Substrate-Directed Regioselective Alkene Functionalizations of (*E*)-β,γ-Unsaturated Carboxylic Acids

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1. General Information:

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian-Mercury-300 (300 MHz) spectrometer. Chemical shifts for protons are reported in parts per million (ppm) downfield from TMS and are referenced to residual proton in the solvent ($CDCl_3$ δ = 7.26). Chemical shifts for carbon are reported in ppm and are referenced to the carbon signal ($CDCl_3$ δ = 77.0 ppm). NMR data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants in Hertz (Hz). TLC was examined by using Merck silica gel 60 F-254 plates, and detection of compounds with UV light or dipping into a solution of $KMnO_4$ followed by heating. Flash column chromatography was performed by using Merck silica gel 60 (40-63 μm). Melting point were performed by using Fargo MP-2D. In relative rate experiments the ratio of the products were determined through NMR by using 1,3,5-trimethoxybenzene as internal standard. The single crystal X-ray diffraction data were obtained using a Bruker APEX DUO. The electron impact (EI) mass spectral data were obtained using a SHIMADZU QP2020 and JEOL AccuTOF GCx-plus.

2. General Procedure:

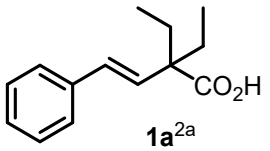
General procedure (Ia) for (*E*)-β,γ-unsaturated carboxylic acids 1a-1j:[1]

1.2 equiv of (2-carboxyethyl)triphenylphosphonium bromide in dry THF (0.5 M), 1 equiv of aryl aldehyde was added. Then it was cooled to −78 °C and 2.5 equiv of *t*-BuOK (1.0 M) was added over 2 h. The mixture was kept for stirring at room temperature for 18 h and the solvent was evaporated under reduced pressure. The obtained residue was dissolved in H_2O:CH_2Cl_2 (1:1). The organic layer was separated and the aqueous layer was then acidified with HCl 1.0 M to pH = 1. Then, extract with Et_2O (100 mL) and the layers were separated. The obtained organic layers were dried over $MgSO_4$ and concentrate under *vacuo*. The residue was purified by flash column chromatography and the pure product of arylbut-3-enoic acids were obtained.

Alkylation of carboxylic acids:[2]

To a 1.0 equiv. of arylbut-3-enoic acids in THF at -78 °C, 2.2 equiv. of *n*-BuLi was added and allow it to stir for 40 minutes. Later, 3.0 equiv. of ethyl bromide was added and allow it to warm up to room temperature and was stirred to overnight. The reaction mixture was quenched with HCl solution (10%) and was extracted with Et_2O (2 x), washed with sodium chloride solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The obtained crude residue was subjected to the next step.

n-BuLi (2.2 equiv.) was added to the crude residue dissolved in THF at -78 °C and allow it to stir for 40 minutes. Later, 3.0 equiv. of ethyl bromide was added and allow it to warm up to room temperature and was stirred to overnight. Then, the mixture was quenched with HCl solution (10%) and was extracted with Et_2O (3 x), washed with sodium chloride solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography and the desired pure products were obtained.



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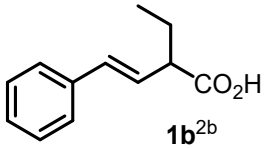

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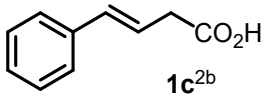

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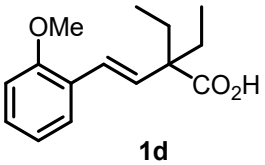

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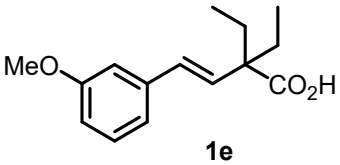

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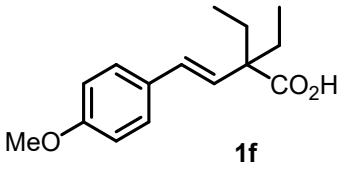

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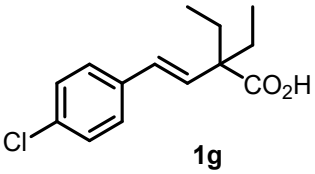

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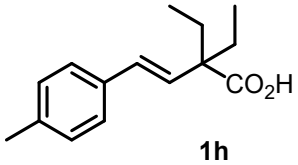

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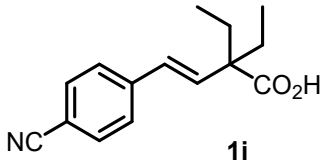

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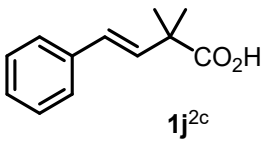

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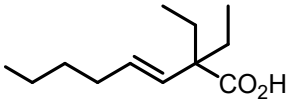

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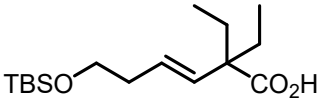


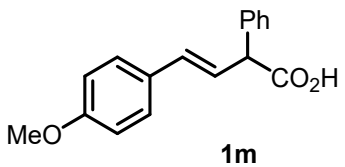
1l

General procedure (Ib) for (*E*)-β,γ-unsaturated carboxylic acids 1m-1o:[3]

In an oven dried 10 mL Schlenk tube under argon were successively placed styrene derivatives (0.5 mmol), alkyl bromide (1 mmol), dry *N,N*-diisopropylethylamine (1 mmol), [Cp*RuCl(PPh_3)$_2$] (0.0005 mmol, 0.1%), dry THF (2.0 mL). Then, the reaction mixture was settled in a pre-heated (100 °C) oil bath for 24 h with stirring. Next, the reaction was concentrated under *vacuo* and purified by silica gel column chromatography (EA/Hexane) to give (*E*)-β,γ-unsaturated carboxylate.

Hydrolysis of esters:

To a solution of (*E*)-β,γ-unsaturated carboxylate (1.0 eq) in water, (0.1 M) NaOH was added (3 eq), and the mixture was reflux in a pre-heated (100 °C) oil bath for 24 h. After cooling to room temperature, the reaction mixture was extracted twice with EtOAc, and the organic phases was discarded. The aqueous phase was acidified with 10% HCl solution then extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and the solvent were removed in *vacuo* to yield carboxylic acid.



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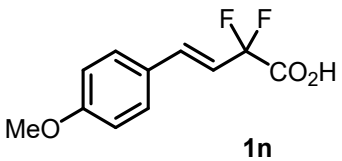

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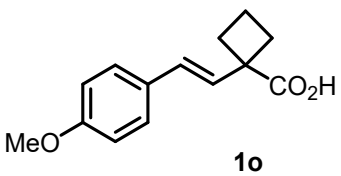
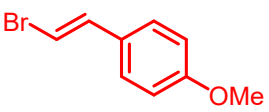


1o

(*E*)-alkenyl bromides **2** were prepared according to the literature procedure[4-8]



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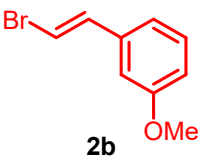

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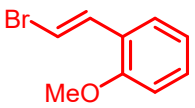

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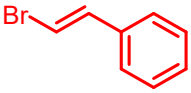

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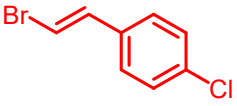

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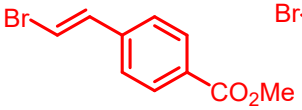

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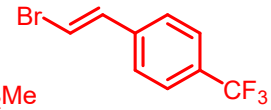

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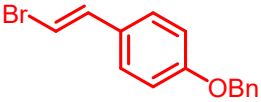

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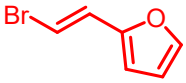

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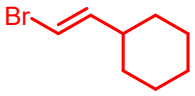

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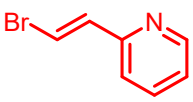

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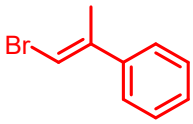

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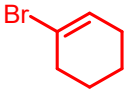

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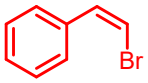
2n

(*Z*)-alkenyl bromides **4** were prepared according to the literature procedure[9]



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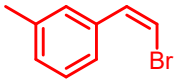

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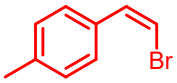

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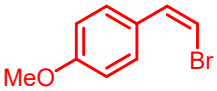

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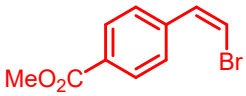

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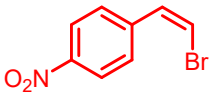

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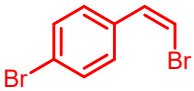

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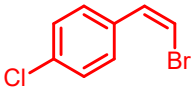

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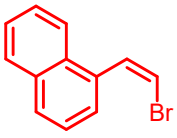

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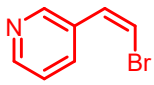

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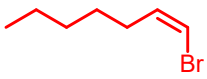

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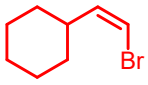

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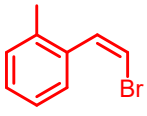
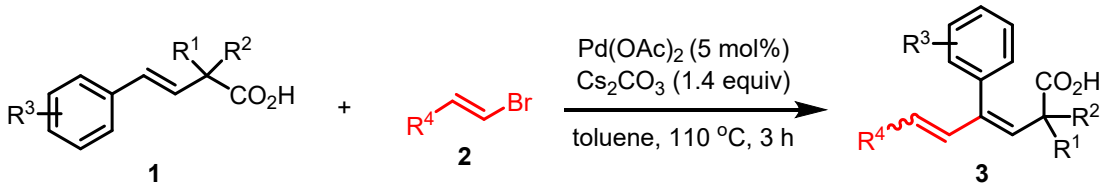


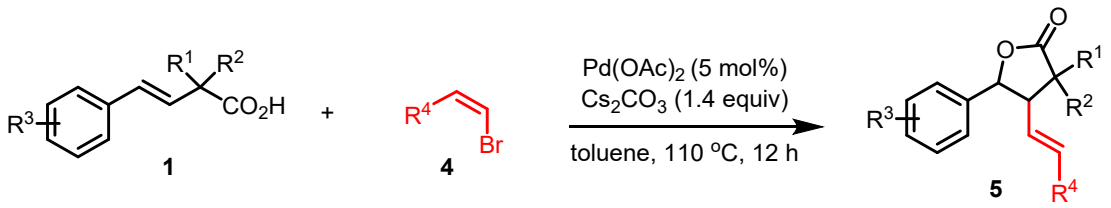
4m

General procedure for Heck-Type alkenylation (II)



To a screw cap schlenk tube (*E*)-β,γ-unsaturated carboxylic acids (**1**, 0.125 mmol), *trans*-alkenyl bromide (**2**, 0.10 mmol), Cs_2CO_3 (0.14 mmol) and $Pd(OAc)_2$ (5 mol%) followed by dry toluene (2 ml) were added. The resulting mixture was kept for stirring in a preheated oil bath at 110 °C for 3 h. The obtained mixture was then diluted with EtOAc and filtered through a pad of celite. The solvent was removed under vacuo and the crude residue was purified by flash column chromatography afforded the desired product **3**.

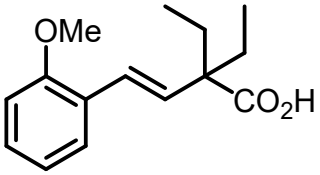
General procedure for alkenylative lactonization (III)



To a screw cap schlenk tube *trans*-β,γ-unsaturated carboxylic acids (**1**, 0.125 mmol), *cis*-alkenyl bromide (**4**, 0.10 mmol), Cs_2CO_3 (0.14 mmol) and $Pd(OAc)_2$ (5 mol%) followed by dry toluene (2 ml) were added. The resulting mixture was kept for stirring in a preheated oil bath at 110 °C for 12 h. The reaction mixture was then diluted with EtOAc and filtered through a pad of celite and concentrated under vacuo. The crude mixture was then purified by flash column chromatography afforded the desired product.

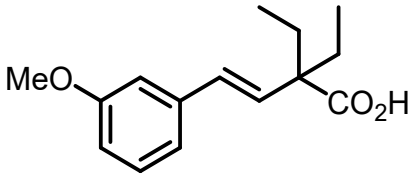
3. Analytical Data

(*E*)-2,2-diethyl-4-(2-methoxyphenyl)but-3-enoic acid (1d)



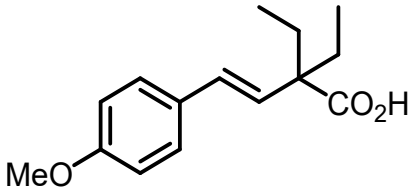
According to general procedure (Ia) with (*E*)-4-(2-methoxyphenyl)but-3-enoic acid (421 mg, 2.2 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1d** as pale-yellow oil (469 mg, 86%).**^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.74 (br, 1H), 7.51 (d, *J* = 6.0 Hz, 1H), 7.29-7.15 (m, 1H), 7.00-6.80 (m, 3H), 6.40 (d, *J* = 18.0 Hz, 1H), 3.85 (s, 3H), 1.92 (q, *J* = 7.3 Hz, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.4, 156.5, 131.2, 128.4, 126.3, 126.3 (overlap), 124.6, 120.6, 110.8, 55.4, 52.8, 28.7, 8.8. **HRMS** (EI) calculated for $C_{15}H_{20}O_3$ ($[M]^+$): 248.1412. Found: 248.1417

(*E*)-2,2-diethyl-4-(3-methoxyphenyl)but-3-enoic acid (1e)



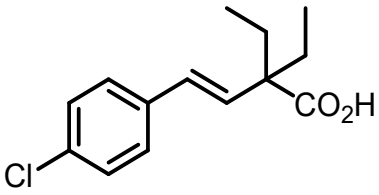
According to general procedure (Ia) with (*E*)-4-(3-methoxyphenyl)but-3-enoic acid (272 mg, 1.4 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1e** as pale-yellow oil (246.6 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29-7.15 (m, 1H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.97-6.90 (m, 1H), 6.85-6.70 (m, 1H), 6.48-6.35 (m, 2H), 3.82 (s, 3H), 1.87 (q, *J* = 7.3 Hz, 4H), 0.90 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.6, 159.8, 138.7, 131.3, 129.9, 129.5, 118.9, 113.1, 111.5, 55.2, 52.6, 28.7, 8.8. **HRMS** (EI) calculated for $C_{15}H_{20}O_3$ ($[M]^+$): 248.1412. Found: 248.1407.

(*E*)-2,2-diethyl-4-(4-methoxyphenyl)but-3-enoic acid (1f)



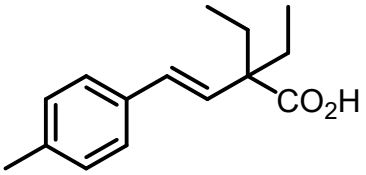
According to general procedure (Ia) with (*E*)-4-(4-methoxyphenyl)but-3-enoic acid (172 mg, 0.9 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1f** as pale-yellow oil (149.6 mg, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.42 (d, *J* = 18.0 Hz, 1H), 6.22 (d, *J* = 18.0 Hz, 1H), 3.81 (s, 3H), 1.86 (q, *J* = 7.3 Hz, 4H), 0.90 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.9, 159.1, 130.0, 129.4, 128.8, 127.4, 113.9, 55.3, 52.5, 28.6, 8.8. **HRMS** (EI) calculated for $C_{15}H_{20}O_3$ ($[M]^+$): 248.1412. Found: 248.1404.

(*E*)-4-(4-chlorophenyl)-2,2-diethylbut-3-enoic acid (1g)



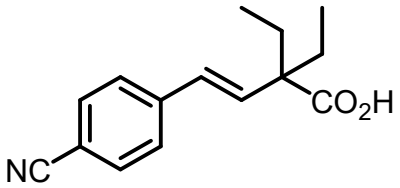
According to general procedure (Ia) with (*E*)-4-(4-chlorophenyl)but-3-enoic acid (197 mg, 1 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1g** as pale-yellow solid, m.p.: 113-115 ^{o}C (129 mg, 51%): **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44-7.20 (m, 4H), 6.39 (q, *J* = 14.0 Hz, 2H), 1.87 (q, *J* = 7.8 Hz, 4H), 0.90 (t, *J* = 7.8 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.8, 135.7, 133.0, 131.7, 128.9, 128.6, 127.5, 52.7, 28.8, 8.8. **HRMS** (EI) calculated for $C_{14}H_{17}ClO_2$ ($[M]^+$): 252.0917. Found: 252.0921.

(*E*)-2,2-diethyl-4-(p-tolyl)but-3-enoic acid (1h)



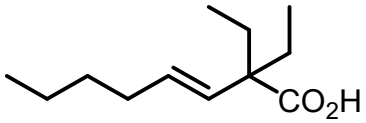
According to general procedure (Ia) with (*E*)-4-(p-tolyl)but-3-enoic acid (405 mg, 2.3 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1h** as pale-yellow oil (277 mg, 52%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 6.0 Hz, 2H), 7.12 (d, *J* = 6.0 Hz, 2H), 6.45 (d, *J* = 16.5 Hz, 2H), 6.31 (d, *J* = 16.5 Hz, 2H), 2.34 (s, 3H), 1.87 (q, *J* = 7.0 Hz, 4H), 0.90 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.8, 137.2, 134.4, 130.0, 129.8, 129.2, 126.2, 52.5, 28.7, 21.2, 8.8. **HRMS** (EI) calculated for $C_{15}H_{20}O_2$ ($[M]^+$): 232.1463. Found: 232.1468.

(*E*)-4-(4-cyanophenyl)-2,2-diethylbut-3-enoic acid (1i)



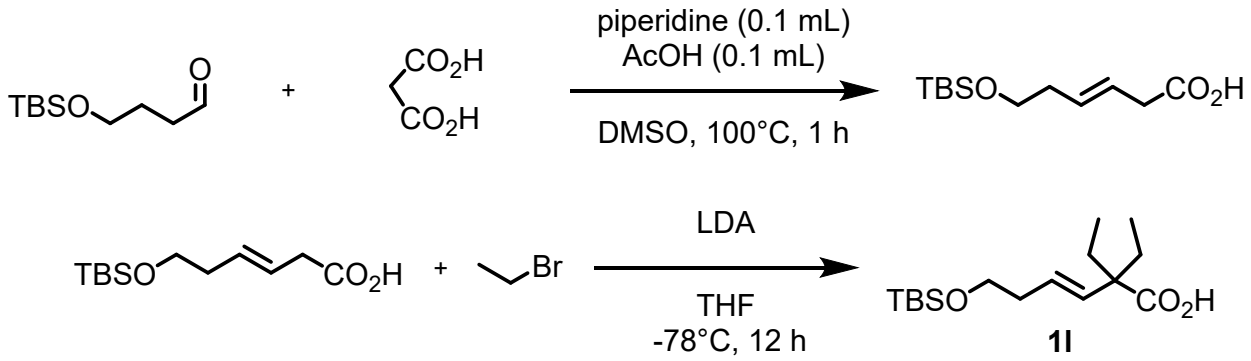
According to general procedure (Ia) with (*E*)-4-(4-cyanophenyl)but-3-enoic acid (488 mg, 2.6 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1i** as a yellow oil (129 mg, 33%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9 Hz, 2H), 7.47 (d, *J* = 6 Hz, 2H), 6.55 (d, *J* = 18 Hz, 1H), 6.47 (d, *J* = 18 Hz, 1H), 1.88 (q, *J* = 9, 3 Hz, 4H), 0.90 (t, *J* = 6 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.1, 141.6, 135.1, 132.3, 128.6, 126.7, 118.9, 110.6, 52.9, 29.0, 8.9. **HRMS** (EI) m/z: ($[M]^+$) calcd for $C_{15}H_{17}NO_2$: 243.1259. Found: 243.1253.

(*E*)-2,2-diethyloct-3-enoic acid (1k)



Compound **1k** were synthesized using a reported procedure[2d] with (*E*)-oct-3-enoic acid (170 mg, 1.2 mmol). The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to provide **1k** as yellow oil (170 mg, 86%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.60-5.45 (m, 2H), 2.15-2.00 (m, 2H), 1.80-1.65 (m, 4H), 1.43-1.25 (m, 4H), 0.95-0.75 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.6 131.1, 130.6, 52.0, 32.5, 31.5, 28.2, 22.1, 13.9, 8.6. **HRMS** (EI) m/z: ($[M]^+$) calcd for $C_{12}H_{22}O_2$: 198.1620. Found: 198.1611.

Preparation of (*E*)-6-((tert-butyldimethylsilyl)oxy)-2,2-diethylhex-3-enoic acid (1l):

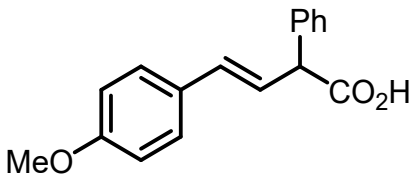


In a flame dried 100 mL round bottom flask with stir bar, 4-((tert-butyl dimethylsilyl)oxy)butanal (640 mg, 3.16 mmol), malonic acid (361.9 mg, 3.48 mmol), DMSO (3.5 mL) were added. Then 0.1 mL of piperidine and 0.1 mL of AcOH were added through syringe while stirring under room temperature. The reaction was then heated to 100 ℃ and stirred for 1 hour. Cool down the reaction to room temperature before quenching the reaction with water. Extract with diethyl ether three times. Collect the organic phase and dry with $MgSO_4$ and remove the solvent with rotary evaporator to afford crude 400 mg (yield = 52%).The product is put into next step without further purification.

In a flame dried 100 mL round bottom flask with stir bar, (*E*)-6-((tert-butyl dimethylsilyl)oxy)hex-3-enoic acid (1.7 g, 6.24 mmol) and dry THF (15 mL) were added. The reaction was cooled down to -78 ℃ before adding LDA (7.8 mL, 2M solution, 15.6 mmol) through syringe dropwise under argon. The reaction was then stirred for another 1 hour. Then dried bromoethane (2.04 g, 18.7 mmol) were added through syringe slowly, the reaction was stirred under room temperature overnight. Quench the reaction with HCl solution (10%), extract with Et_2O three times, collect the organic phase and dry with $MgSO_4$. Remove the solvent with rotary evaporator to afford crude. The crude product was put into flame dried round bottom flask and dry THF (15 mL) was added. The reaction was cooled down to -78 ℃ before adding LDA (7.8 mL, 2M solution, 15.6 mmol) through syringe dropwise under argon. The reaction was then stirred for another 1 hour. Then dried bromoethane (2.04 g, 18.7 mmol) were added through syringe slowly, the reaction was stirred under room temperature overnight. Quench the reaction with HCl solution (10%), extract with Et_2O three times, collect the organic phase and dry with $MgSO_4$. Remove the solvent with rotary evaporator to afford crude. Purify with flash column using Et_2O/hexane = 2/3 as eluent to afford product **1l** as yellow oil (250 mg, 14%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.64-5.48 (m, 2H), 3.66-3.62 (t, *J* = 6.0 Hz, 2H), 2.32-2.26 (q, *J* = 6.0 Hz, 2H), 1.76-1.69 (q, J = 6.0 Hz, 2H), 0.88-0.81

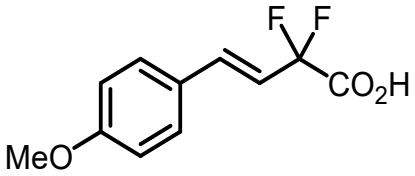
(singlet and triplet stacked, total 15H), 0.04 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.0, 132.7, 127.5, 63.0, 52.2, 36.5, 28.2, 25.9, 18.3, 8.7, -5.3. **HRMS** (EI) m/z: ($[M]^+$)calcd for $C_{16}H_{32}O_3Si$: 300.2121. Found: 300.2115.

(*E*)-4-(4-methoxyphenyl)-2-phenylbut-3-enoic acid (1m)



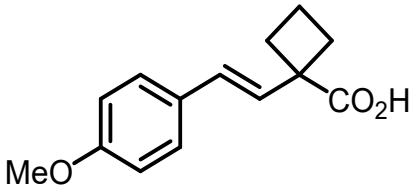
According to general procedure (Ib) with ethyl (*E*)-4-(4-methoxyphenyl)-2-phenylbut-3-enoate (266 mg, 0.89 mmol). The obtained compound was purified by column chromatography to isolate the pure product **1m** as white solid, m.p.: 95-96 ^oC (180 mg, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$) 1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 7H), 6.85 (d, J = 9 Hz, 2H), 6.47 (d, J = 3 Hz, 2H), 4.48 (d, J = 6 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.7, 159.3, 137.8, 132.4, 129.2, 128.7, 128.0, 127.6, 127.5, 124.0, 113.9, 55.2, 54.8. **HRMS** (EI) calculated for $C_{17}H_{16}O_3$ ($[M]^+$): 268.10927. Found: 268.1094.

(*E*)-2,2-difluoro-4-(4-methoxyphenyl)but-3-enoic acid (1n)



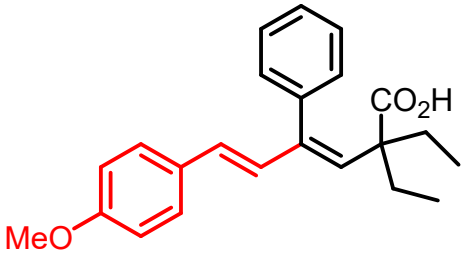
According to general procedure (Ib) with (*E*)-2,2-difluoro-4-(4-methoxyphenyl)but-3-enoate (76.6 mg, 0.299 mmol). The obtained compound was purified by column chromatography to isolate the pure product **1n** as pale-yellow oil (48.6 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 (d, J = 15.0 Hz, 1H), 7.51 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 6.32 (d, J = 15.0 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2, 161.7, 146.6, 130.0 (t, $J^1_{C,\ F}$ = 6 Hz), 126.7, 114.6, 114.3, 55.4. **HRMS** (EI) calculated for $C_{11}H_{10}F_2O_3$ ($[M]^+$): 228.0598. Found: 228.0592.

(*E*)-1-(4-methoxystyryl)cyclobutane-1-carboxylic acid (1o)



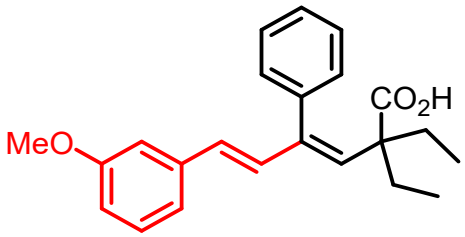
According to general procedure (Ib) with ethyl (*E*)-1-(4-methoxystyryl)cyclobutane-1-carboxylate (200 mg, 0.768 mmol). The product **1o** appears as pale-yellow oil and were used in next step without further purification (150 mg, 84%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 18.0 Hz, 1H), 6.34 (d, *J* = 15.0 Hz, 1H), 3.81 (s, 3H), 2.69-2.59 (m, 2H), 2.33-2.24 (m, 2H), 2.01-1.94 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.5, 159.1 129.5, 128.9, 128.3, 127.5, 113.9, 55.2, 49.6, 30.8, 15.9. **HRMS** (EI) calculated for $C_{14}H_{16}O_3$ ($[M]^+$): 232.1099. Found: 232.1094.

(3*Z*,5*E*)-2,2-diethyl-6-(4-methoxyphenyl)-4-phenylhexa-3,5-dienoic acid (3a)



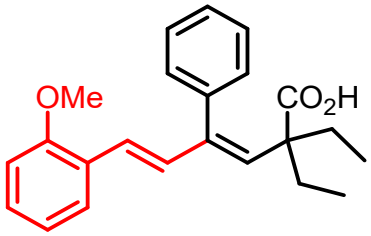
According to general procedure (II) with **1a** (0.137 mmol, 30.0 mg) and **2a** (0.11 mmol, 23.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3a** as pale-yellow oil (36 mg, 93%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.30 (m, 3H), 7.25-7.20 (m, 2H), 7.18-7.12 (m, 2H), 6.94 (d, *J* = 15.0 Hz, 1H), 6.83-6.76 (m, 2H), 5.98 (s, 1H), 5.76 (d, *J* = 15.0 Hz, 1H), 3.78 (s, 3H), 1.62 (q, *J* = 7.3 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.8, 159.0, 142.2, 137.4, 133.7, 133.1, 130.1, 129.8, 129.4, 127.8, 127.5, 127.3, 113.9, 55.2, 52.3, 29.1, 8.8. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1890.

(3*Z*,5*E*)-2,2-diethyl-6-(3-methoxyphenyl)-4-phenylhexa-3,5-dienoic acid (3b)



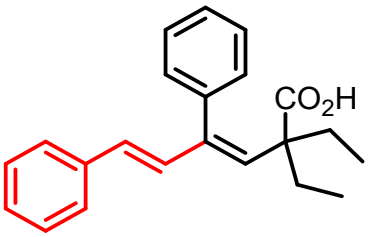
According to general procedure (II) with **1a** (0.206 mmol, 45.0 mg) and **2b** (0.165 mmol, 35.1 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3b** as pale-yellow oil (49 mg, 85%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.32 (m, 3H), 7.22-7.13 (m, 3H), 7.04 (d, *J* = 15.0 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 3.0 Hz, 1H), 6.74 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.06 (s, 1H), 5.80 (d, *J* = 15.0 Hz, 1H), 3.79 (s, 3H), 1.64 (q, *J* = 7.8 Hz, 4H), 0.85 (t, *J* = 7.8 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.9, 159.7, 142.0, 138.7, 137.2, 135.4, 135.0, 130.2, 129.4, 129.3, 127.9, 127.4, 119.1, 113.4, 111.2, 55.2, 52.5, 29.2, 8.9. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1886.

(3*Z*,5*E*)-2,2-diethyl-6-(2-methoxyphenyl)-4-phenylhexa-3,5-dienoic acid (3c)



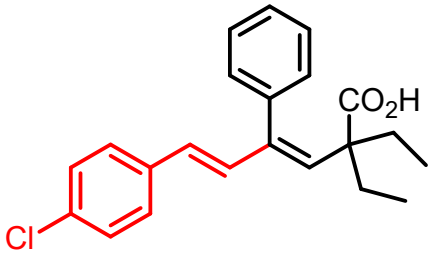
According to general procedure (II) with **1a** (0.206 mmol, 45.0 mg) and **2c** (0.165 mmol, 35.1 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3c** as pale-yellow oil (41.7 mg, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44-7.28 (m, 4H), 7.25-7.04 (m, 4H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 6.15 (d, *J* = 15.0 Hz, 1H), 6.03 (s, 1H), 3.73 (s, 3H), 1.64 (q, *J* = 7.3 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.5, 156.7, 142.7, 137.3, 136.0, 134.3, 129.4, 128.2, 127.8, 127.2, 126.9, 126.3, 125.5, 120.5, 110.8, 55.4, 52.4, 29.1, 8.8. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1877.

(3*Z*,5*E*)-2,2-diethyl-4,6-diphenylhexa-3,5-dienoic acid (3d)



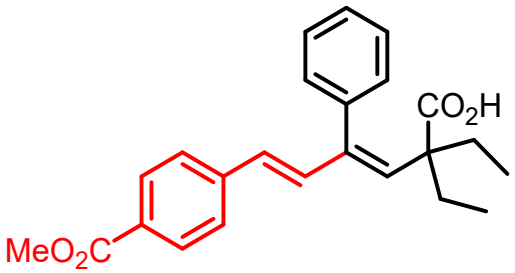
According to general procedure (II) with **1a** (0.115 mmol, 25.0 mg) and **2d** (0.092 mmol, 16.8 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3d** as pale-yellow oil (27.1 mg, 92%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ.42-7.26 (m, 7H), 7.20-7.12 (m, 3H), 7.06 (d, *J* = 15.8 Hz, 1H), 6.04 (s, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 1.66-1.59 (q, *J* = 7.5 Hz, 4H), 0.82 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.4, 142.1, 137.3, 135.0, 134.8, 130.3, 129.4, 128.7, 128.5, 127.9, 127.4, 127.3, 126.4, 52.4, 29.2, 8.9. **HRMS** (EI) calculated for $C_{22}H_{24}O_2$ ($[M]^+$): 320.1776. Found: 320.1777.

(3*Z*,5*E*)-6-(4-chlorophenyl)-2,2-diethyl-4-phenylhexa-3,5-dienoic acid (3e)



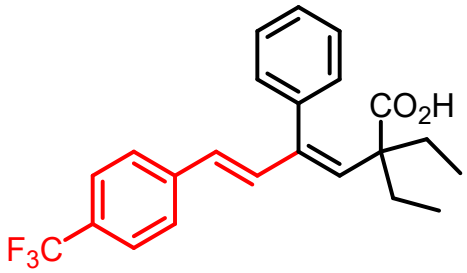
According to general procedure (II) with **1a** (0.206 mmol, 45.0 mg) and **2e** (0.165 mmol, 35.9 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3e** as pale-yellow solid m.p.: 125-127 ^{o}C (44.5 mg, 76%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37-7.32 (m, 3H), 7.26-7.21 (m, 4H), 7.19-7.12 (m, 2H), 7.02 (d, *J* = 15.0 Hz, 1H), 6.05 (s, 1H), 5.75 (d, *J* = 15.0 Hz, 1H), 1.63 (q, *J* = 7.3 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 180.8, 141.9, 137.0, 135.8, 135.7, 135.4, 132.8, 129.3, 129.0, 128.6, 127.9, 127.5, 127.5, 52.4, 29.2, 8.9. **HRMS** (EI) calculated for $C_{22}H_{23}ClO_2$ ($[M]^+$): 354.1387. Found: 354.1382.

(3*Z*,5*E*)-2,2-diethyl-6-(4-(methoxycarbonyl)phenyl)-4-phenylhexa-3,5-dienoic acid (3f)



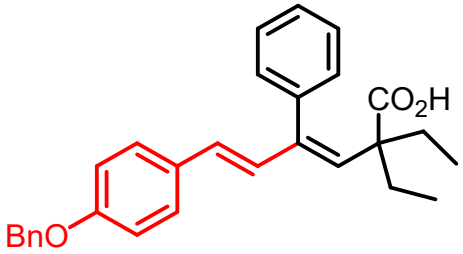
According to general procedure (II) with **1a** (0.206 mmol, 45.0 mg) and **2f** (0.165 mmol, 39.8 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3f** as pale-yellow oil (49 mg, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.38-7.28 (m, 5H), 7.19-7.12 (m, 3H), 6.13 (s, 1H), 5.83 (d, *J* = 15.0 Hz, 1H), 3.89 (s, 3H), 1.62 (q, *J* = 7.3 Hz, 4H), 0.83 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.7, 166.9, 141.9, 141.8, 137.5, 136.8, 136.6, 129.8, 129.3, 129.2, 128.5, 128.0, 127.5, 126.2, 52.6, 52.0, 29.2, 8.9. **HRMS** (EI) calculated for $C_{24}H_{26}O_4$ ($[M]^+$): 378.1831. Found: 378.1836

(3*Z*,5*E*)-2,2-diethyl-4-phenyl-6-(4-(trifluoromethyl)phenyl)hexa-3,5-dienoic acid (3g)



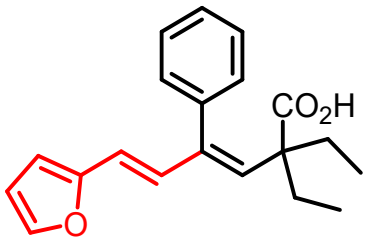
According to general procedure (II) with **1a** (0.151 mmol, 33.0 mg) and **2g** (0.121 mmol, 30.4mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3g** as pale-yellow solid m.p.: 117-119 °C (31 mg, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.0 Hz, 2H), 7.43-7.30 (m, 5H), 7.22-7.08 (m, 3H), 6.12 (s, 1H), 5.83 (d, *J* = 15.0 Hz, 1H), 1.64 (q, *J* = 7.4 Hz, 4H), 0.85 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.2, 141.8, 140.8, 137.4, 136.8, 136.6, 129.3, 129.1, 128.8, 128.0, 127.6, 126.4, 125.4, 125.4, 52.6, 29.2, 8.9. **HRMS** (EI) calculated for $C_{23}H_{23}F_3O_2$ ($[M]^+$): 388.1650. Found: 388.1657.

(3*Z*,5*E*)-6-(4-(benzyloxy)phenyl)-2,2-diethyl-4-phenylhexa-3,5-dienoic acid (3h)



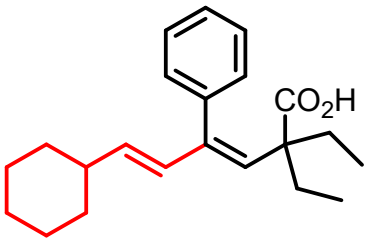
According to general procedure (II) with **1a** (0.161 mmol, 35.0 mg) and **2h** (0.128 mmol, 37.0 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3h** as pale-yellow solid m.p.: 110-112 °C (30 mg, 55%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46-7.28 (m, 7H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.20-7.10 (m, 2H), 6.94 (d, *J* = 16.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.98 (s, 1H), 5.76 (d, *J* = 16.5 Hz, 1H), 5.04 (s, 2H), 1.63 (q, *J* = 7.4 Hz, 4H), 0.84 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.6, 158.2, 142.2, 137.4, 136.9, 133.8, 133.2, 130.3, 129.8, 129.4, 128.5, 127.9, 127.8, 127.5, 127.4, 127.3, 114.9, 69.9, 52.3, 29.1, 8.8. **HRMS** (EI) calculated for $C_{29}H_{30}O_3$ ($[M]^+$): 426.2195. Found: 426.2187.

(3*Z*,5*E*)-2,2-diethyl-6-(furan-2-yl)-4-phenylhexa-3,5-dienoic acid (3i)



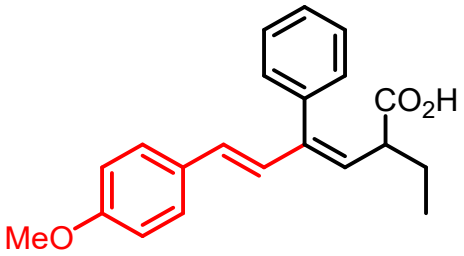
According to general procedure (II) with **1a** (0.137 mmol, 30.0 mg) and **2i** (0.11 mmol, 19.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3i** as pale-yellow oil (21.1 mg, 62%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 4H), 7.15-7.10 (m, 2H), 7.00 (d, *J* = 16.5 Hz, 1H), 6.32 (d, *J* = 3.0 Hz, 1H), 6.09 (d, *J* = 3.0 Hz, 1H), 6.02 (s, 1H), 5.61 (d, *J* = 16.5 Hz, 1H), 1.62 (q, *J* = 7.3 Hz, 4H), 0.83 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.8, 153.3, 141.9, 141.8, 136.9, 134.9, 133.6, 129.3, 127.9, 127.4, 118.2, 111.5, 108.3, 52.4, 29.1, 8.8. **HRMS** (EI) calculated for $C_{20}H_{22}O_3$ ($[M]^+$): 310.1569. Found: 310.1563.

(3*Z*,5*E*)-6-cyclohexyl-2,2-diethyl-4-phenylhexa-3,5-dienoic acid (3j)



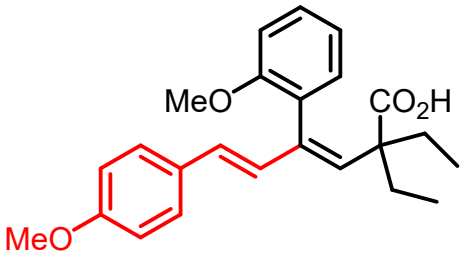
According to general procedure (II) with **1a** (0.161 mmol, 35.0 mg) and **2j** (0.128 mmol, 24.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3j** as pale-yellow oil (22 mg, 52%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35-7.23 (m, 3H), 7.14-7.00 (m, 2H), 6.25 (d, *J* = 18.0 Hz, 1H), 5.72 (s, 1H), 4.91 (q, *J* = 15.0, 9.0 Hz, 1H), 1.75-1.61 (m, 3H), 1.61-1.56 (m, 4H), 1.40-0.90 (m, 8H), 0.80 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 180.6, 142.2, 138.6, 137.9, 133.5, 131.5, 129.3, 127.6, 127.0, 51.9, 40.7, 32.7, 28.9, 26.1, 26.0, 8.8. **HRMS** (EI) calculated for $C_{22}H_{30}O_2$ ($[M]^+$): 326.2246. Found: 326.2245.

(3*Z*,5*E*)-2-ethyl-6-(4-methoxyphenyl)-4-phenylhexa-3,5-dienoic acid (3k)



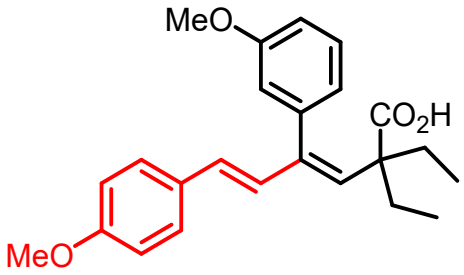
According to general procedure (II) with **1b** (0.137 mmol, 30.0 mg) and **2a** (0.11 mmol, 23.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3k** as pale-yellow oil (21.3 mg, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50-7.30 (m, 3H), 7.27-7.15 (m, 4H), 6.91 (d, *J* = 15.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.00 (d, *J* = 15.0 Hz, 1H), 5.77 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H), 3.05-2.90 (m, 1H), 1.82-1.71 (m, 1H), 1.64-1.54 (m, 1H), 0.85 (d, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 180.4, 159.1, 144.3, 137.3, 131.0, 130.4, 130.0, 129.5, 128.8, 128.3, 127.6, 127.3, 113.9, 55.2, 46.9, 26.0, 11.5. **HRMS** (EI) calculated for $C_{21}H_{22}O_3$ ($[M]^+$): 322.1569. Found: 322.1561.

(3*Z*,5*E*)-2,2-diethyl-4-(2-methoxyphenyl)-6-(4-methoxyphenyl)hexa-3,5-dienoic acid (3m)



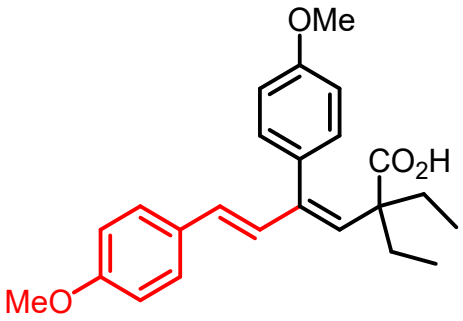
According to general procedure (II) with **1d** (0.20 mmol, 49.0 mg) and **2a** (0.16 mmol, 33.6 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3m** as pale-yellow oil (41 mg, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.27 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.10-7.01 (m, 1H), 6.98-6.86 (m, 3H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.04 (s, 1H), 5.77 (d, *J* = 15.0 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 1.70-1.55 (m, 4H), 0.83 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.6, 158.8, 156.9, 138.9, 134.3, 131.9, 131.0, 130.2, 129.0, 128.6, 127.6, 125.8, 120.0, 113.8, 110.3, 55.2, 55.0, 52.4, 28.6, 28.3, 8.8, 8.7. **HRMS** (EI) calculated for $C_{24}H_{28}O_4$ ($[M]^+$): 380.1988. Found: 380.1985.

(3*Z*,5*E*)-2,2-diethyl-4-(3-methoxyphenyl)-6-(4-methoxyphenyl)hexa-3,5-dienoic acid (3n)



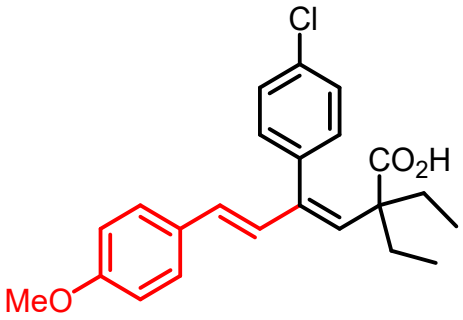
According to general procedure (II) with **1e** (0.20 mmol, 49.0 mg) and **2a** (0.16 mmol, 33.6 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3n** as pale-yellow oil (53 mg, 88%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30-7.20 (m, 3H), 6.96-6.69 (m, 6H), 5.96 (s, 1H), 5.82 (d, *J* = 16.5 Hz, 1H), 3.78 (s, 6H), 1.64 (q, *J* = 7.3 Hz, 4H), 0.83 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.5, 159.0, 159.0, 142.1, 138.8, 133.3, 132.8, 130.1, 129.7, 128.9, 127.5, 121.8, 114.7, 113.9, 113.0, 55.2, 55.1, 52.4, 29.2, 8.9. **HRMS** (EI) calculated for $C_{24}H_{28}O_4$ ($[M]^+$): 380.1988. Found: 380.1993.

(3*Z*,5*E*)-2,2-diethyl-4,6-bis(4-methoxyphenyl)hexa-3,5-dienoic acid (3o)



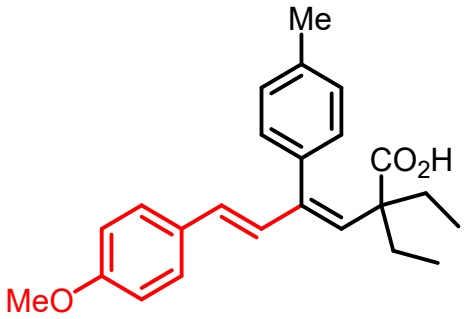
According to general procedure (II) with **1f** (0.16 mmol, 40.0 mg) and **2a** (0.13 mmol, 27.4 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3o** as pale-yellow oil (45 mg, 91%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.95-6.83 (m, 3H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.96 (s, 1H), 5.79 (d, *J* = 15.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 1.67-1.59 (q, *J* = 7.4 Hz, 4H), 0.83 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.1, 159.0, 158.7, 142.0, 134.0, 133.4, 130.4, 130.2, 129.7, 129.5, 127.5, 113.9, 113.3, 55.2, 55.1, 52.3, 29.1, 8.8. **HRMS** (EI) calculated for $C_{24}H_{28}O_4$ ($[M]^+$): 380.1988. Found: 380.1991.

(3*Z*,5*E*)-4-(4-chlorophenyl)-2,2-diethyl-6-(4-methoxyphenyl)hexa-3,5-dienoic acid (3p)



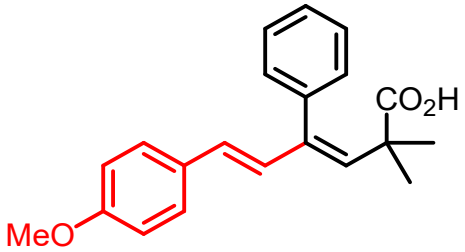
According to general procedure (II) with **1g** (0.15 mmol, 39.0 mg) and **2a** (0.12 mmol, 26.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3p** as pale-yellow oil (27 mg, 59%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 6.0 Hz, 2H), 6.89 (d, *J* = 16.5 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.97 (s, 1H), 5.73 (d, *J* = 16.5 Hz, 1H), 3.79 (s, 3H), 1.64 (q, *J* = 7.4 Hz, 4H), 0.84 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.4, 159.1, 141.1, 135.8, 134.3, 133.3, 132.7, 130.9, 130.0, 129.8, 128.2, 127.6, 114.0, 55.3, 52.2, 29.1, 8.8. **HRMS** (EI) calculated for $C_{23}H_{25}ClO_3$ ($[M]^+$): 384.1492. Found: 384.1501.

(3*Z*,5*E*)-2,2-diethyl-6-(4-methoxyphenyl)-4-(p-tolyl)hexa-3,5-dienoic acid (3q)



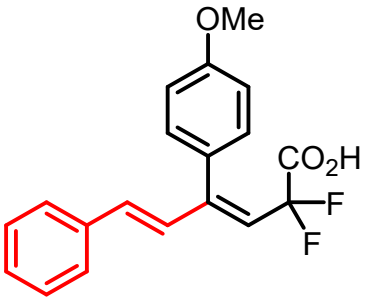
According to general procedure (II) with **1h** (0.25 mmol, 58.1 mg) and **2a** (0.20 mmol, 42.8 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3q** as pale-yellow oil (68.5 mg, 94%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 15.0 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.98 (s, 1H), 5.81 (d, *J* = 15.0 Hz, 1H), 3.79 (s, 3H), 2.38 (s, 3H), 1.70-1.60 (m, 4H), 0.85 (t, *J* = 6.0 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.3, 158.9, 142.3, 136.8, 134.3, 133.7, 133.2, 130.2, 129.6, 129.2, 128.5, 127.5, 113.9, 55.2, 52.3, 29.1, 21.3, 8.8. **HRMS** (EI) calculated for $C_{24}H_{28}O_3$ ($[M]^+$): 364.2038. Found: 364.2034.

(3*Z*,5*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-4-phenylhexa-3,5-dienoic acid (3s)



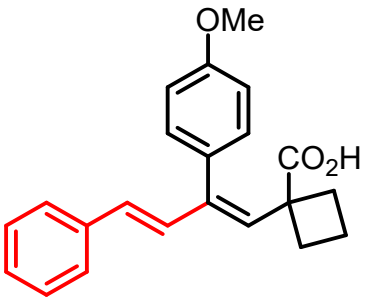
According to general procedure (II) with with **1j** (0.25 mmol, 47.6 mg) and **2a** (0.2 mmol, 42.6 mg) The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) provide pure product **3s** as pale-yellow oil (26.4 mg, 41%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35-7.14 (m, 7H), 6.89-6.78 (m, 3H), 5.89 (s, 1H), 5.81 (d, *J* = 16.5 Hz, 1H), 3.78 (s, 3H), 1.23 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 183.0, 159.0, 142.0, 137.0, 136.0, 132.4, 130.4, 130.0, 129.1, 127.8, 127.5, 127.2, 113.9, 55.2, 43.8, 27.1. **HRMS** (EI) calculated for $C_{21}H_{22}O_3$ ($[M]^+$): 322.1569. Found: 322.1559.

(*3E*,*5E*)-2,2-difluoro-4-(4-methoxyphenyl)-6-phenylhexa-3,5-dienoic acid (3t)



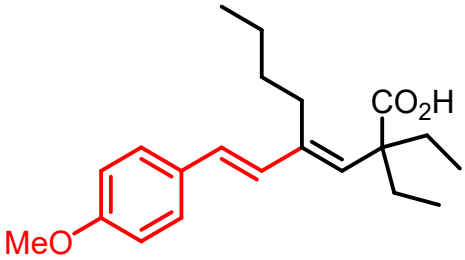
According to general procedure (II) with **1m** (57.2 mg, 0.25 mmol) and **2d** (36.7 mg, 0.2 mmol), the crude was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3t** as yellow oil (24.2 mg, 29%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.15 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 16.5 Hz, 1H), 6.95 (d, J = 9.0 Hz, 2H), 6.44 (d, J = 16.5 Hz, 1H), 6.05 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.1, 159.4, 156.7, 139.2, 136.0, 131.6, 129.9 (t, $J^{l}_{C,F}$ = 9 Hz), 128.9, 128.7, 128.2, 127.2, 118.6, 113.6, 113.4, 55.2. **HRMS** (EI) calculated for $C_{19}H_{16}F_2O_3$ ([M]$^+$): 330.1068. Found: 330.1061.

1-((1*E*,3*E*)-2-(4-methoxyphenyl)-4-phenylbuta-1,3-dien-1-yl)cyclobutane-1-carboxylic acid (3u)



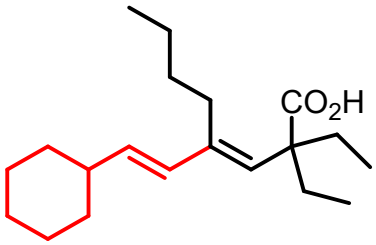
According to general procedure (II) with **1n** (50 mg, 0.215 mmol) and **2d** (31.5 mg, 0.172 mmol), the crude was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3u** as pale-yellow oil (32 mg, 55%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 7H), 7.11 (d, J = 18.0 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 6.37 (d, J = 18.0 Hz, 1H), 5.74 (s, 1H), 3.85 (s, 3H), 2.88-2.79 (m, 2H), 2.46-2.36 (m, 2H), 2.07-1.97 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 180.8, 158.9, 141.3, 137.2, 134.0, 133.3, 133.2, 130.1, 128.6, 127.7, 126.6, 125.6, 113.4, 55.2, 48.6, 33.9, 29.6, 16.8. **HRMS** (EI) calculated for $C_{22}H_{22}O_3$ ([M]$^+$): 334.1569. Found: 334.1564.

(*E*)-2,2-diethyl-4-((*E*)-4-methoxystyryl)oct-3-enoic acid (3v)



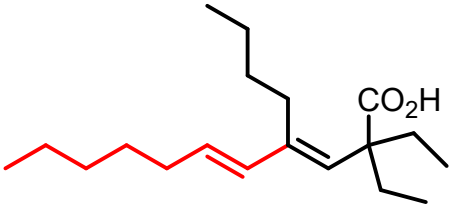
According to general procedure (II) with **1k** (0.129 mmol, 25.6 mg) and **2a** (0.103 mmol, 22.0 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3v** as yellow oil (25.2 mg, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 9 Hz, 2H), 6.86 (d, *J* = 9 Hz, 2H), 6.57 (d, *J* = 15 Hz, 1H), 6.44 (d, *J* = 15 Hz, 1H), 5.49 (s, 1H), 3.81 (s, 3H), 2.35-2.20 (m, 2H), 1.96-1.75 (m, 4H), 1.48-1.30 (m, 4H), 0.99-0.80 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.9, 158.9, 141.1, 133.4, 131.0, 130.4, 127.4, 126.5, 114.0, 55.3, 51.0, 30.3, 28.7, 28.0, 23.4, 13.9, 8.5. **HRMS** (EI) calcd for $C_{21}H_{30}O_3$ ($[M]^+$): 330.2195. Found: 330.2187.

(*E*)-4-((*E*)-2-cyclohexylvinyl)-2,2-diethyloct-3-enoic acid (3w)



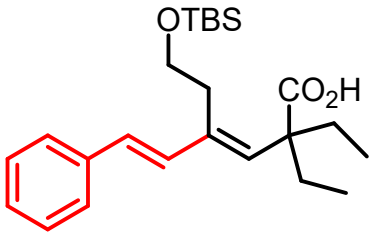
According to general procedure (II) with **1k** (0.14 mmol, 27.7 mg) and **2j** (0.11 mmol, 20.7 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3w** as yellow oil (27.3 mg, 81%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.86 (d, *J* = 15 Hz, 1H), 5.55 (dd, *J* = 15, 6 Hz, 1H), 5.25 (s, 1H), 2.13 (t, *J* = 7.5 Hz, 1H), 1.92-1.65 (m, 8H), 1.37-1.23 (m, 11H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.4, 141.1, 134.9, 131.1, 130.8, 50.6, 41.0, 33.0, 30.2, 28.5, 28.0, 26.2, 26.1, 23.3, 13.9, 8.5. **HRMS** (EI) calcd for $C_{20}H_{34}O_2$ ($[M]^+$): 306.2553. Found: 306.2549.

(3*E*,5*E*)-4-butyl-2,2-diethylundeca-3,5-dienoic acid (3x)



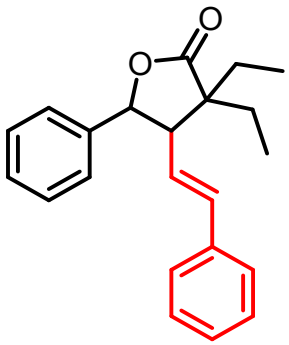
According to general procedure (III) with **1k** (0.14 mmol, 27.8 mg) and **2n** (0.12 mmol, 21.2 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3x** as yellow oil (27.5 mg, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.90 (d, *J* = 15 Hz, 1H), 5.68-5.51(m, 1H), 5.25 (s, 1H), 2.20-2.09 (m, 2H), 2.06 (t, *J* = 7.5 Hz, 1H), 1.90-1.70 (m, 4H), 1.41-1.21 (m, 8H), 0.89 (t, *J* = 7.5 Hz, 6H), 0.82 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.3, 141.0, 133.4, 131.0, 129.3, 50.7, 32.9, 31.5, 30.2, 29.2, 28.6, 28.1, 23.3, 22.5, 14.1, 13.9, 8.5. **HRMS** (EI) calcd for $C_{19}H_{34}O_2$ ($[M]^+$): 294.2553. Found: 294.2549.

(*E*)-6-((tert-butyldimethylsilyl)oxy)hex-3-enoic acid (3y)



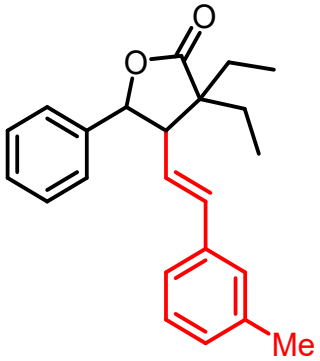
According to general procedure (III) with **1l** (0.19 mmol, 60 mg) and **2d** (0.15 mmol, 27.8 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3y** as yellow oil (20 mg, 42%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.21 (m, 5H), 6.72 (d, *J* = 18.0 Hz, 1H), 6.58 (d, *J* = 18.0 Hz, 1H), 5.71 (s, 1H), 3.75-3.70 (t, *J* = 6.0 Hz, 2H), 2.66-2.61 (t, *J* = 6.0 Hz, 2H), 1.99-1.84 (m, 4H), 0.90-0.84 (singlet and triplet stacked, total 15H), 0.07 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.5, 137.4, 137.0, 136.2, 133.0, 128.6, 127.1, 126.2, 61.6, 51.5, 31.9, 29.3, 26.0, 13.4, 8.7, -5.2. **HRMS** (EI) calcd for $C_{24}H_{38}O_3Si$ ($[M]^+$): 402.2590. Found: 402.2585.

(*E*)-3,3-diethyl-5-phenyl-4-styryldihydrofuran-2(3H)-one (5a)



According to general procedure (III) with **1a** (0.21 mmol, 45.8 mg) and **4a** (0.17 mmol, 30.7 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5a** as white solid m.p.:120-122 °C (47.9 mg, 88%). Compound **5a** dissolves in 6 mL of EA. A few block shaped, colorless crystals of Compound **5a** suitable for X-ray diffraction were obtained after 1 days at room temperature (25 °C), forming just above the solvent line. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.23 (m, 10H), 6.38-6.16 (m, 2H), 5.26 (d, *J* = 9.0 Hz, 1H), 3.18-3.05 (m, 1H), 1.96-1.80 (m, 2H), 1.68-1.53 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.0, 138.3, 136.3, 135.6, 128.6, 128.5, 128.4, 128.0, 126.3, 125.8, 122.6, 81.6, 55.8, 52.6, 26.5, 25.5, 8.9, 8.6. **HRMS** (EI) calculated for $C_{22}H_{24}O_2$ ($[M]^+$): 320.1776. Found: 320.1775.

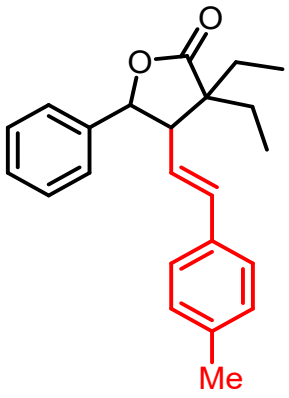
(*E*)-3,3-diethyl-4-(3-methylstyryl)-5-phenyldihydrofuran-2(3H)-one (5b)



According to general procedure (III) with **1a** (0.26 mmol, 58.5 mg) and **4b** (0.21 mmol, 42.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5b** as pale-yellow oil (54.1 mg, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.05 (m, 9H), 6.35-6.15 (m, 2H), 5.26 (d, *J* = 9.0 Hz, 1H), 3.11 (dd, *J* = 9.0, 6.0 Hz, 1H), 2.36 (s, 3H), 1.95-1.83 (m, 2H), 1.75-1.55 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz,

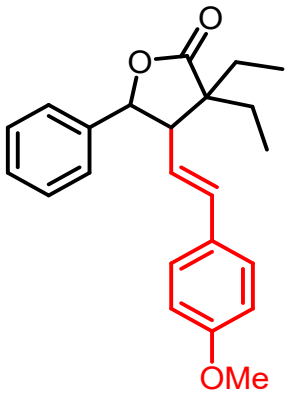
$CDCl_3$) δ 179.0, 138.3, 138.3, 136.3, 135.7, 128.8, 128.5, 128.5, 128.3, 127.0, 125.8, 123.5, 122.4, 81.6, 55.8, 52.5, 26.5, 25.5, 21.3, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_2$ ([M]$^+$): 334.1933. Found: 334.1939.

(*E*)-3,3-diethyl-4-(4-methylstyryl)-5-phenyldihydrofuran-2(3H)-one (5c)



According to general procedure (III) with **1a** (0.21 mmol, 45.0 mg) and **4c** (0.16 mmol, 32.5 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5c** as pale-yellow oil (44.4 mg, 83%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 6.0 Hz, 2H), 6.35-6.15 (m, 2H), 5.25 (d, *J* = 9.0 Hz, 1H), 3.10 (dd, *J* = 10.5, 7.5 Hz, 1H), 2.35 (s, 3H), 1.98-1.80 (m, 2H), 1.74-1.57 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.0, 138.3, 137.9, 135.5, 133.6, 129.3, 128.5, 128.3, 126.2, 125.7, 121.5, 81.6, 55.8, 52.5, 26.5, 25.5, 21.2, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_2$ ([M]$^+$): 334.1933. Found: 334.1932

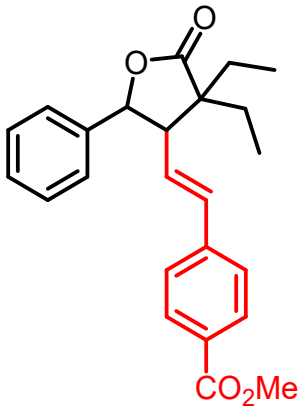
(*E*)-3,3-diethyl-4-(4-methoxystyryl)-5-phenyldihydrofuran-2(3H)-one (5d)



According to general procedure (III) with **1a** (0.24 mmol, 52.6 mg) and **4d** (0.19 mmol, 41.1 mg),

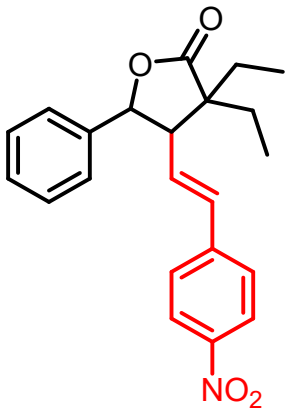
the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5d** as pale-yellow oil (29.3 mg, 44%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.27 (m, 7H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.23 (d, *J* = 15.0 Hz, 1H), 6.07 (dd, *J* = 15.0, 9.0 Hz, 1H), 5.24 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 3.12-3.03 (m, 1H), 1.95-1.80 (m, 2H), 1.78-1.50 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.1, 159.5, 138.4, 135.0, 129.2, 128.5, 128.3, 127.5, 125.8, 120.3, 114.0, 81.7, 55.8, 55.3, 52.5, 26.5, 25.5, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1884

Methyl (*E*)-4-(2-(4,4-diethyl-5-oxo-2-phenyltetrahydrofuran-3-yl)vinyl)benzoate (5e)



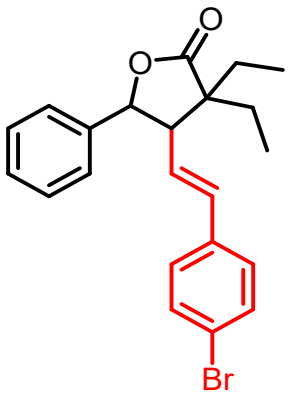
According to general procedure (III) with **1a** (0.20 mmol, 44.0 mg) and **4e** (0.16 mmol, 38.9 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5e** as pale-yellow oil (40.5 mg, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 2H), 7.43-7.28 (m, 7H), 6.39-6.30 (m, 2H), 5.26 (d, *J* = 9.0 Hz, 1H), 3.91 (s, 3H), 3.20-3.10 (m, 1H), 1.98-1.83 (m, 2H), 1.78-1.53 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.00 (d, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.7, 166.7, 140.6, 138.1, 134.8, 130.0, 129.4, 128.6, 128.5, 126.2, 125.8, 125.5, 81.5, 55.8, 52.7, 52.2, 26.5, 25.5, 8.9, 8.7. **HRMS** (EI) calculated for $C_{24}H_{26}O_4$ ($[M]^+$): 378.1831. Found: 378.1828.

***(E)*-3,3-diethyl-4-(4-nitrostyryl)-5-phenyldihydrofuran-2(3H)-one (5f)**



According to general procedure (III) with **1a** (0.23 mmol, 50.4 mg) and **4f** (0.18 mmol, 42.0 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5f** as yellow oil (42.3 mg, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.28-7.13 (m, 5H), 6.43-6.19 (m, 2H), 5.19 (d, *J* = 9.0 Hz, 1H), 3.15-3.00 (m, 3H), 1.88-1.75 (m, 2H), 1.66-1.46 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.4, 147.1, 142.4, 137.8, 133.6, 128.7, 127.9, 127.0, 126.9, 125.8, 124.1, 81.3, 55.9, 52.8, 26.5, 25.5, 8.9, 8.7. **HRMS** (EI) calculated for $C_{22}H_{23}NO_4$ ($[M]^+$): 365.1627. Found: 365.1621.

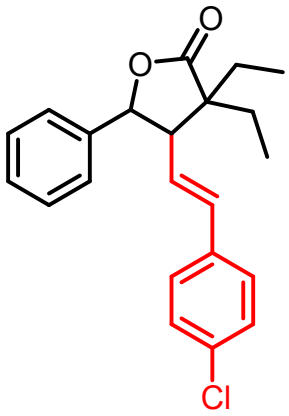
(*E*)-4-(4-bromostyryl)-3,3-diethyl-5-phenyldihydrofuran-2(3H)-one (5g)



According to general procedure (III) with **1a** (0.20 mmol, 43.0 mg) and **4g** (0.16 mmol, 41.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5g** as pale-yellow oil (53.7 mg, 84%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 9.0 Hz, 2H), 7.37-7.27 (m, 5H), 7.23-7.16 (m, 2H), 6.23 (d, *J* = 3.0 Hz, 2H), 5.24 (d, *J* = 12.0 Hz, 1H), 3.17-3.06 (m, 1H), 1.94-1.82 (m, 2H), 1.68-1.59 (m, 2H), 1.15-1.03 (m, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.8, 138.1, 135.2, 134.5, 131.7, 128.6, 128.5, 127.8, 125.8,

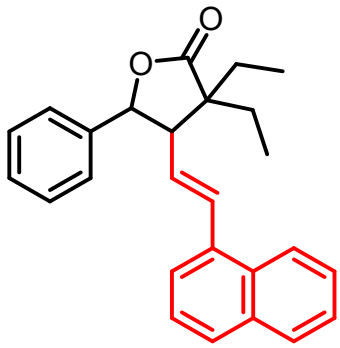
123.5, 121.8, 81.5, 55.8, 52.5, 26.5, 25.5, 8.9, 8.6. **HRMS** (EI) calculated for $C_{22}H_{23}BrO_2$ ($[M]^+$): 398.0881. Found: 398.0885.

(*E*)-4-(4-chlorostyryl)-3,3-diethyl-5-phenyldihydrofuran-2(3H)-one (5h)



According to general procedure (III) with **1a** (0.20 mmol, 43.3 mg) and **4h** (0.16 mmol, 34.6 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5h** as pale-yellow oil (43.7 mg, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.21 (m, 9H), 6.30-6.13 (m, 2H), 5.25 (d, J = 9.0 Hz, 1H), 3.18-3.03 (m, 1H), 1.95-1.83 (m, 2H), 1.73-1.53 (m, 2H), 1.09 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.8, 138.1, 134.7, 134.4, 133.6, 128.8, 128.5, 128.4, 127.5, 125.8, 123.4, 81.5, 55.7, 52.5, 26.5, 25.4, 8.9, 8.6. **HRMS** (EI) calculated for $C_{22}H_{23}ClO_2$ ($[M]^+$): 354.1387. Found: 354.1394.

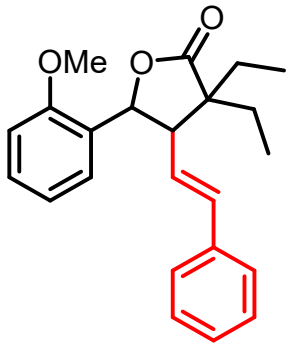
(*E*)-3,3-diethyl-4-(2-(naphthalen-1-yl)vinyl)-5-phenyldihydrofuran-2(3H)-one (5i)



According to general procedure (III) with **1a** (0.41 mmol, 90.0 mg) and **4i** (0.33 mmol, 77.0 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5i** as pale-yellow oil (80.7 mg, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, J = 9.0 Hz, 1H), 8.02 (br, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.63-7.53 (m, 2H), 7.43-7.33 (m, 7H), 6.60-6.35 (m,

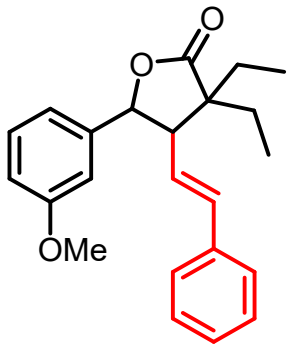
2H), 5.32 (d, J = 12.0 Hz, 1H), 3.25-3.15 (m, 1H), 1.98-1.90 (m, 2H), 1.78-1.58 (m, 2H), 1.13 (t, J = 7.5 Hz, 3H), 1.02 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.8, 138.1, 135.9, 134.9, 133.0, 132.5, 130.7, 130.1, 128.6, 128.5, 128.3, 126.2, 125.8, 125.3, 125.1, 122.5, 122.3, 81.5, 55.9, 52.8, 26.5, 25.6, 8.9, 8.7. **HRMS** (EI) calculated for $C_{26}H_{26}O_2$ ($[M]^+$): 370.1933 Found: 370.1924.

(*E*)-3,3-diethyl-5-(2-methoxyphenyl)-4-styryldihydrofuran-2(3H)-one (5j)



According to general procedure (III) with **1d** (0.20 mmol, 50.0 mg) and **4a** (0.16 mmol, 29.5 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5j** as pale-yellow oil (29.7 mg, 53%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37-7.22 (m, 7H), 7.04-6.93 (m, 1H), 6.89-6.80 (m, 1H), 6.27-6.25 (t, J = 3.0 Hz, 2H), 5.68 (d, J = 9.0 Hz, 1H), 3.73 (s, 3H), 3.30-3.22 (m, 1H), 1.95-1.85 (m, 2H), 1.71-1.53 (m, 2H), 1.08 (t, J = 7.5 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.4, 156.9, 136.7, 133.8, 129.5, 128.6, 127.6, 127.0, 126.4, 126.1, 124.0, 120.8, 110.8, 77.4 (overlap), 55.4, 54.6, 52.6, 26.3, 25.4, 8.9, 8.7. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1891.

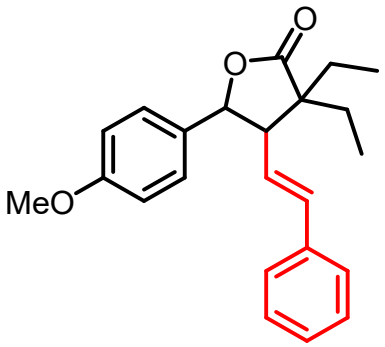
(*E*)-3,3-diethyl-5-(3-methoxyphenyl)-4-styryldihydrofuran-2(3H)-one (5k)



According to general procedure (III) with **1e** (0.20 mmol, 50.0 mg) and **4a** (0.16 mmol, 29.5 mg),

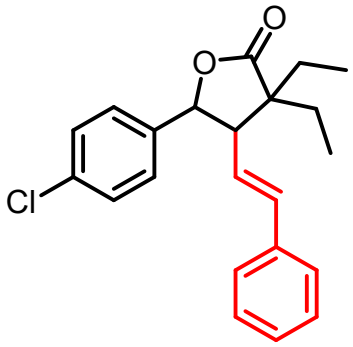
the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5k** as pale-yellow oil (39.8 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.18 (m, 6H), 6.86 (t, *J* = 7.5 Hz, 3H), 6.33 (d, *J* = 15.0 Hz, 1H), 6.22 (dd, *J* = 15.0, 9.0 Hz, 1H), 5.23 (d, *J* = 9.0 Hz, 1H), 3.77 (s, 3H), 3.18-3.05 (m, 1H), 1.95-1.80 (m, 2H), 1.75-1.55 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.0, 159.7, 139.9, 136.4, 135.7, 129.6, 128.7, 128.0, 126.3, 122.8, 118.1, 113.9, 111.1, 81.5, 55.7, 55.2, 52.6, 26.6, 25.6, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1891.

(*E*)-3,3-diethyl-5-(4-methoxyphenyl)-4-styryldihydrofuran-2(3H)-one (5l)



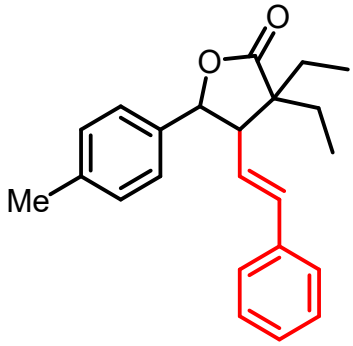
According to general procedure (III) with **1f** (0.20 mmol, 50.0 mg) and **4a** (0.16 mmol, 29.5 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5l** as pale-yellow oil (45.4 mg, 81%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 7H), 6.95-6.80 (m, 2H), 6.31 (d, *J* = 15.0 Hz, 1H), 6.28-6.13 (m, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.18-3.08 (m, 1H), 1.95-1.80 (m, 2H), 1.75-1.55 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.0, 159.7, 136.4, 135.5, 130.1, 128.6, 127.9, 127.3, 126.3, 122.8, 113.9, 81.5, 55.6, 55.2, 52.6, 26.5, 25.4, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_3$ ($[M]^+$): 350.1882. Found: 350.1874.

(*E*)-5-(4-chlorophenyl)-3,3-diethyl-4-styryldihydrofuran-2(3H)-one (5m)



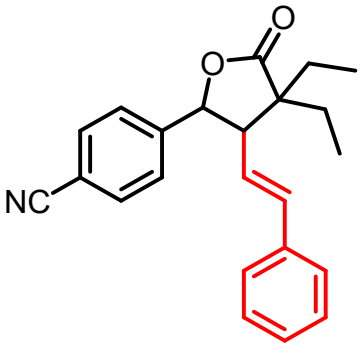
According to general procedure (III) with **1g** (0.20 mmol, 50.5 mg) and **4a** (0.16 mmol, 29.3 g), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5m** as pale-yellow oil (42.6 mg, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.21 (m, 9H), 6.31 (d, *J* = 15.0 Hz, 1H), 6.27-6.15 (m, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 3.10-3.00 (m, 1H), 1.95-1.83 (m, 2H), 1.76-1.70 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.7, 136.9, 136.1, 136.0, 134.2, 128.8, 128.7, 128.1, 127.1, 126.3, 122.2, 80.8, 56.0, 52.5, 26.5, 25.4, 8.9, 8.6. **HRMS** (EI) calculated for $C_{22}H_{23}ClO_2$ ($[M]^+$): 354.1387. Found: 354.1390.

(*E*)-3,3-diethyl-4-styryl-5-(p-tolyl)dihydrofuran-2(3H)-one (5n)



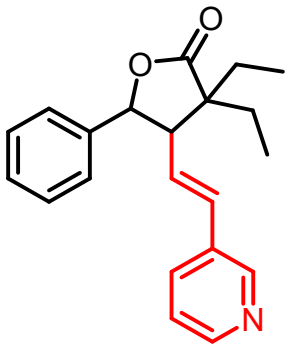
According to general procedure (III) with **1h** (0.20 mmol, 46.5 mg) and **4a** (0.16 mmol, 29.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5n** as pale-yellow oil (32.6 mg, 61%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 9H), 6.32 (d, *J* = 15.0 Hz, 1H), 6.22 (dd, *J* = 15.0, 9.0 Hz, 1H), 5.24 (d, *J* = 9.0 Hz, 1H), 3.20-3.05 (m, 1H), 2.35 (s, 3H), 1.95-1.83 (m, 2H), 1.79-1.60 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.0, 138.2, 136.4, 135.5, 135.2, 129.2, 128.6, 127.9, 126.3, 125.8, 122.8, 81.6, 55.6, 52.6, 26.5, 25.5, 21.1, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_2$ ($[M]^+$): 334.1933. Found: 334.1938.

(*E*)-4-(4,4-diethyl-5-oxo-3-styryltetrahydrofuran-2-yl)benzonitrile (5o)



According to general procedure (III) with **1i** (61.7 mg, 0.254 mmol), **4a** (37.2 mg, 0.203 mmol), the crude was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5o** as yellow oil as yellow liquid (19.4 mg, 28%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9 Hz, 2H), 7.43 (d, *J* = 9 Hz, 2H), 7.35 (m, 5H), 6.31 (d, *J* = 15 Hz, 1H), 6.22 (dd, *J* = 15, 9 Hz, 1H), 5.27 (d, *J* = 9 Hz, 1H), 2.99 (dd, *J* = 9.0, 9.0 Hz, 1H), 1.91-1.84 (m, 2H), 1.78-1.54 (m, 2H), 1.11 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.3, 143.7, 136.5, 135.9, 132.4, 128.7, 128.3, 126.4, 126.1, 121.6, 118.4, 112.2, 56.1, 52.5, 26.4, 25.4, 8.8, 8.5. **HRMS** (EI) m/z: ($[M]^+$) calcd for $C_{23}H_{23}NO_2$; Found: 345.1725.

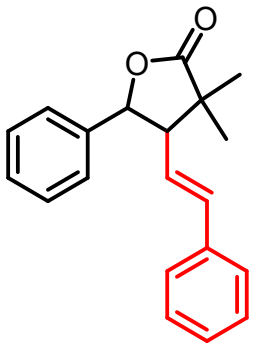
(*E*)-3,3-diethyl-5-phenyl-4-(2-(pyridin-3-yl)vinyl)dihydrofuran-2(3H)-one (5p)



According to general procedure (III) with **1a** (0.20 mmol, 43.6 mg) and **4j** (0.16 mmol, 29.4 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5o** as pale-yellow oil (40.1 mg, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.51 (d, *J* = 18.0 Hz, 2H), 7.69-7.60 (m, 1H), 7.36-7.26 (m, 6H), 6.29 (d, *J* = 9.0 Hz, 2H), 5.25 (d, *J* = 12.0 Hz, 1H), 3.19-3.08 (m, 1H), 1.91-1.84 (m, 2H), 1.70-1.59 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.6, 148.9, 148.0, 138.0, 132.9, 132.1, 132.0, 128.6,

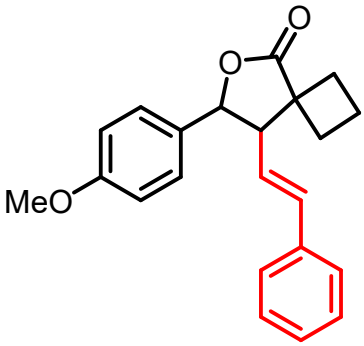
128.6, 125.8, 125.3, 123.5, 81.4, 55.9, 52.6, 26.5, 25.5, 8.9, 8.6. **HRMS** (EI) calculated for $C_{21}H_{23}NO_2$ ([M]$^+$): 321.1729. Found: 321.1723.

(*E*)-3,3-dimethyl-5-phenyl-4-styryldihydrofuran-2(3H)-one (5q)



According to general procedure (III) with **1j** (23.76 mg, 0.125 mmol), **4a** (18.1 mg, 0.1 mmol), the crude was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5q** as white solid, m.p.: 132-133 ^{o}C (21.3 mg, 73%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 (s, 10H), 6.35 (d, J = 16.5 Hz, 1H), 6.16 (dd, J = 16.5, 9 Hz, 1H), 5.26 (d, J = 15 Hz, 1H), 2.82 (dd, J = 9, 9 Hz, 1H), 1.30 (d, J = 2 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.1, 137.7, 136.4, 136.1, 128.9, 128.7, 128.3, 126.6, 126.0, 122.1, 81.9, 59.9, 45.2, 23.5, 19.7. **HRMS** (EI) calcd for $C_{20}H_{20}O_2$ ([M]$^+$): 292.1463. Found: 292.1459

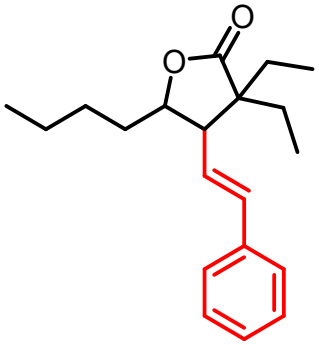
(*E*)-7-(4-methoxyphenyl)-8-styryl-6-oxaspiro[3.4]octan-5-one (5r)



According to general procedure (III) with **1n** (50 mg, 0.215 mmol) and **4a** (31.5 mg 0.172 mmol), the crude was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5r** as yellow oil (34 mg, 59%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41-7.23 (m, 7H), 6.87 (d, J = 9.0 Hz, 2H), 6.47 (d, J = 18.0 Hz, 1H), 6.27 (dd, J = 15.0, 9.0 Hz, 1H), 5.10 (d, J = 9.0 Hz, 1H), 3.79 (s, 3H), 2.92 (dd, J = 9.0, 9.0 Hz, 1H), 2.89-2.56 (m, 1H), 2.45-2.42 (m, 1H), 2.31-2.26 (m, 2H),

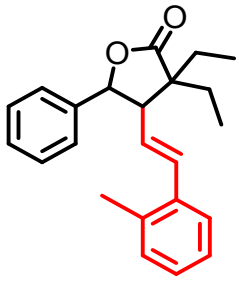
2.03-1.99 (m, 1H), 1.92-1.86 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 180.1, 159.7, 136.3, 135.6, 129.3, 128.7, 128.1, 127.3, 126.4, 122.9, 113.9, 81.9, 57.3, 55.2, 49.1, 27.4, 25.7, 16.6. **HRMS** (EI) calculated for $C_{22}H_{22}O_3$ ([M]$^+$): 334.1569. Found: 334.1565.

(*E*)-5-butyl-3,3-diethyl-4-styryldihydrofuran-2(3H)-one (5s)



According to general procedure (III) with **1k** (0.13 mmol, 25.4 mg) and **4a** (0.14 mmol, 25.7 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5s** as yellow oil (25.3 mg, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 5H), 6.45-6.25 (m, 2H), 5.55-5.46 (m, 2H), 3.08 (t, J = 7.5 Hz, 1H), 2.07-1.94 (m, 2H), 1.85-1.70 (m, 2H), 1.70-1.54 (m, 3H), 1.48-1.24 (m, 3H), 0.93-0.81 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.0, 137.6, 133.1, 131.0, 129.9, 128.5, 127.1, 126.2, 52.5, 51.8, 34.8, 29.7, 24.9, 24.5, 22.5, 13.7, 8.6, 8.4. **HRMS** (EI) calcd for $C_{20}H_{28}O_2$ ([M]$^+$): 300.2089. Found: 300.2083.

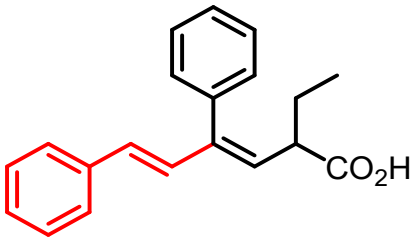
(*E*)-3,3-diethyl-4-(2-methylstyryl)-5-phenyldihydrofuran-2(3H)-one (5t)



According to general procedure (III) with **1a** (0.20 mmol, 43.6 mg) and **4m** (0.16 mmol, 31.5 mg). The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) provide pure product **5t** as pale-yellow oil (10.7 mg, 20%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45-7.23 (m, 6H), 7.22-7.10 (m, 3H), 6.48 (d, J = 16.5 Hz, 1H), 6.12-6.00 (m, 1H), 5.24 (d, J = 9.0 Hz, 1H), 3.18-3.03 (m, 1H), 2.18 (s, 3H), 1.89-1.59 (m, 4H), 1.09 (t, J = 7.5 Hz, 1H), 0.99 (t, J = 7.5

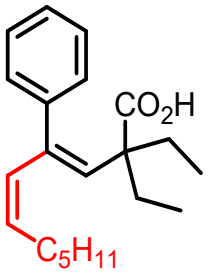
Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.1, 138.3, 135.8, 135.4, 134.0, 130.3, 128.5, 128.4, 127.9, 126.1, 125.8, 125.8 (overlap), 124.4, 81.6, 56.4, 52.3, 26.9, 25.3, 19.6, 8.9, 8.6. **HRMS** (EI) calculated for $C_{23}H_{26}O_2$ ([M]$^+$): 334.1933. Found: 334.1937.

(*E*)-4-(4-methoxyphenyl)-2-phenylbut-3-enoic acid (6a)



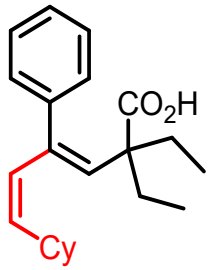
According to general procedure (III) with **1b** (40.0 mg, 0.21 mmol) and **4a** (30.7 mg, 0.168 mmol), the crude was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6a** as yellow liquid. (25 mg, 51%). **^{1}H NMR**, (300 MHz, $CDCl_3$) δ 7.44-7.17 (m, 10H), 7.02 (d, *J* = 18 Hz, 1H), 6.43 (d, *J* = 15 Hz, 1H), 5.82 (d, *J* = 9 Hz, 1H), 2.93-3.02 (m, 1H), 1.82-1.72 (m, 1H), 1.63-1.54 (m, 1H), 0.85 (t, *J* = 6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.5, 144.1, 137.1, 137.0, 132.3, 131.4, 129.8, 129.5, 128.3, 127.4, 127.3, 126.3, 46.8, 26.0, 11.4. **HRMS** (EI) calculated for $C_{20}H_{20}O_2$ ([M]$^+$): 292.1459. Found: 292.1457.

(3*Z*,5*Z*)-2,2-diethyl-4-phenylundeca-3,5-dienoic acid (6b)



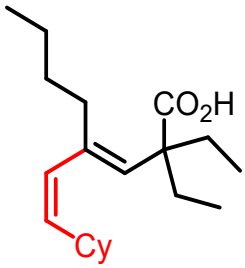
According to general procedure (III) with **1a** (0.27 mmol, 58.0 mg) and **4k** (0.21 mmol, 37.5 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6b** as pale-yellow oil (46.2 mg, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27-7.21 (m, 3H), 7.17-7.10 (m, 2H), 6.03-5.91 (m, 1H), 5.72 (s, 1H), 5.40-5.30 (m, 1H), 1.83-1.70 (m, 2H), 1.68-1.54 (m, 4H), 1.28-1.10 (m, 6H), 0.89-0.75 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.6, 140.3, 140.0, 132.7, 132.7, 132.0, 128.5, 127.8, 127.1, 51.8, 31.5, 29.7, 28.9, 27.8, 22.4, 14.0, 8.7. **HRMS** (EI) calculated for $C_{21}H_{30}O_2$ ([M]$^+$): 314.2246. Found: 314.2242.

(3*Z*,5*Z*)-6-cyclohexyl-2,2-diethyl-4-phenylhexa-3,5-dienoic acid (6c)



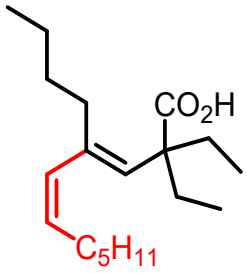
According to general procedure (III) with **1a** (0.20 mmol, 43.6 mg) and **4l** (0.16 mmol, 30.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6c** as pale-yellow oil (41.8 mg, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29-7.21 (m, 3H), 7.18-7.10 (m, 2H), 5.89 (d, *J* = 12.0 Hz, 1H), 5.74 (s, 1H), 5.18 (d, *J* = 9.0 Hz, 1H), 1.65-1.60 (m, 4H), 1.58-1.56 (m, 3H), 0.95-0.88 (m, 8H), 0.82 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.7, 140.6, 140.0, 137.8, 132.5, 131.1, 128.6, 127.8, 127.1, 51.9, 36.3, 33.3, 28.9, 25.9, 25.8, 8.7. **HRMS** (EI) calculated for $C_{22}H_{30}O_2$ ($[M]^+$): 326.2246. Found: 326.2237.

(*E*)-4-((*Z*)-2-cyclohexylvinyl)-2,2-diethyloct-3-enoic acid (6d)



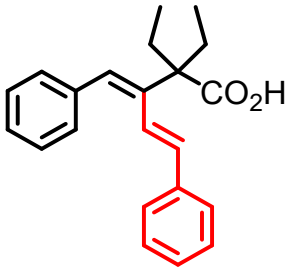
According to general procedure (III) with **1k** (0.18 mmol, 35.7 mg) and **4l** (0.14 mmol, 25.6 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6d** as yellow oil (31.3 mg, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.67 (d, *J* = 12 Hz, 1H), 5.31-5.15 (m, 2H), 2.00 (t, *J* = 7.5 Hz, 2H), 1.92-1.53 (m, 9H), 1.32-1.06 (m, 10H), 0.86 (t, *J* = 7.5 Hz, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 182.3, 140.0, 137.6, 130.0, 129.4, 50.6, 37.2, 33.6, 31.6, 29.7, 28.9, 26.1, 25.9, 22.9, 14.0, 8.5. **HRMS** (EI) calcd for $C_{20}H_{34}O_2$ ($[M]^+$): 306.2553. Found: 306.2554.

(3*E*,5*Z*)-4-butyl-2,2-diethylundeca-3,5-dienoic acid (6e)



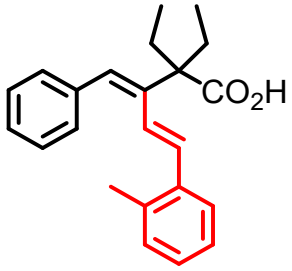
According to general procedure (III) with **1k** (0.25 mmol, 50.0 mg) and **4k** (0.14 mmol, 25.7 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6e** as yellow oil (47.3 mg, 73%).**^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.76 (d, *J* = 12 Hz, 1H), 5.50-5.39 (m, 1H), 5.17 (s, 1H), 2.20 (q, *J* = 7.5 Hz, 1H), 2.03 (t, *J* = 6 Hz, 1H), 1.92-1.73 (m, 6H), 1.45-1.21 (m, 8H), 0.95-0.80 (m, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 183.3, 139.5, 131.8, 130.0, 50.7, 31.7, 31.6, 29.8, 29.7, 28.8, 28.5, 22.9, 22.5, 14.0, 13.9, 8.6. **HRMS** (EI) calcd for $C_{19}H_{34}O_2$ ($[M]^+$): 294.2553. Found: 294.2559.

(*E*)-3-((*E*)-benzylidene)-2,2-diethyl-5-phenylpent-4-enoic acid (6f)



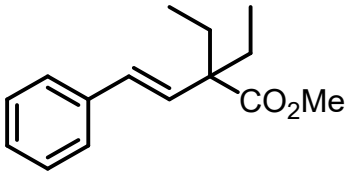
According to general procedure (III) with **1a** (0.20 mmol, 43.6 mg) and **4a** (0.16 mmol, 29.3 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6f** as pale-yellow oil (17.9 mg, 35%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20-7.15 (m, 5H), 7.04-6.96 (m, 6H), 6.15 (s, 1H), 6.03 (d, *J* = 15 Hz, 1H), 1.73-1.65 (m, 4H), 0.83 (t, *J* = 9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.6, 142.1, 137.3, 137.3, 135.1, 134.9, 130.3, 129.4, 128.5, 127.9, 127.4, 127.3, 126.4, 52.4, 29.2, 8.9. **HRMS** (EI) calculated for $C_{22}H_{24}O_2$ ($[M]^+$): 320.1776. Found: 320.1769.

(*E*)-3-((*E*)-benzylidene)-2,2-diethyl-5-(o-tolyl)pent-4-enoic acid (6g)



According to general procedure (III) with **1a** (0.20 mmol, 43.6 mg) and **4m** (0.16 mmol, 31.5 mg), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **6g** as pale-yellow oil (36.9 mg, 69%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55-7.25 (m, 4H), 7.23-7.00 (m, 5H), 6.94 (d, J = 15.0 Hz, 1H), 6.08-6.00 (m, 2H), 2.04 (s, 3H), 1.70-1.60 (m, 4H), 0.85 (t, J = 9.0 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.8, 142.4, 137.4, 136.3, 135.6, 134.5, 130.2, 129.3, 128.7, 128.4, 127.8, 127.3, 127.1, 126.0, 125.0, 52.4, 29.1, 19.4, 8.8. **HRMS** (EI) calculated for $C_{23}H_{26}O_2$ ([M]$^+$): 334.1933. Found: 334.1936.

Methyl (E)-2,2-diethyl-4-phenylbut-3-enoate (7)

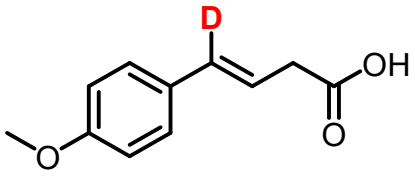


MeI (212 mg, 1.5 mmol) was added to a solution containing K_2CO_3 (166 mg, 1.2 mmol) and **1a** (218 mg, 1 mmol) in dry DMF under Argon and the reaction mixture was kept for stirring in a preheated oil bath at 75 °C for 30 min. After cooling to room temperature, the water was added and extracted with diethyl ether, washed with sodium chloride solution, dried over $MgSO_4$, filtered, and concentrated under *vacuo*. The obtained crude residue was purified by silica gel column chromatography (ethyl acetate/hexane) to provide the **7** as pale-yellow oil (230 mg, 99%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.37-7.32 (m, 2H), 7.28-7.25 (m, 1H), 6.47 (d, J = 3.0 Hz, 2H), 3.75 (s, 3H), 1.91 (q, J = 7.3 Hz, 4H), 0.91 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.7, 137.2, 131.5, 129.3, 128.3, 127.1, 126.1, 52.6, 51.6, 28.7, 8.7. **HRMS** (EI) calculated for $C_{15}H_{20}O_2$ ([M]$^+$): 232.1463. Found: 232.1454.

Mechanistic Studies

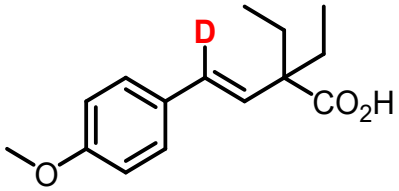
a) Deuterium incorporation experiments

(E)-4-phenylbut-3-enoic-4-*d* acid (8)



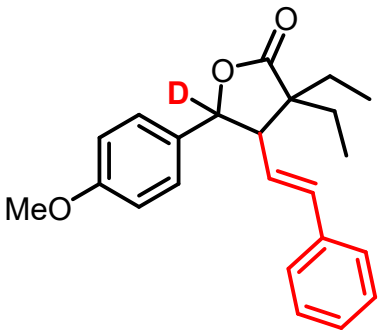
According to general procedure for the synthesis of β,γ-unsaturated carboxylic acids with 4-methoxybenzaldehyde-α-d_1 (100 mg, 0.92 mmol) and (2-carboxyethyl)triphenylphosphonium bromide (0.46 g, 1.10 mmol), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **8** as a yellow liquid (71 mg, 40%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.18-6.05 (m, 1H), 3.80 (s, 3H), 3.25 (d, *J* = 6 Hz, 2H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8, 159.2, 133.2, 132.8, 132.5, 129.4, 127.4, 118.7, 113.9, 55.2, 38.0. **HRMS** (EI) calcd for $C_{11}H_{11}DO_3$ ($[M]^+$): 193.0849. Found: 193.0841.

(E)-2,2-diethyl-4-(4-methoxyphenyl)but-3-enoic-4-*d* acid (1f-*d_1*)



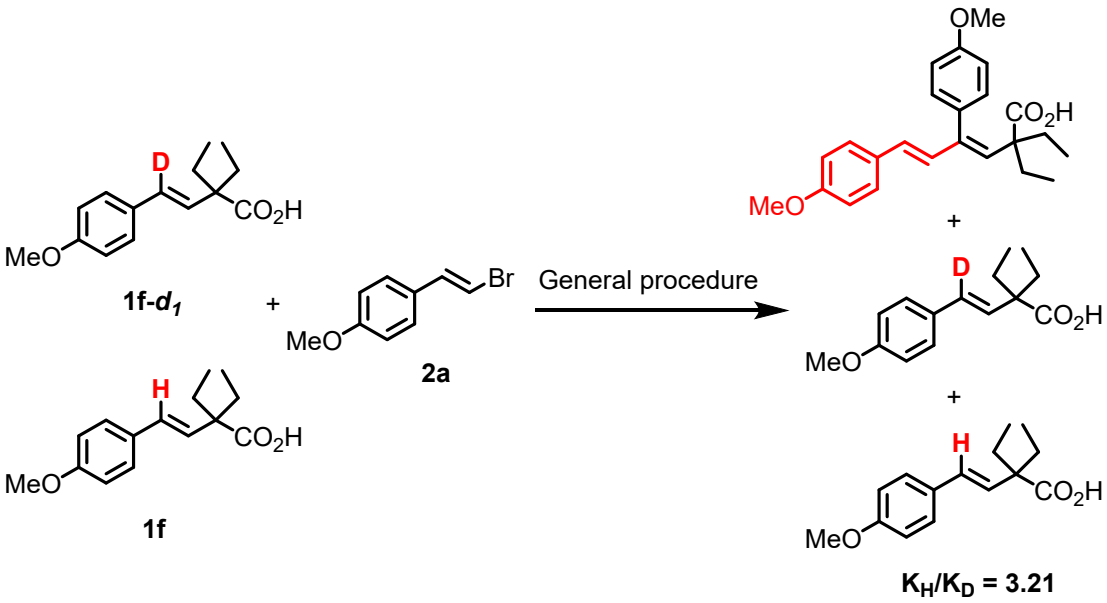
According to general procedure (I) with **8** (67.8 mg, 0.35 mmol), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **1f-*d_1*** as a yellow liquid (41.2 mg, 60%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 9, 1 Hz, 2H), 6.84 (dd, *J* = 4.5, 7.5 Hz, 2H), 6.24 (s, 1H), 3.79 (s, 3H), 1.84 (q, *J* = 6, 15 Hz, 4H), 0.88 (t, *J* = 6 Hz, 6H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 180.3, 158.9, 131.4, 129.2, 127.3, 113.8, 55.2, 52.4, 28.6, 8.8. **HRMS** (EI) calcd for $C_{15}H_{19}DO_3$ ($[M]^+$): 249.1475. Found: 249.1467.

(E)-3,3-diethyl-5-(4-methoxyphenyl)-4-styryldihydrofuran-2(3H)-one-5-d (5l-*d_1*)



According to general procedure III with **1f-*d*$_1$** (41.2 mg, 0.165 mmol), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5l-*d*$_1$** as yellow liquid (30.2 mg, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37-7.22 (m, 7H), 6.88 (d, *J* = 9 Hz, 2H), 6.31 (d, *J* = 18 Hz, 1H), 6.20 (dd, *J* = 15, 9 Hz, 1H), 5.22 (d, *J* = 12 Hz, 1H), 3.80 (s, 3H), 3.12 (d, *J* = 9 Hz, 1H), 1.93-1.82 (m, 2H), 1.75-1.52 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 179.07, 159.67, 136.38, 135.51, 130.05, 128.65, 127.99, 127.37, 126.33, 122.74, 113.95, 81.57, 77.46, 77.04, 76.62, 55.53, 55.28, 52.59, 26.55, 25.50, 8.98, 8.71. **HRMS** (EI) calcd for $C_{23}H_{25}DO_3$ ([M]$^+$): 351.1939. Found: 351.1937.

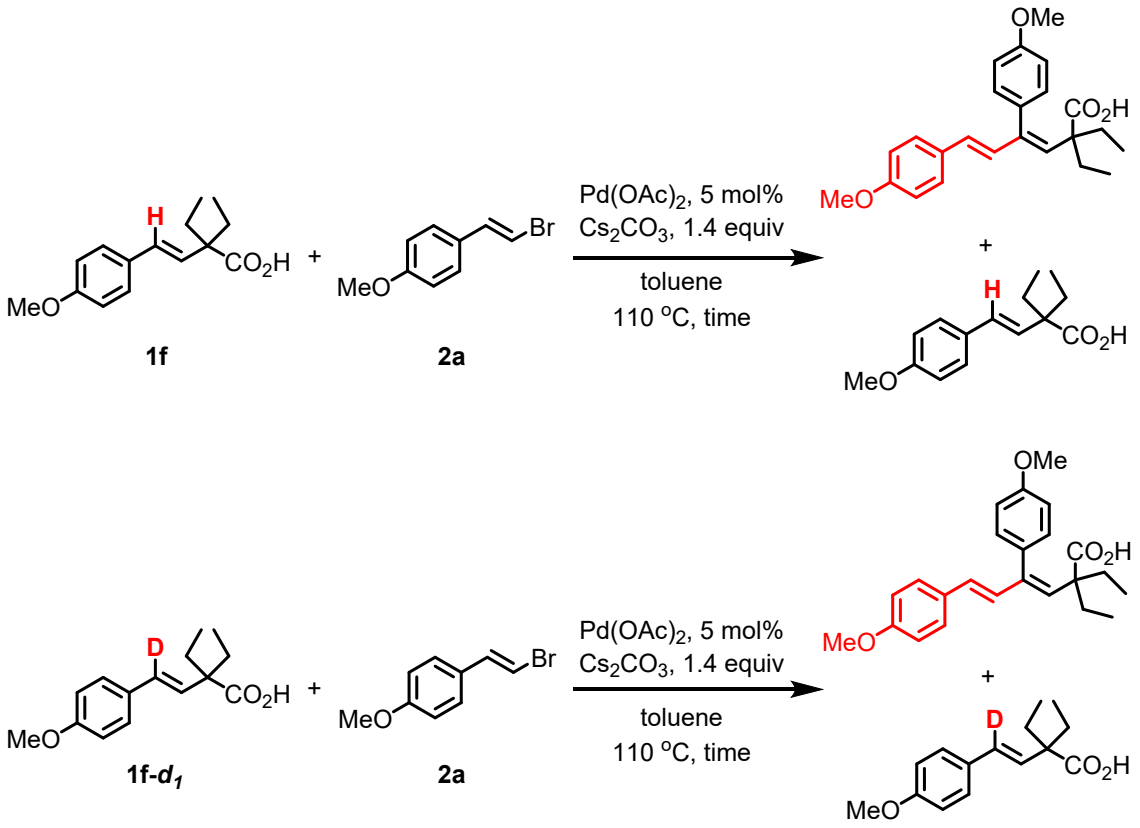
b) Competitive KIE



A screw-cap schlenk tube was charged with **1f** (0.375 mmol), **1f-d1** (0.375 mmol), **2a** (0.3 mmol), Cs_2CO_3 (0.42 mmol) and $Pd(OAc)_2$ (5 mol%) followed by dry toluene (6 ml) were added. The reaction mixture was kept for stirring in a preheated oil bath at 110 °C for 4 minutes. The resulting

mixture was then extracted with ethyl acetate (25 mL). The filtrate was dried over $MgSO_4$ and concentrate under reduced pressure. The ^1H NMR analyses of the products afford the KIE value (K_H/K_D = 3.21).

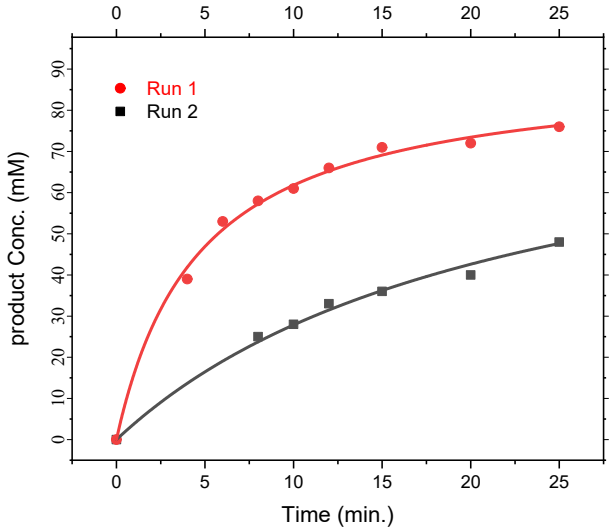
c) Parallel KIE



Run 1: **1f** (0.375 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), Cs_2CO_3 (0.42 mmol), toluene (6 mL)

Run 2: **1f-*d*$_2$** (0.375 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), Cs_2CO_3 (0.42 mmol), toluene (6 mL)

Fig S1. Run 1 and 2 plot of product formation (**3o**)



Run 1:

Rate 1 = $K_H.[\mathbf{1f}]^x\ [\mathbf{2a}]^y$

Rate ($mmol^{-1}.min^{-1}$) = $K_H.[0.375]^x\ [0.30]^y$ ……(eq. I)

Run 2:

Rate 2 = $K_D.[\mathbf{1f}\text{-}\boldsymbol{d_2}]^x\ [\mathbf{2a}]^y$

Rate ($mmol^{-1}.min^{-1}$) = $K_D.[0.375]^x\ [0.30]^y$ ……(eq. II)

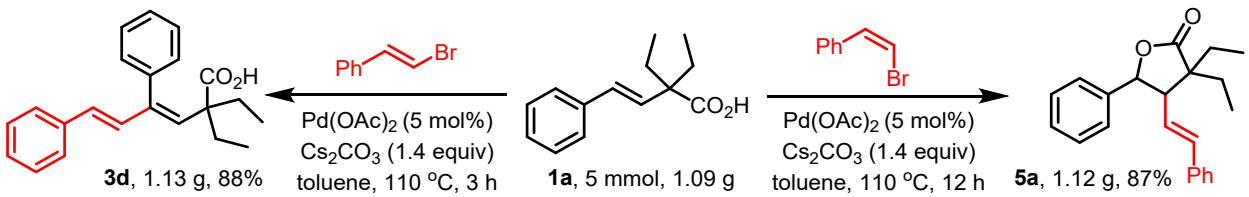
From equation (I) and (II)

K_H/K_D = 1.82802 ($mmol^{-1}.min^{-1}$) / 0.51724 ($mmol^{-1}.min^{-1}$)

K_H/K_D = 3.53

Synthetic Applications

a) Gram-scale synthesis



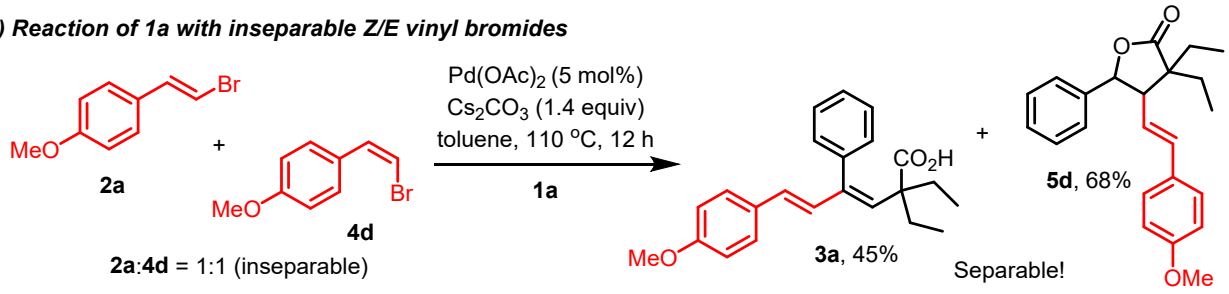
3d, 1.13 g, 88% **1a**, 5 mmol, 1.09 g **5a**, 1.12 g, 87%

For 3d: According to general procedure (II) with **1a** (5.0 mmol, 1.09 g) and **2d** (4.0 mmol, 0.73 g), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **3d** as pale-yellow oil (1.13 g, 88%).

For 5a: According to general procedure (III) with **1a** (5.0 mmol, 1.09g) and **4a** (4.0 mmol, 0.73

g), the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane) to provide **5a** as white solid (1.12 g, 87%).

b) Reaction of 1a with inseparable Z/E vinyl bromides



To a screw cap schlenk tube **1a** (0.58 mmol, 126.6 mg), **2a** (0.26 mmol, 91 mg), and **4d** (0.26 mmol, 91 mg), Cs_2CO_3 (0.73 mmol, 237 mg) and $Pd(OAc)_2$ (0.026 mmol, 5.8 mg) followed by dry toluene (10.4 ml) were added. The resulting mixture was kept for stirring in a preheated oil bath at 110 °C for 12 h. The obtained mixture was then diluted with EtOAc and filtered through a pad of celite. The solvent was removed under vacuo and the crude residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane) to provide **3a** (40.9 mg, 45%) and **5c** (61.9 mg, 68%).

4. Reference:

1. C. Alamillo-Ferrer, M. Karabourniotis-Sotti, A. R. Kennedy, M. Campbell, N. C. O. Tomkinson, *Org. Lett.*, 2016, **18**, 3102.
2. (a) I. Scheipers, E. Koch, A. Studer, *Org. Lett.*, 2017, **19**, 1741; (b) A. H. Mermerian, G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 5604; (c) R. H. Van der Veen, H. Cerfontain, *J. Org. Chem.*, 1985, **50**, 342; (d) A. Manick, H. Tanaka, K. Oisaki, M. Kanai, *Synthesis*, 2018, **50**, 2936.
3. J. M. Muñoz-Molina, P. J. Pérez. *J. Org. Chem.*, 2019, **84**, 8289.
4. P. Pawluc′, G. Hreczycho, J. Szudkowska, M. Kubicki, B. Marciniec, *Org. Lett.*, 2009, **11**, 3390.
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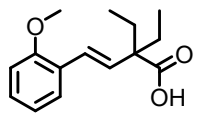
9. J. Mao, W. Bao, *Org. Lett.*, 2014, **16**, 2646.

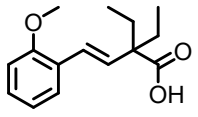
5. NMR Spectra:

^{1}H NMR ($CDCl_3$, 300 MHz)



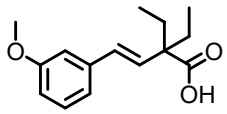
1d

^{13}C NMR ($CDCl_3$, 75 MHz)



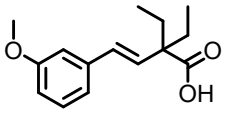
1d

^{1}H NMR ($CDCl_3$, 300 MHz)



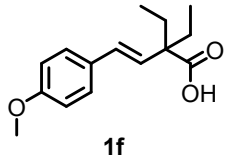
1e

^{13}C NMR ($CDCl_3$, 75 MHz)



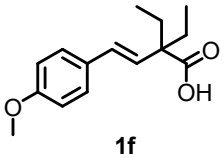
1e

^{1}H NMR ($CDCl_3$, 300 MHz)



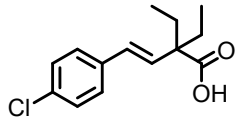
1f

^{13}C NMR ($CDCl_3$, 75 MHz)



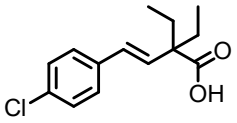
1f

^{1}H NMR ($CDCl_3$, 300 MHz)



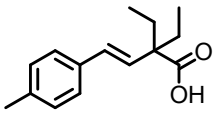
1g

^{13}C NMR ($CDCl_3$, 75 MHz)



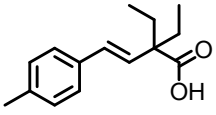
1g

^{1}H NMR ($CDCl_3$, 300 MHz)



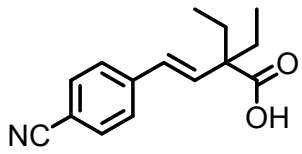
1h

^{13}C NMR ($CDCl_3$, 75 MHz)



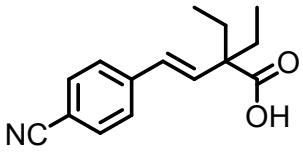
1h

^{1}H NMR ($CDCl_3$, 300 MHz)



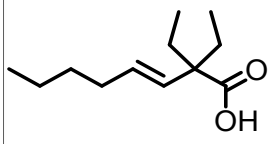
1i

^{13}C NMR ($CDCl_3$, 75 MHz)



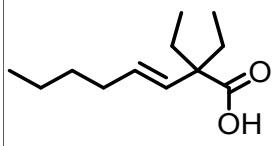
1i

^{1}H NMR ($CDCl_3$, 300 MHz)

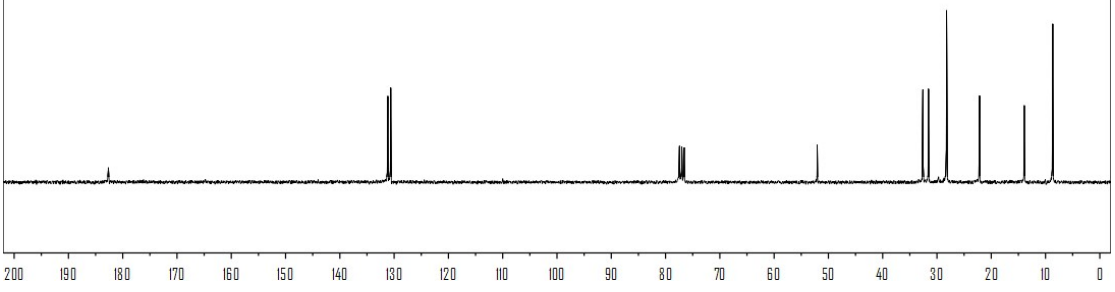


1k

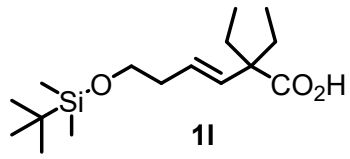
^{13}C NMR ($CDCl_3$, 75 MHz)



1k

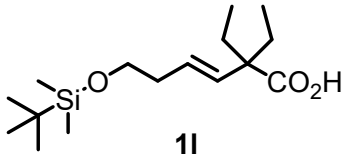


^{1}H NMR ($CDCl_3$, 300 MHz)



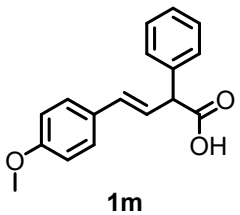
1l

^{13}C NMR ($CDCl_3$, 75 MHz)



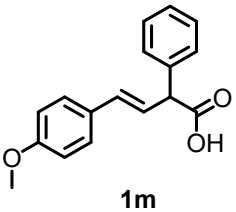
1l

^{1}H NMR ($CDCl_3$, 300 MHz)

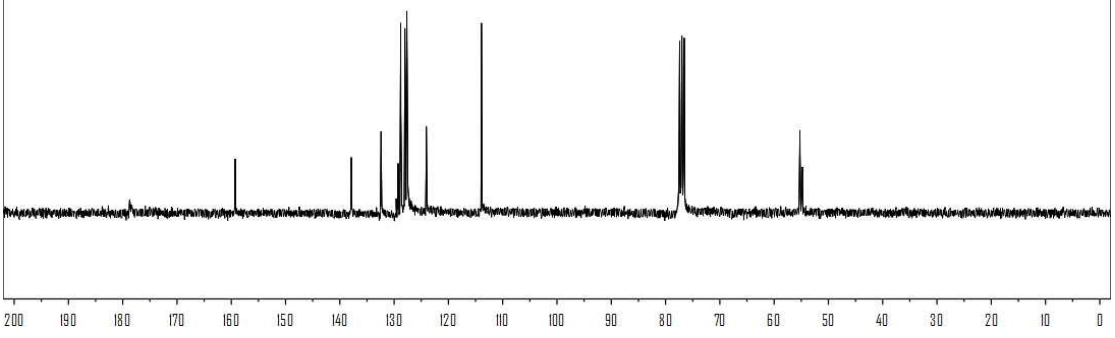


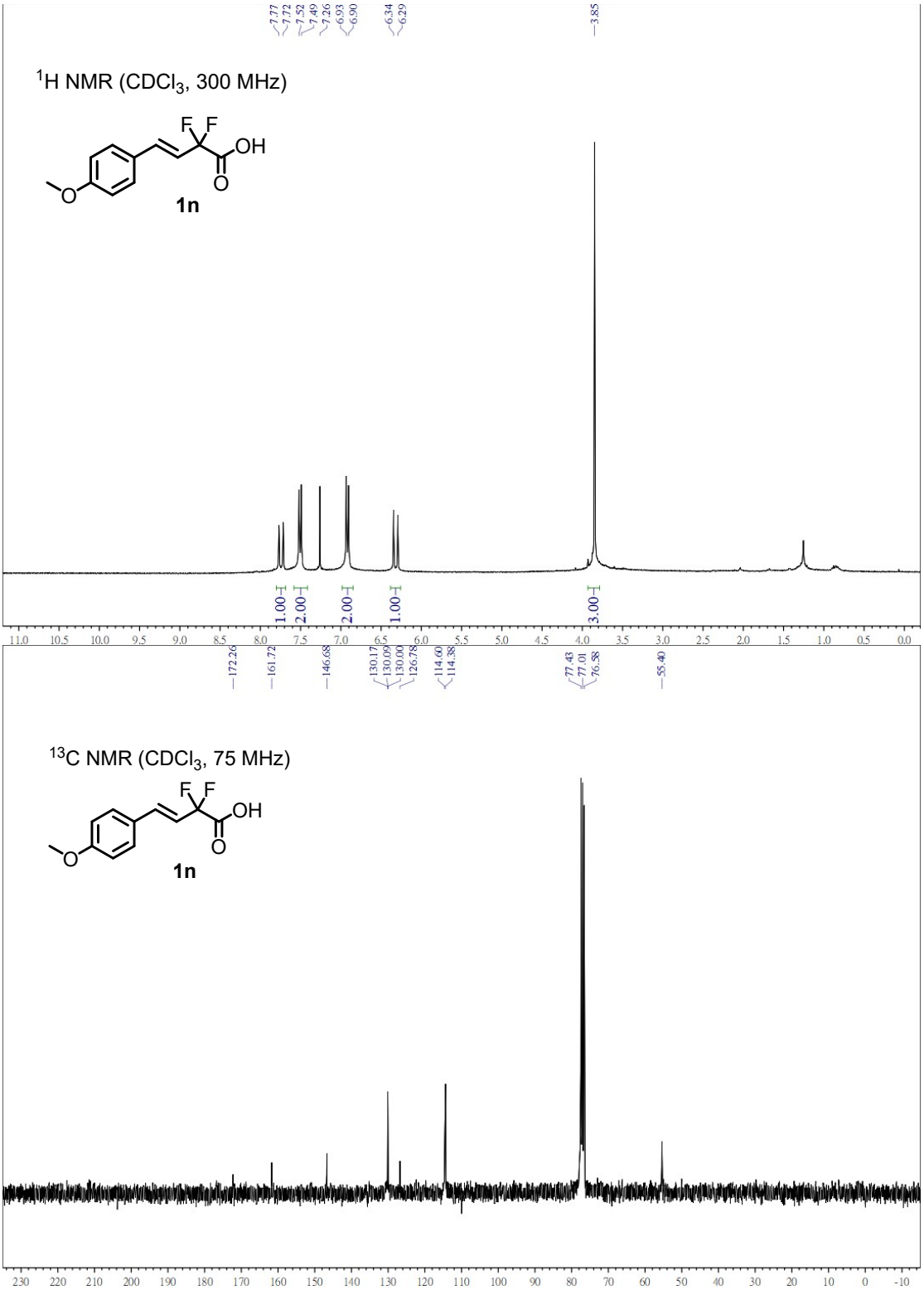
1m

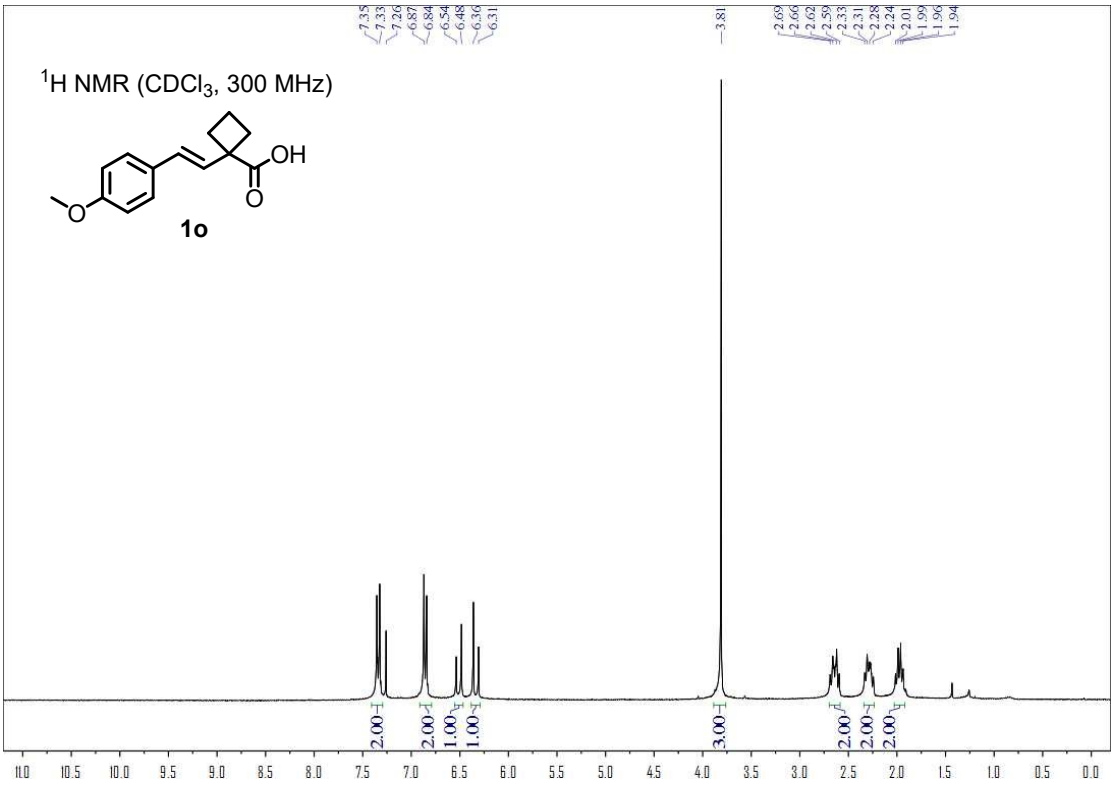
^{13}C NMR ($CDCl_3$, 75 MHz)

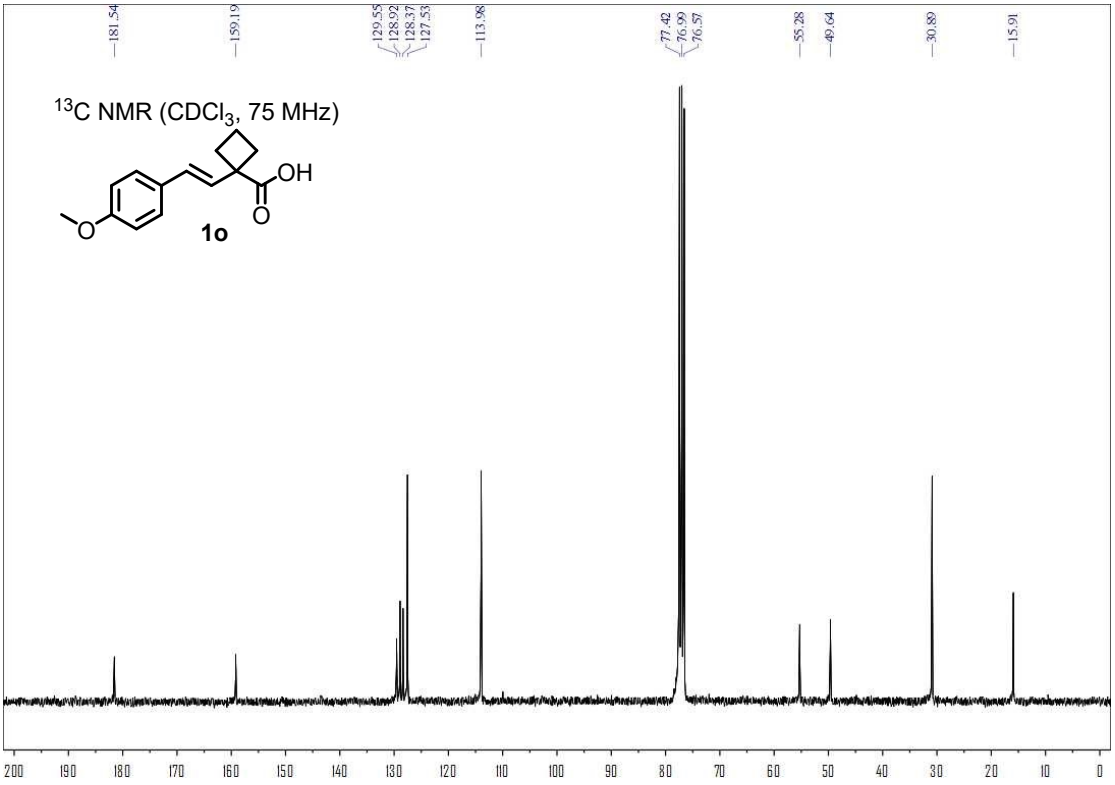


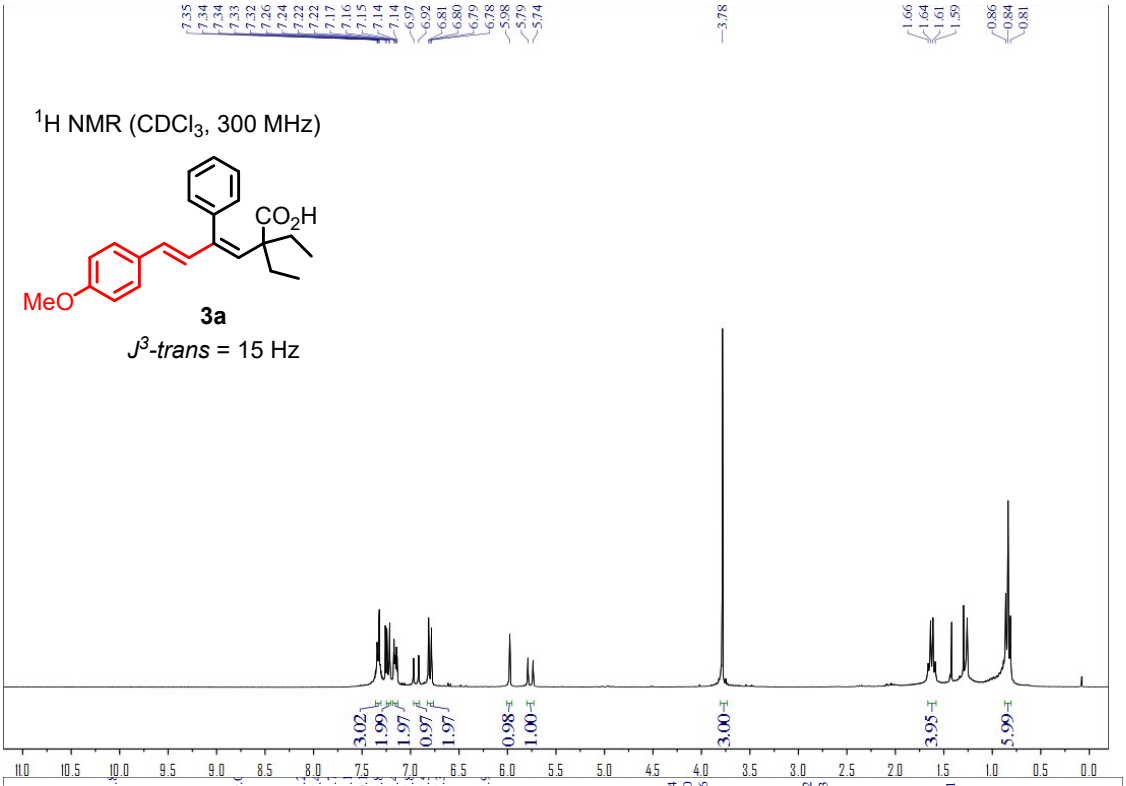
1m




7.77
7.72
7.52
7.49
7.26
6.93
6.90
6.34
6.29
3.85
1H NMR (CDCl3, 300 MHz)
F F
OH
O
O
1n
1.00
2.00
2.00
1.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
172.26
161.72
146.68
130.17
130.09
130.00
126.78
114.60
114.38
77.43
77.01
76.58
55.40
13C NMR (CDCl3, 75 MHz)
F F
OH
O
O
1n
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


^{1}H NMR ($CDCl_3$, 300 MHz)
OH
O
O
1o

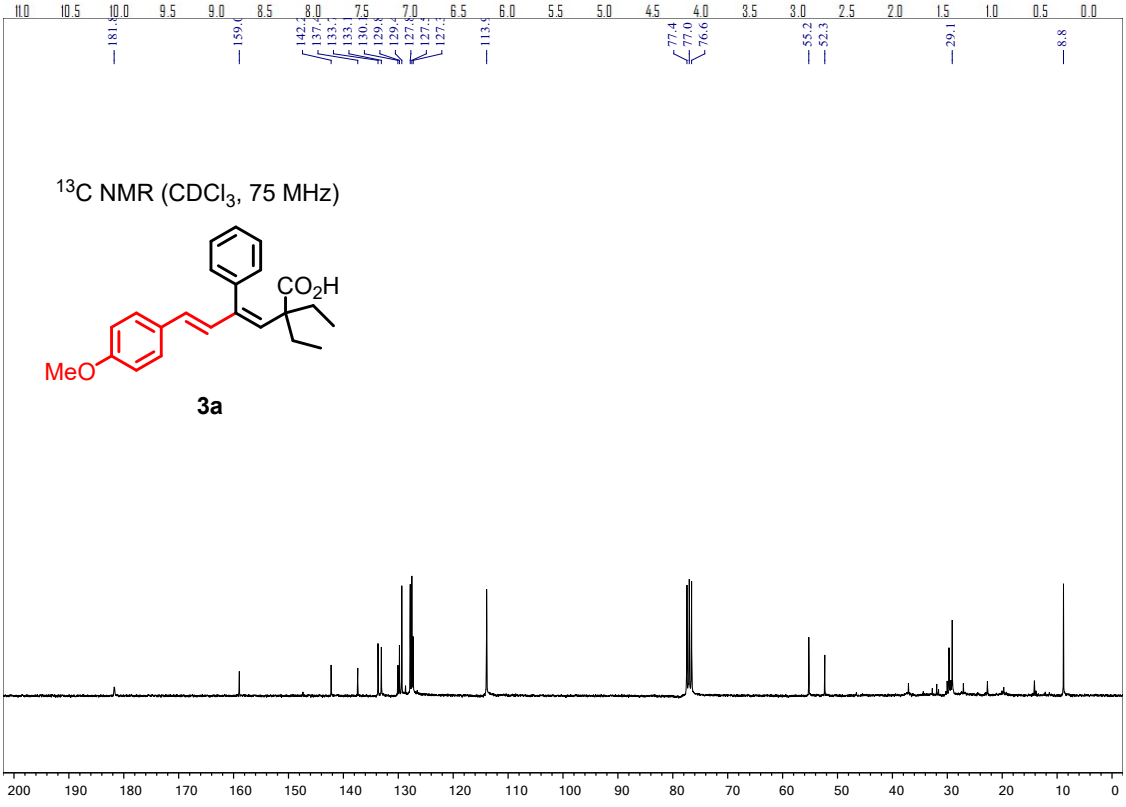

^{13}C NMR ($CDCl_3$, 75 MHz)
OH
O
O
1o



^{1}H NMR ($CDCl_3$, 300 MHz)

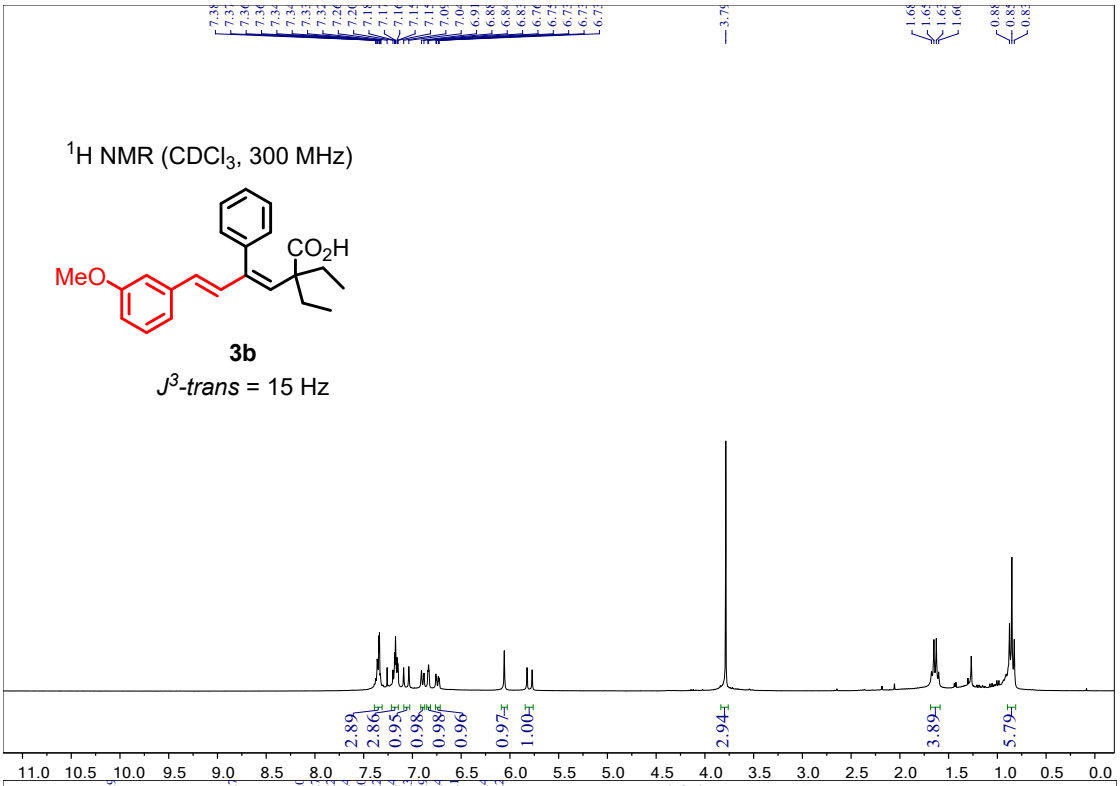
3a

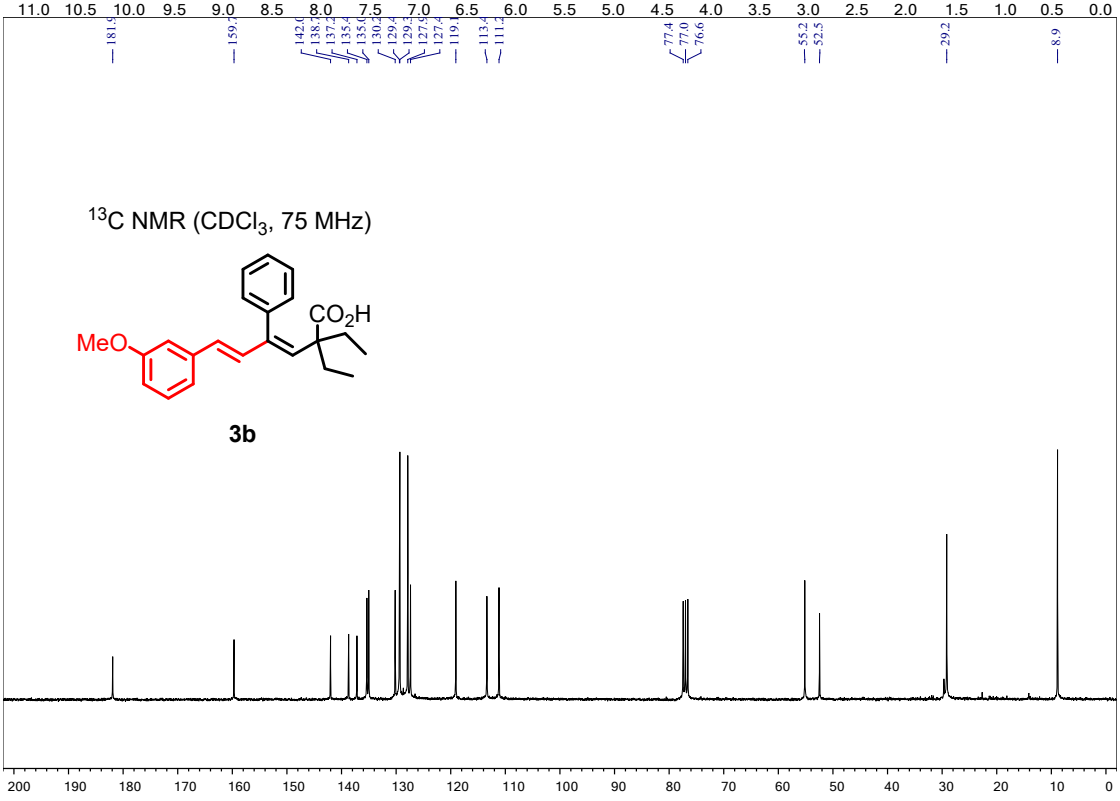
J^{3}-*trans* = 15 Hz



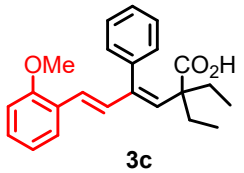
^{13}C NMR ($CDCl_3$, 75 MHz)

3a


^{1}H NMR ($CDCl_3$, 300 MHz)
MeO
CO_2H
3b
J^3-*trans* = 15 Hz


^{13}C NMR ($CDCl_3$, 75 MHz)
MeO
CO_2H
3b

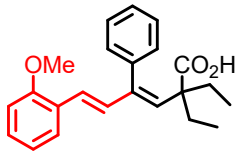
^{1}H NMR ($CDCl_3$, 300 MHz)



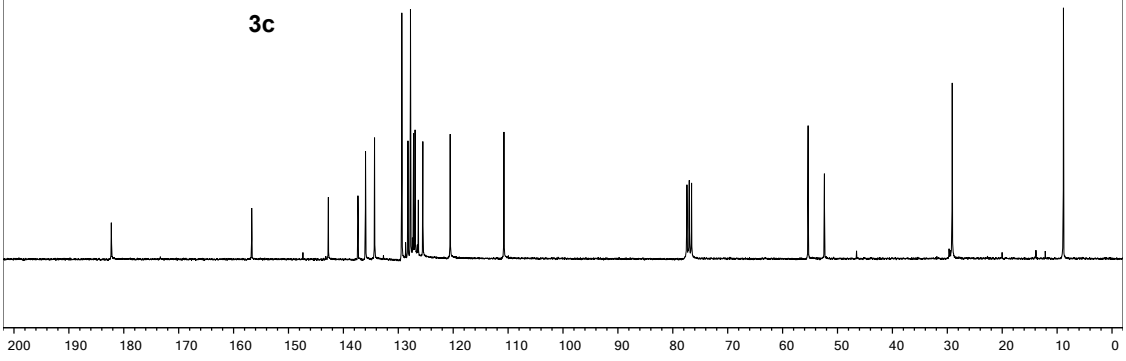
3c

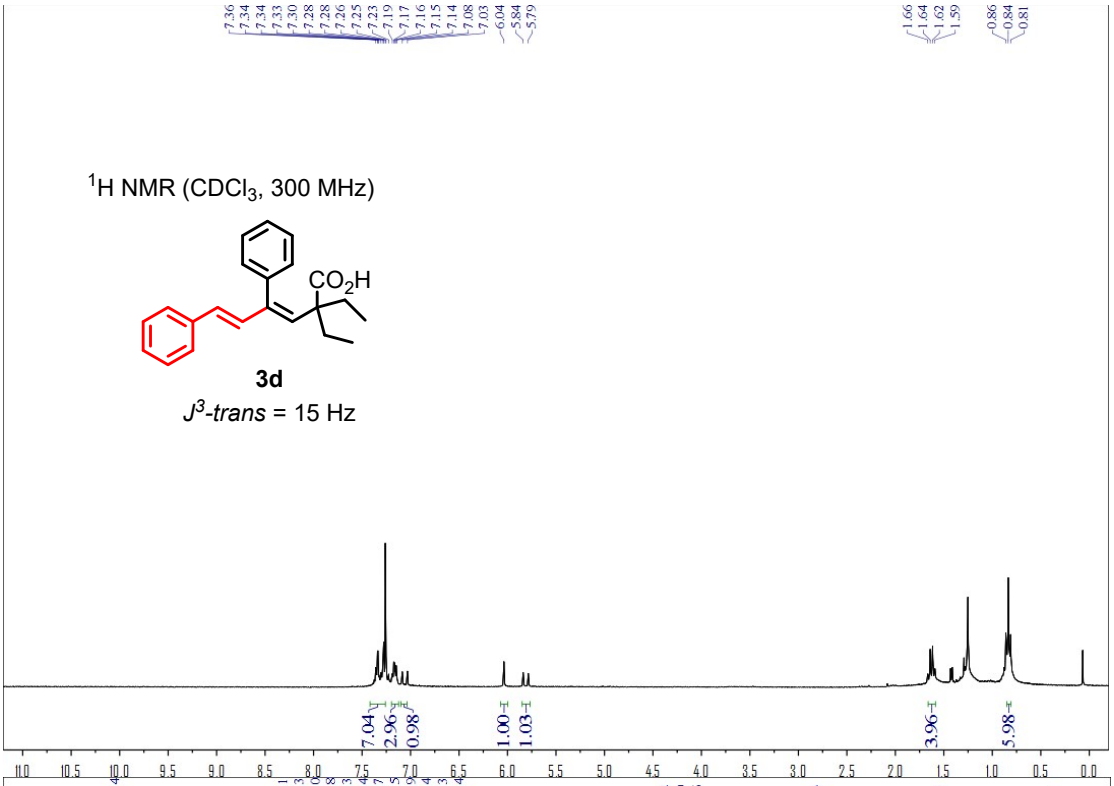
J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



3c

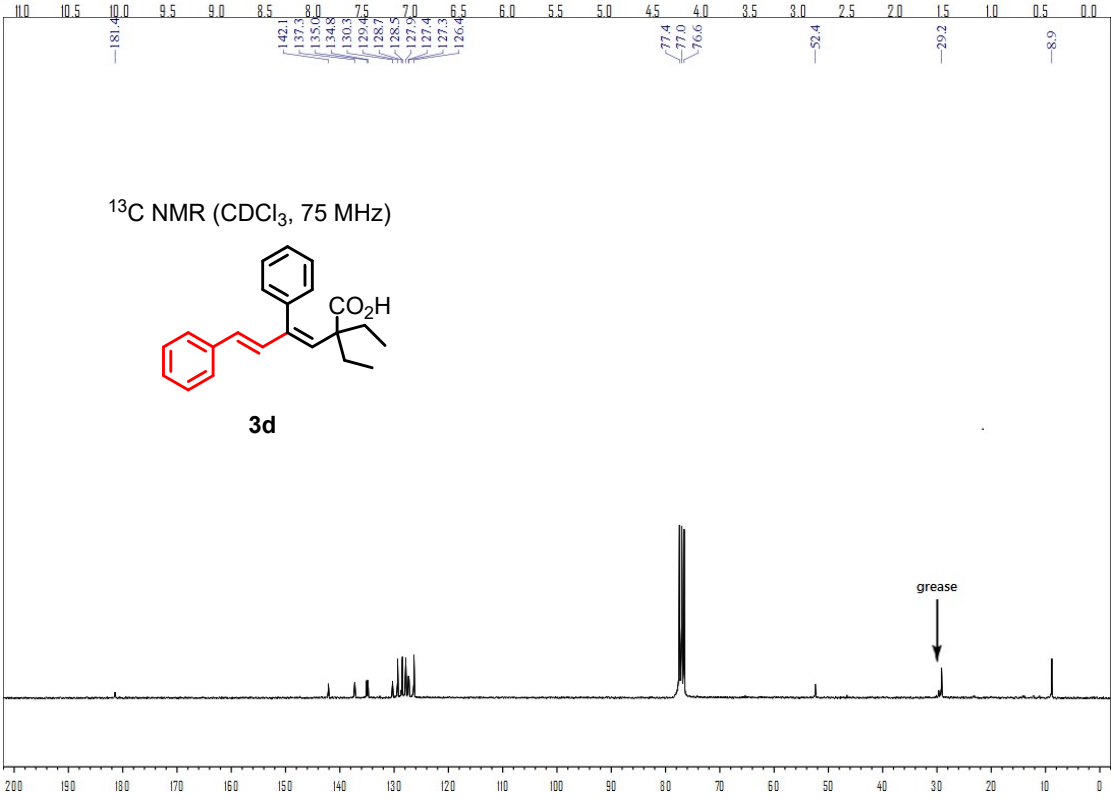




^{1}H NMR ($CDCl_3$, 300 MHz)

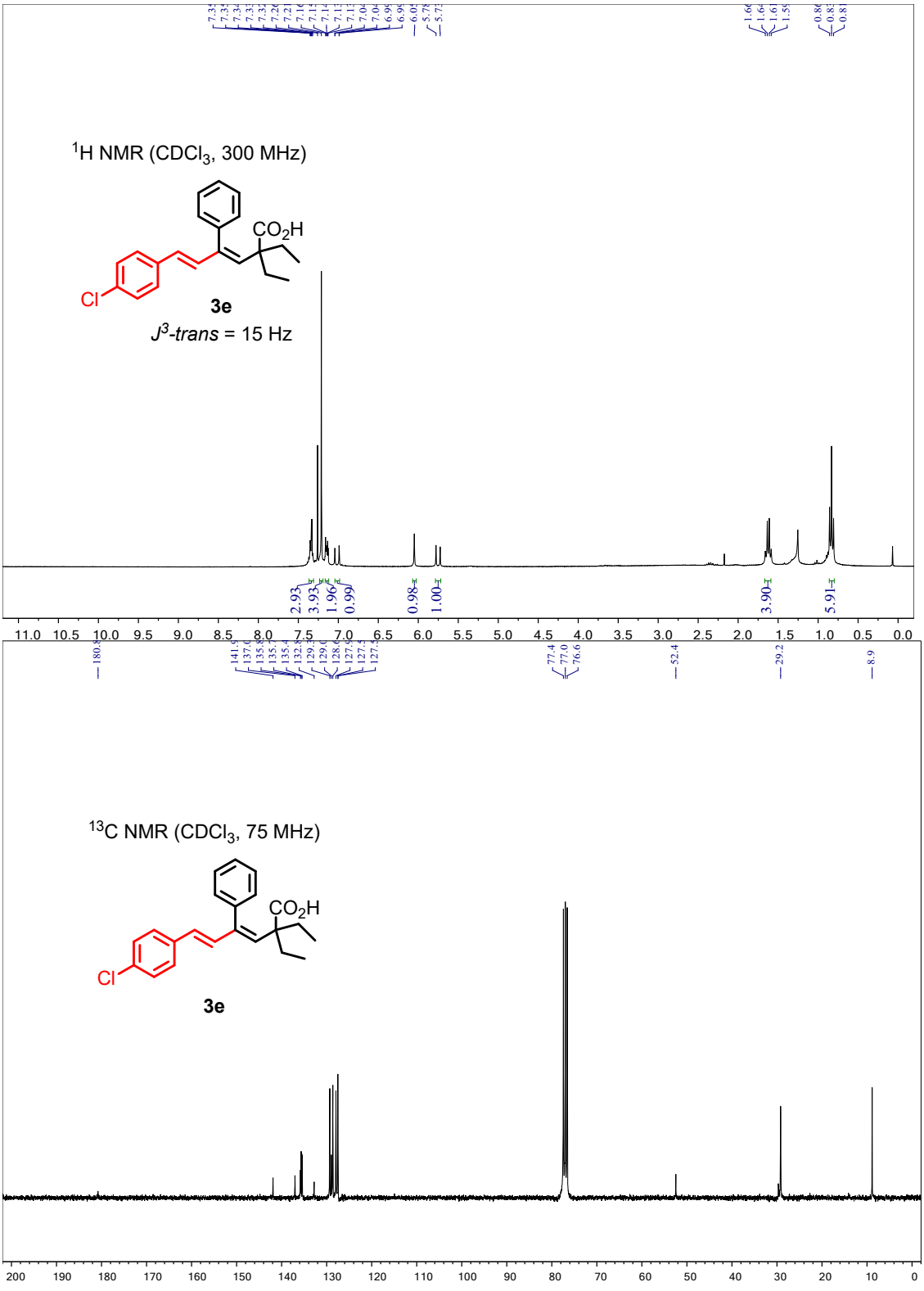
3d

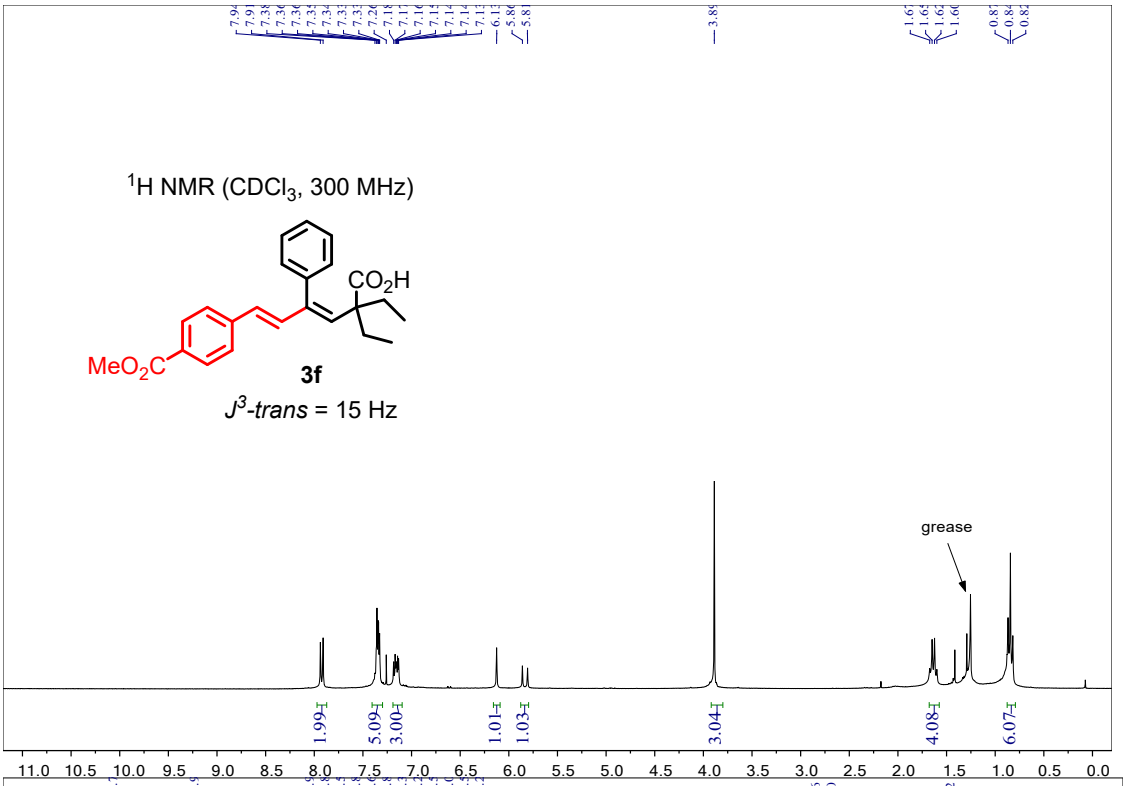
J^{3}-*trans* = 15 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

3d

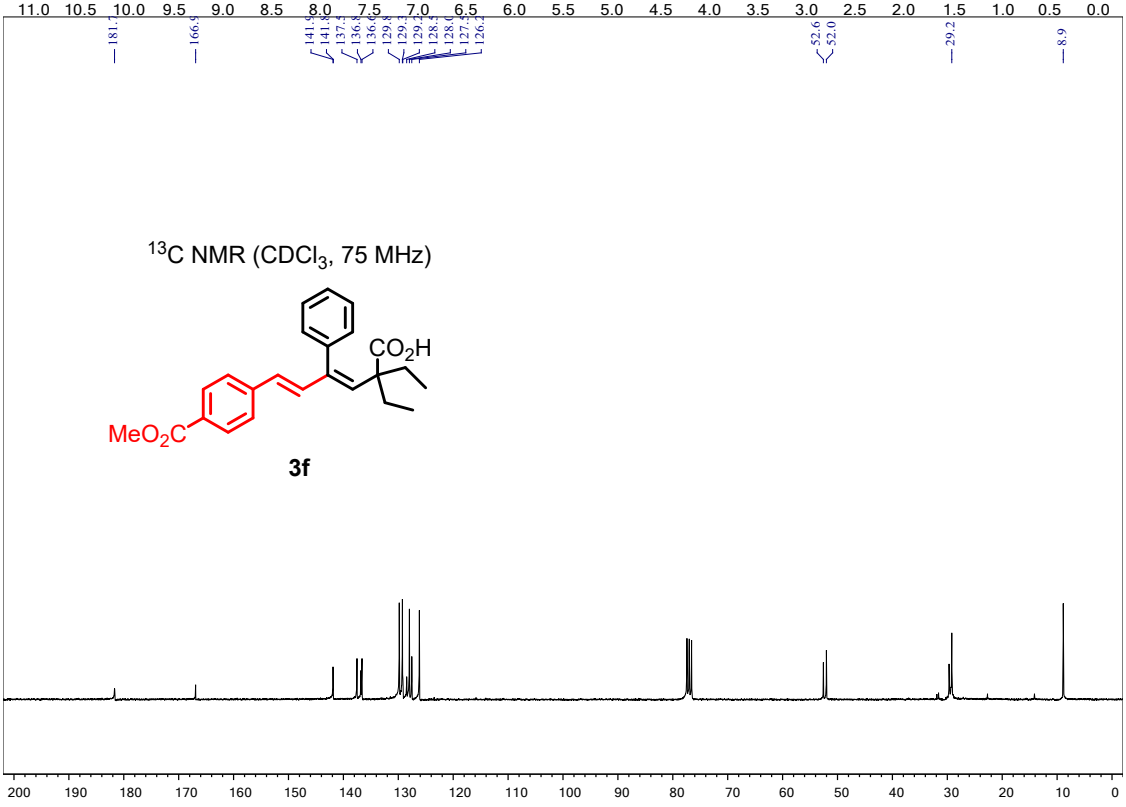

^{1}H NMR ($CDCl_3$, 300 MHz)
CO_2H
Cl
3e
J^3-*trans* = 15 Hz
^{13}C NMR ($CDCl_3$, 75 MHz)
CO_2H
Cl
3e



^{1}H NMR ($CDCl_3$, 300 MHz)

3f

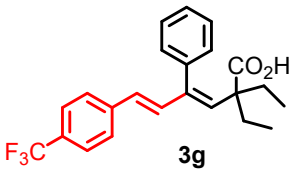
J^{3}-*trans* = 15 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

3f

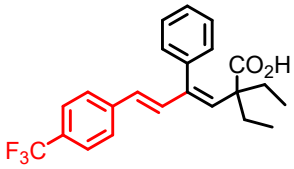
^{1}H NMR ($CDCl_3$, 300 MHz)



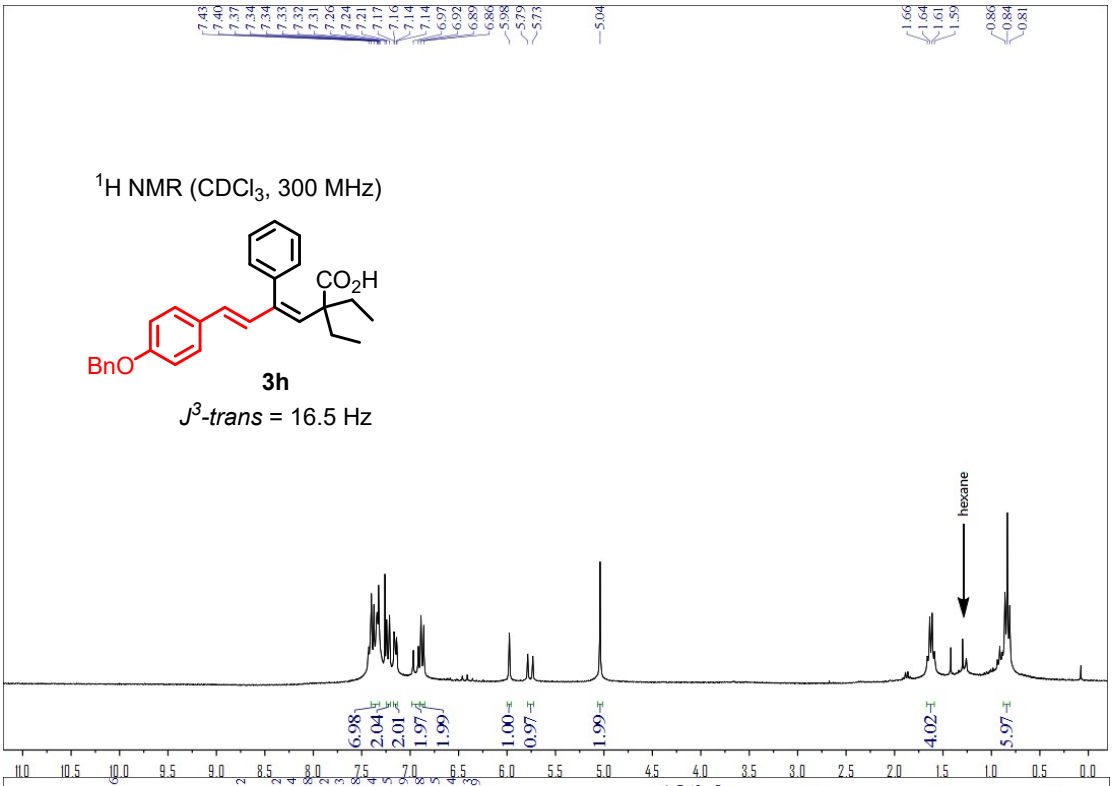
3g

J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



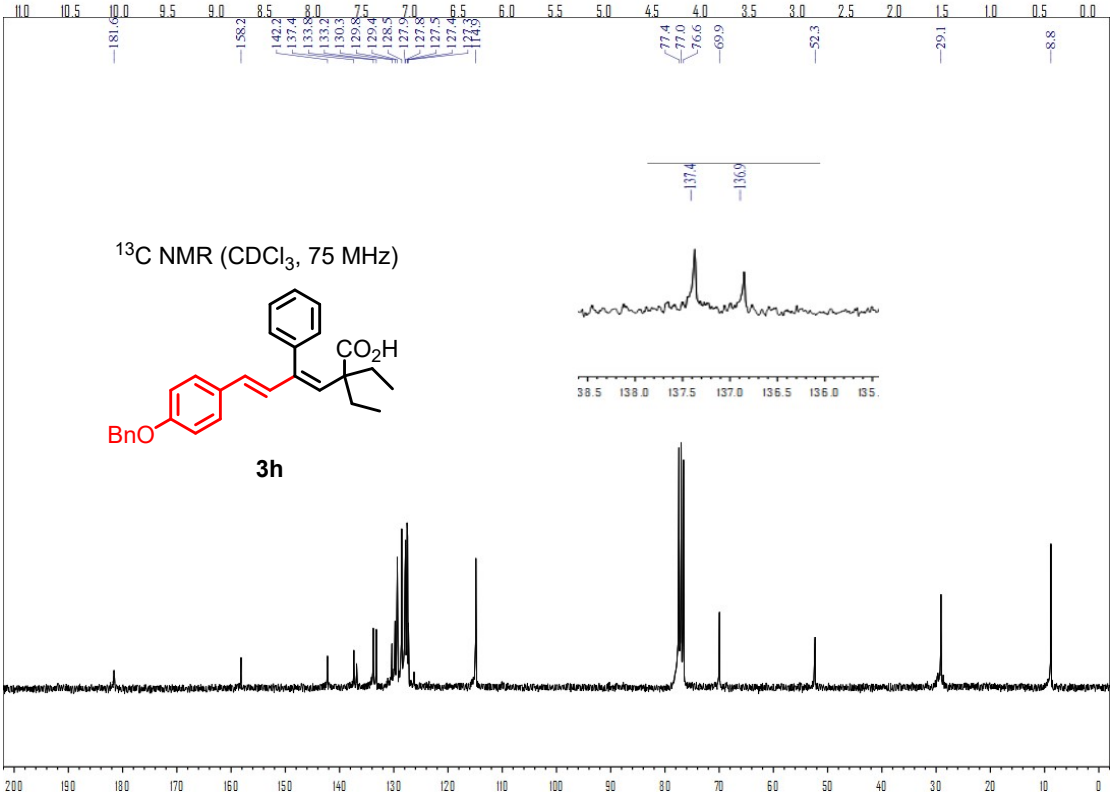
3g



^{1}H NMR ($CDCl_3$, 300 MHz)

3h

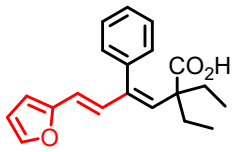
J^{3}-*trans* = 16.5 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

3h

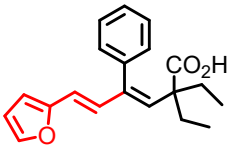
^{1}H NMR ($CDCl_3$, 300 MHz)



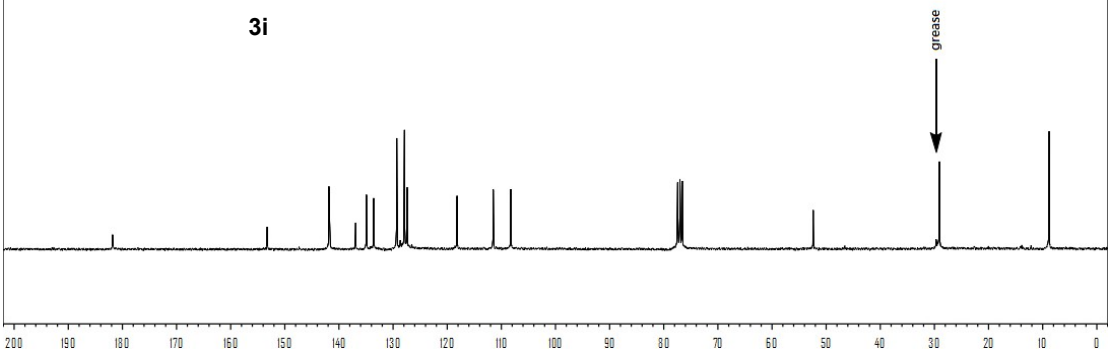
3i

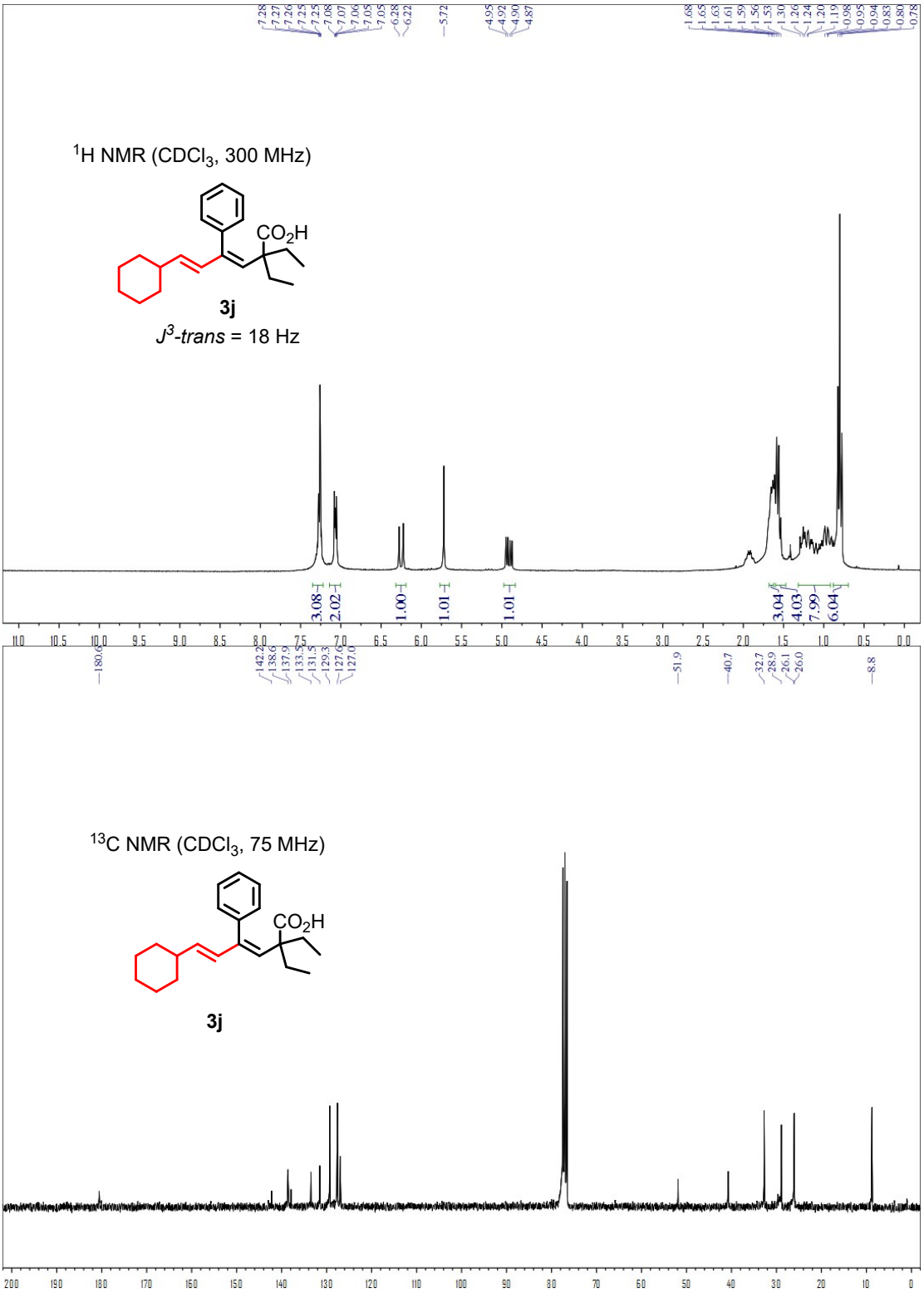
J^{3}-*trans* = 16.5 Hz

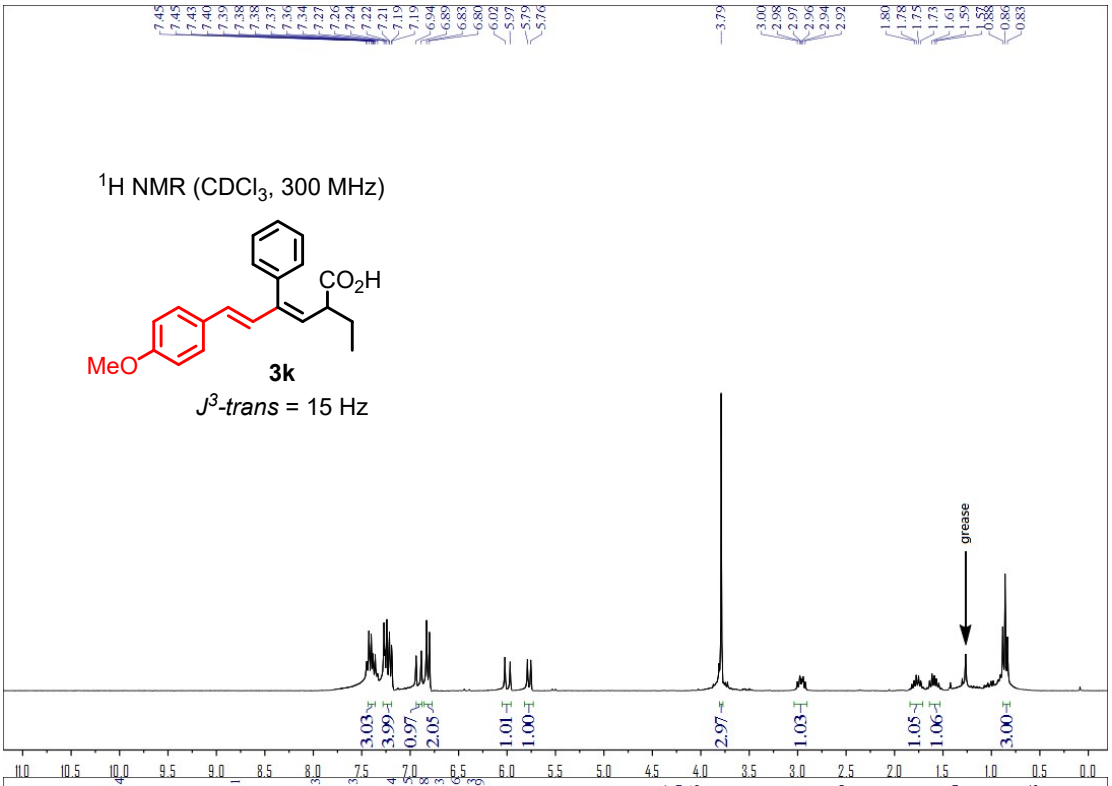
^{13}C NMR ($CDCl_3$, 75 MHz)

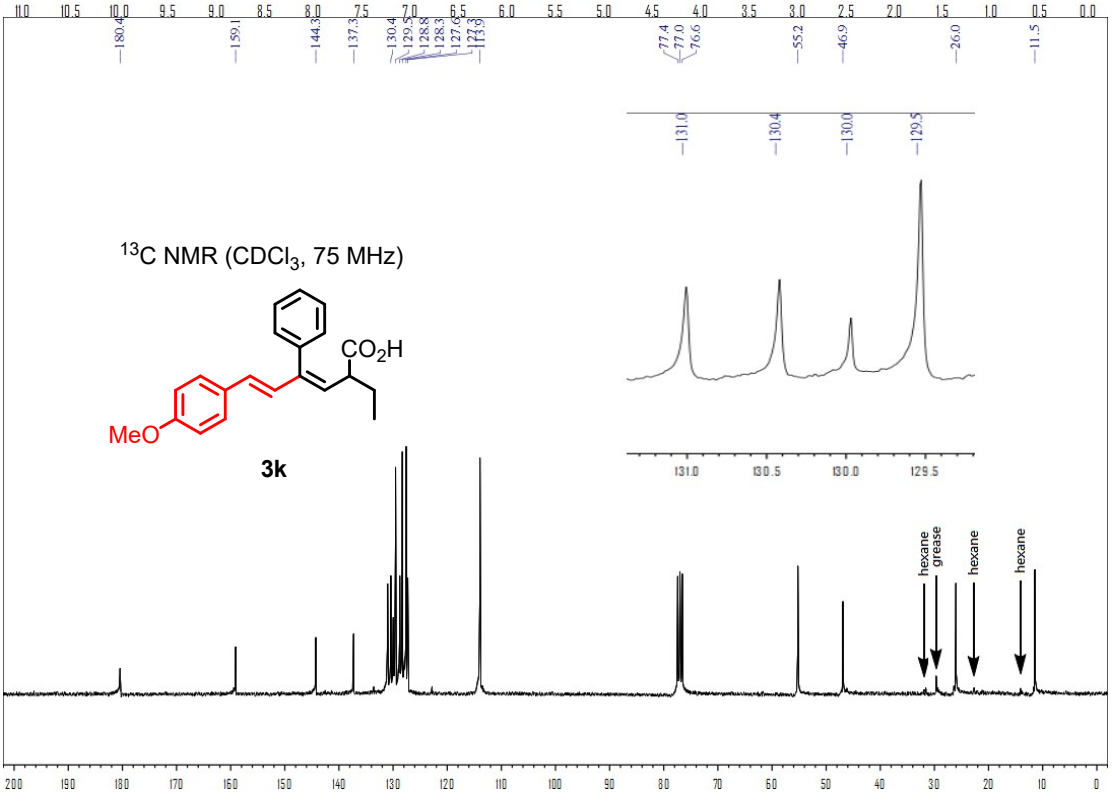


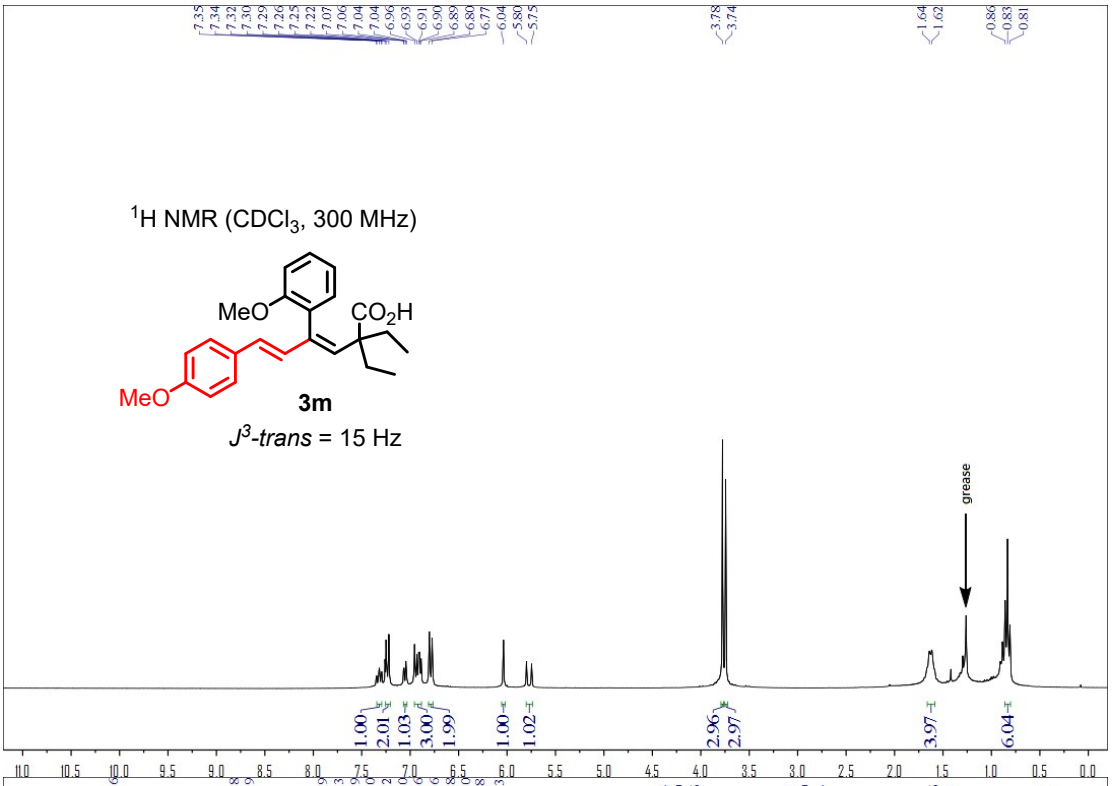
3i




^{1}H NMR ($CDCl_3$, 300 MHz)
CO_2H
3j
J^3-*trans* = 18 Hz
^{13}C NMR ($CDCl_3$, 75 MHz)
CO_2H
3j


7.45
7.45
7.43
7.40
7.39
7.38
7.38
7.37
7.36
7.34
7.27
7.26
7.24
7.22
7.21
7.19
7.19
6.94
6.89
6.83
6.80
6.02
5.97
5.79
5.76
3.79
3.00
2.98
2.97
2.96
2.94
2.92
1.80
1.78
1.75
1.73
1.61
1.59
1.57
0.88
0.86
0.83
^{1}H NMR ($CDCl_3$, 300 MHz)
CO2H
MeO
3k
J^3-trans = 15 Hz
grease
3.03
3.99
0.97
2.05
1.01
1.00
2.97
1.03
1.05
1.06
3.00

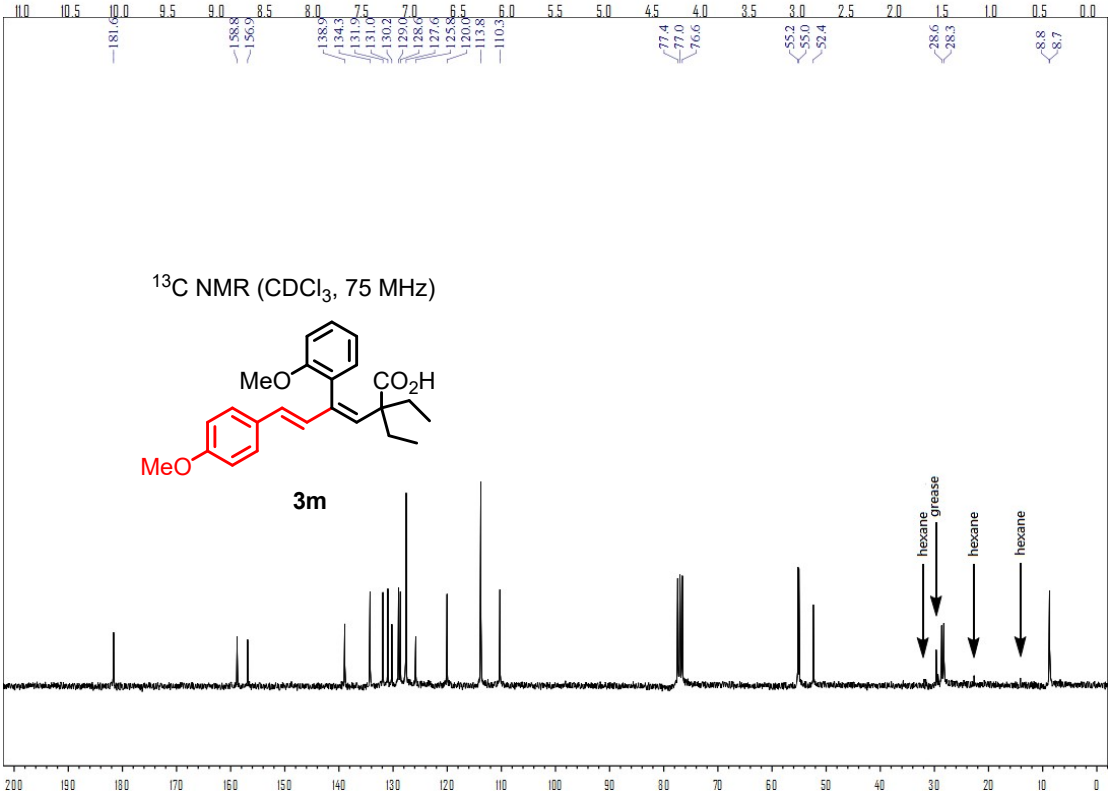

180.4
159.1
144.3
137.3
130.4
129.5
128.8
128.3
127.6
123.3
77.4
77.0
76.6
55.2
46.9
26.0
11.5
131.0
130.4
130.0
129.5
^{13}C NMR ($CDCl_3$, 75 MHz)
CO2H
MeO
3k
hexane
grease
hexane
hexane



^{1}H NMR ($CDCl_3$, 300 MHz)

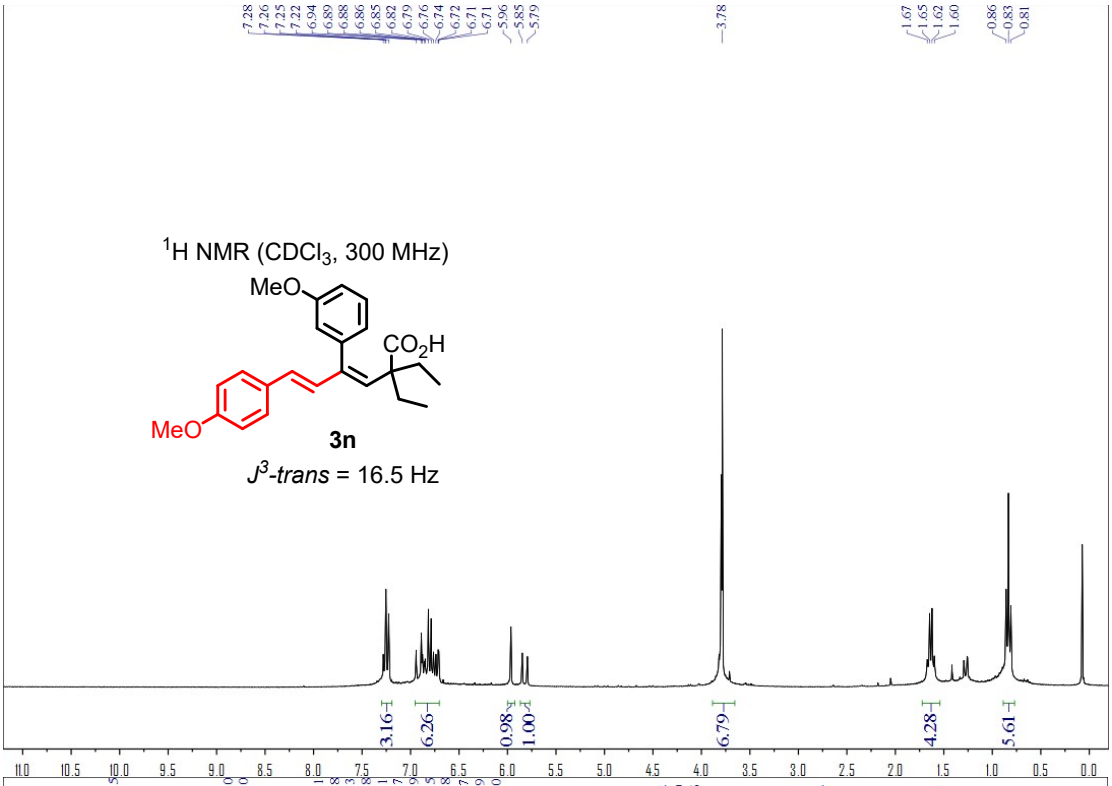
3m

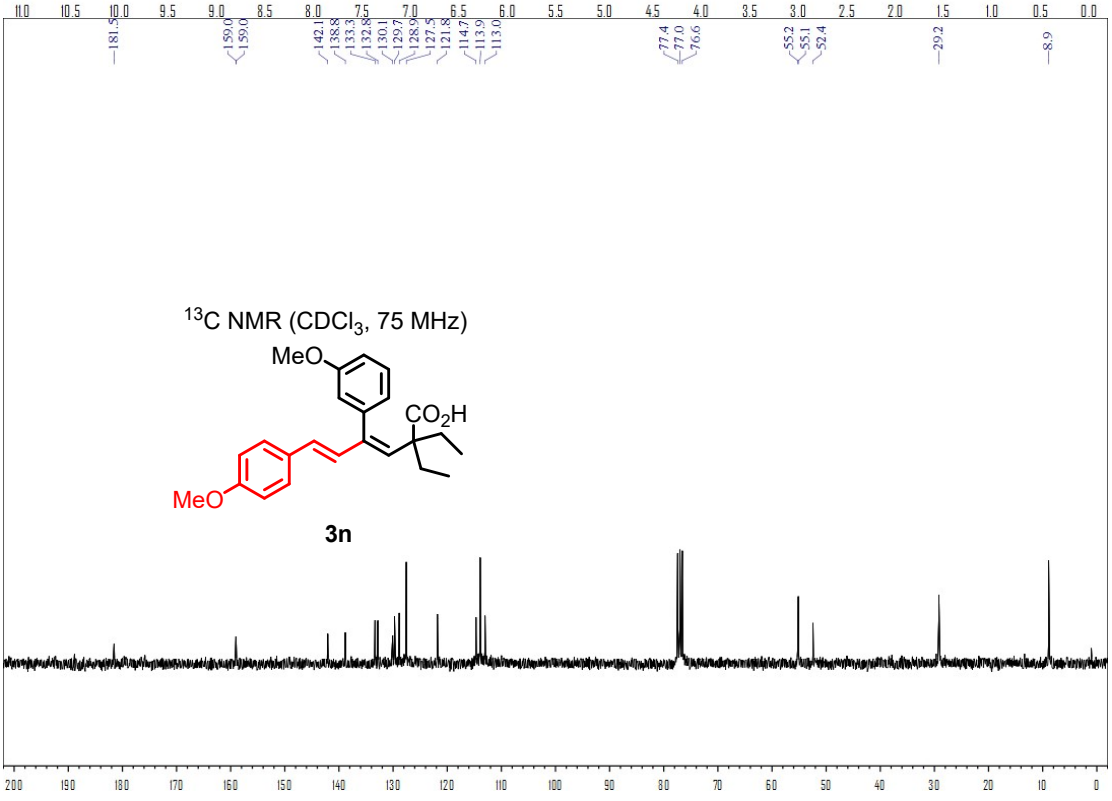
J^{3}-*trans* = 15 Hz

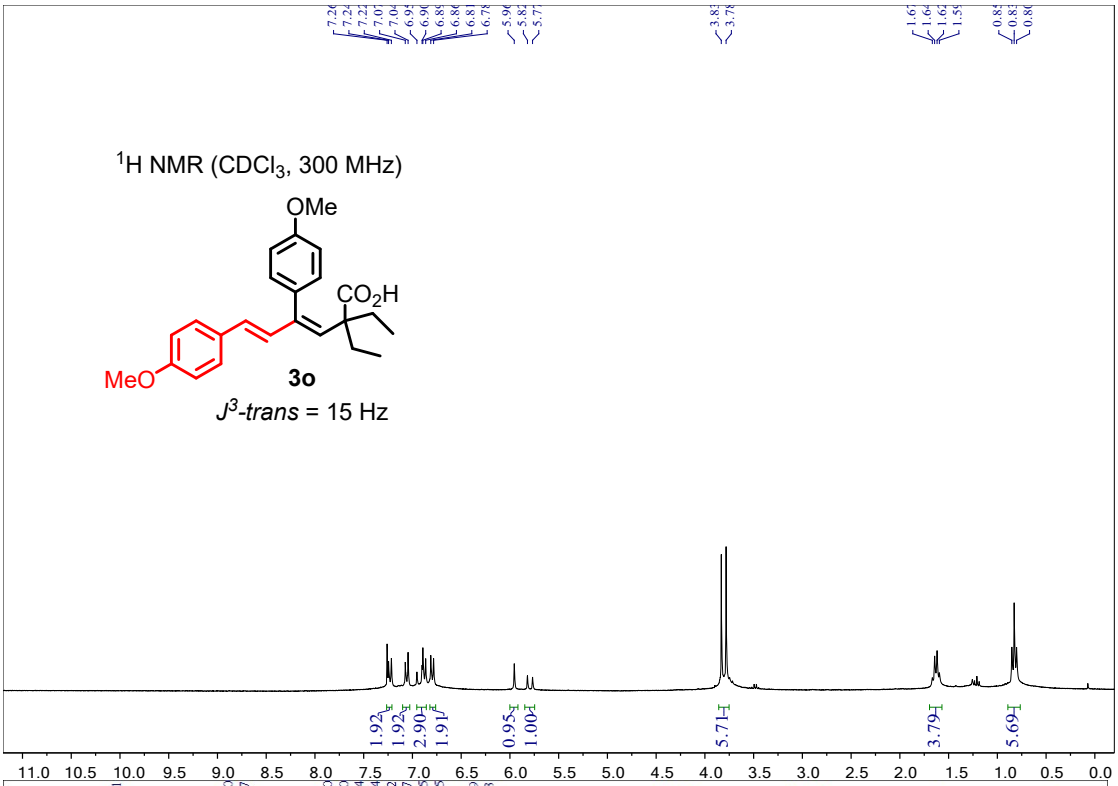


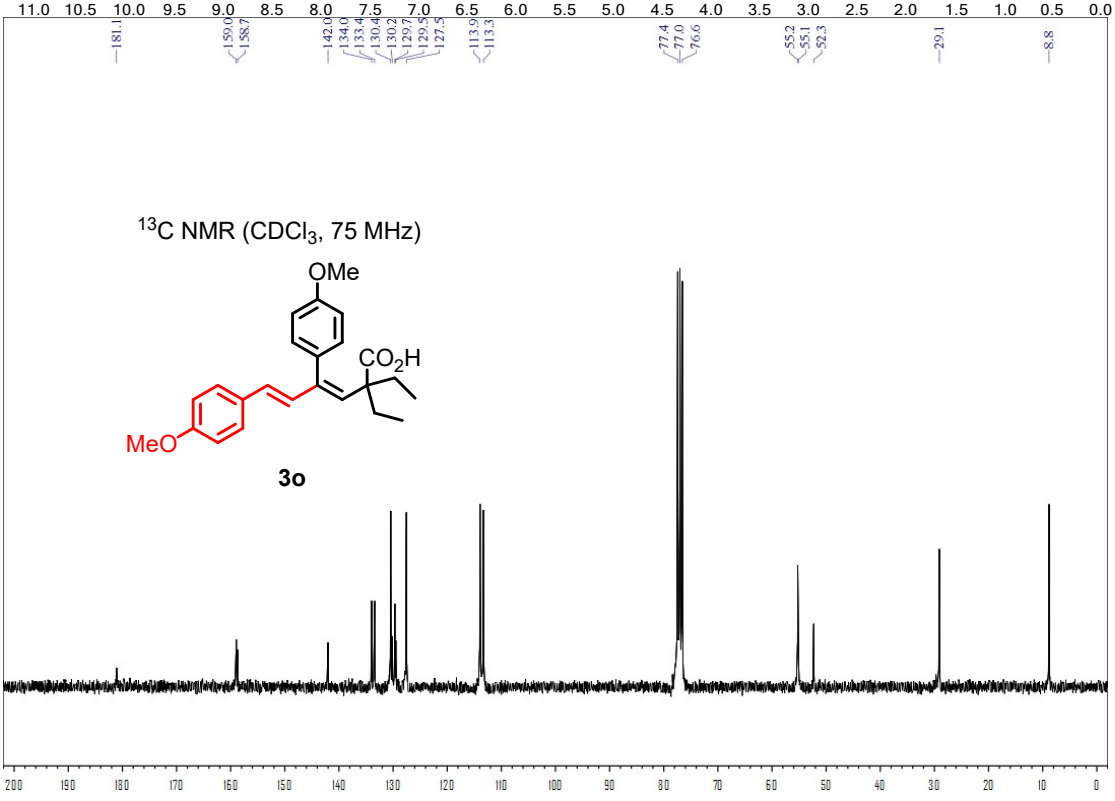
^{13}C NMR ($CDCl_3$, 75 MHz)

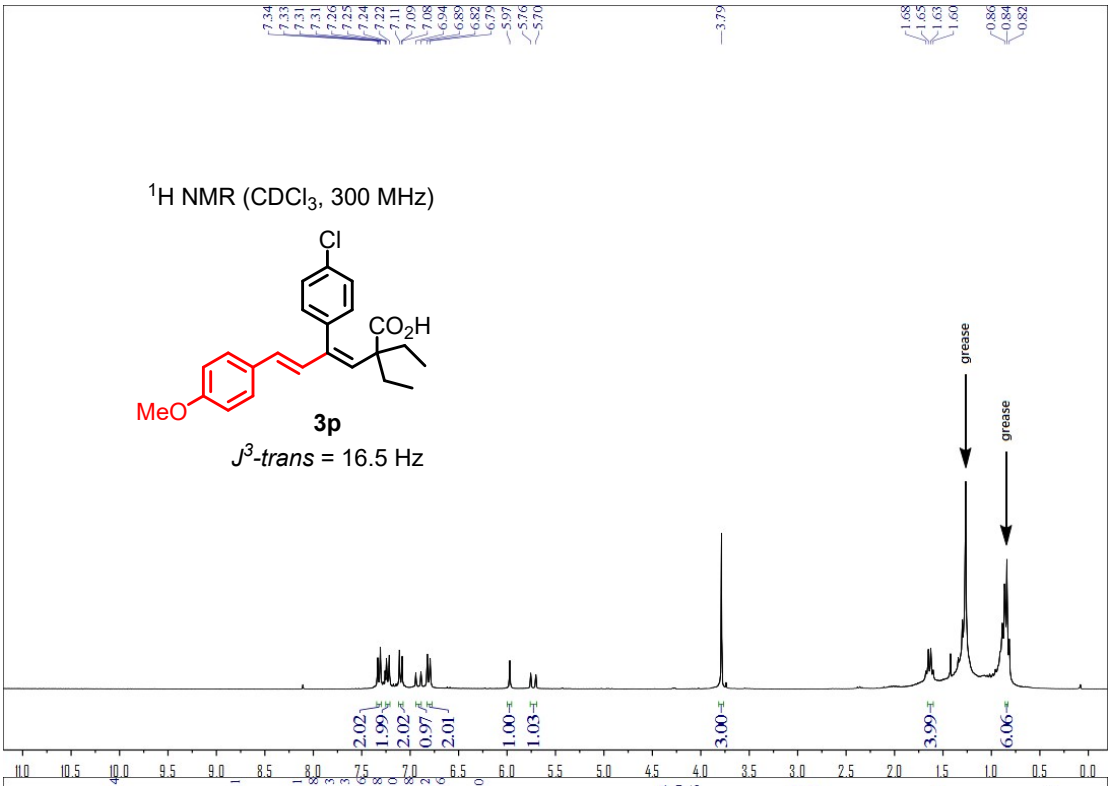
3m


7.28
7.26
7.25
7.22
6.94
6.89
6.88
6.86
6.85
6.82
6.79
6.76
6.74
6.72
6.71
5.96
5.85
5.79
3.78
1.67
1.65
1.62
1.60
0.86
0.83
0.81
^{1}H NMR (CDCl$_3$, 300 MHz)
MeO
CO$_2$H
MeO
3n
J^3-*trans* = 16.5 Hz
3.16
6.26
0.98
1.00
6.79
4.28
5.61
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


181.5
159.0
159.0
142.1
138.8
133.3
132.8
130.1
129.7
128.9
127.5
121.8
114.7
113.9
113.0
77.4
77.0
76.6
55.2
55.1
52.4
29.2
8.9
^{13}C NMR (CDCl$_3$, 75 MHz)
MeO
CO$_2$H
MeO
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


^{1}H NMR ($CDCl_3$, 300 MHz)
OMe
CO_2H
MeO
3o
J^3-*trans* = 15 Hz

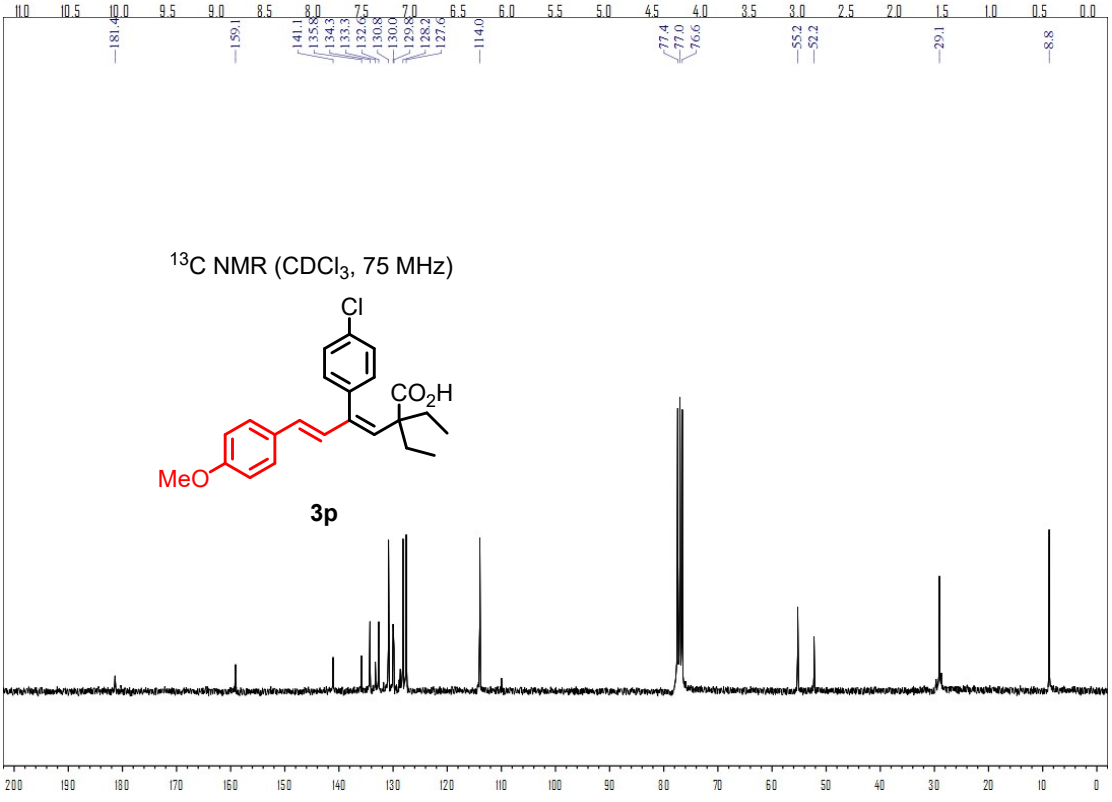

^{13}C NMR ($CDCl_3$, 75 MHz)
OMe
CO_2H
MeO
3o



^{1}H NMR ($CDCl_3$, 300 MHz)

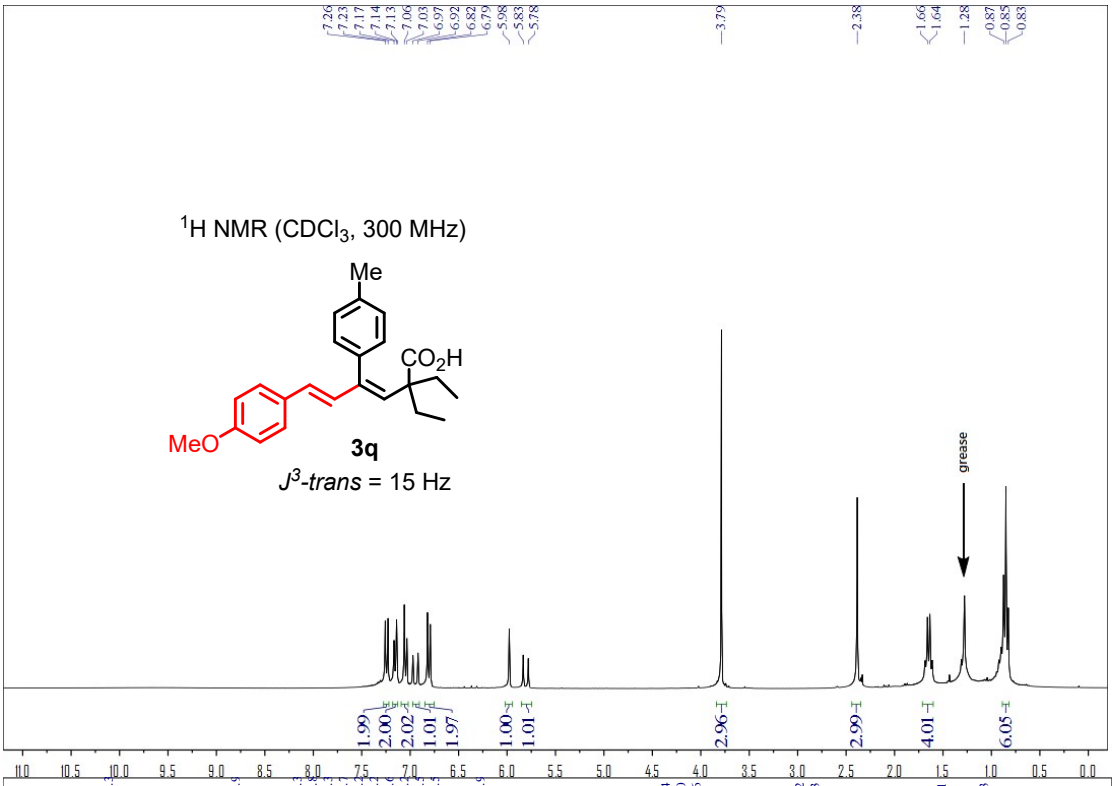
3p

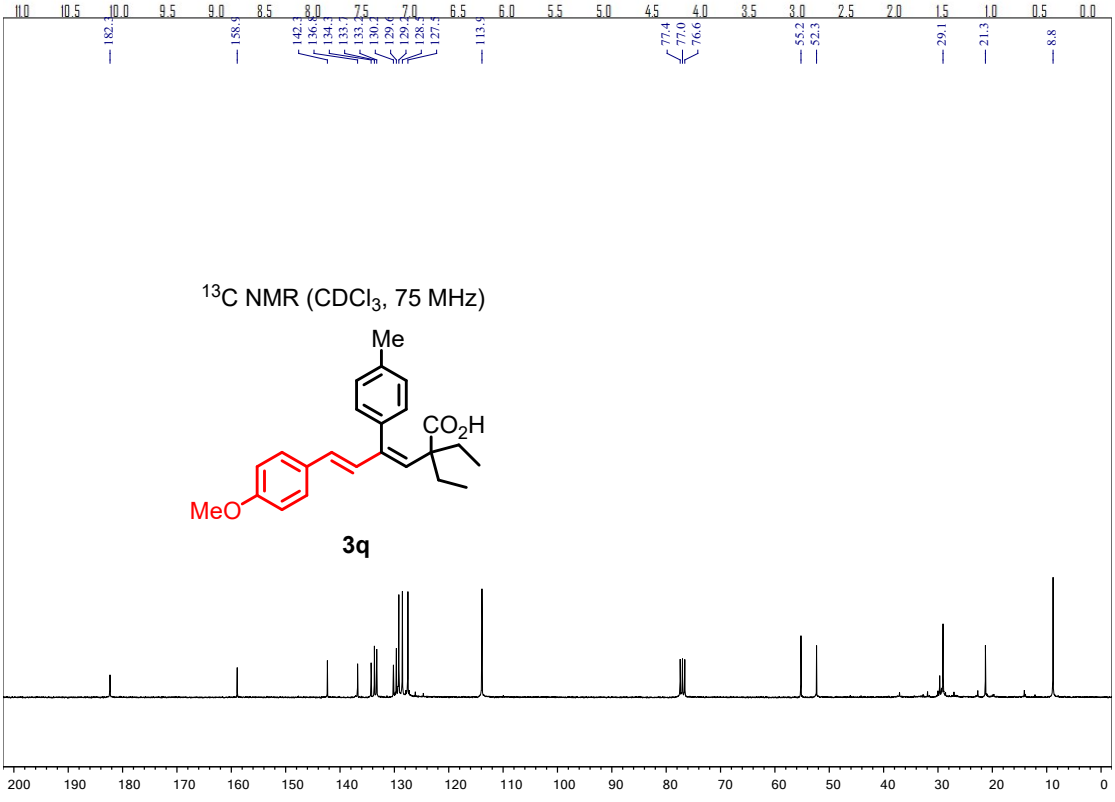
J^3-trans = 16.5 Hz

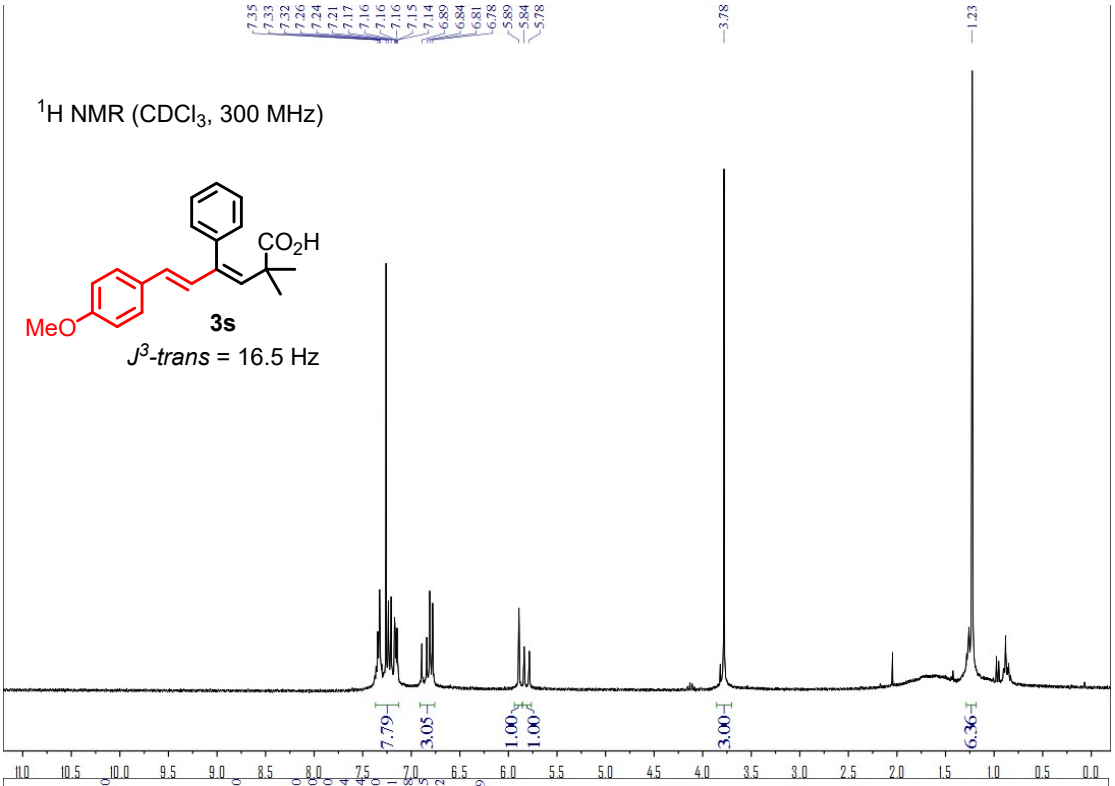


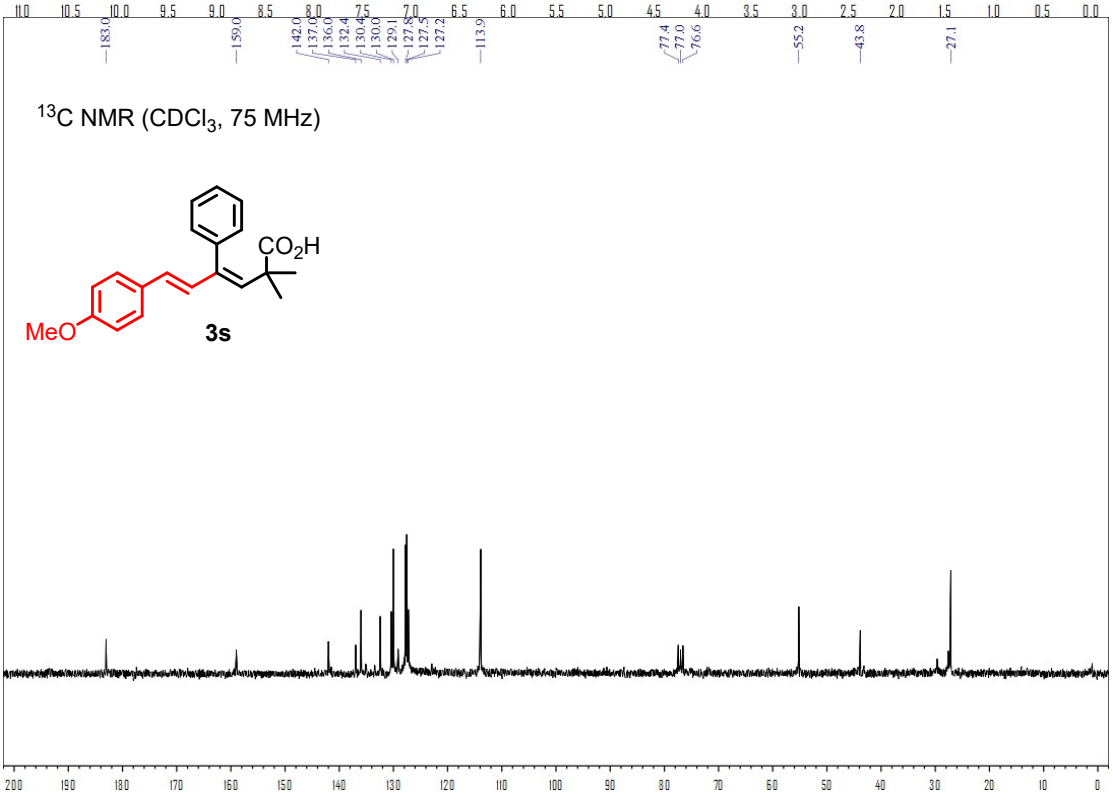
^{13}C NMR ($CDCl_3$, 75 MHz)

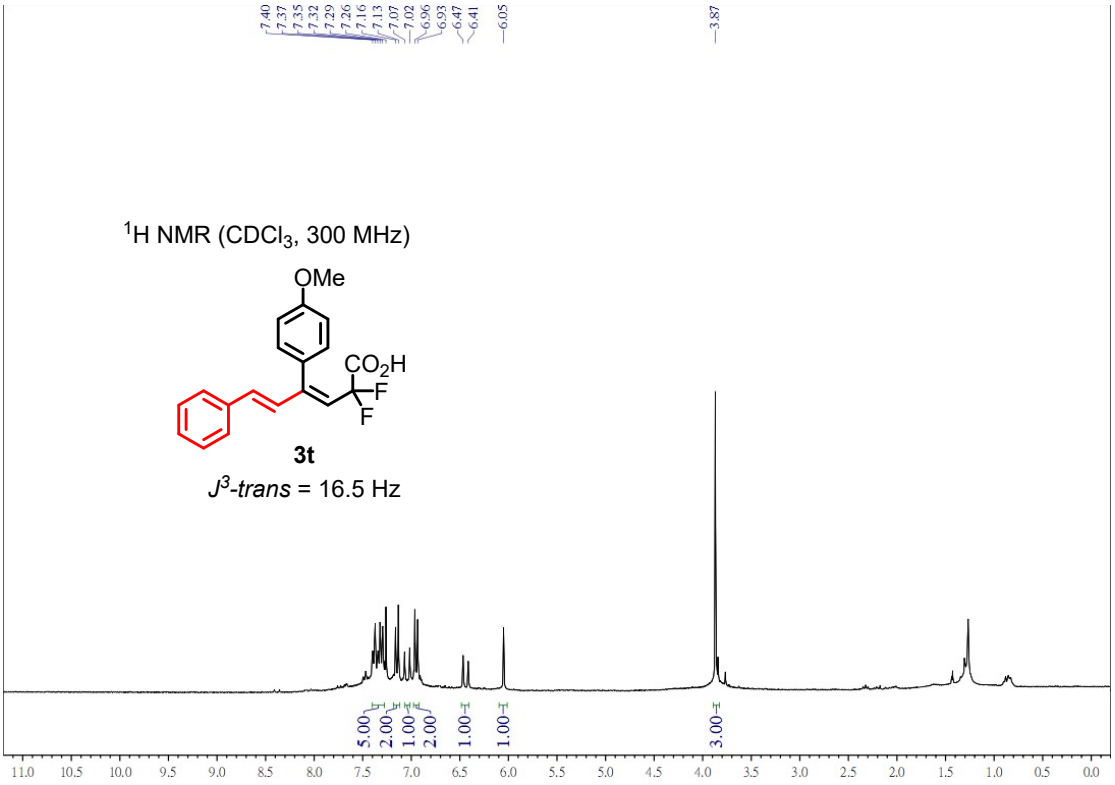
3p

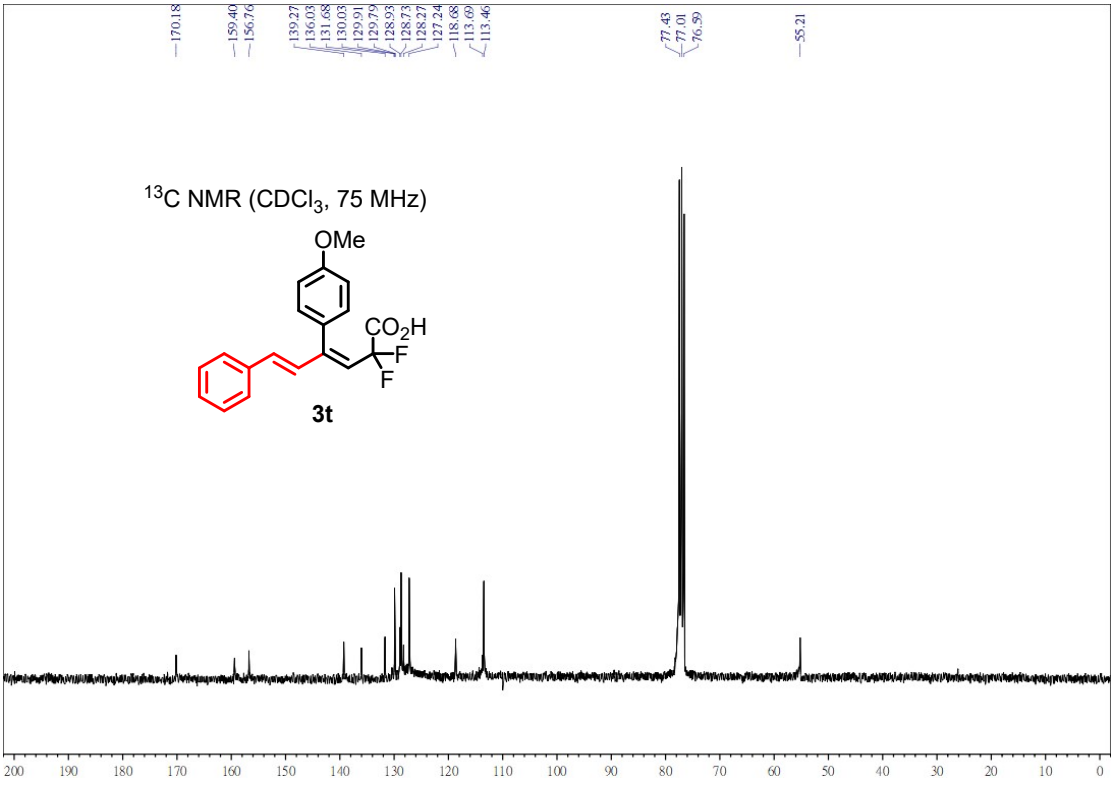

^{1}H NMR ($CDCl_3$, 300 MHz)
Me
CO_2H
MeO
3q
J^3-*trans* = 15 Hz
grease

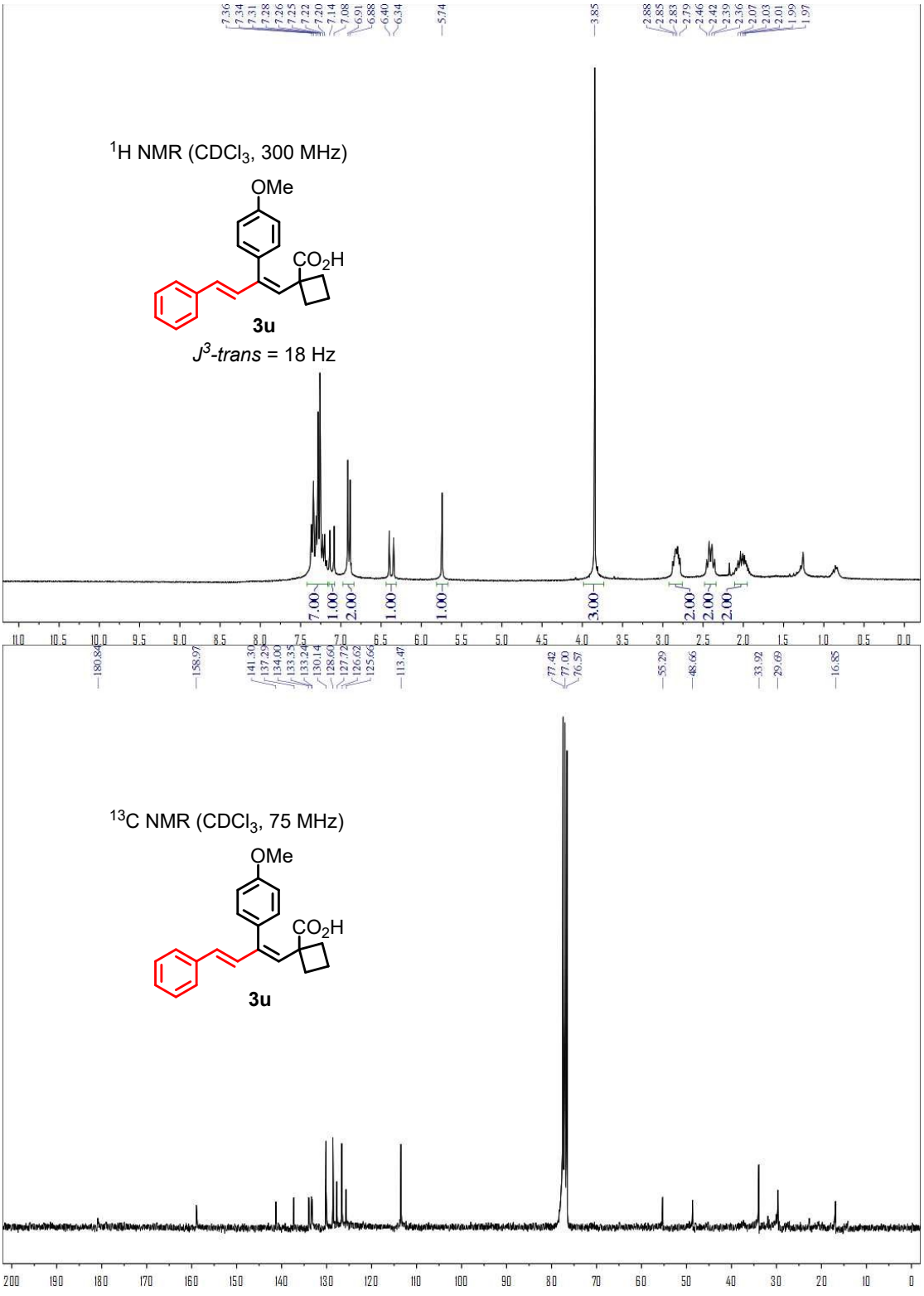

^{13}C NMR ($CDCl_3$, 75 MHz)
Me
CO_2H
MeO
3q


^{1}H NMR ($CDCl_3$, 300 MHz)
CO_2H
MeO
3s
J^3-*trans* = 16.5 Hz

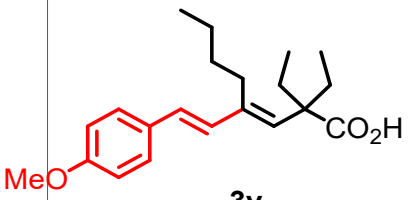

^{13}C NMR ($CDCl_3$, 75 MHz)
CO_2H
MeO
3s


7.40
7.37
7.35
7.32
7.29
7.26
7.16
7.13
7.07
7.02
6.96
6.93
6.47
6.41
6.05
3.87
^{1}H NMR ($CDCl_3$, 300 MHz)
OMe
CO_2H
F
F
3t
J^3-*trans* = 16.5 Hz
5.00
2.00
1.00
2.00
1.00
1.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


170.18
159.40
156.76
139.27
136.03
131.68
130.03
129.91
129.79
128.93
128.73
128.27
127.24
118.68
113.69
113.46
77.43
77.01
76.59
55.21
^{13}C NMR ($CDCl_3$, 75 MHz)
OMe
CO_2H
F
F
3t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


^{1}H NMR ($CDCl_3$, 300 MHz)
OMe
CO_2H
3u
J^3-*trans* = 18 Hz
^{13}C NMR ($CDCl_3$, 75 MHz)
OMe
CO_2H
3u

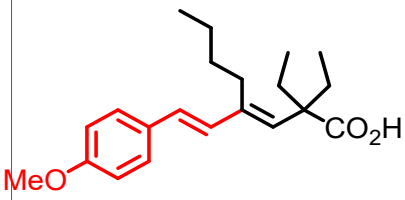
^{1}H NMR ($CDCl_3$, 300 MHz)



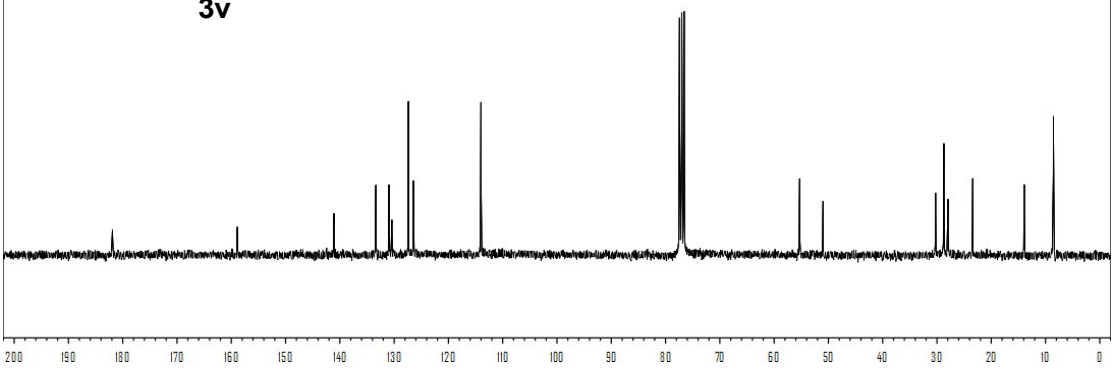
3v

J^{3}-*trans* = 15 Hz

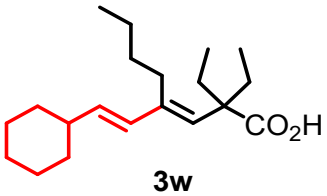
^{13}C NMR ($CDCl_3$, 75 MHz)



3v



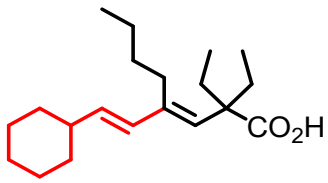
^{1}H NMR ($CDCl_3$, 300 MHz)



3w

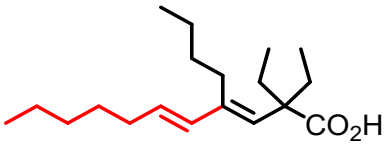
J^3-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



3w

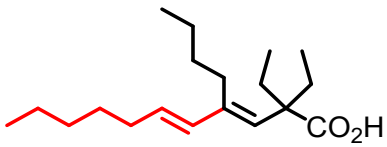
^{1}H NMR ($CDCl_3$, 300 MHz)



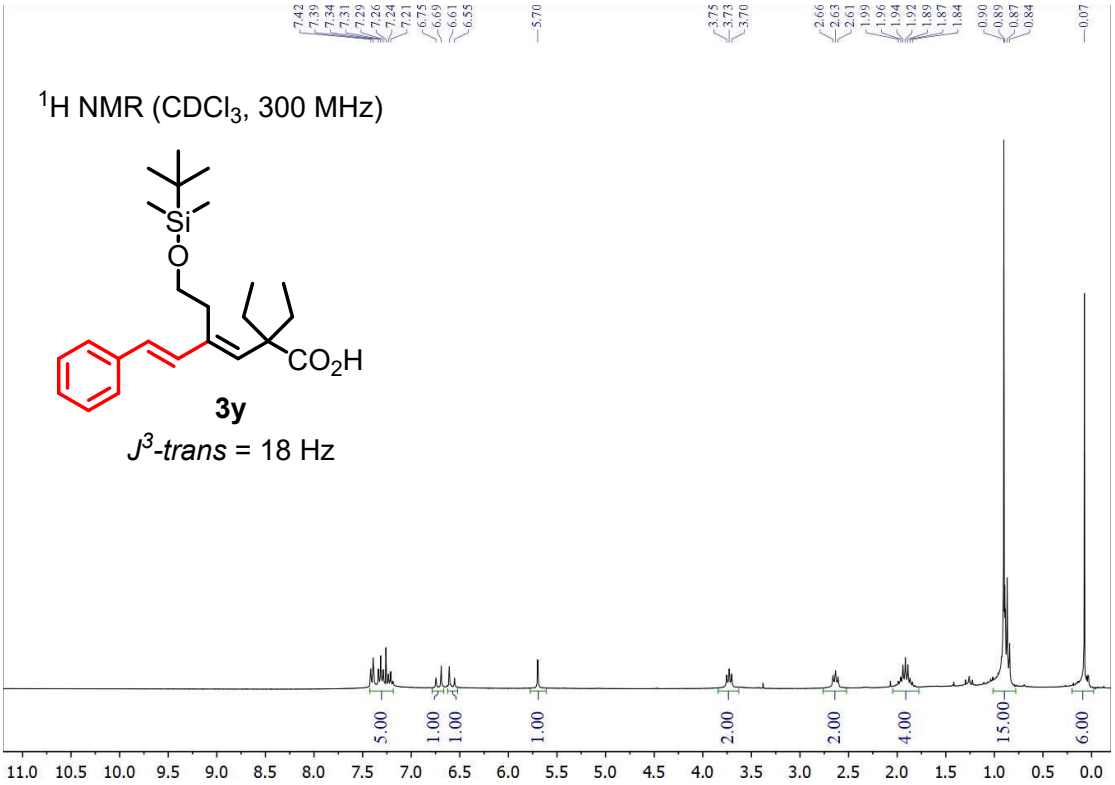
3x

J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



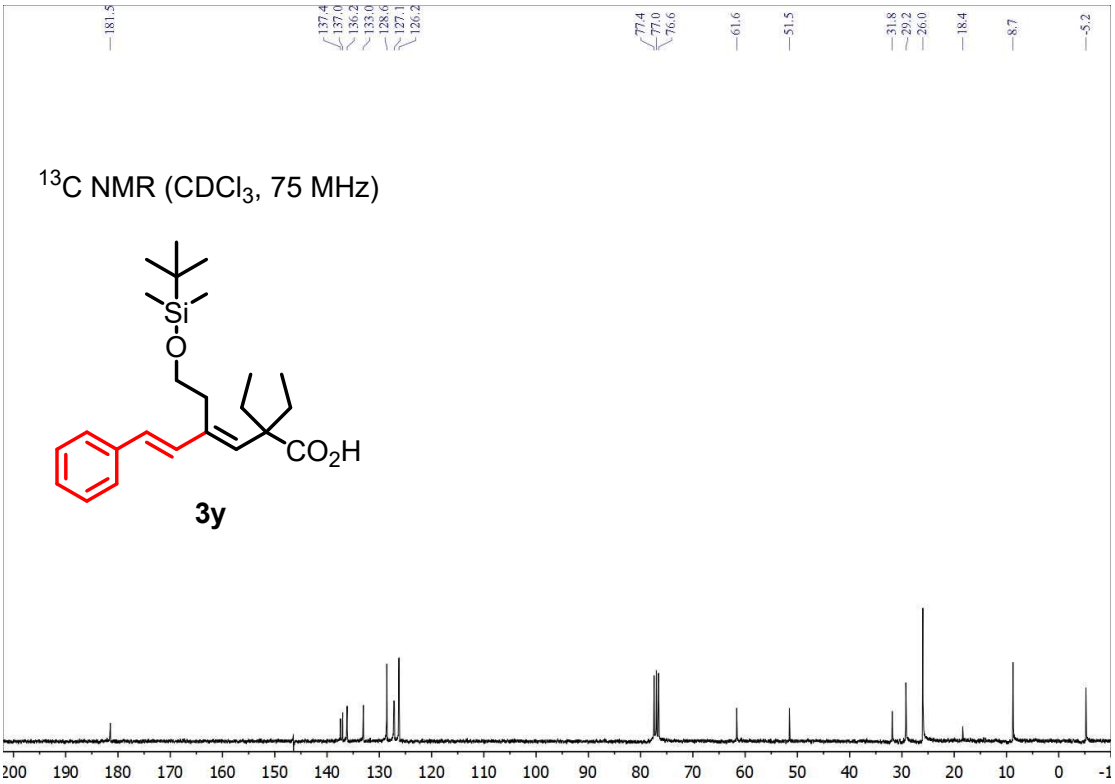
3x



^{1}H NMR ($CDCl_3$, 300 MHz)

3y

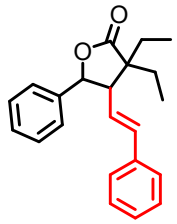
J^{3}-*trans* = 18 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

3y

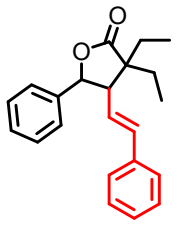
^{1}H NMR ($CDCl_3$, 300 MHz)



5a

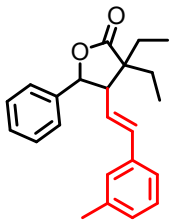
J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



5a

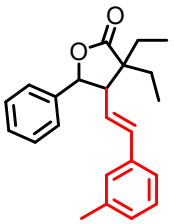
^{1}H NMR ($CDCl_3$, 300 MHz)



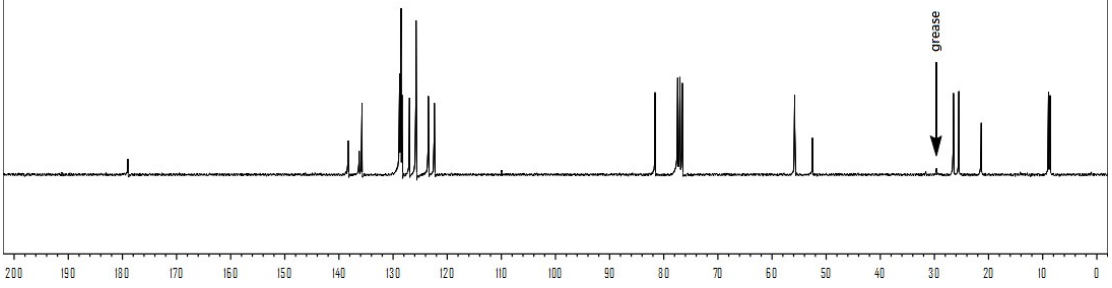
5b

J^3-trans = 15 Hz

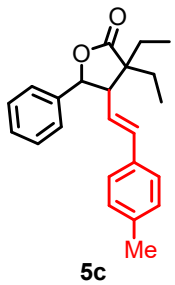
^{13}C NMR ($CDCl_3$, 75 MHz)



5b



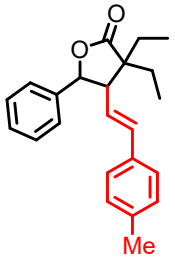
^{1}H NMR ($CDCl_3$, 300 MHz)



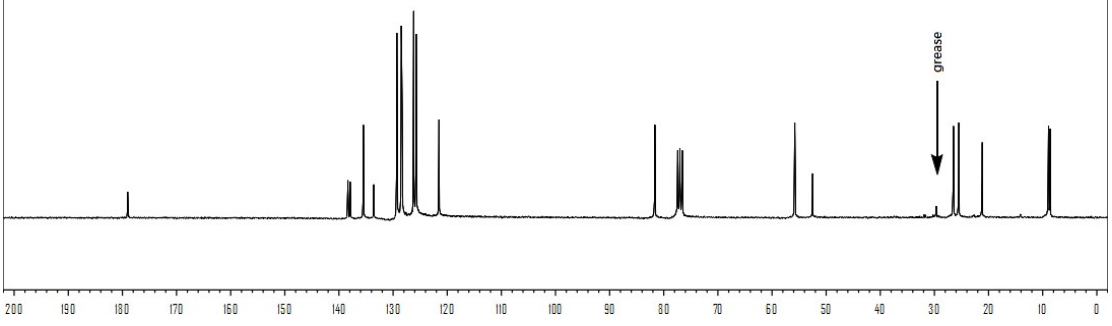
5c

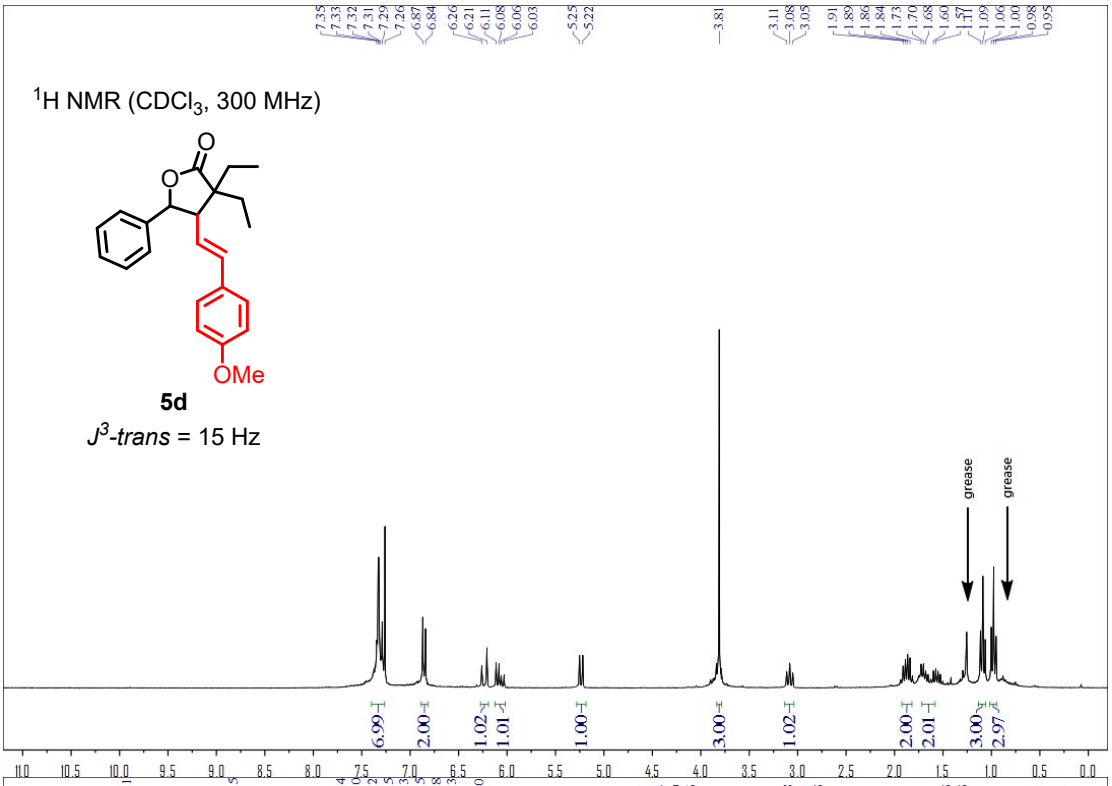
J^3-trans = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



5c

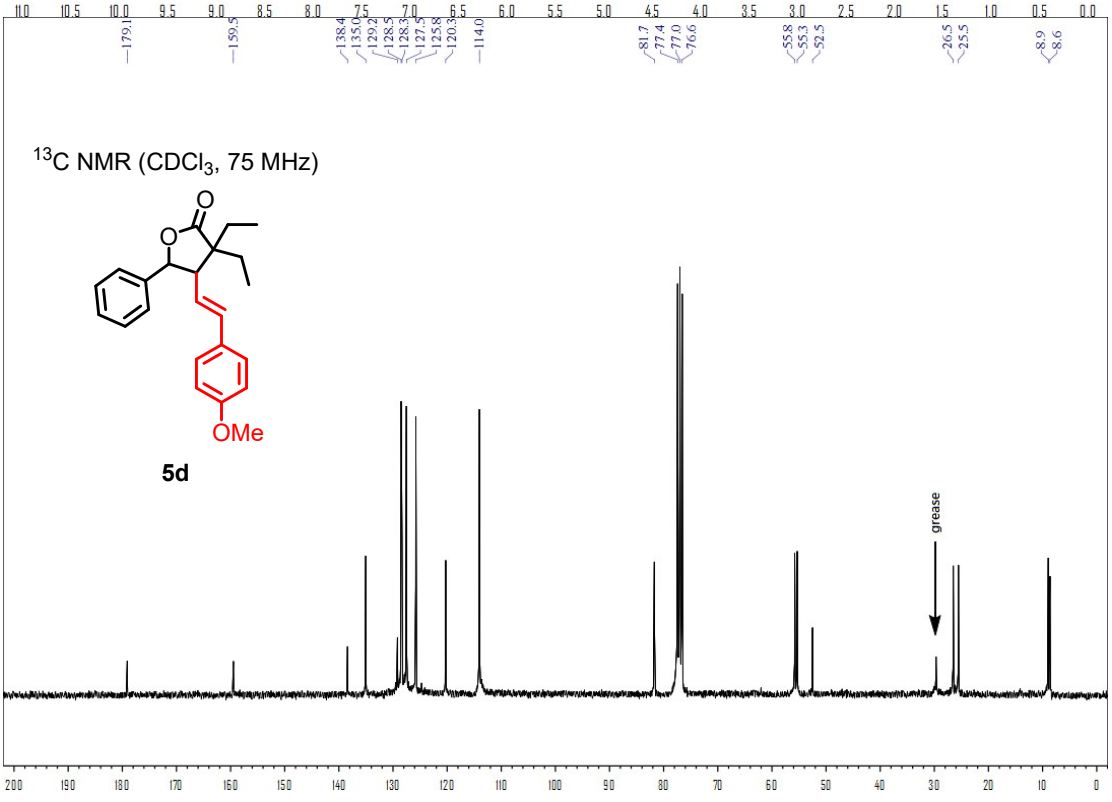




^{1}H NMR ($CDCl_3$, 300 MHz)

5d

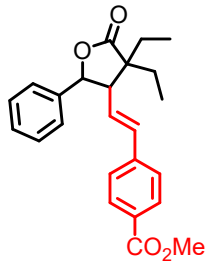
J^{3}-*trans* = 15 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

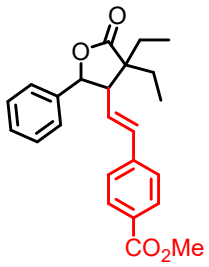
5d

^{1}H NMR ($CDCl_3$, 300 MHz)

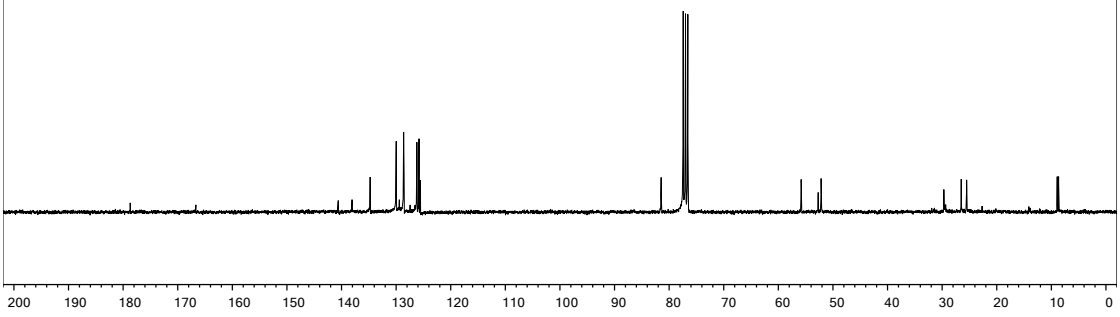


5e

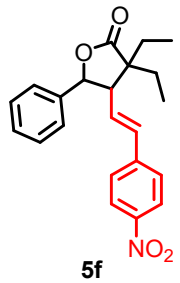
^{13}C NMR ($CDCl_3$, 75 MHz)



5e



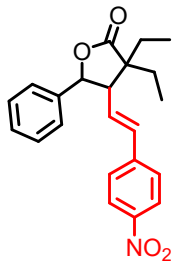
^{1}H NMR ($CDCl_3$, 300 MHz)



5f

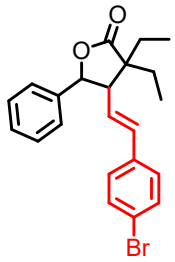
J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



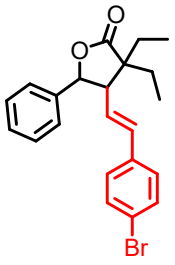
5f

^{1}H NMR ($CDCl_3$, 300 MHz)

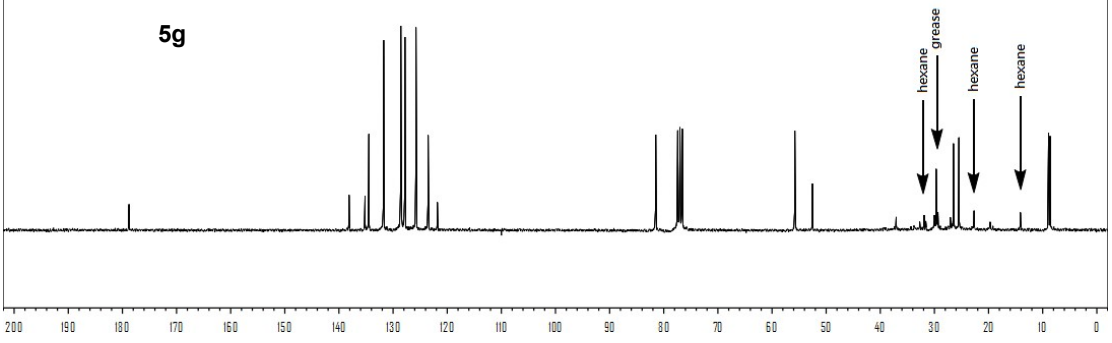


5g

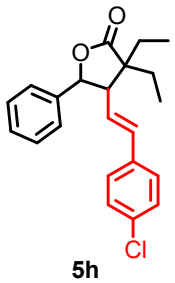
^{13}C NMR ($CDCl_3$, 75 MHz)



5g



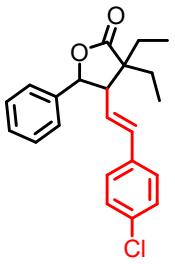
^{1}H NMR ($CDCl_3$, 300 MHz)



5h

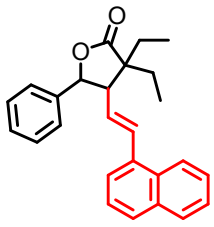
J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



5h

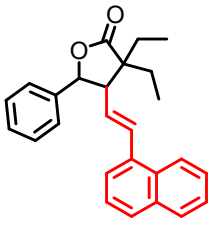
^{1}H NMR ($CDCl_3$, 300 MHz)



5i

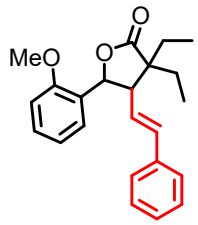
J^{3}-*trans* = 18 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



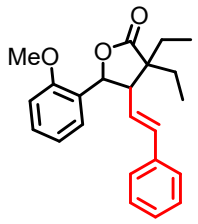
5i

^{1}H NMR ($CDCl_3$, 300 MHz)

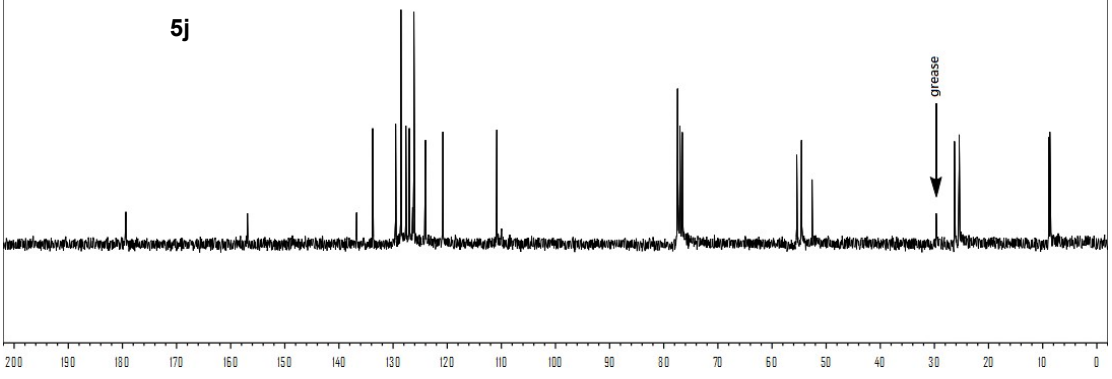


5j

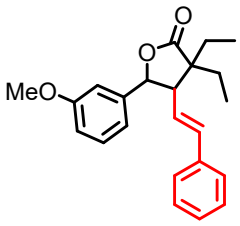
^{13}C NMR ($CDCl_3$, 75 MHz)



5j



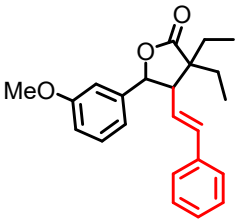
^{1}H NMR ($CDCl_3$, 300 MHz)



5k

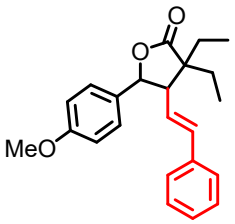
J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



5k

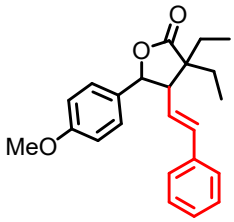
^{1}H NMR ($CDCl_3$, 300 MHz)



5l

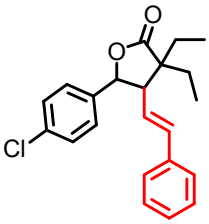
J^{3}-*trans* = 15 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



5l

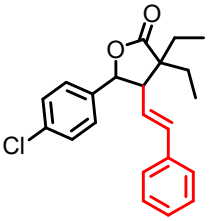
^{1}H NMR ($CDCl_3$, 300 MHz)



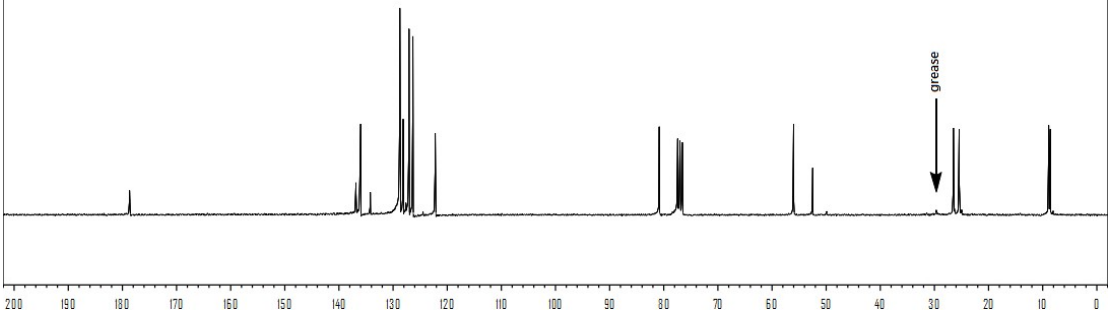
5m

J^{3}-*trans* = 15 Hz

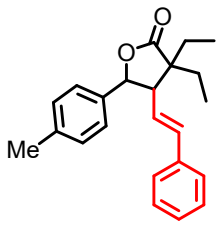
^{13}C NMR ($CDCl_3$, 75 MHz)



5m



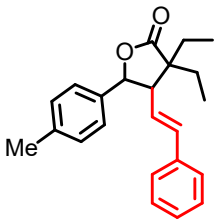
^{1}H NMR ($CDCl_3$, 300 MHz)



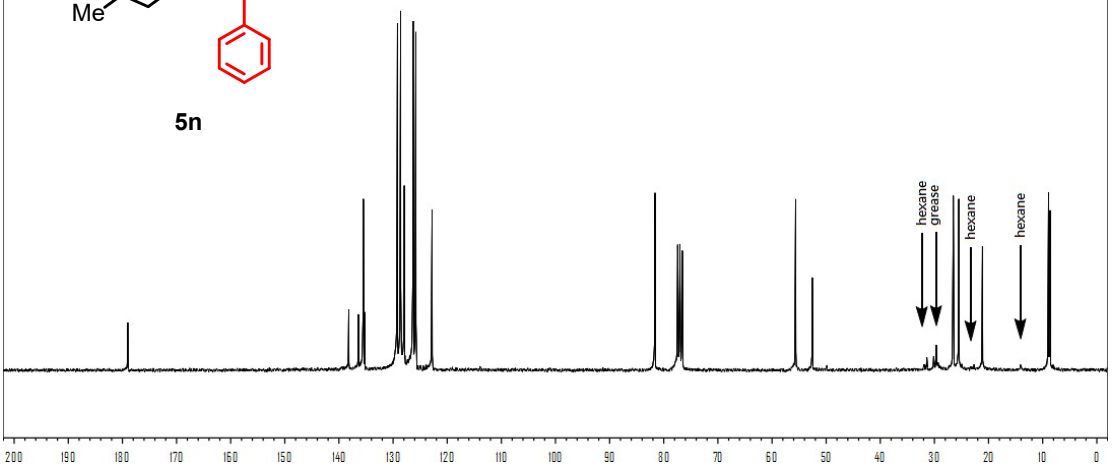
5n

J^{3}-*trans* = 15 Hz

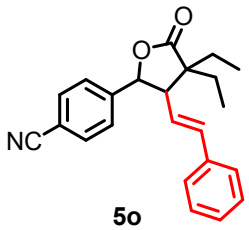
^{13}C NMR ($CDCl_3$, 75 MHz)



5n

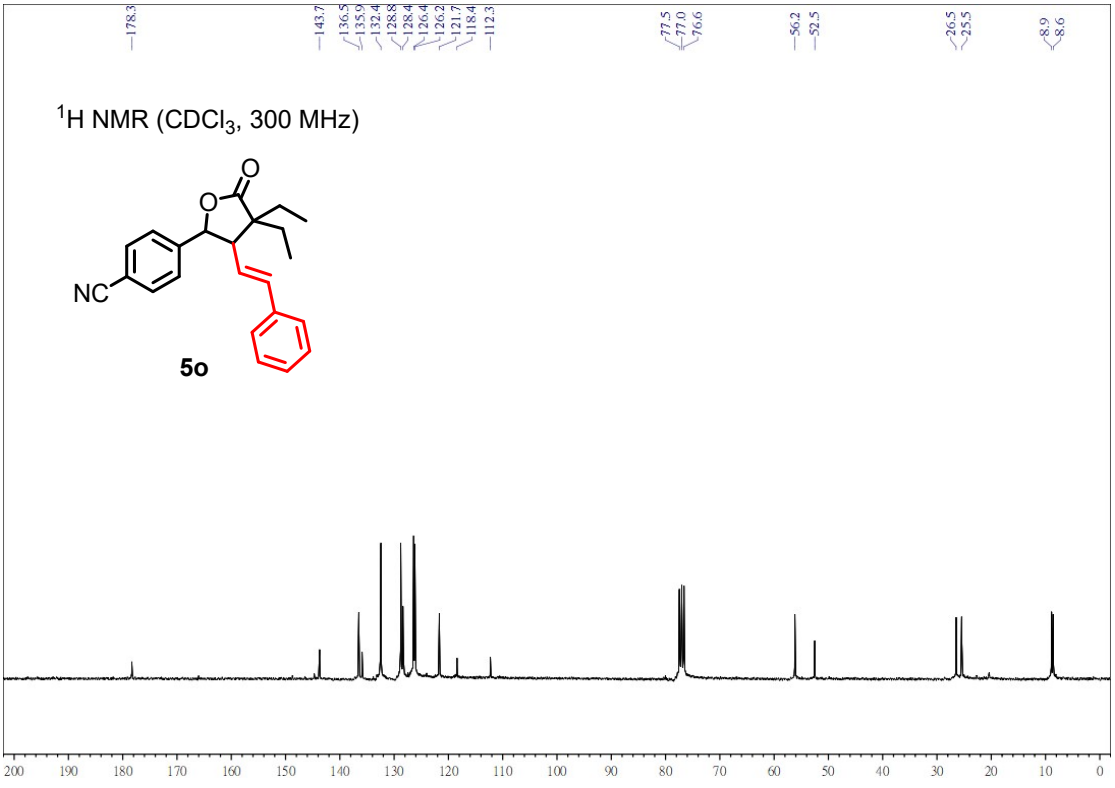


^{1}H NMR ($CDCl_3$, 300 MHz)



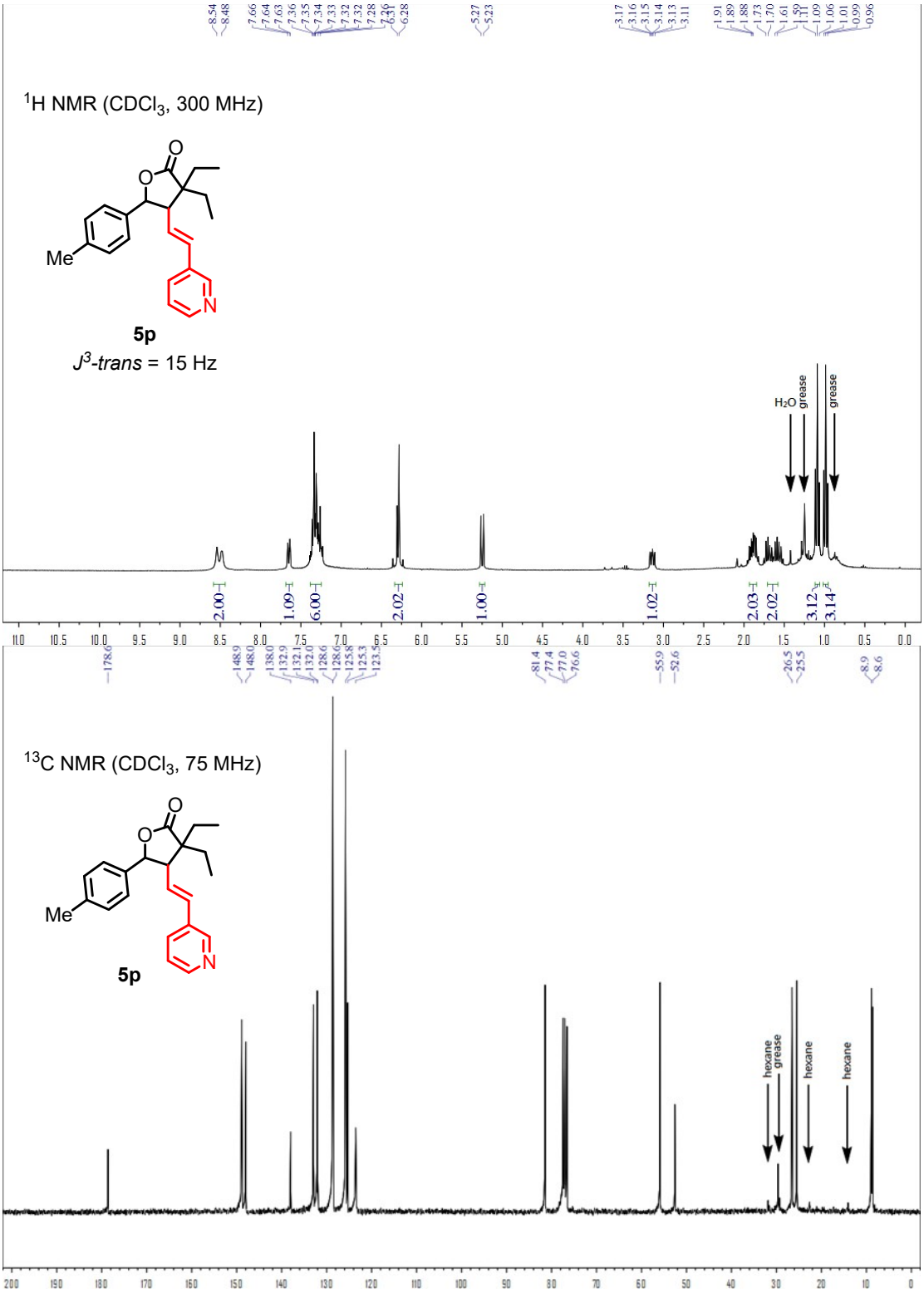
5o

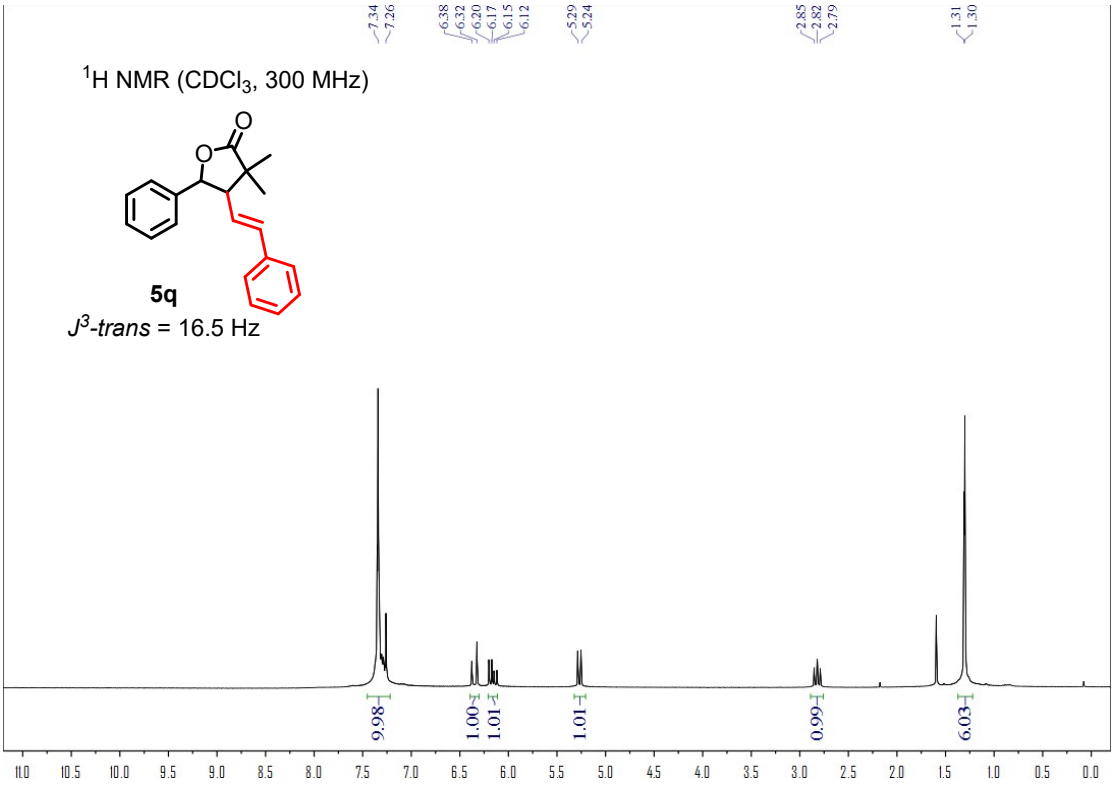
J^3-*trans* = 15 Hz

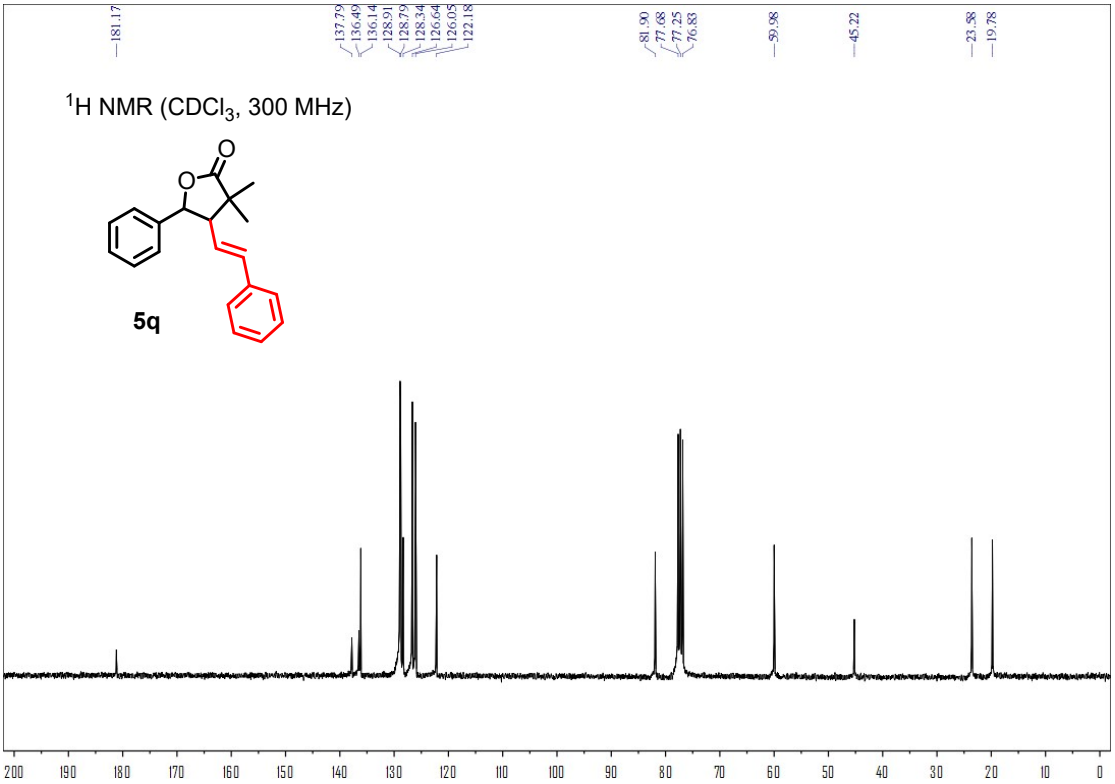


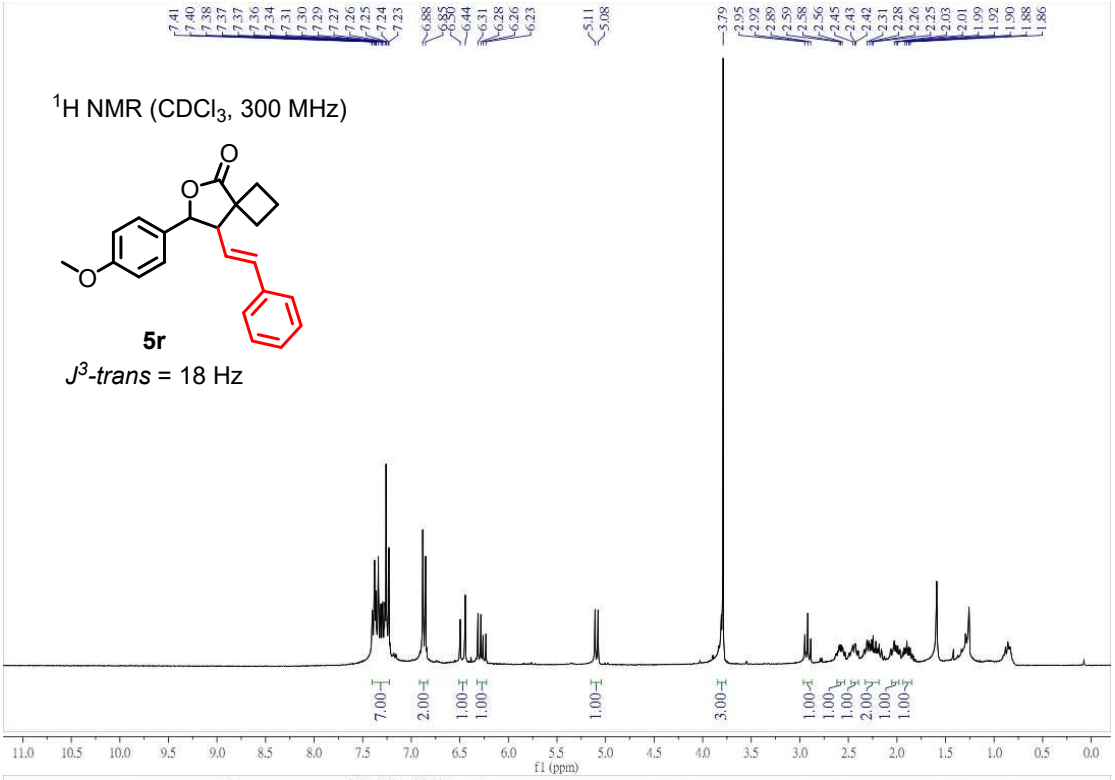
^{1}H NMR ($CDCl_3$, 300 MHz)

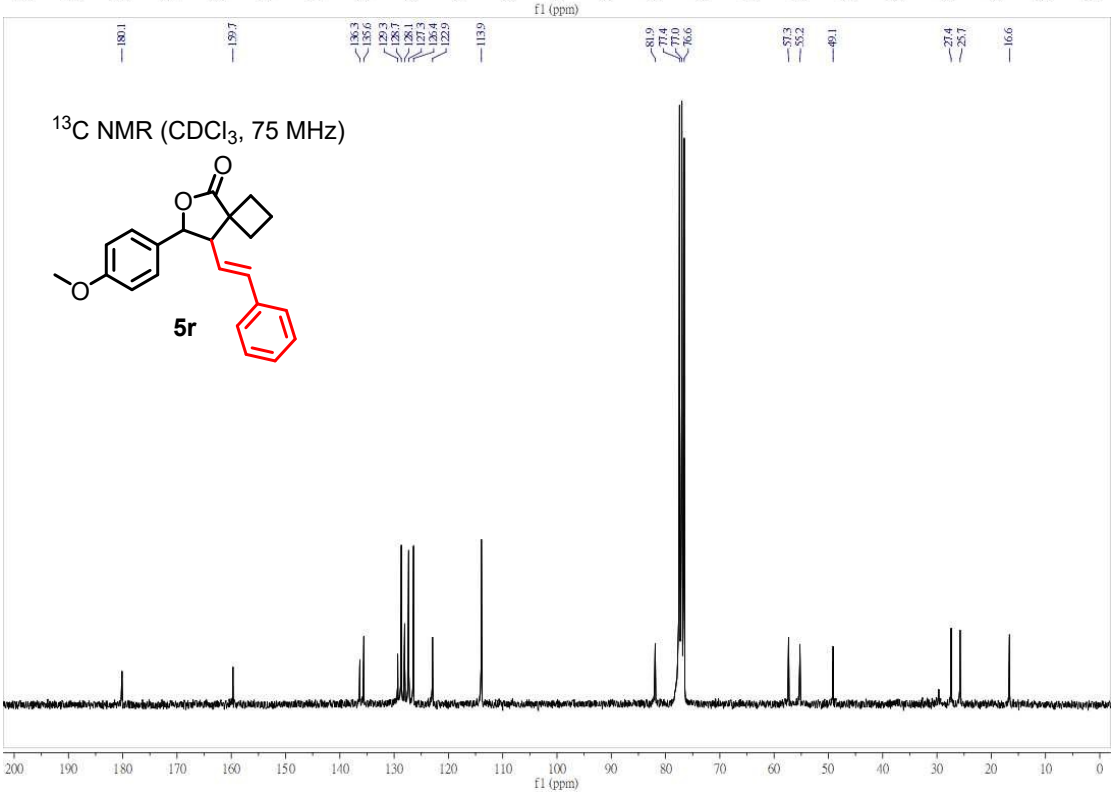
5o


^{1}H NMR ($CDCl_3$, 300 MHz)
Me
5p
J^3-*trans* = 15 Hz
H_2O
grease
grease
^{13}C NMR ($CDCl_3$, 75 MHz)
Me
5p
hexane
grease
hexane
hexane

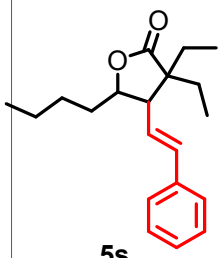

7.34
7.26
6.38
6.32
6.20
6.17
6.15
6.12
5.29
5.24
2.85
2.82
2.79
1.31
1.30
^{1}H NMR ($CDCl_3$, 300 MHz)
5q
J^3-*trans* = 16.5 Hz
9.98
1.00
1.01
1.01
0.99
6.03


181.17
137.79
136.49
136.14
128.91
128.79
128.34
126.64
126.05
122.18
81.90
77.68
77.25
76.83
59.98
45.22
23.38
19.78
^{1}H NMR ($CDCl_3$, 300 MHz)
5q


^{1}H NMR ($CDCl_3$, 300 MHz)
5r
J^3-*trans* = 18 Hz


^{13}C NMR ($CDCl_3$, 75 MHz)
5r

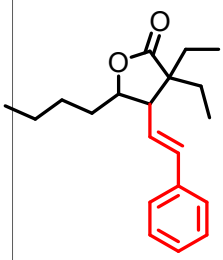
^{1}H NMR ($CDCl_3$, 300 MHz)



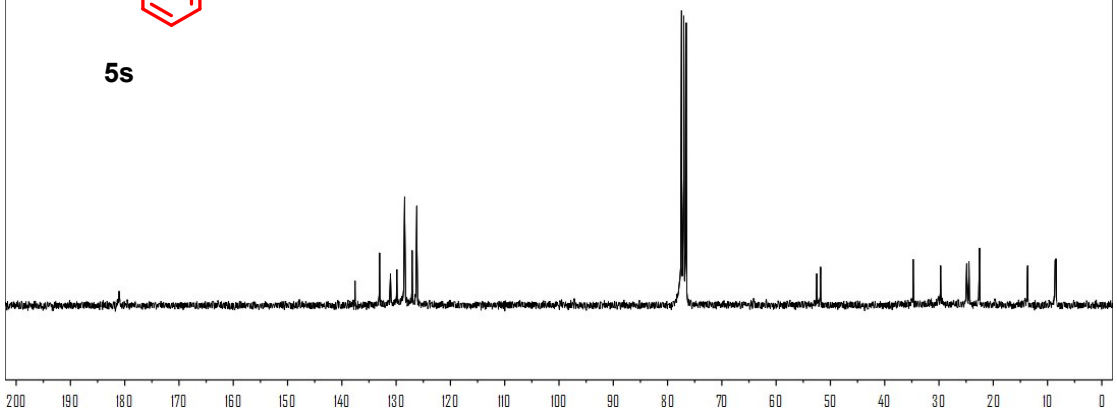
5s

J^3-trans = 15 Hz

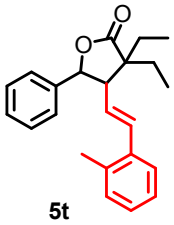
^{13}C NMR ($CDCl_3$, 75 MHz)



5s



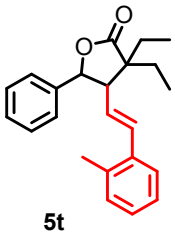
^{1}H NMR ($CDCl_3$, 300 MHz)



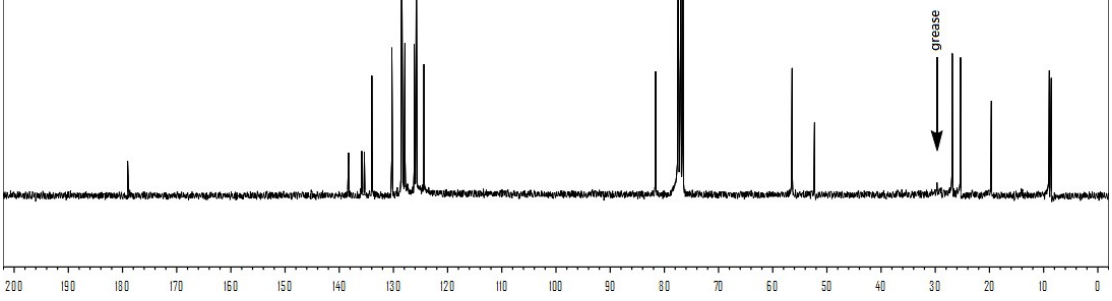
5t

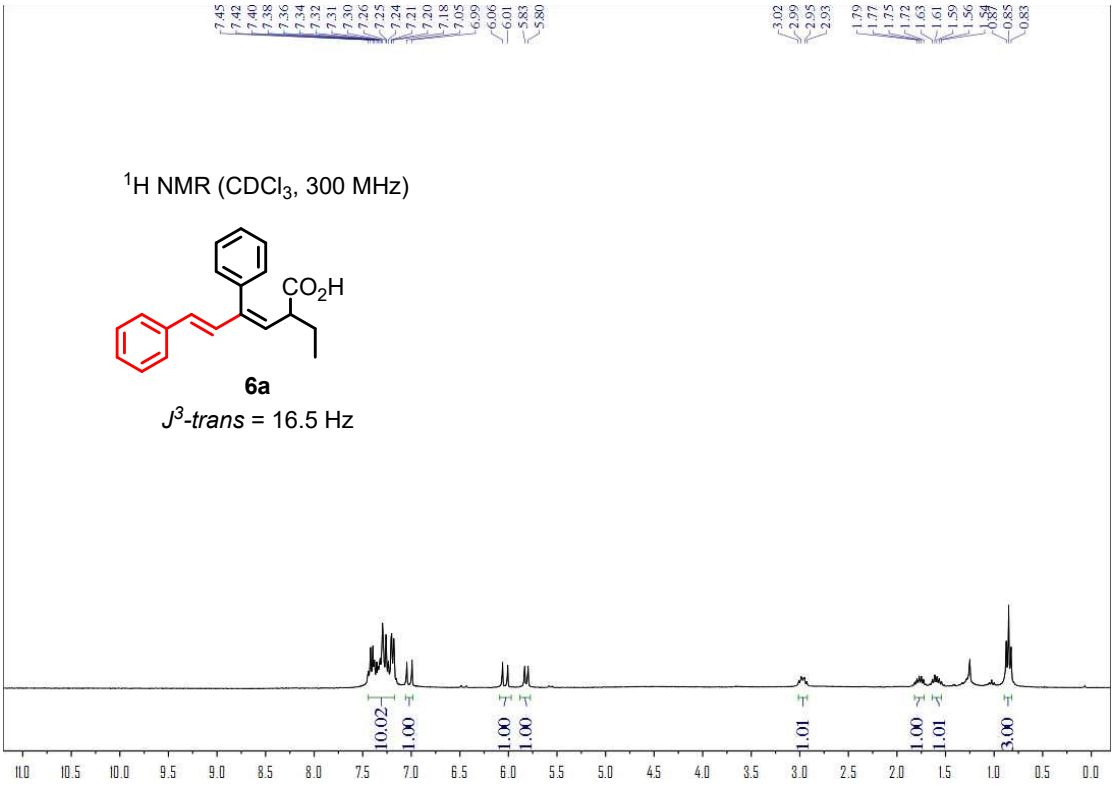
J^{3}-trans = 16.5 Hz

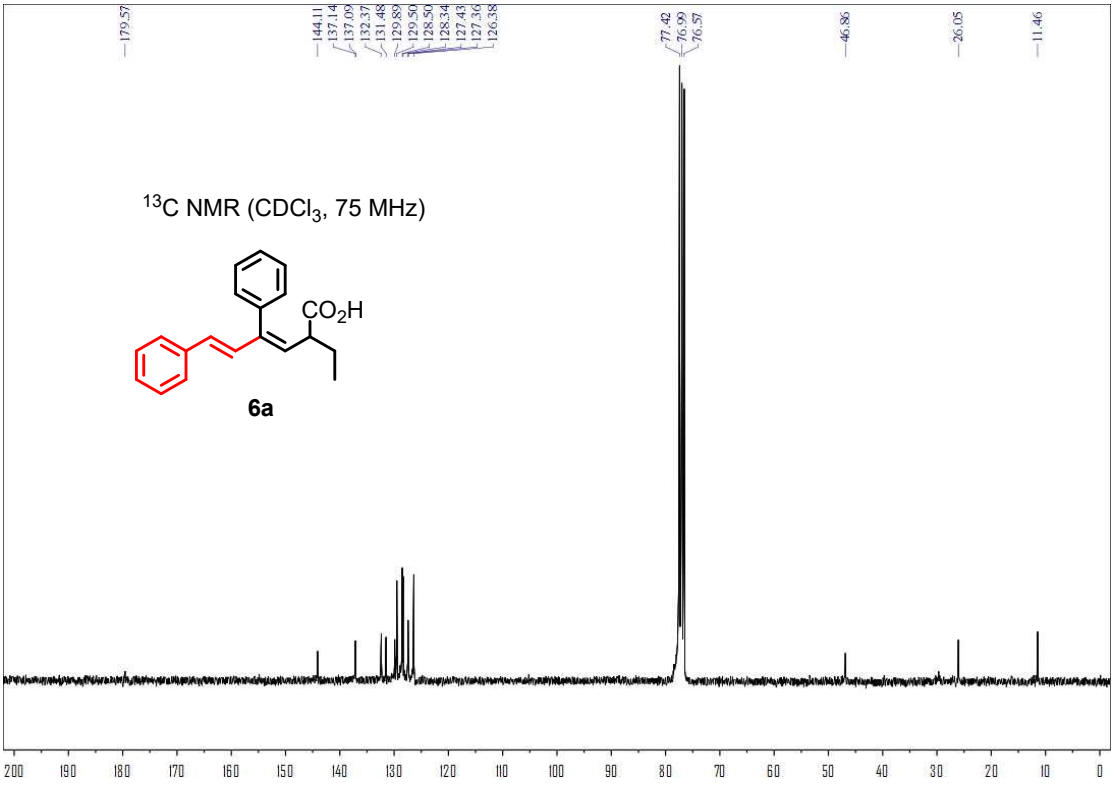
^{13}C NMR ($CDCl_3$, 75 MHz)



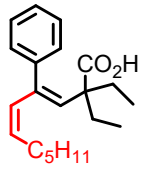
5t




7.45
7.42
7.40
7.38
7.36
7.34
7.32
7.31
7.30
7.26
7.25
7.24
7.21
7.20
7.18
7.05
6.99
6.06
6.01
5.83
5.80
3.02
2.99
2.95
2.93
1.79
1.77
1.75
1.72
1.63
1.61
1.59
1.56
1.54
0.87
0.85
0.83
^{1}H NMR ($CDCl_3$, 300 MHz)
CO_2H
6a
J^3-*trans* = 16.5 Hz
10.02
1.00
1.00
1.00
1.01
1.00
1.01
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


179.57
144.11
137.14
137.09
132.37
131.48
129.89
129.50
128.50
128.34
127.43
127.36
126.38
77.42
76.99
76.57
46.86
26.05
11.46
^{13}C NMR ($CDCl_3$, 75 MHz)
CO_2H
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

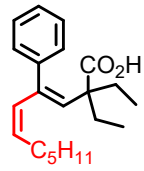
^{1}H NMR ($CDCl_3$, 300 MHz)



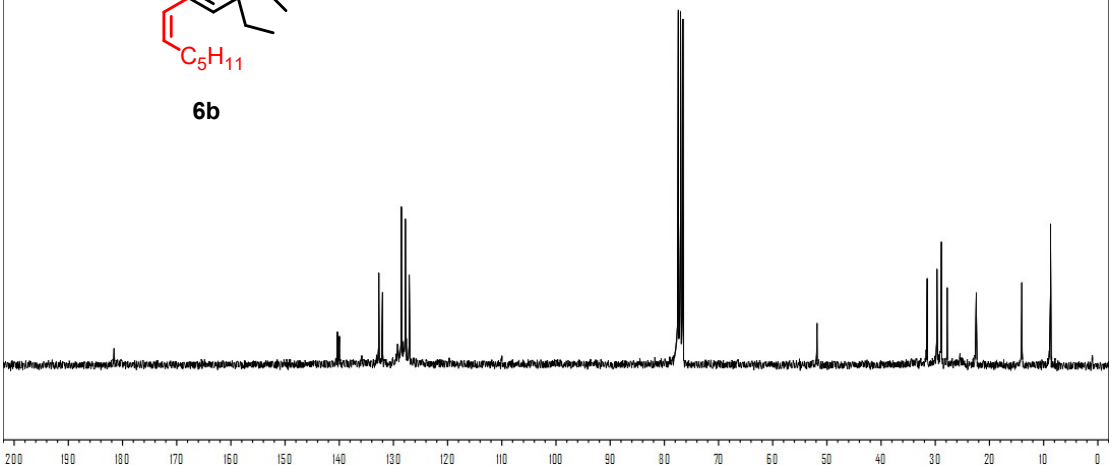
6b

J^{3}-*cis* = 12 Hz

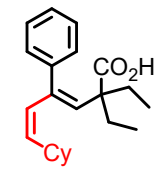
^{13}C NMR ($CDCl_3$, 75 MHz)



6b



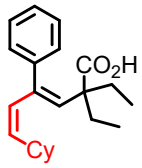
^{1}H NMR ($CDCl_3$, 300 MHz)



6c

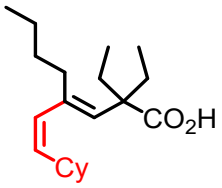
J^{3}-*cis* = 12 Hz

^{13}C NMR ($CDCl_3$, 75 MHz)



6c

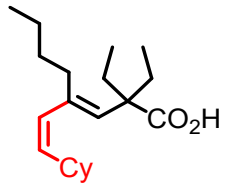
^{1}H NMR ($CDCl_3$, 300 MHz)



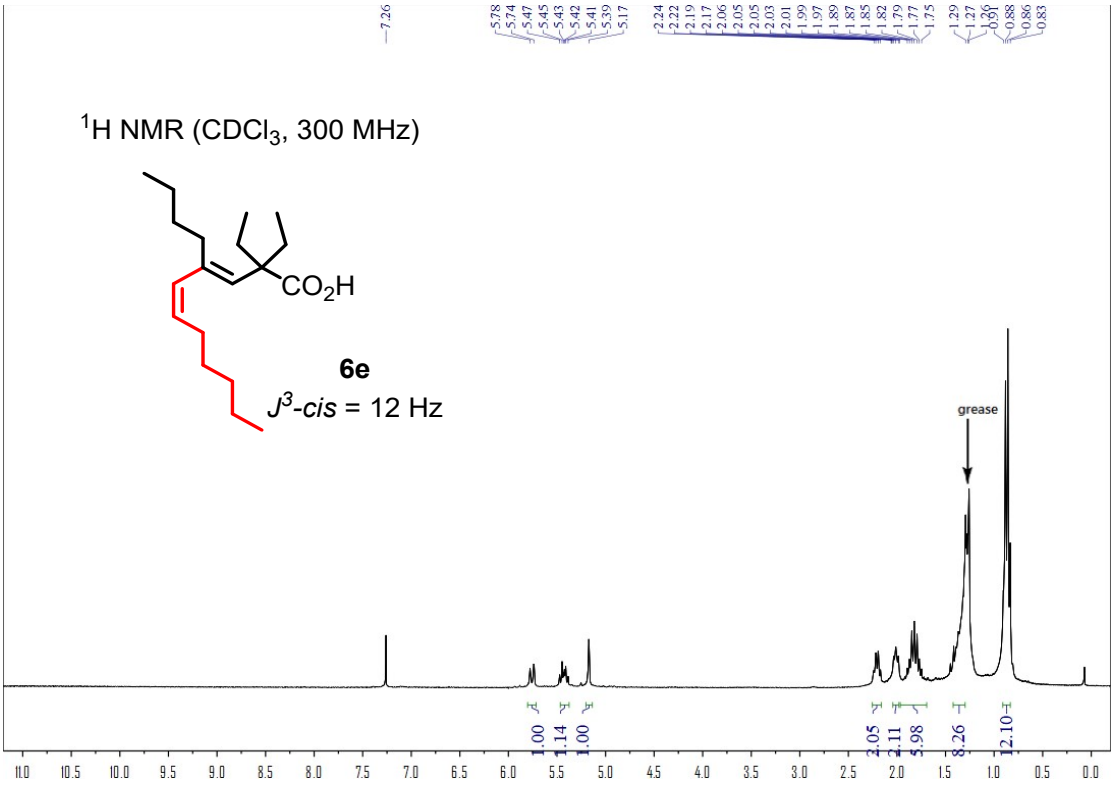
6d

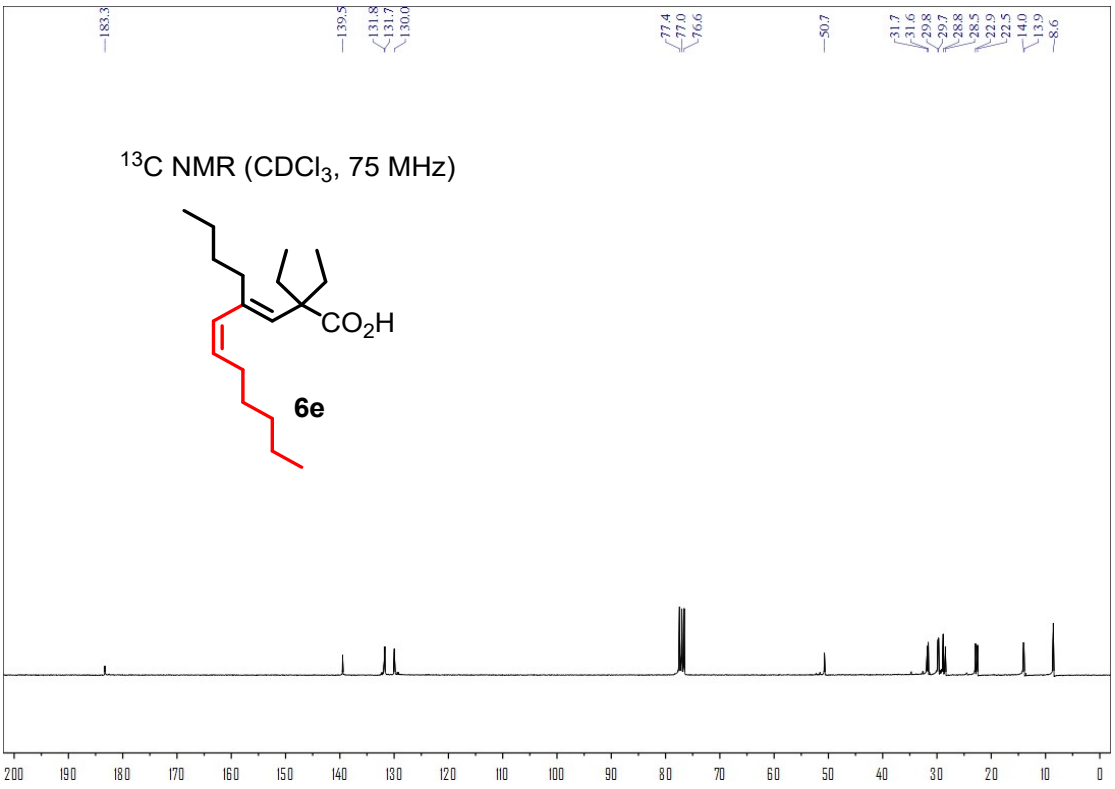
J^{3}-*cis* = 12 Hz

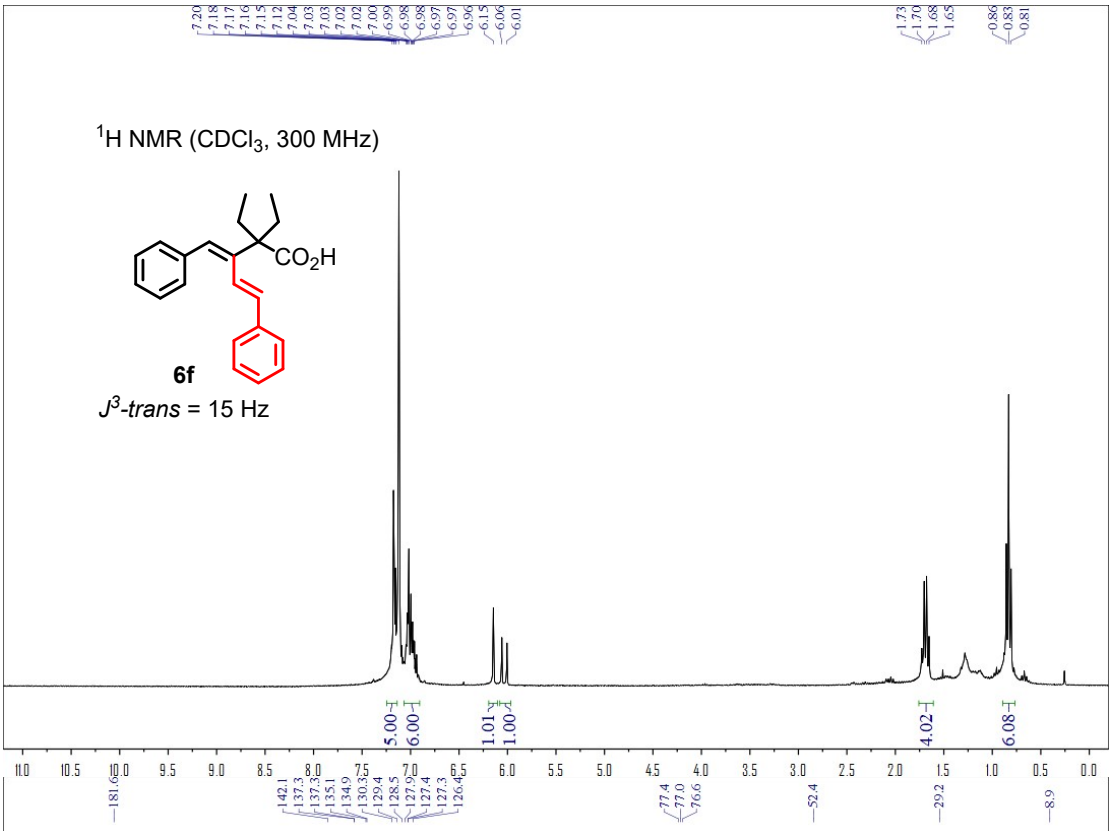
^{13}C NMR ($CDCl_3$, 75 MHz)



6d


^{1}H NMR ($CDCl_3$, 300 MHz)
CO_2H
6e
J^3-*cis* = 12 Hz
grease

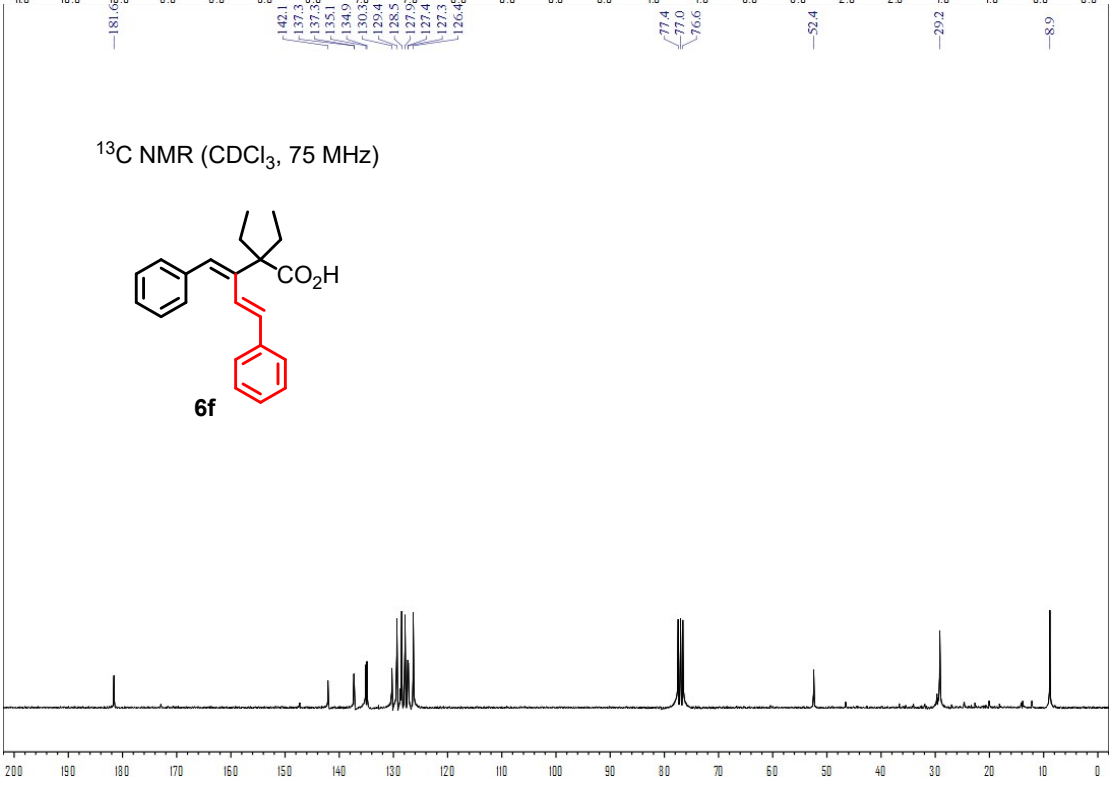

^{13}C NMR ($CDCl_3$, 75 MHz)
CO_2H
6e



^{1}H NMR ($CDCl_3$, 300 MHz)

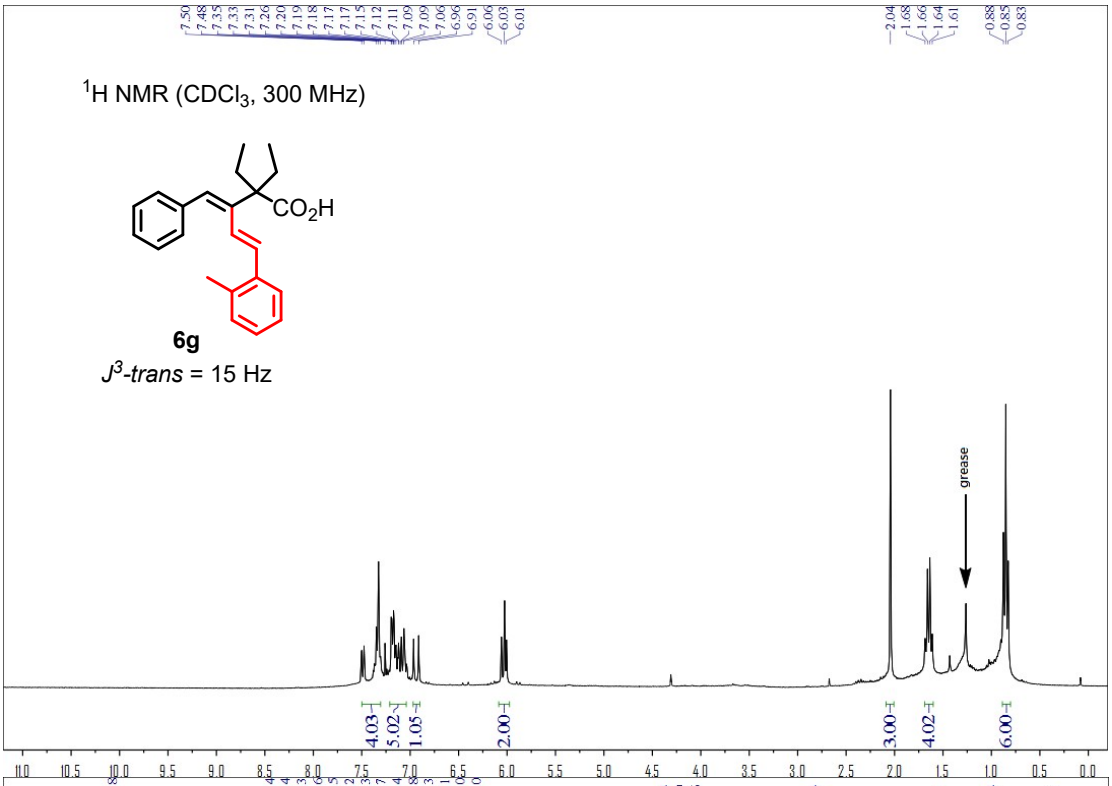
6f

J^3-*trans* = 15 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

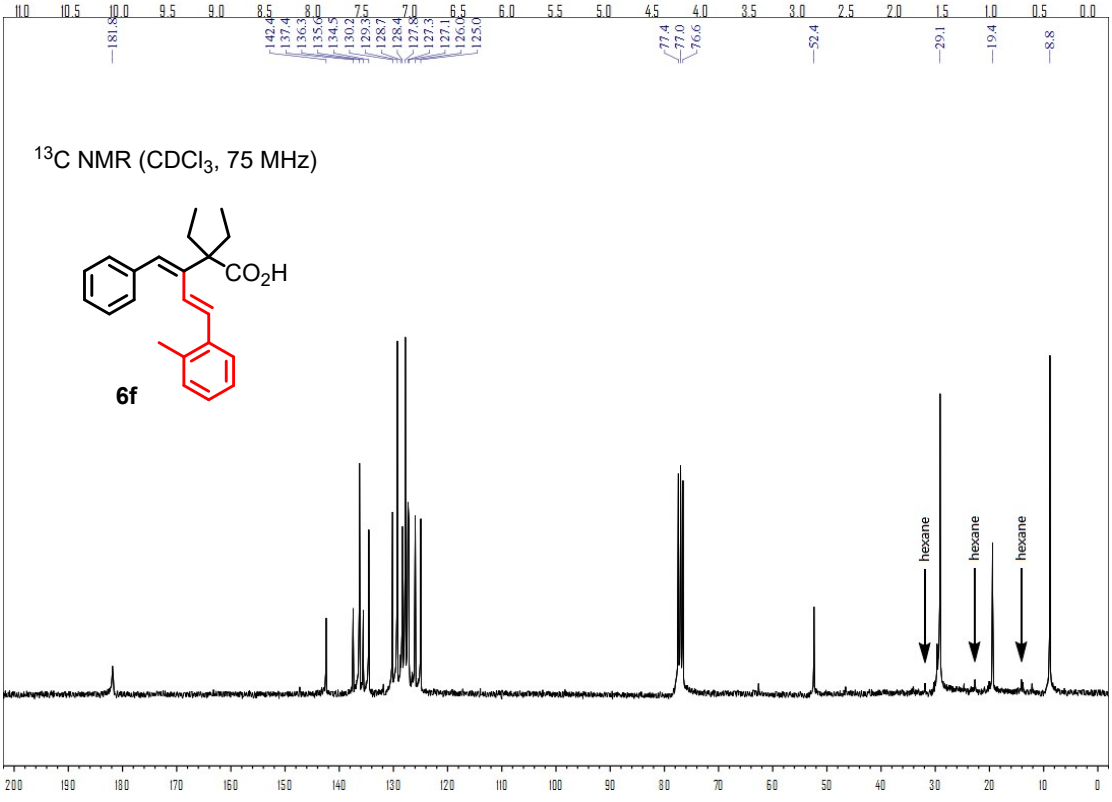
6f



^{1}H NMR ($CDCl_3$, 300 MHz)

6g

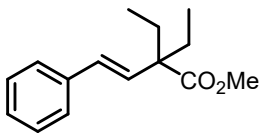
J^{3}-*trans* = 15 Hz



^{13}C NMR ($CDCl_3$, 75 MHz)

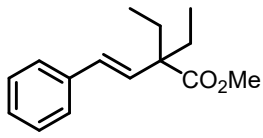
6f

^{1}H NMR ($CDCl_3$, 300 MHz)

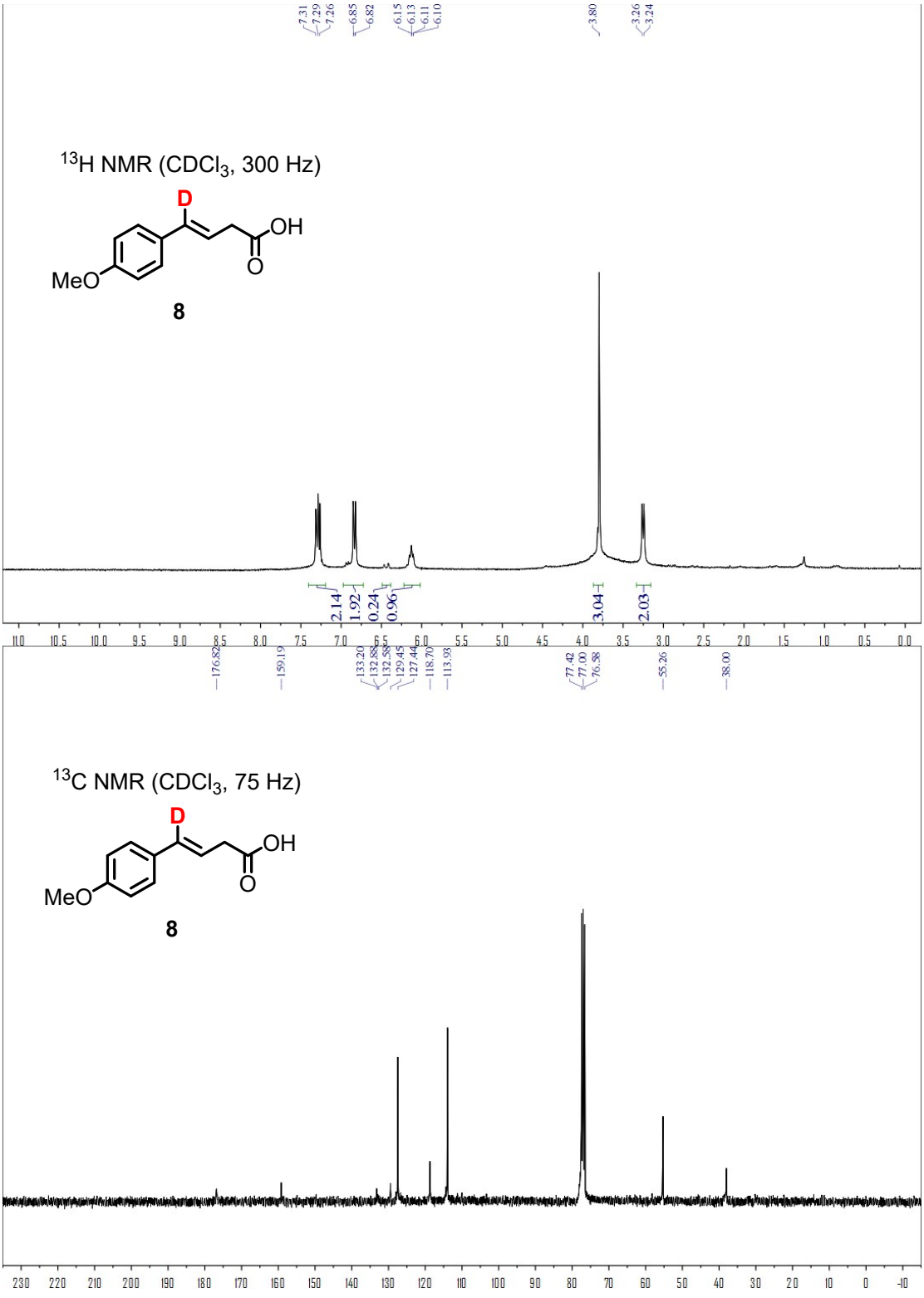


7

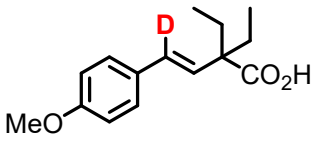
^{13}C NMR ($CDCl_3$, 75 MHz)



7

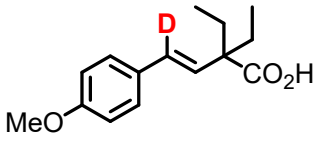

7.31
7.29
7.26
6.85
6.82
6.15
6.13
6.11
6.10
3.80
3.26
3.24
^{13}H NMR ($CDCl_3$, 300 Hz)
D
OH
O
MeO
8
2.14
1.92
0.24
0.96
3.04
2.03
176.82
159.19
133.20
132.88
132.58
129.45
127.44
118.70
113.93
77.42
77.00
76.58
55.26
38.00
^{13}C NMR ($CDCl_3$, 75 Hz)
D
OH
O
MeO
8

^{1}H NMR ($CDCl_3$, 300 Hz)

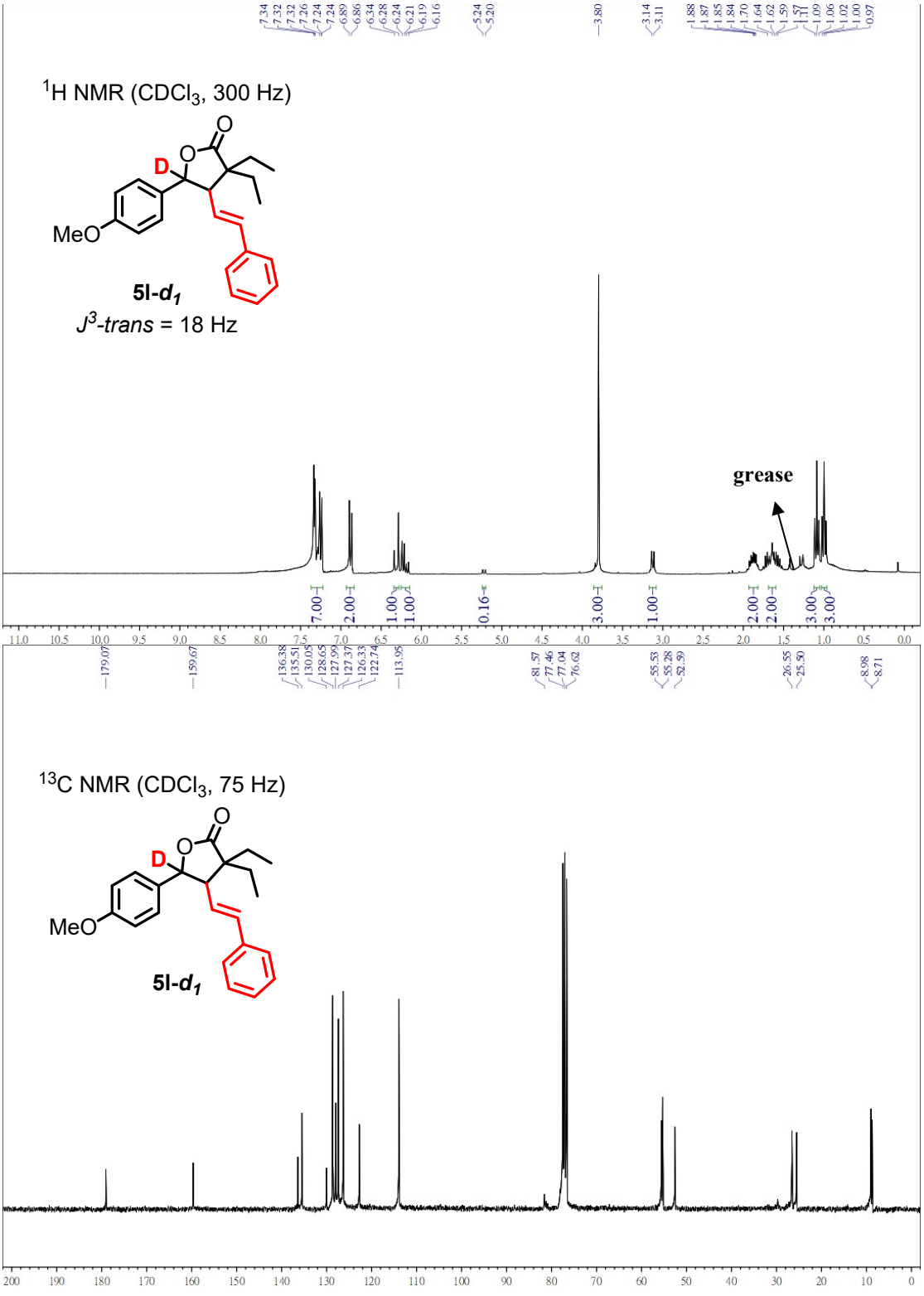


1f-*d*$_1$

^{13}C NMR ($CDCl_3$, 75 Hz)



1f-*d*$_1$


^{1}H NMR ($CDCl_3$, 300 Hz)
D
O
MeO
5l-d_1
J^3-*trans* = 18 Hz
grease
^{13}C NMR ($CDCl_3$, 75 Hz)
5l-d_1

6. X-ray Data:

X-ray structure of 3g

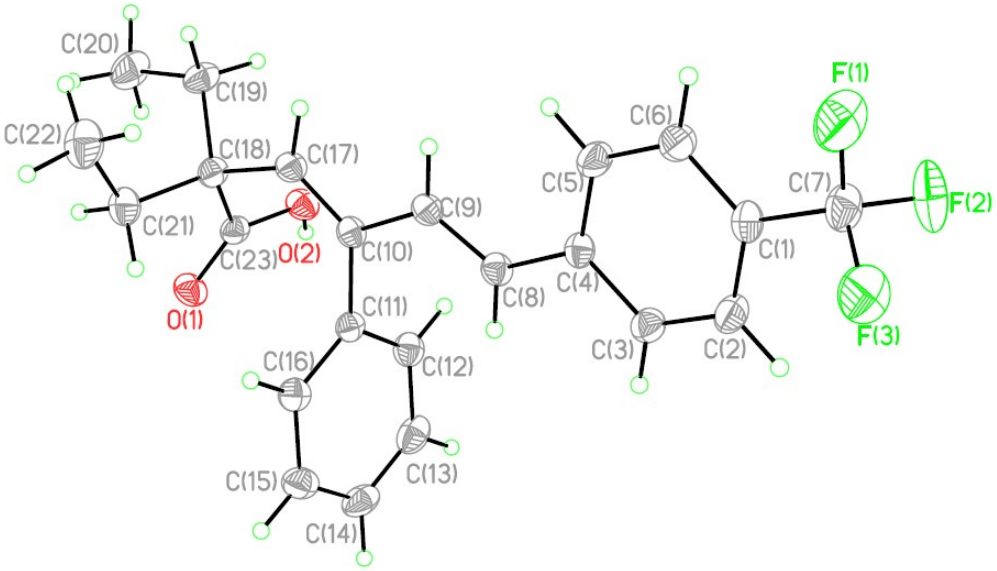


Table 1. Molecular structure and labeling scheme of **3g** with thermal ellipsoids at 50% probability level.

CCDC No	2096072	
Empirical formula	C23 H23 F3 O2	
Formula weight	388.41	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.4578(9) Å	α= 90°.
	b = 22.1975(18) Å	β= 109.640(2)°.
	c = 8.4627(7) Å	γ = 90°.
Volume	2027.1(3) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	816	
Crystal size	0.699 x 0.208 x 0.104 mm^3	
Theta range for data collection	2.098 to 28.386°.	
Index ranges	-15<=h<=13, -29<=k<=29, -11<=l<=11	
Reflections collected	31882	
Independent reflections	5072 [R(int) = 0.0417]	

Completeness to theta = 25.242°	99.8 %
Absorption correction	Numerical
Max. and min. transmission	0.7457 and 0.6494
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5072 / 0 / 255
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1052
R indices (all data)	R1 = 0.0523, wR2 = 0.1089
Extinction coefficient	n/a
Largest diff. peak and hole	0.357 and -0.299 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 21JUL08. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	5423(1)	5042(1)	-1592(2)	56(1)
F(2)	3778(1)	4511(1)	-2277(2)	51(1)
F(3)	4838(1)	4554(1)	-3903(1)	48(1)
O(1)	11145(1)	363(1)	4582(1)	28(1)
O(2)	9719(1)	760(1)	5533(1)	26(1)
C(1)	5672(1)	3986(1)	-1438(2)	24(1)
C(2)	5463(1)	3435(1)	-2258(2)	27(1)
C(3)	6159(1)	2940(1)	-1510(2)	24(1)
C(4)	7077(1)	2983(1)	69(2)	21(1)
C(5)	7251(1)	3539(1)	884(2)	29(1)
C(6)	6560(1)	4038(1)	143(2)	29(1)
C(7)	4940(1)	4522(1)	-2284(2)	30(1)
C(8)	7835(1)	2452(1)	764(2)	21(1)
C(9)	8768(1)	2421(1)	2225(2)	21(1)
C(10)	9520(1)	1884(1)	2864(2)	20(1)
C(11)	9230(1)	1347(1)	1739(2)	20(1)
C(12)	8199(1)	993(1)	1605(2)	25(1)
C(13)	7854(1)	530(1)	440(2)	30(1)
C(14)	8542(1)	413(1)	-591(2)	31(1)
C(15)	9572(1)	758(1)	-464(2)	29(1)
C(16)	9912(1)	1227(1)	692(2)	23(1)
C(17)	10403(1)	1905(1)	4381(2)	22(1)
C(18)	11298(1)	1422(1)	5339(2)	21(1)
C(19)	11609(1)	1571(1)	7230(2)	27(1)
C(20)	12511(2)	1139(1)	8432(2)	38(1)
C(21)	12474(1)	1409(1)	4837(2)	28(1)
C(22)	13230(2)	1989(1)	5224(2)	39(1)
C(23)	10705(1)	795(1)	5080(2)	21(1)

Table 3. Bond lengths [Å] and angles [°] for 21JUL08.

F(1)-C(7)	1.3280(17)
F(2)-C(7)	1.3335(17)
F(3)-C(7)	1.3374(18)
O(1)-C(23)	1.2226(15)
O(2)-C(23)	1.3122(16)
O(2)-H(2A)	0.8375
C(1)-C(2)	1.3862(19)
C(1)-C(6)	1.3866(18)
C(1)-C(7)	1.4929(18)
C(2)-C(3)	1.3814(18)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3988(17)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3945(18)
C(4)-C(8)	1.4644(16)
C(5)-C(6)	1.3828(18)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(8)-C(9)	1.3373(17)
C(8)-H(8)	0.9500
C(9)-C(10)	1.4646(16)
C(9)-H(9)	0.9500
C(10)-C(17)	1.3422(17)
C(10)-C(11)	1.4910(17)
C(11)-C(16)	1.3908(17)
C(11)-C(12)	1.3908(18)
C(12)-C(13)	1.3877(19)
C(12)-H(12)	0.9500
C(13)-C(14)	1.382(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.381(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3905(18)
C(15)-H(15)	0.9500

C(16)-H(16)	0.9500
C(17)-C(18)	1.5175(16)
C(17)-H(17)	0.9500
C(18)-C(23)	1.5309(17)
C(18)-C(21)	1.5432(19)
C(18)-C(19)	1.5540(18)
C(19)-C(20)	1.5209(19)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.524(2)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

C(23)-O(2)-H(2A)	109.4
C(2)-C(1)-C(6)	120.26(12)
C(2)-C(1)-C(7)	119.20(12)
C(6)-C(1)-C(7)	120.54(12)
C(3)-C(2)-C(1)	119.76(12)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	121.07(12)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	118.03(11)
C(5)-C(4)-C(8)	123.12(11)
C(3)-C(4)-C(8)	118.82(11)
C(6)-C(5)-C(4)	121.29(12)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	119.56(12)

C(5)-C(6)-H(6)	120.2
C(1)-C(6)-H(6)	120.2
F(1)-C(7)-F(2)	106.37(13)
F(1)-C(7)-F(3)	106.65(12)
F(2)-C(7)-F(3)	105.15(12)
F(1)-C(7)-C(1)	113.46(12)
F(2)-C(7)-C(1)	112.60(12)
F(3)-C(7)-C(1)	112.02(12)
C(9)-C(8)-C(4)	126.48(12)
C(9)-C(8)-H(8)	116.8
C(4)-C(8)-H(8)	116.8
C(8)-C(9)-C(10)	124.85(11)
C(8)-C(9)-H(9)	117.6
C(10)-C(9)-H(9)	117.6
C(17)-C(10)-C(9)	118.99(11)
C(17)-C(10)-C(11)	125.03(11)
C(9)-C(10)-C(11)	115.97(10)
C(16)-C(11)-C(12)	118.93(12)
C(16)-C(11)-C(10)	120.52(11)
C(12)-C(11)-C(10)	120.27(11)
C(13)-C(12)-C(11)	120.50(13)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	120.07(13)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	120.02(13)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.02(13)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(15)-C(16)-C(11)	120.45(12)
C(15)-C(16)-H(16)	119.8
C(11)-C(16)-H(16)	119.8
C(10)-C(17)-C(18)	129.99(11)

C(10)-C(17)-H(17)	115.0
C(18)-C(17)-H(17)	115.0
C(17)-C(18)-C(23)	112.23(10)
C(17)-C(18)-C(21)	111.22(10)
C(23)-C(18)-C(21)	109.30(10)
C(17)-C(18)-C(19)	106.21(10)
C(23)-C(18)-C(19)	106.14(10)
C(21)-C(18)-C(19)	111.62(11)
C(20)-C(19)-C(18)	115.08(12)
C(20)-C(19)-H(19A)	108.5
C(18)-C(19)-H(19A)	108.5
C(20)-C(19)-H(19B)	108.5
C(18)-C(19)-H(19B)	108.5
H(19A)-C(19)-H(19B)	107.5
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(18)	114.28(12)
C(22)-C(21)-H(21A)	108.7
C(18)-C(21)-H(21A)	108.7
C(22)-C(21)-H(21B)	108.7
C(18)-C(21)-H(21B)	108.7
H(21A)-C(21)-H(21B)	107.6
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(1)-C(23)-O(2)	123.32(12)
O(1)-C(23)-C(18)	123.25(12)
O(2)-C(23)-C(18)	113.32(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 21JUL08. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	60(1)	22(1)	63(1)	6(1)	-11(1)	6(1)
F(2)	32(1)	52(1)	71(1)	27(1)	19(1)	21(1)
F(3)	60(1)	46(1)	36(1)	20(1)	14(1)	16(1)
O(1)	30(1)	20(1)	35(1)	-2(1)	12(1)	3(1)
O(2)	29(1)	20(1)	31(1)	-2(1)	13(1)	-2(1)
C(1)	21(1)	23(1)	27(1)	6(1)	6(1)	4(1)
C(2)	22(1)	29(1)	23(1)	2(1)	1(1)	1(1)
C(3)	23(1)	22(1)	25(1)	-2(1)	5(1)	-1(1)
C(4)	19(1)	20(1)	23(1)	2(1)	6(1)	2(1)
C(5)	29(1)	24(1)	25(1)	-2(1)	-2(1)	5(1)
C(6)	30(1)	21(1)	29(1)	-2(1)	1(1)	4(1)
C(7)	28(1)	26(1)	32(1)	7(1)	4(1)	5(1)
C(8)	22(1)	18(1)	24(1)	1(1)	8(1)	2(1)
C(9)	22(1)	17(1)	23(1)	0(1)	8(1)	1(1)
C(10)	20(1)	17(1)	22(1)	2(1)	8(1)	1(1)
C(11)	21(1)	16(1)	18(1)	3(1)	3(1)	3(1)
C(12)	23(1)	23(1)	28(1)	2(1)	8(1)	1(1)
C(13)	26(1)	22(1)	34(1)	1(1)	0(1)	-2(1)
C(14)	36(1)	20(1)	26(1)	-3(1)	-2(1)	4(1)
C(15)	36(1)	27(1)	22(1)	1(1)	7(1)	8(1)
C(16)	25(1)	21(1)	22(1)	3(1)	7(1)	2(1)
C(17)	24(1)	17(1)	23(1)	-1(1)	6(1)	2(1)
C(18)	22(1)	18(1)	21(1)	1(1)	4(1)	2(1)
C(19)	32(1)	24(1)	21(1)	0(1)	2(1)	0(1)
C(20)	38(1)	41(1)	25(1)	6(1)	-1(1)	3(1)
C(21)	24(1)	27(1)	31(1)	4(1)	8(1)	3(1)
C(22)	32(1)	33(1)	52(1)	6(1)	15(1)	-4(1)
C(23)	23(1)	20(1)	17(1)	1(1)	2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 21JUL08.

	x	y	z	U(eq)
H(2A)	9491	401	5493	39
H(2)	4842	3399	-3331	32
H(3)	6013	2563	-2077	29
H(5)	7856	3575	1969	34
H(6)	6692	4413	713	35
H(8)	7643	2094	113	26
H(9)	8959	2774	2898	25
H(12)	7727	1070	2316	30
H(13)	7146	292	351	36
H(14)	8306	95	-1387	37
H(15)	10048	676	-1166	34
H(16)	10616	1466	767	28
H(17)	10479	2281	4942	26
H(19A)	11961	1982	7437	33
H(19B)	10828	1573	7488	33
H(20A)	12611	1252	9590	56
H(20B)	13315	1160	8264	56
H(20C)	12187	728	8217	56
H(21A)	13007	1072	5431	33
H(21B)	12228	1328	3618	33
H(22A)	12698	2330	4705	58
H(22B)	13914	1961	4776	58
H(22C)	13566	2048	6442	58

X-ray structure of 5a

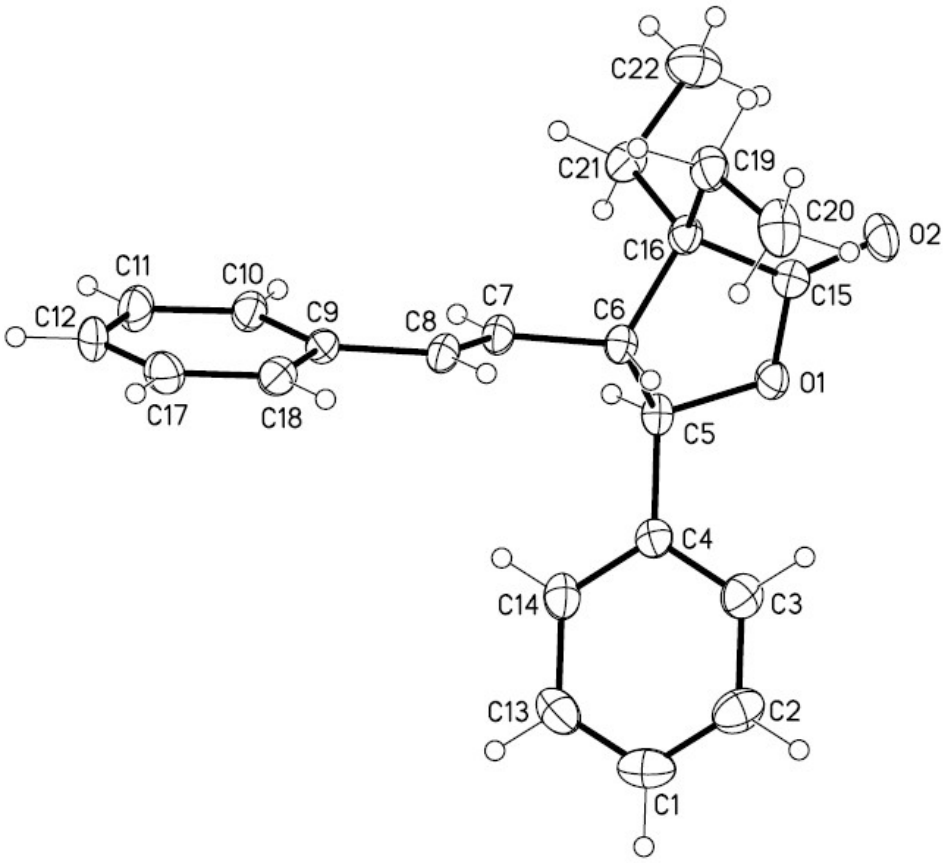


Table 1. Molecular structure and labeling scheme of **5a** with thermal ellipsoids at 50% probability level.

CCDC No	1988572	
Empirical formula	C22 H24 O2	
Formula weight	320.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.8570(6) Å	α= 90°.
	b = 10.6978(9) Å	β= 105.428(5)°.
	c = 11.0526(10) Å	γ = 90°.
Volume	895.52(13) $Å^3$	
Z	2	
Density (calculated)	1.188 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	344	

Crystal size	0.12 x 0.03 x 0.02 mm^3
Theta range for data collection	1.911 to 26.417°.
Index ranges	-9<=h<=9, -12<=k<=12, -13<=l<=13
Reflections collected	8878
Independent reflections	3288 [R(int) = 0.0240]
Completeness to theta = 25.242°	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9485 and 0.8079
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3288 / 1 / 220
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0827
R indices (all data)	R1 = 0.0401, wR2 = 0.0854
Absolute structure parameter	-0.7(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.210 and -0.148 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5243(2)	7260(2)	767(1)	22(1)
O(2)	6726(2)	6241(2)	-388(2)	28(1)
C(1)	3693(3)	7941(3)	4794(2)	34(1)
C(2)	4553(3)	6983(3)	4364(2)	34(1)
C(3)	5132(3)	7143(3)	3294(2)	28(1)
C(4)	4819(3)	8267(2)	2629(2)	20(1)
C(5)	5360(3)	8452(2)	1434(2)	20(1)
C(6)	7280(3)	8880(2)	1581(2)	19(1)
C(7)	7548(3)	10249(2)	1814(2)	21(1)
C(8)	8824(3)	10738(2)	2726(2)	20(1)
C(9)	9158(3)	12077(2)	3017(2)	20(1)
C(10)	8180(3)	13029(2)	2281(2)	23(1)
C(11)	8521(3)	14277(2)	2610(2)	28(1)
C(12)	9849(3)	14602(3)	3664(3)	31(1)
C(13)	3400(3)	9064(3)	4149(2)	32(1)
C(14)	3949(3)	9227(3)	3064(2)	27(1)
C(15)	6563(3)	7170(2)	182(2)	20(1)
C(16)	7645(3)	8367(2)	361(2)	21(1)
C(17)	10842(3)	13672(3)	4394(2)	30(1)
C(18)	10497(3)	12426(2)	4071(2)	24(1)
C(19)	9596(3)	8111(2)	464(2)	28(1)
C(20)	10485(3)	7149(3)	1447(3)	33(1)
C(21)	6831(3)	9236(3)	-767(2)	28(1)
C(22)	6706(4)	8693(3)	-2055(2)	38(1)

Table 3. Bond lengths [Å] and angles [°] for **5a**.

O(1)-C(15)	1.364(3)
O(1)-C(5)	1.464(3)
O(2)-C(15)	1.202(3)
C(1)-C(2)	1.380(4)
C(1)-C(13)	1.384(4)
C(1)-H(1)	0.9500
C(2)-C(3)	1.387(4)
C(2)-H(3)	0.9500
C(3)-C(4)	1.396(3)
C(3)-H(4)	0.9500
C(4)-C(14)	1.389(3)
C(4)-C(5)	1.504(3)
C(5)-C(6)	1.543(3)
C(5)-H(22)	1.0000
C(6)-C(7)	1.493(3)
C(6)-C(16)	1.551(3)
C(6)-H(5)	1.0000
C(7)-C(8)	1.325(3)
C(7)-H(11)	0.9500
C(8)-C(9)	1.477(3)
C(8)-H(10)	0.9500
C(9)-C(18)	1.397(3)
C(9)-C(10)	1.399(3)
C(10)-C(11)	1.391(4)
C(10)-H(6)	0.9500
C(11)-C(12)	1.385(4)
C(11)-H(9)	0.9500
C(12)-C(17)	1.384(4)
C(12)-H(2)	0.9500
C(13)-C(14)	1.389(4)
C(13)-H(24)	0.9500
C(14)-H(23)	0.9500
C(15)-C(16)	1.520(3)
C(16)-C(19)	1.532(3)

C(16)-C(21)	1.550(3)
C(17)-C(18)	1.387(4)
C(17)-H(8)	0.9500
C(18)-H(7)	0.9500
C(19)-C(20)	1.525(4)
C(19)-H(16)	0.9900
C(19)-H(12)	0.9900
C(20)-H(15)	0.9800
C(20)-H(13)	0.9800
C(20)-H(14)	0.9800
C(21)-C(22)	1.516(4)
C(21)-H(17)	0.9900
C(21)-H(18)	0.9900
C(22)-H(20)	0.9800
C(22)-H(21)	0.9800
C(22)-H(19)	0.9800

C(15)-O(1)-C(5)	110.26(16)
C(2)-C(1)-C(13)	119.8(2)
C(2)-C(1)-H(1)	120.1
C(13)-C(1)-H(1)	120.1
C(1)-C(2)-C(3)	120.2(3)
C(1)-C(2)-H(3)	119.9
C(3)-C(2)-H(3)	119.9
C(2)-C(3)-C(4)	120.3(2)
C(2)-C(3)-H(4)	119.9
C(4)-C(3)-H(4)	119.9
C(14)-C(4)-C(3)	119.2(2)
C(14)-C(4)-C(5)	119.1(2)
C(3)-C(4)-C(5)	121.6(2)
O(1)-C(5)-C(4)	109.41(18)
O(1)-C(5)-C(6)	103.89(17)
C(4)-C(5)-C(6)	116.31(17)
O(1)-C(5)-H(22)	109.0
C(4)-C(5)-H(22)	109.0
C(6)-C(5)-H(22)	109.0

C(7)-C(6)-C(5)	113.47(18)
C(7)-C(6)-C(16)	116.58(19)
C(5)-C(6)-C(16)	101.84(17)
C(7)-C(6)-H(5)	108.2
C(5)-C(6)-H(5)	108.2
C(16)-C(6)-H(5)	108.2
C(8)-C(7)-C(6)	124.2(2)
C(8)-C(7)-H(11)	117.9
C(6)-C(7)-H(11)	117.9
C(7)-C(8)-C(9)	127.1(2)
C(7)-C(8)-H(10)	116.5
C(9)-C(8)-H(10)	116.5
C(18)-C(9)-C(10)	117.8(2)
C(18)-C(9)-C(8)	119.4(2)
C(10)-C(9)-C(8)	122.8(2)
C(11)-C(10)-C(9)	120.6(2)
C(11)-C(10)-H(6)	119.7
C(9)-C(10)-H(6)	119.7
C(12)-C(11)-C(10)	120.6(2)
C(12)-C(11)-H(9)	119.7
C(10)-C(11)-H(9)	119.7
C(17)-C(12)-C(11)	119.5(2)
C(17)-C(12)-H(2)	120.3
C(11)-C(12)-H(2)	120.3
C(1)-C(13)-C(14)	120.4(2)
C(1)-C(13)-H(24)	119.8
C(14)-C(13)-H(24)	119.8
C(4)-C(14)-C(13)	120.0(2)
C(4)-C(14)-H(23)	120.0
C(13)-C(14)-H(23)	120.0
O(2)-C(15)-O(1)	120.5(2)
O(2)-C(15)-C(16)	129.1(2)
O(1)-C(15)-C(16)	110.36(19)
C(15)-C(16)-C(19)	111.9(2)
C(15)-C(16)-C(21)	107.66(17)
C(19)-C(16)-C(21)	110.91(19)

C(15)-C(16)-C(6)	100.68(17)
C(19)-C(16)-C(6)	114.32(17)
C(21)-C(16)-C(6)	110.8(2)
C(12)-C(17)-C(18)	119.9(2)
C(12)-C(17)-H(8)	120.0
C(18)-C(17)-H(8)	120.0
C(17)-C(18)-C(9)	121.5(2)
C(17)-C(18)-H(7)	119.2
C(9)-C(18)-H(7)	119.2
C(20)-C(19)-C(16)	115.6(2)
C(20)-C(19)-H(16)	108.4
C(16)-C(19)-H(16)	108.4
C(20)-C(19)-H(12)	108.4
C(16)-C(19)-H(12)	108.4
H(16)-C(19)-H(12)	107.4
C(19)-C(20)-H(15)	109.5
C(19)-C(20)-H(13)	109.5
H(15)-C(20)-H(13)	109.5
C(19)-C(20)-H(14)	109.5
H(15)-C(20)-H(14)	109.5
H(13)-C(20)-H(14)	109.5
C(22)-C(21)-C(16)	115.8(2)
C(22)-C(21)-H(17)	108.3
C(16)-C(21)-H(17)	108.3
C(22)-C(21)-H(18)	108.3
C(16)-C(21)-H(18)	108.3
H(17)-C(21)-H(18)	107.4
C(21)-C(22)-H(20)	109.5
C(21)-C(22)-H(21)	109.5
H(20)-C(22)-H(21)	109.5
C(21)-C(22)-H(19)	109.5
H(20)-C(22)-H(19)	109.5
H(21)-C(22)-H(19)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	18(1)	28(1)	-5(1)	9(1)	-6(1)
O(2)	27(1)	22(1)	35(1)	-11(1)	8(1)	-5(1)
C(1)	26(1)	52(2)	26(1)	0(1)	9(1)	-5(1)
C(2)	32(1)	37(2)	31(1)	12(1)	6(1)	4(1)
C(3)	24(1)	26(2)	32(1)	4(1)	7(1)	5(1)
C(4)	15(1)	21(1)	24(1)	-2(1)	4(1)	-2(1)
C(5)	20(1)	16(1)	24(1)	-2(1)	3(1)	0(1)
C(6)	17(1)	16(1)	22(1)	0(1)	4(1)	0(1)
C(7)	20(1)	15(1)	27(1)	1(1)	6(1)	1(1)
C(8)	20(1)	15(1)	26(1)	2(1)	6(1)	1(1)
C(9)	21(1)	18(1)	24(1)	-2(1)	10(1)	-3(1)
C(10)	23(1)	19(1)	28(1)	0(1)	8(1)	-2(1)
C(11)	32(1)	18(1)	38(1)	3(1)	12(1)	4(1)
C(12)	42(1)	16(1)	38(2)	-7(1)	18(1)	-7(1)
C(13)	27(1)	34(2)	35(1)	-11(1)	11(1)	-1(1)
C(14)	26(1)	20(1)	34(1)	-3(1)	7(1)	-2(1)
C(15)	17(1)	21(1)	22(1)	0(1)	4(1)	0(1)
C(16)	20(1)	18(1)	24(1)	-2(1)	6(1)	-3(1)
C(17)	34(1)	28(2)	27(1)	-9(1)	10(1)	-9(1)
C(18)	26(1)	23(1)	24(1)	1(1)	7(1)	-2(1)
C(19)	22(1)	23(1)	40(1)	-5(1)	12(1)	-5(1)
C(20)	18(1)	28(2)	50(2)	-5(1)	4(1)	3(1)
C(21)	30(1)	24(2)	29(1)	4(1)	9(1)	-2(1)
C(22)	41(2)	47(2)	28(1)	4(1)	11(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **5a**.

	x	y	z	U(eq)
H(1)	3304	7831	5530	41
H(3)	4750	6210	4803	40
H(4)	5744	6486	3012	33
H(22)	4539	9065	891	24
H(5)	8059	8423	2309	23
H(11)	6753	10806	1275	25
H(10)	9609	10164	3250	24
H(6)	7275	12822	1550	28
H(9)	7836	14914	2108	34
H(2)	10076	15456	3883	37
H(24)	2819	9727	4450	38
H(23)	3730	9996	2620	32
H(8)	11758	13886	5117	35
H(7)	11188	11796	4579	29
H(16)	9702	7825	-365	33
H(12)	10252	8909	657	33
H(15)	9826	6361	1288	50
H(13)	10501	7458	2285	50
H(14)	11698	7008	1401	50
H(17)	5629	9474	-729	33
H(18)	7545	10010	-671	33
H(20)	5970	7939	-2178	57
H(21)	7891	8478	-2120	57
H(19)	6175	9311	-2700	57

7. Computational Details

All geometries were calculated at the wB97X-D level of theory.[1] The palladium and cesium atoms were fully described by the SDD basis set, and the rest of the atoms were described by the def2-SVP basis set (BS1 basis set).[2] All geometry computations were performed with ultrafine integration grid (integral(Grid=*UltraFine*)) with Gaussian 16 rev.B program.[3] The ground states and transition states geometries were confirmed by the absence and presence of the imaginary frequency. Then single point energy withn toluene solvent at the same level of theory was used within the SMD solvation model.[4] In order to provide more precise energy, we choose wB97M-V[5] functional which is one of the best performing in the reaction energies and reaction barriers benchmark for metalorganic molecules.[6] Therefore, resulting structures were used for the energy (single points) calculations at wB97M-V/def2-TZVPP/def2-SD (BS2 basis set) level of theory with Orca 4.2.1 software in a vacuum.[7] The def2-SD effective core potential basis set was used for palladium and cesium atoms together with tight SCF criteria. We reported solvated electronic energies ($\Delta E_{toluene}$(wB97M-V/BS2//wB97X-D/BS1)) as it better describe the system with many low frequenscies modes and compounent changes than usually used Gibbs Free energies (also reported here). Post-processing visualization was carried out with the ChemCraft software.[10]

Density functional theory (DFT) calculations were carried out to provide suggestions for the plausible mechanism. *Cis*- and *trans*-1-bromopropene and (*Z*)- and (*E*)-β-phenyl vinyl bromide (**4a** and **2d**) were used as the model substrates to represent alkyl and aryl vinyl bromide substrates, respectively. After the oxidative addition to give the alkenyl-Pd bromide intermediates, the reactions with Cs-carboxylate **1a** (**Cs-1a**) were evaluated. In the case of **2d**, the transition state (TS) energy barrier of the β-alkenylpalladation to **Cs-1a** (where Pd is added β to COOCs, e.g. 1,2-insertion of **Cs-1a** to the alkenyl-Pd bond) is 14.1 kcal/mol and over 23 kcal/mol more favorable than those for γ-alkenylpalladation (2,1-insertion of **Cs-1a**) and C−H activation and oxapalladation (lactonization) of **Cs-1a** pathways, respectively, in good agreement of the excellent regioselectivity a Heck-type process (See Figure S2). Similar trends of reactivity was also observed for *cis*- and *trans*-1-bromopropene, consistent with the formation of Heck-type products when alkyl-vinyl bromides were employed (See Figure S3 and S4). In contrast to these similar reaction profiles for **2d** and 1-bromopropenes, when **4a** was used, the steric interactions between

the (*Z*)-phenyl group to Pd and coordinated **Cs-1a**, appeared to substantially increase the energy barriers. Attempts to locate meaningful structures failed, but the results indicated that the energy difference between the γ-alkenylpalladation and the oxapalladation transition states became much smaller (3.9 kcal/mol) (See Figure S5). While the preliminary computational study was not able to suggest the reaction pathway leading to the alkenylative lactonization product for **4a**, striking differences were observed when compared with substrates that gave Heck-type alkenylation products, γ-alkenylpalladation and oxapalladation may be feasible. We therefore proposed that selective carbopalladation (pathway I, most favorable) at the β-position of **B'** may occur to give **C'-Pd-6** or **B'** may undergo oxapalladation to give **D** (pathway II). After sequential β-Hydride elimination, *E*/*Z* isomerization, carboxypalladation and reductive elimination from intermediate **C'-Pd-6** to give the lactone product **5**. (See Figure S6).

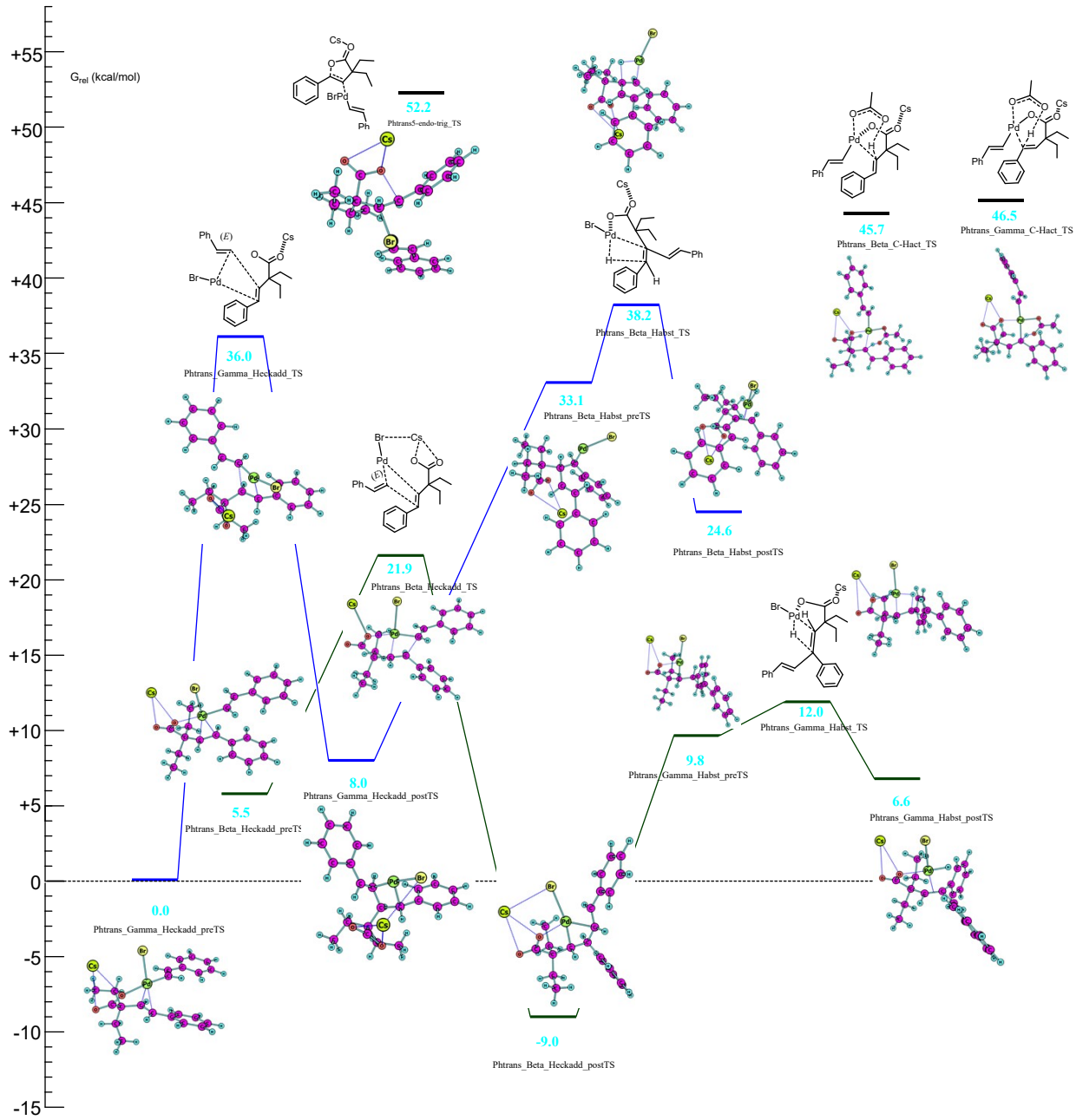


Fig. S2 Model reaction profile of (*E*)-β-phenyl vinyl bromide after oxidation addition.

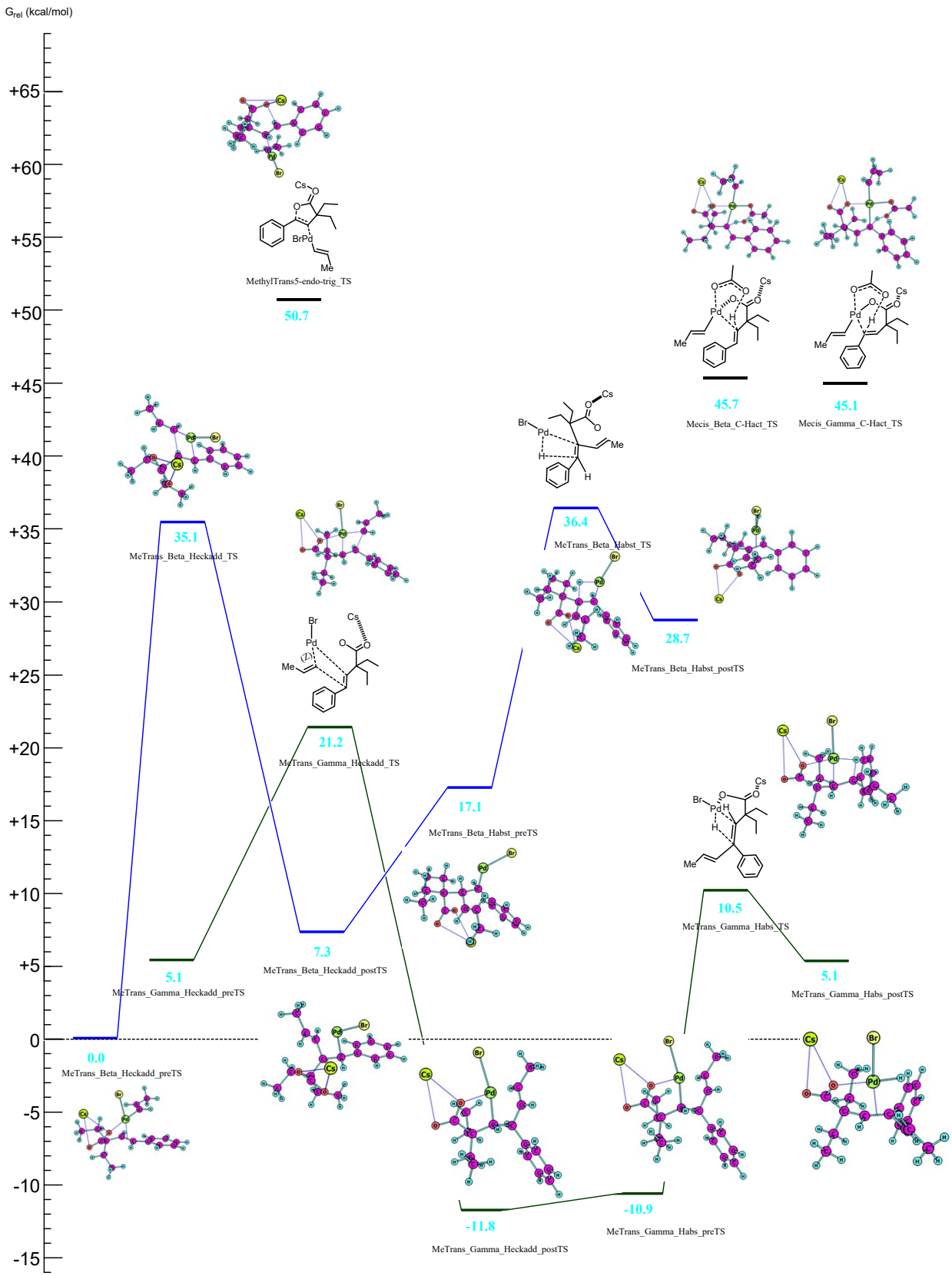


Fig. S3 Model reaction profile of *trans*-1-bromopropene after oxidation addition.

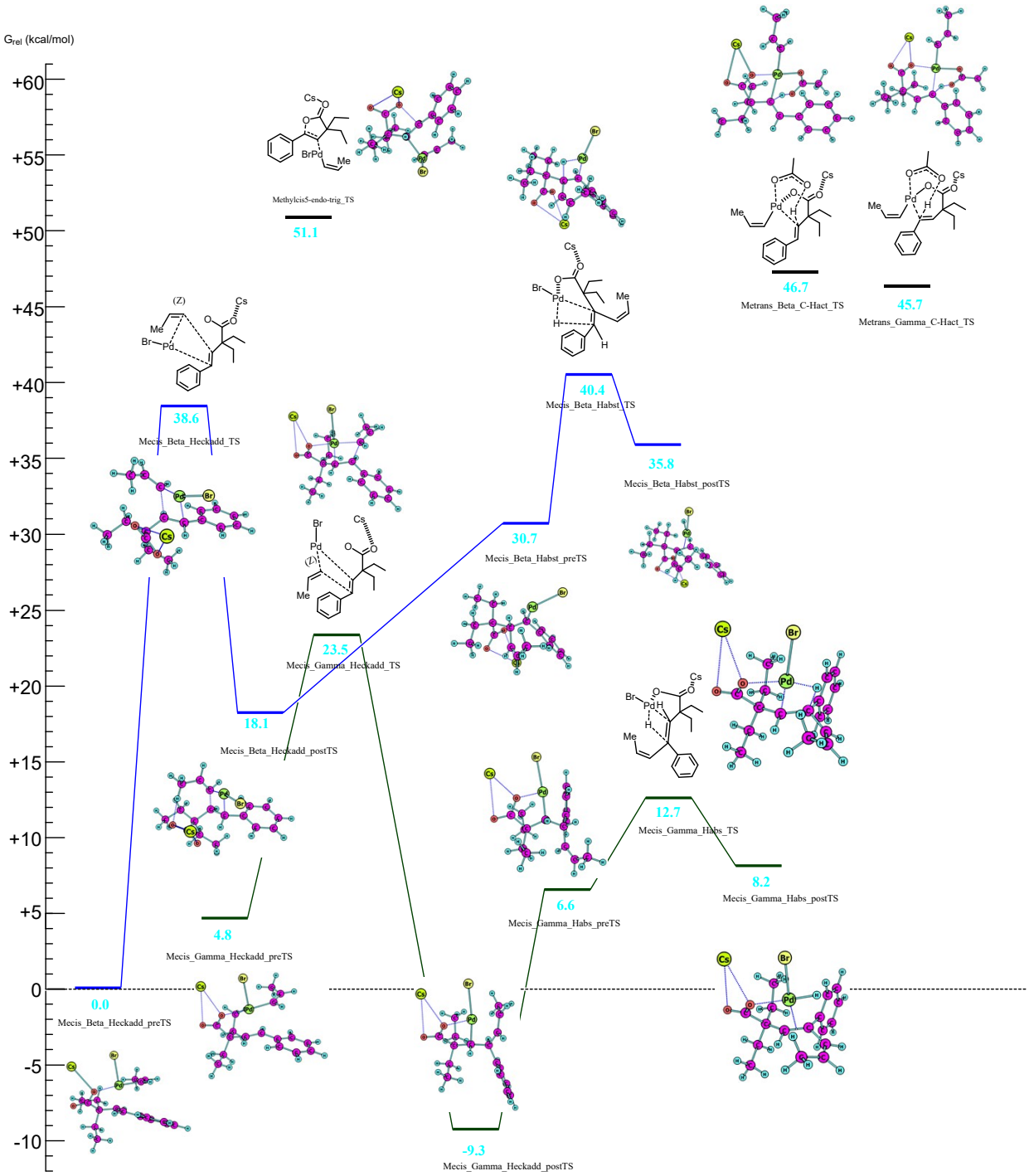


Fig. S4 Model reaction profile of *cis*-1-bromopropene after oxidation addition.

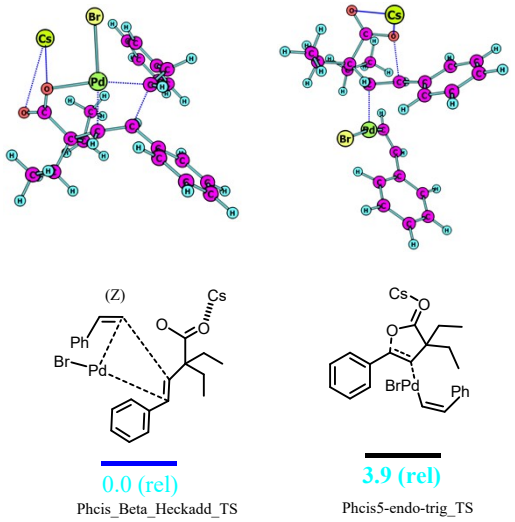


Fig. S5 Computationally located transition states of Heck addition and lactonization for (Z)-β-phenyl vinyl bromide.

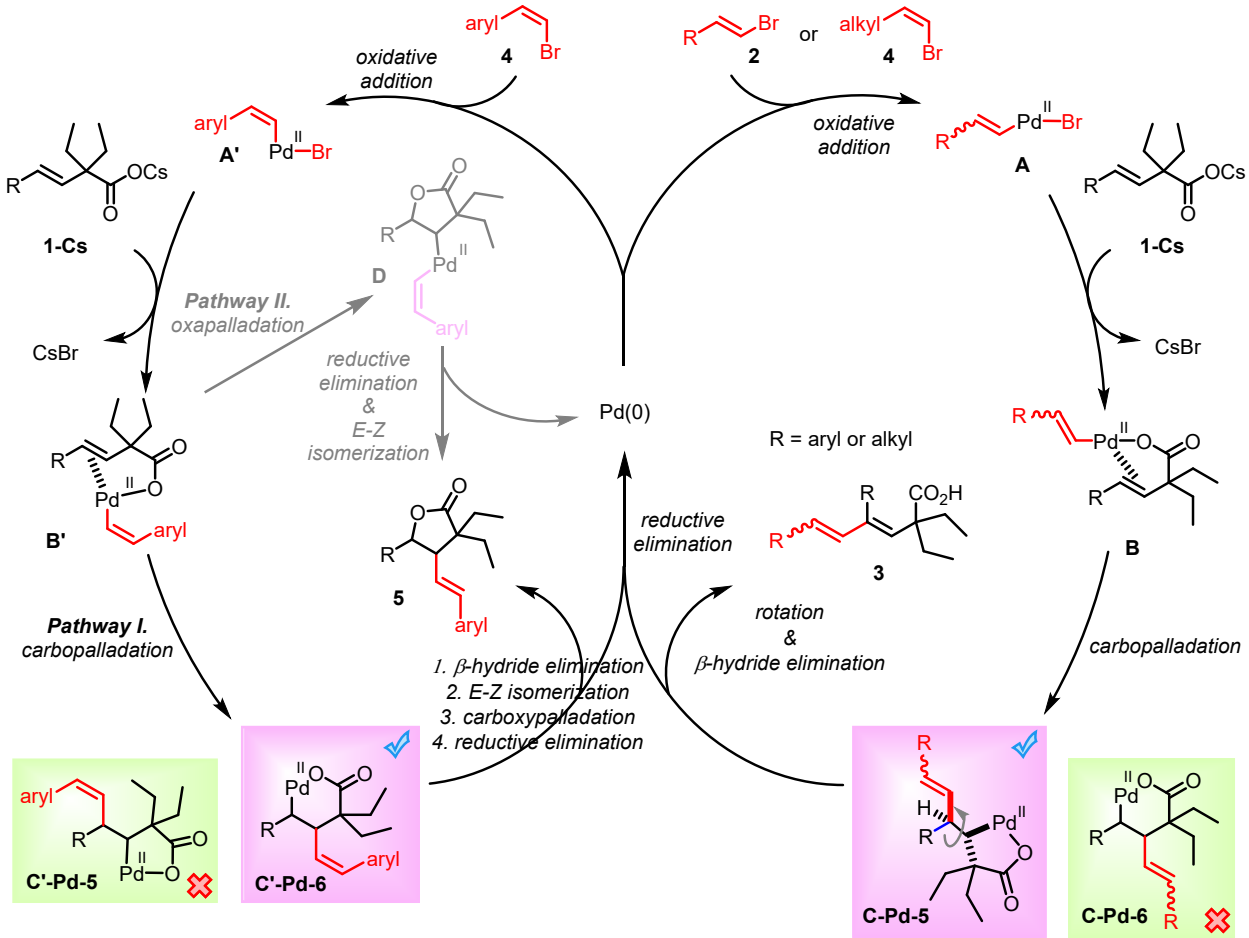


Fig. S6 Proposed mechanisms

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1. Zhao, Y. D.; Truhlar, G. *J. Chem. Phys* **2006**, *125*, 194101.
2. (a) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys* **1987**, *86*, 866. (b) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. *Theor. Chim. Acta* **1990**, *77*, 123. (c) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuß, H. *Mol. Phys.* **1993**, *80*, 1431. (d) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
3. (a) Weigend, F. *Phys Chem Chem Phys* **2006**, *8*, 1057. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Ding, Williams, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. Kitao,; O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J.; *Gaussian 16, Revision B.01, Gaussian Inc.*, Wallingford, CT, **2016**.
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7. (a) F. Neese, *WIRES Comp Mol Sci* **2012**, *2*, 73. (b) Neese, F. *WIRES Comp Mol Sci* **2018**, *8*, e1327.
8. (a) Ryu, H.; Park, J.; Kim, H. K.; Park, J. Y.; Kim, S.-T.; Baik, M.-H.; *Organometallics* **2018**, *37*, 3228. (b) Martin, R. L.; Hay, P. J.; Pratt, L. R. *J. Phys. Chem. A* **1998**, *102*, 3565. (c) Bühl, M.; Sieffert, N.; Wipff, G. *Chem. Phys. Lett.* **2009**, *467*, 287.
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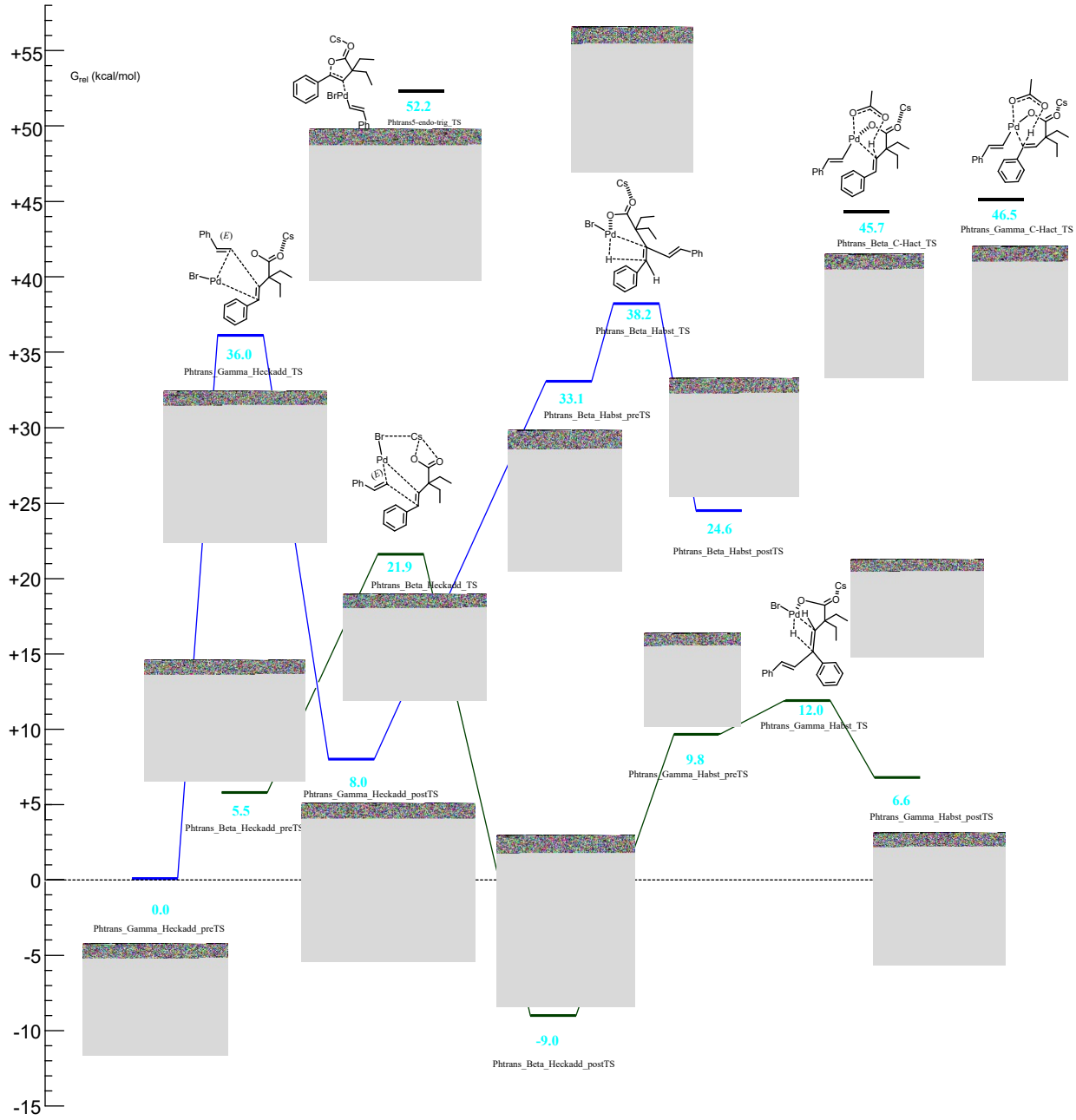
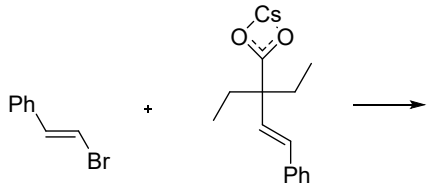


Fig. S2 Model reaction profile of (*E*)-β-phenyl vinyl bromide after oxidation addition.



Cs-1a

			wB97X-D/BS1					wB97M-V/BS2
	1st frequency (cm-1)	Electronic energy	ZPE corr	Thermal corr	Enthalpy corr:	Gibbs corr	Electronic energy in toluene	Electronic energy
Phtrans_Beta_C-Hact_TS	-1178.4	-1378.6326	0.454594	0.503638	0.504851	0.356906	-1378.667289	-1379.726104
Phtrans_Gamma_C-Hact_TS	-1231.1	-1378.63047	0.454423	0.503568	0.504782	0.356042	-1378.665014	-1379.724195
Phtrans_Gamma_Heckadd_preTS	16.8	-3724.3734	0.408193	0.453109	0.454322	0.312926	-3724.41118	-3725.321127
Phtrans_Gamma_Heckadd_TS	-210.4	-3724.31749	0.407706	0.451877	0.45309	0.313377	-3724.351293	-3725.268165
Phtrans_Gamma_Heckadd_postTS	16.9	-3724.37745	0.411364	0.455019	0.456232	0.319534	-3724.411542	-3725.318616
Phtrans_Beta_Heckadd_preTS	16.1	-3724.3632	0.408474	0.453447	0.45466	0.314211	-3724.400413	-3725.31416
Phtrans_Beta_Heckadd_TS	-329.8	-3724.3366	0.407656	0.45172	0.452933	0.313652	-3724.374494	-3725.286845
Phtrans_Beta_Heckadd_postTS	18.5	-3724.39328	0.410676	0.454516	0.455729	0.317548	-3724.429857	-3725.341168
Phtrans_Beta_Habst_preTS	22.4	-3724.34203	0.410457	0.453975	0.455188	0.320273	-3724.379173	-3725.276389
Phtrans_Beta_Habst_TS	-426.6	-3724.32416	0.406027	0.449985	0.451198	0.314126	-3724.362832	-3725.260477
Phtrans_Beta_Habst_postTS	11.7	-3724.34028	0.407241	0.451728	0.452942	0.314137	-3724.379726	-3725.28147
Phtrans_Gamma_Habst_preTS	12.3	-3724.35735	0.407881	0.452351	0.453565	0.311205	-3724.396809	-3725.302126
Phtrans_Gamma_Habst_TS	-754.9	-3724.35308	0.40522	0.449239	0.450452	0.311444	-3724.39127	-3725.300039
Phtrans_Gamma_Habst_postTS	17.9	-3724.36344	0.406979	0.451525	0.452738	0.313188	-3724.400321	-3725.311741
PhtransS-endo-trig_TS	-320.8	-3724.29531	0.408104	0.452127	0.45334	0.314672	-3724.337026	-3725.235642

Cartesian Coordinates

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C -4.7203501075 1.0620360357 -0.7066515827
C -2.9251995283 2.6176474408 -1.0959620367
C -5.6504360014 2.072410746 -0.9318195012
H -5.061762069 0.0537161513 -0.4580826503
C -3.8549593123 3.6319996631 -1.3243075617
H -1.8567156405 2.828582428 -1.1764889831
C -5.2199279446 3.3657216817 -1.2365382275
H -6.7186023816 1.8517191 -0.8682099756
H -3.5051848924 4.6359375411 -1.5749974683
H -5.9487607663 4.1594916331 -1.4163726045
C 1.1129443949 3.577178 1.1634964527
H 0.9636572062 4.2387070461 2.0325372848
C 2.224124787 3.7215443028 0.4196315552
H 2.3498034548 3.0621094469 -0.4504665358
C 3.4007874251 4.5667902698 0.7121040651
C 4.5908149097 4.342101774 -0.0023298832
C 3.4306410493 5.5263991587 1.7395349024
C 5.7644953264 5.0305261132 0.3022433268
H 4.5863918704 3.6126574636 -0.8187774642

C 4.5994763357 6.2174593458 2.04211113
H 2.5192580353 5.7363466682 2.3036433999
C 5.7763170729 5.9707536525 1.3307418579
H 6.6726230733 4.8366543944 -0.2738758795
H 4.5930741972 6.9627918944 2.8411641657
H 6.6912433761 6.5163407797 1.5710467957
Cs 3.6379799661 1.1709072727 1.9903221623

Phtrans_Gamma_C-Hact_TS
C 0.2325438245 1.5841316291 0.1728210309
H 0.0358258561 0.275095758 0.7210255046
C 1.0679761531 -1.4266526497 0.7747814304
C 1.9240966143 -2.4093820436 1.5184821791
O 0.2868214729 -0.685700348 1.4456856033
O 1.1889881131 -1.3418175987 -0.471611834
H 2.2546566482 -3.2160653803 0.8546134443
H 2.8079734483 -1.8650972616 1.8847694539
H 1.3857691806 -2.8067241937 2.3875599974
Pd -0.0751031043 0.0242671624 -1.3669768129
O -1.501002466 1.1876899323 -2.272196602
C -0.6526841963 2.5971854795 0.1139108354
H -0.2946317891 3.5849549714 0.4436057519
C -2.0951906896 2.6242141845 -0.3500484617
C -2.3945523421 1.896178969 -1.6785161164
O -3.5297152738 2.0171229596 -2.1480954505
C -3.0421605664 2.0170783518 0.7222107365
H -2.8181489306 2.5021667549 1.6868810772
H -4.0667616349 2.3118460324 0.4459244242
C -2.5084610496 4.1025441482 -0.5603064933
H -3.5823303381 4.1245511554 -0.7936216626
H -2.3737317769 4.6299593037 0.3997748198
C -1.7407617877 4.8216219878 -1.6640661101
H -1.9281393378 4.3523087781 -2.642033058
H -2.0534150089 5.8740918376 -1.7350945362
H -0.6539181225 4.8061746655 -1.4892666303
C -2.9921843028 0.5036151447 0.8860851807
H -2.0121847669 0.1479568438 1.2278252918
H -3.7399268634 0.1738260138 1.6231254921
H -3.2189494472 -0.0081593921 -0.0640295915
C 1.5986302978 1.8906120371 0.6967150609
C 2.7464692111 1.5035525346 -0.0120334665
C 1.7738962933 2.5385152832 1.9288606497
C 4.0208553898 1.7731330355 0.4836998
H 2.6326558466 0.9907399054 -0.9701090027
C 3.0470746183 2.8069885652 2.427414112
H 0.8910155642 2.8189395789 2.509050026

C 4.1779255392 2.4258700891 1.7061357761
H 4.8988744039 1.471043953 -0.0923989036
H 3.1564879636 3.3109087258 3.3909171699
H 5.1769353474 2.6325175608 2.0968367301
C -0.3677111869 -1.1888042598 -2.9179616257
H -0.3525349418 -0.6651296657 -3.889777106
C -0.8117854958 -2.457557273 -2.8872003826
H -0.8679556019 -2.9856187297 -1.9269517578
C -1.425106693 -3.16432987 -4.0330830818
C -2.3995216785 -4.1484438958 -3.7905796725
C -1.188239477 -2.7982620806 -5.3708750667
C -3.1378317589 -4.7110748201 -4.8309182129
H -2.589129356 -4.4614566395 -2.7595944126
C -1.9247837438 -3.3590733703 -6.4108142191
H -0.4112249424 -2.0633794967 -5.593603352
C -2.9129961455 -4.3106471887 -6.1478066796
H -3.8926815052 -5.470026122 -4.6111280004
H -1.7178718995 -3.0590306033 -7.4410288554
H -3.4875883265 -4.7508049399 -6.9654598593
Cs -3.6499222384 -0.552305509 -3.6305395612

Phtrans_Gamma_Heckadd_preTS
C -1.4756274892 1.377949491 -3.532823105
C -1.576566544 -0.1749800378 -0.8985693465
Pd -1.9262354962 -0.4610102213 -3.0131089641
C -1.8903506692 -2.6866627162 -1.0950281098
Br -1.3236312501 -1.2669775244 -5.2836342091
H -0.8408449224 0.6267698321 -0.7689393029
C -1.1072795677 -1.5392560905 -0.4079443676
C -2.8960704485 0.1905710311 -1.1347047871
H -3.6644690125 -0.5855435647 -1.0599476635
O -1.8761540898 -3.8177974693 -0.6124815689
O -2.4168220516 -2.4085574232 -2.2315999342
C 0.3792717663 -1.6911735233 -0.8480011895
H 0.9297121176 -0.8162681504 -0.4611627072
H 0.4170716831 -1.5945740403 -1.9477717827
C -1.2262950231 -1.636695982 1.1251378011
H -0.8717479782 -2.638231054 1.4085559544
H -0.533986592 -0.9058469836 1.5787698259
C -2.6307113688 -1.4427889173 1.6837309409
H -3.3348589485 -2.1539270452 1.2250922935
H -2.6395026987 -1.6232194282 2.7686649582
H -3.0110580994 -0.4240715892 1.5158697284
C 1.1041016051 -2.9627744163 -0.4197080268
H 0.5420494271 -3.8646713691 -0.701733354
H 2.1026623513 -3.0027590565 -0.8807471084

H 1.2443799054 -3.0074799032 0.6699346881
C -3.4227820651 1.5734646725 -1.173740178
C -4.7510570805 1.7685527304 -1.5762758348
C -2.6488069778 2.6981323744 -0.8553871697
C -5.2882455901 3.0493561433 -1.6753055221
H -5.363651033 0.8994517719 -1.8300320916
C -3.1838983094 3.9788315046 -0.9535344782
H -1.6111758473 2.5791399323 -0.5411707976
C -4.5039038772 4.1601833709 -1.3670471824
H -6.3235849046 3.180537754 -1.9970683839
H -2.5599485834 4.8420721368 -0.713500851
H -4.9209192363 5.1664560258 -1.4461616834
H -2.3426989496 1.9443301652 -3.9015249923
C -0.2815052584 1.9609145784 -3.3811105846
H 0.5713736146 1.3533875799 -3.0531433803
C 0.0253945446 3.3874317762 -3.6150703301
C -0.9736531726 4.3632447462 -3.7705895794
C 1.3637306367 3.8066950753 -3.6611186712
C -0.6429057797 5.6986666481 -3.9791086667
H -2.0251316863 4.0747178473 -3.7119701318
C 1.6965714588 5.1436786026 -3.8682482287
H 2.1569636472 3.0641469179 -3.5376075802
C 0.6936764844 6.0978425841 -4.0302638335
H -1.4386058712 6.4383223923 -4.0969962054
H 2.7471933616 5.4417056602 -3.9037650226
H 0.950442537 7.1472147041 -4.1912867919
Cs -1.1602426687 -4.5161465428 -3.7121244917

Phtrans_Gamma_Heckadd_TS
C -1.2840068268 2.0284929264 -2.6581656899
C -1.8847362125 0.6007576598 -1.107631382
Pd -2.8430342012 0.9280910319 -3.2170678243
C -1.0500057521 -1.577826343 -2.0224053471
Br -4.731907028 0.0101058209 -4.5577250258
H -1.6745492133 1.4824923067 -0.4934833311
C -0.8695577079 -0.5250825677 -0.8844304519
C -3.2685351516 0.30116841 -1.3093140091
H -3.5047768561 -0.7580287018 -1.4535384287
O -1.8473710485 -2.5183254733 -1.8194236969
O -0.4347829903 -1.3567102362 -3.0945096257
C 0.5773482473 0.010879315 -0.8618544118
H 0.6296709059 0.8593036351 -0.1554295735
H 0.8224689589 0.4104918164 -1.8473127676
C -1.1528254665 -1.1304219822 0.5287952956
H -0.5420437735 -2.0427991132 0.585925512
H -0.7309287437 -0.4314990366 1.2730552247

C -2.5696661378 -1.4980466457 0.9563028547
H -3.0202754314 -2.1894655164 0.2337807157
H -2.5290656894 -2.0021183792 1.9342029959
H -3.2244740665 -0.6223631231 1.0794522059
C 1.6422428735 -1.0223990061 -0.5069165891
H 1.5687354133 -1.8959409033 -1.1727685221
H 2.6449414073 -0.5892822564 -0.6394731779
H 1.5733543324 -1.3738134941 0.5327398745
C -4.3852536864 1.1231959427 -0.7814021546
C -5.6735712485 0.5715867223 -0.7849250315
C -4.2131757811 2.4207185178 -0.2778183364
C -6.7590120477 1.2926047882 -0.2979851238
H -5.8191423314 -0.4311021638 -1.192435232
C -5.2987377512 3.1438258781 0.2064754092
H -3.2224540933 2.8801834029 -0.2658837641
C -6.5757223666 2.5823421794 0.1990257676
H -7.7555277804 0.8465308398 -0.3114232285
H -5.1467647729 4.1537502365 0.5931925892
H -7.4268682151 3.1510587167 0.5793317084
H -1.4783099332 2.9906550843 -2.1697231873
C -0.1980478449 1.7665262034 -3.4063787538
H -0.0368666928 0.7181335012 -3.6950516516
C 0.8376675214 2.730500624 -3.8137126361
C 0.6668028778 4.1213300701 -3.726934037
C 2.0560669218 2.2353337003 -4.3025786051
C 1.6899301427 4.9860881325 -4.1009748384
H -0.2839741825 4.5310711297 -3.3786314606
C 3.081266875 3.1014058085 -4.675364842
H 2.196654741 1.1539590162 -4.378981918
C 2.902113487 4.4799344951 -4.5740694892
H 1.53925125 6.065634262 -4.0307409702
H 4.025037738 2.6973304243 -5.0481170902
H 3.7028258588 5.1613876096 -4.8694656404
Cs -2.4807415272 -2.7792882659 -4.6835323083

Phtrans_Gamma_Heckadd_postTS
C -0.832277487 1.8435021064 -1.6474143152
C -1.4484284046 0.7357750167 -0.7850886798
Pd -2.3077382558 1.6905647284 -3.228151018
C -0.7934681974 -1.4992250624 -1.8630769244
Br -4.0420509516 1.3217210497 -4.9560552988
H -1.6095692897 1.151507297 0.2212273327
C -0.6688585559 -0.6066487653 -0.5828407765
C -2.7701460523 0.6246935549 -1.528723012
H -2.9720646213 -0.378300494 -1.9222936899
O -1.800169572 -2.2368527376 -1.9554136313

O 0.0773881999 -1.3657827864 -2.7605514531
C 0.8095637749 -0.2789656151 -0.2907125485
H 0.8465243654 0.4594668278 0.5316542421
H 1.2496169771 0.2070224634 -1.1703442691
C -1.2676617064 -1.3364951629 0.6486542029
H -0.8598821606 -2.3583446816 0.6577793622
H -0.8658579823 -0.8379778036 1.5501121353
C -2.78498332 -1.4313044202 0.7871949452
H -3.2191879308 -1.9307785983 -0.087329664
H -3.038220951 -2.0185754942 1.6832586002
H -3.2627456953 -0.4470683619 0.9089625398
C 1.6800676662 -1.4810389056 0.0614866343
H 1.6355641507 -2.2324944877 -0.7407512166
H 2.7306536443 -1.1734841352 0.1737526063
H 1.3760173911 -1.9602963895 1.003702842
C -3.9809876895 1.3176974773 -1.0330827667
C -5.2417966994 0.8074239939 -1.3812258963
C -3.9258932749 2.4673849944 -0.2282522784
C -6.4074892427 1.4197443322 -0.937721668
H -5.296403882 -0.0772559371 -2.0190732305
C -5.0926250685 3.0843937375 0.2123053883
H -2.9599127739 2.890363245 0.0557164835
C -6.3370323374 2.5627537009 -0.1406352293
H -7.3781059733 1.0064628212 -1.2189201546
H -5.0304688348 3.9788681301 0.8356141571
H -7.2522947071 3.0478719551 0.2050874915
H -0.8611051597 2.8580645409 -1.234116894
C -0.1521427574 1.5982547086 -2.8295541886
H 0.1085802616 0.552906623 -3.0481155199
C 0.5194330849 2.6167822019 -3.6604984751
C 0.2246643931 3.9880701454 -3.5886330295
C 1.4829575299 2.1836450204 -4.5836355463
C 0.8826779941 4.8968941672 -4.4109889365
H -0.5400049677 4.3473676756 -2.8956466646
C 2.1442461316 3.0940706896 -5.4031695946
H 1.7168002335 1.1174944445 -4.6428143686
C 1.8451513422 4.4534360546 -5.3191347577
H 0.6383216281 5.9592581843 -4.3482013823
H 2.8963960516 2.7415340156 -6.1120860193
H 2.3584578284 5.1688769163 -5.9650373893
Cs -1.9838451461 -1.750625981 -4.8825164758

Phtrans_Beta_Heckadd_preTS
C 0.0457702492 2.1081710008 0.0304726742
C 0.1701687931 0.8054026777 -2.4108181601
Br -1.8619580631 1.9385644329 -4.3774661599

H -0.4727094969 1.2415837989 0.4490818537
O -2.3505114215 4.0361905495 -1.8491308742
C -0.6290871386 3.2958786482 -0.0707926903
H -0.0537037246 4.1786749795 -0.3646692117
C -2.005219836 3.6305553605 0.4809134247
C -2.8495407312 4.2011716423 -0.6796545119
O -3.9487740623 4.7080254981 -0.4655771976
C -2.773159105 2.4339750191 1.0890989592
H -2.1223170929 1.9413344857 1.8306711557
H -3.611479836 2.8625588866 1.6585953483
C -1.8655493016 4.7091224616 1.5820499539
H -2.8910424499 4.9493175455 1.9016426784
H -1.3515377553 4.2596177833 2.4488706997
C -1.1688778767 6.0028221648 1.1731338081
H -1.6309439995 6.4349416177 0.2719318618
H -1.2536726968 6.7488619335 1.9766827811
H -0.0952980803 5.8649912137 0.9755809638
C -3.3442736391 1.3983233175 0.1239177862
H -2.5775785582 0.9107872617 -0.4962420123
H -3.8773883541 0.6131917525 0.6800014638
H -4.0701531711 1.864462555 -0.5599362887
C 1.5114027786 1.9289892127 -0.095671849
C 2.3709122981 2.9395843324 -0.5492362826
C 2.0610977415 0.6869472627 0.2417570143
C 3.7382160284 2.7104985656 -0.6579174323
H 1.9693839929 3.9120859962 -0.8415641705
C 3.4312134292 0.4564888552 0.1380124137
H 1.4005060233 -0.1206357346 0.5654331489
C 4.2750300069 1.467940779 -0.3135051912
H 4.3918702759 3.5074052281 -1.0190573288
H 3.8341168067 -0.5251948379 0.394828456
H 5.34878823 1.2902560421 -0.4036944341
Pd -1.0025624029 2.3687612812 -2.1019180076
H 1.1774965657 1.0971061334 -2.7384682476
C -0.1497423191 -0.4775035089 -2.2130874378
H -1.1763342395 -0.7318101479 -1.9221115513
C 0.7607749725 -1.6336423561 -2.3405812802
C 0.2420971993 -2.9327109783 -2.2255951506
C 2.1442589066 -1.4983388245 -2.5481553073
C 1.0647868616 -4.0533827312 -2.320081228
H -0.8314441687 -3.0621080092 -2.0621784885
C 2.9670546106 -2.6159430234 -2.6441117233
H 2.585850911 -0.5028199336 -2.6235149223
C 2.4339049966 -3.9012066442 -2.5306522277
H 0.6320701214 -5.0525935578 -2.2288405874
H 4.0394723459 -2.4818568417 -2.8058250916

H 3.0826930514 -4.7768097593 -2.6043611402
Cs -4.7889716753 3.711527613 -3.3403572586

Phtrans_Beta_Heckadd_TS
C 0.0653989626 1.8906491361 -0.2905867083
C 0.1747393627 0.8969340608 -1.964836637
Br -2.2625369247 1.3838342434 -4.3729462981
H -0.4437572654 1.1393810489 0.3182920979
O -2.6073912651 3.9730857781 -1.9823231814
C -0.6511387043 3.127647548 -0.4537182313
H -0.0326320706 3.9917674655 -0.7190150774
C -1.9251133863 3.5441157448 0.2955779498
C -2.9377583531 4.1051130052 -0.7427557871
O -4.0091724386 4.5740528254 -0.3740948268
C -2.6269490463 2.3977742084 1.0592766401
H -1.8987941314 1.9359070378 1.7475646849
H -3.3891683555 2.8687394979 1.6977569278
C -1.5983450074 4.6552764083 1.3213992625
H -2.5465355987 4.9098705395 1.8198300933
H -0.9312910517 4.2311716 2.0921642037
C -0.9934148141 5.9351194935 0.7540966085
H -1.6263960103 6.3526835601 -0.0440420509
H -0.908806416 6.6975151085 1.5423911077
H 0.0162786352 5.7839617393 0.3437758507
C -3.3170225829 1.3226544103 0.2244616897
H -2.6447459979 0.8305433382 -0.494323782
H -3.7494404627 0.5474425938 0.8742532025
H -4.1436285686 1.7607724163 -0.3551826162
C 1.5495568022 1.8642374163 -0.0657493899
C 2.3953922295 2.9028272759 -0.4705447403
C 2.1134842093 0.7417008329 0.5518727376
C 3.7689359364 2.8225568673 -0.251875554
H 1.9856358237 3.7810851764 -0.9730769996
C 3.4843196092 0.6638660724 0.7802572587
H 1.4664203382 -0.0914459295 0.8395551843
C 4.3185361894 1.7058901714 0.3768918223
H 4.4148879711 3.6411006781 -0.5765283493
H 3.9032318605 -0.2192321664 1.2670752275
H 5.3954124625 1.6461976509 0.5480030957
Pd -1.2475906626 2.3626788817 -2.2293322916
H 1.1064143984 1.1695521876 -2.4741846395
C -0.1235406998 -0.4072664086 -1.7907385027
H -1.0510818317 -0.6716391006 -1.2690682153
C 0.6973884377 -1.539863682 -2.2327855358
C 0.1133322301 -2.8099143451 -2.3659284471
C 2.0702685478 -1.405083336 -2.5009511667

C 0.8674227792 -3.9043463599 -2.7781286777
H -0.9523753398 -2.9304097871 -2.1548641175
C 2.8245937437 -2.5012568911 -2.9072220726
H 2.5555205163 -0.4358126705 -2.3674441581
C 2.2268434113 -3.7537152378 -3.0521262864
H 0.3921562659 -4.881885746 -2.8858996492
H 3.8913494242 -2.3781785749 -3.1071874021
H 2.8212471043 -4.612304716 -3.3721106516
Cs -5.0750372659 3.2342099328 -3.2270236019

Phtrans_Beta_Heckadd_postTS
C 0.5140669152 1.4165021223 0.0286247598
C 0.7434992845 0.6064293498 -1.2404208385
Br -2.6526757642 -0.1334909884 -3.7358645247
H -0.0567871366 0.7981939482 0.7370433842
O -2.3977269411 2.9322075363 -2.1875376392
C -0.3936898974 2.423381157 -0.6498638602
H 0.2128901536 3.1465107782 -1.2136477512
C -1.5489398666 3.1444824142 0.0543358372
C -2.5950660959 3.4801924653 -1.0319123978
O -3.5824473502 4.162591038 -0.7806840216
C -2.2581054371 2.3053717515 1.1412151682
H -1.5127444578 2.027497246 1.905714844
H -2.9700854556 2.9784554393 1.6432102455
C -1.0611850017 4.4482143832 0.7289449083
H -1.9507854944 4.9229429033 1.1724168712
H -0.3897290994 4.1771350609 1.5619433351
C -0.3701179531 5.4577398942 -0.1806931108
H -0.9856983597 5.6855710959 -1.0650784928
H -0.202529427 6.4022011212 0.3576128534
H 0.6131483584 5.1064365426 -0.527168703
C -3.0170032372 1.0661742875 0.6807592165
H -2.375864727 0.3348303717 0.1673564263
H -3.4895218431 0.5619199563 1.5367633116
H -3.8187480686 1.3355229514 -0.0237756634
C 1.7338159515 1.9636400163 0.7300229823
C 2.6755031231 2.7408504213 0.0438896792
C 1.9254466514 1.7389675248 2.0966194169
C 3.7781311672 3.275772195 0.7055393153
H 2.545468194 2.9383616665 -1.0238249451
C 3.0256591451 2.2760230856 2.7642492718
H 1.1990517161 1.1349432348 2.6474413396
C 3.9561336172 3.0463505076 2.0699375085
H 4.5022693748 3.8784808554 0.1529008092
H 3.156114818 2.090195605 3.8326955452
H 4.8190342485 3.4678430114 2.5899398559

Pd -1.1664779435 1.2440482105 -2.1115358245
H 1.5713697337 0.929475304 -1.8808696584
C 0.0385945545 -0.5413783723 -1.567092006
H -0.5937614083 -0.9919673564 -0.7935539785
C 0.3877222005 -1.4494905949 -2.6851245125
C -0.0178270996 -2.7863406269 -2.619704234
C 1.1173697955 -1.0249645167 -3.8038165594
C 0.3114933929 -3.6838775082 -3.6328926668
H -0.60716357 -3.1255574304 -1.7643294035
C 1.446781218 -1.9187940814 -4.8159707769
H 1.4030143514 0.0247330007 -3.9020440563
C 1.0482164805 -3.2539289163 -4.7336544244
H -0.0162886441 -4.7234025367 -3.5638730581
H 2.0082637528 -1.5681930796 -5.6846596632
H 1.3028125407 -3.9533326492 -5.5329023679
Cs -5.0797964598 2.3340892038 -2.9887817469

TransPath_5-NoCsBr_TS_HeckAdd_Beta__2373
C 0.4582442964 2.6473587972 -2.5828916398
C -0.7715748531 0.6137768671 -0.5195486866
Pd -0.4032137569 0.8837501279 -2.5894378962
C -1.2855952179 -1.6495874597 -1.5263674445
H -0.0863007203 1.2198801673 0.0854328417
C -0.6735292348 -0.8891909703 -0.3063326887
C -1.9086470499 1.2433892696 -1.0558239885
H -2.697203305 0.588602292 -1.4436540383
O -1.7916894957 -2.7412937661 -1.3729296615
O -1.1523504183 -1.038948783 -2.6636829033
C 0.8307627976 -1.2651169279 -0.2216022042
H 1.2890974233 -0.6477008473 0.5719414119
H 1.3156128697 -0.9565364393 -1.1642983444
C -1.393373258 -1.2771790416 1.0016721939
H -1.339928246 -2.3732944243 1.0619160838
H -0.8210153797 -0.8738262227 1.8556703831
C -2.8563388124 -0.8636123093 1.1090448846
H -3.4319944312 -1.2486609854 0.2541639269
H -3.3029357053 -1.28393871 2.0218504292
H -2.9876819047 0.228862062 1.158265837
C 1.1367229515 -2.7359461865 0.0370498955
H 0.6357508616 -3.3842244566 -0.6955207258
H 2.2203915325 -2.9124420881 -0.0267772897
H 0.8105420139 -3.0509121265 1.0387903835
C -2.3374441866 2.6366921588 -0.8360289069
C -3.4755977489 3.0918619839 -1.515711492
C -1.6505114902 3.5272076898 0.0014263686
C -3.9089461645 4.4088517211 -1.3782205639

H -4.0196954702 2.4042704952 -2.1683420433
C -2.0825975535 4.8405643901 0.1404794856
H -0.7603923896 3.198129342 0.5396483425
C -3.2108353863 5.2866247246 -0.5512022022
H -4.7953072143 4.7485396568 -1.9175835402
H -1.532986959 5.5250838208 0.7891740712
H -3.5460804957 6.3200490044 -0.440833421
H 1.5492415949 2.5907827439 -2.4249946901
C -0.13733816 3.8153974051 -2.8592913317
H -1.2334224976 3.8437770014 -2.9161675453
C 0.5061386431 5.1305547271 -3.0473237955
C 1.883738767 5.2845754678 -3.2672443837
C -0.2916261113 6.283038032 -2.9884217354
C 2.4439629067 6.550163337 -3.4073580937
H 2.5230591432 4.4021866816 -3.3427461205
C 0.2686135152 7.5508343089 -3.1273337914
H -1.366624636 6.17555221 -2.8196924921
C 1.6396266817 7.6890527355 -3.3357644477
H 3.5176535865 6.650386911 -3.581334857
H -0.3695827801 8.435728919 -3.0747065164
H 2.0817684481 8.6811986938 -3.4491180577

Phtrans_Beta_Habst_preTS
H -0.0021610124 -1.0079211161 -1.3457301398
C -0.8440552661 -0.7377683832 -0.5474049263
C -1.3898714138 1.1131450471 0.9853999826
Br -2.1336973076 -3.4396811016 -3.9935341135
Pd -0.9764416824 -2.0295709346 -2.4589585448
C -0.5401883516 0.7948477472 -0.3061158555
C -2.1723569659 -1.0405987336 -1.2151650108
H -2.5340475497 -0.1989751215 -1.8117758858
O -0.797337962 1.1473772314 2.0844545618
O -2.6266162535 1.1645365676 0.8112758576
C 0.9730161272 1.0557808357 -0.1318077838
H 1.0687886927 2.0876629853 0.2342261489
H 1.4215523525 1.047913617 -1.1430628459
C -1.0492692097 1.6561573273 -1.4774713544
H -0.6790298543 1.2328061304 -2.4305468497
H -2.144096188 1.5962927776 -1.4915700128
C -0.6837442049 3.1357042276 -1.3958782183
H 0.3926826703 3.3179632994 -1.5239947287
H -1.2076136045 3.6956605842 -2.184289931
H -0.9894852996 3.5611387507 -0.427300703
C 1.8275468726 0.1740269191 0.7759968465
H 1.883253938 -0.8706963024 0.4351342292
H 2.8574491421 0.5621538251 0.7875982629

H 1.4430184379 0.1973725365 1.803653357
C -3.3283705162 -1.7133821072 -0.5503759069
C -3.381424423 -3.0739575673 -0.2194058284
C -4.4386853049 -0.9112978475 -0.2377583611
C -4.4755740216 -3.6038185606 0.4625804625
H -2.5777933029 -3.7341944393 -0.540486912
C -5.5377056642 -1.4411685724 0.4361330734
H -4.4040450206 0.1512750486 -0.4784424507
C -5.5549338034 -2.7880409283 0.8034580584
H -4.4951102528 -4.66880977 0.7036780986
H -6.388235736 -0.7961341182 0.6691410549
H -6.419202632 -3.2076128294 1.3237980986
C -0.5613051814 -1.5439998352 0.6888810081
H -0.4904320711 -0.9188417764 1.5796577664
C -0.4572732486 -2.8657022123 0.8459672661
H -0.4924268944 -3.5447125893 -0.0126836071
C -0.4462233844 -3.4624785675 2.1972616256
C 0.1130431205 -2.7899912473 3.2974784401
C -1.1266615994 -4.6671190452 2.4269186886
C -0.04427925 -3.2867197217 4.5893090979
H 0.6802197675 -1.8701114572 3.1337055552
C -1.284330608 -5.1629282468 3.7200108324
H -1.5564760164 -5.2085407092 1.5803305672
C -0.7534141956 -4.469523473 4.8076303741
H 0.4030659673 -2.752668027 5.4309015679
H -1.8254666688 -6.0983272511 3.8788721247
H -0.873268013 -4.8601743891 5.8203481458
Cs -3.027090154 -0.9179424765 3.0104898173

Phtrans_Beta_Habst_TS
H 0.1695708916 -1.0505242646 -1.6286406998
C -1.0668983637 -0.663020806 -0.4520866099
C -1.2702938458 1.1940175376 1.0689048662
Br 0.0063011774 -3.0770492218 -4.1992386662
Pd -0.9036820228 -1.7999259761 -2.3904600527
C -0.5817940336 0.8073847984 -0.3141134087
C -2.3079067287 -0.9162789023 -1.1044880113
H -2.7120405923 -0.0718205336 -1.6679150993
O -0.547451133 1.2518210291 2.082216913
O -2.5182864401 1.2774062323 1.0403633116
C 0.9548937856 0.965031759 -0.2951285948
H 1.1593110465 1.9798557662 0.0733429468
H 1.2907943807 0.9475470824 -1.3487489189
C -1.1555448977 1.7202535907 -1.4139636601
H -0.9035392246 1.2982501492 -2.4042366788
H -2.2486264816 1.7206336303 -1.3182591517

C -0.6961402641 3.1740280517 -1.3430844565
H 0.3701334701 3.2955670238 -1.5808073827
H -1.2631797072 3.7817895764 -2.0632907945
H -0.8725533757 3.5957540144 -0.3411474393
C 1.8380749283 0.0059917737 0.4993992877
H 1.7621856742 -1.0366646326 0.1537733744
H 2.8901172748 0.3050812215 0.3784873192
H 1.5946011536 0.0511259118 1.5690211098
C -3.3931710061 -1.7868877802 -0.5558128006
C -3.5088696653 -3.1645964282 -0.7597095803
C -4.3656291534 -1.1352958182 0.2201020109
C -4.5399481531 -3.8879651116 -0.158162475
H -2.7893656205 -3.6843755075 -1.3982873656
C -5.3891919459 -1.8599742103 0.8274403053
H -4.2671716203 -0.0550000946 0.3645312871
C -5.4741625237 -3.2425783639 0.6491370533
H -4.6136138755 -4.9641383528 -0.3294004201
H -6.1388865617 -1.3387290958 1.4295414762
H -6.2812475296 -3.8105489513 1.1171456279
C -0.6901185953 -1.5030103944 0.7172089933
H -0.3654387799 -0.8931779163 1.5619667502
C -0.7972714135 -2.8213405888 0.9195796816
H -1.0803177597 -3.5050387952 0.1167528317
C -0.6888652476 -3.3728955156 2.2847879039
C 0.1947525658 -2.8356908024 3.2355876599
C -1.6037730819 -4.3539700777 2.6979405647
C 0.1349449497 -3.2396605232 4.5677501131
H 0.9321976396 -2.0924817841 2.9228249086
C -1.664773019 -4.7539816163 4.03178717
H -2.2972787285 -4.7769215266 1.9661892814
C -0.8024663451 -4.1913747726 4.9739917563
H 0.8326950735 -2.8140735986 5.2925210633
H -2.390645 -5.5108441732 4.3376409479
H -0.8468556161 -4.5083083692 6.0181164101
Cs -2.7396806584 -0.6449886429 3.3494583413

Phtrans_Beta_Habst_postTS
H -0.3802218913 -1.4862410321 -2.9733272941
C -1.1940087306 -0.5705549276 -0.3175988825
C -1.172631837 1.2705096213 1.1937695971
Br 1.0426160866 -3.8159404339 -2.4421102801
Pd -0.4139657975 -2.0985766351 -1.6033771066
C -0.632289967 0.8588395904 -0.2377734799
C -2.2121096689 -0.9562165207 -1.2049564777
H -2.4404945309 -0.259646566 -2.0143095862
O -0.3520622723 1.3782232846 2.1251741297

O -2.4219707416 1.3189371006 1.2994721635
C 0.9037437272 0.9649224328 -0.3669956473
H 1.1720256559 1.9835018347 -0.0524691755
H 1.1387805426 0.8933715496 -1.4436324688
C -1.2913032246 1.7781000863 -1.2822455464
H -1.0631794607 1.4006026714 -2.2950360644
H -2.3790613713 1.7189106759 -1.1381352394
C -0.8784563605 3.243991197 -1.1878885172
H 0.1764558321 3.4022997405 -1.4544559547
H -1.4853694567 3.8538958118 -1.8732377353
H -1.0338738051 3.6332165166 -0.1696549197
C 1.8235113693 0.0030152071 0.381422463
H 1.7004295555 -1.04438912 0.0625028677
H 2.8698773005 0.2707002992 0.1715440642
H 1.6704125361 0.0814827776 1.4666434113
C -3.3758412315 -1.8026025018 -0.7955199451
C -3.7216510743 -3.0085557205 -1.4092378701
C -4.1553732234 -1.3211609643 0.2679572629
C -4.8057888802 -3.7498687148 -0.9361209609
H -3.1173282771 -3.3846148726 -2.2386956342
C -5.2373118716 -2.062524551 0.7348763874
H -3.8766447648 -0.356672285 0.7087871774
C -5.5590136661 -3.2857014429 0.141276938
H -5.059349798 -4.6993657197 -1.4123884816
H -5.8454362569 -1.6803612608 1.5595699534
H -6.4059792774 -3.8694385259 0.5088050139
C -0.8563414175 -1.4168754805 0.8444282859
H -0.1735165404 -0.9255915534 1.5385868556
C -1.2519307612 -2.6710506516 1.1626949461
H -1.9794144123 -3.2218528324 0.5633752076
C -0.8931527142 -3.2762444169 2.4564711137
C 0.2706475783 -2.9208305759 3.15950352
C -1.8202769157 -4.128558802 3.077140209
C 0.4757350936 -3.3720715685 4.460339119
H 1.0219928713 -2.2905292502 2.677947669
C -1.614706725 -4.5756713226 4.3811828833
H -2.7222606867 -4.4207780477 2.532135467
C -0.4706575558 -4.1909681256 5.0806363635
H 1.3880417239 -3.0913828913 4.991110346
H -2.34947759 -5.2327726881 4.8516916266
H -0.3053257176 -4.5451156807 6.100316386
Cs -2.3526033988 -0.3133887145 3.75033184

Phtrans_Gamma_Habst_preTS
C 0.0249845917 1.8000701993 0.311608036
H 0.1523993994 1.4348422421 -0.8261598713

Br -0.6551127602 2.0112553579 -4.1791276697
Pd -0.7190922757 2.7581806677 -1.72532286
O -2.0971760268 4.342535078 -1.6026818834
C -0.7917923496 3.058588816 0.2307180388
H -0.1652204878 3.9437695357 0.403249785
C -2.2490908522 3.3633272599 0.612122307
C -2.7696447256 4.3390016894 -0.4904231603
O -3.7958788606 4.9763957451 -0.3315257789
C -3.2555199669 2.1820200196 0.627250941
H -2.9108528559 1.4234265564 1.3419393789
H -4.1877849721 2.5923351713 1.0449321048
C -2.3359321194 4.0482634832 1.9942201085
H -3.3828702798 4.3683766344 2.1101291565
H -2.1457573864 3.288716346 2.7721928704
C -1.4327475364 5.2576180302 2.2101665524
H -1.559660998 5.9949021048 1.4020441691
H -1.6877342597 5.7591521079 3.1553390088
H -0.3664887402 4.9899745974 2.2628901274
C -3.5953513561 1.5190904307 -0.7031860437
H -2.706558346 1.174696328 -1.2544545246
H -4.2454497343 0.6473317109 -0.5386059331
H -4.14267131 2.2166761155 -1.3568193498
C -0.5637424033 0.5832038388 0.9969768544
C -0.6930966787 0.5708746313 2.3908686226
C -0.9835042837 -0.5299063719 0.2683775177
C -1.2559259823 -0.5241826811 3.039346631
H -0.3725958354 1.4391009713 2.9728619412
C -1.5507799165 -1.6271041007 0.9161489092
H -0.8804142576 -0.5307681192 -0.8204624576
C -1.692630367 -1.6257948079 2.3017875474
H -1.3604566136 -0.516170244 4.1264323833
H -1.8825781081 -2.4875296812 0.3311971835
H -2.1389486672 -2.4835186232 2.8093173022
C 1.4564991503 2.0582936222 0.7234312113
H 1.645143302 2.0235796798 1.8009855534
C 2.4376185652 2.3424757923 -0.1391666136
H 2.1876552892 2.3553022213 -1.208576871
C 3.8431818002 2.6535876571 0.176001636
C 4.346233167 2.6945446562 1.4862108496
C 4.7249078325 2.9241888611 -0.8803833182
C 5.6826811404 2.9942574875 1.7272221577
H 3.6869431104 2.4894283245 2.3322168656
C 6.0638480962 3.2254333992 -0.6406460536
H 4.3501109938 2.8970366821 -1.9068931853
C 6.5483194357 3.2613903942 0.6649697781
H 6.0538895466 3.0203764535 2.7541847889

H 6.7314065413 3.4328117783 -1.479783961
H 7.5972791822 3.496961152 0.8571051156
Cs -3.5990148311 4.0370147985 -4.0017748986

Phtrans_Gamma_Habst_TS
C -0.0040089671 1.8617117492 0.3791695841
H 0.2196802152 1.4031672869 -1.0764293128
Br -0.7819139736 1.8945650483 -4.0387009478
Pd -0.6730641581 2.5978325353 -1.613336756
O -2.0420954106 4.2454889962 -1.6200260096
C -0.7793818972 3.0847720815 0.3542297738
H -0.1460116228 3.9751154861 0.4431586595
C -2.2470581088 3.4210702155 0.6528990152
C -2.7566873768 4.2877799775 -0.5447517007
O -3.8248601205 4.8784802532 -0.4661288739
C -3.2443243168 2.2393703879 0.7790580235
H -2.8597159586 1.5211536916 1.5146135589
H -4.1594948149 2.6648032162 1.217816924
C -2.3471827439 4.2429081273 1.9586203783
H -3.4004644598 4.5508313925 2.0427632985
H -2.1397011909 3.5706334533 2.8096726793
C -1.4712385408 5.488173162 2.048058017
H -1.6112201739 6.1339715842 1.1671188075
H -1.7418902016 6.0794478565 2.935170506
H -0.3996178477 5.2529258996 2.131906549
C -3.6440994182 1.5087617509 -0.4993605552
H -2.7804011596 1.1747123493 -1.0938785141
H -4.2483695687 0.621937047 -0.259159759
H -4.261126128 2.1628799917 -1.135202173
C -0.5710438992 0.5758074744 0.9429216948
C -0.6876487299 0.4663856674 2.3352935726
C -0.9523051067 -0.505333649 0.1480992428
C -1.1959826139 -0.6905598393 2.9170831184
H -0.3988642792 1.3098258206 2.9684881406
C -1.4647081801 -1.6650983508 0.7301431812
H -0.8626069772 -0.431717933 -0.9387457218
C -1.5913206691 -1.7609476027 2.1134157392
H -1.2900151177 -0.755210377 4.0032142475
H -1.7658398225 -2.4986898394 0.0921946044
H -1.9944672151 -2.6686465643 2.5673796791
C 1.454205041 2.0382782884 0.7203068045
H 1.6936284425 1.8008845685 1.7622956861
C 2.4096207792 2.4591447645 -0.115287991
H 2.1325519869 2.6317929577 -1.1626724011
C 3.8256051938 2.6998258245 0.2149920423
C 4.3098471946 2.7410293029 1.5321751105

C 4.736660346 2.9004371224 -0.8323132408
C 5.659425095 2.9590777061 1.7888146431
H 3.6221406893 2.6127585286 2.370844185
C 6.0884277806 3.119551211 -0.576946377
H 4.375175968 2.8785125358 -1.8636567999
C 6.555684745 3.1475650286 0.7354190412
H 6.0154801873 2.9887646753 2.8210508896
H 6.7799032246 3.2699824642 -1.4088516714
H 7.6144235242 3.3212890684 0.9394937602
Cs -3.7927036437 3.8582316068 -3.8239803529

Phtrans_Gamma_Habst_postTS
C -0.0275121992 1.8710963908 0.5377263604
H 0.3362194154 1.176664564 -1.7052123076
Br -0.7579113999 1.9723976912 -4.0658718918
Pd -0.5704450752 2.3885692194 -1.6390223649
O -1.8844872596 4.1135585759 -1.636009946
C -0.760644092 3.0501092679 0.4125256279
H -0.1362175729 3.9490483462 0.374889368
C -2.2302667747 3.4063466947 0.6279244733
C -2.657408791 4.2289520056 -0.6169024596
O -3.713573891 4.8544095976 -0.6247296213
C -3.2517992593 2.2473572546 0.7579877231
H -2.9068324462 1.54795759 1.5304616398
H -4.1736323027 2.7042985577 1.1489938047
C -2.3615059313 4.2787542291 1.8986799397
H -3.4058770094 4.6255594445 1.9183283377
H -2.2198459151 3.6308959458 2.7810464418
C -1.4426924424 5.492673084 1.987909307
H -1.516363939 6.1131726849 1.0809594605
H -1.7297533185 6.1237608003 2.8417501253
H -0.3866376833 5.2176861909 2.1288119261
C -3.617459169 1.4813830044 -0.5095293538
H -2.7387787582 1.0988167853 -1.0495906246
H -4.2588322149 0.6226359429 -0.2636558237
H -4.1836243702 2.126139801 -1.1998365283
C -0.6068169859 0.5861283503 1.0699548053
C -0.764577982 0.4841706747 2.4601178522
C -0.9401593864 -0.5131693202 0.2766001614
C -1.2729782194 -0.6749105109 3.0389515576
H -0.5015988765 1.3372303975 3.0918011518
C -1.4532793554 -1.6742990021 0.8551657134
H -0.8090299634 -0.4507778266 -0.8050569396
C -1.6256714037 -1.7588426171 2.2345020146
H -1.3989902208 -0.7303205357 4.1224620667
H -1.7179353458 -2.5200231653 0.2167947514

H -2.0290436358 -2.6687063745 2.6841214602
C 1.450582453 1.9701131723 0.748969175
H 1.7949038288 1.4496762329 1.649980008
C 2.3353130149 2.6231961671 -0.0158552482
H 1.9805707278 3.0550069617 -0.9592372086
C 3.7732377561 2.7883984814 0.2561632141
C 4.3514256192 2.528698952 1.5092622867
C 4.6106332415 3.2262963897 -0.7809458741
C 5.7192534343 2.6839094957 1.7094398191
H 3.7219706401 2.2134091111 2.3442706569
C 5.9801594483 3.3836946755 -0.5815409813
H 4.1760869217 3.4383407312 -1.7613205494
C 6.5407748262 3.1105139188 0.6646861138
H 6.1485471848 2.4774893919 2.6924766353
H 6.6127211402 3.7216625916 -1.4053280132
H 7.6139031969 3.2348423369 0.8251352452
Cs -3.7330866589 4.0214636514 -3.7907514881

Phtrans5-endo-trig_TS
C -0.6527042689 2.3418803762 1.0365099367
O -1.1270861627 0.6381298459 -0.1648543046
H -1.3779043236 1.9611195363 1.7496083763
Pd -1.0011398268 4.9100781251 1.0795877726
C -1.0905825139 3.1709418777 -0.0278003697
H -0.277123642 3.3959579482 -0.7275365344
C -2.2891934683 2.6469943503 -0.8024964726
C -1.8297026903 1.1677821592 -1.0921338378
O -2.0874207134 0.6393067803 -2.1721530903
C -3.6648237402 2.5952938432 -0.0936770898
H -3.9435670783 3.6297637848 0.1650667489
H -4.3803981174 2.2753798976 -0.868145107
C -2.4885775712 3.4273626415 -2.1165012712
H -3.2673135024 2.8999482632 -2.6865047462
H -2.8878259997 4.4229279084 -1.8610923733
C -1.2691587263 3.600232394 -3.0160747184
H -0.8599233117 2.617282448 -3.299067605
H -1.5600235359 4.100989408 -3.9510793944
H -0.4855735262 4.2221103863 -2.5556963468
C -3.8570786691 1.6861547481 1.1185096238
H -3.3495145039 2.0632907786 2.016896492
H -4.9278483442 1.6242299758 1.3647363901
H -3.4979388295 0.6651647197 0.9251889825
C 0.7609201467 2.0244424985 1.3219590016
C 1.8339942507 2.8030859926 0.8583840194
C 1.0301510094 0.8060728852 1.9631229971
C 3.1437149015 2.3519481665 1.0127012385

H 1.6468223864 3.7769384387 0.3931108729
C 2.3394510823 0.3513355387 2.1004372214
H 0.1952969723 0.1946336201 2.3106217277
C 3.4008083699 1.1210890723 1.6208149683
H 3.9693968165 2.9769354217 0.665039842
H 2.5328810854 -0.6057121414 2.5897664132
H 4.4289997296 0.7718259071 1.7404096885
C -2.3116375196 4.3817004383 2.4419050755
H -3.3655424785 4.5394491145 2.167749616
C -1.9837972308 4.0326362815 3.6967295814
H -0.9286760151 3.8500475619 3.9410991395
C -2.9122502688 3.8675447334 4.8356468217
C -2.3928973508 3.7759394363 6.1358147228
C -4.3047646714 3.7810771114 4.6740924998
C -3.2306923683 3.6196461973 7.2377429449
H -1.3108521792 3.8352587096 6.2817521781
C -5.1428120679 3.6238869146 5.7733857666
H -4.7381451225 3.8248286245 3.6725877003
C -4.6111563383 3.5447989726 7.0615185999
H -2.8019173683 3.5556745008 8.2404891781
H -6.2228236552 3.5565415872 5.6233915307
H -5.2711251671 3.4202266103 7.9227376305
Br 0.6249561128 6.1250495565 -0.4143513476
Cs 1.2447840043 0.6128080527 -1.8810736905

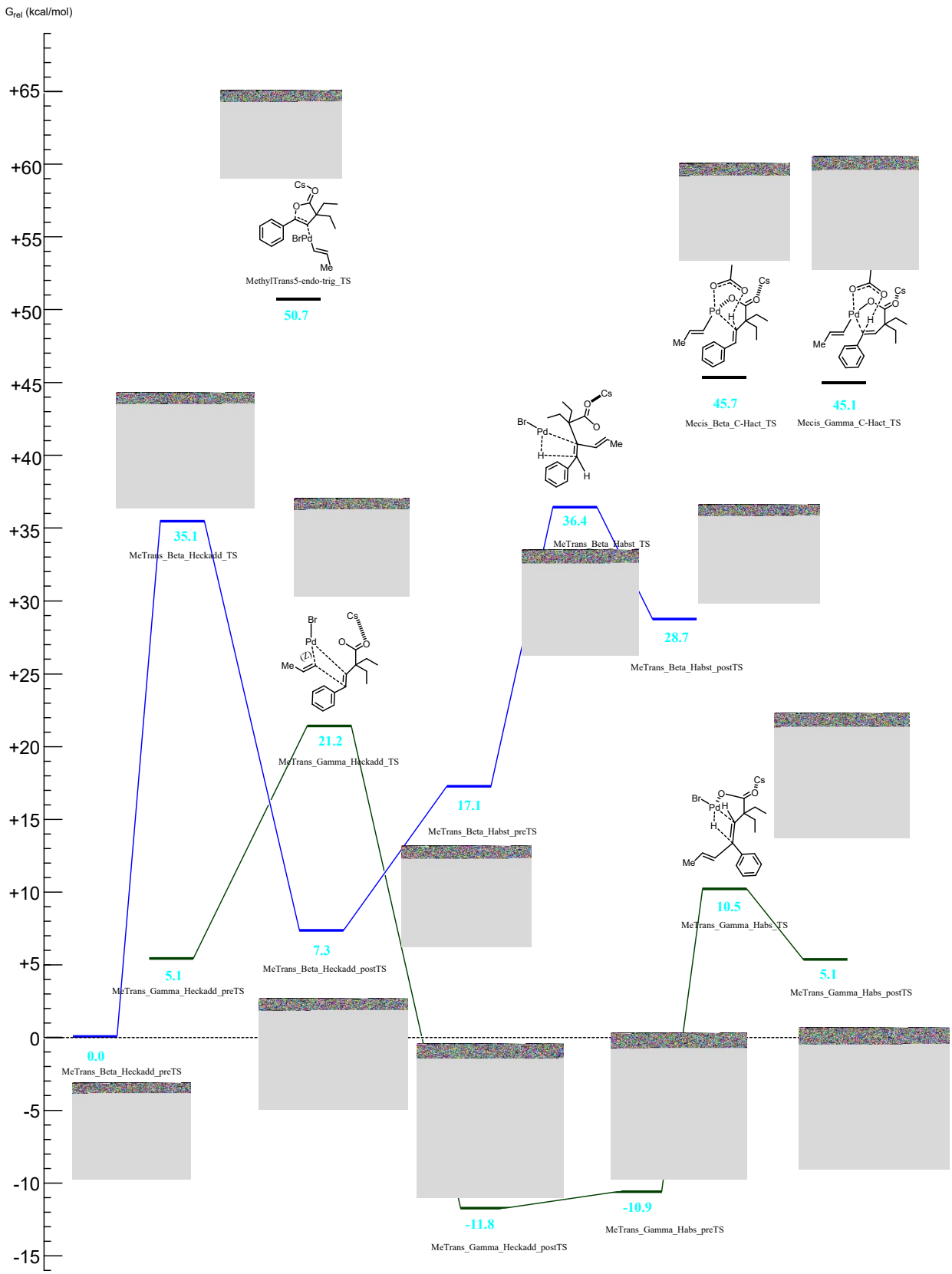
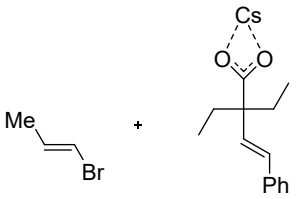


Fig. S3 Model reaction profile of *trans*-1-bromopropene after oxidation addition.



			wB97X-D/BS1					wB97M-V/BS2
	1st frequency (cm-1)	Electronic energy	ZPE corr	Thermal corr	Enthalpy corr:	Gibbs corr	Electronic energy in toluene	Electronic energy
Metrans_Gamma_C-Hact_TS	-1202.2	-1187.082030	0.399551	0.443876	0.445090	0.308052	-1187.113549	-1187.976255
Metrans_Beta_C-Hact_TS	-1122.5	-1187.086090	0.400193	0.444192	0.445406	0.310765	-1187.116763	-1187.978907
Metrans_Beta_Heckadd_preTS	17.9	-3532.831350	0.353958	0.393865	0.395078	0.266424	-3532.863461	-3533.575198
Metrans_Beta_Heckadd_TS	-230.3	-3532.778000	0.353545	0.392615	0.393829	0.267875	-3532.806071	-3533.524765
Metrans_Beta_Heckadd_postTS	23.6	-3532.836330	0.357104	0.395623	0.396836	0.273542	-3532.864823	-3533.574298
Metrans_Gamma_Heckadd_preTS	20.6	-3532.820550	0.353870	0.393995	0.395208	0.266605	-3532.852179	-3533.567773
Metrans_Gamma_Heckadd_TS	-340.3	-3532.796030	0.353392	0.392453	0.393666	0.267530	-3532.828124	-3533.542508
Metrans_Gamma_Heckadd_postTS	18.6	-3532.857240	0.356685	0.395335	0.396548	0.271493	-3532.887943	-3533.600538
Metrans_Beta_Habst_preTS	14.2	-3532.788300	0.353244	0.392530	0.393743	0.266839	-3532.826093	-3533.542744
Metrans_Beta_Habst_TS	-607.4	-3532.777320	0.351469	0.390525	0.391739	0.266936	-3532.812915	-3533.514263
Metrans_Beta_Habst_postTS	22.0	-3532.794970	0.355593	0.394314	0.395527	0.271399	-3532.829420	-3533.532060
Metrans_Gamma_Habs_preTS	22.1	-3532.857260	0.357179	0.395597	0.396810	0.273069	-3532.888005	-3533.600536
Metrans_Gamma_Habs_TS	-774.6	-3532.815120	0.350912	0.389843	0.391056	0.265935	-3532.847365	-3533.557833
Metrans_Gamma_Habs_postTS	21.8	-3532.824910	0.352626	0.392207	0.393420	0.266970	-3532.855894	-3533.568736
MethylTrans5-endo-trig_TS	-326.2	-3532.755410	0.353261	0.392524	0.393738	0.266828	-3532.791189	-3533.491111

Cartesian Coordinates

Metrans_Gamma_C-Hact_TS
C 0.5322070982 1.8507147918 0.1956868463
H 0.7926091854 0.4594700958 0.5342837548
C 2.3644181294 -0.7268798065 0.3225641952
C 3.5510814031 -1.4217483284 0.9222980235
O 1.3887102384 -0.445129335 1.0864244262
O 2.3963880115 -0.4087813125 -0.8897436582
H 4.1316516956 -1.9362905377 0.148353336
H 4.1833713102 -0.648623049 1.3853039995
H 3.2338717212 -2.1171268256 1.7089639404
Pd 0.6731563277 0.5186737078 -1.5667005075
O -1.1650192664 1.1530738506 -2.2103340387
C -0.6265305329 2.5280730746 0.2976321305
H -0.5868450623 3.5229798453 0.7699140526
C -2.028912557 2.1424850361 -0.1182125486
C -2.17232714 1.3503757132 -1.433888838
O -3.2985636682 0.9425361495 -1.7317423518
C -2.7049710816 1.3210523743 1.0096403266
H -2.6253583003 1.8972390039 1.9469054084
H -3.7755136685 1.2497964664 0.7640294598
C -2.8518037503 3.440026801 -0.3285955856
H -3.8942291139 3.1513614734 -0.529526845

H -2.8498873443 3.9978970416 0.6237660473
C -2.340294284 4.3314809009 -1.4548365898
H -2.3968804464 3.817713355 -2.4266274173
H -2.9391018688 5.2516038196 -1.526968034
H -1.2902592866 4.6226259184 -1.2981246869
C -2.1445157544 -0.0784834689 1.2229090519
H -1.0856969122 -0.0649681185 1.5124771711
H -2.702064362 -0.6045267361 2.0123647019
H -2.2317066033 -0.6814811172 0.3039486284
C 1.7572766453 2.4974508754 0.7574004554
C 2.9197178448 2.6462668901 -0.0150648572
C 1.7920421151 2.9392572233 2.088859204
C 4.0661521211 3.2316399414 0.5193138758
H 2.9183885156 2.3024959817 -1.0521078453
C 2.9380799892 3.522273355 2.6259969159
H 0.9043607286 2.8054451116 2.7125411566
C 4.0819163686 3.6718018411 1.8427420038
H 4.9548582208 3.3459576838 -0.1061642609
H 2.9394438087 3.8563675336 3.6665199645
H 4.9824115931 4.1262389002 2.2622915685
C 0.8318402192 -0.4358696206 -3.3209847784
H 0.4388987465 0.1391651384 -4.1806506523
C 1.3105957613 -1.6650413683 -3.5580127302
H 1.7278242251 -2.242148409 -2.7209010586
Cs -2.2893823381 -1.5406473772 -3.0159574515
C 1.3728352109 -2.3313929453 -4.9076400444
H 2.4123736845 -2.5600040367 -5.195309318
H 0.8338408586 -3.296253527 -4.9159868225
H 0.942436564 -1.6898209756 -5.6929387241

Metrans_Beta_C-Hact_TS
H -2.0012737464 1.0683934829 1.5687465509
C -1.4154637218 0.2304186353 0.5076710576
C 0.9268964728 -0.6339381936 0.7571448772
C -2.5409476125 2.9054129751 2.1498391146
C -3.6198317052 3.8551018596 2.5776791335
O -2.7632639749 1.6618746859 2.2819479954
O -1.4975453508 3.3676416673 1.633107173
H -4.153254192 3.4682520808 3.4543763051
H -3.2074749705 4.8519394585 2.7701139712
H -4.3337442679 3.9203579999 1.7409477188
Pd -0.140168599 1.9765144764 0.9159852377
C -0.5675104299 -1.0199028254 0.7995758164
C -2.4172464788 0.2114402304 -0.396629857
H -2.6875240443 -0.708408835 -0.9306799538
O 1.2297651456 0.571255193 0.3883700577

O 1.7975279278 -1.4267851916 1.1125395654
C -0.8780704975 -1.5428584485 2.2268565105
H -0.3722150871 -2.5112685904 2.3515119813
H -1.9625684998 -1.7356342078 2.2775753946
C -0.8205470503 -2.1542443724 -0.2283862282
H -1.8872618125 -2.4235794977 -0.1535626603
H -0.6847891054 -1.7296168482 -1.2368440026
C -0.0004050739 -3.437886395 -0.1231579889
H -0.1535848853 -3.9522499669 0.8371972052
H -0.3107415447 -4.1340529912 -0.9177100422
H 1.0749537512 -3.2471245828 -0.2250948524
C -0.464574208 -0.6474038635 3.3913211701
H -0.9333042213 0.3451614168 3.35468617
H -0.7436219606 -1.1127608995 4.3486261547
H 0.6288231505 -0.514466689 3.4065456393
C -3.3068065884 1.3570191426 -0.7093832283
C -4.6993269477 1.1985213234 -0.6294057756
C -2.8027781788 2.609588879 -1.0827504116
C -5.5576319131 2.267115483 -0.8707504431
H -5.1086738431 0.2243209258 -0.3493198193
C -3.6604821451 3.6819978031 -1.3272666889
H -1.7231092484 2.7408510598 -1.1812904429
C -5.0397754496 3.517511006 -1.2160859931
H -6.6379153947 2.1258306525 -0.7880882891
H -3.2430238572 4.6512749958 -1.6090216142
H -5.712126291 4.3568294729 -1.4088109894
C 1.257139052 3.4125582102 1.0397175258
H 1.0308734388 4.2527997625 1.7188617218
C 2.3756272662 3.4905434867 0.3026504723
H 2.5909651509 2.6812719908 -0.4121083975
Cs 3.3591886986 0.899896587 2.3613573491
C 3.3695861196 4.6219844327 0.3279896067
H 3.0934262023 5.3836148428 1.0732359023
H 4.3912240093 4.2700409494 0.5620701927
H 3.4358873972 5.1188327284 -0.6542199375

Metrans_Beta_Heckadd_preTS
C -1.0802402998 1.8854202472 -2.9933517738
C -1.5736186771 -0.098327942 -0.7146676273
Pd -1.4357504393 -0.045856632 -2.8667184607
C -1.5280797874 -2.5592868657 -1.3403334714
Br -0.2796385257 -0.4089397223 -5.0401017817
H -0.9903388699 0.7326096204 -0.3020441097
C -1.0510714047 -1.479059069 -0.3355082677
C -2.8510191064 0.1788218837 -1.1868298935
H -3.5096308395 -0.667884824 -1.4046894774

O -1.4636335188 -3.7505398224 -1.0379469966
O -1.8513814308 -2.1412197012 -2.5082166085
C 0.5013971047 -1.4212720354 -0.4467101596
H 0.8458833943 -0.5774027285 0.1757747094
H 0.7546611982 -1.1383699094 -1.4840119673
C -1.473687604 -1.845243771 1.1003284053
H -1.064805577 -2.844726712 1.3075950523
H -0.9875275344 -1.1429310371 1.8002139156
C -2.9767463259 -1.8747327996 1.3496126689
H -3.4754839182 -2.5585231146 0.6456116645
H -3.189636605 -2.2353493306 2.3667129746
H -3.4373057596 -0.8806017286 1.2485580772
C 1.2751054886 -2.6753906604 -0.0537397783
H 0.9050597255 -3.5637861372 -0.5852864487
H 2.3452981732 -2.5442708406 -0.2748816952
H 1.1866966015 -2.8919435472 1.0206955998
C -3.5399685329 1.4873152183 -1.1314584681
C -4.7752702385 1.6163422809 -1.7807217308
C -3.0109052912 2.606629642 -0.4741215816
C -5.4580480751 2.8298030499 -1.7877695364
H -5.1967748241 0.7508244368 -2.2986084962
C -3.6920895103 3.8197914013 -0.479466598
H -2.0522358231 2.5341026043 0.0411577014
C -4.9163353151 3.9378807211 -1.1381669024
H -6.4168733754 2.9105841434 -2.3043188149
H -3.2626964165 4.6819037424 0.0354786748
H -5.4481662505 4.8917642677 -1.1418218153
H -1.8922036867 2.4472298144 -3.48072721
C -0.0162527839 2.5187811635 -2.4998001731
H 0.7891425299 1.9369133217 -2.030978493
Cs -0.0664283657 -3.8446551457 -3.9654486073
C 0.182947438 4.0086938494 -2.5402552627
H -0.6678949892 4.5111559195 -3.0239780603
H 0.2900608217 4.425518423 -1.5242768516
H 1.0981082262 4.2758873255 -3.0939503245

Metrans_Beta_Heckadd_TS
C -0.3453229807 1.8385333489 -2.0882391827
C -1.5376041751 0.4345607582 -0.9217399877
Pd -1.8454617957 1.0545899416 -3.1466751455
C -0.8411034104 -1.8009120387 -1.8143448784
Br -3.4264818945 0.5814373902 -5.0151865385
H -1.381800385 1.2214073962 -0.1764069173
C -0.7920985312 -0.8581872487 -0.5712445387
C -2.8488722311 0.3766275363 -1.4930175533
H -3.1848613323 -0.6197305276 -1.7985814164

O -1.7836506538 -2.6194210864 -1.8829336662
O 0.0316771947 -1.6104609922 -2.6957841631
C 0.670126108 -0.5830628537 -0.1643295214
H 0.6841312316 0.2223572814 0.5927231015
H 1.2067538976 -0.2070567799 -1.0375568698
C -1.5062761194 -1.4793397693 0.6715615418
H -1.0818069718 -2.4872058101 0.7842488661
H -1.1778392281 -0.9060539362 1.5572113494
C -3.0247874047 -1.6119355046 0.7151543481
H -3.3842723451 -2.1770153124 -0.1534839949
H -3.3113886547 -2.1621757902 1.6246076884
H -3.5414677197 -0.6413086698 0.7559481175
C 1.431836789 -1.7974709436 0.3582538959
H 1.3804804631 -2.6258983827 -0.3650490084
H 2.4941191587 -1.5461110982 0.4966739711
H 1.0537032359 -2.1605027772 1.324844146
C -3.9408108146 1.3292767279 -1.1743357721
C -5.2482361684 0.9883127705 -1.5460939519
C -3.7280791881 2.5502791334 -0.5182629257
C -6.3133494377 1.8393032804 -1.2693647072
H -5.4204482707 0.047603355 -2.0734119429
C -4.7922107869 3.4035483367 -0.243614856
H -2.7198378731 2.8473214077 -0.2217068198
C -6.0892122706 3.0511115328 -0.6172795125
H -7.3245429319 1.5567961496 -1.5692915772
H -4.607652771 4.3516666937 0.2659396221
H -6.92349213 3.7218444267 -0.4013581183
H -0.5232457387 2.7860373516 -1.5635666685
C 0.847786225 1.4858975419 -2.5862822245
H 0.9506058639 0.4650981574 -2.9804219103
Cs -1.7802873572 -2.5907339957 -4.8236136701
C 2.0588391246 2.3679783144 -2.5974850073
H 1.8546637107 3.3583122835 -2.1660259475
H 2.8744349358 1.8970315136 -2.0244599015
H 2.4299572485 2.5053152077 -3.625184667

Metrans_Beta_Heckadd_postTS
C -0.4242308173 1.5766084196 -1.4529982467
C -1.2669282109 0.5493273751 -0.6873050021
Pd -1.7039955271 1.5775731501 -3.2146016915
C -0.756174804 -1.7528655464 -1.6837846778
Br -3.1855401152 1.3835676566 -5.1894111345
H -1.5090886052 0.9902451011 0.2918132527
C -0.6785902056 -0.870584325 -0.3938899913
C -2.4838588475 0.5789729125 -1.5947751358
H -2.7412935921 -0.3983312964 -2.0200428731

O -1.8095973893 -2.4017363871 -1.8760452734
O 0.2038501256 -1.6947277033 -2.4926242825
C 0.7842444903 -0.7165845397 0.067875948
H 0.8156915937 0.0226649052 0.8898125481
H 1.3745586894 -0.2986978787 -0.7570162558
C -1.4999217786 -1.5099891345 0.7562063133
H -1.2213201815 -2.5728620872 0.8107151654
H -1.1517543677 -1.0518255505 1.7004749196
C -3.0234222213 -1.4223788311 0.7114853865
H -3.4058231247 -1.8787054867 -0.2096147565
H -3.4507690621 -1.96379852 1.5694905095
H -3.3918453073 -0.3869666677 0.7756937844
C 1.45829997 -2.0096628656 0.5154993113
H 1.4149266572 -2.7611541976 -0.2869787636
H 2.5189363249 -1.8294601112 0.7469928947
H 0.9941248093 -2.4374411189 1.4162679321
C -3.6683136936 1.4019586949 -1.2619485476
C -4.9157024882 1.0339994039 -1.7909147239
C -3.6007313072 2.5395124866 -0.4409624277
C -6.0581471924 1.7719701251 -1.5064817369
H -4.9767697051 0.160243577 -2.4431945762
C -4.7430938034 3.2819818553 -0.1594051697
H -2.6435204216 2.8533352483 -0.0194096974
C -5.9751945172 2.9006835437 -0.6907073629
H -7.0189288775 1.4685606134 -1.9269088367
H -4.6717327233 4.1649773584 0.4790413043
H -6.8711135872 3.4845712922 -0.4694125816
H -0.4053507426 2.5948585503 -1.0434899177
C 0.3758391811 1.2846433384 -2.5413233355
H 0.5407968262 0.2228432813 -2.7757929233
Cs -1.6676775456 -1.9613244241 -4.7980558794
C 1.3025902923 2.2828368154 -3.1701255859
H 1.0735796415 3.316279743 -2.8715187529
H 2.3398455667 2.0562958272 -2.8731352919
H 1.2657595938 2.2182453972 -4.2686648379

Metrans_Gamma_Heckadd_preTS
C 0.0971423061 2.0723288375 -0.1400312192
C -0.0887991608 0.9454873246 -2.6629833017
Br -2.4712793203 2.0831199989 -4.1925375155
H -0.2626453213 1.1254801402 0.2708958598
O -2.7152552478 3.918879233 -1.4254560398
C -0.6863398868 3.1895414087 -0.0152002383
H -0.2441985563 4.1471588526 -0.3052691345
C -1.9769336197 3.3407363148 0.7723475495
C -3.0384587219 3.9259882275 -0.185502061

O -4.1298896377 4.2985842614 0.2417364199
C -2.5355516892 2.0287921523 1.3700284724
H -1.7339467819 1.5393865398 1.9481980882
H -3.3011249722 2.3242665741 2.103171123
C -1.7508688797 4.3306939817 1.9404003784
H -2.7281049097 4.4433685645 2.434234089
H -1.0696459772 3.8610068622 2.6705533664
C -1.2365211233 5.7153316663 1.5603239161
H -1.8705435311 6.1757514645 0.7867560349
H -1.2521132633 6.3790235014 2.4371575267
H -0.2008700926 5.6982772707 1.1892611596
C -3.1706895947 1.0293888448 0.4068802011
H -2.4794051711 0.6766766192 -0.3728094934
H -3.5367565693 0.1500130806 0.9571372234
H -4.0365656449 1.4794844738 -0.1024994875
C 1.533542482 2.0660380352 -0.5052318573
C 2.1970781915 3.1864040609 -1.0241297109
C 2.2606310275 0.8830916978 -0.3303321648
C 3.5475243778 3.1233552491 -1.350395087
H 1.6503257592 4.1155265645 -1.1980930905
C 3.6144323028 0.8183135829 -0.6529204441
H 1.7499121779 -0.0043857027 0.0507168945
C 4.2635306574 1.9392851261 -1.164810827
H 4.0455265518 4.0052084353 -1.7591537122
H 4.1615126926 -0.1160568607 -0.5102869745
H 5.323130721 1.8916889326 -1.4247854336
Pd -1.2959113999 2.3920228622 -2.035723308
H 0.825071801 1.3312883203 -3.1398190238
C -0.2861756472 -0.365546821 -2.5358841166
H -1.2129818397 -0.7311652926 -2.0735990745
Cs -5.315265871 3.4779158158 -2.561145091
C 0.6806800918 -1.418934676 -3.002083701
H 1.00497719 -2.0641482371 -2.1676144659
H 0.2216201706 -2.0787207896 -3.7569700238
H 1.5789329295 -0.9649224984 -3.4465707053

Metrans_Gamma_Heckadd_TS
C 0.0614578516 1.8829253266 -0.5458174188
C -0.0850991263 1.1188423267 -2.3861545909
Br -2.8327506095 1.9101188936 -4.2825888624
H -0.2755927787 0.9957981862 -0.0043434303
O -2.9329121205 4.0044218539 -1.4281118894
C -0.7391494526 3.0609752296 -0.3626924327
H -0.2136139492 4.004180899 -0.5497292527
C -1.9045364727 3.2409774963 0.6196008785
C -3.0871272428 3.8906476764 -0.1528702109

O -4.118045374 4.2001662416 0.4351184751
C -2.4202026861 1.9304284106 1.2567263807
H -1.5696255004 1.413050088 1.7322361834
H -3.0916426955 2.2241074144 2.077345238
C -1.4861045929 4.1854490057 1.771543591
H -2.3611775301 4.2775845409 2.4334262163
H -0.6901277861 3.6902041664 2.3547197529
C -1.04027891 5.5857679834 1.3638297335
H -1.8060021919 6.081724008 0.7475277325
H -0.8801679255 6.2081177609 2.2565322612
H -0.0962075807 5.5850009184 0.7988690243
C -3.1824245929 0.9670141847 0.3517033482
H -2.6109212826 0.6623324698 -0.5375441226
H -3.4654982256 0.0590795428 0.9046735693
H -4.1126443845 1.4345461394 -0.005243371
C 1.5551617289 1.9894060728 -0.5801462395
C 2.2141751006 3.0705682521 -1.1777113087
C 2.3196962144 0.9793385155 0.0110303723
C 3.6039036783 3.144960802 -1.1675553561
H 1.6350434017 3.8534082079 -1.6738635164
C 3.7110483505 1.0560019391 0.0288461023
H 1.8165417574 0.1198220913 0.46218378
C 4.3581744759 2.1403410809 -0.5601029909
H 4.1026616459 3.9929376178 -1.6417846738
H 4.2917577422 0.2615980148 0.5027306093
H 5.4484802644 2.2008967031 -0.551985688
Pd -1.5544295057 2.5521344296 -2.1427422824
H 0.7162093229 1.5097343213 -3.0270375484
C -0.3327155513 -0.199139652 -2.372419009
H -1.0884322361 -0.5919864348 -1.6797425798
Cs -5.5247914308 3.2890600248 -2.4148825623
C 0.3265114127 -1.2013565057 -3.2649726063
H 0.8002740049 -2.0066595052 -2.6790076176
H -0.421351143 -1.6758434772 -3.9208829849
H 1.0912059255 -0.7336592616 -3.9007487029

Metrans_Gamma_Heckadd_postTS
C 0.2764233559 1.5157075438 -0.8097085159
C 0.1201201178 1.2003791193 -2.292807676
Br -3.8494759282 1.1879232869 -3.9211986014
H -0.0819385351 0.6504706793 -0.2326718226
O -3.0991490271 3.4851189818 -1.4661409136
C -0.7620091192 2.6202613173 -0.8135488207
H -0.321229148 3.5397821534 -1.2251409314
C -1.6549029901 2.9596352752 0.3860033218
C -2.9531385072 3.5747225284 -0.1838942308

O -3.8139338863 4.0471678915 0.5511506663
C -2.0574271696 1.7425118587 1.2492128058
H -1.1373436015 1.2710389682 1.6344419933
H -2.5842807689 2.1422442904 2.1293473596
C -0.9645928068 3.9766270647 1.3250526962
H -1.6859099901 4.201897 2.1265757258
H -0.0997410396 3.4801897151 1.7982090661
C -0.5178853521 5.2864244144 0.6854833531
H -1.342938153 5.7635825887 0.1335040063
H -0.1854022617 5.9936609007 1.4595767402
H 0.3251960186 5.1484315669 -0.0076640724
C -2.9469096238 0.689224544 0.598886446
H -2.4901107024 0.2298485042 -0.289699883
H -3.1807168875 -0.1136979579 1.3138056564
H -3.9033070442 1.1278463713 0.2750526819
C 1.6573429027 1.8869617165 -0.3249639873
C 2.385752579 2.9159672375 -0.9353397818
C 2.2211558133 1.2367536412 0.7770693907
C 3.6421183215 3.2819163599 -0.4584956189
H 1.9647252907 3.4463695749 -1.7939636649
C 3.4770076062 1.6024760307 1.2606525117
H 1.6652564926 0.4320386222 1.2663140409
C 4.1919772757 2.6268361884 0.6435130579
H 4.1948089423 4.0865236906 -0.9486499636
H 3.8985424751 1.0831407373 2.1242491663
H 5.1757722112 2.9153459966 1.0198205407
Pd -1.9376360426 1.9788122868 -2.3354351413
H 0.7316843527 1.7871873706 -2.9893225832
C -0.6835179846 0.1965483275 -2.8000098602
H -1.1071152126 -0.5289032294 -2.093964961
Cs -5.9118592926 3.0188424023 -1.6865176306
C -0.6422126541 -0.2418166447 -4.2369692899
H 0.0213618718 -1.1167921317 -4.3351899798
H -1.6429619293 -0.5221135246 -4.5898894965
H -0.2628719692 0.5579307412 -4.8887678

Metrans_Beta_Habst_preTS
H -0.4574565271 -1.7990576753 -2.710780944
C -1.3018215145 -0.3487151905 -0.1813671446
C -0.8880508317 1.6538120804 1.1478386166
Br 0.8113412954 -4.0410050325 -1.5813405147
Pd -0.5661768884 -2.0800365186 -1.2206461699
C -0.5964757488 1.0159498267 -0.2472522148
C -2.2830707702 -0.754682742 -1.1013931036
H -2.4023351824 -0.1302636733 -1.9884032817
O 0.0149273634 2.3140310994 1.7024380901

O -2.0451102075 1.4632980674 1.6037858781
C 0.9120772818 0.9616867113 -0.5680102574
H 1.2717760471 1.9972703808 -0.5039703737
H 1.0183879206 0.6426438151 -1.6190131613
C -1.294624129 1.9366374049 -1.2793644063
H -1.1740607444 1.4990658549 -2.2852457548
H -2.3714050957 1.9364458461 -1.0507637141
C -0.8019080339 3.381333681 -1.3152553208
H 0.2256389339 3.4602289357 -1.6982336375
H -1.4448739386 3.9805769755 -1.9772032247
H -0.8167956197 3.8389047679 -0.3149603546
C 1.8326943847 0.1123265155 0.3033391134
H 1.6588699907 -0.9680810004 0.1876982999
H 2.8784286473 0.2950806315 0.0142910433
H 1.730157941 0.3896057893 1.3629580315
C -3.5193300778 -1.5100591575 -0.7436417506
C -4.0109029917 -2.5592684008 -1.5281257826
C -4.2432492561 -1.0968801453 0.3841813105
C -5.1967031479 -3.202526214 -1.1782796763
H -3.4422721037 -2.8868185276 -2.4019590963
C -5.4292803189 -1.7414228314 0.7283476975
H -3.8501302326 -0.2658823398 0.9783684992
C -5.9070967248 -2.7976950462 -0.0481516318
H -5.5649621988 -4.028772282 -1.7902790621
H -5.9879702821 -1.4151970406 1.6090273406
H -6.8352249747 -3.3045896487 0.2255594641
C -0.9543794707 -1.1974053489 0.9742239623
H -0.1697025561 -0.7900760589 1.6163273208
C -1.3084729232 -2.4934865586 1.1925197162
H -2.1455950246 -2.9496283498 0.6564147077
Cs -1.4583129683 2.6041038432 4.1828799078
C -0.6384043946 -3.3651638789 2.2041157055
H -1.3700378532 -3.788564729 2.9099444854
H -0.1537822246 -4.2100739303 1.6873820962
H 0.1343661501 -2.8224309055 2.7673892914

Metrans_Beta_Habst_TS
H 0.0054724053 -0.9972903511 -1.6636820291
C -1.1599329359 -0.4967700822 -0.4395020677
C -1.3695271054 1.445084027 0.9431793714
Br -0.2389611449 -3.0122222575 -4.1507831662
Pd -1.1478841758 -1.673164161 -2.3819696412
C -0.582613808 0.9427778736 -0.347681195
C -2.4304421034 -0.6483046606 -1.0690227087
H -2.7478601003 0.2227965916 -1.6433629014
O -0.7826963516 1.3799274794 2.0413606411

O -2.5734346419 1.7278269143 0.7583603692
C 0.9550800152 1.0269737754 -0.2093582909
H 1.1719604375 2.0598148489 0.0976494043
H 1.3717489393 0.9226236851 -1.2286255527
C -0.9973914497 1.8219892519 -1.5462057551
H -0.6949426256 1.3206768103 -2.483785558
H -2.0897973642 1.9078903464 -1.5484674251
C -0.4496163322 3.2466138533 -1.5230681518
H 0.6377069396 3.2909070223 -1.676855775
H -0.9170899977 3.8377628487 -2.3242091405
H -0.6824667173 3.7419966968 -0.5675315892
C 1.7456515265 0.1095492474 0.7198028698
H 1.7225009518 -0.9423669526 0.4038195482
H 2.8001911994 0.4254510104 0.7112552433
H 1.3772462219 0.1862168072 1.7503612469
C -3.6073460142 -1.3682661067 -0.5168229931
C -3.6621260602 -2.7221953791 -0.1560859008
C -4.7459262131 -0.5734136695 -0.2834020144
C -4.7932476912 -3.2480309781 0.4701256713
H -2.8231992478 -3.3777524625 -0.3822935261
C -5.8752895142 -1.0990443737 0.3389664491
H -4.7083037168 0.4850431584 -0.5506082175
C -5.8985517786 -2.4395497696 0.7318277599
H -4.8143312446 -4.3066404952 0.7382310355
H -6.7438371552 -0.4592601276 0.5131424998
H -6.7853889335 -2.8584809485 1.2126387891
C -0.7886037222 -1.3824265205 0.7047861667
H -0.6135501563 -0.8248423472 1.6297813405
C -0.5902402937 -2.7028250954 0.7098916299
H -0.6340623301 -3.2562388112 -0.2365007471
Cs -3.3396869064 -0.1661739532 2.8794376372
C -0.2341001009 -3.4889509983 1.9315137627
H -0.9679338959 -4.2912957273 2.1139761757
H 0.7437950299 -3.9811938191 1.80888404
H -0.1822761596 -2.8500023686 2.8262247218

Metrans_Beta_Habst_postTS
H -0.1211975602 -0.8925287126 -1.3627122253
C -0.9383213605 -0.5707148316 -0.5592088575
C -1.4538253448 1.3570388206 0.8751013856
Br -2.4498500543 -3.0539795194 -4.0909881256
Pd -1.1669524767 -1.808705256 -2.5112908468
C -0.5412632528 0.9412761291 -0.334552358
C -2.2807207836 -0.7766803942 -1.2271135405
H -2.5974227996 0.0932893445 -1.806299508
O -0.9601284507 1.3258028557 2.0230847872

O -2.658943518 1.5542491792 0.5995121392
C 0.9704678284 1.1253181288 -0.0657649648
H 1.0932677593 2.1697412933 0.2545249503
H 1.4834797372 1.0485363697 -1.0429600043
C -0.9082581256 1.7930701395 -1.5680036951
H -0.5017655979 1.3108929107 -2.4772654921
H -1.9998182886 1.8078796228 -1.6611793518
C -0.4542805475 3.2492168564 -1.5113589166
H 0.6371669194 3.3624855506 -1.574987981
H -0.8912329088 3.8093768466 -2.3510492591
H -0.7953920834 3.728661802 -0.5805545323
C 1.7252291018 0.2582804519 0.9391873779
H 1.8037593883 -0.7917949795 0.625867832
H 2.7516708723 0.6438477464 1.0396971588
H 1.2447566478 0.3038906867 1.9241269963
C -3.4710865181 -1.3986307204 -0.5831669209
C -3.5346742422 -2.7177202836 -0.1107665593
C -4.6089762376 -0.5867337384 -0.4395464779
C -4.6771740885 -3.1909104109 0.5330195746
H -2.6960291055 -3.3899982557 -0.2815920824
C -5.7547502021 -1.0609128937 0.1963811902
H -4.5650473553 0.4446864757 -0.7920030409
C -5.7894213862 -2.3635708543 0.6977002256
H -4.7083957214 -4.2255727373 0.8816197183
H -6.6272193265 -0.4103084423 0.2929353091
H -6.6900034328 -2.7432162731 1.1861215063
C -0.6815283577 -1.4356829199 0.651816882
H -0.7017205384 -0.8915116243 1.599499308
C -0.3939192117 -2.7365973734 0.6547800288
H -0.3107371845 -3.2674650616 -0.3044036474
Cs -3.4378665125 -0.214679074 2.8301274357
C -0.1680136968 -3.5483343772 1.8911583225
H -0.8968148096 -4.3728581245 1.9615977016
H 0.8313585071 -4.011517495 1.8850975559
H -0.2497106812 -2.9316938574 2.7991990016

Metrans_Gamma_Habs_preTS
C -0.3939585386 1.4111581931 0.6069169607
H -0.8287402055 0.7458308543 -0.1535807711
Br 1.2742695491 4.6037798832 -3.1107940234
Pd 0.2151311049 3.5475433352 -0.9767042886
O -1.3055421591 4.9789465686 -0.8571246316
C -0.9752768198 2.806032515 0.4875249714
H -0.6799718521 3.4055382364 1.3607669434
C -2.436707236 3.0950935298 0.1245968586
C -2.4617196794 4.4808753714 -0.5590943786

O -3.5179551258 5.0266703734 -0.8606054237
C -3.0638638448 2.0801854997 -0.8578262337
H -3.0154293767 1.0782662355 -0.3984475288
H -4.1337851675 2.3298685258 -0.9280319621
C -3.3300437612 3.1204471562 1.3870683195
H -4.3444677702 3.3829395817 1.0471689358
H -3.3807329467 2.0968064051 1.7968046804
C -2.9139869269 4.0928697534 2.4850158236
H -2.7733956108 5.1098272226 2.0861086778
H -3.6921260012 4.1466211522 3.2606065382
H -1.9824299625 3.7875353162 2.9843185869
C -2.4916830303 2.031622017 -2.2699073841
H -1.4191928726 1.7890233535 -2.290868148
H -3.0218295681 1.2822387896 -2.8763590203
H -2.6087573806 3.0029543965 -2.7746697479
C -0.5024041593 0.744235154 1.957153448
C 0.0320749281 1.3430250746 3.1051184888
C -1.1799429983 -0.4710651149 2.0952629118
C -0.1056441069 0.7421849466 4.3540758521
H 0.5601009182 2.297395333 3.0262905701
C -1.3238458929 -1.0744021882 3.3442739198
H -1.6044614469 -0.9513310284 1.2092252774
C -0.7863413902 -0.4690934833 4.4783054587
H 0.318806611 1.224419164 5.2374779235
H -1.8586748954 -2.0229120909 3.430695062
H -0.8972256532 -0.9391277332 5.4578327294
C 0.9981967739 1.8229248792 0.1431158359
H 1.6872355502 2.1889008485 0.9143589086
C 1.4575080937 1.7062959802 -1.1554741132
H 0.8508945772 1.1297286032 -1.865312557
Cs -1.8618879879 6.2432830183 -3.3628375287
C 2.8981148812 1.8993026857 -1.5377286035
H 3.4229234238 2.5369968375 -0.8123059502
H 3.4033522283 0.9199161053 -1.5716963901
H 2.9818187277 2.3687557432 -2.5262229978

Metrans_Gamma_Habs_TS
C -0.0250990088 1.8950694435 0.4135778601
H 0.2216062458 1.2849628382 -0.9883964757
Br -0.7762083075 1.4163134651 -3.9839808976
Pd -0.698616819 2.3876027913 -1.6502660562
O -2.1092747377 3.9922258058 -1.8430466587
C -0.8273399417 3.0878851651 0.2521555545
H -0.2144372651 3.9967853663 0.2420805152
C -2.3037662003 3.4223524541 0.5071097267
C -2.8268102538 4.1407796459 -0.7793606515

O -3.9060803265 4.7165718037 -0.7670656151
C -3.274880648 2.2391147072 0.7596242222
H -2.8750064286 1.6120317489 1.5668885795
H -4.2000795153 2.6877765497 1.1517933434
C -2.4290198333 4.379110462 1.7150702263
H -3.4891126578 4.6712352797 1.7616740998
H -2.2115450128 3.8083976905 2.6349791622
C -1.5808096251 5.6457832342 1.671163785
H -1.7309023363 6.1890377319 0.7250664095
H -1.8681926661 6.323500874 2.4885018468
H -0.5048407229 5.4440265237 1.7823518674
C -3.6562267266 1.3682578762 -0.4339133049
H -2.7840454309 0.9984829233 -0.9941990136
H -4.2350630759 0.4947690129 -0.1003141668
H -4.2923054545 1.9358160346 -1.1312778716
C -0.5667278783 0.6631865891 1.1078984443
C -0.6830876826 0.6962956054 2.5042694875
C -0.9259121056 -0.5023176011 0.4303988433
C -1.1697510674 -0.4037161801 3.2033702859
H -0.410953952 1.6060083779 3.0463841829
C -1.4162103057 -1.6052795015 1.1299901075
H -0.8366228865 -0.5398864591 -0.6583309797
C -1.5429996775 -1.5594802622 2.5158310972
H -1.2639670578 -0.3568937351 4.2904402044
H -1.700386688 -2.506195872 0.5820735005
H -1.929165676 -2.4227171272 3.0619950289
C 1.429929681 2.1372710619 0.7365168712
H 1.6616608094 2.0798346866 1.8072597599
C 2.4016173186 2.4221546388 -0.1315138233
H 2.1522295554 2.4496679307 -1.2003908307
Cs -3.8279567969 3.3171419778 -3.9973779037
C 3.8236934212 2.706489769 0.2374228612
H 3.986191347 2.6469921162 1.3233865212
H 4.5044944573 1.9935355956 -0.2541844305
H 4.1203860476 3.7121171653 -0.1011622719

Metrans_Gamma_Habs_postTS
C -0.0520603863 1.9162691347 0.5480278404
H 0.3144620011 1.0207551177 -1.6224167775
Br -0.8199617995 1.5524922008 -4.0383885766
Pd -0.6196413629 2.2121236109 -1.6655202483
O -1.9743493489 3.9002782248 -1.8180635565
C -0.8114846661 3.0609573628 0.3162524264
H -0.2057210115 3.9639131493 0.185365135
C -2.2879494766 3.4056268535 0.5067690527
C -2.7433264215 4.0928417705 -0.8080870088

O -3.8164461835 4.6867995421 -0.8668990634
C -3.281675488 2.2428706885 0.7601434764
H -2.9142291252 1.6306630031 1.5937370156
H -4.2108238814 2.7150709238 1.1139249343
C -2.431846166 4.395696362 1.6868002819
H -3.4845206391 4.7170033562 1.6827413414
H -2.2668232994 3.8419228971 2.6272594411
C -1.5443443965 5.6352984872 1.647185584
H -1.6397680533 6.1603908738 0.6837390847
H -1.8424707357 6.3407361728 2.4367082027
H -0.4807563501 5.4020265865 1.8054923933
C -3.6398971216 1.347784454 -0.4221058091
H -2.7571982703 0.9386429632 -0.9354934046
H -4.2539105979 0.4998351279 -0.0855693647
H -4.2325469424 1.9074249579 -1.1625471381
C -0.6004012513 0.673550133 1.2003104587
C -0.7516822321 0.6967163125 2.5947949954
C -0.9114958945 -0.5019849784 0.5142653775
C -1.2325114843 -0.414655714 3.2809008007
H -0.5058623859 1.6099446549 3.1438161469
C -1.396659679 -1.6156898139 1.2001854822
H -0.7853854194 -0.5367427272 -0.5692366808
C -1.5632954187 -1.5760495275 2.5822584695
H -1.3541372652 -0.3720346987 4.36552538
H -1.6445027387 -2.5223373614 0.6438931784
H -1.9451860708 -2.4488809109 3.1162127198
C 1.4268904019 2.0656985952 0.7444743762
H 1.7730583401 1.7044205923 1.7217501472
C 2.3185887354 2.5947806581 -0.0970688506
H 1.9785124142 2.9011415671 -1.094494723
Cs -3.850779132 3.5313780168 -3.9198312529
C 3.771781005 2.7822856319 0.2071076044
H 4.0280169927 2.4302459171 1.2170644699
H 4.3971738991 2.237808584 -0.5184793984
H 4.0535729066 3.8450832477 0.1319900366

MethylTrans5-endo-trig_TS
C -0.6819270994 2.2529193004 1.0285518715
O -1.3120398391 0.671732146 -0.2354023237
H -1.4319893472 1.9139973568 1.7370342994
Pd -0.7876030858 4.8476922606 1.1966965336
C -1.0474577764 3.1779885635 0.0166178481
H -0.2222212341 3.3576710438 -0.6828193924
C -2.295186996 2.8023118514 -0.7674783356
C -1.9774584046 1.3027769868 -1.127778908
O -2.2964083071 0.8449863058 -2.2233239171

C -3.6632580463 2.8467748297 -0.0438990963
H -3.8392158286 3.8890926813 0.267721684
H -4.4134365604 2.6319568404 -0.8219494984
C -2.4341873772 3.6574159908 -2.0422307932
H -3.2655254197 3.232659598 -2.6237554862
H -2.7350109423 4.6727531447 -1.7352327438
C -1.2147203221 3.758905842 -2.9524835317
H -0.9079009478 2.7578218024 -3.2952293852
H -1.4665004025 4.3359000635 -3.8543444695
H -0.3683919772 4.2758807048 -2.4736528217
C -3.9276531744 1.9049087782 1.1288369695
H -3.3803323674 2.1993613196 2.0347715528
H -4.9977188077 1.9294548657 1.3843551017
H -3.6638911121 0.8651478004 0.887377363
C 0.7000564379 1.795152041 1.2828638831
C 1.8364569988 2.5029296909 0.858612718
C 0.8634248593 0.5216531115 1.8481700908
C 3.1020906665 1.9306455427 0.9767599027
H 1.7350163457 3.5145744365 0.4508694085
C 2.1280666176 -0.0530652302 1.9494419725
H -0.0212517501 -0.0349888587 2.1629293842
C 3.2520860728 0.6482886444 1.5091655558
H 3.9783176594 2.5009461989 0.660101003
H 2.2377466523 -1.051096778 2.3793136514
H 4.2460121342 0.2041788399 1.6005948734
C -2.1193368544 4.4005052127 2.5689611281
H -3.1594489242 4.6853939442 2.3390847785
C -1.8037539153 3.9919122131 3.8049816557
H -0.7799070915 3.6504172721 4.0150869815
Br 0.9367259398 5.9707530721 -0.2736375518
Cs 1.0354702372 0.550390169 -1.9931093053
C -2.7524707849 3.9596767859 4.9707893281
H -3.7560483462 4.3052634375 4.6820036039
H -2.8438018539 2.9384956079 5.3771633322
H -2.3931807665 4.5989230118 5.793603047

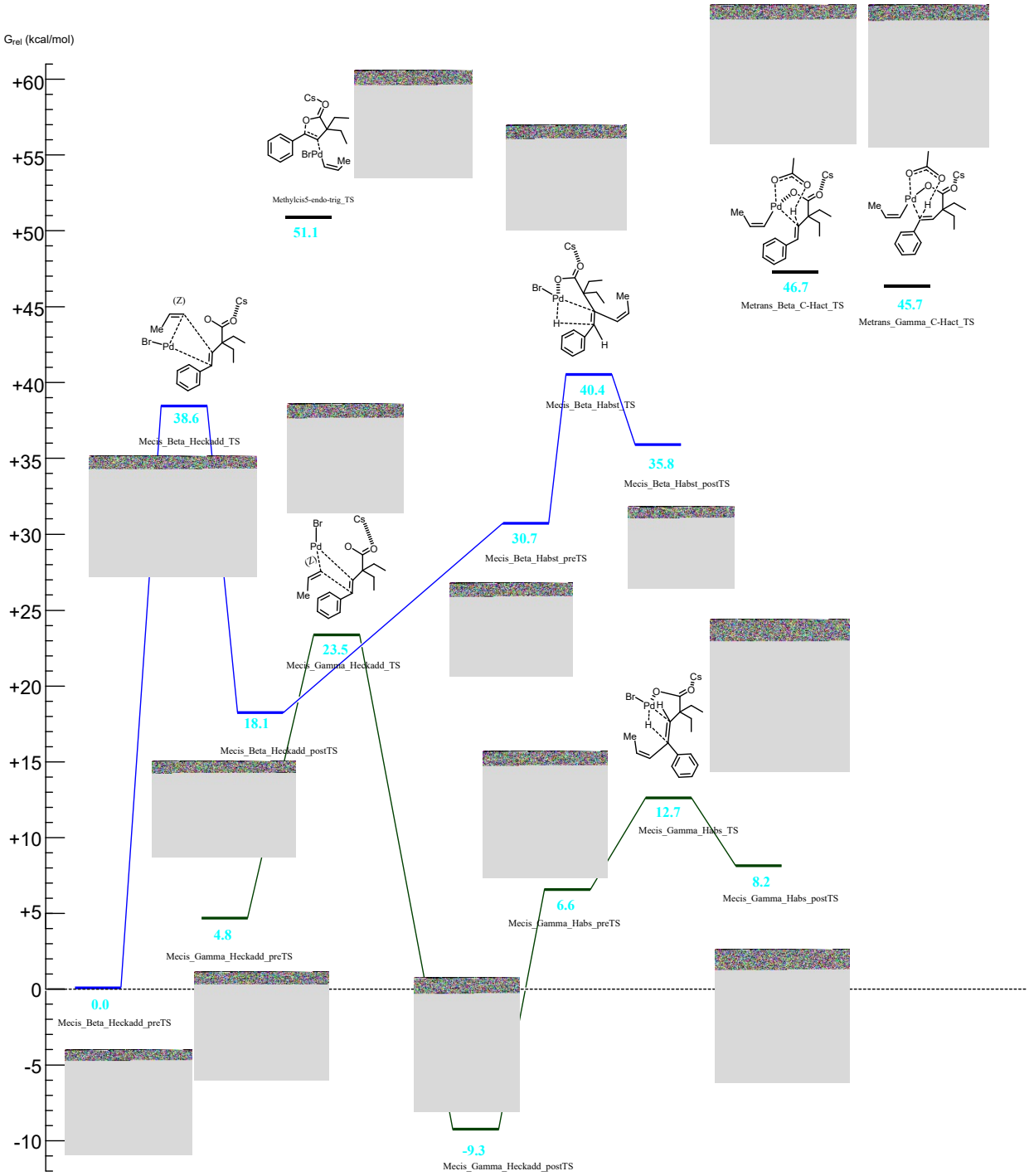
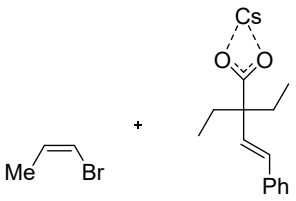


Fig. S4 Model reaction profile of *cis*-1-bromopropene after oxidation addition.



	wB97X-D/BS1							wB97M-V/BS2
	1st frequency (cm-1)	Electronic energy	ZPE corr	Thermal corr	Enthalpy corr:	Gibbs corr	Electronic energy in toluene	Electronic energy
Mecis_Gamma_C-Hact_TS	-1215.4	-1187.083690	0.399927	0.443977	0.445190	0.309308	-1187.114778	-1187.977221
Mecis_Beta_C-Hact_TS	-1143.4	-1187.087370	0.400628	0.444407	0.445620	0.312008	-1187.117607	-1187.979081
Mecis_Beta_Heckadd_preTS	20.2	-3532.833130	0.354088	0.393845	0.395058	0.267053	-3532.864999	-3533.576233
Mecis_Beta_Heckadd_TS	-296.5	-3532.776930	0.354499	0.393078	0.394291	0.270386	-3532.804902	-3533.522003
Mecis_Beta_Heckadd_postTS	23.2	-3532.823030	0.357626	0.395846	0.397060	0.275096	-3532.851580	-3533.558673
Mecis_Gamma_Heckadd_preTS	18.2	-3532.821580	0.353874	0.393928	0.395141	0.266365	-3532.853123	-3533.568230
Mecis_Gamma_Heckadd_TS	-375.4	-3532.795900	0.354029	0.392678	0.393892	0.269210	-3532.827848	-3533.540849
Mecis_Gamma_Heckadd_postTS	16.4	-3532.856750	0.357581	0.395756	0.396969	0.273807	-3532.887870	-3533.598511
Mecis_Beta_Habst_preTS	27.0	-3532.790780	0.355988	0.394764	0.395978	0.271465	-3532.825689	-3533.528679
Mecis_Beta_Habst_TS	-576.9	-3532.771560	0.351650	0.390585	0.391798	0.267338	-3532.806974	-3533.508638
Mecis_Beta_Habst_postTS	26.5	-3532.782360	0.353879	0.392744	0.393957	0.271144	-3532.817391	-3533.520100
Mecis_Gamma_Habs_preTS	26.1	-3532.832430	0.356597	0.395045	0.396258	0.273504	-3532.863028	-3533.573373
Mecis_Gamma_Habs_TS	-795.2	-3532.812890	0.350884	0.389779	0.390993	0.265475	-3532.844954	-3533.554159
Mecis_Gamma_Habs_postTS	22.7	-3532.824040	0.353483	0.392592	0.393805	0.269279	-3532.854891	-3533.566419
Methylcis5-endo-trig_TS	-328.1	-3532.757150	0.353393	0.392415	0.393628	0.268305	-3532.792568	-3533.492491

Cartesian Coordinates

Mecis_Gamma_C-Hact_TS
C 0.48924622 1.8508732304 0.1855775817
H 0.7302877362 0.4568566 0.5144018205
C 2.2966260952 -0.7328416058 0.2881169493
C 3.4863792879 -1.4314484643 0.876500217
O 1.3219797942 -0.4593531213 1.0566941841
O 2.322843026 -0.4047593904 -0.9213248359
H 4.0564891523 -1.9485206325 0.0964610902
H 4.1267710476 -0.6607347278 1.3323929342
H 3.174325583 -2.1257899405 1.6660592997
Pd 0.5923882726 0.5221428626 -1.5831662395
O -1.2293874889 1.2044544138 -2.217654653
C -0.6554129664 2.5492857025 0.3012430661
H -0.591209686 3.5392673804 0.7807365887
C -2.0671815889 2.1965940295 -0.1118877854
C -2.2345554464 1.4555340448 -1.4545664495
O -3.3795934724 1.1300809973 -1.7809238555
C -2.7443385095 1.334545103 0.9857818582
H -2.6452729075 1.8658505188 1.947292933
H -3.8184986874 1.2937285036 0.7485233167
C -2.8764346401 3.5107058652 -0.2578117271
H -3.9249658938 3.2431326694 -0.4543860483
H -2.8525068267 4.031313288 0.7150811998
C -2.3714875829 4.4380567217 -1.3576790174

H -2.4528751408 3.9617916275 -2.3467910797
H -2.9592538975 5.367646681 -1.3853730097
H -1.3153486467 4.7107845422 -1.2088202769
C -2.2087219908 -0.0835239123 1.1298325932
H -1.1498803201 -0.1040065416 1.4179517392
H -2.7749378432 -0.6362737026 1.8944718103
H -2.3064229685 -0.6414474051 0.1836562334
C 1.7301241258 2.4734305557 0.7401615243
C 2.8807884958 2.6280961504 -0.0482939708
C 1.790928367 2.8858314703 2.0799984061
C 4.0418064245 3.1904341852 0.4793191647
H 2.8584388774 2.3069089841 -1.092247398
C 2.9515611241 3.4457160386 2.6104433094
H 0.912001355 2.7475029773 2.7149654325
C 4.0838331199 3.60105108 1.8116189499
H 4.9211762935 3.3097664897 -0.1582747652
H 2.9733766743 3.7572395183 3.6577044473
H 4.9956889569 4.0373168436 2.2258801467
C 0.7832088425 -0.4175307631 -3.3500632437
H 0.8068627688 0.2725715327 -4.2093005493
C 0.9192570914 -1.7257423645 -3.6117530197
H 1.0821608514 -2.0493824202 -4.652376876
Cs -2.5097609731 -1.3340388553 -3.1683653451
C 0.9111197627 -2.8358583177 -2.5941651991
H 0.2173970697 -3.6499640193 -2.8759068668
H 1.9057344384 -3.3020873928 -2.5017014843
H 0.6285756236 -2.4599700303 -1.5986861007

Mecis_Beta_C-Hact_TS
H -1.9801334685 1.0618176883 1.5204195991
C -1.4353871514 0.2029405199 0.4655632616
C 0.8982210293 -0.6918437284 0.6146027625
C -2.4811702202 2.9127691668 2.0945053654
C -3.5331963331 3.883302884 2.5425703234
O -2.7154978525 1.6746318379 2.2495701799
O -1.4482134703 3.3550405115 1.5400487042
H -4.0464361534 3.5140646712 3.4386699975
H -3.1005715377 4.875747771 2.7117538976
H -4.2700070597 3.9505440093 1.7261226907
Pd -0.1251788453 1.9443184768 0.7978440147
C -0.5948679043 -1.0489173399 0.770841503
C -2.458025368 0.1762753491 -0.4149301565
H -2.7535900877 -0.7523949191 -0.9193302927
O 1.1910278036 0.5074961924 0.2179656459
O 1.7829179391 -1.4935474547 0.907656902
C -0.8134011101 -1.4870025515 2.2436985854
H -0.3125642798 -2.455593573 2.3851116776
H -1.8939288352 -1.6589351457 2.3811781142
C -0.9361822861 -2.2306831287 -0.1742082781
H -2.0087540095 -2.4487521441 -0.0395497292
H -0.82789941 -1.872964812 -1.2116498127
C -0.1651589448 -3.5402139291 -0.0254826809
H -0.3115366766 -3.9983032598 0.9640570253
H -0.5271590825 -4.2626675466 -0.7732953499

H 0.9130905146 -3.3984660077 -0.1670666568
C -0.3047455894 -0.5381422506 3.3253316287
H -0.7820371636 0.4500703332 3.2850739059
H -0.4962624323 -0.9606239552 4.3231701493
H 0.7847955152 -0.3979423509 3.238365816
C -3.3426631295 1.3244440516 -0.7306359655
C -4.7349087895 1.1750888522 -0.6297528619
C -2.8367596274 2.5701825414 -1.123625207
C -5.5901793579 2.2466066303 -0.8684858577
H -5.1460874707 0.2060474246 -0.3347957168
C -3.6913772647 3.6455816928 -1.3653915849
H -1.7579289296 2.6944379767 -1.2388234122
C -5.0698483785 3.4906483306 -1.232404803
H -6.6699553142 2.1126827915 -0.7689209528
H -3.2721557825 4.6096468888 -1.661967798
H -5.7398463027 4.3323744736 -1.4227411532
C 1.2784506429 3.3848799209 0.9356999813
H 1.112598482 4.0780714076 1.7761869075
C 2.3002920064 3.6850896095 0.1163624306
H 2.9028328849 4.5815474491 0.3376956606
Cs 3.5456660165 0.8670360814 1.8463735831
C 2.6884381567 2.9588242626 -1.144062595
H 3.7571727935 2.671488738 -1.1428662748
H 2.0832426074 2.0536447873 -1.2881143629
H 2.5571531429 3.6108064081 -2.0234447496

Mecis_Beta_Heckadd_preTS
C -1.7271542387 1.7658125508 -3.4159038001
C -1.6904896043 -0.0235223335 -0.9067319694
Pd -1.8712863186 -0.1676656001 -3.0517549195
C -1.5777220419 -2.5281481301 -1.3062395506
Br -0.972451065 -0.6745799074 -5.3159368426
H -1.115269935 0.8742909967 -0.6531482184
C -1.0338852482 -1.3326643177 -0.4826274186
C -3.0404753343 0.1272714812 -1.2026808901
H -3.6547191197 -0.7777532563 -1.2445061298
O -1.4036106848 -3.6791945591 -0.9065656229
O -2.0721946061 -2.243009983 -2.4536493479
C 0.4820869099 -1.2264322692 -0.8205686321
H 0.859983582 -0.2898740056 -0.3758222514
H 0.5728249756 -1.0842339958 -1.9117379491
C -1.2310976002 -1.5702862701 1.0272170488
H -0.7458286685 -2.5281015908 1.2640446652
H -0.6877748709 -0.7845057986 1.581217296
C -2.6799908268 -1.6325907705 1.4952205582
H -3.2375302814 -2.4003409086 0.9369235885
H -2.7268210349 -1.900433175 2.5610029329
H -3.2014740232 -0.6715774785 1.372497776
C 1.3735917506 -2.3837469232 -0.3822497364
H 0.974368161 -3.350747879 -0.7207652536
H 2.3897679442 -2.2519879655 -0.7843052411
H 1.4605981385 -2.4426807546 0.7122518488
C -3.8183244429 1.3839813328 -1.1415836271
C -5.1439237346 1.3678728722 -1.5964565169

C -3.2927710641 2.5892775717 -0.6568422524
C -5.921122664 2.5228828837 -1.5805331864
H -5.5635290621 0.4336727421 -1.9788168254
C -4.0687387201 3.7440214656 -0.6380901561
H -2.2640993536 2.6300208221 -0.2959446299
C -5.3843095303 3.7170139452 -1.1017106588
H -6.9503751419 2.4902640977 -1.9442028668
H -3.6420826206 4.6748308673 -0.2582178675
H -5.9903853478 4.6254144693 -1.0868345651
H -2.6850158922 2.2000827001 -3.735759635
C -0.6558630061 2.5457602797 -3.2689933583
H -0.7804460234 3.6180297798 -3.4765905802
Cs -0.3460084157 -3.9575544731 -3.9660791814
C 0.7232667777 2.1164055296 -2.8621444795
H 1.019706797 2.5661675987 -1.8984636656
H 0.788552659 1.0235748472 -2.7694399669
H 1.4701638267 2.436612512 -3.6063449214

Mecis_Beta_Heckadd_TS
C -0.5656867248 1.8084430163 -2.2093412374
C -1.5584887267 0.3965688619 -1.0441056451
Pd -1.9910913486 0.8428233592 -3.2881977284
C -1.0357826354 -1.9623179975 -1.756384009
Br -3.549220089 0.2554046168 -5.1270180479
H -1.3993384223 1.180328284 -0.2972621089
C -0.8089864618 -0.8833920802 -0.6530273356
C -2.9057281597 0.306643668 -1.5500144823
H -3.2558833607 -0.7115410326 -1.7534512167
O -2.0713976357 -2.6611475418 -1.6759569817
O -0.2017271652 -2.0046437091 -2.6911612696
C 0.6927868602 -0.6068521204 -0.455238805
H 0.8061748953 0.2666543511 0.2120735835
H 1.1203486007 -0.3268196844 -1.419316241
C -1.3920704817 -1.3339674258 0.7242626394
H -1.0022558611 -2.3469296607 0.9018634375
H -0.9356217146 -0.6901373065 1.49764191
C -2.9009263441 -1.3668476238 0.9456498529
H -3.3845631774 -1.9932439196 0.1865446264
H -3.1131658304 -1.797604746 1.9362275062
H -3.3583044323 -0.3659301759 0.9299598639
C 1.4984874424 -1.7816397828 0.0901004857
H 1.3638383152 -2.6682770948 -0.5474448375
H 2.5710345335 -1.5357353892 0.0931603898
H 1.2222309823 -2.0490870265 1.1205718135
C -3.9788253029 1.2806995359 -1.2361585304
C -5.2836524029 0.9841114424 -1.6566374196
C -3.7579814884 2.476644117 -0.5381256898
C -6.3340831336 1.8563601749 -1.39426709
H -5.4617857526 0.0630987335 -2.2158925501
C -4.8085885358 3.3513533705 -0.2758237014
H -2.7569291866 2.73379908 -0.1859088792
C -6.1000290731 3.0453432965 -0.7034608907
H -7.3416936722 1.6092033752 -1.734655384
H -4.6173164876 4.2777446127 0.2699015692

H -6.9232926314 3.7324577242 -0.4969560754
H -0.8774077731 2.70877587 -1.6703783432
C 0.6430742965 1.7821953575 -2.7966834368
H 1.216192026 2.7171137166 -2.7167009692
Cs -2.1965757101 -3.0067425648 -4.6018539766
C 1.2821111886 0.6936331738 -3.6035661774
H 2.3358048884 0.5686411843 -3.3079494668
H 0.7661715235 -0.2725175408 -3.4833022932
H 1.2882820123 0.9789627102 -4.6695826038

Mecis_Beta_Heckadd_postTS
C -0.6276312929 1.581145717 -1.8518708309
C -1.3323163633 0.5490476077 -0.9590098463
Pd -2.0373534301 1.3941621013 -3.5192174573
C -0.9485038833 -1.910018023 -1.6889619233
Br -3.669030469 0.8597816455 -5.2946884167
H -1.4853458381 1.0607306487 0.0036025992
C -0.7074962457 -0.834417436 -0.5799779772
C -2.6343019303 0.5213683949 -1.7398384395
H -2.9149593511 -0.4848448124 -2.0738079082
O -2.1223618134 -2.3326935646 -1.8289129513
O 0.0157391533 -2.2524290384 -2.4116882522
C 0.7951079187 -0.6184504201 -0.3120166379
H 0.900227943 0.2540698076 0.3597529333
H 1.2876822409 -0.3468305864 -1.2534397677
C -1.3808725972 -1.3088062296 0.739891802
H -1.0676836979 -2.3494024774 0.9159073198
H -0.9374604515 -0.71673216 1.5619999749
C -2.9013909382 -1.2409939033 0.856807902
H -3.3740018028 -1.8074453056 0.045376123
H -3.2181874199 -1.6712476191 1.8192797414
H -3.2811775344 -0.2080831183 0.8317174524
C 1.5414501278 -1.8077017333 0.2846614737
H 1.4172859234 -2.6919879203 -0.3558712752
H 2.6175088959 -1.5868017019 0.3524550208
H 1.1949222189 -2.0551417911 1.2989569863
C -3.7884716225 1.3568326509 -1.3406672542
C -5.0699617561 0.9734510777 -1.7697277904
C -3.669568017 2.5093857008 -0.5462440237
C -6.1931047257 1.7114295011 -1.416291531
H -5.1720561972 0.0886702892 -2.4015003941
C -4.7927489443 3.2507665246 -0.1945376309
H -2.6888954019 2.8348933093 -0.1933680533
C -6.0580343293 2.8548408113 -0.6286954314
H -7.1798878771 1.3954744808 -1.7602606561
H -4.6805807106 4.143752504 0.4238633766
H -6.9388817998 3.4383178705 -0.3525000306
H -0.7664733144 2.6049393727 -1.4846107766
C 0.1197967335 1.50479751 -3.016766331
H 0.4386292995 2.4914274906 -3.3812811119
Cs -1.8773135388 -2.3259350073 -4.7621097294
C 0.8628539738 0.3797027632 -3.6740335101
H 1.9408490859 0.5258064251 -3.4876095034
H 0.5927907111 -0.6159881045 -3.2957242067

H 0.7293500679 0.4327787481 -4.7669080568

Mecis_Gamma_Heckadd_preTS
C 0.0164922234 2.0296814861 -0.193953301
C -0.1327605152 1.1037281378 -2.8272316607
Br -2.5722405263 2.3018627885 -4.2347095
H -0.384128344 1.0861515139 0.1867015123
O -2.7633140296 3.9836903694 -1.3912382089
C -0.718811656 3.1755403539 -0.0329577428
H -0.232737945 4.1207781694 -0.2914981711
C -1.9897504163 3.3604644499 0.7803425544
C -3.0589880222 3.9790986757 -0.1450983092
O -4.1336220672 4.3665075956 0.3109747132
C -2.5700403462 2.0626399741 1.3863265601
H -1.7689611955 1.5482001345 1.943101256
H -3.3113115228 2.3742748369 2.137409624
C -1.7071421975 4.3388692287 1.9463578836
H -2.664575668 4.4634474896 2.4748522178
H -1.0087325753 3.8534289254 2.6495324466
C -1.1857664831 5.7186990132 1.5582395849
H -1.8416633674 6.1955745858 0.8135303484
H -1.1575499962 6.3744286508 2.4407297213
H -0.1653854166 5.6902410372 1.1476962752
C -3.2500943036 1.0892944407 0.4285203565
H -2.5842287371 0.735352294 -0.3706135536
H -3.6195824454 0.2085722506 0.9742378507
H -4.1189410583 1.5640458189 -0.0529057368
C 1.4570224223 1.9806980877 -0.5368237818
C 2.1690448756 3.0899176387 -1.0142041027
C 2.1411277127 0.7714290143 -0.3716576105
C 3.5246025553 2.9905819836 -1.3082532784
H 1.6569591252 4.0399549685 -1.1807417059
C 3.5002977168 0.6704201256 -0.6604502358
H 1.5933174362 -0.1070790466 -0.022422613
C 4.1978731369 1.7806254374 -1.1301548815
H 4.060464553 3.8644603848 -1.6850069134
H 4.0140071391 -0.2836827429 -0.5245033058
H 5.2620042019 1.7045826384 -1.3634852921
Pd -1.3615563685 2.4805646621 -2.0831934976
H 0.8052979083 1.5471765212 -3.1887366984
C -0.3198742192 -0.2135143672 -2.9028106947
H 0.4986612424 -0.811581705 -3.3271172168
Cs -5.3933955513 3.5972756695 -2.4731588727
C -1.5386497685 -0.9772311715 -2.4722231894
H -1.8122472854 -1.7385448323 -3.2195386986
H -1.3713923351 -1.5099999587 -1.5190569003
H -2.3999088866 -0.3053375279 -2.3474832316

Mecis_Gamma_Heckadd_TS
C -0.0201304357 1.8738980788 -0.6991242448
C -0.1901054475 1.2075785007 -2.5635825807
Br -3.0661083745 2.0257410404 -4.3040219597
H -0.3527835548 0.9653330809 -0.1911034433
O -2.9588602445 4.1231285331 -1.4374636698

C -0.8087895417 3.0492073879 -0.4473445787
H -0.2735558397 3.9935232005 -0.5975721201
C -1.9561745467 3.2189036537 0.5575342242
C -3.0555222126 4.0599470301 -0.1517451029
O -3.9871271541 4.5407176846 0.4816888826
C -2.6168902524 1.8967744422 1.0309762345
H -1.8232681356 1.1614151558 1.2430691169
H -3.0891912416 2.1041213482 2.0029466949
C -1.4620041677 3.9683377241 1.8155703328
H -2.357530255 4.1546531418 2.4285675226
H -0.8078143029 3.2902694929 2.3912729405
C -0.7510600726 5.2958021539 1.5753818523
H -1.3542522614 5.9577862247 0.9343776836
H -0.590406278 5.8187533246 2.5295990718
H 0.2364556435 5.1690544239 1.1067589272
C -3.6781907429 1.2744175044 0.1251318748
H -3.334104471 1.1513329758 -0.9141261493
H -3.9780988098 0.2854663086 0.5021752055
H -4.5779689129 1.9084531437 0.1161092743
C 1.4737029341 1.9858925662 -0.7356918412
C 2.1289391859 3.0922732068 -1.2898182721
C 2.2418400695 0.9561643251 -0.1846572297
C 3.5184825642 3.1711013691 -1.2766831954
H 1.5474682373 3.8925932831 -1.7543538008
C 3.632868539 1.0370896319 -0.1635540875
H 1.7418577534 0.0777970472 0.2324065953
C 4.2762341499 2.1460769907 -0.7091734333
H 4.0141508403 4.0390188745 -1.7168370393
H 4.2162985398 0.2266740597 0.2788077327
H 5.366308238 2.2102007416 -0.6982706732
Pd -1.6652242973 2.6255915845 -2.2224245601
H 0.6135014585 1.6513267232 -3.1619736969
C -0.4239047646 -0.1096625372 -2.6803625504
H 0.1619394939 -0.6532289979 -3.432454389
Cs -5.5778911546 3.722081818 -2.4581128333
C -1.4492893697 -0.9100931723 -1.9469227517
H -2.3470563865 -1.0164394285 -2.5794467445
H -1.0846457048 -1.9214317163 -1.7116901805
H -1.7722787144 -0.4223619247 -1.0165410385

Mecis_Gamma_Heckadd_postTS
C 0.0691936454 1.6452343646 -1.0553663168
C -0.1952725294 1.5232724303 -2.5516726824
Br -4.1091391972 1.9067734032 -4.0942590688
H -0.2884416035 0.7386003509 -0.5491756701
O -3.2120432713 3.8731409932 -1.3364828005
C -0.9232304129 2.7823254398 -0.8767424589
H -0.4542701694 3.7289560493 -1.1821642762
C -1.7669711692 3.0112606254 0.3844476397
C -3.0039456857 3.8286049984 -0.0591324434
O -3.7742961231 4.3208498913 0.7566709722
C -2.289394768 1.7162920553 1.0549167333
H -1.4363653482 1.0328015456 1.2001158412
H -2.6247727633 1.9918477811 2.0665595182

C -0.9709640226 3.7907625442 1.4559190444
H -1.6812028902 4.0080331182 2.269466215
H -0.1973488848 3.1210960031 1.8704550994
C -0.3284184049 5.0962754539 1.0013709385
H -1.0591179661 5.7445909791 0.4922119646
H 0.0578007298 5.6520669478 1.8684940957
H 0.5197484292 4.9302450878 0.3206936172
C -3.4350089007 0.9822532873 0.3643614232
H -3.2287669152 0.7657712627 -0.6944384864
H -3.6500204362 0.0303999212 0.8721702441
H -4.3538770467 1.5873962151 0.4060259315
C 1.4912642961 1.9105218948 -0.6236376139
C 2.2312200251 2.966563409 -1.1706205779
C 2.0863796092 1.1272053507 0.3700693391
C 3.528826748 3.2290773442 -0.737724172
H 1.7870907556 3.601043197 -1.9425869707
C 3.3838302266 1.3882971315 0.8092302955
H 1.522091452 0.2998298899 0.8094359083
C 4.1098158594 2.440858564 0.2557426755
H 4.0896096887 4.0570546605 -1.1771272669
H 3.829187559 0.7651037328 1.5879947915
H 5.1262609206 2.6479577892 0.597258253
Pd -2.1830743995 2.4107010873 -2.4217624946
H 0.3805032446 2.194169728 -3.1988421507
C -1.0842114968 0.6437555083 -3.1530670904
H -1.1322877563 0.6870192186 -4.2460414193
Cs -6.0299820077 3.5950906527 -1.6102388424
C -1.6510005607 -0.6169536173 -2.5586481007
H -2.7021300002 -0.7338579717 -2.8574028734
H -1.0930304857 -1.4851558848 -2.9467032936
H -1.5944169734 -0.6418474333 -1.462451471

Mecis_Beta_Habst_preTS
H -0.2744000897 -0.9535422693 -1.4754793231
C -1.0247522803 -0.6371145534 -0.6213725923
C -1.483706184 1.2900101866 0.8484589018
Br -2.9768589651 -2.646237606 -4.2472101057
Pd -1.4589265804 -1.6963661345 -2.6693065123
C -0.5640493088 0.8520062849 -0.3463088392
C -2.414526645 -0.7319180022 -1.2220495464
H -2.7286821277 0.1995558311 -1.6945622812
O -1.0284724811 1.1902739619 2.0089179758
O -2.6636159028 1.5846073102 0.5486316491
C 0.9474016934 0.9744779873 -0.0395994425
H 1.0958040199 2.0131603417 0.2884126646
H 1.4827328564 0.8874252831 -1.0039174693
C -0.8583066646 1.7417218224 -1.5748637951
H -0.4299327028 1.2651331792 -2.4768844955
H -1.9426453098 1.7962361328 -1.7172095631
C -0.3644656467 3.1824350671 -1.4711398345
H 0.731414301 3.2647359127 -1.4894792628
H -0.7514004111 3.7707873679 -2.3161223322
H -0.7295498565 3.653625256 -0.545321118
C 1.6496031961 0.0835056656 0.9824148452

H 1.7588196554 -0.9544113101 0.6426066723
H 2.6633179414 0.4770954099 1.15638626
H 1.1092728628 0.0936967005 1.9364704403
C -3.5922421037 -1.3624448037 -0.568786111
C -3.6281446546 -2.668744741 -0.0588219642
C -4.7513869801 -0.5754523261 -0.4587941774
C -4.7667401298 -3.1518580281 0.5839427983
H -2.7664271884 -3.3201696223 -0.188945618
C -5.8941392449 -1.0605966405 0.1734117521
H -4.7296120108 0.4449611997 -0.8449623696
C -5.9024410798 -2.349790274 0.7096889729
H -4.7756317967 -4.1753474827 0.9652633956
H -6.7845891719 -0.4308397972 0.2397867785
H -6.7994785336 -2.7391012033 1.1969329949
C -0.7806694385 -1.5601332665 0.5482283564
H -0.9820185734 -1.0837756842 1.5098534936
C -0.3156859057 -2.8126757395 0.5717017163
H -0.2382478897 -3.272346027 1.5639147201
Cs -3.6439790002 -0.0267534886 2.8019964337
C 0.1324619736 -3.6808939842 -0.5655141966
H 0.9666937867 -4.3244542034 -0.250490129
H -0.676846415 -4.3475192332 -0.9102152588
H 0.4690049869 -3.1064904797 -1.4410784839

Mecis_Beta_Habst_TS
H -0.0651578993 -1.0153483441 -1.7746500302
C -1.2033677873 -0.5286537585 -0.487195045
C -1.3539263743 1.396610617 0.9498721926
Br -0.4226717308 -2.5185949009 -4.536290283
Pd -1.2829513446 -1.4793081236 -2.5507761874
C -0.5898254161 0.9002734994 -0.3558117462
C -2.5001008694 -0.6038746331 -1.0681256688
H -2.8233430909 0.3178435916 -1.5521014619
O -0.7703711097 1.277083623 2.0456865043
O -2.5448951673 1.736063734 0.7760183827
C 0.9512264113 0.9496446878 -0.2311803705
H 1.1883206429 1.9733991563 0.0905876743
H 1.3558440426 0.8569014461 -1.2563589108
C -0.9864559484 1.8254584893 -1.5278699914
H -0.6857096104 1.352579354 -2.4802373037
H -2.0766812727 1.9314639054 -1.5356311706
C -0.419377891 3.2412164539 -1.4552986086
H 0.6684235941 3.2765500989 -1.6075512176
H -0.8782459457 3.8644026613 -2.2369205656
H -0.6474544294 3.7077079924 -0.4842861706
C 1.7396048384 0.0078330326 0.6748366739
H 1.7153027198 -1.0354883647 0.3330287089
H 2.7944174449 0.3233587012 0.6734597211
H 1.3715606397 0.0585829095 1.7069775271
C -3.6694295169 -1.3524596891 -0.5468774753
C -3.6902742647 -2.7054791289 -0.1801694724
C -4.8340610418 -0.5897507395 -0.3345740079
C -4.8163116525 -3.2612843033 0.4278752673
H -2.8283367151 -3.3348191277 -0.3858300893

C -5.958252549 -1.1450984575 0.2710063301
H -4.8260380206 0.4674420639 -0.6098819793
C -5.9492244655 -2.4844001402 0.6678547036
H -4.8107393183 -4.3186152739 0.7018065947
H -6.8476634727 -0.5302651657 0.4284974413
H -6.8311779762 -2.9269889901 1.1361874443
C -0.8167077774 -1.4489683573 0.630093605
H -0.6770414899 -0.875630224 1.5510691354
C -0.531182683 -2.7556359994 0.7183673426
H -0.2578217808 -3.0901368946 1.7273209111
Cs -3.4002123884 -0.1641548556 2.836354734
C -0.4150295786 -3.8249675652 -0.3205954954
H 0.6317574995 -4.1645677021 -0.3803968109
H -1.0114686186 -4.7085335733 -0.0405270182
H -0.7109913167 -3.5049146502 -1.3291785458

Mecis_Beta_Habst_postTS
H -1.0166262301 -0.5052355141 -3.1883267084
C -1.1817702568 -0.5534021488 -0.4026786267
C -1.3225576667 1.373675384 0.9989554085
Br 0.1907871636 -2.7479627221 -4.1132974385
Pd -0.9355556713 -1.6790689039 -2.2708180437
C -0.56789983 0.866603535 -0.3126389068
C -2.4269178476 -0.7055018923 -1.050331592
H -2.7307927702 0.1618794646 -1.633373472
O -0.749370403 1.2212271889 2.0963116142
O -2.500443767 1.7528702108 0.8213431133
C 0.9751001392 0.9218422099 -0.2079893477
H 1.2162968697 1.9445887983 0.1151545212
H 1.3647924358 0.8270586246 -1.2371997032
C -0.9850110753 1.79694437 -1.4726832771
H -0.6336667689 1.3676223242 -2.4265406414
H -2.0787226363 1.8503579825 -1.5049317623
C -0.4843573227 3.2345245278 -1.3537972236
H 0.6054979262 3.3184070287 -1.4689920136
H -0.9439206003 3.8544254575 -2.1378720832
H -0.7655348927 3.6684896465 -0.3821049353
C 1.7728510634 -0.0240805049 0.6842409183
H 1.7391202936 -1.0652121537 0.336096563
H 2.8291521188 0.286225164 0.6689060662
H 1.4214982316 0.023817451 1.7226250298
C -3.6320378119 -1.4120928623 -0.5382623389
C -3.7100257305 -2.7214227 -0.0426323119
C -4.786920974 -0.6100577876 -0.4461685007
C -4.8766899057 -3.1920704641 0.5626100016
H -2.8621839251 -3.3934149792 -0.133365243
C -5.9517949347 -1.078500955 0.1554070625
H -4.7430462739 0.41690051 -0.8153602532
C -5.9993111789 -2.3735355424 0.6759181099
H -4.9087137661 -4.2183882628 0.9353455072
H -6.8278619952 -0.4283740135 0.2145443224
H -6.912579555 -2.7499033203 1.1420093141
C -0.7845713125 -1.4601905139 0.7161352131
H -0.6127921171 -0.9099554422 1.6461682666

C -0.5185160071 -2.7728778369 0.7384396398
H -0.2102331575 -3.1835508439 1.7064599677
Cs -3.4562497947 -0.1516780974 2.8075728741
C -0.4441336271 -3.7465995237 -0.3977019342
H 0.5886384326 -3.8443892372 -0.7678817253
H -0.7705646705 -4.7510763582 -0.0882879365
H -1.0883971979 -3.5124412977 -1.2724134944

Mecis_Gamma_Habs_preTS
C 0.0907096647 1.9024804471 0.3308450963
H 0.9106485004 1.7696212508 -0.3931385315
Br -3.3576234609 -0.2050475572 -3.2363294988
Pd -1.9612044407 1.3614388646 -1.6819884662
O -3.0704294601 3.0728112012 -1.9289241655
C -1.0085104025 2.6575615441 -0.456841125
H -0.517141817 3.3318318341 -1.1743910932
C -2.1238323642 3.4561384151 0.2567054146
C -3.1998586026 3.7351422962 -0.819666487
O -4.1519568765 4.4754812774 -0.6110424748
C -2.8310704944 2.717907643 1.4252942244
H -2.0619639882 2.3744356299 2.1340059562
H -3.421344175 3.476801596 1.9624227381
C -1.643512192 4.8193633321 0.8156294979
H -2.5585208782 5.3735537584 1.0783793508
H -1.0910470026 4.6511905936 1.7527286772
C -0.8008965704 5.6701736685 -0.1257827628
H -1.2898645601 5.7915087331 -1.105732773
H -0.6535179264 6.6756109893 0.295937517
H 0.1957527038 5.2361320669 -0.2946088566
C -3.759252175 1.5540418451 1.0937340552
H -3.2538750244 0.7323296409 0.5661617009
H -4.1919251898 1.1410357724 2.0171261096
H -4.5994244295 1.8927671061 0.4675441541
C -0.4093050984 0.4960143531 0.6077466534
C -0.5760738194 -0.0753583489 1.8681937328
C -0.8191299093 -0.249873694 -0.5169788461
C -1.1520084154 -1.3404736324 1.9999362335
H -0.2653726109 0.4682895528 2.7617202417
C -1.406491542 -1.5104252265 -0.387552133
H -0.5017925337 0.081312952 -1.5478708727
C -1.5766680906 -2.0572735166 0.8811852798
H -1.2762902909 -1.7698778663 2.9969548443
H -1.7429503274 -2.0340658208 -1.2838346455
H -2.0369260294 -3.0400531007 0.9988115806
C 0.6513662529 2.6440793926 1.5135319529
H 0.0663158497 2.6102620701 2.4379510139
C 1.7686017162 3.3799472361 1.5296674305
H 2.0236404806 3.8780515592 2.4723179808
Cs -5.7724876749 2.3285797534 -2.5482355329
C 2.7179398463 3.6336301823 0.3986196812
H 3.740286445 3.3236334013 0.6682950141
H 2.43619013 3.1133584995 -0.5268702564
H 2.7647427835 4.7114483052 0.1728593889

Mecis_Gamma_Habs_TS
C -0.0213976041 1.7921318359 0.3006244751
H 0.16167205 1.1388618697 -1.0849574517
Br -1.0622893537 1.0805321225 -4.0198398818
Pd -0.8153831906 2.1938531021 -1.7600242309
O -2.2080758275 3.8174290562 -1.9477598783
C -0.8187091386 2.9852623623 0.10931764
H -0.2030552728 3.8883226595 0.0422061374
C -2.2720192921 3.3608817718 0.43270301
C -2.848502563 4.0456221572 -0.8491419291
O -3.9000145034 4.6674668254 -0.7958644983
C -3.2600261846 2.2158718692 0.7811867952
H -2.8301663257 1.5997923408 1.5810805896
H -4.1439355067 2.705966762 1.2166399725
C -2.3053480649 4.3614850277 1.6111639815
H -3.3509083327 4.6946348653 1.6949574001
H -2.0655861624 3.81363552 2.5392466952
C -1.4141103878 5.5928721362 1.4859295595
H -1.5811162198 6.1058995299 0.525738061
H -1.6449848572 6.3111316907 2.2863261722
H -0.3427166861 5.3544262681 1.5661896429
C -3.7456001579 1.3237787466 -0.3577341714
H -2.9240423707 0.909353886 -0.9615040055
H -4.3265773384 0.4793916301 0.0406991939
H -4.4105347426 1.8913316928 -1.0277345608
C -0.5811507261 0.5986808541 1.0468980791
C -0.6173128431 0.6674835935 2.4465869666
C -1.041553481 -0.5579774774 0.4179899723
C -1.1305017076 -0.3854024684 3.1969648751
H -0.2583408326 1.5694276584 2.9497446573
C -1.5569104506 -1.6148104337 1.1695547235
H -1.011308249 -0.625380726 -0.6725266487
C -1.608232541 -1.5310084138 2.5581895783
H -1.1627445371 -0.3101345183 4.2860382241
H -1.9199429513 -2.5095911911 0.6594599966
H -2.0147455828 -2.3576140485 3.144763888
C 1.4494587895 1.9925285759 0.5865760337
H 1.7968739554 1.4291353357 1.4576569922
C 2.3538630783 2.7407652511 -0.0586965469
H 3.3603092034 2.7355158026 0.3742038268
Cs -4.0460248148 3.0741515627 -3.9784015682
C 2.1833484281 3.5780394834 -1.288479218
H 3.1152570048 3.6051447792 -1.8704267335
H 1.3755212001 3.2064702647 -1.9420351578
H 1.9314976287 4.6201559189 -1.0289932509

Mecis_Gamma_Habs_postTS
C -0.0522711742 1.8195994342 0.4081123148
H 0.1935744006 0.8358085199 -1.7621460915
Br -1.1167999466 1.2486498906 -4.1148684429
Pd -0.7475640979 2.0229186644 -1.7969885538
O -2.0866062117 3.7275570402 -1.935160675
C -0.807179296 2.9630036512 0.1586941123
H -0.2103858621 3.8549393819 -0.0439696741

C -2.2611569248 3.3482864096 0.4257696478
C -2.7814143881 3.9912351061 -0.8877598751
O -3.837536541 4.6167519911 -0.9058886629
C -3.267167822 2.2255938208 0.7881730616
H -2.8601800916 1.6288427302 1.6142430836
H -4.1551458168 2.7371310454 1.1897518837
C -2.3059484306 4.390662018 1.5683661352
H -3.346152517 4.748073626 1.607706344
H -2.1058725675 3.870787215 2.521143594
C -1.3814225637 5.5954865401 1.426521855
H -1.5073809206 6.0786866864 0.4446746571
H -1.616137664 6.3468441501 2.1946750436
H -0.3194637711 5.3322233976 1.5453945365
C -3.7339483297 1.3068103111 -0.3370758393
H -2.9013278596 0.8692076469 -0.9074551424
H -4.3319796082 0.4785541877 0.0697169124
H -4.37536221 1.8591415755 -1.0415373258
C -0.612012767 0.6173276294 1.1253000583
C -0.6584976972 0.6813026378 2.5260397362
C -1.0322527583 -0.5554547775 0.4957268338
C -1.1482305658 -0.38453504 3.2747564732
H -0.3200535437 1.5907896465 3.0298747758
C -1.5251401421 -1.6244371005 1.245079175
H -0.9847470901 -0.6244762097 -0.5924338452
C -1.5909048044 -1.542117201 2.633498246
H -1.1878716199 -0.3099881691 4.3637416781
H -1.858696987 -2.5296561444 0.7329934397
H -1.9795071474 -2.3795039503 3.2170663428
C 1.4383756028 1.893797128 0.5153742494
H 1.8437152209 1.1614557694 1.2206728932
C 2.3286487702 2.6997562113 -0.0845629281
H 3.370044228 2.5546350899 0.2220636274
Cs -4.0884382608 3.3006542733 -3.9052316097
C 2.0976634036 3.7408343975 -1.135699901
H 3.0179315599 3.9314342665 -1.7046388107
H 1.308883507 3.4333407732 -1.8453584575
H 1.7798513054 4.7035707293 -0.6998328756

Methylcis5-endo-trig_TS
C -0.669547451 2.4754349093 1.0362757644
O -1.2999475148 0.7578833008 -0.0384008013
H -1.4041252978 2.2107353495 1.7916874447
Pd -0.8027212638 5.0700358524 0.9212119795
C -1.0606304534 3.2793455073 -0.0652284368
H -0.2466116084 3.3896512028 -0.7916047345
C -2.312683441 2.8076483911 -0.7882068159
C -1.9788947938 1.2818184931 -0.98769012
O -2.2994683145 0.705137043 -2.0252630644
C -3.6736401278 2.9129176272 -0.0578918147
H -3.8576975667 3.9796573021 0.1481352803
H -4.4291657023 2.6129360936 -0.8018671052
C -2.475445337 3.5168975126 -2.1467866308
H -3.3020454937 3.0158760562 -2.6715388922
H -2.7937622291 4.5539699912 -1.9497847138

C -1.2633110353 3.5404957271 -3.0720380075
H -0.9351077004 2.5139700691 -3.3010239029
H -1.5325428787 4.0052507059 -4.0318266655
H -0.4260340567 4.1261887755 -2.6614594367
C -3.91572444 2.0925938307 1.2071682057
H -3.360380036 2.4820866771 2.0711767806
H -4.9827798235 2.135594281 1.4726003126
H -3.6464302504 1.0356401215 1.068738349
C 0.7215859855 2.0569303734 1.3097103402
C 1.8418969908 2.7215345419 0.785668281
C 0.9086875208 0.8579401436 2.01302161
C 3.1158201118 2.1778810164 0.944353446
H 1.7222759862 3.6801254367 0.2691400085
C 2.1809797251 0.3096580289 2.1549361441
H 0.0360268124 0.3345477034 2.408099999
C 3.2893915304 0.9661258012 1.6164414772
H 3.9799182806 2.7162684598 0.5484499919
H 2.3092738423 -0.6315599969 2.6939293941
H 4.2896104036 0.5443691154 1.7393969168
C -2.1238694293 4.7683829608 2.3490515464
H -3.1563670226 5.0336708591 2.0748925801
C -1.8487318287 4.4829826054 3.6290428498
H -2.6650815792 4.5862639898 4.3595478981
Br 0.8899495848 6.054435369 -0.6764234098
Cs 1.0203936601 0.4372147601 -1.803392078
C -0.5357369145 4.0285258474 4.1983925114
H -0.6338257399 3.0355886444 4.6694263398
H 0.2471190134 3.9693087143 3.4279956631
H -0.1863235435 4.7169973329 4.9846993668

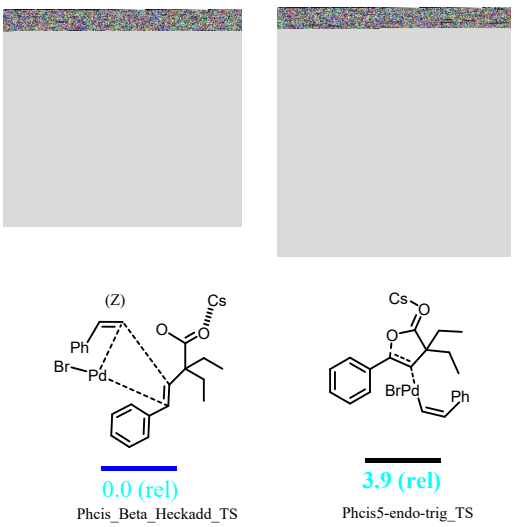


Fig. S5 Computationally located transition states of Heck addition and lactonization for (*Z*)-β-phenyl vinyl bromide.

	wB97X-D/BS1							wB97M-V/BS2
	1st frequency (cm-1)	Electronic energy	ZPE corr	Thermal corr	Enthalpy corr:	Gibbs corr	Electronic energy in toluene	Electronic energy
(Z)-2-bromoalkenylbenzene	23.3	-2882.61857	0.125417	0.137623	0.138837	0.077378	-2882.629994	-2883.039125
Phcis_Beta_Heckadd_TS	-376.4	-3724.33887	0.408436	0.451872	0.453085	0.319339	-3724.375226	-3725.282303
Phcis5-endo-trig_TS	-311.9	-3724.30096	0.407881	0.451597	0.45281	0.316569	-3724.340653	-3725.244044

(*Z*)-β-phenyl vinyl bromide
C 3.850227 0.496597 -1.179266
H 4.574594 0.863396 -1.907709
C 4.126739 -0.564801 -0.414785
H 5.126986 -0.97831 -0.589754
C 3.359989 -1.251352 0.640406
C 4.080141 -1.928488 1.638427
C 1.957929 -1.293134 0.687889
C 3.42615 -2.597743 2.668094
H 5.172864 -1.921813 1.606859
C 1.30428 -1.97125 1.713884
H 1.372016 -0.805023 -0.090462
C 2.032569 -2.618909 2.710588
H 4.00711 -3.109298 3.438473
H 0.212547 -1.996195 1.73097
H 1.515087 -3.146564 3.514669
Br 2.297241 1.562604 -1.14755

Phcis_Beta_Heckadd_TS
C -0.0809834286 1.848455356 -0.7514214744
C -0.159994594 1.385543423 -2.6183515187
Br -2.8086728724 2.6226956203 -4.5134722313
H -0.5101881607 0.9402941759 -0.3200657979
O -3.1114894834 4.0052615111 -1.2925438767

C -0.7850393837 3.0711241657 -0.4254675382
H -0.1692120568 3.9717255187 -0.5384191388
C -1.8727516069 3.2561709293 0.6462890682
C -3.174605109 3.772275448 -0.0240568192
O -4.2013757458 3.8875689637 0.6345038047
C -2.1892060559 1.9690841964 1.438182161
H -1.2345947586 1.5202770101 1.7613790903
H -2.7111753061 2.2681929048 2.3589368583
C -1.4056826695 4.3352222833 1.6552363911
H -2.1634737686 4.3748992045 2.4530101182
H -0.4669575682 3.9867219587 2.1210044347
C -1.2263475569 5.7418455553 1.0935445665
H -2.1661782141 6.1194144172 0.663565094
H -0.9230537296 6.4338297085 1.8928944949
H -0.4571585717 5.7957009899 0.3086045034
C -3.0510966791 0.9303339284 0.7272441716
H -2.7088379991 0.7198681187 -0.2967125367
H -3.0546387102 -0.0243938829 1.271838736
H -4.0913088819 1.2840587288 0.6796890174
C 1.4195071917 1.8398388223 -0.6668191274
C 2.2059315363 2.8985397785 -1.1357664517
C 2.0507614173 0.741766694 -0.0762079898
C 3.5911342705 2.8609519563 -1.0068485423
H 1.7320961845 3.7552743141 -1.6220145025
C 3.4374846148 0.7060349015 0.0609648212
H 1.4462246128 -0.0942766208 0.2858793563
C 4.2123727176 1.7658890899 -0.404825588
H 4.1911575841 3.6927544708 -1.3818770063
H 3.9135588839 -0.155983892 0.5332572663
H 5.2992207826 1.738863061 -0.3028883126
Pd -1.64851129 2.7996015772 -2.2215707798
H 0.6838211185 1.8408449932 -3.1477533213
C -0.4304814396 0.0928847527 -2.8742563483
H 0.1775982627 -0.4215234227 -3.6293294105
C -1.5074339471 -0.7129079805 -2.2416454258
C -1.2182268467 -1.6307963382 -1.2246467796
C -2.8353102153 -0.5777784977 -2.6726377116
C -2.235478746 -2.3712141548 -0.6229152785
H -0.1832531102 -1.7589561997 -0.8966999226
C -3.8474036542 -1.3317982575 -2.0806983398
H -3.0492460752 0.1290667212 -3.479712237
C -3.5547016772 -2.2215163898 -1.0468178766
H -1.9950980979 -3.071781864 0.1797905163
H -4.8770723222 -1.238402154 -2.4397674519
H -4.3501825187 -2.8072415482 -0.5808919104
Cs -5.4075453258 2.353142954 -2.0619562239

Phcis5-endo-trig_TS
C -0.6673793325 2.1836898481 1.012701908
O -1.3276667772 0.6457076535 -0.3112543438
H -1.4210777816 1.817745726 1.7053639209
Pd -0.7517878177 4.7670786856 1.3175352502
C -1.023272291 3.144104043 0.0374704558
H -0.1971394626 3.3472541019 -0.65241371

C -2.278753753 2.8113127541 -0.7585197917
C -1.9967651081 1.3164239387 -1.1694846332
O -2.3552773877 0.9008397151 -2.2699260313
C -3.640904816 2.8640403198 -0.0179724845
H -3.6927278693 3.8219863731 0.5228292817
H -4.4137147539 2.9189222895 -0.8004366116
C -2.4040873557 3.7130671421 -2.0027662896
H -3.2694132698 3.3484642046 -2.5754279097
H -2.6456341633 4.7315167841 -1.6557279011
C -1.2079834833 3.778054871 -2.9467896473
H -0.9925434405 2.7771128936 -3.3533150859
H -1.4434519394 4.423366194 -3.8058642147
H -0.3127257512 4.2073997707 -2.4705549301
C -4.0303191706 1.7067201237 0.9009667564
H -3.3636555756 1.5807763189 1.7649143267
H -5.0419689025 1.8784841462 1.2988268582
H -4.0428378149 0.7501272527 0.3587941202
C 0.7091589518 1.7041983537 1.2603166179
C 1.8537948673 2.4325957945 0.8992371532
C 0.8593377836 0.3984107914 1.7500125061
C 3.1159586824 1.8504150666 1.0049400338
H 1.7596919025 3.4634982189 0.5419365578
C 2.1208689651 -0.1850946832 1.838356916
H -0.0318063319 -0.1736173763 2.0145712987
C 3.2540571839 0.5381882036 1.4618483994
H 3.9985680286 2.4353884309 0.7365110343
H 2.220601066 -1.2078741986 2.208314074
H 4.2452321653 0.0860602027 1.5432249215
C -2.025353245 4.1790065505 2.7315839602
H -2.8576233142 3.488807195 2.5629371694
C -1.8099244694 4.6647946679 3.9670656227
H -2.4417296767 4.3846578848 4.8190474003
C -0.6681171805 5.5627825205 4.2020864919
C 0.068422925 5.5651146643 5.3948397422
C -0.2241443811 6.3862321847 3.1494177232
C 1.2272948667 6.328057998 5.5069031514
H -0.2584588068 4.93891894 6.2285516023
C 0.9567846562 7.1230117873 3.246318261
H -0.8970659606 6.5837907305 2.2870123517
C 1.6855347293 7.0950731129 4.4313305794
H 1.793172099 6.3140161829 6.4415335322
H 1.2879582938 7.7154521479 2.3916504824
H 2.6042234807 7.6775498459 4.5247126397
Br 0.9026972057 5.8361722066 -0.3258194041
Cs 1.0422695306 0.686727426 -2.0649811125