Supporting Information

For

Photoredox-catalyzed selective head-to-head reductive coupling of activated alkenes

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1. General Information

Unless otherwise noted, all the reactions were carried out in oven-dried sealed tube with Teflon-lined-septum under N_2 atmosphere. Materials were obtained from commercial sources and used as received, or synthesized according to previous literatures. Super dry acetonitrile with molecular sieves was use in the reaction. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on 400 MHz at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, and s referred to multiplet, quartet, triplet, doublet, and singlet. The reaction progress was monitored by GC-MS if applicable. Column chromatography was performed with silica gel (200-300 meshes). Thin layer chromatography (TLC) was visualized using UV light. HRMS(EI^+) analysis was performed on a Shimadzu GCMS-FT/TOF spectrometer. HRMS(ESI^+) analysis was performed on a Shimadzu LCMS-IT/TOF spectrometer.

The photoreactor used in this research was built by our group, which was made up of 8 blue LED bulbs (15 W for each) with a circulating coolant pump to keep the reactor at the set temperature. Spectral distribution: 425 nm. In the reaction, each Schlenk tube is irradiated by one of the light bulbs separately. The approximate distance of the tube to the closest light bulb is 2 cm. A magnetic stirrer is placed under the photoreactor to keep the reaction stirred.

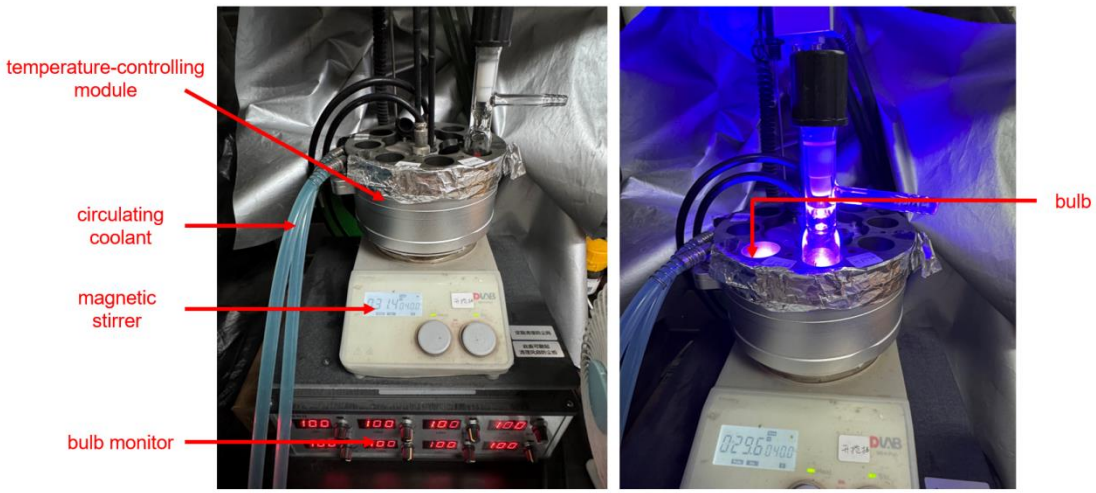
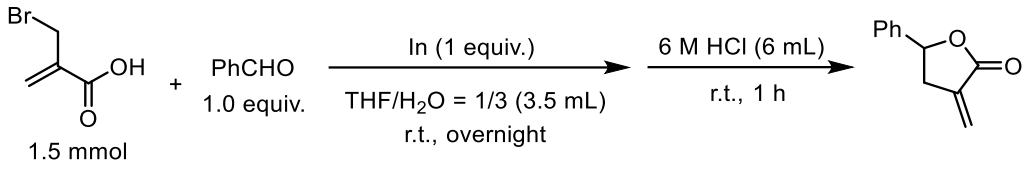


Fig. S1 Photos of the photoreactor

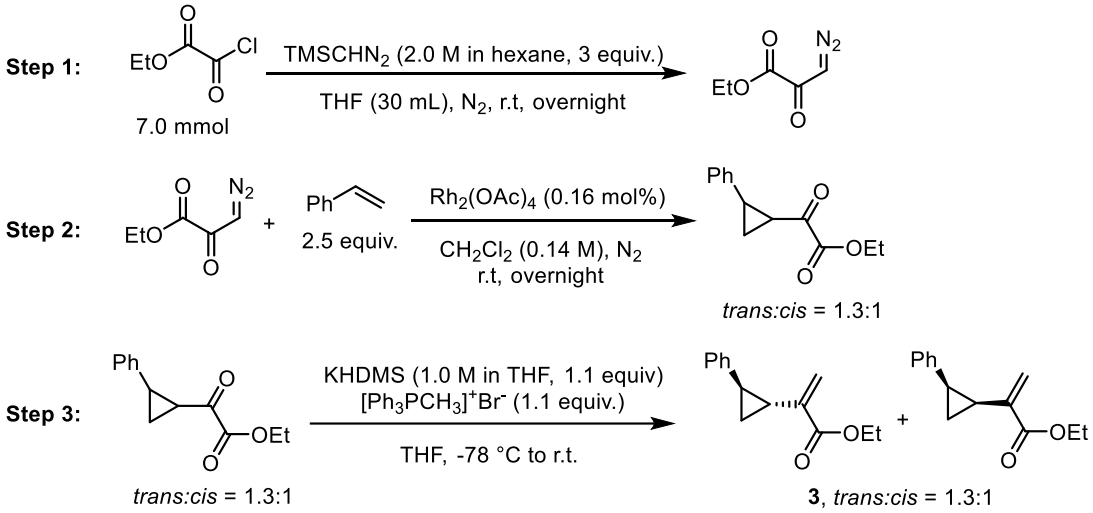
2. General Procedures for Synthesis of Substrates:

General procedures for synthesis of substrates ***1g****:*[1]



To a stirred of solution of benzaldehyde (1.5 mmol, 1.0 equiv.) in THF/H_2O (1/3, 3.5 mL), 2-(bromomethyl)acrylic acid (1.5 mmol, 1.0 equiv.) and indium (1.5 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 25 °C overnight, then quenched by 6 M HCl (6 mL) and concentrated *in vacuo.* The residue was purified by flash column chromatography (hexane/EtOAc: 2/1) to give product **1g** (85%, white solid), which was identified by ^1H and ^{13}C NMR.

General procedures for synthesis of substrates ***3****:*[2]

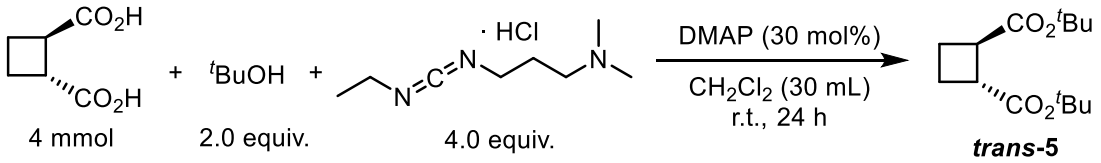


Step 1: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with N_2 for 3 times. Ethyl chloroglyoxylate (0.78 mL, 7.0 mmol, 1.0 equiv.) was dissolved in THF (30 mL) and trimethyl silyl diazomethane (2.0 M in hexane, 21 mmol, 3.0 equiv.) was added dropwise. The reaction was stirred at room temperature overnight before it was concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EtOAc: 2/1) and ethyl 3-diazo-2-oxopropanoate was isolated as yellow crystals.

Step 2: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with N_2 for 3 times. $Rh_2(OAc)_4$ (7.0 mg, 0.16 mol%) and styrene (2.9 mL, 25 mmol, 2.5 equiv.) were dissolved in CH_2Cl_2 (20 mL) and ethyl 3-diazo-2-oxopropanoate (1.40 g, 10 mmol, 1.0 equiv.) in CH_2Cl_2 (50 mL) was added within 2 h. The reaction mixture was further stirred for 2 h. Evaporation of the volatile substances under reduced pressure followed by flash column chromatography (hexane/EtOAc: 10/1) afforded ethyl 2-oxo-2-(2-phenylcyclopropyl)acetate as a mixture of diastereoisomers (*trans*:*cis* = 1.3:1).

Step 3: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with N_2 for 3 times. Methyltriphenylphosphonium bromide (1.08 g, 3.0 mmol, 1.1 equiv.) was suspended in THF (5.5 mL) and KHMDS (1.0 M in THF, 3.0 mL, 3.0 mmol, 1.1 equiv.) was added at -78 °C. The reaction was further stirred at -78 °C for 15 min and at room temperature for 30 min. Then, ethyl 2-oxo-2-(2-phenylcyclopropyl)acetate (0.60 g, 2.75 mmol, 1.0 equiv.) was added at -78 °C and the reaction mixture was allowed to warm up to room temperature overnight. After the reaction, HCl (2.0 M, 3 mL) was carefully added and the mixture was extracted with EtOAc (3x4 mL). The combined organic phases were washed with brine (4 mL) and dried with Na_2SO_4. Flash column chromatography (hexane/EtOAc: 30/1) afforded ethyl 2-(2-phenylcyclopropyl)acrylate **3** (30%, colorless liquid) as a mixture of diastereoisomers (*trans*:*cis* = 1.3:1), known as colorless oil.

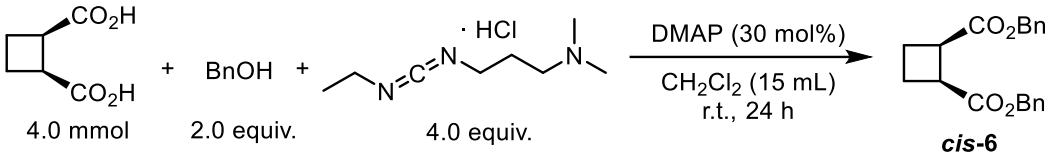
General procedures for synthesis of substrates ***trans-5****:*[3]



To a stirred of solution of *trans*-cyclobutane-1,2-dicarboxylic acid (4.0 mmol, 1.0 equiv.) and EDCI (*N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride) (16.0 mmol, 4.0 equiv.) in CH_2Cl_2 (30 mL), DMAP (4-dimethylaminepyridine) (0.60 mmol, 0.15 equiv.) and *tert*-butanol (8.0 mmol, 2.0 equiv) were added. The reaction

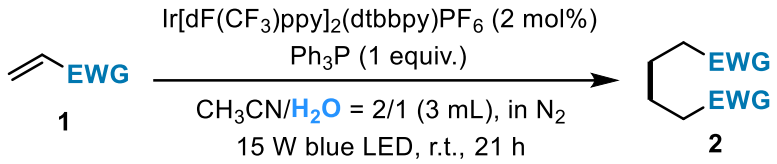
mixture was stirred at 25 °C for 24 h, then concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give product ***trans*-5**, which was identified by ^{1}H and ^{13}C NMR.

General procedures for synthesis of substrates ***cis*-6**.[3]

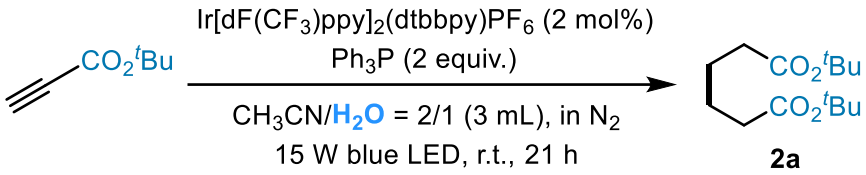


To a stirred of solution of *cis*-cyclobutane-1,2-dicarboxylic acid (4.0 mmol, 1.0 equiv.) and EDCI (16.0 mmol, 4.0 equiv.) in CH_2Cl_2 (30 mL), DMAP (0.60 mmol, 0.15 equiv.) and *tert*-butanol (8.0 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 25 °C for 24 h, then concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give product ***cis*-6**, which was identified by ^{1}H and ^{13}C NMR.

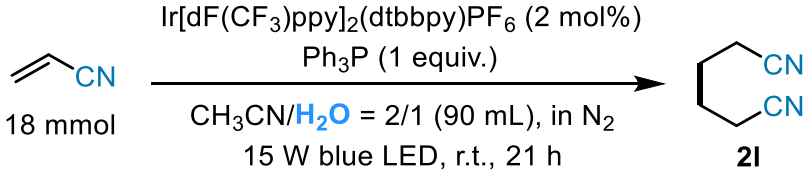
3. General Procedures for Synthesis of Products 2:



General procedures for synthesis of products ***2****:* A sealed tube equipped with a stirrer bar was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (4.4 mg, 2.0 mol%), PPh$_3$ (52.5 mg, 1.0 equiv.), substrate **1** (0.2 mmol, for solid substrates), then degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (2 mL), H_2O (1 mL), and substrate **1** (0.2 mmol, for liquid substrates) were added under N_2. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products **2**, which were identified by ^{1}H, ^{13}C, and ^{19}F NMR.



Procedure for synthesis of products ***2a*** *from propiolate:* A sealed tube equipped with a stirrer bar was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (4.4 mg, 2.0 mol%) and PPh$_3$ (104.9 mg, 2.0 equiv.), then degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (2 mL), H_2O (1 mL), and *tert*-butyl propiolate (0.2 mmol) were added under N_2. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products **2a**, which were identified by ^{1}H and ^{13}C NMR.



*Procedure for gram-scale synthesis of product **2l**:* A sealed tube equipped with a stirrer bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (396.0 mg, 2.0 mol%) and PPh_3 (4.725 g, 1.0 equiv.), then degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (60 mL), H_2O (30 mL), and acrylonitrile (18.0 mmol) were added under N_2. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give product **2l** (0.64 g, 66%), which was identified by ^1H and ^{13}C NMR.

4. Discussion on the Exploration of Substrate Scope

4.1 Failed examples of substrate scope

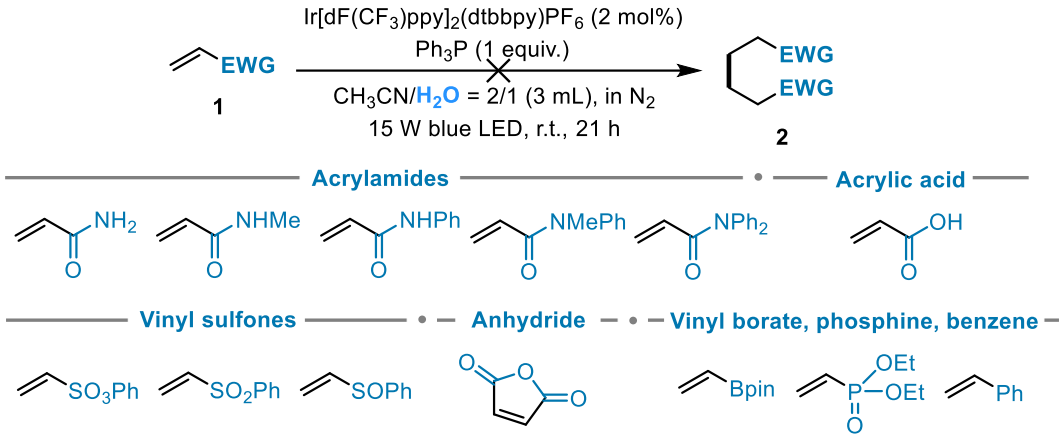
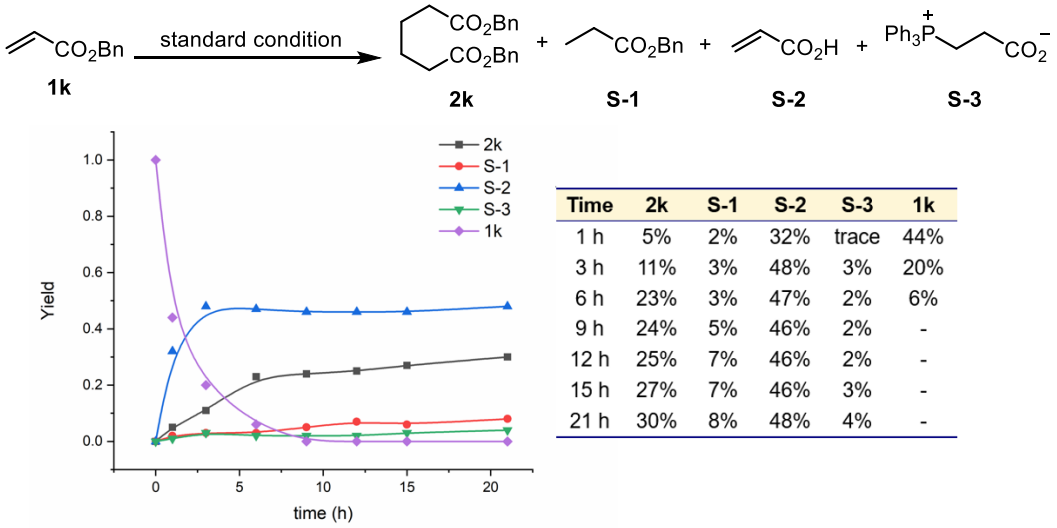


Fig. S2 Substrate scope in failed examples

4.2 Time-scale profile for the reductive hydrogenation of 1k



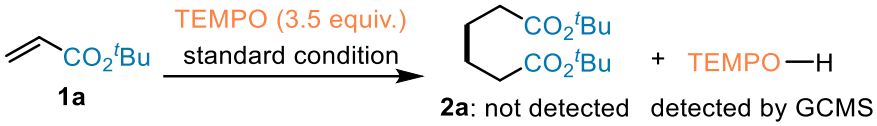
Time	2k	S-1	S-2	S-3	1k
1 h	5%	2%	32%	trace	44%
3 h	11%	3%	48%	3%	20%
6 h	23%	3%	47%	2%	6%
9 h	24%	5%	46%	2%	-
12 h	25%	7%	46%	2%	-
15 h	27%	7%	46%	3%	-
21 h	30%	8%	48%	4%	-

Fig. S3 Time-scale profile for the reaction of **1k** under standard condition

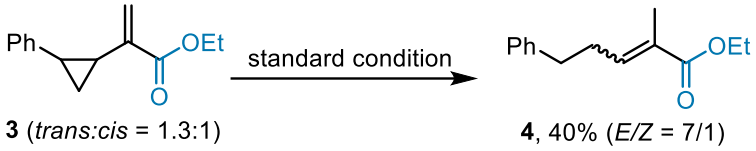
To illustrate the unexpected poor yield of **2k** under standard condition, we built a time-scale profile for this reaction with **1k** as substrate. The hydronation of the vinyl group of **1k** acted as the minor side-reaction to generate **S-1**. A large proportion of **1k** underwent hydrolysis with water to produce **S-2** that was unsuitable for the hydrogenation reaction, while **S-3** from the Michael addition of PPh_3 to **S-2** was also detected. Since acrylic acid was inappropriate for this reaction, we supposed that the hydrolysis of acrylates provided negative effect on the reaction.

5. General Procedures for Mechanism Studies

5.1 Radical capturing experiments



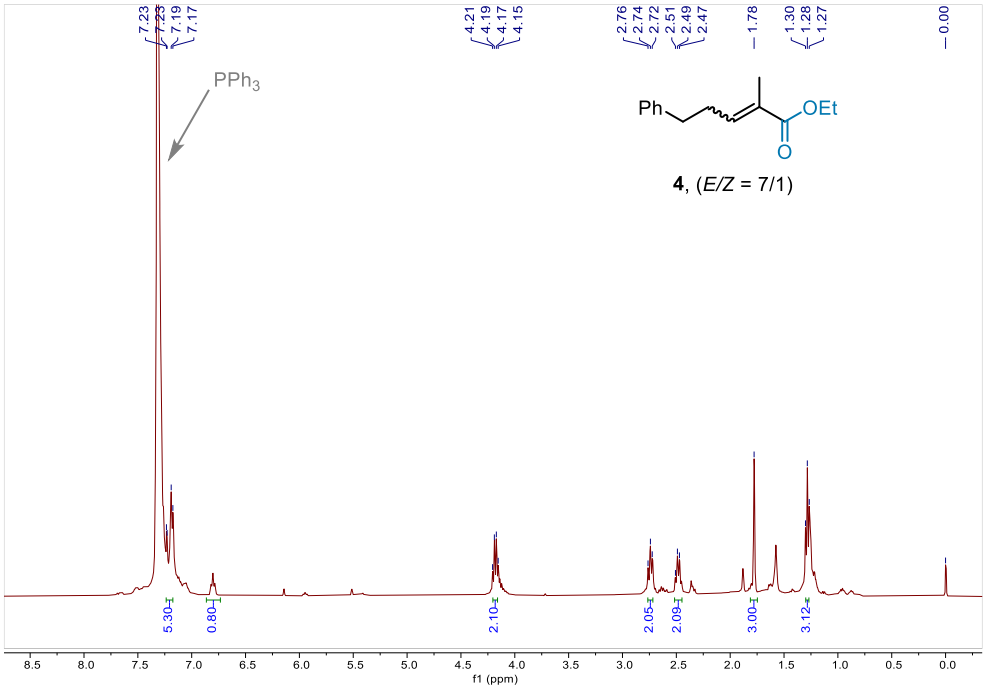
A sealed tube equipped with a stirrer bar was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (4.4 mg, 2.0 mol%), PPh$_3$ (52.5 mg, 1.0 equiv.), and TEMPO (109.4 mg, 3.5 equiv.), then degassed and refilled with N$_2$ for 3 times. After that, anhydrous CH$_3$CN (2 mL), H$_2$O (1 mL), and substrate **1a** (0.2 mmol) were added under N$_2$. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. Products **2a** was not detected, while TEMPO-H was observed by GCMS.



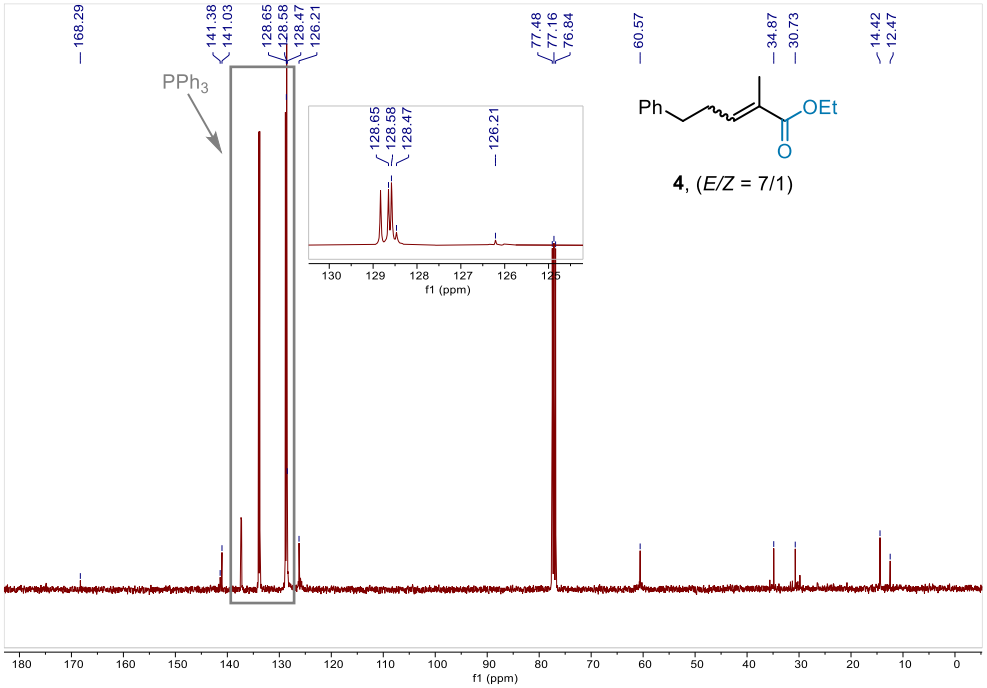
A sealed tube equipped with a stirrer bar was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (4.4 mg, 2.0 mol%) and PPh$_3$ (52.5 mg, 1.0 equiv.), then degassed and refilled with N$_2$ for 3 times. After that, anhydrous CH$_3$CN (2 mL), H$_2$O (1 mL), and substrate **3** (0.2 mmol) were added under N$_2$. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products **4**, which were identified by ^{1}H and ^{13}C NMR.

Ethyl 2-methyl-5-phenylpent-2-enoate (4) (*E*/*Z* = 7:1): colorless liquid. ***E*-isomer:** ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.24 – 7.17 (m, 5H), 6.80 (s, 1H), 4.18 (d, *J* = 7.3 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.52 – 2.45 (m, 2H), 1.78 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 168.3, 141.4, 141.0, 128.6, 128.6, 128.5, 126.2, 60.6, 34.9, 30.7, 14.4, 12.5. The spectroscopic data corresponds to the reported data.[4] ***Z*-isomer:** The NMR peak of the *Z*-isomer was too weak to be assigned one-by-one due to the low ratio of this minor isomer. The *E*/*Z* ratio was

calculated by the crude ^{1}H NMR according to the integral of the peak of benzylic hydrogen (Ph-CH_2-). The spectroscopic data of the *Z*-isomer corresponds to the reported data.[5]

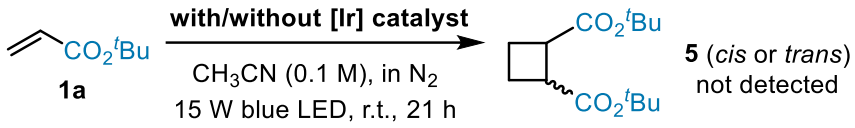


^{1}H NMR for compound **4**

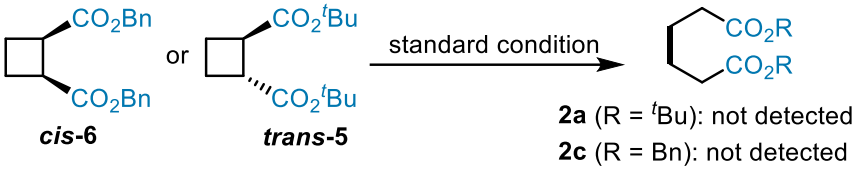


^{13}C{^{1}H} NMR for compound **4**

5.2 Intermediate study

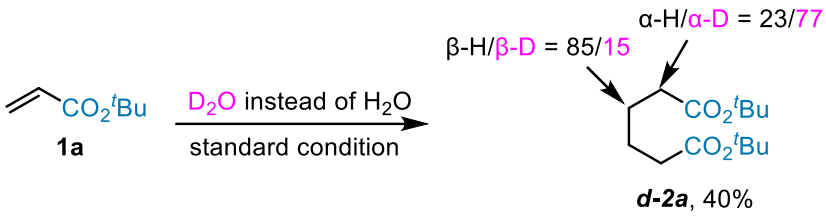


A sealed tube equipped with a stirrer bar was charged with/without Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.4 mg, 2.0 mol%), then degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (2 mL) and substrate **1a** (0.2 mmol) were added under N_2. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was tested by ^{1}H NMR and GCMS to determine the result.



A sealed tube equipped with a stirrer bar was charged with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.4 mg, 2.0 mol%) and PPh_3 (52.5 mg, 1.0 equiv.), then degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (2 mL), H_2O (1 mL), and substrate ***cis*-6** or ***trans*-5** (0.2 mmol) were added under N_2. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was tested by ^{1}H NMR and GCMS to determine the result.

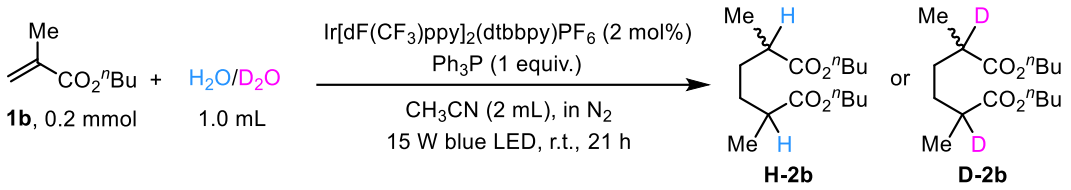
5.3 Deuterium-labelled experiments



A sealed tube equipped with a stirrer bar was charged with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.4 mg, 2.0 mol%) and PPh_3 (52.5 mg, 1.0 equiv.), then

degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (2 mL), D_2O (1 mL), and substrate **1a** (0.2 mmol) were added under N_2. The reaction mixture was irradiated by 15 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was tested by ^1H NMR to determine the deuterium ratio.

5.4 Studies on kinetic isotope effect (KIE)

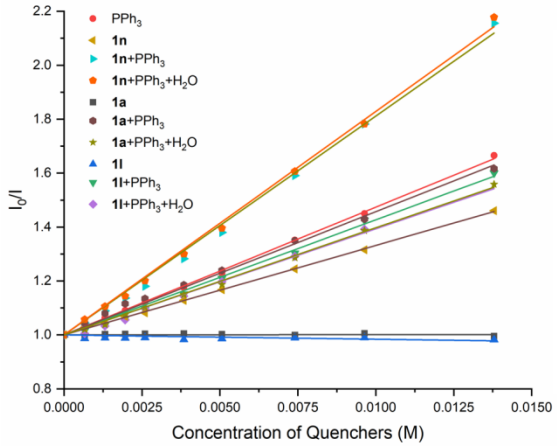


Time	H-2b	D-2b	H-2b/D-2b
1 h	5%	trace	>5.0
2 h	12%	trace	>5.0
4 h	21%	3%	>5.0
6 h	29%	5%	5.8

Fig. S4 Time-scale profile for the reaction of **1b** under standard condition

Time-scale reactions of **1b** under standard condition with H_2O or D_2O were studied to explore the kinetic isotope effect (KIE). To calculate the accurate KIE value, the yield changing in the very beginning of this reaction was needed to be measured. However, the reaction proceeded slowly, making the yield of **2b** hard to be measured accurately. Instead, the ratios of the yield of **H-2b**/**D-2b** (as an index of the average rate) within 6 hours were used to approximate the k_H/k_D. The reactions with D_2O were obviously slower than reactions with H_2O, showing a ratio of **H-2b**/**D-2b** over 5.0 in the beginning, which indicated a primary isotope effect.

6. Stern-Volmer Fluorescence Quenching Experiments



Stern-Volmer constant of various quenchers

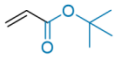
Structure	Quencher	K_{sv} (M^{-1})
-	PPh_3	47.4
 **1n**	**1n**	33.2
	1n +Ph_3P	81.1
	1n +Ph_3P + H_2O	82.9
 **1a**	**1a**	0.102
	1a +Ph_3P	45.7
	1a +Ph_3P + H_2O	39.7
 **1l**	**1l**	-1.61
	1l +Ph_3P	42.7
	1l +Ph_3P + H_2O	39.3

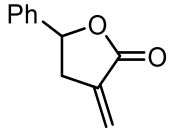
Fig. S5 Fluorescence quenching experiment between photocatalyst and substrate

Fluorescence quenching experiments were measured on an Ahilent Technologies Cary Eclipse Fluoresence Spectrophotometer. The complex Ir[dF(CF_3)ppy]$_2$(dtbbpy) was excited at 375 nm and the emission spectrum max = 475 nm was recorded. Gradient dilution to get 1.0 x 10^{-5} M Ir[dF(CF_3)ppy]$_2$(dtbbpy) solution in CH_3CN, 0.1 M PPh_3 solution in CH_3CN, 0.1 M *tert*-butyl acrylate (**1a**) solution in CH_3CN, 0.1 M *tert*-butyl acrylate + 0.1 M PPh_3 (**1a** + PPh_3) solution in CH_3CN, 0.1 M *tert*-butyl acrylate + 0.1 M PPh_3 + 0.1 M H_2O (**1a** + PPh_3 + H_2O) solution in CH_3CN, and the solutions of **1l** and **1n** were prepared in similar method. 3.0 mL 1.0 x 10^{-5} M Ir[dF(CF_3)ppy]$_2$(dtbbpy) solution in CH_3CN and a stirrer bar were added into the 4.0 mL quartz cuvette covered with Teflon cap. 20 μL of the above solutions were added each time, separately. Then, the emission spectrum of the solution was collected at each addition.

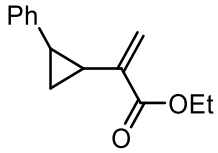
Quenching effects of various quenchers under different concentration were shown in Fig S3. Linear fit based on the Stern-Volmer equation was performed to calculate the Stern-Volmer constant.

$$\frac{I_0}{I} = 1 + K_{sv} \cdot [Q], \quad Q \text{ represents quencher}$$

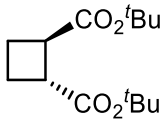
7. Spectra Data for Synthesized Substrates



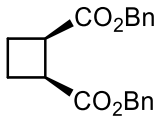
2-Methylene-4-phenylbutyrolactone (1g): ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 – 7.29 (m, 5H), 6.28 (t, *J* = 3.0 Hz, 1H), 5.67 (t, *J* = 2.5 Hz, 1H), 5.51 – 5.48s (m, 1H), 3.38 (ddt, *J* = 17.0, 8.3, 2.8 Hz, 1H), 2.88 (ddt, *J* = 17.4, 6.4, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 170.2, 139.8, 134.2, 128.8, 128.5, 125.4, 122.4, 78.0, 36.2. The spectroscopic data corresponds to the reported data.[1]



Ethyl 2-(2-phenylcyclopropyl)acrylate (*trans:cis* = 1.3:1)(3): Major isomer (*trans*) ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.26 – 7.04 (m, *5*H), 6.10 (s, 1H), 5.39 (s, 1H), 4.24 – 4.18 (m, 2H), 2.08 – 1.96 (m, 2H), 1.28 – 1.15 (m, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.0, 141.6, 137.5, 128.4, 126.3, 125.9, 121.8, 60.8, 26.4, 23.4, 14.2, 8.9. **Minor isomer (*cis*)** ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.26 – 7.04 (m, *5*H), 6.01 (s, 1H), 5.22 (s, 1H), 4.09 – 4.04 (m, 2H), 2.49 – 2.19 (m, 2H), 1.28 – 1.15 (m, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.0, 142.1, 137.6, 129.0, 127.7, 126.0, 124.9, 60.5, 23.7, 21.3, 16.2, 14.2. The spectroscopic data corresponds to the reported data.[2]



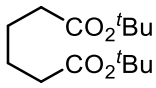
Di*tert*-butyl (1R,2R)-cyclobutane-1,2-dicarboxylate (*trans*-5): ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 3.23 – 3.19 (m, 2H), 2.12 – 2.04 (m, 4H), 1.45 (s, 18H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 173.2, 80.4, 41.8, 28.2, 21.5. The spectroscopic data corresponds to the reported data.[6]



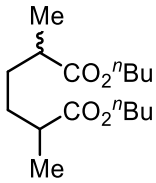
***Rel*-1,2-Bis(phenylmethyl) (1R,2S)-1,2-cyclobutanedicarboxylate (*cis*-6):** ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.34 – 7.27 (m, 10H), 4.98 (ABq, J = 29.7 Hz, 4H), 3.48 – 3.42 (m, 2H), 2.45 – 2.39 (m, 2H), 2.23 – 2.16 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 173.1, 135.9, 128.6, 128.4, 128.3, 66.5, 40.7, 22.2. The spectroscopic data corresponds to the reported data.[7]

8. Spectral Data for All Products

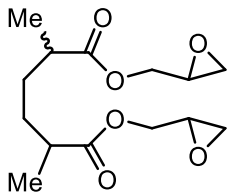
For products with diastereoisomers, **2b-2i**, **2l, 2o-2q** were isolated and characterized as the mixture of the *dl* and *meso* isomer.



Di-*tert*-butyl adipate (2a): colorless oil (18.6 mg, 72%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.25 – 2.20 (m, 4H), 1.63 – 1.58 (m, 4H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 173.0, 80.2, 35.4, 28.2, 24.7. The spectroscopic data corresponds to the reported data.[8]

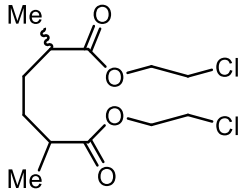


Dibutyl 2,5-dimethylhexanedioate (d.r. 5:1) (2b): colorless oil (24.9 mg, 87%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 4.07 (t, *J* = 6.9 Hz, 4H), 2.48 – 2.33 (m, 2H), 1.65 – 1.57 (m, 6H), 1.44 – 1.34 (m, 6H), 1.15 (d, *J* = 6.9 Hz, 6H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 176.7, 176.6, 64.5, 64.3, 39.8, 39.6, 31.6, 31.3, 30.8, 30.7, 19.4, 19.3, 17.3, 17.1, 13.8. The spectroscopic data corresponds to the reported data.[9]

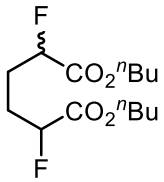


Bis(oxiran-2-ylmethyl) 2,5-dimethylhexanedioate (d.r. 1.2:1) (2c): colorless oil (26.9 mg, 94%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 2/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 4.45 – 4.41 (m, 2H), 3.95 – 3.90 (m, 2H), 3.21 (dd, *J* = 5.7, 3.0 Hz, 2H), 2.84 (t, *J* = 4.4 Hz, 2H), 2.65 (dd, *J* = 4.8, 2.5 Hz, 2H), 2.54 – 2.47 (m, 2H), 1.72 – 1.64 (m, 2H), 1.51 – 1.40 (m, 2H), 1.18 (dd, *J* = 6.9, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 176.2,

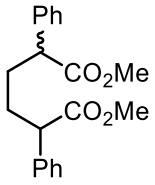
176.2, 65.0, 64.9, 49.5, 44.7, 39.5, 39.4, 39.4, 39.3, 31.3, 31.2, 17.2, 17.2, 17.1, 17.0. The spectroscopic data corresponds to the reported data.[10]



Bis(2-chloroethyl) 2,5-dimethylhexanedioate (d.r. 1.1:1) (2d): colorless oil (26.9 mg, 90%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 4.38 – 4.27 (m, 4H), 3.72 – 3.66 (m, 4H), 2.52 – 2.46 (m, 2H), 1.73 – 1.65 (m, 2H), 1.53 – 1.43 (m, 2H), 1.18 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 176.2, 176.1, 64.0, 41.8, 39.5, 39.4, 31.3, 31.2, 17.2, 17.1. HRMS (ESI+) calculated *m/z* for $C_{12}H_{20}Cl_2NaO_4^+$ $[M+Na]^+$: 321.0631, found 321.0633.

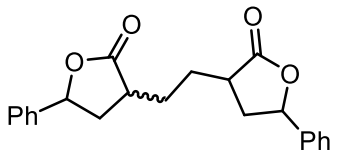


Dibutyl 2,5-difluorohexanedioate (d.r. 1:1) (2e): colorless oil (22.4 mg, 76%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 10/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 5.03 – 4.87 (m, 2H), 4.21 (t, *J* = 6.9 Hz, 4H), 2.17 – 1.98 (M, 4H), 1.70 – 1.62 (m, 4H), 1.44 – 1.35 (M, 4H), 0.95 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 169.6 (d, *J* = 4.0 Hz), 169.3 (d, *J* = 4.0 Hz), 88.3 (d, *J* = 186.8 Hz), 88.1 (d, *J* = 185.8 Hz), 65.7, 30.6, 27.7 (dd, *J* = 21.2, 3.0 Hz), 27.5 (dd, *J* = 21.2, 3.0 Hz), 19.1, 13.8. ^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ -192.5 – -192.8 (m). HRMS (ESI+) calculated *m/z* for $C_{14}H_{24}F_2NaO_4^+$ $[M+Na]^+$: 317.1535, found 317.1537.

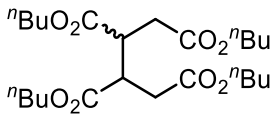


Dimethyl 2,5-diphenylhexanedioate (d.r. 1.1:1) (2f): colorless oil (10.8 mg, 33%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 2/1. ^{1}H NMR (400 MHz, CHLOROFORM-

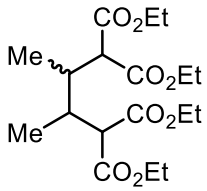
D) δ 7.33 – 7.17 (m, 10H), 3.76 – 3.52 (m, 8H), 2.27 – 1.68 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 174.3, 174.2, 138.8, 138.6, 128.8, 128.8, 128.0, 128.0, 127.5, 52.2, 51.5, 51.5, 31.5, 31.2. The spectroscopic data corresponds to the reported data.[11]



3,3'-(Ethane-1,2-diyl)bis(5-phenyldihydrofuran-2(3*H*)-one) (d.r. 10:1) (2g): white solid (23.1 mg, 66%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 2/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.40 – 7.31 (m, 10H), 5.37 (dd, *J* = 10.5, 5.5 Hz, 2H), 2.85 – 2.76 (m, 4H), 2.12 – 2.02 (m, 2H), 1.94 – 1.82 (m, 2H), 1.72 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 178.1, 138.9, 128.9, 128.7, 125.6, 79.6, 41.3, 37.8, 27.8. HRMS (ESI+) calculated *m/z* for $C_{22}H_{22}NaO_4^+$ $[M+Na]^+$: 373.1410, found 373.1411.

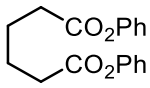


Butan-1,2,3,4-tetracarbonsaeure-tetrabutylester (d.r. 1:1) (2h): colorless oil (34.4 mg, 75%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 10/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 4.09 (tt, *J* = 6.9, 3.9 Hz, 8H), 3.36 – 3.29 (m, 2H), 2.81 (ddd, *J* = 16.5, 14.9, 9.6 Hz, 2H), 2.42 (td, *J* = 17.0, 3.9 Hz, 2H), 1.65 – 1.56 (m, 8H), 1.41 – 1.34 (m, 8H), 0.93 (td, *J* = 7.3, 1.4 Hz, 12H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 172.4, 172.2, 171.6, 171.6, 65.3, 65.2, 64.9, 64.8, 42.5, 42.4, 33.4, 33.4, 30.7, 30.6, 19.2, 13.8. The spectroscopic data corresponds to the reported data.[12]

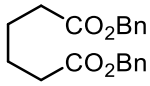


Tetraethyl 2,3-dimethylbutane-1,1,4,4-tetracarboxylate (d.r. 1.5:1) (2i): colorless oil (31.1 mg, 66%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 4.25 – 4.16 (m, 8H), 3.48 (d, *J* = 6.4 Hz, 2H), 3.33 (d, *J* = 10.1 Hz, 2H), 2.42

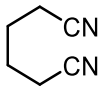
– 2.35 (m, 2H), 1.30 – 1.25 (m, 12H), 1.07 (d, J = 6.4 Hz, 6H), 0.90 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 169.1, 168.6, 168.5, 168.2, 61.5, 61.4, 61.2, 56.7, 54.1, 36.6, 34.8, 14.7, 14.1, 14.1, 11.6. The spectroscopic data corresponds to the reported data.[13]



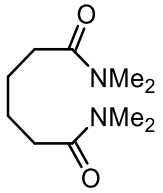
Diphenyl adipate (2j): colorless oil (9.2 mg, 31%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 (t, J = 8.3 Hz, 4H), 7.23 (t, J = 7.3 Hz, 2H), 7.09 (d, J = 7.8 Hz, 4H), 2.67 – 2.61 (m, 4H), 1.91 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 171.9, 150.8, 129.6, 126.0, 121.7, 34.1, 24.4. The spectroscopic data corresponds to the reported data.[8]



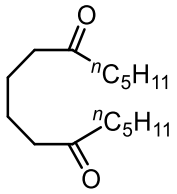
Dibenzyl adipate (2k): colorless oil (9.8 mg, 30%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 – 7.29 (m, 10H), 5.11 (s, 4H), 2.40 – 2.35 (m, 4H), 1.71 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 173.2, 136.1, 128.7, 128.3, 66.4, 34.0, 24.5. The spectroscopic data corresponds to the reported data.[8]



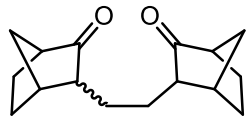
Adiponitrile (2l): colorless oil (9.4 mg, 87%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 1/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.47 – 2.42 (m, 4H), 1.90 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 118.8, 24.4, 16.8. The spectroscopic data corresponds to the reported data.[8]



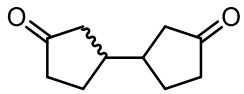
***N,N,N′,N′*-tetramethyladipamide (2m):** light yellow oil (4.0 mg, 20%). Eluent for the flash chromatography with silica gel: CH_2Cl_2 / MeOH: 20/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 3.01 (s, 6H), 2.94 (s, 6H), 2.38 – 2.32 (m, 4H), 1.70 – 1.67 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 172.9, 37.4, 35.4, 33.3, 25.1. The spectroscopic data corresponds to the reported data.[14]



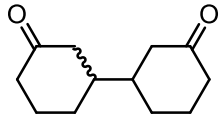
Hexadecane-6,11-dione (2n): white solid (22.9 mg, 90%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 10/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.42 – 2.36 (m, 8H), 1.60 – 1.52 (m, 8H), 1.33 – 1.24 (m, 8H), 0.89 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 211.2, 43.0, 42.6, 31.5, 23.7, 23.4, 22.6, 14.0. The spectroscopic data corresponds to the reported data.[15]



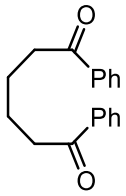
(1R,3S,4S)-3-(2-((1R,4S)-3-oxobicyclo[2.2.1]heptan-2-yl)ethyl)bicyclo[2.2.1]heptan-2-one (d.r. 1:1) (2o): white solid (18.5 mg, 75%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 2/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.64 – 2.61 (m, 4H), 2.04 – 1.96 (m, 2H), 1.84 – 1.80 (m, 2H), 1.76 – 1.66 (m, 4H), 1.62 – 1.54 (m, 6H), 1.43 – 1.38 (m, 2H), 1.25 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 219.9, 219.7, 54.0, 53.2, 50.6, 50.5, 38.2, 37.9, 37.1, 25.5, 25.4, 25.2, 24.4, 21.2, 21.1. HRMS (EI+) calculated *m/z* for $C_{16}H_{22}O_2^+$ $[M]^+$: 246.1614, found 246.1615.



[1,1′-Bicyclopentyl]-3,3′-dione (d.r. 1:1) (2p): colorless oil (12.5 mg, 75%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.50 – 2.32 (m, 4H), 2.31 – 2.08 (m, 6H), 1.99 – 1.81 (m, 2H), 1.66 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 218.4, 218.3, 44.1, 43.6, 42.9, 42.7, 38.6, 38.6, 28.7, 27.8. The spectroscopic data corresponds to the reported data.[16]



[1,1′-Bicyclohexyl]-3,3′-dione (d.r. 1:1) (2q): colorless oil (13.2 mg, 68%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 5/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.47 – 2.37 (m, 4H), 2.31 – 2.22 (m, 2H), 2.13 – 2.07 (m, 4H), 1.93 – 1.90 (m, 2H), 1.77 – 1.59 (m, 4H), 1.45 – 1.37 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 211.4, 211.4, 45.4, 45.0, 43.9, 43.8, 41.5, 28.5, 28.3, 25.4, 25.3. The spectroscopic data corresponds to the reported data.[16]



1,6-Diphenylhexane-1,6-dione (2r): white solid (8.0 mg, 30%). Eluent for the flash chromatography with silica gel: hexane / EtOAc: 10/1. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.00 – 7.92 (m, 4H), 7.58 – 7.54 (m, 2H), 7.48 – 7.44 (m, 4H), 3.07 – 3.02 (m, 4H), 1.87 – 1.83 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 200.2, 137.1, 133.1, 128.7, 128.2, 38.6, 24.0. The spectroscopic data corresponds to the reported data.[15]

9. Details and notes on calculations

9.1 Calculation Methods[17]

All efforts to find the HAT transition state of $Ph_3POH^{\cdot}$ to acrylonitrile were failed, but the leap of the spin population between these two fragments during the scanning of O-H bond length suggests a potential energy surface(PES) crossing. These pre-exploration are done in the level of ωB97X-D/def2-SVP(with SMD implicit solvation model for acetonitrile solvents) by Gaussian16 B.01 for geometry optimization, frequency analysis and PES scan. KST48 are used for searching fof PCET crossing point combined with single point energy and force information from Gaussian. A concerted PCET crossing point between $^{\cdot}Ph_3P\text{-}OH...NC\text{-}CH{=}CH_2$ and $Ph_3P{=}O...HN{=}C{=}CH\text{-}CH_2^{\cdot}$ is found. The downhill curve lead to correct pre-complex reactant and product with their correct and stable wavefunction. Optimization of these two points give the exact pre-complex reactant and product. The other two paths are also dealt in this process.

Describing the electron structure of $Ph_3POH^{\cdot}$ and the PCET crossing points of with significant static correlation effects is challenging for both DFT and post Hartree-Fock methods. Benchmarks with criterion of the relative energy of the PCET crossing point for the H transferred to the N were carried out. The reference single point energy is done in the level of NEVPT2(15e,14o)/def2-TZVPP(with SMD implicit solvation model for acetonitrile solvents) by ORCA 6.0 with the geometry in ωB97X-D/def2-SVP(with SMD implicit solvation model for acetonitrile solvents). The methods tested include DLPNO-CCSD(T), PBE-D3(BJ), PBE0-D3(BJ), B3LYP-B3(BJ), TPSSh-D3(BJ), M06-D3, M06-2X-D3, ωB97X-D and CAM-B3LYP-D3(BJ) with def2-TZVPP basis and geometry in ωB97X-D/def2-SVP. Auxiliary basis def2/J and def2-TZVPP/C are utilized in NEVPT2 and DLPNO-CCSD(T) calculations by ORCA 6.0. It was found that ωB97X-D gives a correct description and performs better than the post-Hartree-Fock method DLPNO-CCSD(T). Therefore, all DFT calculations were performed at the ωB97X-D/def2-TZVPP//ωB97X-D/def2-SVP (with SMD) level by Gaussian16B. The Gibbs free energy is obtained from the sum of the single point energy

at ωB97X-D/def2-TZVPP (with SMD) level and the thermodynamic corrections from the frequency analysis at ωB97X-D/def2-SVP (with SMD) level. Thermodynamic corrections of crossing points are conducted by KST48-freq and Goodvibes with quasi-RRHO method. All transition states and crossing points are confirmed by IRC or keyword IRC=downhill. The Gibbs free energy is NEVPT2(13e,12o)/def2-TZVPP with SMD calculation is also done for $Ph_3POH^{\cdot}$. The $E_{1/2}$ of $Ph_3POH^{+} + e^{-} \rightarrow Ph_3POH^{\cdot}$ is approximated by absolute potential from Gibbs free energy minus 4.28V.

The spin population colouring maps are drafted by GaussView 6.0. All visualization of molecular orbitals(MOs) and isosurfaces are done by Multiwfn 3.8 and VMD 1.9.3. The Independent Gradient Model based on Hirshfeld partition(IGMH) analysis for weak interactions and Extended Transition State-Natural Orbitals for Chemical Valence(ETS-NOCV) analysis for orbital interactions are done by Multiwfn 3.8. In IGMH and ETS-NOCV analysis, the wavefunction of $^{\cdot}Ph_3P\text{-}OH...NC\text{-}CH{=}CH_2$ with two fragments of radical $Ph_3POH^{\cdot}$ and neutral acrylonitrile before SET are chosen.

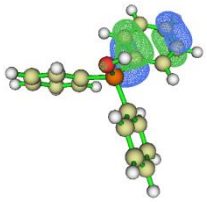
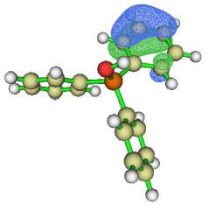
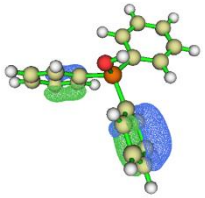
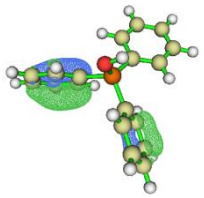
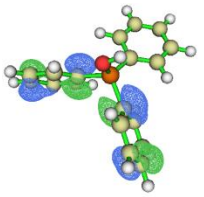
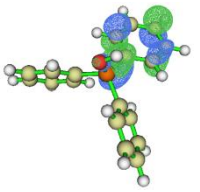
9.2 Benchmark

Table S1. Relative Single Point Energy of [N-cp]

Method	E_{rel}(kcal/mol) of [N-cp]
NEVPT2(15,14)	4.64
DLPNO-CCSD(T)	7.10
PBE-D3(BJ)	-1.40
PBE0-D3(BJ)	2.23
B3LYP-D3(BJ)	1.29
TPSSh-D3(BJ)	0.51
M06-D3	2.90
M06-2X-D3	3.47
ωB97X-D	**3.58**
CAM-B3LYP-D3(BJ)	3.52

9.3 NEVPT2 Calculations of $Ph_3POH^{\cdot}$,[N-pre] and [N-cp]

Table S2. Active Orbitals and Occupation Numbers from NEVPT2(13e,12o) of $Ph_3POH^{\cdot}$

MO Number	Energy (Hartree)	MO Type	MO Diagram (isovalue = 0.05)	Occupation Number
68	-0.344428	π(-Ph1)		1.97
69	-0.369232	π(-Ph1)		1.94
70	-0.383087	π(-Ph2) π(-Ph3)		1.92
71	-0.379539	π(-Ph2) π(-Ph3)		1.92
72	-0.329388	π(-Ph2) π(-Ph3)		1.75
73	-0.299492	π(-Ph2) π(-Ph3)		1.69
74	-0.013149	π^*(-Ph1)		0.78

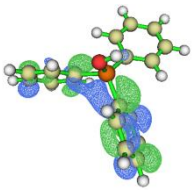
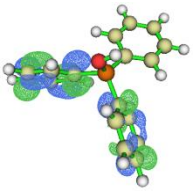
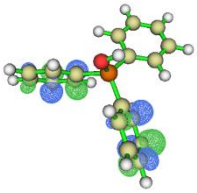
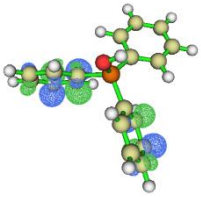
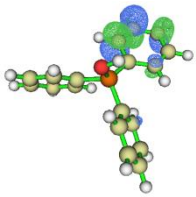
75	0.036726	π(P) π*(-Ph2) π*(-Ph3)		0.56
76	0.100074	π*(-Ph2) π*(-Ph3)		0.25
77	0.222558	π*(-Ph2) π*(-Ph3)		0.08
78	0.229542	π*(-Ph2) π*(-Ph3)		0.08
79	0.243343	π*(-Ph1)		0.07

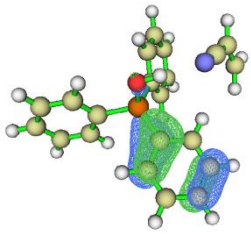
Table S3. Configurations from NEVPT2(13e,12o) of $Ph_3POH^{\cdot}$

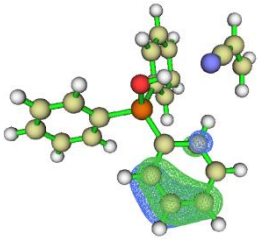
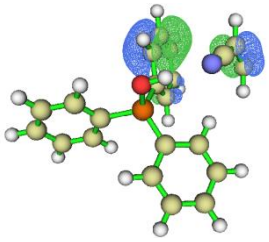
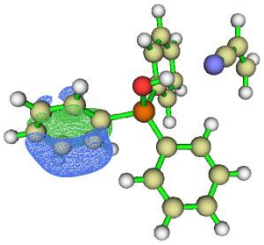
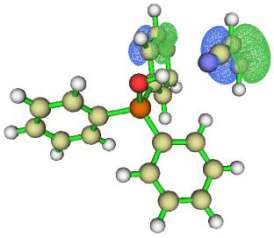
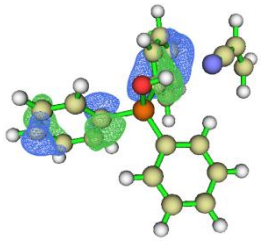
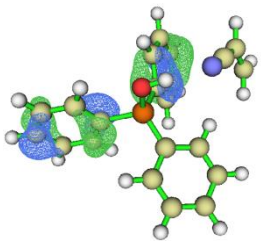
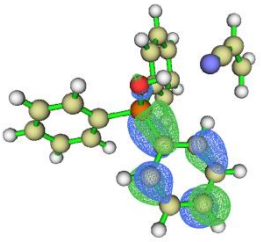
Root	Configuration Factor	Configuration
Doublet Root 0 0 eV	0.82883	222222100000
	0.01772	222211111000
	0.01500	212222100001
	0.01411	202222100002
	0.00944	221122100110
	0.00604	222220102000
	0.00524	222121101010
	0.00522	222202120000
	0.00488	222220120000
	0.00487	112222200001
	0.00474	221212110100
	0.00471	222022100020
	0.00452	220222100200
	0.00420	221221110010

	0.00385	222202102000
	0.00371	222121110100
	0.00359	222112101100
	0.00348	221221101100
	0.00333	222112110010
	0.00291	222022100200
	0.00281	221212101010
	0.00256	220222100020
Doublet Root 1 2.341 eV	0.79227	222222010000
	0.01591	122222110000
	0.01403	112222110001
	0.01292	022222210000
	0.01230	202222010002
	0.00895	221122010110
	0.00770	222211021000
	0.00663	222220012000
	0.00555	222221011000
	0.00516	222121011010
	0.00455	222022010020
	0.00435	220222010200
	0.00433	221222010100
	0.00323	222221101000
	0.00317	221221011100
	0.00312	222202012000
	0.00309	222212020000
	0.00287	222222000100
	0.00279	222112011100
	0.00274	222022010200
	0.00265	222222000001
Quartet Root 0 0 eV	0.49513	222221110000
	0.26228	222212101000
	0.02421	222122100100
	0.02239	221222100010
	0.01435	222212110000
	0.01117	222221101000
	0.00931	222210121000
	0.00886	212221110001
	0.00849	202221110002
	0.00814	222201112000
	0.00695	221121110110
	0.00524	222111111100
	0.00477	212212101001

	0.00476	221211111010
	0.00463	221222100100
	0.00449	202212101002
	0.00411	222122100010
	0.00385	221112101110
	0.00297	220221110200
	0.00295	222021110020
	0.00286	112221210001
Quartet Root 1 0.092 eV	0.39984	222212110000
	0.36493	222221101000
	0.02937	222122100010
	0.02741	221222100100
	0.00931	222210112000
	0.00923	222212101000
	0.00876	222201121000
	0.00723	212212110001
	0.00688	202212110002
	0.00659	212221101001
	0.00622	202221101002
	0.00604	222111111010
	0.00599	221211111100
	0.00597	221112110110
	0.00550	221121101110
	0.00303	220212110200
	0.00291	222012110020
	0.00290	222021101020
	0.00282	222221110000
	0.00258	220221101200

Table S4. Active Orbitals and Occupation Numbers from NEVPT2(15e,14o) of [N-pre]

MO Number	Energy (Hartree)	MO Type	MO Diagram (isovalue = 0.05)	Occupation Number
81	-0.342245	π(-Ph1)		1.97

82	-0.367758	π(-Ph1)		1.94
83	-0.390186	π(-Ph2) π(acrylonitrile)		1.92
84	-0.380934	π(-Ph3)		1.92
85	-0.385629	π(-Ph2) π(acrylonitrile)		1.91
86	-0.328418	π(-Ph2) π(-Ph3)		1.75
87	-0.298450	π(-Ph2) π(-Ph3)		1.69
88	-0.010020	π(P) π*(-Ph1)		0.78

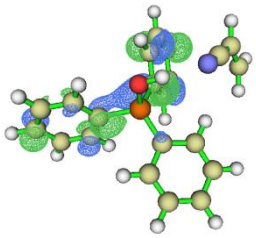
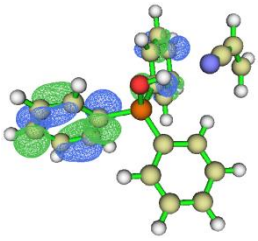
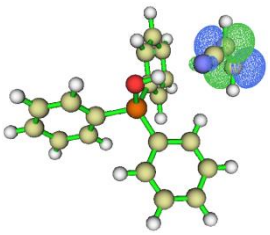
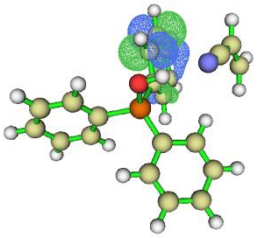
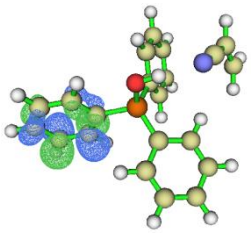
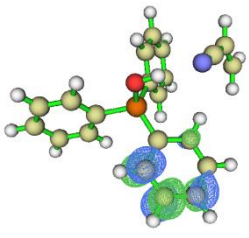
89	0.038712	π(P) π*(-Ph2) π*(-Ph3)		0.56
90	0.099763	π*(-Ph2) π*(-Ph3)		0.25
91	0.181654	π*(acrylonitrile)		0.09
92	0.229523	π*(-Ph2)		0.08
93	0.223158	π*(-Ph3)		0.08
94	0.245698	π*(-Ph1)		0.07

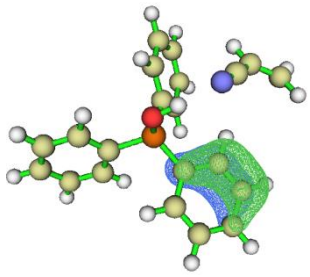
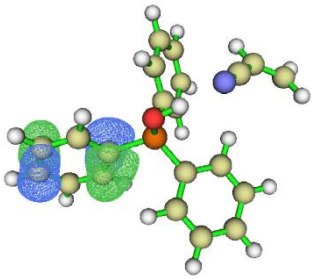
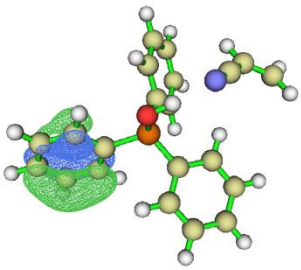
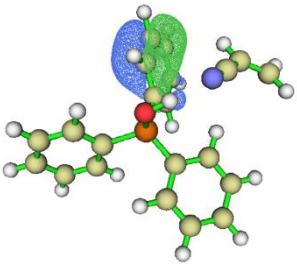
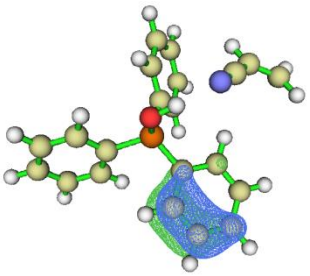
Table S5. Configurations from NEVPT2(15e,14o) of [N-pre]

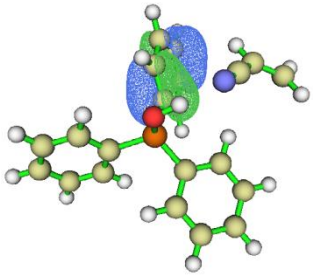
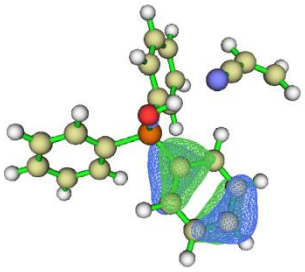
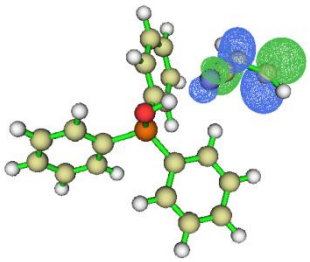
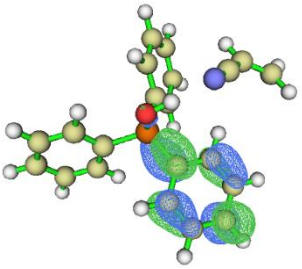
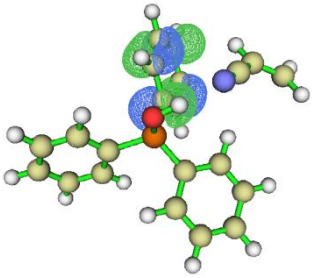
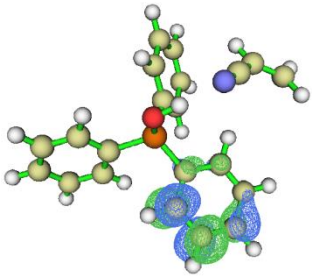
Root	Configuration Factor	Configuration
Doublet Root 0 0 eV	0.79320	22222212000000
	0.02165	22222210000002
	0.01678	12212212100100

	0.01410	22122212001000
	0.01400	22022212002000
	0.01382	22222012020000
	0.01022	21222211000002
	0.00767	20222212000020
	0.00616	22212112010100
	0.00578	22202212000200
	0.00499	02222212200000
	0.00478	12222112010100
	0.00474	22121222001000
	0.00472	22202212200000
	0.00425	21212212100010
	0.00422	21222211000020
	0.00420	11222212100010
	0.00373	02222212000200
	0.00334	22212112110000
	0.00268	12222112110000
Doublet Root 1 3.699 eV	0.76065	22222202100000
	0.02110	22222200100002
	0.01478	22221212100000
	0.01376	22121212101000
	0.01323	22222002120000
	0.01274	22220222100000
	0.01224	22022202102000
	0.00977	21222201100002
	0.00760	20222202100020
	0.00738	12212202200100
	0.00639	22202202100200
	0.00628	22212102110100
	0.00516	22212202100100
	0.00415	21222201100020
	0.00402	12222102110100
	0.00333	12222202200000
	0.00308	02222202100200
	0.00281	21222202100010
	0.00271	22212212000100
Quartet Root 0 0 eV	0.47277	22212212100000
	0.24932	12222212000100
	0.02411	22222112010000
	0.02154	21222212000010
	0.01940	12222212100000
	0.01292	22212210100002

	0.00940	22212012120000
	0.00885	12202212200100
	0.00865	22212212000100
	0.00838	22012212102000
	0.00830	22112212101000
	0.00791	02212212100200
	0.00697	22222211000010
	0.00682	12222210000102
	0.00634	12212112110100
	0.00607	21212211100002
	0.00561	20212212100020
	0.00543	12222012020100
	0.00446	12122212001100
	0.00442	12022212002100
	0.00388	11212212100110
	0.00320	11222211000102
	0.00312	21212211100020
	0.00291	10222212000120
	0.00278	22111222101000
Quartet Root 1 0.083 eV	0.37387	12222212100000
	0.35489	22212212000100
	0.03245	22222112010000
	0.01841	21222212000010
	0.01365	12222212000100
	0.01023	12222210100002
	0.00969	22212210000102
	0.00878	12202212100200
	0.00849	02212212200100
	0.00783	22212012020100
	0.00762	12222012120000
	0.00665	12022212102000
	0.00664	12122212101000
	0.00630	22112212001100
	0.00627	22012212002100
	0.00587	12212112110100
	0.00552	22222211000010
	0.00479	11222211100002
	0.00472	11212212100110
	0.00456	21212211000102
	0.00449	10222212100020
	0.00397	20212212000120

Table S6. Active Orbitals and Occupation Numbers from NEVPT2(15e,14o) of [N-cp]

MO Number	Energy (Hartree)	MO Type	MO Diagram (isovalue = 0.05)	Occupation Number
81	-0.449713	π(-Ph1)		1.97
82	-0.356297	π(-Ph3)		1.94
83	-0.367438	π(-Ph3)		1.93
84	-0.384719	π(-Ph2)		1.92
85	-0.404348	π(-Ph1)		1.91

86	-0.318497	π(-Ph2)		1.71
87	-0.297588	π(-Ph1)		1.48
88	-0.018317	π*(acrylonitrile)		1.00
89	0.021676	π(P) π*(-Ph1)		0.53
90	0.075960	π*(-Ph2)		0.29
91	0.226983	π*(-Ph1)		0.09

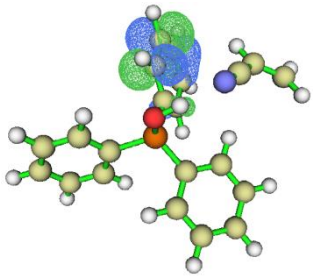
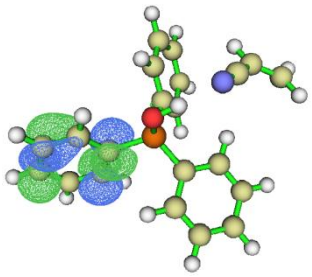
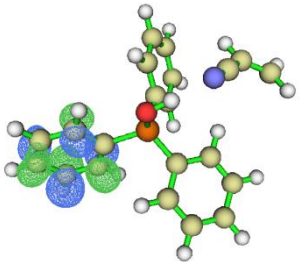
92	0.219074	π^*(-Ph2)		0.08
93	0.138576	π^*(-Ph3)		0.07
94	0.192461	π^*(-Ph3)		0.06

Table S7. Configurations from NEVPT2(15e,14o) of [N-cp]

Root	Configuration Factor	Configuration
Doublet Root 0 0 eV	0.80527	22222221000000
	0.02361	22222201200000
	0.02020	22222021020000
	0.01776	22221211101000
	0.01767	22212121010100
	0.01660	21122221000011
	0.01538	22022221000002
	0.01466	20222221000020
	0.01449	22202221000200
	0.01353	22220221002000
Doublet Root 1 3.699 eV	0.77502	22222211100000
	0.03070	22221221001000
	0.01967	22222011120000
	0.01826	22220211102000
	0.01712	22212111110100
	0.01599	21122211100011
	0.01482	22022211100002
	0.01412	20222211100020

	0.01395	22202211100200
	0.01293	22222220100000
	0.00657	22220221101000
	0.00441	22221201201000
	0.00388	22221211002000
	0.00339	22221211101000
	0.00333	22221211200000
	0.00329	22222201101000
Quartet Root 0 0 eV	0.79121	22222211100000
	0.03080	22221221001000
	0.02008	22222011120000
	0.01862	22220211102000
	0.01747	22212111110100
	0.01632	21122211100011
	0.01512	22022211100002
	0.01441	20222211100020
	0.01424	22202211100200
	0.00659	22220221101000
	0.00445	22221201201000
	0.00395	22221211002000
	0.00341	22221211101000
	0.00337	22221211200000
	0.00332	22222201101000
Quartet Root 1 0.526 eV	0.74523	22222121010000
	0.05884	22212221000100
	0.02234	22222101210000
	0.01908	22202121010200
	0.01663	22221111111000
	0.01545	21122121010011
	0.01424	22022121010002
	0.01371	20222121010020
	0.01252	22220121012000
	0.00821	22222121100000
	0.00573	22212021020100
	0.00524	22202221010100
	0.00362	22212121020000
	0.00358	22212121000200
	0.00342	22222021010100
	0.00342	22212121010100
	0.00286	21222221000010

9.4 Attachment details of Gibbs free energy diagram

Gibbs free energy change of red-ox and acid-base reactions in Figure 5, which is difficult to get exact activation energy barriers by DFT calculations are shown in Table S8. Formation of the active species as $[Ir^{II}]$+$Ph_3P^{+\cdot}$ and $Ph_3POH^{\cdot}$ are feasible, and reactions in work-up stage are all spontaneous. The SET pathway with a Gibbs free energy change of +18.79 kcal/mol are higher than the PCET pathway via [N-cp] with a +12.73 kcal/mol barrier in energy. The SET pathway similarly generating linear products is also a possible pathway, however, should be a side pathway based on the following considerations. Firstly, it is unfavorable both thermodynamically and kinetically compared to the PCET reaction undergoing [N-cp]. Secondly, when an equivalent of acrylonitrile radical anion is generated, an equivalent amount of $Ph_3P^{+\cdot}$ is simultaneously generated, followed by the generation of an equivalent amount of $Ph_3POH^{\cdot}$ and the PCET reaction. Therefore, there must be more molecules undergoing PCET pathway than undergoing SET pathway. The unsuccessful substrates scope also confirms this inference, where vinyl benzene and vinyl sulfones that promote the SET cannot be converted to the desired products. Only carbonyl and carboxylic acid derivatives with heteroatoms and isomeric forms of enolized derivatives are capable of this reaction.

Table S8. Red-Ox and Acid-Base Reactions in Figure 5

Reaction Formula	$\Delta_r G$(kcal/mol)
T-$[Ir^{III}]^+$ + Ph_3P → $[Ir^{II}]$ + $Ph_3P^{+\cdot}$	-5.29
$Ph_3P^{+\cdot}$ + Ph_3P + H_2O → $Ph_3POH^{\cdot}$ + Ph_3PH^+	+3.61
$[Ir^{II}]$ + CH_2CHCN → $[Ir^{III}]^+$ + $CH_2CHCN^{-\cdot}$	+13.30
[SET-Int4] + Ph_3PH^+ → [α-Int4] + Ph_3P	-46.79
[N-Int4] + $[Ir^{II}]$ + Ph_3PH^+ → [L-P] + $[Ir^{III}]^+$ + Ph_3P	-84.64
[α-Int4] + $[Ir^{II}]$ + Ph_3PH^+ → [L-P] + $[Ir^{III}]^+$ + Ph_3P	-59.31
[β-Int4] + $[Ir^{II}]$ + Ph_3PH^+ → [B-P] + $[Ir^{III}]^+$ + Ph_3P	-60.20

The Giese addition reaction from complex **[SET-Int3]** to **[SET-Int4]** is a nearly barrierless process. As shown in Fig. S6, the scan curve of C-C bond is monotonically increasing. This suggests the possibility that this Giese addition reaction may either be a diffusion-controlled process, or a process with a transition state of conformation rotation, making it difficult to identify a clear transition state. The total barrier of this pathway is approximated by the barrier of **[SET-Int3]**.

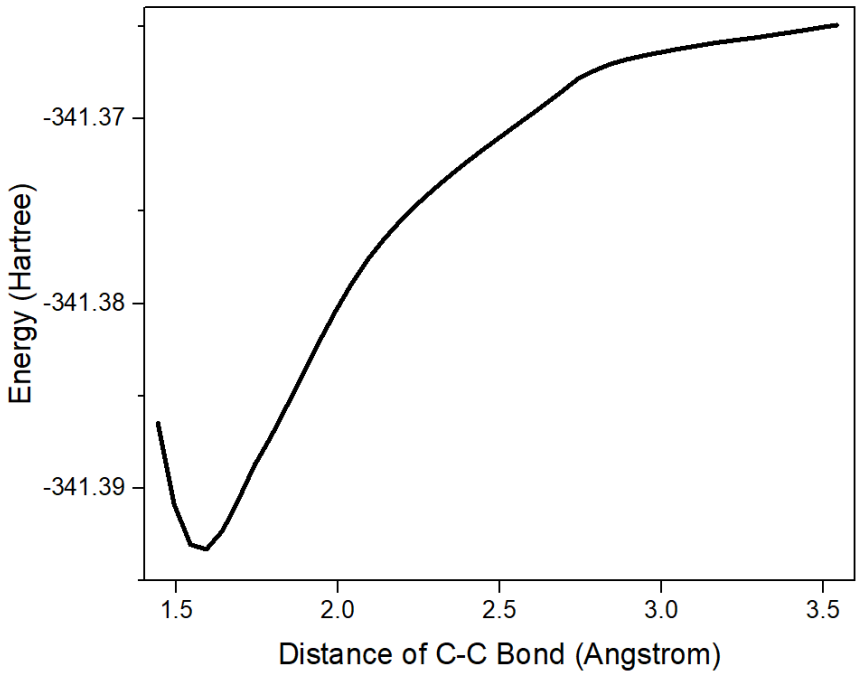


Fig. S6 Energy profile of C-C bond length from flexible PES scan of **[SET-Int4]**

9.5 Electron structure details of PCET crossing points[18]

The electronic structural details of the PCET crossing points will be discussed to explain the selectivity. Fig. S7a shows the relative electronic energies of five points along the downhill curves in both the forward and reverse directions at the crossing point of three reaction sites. The shape of the curves clearly reveals the intersection of two PESs. The attached pictures in Fig. S7a show the spin densities of the wavefunctions at the geometry of **[N-cp]** on two PESs. These surfaces correspond to electronic structures where the single electron is mainly distributed on $Ph_3POH^{\cdot}$ and acrylonitrile, respectively. The crossing point represents the SET from $Ph_3POH^{\cdot}$ to acrylonitrile, followed by proton transfer to acrylonitrile with no energy barrier. Fig.

S7b to S7d visualize the intermolecular interaction derived from IGMH analysis; the deformation density maps, eigenvalue of charge transfer, interaction energies, and the percentage of total orbital interaction energy for the most significant contributing orbitals from the ETS-NOCV analysis are also shown in the right part. For **[α-cp]** and **[β-cp]**, the isosurfaces from IGMH analysis primarily appear in green, indicating that the weak interaction between acrylonitrile and $Ph_3POH^{\cdot}$ is dominated by dispersion. The deformation density of the orbital interactions shows that the charge is transferring from the p orbital of a neighboring C to the region between the H and C, corresponding to the inductive polarization effect of the hydrogen on the double bond of acrylonitrile. For **[N-cp]**, the isosurfaces from IGMH analysis show a blue region at the center of the N...H bond, indicating a strong hydrogen bond. The deformation density of the orbital interactions also aligns with the formation of hydrogen bond, and both the charge transfer eigenvalue and interaction energy are significantly higher than those at the other two crossing points. These analyses suggest that the formation of the hydrogen bond is the main reason for the significantly lower energy of **[N-cp]** compared to **[α-cp]** and **[β-cp]**.

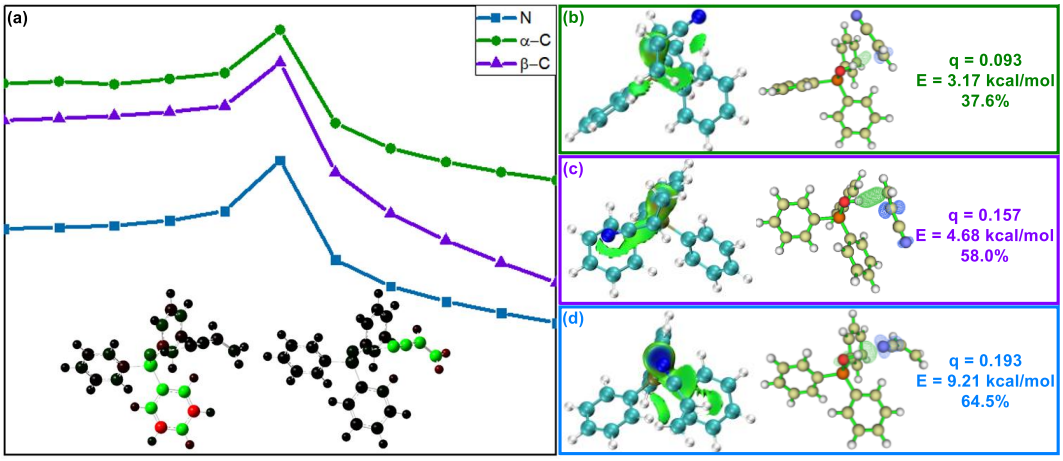


Fig. S7 Details of three PCET conical crossing points.

Table S9. Points in Downhill Curve of [N-cp]

Reaction Coordinate	Electron Energy (Hartree)
-3.65969	-1281.849026
-3.55021	-1281.848963
-3.23164	-1281.848992

-2.902	-1281.848793
-2.57354	-1281.848832
-2.24688	-1281.848756
-1.91465	-1281.848697
-1.58254	-1281.848629
-1.25238	-1281.84855
-0.93562	-1281.84841
-0.60635	-1281.848053
-0.28557	-1281.847348
0	-1281.843681
0.31312	-1281.850893
0.62488	-1281.852805
0.9572	-1281.853887
1.29176	-1281.854736
1.62654	-1281.855446
1.96162	-1281.856204
2.2955	-1281.857341
2.62895	-1281.859639
2.94758	-1281.862484
3.27486	-1281.864687
3.59324	-1281.862348
3.71297	-1281.865879

Table S10. Points in Downhill Curve of [α-cp]

Reaction Coordinate	Electron Energy (Hartree)
-1.36379	-1281.838127
-1.26126	-1281.837972
-0.93673	-1281.838179
-0.60901	-1281.83779
-0.28867	-1281.837358
0	-1281.834229
0.32149	-1281.840986
0.63813	-1281.842821
0.97375	-1281.843804
1.31153	-1281.844535
1.6492	-1281.845127
1.98553	-1281.8456
2.31999	-1281.846064
2.65217	-1281.846632
2.97306	-1281.846441
3.30634	-1281.847563
3.64505	-1281.848198

3.9835	-1281.848903
4.32133	-1281.849981
4.65992	-1281.852251
4.99833	-1281.857252
5.31212	-1281.861699
5.63619	-1281.863929
5.9627	-1281.865816
6.277	-1281.866617
6.60831	-1281.869483
6.94397	-1281.872205
7.27787	-1281.874124
7.61661	-1281.875716
7.95435	-1281.876815
8.29419	-1281.877865
8.6328	-1281.878575
8.97098	-1281.879234
9.30536	-1281.879537
9.63245	-1281.879671
9.73553	-1281.879477

Table S11. Points in Downhill Curve of [β-cp]

Reaction Coordinate	Electron Energy (Hartree)
-4.47294	-1281.841569
-4.38221	-1281.841682
-4.06539	-1281.841637
-3.74508	-1281.841544
-3.42354	-1281.841419
-3.10503	-1281.841332
-2.79717	-1281.841243
-2.4799	-1281.841188
-2.16291	-1281.841073
-1.84843	-1281.840943
-1.53205	-1281.840784
-1.21231	-1281.840659
-0.89361	-1281.840465
-0.57465	-1281.840191
-0.27827	-1281.83975
0	-1281.836615
0.30587	-1281.844562
0.61319	-1281.847548
0.93241	-1281.849481
1.25229	-1281.851083

1.57401	-1281.852541
1.89648	-1281.854065
2.21798	-1281.855802
2.53876	-1281.858189
2.8578	-1281.862778
3.17754	-1281.873091
3.49127	-1281.884049
3.78585	-1281.887455
4.09041	-1281.888577
4.39578	-1281.890288
4.69403	-1281.89224
4.78774	-1281.889338

9.6 Overall Picture of Hydrogen Transfer to Electron-Deficient Alkenes

Fig. S8 combines several hypothetical scenarios to provide a brief description of the overall mechanism for hydrogen transfer to electron-deficient olefins, illustrating why hydrogen bonding and the concerted PCET mechanism lead to reverse selectivity. Figure 8a depicts the situation where the weak interactions between the two species are neglected, treating them as isolated species. The reaction coordinates of the two PES before and after electron transfer are defined by the species before and after proton transfer, and the crossing point is approximated by a straight line connecting the two surfaces. Since the radical **[β-Int2]** formed by β-H addition is a stable radical, the crossing point energy of **[β-cp]** is lower than **[N-cp]′**, leading to the formation of branched products. When weak interactions between the two species are considered (Fig. S8b), both the reactant and product complexes will experience a significant energy decrease, lowering the crossing point energy of **[N-cp]**, thereby selectively generating the linear product. Fig. S8c illustrates the mechanism when a 2-aminopropyl radical acts as the H donor. The reaction first proceeds via a SET to form a hydrogen-bonded intermediate of iminium cation and an acrylonitrile radical anion. However, the barrier for proton transfer to β-C is lower than to N in the presence of the [N-H···N] hydrogen bond, leading to the branched product that is contradictory to the experimental results. Fig. S8d shows the mechanism with a cyclohexadienyl radical as the H donor. The hydrogen atom is favored of transferring to the β-C to generates the most stable radical

through the classical concerted HAT, which is inconsistent with the formation of linear products. In summary, the active species $Ph_3POH^{\cdot}$, acting as both an active electron and proton donor, leads to a concerted PCET mechanism. The formation of hydrogen bonds lowers the energy of the crossing point for H transfer to the heteroatom compared to the C atom, which also accounts for the anomalous selectivity observed in the reactions.

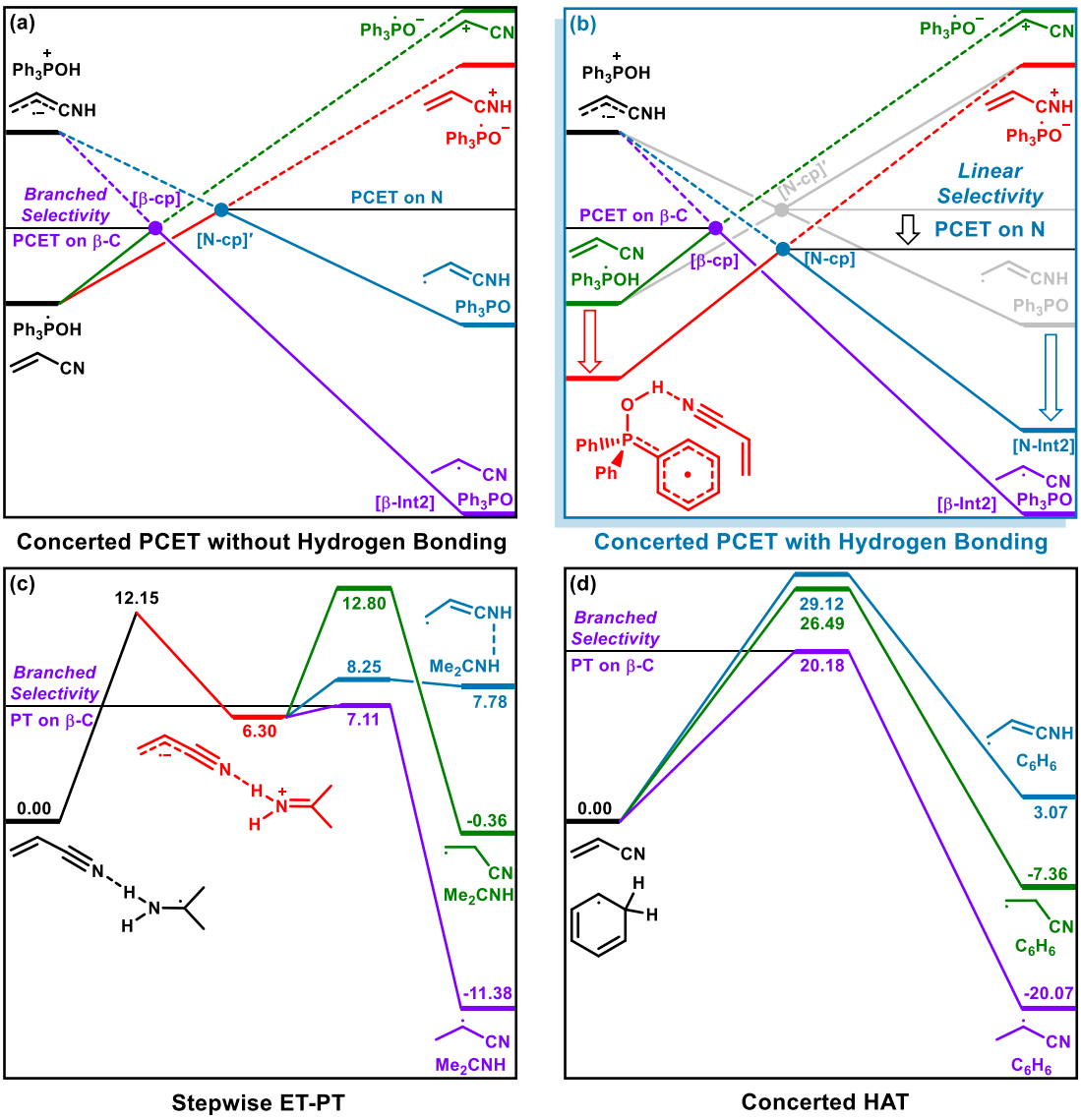


Fig. S8 Schematic mechanism picture of hydrogen transfer to activated alkenes

9.7 Cartesian Geometry Coordinations of all Species

[Ir^+]

1 1

N	-0.91942700	-0.25295400	1.29696500
C	-0.85681300	-0.56565800	2.59704900
C	-1.98757900	-0.72152200	3.37925200
C	-3.25855700	-0.54905400	2.81496600
C	-3.30049200	-0.20826500	1.46124100
C	-2.12452400	-0.06763700	0.72601300
N	-0.89825700	0.36677900	-1.29506700
C	-0.81335500	0.67557400	-2.59484300
C	-1.93003200	0.92095700	-3.37437400
C	-3.20959200	0.84616200	-2.80792500
C	-3.27543600	0.51160700	-1.45363200
C	-2.11261700	0.27898100	-0.72090500
H	0.14104700	-0.70338700	3.01764000
H	-1.86149500	-0.98245000	4.43075000
H	-4.25648600	-0.05226400	0.96804000
H	0.19164900	0.73374600	-3.01710200
H	-1.78679100	1.17326400	-4.42586600
H	-4.23955900	0.43184100	-0.95824800
C	2.86372100	-1.55779100	1.66486800
C	2.60425500	0.81814000	2.11250800
C	3.81094200	-1.61502800	2.67685000
H	2.62453400	-2.47503100	1.12302400
C	3.56830700	0.69729900	3.12297100
C	1.90524800	2.05268800	1.74199400
C	4.18510100	-0.50501800	3.42528500
C	2.08591700	3.32182600	2.31006500
N	1.00516800	1.89002300	0.73658800
H	4.93159700	-0.57005000	4.21705100
C	1.35223500	4.39784800	1.84286700
H	2.80237300	3.46005800	3.11439000
C	0.29549400	2.92789200	0.27985800
C	0.43899300	4.19941200	0.80518900
H	1.49228400	5.38778000	2.28220800
H	-0.40230600	2.72681300	-0.53261200
N	0.79724400	-1.96027100	-0.73773200
C	-0.00773500	-2.91797000	-0.26407100
C	1.66779600	-2.22224000	-1.74826400
C	0.00338600	-4.20250500	-0.77683000
H	-0.67322700	-2.64069300	0.55292200
C	1.71670800	-3.50878500	-2.30356600

C	2.48640200	-1.06843700	-2.13375800
C	0.88367900	-4.50159900	-1.81870000
H	2.40945800	-3.72608400	-3.11125800
C	3.44667900	-1.05259900	-3.15489500
H	0.92045200	-5.50518300	-2.24741300
C	4.18280800	0.07750600	-3.46877300
C	2.99733600	1.26907300	-1.70007600
C	3.93488400	1.22326900	-2.72168400
H	4.92314600	0.06119000	-4.26880800
H	2.85920000	2.20779800	-1.15988900
Ir	0.80848600	-0.02937200	-0.00495600
F	3.68667300	-2.15172400	-3.87773600
F	4.63437600	2.32389600	-3.00758400
F	3.93033300	1.76208900	3.84642900
F	4.39451500	-2.78409800	2.95116200
C	-0.92035000	-5.25526900	-0.22939600
C	-0.37334200	5.34700000	0.27178900
F	-0.24497300	-6.33790400	0.17172900
F	-1.62523300	-4.81403300	0.81551200
F	-1.79615100	-5.66713400	-1.15409100
F	-1.14905800	5.88049800	1.22304800
F	0.41025800	6.33137500	-0.18370200
F	-1.17229200	4.97676400	-0.73182100
C	-4.45049000	1.12917500	-3.65492100
C	-4.48901100	0.13124900	-4.82617600
C	-5.74410000	0.99294100	-2.84502700
C	-4.35362300	2.56618600	-4.19865400
H	-3.60437300	0.22346700	-5.47389600
H	-4.54072800	-0.90612400	-4.46008700
H	-5.37917800	0.31932100	-5.44637800
H	-5.77915500	1.70347100	-2.00470800
H	-6.60579400	1.20553100	-3.49526100
H	-5.87284400	-0.02454100	-2.44462100
H	-5.24267600	2.79594600	-4.80626500
H	-4.30331400	3.29720700	-3.37642300
H	-3.46720000	2.70433900	-4.83567400
C	-4.51604300	-0.73912000	3.66334100
C	-4.47708100	0.25605600	4.83684900
C	-5.79700700	-0.50371600	2.85603600
C	-4.52751700	-2.18089000	4.20339000
H	-3.60100800	0.09508400	5.48272700
H	-4.45008800	1.29522800	4.47325000
H	-5.37796400	0.13485100	5.45821800
H	-5.88835100	-1.20908200	2.01560300

H	-6.67096500	-0.65022800	3.50813300
H	-5.84865100	0.52101500	2.45680000
H	-5.43177700	-2.34458200	4.80995700
H	-4.53204400	-2.91130600	3.37907900
H	-3.65458600	-2.38783300	4.84051700
C	2.25527100	0.12264900	-1.39220500
C	2.24218500	-0.33873000	1.36863300

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0 2

N	0.89441800	-0.25294900	-1.29507600
C	0.88555000	-0.65304500	-2.57659400
C	2.01936700	-0.77145900	-3.34918600
C	3.29011100	-0.45891400	-2.77434100
C	3.30048000	-0.03337400	-1.46663400
C	2.09731400	0.08443000	-0.70450300
N	0.81077800	0.54085200	1.25985200
C	0.71758700	0.93559100	2.53961100
C	1.79581300	1.33457500	3.29785200
C	3.09854600	1.33631300	2.71002800
C	3.19814100	0.92446000	1.40161000
C	2.05179700	0.51442100	0.65312200
H	-0.09598400	-0.89796200	-2.99169900
H	1.92466200	-1.10893400	-4.38166300
H	4.24167800	0.21681900	-0.98123700
H	-0.28915600	0.93215000	2.96635300
H	1.63256900	1.64470300	4.33037300
H	4.16703500	0.90913100	0.90649400
C	-2.72416500	-1.88537300	-1.60809100
C	-2.68387100	0.48515900	-2.14361900
C	-3.66336500	-2.06720400	-2.61174700
H	-2.39848000	-2.75537100	-1.03350700
C	-3.63377200	0.23924700	-3.14471500
C	-2.10234400	1.79273400	-1.82189900
C	-4.13891300	-1.02461200	-3.39980400
C	-2.40256800	3.01860500	-2.43393300
N	-1.18980000	1.75218300	-0.81517400
H	-4.87688700	-1.18696200	-4.18544800
C	-1.76924000	4.17422300	-2.01218100
H	-3.13280300	3.06108600	-3.23674300
C	-0.57390400	2.86638100	-0.40495300
C	-0.83503300	4.09896500	-0.97687500
H	-2.00320900	5.12950200	-2.48652300

H	0.14277900	2.75228300	0.40841500
N	-0.59826700	-1.97995100	0.82605500
C	0.30461300	-2.86506700	0.39000900
C	-1.41941100	-2.27975600	1.86689000
C	0.44544500	-4.11272200	0.97082600
H	0.92345500	-2.55223800	-0.45070500
C	-1.31507900	-3.53192300	2.49097000
C	-2.35479000	-1.20264500	2.20868000
C	-0.38169300	-4.45050800	2.04430700
H	-1.96689600	-3.78040600	3.32337000
C	-3.30294500	-1.24334000	3.24041900
H	-0.29881800	-5.42603700	2.52799700
C	-4.15659400	-0.18724500	3.51171400
C	-3.12352300	1.04032100	1.67366100
C	-4.04180700	0.94177700	2.70787600
H	-4.88427800	-0.24634400	4.32123300
H	-3.09367700	1.96202300	1.08820800
Ir	-0.81423200	-0.10190800	0.00317000
F	-3.41740800	-2.32757200	4.01732100
F	-4.85774400	1.97187400	2.95225500
F	-4.09364700	1.23902600	-3.90716500
F	-4.13946700	-3.29493100	-2.84121100
C	1.47619300	-5.08292900	0.46517100
C	-0.11801100	5.33285500	-0.50478800
F	0.92386900	-6.25791500	0.13877800
F	2.11334000	-4.62745800	-0.61649400
F	2.40556000	-5.34066100	1.39429200
F	0.68853300	5.82577400	-1.45391700
F	-0.97818000	6.30805500	-0.18779900
F	0.63555300	5.09981400	0.57261900
C	4.30166800	1.79116400	3.53969800
C	4.43138000	0.88209600	4.77526900
C	5.61179500	1.72679100	2.74720200
C	4.07407200	3.24466400	3.99351000
H	3.53473600	0.92404000	5.41192100
H	4.58877300	-0.16692200	4.47769700
H	5.29159000	1.19429500	5.38889800
H	5.58783000	2.38057400	1.86157700
H	6.44600800	2.06025300	3.38352100
H	5.83833600	0.70262300	2.41225800
H	4.93021700	3.59521400	4.59196800
H	3.96714700	3.91584300	3.12636700
H	3.17044800	3.34401300	4.61375100
C	4.55955700	-0.61831800	-3.61431000

C	4.45749200	0.28248800	-4.85833100
C	5.82298400	-0.23433000	-2.83652400
C	4.68206800	-2.08901500	-4.05358900
H	3.59170700	0.02105700	-5.48527400
H	4.36238200	1.34178100	-4.57094500
H	5.36207900	0.17828800	-5.47867200
H	5.96595000	-0.86837900	-1.94775900
H	6.70691700	-0.36123400	-3.48037200
H	5.79855500	0.81648300	-2.50847500
H	5.59347300	-2.23236800	-4.65594900
H	4.74250900	-2.75706300	-3.17951600
H	3.82410100	-2.40687800	-4.66517800
C	-2.25844100	-0.02996700	1.40664000
C	-2.21292000	-0.60437500	-1.35720100

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1 3

N	0.77946800	0.48248900	1.27033900
C	0.67003900	0.83027400	2.57095600
C	1.74060200	1.20263500	3.34372000
C	3.05048000	1.23139800	2.76876700
C	3.16200400	0.86749400	1.44869700
C	2.02574300	0.47963900	0.67784000
N	0.87303500	-0.24361600	-1.27698600
C	0.86436800	-0.61491400	-2.57479900
C	1.99639300	-0.70046300	-3.34574900
C	3.26737200	-0.38607600	-2.77077400
C	3.27674000	0.00336900	-1.45316600
C	2.07670200	0.08591800	-0.68600400
H	-0.33631400	0.81237200	2.99363000
H	1.56693600	1.47518400	4.38498600
H	4.13399000	0.87039900	0.96022400
H	-0.10924400	-0.86369900	-3.00086400
H	1.90035000	-1.01564600	-4.38495800
H	4.21502200	0.25489800	-0.96352100
C	-3.05167600	1.13746000	1.70680800
C	-2.37310900	-1.15995000	2.22914000
C	-3.97372900	1.06717900	2.73997600
H	-2.97387800	2.05957000	1.12885200
C	-3.32187300	-1.16885400	3.25332900
C	-1.46867100	-2.26517000	1.88576500
C	-4.12800000	-0.07029700	3.52403900
C	-1.37721000	-3.50439200	2.52594200

N	-0.65567900	-1.99080000	0.83438100
H	-4.85860500	-0.10717600	4.33320300
C	-0.45246300	-4.43712300	2.08176700
H	-2.02358200	-3.73536700	3.36776400
C	0.24189200	-2.88015800	0.40259100
C	0.37326300	-4.12064700	1.00361400
H	-0.37566100	-5.40667900	2.57775900
H	0.85959600	-2.58092700	-0.44414500
N	-1.17681000	1.75950000	-0.81479200
C	-0.58676100	2.86806800	-0.36032400
C	-1.99771000	1.79227900	-1.89513900
C	-0.79259900	4.09506200	-0.96811900
H	0.05997500	2.75763000	0.51015100
C	-2.24051400	3.00693100	-2.54295800
C	-2.53795600	0.47676200	-2.26195000
C	-1.63519200	4.16381000	-2.07723200
H	-2.89598700	3.04464000	-3.40817100
C	-3.42073300	0.22056100	-3.31404500
H	-1.81991500	5.11508200	-2.58041500
C	-3.86789700	-1.06034900	-3.60931100
C	-2.54359400	-1.92142800	-1.75798500
C	-3.41585600	-2.11107100	-2.81965200
H	-4.55465800	-1.22858600	-4.43964800
H	-2.21963900	-2.78631200	-1.17717700
Ir	-0.86555700	-0.10807100	0.01101400
F	-3.86835100	1.21125600	-4.08304400
F	-3.84111700	-3.33931700	-3.09944800
F	-3.48779400	-2.24519900	4.01914500
F	-4.74299800	2.12048100	2.99801300
C	-0.13033800	5.33565600	-0.42833300
C	1.38035700	-5.11621700	0.49122300
F	-1.02792900	6.17807100	0.09484900
F	0.75627400	5.05417800	0.52833000
F	0.51348800	6.00131700	-1.39140600
F	2.17655200	-5.55068500	1.47258500
F	0.77868100	-6.19172000	-0.02771600
F	2.16014600	-4.59736800	-0.45914800
C	4.53249600	-0.49965400	-3.62228200
C	4.40839600	0.44565000	-4.83096600
C	5.79479700	-0.12784900	-2.83709800
C	4.67043000	-1.95153500	-4.11601600
H	3.54074800	0.19634900	-5.46031500
H	4.30286800	1.49208500	-4.50329400
H	5.30927500	0.37532100	-5.46106600

H	5.94923200	-0.79110600	-1.97187400
H	6.67647100	-0.22172200	-3.48933900
H	5.75983300	0.91062800	-2.47286200
H	5.58019300	-2.05876600	-4.72792800
H	4.74575200	-2.65046500	-3.26777100
H	3.81384700	-2.25820100	-4.73513000
C	4.24250700	1.65943800	3.62569700
C	4.35945700	0.70794400	4.83023900
C	5.56026600	1.62433500	2.84443100
C	4.00484900	3.09611400	4.12564400
H	3.45627800	0.72714000	5.45866900
H	4.52209500	-0.32976600	4.49815300
H	5.21255900	1.00072000	5.46273500
H	5.54284600	2.30715300	1.98087800
H	6.38684700	1.93852000	3.49991300
H	5.79256500	0.61221100	2.47825100
H	4.85296000	3.42662900	4.74618000
H	3.90747500	3.79619400	3.28063800
H	3.09358500	3.17209900	4.73796100
C	-2.10933600	-0.62359800	-1.46474900
C	-2.25037100	0.01991800	1.43653700

Ph_3P

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P	0.00124900	0.00010000	-1.24412200
C	-0.97000900	1.33972400	-0.43271700
C	-0.54210500	2.05055600	0.69574600
C	-2.21497700	1.65378900	-0.99844300
C	-1.34563200	3.04834800	1.24980000
H	0.42411000	1.82532900	1.15340900
C	-3.02268800	2.64191600	-0.43769700
H	-2.55928700	1.11634000	-1.88733900
C	-2.58766800	3.34360400	0.68784600
H	-0.99843500	3.59548000	2.12966800
H	-3.99206900	2.87082900	-0.88695900
H	-3.21581600	4.12376100	1.12448800
C	1.64672800	0.17078300	-0.43226200
C	2.54112900	1.09267400	-0.99670900
C	2.04809600	-0.55668800	0.69547600
C	3.80067000	1.29719300	-0.43553800
H	2.24789500	1.66056900	-1.88502300
C	3.31393100	-0.36057300	1.24990800
H	1.36955100	-1.28148100	1.15147800
C	4.19068600	0.56812800	0.68908000

H	4.48378400	2.02272900	-0.88371000
H	3.61404900	-0.93596200	2.12907300
H	5.18050200	0.72120900	1.12576700
C	-0.67465300	-1.51040400	-0.43308700
C	-0.31641600	-2.74639400	-0.99206200
C	-1.51381800	-1.49377700	0.68831700
C	-0.77065400	-3.93924100	-0.43170800
H	0.32912200	-2.77686200	-1.87521400
C	-1.97871500	-2.68789000	1.24167600
H	-1.80779600	-0.54338800	1.14004900
C	-1.60602500	-3.91192000	0.68630100
H	-0.47803000	-4.89393400	-0.87538300
H	-2.63393600	-2.65958600	2.11572400
H	-1.96966900	-4.84550400	1.12221700

Ph_3PH^+

1 1

P	0.00323700	-0.00738500	-0.88604800
C	-1.20105500	-1.21863100	-0.32785400
C	-2.02083500	-0.95030600	0.77377000
C	-1.26526200	-2.45374100	-0.98676900
C	-2.91197900	-1.92726600	1.21461200
H	-1.96888000	0.01354100	1.28553800
C	-2.16103100	-3.42031400	-0.53906400
H	-0.62213300	-2.66034700	-1.84567000
C	-2.98160400	-3.15685600	0.55985800
H	-3.55570200	-1.72409200	2.07275100
H	-2.22048900	-4.38254900	-1.05155000
H	-3.68410600	-3.91770600	0.90728300
C	-0.45402200	1.64487900	-0.34421800
C	-1.55144000	2.27195100	-0.95099100
C	0.24533500	2.27035400	0.69327100
C	-1.94352800	3.53327500	-0.51340300
H	-2.09656800	1.77825200	-1.76031000
C	-0.15812800	3.53349600	1.12390000
H	1.10010700	1.78029400	1.16495000
C	-1.24802000	4.16158400	0.52252900
H	-2.79462500	4.02940300	-0.98413200
H	0.38410300	4.02734300	1.93264000
H	-1.55904400	5.15214300	0.86194400
C	1.65642100	-0.43351000	-0.32813100
C	2.75864000	0.01833300	-1.06600400
C	1.83358100	-1.15947200	0.85559100
C	4.04428400	-0.26676600	-0.61422200

H	2.61454000	0.58653500	-1.98867700
C	3.12528600	-1.43696800	1.29802600
H	0.97191300	-1.50904400	1.42930500
C	4.22586600	-0.99244700	0.56471400
H	4.90820500	0.07646200	-1.18684700
H	3.27104800	-2.00572700	2.21855100
H	5.23655600	-1.21615200	0.91345700
H	0.01148000	-0.02315100	-2.29221500

Ph_3P^+

1 2

P	0.00050100	0.00108500	-0.66107100
C	-1.27440400	1.16870400	-0.23385300
C	-2.56493600	0.96633000	-0.75778500
C	-1.00356900	2.28159700	0.58138300
C	-3.57967600	1.86284800	-0.44435100
H	-2.77153500	0.11056300	-1.40510000
C	-2.02930100	3.17150100	0.88275400
H	-0.00489900	2.44265200	0.99161500
C	-3.31241200	2.96354800	0.37309800
H	-4.58290100	1.70599900	-0.84498500
H	-1.82563800	4.03058900	1.52483700
H	-4.11222500	3.66718300	0.61401100
C	1.64917200	0.51976300	-0.23250700
C	2.12376400	1.73410100	-0.76230100
C	2.47306300	-0.26901200	0.58900600
C	3.40848600	2.16230000	-0.44922000
H	1.48943000	2.33925700	-1.41480100
C	3.75762200	0.17180400	0.88999700
H	2.10877200	-1.21092800	1.00391300
C	4.22413400	1.38248100	0.37409200
H	3.77805100	3.10587200	-0.85510800
H	4.39677900	-0.43251400	1.53657200
H	5.23433900	1.72120100	0.61433200
C	-0.37371500	-1.68664300	-0.23304100
C	0.44265900	-2.70419700	-0.76121700
C	-1.47004100	-2.00697500	0.58653700
C	0.17145100	-4.03112100	-0.44916600
H	1.28530300	-2.45616900	-1.41113600
C	-1.72993900	-3.34016500	0.88683300
H	-2.10485300	-1.22119400	1.00065300
C	-0.91317000	-4.34868000	0.37179000
H	0.80511700	-4.82247900	-0.85400800
H	-2.57380000	-3.59229200	1.53187300

H	-1.12458100	-5.39311300	0.61111800

Ph_3PO

0 1

P	-0.00017900	-0.03012900	0.90780600
C	0.04410100	1.68257100	0.29226200
C	1.27024700	2.35351800	0.18714900
C	-1.14477900	2.37916900	0.03936200
C	1.30616600	3.69770000	-0.17950100
H	2.20589200	1.82528000	0.38906800
C	-1.10629000	3.72395000	-0.32726100
H	-2.10946700	1.87259600	0.12536800
C	0.11832300	4.38289600	-0.43921900
H	2.26626700	4.21174600	-0.26393400
H	-2.03772300	4.25844800	-0.52715800
H	0.14762800	5.43577700	-0.72952000
C	-1.47755000	-0.79917000	0.16763200
C	-2.34113400	-1.48087300	1.03024300
C	-1.76122800	-0.74758300	-1.20369000
C	-3.48032100	-2.11050200	0.52669100
H	-2.11293000	-1.51142900	2.09823700
C	-2.89920400	-1.37654800	-1.70324900
H	-1.09863000	-0.20858900	-1.88579000
C	-3.75884200	-2.05889400	-0.83852100
H	-4.15252700	-2.64154100	1.20467800
H	-3.11888800	-1.33244900	-2.77238700
H	-4.65123900	-2.55036800	-1.23342600
C	1.43979400	-0.87004500	0.17133700
C	2.17900900	-1.71353200	1.00673300
C	1.80816800	-0.72526200	-1.17286900
C	3.27443000	-2.41460200	0.50137300
H	1.89023700	-1.81273000	2.05579200
C	2.90232400	-1.42689300	-1.67449700
H	1.24827800	-0.05577100	-1.83106400
C	3.63481300	-2.27289400	-0.83833100
H	3.84923700	-3.07183400	1.15800800
H	3.18807600	-1.30998400	-2.72232200
H	4.49332500	-2.82066500	-1.23429800
O	-0.00662600	-0.14682200	2.40972300

$Ph_3POH^{\cdot}$

0 2

P	0.03497500	-0.00715100	0.72402200
C	1.66149000	-0.25161000	0.24423000

C	2.23235300	-1.57617900	0.10372400
C	2.57879800	0.86683200	0.14622000
C	3.57029200	-1.74052500	-0.17971100
H	1.59546000	-2.45679600	0.21744300
C	3.91257600	0.66211700	-0.13630000
H	2.20740200	1.88550700	0.28468100
C	4.44197700	-0.63505400	-0.31449600
H	3.96306600	-2.75491500	-0.29606200
H	4.57230600	1.53071900	-0.22143000
H	5.50109100	-0.78179300	-0.53344500
C	-0.59669300	1.58433800	0.13417000
C	-1.34884800	2.43536300	0.95275100
C	-0.36900000	1.93021700	-1.20508100
C	-1.86398100	3.62284800	0.43343900
H	-1.52611400	2.16854700	1.99483900
C	-0.88171800	3.11915100	-1.71716800
H	0.21978300	1.26821700	-1.84496000
C	-1.63119400	3.96567400	-0.89810500
H	-2.44876500	4.28468900	1.07553800
H	-0.69648200	3.38565600	-2.75956900
H	-2.03510400	4.89709700	-1.30070100
C	-1.02564100	-1.35835700	0.15193300
C	-2.09686300	-1.79883400	0.93997500
C	-0.83491000	-1.90549500	-1.12571100
C	-2.95798900	-2.78513000	0.46033100
H	-2.25464100	-1.36799700	1.92994400
C	-1.69403200	-2.89437100	-1.59714600
H	-0.00749200	-1.55930700	-1.74913500
C	-2.75656300	-3.33487800	-0.80515300
H	-3.78944300	-3.12556600	1.08079900
H	-1.53614200	-3.32088100	-2.58968900
H	-3.43118300	-4.10833800	-1.17836800
O	-0.36880800	0.15699800	2.32970200
H	0.05176900	-0.53019100	2.86474200

Ph_3POH^+

1 1

P	-0.00489000	-0.01296000	0.72997600
C	-0.25042400	1.67519300	0.18650900
C	0.77959600	2.61088700	0.37673800
C	-1.46583800	2.06476700	-0.39213100
C	0.58450900	3.93284600	-0.00825500
H	1.73489900	2.31197200	0.81504000
C	-1.64798000	3.39066800	-0.77727600

H	-2.26541400	1.33835600	-0.54994200
C	-0.62683900	4.32062500	-0.58454600
H	1.38282400	4.66225000	0.13708900
H	-2.59114400	3.69599000	-1.23298000
H	-0.77344600	5.35840100	-0.89026000
C	-1.32077900	-1.08077400	0.16457000
C	-2.50673800	-1.16827300	0.90747900
C	-1.17636600	-1.78228000	-1.03912900
C	-3.54862600	-1.96146400	0.43597200
H	-2.61296200	-0.62503000	1.84812300
C	-2.22729100	-2.57012500	-1.50103400
H	-0.24918800	-1.72340000	-1.61322900
C	-3.40940200	-2.65816900	-0.76547200
H	-4.47317700	-2.03656000	1.01070100
H	-2.11914200	-3.12081500	-2.43672600
H	-4.23002900	-3.27906600	-1.13016400
C	1.59801100	-0.59995500	0.19359300
C	2.25954400	-1.55708800	0.97575700
C	2.15143300	-0.15867100	-1.01654400
C	3.48059800	-2.06610900	0.54395400
H	1.82609400	-1.89630000	1.91871300
C	3.37054300	-0.68052000	-1.44075400
H	1.63841300	0.58881400	-1.62571300
C	4.03252900	-1.62983900	-0.66162100
H	4.00363000	-2.80621600	1.15172700
H	3.80614100	-0.34003300	-2.38142200
H	4.99046500	-2.03270900	-0.99631200
O	-0.10338400	-0.11958400	2.32730800
H	0.37358000	0.56510200	2.82039300

H_2O

0 1

O	0.00000000	0.00000000	0.12034800
H	0.00000000	0.75335200	-0.48139300
H	0.00000000	-0.75335200	-0.48139300

H_3O^+

1 1

O	0.00000000	0.00000000	0.09190400
H	0.00000000	0.92924000	-0.24507600
H	0.80474600	-0.46462000	-0.24507600
H	-0.80474600	-0.46462000	-0.24507600

CH_2CHCN

0 1

C	-1.60065700	-0.36393800	0.00000000
C	-0.59002600	0.51103600	0.00000000
C	0.78278900	0.09383200	0.00000000
N	1.89572200	-0.22655300	0.00000000
H	-0.75827900	1.59209200	0.00000000
H	-1.43080800	-1.44385500	0.00000000
H	-2.63360200	-0.00794900	0.00000000

CH_2CHCN^-
[SET-Int2]
-1 2

C	-1.66968100	-0.35510900	-0.00023100
C	-0.53760100	0.51133600	0.00002500
C	0.78951700	0.10126900	0.00000900
N	1.92022300	-0.25109700	0.00000900
H	-0.69283600	1.59694100	0.00005000
H	-1.56101900	-1.44416600	0.00046800
H	-2.68110900	0.05992900	0.00060700

[N-Int1]
0 2

P	0.54066900	0.03902700	0.49604900
C	-0.51089500	-1.19730200	-0.31298300
C	-0.71251200	-1.14577400	-1.69979200
C	-1.07186000	-2.24340900	0.42993000
C	-1.48031700	-2.12228300	-2.33023300
H	-0.27167600	-0.33680600	-2.28708100
C	-1.84078100	-3.21792100	-0.20578500
H	-0.91146900	-2.29472100	1.50820500
C	-2.04606100	-3.15819600	-1.58385100
H	-1.63789100	-2.07404700	-3.40987800
H	-2.28085400	-4.02743000	0.38067500
H	-2.64897000	-3.92220500	-2.08009900
C	2.28619200	-0.40017100	0.29399200
C	3.00457400	-1.03589700	1.31371400
C	2.90227300	-0.14718700	-0.93923200
C	4.33100500	-1.41003900	1.09965100
H	2.52619600	-1.23426000	2.27376100
C	4.22800200	-0.52075200	-1.14635000
H	2.34368400	0.34900800	-1.73708800
C	4.94272900	-1.15309700	-0.12720400
H	4.88910300	-1.90389200	1.89830100
H	4.70539000	-0.31731700	-2.10742000

H	5.98236200	-1.44646200	-0.29099200
C	0.20815800	1.60819300	-0.11220000
C	1.18451900	2.67425000	0.02452200
C	-1.10470500	1.98679000	-0.60027100
C	0.88098800	3.96245100	-0.35929700
H	2.17638000	2.45100900	0.42776800
C	-1.37120200	3.28499800	-0.97385000
H	-1.89220600	1.23375900	-0.68106700
C	-0.39261400	4.30500700	-0.87325600
H	1.64759200	4.73713800	-0.25746100
H	-2.36905900	3.52928400	-1.35150300
H	-0.62075100	5.33141000	-1.16760600
O	0.37414200	-0.26127100	2.10189700
H	-0.52633000	-0.00261400	2.39778300
C	-4.35445500	-0.37098000	-0.31908900
C	-4.44510300	0.07678100	0.93796400
H	-5.25477300	-0.47528400	-0.92915000
H	-5.39767900	0.35006800	1.40024700
C	-3.28069100	0.21769900	1.75872500
N	-2.33014800	0.31987700	2.41070500
H	-3.39465200	-0.63998600	-0.76886600

[N-cp]
0 2

P	0.55046200	0.04865000	0.48779300
C	-0.47624800	-1.18271400	-0.33991700
C	-0.93793900	-1.00132700	-1.64930900
C	-0.76180800	-2.37080600	0.34631900
C	-1.72369800	-1.98465100	-2.24662100
H	-0.69315500	-0.09043900	-2.19985700
C	-1.53581600	-3.35497300	-0.26191800
H	-0.38961700	-2.51897500	1.36191900
C	-2.02772900	-3.15696400	-1.55286000
H	-2.10410500	-1.82980700	-3.25842200
H	-1.76310600	-4.27511700	0.28057400
H	-2.65135000	-3.92170400	-2.02083300
C	2.28405400	-0.35688300	0.22656800
C	2.96461700	-1.15849000	1.15012900
C	2.91475500	0.05124900	-0.95568000
C	4.28269400	-1.53334800	0.89649000
H	2.46232000	-1.48701700	2.06155400
C	4.23399600	-0.32112300	-1.19811000
H	2.37522100	0.66361800	-1.68260200
C	4.91768100	-1.11113100	-0.27173800

H	4.81520500	-2.15803600	1.61682200
H	4.72844500	0.00589700	-2.11517900
H	5.95291100	-1.40159900	-0.46368300
C	0.17808500	1.67252400	-0.02710600
C	1.16156000	2.70327200	0.11352300
C	-1.14038600	2.05002900	-0.43345300
C	0.85265200	4.01298500	-0.20542200
H	2.16386000	2.45879600	0.47495200
C	-1.42313700	3.36638200	-0.74827900
H	-1.93400900	1.30179900	-0.49360100
C	-0.43523300	4.36573500	-0.65154400
H	1.62351900	4.78139100	-0.10089500
H	-2.43556800	3.62707800	-1.06821900
H	-0.66892000	5.40310500	-0.90086100
O	0.38208100	-0.22681500	2.07276400
H	-0.57094700	-0.10453800	2.34167900
C	-4.87647000	0.34579000	0.00369900
C	-3.98681800	-0.55356500	0.52269600
H	-5.53059200	0.04461400	-0.81805800
H	-3.90991300	-1.56840000	0.11720800
C	-3.08591600	-0.27003400	1.56778500
N	-2.29812700	-0.06881800	2.40946900
H	-4.97026900	1.36409100	0.39070800

[N-Int2]

0 2

P	0.51645200	-0.03677100	0.60901600
C	-0.45884000	-1.20543800	-0.38358200
C	-0.75544600	-1.00400400	-1.73691900
C	-0.91238300	-2.36070600	0.26525300
C	-1.50724200	-1.95065400	-2.43147400
H	-0.41105300	-0.10400700	-2.25211600
C	-1.66109600	-3.30546700	-0.43366900
H	-0.68877200	-2.50886900	1.32429700
C	-1.96090700	-3.09907100	-1.78099000
H	-1.74338100	-1.78780400	-3.48535600
H	-2.01699500	-4.20289800	0.07724300
H	-2.55318800	-3.83683600	-2.32742100
C	2.26609800	-0.40692400	0.30542600
C	3.08949600	-0.65181300	1.40804800
C	2.79398400	-0.46082100	-0.99114800
C	4.43951700	-0.94748900	1.21514200
H	2.66599900	-0.61103500	2.41408500
C	4.14205600	-0.75520400	-1.17850400

H	2.15451100	-0.27017400	-1.85732500
C	4.96463500	-0.99846400	-0.07552000
H	5.08216300	-1.13923000	2.07739200
H	4.55371600	-0.79652800	-2.18934800
H	6.02176000	-1.23021700	-0.22569500
C	0.19824400	1.62300800	-0.05527000
C	1.23270200	2.55807000	-0.18402400
C	-1.12127100	2.00789500	-0.33382700
C	0.95070500	3.86030100	-0.59611300
H	2.26495300	2.27386100	0.03431400
C	-1.39848800	3.30919200	-0.74555500
H	-1.93940600	1.28890100	-0.24014000
C	-0.36269800	4.23582600	-0.87762200
H	1.76258200	4.58376800	-0.69824800
H	-2.42806600	3.59915600	-0.96676400
H	-0.58090700	5.25579800	-1.20273200
O	0.18867000	-0.16509500	2.08675500
H	-1.47559100	-0.21111500	2.54703800
C	-4.68036300	0.70976900	0.01642500
C	-4.07599700	-0.38789400	0.65166300
H	-5.34142600	0.54541400	-0.83616300
H	-4.26542000	-1.40296000	0.28165000
C	-3.21416000	-0.32305200	1.69373200
N	-2.51614200	-0.28396900	2.68905400
H	-4.51590400	1.73251500	0.36379900

[α-Int1]

0 2

P	-0.33346400	0.01674000	-0.32333200
C	0.73260600	0.90276800	0.68412600
C	0.69945200	2.35220700	0.72676700
C	1.82965900	0.25315500	1.37356300
C	1.63964600	3.05713700	1.44720900
H	-0.08259400	2.89324800	0.18713200
C	2.75279700	0.99170200	2.08087700
H	1.92249600	-0.83507200	1.33603800
C	2.68386800	2.40455000	2.14368900
H	1.57594200	4.14944000	1.47006300
H	3.55874500	0.46697800	2.60300900
H	3.42531100	2.97656500	2.70496900
C	-0.44042600	-1.71247800	0.19247100
C	-0.06981800	-2.76026200	-0.65760400
C	-0.90676500	-1.99031900	1.48479400
C	-0.16215800	-4.07890200	-0.21194900

H	0.29480400	-2.54340500	-1.66235200
C	-0.99712700	-3.30878700	1.92318500
H	-1.19622900	-1.17306700	2.15090800
C	-0.62405300	-4.35341500	1.07476900
H	0.13151200	-4.89549600	-0.87527200
H	-1.35931600	-3.52214900	2.93119900
H	-0.69420400	-5.38751000	1.42026900
C	-1.97663400	0.77712500	-0.36888000
C	-2.75207000	0.71374800	-1.53427600
C	-2.51215700	1.35684000	0.79054500
C	-4.04567500	1.23374100	-1.54066500
H	-2.34126000	0.25908800	-2.43753100
C	-3.80323900	1.87932200	0.77655700
H	-1.91514200	1.40267600	1.70434400
C	-4.57110100	1.81745800	-0.38793200
H	-4.64474500	1.18362100	-2.45263700
H	-4.21295700	2.33480400	1.68075400
H	-5.58455600	2.22542000	-0.39561800
O	0.02644300	-0.20504200	-1.92856600
H	0.39780300	0.60720200	-2.30843200
C	3.24902700	1.78114800	-1.57734200
C	3.13968000	0.65354700	-2.28877400
H	3.15679700	2.75081900	-2.07243300
H	2.95754900	0.66121800	-3.36768700
C	3.24602500	-0.64381000	-1.68634400
N	3.32870400	-1.69901100	-1.21540300
H	3.43032000	1.76908700	-0.49910600

[α-cp]
0 2

P	-0.30704700	-0.04766500	-0.25880700
C	0.91491400	-0.31327800	0.95498200
C	0.97348300	0.43388200	2.17081300
C	1.81916700	-1.41054000	0.78191500
C	1.91867500	0.12470500	3.13040900
H	0.26714300	1.24837700	2.34902900
C	2.76340100	-1.68984100	1.75462300
H	1.78569900	-2.01343200	-0.12937300
C	2.83732400	-0.92900300	2.93530400
H	1.94197100	0.70026400	4.05956700
H	3.45924600	-2.51823900	1.59695900
H	3.58329900	-1.16060600	3.69869700
C	-1.63575600	-1.27333900	-0.27392800
C	-2.25888500	-1.66868600	-1.46445100

C	-2.06728000	-1.79390900	0.95257000
C	-3.31276000	-2.57930200	-1.42117600
H	-1.92126800	-1.26892300	-2.42225400
C	-3.12395700	-2.70211400	0.98777000
H	-1.57615800	-1.49191500	1.88140900
C	-3.74811500	-3.09172800	-0.19766300
H	-3.79695000	-2.89034300	-2.34932400
H	-3.45839200	-3.10990500	1.94403900
H	-4.57835700	-3.80157700	-0.16887000
C	-1.02965800	1.59355500	-0.09180000
C	-0.16877700	2.70206400	-0.11701100
C	-2.41305200	1.78594100	0.01953100
C	-0.68834600	3.98960600	-0.02905700
H	0.90940600	2.55383400	-0.21152000
C	-2.92623600	3.07989300	0.10676200
H	-3.09338900	0.93199100	0.04484300
C	-2.06707900	4.17872700	0.08129700
H	-0.01259100	4.84727300	-0.05173000
H	-4.00410800	3.22894100	0.19825400
H	-2.47435400	5.19020000	0.14750900
O	0.31338900	-0.25411500	-1.74116300
H	1.17631000	0.19720900	-1.84403300
C	3.22862600	1.40339700	-1.06640000
C	3.34581500	0.64598900	-2.20413000
H	2.97678400	2.46362000	-1.14458800
H	3.19244400	1.09084600	-3.19337300
C	3.70694300	-0.72504400	-2.19769500
N	3.98413500	-1.85842800	-2.19973500
H	3.42223000	0.99343300	-0.07167300

[α-Int2]

0 2

P	-0.41223500	-0.05325500	-0.58203600
C	0.72904200	-0.74930200	0.65204600
C	0.84694600	-0.26542300	1.95959300
C	1.54764100	-1.80239100	0.22410200
C	1.77589300	-0.83332200	2.83134900
H	0.22501100	0.56418100	2.30286000
C	2.47860000	-2.36310900	1.09564100
H	1.46932000	-2.16878700	-0.80248100
C	2.59338800	-1.87837500	2.39970900
H	1.86731400	-0.45019300	3.85012900
H	3.12424300	-3.17411700	0.75144100
H	3.32641000	-2.31523400	3.08198100

C	-1.95613600	-1.00441800	-0.45698600
C	-2.71613800	-1.15206100	-1.62374000
C	-2.40004900	-1.57664400	0.74120800
C	-3.91826500	-1.85655100	-1.58813200
H	-2.35697500	-0.71945000	-2.56071100
C	-3.60462200	-2.27852800	0.77277900
H	-1.80515300	-1.48150200	1.65329800
C	-4.36370900	-2.41719400	-0.39002800
H	-4.50809200	-1.97161300	-2.50040800
H	-3.94858900	-2.72404300	1.70888400
H	-5.30524700	-2.97084600	-0.36361800
C	-0.79864400	1.64561000	-0.05684500
C	-0.13462100	2.68297200	-0.72233200
C	-1.71221400	1.94480700	0.96168300
C	-0.36860000	4.00871000	-0.35910600
H	0.55908300	2.44677400	-1.53267400
C	-1.94278600	3.27160300	1.32231600
H	-2.24971800	1.14455200	1.47657900
C	-1.26989400	4.30275300	0.66461100
H	0.15118800	4.81520800	-0.88127100
H	-2.65515400	3.50117400	2.11784700
H	-1.45428500	5.34175900	0.94781000
O	0.16902700	-0.09418600	-1.97631300
H	2.25717400	0.42346700	-1.83016000
C	3.29547300	1.29846800	-0.15242800
C	3.28926400	0.70605300	-1.52166900
H	2.89491400	2.30507700	-0.01637500
H	3.64077400	1.43044200	-2.27641700
C	4.10774700	-0.49902900	-1.63701700
N	4.74011800	-1.46433600	-1.71580000
H	3.54834500	0.69804100	0.72443200

[β-Int1]

0 2

P	-0.34602600	-0.03450100	0.31850600
C	-0.50228600	1.63681600	-0.35496500
C	-0.77791000	1.81183300	-1.71898100
C	-0.39763000	2.75407900	0.48190400
C	-0.92853200	3.09423700	-2.23981500
H	-0.87076300	0.94312100	-2.37541900
C	-0.55003900	4.03646500	-0.04552300
H	-0.19956700	2.62575000	1.54758400
C	-0.81299100	4.20726300	-1.40402500
H	-1.13965200	3.22576400	-3.30330000

H	-0.46399500	4.90495400	0.61116200
H	-0.93228900	5.21247700	-1.81493700
C	-1.97665200	-0.81636300	0.44959500
C	-2.74659500	-0.71970700	1.61599800
C	-2.49957900	-1.46337400	-0.67788800
C	-4.02647700	-1.27128100	1.65108600
H	-2.34343900	-0.21758800	2.49648200
C	-3.77748400	-2.01711000	-0.63513900
H	-1.90133900	-1.53925000	-1.58945500
C	-4.54192000	-1.91999400	0.52849900
H	-4.62316400	-1.19569600	2.56292700
H	-4.17763700	-2.52618600	-1.51467200
H	-5.54461300	-2.35269200	0.56057500
C	0.75162200	-0.96947200	-0.60770700
C	0.81067900	-2.40671300	-0.41549700
C	1.75128800	-0.38457700	-1.47874900
C	1.75419700	-3.16688700	-1.07350300
H	0.09797800	-2.89272500	0.25687000
C	2.67734200	-1.17700200	-2.11919800
H	1.76653600	0.69622400	-1.63903600
C	2.70553300	-2.58185000	-1.93971100
H	1.76495900	-4.24934200	-0.91233000
H	3.40944500	-0.70241100	-2.77970200
H	3.45166300	-3.19572600	-2.44810000
O	-0.06187300	0.17997000	1.93268300
H	0.85321000	0.46236000	2.09063600
C	2.99452000	1.65880000	2.52459300
C	3.13963900	0.95150700	1.39714200
H	2.63808600	2.69057200	2.47852000
H	2.91421800	1.37595500	0.41383100
C	3.60643800	-0.40669200	1.39205900
N	3.97767200	-1.50339400	1.37594800
H	3.22306500	1.23608100	3.50661800

[β-cp]
0 2

P	-0.36511300	-0.03807200	0.37241900
C	-0.61883300	1.59653600	-0.34382300
C	-1.22045800	1.70489900	-1.60534700
C	-0.25288400	2.74737600	0.36301800
C	-1.44530700	2.96192400	-2.15929900
H	-1.51799000	0.80519100	-2.15040800
C	-0.47980900	4.00349600	-0.19985000
H	0.20246900	2.66897800	1.35269600

C	-1.07430600	4.11049000	-1.45672200
H	-1.91804200	3.04678400	-3.14004200
H	-0.19417700	4.90337600	0.34887400
H	-1.25618100	5.09588900	-1.89181200
C	-1.95913500	-0.88350700	0.46820300
C	-2.89061300	-0.51598900	1.44989000
C	-2.29382400	-1.84591000	-0.49139200
C	-4.14605100	-1.11811300	1.47028200
H	-2.63531400	0.23716600	2.19838600
C	-3.54979000	-2.45054400	-0.45894300
H	-1.57101200	-2.12638700	-1.26122100
C	-4.47512400	-2.08582900	0.51861200
H	-4.87270300	-0.83250700	2.23400400
H	-3.80518400	-3.20860500	-1.20232400
H	-5.46012400	-2.55780900	0.54012800
C	0.82713100	-0.94713500	-0.50691500
C	1.09278700	-2.29798600	-0.10298400
C	1.58153800	-0.40230300	-1.59263900
C	2.03503300	-3.05307500	-0.77823100
H	0.55103600	-2.73460300	0.74080700
C	2.51294400	-1.18174000	-2.25143800
H	1.41569600	0.62971200	-1.91080300
C	2.75135600	-2.51753700	-1.86354900
H	2.22591000	-4.08059500	-0.45622900
H	3.07567600	-0.75007700	-3.08347700
H	3.49063500	-3.12333000	-2.39177700
O	-0.03913400	0.15430700	1.94916500
H	0.88761000	0.43249800	2.12068500
C	2.69116600	1.28467500	2.76785200
C	3.08643700	1.12468400	1.46749700
H	2.07988500	2.14355300	3.05809000
H	2.75543400	1.81371900	0.68315800
C	3.94340000	0.07420100	1.05005100
N	4.65894000	-0.78328500	0.71582600
H	3.02961500	0.60498900	3.55523900

[β-Int2]

0 2

P	-0.59824600	0.01263700	0.73704400
C	-0.41589600	1.63961700	-0.05962100
C	-0.92617500	1.93400900	-1.33033000
C	0.26368100	2.62836800	0.66175900
C	-0.73443700	3.19970100	-1.88213400
H	-1.47969900	1.17896500	-1.89415400

C	0.45298000	3.89354500	0.10660800
H	0.63904700	2.40172600	1.66230600
C	-0.04246300	4.17810100	-1.16616900
H	-1.13227600	3.42447000	-2.87424700
H	0.98525700	4.66126700	0.67282300
H	0.10458600	5.16980900	-1.60045900
C	-2.27509600	-0.57246300	0.33883200
C	-3.26790900	-0.36261300	1.30382500
C	-2.59999900	-1.20603500	-0.86673700
C	-4.57761900	-0.77202500	1.05860500
H	-3.00707700	0.11589800	2.25091200
C	-3.91188500	-1.61201100	-1.10902400
H	-1.83027900	-1.39085100	-1.62029900
C	-4.90030200	-1.39443700	-0.14816400
H	-5.34885800	-0.60809000	1.81473300
H	-4.16116200	-2.10646100	-2.05059700
H	-5.92680600	-1.71647900	-0.33883300
C	0.55656000	-1.13215800	-0.08231800
C	1.06648900	-2.17311200	0.70405800
C	0.94043700	-1.02493300	-1.42434800
C	1.94402500	-3.10305900	0.14989100
H	0.78020900	-2.24368100	1.75611900
C	1.81411200	-1.96089800	-1.97656400
H	0.56666000	-0.20859900	-2.04633200
C	2.31497500	-2.99982200	-1.19140700
H	2.34238700	-3.91010700	0.76897100
H	2.11226200	-1.87159300	-3.02348700
H	3.00581400	-3.72685300	-1.62455300
O	-0.36263200	0.08502200	2.22627200
H	1.95907800	0.35210100	2.32253100
C	3.03391700	0.54264000	2.15312800
C	3.30017200	0.69916800	0.69913900
H	3.27466700	1.48107200	2.68288600
H	2.75972500	1.45667200	0.12263500
C	4.22705800	-0.07077200	0.00154100
N	5.00513200	-0.72010600	-0.58395200
H	3.61954500	-0.27312800	2.59745800

[N-H]
0 2

C	1.73100700	-0.36640300	0.00274900
C	0.62922600	0.49893000	0.00446600
C	-0.67100900	0.12633200	0.02958800
N	-1.83785700	-0.19616300	-0.13543400

H	0.79000100	1.58395000	0.01819900
H	1.60593400	-1.45164500	-0.00519400
H	2.74155200	0.04558900	0.00874300
H	-2.40783000	-0.35790000	0.70547300

[α-H]
0 2

C	1.58701300	-0.48258500	-0.03573300
C	0.55948100	0.59649300	0.03621300
H	0.67938800	1.32002200	-0.78788300
C	-0.81628200	0.09969700	-0.00187100
N	-1.90111000	-0.29882000	-0.02948500
H	0.66327200	1.19130000	0.96598500
H	1.36726600	-1.49593700	0.30748500
H	2.61657100	-0.20527700	-0.27085000

[β-H]
0 2

C	1.63177000	-0.33906800	0.00002500
C	0.45124600	0.56461100	0.00003000
H	2.26112600	-0.13802600	0.88378900
H	0.59373400	1.64967600	0.00022900
C	-0.86431400	0.10640000	-0.00002200
N	-1.96817000	-0.28100700	-0.00008900
H	1.34808100	-1.39940700	-0.00078500
H	2.26203400	-0.13685200	-0.88280700

[N-Int3]
0 2

C	1.68018800	1.48795300	-0.64068100
C	1.97402400	0.49430100	0.30223600
C	-1.49063500	0.84511400	1.46279400
C	-1.91394000	-0.13688700	0.66065200
H	-1.68783600	0.80014600	2.53654000
H	-0.94219100	1.70873200	1.07683200
H	-2.45934200	-1.00586700	1.03993300
C	-1.66809800	-0.11836000	-0.75242800
N	-1.46767300	-0.10806800	-1.89327700
H	2.08334600	2.49349400	-0.50924900
H	1.05732400	1.27899000	-1.51330500
C	1.57022200	-0.79580200	0.23593900
N	1.02815300	-1.88955400	0.28739500
H	2.60995300	0.73083900	1.16390000
H	1.50481300	-2.68089000	-0.16454800

[α-Int3]
0 2

C	-1.03494100	1.38780900	0.69636900
C	-2.09371400	1.10797700	-0.31792100
H	-2.93293500	1.82760700	-0.23611000
C	0.75162000	-1.07349900	-0.16012300
C	1.91713300	-0.88483300	0.46912800
H	0.00064900	-1.74511600	0.26264700
H	0.52221100	-0.58278800	-1.10968000
H	2.15297100	-1.38020600	1.41557700
C	2.92847500	-0.01108800	-0.04952200
N	3.75219400	0.69443100	-0.45643100
H	-0.29099400	2.15723400	0.48097800
H	-1.11436800	0.98742500	1.70952400
C	-2.66681300	-0.23356400	-0.19669800
N	-3.10099700	-1.29986800	-0.09021300
H	-1.70647200	1.21710200	-1.34382600

[β-Int3]
0 2

C	1.24879300	1.26359400	1.21448600
C	1.61082300	0.81647000	-0.15616400
H	0.31084100	1.84395400	1.18471000
H	1.73442400	1.55192500	-0.95691800
C	1.79977300	-0.52054100	-0.49863400
N	1.94682700	-1.64598700	-0.78280000
H	1.13019700	0.42422300	1.91190700
H	2.02321600	1.94542700	1.60644100
C	-1.61097300	-1.08444400	1.27122100
C	-1.58686900	-0.90720200	-0.05356500
H	-1.49677200	-2.08637500	1.69172100
H	-1.74445900	-0.24992500	1.96438300
H	-1.44871600	-1.73954100	-0.74971900
C	-1.71538000	0.39147400	-0.64882700
N	-1.80193200	1.43944500	-1.13486100

[N-TS]
0 2

C	0.58420500	-0.74387400	0.57654100
C	1.75267200	-0.87669300	-0.23276000
C	-0.75599900	0.74958300	-0.47995500
C	-1.91342500	0.90035400	0.23887800
H	0.02774500	1.50341200	-0.38444300

H	-0.74045200	0.13227000	-1.38079700
H	-1.98800700	1.62343500	1.05596600
C	-3.04185500	0.06429400	0.03524700
N	-3.97098900	-0.61581000	-0.12833900
H	-0.14838500	-1.55239400	0.54378400
H	0.64271200	-0.17742700	1.50852600
C	2.85932100	-0.13676900	-0.08820700
N	3.81570700	0.61381600	-0.03231200
H	1.76584900	-1.59228100	-1.06245900
H	4.61799700	0.33557700	0.54552000

[α-TS]
0 2

C	-0.68859400	1.01975600	0.60024600
C	-1.92106400	1.07515500	-0.24728600
H	-2.53443500	1.95727100	0.01998200
C	0.61978300	-0.78071000	-0.36239800
C	1.77872000	-0.87971900	0.33597400
H	-0.20739300	-1.45375900	-0.12701000
H	0.56648100	-0.21557900	-1.29581100
H	1.86581700	-1.52209100	1.21670500
C	2.93068900	-0.10940900	0.00253000
N	3.87340800	0.51420800	-0.26111000
H	0.05062400	1.80640500	0.43230000
H	-0.76284300	0.61603700	1.61315300
C	-2.77647600	-0.10401500	-0.11338500
N	-3.44004000	-1.04404100	-0.00168600
H	-1.67015900	1.19421300	-1.31383300

[β-TS]
0 2

C	-2.21551100	-1.42935200	-0.22875700
C	-1.22866100	-0.34874800	-0.54074400
H	-1.73561900	-2.41548700	-0.29302700
H	-0.58434500	-0.47214600	-1.41643800
C	-1.54619000	0.99921300	-0.23740900
N	-1.77604000	2.10212900	0.05142900
H	-2.65628600	-1.30476200	0.77044200
H	-3.03651800	-1.40974400	-0.96710900
C	0.42341800	-0.78460500	0.94499800
C	1.38439400	0.18273600	0.83181400
H	-0.29159100	-0.72396600	1.76851000
H	0.55500600	-1.75641000	0.46326700
H	1.33604400	1.10802900	1.41270600

C	2.44912200	0.08227300	-0.10575900
N	3.32087800	0.00721200	-0.86903100

[β-Int4]
0 2

C	-2.02851800	-1.55199100	-0.11615000
C	-1.00519200	-0.43249900	-0.32986300
H	-1.54380100	-2.52330400	-0.28850900
H	-0.63254200	-0.47537100	-1.36606800
C	-1.63909100	0.88480700	-0.18231800
N	-2.13933400	1.91960200	-0.05492200
H	-2.42060100	-1.53437500	0.91141000
H	-2.86960900	-1.45490600	-0.81667500
C	0.20010100	-0.57661500	0.63073100
C	1.25210800	0.46347100	0.43407500
H	-0.17204900	-0.51314800	1.66779300
H	0.61753600	-1.58247100	0.48681400
H	1.03481700	1.51462400	0.65022600
C	2.52332100	0.16700100	-0.05118100
N	3.59217300	-0.08475800	-0.45318700

[N-Int4]
0 2

C	0.48983700	-0.03334600	0.60352600
C	1.73156200	-0.73605000	0.11344200
C	-0.61734500	-0.00870500	-0.46563300
C	-1.84482400	0.69461100	0.00827100
H	-0.23335200	0.52760200	-1.35291800
H	-0.85886900	-1.03280100	-0.78731900
H	-1.77059700	1.71538700	0.39741500
C	-3.11130500	0.11675700	-0.01116000
N	-4.17383200	-0.37260700	-0.02981400
H	0.10745200	-0.54829000	1.50020000
H	0.73106100	0.99760100	0.90550200
C	2.89635900	-0.14657900	-0.04557300
N	3.95372800	0.42588700	-0.28993200
H	1.67704800	-1.80292800	-0.13055000
H	4.62227500	0.45034200	0.48865500

[α-Int4]
0 2

C	-0.59431000	0.96997100	0.33092400
C	-1.94013900	0.90611700	-0.39949500
H	-2.57465500	1.75519100	-0.10440000

C	0.37738400	-0.13023700	-0.10321900
C	1.66842300	-0.06962700	0.64124200
H	-0.08090800	-1.11896800	0.09684000
H	0.55511700	-0.08179200	-1.18835000
H	1.66587300	0.06318200	1.72803600
C	2.90816800	-0.21086000	0.02326600
N	3.94812200	-0.32481200	-0.49996600
H	-0.15349700	1.95603200	0.12214400
H	-0.76070000	0.91518700	1.41826400
C	-2.68934500	-0.31900800	-0.12471600
N	-3.26744200	-1.29491000	0.10126500
H	-1.79706800	0.97107500	-1.48964400

[β-Int4]$^-$

-1 1

C	-2.09563400	-1.40385700	-0.29243400
C	-0.92556500	-0.41570900	-0.31014600
H	-1.70701500	-2.42603000	-0.41144900
H	-0.40979300	-0.47910300	-1.28313000
C	-1.41042400	0.96443000	-0.20377100
N	-1.80345300	2.04769600	-0.09257400
H	-2.63868100	-1.35292400	0.66389300
H	-2.80803800	-1.21041000	-1.10768900
C	0.12719700	-0.69590500	0.80335200
C	1.31993500	0.22151100	0.85311200
H	-0.41105700	-0.68053100	1.76819900
H	0.43514000	-1.74576300	0.65007700
H	1.19930600	1.19991400	1.33235100
C	2.35035400	0.09920300	-0.06001300
N	3.25273300	-0.03672300	-0.81497700

[N-Int4]$^-$

-1 1

C	0.39914100	0.55833700	-0.55343300
C	1.80721400	0.73634800	-0.03092300
C	-0.68665100	0.85504300	0.50323500
C	-2.11327300	0.76623200	0.01064100
H	-0.52953000	0.16198800	1.35062000
H	-0.48300700	1.86353100	0.91243900
H	-2.46327700	1.54109900	-0.68332400
C	-2.78822300	-0.43814000	-0.02082200
N	-3.38389000	-1.46325200	-0.00005900
H	0.24384500	1.23335900	-1.41376700
H	0.26594800	-0.46779100	-0.93342600

C	2.70197400	-0.22363600	0.03809200
N	3.49830500	-1.14771900	0.19401700
H	2.11629900	1.72435200	0.33073800
H	4.12771700	-1.30483500	-0.60172400

[α-Int4]$^-$

-1 1

C	-0.39243100	0.64791500	0.50402100
C	-1.74742200	1.05681500	-0.09361700
H	-2.19249200	1.89173900	0.46913100
C	0.34135200	-0.44619500	-0.28738100
C	1.67876600	-0.87192600	0.27671400
H	-0.33195000	-1.32209600	-0.35990100
H	0.46183800	-0.08808600	-1.32724400
H	1.67640900	-1.45329500	1.20746500
C	2.83236400	-0.16646700	-0.00424500
N	3.83055500	0.40802300	-0.28633100
H	0.23370500	1.55376500	0.54284900
H	-0.53665900	0.31927900	1.54670000
C	-2.72516900	-0.03016900	-0.10204100
N	-3.48917600	-0.89916700	-0.10009300
H	-1.62526800	1.39687000	-1.13473900

[B-P]

0 1

C	-2.02697500	-1.37872300	-0.40981600
C	-0.85409500	-0.39871100	-0.30029700
H	-1.63616300	-2.39369200	-0.56905600
H	-0.28407300	-0.42175600	-1.24495000
C	-1.34502100	0.97993400	-0.16409700
N	-1.72913000	2.06417200	-0.04331500
H	-2.62699700	-1.37725900	0.51227500
H	-2.68062200	-1.12268100	-1.25530400
C	0.08546800	-0.76056900	0.86166400
C	1.31901000	0.13697500	1.00202200
H	-0.47272500	-0.71704400	1.80880200
H	0.40157600	-1.80444100	0.71902700
H	1.90838400	-0.17311000	1.87765500
C	2.20092000	0.09277100	-0.16321400
N	2.88367100	0.04890700	-1.09548700
H	1.03299400	1.18837500	1.16559500

[L-P]

0 1

C	-0.74348000	1.11588600	0.20910100
C	-2.09623900	0.76455900	-0.42037200
H	-2.85881400	1.50354700	-0.13230600
C	0.38346300	0.18367800	-0.22029400
C	1.71622900	0.59364300	0.41596500
H	0.14887600	-0.85369300	0.06900700
H	0.48078200	0.19757100	-1.31761800
H	1.64533600	0.57426300	1.51497700
C	2.82097000	-0.27959900	0.02924200
N	3.68756400	-0.97831500	-0.28423000
H	-0.50404500	2.14910700	-0.08595700
H	-0.83791900	1.11229200	1.30678800
C	-2.59161500	-0.55281200	-0.02353000
N	-2.96847100	-1.59794700	0.29799000
H	-2.03104000	0.77692400	-1.51982500
H	1.98720400	1.62170000	0.12793900

[SET-TS]
-1 2

C	-2.34693900	-1.39149300	-0.23002600
C	-1.29149900	-0.48720000	-0.47767200
H	-2.26307900	-2.42778800	-0.56722800
H	-0.61174400	-0.69948900	-1.31033300
C	-1.51266300	0.91210000	-0.28874100
N	-1.64865100	2.04924800	-0.08146600
H	-3.15941100	-1.13835500	0.45700800
C	0.28605000	-0.66540600	0.96107100
C	1.34030100	0.25336300	0.80503100
H	-0.37847600	-0.53130900	1.82030700
H	0.45478000	-1.71169900	0.68803900
H	1.28014900	1.24802600	1.25688300
C	2.39446500	0.03881700	-0.09434400
N	3.28572200	-0.14931600	-0.83233300

[SET-Int5]
-1 2

C	2.07238300	1.46187200	-0.33719200
C	0.96133900	0.47081900	-0.33373600
H	1.90324900	2.44174500	-0.79047300
H	0.40125300	0.52586600	-1.28243000
C	1.47022400	-0.90002900	-0.22722600
N	1.87582900	-1.97800600	-0.11180900
H	2.94557100	1.32331100	0.30626900
C	-0.10340400	0.72389200	0.81987100

C	-1.25994900	-0.22908300	0.86511700
H	0.45583800	0.71190300	1.77055900
H	-0.43489800	1.76497200	0.66756000
H	-1.09974600	-1.21325900	1.32000700
C	-2.29370200	-0.12969800	-0.04989500
N	-3.19763100	-0.01359200	-0.80435300

[SET-Int4]
-1 2

C	0.43367800	-0.49895400	-0.48407300
C	1.70998000	-0.90794900	0.11253600
H	-0.22003600	-1.36427900	-0.66902600
H	1.73130000	-1.71836900	0.84824500
C	2.84438600	-0.10596000	0.03862800
N	3.80471500	0.56597200	-0.05174300
H	0.56574000	0.04768600	-1.42969900
C	-0.43377300	0.49861800	0.48502500
C	-1.70982600	0.90802400	-0.11186000
H	0.21977700	1.36383800	0.67086600
H	-0.56634200	-0.04866800	1.43023800
H	-1.73070000	1.71907200	-0.84691800
C	-2.84431800	0.10606400	-0.03930100
N	-3.80478600	-0.56573400	0.05039600

$Me_2CNH_2^{\cdot}$
0 2

C	0.00001400	0.02785900	-0.21321400
H	-0.83345200	1.89139000	-0.18179000
C	-1.28832500	-0.69481400	0.02210300
H	-1.27608900	-1.69197300	-0.44454200
H	-2.14805300	-0.13864300	-0.38937500
C	1.28849900	-0.69454400	0.02216900
H	2.14811200	-0.13823200	-0.38936800
H	1.49324200	-0.84430200	1.10458200
H	1.27645900	-1.69175000	-0.44437600
N	-0.00011600	1.39077400	0.11956400
H	0.83253000	1.89187300	-0.18292600
H	-1.49306600	-0.84478300	1.10449400

$Me_2{}^{\cdot}CNH_2...NCCHCH_2$
0 2

C	2.51810900	-0.10493400	-0.19661100
H	0.86800100	1.03725100	0.18916500
C	-2.39595400	0.39164900	0.28521000

N	-1.27670100	0.68538100	0.28238600
C	-3.78503700	0.03711900	0.30710900
C	-4.38667200	-0.53984700	-0.73790400
H	-4.31996300	0.26942000	1.23275500
H	-5.44751500	-0.79602100	-0.68605800
H	-3.84773200	-0.77020700	-1.66073700
C	2.00246300	-1.31273400	0.52125700
H	2.39544800	-2.23979900	0.07544600
H	0.90073800	-1.36239800	0.49281000
C	3.98183100	-0.01417000	-0.49297500
H	4.20354400	0.80033400	-1.20402300
H	4.58299200	0.18781800	0.42054200
H	4.36057100	-0.95295800	-0.92638500
N	1.88373100	1.10325500	0.12191900
H	2.15184000	1.88276600	-0.47448900
H	2.29442600	-1.31915600	1.59432500

$Me_2{}^{\cdot}CNH_2$...$NCCHCH_2$_SET_cp

0 2

C	2.50332900	0.07105900	0.04478900
H	0.70876100	-0.93135800	-0.08647000
C	-2.26072600	-0.36818500	-0.29771800
N	-1.11932200	-0.62891500	-0.29683900
C	-3.63116500	-0.05864400	-0.31113500
C	-4.30550000	0.51756700	0.74299000
H	-4.15540200	-0.30710700	-1.23976900
H	-5.37380500	0.72737000	0.65177700
H	-3.80745400	0.77439400	1.68234000
C	1.96542600	1.32289200	-0.54856100
H	2.35900900	2.20528700	-0.02027600
H	0.86580300	1.33969600	-0.51837700
C	3.93266900	-0.03570600	0.43254000
H	4.10200000	-0.88053400	1.11753100
H	4.57886500	-0.18825600	-0.45485200
H	4.27175700	0.89349900	0.91642500
N	1.71658700	-1.00273100	0.11152100
H	2.06122700	-1.85624800	0.53932900
H	2.27206100	1.42315100	-1.60898800

$Me_2CNH_2{}^{+}$...$^{-}NCCHCH_2$

0 2

C	-2.45993200	0.00117600	-0.04569800
H	-0.56104600	-0.75570900	0.08818200
C	2.22529100	-0.19856500	0.34719700

N	1.04419200	-0.29527700	0.29948800
C	3.59893000	-0.07840600	0.39916100
C	4.43860900	0.24483800	-0.70171900
H	4.04425700	-0.25254800	1.38562000
H	5.51988700	0.31922000	-0.56252800
H	4.03214100	0.42871100	-1.70051200
C	-3.90381100	-0.27932000	-0.24294300
H	-4.45648000	0.07465900	0.64072900
H	-4.10352000	-1.34593400	-0.40480200
C	-2.01216000	1.40286700	0.15817800
H	-0.92877100	1.46466300	0.31793800
H	-2.29888200	1.99647600	-0.72334800
H	-2.54951300	1.82721100	1.01957200
N	-1.59444700	-0.94853200	-0.04972200
H	-1.90167700	-1.91075200	-0.19217300
H	-4.26618100	0.30512600	-1.10210700

$Me_2CNH_2^+$...$^-$NCCHCH$_2$_N_PT_TS

0 2

C	-2.01798300	0.11972700	-0.00801000
H	-0.21898000	-1.29348500	-0.21624300
C	1.87811700	-0.80636900	0.06481400
N	1.00634500	-1.52474900	-0.33989300
C	2.88934600	-0.00116800	0.50409200
C	3.47965300	1.05059100	-0.23253700
H	3.24253600	-0.21431500	1.51988700
H	4.28449000	1.64115700	0.21008600
H	3.15679000	1.28928900	-1.24942700
C	-3.48421200	0.33462100	0.18198700
H	-3.65135800	1.00258700	1.04054300
H	-4.02295600	-0.60947200	0.33779200
C	-1.15435000	1.33402600	-0.12244600
H	-0.11560400	1.08403200	-0.37049500
H	-1.56563500	2.01024100	-0.88670600
H	-1.17727600	1.87959100	0.83405400
N	-1.49629800	-1.04677300	-0.07010000
H	-2.15472100	-1.82267500	0.02801300
H	-3.89104400	0.84514100	-0.70495300

$Me_2CNH_2^+$_$^-$NCCHCH$_2$_α_PT_TS

0 2

C	-1.68818600	-0.06522200	-0.01035600
H	0.37929800	-0.70219800	-0.59684300
C	2.04694200	0.74069600	-0.37989500

N	2.13186700	1.90353000	-0.34069400
C	1.81594100	-0.66632700	-0.41288200
C	2.08706300	-1.44230500	0.78842100
H	2.14544700	-1.11458700	-1.36271300
H	2.05357300	-2.53389800	0.73137700
H	2.01856400	-0.98214900	1.77897900
C	-3.14527300	0.04146800	-0.31233100
H	-3.71126200	-0.48137300	0.47460600
H	-3.39901200	-0.38663600	-1.29099600
C	-1.17986200	0.61791500	1.21752500
H	-0.20016900	0.23261400	1.52675100
H	-1.08713200	1.69482900	1.00166000
H	-1.90126500	0.50960300	2.03941900
N	-0.87423800	-0.69949100	-0.76767200
H	-1.27120800	-1.12037900	-1.61032200
H	-3.44999000	1.09855000	-0.27624900

$Me_2CNH_2^+_^-NCCHCH_2$_β_PT_TS

0 2

C	1.78305200	-0.04098300	0.03111300
H	0.06677100	1.31208700	0.21438100
C	-2.42177100	-0.56280400	-0.28856600
N	-2.66125500	-1.70785500	-0.17299200
C	-2.13136400	0.79618400	-0.40913100
C	-1.38990400	1.53821600	0.56882400
H	-2.38778900	1.25353200	-1.37071700
H	-1.47187200	2.63230200	0.49813300
H	-1.41642600	1.16691600	1.60453300
C	3.18599700	-0.27938700	-0.41225100
H	3.80212700	-0.51292700	0.47013600
H	3.60784000	0.58853400	-0.93540100
C	1.03503300	-1.18312800	0.63253200
H	0.10792100	-0.86247700	1.12164300
H	0.78954800	-1.89928300	-0.16799200
H	1.67762000	-1.71025200	1.35211900
N	1.21585800	1.09902600	-0.10135700
H	1.75960800	1.84789000	-0.53415100
H	3.21617800	-1.16311200	-1.06736600

$Me_2CNH...HNCCHCH_2$

0 2

C	-2.08539800	-0.09669800	0.01032700
H	0.13389900	1.44174700	0.23009800
C	1.96226600	0.79143800	-0.09057400

N	1.18178800	1.62763500	0.31573100
C	2.91429500	-0.07655400	-0.50977100
C	3.47514600	-1.11137100	0.25967900
H	3.23424000	0.06032600	-1.54972000
H	4.22793700	-1.76765900	-0.18060300
H	3.17718000	-1.27739900	1.29778700
C	-3.55570200	-0.34914700	-0.16163800
H	-3.72718100	-0.97386300	-1.05226400
H	-4.12252200	0.58695000	-0.26149300
C	-1.21213600	-1.31196000	0.11941200
H	-0.16134600	-1.04398700	0.29018200
H	-1.56217000	-1.95536500	0.94176500
H	-1.28654100	-1.90688700	-0.80482300
N	-1.56620100	1.06841700	0.06294700
H	-2.27361900	1.80305700	-0.02905000
H	-3.93980400	-0.91352600	0.70277100

$Me_2CNH\_NCCH_2CH_2$

0 2

C	2.06478500	-0.13719400	-0.05472700
H	-0.93414700	-0.11717800	-0.79122700
C	-2.70380400	-0.66812800	0.15121400
N	-3.26706900	-1.41689300	0.82942000
C	-1.97600600	0.27438900	-0.69516100
C	-1.96947700	1.67001700	-0.17031200
H	-2.40927500	0.22631100	-1.70869900
H	-1.66668800	2.47756800	-0.84000500
H	-2.09462000	1.87668000	0.89493800
C	3.47766500	-0.62212200	0.12583300
H	4.18574700	0.13082800	-0.25546800
H	3.65141300	-1.57430800	-0.39525000
C	1.72223300	1.15243000	0.63588500
H	0.67986000	1.44332800	0.44576200
H	1.87764600	1.05280200	1.72217300
H	2.39134600	1.95702900	0.29106300
N	1.17666200	-0.74483300	-0.73981400
H	1.56144500	-1.60461500	-1.14422900
H	3.69774600	-0.75271100	1.19731200

$Me_2CNH\_HNCCHCH_3$

0 2

C	-1.56206800	-0.33871800	-0.07052800
H	1.17196900	-2.01279500	-0.01335500
C	1.60631100	1.07923700	-0.07822100

N	1.25421000	2.10943800	0.35110700
C	2.01566400	-0.15376200	-0.58029400
C	2.05162700	-1.39275800	0.23983600
H	2.25580300	-0.19266700	-1.64721800
H	2.94956300	-1.98416800	0.00411600
H	2.02398600	-1.18133300	1.31727200
C	-2.09986700	0.96084000	-0.60711900
H	-3.10186200	1.15605400	-0.19260400
H	-2.16088000	0.95384600	-1.70482800
C	-1.40158400	-0.41108700	1.42220000
H	-1.04308000	-1.40160100	1.73219200
H	-0.68908000	0.35807000	1.76163700
H	-2.36033700	-0.19890400	1.92210000
N	-1.23435300	-1.34141100	-0.78920400
H	-1.39260700	-1.12868100	-1.78015800
H	-1.45297700	1.79348000	-0.28771800

C_6H_6H

0 2

H	-0.86748400	-2.13940700	0.00000000
C	0.00011100	1.45719200	0.00000000
C	0.00013900	0.74067900	-1.22731800
C	0.00013900	-0.62583800	-1.25320900
C	-0.00013600	-1.44552700	0.00000000
C	0.00013900	-0.62583800	1.25320900
C	0.00013900	0.74067900	1.22731800
H	-0.00090000	2.54908500	0.00000000
H	-0.00035700	1.29819400	-2.16841600
H	-0.00066500	-1.15762500	-2.20896300
H	0.86724800	-2.13890300	0.00000000
H	-0.00066500	-1.15762500	2.20896300
H	-0.00035700	1.29819400	2.16841600

$C_6H_6H\_NCCHCH_2\_N\_HAT\_TS$

0 2

H	0.27961500	-1.71553800	-0.10707400
C	-1.69687900	-1.05918500	-0.14453000
N	-0.98989200	-1.95588300	-0.46309400
C	-2.44898700	0.05679100	0.23802800
C	-2.47757800	1.21161900	-0.48012300
H	-3.01366700	-0.04760400	1.17030000
H	-3.08479500	2.05304700	-0.13961300
H	-1.91950000	1.32175400	-1.41299500
C	1.02274200	1.62404100	-0.01492600

C	1.57377000	0.88176100	-1.08025100
C	1.83853300	-0.46488000	-0.93481300
C	1.45857200	-1.16077300	0.26925600
C	1.03096000	-0.35381100	1.38351100
C	0.78642400	0.99711900	1.22115200
H	0.82745500	2.69205900	-0.13419400
H	1.81289000	1.38459300	-2.02103800
H	2.28254000	-1.03041600	-1.75806400
H	1.95321300	-2.11658100	0.48720200
H	0.85433000	-0.83175000	2.35051900
H	0.41182700	1.58552600	2.06279200

$C_6H_6H\_NCCHCH_2\_\alpha\_HAT\_TS$

0 2

H	0.62503100	0.40304100	0.92593800
C	2.26300900	-0.49698600	-0.15104500
N	2.51302100	-1.59353400	-0.43309700
C	1.87467800	0.83319300	0.23161500
C	1.46308500	1.74666300	-0.73817300
H	2.36808100	1.19956500	1.13987600
H	1.17922700	1.42387000	-1.74224900
H	1.36357200	2.80306500	-0.48175400
C	-0.58421700	0.07797700	1.35126900
C	-0.76263700	-1.26268800	0.84148200
C	-1.40613500	-1.46889100	-0.36286100
C	-1.99020800	-0.39059600	-1.05360400
C	-1.96704600	0.90124700	-0.49355200
C	-1.33133000	1.13193500	0.71035600
H	-0.36918300	0.18573700	2.42202800
H	-0.32459700	-2.10201200	1.38653200
H	-1.48332400	-2.47887800	-0.77332500
H	-2.49745400	-0.56272200	-2.00559000
H	-2.47878000	1.72068000	-1.00478600
H	-1.32890300	2.13127100	1.15207700

$C_6H_6H\_NCCHCH_2\_\beta\_HAT\_TS$

0 2

H	-0.06443300	1.27491900	0.51049100
C	-2.63978900	-0.30019700	-0.27378300
N	-3.38961500	-1.03844900	0.22519900
C	-1.73590500	0.59889400	-0.88922200
C	-1.26863500	1.73047000	-0.24660100
H	-1.35828400	0.30800000	-1.87344100
H	-1.78403000	2.10432900	0.64480800

H	-0.70735700	2.46656000	-0.83094900
C	2.04369600	1.02390500	0.18918500
C	0.94550000	0.73409400	1.09473600
C	0.50915900	-0.64572400	1.16745800
C	0.92160500	-1.55801000	0.21955900
C	1.86769100	-1.19614100	-0.76130400
C	2.44095800	0.09237800	-0.74506800
H	2.49824000	2.01732200	0.21108100
H	0.90106100	1.31978400	2.02238000
H	-0.21094500	-0.93467700	1.93680900
H	0.53387900	-2.57969700	0.24351700
H	2.18831700	-1.92742400	-1.50645700
H	3.22517000	0.34200600	-1.46438000

C_6H_6_$HNCCHCH_2$

0 2

H	0.01738500	1.89000200	-0.17275500
C	1.76167400	1.08625900	-0.12918000
N	0.95510200	1.87342100	-0.59971200
C	2.77338000	0.28153400	0.26780000
C	3.01340600	-1.01701900	-0.20204500
H	3.41627200	0.70668000	1.04801600
H	3.84471200	-1.59469400	0.20557600
H	2.39002200	-1.46799800	-0.97736500
C	-0.58073600	-1.32222900	0.57584200
C	-0.96519000	-1.31773800	-0.76645600
C	-1.85316800	-0.34797400	-1.23589000
C	-2.35807700	0.61753300	-0.36253600
C	-1.97007900	0.61584200	0.97999300
C	-1.08109000	-0.35430400	1.44889700
H	0.11933500	-2.07777500	0.94100100
H	-0.56922400	-2.07268600	-1.45028500
H	-2.15285500	-0.34400400	-2.28671800
H	-3.05311700	1.37682700	-0.72933000
H	-2.36282000	1.37303800	1.66311700
H	-0.77615300	-0.35475500	2.49818700

C_6H_6H_$NCCH_2CH_2$

0 2

H	1.53850900	1.09069300	1.30055200
C	2.53544000	-0.24441600	0.05182600
N	2.89988100	-1.31779700	-0.17595100
C	2.06802800	1.11298100	0.33272600
C	1.20262300	1.68183600	-0.74066800

H	2.96760400	1.73817200	0.50193800
H	1.27293400	1.32860600	-1.77154700
H	0.62146800	2.57874100	-0.51780800
C	-1.40536800	0.09037500	1.42971600
C	-0.70435700	-1.03937200	1.00356000
C	-0.76309200	-1.43429800	-0.33446300
C	-1.52575400	-0.70136700	-1.24581400
C	-2.22808500	0.42790000	-0.81957100
C	-2.16669500	0.82464300	0.51781500
H	-1.35689700	0.40083200	2.47645600
H	-0.10418100	-1.61166300	1.71533600
H	-0.20620900	-2.31315300	-0.66835400
H	-1.57106200	-1.01002100	-2.29317900
H	-2.82348600	1.00278300	-1.53327600
H	-2.71428600	1.70989700	0.85077300

$C_6H_6H\_NCCHCH_3$

0 2

H	-2.12269800	-2.11794000	-0.06171200
C	-1.76753200	1.17871600	0.13994100
N	-1.44096100	2.23686100	-0.23801100
C	-2.15166900	-0.08396300	0.58520500
C	-2.60711500	-1.16552700	-0.32825700
H	-2.14055300	-0.24719700	1.66704600
H	-2.39941400	-0.93657200	-1.38186000
H	-3.69496900	-1.32263300	-0.21434800
C	1.42951500	-0.36517300	1.37453200
C	0.96928000	-1.42576000	0.59143400
C	0.95898500	-1.31325000	-0.80050000
C	1.40821400	-0.13985300	-1.40888400
C	1.87043400	0.91998700	-0.62589300
C	1.88032600	0.80764000	0.76574400
H	1.43549500	-0.45294400	2.46384600
H	0.61469900	-2.34313000	1.06800600
H	0.59582700	-2.14220200	-1.41303500
H	1.39766100	-0.05034600	-2.49801000
H	2.21951400	1.83942000	-1.10225300
H	2.23853500	1.63861700	1.37846300

$C_6H_6H\_NCCH_2CH_2$

0 2

H	1.53850900	1.09069300	1.30055200
C	2.53544000	-0.24441600	0.05182600
N	2.89988100	-1.31779700	-0.17595100

C	2.06802800	1.11298100	0.33272600
C	1.20262300	1.68183600	-0.74066800
H	2.96760400	1.73817200	0.50193800
H	1.27293400	1.32860600	-1.77154700
H	0.62146800	2.57874100	-0.51780800
C	-1.40536800	0.09037500	1.42971600
C	-0.70435700	-1.03937200	1.00356000
C	-0.76309200	-1.43429800	-0.33446300
C	-1.52575400	-0.70136700	-1.24581400
C	-2.22808500	0.42790000	-0.81957100
C	-2.16669500	0.82464300	0.51781500
H	-1.35689700	0.40083200	2.47645600
H	-0.10418100	-1.61166300	1.71533600
H	-0.20620900	-2.31315300	-0.66835400
H	-1.57106200	-1.01002100	-2.29317900
H	-2.82348600	1.00278300	-1.53327600
H	-2.71428600	1.70989700	0.85077300

$C_6H_6H\_NCCHCH_3$

0 2

H	-2.12269800	-2.11794000	-0.06171200
C	-1.76753200	1.17871600	0.13994100
N	-1.44096100	2.23686100	-0.23801100
C	-2.15166900	-0.08396300	0.58520500
C	-2.60711500	-1.16552700	-0.32825700
H	-2.14055300	-0.24719700	1.66704600
H	-2.39941400	-0.93657200	-1.38186000
H	-3.69496900	-1.32263300	-0.21434800
C	1.42951500	-0.36517300	1.37453200
C	0.96928000	-1.42576000	0.59143400
C	0.95898500	-1.31325000	-0.80050000
C	1.40821400	-0.13985300	-1.40888400
C	1.87043400	0.91998700	-0.62589300
C	1.88032600	0.80764000	0.76574400
H	1.43549500	-0.45294400	2.46384600
H	0.61469900	-2.34313000	1.06800600
H	0.59582700	-2.14220200	-1.41303500
H	1.39766100	-0.05034600	-2.49801000
H	2.21951400	1.83942000	-1.10225300
H	2.23853500	1.63861700	1.37846300

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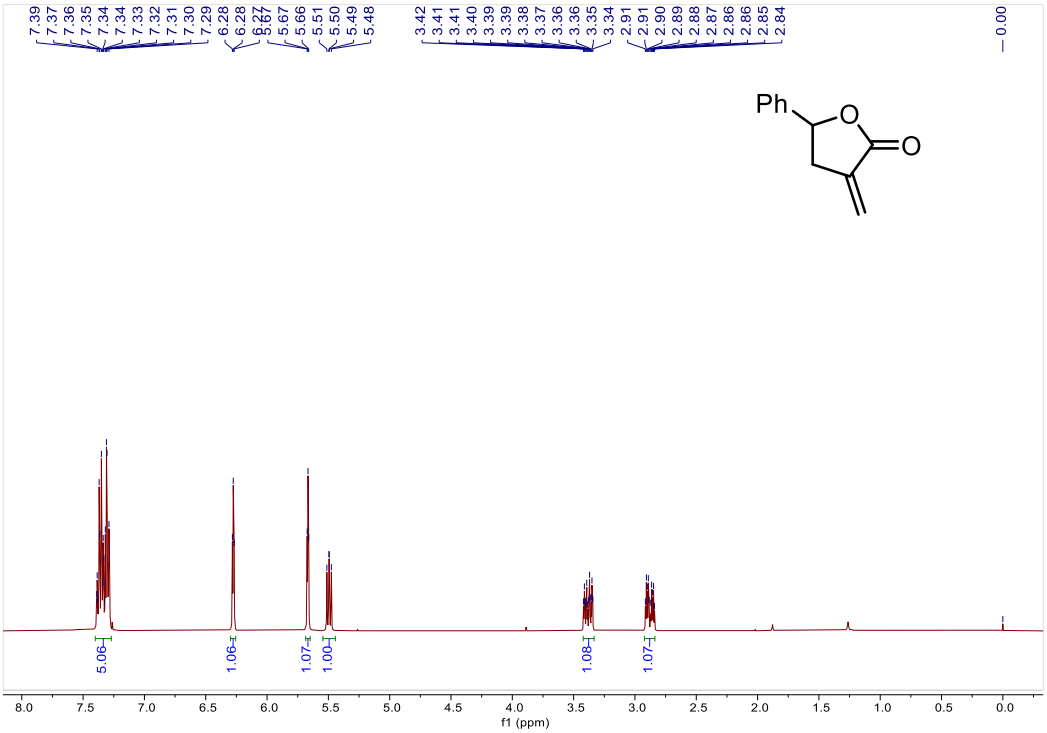
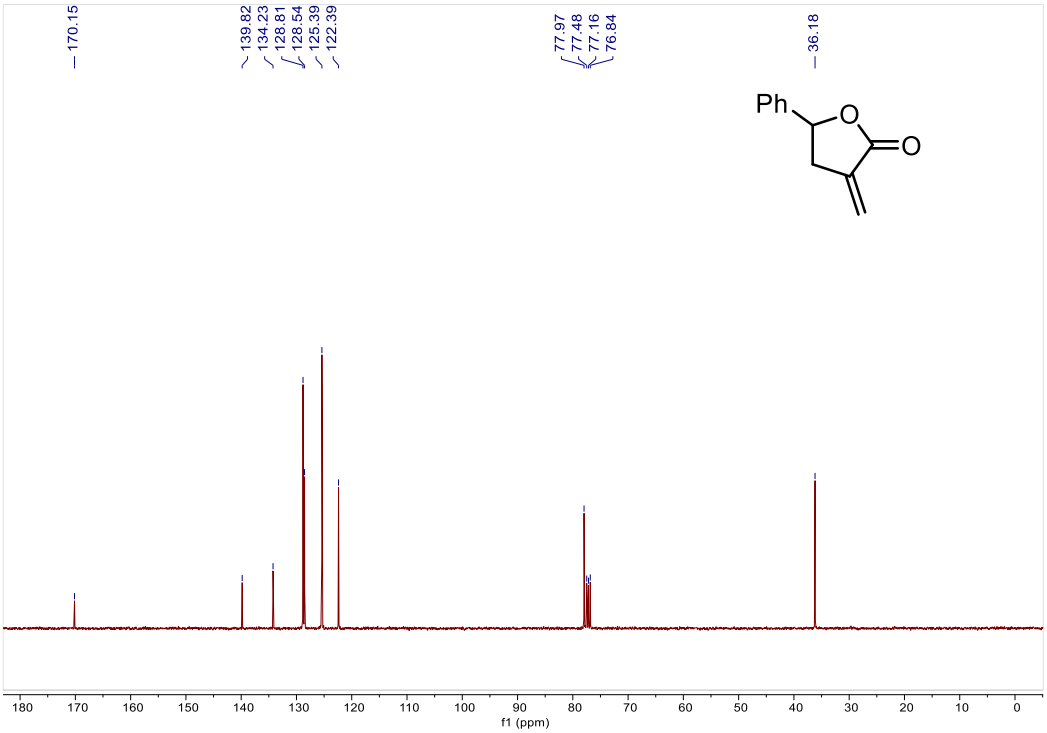
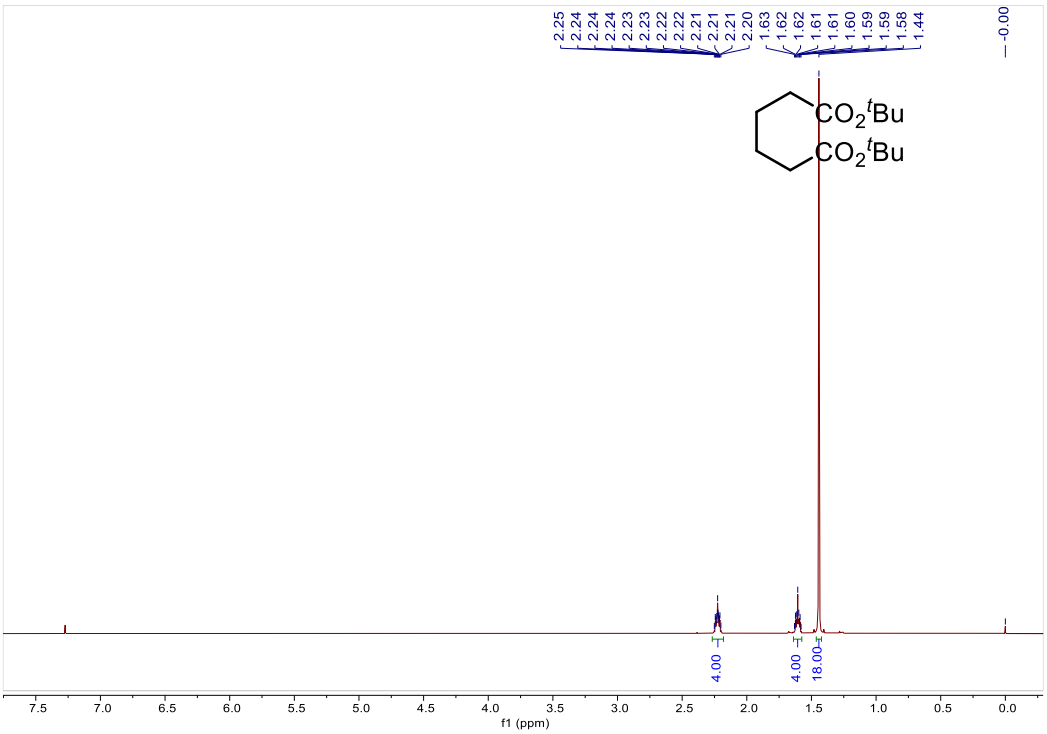
11. Copies of ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F NMR Spectra for Synthesized Compounds



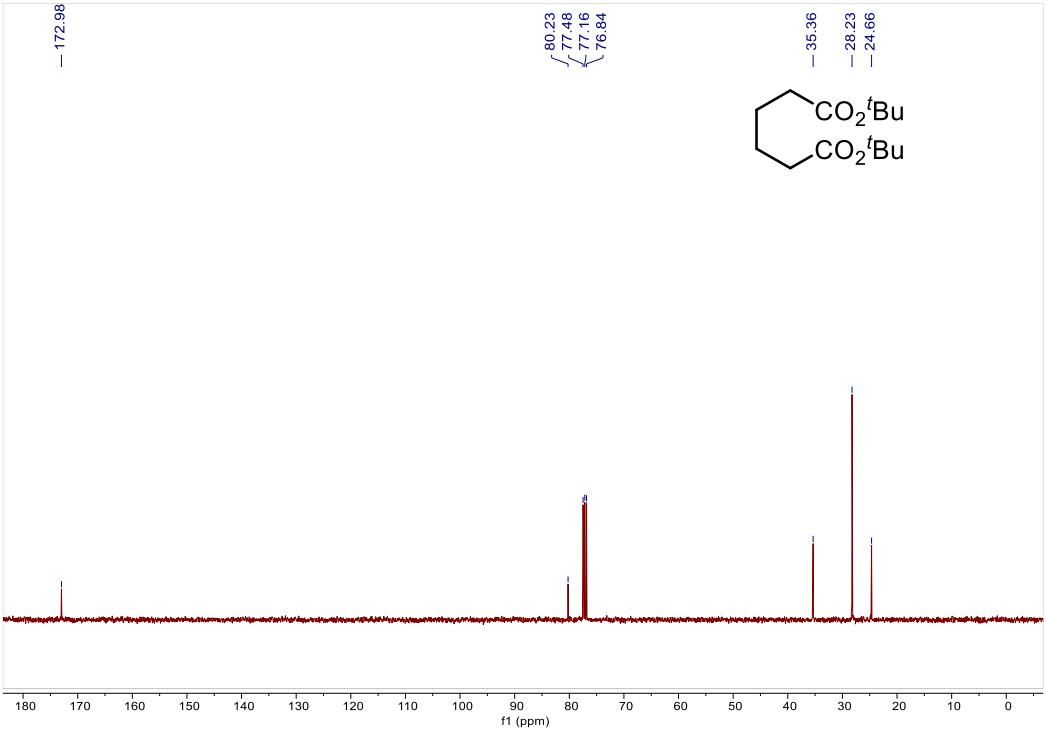
^{1}H NMR for compound **1g**



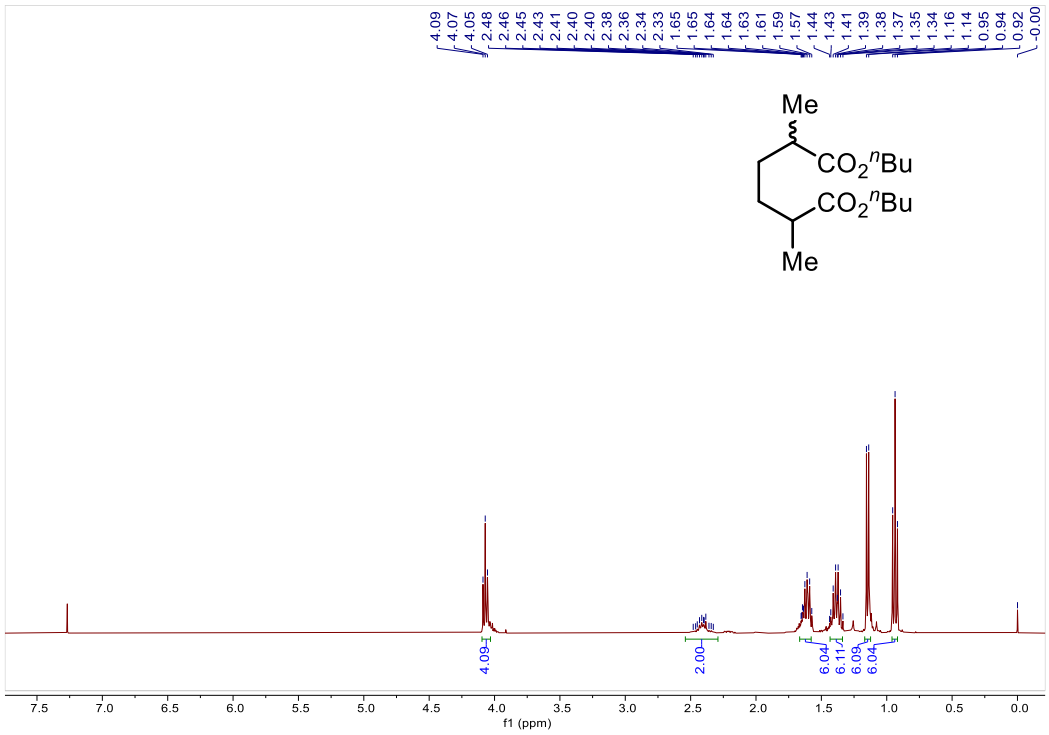
$^{13}C\{^{1}H\}$ NMR for compound **1g**



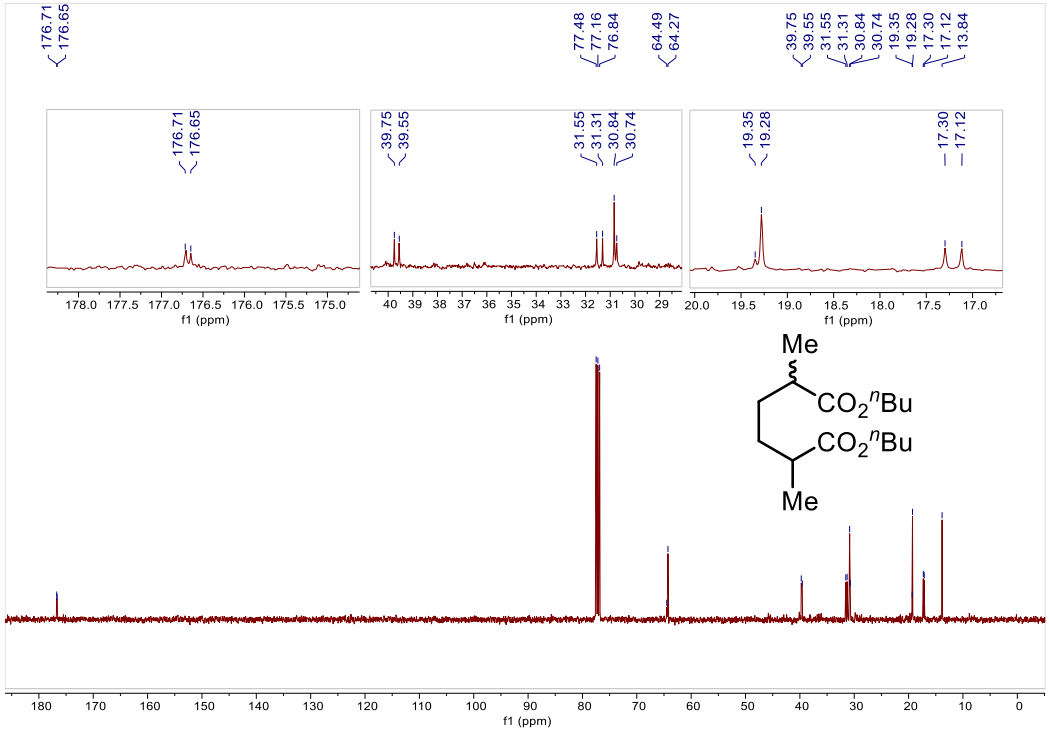
^{1}H NMR for compound **2a**



^{13}C{^{1}H} NMR for compound **2a**



^{1}H NMR for compound **2b**



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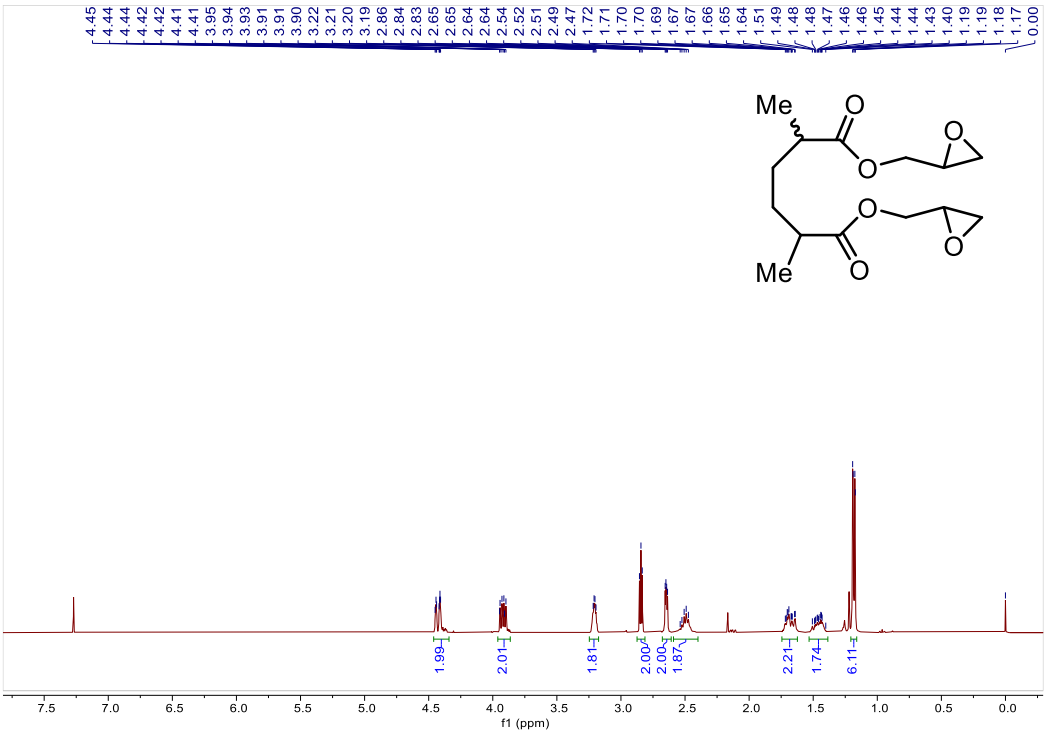

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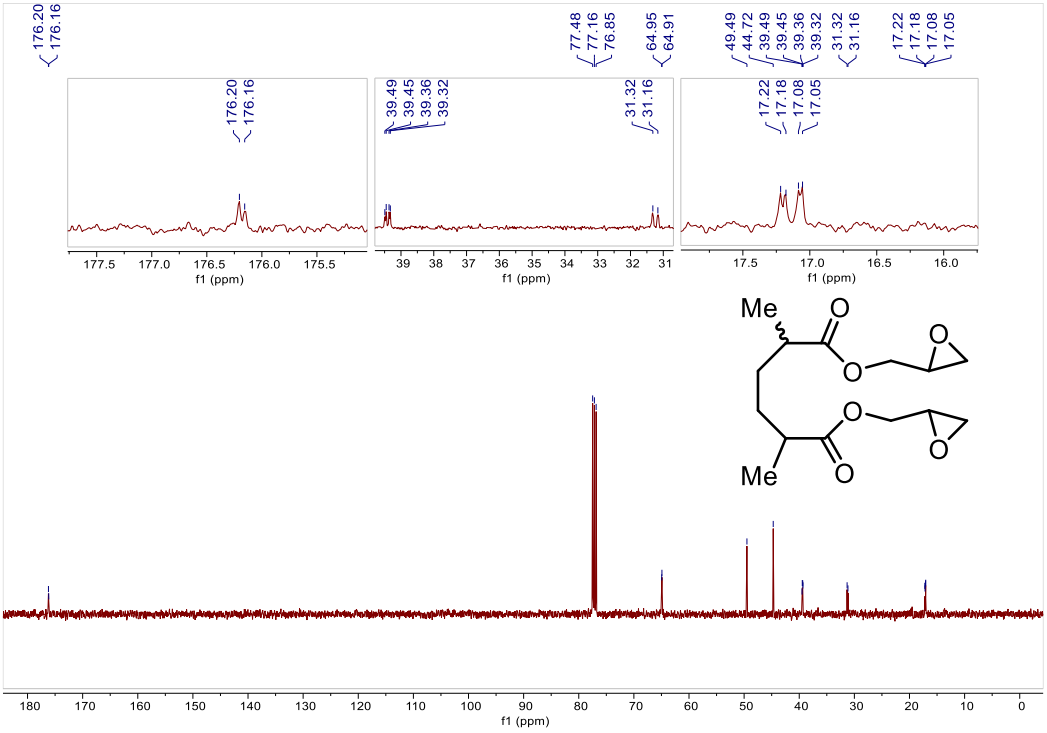
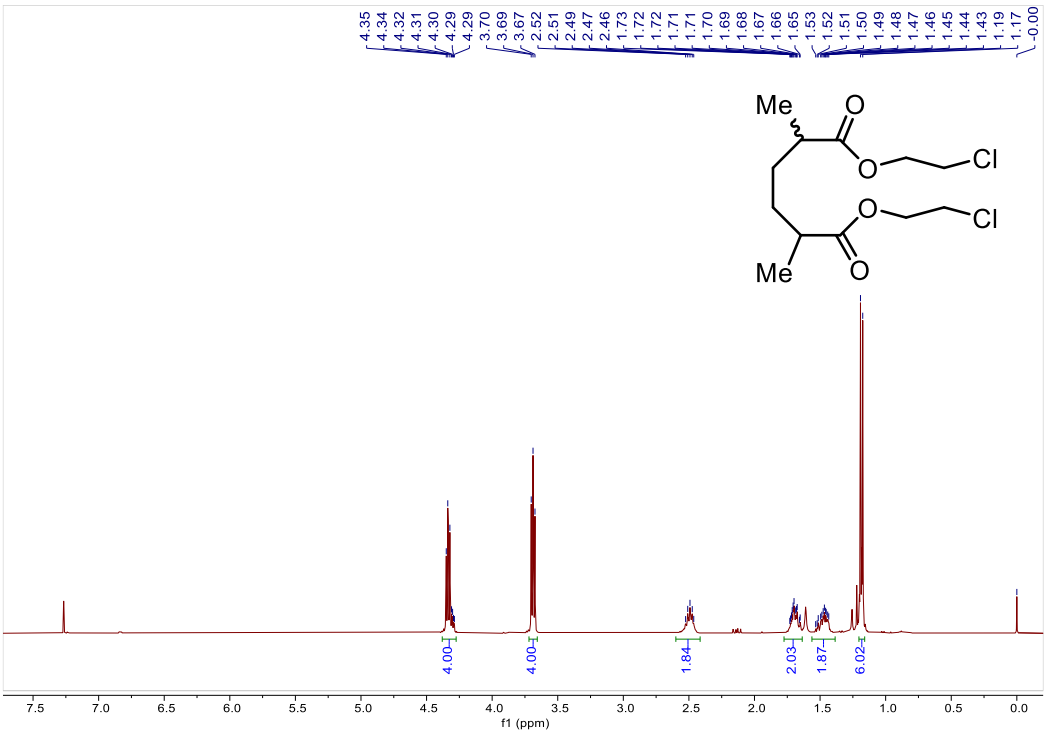


^{13}C{^{1}H} NMR for compound **2c**



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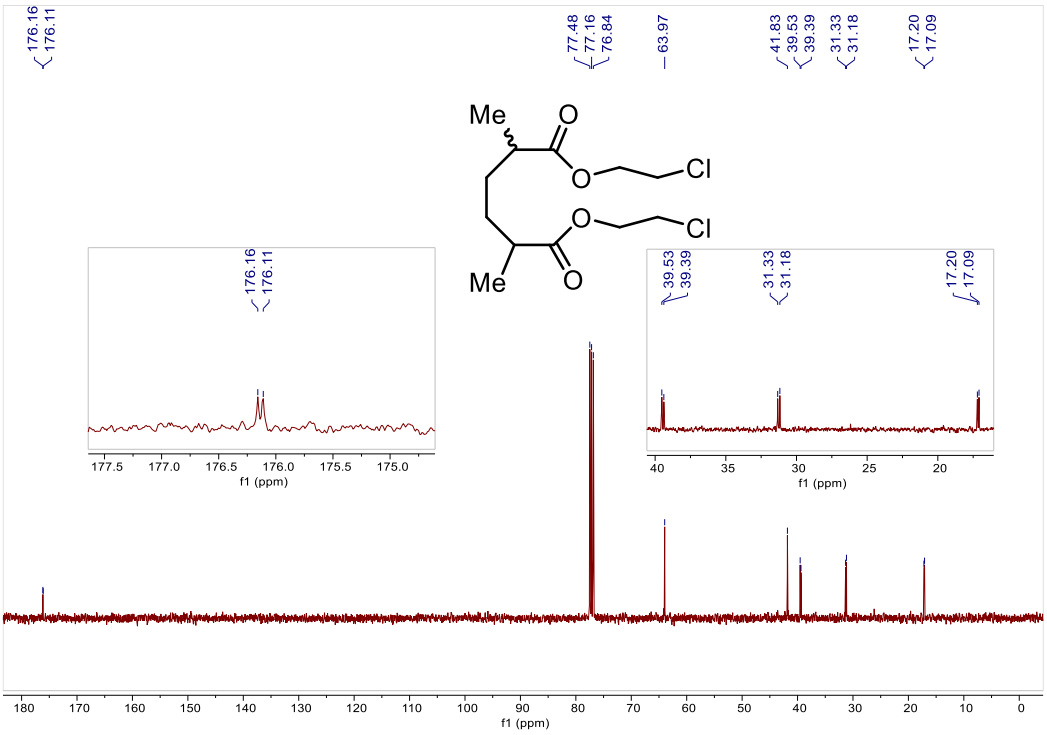

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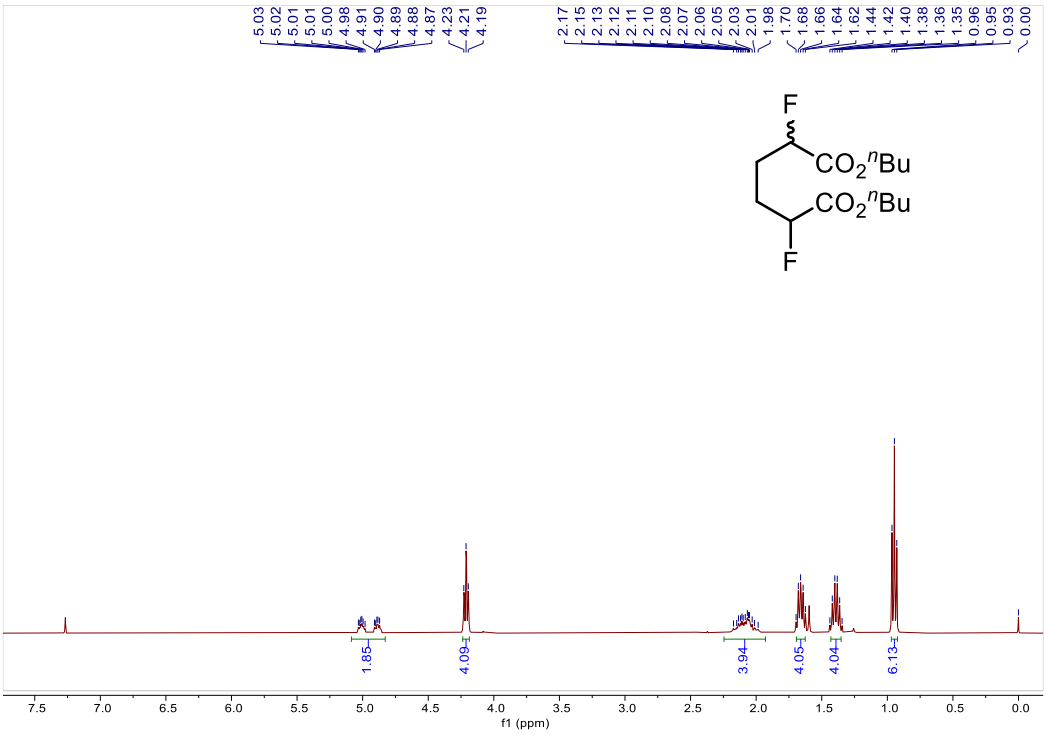

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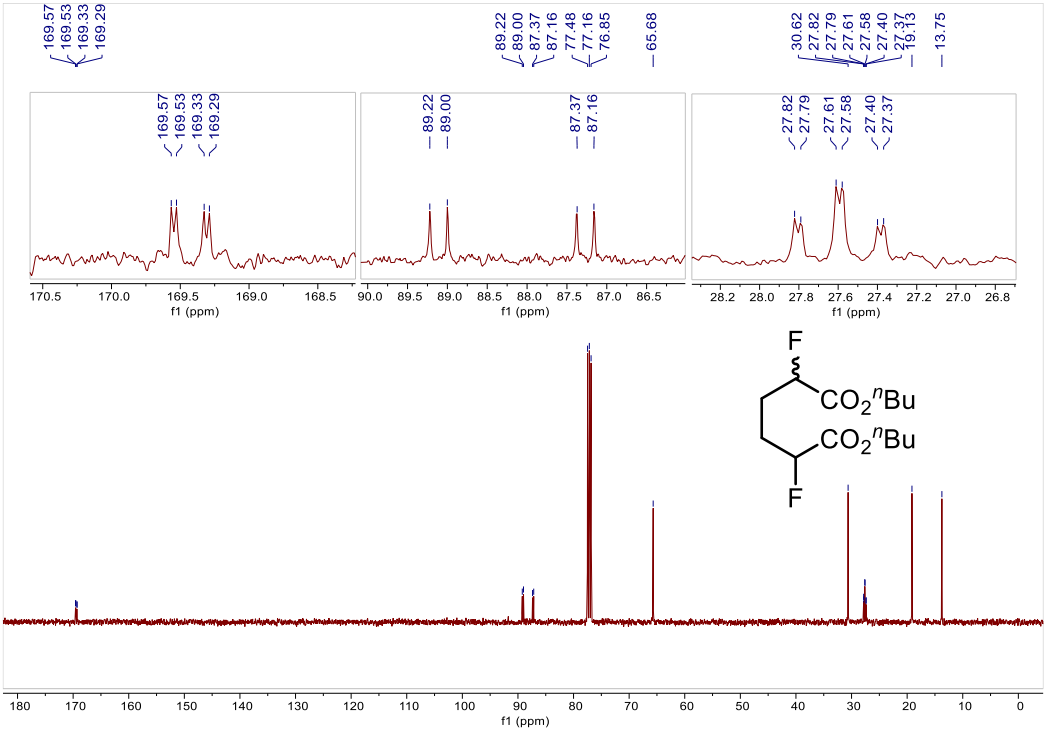

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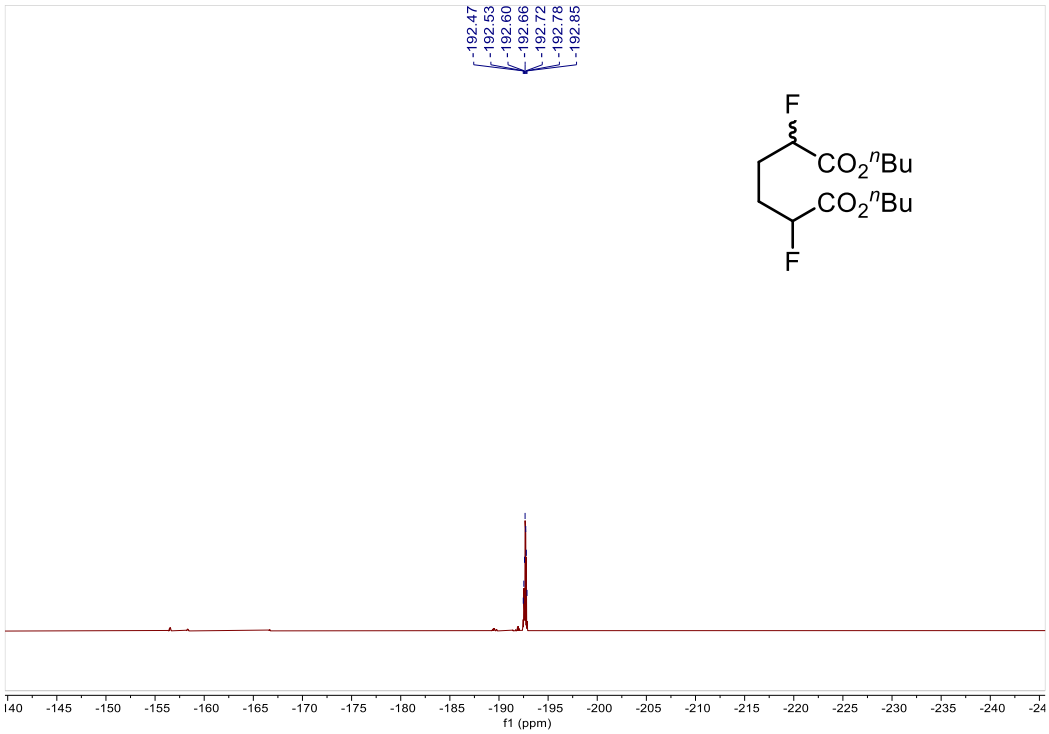
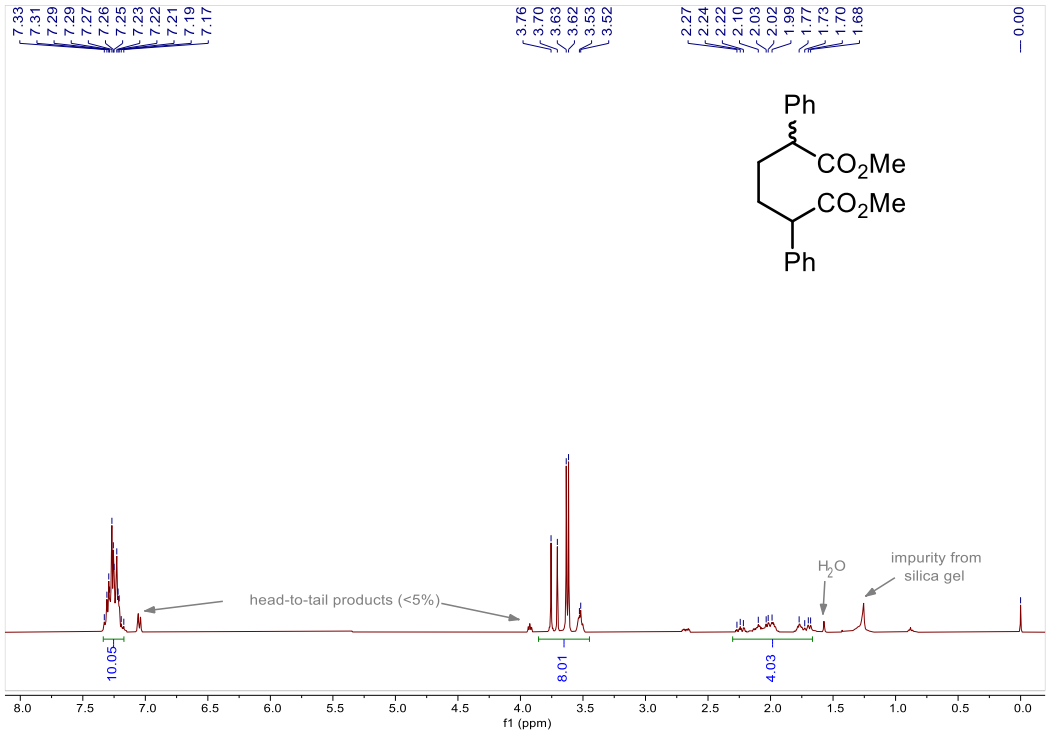


^{19}F NMR for compound **2e**



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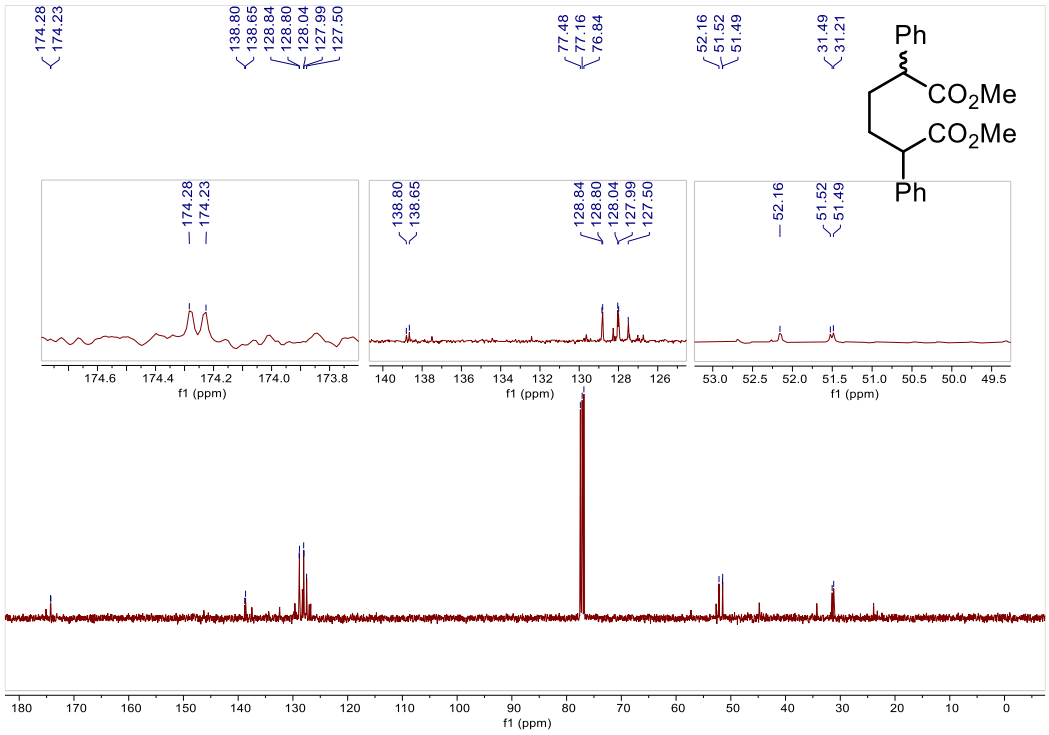

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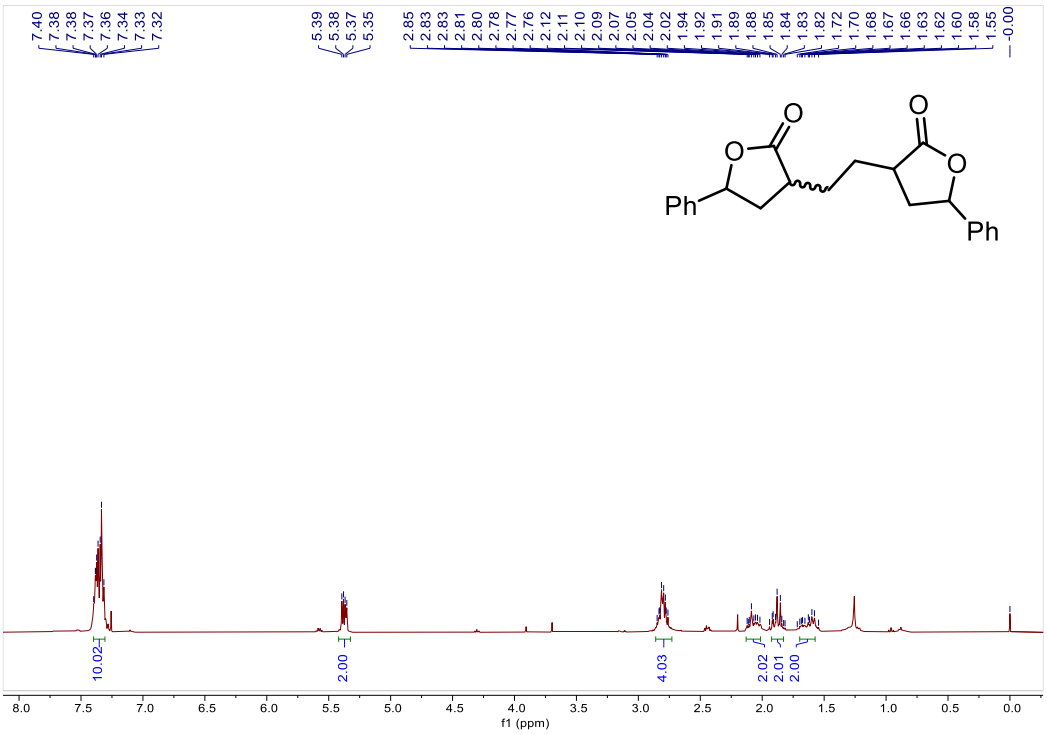
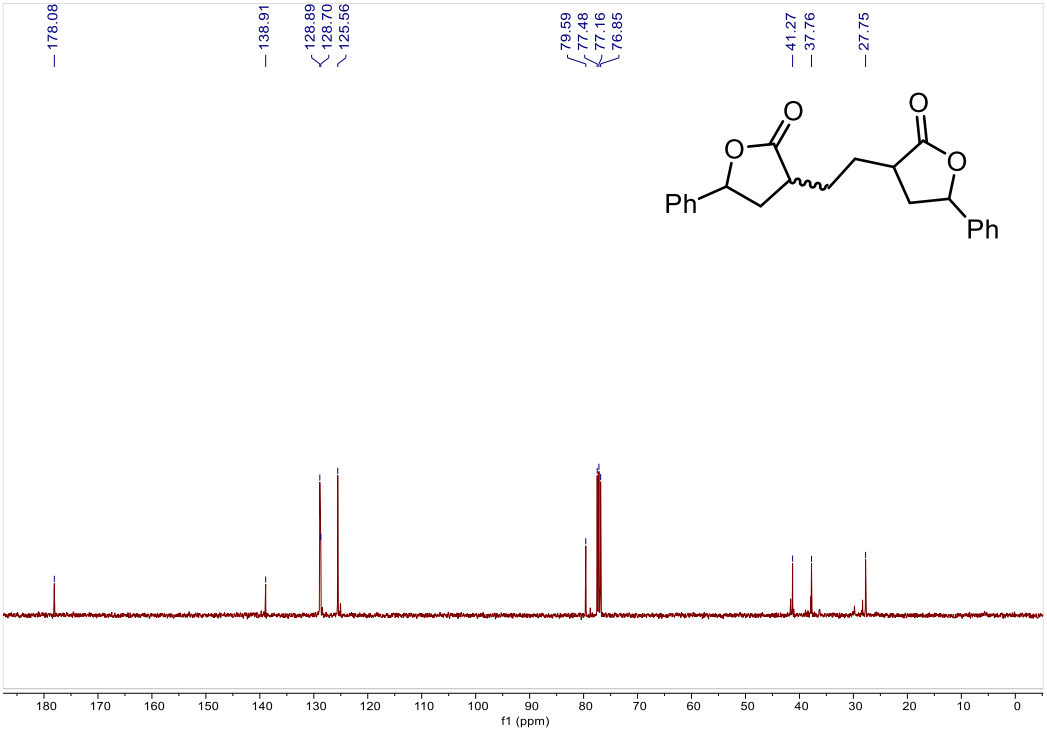


^{1}H NMR for compound **2g**



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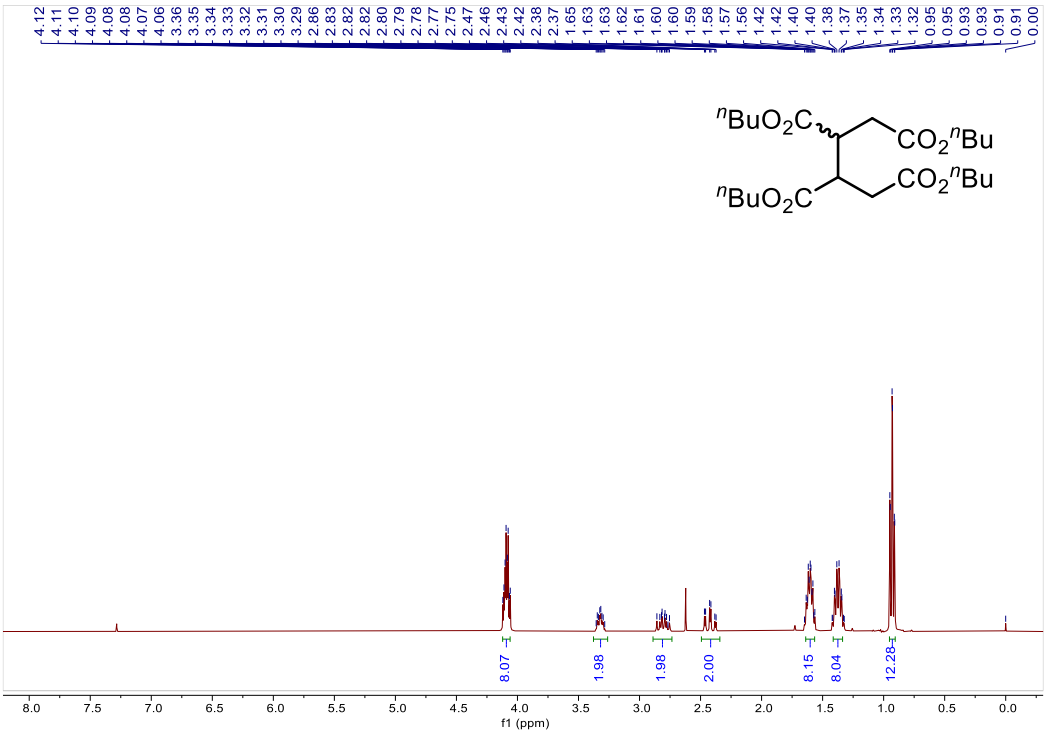

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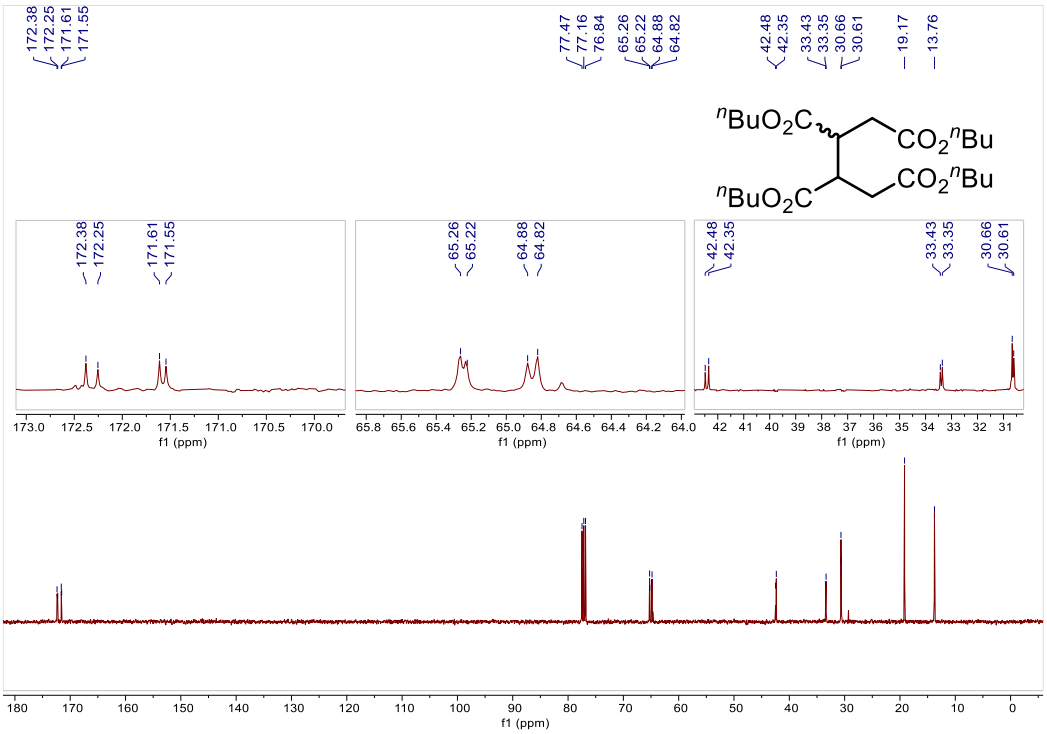

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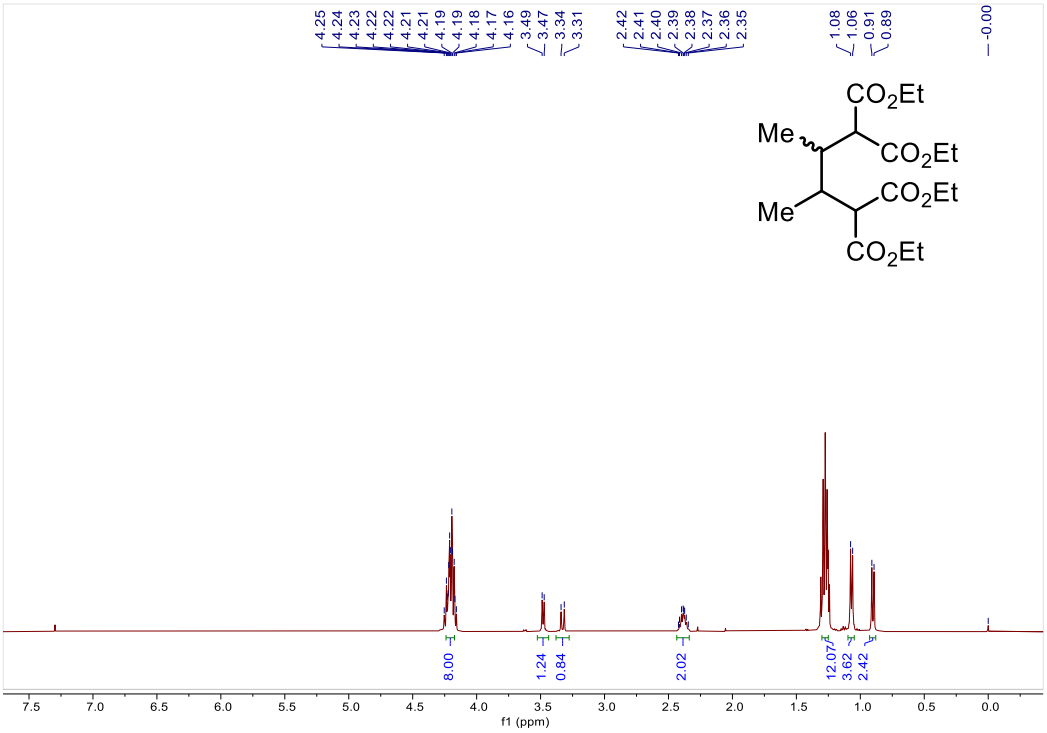
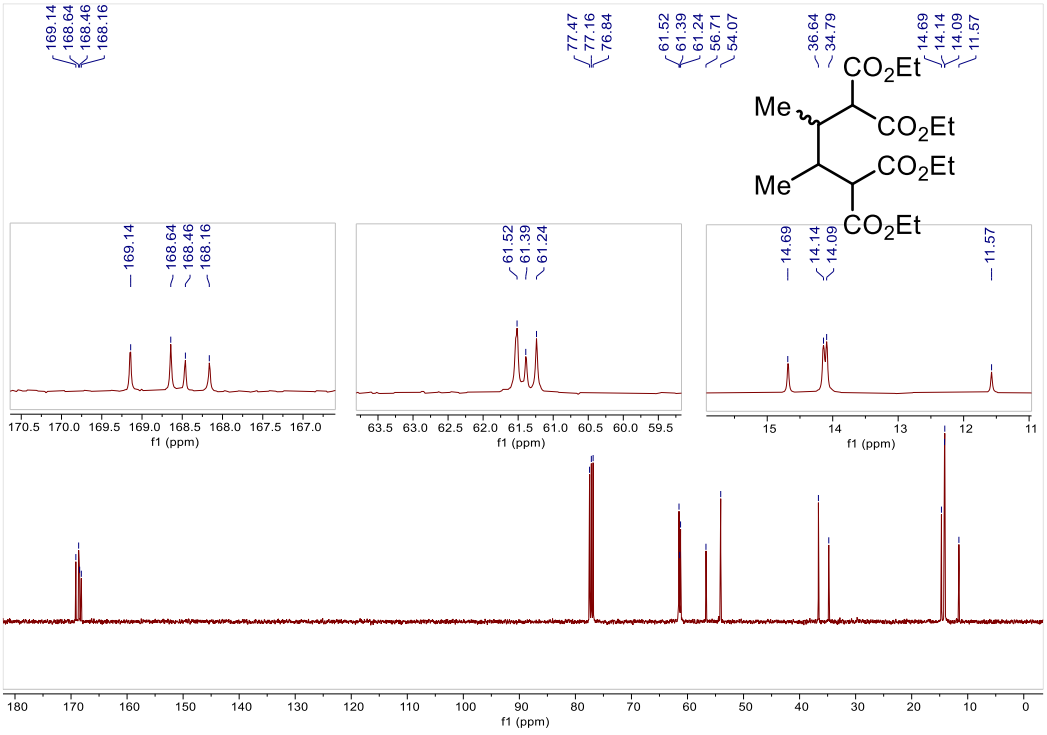
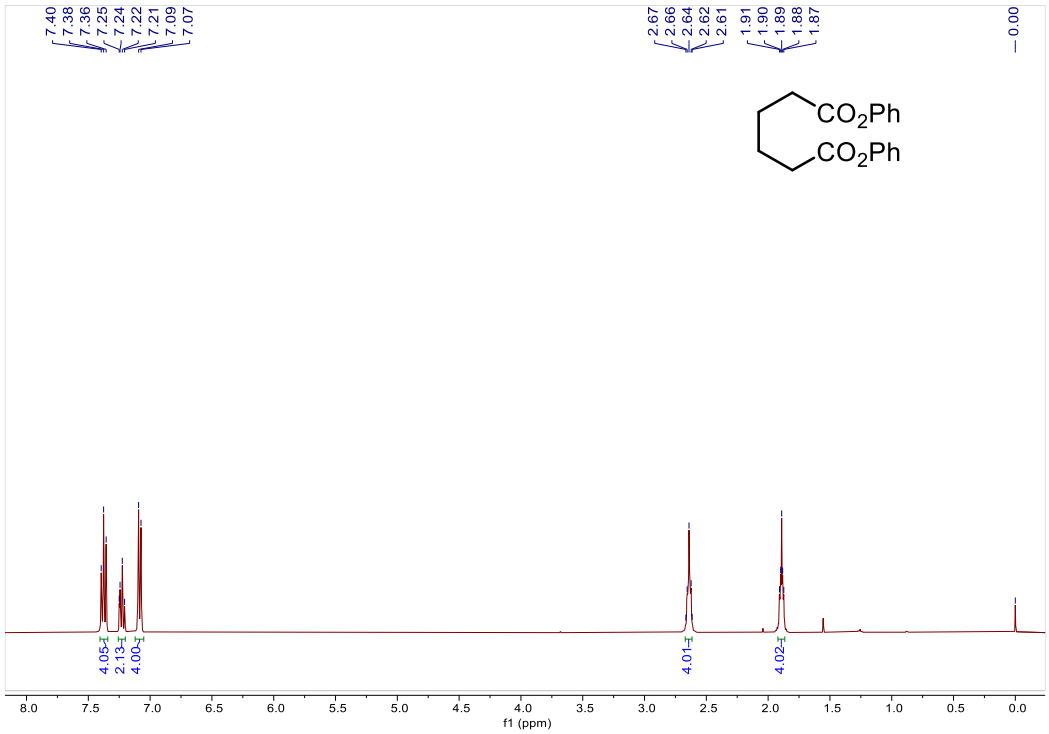


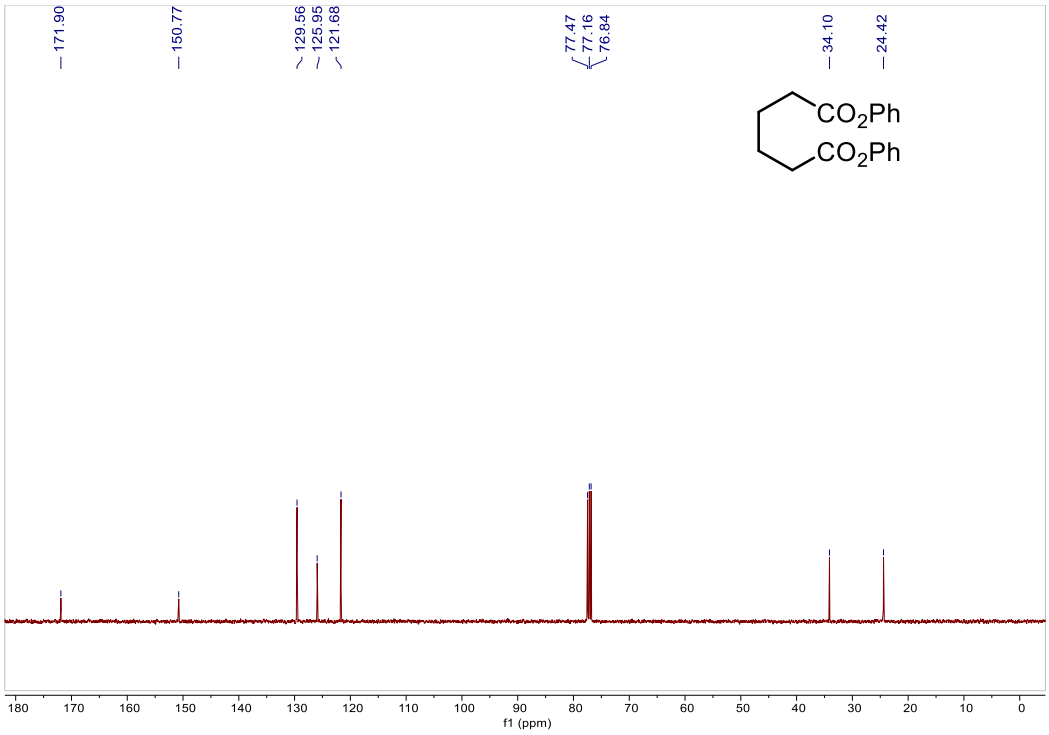
^{1}H NMR for compound **2i**



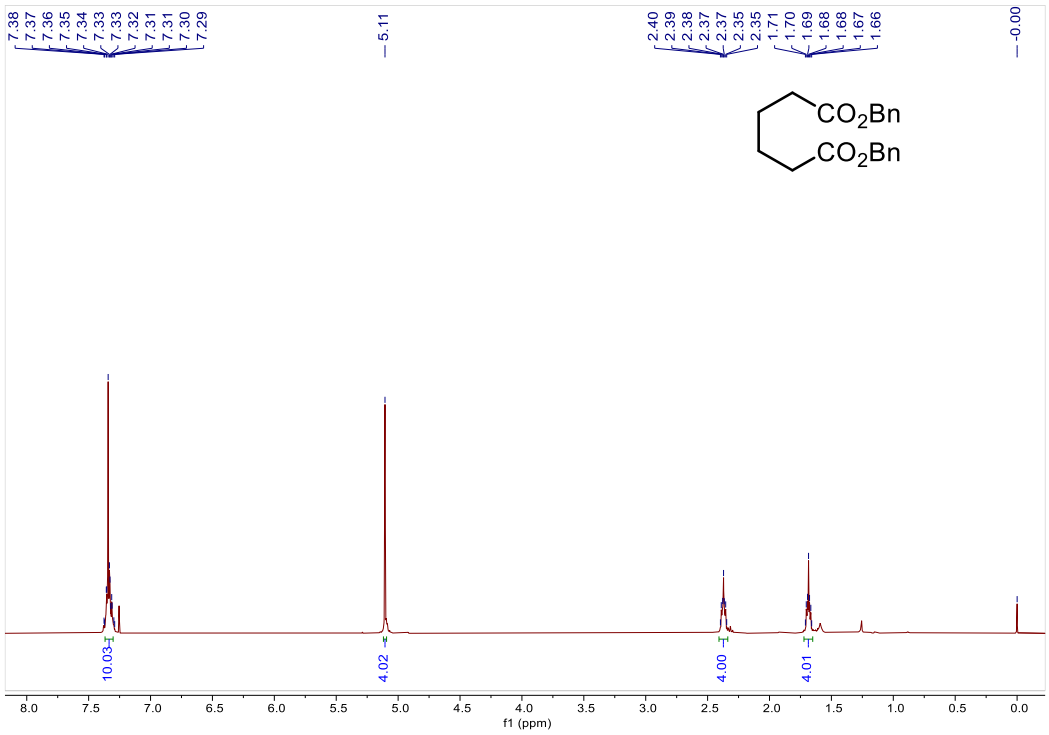
^{13}C{^{1}H} NMR for compound **2i**



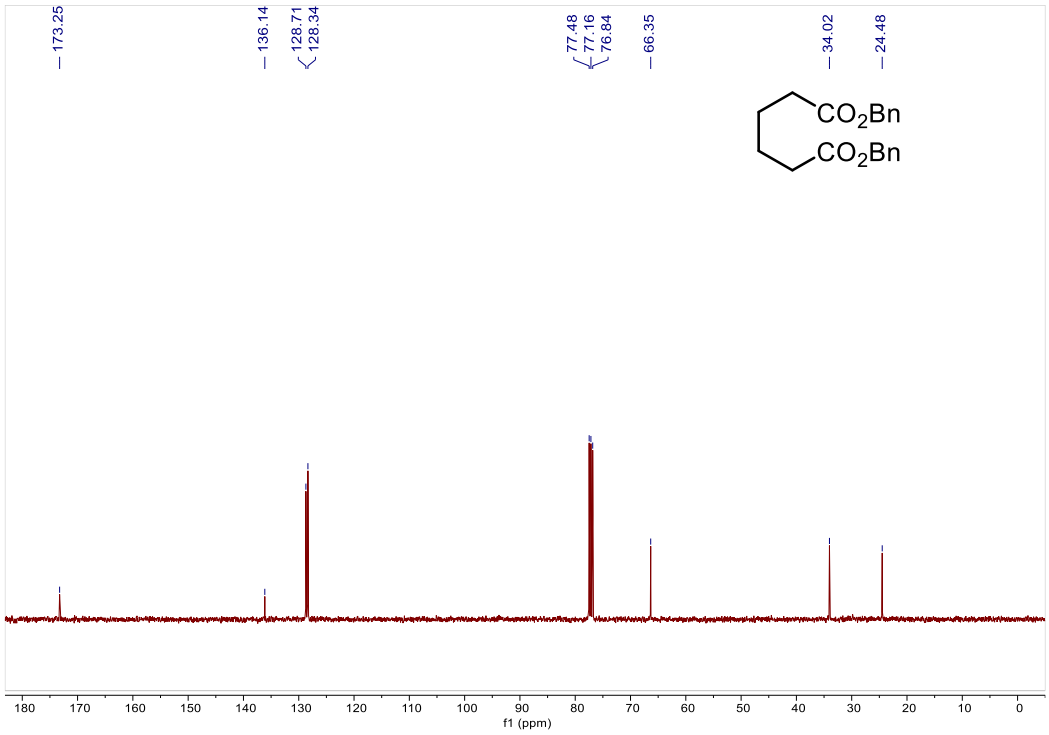
^{1}H NMR for compound **2j**



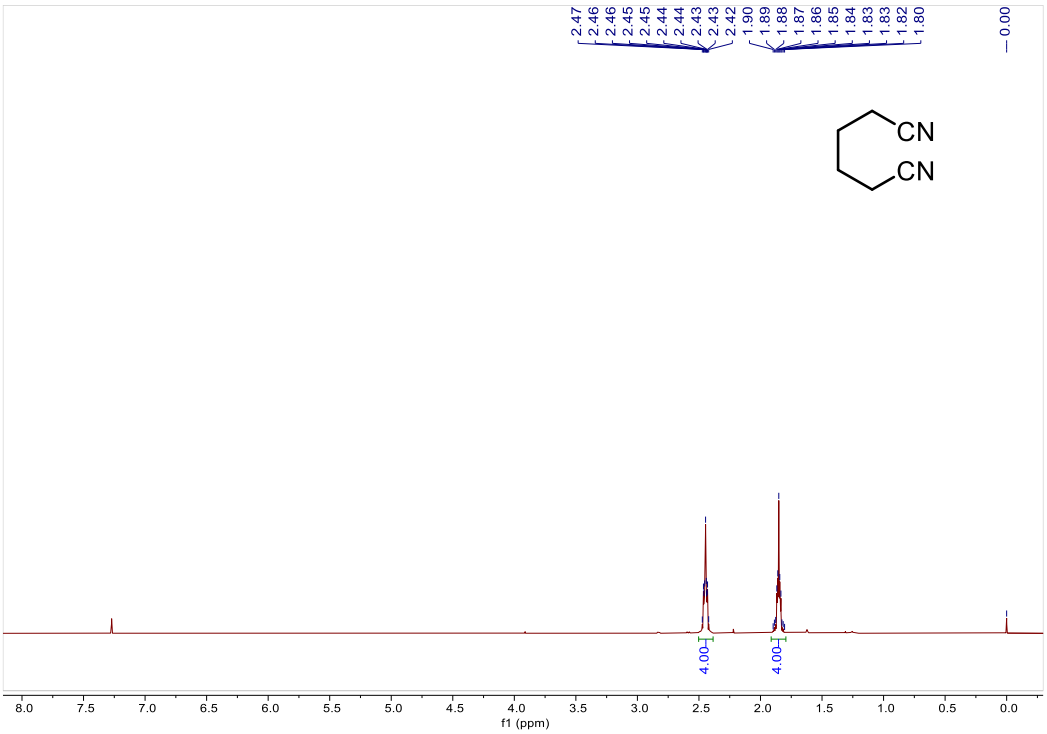
^{13}C{^{1}H} NMR for compound **2j**



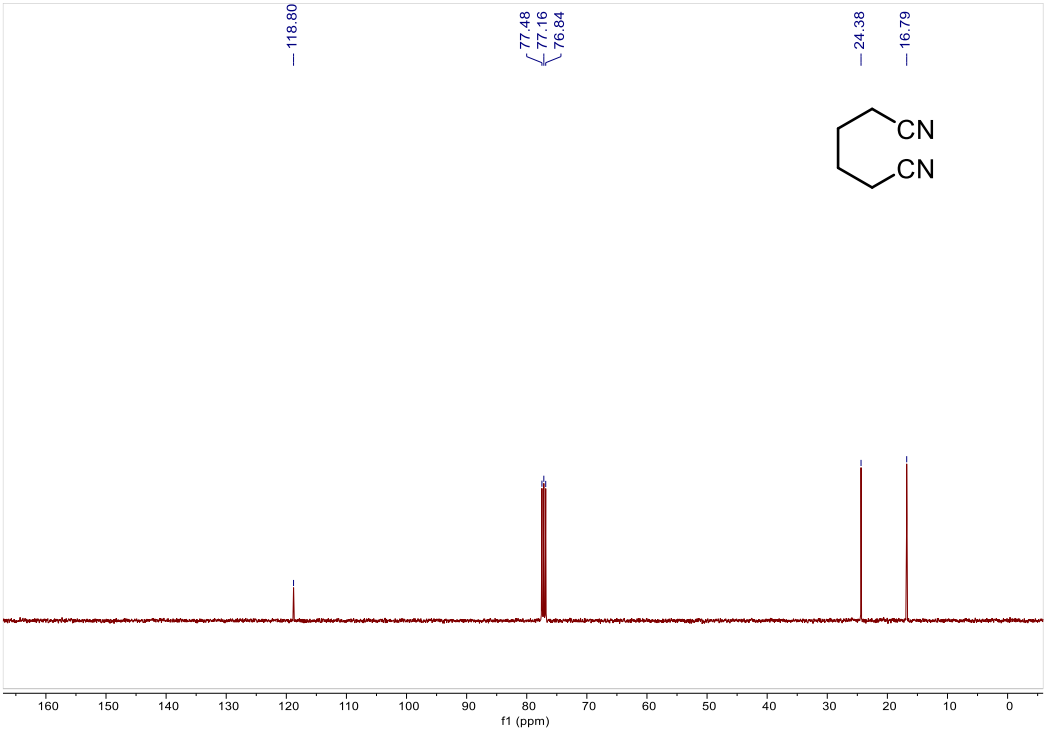
^{1}H NMR for compound **2k**



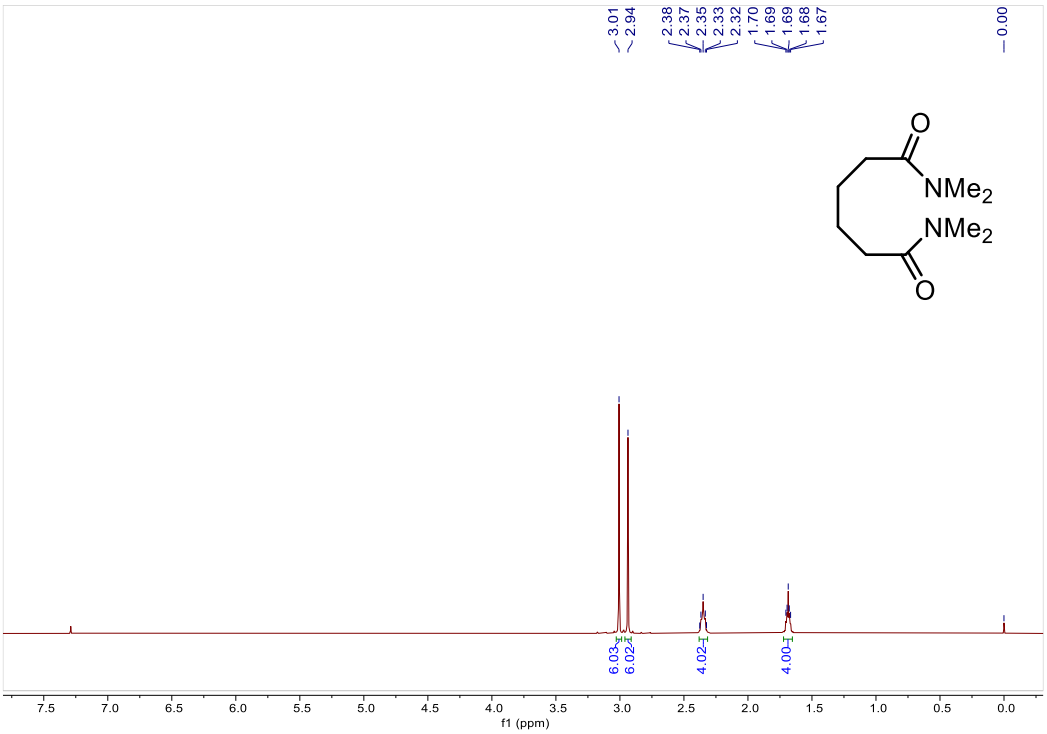
^{13}C{^{1}H} NMR for compound **2k**



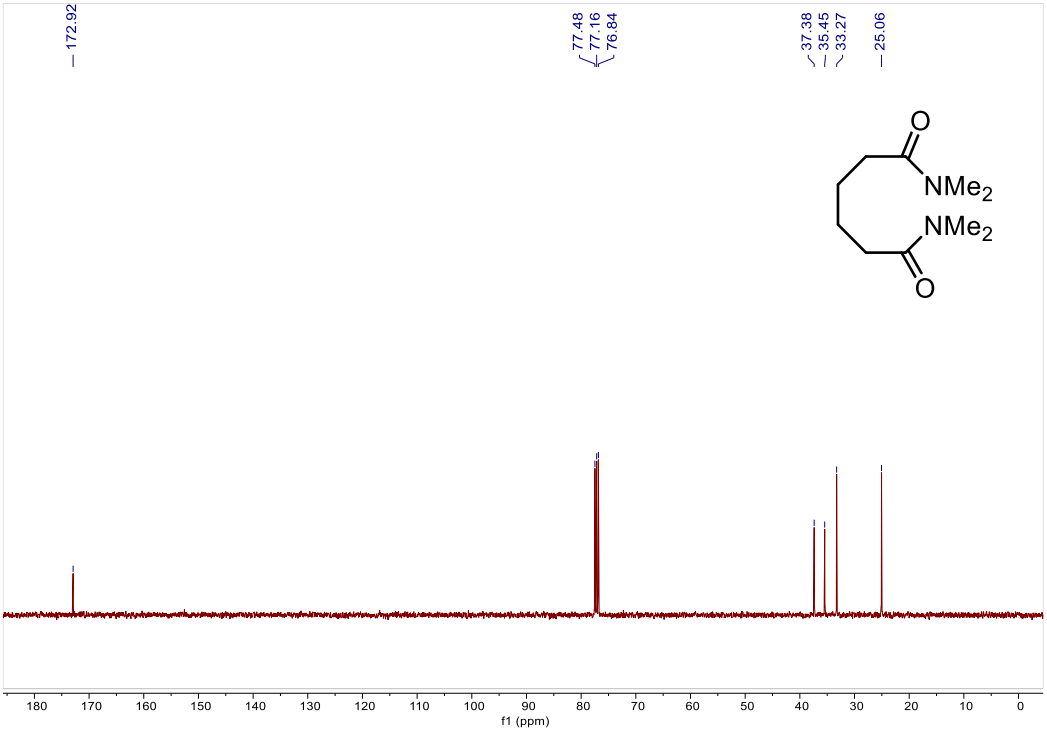
^{1}H NMR for compound **2l**



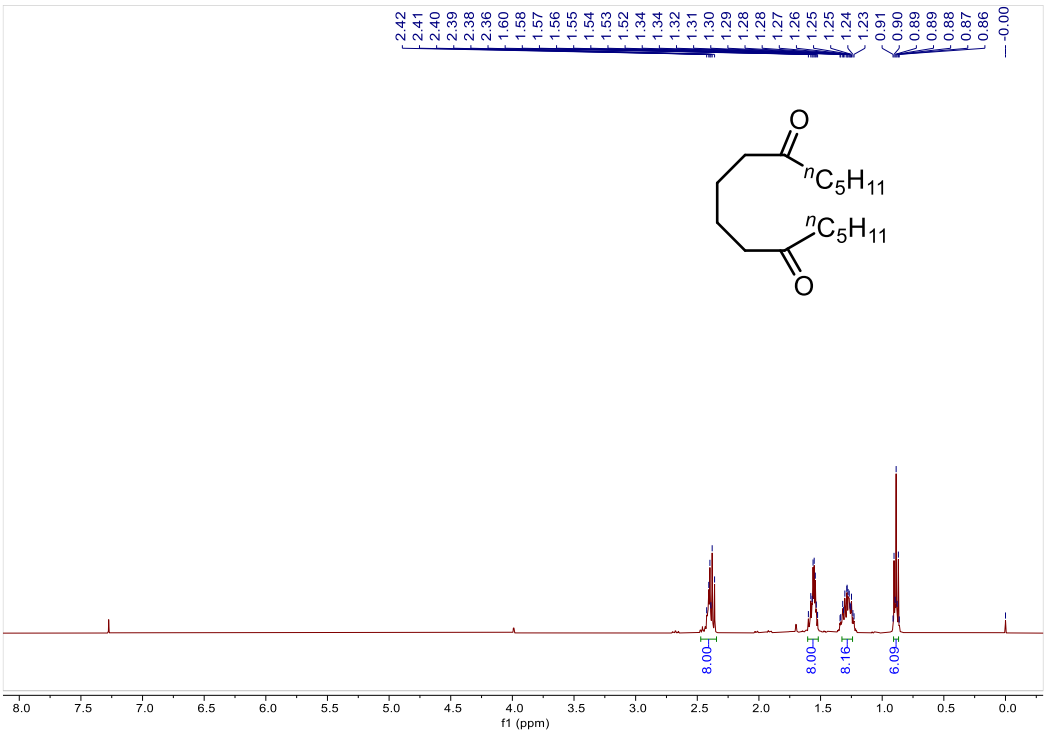
^{13}C{^{1}H} NMR for compound **2l**



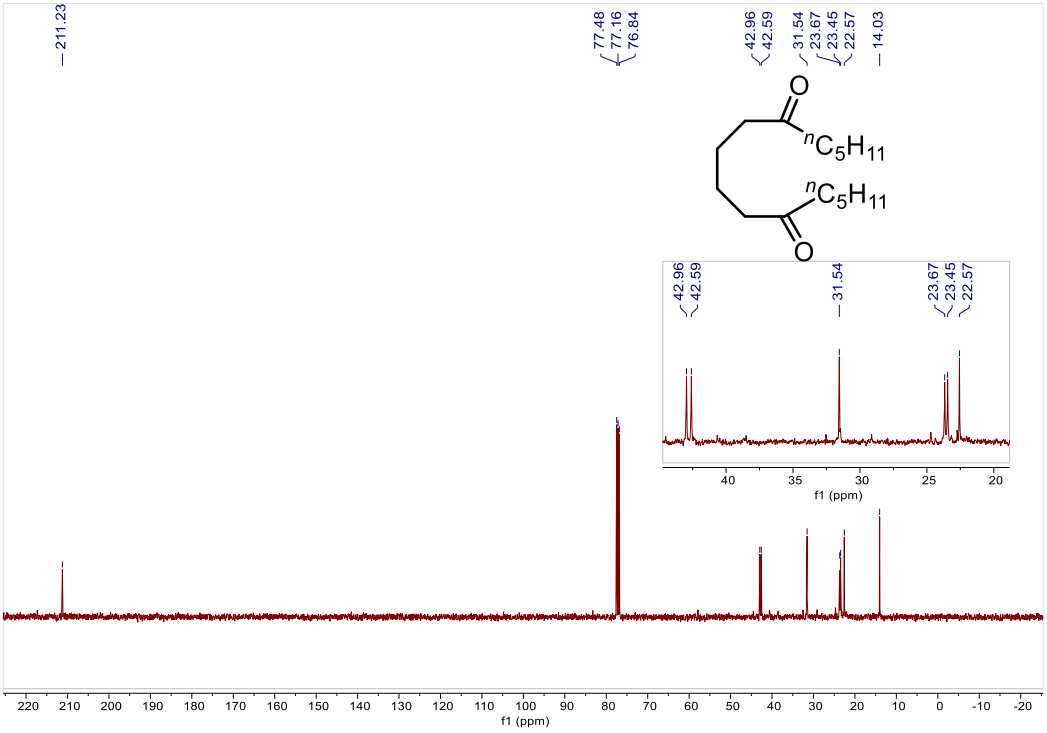
^{1}H NMR for compound **2m**



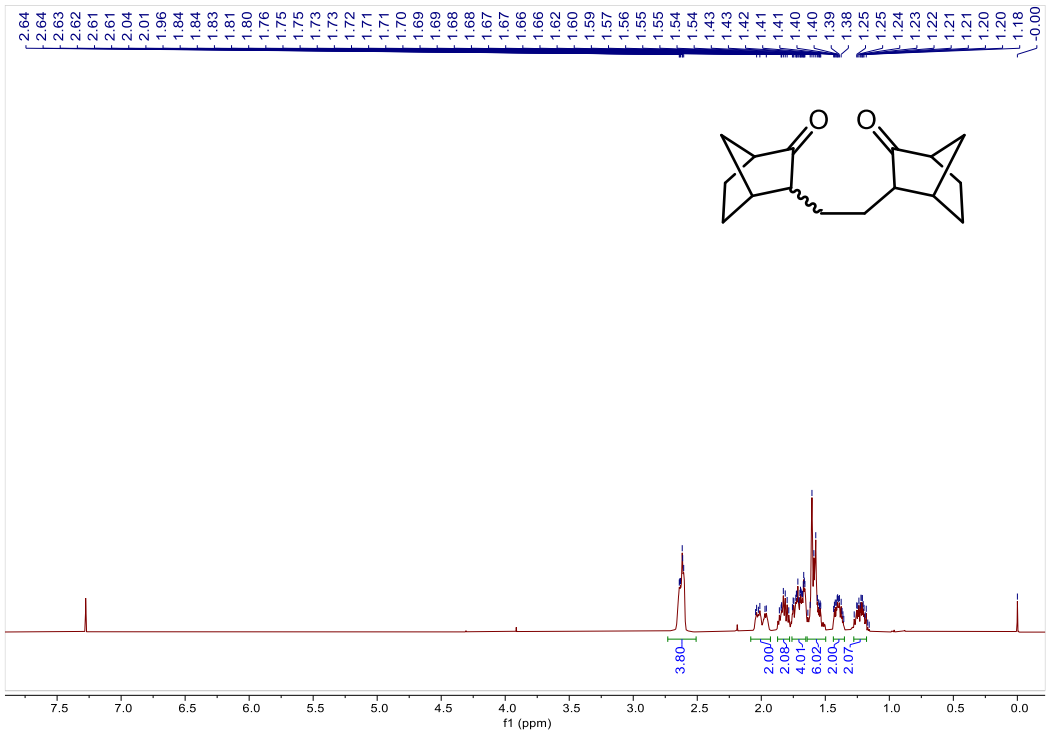
^{13}C{^{1}H} NMR for compound **2m**



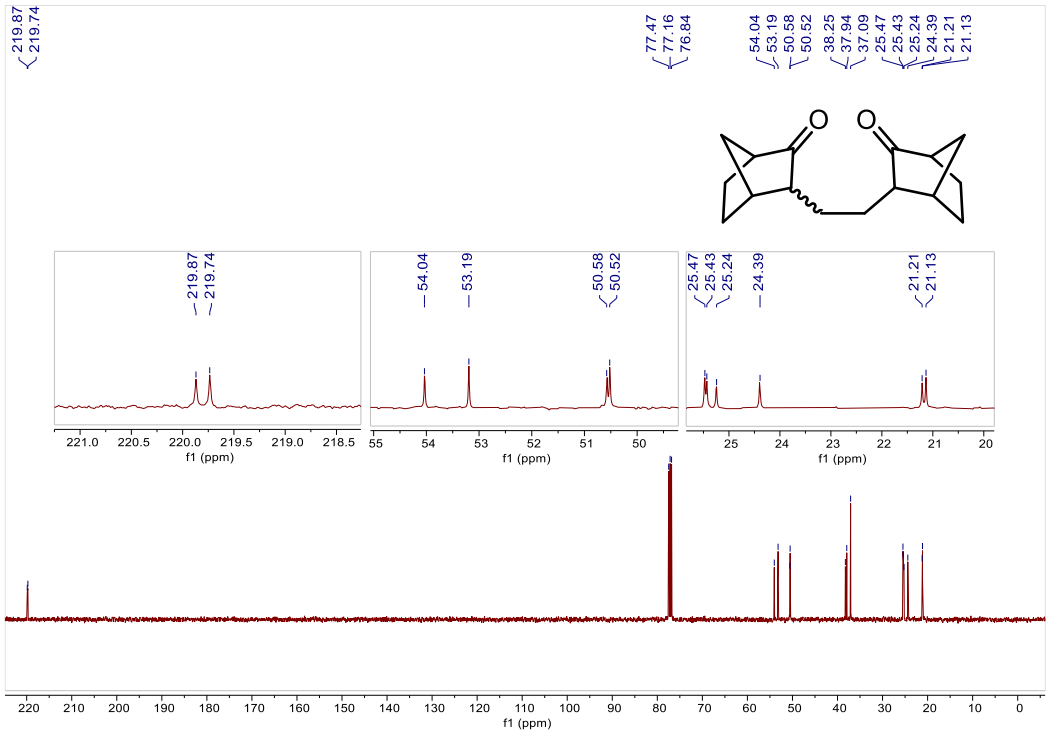
^{1}H NMR for compound **2n**



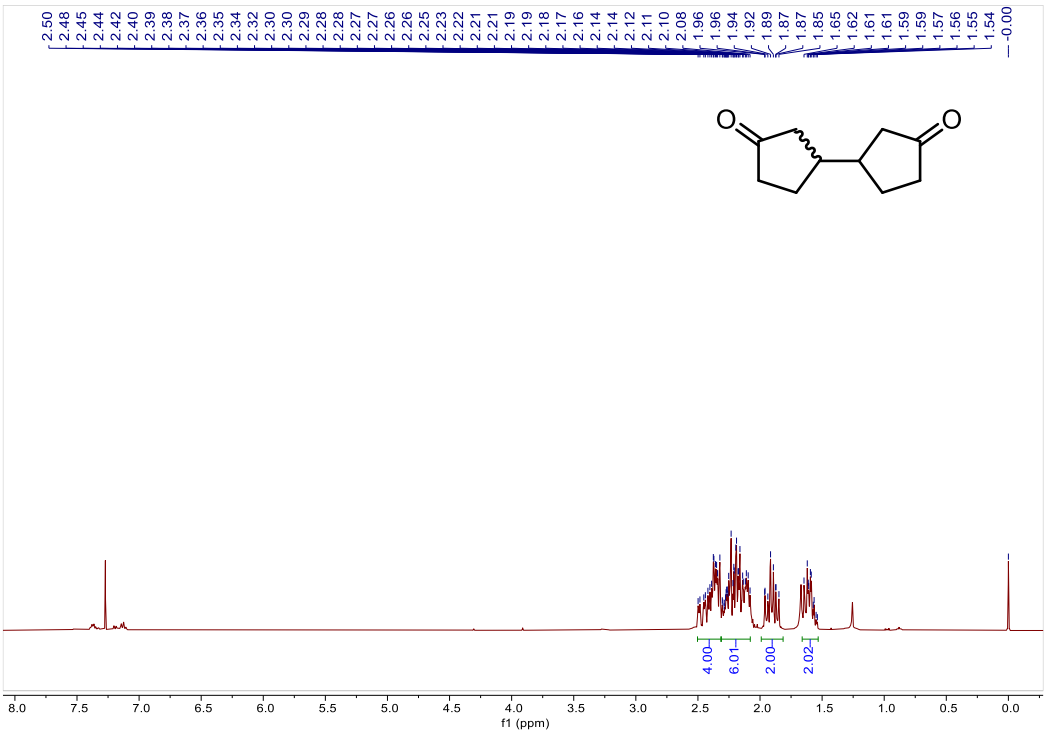
^{13}C{^{1}H} NMR for compound **2n**



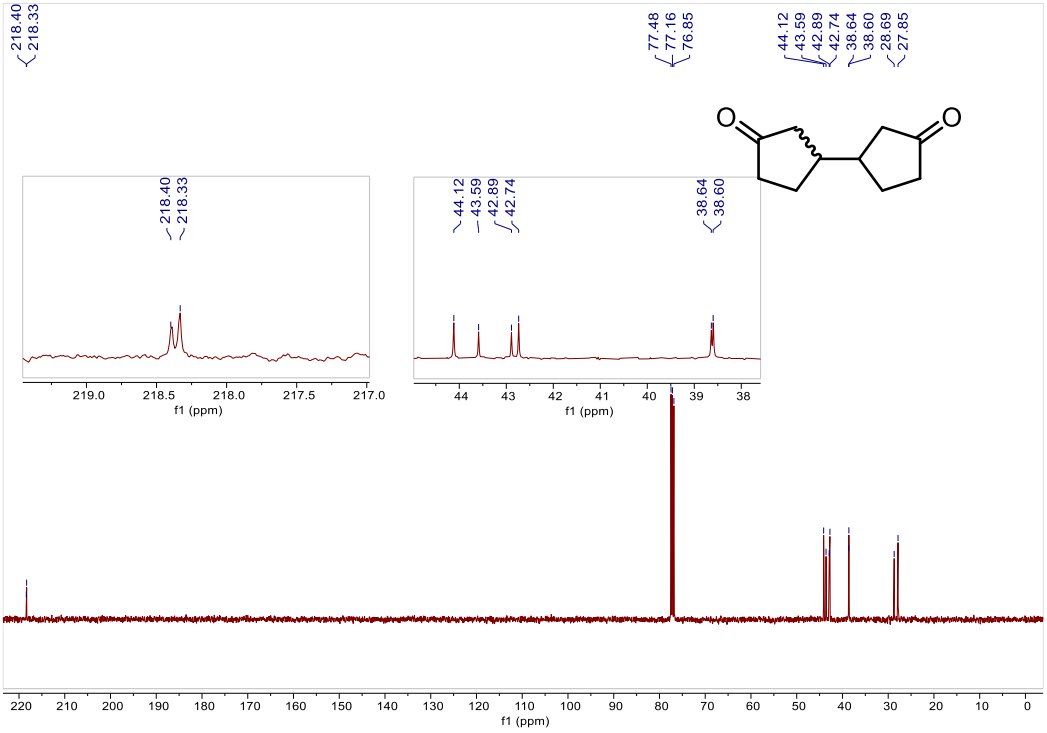
^{1}H NMR for compound **2o**



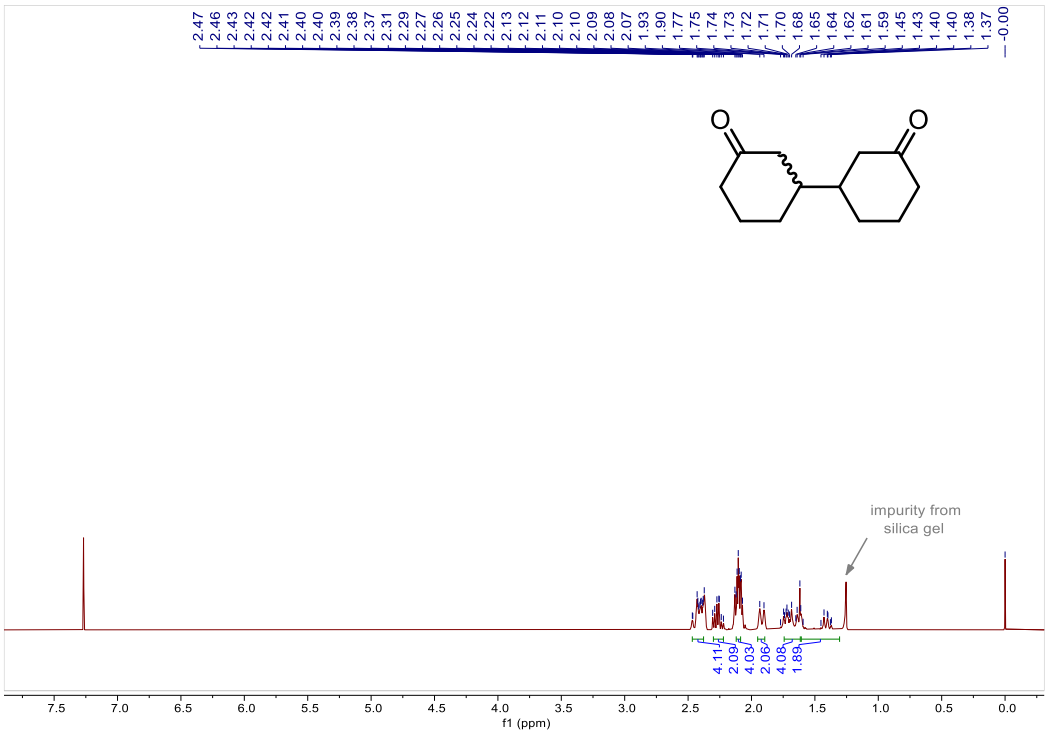
^{13}C{^{1}H} NMR for compound **2o**



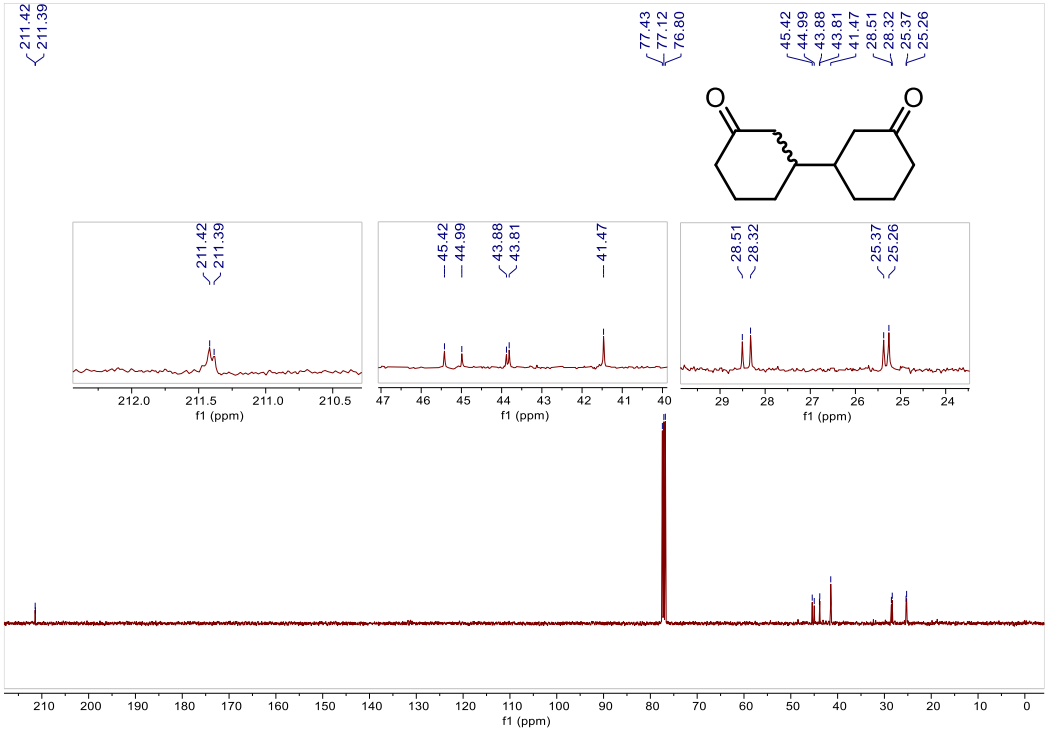
^{1}H NMR for compound **2p**



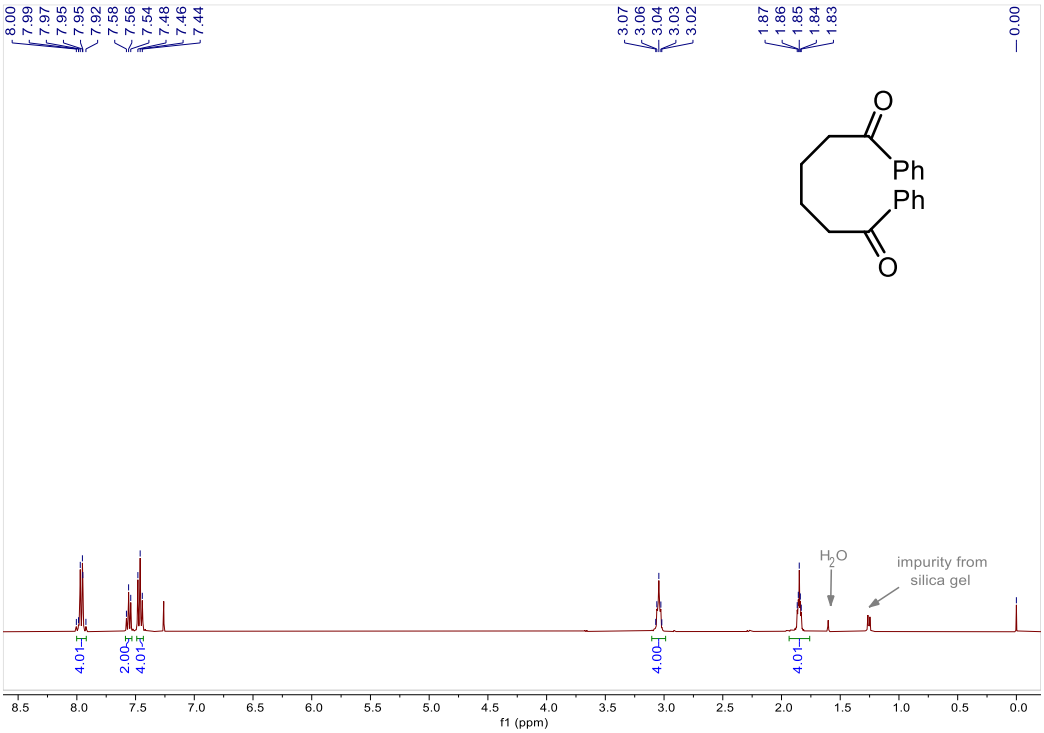
^{13}C{^{1}H} NMR for compound **2p**



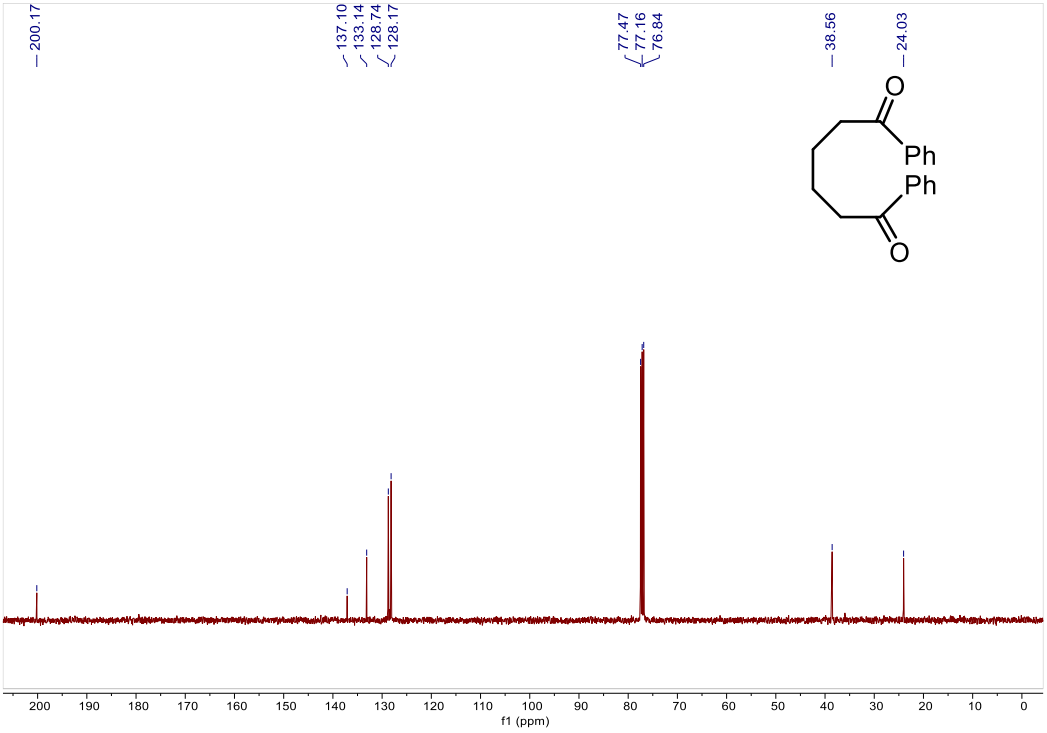
^{1}H NMR for compound **2q**



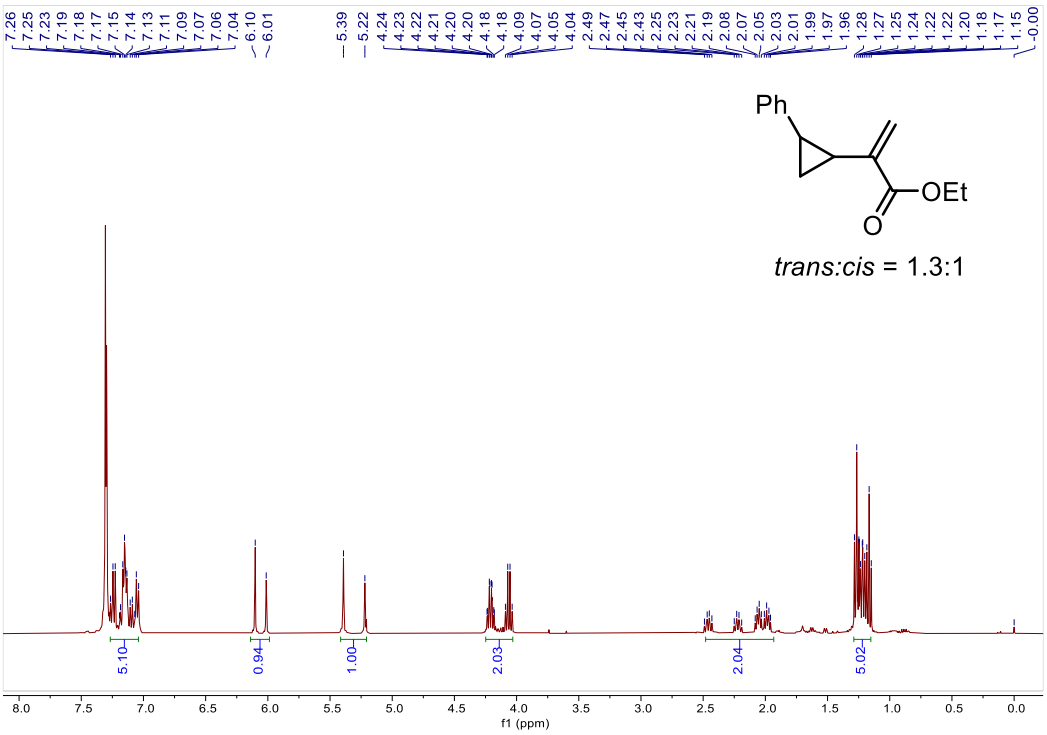
^{13}C{^{1}H} NMR for compound **2q**



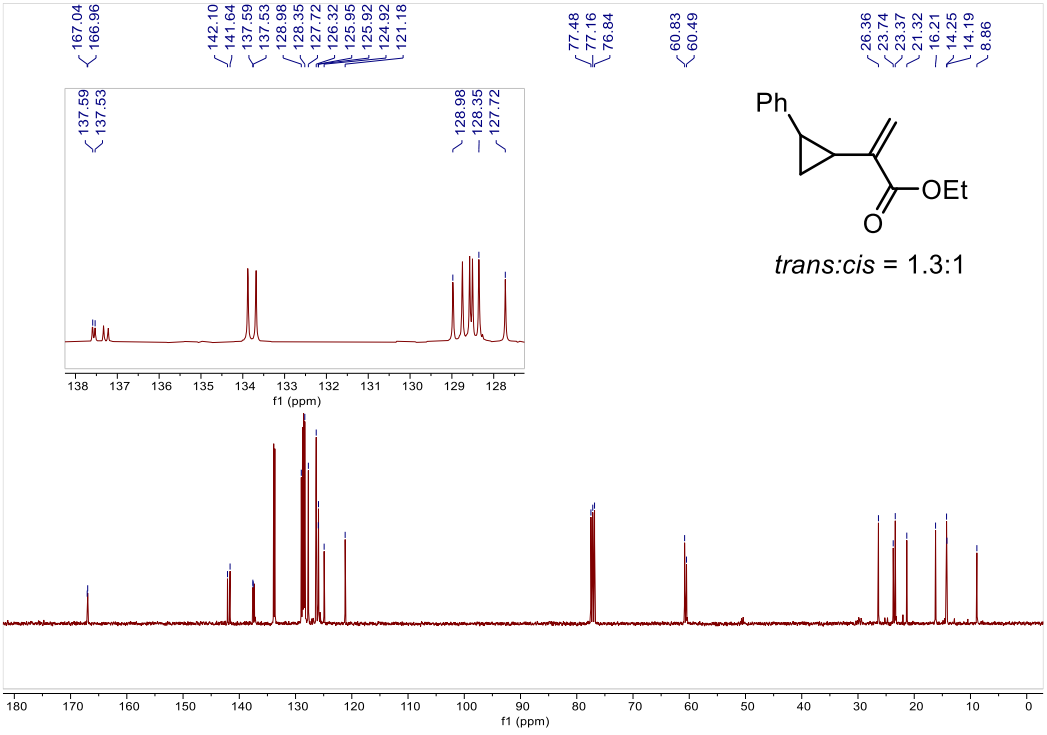
^{1}H NMR for compound **2r**



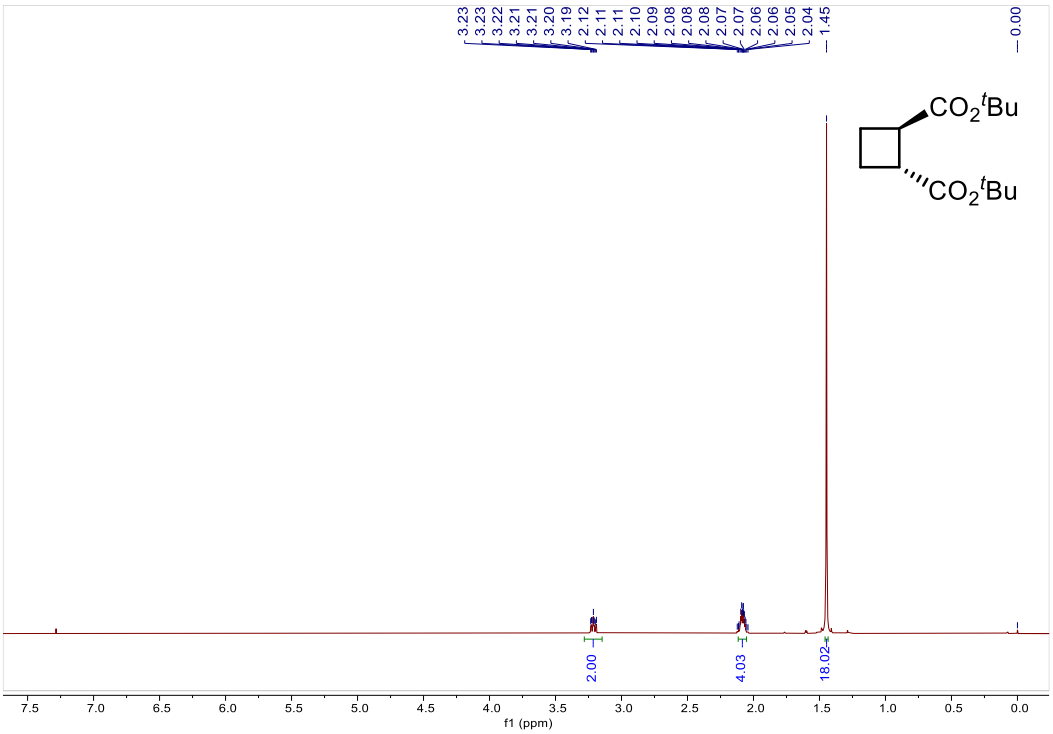
^{13}C{^{1}H} NMR for compound **2r**



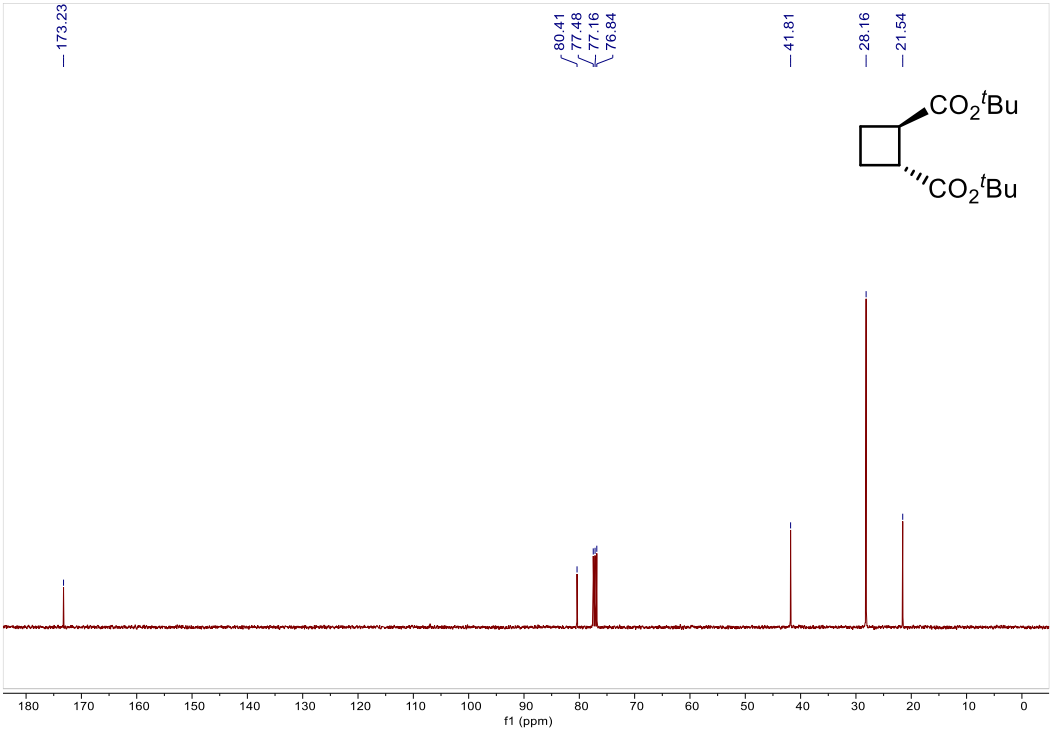
^{1}H NMR for compound **3**



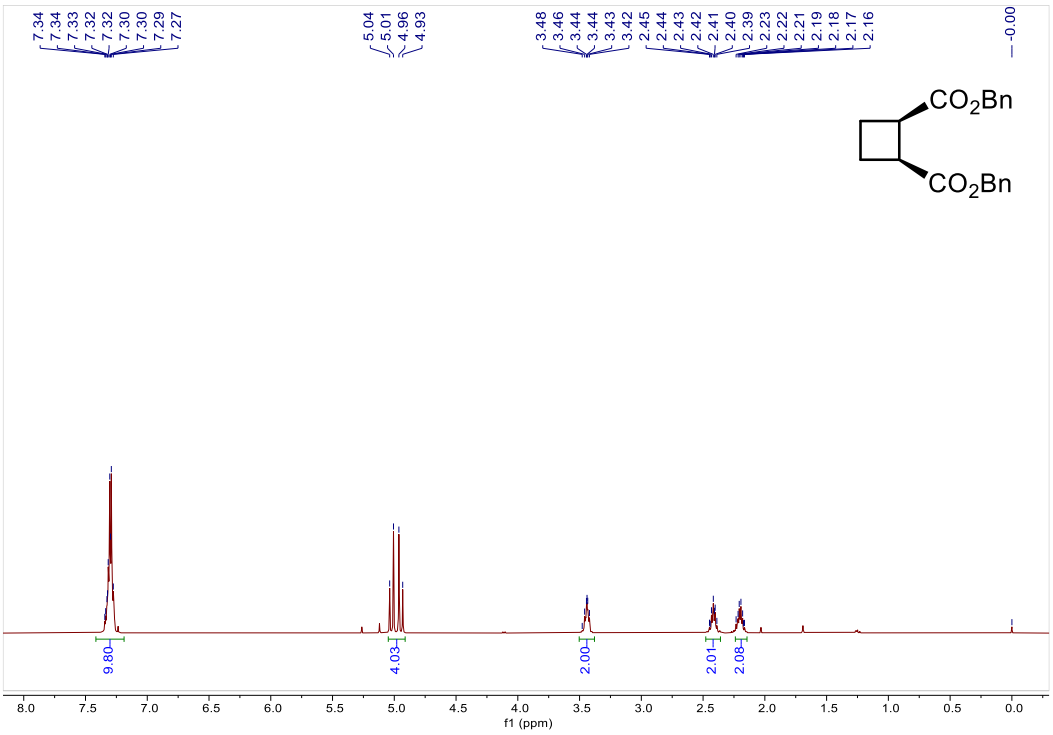
^{13}C{^{1}H} NMR for compound **3**



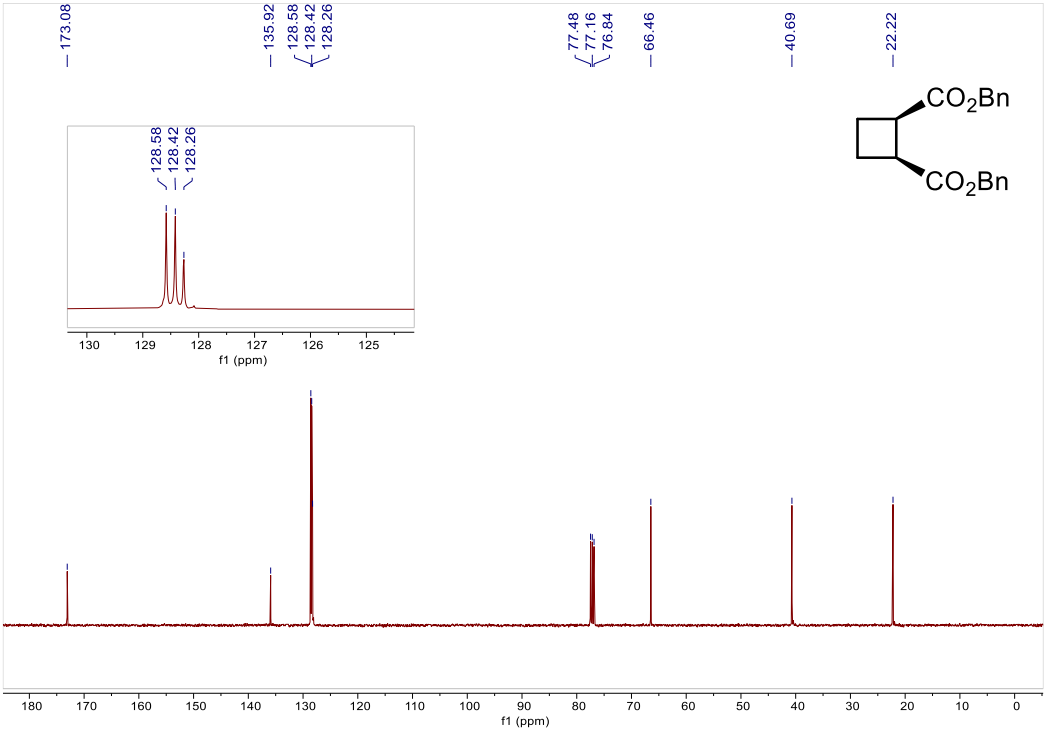
^{1}H NMR for compound ***trans*-5**



^{13}C{^{1}H} NMR for compound ***trans*-5**



^{1}H NMR for compound ***cis*-6**



^{13}C{^{1}H} NMR for compound ***cis*-6**