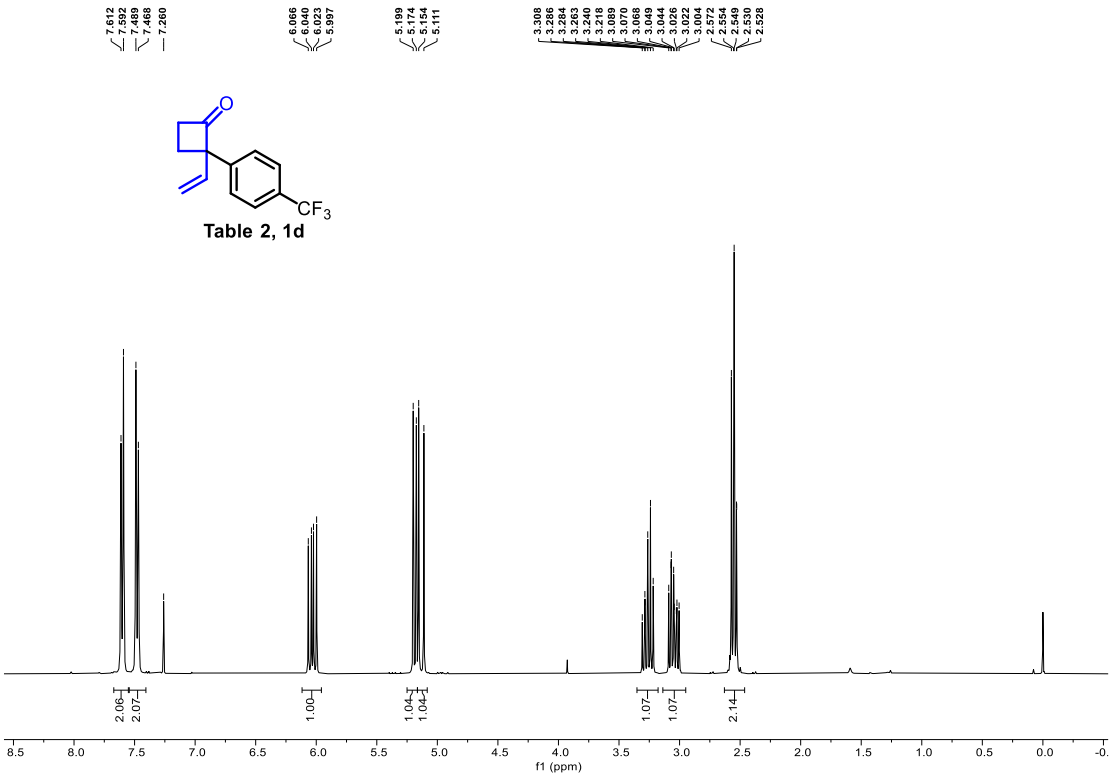


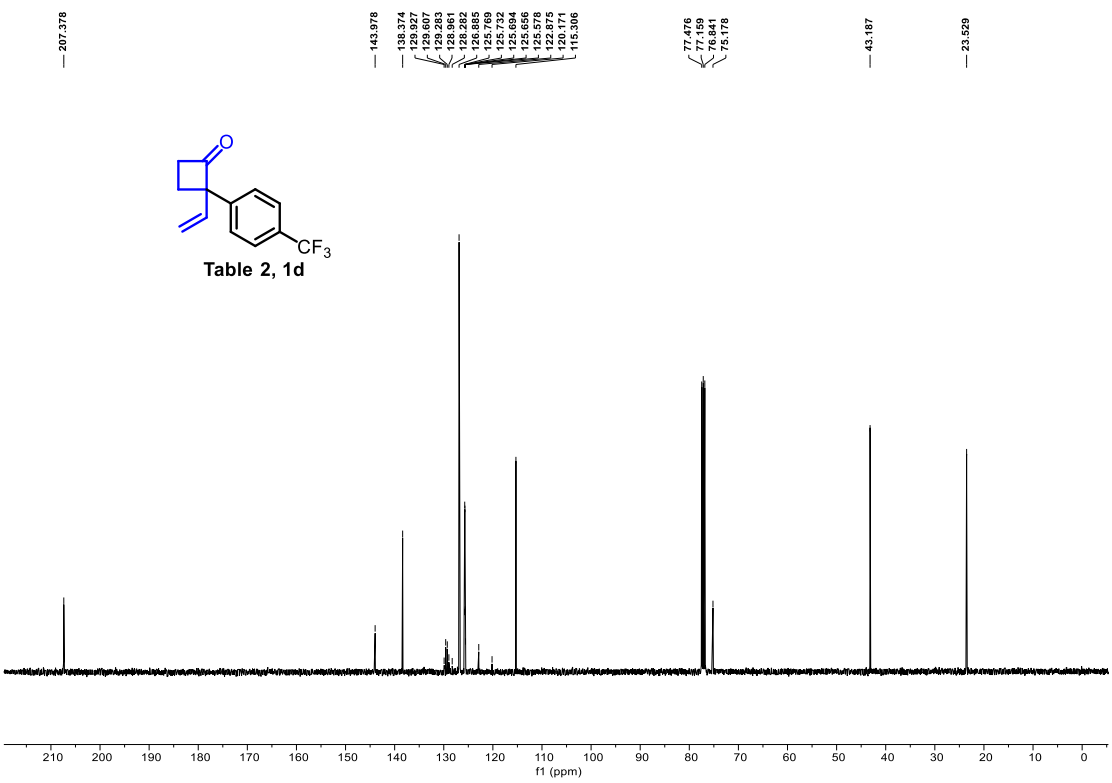
Table 2, 1c



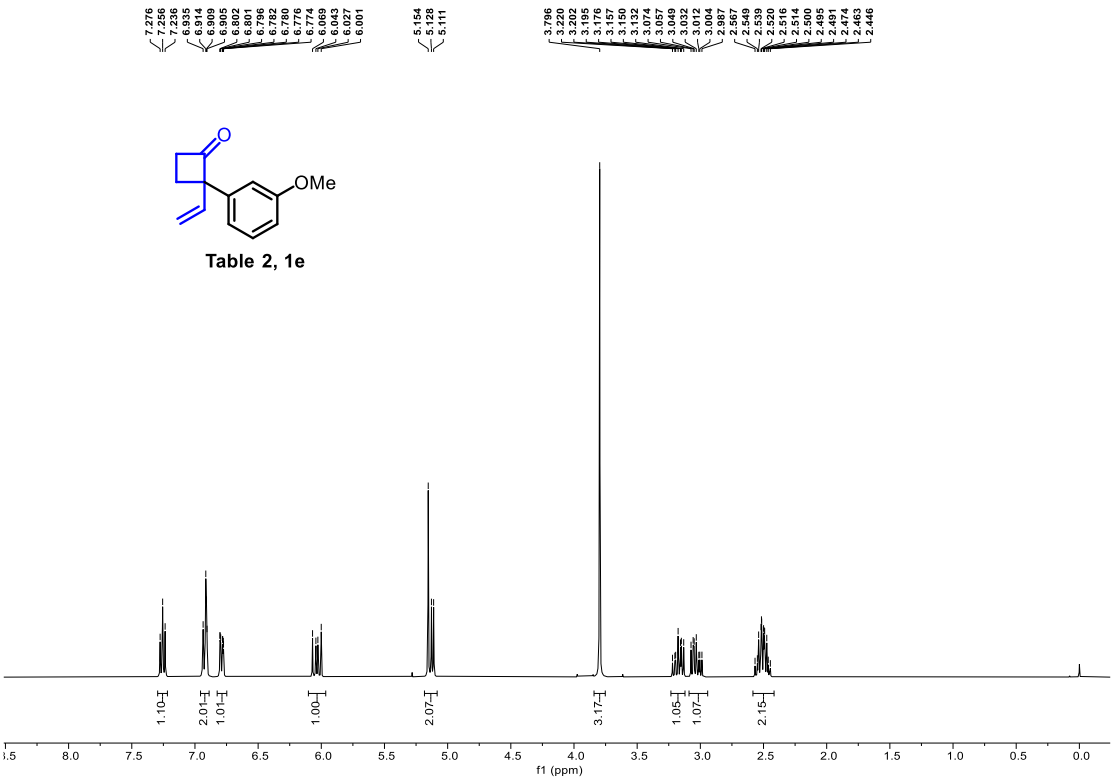
^{1}H NMR in $CDCl_3$, 400 MHz



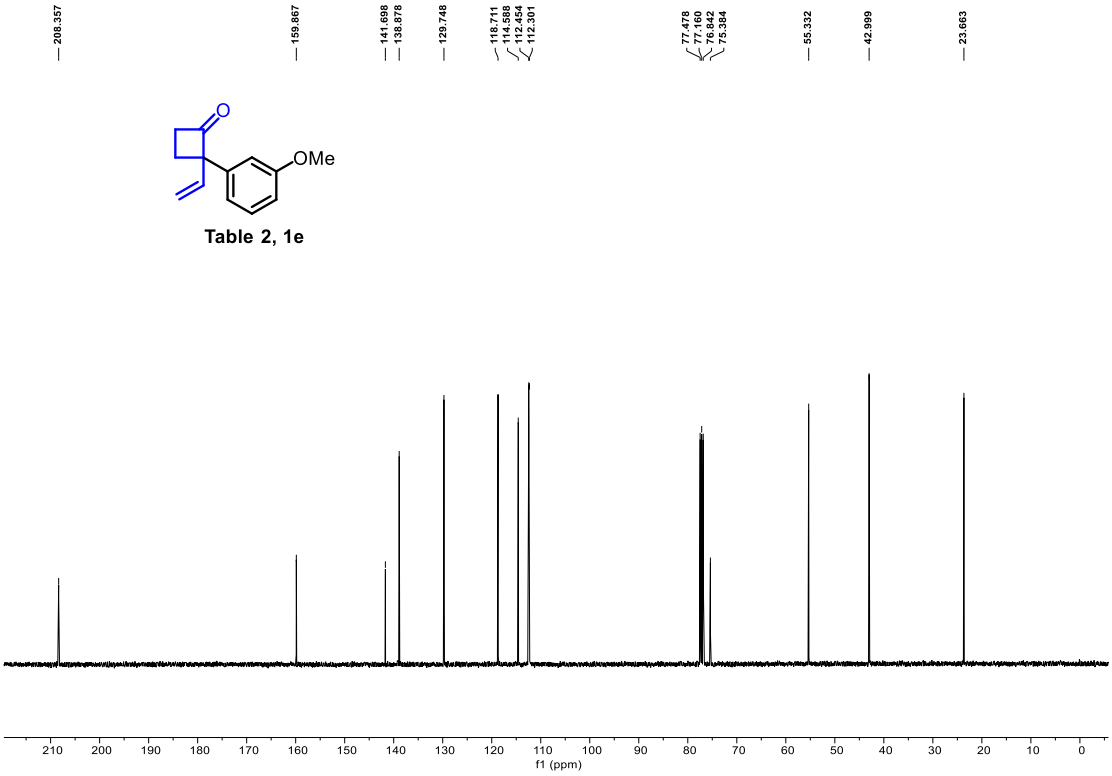
^{13}C NMR in $CDCl_3$, 100 MHz



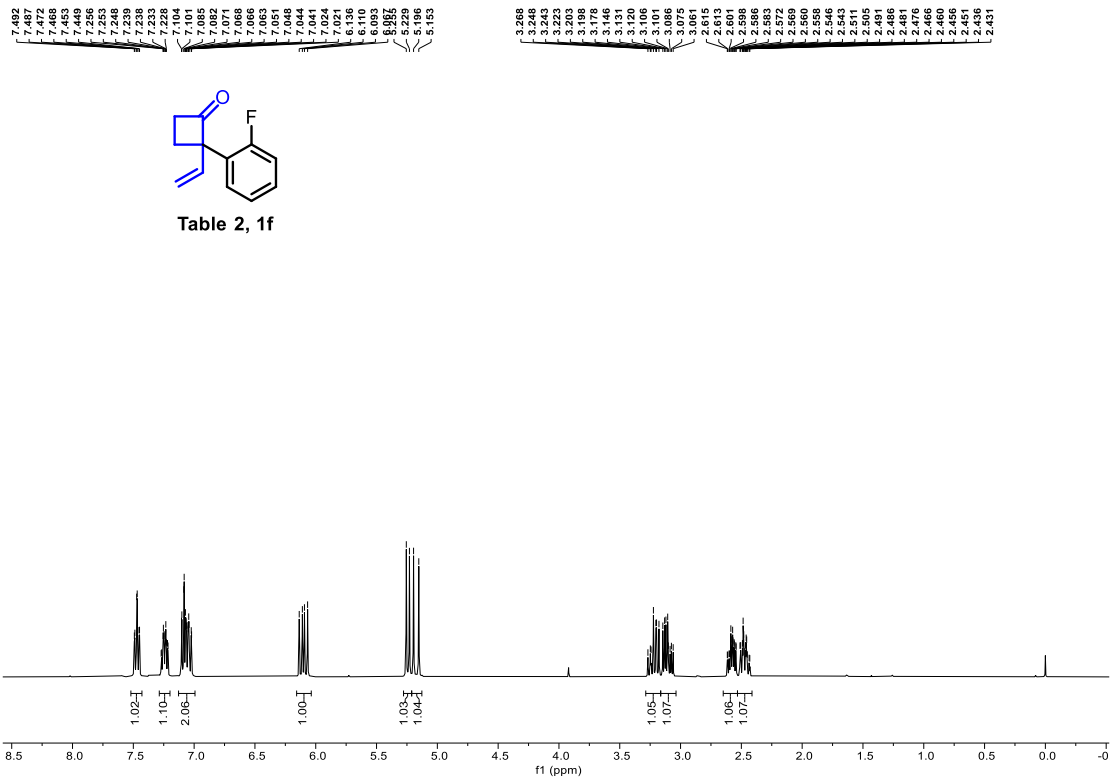
^{1}H NMR in $CDCl_3$, 400 MHz



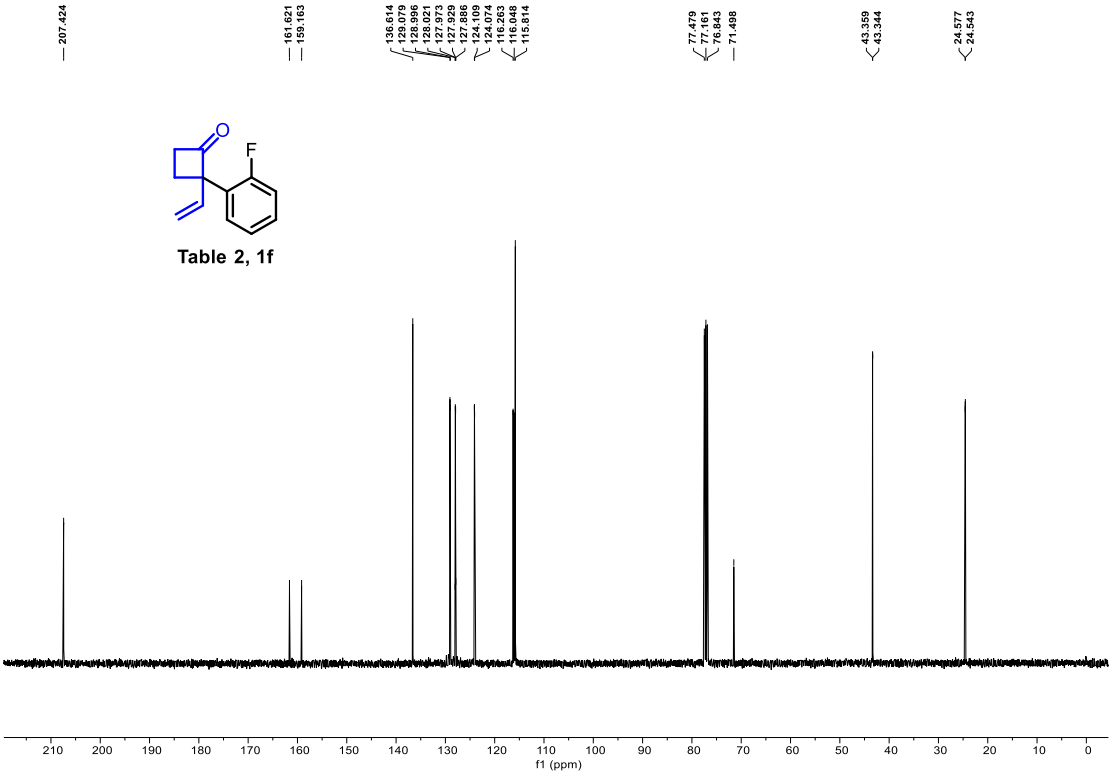
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



^{19}F NMR in $CDCl_3$, 471 MHz

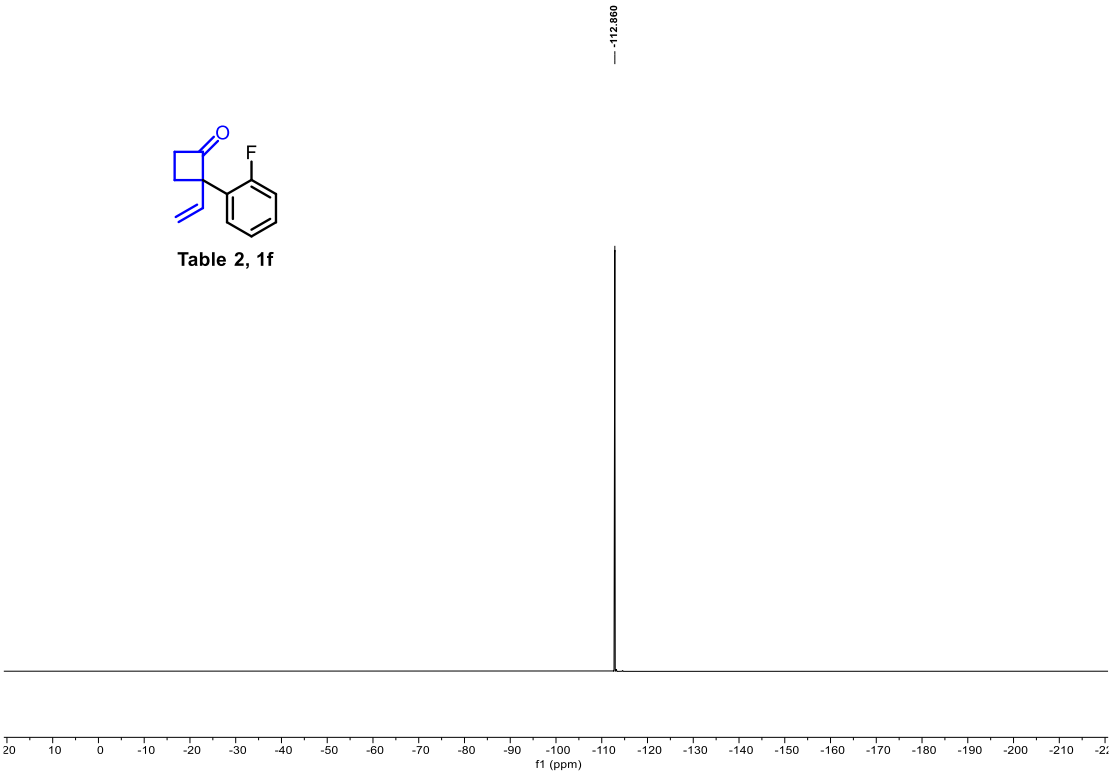
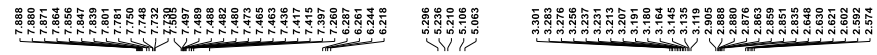


Table 2, 1f

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



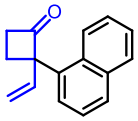
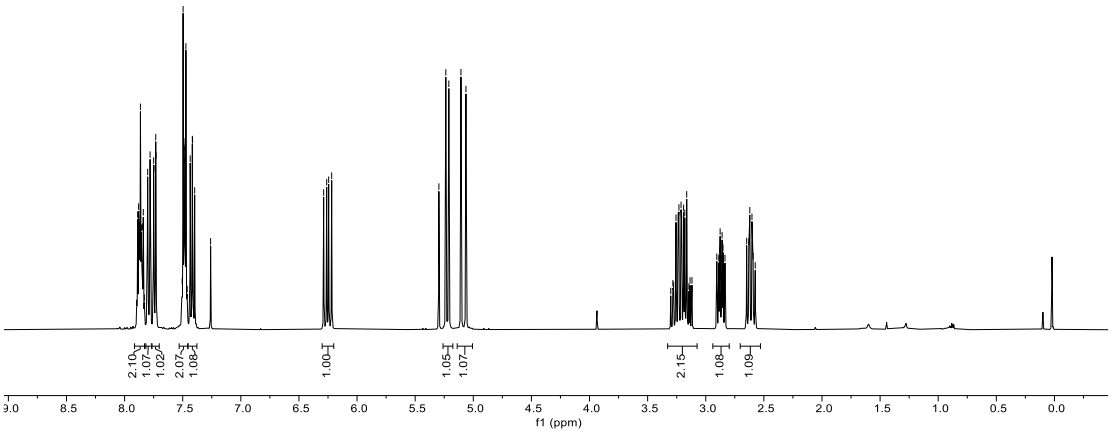


Table 2, 1g



^{13}C NMR in $CDCl_3$, 100 MHz

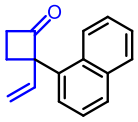
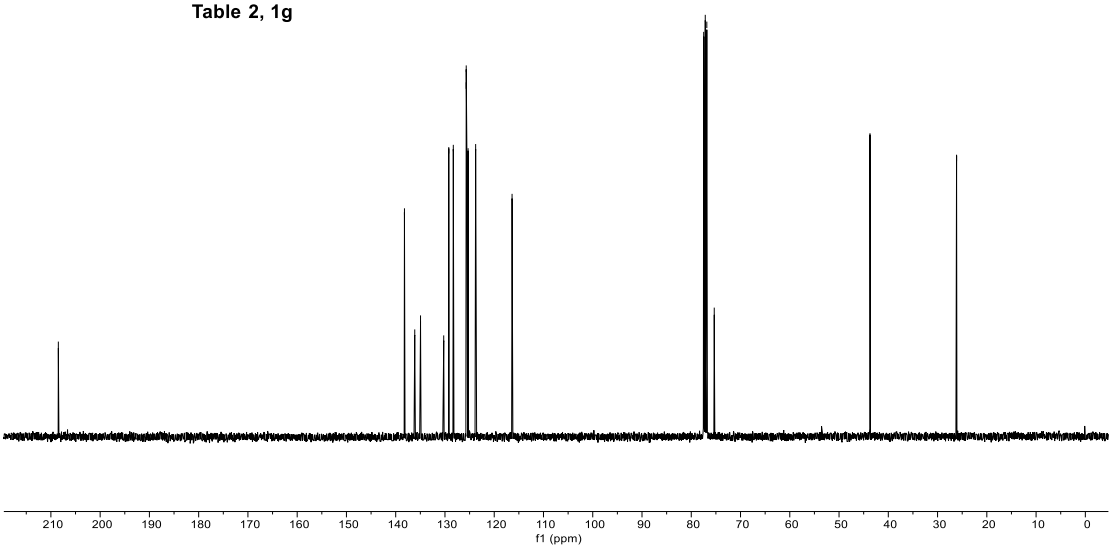


Table 2, 1g



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

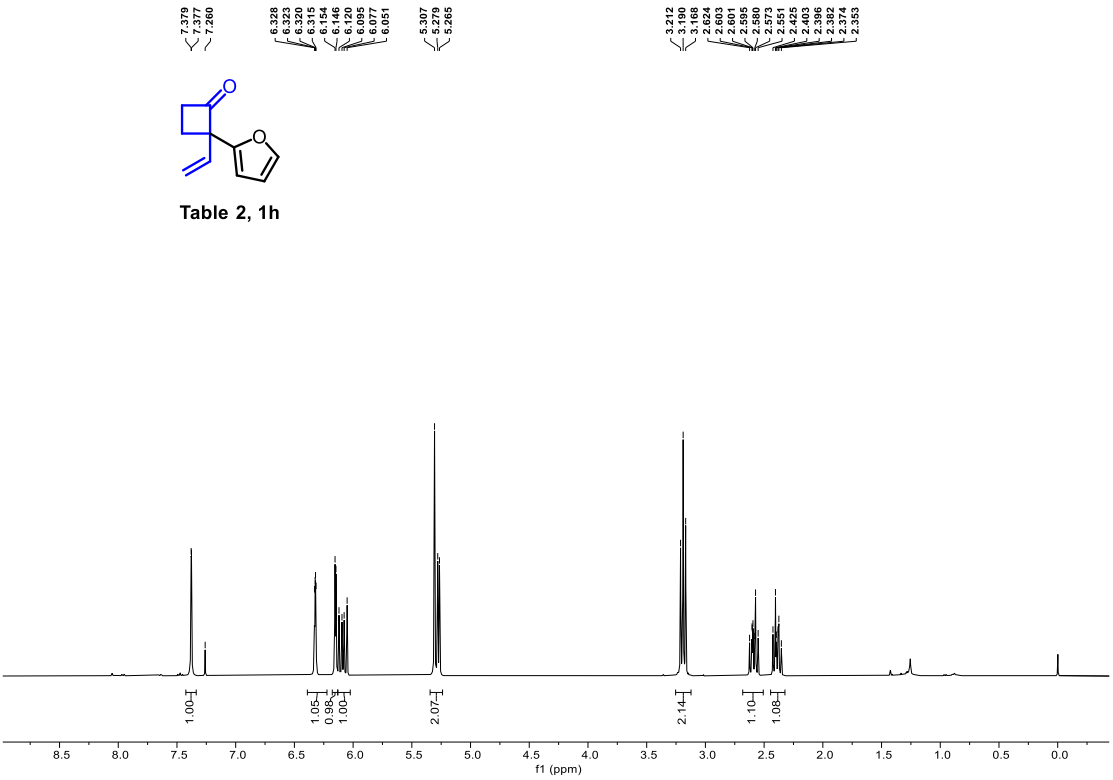


Table 2, 1h

^{13}C NMR in $CDCl_3$, 100 MHz

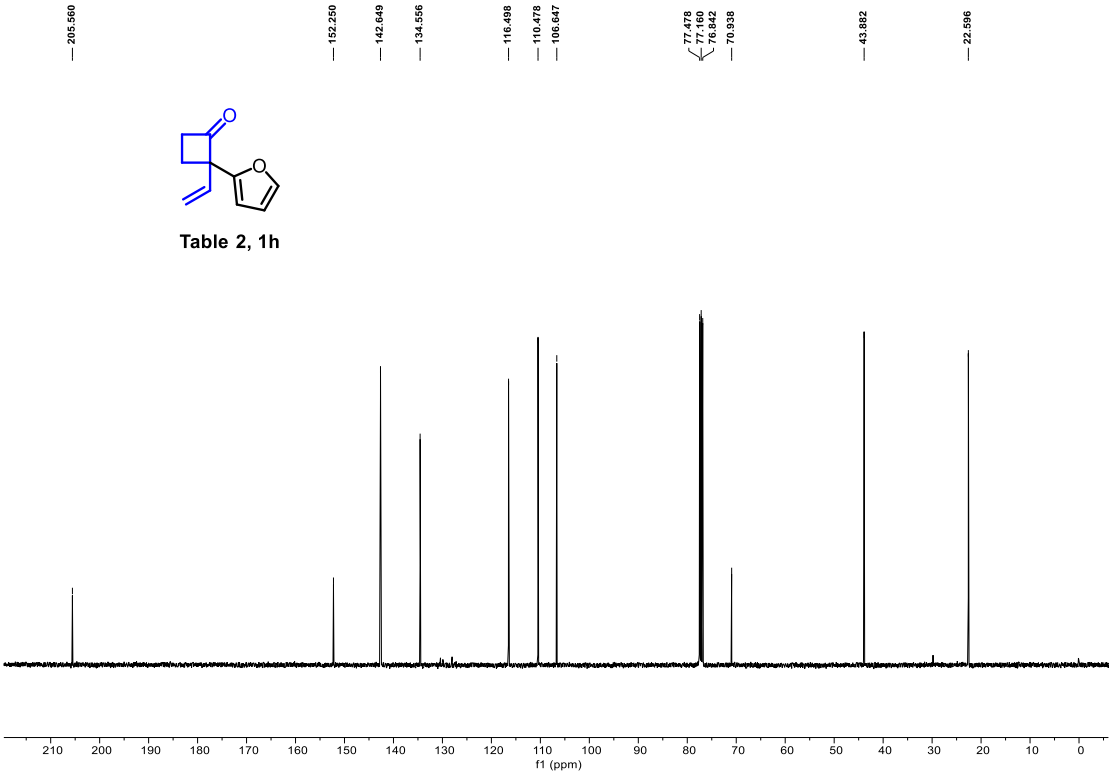


Table 2, 1h

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

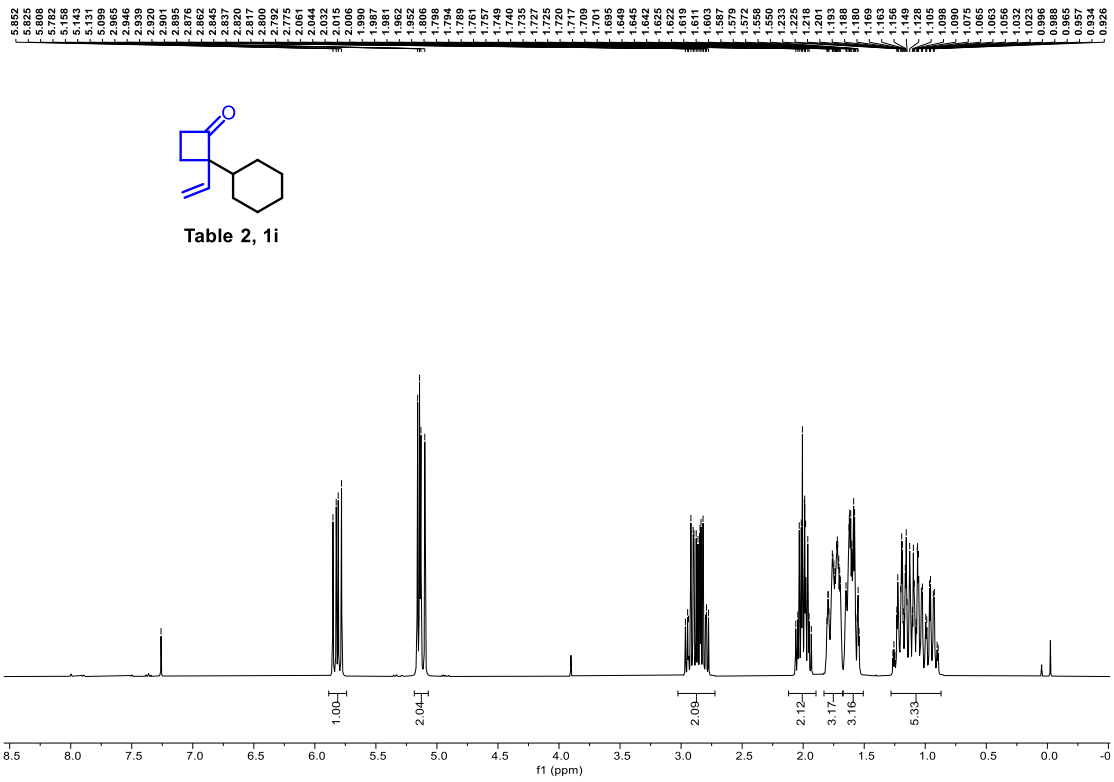


Table 2, 1i

^{13}C NMR in $CDCl_3$, 100 MHz

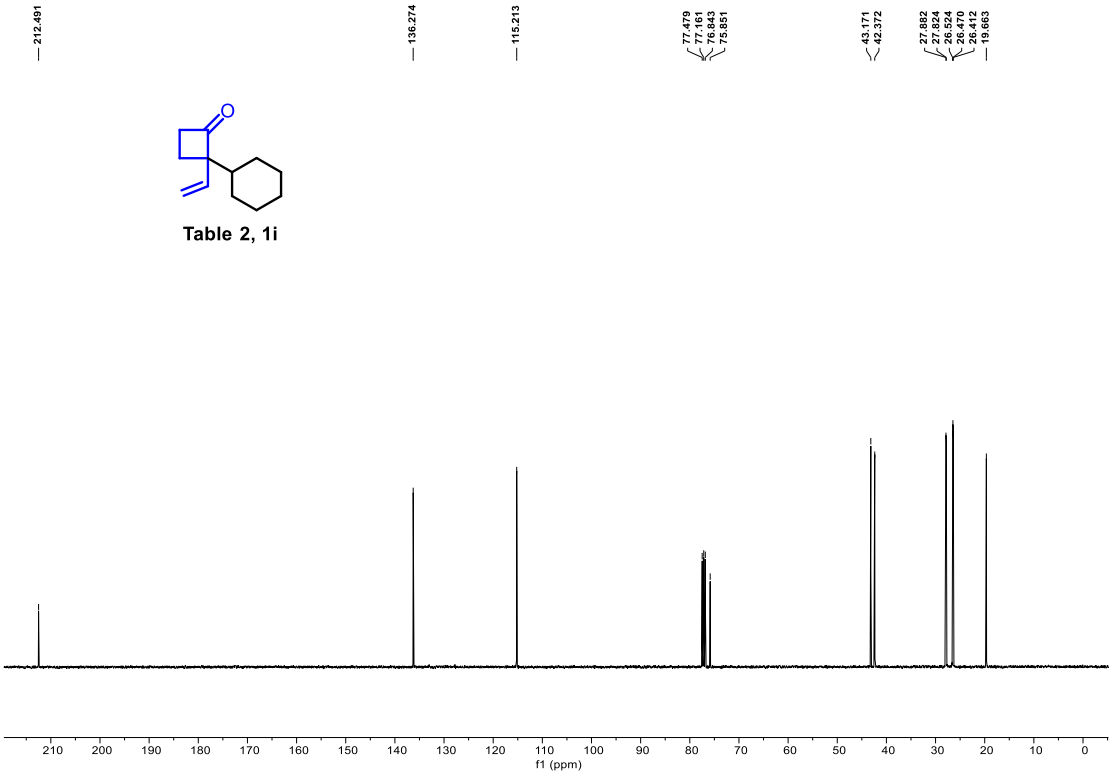


Table 2, 1i

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

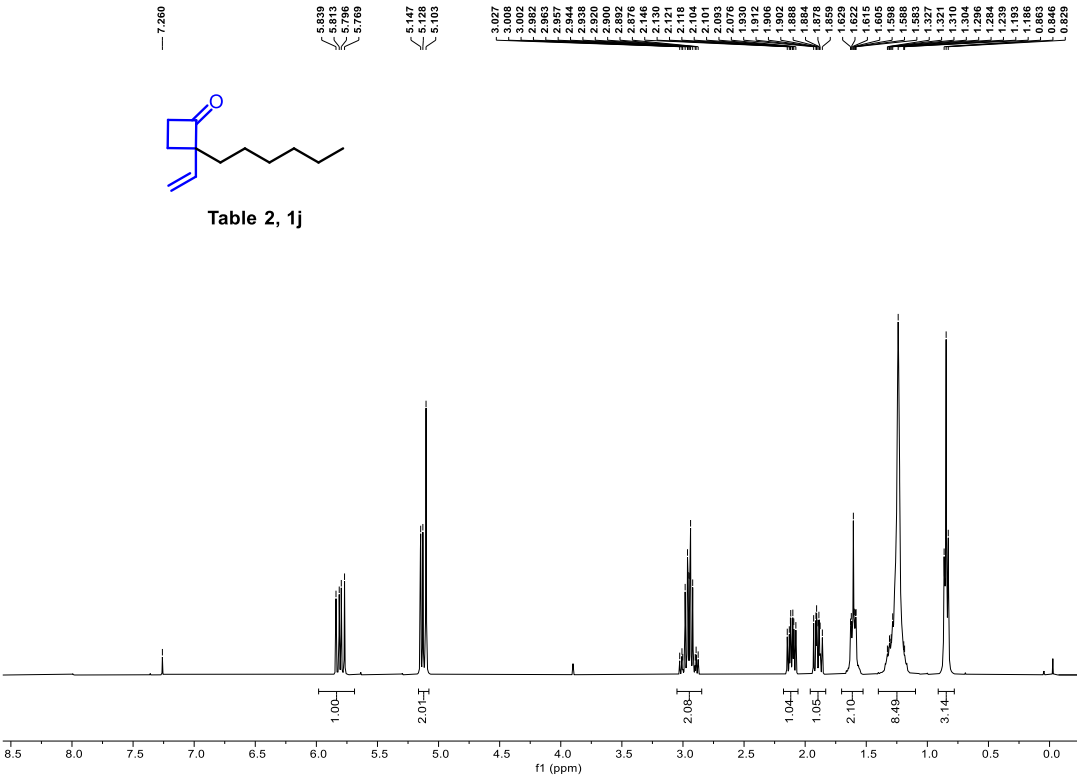


Table 2, 1j

^{13}C NMR in $CDCl_3$, 100 MHz

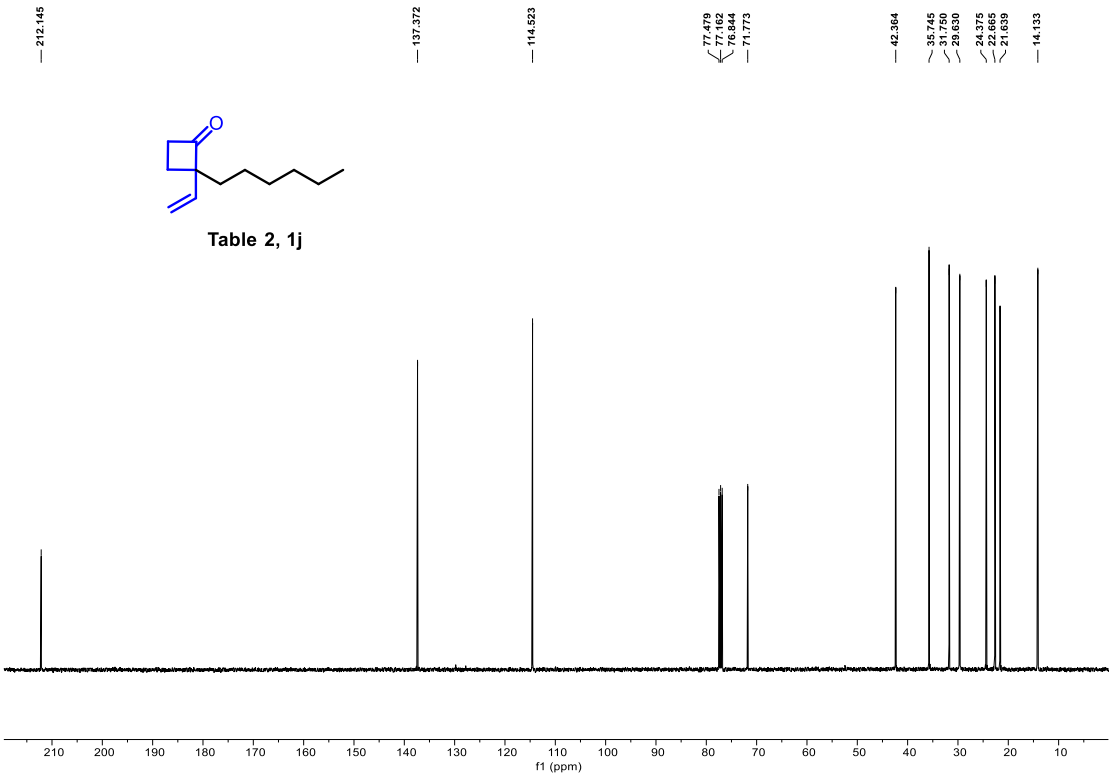
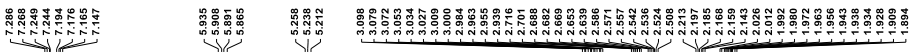


Table 2, 1j

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



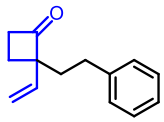
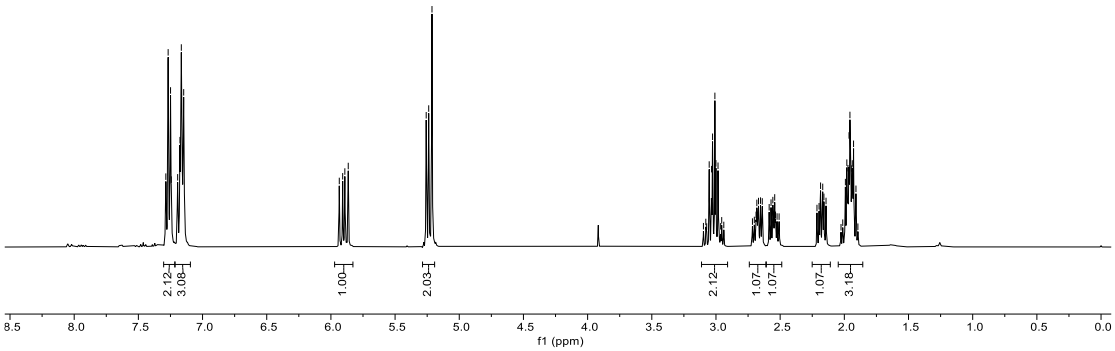
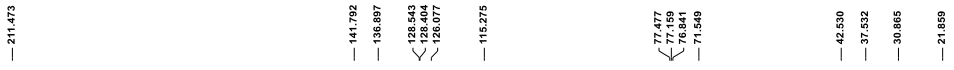


Table 2, 1k



^{13}C NMR in $CDCl_3$, 100 MHz



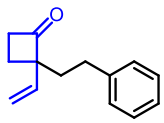
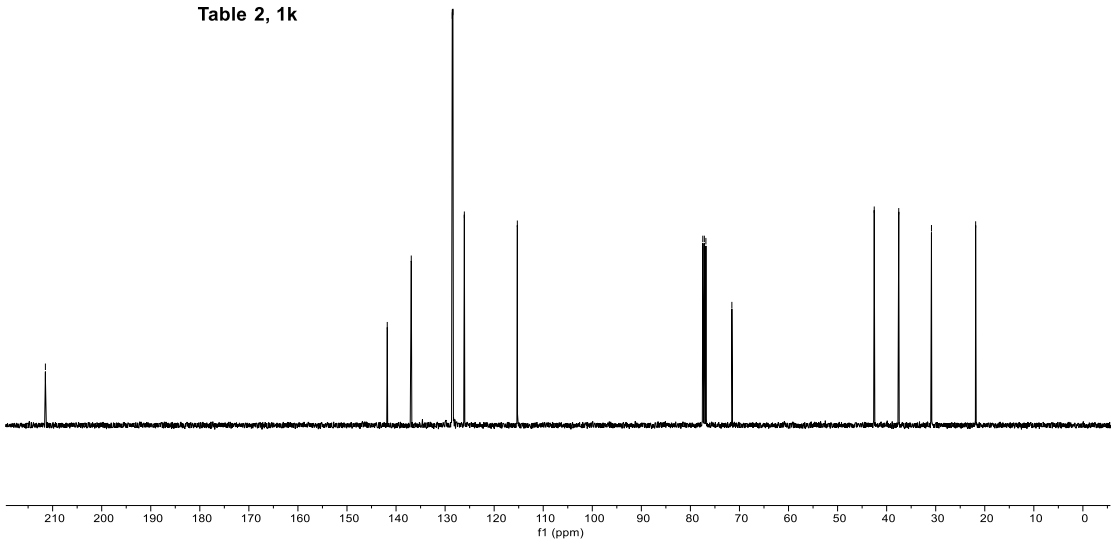


Table 2, 1k



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

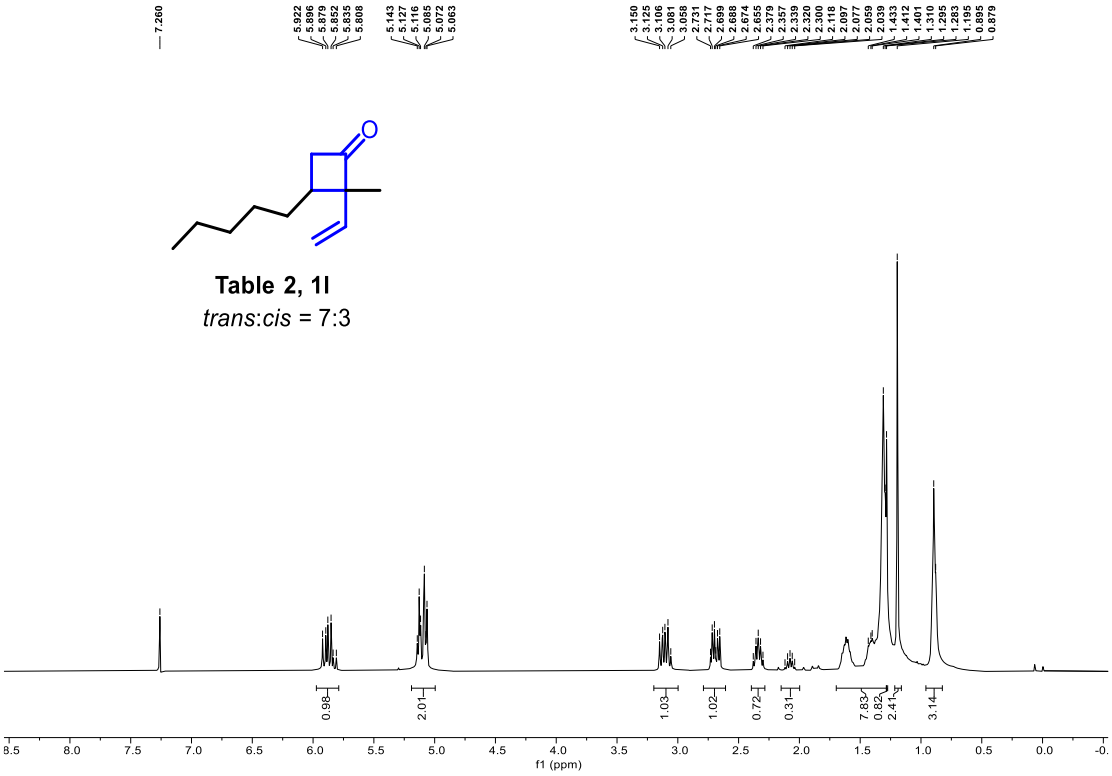


Table 2, 1l

trans:*cis* = 7:3

^{13}C NMR in $CDCl_3$, 100 MHz

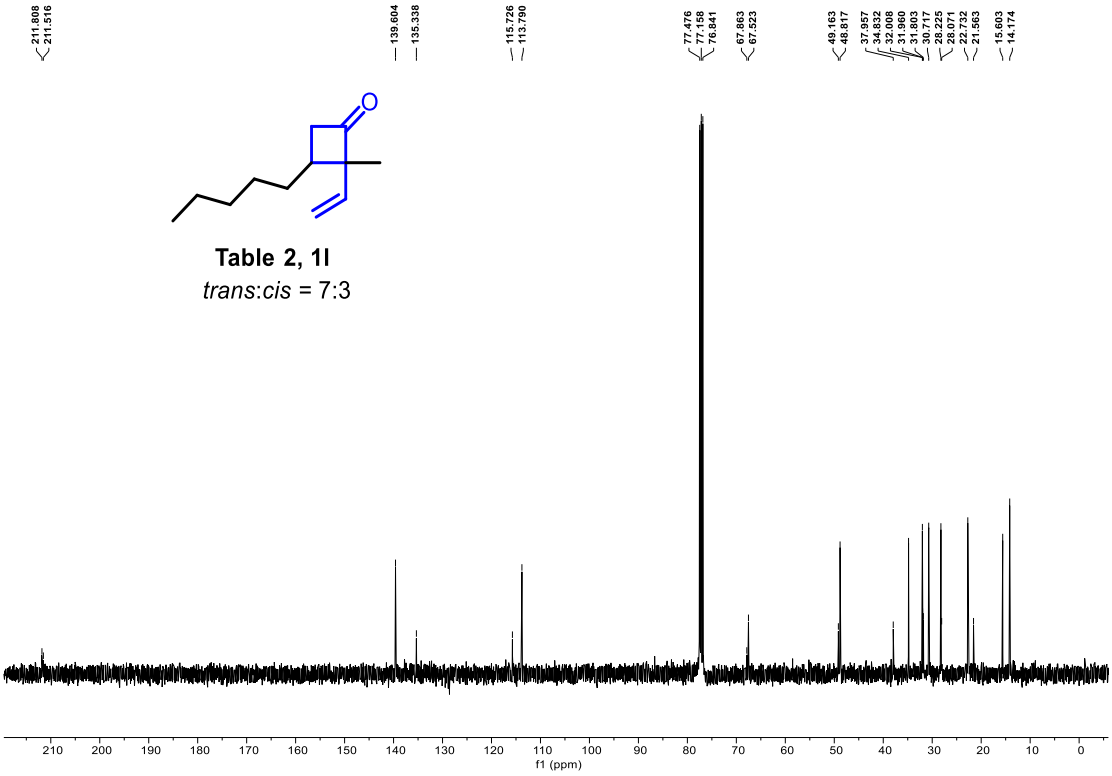
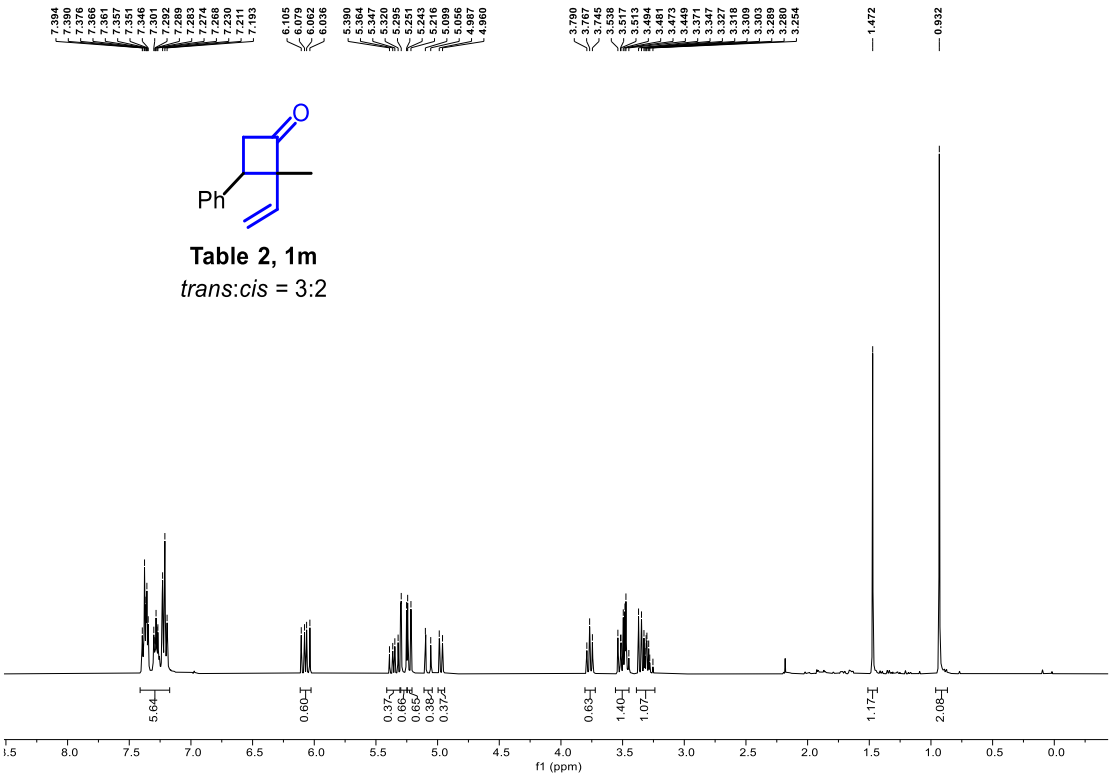


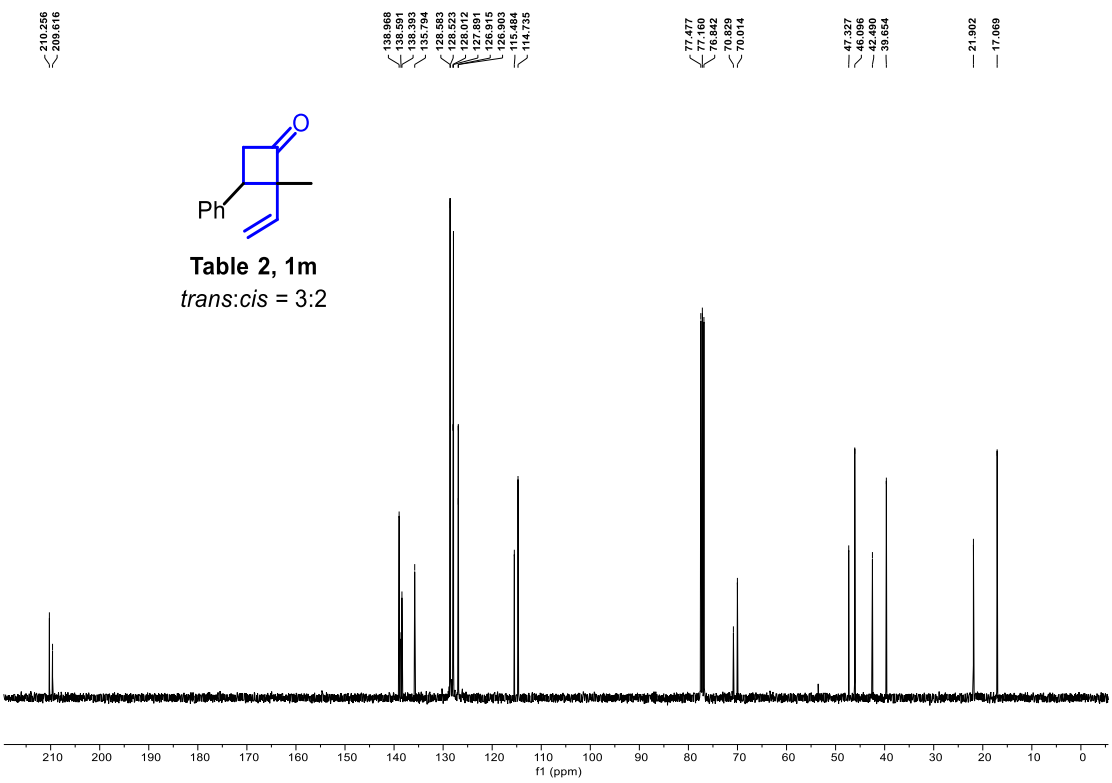
Table 2, 1l

trans:*cis* = 7:3

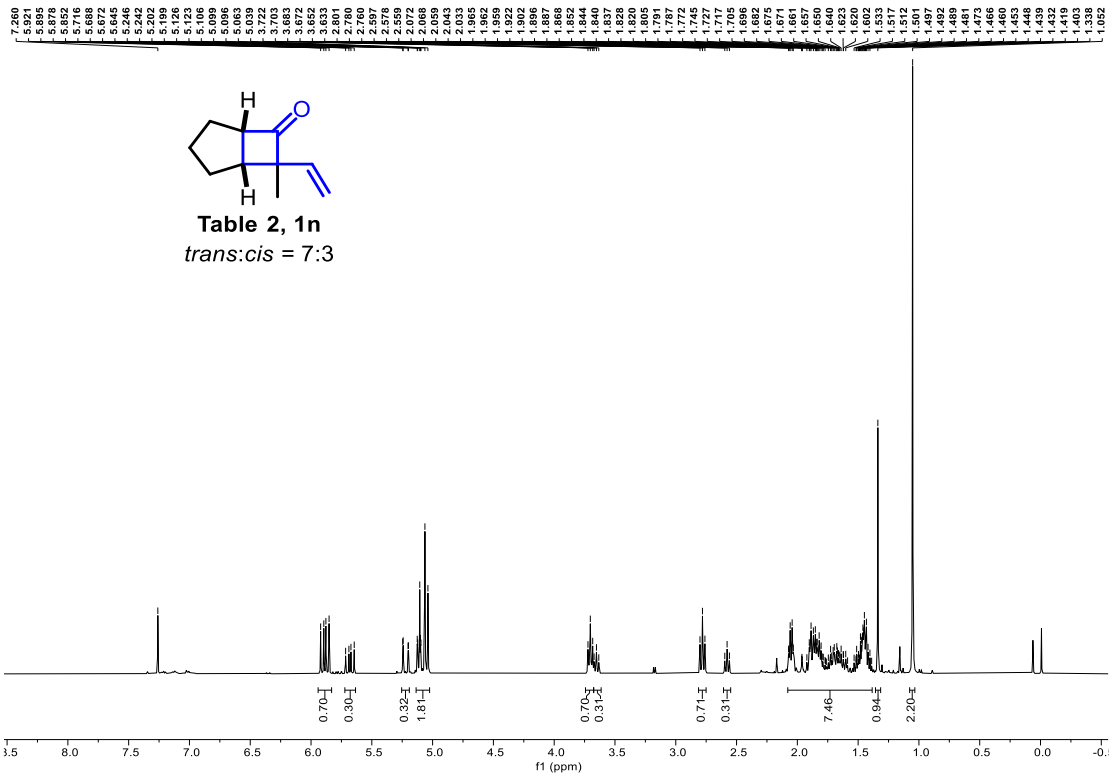
^{1}H NMR in $CDCl_3$, 400 MHz



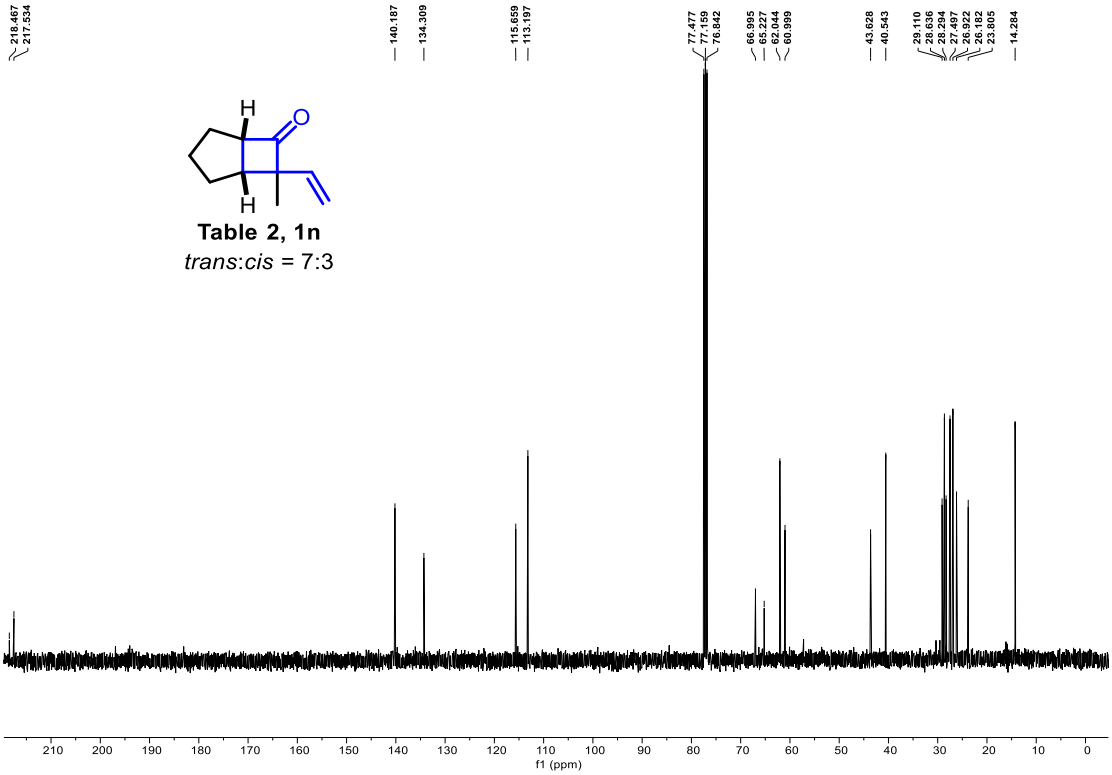
^{13}C NMR in $CDCl_3$, 100 MHz



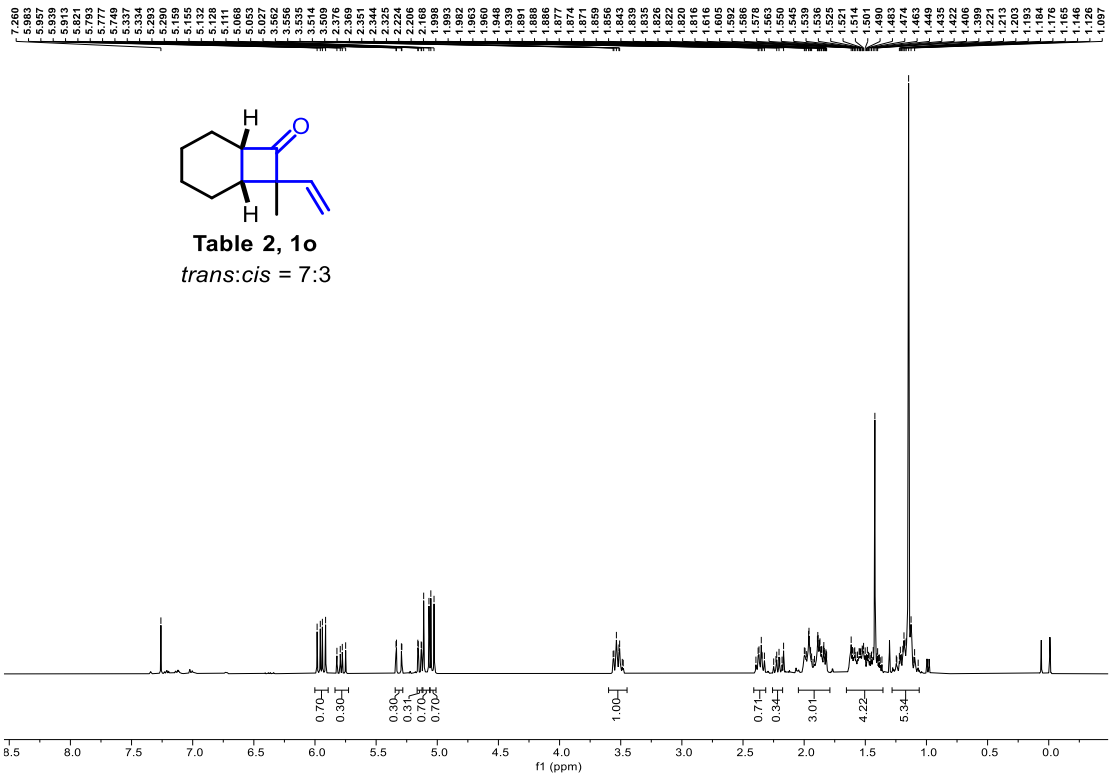
^{1}H NMR in $CDCl_3$, 400 MHz



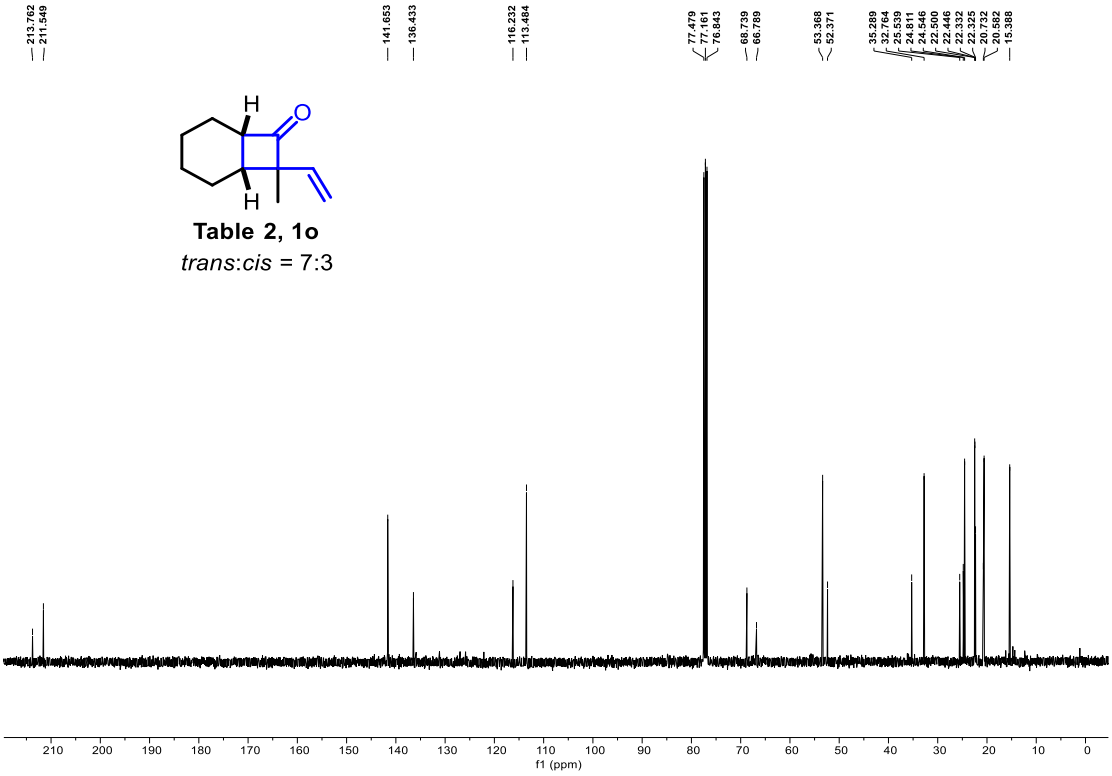
^{13}C NMR in $CDCl_3$, 100 MHz



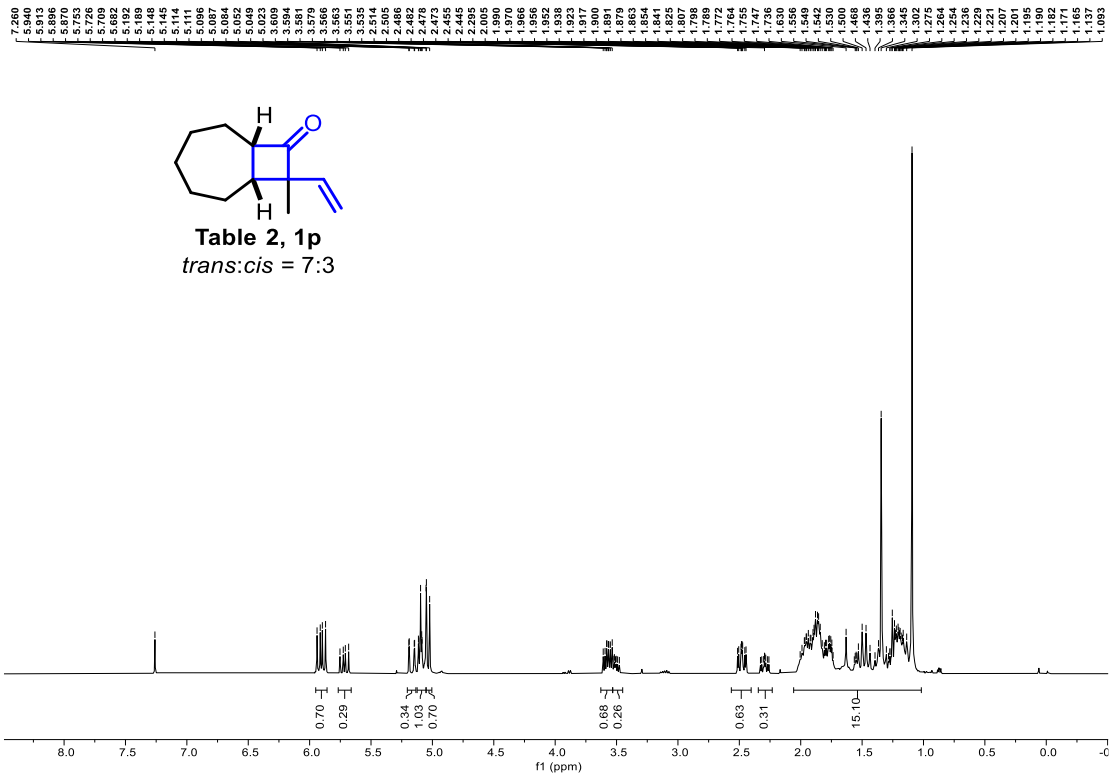
^{1}H NMR in $CDCl_3$, 400 MHz



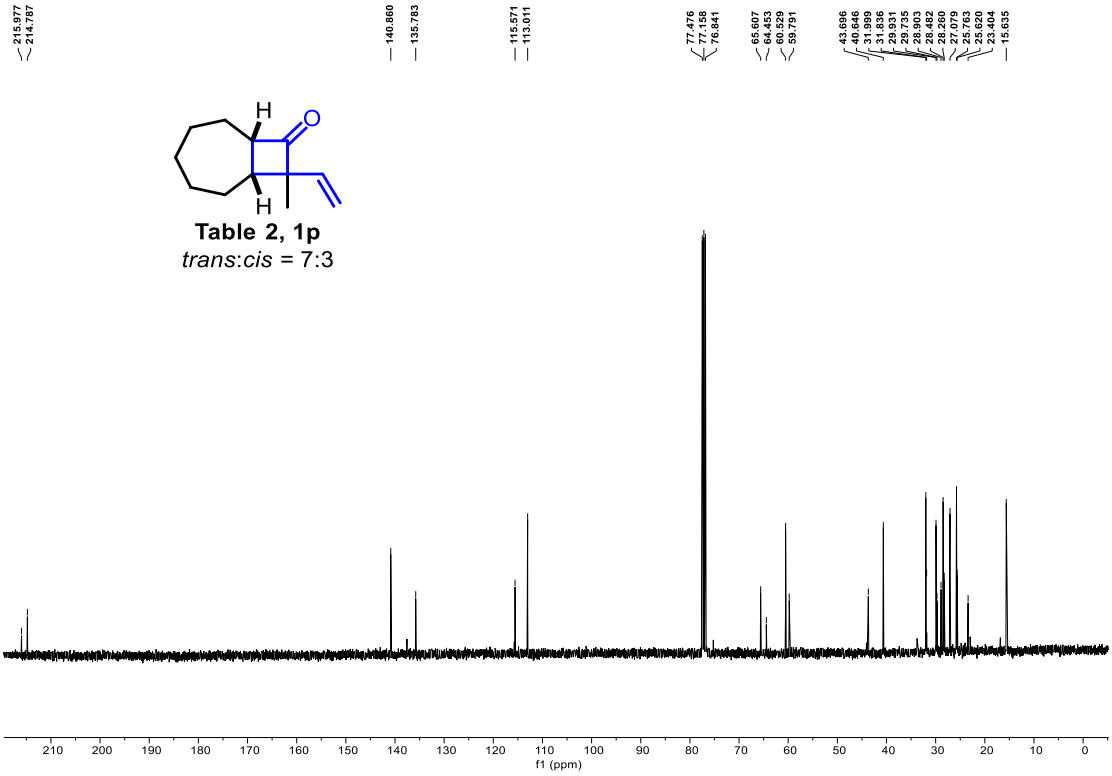
^{13}C NMR in $CDCl_3$, 100 MHz



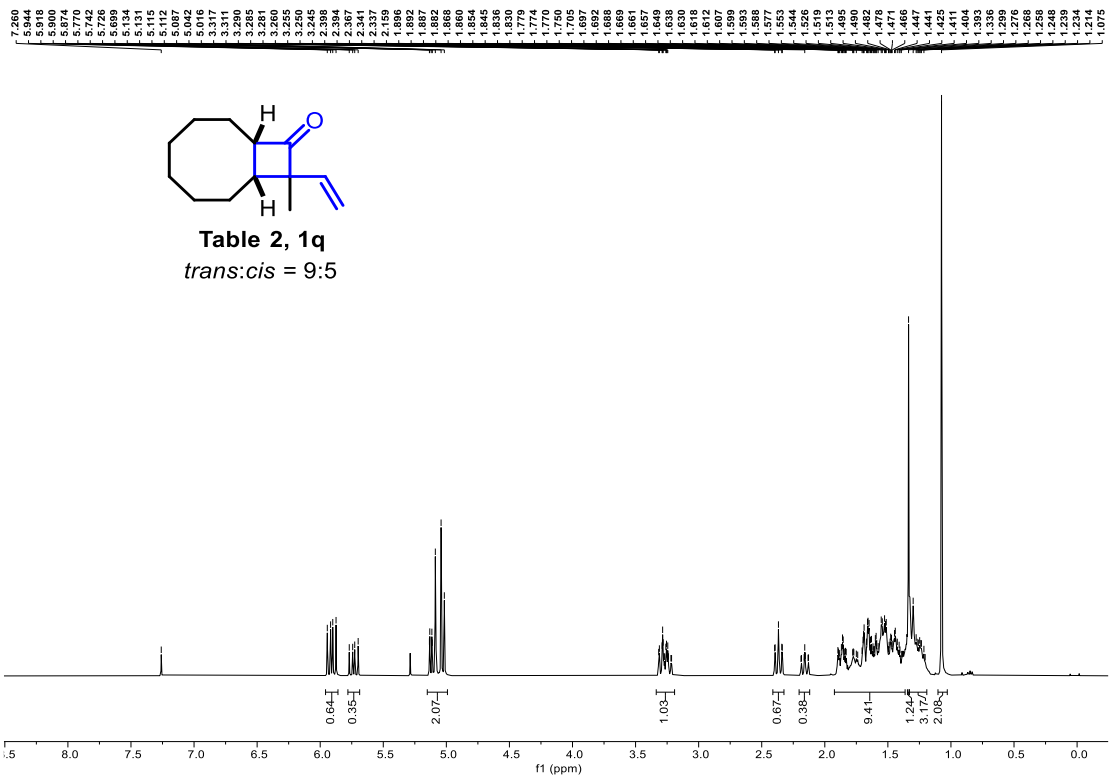
^{1}H NMR in $CDCl_3$, 400 MHz



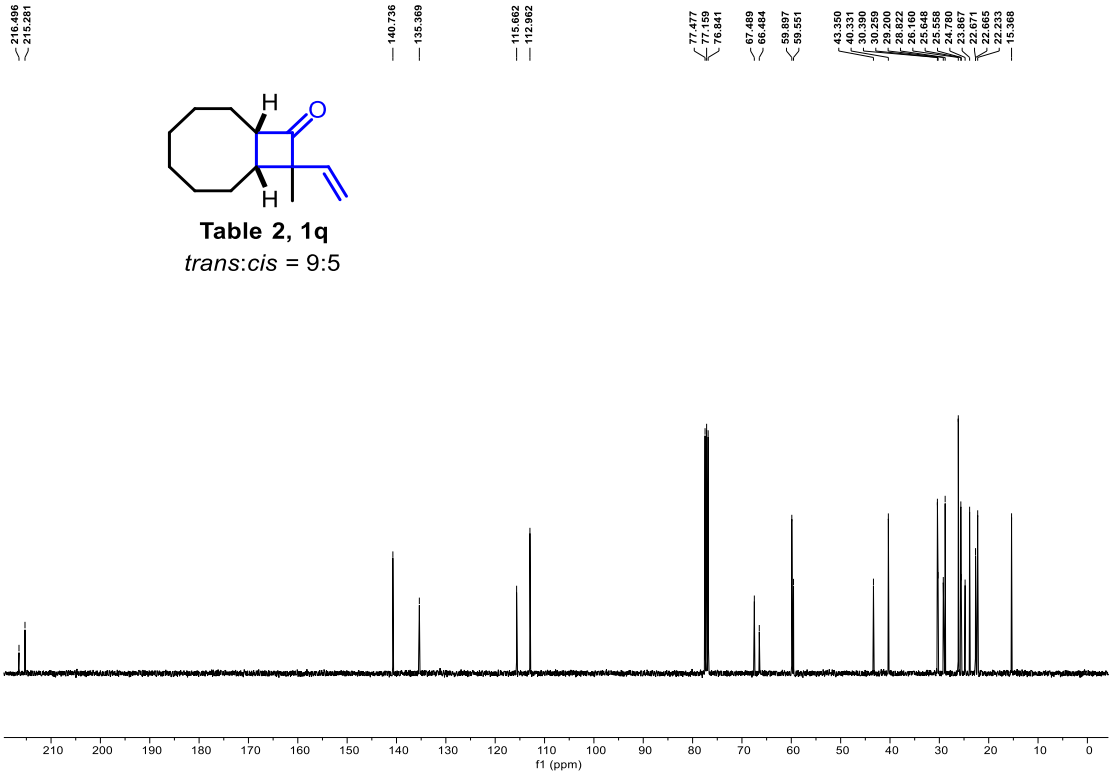
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

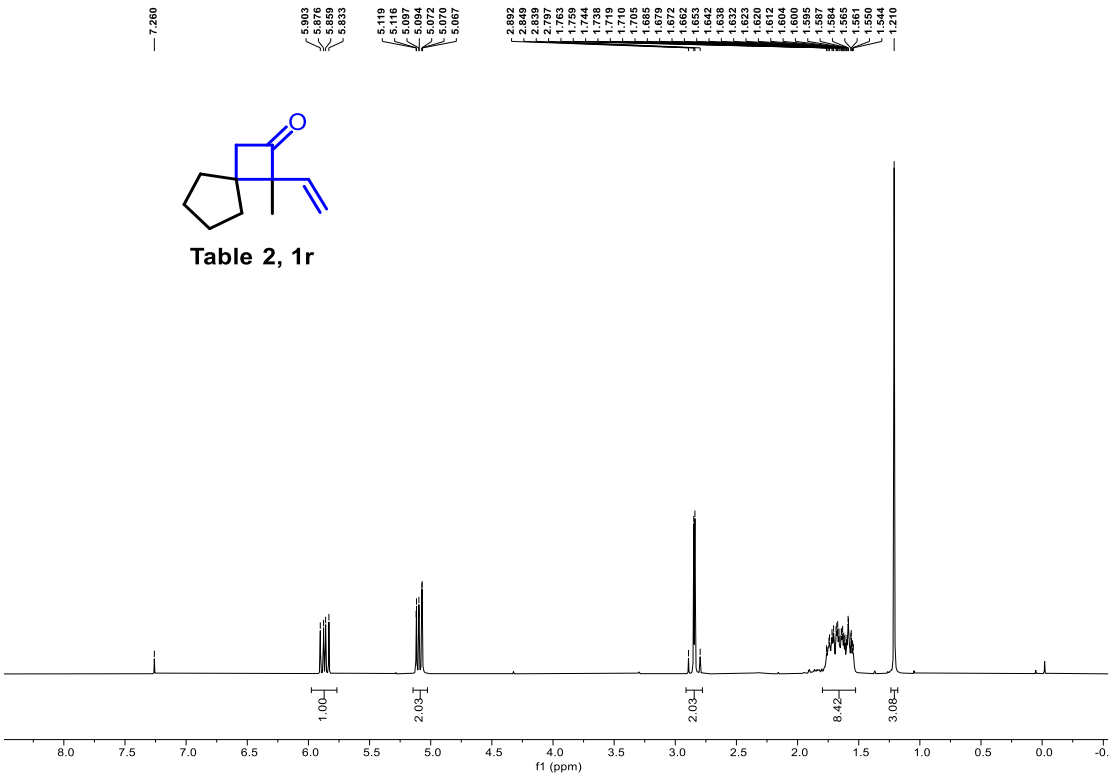


Table 2, 1r

^{13}C NMR in $CDCl_3$, 100 MHz

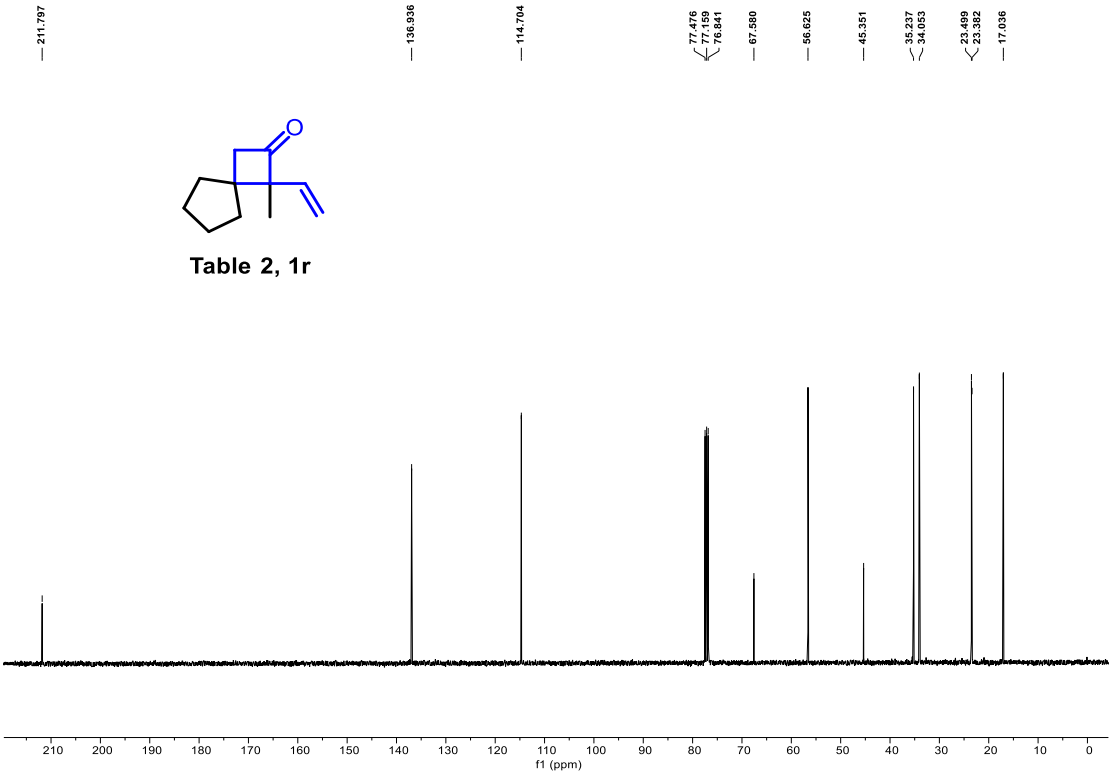
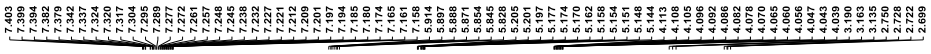


Table 2, 1r

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



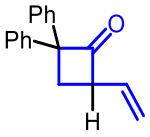
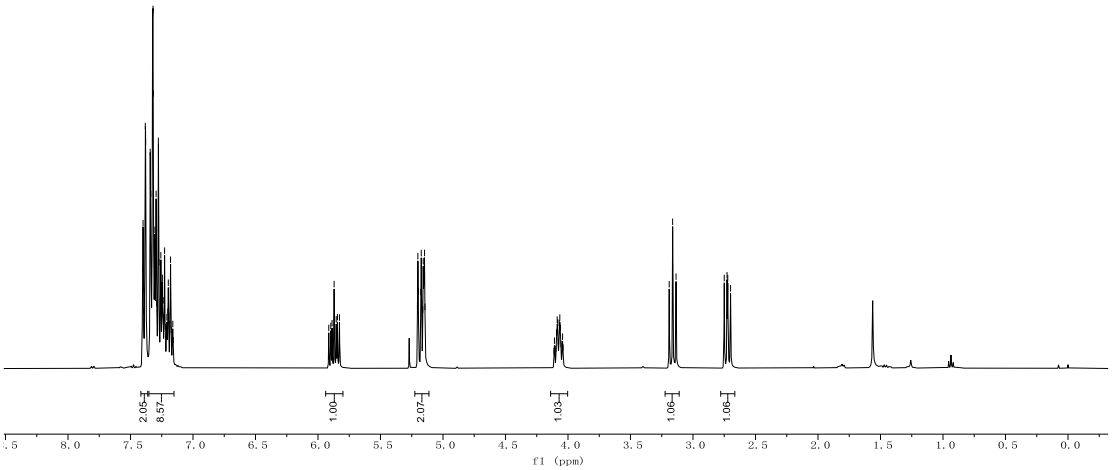


Table 2, 1s



^{13}C NMR in $CDCl_3$, 100 MHz

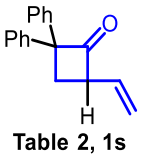
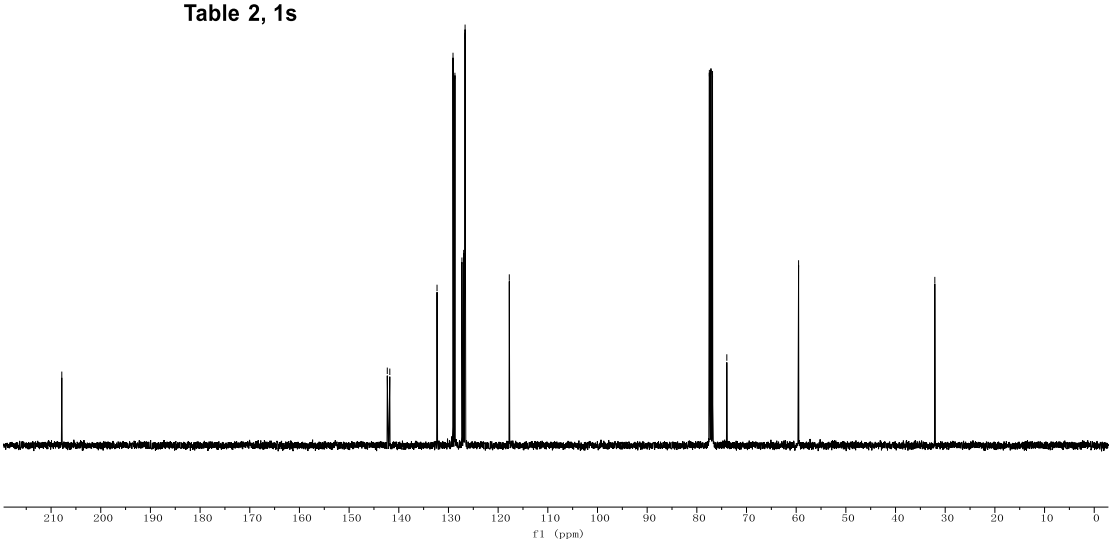
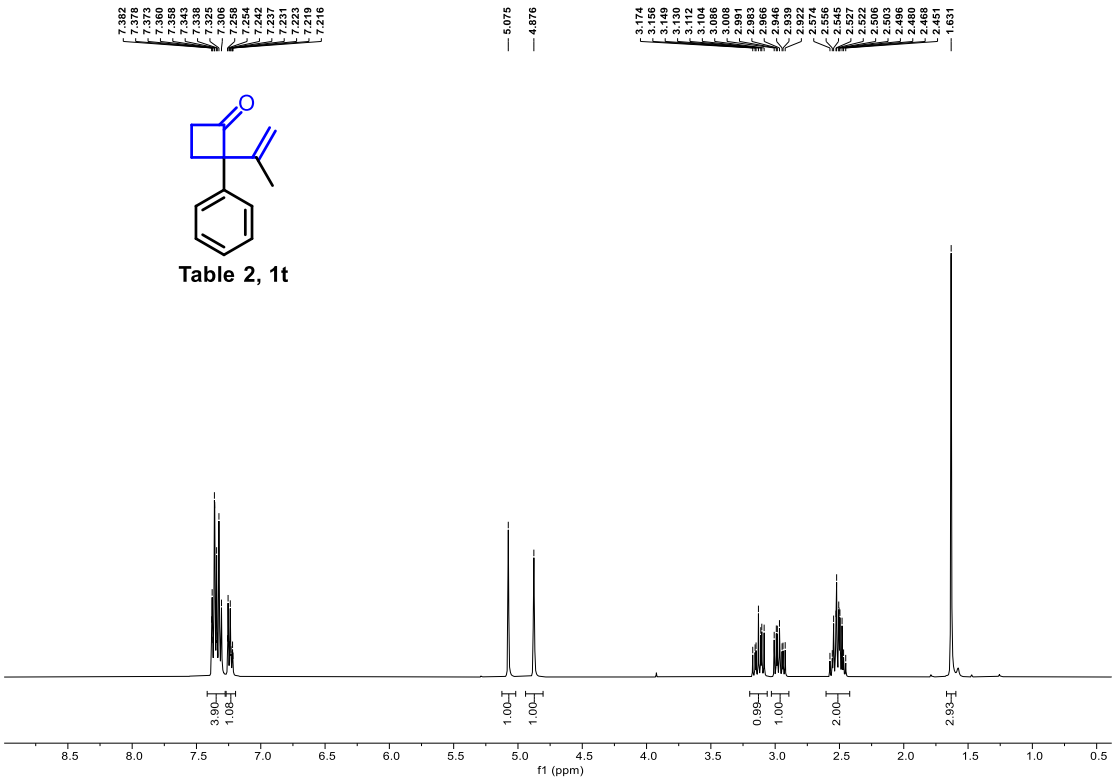


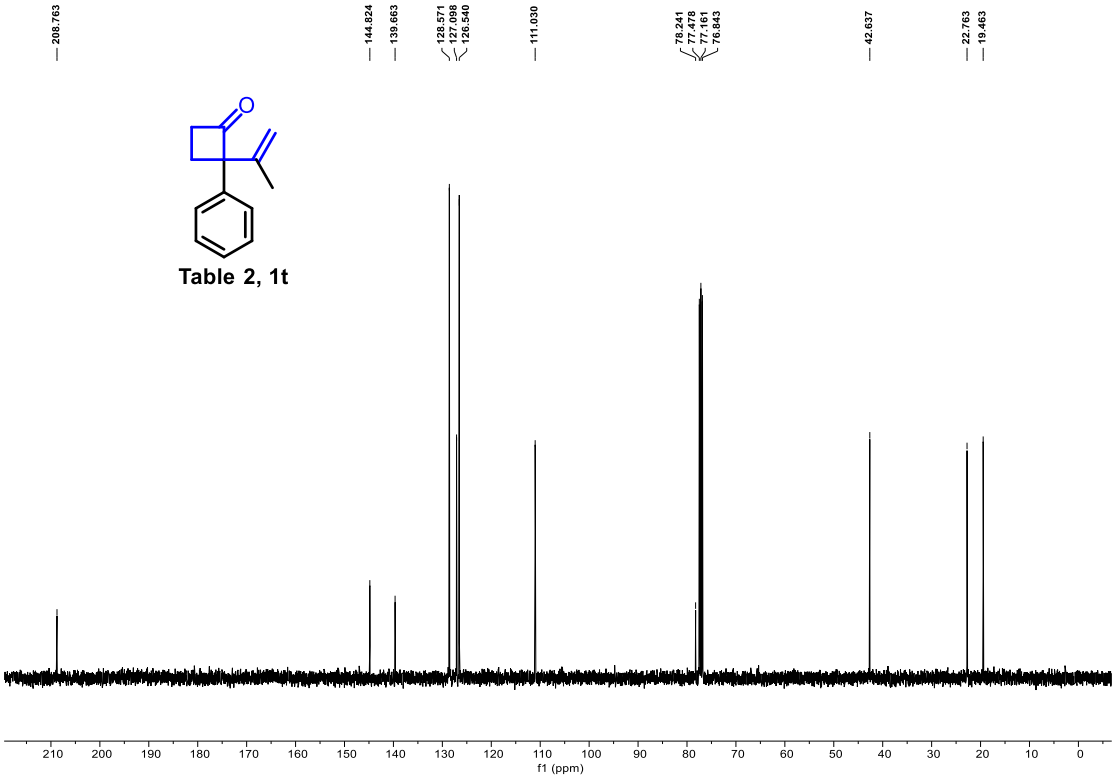
Table 2, 1s



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

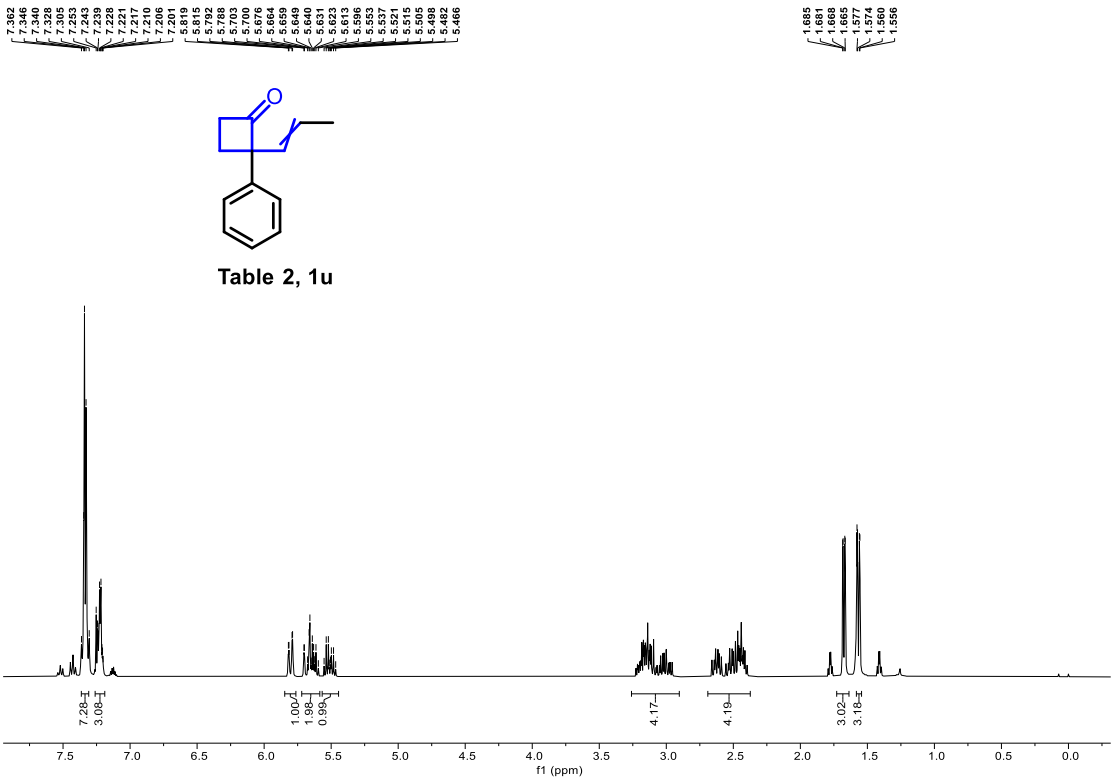


Table 2, 1u

^{13}C NMR in $CDCl_3$, 100 MHz

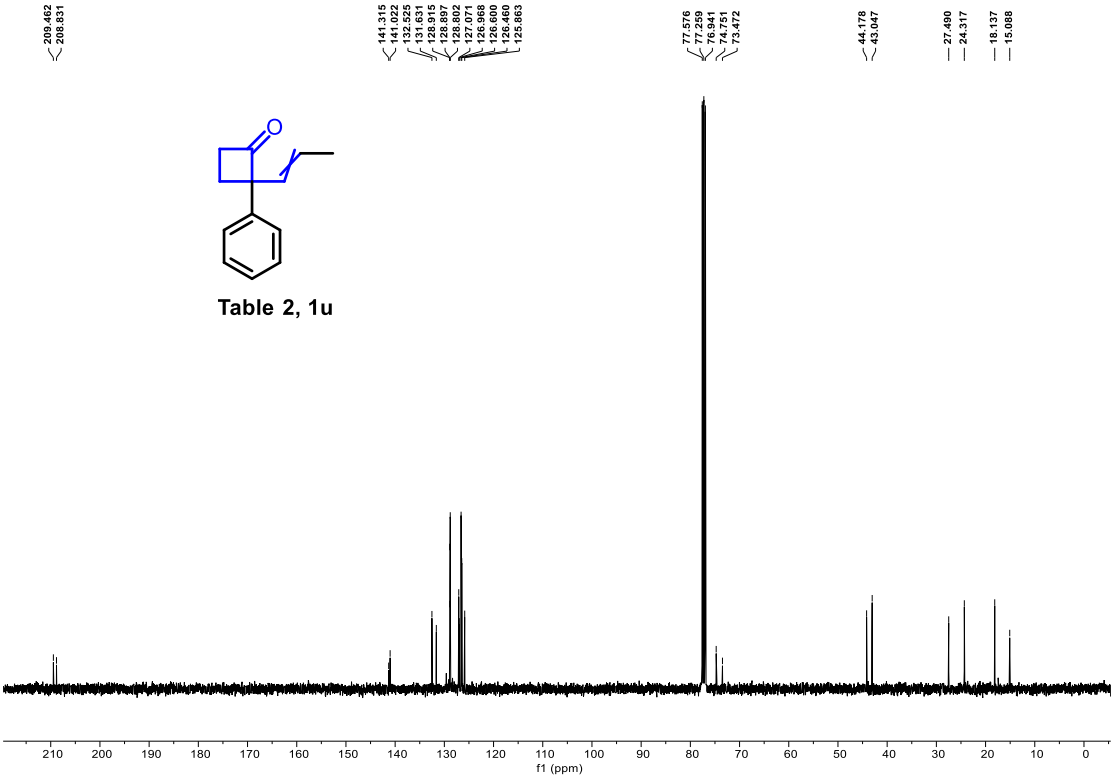
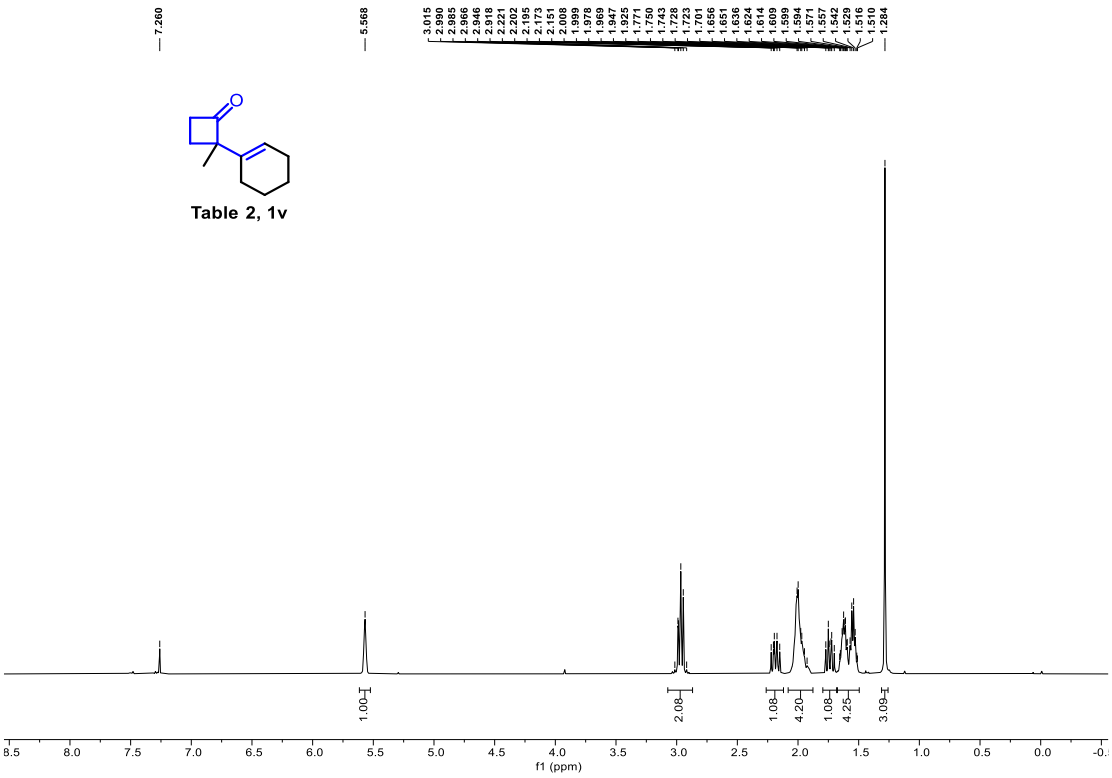
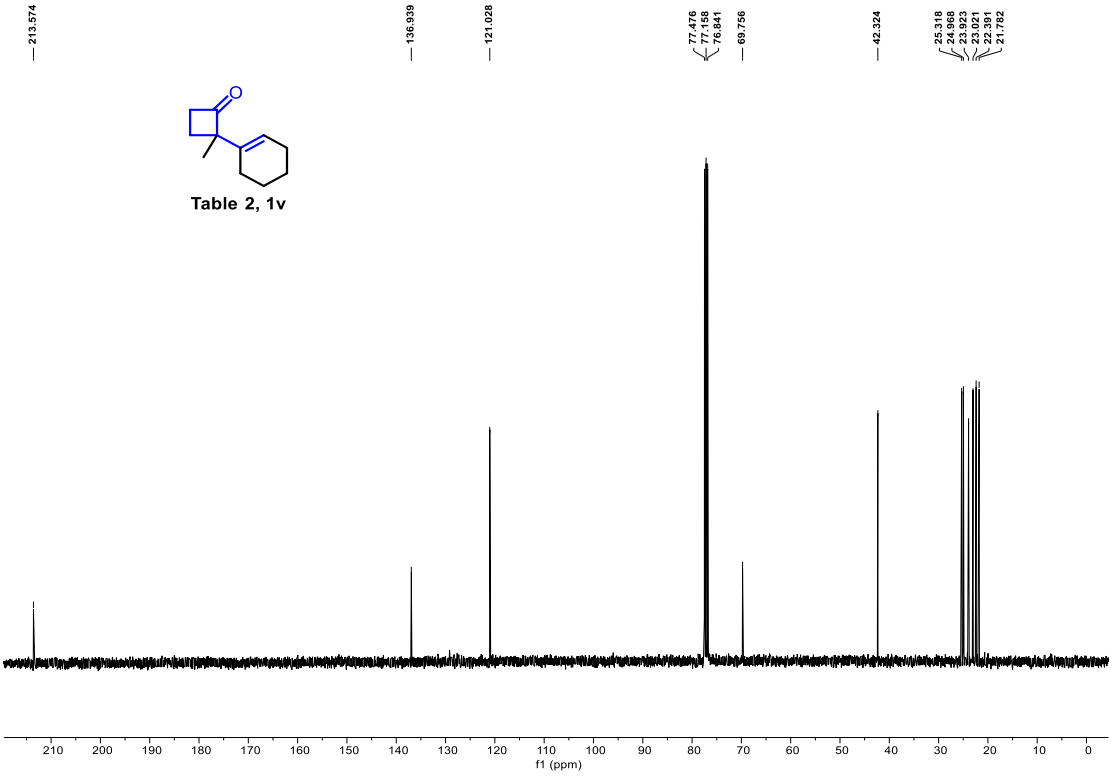


Table 2, 1u

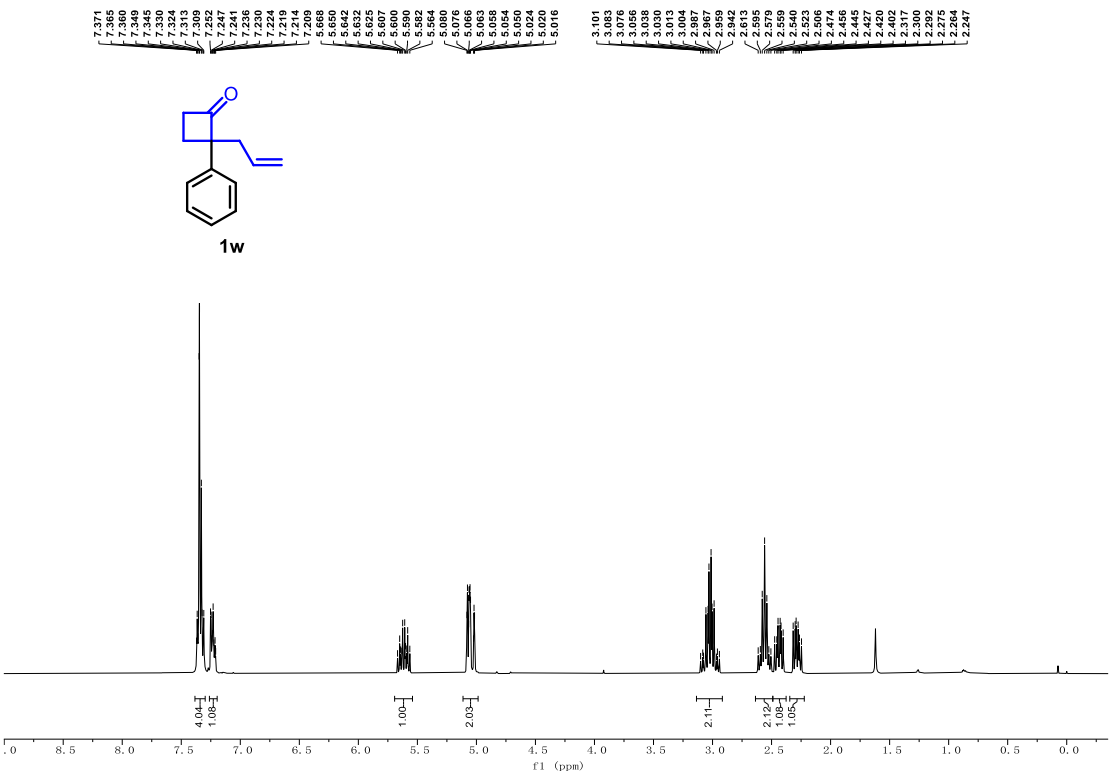
^{1}H NMR in $CDCl_3$, 400 MHz



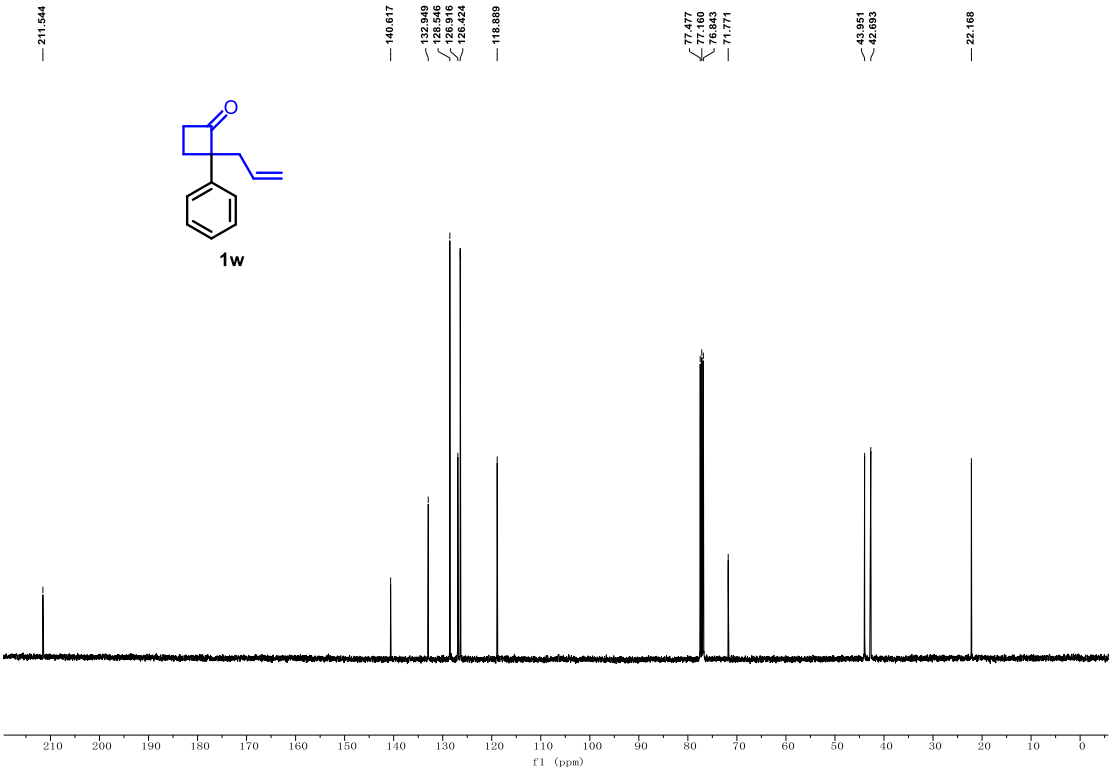
^{13}C NMR in $CDCl_3$, 100 MHz



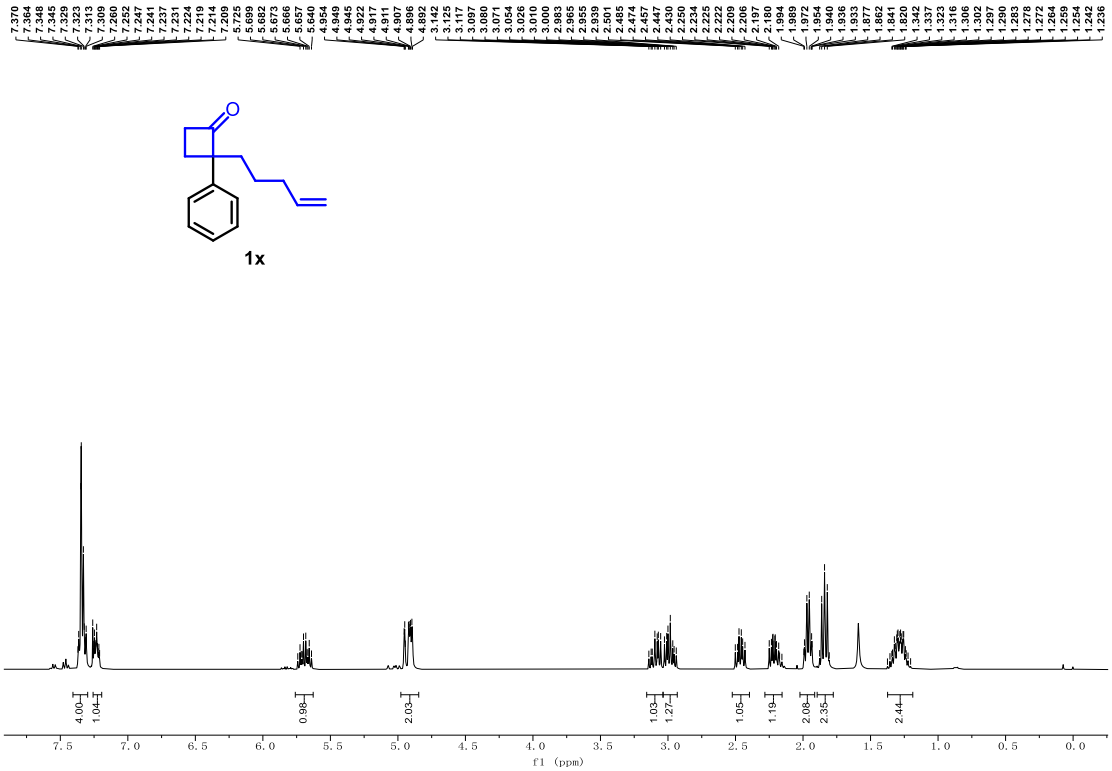
^{1}H NMR in $CDCl_3$, 400 MHz



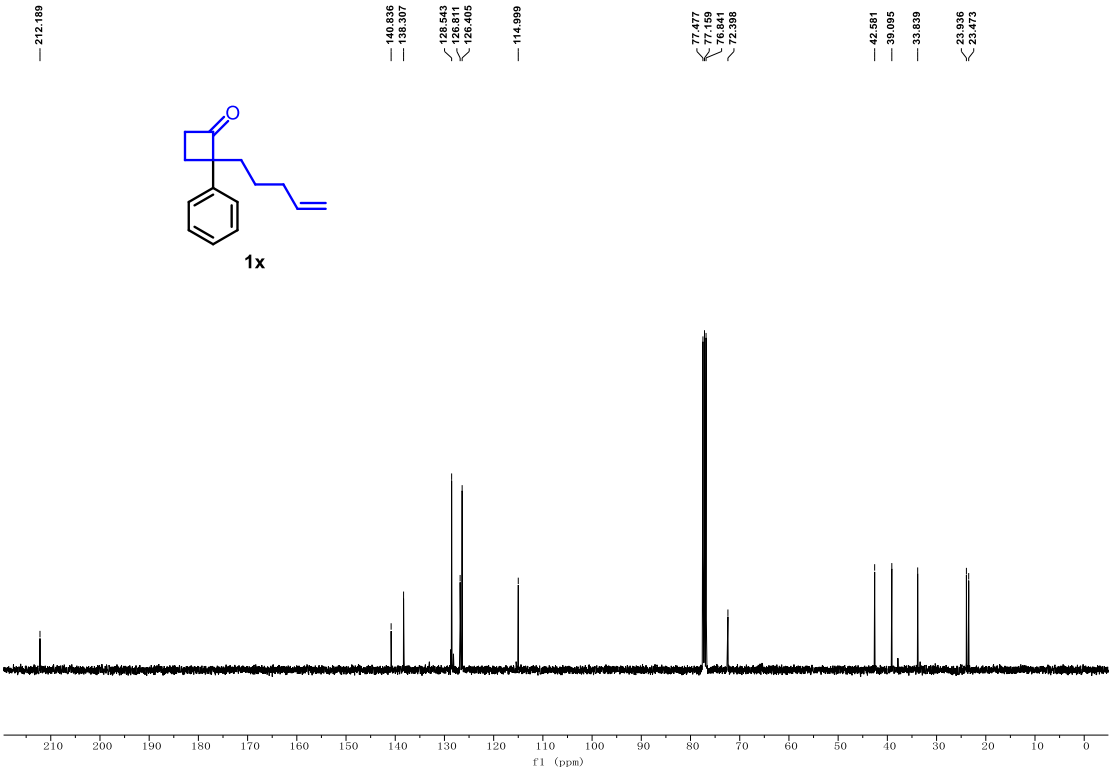
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

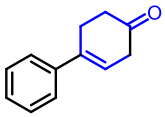
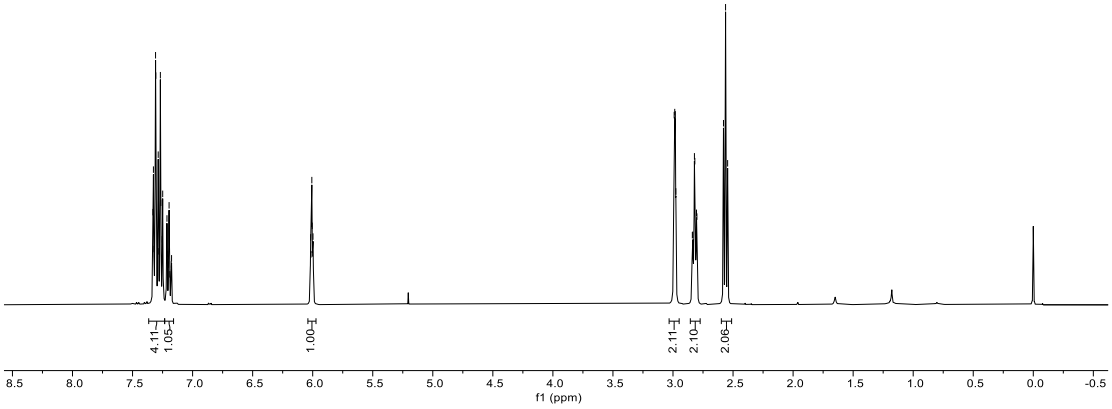


Table 2, 2a



^{13}C NMR in $CDCl_3$, 100 MHz

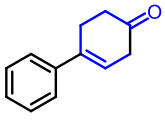
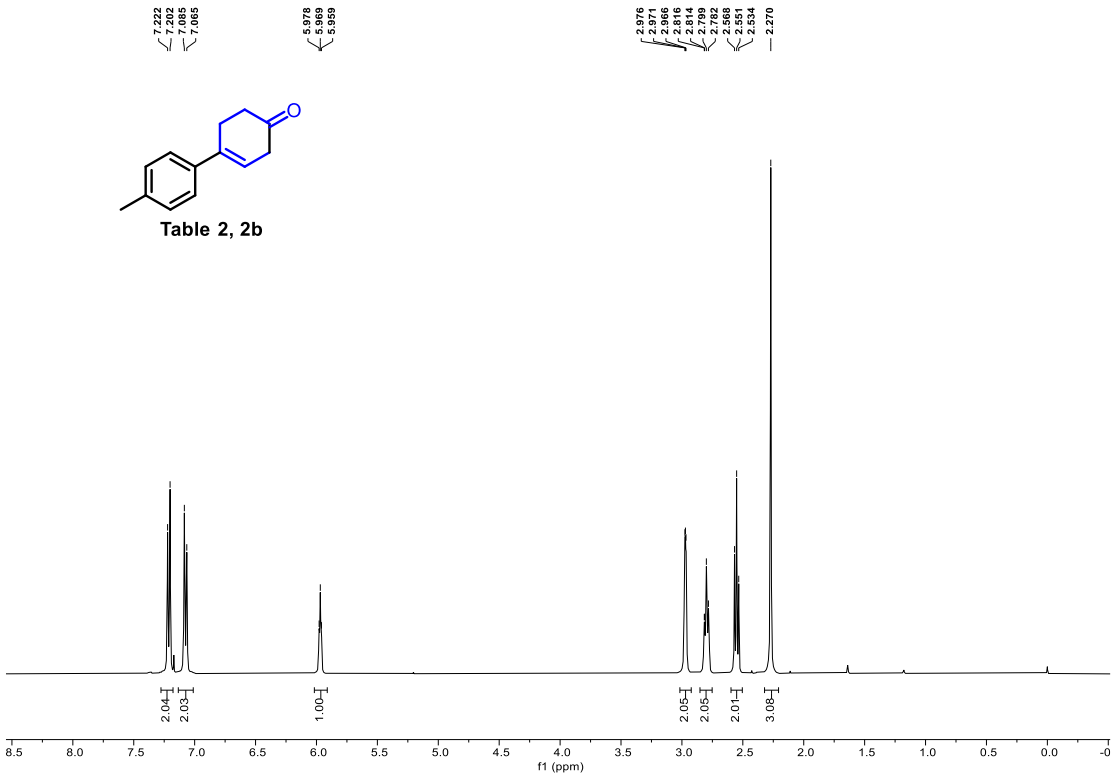
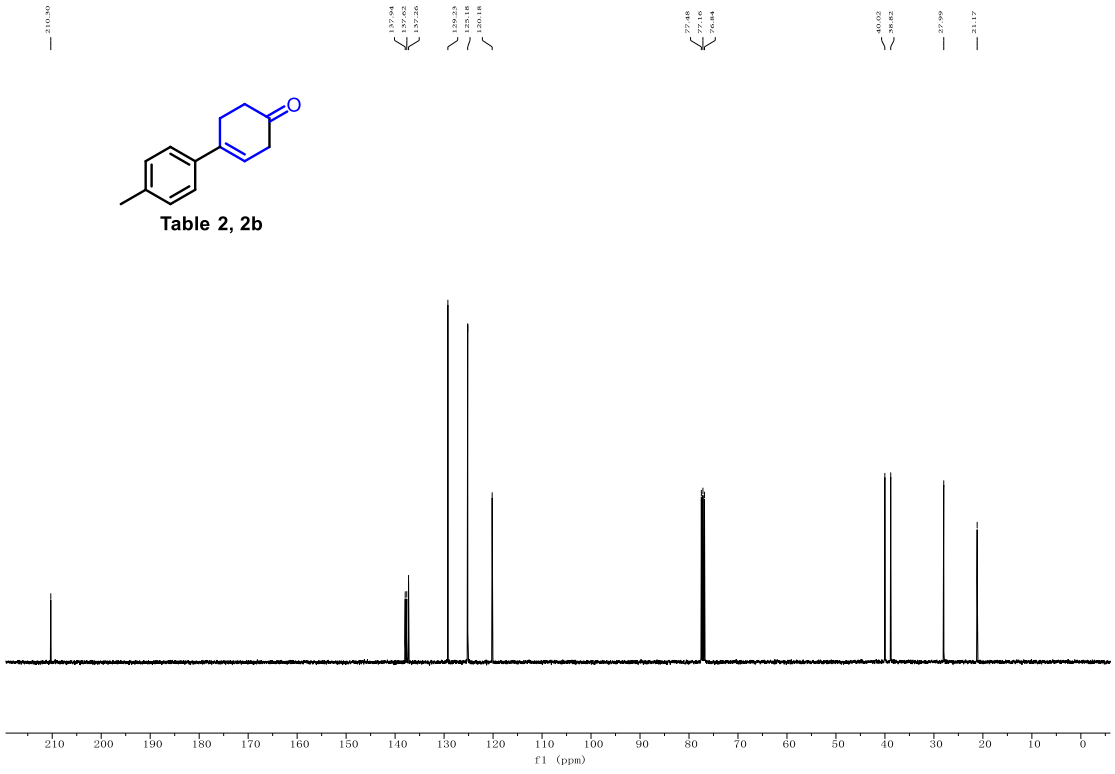


Table 2, 2a

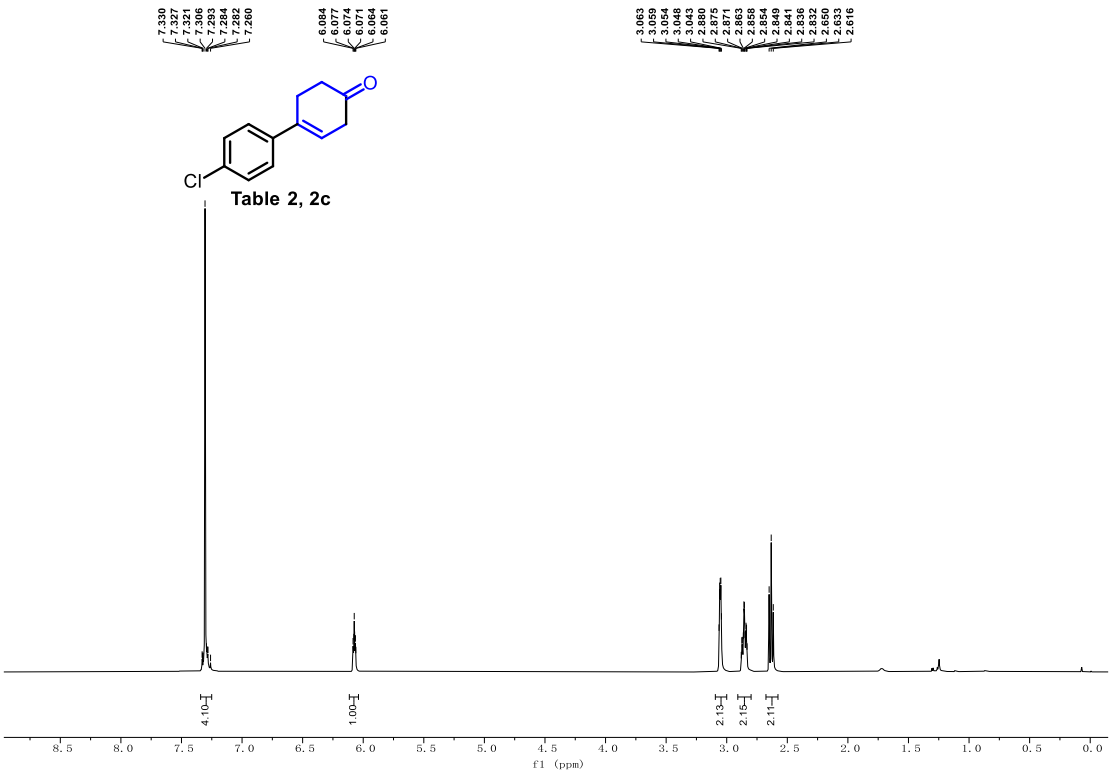
^{1}H NMR in $CDCl_3$, 400 MHz



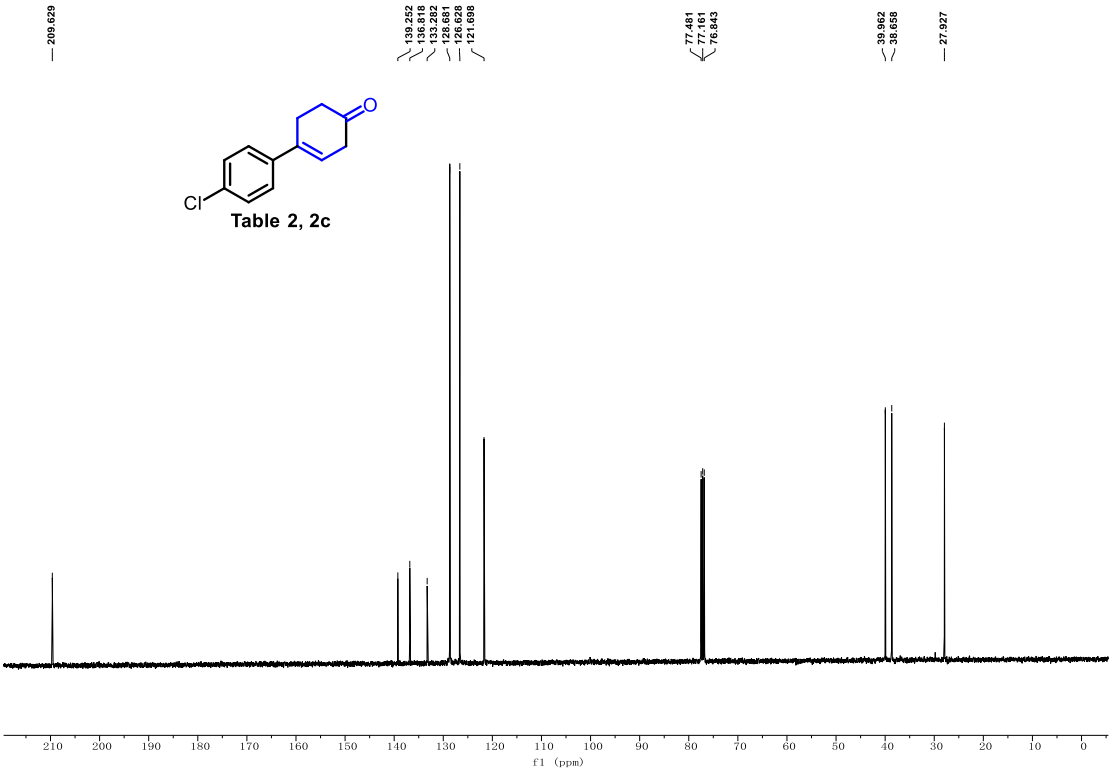
^{13}C NMR in $CDCl_3$, 100 MHz



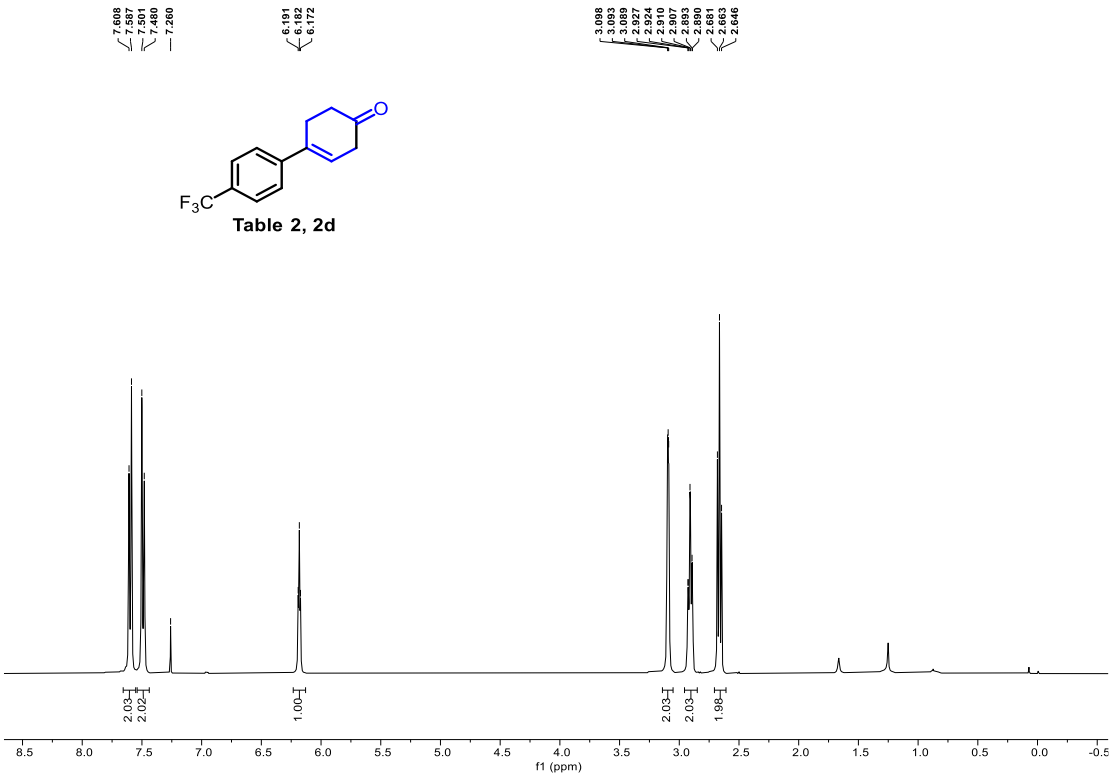
^{1}H NMR in $CDCl_3$, 400 MHz



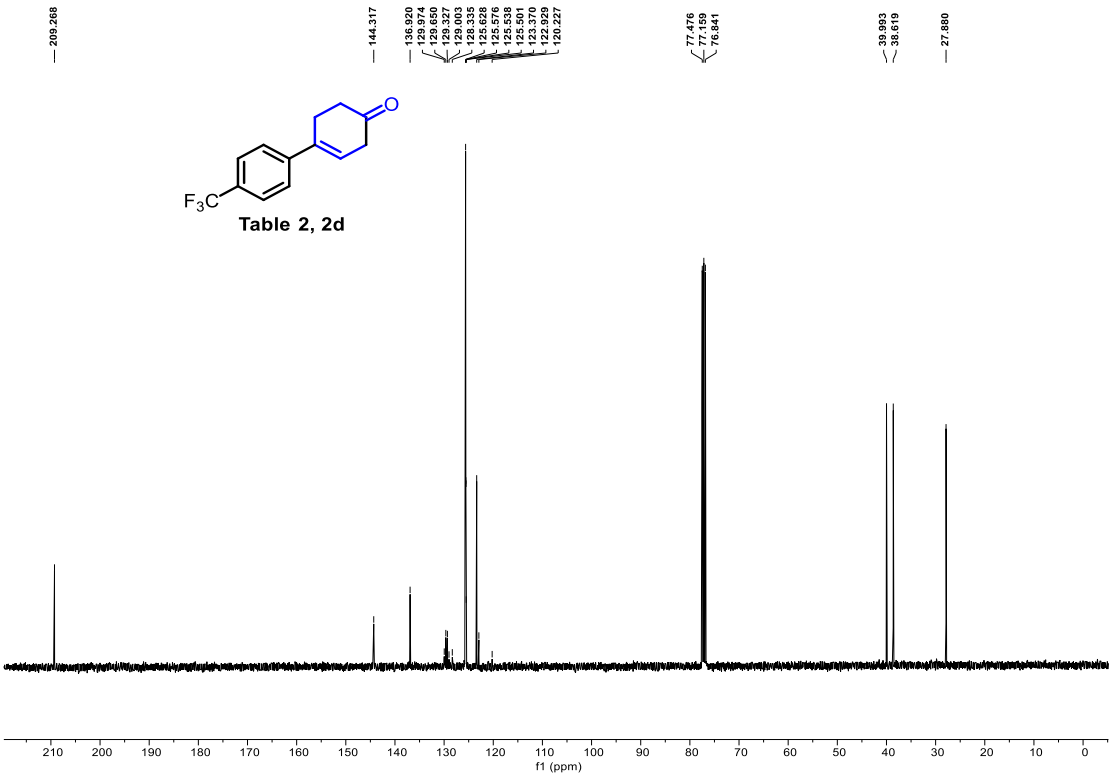
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

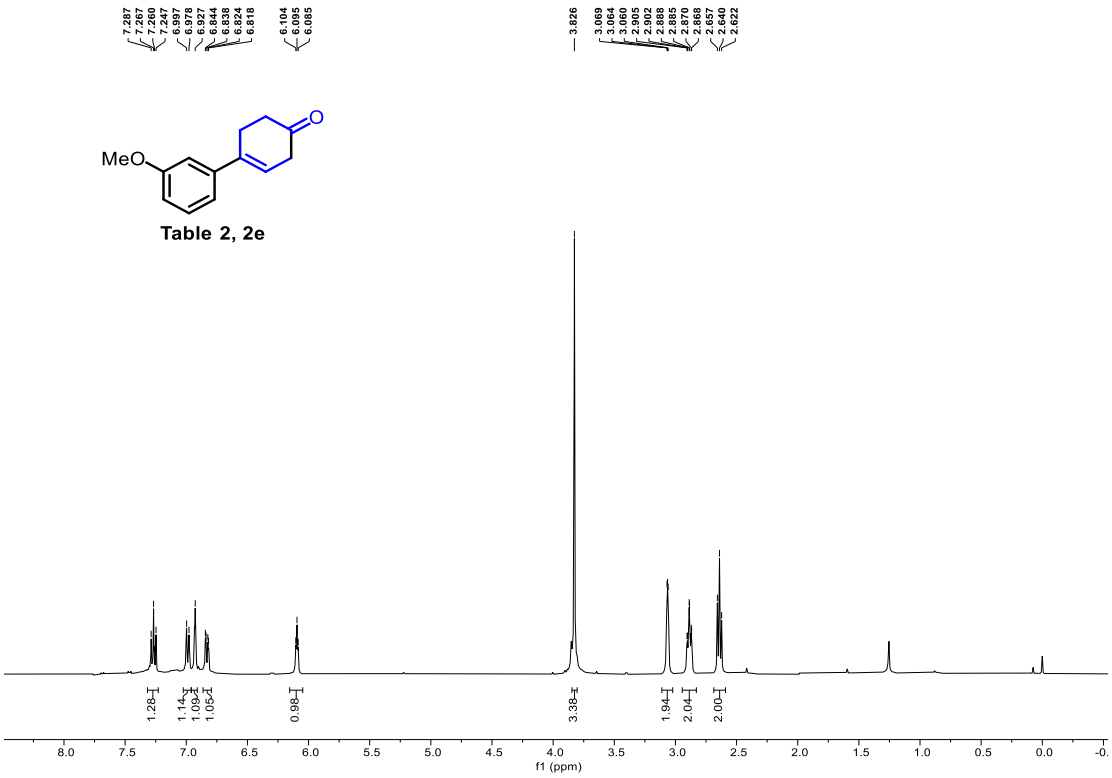


Table 2, 2e

^{13}C NMR in $CDCl_3$, 100 MHz

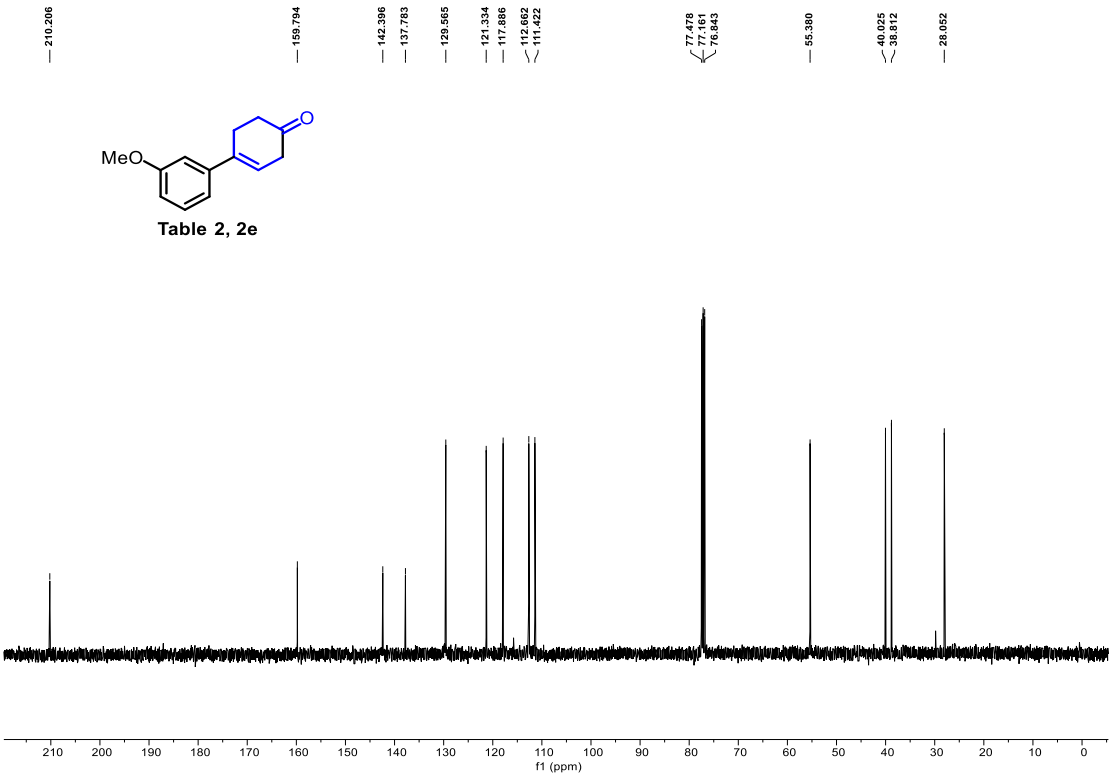
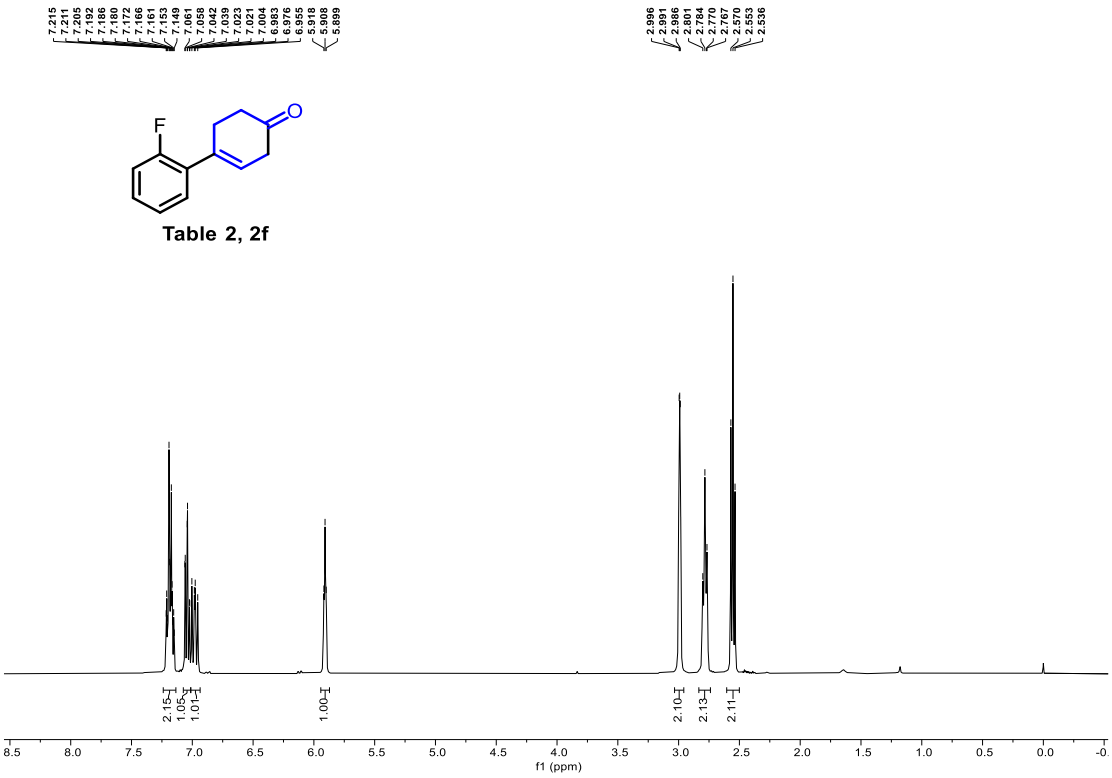
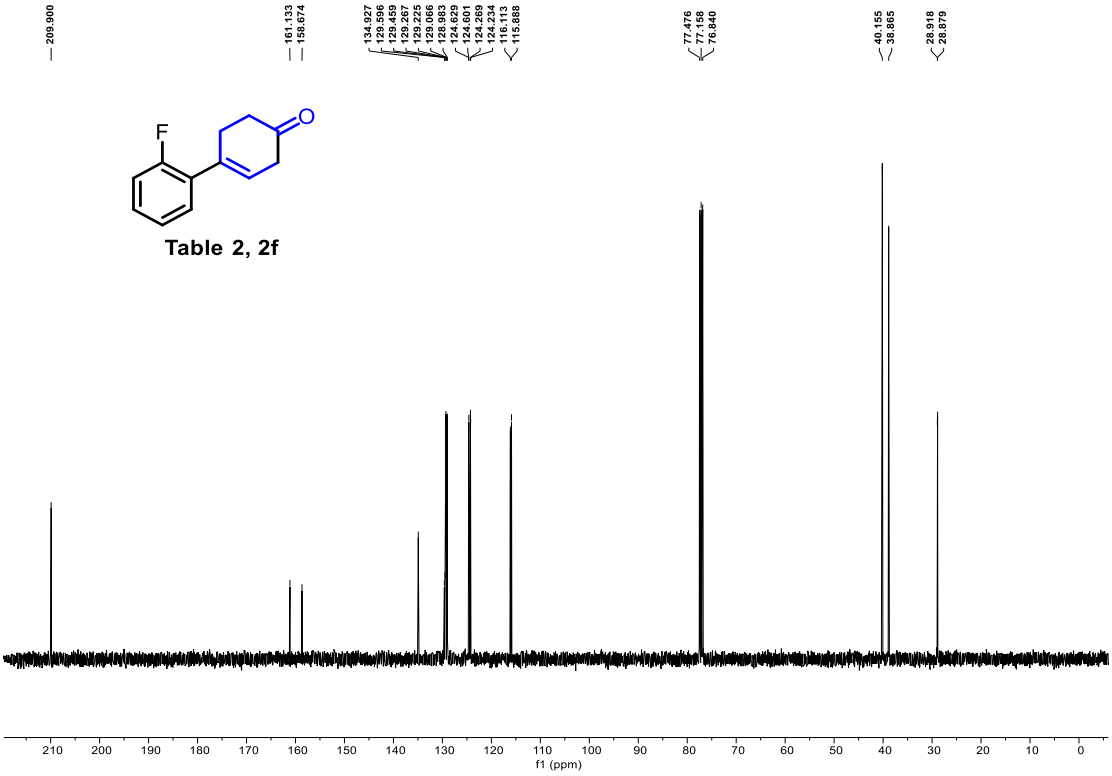


Table 2, 2e

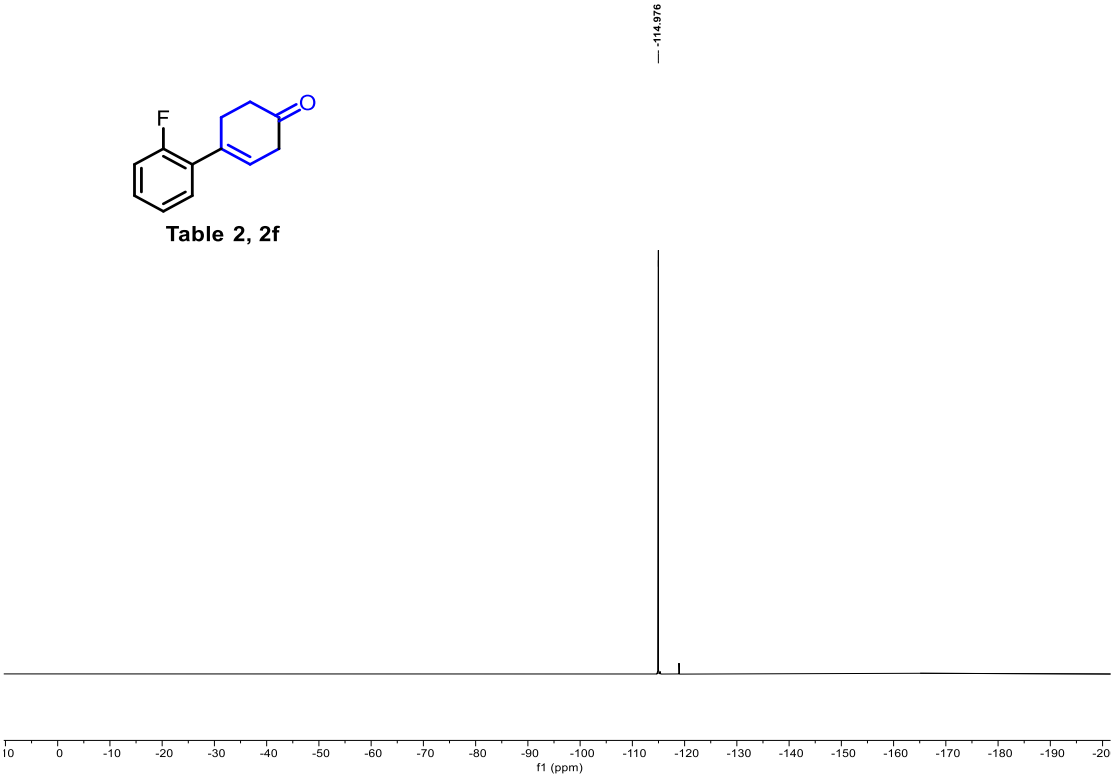
^{1}H NMR in $CDCl_3$, 400 MHz



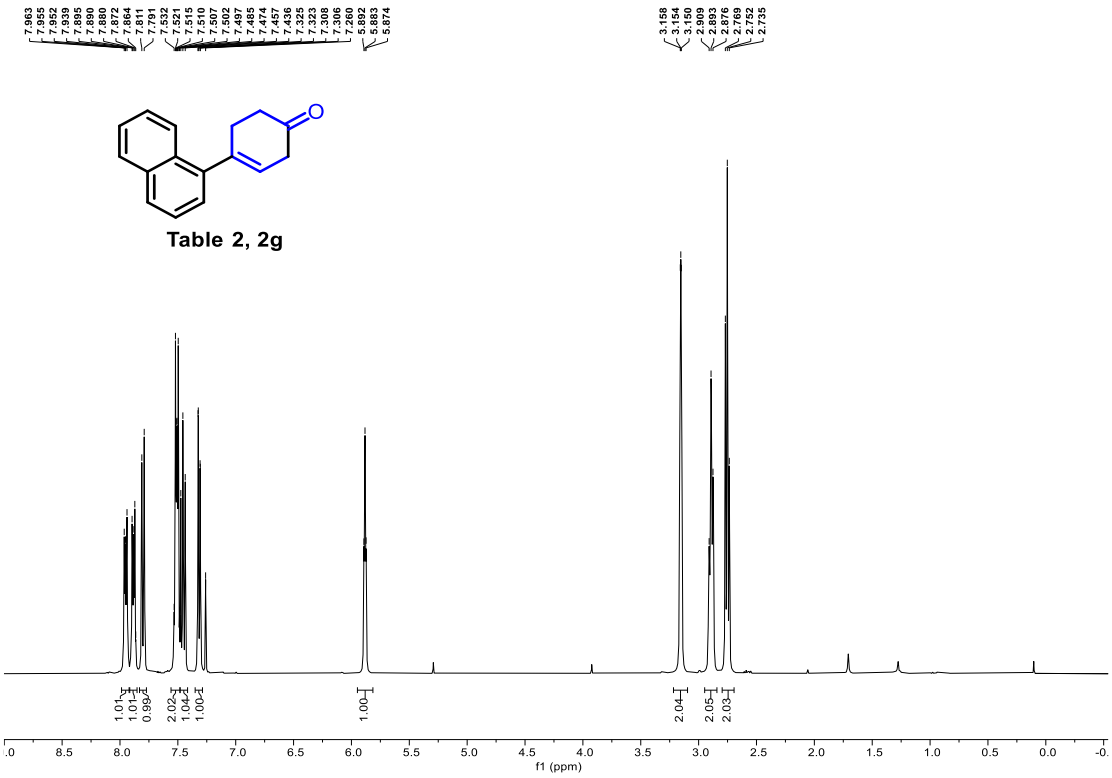
^{13}C NMR in $CDCl_3$, 100 MHz



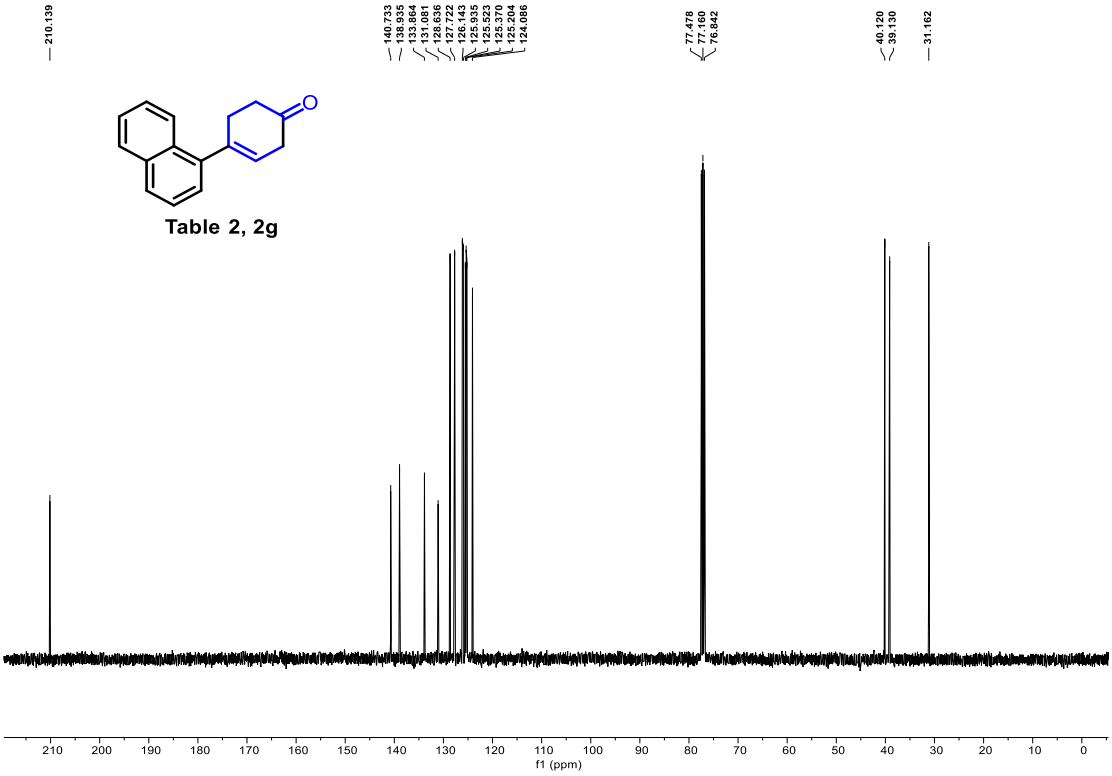
^{19}F NMR in $CDCl_3$, 471 MHz



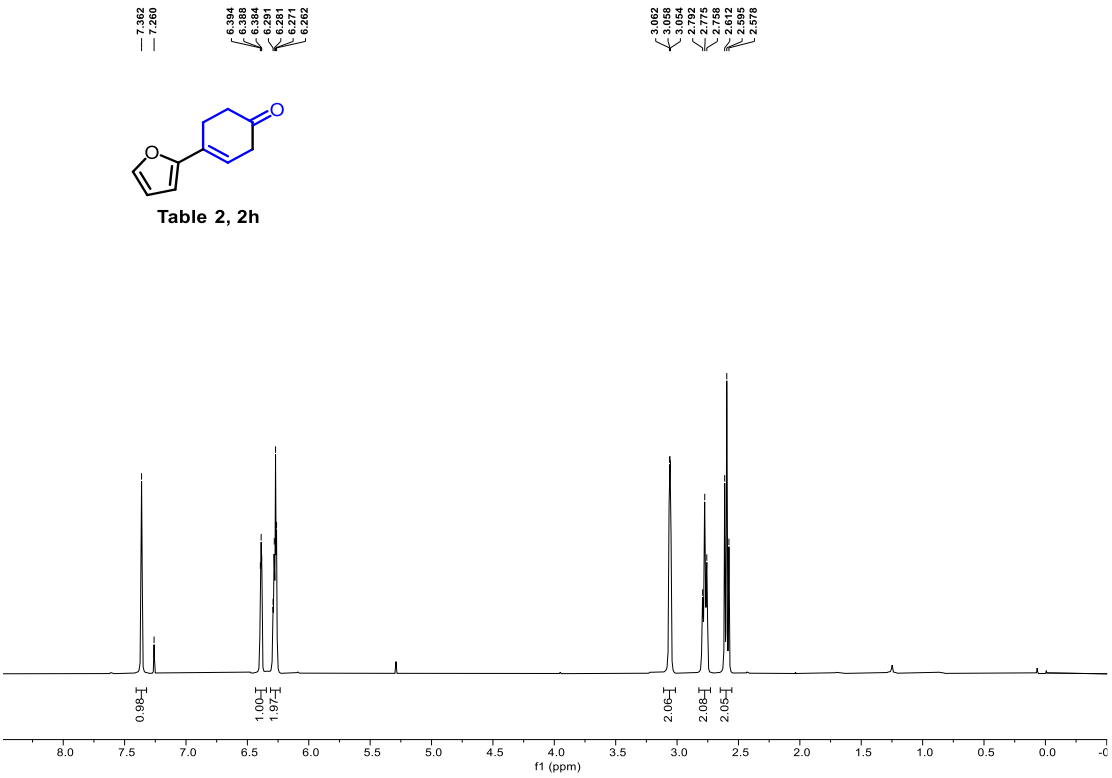
^{1}H NMR in $CDCl_3$, 400 MHz



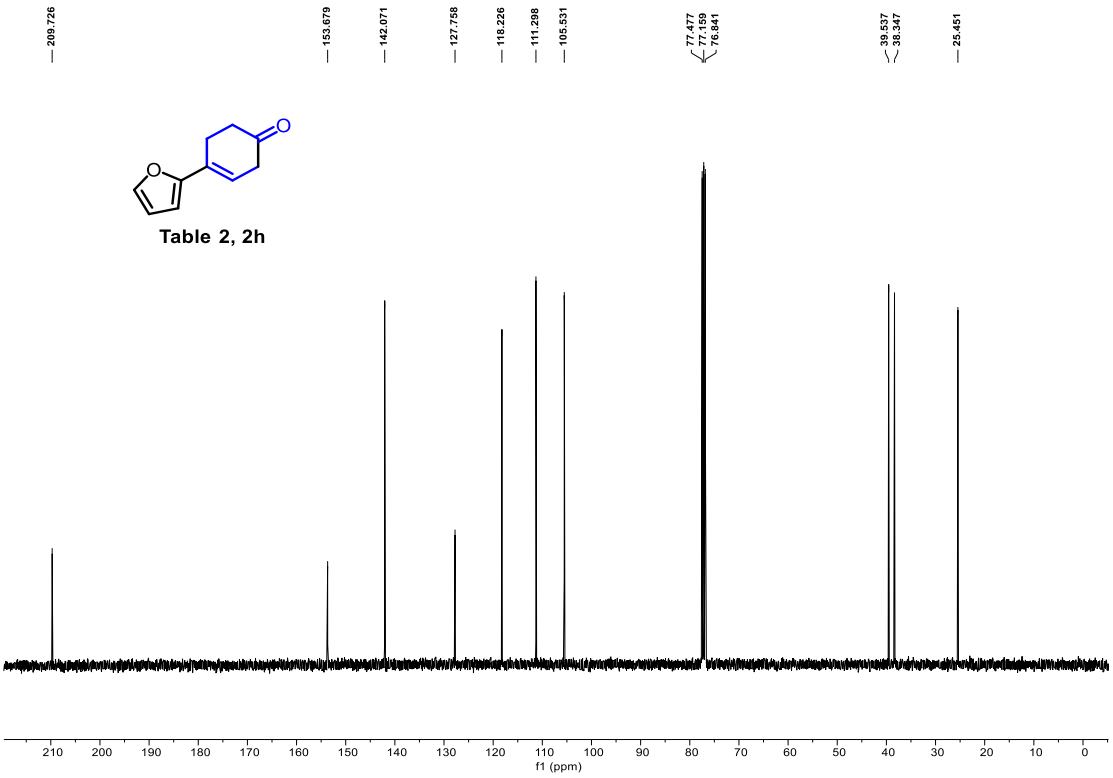
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

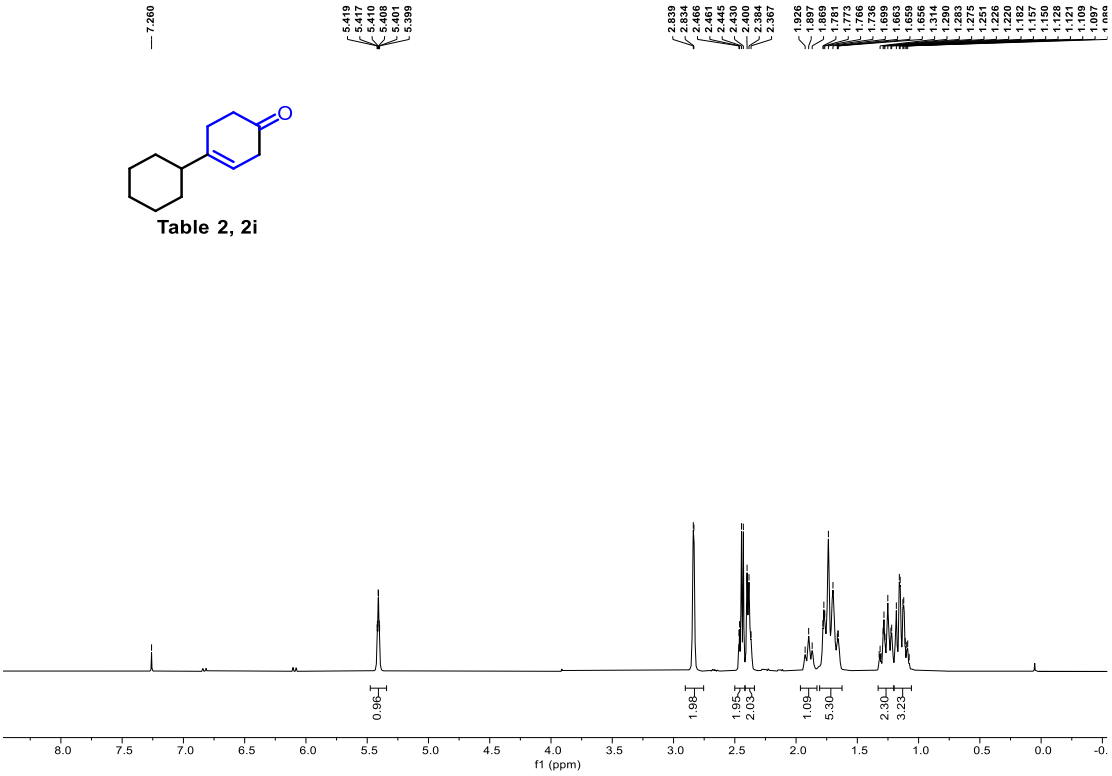


Table 2, 2i

^{13}C NMR in $CDCl_3$, 100 MHz

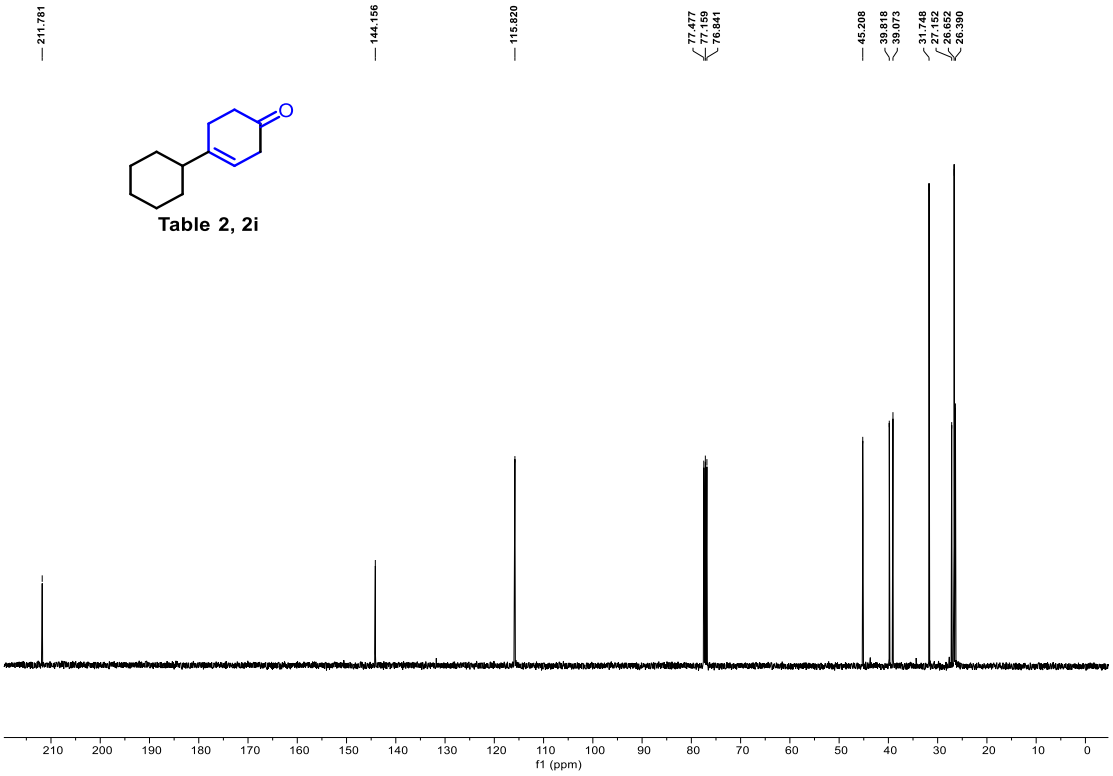
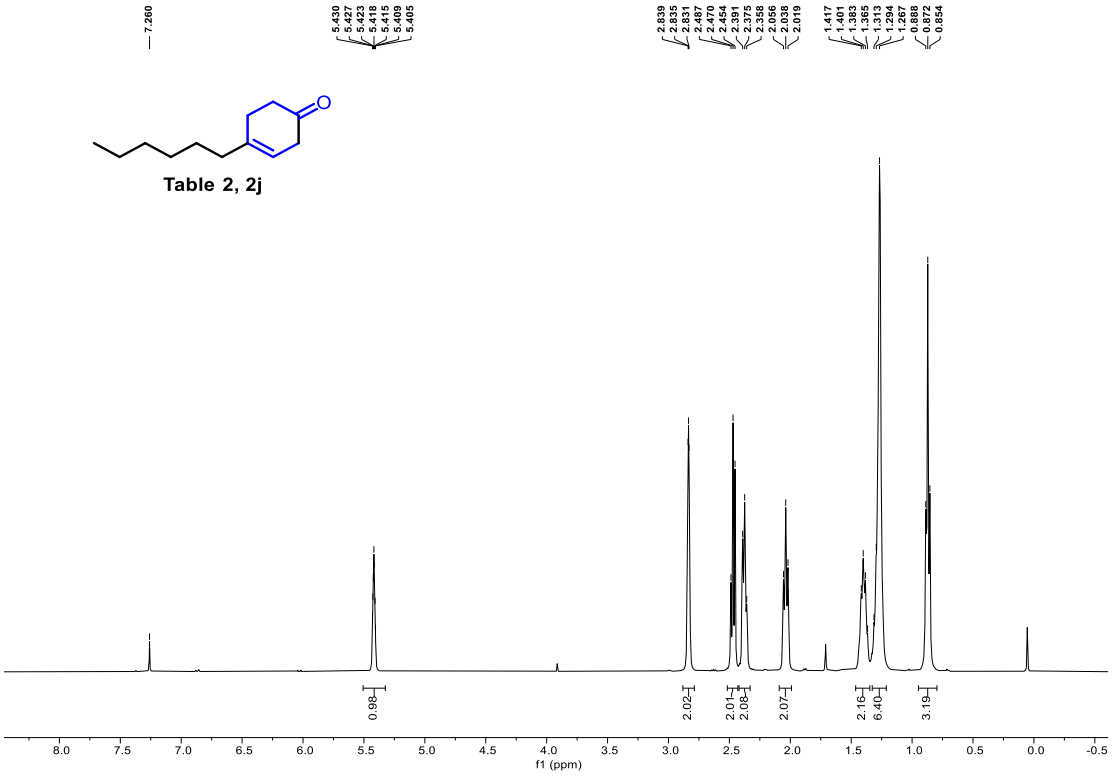
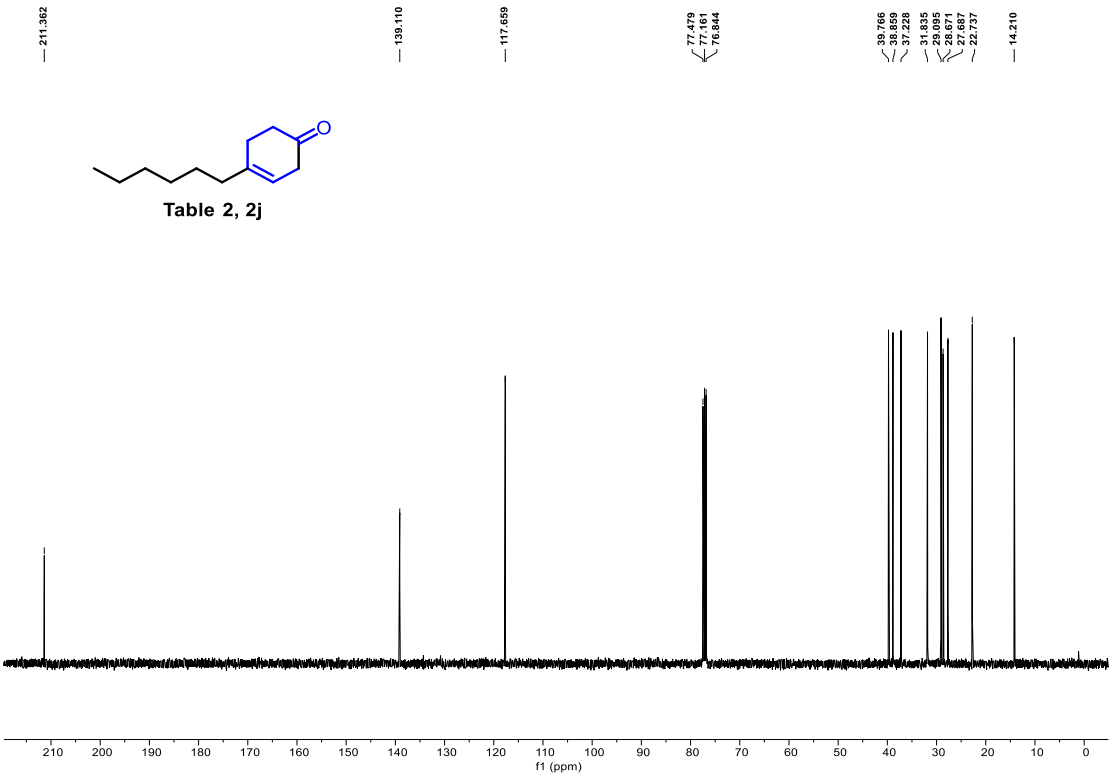


Table 2, 2i

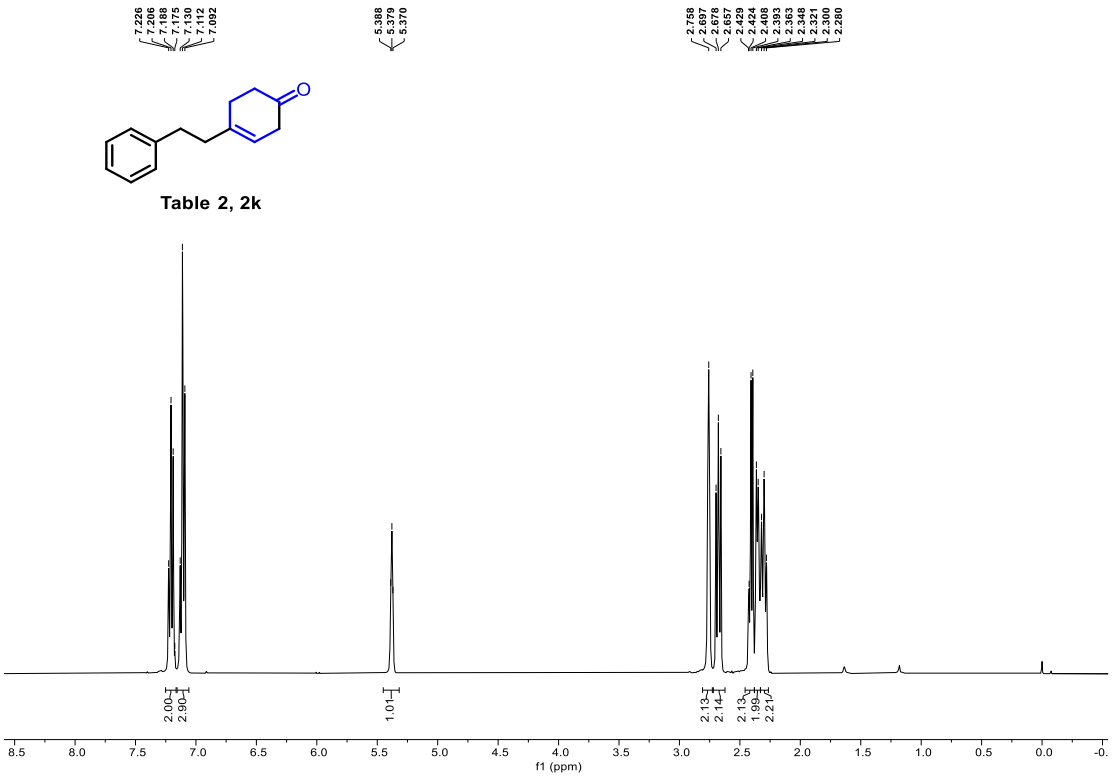
^{1}H NMR in $CDCl_3$, 400 MHz



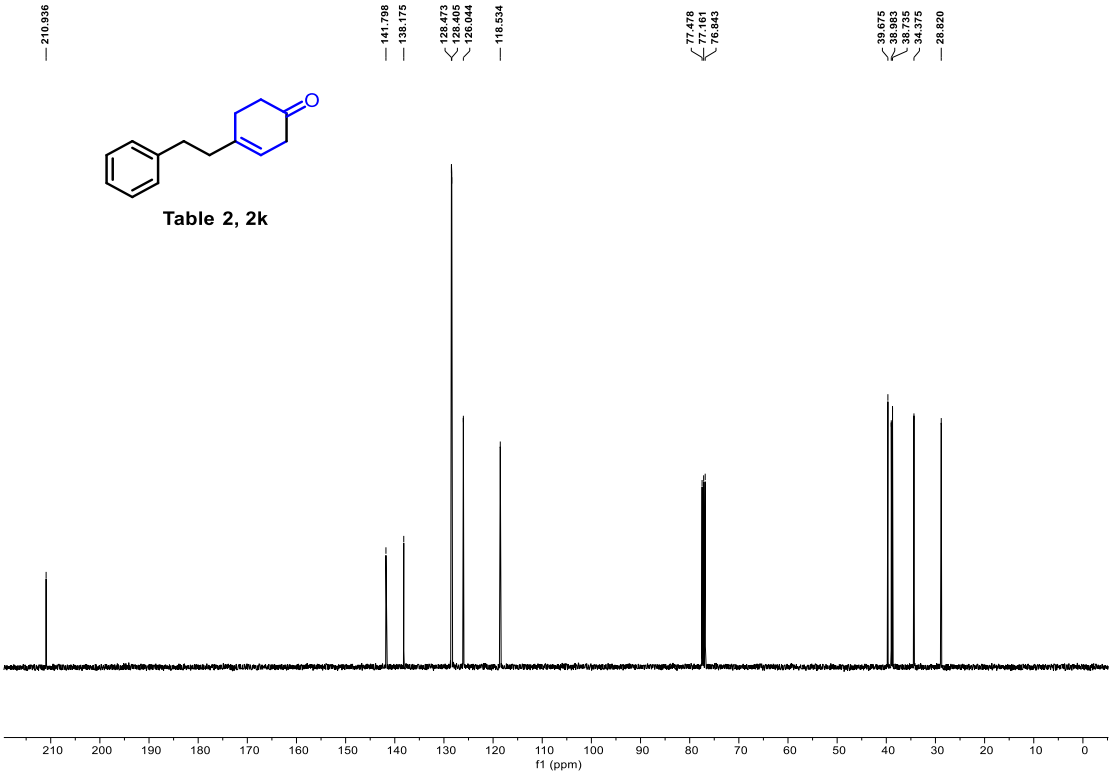
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

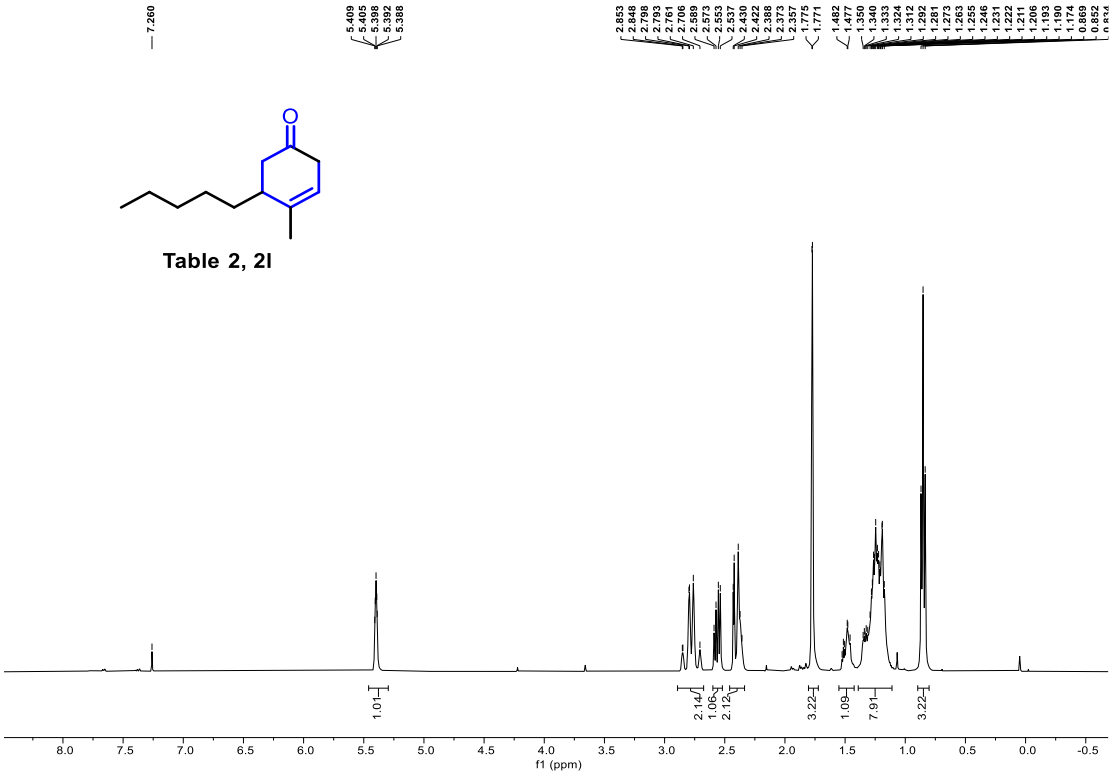


Table 2, 2l

^{13}C NMR in $CDCl_3$, 100 MHz

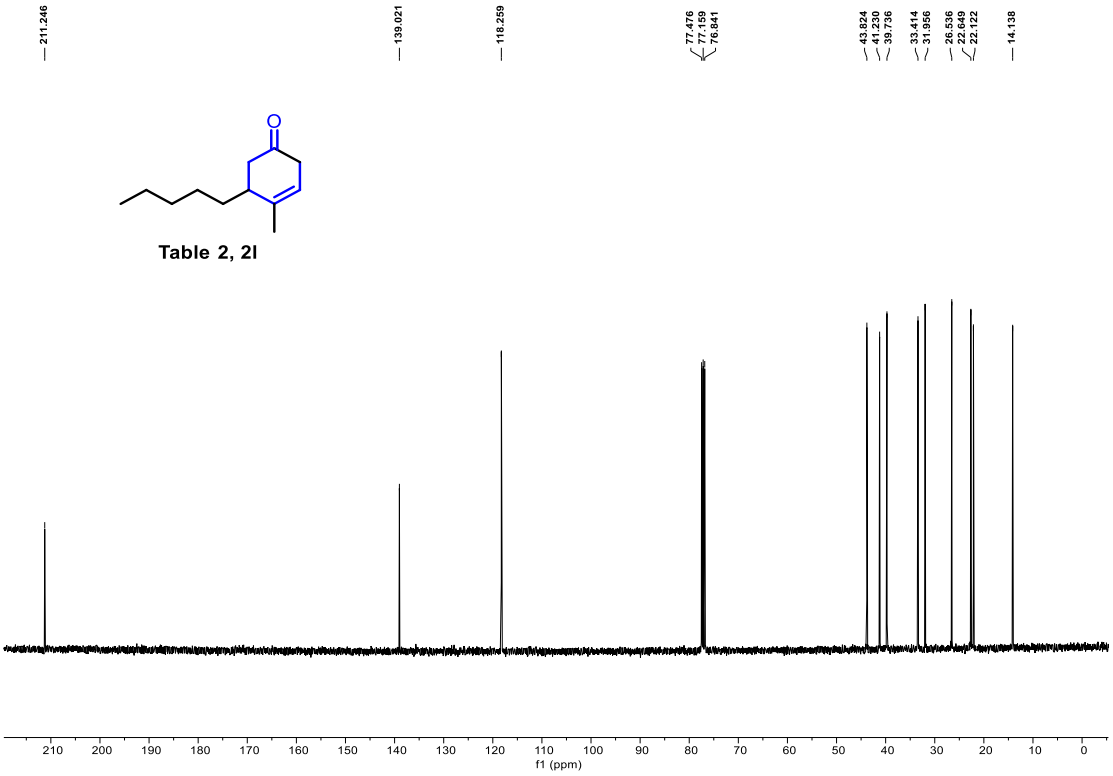
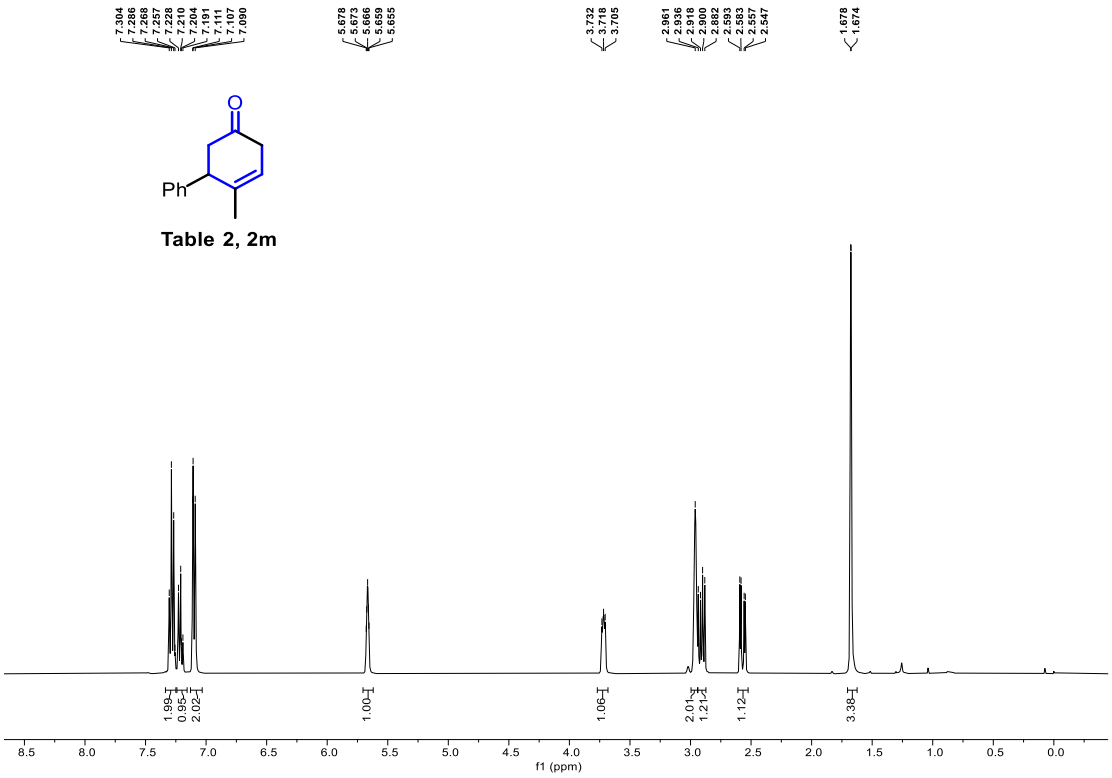
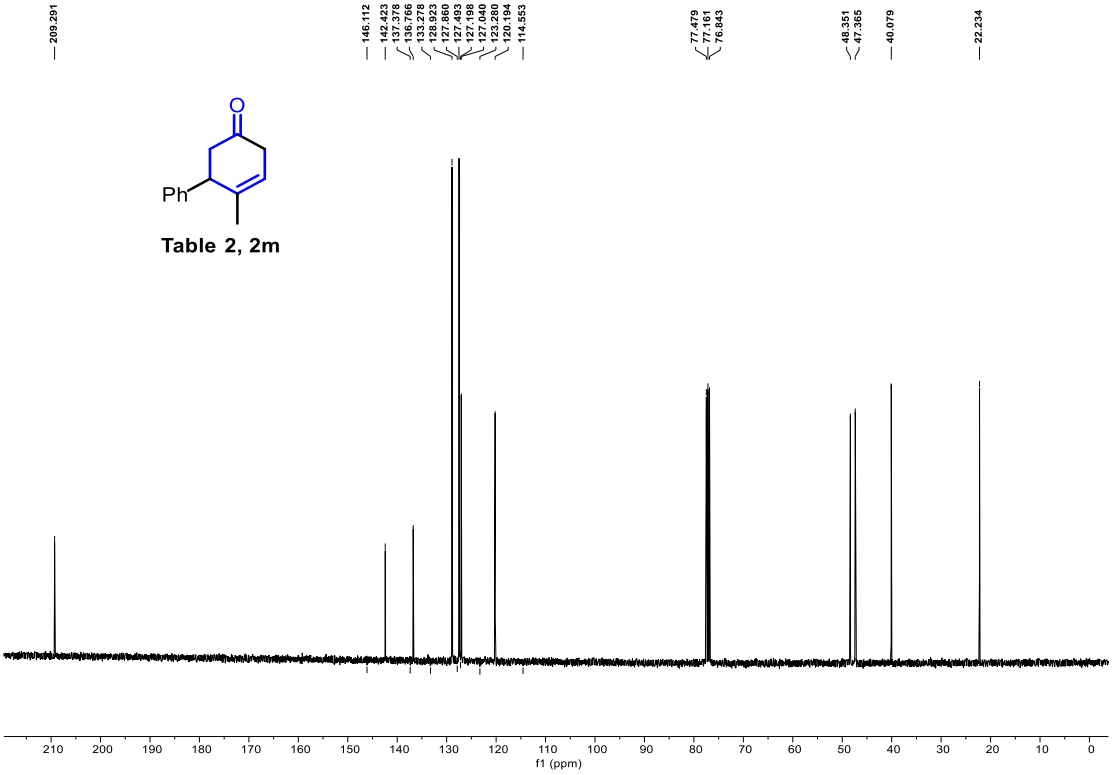


Table 2, 2l

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



^{13}C NMR in $CDCl_3$, 100 MHz



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

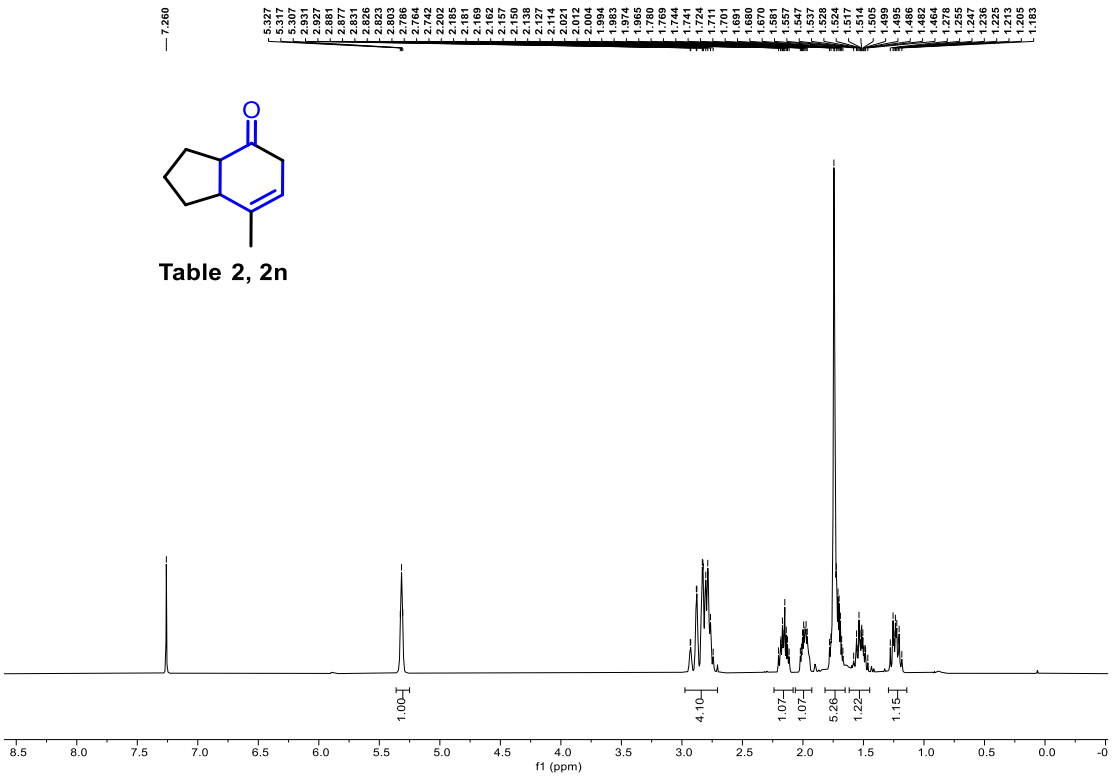


Table 2, 2n

^{13}C NMR in $CDCl_3$, 100 MHz

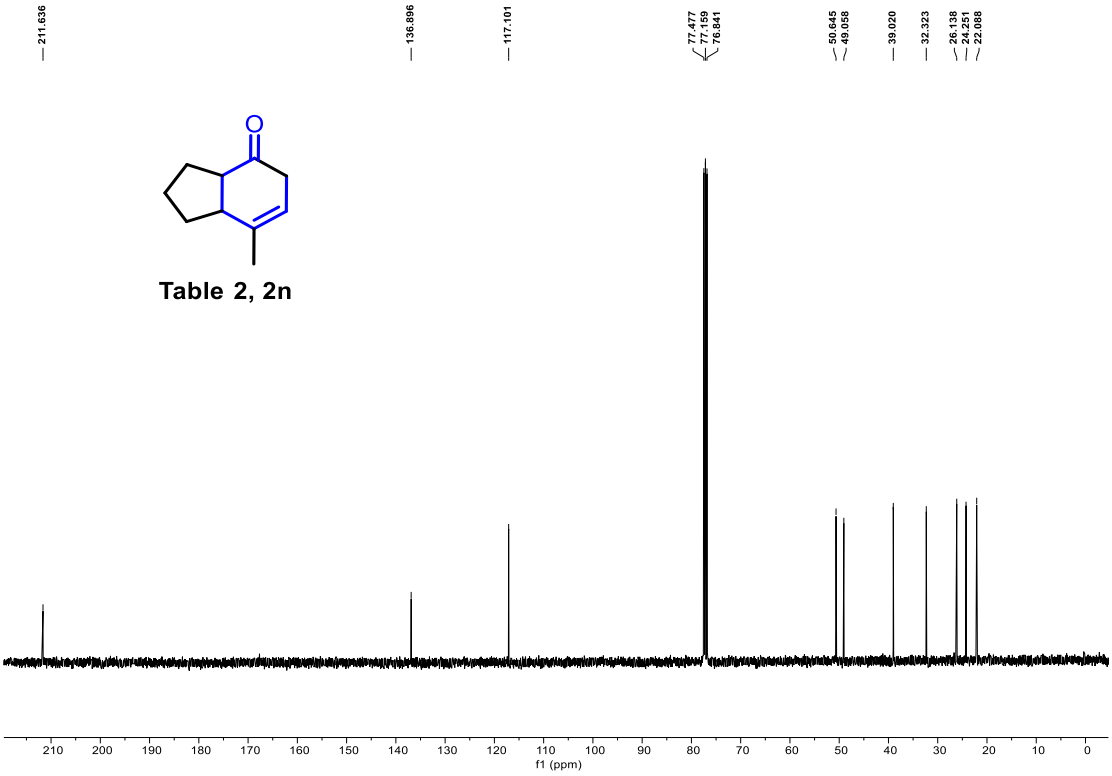
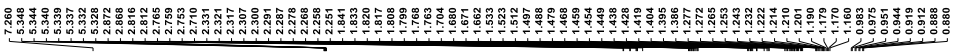


Table 2, 2n

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



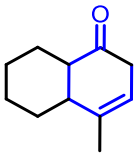


Table 2, 2o

^{13}C NMR in $CDCl_3$, 100 MHz

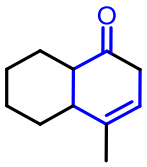
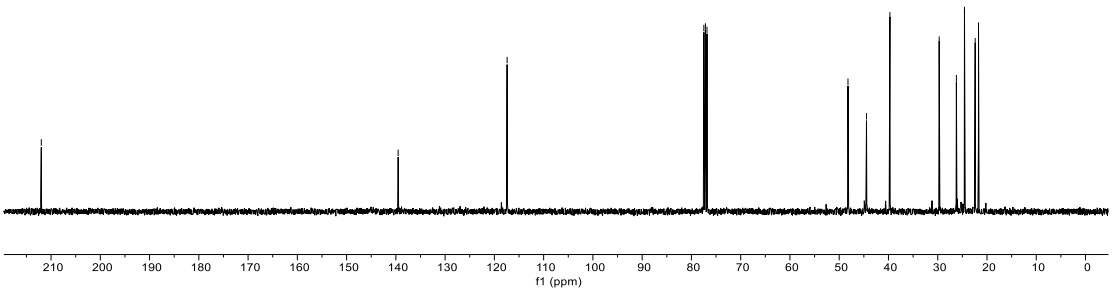


Table 2, 2o



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

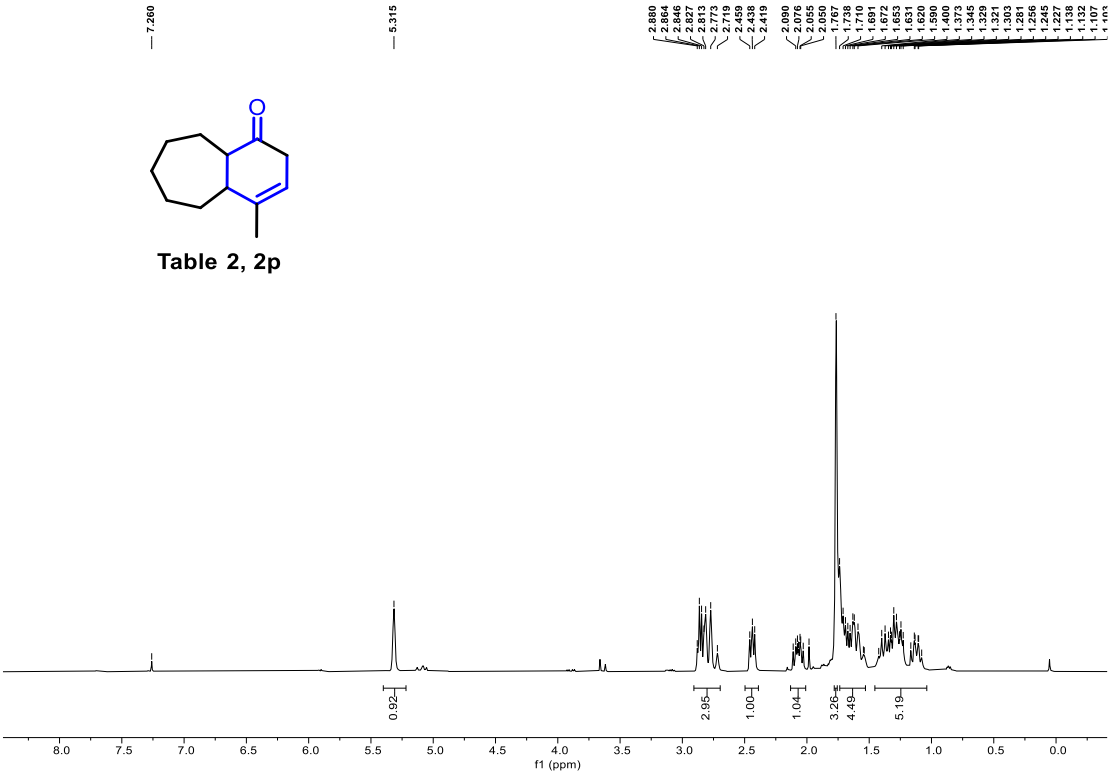


Table 2, 2p

^{13}C NMR in $CDCl_3$, 100 MHz

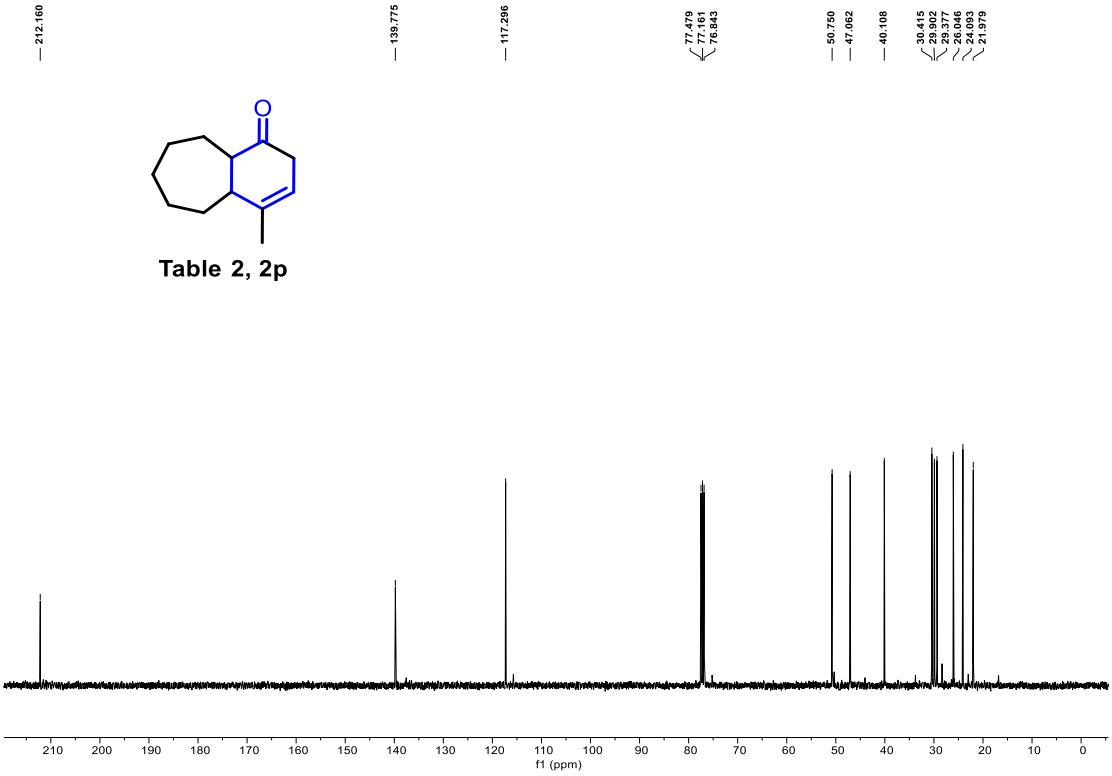


Table 2, 2p

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

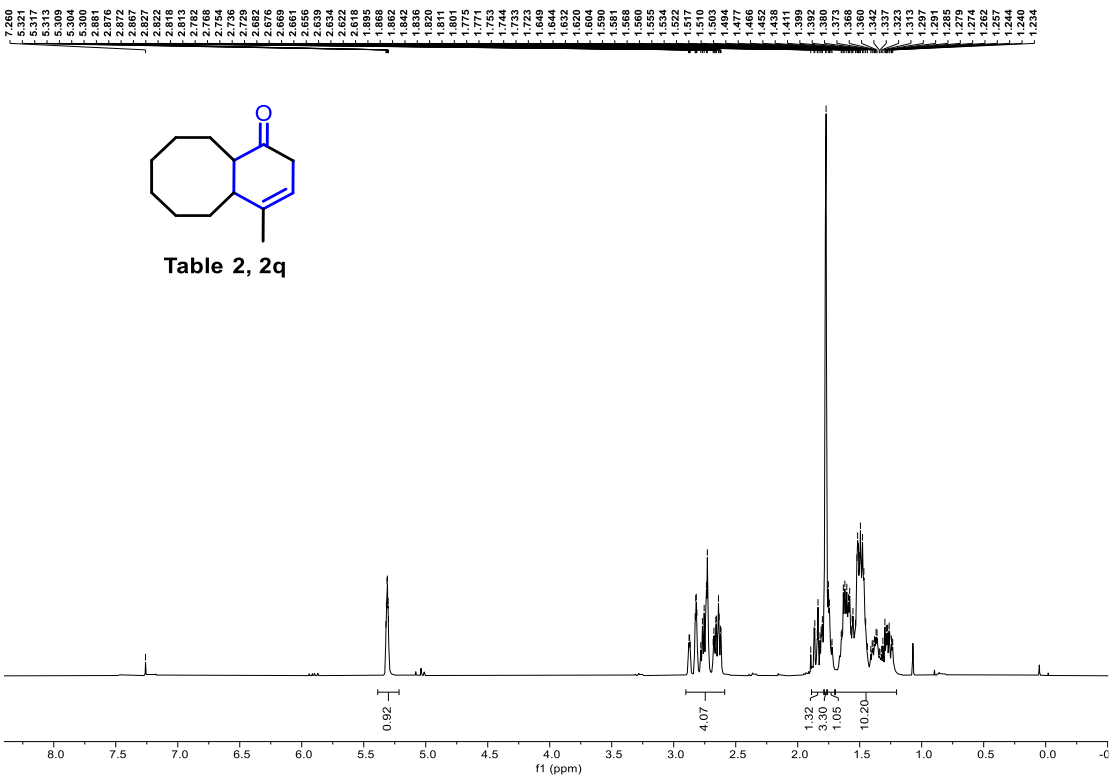


Table 2, 2q

^{13}C NMR in $CDCl_3$, 100 MHz

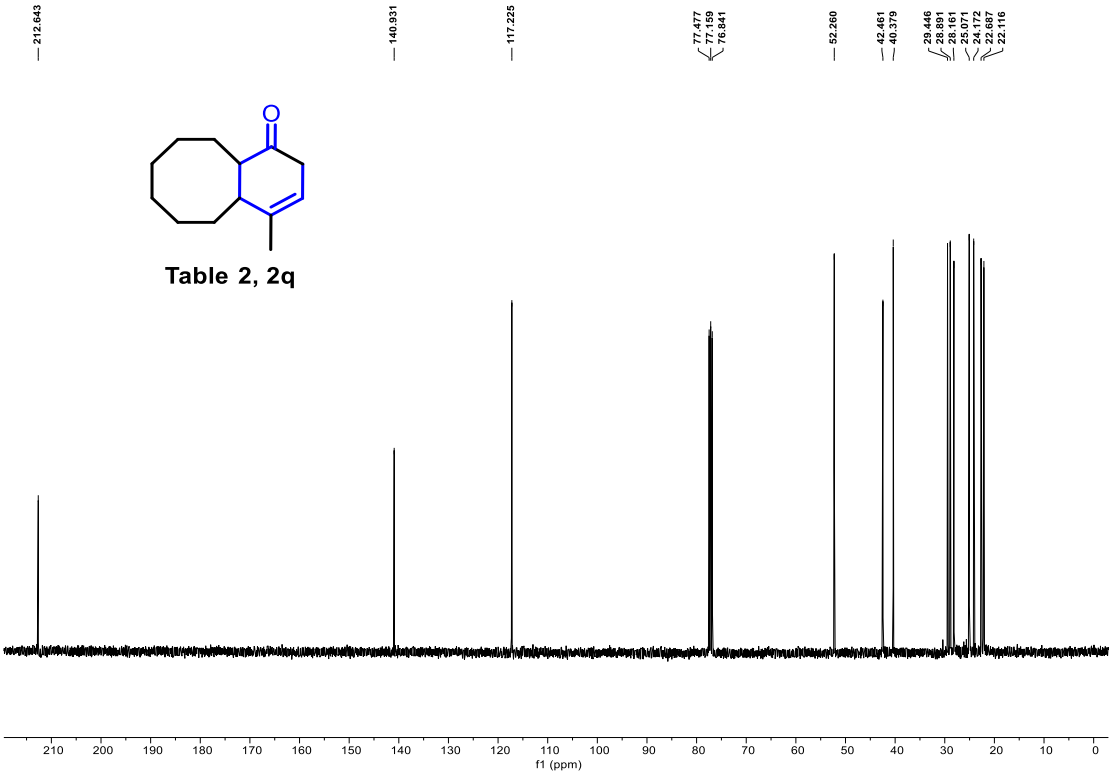


Table 2, 2q

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

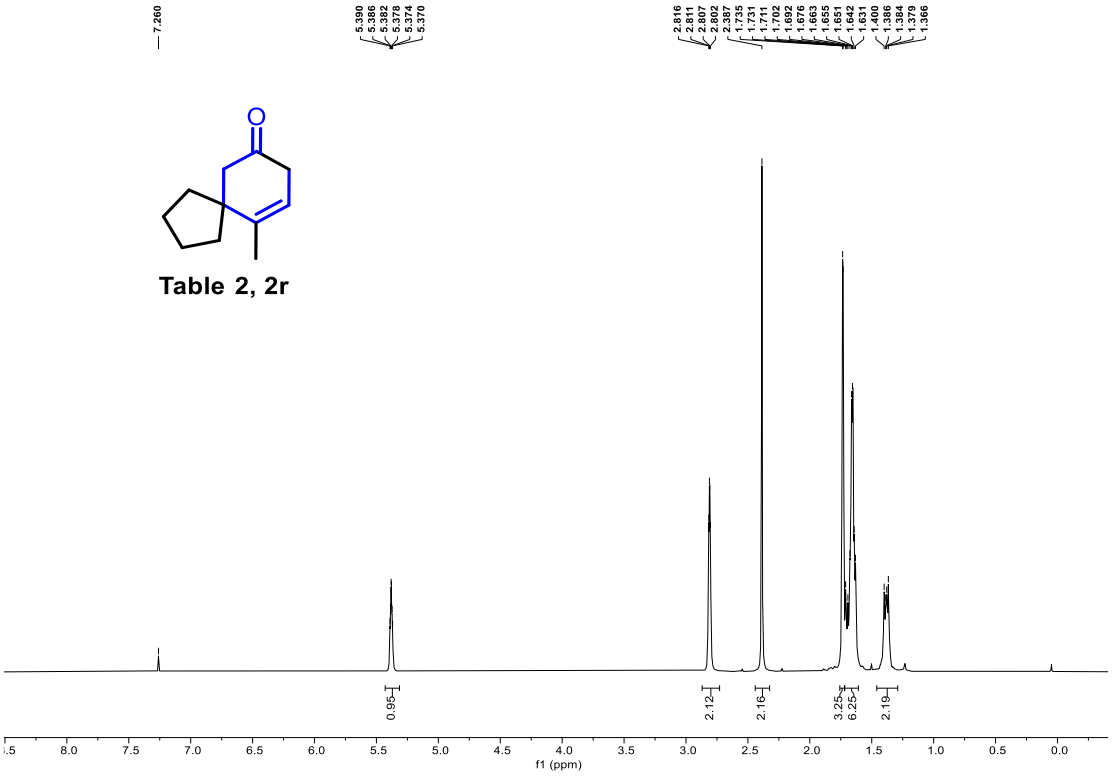


Table 2, 2r

^{13}C NMR in $CDCl_3$, 100 MHz

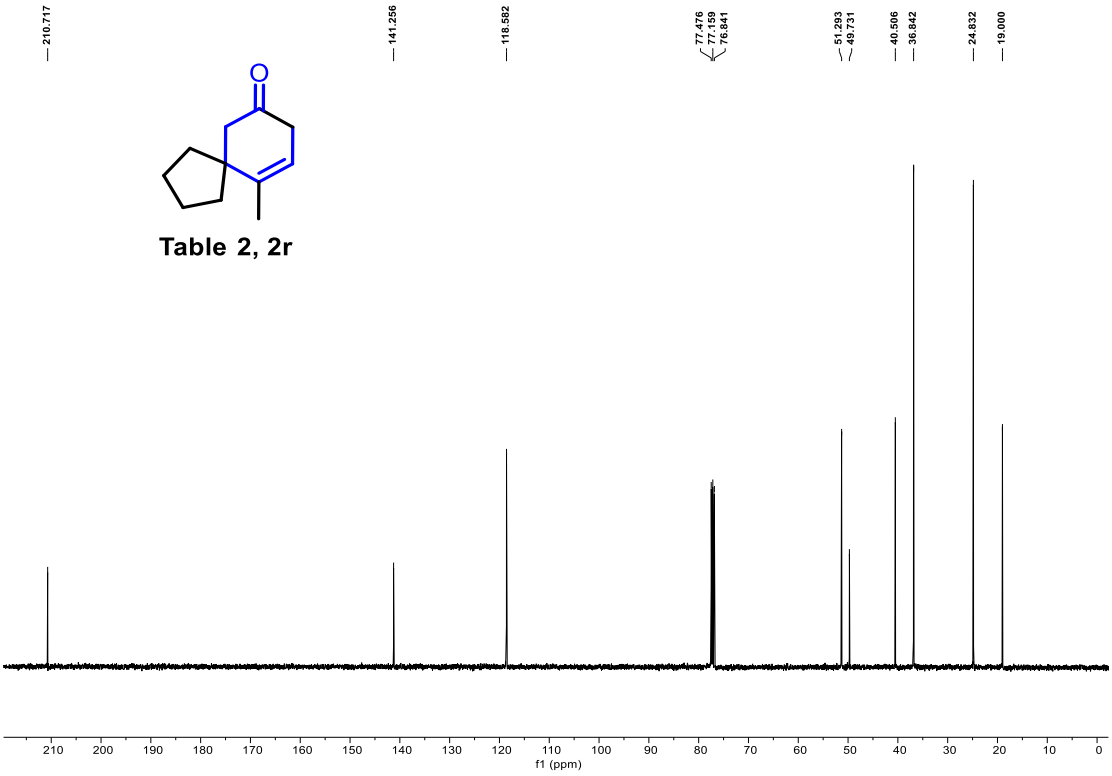


Table 2, 2r

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

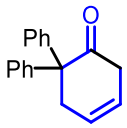
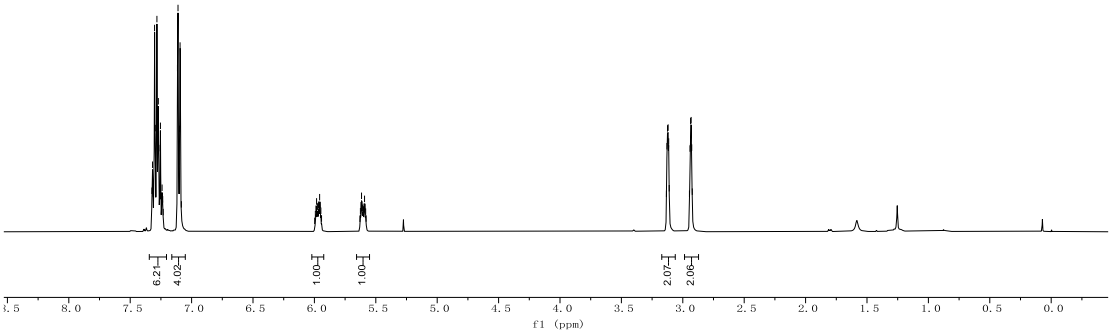
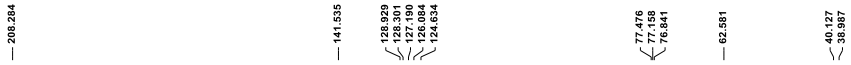


Table 2, 2s



^{13}C NMR in $CDCl_3$, 100 MHz



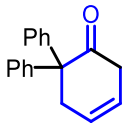
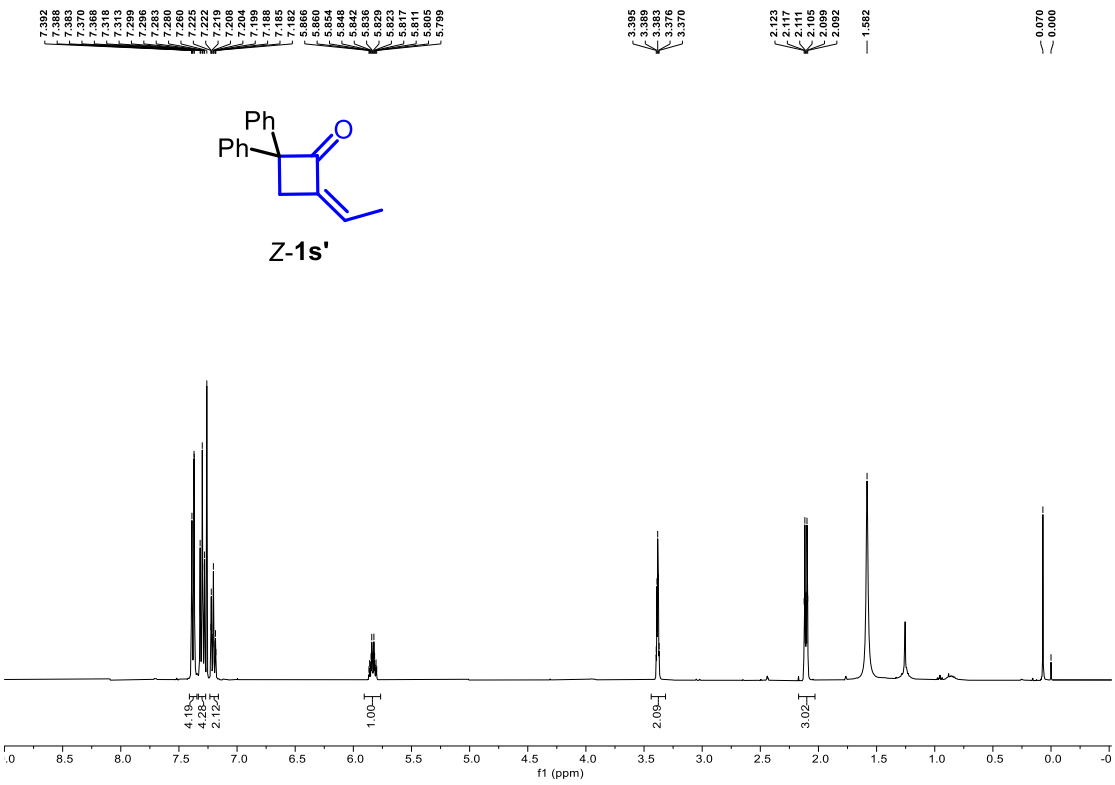
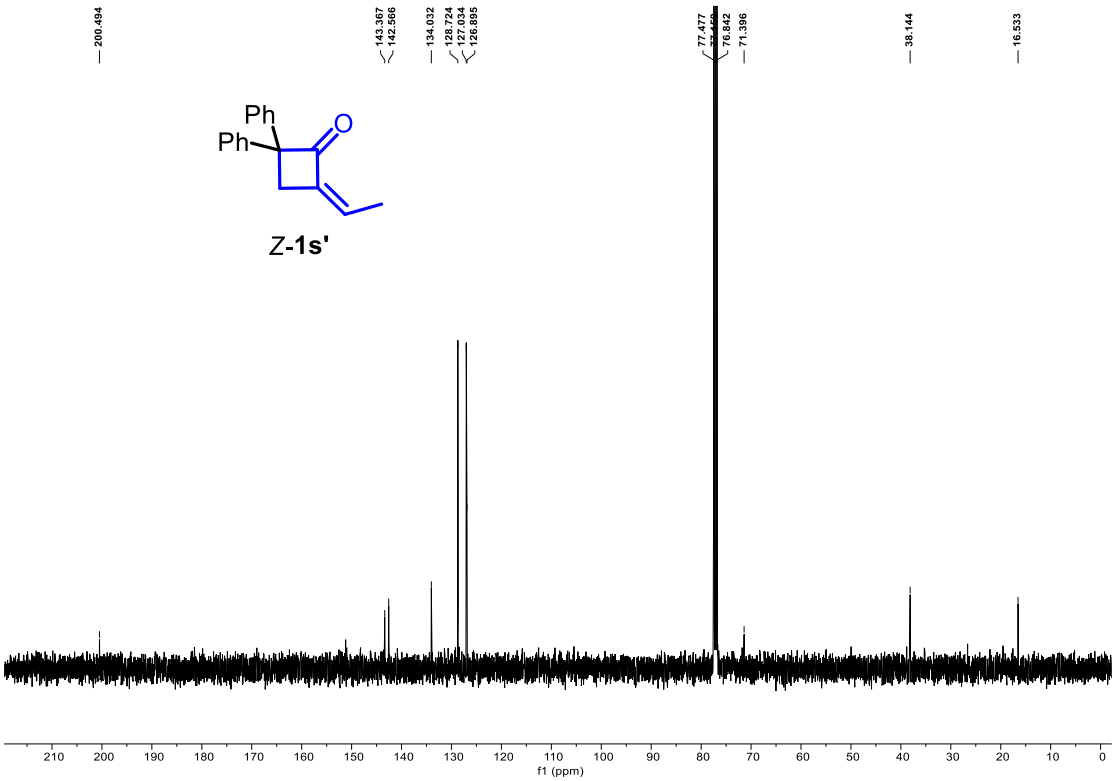


Table 2, 2s

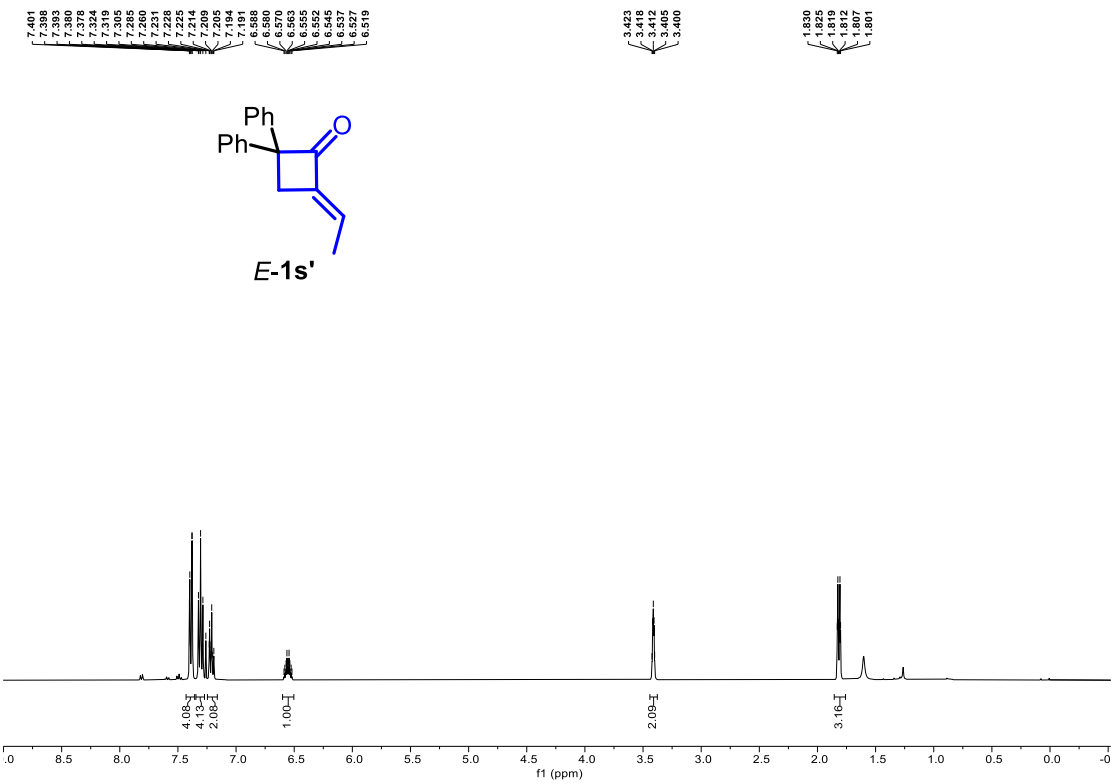
^{1}H NMR in $CDCl_3$, 400 MHz



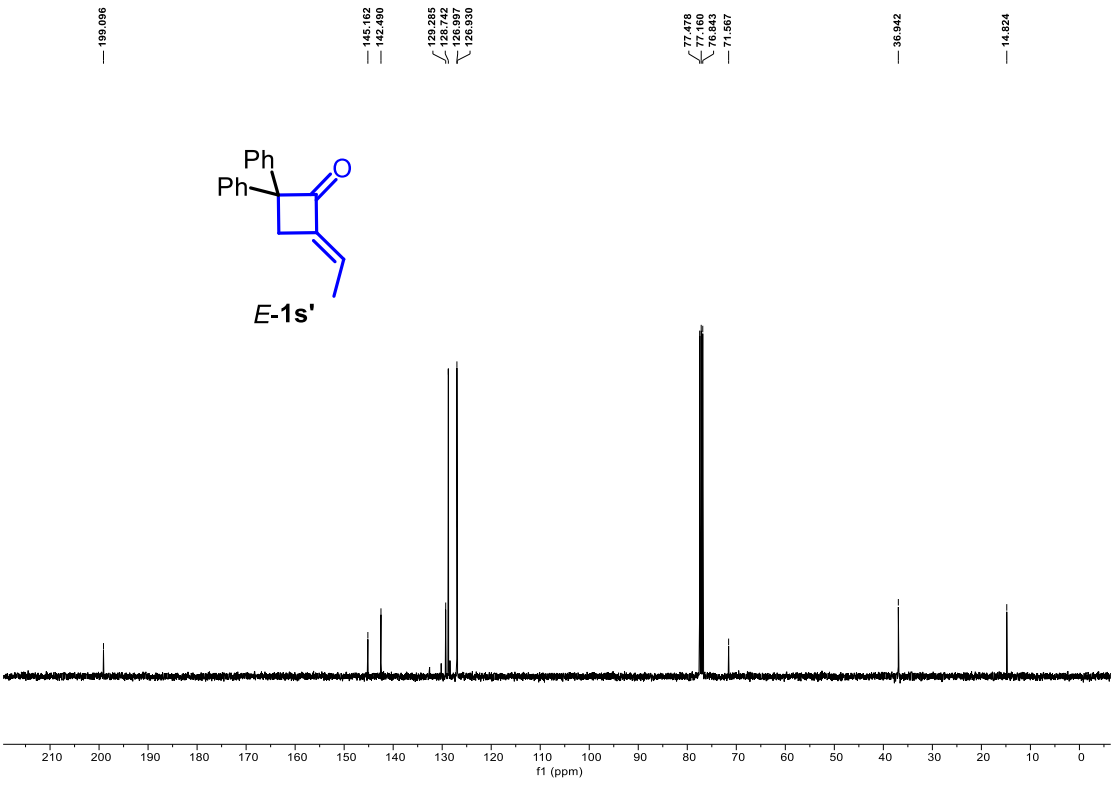
^{13}C NMR in $CDCl_3$, 100 MHz



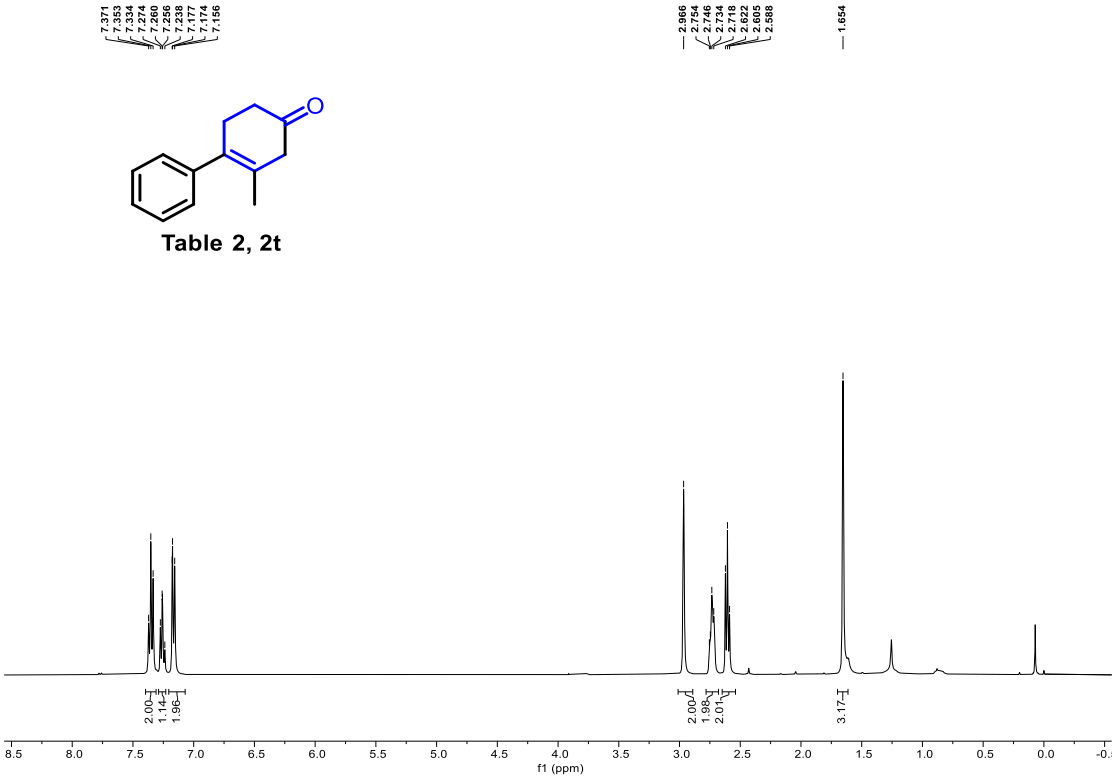
^{1}H NMR in $CDCl_3$, 400 MHz



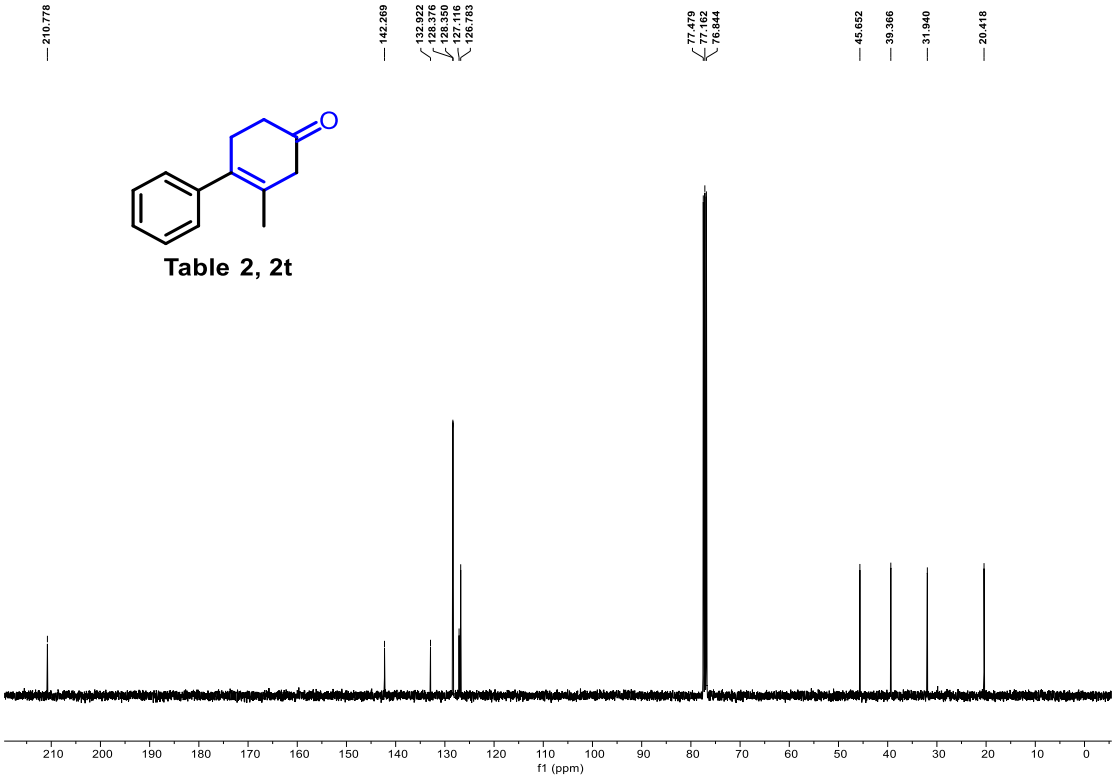
^{13}C NMR in $CDCl_3$, 100 MHz



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



^{13}C NMR in $CDCl_3$, 100 MHz



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

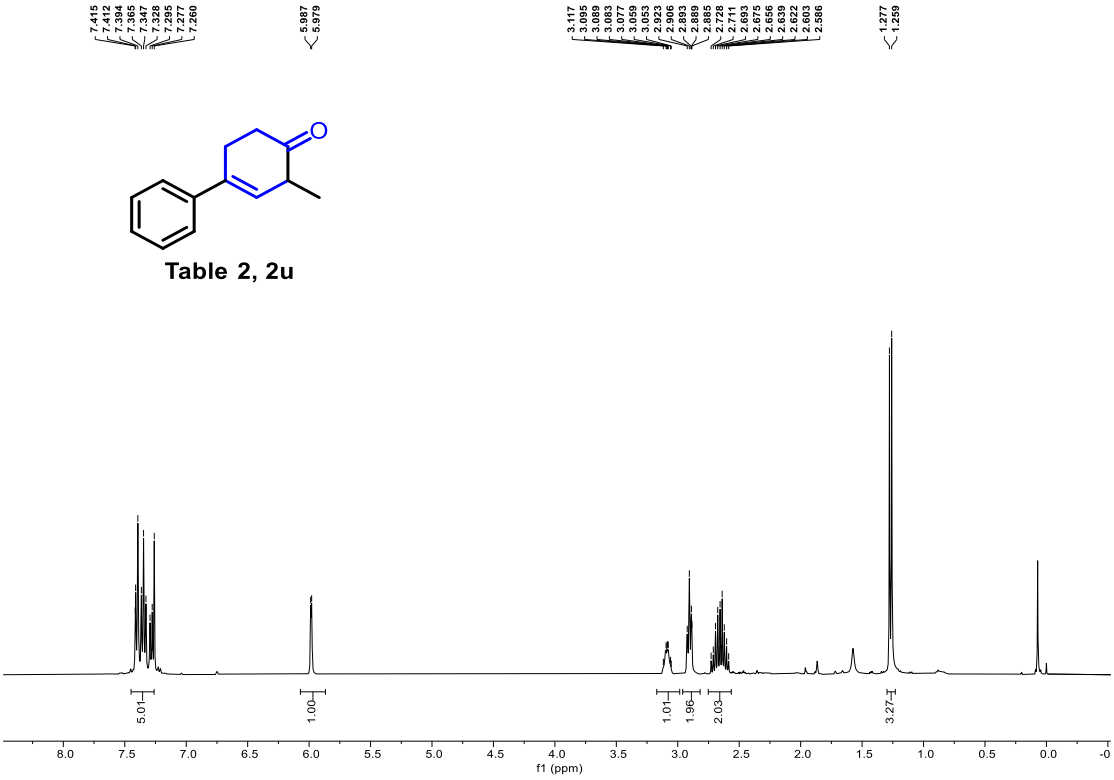


Table 2, 2u

^{13}C NMR in $CDCl_3$, 100 MHz

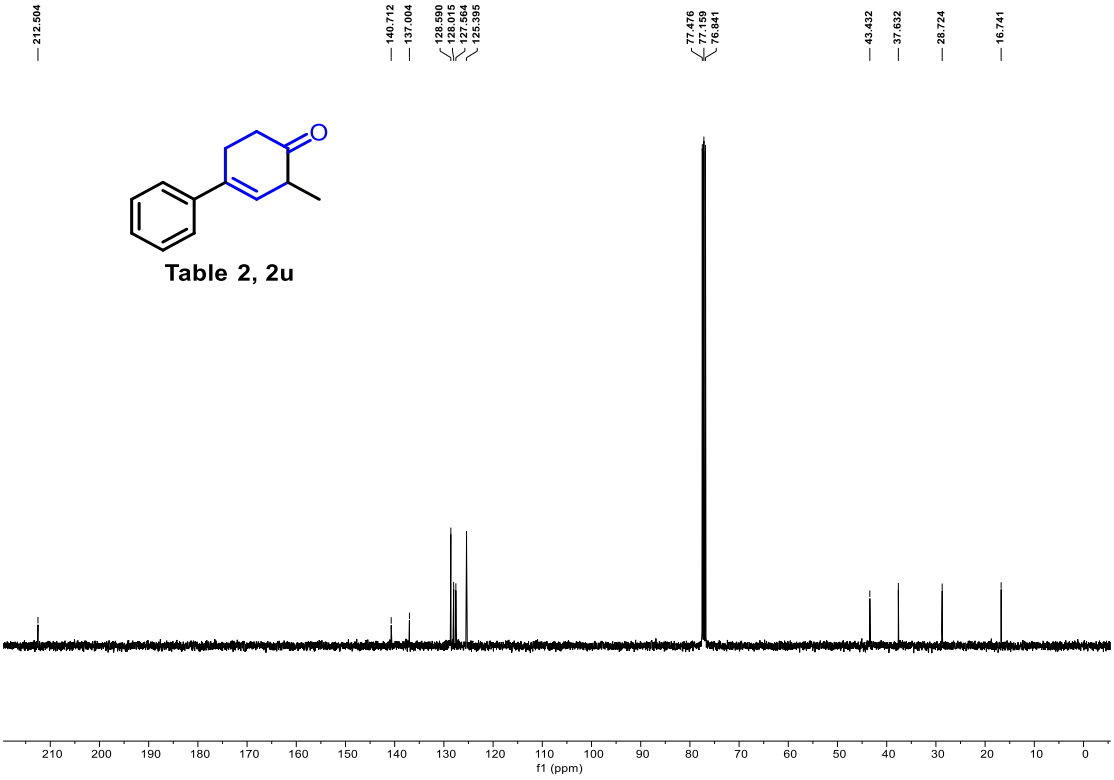
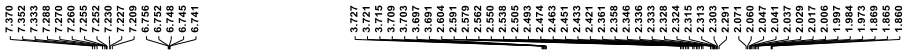


Table 2, 2u

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



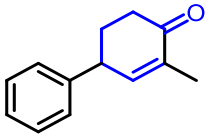
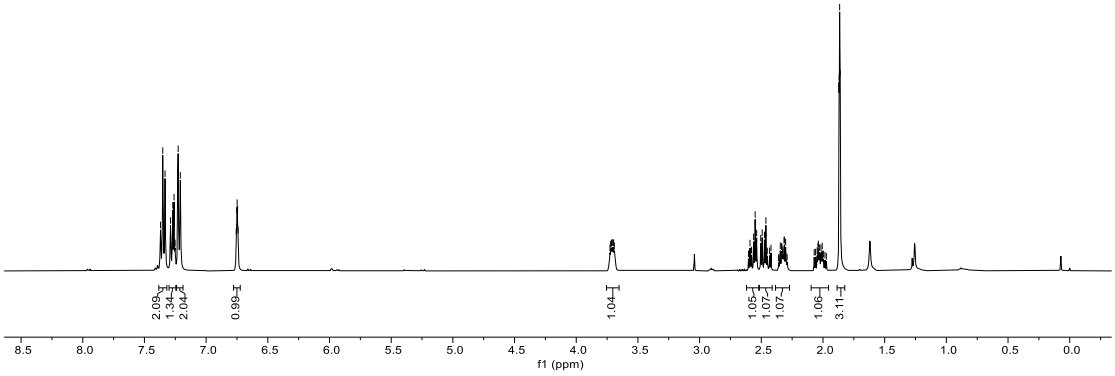


Table 2, 2u'



^{13}C NMR in $CDCl_3$, 100 MHz

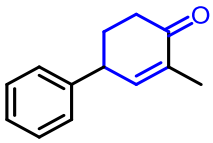
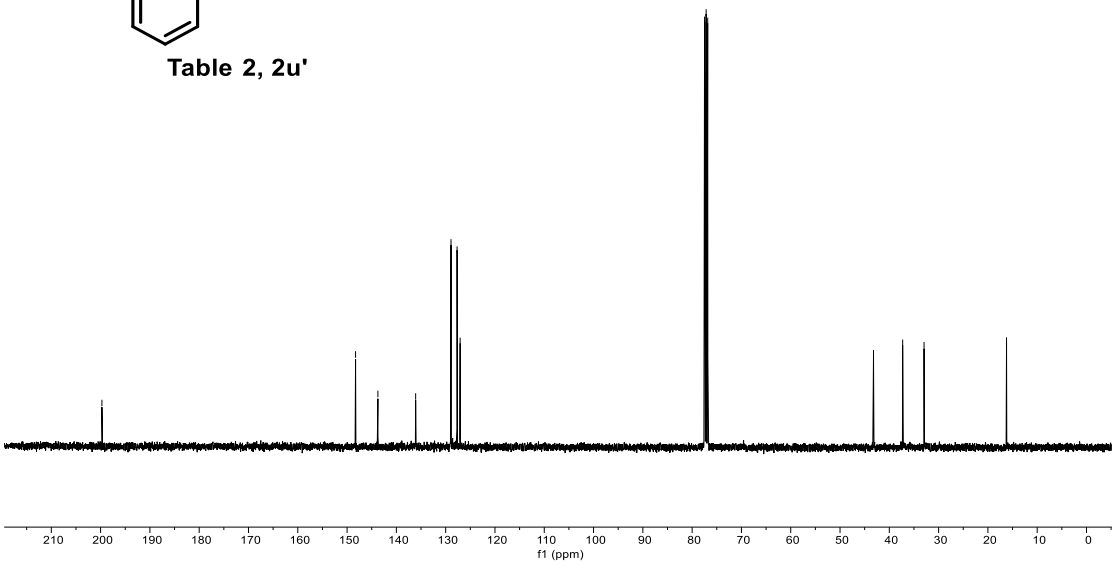
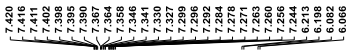
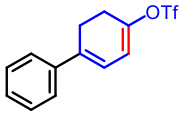


Table 2, 2u'

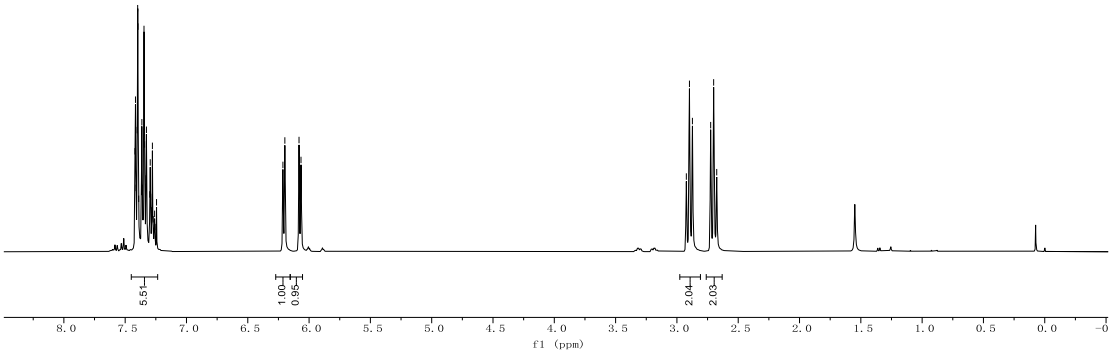


^{1}H NMR in $CDCl_3$, 400 MHz

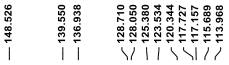


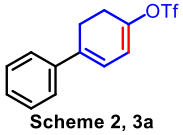


Scheme 2, 3a

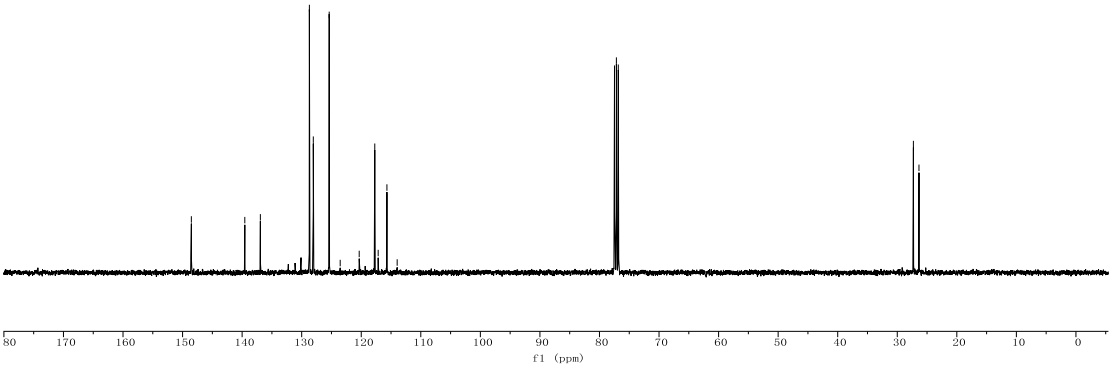


^{13}C NMR in $CDCl_3$, 100 MHz

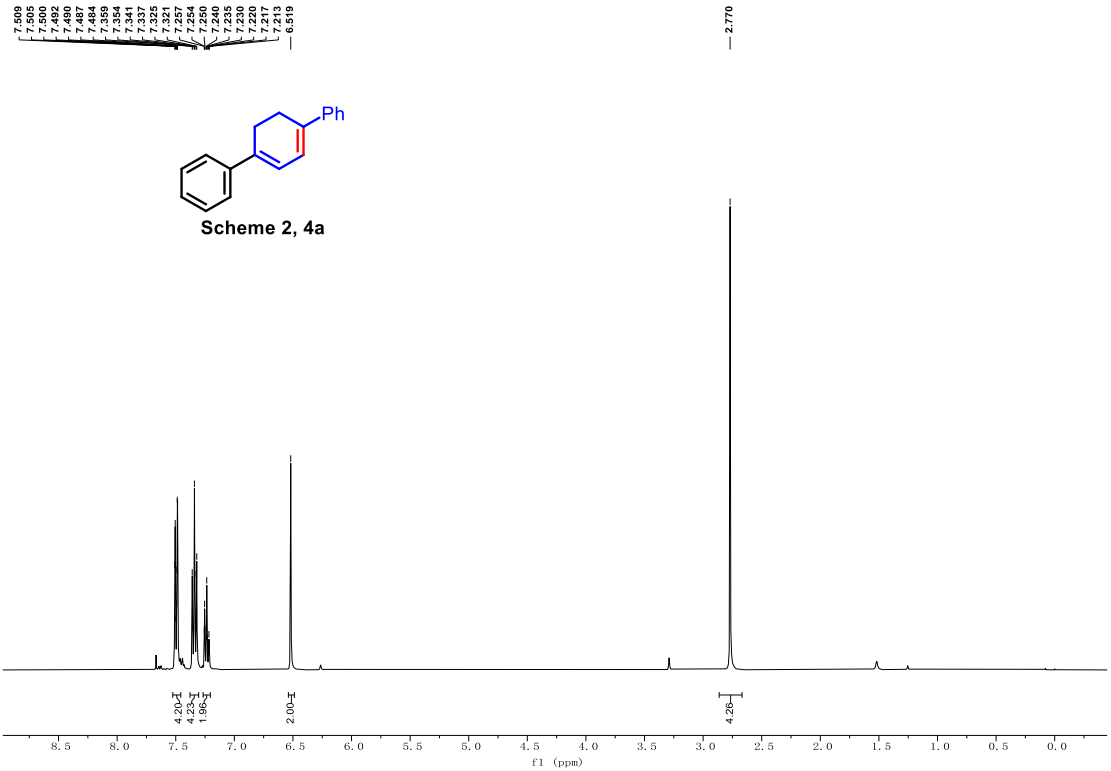




Scheme 2, 3a

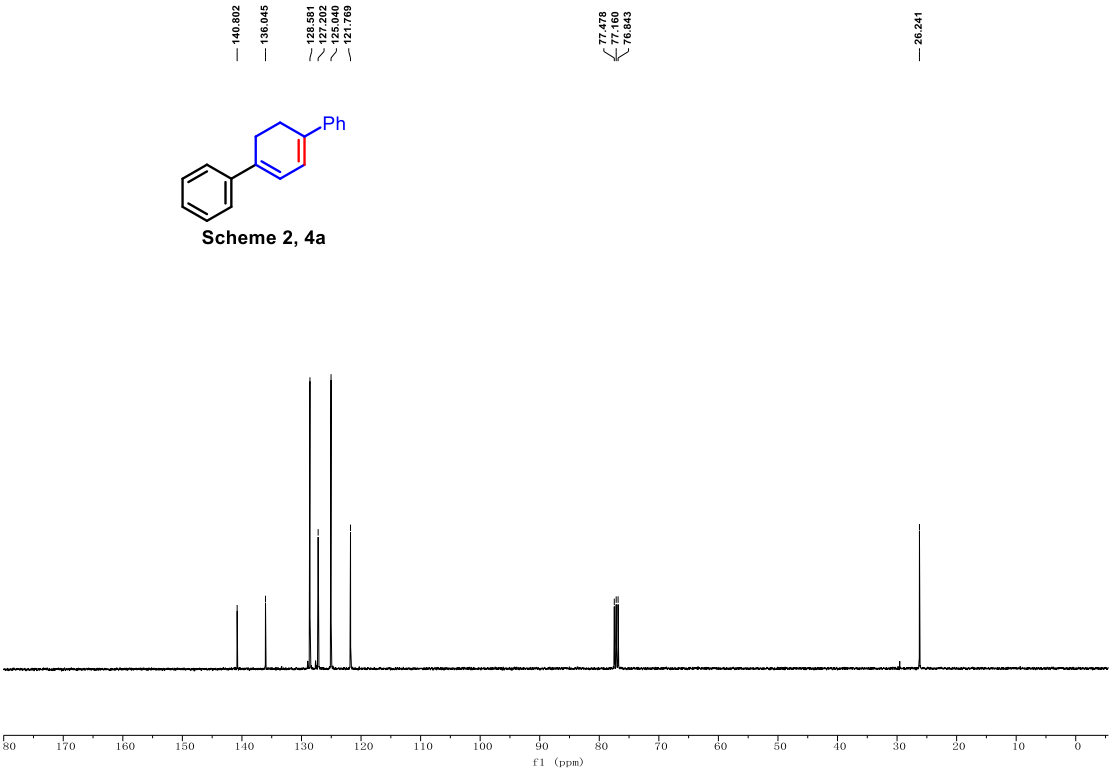


^{1}H NMR in $CDCl_3$, 400 MHz



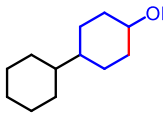
Scheme 2, 4a

^{13}C NMR in $CDCl_3$, 100 MHz

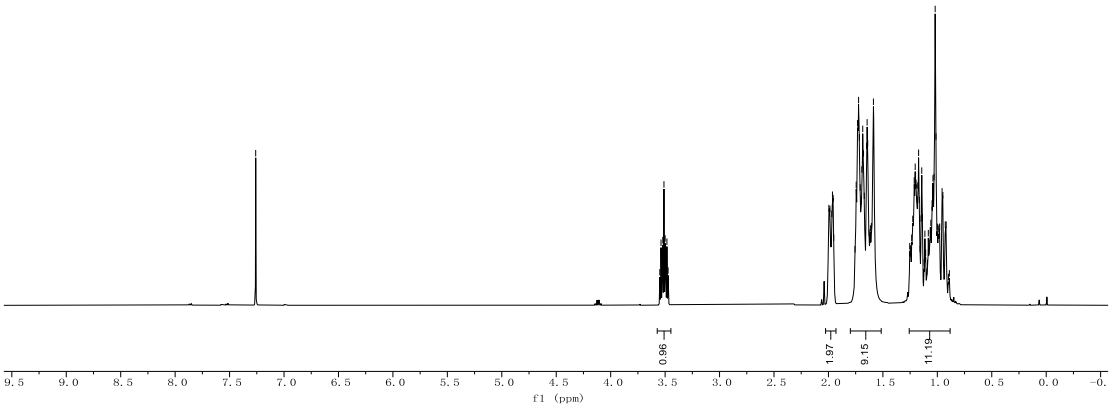


Scheme 2, 4a

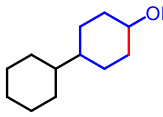
^{1}H NMR in $CDCl_3$, 400 MHz



Scheme 2, *trans*-**5a**

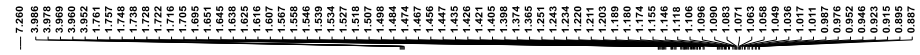


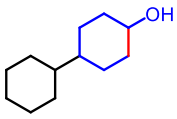
^{13}C NMR in $CDCl_3$, 100 MHz



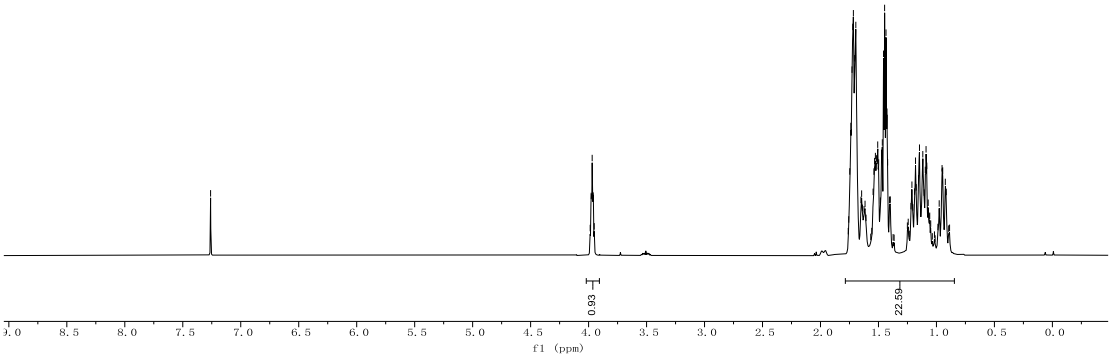
Scheme 2, *trans*-**5a**

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

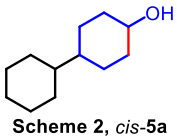




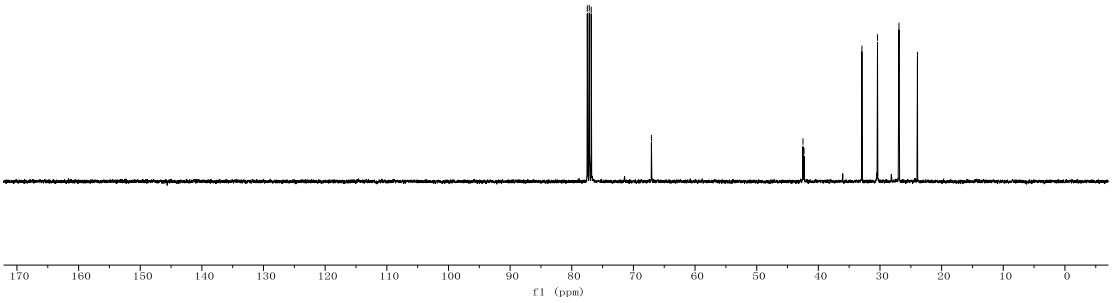
Scheme 2, *cis*-**5a**



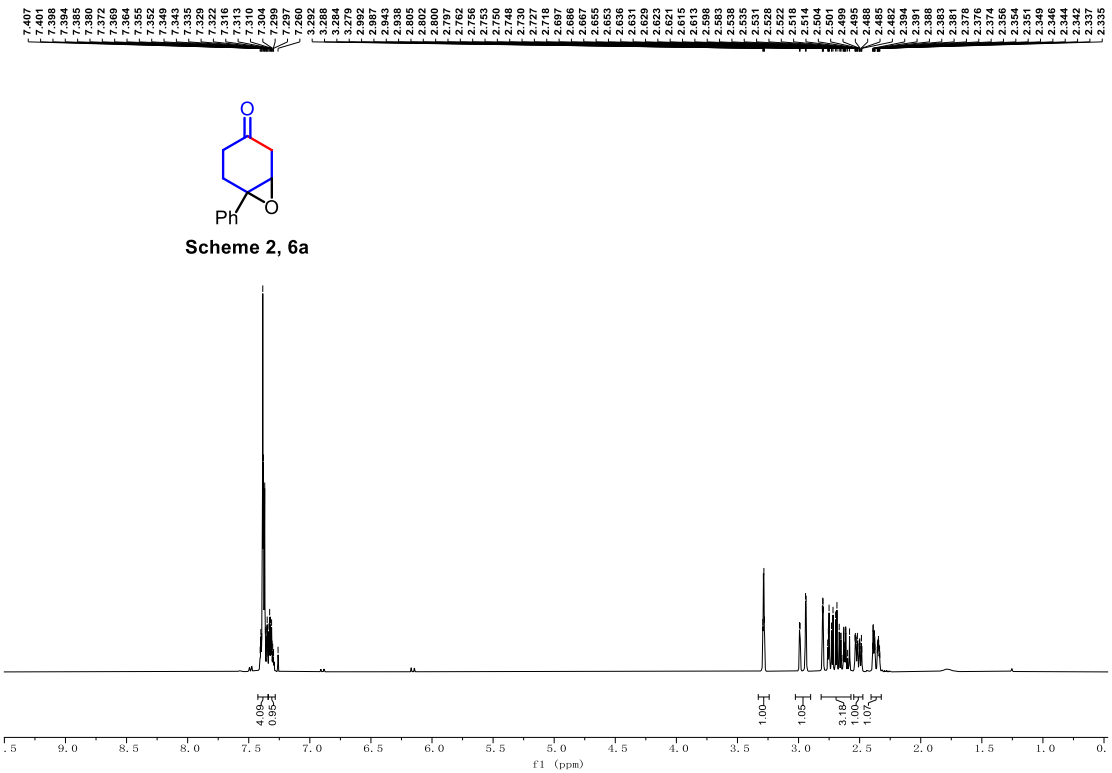
^{13}C NMR in $CDCl_3$, 100 MHz



Scheme 2, *cis*-**5a**

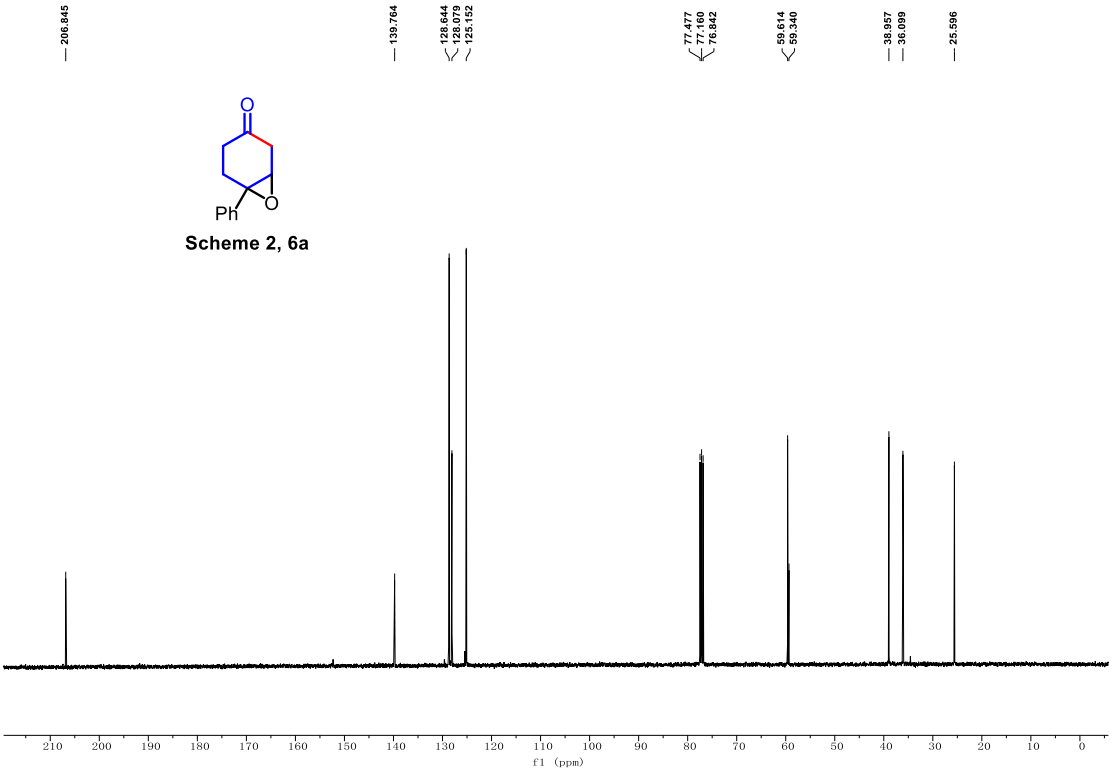


^{1}H NMR in $CDCl_3$, 400 MHz



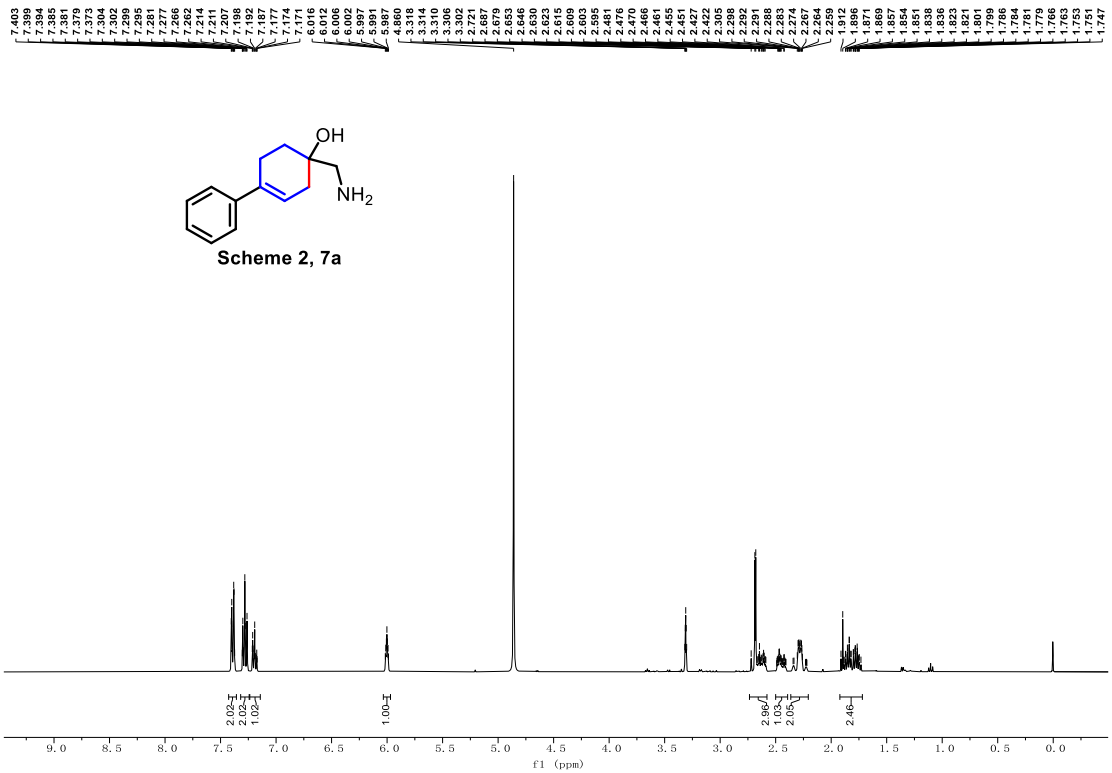
Scheme 2, 6a

^{13}C NMR in $CDCl_3$, 100 MHz

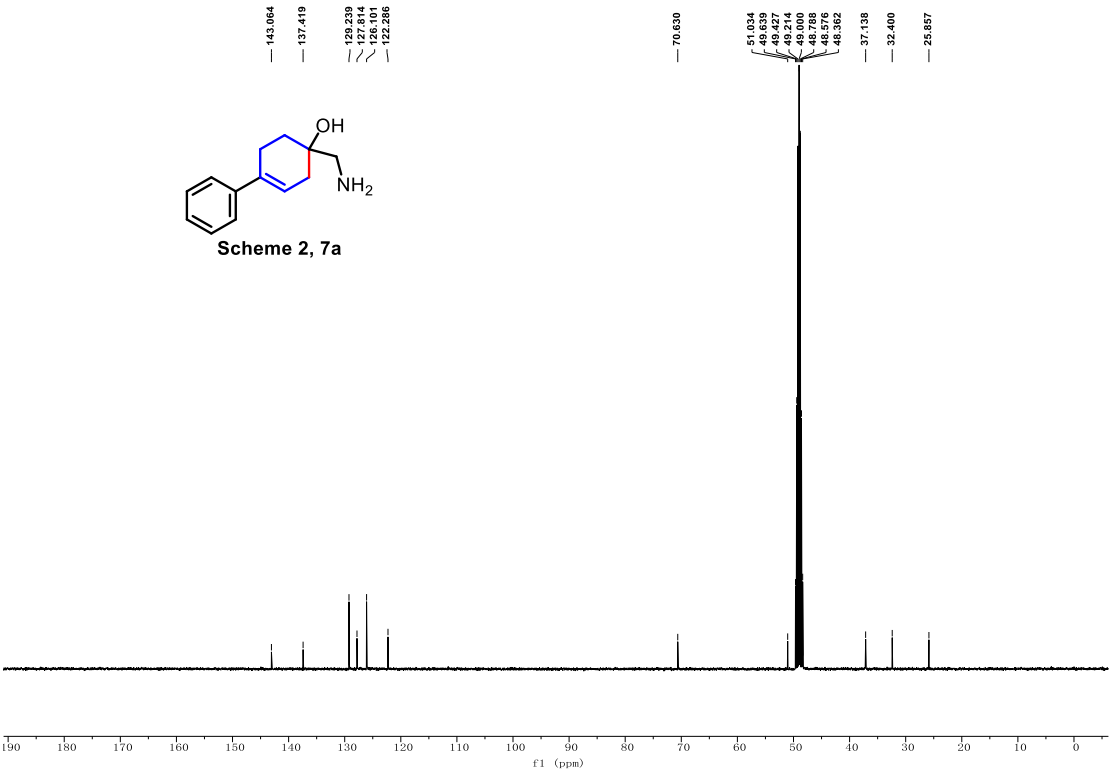


Scheme 2, 6a

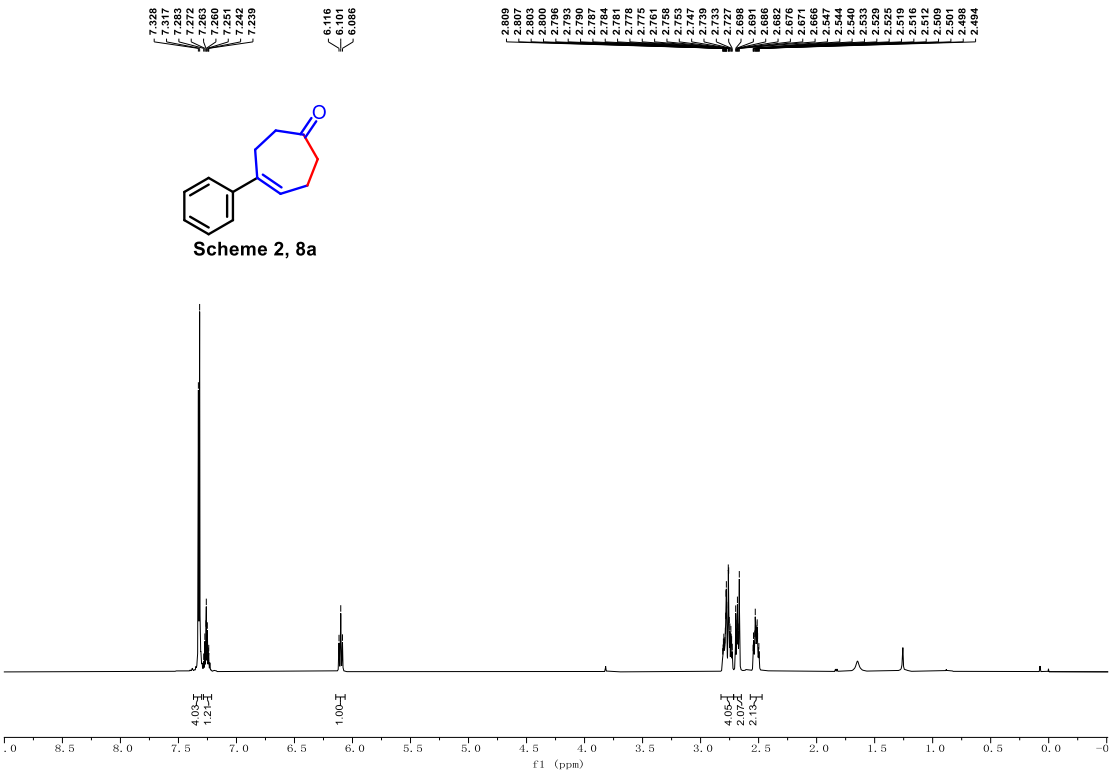
^{1}H NMR in CD_3OD, 400 MHz



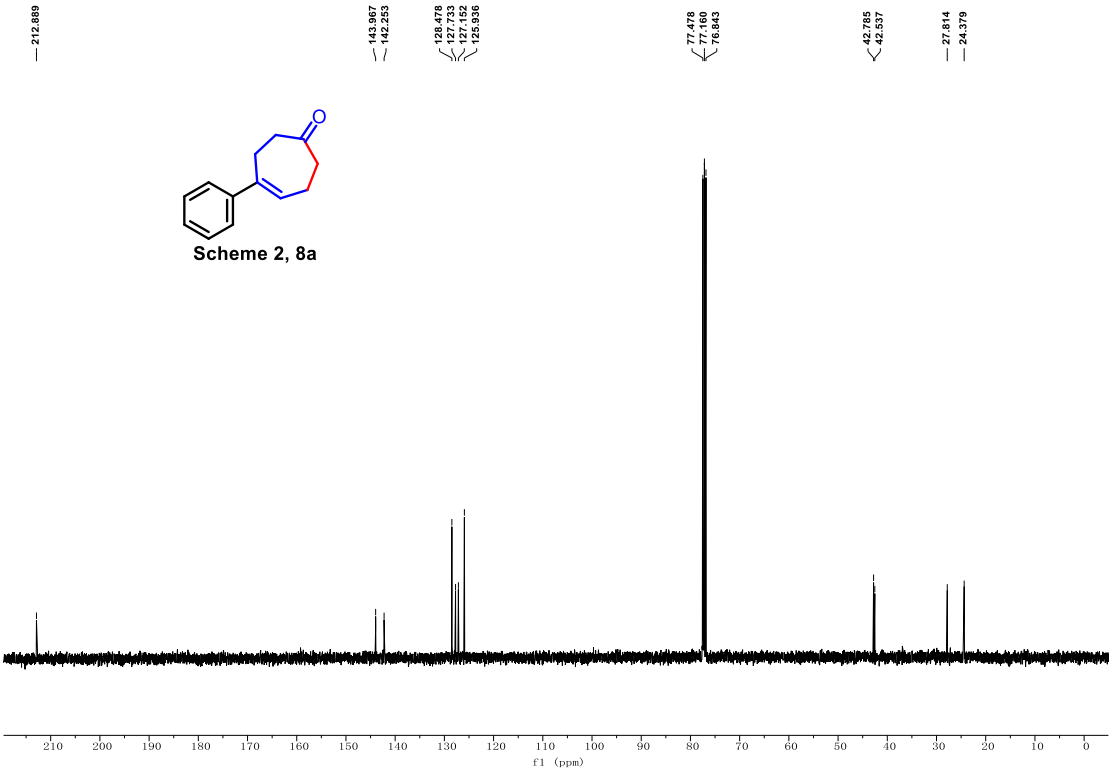
^{13}C NMR in CD_3OD, 100 MHz



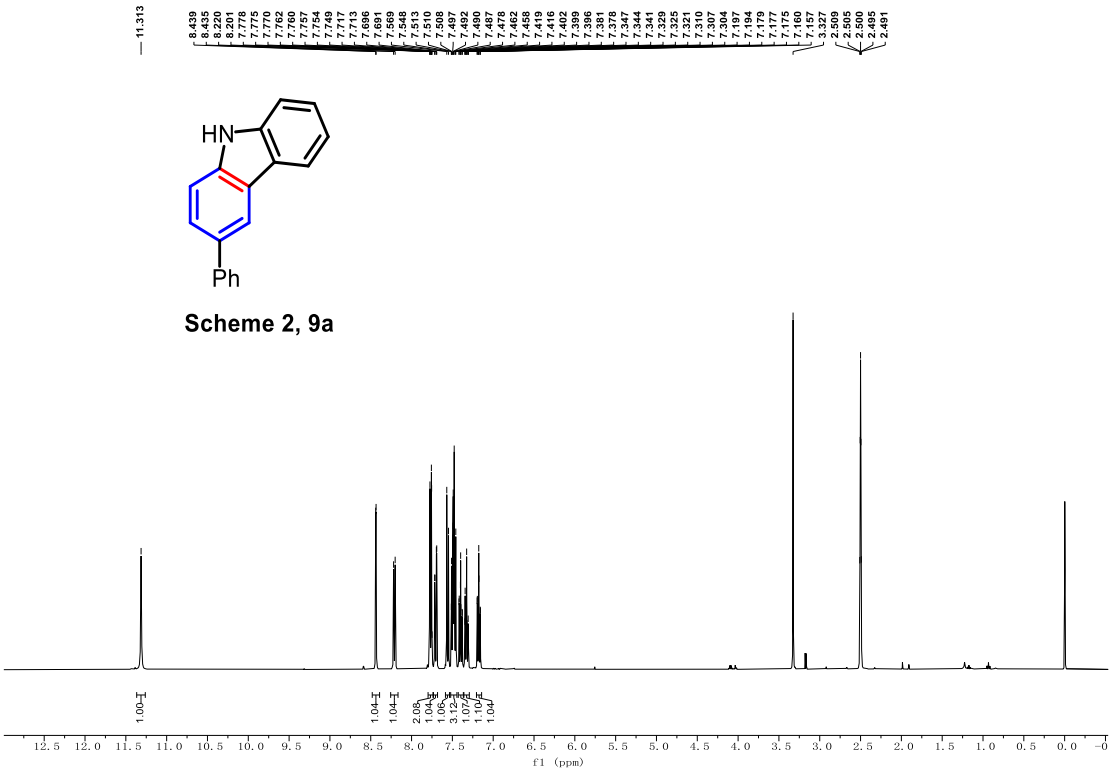
^{1}H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 100 MHz

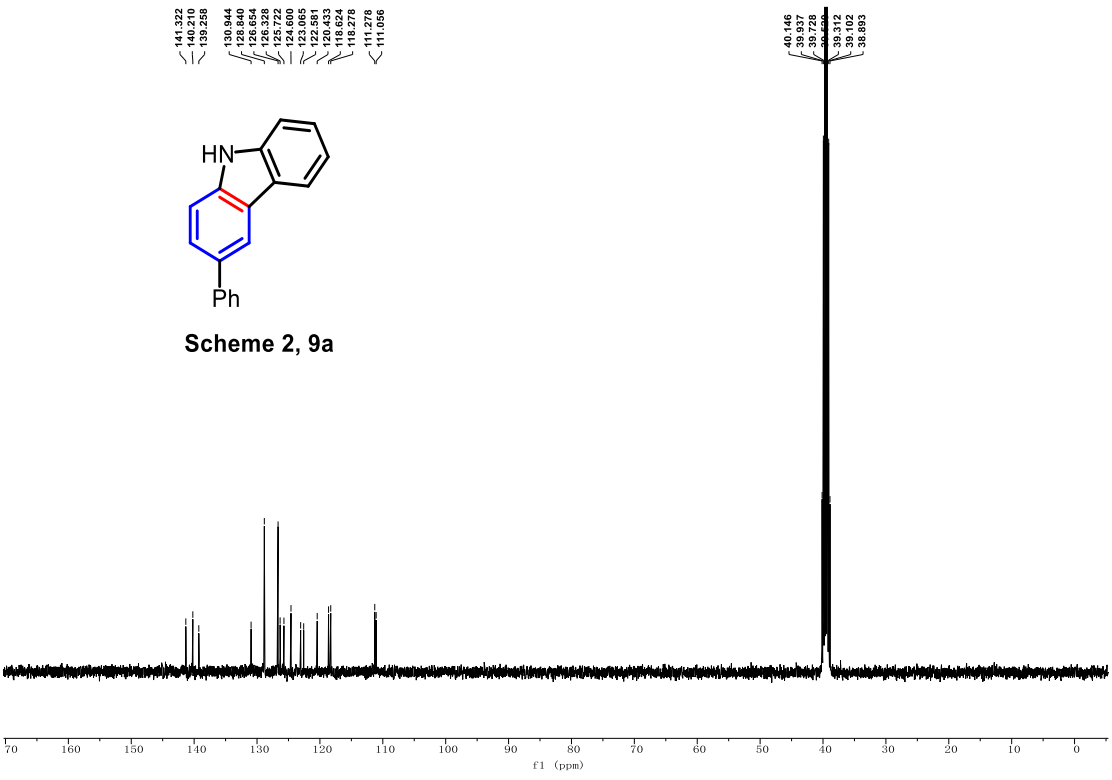


^{1}H NMR in DMSO-d_6, 400 MHz



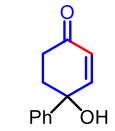
Scheme 2, 9a

^{13}C NMR in DMSO-d_6, 100 MHz

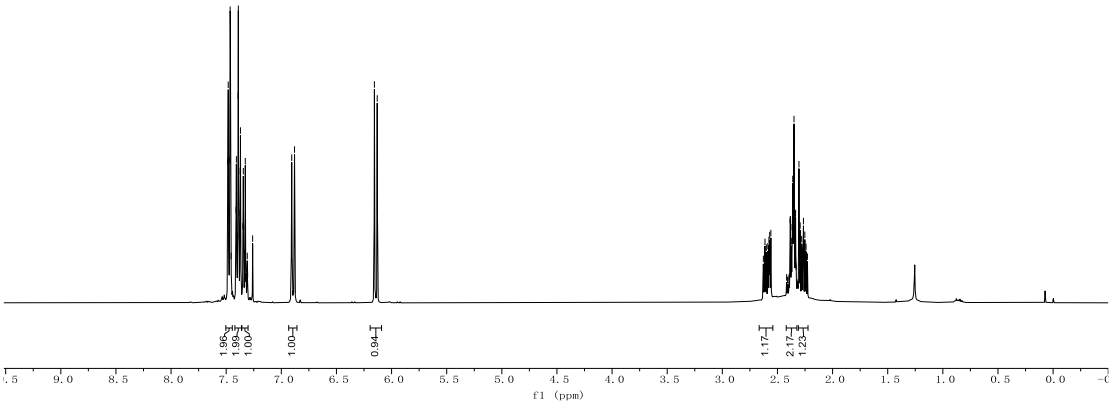


Scheme 2, 9a

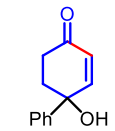
^{1}H NMR in $CDCl_3$, 400 MHz



Scheme 2, 10a



^{13}C NMR in $CDCl_3$, 100 MHz



Scheme 2, 10a