Supplementary Materials

Development of Silicon Carbide-Supported Palladium Catalysts and Their Application as Semihydrogenation Catalysts for Alkynes under Batch- and Continuous-Flow Conditions

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Contents

1. General

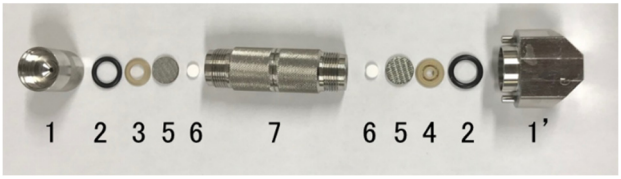
All reagents and solvents were obtained from commercial sources and used without further purification. Silicon carbide was obtained from Cataler Corporation (Shizuoka, Japan). $Pd(OAc)_2$ was obtained from N.E. Chemcat Corporation (Tokyo, Japan). The ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JNM ECA-500 (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR) and ECZ-400 (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) spectrometers. $CDCl_3$ was used as the solvent for the NMR measurements. The chemical shifts (d) are expressed in parts per million and internally referenced (0.00 ppm for tetramethylsilane and 77.0 ppm for $CDCl_3$ for ^{13}C NMR). FlowFactory Flow reactor FFX-1000G (EYELA) was used for the continuous-flow hydrogenation reactions. Thermo Fisher Helios G4 PFIB UX, ULVAC-PHI QuanteraSXM, OXFORD X-MaxN 150, and Shimadzu AA-7000 instruments were used for focused ion beam scanning electron microscopy (FIB-SEM) analysis, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectrometry (EDX), and atomic absorption spectrometry (AAS), respectively. All of the ^1H NMR spectra of the known products were identical to those reported in the literature.

2. Preparation of 3% Pd/SiC catalyst (Scheme 3)

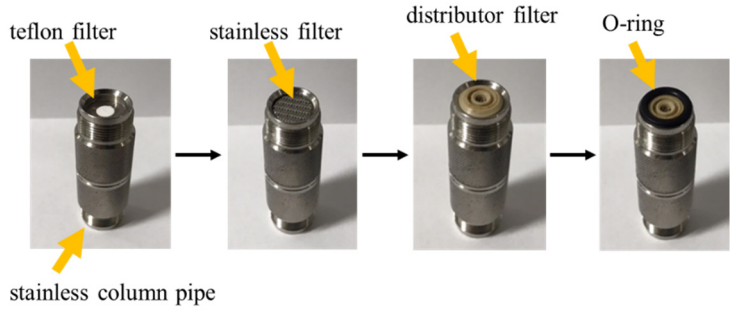
Cubic SiC (grayish color) was crushed to small particles by using a mortar and pestle, passed through a filter (diameter of the filter is < 63 μm), and deaerated in vacuo. A solution of $Pd(OAc)_2$ [39.1 mg, 174.1 μmol (18.5 mg, palladium quantity)] in MeOH (6.0 mL) was poured into SiC particles (600 mg) placed in a 50 mL-round-bottom flask, stirred under argon atmosphere at 25 °C for 24 h. The resulting dark gray solid was collected by filtration (1.0 μm filter paper), washed with H_2O (10 mL× 3) and MeOH (10 mL × 3), and dried in vacuo for 24 h to give Pd/SiC (608.5 mg). The filtrate was transferred to a 100 mL volumetric flask and diluted to 100 mL with MeOH; 7.2 ppm (0.7 mg) of palladium species was observed in the diluted filtrate by using AAS (SHIMADZU AA-7000). The total palladium species that was not absorbed in SiC was 0.7 mg; thus, the palladium content of Pd/SiC was estimated to be approximately 3% [(18.5 – 0.7)/(600 + 18.5 – 0.7) × 100].

3. Preparation of catalyst cartridge

(1 and 1') Prepare column ends, (2) O-ring, (3) filter pressing ring, (4) distributor filter, (5) stainless filters, (6) Teflon filters, and (7) stainless column pipe.



2) Insert the Teflon filter inside the stainless column pipe. Put stainless filter, distributor filter and O-ring on the stainless column pipe.

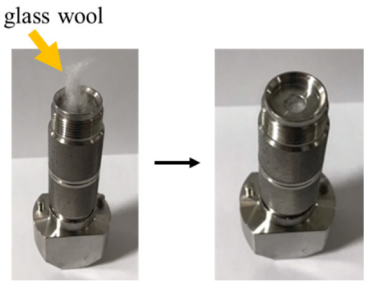


↓ Assemble the column end.

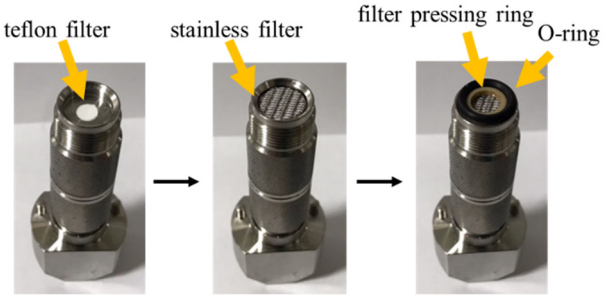
3) Insert ca. 0.48 mL of glass wool tightly into the pipe.

4) Fill the pipe with 50 mg of 3% Pd/SiC.

5) Fill the pipe with glass wool tightly to the end of the pipe to fix the catalyst.



6) Insert the Teflon filter inside the stainless column pipe. Put stainless filter, filter pressing ring and O-ring on the pipe.



↓ Tighten the column end.

4. Preparation of 3% Pd(DETA)/SiC catalyst (Scheme 4)

A suspension of 3% Pd/SiC [100 mg, 25.3 μmol (2.7 mg, palladium quantity)] and DETA (191.0 μL, 1.77 mmol) in MeOH (1.0 mL) was stirred under argon atmosphere at 25 °C for 7 d. The resulting dark gray solid was collected by filtration (1 μm filter paper), washed with MeOH (5 mL × 3) and Ether (5 mL × 3), and dried in vacuo for 24 h to give Pd(DETA)/SiC (98.7 mg). The filtrate was transferred to a 50 mL volumetric flask and diluted to 50 mL with MeOH; 0.02 ppm (2.0 μg) of palladium species was observed in the diluted filtrate using AAS (SHIMADZU AA-7000). The total palladium species that was leaked from Pd/SiC was 2.0 μg; thus, the palladium contents of Pd(DETA)/SiC were estimated to be approximately 3% [(2.7 – 0.002)/(100 – 0.002) × 100].

5. General procedure for chemoselective hydrogenation under batch conditions (Table 1)

A mixture of the substrate (250 μmol) and 3% Pd/SiC (8.8 mg, 2.5 μmol) in MeOH or EtOAc (1.0 mL) was stirred at 25 or 50 °C using a test tube equipped with an H_2 balloon. The reaction was continuously monitored by thin-layer chromatography. After a specific time, as indicated in Table 1, the mixture was filtered by a membrane filter (pore size: 0.45 μm). The catalyst on the filter was washed with diethyl ether (5 mL × 3). The combined filtrates were concentrated in vacuo to afford the corresponding analytically pure product. If necessary, the product was further purified by silica-gel column chromatography (hexane/EtOAc or hexane/diethyl ether).

6. General procedures for semihydrogenation of alkynes under batch and continuous-flow conditions

6-1. General procedure for semihydrogenation of alkynes under batch conditions (Table 3)

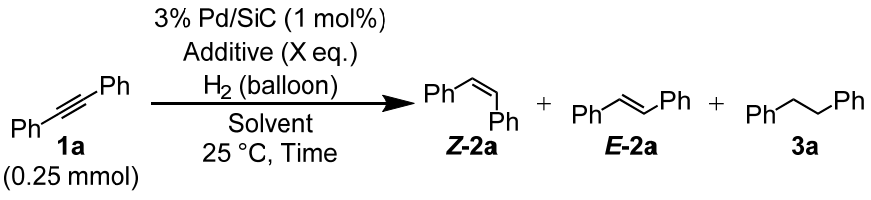
A mixture of the substrate (250 μmol), 3% Pd/SiC (8.8 mg, 2.5 μmol), and DETA (40.5 μL, 375 μmol) in MeOH (1.0 mL) was stirred at 25 °C using a test tube equipped with an H_2 balloon. The reaction was continuously monitored by thin-layer chromatography. After a specific time, as indicated in Table 3, the mixture was filtered by a membrane filter (pore size: 0.45 μm). The catalyst on the filter was washed with diethyl ether (5 mL × 3). The combined filtrates were washed with saturated NH_4Cl aq. (3 mL × 3) and brine (3 mL × 1) if additive was used, dried over Na_2SO_4, and concentrated in vacuo to afford the corresponding alkenes with small amounts of substrates and/or alkanes.

6-2. General procedure semihydrogenation of alkynes under continuous-flow conditions (Table 4)

A solution of the substrate (500 μmol) and DETA (162.0 μL, 1.5 mmol) in MeOH (10 mL, 0.05 M) was pumped into the 3% Pd/SiC (50 mg) catalyst-packed cartridge [φ 5 × 50 mm, stainless] at a flow rate of 0.1 mL/min together with hydrogen gas at a flow rate of 10 mL/min at 25 °C after introducing a flow of MeOH and hydrogen gas into the cartridge under the same condition for ca. 5 min. The cartridge was washed with MeOH (10 mL) and CH_2Cl_2 (10 mL), and the combined reaction mixture was collected and concentrated in vacuo. The solution was added to water (3 mL) and extracted with *n*-Hexane / AcOEt = 1 / 1 (6 mL × 3), dried over Na_2SO_4, and concentrated in vacuo to afford the corresponding alkenes with small amounts of substrates and/or alkanes.

7. Optimization of semihydrogenation under batch and continuous-flow conditions

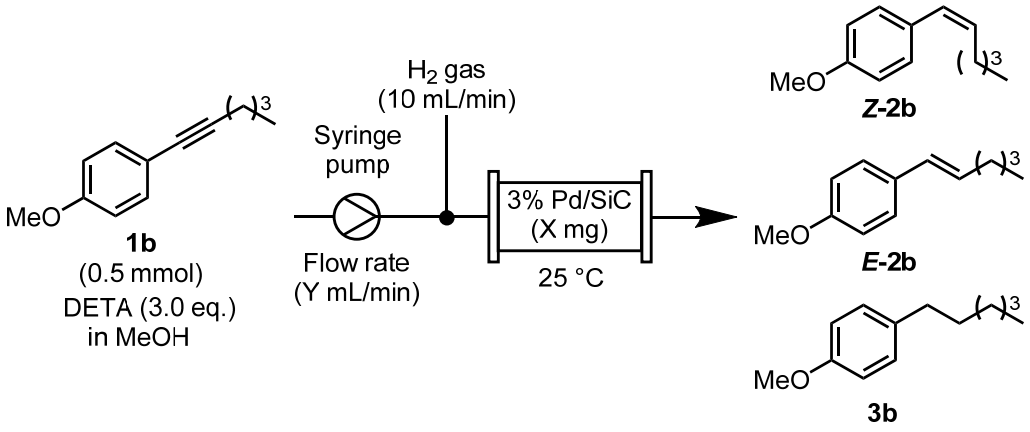
Table S1. Optimization of semihydrogenation reaction under batch conditions



Entry	Solvent	Additive (X eq.)	Time (h)	Ratio[a)]			
				1a	***Z*-2a**	***E*-2a**	**3a**
1	MeOH	-	1	2	38	2	58
2	AcOEt	-	2	2	43	2	53
3	MeOH	Pyridine (1.0 eq.)	2	4	51	3	42
4	MeOH	DETA (1.0 eq.)	2	3	86	2	9
5	MeOH	DETA (1.5 eq.)	2	2	93	2	3
6	MeOH	DETA (2.0 eq.)	2	2	93	2	3

a) Determined by ^{1}H NMR of the crude mixture.

Table S2. Optimization of semihydrogenation reaction under continuous-flow conditions



Entry	Pd/SiC (X mg)	Flow rate (Y mL/min)	Yield[a)]			
			1b	***Z*-2b**	***E*-2b**	**3b**
1	50	0.1	22	72	1	2
2	70	0.1	7	88	2	3
3	100	0.1	6	84	2	3
4[b)]	50	0.1	0	81	3	6
5	50	0.05	3	91	2	4
6	50	0.025	5	84	3	4
7	70	0.05	3	90	2	5

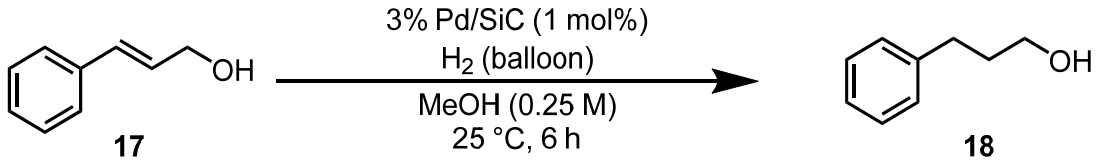
a) Determined by ^{1}H NMR of the crude mixture using ethylene carbonate as an internal standard. b) 50 °C.

8. Reuse test of 3% Pd/SiC (Table 2)

A mixture of cinnamyl alcohol (**17**, 1.07 g, 8.0 mmol) and 3% Pd/SiC (293.8 mg, 80.0 μmol) in MeOH (32 mL) was stirred under an H_2 atmosphere (balloon). After 4 h, the mixture was filtered through a funnel (1 mm filter paper). The catalyst on the filter was washed with EtOAc (3 mL × 5), and the filtrate was concentrated in vacuo to afford 3-

pnenylpropanol (**18**). The catalyst on the filter was dried in vacuo at room temperature overnight and then weighted. The reaction for the second run was carried out in a procedure similar to the first run except for the amount of cinnamyl alcohol (1.01 mg, 7.5 mmol) and 3% Pd/SiC (275.2 mg, 75.0 μmol) for 4 h. The reaction for the third run was also carried out likewise the first run except for the usage of substrate and catalyst. The detailed results were summarized below (Table S3).

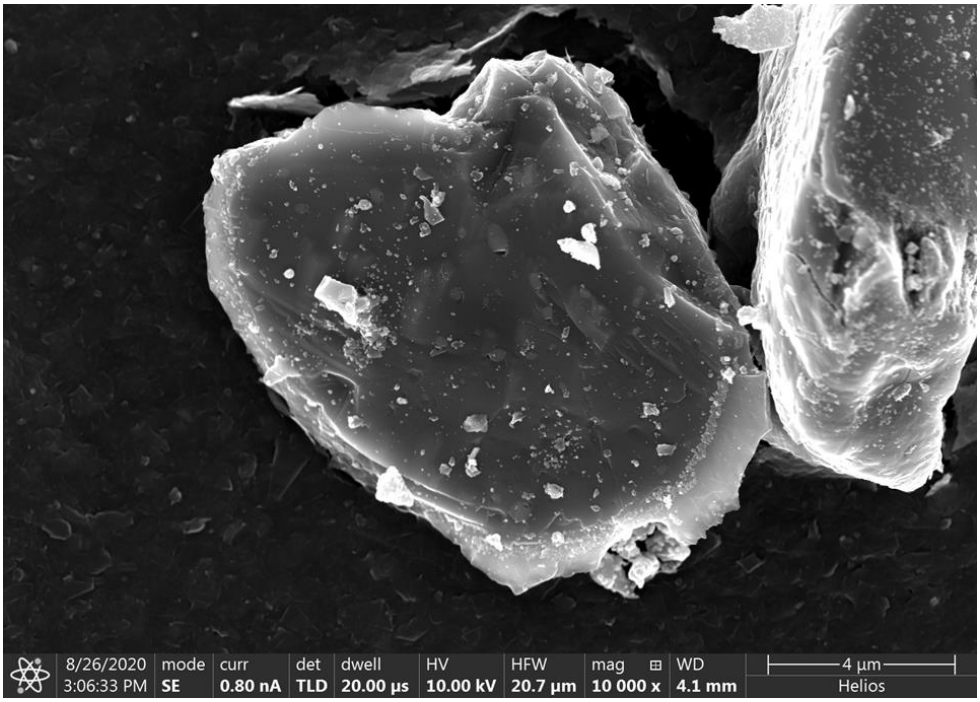
Table S3. Reuse test of Pd/SiC



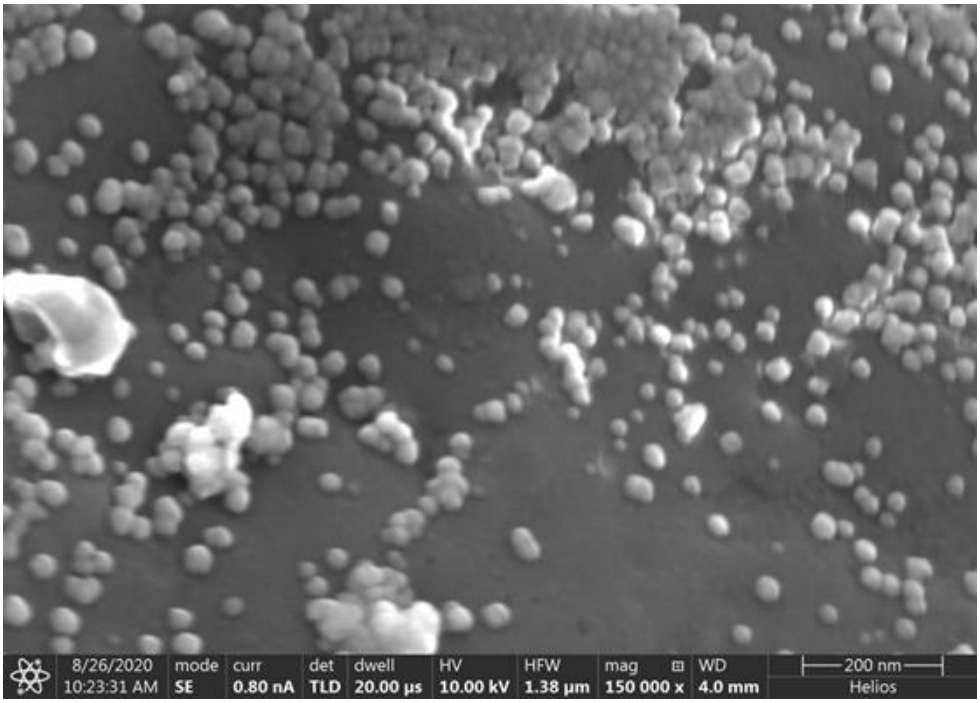
17 **18**

Run	**17** usage	Catalyst usage	Yield (%)	Catalyst recovery yield (%)
1	1.07 g (8.0 mmol)	293.8 mg (80.0 μmol)	99 (1.08 g, 8.0 mmol)	99 (293.5 mg, 80.0 μmol)
2	1.01 g (7.5 mmol)	275.2 mg (75.0 μmol)	quant. (1.03 g, 7.6 mmol)	quant. (277.3 mg, 75.6 μmol)
3	0.94 g (7.0 mmol)	256.9 mg (70.0 μmol)	97 (921.5 mg, 6.8 mmol)	95 (244.8 mg, 66.7μmol)

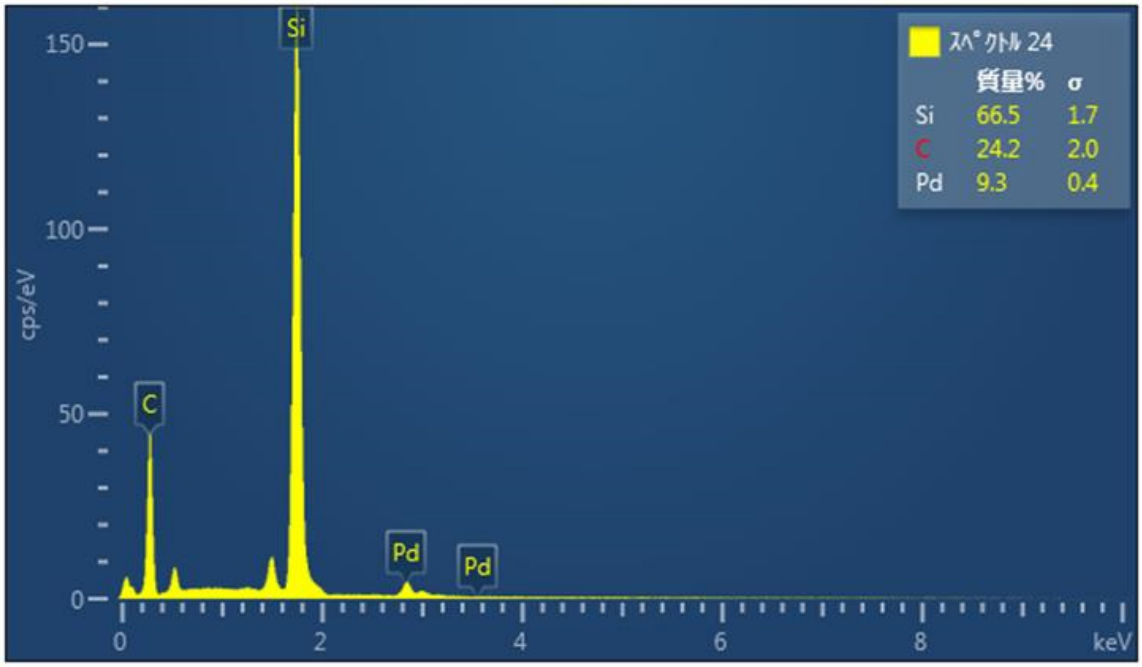
9. FIB-SEM image, EDX analysis, and XPS spectra of 3% Pd/SiC before and after use



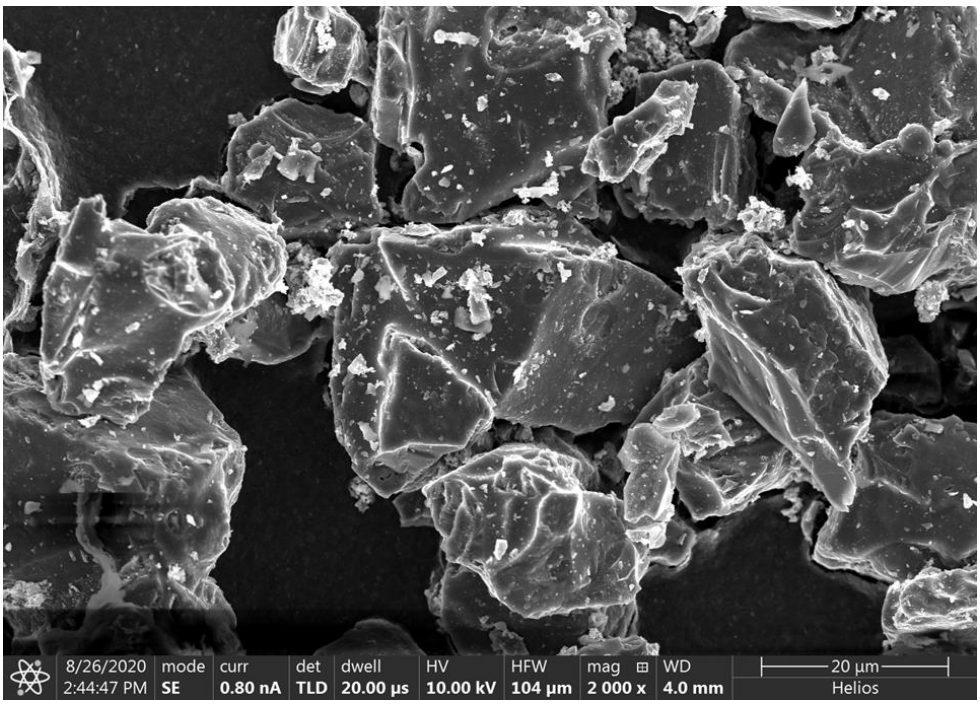
FIB-SEM image of 3% Pd/SiC before use



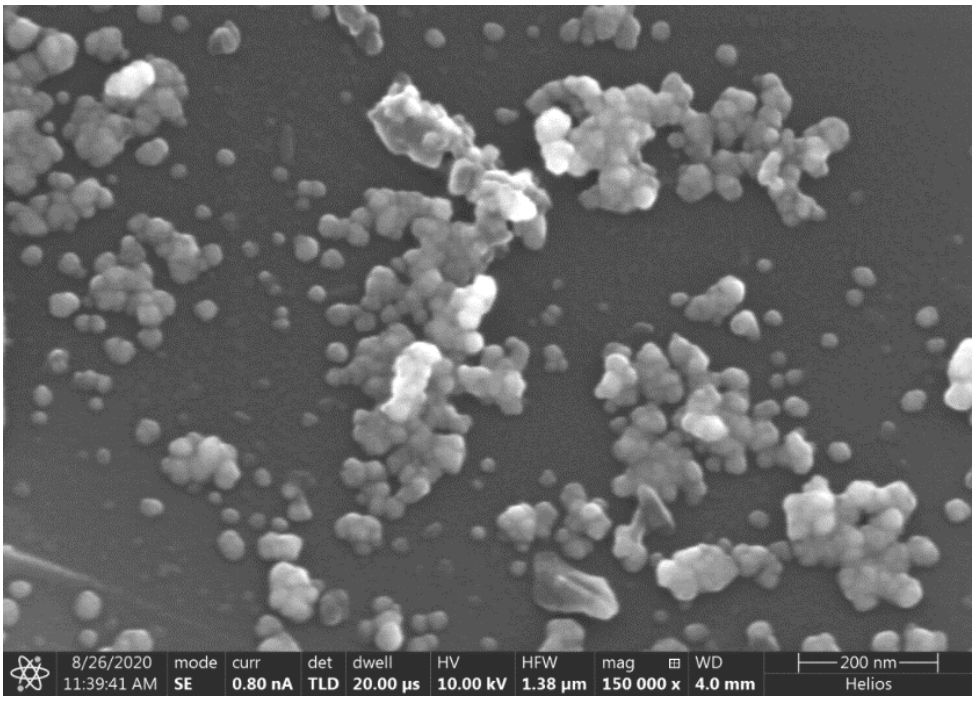
FIB-SEM image of 3% Pd/SiC before use



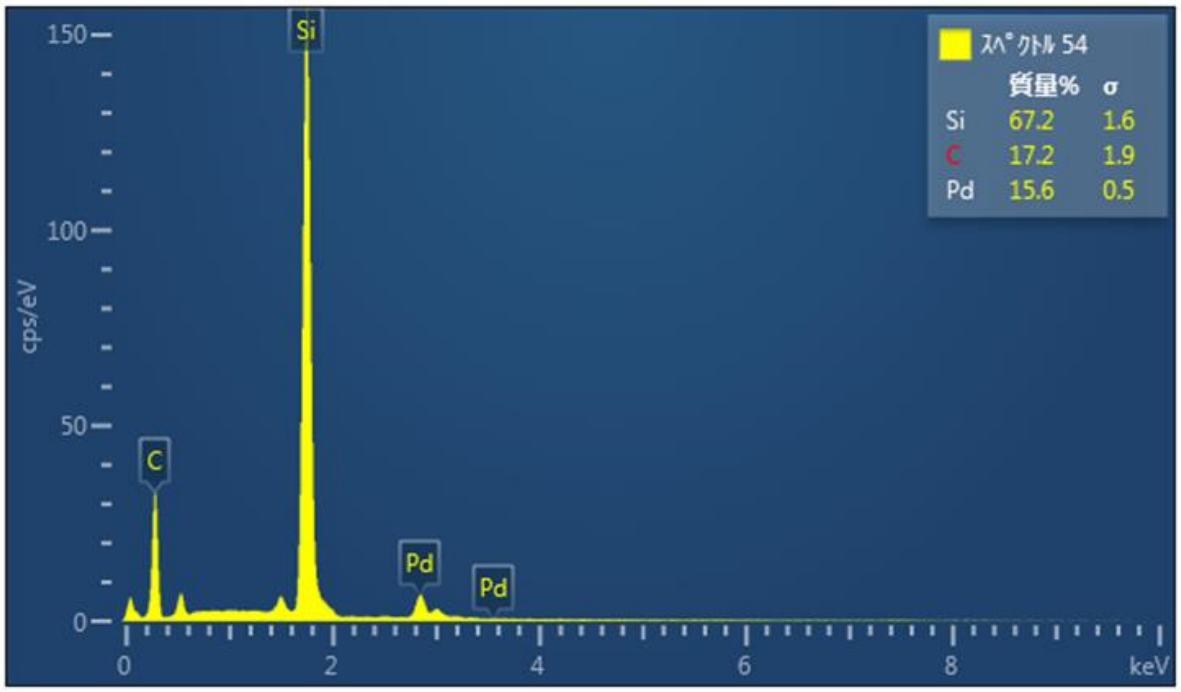
EDX analysis of 3% Pd/SiC before use



FIB-SEM image of 3% Pd/SiC after use

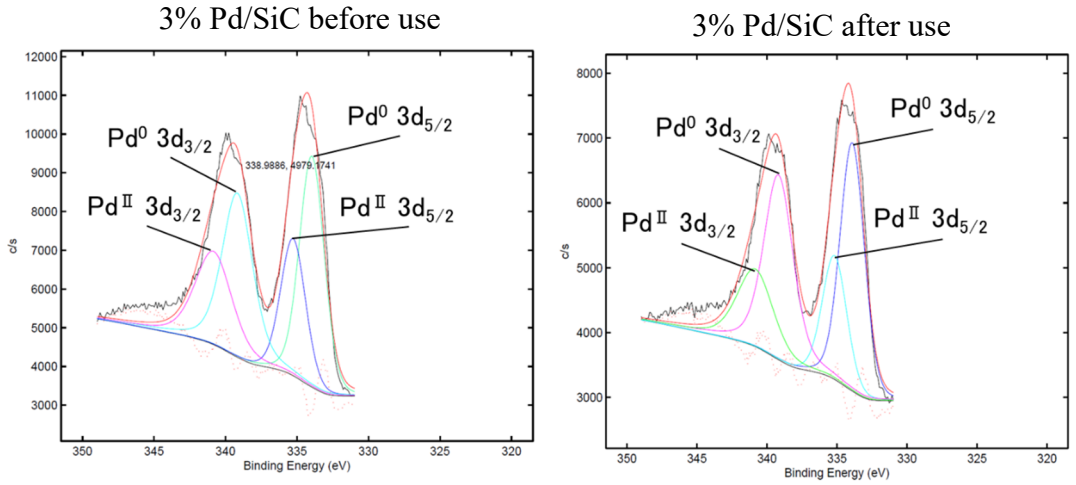


FIB-SEM image of 3% Pd/SiC after use



EDX analysis of 3% Pd/SiC after use

10. XPS data of 3% Pd/SiC

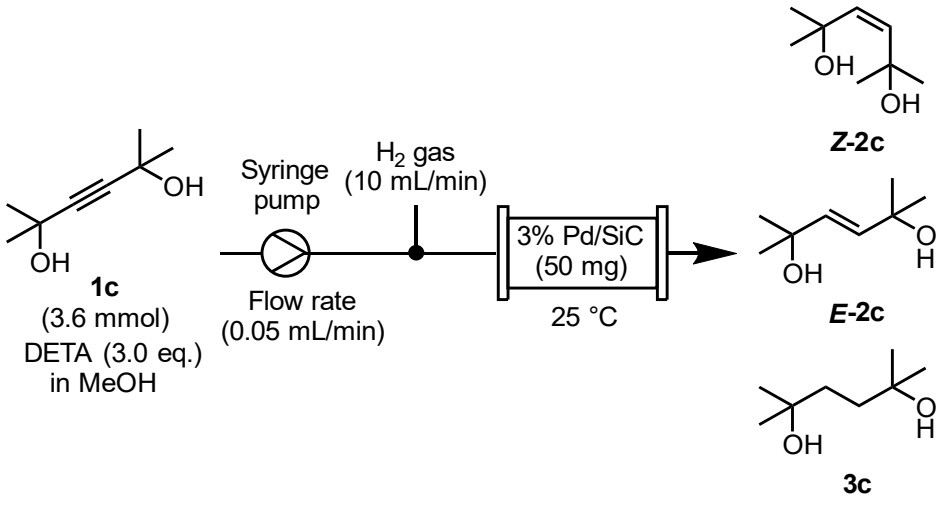


Binding energy (eV)	342.9	341.0	337.7	335.7
Species	Pd^{II} $3d_{3/2}$	Pd^{0} $3d_{3/2}$	Pd^{II} $3d_{5/2}$	Pd^{0} $3d_{5/2}$
Brfore reaction: Pd/SiC Area%	20.42	29.87	18.52	33.45
After reaction : Pd/SiC Area%	16.93	32.95	16.68	33.45

Figure S1. XPS spectra of 3% Pd/SiC before and after the reaction

11. Long-term continuous-flow semihydrogenation (Figure 3)

Table S4. Long-term Continuous-flow semihydrogenation of 1c using 3% Pd/SiC

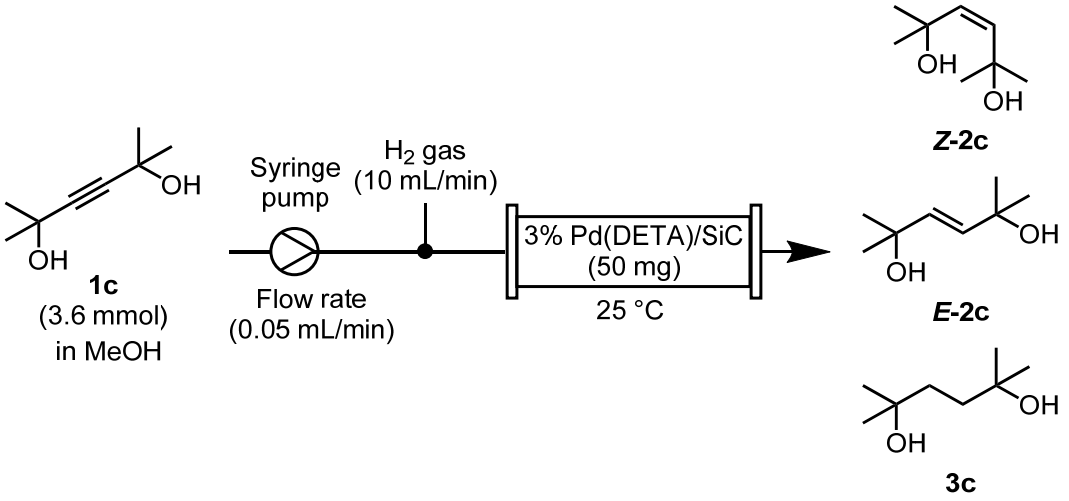


Entry	Reaction time (h)	Total theoretical amount of material	Yield[a)]			
			1c	***Z*-2c**	***E*-2c**	**3c**
1	0–3	0.45 mmol	4	94	2	Trace
2	3–6	0.45 mmol	11	85	4	Trace
3	6–12	0.90 mmol	20	77	2	1

4	12–18	0.90 mmol	26	71	2	1
5	18–24	0.90 mmol	34	65	1	0

a) Determined by ^{1}H NMR using ethylene carbonate as an internal standard.

Table S5. Long-term Continuous-flow semihydrogenation of 1c using 3% Pd(DETA)/SiC

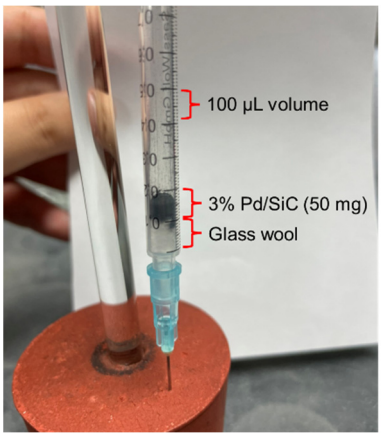


Entry	Reaction time (h)	Total theoretical amount of material	Yield[a)]			
			1c	***Z*-2c**	***E*-2c**	**3c**
1	0–3	0.45 mmol	0	89	2	1
2	3–6	0.45 mmol	0	89	2	1
3	6–12	0.90 mmol	0	90	4	3
4	12–18	0.90 mmol	trace	90	4	2
5	18–24	0.90 mmol	3	90	3	2

a) Determined by ^{1}H NMR using ethylene carbonate as an internal standard.

12. Calculation of the residence time

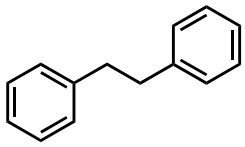
Since 3% Pd/SiC are small particles with a size of about <63 μm diameter, the void space would be ignored. Considering the accuracy of the 1 mL disposable syringe and the calculational convenience used in this experiment, the volume of 50 mg 3% Pd/SiC was calculated in this paper as ca. 100 μ L (see, below picture). Therefore, the residence time when the flow rate is 0.1 mL/min is 0.1 (mL)/0.1 (mL/min) = 1min. (60 seconds). In the case that the flow rate is 0.05 mL/min, the residence time is 0.1 (mL)/0.05 (mL/min) = 2 min. (120 seconds).



13. Spectroscopic data of products

Diphenylethane (Table 1 Entry 1) [CAS Reg. No. 103-29-7][73]

Obtained in quantitative yield (45.3 mg, 0.25 mmol; colorless solid) from diphenylacetylene (44.6 mg, 0.25 mmol).

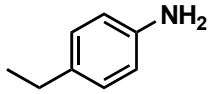


3a

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.28 (4H, dd, J = 7.5, 7.5 Hz), 7.19 (6H, m), 2.92 (4H, s); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 141.7, 128.4, 128.3, 125.8, 37.9.

***p*-Ethylaniline (Table 1, Entry 2 and 3) [CAS Reg. No. 589-16-2][74]**

Obtained in quantitative yield (30.6 mg, 0.25 mmol; yellow liquid) from *p*-ethylnitrobenzene (37.8 mg, 0.25 mmol) or *p*-ethylphenyl azide (36.8 mg, 0.25 mmol).



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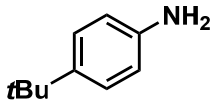
^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 6.89 (2H, d, J = 8.0 Hz), 6.62 (2H, d, J = 8.0 Hz), 3.52 (2H, brs), 2.54 (2H, q, J = 7.6 Hz), 1.18 (3H, t, J = 7.6 Hz); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 143.9, 134.4, 128.5, 115.2, 27.9, 15.9.

4-*tert* Butylaniline (Table1, Entry 4) [CAS Reg. No. 769-92-6][75]

Obtained in quantitative yield (31.0 mg, 0.25 mmol; brown liquid) from N-*Cbz*-4-*tert* butylaniline (36.8 mg, 0.25 mmol).



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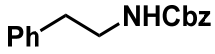
^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.18 (2H, d, *J* = 8.5 Hz), 6.23 (2H, d, *J* = 8.5 Hz), 3.54 (2H, brs), 1.27 (9H, s); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 143.7, 141.3, 125.9, 114.8, 33.8, 31.4.

Benzyl phenethylcarbamate (Table 1, Entry 5) [CAS Reg. No. 70867-38-8][76]

Obtained in quantitative yield (64.3 mg, 0.25 mmol; peal yellow liquid) from benzyl phenethylcarbamate (63.8 mg, 0.25 mmol).



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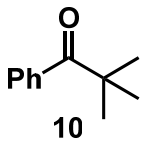
^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.36–7.16 (10H, m), 5.08 (2H, s), 4.80 (1H, brs), 3.45 (2H, m), 2.80 (2H, t, *J* = 7.3 Hz); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 156.2, 138.6, 136.4, 128.7, 128.5, 128.4, 128.0, 126.4, 66.5, 42.1, 35.9.

2,2-Dimethylpropiophenone (Table 1, Entry 6) [CAS Reg. No. 938-16-9][77]

Obtained in quantitative yield (40.8 mg; 0.25 mmol, colorless liquid) from 2,2-dimethylpropiophenone (40.6 mg, 0.25 mmol).



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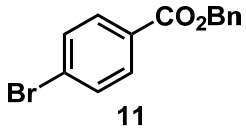
^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 7.69–7.67 (2H, m), 7.47–7.37 (3H, m), 1.35 (9H, s); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 209.2, 138.4, 130.7, 127.9, 127.7, 44.1, 27.9.

Benzyl-4-bromobenzoate (Table 1, Entry 7) [CAS Reg. No. 120-51-4][78]

Obtained in quantitative yield (73.4 mg, 0.25 mmol; yellow liquid) from benzyl-4-bromobenzoate (72.8 mg, 0.25 mmol).



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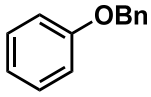
^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.92 (2H, d, *J* = 7.5 Hz), 7.56 (3H, d, *J* = 7.5 Hz), 7.44–7.33 (5H, m), 5.35 (2H, s); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 165.3, 135.5, 131.4, 130.9, 128.7, 128.4, 128.1, 128.0, 127.9, 66.6.

Benzyl phenyl ether (Table 1, Entry 8) [CAS Reg. No. 946-80-5][79]

Obtained in quantitative yield (46.4 mg, 0.25 mmol; colorless liquid) from benzyl phenyl ether (46.1 mg, 0.25 mmol).

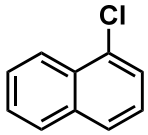


12

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.42 (2H, d, J = 7.5 Hz), 7.38–7.35(2H, m), 7.32–7.26 (3H, m), 6.98–6.93 (3H, m), 5.04(2H, s); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 158.7, 136.9, 129.4, 128.5, 127.8, 127.4, 120.8, 114.7, 69.8.

1-Chloronaphthalene (Table 1, Entry 9) [CAS Reg. No. 90-13-1][80]

Obtained in quantitative yield (41.0 mg, 0.25 mmol; brown liquid) from 1-chloronaphthalene (40.6 mg, 0.25 mmol).

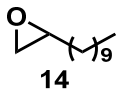


13

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 8.26 (1H, d, J = 8.0 Hz), 7.82 (1H, d, J = 8.0 Hz), 7.72 (1H, d, J = 8.0 Hz), 7.58–7.49 (3H, m), 7.34 (1H, m); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 134.4, 131.8, 130.7, 128.1, 127.1, 127.0, 126.6, 126.1, 125.6, 124.3.

1, 2-Epoxydodecane (Table 1, Entry 10) [CAS Reg. No. 2855-19-8][81]

Obtained in 97% (recovery) yield (44.8 mg, 0.24 mmol; colorless liquid) from 1, 2-Epoxydodecane (46.1 mg, 0.25 mmol).

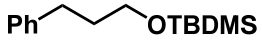


14

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 2.92–2.89 (1H, m), 2.74 (1H, dd, J = 4.5, 4.5 Hz), 2.46 (1H, dd, J = 4.5, 2.0 Hz), 1.53–1.26 (18H, m), 0.88 (3H, t, J = 7.5 Hz); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 52.3, 47.0, 32.4, 31.8, 29.5, 29.5, 29.4, 29.2, 25.9, 22.6, 14.0.

1-(*tert*-Butyldimethylsilyl)oxy-3-phenylpropane (Table 1, Entry 11) [CAS Reg. No. 69404-95-1][82]

Obtained in quantitative yield (62.8 mg, 0.25 mmol; colorless liquid) from *tert*-butyl(cinnamyloxy)dimethylsilane (62.1 mg, 0.25 mmol).

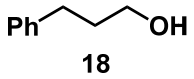


16

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.28 (2H, m), 7.20–7.16 (3H, m), 3.64 (2H, t, J = 6.1 Hz), 2.67 (2H, t, J = 8.0 Hz), 1.84 (2H, tt, J = 6.1, 8.0 Hz), 0.91 (9H, s), 0.05 (6H, s); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 142.2, 128.4, 128.2, 125.6, 62.3, 34.4, 32.0, 25.9, 18.3, -5.2.

3-Phenyl-1-propanol (Table 2) [CAS Reg. No. 122-97-4][73]

Obtained in 99% yield (1.08 g, 8.0 mmol; colorless oil) from cinnamyl alcohol (1.07 g, 8.0 mmol).



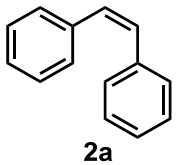
18

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.28–7.25 (2H, m), 7.19–7.16 (3H, m), 3.62 (2H, t, J = 6.3 Hz), 2.68 (2H, t, J = 7.8 Hz), 1.89–1.83 (2H, m); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ141.6, 128.1, 128.0, 125.5, 61.4, 33.8, 31.7.

(*Z*)-1,2-Diphenylethene [CAS Reg. No. 645-49-8][83]

Table 3, Entry 1: Purification by crystallization with $CHCl_3$ and hexane at 0 ºC to obtain **2a** in 52% isolated yield (23.4 mg, 0.13 mmol; colorless solid).

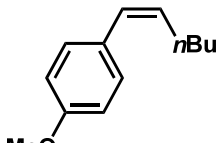
Table 4, Entry 1: Purification by crystallization with $CHCl_3$ and hexane at 0 ºC to obtain **2a** in 44% isolated yield (39.3 mg, 0.26 mmol; colorless solid).



2a

^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 7.26–7.16 (m, 10H), 6.60 (s, 2H); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 137.2, 130.2, 128.8, 128.2, 127.1.

(*Z*)-1-(Hex-1-enyl)-4-methoxybenzene (Table 4, Entry 2) [CAS Reg. No. 146646-32-4][84]



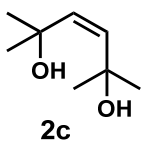
2b

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.22 (d, J = 10.0 Hz, 2H), 6.87 (d, J = 10.0 Hz, 2H) 6.34 (d, J = 12.0 Hz, 1H), 5.60–5.54 (m, 1H), 3.81 (s, 1H), 2.34–2.30 (m, 2H), 1.46–1.32 (m, 4H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 158.0, 131.7, 130.5, 129.9, 128.0, 113.5, 55.2, 32.2, 28.3, 22.4, 14.0.

(*Z*)-2,5-Dimethylhex-3-ene-2,5-diol [CAS Reg. No. 6177-86-4] [85]

Table 3, Entry 1: Purification by crystallization with $CHCl_3$ and hexane to obtain **2c** in 85% isolated yield (30.6 mg, 0.21 mmol; colorless solid).

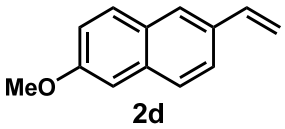
Table 4, Entry 1: Purification by crystallization with $CHCl_3$ and hexane to obtain **2c** in 83% isolated yield (59.7 mg, 0.42 mmol; colorless solid).



2c

^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 5.35 (s, 2H), 4.29 (br, 2H), 1.40 (s, 12H); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 135.4, 71.2, 31.6.

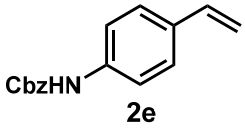
2-Methoxy-6-vinylnaphthalene (Table 4, Entry 4) [CAS Reg. No. 63444-51-9][83]



2d

^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 7.71–7.67 (m, 3H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.13–7.10 (m, 2H), 6.84 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.81 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 11.0 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 157.7, 136.9, 134.2, 132.9, 129.5, 128.9, 127.0, 126.2, 123.7, 118.9, 113.1, 105.7, 55.3.

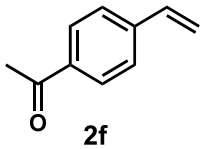
***N*-Benzyloxycarbonyl-4-aminostyrene (Table 4, Entry 5) [CAS Reg. No. 227778-64-5][86]**



2e

^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 7.42–7.36 (m, 9H), 6.66 (dd, *J* = 17.3, 11.0 Hz, 2H), 5.67 (d, *J* = 17.3 Hz, 1H), 5.21–5.17 (m, 3H); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 153.1, 137.3, 136.0, 135.9, 133.0, 128.6, 128.4, 128.3, 126.9, 118.5, 112.7, 67.1.

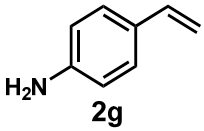
1-(4-Vinylphenyl)ethanone (Table 4, Entry 6) [CAS Reg. No. 10537-63-0][87]



2f

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.88 (d, *J* = 17.7 Hz, 1H), 5.40 (d, *J* = 11.1 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR [125 MHz (ECA-500, $CDCl_3$)] δ 197.6, 142.1, 136.2, 135.9, 128.7, 126.3, 116.7, 26.6.

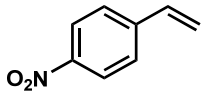
4-Vinylaniline (Table 4, Entry 7) [CAS Reg. No. 1520-21-4][88]



2g

^{1}H NMR [400 MHz (ECZ-400, $CDCl_3$)] δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.65–6.55 (m, 3H), 5.54 (d, *J* = 17.2 Hz, 1H) 5.04 (d, *J* = 10.8 Hz, 1H) 3.69 (br, 2H); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 146.1, 136.5, 128.3, 127.3, 115.0, 110.0.

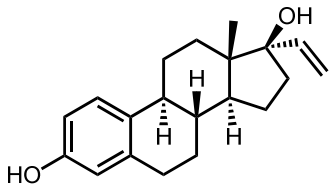
1-Nitoro-4-vinylbenzene (Table 3, Entry 10) [CAS Reg. No. 1520-21-4][89]



2h

^{1}H NMR [500 MHz (ECA-500, $CDCl_3$)] δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 6.79 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.94 (d, *J* = 17.5, 1H), 5.51 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR [100 MHz (ECZ-400, $CDCl_3$)] δ 147.1, 143.8, 134.9, 126.8, 123.9, 118.6.

17α-Vinyl-1,3,5(10)-estratriene-3,17β-diol (Table 4, Entry 9) [CAS Reg. No. 7678-95-7][73]

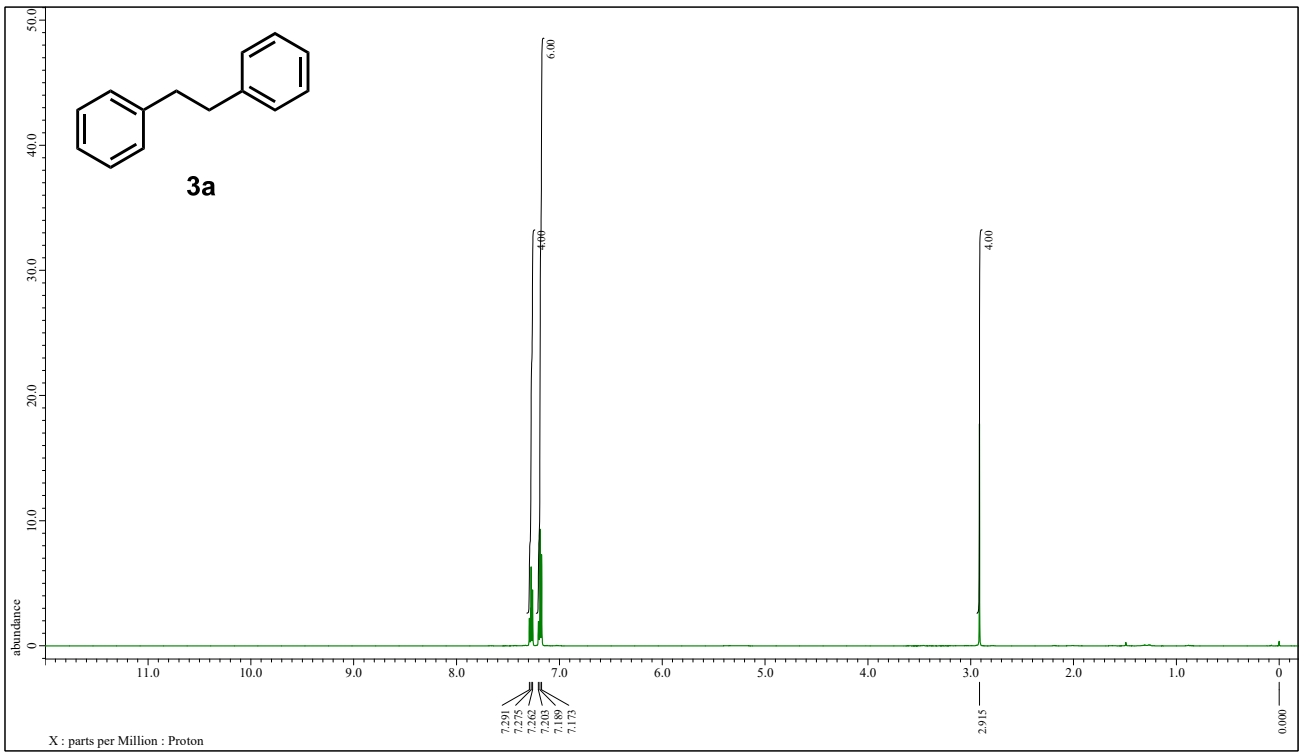


2i

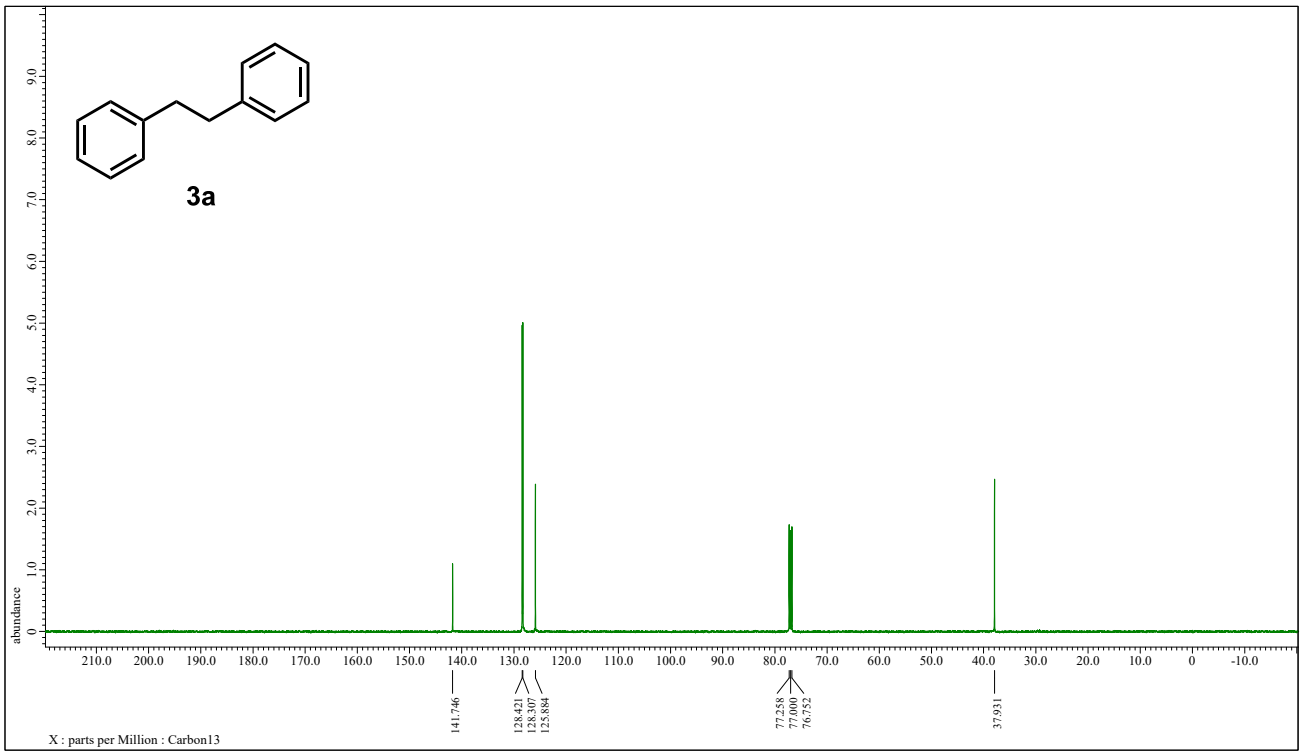
^{1}H NMR [500 MHz (ECA-500, CD_3OD)] δ 7.08 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 6.50 (s, 1H), 6.13 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.19 (d, *J* = 17.3 Hz, 1H), 5.13 (d, *J* = 10.9 Hz, 1H), 2.86–2.78 (m, 2H), 2.30–2.27 (m, 1H), 2.00–1.89 (m, 4H), 1.79–1.73 (m, 1H), 1.67–1.64 (m, 1H), 1.53–1.41 (m, 6H), 0.96 (s, 3H); ^{13}C NMR [125 MHz (ECA-500, CD_3OD)] δ 156.8, 145.5, 140.0, 133.4, 128.0, 116.9, 114.6, 113.1, 85.9, 51.0, 48.7, 46.0, 42.0, 37.2, 34.3, 31.6, 29.6, 28.5, 25.1, 15.6.

14. ^{1}H and ^{13}C spectra of products

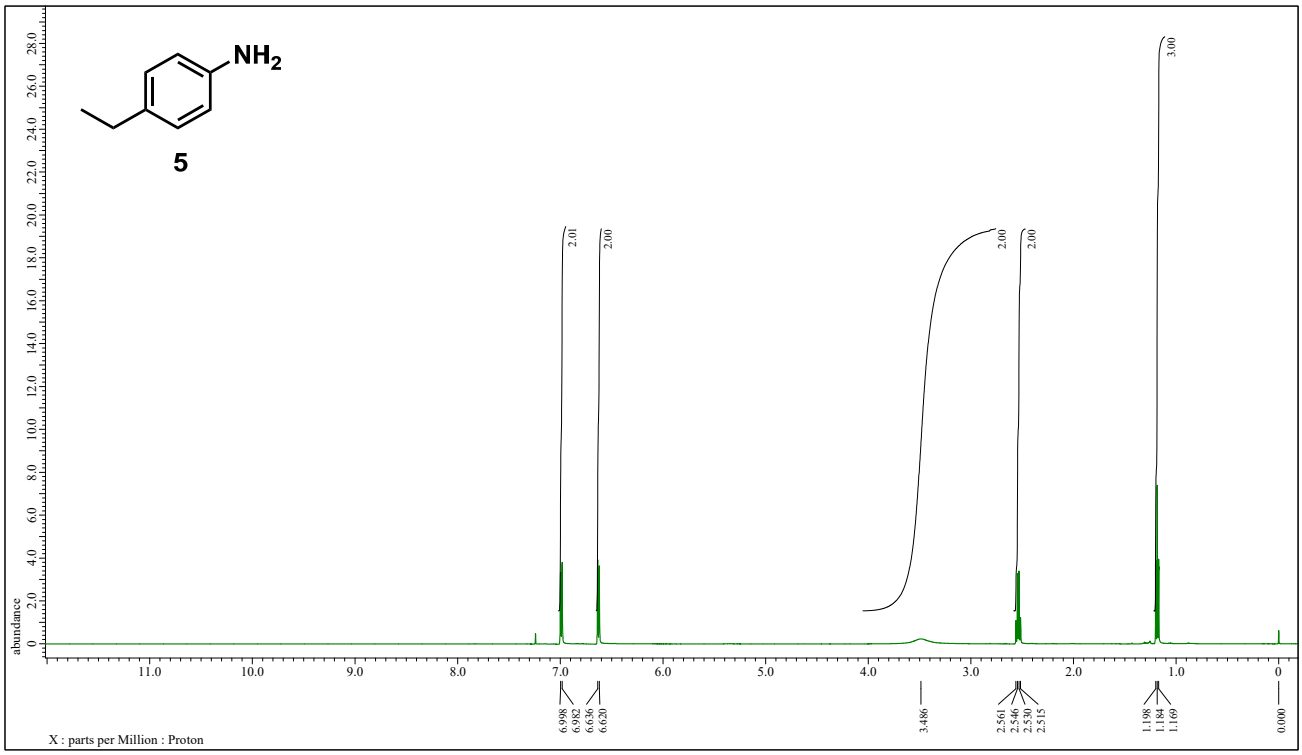
^{1}H NMR of diphenylethane (3a)



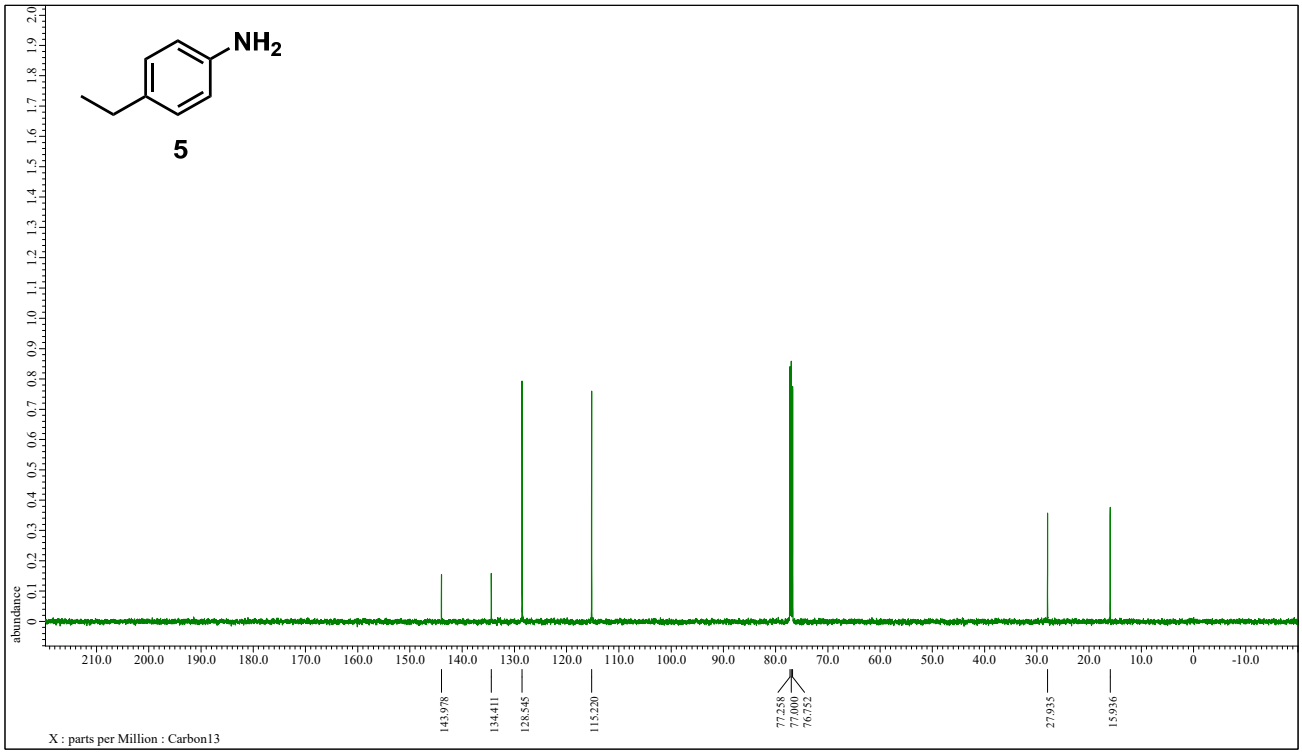
^{13}C NMR of diphenylethane (3a)



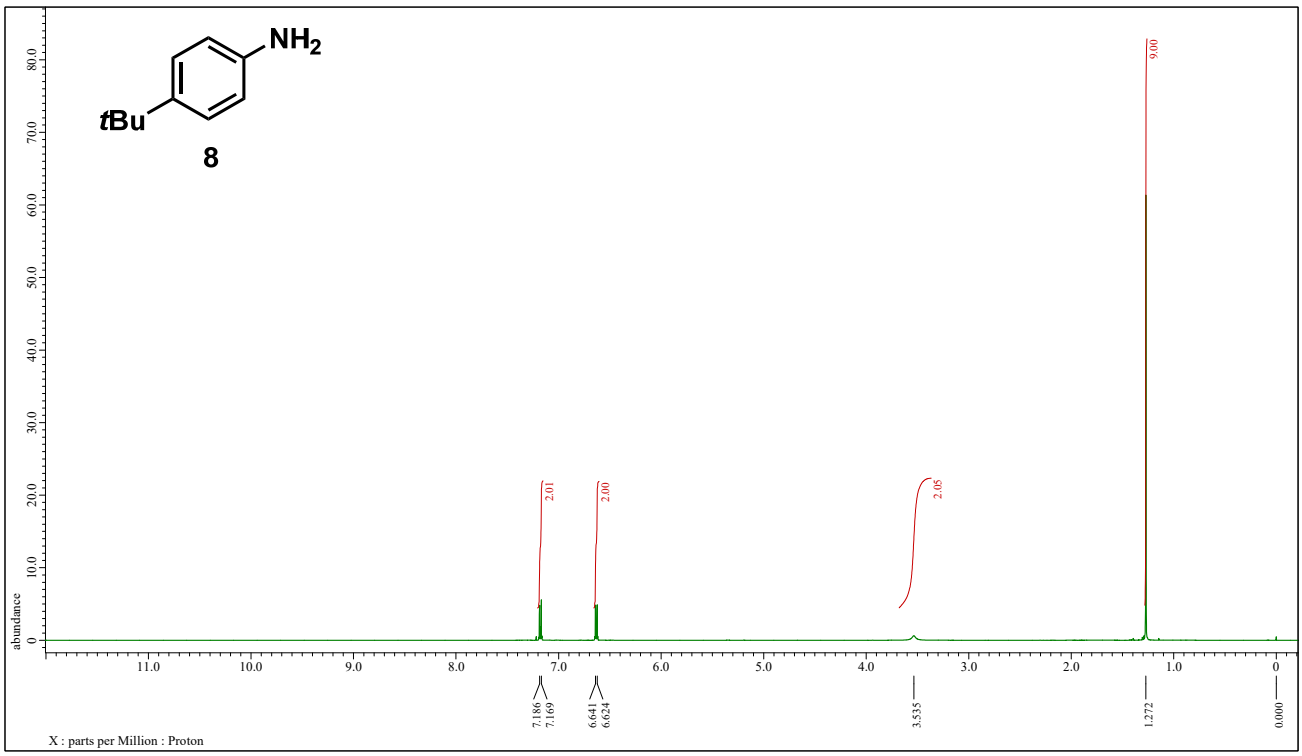
^{1}H NMR of *p*-ethylaniline (5)



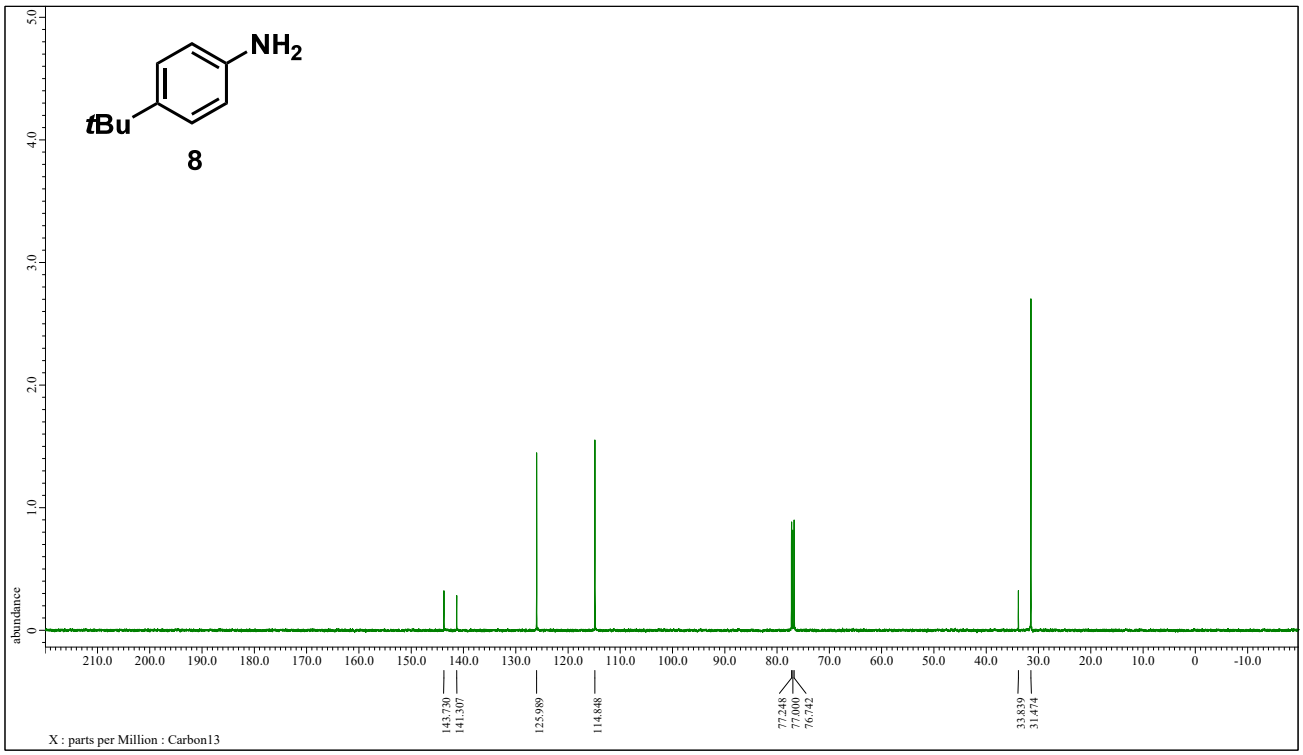
^{13}C NMR of *p*-ethylaniline (5)



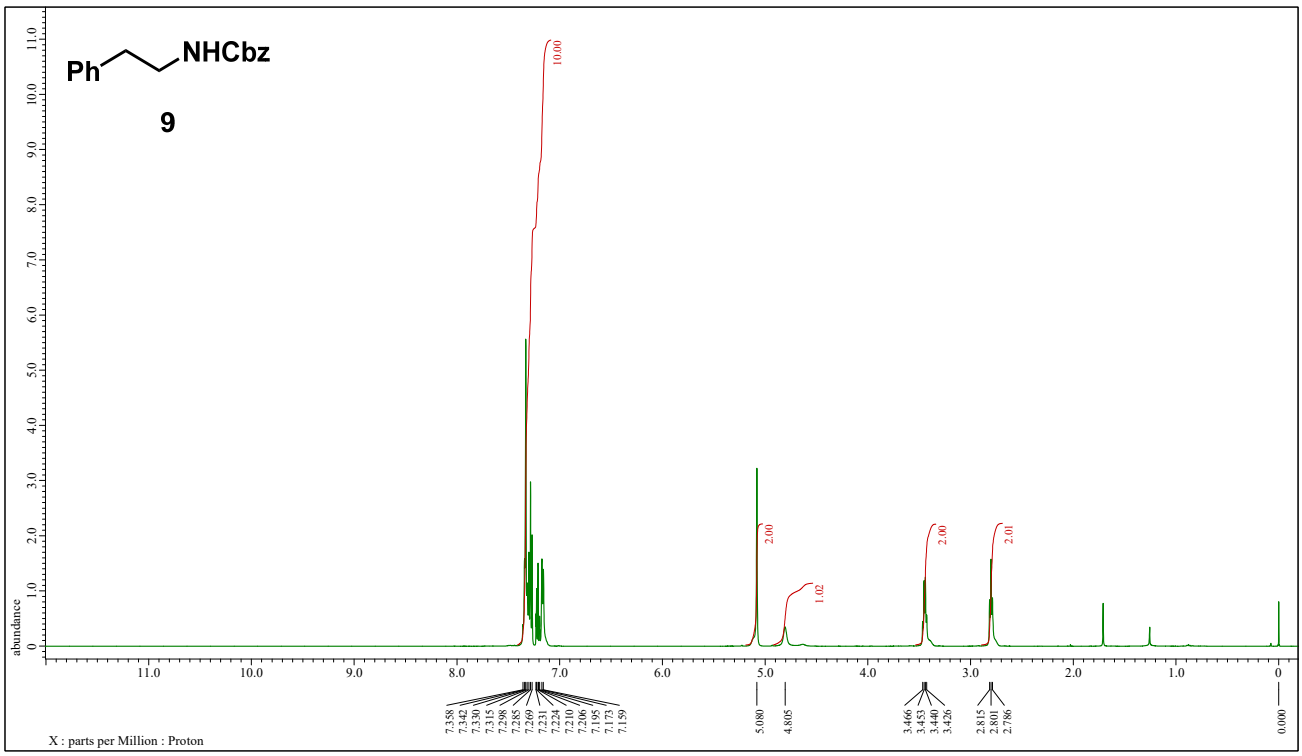
^{1}H NMR of 4-*tert* butylaniline (8)



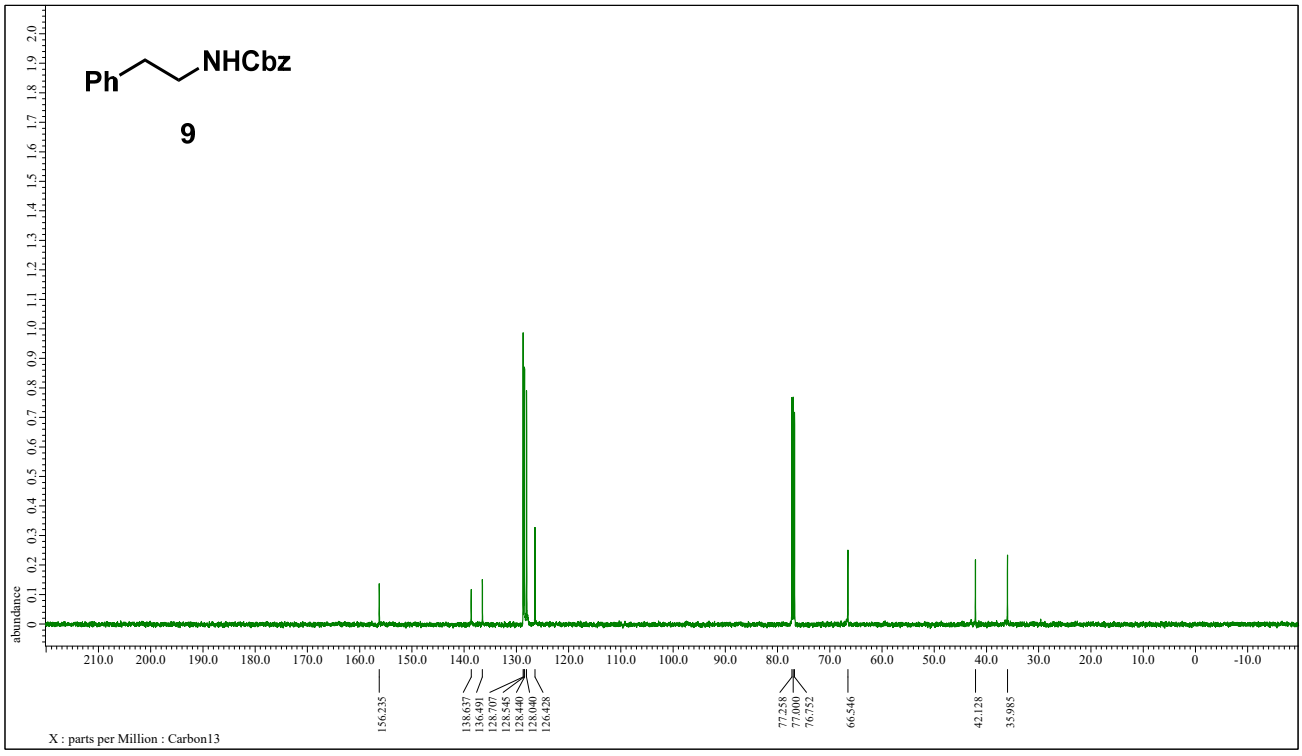
^{13}C NMR of 4-*tert* butylaniline (8)



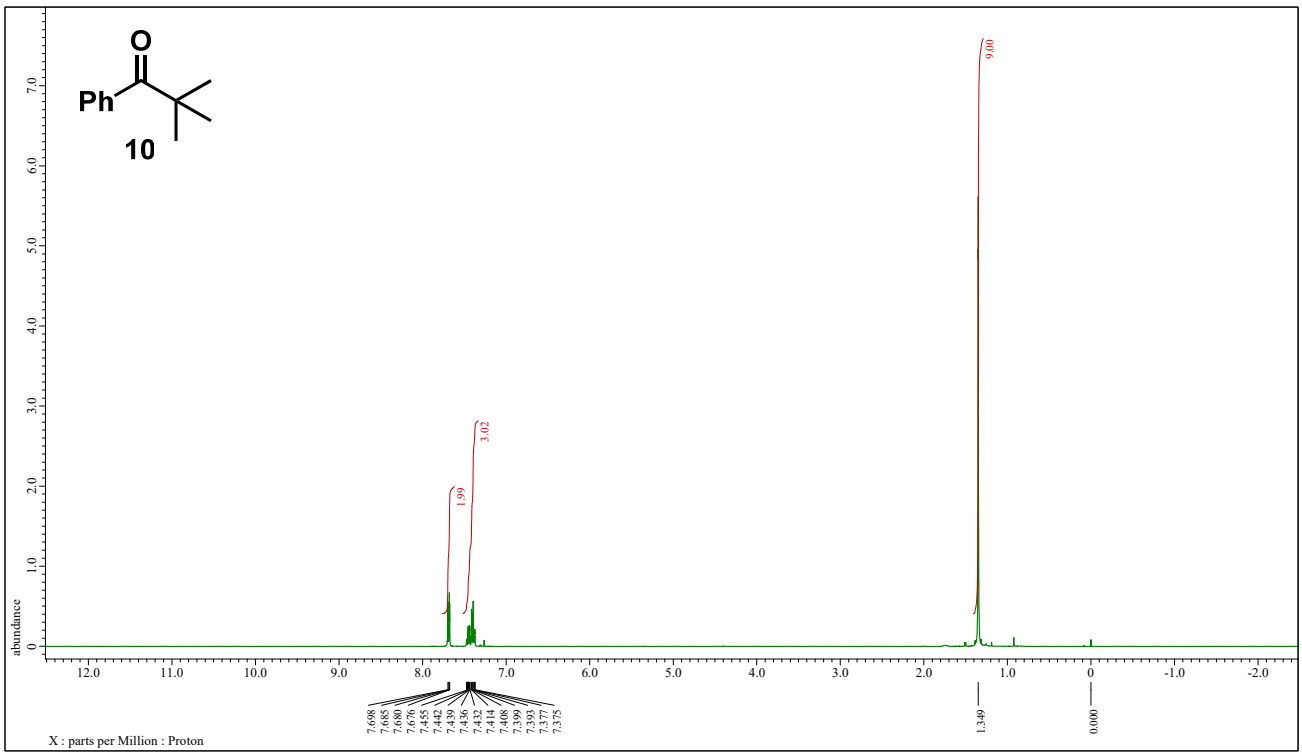
^{1}H NMR of benzyl phenethylcarbamate (9)



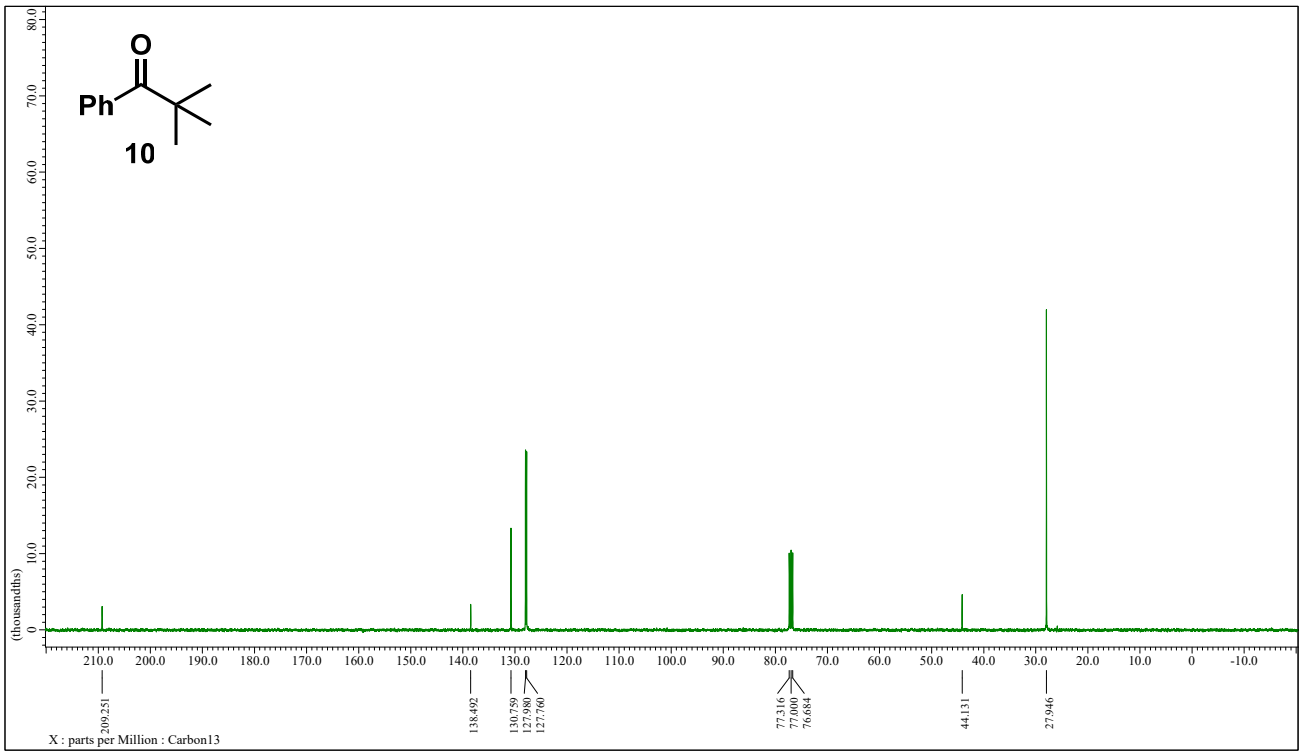
^{13}C NMR of benzyl phenethylcarbamate (9)



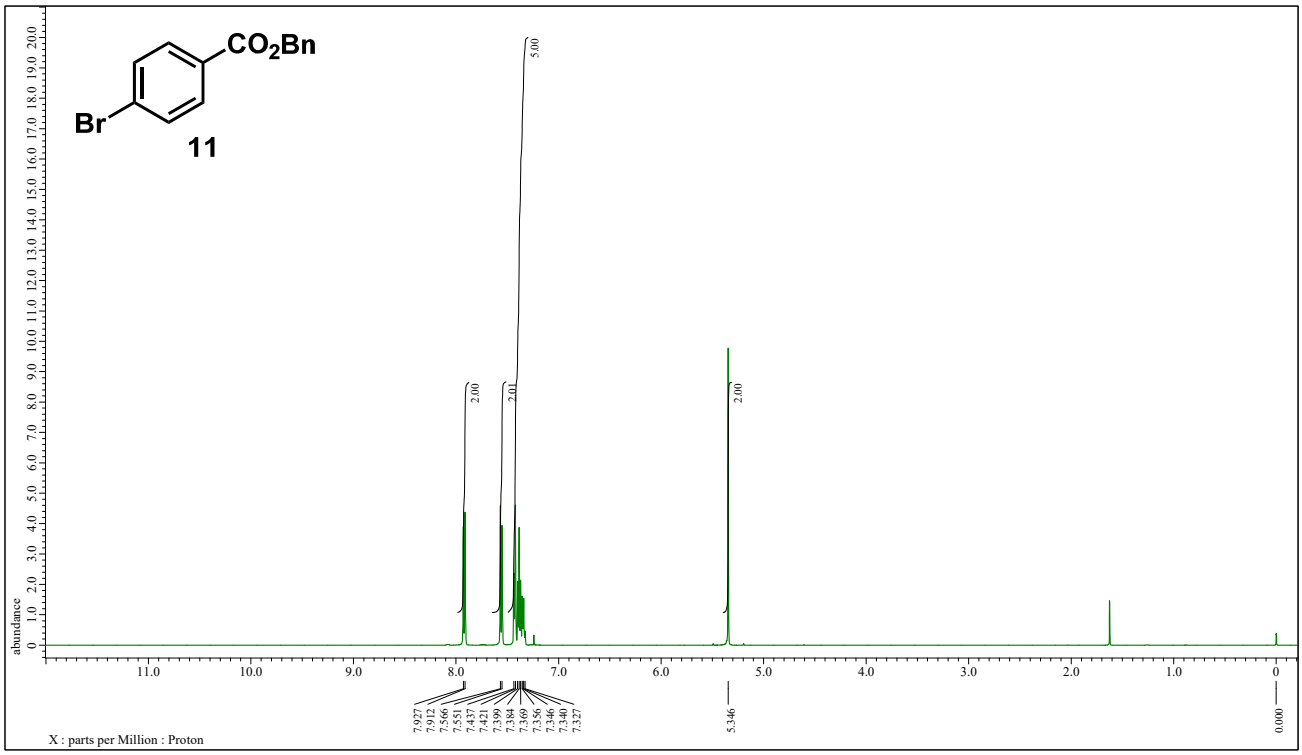
^{1}H NMR of 2,2-dimethylpropiophenone (10)



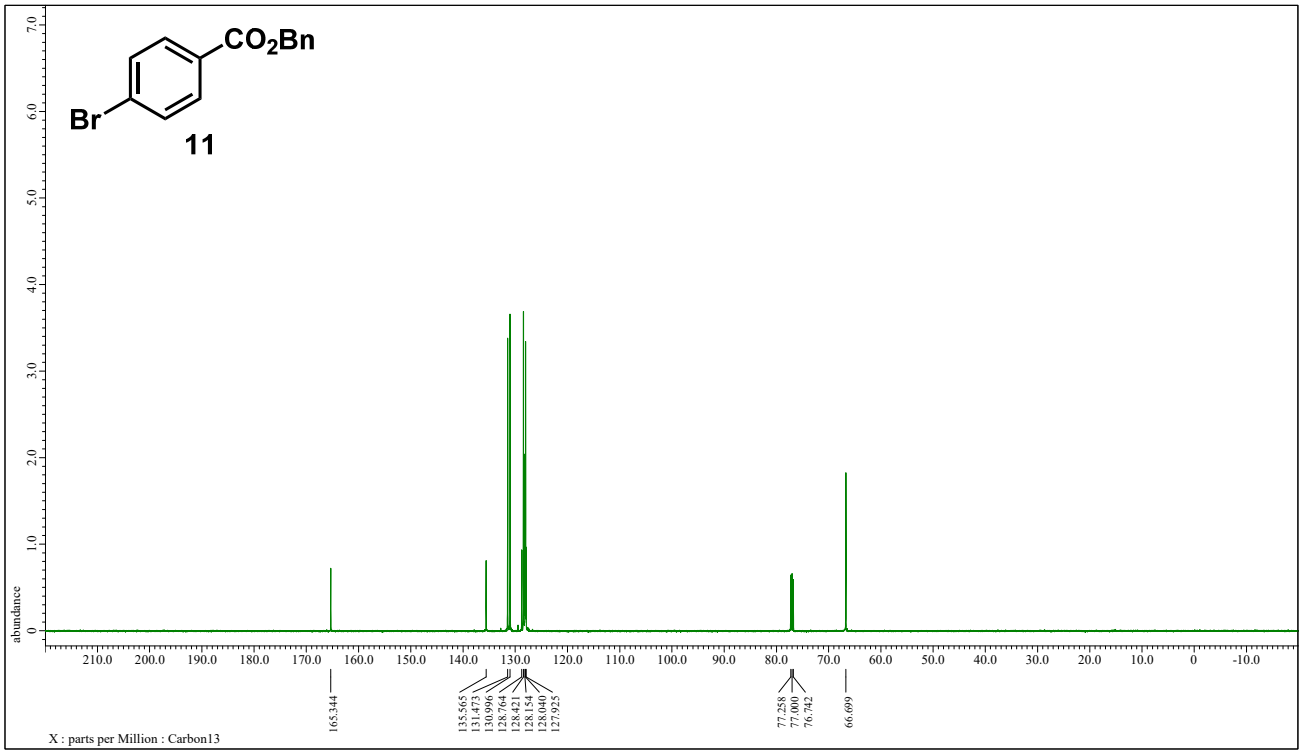
^{13}C NMR of 2,2-dimethylpropiophenone (10)



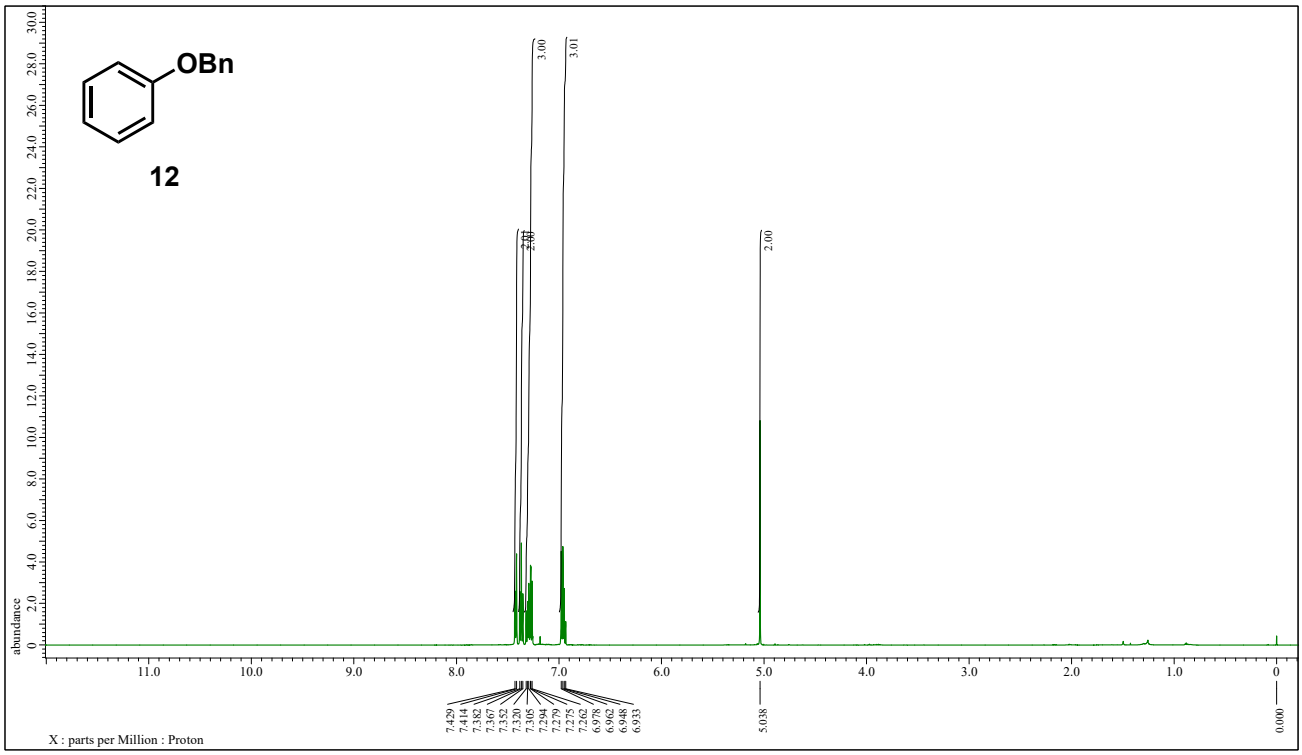
^{1}H NMR of benzyl-4-bromobenzoate (11)



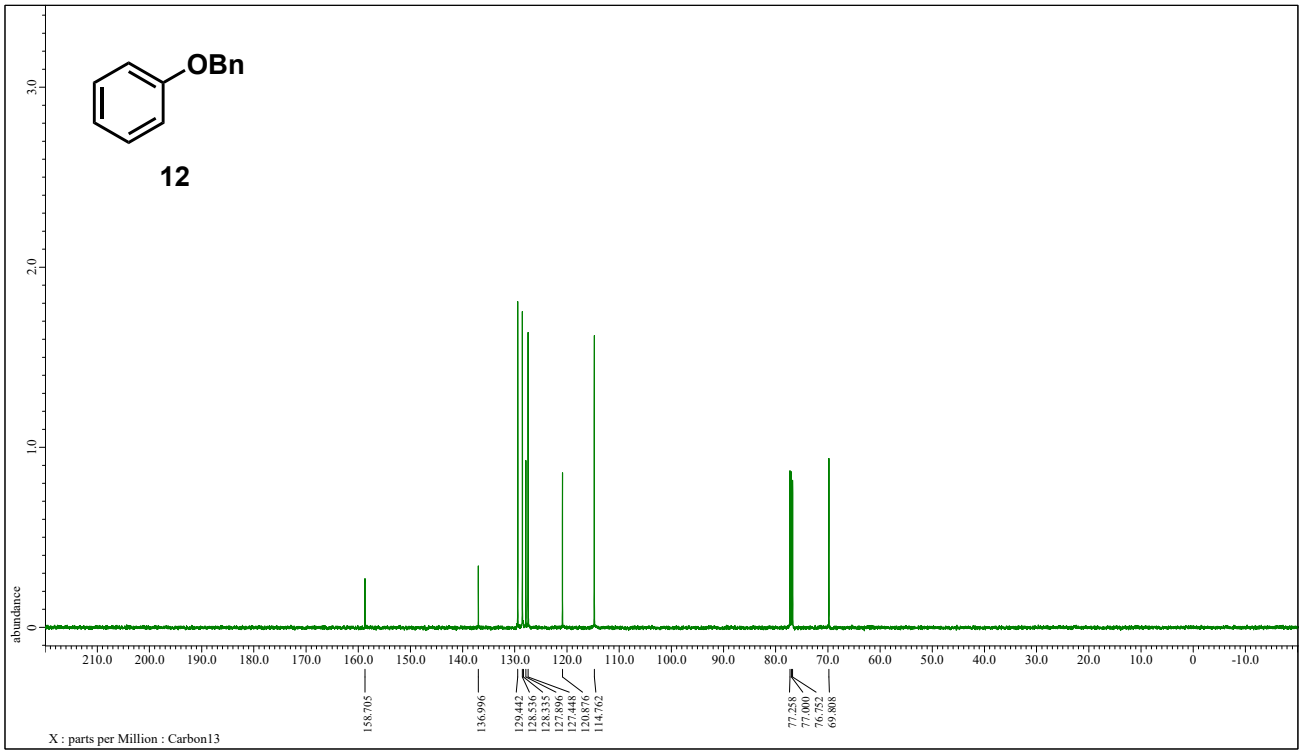
^{13}C NMR of benzyl-4-bromobenzoate (11)



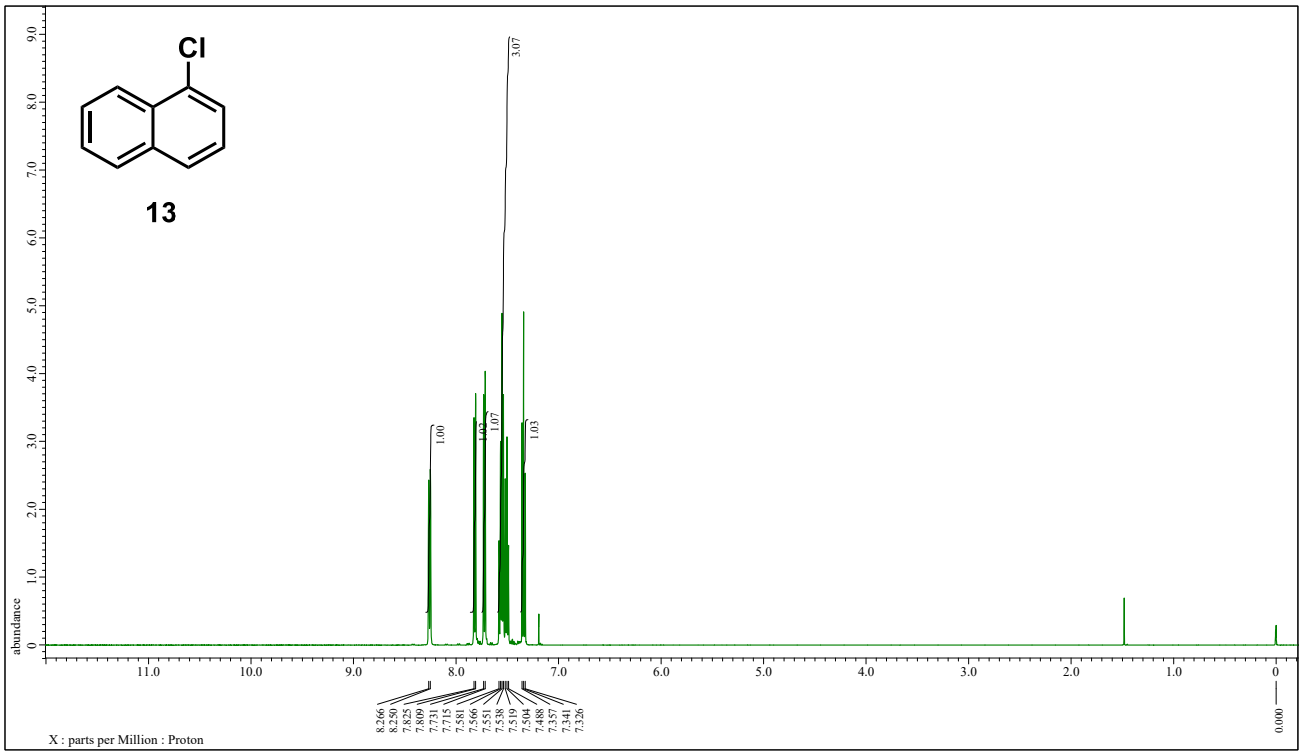
^{1}H NMR of benzyl phenyl ether (12)



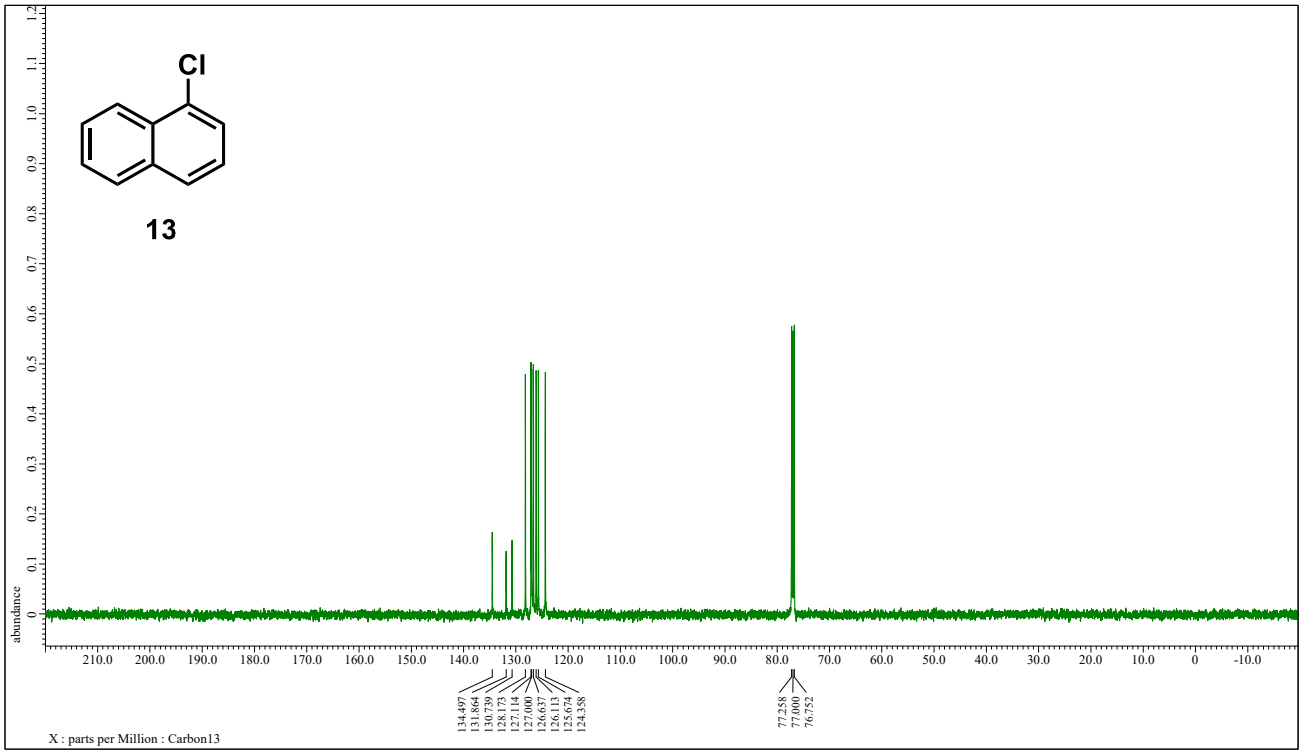
^{13}C NMR of benzyl phenyl ether (12)



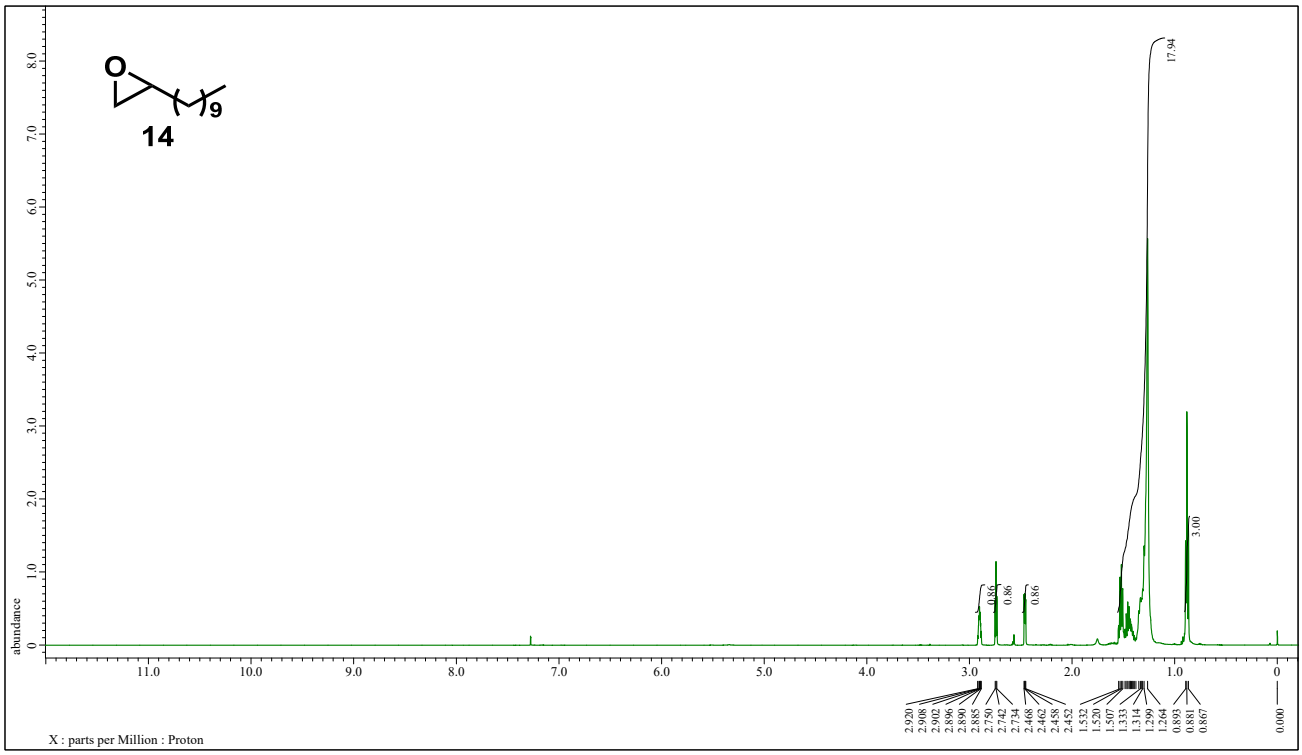
^{1}H NMR of 1-chloronaphthalene (13)



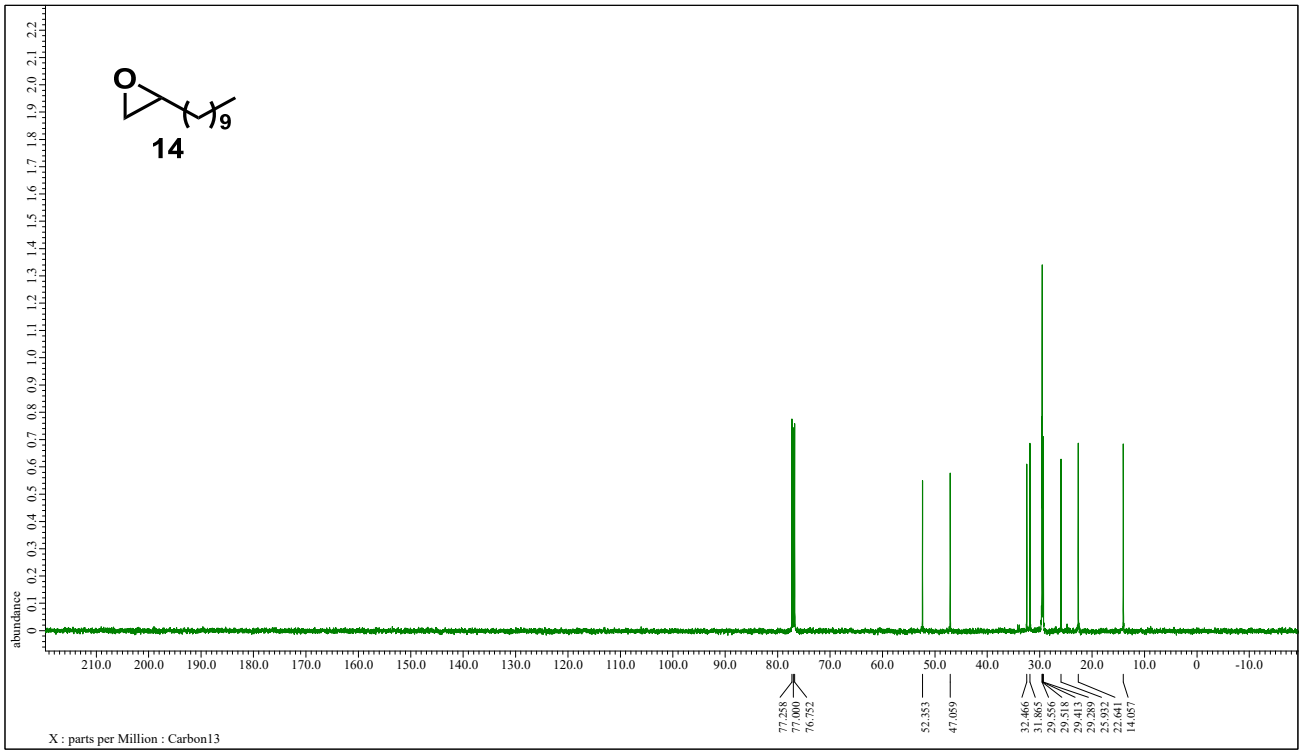
^{13}C NMR of 1-chloronaphthalene (13)



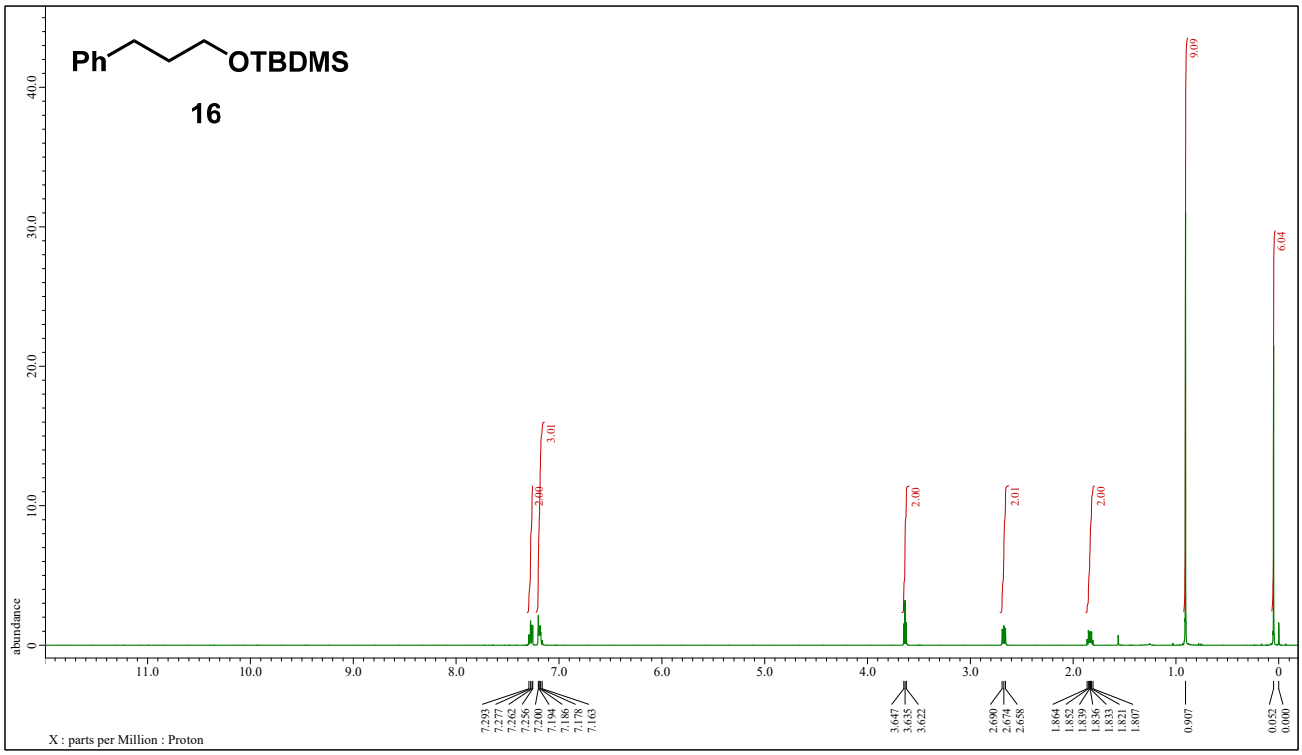
^{1}H NMR of 1,2-epoxydodecane (14)



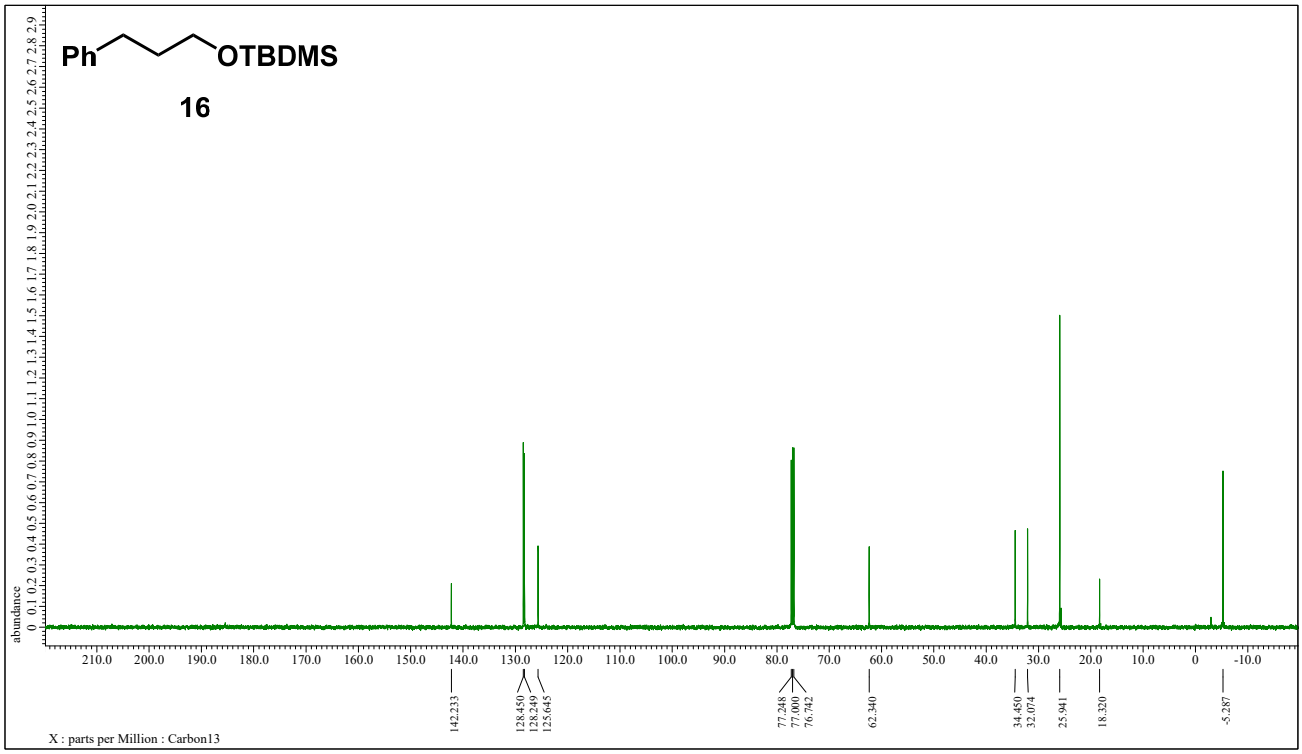
^{13}C NMR of 1,2-epoxydodecane (14)



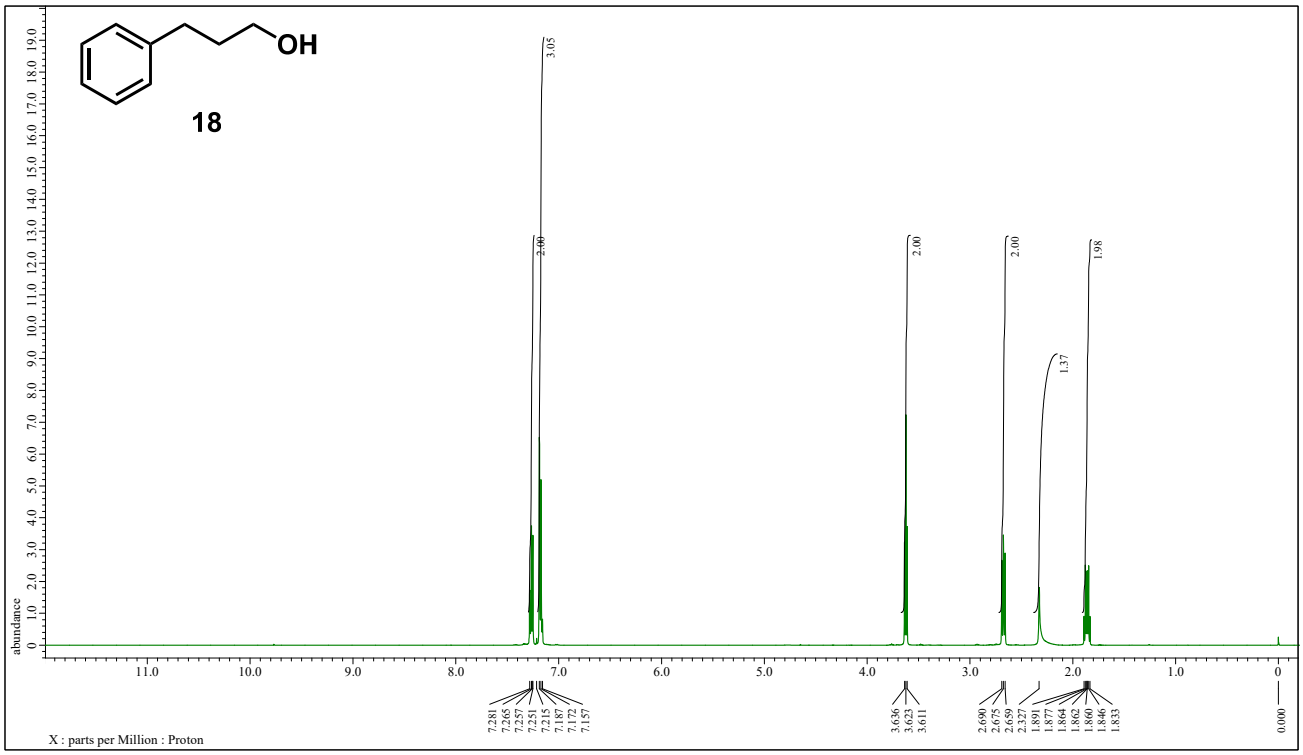
^{1}H NMR of 1-(*tert*-butyldimethylsilyl)oxy-3-phenylpropane (16)



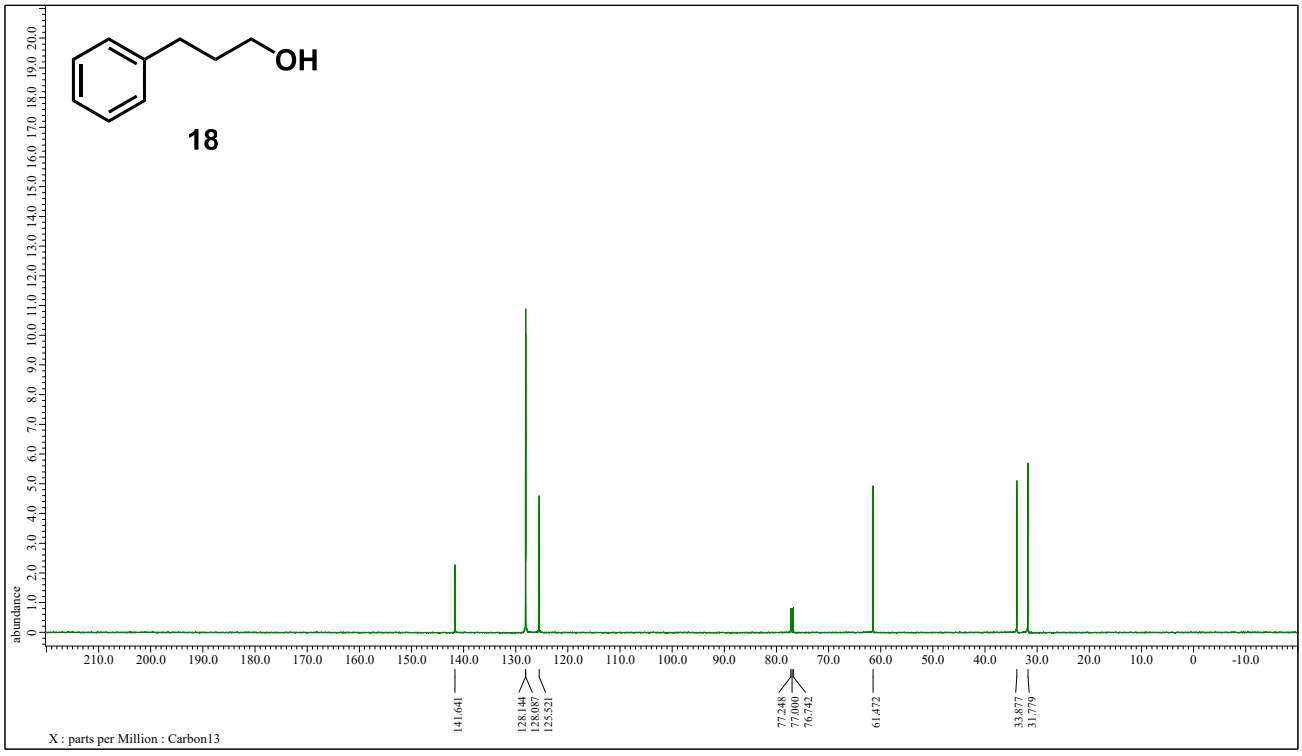
^{13}C NMR of 1-(*tert*-butyldimethylsilyl)oxy-3-phenylpropane (16)



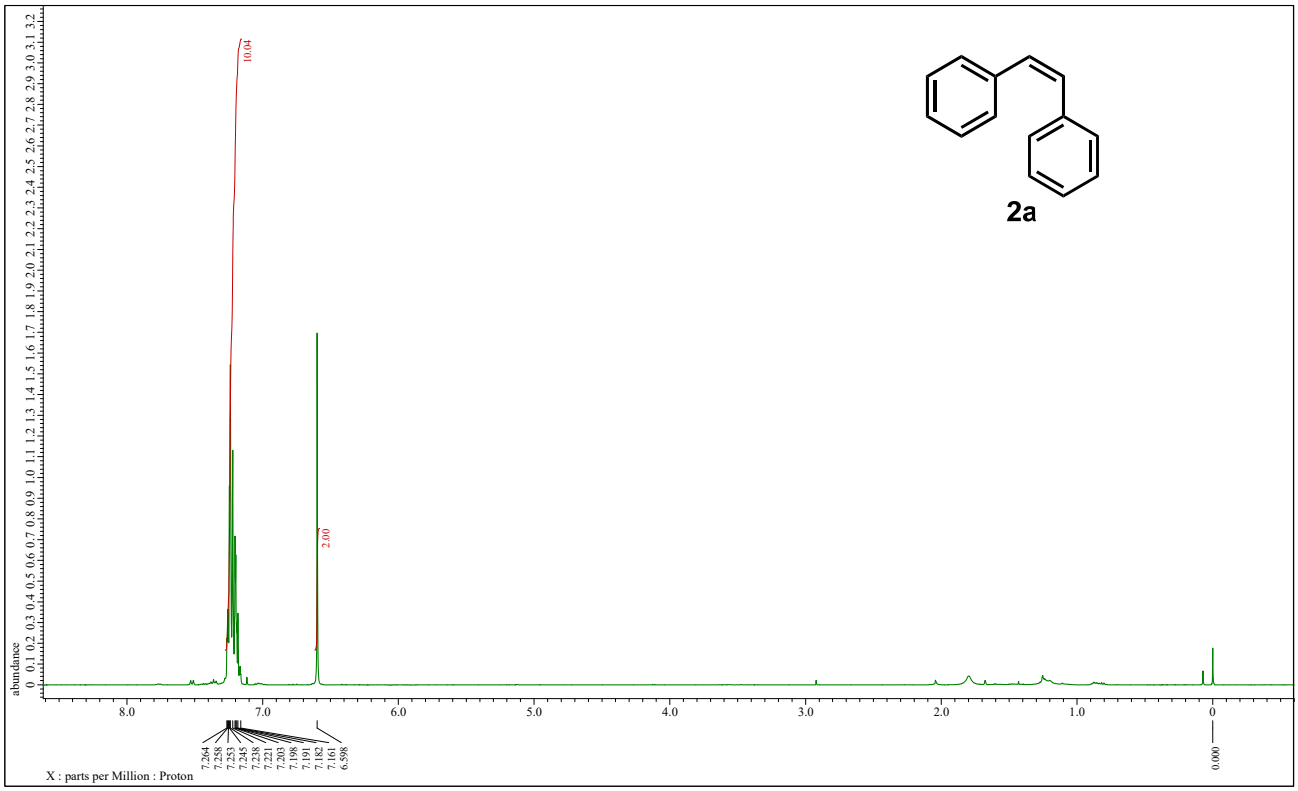
^{1}H NMR of 3-phenyl-1-propanol (18)



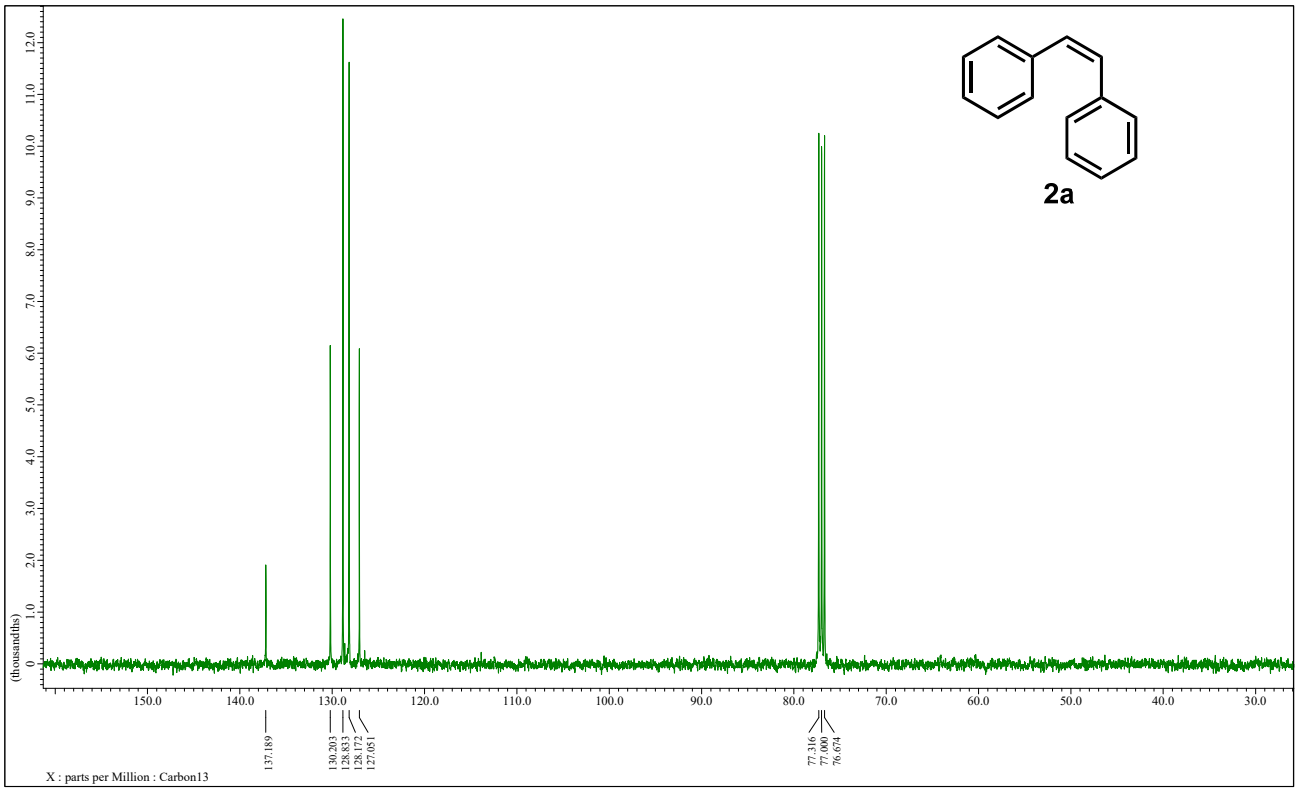
^{13}C NMR of 3-phenyl-1-propanol (18)



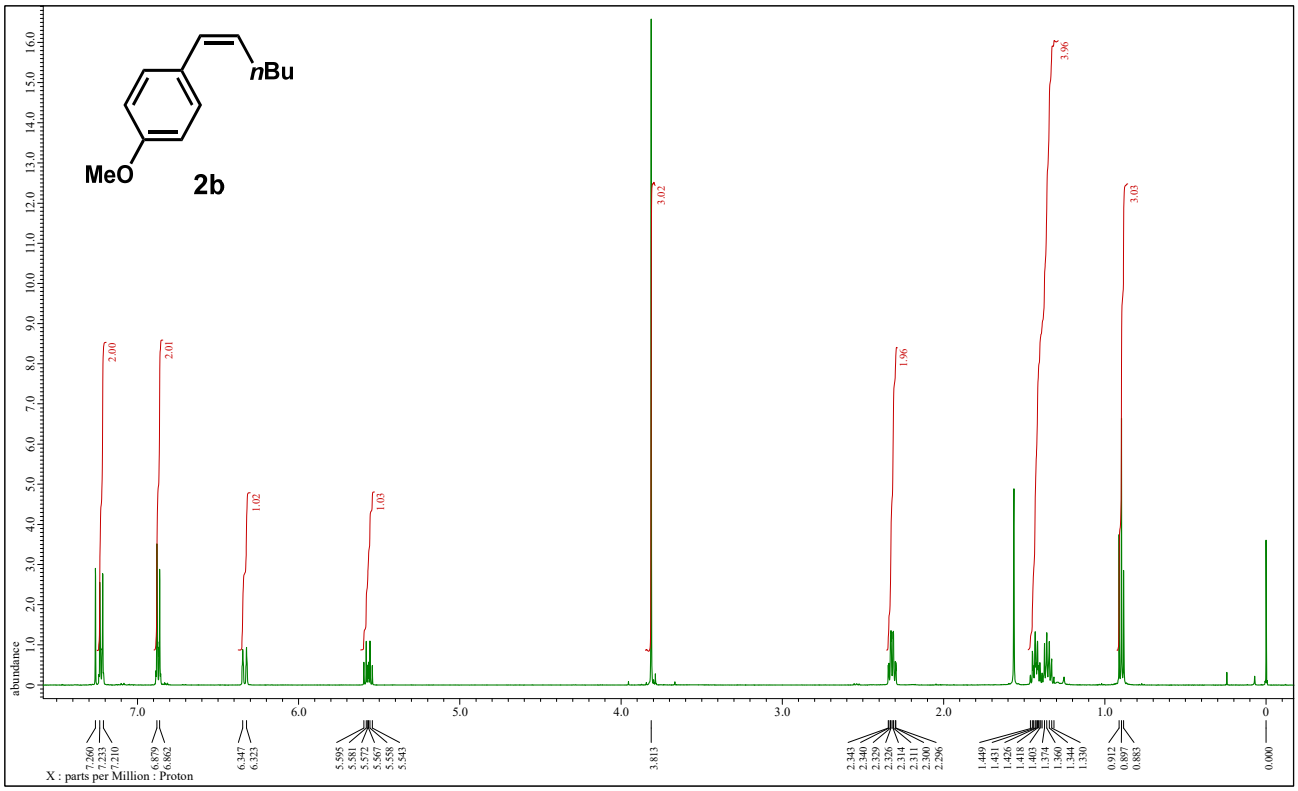
^{1}H NMR of (*Z*)-1,2-diphenylethene (2a)



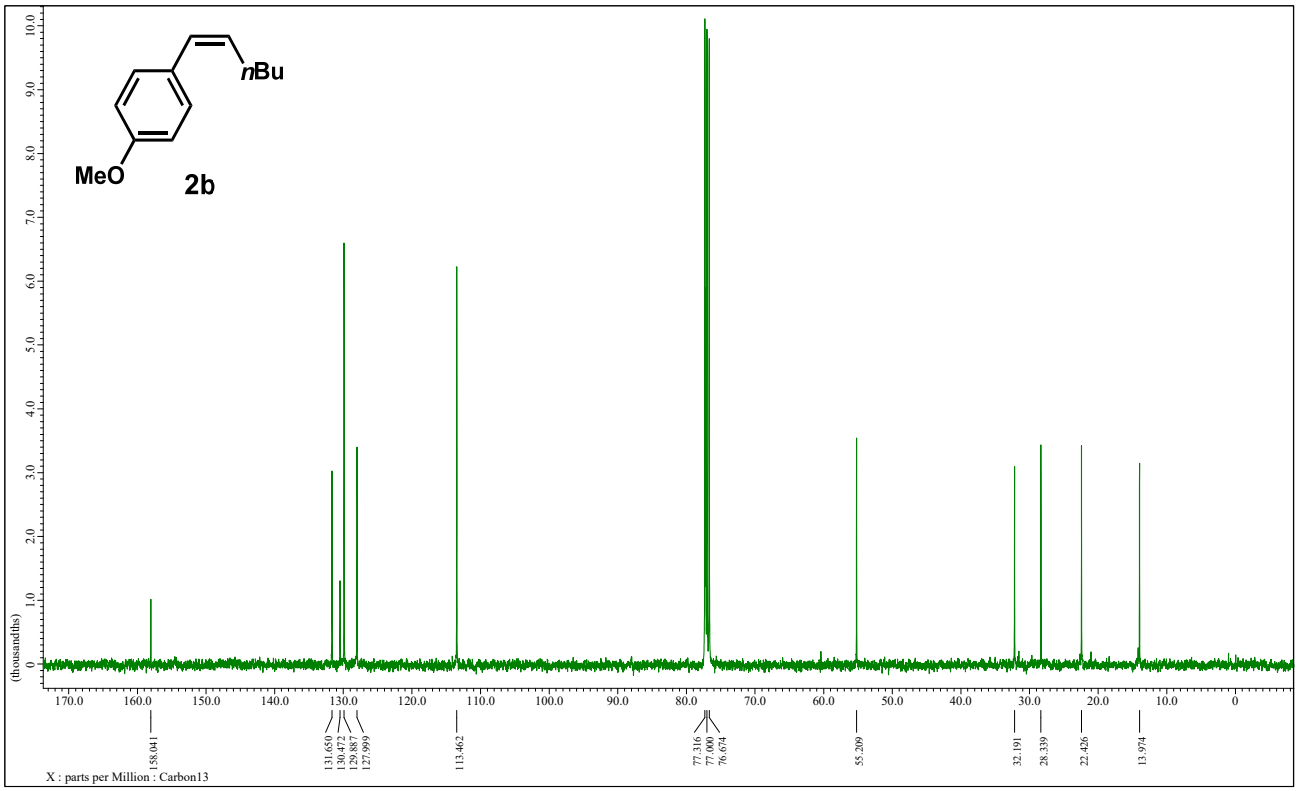
^{13}C NMR of (*Z*)-1,2-diphenylethene (2a)



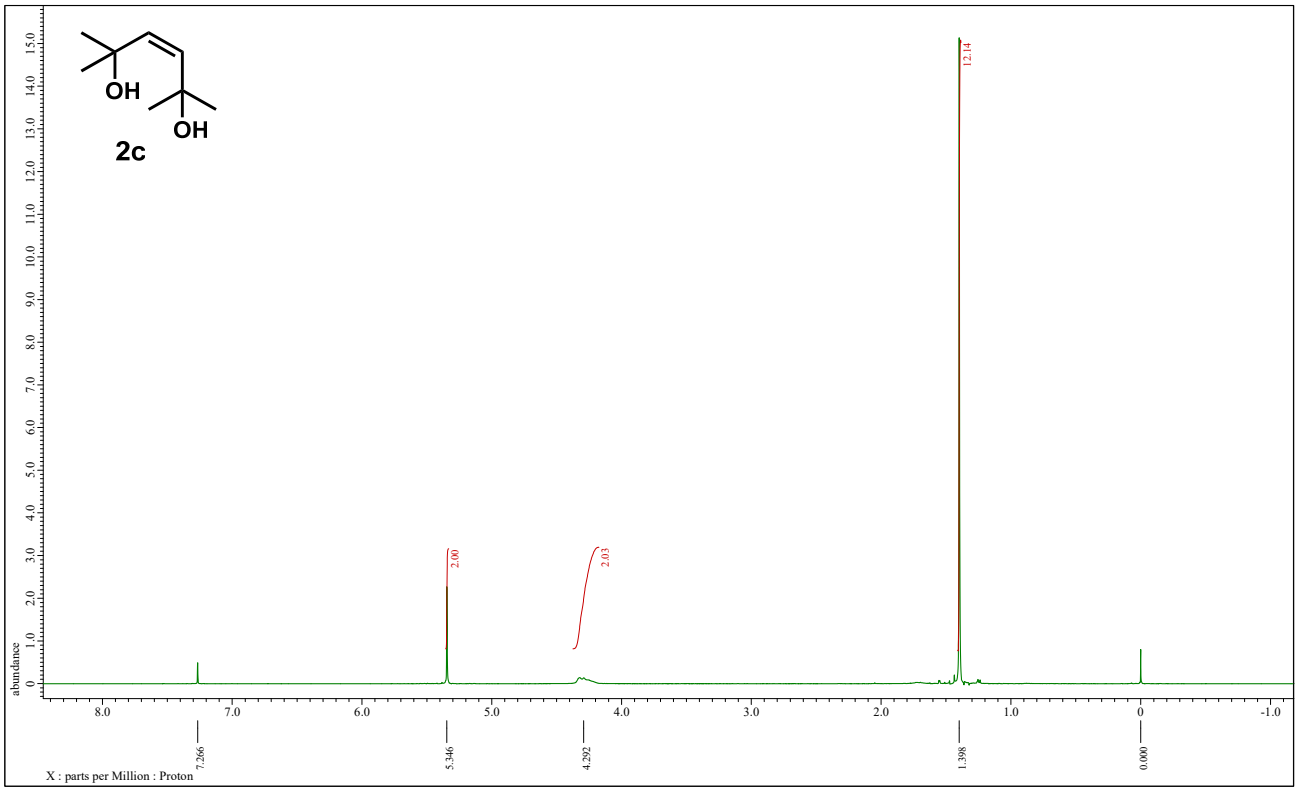
^{1}H NMR of (*Z*)-1-(hex-1-enyl)-4-methoxybenzene (2b)



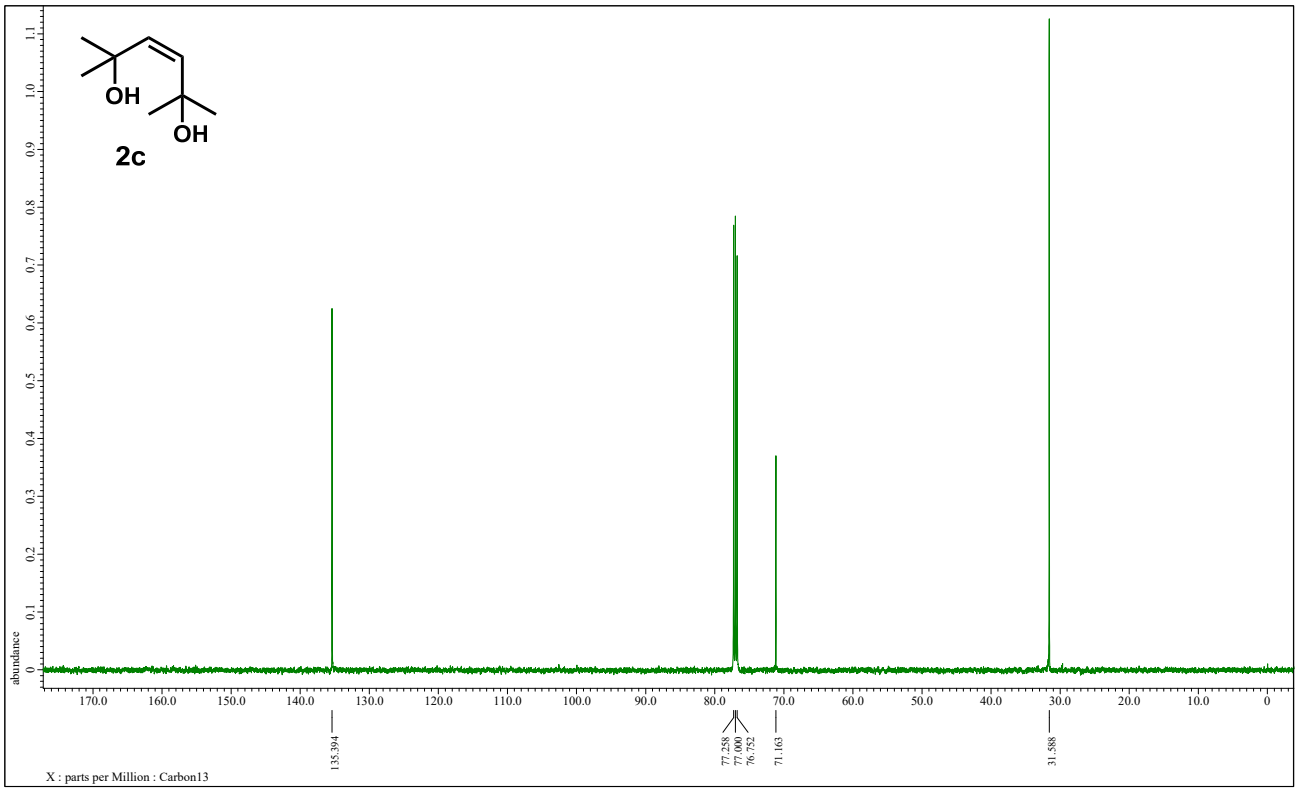
^{13}C NMR of (*Z*)-1-(hex-1-enyl)-4-methoxybenzene (2b)



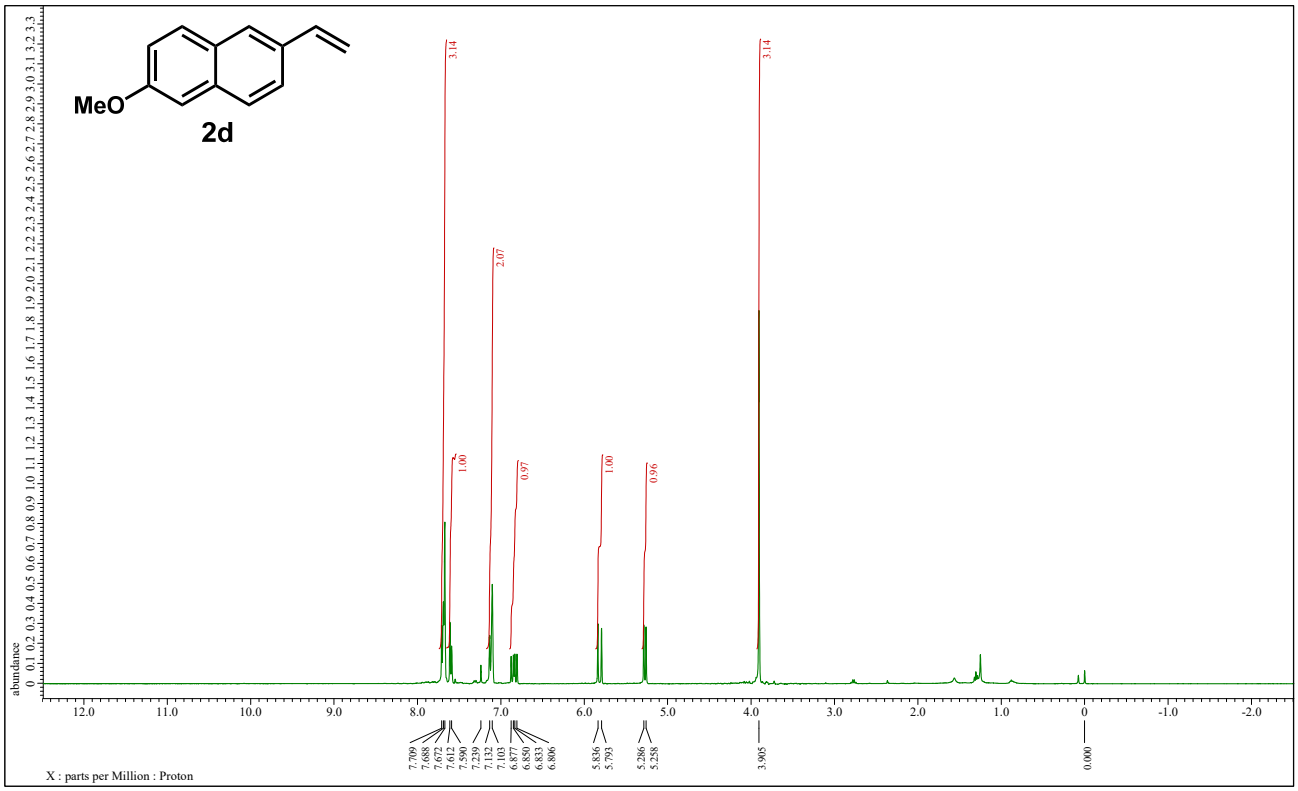
^{1}H NMR of (*Z*)-2,5-dimethylhex-3-ene-2,5-diol (2c)



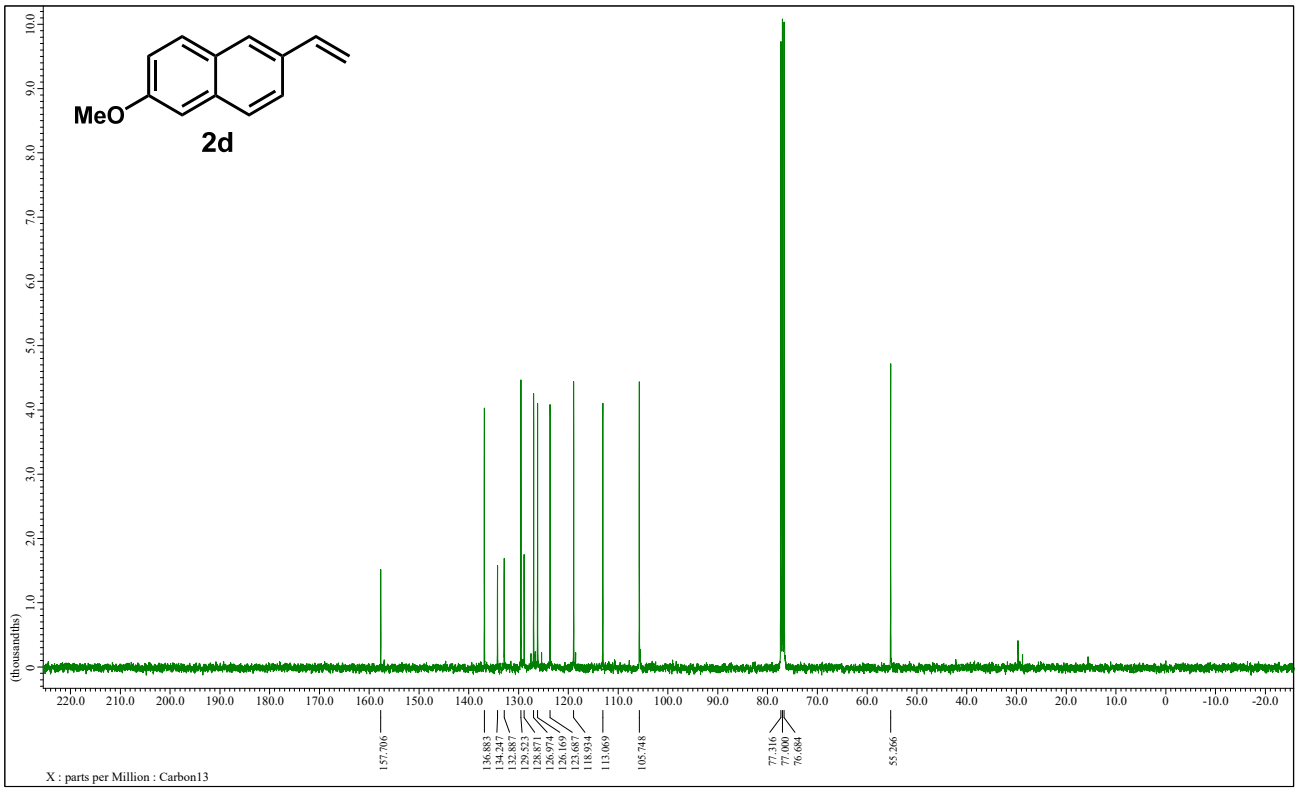
^{13}C NMR of (*Z*)-2,5-dimethylhex-3-ene-2,5-diol (2c)



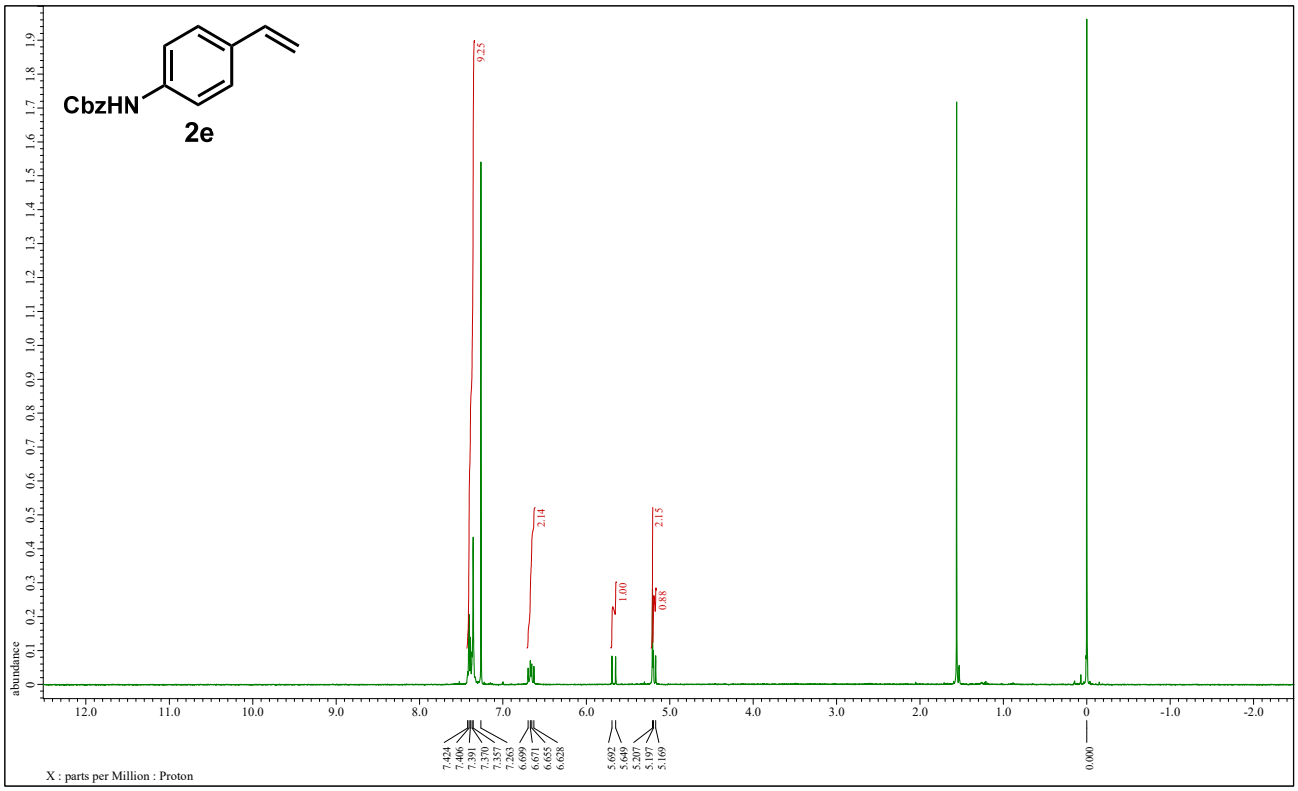
^{1}H NMR of 2-methoxy-6-vinylnaphthalene (2d)



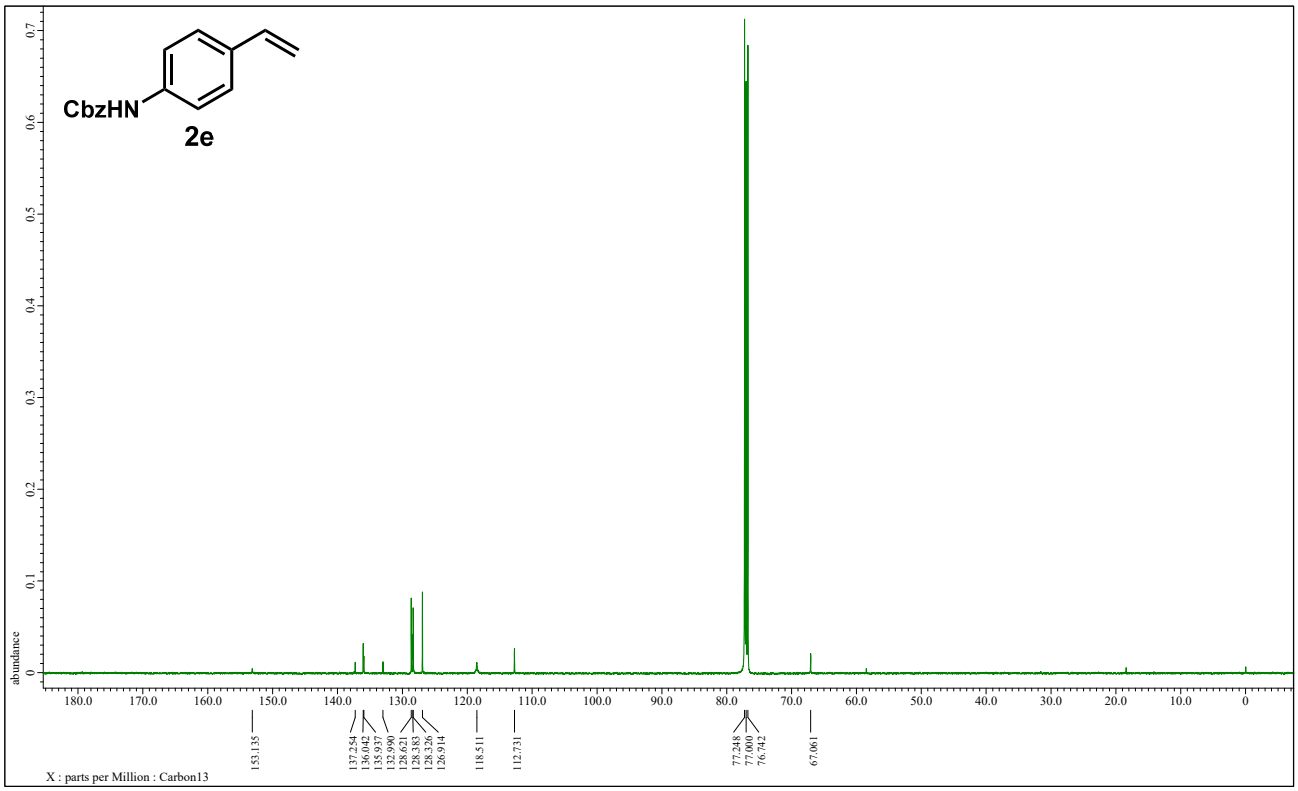
^{13}C NMR of 2-methoxy-6-vinylnaphthalene (2d)



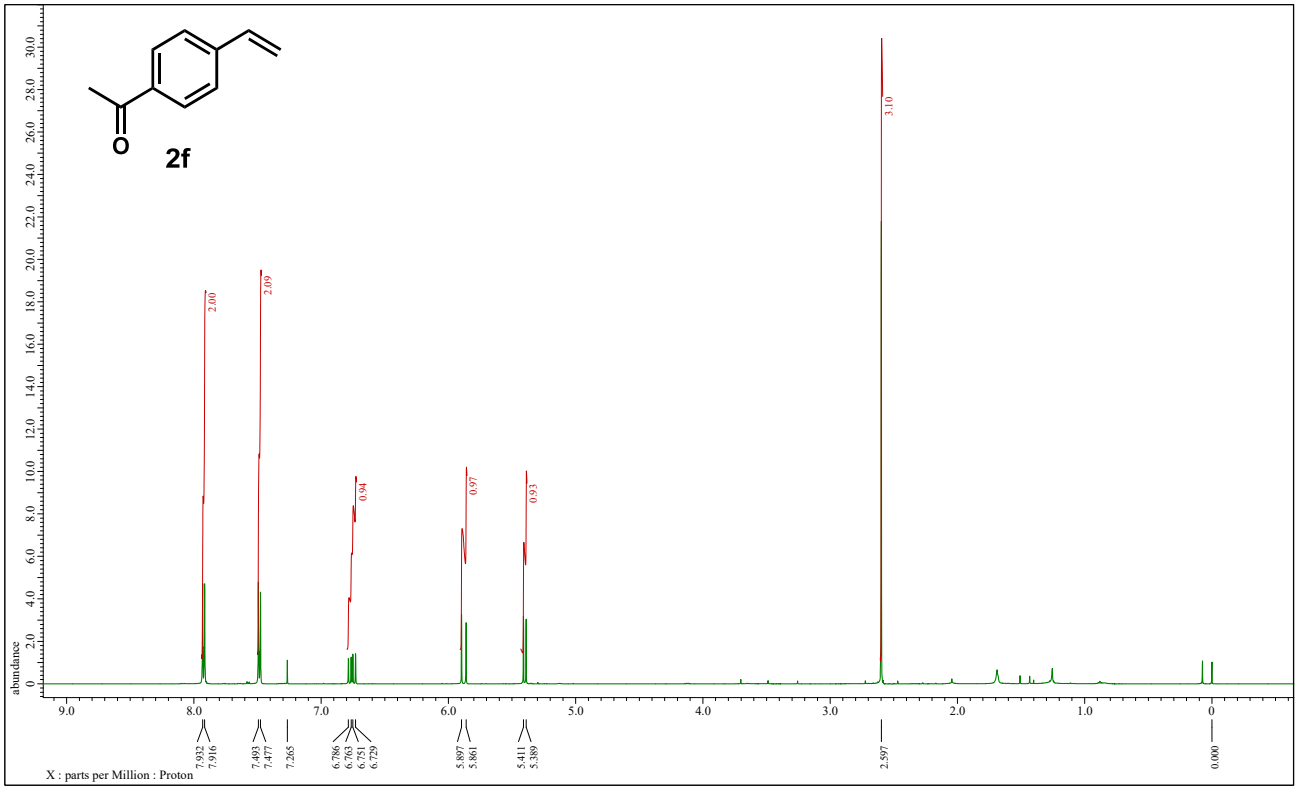
^{1}H NMR of *N*-benzyloxycarbonyl-4-aminostyrene (2e)



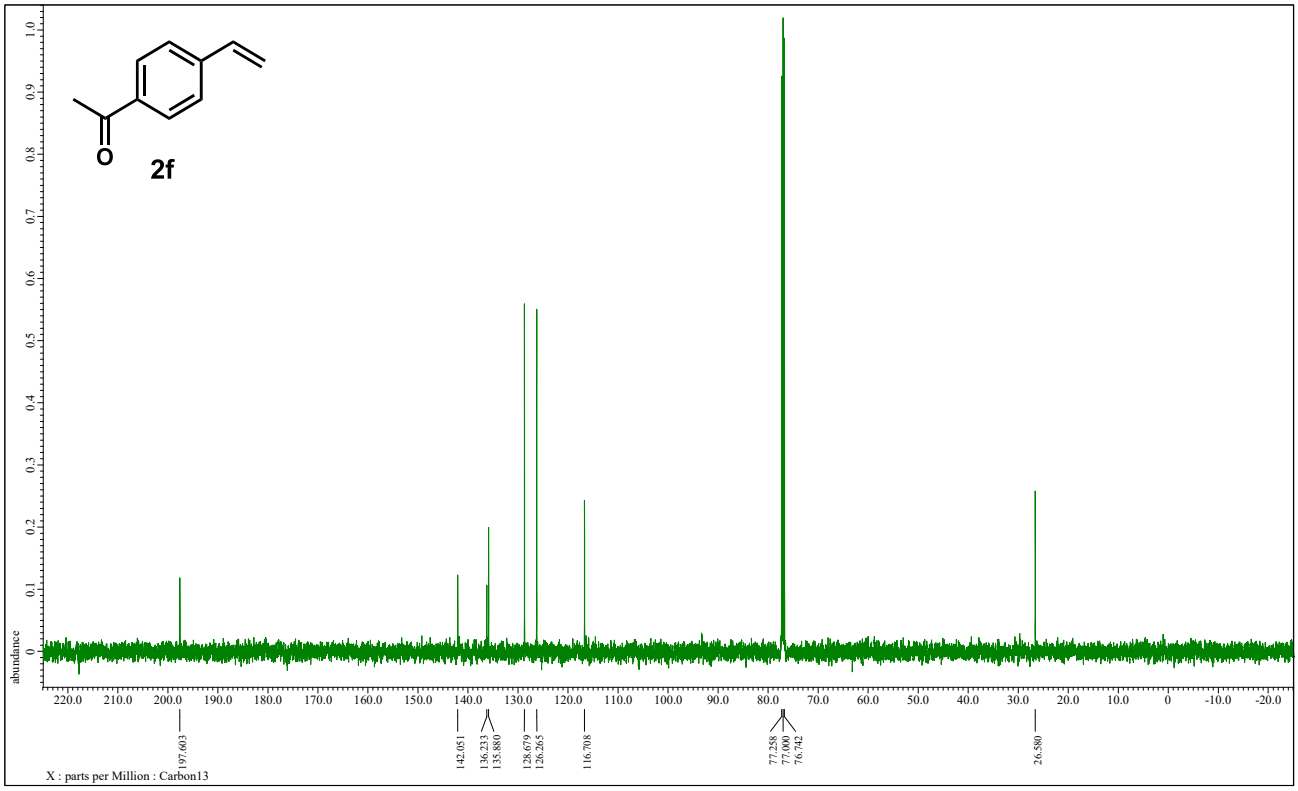
^{13}C NMR of *N*-benzyloxycarbonyl-4-aminostyrene (2e)



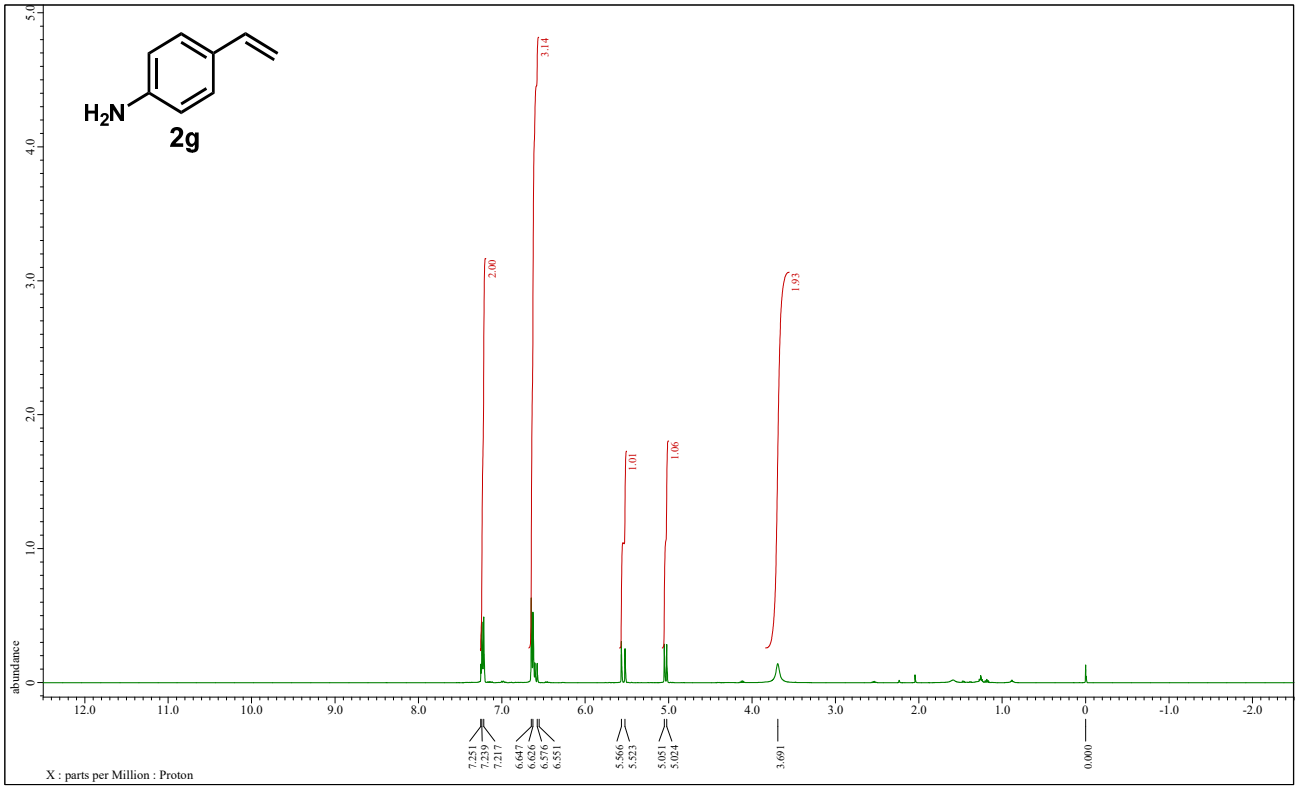
^{1}H NMR of 1-(4-vinylphenyl)ethenone (2f)



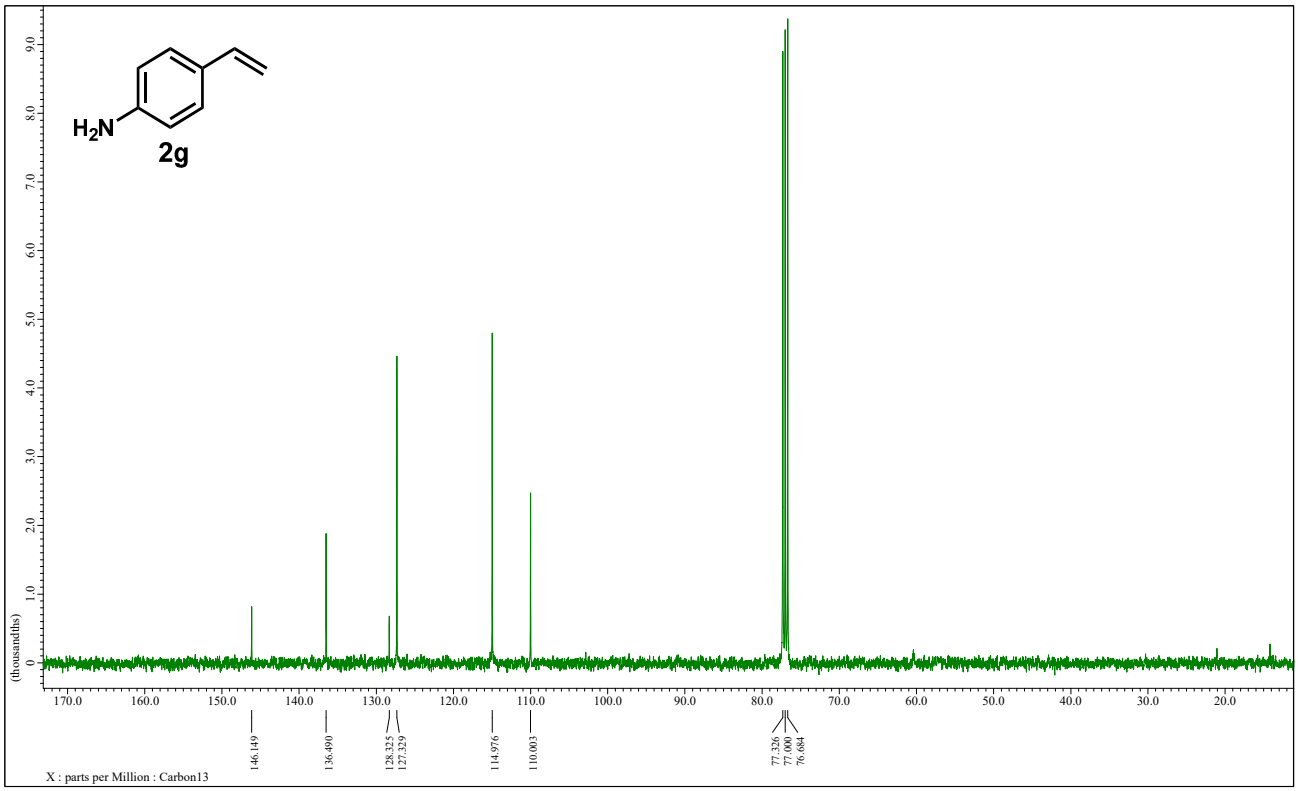
^{13}C NMR of 1-(4-vinylphenyl)ethenone (2f)



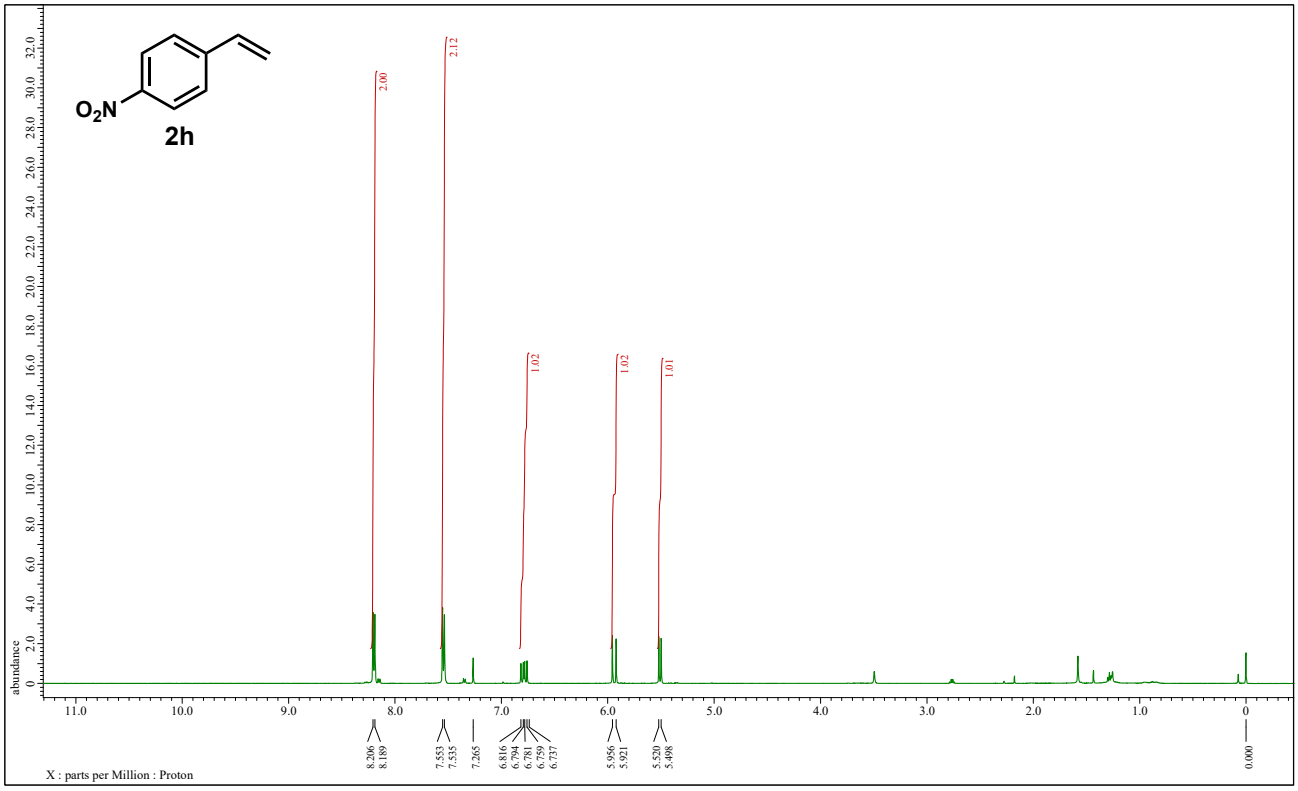
^{1}H NMR of 4-vinylaniline (2g)



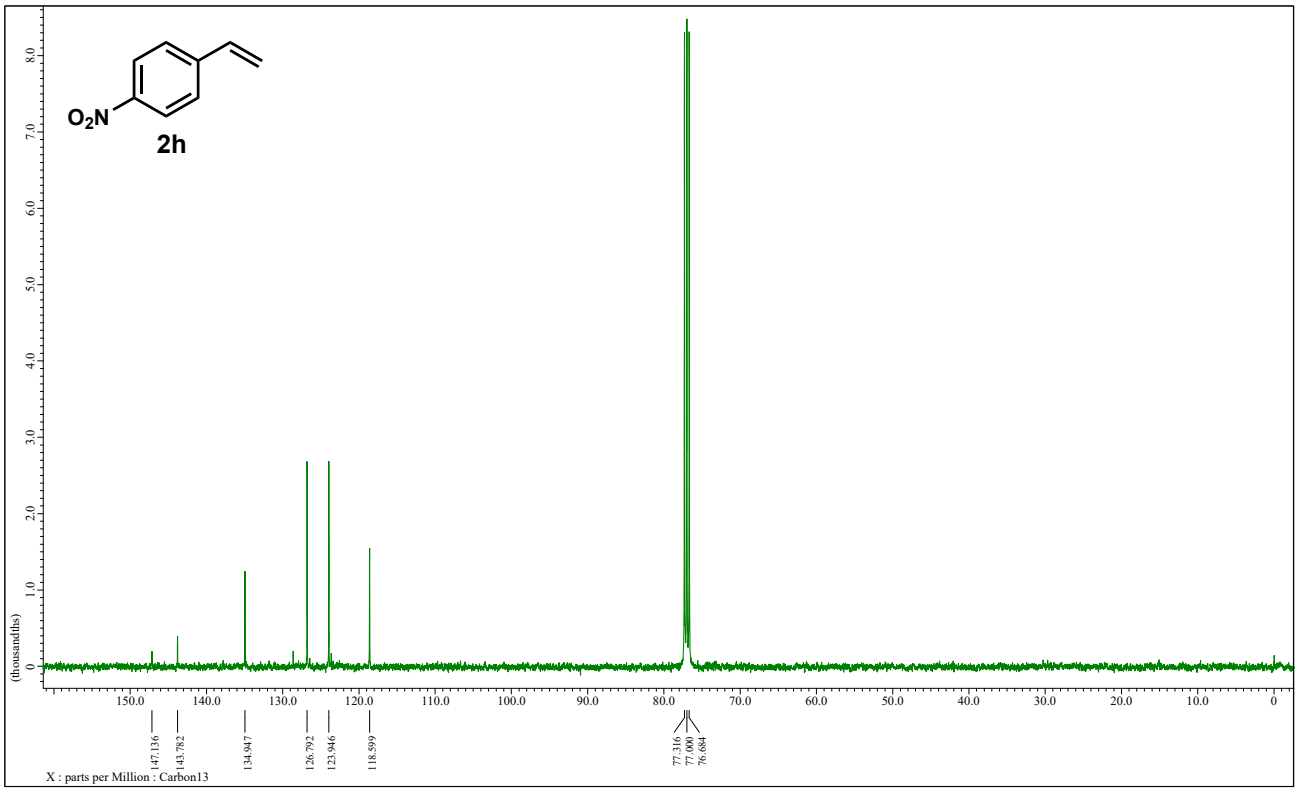
^{13}C NMR of 4-vinylaniline (2g)



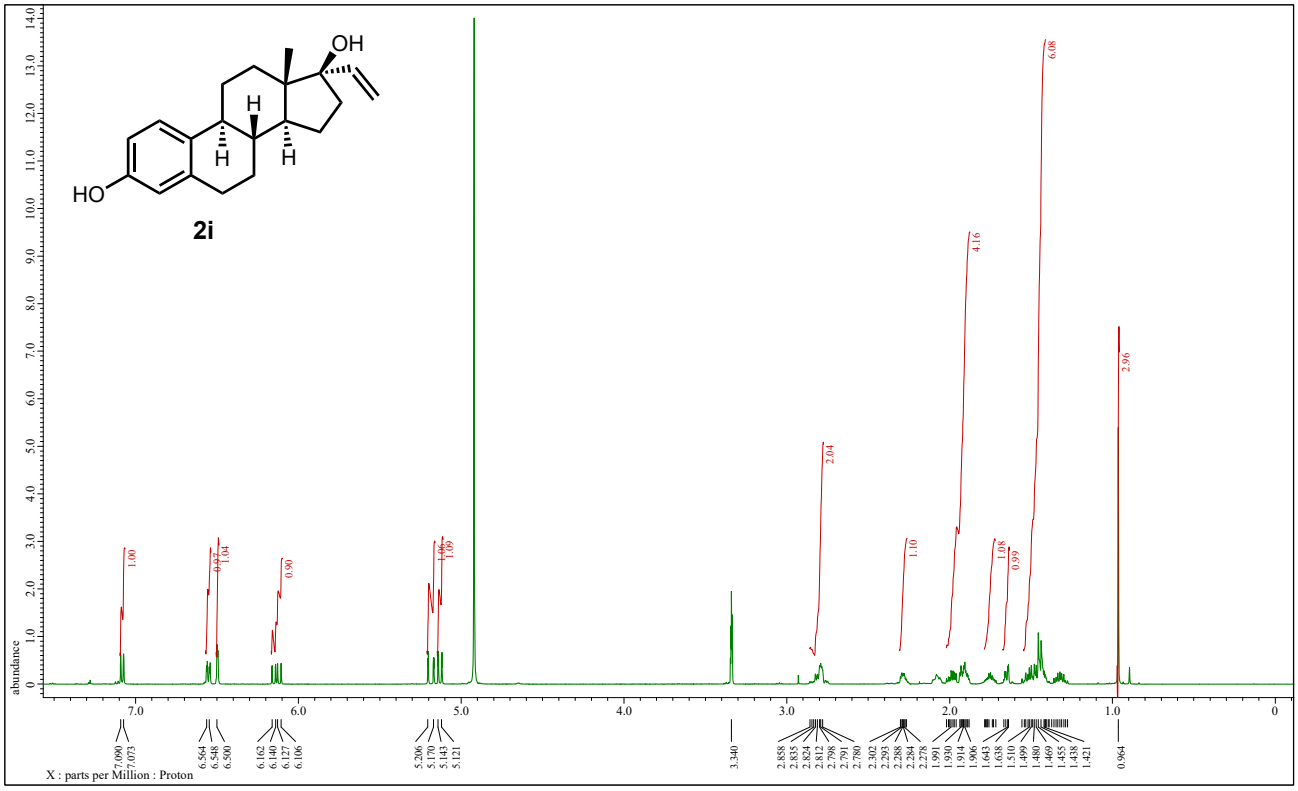
[1]H NMR of 1-nitoro-4-vinylbenzene (2h)



[13]C NMR of 1-nitoro-4-vinylbenzene (2h)



^{1}H NMR of 17α-vinyl-1,3,5(10)-estratriene-3,17β-diol (2i)



^{13}C NMR of 17α-vinyl-1,3,5(10)-estratriene-3,17β-diol (2i)