Intra/Intermolecular Direct Allylic Alkylation *via* Pd(II)-Catalyzed sp^3 C-H Activation

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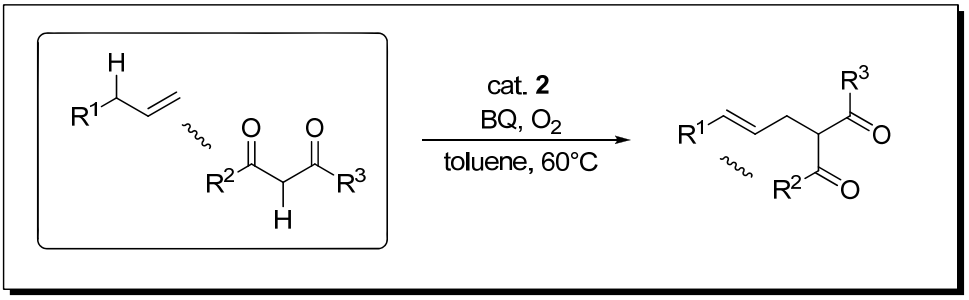
Table of Contents for SI:

General information. Unless otherwise noted, the reactions were carried out under oxygen atmosphere. Toluene, dioxane were freshly distilled over sodium wire and benzophenone. Dichloroethane was freshly distilled over phosphorus pentoxide. Nitromethane, dimethyl sulfoxide, diketones and part of allyl arenes were purchased as analytical pure and used without further purification. Benzoquinone was freshly recrystallizated in petroleum ether. $Pd(OAc)_2$ was purchased from Alfa Aesar. ^1H NMR (300 MHz or 200MHz) and ^{13}C NMR (75 MHz or 50 MHz) were registered on Varian 300/200 M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. IR, X-ray, GC, MS, ESI-MS and HRMS were performed by the State-authorized Analytical Center in Peking University.

General procedures.

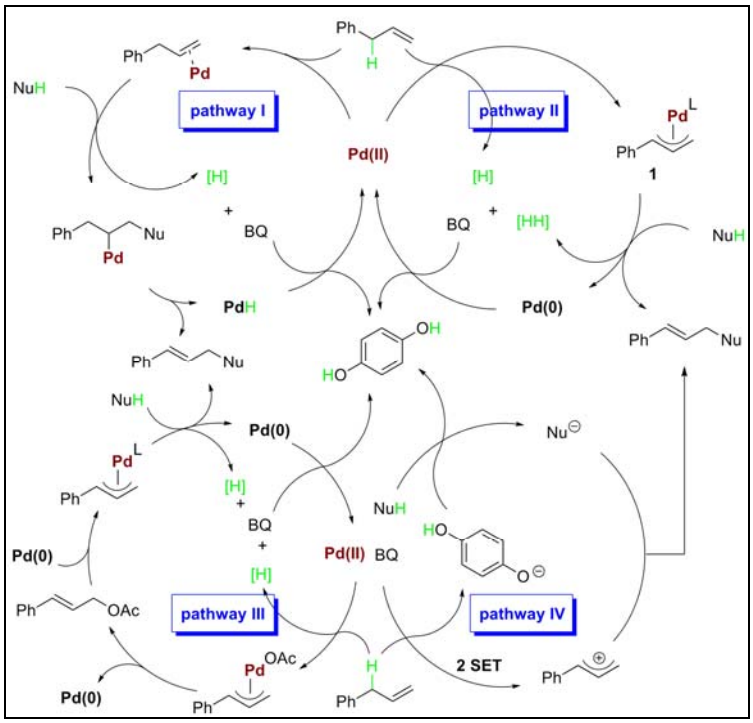


General procedures I for direct intramolecular allylic alkylation. The reactions were performed on 0.3 mmol scale. A 25 mL Schlenck tube was charged sequentially with a stir bar, 1,2-bis(benzylsulfinyl)ethane-supported $Pd(OAc)_2$ **2** (10-20 mol%), BQ (1.3 equiv.). **3** (1 equiv.) was dissolved in toluene (2.1 mL) in a flask and transferred into the tube. The reaction was stirred at 60 °C under 1 atm of oxygen (balloon pressure) for 60-84 h. After cooling down, the mixture was directly applied to a flash column chromatography.

General procedures II for direct intermolecular allylic alkylation. The reactions were performed on 0.5 mmol scale. A 25 mL Schlenck tube was charged sequentially with a stir bar, diketone **6** (0.70 mmol), 1,2-bis(benzylsulfinyl)ethane-supported $Pd(OAc)_2$ **2** (0.05 mmol), BQ (0.65 mmol). To the mixture, toluene (2.5 mL) and allyl arenes **5** (0.5 mmol) were added. The reaction was stirred at 60 °C under 1 atm of oxygen (balloon pressure) for 48 h. After cooling down, the mixture was directly applied to a flash column chromatography.

Mechanistic investigation.

The reaction is proposed to proceed *via* the following pathways.



Confirmation of pathway II: ESI-MS study.

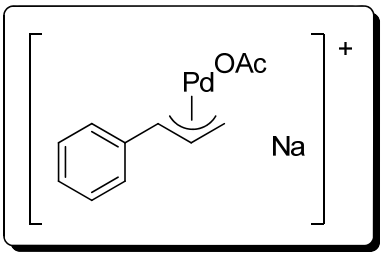
A Schlenck tube was charged with a stir bar, **2** (138.0 mg, 0.26 mmol), d8-toluene (1 mL) and allyl benzene (26.6 μL, 0.2 mmol). The tube was sealed and the reaction was then stirred at 60 °C. Samples were taken at 30 min, 2h and 4h. Every sample (~5 μL) was taken by a dropper directly from the reaction mixture, diluted with CH_3CN (0.5 mL) and applied to ESI-MS to investigate the mechanism. The reaction mixture was stirred for 6h as a whole and further applied to the stoichiometric reaction study. Please check page SI 8 to see the ESI-MS spectrum.

Results:

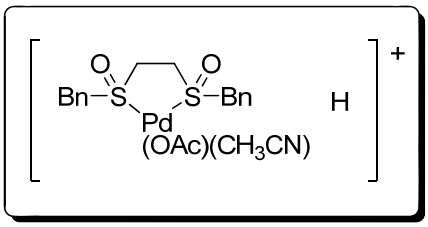
Major peaks and plausible formulas	Relative abundance (%)		
	30 min	2 h	4 h
305 $[(C_{11}H_{12}O_2)Pd + Na]^+$	6	14	9
329 $[C_{16}H_{18}O_2S_2 + Na]^+$	100	100	100
513 $[(C_{16}H_{18}O_2S_2)Pd(CH_3CN)(OAc) + H]^+$	0	18	16
635 $[(C_{16}H_{18}O_2S_2)_2 + Na]^+$	55	51	66
981 $[(C_{16}H_{18}O_2S_2)_2Pd_2(OAc)_2 + K]^+$	19	4	3
1647 $[(C_{16}H_{18}O_2S_2)_2(C_9H_9)_2(OAc)_6Pd_4 + Na]^+$	12	23	2

Plausible structures:

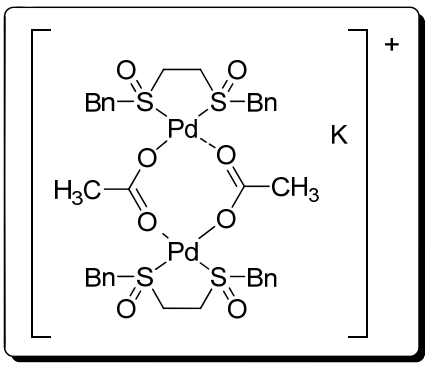
$[(C_{11}H_{12}O_2)Pd + Na]^+$



$[(C_{16}H_{18}O_2S_2)Pd(CH_3CN)(OAc) + H]^+$



$[(C_{16}H_{18}O_2S_2)_2Pd_2(OAc)_2 + K]^+$



The study shows that the coupling reaction was likely to happen through a π-allylpalladium intermediate.

Effect of benzoquinone: Stoichiometric reaction study.

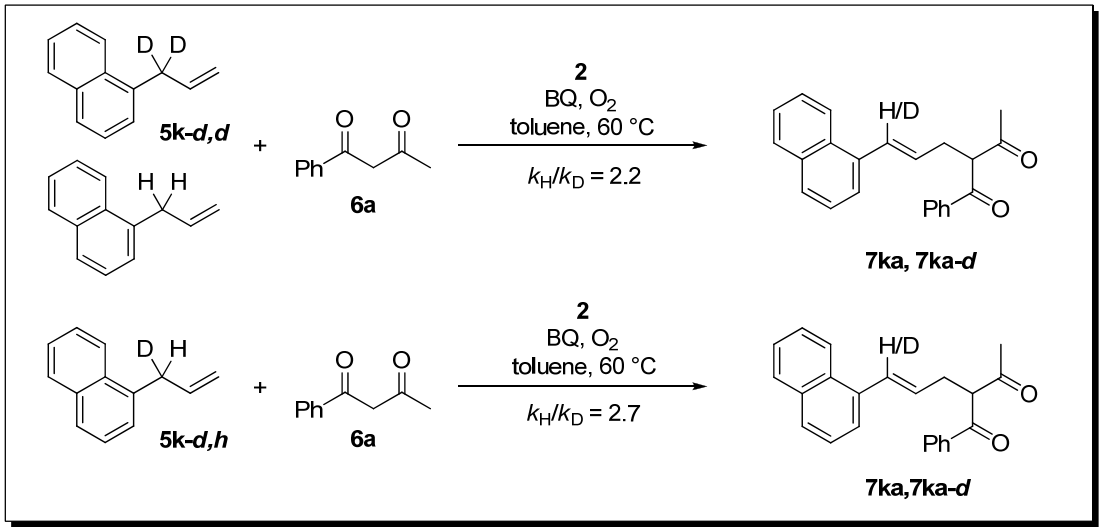
The reaction mixture above was separated into 3 parts, each of which was 0.25 mL in total volume. Part I was mixed with BQ (7.0 mg, 0.065 mmol); part II was mixed with benzoylacetone (11.4 mg, 0.07 mmol); part III was mixed with both BQ (7.0 mg, 0.065 mmol) and benzoylacetone (11.4 mg, 0.07 mmol). All of them were stirred at 60 °C for additional 20h and applied to GC to determine the products.

Results:

Part	GC yield of cinnamyl acetate (%)	GC yield of product **7aa** (%)
I	43	0
II	30	0
III	33	21

The study shows that benzoquinone performed as an H-acceptor other than oxidant.

Confirmation of pathway II and disproval of pathway I: Kinetic isotopic effect study.



Synthesis of substrates for isotopic effect study.

1-(1',1'-dideuterated allyl)naphthalene (5k-*d,d*). To a stirred suspension of $LiAlD_4$ (127.2 mg, 3 mmol) in THF (10 mL) at 0 °C was added a solution of methyl 1-naphthoate (1.02 g, 5.5 mmol) in THF (5 mL). The reaction was stirred at r. t. for 1 h. The resulting solution was quenched at 0 °C with diluted HCl and was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated to give **1,1-dideuterated naphthalen-1-ylmethanol** (889 mg, >99%). 1,1-dideuterated naphthalen-1-ylmethanol (750.3 mg, 4.69 mmol) was dissolved in DCE in ice bath, and PBr_3 (0.67 mL, 7 mmol) was added dropwise. The reaction was conducted at r. t. for 6 min and quenched with ice water. Workup by extraction with ether, washing with water, drying over $MgSO_4$, and concentrating to afford a crude product, which was chromatographed to afford **1,1-dideuterated 1-(bromomethyl)naphthalene** (672.7 mg, 64%). To a stirred mixture of 1,1-dideuterated 1-(bromomethyl)naphthalene (655.2 mg, 2.94 mmol), CuI (56.0 mg, 0.294 mmol), bipyridine (45.9 mg, 0.294 mmol) and benzene (1.1 mL) was rapidly added vinyl magnesium bromide (0.7 M in THF, 6.5 mL, 4.56 mmol) at 5 °C. After the reaction was complete, the ice bath was removed and the mixture was stirred at 20 °C for 3 h. Saturated NH_4Cl (12 mL) and 27% ammonia aq. (4 mL) were added and the mixture was stirred for 30 min and extracted with ether. After washed with brine, dried over $MgSO_4$ and concentrated, the crude product was applied to flash column chromatograph to give the final product (344.2 mg, 69%, deuterated ratio >99%).
^{1}H NMR ($CDCl_3$, 300MHz) δ 8.00 (d, 1H, J = 7.8), 7.85-1.82 (m, 1H), 7.71 (d, 1H, J = 8.4), 7.51-7.33 (m, 4H), 6.14-6.05 (q, 1H), 5.11-5.05 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 136.9, 136.0, 133.8, 131.9, 128.6, 126.9, 126.2, 125.7, 125.6, 125.5, 124.0, 116.2, 36.5 (t, J = 19.0) ppm; IR 3054, 1632, 1595, 1510, 1397, 993, 917, 781 cm^{-1}; MS: (m/z) (%): 170 (100) [M$^+$], 154 (30); HRMS: Anal. Calcd. for $C_{13}H_{10}D_2$ 170.10645, Found: 170.10609.

1-(1'-deuterated allyl)naphthalene (5k-*d,h*). To a suspension of $LiAlD_4$ (167.9 mg, 4 mmol) in ether (5.8 mL) at 0 °C was added a solution of 1-naphthaldehyde (1.09 mL, 8 mmol) in ether (3.3 mL) dropwise. After stirred for 1 h at reflux, the mixture was

quenched with diluted HCl at 0 °C. After extracted with ether, washed with brine, dried over $MgSO_4$ and concentrated, the crude product was applied to flash column chromatograph to give **1-deuterated naphthalen-1-ylmethanol** (651.8 mg, 51%). 1-deuterated naphthalen-1-ylmethanol was treated as the same procedures above to afford the final product **5k-*d,h*** (deuterated ratio >99%).

^{1}H NMR ($CDCl_3$, 300MHz) δ 8.02 (d, 1H, J = 8.7), 7.85-1.82 (m, 1H), 7.72 (d, 1H, J = 8.1), 7.51-7.32 (m, 4H), 6.16-6.05 (m, 1H), 5.12-5.06 (m, 2H), 3.81 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 136.9, 136.1, 133.8, 132.0, 128.6, 126.9, 126.2, 125.8, 125.6, 125.5, 124.0, 116.2, 36.9 (t, J = 19.1) ppm; IR 3045, 2923, 1637, 1596, 1510, 1397, 1166, 998, 914, 786, 775 cm^{-1}; MS: (m/z) (%): 169 (100) [M^+], 154 (46); HRMS: Anal. Calcd. for $C_{13}H_{11}D$ 169.10018, Found: 169.10031.

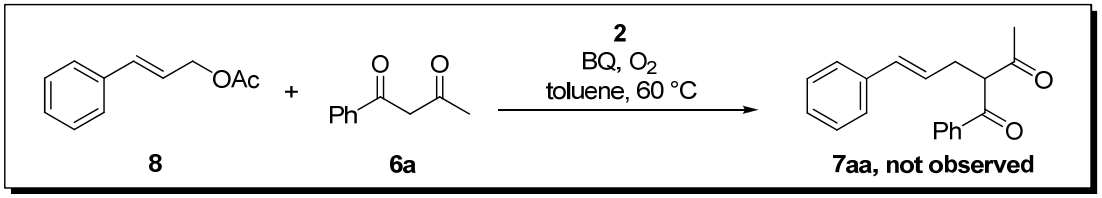
Procedures of determination of isotopic effect.

Intermolecular isotopic effect. Following the general procedures I and reacting for 30 h. Startinging from **5k** (42.1 mg, 0.25 mmol) and **5k-*d,d*** (42.6 mg, 0.25 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ka** and **7ka-*d***. The products were isolated and applied to NMR spectrum. The kinetic isotopic effect (k_H/k_D) was determined to be **2.2**.

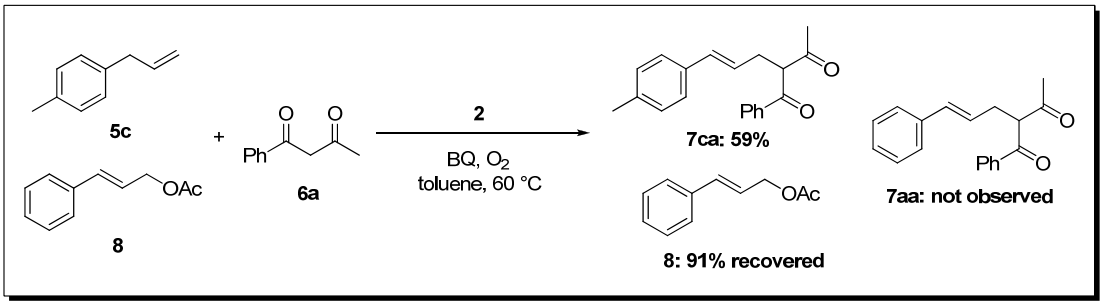
Intramolecular isotopic effect. Following the general procedures I and reacting for 30 h. Startinging from **5k-*d,h*** (42.3 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ka** and **7ka-*d***. The products were isolated and applied to NMR spectrum. The kinetic isotopic effect (k_H/k_D) was determined to be **2.7**.

The study shows that the allylic C-H cleavage was involved in the rate determining step of the reaction pathway, which indicates pathway II including β-H elimination was not likely to happen and confirms the existence of pathway II.

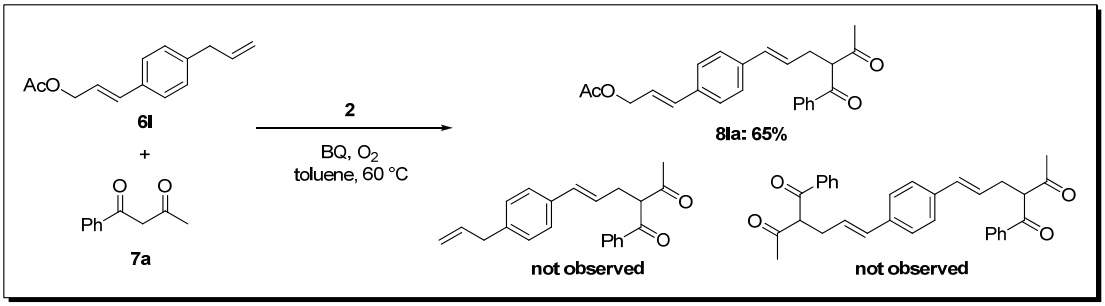
Elimination of pathway III: Control experiments.



Following the general procedures I. Starting from cinnamyl acetate **8** (35.2 mg, 0.2 mmol) with **6a** (45.4 mg, 0.28 mmol). The reaction mixture was detected by GC and no product **7aa** was observed.



Following the general procedures I and 15% of catalyst **2** was used, reacting for 29h. Starting from **5c** (26.4 mg, 0.2 mmol) and cinnamyl acetate **8** (18.2 mg, 0.1 mmol) with **6a** (68.0 mg, 0.42 mmol) and benzoquinone (42.1 mg, 0.39 mmol) in 2 mL toluene. The reaction mixture was analyzed by GC and no product **7aa** was observed.



Following the general procedures I and 15% of catalyst **2** was used, reacting for 26h. Starting from **5l** (18.6 mg, 0.086 mmol) with **6a** (43.7 mg, 0.27 mmol) and benzoquinone (29.2 mg, 0.27 mmol) in 0.7 mL toluene. The reaction mixture was analyzed by GC-MS and **7la** was observed and isolated as a single product.

The study shows that pathway III was not possible in this reaction condition.

Disproval of pathway IV: Control experiments.

BQ or DDQ-mediated reactions were carried out in the absence of Pd catalyst.
Following the general procedures II and **2** was excluded. Starting from **5a** (26.6 μL, 0.2 mmol), **6a** (45.4 mg, 0.28 mmol), and BQ (28.1 mg, 0.26 mmol) or DDQ (58.9 mg, 0.26 mmol). The reaction mixture was analyzed by GC and no coupling product was detected.

4-Methoxyphenol was used as the radical inhibitor in the model reaction.
Following the general procedures II. Starting from **5a** (26.6 μL, 0.2 mmol) and **6a** (45.4 mg, 0.28 mmol), and 4-methoxyphenyl (5 mg) was added. The yield was determined by GC to be 76%.

The study shows that pathway IV involving a SET process was not possible in this reaction condition.

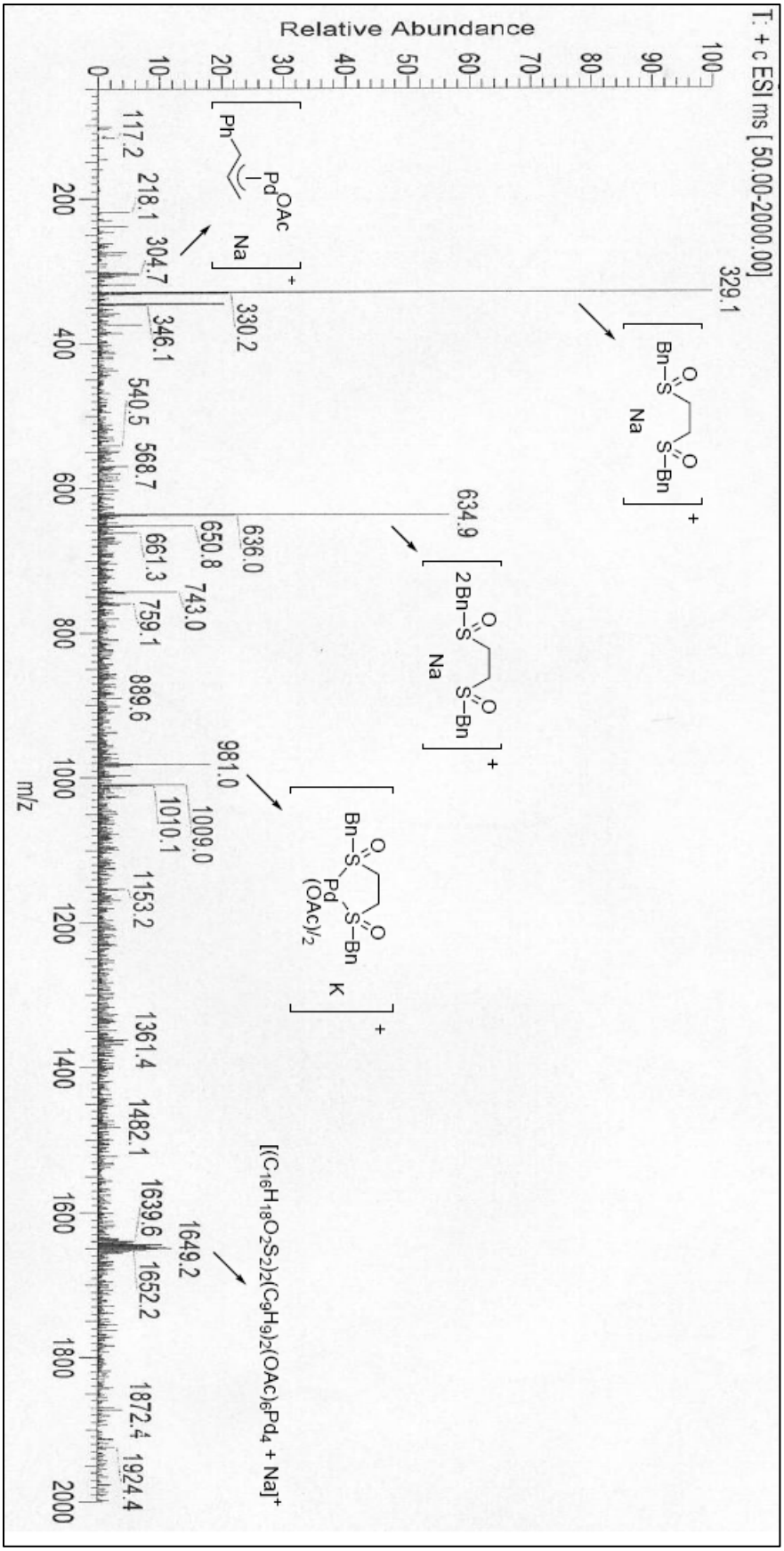
Study of the mechanism for the formation of 4k': Control experiments.

The Pd catalyst was removed from the reaction condition of **3k** to **4k'**.
Following the general procedures I. Starting from **3k** (40.4 mg, 0.2 mmol), and **2** was ***not*** added. TLC showed that no desired product **4k'** was formed, and **3k** remained.

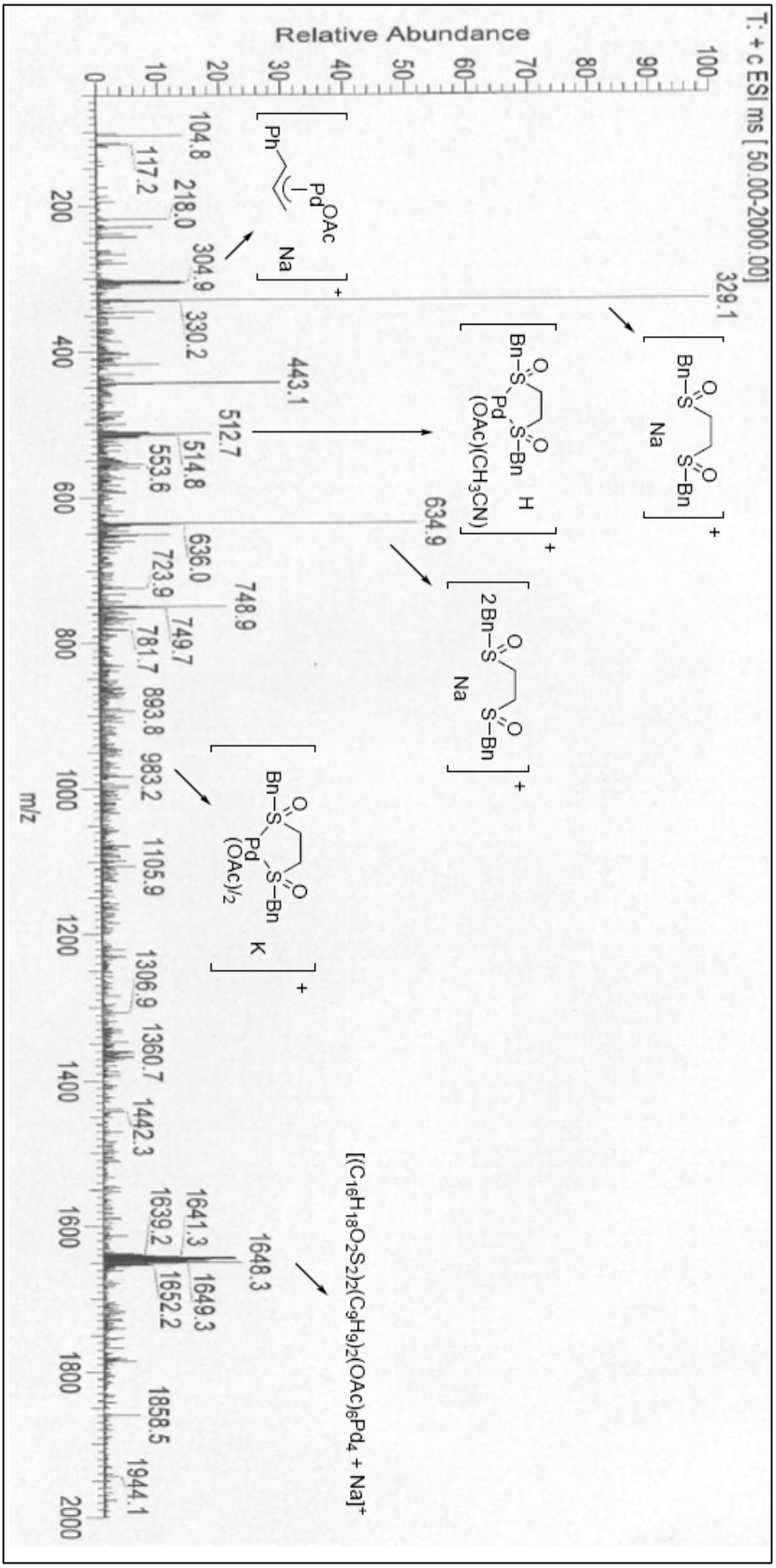
The study shows that 4k' was formed through β-elimination of π-allylpalladium species, rather than direct dehydrogenation by BQ.

ESI-Mass spectrum for mechanistic investigation.

30min



2h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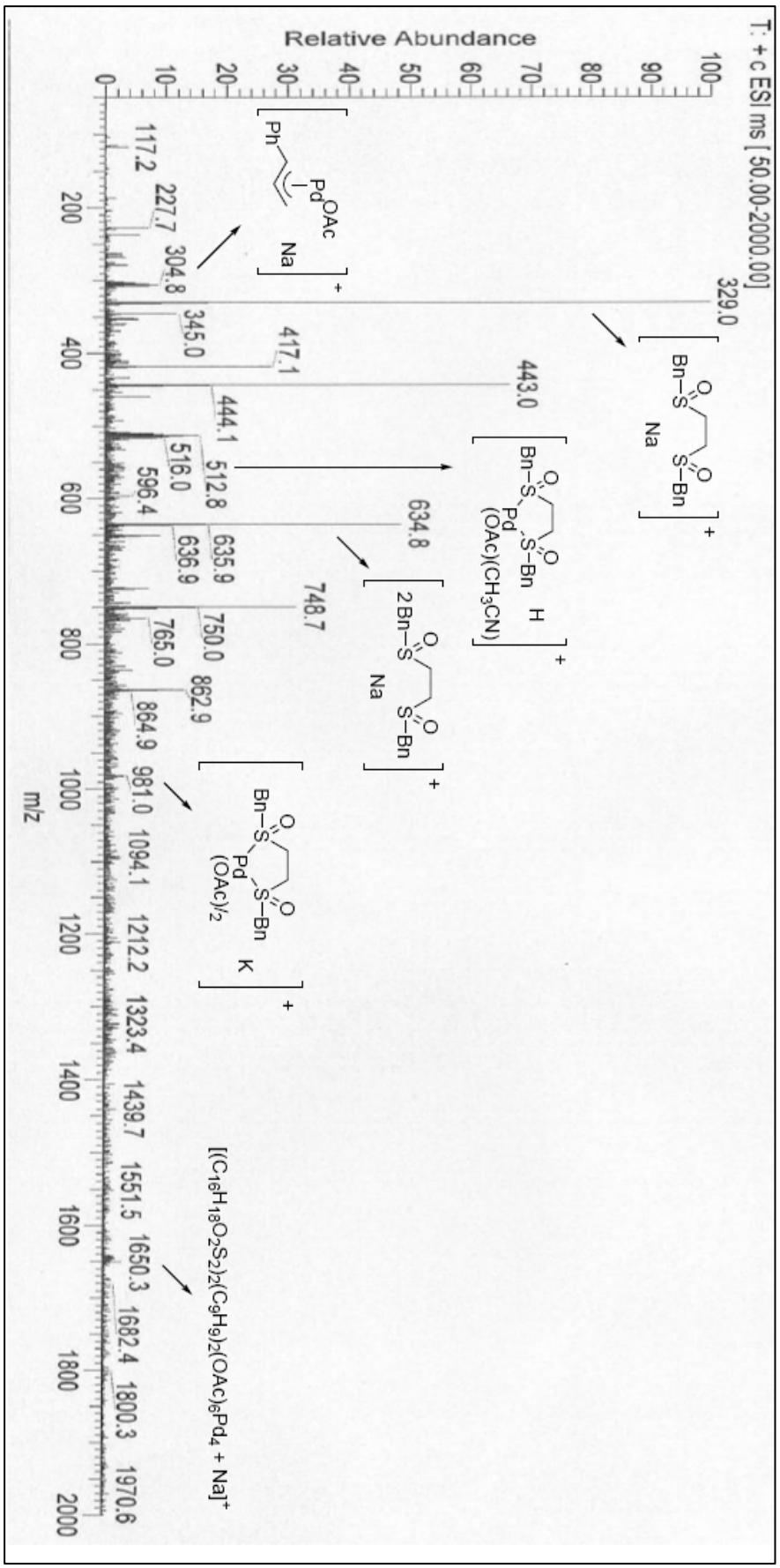
4h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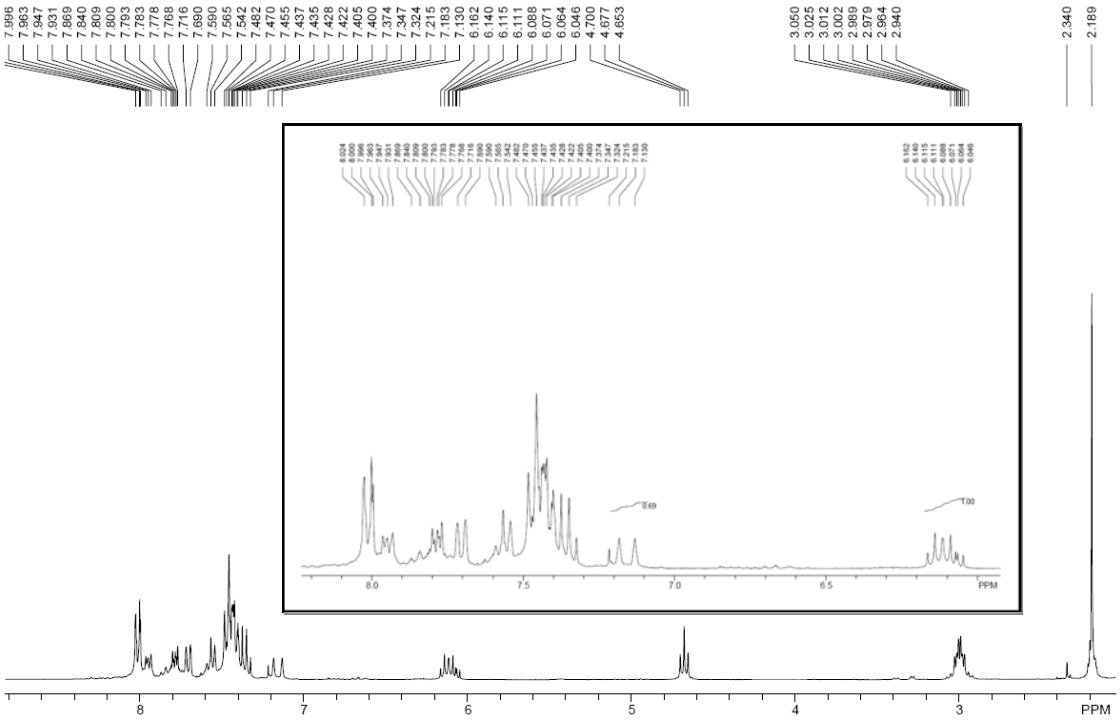
NMR spectrum for isotopic effect study.

From 5k and 5k-*d,d*



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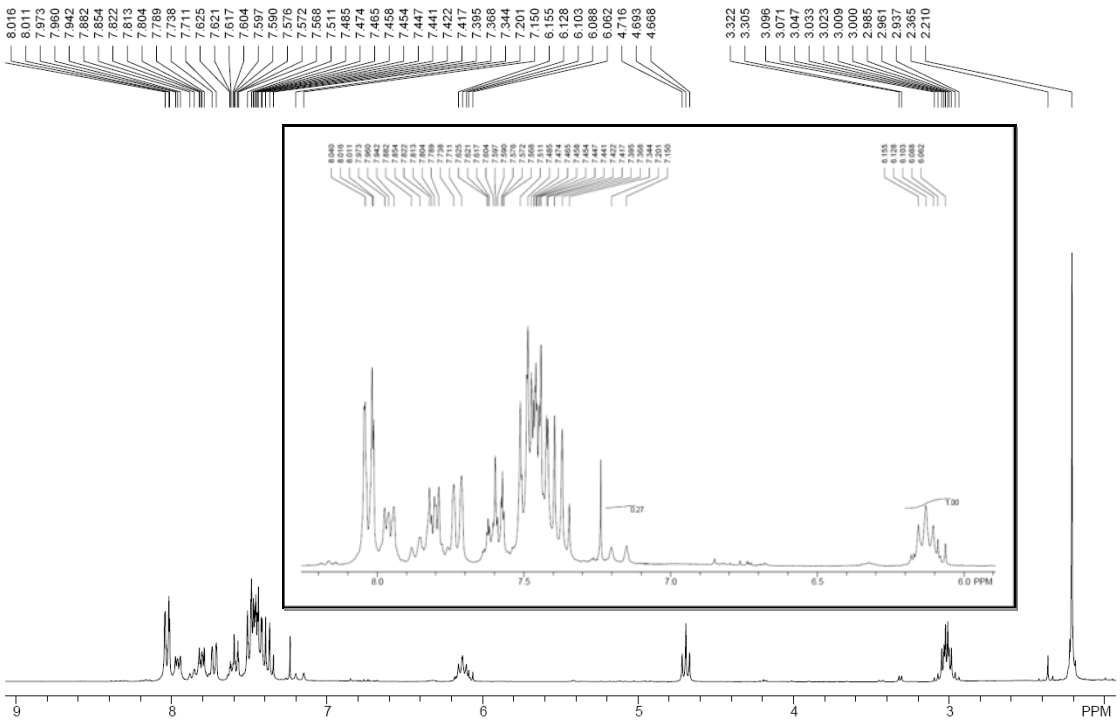
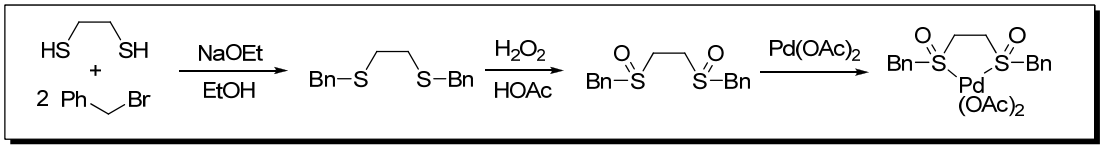


Synthesis and characterization data for catalyst 2.



1,2-Bis(benzylthio)ethane.[1a] A dry round bottom flask was charged with a stir bar, NaOEt (3.4 g, 50 mmol) and EtOH (100 mL) under a N_2 atmosphere. After the mixture became homogeneous, 1,2-ethanedithol (1.67 mL, 20 mmol) was added dropwise *via* syringe to the solution and the mixture was allowed to stir for 20 minutes. A solution of benzyl bromide (4.8 mL, 40 mmol) in benzene (60 mL) was added dropwise *via* dropping funnel. The reaction was stirred overnight at room temperature. Solvents were removed under reduced pressure. The residue was diluted with $CHCl_3$ and washed with brine. The separated aqueous phase was extracted three times with $CHCl_3$. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated in *vacuo* to give a yellow oil. The yellow oil was suspended in EtOH and allowed to sit at 0°C for 1h. A yellow solid crashed out and was washed with EtOH until the solid became white. The solid was dried under high vacuum to afford compound 1,2-bis(benzylthio)ethane.
^{1}H NMR ($CDCl_3$, 200MHz) δ 7.33-7.25 (m, 10H), 3.69 (s, 4H), 2.57 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 138.1, 128.8, 128.5, 127.0, 36.2, 30.9 ppm.

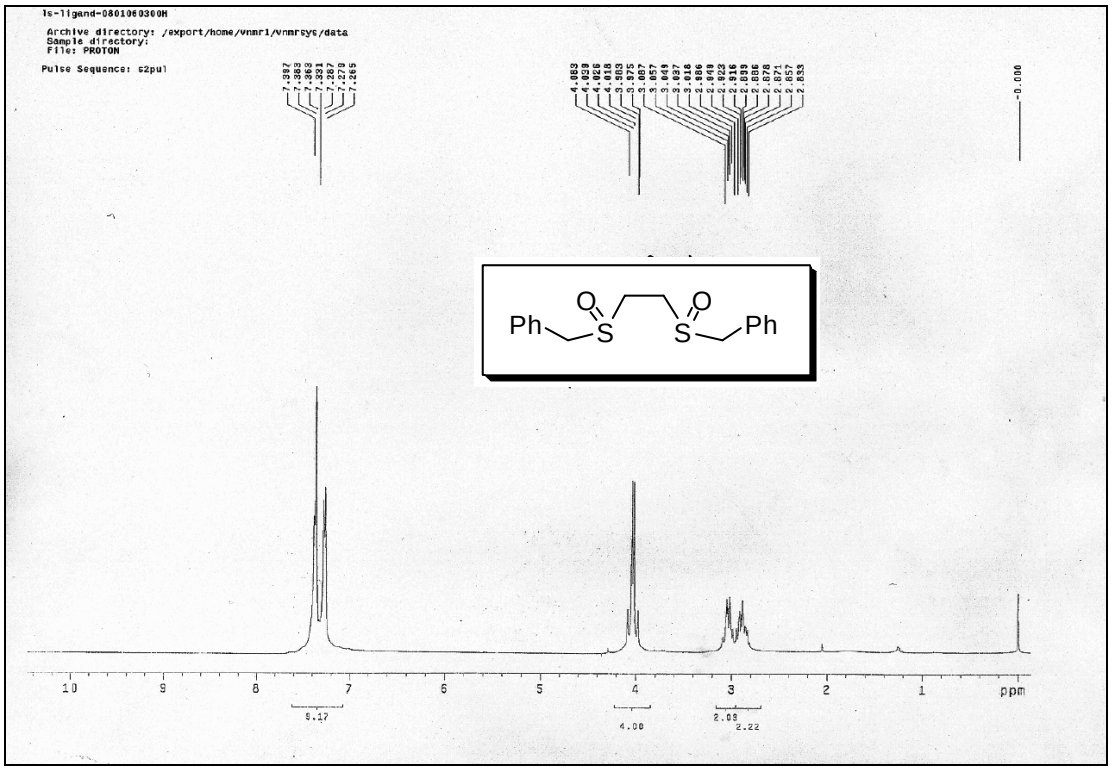
1,2-Bis(benzylsulfinyl)ethane (2l).[1a] A round bottom flask was charged with a stir bar, 1,2-bis(benzylthio)ethane (5.17 g, 18.9 mmol), and 45 mL of glacial acetic acid. The mixture was allowed to stir at room temperature until it became homogeneous at which time it was cooled to 0°C and H_2O_2 (30% aq., 4.28 mL, 37.8 mmol) was added dropwise. The reaction was allowed to come to room temperature and was stirred overnight. The acetic acid was removed with mild heating (50°C) under high vacuum and the white solid was washed with EtOH. The product was dried under high vacuum to afford **2l**.
The ligand **2l** is a mixture of two diastereoisomers with a ratio of 1.8:1 (by ^{1}H NMR).
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.40-7.37 (m, 5H), 7.29-7.26 (m, 5H), 4.04 (dd, 1.4H, J = 13.2), 4.03 (dd, 2.6H, J = 12.9), 3.09-3.00 (m, 2H), 2.97-2.83 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 130.0, 129.1, 128.6, 58.8, 58.6, 43.4, 42.6 ppm; IR 2962, 1495, 1455, 1417, 1072, 1030, 1020, 1002, 947, 881, 767, 698 cm^{-1} ; MS: (m/z) (%): 306 (2) [M^+], 91 (100).

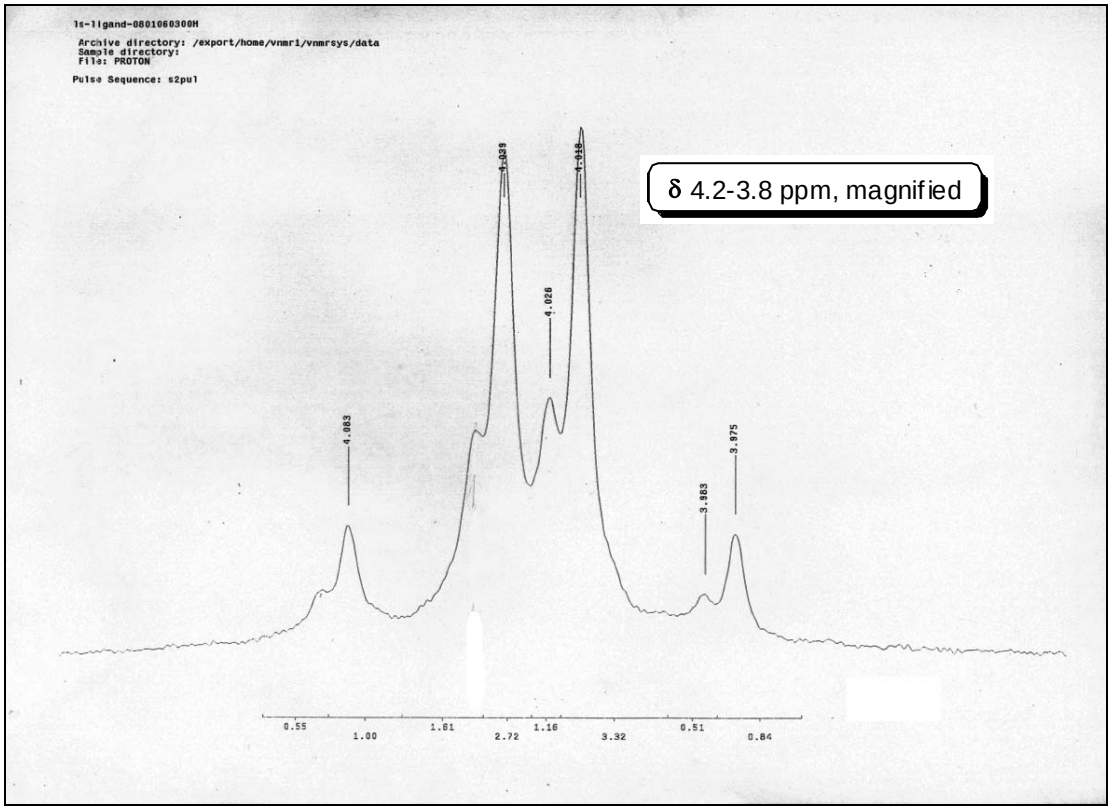
Catalyst 2.[1] A dry round bottom flask was charged with a stir bar, 1,2-bis(benzylsulfinyl)ethane (1 equiv.), $Pd(OAc)_2$ (1 equiv.) and CH_2Cl_2 (0.067 M). The mixture was stirred at reflux under a N_2 atmosphere for 24h. The solution was concentrated in *vacuo* and dried over a N_2 stream for 6h to give a black solid that was used without further purification.
The catalyst is a mixture. Characterization data listed as:
^{1}H NMR (d8-toluene, 300MHz) main peaks: δ 7.22-7.00 (m, 5H), 6.16-6.07 (dd, 1H, J = 9.3), 5.99-5.93 (d, 1H, J = 16.5), 5.42 (d, 1H, J = 9.3), 3.59 (dd, 2H, J = 12.6), 1.80 (s, 3H) ppm; ^{13}C NMR (d8-toluene, 75MHz) δ 140.4, 137.2, 130.2, 128.3, 127.8, 121.2, 59.5, 30.0 ppm; IR 2924, 1738, 1560, 1494, 1454, 1415, 1347, 1299, 1232, 1128, 1072, 1029,

958, 877, 767, 698 cm^{-1}; MS (ESI): (m/z) (%): 981 (46) $[(C_{16}H_{18}O_2S_2)_2Pd_2(OAc)_2K]^+$, 965 (17) $[(C_{16}H_{18}O_2S_2)_2Pd_2(OAc)_2Na]^+$, 329 (100) $[C_{16}H_{18}O_2S_2Na]^+$.

NMR spectrum for ligand 2l and catalyst 2

2l





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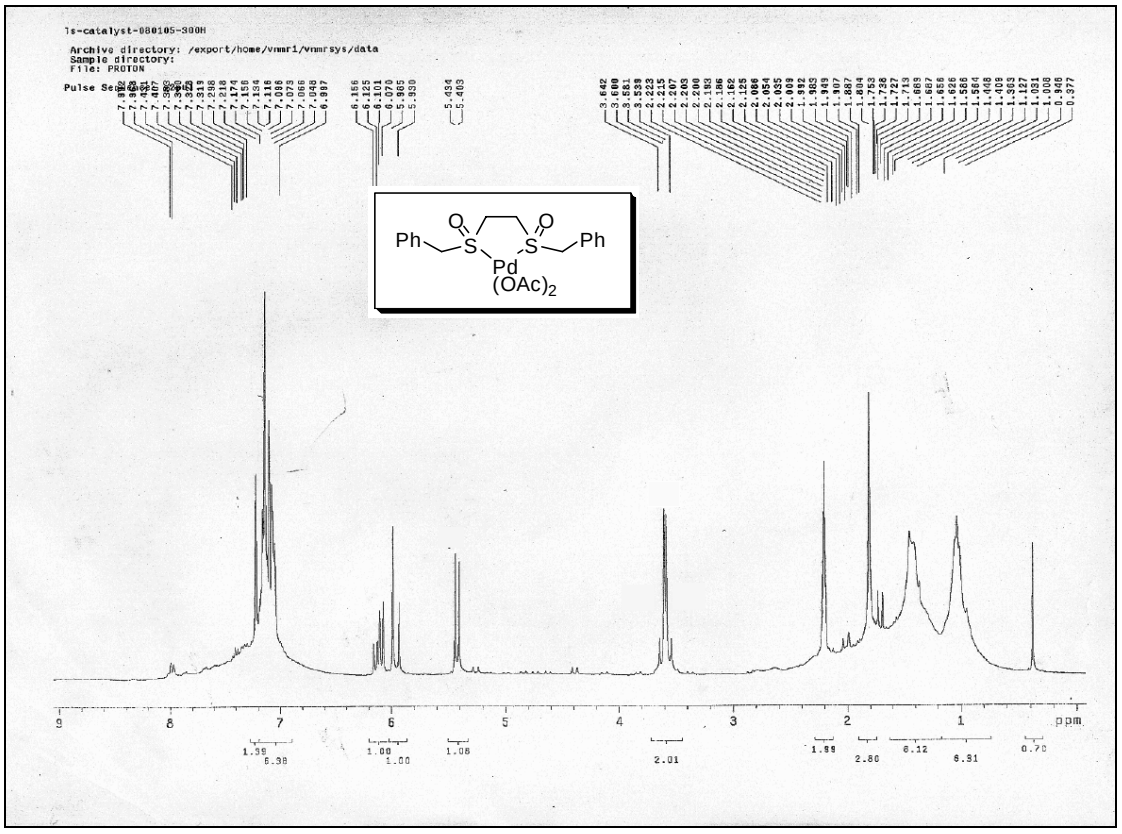
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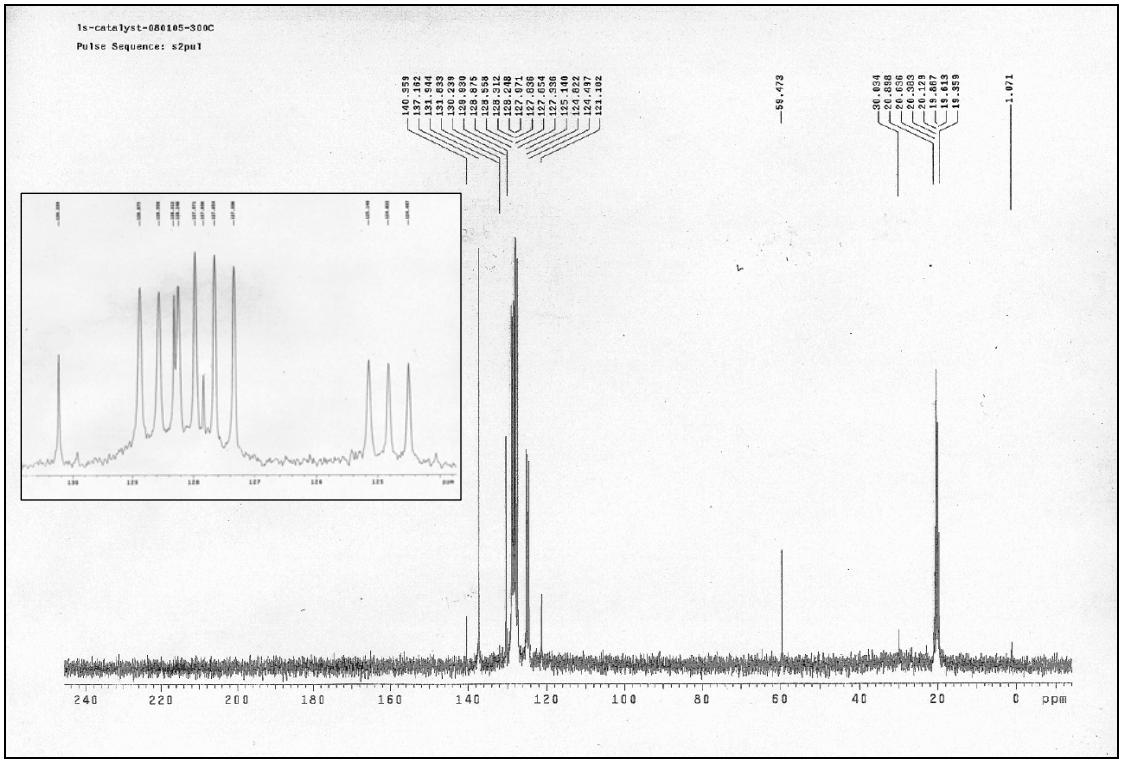
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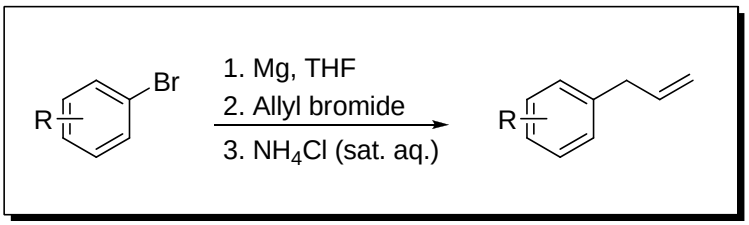
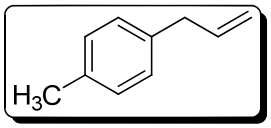
Synthesis and characterization data for allyl arenes 5c-5i, 5k, 5l.



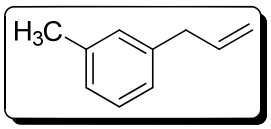
General procedures for 5c-5i, 5k.[2a] A dry round bottom flask was charged with a stir bar and Mg (1.2 equiv.) under a N_2 atmosphere. Aryl bromide (1 equiv.) and an iodide grain were dissolved in Et_2O (1.6 M, for **5c-5e**, **5h**, **5i**, **5k**) or THF (1.6 M, for **5f**, **5g**) in a dry conical flask. Part of the solution (~2 mL) was added to the flask and stirred. After the color of the mixture suddenly faded, the rest solution was added dropwise *via* dropping funnel. Then the mixture was stirred at reflux for 2h. The reaction solution was decanted into another dry flask and allyl bromide (1.5 equiv.) was carefully added in ice bath. When the mixture had reached room temperature, it was carefully hydrolyzed with aqueous saturated NH_4Cl solution. The aqueous phase was removed and extracted with Et_2O. The combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The rough product was applied to flash column chromatography afford pure allyl arene.

Analytical and spectral data.



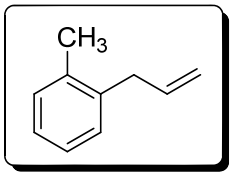
1-allyl-4-methylbenzene (5c).

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.10 (s, 4H), 6.03-5.89 (m, 1H), 5.11-5.03 (m, 2H), 3.35 (d, 2H, J = 6.6), 2.32 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 137.7, 136.9, 135.5, 129.1, 128.4, 115.5, 39.8, 21.0 ppm; IR 2920, 2849, 1658, 1632, 1469 cm^{-1} ; MS: (m/z) (%): 132 (59) [M$^+$], 117 (100).



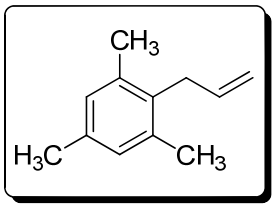
1-allyl-3-methylbenzene (5d).

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.26-7.17 (m, 1H), 7.04-3.99 (m, 3H), 6.04-5.90 (m, 1H), 5.12-5.05 (m, 2H) 3.35 (d, 2H, J = 6.6), 2.33 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 140.0, 138.0, 137.6, 129.3, 128.3, 126.8, 125.6, 115.6, 40.2, 21.4 ppm; IR 2953, 2923, 2854, 1459, 1376, 1027 cm^{-1} ; MS: (m/z) (%): 132 (62) [M$^+$], 117 (100).



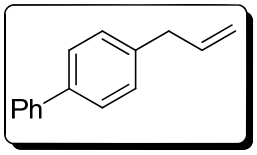
1-allyl-2-methylbenzene (5e).

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.14 (s, 4H), 6.02-5.89 (m, 1H), 5.08-4.96 (m, 2H) 3.36 (d, 2H, *J* = 6.6), 2.28 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 138.1, 136.6, 136.3, 130.1, 129.1, 126.2, 126.0, 115.6, 37.7, 19.3 ppm; IR 2953, 2924, 2855, 1458 cm^{-1} ; MS: (m/z) (%): 132 (56) [M^+], 117 (100).



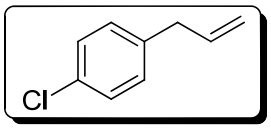
2-allyl-1,3,5-trimethylbenzene (5f).

^{1}H NMR ($CDCl_3$, 300MHz) δ 6.85 (s, 2H), 5.95-5.82 (m, 1H), 5.00-4.82 (m, 2H) 3.37-3.34 (m, 2H), 2.25 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 136.5, 135.5, 135.3, 133.0, 128.7, 126.9, 33.3, 20.8, 19.7 ppm; IR 2921, 2851, 1639, 1443, 1260 cm^{-1} ; MS: (m/z) (%): 160 (51) [M^+], 145 (100).



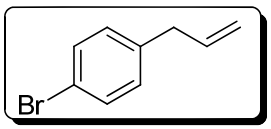
4-allylbiphenyl (5g).

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.60-7.24 (m, 9H), 6.10-5.90 (m, 1H), 6.02-5.89 (m, 1H) 5.17-5.06 (m, 2H), 3.42 (d, 2H, *J* = 7.0) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 141.1, 139.2, 139.1, 137.4, 129.0, 128.8, 127.2, 127.1, 116.0, 39.8 ppm; IR 3057, 1638, 1486 cm^{-1} ; MS: (m/z) (%): 194 (100) [M^+], 178 (42).



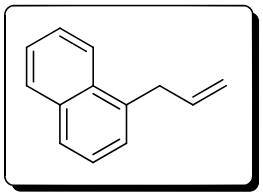
1-allyl-4-chlorobenzene (5h).

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.24 (d, 1H, *J* = 8.4), 7.09 (d, 1H, *J*= 8.4), 5.98-5.85 (m, 1H), 5.09-5.03 (m, 2H), 3.32 (d, 2H, *J* = 6.6) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 138.4, 136.8, 131.8, 129.9, 128.4,116.2, 39.4 ppm; IR 2954, 2924, 2855, 1456, 1377, 1091 cm^{-1} ; MS: (m/z) (%): 152 (50) [M^+], 117 (100).



1-allyl-4-bromobenzene (5i).

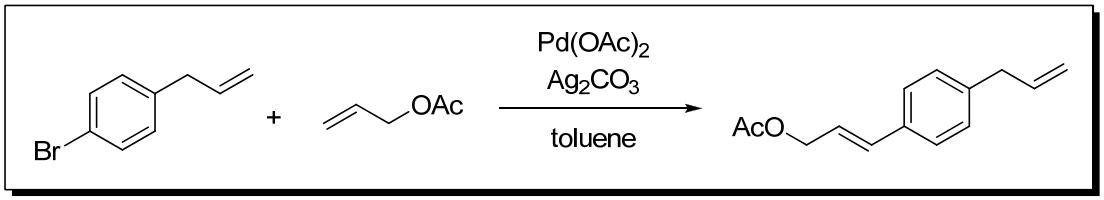
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.42 (d, 1H, *J* = 8.4), 7.07 (d, 1H, *J* = 8.4), 6.02-5.87 (m, 1H), 5.14-5.05 (m, 2H), 3.34 (d, 2H, *J* = 6.9) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 138.9, 136.7, 131.4, 130.3, 119.8, 116.2, 39.5 ppm; IR 2953, 2924, 2853, 1488, 1460,1024 cm^{-1} ; MS: (m/z) (%): 196 (56) [M^+], 117 (100).



1-allylnaphthalene (5k).

^{1}H NMR ($CDCl_3$, 300MHz) δ 8.00 (d, 2H, *J* = 9.0), 7.83-7.80 (m, 1H), 7.70 (d, 1H, *J* = 8.1), 7.47-7.43 (m, 2H), 7.37 (d, 2H, *J* = 8.1), 7.31 (d, 2H, *J* = 7.2), 6.16-6.02 (m, 1H), 5.11-5.04 (m, 2H), 3.80 (d, 2H, *J* = 6.3) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 136.9, 136.0, 131.9, 128.6, 127.8, 126.9, 126.2, 125.8, 125.5, 124.0, 116.1, 37.2 ppm; IR 2976, 1638, 1597, 1510, 1396, 993, 913 cm^{-1} ; MS: (m/z) (%): 168 (100) [M^+], 153 (87).

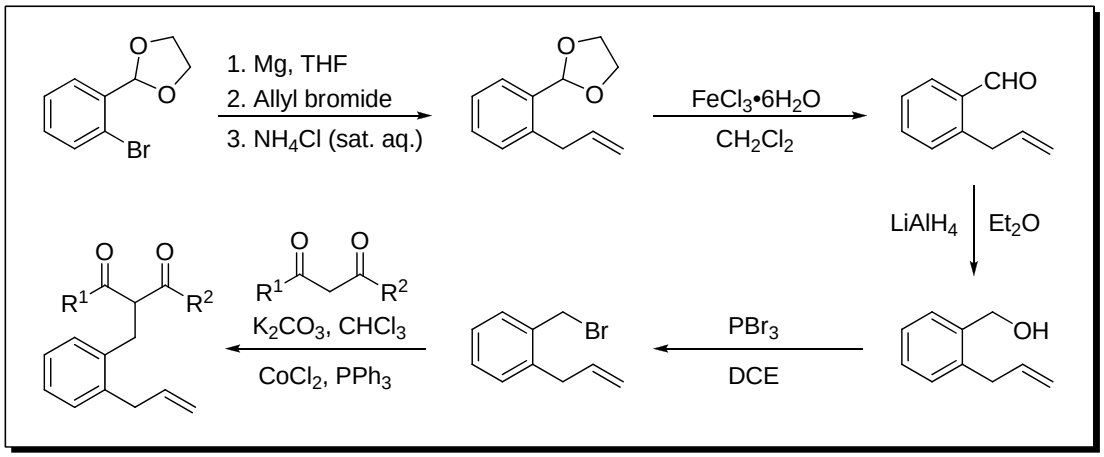
Procedures and characterization data for 5l.[2b]



(*E*)-3-(4-allylphenyl)allyl acetate (**5l**). To a mixture of $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), Ag_2CO_3 (331 mg, 1.2 mmol) in 12 mL toluene was added 1-allyl-4-bromobenzene (473 mg, 2.4 mmol) and allyl acetate (200 mg, 2 mmol) subsequently. The mixture was refluxed for 15 h. After filtration and evaporation, the residue was directly applied to the flash column chromatography.

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.34-7.13 (m, 4H), 6.63 (d, 1H, *J* = 15.9), 6.32-6.20 (m, 1H), 6.02-5.88 (m, 1H), 5.10-5.05 (m, 2H), 4.71 (d, 2H, *J* = 6.6), 3.36 (d, 2H, *J* = 6.3), 2.09 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 170.8, 140.9, 137.1, 134.0, 128.8, 126.6, 122.4, 115.9, 65.2, 39.9, 21.0 ppm; MS: (m/z) (%): 216 (30) [M^+], 157 (100).

Procedures and characterization data for 3a-d.



2-(2-allylphenyl)-1,3-dioxolane. Following the general procedures for **2c**-**2i**, **2k**. Starting from 2-(2-bromophenyl)-1,3-dioxolane (5.8 mL, 38 mmol), yield 77%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.60-7.48 (m, 1H), 7.40-7.19 (m, 3H), 6.08-5.95 (m, 2H), 4.20-4.10 (m, 2H), 4.09-4.00 (m, 2H), 3.55 (d, 2H, J = 6.3); ^{13}C NMR ($CDCl_3$, 50MHz) δ 138.3, 137.1, 129.8, 129.1, 126.3, 126.0, 115.8, 101.5, 65.2, 63.6, 36.4 ppm.

2-allylbenzaldehyde. Refer to the reference 2c, yield 91%.
^{1}H NMR ($CDCl_3$, 200MHz) δ 10.14 (s, 1H), 7.75-7.74 (m, 1H), 7.46-7.37 (m, 1H), 7.31-7.16 (m, 2H), 6.02-5.82 (m, 1H), 5.01-4.82 (m, 2H), 3.70 (d, 2H, J = 6.3); ^{13}C NMR ($CDCl_3$, 75MHz) δ 192.6, 142.2, 136.9, 134.0, 133.7, 131.5, 131.0, 126.9, 116.4, 36.4 ppm.

(2-allylphenyl)methanol. A dry round bottom flask was charged with a stir bar, $LiAlH_4$ (190 mg, 5 mmol) and ethyl ether (4 mL). 2-allylbenzaldehyde (1.41 g, 9.7 mmol) was added to the mixture dropwise, keeping the solution mildly refluxing. The solution was stirred for another 10 minutes and cooled to 0°C. Water was added carefully to decompose $LiAlH_4$ and the reaction mixture was then poured into ice water. The aqueous phase was extracted with Et_2O. The combined organic layers were dried with K_2CO_3 and concentrated under reduced pressure. The rough product was applied to flash column chromatography, yield 72%.
^{1}H NMR ($CDCl_3$, 200MHz) δ 7.40-7.35 (m, 1H), 7.29-7.19 (m, 3H), 6.07-5.94 (m, 1H), 5.10-4.96 (m, 2H), 3.48 (d, 2H, J = 6.0), 1.67 (s, 1H) ppm.

1-allyl-2-(bromomethyl)benzene. (2-allylphenyl)methanol (1.02 g, 7 mmol) was dissolved in DCE (11 mL) in ice bath. PBr_3 (0.88 mL, 9.1 mmol) was added dropwise to the above solution. The reaction was conducted at room temperature until TLC showed that the substrate disappeared (30 minutes). Ice water was added carefully to the mixture. The aqueous phase was extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The rough product was applied to flash column chromatography, yield 100%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.36-7.20 (m, 4H), 6.09-5.96 (m, 1H), 5.13-5.00 (m, 2H),

4.54 (s, 2H), 3.54 (d, 2H, J = 6.3) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 138.9, 136.5, 135.9, 130.5, 130.3, 129.1, 126.9, 116.2, 36.7, 31.7 ppm.

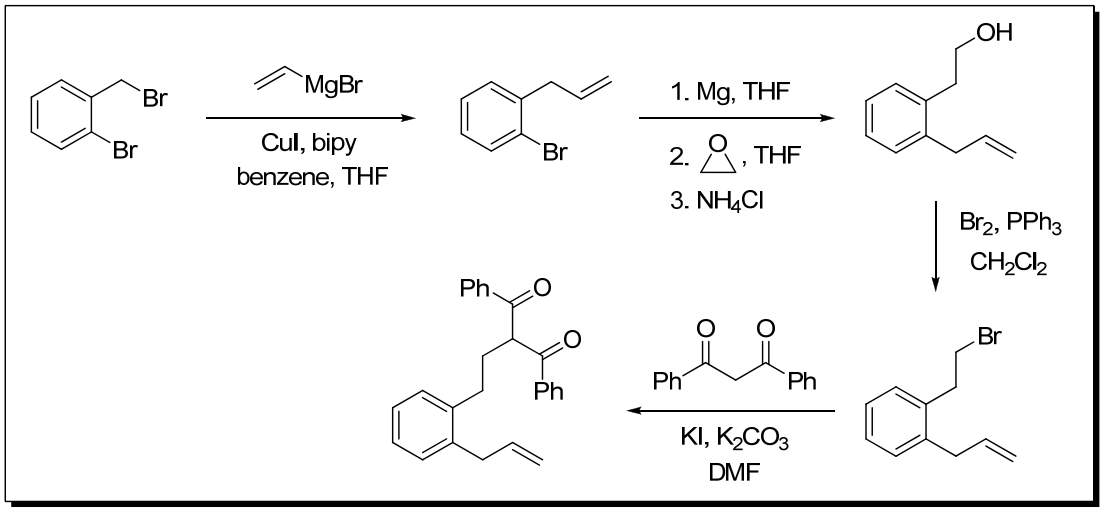
2-(2-allylbenzyl)-1,3-diphenylpropane-1,3-dione (3a). Refer to the reference 2d.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.88-7.86 (m, 3H), 7.54-7.49 (m, 3H), 7.39-7.35 (m, 4H), 7.14-7.00 (m, 4H), 6.00-5.89 (m, 1H), 5.55 (t, 1H, J = 6.9), 5.05-4.90 (m, 2H), 3.48 (d, 2H, J = 6.9), 3.43 (d, 2H, J = 6.3) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 195.7, 137.8, 137.0, 136.8, 136.0, 133.5, 130.0, 129.7, 128.7, 128.6, 126.9, 126.5, 116.0 ppm; IR 2924, 1696, 1668, 1596, 1580, 1491, 1448, 1324, 1269, 1229, 1197, 1180, 1000, 917, 754, 691 cm^{-1} ; MS: (m/z) (%): 354 (3) [M^+], 130 (100); HRMS: Anal. Calcd. for $C_{25}H_{22}O_2$ 354.16198, Found: 354.16261.

3-(2-allylbenzyl)pentane-2,4-dione (3b). Refer to the reference 2d.
^{1}H NMR ($CDCl_3$, 300MHz) δ 16.9 (s, 0.7H), 7.19-7.01 (m, 4H), 6.04-5.93 (m, 1H), 5.12-4.96 (m, 2H), 4.03 (t, 0.3H, J = 9.9), 3.60 (s, 1.4H), 3.46 (d, 1.4H, J = 6.3), 3.41 (d, 0.6H, J = 6.3), 3.17 (d, 0.6H, J = 7.2), 2.11 (s, 1.8H), 1.99 (s, 4.2H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.5, 192.0, 137.4, 137.1, 136.3, 136.2, 134.6, 129.8, 129.7, 129.2, 126.8, 126.7, 126.5, 126.3, 126.0, 115.9, 115.8, 107.1, 68.5, 37.2, 36.9, 30.8, 29.8, 29.7, 29.4, 39.3, 23.0 ppm; IR 2924, 1697, 1601, 1452, 1429, 1358, 1151, 917, 747 cm^{-1}; MS: (m/z) (%): 230 (8) [M^+], 130 (100).

ethyl 2-(2-allylbenzyl)-3-oxobutanoate (3c). Refer to the reference 2d.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.16-7.12 (m, 4H), 6.05-5.90 (m, 1H), 5.11-4.95 (m, 2H), 4.14 (q, 2H, J = 7.8), 3.79 (t, 1H, J = 7.2), 3.42 (d, 2H, J = 6.0), 3.20-3.16 (m, 2H), 2.17 (s, 3H), 1.19 (t, 3H, J =7.5) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.4, 169.2, 137.8, 137.0, 130.0, 129.5, 129.1, 126.9, 126.4, 115.9, 61.4, 60.1, 36.9, 30.5, 29.6, 13.9 ppm; IR 2980, 1737, 1716, 1451, 1359, 1248, 1213, 1148, 1021, 916, 858, 754 cm^{-1}; MS: (m/z) (%): 260 (4) [M^+], 130 (100).

2-(2-allylbenzyl)-1-phenylbutane-1,3-dione (3d). Refer to the reference 2d.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.90-7.86 (m, 2H), 7.61-7.09 (m, 7H), 6.08-5.86 (m, 1H), 5.11-4.92 (m, 2H), 4.81 (t, 1H, J = 10.8), 3.44 (d, 2H, J = 9.0), 3.34 (dd, 2H, J = 5.1), 2.13 (s, 3H) ppm; IR 2924, 2854, 1718, 1675, 1596, 1448, 1358, 1265, 1221, 918, 755, 694 cm^{-1}; MS: (m/z) (%): 292 (5) [M^+], 131 (100).

Procedures and characterization data for 3e.



1-allyl-2-bromobenzene. Refer to the reference 2e, yield 75%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.54 (d, 1H, *J* = 8.1), 7.27-7.11 (m, 2H), 7.09-7.03 (m, 1H), 6.03-5.90 (m, 1H), 5.14-5.04 (m, 2H), 3.51 (d, 2H, *J* = 7.8) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 138.0, 135.5, 132.7, 130.4, 127.8, 127.4, 124.5, 116.5, 40.1 ppm; IR 1638, 1567, 1469, 1439, 1023, 993, 916, 747 cm^{-1} ; MS: (m/z) (%): 196 (4), 198 (4) [M^+], 169 (100).

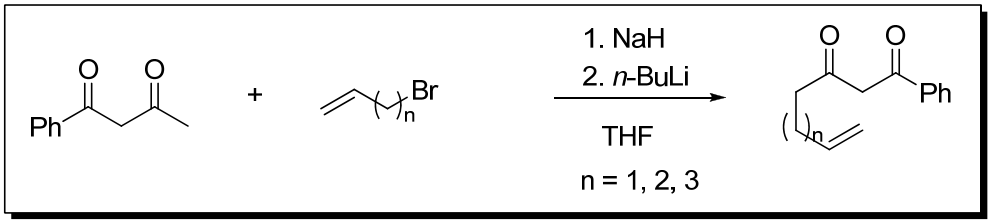
2-(2-allylphenyl)ethanol. A dry round bottom flask was charged with a stir bar and Mg (1.2 equiv.) under a N_2 atmosphere. Part of the solution of 1-allyl-2-bromobenzene (877 mg, 4.45 mmol) in THF (3 mL) was added to the flask and stirred. After the color of the mixture suddenly faded, the rest solution was added dropwise *via* dropping funnel. Then the mixture was stirred at reflux for 1h. After that, oxirane (0.5 mmol, 9.8 mmol, excessive) in THF (3 mL) was added dropwise in ice bath. The reaction was allowed to stir at r. t. for 1 h, and then quenched with NH_4Cl. After extracted with ethyl acetate, dried over Na_2SO_4 and concentrated, the crude product was applied to flash column chromatography to afford the product (716 mg, 4.42 mmol, 99% yield).
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.16-7.10 (m, 4H), 5.99-5.85 (m, 1H), 5.07-4.90 (m, 2H), 3.71 (t, 2H, *J* = 7.2), 3.32 (d, 2H, *J* = 6.3), 2.58 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 137.6, 136.6, 135.9, 129.4, 129.3, 126.1, 125.9, 115.2, 62.4, 62.0, 36.5, 35.2 ppm; IR 3329, 3075, 2946, 1638, 1490, 1450, 1432, 1042, 996, 914, 751 cm^{-1} ; MS: (m/z) (%): 162 (31) [M^+], 129 (100).

1-allyl-2-(2-bromoethyl)benzene.[2f] Refer to the reference 2f, yield 72%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.23-7.13 (m, 4H), 6.02-5.89 (m, 1H), 5.09-4.96 (m, 2H), 3.51 (t, 2H, *J* = 12.9), 3.40 (d, 2H, *J* = 6.0), 3.19 (t, 2H, *J* = 9.9) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 137.7, 137.0, 136.9, 130.0, 129.6, 127.2, 126.6, 116.0, 37.4, 36.3, 32.0 ppm; IR 3075, 3018, 2975, 1637, 1489, 1453, 1314, 1262, 1209, 995, 916, 755 cm^{-1}; MS: (m/z) (%): 224 (100), 226 (99) [M^+].

2-(2-allylphenethyl)-1,3-diphenylpropane-1,3-dione (3e). To a mixture of KI (668.2 mg, 1 mmol), K_2CO_3 (152.2 mg, 1.1 mmol) and dibenzoylmethane (485.6 mg, 1.1 mmol) was added 1-allyl-2-(2-bromoethyl)benzene (225 mg, 1 mmol) in DMF (1.4 mL). The mixture was stirred at 100 ^oC for 3 h and quenced with water. After extracted with ether, washed with water for three times, dried over Na_2SO_4 and concentrated, the crude product was applied to flash column chromatography to afford **3e** (149.6 mg, 0.407 mmol, 41% yield).

^1H NMR ($CDCl_3$, 300MHz) δ 7.88 (d, 4H, *J* = 7.8), 7.56-7.51 (m, 2H), 7.47-7.38 (m, 4H), 7.23-7.15 (m, 4H), 5.94-5.81 (m, 1H), 5.24 (t, 1H, *J* = 6.6), 4.98-4.90 (m, 2H), 3.36 (d, 2H, *J* = 6.6), 2.78 (t, 2H, *J* = 7.5), 3.38 (q, 2H, *J* = 6.6) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 196.0, 139.0, 137.9, 137.1, 135.8, 133.5, 129.8, 129.6, 128.8, 128.4, 126.6, 126.4, 115.8, 55.8, 36.8, 30.9, 30.1 ppm; IR 2960, 2924, 1695, 1671, 1596, 1580, 1448, 1346, 1259, 1198, 1094, 1024, 797, 757, 692 cm^{-1}; MS: (m/z) (%): 368 (2) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{20}H_{20}O_3$ 368.17763, Found: 368.17843.

Procedures and characterization data for 3f-g, 3l.



1-phenylhept-6-ene-1,3-dione (3l). Refer to the reference 2g.

^1H NMR ($CDCl_3$, 200MHz) δ 16.14 (s, 1H), 7.88-7.85 (m, 2H), 7.56-7.42 (m, 3H), 6.18 (s, 1H), 5.93-5.80 (m, 1H), 5.13-5.00 (m, 2H), 4.10 (s, 0.2H), 2.57-2.40 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 196.1, 183.2, 136.8, 134.8, 132.3, 128.6, 127.0, 115.6, 96.2, 38.4, 29.5 ppm; IR 3078, 2927, 1607, 1574, 1492, 1450, 1272, 1182, 1145, 1078, 1000, 915 cm^{-1}; MS: (m/z) (%): 202 (10) [M^+], 105 (100).

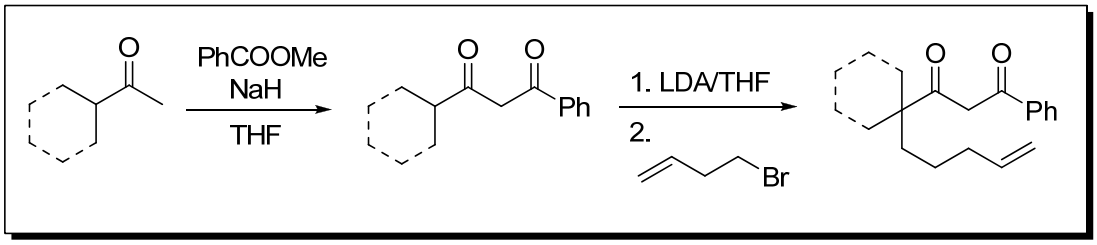
1-phenyloct-7-ene-1,3-dione (3f). Refer to the reference 2g.

^1H NMR ($CDCl_3$, 200MHz) δ 7.92-7.87 (m, 2H), 7.57-7.41 (m, 3H), 6.18 (s, 0.9H), 5.89-5.72 (m, 1H), 5.11-5.00 (m, 2H), 4.09 (s, 0.2H), 2.60 (t, 0.8H, *J* = 7.2), 2.45 (t, 1.5H, *J* = 7.4), 2.20-2.09 (m, 2H), 1.86-1.67 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 196.8, 183.5, 137.9, 135.0, 132.3, 128.6, 127.0, 115.4, 96.2, 38.4, 33.1, 24.8 ppm; IR 3073, 2930, 2359, 2342, 1602, 1574, 1457, 1027, 913, 799, 692 cm^{-1}; MS: (m/z) (%): 215 (18) [M^+], 105 (100).

1-phenylnon-8-ene-1,3-dione (3g). Refer to the reference 2g.

^1H NMR ($CDCl_3$, 300MHz) δ 16.20 (s, 1H), 7.90-7.87 (m, 2H), 7.55-7.42 (m, 3H), 6.18 (s, 1H), 5.88-5.75 (m, 1H), 5.06-4.96 (m, 2H), 4.09 (s, 0.2H), 2.44 (t, 2H, *J* = 7.5), 2.10 (q, 2H, *J* = 7), 1.76-1.66 (m, 2H), 1.53-1.43 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 196.8, 183.4, 138.4, 135.0, 132.2, 128.6, 127.0, 114.7, 96.1, 39.1, 33.5, 28.4, 25.2 ppm; IR 3068, 2931, 1602, 1575, 1459, 1262, 911, 765, 689 cm^{-1}; MS: (m/z) (%): 230 (15) [M^+], 105 (100).

Procedures and characterization data for 3i-j.



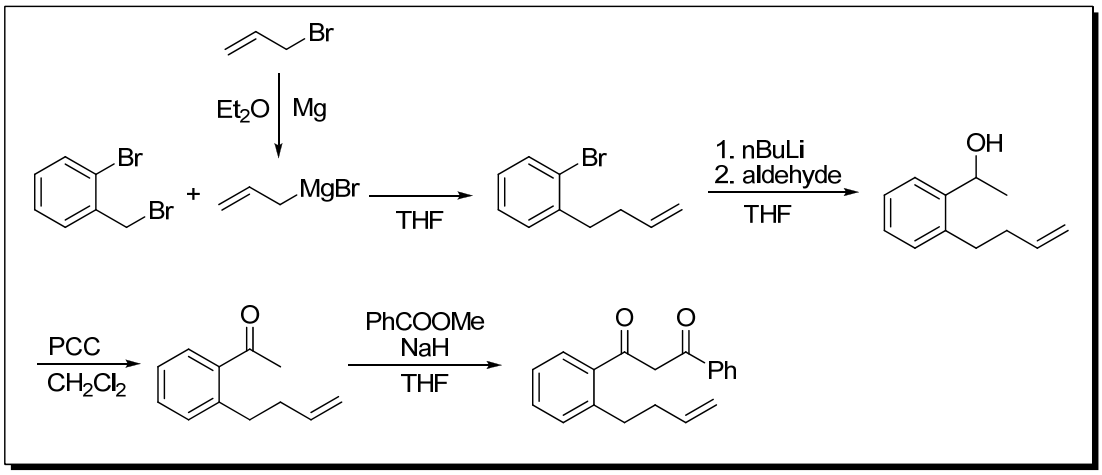
4-methyl-1-phenylpentane-1,3-dione. Refer to the reference 2h.
^{1}H NMR ($CDCl_3$, 200MHz) δ 16.26 (s, 1H), 7.91-7.86 (m, 2H), 7.55-7.431 (m, 3H), 6.19 (s, 1H), 2.65-2.58 (m, 1H), 1.24 (s, 3H), 1.20 (s, 3H) ppm; MS: (m/z) (%): 190 (21) [M^+], 147 (100).

1-cyclohexyl-3-phenylpropane-1,3-dione. Refer to the reference 2h.
^{1}H NMR ($CDCl_3$, 300MHz) δ 16.30 (s, 1H), 7.88 (m, 2H), 7.54-7.41 (m, 3H), 6.18 (s, 1H), 2.36-2.27 (m, 1H), 1.96-1.18 (m, 10H) ppm.

4,4-dimethyl-1-phenylnon-8-ene-1,3-dione (3i). Refer to the reference 2i.
^{1}H NMR ($CDCl_3$, 200MHz) δ 16.54 (s, 1H), 7.91-7.87 (m, 2H), 7.52-7.40 (m, 3H), 6.28 (s, 1H), 5.88-5.68 (m, 1H), 5.05-4.91 (m, 2H), 2.09-1.98 (m, 2H), 1.64-1.56 (m, 2H), 1.41-1.28 (m, 2H), 1.22 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 202.4, 184.2, 138.5, 135.5, 132.1, 128.6, 127.0, 114.7, 92.9, 43.1, 40.4, 34.2, 25.3, 24.0 ppm; IR 2936, 1601, 1570, 1461, 1272, 1073, 990, 993, 912, 768, 694 cm^{-1}; MS: (m/z) (%): 258 (4) [M^+], 147 (100).

1-(1-(pent-4-enyl)cyclohexyl)-3-phenylpropane-1,3-dione (3j). Refer to the reference 2i.
^{1}H NMR ($CDCl_3$, 300MHz) δ 16.69 (s, 1H), 7.90 (m, 2H), 7.53-7.41 (m, 3H), 6.32 (s, 1H), 5.85-5.65 (m, 1H), 5.02-4.91 (m, 2H), 2.08-1.94 (m, 3H), 1.59-1.23 (m, 14H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.8, 183.1, 138.5, 135.4, 132.0, 128.5, 126.9, 114.6, 94.1, 47.5, 40.1, 34.2, 33.8, 26.1, 23.0, 22.8 ppm; IR 3064, 2932, 2856, 1602, 1569, 1457, 1258, 1184, 1076, 990, 909, 768, 692 cm^{-1}; MS: (m/z) (%): 298 (5) [M^+], 147 (100).

Procedures and characterization data for 3k.



allylmagnesium bromide. Refer to the reference 2j.

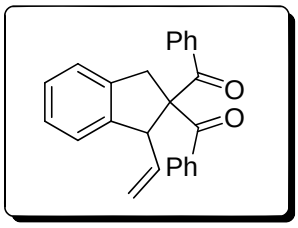
1-bromo-2-(but-3-enyl)benzene. Refer to the reference 2k, yield 100%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.52 (d, 1H, *J* = 8.4), 7.26-7.19 (m, 2H), 7.08-7.02 (m, 1H), 5.95-5.81 (m, 1H), 5.10-4.98 (m, 2H), 2.85-2.80 (m, 2H), 2.41-2.33(q, 2H, *J* = 7.2) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 141.0, 137.6, 132.8, 130.3, 137.6, 127.3, 124.3, 115.2, 35.6, 33.8 ppm.

1-(2-(but-3-enyl)phenyl)ethanol. Refer to the reference 2l, yield 100%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.55-7.52 (m, 1H), 7.28-7.14 (m, 3H), 5.95-5.81 (m, 1H), 5.14 (q, 1H, *J* = 6.6), 5.09-4.98 (m, 2H), 2.78-2.72 (m, 2H), 2.39-2.31 (m, 2H), 1.85 (s, 1H), 1.48 (d, 3H, *J* = 6) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 143.3, 138.1, 137.9, 129.3, 127.3, 136.6, 135.0, 115.1, 66.1, 35.6, 31.6, 24.7 ppm.

1-(2-(but-3-enyl)phenyl)ethanone.
1-(2-(but-3-enyl)phenyl)ethanol was dissolved in DCM at 0°C, PCC was then added under stirring. The mixture was stirred for 40 min in ice bath and then at room temperature until TLC showed complete conversion, yield 81%.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.67-7.64 (m, 1H), 7.43-7.37 (m, 1H), 7.30-7.24 (m, 2H), 5.94-5.80 (m, 1H), 5.06-4.94 (m, 2H), 2.97-2.93(m, 2H), 2.58 (s, 3H), 2.38-2.30 (m, 2H), ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.0, 141.9, 138.2, 137.9, 131.3, 129.1, 125.8, 114.8, 35.7, 33.5, 29.8 ppm.

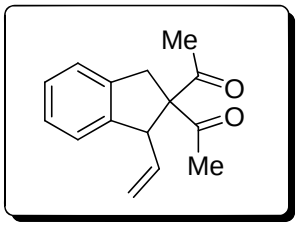
1-(2-(but-3-enyl)phenyl)-3-phenylpropane-1,3-dione (3k). Refer to the reference 2h.
^{1}H NMR ($CDCl_3$, 300MHz) δ 16.65 (s, 1H), 7.95 (d, 2H, J =7.2), 7.57-7.25 (m, 7H), 6.52 (s, 1H), 5.94-5.80 (m, 1H), 5.07-4.59 (m, 2H), 2.98 (d, 2H, *J* = 7.5), 2.41 (q, 2H, J = 7.5) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 191.0, 184.8, 140.9, 138.0, 136.7, 135.1, 132.5, 130.7, 128.7, 128.4, 127.1, 126.0, 115.0, 97.3, 35.7, 33.1 ppm; IR 3067, 1602, 1560, 1490, 1458, 1302, 1221, 913, 759, 689 cm^{-1}; MS: (m/z) (%): 278 (6) [M^+], 105 (100).

Characterization data for 4a-4l', 7aa-7la, 7ab-7ae.



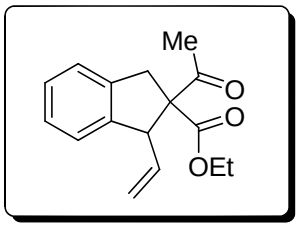
(1-vinyl-2,3-dihydro-1*H*-indene-2,2-diyl)bis(phenylmethanone) (4a).

Following the general procedures I. Startinging from **3a** (175.5 mg, 0.50 mmol), reacting for 60 h, to afford **4a** (112.4 mg), yield 65%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.90-7.82 (m, 4H), 7.40-7.12 (m, 10H), 5.64-5.52 (m, 1H), 5.19 (d, 1H, *J* = 9.6), 4.92 (d, 1H, *J* = 16.8), 4.81 (d, 1H, *J* = 10.2), 4.72 (d, 1H, *J* = 16.8), 3.38 (d, 1H, *J* = 17.1) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 197.1, 196.8, 143.3, 138.4, 137.1, 135.9, 134.8, 133.1, 133.0, 129.3, 129.0, 128.5, 127.3, 127.2, 124.6, 124.4, 117.2, 74.3, 56.4, 39.9 ppm; IR 2924, 1662, 1596, 1579, 1482, 1447, 1249, 1232, 1177, 1026, 994, 924, 756, 689 cm^{-1} ; MS: (m/z) (%): 352 (6) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{25}H_{20}O_2$ 352.14633, Found: 352.14632.



1,1'-(1-vinyl-2,3-dihydro-1H-indene-2,2-diyl)diethanone (4b).

Following the general procedures I. Startinging from **3b** (69.1 mg, 0.3 mmol), reacting for 60 h, to afford **4b** (29.4 mg), yield 43%. ^{1}H NMR ($CDCl_3$, 200MHz) δ 7.20-7.17 (m, 4H), 5.73-5.55 (m, 1H), 5.34-5.09 (m, 2H), 4.64 (d, 1H, *J* = 9.0), 3.83 (d, 1H, *J* = 17.0), 3.18 (d, 1H, *J* = 16.8), 2.17 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 204.8, 204.3 142.7, 138.7, 135.7, 127.6, 127.3, 124.8, 124.4, 117.9, 79.3, 53.4, 36.3, 28.5, 27.0 ppm; IR 2926, 1709, 1698, 1479, 1356, 1202, 1146, 927, 751 cm^{-1} ; MS: (m/z) (%): 228 (1) [M^+], 43 (100); HRMS (ESI): Anal. Calcd. for [$C_{15}H_{16}O_2$ + Na^+] 251.10425, Found: 251.10439.



ethyl 2-acetyl-1-vinyl-2,3-dihydro-1*H*-indene-2-carboxylate (4c).

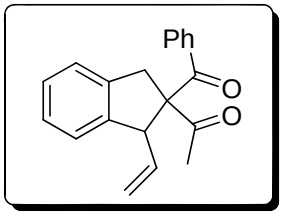
Following the general procedures I. Startinging from **3c** (131.2 mg, 0.5 mmol), reacting for 60 h, to afford **4c** (80.2 mg), yield 63%, the ratio of **4c-*trans*/*cis*** was determined by GC-MS to be 1/2.4.

4c-*trans*.

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.20-7.13 (m, 4H), 5.70-5.57 (m, 1H), 5.34-5.25 (m, 2H), 4.60 (d, 1H, *J* = 9.4), 4.20 (q, 2H, *J* = 7.4), 3.84 (d, 1H, *J* = 17.0), 3.21 (d, 1H, *J* = 16.8), 2.13 (s, 3H), 1.24 (t, 3H, *J* = 7.2) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ (208.6), (171.1), 142.3, (140.1), 135.7, 127.4, 127.1, 124.6, 124.3, 117.7, 71.8, 61.8, 55.0, 37.4, 28.0, 13.9 ppm; IR 2979, 2826, 1735, 1713, 1479, 1356, 1243, 1211, 1156, 1019, 928, 753, 684 cm^{-1} ; MS: (m/z) (%): 258 (4) [M^+], 43 (100); HRMS (ESI): Anal. Calcd. for [$C_{16}H_{18}O_3$ + H^+] 259.13287, Found: 259.13298.

4c-*cis*.

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.18-7.11 (m, 4H), 5.82-5.64 (m, 1H), 5.23-4.93 (m, 2H), 4.56 (d, 1H, *J* = 9.2), 4.18 (q, 2H, *J* = 7.4), 3.82 (d, 1H, *J* = 16.6), 3.20 (d, 1H, *J* = 16.4), 2.23 (s, 3H), 1.24 (t, 3H, *J* = 7.0) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 202.1, 170.2, 142.7, 138.7, 136.0, 127.3, 127.1, 124.2, 117.7, 71.0, 61.4, 53.5, 37.8, 26.4, 14.0 ppm; IR 2981, 1740, 1713, 1479, 1356, 1237, 1149, 1078, 1020, 920, 856, 750 cm^{-1} ; MS: (m/z) (%): 258 (4) [M^+], 43 (100); HRMS (ESI): Anal. Calcd. for [$C_{16}H_{18}O_3$ + H^+] 259.13287, Found: 259.13301.



1-(2-benzoyl-1-vinyl-2,3-dihydro-1H-inden-2-yl)ethanone (4d).

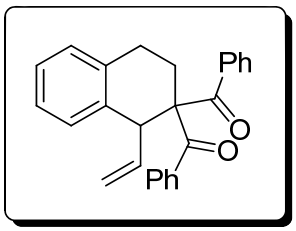
Following the general procedures I. Startinging from **3d** (88.1 mg, 0.3 mmol), reacting for 60 h, to afford **4d-*trans*** (23.2 mg), yield 27%, and **4d-*cis*** (25.5 mg), yield 29%.

4d-*cis*.

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.92-7.87 (m, 2H), 7.59-7.42 (m, 3H), 7.19-7.17 (m, 4H), 5.59-5.46 (m, 1H), 4.88-4.77 (m, 3H), 4.30 (d, 1H, *J* = 17.4), 3.14 (d, 1H, *J* = 17.4), 2.07(s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 204.7, 195.8, 143.4, 137.8, 136.4, 135.7, 133.5, 128.9, 128.8, 127.4, 127.3, 124.7, 124.4, 117.4, 54.5, 38.0, 26.8 ppm; IR 3074, 2925, 2855, 1715, 1674, 1597, 1448, 1242, 1153, 923, 760 cm^{-1} ; MS: (m/z) (%): 290 (2) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{20}H_{18}O_2$ + H^+] 291.13796, Found: 291.13839.

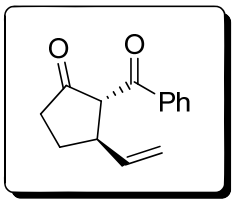
4d-*trans*.

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.87-7.84 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.41 (m, 2H), 7.19-7.08 (m, 4H), 5.69-5.56 (m, 1H), 5.35 (dd, 1H, *J* = 1.8), 5.11 (dd, 1H, *J* = 1.8), 5.00 (d, 1H, *J* = 9.9), 4.32 (d, 1H, *J* = 17.1), 3.26 (d, 1H, *J* = 17.4), 2.05(s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 204.9, 196.2, 142.5, 138.9, 136.3, 134.7, 133.4, 129.2, 128.8, 127.4, 127.2, 124.7, 124.4, 117.4, 76.7, 54.8, 38.1, 29.7 ppm; IR 2926, 1714, 1671, 1597, 1580, 1447, 1356, 1242, 1153, 923, 762, 749, 694 cm^{-1} ; MS: (m/z) (%): 290 (3) [M^+], 247 (100); HRMS (ESI): Anal. Calcd. for [$C_{20}H_{18}O_2$ + H^+] 291.13796, Found: 291.13836.



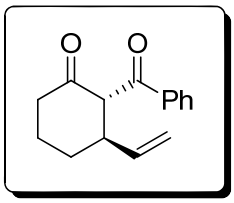
(1-vinyl-1,2,3,4-tetrahydronaphthalene-2,2-diyl)bis(phenylmethanone) (4e).

Following the general procedures I. Startinging from **3e** (139.4 mg, 0.379 mmol), reacting for 60 h, to afford **4e** (65.9 mg), yield 48%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.92 (d, 2H, *J* = 8.1), 7.78 (d, 2H, *J* = 7.8), 7.41-6.91 (m, 10H), 5.65-5.53 (m, 1H), 4.74 (d, 1H, *J* = 9.6), 4.59-4.48 (m, 2H), 2.76-2.68 (m, 1H), 2.60-2.51 (m, 2H), 2.34-2.22 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 198.0, 197.9, 137.3, 137.0, 136.7, 135.4, 133.0, 132.9, 132.8, 129.5, 128.73, 128.66, 128.4, 128.33, 128.30, 125.9, 125.8, 117.1, 66.4, 49.1, 26.3, 25.0 ppm; IR 2963, 1661, 1597, 1579, 1490, 1447, 1248, 1227, 1177, 1026, 970, 908, 734 cm^{-1} ; MS: (m/z) (%): 366 (4) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{26}H_{22}O_2$ 366.16198, Found: 366.16299.



(*E*)-2-benzoyl-3-vinylcyclopentanone (4f).

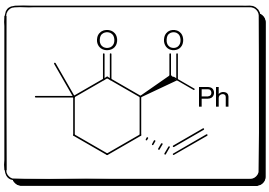
Following the general procedures I. Startinging from **3f** (64.8 mg, 0.3 mmol), reacting for 84 h, to afford **4f** (33.2 mg), yield 52%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.92-7.89 (m, 2H), 7.52-7.40 (m, 3H), 6.57 (s, 1H), 5.96-5.84 (m, 1H), 5.40-5.25 (m, 2H), 4.90 (q, 1H, *J* = 6.9), 3.51-3.40 (m, 1H), 3.25-3.13 (m, 1H), 2.39-2.28 (m, 1H), 1.98-1.85 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 190.3, 178.4, 139.7, 135.7, 131.7, 128.3, 127.5, 117.9, 95.1, 84.1, 31.4, 29.7 ppm; IR 3054, 2929, 1637, 1586, 1563, 1447, 1426, 1382, 1336, 1300, 1250, 1171, 1062, 996, 975, 931, 900, 839, 793, 702, 689 cm^{-1} ; MS: (m/z) (%): 214 (95) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{14}H_{14}O_2$ 214.09938, Found: 214.09959.



***trans*-2-benzoyl-3-vinylcyclohexanone (4g).**

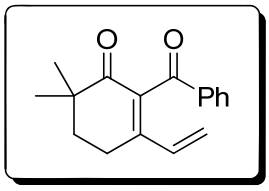
Following the general procedures I. Startinging from **3a** (64.9 mg, 0.3 mmol), reacting for 60 h, to afford **4a** (17.2 mg), yield 25%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.88-7.85 (m, 2H), 7.58-7.43 (m, 3H), 5.79-5.67 (m, 1H), 5.07-4.97 (m, 2H), 4.32 (d, 1H, *J* = 10.2), 3.24-3.16 (m, 1H), 3.60-2.41 (m, 2H), 2.17-2.06 (m, 2H), 1.91-1.65 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 207.8, 197.3, 139.3, 137.4, 133.1, 128.6, 128.2, 115.6, 62.6, 44.4, 41.7, 29.6, 24.3 ppm; IR 2933, 2864, 1711, 1681, 1598, 1582, 1448, 1346, 1291,

1239, 1171, 1001, 918, 765, 693 cm^{-1} ; MS: (m/z) (%): 228 (5) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{15}H_{16}O_2 + H^+$] 229.12231, Found: 229.12210.



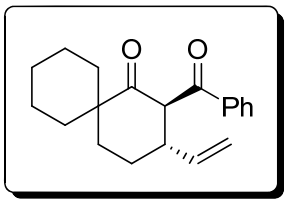
6-benzoyl-2,2-dimethyl-5-vinylcyclohexanone. (4i)

Following the general procedures I. Startinging from **3i** (78.4 mg, 0.3 mmol), reacting for 80 h, to afford **4i** (30.8 mg), yield 40%, and **4i'** (10.8 mg), yield 14%. ^1H NMR ($CDCl_3$, 300MHz) δ 7.81-7.79 (m, 2H), 7.55-7.40 (m, 3H), 5.76-5.64 (m, 1H), 5.04-4.92 (m, 2H), 4.53 (d, 1H, *J* = 11.4), 3.19-3.13 (m, 1H), 1.93-1.73 (m, 4H), 1.35 (s, 3H), 1.07 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 212.1, 197.8, 139.6, 138.0, 132.9, 128.5, 127.9, 115.3, 58.6, 45.4, 45.0, 38.9, 26.5, 24.9, 24.8 ppm; IR 2927, 2853, 1706, 1684, 1598, 1581, 1448, 1344, 1288, 1205, 1077, 1001, 913 cm^{-1} ; MS: (m/z) (%): 256 (4) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{17}H_{20}O_2 + H^+$] 257.15361, Found: 257.15379.



2-benzoyl-6,6-dimethyl-3-vinylcyclohex-2-enone (4i').

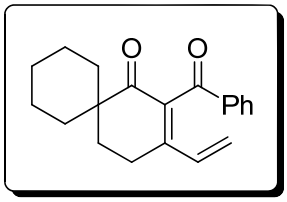
^1H NMR ($CDCl_3$, 300MHz) δ 7.82-7.79 (m, 2H), 7.58-7.41 (m, 3H), 6.45-6.36 (m, 1H), 5.77 (d, 1H, *J* = 17.1), 5.45 (d, 1H, *J* = 10.5), 2.69 (t, 2H, *J* = 6.0), 2.00 (t, 2H, *J* = 6.3), 1.22 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.7, 197.2, 151.1, 137.0, 136.2, 134.1, 133.6, 128.9, 128.7, 122.8, 41.1, 35.1, 24.0, 21.6 ppm; IR 2963, 2927, 1675, 1656, 1619, 1597, 1580, 1449, 1367, 1321, 1263, 1242, 1151, 950, 818 cm^{-1} ; MS: (m/z) (%): 254 (68) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{17}H_{18}O_2$ + H^+] 255.13796, Found: 255.13815.



***trans*-2-benzoyl-3-vinylspiro[5.5]undecan-1-one (4j).**

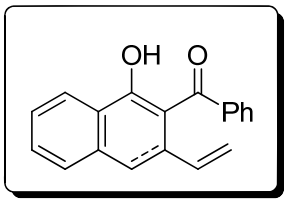
Following the general procedures I. Startinging from **3j** (89.4 mg, 0.3 mmol) and 1.8 equiv. of BQ was used, reacting for 84 h, to afford **4j** (46.8 mg), yield 53%, and **4j'** (31.2 mg), yield 35%. ^1H NMR ($CDCl_3$, 200MHz) δ 7.84-7.80 (m, 2H), 7.58-7.39 (m, 3H), 5.79-5.62 (m, 1H), 5.05-4.90 (m, 2H), 4.61 (d, 1H, *J* = 12.0), 3.26-3.08 (m, 1H), 2.11-1.09 (m, 14H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 212.3, 197.5, 139.7, 137.9, 132.9, 128.6, 127.9, 115.1, 58.4, 49.0, 45.3, 36.4, 33.5, 33.4, 26.1, 25.7, 22.3, 21.7 ppm; IR 2932,

2851, 1697, 1681, 1597, 1361, 1293, 1212, 1066, 991, 907, 784, 755, 692 cm^{-1} ; MS: (m/z) (%): 296 (8) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{20}H_{24}O_2 + H^+$] 297.18491, Found: 297.18516.



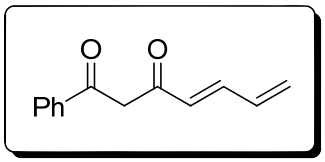
2-benzoyl-3-vinylspiro[5.5]undec-2-en-1-one (4j').

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.84-7.79 (m, 2H), 7.59-7.39 (m, 3H), 6.47-6.33 (m, 1H), 5.76 (d, 1H, *J* = 17.4), 5.44 (d, 1H, *J* = 11.0), 2.66 (t, 2H, *J* = 6.0), 2.08 (t, 2H, *J* = 6.4), 1.87-1.27 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 203.1, 197.4, 150.4, 137.0, 136.5, 134.0, 133.6, 128.9, 128.7, 122.6, 44.0, 31.5, 29.8, 26.5, 25.9, 21.5, 21.0 ppm; IR 2926, 2857, 1807, 1675, 1655, 1581, 1448, 1318, 1244, 1198, 1043, 1002, 943, 806, 690 cm^{-1} ; MS: (m/z) (%): 294 (56) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{20}H_{22}O_2 + H^+$] 295.16926, Found: 295.16927.



(1-hydroxy-3-vinyl-3,4-dihydronaphthalen-2-yl)(phenyl)methanone and (1-hydroxy-3-vinylnaphthalen-2-yl)(phenyl)methanone (4k/4k').

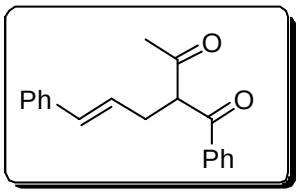
Following the general procedures I. Startinging from **3k** (83.8 mg, 0.3 mmol) and 1.3 equiv. of BQ was used, reacting for 60 h, to afford **4k** and **4k'** as an unseperable mixture (39.0 mg), yield 47%. ^{1}H NMR ($CDCl_3$, 200MHz) δ 17.2 (s, 1H), 11.9 (s, 0.7H), 8.41 (d, 0.7H, *J* = 8.2), 8.04-7.13 (m, 15.3H), 6.33 (dd, 0.7H, *J* = 10.6), 5.87-5.71 (m, 1H), 5.45 (d, 0.7H, *J* = 17.0), 4.99-4.85 (m, 2.7H), 3.58 (m, 1H), 3.27-3.12 (dd, 1H, *J* = 6.6), 3.77 (d, 1H, *J* = 15.8) ppm; IR 3064, 2924, 1667, 1599, 1555, 1490, 1448, 1324, 1304, 1263, 1224, 1023, 1001, 970, 919, 804, 781, 754, 694 cm^{-1} ; MS (GC-MS): (m/z) (%): **4k**: 276 (18) [M^+], 105 (100); **4k'**: 274 (42) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{19}H_{16}O_2 + H^+$] 277.12231, Found: 277.12259.



(E)-1-phenylhepta-4,6-diene-1,3-dione (4l').

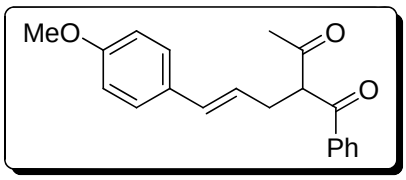
Following the general procedures I. Startinging from **3l** (59.2 mg, 0.3 mmol), reacting for 60 h, to afford **4l** (33.1 mg), yield 58%. ^{1}H NMR ($CDCl_3$, 200MHz) δ 16.0 (s, 1H), 7.95-7.91 (m, 2H), 7.55-7.36 (m, 3H), 7.31-7.23 (m, 1H), 6.61-6.42 (m, 1H), 6.26 (s, 1H),

6.12 (d, 1H, J = 15.2), 5.62 (d, 1H, J = 16.8), 5.49 (d, 1H, J = 9.8) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 189.8, 178.8, 140.3, 136.2, 135.4, 132.6, 128.6, 127.4, 127.3, 124.9, 97.5 ppm; IR 1636, 1610, 1558, 1261, 1088, 1008, 805, 765, 679 cm^{-1} ; MS: (m/z) (%): 200 (43) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{13}H_{12}O_2$ + H^+] 201.09101, Found: 201.09128.



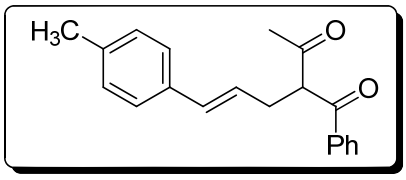
2-cinnamyl-1-phenylbutane-1,3-dione (7aa).[3a]

Following the general procedures I. Startinging from **5a** (66.4 μL, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7aa** (113.9 mg), yield 82%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.05-8.01 (m, 2H), 7.64-7.53 (m, 1H), 7.52-7.47 (m, 2H), 7.32-7.21 (m, 5H), 6.51-8.45 (m, 1H), 6.21-6.10 (m, 1H), 4.64 (t, 1H, J = 7.2), 2.94-2.88 (m, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.4, 195.7, 136.8, 136.2, 133.7, 132.6, 128.8, 128.7, 128.4, 127.3, 126.1, 126.0, 125.8, 62.9, 32.3, 28.2 ppm; IR 3027, 1720, 1675, 1596, 1493, 1448, 1357, 1271, 1182, 968, 742, 692 cm^{-1} ; MS: (m/z) (%): 278 (6) [M^+], 91 (100).



(*E*)-2-(3-(4-methoxyphenyl)allyl)-1-phenylbutane-1,3-dione (7ba).

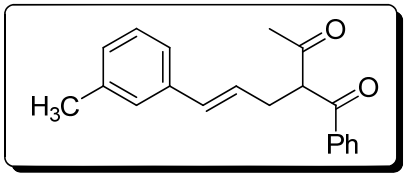
Following the general procedures I. Startinging from **5b** (77.0 μL, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ba** (99.9 mg), yield 65%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.01-7.98 (m, 2H), 7.62-7.19 (m, 5H), 6.88-6.78 (m, 2H), 6.40 (d, 1H, J = 15.6), 6.03-5.93 (m, 1H), 4.60 (t, 1H, J = 7.2), 3.77 (s, 3H), 2.89-2.84 (m, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.5, 195.8, 159.0, 136.3, 133.7, 132.0, 129.7, 128.8, 128.7, 127.2, 123.6, 113.8, 63.2, 55.2, 32.3, 28.2 ppm; IR 2934, 1720, 1674, 1607, 1511, 1448, 1248, 1175, 1033, 969, 842, 742, 694 cm^{-1}; MS: (m/z) (%): 308 (16) [M^+], 265 (100); HRMS: Anal. Calcd. for $C_{20}H_{20}O_3$ 308.14124, Found: 308.14229.



(*E*)-1-phenyl-2-(3-*p*-tolylallyl)butane-1,3-dione (7ca).

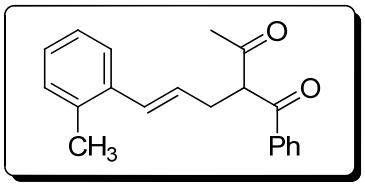
Following the general procedures I and reacting for 72 h. Startinging from **5c** (66.8 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ca** (110.0 mg), yield 75%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.00-7.98 (m, 2H), 7.61-7.56 (m, 1H), 7.48-7.44 (m, 2H), 7.18-7.15

(m, 2H), 7.08-7.05 (m, 2H), 6.42 (d, 1H, *J* = 15.3), 6.12-6.02 (m, 1H), 4.60 (t, 1H, *J* = 7.2), 2.95-2.80 (m, 2H), 2.29 (s, 3H), 2.27 (s, 0.2H), 2.16 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.5, 195.9, 137.2, 136.4, 134.2, 133.8, 132.5, 129.2, 128.9, 128.8, 126.1, 124.8, 63.2, 32.4, 28.3, 21.1 ppm; IR 3027, 2920, 1720, 1675, 1596, 1513, 1448, 1357, 1214, 1181, 1155, 969, 796, 693 cm^{-1} ; MS: (m/z) (%): 292 (4) [M$^+$], 105 (100); HRMS: Anal. Calcd. for $C_{20}H_{20}O_2$ 292.14633, Found: 292.14700.



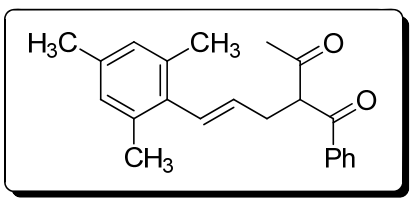
(*E*)-1-phenyl-2-(3-*m*-tolylallyl)butane-1,3-dione (7da).

Following the general procedures I and reacting for 72 h. Startinging from **5d** (66.1 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7da** (62.3 mg), yield 43%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.00-7.98 (m, 2H), 7.61-7.56 (m, 1H), 7.50-7.45 (m, 2H), 7.28-7.26 (m, 1H), 7.14-7.085 (m, 3H), 6.63 (d, 1H, *J* = 15.6), 6.02-5.92 (m, 1H), 4.61 (t, 1H, *J* = 6.9), 2.99-2.82 (m, 2H), 2.30 (s, 0.8H), 2.24 (s, 3H), 2.17 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.5, 195.8, 136.4, 136.1, 135.1, 133.8, 130.1, 128.9, 128.7, 127.3, 127.2, 126.0, 125.6, 63.2, 32.7, 28.2, 19.7 ppm; IR 2920, 2849, 1720, 1675, 1596, 1484, 1448, 1357, 1218, 1183, 1157, 968, 743, 694 cm^{-1} ; MS: (m/z) (%): 292 (5) [M$^+$], 249 (100); HRMS: Anal. Calcd. for $C_{20}H_{20}O_2$ 292.14633, Found: 292.14708.



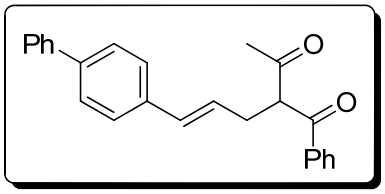
(*E*)-1-phenyl-2-(3-*o*-tolylallyl)butane-1,3-dione (7ea).

Following the general procedures I and reacting for 72 h. Startinging from **5e** (64.7 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ea** (49.8 mg), yield 34%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.03-8.00 (m, 2H), 7.64-7.59 (m, 1H), 7.53-7.48 (m, 2H), 7.31-7.26 (m, 1H), 7.17-7.09 (m, 3H), 6.65 (d, 1H, *J* = 15.6), 6.04-5.94 (m, 1H), 4.63 (t, 1H, *J* = 7.5), 3.01-2.84 (m, 2H), 2.31 (s, 0.4H), 2.25 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.6, 195.8, 136.3, 135.1, 133.8, 130.6, 130.1, 128.9, 127.3, 127.1, 126.0, 125.5, 63.1, 32.7, 28.2, 19.7 ppm; IR 3055, 2917, 1721, 1675, 1596, 1484, 1448, 1357, 1217, 1182, 1156, 968, 746, 699 cm^{-1} ; MS: (m/z) (%): 292 (4) [M$^+$], 105 (100); HRMS: Anal. Calcd. for $C_{20}H_{20}O_2$ 292.14633, Found: 292.14594.



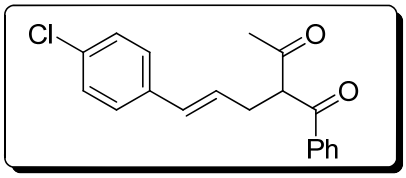
(*E*)-2-(3-mesitylallyl)-1-phenylbutane-1,3-dione (7fa).

Following the general procedures I and reacting for 72 h. Startinging from **5f** (80.0 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7fa** (26.0 mg), yield 16%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.05-8.01 (m, 2H), 7.65-7.59 (m, 1H), 7.53-7.48 (m, 2H), 6.82 (s, 2H), 6.40 (d, 1H, *J* = 15.6), 5.63-5.53 (m, 1H), 4.65 (t, 1H, *J* = 6.9), 2.99-2.91 (m, 2H), 2.24 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.6, 195.8, 136.3, 136.0, 135.7, 133.8, 133.6, 130.4, 130.3, 128.9, 128.7, 128.4, 63.2, 33.0, 30.9, 28.0, 20.8, 20.7 ppm; IR 3668, 2971, 2919, 1720, 1677, 1596, 1448, 1356, 1251, 1217, 1056, 975, 854, 741 cm^{-1} ; MS: (m/z) (%): 320 (12) [M^+], 133 (100); HRMS: Anal. Calcd. for $C_{22}H_{24}O_2$ 320.17763, Found: 320.17787.



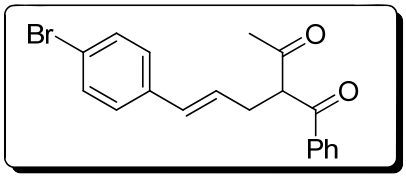
(*E*)-2-(3-(biphenyl-4-yl)allyl)-1-phenylbutane-1,3-dione (7ga).

Following the general procedures I. Startinging from **5g** (97.6 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ga** (136.7 mg), yield 77%.^{1}H NMR ($CDCl_3$, 300MHz) δ 8.02-7.99 (m, 2H), 7.63-7.30 (m, 12H), 6.50 (d, 1H, *J* = 16.2), 6.22-6.12 (m, 1H), 4.62 (t, 1H, *J* = 7.2), 3.23-3.24 (m, 0.2H), 3.00-2.84 (m, 2H), 2.30 (s, 0.4H), 2.19 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.3, 195.7, 140.6, 140.1, 136.3, 135.8, 133.7, 132.1, 130.3, 128.8, 128.7, 127.2, 127.1, 126.8, 126.5, 125.9, 63.0, 32.3, 28.2 ppm; IR 2982, 2142, 2088, 1726, 1701, 1598, 1449, 1370, 1323, 1298, 1266, 1204, 1162, 1120, 1089, 1019, 815, 748, 693 cm^{-1} ; MS: (m/z) (%): 354 (8) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{25}H_{22}O_2$ 354.16198, Found: 354.16226.



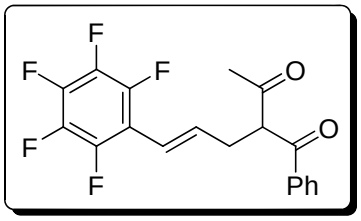
(*E*)-2-(3-(4-chlorophenyl)allyl)-1-phenylbutane-1,3-dione (7ha).

Following the general procedures I and 15 mol% of catalyst **2** was used. Startinging from **5h** (76.9 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ha** (92.7 mg), yield 59%. ^{1}H NMR ($CDCl_3$, 200MHz) δ 8.02-7.99 (m, 2H), 7.63-7.58 (m, 1H), 7.51-7.46 (m, 2H), 7.24-7.17 (m, 4H), 6.39 (d, 1H, *J* = 15.6), 6.16-6.06 (m, 1H), 4.62 (t, 1H, *J* = 7.2), 3.21-3.20 (m, 0.1H), 2.96-2.81 (m, 2H), 2.27 (s, 0.4H), 2.17 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.3, 195.6, 136.1, 135.2, 133.8, 132.8, 131.3, 128.8, 128.6, 128.5, 127.2, 126.5, 62.6, 32.1, 28.3 ppm; IR 3028, 1720, 1676, 1580, 1491, 1448, 1357, 1255, 1218, 1182, 1091, 1012, 969, 801, 691 cm^{-1} ; MS: (m/z) (%): 312 (4) [M^+], 269 (100); HRMS: Anal. Calcd. for $C_{19}H_{17}ClO_2$ 312.09171, Found: 312.09110.



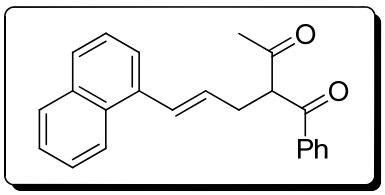
(*E*)-2-(3-(4-bromophenyl)allyl)-1-phenylbutane-1,3-dione (7ia).

Following the general procedures I and 15 mol% of catalyst **2** was used. Startinging from **5i** (99.3 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ia** (111.9 mg), yield 63%. ^{1}H NMR ($CDCl_3$, 200MHz) δ 8.01-7.99 (m, 2H), 7.64-7.59 (m, 1H), 7.52-7.47 (m, 2H), 7.39-7.36 (m, 2H), 7.15-7.12 (m, 2H), 6.39 (d, 1H, *J* = 16.2), 6.17-6.07 (m, 1H), 4.60 (t, 1H, *J* = 6.9), 3.20-3.19 (m, 0.1H), 2.90-2.84 (m, 2H), 2.27 (s, 0.2H), 2.17 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) δ 203.3, 195.6, 136.1, 135.7, 133.8, 131.5, 131.4, 128.9, 128.7, 127.6, 126.7, 121.0, 62.7, 28.3 ppm; IR 2923, 2855, 1721, 1676, 1596, 1487, 1448, 1357, 1217, 1181, 1072, 1008, 970, 799, 694 cm^{-1} ; MS: (m/z) (%): 356 (3) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{19}H_{17}BrO_2$ 356.04119, Found: 356.04016.



(*E*)-2-(3-(perfluorophenyl)allyl)-1-phenylbutane-1,3-dione (7ja).

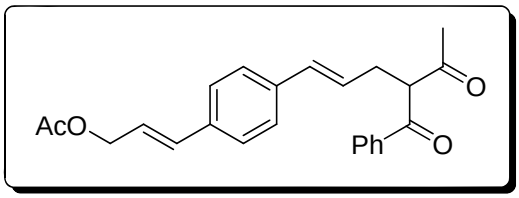
Following the general procedures I and 15 mol% of catalyst **2** was used. Startinging from **5j** (76.6 μL, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ja** (114.4 mg), yield 63%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.02-7.99 (m, 2H), 7.65-7.60 (m, 1H), 7.53-7.41 (m, 2H), 6.55-6.45 (m, 1H), 6.36 (d, 1H, *J* = 16.5), 4.68 (t, 1H, *J* = 6.9), 3.31-3.30 (m, 0.1H), 2.88-3.04 (m, 2H), 2.29 (s, 0.2H), 2.20 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.6, 195.3, 146.0, 142.8, 141.3, 139.0, 137.9, 135.9, 133.8, 128.8, 128.6, 128.2, 127.2, 116.8, 62.1, 33.2, 28.2 ppm; IR 1722, 1677, 1521, 1496, 1449, 1359, 1265, 1133, 997, 973, 693 cm^{-1} ; MS: (m/z) (%): 368 (6) [M^+], 105 (100); HRMS: Anal. Calcd. for $C_{19}H_{13}F_5O_2$ 368.08357, Found: 368.08257.



(*E*)-2-(3-(naphthalen-1-yl)allyl)-1-phenylbutane-1,3-dione (7ka).

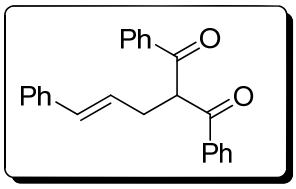
Following the general procedures I. Startinging from **5k** (84.0 mg, 0.5 mmol) with **6a** (113.5 mg, 0.7 mmol) to afford **7ka** (109.8 mg), yield 67%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.03-7.94 (m, 3H), 7.81-7.70 (m, 2H), 7.60-7.55 (m, 1H), 7.49-7.33 (m, 6H), 7.16 (d, 1H, *J* = 15.6), 6.17-6.07 (m, 1H), 4.68 (t, 1H, *J* = 6.9), 3.31-3.28 (m, 0.1H), 2.92-3.08 (m, 2H), 2.35 (s, 0.2H), 2.20 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.4, 195.9, 136.4, 134.7,

133.7, 133.4, 130.9, 130.0, 129.0, 128.9, 128.7, 128.4, 127.7, 125.9, 125.6, 125.5, 123.7, 123.6, 62.9, 32.7, 28.3 ppm; IR 3059, 1720, 1674, 1595, 1448, 1356, 1262, 1217, 1182, 1157, 970, 796, 777, 693 cm^{-1} ; MS: (m/z) (%): 328 (30) [M^+], 285 (100); HRMS: Anal. Calcd. for $C_{23}H_{20}O_2$ 328.14633, Found: 328.14694.



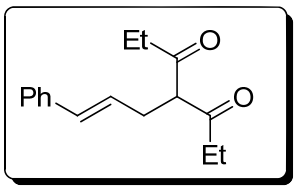
(*E*)-3-(4-((*E*)-4-benzoyl-5-oxohex-1-enyl)phenyl)allyl acetate (7la).

Following the general procedures I. Startinging from **5l** (18.6 mg, 0.086 mmol) with **6a** (43.7 mg, 0.27 mmol) and benzoquinone (29.2 mg, 0.27 mmol) in 0.7 mL toluene, to afford **7ka** (21.2 mg), yield 65%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.02-7.98 (m, 1H), 7.67-7.47 (m, 4H), 7.35-7.22 (m, 4H), 6.60 (d, 1H, *J* = 16.2), 6.44 (d, 1H, *J* = 15.6), 6.30-6.09 (m, 2H), 4.71 (d, 2H, *J* = 6.0), 4.61 (t, 1H, *J* = 7.2), 2.92-2.87 (m, 2H), 2.18 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 205.8, 197.9, 173.1, 138.8, 138.4, 137.4, 136.1, 136.0, 134.4, 132.4, 131.1, 130.9, 128.9, 128.6, 128.3, 125.0, 119.0, 67.3, 65.2, 34.6, 30.5, 23.2 ppm; IR 2917, 2849, 1735, 1676, 1597, 1448, 1361, 1230, 1189, 1024, 967, 909, 788, 731 cm^{-1}; MS: (m/z) (%): 376 (7) [M^+], 105 (100); HRMS (ESI): Anal. Calcd. for [$C_{24}H_{24}O_4$ + Na] 399.15723, Found: 399.15703.



2-cinnamyl-1,3-diphenylpropane-1,3-dione (7ab). [3a]

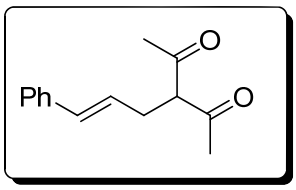
Following the general procedures I. Startinging from **5a** (66.4 μL, 0.5 mmol) with **6b** (157.0 mg, 0.7 mmol) to afford **7ab** (117.8 mg), yield 69%. ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.05 (d, 4H, *J* = 7.8), 7.64-7.59 (m, 2H), 7.53-7.47 (m, 4H), 7.32-7.24 (m, 5H), 6.53 (d, 1H, *J* = 15.9), 6.38-6.28 (m, 1H), 5.47 (t, 1H, *J* = 6.6), 3.10 (t, 2H, *J* = 6.6) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 195.4, 136.9, 135.8, 133.4, 132.4, 128.8, 128.5, 128.3, 127.2, 126.6, 126.0, 56.9, 32.8 ppm; IR 3058, 1694, 1671, 1596, 1580, 1448, 1329, 1263, 1232, 1198, 1181, 1001, 966, 940, 744, 691 cm^{-1} ; MS: (m/z) (%): 340 (2) [M^+], 235 (100).



4-cinnamylheptane-3,5-dione (7ac).

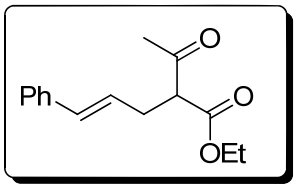
Following the general procedures I. Startinging from **5a** (66.4 μL, 0.5 mmol) with **6c** (95.0 μL, 0.7 mmol) to afford **7ac** (65.9 mg), yield 54%. ^{1}H NMR ($CDCl_3$, 300MHz) δ

17.0 (s, 0.2H), 7.32-7.20 (m, 5H), 6.43 (d, 0.7H, *J* = 15.9), 6.34 (d, 0.3H, *J* = 16.2), 6.26-6.18 (m, 0.3H), 6.10-6.00 (m, 0.7H), 3.83 (t, 1H, *J* = 7.5), 3.18-3.16 (m, 0.4H), 2.74 (t, 1.6H, *J* = 7.4), 2.61-2.40 (m, 4.2H), 1.14 (t, 1.5H, *J* = 7.8), 1.04 (t, 4.5H, *J* = 7.5) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 206.9, 195.4, 137.4, 133.2, 130.5, 129.11, 129.08, 128.9, 128.0, 127.8, 126.7, 126.6, 126.3, 67.2, 36.2, 32.4, 29.9, 29.2, 10.1, 8.1 ppm; IR 3026, 2978, 2939, 1725, 1699, 1598, 1494, 1459, 1449, 1409, 1377, 1349, 1106, 1027, 968, 745, 693 cm^{-1} ; MS: (m/z) (%): 244 (3) [M$^+$], 187 (100); HRMS: Anal. Calcd. for $C_{16}H_{20}O_2$ 244.14633, Found: 244.14633.



3-cinnamylpentane-2,4-dione (7ad). [3a]

Following the general procedures I. Startinging from **5a** (66.4 μL, 0.5 mmol) with **6d** (72.0 μL, 0.7 mmol) to afford **7ad** (59.7 mg), yield 55%. ^{1}H NMR ($CDCl_3$, 200MHz) δ 16.8 (s, 0.4H), 7.36-7.20 (m, 5H), 6.48-5.99 (m, 2H), 3.79 (t, 0.4H, *J* = 7.4), 3.14 (d, 1H, *J* = 4.8), 2.73 (t, 1H, *J* = 7.4), 2.20 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 203.6, 191.5, 137.0, 136.7, 132.7, 130.0, 128.5, 127.6, 127.5, 127.2, 126.1, 126.0, 125.4, 107.4, 68.2, 31.5, 30.4, 29.3, 23.0 ppm; IR 3026, 2924, 2852, 1726, 1699, 1598, 1495, 1448, 1420, 1358, 1282, 1201, 1152, 967, 749, 693 cm^{-1} ; MS: (m/z) (%): 216 (4) [M$^+$], 43 (100).



(*E*)-ethyl 2-acetyl-5-phenylpent-4-enoate (7ae). [3b]

Following the general procedures I. Startinging from **5a** (66.4 μL, 0.5 mmol) with **6e** (89.0 mg, 0.7 mmol) to afford **7ae** (30.8 mg), yield 25%, and byproduct cinnamyl acetate (10.9mg), yield 12%; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.33-7.21 (m, 5H), 6.46 (d, 1H, *J* = 15.6), 6.17-6.07 (m, 1H), 4.21 (q, 2H, *J* = 7.5), 3.59 (t, 1H, *J* = 7.5), 2.77-2.72 (m, 2H), 2.26 (s, 3H), 1.26 (t, 3H, *J* = 6.8) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.7, 169.5, 132.9, 128.8, 127.6, 126.4, 125.9, 61.8, 59.8, 31.8, 29.5, 14.4 ppm; IR 2919, 1739, 1715, 1653, 1494, 1448, 1358, 1247, 1217, 1150, 1095, 1024, 967, 857, 746, 693 cm^{-1} ; MS: (m/z) (%): 246 (30) [M$^+$], 157 (100).

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(1) (a) M. S. Chen, C. M. White, *J. Am. Chem. Soc.* **2004**, *126*, 1346. (b) M. S. Chen, N. Prabagaran, N. A. Labenz, C. M. White, *J. Am. Chem. Soc.* **2005**, *127*, 6970.

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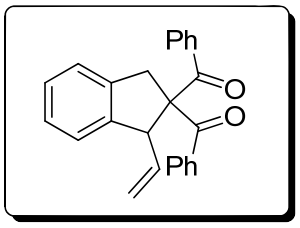
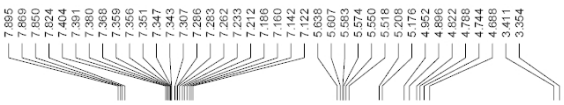
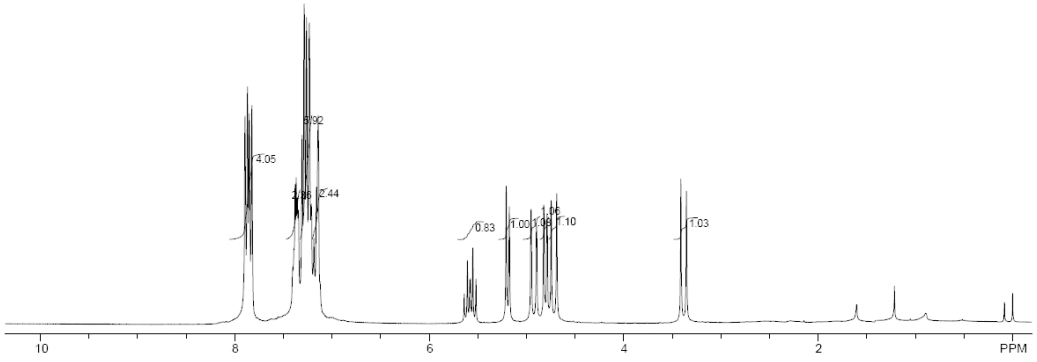
(3) (a) M. Rueping, B. J. Nachtsheim; A. Kuenkel, *Org. Lett*. **2007**, *9*, 825. (b) F. Ozawa; H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 10968.

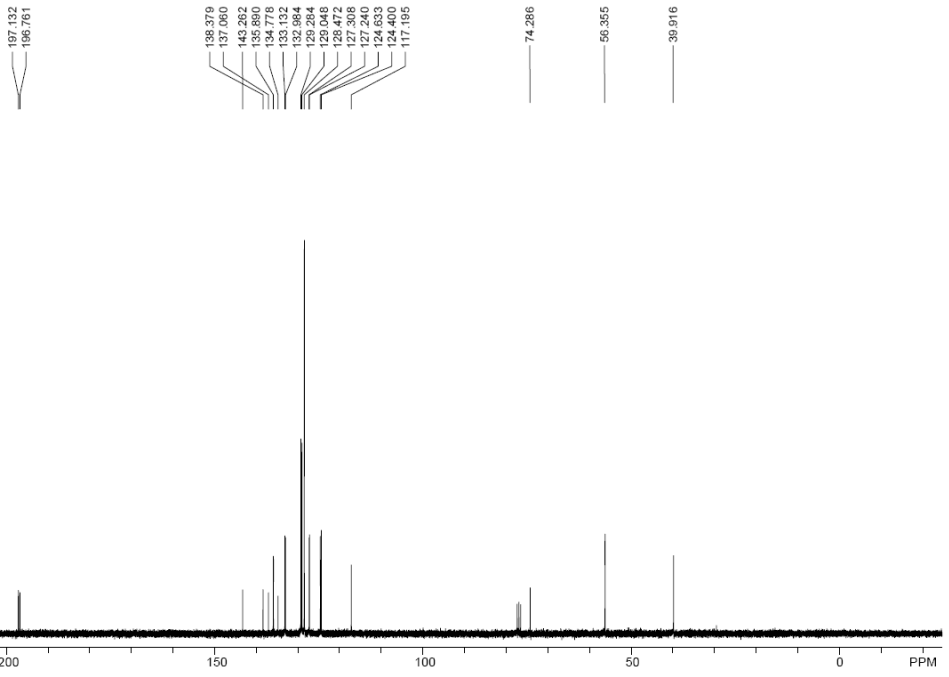
NMR spectrum of compounds 4a-4l’, **7aa-7la**, **7ab-7ae.**

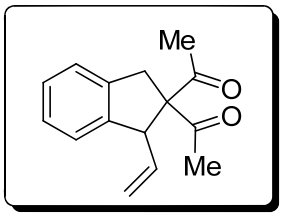


4a





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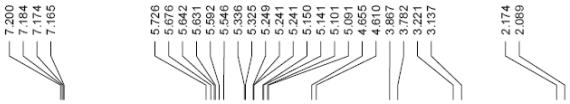
4b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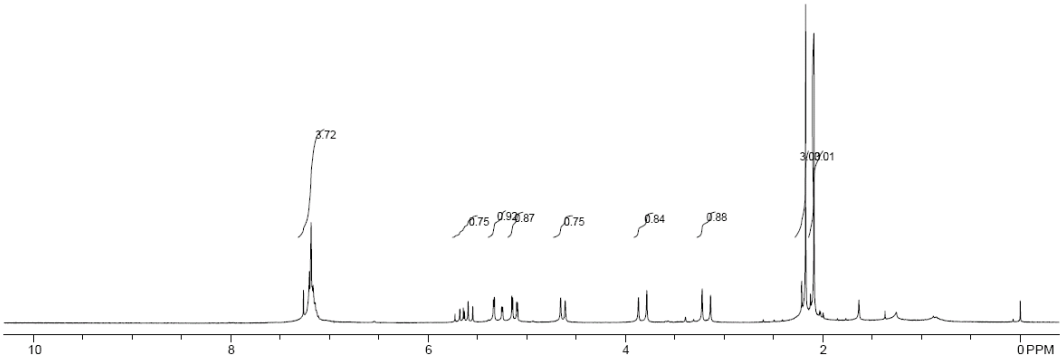
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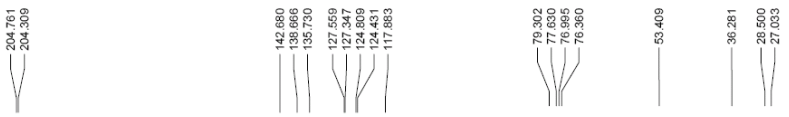
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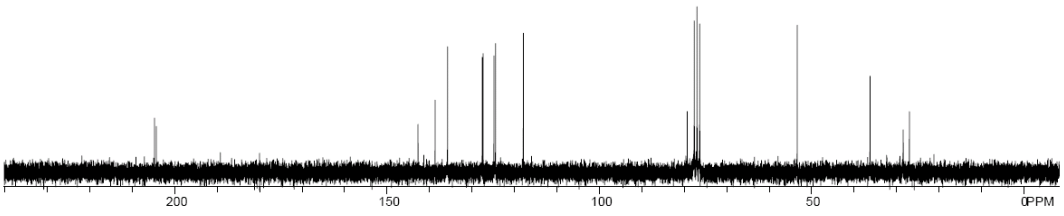
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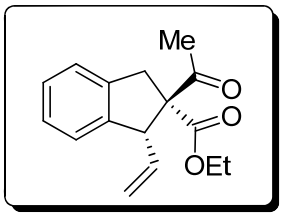
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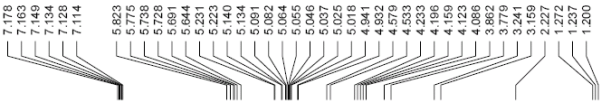
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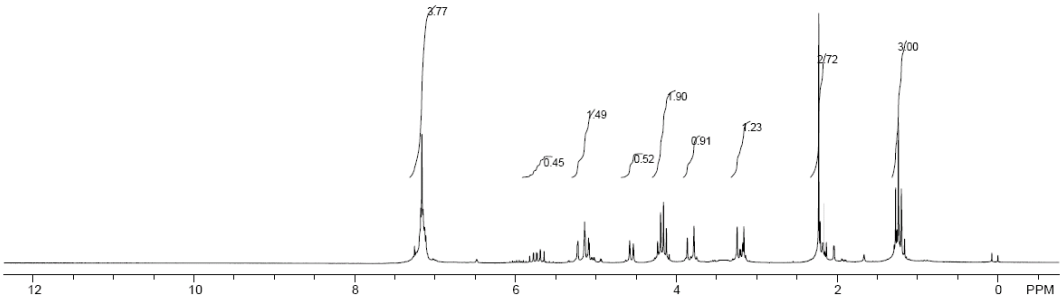
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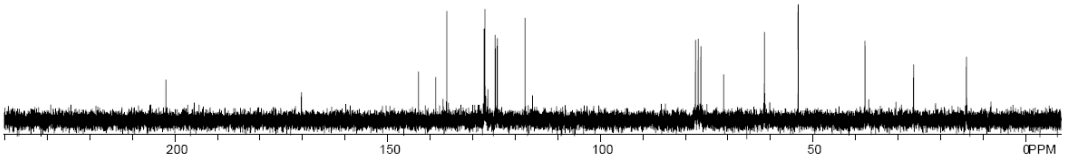
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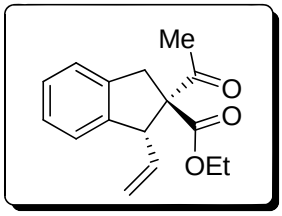
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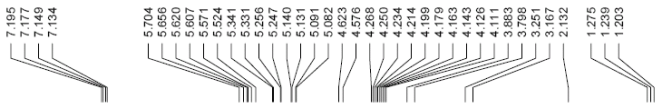
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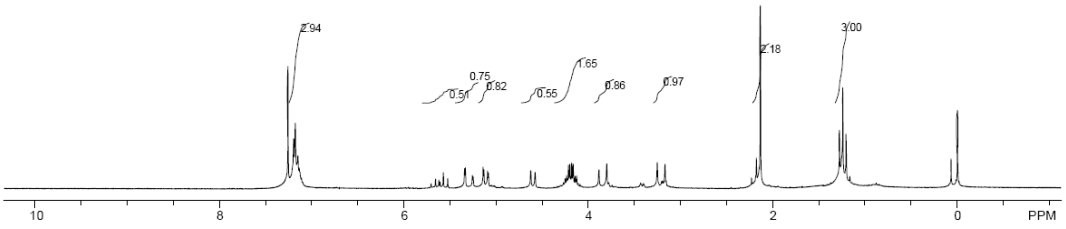
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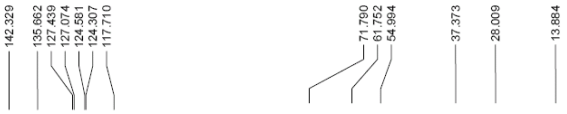
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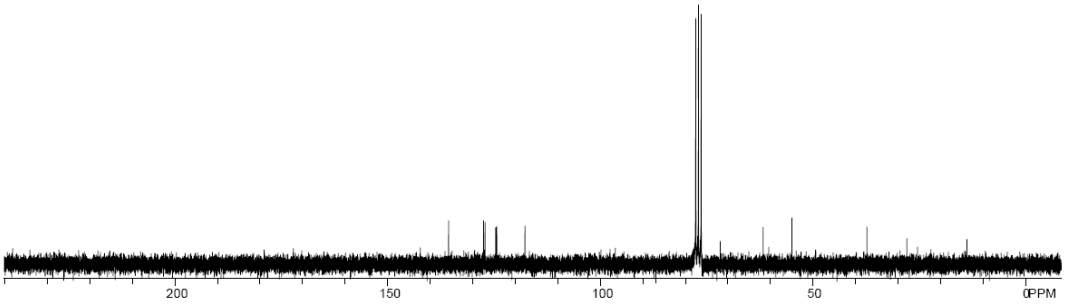
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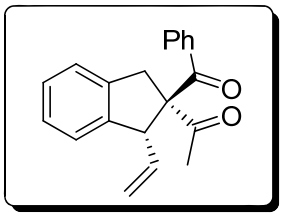
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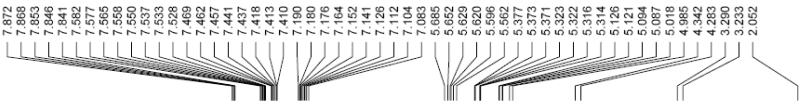
4d-*trans*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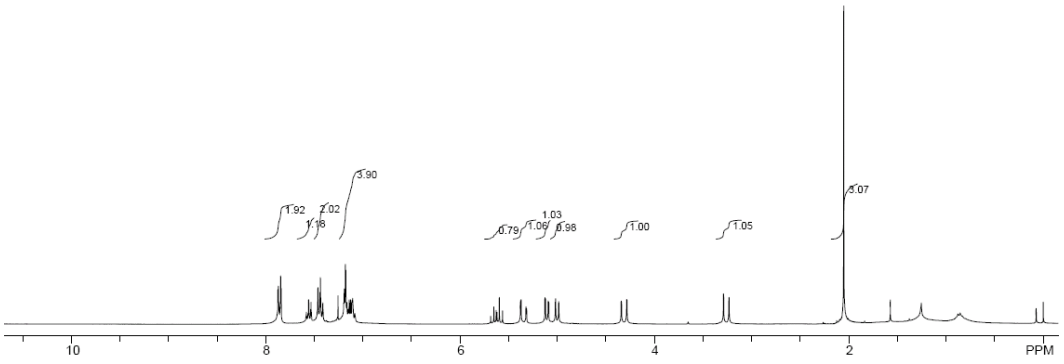
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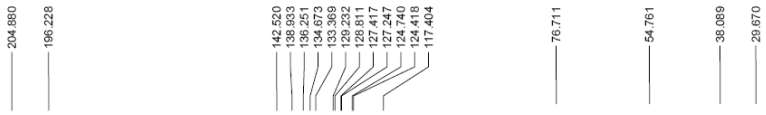
PPM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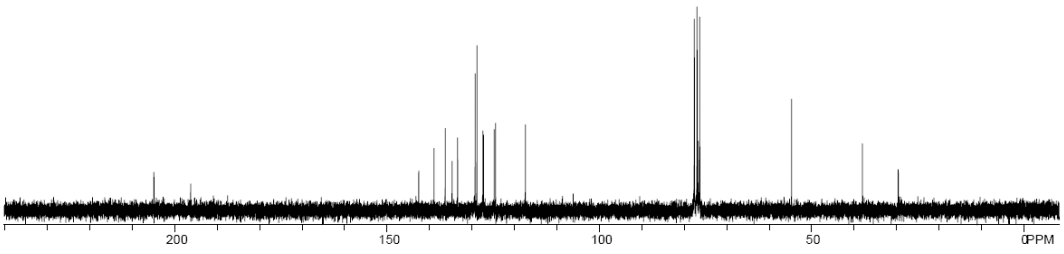
29.670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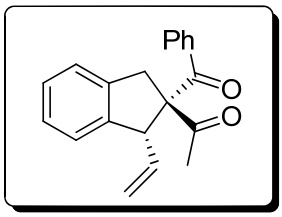
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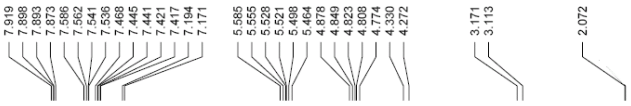
4d-*cis*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7.417
7.194
7.171
5.585
5.555
5.528
5.521
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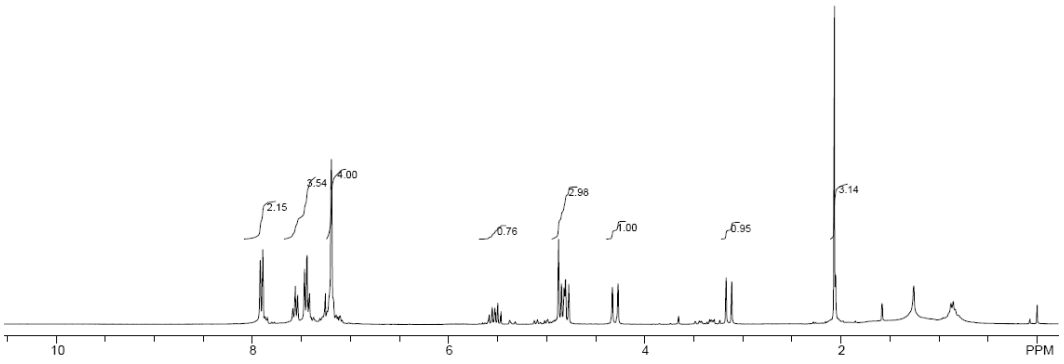
3.171
3.113
2.072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10
8
6
4
2
PPM


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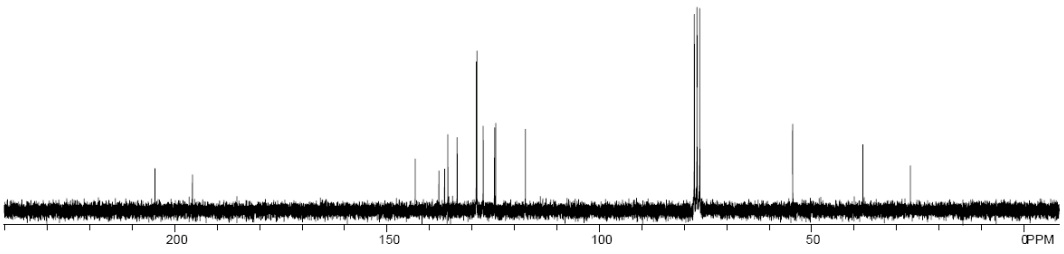
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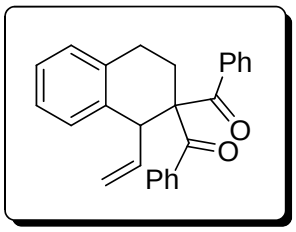
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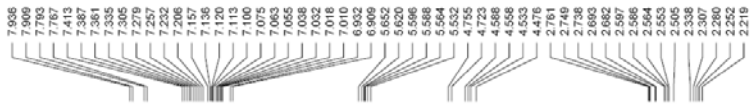
Ph

4e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7.113
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7.075
7.063
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7.016
7.010
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6.909
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5.620
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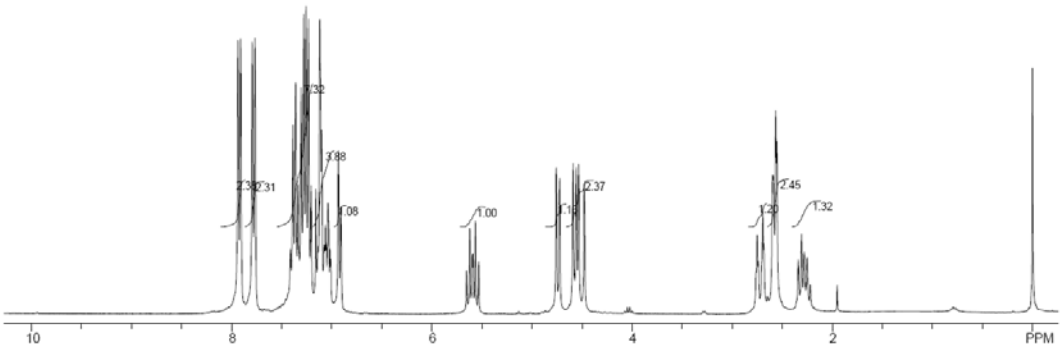
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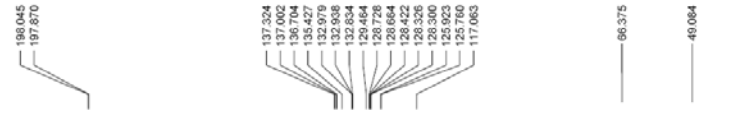
6
4
2
PPM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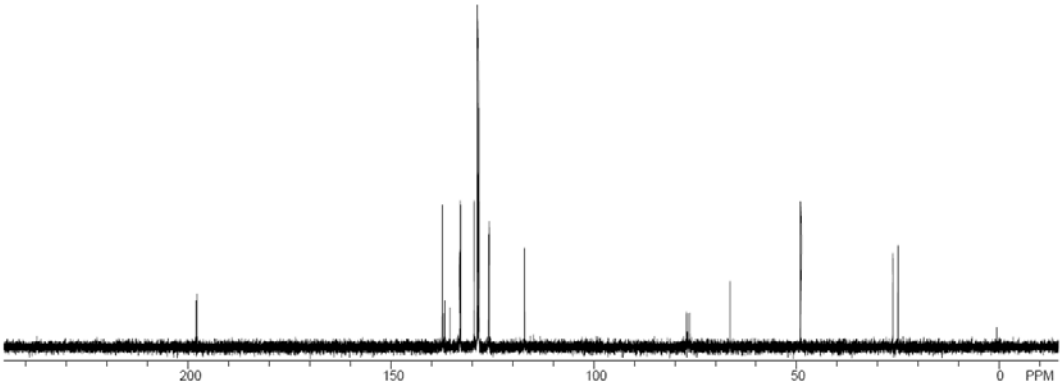
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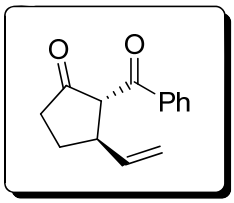
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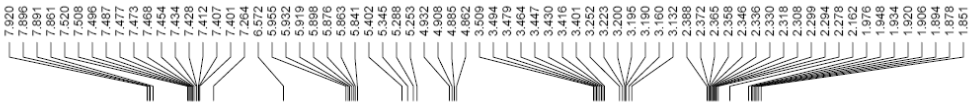
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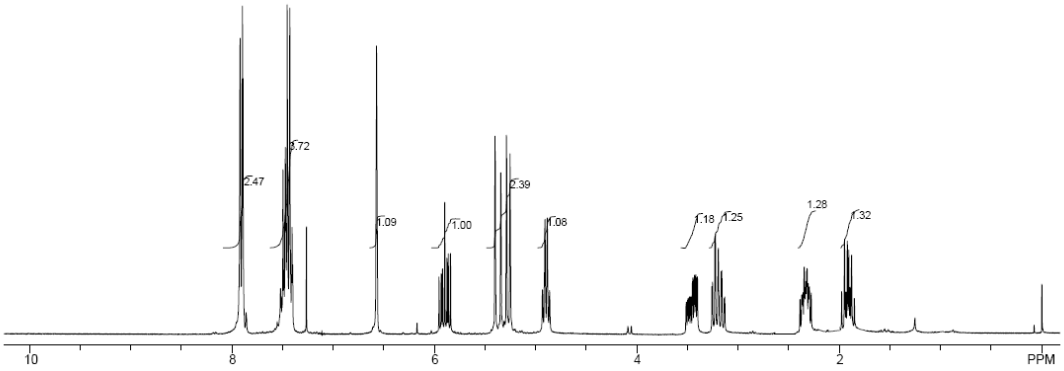
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6
4
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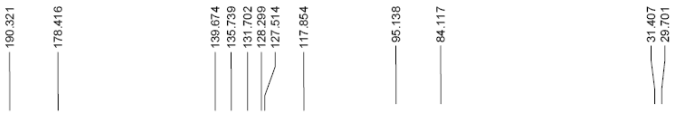
PPM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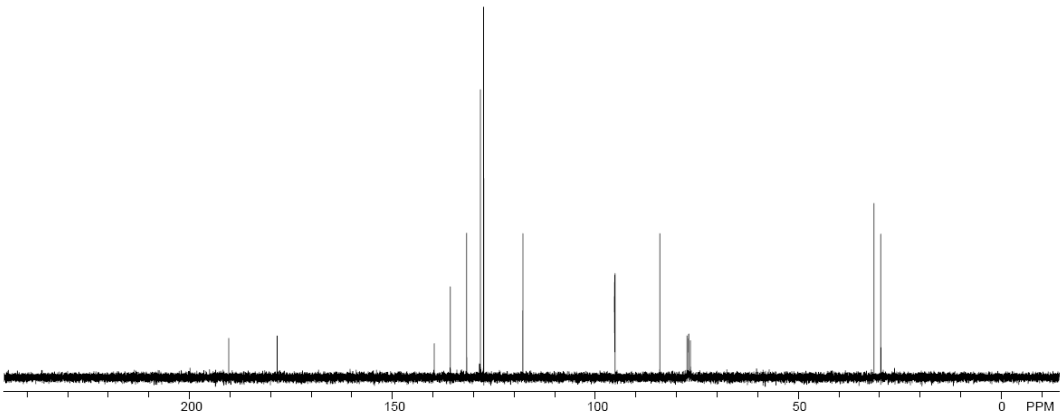
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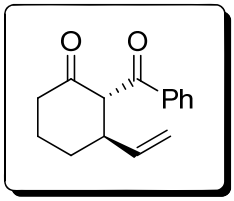
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O
Ph

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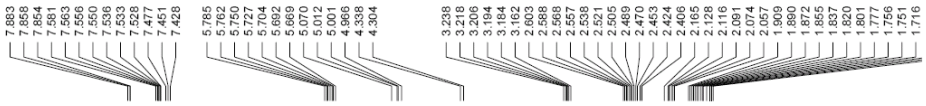
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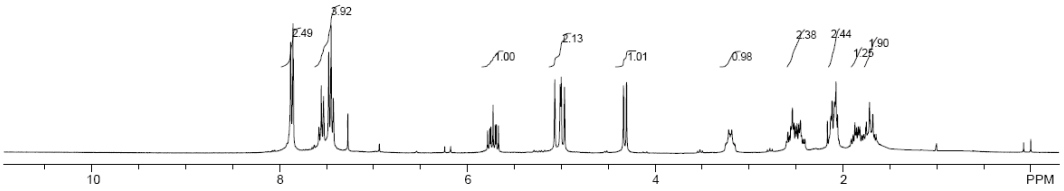
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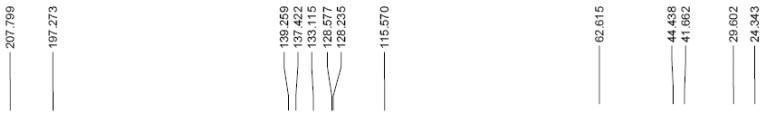
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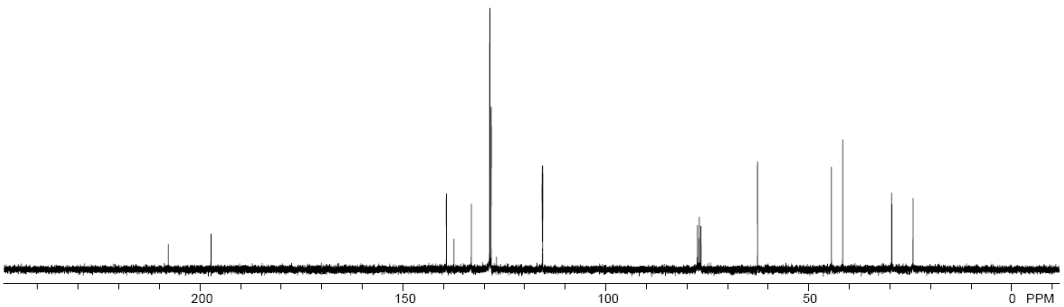
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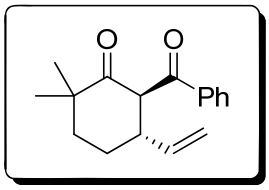
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Ph

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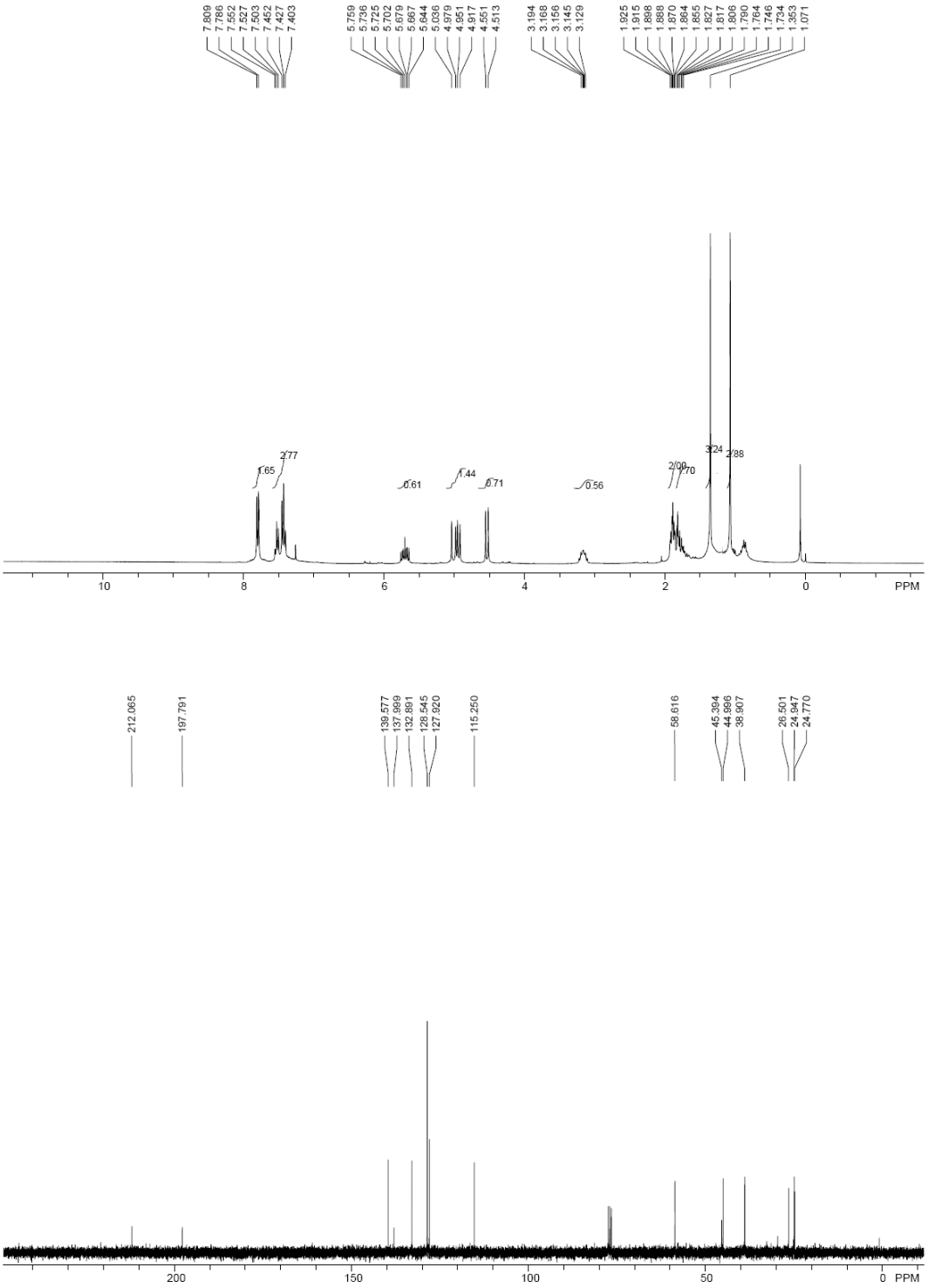
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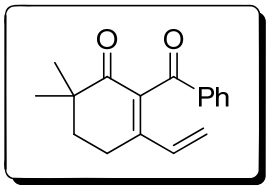
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Ph

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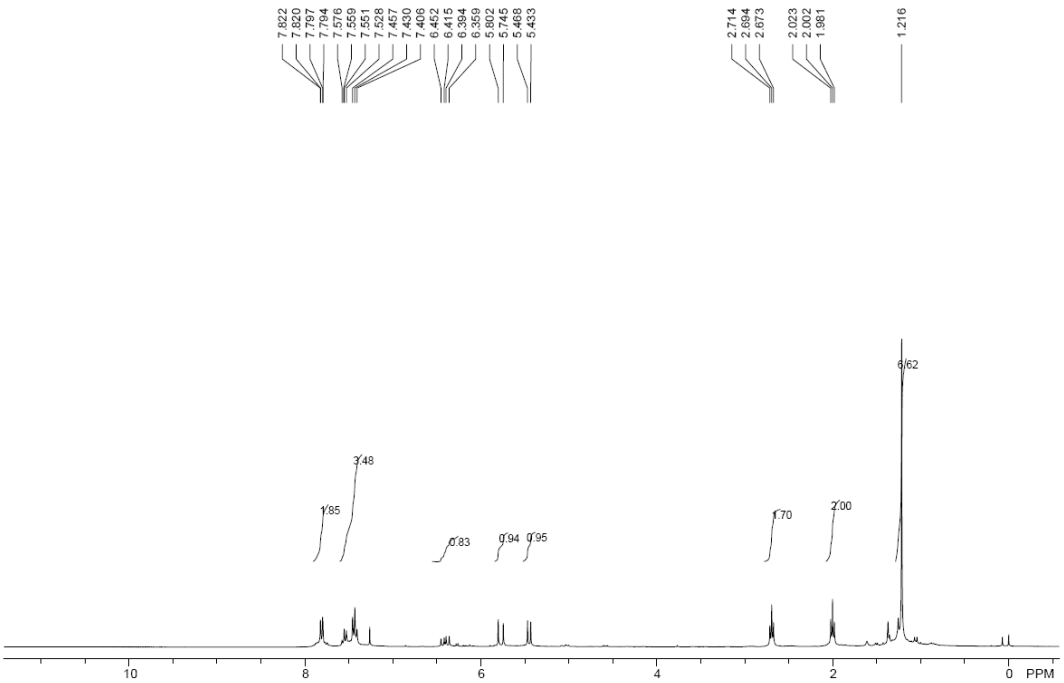
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6.415
6.394
6.359
5.802
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5.468
5.433
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2.694
2.673
2.023
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1.981
1.216
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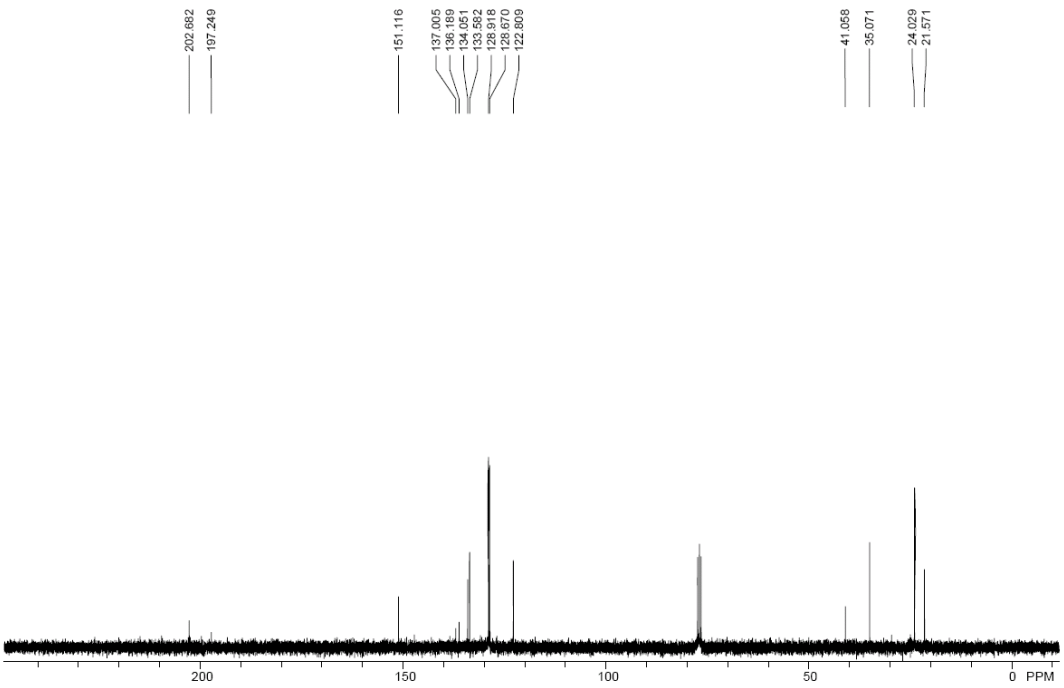
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21.571
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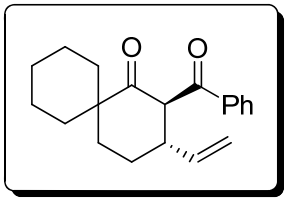
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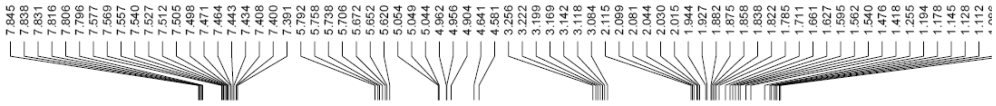

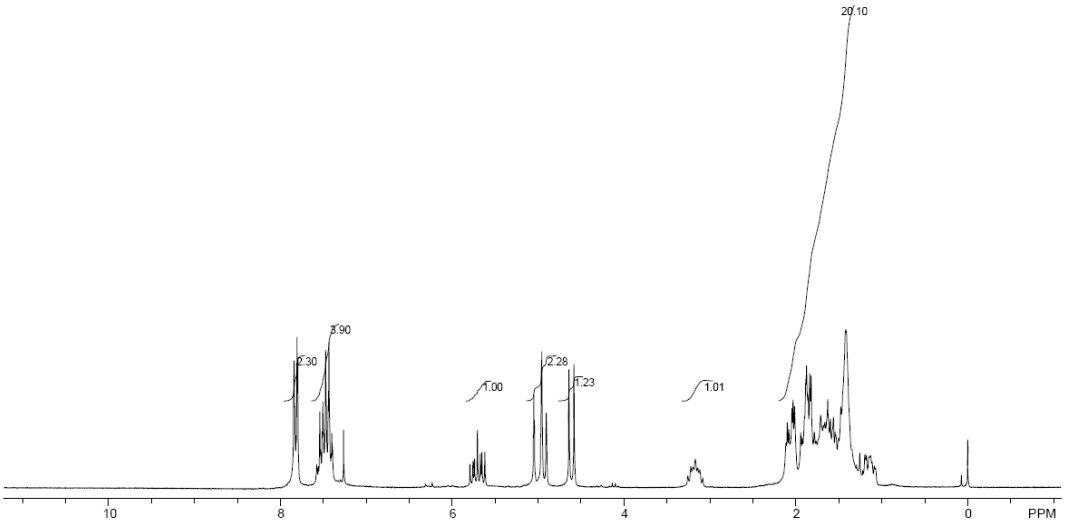
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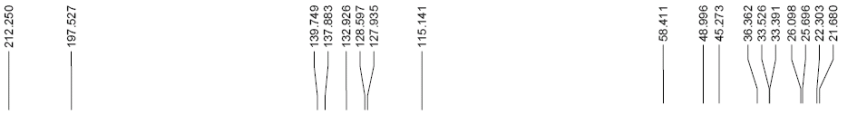
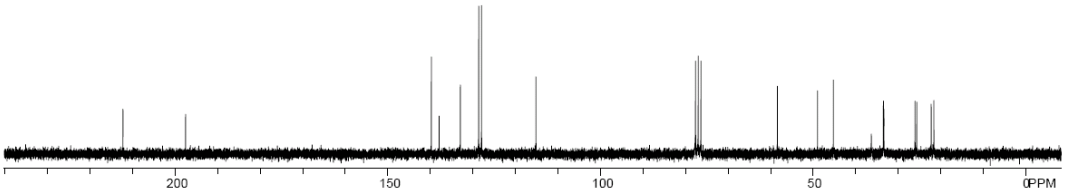
1.00
1.01
10
8
6
4
2
0
PPM

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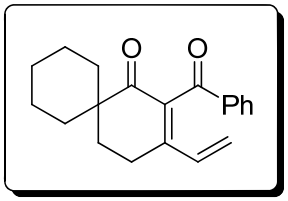
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4j'


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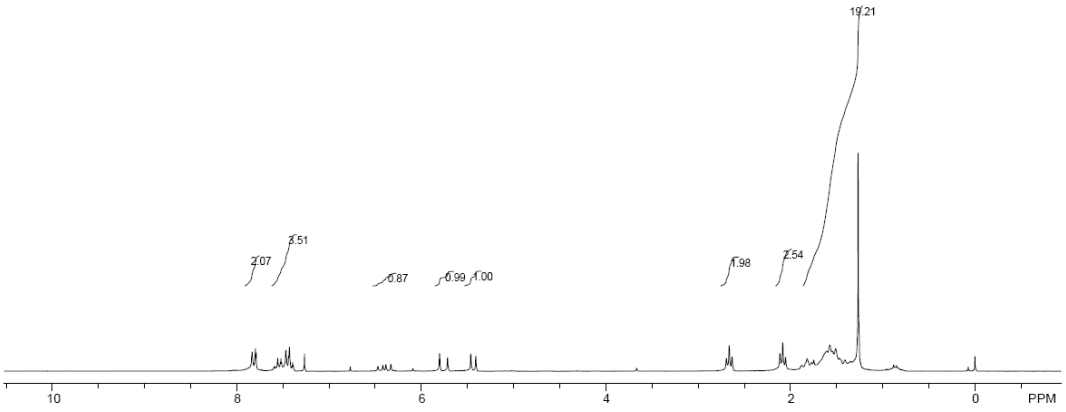
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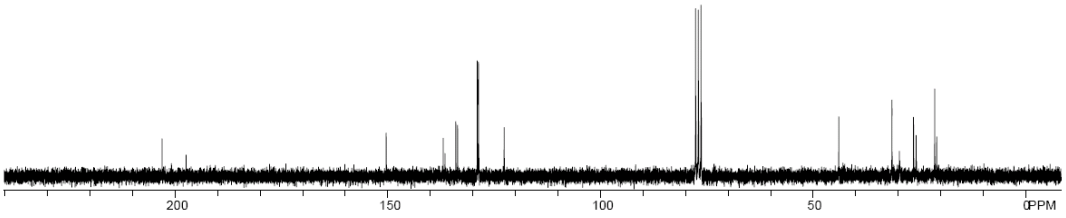
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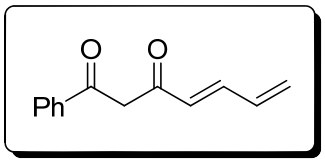
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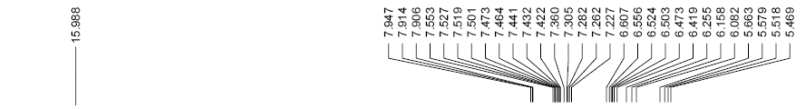
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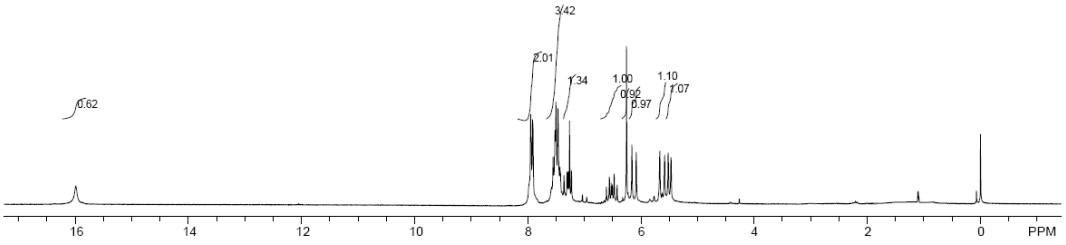
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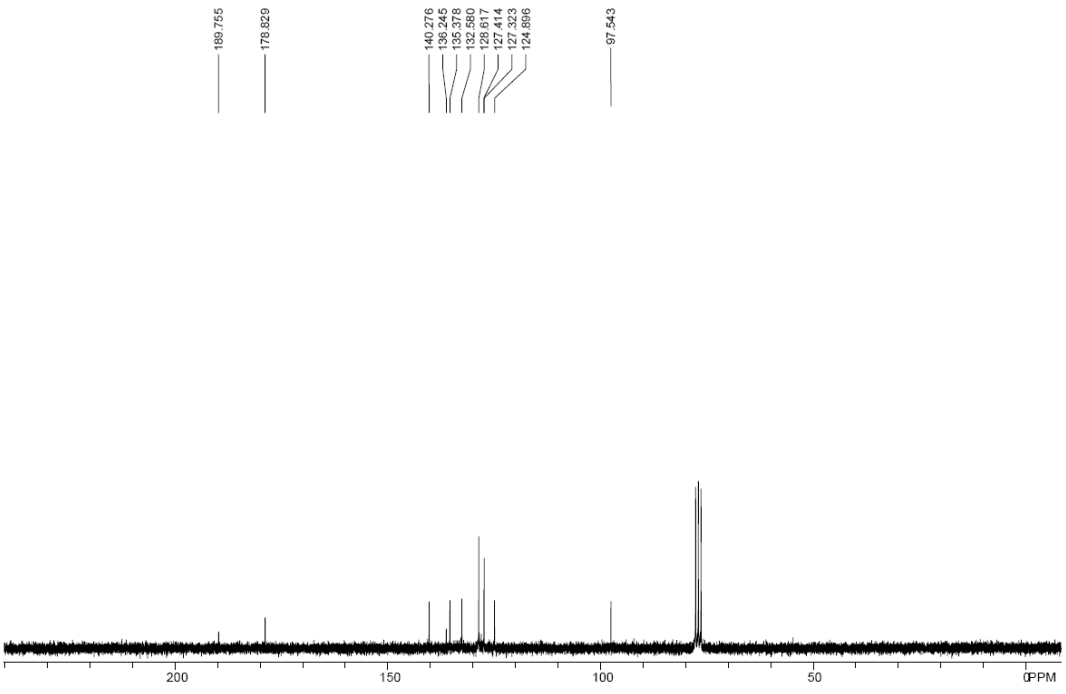
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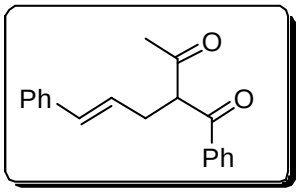
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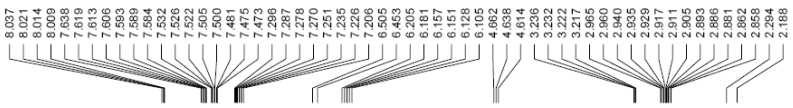
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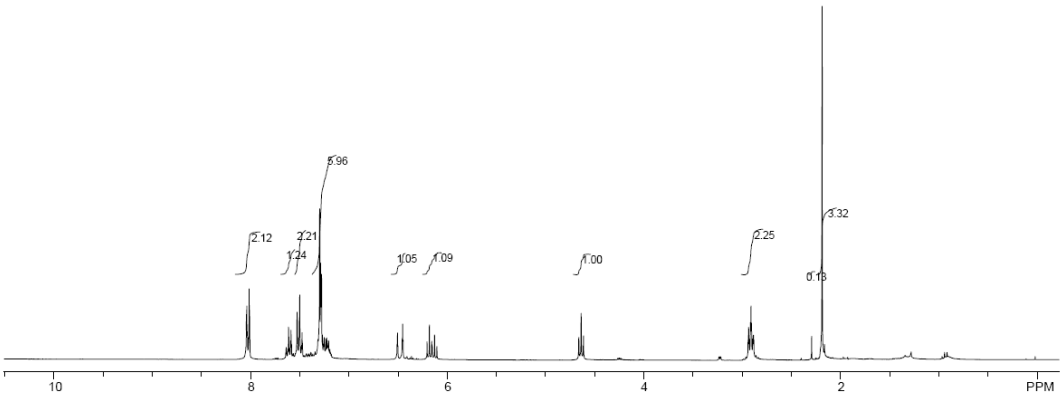
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PPM


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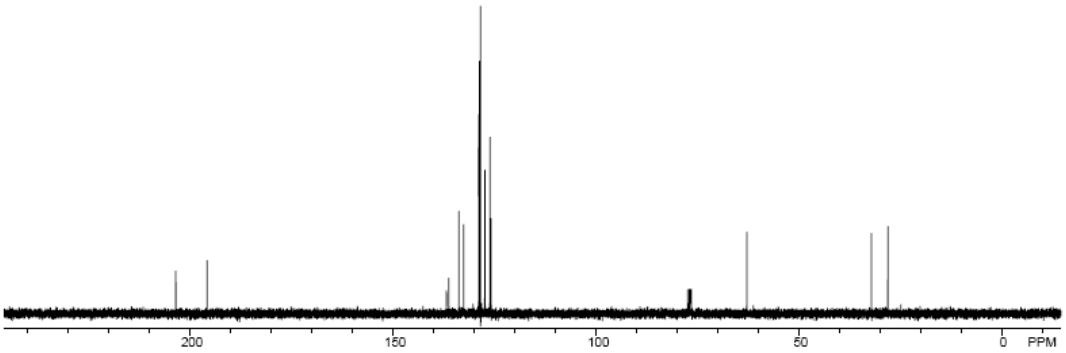
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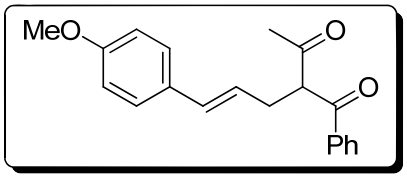
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Ph

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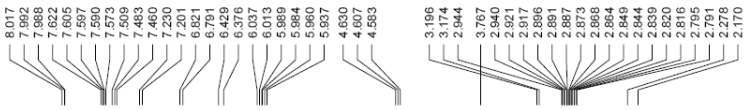
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6.013
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4.607
4.583
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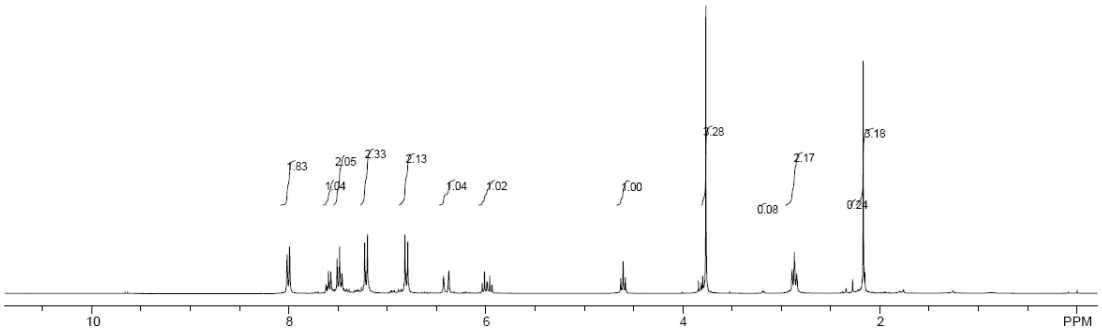
2.170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4
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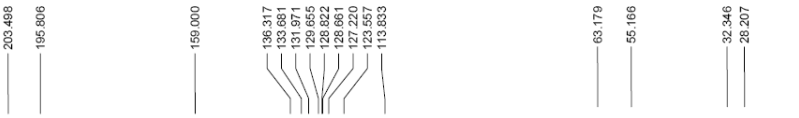
PPM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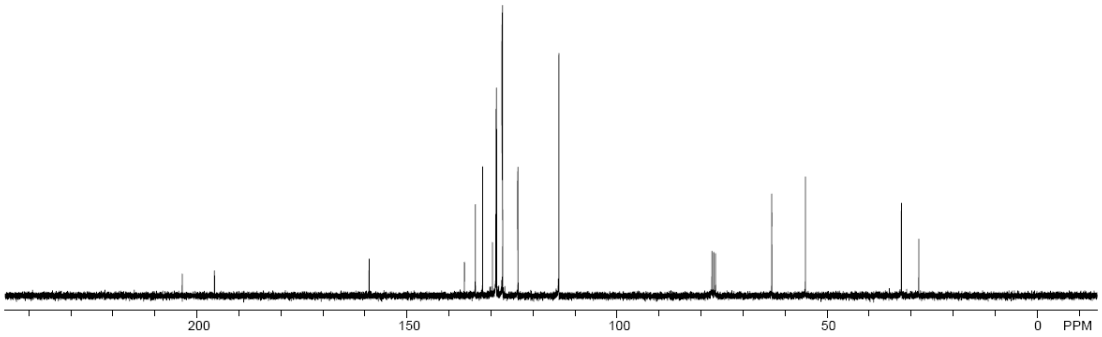
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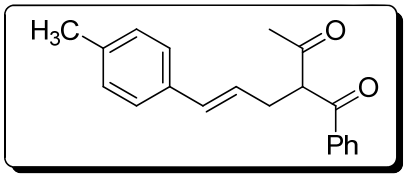
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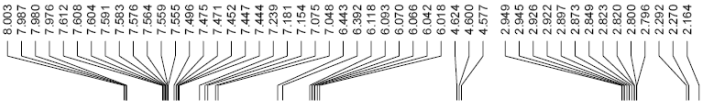
7ca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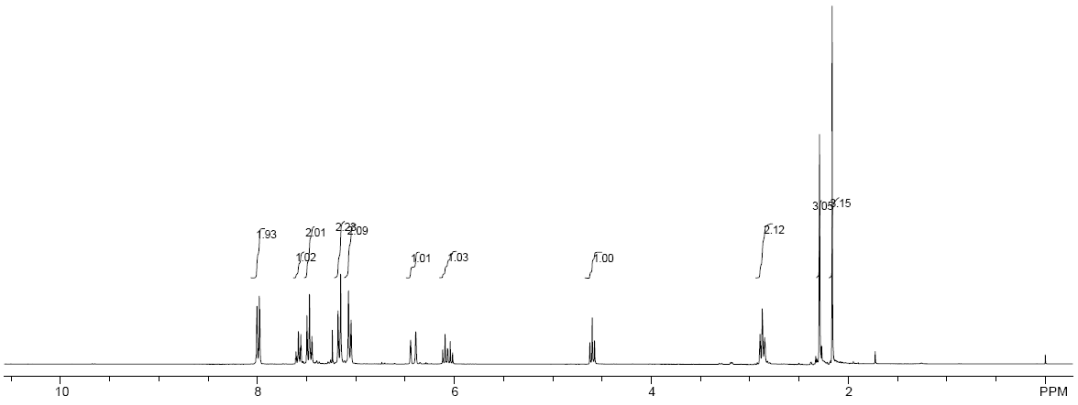
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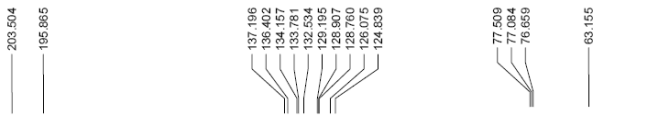
PPM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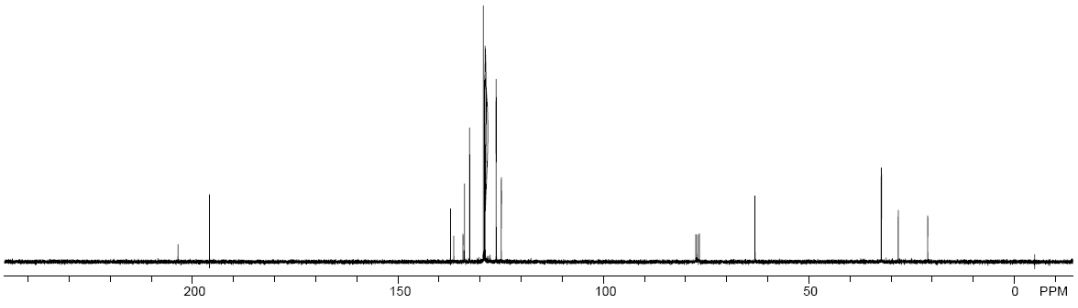
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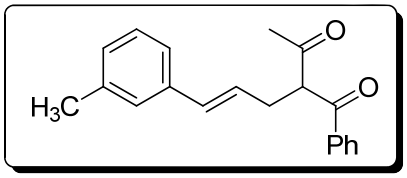
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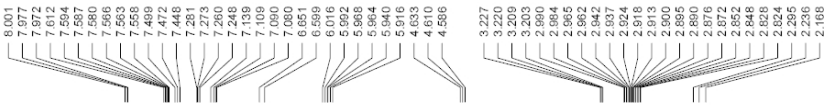
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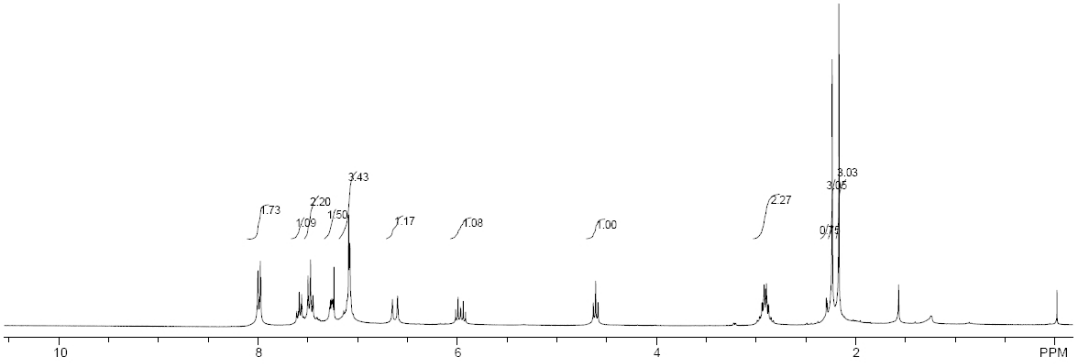
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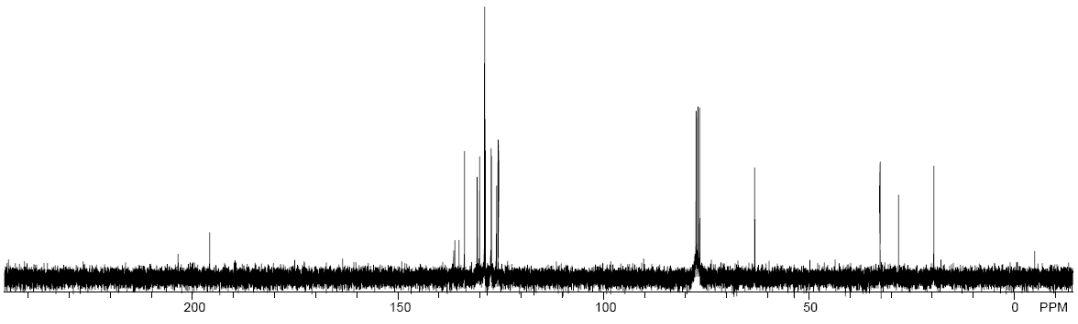
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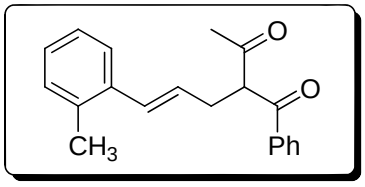
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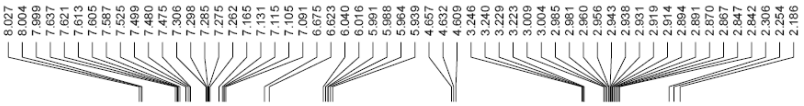
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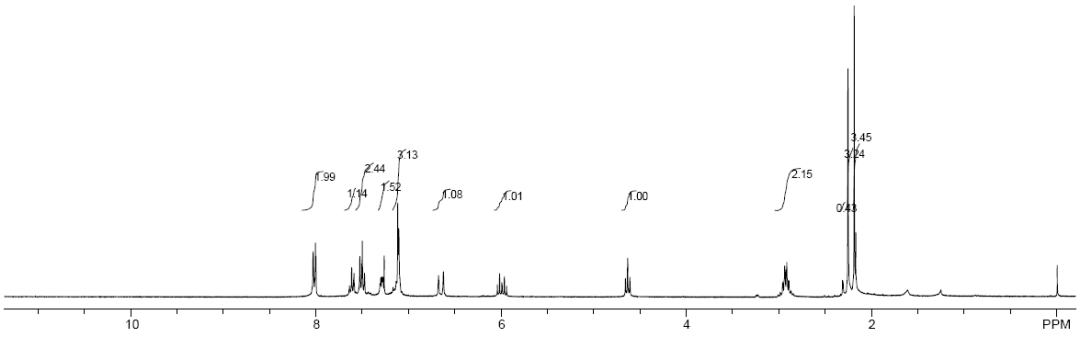
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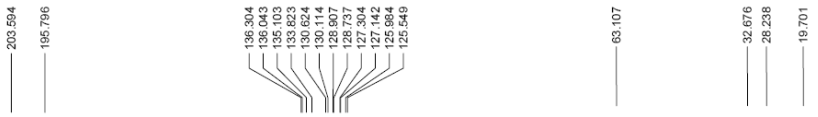
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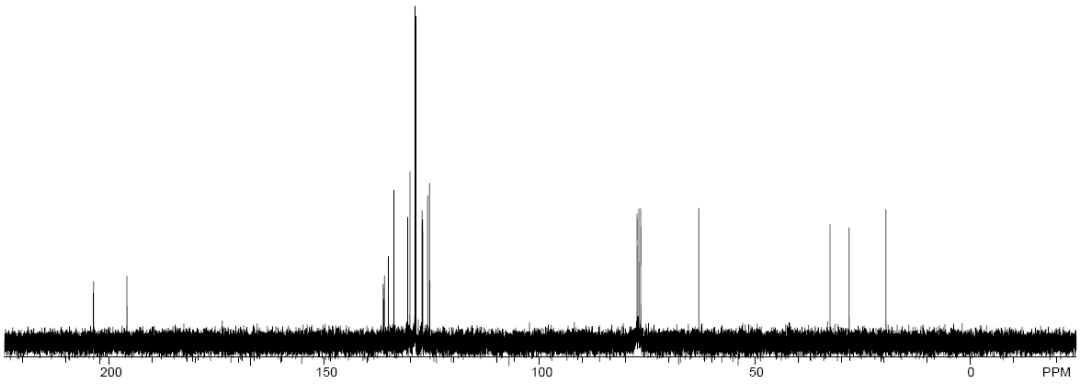
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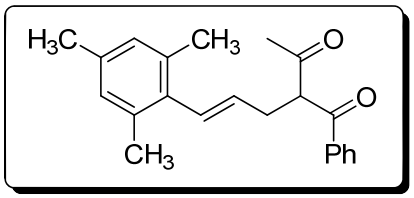
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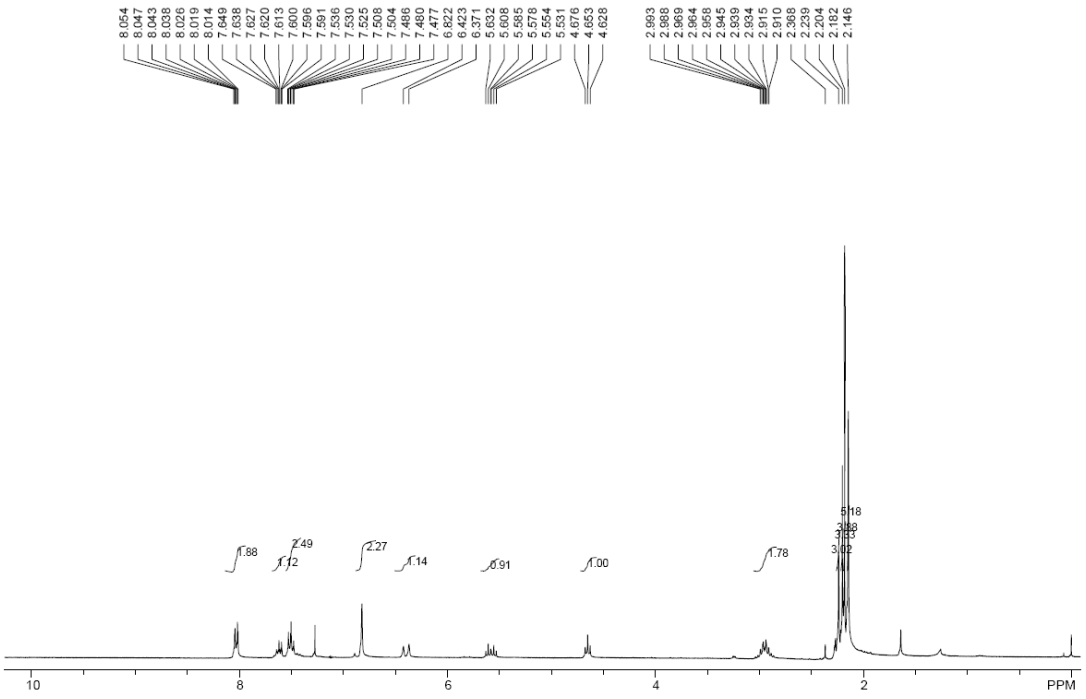
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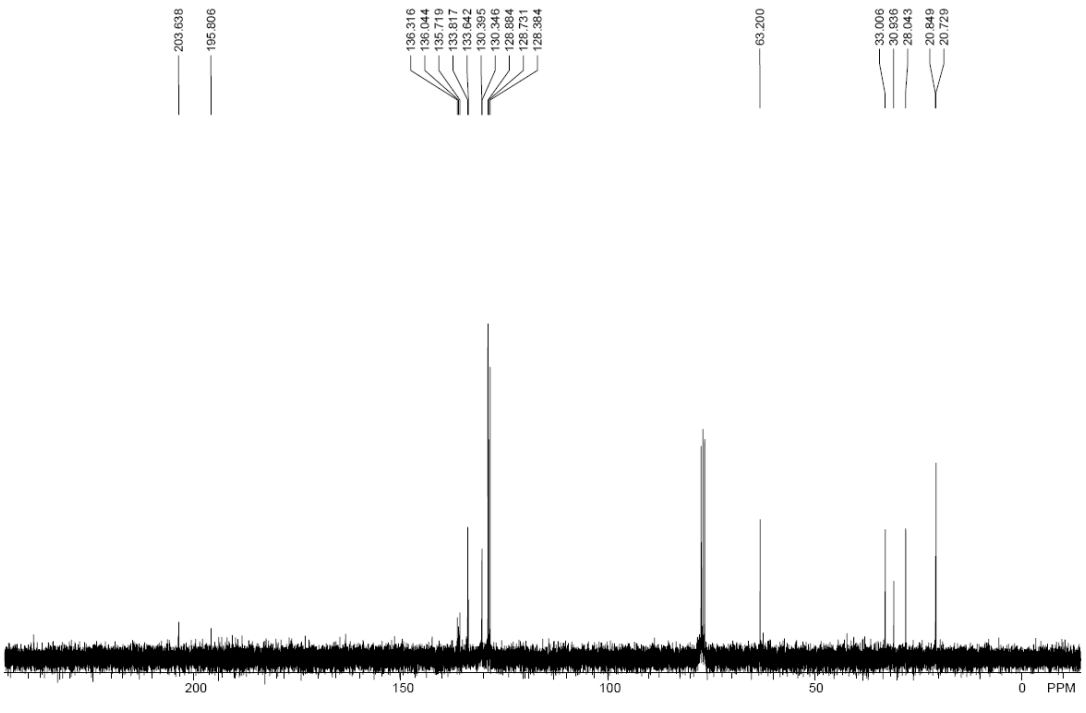
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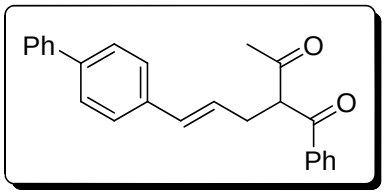
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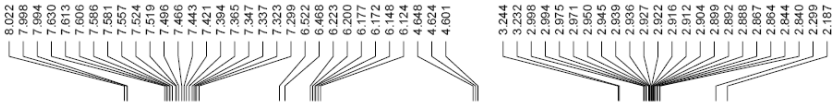
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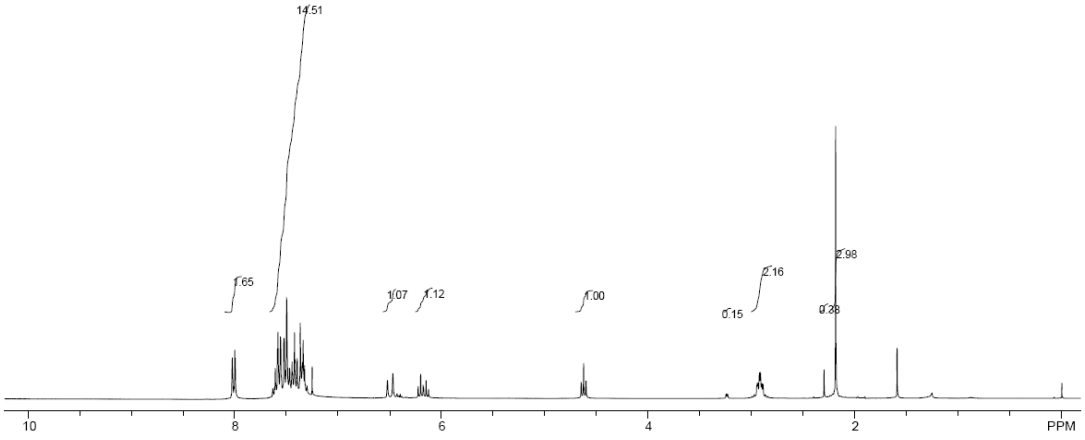
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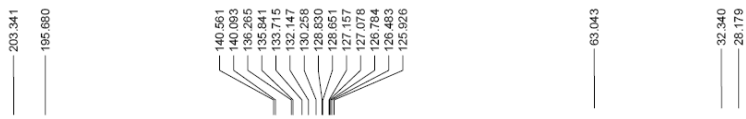
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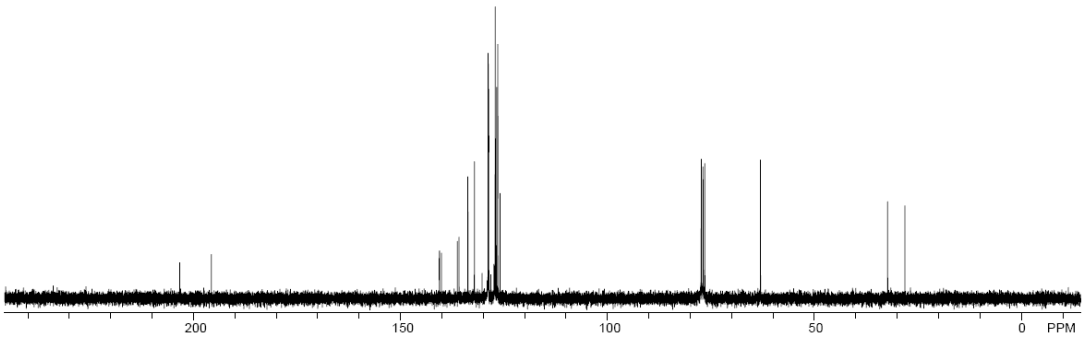
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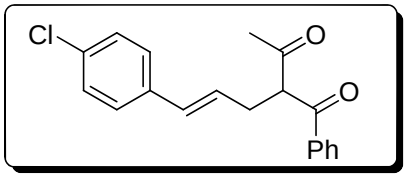
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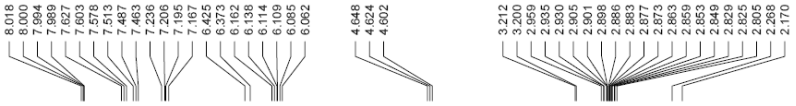
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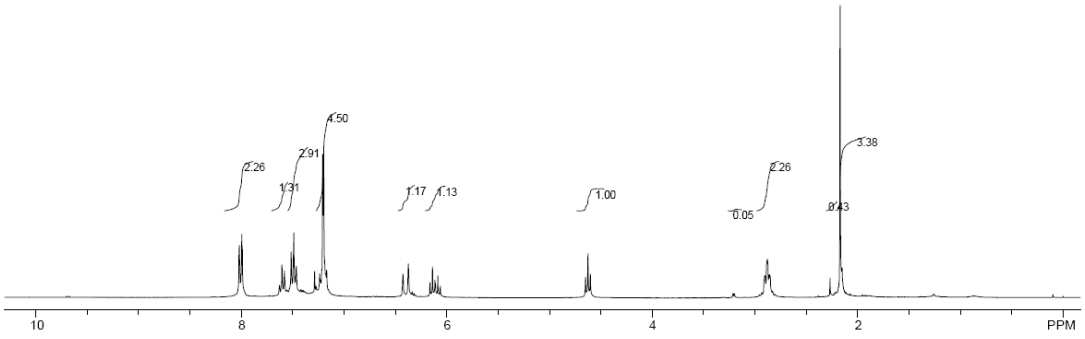
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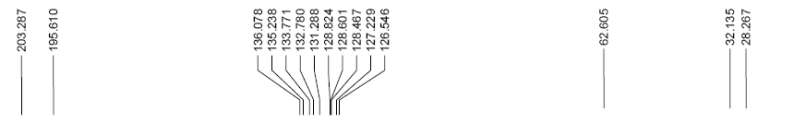
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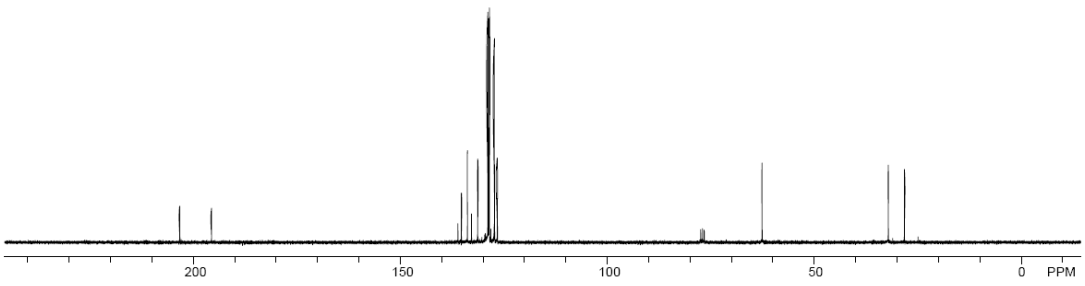
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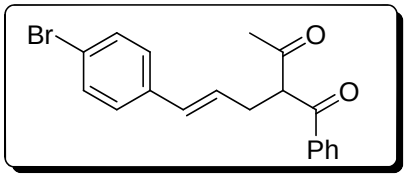
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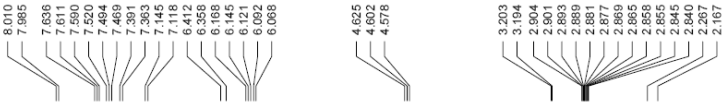
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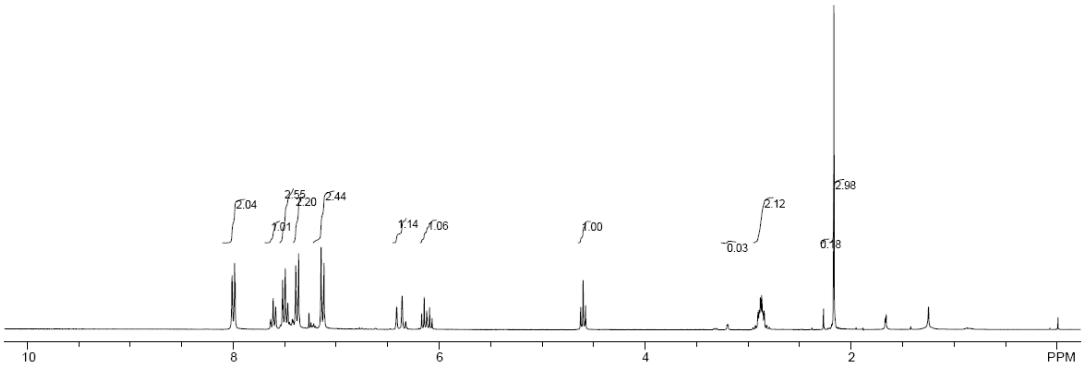
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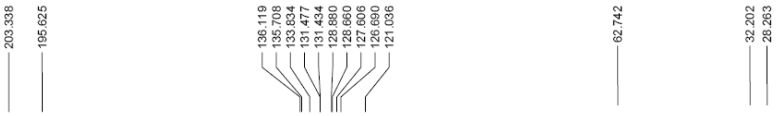
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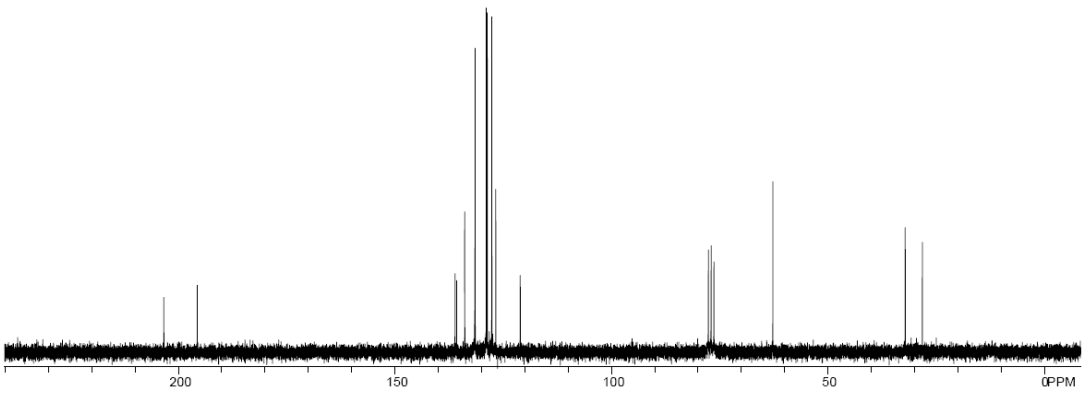
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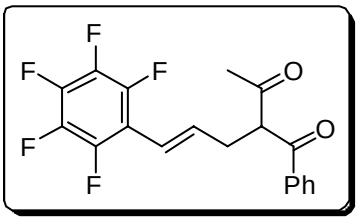
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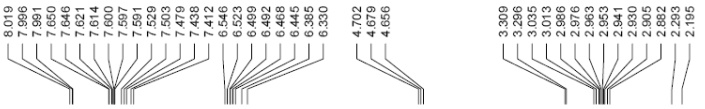
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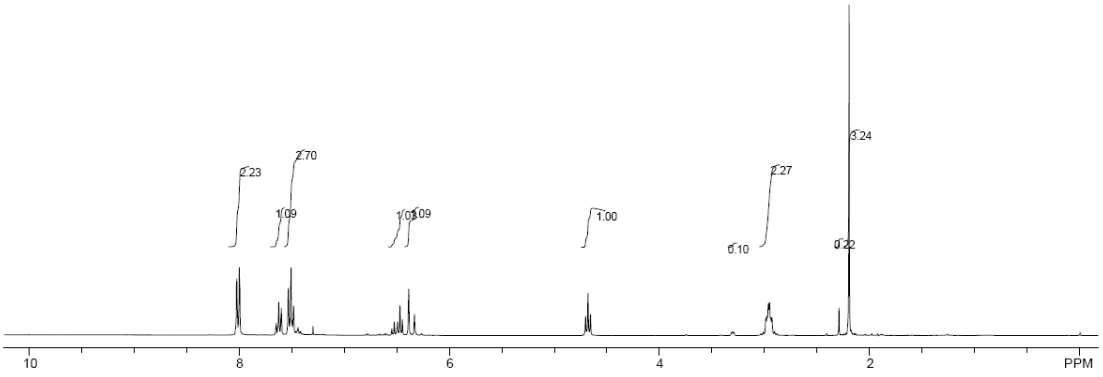
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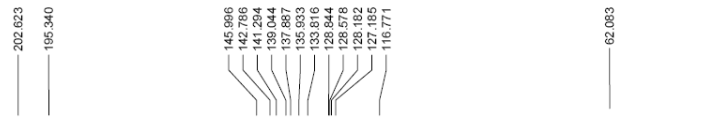
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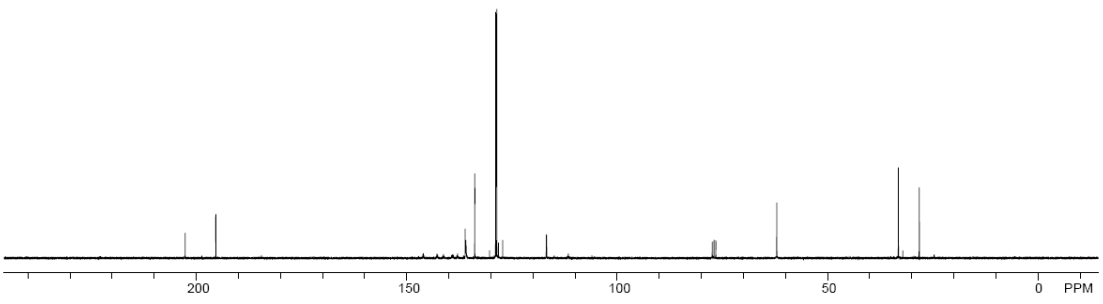
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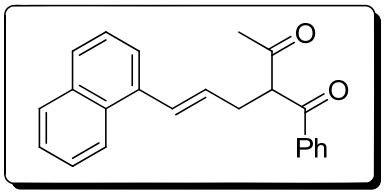
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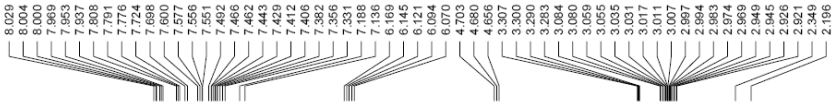
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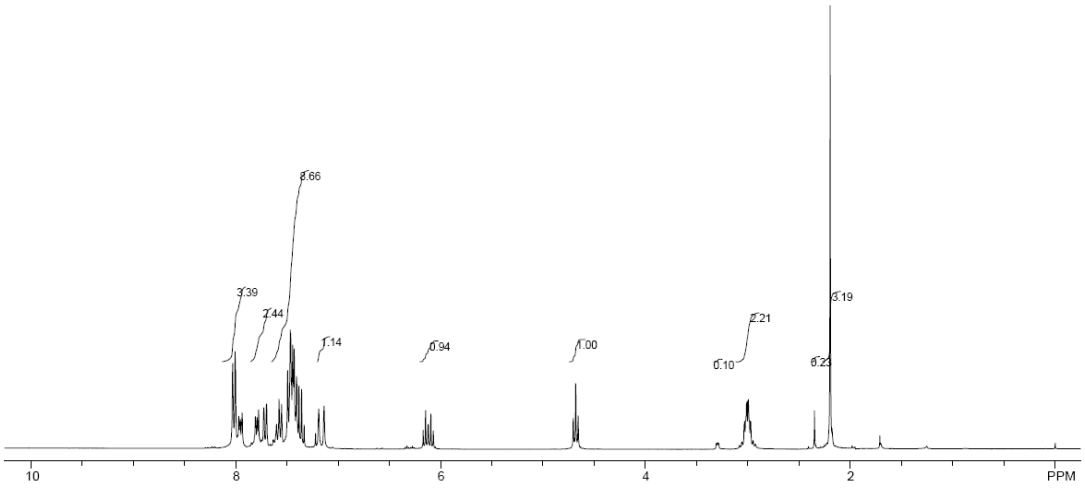
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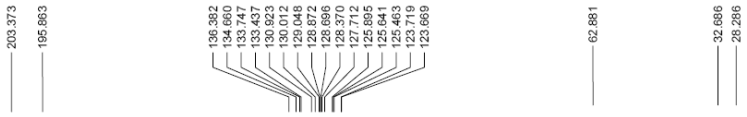
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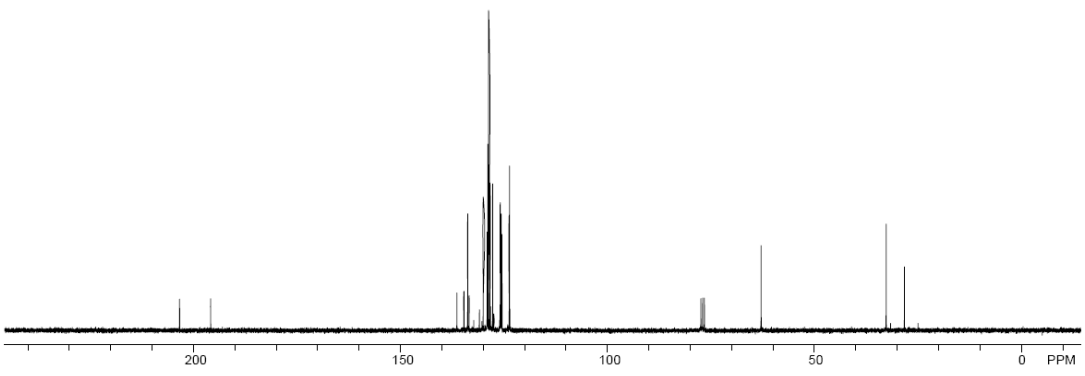
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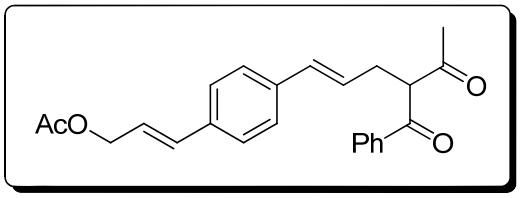
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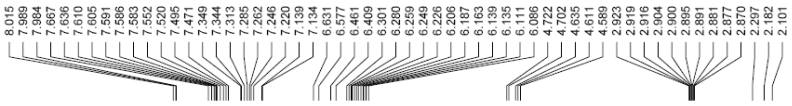
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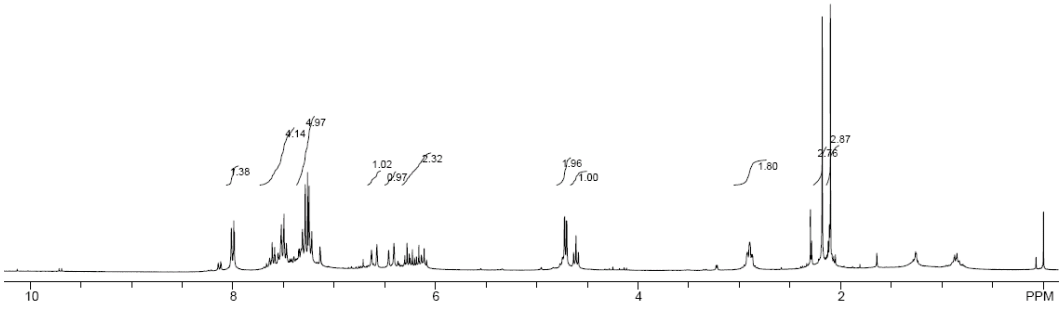
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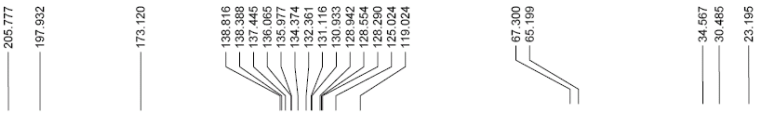
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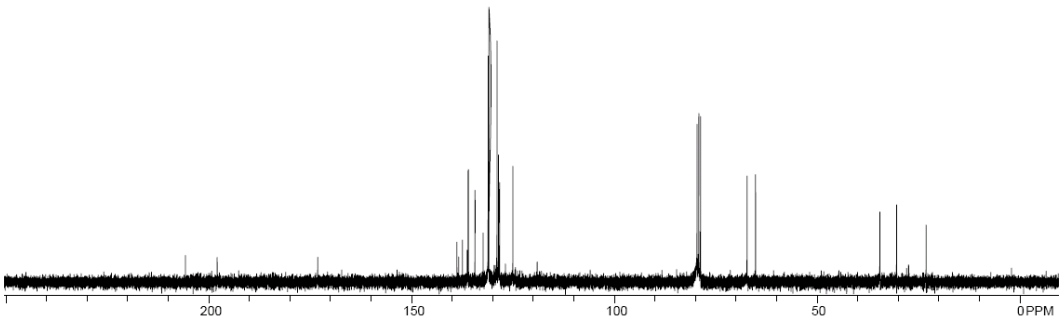
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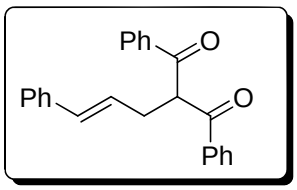
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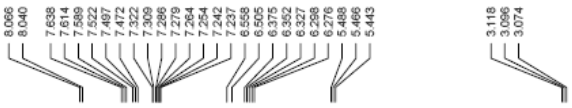
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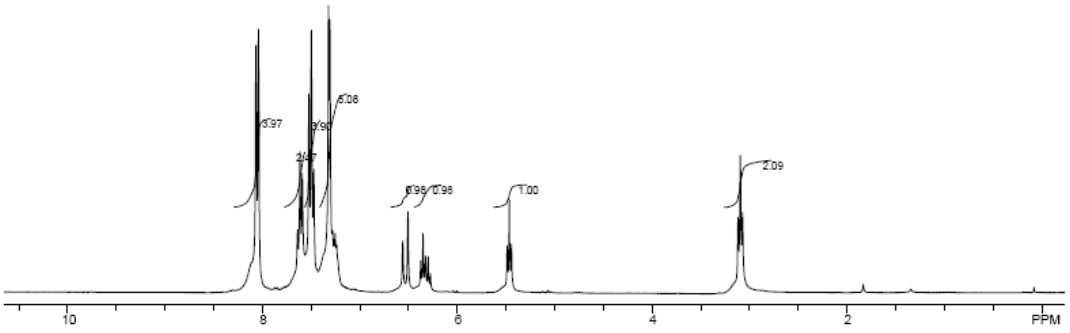
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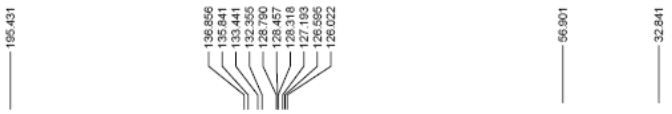
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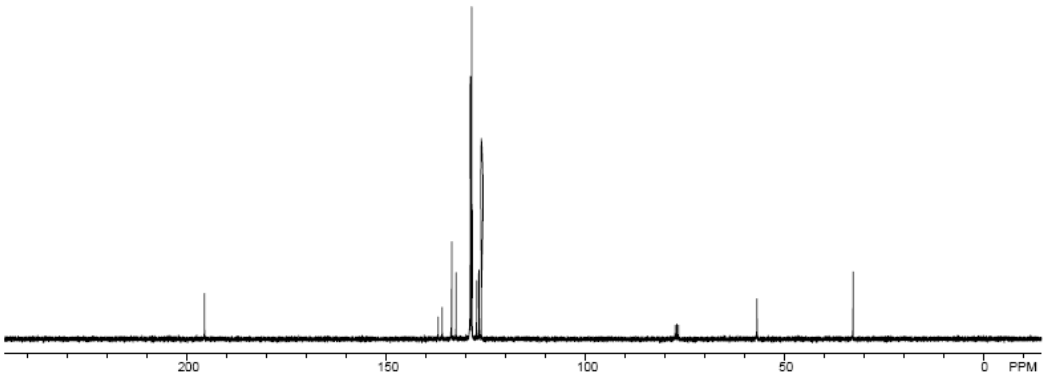
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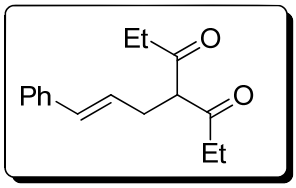
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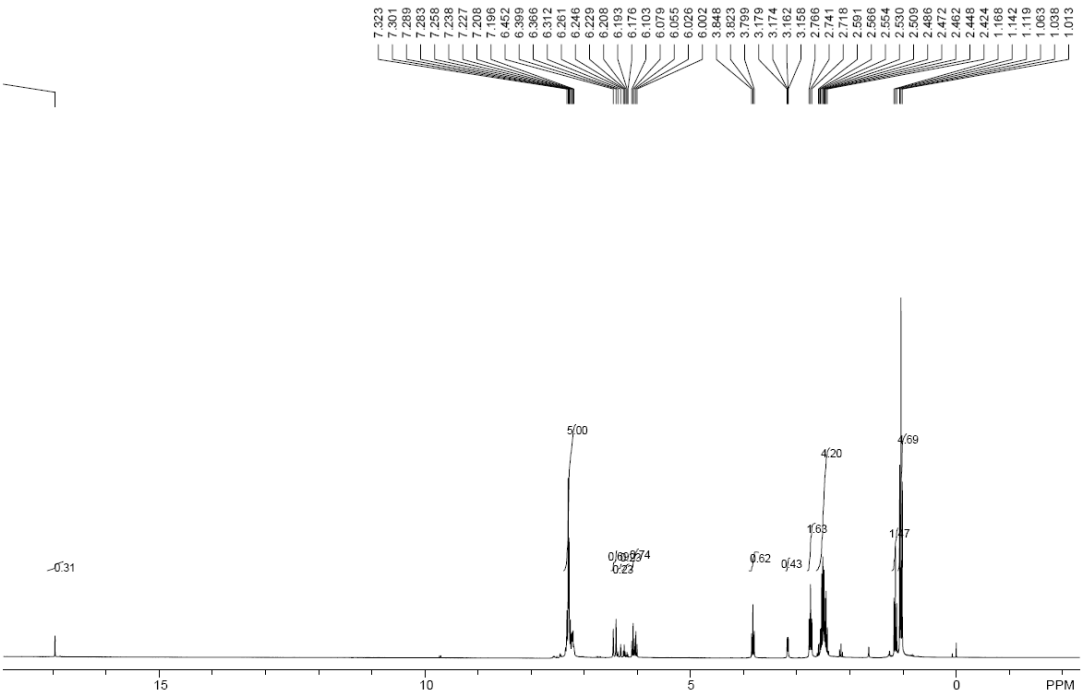
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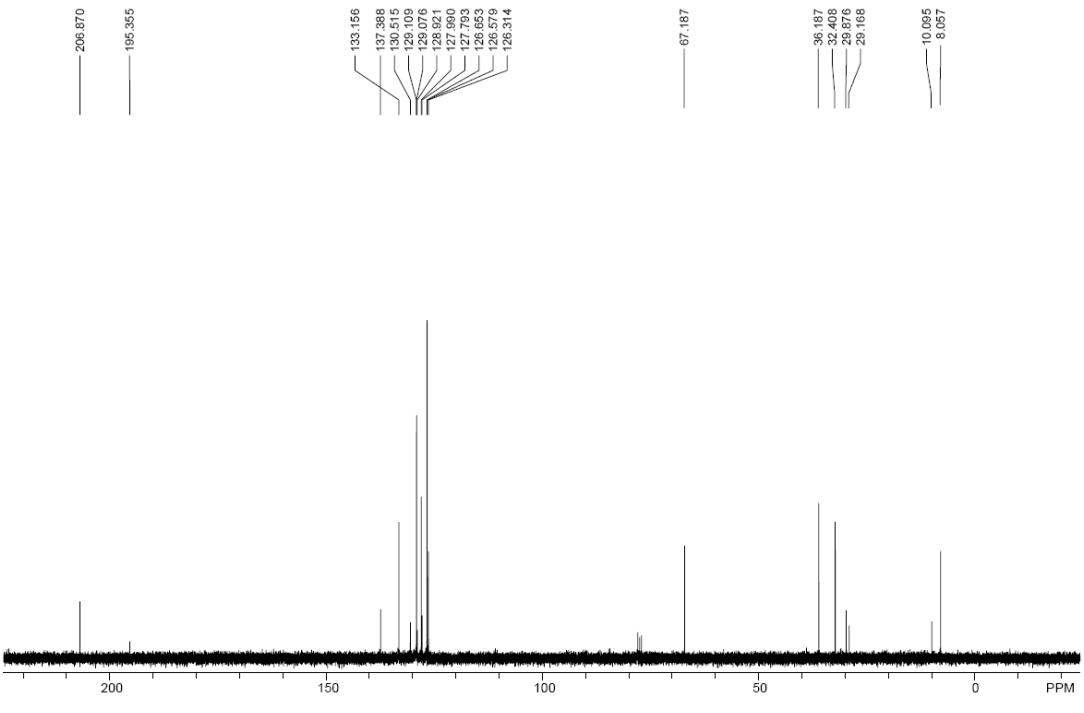
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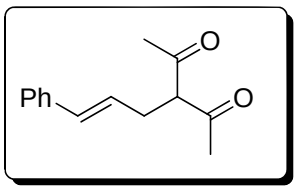
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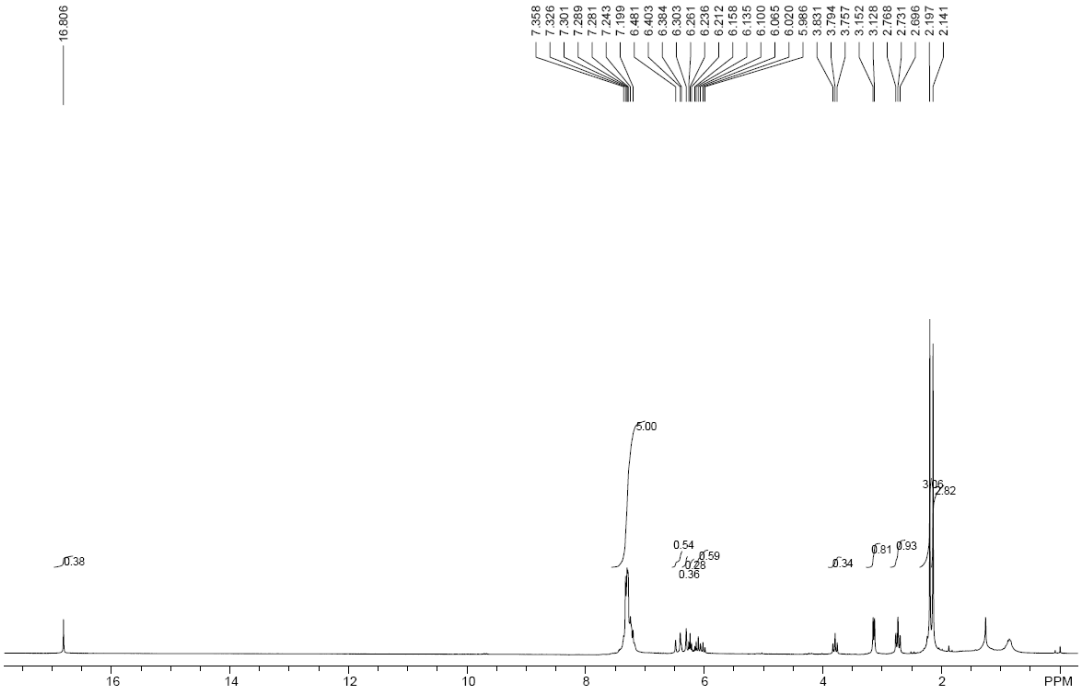
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2.696
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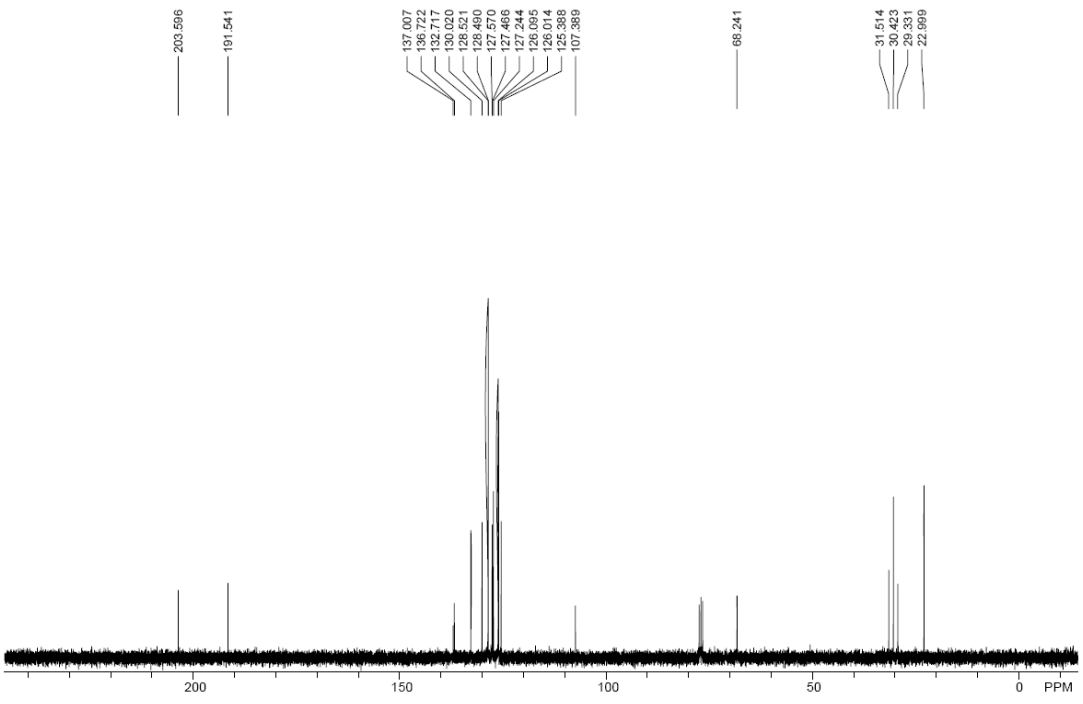
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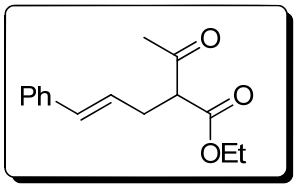
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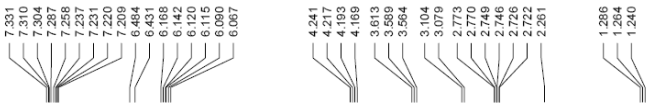
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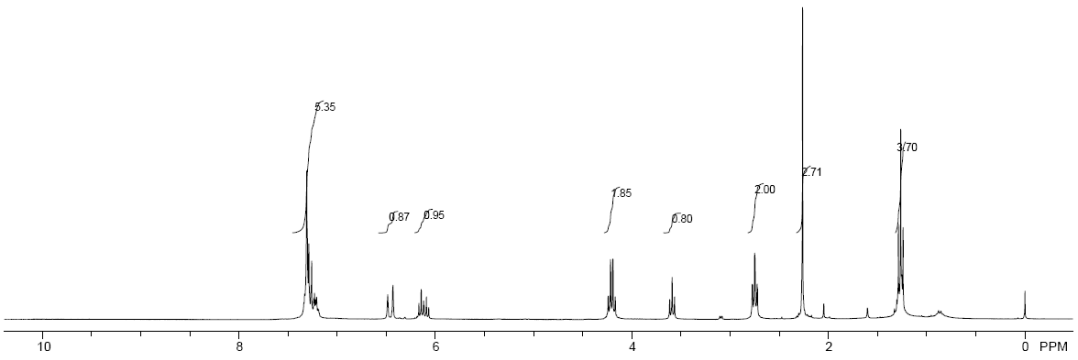
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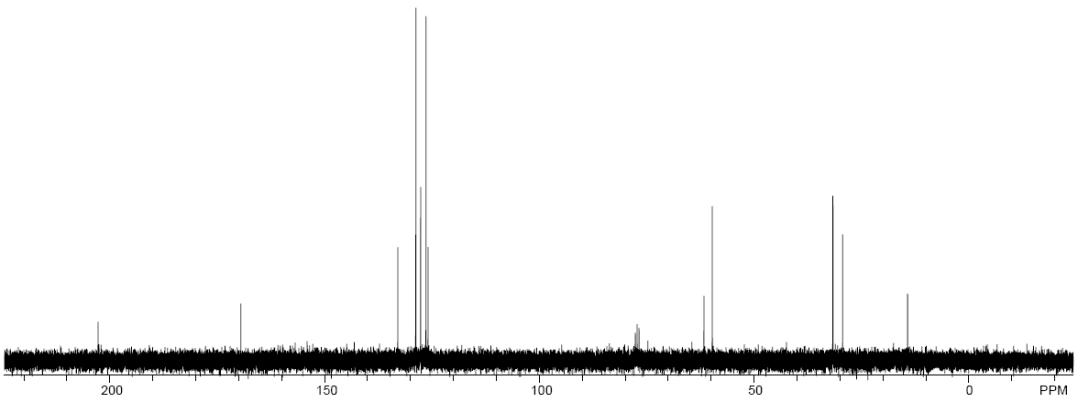
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Data for Crystal Structure of *cis*-4d.

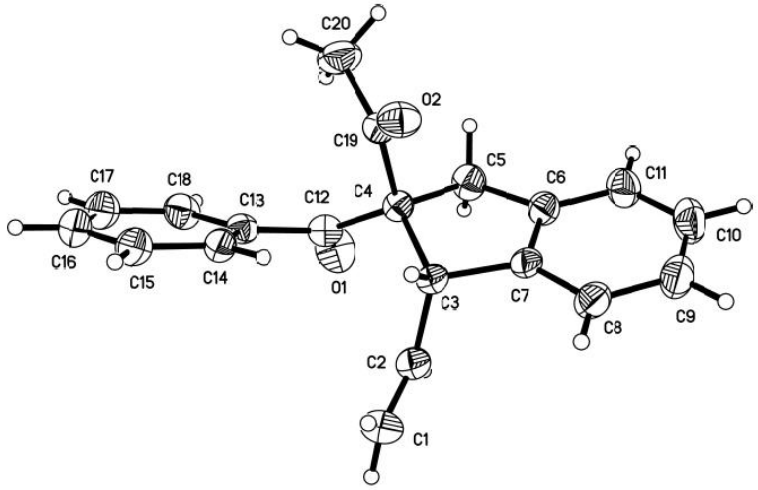

Figure 1 ORTEP drawing of ***cis*-4d** with 30% probability ellipsoids.

Table 1. Crystal data and structure refinement for *cis*-4d.

Identification code	*cis*-4d
Empirical formula	$C_{20}H_{18}O_2$
Formula weight	290.34
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 8.6769(15) A alpha = 90 deg.
	b = 17.545(2) A beta = 90 deg.
	c = 20.948(2) A gamma = 90 deg.
Volume	3189.0(7) A^3
Z, Calculated density	8, 1.209 Mg/m^3
Absorption coefficient	0.077 mm^-1
F(000)	1232
Crystal size	0.49 x 0.48 x 0.45 mm
Theta range for data collection	1.94 to 25.01 deg.
Limiting indices	-10<=h<=9, -20<=k<=13, -23<=l<=24
Reflections collected / unique	14929 / 2798 [R(int) = 0.0608]
Completeness to theta = 25.01	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9662 and 0.9633
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2798 / 0 / 200
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.0966
R indices (all data)	R1 = 0.1039, wR2 = 0.1348
Largest diff. peak and hole	0.145 and -0.162 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for *cis*-4d.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5398(3)	8940(1)	7264(1)	81(1)
O(2)	6103(2)	10569(1)	5553(1)	60(1)
C(1)	1676(4)	8932(2)	5945(2)	88(1)
C(2)	2447(3)	9350(2)	6342(2)	57(1)
C(3)	3556(3)	9958(1)	6146(1)	43(1)
C(4)	5165(3)	9928(1)	6484(1)	42(1)
C(5)	5029(3)	10493(2)	7052(1)	58(1)
C(6)	3784(3)	11030(2)	6849(1)	51(1)
C(7)	2965(3)	10733(2)	6343(1)	46(1)
C(8)	1742(3)	11130(2)	6082(2)	60(1)
C(9)	1368(4)	11835(2)	6338(2)	71(1)
C(10)	2188(4)	12129(2)	6837(2)	75(1)
C(11)	3405(4)	11735(2)	7102(2)	67(1)
C(12)	5601(3)	9122(2)	6712(1)	48(1)
C(13)	6287(3)	8572(1)	6256(1)	45(1)
C(14)	5938(3)	8563(1)	5615(1)	48(1)
C(15)	6571(3)	8017(2)	5219(2)	62(1)
C(16)	7601(4)	7494(2)	5460(2)	74(1)
C(17)	7986(4)	7510(2)	6089(2)	75(1)
C(18)	7328(3)	8038(2)	6493(2)	64(1)
C(19)	6412(3)	10251(2)	6043(1)	45(1)
C(20)	8059(3)	10208(2)	6269(2)	78(1)

Table 3. Bond lengths [A] and angles [deg] for *cis*-4d.

O(1)-C(12)	1.212(3)
O(2)-C(19)	1.200(3)
C(1)-C(2)	1.297(4)
C(1)-H(1A)	0.9300
C(1)-H(1B)	0.9300

C(2)-C(3)	1.494(4)
C(2)-H(2)	0.9300
C(3)-C(7)	1.511(4)
C(3)-C(4)	1.568(4)
C(3)-H(3)	0.9800
C(4)-C(19)	1.531(4)
C(4)-C(12)	1.539(4)
C(4)-C(5)	1.553(3)
C(5)-C(6)	1.495(4)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.378(4)
C(6)-C(11)	1.386(4)
C(7)-C(8)	1.382(4)
C(8)-C(9)	1.387(4)
C(8)-H(8)	0.9300
C(9)-C(10)	1.366(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.379(4)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(12)-C(13)	1.483(4)
C(13)-C(14)	1.377(4)
C(13)-C(18)	1.392(4)
C(14)-C(15)	1.380(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.377(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.359(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.378(4)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.507(4)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600

C(2)-C(1)-H(1A)	120.0
C(2)-C(1)-H(1B)	120.0
H(1A)-C(1)-H(1B)	120.0
C(1)-C(2)-C(3)	124.0(3)
C(1)-C(2)-H(2)	118.0
C(3)-C(2)-H(2)	118.0

C(2)-C(3)-C(7)	110.4(2)
C(2)-C(3)-C(4)	115.1(2)
C(7)-C(3)-C(4)	102.0(2)
C(2)-C(3)-H(3)	109.7
C(7)-C(3)-H(3)	109.7
C(4)-C(3)-H(3)	109.7
C(19)-C(4)-C(12)	110.7(2)
C(19)-C(4)-C(5)	106.3(2)
C(12)-C(4)-C(5)	111.6(2)
C(19)-C(4)-C(3)	110.1(2)
C(12)-C(4)-C(3)	112.9(2)
C(5)-C(4)-C(3)	104.9(2)
C(6)-C(5)-C(4)	103.9(2)
C(6)-C(5)-H(5A)	111.0
C(4)-C(5)-H(5A)	111.0
C(6)-C(5)-H(5B)	111.0
C(4)-C(5)-H(5B)	111.0
H(5A)-C(5)-H(5B)	109.0
C(7)-C(6)-C(11)	120.6(3)
C(7)-C(6)-C(5)	110.7(2)
C(11)-C(6)-C(5)	128.7(3)
C(6)-C(7)-C(8)	120.7(3)
C(6)-C(7)-C(3)	112.1(2)
C(8)-C(7)-C(3)	127.2(3)
C(7)-C(8)-C(9)	118.4(3)
C(7)-C(8)-H(8)	120.8
C(9)-C(8)-H(8)	120.8
C(10)-C(9)-C(8)	120.7(3)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	121.2(3)
C(9)-C(10)-H(10)	119.4
C(11)-C(10)-H(10)	119.4
C(10)-C(11)-C(6)	118.4(3)
C(10)-C(11)-H(11)	120.8
C(6)-C(11)-H(11)	120.8
O(1)-C(12)-C(13)	120.0(3)
O(1)-C(12)-C(4)	120.1(3)
C(13)-C(12)-C(4)	119.9(2)
C(14)-C(13)-C(18)	118.9(3)
C(14)-C(13)-C(12)	123.1(2)
C(18)-C(13)-C(12)	118.0(3)
C(13)-C(14)-C(15)	120.4(3)
C(13)-C(14)-H(14)	119.8

C(15)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	120.0(3)
C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.1(3)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	120.5(3)
C(16)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(17)-C(18)-C(13)	120.1(3)
C(17)-C(18)-H(18)	120.0
C(13)-C(18)-H(18)	120.0
O(2)-C(19)-C(20)	120.3(3)
O(2)-C(19)-C(4)	122.0(2)
C(20)-C(19)-C(4)	117.5(3)
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

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for *cis*-4d. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	124(2)	78(2)	42(1)	13(1)	5(1)	9(1)
O(2)	60(1)	66(1)	56(1)	14(1)	1(1)	-10(1)
C(1)	62(2)	69(2)	133(3)	-15(2)	-2(2)	-17(2)
C(2)	46(2)	53(2)	71(2)	1(2)	8(2)	-3(1)
C(3)	38(1)	48(2)	43(2)	1(1)	3(1)	-2(1)
C(4)	43(1)	47(2)	37(2)	-3(1)	0(1)	1(1)
C(5)	63(2)	64(2)	47(2)	-11(1)	-4(2)	3(2)
C(6)	52(2)	52(2)	49(2)	-5(1)	9(1)	2(1)
C(7)	39(2)	47(2)	51(2)	4(1)	11(1)	-2(1)
C(8)	48(2)	62(2)	70(2)	6(2)	7(2)	4(2)

C(9)	64(2)	64(2)	84(3)	4(2)	12(2)	18(2)
C(10)	91(3)	54(2)	81(3)	-9(2)	21(2)	15(2)
C(11)	75(2)	61(2)	66(2)	-15(2)	7(2)	2(2)
C(12)	51(2)	55(2)	40(2)	5(1)	-3(1)	-3(1)
C(13)	44(2)	41(2)	49(2)	7(1)	-3(1)	-3(1)
C(14)	45(2)	47(2)	53(2)	0(1)	3(1)	3(1)
C(15)	62(2)	64(2)	61(2)	-9(2)	10(2)	-4(2)
C(16)	61(2)	59(2)	100(3)	-15(2)	16(2)	5(2)
C(17)	58(2)	55(2)	113(3)	7(2)	-7(2)	13(2)
C(18)	65(2)	51(2)	75(2)	13(2)	-14(2)	3(2)
C(19)	44(2)	42(2)	50(2)	-4(1)	-2(1)	-2(1)
C(20)	46(2)	88(2)	98(3)	3(2)	-9(2)	-10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ***cis*-4d**.

	x	y	z	U(eq)
H(1A)	1796	9001	5508	106
H(1B)	1002	8562	6097	106
H(2)	2302	9267	6777	68
H(3)	3697	9944	5681	52
H(5A)	4748	10229	7442	69
H(5B)	5992	10762	7121	69
H(8)	1183	10929	5742	72
H(9)	549	12111	6168	85
H(10)	1921	12604	7001	90
H(11)	3959	11938	7442	81
H(14)	5272	8927	5448	58
H(15)	6301	8003	4790	75
H(16)	8034	7130	5192	88
H(17)	8698	7162	6247	90
H(18)	7581	8038	6925	76
H(20A)	8686	9985	5941	116
H(20B)	8113	9899	6647	116
H(20C)	8427	10711	6363	116

Table 6. Torsion angles [deg] for *cis*-4d.

C(1)-C(2)-C(3)-C(7)	114.0(3)
C(1)-C(2)-C(3)-C(4)	-131.2(3)
C(2)-C(3)-C(4)-C(19)	150.4(2)
C(7)-C(3)-C(4)-C(19)	-90.1(2)
C(2)-C(3)-C(4)-C(12)	26.1(3)
C(7)-C(3)-C(4)-C(12)	145.7(2)
C(2)-C(3)-C(4)-C(5)	-95.6(3)
C(7)-C(3)-C(4)-C(5)	23.9(2)
C(19)-C(4)-C(5)-C(6)	92.5(2)
C(12)-C(4)-C(5)-C(6)	-146.8(2)
C(3)-C(4)-C(5)-C(6)	-24.2(3)
C(4)-C(5)-C(6)-C(7)	15.4(3)
C(4)-C(5)-C(6)-C(11)	-164.7(3)
C(11)-C(6)-C(7)-C(8)	-0.7(4)
C(5)-C(6)-C(7)-C(8)	179.2(2)
C(11)-C(6)-C(7)-C(3)	-179.6(2)
C(5)-C(6)-C(7)-C(3)	0.3(3)
C(2)-C(3)-C(7)-C(6)	107.3(3)
C(4)-C(3)-C(7)-C(6)	-15.6(3)
C(2)-C(3)-C(7)-C(8)	-71.6(3)
C(4)-C(3)-C(7)-C(8)	165.6(3)
C(6)-C(7)-C(8)-C(9)	0.5(4)
C(3)-C(7)-C(8)-C(9)	179.2(3)
C(7)-C(8)-C(9)-C(10)	-0.1(4)
C(8)-C(9)-C(10)-C(11)	-0.2(5)
C(9)-C(10)-C(11)-C(6)	0.0(5)
C(7)-C(6)-C(11)-C(10)	0.4(4)
C(5)-C(6)-C(11)-C(10)	-179.5(3)
C(19)-C(4)-C(12)-O(1)	137.7(3)
C(5)-C(4)-C(12)-O(1)	19.5(4)
C(3)-C(4)-C(12)-O(1)	-98.4(3)
C(19)-C(4)-C(12)-C(13)	-41.6(3)
C(5)-C(4)-C(12)-C(13)	-159.7(2)
C(3)-C(4)-C(12)-C(13)	82.4(3)
O(1)-C(12)-C(13)-C(14)	149.1(3)
C(4)-C(12)-C(13)-C(14)	-31.7(4)
O(1)-C(12)-C(13)-C(18)	-30.7(4)
C(4)-C(12)-C(13)-C(18)	148.6(2)
C(18)-C(13)-C(14)-C(15)	2.2(4)
C(12)-C(13)-C(14)-C(15)	-177.5(2)

C(13)-C(14)-C(15)-C(16)	-2.3(4)
C(14)-C(15)-C(16)-C(17)	0.6(5)
C(15)-C(16)-C(17)-C(18)	1.3(5)
C(16)-C(17)-C(18)-C(13)	-1.5(5)
C(14)-C(13)-C(18)-C(17)	-0.3(4)
C(12)-C(13)-C(18)-C(17)	179.4(3)
C(12)-C(4)-C(19)-O(2)	134.9(3)
C(5)-C(4)-C(19)-O(2)	-103.8(3)
C(3)-C(4)-C(19)-O(2)	9.3(3)
C(12)-C(4)-C(19)-C(20)	-49.5(3)
C(5)-C(4)-C(19)-C(20)	71.8(3)
C(3)-C(4)-C(19)-C(20)	-175.0(2)

Data for Crystal Structure of 4j.

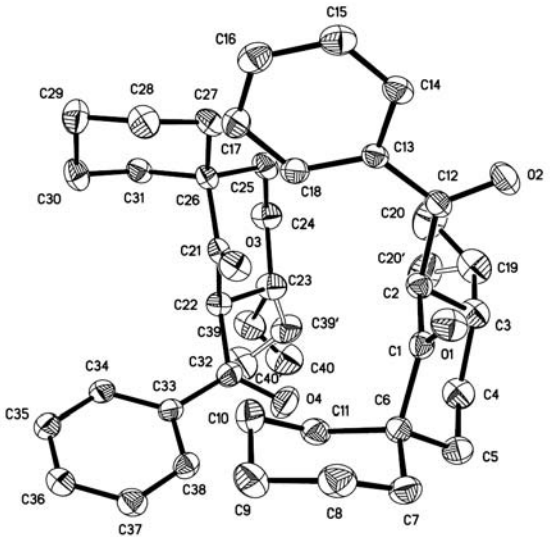

Figure 2 ORTEP drawing of **4j** with 30% probability ellipsoids.

Table 7. Crystal data and structure refinement for 4j.

Identification code	4j
Empirical formula	$C_{20}H_{24}O_2$
Formula weight	296.39
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.4799(13) A alpha = 90 deg.
	b = 17.225(2) A beta = 103.884(2) deg.
	c = 17.214(2) A gamma = 90 deg.
Volume	3304.5(7) A^3
Z, Calculated density	8, 1.192 Mg/m^3
Absorption coefficient	0.075 mm^-1
F(000)	1280
Crystal size	0.40 x 0.38 x 0.05 mm
Theta range for data collection	1.70 to 25.01 deg.
Limiting indices	-13<=h<=13, -20<=k<=19, -13<=l<=20
Reflections collected / unique	16407 / 5801 [R(int) = 0.0667]
Completeness to theta = 25.01	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9963 and 0.9706
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5801 / 0 / 426
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1158
R indices (all data)	R1 = 0.1663, wR2 = 0.1760
Largest diff. peak and hole	0.165 and -0.178 e.A^-3

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **4j**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	2504(2)	649(1)	6927(2)	70(1)
O(2)	3521(3)	2100(2)	8049(2)	83(1)
O(3)	7682(2)	1112(2)	7068(2)	73(1)
O(4)	8622(3)	-398(2)	8204(2)	100(1)
C(1)	3525(3)	430(2)	7199(2)	49(1)
C(2)	4471(3)	999(2)	7648(2)	51(1)
C(3)	4840(3)	743(2)	8528(2)	63(1)
C(4)	5212(3)	-109(2)	8593(2)	73(1)
C(5)	4270(3)	-638(2)	8085(2)	67(1)
C(6)	3908(3)	-411(2)	7191(2)	51(1)
C(7)	2877(3)	-923(2)	6747(2)	66(1)
C(8)	2547(4)	-808(2)	5852(3)	79(1)
C(9)	3628(4)	-885(3)	5493(3)	90(1)
C(10)	4627(4)	-345(2)	5915(3)	78(1)
C(11)	4966(3)	-505(2)	6804(2)	62(1)
C(12)	3958(3)	1816(2)	7540(2)	53(1)
C(13)	3925(3)	2234(2)	6782(2)	47(1)
C(14)	3090(3)	2823(2)	6560(2)	56(1)
C(15)	2990(3)	3213(2)	5850(3)	64(1)
C(16)	3722(4)	3034(2)	5355(2)	68(1)
C(17)	4571(3)	2467(2)	5580(2)	64(1)
C(18)	4674(3)	2060(2)	6283(2)	55(1)
C(19)	5798(4)	1240(3)	9037(3)	89(2)
C(20)	6472(10)	1736(10)	8824(7)	114(4)
C(20')	6950(40)	1140(40)	9050(20)	114(17)
C(21)	8731(3)	1278(2)	7339(2)	53(1)
C(22)	9612(3)	671(2)	7771(2)	56(1)
C(23)	10084(4)	903(2)	8654(2)	77(1)
C(24)	10495(4)	1750(2)	8735(2)	79(1)
C(25)	9580(3)	2305(2)	8256(2)	68(1)
C(26)	9211(3)	2106(2)	7360(2)	51(1)
C(27)	8245(3)	2670(2)	6929(2)	65(1)
C(28)	7936(4)	2594(3)	6029(2)	80(1)
C(29)	9039(4)	2647(3)	5689(2)	84(1)

C(30)	9950(3)	2053(2)	6090(2)	75(1)
C(31)	10288(3)	2164(2)	6980(2)	62(1)
C(32)	8996(3)	-112(2)	7667(3)	62(1)
C(33)	8789(3)	-516(2)	6877(2)	51(1)
C(34)	9425(3)	-355(2)	6312(2)	61(1)
C(35)	9156(4)	-732(2)	5588(3)	69(1)
C(36)	8237(4)	-1268(2)	5417(3)	68(1)
C(37)	7615(3)	-1434(2)	5982(3)	68(1)
C(38)	7894(3)	-1066(2)	6705(2)	57(1)
C(39)	11220(30)	413(17)	8925(19)	94(7)
C(40)	11543(18)	7(12)	9580(20)	128(9)
C(39')	10870(30)	389(19)	9260(18)	93(9)
C(40')	11573(17)	-75(19)	8990(20)	116(9)

Table 9. Bond lengths [A] and angles [deg] for **4j**.

O(1)-C(1)	1.212(4)
O(2)-C(12)	1.213(4)
O(3)-C(21)	1.217(4)
O(4)-C(32)	1.214(4)
C(1)-C(6)	1.516(4)
C(1)-C(2)	1.528(4)
C(2)-C(12)	1.519(4)
C(2)-C(3)	1.537(5)
C(2)-H(2)	0.9800
C(3)-C(19)	1.499(5)
C(3)-C(4)	1.526(5)
C(3)-H(3)	0.9800
C(4)-C(5)	1.520(5)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.544(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.527(4)
C(6)-C(11)	1.528(5)
C(7)-C(8)	1.508(5)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.520(6)
C(8)-H(8A)	0.9700

C(8)-H(8B)	0.9700
C(9)-C(10)	1.520(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.512(5)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.482(5)
C(13)-C(14)	1.386(4)
C(13)-C(18)	1.387(4)
C(14)-C(15)	1.376(5)
C(14)-H(14)	0.9300
C(15)-C(16)	1.368(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.368(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.378(5)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.266(12)
C(19)-C(20')	1.33(5)
C(19)-H(19)	0.9300
C(19)-H(19')	0.9300
C(20)-H(20A)	0.9300
C(20)-H(20B)	0.9300
C(20')-H(20C)	0.9300
C(20')-H(20D)	0.9300
C(21)-C(22)	1.520(5)
C(21)-C(26)	1.525(5)
C(22)-C(32)	1.514(5)
C(22)-C(23)	1.539(5)
C(22)-H(22)	0.9800
C(23)-C(39')	1.50(3)
C(23)-C(24)	1.528(5)
C(23)-C(39)	1.53(3)
C(23)-H(23)	0.9800
C(23)-H(23')	0.9800
C(24)-C(25)	1.511(5)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-C(26)	1.537(5)
C(25)-H(25A)	0.9700

C(25)-H(25B)	0.9700
C(26)-C(27)	1.527(4)
C(26)-C(31)	1.534(4)
C(27)-C(28)	1.509(5)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-C(29)	1.520(5)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-C(30)	1.507(5)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.500(5)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-C(33)	1.496(5)
C(33)-C(38)	1.377(4)
C(33)-C(34)	1.378(5)
C(34)-C(35)	1.373(5)
C(34)-H(34)	0.9300
C(35)-C(36)	1.379(5)
C(35)-H(35)	0.9300
C(36)-C(37)	1.369(5)
C(36)-H(36)	0.9300
C(37)-C(38)	1.364(5)
C(37)-H(37)	0.9300
C(38)-H(38)	0.9300
C(39)-C(40)	1.30(7)
C(39)-H(39)	0.9300
C(40)-H(40A)	0.9300
C(40)-H(40B)	0.9300
C(39')-C(40')	1.29(7)
C(39')-H(39')	0.9300
C(40')-H(40C)	0.9300
C(40')-H(40D)	0.9300

O(1)-C(1)-C(6)	123.3(3)
O(1)-C(1)-C(2)	120.0(3)
C(6)-C(1)-C(2)	116.4(3)
C(12)-C(2)-C(1)	108.9(3)
C(12)-C(2)-C(3)	113.1(3)
C(1)-C(2)-C(3)	108.0(3)

C(12)-C(2)-H(2)	108.9
C(1)-C(2)-H(2)	108.9
C(3)-C(2)-H(2)	108.9
C(19)-C(3)-C(4)	110.7(3)
C(19)-C(3)-C(2)	113.8(4)
C(4)-C(3)-C(2)	110.7(3)
C(19)-C(3)-H(3)	107.1
C(4)-C(3)-H(3)	107.1
C(2)-C(3)-H(3)	107.1
C(5)-C(4)-C(3)	112.8(3)
C(5)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
C(3)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(4)-C(5)-C(6)	113.9(3)
C(4)-C(5)-H(5A)	108.8
C(6)-C(5)-H(5A)	108.8
C(4)-C(5)-H(5B)	108.8
C(6)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7
C(1)-C(6)-C(7)	111.4(3)
C(1)-C(6)-C(11)	111.6(3)
C(7)-C(6)-C(11)	108.8(3)
C(1)-C(6)-C(5)	104.1(3)
C(7)-C(6)-C(5)	110.1(3)
C(11)-C(6)-C(5)	110.8(3)
C(8)-C(7)-C(6)	114.2(3)
C(8)-C(7)-H(7A)	108.7
C(6)-C(7)-H(7A)	108.7
C(8)-C(7)-H(7B)	108.7
C(6)-C(7)-H(7B)	108.7
H(7A)-C(7)-H(7B)	107.6
C(7)-C(8)-C(9)	112.0(4)
C(7)-C(8)-H(8A)	109.2
C(9)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8B)	109.2
C(9)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
C(10)-C(9)-C(8)	110.3(3)
C(10)-C(9)-H(9A)	109.6
C(8)-C(9)-H(9A)	109.6
C(10)-C(9)-H(9B)	109.6
C(8)-C(9)-H(9B)	109.6

H(9A)-C(9)-H(9B)	108.1
C(11)-C(10)-C(9)	110.7(4)
C(11)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
C(10)-C(11)-C(6)	112.6(3)
C(10)-C(11)-H(11A)	109.1
C(6)-C(11)-H(11A)	109.1
C(10)-C(11)-H(11B)	109.1
C(6)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8
O(2)-C(12)-C(13)	120.8(3)
O(2)-C(12)-C(2)	120.1(4)
C(13)-C(12)-C(2)	119.0(3)
C(14)-C(13)-C(18)	118.6(4)
C(14)-C(13)-C(12)	117.9(3)
C(18)-C(13)-C(12)	123.5(3)
C(15)-C(14)-C(13)	120.5(4)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	120.7(4)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(17)-C(16)-C(15)	119.1(4)
C(17)-C(16)-H(16)	120.4
C(15)-C(16)-H(16)	120.4
C(16)-C(17)-C(18)	121.2(4)
C(16)-C(17)-H(17)	119.4
C(18)-C(17)-H(17)	119.4
C(17)-C(18)-C(13)	119.9(4)
C(17)-C(18)-H(18)	120.1
C(13)-C(18)-H(18)	120.1
C(20)-C(19)-C(20')	54(2)
C(20)-C(19)-C(3)	129.0(6)
C(20')-C(19)-C(3)	122(2)
C(20)-C(19)-H(19)	115.5
C(3)-C(19)-H(19)	115.5
C(20')-C(19)-H(19')	118.5
C(3)-C(19)-H(19')	119.5
C(19)-C(20)-H(20A)	120.3
C(19)-C(20)-H(20B)	119.7
H(20A)-C(20)-H(20B)	120.0

H(20A)-C(20)-H(20D)	124.5
C(19)-C(20')-H(20C)	120.5
C(19)-C(20')-H(20D)	119.5
H(20C)-C(20')-H(20D)	120.0
O(3)-C(21)-C(22)	120.5(3)
O(3)-C(21)-C(26)	123.2(3)
C(22)-C(21)-C(26)	115.9(3)
C(32)-C(22)-C(21)	108.5(3)
C(32)-C(22)-C(23)	113.1(3)
C(21)-C(22)-C(23)	109.9(3)
C(32)-C(22)-H(22)	108.4
C(21)-C(22)-H(22)	108.4
C(23)-C(22)-H(22)	108.4
C(39')-C(23)-C(24)	112.3(11)
C(39')-C(23)-C(39)	29.7(9)
C(24)-C(23)-C(39)	106.1(11)
C(39')-C(23)-C(22)	123.1(14)
C(24)-C(23)-C(22)	111.4(3)
C(39)-C(23)-C(22)	103.3(11)
C(39')-C(23)-H(23)	83.1
C(24)-C(23)-H(23)	111.9
C(39)-C(23)-H(23)	111.9
C(22)-C(23)-H(23)	111.9
C(39')-C(23)-H(23')	102.4
C(24)-C(23)-H(23')	102.4
C(39)-C(23)-H(23')	131.2
C(22)-C(23)-H(23')	102.0
H(23)-C(23)-H(23')	19.3
C(25)-C(24)-C(23)	113.3(3)
C(25)-C(24)-H(24A)	108.9
C(23)-C(24)-H(24A)	108.9
C(25)-C(24)-H(24B)	108.9
C(23)-C(24)-H(24B)	108.9
H(24A)-C(24)-H(24B)	107.7
C(24)-C(25)-C(26)	113.2(3)
C(24)-C(25)-H(25A)	108.9
C(26)-C(25)-H(25A)	108.9
C(24)-C(25)-H(25B)	108.9
C(26)-C(25)-H(25B)	108.9
H(25A)-C(25)-H(25B)	107.8
C(21)-C(26)-C(27)	111.5(3)
C(21)-C(26)-C(31)	112.0(3)
C(27)-C(26)-C(31)	108.4(3)
C(21)-C(26)-C(25)	104.1(3)

C(27)-C(26)-C(25)	109.8(3)
C(31)-C(26)-C(25)	110.9(3)
C(28)-C(27)-C(26)	114.1(3)
C(28)-C(27)-H(27A)	108.7
C(26)-C(27)-H(27A)	108.7
C(28)-C(27)-H(27B)	108.7
C(26)-C(27)-H(27B)	108.7
H(27A)-C(27)-H(27B)	107.6
C(27)-C(28)-C(29)	112.2(3)
C(27)-C(28)-H(28A)	109.2
C(29)-C(28)-H(28A)	109.2
C(27)-C(28)-H(28B)	109.2
C(29)-C(28)-H(28B)	109.2
H(28A)-C(28)-H(28B)	107.9
C(30)-C(29)-C(28)	109.5(4)
C(30)-C(29)-H(29A)	109.8
C(28)-C(29)-H(29A)	109.8
C(30)-C(29)-H(29B)	109.8
C(28)-C(29)-H(29B)	109.8
H(29A)-C(29)-H(29B)	108.2
C(31)-C(30)-C(29)	111.2(3)
C(31)-C(30)-H(30A)	109.4
C(29)-C(30)-H(30A)	109.4
C(31)-C(30)-H(30B)	109.4
C(29)-C(30)-H(30B)	109.4
H(30A)-C(30)-H(30B)	108.0
C(30)-C(31)-C(26)	113.0(3)
C(30)-C(31)-H(31A)	109.0
C(26)-C(31)-H(31A)	109.0
C(30)-C(31)-H(31B)	109.0
C(26)-C(31)-H(31B)	109.0
H(31A)-C(31)-H(31B)	107.8
O(4)-C(32)-C(33)	119.7(4)
O(4)-C(32)-C(22)	120.8(4)
C(33)-C(32)-C(22)	119.4(4)
C(38)-C(33)-C(34)	118.8(4)
C(38)-C(33)-C(32)	117.6(4)
C(34)-C(33)-C(32)	123.6(4)
C(35)-C(34)-C(33)	120.2(4)
C(35)-C(34)-H(34)	119.9
C(33)-C(34)-H(34)	119.9
C(34)-C(35)-C(36)	120.3(4)
C(34)-C(35)-H(35)	119.8
C(36)-C(35)-H(35)	119.8

C(37)-C(36)-C(35)	119.4(4)
C(37)-C(36)-H(36)	120.3
C(35)-C(36)-H(36)	120.3
C(38)-C(37)-C(36)	120.2(4)
C(38)-C(37)-H(37)	119.9
C(36)-C(37)-H(37)	119.9
C(37)-C(38)-C(33)	121.0(4)
C(37)-C(38)-H(38)	119.5
C(33)-C(38)-H(38)	119.5
C(40)-C(39)-C(23)	127(4)
C(40)-C(39)-H(39)	116.3
C(23)-C(39)-H(39)	116.3
C(39)-C(40)-H(40A)	120.0
C(39)-C(40)-H(40B)	120.0
H(40A)-C(40)-H(40B)	120.0
C(40')-C(39')-C(23)	116(4)
C(40')-C(39')-H(39')	121.9
C(23)-C(39')-H(39')	121.9
C(39')-C(40')-H(40C)	120.0
C(39')-C(40')-H(40D)	120.0
H(40C)-C(40')-H(40D)	120.0

Table 10. Anisotropic displacement parameters (A^2 x 10^3) for **4j**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	50(2)	65(2)	89(2)	-1(2)	6(2)	9(1)
O(2)	107(2)	76(2)	78(2)	-4(2)	42(2)	28(2)
O(3)	45(2)	77(2)	91(2)	-14(2)	7(2)	-8(1)
O(4)	138(3)	99(2)	72(2)	-3(2)	41(2)	-43(2)
C(1)	45(2)	53(2)	51(2)	6(2)	16(2)	4(2)
C(2)	48(2)	49(2)	57(3)	0(2)	13(2)	5(2)
C(3)	62(3)	65(3)	58(3)	0(2)	6(2)	10(2)
C(4)	77(3)	75(3)	61(3)	10(2)	4(2)	17(2)
C(5)	79(3)	55(2)	68(3)	15(2)	18(2)	13(2)
C(6)	49(2)	47(2)	57(3)	5(2)	17(2)	8(2)
C(7)	64(3)	52(2)	82(3)	0(2)	22(2)	-8(2)

C(8)	81(3)	72(3)	79(3)	−14(3)	9(3)	−18(2)
C(9)	118(4)	80(3)	76(3)	−19(3)	30(3)	−3(3)
C(10)	83(3)	76(3)	86(3)	1(3)	43(3)	6(3)
C(11)	59(2)	49(2)	80(3)	2(2)	23(2)	10(2)
C(12)	51(2)	50(2)	61(3)	−9(2)	18(2)	1(2)
C(13)	45(2)	39(2)	56(2)	−5(2)	14(2)	−2(2)
C(14)	51(2)	48(2)	68(3)	−9(2)	14(2)	−2(2)
C(15)	51(3)	55(3)	80(3)	6(2)	4(2)	4(2)
C(16)	70(3)	61(3)	69(3)	3(2)	11(2)	−14(2)
C(17)	67(3)	60(3)	74(3)	−1(2)	31(2)	−7(2)
C(18)	55(2)	45(2)	67(3)	0(2)	19(2)	1(2)
C(19)	84(4)	101(4)	72(3)	−10(3)	1(3)	8(3)
C(20)	89(6)	153(12)	95(6)	5(7)	12(5)	−33(7)
C(20')	90(30)	150(40)	100(20)	0(30)	13(19)	−30(30)
C(21)	50(2)	61(2)	49(2)	−10(2)	14(2)	1(2)
C(22)	47(2)	57(2)	61(3)	−1(2)	8(2)	−3(2)
C(23)	81(3)	74(3)	63(3)	−4(2)	−7(2)	−4(3)
C(24)	84(3)	75(3)	64(3)	−12(2)	−7(2)	−10(3)
C(25)	69(3)	68(3)	63(3)	−22(2)	12(2)	−8(2)
C(26)	44(2)	55(2)	53(2)	−10(2)	13(2)	1(2)
C(27)	57(2)	61(3)	77(3)	−11(2)	15(2)	10(2)
C(28)	74(3)	90(3)	70(3)	1(3)	4(3)	15(3)
C(29)	88(3)	104(4)	63(3)	4(3)	24(3)	4(3)
C(30)	60(3)	93(3)	77(3)	−20(3)	27(2)	−3(2)
C(31)	51(2)	58(2)	78(3)	−11(2)	21(2)	−3(2)
C(32)	60(3)	60(3)	67(3)	4(2)	17(2)	−4(2)
C(33)	47(2)	42(2)	64(3)	3(2)	17(2)	0(2)
C(34)	64(3)	50(2)	75(3)	−4(2)	26(2)	−12(2)
C(35)	78(3)	59(3)	81(3)	4(2)	37(3)	−1(2)
C(36)	73(3)	64(3)	68(3)	−8(2)	15(2)	5(2)
C(37)	58(3)	65(3)	82(3)	−12(2)	17(2)	−13(2)
C(38)	46(2)	61(2)	68(3)	5(2)	18(2)	−3(2)
C(39)	121(16)	87(12)	61(13)	3(11)	−7(10)	21(11)
C(40)	137(11)	119(11)	110(20)	14(12)	−8(11)	32(9)
C(39')	117(19)	88(12)	63(14)	24(13)	−1(13)	7(12)
C(40')	129(12)	122(18)	85(17)	19(14)	3(11)	49(11)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **4j**.

	x	y	z	U(eq)
H(2)	5175	975	7420	61
H(3)	4127	789	8745	76
H(4A)	5957	-165	8426	88
H(4B)	5359	-270	9148	88
H(5A)	3560	-631	8297	81
H(5B)	4576	-1166	8130	81
H(7A)	3096	-1463	6860	79
H(7B)	2176	-818	6952	79
H(8A)	2197	-296	5731	95
H(8B)	1947	-1188	5609	95
H(9A)	3913	-1418	5545	109
H(9B)	3397	-759	4927	109
H(10A)	5323	-417	5696	93
H(10B)	4364	190	5823	93
H(11A)	5602	-152	7059	74
H(11B)	5274	-1030	6894	74
H(14)	2594	2957	6894	67
H(15)	2418	3603	5704	77
H(16)	3644	3294	4872	81
H(17)	5088	2355	5254	77
H(18)	5245	1669	6421	66
H(19)	5904	1180	9587	107
H(19')	5583	1632	9347	107
H(20A)	6417	1827	8283	137
H(20B)	7030	2007	9209	137
H(20C)	7193	757	8750	137
H(20D)	7519	1468	9374	137
H(22)	10293	651	7520	67
H(23)	9498	793	8970	92
H(23')	9344	921	8843	92
H(24A)	10666	1897	9294	94
H(24B)	11234	1796	8559	94
H(25A)	9908	2826	8319	81
H(25B)	8871	2300	8470	81
H(27A)	7524	2586	7117	78
H(27B)	8516	3196	7070	78

H(28A)	7376	3001	5798	96
H(28B)	7543	2099	5880	96
H(29A)	8814	2554	5117	101
H(29B)	9382	3164	5779	101
H(30A)	9621	1537	5966	90
H(30B)	10662	2097	5882	90
H(31A)	10659	2670	7101	74
H(31B)	10876	1774	7218	74
H(34)	10040	10	6421	74
H(35)	9595	-626	5211	83
H(36)	8042	-1514	4921	82
H(37)	7001	-1799	5873	81
H(38)	7473	-1189	7087	69
H(39)	11736	404	8583	113
H(40A)	11061	-5	9940	153
H(40B)	12258	-271	9680	153
H(39')	10863	403	9799	112
H(40C)	11565	-76	8450	139
H(40D)	12084	-408	9341	139

Table 12. Torsion angles [deg] for **4j**.

O(1)-C(1)-C(2)-C(12)	-9.9(5)
C(6)-C(1)-C(2)-C(12)	176.0(3)
O(1)-C(1)-C(2)-C(3)	113.3(4)
C(6)-C(1)-C(2)-C(3)	-60.8(4)
C(12)-C(2)-C(3)-C(19)	-61.1(4)
C(1)-C(2)-C(3)-C(19)	178.2(3)
C(12)-C(2)-C(3)-C(4)	173.5(3)
C(1)-C(2)-C(3)-C(4)	52.9(4)
C(19)-C(3)-C(4)-C(5)	-179.9(4)
C(2)-C(3)-C(4)-C(5)	-52.8(5)
C(3)-C(4)-C(5)-C(6)	55.6(5)
O(1)-C(1)-C(6)-C(7)	4.4(5)
C(2)-C(1)-C(6)-C(7)	178.3(3)
O(1)-C(1)-C(6)-C(11)	126.2(4)
C(2)-C(1)-C(6)-C(11)	-59.9(4)
O(1)-C(1)-C(6)-C(5)	-114.2(4)
C(2)-C(1)-C(6)-C(5)	59.7(4)
C(4)-C(5)-C(6)-C(1)	-55.0(4)
C(4)-C(5)-C(6)-C(7)	-174.5(3)

C(4)-C(5)-C(6)-C(11)	65.1(4)
C(1)-C(6)-C(7)-C(8)	71.5(4)
C(11)-C(6)-C(7)-C(8)	-51.9(4)
C(5)-C(6)-C(7)-C(8)	-173.6(3)
C(6)-C(7)-C(8)-C(9)	53.0(5)
C(7)-C(8)-C(9)-C(10)	-53.8(5)
C(8)-C(9)-C(10)-C(11)	56.7(5)
C(9)-C(10)-C(11)-C(6)	-58.6(4)
C(1)-C(6)-C(11)-C(10)	-68.7(4)
C(7)-C(6)-C(11)-C(10)	54.6(4)
C(5)-C(6)-C(11)-C(10)	175.8(3)
C(1)-C(2)-C(12)-O(2)	96.7(4)
C(3)-C(2)-C(12)-O(2)	-23.4(5)
C(1)-C(2)-C(12)-C(13)	-79.1(4)
C(3)-C(2)-C(12)-C(13)	160.7(3)
O(2)-C(12)-C(13)-C(14)	-19.5(5)
C(2)-C(12)-C(13)-C(14)	156.3(3)
O(2)-C(12)-C(13)-C(18)	161.2(3)
C(2)-C(12)-C(13)-C(18)	-23.0(5)
C(18)-C(13)-C(14)-C(15)	1.6(5)
C(12)-C(13)-C(14)-C(15)	-177.7(3)
C(13)-C(14)-C(15)-C(16)	-0.9(5)
C(14)-C(15)-C(16)-C(17)	-0.9(6)
C(15)-C(16)-C(17)-C(18)	2.1(6)
C(16)-C(17)-C(18)-C(13)	-1.4(5)
C(14)-C(13)-C(18)-C(17)	-0.5(5)
C(12)-C(13)-C(18)-C(17)	178.8(3)
C(4)-C(3)-C(19)-C(20)	111.7(12)
C(2)-C(3)-C(19)-C(20)	-13.7(12)
C(4)-C(3)-C(19)-C(20')	44(3)
C(2)-C(3)-C(19)-C(20')	-81(3)
O(3)-C(21)-C(22)-C(32)	8.6(5)
C(26)-C(21)-C(22)-C(32)	-178.3(3)
O(3)-C(21)-C(22)-C(23)	-115.5(4)
C(26)-C(21)-C(22)-C(23)	57.5(4)
C(32)-C(22)-C(23)-C(39')	52.4(17)
C(21)-C(22)-C(23)-C(39')	173.8(17)
C(32)-C(22)-C(23)-C(24)	-169.8(3)
C(21)-C(22)-C(23)-C(24)	-48.4(5)
C(32)-C(22)-C(23)-C(39)	76.7(14)
C(21)-C(22)-C(23)-C(39)	-161.9(14)
C(39')-C(23)-C(24)-C(25)	-167.7(18)
C(39)-C(23)-C(24)-C(25)	161.5(14)
C(22)-C(23)-C(24)-C(25)	49.8(5)

C(23)-C(24)-C(25)-C(26)	-56.6(5)
O(3)-C(21)-C(26)-C(27)	-5.6(5)
C(22)-C(21)-C(26)-C(27)	-178.5(3)
O(3)-C(21)-C(26)-C(31)	-127.4(4)
C(22)-C(21)-C(26)-C(31)	59.8(4)
O(3)-C(21)-C(26)-C(25)	112.7(4)
C(22)-C(21)-C(26)-C(25)	-60.1(4)
C(24)-C(25)-C(26)-C(21)	57.8(4)
C(24)-C(25)-C(26)-C(27)	177.4(3)
C(24)-C(25)-C(26)-C(31)	-62.8(4)
C(21)-C(26)-C(27)-C(28)	-72.9(4)
C(31)-C(26)-C(27)-C(28)	50.9(4)
C(25)-C(26)-C(27)-C(28)	172.3(3)
C(26)-C(27)-C(28)-C(29)	-53.5(5)
C(27)-C(28)-C(29)-C(30)	54.8(5)
C(28)-C(29)-C(30)-C(31)	-57.6(5)
C(29)-C(30)-C(31)-C(26)	58.9(4)
C(21)-C(26)-C(31)-C(30)	70.0(4)
C(27)-C(26)-C(31)-C(30)	-53.6(4)
C(25)-C(26)-C(31)-C(30)	-174.2(3)
C(21)-C(22)-C(32)-O(4)	-102.4(4)
C(23)-C(22)-C(32)-O(4)	19.8(5)
C(21)-C(22)-C(32)-C(33)	74.4(4)
C(23)-C(22)-C(32)-C(33)	-163.4(3)
O(4)-C(32)-C(33)-C(38)	19.0(5)
C(22)-C(32)-C(33)-C(38)	-157.8(3)
O(4)-C(32)-C(33)-C(34)	-162.4(4)
C(22)-C(32)-C(33)-C(34)	20.7(5)
C(38)-C(33)-C(34)-C(35)	0.8(5)
C(32)-C(33)-C(34)-C(35)	-177.8(3)
C(33)-C(34)-C(35)-C(36)	0.8(6)
C(34)-C(35)-C(36)-C(37)	-1.6(6)
C(35)-C(36)-C(37)-C(38)	0.7(6)
C(36)-C(37)-C(38)-C(33)	0.9(6)
C(34)-C(33)-C(38)-C(37)	-1.7(5)
C(32)-C(33)-C(38)-C(37)	177.0(3)
C(39')-C(23)-C(39)-C(40)	2(2)
C(24)-C(23)-C(39)-C(40)	109(2)
C(22)-C(23)-C(39)-C(40)	-134(2)
C(24)-C(23)-C(39')-C(40')	-108(2)
C(39)-C(23)-C(39')-C(40')	-24(3)
C(22)-C(23)-C(39')-C(40')	30(3)