Supplementary Material (ESI) for Chemical Communications


# Preparation of cyclic Alkenylmagnesium Reagents via Iodine/Magnesium Exchange

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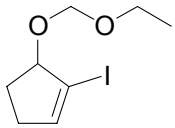
## Supporting Information

### General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under argon. Syringes used to transfer reagents and solvent were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC).



**5-Ethoxymethoxy-1-iodo-cyclopentene** (**1a**).

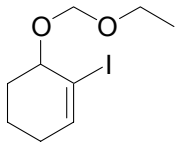
To a solution of 2-iodo-cyclopent-2-enol (390 mg, 1.86 mmol) and (*i*-Pr)$_2$NEt (311 mg, 2.41 mmol) in $CH_2Cl_2$ (4.0 mL) was slowly added chloromethoxy-ethane (228 mg, 2.41 mmol) at -20 °C. The reaction mixture was stirred for 1 h at this temperature and then warmed to rt for 2 h. $CH_2Cl_2$ (10 mL) was added and the organic phase was washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography yielded the pure product **1a** (430 mg, 86 %) as a colorless oil.

$^1$H NMR ($CDCl_3$, 300 MHz): 6.30-6.35 (m, 1 H), 4.76 (s, 2 H), 4.58-4.64 (m, 1 H), 3.55-3.81 (m, 2 H), 2.40-2.55 (m, 1 H), 2.18-2.34 (m, 2 H), 1.84-1.95 (m, 1 H), 1.21 (t, $J$ = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 143.6, 96.4, 94.2, 86.6, 63.4, 32.8, 29.9, 15.0;

IR (film): 2931, 1606, 1391, 1098, 1036, 1012;

MS (IE, 70 ev): 268 ($M^+$, 0.3 %), 238 (9 %), 222 (35 %), 192 (100 %), 111 (47 %).



**6-Ethoxymethoxy-1-iodo-cyclohexene** (**1b**).

To a solution of 2-iodo-cyclohex-2-enol (1.63 g, 7.3 mmol) and (*i*-Pr)$_2$NEt (1.41 g, 11 mmol) in $CH_2Cl_2$ (10.0 mL) was slowly added chloromethoxy-ethane (897 mg, 9.5 mmol) at - 20 °C. The reaction mixture was stirred for 1 h at this temperature and then warmed to rt for 2 h. $CH_2Cl_2$ (25 mL) was added and the organic phase was washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography yielded the pure product **1b** (1.91 g, 93 %) as a colorless oil.

$^1$H NMR ($CDCl_3$, 300 MHz): 6.52 (t, *J* = 4.0 Hz, 1 H), 4.77 (d, *J* = 7.1 Hz, 1 H ), 4.73 (d, *J* = 7.1 Hz, 1 H), 4.09 (t, *J* = 4.2 Hz, 1 H), 3.74-3.84 (m, 1 H), 3.58-3.68 (m, 1 H), 1.55-2.17 (m, 6 H), 1.20 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 142.0, 99.0, 94.2, 77.1, 63.7, 30.0, 29.3, 17.0, 14.9;

IR (film): 2936, 1629, 1440, 1391, 1028 cm$^{-1}$;

MS (EI, 70 ev): 282 ($M^+$, 0.5 %), 252 (4 %), 236 (33 %), 206 (99 %), 125 (100 %), 79 (98 %).

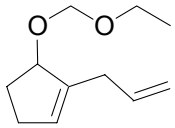
Typical Procedure for the compounds of **3a**, **3b**, **3d**:

To a solution of 5-ethoxymethoxy-1-iodo-cyclopentene (**1a**) (268 mg, 1.0 mmol) in THF (0.3 mL) was slowly added *i*-PrMgCl·LiCl (0.51 mL, 1.1 mmol, 2.16 M in THF) at - 25 °C. After 5 h, a complete conversion to the Grignard reagent (**2a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Electrophiles (allylbromide, PhSSPh, PhCHO, 1.1 mmol) in THF(1.0 mL) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography yielded the pure product.

Typical Procedure for the compounds of **3g**, **3h**, **3i**:

To a solution of 6-ethoxymethoxy-1-iodo-cyclohexene (**1b**) (282 mg, 1.0 mmol) in THF (0.3 mL) was slowly added *i*-PrMgCl·LiCl (0.51 mL, 1.1 mmol, 2.16 M in THF) at – 40 °C. After 12 h, a complete conversion to the Grignard reagent (**2b**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Electrophiles (allylbromide, PhSSPh, PhCHO, 1.1

mmol) in THF(1.0 mL) was added and the reaction mixture was warmed up to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography yielded the pure product.




**1-Allyl-5-ethoxymethoxy-cyclopentene** (**3a**).

Yield: 91 %; colorless oil.

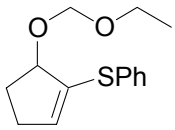
$^1$H NMR ($CDCl_3$, 400 MHz): 5.79-5.90 (m, 1 H), 5.57-5.60 (m, 1 H), 4.99-5.07 (m, 2 H), 4.74 (d, *J* = 6.9 Hz, 1 H), 4.68 (d, *J* = 6.9 Hz, 1 H), 4.56-4.59 (m, 1 H), 3.54-3.67 (m, 2 H), 2.75-2.96 (m, 2 H), 2.34-2.47 (m, 1 H), 2.11-2.28 (m, 2 H), 1.75-1.85 (m, 1 H), 1.20 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 142.8, 135.9, 128.9, 115.7, 94.2, 83.6, 63.2, 32.9, 30.9, 30.0, 15.1;

IR (film): 2976, 1738, 1640, 1391, 1364, 1099, 1039 cm$^{-1}$;

MS (EI, 70 ev): 181 ($M^+$-H, 0.2 %), 141 (21 %), 106 (95 %), 91 (53 %), 79 (62 %);

HRMS (EI): calcd. for $C_{11}H_{17}O_2$ ($M^+$-H): 181.1229, found: 181.1243 ($M^+$-H).




**(5-Ethoxymethoxy-cyclopent-1-enylsulfanyl)-benzene** (**3b**).

Yield: 82 %; colorless oil.

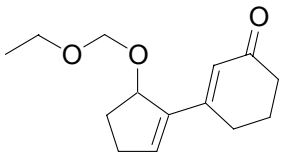
$^1$H NMR (CDCl3, 300 MHz): 7.32-7.40 (m, 2 H), 7.14-7.26 (m, 3 H), 5.69-5.75 (m, 1 H), 4.63 (d, *J* = 7.0 Hz, 1 H), 4.56-4.61 (m, 1 H), 4.55 (d, *J* = 7.0 Hz, 1 H), 3.43-3.57 (m, 2 H), 2.36-2.51 (m, 1 H), 2.13-2.31 (m, 2 H), 1.83-1.95 (m, 1 H), 1.07 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 137.8, 134.1, 133.7, 131.7, 129.0, 127.2, 94.1, 82.0, 63.1, 31.2, 30.6, 14.9;

IR (film): 2974, 1738, 1584, 1477, 1440, 1098, 1042 cm$^{-1}$;

MS (EI, 70 ev), m/z (%): 250 ($M^+$, 13 %), 174 (100 %), 147 (15 %), 110 (14 %);

HRMS (EI): calcd. for $C_{14}H_{18}O_2S$: 250.1028, found: 250.1031.



**3-(5-Ethoxymethoxy-cyclopent-1-enyl)-cyclohex-2-enone** (**3c**).

To a solution of 5-ethoxymethoxy-1-iodo-cyclopentene (**1a**) (268 mg, 1.0 mmol) in THF (0.3 mL) was slowly added *i*-PrMgCl·LiCl (0.51 mL, 1.1 mmol, 2.16 M in THF) at - 25 °C. After 5 h, a complete conversion to the Grignard reagent (**2a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (2.0 mL) and CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) were added at this temperature and stirred for 15 min. The solution of 3-iodo-cyclohex-2-enone (244 mg, 1.1 mmol) in THF (1.0 mL) was added and the reaction mixture was stirred continuously 4 h at –25 °C. Then the reaction mixture was warmed up to 25 °C and quenched with aq. $NH_3$ (2 ml). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography yielded the pure product **3c** (144 mg, 61 %) as a yellow oil.

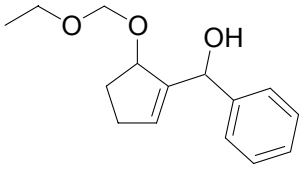
$^1$H NMR ($CDCl_3$, 300 MHz): 6.47 (t, $J$ = 2.7 Hz, 1 H), 6.08 (s, 1 H), 4.90 (dt, $J_1$ = 6.6 Hz, $J_2$ = 2.2 Hz, 1 H), 4.75 (d, $J$ = 7.1 Hz, 1 H), 4.68 (d, $J$ = 7.1 Hz, 1 H), 3.49-3.67 (m, 2 H), 2.32-2.70 (m, 6 H), 1.95-2.18 (m, 4 H), 1.20 (t, $J$ = 7.1 Hz, 3 H);

$^{13}$C NMR (CDCl3, 75 MHz): 200.3, 152.9, 143.1, 140.1, 124.9, 94.4, 81.0, 64.0, 37.4, 31.3, 30.7, 26.6, 22.4, 14.9;

IR (film): 2972, 1659, 1613, 1584, 1448, 1101, 1030 cm$^{-1}$;

MS (EI, 70 ev), m/z (%): 236 ($M^+$, 0.1 %), 206 (2 %), 192 (2 %), 160 (100 %), 147 (11 %), 133 (19 %), 91 (51 %);

HRMS (EI): calcd. for $C_{14}H_{20}O_3$: 236.1413, found: 236.1435.



**(5-Ethoxymethoxy-cyclopent-1-enyl)-phenyl-methanol** (**3d**).

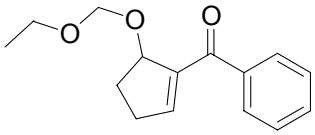
Yield: 89 %, colorless oil, dr = 80:20 (determined by GC).

$^1$H NMR ($CDCl_3$, 300 MHz): 7.08-7.32 (m, 5 H), 5.62 (s, 1 H), 5.34 (s, 1 H), 4.58 (d, *J* = 7.0 Hz, 1 H), 4.49 (d, *J* = 7.0 Hz, 1 H), 3.42 (q, *J* = 7.1 Hz, 2 H), 2.25-2.40 (m, 1 H), 2.03-2.16 (m, 2 H), 1.67-1.79 (m, 1 H), 1.03 (t, *J* = 7.1 Hz, 3 H). The following signals is discernible for the minor isomer: 5.58 (s, 1 H), 5.23 (s, 1 H), 4.60-4.62 (m, 1 H), 4.51-4.52 (m, 1 H), 3.45 (q, *J* = 7.1 Hz, 2 H);

$^{13}$C NMR (CDCl3, 75 MHz): 145.1, 142.7, 132.8, 128.0, 126.9, 125.8, 94.2, 82.7, 71.9, 63.6, 31.2, 29.9, 14.8.

IR (film): 3437, 2932, 1603, 1493, 1452, 1106, 1029 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 247 ($M^+$-H, 0.1 %), 230 (0.2 %), 172 (100 %), 143 (10 %), 105 (79 %).




**(5-Ethoxymethoxy-cyclopent-1-enyl)-phenyl-methanone** (**3e**).

To a solution of 5-ethoxymethoxy-1-iodo-cyclopentene (**1a**) (268 mg, 1.0 mmol) in THF (0.3 mL) was slowly added *i*-PrMgCl·LiCl (0.51 mL, 1.1 mmol, 2.16 M in THF) at - 25 °C. After 5 h, a complete conversion to the Grignard reagent (**2a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (2.0 mL) and CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) were added at this temperature and stirred for 15 min. Benzoyl chloride (211 mg, 1.5 mmol) was added and the reaction mixture was stirred continuously 1 h at – 25 °C. Then the reaction mixture was warmed up to 25 °C and stirred for 2 h and quenched with aq. $NH_3$ (2 ml). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography yielded the pure product **3e** (144 mg, 61 %) as a yellow oil.

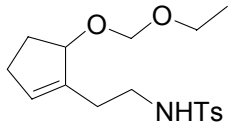
$^1$H NMR ($CDCl_3$, 300 MHz): 7.75-7.80 (m, 2 H), 7.47-7.54 (m, 1 H), 7.37-7.44 (m, 2 H), 6.61 (t, *J* = 2.2 Hz, 1 H), 5.20-5.26 (m, 1 H), 4.83 (d, *J* = 7.1 Hz, 1 H), 4.72 (d, *J* = 7.1 Hz, 1 H), 3.58 (q, *J* = 7.1 Hz, 2 H), 2.70-2.84 (m, 1 H), 2.39-2.52 (m, 1 H), 2.23-2.36 (m, 1 H), 1.93-2.05 (m, 1 H), 1.16 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR (CDCl3, 75 MHz): 193.0, 148.0, 144.6, 138.6, 132.1, 129.0, 128.2, 94.7, 81.0, 63.2, 31.9, 30.7, 15.0;

IR (film): 2974, 1738, 1651, 1447, 1107, 1037 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 201 ($M^+$- $OC_2H_5$, 1 %), 187 (8 %), 172 (100 %), 157 (7 %), 144 (9 %), 105 (89 %);

HRMS (EI): calcd. for $C_{13}H_{13}O_2$ ($M^+$- $OC_2H_5$): 201.0916, found: 201.0907 ($M^+$- $OC_2H_5$).




**N-[2-(5-Ethoxymethoxy-cyclopent-1-enyl)-ethyl]-4-methyl-benzenesulfonamide** (**3f**).

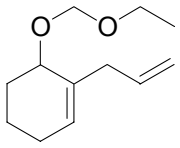
To a solution of 5-ethoxymethoxy-1-iodo-cyclopentene (**1a**) (268 mg, 1.0 mmol) in THF (0.3 mL) was slowly added *i*-PrMgCl·LiCl (0.51 mL, 1.1 mmol, 2.16 M in THF) at - 25 °C. After 5 h, a complete conversion to the Grignard reagent (**2a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (2.0 mL) and CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) were added at this temperature and stirred for 15 min. The solution of 1-(toluene-4-sulfonyl)-aziridine (217 mg, 1.1 mmol) in THF (1.0 mL) was added and the reaction mixture was stirred continuously 1 h at – 25 °C. Then the reaction mixture was warmed up to 25 °C and stirred for 12 h and then quenched with aq. $NH_3$ (2 ml). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:2) yielded the pure product **3f** (214 mg, 63 %) as a colorless oil.

$^1$H NMR ($CDCl_3$, 300 MHz): 7.70, (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 5.50-5.54 (m, 1 H), 5.00-5.10 (m, 1 H), 4.66 (d, *J* = 7.1 Hz, 1 H), 4.60 (d, *J* = 7.1 Hz, 1 H), 4.40-4.48 (m, 1 H), 3.48-3.58 (m, 2 H), 2.93-3.17 (m, 2 H), 2.39 (s, 3 H), 2.05-2.39 (m, 5 H), 1.65-1.81 (m, 1 H), 1.16 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 143.1, 140.3, 137.0, 131.9, 129.5, 127.1, 94.1, 83.8, 63.5, 41.9, 30.7, 30.1, 28.4, 21.4, 15.0;

IR (film): 3279, 2930, 1598, 1495, 1435, 1328, 1160 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 280 ($M^+$- $CH_2OCH_2CH_3$, 8 %), 263 (9 %), 184 (60 %), 155 (100 %), 138 (12 %), 108 (12 %).



**1-Allyl-6-ethoxymethoxy-cyclohexene** (**3g**).

Yield: 81 %; colorless oil.

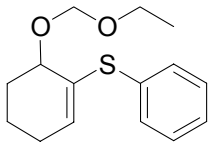
$^1$H NMR ($CDCl_3$, 300 MHz): 5.70-5.86 (m,1 H), 5.56-5.65 (m, 1 H), 4.96-5.05 (m, 1 H), 4.98 (t, *J* = 1.3 Hz, 1 H), 4.77 (d, *J* = 7.1 Hz, 1 H), 4.66 (d, *J* = 7.1 Hz, 1 H), 3.94 (s, 1 H), 3.54-3.73 (m, 2 H), 2.77-2.82 (m, 2 H), 1.82-2.09 (m, 3 H), 1.47-1.73 (m, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 136.7, 136.1, 127.0, 115.8, 94.0, 72.0, 63.3, 38.6, 28.5, 25.3, 17.8, 15.0;

IR (film): 2975, 1738, 1639, 1440, 1391, 1099, 1033 cm$^{-1}$;

MS (EI, 70 ev), m/z (%): 195 ($M^+$- H, 0.1 %), 166 (1 %), 155 (10 %), 120 (100 %), 105 (21 %), 79 (80 %);

HRMS (EI): calcd. for $C_{12}H_{19}O_2$ ($M^+$- H): 195.1385 , found: 195.1390 ($M^+$- H).




**(6-Ethoxymethoxy-cyclohex-1-enylsulfanyl)-benzene** (**3h**).

Yield: 81 %; colorless oil.

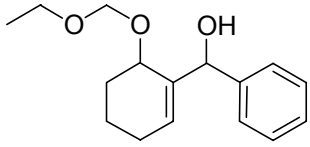
$^1$H NMR ($CDCl_3$, 300 MHz): 7.08-7.30 (m, 5 H), 6.07 (t, *J* = 4.0 Hz, 1 H), 4.66 (d, *J* = 7.1 Hz, 1 H), 4.58 (d, J = 7.1 Hz, 1 H), 3.98 (s, 1 H), 3.46-3.68 (m, 2 H), 1.50-2.19 (m, 6 H), 1.07 (t, *J* = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 136.9, 135.3, 132.8, 130.3, 128.9, 126.4, 94.2, 71.4, 63.2, 29.3, 27.0, 16.9, 14.9;

IR (film): 2933, 1582, 1478, 1440, 1106, 1032 cm$^{-1}$;

MS (EI, 70 ev), m/z (%): 264 ($M^+$, 11 %), 188 (100 %), 173 (8 %), 147 (12 %), 110 (14 %);

HRMS (EI): calcd. for $C_{12}H_{20}O_2S$: 264.1184 , found: 264.1190.




**(6-Ethoxymethoxy-cyclohex-1-enyl)-phenyl-methanol** (**3i**).

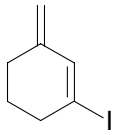
Yield: 81 %, colorless oil, dr = 80:20 (determined by GC). The two isomers can be separated by repeated flash chromatography on silica gel.

Less polar isomer: $^1$H NMR ($CDCl_3$, 300 MHz): 7.18-7.38 (m, 5 H), 5.87 (t, $J$ = 3.5 Hz, 1 H), 5.23 (d, $J$ = 6.6 Hz, 1 H ), 4.68 (d, $J$ = 6.6 Hz, 1 H), 4.49 (d, $J$ = 6.6 Hz, 1 H), 4.06-4.09 (m, 1 H), 3.67 (d, $J$ = 7.1 Hz, 1 H), 3.43-3.58 (m, 2 H), 1.49-2.24 (m, 6 H), 1.13 (t, $J$ = 7.1 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 143.0, 138.8, 131.3, 128.0, 126.7, 125.8, 94.2, 77.8, 72.0, 63.8, 28.6, 25.2, 18.2, 14.9;

IR (film): 3450, 2932, 1602, 1492, 1450, 1104, 1031 cm$^{-1}$;

MS (EI, 70 ev), m/z (%): 262 ($M^+$, 0.1 %), 203 (3 %), 186 (100 %), 168 (11 %), 157 (22 %), 129 (21 %), 105 (48 %).




**1-Iodo-3-methylene-cyclohexene** (**4**).

To a solution of methyltriphenylphosphonium bromide (1.18 g, 3.3 mmol) in THF (15 mL) was slowly added *n*-BuLi (2.2 mL, 3.3 mmol, 1.50 M in Hexane) at - 78°C, then warmed to 0 $^o$C and stirred for 1 h. The reaction mixture was cooled to - 78°C and slowly transfered to a solution of 3-iodo-cyclohex-2-enone (666 mg, 3.0 mmol) in THF (20 mL) and stirred overnight at room temperature. Quenched with $NH_4Cl$ (aq) and the aqueous phase was extracted with diethyl ether (3 × 200 mL). The organic fractions were washed with brine (20 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane) yielded the pure product (554 mg, 84 %) as a colorless oil.

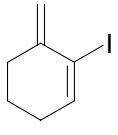
$^1$H NMR ($CDCl_3$, 300 MHz): 6.79 (s, 1 H), 4.72 (s, 1 H), 4.65 (s, 1 H), 2.60 (t, $J$ = 6.2 Hz, 2 H), 2.29-2.35 (m, 2 H), 1.70-1.79 (m, 2 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 143.2, 139.9, 111.6, 100.8, 39.6, 29.0, 24.9;

IR (film): 2937, 1676, 1624, 1589, 1426, 1335, 892 cm$^{-1}$;

MS (EI, 70 ev), m/z (%): 220 ($M^+$, 100 %), 192 (0.2 %), 127 (1 %), 91 (15 %), 77 (16 %);

HRMS (EI): calcd. for $C_7H_9I$: 219.9747, found: 219.9771.

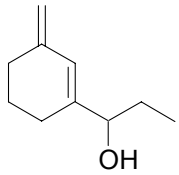


**1-Iodo-6-methylene-cyclohexene** (**5**).

The reaction was carried out according to the procedure for 1-iodo-3-methylene-cyclohexene (**4**). Methyltriphenylphosphonium bromide (1.18 g, 3.3 mmol) and 3-iodo-cyclohex-2-enone (666 mg, 3.0 mmol) yielded the product 1-iodo-6-methylene-cyclohexene (**5**) (67 mg , 10 %) as a colorless oil.

$^1$H NMR ($CDCl_3$, 200 MHz): 6.65-6.69 (m, 1 H), 5.17 (s, 1 H), 5.04 (s, 1 H), 2.51-2.61 (m, 2 H), 2.18-2.30 (m, 2 H), 1.75-1.84 (m, 2 H);

MS (EI, 70 ev), m/z (%): 220 ($M^+$, 100 %), 205 (1 %), 127 (5 %), 91 (64 %), 77 (63 %).




**1-(3-Methylene-cyclohex-1-enyl)-propan-1-ol** (**7**).

To a solution of 1-iodo-3-methylene-cyclohexene (**4**) (110 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.26 mL, 0.55 mmol, 2.16 M in THF) at - 40 °C. After 4 h, a complete conversion to the Grignard reagent (**6**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. The solution of propionaldehyde (32 mg, 0.55 mmol) in THF (0.5 mL) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:3) yielded the pure product **7** (69 mg, 91 %) as a colorless oil.

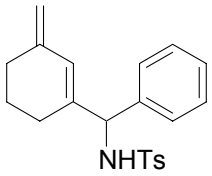
$^1$H NMR ($CDCl_3$, 300 MHz): 6.09 (s, 1 H), 4.76(s, 1 H), 4.75 (s, 1 H), 3.96 (t, $J$ = 6.6 Hz, 1 H), 2.25-2.35 (m, 2 H), 2.06-2.19 (m, 1 H), 1.92-2.03 (m, 1 H), 1.50-1.76 (m, 4 H), 0.87 (t, $J$ = 7.5 Hz, 3 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 143.6, 143.2, 125.2, 110.6, 77.3, 30.8, 27.8, 24.1, 23.0, 9.9;

IR (film): 3391, 2960, 1662, 1607, 1455 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 152 ($M^+$, 11 %), 134 (4 %), 123 (100 %), 95 (55 %), 77 (20 %);

HRMS (EI): calcd. for $C_{10}H_{16}O$: 152.1201, found: 152.1203.




**4-Methyl-N-[(3-methylene-cyclohex-1-enyl)-phenyl-methyl]-benzenesulfonamide** (**8**).

To a solution of 1-iodo-3-methylene-cyclohexene (**4**) (110 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.26 mL, 0.55 mmol, 2.16 M in THF) at - 40 °C. After 4 h, a complete conversion to the Grignard reagent (**6**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. The solution of N-benzylidene-4-methyl-benzenesulfonamide (142 mg, 0.55 mmol) in THF (0.5 mL) was added and the reaction mixture was warmed to 25 °C and quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:2) yielded the pure product **8** (150 mg, 85 %) as a white solid, mp: 127.1-127.7 $^oC$.

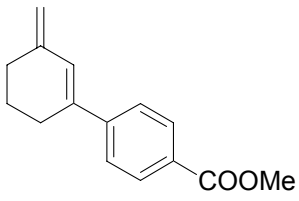
$^1H$ NMR ($CDCl_3$, 300 MHz): 7.61 (d, $J$ = 8.4 Hz, 2 H), 7.03-7.22 (m, 7 H), 5.99 (s, 1 H), 5.02 (d, $J$ = 7.7 Hz, 1 H), 4.90 (d, $J$ = 7.7 Hz, 1 H), 4.73 (s, 1 H), 4.68 (s, 1 H), 2.36 (s, 3 H), 1.40-2.30 (m, 6 H);

$^{13}C$ NMR ($CDCl_3$, 75 MHz): 143.2, 142.5, 138.9, 138.8, 137.5, 129.3, 128.5, 127.7, 127.6, 127.3, 126.9, 111.7, 62.8, 30.2, 25.6, 22.5, 21.4;

IR (KBr): 3436, 3290, 1643, 1599, 1494, 1455, 1435, 1320, 1160 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 353 ($M^+$, 2 %), 260 (3 %), 198 (100 %), 182 (19 %), 167 (22 %), 91 (43 %);

HRMS (EI): calcd. for $C_{21}H_{23}NO_2S$: 353.1449, found: 353.1463.




**4-(3-Methylene-cyclohex-1-enyl)-benzoic acid methyl ester** (**9**).

To a solution of 1-iodo-3-methylene-cyclohexene (**4**) (110 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.26 mL, 0.55 mmol, 2.16 M in THF) at - 40 °C. After 4 h, a complete conversion to the Grignard reagent (**6**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. The solution of $ZnBr_2$ (0.55 mL, 0.55 mmol, 1.0 M in THF) was added at -40 °C and warmed to 0 $^oC$ and stirred for 20 min. The solution of methyl 4-

iodobenzoate (144 mg, 0.55 mmol) in THF (0.5 mL), Pd(dba)2 (14.4 mg, 5 mol %) and tri(2-furyl)phosphine (12 mg, 10 mol %) were added and the reaction mixture was stirred overnight at room temperature then quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:2) yielded the pure product **9** (107 mg, 94 %) as a white solid, mp: 59.3 - 60.7 $^oC$.

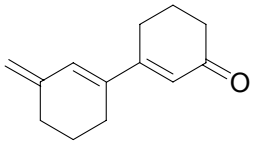
$^1H$ NMR ($CDCl_3$, 300 MHz): 7.97 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 6.67 (s, 1 H), 4.97 (s, 1 H), 4.92 (s, 1 H), 3.89 (s, 3 H), 2.51 (t, *J* = 5.7 Hz, 2 H), 2.36-2.42 (m, 2 H), 1.81-1.89 (m, 2 H);

$^{13}C$ NMR ($CDCl_3$, 75 MHz): 166.9, 145.8, 143.5, 138.1, 129.6, 128.6, 128.4, 125.0, 113.0, 52.0, 30.1, 27.3, 23.0;

IR (KBr): 2948, 1718, 1601, 1434, 1289, 1111 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 228 ($M^+$, 100 %), 213 (7 %), 197 (19 %), 169 (22 %), 154 (18 %), 141 (23 %);

HRMS (EI): calcd. for $C_{15}H_{16}O_2$: 228.1150, found: 228.1132.




**3-(3-Methylene-cyclohex-1-enyl)-but-2-enal** (**10**).

To a solution of 1-iodo-3-methylene-cyclohexene (**4**) (110 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.26 mL, 0.55 mmol, 2.16 M in THF) at - 40 °C. After 4 h, a complete conversion to the Grignard reagent (**6**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. The solution of $ZnBr_2$ (0.55 mL, 0.55 mmol, 1.0 M in THF) was added at -40 °C and warmed to 0 $^oC$ and stirred for 20 min. The solution 3-bromo-cyclohex-2-enone (88 mg, 0.5 mmol) in THF (0.5 mL), $Pd(dba)_2$ (14.4 mg, 5 mol %) and tri(2-furyl)phosphine (12 mg, 10 mol %) were added and the reaction mixture was stirred overnight at room temperature then quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:1) yielded the pure product **10** (66 mg, 70 %) as a yellow oil.

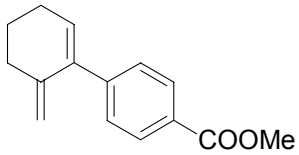
$^1H$ NMR ($CDCl_3$, 300 MHz): 6.63 (s, 1 H), 6.10 (s, 1 H), 5.00-5.04 (m, 2 H), 2.54 (t, *J* = 6.0 Hz, 2 H), 2.23-2.41 (m, 6 H), 1.97-2.06 (m, 2 H), 1.71-1.79 (m, 2 H);

$^{13}$C NMR ($CDCl_3$, 75 MHz): 200.4, 158.5, 143.4, 137.8, 131.9, 123.9, 115.8, 37.5, 29.9, 25.7, 25.3, 22.54, 22.51;

IR (film): 2927, 1706, 1662, 1187 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 188 ($M^+$, 100 %), 173 (11 %), 160 (32 %), 145 (31 %), 117 (53 %);

HRMS (EI): calcd. for $C_{13}H_{16}O$: 188.1201, found: 188.1189.




**4-(6-Methylene-cyclohex-1-enyl)-benzoic acid methyl ester** (**12**).

To a solution of 1-iodo-3-methylene-cyclohexene (**5**) (60 mg, 0.27 mmol) in THF (0.1 mL) was slowly added *i*-PrMgCl·LiCl (0.15 mL, 0.30 mmol, 2.0 M in THF) at - 40 °C. After 4 h, a complete conversion to the Grignard reagent (**11**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. The solution of $ZnBr_2$ (0.3 mL, 0.3 mmol, 1.0 M in THF) was added at -40 °C and warmed to 0 $^oC$ and stirred for 20 min. The solution of methyl 4-iodobenzoate (78 mg, 0.3 mmol) in THF (0.3 mL), $Pd(dba)_2$ (8 mg, 5 mol %) and tri (2-furyl) phosphine (6 mg, 10 mol %) were added and the reaction mixture was stirred overnight at room temperature then quenched as usual. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:5) yielded the pure product **12** (55 mg, 90 %) as a yellow oil.

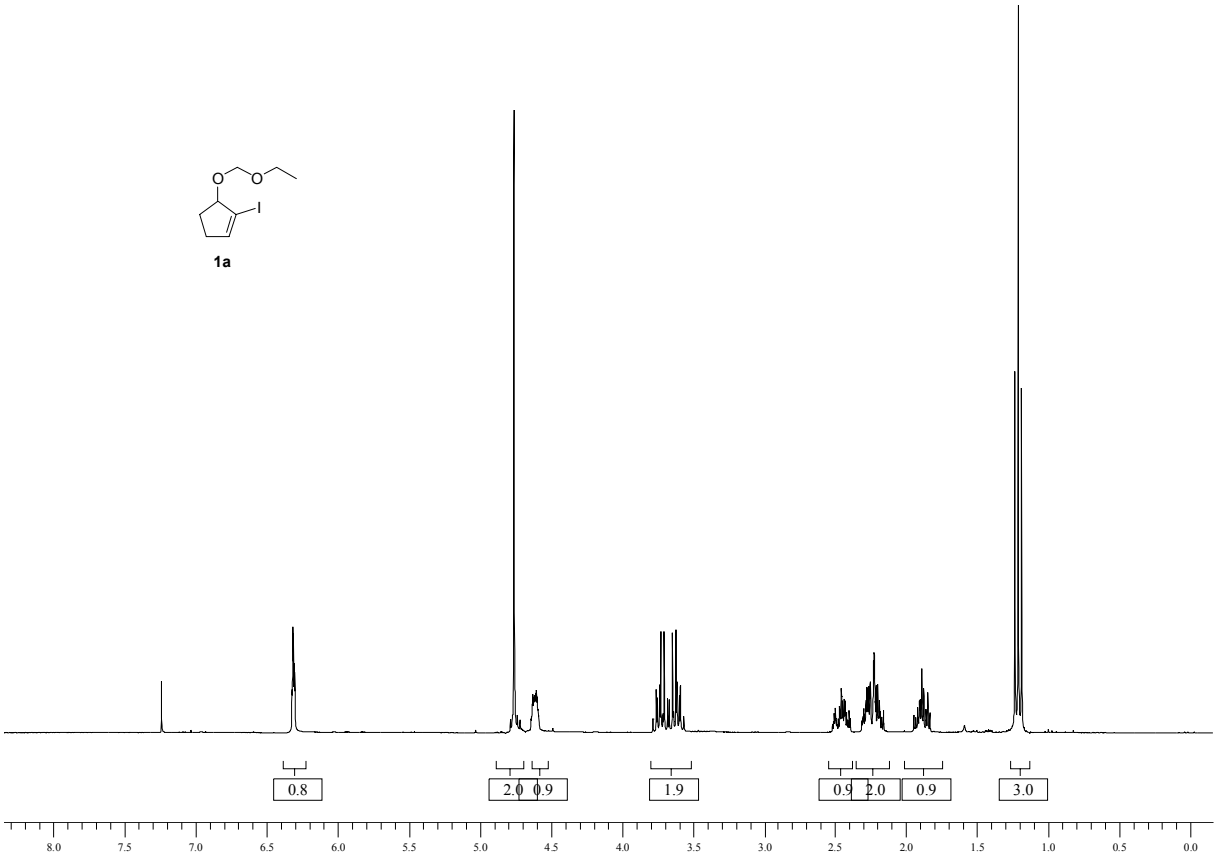
$^1$H NMR ($CDCl_3$, 300 MHz): 7.96 (d, $J$ = 8.4 Hz, 2 H), 7.30 (d, $J$ = 8.4 Hz, 2 H), 5.78-5.82 (m, 1 H), 4.88 (s, 1 H), 4.64 (s, 1 H), 3.89 (s, 3 H), 2.47 (t, $J$ = 6.2 Hz, 2 H), 2.26-2.33 (m, 2 H), 1.75-1.84 (m, 2 H);

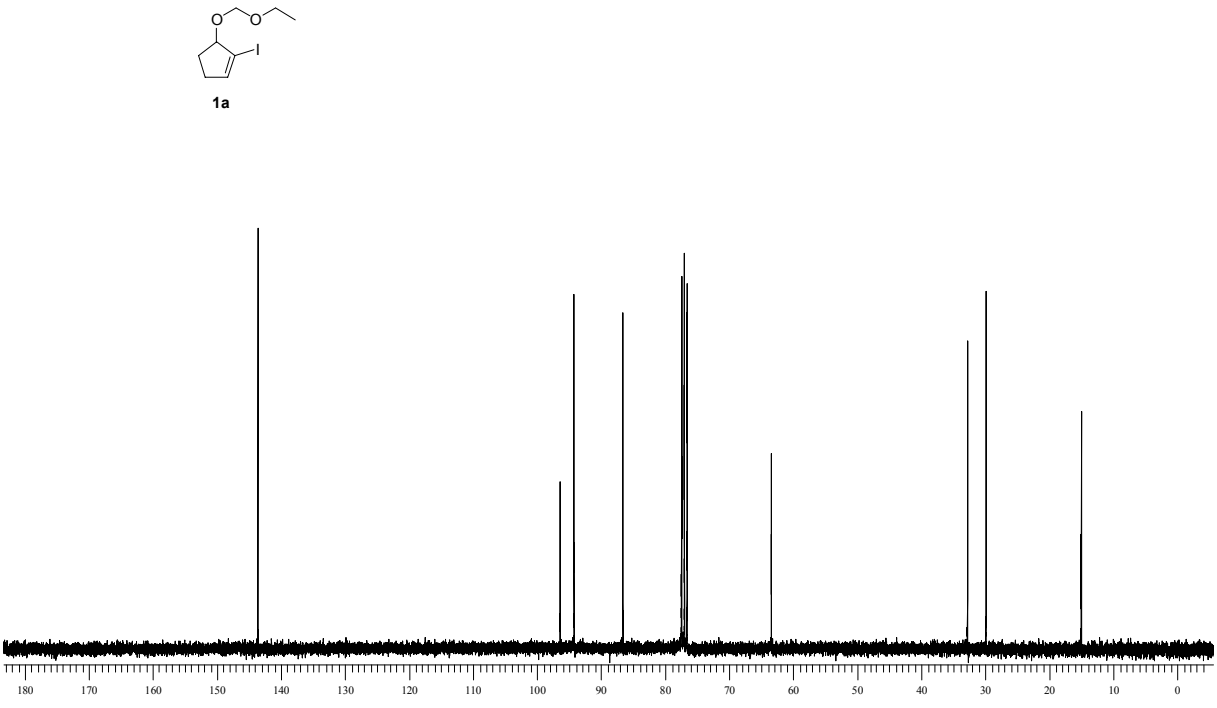
$^{13}$C NMR ($CDCl_3$, 75 MHz): 167.1, 146.6, 143.3, 139.8, 131.0, 129.2, 129.0, 128.5, 111.9, 52.0, 32.6, 26.6, 23.1;

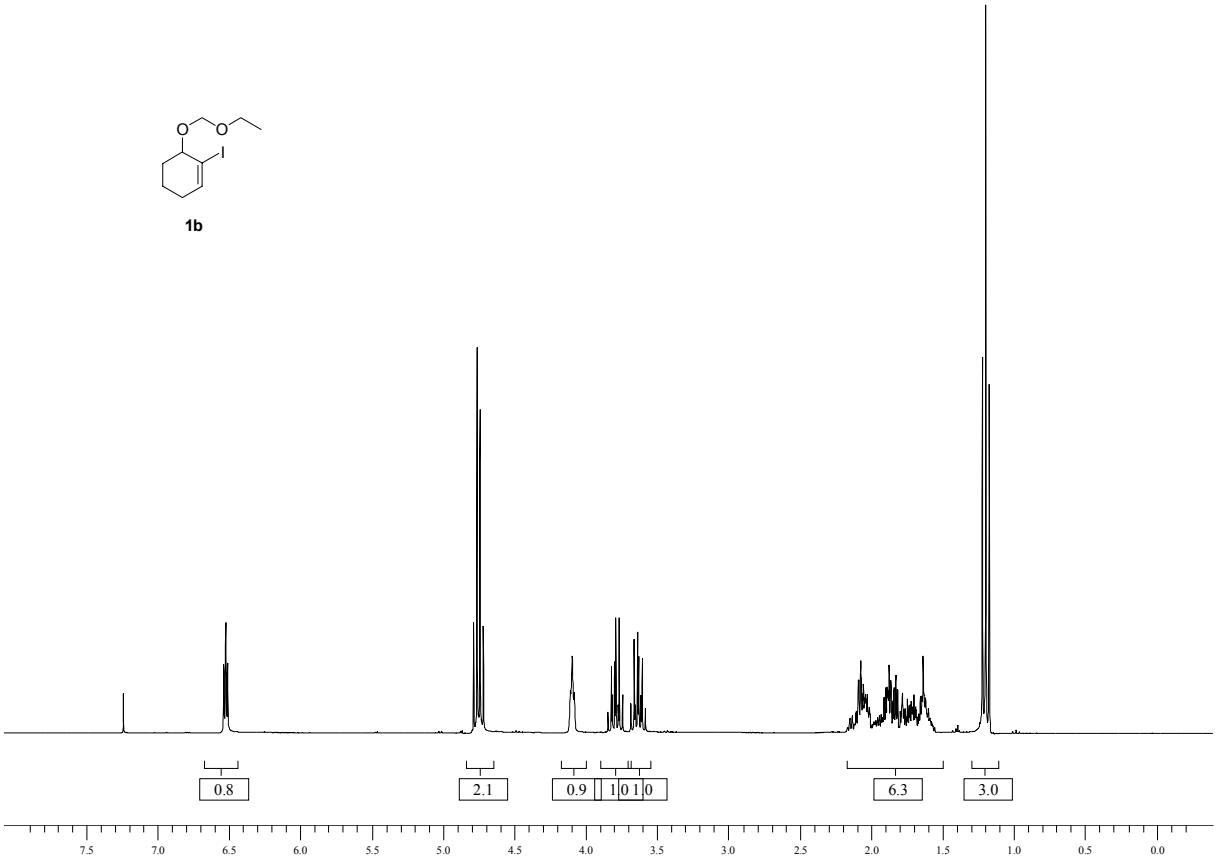
IR (film): 2936, 1724, 1608, 1435, 1277, 1112 $cm^{-1}$;

MS (EI, 70 ev), m/z (%): 228 ($M^+$, 82 %), 213 (11 %), 197 (12 %), 169 (100 %), 153 (13 %), 141 (63 %);

HRMS (EI): calcd. for $C_{15}H_{16}O_2$: 228.1150, found: 228.1133.

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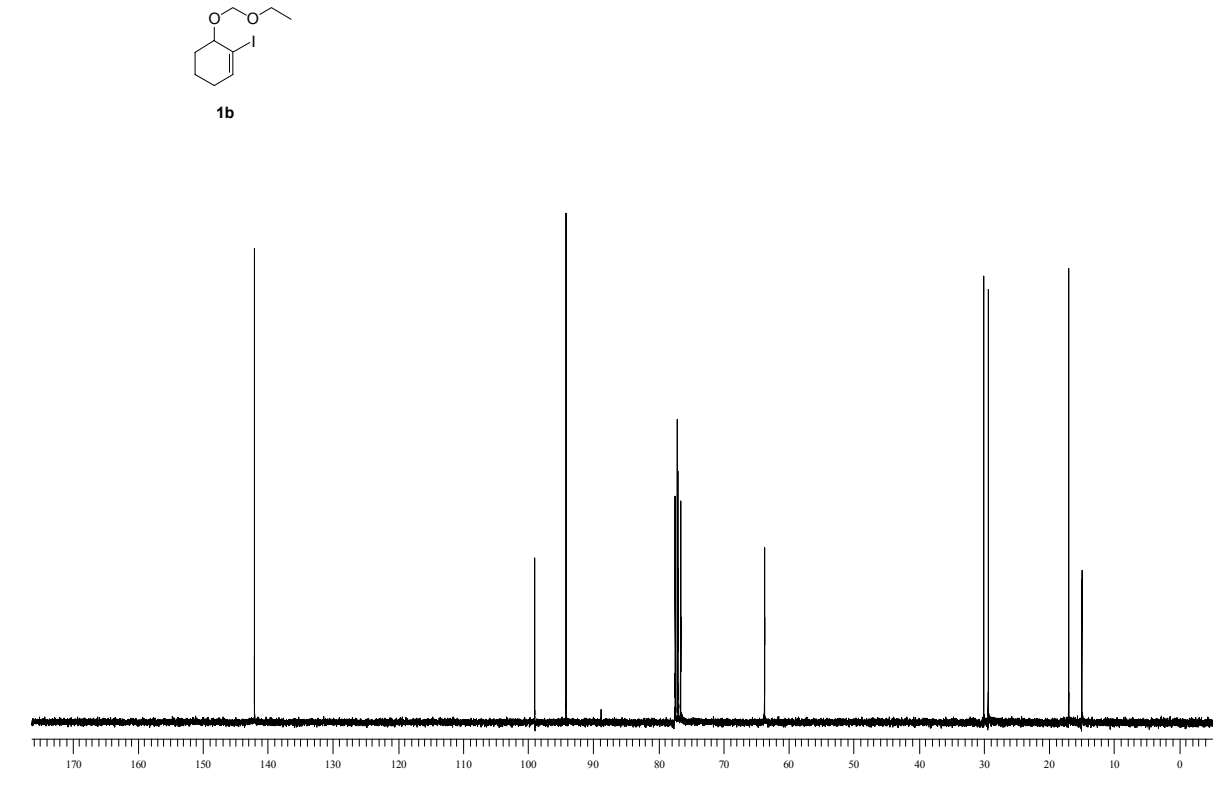
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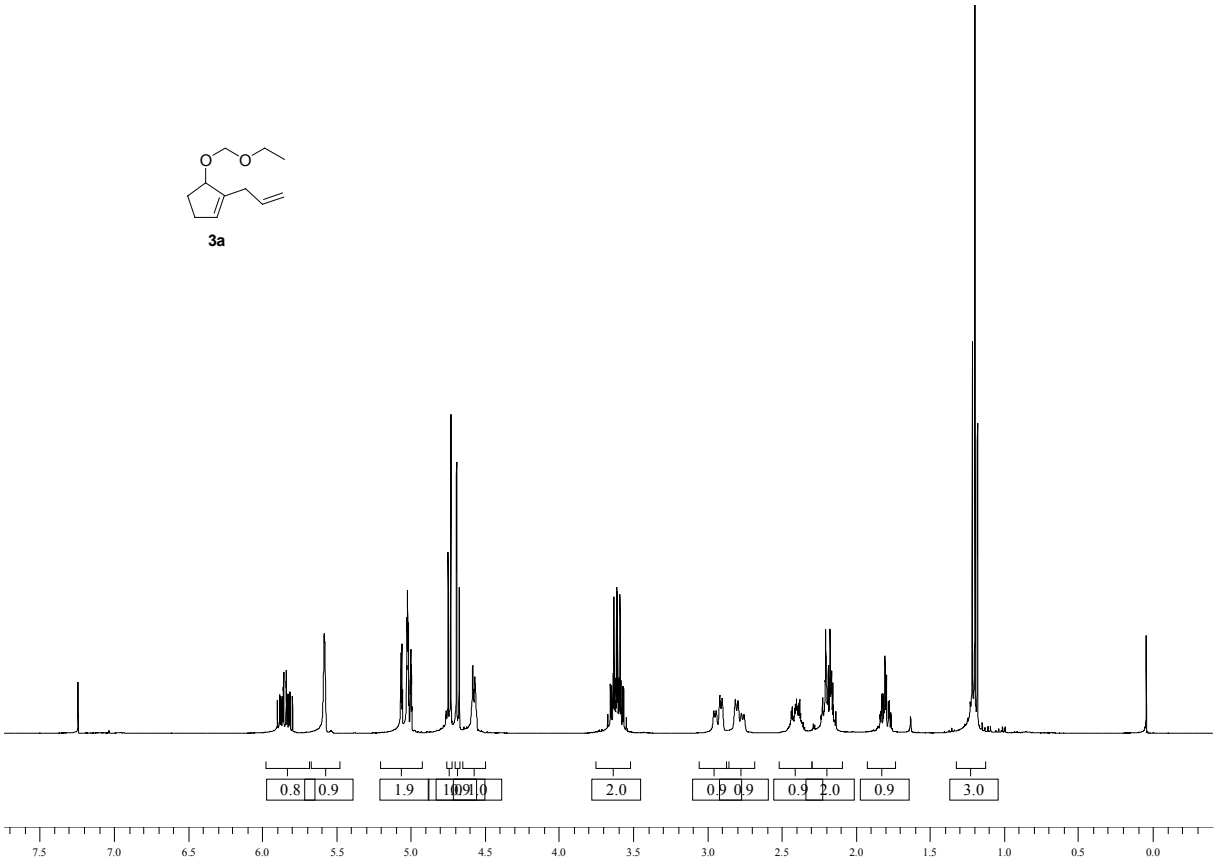


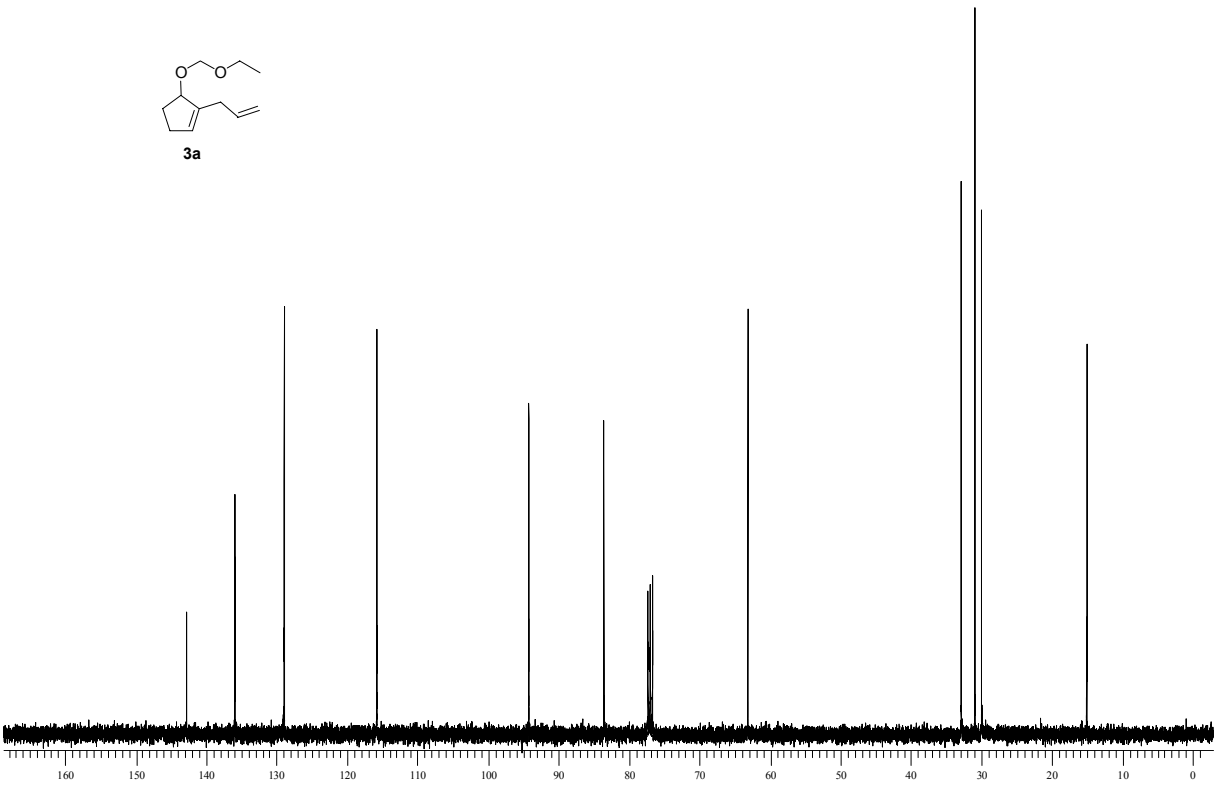

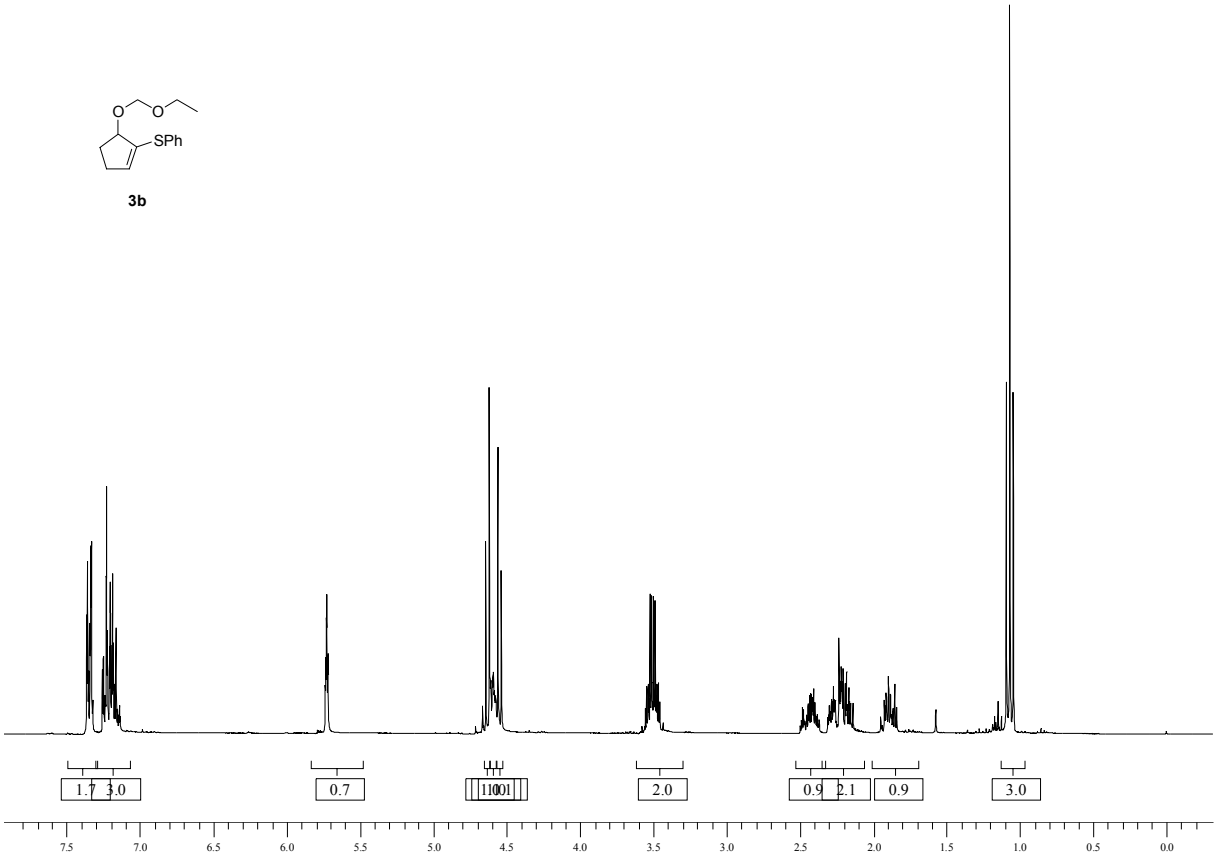


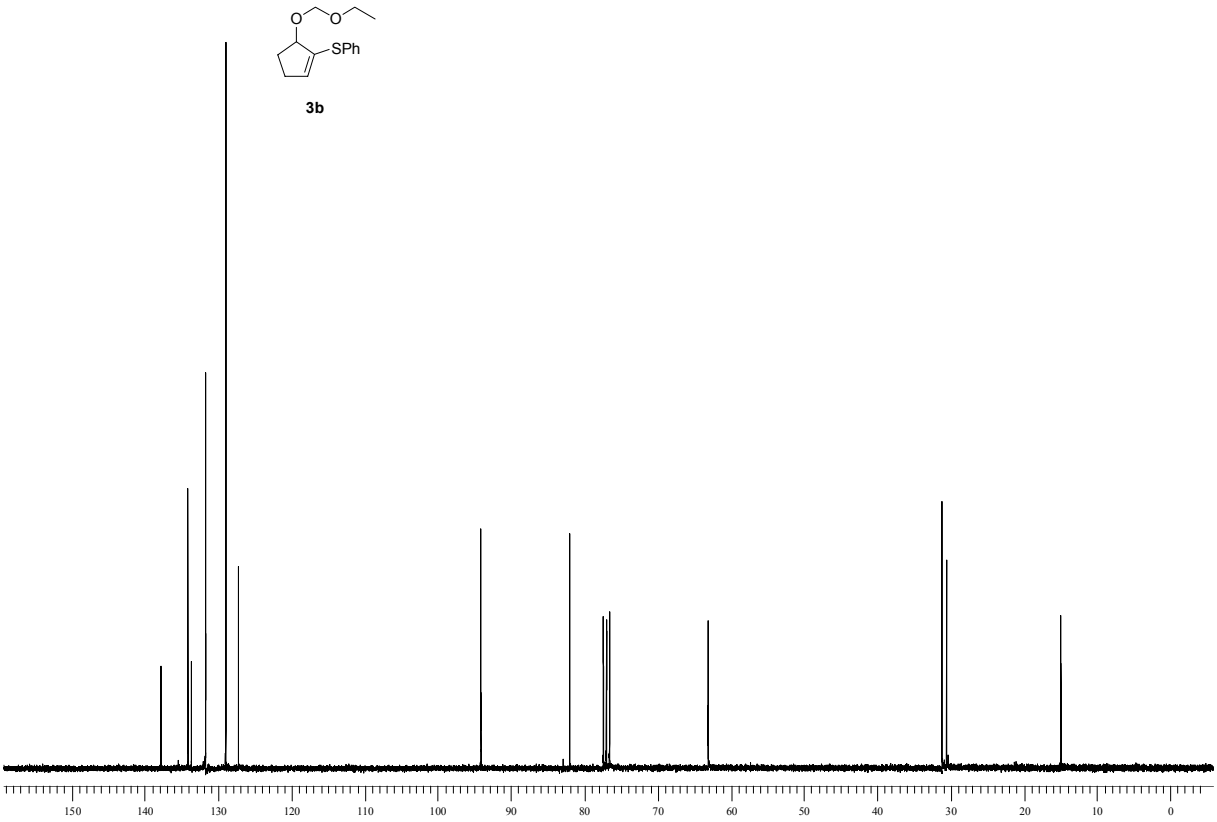

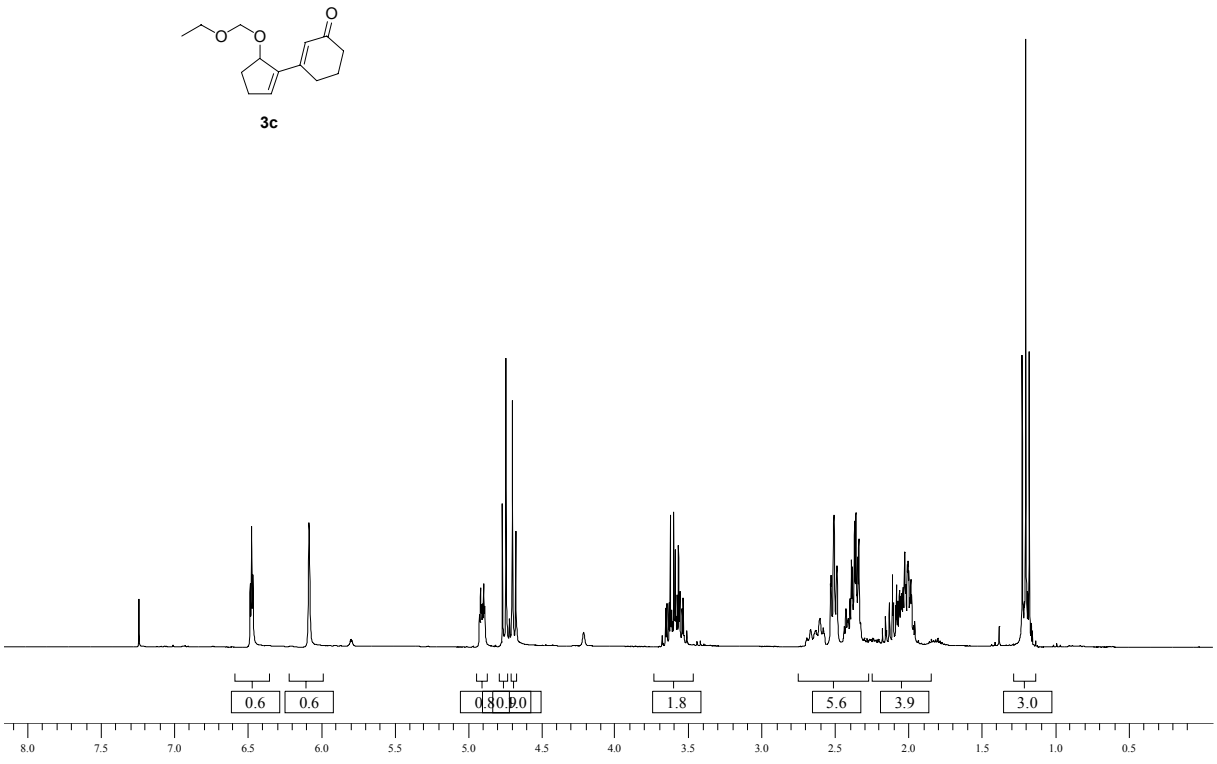


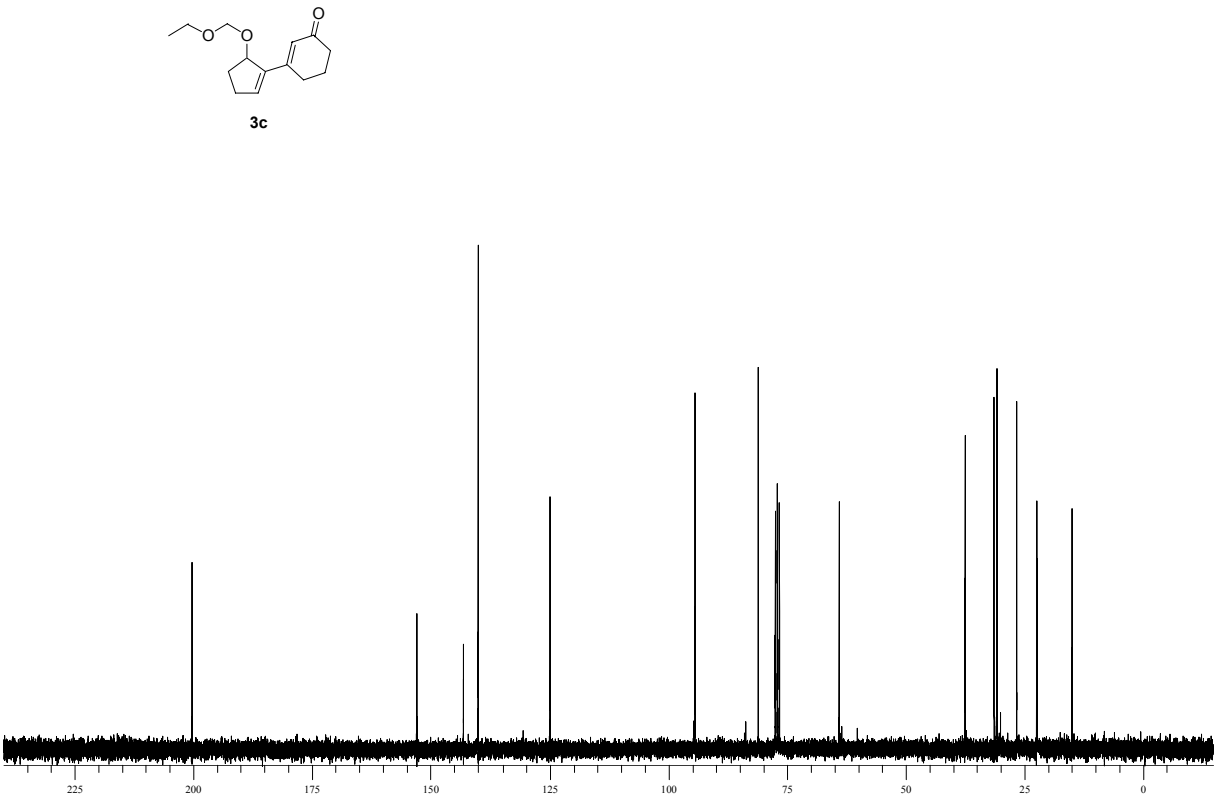

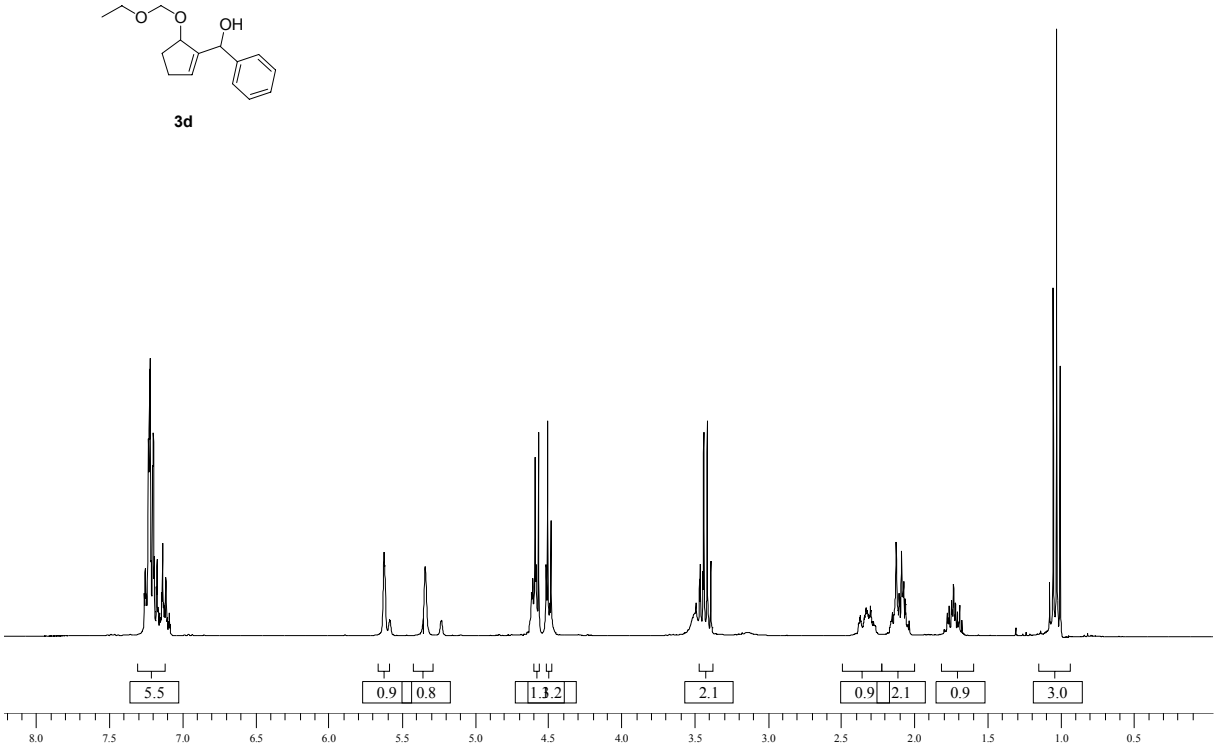
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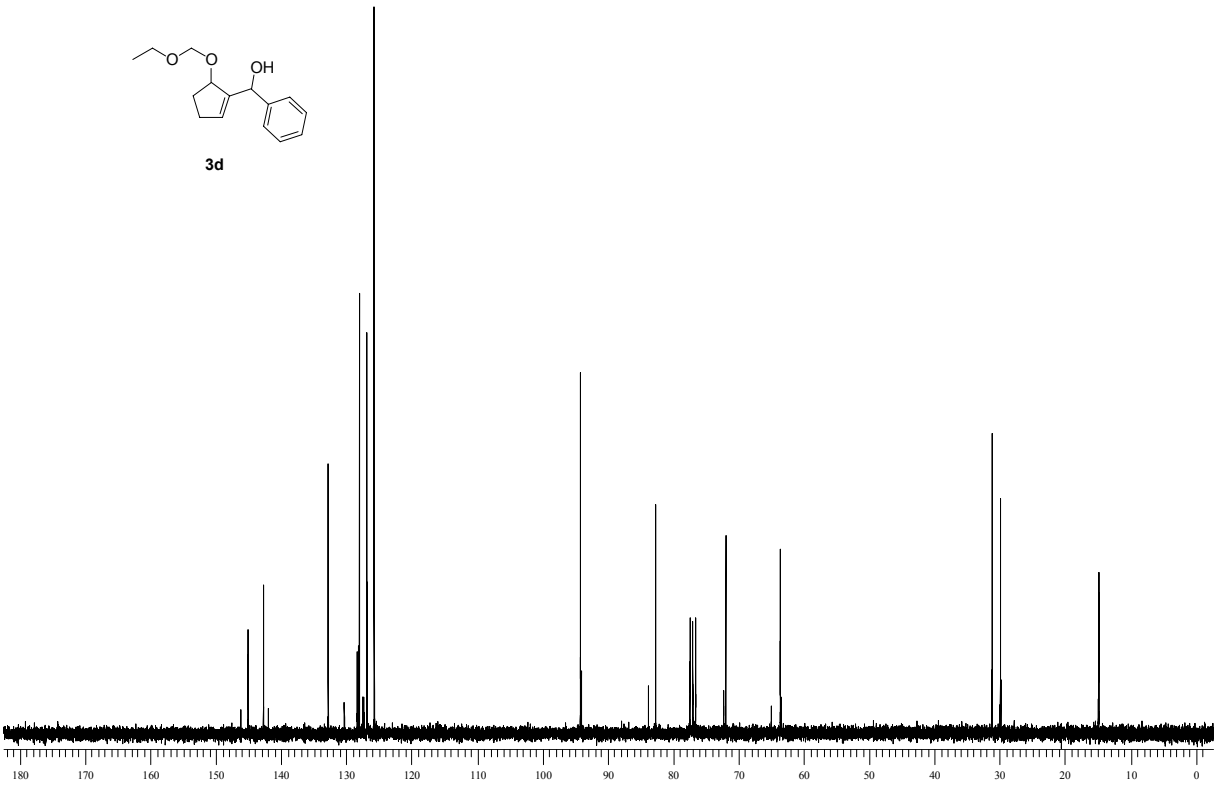
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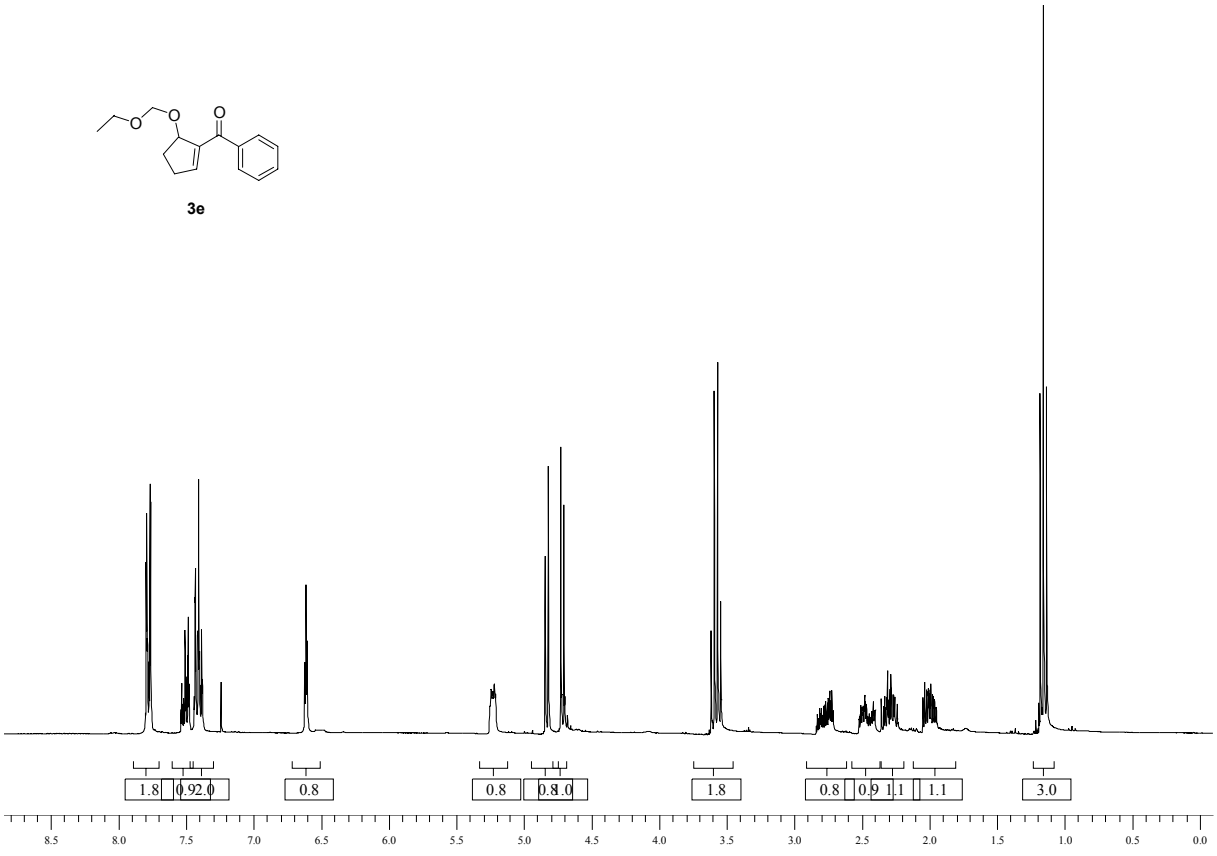


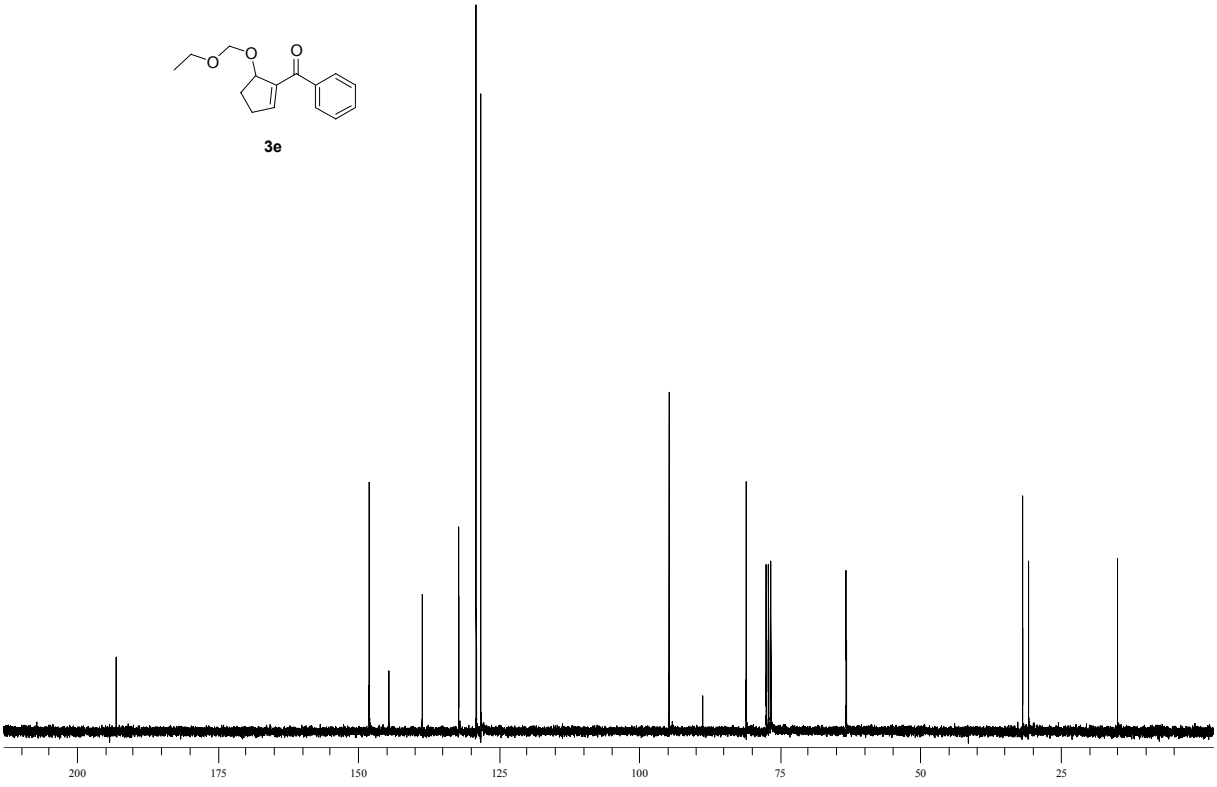

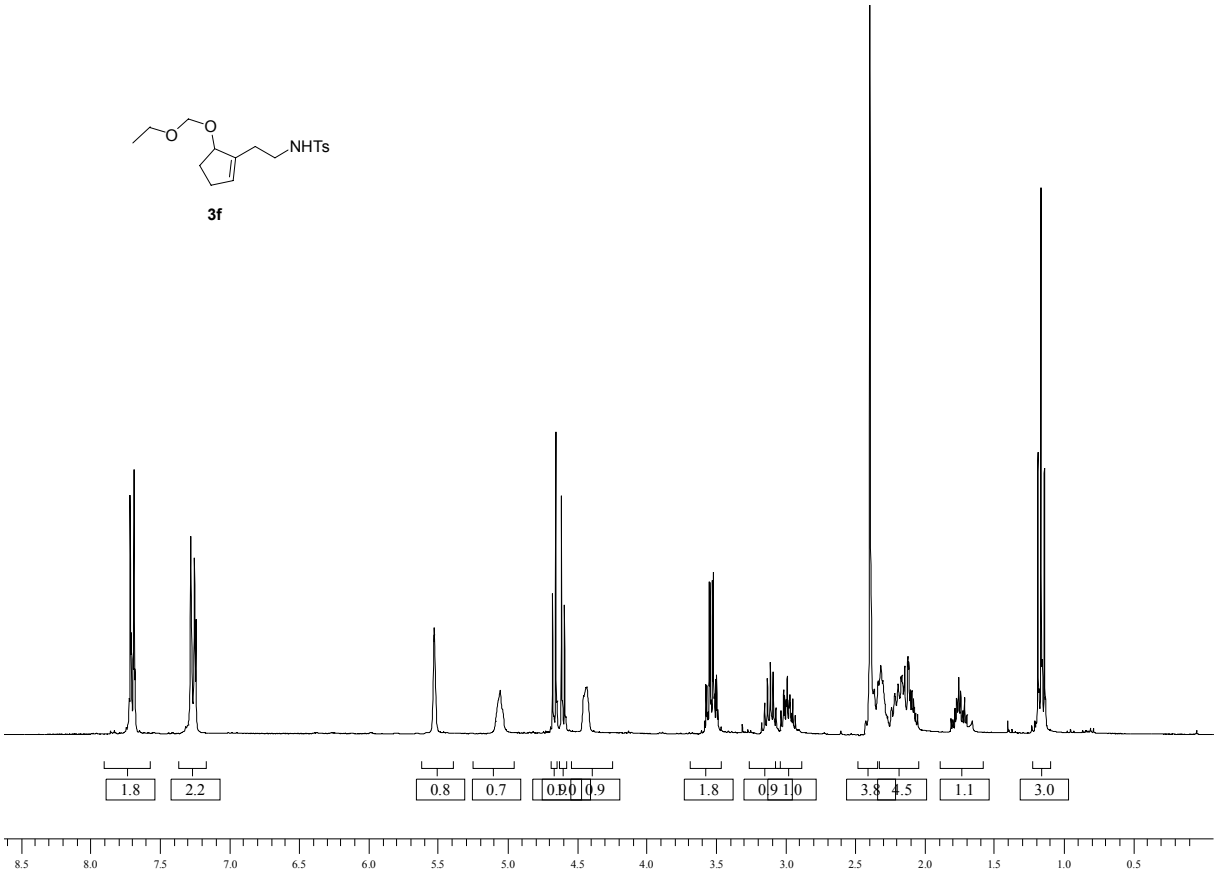
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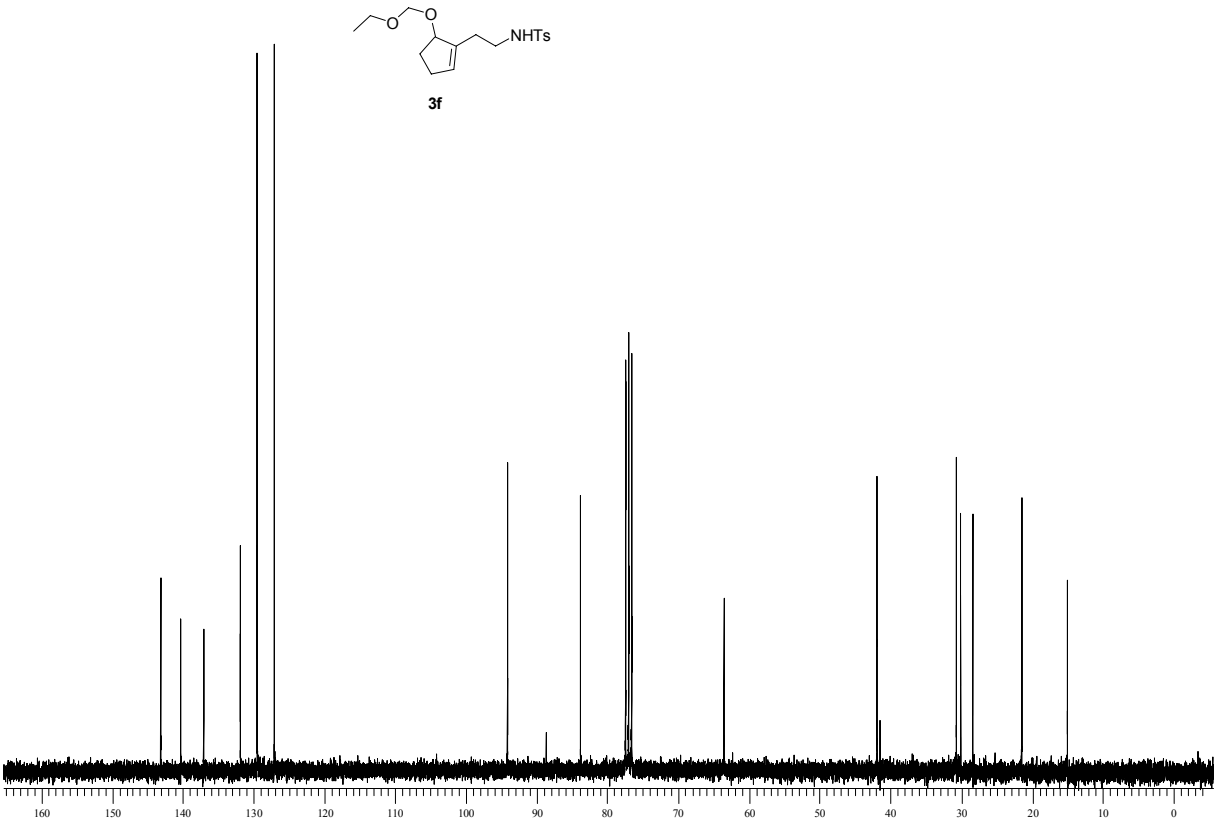
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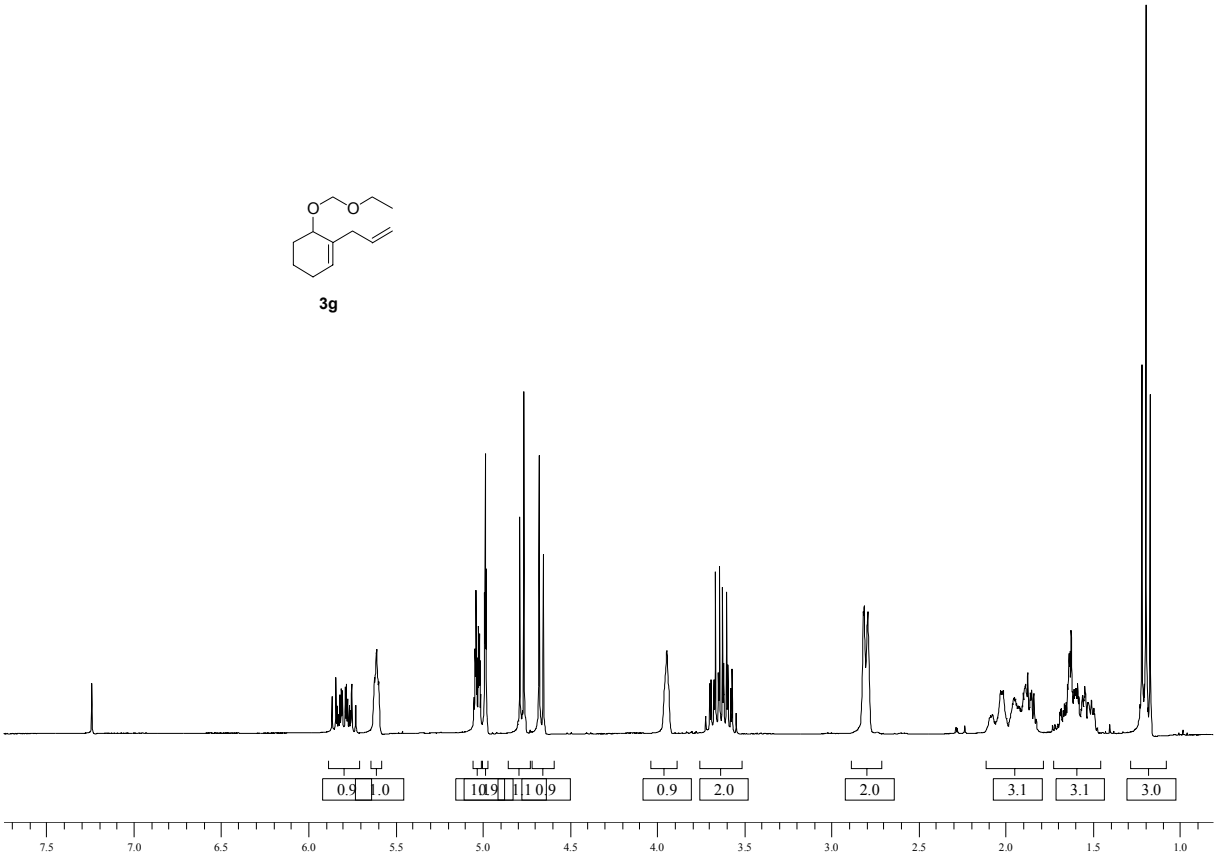


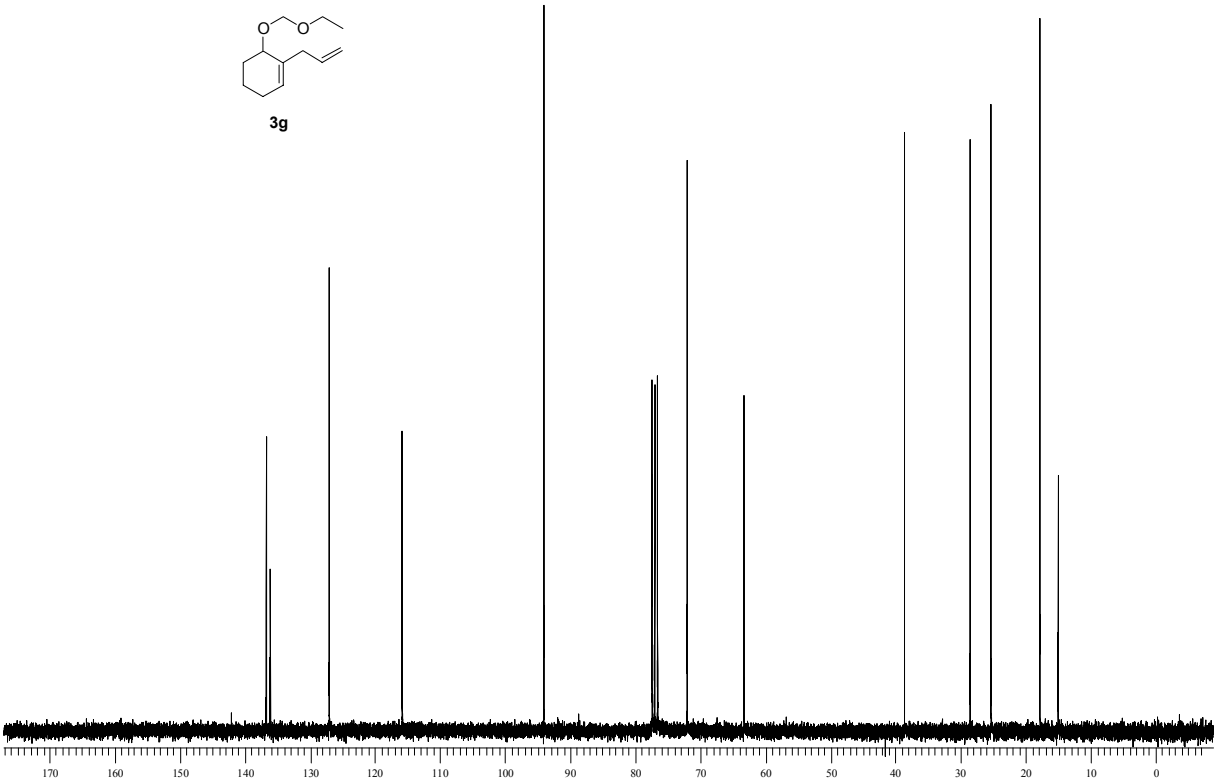

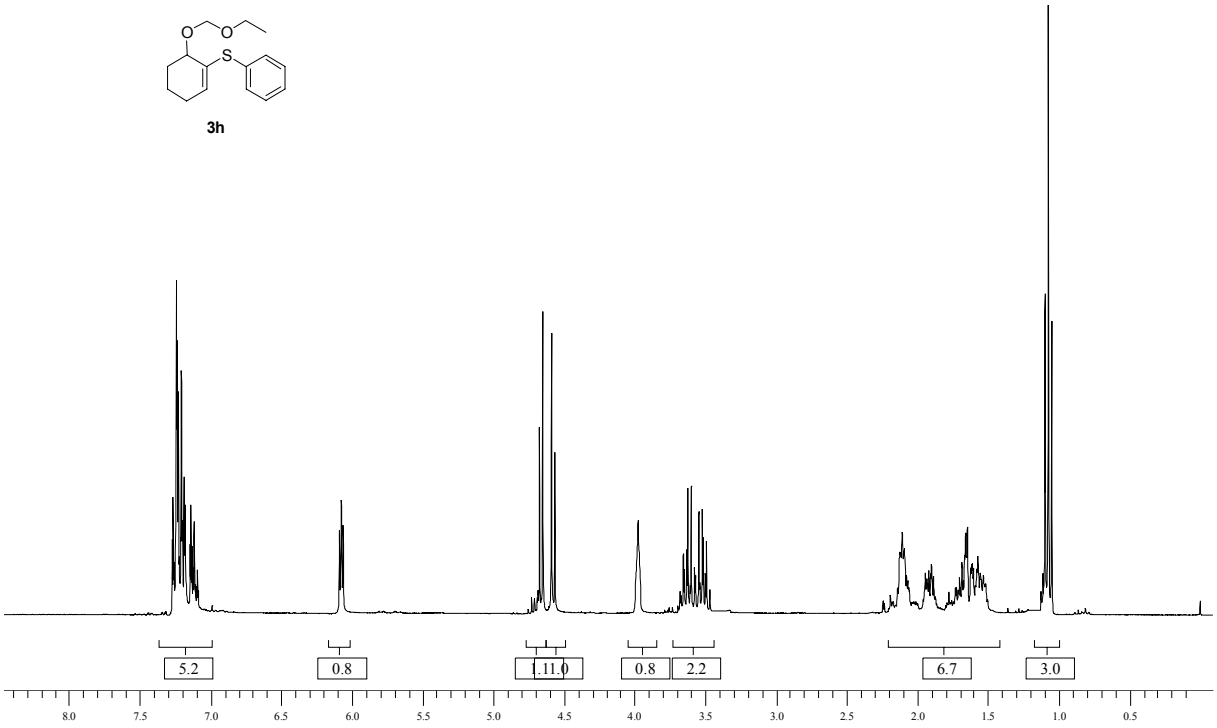


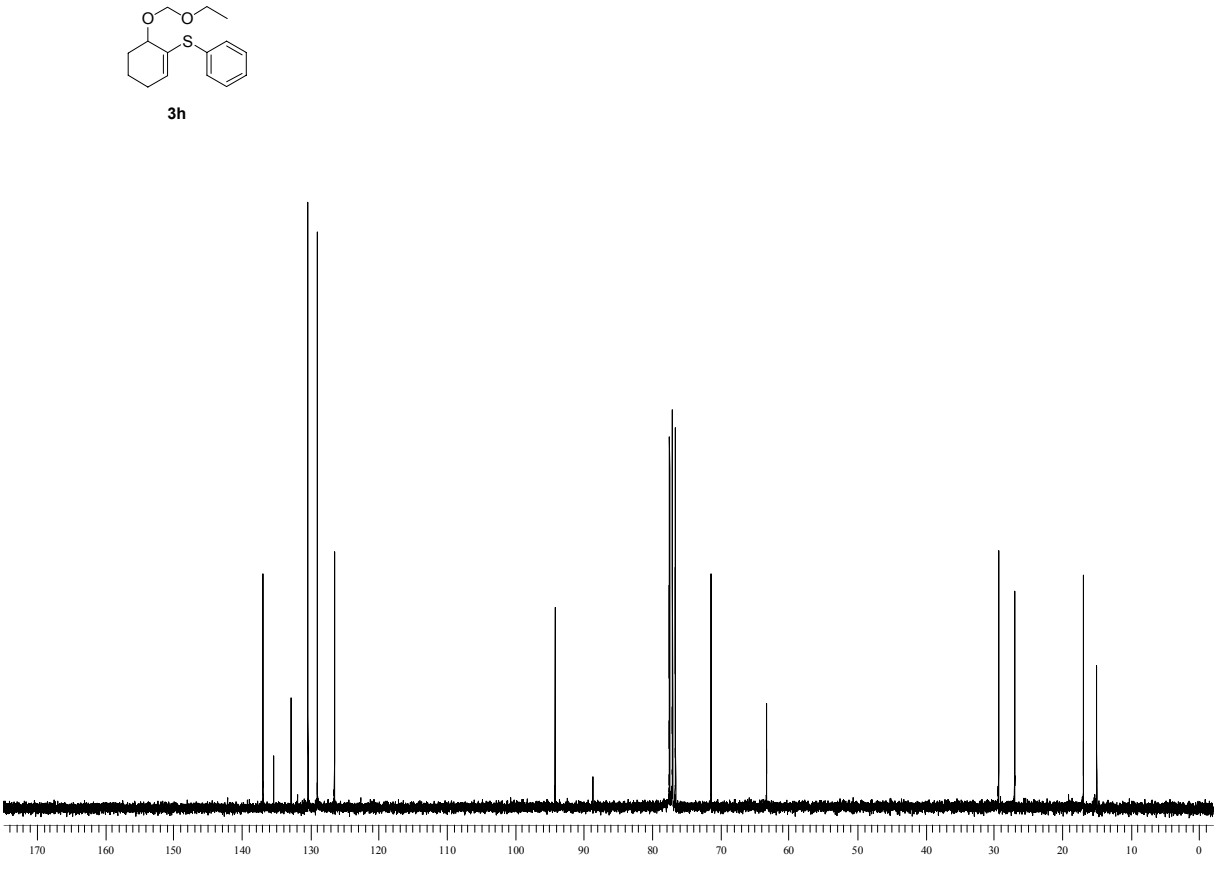

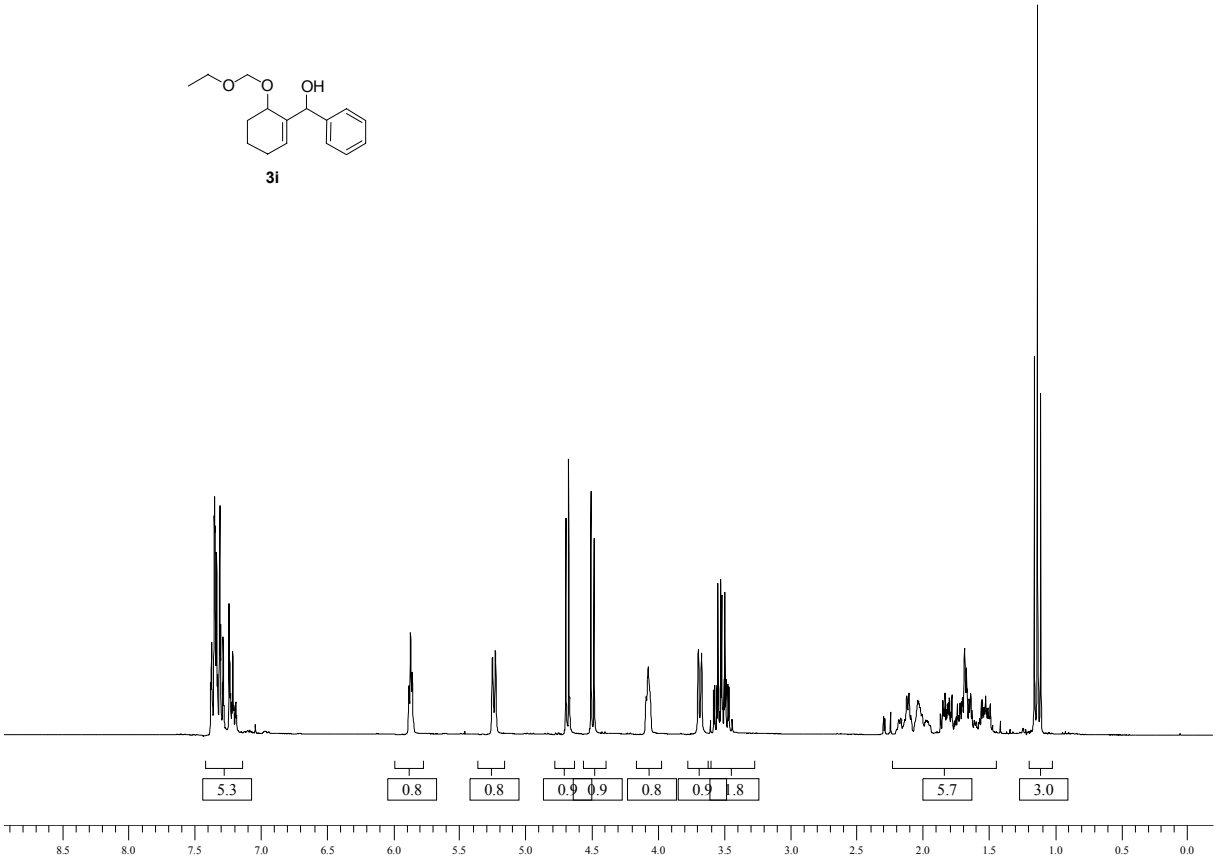


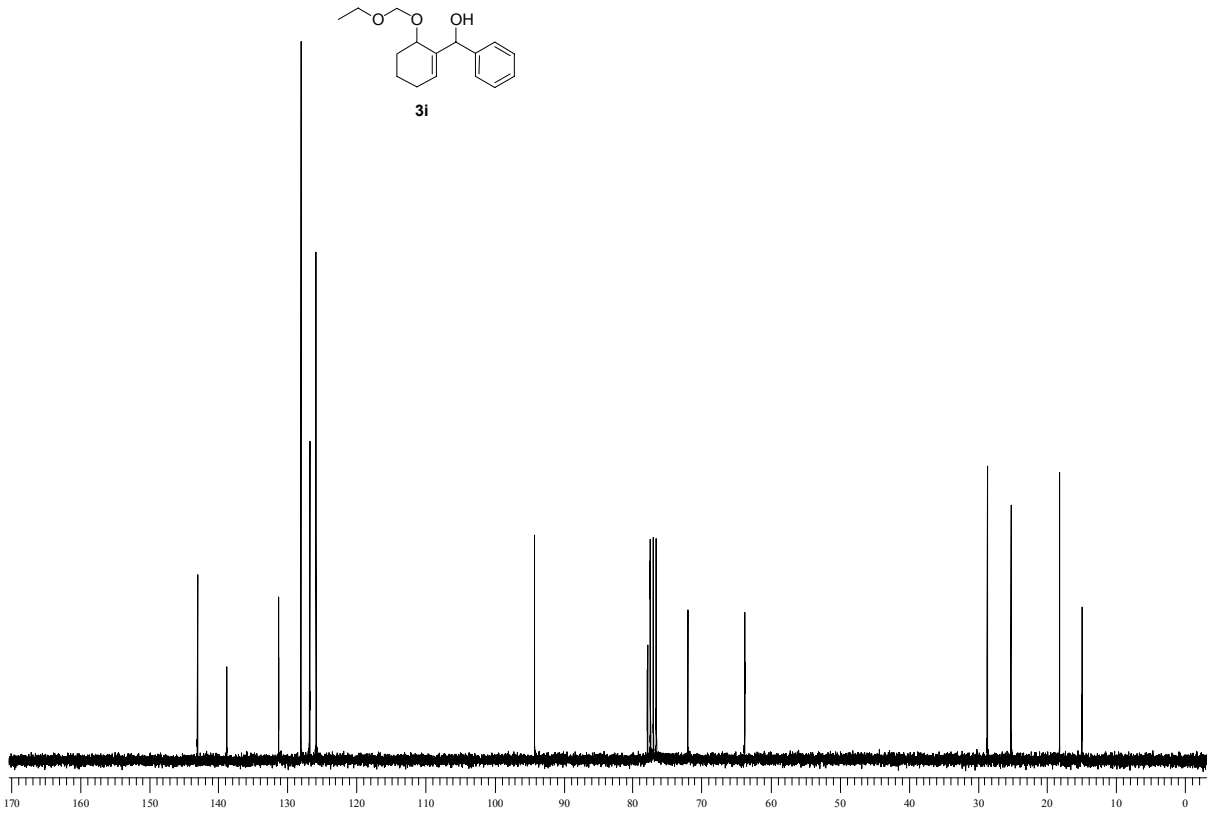

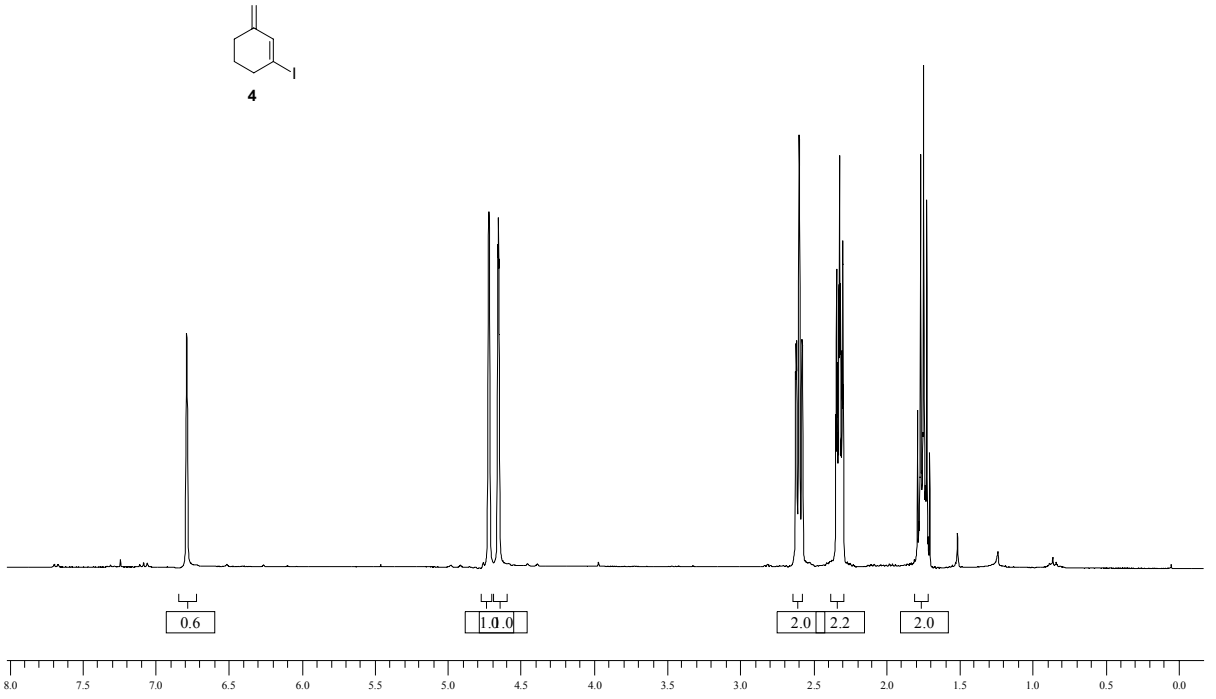


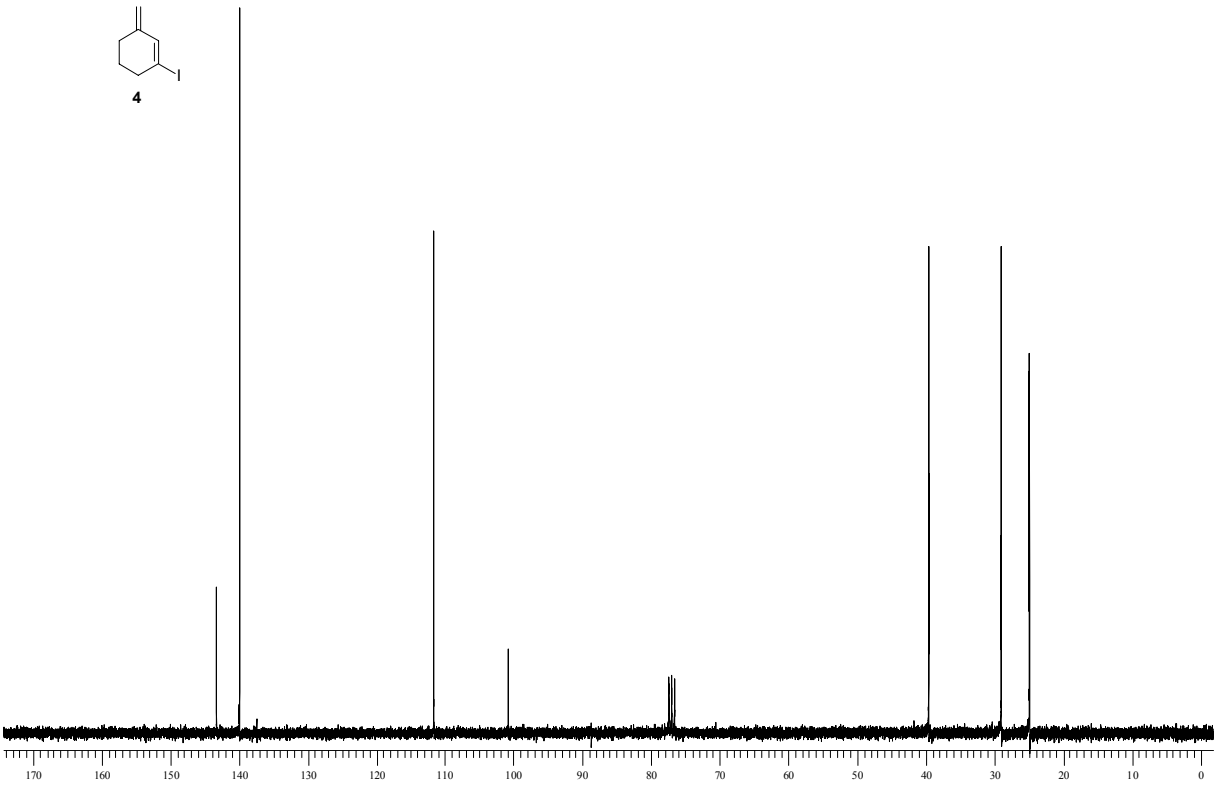

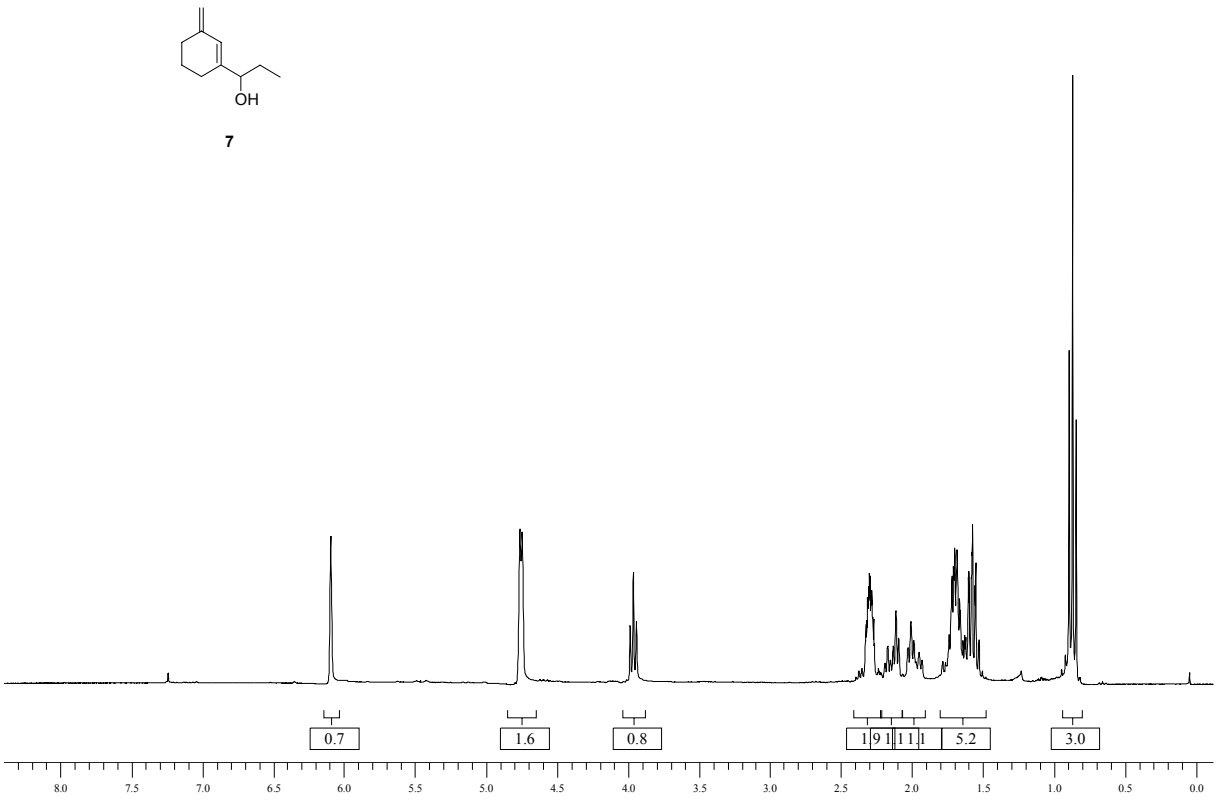


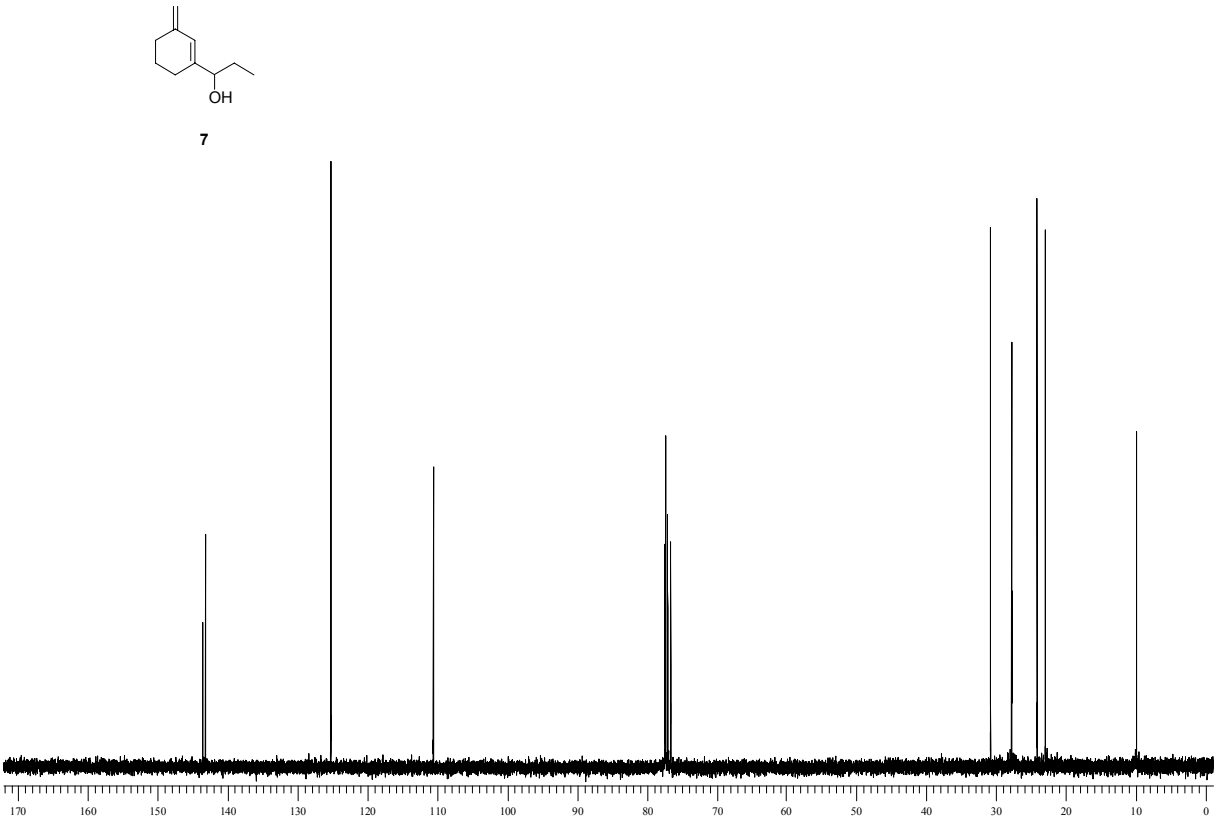

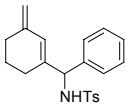
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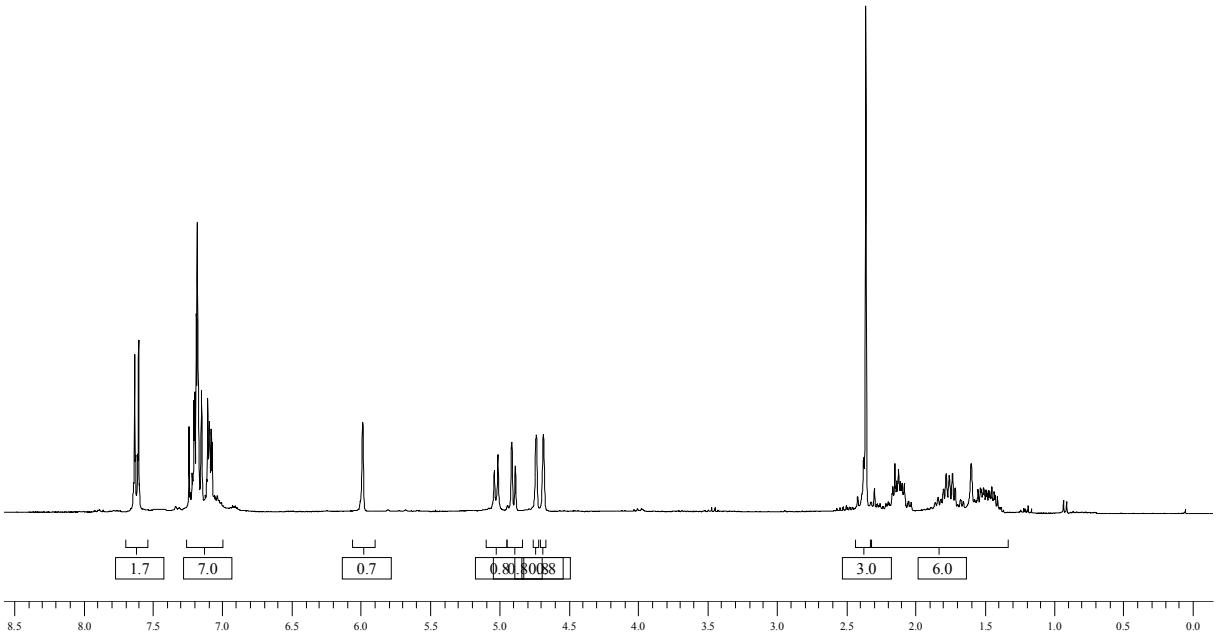
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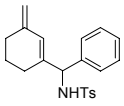
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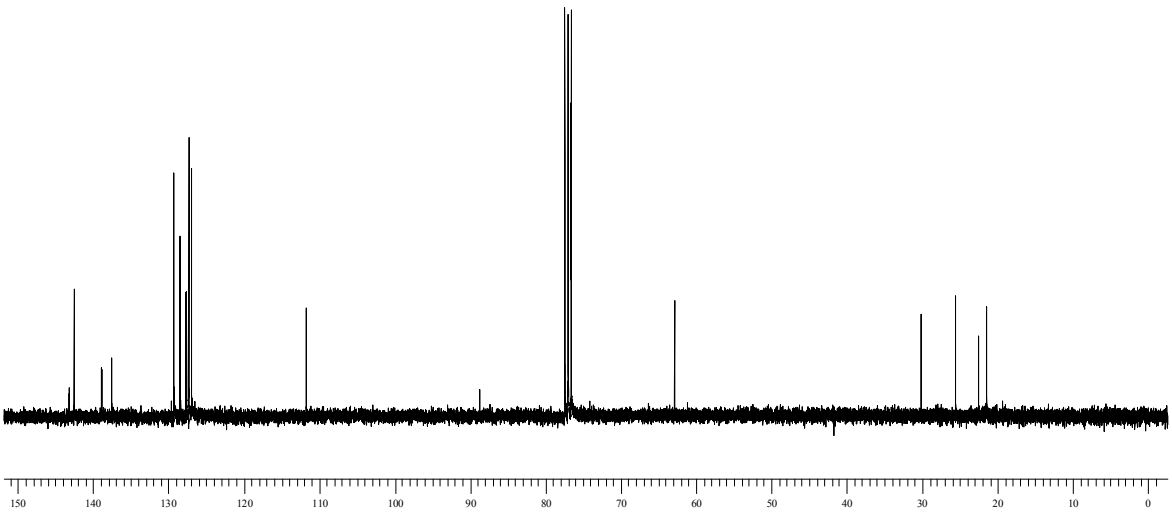
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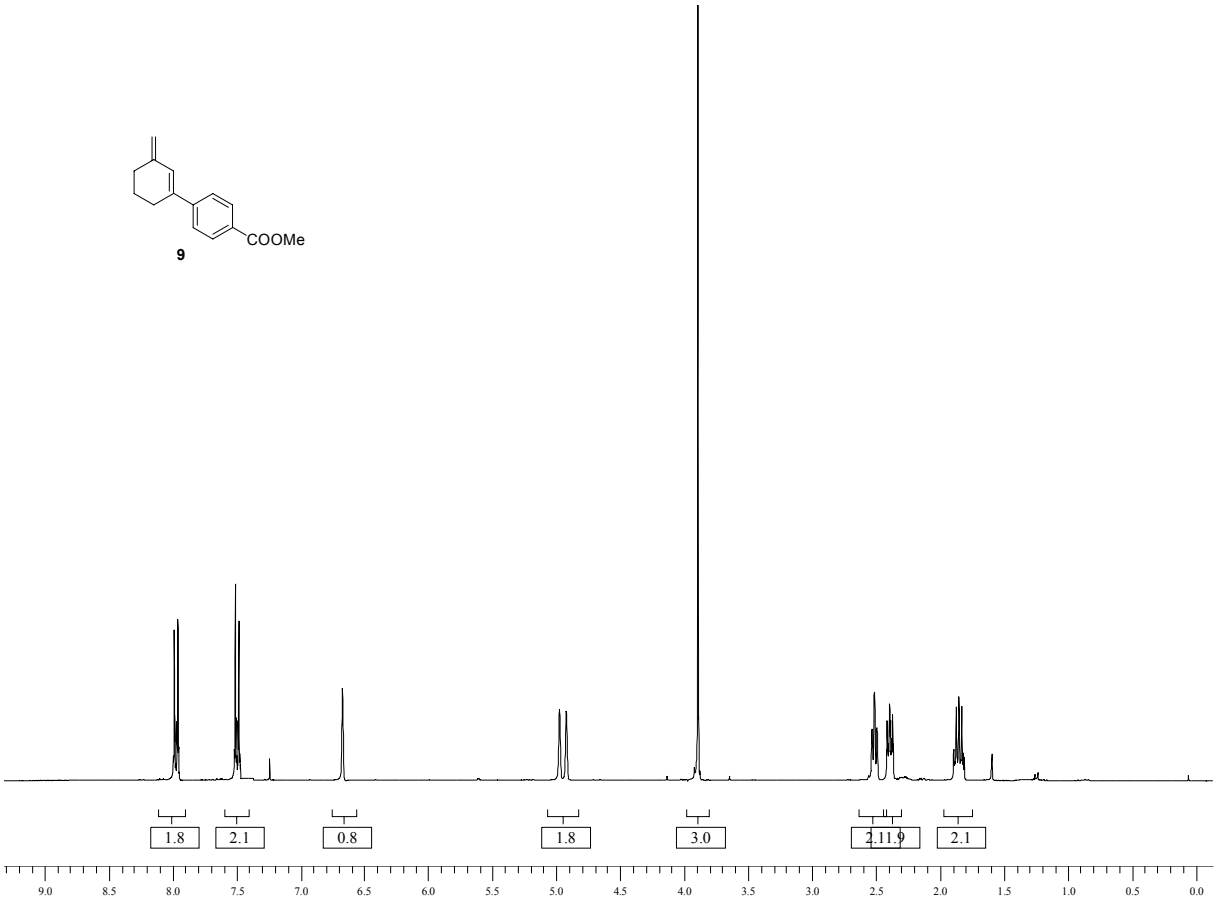


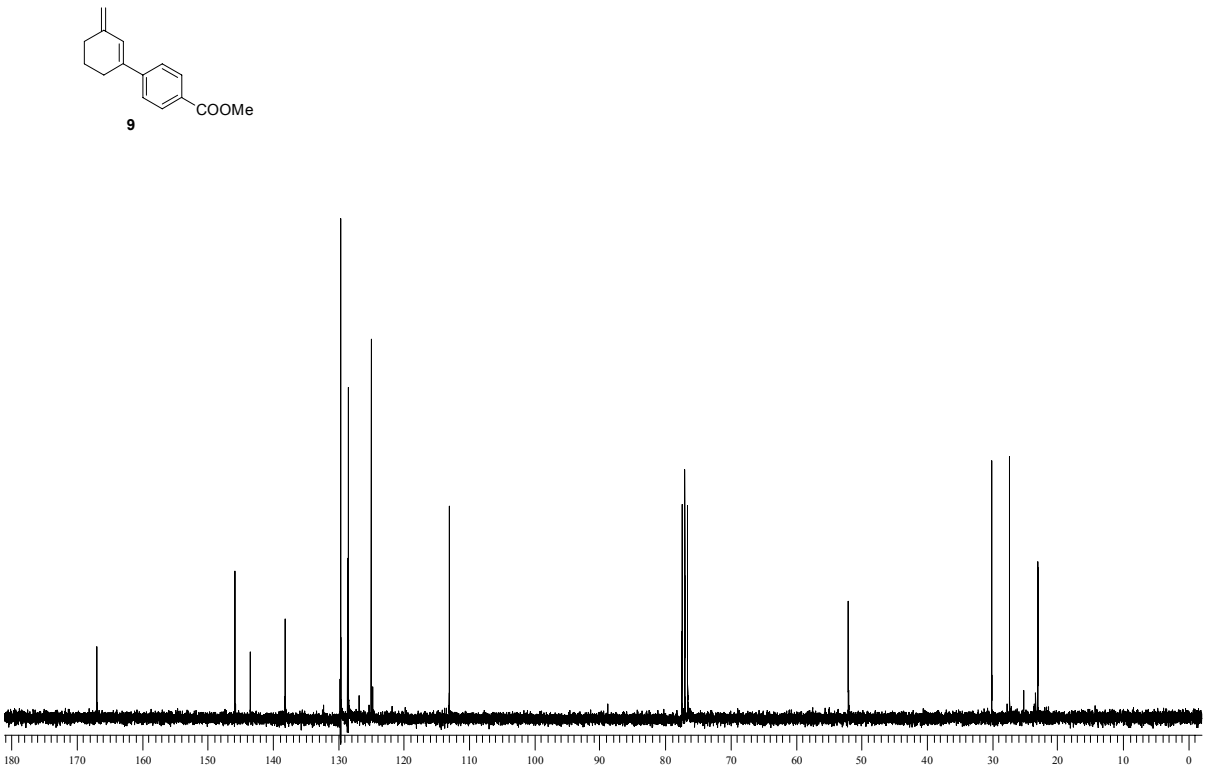

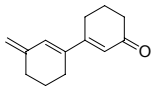


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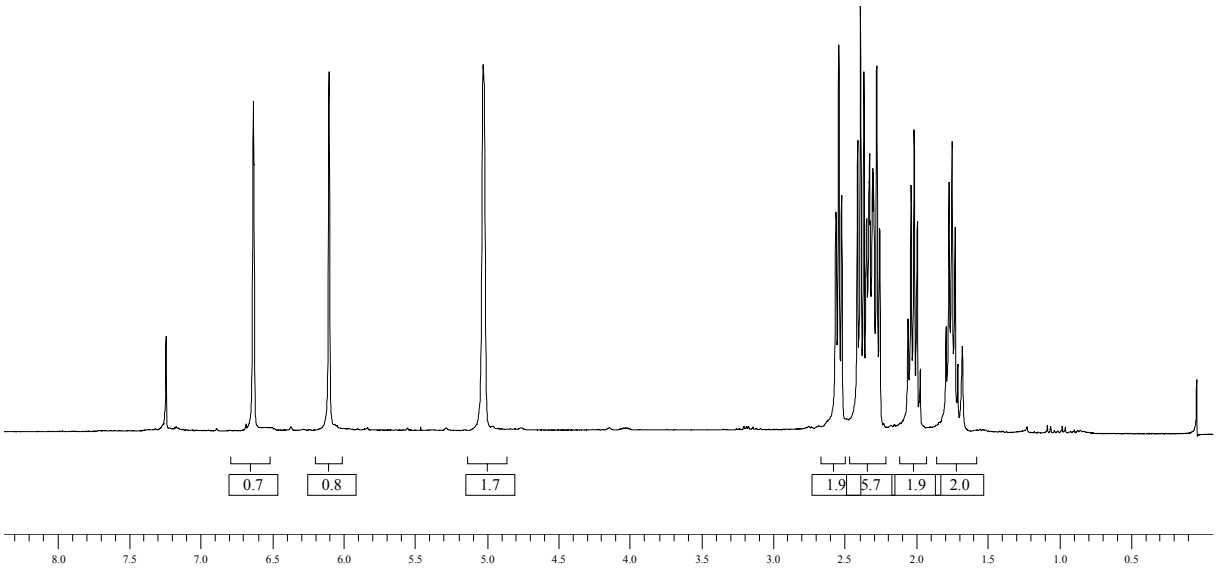


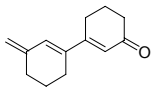


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