# Supporting Information

**for**

# Ambient gold-catalyzed *O*-vinylation of cyclic 1,3-diketone: A vinyl ether synthesis

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## General methods, characterization data and NMR spectra of synthesized compounds

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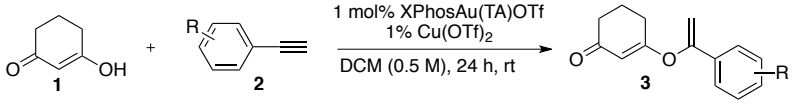
# I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. All gold complexes were synthesized from $HAuCl_4$, which was purchased from Strem. XPhos was purchased from Acros and used as received (stored at 4°C and handled in glovebox). $^1H$ NMR and $^{13}C$ NMR spectra were recorded on Varian/Agilent 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for $^1H$ and $CDCl_3$ (δ 77.0 ppm) for $^{13}C$. Flash column chromatography was performed on 230-430 mesh silica gel. HRMS were recorded on LTQ-FTUHRA spectrometer.

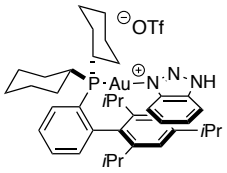
**Representative procedure for Gold-catalyzed O-Vinylation of 1,3-Cyclic Diketone**




1 2 3

A 4 mL screw-cap vial was charged with 1,3-cyclohexanedione (46 mg, 0.4 mmol) and alkyne (0.8 mmol, 1.2 equiv.) in dry DCM (0.8 mL), followed by the addition of catalysts XPhosAu(TA)OTf (3.7 mg, 1 mol%) and $Cu(OTf)_2$ (1.4 mg, 1 mol%). The vial was allowed to stir at rt and monitored by TLC. After the reaction was completed (about 24 h), the reaction mixture was directly purified by flash chromatography on silica gel (ethyl acetate/hexane = 1:3, V/V) to give desired addition product.

**Procedure for Synthesis of XPhosAu(TA)OTf**

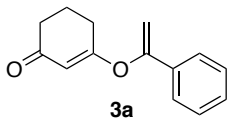



**XPhosAu(TA)OTf**

A 20 mL screw-cap vial was charged with XPhosAuCl (355 mg, 0.5 mmol) and 1H-benzotriazole (1.1 equiv.) in dry DCM (5 mL), followed by the addition of AgOTf (1.05 equiv.). The vial was allowed to stir at ambient temperature. After 4h, the reaction mixture was filtered through two celite pads and concentrated *in vacuo* to give the product as white foam. Pure white powder was obtained via recrystallization through diffusion of hexane into DCM solution of crude product.

For the synthesis of $Ph_3PAu(TA)OTf$ and IPrAu(TA)OTf, see: ref 1-2.

## II. Compounds Characterizaton

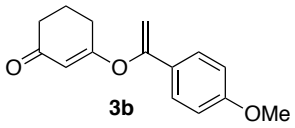


**3a**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.33-7.30 (m, 2H), 5.43 (d, *J* = 2.0 Hz, 1H), 5.42 (s, 1H), 4.97 (d, *J* = 2.4 Hz, 1H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 2.61 (quint, *J* = 6.4 Hz, 2H), 2.00 (s, 6H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.6, 176.5, 154.9, 133.2, 129.3, 128.7, 125.0, 106.5, 101.9, 36.5, 28.2, 21.1.

HRMS Calculated for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.1067, Found: 215.1067.

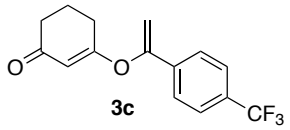


**3b**

$^1$H-NMR (400 MHz, $CDCl_3$) δ7.37-7.35 (m, 2H), δ6.87-6.84 (m, 2H), 5.31 (t, *J* = 1.6 Hz, 1H), 4.87 (d, *J* = 1.6 Hz, 1H), 3.80 (s, 3H), 2.63 (t, *J* = 1.6 Hz, 2H), 2.34 (t, *J* = 1.6 Hz, 2H), 2.05-2.02 (m, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.7, 176.7, 160.3, 154.6, 126.4, 125.6, 114.0, 106.3, 99.9, 55.2, 36.4, 28.1, 21.0.

HRMS Calculated for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.1172, Found: 245.1172.

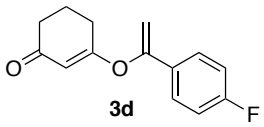


**3c**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.57 (d, *J* = 2.4 Hz, 1H), 5.39 (s, 1H), 5.13 (d, *J* = 2.0 Hz, 1H), 2.64 (t, *J* = 6.2 Hz, 2H), 2.34 (t, *J* = 6.6 Hz, 2H), 2.06 (quint, *J* = 6.4 Hz, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.3, 176.0, 153.5, 136.6, 126.0, 125.7 (q, *J* = 3.8 Hz), 125.3, 104.6, 104.1, 36.4, 28.1, 21.0.

HRMS Calculated for $C_{15}H_{14}F_3O_2$ $[M+H]^+$: 283.0940, Found: 283.0942.

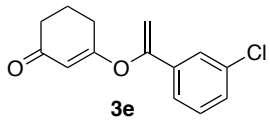


**3d**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.06-7.00 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 5.41 (s, 1H), 5.38 (d, *J* = 2.4 Hz, 1H), 4.97 (d, *J* = 2.4 Hz, 1H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.33 (t, *J* = 6.8 Hz, 2H), 2.04 (quint, *J* = 6.8 Hz, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.3, 176.2, 164.4, 161.9, 153.9, 129.4, 126.9, 126.9, 115.6 (q, *J* = 22.0 Hz), 106.4, 101.6, 36.4, 28.1, 21.0.

HRMS Calculated for $C_{14}H_{14}FO_2$ [M+H]$^+$: 233.0972, Found: 233.0971.

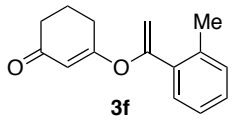



**3e**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.40 (m, 1H), 7.34-7.27 (m, 3H), 5.47 (d, *J* = 2.4 Hz, 1H), 5.04 (d, *J* = 2.4 Hz, 1H), 2.63 (t, *J* = 6.2 Hz, 2H), 2.34 (t, *J* = 6.6 Hz, 2H), 2.05 (quint, *J* = 6.4 Hz, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.4, 176.1, 153.5, 135.1, 134.7, 130.0, 129.3, 125.1, 123.2, 106.6, 103.2, 36.5, 28.1, 21.0.

HRMS Calculated for $C_{14}H_{14}ClO_2$ [M+H]$^+$: 249.0677, Found: 249.0678.

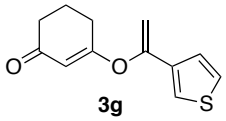



**3f**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 1H), 7.26-7.21 (m, 1H), 7.18-7.14 (m, 2H), 5.44 (s, 1H), 5.15 (d, *J* = 2.0 Hz, 1H), 5.06 (d, *J* = 1.6 Hz, 1H), 2.50 (t, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 2.27 (t, *J* = 6.4 Hz, 2H), 1.97 (quint, *J* = 6.4 Hz, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.3, 175.5, 155.6, 135.8, 133.8, 130.9, 129.0,128.9, 125.8, 106.7, 106.5, 36.4, 28.3, 210.0, 20.7.

HRMS Calculated for $C_{15}H_{17}O_2$ [M+H]$^+$: 229.1223, Found: 229.1224.

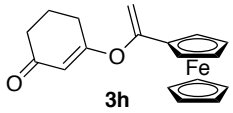



**3g**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.14 (dd, *J* = 5.0, 1.4 Hz, 1H), 5.49 (s, 1H), 5.32 (d, *J* = 2.0 Hz, 1H), 4.91 (d, *J* = 2.0 Hz, 1H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.34 (t, *J* = 6.4 Hz, 2H), 2.04 (quint, *J* = 6.4 Hz, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.5, 176.4, 151.0, 135.3, 126.6, 124.7, 122.4, 106.1, 101.1, 36.4, 28.1, 21.0.

HRMS Calculated for $C_{12}H_{13}O_2S$ [M+H]$^+$: 221.0631, Found: 221.0631.

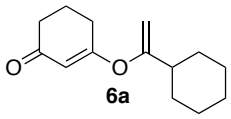



**3h**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H), 5.11 (d, *J* = 2.0 Hz, 1H), 4.75 (d, *J* = 2.0 Hz, 1H), 4.31 (t, *J* = 1.8 Hz, 2H), 4.22 (t, *J* = 1.8 Hz, 2H), 4.13 (s, 5H), 2.58 (t, *J* = 6.2 Hz, 2H), 2.35 (t, *J* = 6.2 Hz, 2H), 2.04 (quint, *J* = 6.4 Hz, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.5, 176.6, 155.2, 105.8, 98.6, 78.4, 69.7, 69.2, 66.3, 36.6, 28.2, 21.1.

HRMS Calculated for $C_{18}H_{19}FeO_2$ [M+H]$^+$: 323.0734, Found: 321.0729.

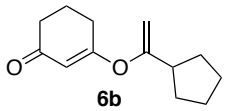


**6a**

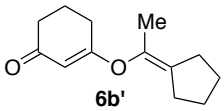
$^{1}$H-NMR (400 MHz, $CDCl_3$) δ 5.41 (s, 1H), 4.64 (m, 1H), 4.51 (m, 1H), 2.41 (t, *J* = 6.3 Hz, 2H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.98-1.90 (m, 3H), 1.79-1.57 (m, 4H), 1.17-1.04 (m, 6H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.6, 176.7, 162.2, 105.2, 99.2, 40.7, 36.4, 30.5, 28.3, 25.8, 25.7, 21.0.

HRMS Calculated for $C_{14}H_{21}O_2$ $[M+H]^+$: 221.1536, Found: 221.1535.



**6b**



**6b'**

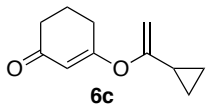
Obtained as inseparable mixtures (**6b:6b'**=1:0.4).

Major isomer (6b):

$^{1}$H-NMR (400 MHz, $CDCl_3$) δ7.37-7.35 (m, 2H), δ 5.56 (s, 1H), 4.80 (dd, *J* = 1.6, 1.0 Hz, 1H), 4.60 (d, *J* = 1.6 Hz, 1H), 2.59 (quint, *J* = 8.0 Hz, 1H), 2.50 (t, *J* = 6.4 Hz, 2H), 2.36 (t, *J* = 6.4 Hz, 2H), 1.84-1.80 (m, 2H), 1.71-1.47 (m, 6H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.8, 176.8, 161.0, 105.4, 99.5, 42.9, 36.6, 30.6, 28.4, 24.8, 21.1.

HRMS Calculated for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1380, Found: 207.1378.

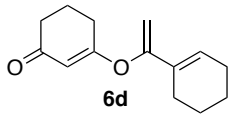


**6c**

$^{1}$H-NMR (400 MHz, $CDCl_3$) δ 5.60 (s, 1H), 4.75 (d, *J* = 2.0 Hz, 1H), 4.57 (d, *J* = 1.6 Hz, 1H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 2.02 (quint, *J* = 6.4 Hz, 2H), 1.49 (tt, *J* = 8.4, 5.2 Hz, 1H), 0.75-0.70 (m, 2H), 0.61-0.57 (m, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.7, 176.7, 158.3, 105.6, 98.9, 36.5, 28.2, 21.1, 13.0, 6.0.

HRMS Calculated for $C_{11}H_{15}O_2$ $[M+H]^+$: 179.1067, Found: 179.1066.

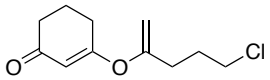


**6d**

$^{1}$H-NMR (400 MHz, $CDCl_3$) δ 5.91 (t, *J* = 5.4 Hz, 1H), 5.42 (s, 1H), 4.94 (d, *J* = 1.2 Hz, 1H), 4.69 (d, *J* = 0.8 Hz, 1H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.35 (t, *J* = 6.4 Hz, 2H), 2.15-2.10 (m, 4H), 2.03 (quint, *J* = 6.6 Hz, 2H), 1.71-1.66 (m, 2H), 1.60-1.55 (m, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.9, 177.5, 155.8, 129.0, 126.7, 105.2, 99.9, 36.5, 28.1, 25.5, 24.6, 22.1, 21.6, 21.1.

HRMS Calculated for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, Found: 219.1380.

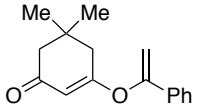


**6e**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 5.45 (s, 1H), 4.78 (m, 1H), 4.68 (d, *J* = 1.6 Hz, 1H), 3.53 (t, *J* = 6.4 Hz, 2H), 2.44 (t, *J* = 6.0 Hz, 2H), 2.33-2.29 (m, 4H), 1.98 (quint, *J* = 6.4 Hz, 2H), 1.94-1.87 (m, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.5, 175.8, 156.1, 105.5, 102.4, 43.7, 36.5, 29.4, 29.3, 28.3, 21.0.

HRMS Calculated for $C_{11}H_{16}ClO_2$ $[M+H]^+$: 215.0833, Found: 215.0832.

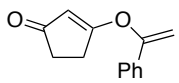


**10a**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.35-7.32 (m, 3H), 5.44 (t, *J* = 2.4 Hz, 1H), 5.42 (s, 1H), 4.98 (d, *J* = 2.0 Hz, 1H), 2.49 (s, 2H), 2.19 (s, 2H), 1.10 (s, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 199.4, 175.0, 155.0, 133.2, 129.3, 128.7, 125.0, 105.4, 101.9, 50.6, 42.1, 32.7, 28.2.

HRMS Calculated for $C_{16}H_{18}O_2Na$ $[M+H]^+$: 265.1199, Found: 265.1199.

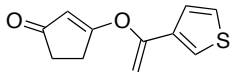


**10b**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.34-7.31 (m, 3H), 5.42 (d, *J* = 2.8 Hz, 1H), 5.26 (t, *J* = 1.2 Hz, 1H), 5.04 (d, *J* = 2.4 Hz, 1H), 2.77-2.74 (m, 2H), 2.47-2.44 (m, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 205.5, 188.7, 156.8, 132.6, 129.4, 128.7, 125.0, 108.4, 101.1, 34.3, 28.0.

HRMS Calculated for $C_{13}H_{13}O_2$ $[M+H]^+$: 201.0910, Found: 201.0909.

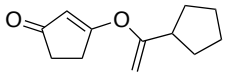


**10c**

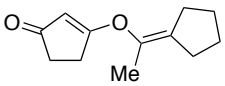
$^1$H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.17 (d, *J* = 5.4, 2.4 Hz, 1H), 5.37 (t, *J* = 0.9 Hz, 1H), 5.33 (d, *J* = 2.4 Hz, 1H), 5.00 (d, *J* = 2.4 Hz, 1H), 2.81-2.78 (m, 2H), 2.53-2.50 (m, 2H).

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ 205.5, 188.7, 153.1, 134.8, 126.9, 124.7, 122.7, 108.1, 100.2, 34.4, 28.0.

HRMS Calculated for $C_{11}H_{11}O_2$ $[M+H]^+$: 207.0474, Found: 207.0473.



**10d**



**10d'**

Obtained as inseparable mixtures (**10d:10d'**=1:2.6).

HRMS Calculated for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1223, Found: 193.1222.

## III. ORTEP Drawing of the Crystal Structure

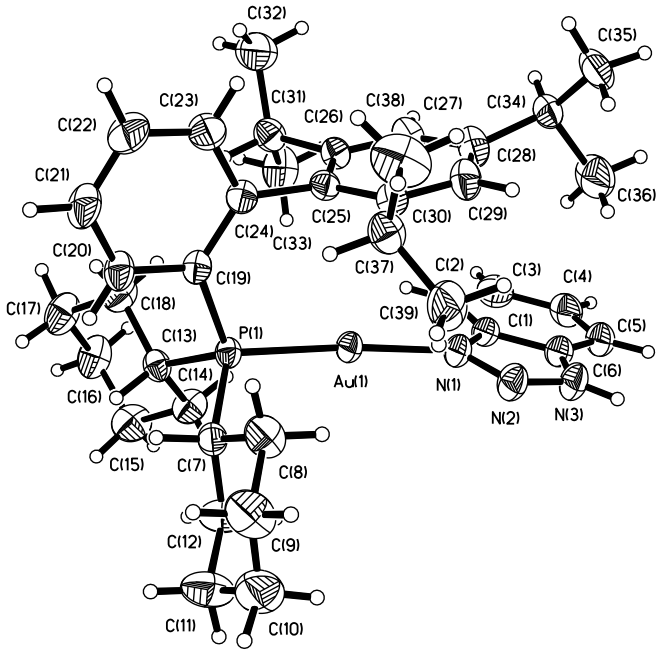
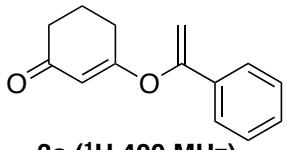



**Figure S1.** Perspective view of the molecular structure of the $(C_6H_5N_3)Au[P(C_6H_{11})_2(C_6H_4(C_6H_2(i\text{-}C_3H_7)_3))]^+$ cation with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

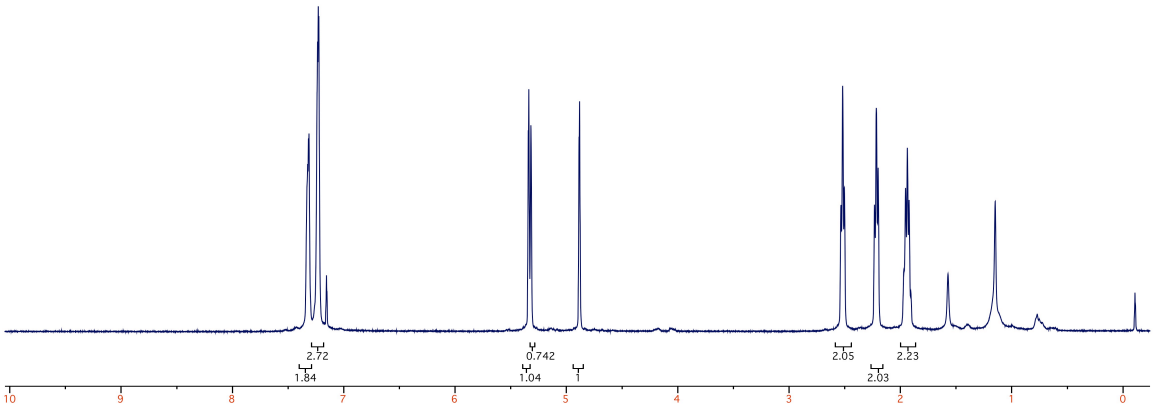
## IV. Reference


1. Duan, H.; Sengupta, S.; Petersen, J. L.; Akhmedov, N.; Shi, X. *J. Am. Chem. Soc.* **2009,** *131*, 12100-12102.
2. Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.;Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012-9019.

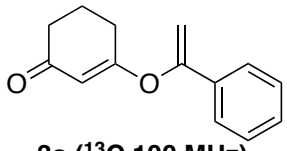
## V. NMR Spectra of New Compounds



**3a ($^{1}$H 400 MHz)**







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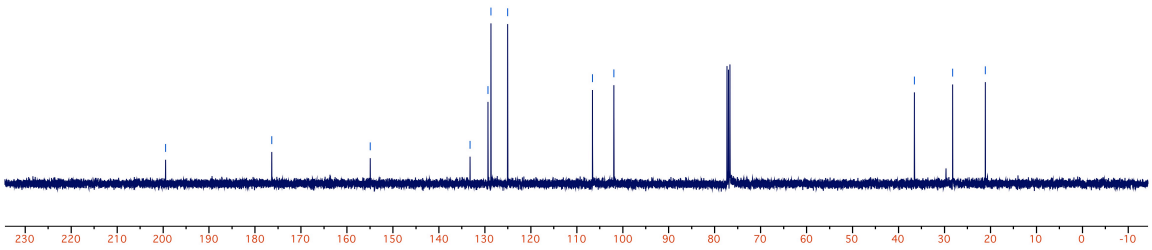

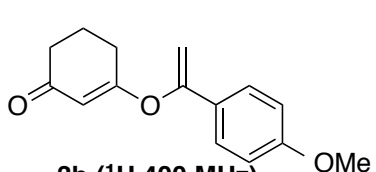


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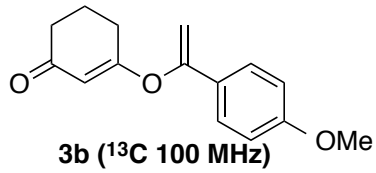


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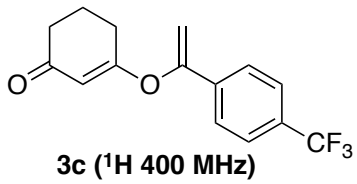

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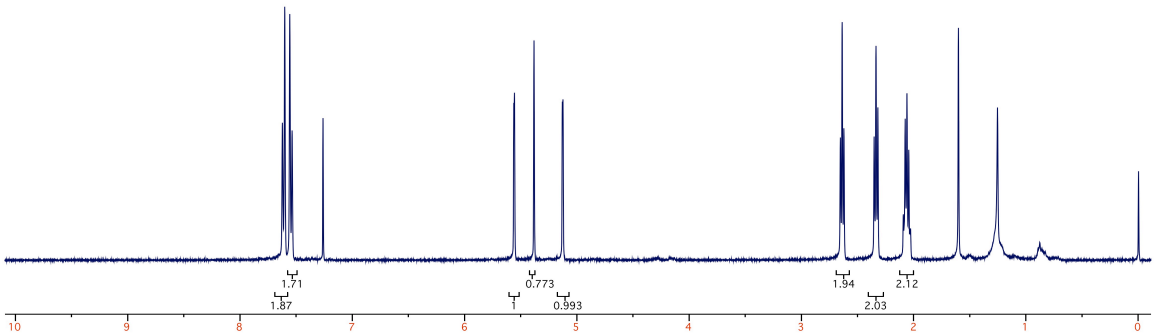



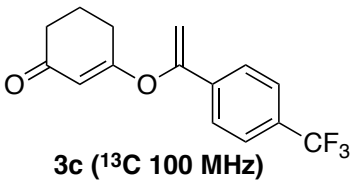

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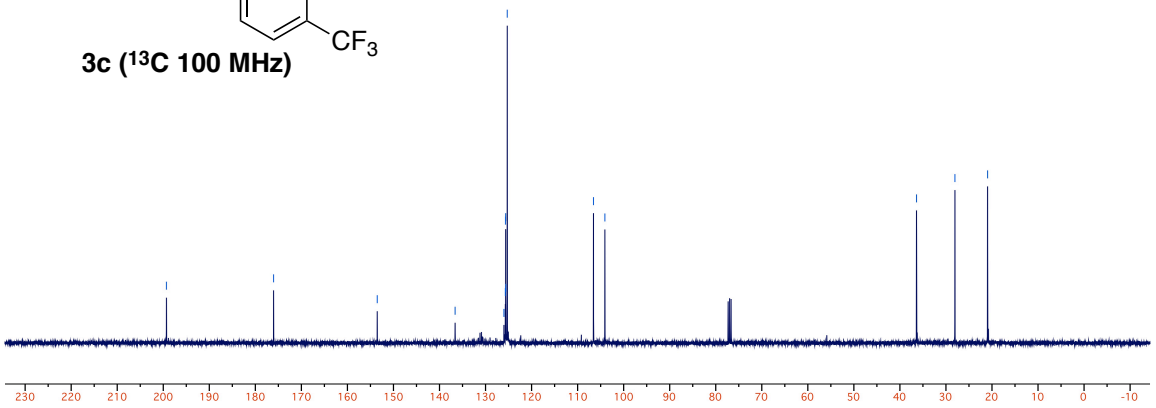

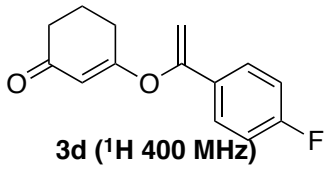


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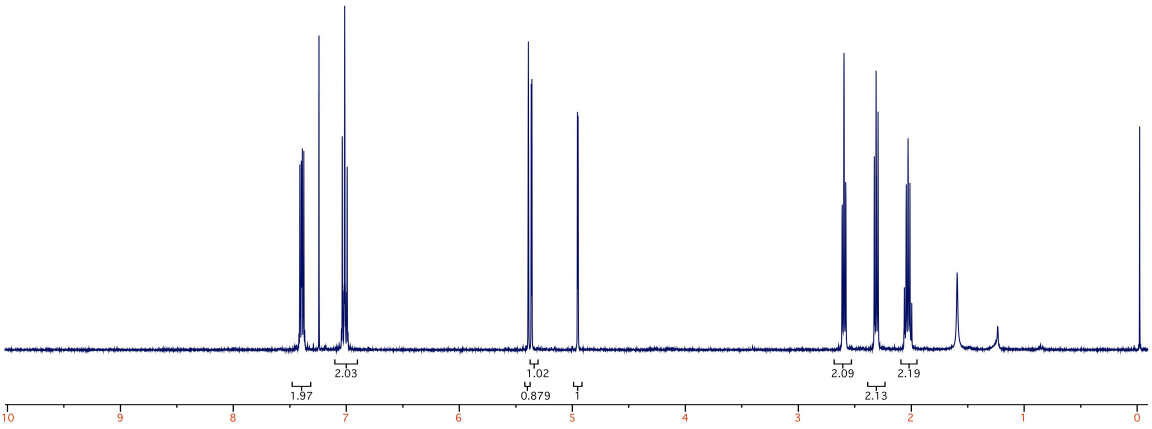



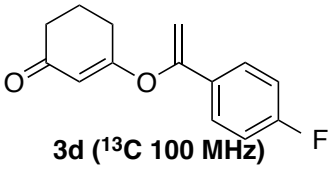


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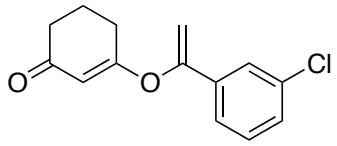


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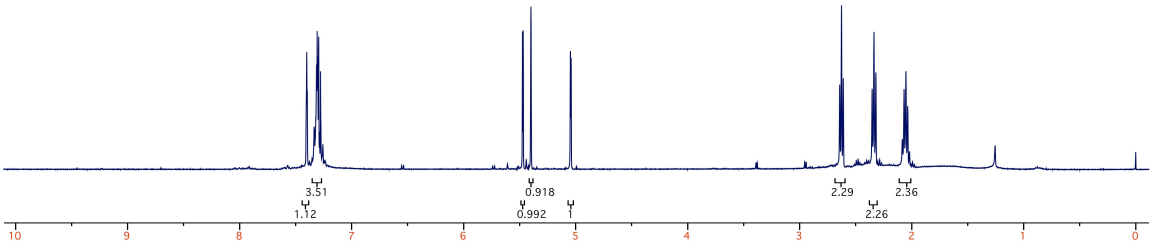



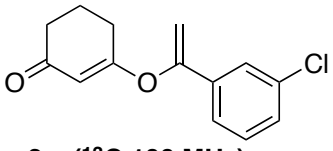


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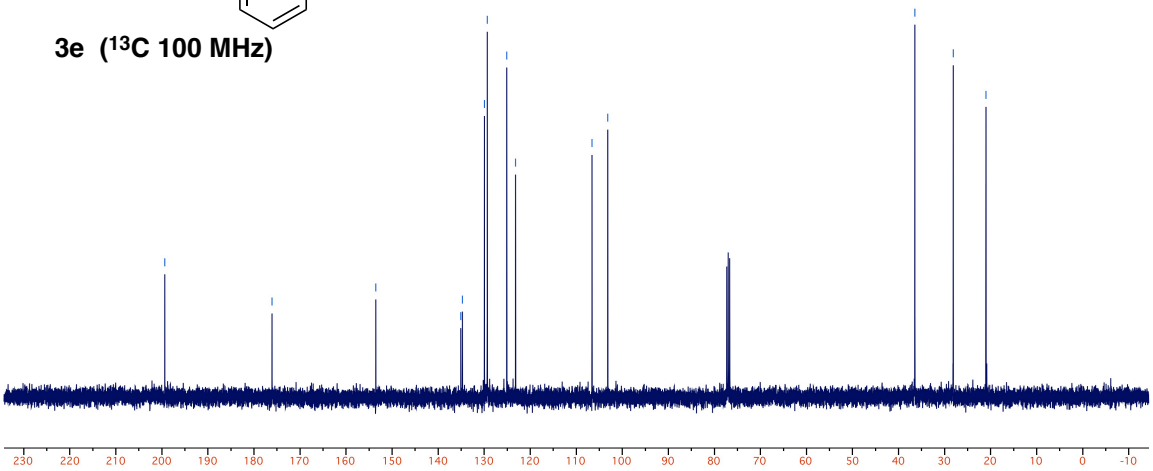

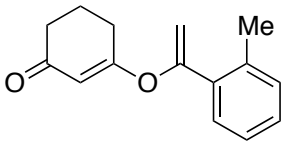


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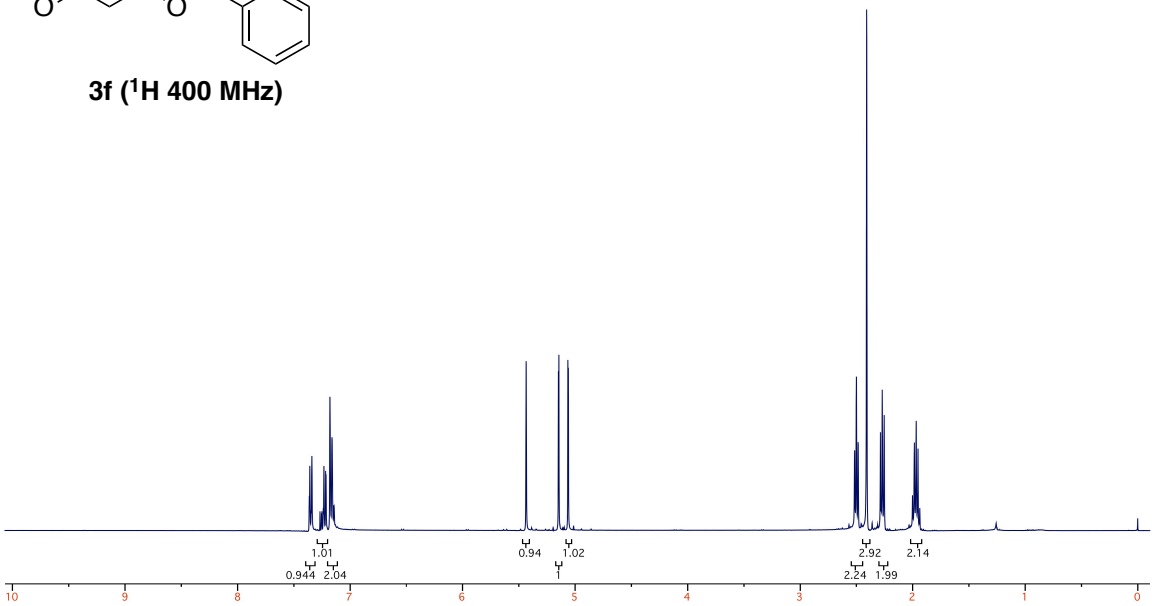


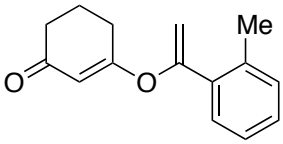


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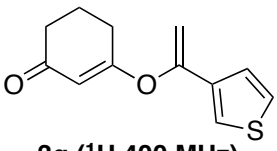

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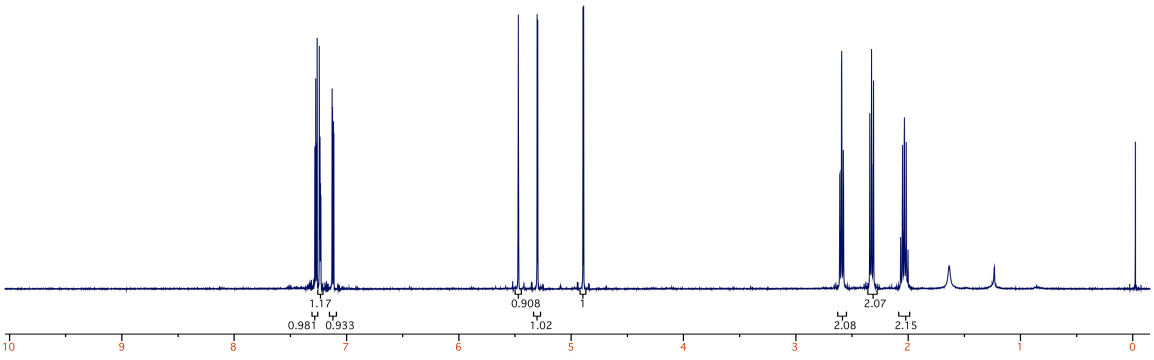


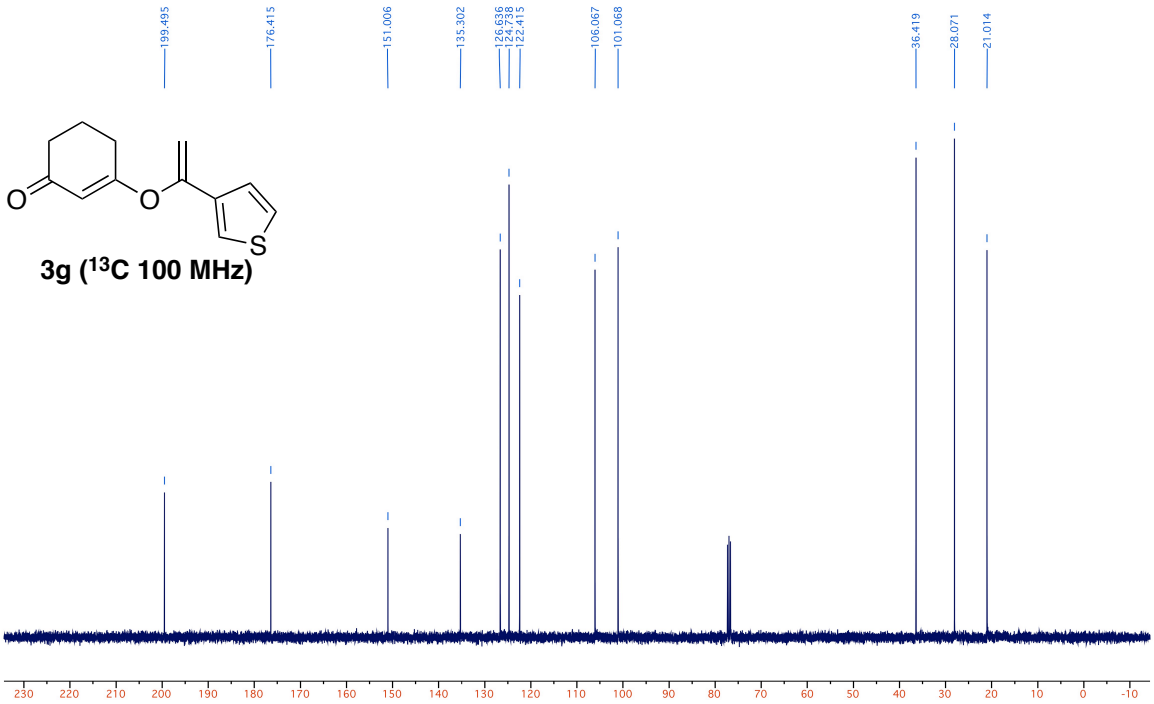




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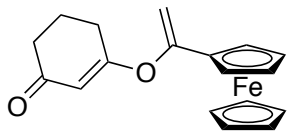


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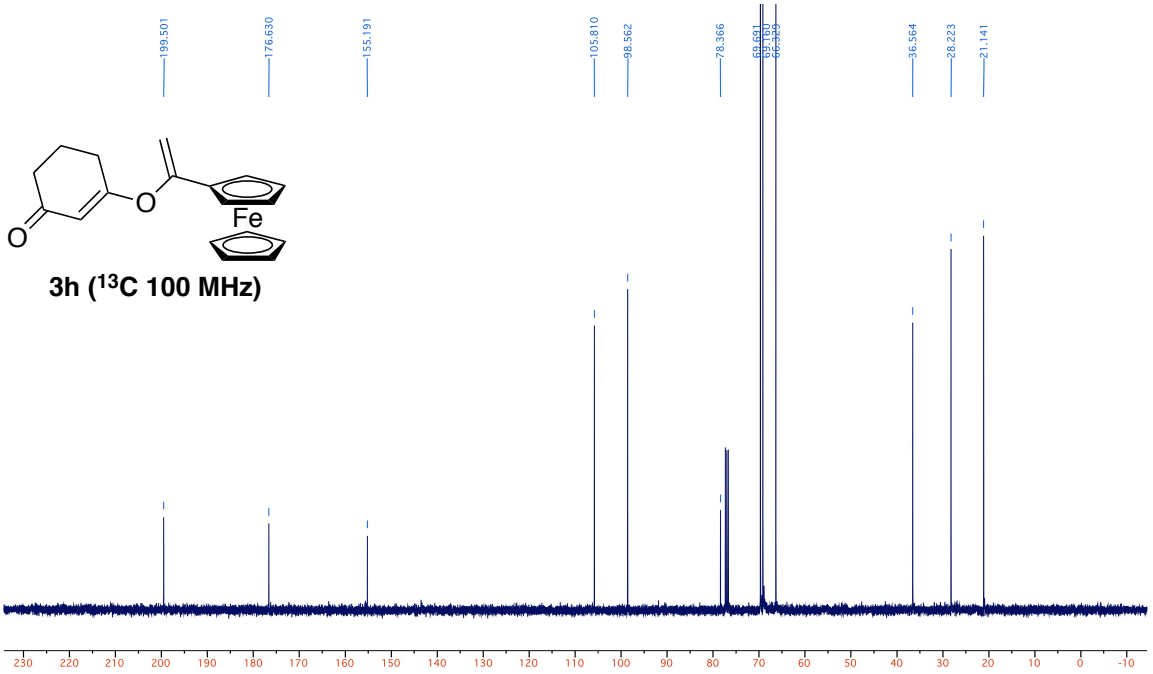





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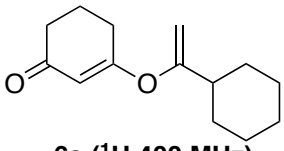

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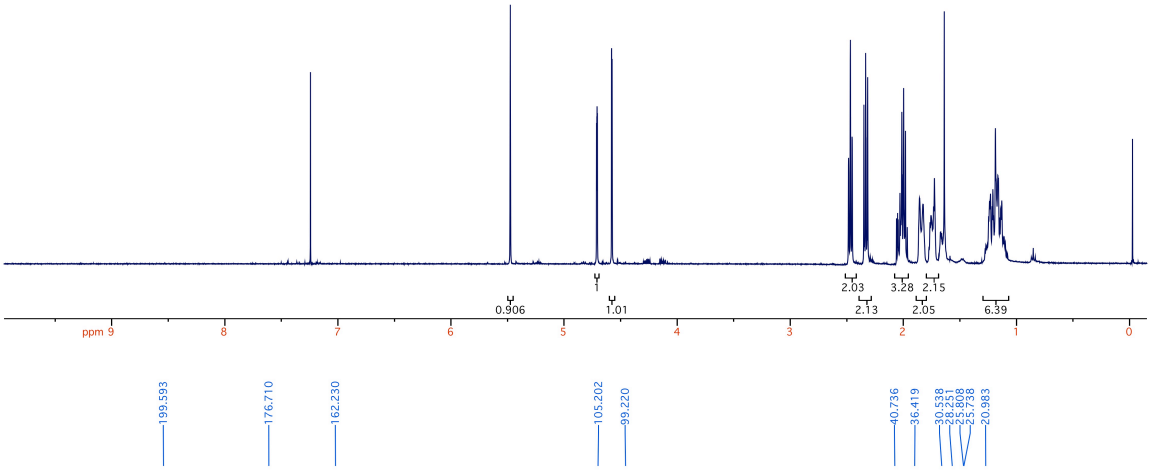





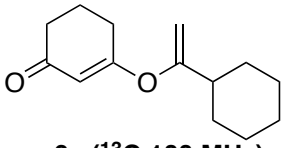

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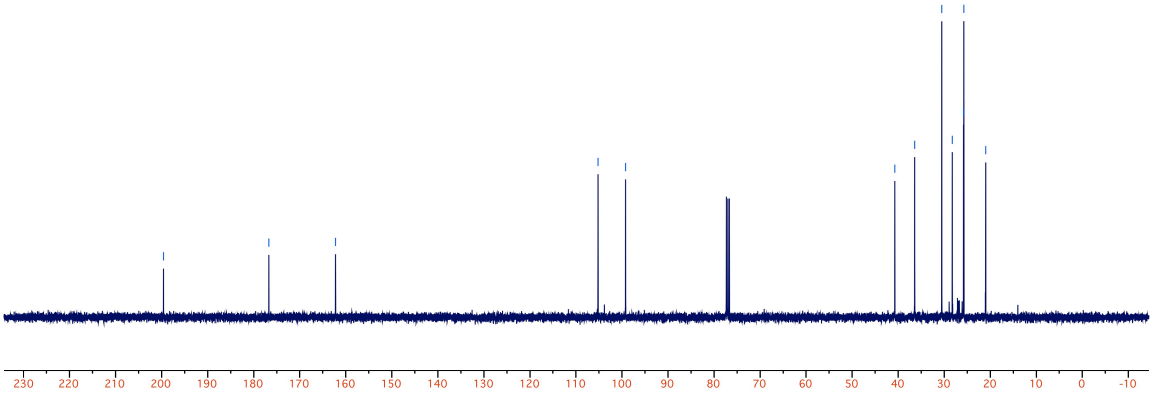

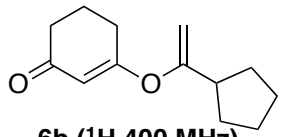

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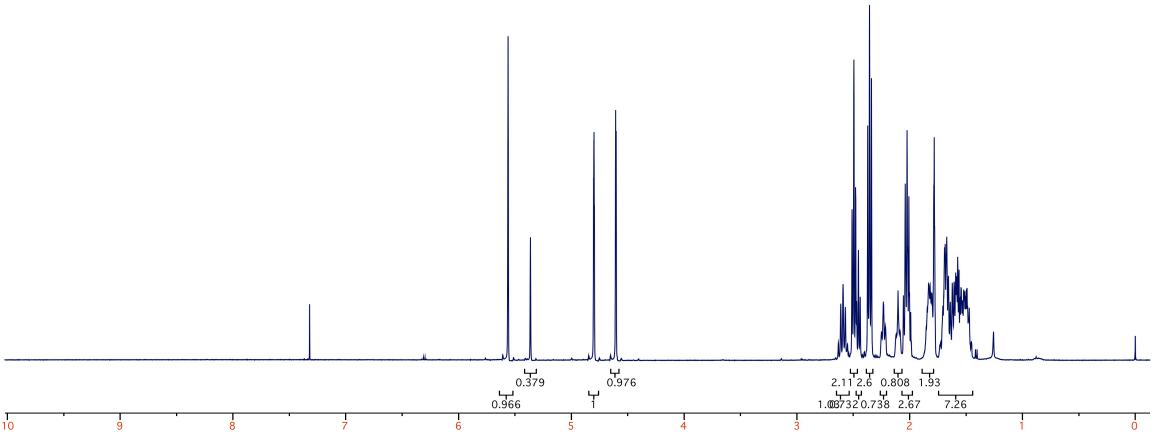



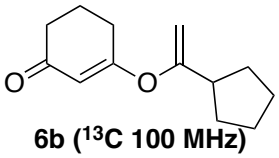

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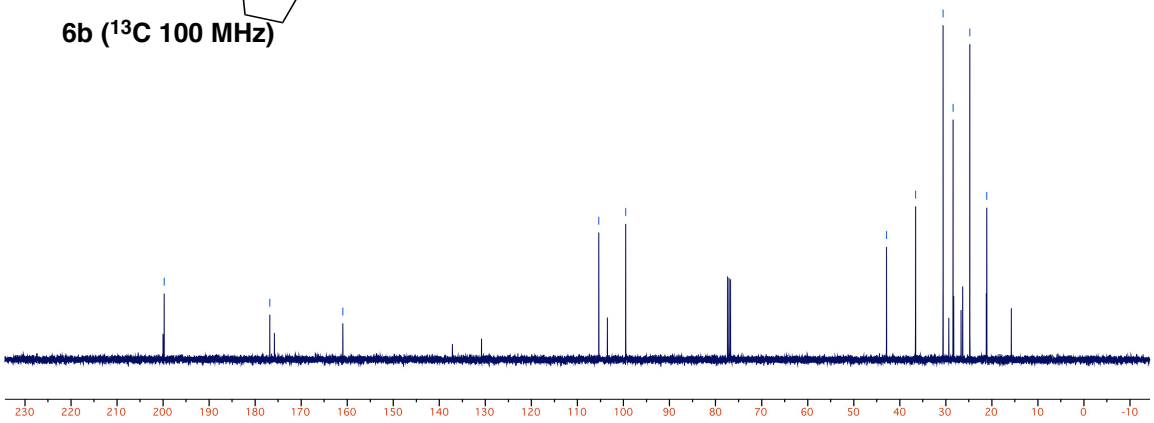

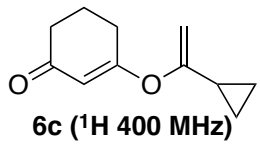

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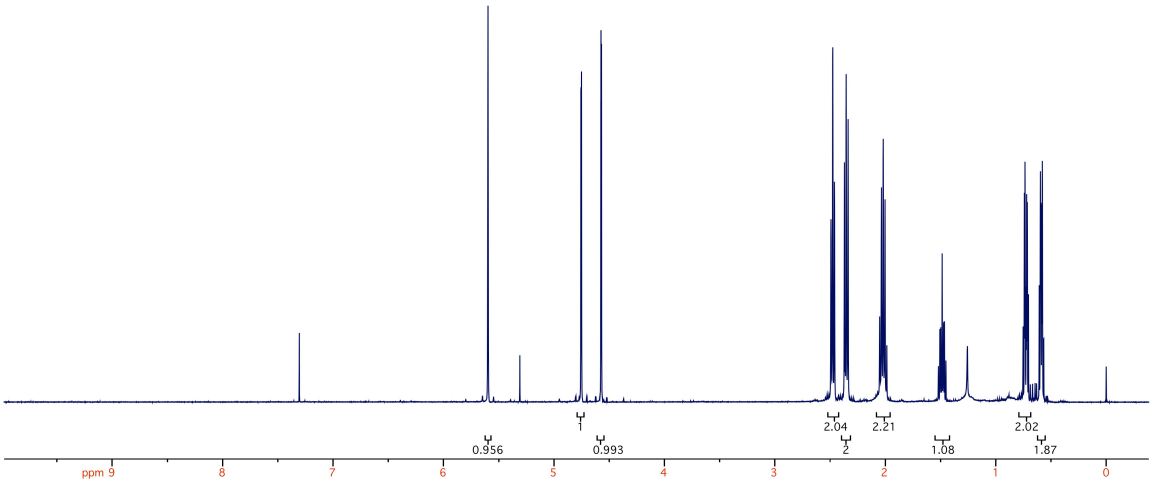


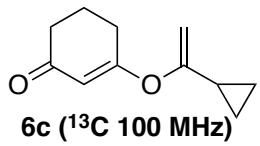

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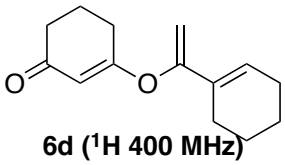

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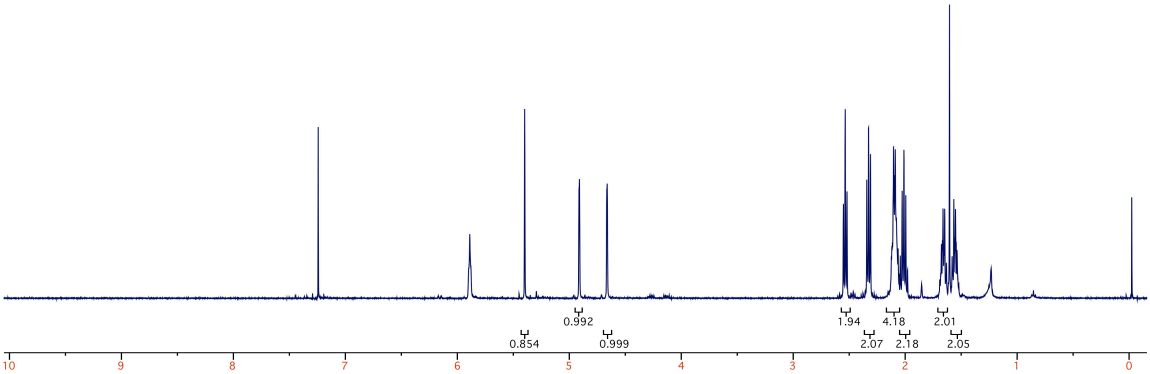



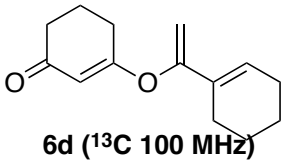

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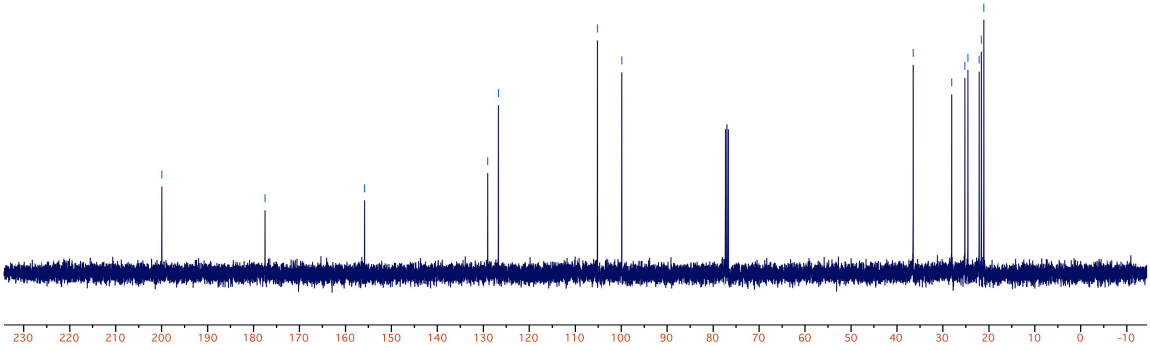

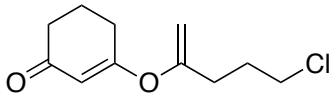


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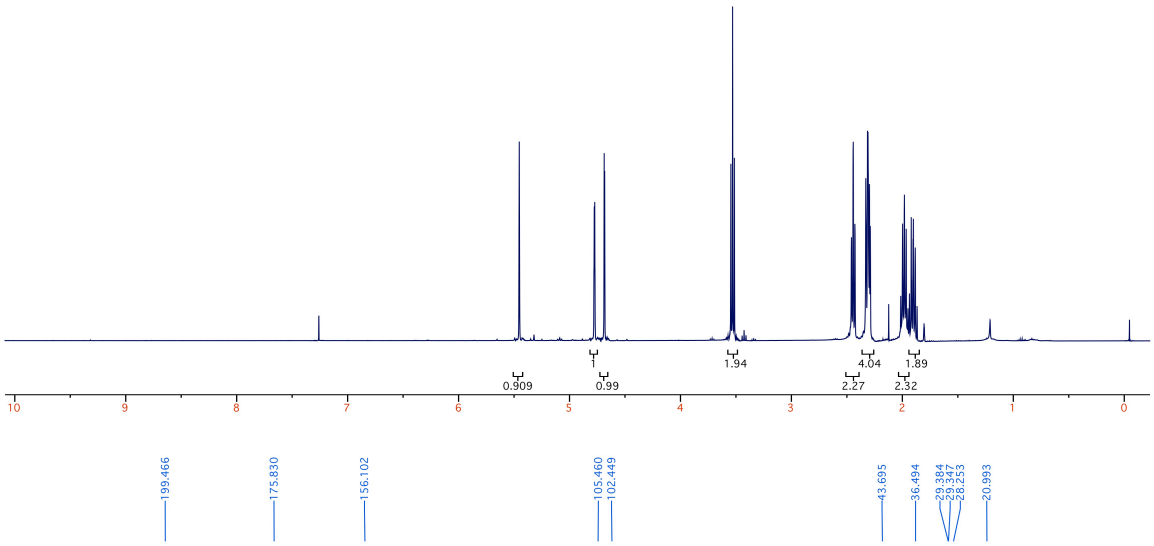





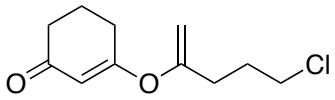


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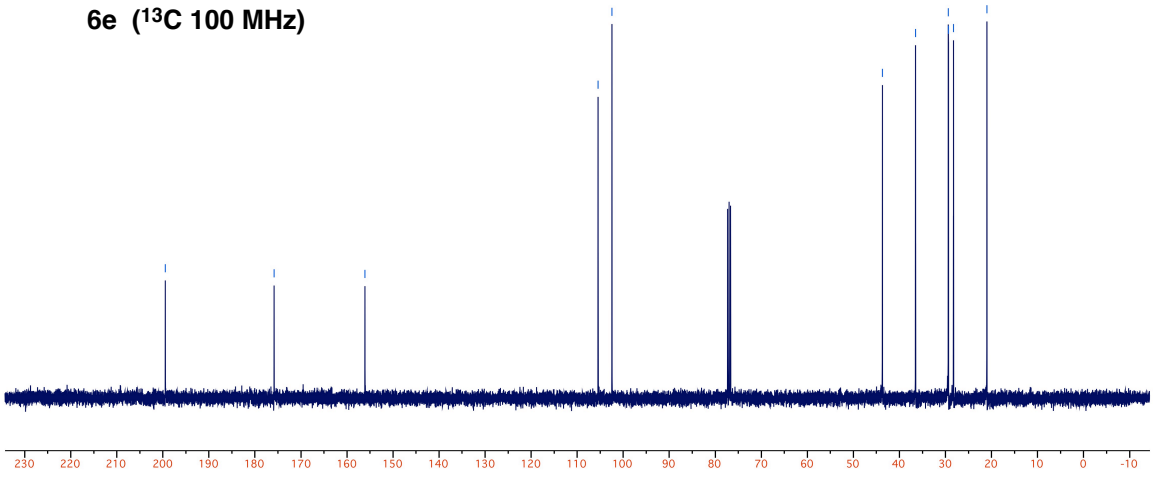
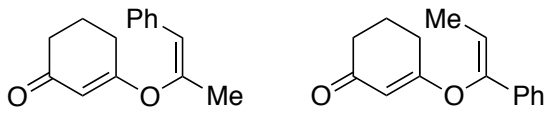


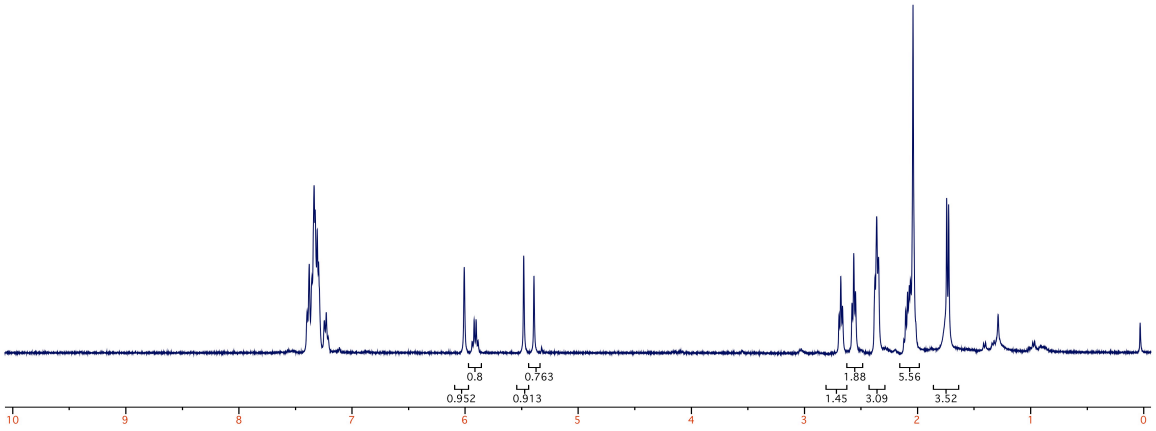


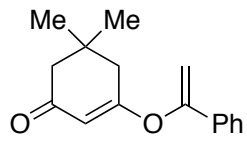

**8a**




**8b**

(**$^1$H 400 MHz**)

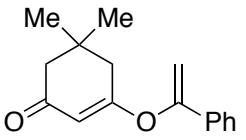




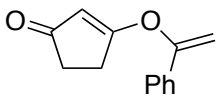

**10a ($^{1}$H 400 MHz)**








**10a ($^{13}$C 100 MHz)**

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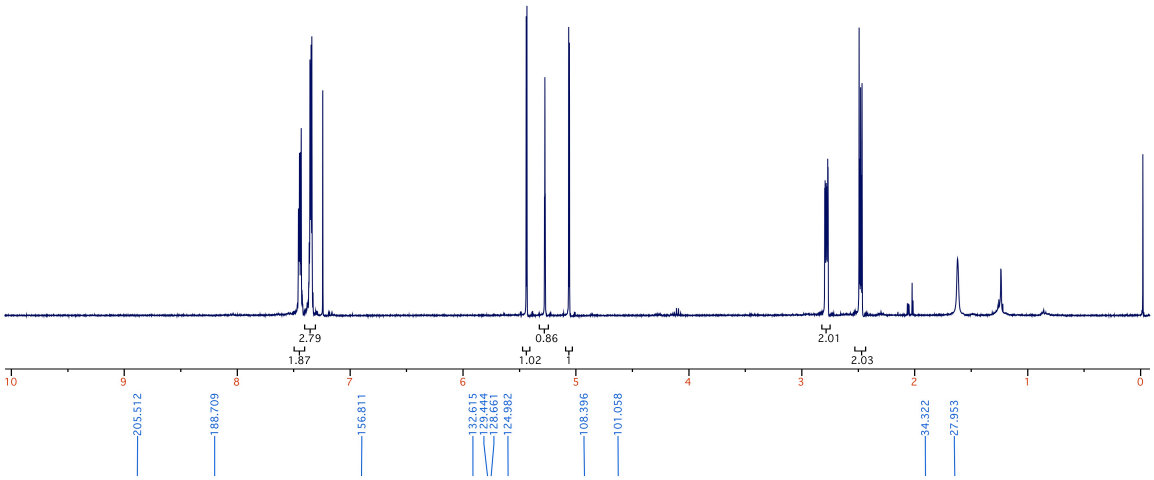


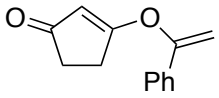


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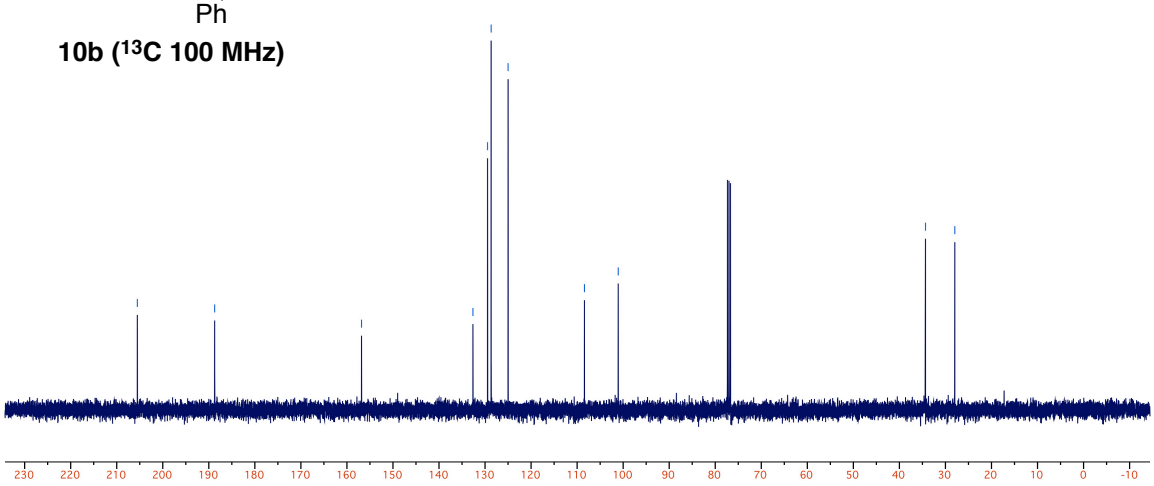

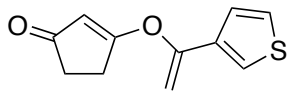

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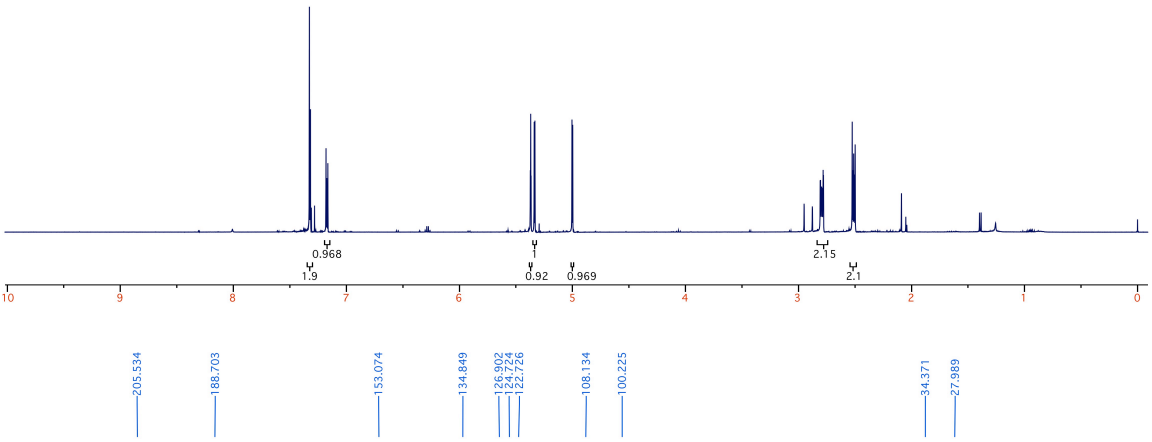
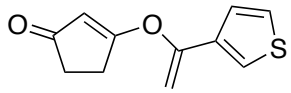
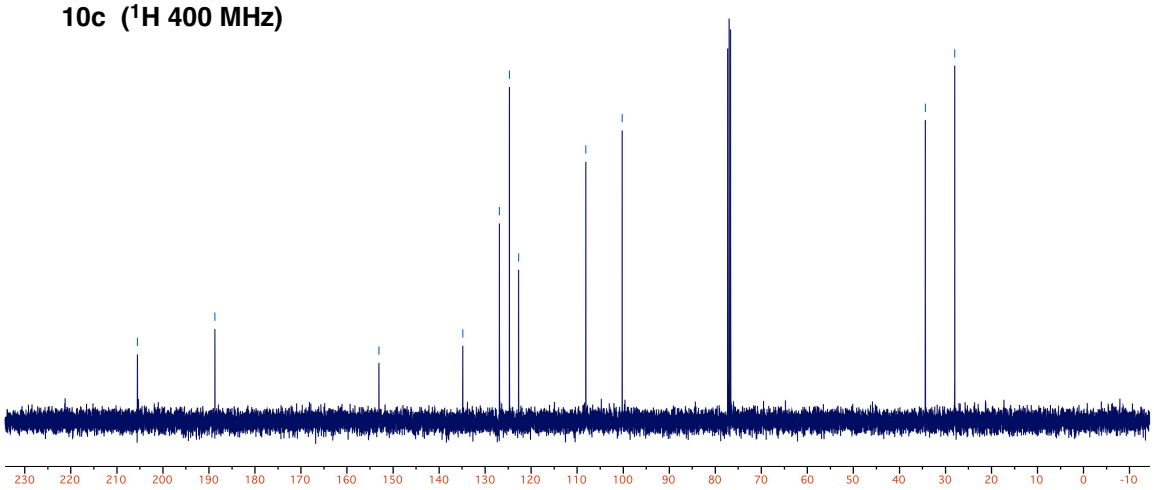


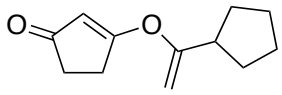




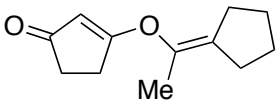


**10c (¹H 400 MHz)**






**10d**




**10d'**

**($^1$H 400 MHz)**