

Supporting Information

Breaking the Dichotomy of Reactivity vs Chemoselectivity in Catalytic Dehydrative Reactions

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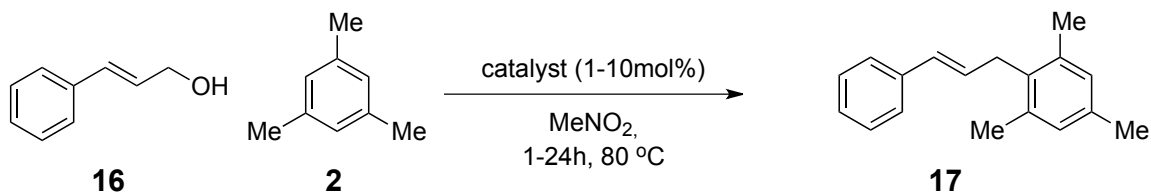
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Survey of boron catalysts for the reaction of cinnamyl alcohol **16 with **2**.^[a]**



Entry	Catalyst	Cat. loading [mol%]	<i>t</i> [h]	Yield ^[b] [%]
1	B(C ₆ F ₅) ₃	10	1	65
2	B(C ₆ F ₅)(OH) ₂ (A)	10	1	22
3	B(2-HC ₆ F ₄)(OH) ₂ (B)	10	1	13
4	Ph ₃ B	10	1	31
5	Ph ₂ BOH	10	1	17
6	PhB(OH) ₂	10	1	<5
7	B(OH) ₃	10	1	12
8	none	n/a	1	<5
9	B(C ₆ F ₅) ₃	1	1	86
10	A, B	1	1	<5
11	B(C ₆ F ₅) ₃ ^[c]	1	1	63
12	BF ₃ •THF	1	1	68
13	B(C ₆ F ₅) ₂ OH (C)	1	1	59
14	B(C ₆ F ₅) ₃	0.1	24	66

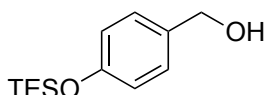
[a] Conditions: 1.0 equiv **16** (0.2 M in MeNO₂), 3.0 equiv **2**, 80 °C. [b] Yields of isolated product purified by column chromatography on silica gel. [c] MgSO₄ was added.

General Information. All reactions were performed in air-dried flasks under a nitrogen atmosphere, unless otherwise noted. All dehydrative transformations were performed in 10 mL sealed tubes under an air atmosphere. Purification of reaction products was carried out by flash column chromatography using Merck silica gel (40-63 μm). Analytical thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel 60 F254 (E. Merck), cut to size. Visualization was accomplished with UV light followed by dipping in a potassium permanganate and/or Seebach's staining solutions and heating.

¹H NMR spectra were recorded on a Bruker Avance400 (400 MHz) spectrometer at ambient temperature unless otherwise noted and are reported in ppm using solvent as the internal standard (CDCl₃ at 7.26 ppm, C₆D₆ at 7.15 ppm). Data are reported as: multiplicity (ap = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. ¹³C NMR spectra were recorded on a Bruker Avance400 (100 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the residual solvent resonance employed as the internal standard (CDCl₃ at 77.0 ppm, C₆D₆ at 128.02 ppm).

Materials. Unless otherwise noted, all commercial materials were purchased from *Sigma-Aldrich* and used without further purification. 1-Vinyl-1-cyclohexanol **1**,¹ (2-(Triisopropylsilyloxy)phenyl)methanol **4a**,² 4-(4'-Methoxybenzyloxy)benzylalcohol **4c**,³ (*E*)-6-Phenylhex-5-ene-1,4-diol **6**,⁶ 6-Phenylhex-5-yne-1,4-diol **8**,⁶ 4-Benzyl-5-phenylpentane-1,4-diol **10**⁶ and *N*-Tosyl butanolamine **12**⁴ were prepared following a literature procedure. Tris(pentafluorophenyl)borane was purchased from *Strem Chemicals Inc.* and used under air, without any precaution to exclude moisture or air.

Preparation of alcohols.

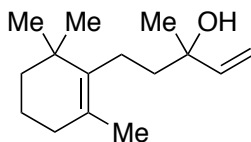


4-(Triethylsilyloxyphenyl)methanol (**4b**). To a stirred solution of 4-hydroxybenzaldehyde (7.3 mmol, 1.0 g, 1.0 equiv) in anhydrous CH₂Cl₂ (50 mL) was added imidazole (14.7 mmol, 1.0 g, 2.0 equiv) and triethylsilyl chloride (8.8 mmol, 1.5 mL, 1.2 equiv) in several portions. The reaction mixture was stirred for 20 h at room temperature. Then the reaction was filtered through Celite, rinsing with CH₂Cl₂ and the solvent was removed in vacuo obtaining a white solid (3.04 g). The residue was dissolved in anhydrous CH₂Cl₂ (10 mL) and cooled to -78°C. A solution of diisobutylaluminum hydride (14.68 mmol, 1M in CH₂Cl₂, 14.68 mL) was added dropwise. The reaction mixture was stirred for 90 min at -78°C, was quenched with MeOH (1 mL), warmed to room temperature and a 1 M aqueous solution of potassium tartrate was added. The aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL). The organic layer was washed with water and brine, then dried over Na₂SO₄, filtered and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether 1:5) affording a colorless oil (72%).

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 4.58 (s, 2H), 0.98 (t, *J* = 7.7 Hz, 9H), 0.72 (q, *J* = 15.4 Hz, 7.7 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 155.1, 133.8, 128.5, 119.9, 64.8, 6.59, 5.09.

HRMS (ESI) for C₁₃H₂₂OSi: calcd. 238.1389; found 238.1398.



¹ U. Albrecht, P. Langer, *Tetrahedron* **2007**, *63*, 4648-4654.

² H. Y. Lee, X. Jiang, D. Lee, *Org. Lett.* **2009**, *11*, 2065-2068.

³ H. Taguchi, I. Yosioka, K. Yamasaki, I. H. Kim, *Chem. Pharm. Bull.* **1981**, *29*, 55-62.

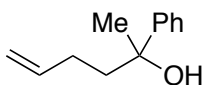
⁴ L. D. Elliott, J. W. Wrigglesworth, B. Cox, G. C. Lloyd-Jones, and K. I. Booker-Milburn, *Org. Lett.* **2011**, *13*, 728-731.

3-Methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pent-1-en-3-ol (**4g**).⁵ To a solution at 0°C of vinylmagnesiumbromide (1M solution in THF) was added dropwise a solution of dihydro-beta-ionone (1.94 g, 10 mmol) in THF (10 mL). After stirring for 1 h at rt, an aqueous solution of NH₄Cl was added. The organic and the aqueous layers were separated and the latter was extracted twice with EtOAc. The combined organic layers were dried (Na₂SO₄), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/EtOAc 5 to 10%) to give a colorless oil (2.03 g, 9.15 mmol, 92%). R_f = 0.34 (Petroleum ether/EtOAc 5%).

¹H NMR (400 MHz, CDCl₃) δ 6.0 (dd, *J* = 17.4 and 10.8 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.13 (d, *J* = 10.8 Hz, 1H), 2.11-1.90 (m, 4H), 1.71-1.56 (m, 4H), 1.62 (s, 3H), 1.48-1.42 (m, 2H), 1.35 (s, 3H), 1.03 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 145.0, 136.6, 127.1, 111.8, 73.6, 42.3, 39.9, 35.1, 32.8, 28.7, 27.5, 22.7, 19.8, 19.5.

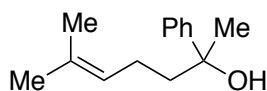
The analytical data are in accordance with those reported in the literature.



2-Phenylhex-5-en-2-ol (**4h**).⁶ To a solution at 0 °C of phenylmagnesiumbromide (1M solution in THF) was added dropwise a solution of 5-hexen-2-one (981 mg, 10 mmol) in dry THF (10 mL). After stirring for 1 h at rt, an aqueous solution of NH₄Cl was added. The organic and the aqueous layers were separated and the latter was extracted twice with EtOAc. The combined organic layers were dried (Na₂SO₄), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/EtOAc 5 to 10%) to give a colorless oil (1.73 g, 9.82 mmol, 98%). R_f = 0.30 (Petroleum ether/EtOAc 5%)

¹H NMR (400 MHz, CDCl₃) δ 7.50-7.26 (m, 5H), 5.91-5.78 (m, 1H), 5.08-4.93 (m, 2H), 2.16-1.92 (m, 4H), 1.63 (s, 3H).

The analytical data are in accordance with those reported in the literature.



6-Methyl-2-phenylhept-5-en-2-ol (**4i**). To a solution at 0°C of phenylmagnesiumbromide (1M solution in THF) was added dropwise a solution of 6-methyl-5-heptene-2-one (1.26 g, 10 mmol) in THF (10 mL). After stirring for 1 h at rt, an aqueous solution of NH₄Cl was added. The organic and the aqueous layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried (Na₂SO₄), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/EtOAc 5 to 10%) to give a colorless oil (1.78 g, 8.71 mmol, 87%). R_f = 0.31 (Petroleum ether/EtOAc 5%)

⁵ A.F. Barrero, J. Altarejos, E.J. Alvarez-Manzaneda, J. M. Ramos, S. Salido, *J. Org. Chem.* **1996**, *61*, 2215-2218.

⁶ M.B. Hay, A.R. Hardin, J. P. Wolfe, *J. Org. Chem.* **2005**, *70*, 3099-3107.

¹H NMR (400 MHz, CDCl₃) δ 7.52-7.26 (m, 5H), 5.20-5.11 (m, 1H), 2.06-1.86 (m, 5H), 1.71 (s, 3H), 1.60 (s, 3H), 1.54 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ 147.9, 132.2, 128.1, 126.5, 124.8, 124.2, 75.0, 43.7, 30.5, 25.7, 23.0, 17.6;
HRMS (ESI) for C₁₄H₂₀O: calcd. 204.15141; found 204.15673.

General procedure for the dehydrative substitution of alcohols

General procedure A.

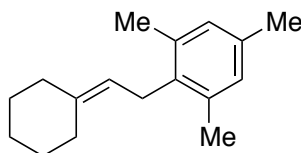
To a 10 mL reaction tube containing the alcohol (0.5 mmol) in nitromethane (2.5 mL) was added the nucleophile (1.1 to 3 equiv), followed by B(C₆F₅)₃ (1 to 5 mol%). The vial was capped and the mixture allowed to stir for 0.5 to 2 h at room temperature, 80 or 100 °C. After cooling to room temperature, the reaction mixture was diluted with water and extracted twice with EtOAc. The organic layers were combined, washed with brine, dried over Na₂SO₄, filtered and volatiles were removed in vacuo. The residue was purified by flash chromatography on SiO₂.

General procedure B.

To a 10 mL reaction tube containing the alcohol (0.5 mmol) in nitromethane (2.5 mL) was added the nucleophile (1.1 to 3 equiv), followed by B(C₆F₅)₃ (1 to 5 mol%). The vial was capped and the mixture allowed to stir for 0.5 to 2 h at room temperature, 80 or 100 °C. After cooling to room temperature, volatiles were removed in vacuo. The residue was purified by flash chromatography on SiO₂.

General procedure C.

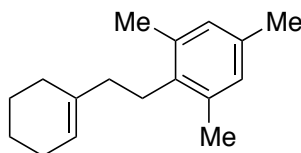
To a 10 mL reaction tube containing the alcohol (0.5 mmol) in nitromethane (2.5 mL) was added B(C₆F₅)₃ (1 to 15 mol%). The vial was capped and the mixture allowed to stir for 1 to 18 h at room temperature, 80 or 100 °C. After cooling to room temperature, volatiles were removed in vacuo. The residue was purified by flash chromatography on SiO₂.



1-(2-Cyclohexylidenethyl)-2,4,6-trimethylbenzene (**3a**). Synthesized according to general procedure A after 1 h at 80 °C starting with the alcohol **1** (63 mg, 0.5 mmol), mesitylene **2** (180 mg, 1.5 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (105 mg, 92%) as a colorless liquid after column chromatography (100% Petroleum ether). R_f = 0.64 (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 6.92 (s, 2H), 5.03 (t, *J* = 6.8 Hz, 1H), 3.39 (d, *J* = 6.8 Hz, 2H), 2.41-2.37 (m, 2H), 2.36 (s, 6H), 2.33 (s, 3H), 2.16-2.10 (m, 2H), 1.70-1.34 (m, 6H);
¹³C NMR (100 MHz, CDCl₃) δ 139.2, 136.2, 135.5, 135.1, 128.9, 118.9, 37.2, 29.0, 28.6, 27.8, 27.6, 27.0, 20.9, 20.0;

HRMS (ESI) for C₁₇H₂₄: calcd. 228.1878; found 228.1888.

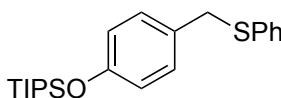


2-(2-(Cyclohex-1-en-1-yl)ethyl)-1,3,5-trimethylbenzene (**3b**).

¹H NMR (400 MHz, CDCl₃) δ 6.97 (s, 2H), 5.65 (s, 1H), 2.87-278 (m, 2H), 2.44 (s, 6H), 2.39 (s, 3H), 2.22-2.13 (m, 6H), 1.85-1.70 (m, 4H);

¹³C NMR (100 MHz, CDCl₃) δ 138.0, 136.2, 135.9, 134.9, 128.9, 120.9, 37.5, 28.4, 28.4, 25.3, 23.1, 22.6, 20.1, 19.7.

HRMS (ESI) for C₁₇H₂₄: calcd. 228.1878; found 228.1888.

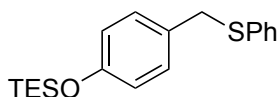


4-Triisopropylsilyloxybenzyl-phenyl sulfide (**5a**). Synthesized according to general procedure A after 2 h at 80 °C starting the alcohol **4a** (140.2 mg, 0.5 mmol), thiophenol (56 μL, 60.6 mg, 0.55 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (171.3 mg, 92%) as a colorless oil after column chromatography (Petroleum ether). R_f = 0.71 (Petroleum ether/CH₂Cl₂ 8:2).

¹H NMR (400 MHz, CDCl₃): δ 7.32–7.16 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.06 (s, 2H), 1.32–1.20 (m, 3H), 1.11 (d, *J* = 7.1 Hz, 18H);

¹³C NMR (100 MHz, CDCl₃): δ 155.3, 136.5, 130.3, 130.0, 129.9, 128.9, 126.5, 120.0, 38.9, 18.0, 12.8.

HRMS (ESI) for C₂₂H₃₂OSSi: calcd. 372.1943; found 372.1960.

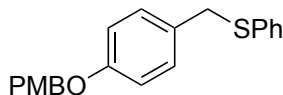


4-Triethylsilyloxybenzyl-phenyl sulfide (**5b**). Synthesized according to general procedure A after 2 h at 80 °C starting the alcohol **4b** (119.2 mg, 0.5 mmol), thiophenol (154 μL, 165.3 mg, 1.5 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (113.4 mg, 69%) as a colorless oil after column chromatography (10% CH₂Cl₂ in Petroleum ether). R_f = 0.33 (Petroleum ether/CH₂Cl₂ 8:2).

¹H NMR (400 MHz, CDCl₃): δ 7.32–7.16 (m, 5H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 4.06 (s, 2H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.73 (q, *J* = 7.9 Hz, 6H);

¹³C NMR (100 MHz, CDCl₃): δ 154.9, 136.6, 130.2, 130.1, 130.1, 128.9, 126.4, 120.1, 38.8, 6.7, 5.1.

HRMS (ESI) for C₁₉H₂₆OSSi: calcd. 330.1473; found 330.1466.

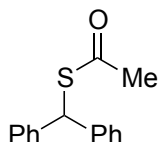


p-Methoxybenzyl-4-oxybenzyl-phenyl sulfide (**5c**). Synthesized according to general procedure A after 4 h at 22 °C starting with the alcohol **4c** (122.1 mg, 0.5 mmol), thiophenol (56 μ L, 60.6 mg, 0.55 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (136.2 mg, 81%) as a colorless solid after column chromatography (25% CH₂Cl₂ in Petroleum ether). R_f = 0.21 (Petroleum ether/CH₂Cl₂ 8:2).

¹H NMR (400 MHz, CDCl₃): δ 7.39–7.16 (m, 9H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 4.09 (s, 2H), 3.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 159.6, 158.2, 136.7, 130.1, 129.9, 129.7, 129.3, 129.2, 128.9, 126.4, 115.0, 114.2, 70.0, 55.4, 38.6.

HRMS (ESI) for C₂₁H₂₀O₂S: calcd. 336.1184; found 330.1183.

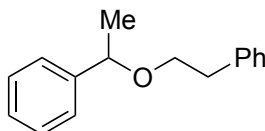


S-Benzhydryl-ethanethioate (**5d**).⁷ Synthesized according to general procedure A after 3 h at 22 °C starting with the alcohol **4d** (92.1 mg, 0.5 mmol), thioacetic acid (107 μ L, 114.2 mg, 1.5 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (103.1 mg, 85%) as a white solid after column chromatography (10% CH₂Cl₂ to 20% CH₂Cl₂ in Petroleum ether). R_f = 0.28 (Petroleum ether/CH₂Cl₂ 8:2).

¹H NMR (400 MHz, CDCl₃): δ 7.38–7.21 (m, 10H), 5.97 (s, 1H), 2.35 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 193.9, 141.1, 128.7, 128.5, 127.4, 52.0, 30.4.

The analytical data are in accordance with those reported in the literature.



1-(2-Phenylethoxy)ethyl-benzene (**5e**).⁸ Synthesized according to general procedure A after 2 h at 80 °C starting with the alcohol **5e** (61.1 mg, 0.5 mmol), 2-phenyl ethanol (122.2 mg, 1.0 mmol) and B(C₆F₅)₃ (5.2 mg, 0.010 mmol, 2.0 mol%). Isolated (108.7 mg, 96%) as a white solid after column chromatography (3% EtOAc in Petroleum ether).

R_f = 0.34 (Petroleum ether/EtOAc 30:1).

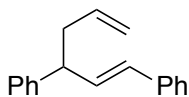
¹H NMR (400 MHz, CDCl₃): δ 7.45–7.21 (m, 10H), 4.47 (q, *J* = 6.4 Hz, 1H), 3.58 (t, *J* = 7.4 Hz, 2H), 3.03–2.88 (m, 2H), 1.50 (d, *J* = 1.5 Hz, 3H);¹

¹³C NMR (100 MHz, CDCl₃): δ 144.1, 139.2, 129.1, 128.5, 128.4, 127.5, 126.2, 126.2, 78.2, 69.7, 36.7, 24.2.

⁷ C. Liu, M.-B. Li, C.-F. Yang, S.-K. Tian, *Chem. Eur. J.* **2009**, *15*, 793–797.

⁸ D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Utsunomiya, J. F. Hartwig, *Org. Lett.* **2006**, *8*, 4179-4182.

The analytical data are in accordance with those reported in the literature.

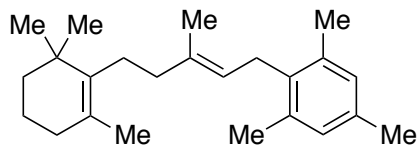


(*E*)-Hexa-1,5-diene-1,3-diyl dibenzene (**5f**).⁹ Synthesized according to general procedure A after 1 h at 22 °C starting with the alcohol **4f** (105 mg, 0.5 mmol), allyltrimethylsilane (238 μ L, 171 mg, 1.5 mmol) and $B(C_6F_5)_3$ (7.8 mg, 0.015 mmol, 3.0 mol%). Isolated (116 mg, 99%) as a colorless liquid without further purification. $R_f = 0.33$ (Petroleum ether).

¹H NMR (400 MHz, $CDCl_3$) δ 7.49-7.27 (m, 10H), 6.56-6.45 (m, 2H), 5.96-5.84 (m, 1H), 5.23-5.10 (m, 2H), 3.69-3.61 (m, 1H), 2.78-2.65 (m, 2H);

¹³C NMR (100 MHz, $CDCl_3$) δ 144.0, 137.6, 136.6, 133.6, 129.9, 128.6, 128.6, 127.9, 127.2, 126.5, 126.3, 116.5, 49.1, 40.3.

The analytical data are in accordance with those reported in the literature.

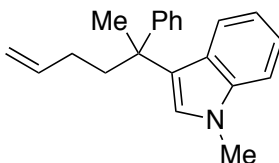


1,3,5-Trimethyl-2-(3-methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pent-2-en-1-yl)benzene (**5g**). Synthesized according to general procedure A after 1 h at 80 °C starting with the alcohol **4g** (111.2 mg, 0.5 mmol), mesitylene **2** (180 mg, 1.5 mmol) and $B(C_6F_5)_3$ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (90 mg, 55%) as a colorless liquid after column chromatography (100% Petroleum ether). $R_f = 0.52$ (Petroleum ether).

¹H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 5.16 (t, $J = 6.2$ Hz, 1H), 3.44 (d, $J = 6.2$ Hz, 2H), 2.49-2.38 (m, 9H), 2.24-1.54 (m, 16H), 1.12 (s, 6H);

¹³C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.4, 136.3, 135.7, 135.1, 128.9, 127.0, 121.8, 40.4, 40.0, 35.1, 32.9, 28.7, 28.5, 28.0, 20.9, 20.1, 19.9, 19.7, 16.4;

HRMS (ESI) for $C_{24}H_{36}$: calcd. 324.28170; found 324.28247.



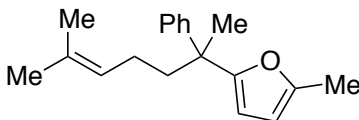
1-Methyl-3-(2-phenylhex-5-en-2-yl)indole (**5h**). Synthesized according to general procedure A after 1 h at 80 °C starting with the alcohol **4h** (105.7 mg, 0.5 mmol), *N*-methylindole (65.6 mg, 0.5 mmol) and $B(C_6F_5)_3$ (13.25 mg, 0.025 mmol, 5.0 mol%). Isolated (139 mg, 96%) as a white solid after column chromatography (100% Petroleum ether). $R_f = 0.23$ (Petroleum ether).

⁹ G. G. K. S. Narayana Kumar, Kenneth K. Laali, *Org. Biomol. Chem.* **2012**, *10*, 7347-7355.

¹H NMR (400 MHz, CDCl₃) δ 7.52-7.25 (m, 7H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 7.03-6.98 (m, 1H), 6.01-5.87 (m, 1H), 5.16-5.01 (m, 2H), 3.88 (s, 3H), 2.54-2.32 (m, 2H), 2.09-1.98 (m, 2H), 1.88 (s, 3H) ;

¹³C NMR (100 MHz, CDCl₃) δ 148.9, 139.5, 137.8, 128.0, 129.1, 126.6, 126.3, 125.7, 123.2, 121.5, 121.3, 118.4, 114.1, 109.2, 42.3, 40.9, 32.8, 29.3, 27.8 ;

HRMS (ESI) for C₂₁H₂₃N: calcd. 289.18305 ; found 289.18402.

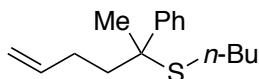


2-Methyl-5-(6-methyl-2-phenylhept-5-en-2-yl)furan (**5i**). Synthesized according to general procedure A after 1 h at 80 °C starting with the alcohol **4i** (102.1 mg, 0.5 mmol), 2-methylfuran (123.1 mg, 1.5 mmol) and B(C₆F₅)₃ (7.95 mg, 0.015 mmol, 3.0 mol%). Isolated (118 mg, 88%) as a colorless liquid after column chromatography (100% Petroleum ether). R_f = 0.35 (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.45-7.27 (m, 5H), 6.16 (d, *J* = 3.0 Hz, 1H), 6.02 (dd, *J* = 3.0 and 1.0 Hz, 1H), 5.28 (m, 1H), 2.36 (s, 3H), 2.28-2.10 (m, 2H), 2.07-1.91 (m, 2H), 1.82 (s, 3H), 1.77 (s, 3H), 1.67 (s, 3H) ;

¹³C NMR (100 MHz, CDCl₃) δ 159.6, 150.7, 147.6, 131.5, 128.1, 126.5, 126.0, 124.6, 106.3, 105.6, 43.8, 40.8, 28.5, 25.2, 23.6, 17.6, 13.7 ;

HRMS (ESI) for C₁₉H₂₄O: calcd. 268.18271; found 268.18617.

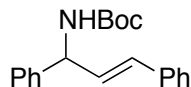


Butyl(2-phenylhex-5-en-2-yl)sulfide (**5j**). Synthesized according to general procedure A after 1 h at 80 °C starting with the alcohol **4h** (88.1 mg, 0.5 mmol), 1-butanethiol (49.6 mg, 10.55 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (112 mg, 90%) as a colorless liquid after column chromatography (100% Petroleum ether). R_f = 0.31 (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.65-7.24 (m, 5H), 5.93-5.77 (m, 1H), 5.13-4.96 (m, 2H), 2.45-2.33 (m, 1H), 2.26-2.12 (m, 3H), 2.07-1.92 (m, 2H), 1.81 (s, 3H), 1.48-1.31 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H) ;

¹³C NMR (100 MHz, CDCl₃) δ 145.2, 138.4, 128.1, 127.0, 126.3, 114.5, 51.0, 42.1, 31.3, 29.1, 28.5, 26.2, 22.2, 13.7 ;

HRMS (ESI) for C₁₆H₂₄S: calcd. 248.15987; found 248.16013.



tert-Butyl *N*-[(2*E*)-1,3-diphenyl-2-propen-1-yl]carbamate (**5k**).¹⁰ Synthesized according to general procedure B after 1 h at 22 °C starting with the alcohol **4f** (105 mg, 0.5 mmol),

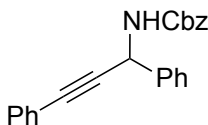
¹⁰ K. Das, R. Shibuya, Y. Nakahara, N. Germain, T. Ohshima, K. Mashima, *Angew. Chem. Int. Ed.* **2012**, *51*, 150-154.

tert-butyl carbamate (117 mg, 1.0 mmol) and B(C₆F₅)₃ (5.2 mg, 0.010 mmol, 2.0 mol%). Isolated (146 mg, 94%) as a white solid after column chromatography (1 to 10% EtOAc in Petroleum ether). R_f = 0.39 (Petroleum ether/EtOAc 9:1).

¹H NMR (400 MHz, CDCl₃) δ 7.43-7.24 (m, 10H), 6.58 (dd, *J* = 15.9 and 1.0 Hz, 1H), 6.36 (dd, *J* = 15.9 and 6.0 Hz, 1H), 5.50 (br, 1H), 5.03 (br, 1H), 1.50 (s, 9H);

¹³C NMR (100 MHz, CDCl₃) δ 155.0, 141.4, 136.6, 131.0, 129.6, 128.7, 128.6, 127.7, 127.5, 127.0, 126.5, 79.8, 56.3, 28.4.

The analytical data are in accordance with those reported in the literature.

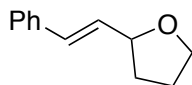


N-(1,3-Diphenylpropynyl)-benzyl-carbamate (**5i**).¹¹ Synthesized according to general procedure A after 2 h at 80 °C starting with the alcohol **4j** (104.1 mg, 0.5 mmol), benzyl carbamate (151.2 mg, 1.0 mmol) and 1 mol% of B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (167.2 mg, 98%) as a white solid after column chromatography (5% CH₂Cl₂ in Petroleum ether). R_f = 0.16 (Petroleum ether/CH₂Cl₂ 20:1).

¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 6.7 Hz, 2H), 7.55–7.47 (m, 2H), 7.46–7.31 (m, 11H), 6.03 (d, *J* = 8.3 Hz, 1H), 5.55 (d, *J* = 8.3 Hz, 1H), 5.28–5.13 (m, 2H);

¹³C NMR (100 MHz, CDCl₃): δ = 155.5, 139.2, 136.3, 131.9, 128.8, 128.6, 128.6, 128.4, 128.3, 127.1, 122.5, 87.1, 85.2, 67.2, 47.5.

The analytical data are in accordance with those reported in the literature.

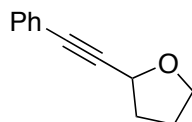


(*E*)-2-Styryltetrahydrofuran (**7**).⁶ Synthesized according to general procedure C after 1 or 2 h at 22 °C starting with alcohol **6** (39 mg, 0.2 mmol) and B(C₆F₅)₃ (1.0 mg, 0.002 mmol, 1.0 mol%). Isolated (32 and 29 mg, 91 and 82 %, respectively) as a colorless liquid after column chromatography (0 to 5% EtOAc in Petroleum ether). R_f = 0.35 (Petroleum ether/EtOAc 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.46-7.24 (m, 5H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9 and 6.6 Hz, 1H), 4.56-4.48 (m, 1H), 4.05-3.98 (m, 1H), 3.93-3.85 (m, 1H), 2.22-1.92 (m, 4H);

¹³C NMR (100 MHz, CDCl₃) δ 136.9, 130.6, 130.4, 128.5, 127.5, 126.5, 79.7, 68.2, 32.4, 25.9. The analytical data are in accordance with those reported in the literature.

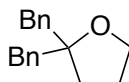
¹¹ B. G. Das, R. Nallagonda, P. Ghorai, *J. Org. Chem.* **2012**, *77*, 5577–5583.



2-(Phenylethynyl)tetrahydrofuran (**9**).¹² Synthesized according to general procedure C after 18 h at 80 °C starting with the alcohol **8** (95 mg, 0.5 mmol) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (75 mg, 87%) as a colorless liquid after column chromatography (0 to 5% EtOAc in Petroleum ether). R_f = 0.31 (Petroleum ether/EtOAc 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.50-7.42 (m, 2H), 7.35-7.28 (m, 3H), 4.87-4.79 (m, 1H), 4.08-3.98 (m, 1H), 3.92-3.82 (m, 1H), 2.30-1.88 (m, 4H);

¹³C NMR (100 MHz, CDCl₃) δ 131.7, 128.2, 128.8, 122.8, 89.1, 84.5, 68.6, 67.9, 33.4, 25.5. The analytical data are in accordance with those reported in the literature.



2,2-Dibenzyltetrahydrofuran (**11**).⁶ Synthesized according to general procedure C after 4 h at 100 °C starting with the alcohol **10** (27 mg, 0.1 mmol) and B(C₆F₅)₃ (1.0 mg, 0.002 mmol, 2.0 mol%). Isolated (20 mg, 79%) as a colorless liquid after column chromatography (0 to 4% EtOAc in Petroleum ether). R_f = 0.42 (Petroleum ether/EtOAc 20:1).

¹H NMR (400 MHz, CDCl₃) δ 7.33-7.21 (m, 10H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.93 (d, *J* = 13.5 Hz, 2H), 2.80 (d, *J* = 13.5 Hz, 2H), 1.78 (t, *J* = 7.2 Hz, 2H), 1.43-1.35 (m, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 138.3, 130.7, 127.9, 126.1, 85.3, 68.3, 46.2, 32.9, 26.2. The analytical data are in accordance with those reported in the literature.



N-Tosyl pyrrolidine (**13**).¹³ Synthesized according to general procedure C after 4 h at 100 °C starting with the alcohol **12** (49 mg, 0.2 mmol) and B(C₆F₅)₃ (5.2 mg, 0.001 mmol, 5.0 mol%). Isolated (45 mg, 99%) as a white solid after column chromatography (10 to 20% EtOAc in Petroleum ether). R_f = 0.25 (Petroleum ether/EtOAc 10:1).

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.26-3.14 (m, 4H), 2.41 (s, 3H), 1.78-1.68 (m, 4H);

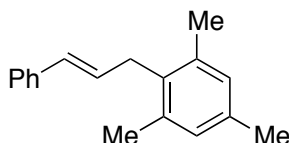
¹³C NMR (100 MHz, CDCl₃) δ 143.3, 134.0, 129.6, 127.5, 47.9, 25.2, 21.5. The analytical data are in accordance with those reported in the literature.

¹² D. S. B. Daniels, A. L. Thompson, E. A. Anderson, *Angew. Chem. Int. Ed.* **2011**, *50*, 11506-11510.

¹³ T. Nishikata, H. Nagashima, *Angew. Chem. Int. Ed.* **2012**, *51*, 5363-5366.



Tetrahydrofuran (**15**). A NMR tube was charged with 1,4-butane diol **14** (9.0 mg, 0.1 mmol) and $B(C_6F_5)_3$ (7.8 mg, 0.015 mmol, 15 mol%), then C_6D_6 (0.5 mL) was added. The reaction mixture was heated to 100 °C for 16 h and the conversion was determined by 1H -NMR based on the relative integration of the methylene resonance of the product at 3.46 ppm with the methylene resonance of the starting material at 3.26 ppm.

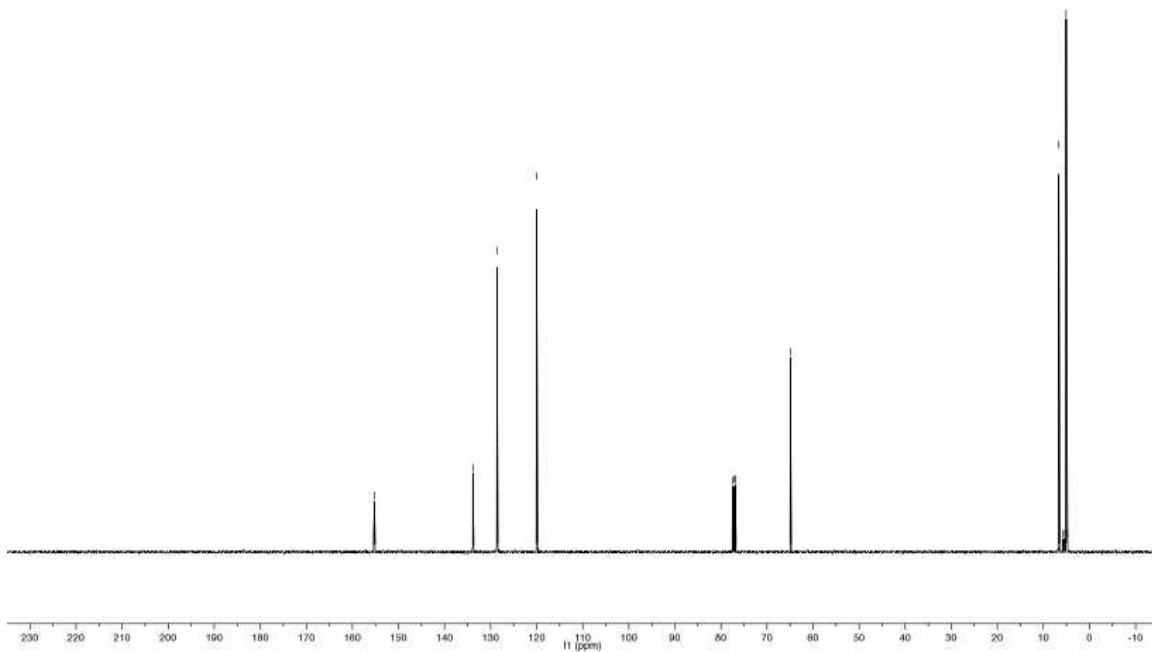
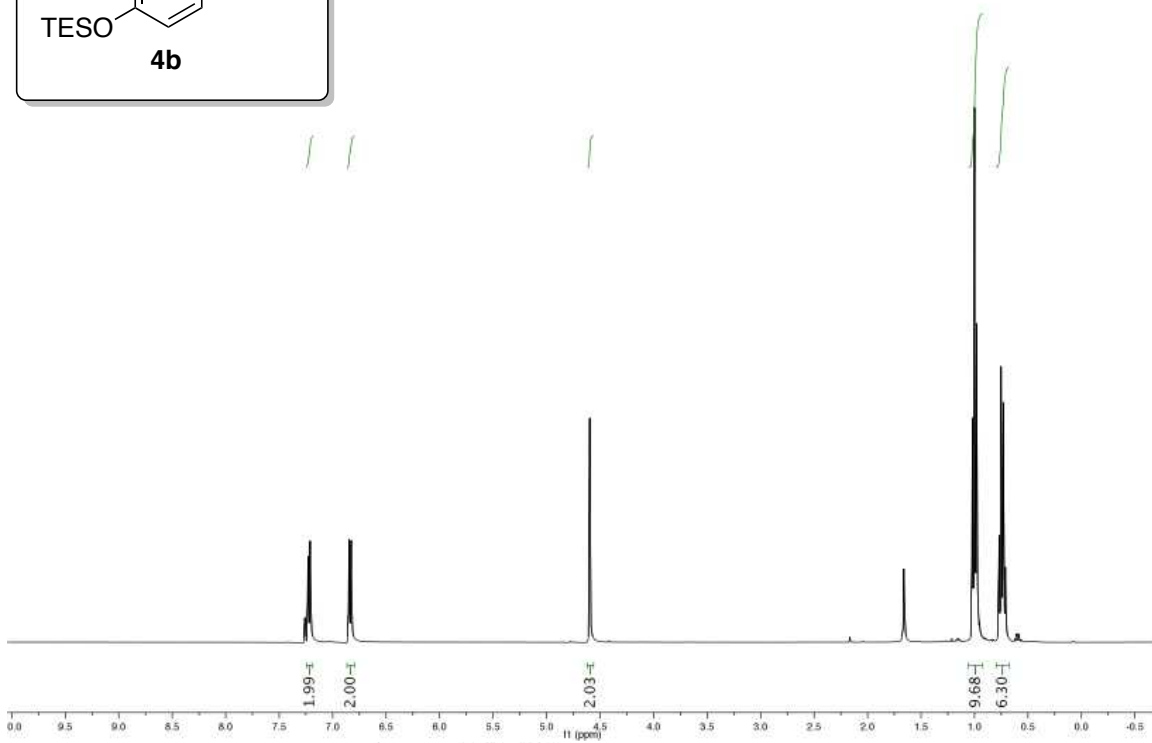
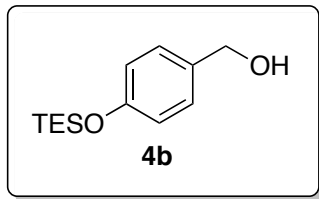


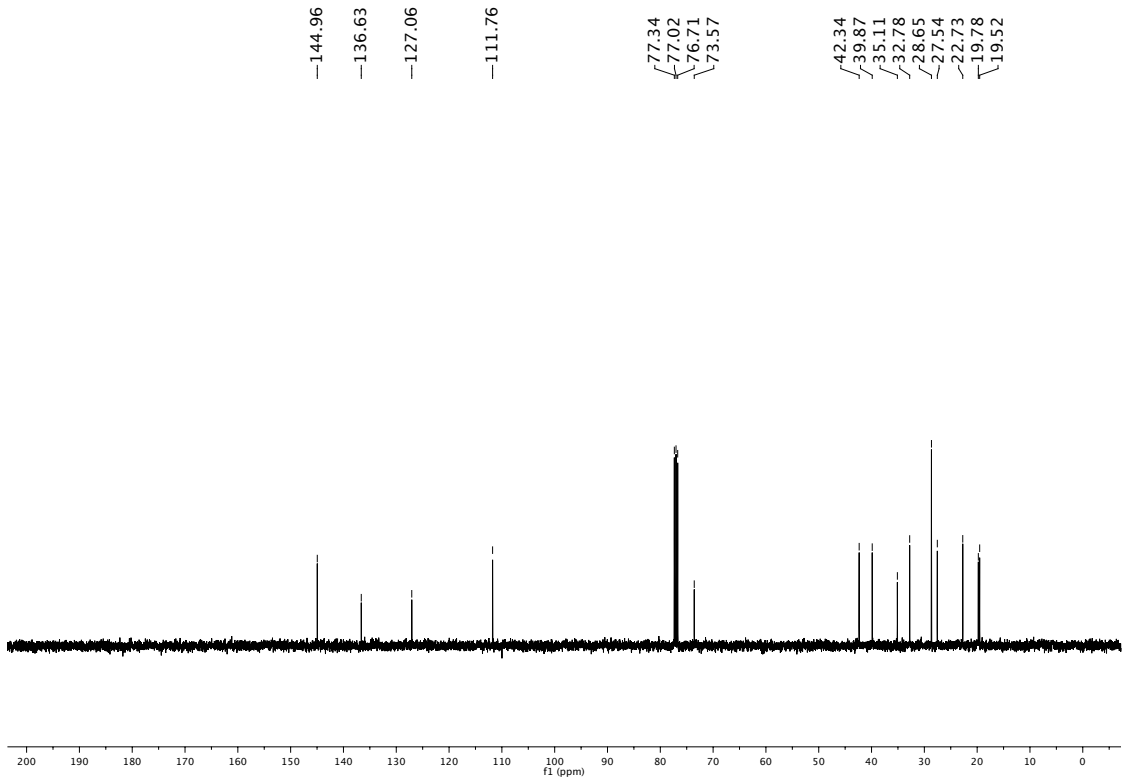
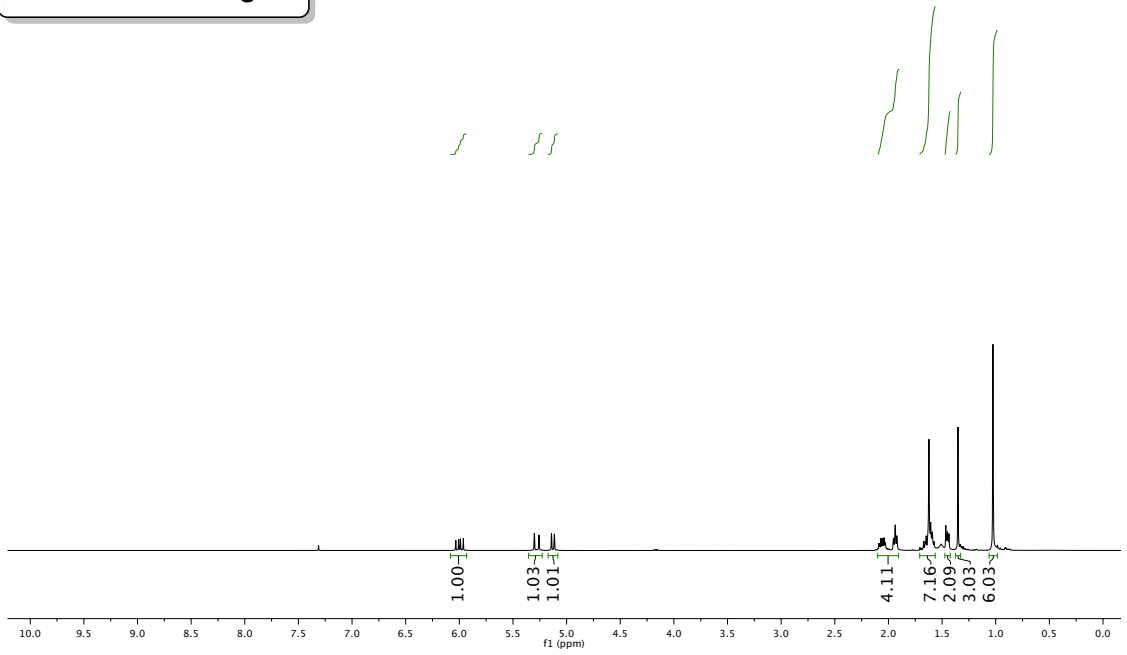
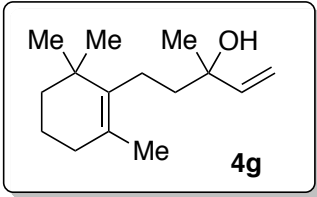
1-Cinnamyl-2,4,6-trimethylbenzene (**17**).¹⁴ Synthesized according to general procedure A after 1 h at 80 °C starting with the alcohol **16** (67 mg, 0.5 mmol), mesitylene **2** (180 mg, 1.5 mmol) and $B(C_6F_5)_3$ (2.6 mg, 0.005 mmol, 1.0 mol%). Isolated (102 mg, 86%) as a colorless liquid after column chromatography (100% Petroleum ether). $R_f = 0.24$ (Petroleum ether).

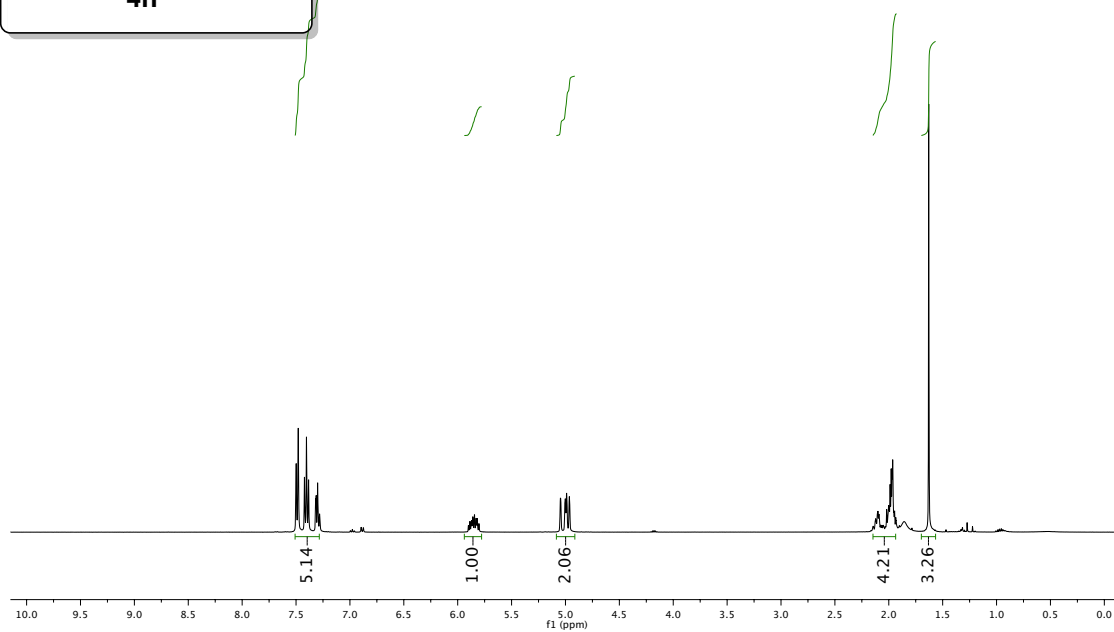
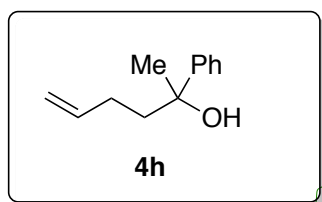
1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.14 (m, 5H), 6.88 (s, 2H), 6.31-6.21 (m, 2H), 3.55 (d, $J = 4.0$ Hz, 1H), 2.31 (s, 6H), 2.28 (s, 3H);

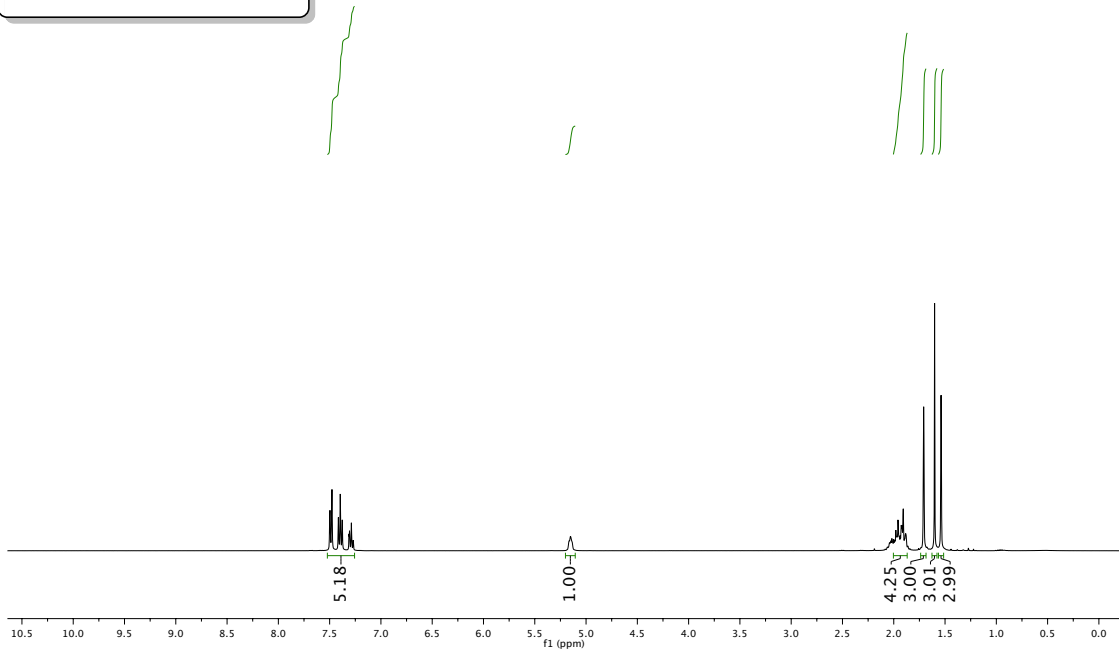
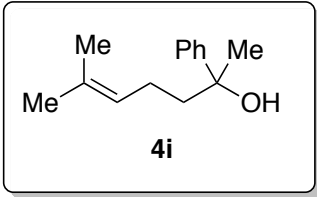
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.7, 135.6, 133.2, 130.0, 129.0, 128.5, 127.8, 127.0, 126.1, 32.7, 21.0, 20.0. The analytical data are in accordance with those reported in the literature.

¹⁴ X.-L. Tang, Z. Wu, M.-B. Li, Y. Gu, S.-K. Tian, *Eur. J. Org. Chem.* **2012**, 22, 4107-4109.

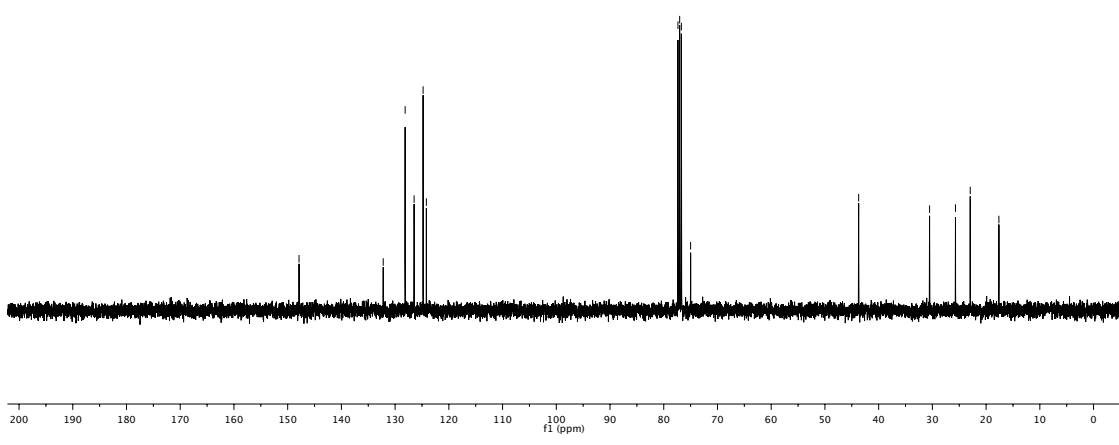


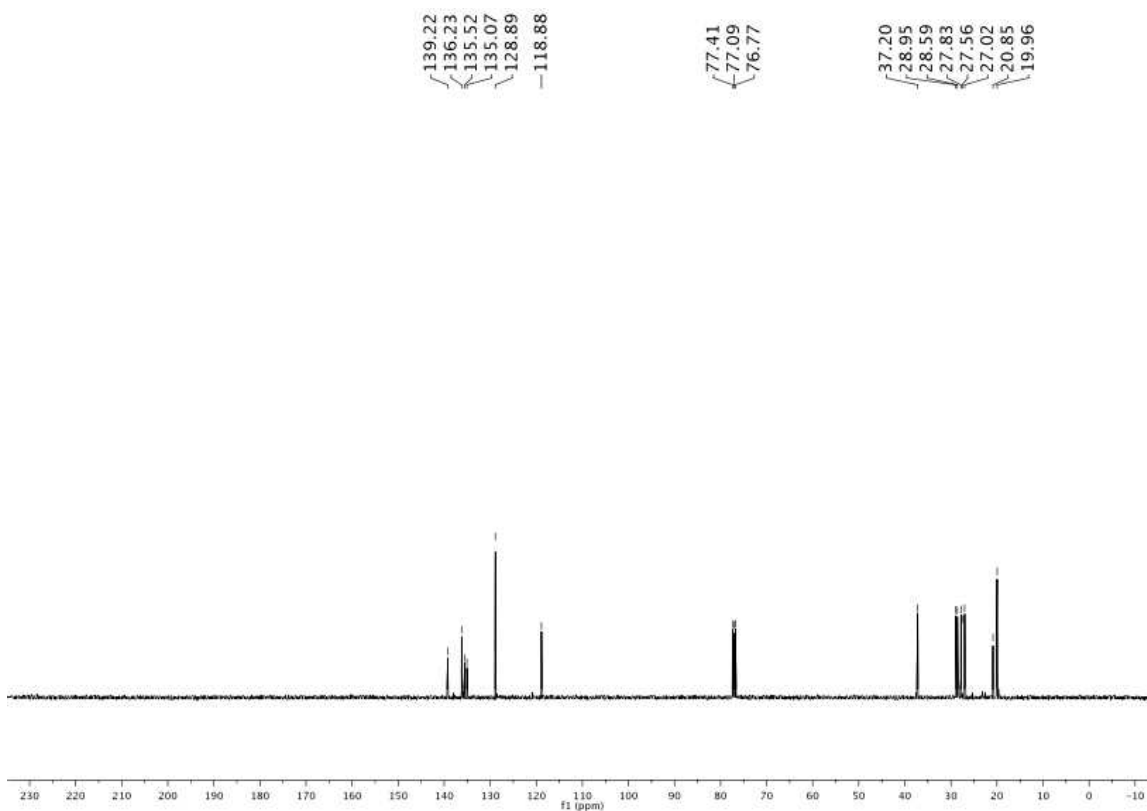
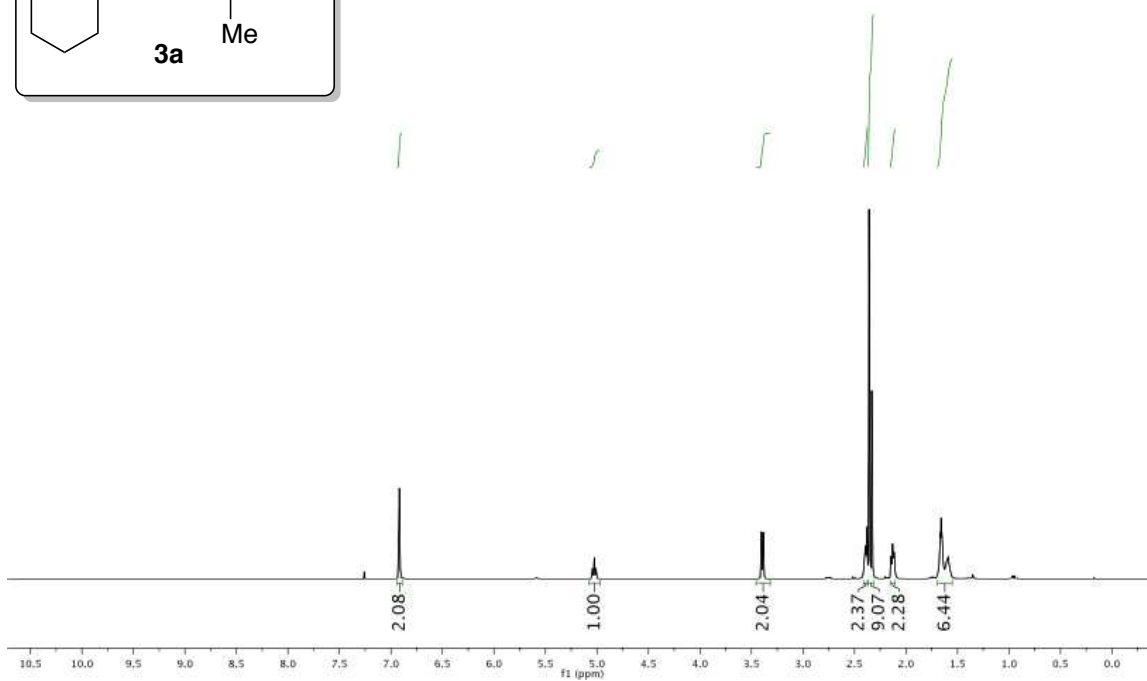
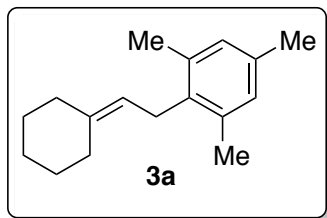


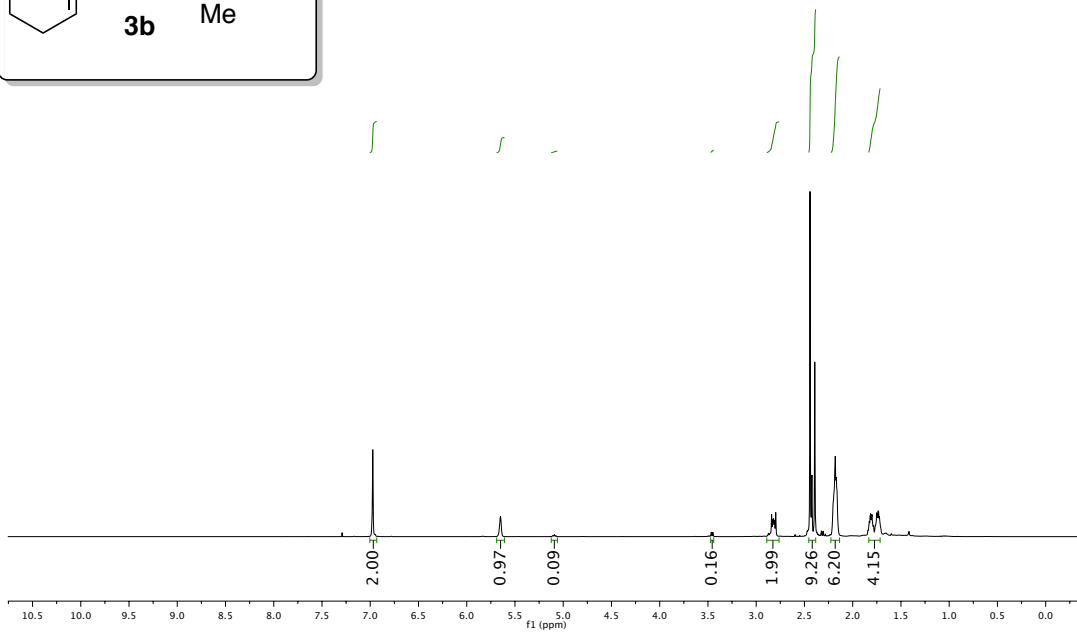
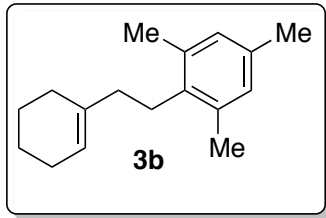




- 147.88
- 132.22
- 128.13
- 126.47
- 124.79
- 124.18
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- 77.04
- 76.72
- 75.00
- 43.72
- 30.52
- 25.70
- 22.95
- 17.62



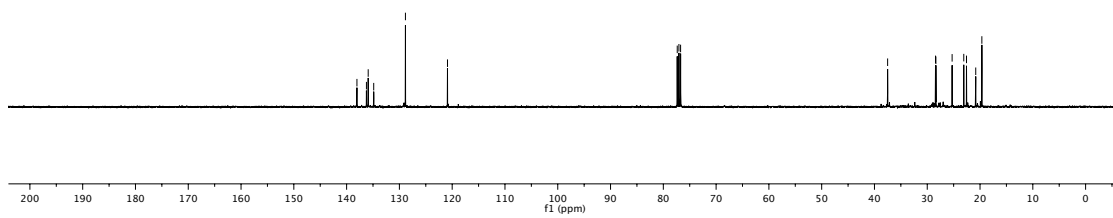


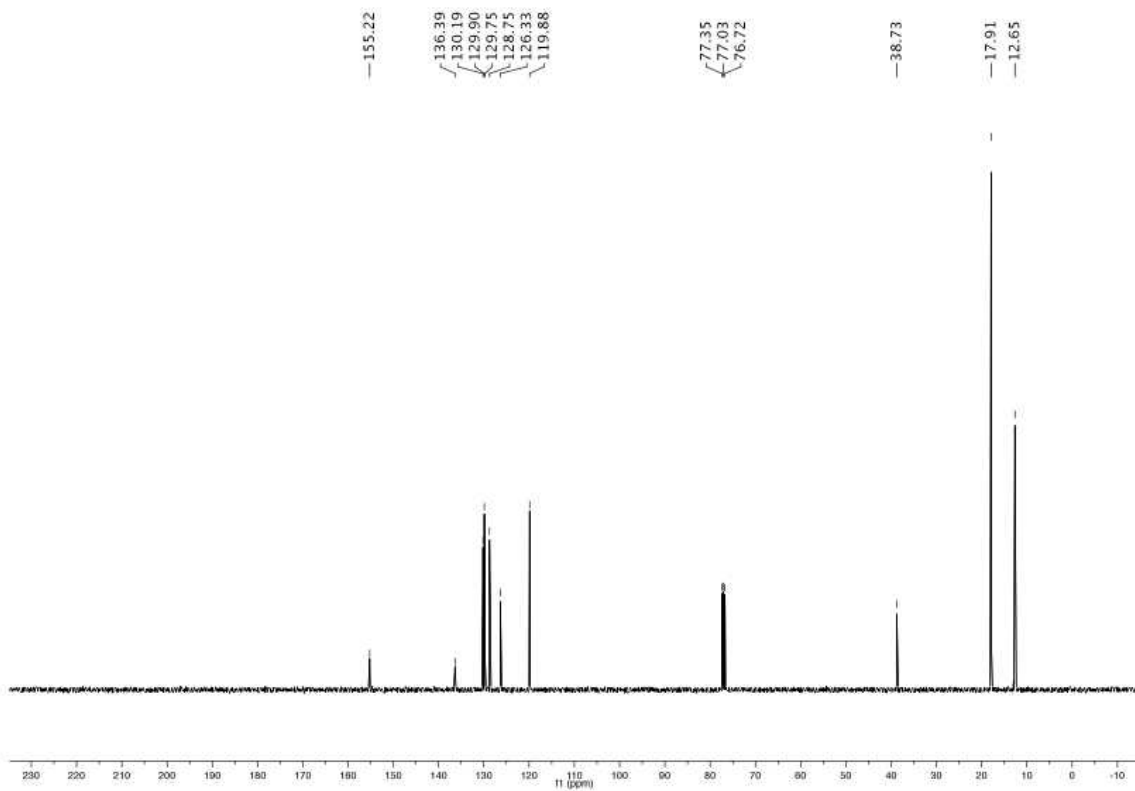
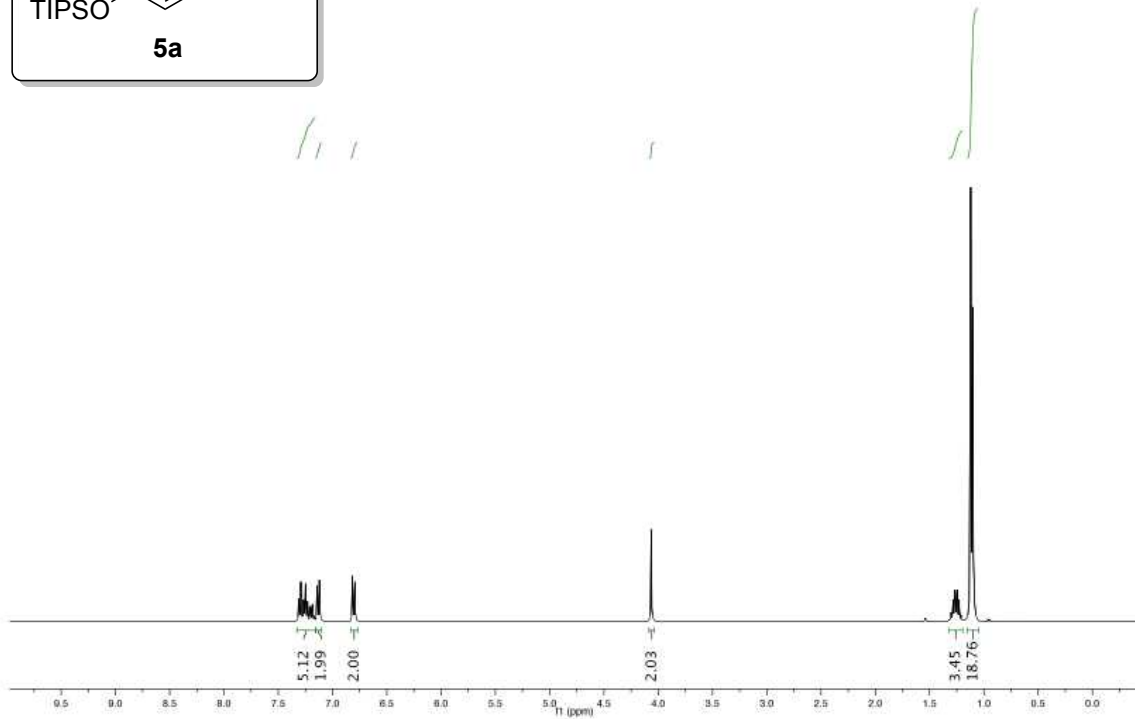
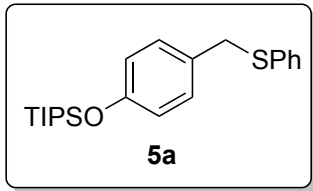


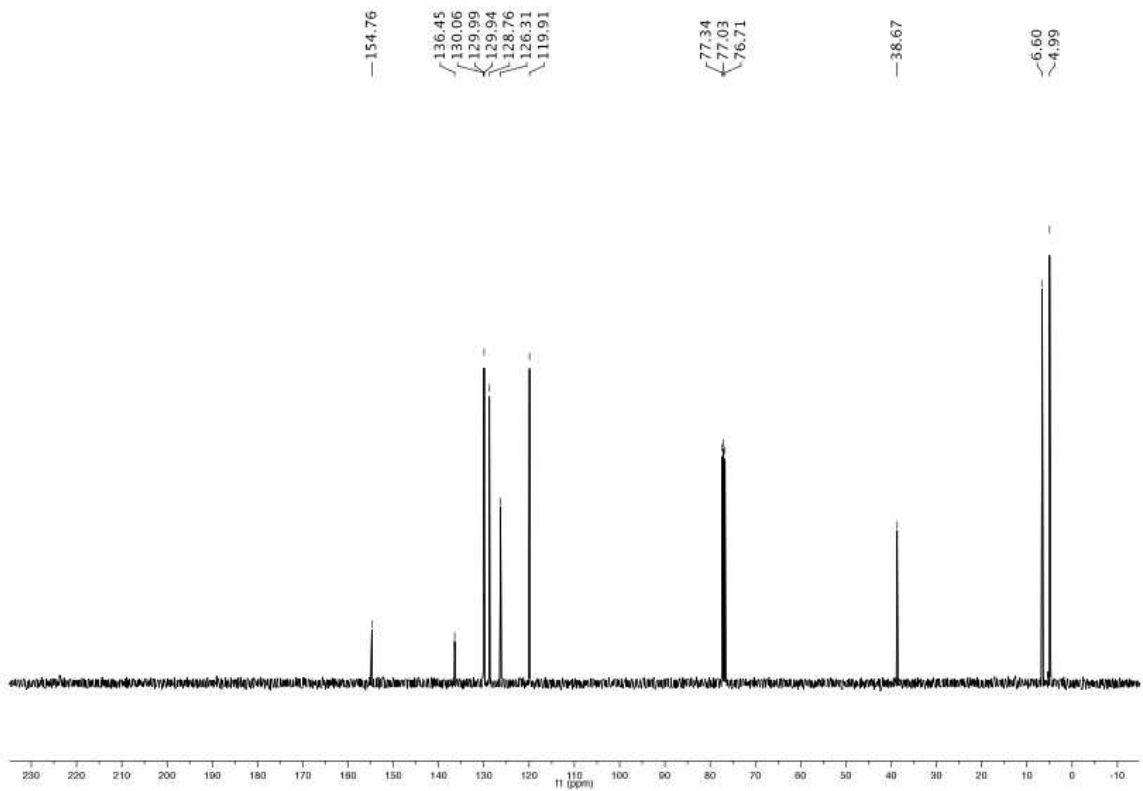
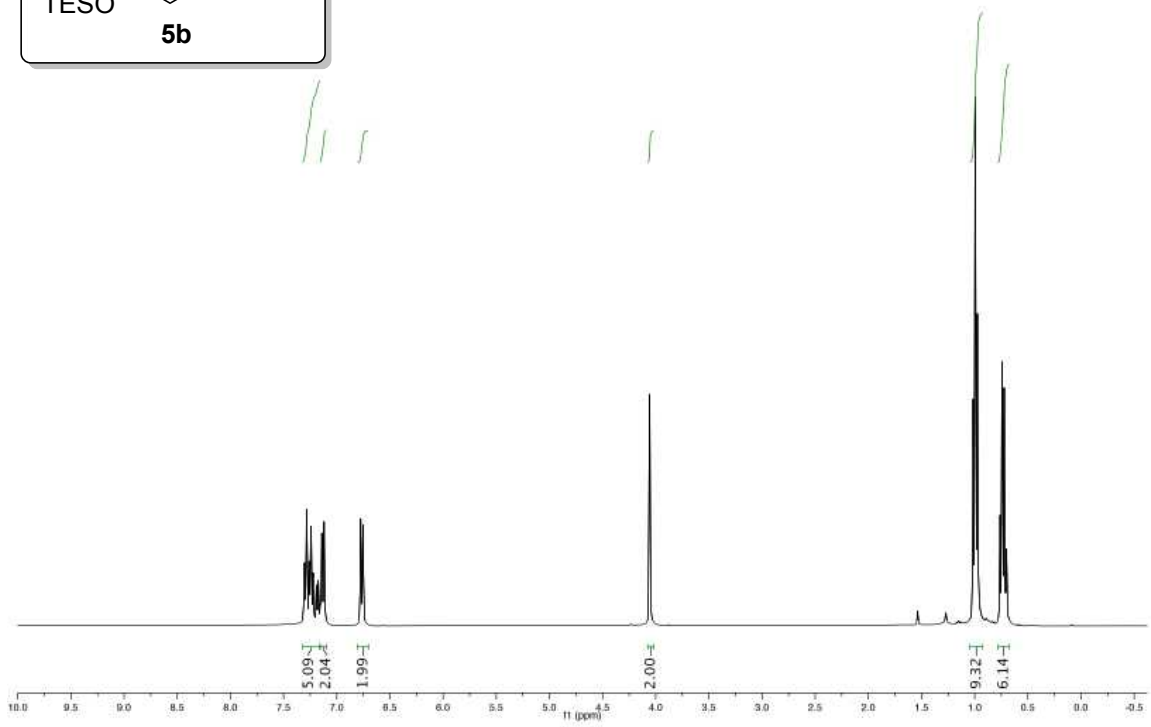
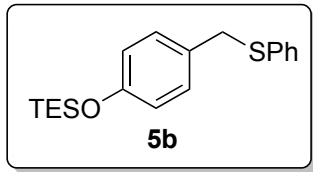
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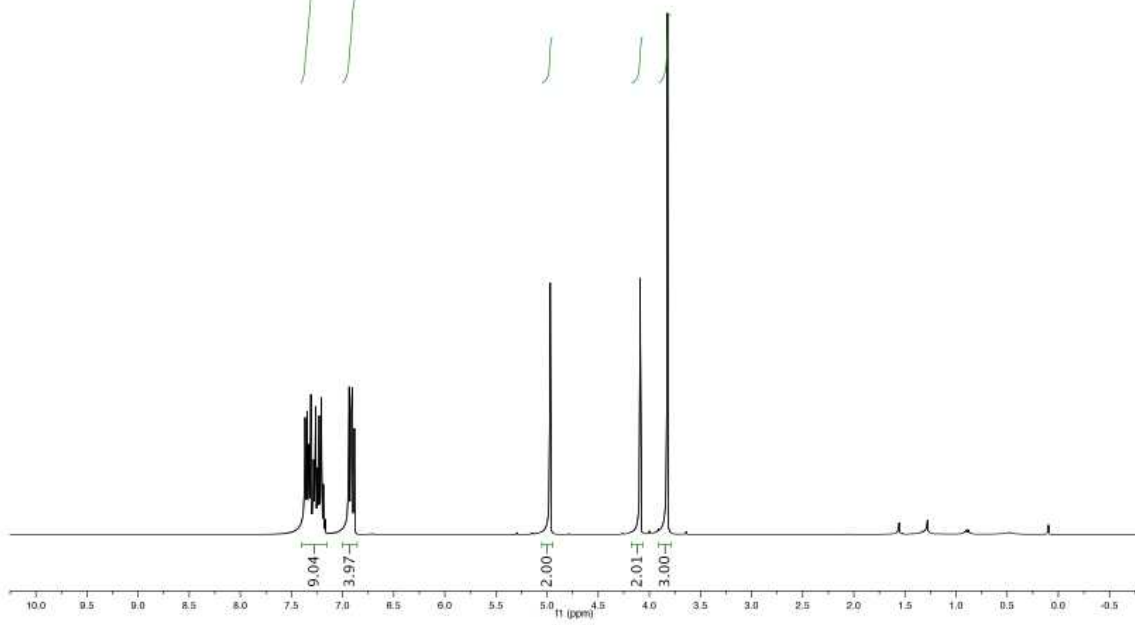
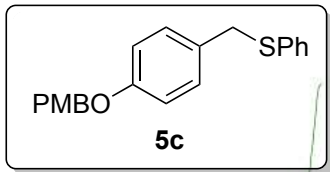
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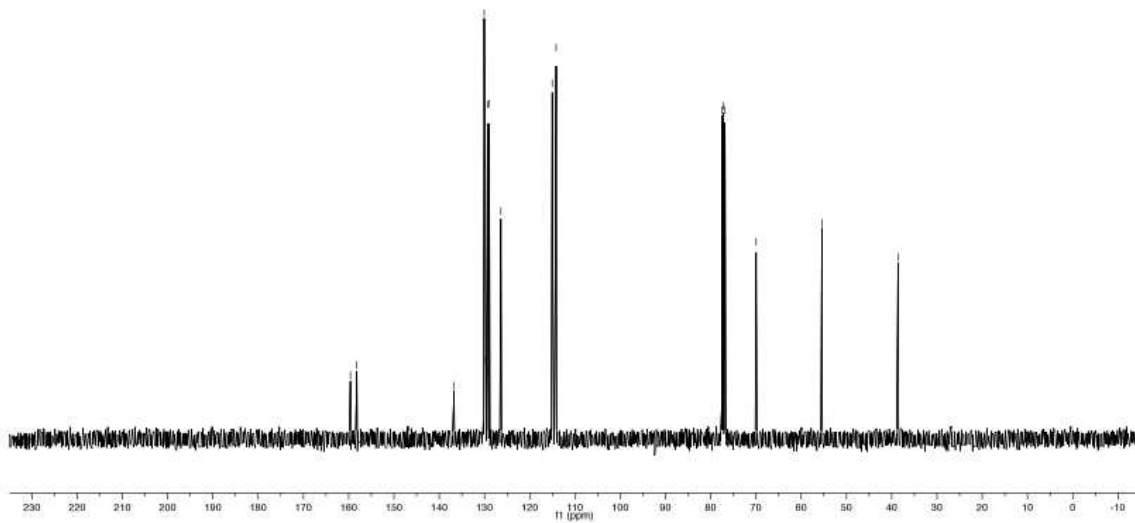


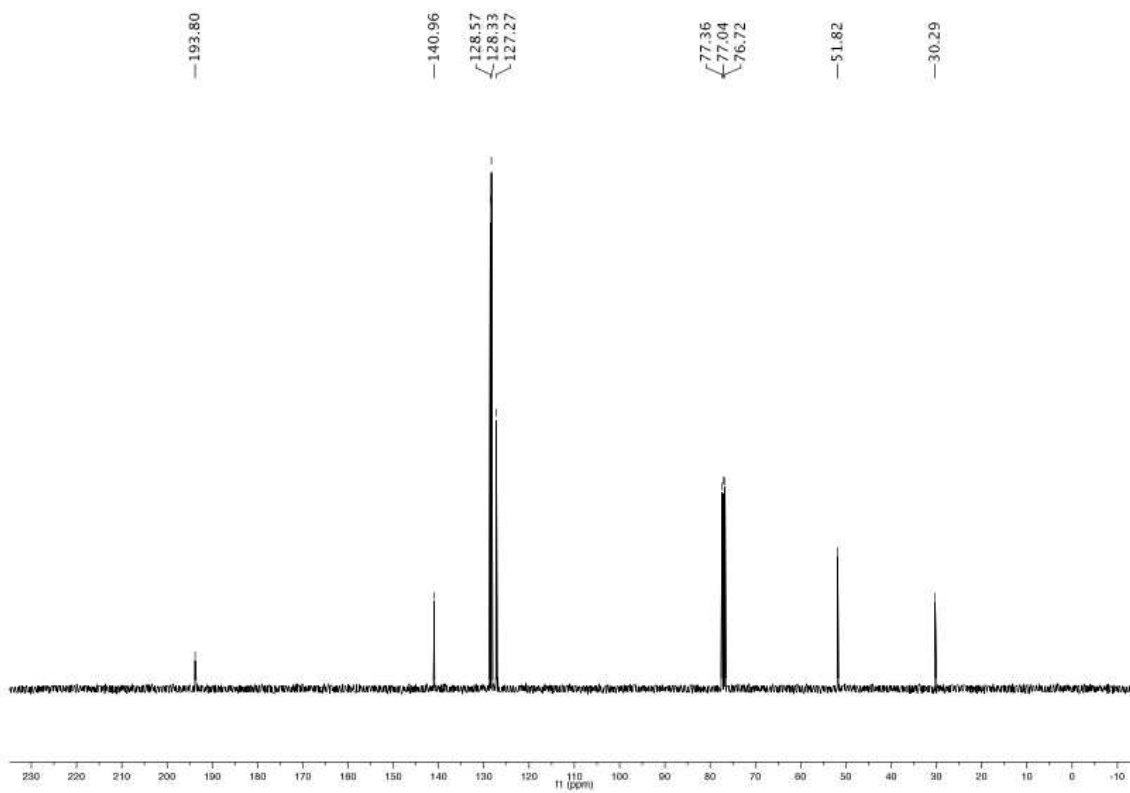
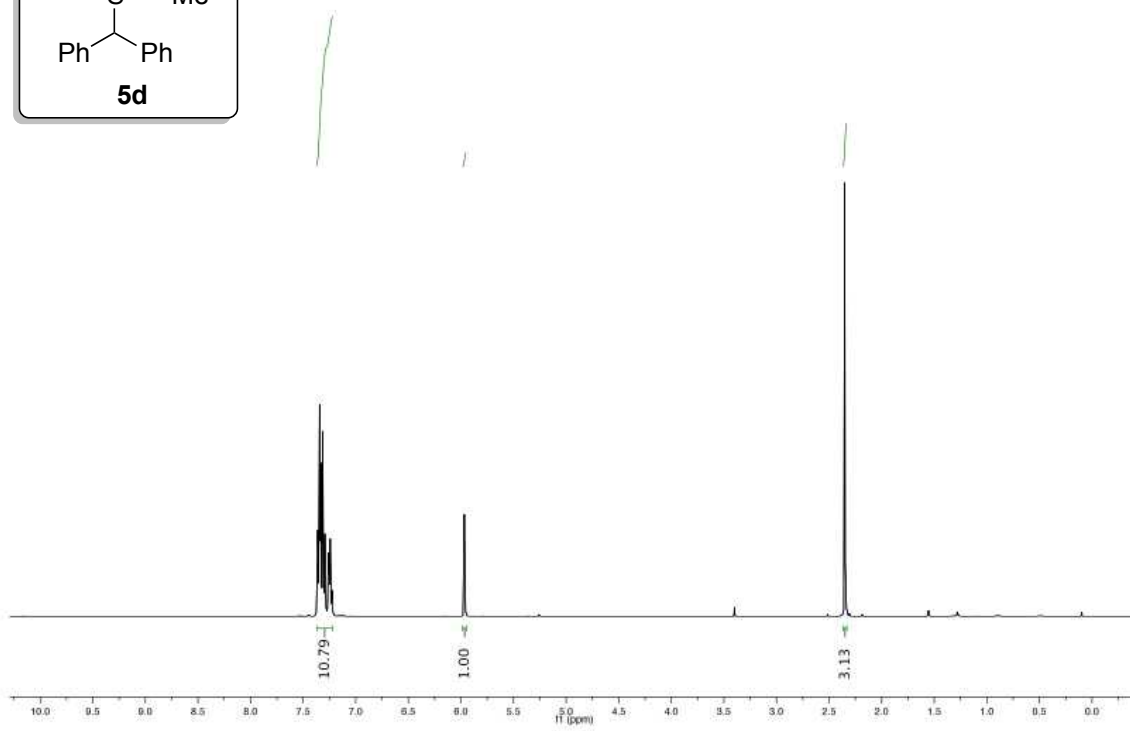
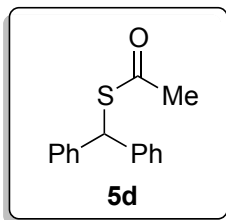


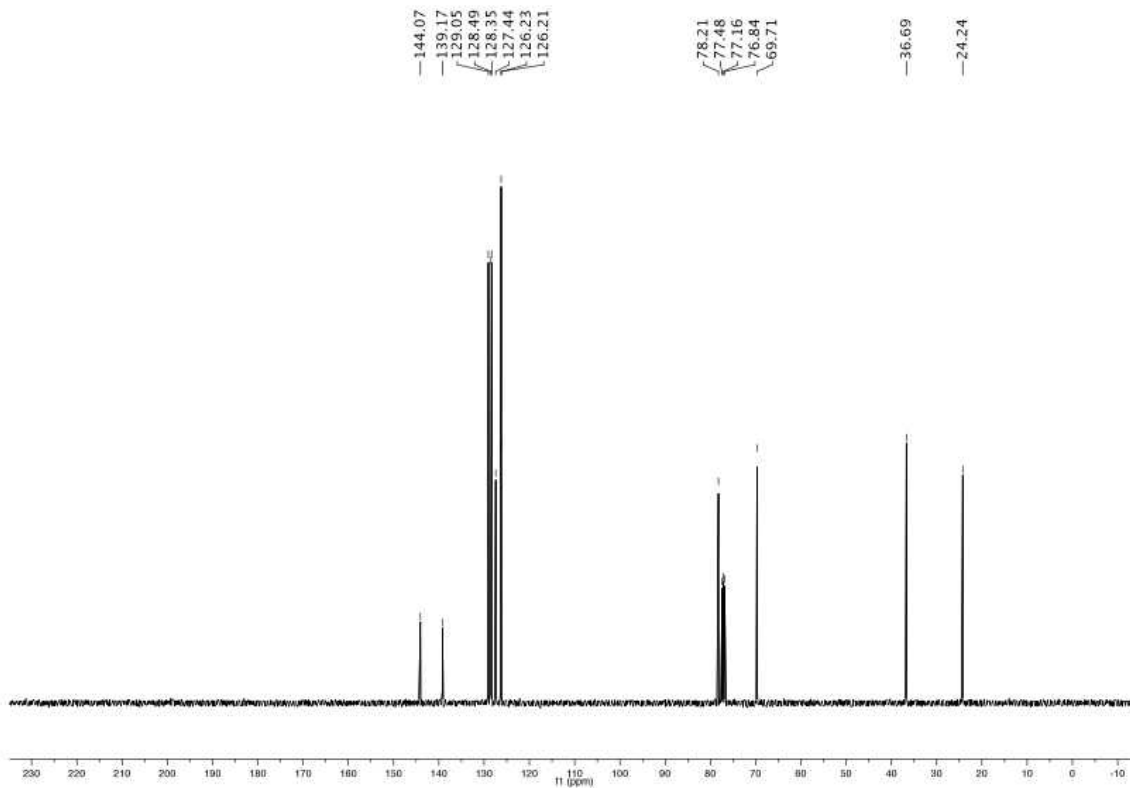
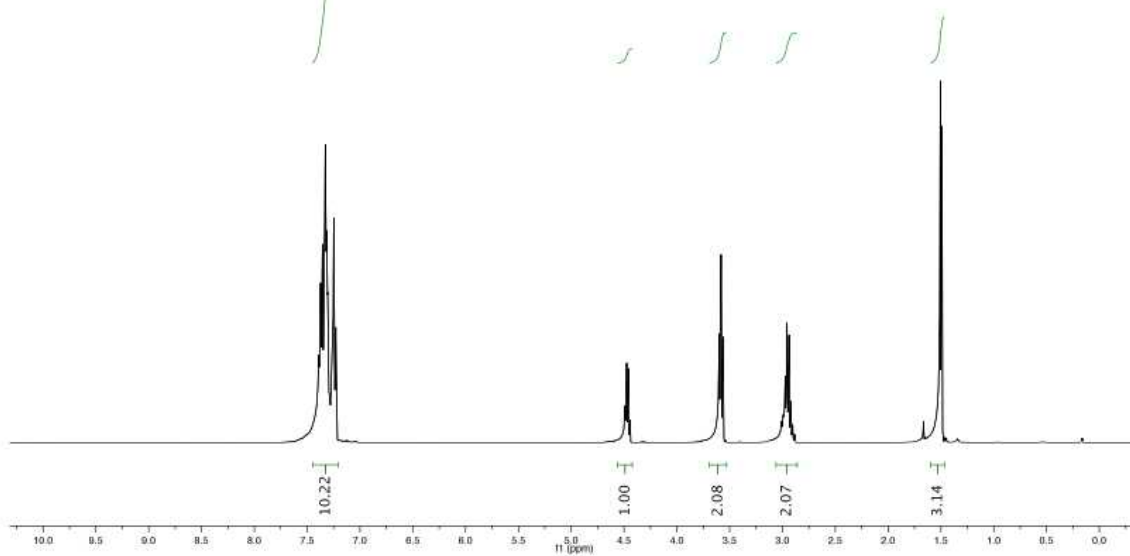
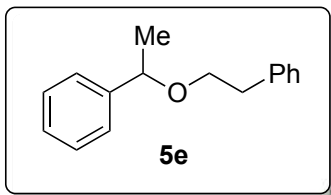


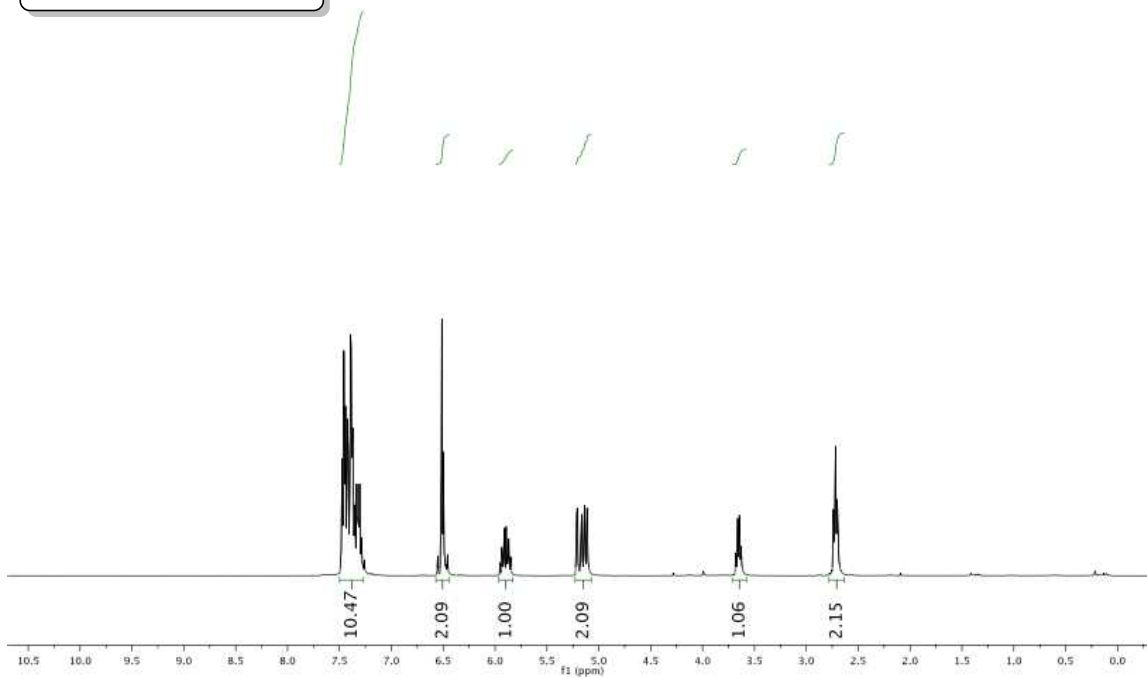
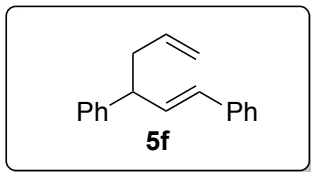


159.62, 158.20, 136.72, 130.06, 129.91, 129.73, 129.34, 129.15, 128.04, 126.37, 115.03, 114.15, 77.48, 77.16, 76.84, 69.97, 55.43, 38.61





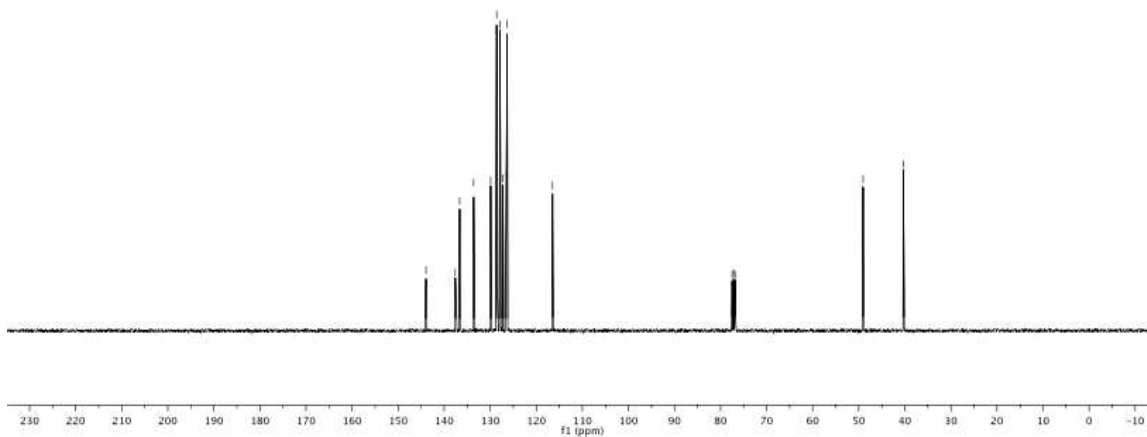


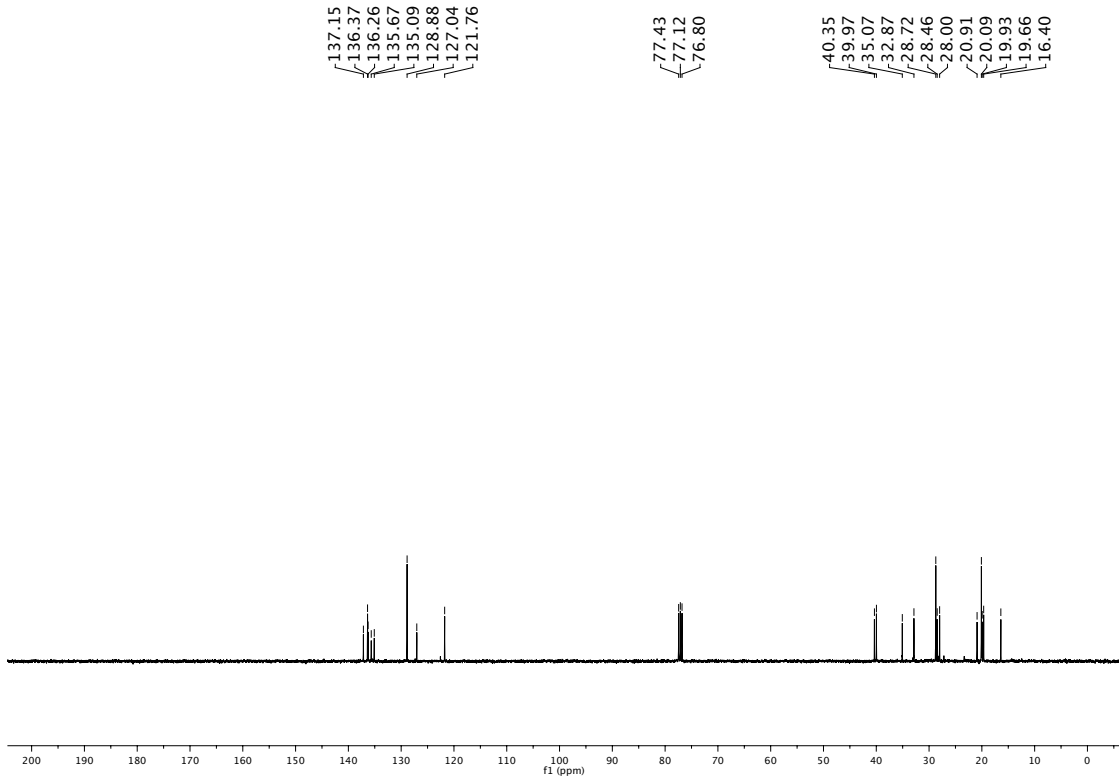
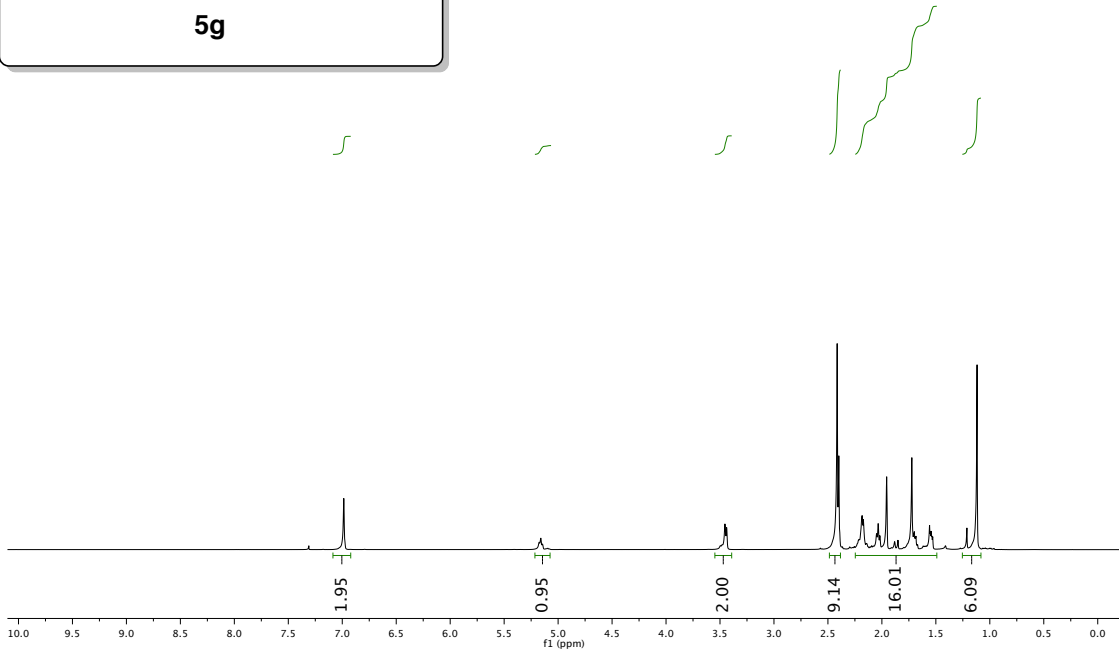
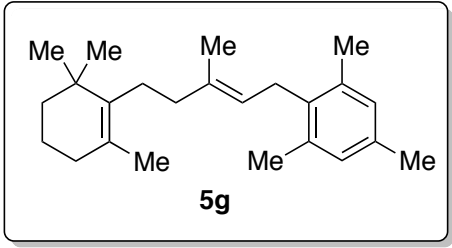


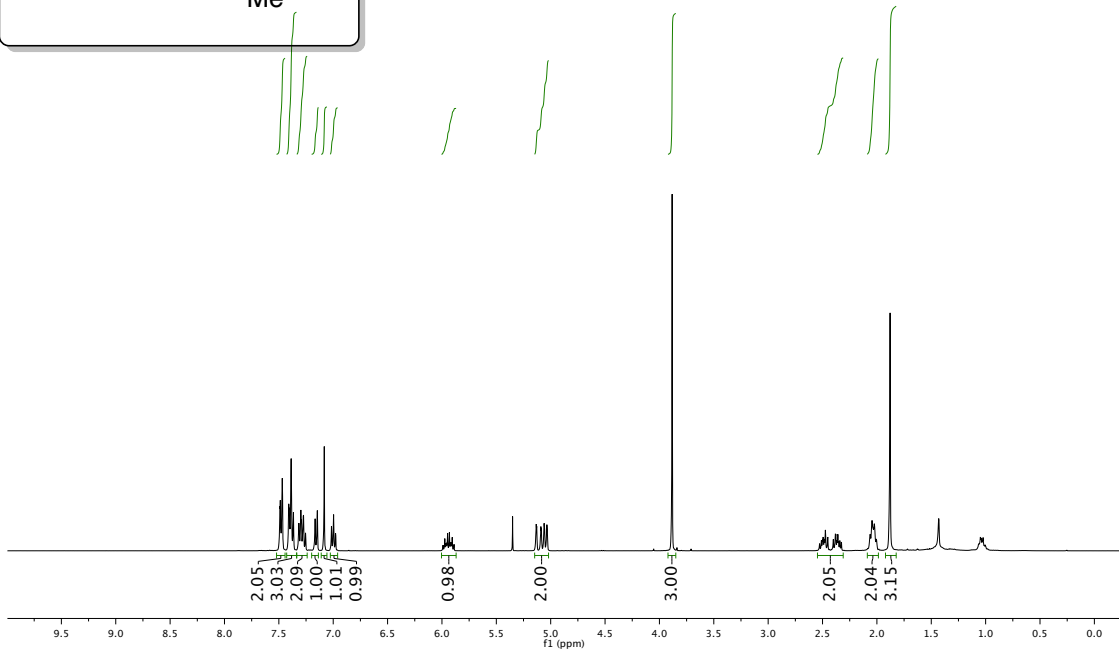
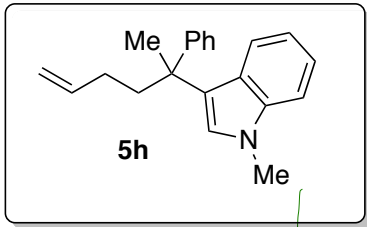
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49.05
40.32

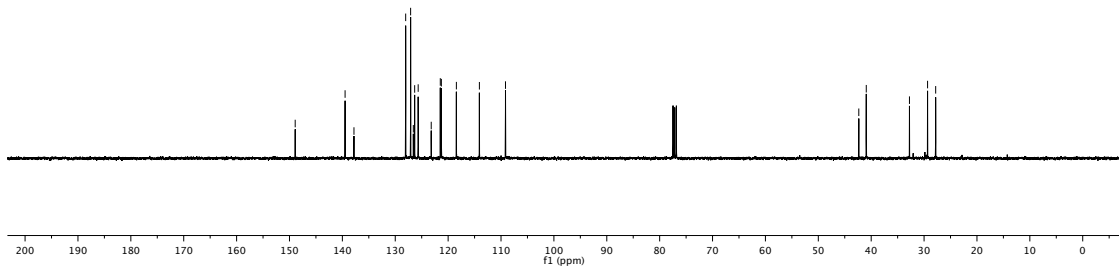


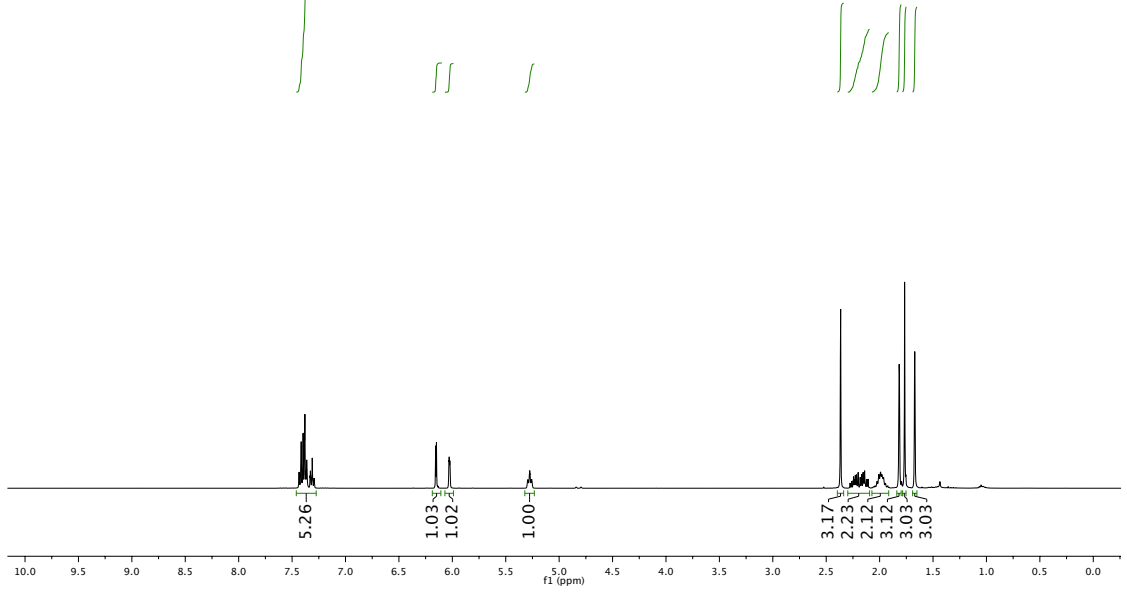
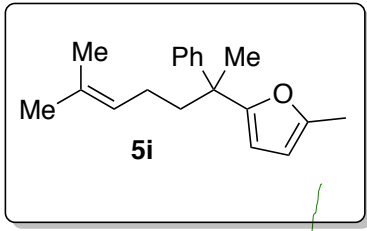




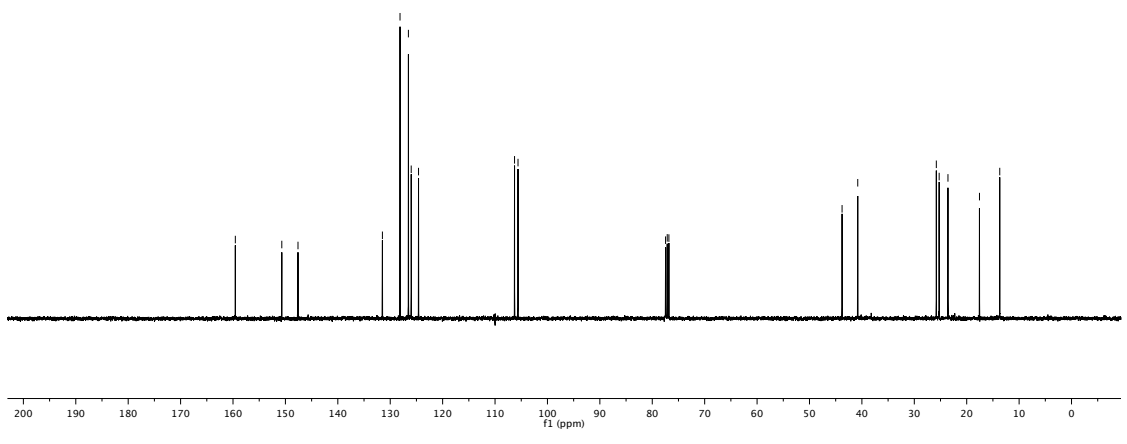
-148.92
 ~139.49
 ~137.81
 ~128.03
 ~127.09
 ~126.58
 ~126.33
 ~125.66
 ~123.20
 ~121.48
 ~121.28
 ~118.44
 ~114.09
 ~109.15

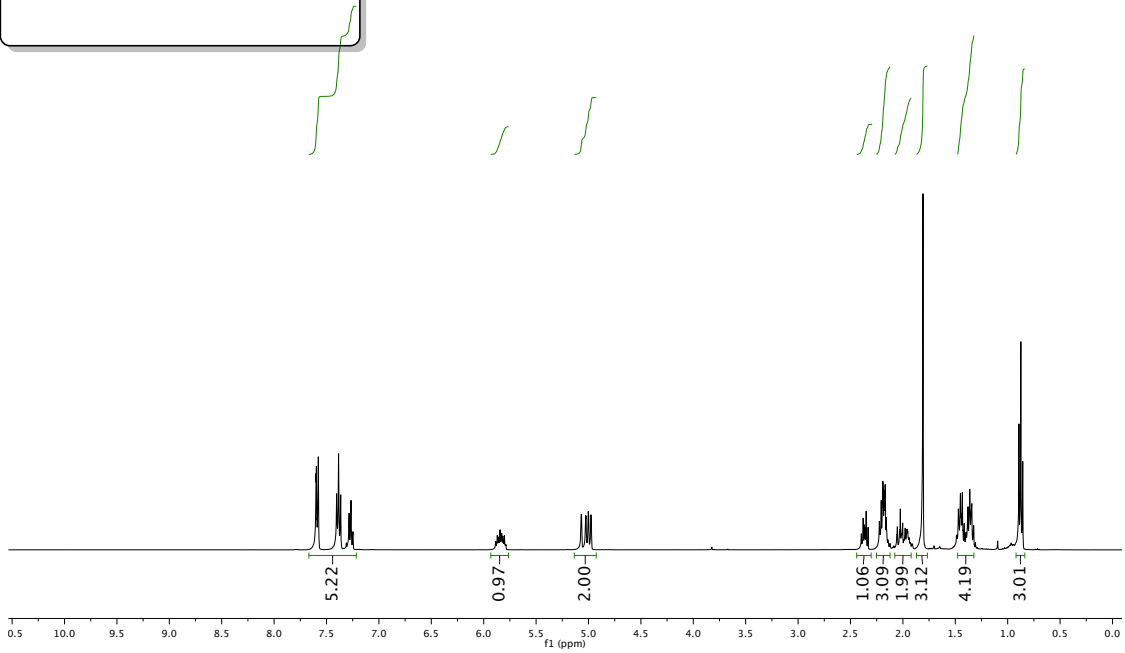
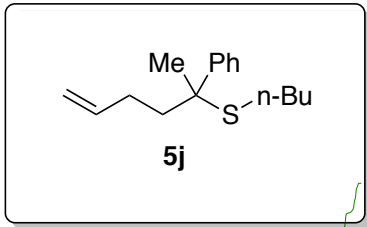
~42.34
 ~40.93
 ~32.76
 ~29.34
 ~27.81





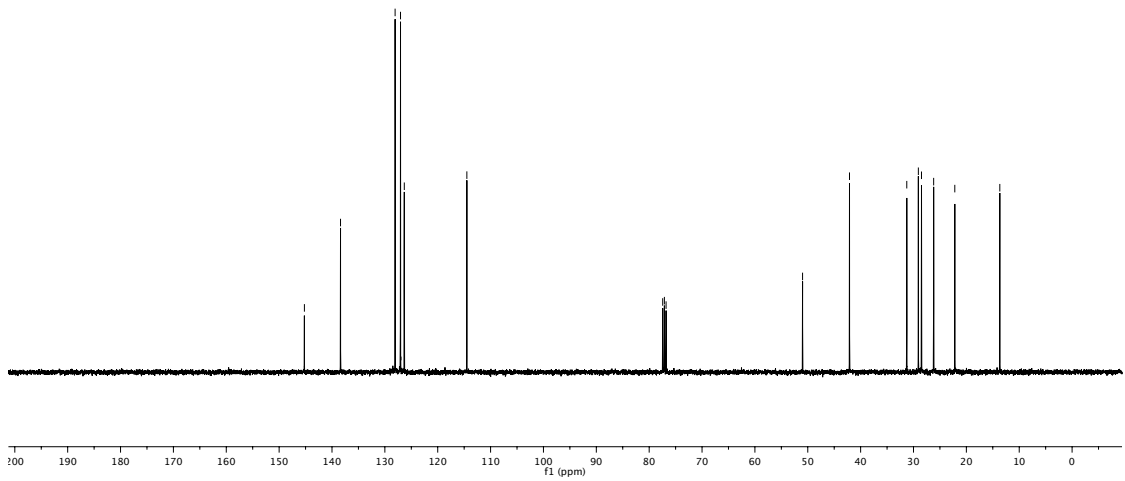
- 159.56
- 150.69
- 147.60
- 131.49
- 128.13
- 126.53
- 126.00
- 124.60
- 106.28
- 105.62
- 77.46
- 77.14
- 76.83
- 43.78
- 40.79
- 25.80
- 25.25
- 23.58
- 17.56
- 13.69

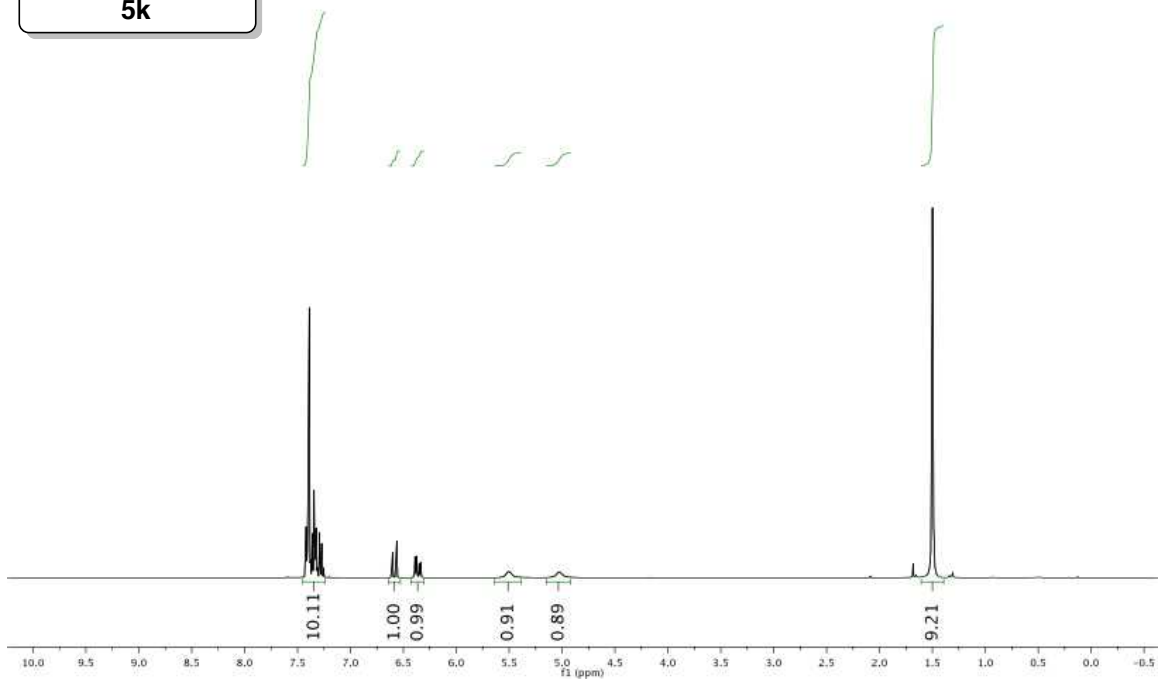
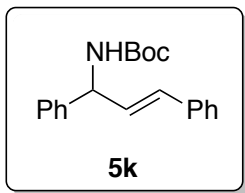




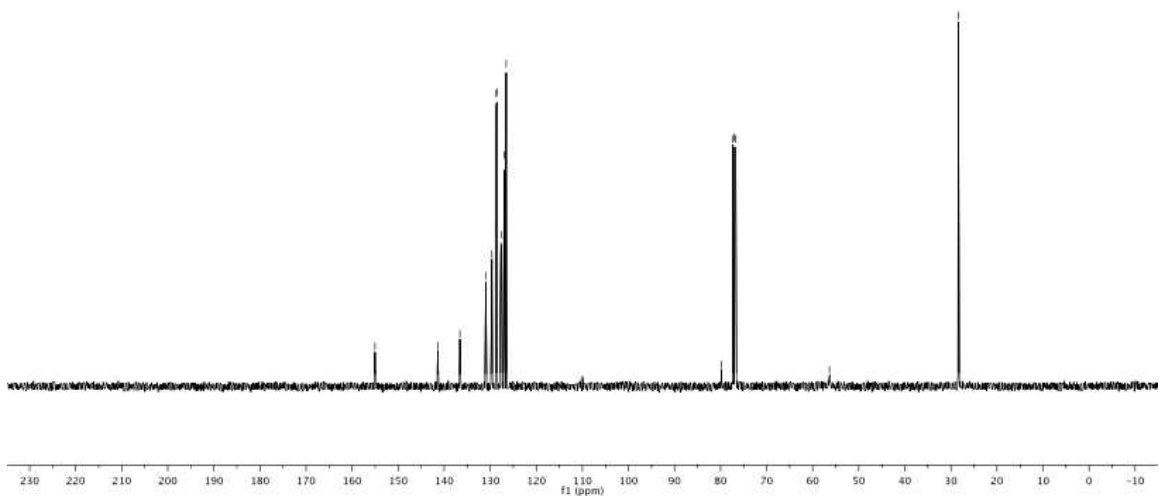
Chemical shift values (ppm) for $^{13}\text{C NMR}$ spectrum:

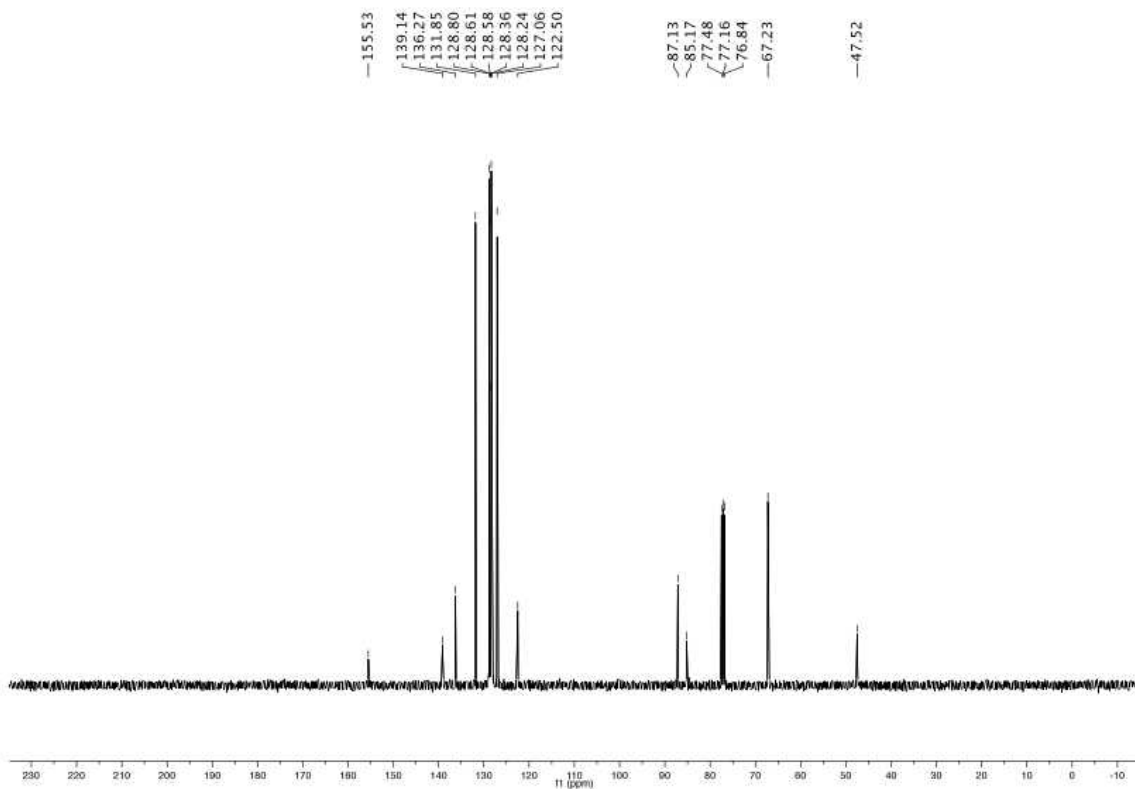
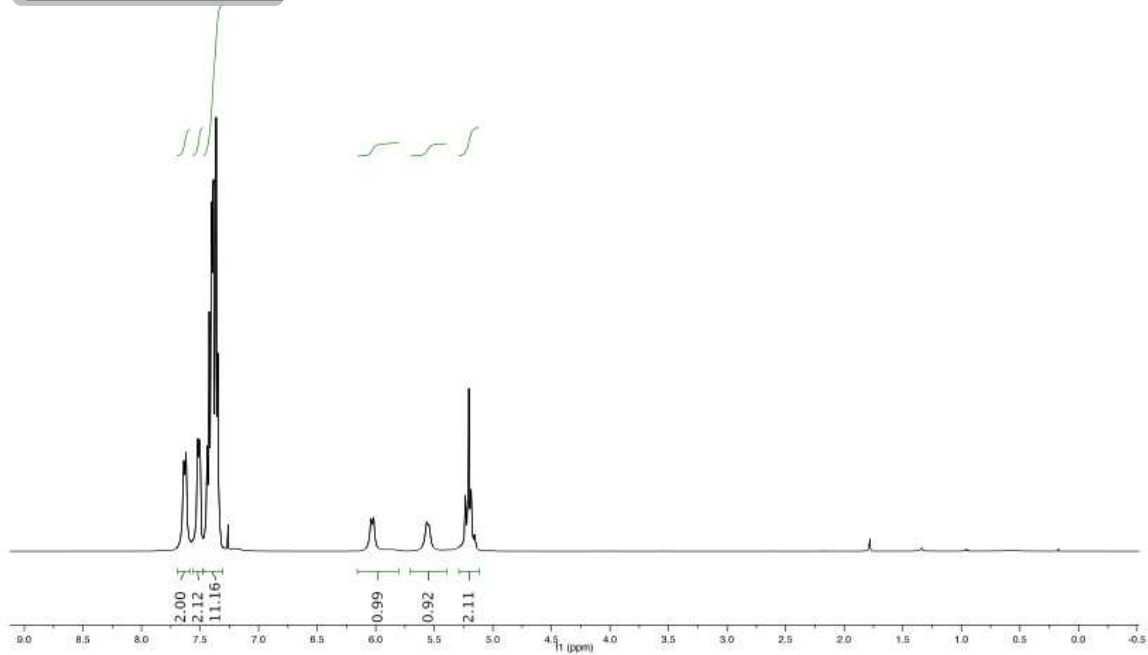
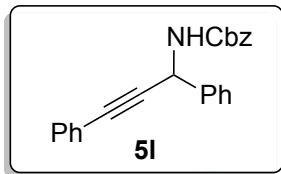
- 145.22
- 138.39
- 128.06
- 127.04
- 126.32
- 114.49
- 77.44
- 77.12
- 76.80
- 50.98
- 42.11
- 31.27
- 29.08
- 28.49
- 26.19
- 22.19
- 13.67

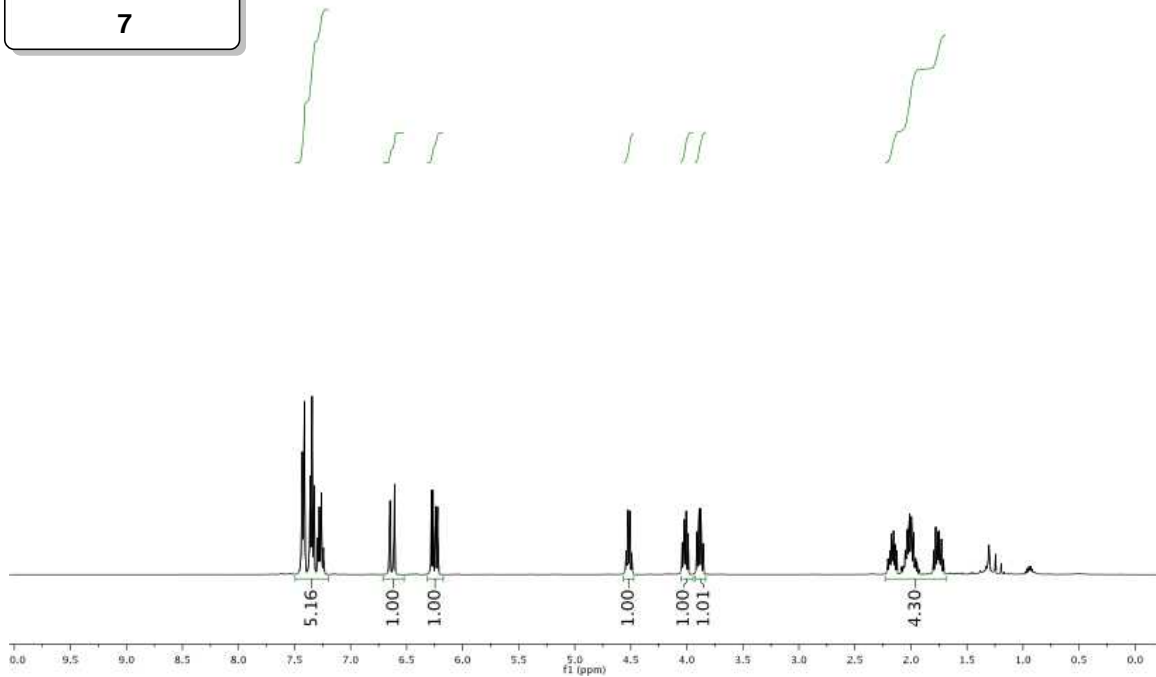
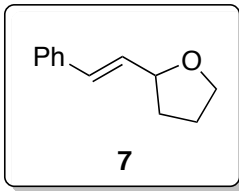




155.02, 136.60, 130.96, 129.64, 128.73, 128.55, 127.69, 127.54, 126.99, 126.85, 79.80, 77.34, 77.03, 76.71, 56.35, 28.40



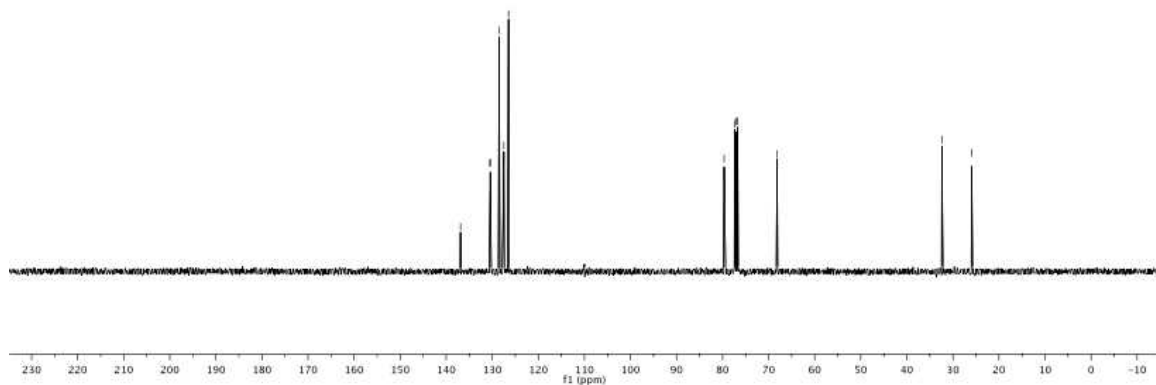


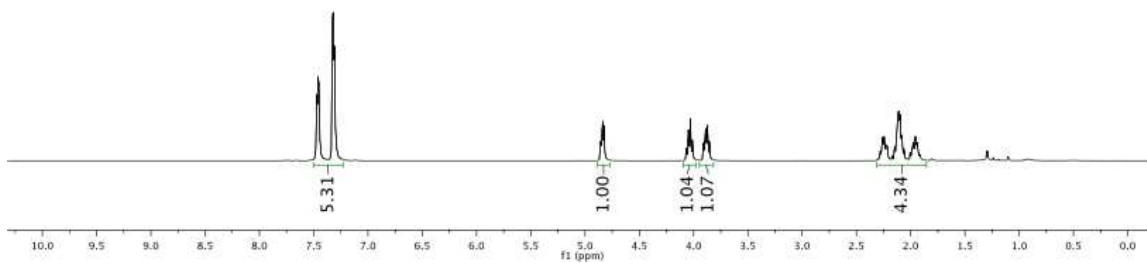
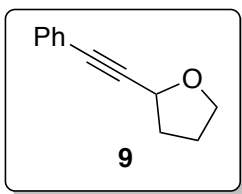


136.88
 130.55
 130.42
 128.50
 127.48
 126.46

79.66
 77.37
 77.05
 76.73
 68.17

-32.40
 -25.91

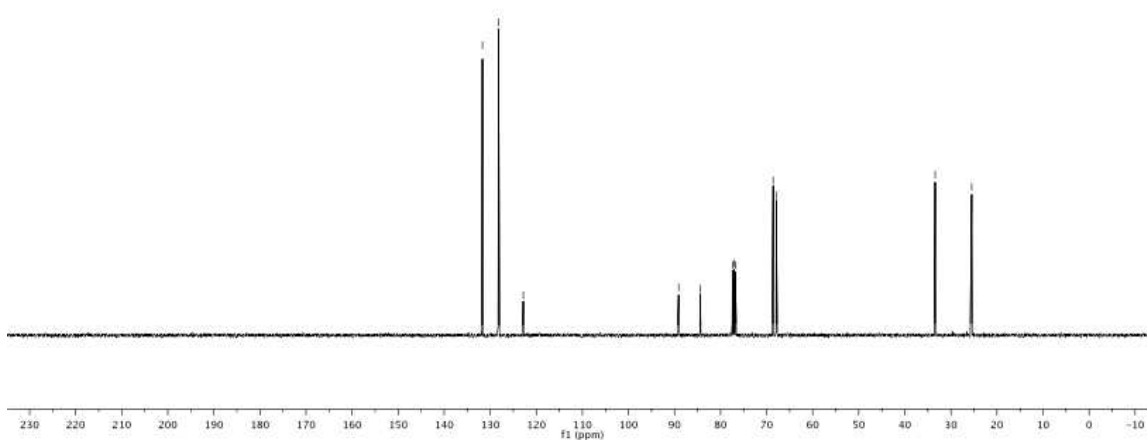


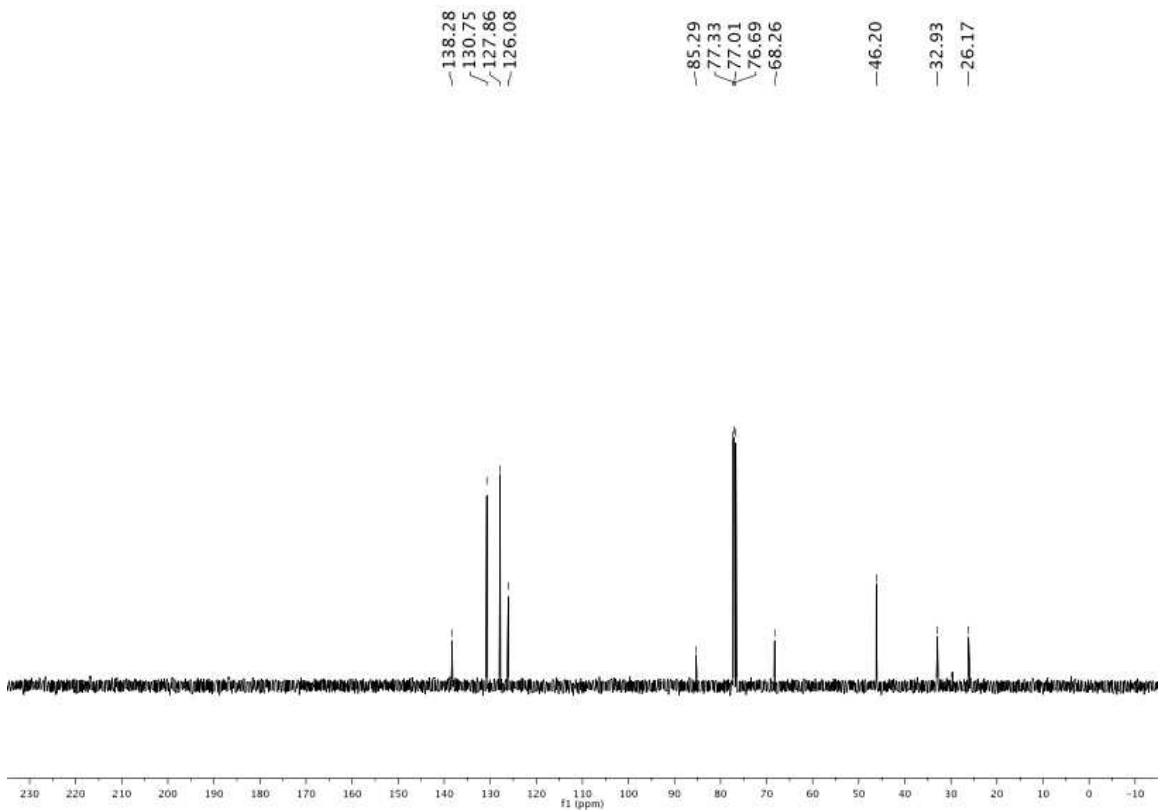
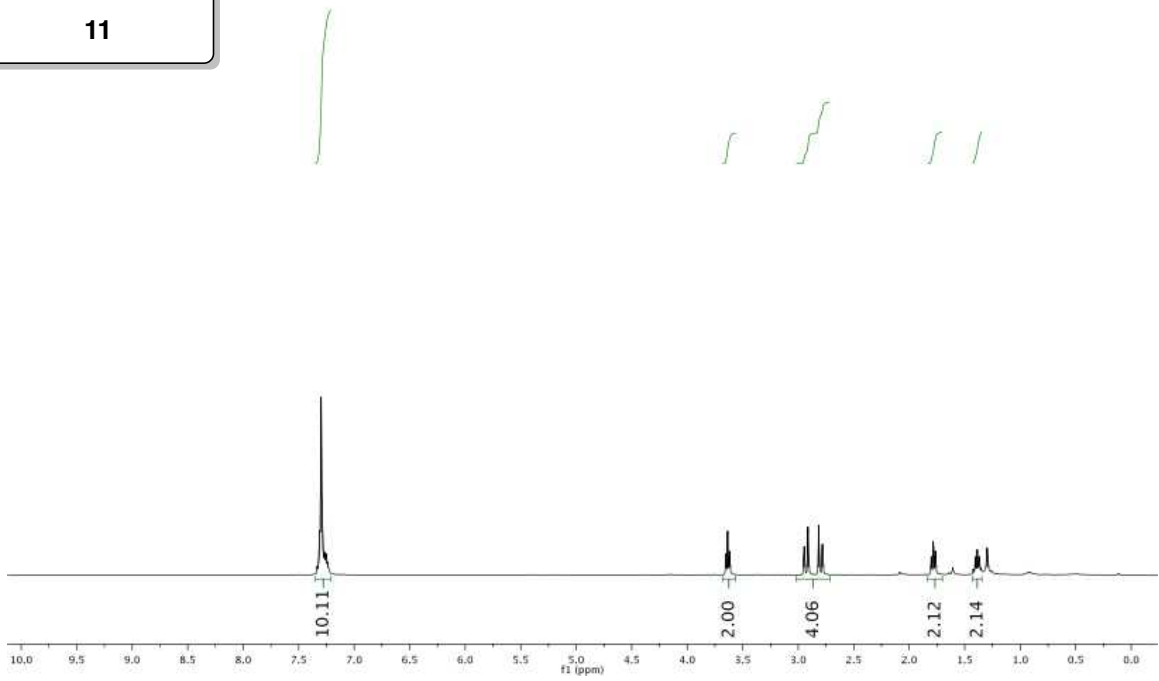
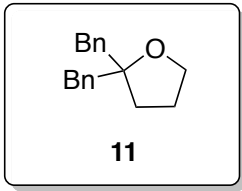


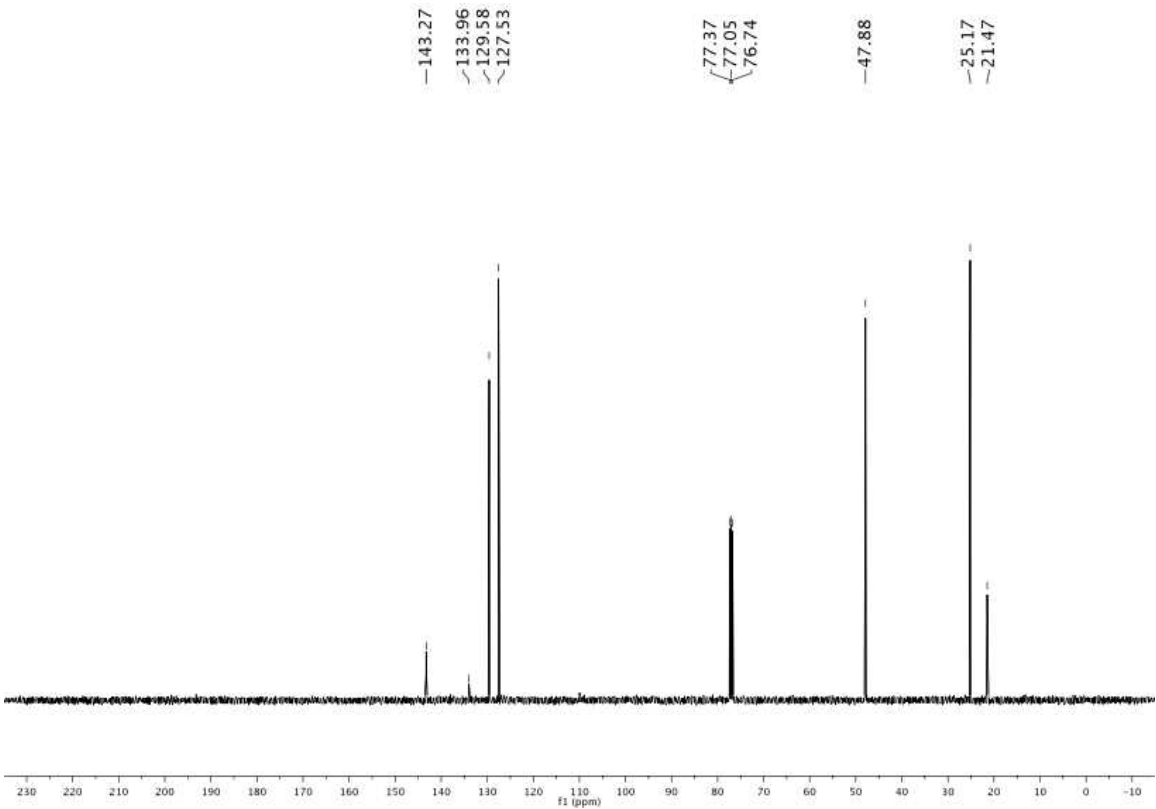
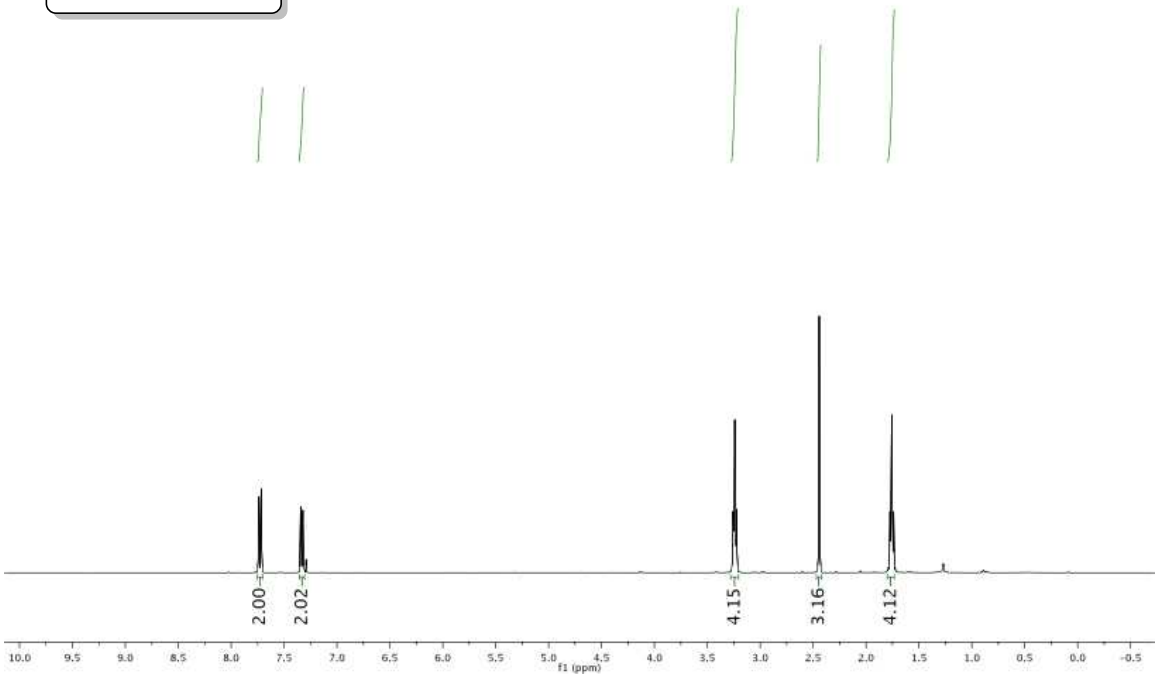
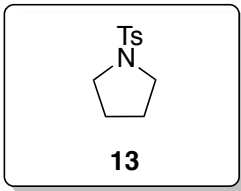
131.69
128.23
128.20
122.82

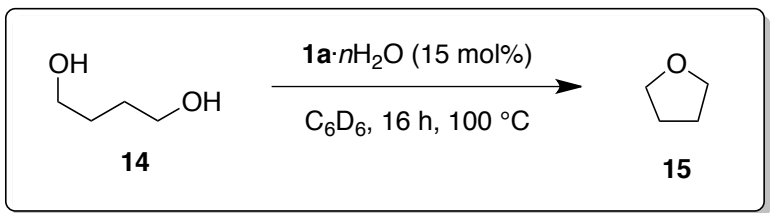
89.10
84.45
77.42
77.10
76.78
68.59
67.92

-33.42
-25.49









h

