

Supporting Information for
Bottleable NiCl₂(dppe) as a catalyst for the Markovnikov-selective
hydroboration of styrenes with bis(pinacolato)diboron

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General procedures.

All manipulations involving air- and moisture-sensitive organometallic compounds were performed under an atmosphere of nitrogen dried with SICAPENT (Merck Co., Inc.) using standard Schlenk-line or high-vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. $\text{NiCl}_2(\text{PPh}_3)_2$,¹ $\text{NiCl}_2(\text{PCy}_3)_2$,¹ $\text{NiCl}_2(\text{dppe})$,¹ $\text{NiCl}_2(\text{dppp})$,¹ and nickel complexes **1**² were prepared according to literature procedures. Vinylarenes **2a**, **2b**, **2c**, **2d**, **2h**, **13**, and **15** were purchased from commercial suppliers and distilled before use. Vinylarenes **2e**, **2f**, **2g**, **2i**, **2j**, **2k**, **2l**, and **10** were prepared by Wittig reactions involving the corresponding aldehydes. All other reagents employed in this study were obtained from commercial suppliers and used without further purification.

Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C{¹H} NMR) spectra were recorded using BRUKER DRX-500 and JEOL ECX 500 spectrometers at ambient temperature. ¹H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard (TMS: 0.00 ppm). ¹³C{¹H} NMR chemical shifts are reported in ppm relative to the solvent resonance peak as the internal standard (CDCl₃: 77.0 ppm). Data are presented in the following form: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constants (Hz), and signal area integration in natural numbers.

Analytical thin-layer chromatography (TLC) was performed on alumina plates (Merck, 1.05554.0001), which were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at *ca.* 30–400 mmHg. Flash column chromatography was performed on Kanto silica gel 60N (spherical, neutral, 63–210 mesh). Gas chromatograms were recorded using a Shimadzu GC-17A gas chromatograph using an ULBON HR-1 capillary column (0.25 ID × 25 m, Shinwa Chemical Industries Ltd.). IR spectra were recorded using a JASCO FT/IR-460 Plus. Characteristic IR absorptions are reported in cm⁻¹. High-resolution mass spectra (HRMS) were recorded using the electron impact (EI) method with a JEOL JMS-700 Mass Spectrometer.

Experimental Procedures

Optimization of Reaction Conditions

General Procedure for the Hydroboration of 4-Methoxystyrene (**2a**) Catalysed by Nickel Catalysts (Table 1).

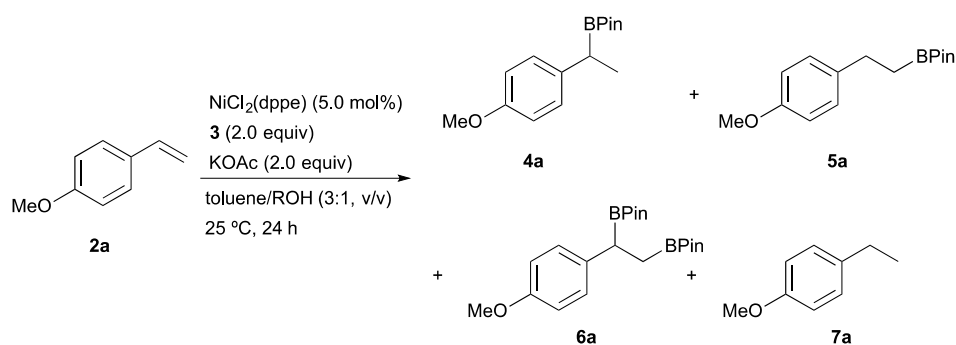
A Schlenk tube was charged with the nickel catalyst (5 mol%), KOAc (1.00 mmol), toluene (3.0 mL), and MeOH (1.0 mL). The mixture was stirred at room temperature for 5 min. Subsequently, **2a** (0.50 mmol) and **3** (1.00 mmol) were added sequentially, and stirring was continued for 24 h at 25 °C. The resulting mixture was filtered through a short pad of silica gel using EtOAc as the eluent. The yield of the product **7a** and the recovery of **2a** were determined by GC analysis of the crude product using undecane as the internal standard. The filtrate was concentrated under reduced pressure, and 1,1,2,2-tetrachloroethane was added as an internal standard. The yields of the products **4a**, **5a**, and **6a** were determined by ¹H NMR analysis.

General Procedure for the NiCl₂(dppe)-catalysed Hydroboration of **2**, **10**, **13**, and **15** (Table 2 and Scheme 1).

A Schlenk tube was charged with NiCl₂(dppe) (5–10 mol%), KOAc (2.0–3.0 equiv), toluene (3.0 mL), and MeOH (1.0 mL). The mixture was stirred at room temperature for 5 min. Then, **2**, **10**, **13**, or **15** (0.50–1.0 mmol) and **3** (2.0–3.0 equiv) and were added sequentially, and stirring was continued for 24–48 h at 25 °C. The resulting solution was filtered through a pad of silica gel using EtOAc as the eluent, and the resulting filtrates were concentrated. The residue was re-solvated in THF (6.0 mL), and a mixture of aqueous NaOH (1.8 mL, 3.0 M) and hydrogen peroxide (0.20 mL, 30% aqueous solution) was added at 0 °C. The mixture was stirred at room temperature for 0.5–1.5 h and subsequently extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel to afford the corresponding alcohol **8** or **14**.

Effect of the Alcohol on the NiCl₂(dppe)-catalysed Hydroboration of **2a**.

A Schlenk tube was charged with NiCl₂(dppe) (5 mol%), KOAc (1.00 mmol), toluene (3.0 mL), and alcohol (1.0 mL). The mixture was stirred at room temperature for 5 min. Subsequently, **2a** (0.50 mmol) and **3** (1.00 mmol) were added sequentially, and stirring was continued for 24 h at 25 °C. The resulting mixture was filtered through a short pad of silica gel using EtOAc as the eluent. The yield of the product **7a** and the recovery of **2a** were determined by GC analysis of the crude product using undecane as the internal standard. The filtrate was concentrated under reduced pressure, and 1,1,2,2-tetrachloroethane was added as an internal standard. The yields of the products **4a**, **5a**, and **6a** were determined by ¹H NMR analysis.



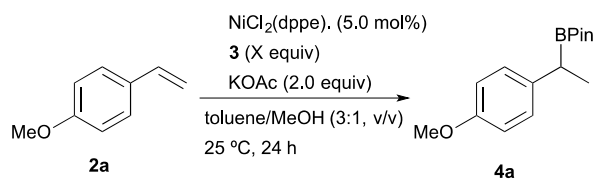
Entry	ROH	Yield of 4a (%) ^a	Yield of 5a (%) ^a	Yield of 6a (%) ^a	Yield of 7a (%) ^b	Recovery of 2a (%) ^b
1	MeOH	97	0	0	0	0
2	EtOH	48	5	0	0	46
3	<i>i</i> -PrOH	15	0	0	0	84
4	<i>t</i> -BuOH	0	0	0	0	97

^a Determined by NMR analysis using an internal standard.

^b Determined by GC analysis using an internal standard.

Procedure for the NiCl₂(dppe)-Catalyzed Hydroboration of **2a** using Different Amounts of **3**.

A Schlenk tube was charged with NiCl₂(dppe) (5 mol%), KOAc (1.00 mmol), toluene (3.0 mL), and MeOH (1.0 mL). The mixture was stirred at room temperature for 5 min. Subsequently, **2a** (0.50 mmol) and **3** (0.1–2.0 equiv, 0.05–1.00 mmol) were added sequentially, and stirring was continued for 24 h at 25 °C. The resulting mixture was filtered through a short pad of silica gel using EtOAc as the eluent. The recovery of **2a** was determined by GC analysis of the crude product using undecane as the internal standard. The filtrate was concentrated under reduced pressure, and 1,1,2,2-tetrachloroethane was added as an internal standard. The yield of the product **4a** was determined by ¹H NMR analysis.

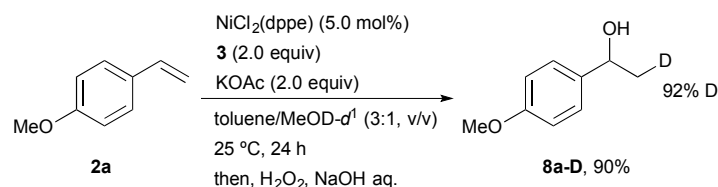


Entry	3 (X equiv)	Yield of 4a (%) ^a	Recovery of 2a (%) ^b
1	0.1	n.d	>98
2	0.2	n.d	>98
3	0.3	10	90
4	0.4	15	79
5	0.5	29	69
6	0.8	35	59
7	1.0	54	42
8	1.5	76	19
9	2.0	97	0

^a Determined by NMR analysis using an internal standard.

^b Determined by GC analysis using an internal standard.

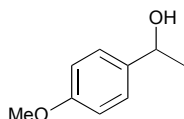
Isotope-labelling Experiment (Scheme 2)



A Schlenk tube was charged with $\text{NiCl}_2(\text{dppe})$ (13.2 mg, 0.025 mmol, 5 mol%), KOAc (98.1 mg, 1.00 mmol), toluene (3.0 mL), and CH_3OD (1.0 mL). The mixture was stirred at room temperature for 5 min. Subsequently, **2a** (58.6 mg, 0.50 mmol) and **3** (254.0 mg, 1.00 mmol) were added sequentially and stirring was continued for 24 h at 25 °C. The resulting solution was filtered through a pad of silica gel using EtOAc as the eluent and concentrated. To a solution of the residue in THF (4.0 mL), hydrogen peroxide (0.20 mL, 30% aqueous solution) and an aqueous solution of NaOH (1.8 mL, 3.0 M) were added at 0 °C. The mixture was stirred at room temperature for 1 h and subsequently extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel to afford the corresponding alcohol **8a-D** (70.3 mg, 0.46 mmol, 90%). The amount of deuterium incorporated into the alcohol **8a-D** was measured using ^1H NMR analysis. ^1H NMR (500 MHz, CDCl_3) δ 1.46–1.49 (m, 2H), 1.72 (br, 1H), 4.86 (t, $J = 6.0$ Hz, 1H), 6.87–6.90 (m, 2H), 7.29–7.32 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 24.7 (t, $J = 19.1$ Hz), 55.3, 69.9, 113.8, 126.6, 138.0, 159.0 ppm. IR (Diamond-ATR, neat) 3370, 2928, 2850, 1612, 1510, 1461, 1299, 1241, 1174, 1064, 1032, 829, 545 cm^{-1} , HRMS (EI^+): calcd for $\text{C}_9\text{H}_{11}\text{DO}_2$ [$\text{M}]^+$: 153.0900. found: 153.0901. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached.

Characterization Data for the Isolated Products

Synthesis of 1-(4-Methoxyphenyl)ethanol (**8a**)



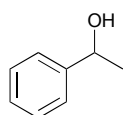
Compound **8a** was prepared according to the general procedure using **2a** (68.4 mg, 0.51 mmol), **3** (254.0 mg, 1.00 mmol), KOAc (98.1 mg, 1.00 mmol), and NiCl₂(dppe) (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8a** was obtained in 85% yield (65.9 mg, 0.433 mmol) as a colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.48 (d, *J* = 6.5 Hz, 3H), 1.78 (br, 1H), 3.81 (s, 3H), 4.86 (q, *J* = 6.5 Hz, 1H), 6.87–6.90 (m, 2H), 7.29–7.32 (m, 2H) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 25.0, 55.3, 70.0, 113.8, 126.6, 138.0, 159.0 ppm. ¹H and ¹³C{¹H} NMR spectra have been attached. The product was characterized by comparison with previously reported ¹H and ¹³C{¹H} NMR data.³

Synthesis of 1-Phenylethanol (**8b**)



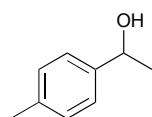
Compound **8b** was prepared according to the general procedure using **2b** (53.5 mg, 0.51 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.3 mg, 1.00 mmol), and NiCl₂(dppe) (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8b** was obtained in 84% yield (52.8 mg, 0.43 mmol) as a colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.51 (d, *J* = 6.5 Hz, 3H), 1.81 (br, 1H), 4.91 (q, *J* = 6.5 Hz, 1H), 7.26–7.29 (m, 2H), 7.34–7.39 (m, 2H) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 25.1, 70.4, 125.3, 127.4, 128.5, 145.8 ppm. ¹H and ¹³C{¹H} NMR spectra have been attached. The product was characterized by comparison with previously reported ¹H and ¹³C{¹H} NMR data.³

Synthesis of 1-(*p*-Tolyl)ethanol (**8c**)



Compound **8c** was prepared according to the general procedure using **2c** (59.6 mg, 0.50 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.1 mg, 1.00 mmol), and NiCl₂(dppe) (13.2 mg, 0.025 mmol, 5 mol%).

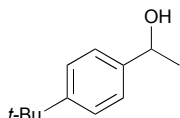
Reaction conditions: 24 h, 25 °C.

The product **8c** was obtained in 89% yield (61.0 mg, 0.45 mmol) as a colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.48 (d, *J* = 6.5 Hz, 3H), 1.77 (br, 1H), 4.87 (q, *J* = 6.5 Hz, 1H), 7.15–7.17 (m, 2H), 7.26–7.28 (m, 2H) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 21.0, 25.0, 70.2, 125.3,

129.1, 137.1, 142.8 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.³

Synthesis of 1-(4-*t*-Butylphenyl)ethanol (**8d**)



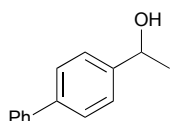
Compound **8d** was prepared according to the general procedure using **2d** (80.1 mg, 0.50 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.1 mg, 1.00 mmol), and $\text{NiCl}_2(\text{dppe})$ (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8d** was obtained in 86% yield (77.0 mg, 0.43 mmol) as a colourless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.32 (s, 9H), 1.49 (d, $J = 6.0$ Hz, 3H), 1.87 (br, 1H), 4.86 (q, $J = 6.0$ Hz, 1H), 7.30–7.31 (m, 2H), 7.37–7.38 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 24.9, 31.3, 34.5, 70.2, 125.1, 125.4, 142.8, 150.4 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.⁴

Synthesis of 1-(4-Biphenyl)ethanol (**8e**)



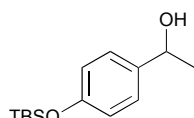
Compound **8e** was prepared according to the general procedure using **2e** (90.1 mg, 0.50 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.2 mg, 1.00 mmol), and $\text{NiCl}_2(\text{dppe})$ (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8e** was obtained in 73% yield (72.1 mg, 0.36 mmol) as a white solid.

^1H NMR (500 MHz, CDCl_3) δ 1.53 (d, $J = 6.5$ Hz, 3H), 1.81 (br, 1H), 4.94–4.97 (m, 1H), 7.33–7.36 (m, 1H), 7.42–7.46 (m, 4H), 7.58–7.60 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 25.2, 70.2, 125.8, 127.1, 127.3, 128.9, 140.5, 140.9, 144.8 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.⁵

Synthesis of 1-[(4-*tert*-Butyldimethylsilyloxy)phenyl]ethanol (**8f**)



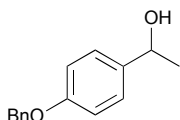
Compound **8f** was prepared according to the general procedure using **2f** (118.3 mg, 0.50 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.2 mg, 1.00 mmol), and $\text{NiCl}_2(\text{dppe})$ (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8f** was obtained in 70% yield (89.9 mg, 0.36 mmol) as a colourless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.19 (s, 6H), 0.98 (s, 9H), 1.48 (d, $J = 6.5$ Hz, 3H), 1.71 (br, 1H), 4.85 (q, $J = 6.5$ Hz, 1H), 6.80–6.82 (m, 2H), 7.22–7.25 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ -4.4, 18.2, 25.0, 25.7, 70.1, 120.0, 126.6, 138.5, 155.0 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.⁶

Synthesis of 1-[4-(Benzyloxy)phenyl]ethanol (**8g**)



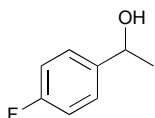
Compound **8g** was prepared according to the general procedure using **2g** (105.2 mg, 0.50 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.1 mg, 1.00 mmol), and $\text{NiCl}_2(\text{dppe})$ (13.3 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8g** was obtained in 53% yield (60.2 mg, 0.26 mmol) as a white solid.

^1H NMR (500 MHz, CDCl_3) δ 1.48 (d, $J = 6.5$ Hz, 3H), 1.69 (br, 1H), 4.86 (dq, $J = 3.5$ and 6.5 Hz, 1H), 5.07 (s, 2H), 6.95–6.98 (m, 2H), 7.29–7.34 (m, 3H) 7.37–7.44 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 25.0, 69.9, 70.0, 114.8, 126.7, 127.4, 127.9, 128.6, 137.0, 138.2, 158.2 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.⁶

Synthesis of 1-(4-Fluorophenyl)ethanol (**8h**)



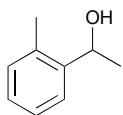
Compound **8h** was prepared according to the general procedure using **2h** (123.1 mg, 1.01 mmol), **3** (507.8 mg, 2.00 mmol), KOAc (196.3 mg, 2.00 mmol), and $\text{NiCl}_2(\text{dppe})$ 52.8 mg, 0.10 mmol, 10 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8h** was obtained in 41% yield (57.8 mg, 0.41 mmol) as a colourless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.49 (d, $J = 6.5$ Hz, 3H), 1.78 (br, 1H), 4.90 (qd, $J = 3.5$ and 6.5 Hz, 1H), 7.01–7.06 (m, 2H), 7.33–7.37 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 25.2, 69.7, 115.2 ($J = 21.4$ Hz), 127.0 ($J = 8.4$ Hz), 141.5 ($J = 2.4$ Hz), 162.1 ($J = 243.3$ Hz) ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.³

Synthesis of 1-(*o*-Tolyl)ethanol (**8i**)



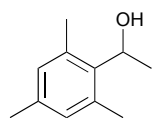
Compound **8i** was prepared according to the general procedure using **2i** (58.8 mg, 0.50 mmol), **3** (253.8 mg, 1.00 mmol), KOAc (98.3 mg, 1.00 mmol), and NiCl₂(dppe) (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8i** was obtained in 70% yield (47.5 mg, 0.35 mmol) as a colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.47 (d, *J* = 6.5 Hz, 3H), 1.70 (br, 1H), 2.35 (s, 3H), 5.14 (dq, *J* = 3.0 and 6.5 Hz, 1H), 7.13–7.19 (m, 2H), 7.22–7.26 (m, 1H), 7.51–7.52 (m, 1H) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 18.9, 23.9, 66.8, 124.4, 126.4, 127.2, 130.4, 134.2, 143.8 ppm. ¹H and ¹³C{¹H} NMR spectra have been attached. The product was characterized by comparison with previously reported ¹H and ¹³C{¹H} NMR data.³

Synthesis of 1-Mesitylethan-1-ol (**8j**)



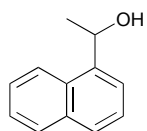
Compound **8j** was prepared according to the general procedure using **2j** (74.0 mg, 0.51 mmol), **3** (253.8 mg, 1.00 mmol), KOAc (98.3 mg, 1.00 mmol), and NiCl₂(dppe) (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8j** was obtained in 63% yield (52.2 mg, 0.32 mmol) as a colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.53 (d, *J* = 6.5 Hz, 3H), 2.10 (br, 1H), 2.25 (s, 3H), 2.41 (s, 6H), 5.37 (q, *J* = 6.5 Hz, 1H), 6.82 (s, 2H) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 20.5, 20.7, 21.6, 67.5, 130.1, 135.6, 136.4, 137.6 ppm. ¹H and ¹³C{¹H} NMR spectra have been attached. The product was characterized by comparison with previously reported ¹H and ¹³C{¹H} NMR data.⁷

Synthesis of 1-(1-Naphthyl)ethanol (**8k**)



Compound **8k** was prepared according to the general procedure using **2k** (77.6 mg, 0.50 mmol), **3** (254.1 mg, 1.00 mmol), KOAc (98.7 mg, 1.01 mmol), and NiCl₂(dppe) (13.4 mg, 0.025 mmol, 5 mol%).

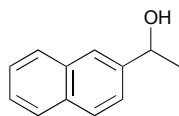
Reaction conditions: 24 h, 25 °C.

The product **8k** was obtained in 83% yield (71.4 mg, 0.41 mmol) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 1.68 (d, *J* = 6.5 Hz, 3H), 1.89 (br, 1H), 5.70 (dq, *J* = 3.5 and 6.5 Hz, 1H), 7.47–7.55 (m, 3H), 7.68–7.70 (m, 1H), 7.78–7.80 (m, 1H), 7.87–7.89 (m, 1H), 8.13–8.14 (m,

1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 24.3, 67.1, 122.0, 123.1, 125.52, 125.54, 126.0, 127.9, 128.9, 130.3, 133.8, 141.3 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.⁸

Synthesis of 1-(2-Naphthyl)ethanol (**8I**)



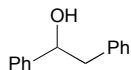
Compound **8I** was prepared according to the general procedure using **2I** (77.0 mg, 0.50 mmol), **3** (253.9 mg, 1.00 mmol), KOAc (98.1 mg, 1.00 mmol), and $\text{NiCl}_2(\text{dppe})$ (13.2 mg, 0.025 mmol, 5 mol%).

Reaction conditions: 24 h, 25 °C.

The product **8I** was obtained in 88% yield (75.3 mg, 0.44 mmol) as a white solid.

^1H NMR (500 MHz, CDCl_3) δ 1.55 (d, $J = 6.5$ Hz, 3H), 2.11 (br, 1H), 5.02 (q, $J = 6.5$ Hz, 1H), 7.43–7.48 (m, 3H), 7.79–7.82 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 25.1, 70.5, 123.75, 123.78, 125.8, 126.1, 127.6, 127.9, 128.3, 132.9, 133.3, 143.1 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.³

Synthesis of 1,2-Diphenylethan-1-ol (**14**)



Compound **14** was prepared according to the general procedure using **13** (90.5 mg, 0.50 mmol), **3** (381.1 mg, 1.50 mmol), KOAc (147.3 mg, 1.50 mmol), and $\text{NiCl}_2(\text{dppe})$ (26.4 mg, 0.05 mmol, 10 mol%).

Reaction conditions: 48 h, 25 °C.

The product **14** was obtained in 85% yield (84.2 mg, 0.42 mmol) as a white solid.

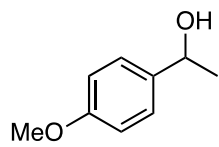
^1H NMR (500 MHz, CDCl_3) δ 1.93 (d, $J = 3.0$ Hz, 1H), 2.99 (dd, $J = 8.5$ and 13.5 Hz, 1H), 3.05 (dd, $J = 4.5$ and 13.5 Hz, 1H), 4.89–4.93 (m, 1H), 7.20–7.38 (m, 10H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 46.1, 125.9, 126.6, 127.6, 128.4, 128.5, 129.5, 138.0, 143.8 ppm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data.³

Compound **14** was also prepared according to the general procedure using **15** (90.8 mg, 0.50 mmol), **3** (381.3 mg, 1.50 mmol), KOAc (147.2 mg, 1.50 mmol), and $\text{NiCl}_2(\text{dppe})$ (26.5 mg, 0.050 mmol, 10 mol%).

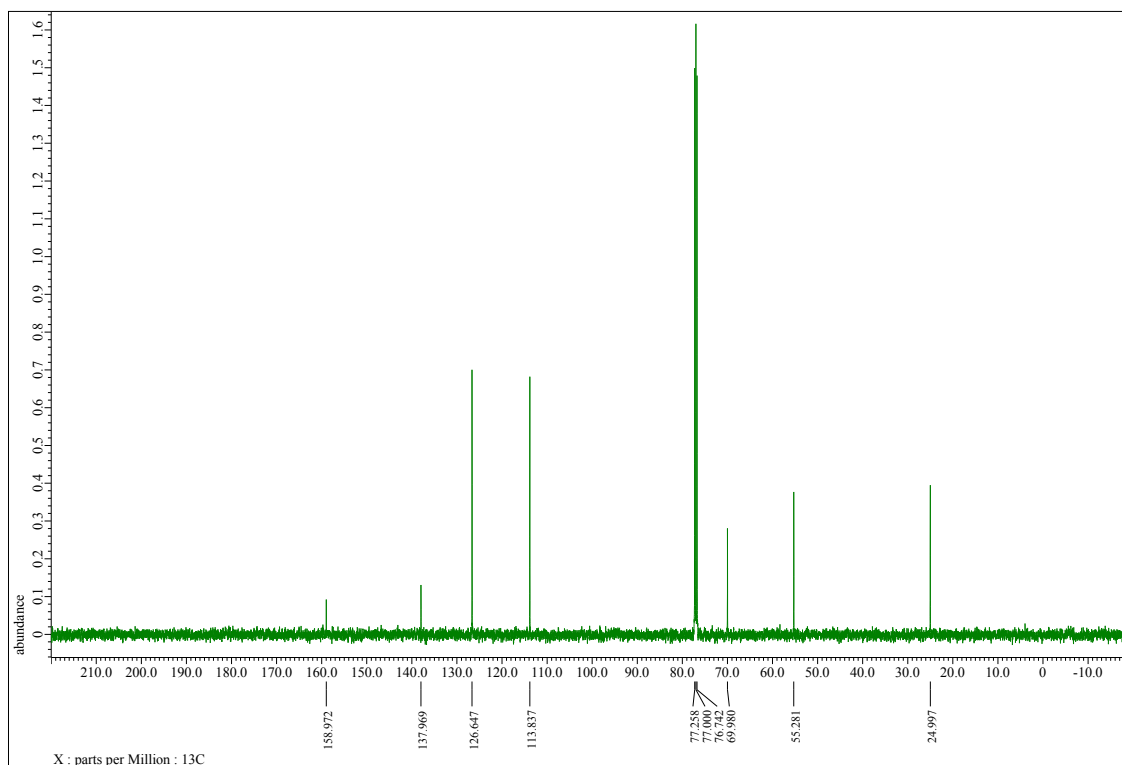
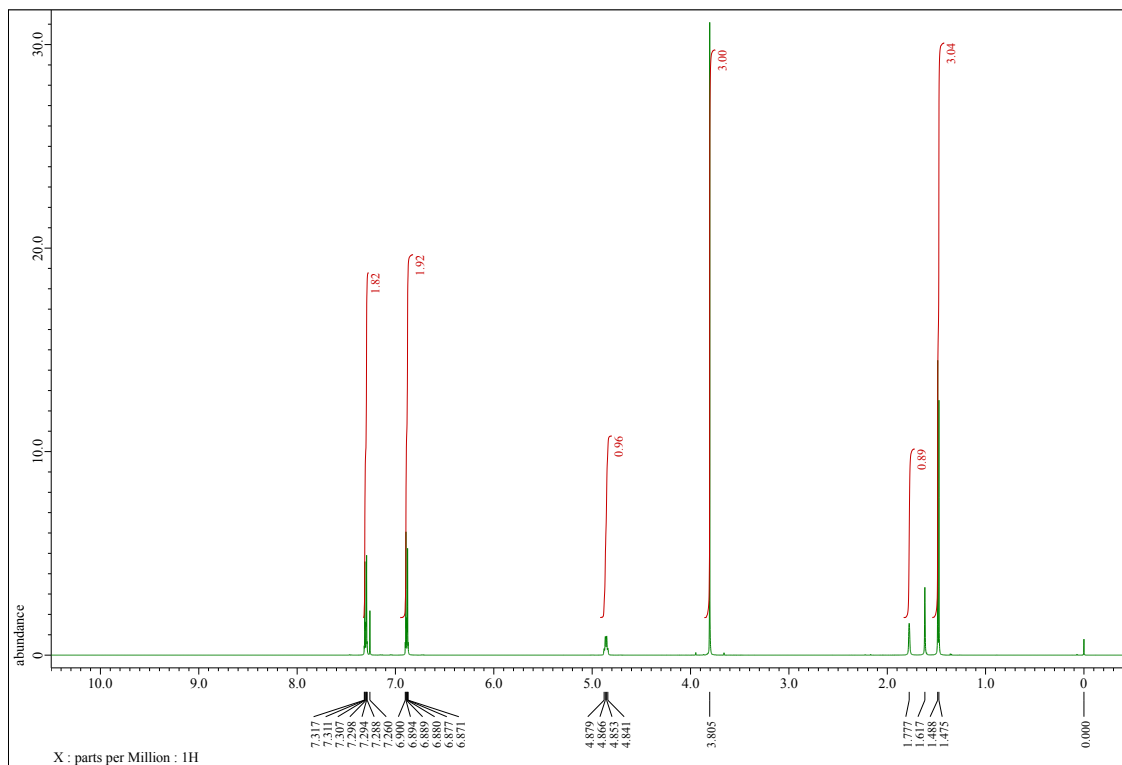
Reaction conditions: 48 h, 25 °C.

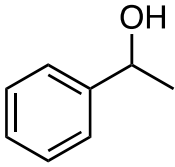
The product **14** was obtained in 81% yield (81.3 mg, 0.41 mmol) as a white solid.

^1H NMR and ^{13}C NMR Spectra

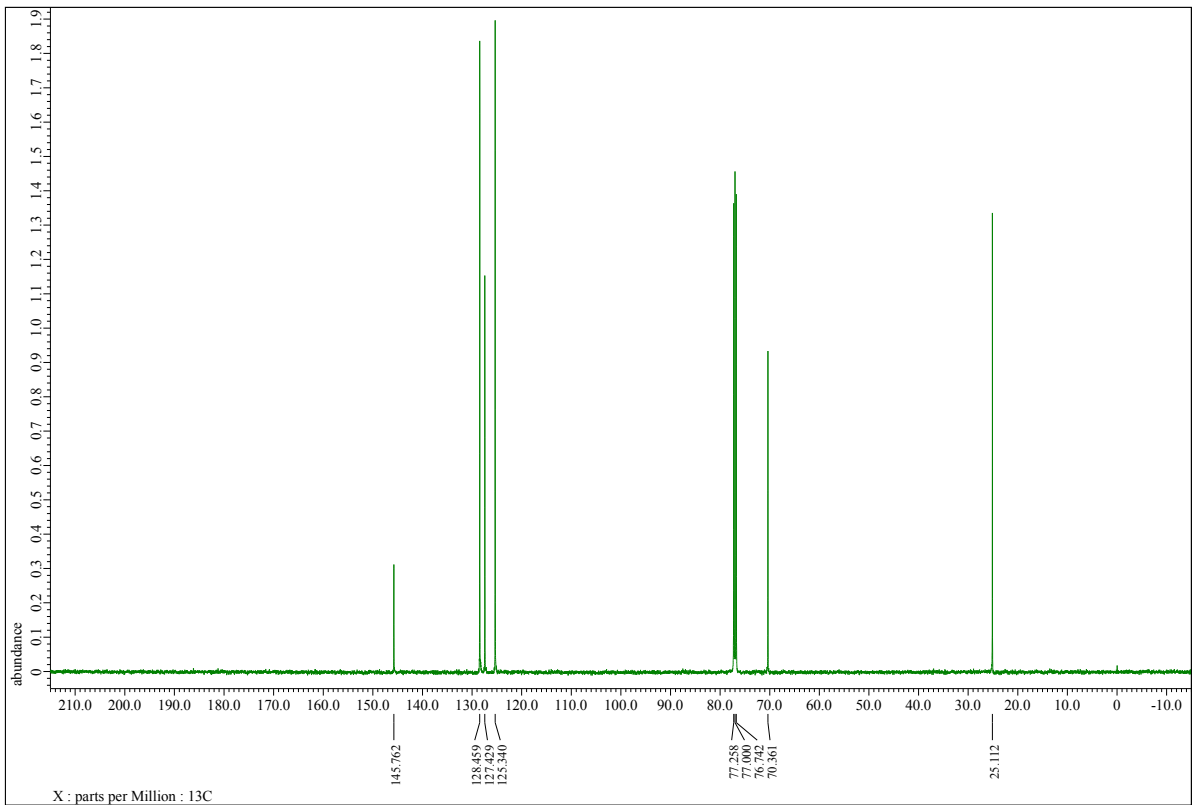
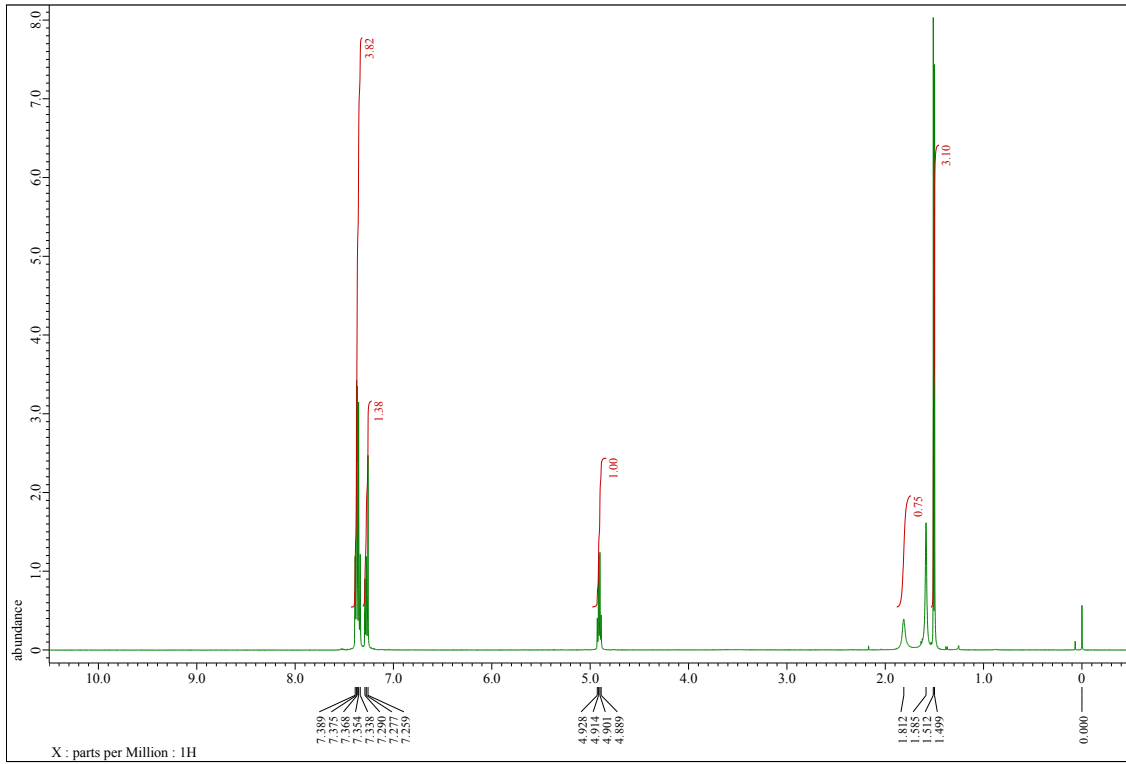


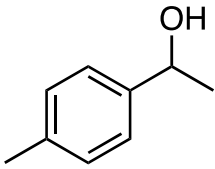
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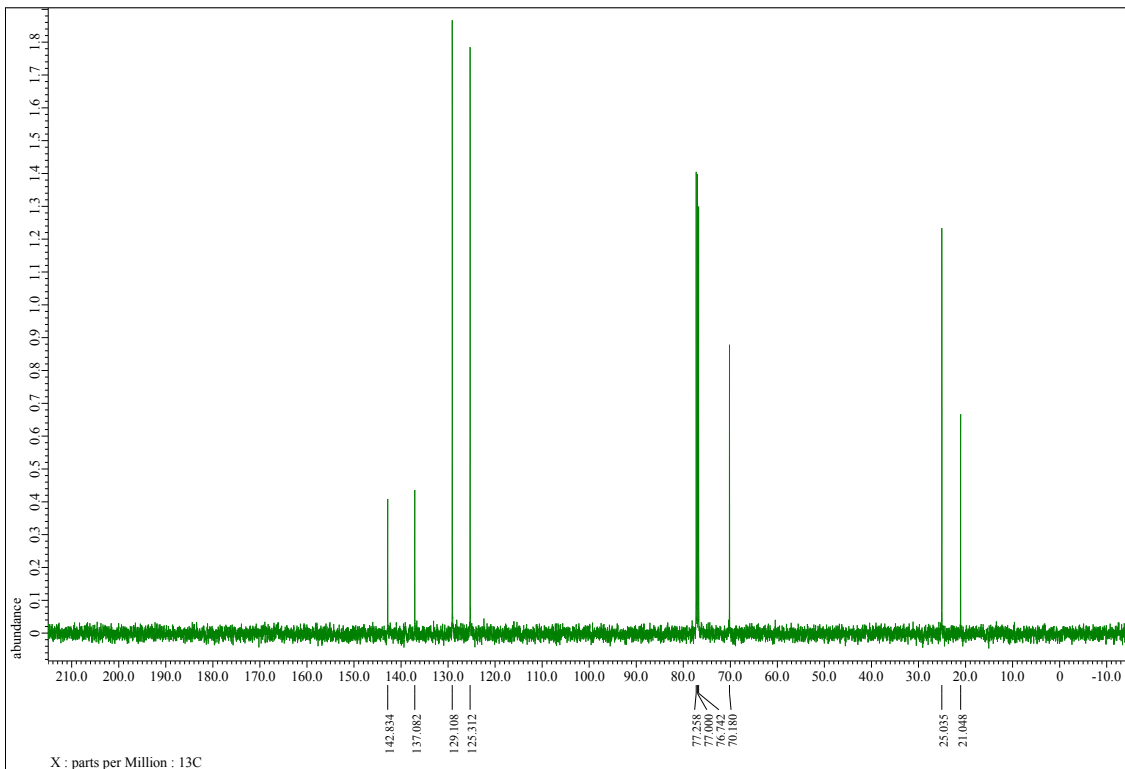
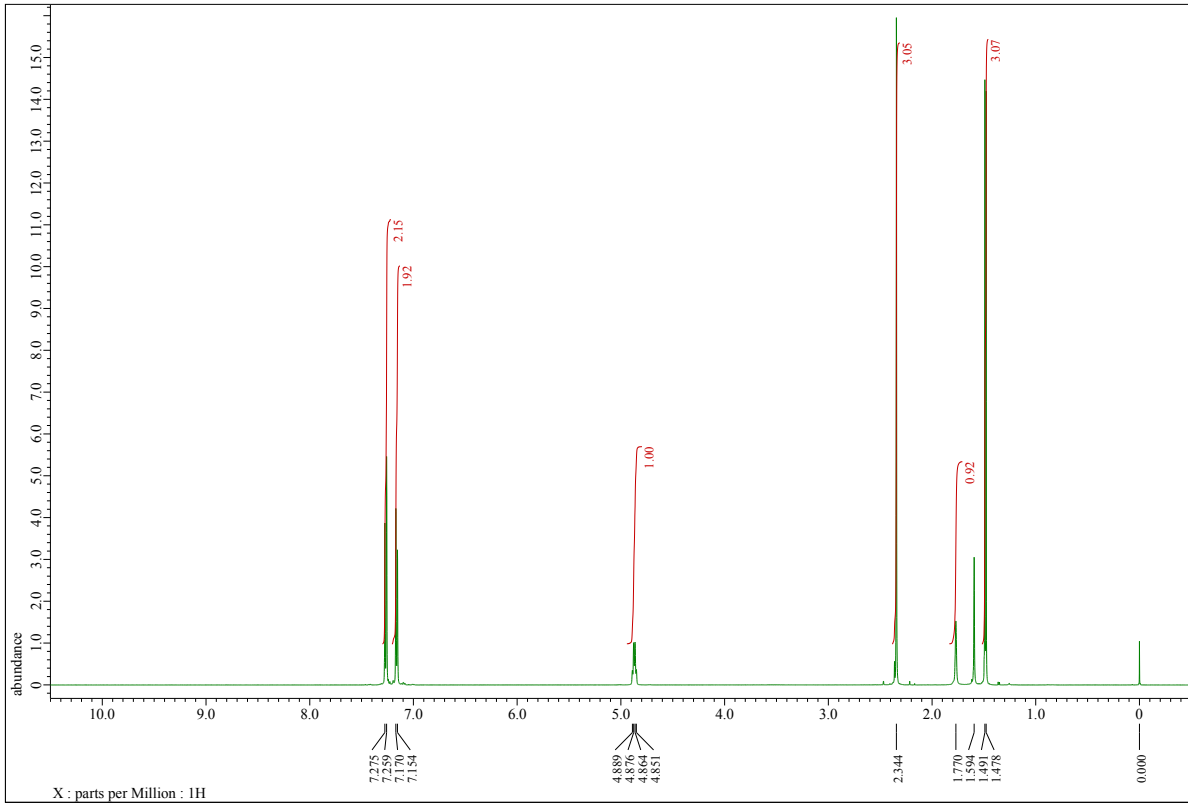


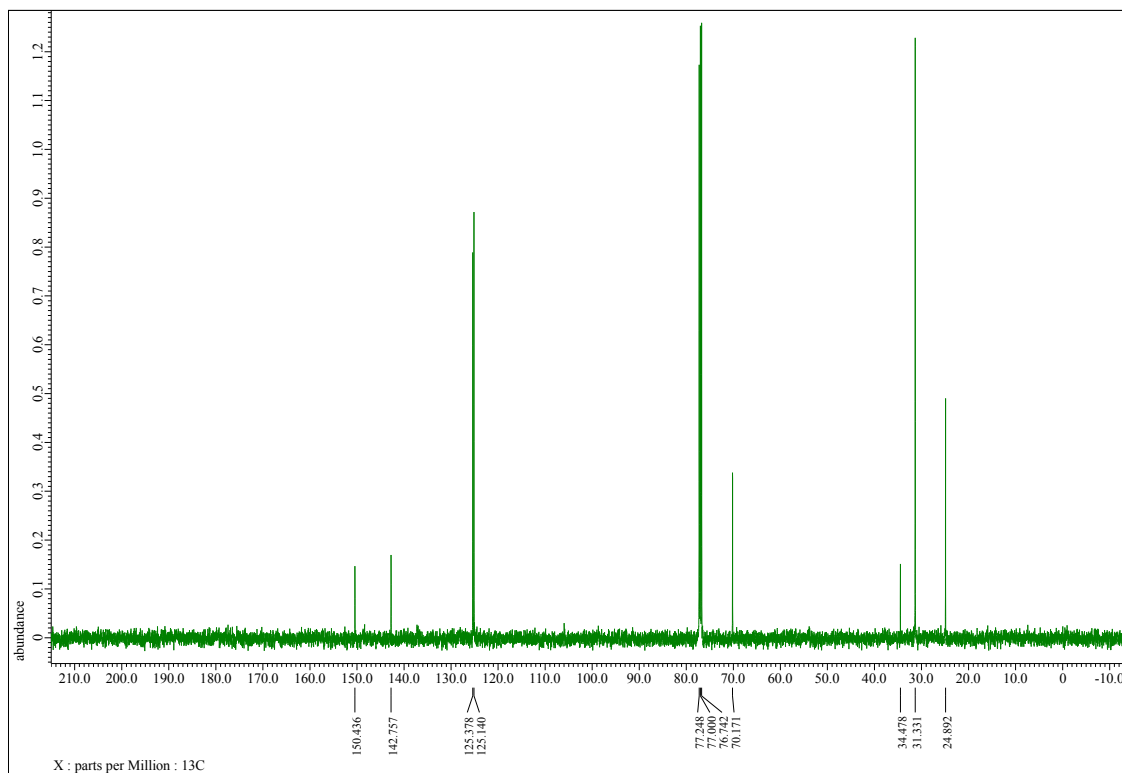
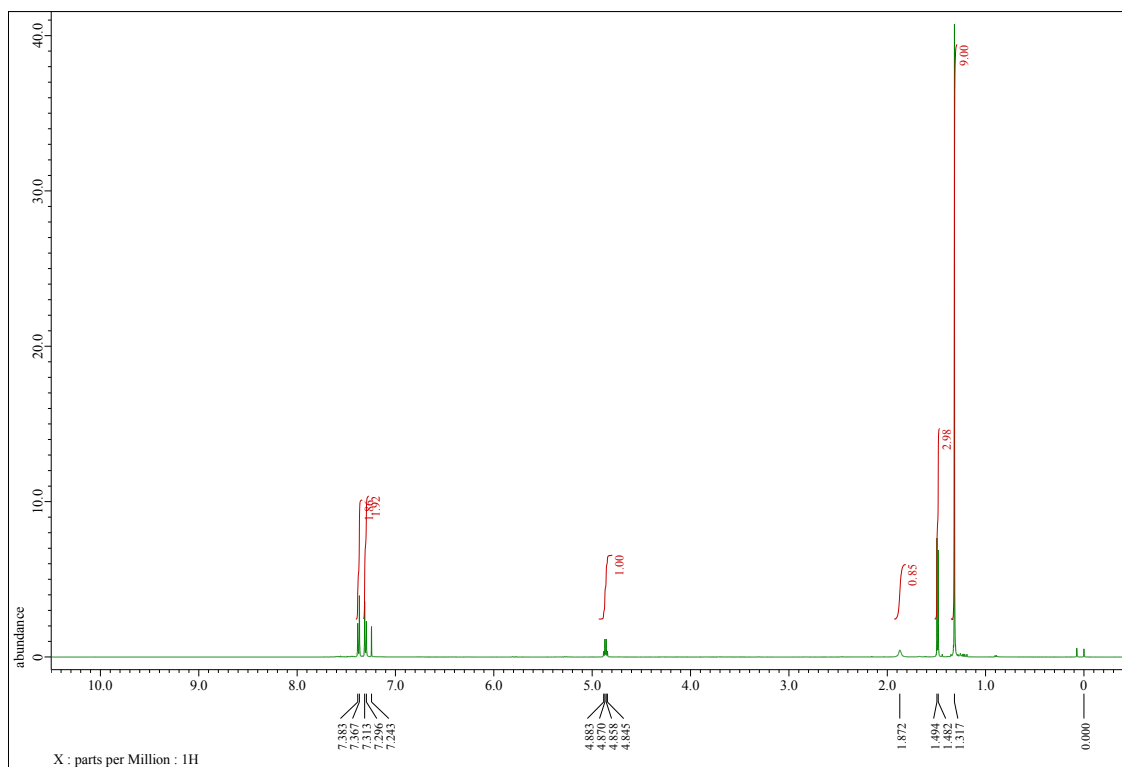
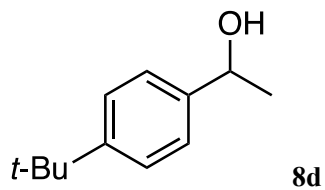
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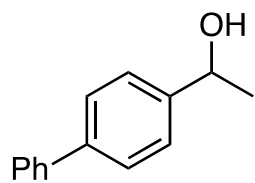




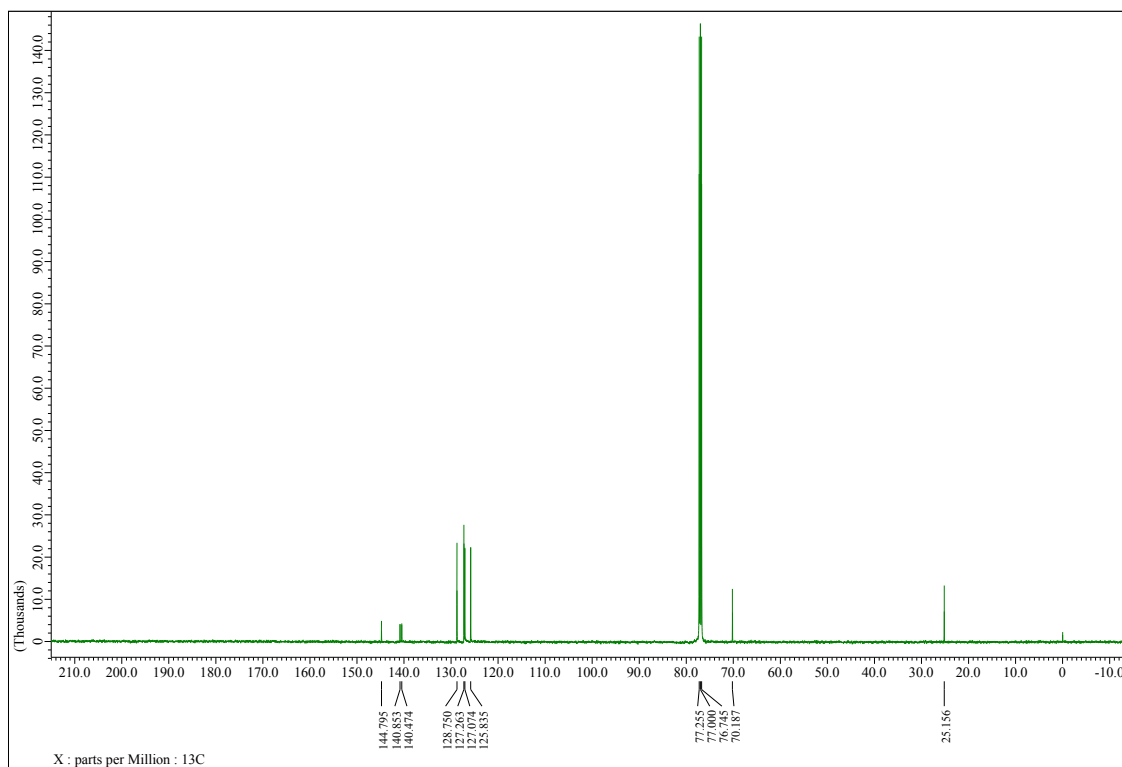
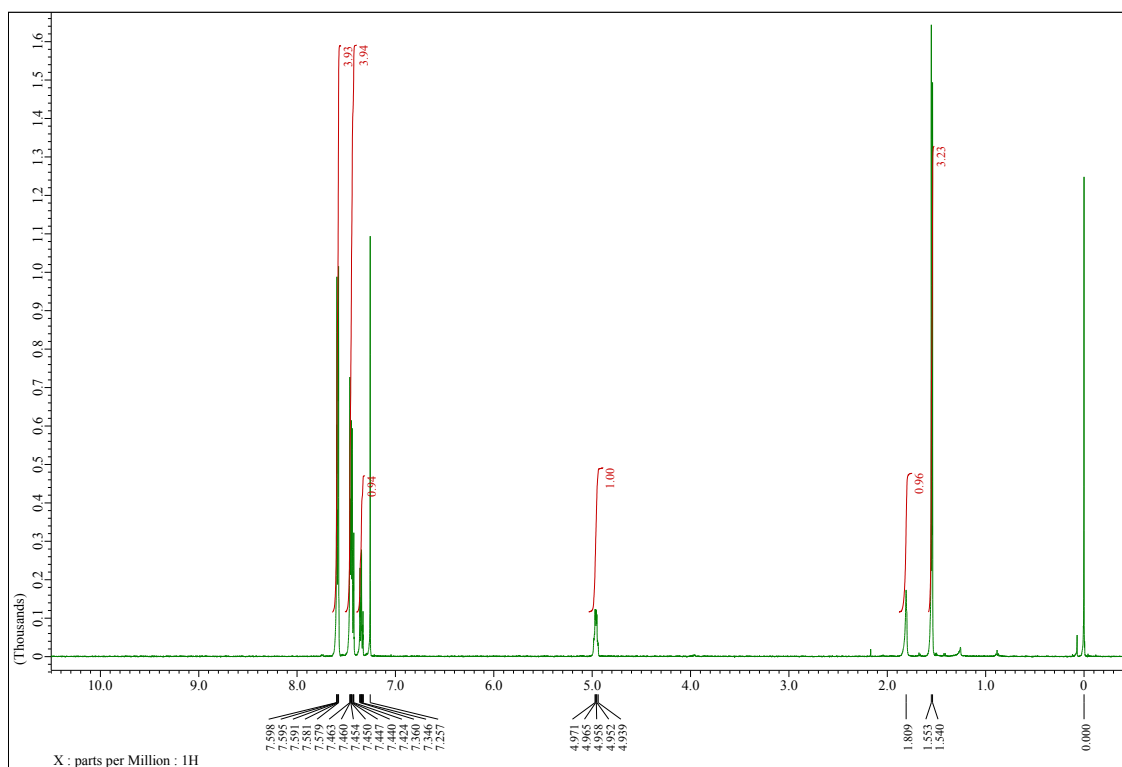
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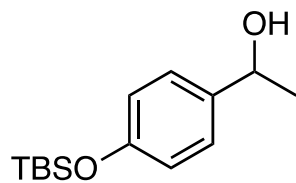




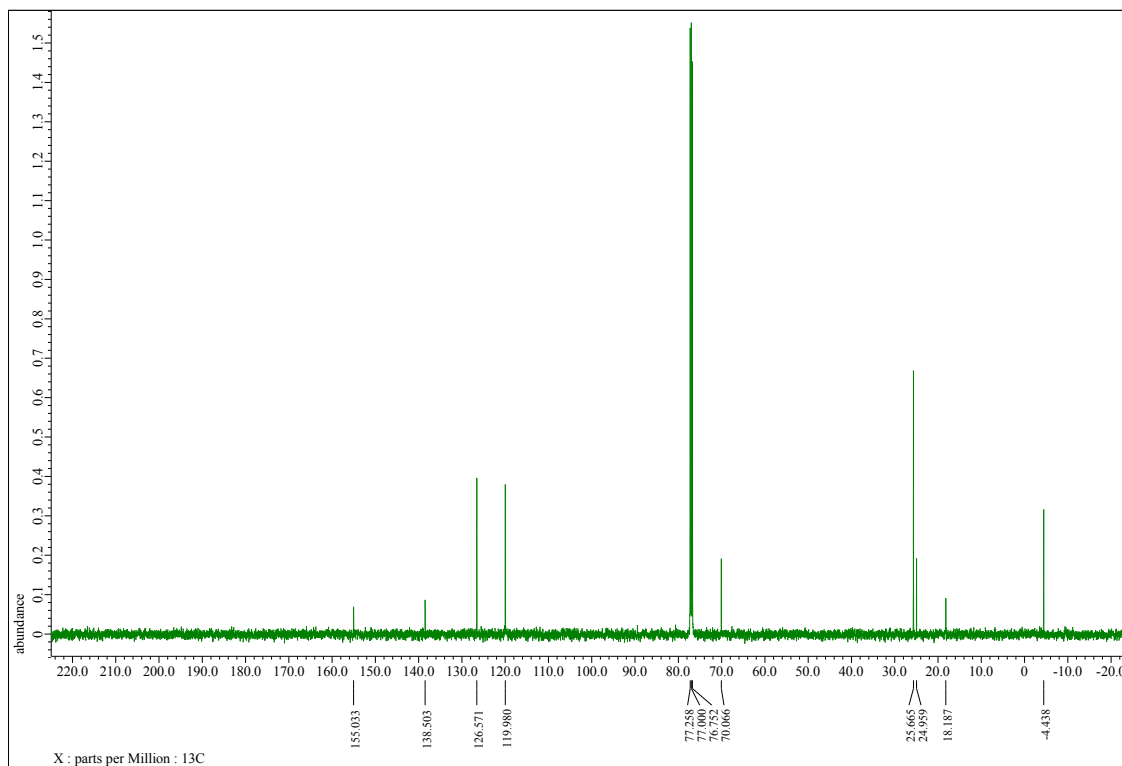
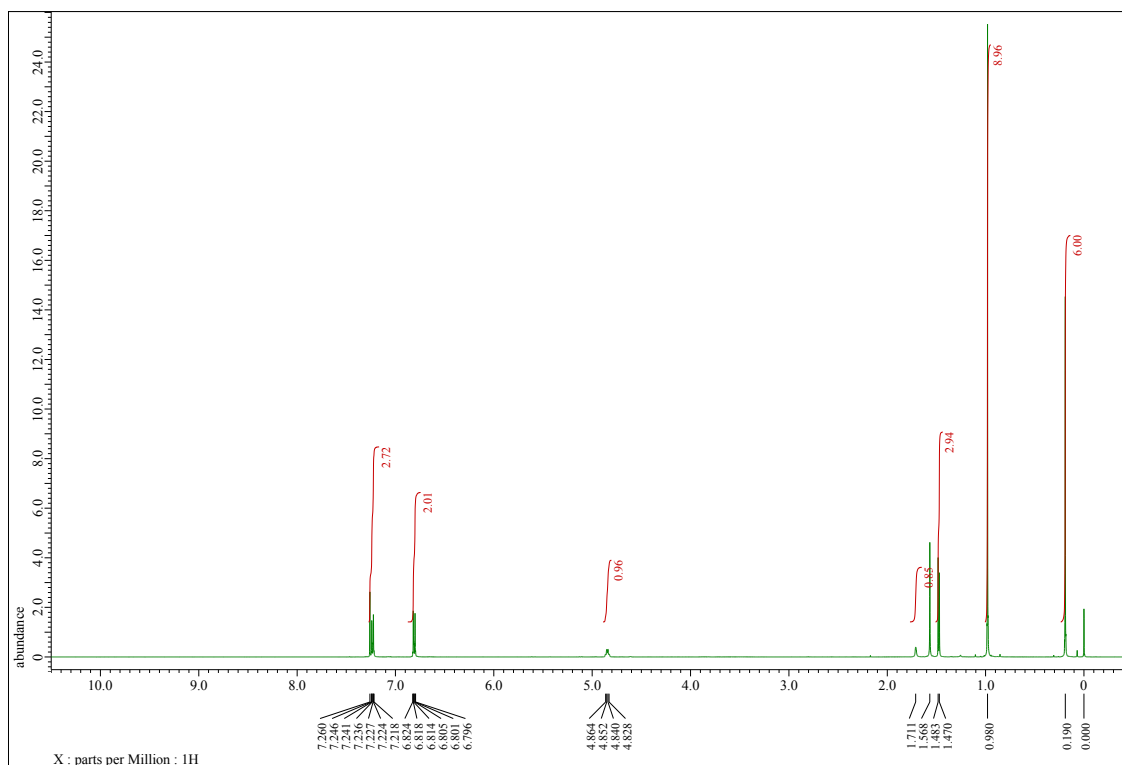


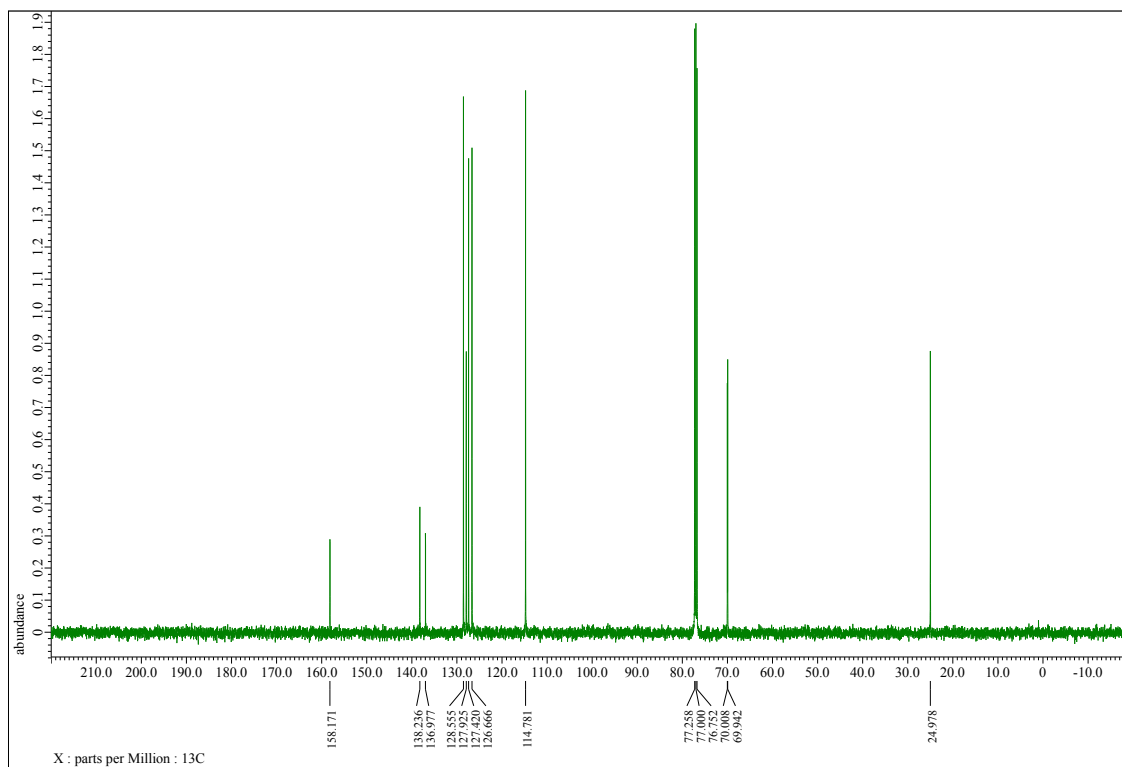
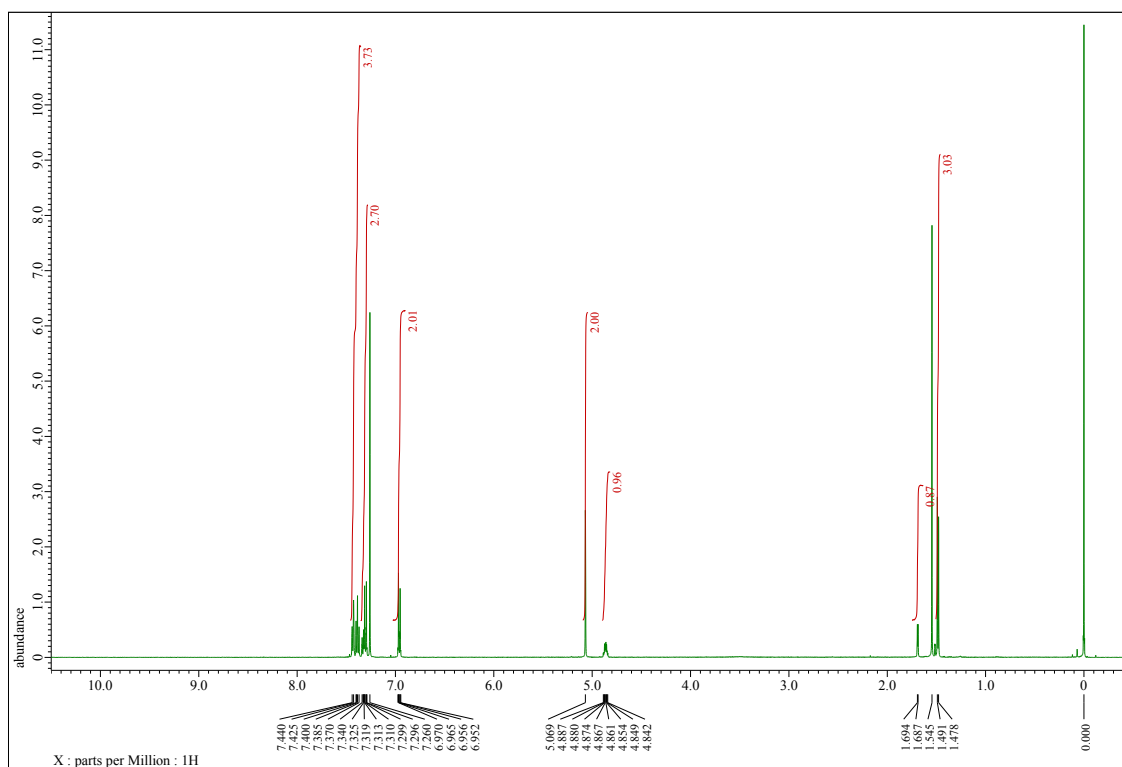
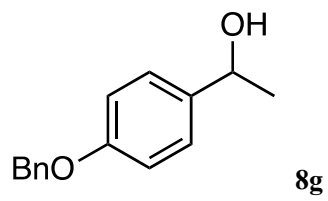
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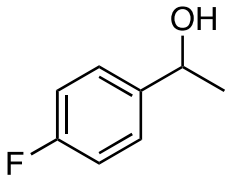




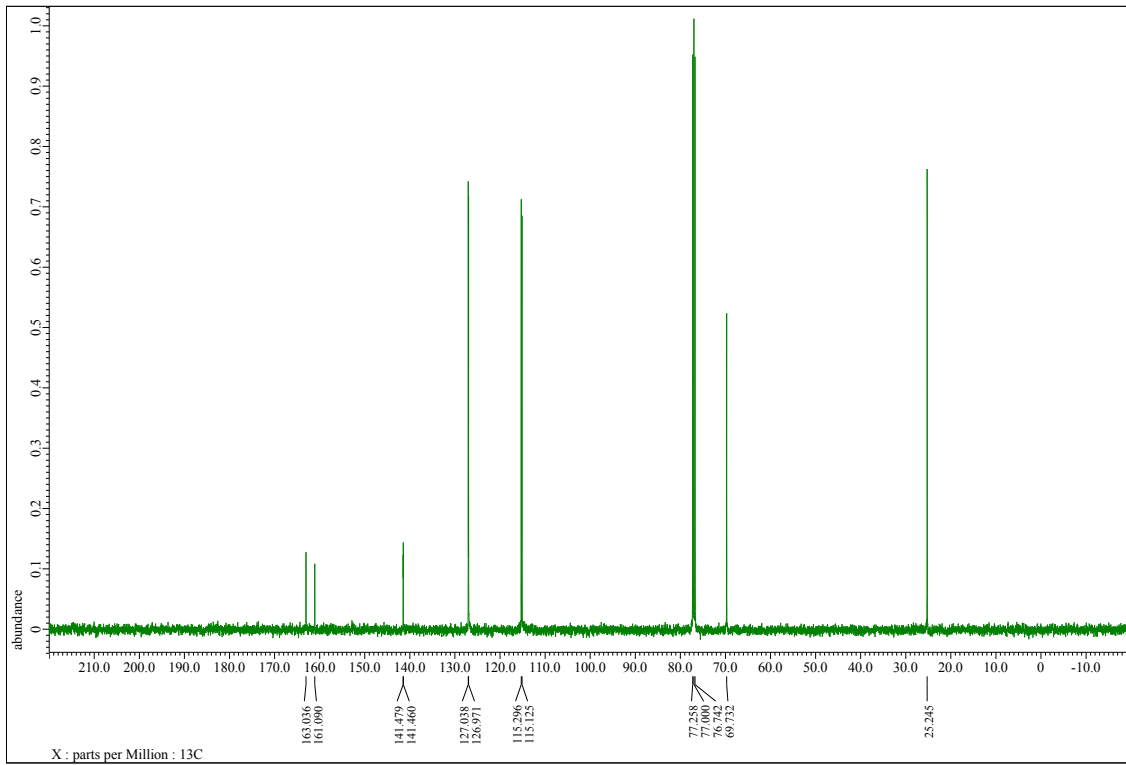
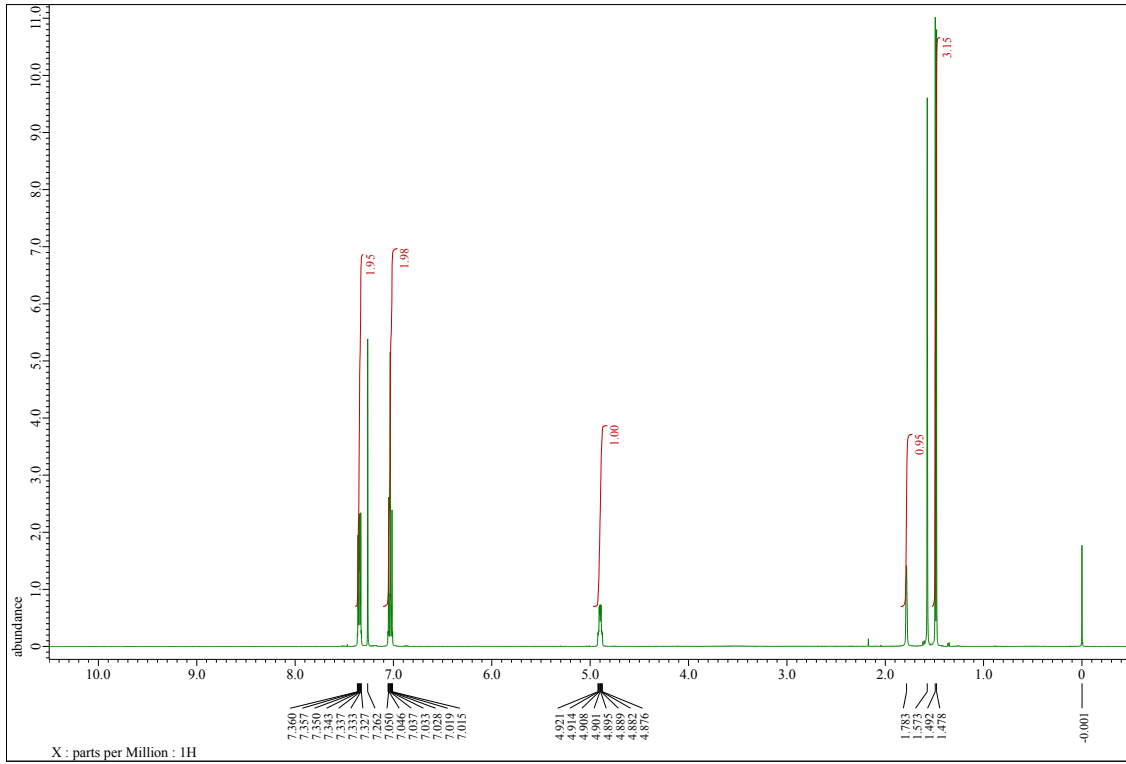
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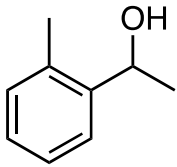




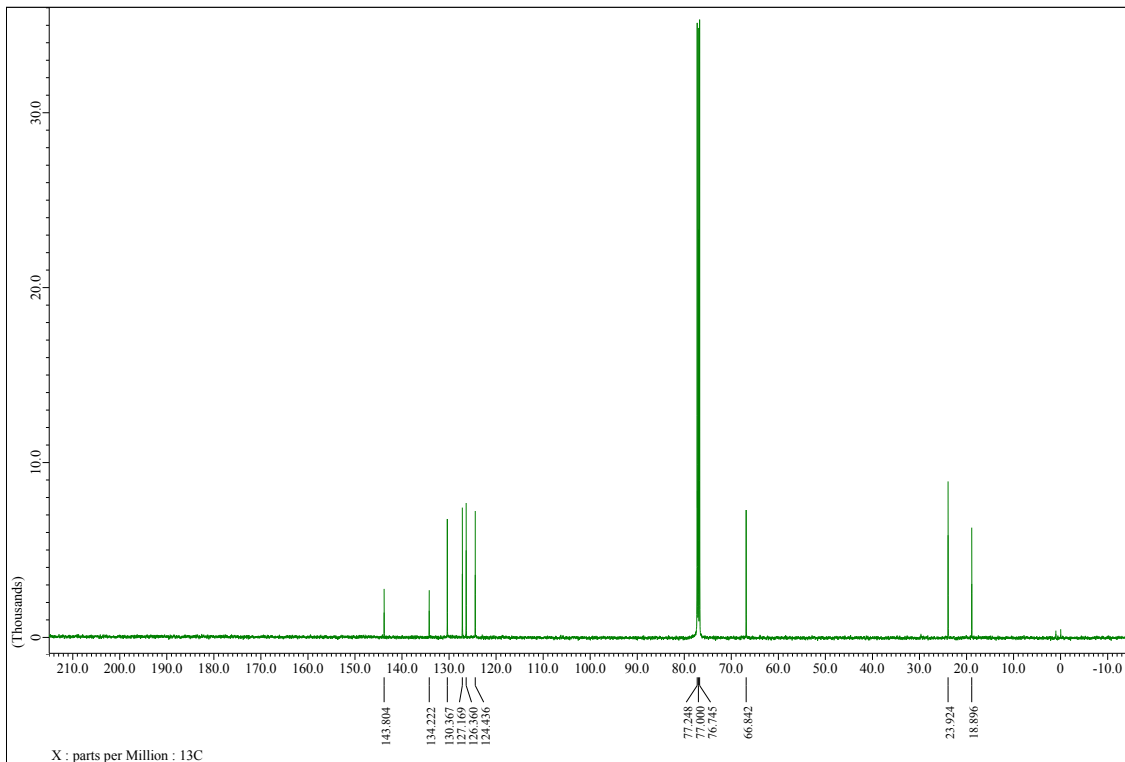
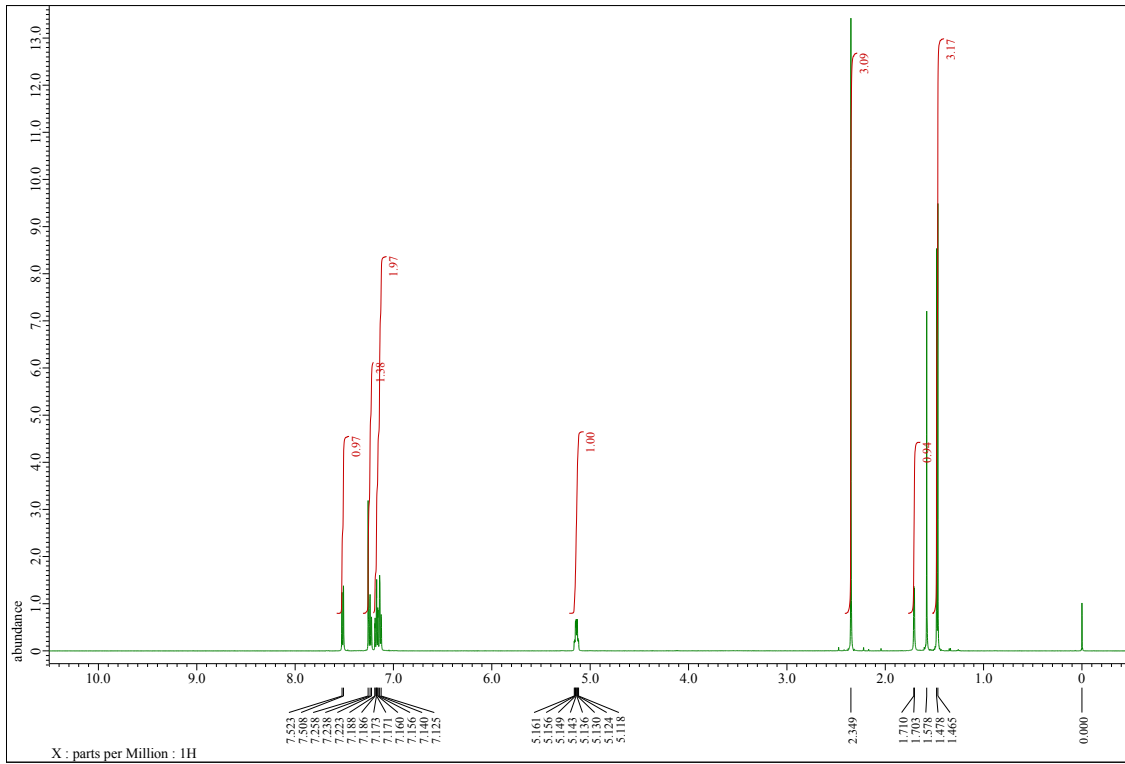


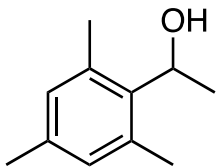
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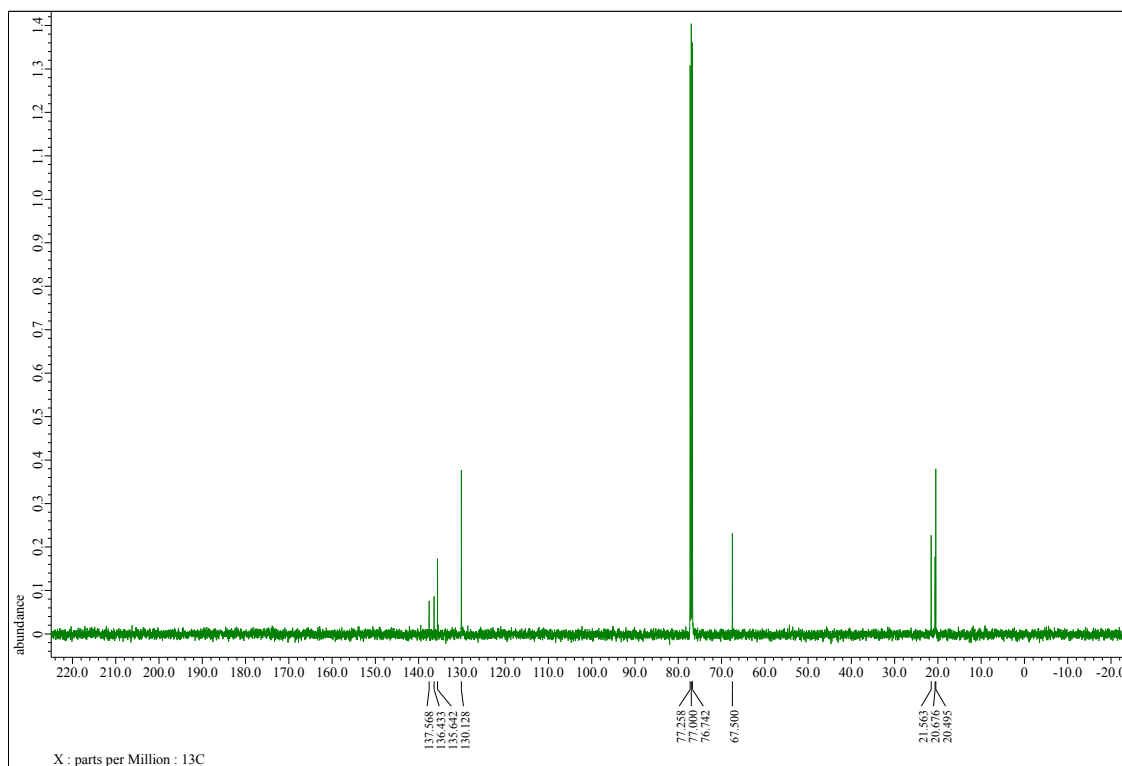
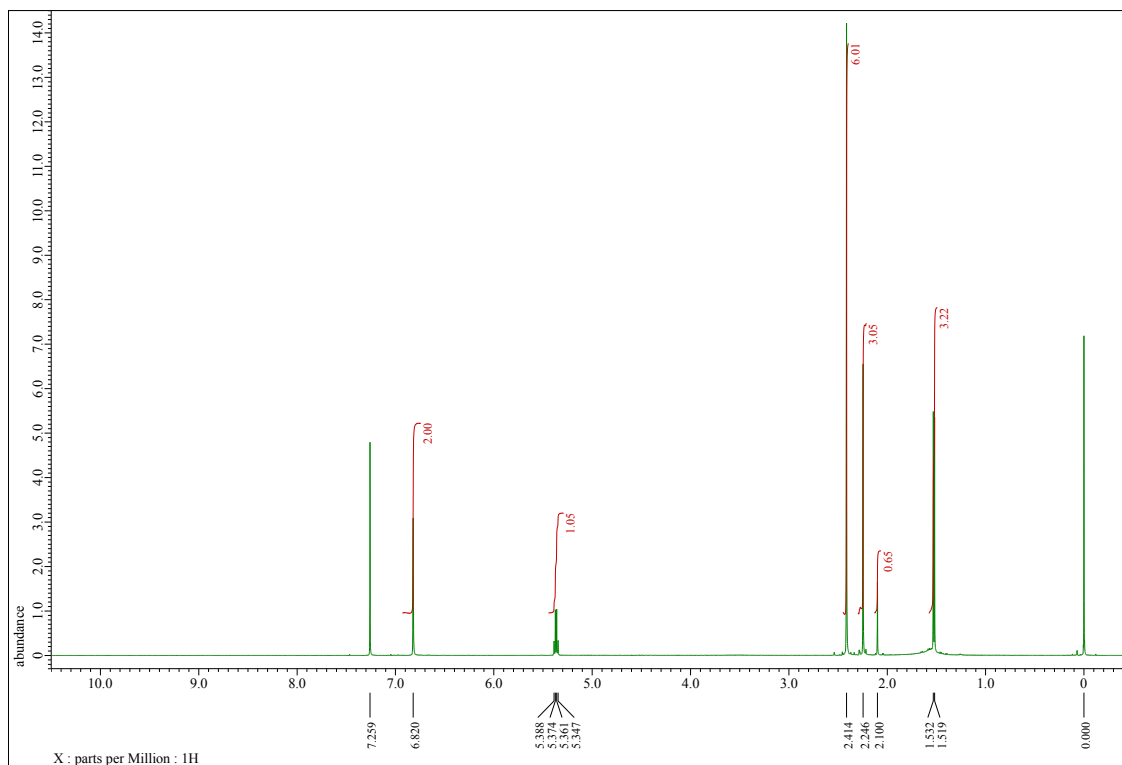


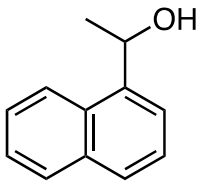
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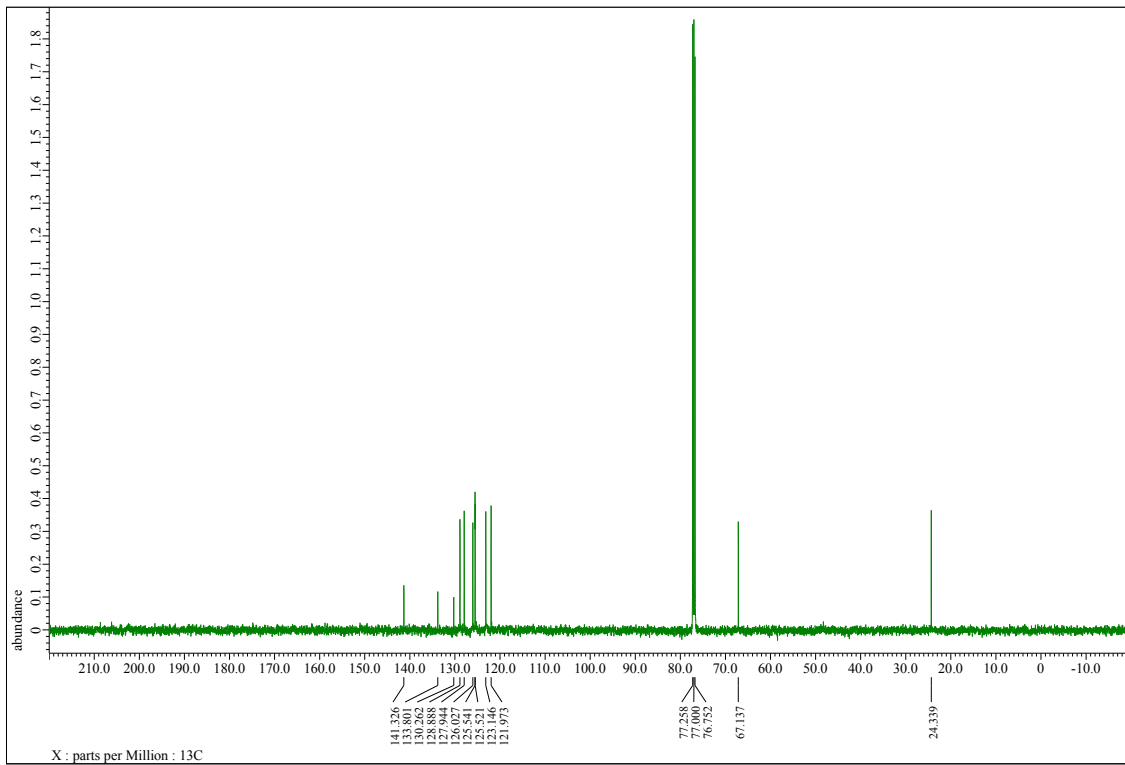
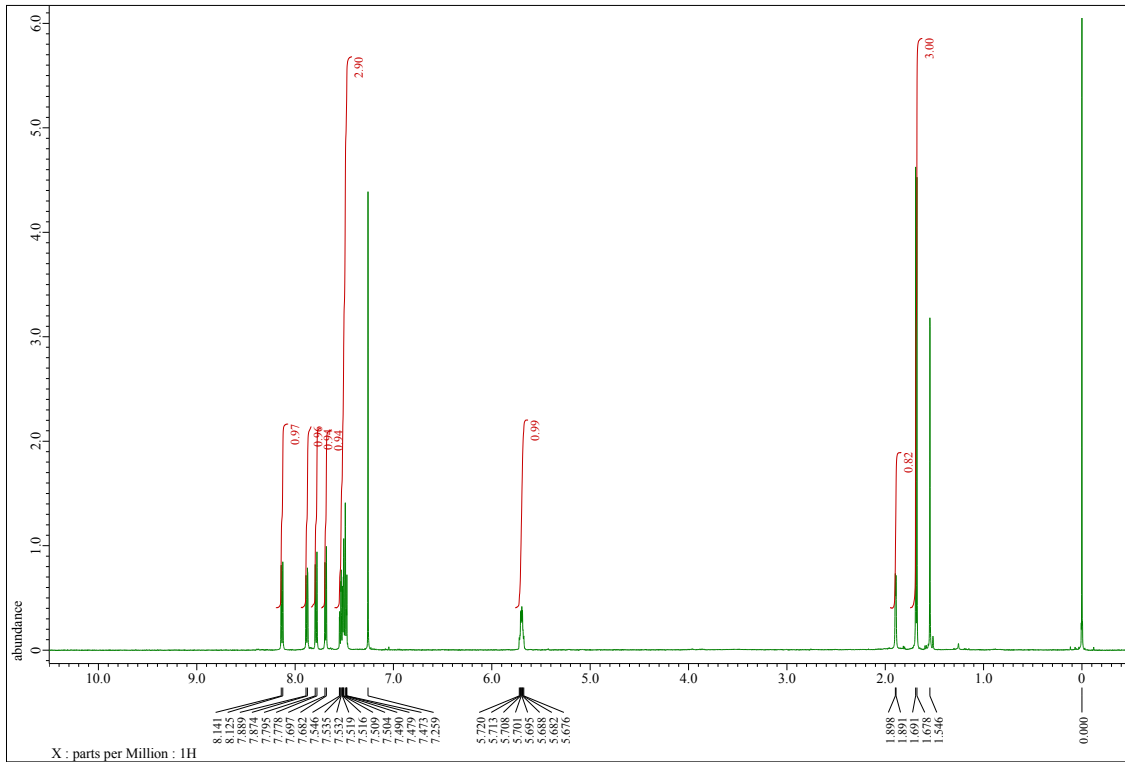


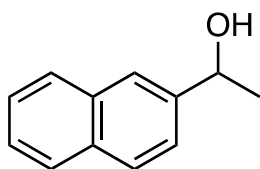
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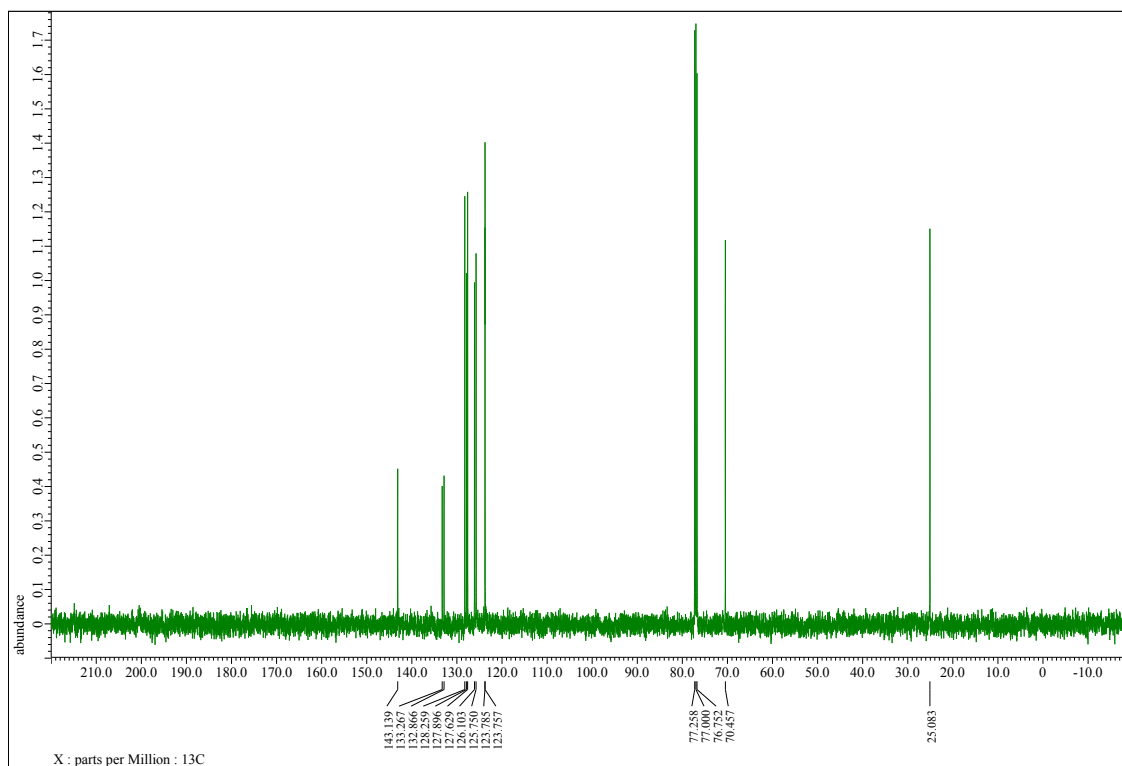
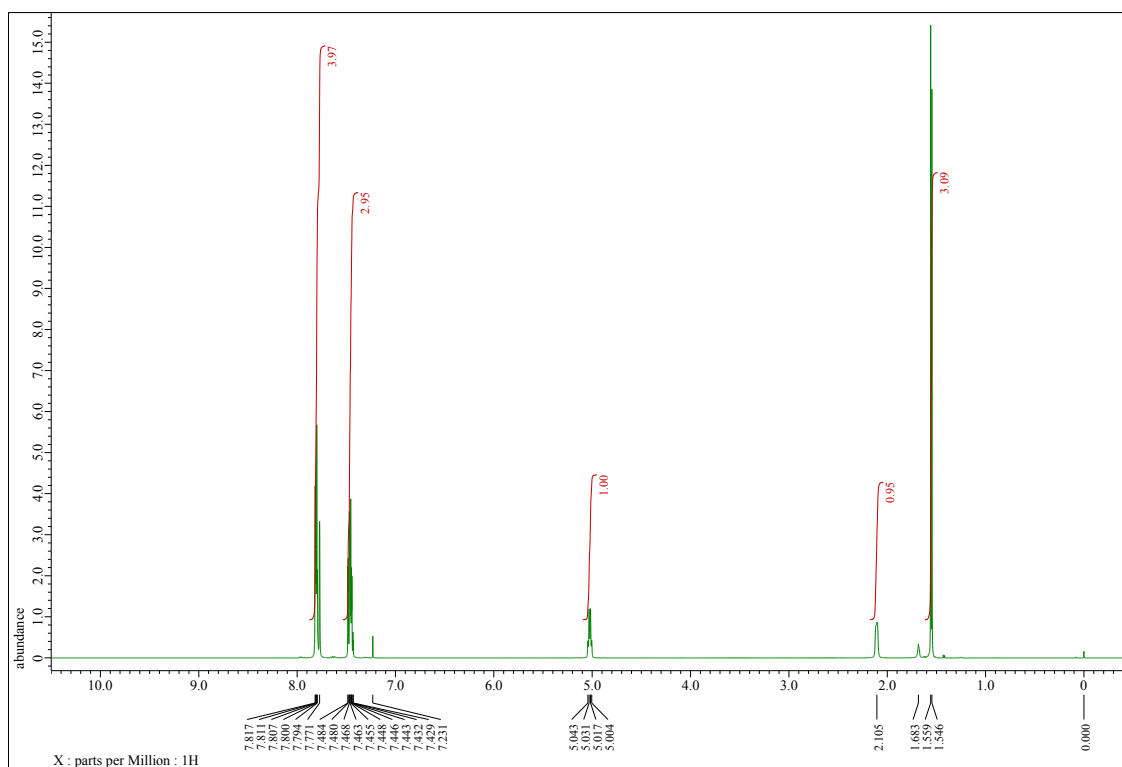


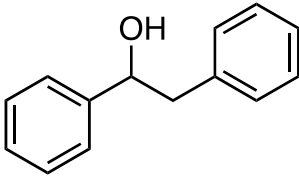
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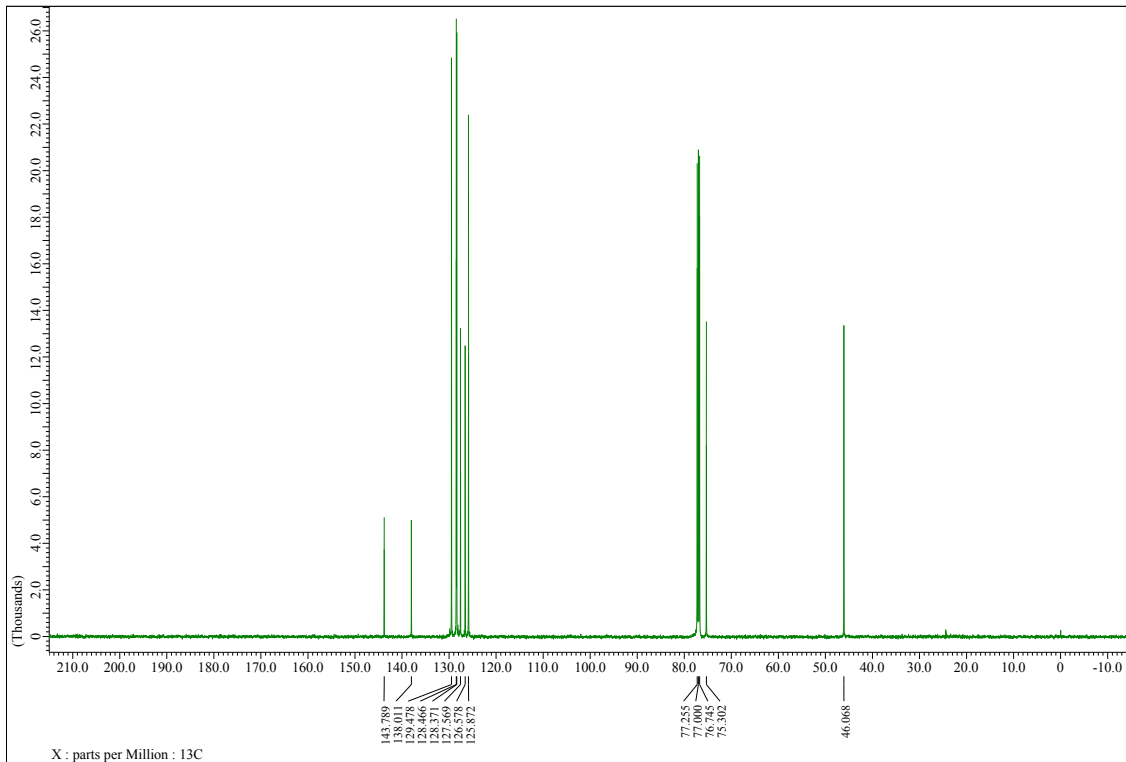
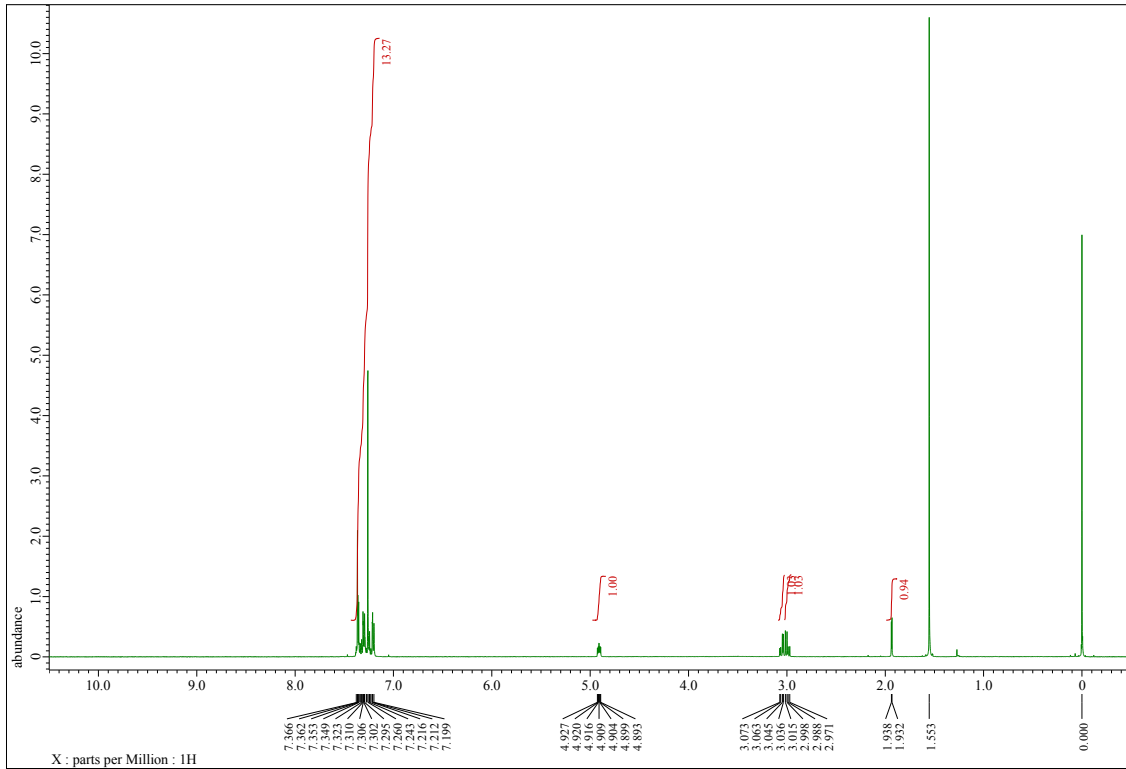


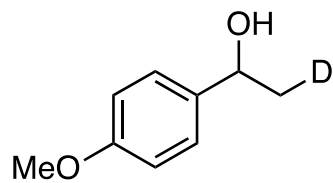
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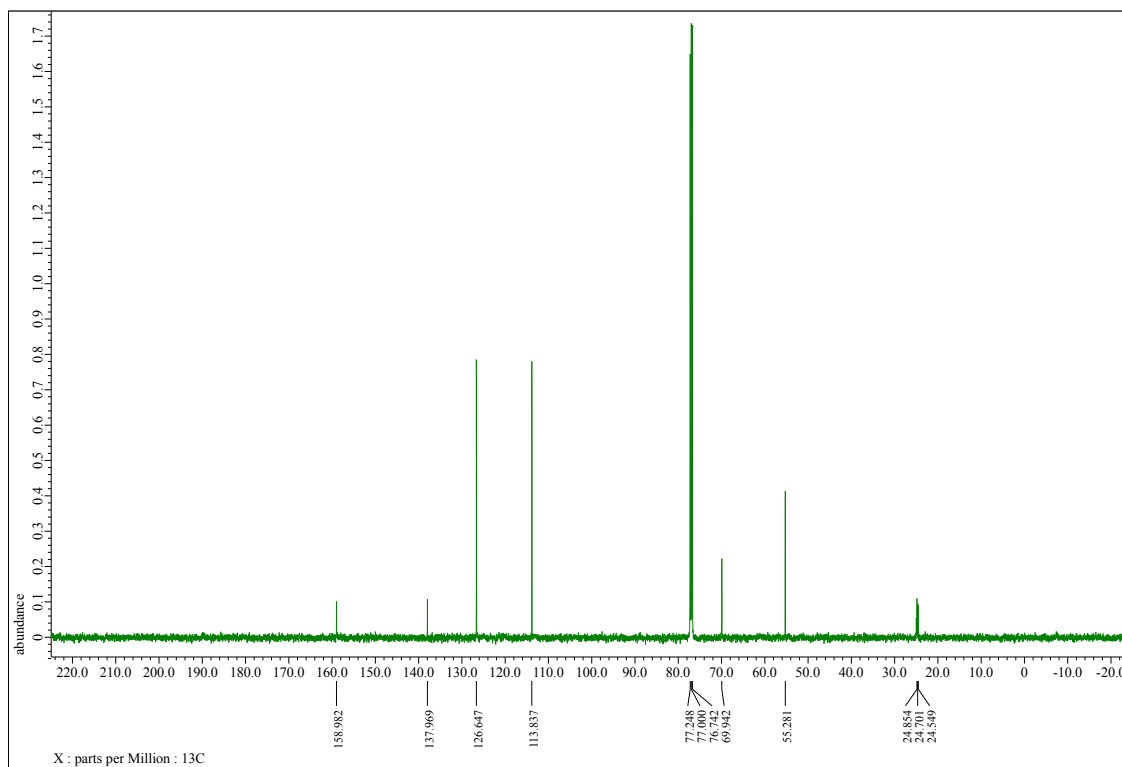
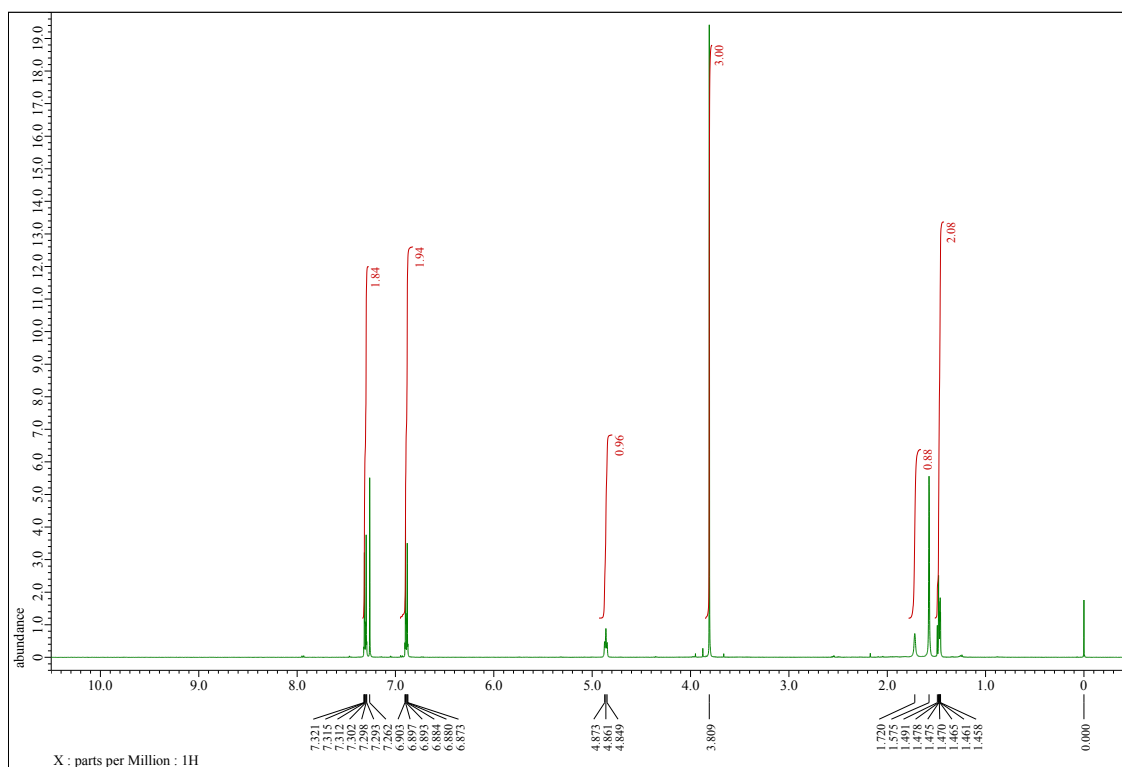


14





8a-D



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