Supporting Information

Direct activation of alcohols via perrhenate ester formation for an intramolecular dehydrative Friedel-Crafts reaction

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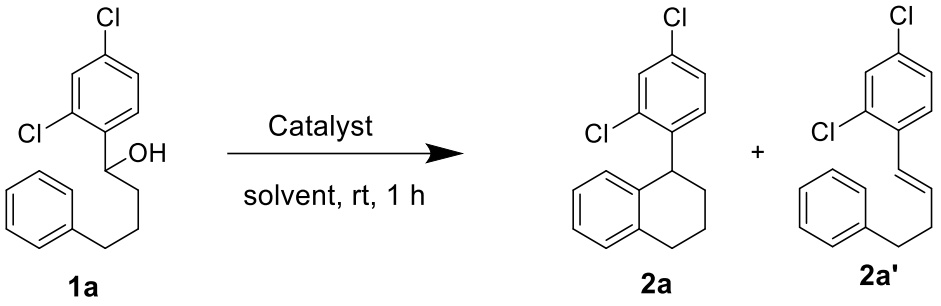
Table of Contents

1 General information

Re_2O_7 was purchased from Sigma Aldrich. Unless otherwise stated, Other chemicals used in this manuscript were purchased from Energy chemical company, Bide Pharmatech Ltd, Inno-Chem Ltd, Adamas Company, and Alfa Aesar Company. Other commercially available compounds were used as provided without further purification. HFIP used in the reactions were dried from anhydrous Mg_2SO_4 and distilled in N_2 prior to use. Other solvents are used after processing in accordance with conventional methods. Unless otherwise noted, all reactions were performed under air. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated plastic sheets (0.2 mm). Visualization was accomplished by irradiation with p-methoxybenzaldehyde, ultraviolet lamp (254 nm), alkaline potassium permanganate solution, iodine cylinder and phosphomolybdic acid solution. Flash column chromatography was performed over silica gel (200-300 mesh). The nuclear magnetic resonance data in this paper is measured by Bruker AVANCE III-400 or Bruker AscendTM 600MHZ nuclear magnetic resonance instrument at room temperature. The internal standards of ^1H NMR and ^{13}C NMR are TMS (δ = 0.00 ppm) or $CDCl_3$ (δ = 7.26 ppm) or CD_2Cl_2 (δ = 5.31 ppm). Proton spectrum description analysis is as follows: chemical shift (ppm), multiplet analysis (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), unidentified coupling the methods are all analyzed by multiple peak processing, and the carbon spectrum is described in ppm. High-resolution mass spectrometry data were measured by a Fourier transform high-resolution mass spectrometer Apex III (7.0 Tesla) FTMS (Bruker, Billerica, MA, USA) (ESI source) or Waters Micromass GCT Premier (EI source).

2 Optimization of reaction conditions[a]

Table S1. Reaction condition optimization.



1a **2a** **2a'**

Entry	Catalyst	Solvent	Yield.[b] (**2a**+**2a**')	Yield[b] (**2a**)
1	1 mol% V_2O_5 ($H_4V_6O_{17}$)	HFIP	32%	32%
2	10 mol% CF_3CO_2H	HFIP	12%	12%
3	**0.1 mol% Re_2O_7 ($HReO_4$)**	**HFIP**	**96%**	**96%**
4	10 mol% TsOH	HFIP	67%	67%
5	10 mol% H_2SO_4	HFIP	0%	0%
6	10 mol% HCl	HFIP	58%	58%
7	10 mol% TfOH	HFIP	92%	92%
8	10 mol% $FeCl_3$	HFIP	0%	0%
9	10 mol% $SnCl_4$	HFIP	65%	65%
10	0.1 mol% Re_2O_7	DCM	42%	17%
11	0.1 mol% Re_2O_7	Toluene	22%	7%
12	0.1 mol% Re_2O_7	AcOEt	0%	0%
13	0.1 mol% Re_2O_7	1,4-Dioxane	0%	0%
14	0.1 mol% Re_2O_7	MeCN	17%	4%
15	0.1 mol% Re_2O_7	DMF	0%	0%
16	0.1 mol% Re_2O_7	MeOH	0%	0%
17	1 mol% TfOH	HFIP	94%	94%
18	0.1 mol% TfOH	HFIP	93%	93%

[a] Unless otherwise specified, the reaction was carried out under air atmosphere, with Re_2O_7•SiO_2 (0.0001 mmol), solvent (0.2 mL), and **1a** (29.5 mg, 0.1 mmol) in a sealed tube for 1 hour, after which 20 μl Et_3N was added to quench the reaction; [b] yield is determined by analyzing HPLC traces of the reaction mixture with 1,3,5-trimethyl benzene as the internal standard.

Note: TfOH was used as a 5.0 mM solution in HFIP, if a 5.0 mM solution of TfOH in Et_2O was used, catalytic efficiency was much lower.

3 Additional Substrate Scope

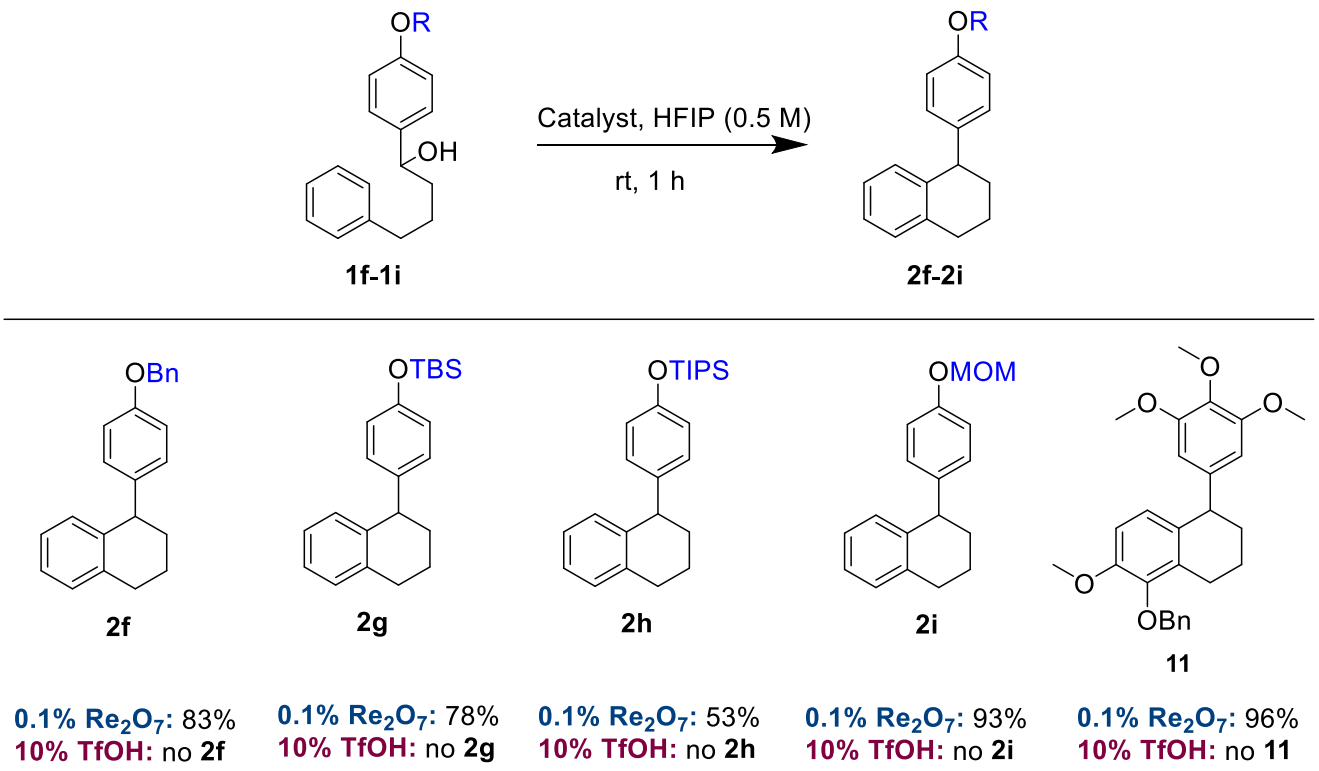


Figure S1. Efficiency comparison between TfOH and Rhenium catalysts.

Comments: When the highly acidic and corrosive triflic acid was used to catalyzed the dehydrative Friedel-Crafts reactions, the high acidity and corrosiveness of TfOH made it less tolerant of acid-sensitive substrates (**1f, 1g**, **1h**, **1i, 10**), while Re_2O_7 did not have this problem.

4 Syntheses of starting materials and Spectroscopic Data

All substrates were prepared by following literature procedures or the procedures provided in this manuscript. ^{1}H NMR, ^{13}C NMR and HRMS were provided for all compounds not previously reported, for cases where HRMS were not obtained after several tries, GC-MS were provided. Only ^{1}H NMR (and ^{13}C NMR) were provided for known compounds to show excellent agreement with reported data.

4.1 General synthetic **method A** for the preparation of reaction substrates

Figure S2. General synthetic method A

Add Mg metal (6 mmol, 1.2 equiv, 0.144 g), THF (20.0 mL) and a small crystal of iodine to a flame-dried Schlenk flask under argon. Dilute the 1-bromo-3-phenylpropane (6.0 mmol, 1.2 equiv, 1.195 g) with THF (3.0 mL) and add 1.0 mL of the solution to the above reaction mixture. Stir the solution to boil. Add the remaining bromide solution dropwise to the reaction mixture. Allow the reaction to stir at room temperature for 1–2 hours. The freshly made alkyl magnesium bromide (1.2 equiv) was added dropwisely to aldehyde (1 equiv) in anhydrous THF at 0 °C, and the reaction was stirred for 1–2 hours. After quenching with saturated NH_4Cl solution, the reaction mixture was extracted with EtOAc, and the organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. Purification by flash column chromatography on silica gel afforded the corresponding alcohol.

4.2 General synthetic **method B** for the preparation of reaction substrates

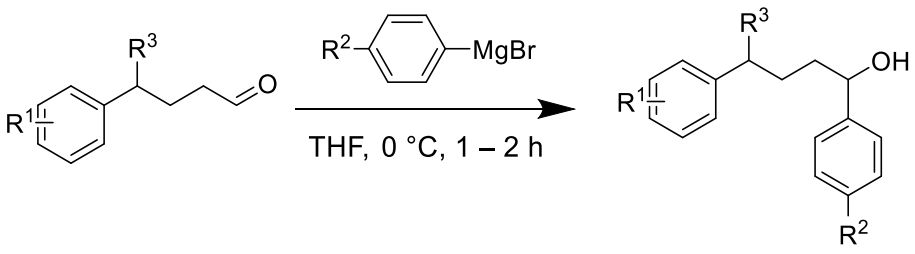
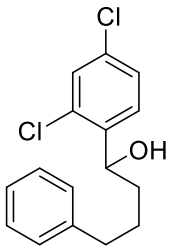


Figure S3. General synthetic method B

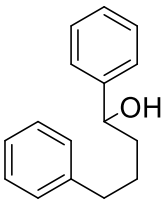
Add Mg metal (6 mmol, 1.2 equiv, 0.144 g), THF (20.0 mL) and a small crystal of iodine to a flame-dried Schlenk flask under argon. Dilute the aryl bromide (6.0 mmol, 1.2 equiv.) with THF (3.0 mL) and add 1.0 mL of the solution to the above reaction mixture. Stir the solution to boil. Add the remaining bromide solution dropwisely to the reaction mixture. Allow the reaction to stir at room temperature for 1-

2 hours. The freshly made aryl magnesium bromide (1.2 equiv.) was added dropwisely to aldehyde (1 equiv.) in anhydrous THF at 0 °C, and the reaction was stirred for 1-2 hours. After quenching with saturated NH_4Cl solution, the reaction mixture was extracted with EtOAc, and the organic layer was dried over anhydrous Na_2SO_4, and concentrated under cacuum. Purification by flash column chromatography on silica gel afforded the corresponding alcohol.



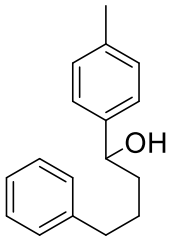
1a: 1-(2,4-dichlorophenyl)-4-phenyl-1-butanol. **1a** was synthesized according to the general synthetic **method A**.

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.48 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.26 (t, *J* = 3.8 Hz, 5H), 7.18 (t, *J* = 6.8 Hz, 3H), 5.11 (m, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.69 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.2, 140.9, 133.5, 132.5, 129.2, 128.5, 128.5, 128.3, 127.6, 125.9, 70.3, 37.2, 35.7, 27.5; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{16}Cl_3O$ $[M+Cl]^-$: 329.0272; found: 329.0274.



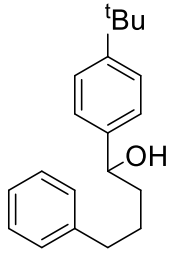
1b: 1,4-diphenylbutan-1-ol.[1] **1b** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.34 (m, 4H), 7.30 – 7.23 (m, 3H), 7.20 – 7.14 (m, 3H), 4.69 (t, *J* = 7.2 Hz, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.58 (m, 4H).



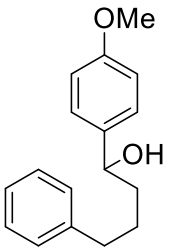
1c: 4-phenyl-1-(p-tolyl)butan-1-ol.[2] **1c** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.29 – 7.24 (m, 2H), 7.23 – 7.20 (m, 2H), 7.19 – 7.12 (m, 5H), 4.67 – 4.64 (m, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.90 – 1.68 (m, 4H).



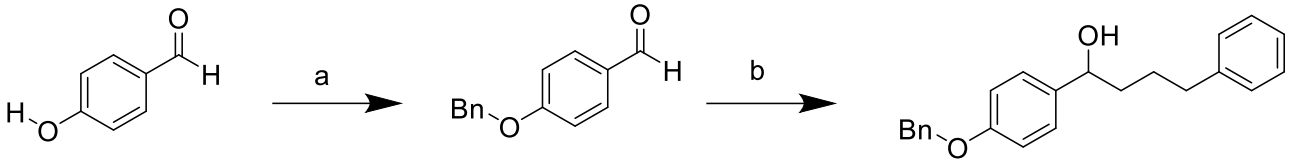
1d: 1-(4-(tert-butyl)phenyl)-4-phenylbutan-1-ol. **1d** was synthesized according to the general synthetic **method A.**

Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54 – 7.47 (m, 2H), 7.44 – 7.37 (m, 4H), 7.37 – 7.32 (m, 3H), 4.74 – 4.71 (m, 1H), 2.82 – 2.77 (m, 3H), 2.03 – 1.73 (m, 4H), 1.52 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 150.2, 142.3, 141.8, 128.4, 128.3, 125.7, 125.2, 74.0, 38.4, 35.8, 34.4, 31.4, 27.6. **HRMS** m/z (ESI): calcd. for $C_{20}H_{26}NaO$ $[M+Na]^+$: 305.1876; found: 305.1877.



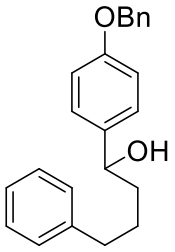
1e: 1-(4-methoxyphenyl)-4-phenylbutan-1-ol.[2] **1e** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.26 – 7.13 (m, 7H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.62 (t, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 2.65 (t, *J* = 7.1 Hz, 2H), 2.09 – 1.72 (m, 3H), 1.61 – 1.57 (m, 1H).



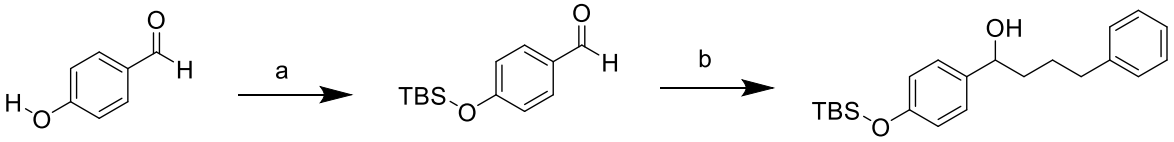
Reaction Condition：
a) Cs_2CO_3, CH_3CN, BnBr, rt, 12 h, 53%. b) $Ph(CH_2)_3MgBr$, THF, 0 °C, 1 h, 78%.

Figure S4. Synthesis of 1f



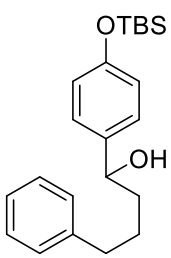
1f: 1-(4-(benzyloxy)phenyl)-4-phenylbutan-1-ol. **1f** was synthesized via the route shown in **Figure S4**.

White solid. ^{1}H NMR (400 MHz, Chloroform-d) δ **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.42 (m, 4H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.23 – 7.21 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 2H), 4.64 (t, *J* = 6.1 Hz, 1H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.19 – 2.04 (m, 1H), 1.92 – 1.75(m, 3H), 1.98 – 1.59 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.3, 142.4, 137.2, 137.1, 128.6, 128.5, 128.4, 128.0, 127.5, 127.2, 125.8, 114.8, 74.1, 70.1, 38.5, 35.8, 27.7. **HRMS** m/z (ESI): calcd. for $C_{23}H_{24}NaO_2$ $[M+Na]^+$: 355.1669; found: 355.1679.



Reaction Condition：
a) Et_3N, DCM, TBSCl, rt, 12 h, 90%. b) $Ph(CH_2)_3MgBr$, THF, 0 °C, 1 h, 81%.

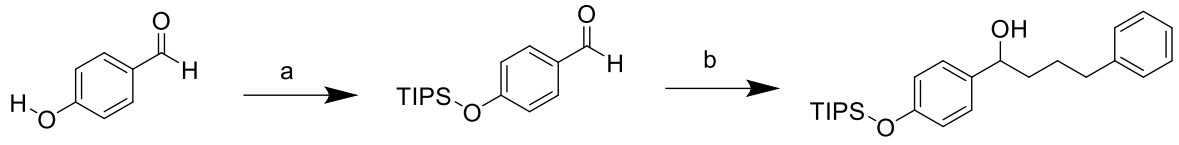
Figure S5. Synthesis of 1g



1g: 1-(4-((tert-butyldimethylsilyl)oxy)phenyl)-4-phenylbutan-1-ol. **1g** was synthesized via the route shown in **Figure S5**.

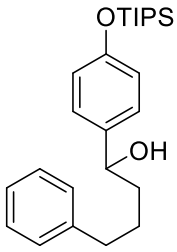
Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ *7.28* (t, *J* = 7.5 Hz, 2H), 7.18 (dt, *J* = 13.5, 5.2 Hz, 5H), 6.82 (d, *J* = 8.1 Hz, 2H), 4.62 (t, *J* = 6.3 Hz, 1H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.92 (s, 1H), 1.87 – 1.82 (m, 1H), 1.78 – 1.70 (m, 2H), 1.63 – 1.56 (m, 1H), 1.02 (s, 9H), 0.22 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.1, 142.4, 137.6, 128.5, 128.4,

127.2, 125.8, 120.1, 74.2, 38.5, 35.8, 27.7, 25.8, 18.3, -4.30; **HRMS** m/z (ESI): calcd. for $C_{22}H_{32}O_2NaSi$ $[M+Na]^+$: 379.2064; found: 379.2050.



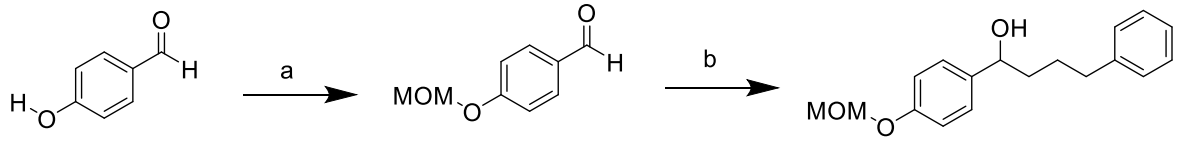
Reaction Condition：
a)Imidazole，DCM, TIPSCl, rt, 12 h, 75%. b) $Ph(CH_2)_3MgBr$, THF, 0 °C, 1 h, 45%.

Figure S6. Synthesis of 1h



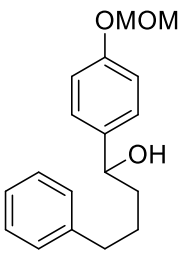
1h: 4-phenyl-1-(4-((triisopropylsilyl)oxy)phenyl)butan-1-ol. **1h** was synthesized via the route shown in **Figure S6**.

Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.19 (m, 5H), 6.94 (dd, *J* = 8.6, 2.2 Hz, 2H), 4.60 (t, *J* = 6.1 Hz, 1H), 2.76 – 2.63 (m, 3H), 1.91 – 1.84 (m, 1H), 1.82 – 1.70 (m, 2H), 1.66 – 1.59 (m, 1H), 1.42 – 1.33 (m, 3H), 1.22 (dd, *J* = 7.4, 2.8 Hz, 18H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.4, 142.4, 137.3, 128.4, 128.2, 127.1, 125.7, 119.7, 74.0, 38.5, 35.8, 27.6, 18.0, 12.7; .**HRMS** m/z (ESI): calcd. for $C_{25}H_{38}O_2NaSi$ $[M+Na]^+$: 421.2533; found: 421.2529.



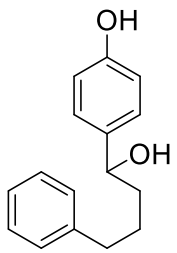
Reaction Condition：
a)K_2CO_3, acetone,MOMCl, rt, 12 h, 45%. b) $Ph(CH_2)_3MgBr$, THF, 0 °C, 1 h, 56%.

Figure S7. Synthesis of 1i



1i 1-(4-(methoxymethoxy)phenyl)-4-phenylbutan-1-ol **1h** was synthesized via the route shown in **Figure S7**.

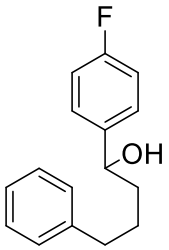
Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.25 (m, 6H), 7.12 – 7.08 (m, 2H), 5.21 (s, 2H), 4.64 (t, J = 6.0 Hz, 1H), 3.53 (s, 3H), 3.19 (s, 1H), 2.70 (d, *J* = 7.2 Hz, 2H), 1.95 – 1.75 (m, 3H), 1.70 – 1.64 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 156.4, 142.2, 138.3, 128.3, 128.2, 127.1, 125.6, 116.0, 94.2, 73.7, 55.7, 38.4, 35.6, 27.5; **HRMS** m/z (ESI): calcd. for $C_{18}H_{22}O_3Na$ $[M+Na]^+$: 309.1461; found: 309.1445.



1j: 4-(1-hydroxy-4-phenylbutyl) phenol. **1j** was synthesized according to the general synthetic **method A.**

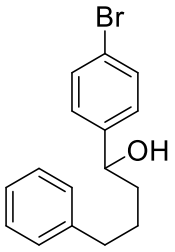
White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.28 – 7.24 (m, 2H), 7.22 – 7.13 (m, 5H), 6.82 – 6.77 (m, 2H), 4.73 (s, 1H), 4.63 (t, *J* = 6.4 Hz, 1H), 2.62 (t, *J* = 7.3 Hz, 2H), 1.88 – 1.79 (m, 1H), 1.77 – 1.67 (m, 3H), **^{13}C NMR** (101 MHz, DMSO-d^6) δ 156.1, 142.5,

136.7, 128.4, 128.4, 127.1, 125.8, 114.9, 72.2, 39.0, 35.3, 27.7; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$: 265.1199; found: 265.1176.



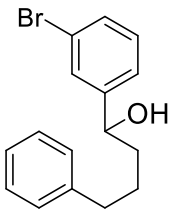
1k: 1-(4-fluorophenyl)-4-phenylbutan-1-ol. **1k** was synthesized according to the general synthetic **method A.**

Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.32 – 7.26 (m, 3H), 7.25 (s, 1H), 7.21 – 7.11 (m, 3H), 7.06 – 6.98 (m, 2H), 4.69 – 4.66 (m, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 1.88 – 1.67 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 163.4 (d, *J* = 243.0 Hz), 142.2, 140.5 (d, *J* = 3.0 Hz), 128.5, 128.4, 127.6 (d, *J* = 8.1 Hz), 125.9, 115.3 (d, *J* = 21.2 Hz), 73.9, 38.7, 35.8, 27.6; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{18}FO$ $[M+H]^+$: 245.1336; found: 245.1362.



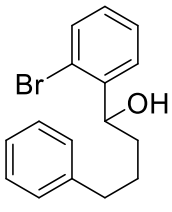
1l: 1-(4-bromophenyl)-4-phenylbutan-1-ol. **1l** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.30 – 7.24 (m, 2H), 7.27 – 7.17 (m. 3H), 7.16 – 7.12 (m, 2H), 4.67 – 4.64 (m, 1H), 2.62 (t, *J* = 7.1 Hz, 2H), 1.84 – 1.68 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 143.8, 142.2, 131.6, 128.5, 128.5, 127.8, 125.9, 121.4, 74.0, 38.7, 35.8, 27.5; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{17}BrClO$ $[M+Cl]^-$: 339.0157; found: 339.0171.



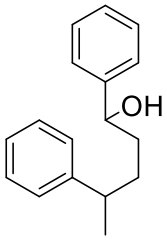
1m: 1-(3-bromophenyl)-4-phenylbutan-1-ol. **1m** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.49 (d, *J* = 1.7 Hz, 1H), 7.41 (m, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.19 (m, 5H), 4.62 ((t, *J* = 7.1 Hz, 1H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.18 (s, 1H), 1.82 – 1.71 (m, 3H), 1.65 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.1, 142.1, 130.6, 130.1, 129.1, 128.5, 128.4, 125.9, 124.6, 122.7, 73.9, 38.6, 35.7, 27.5; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{18}BrO$ $[M+H]^+$: 295.0651; found: 295.0646.



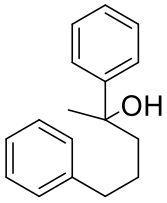
1n: 1-(2-bromophenyl)-4-phenylbutan-1-ol. **1n** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.52 (m, 2H), 7.36 – 7.26 (m, 3H), 7.20 (m, 3H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 5.12 – 5.09 (m, 1H), 2.73 – 2.62 (m, 2H), 1.98 (s, 1H), 1.89 – 1.72 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 143.8, 142.4, 132.8, 128.9, 128.5, 128.4, 127.8, 127.5, 125.9, 72.9, 37.3, 35.8, 27.6; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{17}BrNaO$ $[M+Na]^+$: 327.0355; found: 327.0316.



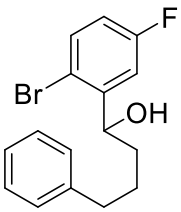
1o: 1,4-diphenyl-1-pentanol. **1o** was synthesized according to the general synthetic **method B.**

Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.40 – 7.24 (m, 7H), 7.20 – 7.12 (m, 3H), 4.64 – 4.59 (m, 1H), 2.72 – 2.65 (m, 1H), 1.80 – 1.61 (m, 4H), 1.23 (d, J = 2.4 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.4, 144.8, 128.6, 128.5, 127.7, 127.1, 126.7, 126.0, 74.9, 40.0, 37.2, 34.4, 22.5; **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{20}NaO$ $[M+Na]^+$: 263.1406; found 263.1380.



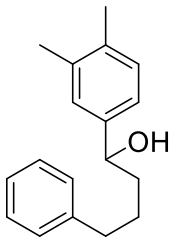
1p: 2,5-diphenylpentan-2-ol.[1] **1p** was synthesized according to the general synthetic **method A.**

Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.27 – 7.20 (m, 3H), 7.19 – 7.08 (m, 3H), 2.56 (t, *J* = 7.0 Hz, 2H), 1.84 (dt, *J* = 10.4, 5.6 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.55 (s, 3H).



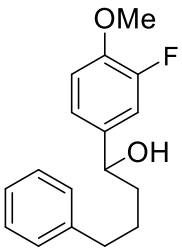
1q: 1-(5-bromo-2-fluorophenyl)-4-phenylbutan-1-ol. **1q** was synthesized according to the general synthetic **method A.**

Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.59 (dd, *J* = 6.4, 2.6 Hz, 1H), 7.34 (ddd, *J* = 8.7, 4.6, 2.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 – 7.13 (m, 3H), 6.90 (dd, *J* = 9.8, 8.7 Hz, 1H), 5.01 – 4.98 (m, 1H), 2.69 – 2.60 (m, 2H), 1.89 (s, 1H), 1.83 – 1.73 (m, 3H), 1.72 – 1.61 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 158.8 (d, *J* = 245.8 Hz), 142.1, 134.1, 134.0, 131.7 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 4.8 Hz), 128.5, 128.5, 126.0, 117.2 (d, *J* = 23.9 Hz), 67.9 (d, *J* = 2.1 Hz), 37.7, 35.7, 27.4; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{16}BrClFO$ $[M+Cl]^-$: 357.0063; found: 357.0085.



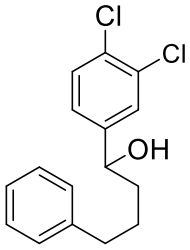
1r: 1-(3,4-dimethylphenyl)-4-phenylbutan-1-ol. **1r** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 7.15 – 7.10 (m, 2H), 7.10 – 7.05 (m, 1H), 4.64 (t, *J* = 7.3 Hz, 1H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.89 – 1.64 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.4, 142.3, 136.7, 135.9, 129.7, 128.5, 128.3, 127.2, 125.7, 123.4, 74.5, 38.5, 35.8, 27.7, 19.9, 19.5; **HRMS** *m/z* (ESI): calcd. for $C_{18}H_{22}NaO$ $[M+Na]^+$: 277.1563; found: 277.1548.



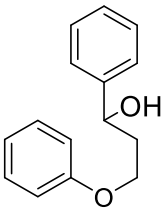
1s: 1-(3-fluoro-4-methoxyphenyl)-4-phenylbutan-1-ol. **1s** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.27 (m, 1H), 7.26 – 7.25 (m, 1H), 7.21 – 7.17 (m, 1H), 7.17 – 7.14 (m, 2H), 7.07 (dd, *J* = 12.2, 2.1 Hz, 1H), 7.01 (m, 1H), 6.91 (t, *J* = 8.4 Hz, 1H), 4.62 – 4.59 (m, 1H), 3.88 (s, 3H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.89 (s, 1H), 1.84 – 1.68 (m, 3H), 1.62 – 1.56 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 152.5 (d, *J* = 246.4 Hz), 147.0 (d, *J* = 10.7 Hz), 142.3, 138.0 (d, *J* = 5.1 Hz), 128.5, 128.4, 125.9, 121.7 (d, *J* = 3.5 Hz), 113.8 (d, *J* = 18.6 Hz), 113.4 (d, *J* = 2.6 Hz), 73.8 (d, *J* = 1.4 Hz), 56.5, 38.6, 35.8, 27.6; **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{19}FNaO_2$ [M+Na]$^+$: 297.1261; found: 297.1244.



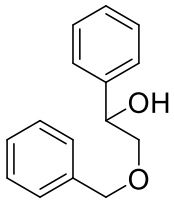
1t: 1-(3,4-dichlorophenyl)-4-phenylbutan-1-ol. **1t** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.43 – 7.38 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.12 (m, 4H), 4.66 – 4.63 (m, 1H), 2.63 (t, *J* = 7.1 Hz, 2H), 1.81 – 1.68 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.0, 142.0, 132.6, 131.3, 130.5, 128.5, 128.5, 128.0, 126.0, 125.3, 73.3, 38.6, 35.7, 27.4; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{18}Cl_2O$ [M+H]$^+$: 295.0651; found 295.0632.



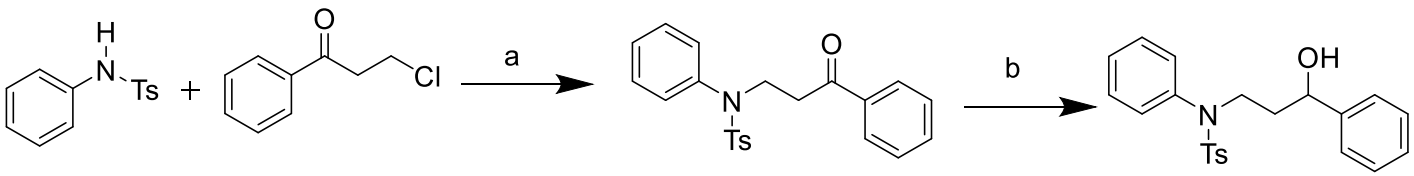
1u: 3-phenoxy-1-phenylpropan-1-ol.[3]

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.43 – 7.33 (m, 4H), 7.33 – 7.26 (m, 3H), 6.96 (tt, J = 7.4, 1.1 Hz, 1H), 6.94 – 6.89 (m, 2H), 5.03 (ddd, *J* = 7.7, 4.4, 2.5 Hz, 1H), 4.18 (ddd, *J* = 9.4, 7.0, 4.9 Hz, 1H), 4.06 (ddd, *J* = 9.4, 6.6, 5.0 Hz, 1H), 2.52 (d, *J* = 3.2 Hz, 1H), 2.31 – 2,16 (m, 2H).



1v: 2-(benzyloxy)-1-phenylethan-1-ol.[4]

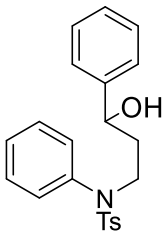
Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.41 – 7.26 (m, 10H), 4.94 (dd, *J* = 9.1, 3.1 Hz, 1H), 4.64 – 4.58 (m, 2H), 3.65 (dd, *J* = 9.7, 3.2 Hz, 1H), 3.51 (t, *J* = 9.4 Hz, 1H), 2.84 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 140.3, 137.9, 128.6, 128.5, 128.0, 128.0, 127.9, 126.3, 75.9, 73.5, 73.0.



Reaction Condition:

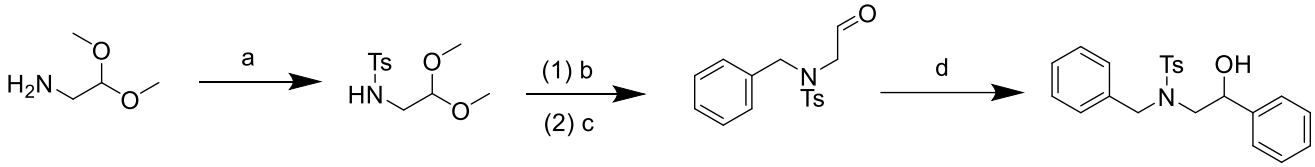
a) Et_3N, THF, reflux, 12 h, 72%. b) $NaBH_4$,THF, 0 °C, 1 h, 57%.

Figure S8. Synthesis of 1w



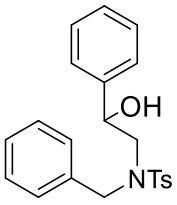
1w: *N*-(3-hydroxy-3-phenylpropyl)-4-methyl-*N*-phenylbenzenesulfonamide. **1w** was synthesized via the route shown in **Figure S8**.

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.51 – 7.48 (m, 2H), 7.38 – 7.29 (m, 7H), 7.27 (d, *J* = 7.9 Hz, 3H), 7.11 – 7.10 (m, 2H), 4.92 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.95 (dt, *J* = 14.3, 7.5 Hz, 1H), 3.57 (dt, *J* = 12.8, 5.7 Hz, 1H), 3.15 (s, 1H), 2.44 (s, 3H), 1.87 – 1.79 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.2, 143.6, 139.1, 135.0, 129.6, 129.2, 128.8, 128.4, 128.1, 127.7, 127.4, 125.8, 70.7, 47.7, 37.6, 21.6; **HRMS** *m/z* (ESI): calcd. for $C_{22}H_{24}NO_3S$ $[M+H]^+$: 382.1471; Wound: 382.1473.



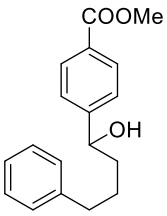
Reaction Condition：
a) Et_3N, DCM, 0 °C, then 4-methylbenzenesulfonyl chloride, 0 °C to rt, 12 h, 72%. b) $PhCH_2Br$, NaH, THF, 1 h, 89%. c) HCl, acetone, reflux, 3 h, 78%. d) PhMgBr, THF, 0 °C, 1 h, 84%.

Figure S9. Synthesis of 1x



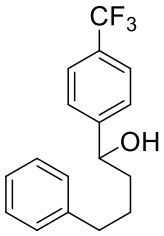
1x: *N*-benzyl-*N*-(2-hydroxy-2-phenylethyl)-4-methylbenzenesulfonamide. **1x** was synthesized via the route shown in **Figure S9**.

Yellow solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.19 (m, 10H), 7.11 (d, *J* = 6.7 Hz, 2H), 4.62 (d, *J* = 14.4 Hz, 1H), 4.52 (dd, *J* = 9.4, 2.7 Hz, 1H), 4.14 (d, *J* = 14.4 Hz, 1H), 3.36 (dd, *J* = 15.1, 9.4 Hz, 1H), 3.07 (dd, *J* = 15.1, 2.8 Hz, 1H), 2.89 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 143.9, 141.4, 136.1, 136.0, 130.0, 129.0, 128.9, 128.5, 128.4, 127.9, 127.5, 125.9, 72.6, 56.8, 54.2, 21.7; **HRMS** *m/z* (ESI): calcd. for $C_{22}H_{23}ClNO_3S$ $[M+Cl]^-$: 416.1093; found: 416.1076.



1y: methyl-4-(1-hydroxy-4-phenylbutyl)benzoate.[2] **1y** was synthesized according to the general synthetic **method A.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.03 – 8.02 (m, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.29 (q, *J* = 1.3 Hz, 2H), 7.21 – 7.20 (m, 1H), 7.19 – 7.16(m, 2H), 4.78 – 4.76 (m, 1H), 3.93 (s, 3H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.00 (s, 1H), 1.87 – 1.73 (m, 3H), 1.66 – 1.62 (m, 1H).



1z: 4-phenyl-1-(4-(trifluoromethyl)phenyl)butan-1-ol.[2] **1z** was synthesized according to the general synthetic **method A.**

Light yellow solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.44(d, *J*= 8.4 Hz, 2H), 7.30 – 7.24 (m, 2 H), 7.21 – 7.13 (m, 3 H), 4.77 (t, *J* = 6.8 Hz, 1H), 2.64 (t, *J* = 6.8 Hz, 2H), 1.84 – 1.65 (m, 4H).

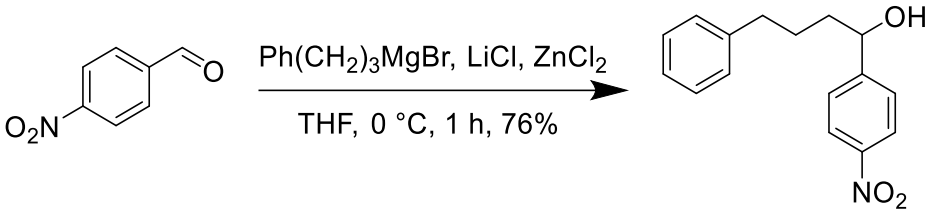
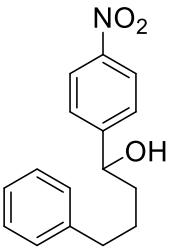
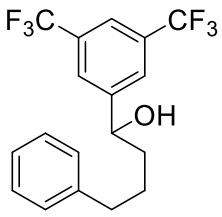


Figure S10. Synthesis of 1aa



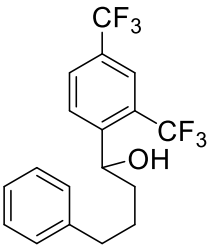
1aa: 1-(4-nitrophenyl)-4-phenylbutan-1-ol. **1aa** was synthesized via the route shown in **Figure S10**.

Yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.21 – 8.18 (m, 2H), 7.50 – 7.47 (m, 2H), 7.29 – 7.26 (m, 1H), 7.25 (s, 1H), 7.21 – 7.14 (m, 1H), 7.16 – 7.12 (m, 2H), 4.83 (t, *J* = 6.8 Hz, 1H), 2.64 (t, *J* = 7.0 Hz, 2H), 1.83 – 1.75 (m, 3H), 1.68 – 1.63 (m, 1H).**^{13}C NMR** (101 MHz, Chloroform-d) δ 152.1, 141.9, 128.6, 128.5, 126.7, 126.1, 123.9, 73.6, 38.9, 35.7, 27.3; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$: 294.1101; found: 294.1125.



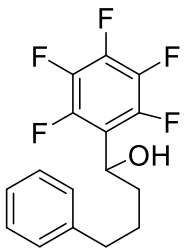
1bb: 1-(3,5-bis(trifluoromethyl)phenyl)-4-phenylbutan-1-ol. **1bb** was synthesized according to the general synthetic **method A.**

Yellow solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.79 (s, 3H), 7.29 (m, 2H), 7.24 – 7.13 (m, 3H), 4.84 – 4.81 (m, 1H), 2.67 (t, *J* = 7.0 Hz,, 2H), 2.03 (s, 1H), 1.85 – 1.75 (m, 3H), 1.73 – 1.66 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.5, 141.8, 131.8 (q, *J* = 33.1 Hz), 128.6, 128.5, 126.2, 126.1, 123.49 (q, *J* = 270.9 Hz), 121.5 (q, *J* = 3.8 Hz), 73.4, 38.9, 35.6, 27.3; **HRMS** *m/z* (ESI): calcd. for $C_{18}H_{16}ClF_6O$ $[M+Cl]^-$: 397.0799; found: 397.0811.



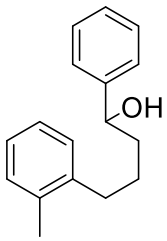
1cc: 1-(2,4-bis(trifluoromethyl)phenyl)-4-phenylbutan-1-ol. The synthetic of **1cc** was according to the general synthetic **method A.**

Yellow solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.95 – 7.83 (m, 3H), 7.32 – 7.29 (m, 2H), 7.23 – 7.19 (m, 3H), 5.21 – 5.17 (m, 1H), 2.71 – 2.66 (m, 2H), 1.96 – 1.88 (m, 1H), 1.80 – 1.72 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.0, 128.8, 128.5, 128.5, 126.0, 69.3, 39.0, 35.7, 27.9; **HRMS** *m/z* (ESI): calcd. for $C_{18}H_{16}ClF_6O$ $[M+Cl]^-$: 397.0799; found: 397.0801.



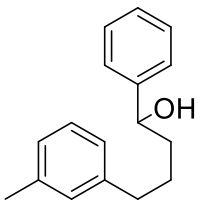
1dd: 1-(perfluorophenyl)-4-phenylbutan-1-ol. **1dd** was synthesized according to the general synthetic **method A.**

Yellow solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 5.07 – 5.04 (m, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.07 – 2.02 (m, 1H), 1.88 – 1.77 (m, 2H), 1.63 – 1.57 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 141.7, 128.6, 128.5, 126.2, 66.5, 36.6, 35.5, 27.7; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{13}ClF_5O$ $[M+Cl]^-$: 351.0581; found: 351.0615.



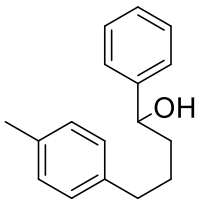
1ee: 1-phenyl-4-(o-tolyl)butan-1-ol. **1ee** was synthesized according to the general synthetic **method B**.

Yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 4.1 Hz, 4H), 7.31 – 7.26 (m, 1H), 7.14 – 7.07 (m, 4H), 4.70 (t, *J* = 6.6 Hz, 1H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.27 (s, 3H), 1.96 – 1.70 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.8, 140.6, 136.0, 130.3, 128.9, 128.6, 127.7, 126.0, 126.0, 126.0, 74.7, 39.0, 33.2, 26.5, 19.4; **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{20}NaO$ $[M+Na]^+$: 263.1406; found: 263.1397.



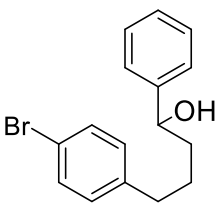
1ff: 1-phenyl-4-(m-tolyl)butan-1-ol. **1ff** was synthesized according to the general synthetic **method B**.

Yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 –7.32 (m, *J* = 7.35 Hz, 4H), 7.31 – 7.26 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.96 (m, 3H), 4.70 – 4.67 (m, 1H), 2.63 – 2.59 (m, 2H), 2.34 (s, 3H), 1.97(s, 1H), 1.97 – 1.72 (m, 3H), 1.68 – 1.59 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.7, 142.2, 137.8, 129.3, 128.5, 128.2, 127.6, 126.5, 126.0, 125.4, 74.4, 38.6, 35.7, 27.6, 21.4; **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{20}NaO$ $[M+Na]^+$: 263.1406; found: 263.1408.



1gg: 1-phenyl-4-(p-tolyl)butan-1-ol. **1gg** was synthesized according to the general synthetic **method B**.

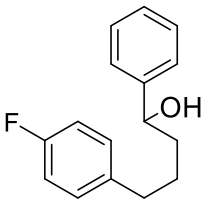
Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.36 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 7.09 – 7.03 (m, 4H), 4.70 – 4.67 (m, 1H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.89 – 1.68 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.8, 139.3, 135.2, 129.1, 128.5, 128.4, 127.6, 126.0, 74.6, 38.7, 35.4, 27.8, 21.1; **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{20}NaO$ $[M+Na]^+$: 263.1406; found: 263.1409.



1hh: 4-(4-bromophenyl)-1-phenylbutan-1-ol. **1hh** was synthesized according to the general synthetic **method B**.

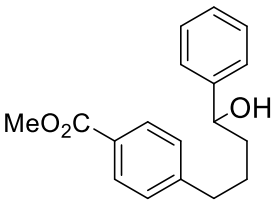
Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.39 – 7.34 (m, 3H), 7.34 – 7.26 (m, 4H), 7.04 – 7.00 (m, 2H), 4.69 – 4.66 (m, 1H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.74 – 1.70 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.6, 141.1,

131.3, 130.2, 128.5, 127.7, 125.8, 119.5, 74.5, 38.4, 35.1, 27.5; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{17}BrNaO$ $[M+Na]^+$: 327.0355; found: 327.0357.



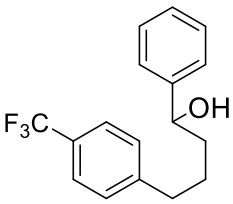
1ii: 4-(4-fluorophenyl)-1-phenylbutan-1-ol. **1ii** was synthesized according to the general synthetic **method B.**

Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.39 – 7.26 (m, 5H), 7.14 – 7.06 (m, 2H), 6.99 – 6.91 (m, 2H), 4.68 – 4.65 (m, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.04 (s, 1H), 1.88 – 1.69 (m, 3H), 1.65 – 1.53 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.2 (d, *J* = 244.4 Hz), 144.7, 137.8, 137.8, 129.7 (d, *J* = 7.1 Hz), 128.5, 127.6, 126.6, 125.9, 115.0 (d, *J* = 21.2 Hz), 74.5, 38.4, 34.9, 27.7. **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{17}FNaO$ $[M+Na]^+$: 267.1156; found: 267.1155.



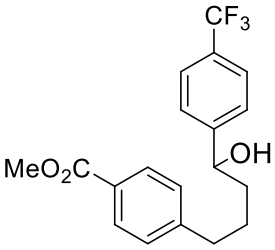
1jj: methyl 4-(4-hydroxy-4-phenylbutyl)benzoate. **1jj** was synthesized according to the general synthetic **method B.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.96 – 7.92 (m, 2H), 7.38 – 7.26 (m, 5H), 7.24 – 7.21 (m, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.54 (s, 1H), 1.86 – 1.62 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.3, 147.9, 144.8, 129.7, 128.7, 128.5, 128.0, 127.6, 125.9, 74.3, 52.0, 38.52, 35.8, 27.2; **HRMS** *m/z* (ESI): calcd. for $C_{18}H_{20}NaO_3$ $[M+Na]^+$: 307.1305; found: 307.1307.



1kk: 1-phenyl-4-(4-(trifluoromethyl)phenyl)butan-1-ol. **1kk** was synthesized according to the general synthetic **method B.**

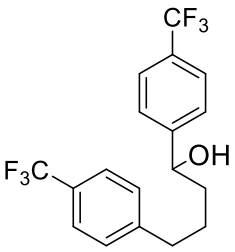
White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.30 – 7.25 (m, 2H), 4.71 (t, *J* = 5.9 Hz, 1H), 2.71 (t, *J* = 7.2 Hz, 2H), 1.94 (s, 1H), 1.91 – 1.74 (m, 3H), 1.70 – 1.62 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.5 (q, *J* = 2.0 Hz), 144.7, 128.8, 128.7, 128.3 (q, *J* = 32.3 Hz), 127.8, 126.0, 125.4(q, *J* =4.0 Hz), 124.5 (q, *J* = 272.7 Hz), 74.6, 38.5, 35.7, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2 (s); **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{17}F_3NaO$ $[M+Na]^+$: 317.1124; found: 317.1126.



1ll: methyl 4-(4-hydroxy-4-(4-(trifluoromethyl)phenyl)butyl)benzoate. **1ll** was synthesized according to the general synthetic **method B.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.95 – 7.90 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 4.75 (t, *J* = 5.9 Hz, 1H), 3.88 (s, 3H), 2.68 (t, *J* = 7.1 Hz, 2H), 2.14 (s, 1H), 1.85 – 1.70 (m, 3H), 1.67 – 1.60 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.30, 148.7 (q, *J* = 1.0 Hz), 147.6, 129.9, 129.7, 129.9 (q, *J* = 32.3 Hz), 128.6, 126.8 (q, *J* = 248.5 Hz), 126.2, 125.6 (q, *J*

= 4.0 Hz), 73.8, 52.1, 38.7, 35.8, 27.1; **^{19}F** NMR (376 MHz, $CDCl_3$) δ -62.4 (s); **HRMS** *m/z* (ESI): calcd. for $C_{19}H_{20}F_3O_3$ $[M+Na]^+$: 353.1359; found: 353.1361.



1mm: 1,4-bis(4-(trifluoromethyl)phenyl)butan-1-ol. **1mm** was synthesized according to the general synthetic **method B.**

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.80 – 4.77 (m, 1H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.05 – 2.04 (m, 1H), 1.86 – 1.72 (m, *J* = 18.1, 10.9, 9.1, 4.9 Hz, 3H), 1.71 – 1.64 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 148.6, 146.2, 129.9 (q, *J* = 32.3 Hz), 128.8, 128.4 (q, J = 29.3 Hz), 126.2, 125.4 (q, *J* = 3.0 Hz), 125.3 (q, *J* = 4.0 Hz), 73.9, 38.6, 35.6, 27.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3 (s), -62.4 (s); **HRMS** *m/z* (ESI): calcd. for $C_{18}H_{16}F_6NaO$ $[M+Na]^+$: 385.0998; found: 385.0996.

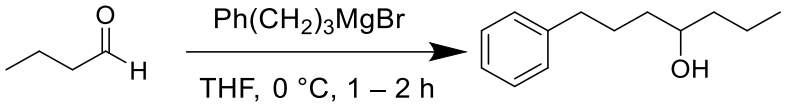
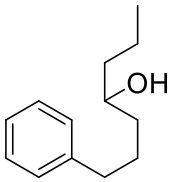


Figure S11. Synthesis of 1oo



1oo: 1-phenylheptan-4-ol. **1ll** was synthesized via the route shown in **Figure S11**.

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 3.63 (tt, *J* = 7.4, 4.5 Hz, 1H), 2.71 – 2.57 (m, 2H), 1.85 – 1.61 (m, 2H), 1.51 – 1.41 (m, 6H), 0.95 – 0.89 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.5, 128.5, 128.4, 125.8, 71.6, 39.8, 37.1, 36.0, 27.6, 18.9, 14.2; **HRMS** *m/z* (ESI): calcd. for $C_{13}H_{19}O$ $[M-H]^-$: 191.1441; found: 191.1426.

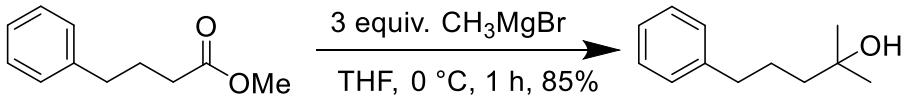
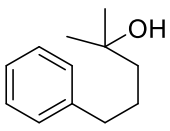


Figure S12. Synthesis of 1pp



1pp: 1-phenylheptan-4-ol.[5] **1pp** was synthesized via the route shown in **Figure S12**.

White solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.31 – 7.26 (m, 2H), 7.20 – 7.16 (m, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.68 (m, 2H), 1.67 – 1.49 (m, 2H), 1.21 (s, 6H).

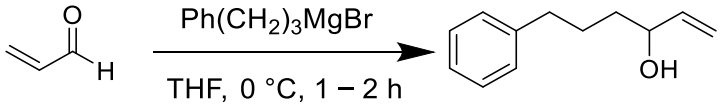
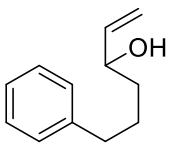
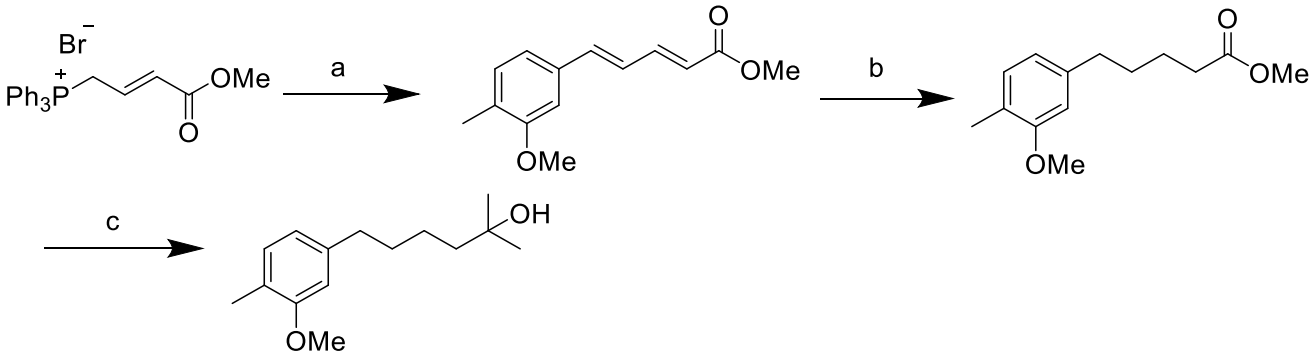


Figure S13. Synthesis of 1qq

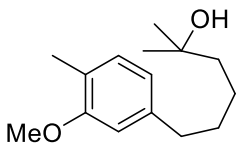


1qq: 1-phenylheptan-4-ol.[6] **1qq** was synthesized via the route shown in **Figure S13**. Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 2.1 Hz, 3H), 5.99 (dddd, *J* = 16.8, 10.5, 6.1, 2.1 Hz, 1H), 5.36 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.24 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 1H), 3.36 (s, 1H), 2.79 (td, *J* = 7.5, 2.1 Hz, 2H), 1.96 – 1.69 (m, 4H).



Reaction Condition:
a) NaH, THF, then 3-methoxy-4-methylbenzaldehyde, THF, 12 h, 72%. b) Pd/C, H_2, MeOH, rt, 12 h, 94%. c) CH_3MgBr, THF, 0 °C to rt, 1 h, 84%.

Figure S14. Synthesis of 1rr



1rr: 6-(3-methoxy-4-methylphenyl)-2-methylhexan-2-ol. **1rr** was synthesized via the route shown in **Figure S14**.

Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.04 (dd, *J* = 7.4, 0.9 Hz, 1H), 6.69 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.66 (d, *J* = 1.5, 0.9 Hz, 1H), 3.83 (s, 3H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.19 (s, 3H), 1.68 – 1.59 (m, 2H), 1.55 – 1.49 (m, 2H), 1.46 – 1.39 (m, 2H), 1.22 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.7, 141.6, 130.5, 123.9, 120.2, 110.4, 71.2, 55.4, 43.9, 36.1, 32.4, 29.4, 24.2, 16.0; **HRMS** *m/z* (ESI): calcd. for $C_{15}H_{24}ClO_2$ $[M+Cl]^-$: 271.1470; found 271.1488.

5 Products of intramolecular dehydrative Friedel-Crafts reaction and spectral data

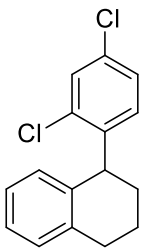
5.1 Preparation of (5% w/w) **Re_2O_7•SiO_2** or (10% w/w) **Re_2O_7•SiO_2** [7]

A slurry of SiO_2 (3.27 g) and of Re_2O_7 (0.172 g) in Et_2O (10 mL) was stirred in a round bottom flask at room temperature for 3 h, then the solvent was removed under reduced pressure. The resulting powder was dried under vacuum overnight. The catalyst was transferred to a vial, wrapped in aluminum foil, and stored in a desiccator.

A slurry of SiO_2 (2.98 g) and of Re_2O_7 (0.327 g) in Et_2O (10 mL) was stirred in a round bottom flask at room temperature for 3 h, then the solvent was removed under reduced pressure. The resulting powder was dried under vacuum overnight. The catalyst was transferred to a vial, wrapped in aluminum foil, and stored in a desiccator.

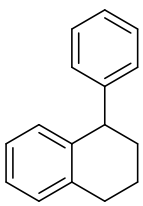
5.2 General **procedure C** for the Re_2O_7•SiO_2 mediated Friedel-Crafts alkylation.

To a solution of the substrate (0.1 mmol) in HFIP (0.2 mL) was added Re_2O_7•SiO_2 (5% w/w, 0.001 equiv). The reaction mixture was sealed in the reaction tube and stirred at room temperature for 1 hour. Then the reaction was quenched by adding 20 µl Et_3N, and the solvent was removed under vacuum. The crude mixture was then purified by flash column chromatography to afford the target product.



2a: 1-(2,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalene.

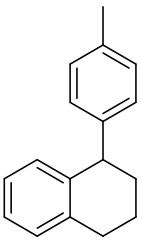
2a was synthesized according to the general synthetic **method C** with **1a** (29.5 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 µl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (26.6 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.40 (d, *J* = 2.2 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.06 (m, 2H), 6.78 (dd, *J* = 2.3, 8.6 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.60 (t, *J* = 6.2 Hz, 1H), 2.96 – 2.78 (m, 2H), 2.19 – 2.08 (m, 1H), 1.88 – 1.74 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 143.5, 138.1, 138.1, 134.5, 132.3, 131.9, 130.1, 129.3, 129.2, 127.0, 126.4, 126.1, 41.4, 30.6, 29.8, 20.6; **GC-MS** *m/z* (EI): calcd. for $C_{16}H_{14}Cl_2$ $[M]^+$: 276.05, found 276.10.



2b: 1-phenyl-1,2,3,4-tetrahydronaphthalene.[1]

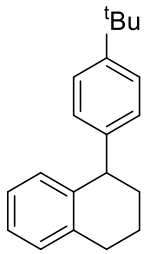
2b was synthesized according to the general synthetic **method C** with **1b** (22.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 µl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (20.0 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 7.16 – 7.07 (m, 4H), 7.06 – 7.00 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.12 (t, *J* = 6.8

Hz, 1H), 2.87 (m, 2H), 2.16 (m, 1H), 1.95 – 1.83 (m, 2H), 1.81 – 1.71 (m, 1H).



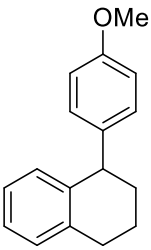
2c: 1-(p-tolyl)-1,2,3,4-tetrahydronaphthalene.[8]

2c was synthesized according to the general synthetic **method C** with **1c** (24.0 mg, 0.1 mmol), Re_2O_7•SiO_2 (9.6 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (20.7 mg, 93% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.16 – 7.07 (m, 4H), 7.06 – 6.97 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 1H), 2.88 (m, 2H), 2.33 (s, 3H), 2.15 (m, 1H), 1.95 – 1.69 (m, 3H).



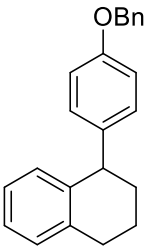
2d: 1-(4-*t*-butylphenyl)-1,2,3,4-tetrahydronaphthalene.

2d was synthesized according to the general synthetic **method C** with **1d** (28.2 mg, 0.1 mmol), Re_2O_7•SiO_2 (9.6 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (24.8 mg, 94% yield). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.29 – 7.27 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 1H), 3.17 (ddd, *J* = 17.0, 7.7, 5.4 Hz, 1H), 3.09 (dt, *J* = 16.9, 6.0 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.18 – 2.12 (m, 2H), 2.03 – 1.97 (m, 1H), 1.59 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 148.6, 144.4, 139.6, 137.5, 130.3, 129.0, 128.5, 125.9, 125.7, 125.1, 45.2, 34.4, 33.3, 31.6, 29.9, 21.0. **GC-MS** *m/z* (EI): calcd. for $C_{20}H_{24}$ $[M]^+$: 264.19; found: 264.19.



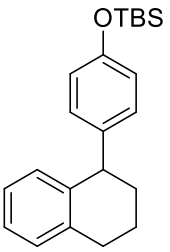
2e: 1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene.[2]

2e was synthesized according to the general synthetic **method C** with **1e** (25.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (23.3 mg, 98% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.15 – 7.11 (m, 2H), 7.07 – 7.01 (m, 3H), 6.88 – 6.83 (m, 3H), 4.09 (t, *J* = 6.7 Hz, 1H), 3.80 (s, 3H), 2.88 (m, 2H), 2.16 (m, 1H), 1.93 – 1.85 (m, 2H), 1.77 – 1.72 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.8, 139.8, 139.7, 137.5, 130.0, 129.7, 129.0, 125.6, 125.6, 113.4, 55.3, 44.8, 33.4, 29.8, 21.0.



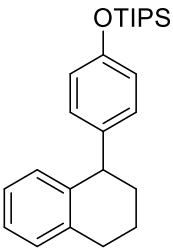
2f: 1-(4-(benzyloxy)phenyl)-1,2,3,4-tetrahydronaphthalene.

2f was synthesized according to the general synthetic **method C** with **1f** (33.2 mg, 0.1 mmol), Re_2O_7•SiO_2 (9.6 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 µl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a white solid (26.2 mg, 83% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.47 – 7.36 (m, 4H), 7.36 – 7.31 (m, 1H), 7.16 – 7.11 (m, 2H), 7.07 – 6.99 (m, 3H), 6.94 – 6.89 (m, 2H), 6.89 – 6.84 (m, 1H), 5.04 (s, 2H), 4.08 (t, J = 6.7 Hz, 1H), 2.98 – 2.79 (m, 2H), 2.21 – 2.10 (m, 1H), 1.95 – 1.69 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.2, 140.1, 139.8, 137.6, 137.3, 130.3, 129.8, 129.1, 128.7, 128.0, 127.6, 126.0, 125.7, 114.6, 70.1, 44.9, 33.4, 29.9, 21.1. **HRMS** *m/z* (ESI): calcd: for $C_{23}H_{22}NaO$ $[M+Na]^+$: 337.1563; found: 337.1516.



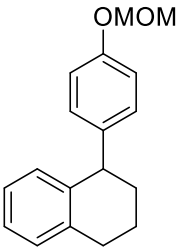
2g: tert-butyldimethyl(4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenoxy)silane.

2g was synthesized according to the general synthetic **method C** with **1g** (35.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (9.6 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 µl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a white solid (26.3 mg, 78% yield). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.16 – 7.11 (m, 2H), 7.05 (t, *J* = 7.0 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.78 – 6.76 (m, 2H), 4.07 (t, *J* = 6.7 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.18 – 2.13 (m, 1H), 1.94 – 1.83 (m, 2H), 1.80 – 1.75 (m, 1H), 1.01 (s, 9H), 0.22 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.8, 140.3, 139.9, 137.6, 130.3, 129.8, 129.0, 125.9, 125.7, 119.8, 45.0, 33.4, 29.9, 25.8, 21.1, 18.3, -4.2; **HRMS** *m/z* (ESI): calcd: for $C_{22}H_{31}OSi$ $[M+H]^+$: 339.2139; found: 339.2122



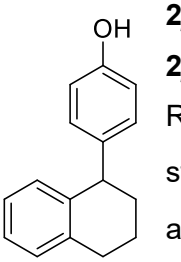
2h: triisopropyl(4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenoxy)silane.

2h was synthesized according to the general synthetic **method C** with **1h** (39.8 mg, 0.1 mmol), Re_2O_7•SiO_2 (9.6 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 µl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a white solid (20.1 mg, 53% yield). **^{1}H NMR** (600 MHz, Chloroform-d) 7.13 – 7.11 (m, 2H), 7.05 – 7.03 (m, 1H), 6.94 (dd, J = 8.5, 2.7 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.83 – 6.80 (m, 2H), 4.05 (t, *J* = 6.8 Hz, 1H), 2.94 – 2.82 (m, 2H), 2.17 – 2.12 (m, 1H), 1.91 – 1.83 (m, 2H), 1.79 – 1.73 (m, 1H), 1.27 (tdd, *J* = 15.1, 8.6, 5.0 Hz, 3H), 1.12 (dd, *J* = 7.7, 2.9 Hz, 18H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 154.3, 140.0, 134.0, 137.6, 130.2, 129.7, 129.0, 125.9, 125.7, 119.7, 45.0, 33.4, 29.9, 21.2, 18.1, 12.8. **HRMS** *m/z* (ESI): calcd: for $C_{25}H_{37}OSi$ $[M+H]^+$: 381.2608; found: 381.2602.



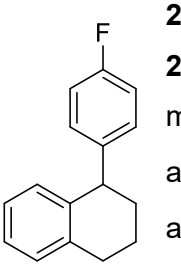
2i: 1-(4-(methoxymethoxy)phenyl)-1,2,3,4-tetrahydronaphthalene

2i was synthesized according to the general synthetic **method C** with **1i** (28.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (9.6 mg, 0.0001 mmol), and HFIP : DCM = 1:1 (0.2 mL). The reaction was stirred at - 20 °C for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a white solid (24.9 mg, 93% yield). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.21 – 7.16 (m, 2H), 7.11 – 7.08 (m, 3H), 7.04 – 7.03 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 2H), 4.15 (t, *J* = 6.6 Hz, 1H), 3.55 (s, 3H), 3.02 – 2.88 (m, 2H), 2.24 – 2.19 (m, 1H), 1.99 – 1.89 (m, 2H), 1.85 – 1.79 (m, 1H); ^{13}C NMR (151 MHz, Chloroform-d) δ 155.6, 141.1, 139.7, 137.6, 130.2, 129.8, 129.0, 126.0, 125.7, 116.1, 94.7, 56.0, 44.9, 33.4, 29.9, 21.0; **HRMS** *m/z* (ESI): calcd: for $C_{18}H_{20}NaO_2Si$ $[M+Na]^+$: 291.1356; found: 291.1362.



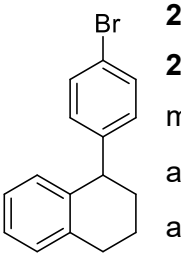
2j: 4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenol.[2]

2j was synthesized according to the following method with **1j** (24.3 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP : DCM = 1:1 (0.2 mL). The reaction was stirred at - 20 °C for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a white solid (22.0 mg, 98% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.13 (d, *J* = 6.0 Hz, 2H), 7.06 – 7.02 (m, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.78 (s, 1H), 4.08 (t, *J* = 6.7 Hz, 1H), 2.95 – 2.80 (m, 2H), 2.18 – 2.08 (m, 1H), 1.95 – 1.72 (m, 3H).



2k: 1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene.[9]

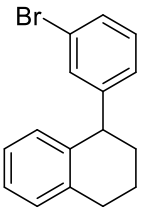
2k was synthesized according to the general synthetic **method C** with **1k** (24.4 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (20.1 mg, 89% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.15 – 7.09 (m, 2H), 7.04 (m, 3H), 7.00 – 6.92 (m, 2H), 6.83 – 6.80 (m, 1H), 4.11 (t, *J* = 6.6 Hz, 1H), 2.97 – 2.80 (m, 2H), 2.20 – 2.10 (m, 1H), 1.92 – 1.75 (m, 3H).



2l: 1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene.

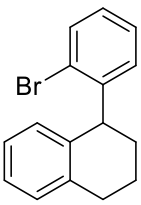
2l was synthesized according to the general synthetic **method C** with **1l** (30.5 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired

product as a colorless oil (26.4 mg, 92% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.41 – 7.26 (m, 2H), 7.21 – 6.93 (m, 5H), 6.86 – 6.73 (m, 1H), 4.09 (t, *J* = 6.7 Hz, 1H), 2.95 – 2.80 (m, 2H), 2.17 – 2.13 (m, 1H), 1.90 – 1.75 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.7, 138.8, 137.7, 131.4, 130.7, 130.2, 129.2, 126.3, 125.9, 119.9, 45.2, 33.3, 29.8, 20.9; **GC-MS** *m/z* (EI): $C_{16}H_{15}Br$ $[M]^+$: calcd. 286.04; found: 286.10.



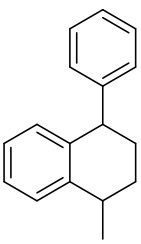
2m: 1-(3-bromophenyl)-1,2,3,4-tetrahydronaphthalene.

2m was synthesized according to the general synthetic **method C** with **1m** (30.5 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (27.3 mg, 95% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 – 7.34 (m, 1H), 7.16 (d, *J* = 4.0 Hz, 1H), 7.07 (ddd, *J* = 8.4, 5.2, 3.3 Hz, 3H), 7.06 – 7.02 (m, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.11 (t, *J* = 6.7 Hz, 1H), 3.01 – 2.83 (m, 2H), 2.24 – 2.15 (m, 1H), 1.96 – 1.72 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 150.1, 138.6, 137.7, 131.9, 130.2, 129.9, 129.2, 127.7, 126.3, 125.9, 122.6, 45.5, 33.3, 29.8, 21.0; **GC-MS** *m/z* (EI): calcd. for $C_{16}H_{15}Br$ $[M]^+$: 286.04; found: 286.10.



2n: 1-(2-bromophenyl)-1,2,3,4-tetrahydronaphthalene.

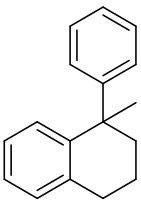
2n was synthesized according to the general synthetic **method C** with **1n** (30.5 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (28.1 mg, 98% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.59 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.06 (m, 2H), 6.86 – 6.80 (m, 2H), 4.65 (t, *J* = 6.4 Hz, 1H), 2.96 – 2.84 (m, 2H), 2.20 – 2.15 (m, 1H), 1.90 – 1.77 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.5, 138.8, 138.0, 132.8, 131.1, 130.2, 129.2, 127.6, 127.4, 126.2, 126.0, 124.8, 44.5, 31.0, 29.9, 20.8; **GC-MS** *m/z* (EI): calcd. for $C_{16}H_{15}Br$ $[M]^+$: 286.04; found: 286.10.



2o: 1-methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene.[10]

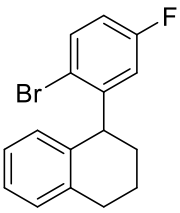
2o was synthesized according to the general synthetic **method C** with **1o** (24.0 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at r.t. for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (20.2 mg, 91% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 2H), 7.25 (d, *J* = 6.7 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.09 (m, 2H), 7.03 (m, 1H), 6.83 (m, 1H), 4.12 (t, J = 6.7 Hz, 1H), 3.02 (m, 1H), 2.07 – 1.88 (m, 3H), 1.60 (m, 1H), 1.35 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ

147.4, 142.8, 139.0, 130.0, 128.9, 128.2, 129.2, 126.0, 125.9, 125.6, 46.0, 32.7, 29.8, 28.7, 23.3.



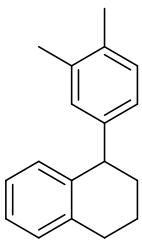
2p: 1-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene.[11]

2p was synthesized according to the general synthetic **method C** with **1p** (24.0 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (20.7 mg, 93% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.27 – 7.23 (m, 2H), 7.18 – 7.06 (m, 6H), 7.02 – 6.99 (m, 1H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.09 – 2.04 (m, 1H), 1.92 – 1.89 (m, 1H), 1.88 – 1.75 (m, 1H), 1.74 (s, 3H), 1.71 – 1.68 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 151.7, 144.5, 137.2, 129.3, 129.1, 127.9, 127.6, 125.9, 125.8, 125.6, 43.1, 41.6, 30.4, 30.2, 19.7.



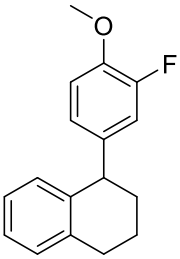
2q: 1-(5-bromo-2-fluorophenyl)-1,2,3,4-tetrahydronaphthalene.

2q was synthesized according to the general synthetic **method C** with **1q** (33.7 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (28.7 mg, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 (ddd, J = 8.6, 4.5, 2.6 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.11 – 7.04 (m, 1H), 7.00 – 6.97 (m, 1H), 6.97 – 6.92 (m, 1H), 6.83 (dd, *J* = 7.6, 1.0 Hz, 1H), 4.44 (t, *J* = 6.5 Hz, 1H), 2.96 – 2.80 (m, 2H), 2.15 – 2.09 (m, 1H), 1.93 – 1.76 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.0 (d, *J* = 246.1 Hz), 137.9, 137.4, 136.7 (d, *J* = 15.5 Hz), 133.6 (d, *J* = 4.8 Hz), 130.6 (d, *J* = 8.4 Hz), 129.8, 129.4, 126.5, 126.1, 117.2 (d, *J* = 24.4 Hz), 116.6 (d, *J* = 3.3 Hz), 38.5 (d, *J* = 2.2 Hz), 31.2, 29.7, 21.0; **GC-MS** *m/z* (EI) calcd. for $C_{16}H_{14}BrF$ $[M]^+$: 304.03; found: 304.10.



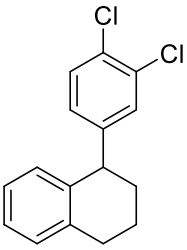
2r: 1-(3,4-dimethylphenyl)-1,2,3,4-tetrahydronaphthalene.

2r was synthesized according to the general synthetic **method C** with **1r** (25.4 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (22.2 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.20 – 7.12 (m, 2H), 7.11 – 7.04 (m, 2H), 6.95 (d, *J* = 1.9 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.87 (dd, *J* = 7.7, 1.9 Hz, 1H), 4.10 (t, *J* = 6.9 Hz, 1H), 2.93 (m, 2H), 2.29 (s, 3H), 2.29 (s, 3H), 2.23 – 2.15 (m, 1H), 2.01 – 1.75 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.1, 139.8, 137.6, 136.4, 134.2, 130.3, 130.2, 129.6, 129.0, 126.4, 125.9, 125.7, 45.4, 33.5, 30.0, 21.3, 20.0, 19.5; **GC-MS** *m/z* (EI): calcd. for $C_{18}H_{20}$ $[M]^+$: 236.16; found: 236.20.



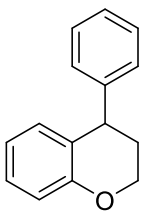
2s: 1-(3-fluoro-4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene.

2s was synthesized according to the general synthetic **method C** with **1s** (27.4 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (24.9 mg, 97% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.14 – 7.13 (m, 2H), 7.06 – 7.04 (m, 1H), 6.89 – 6.84 (m, 2H), 6.83 – 6.80 (m, 2H), 4.06 (t, *J* = 6.5 Hz, 1H), 3.88 (m, 3H), 2.93 – 2.81 (m, 2H), 2.16 – 2.12 (m, 1H), 1.90 – 1.74 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 152.4 (d, *J* = 245.1 Hz), 145.9 (d, *J* = 10.9 Hz), 140.9 (d, *J* = 5.4 Hz), 139.1, 137.6, 130.2, 129.2, 126.2, 125.8, 124.4 (d, *J* = 3.4 Hz), 116.5 (d, *J* = 18.1 Hz), 113.3 (d, *J* = 2.3 Hz), 56.5, 44.8 (d, *J* = 1.4 Hz), 33.3, 29.8, 20.9; **HRMS** *m/z* (ESI): calcd. for $C_{17}H_{18}FO$ $[M+H]^+$: 257.1336; found: 257.1338.



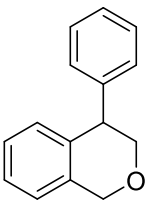
2t: 1-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalene.[12]

2t was synthesized according to the general synthetic **method C** with **1t** (29.5 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (25.5 mg, 92% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.33 (d, *J* = 8.3 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.06 (m, 1H), 6.92 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 1H), 2.97 – 2.78 (m, 2H), 2.21 – 2.10 (m, 1H), 1.91 – 1.71 (m, 3H).



2u: 4-phenylchromane.[13]

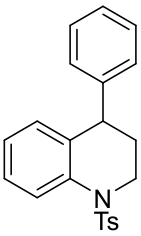
2u was synthesized according to the general synthetic **method C** with **1u** (22.8 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (20.6 mg, 98% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 7.15 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 3H), 6.92 – 6.79 (m, 3H), 4.24 – 4.18 (m, 3H), 2.33 (dq, *J* = 13.8, 5.8 Hz, 1H), 2.17 – 2.08 (m, 1H).



2v: 4-phenylisochromane.[14]

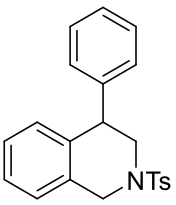
2v was synthesized according to the general synthetic **method C** with **1v** (22.8 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light

yellow oil (20.2 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.16 (m, 4H), 7.12 (ddd, *J* = 7.2, 6.8, 1.2 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.98 – 4.86 (m, 2H), 4.21 – 4.16 (m, 2H), 3.94 – 3.88 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 143.2, 136.5, 135.0, 129.7, 129.1, 128.6, 126.9, 126.8, 126.5, 124.3, 72.3, 68.6, 44.6.



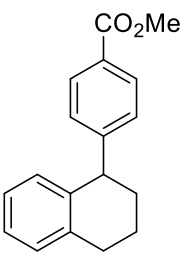
2w: 4-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline.

2w was synthesized according to the general synthetic **method C** with **1w** (38.1 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether to 5% ethyl acetate in petroleum ether) to give the desired product as a white solid (34.3 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.25 – 7.19 (m, 3H), 7.18 – 7.12 (m, 3H), 7.01 (td, *J* = 7.5, 1.3 Hz, 1H), 6.75 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.77 – 6.61 (m, 2H), 4.11 (ddd, *J* = 13.8, 5.8, 3.7 Hz, 1H), 3.86 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.73 (ddd, *J* = 13.6, 10.2, 3.2 Hz, 1H), 2.43 (s, 3H), 1.98 – 1.90 (m, 1H), 1.73 – 1.64 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.0, 143.7, 137.1, 136.8, 132.7, 130.3, 129.7, 128.4, 128.3, 127.4, 123.0, 126.5, 125.1, 124.7, 45.5, 43.4, 30.3, 21.6; **HRMS** *m/z* (ESI): calcd. for $C_{22}H_{22}NO_2S$ $[M+H]^+$: 364.1366; found: 364.1367.



2x: 4-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinoline.[15]

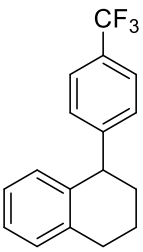
2x was synthesized according to the general synthetic **method C** with **1x** (38.1 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then was quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether to 5% ethyl acetate in petroleum ether) to give the desired product as a light yellow oil (34.9 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.67 – 7.65 (m, 2H), 7.31 – 7.23 (m, 5H), 7.21 – 7.14 (m, 1H), 7.13 – 7.07 (m, 4H), 6.87 – 6.85 (m, 1H), 4.51 (d, *J* = 14.9 Hz, 1H), 4.35 – 4.26 (m, 1H), 4.17 (d, *J* = 15.0 Hz, 1H), 3.80 (m, 1H), 3.06 (m, 1H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.5, 136.6, 132.1, 129.8, 129.7, 129.1, 128.7, 127.9, 127.2, 127.1, 126.8, 126.3, 51.2, 48.2, 45.4, 21.7.



2y: methyl-4-(1,2,3,4-tetrahydronaphthalen-1-yl)benzoate.[2]

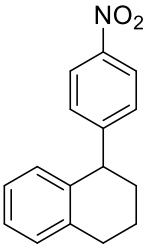
2y was synthesized according to the following method with **1y** (28.4 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 4 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether to 5% ethyl acetate in petroleum ether) to give the desired product as a light yellow oil (24.0 mg, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.97 – 7.94 (m, 2H), 7.19 – 7.13 (m, 4H), 7.03 (ddd, *J* = 7.6,

5.9, 2.8 Hz, 1H), 6.80 – 6.78 (m, 1H), 4.18 (t, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 2.97 – 2.82 (m, 2H), 2.20 – 2.15 (m, 1H), 1.93 – 1.83 (m, 3H), 1.80 – 1.76 (m, 1H).



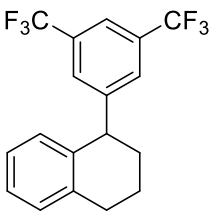
2z: 1-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalene.[2]

2z was synthesized according to the following method with **1z** (29.4 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 2 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (25.1 mg, 91% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.12 (m, 2H), 7.05 (m, 1H), 6.78 (d, J = 7.7 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 1H), 2.99 – 2.80 (m, 2H), 2.19 (m, 1H), 1.92 – 1.75 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 151.8 (q, *J* = 1.4 Hz), 138.4, 137.8, 130.2, 129.3, 129.3, 128.4 (q, *J* = 32.4 Hz), 125.8, 125.3 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 270.1 Hz), 45.6, 33.3, 29.8, 20.9.



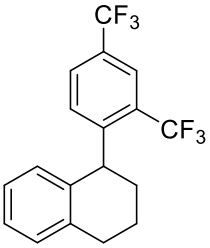
2aa: 1-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalene.

2aa was synthesized according to the following method with **1aa** (27.1 mg, 0.1 mmol), Re_2O_7•SiO_2 (4.8 mg, 0.0005 mmol), and HFIP (0.2 mL). The reaction was stirred at 50 °C for 8 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (22.8 mg, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.16 – 8.12 (m, 2H), 7.27 – 7.22 (m, 2H), 7.20 – 7.13 (m, 2H), 7.10 – 7.03 (m, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.25 (t, *J* = 6.5 Hz, 1H), 3.01 – 2.80 (m, 2H), 2.21 (m, 1H), 1.92 – 1.77 (m, 3H), **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.5, 146.5, 137.7, 130.1, 129.7, 129.5, 126.7, 126.1, 123.7, 45.7, 33.2, 29.7, 20.8; **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1176; found: 254.1177.



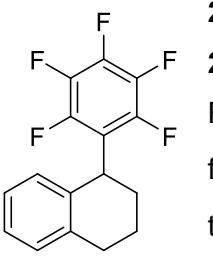
2bb: 1-(3,5-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalene.

2bb was synthesized according to the following method with **1bb** (36.2 mg, 0.1 mmol), Re_2O_7•SiO_2 (4.8 mg, 0.0005 mmol), and HFIP (0.2 mL). The reaction was stirred at 50 °C for 8 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (32.4 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.73 (d, *J* = 1.6 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.07 – 7.05 (m, 1H), 6.75 – 6.73 (m, 1H), 4.27 (t, *J* = 6.6 Hz, 1H), 3.00 – 2.84 (m, 2H), 2.25 – 2.19 (m, 1H), 1.91 – 1.77 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 150.2, 137.8, 137.3, 131.7 (q, *J* = 33.4, 33.0 Hz), 129.9, 129.6, 129.0 (q, *J* = 3.8 Hz), 126.9, 126.3, 123.6 (q, *J* = 272.5 Hz), 120.4 (q, *J* = 4.0 Hz), 45.7, 33.5, 29.7, 21.0; **GC-MS** *m/z* (EI): $C_{18}H_{14}F_6$ $[M]^+$: calcd. 344.10; found: 344.10.



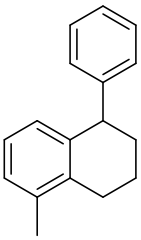
2cc: 1-(2,4-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalene.

2cc was synthesized according to the following method with **1cc** (36.2 mg, 0.1 mmol), Re_2O_7•SiO_2 (4.8 mg, 0.0005 mmol), and HFIP (0.2 mL). The reaction was stirred at 50 °C for 8 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (31.7 mg, 96% yield).**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.94 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.02 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.64 – 4.62 (m, 1H), 3.02 – 2.86 (m, 2H), 2.30 – 2.24 (m, 1H), 2.04 – 1.98 (m, 1H), 1.88 – 1.71 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 151.5, 138.6, 137.8, 132.3, 130.2, 129.3, 128.6 (q, J = 2.9 Hz), 126.5, 126.3, 122.9 (q, J = 11.2 Hz), 77.5, 77.2, 76.8, 41.5, 33.7, 29.9, 21.9; **GC-MS** *m/z* (EI): calcd. for $C_{18}H_{14}F_6$ $[M]^+$: 304.10; found: 304.10.



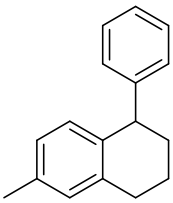
2dd: 1-(perfluorophenyl)-1,2,3,4-tetrahydronaphthalene.

2dd was synthesized according to the following method with **1dd** (31.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (4.8 mg, 0.0005 mmol), and HFIP (0.2 mL). The reaction was stirred at 50 °C for 8 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a yellow oil (28.6 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.15 – 7.09 (m, 2H), 7.08 – 6.99 (m, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.54 (m, 1H), 3.00 – 2.82 (m, 2H), 2.19 – 1.93 (m, 3H), 1.88 – 1.80 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 137.1, 136.5, 129.4, 127.6, 126.5, 126.2, 35.4, 30.2, 29.7, 23.1; **GC-MS** *m/z* (EI): calcd. for $C_{16}H_{11}F_5$ $[M]^+$: 298.08; found: 298.10.



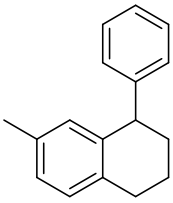
2ee: 5-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene.

2ee was synthesized according to the general synthetic **method C** with **1ee** (24.0 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (21.6 mg, 97% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.25 – 7.18 (m, 1H), 7.13 – 7.06 (m, 2H), 7.02 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 4.16 (t, *J* = 6.4 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.29 (s, 3H), 2.17 – 2.12 (m, 1H), 1.98 – 1.84 (m, 2H), 1.84 – 1.78 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.8, 139.4, 136.4, 136.2, 129.0, 128.3, 128.2, 127.6, 126.0, 125.3, 46.0, 32.7, 27.1, 20.7, 19.9; **GC-MS** *m/z* (EI): calcd. for $C_{17}H_{18}$ $[M]^+$: 222.14; found: 222.20.



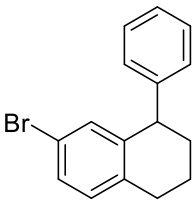
2ff: 6-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene.

2ff was synthesized according to the general synthetic **method C** with **1ff** (24.0 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (20.0 mg, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.33 – 7.19 (m, 3H), 7.15 – 7.10 (m, 2H), 6.99 (dd, *J* = 5.5 Hz, 1.8 Hz, 1H), 6.88 (dd, *J* = 7.9 Hz, 1.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H),4.25 (t, *J* = 6.8 Hz, 0.16H), 4.10 (t, *J* = 6.8 Hz, 0.84H), 2.95 – 2.78 (m, 2H), 2.32 (s, 3H), 2.21 – 2.12 (m, 1H), 1.94 – 1.86 (m, 2H) , 1.81 – 1.70 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.8, 140.6, 136.0, 130.3, 128.9, 128.6, 127.7, 126.0, 126.0, 126.0, 74.7, 39.0, 33.2, 26.5, 19.4; **GC-MS** *m/z* (EI): calcd. for $C_{17}H_{18}$ $[M]^+$: 222.14; found: 222.20.



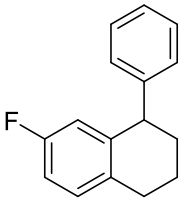
2gg: 7-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene.

2gg was synthesized according to the general synthetic **method C** with **1gg** (24.0 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (20.7 mg, 93% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.12 – 7.07 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.66 (s, 1H), 4.08 (t, *J* = 6.6 Hz, 1H), 2.91 – 2.76 (m, 2H), 2.18 (s, 3H), 2.16 – 2.10 (m, 1H), 1.90 – 1.83 (m, 2H), 1.78 – 1.68 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.8, 139.2, 135.1, 134.7, 130.8, 129.0, 129.0, 128.3, 127.0, 126.0, 45.7, 33.5, 29.5, 21.1, 21.1; **GC-MS** *m/z* (EI): calcd. for $C_{17}H_{18}$ $[M]^+$: 222.14; found: 222.20.



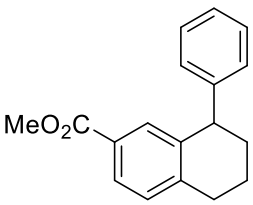
2hh: 7-bromo-1-phenyl-1,2,3,4-tetrahydronaphthalene.

2hh was synthesized according to the following method with **1hh** (30.5 mg, 0.1 mmol), Re_2O_7 (0.48 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at 80 °C for 2 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a lolorless oil (24.4 mg, 85% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 (dd, *J* = 8.1 Hz, 6.5Hz, 2H), 7.25 – 7.20 (m, 2H), 7.10 – 7.05 (m, 2H), 7.03 – 6.97 (m, 2H), 4.08 (t, *J* = 6.8 Hz, 1H), 2.92 – 2.72 (m, 2H), 2.18 – 2.10 (m, 1H), 1.93 – 1.81 (m, 2H), 1.78 – 1.68 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.9, 142.0, 136.8, 133.0, 130.9, 129.3, 129.0, 128.7, 126.5, 119.5, 45.8, 33.2, 29.6, 21.0; **GC-MS** *m/z* (EI): calcd. for $C_{16}H_{15}Br$ $[M]^+$: 286.04; found: 286.00.



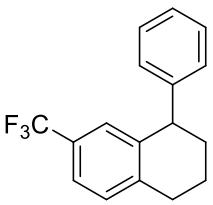
2ii: 7-fluoro-1-phenyl-1,2,3,4-tetrahydronaphthalene.

2ii was synthesized according to the following method with **1ii** (24.4 mg, 0.1 mmol), Re_2O_7 (0.48 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at 80 °C for 2 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (10.2 mg, 45% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 7.14 – 7.06 (m, 3H), 6.84 (td, *J* = 8.4 Hz, 2.8 Hz, 1H), 6.55 (dd, *J* = 10.2 Hz, 2.7 Hz, 1H), 4.09 (t, *J* = 6.9 Hz, 1H), 2.93 – 2.76(m, 2H), 2.22 – 2.11 (m, 1H), 1.96 – 1.83 (m, 2H), 1.82 – 1.70 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.0 (d, *J* = 244.4 Hz), 146.7, 141.4 (d, *J* = 6.1 Hz), 133.1 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 7.1 Hz), 128.8, 128.4, 126.2, 116.2 (d, *J* = 15.1 Hz), 113.1 (d, *J* = 21.2 Hz), 45.9, 45.9, 33.0, 29.1, 21.2; **GC-MS** *m/z* (EI): calcd. for $C_{16}H_{15}F$ $[M]^+$: 226.12; found: 226.20.



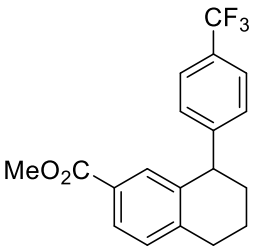
2jj: methyl-8-phenyl-5,6,7,8-tetrahydronaphthalene-2-carboxylate.

2jj was synthesized according to the following method with **1jj** (28.4 mg, 0.1 mmol), Re_2O_7 (0.48 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at 100 °C for 12 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether to 5% ethyl acetate in petroleum ether) to give the desired product as a colorless oil (11.9 mg, 45% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.78 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.56 (t, *J* = 1.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 2H), 7.08 – 7.02 (m, 2H), 4.17 (t, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 2.92 (qt, J = 17.4, 6.4 Hz, 2H), 2.20 – 2.13 (m, 1H), 1.93 – 1.83 (m, 2H), 1.80 – 1.70 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ167.3, 146.9, 143.3, 139.4, 131.6, 129.2, 128.8, 128.4, 127.7, 1267.0, 126.1, 51.9, 45.3, 33.0, 30.0, 20.3; **HRMS** *m/z* (ESI): calcd. for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1380; found: 267.1380.



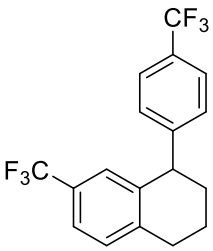
2kk: 1-phenyl-7-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene.

2kk was synthesized according to the following method with **1kk** (29.4 mg, 0.1 mmol), Re_2O_7 (0.48 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at 100 °C for 2 h, then was quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (12.4 mg, 45% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.30 (dd, *J* = 8.2 Hz, 6.5 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.12 (s, 1H), 7.07 (dd, *J* = 7.1 Hz, 1.7 Hz, 2H), 4.15 (t, *J* = 6.6 Hz, 1H), 2.91(m, ddt, *J* = 23.5, 17.3, 8.3 Hz, 2H), 2.22 – 2.14 (m, 1H), 1.96 – 1.85 (m, 2H), 1.83 – 1.70 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.6, 141.9 (q, *J* = 2.0 Hz), 140.2, 129.6, 128.8, 128.6, 127.1(q, *J* = 4.0 Hz), 126.5, 124.3 (q, *J* = 223.2 Hz), 122.7 (q, *J* = 4.0 Hz), 45.6, 33.1, 29.9, 20.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3 (s); **GC-MS** *m/z* (EI): calcd. for $C_{17}H_{15}F_3$ $[M]^+$: 276.11; found: 276.10.



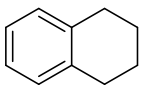
2ll: methyl-8-(4-(trifluoromethyl)phenyl)-5,6,7,8-tetrahydronaphthalene-2-carboxylate.

2ll was synthesized according to the following method with **1ll** (35.2 mg, 0.1 mmol), Re_2O_7 (0.96mg, 0.002 mmol), and HFIP (0.2 mL). The reaction was stirred at 100 °C for 48 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether to 10 ethyl acetate in petroleum ether) to give the desired product as a colorless oil (28.4mg, 85% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.81 (ddd, *J* = 8.0, 1.9, 0.6 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.16 (m, 2H), 4.24 (t, *J* = 6.3 Hz, 1H), 3.82 (s, 3H), 3.02 – 2.84 (m, 2H), 2.23 – 2.14 (m, 1H), 1.92 – 1.82 (m, 2H), 1.79 – 1.76 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.2, 151.1, 143.4, 138.5, 131.6, 129.5, 129.2, 128.1, 127.5, 125.5 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 272.7 Hz), 52.1, 45.3, 33.0, 30.0, 20.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3 (s); **HRMS** *m/z* (ESI): calcd. for $C_{19}H_{18}F_3O_2$ $[M+H]^+$: 335.1253; found: 335.1256.



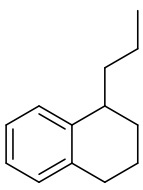
2mm: 7-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalene.

2mm was synthesized according to the following method with **1mm** (36.2 mg, 0.1 mmol), Re_2O_7 (0.96 mg, 0.002 mmol), and HFIP (0.2 mL). The reaction was stirred at 100 °C for 48 hours, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (21.3 mg, 62% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.39 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 4.23 (t, *J* = 6.5 Hz, 1H), 3.04 – 2.83 (m, 2H), 2.26 – 2.12 (m, 1H), 1.95 – 1.72 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 150.6, 141.9, 139.1, 129.8, 129.1, 129.0, 128.7, 128.3, 126.9 (q, *J* = 3.0 Hz), 125.6 (q, *J* = 3.0 Hz), 125.3, 123.4, 123.1 (q, *J* = 3.0 Hz), 45.4, 33.0, 29.8, 20.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3 (s); **GC-MS** *m/z* (EI): calcd. for $C_{18}H_{14}F_6$ $[M]^+$: 334.10; found: 334.10.



2nn: 1,2,3,4-tetrahydronaphthalene. [16]

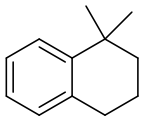
2nn was synthesized according to the following method with **1nn** (15 mg, 0.1 mmol), Re_2O_7 (0.96 mg, 0.001 mmol), and HFIP (0.2 mL). The reaction was stirred at 100 °C for 48 hours, then quenched with 20 μl Et_3N, the yield was determined by analyzing ^{1}H NMR of the reaction mixture using Mesitylene as the internal standard.



2oo: 1-propyl-1,2,3,4-tetrahydronaphthalene.[9]

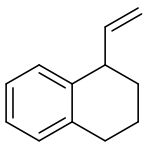
2oo was synthesized according to the general synthetic **method C** with **1oo** (19.2 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then was quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product

as a light yellow oil (16.4 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7. 26 – 7.22 (m, 1H), 7.18 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.14 – 7.10 (m, 2H), 2.84 – 2.79 (m, 3H), 1.92 – 1.81 (m, 2H), 1.74 – 1.38 (m, 6H), 0.96 (t, *J* = 7.3 Hz, 3H).



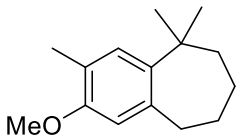
2pp: 1,1-dimethyl-1,2,3,4-tetrahydronaphthalene.[17]

2pp was synthesized according to the general synthetic **method C** with **1pp** (17.8 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (15.2 mg, 95% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.11 – 7.04 (m, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.72 – 1.66 (m, 2H), 1.31 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.9, 136.3, 126.8, 125.9, 125.4, 39.5, 34.0, 32.0, 30.9, 19.9.



2qq: 1-vinyl-1,2,3,4-tetrahydronaphthalene.[6]

2qq was synthesized according to the general synthetic **method C** with **1qq** (17.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a colorless oil (13.1 mg, 83% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.19 – 7.07 (m, 4H), 7.34 (d, *J* = 2.1 Hz, 3H), 5.89 (ddd, *J* = 16.8, 10.5, 8.1 Hz, 1H), 5.10 (ddd, *J* = 10.1, 1.9, 0.7 Hz, 1H), 5.04 (ddd, *J* = 17.0, 2.0, 1.1 Hz, 1H), 3.47 (q, *J* = 6.9 Hz, 1H), 2.84 – 2.75 (m, 2H), 2.01 – 1.84 (m, 2H), 1.82 – 1.69 (m, 2H).



2rr: 2-methoxy-3,5,5-trimethyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene.

2rr was synthesized according to the general synthetic **method C** with **1rr** (23.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at room temperature for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (21.4 mg, 98% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.13 (s, 1H), 6.56 (s, 1H),3.81 (s, 3H) 2.93 – 2.90(m, 2H), 2.19 (s, 3H), 1.90 – 1.80 (m, 2H), 1.66 (ddd, *J* = 9.3, 5.8, 2.9 Hz, 4H), 1.35 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.3, 140.7, 140.3, 129.4, 123.1, 113.4, 55.4, 42.1, 38.7, 37.6, 30.6, 28.5, 26.7, 16.1; **HRMS** *m/z* (ESI): calcd. for $C_{15}H_{23}O$ $[M+H]^+$: 219.1743; found: 219.1745.

6 Gram scale experiments

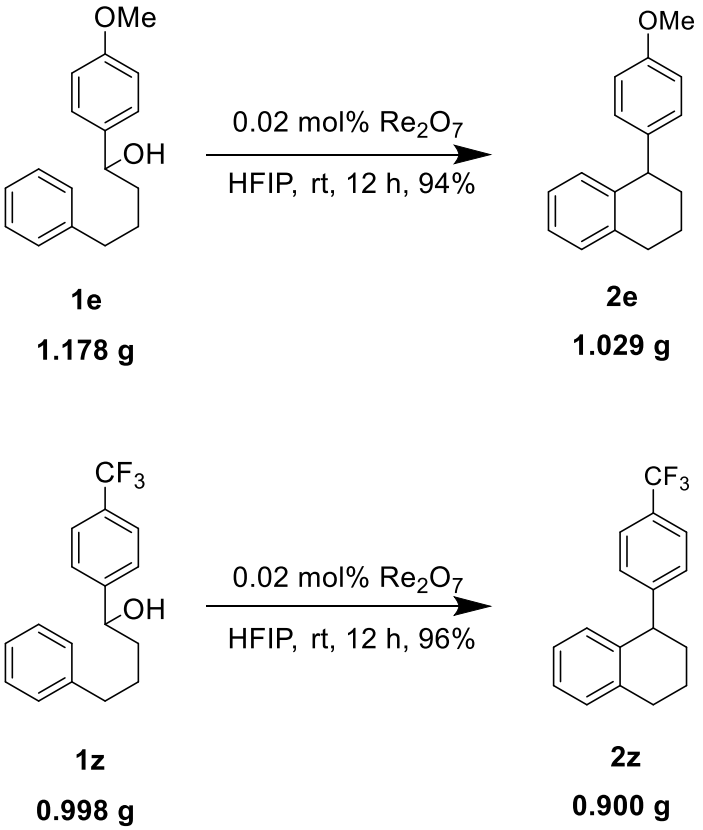


Figure S15. Gram scale experiments

Detailed **experimental procedure** for the gram experiments:

General reaction protocol was followed with **1e** (1.178 g, 5 mmol, 1 equiv.), Re_2O_7 (0.48 mg, 0.001 mmol, 0.0002 equiv.), and HFIP (10.0 mL). The reaction was stirred at room temperature for 12 hours, then quenched with 20 µl Et_3N, concentrated under vacuum followed by purification through flash chromatography (100% petroleum ether) to give the desired product (1.029 g, 94% yield).

General reaction protocol was followed with **1z** (0.998 g, 3.3 mmol, 1 equiv.), Re_2O_7 (0.32 mg, 0.00066 mmol, 0.0002 equiv.), and HFIP (0.2 mL). The reaction was stirred at room temperature for 12 hours, then quenched with 20 µl Et_3N, concentrated under vacuum followed by purification through flash chromatography (100% petroleum ether) to give the desired product (0.900 g, 96% yield).

7 Synthetic applications and spectral data

7.1 formal synthesis of **Nafenopine.**

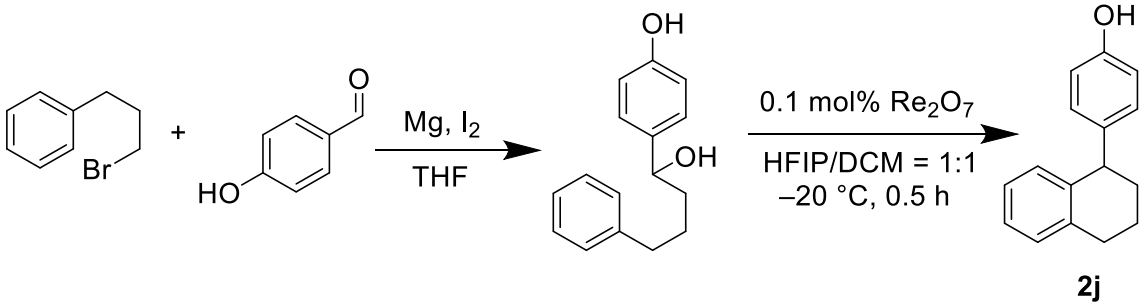


Figure S16. Synthesis of key intermediate 2e to Nafenopine

7.2 formal synthesis of **Sertraline.**

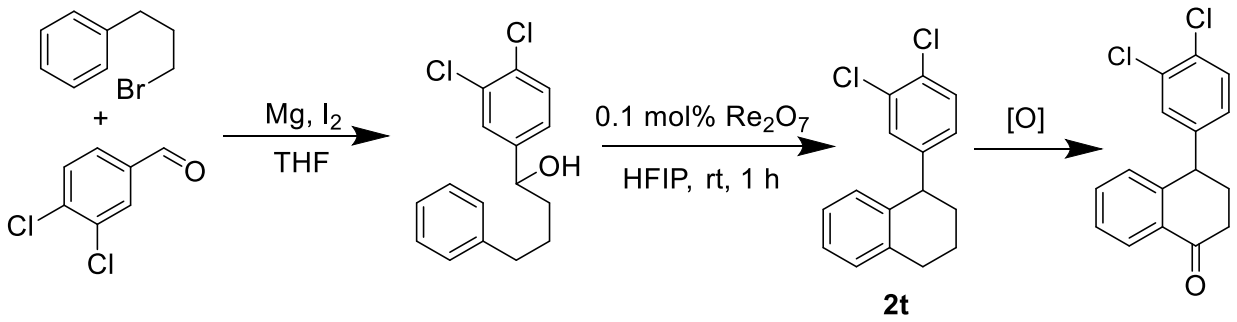


Figure S17. Synthesis of key intermediate 2q to Sertraline

7.3 formal synthesis of **9 (estrogen and androgen receptor).**

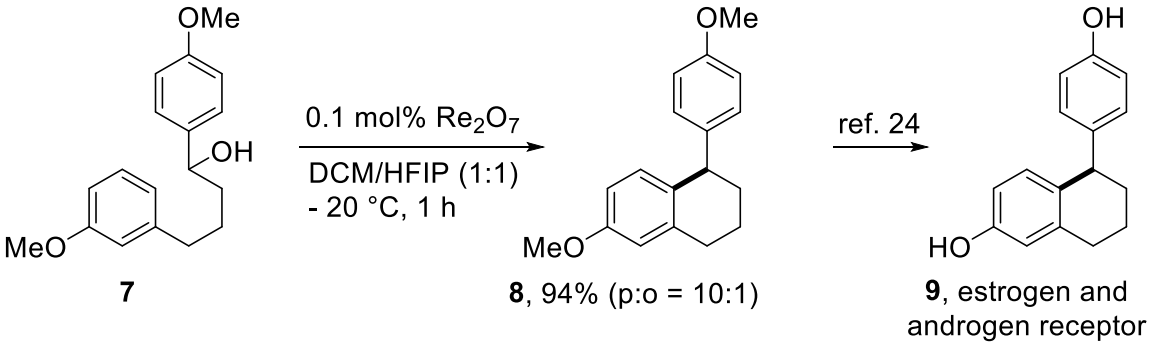
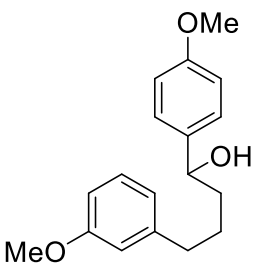


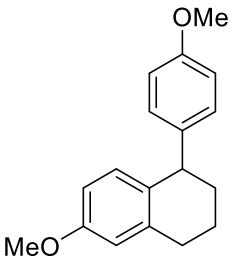
Figure S18. Synthesis of key intermediate 8 to estrogen and androgen receoptor 9



7: 4-(3-methoxyphenyl)-1-(4-methoxyphenyl)butan-1-ol[18].

7 was synthesized according to the general synthetic **method B** as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d)) δ 7.32 – 7.15 (m, 3H), 6.92 – 6.86 (m, 2H), 6.76 – 6.68 (m, 3H), 4.65 (d, *J* = 5.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.62 (dd, *J* = 8.4, 6.3 Hz, 2H), 1.94 – 1.71 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ

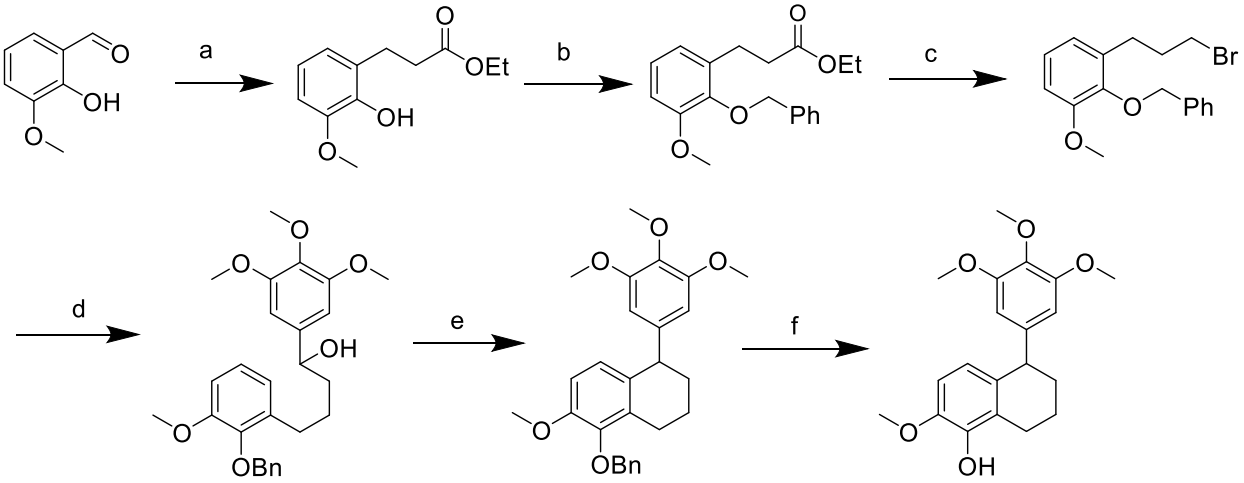
159.6, 159.0, 144.0, 136.9, 129.2, 127.2, 120.9, 114.2, 113.8, 111.0, 74.1, 55.3, 55.1, 38.5, 35.8, 27.6.



8: 6-methoxy-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene[19].

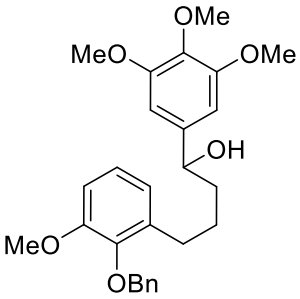
8 was synthesized according to the following method with **7** (28.6 mg, 0.1 mmol), Re_2O_7•SiO_2 (0.96 mg, 0.0001 mmol), and HFIP : DCM = 1:1 (0.2 mL). The reaction was stirred at – 20 °C for 1 hour, then quenched with 20 μl Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether) to give the desired product as a light yellow oil (25.2 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.04 – 6.98 (m, 2H), 6.85 – 6.79 (m, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 6.61 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.91 – 2.77 (m, 2H), 2.11 (s, 1H), 1.91 – 1.68 (m, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.9, 157.7, 138.8, 132.1, 131.2, 129.7, 113.7, 113.4, 112.2, 55.4, 55.3, 44.2, 33.7, 30.3, 21.1.

7.4 total synthetic of an isoCA-4 analogue.

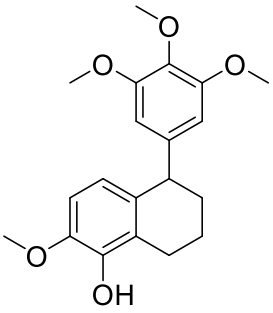


Reaction Condition:a)
(1) 2-Ethoxy-2-oxoethylidene)triphenylphosphorane, DCM, rt, 12 h, (2) Pd/C, H_2 ,MeOH, 12 h, 2 steps, 86%.b) (bromomethyl)benzene, MeCN, K_2CO_3, reflux, 36 h, 95%. c) (1) $LiAlH_4$,THF, 0 °C to rt, 1 h.(2) NBS, PPh_3, DCM , 0 °C to rt, 2 h, 2 steps, 86%. d) Mg, I_2, THF, then 3,4,5-trimethoxybenzaldehyde, THF, 0 °C to rt, 1 h, 36%.e) 0.001 equiv Re_2O_7, HFIP, rt, 1 h, 96%. f) Pd/C, H_2, MeOH, rt, 12 h, 95%.

Figure 19. Total synthesis of an isoCA-4 analogue

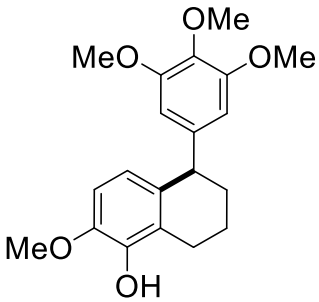


10: 4-(2-(benzyloxy)-3-methoxyphenyl)-1-(3,4,5-trimeth-oxyphenyl)butan-1-ol. Light yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.51 (s, 2H), 4.97 (s, 2H), 4.57 (m, 1H), 3.87 (s, 3H), 3.83 (s, 6H), 3.82 (s, 3H), 2.63 (t, *J* = 7.0 Hz, 2H), 1.81 – 1.64 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.3, 152.9, 140.8, 138.2, 136.4, 128.4, 128.1, 127.9, 124.0, 122.0, 110.3, 102.9, 74.8, 74.6, 60.9, 56.2, 55.8, 38.8, 29.8, 26.9; **HRMS** *m/z* (ESI): calcd. for $C_{27}H_{32}NaO_6$ [M+Na]$^+$: 475.2901; found: 475.2917.



11: 5-(benzyloxy)-6-methoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene.

General reaction protocol was followed with **9** (45.35 mg, 0.1 mmol), Re_2O_7 (0.97 mg, 0.0001 mmol), and HFIP (0.2 mL). The reaction was stirred at at 100 °C for 48 hours, then quenched with Et_3N, concentrated under vacuum and purified through flash chromatography (100% petroleum ether to 20% ethyl acetate in petroleum ether) to give the desired product as a light yellow oil (41.2 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.52 – 7.48 (m, 2H), 7.42 – 7.30 (m, 3H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 1H), 6.29 (s, 2H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 3.98 (t, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.78 (s, 6H), 2.81 (m, 2H), 2.10 – 2.03 (m, 1H), 1.87 – 1.77 (m, 2H), 1.72 – 1.63 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.0, 150.7, 145.1, 143.5, 138.3, 136.2, 132.7, 132.3, 128.5, 128.2, 128.0, 125.7, 110.2, 106.0, 74.1, 61.0, 56.2, 55.9, 45.7, 33.0, 24.2, 20.7; **GC-MS** *m/z* (EI): calcd. for $C_{27}H_{30}O_5$ [M]$^+$: 434.21; found: 434.20.



isoCA-4 analogue (5): (R)-2-methoxy-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphthalen-1-ol.[20]

^{1}H NMR (400 MHz, Chloroform-d) δ 6.65 (d, *J* = 8.5 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 6.34 (s, 2H), 5.72 (s, 1H), 3.99 (dd, *J* = 7.9, 5.4 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.81 (s, 6H), 2.83 (dt, *J* = 19.9, 6.5 Hz, 2H), 2.20 – 2.02 (m, 1H), 2.02 – 1.71 (m, 4H).

8 Catalyst Recovery Experiment

8.1 Experimental details I

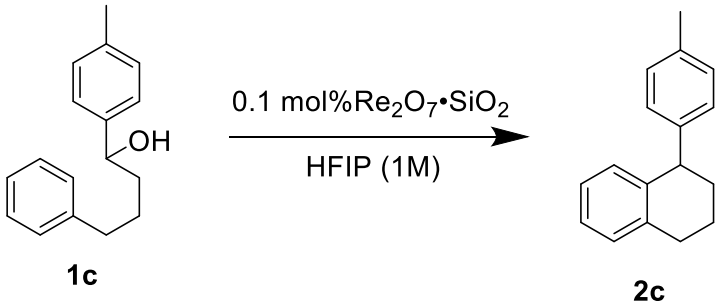


Figure 20. Catalyst Recovery Experiment I

Initial experiment: Select **1c** as the substrate for the catalyst recycling experiment. To a solution of the **1c** (0.608 g, 2.69 mmol) in HFIP (2.7 mL) was added Re_2O_7•SiO_2 (13.5 mg, 10% w/w, 0.001 equiv). The reaction mixture was sealed in the reaction tube and stirred at room temperature for 5 minutes. After monitoring the reaction, it was found that the cyclic product **2c** was the only product, and no starting material remained in the system. Then the reaction was not quenched, and the solvent was removed under vacuum. The crude product was filtered through a simple small silica gel column with a small amount of silica gel. The catalyst catalyzed the Friedel-Crafts dehydration alkylation of **1c** for the first time with a yield of 99%.The catalyst in the reaction was supported on a small amount of silica gel on the small silica gel column.

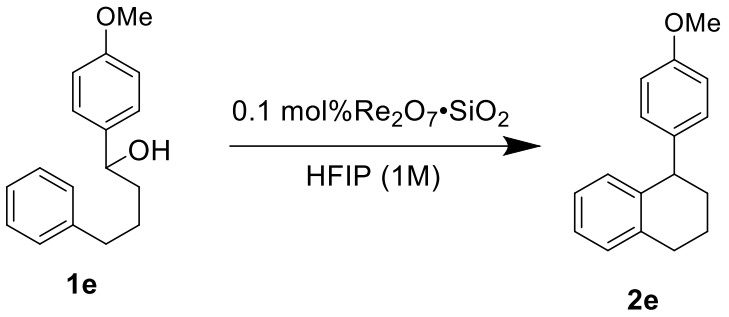
First recycling: The catalyst recovered for the first time was added to the solution of the **1c** (0.589 g, 2.60 mmol) in HFIP (2.6 ml), the reaction mixture was sealed in the reaction tube and stirred at room temperature for 5 minutes. The cyclic product **2c** was found to be the only product by monitoring the reaction, and there was no remaining raw material in the system. The reaction results were similar to the first catalytic cycle of the catalyst. The yield of the catalyst for the second catalyzed Friedel-Crafts dehydration alkylation of **1c** was 96%, and the catalyst recovered for the second time was obtained by the same method.

Second recycling: The catalyst recovered for the second time was added to the solution of the **1c** (0.597 g, 2.64 mmol) in HFIP (2.7 ml), the reaction mixture was sealed in the reaction tube and stirred at room temperature for 5 minutes. The cyclic product **2c** was found to be the only product by monitoring the reaction, and there was no remaining raw material in the system. The third reaction results were the same as the first two catalytic cycles of the catalyst. The yield of the catalyst for the third Friedel-Crafts alkylation dehydration alkylation of **1c** was 99%, and the catalyst recovered for the third time was obtained by the same method.

Third recycling: The catalyst recovered for the third time was added to the solution of the **1c** (0.608 g, 2.69 mmol) in HFIP (2.7 ml), the reaction mixture was sealed in the reaction tube and stirred at room temperature for 5 minutes. After monitoring the reaction, it was found that there was basically no product

in the system. The system was stirred at room temperature for 41 hours, and a large amount of raw materials remained in the system. **This results indicated that Re_2O_7 was active for at least three cycles of reactions, but gradually lost catalytic efficiency.**

8.2 Experimental details Ⅱ



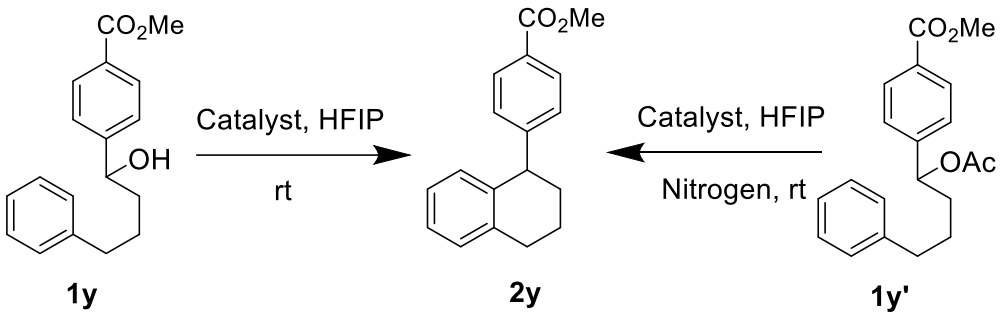
1e **2e**

Figure 21. Catalyst Recovery Experiment Ⅱ

Select **1e** as the substrate for the catalyst recycling experiment . To a solution of the **1e** (0.604 g, 2.36 mmol) in HFIP (2.4 mL) was added Re_2O_7•SiO_2 (11.5 mg, 10% w/w, 0.001 equiv). The reaction mixture was sealed in the reaction tube and stirred at room temperature for 5 minutes. After monitoring the reaction, it was found that the cyclic product **2e** was the only product, and no starting material remained in the system. Then the reaction was not quenched, and the solvent was not removed under vacuum. The reaction system was directly filtered with a simple column with only cotton, and the residual material on the cotton was used as the recovered catalyst.

The residues from the cotton was added to the solution of the **1e** (0.615 g, 2.40 mmol) in HFIP (2.4 ml), the reaction mixture was sealed in the reaction tube and stirred at room temperature for 5 minutes. After monitoring the reaction, it was found that there was basically no product in the system. **This results indicated that Re_2O_7 was dissolved in the highly polar HFIP, and pointed to a homogeneous catalysis.**

9 Control Experiments



0.1 mol% Re_2O_7 (98%, 4h)

0.2 mol% $HReO_4$ (97%, 2.5h)

0.2 mol% TfOH (98%, 2.5h)

pK_a of $HReO_4$: -1.25
pK_a of TfOH : -14

0.1 mol% Re_2O_7 (trace, 4h)

0.2 mol% $HReO_4$ (10%, 2.5h)

0.2 mol% TfOH (94%, 2.5h)

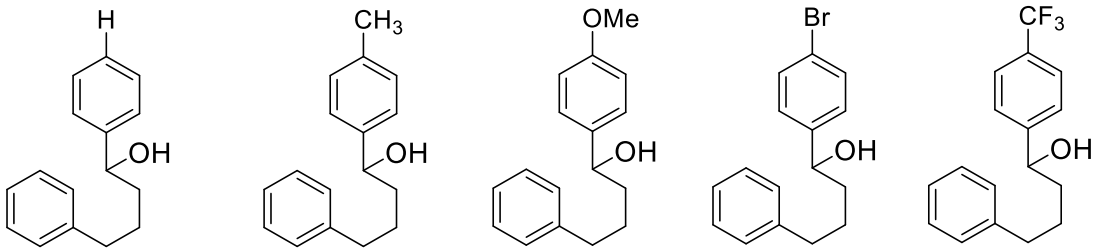
Figure 22. Control experiment details

1y' was chosen as the substrate to verify the possible mechanism in the Rhenium oxide catalytic system. **1y'** was placed into a Schlenk reaction tube, then ultra-dry toluene was used to remove the possible residual water in the substrate under a vacuum pump, then store the system in a nitrogen environment, add Hexafluoroisopropanol (it was dry and kept under nitrogen), and 0.1 mol% of Re_2O_7 was added as a catalyst, the entire reaction system was initially guaranteed to be under anhydrous conditions, and the reaction was carried out at room temperature for four hours, then the reaction was quenched with triethylamine. Using *p*-nitrotoluene as the internal standard, the yield of **2y** was calculated by NMR analysis. Using the same method, in an anhydrous and oxygen-free system, the yield of **2y** was determined when 0.2 mol% perrhenic acid ($HOReO_3$) or 0.2 mol% of trifluoromethanesulfonic acid (TfOH) was used as catalysts.

Note: $HOReO_3$ was used as a 10.0 mM solution in HFIP, TfOH was used as a 5.0 mM solution in HFIP, if a 5.0 mM solution of TfOH in Et_2O was used, catalytic efficiency was much lower.

10 Kinetic Study

10.1 Hammett equation



1b **1c** **1e** **1l** **1z**

A mixture two different *p*-substituted **1** (**1b** and **1c**; **1b** and **1e**; **1b** and **1l**; **1b** and **1z**, 0.25 mmol each) was dissolved in HFIP (1.0 mL), and it was cooled to 0 °C before $Re_2O_7{\cdot}SiO_2$ (0.000125 mmol, 0.0005 equiv) was added. The reaction was stirred at room temperature for 5 minute, 10 minutes, or 15 minutes, then quenched with 20 μl Et_3N, Then solvent was removed under vacuum and add p-nitrotoluene as internal standard analyzed by ^1H NMR. The k_X/k_H data was calculated based on the reduced molar amount of **1** and the results were summarized as follows equation:

$$\frac{K_X}{K_H} = \frac{\frac{C_{X0}-C_{Xt}}{t}}{\frac{C_{H0}-C_{Ht}}{t}} = \frac{\frac{m_{X0}-m_{Xt}}{V}}{\frac{m_{H0}-m_{Ht}}{V}} = \frac{m_{X0}-m_{Xt}}{m_{H0}-m_{Ht}}$$

Each group of experiments was repeated three times, and the average value of the three times was taken as the final k_X/k_H data.

Table S2. the datas of k_X/k_H

X	σ	k_X/k_H(1)	k_X/k_H(2)	k_X/k_H(3)	Average
OMe	-0.27	3.592	4.079	3.5457	3.739
CH_3	-0.17	2.232	1.254	2.37	1.952
H	0.0	1	1	1	1
Br	0.23	0.2822	0.3854	0.3384	0.335
CF_3	0.54	0.0451	0.0670	0.0568	0.056

Table S3. the datas of log(k_X/k_H) and σ_p

entry	k_X/k_H	*p*-substituted X	σ_p[a]	log(k_X/k_H)
1	3.739	OMe	-0.27	0.5728
2	1.852	CH_3	-0.17	0.2676
3	1	H	0.0	0.0000
4	0.335	Br	0.23	-0.4750
5	0.056	CF_3	0.54	-1.2518

[a]Data from: Hansch, Corwin.; Leo, A.; Taft R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev*. 1991, **91**, 165–195.

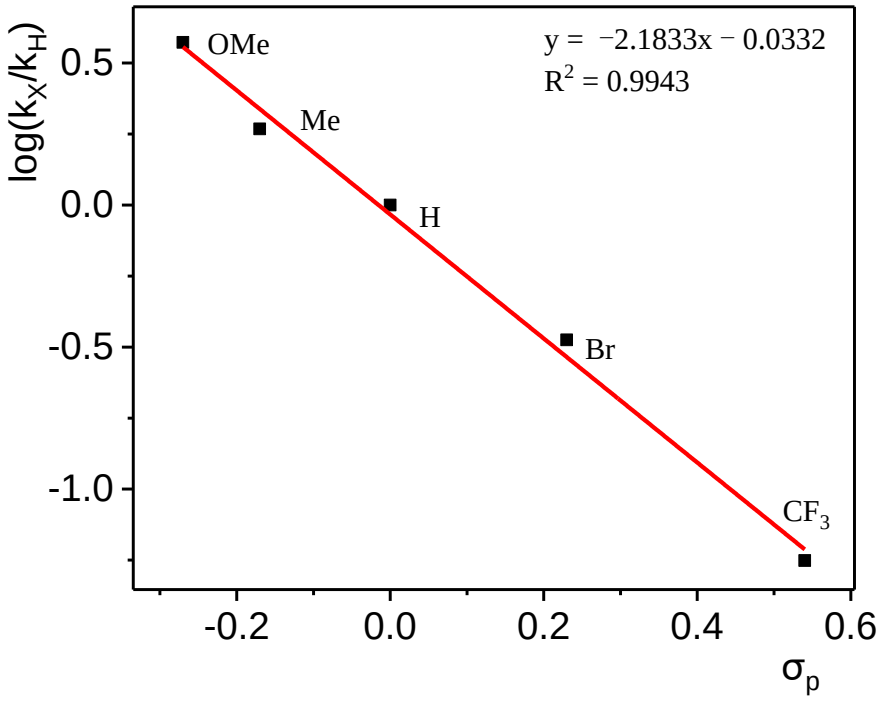


Figure 23. Hammett plots of log(k_X/k_H) vs σ_p

Table S4. the datas of log(k_X/k_H) and σ_p^+

entry	*k*X/*k*H	*p*-substituted X	σ_p^{+a}	log(k_X/k_H)
1	3.739	OMe	-0.78	0.5728
2	1.852	CH_3	-0.31	0.2676
3	1	H	0.0	0.0000
4	0.335	Br	0.15	-0.4750
5	0.056	CF_3	0.61	-1.2518

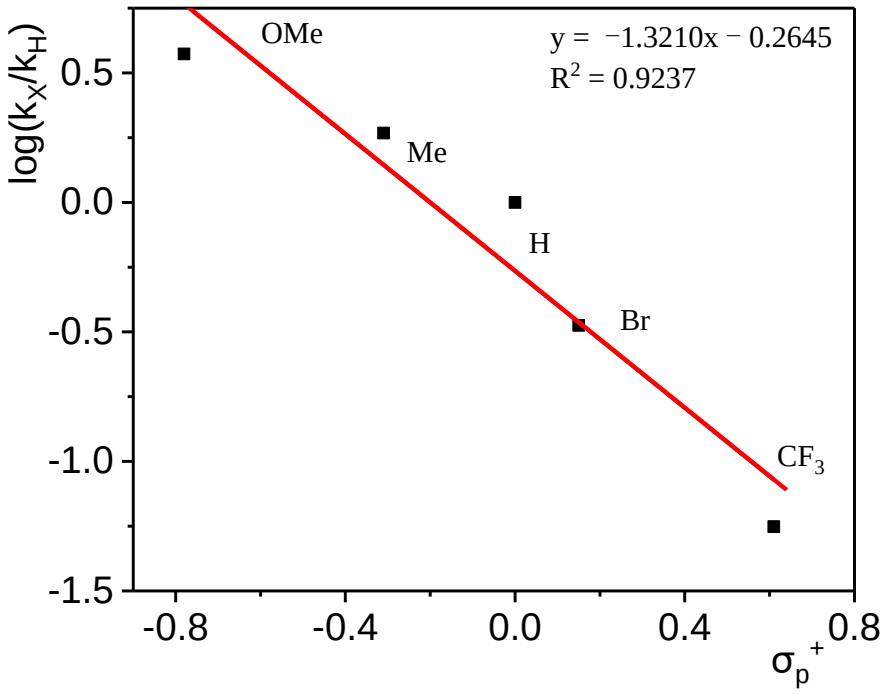
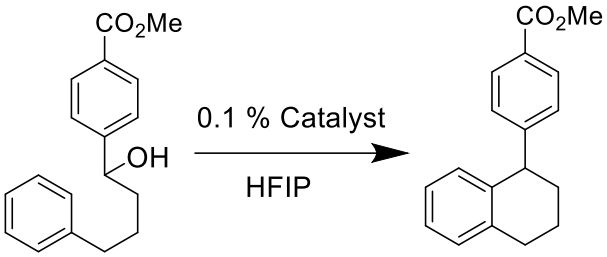


Figure 24. Hammett plots of log(k_X/k_H) vs σ_p^+

10.2 Reaction rate constant determination



1y **2y**

The activation energy of the reaction system with 0.1 mol% of the catalyst was measured with **1y** as the substrate. **1y** (0.25 mmol) and p-nitrotoluene (certain amount) was dissolved in HFIP (0.25 mL), and the reaction was heated to 30 °C before $Re_2O_7{\cdot}SiO_2$ (0.00025 mmol, 0.001 equiv) was added. Continuously monitor the reaction, small aliquots were at different times and quenched with triethylamine, determination of the residual concentration of **1y** in the system was made by ^{1}H NMR(*p*-nitrotoluene as an internal standard). Then the natural logarithm of the ratio of the initial concentration of **1y** to the concentration at a certain time was ploted against the reaction time, through which the k value can be obtained. the reaction rate constants at 35 °C, 40 °C, 45 °C, and 50 °C of the 0.1 mol% Rhenium catalyst system were measured in the same way, and the same method was used to measure the reaction rate constants at 30 °C, 40 °C, 45 °C, and 50 °C of the 0.1 mol% Trifluoromethanesulfonic acid-catalyzed reaction.

Note: $HOReO_3$ was used as a 10.0 mM solution in HFIP, TfOH was used as a 5.0 mM solution in HFIP, if a 5.0 mM solution of TfOH in Et_2O was used, catalytic efficiency was much lower.

Table S5. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Rhenium oxide at 30 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0	0.46556	1.0000	0.0000
2	0.5	0.15896	2.9288	1.0746
3	1	0.09856	4.7236	1.5526
4	2	0.05087	9.1520	2.2140
5	4	0.00954	48.8008	3.8877

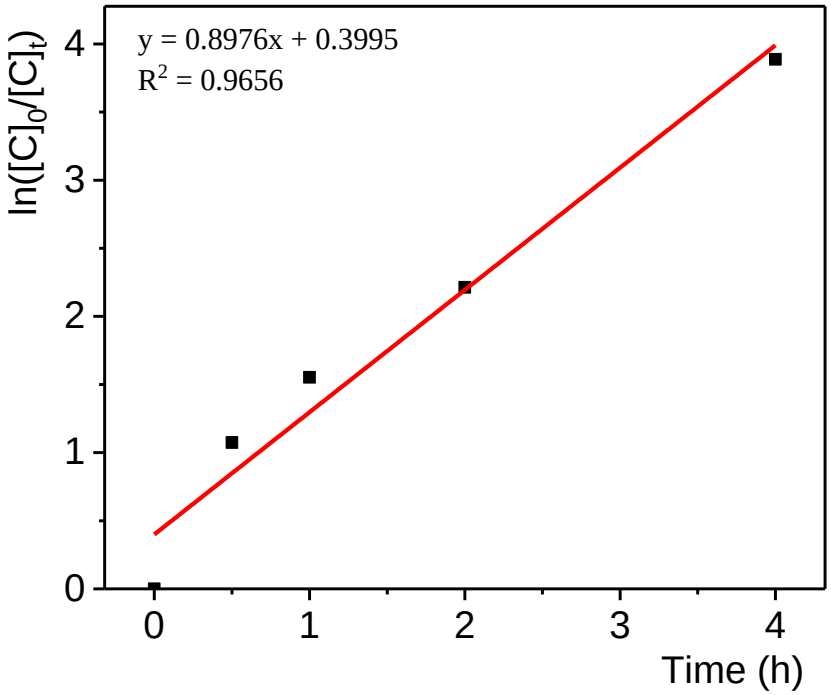


Figure 25. Rate constants of systems catalyzed by Rhenium oxide at 30 °C

Table S6. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Trifluoromethanesulfonic acid at 30 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0	0.47675	1.0000	0.0000
2	0.5	0.06166	7.7319	2.0454
3	1	0.01822	26.1663	3.2645

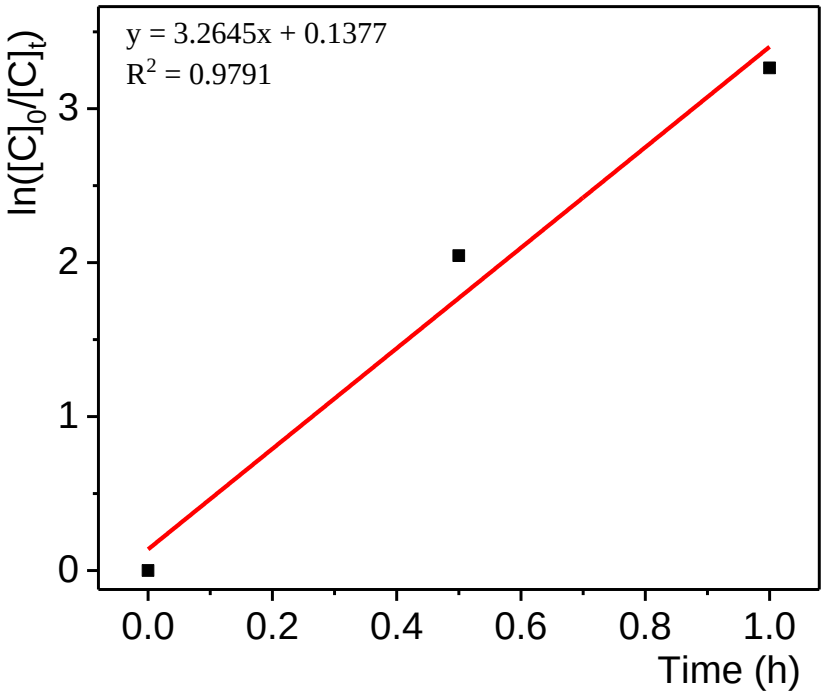


Figure 26. Rate constants of systems catalyzed by Trifluoromethanesulfonic acid at 30 °C

Table S7. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Rhenium oxide at 35 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0.0000	0.4679	1.0000	0.0000
2	0.1670	0.2685	1.7426	0.5554
3	0.5000	0.1611	2.9044	1.0662
4	1.0000	0.0917	5.1025	1.6297

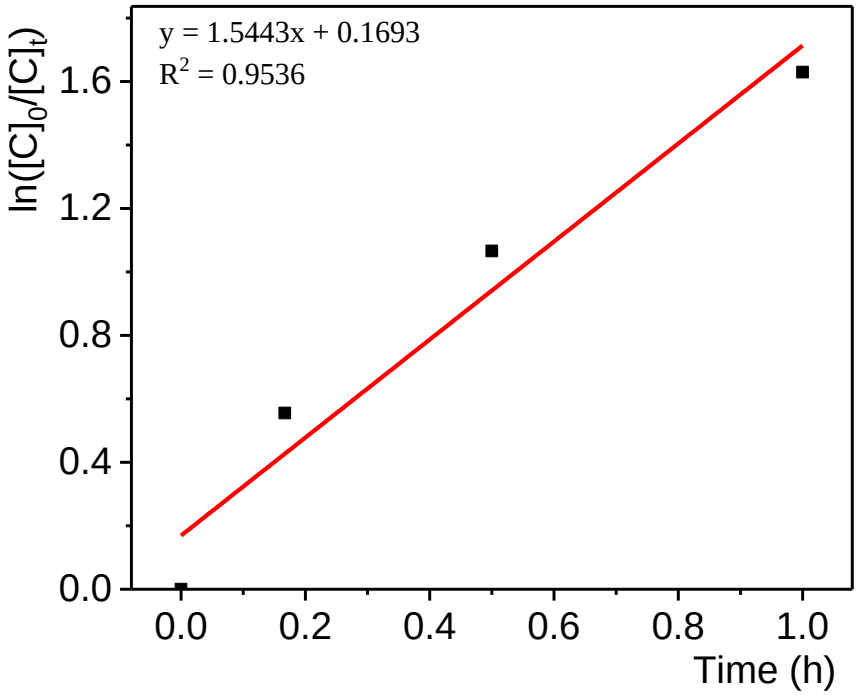


Figure 27. Rate constants of systems catalyzed by Rhenium oxide at 35 °C

Table S8. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Rhenium oxide at 40 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0.0000	0.4961	1.0000	0.0000
2	0.2500	0.1913	2.5933	0.9529
3	0.7500	0.0466	10.6459	2.3652
4	1.2500	0.0264	18.7917	2.9334
5	1.7500	0.0088	56.3750	4.0320

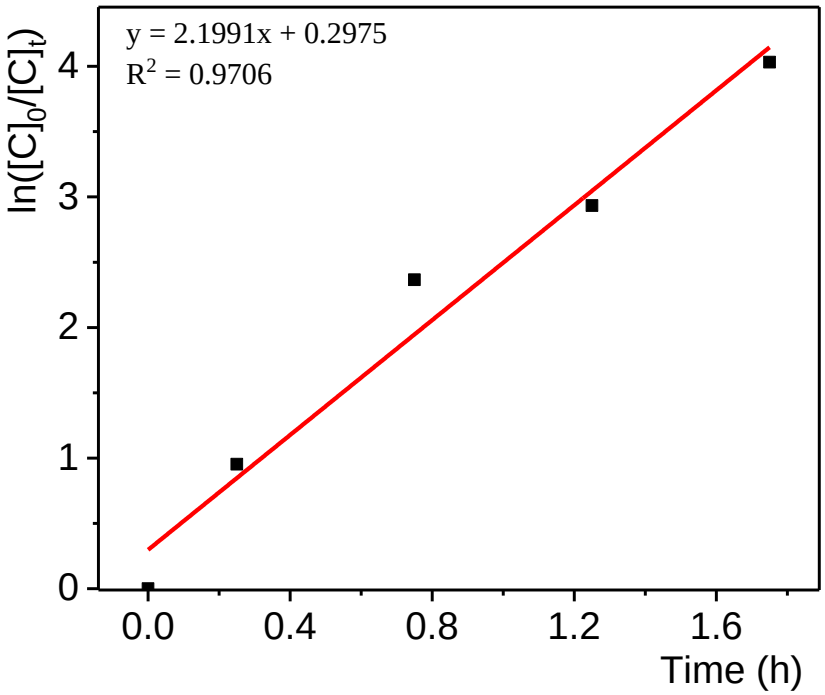


Figure 28. Rate constants of systems catalyzed by Rhenium oxide at 40 °C

Table S9. Data of ln([C]$_0$/[C]$_t$) and t catalyzed by Trifluoromethanesulfonic acid at 40 °C

entry	t (h)	[C]$_t$	[C]$_0$/[C]$_t$	ln([C]$_0$/[C]$_t$)
1	0.0000	0.4545	1.0000	0.0000
2	0.2500	0.0879	5.1703	1.6429
3	0.7500	0.0113	40.0767	3.6908

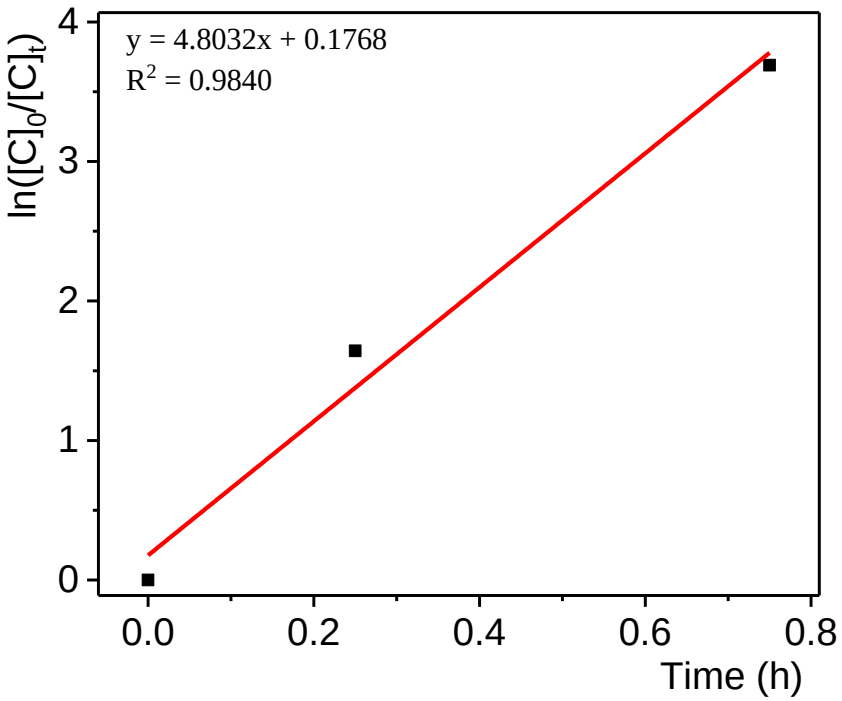


Figure 29. Rate constants of systems catalyzed by Trifluoromethanesulfonic acid at 40 °C

Table S10. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Rhenium oxide at 45 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0.0000	0.4802	1.0000	0.0000
2	0.0830	0.2551	1.8824	0.6325
3	0.2500	0.1206	3.9818	1.3817
4	0.4170	0.0729	6.5871	1.8851
5	0.5000	0.0566	8.4841	2.1382

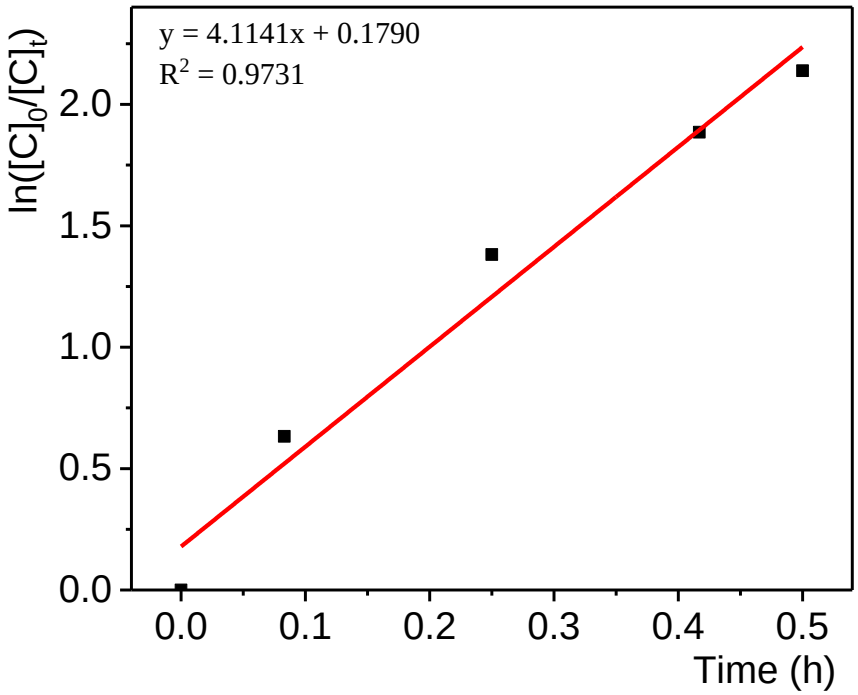


Figure 30. Rate constants of systems catalyzed by Rhenium oxide at 45 °C

Table S11. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Trifluoromethanesulfonic acid at 45 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0.0000	0.4744	1.0000	0.0000
2	0.0830	0.1883	2.5194	0.9240
3	0.2500	0.0491	9.6619	2.2682
4	0.4170	0.0211	22.4834	3.1128

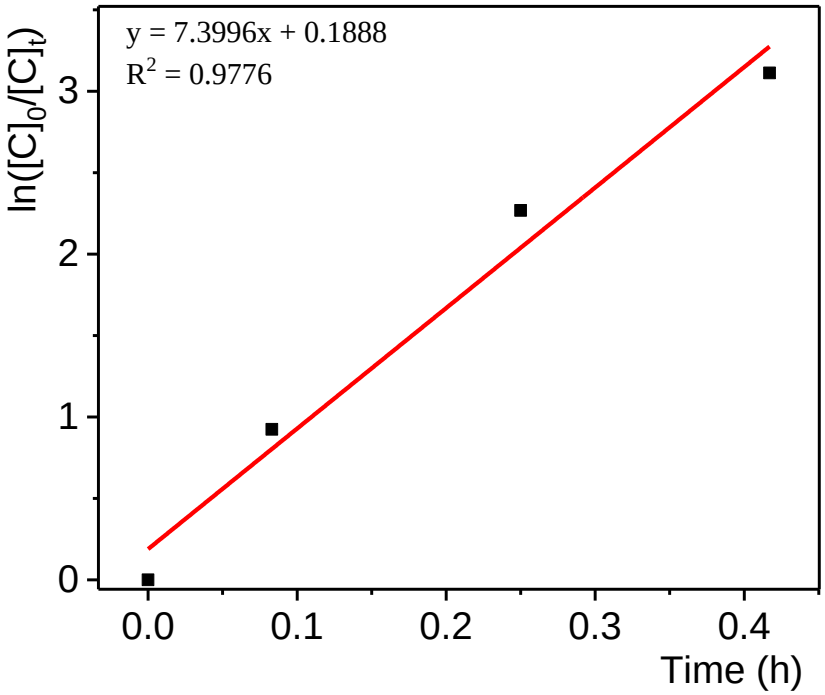


Figure 31. Rate constants of systems catalyzed by Trifluoromethanesulfonic acid at 45 °C

Table S12. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Rhenium oxide at 50 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0.0000	0.4960	1.0000	0.0000
2	0.0830	0.1815	2.7328	1.0053
t3	0.2500	0.0928	5.0168	1.6128
4	0.4170	0.0544	8.5581	2.1469
5	0.5830	0.0202	23.0475	3.1376

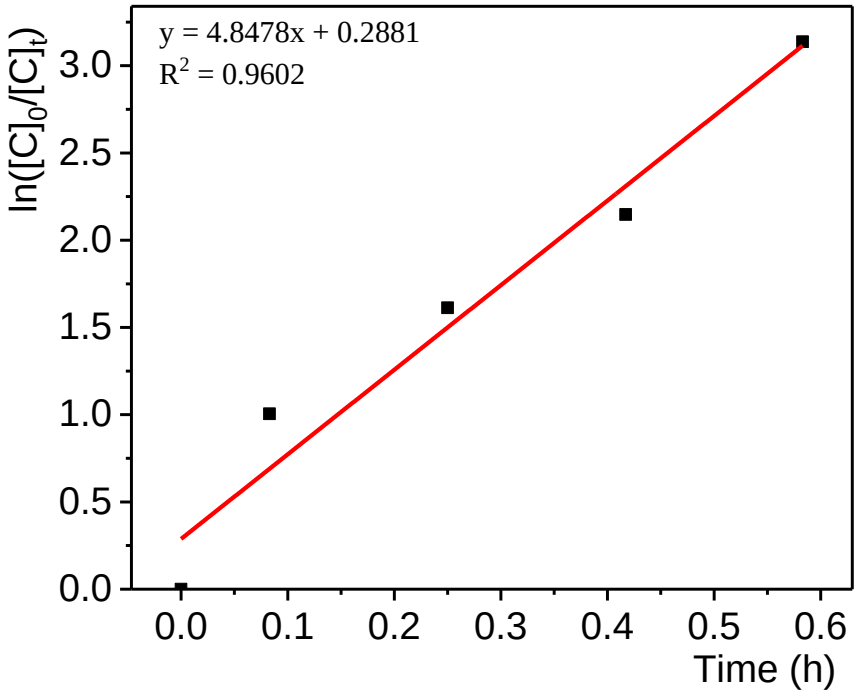


Figure 32. Rate constants of systems catalyzed by Rhenium oxide at 50 °C

Table S13. Data of $\ln([C]_0/[C]_t)$ and t catalyzed by Trifluoromethanesulfonic acid at 50 °C

entry	t (h)	$[C]_t$	$[C]_0/[C]_t$	$\ln([C]_0/[C]_t)$
1	0.0000	0.4821	1.0000	0.0000
2	0.0830	0.0752	6.4109	1.8580
t3	0.2500	0.0217	22.2166	3.1008

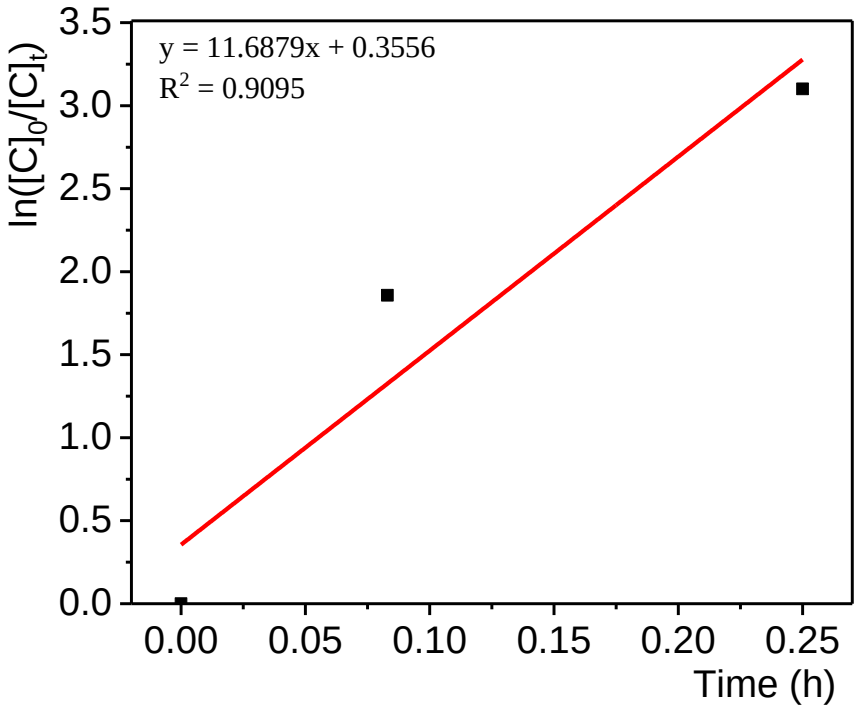


Figure 33. Rate constants of systems catalyzed by Trifluoromethanesulfonic acid at 50 °C

10.3 Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

k is the rate constant of the reaction; E_a is activation energy; A is preexponential factor; E_a and A are two very important parameters in chemical kinetics; R is the molar gas constant; T is the thermodynamic temperature. The value of k is obtained at various temperatures, the relationship between lnk and 1/T is a straight line, the slope of the straight line is -Ea/R, and the intercept is lnA. The k value at different temperatures is measured experimentally, and the E_a value can be obtained by plotting lnk against 1/T.

Table S14. Calculation of Activation Energy of Rhenium oxide Catalytic System

t (°C)	T (K)	1/T	Rate k (h^{-1})	ln(k)
30	303.15	0.0033	0.8975	-0.1081
35	308.15	0.0032	1.5443	0.4346
40	313.15	0.0032	2.1991	0.7880
45	318.15	0.0031	4.1141	1.4144
50	323.15	0.0031	4.8478	1.5785

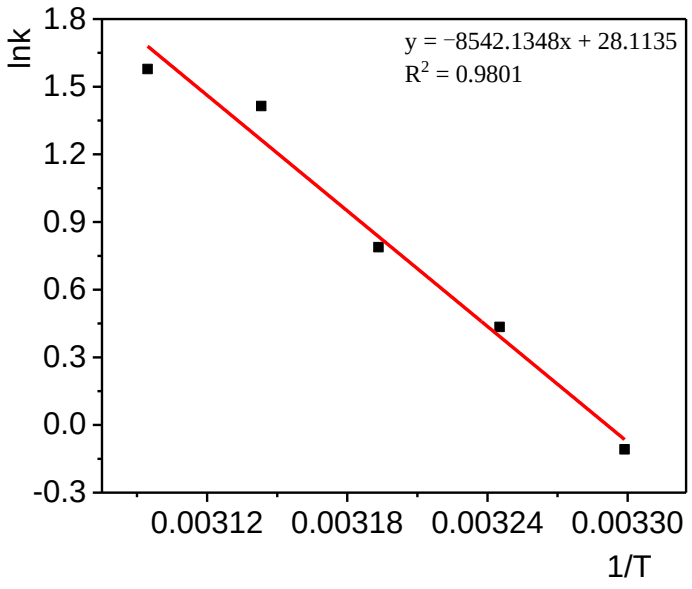


Figure 34. Calculation of Activation Energy of Rhenium oxide Catalyzed Reaction

E_a= R*8542.1348 J/mol = 71.019 kJ/mol = 16.990 kcal/mol

The activation energy of Rhenium oxide catalyzed **1y** dehydrated Friedel-Crafts alkylation is 16.990 kcal/mol**.**

Table S15. Calculation of Activation Energy of Trifluoromethanesulfonic acid Catalytic System

t (°C)	T (K)	1/T	Rate k (h^{-1})	ln(k)
30	303.15	0.0033	3.2645	1.1831
40	313.15	0.0032	4.8032	1.5693
45	318.15	0.0031	7.3996	2.0014
50	323.15	0.0031	11.6879	2.4586

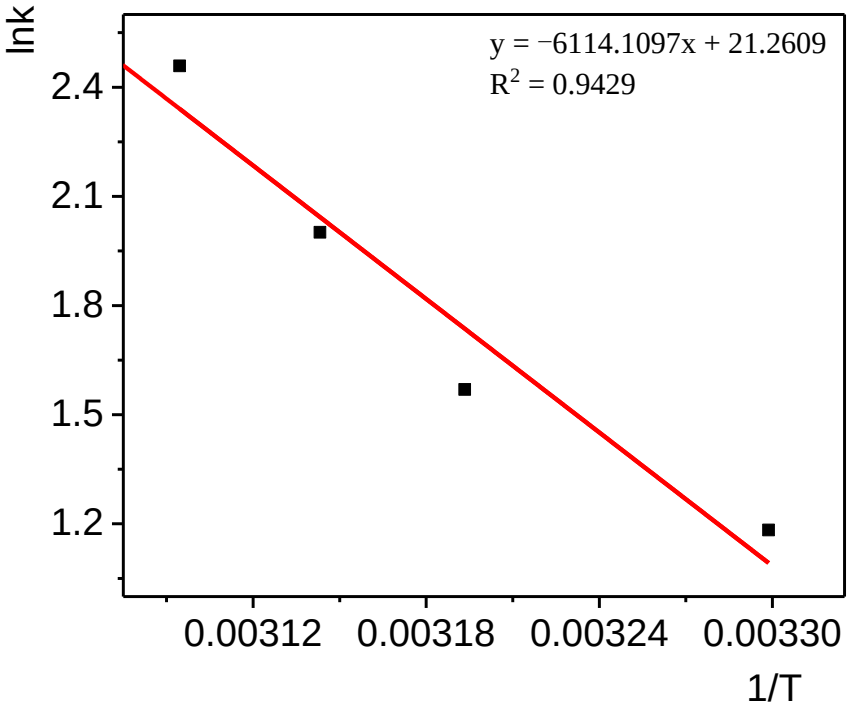


Figure 35. Calculation of Activation Energy of TfOH Catalyzed reaction

E_a=R*6114.1097 J/mol =50.832 kJ/mol =12.161 kcal/mol

The activation energy of Trifluoromethanesulfonic acid catalyzed **1y** dehydrated Friedel-Crafts alkylation is 12.161 kcal/mol**.**

11 DFT results

The density functional calculations were performed at the B3LYP-D3[21,22] level using the Gaussian 16 program package.[23] Geometries were optimized using the def2-SVP basis sets for all atoms, with SDD pseudopotential[24] for Re, followed by analytic frequency calculations at the same theory level. The final and solvation energies in the HFIP solvent were calculated using the SMD continuum solvation model[25] (with the related 2-Propanol as the model solvent) at the B3LYP-D3/def2-TZVPP level. The Gibbs energies are reported, including solvation correction and Gibbs free energy correction.

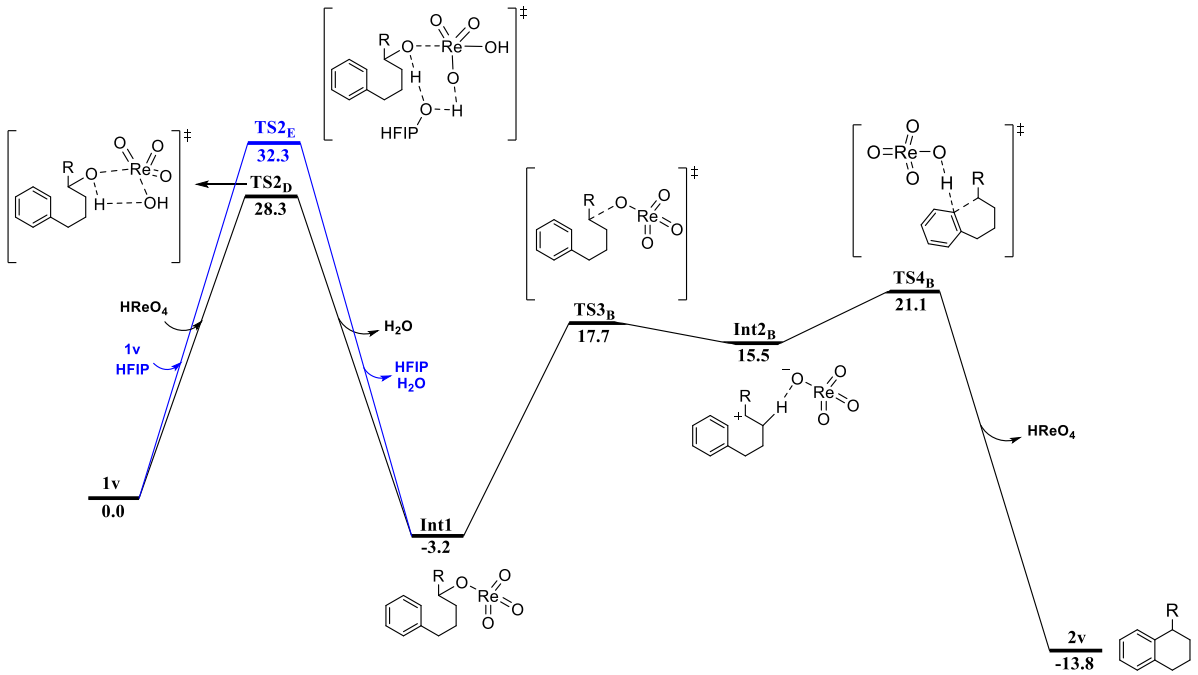


Figure S36. Gibbs energy diagram (in kcal/mol) at the SMD-B3LYP-D3/def2-TZVPP level for $HReO_4$ catalyzed reaction.

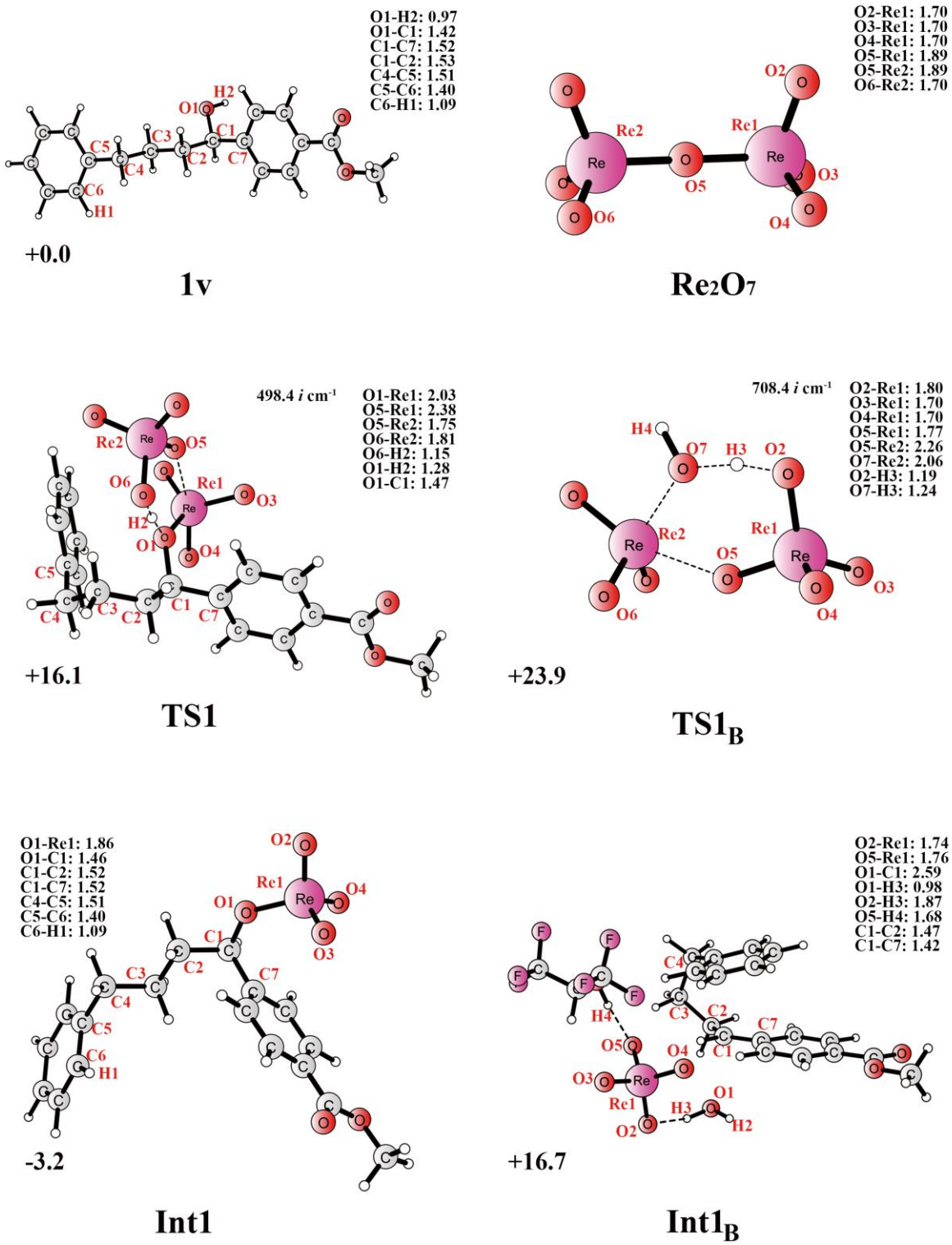


Figure S37. Optimized geometries of the reactants, intermediates, and transition states for the possible catalytic reactions. All distances are given in Å. Energies evaluated at the level of SMD-B3LYP-D3/def2-TZVPP are given in kcal/mol.

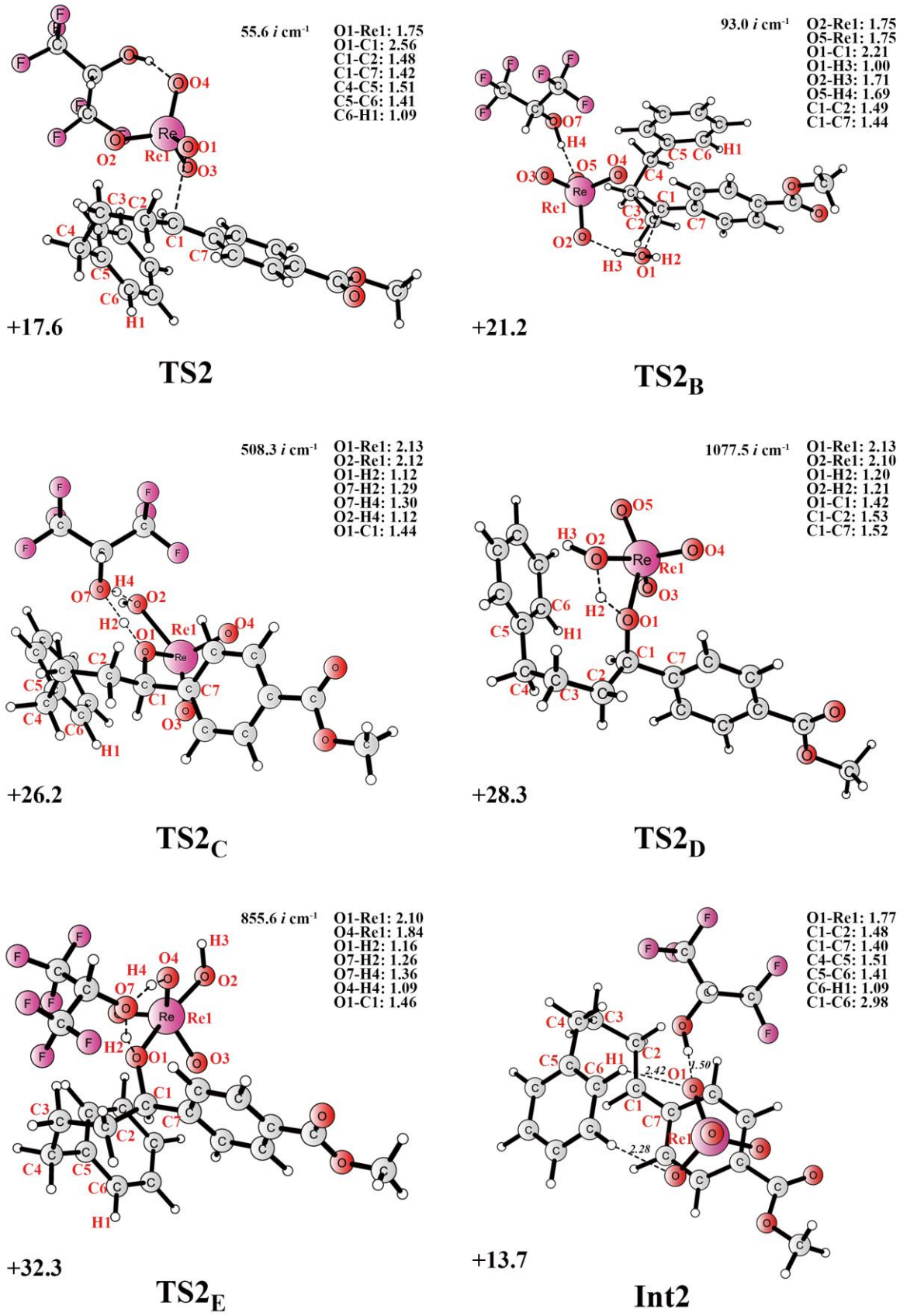


Figure S38. Optimized geometries of the transition states and intermediates for the possible catalytic reactions. All distances are given in Å. Energies evaluated at the level of SMD-B3LYP-D3/def2-TZVPP are given in kcal/mol.

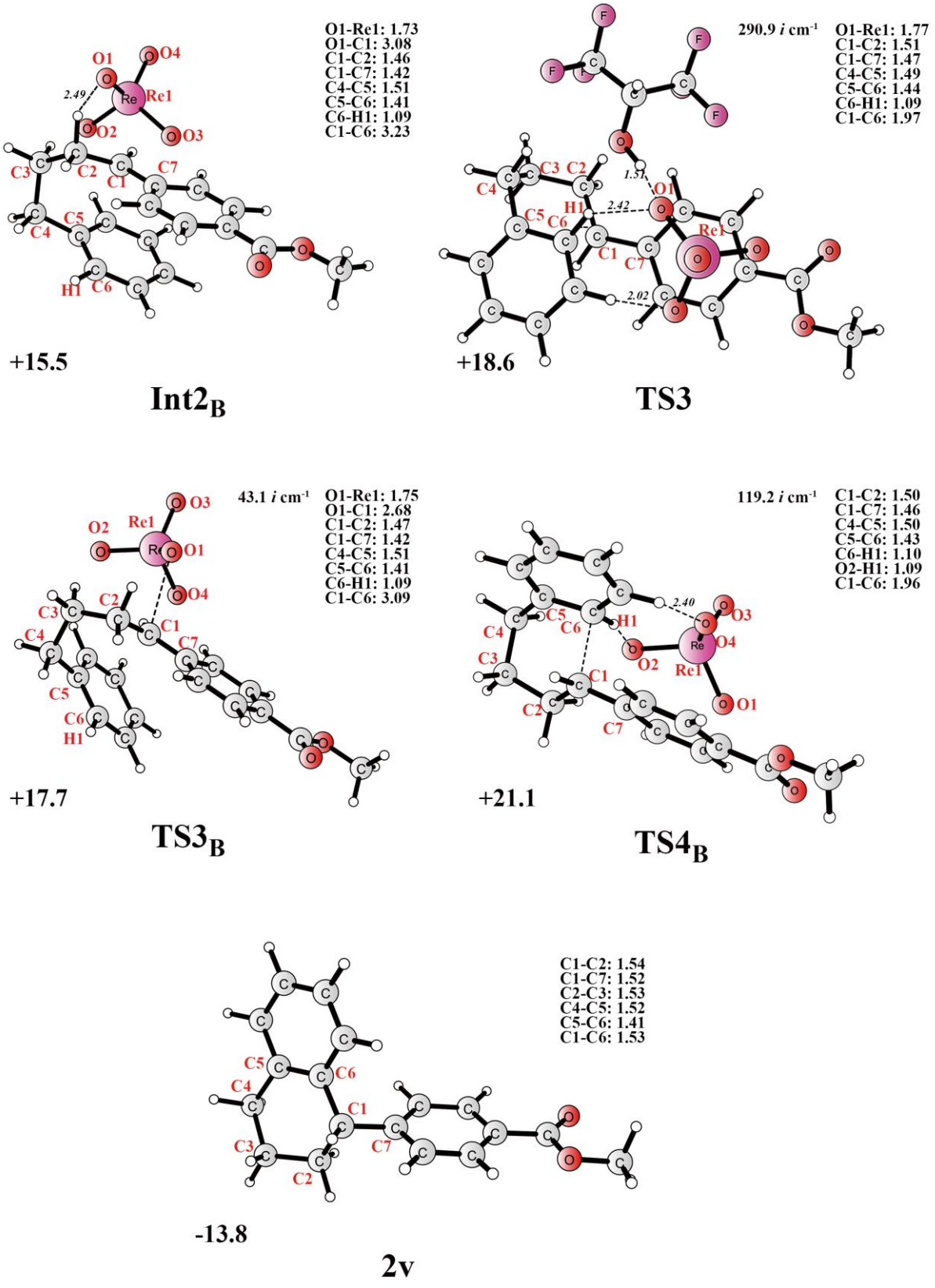


Figure S39. Optimized geometries of the transition states, intermediates, and the product for the possible catalytic reactions. All distances are given in Å. Energies evaluated at the level of SMD-B3LYP-D3/def2-TZVPP are given in kcal/mol.

12 Cartesian coordinates for all optimized structures

Re_2O_7

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	0.00000000	0.00000000	1.88983500
2	O	0.00000000	1.59814700	2.47923800
3	O	-1.38403600	-0.79907400	2.47923800
4	O	1.38403600	-0.79907400	2.47923800
5	O	0.00000000	0.00000000	0.00000000
6	Re	0.00000000	0.00000000	-1.88983500
7	O	-1.38403600	-0.79907400	-2.47923800
8	O	1.38403600	-0.79907400	-2.47923800
9	O	0.00000000	1.59814700	-2.47923800

1v

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	O	0.43009700	1.96947400	1.11411400
2	C	0.05245100	0.60877100	0.98555600
3	H	0.25990300	0.05987500	1.92858700
4	C	0.93527000	0.00293400	-0.11198200
5	H	0.62312600	-1.04275500	-0.27462500
6	H	0.72330200	0.54414200	-1.05081600
7	C	-1.42445200	0.44759200	0.66047200
8	C	-2.10797400	-0.72787000	1.00711900
9	C	-2.11405300	1.45536500	-0.03080300
10	C	-3.44937800	-0.90040100	0.66895500
11	H	-1.58182300	-1.51690500	1.55292100
12	C	-3.45606100	1.29035500	-0.36901300
13	H	-1.58161700	2.37137000	-0.29439100
14	C	-4.13427300	0.11140600	-0.02368600
15	H	-3.97756200	-1.81456400	0.94248000
16	H	-4.00328700	2.06744800	-0.90648500
17	C	-5.57015100	-0.01135900	-0.40963400
18	O	-6.19763700	0.83761500	-1.00107900
19	O	-6.11058900	-1.18657100	-0.02706000
20	C	-7.48346200	-1.38208000	-0.36147800
21	H	-7.75425400	-2.37505200	0.01886500
22	H	-8.11459100	-0.60860300	0.10350300
23	H	-7.63208800	-1.33590200	-1.45168000
24	C	2.42827000	0.06929700	0.20918000
25	H	2.70616300	1.11563800	0.41103700
26	H	2.63401900	-0.48850500	1.14059700
27	C	3.30951600	-0.49079000	-0.91936100
28	H	3.02039900	-1.53605500	-1.12447800
29	H	3.10606900	0.07503400	-1.84521000
30	C	4.78444500	-0.42308000	-0.59560500
31	C	5.45649300	-1.52355800	-0.04159000
32	C	5.50574400	0.76576300	-0.79301400
33	C	6.80930900	-1.44248900	0.30278800
34	H	4.91160000	-2.45895200	0.11840800
35	C	6.85755700	0.85249800	-0.45056300
36	H	4.99822900	1.63418200	-1.22396000
37	C	7.51501600	-0.25296100	0.09952200
38	H	7.31477600	-2.31325400	0.72906500
39	H	7.40161000	1.78624100	-0.61648000
40	H	8.57321800	-0.18798200	0.36551300
41	H	-0.08775800	2.36409100	1.82817800

TS1

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-0.04901000	0.61988200	-1.43617400
2	O	1.13710100	0.96630100	-2.60876200
3	O	-0.95378800	2.06165300	-1.31726600
4	O	-1.13553000	-0.52059400	-2.08203400
5	O	0.15224300	0.46220600	0.57377000
6	C	-0.82073400	1.12300700	1.46142600
7	H	-0.77524400	2.18850200	1.19685000
8	C	-0.44594400	0.93189900	2.93419900
9	H	-1.21773800	1.50048000	3.48127300
10	H	-0.60464200	-0.12395600	3.20912000
11	C	-2.20164100	0.57894300	1.16400000
12	C	-3.26816100	1.44384200	0.89258200
13	C	-2.41498400	-0.80854600	1.13675400
14	C	-4.53608700	0.93515400	0.60996800
15	H	-3.09903700	2.52313300	0.87907500
16	C	-3.67591000	-1.32109300	0.84704400
17	H	-1.58065800	-1.48923200	1.32416300
18	C	-4.74607300	-0.45142100	0.58579400
19	H	-5.36635700	1.60753600	0.39237700
20	H	-3.85571300	-2.39700600	0.81233300
21	C	-6.07847700	-1.05543700	0.27778500
22	O	-6.30029400	-2.24396000	0.25964200
23	O	-7.01820000	-0.12653000	0.02085900
24	C	-8.32099400	-0.62145700	-0.29033200
25	H	-8.94895900	0.25984500	-0.47040300
26	H	-8.29171800	-1.26130200	-1.18586200
27	H	-8.72317800	-1.21567100	0.54485500
28	C	0.94678000	1.37161500	3.41697400
29	H	0.90527600	1.38606600	4.51852700
30	H	1.68537500	0.59696500	3.16694800
31	C	1.45322000	2.73747100	2.92244500
32	H	0.65626300	3.49476000	3.01825700
33	H	2.26018000	3.06398200	3.60146600
34	C	1.99628300	2.74131100	1.50622900
35	C	1.50721400	3.63112400	0.54069600
36	C	3.01053500	1.84394900	1.12674800
37	C	2.01049700	3.62882800	-0.76518300
38	H	0.71208500	4.33302700	0.80841400
39	C	3.51340000	1.83176900	-0.17580600
40	H	3.41356500	1.13636800	1.85605100
41	C	3.01500400	2.72889900	-1.12749400
42	H	1.59845600	4.31707600	-1.50658000
43	H	4.28593300	1.10922900	-0.44703800
44	H	3.38608700	2.70388000	-2.15335800
45	O	1.45013100	-1.20116800	-1.09548300
46	H	0.87262400	-0.38239300	1.21376900
47	Re	2.38750800	-1.90427100	0.20246800
48	O	4.02059000	-1.40182400	0.15210400
49	O	2.31565200	-3.60808500	0.19289000
50	O	1.53666200	-1.21816100	1.63987700

$TS1_B$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	1.87372400	-0.07326300	0.00000700
2	O	2.04069100	-1.04209900	1.38936400
3	O	3.27690400	0.89960200	-0.00021600
4	O	2.04042600	-1.04234100	-1.38921600
5	O	0.78281000	1.66957700	-0.00012900
6	O	-0.29999800	-0.67594800	0.00004000
7	H	-0.44554400	1.83591900	-0.00009900
8	Re	-1.94729100	-0.03955200	0.00000400
9	O	-2.81510100	-0.50947000	1.38918600
10	O	-2.81504300	-0.50952900	-1.38919200
11	O	-1.62658200	1.72640500	-0.00002700
12	H	1.29024700	2.49559000	0.00078800

Int1

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	R	2.69176200	-1.57638600	0.04018700
2	O	3.56666200	-2.96281400	-0.44307400
3	O	2.98128800	-1.25015400	1.69464600
4	O	3.19654900	-0.23084200	-0.88540100
5	O	0.88009500	-1.92966200	-0.22304600
6	C	-0.28729700	-1.19458000	0.24820200
7	H	-0.39201200	-1.44112700	1.31854200
8	C	-1.48996400	-1.73564000	-0.51580400
9	H	-1.34096700	-1.55799800	-1.59373000
10	H	-1.50549900	-2.82984500	-0.38208700
11	C	-0.03219900	0.29200300	0.10988900
12	C	0.23984900	1.06367500	1.24797300
13	C	0.03975400	0.89207700	-1.15814000
14	C	0.56919400	2.41486000	1.12917700
15	H	0.20876600	0.59885400	2.23669000
16	C	0.36914300	2.23797000	-1.28160300
17	H	-0.14172000	0.29691400	-2.05547500
18	C	0.63389700	3.00857300	-0.13845900
19	H	0.78381800	3.01264200	2.01529800
20	H	0.43616600	2.71664400	-2.26013900
21	C	0.98676900	4.44909500	-0.33243200
22	O	1.03381400	4.99938300	-1.40802600
23	O	1.24815700	5.07548700	0.82904800
24	C	1.60227300	6.45571400	0.73264400
25	H	1.78060700	6.79881700	1.75919000
26	H	2.50940100	6.58362400	0.12199500
27	H	0.78939800	7.03595900	0.26909600
28	C	-2.81136100	-1.12134100	-0.05087500
29	H	-2.94435600	-1.29140300	1.03226900
30	H	-2.78283200	-0.02675700	-0.18436300
31	C	-4.02840200	-1.68683800	-0.80184800
32	H	-3.89213600	-1.51565400	-1.88364200
33	H	-4.06559400	-2.78055900	-0.66152000
34	C	-5.32853800	-1.06506200	-0.34550100
35	C	-5.77731500	0.14416900	-0.90037800
36	C	-6.08741000	-1.65005900	0.68002400
37	C	-6.95095300	0.75144300	-0.44587600
38	H	-5.19968700	0.61358300	-1.70263400
39	C	-7.26245500	-1.04678200	1.13807500
40	H	-5.75477000	-2.59408000	1.12235900
41	C	-7.69793700	0.15727700	0.57644500
42	H	-7.28581000	1.69066400	-0.89402200
43	H	-7.84199400	-1.52090100	1.93462200
44	H	-8.61773300	0.62911800	0.93125900

$Int1_B$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	1.16857300	-2.06068100	0.02975500
2	O	1.58077800	-0.80762500	1.19228100
3	O	-0.12908900	-1.46766100	-0.96172300
4	O	2.54985600	-2.43988400	-0.92660400
5	O	0.60522200	-3.45455400	0.90377000
6	C	-1.57216400	0.15789300	1.71655800
7	H	-0.74709300	-0.20729300	1.11099400
8	C	-1.22560600	0.54984600	3.09314100
9	H	-2.05621400	1.04555000	3.61692900
10	H	-1.05465300	-0.42422300	3.59182900
11	C	-2.85162800	0.16396900	1.09457600
12	C	-2.93861700	-0.29998100	-0.24449900
13	C	-4.02875600	0.61727000	1.74790800
14	C	-4.16815900	-0.32555100	-0.89889000
15	H	-2.03131000	-0.65883100	-0.73902700
16	C	-5.24479400	0.59226800	1.08960600
17	H	-3.97712900	0.98830200	2.77206200
18	C	-5.32061100	0.11917500	-0.23740400
19	H	-4.23973500	-0.68732500	-1.92460800
20	H	-6.16174900	0.93335400	1.57287800
21	C	-6.67019000	0.12224000	-0.89593500
22	O	-7.67853600	0.51097500	-0.35507100
23	O	-6.62789800	-0.35212700	-2.14777500
24	C	-7.87239200	-0.38975400	-2.85442600
25	H	-7.64759600	-0.80118000	-3.84553000
26	H	-8.59728700	-1.02780600	-2.32646200
27	H	-8.29747100	0.62163800	-2.94282300
28	C	0.07734400	1.36960500	3.17462100
29	H	0.38168500	1.45976800	4.22875600
30	H	0.86824400	0.80710500	2.65867300
31	C	-0.08023700	2.77099600	2.55044900
32	H	-0.69019600	3.40784600	3.21158600
33	H	0.91942100	3.23342200	2.48830000
34	C	-0.70829000	2.72468500	1.17868400
35	C	-1.97417600	3.29477300	0.93783800
36	C	-0.04501900	2.08256300	0.10853200
37	C	-2.57739600	3.19081500	-0.31289600
38	H	-2.49495600	3.80626200	1.75206600
39	C	-0.64669600	1.98218900	-1.14741800
40	H	0.94975400	1.66302000	0.26207500
41	C	-1.91798200	2.52318900	-1.35715800
42	H	-3.56789500	3.62153700	-0.47840400
43	H	-0.11788100	1.46725600	-1.94959400
44	H	-2.39500900	2.43693500	-2.33642600
45	O	3.28456800	1.15373000	0.70777600
46	H	2.70557400	0.42680100	1.03331200
47	C	4.01375600	0.66155000	-0.37058400
48	H	4.02664600	-0.44097700	-0.42869900
49	C	5.47276100	1.10638100	-0.20917500
50	C	3.38523100	1.13247700	-1.69133900
51	F	4.04175200	0.67233100	-2.75920700

52	F	3.31556500	2.46446100	-1.77861900
53	F	2.11657900	0.66175600	-1.76030400
54	F	5.58897200	2.43908400	-0.16667200
55	F	6.23509700	0.65586500	-1.21784000
56	F	5.96641400	0.60998500	0.93181700
57	O	-1.62802700	-2.38549200	2.19520600
58	H	-0.82827700	-2.91139400	1.97557400
59	H	-2.26251800	-2.67851500	1.52632400

TS2

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-0.64158400	-0.84451300	-0.80696500
2	O	-1.66433800	0.55124600	-0.92417600
3	O	0.10836300	-0.85913500	0.75562100
4	O	-1.60165500	-2.27374100	-1.05132900
5	O	0.64215300	-0.66375700	-1.98514700
6	C	1.90437300	1.33023100	-1.00048800
7	H	1.10408200	1.14428400	-0.29117800
8	C	1.61918000	2.20163300	-2.15841200
9	H	2.49206400	2.84012000	-2.38140000
10	H	1.54479800	1.49163800	-3.00684300
11	C	3.13638800	0.69981900	-0.68505200
12	C	3.16015100	-0.16992200	0.43909600
13	C	4.31756000	0.87982500	-1.45411300
14	C	4.33166500	-0.83440300	0.78156400
15	H	2.23815200	-0.32861100	1.00388700
16	C	5.48074100	0.21832600	-1.10257900
17	H	4.31100100	1.53815100	-2.32421900
18	C	5.49274700	-0.63957100	0.01660600
19	H	4.35643000	-1.51026000	1.63621700
20	H	6.40219300	0.33967000	-1.67429100
21	C	6.78866400	-1.32839100	0.34277700
22	O	7.80513000	-1.17291500	-0.29148900
23	O	6.68468500	-2.12799000	1.41042400
24	C	7.86988900	-2.83572900	1.79211400
25	H	7.59795600	-3.43318000	2.67016400
26	H	8.21102700	-3.48601900	0.97243200
27	H	8.67793300	-2.13030300	2.03851800
28	C	0.31857800	3.00923300	-2.07261600
29	H	0.15206800	3.50601800	-3.04135300
30	H	-0.52113400	2.31418900	-1.91878000
31	C	0.32045000	4.06687900	-0.94495300
32	H	1.10156200	4.82053300	-1.14073200
33	H	-0.64782000	4.59264400	-0.96617700
34	C	0.53819800	3.43234500	0.40677100
35	C	1.80310300	3.46411300	1.02562600
36	C	-0.48612600	2.67058200	1.00556100
37	C	2.04269000	2.74526000	2.20473400
38	H	2.60474400	4.06025300	0.57989300
39	C	-0.24005000	1.93529400	2.16256200
40	H	-1.46548000	2.60015400	0.52892800
41	C	1.02760000	1.97076200	2.76594300
42	H	3.03011500	2.78162300	2.67176400
43	H	-1.03185600	1.30831900	2.57504300
44	H	1.21588900	1.38630400	3.66960100
45	O	-4.03621600	-2.21634300	0.32059500
46	H	-3.21599800	-2.41076600	-0.17475100
47	C	-4.33009700	-0.86629200	0.19158800
48	H	-3.79001800	-0.36465100	-0.62739700
49	C	-5.82116600	-0.72170000	-0.13607100
50	C	-3.93105000	-0.10119900	1.46829400
51	F	-6.18817300	0.57334400	-0.15525600

52	F	-6.06156500	-1.23124000	-1.35218400
53	F	-6.60212400	-1.35851200	0.73988200
54	F	-3.96038600	1.22991400	1.28029800
55	F	-2.67032500	-0.42579300	1.81517700
56	F	-4.71907800	-0.38584100	2.51134800

$TS2_B$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-1.22192800	1.95801000	-0.26695000
2	O	-1.67515700	0.88128100	1.04065000
3	O	0.02754100	1.18975500	-1.19156700
4	O	-2.59275200	2.31048800	-1.24507800
5	O	-0.54128300	3.40147300	0.44735000
6	C	1.68419800	0.47982400	1.72793100
7	H	0.82940200	0.53856400	1.05949600
8	C	1.36630400	0.30279200	3.16770300
9	H	2.23663900	-0.05153700	3.73961200
10	H	1.12860700	1.31149000	3.54398600
11	C	2.94976600	0.26939900	1.08036000
12	C	2.98015000	0.30557300	-0.33529400
13	C	4.15084500	0.03764800	1.79442800
14	C	4.18085500	0.11377300	-1.01490300
15	H	2.05223000	0.49270000	-0.88197800
16	C	5.34020600	-0.15676700	1.11188500
17	H	4.14395200	0.00804900	2.88463600
18	C	5.36108400	-0.12083700	-0.29671400
19	H	4.20735000	0.13691800	-2.10431200
20	H	6.27653300	-0.34033700	1.64144100
21	C	6.67978400	-0.34726600	-0.97598800
22	O	7.71302700	-0.55544200	-0.38457900
23	O	6.58168800	-0.29472100	-2.31170100
24	C	7.79372800	-0.49953600	-3.04466000
25	H	7.52546800	-0.42277300	-4.10504000
26	H	8.54042200	0.26420700	-2.77896800
27	H	8.21656100	-1.49151000	-2.82396600
28	C	0.12740300	-0.58865400	3.40943600
29	H	-0.17261000	-0.47957300	4.46368600
30	H	-0.70222500	-0.19841700	2.80131200
31	C	0.36594000	-2.07651700	3.09774500
32	H	1.06800900	-2.50019900	3.83490100
33	H	-0.59124800	-2.60936600	3.22994700
34	C	0.89550700	-2.32123200	1.70359900
35	C	2.17883800	-2.86249600	1.50463800
36	C	0.12238800	-1.99111900	0.57098800
37	C	2.68865500	-3.04557000	0.21973400
38	H	2.78816500	-3.12991300	2.37257300
39	C	0.63266200	-2.16915600	-0.71643000
40	H	-0.88620400	-1.59325700	0.69257500
41	C	1.91846000	-2.69007000	-0.89499600
42	H	3.69301300	-3.45470600	0.08499900
43	H	0.01936800	-1.89178400	-1.57390300
44	H	2.31929000	-2.82469200	-1.90272100
45	O	-3.39970200	-1.12657100	0.89496400
46	H	-2.79514300	-0.38299800	1.11168700
47	C	-4.09812500	-0.77306700	-0.25427800
48	H	-4.08982800	0.31188900	-0.46170500
49	C	-5.56901400	-1.16431000	-0.06355200
50	C	-3.45695700	-1.42951400	-1.48679500
51	F	-4.07731300	-1.09225400	-2.62118100

52	F	-3.42599700	-2.76185700	-1.40157400
53	F	-2.17432300	-1.00344100	-1.58471000
54	F	-5.71428600	-2.47464200	0.16367300
55	F	-6.30157900	-0.84679400	-1.14283600
56	F	-6.07433300	-0.50202800	0.98440100
57	O	1.73265900	2.69038400	1.68224900
58	H	0.86959600	3.07010000	1.35641700
59	H	2.35346800	2.90500800	0.96929700

$TS2_C$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-0.03642500	-1.52843500	-1.24805700
2	O	-0.82239100	-2.67224800	-2.25131400
3	O	0.99661200	-2.49769600	-0.28771600
4	O	0.97501700	-0.61557300	-2.26614600
5	O	-0.12666000	-0.25008500	0.45847800
6	C	0.76896900	-0.36001700	1.58551200
7	H	0.77061000	-1.42062200	1.87633200
8	C	0.27242600	0.48762500	2.76245000
9	H	1.00840200	0.31685400	3.56609900
10	H	0.37087300	1.55421500	2.49436100
11	C	2.17320100	0.03075100	1.17443000
12	C	3.27643600	-0.65860200	1.69351300
13	C	2.38337600	1.10112400	0.29336400
14	C	4.57410500	-0.28026300	1.35186400
15	H	3.11721700	-1.51077600	2.35989700
16	C	3.67772200	1.47949500	-0.05546700
17	H	1.52759200	1.62306800	-0.13713600
18	C	4.78223800	0.79525400	0.47432400
19	H	5.43262200	-0.82059700	1.75186800
20	H	3.85651600	2.30517700	-0.74657200
21	C	6.14654600	1.24423400	0.06677300
22	O	6.36943900	2.17263400	-0.67596400
23	O	7.12330600	0.49890000	0.62181400
24	C	8.45955800	0.86243000	0.27829900
25	H	9.11507900	0.16054900	0.80889100
26	H	8.61851100	0.78802400	-0.80879600
27	H	8.67601000	1.89719200	0.58680300
28	C	-1.14567800	0.22167800	3.30235100
29	H	-1.20221000	0.70698300	4.29023800
30	H	-1.88784100	0.73320900	2.67416600
31	C	-1.55884000	-1.25900800	3.45415100
32	H	-0.69948000	-1.86410500	3.78895900
33	H	-2.30119300	-1.32031200	4.26780300
34	C	-2.18437400	-1.88752900	2.22201700
35	C	-1.60693100	-2.99309200	1.57831300
36	C	-3.38941400	-1.38059400	1.70861200
37	C	-2.21138700	-3.57623800	0.45807600
38	H	-0.66337700	-3.40349800	1.94610000
39	C	-4.00464800	-1.96481800	0.59804500
40	H	-3.85222400	-0.50871600	2.17696200
41	C	-3.41879200	-3.06732700	-0.03320300
42	H	-1.73153100	-4.42237700	-0.03744700
43	H	-4.94514300	-1.55072400	0.22417400
44	H	-3.89111600	-3.52755800	-0.90474900
45	O	-1.90232600	-0.51801800	-1.35104800
46	H	-0.94932600	0.50613000	0.53957200
47	H	-2.65512500	-1.07141500	-1.60685300
48	O	-2.07576300	1.11072100	0.37162500
49	H	-2.18261300	0.28689500	-0.62973000
50	C	-2.20981000	2.47260300	0.22302300
51	H	-1.63519100	3.03374100	0.98428900

52	C	-3.68611300	2.83015600	0.45329600
53	C	-1.67377600	2.94085700	-1.14032600
54	F	-4.02611400	2.50736500	1.71230700
55	F	-3.91792900	4.13780100	0.28492400
56	F	-4.48956200	2.14927600	-0.37373100
57	F	-1.66061100	4.27242600	-1.24382200
58	F	-0.40693900	2.50055700	-1.28186800
59	F	-2.38906300	2.44144900	-2.15506400

$TS2_D$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-1.18529200	-1.44996700	-0.05600600
2	O	-2.51158900	-2.40472200	0.45878400
3	O	-0.41554500	-0.98449500	1.40150400
4	O	-0.12888400	-2.48988900	-0.89707800
5	O	-0.57421000	0.42497900	-0.86921400
6	C	0.20995000	1.44507100	-0.26617400
7	H	-0.14779700	1.58814400	0.76754300
8	C	0.04016600	2.75163200	-1.05072400
9	H	0.63758400	3.51796700	-0.52837600
10	H	0.50323600	2.61866400	-2.04256100
11	C	1.66346900	1.02028700	-0.19522700
12	C	2.50504700	1.58748300	0.77259800
13	C	2.19229500	0.09172800	-1.10200700
14	C	3.85420800	1.24446100	0.83226500
15	H	2.09595600	2.29883700	1.49613000
16	C	3.53999500	-0.25922500	-1.04265200
17	H	1.53612200	-0.37229000	-1.83949700
18	C	4.38199200	0.31622100	-0.07972700
19	H	4.50536100	1.68349100	1.58882700
20	H	3.96218800	-0.98773100	-1.73734100
21	C	5.81591800	-0.09610900	-0.06348500
22	O	6.31342900	-0.88371400	-0.83529500
23	O	6.51762500	0.51056800	0.91624700
24	C	7.89908400	0.16578100	1.00081500
25	H	8.30897700	0.74143000	1.84026300
26	H	8.02363100	-0.91366300	1.17977600
27	H	8.42535900	0.42137600	0.06776100
28	C	-1.39876600	3.25657500	-1.22456100
29	H	-1.33873600	4.22533000	-1.74652800
30	H	-1.95241600	2.59208900	-1.90981500
31	C	-2.21733300	3.43999700	0.07933400
32	H	-1.54186500	3.70096100	0.91088900
33	H	-2.88513000	4.30729700	-0.05036600
34	C	-3.07524800	2.25050500	0.46315300
35	C	-2.75744900	1.40956400	1.54147400
36	C	-4.22865200	1.95548900	-0.28355200
37	C	-3.54768700	0.29753800	1.85187100
38	H	-1.87067500	1.61302600	2.14600800
39	C	-5.02869900	0.84845500	0.02512600
40	H	-4.50411400	2.60154100	-1.12233100
41	C	-4.68483100	0.00858900	1.09143500
42	H	-3.25828900	-0.35793000	2.67528900
43	H	-5.92480100	0.64368100	-0.56680100
44	H	-5.28901400	-0.87090600	1.32224900
45	O	-2.48585700	-0.51348000	-1.41039500
46	H	-1.68126800	0.38897600	-1.33364000
47	H	-3.40792700	-0.37100800	-1.13322600

$TS2_E$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	0.68358200	1.14270400	-1.66677600
2	O	2.13120000	1.87912700	-1.16469200
3	O	-0.67599900	2.00986500	-1.10547800
4	O	0.52428700	1.74762900	-3.44809500
5	O	0.49919400	0.05674100	0.11597300
6	C	-0.46820800	0.32202600	1.17063100
7	H	-0.53480800	1.41112500	1.24349900
8	C	0.07096000	-0.25494500	2.48499300
9	H	-0.69214100	-0.06197700	3.25844000
10	H	0.12593500	-1.35019400	2.38135000
11	C	-1.82997900	-0.22179600	0.79667300
12	C	-2.94815500	0.62162500	0.85829500
13	C	-1.99922300	-1.55981200	0.40246700
14	C	-4.21951300	0.14173800	0.54429100
15	H	-2.81346300	1.66831700	1.14235000
16	C	-3.26668400	-2.03953300	0.08020600
17	H	-1.13668100	-2.22525300	0.33280200
18	C	-4.38600300	-1.19496300	0.15148200
19	H	-5.08743800	0.80034900	0.59025200
20	H	-3.41398700	-3.07521300	-0.23191300
21	C	-5.71831600	-1.76550500	-0.20632100
22	O	-5.90362600	-2.90897500	-0.55583100
23	O	-6.71374700	-0.86254100	-0.09883600
24	C	-8.02113700	-1.33021300	-0.42617900
25	H	-8.69679800	-0.47711600	-0.28616500
26	H	-8.06151200	-1.68388900	-1.46830200
27	H	-8.31525500	-2.16384900	0.23054900
28	C	1.43595700	0.29231600	2.92943300
29	H	1.88506200	-0.43146000	3.62796100
30	H	2.10994400	0.32179800	2.05951100
31	C	1.40454500	1.66967100	3.62227900
32	H	0.81727700	1.59136900	4.55275300
33	H	2.43522700	1.92323000	3.92512300
34	C	0.84311700	2.78485800	2.76776000
35	C	-0.39691400	3.37280100	3.06091000
36	C	1.51750100	3.19665700	1.60640100
37	C	-0.96104300	4.32720300	2.20682700
38	H	-0.93710100	3.06472500	3.96094600
39	C	0.95786800	4.14759600	0.75121700
40	H	2.47632200	2.74157600	1.34602600
41	C	-0.28792700	4.71225100	1.04422900
42	H	-1.93295700	4.76571700	2.44848000
43	H	1.49054900	4.42985100	-0.15962900
44	H	-0.73296800	5.44417500	0.36603900
45	O	0.88269600	-0.57262900	-2.29857100
46	H	0.83554700	-1.04712700	0.01476300
47	H	1.02322600	1.27101500	-4.13147700
48	C	2.23383700	-2.86890200	-0.23592100
49	H	2.34644000	-3.73733700	-0.91046400
50	O	1.07460100	-2.17023900	-0.50997900
51	H	0.98251500	-1.45219600	-1.65970500

52	C	2.18076000	-3.45446400	1.18652200
53	C	3.47688000	-1.98956900	-0.46796700
54	F	3.57210000	-1.69981100	-1.77563600
55	F	3.38523200	-0.82405900	0.19365800
56	F	4.60680700	-2.59780000	-0.09334000
57	F	3.14823800	-4.35888500	1.37475000
58	F	2.31805600	-2.50012300	2.12561800
59	F	1.00286000	-4.05448600	1.38936300

Int2

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	2.02247100	-0.10072600	-1.45299300
2	O	0.28059100	-0.26466800	-1.22051900
3	O	2.42658800	-0.39213200	-3.09992100
4	O	2.49088900	1.50849000	-1.01144100
5	O	2.85723400	-1.22990900	-0.43596000
6	C	-1.55412700	1.75545600	2.02400800
7	H	-1.51781600	2.84871900	2.07591000
8	C	-2.88967200	1.12368600	2.05073900
9	H	-2.84424700	0.11569200	1.61948400
10	H	-3.11838700	0.99611400	3.13221000
11	C	-0.32013200	1.08891900	2.06424900
12	C	0.88349400	1.85897000	2.00952500
13	C	-0.22261500	-0.33500600	2.15984800
14	C	2.11752600	1.23845000	2.03380500
15	H	0.81383500	2.94299600	1.89929500
16	C	1.01355300	-0.94194700	2.22653900
17	H	-1.12377200	-0.94208800	2.18426100
18	C	2.18561600	-0.16374500	2.15222900
19	H	3.03746600	1.81095300	1.92927500
20	H	1.11151800	-2.02561300	2.29059100
21	C	3.49907900	-0.89721400	2.16567100
22	O	3.60845300	-2.04586400	2.51654600
23	O	4.50238600	-0.12044300	1.75310000
24	C	5.73894400	-0.78687500	1.48182000
25	H	6.44331900	-0.00684000	1.16957300
26	H	6.10677800	-1.31055400	2.37685100
27	H	5.58691000	-1.51536200	0.67088600
28	C	-4.03001100	1.93137100	1.41148200
29	H	-4.96228700	1.36025600	1.54294800
30	H	-4.16094000	2.88532900	1.95097600
31	C	-3.80282900	2.21242500	-0.08942900
32	H	-3.70053900	1.25994600	-0.62736800
33	H	-4.69898300	2.72166200	-0.48224300
34	C	-2.58184900	3.07141100	-0.31349300
35	C	-1.39633500	2.53345000	-0.84730500
36	C	-2.58276600	4.42348800	0.09200100
37	C	-0.23442600	3.31150600	-0.94907400
38	H	-1.37173900	1.49652000	-1.17940700
39	C	-1.43054200	5.19955600	-0.00922700
40	H	-3.50057500	4.86359300	0.49353500
41	C	-0.24797700	4.63983500	-0.52296400
42	H	0.68542500	2.86821900	-1.33421100
43	H	-1.44796200	6.24584600	0.30737500
44	H	0.65804800	5.24662800	-0.59761700
45	O	-1.99533800	-0.73099600	-0.26853300
46	H	-1.06357100	-0.57978500	-0.63398400
47	C	-2.46684900	-1.96759400	-0.65657200
48	H	-2.15445800	-2.26287500	-1.67587100
49	C	-3.99910000	-1.88681200	-0.67641700
50	C	-1.93466100	-3.06086400	0.28804900
51	F	-2.31436300	-4.28541900	-0.08345300

52	F	-2.35094900	-2.86237500	1.55724800
53	F	-0.59422300	-3.02071400	0.30040000
54	F	-4.48763800	-1.46371600	0.50474500
55	F	-4.56070400	-3.06692500	-0.95639000
56	F	-4.39164100	-1.00657400	-1.60889600

Int2$_B$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-2.92033100	-0.97802200	-0.00968900
2	O	-3.58707200	0.41541400	0.79002900
3	O	-1.37149800	-1.33208400	0.73386200
4	O	-3.98725700	-2.33074800	0.08410100
5	O	-2.59306200	-0.53547700	-1.66397500
6	C	0.12416200	0.78954500	-1.08197400
7	H	-0.56435300	0.14756100	-0.53404700
8	C	-0.49007600	1.76177300	-1.99090900
9	H	0.24108400	2.37544400	-2.53827400
10	H	-1.03557700	1.10969300	-2.70707200
11	C	1.48085300	0.40887600	-0.94021000
12	C	1.74479900	-0.68996400	-0.07595500
13	C	2.56466100	1.06282100	-1.58883000
14	C	3.05205400	-1.13433200	0.11082800
15	H	0.89689500	-1.18126800	0.41200200
16	C	3.85764100	0.61658800	-1.39424700
17	H	2.37441300	1.91860300	-2.23834100
18	C	4.10599000	-0.48550900	-0.54554500
19	H	3.26188100	-1.98214800	0.76279200
20	H	4.70756500	1.09655500	-1.88206500
21	C	5.53566100	-0.91625000	-0.37828100
22	O	6.46690300	-0.36767600	-0.91880300
23	O	5.65826300	-1.97188700	0.43588900
24	C	6.98804100	-2.45803900	0.64932600
25	H	6.89421100	-3.31265000	1.32964800
26	H	7.44217900	-2.77039000	-0.30326600
27	H	7.61866600	-1.67465000	1.09653100
28	C	-1.57313500	2.62614300	-1.30643600
29	H	-2.09935700	3.21435200	-2.07335600
30	H	-2.32266700	1.96408500	-0.84830900
31	C	-0.95872100	3.55711700	-0.24325900
32	H	-0.36316000	4.34750000	-0.72856500
33	H	-1.78476400	-0.97802200	0.29018800
34	C	-0.09782000	0.41541400	0.73757600
35	C	1.27455200	-1.33208400	0.88540200
36	C	-0.65583700	-2.33074800	1.50901400
37	C	2.07270600	-0.53547700	1.73169200
38	H	1.71731400	0.78954500	0.30487000
39	C	0.14582000	0.14756100	2.36086200
40	H	-1.72386100	1.76177300	1.43324700
41	C	1.51098200	2.37544400	2.46324300
42	H	3.13981500	1.10969300	1.81934500
43	H	-0.30372100	0.40887600	2.91077000
44	H	2.14406900	-0.68996400	3.11795700

TS3

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-0.64158400	-0.84451300	-0.80696500
2	O	-1.66433800	0.55124600	-0.92417600
3	O	0.10836300	-0.85913500	0.75562100
4	O	-1.60165500	-2.27374100	-1.05132900
5	O	0.64215300	-0.66375700	-1.98514700
6	C	1.90437300	1.33023100	-1.00048800
7	H	1.10408200	1.14428400	-0.29117800
8	C	1.61918000	2.20163300	-2.15841200
9	H	2.49206400	2.84012000	-2.38140000
10	H	1.54479800	1.49163800	-3.00684300
11	C	3.13638800	0.69981900	-0.68505200
12	C	3.16015100	-0.16992200	0.43909600
13	C	4.31756000	0.87982500	-1.45411300
14	C	4.33166500	-0.83440300	0.78156400
15	H	2.23815200	-0.32861100	1.00388700
16	C	5.48074100	0.21832600	-1.10257900
17	H	4.31100100	1.53815100	-2.32421900
18	C	5.49274700	-0.63957100	0.01660600
19	H	4.35643000	-1.51026000	1.63621700
20	H	6.40219300	0.33967000	-1.67429100
21	C	6.78866400	-1.32839100	0.34277700
22	O	7.80513000	-1.17291500	-0.29148900
23	O	6.68468500	-2.12799000	1.41042400
24	C	7.86988900	-2.83572900	1.79211400
25	H	7.59795600	-3.43318000	2.67016400
26	H	8.21102700	-3.48601900	0.97243200
27	H	8.67793300	-2.13030300	2.03851800
28	C	0.31857800	3.00923300	-2.07261600
29	H	0.15206800	3.50601800	-3.04135300
30	H	-0.52113400	2.31418900	-1.91878000
31	C	0.32045000	4.06687900	-0.94495300
32	H	1.10156200	4.82053300	-1.14073200
33	H	-0.64782000	4.59264400	-0.96617700
34	C	0.53819800	3.43234500	0.40677100
35	C	1.80310300	3.46411300	1.02562600
36	C	-0.48612600	2.67058200	1.00556100
37	C	2.04269000	2.74526000	2.20473400
38	H	2.60474400	4.06025300	0.57989300
39	C	-0.24005000	1.93529400	2.16256200
40	H	-1.46548000	2.60015400	0.52892800
41	C	1.02760000	1.97076200	2.76594300
42	H	3.03011500	2.78162300	2.67176400
43	H	-1.03185600	1.30831900	2.57504300
44	H	1.21588900	1.38630400	3.66960100
45	O	-4.03621600	-2.21634300	0.32059500
46	H	-3.21599800	-2.41076600	-0.17475100
47	C	-4.33009700	-0.86629200	0.19158800
48	H	-3.79001800	-0.36465100	-0.62739700
49	C	-5.82116600	-0.72170000	-0.13607100
50	C	-3.93105000	-0.10119900	1.46829400
51	F	-6.18817300	0.57334400	-0.15525600

52	F	-6.06156500	-1.23124000	-1.35218400
53	F	-6.60212400	-1.35851200	0.73988200
54	F	-3.96038600	1.22991400	1.28029800
55	F	-2.67032500	-0.42579300	1.81517700
56	F	-4.71907800	-0.38584100	2.51134800

$TS3_B$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	-2.46250400	-1.27518400	0.02734900
2	O	-3.49519700	0.11581500	0.18269400
3	O	-1.23952600	-1.17556400	1.27053400
4	O	-3.36354400	-2.73864300	0.15689800
5	O	-1.63746800	-1.16572800	-1.51572800
6	C	-0.03572300	0.93613000	-1.03762000
7	H	-0.67077600	0.63018000	-0.21674600
8	C	-0.67630700	1.68247200	-2.12871700
9	H	0.04612400	2.26567600	-2.72192800
10	H	-1.05509400	0.86605400	-2.78003900
11	C	1.30742100	0.50716500	-0.90906500
12	C	1.61336200	-0.32011900	0.20715500
13	C	2.33822400	0.86851000	-1.81911600
14	C	2.91630500	-0.76885500	0.40242400
15	H	0.80304500	-0.61900200	0.88013200
16	C	3.63011900	0.42355400	-1.61067500
17	H	2.11253700	1.50392900	-2.67698300
18	C	3.92397900	-0.39514600	-0.49817000
19	H	3.15990400	-1.41037900	1.24913600
20	H	4.44292400	0.68894100	-2.28860200
21	C	5.34940700	-0.84125300	-0.33064500
22	O	6.24096600	-0.52795400	-1.08375600
23	O	5.51632500	-1.62100500	0.74443400
24	C	6.84403400	-2.10228000	0.97963600
25	H	6.78906700	-2.71643500	1.88616800
26	H	7.19335000	-2.70322500	0.12635100
27	H	7.53993700	-1.26168700	1.12300000
28	C	-1.88437700	2.51347500	-1.66711100
29	H	-2.39345900	2.93174300	-2.54908300
30	H	-2.60260400	1.84102200	-1.17077200
31	C	-1.48056300	3.65183500	-0.70507200
32	H	-0.88551600	4.40623600	-1.24590800
33	H	-2.40004200	4.15487000	-0.36197100
34	C	-0.69773800	3.14304100	0.48253800
35	C	0.67004100	3.44269400	0.63741400
36	C	-1.31206300	2.29125600	1.42903000
37	C	1.40973200	2.89484100	1.68767600
38	H	1.15806600	4.10391800	-0.08433000
39	C	-0.56970000	1.72938100	2.46536400
40	H	-2.36214500	2.01247800	1.30695800
41	C	0.79428500	2.02776300	2.59616300
42	H	2.47188200	3.13153500	1.78750800
43	H	-1.04970900	1.02964300	3.15121800
44	H	1.37522500	1.58113800	3.40686000

$TS4_B$

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	Re	0.41029200	2.16986500	-0.25869100
2	O	1.74567600	1.52107700	0.69322100
3	O	0.90569000	3.57719600	-1.12310600
4	O	-0.06150300	0.90920700	-1.36542000
5	O	-0.91271700	2.53595300	0.79930900
6	C	1.10026600	-1.95255100	1.17842200
7	H	1.37986800	-2.99960900	1.01335600
8	C	1.86168000	-1.25637400	2.27082600
9	H	1.69788100	-0.16968800	2.20195800
10	H	1.39007200	-1.60004000	3.21227000
11	C	-0.32264400	-1.68797600	0.97549500
12	C	-1.11033300	-2.63072600	0.27497000
13	C	-0.93357900	-0.50829200	1.44414500
14	C	-2.45688300	-2.39543700	0.04260600
15	H	-0.64427100	-3.54504800	-0.10188900
16	C	-2.28203400	-0.26406500	1.20300100
17	H	-0.35546700	0.24568500	1.97503900
18	C	-3.04914800	-1.20245300	0.50202200
19	H	-3.06359200	-3.11945600	-0.50146300
20	H	-2.73187700	0.67674300	1.52135500
21	C	-4.49362800	-0.88867200	0.25956700
22	O	-5.06149500	0.08041200	0.70160800
23	O	-5.09557300	-1.81490700	-0.50980100
24	C	-6.47616900	-1.58599200	-0.79869900
25	H	-6.80016500	-2.42255500	-1.42995100
26	H	-7.06822400	-1.55165700	0.12896100
27	H	-6.60880100	-0.63021400	-1.32856200
28	C	3.35754400	-1.55622300	2.30725000
29	H	3.81078900	-1.05511300	3.17613500
30	H	3.52887900	-2.63981900	2.43236200
31	C	4.05992000	-1.07005700	1.01385000
32	H	3.95148800	0.02431800	0.94825300
33	H	5.12972500	-1.32513500	1.04766400
34	C	3.39160500	-1.70146800	-0.16585800
35	C	2.07688500	-1.24408100	-0.50492500
36	C	3.92697500	-2.79018100	-0.86007200
37	C	1.39227300	-1.81391200	-1.61975900
38	H	1.81701600	-0.22222400	-0.20016700
39	C	3.21179600	-3.36914500	-1.91340900
40	H	4.91311200	-3.17692200	-0.59092700
41	C	1.94850700	-2.87846700	-2.30501900
42	H	0.42859400	-1.37863900	-1.89158300
43	H	3.64695100	-4.21591600	-2.45185600
44	H	1.42732900	-3.32966400	-3.15210400

2v

Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.42975800	-0.93109600	-0.59684000
2	H	1.52603000	-1.19622200	-1.66590900
3	C	1.82065000	-2.18603100	0.21159500
4	H	1.53811100	-2.03856800	1.26914000
5	H	1.23290500	-3.04422200	-0.15143100
6	C	-0.02847100	-0.58068700	-0.35174400
7	C	-1.01181400	-0.88270300	-1.30475700
8	C	-0.43088400	0.00987600	0.85969300
9	C	-2.35927000	-0.60724300	-1.06394000
10	H	-0.71664400	-1.33929200	-2.25378600
11	C	-1.77129500	0.28677700	1.10905200
12	H	0.32448300	0.26502100	1.60726400
13	C	-2.74932100	-0.01976900	0.14800700
14	H	-3.11521900	-0.84337400	-1.81383400
15	H	-2.08872100	0.74690500	2.04687500
16	C	-4.17059300	0.30081300	0.46501300
17	O	-4.54768500	0.80670100	1.49782600
18	O	-5.01344100	-0.03605900	-0.53349400
19	C	-6.39407400	0.23910400	-0.30572300
20	H	-6.92663100	-0.09326300	-1.20573700
21	H	-6.76199000	-0.30368400	0.57910900
22	H	-6.55786800	1.31543600	-0.13961100
23	C	3.32121500	-2.45551300	0.12219600
24	H	3.57590100	-3.40449600	0.62126800
25	H	3.61358600	-2.56437300	-0.93777600
26	C	4.09475700	-1.29943400	0.75714300
27	H	3.95428800	-1.33311700	1.85427300
28	H	5.17853000	-1.41413100	0.59033300
29	C	3.64449100	0.05849100	0.25177800
30	C	2.38514600	0.24100100	-0.35557400
31	C	4.49430700	1.16739100	0.40498200
32	C	2.02588800	1.52441700	-0.80366700
33	C	4.12329100	2.43685000	-0.03437300
34	H	5.47016100	1.02185400	0.87845500
35	C	2.87855700	2.61567900	-0.64748400
36	H	1.05173200	1.66644200	-1.27841900
37	H	4.80278700	3.28311600	0.09573900
38	H	2.57354600	3.60329900	-1.00275500

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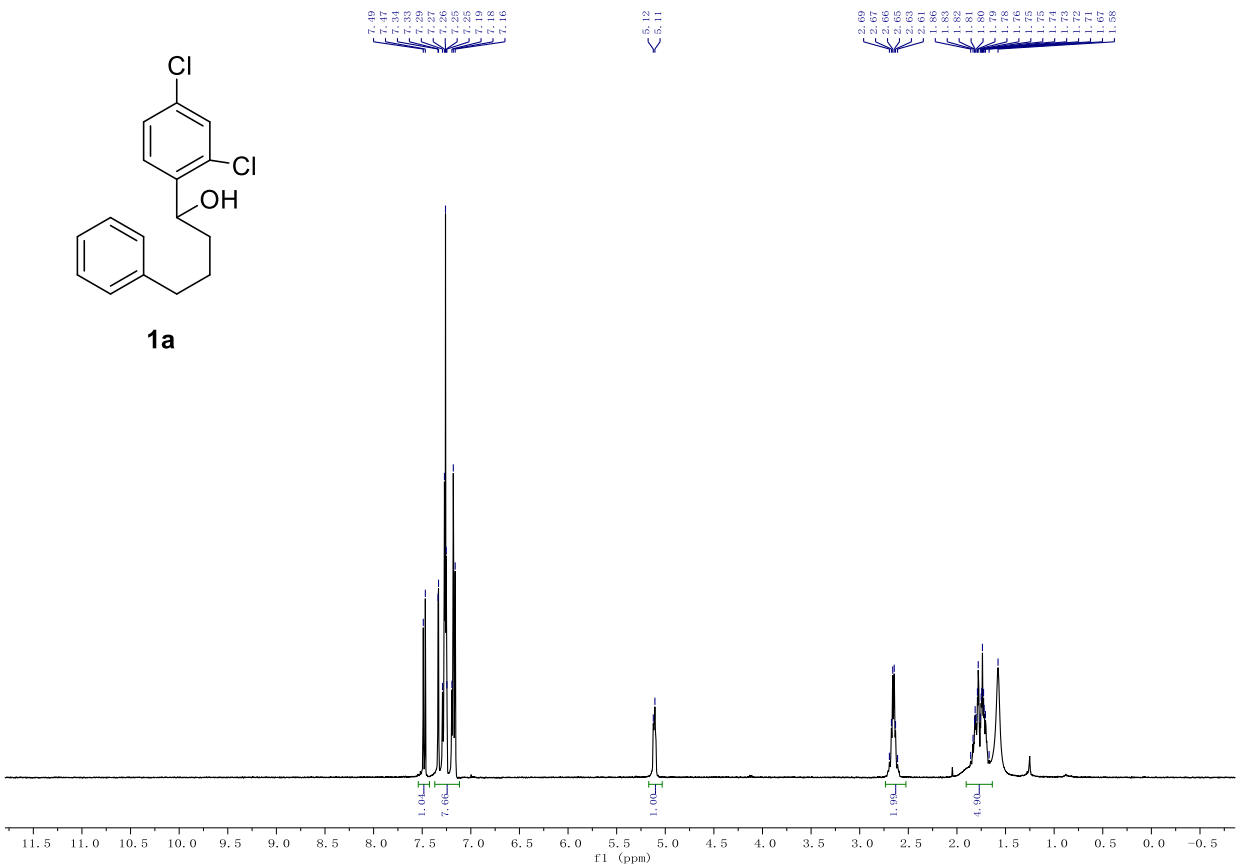
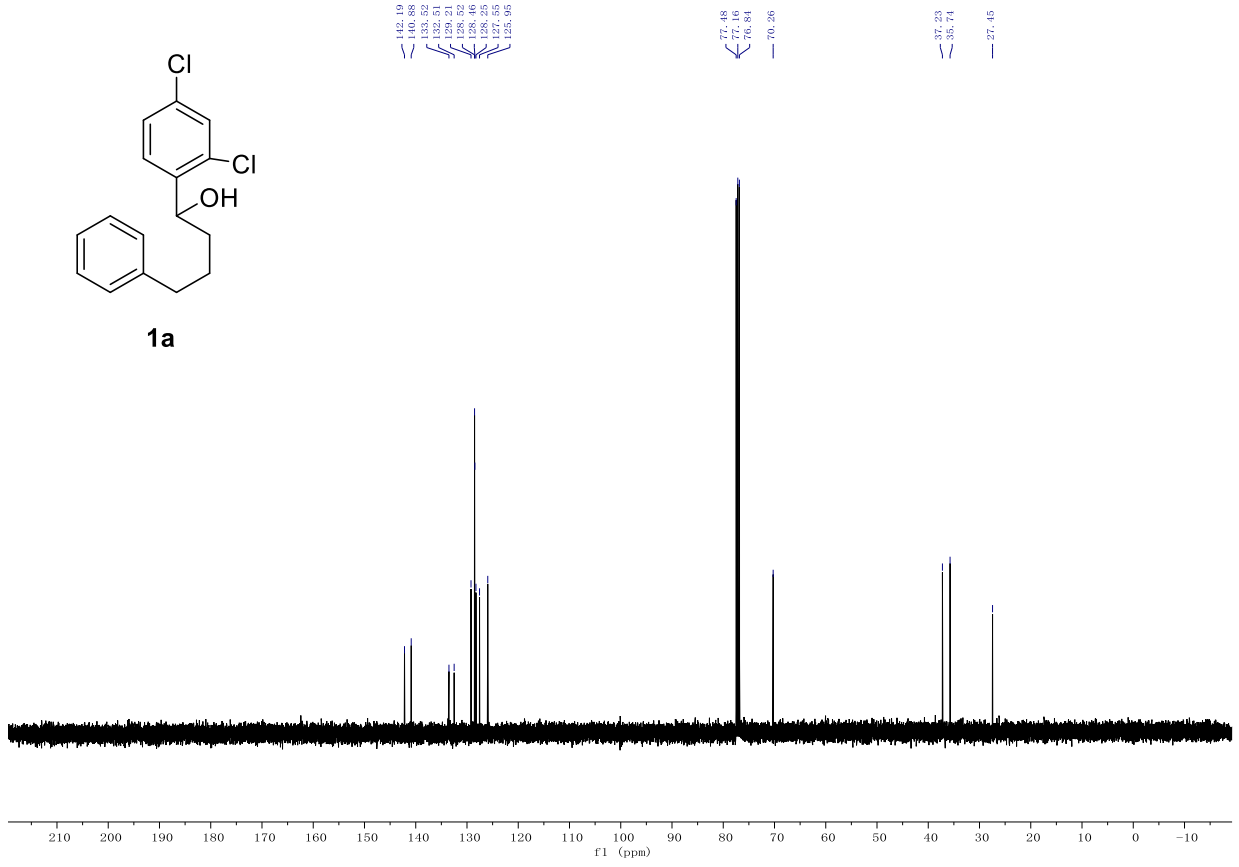
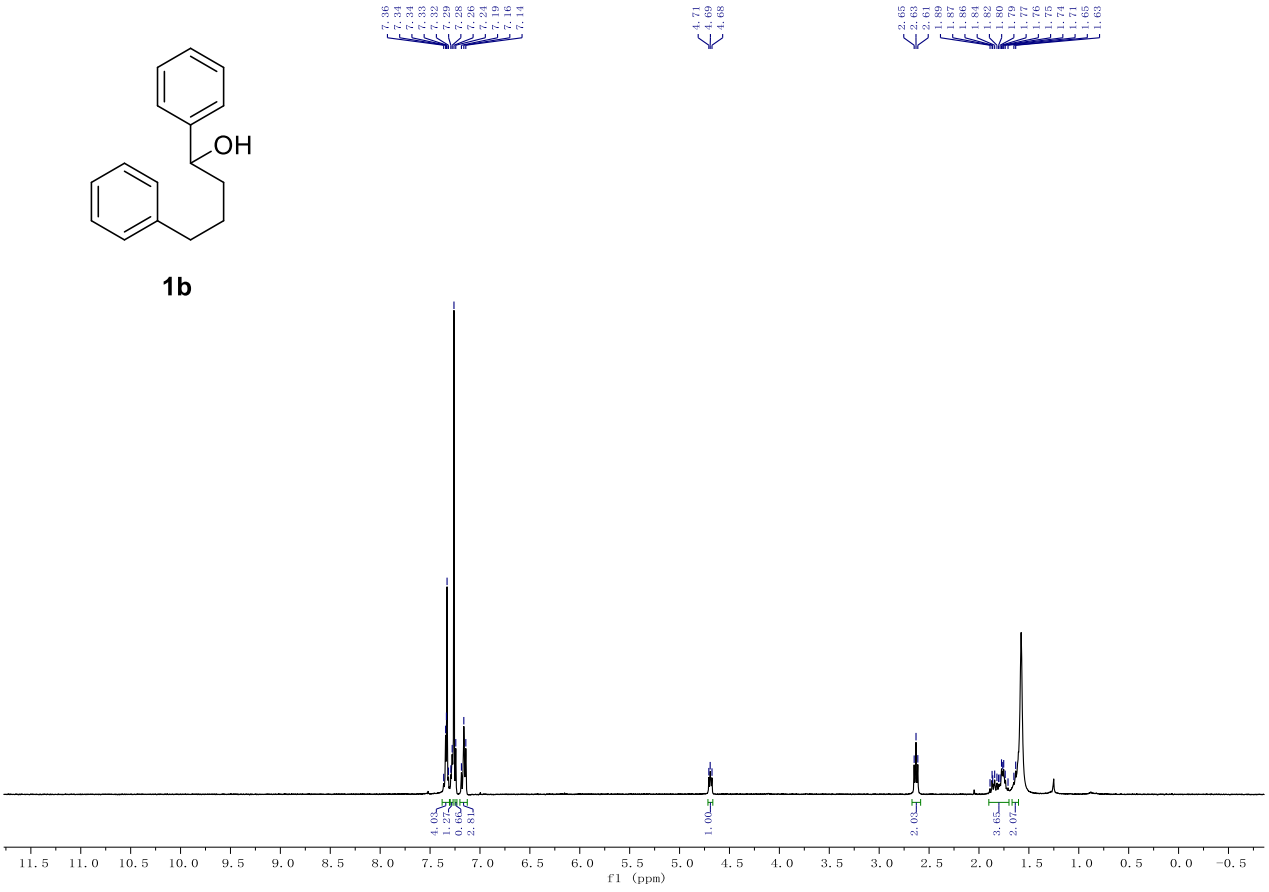
14 NMR spectroscopic data







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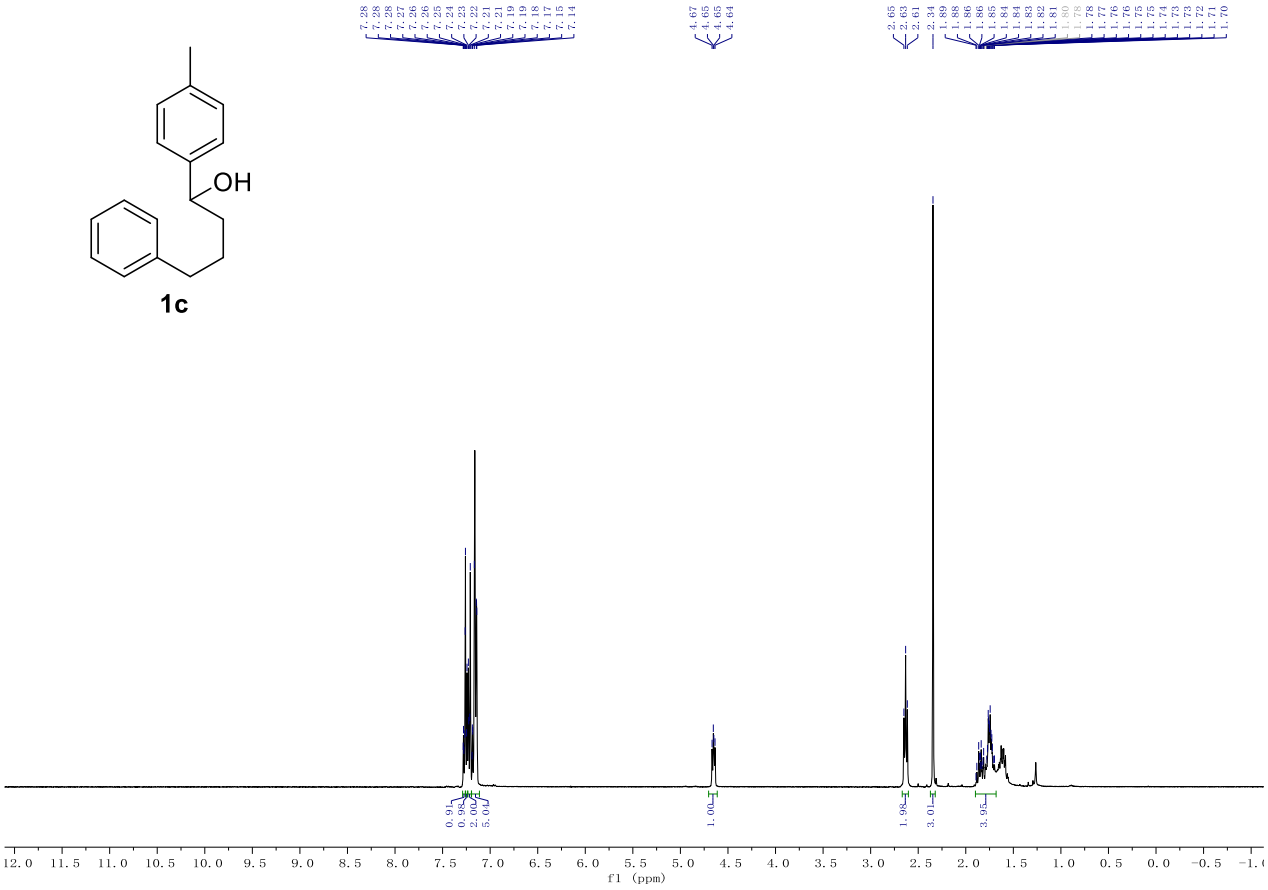

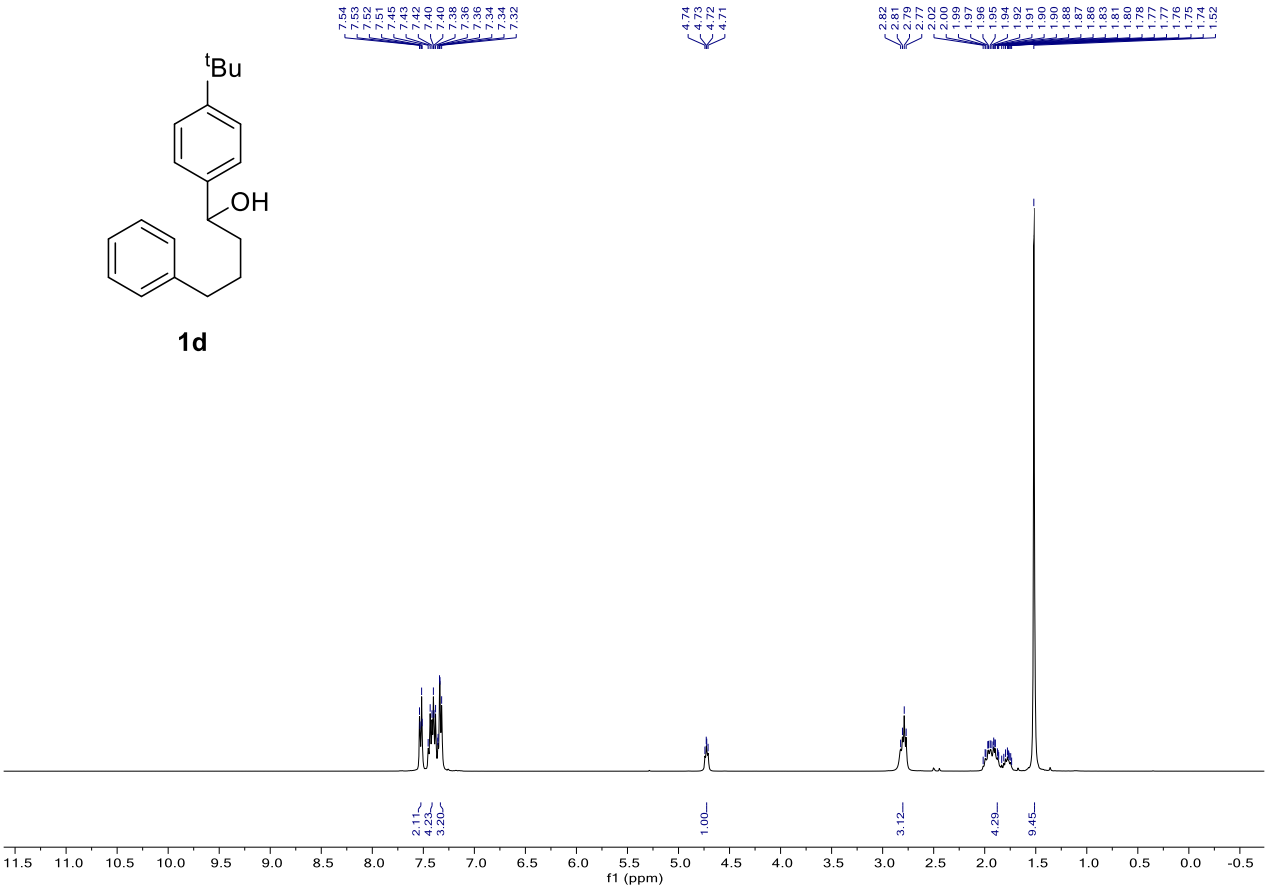

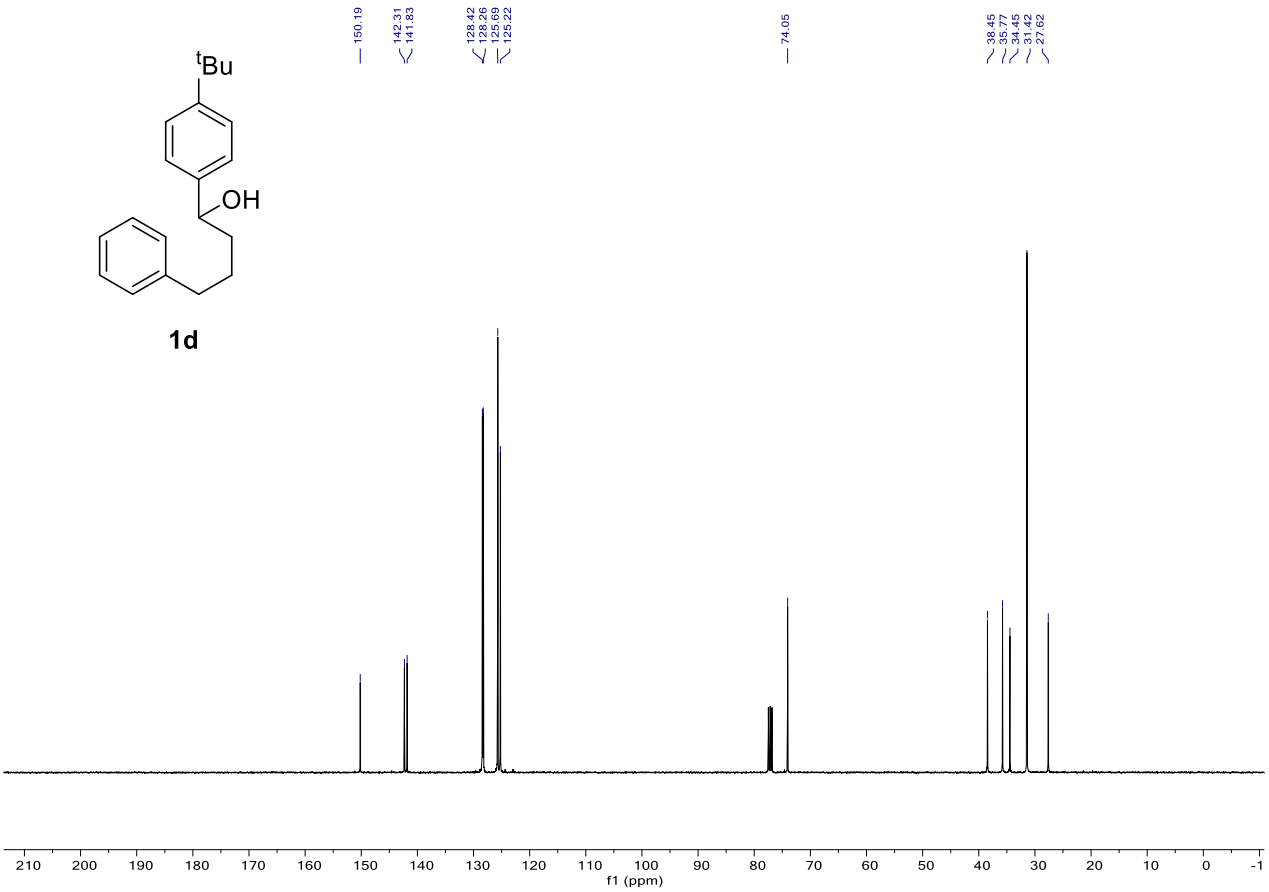

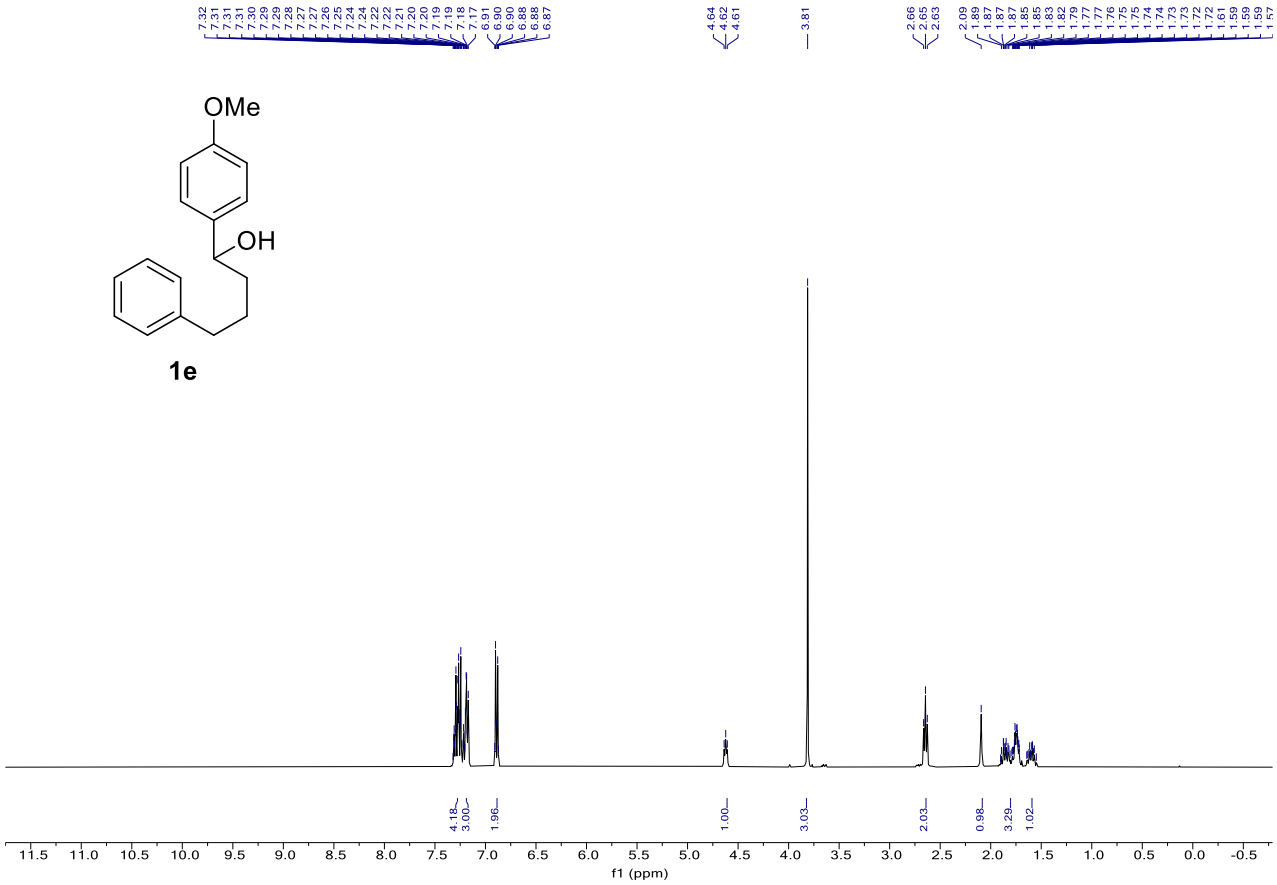

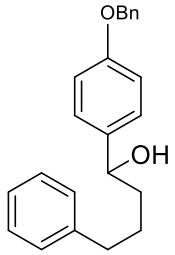

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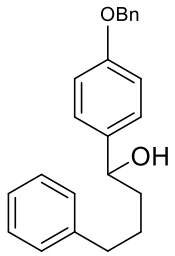

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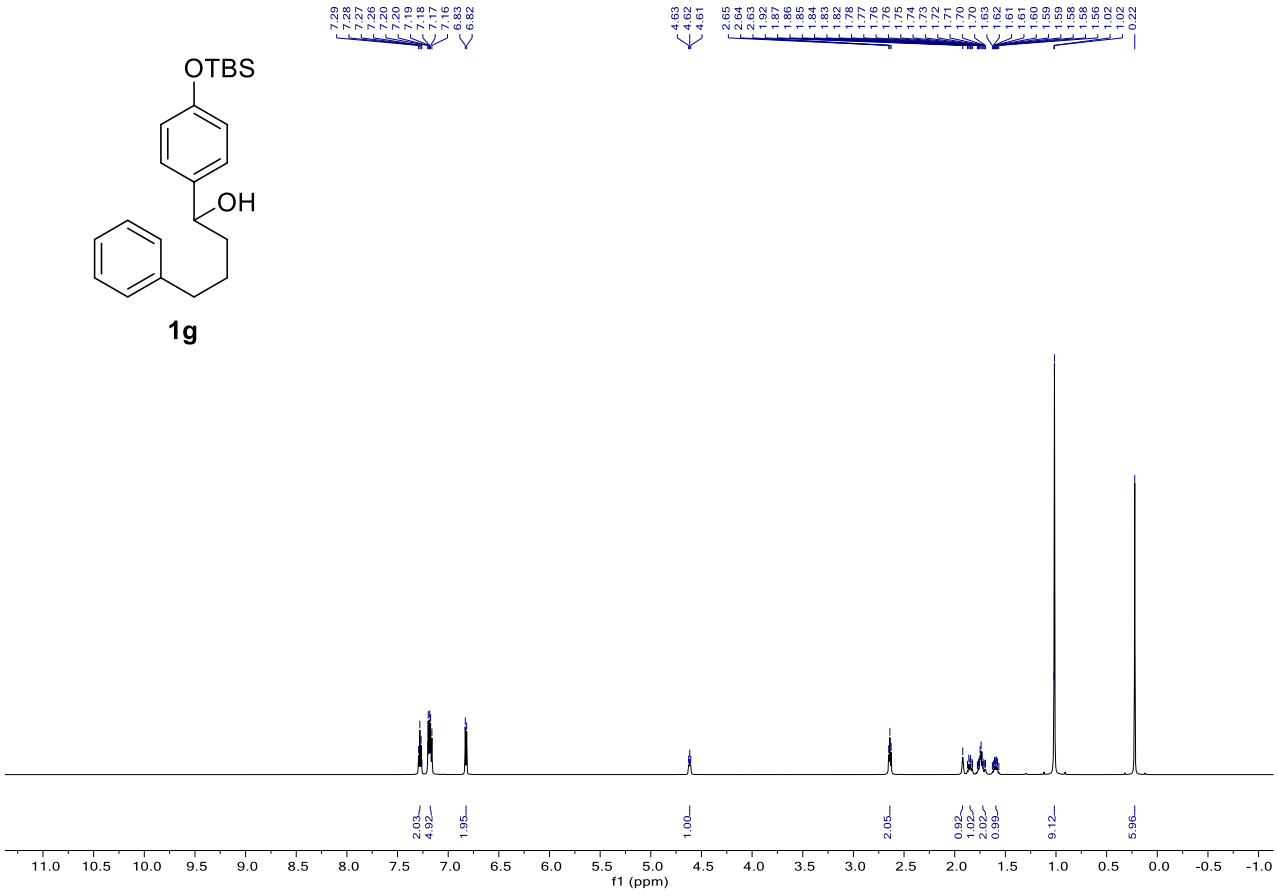

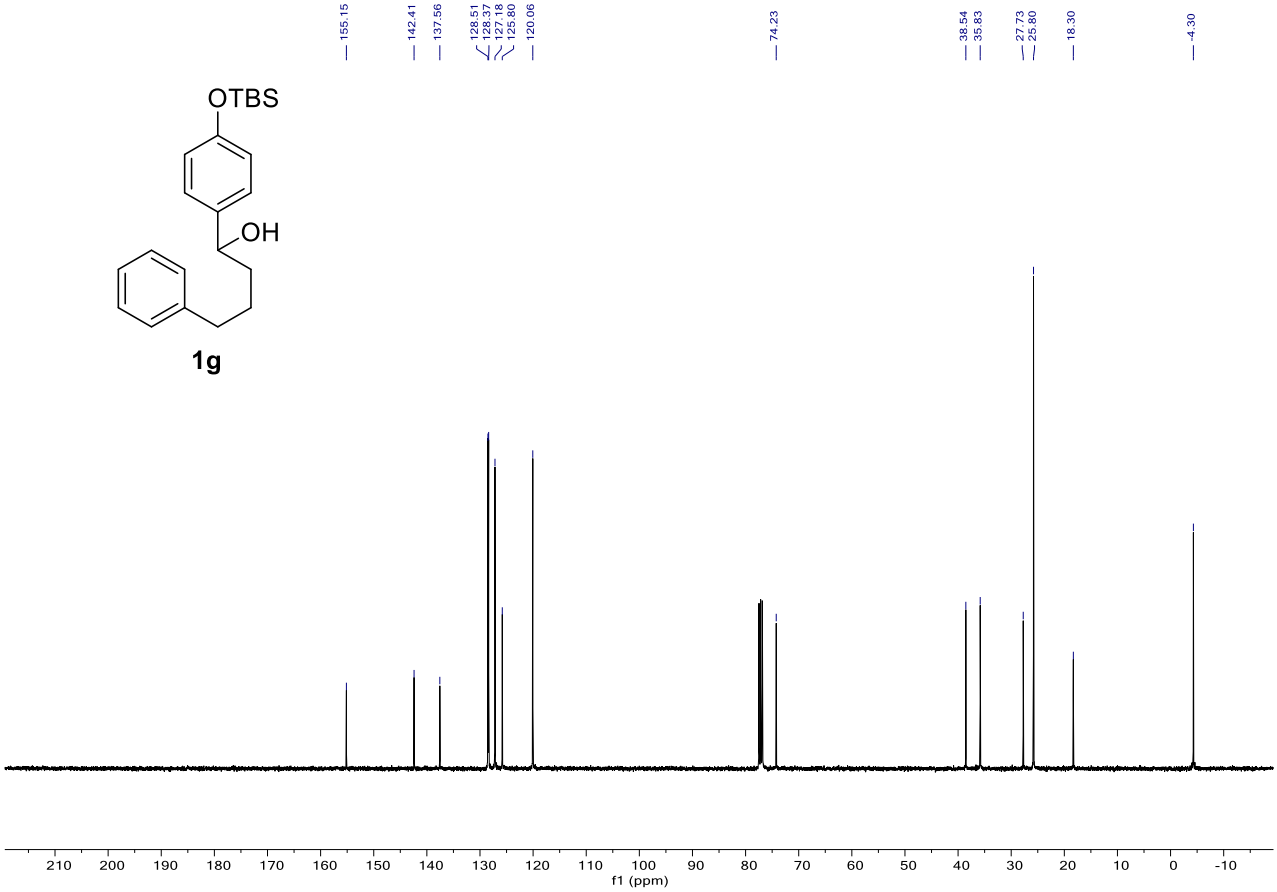

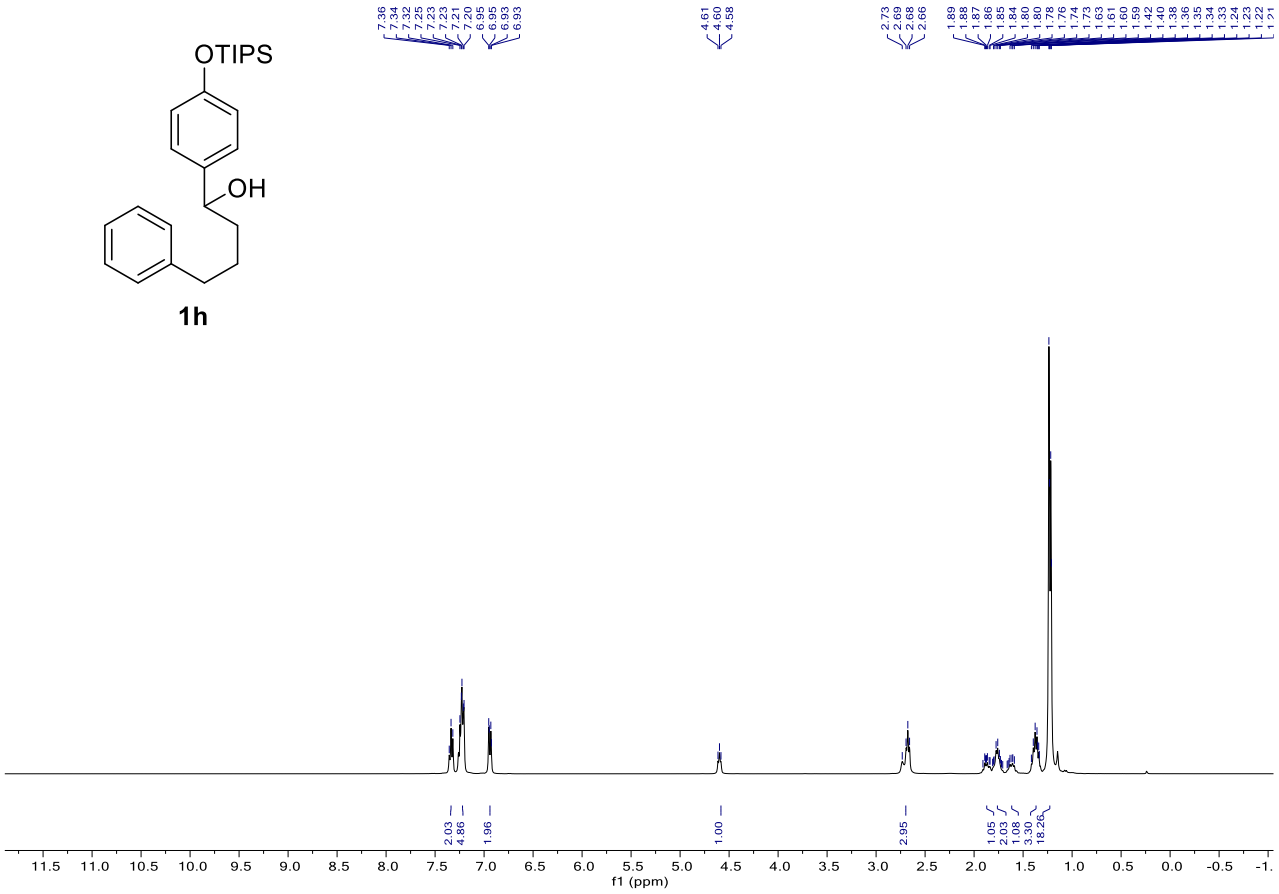

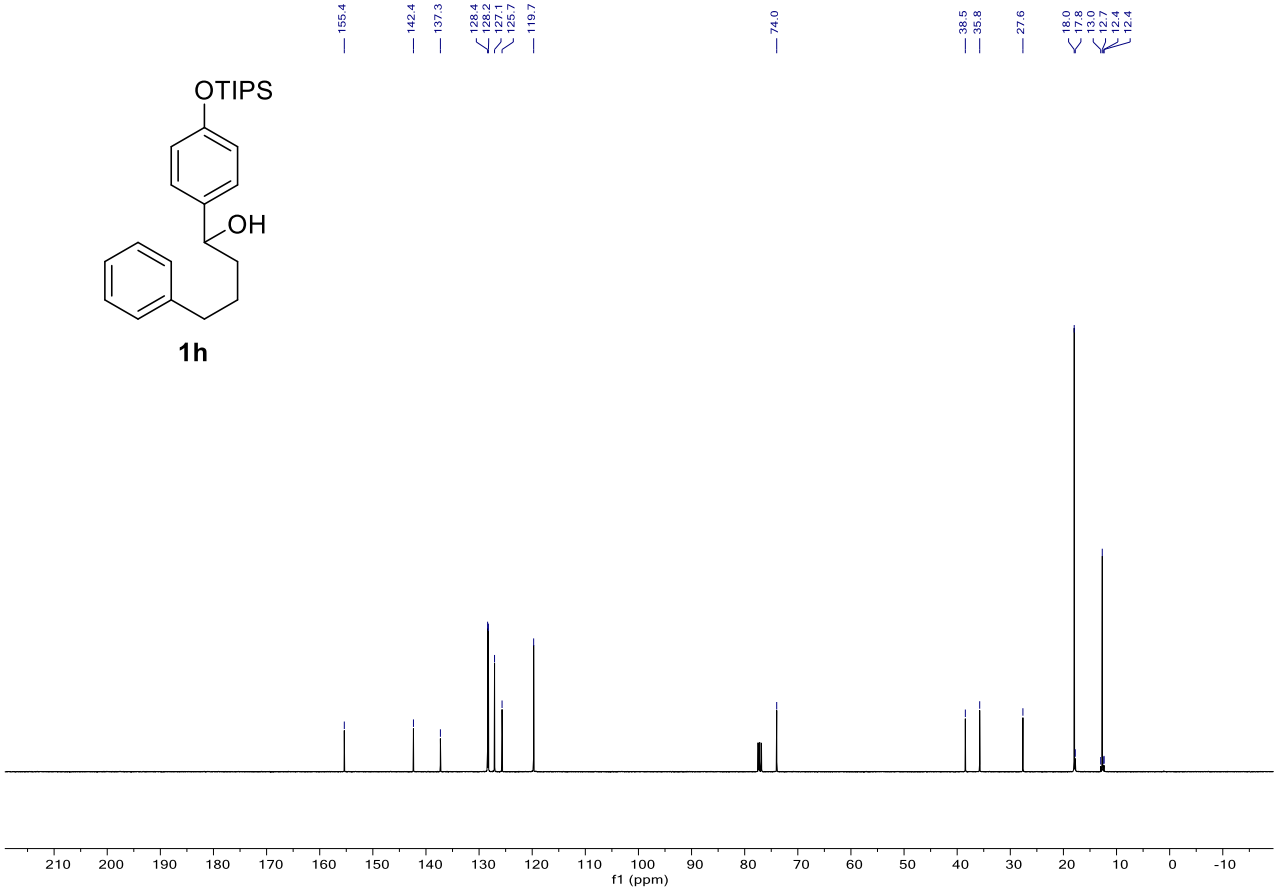

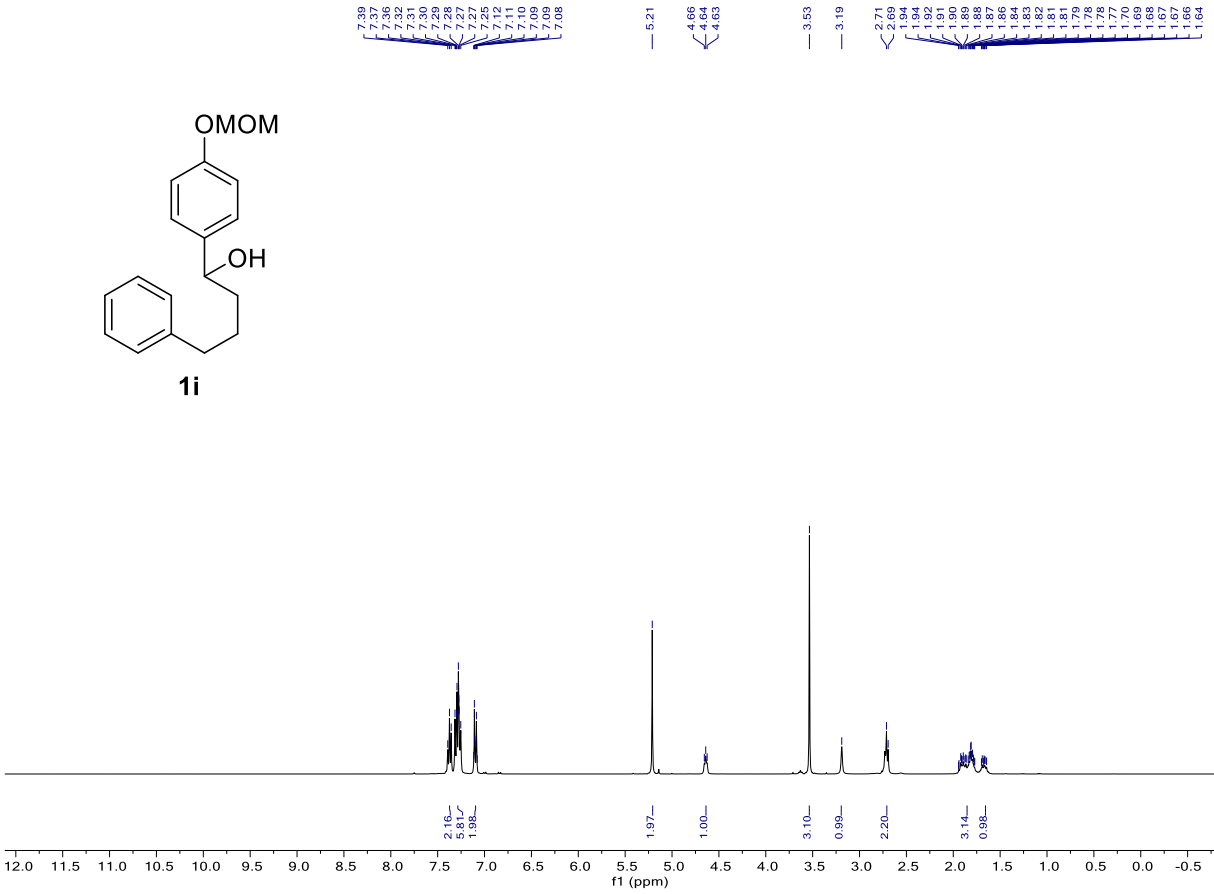

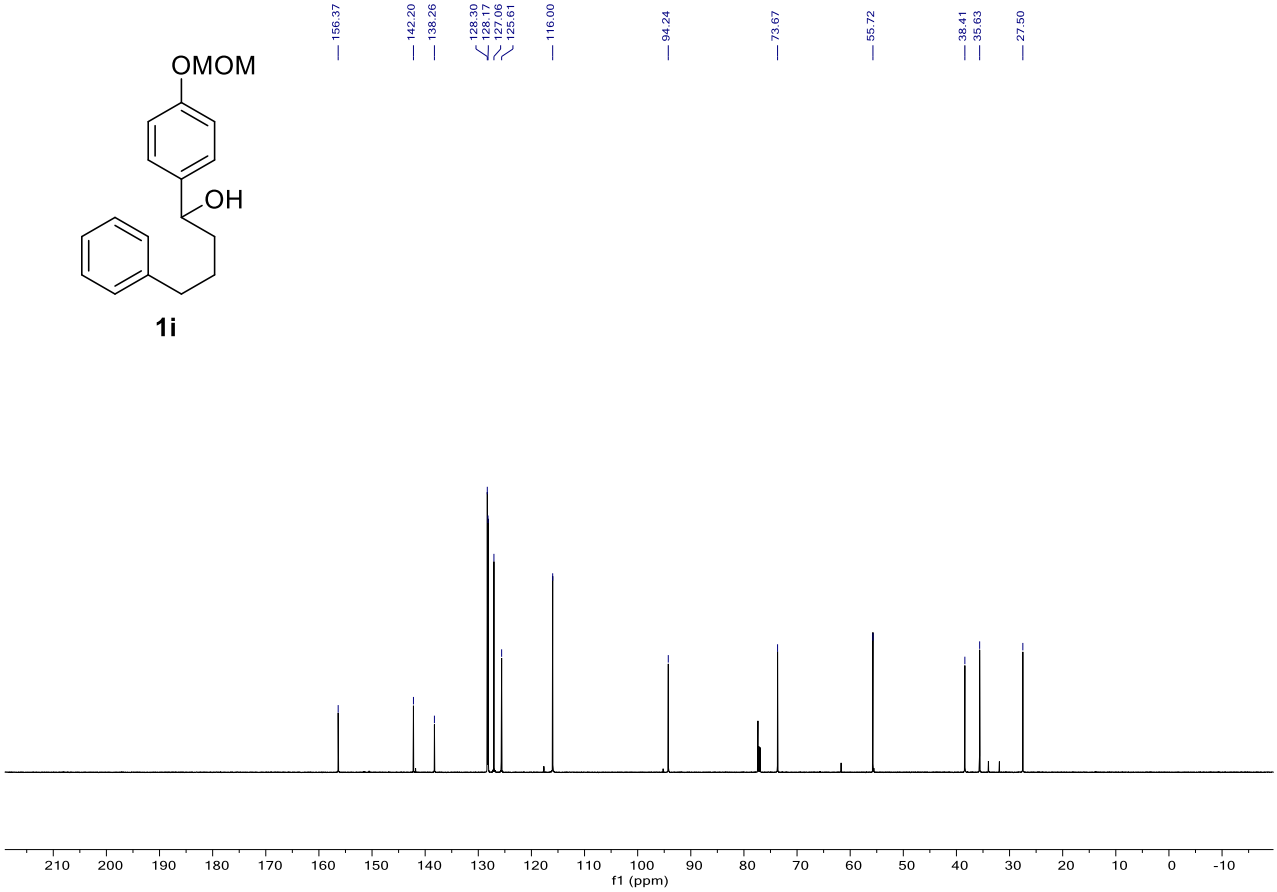

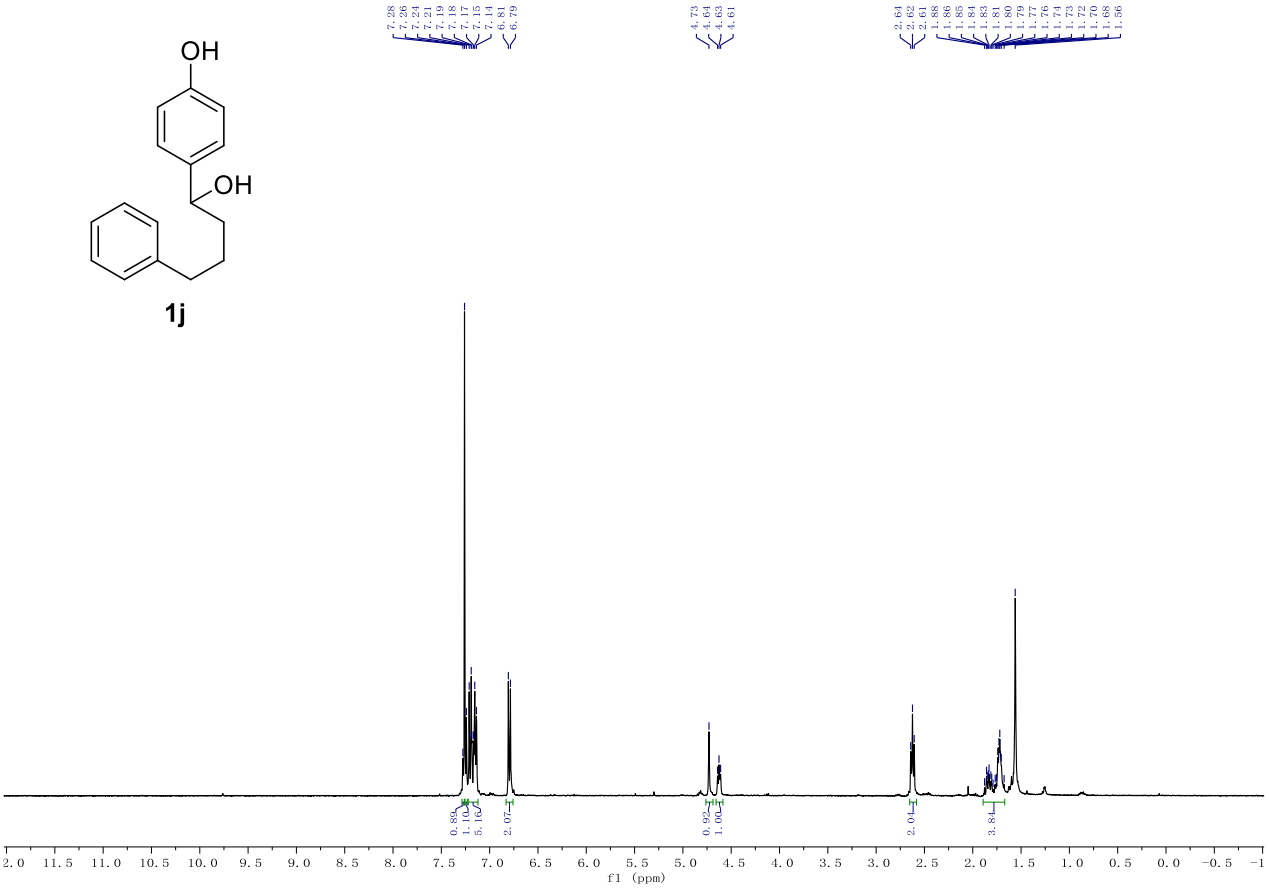

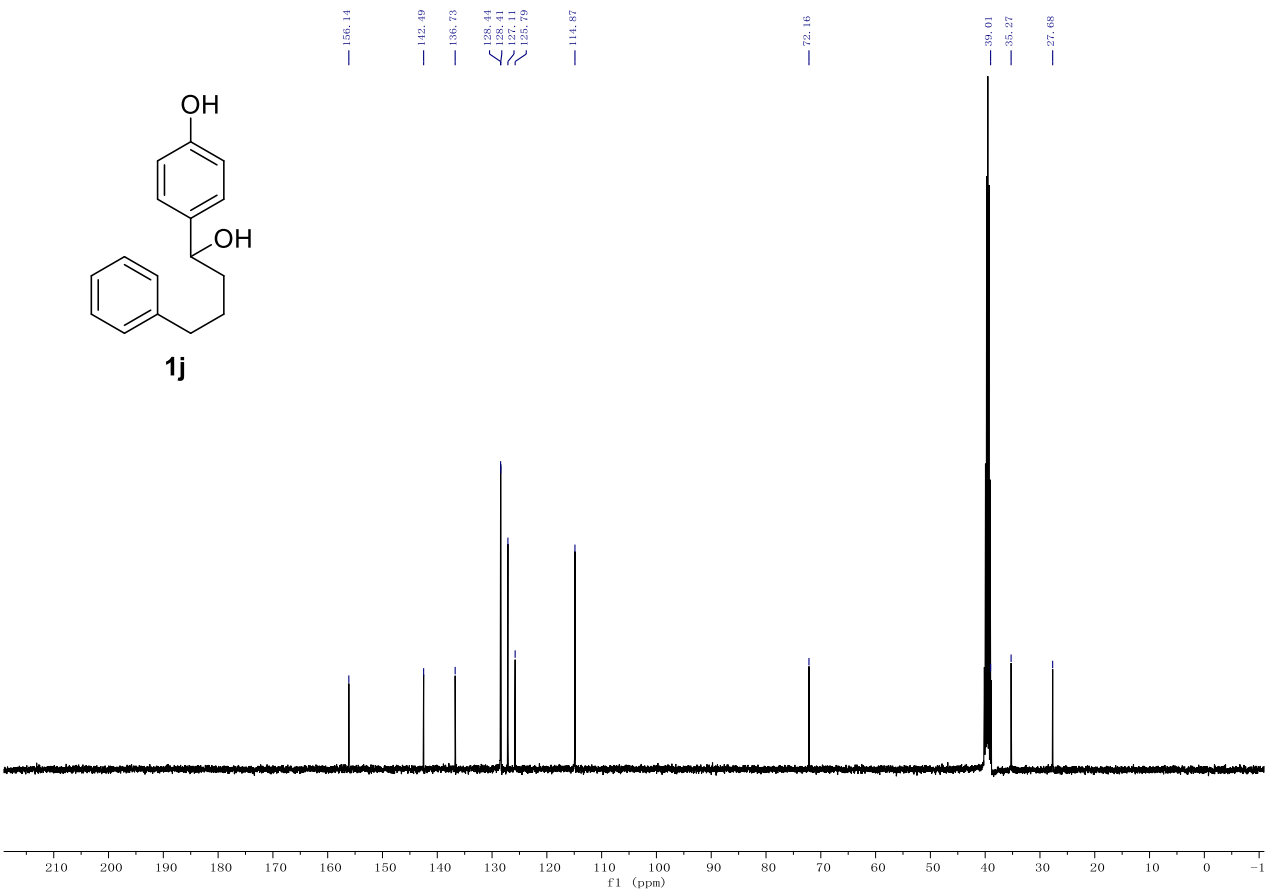

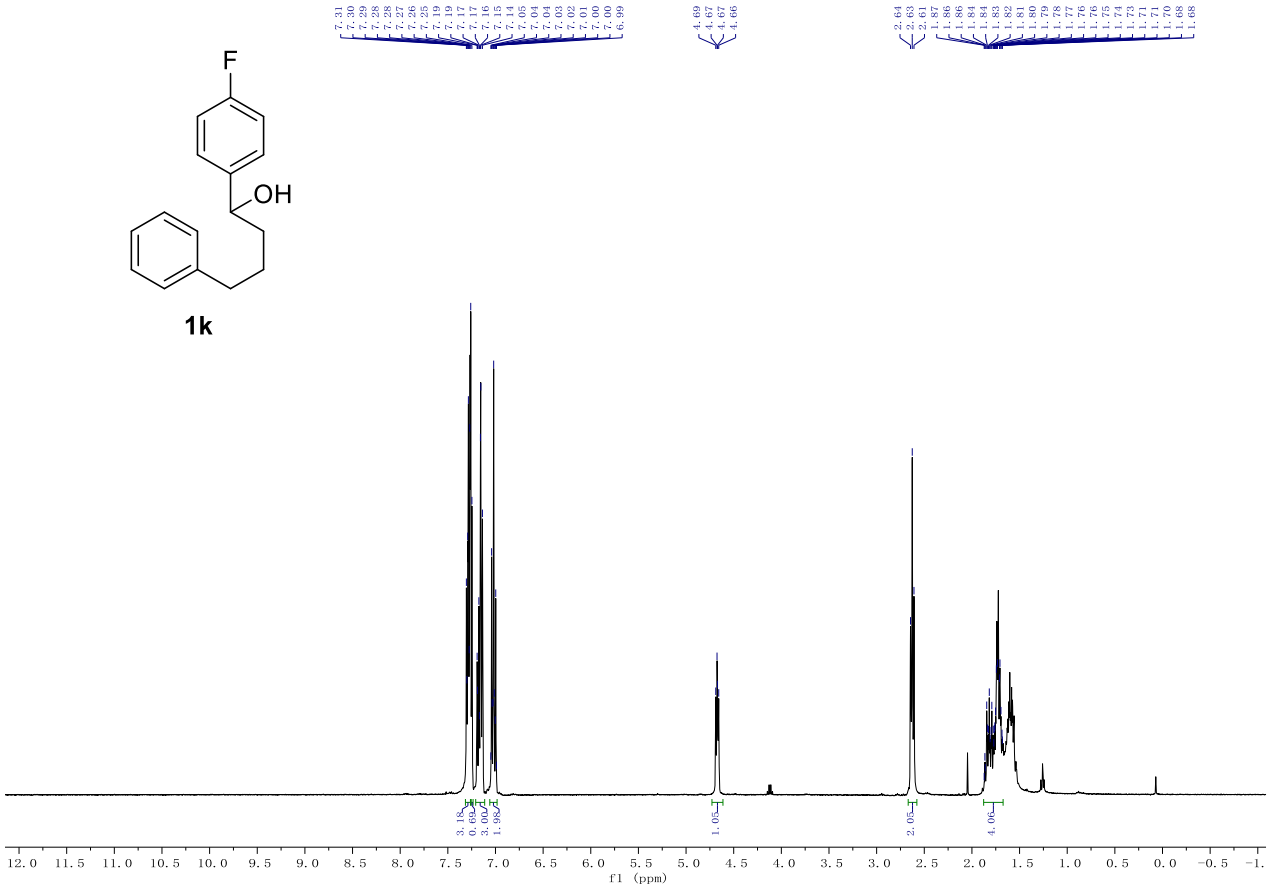

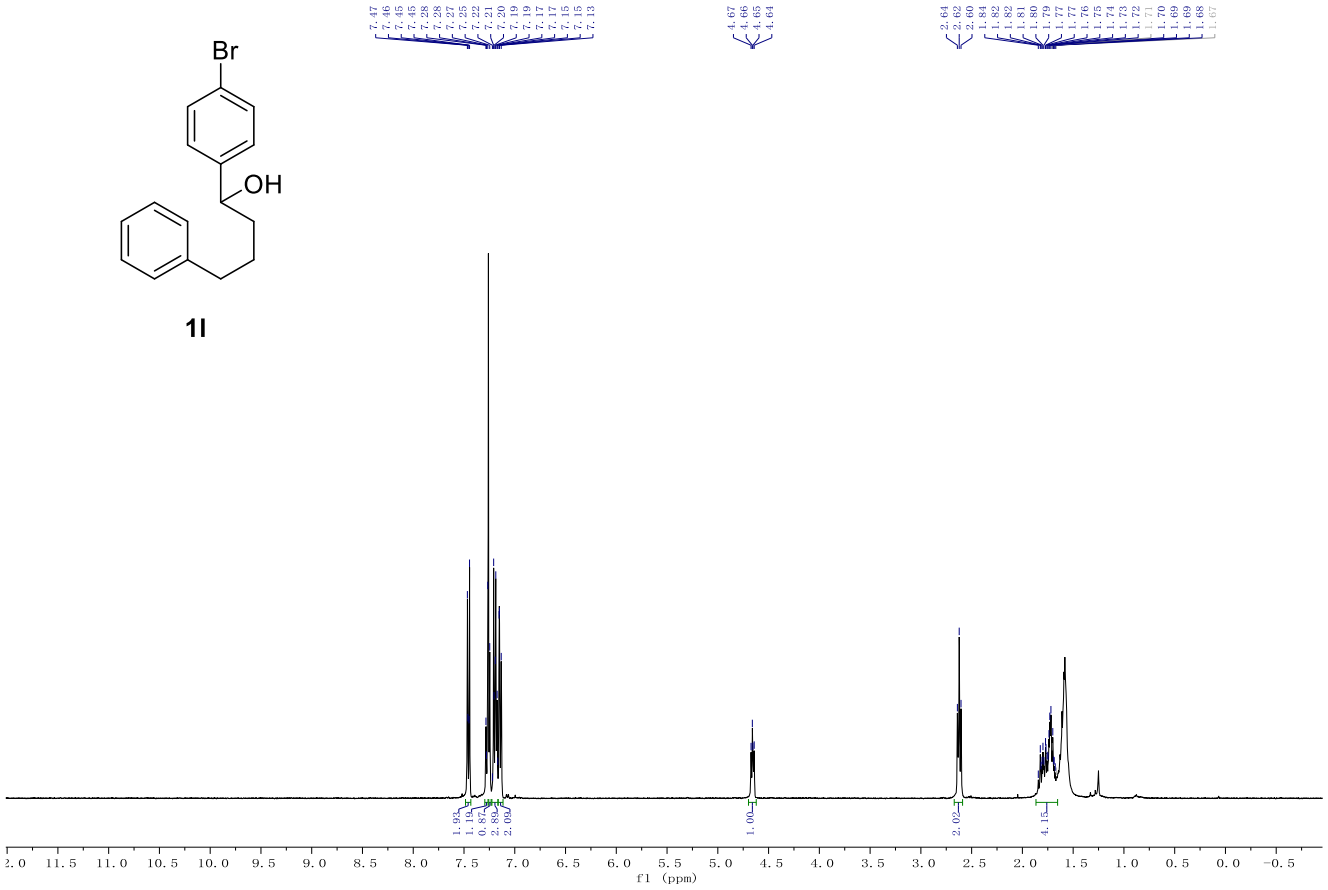

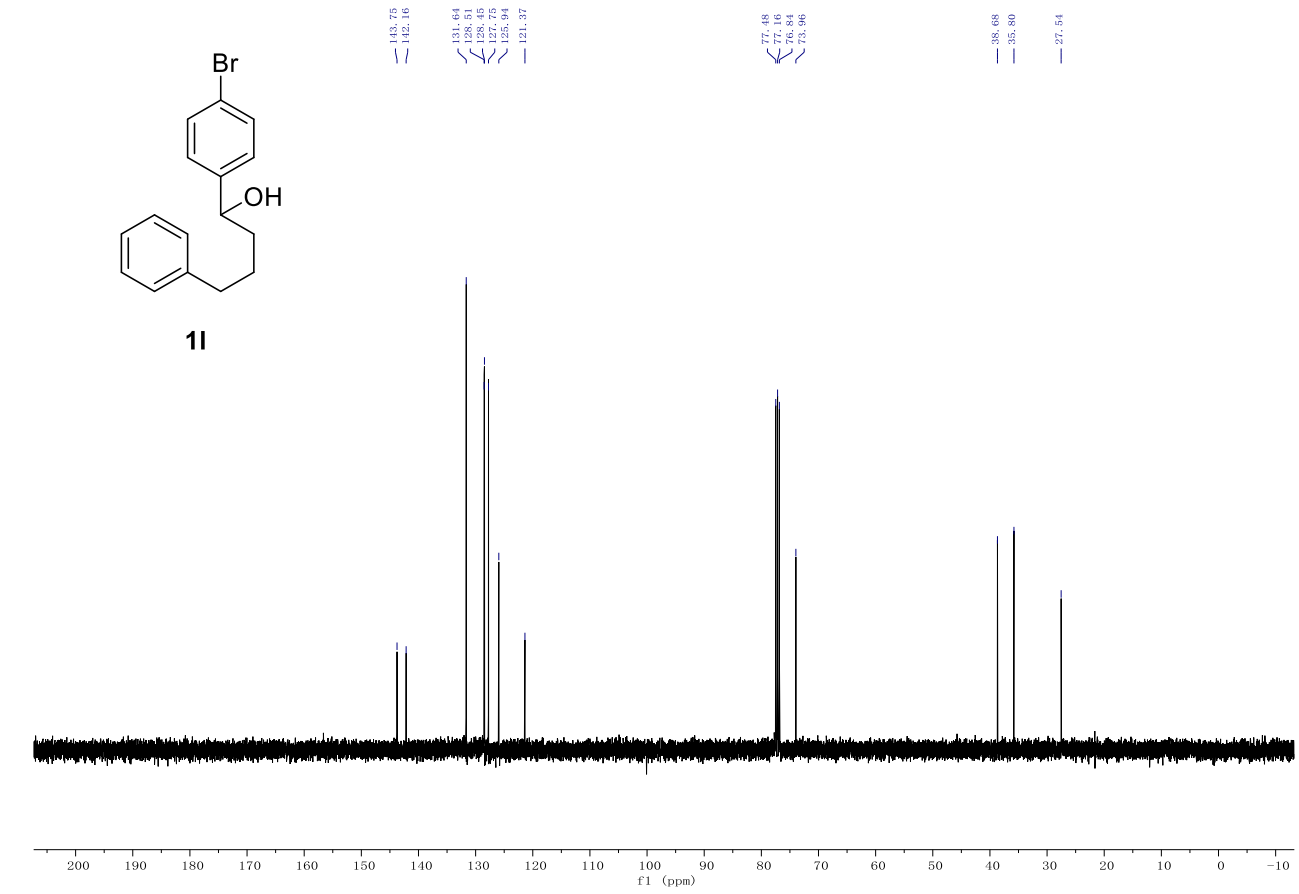

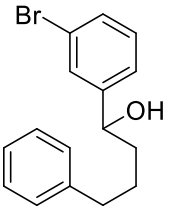

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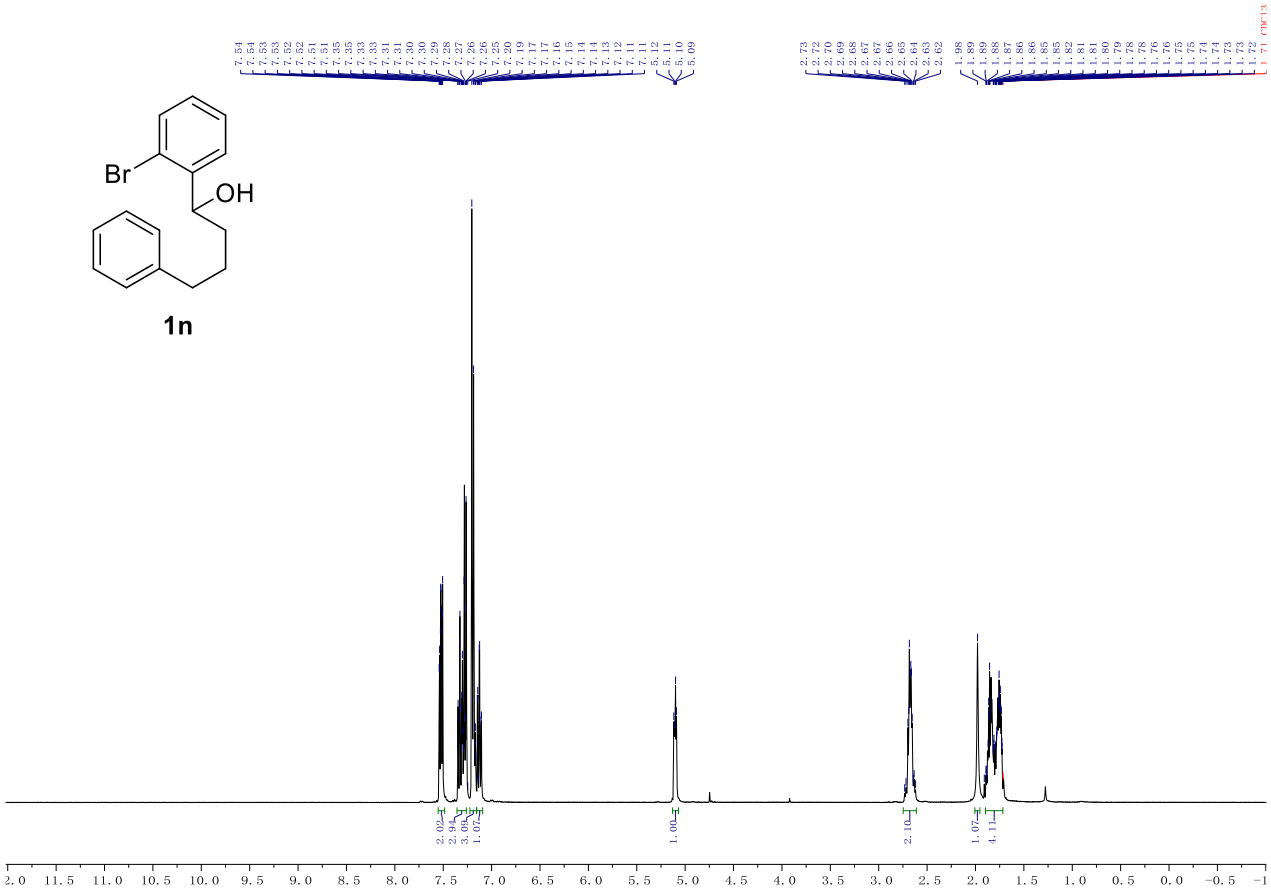

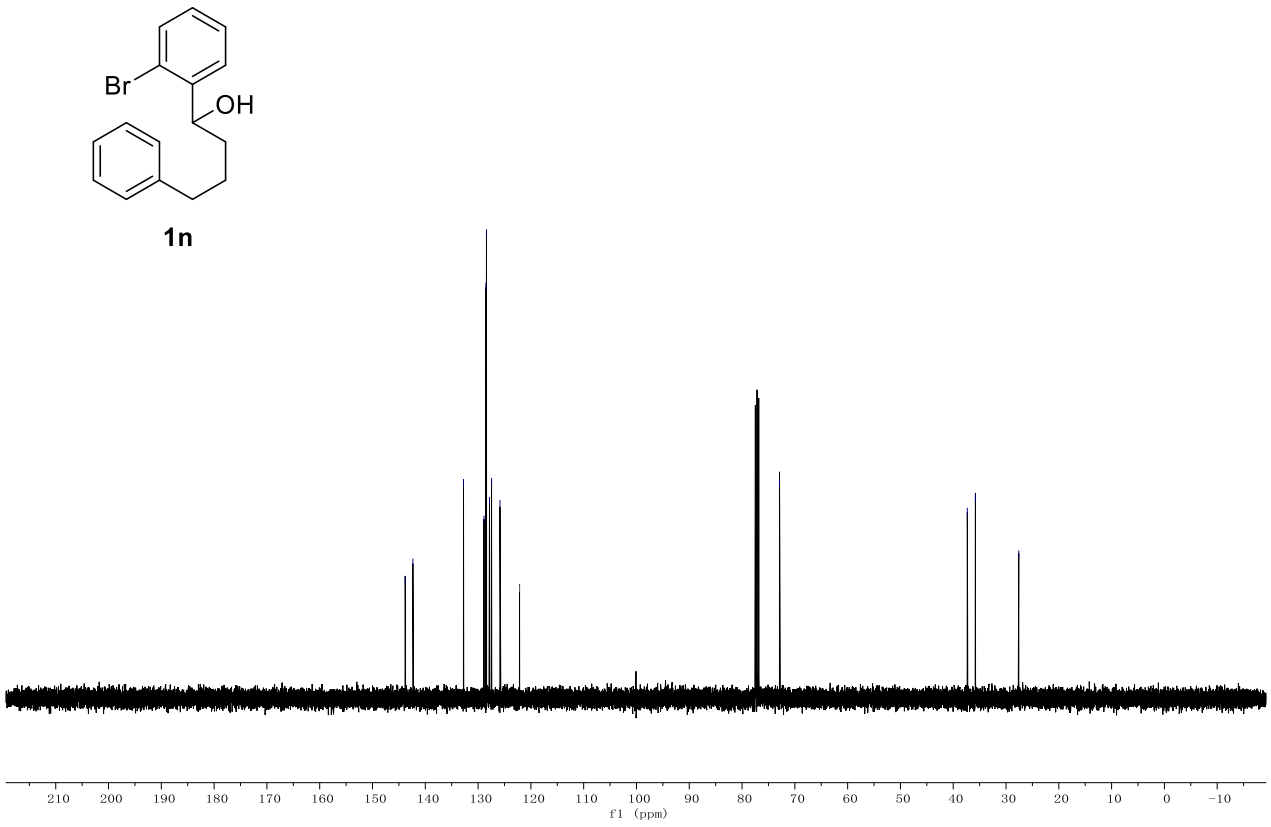

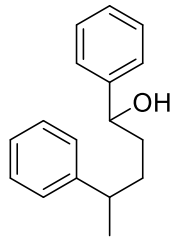

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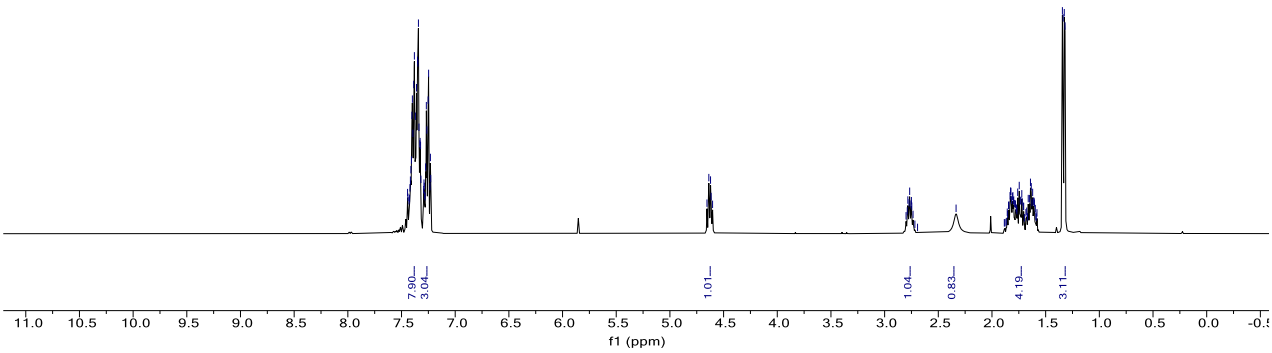

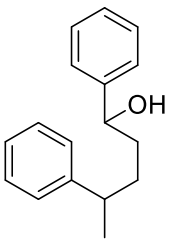

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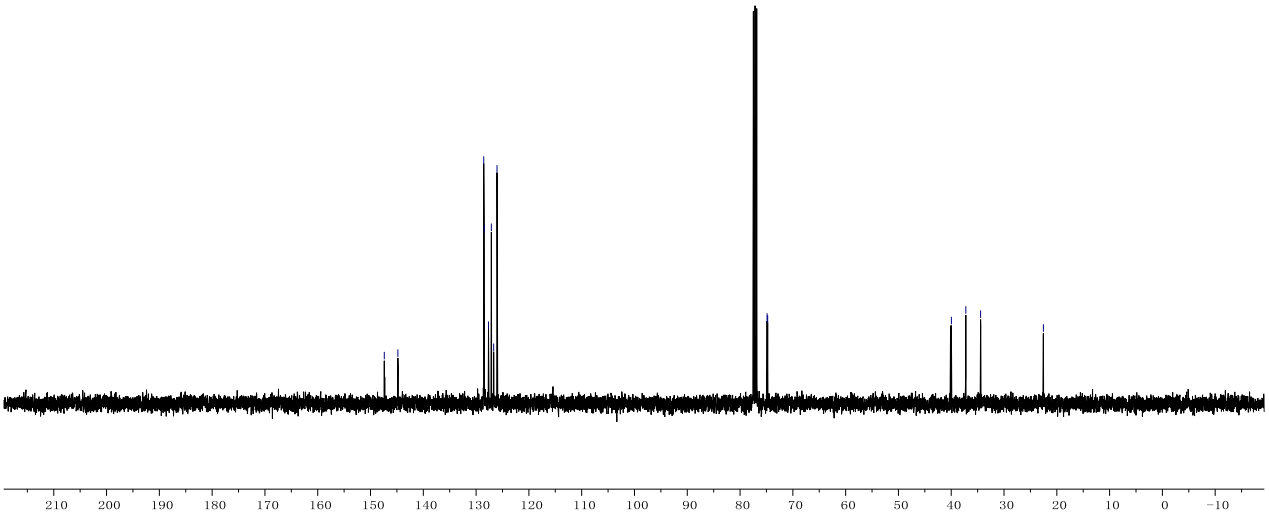

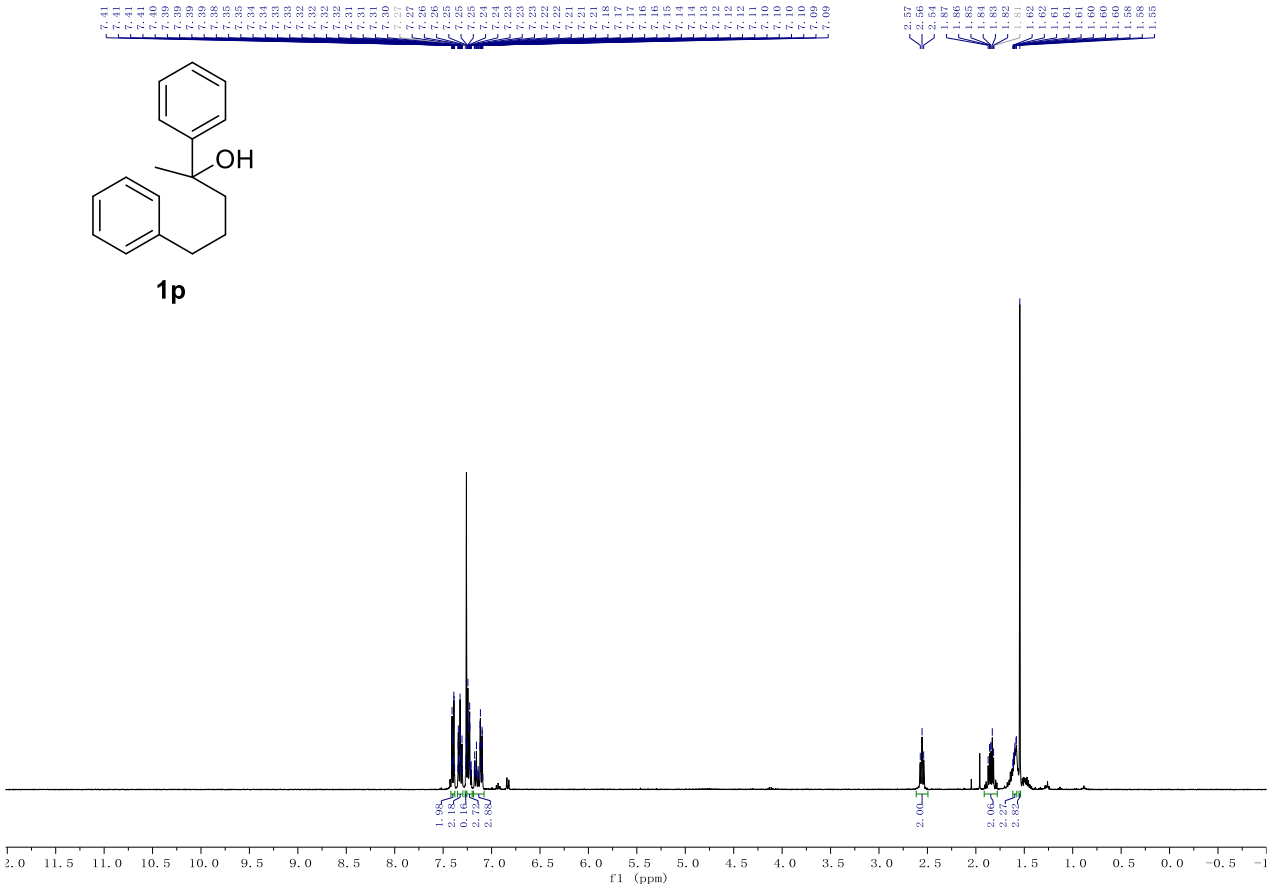

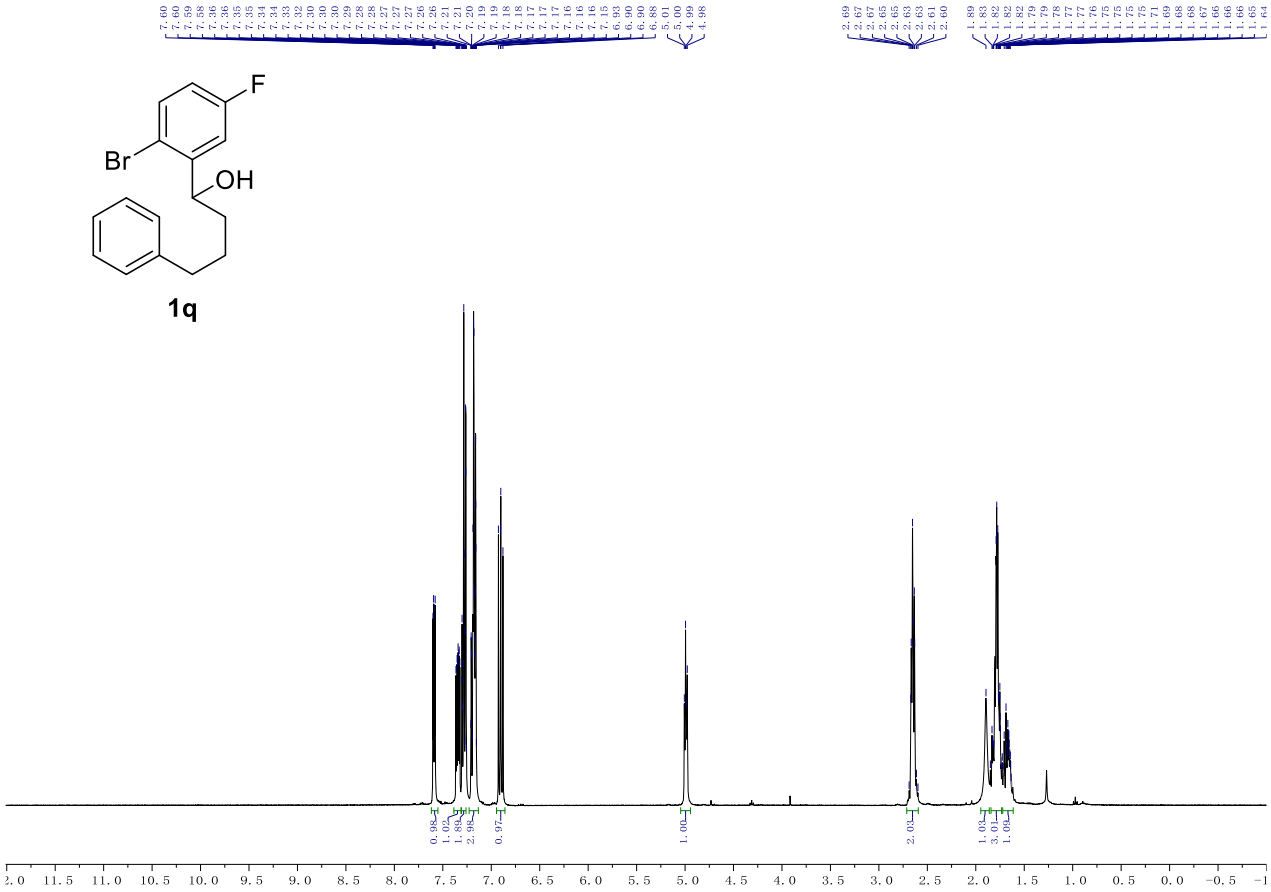

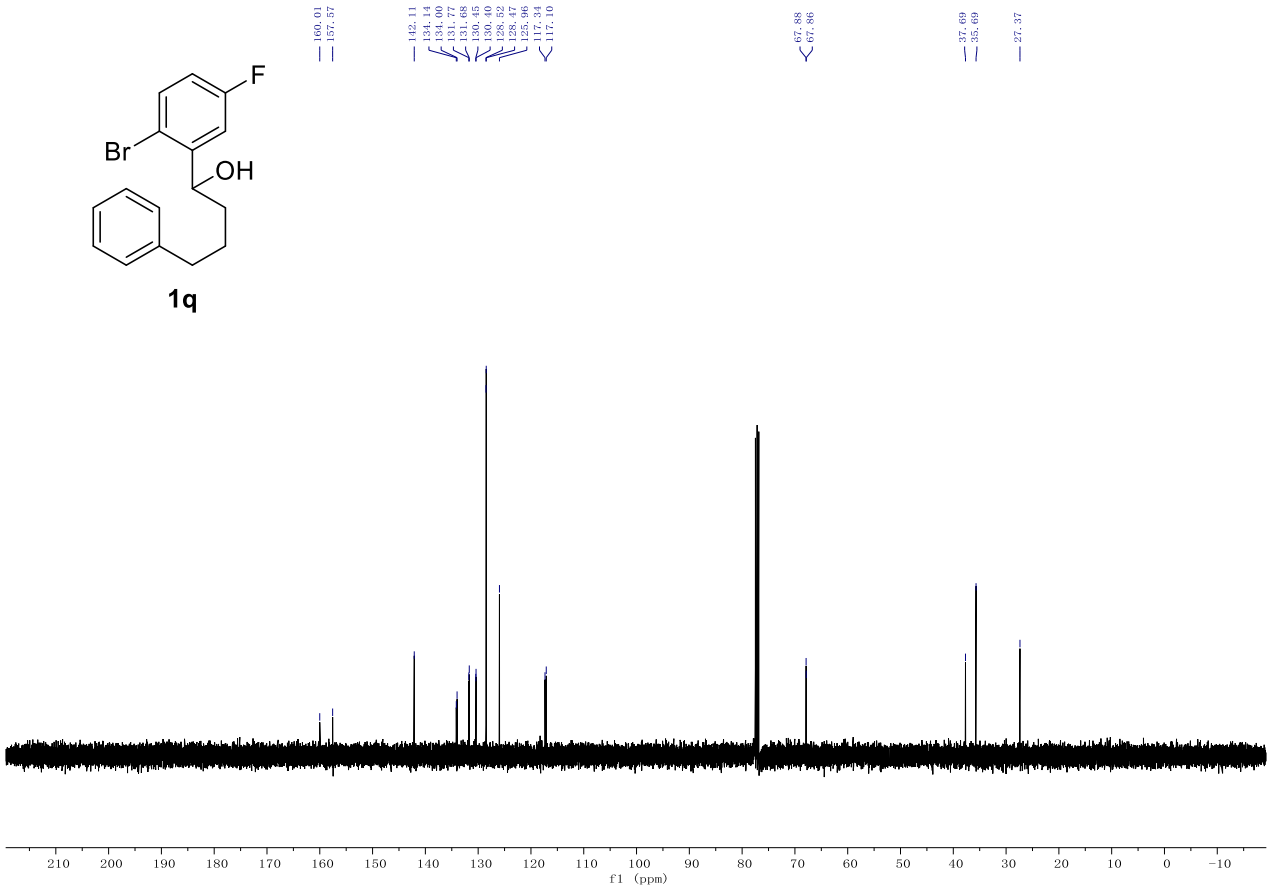

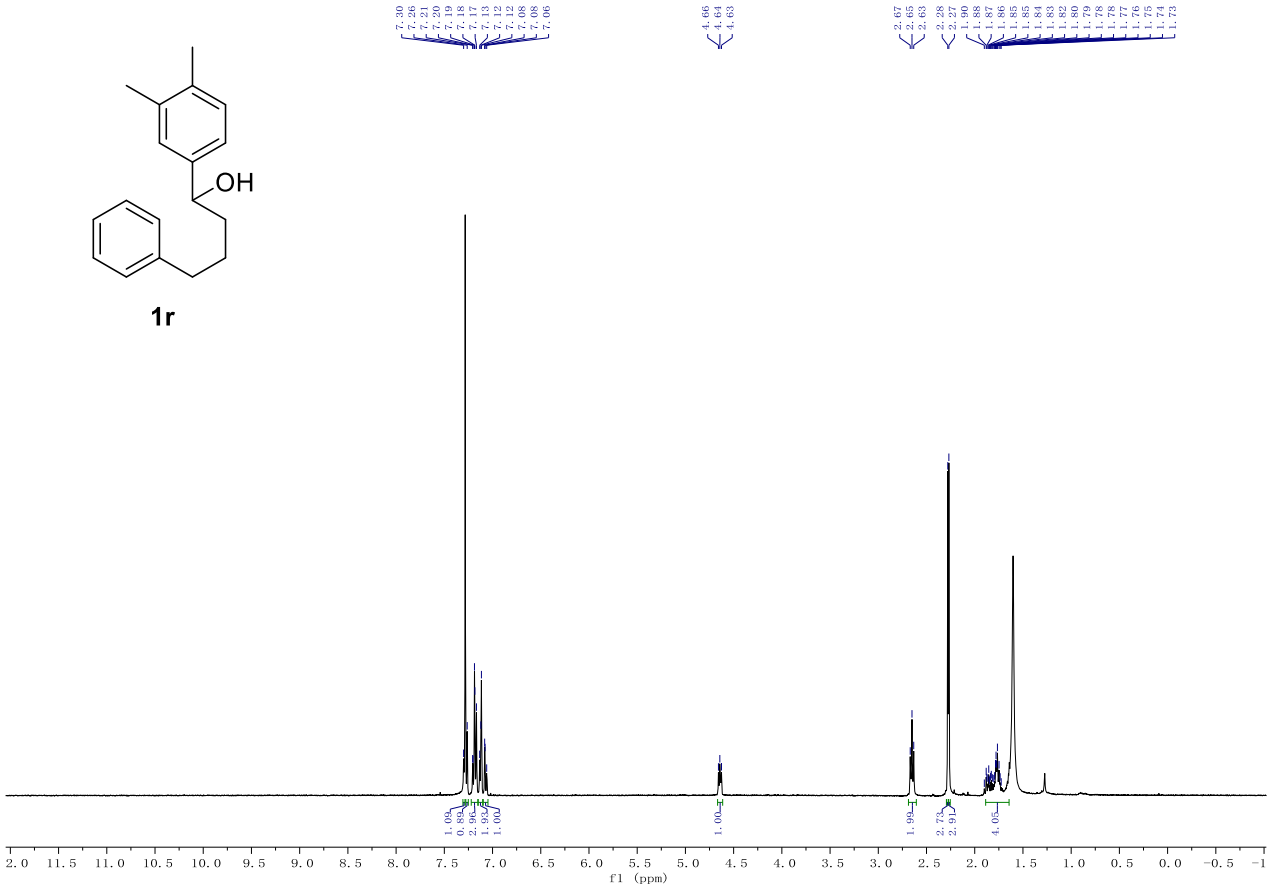

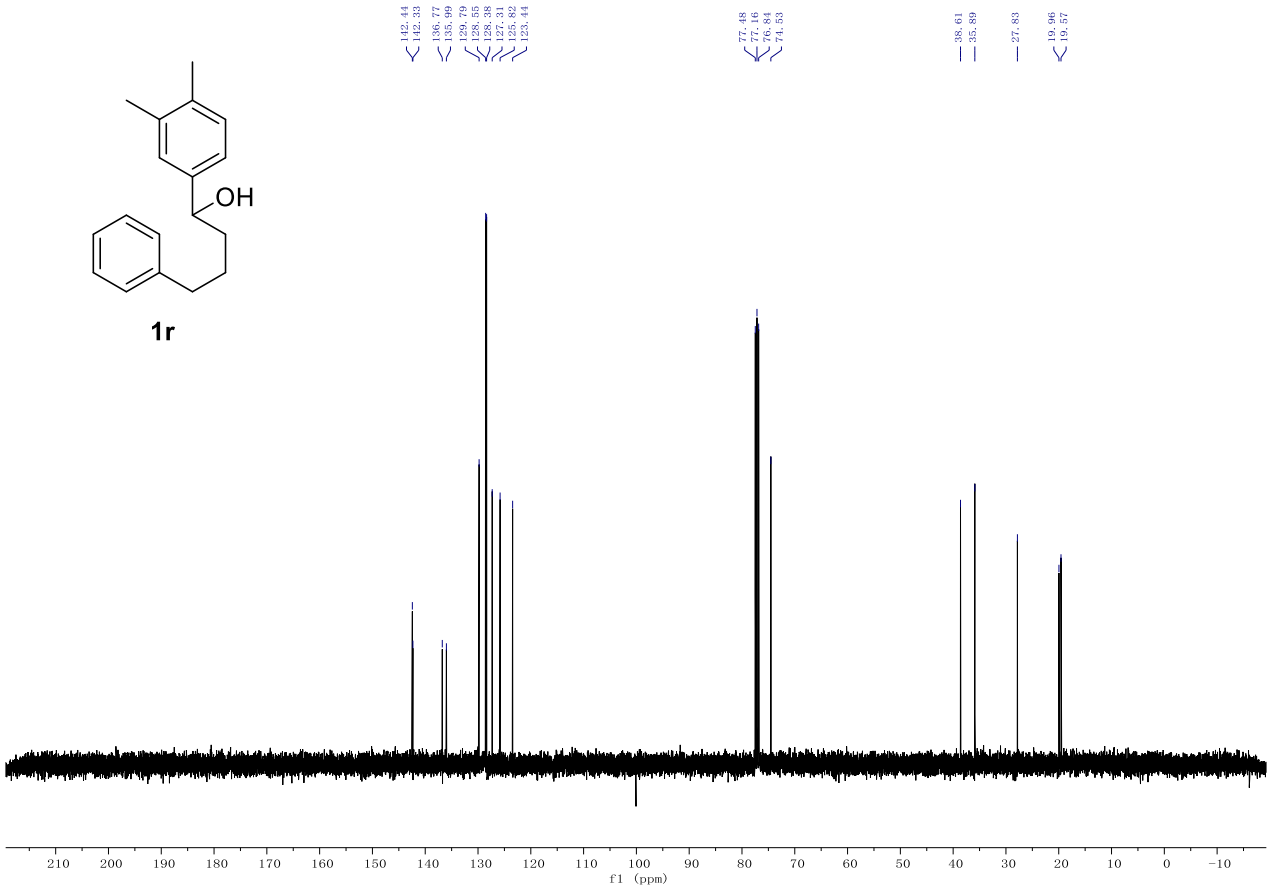

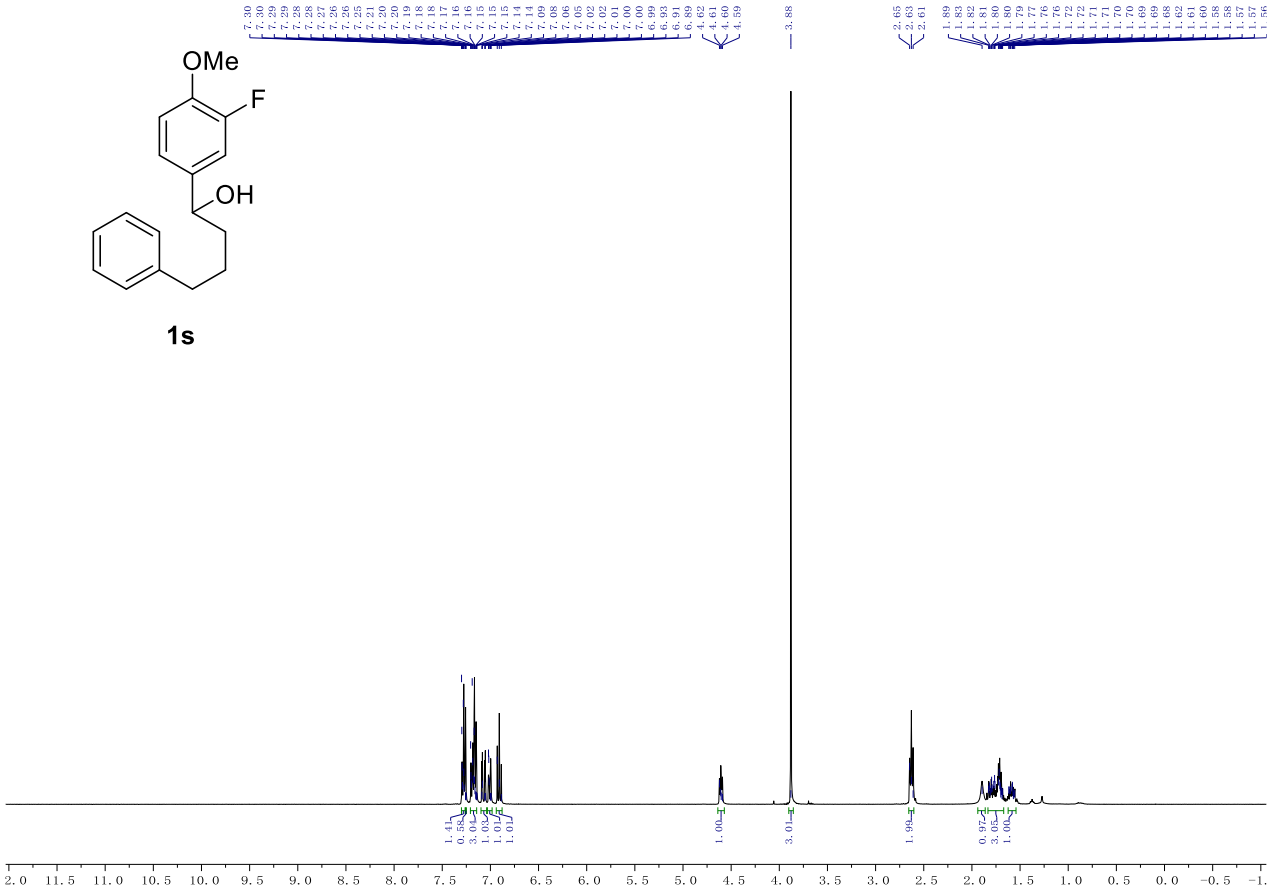

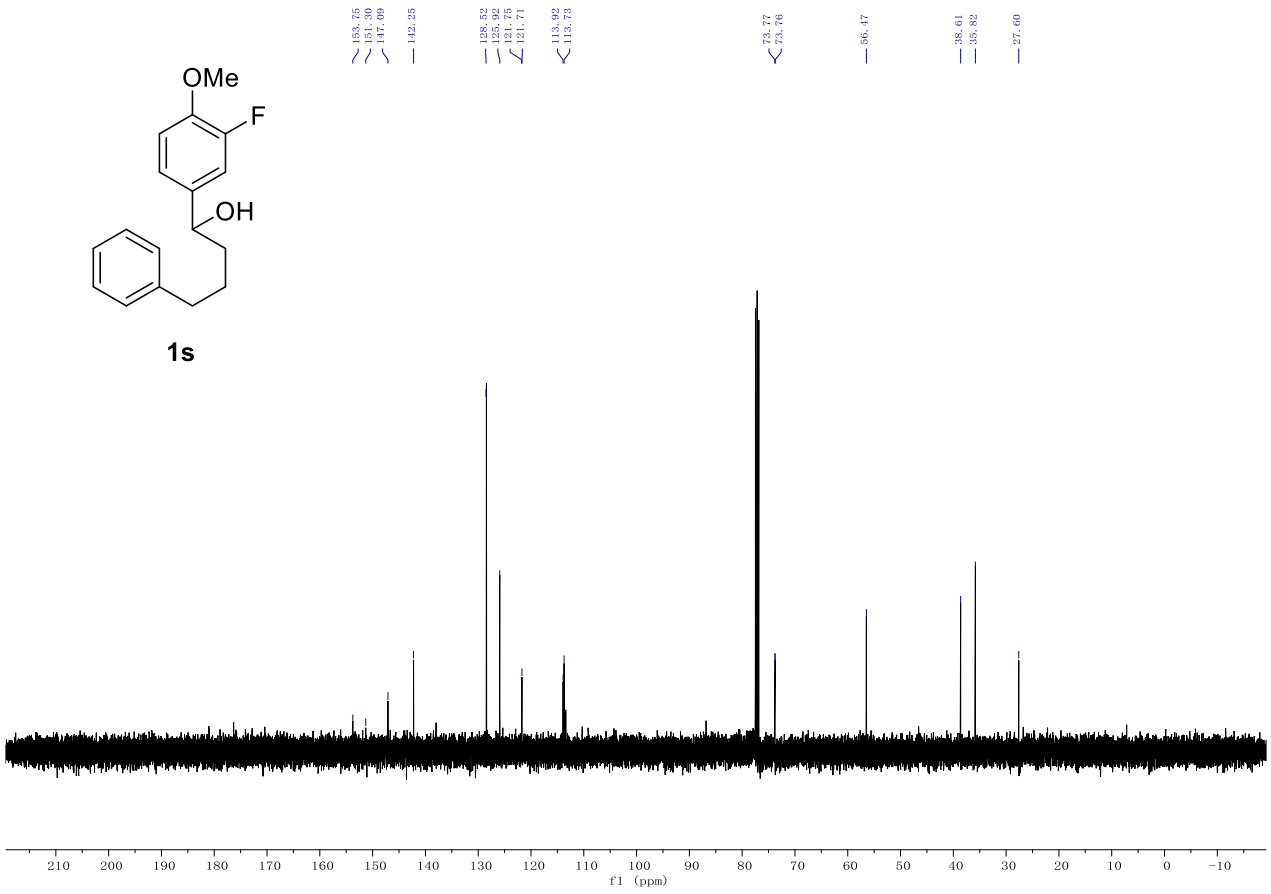

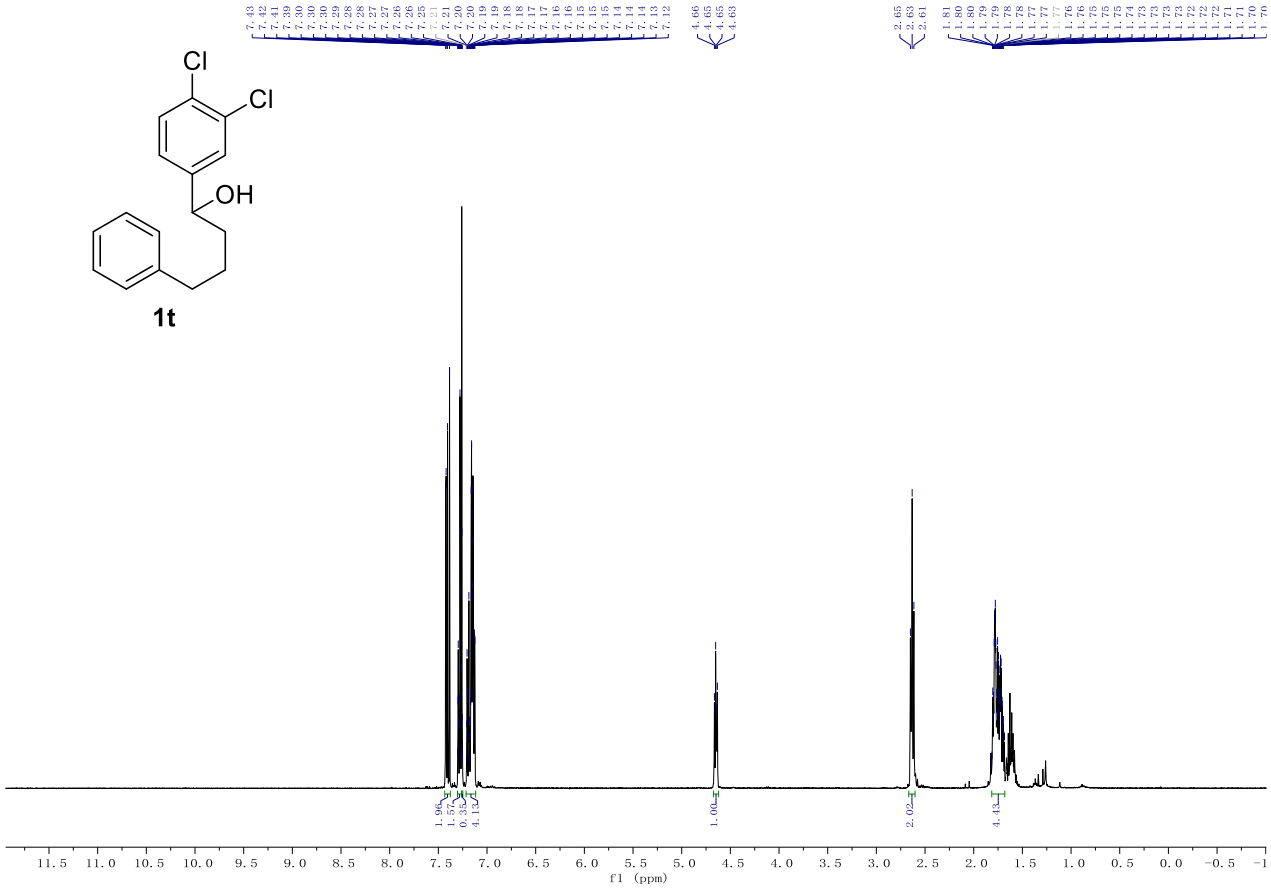

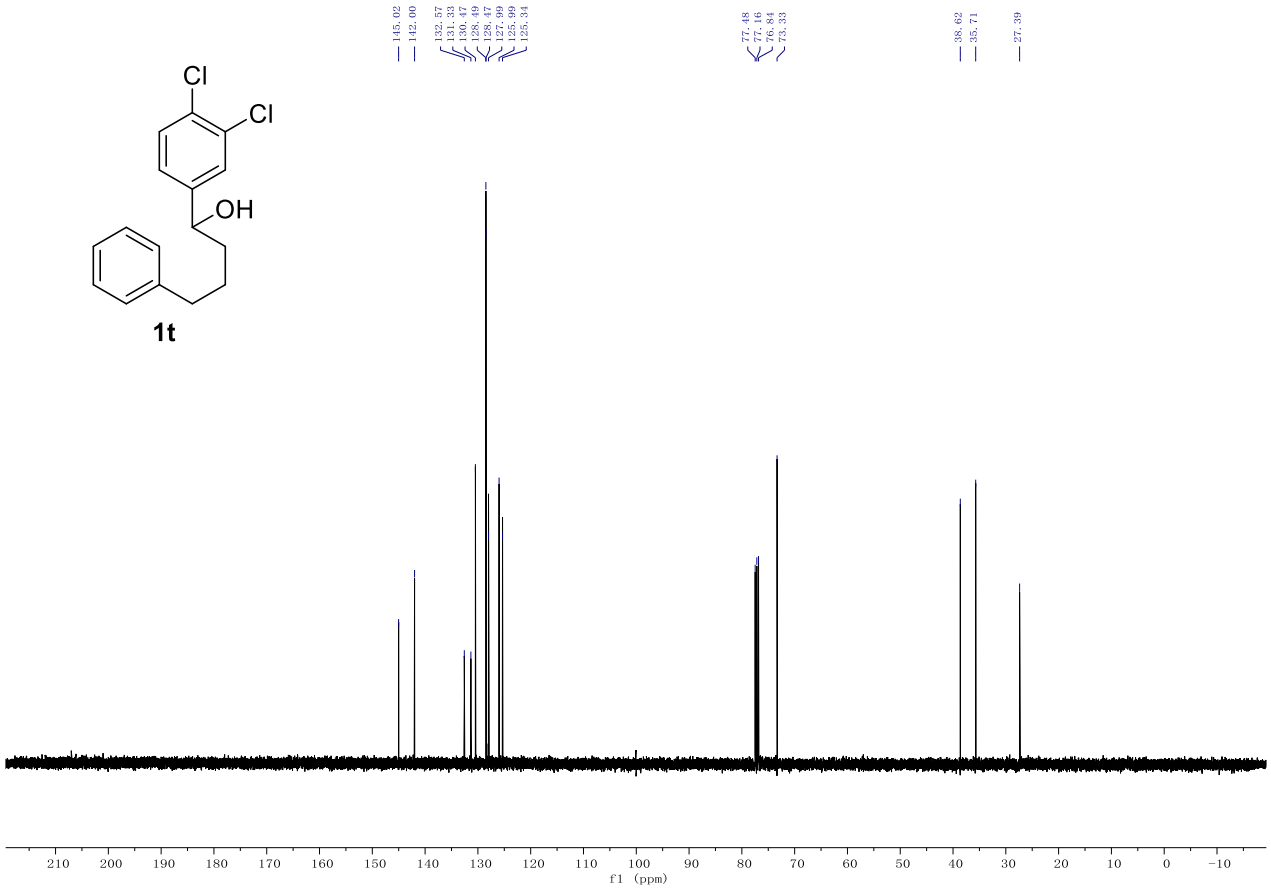

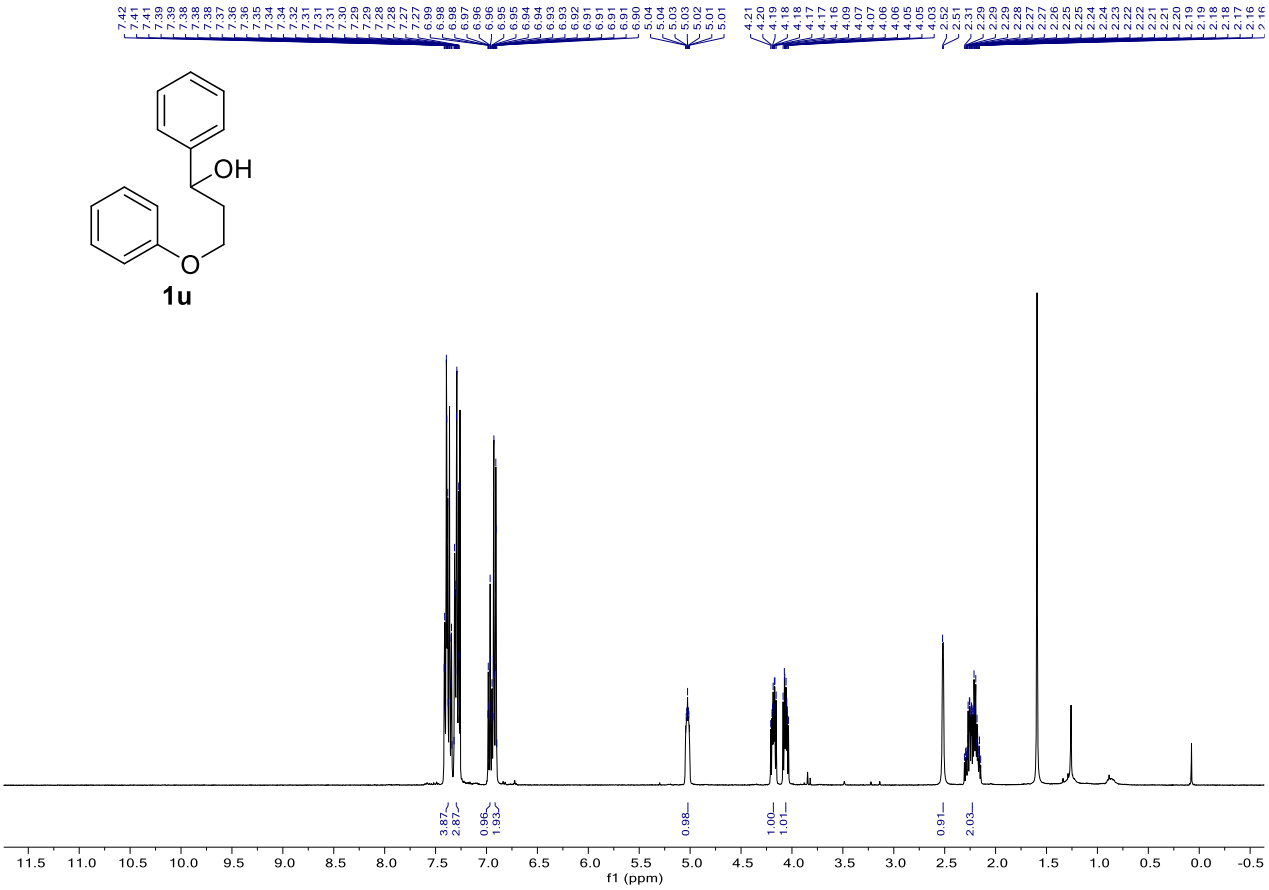

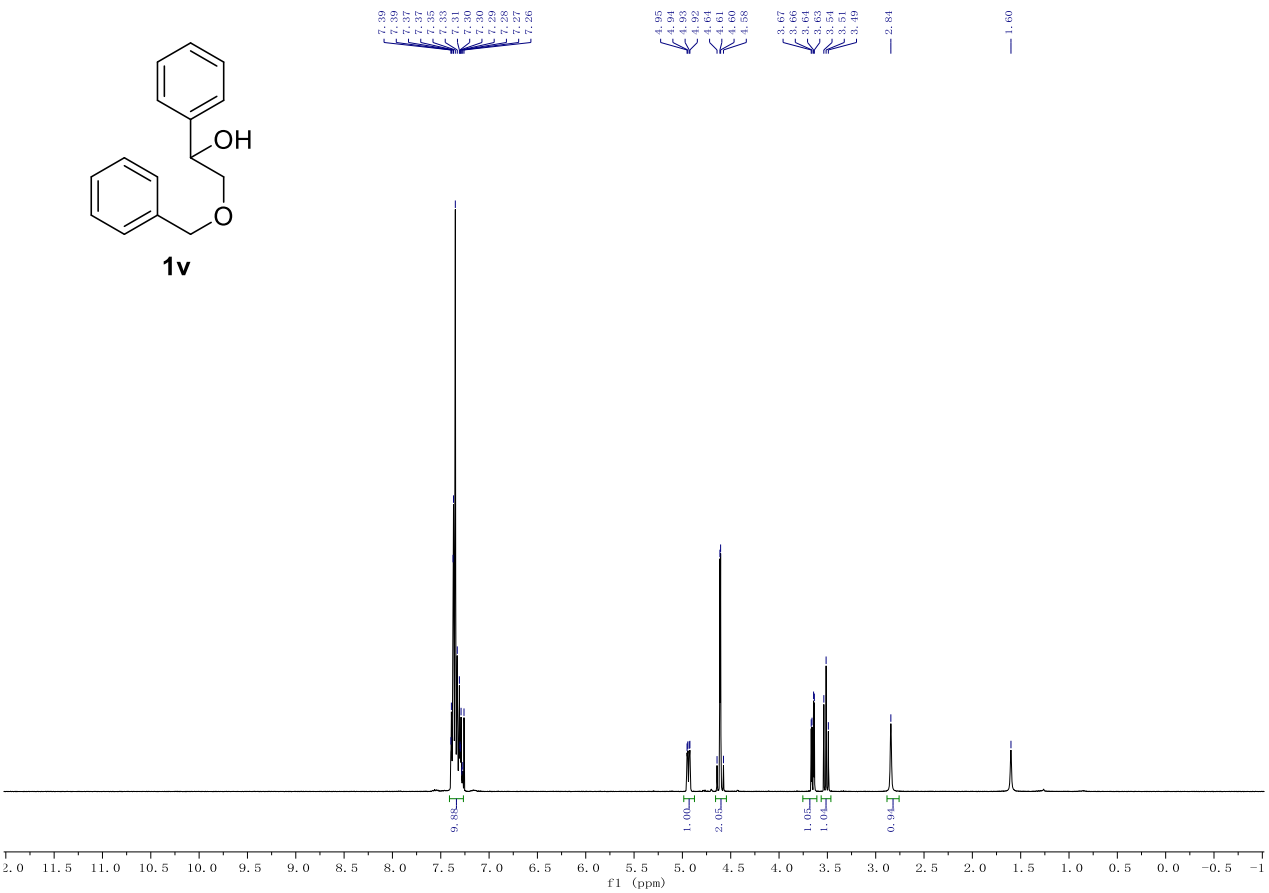

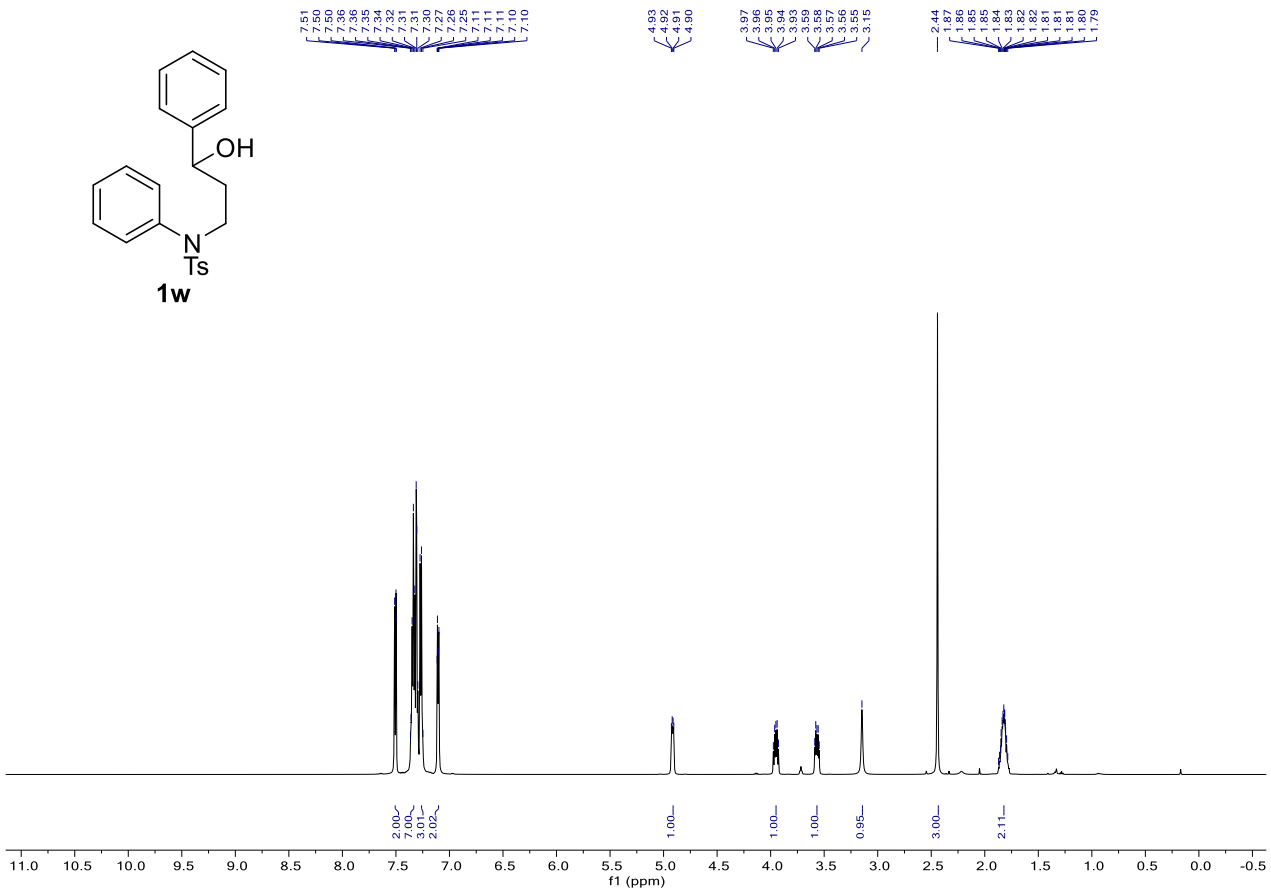

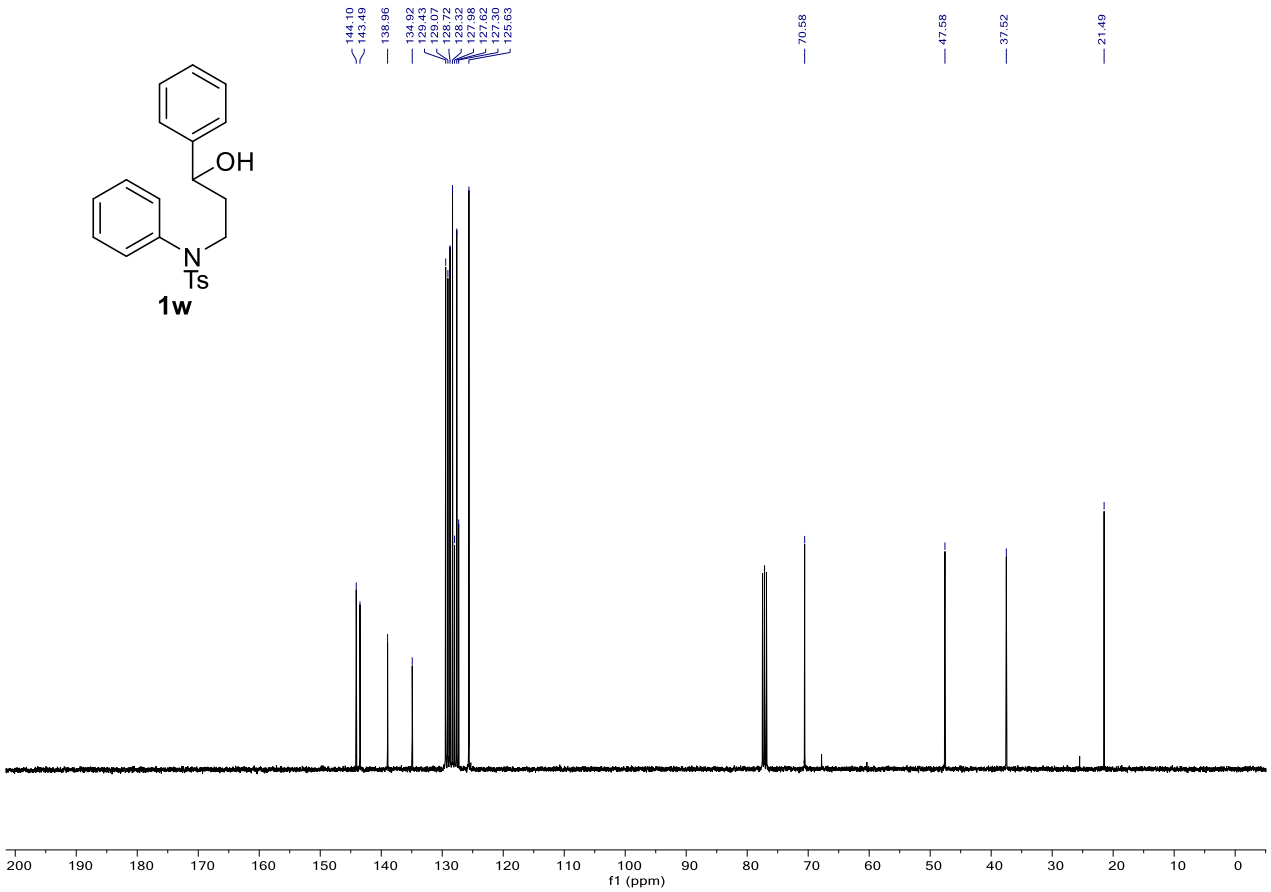

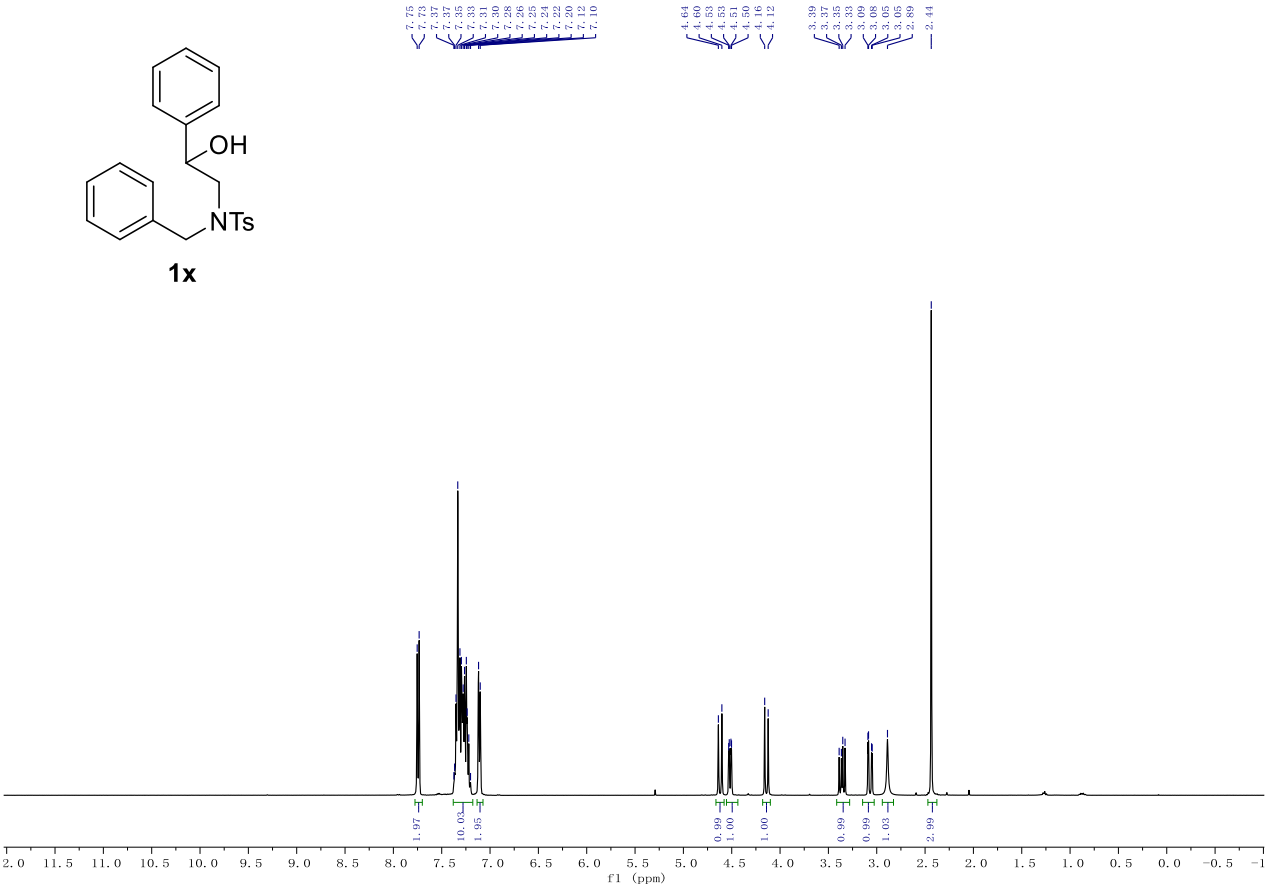

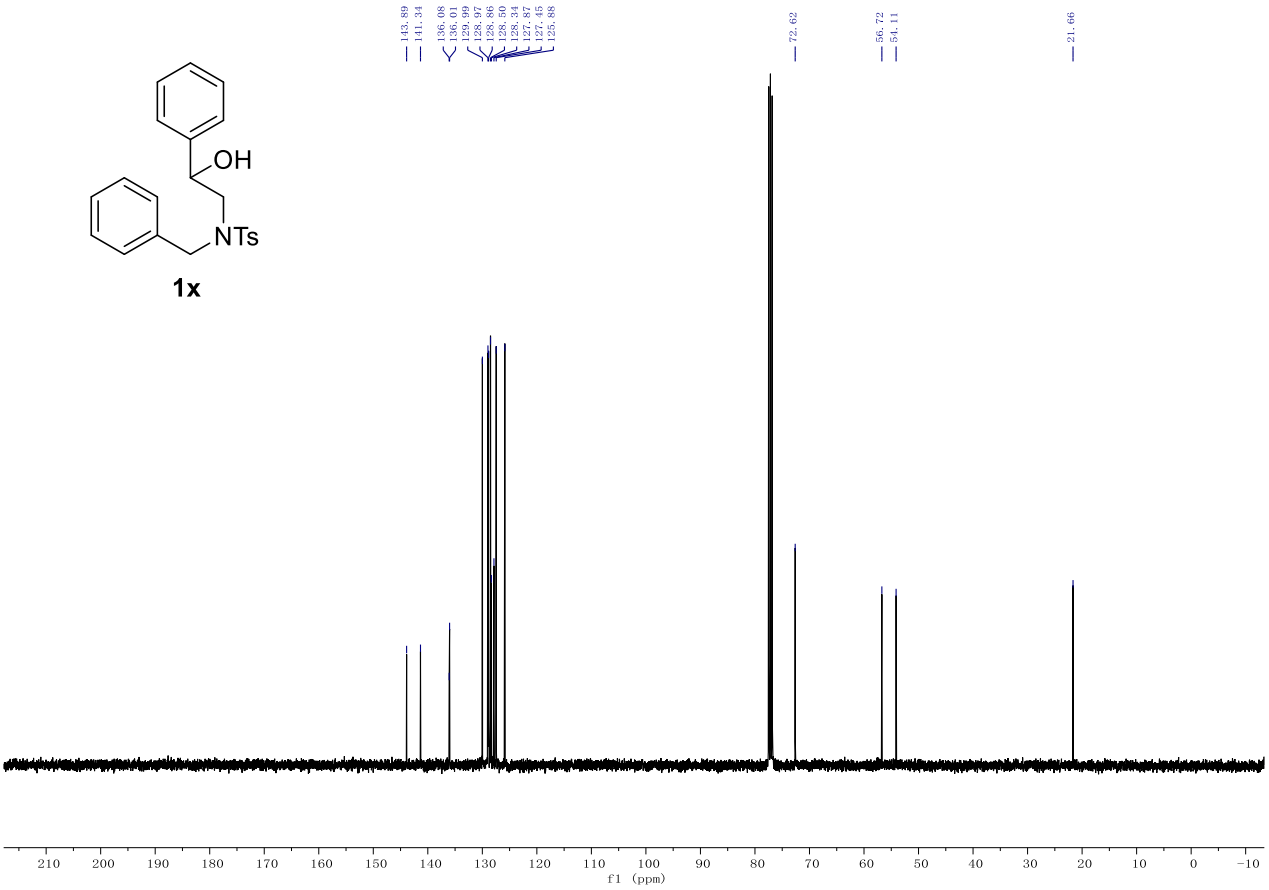

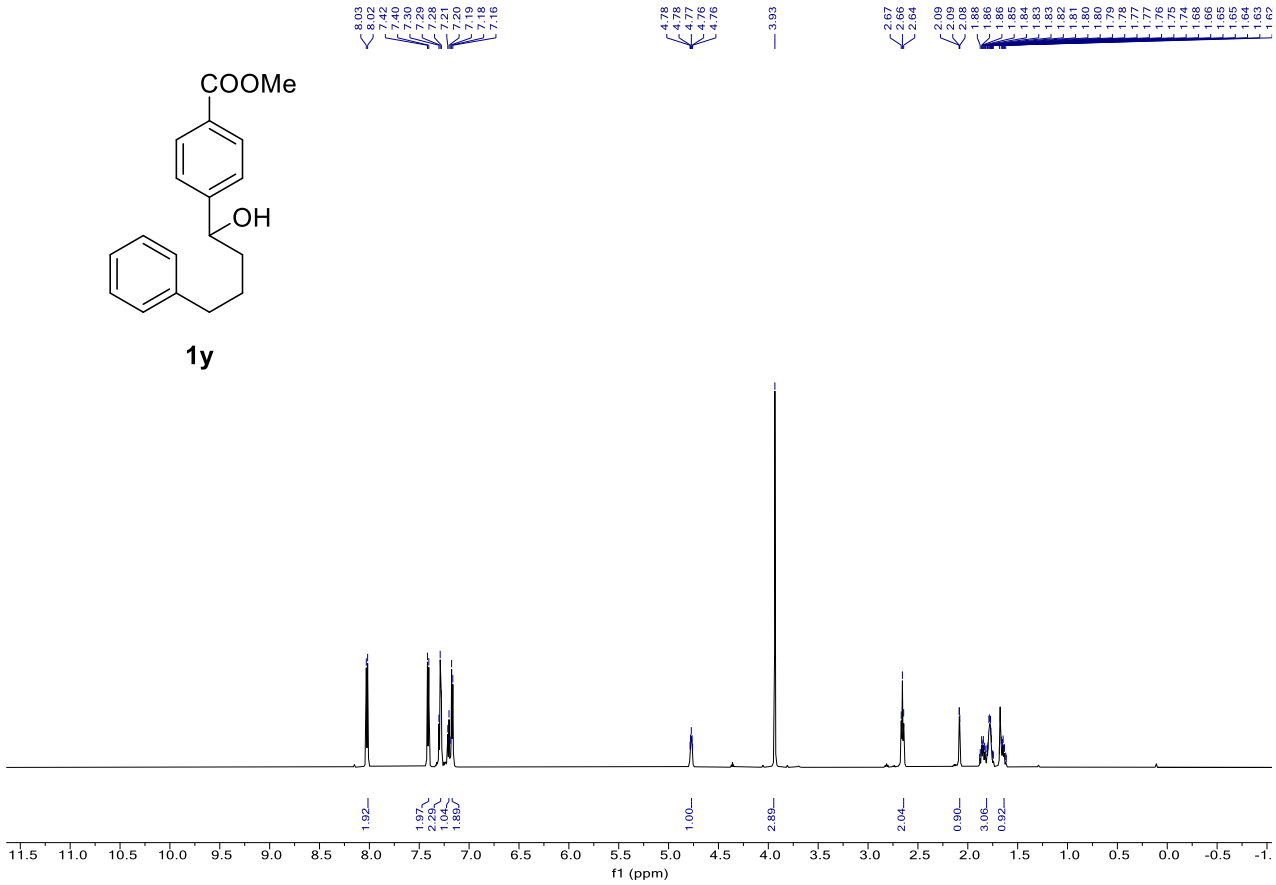

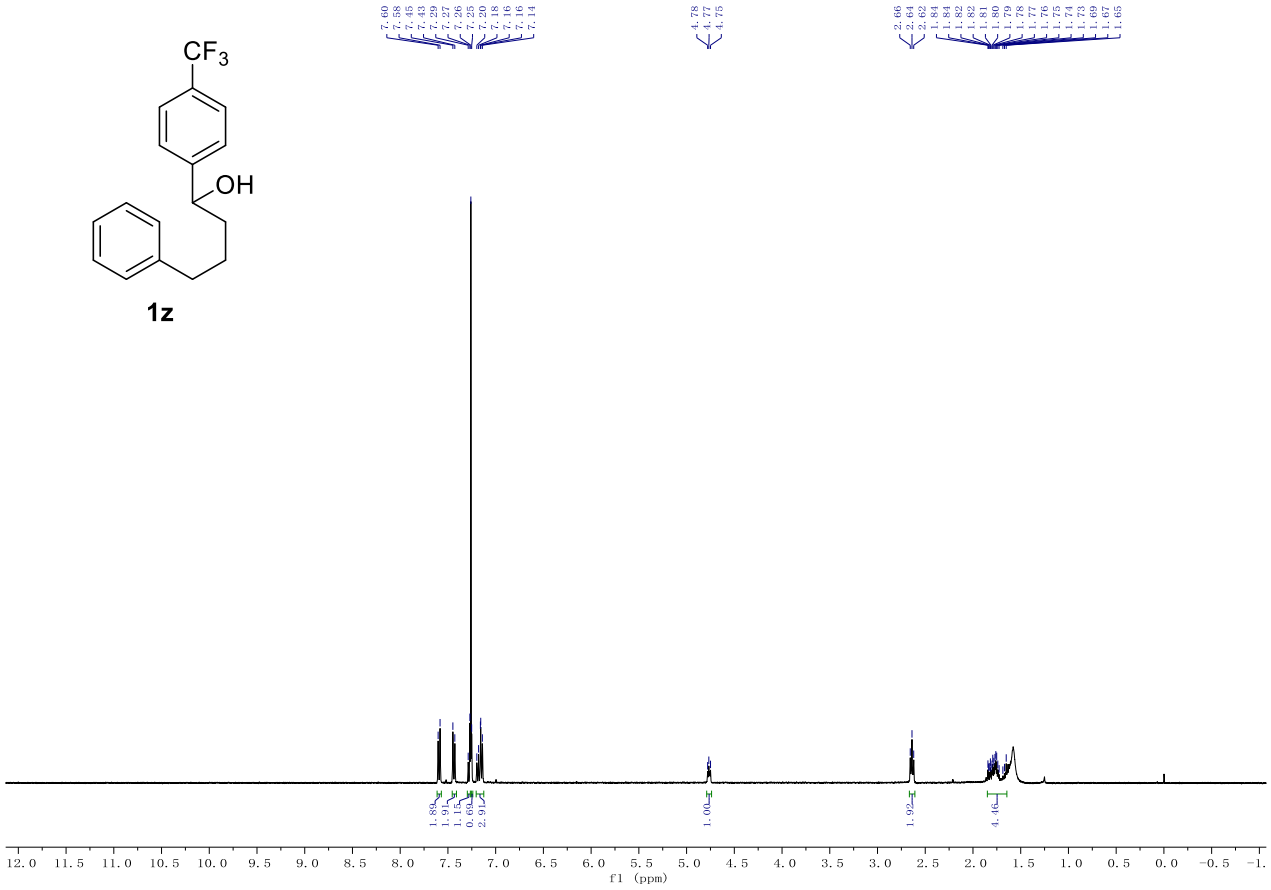

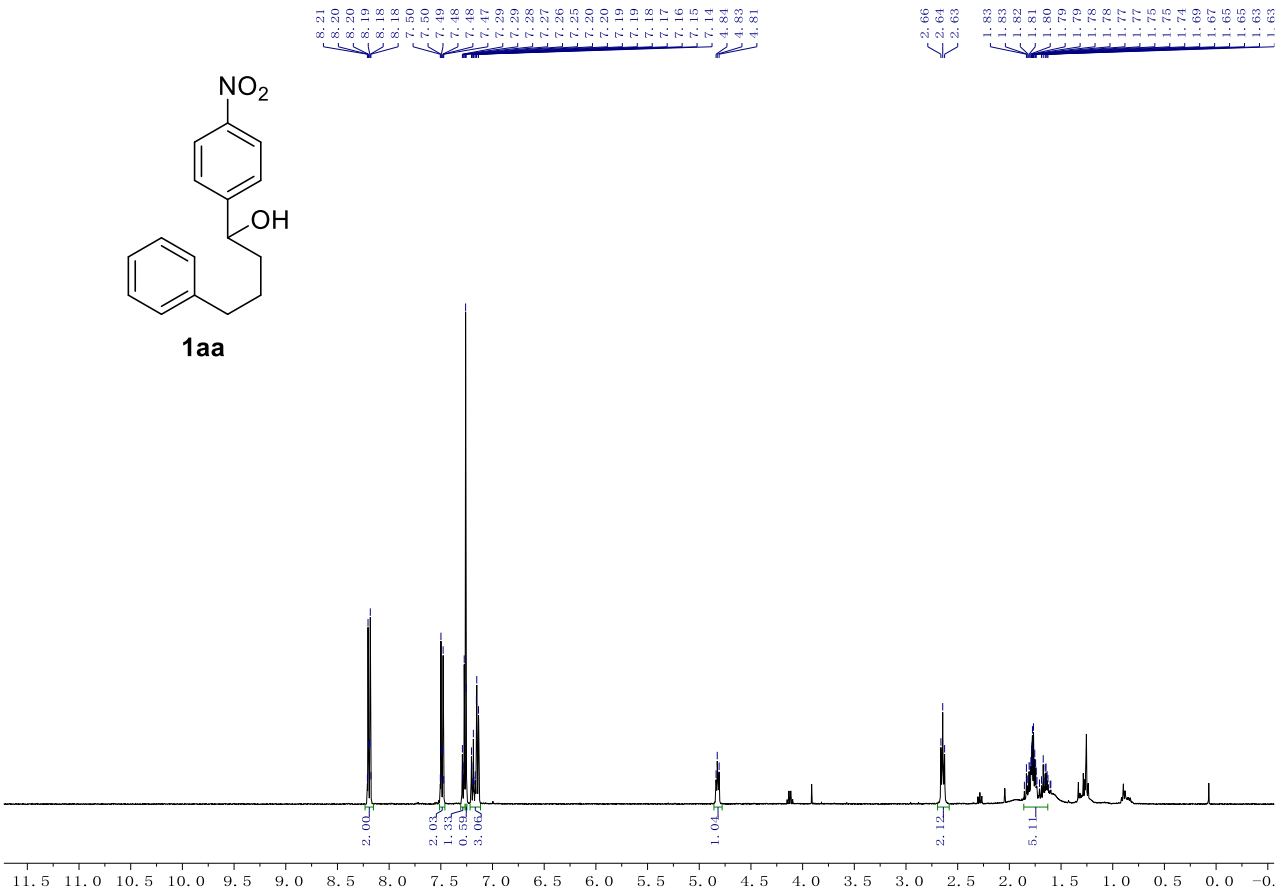

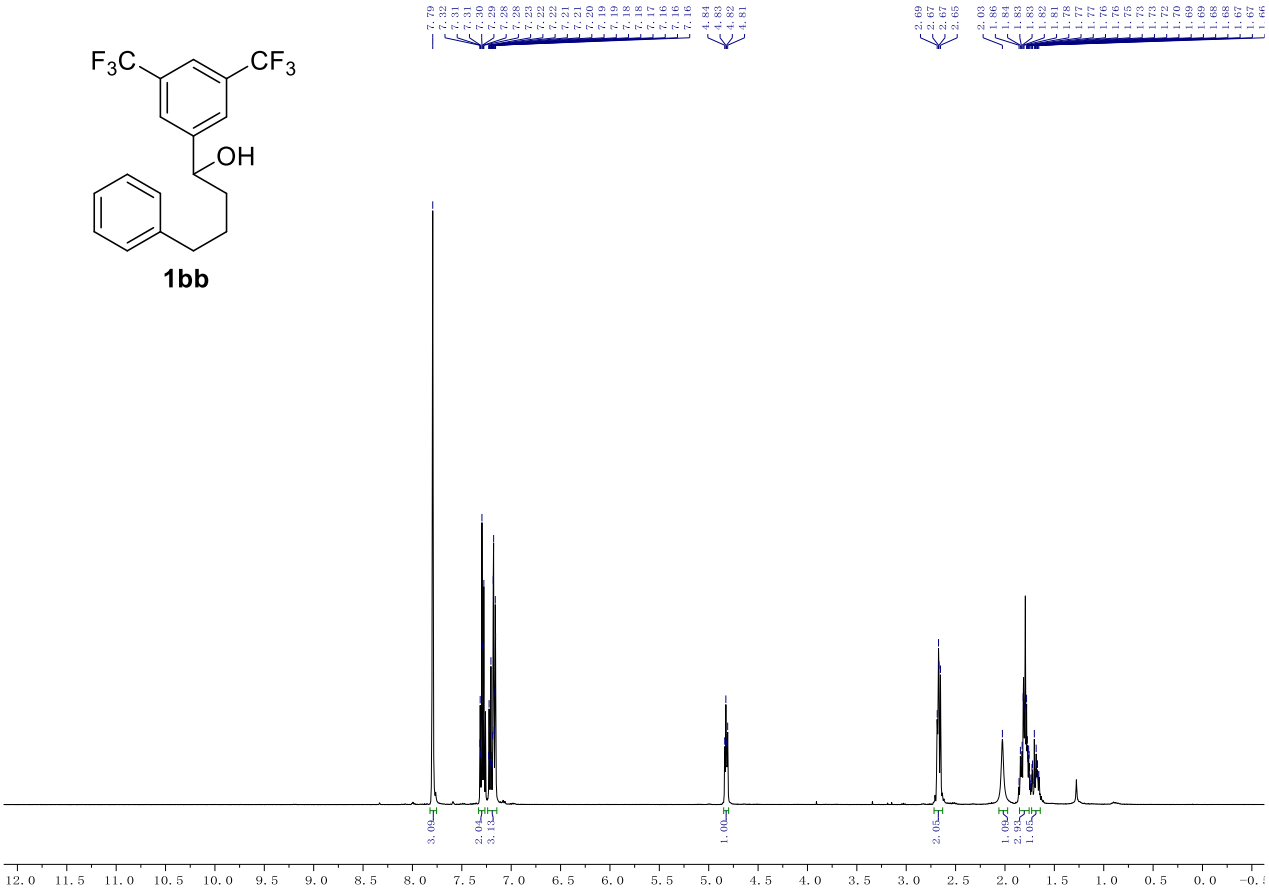

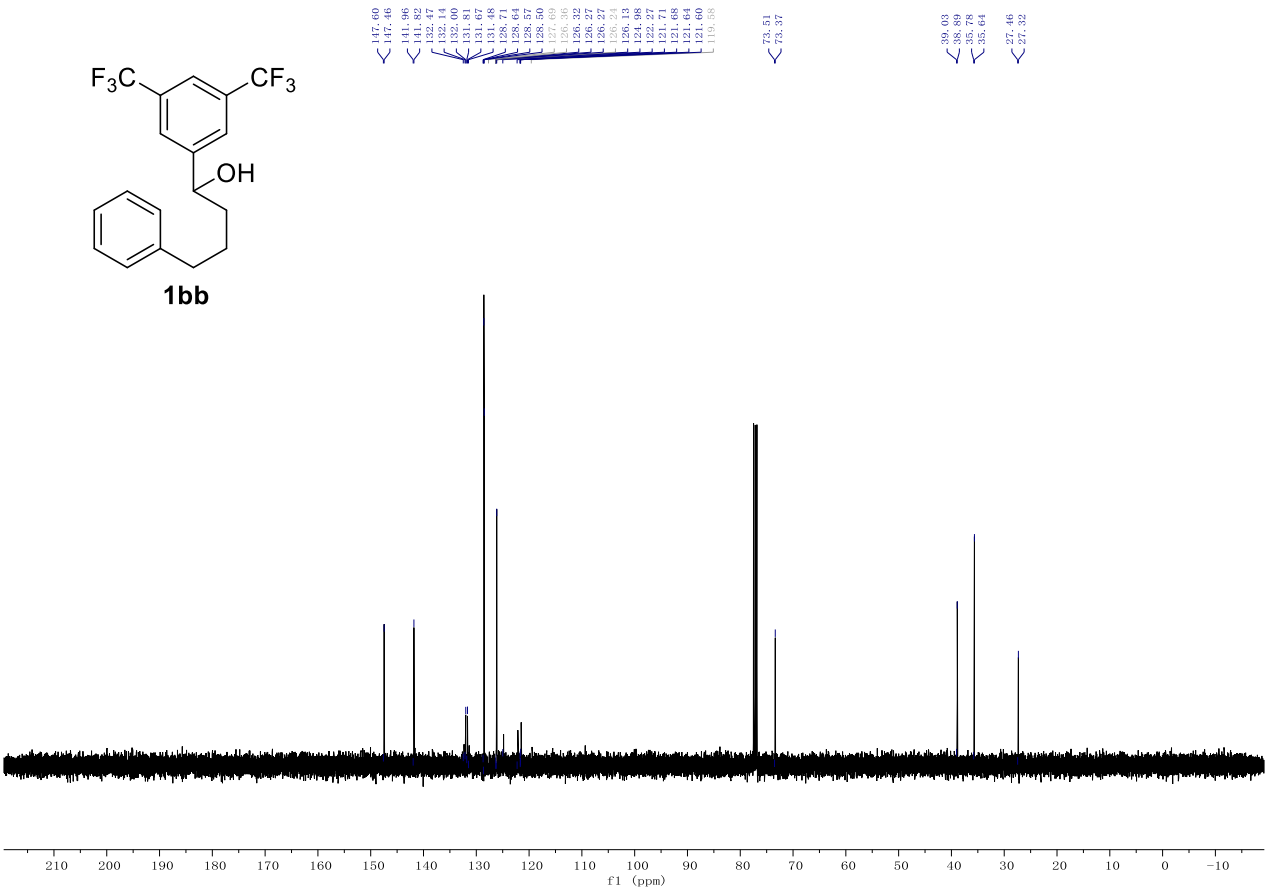

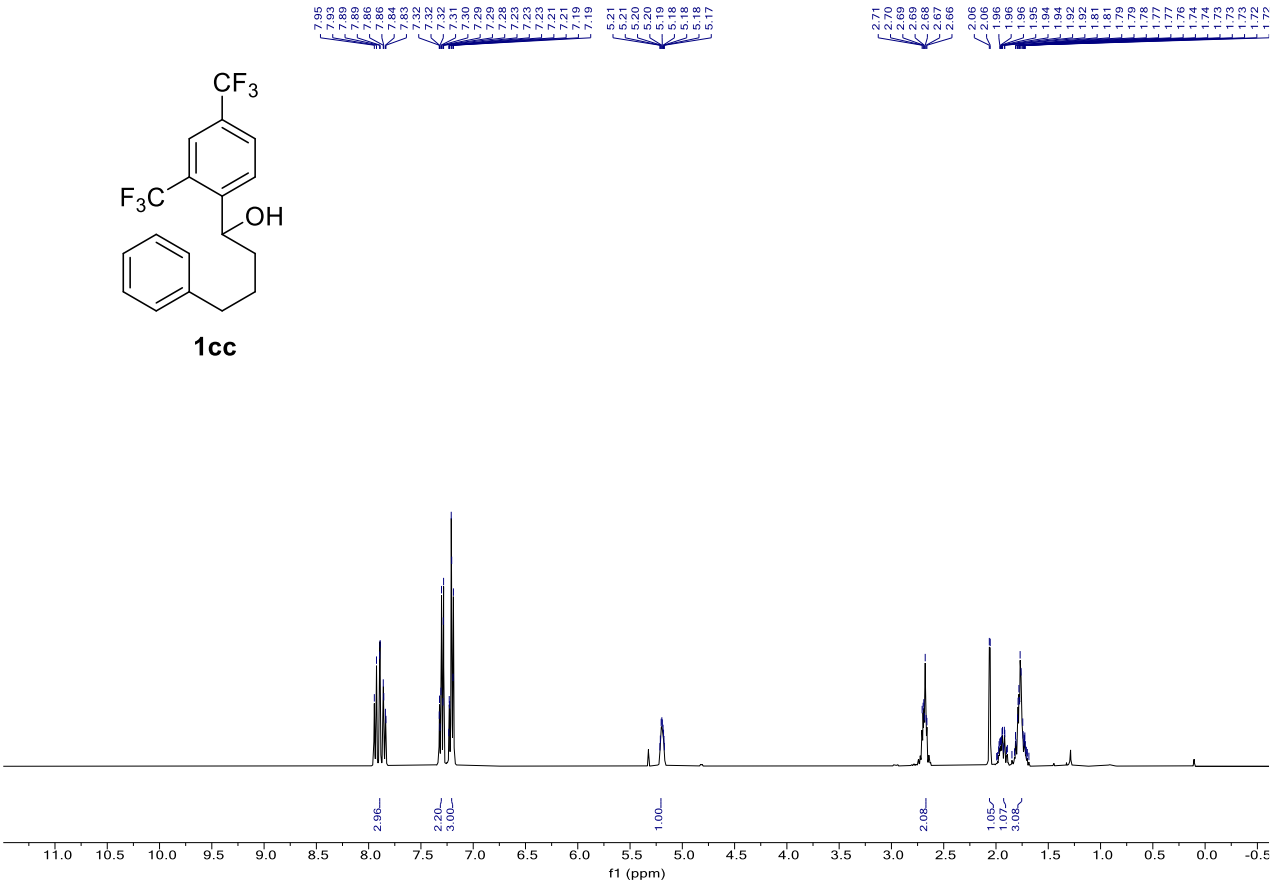

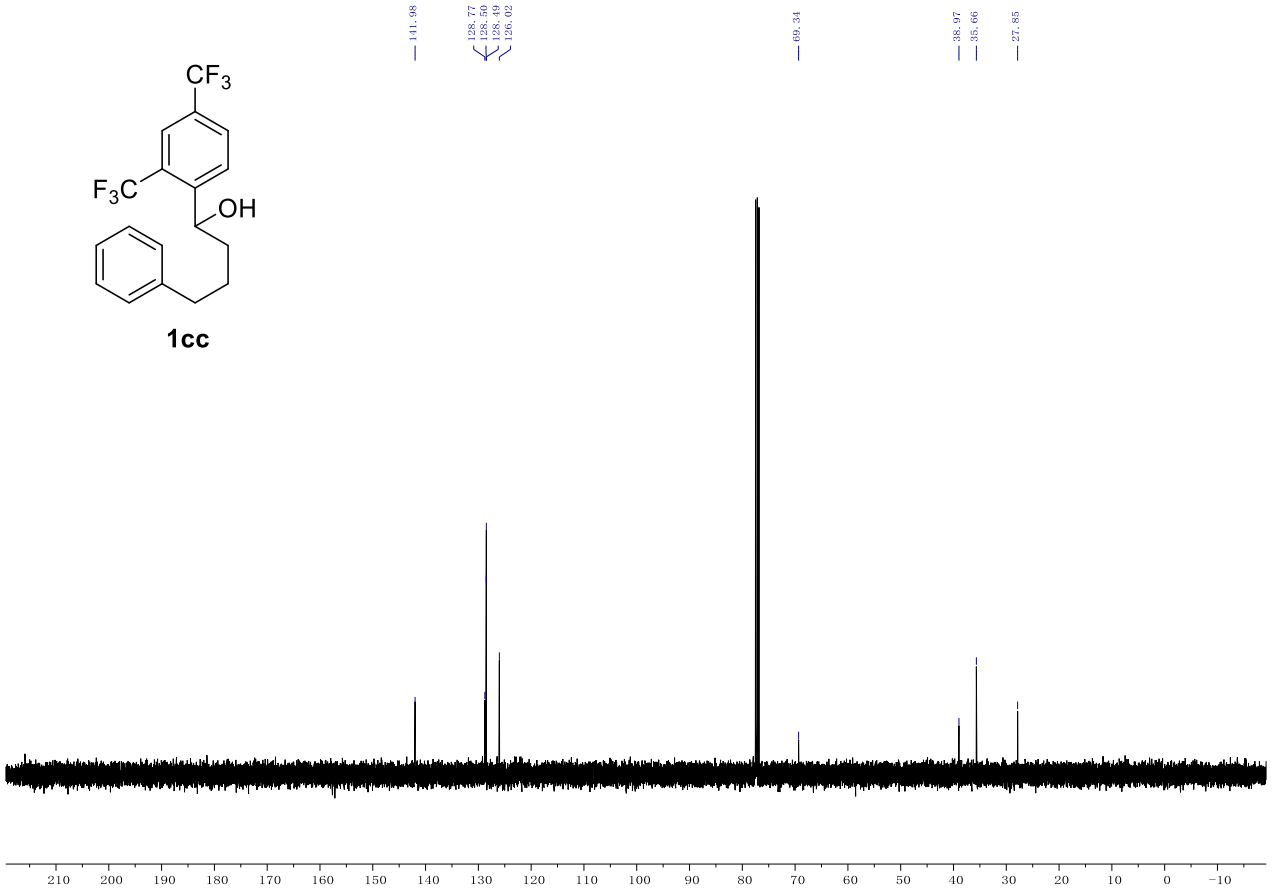

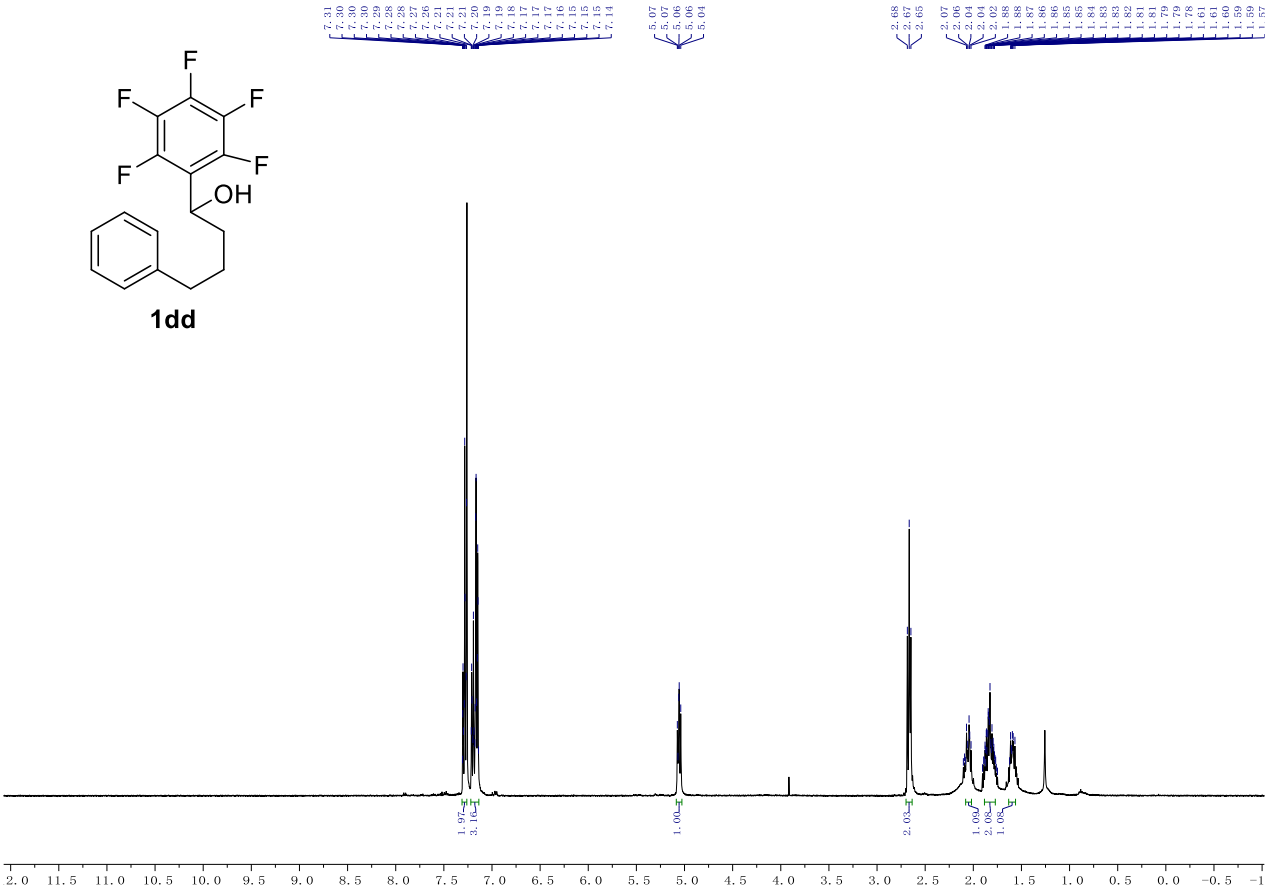

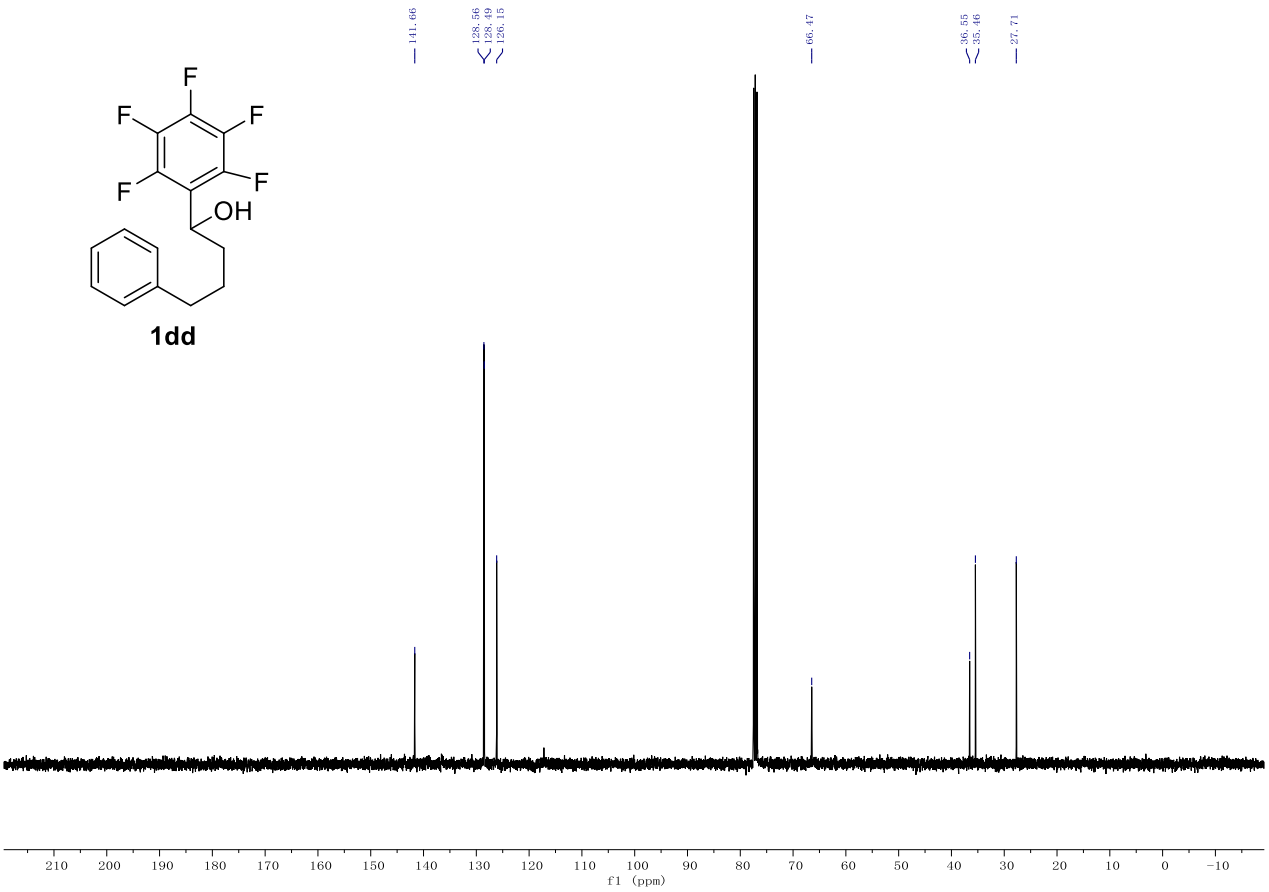

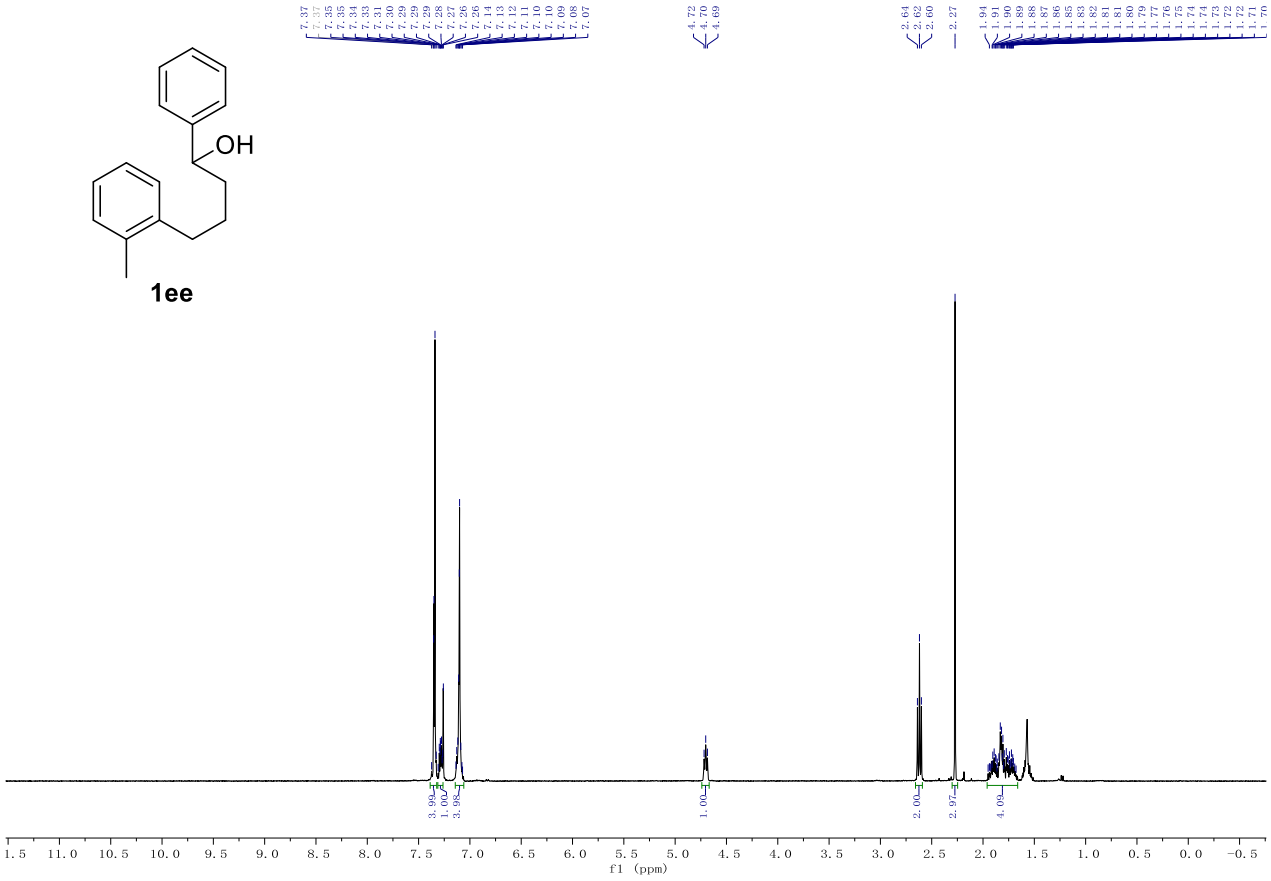

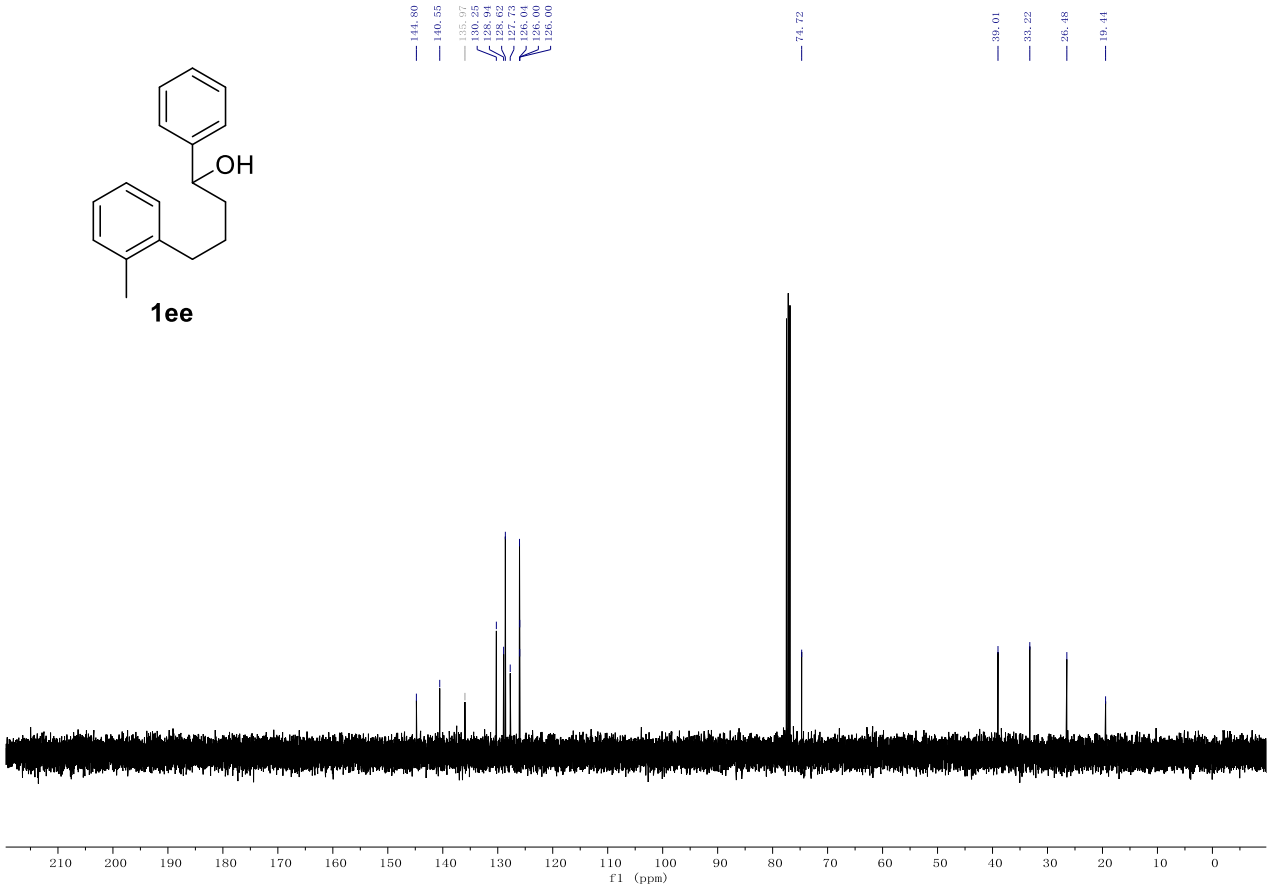

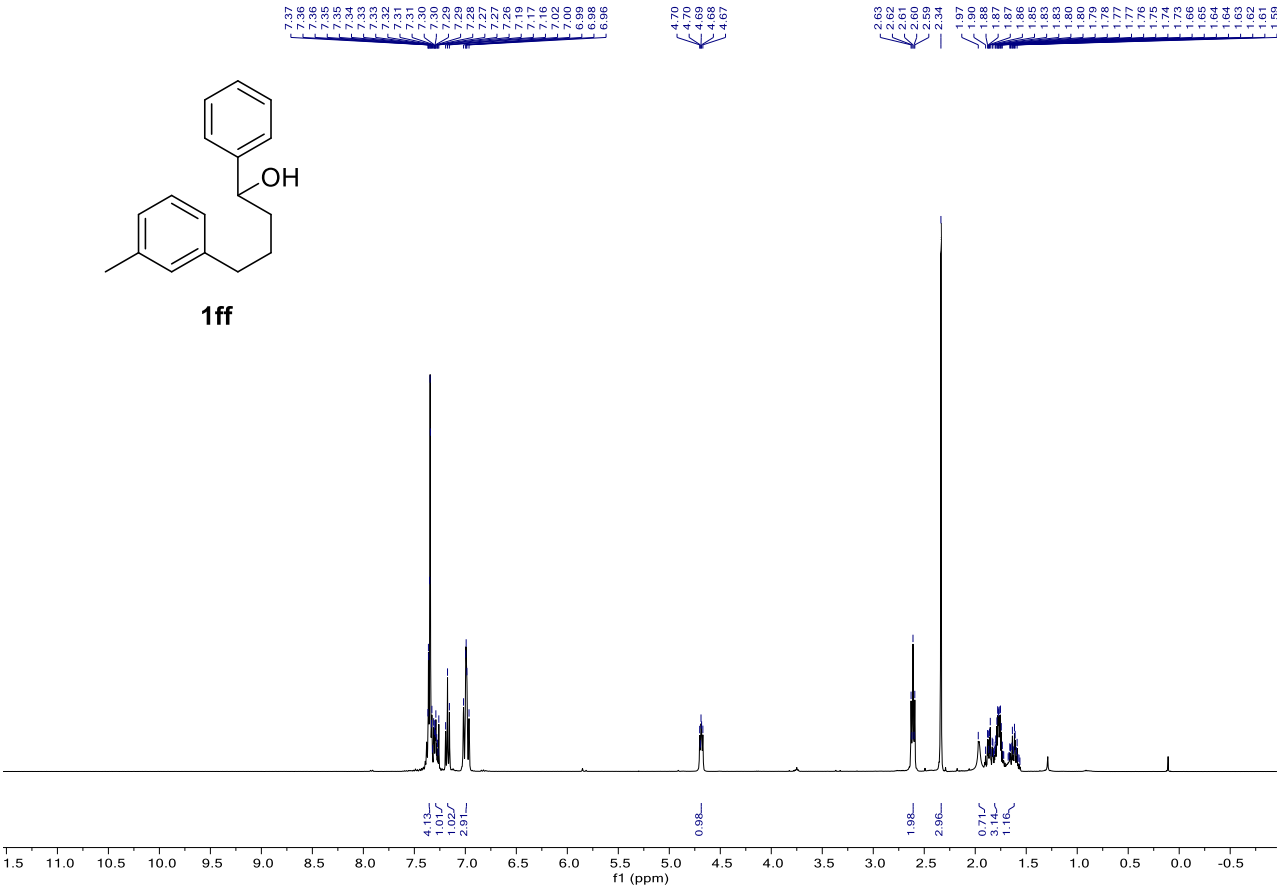

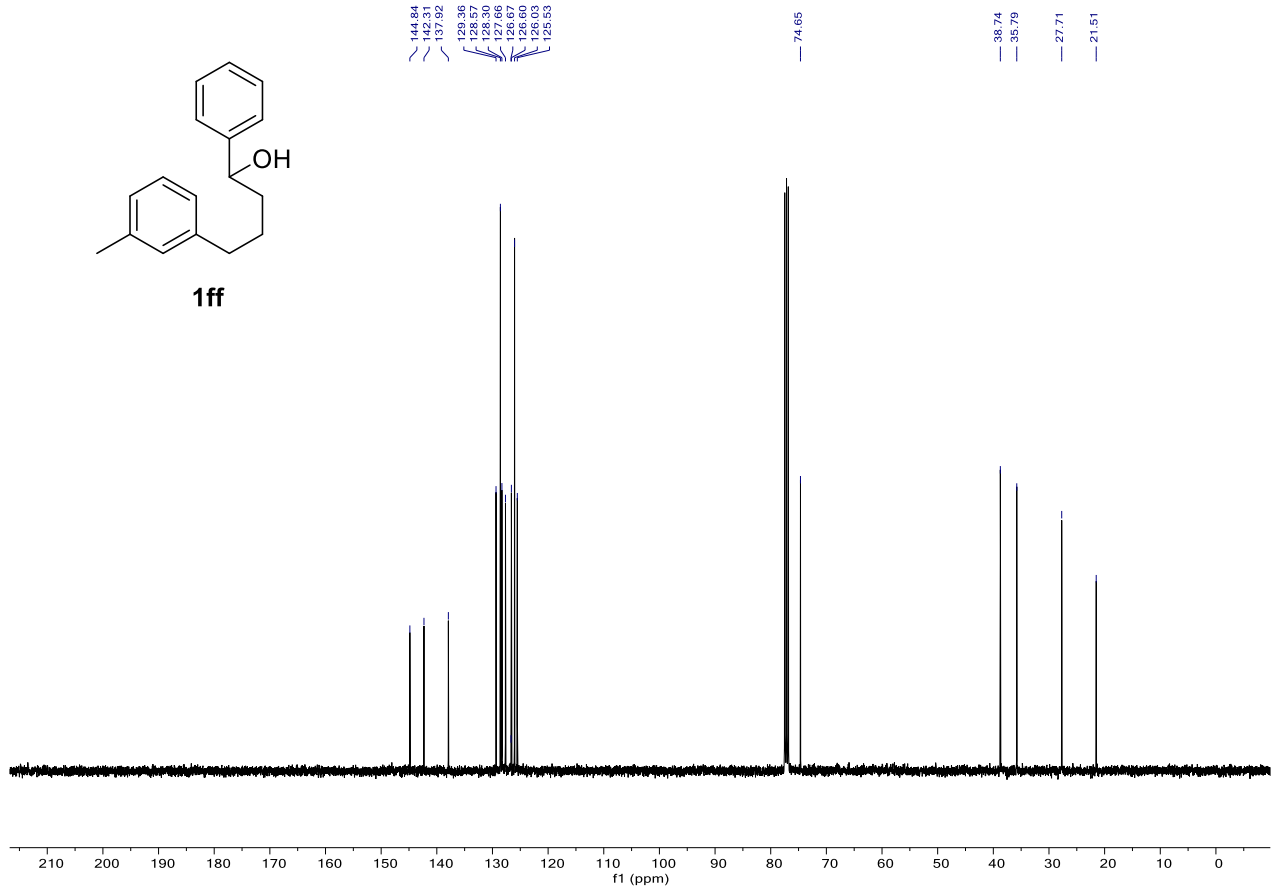

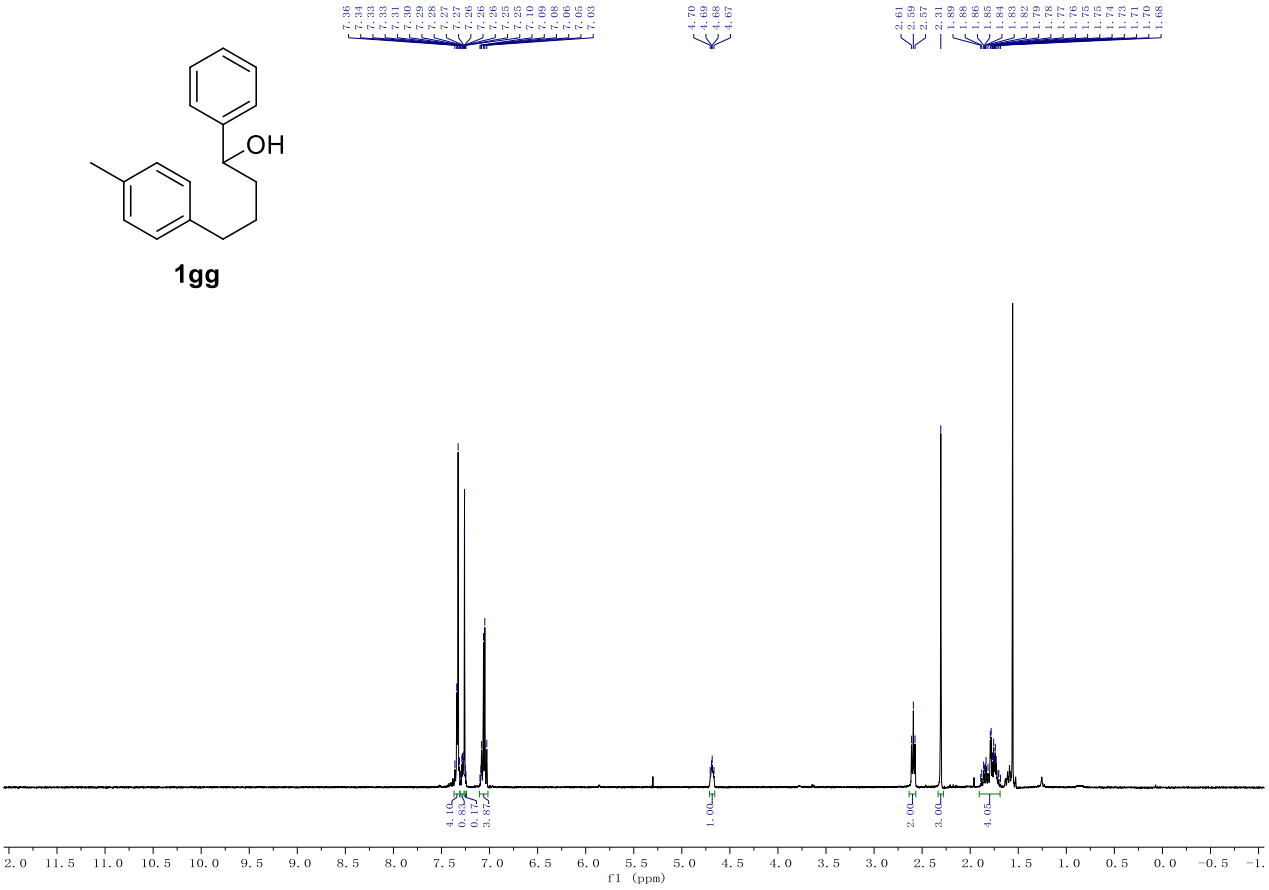

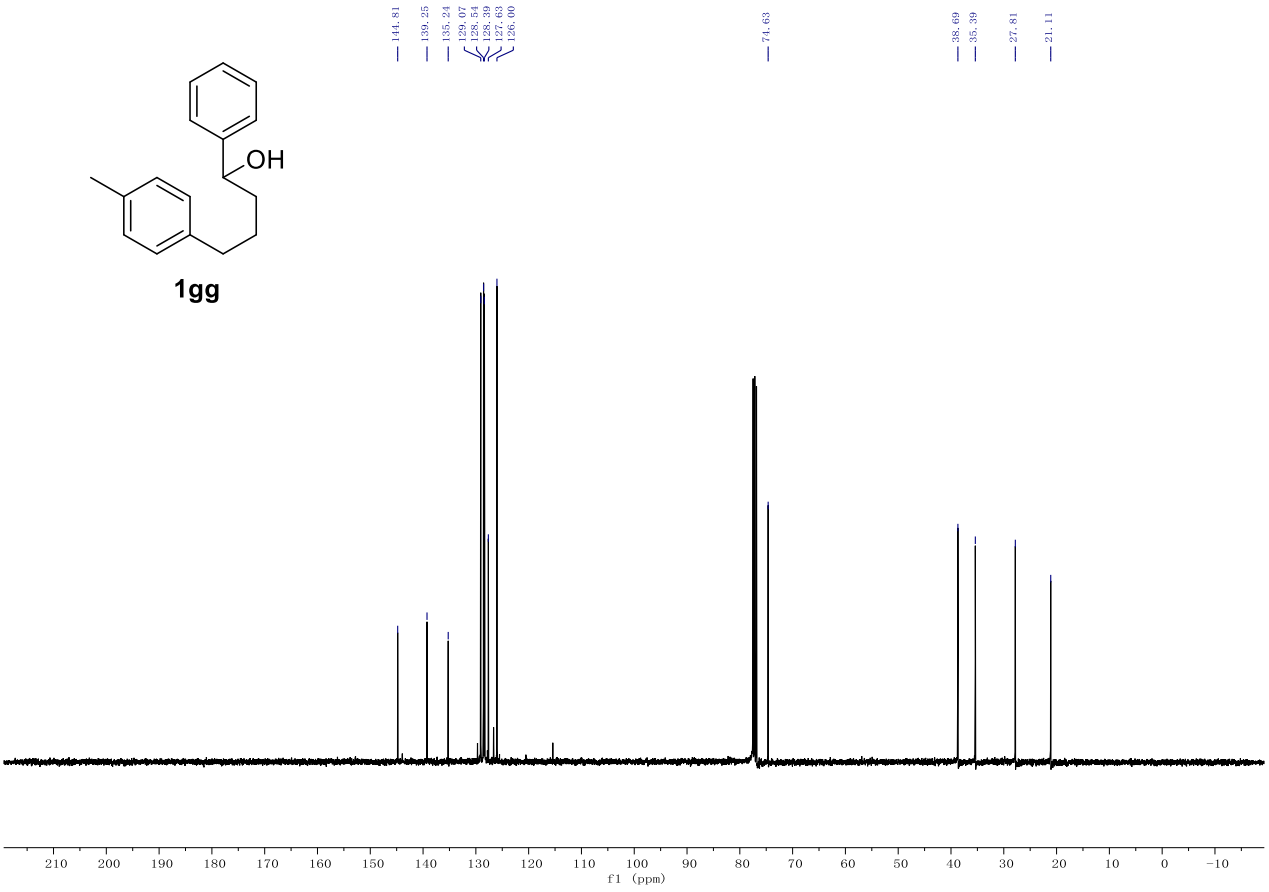

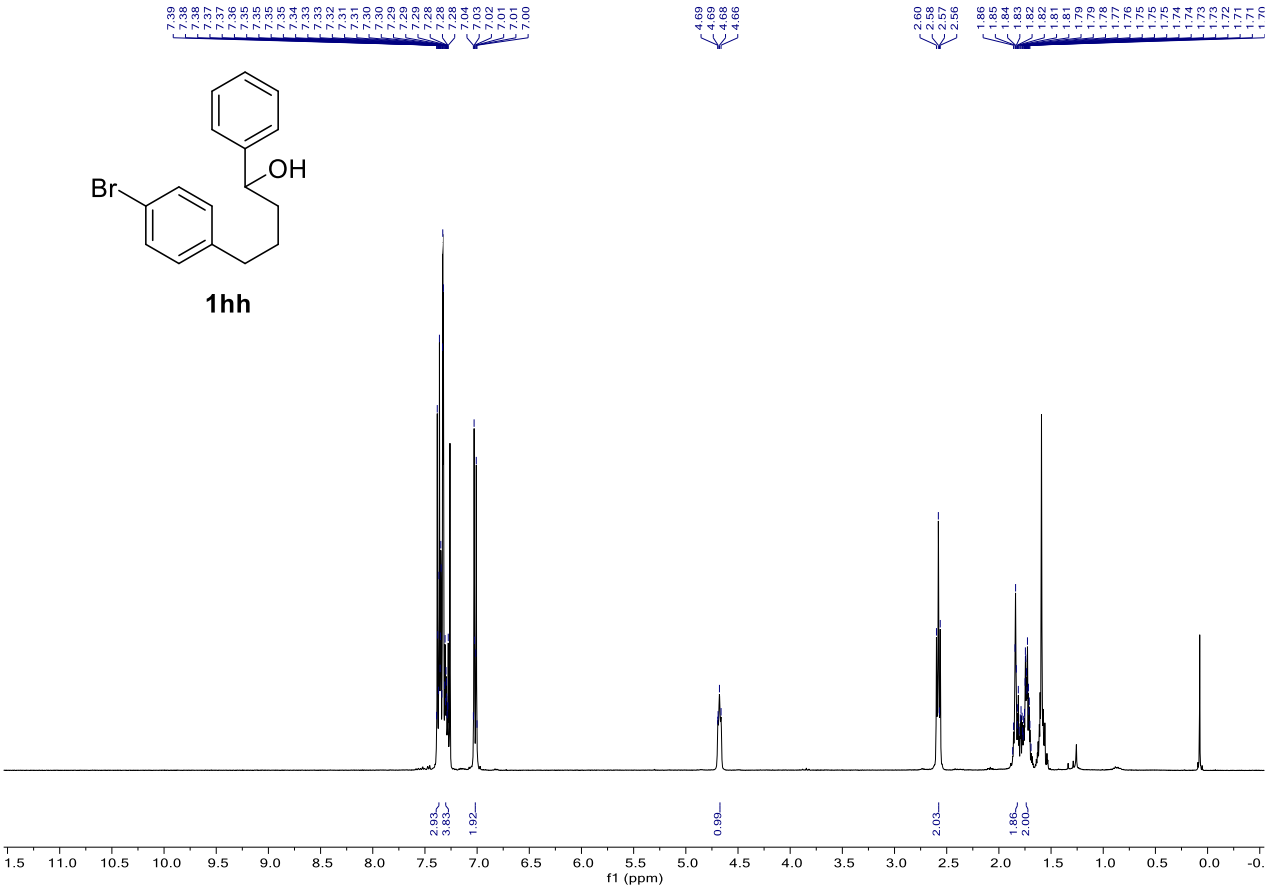

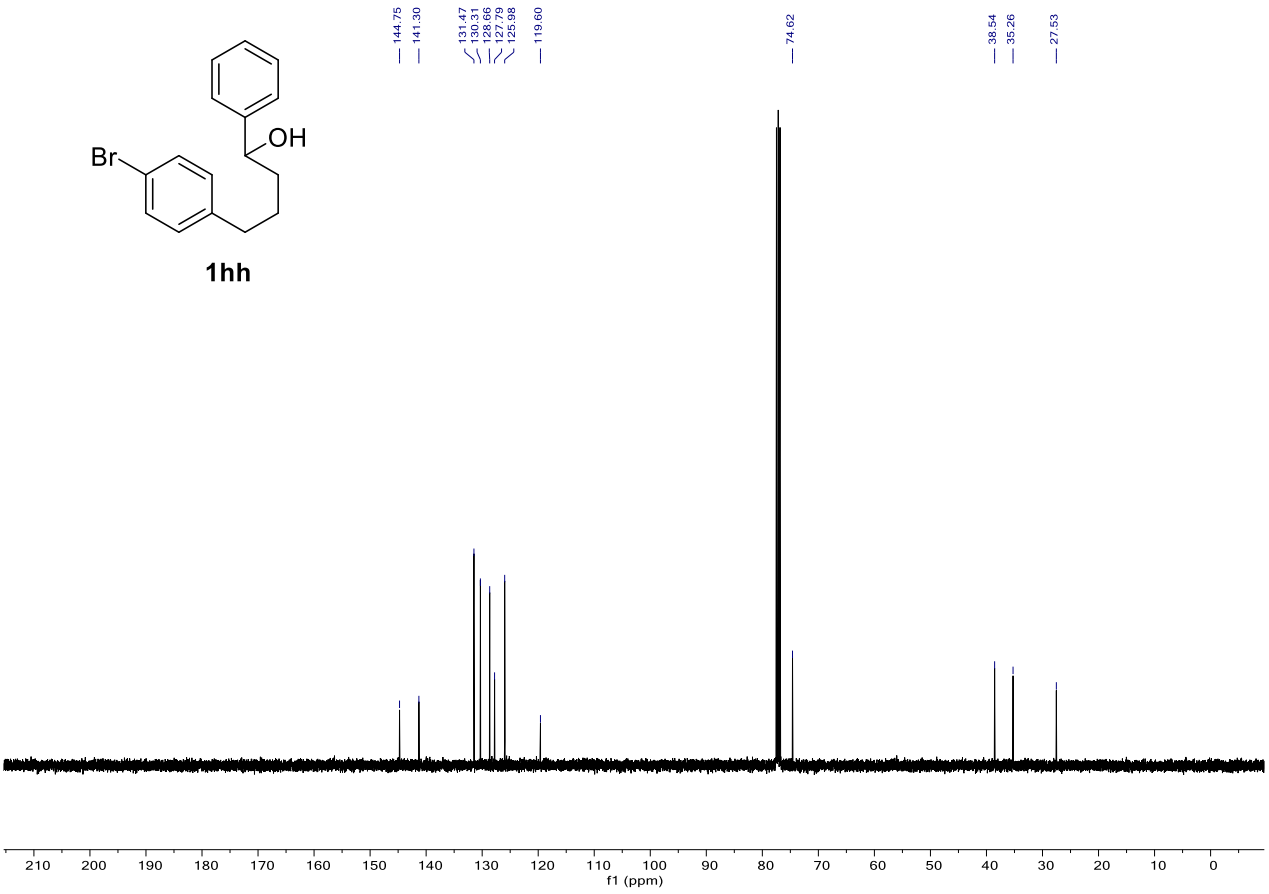

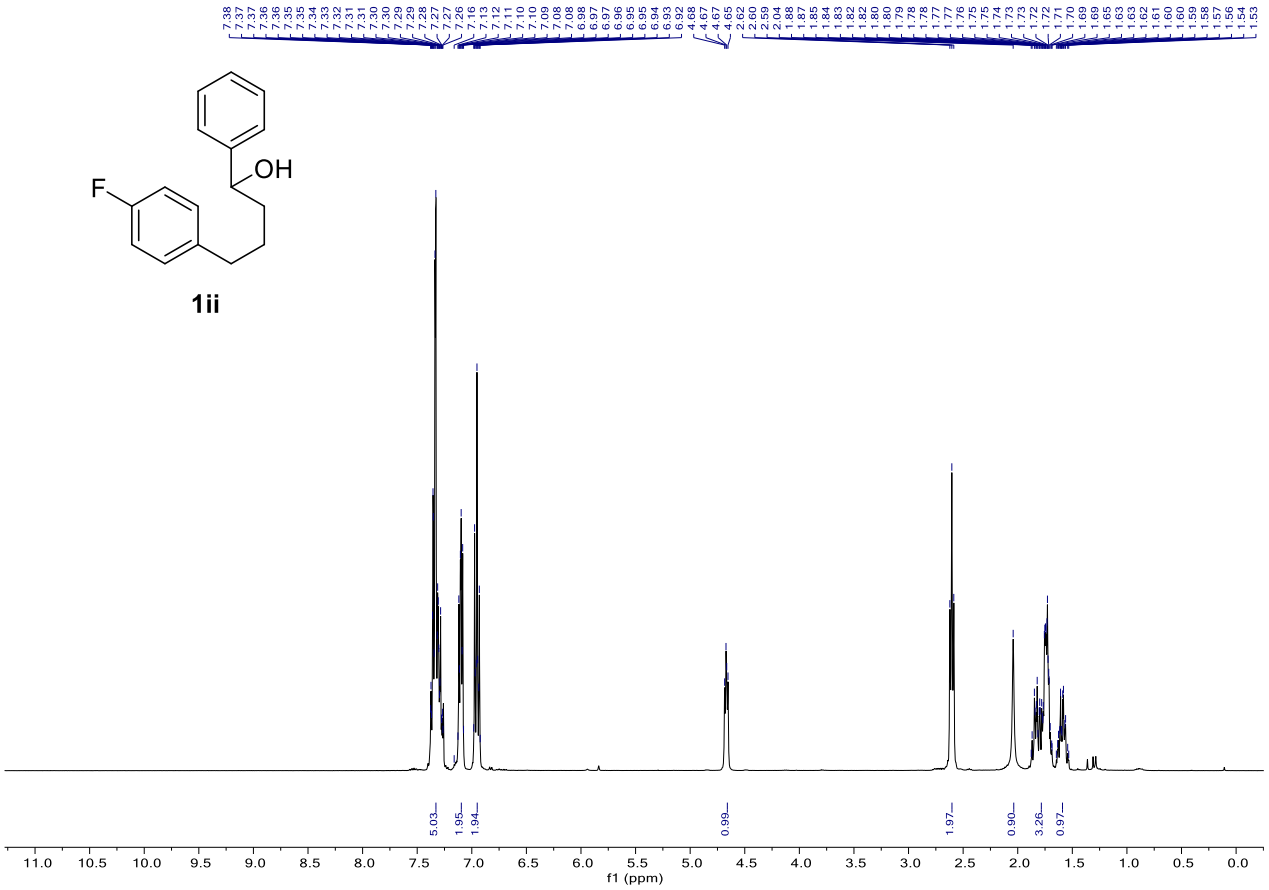

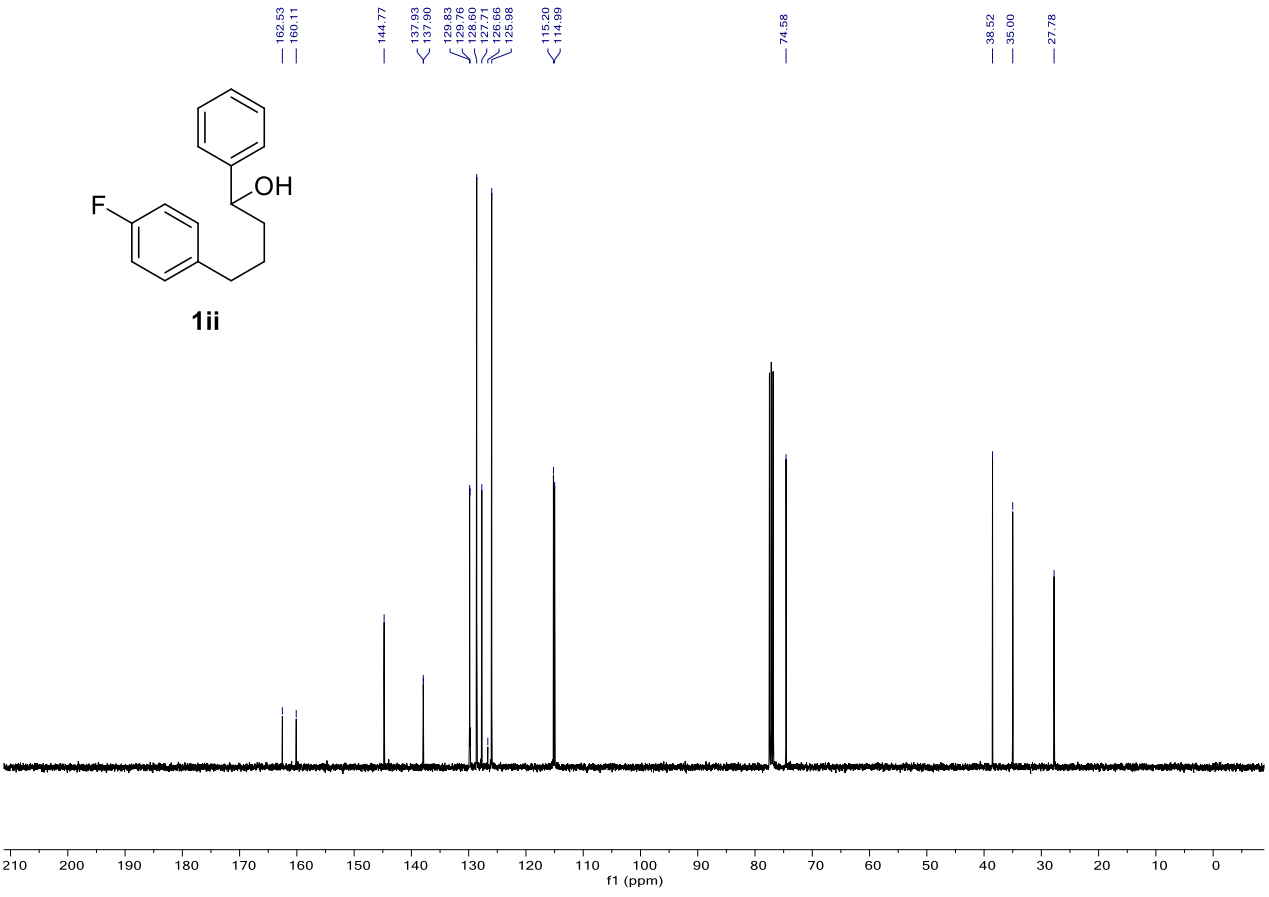

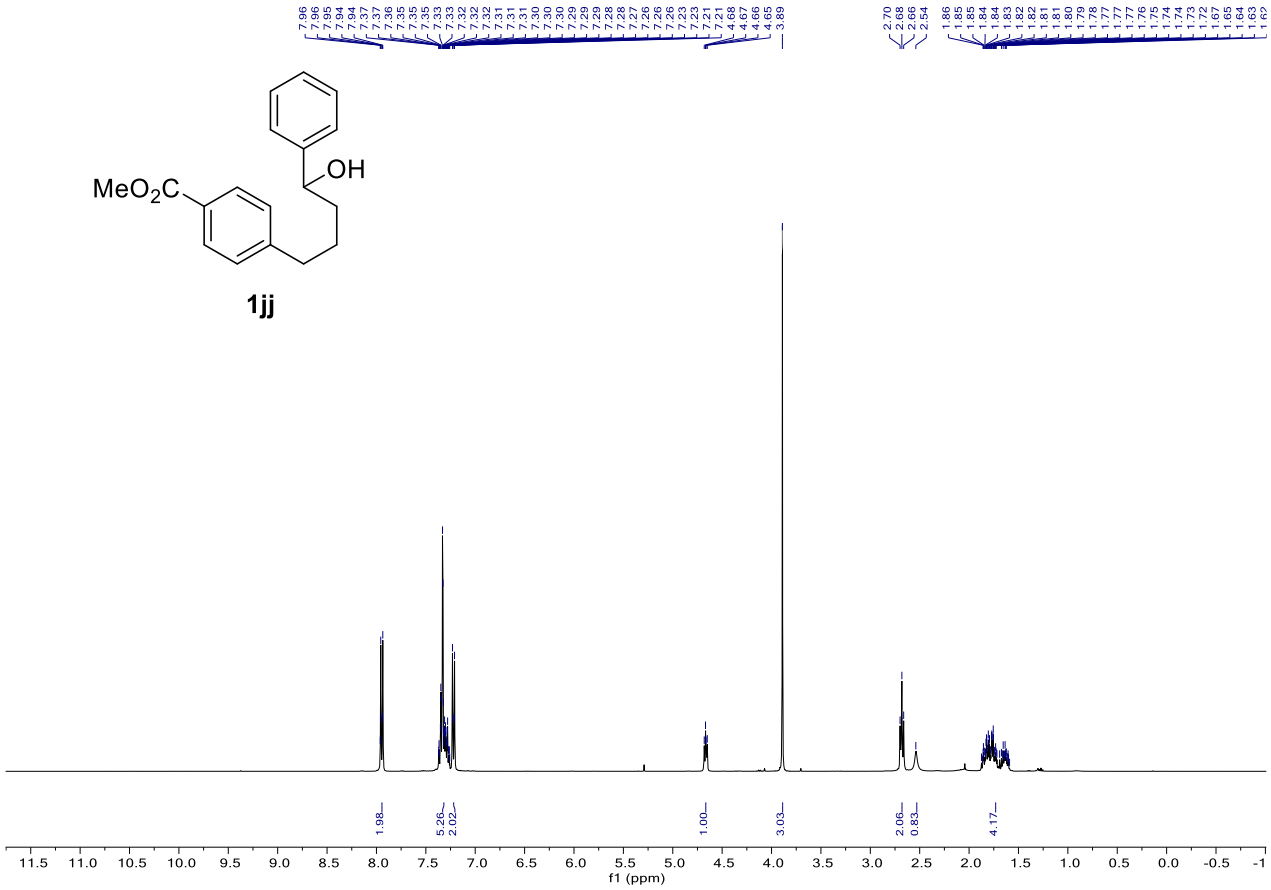

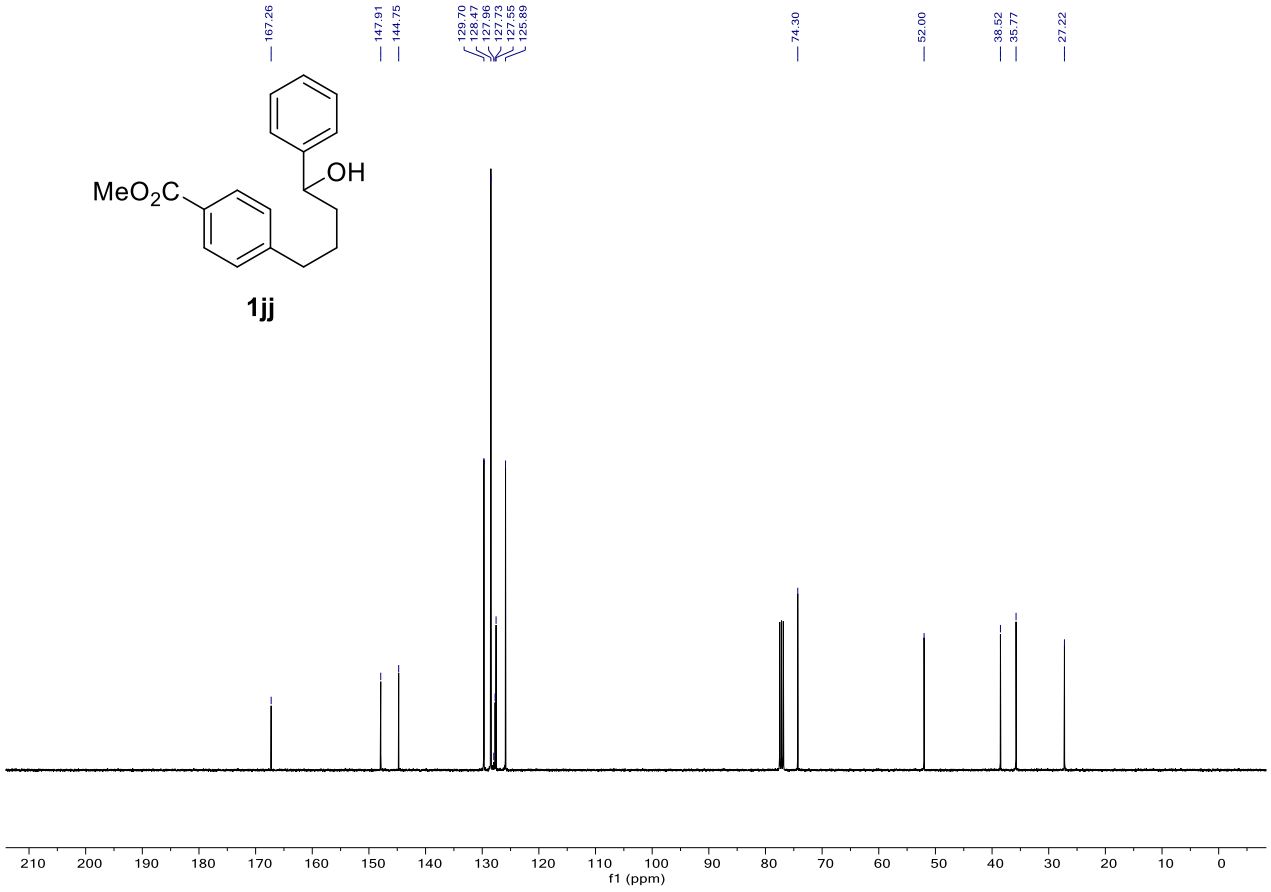

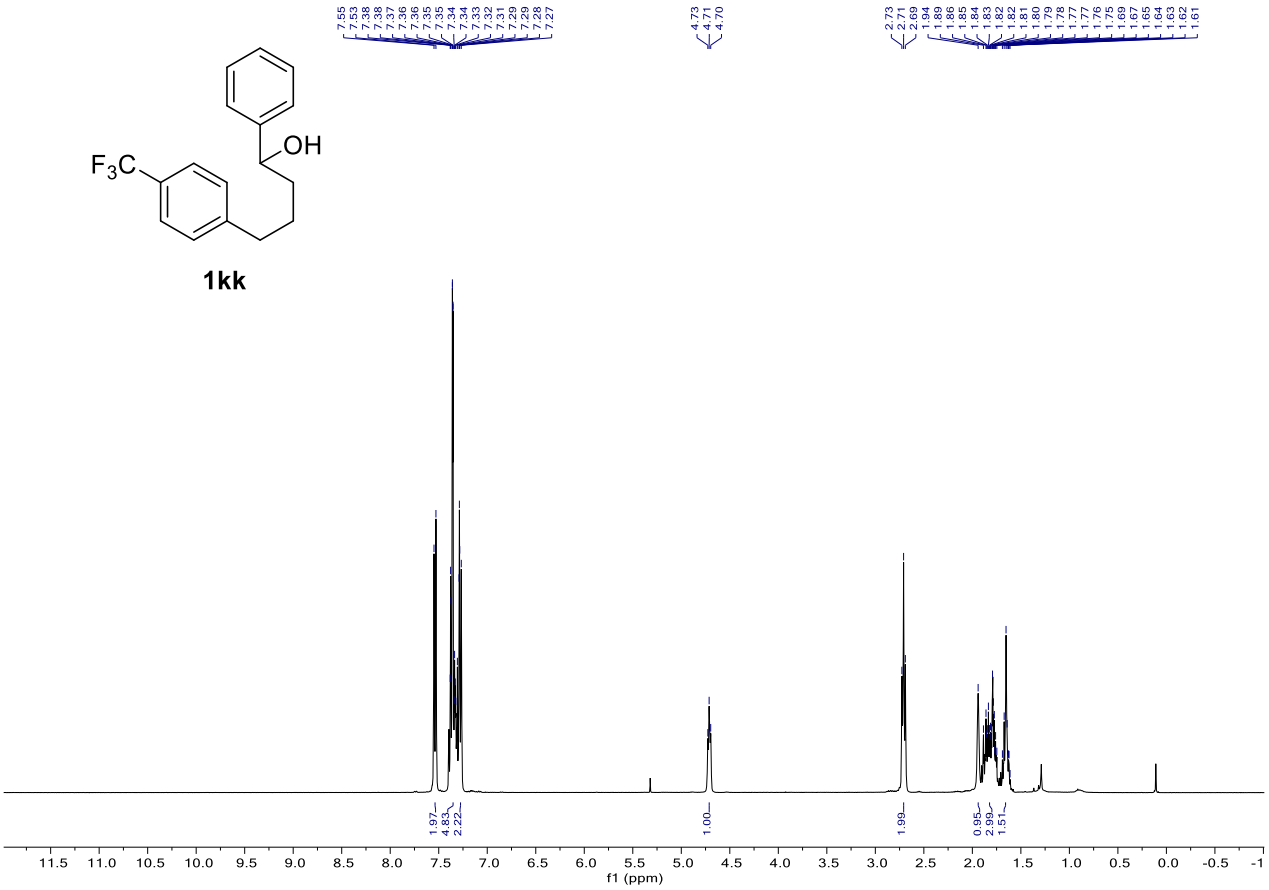

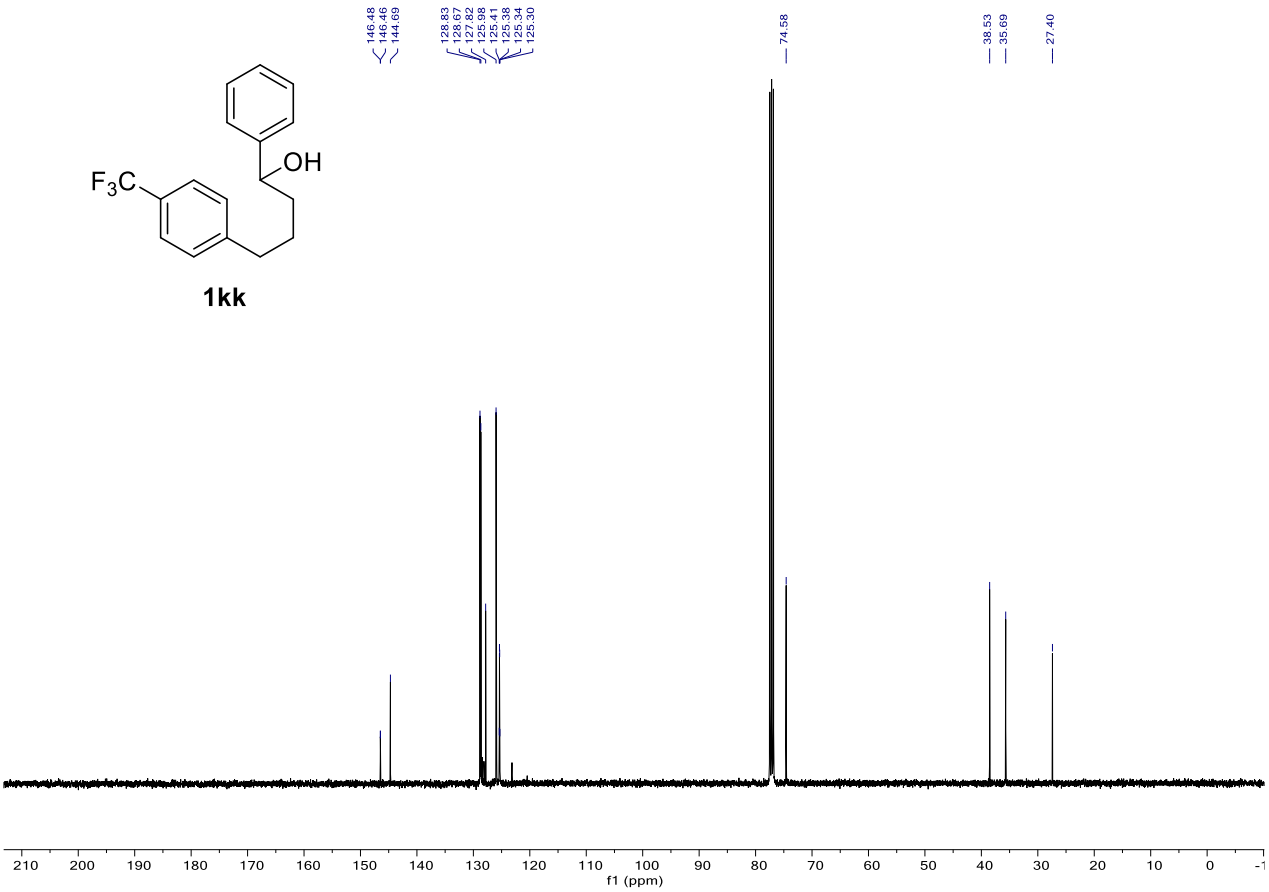

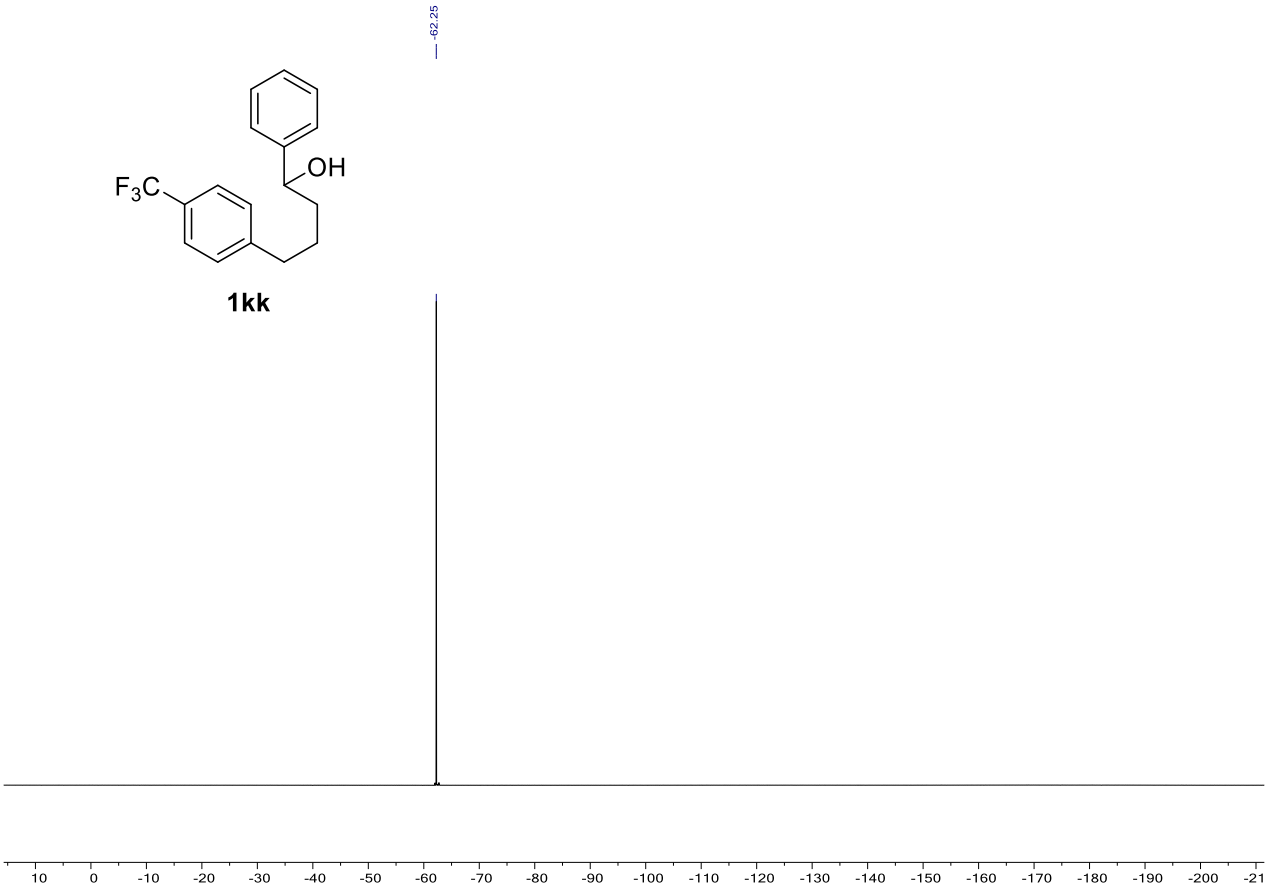

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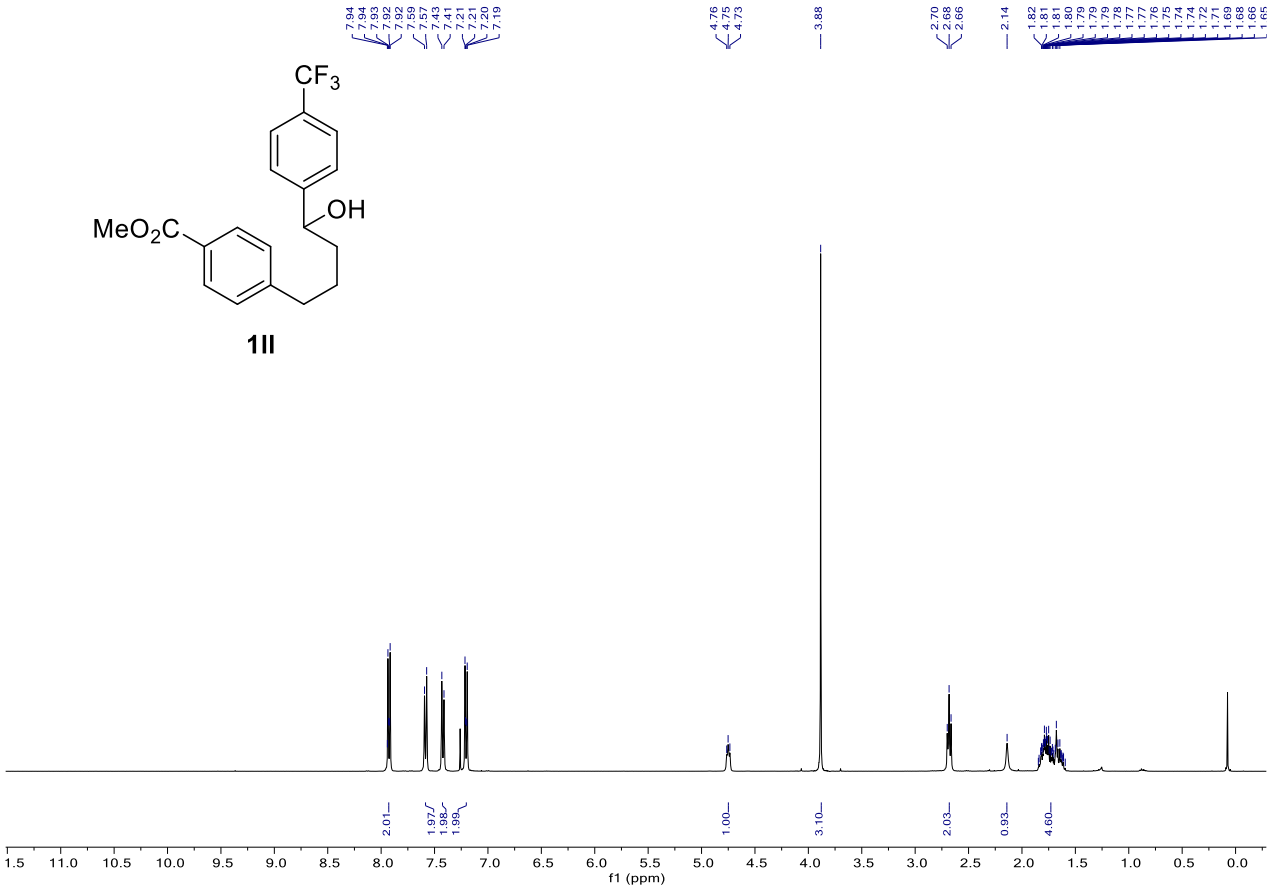

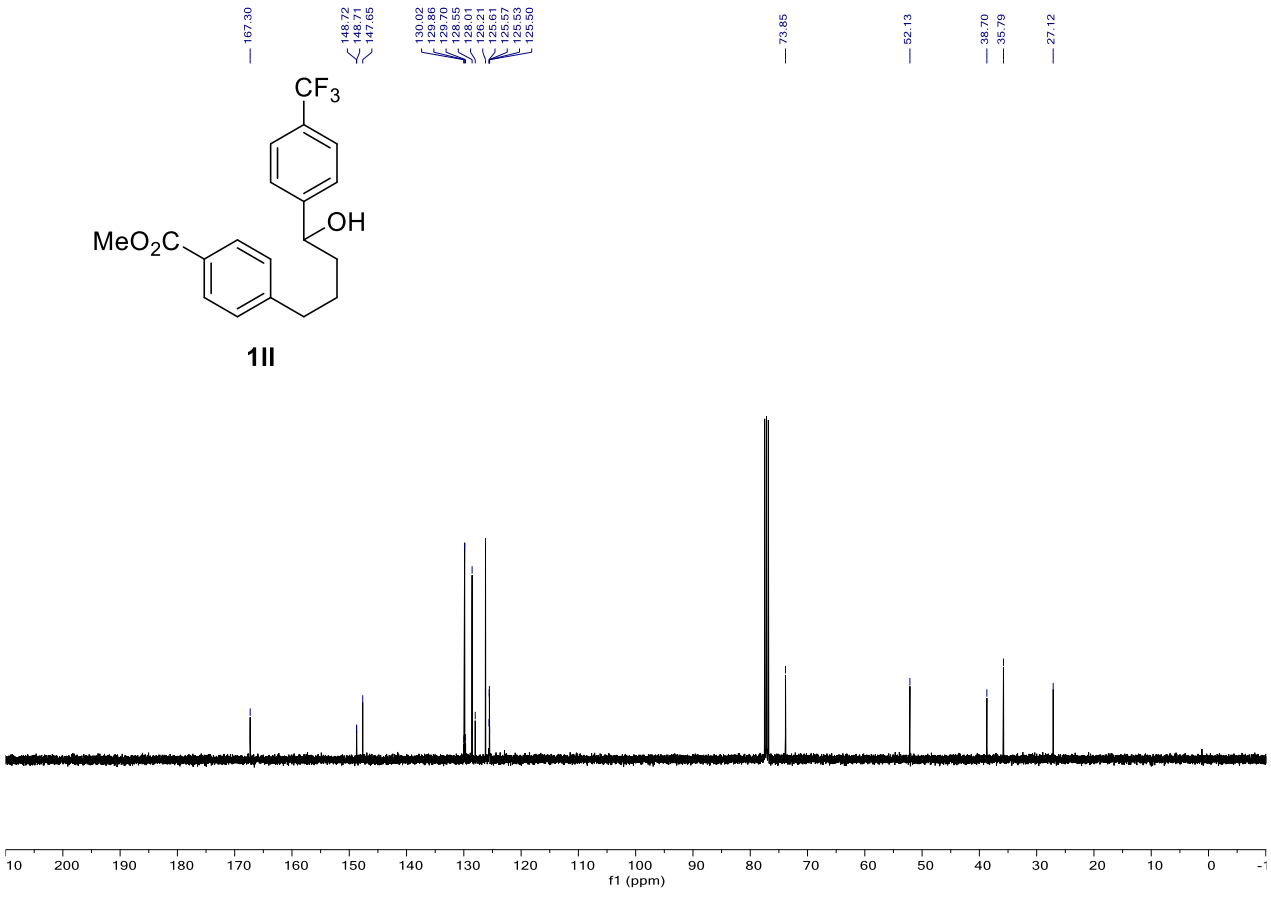

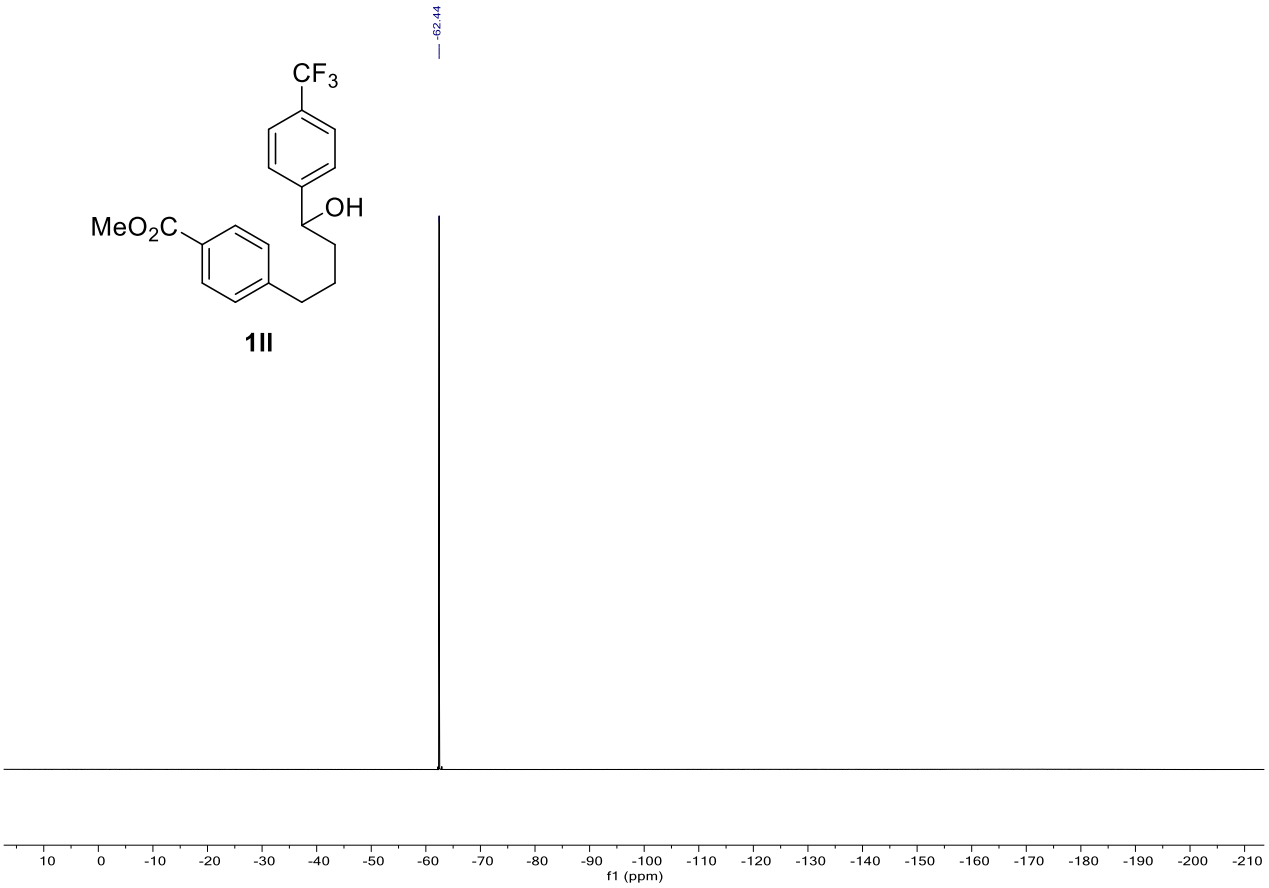

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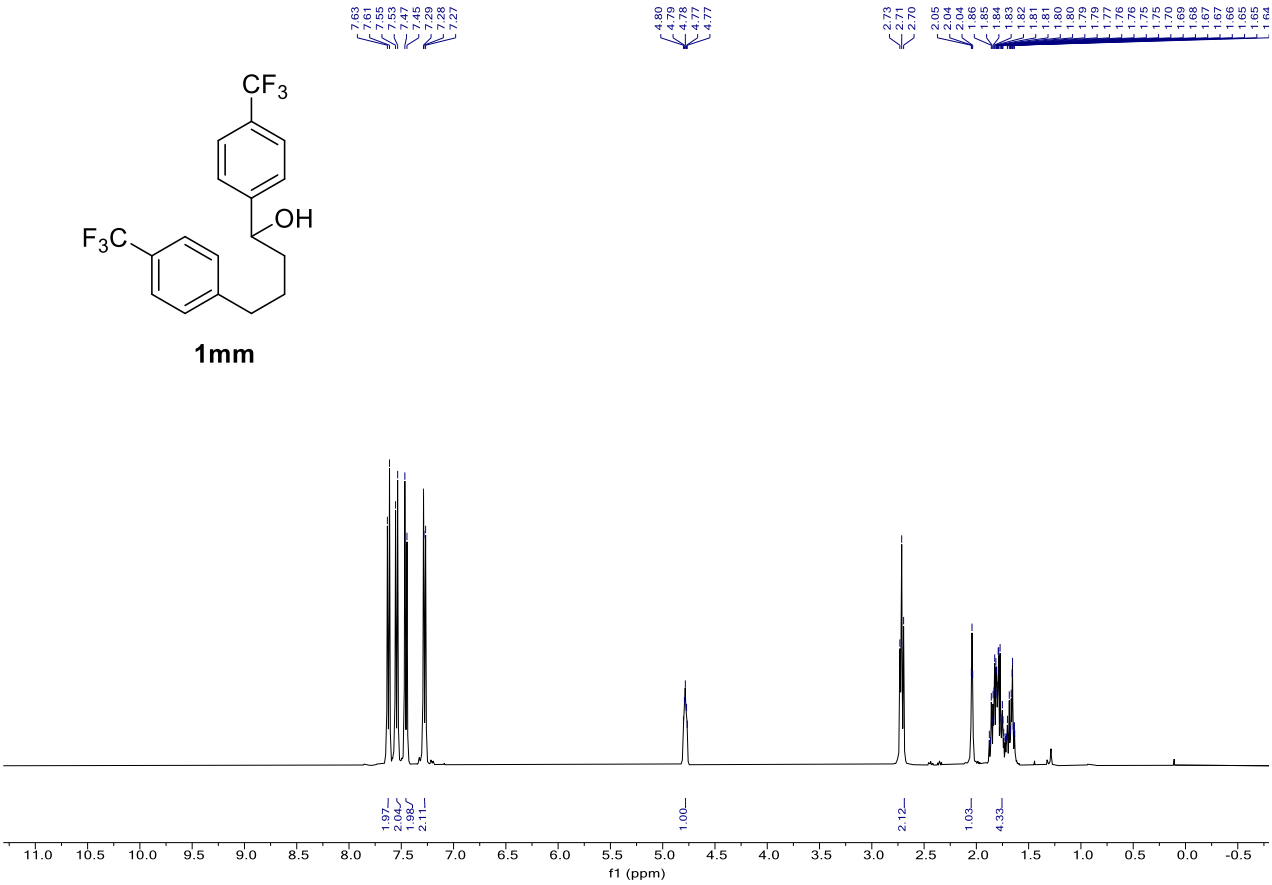

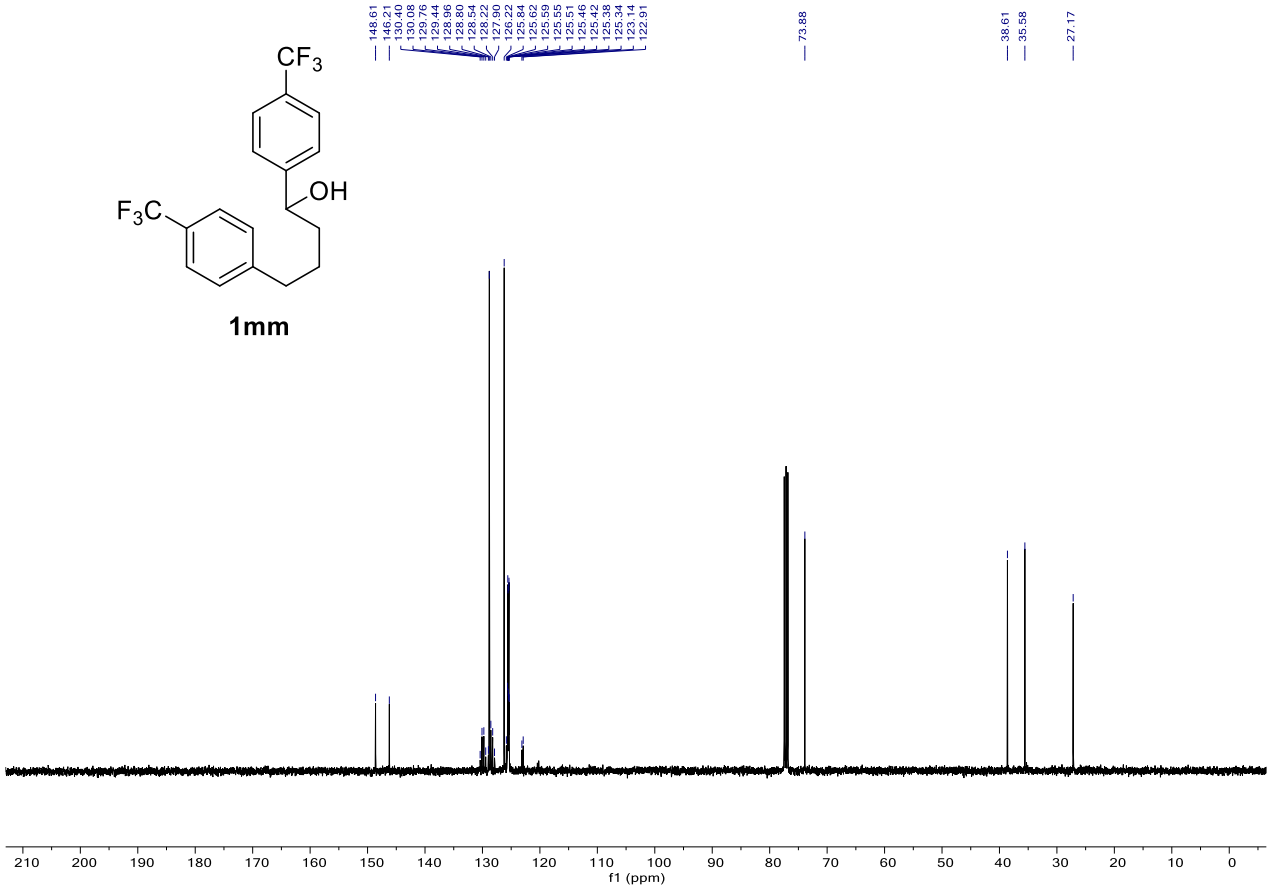

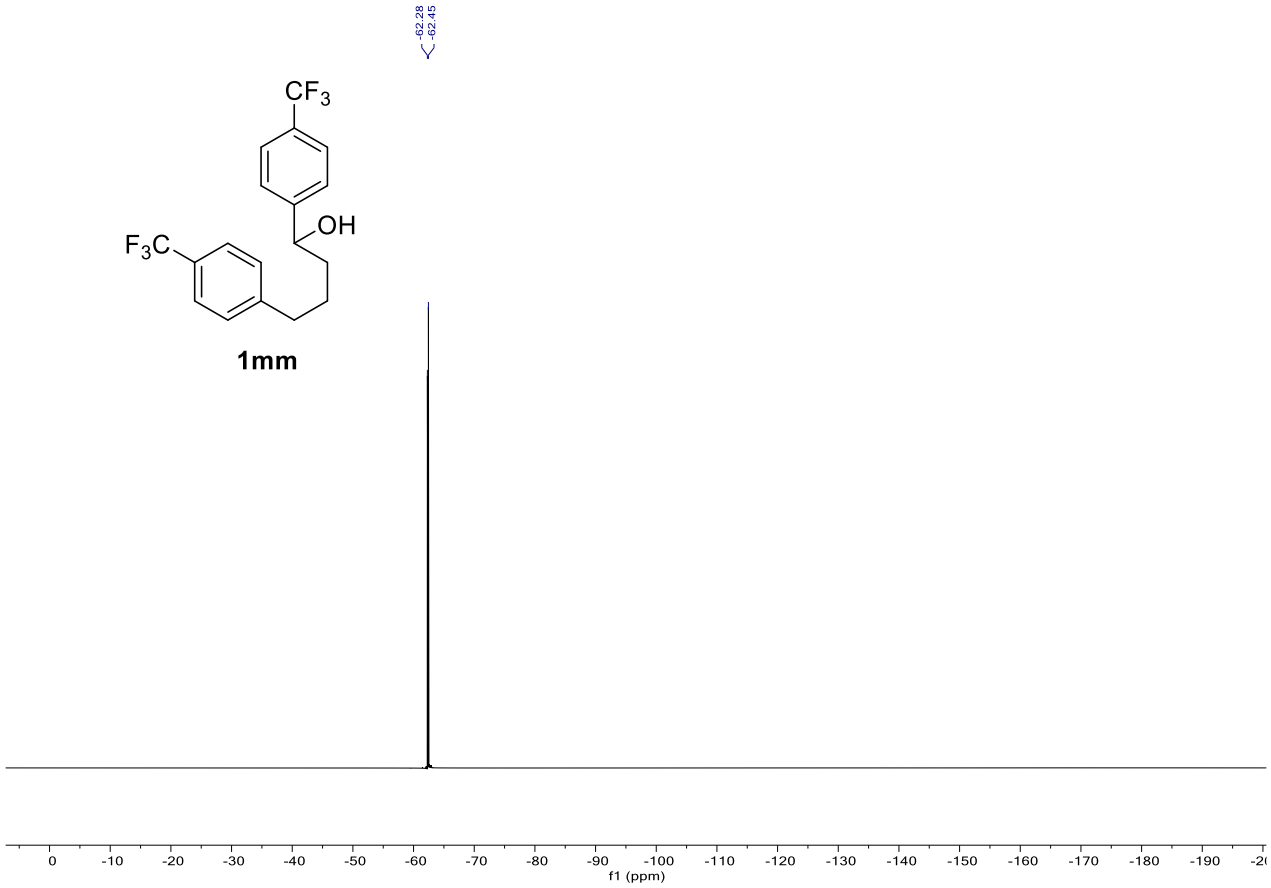

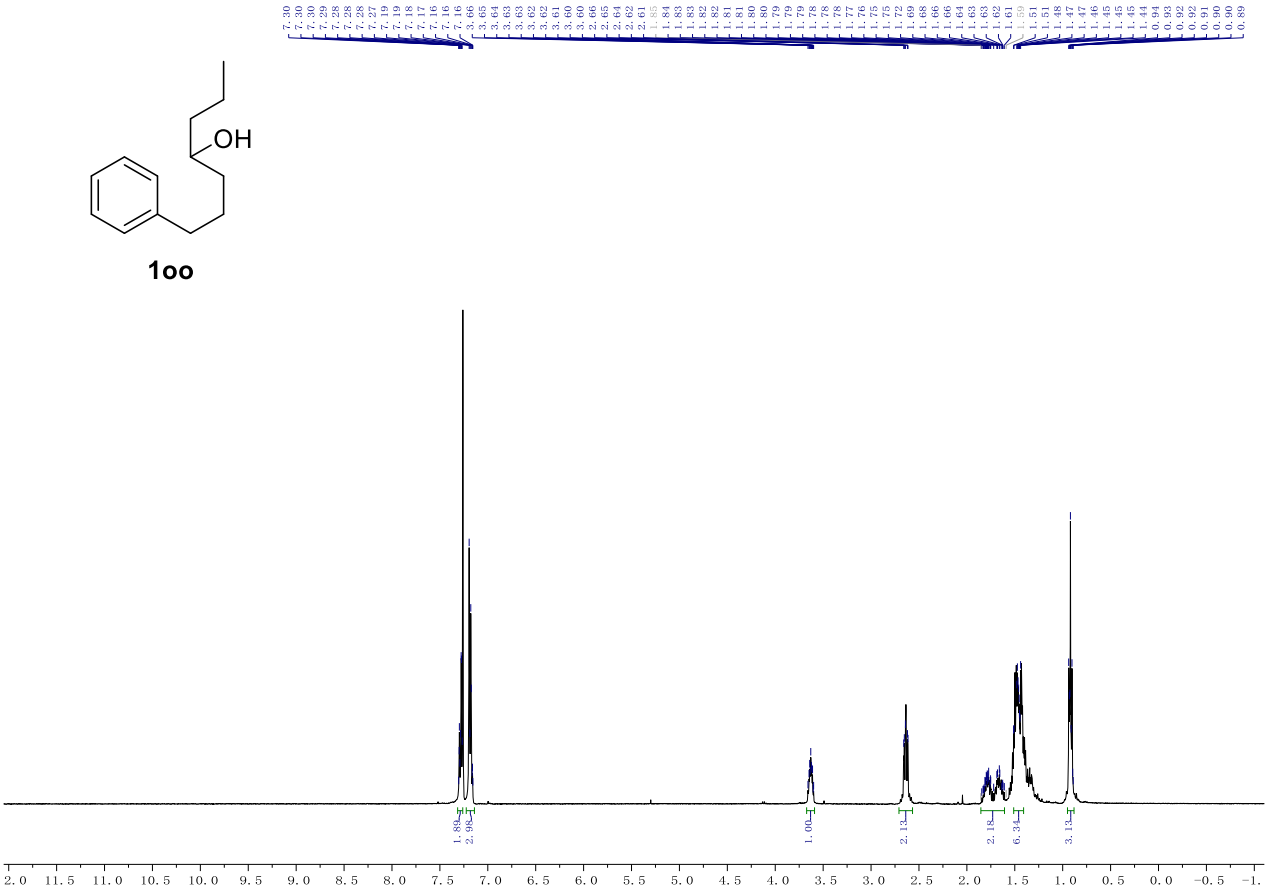

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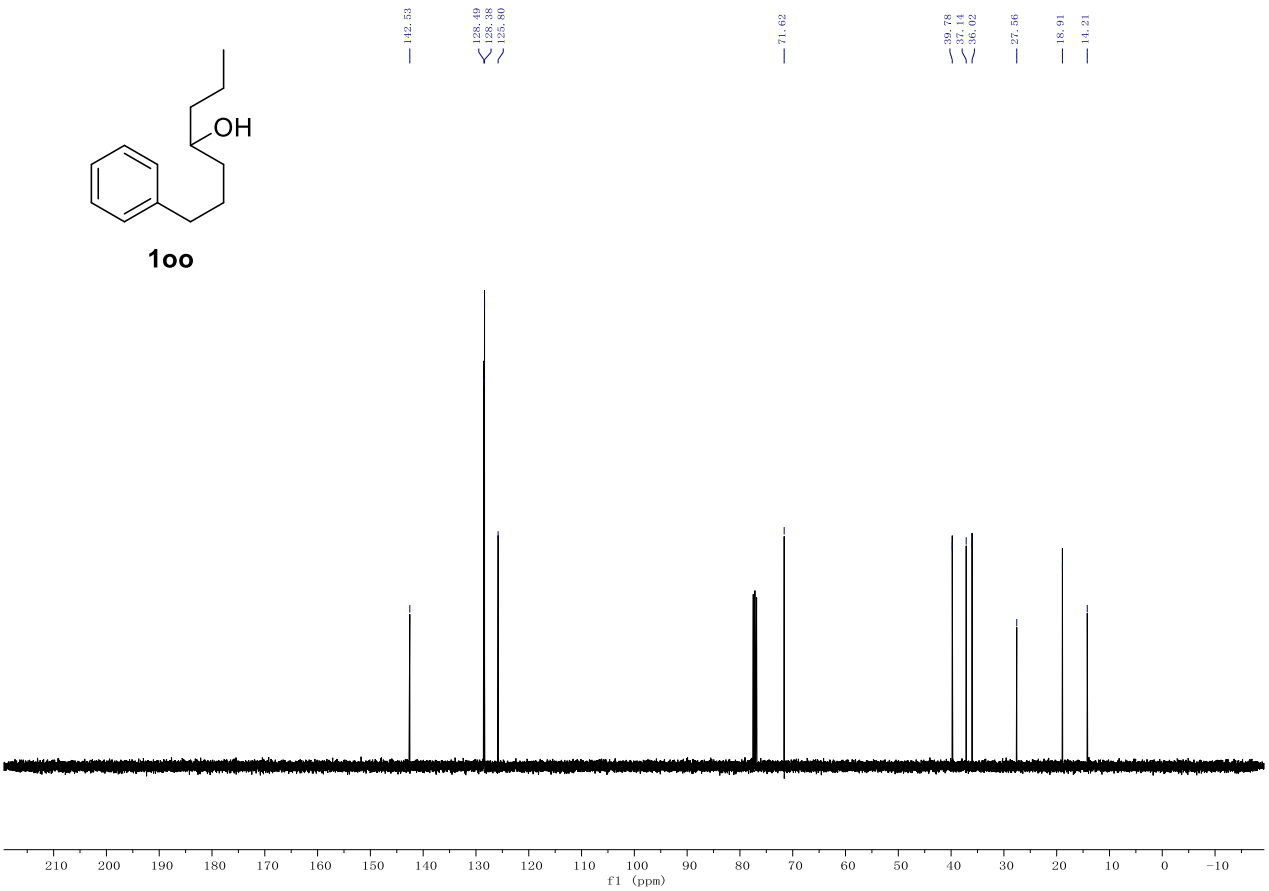

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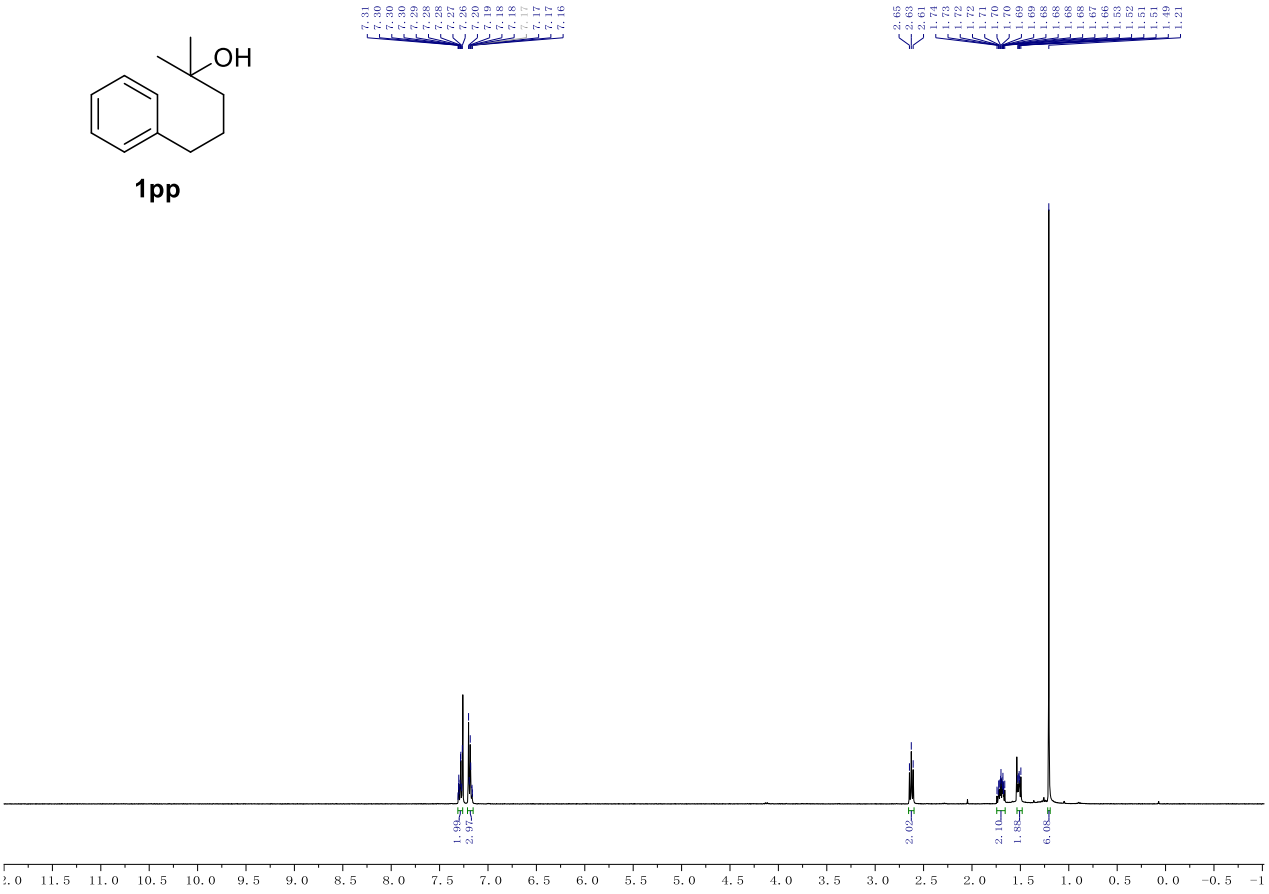

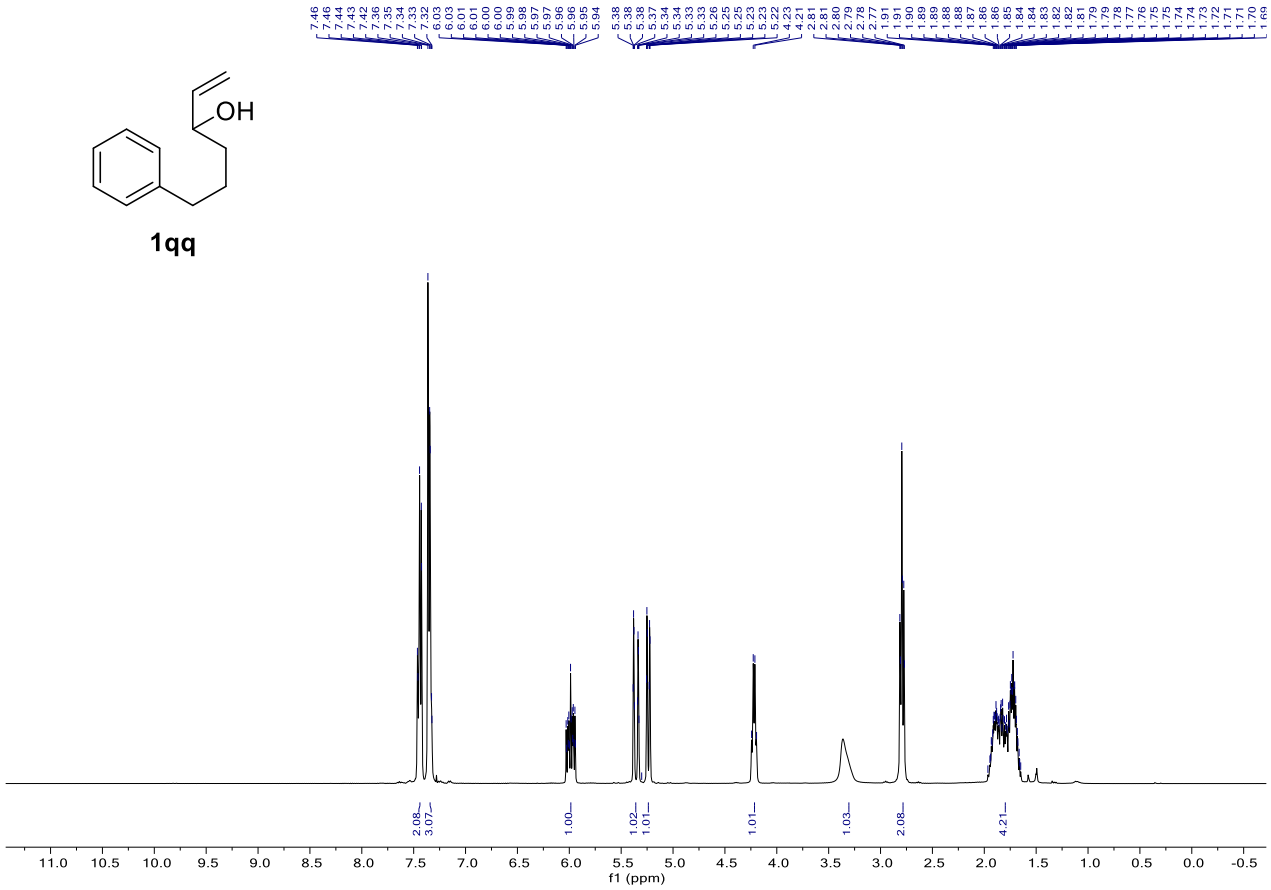

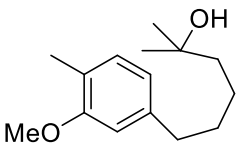

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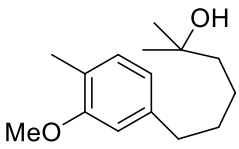

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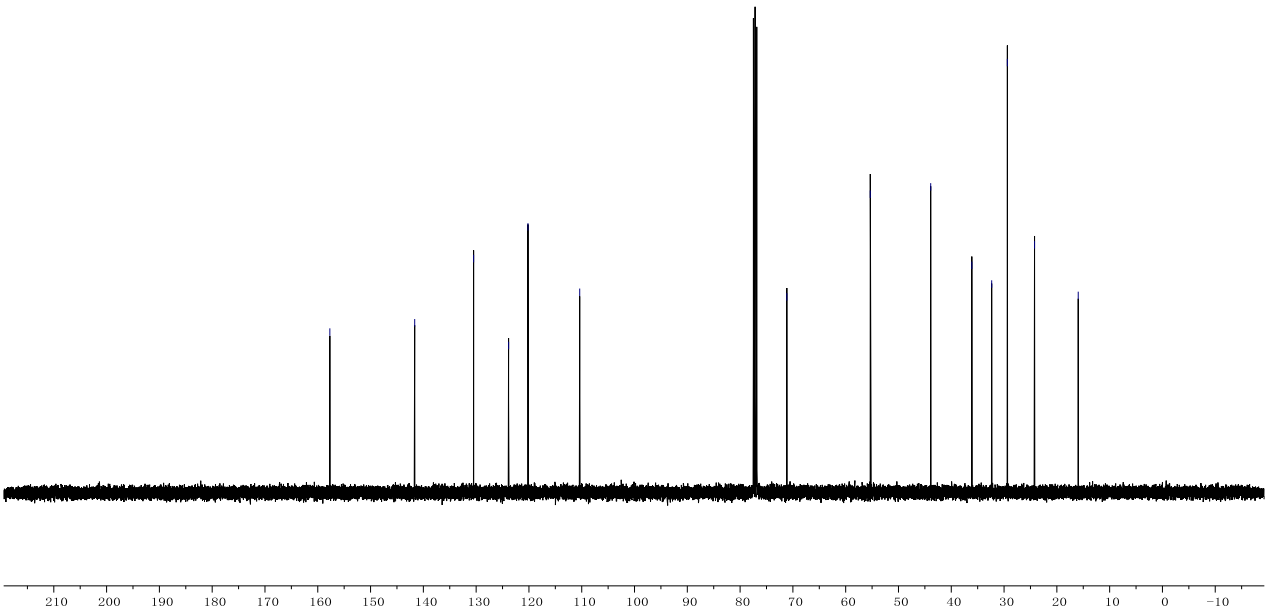

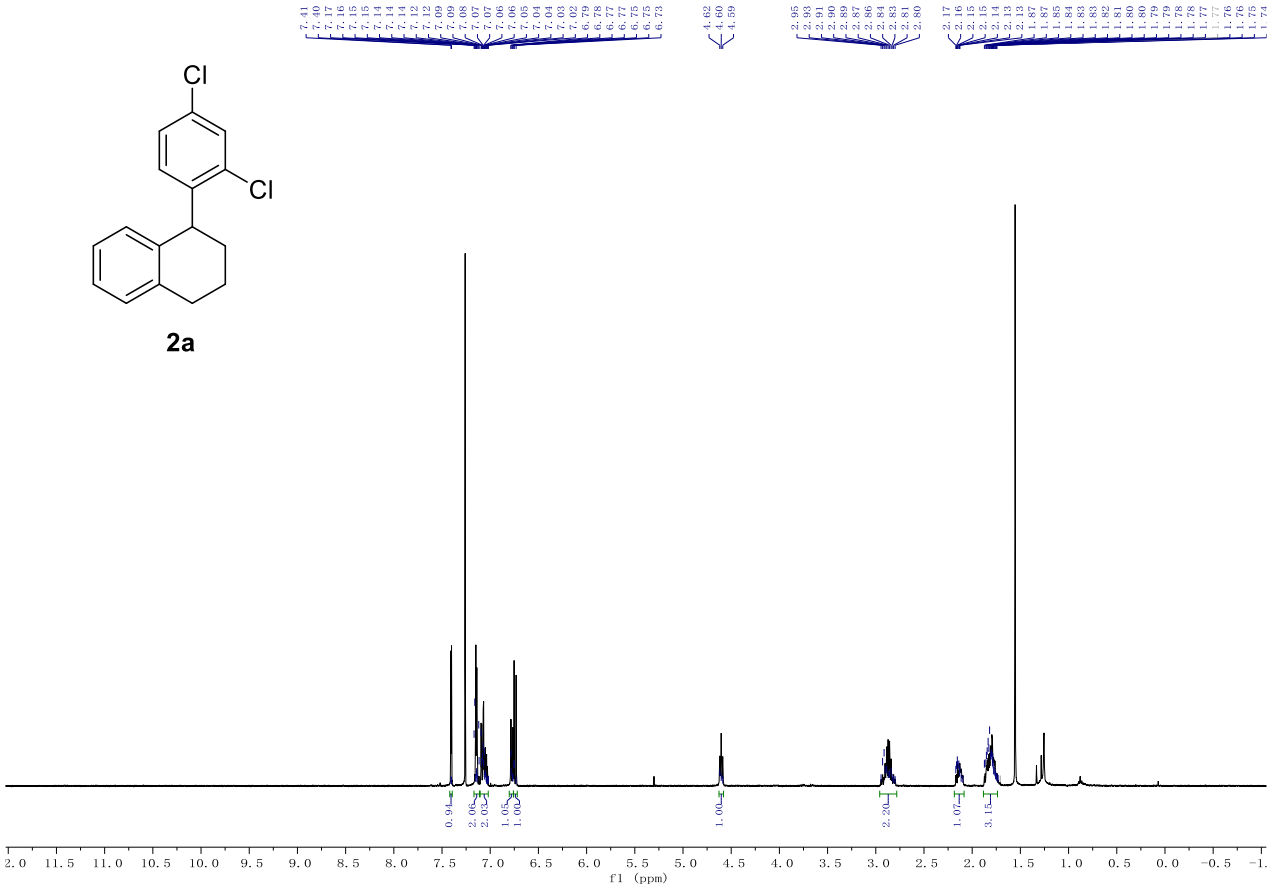

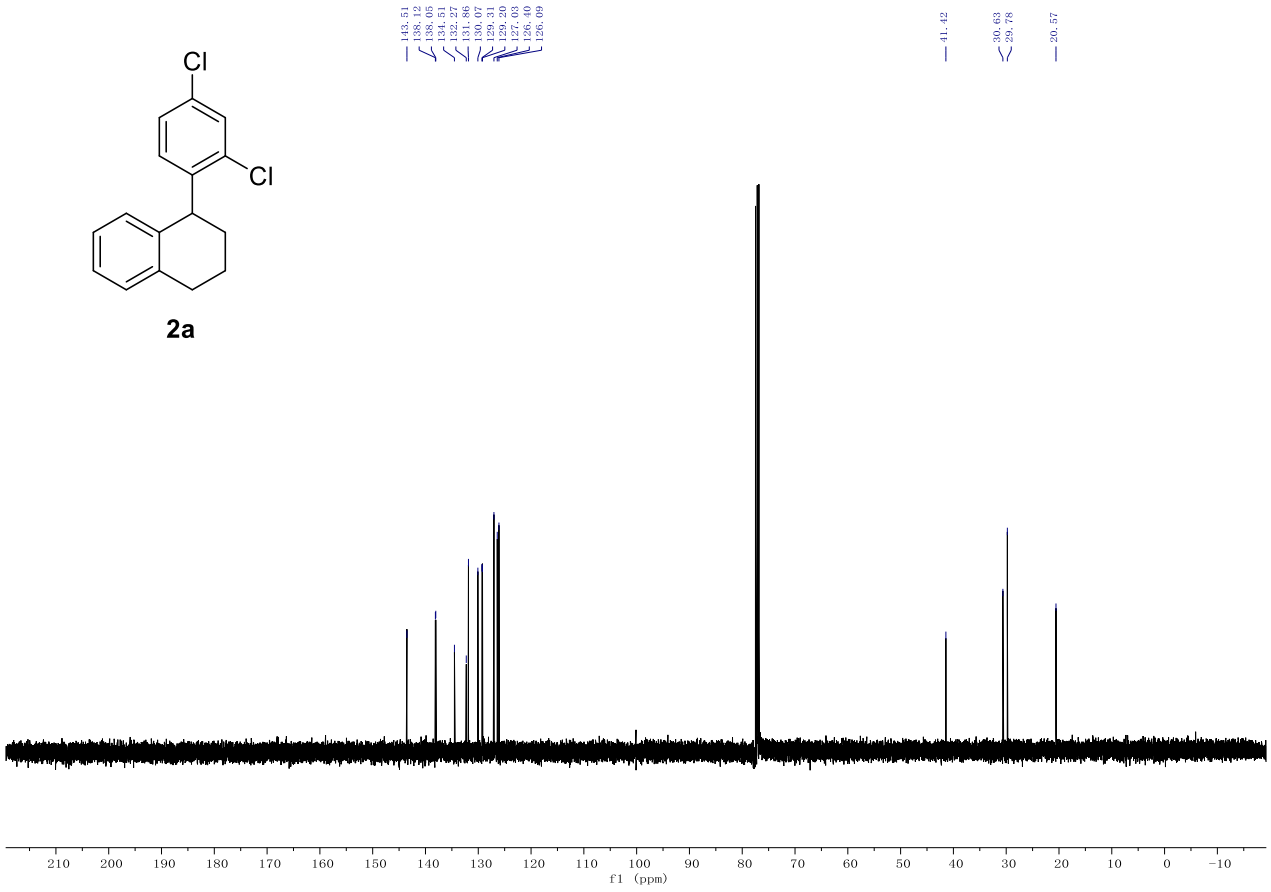

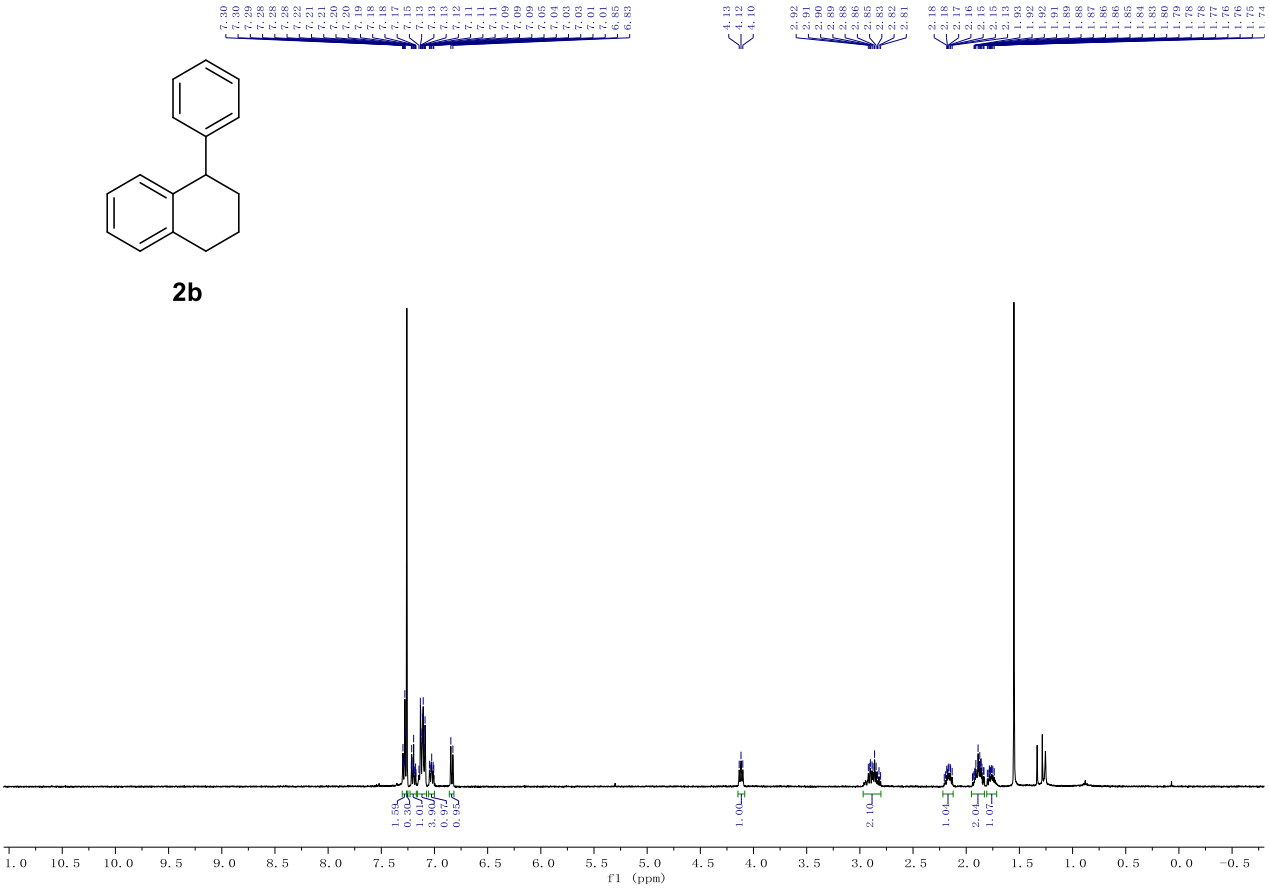

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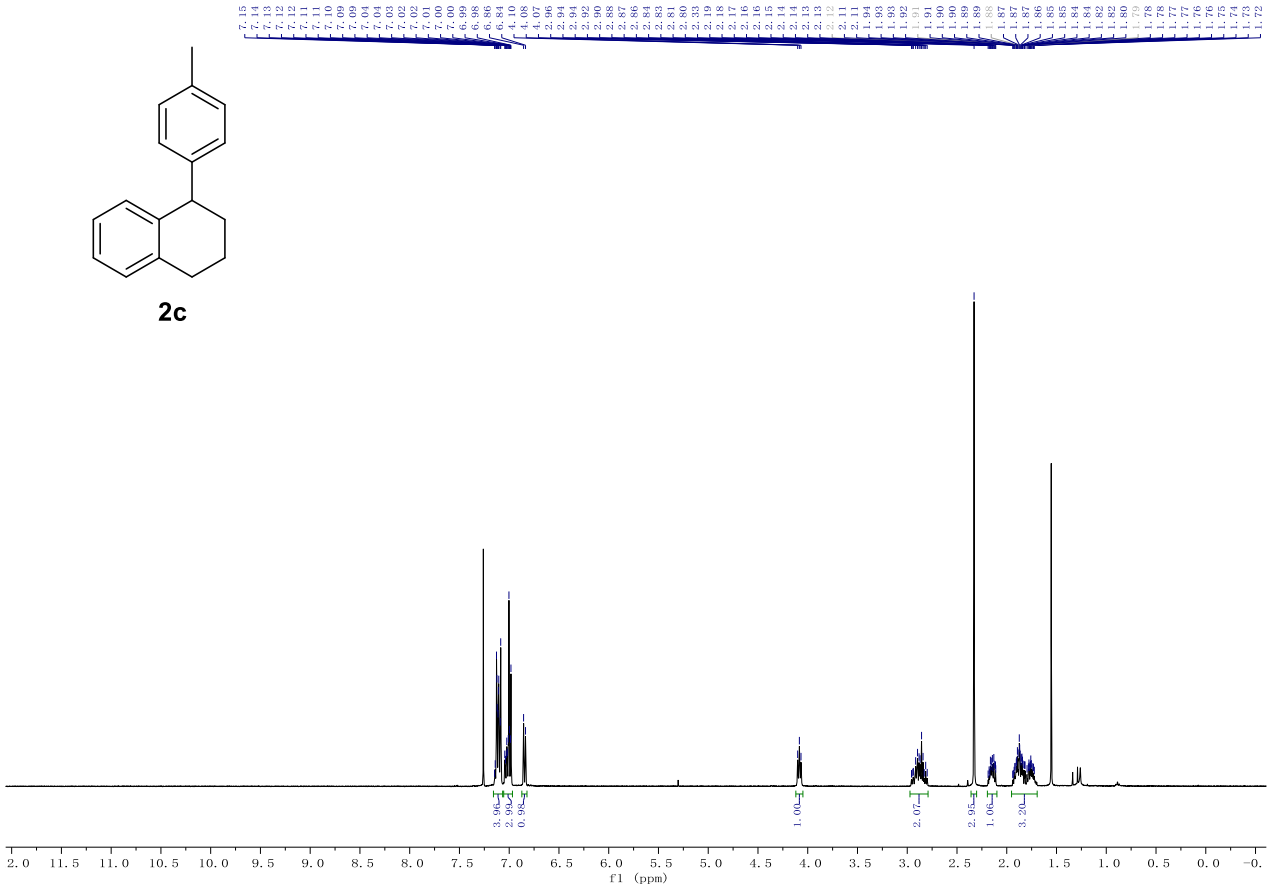

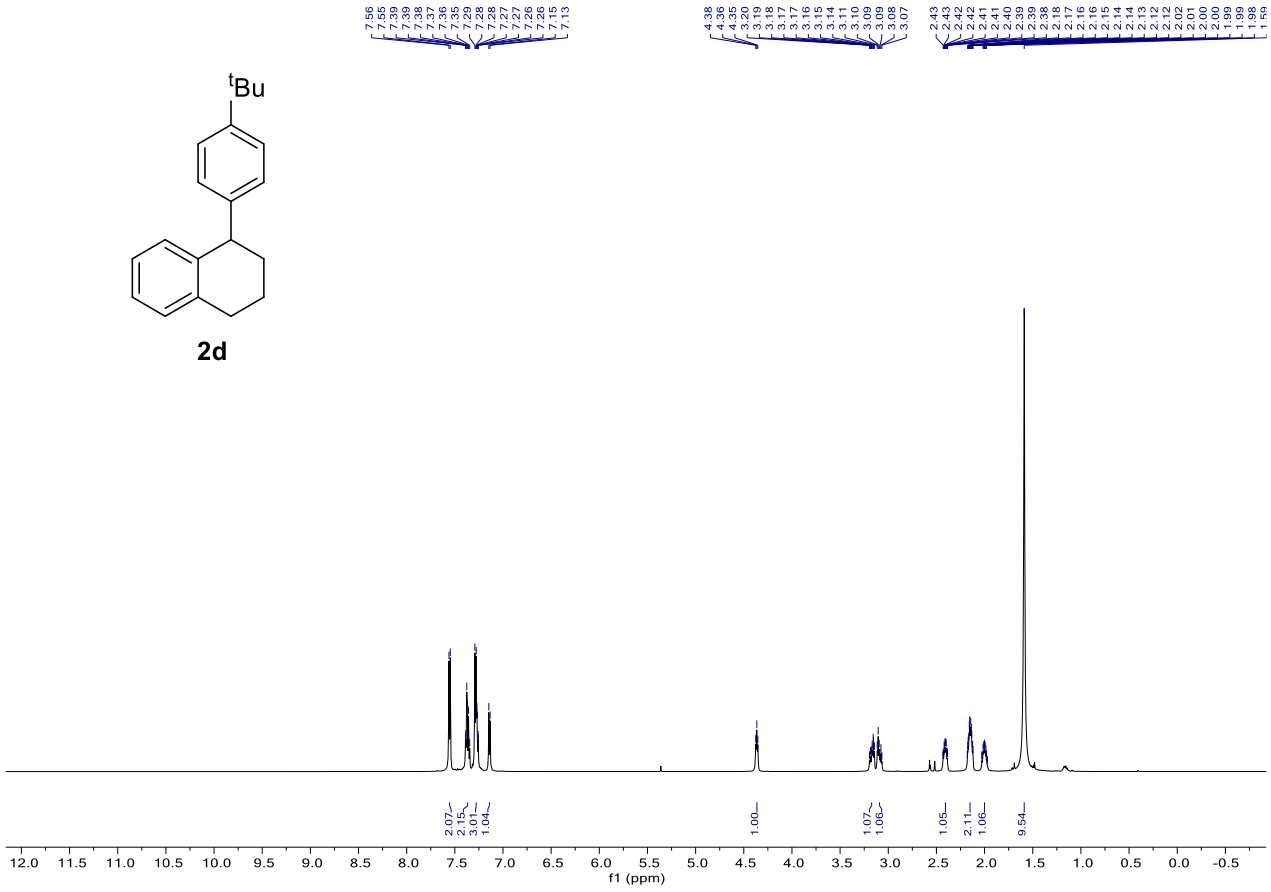

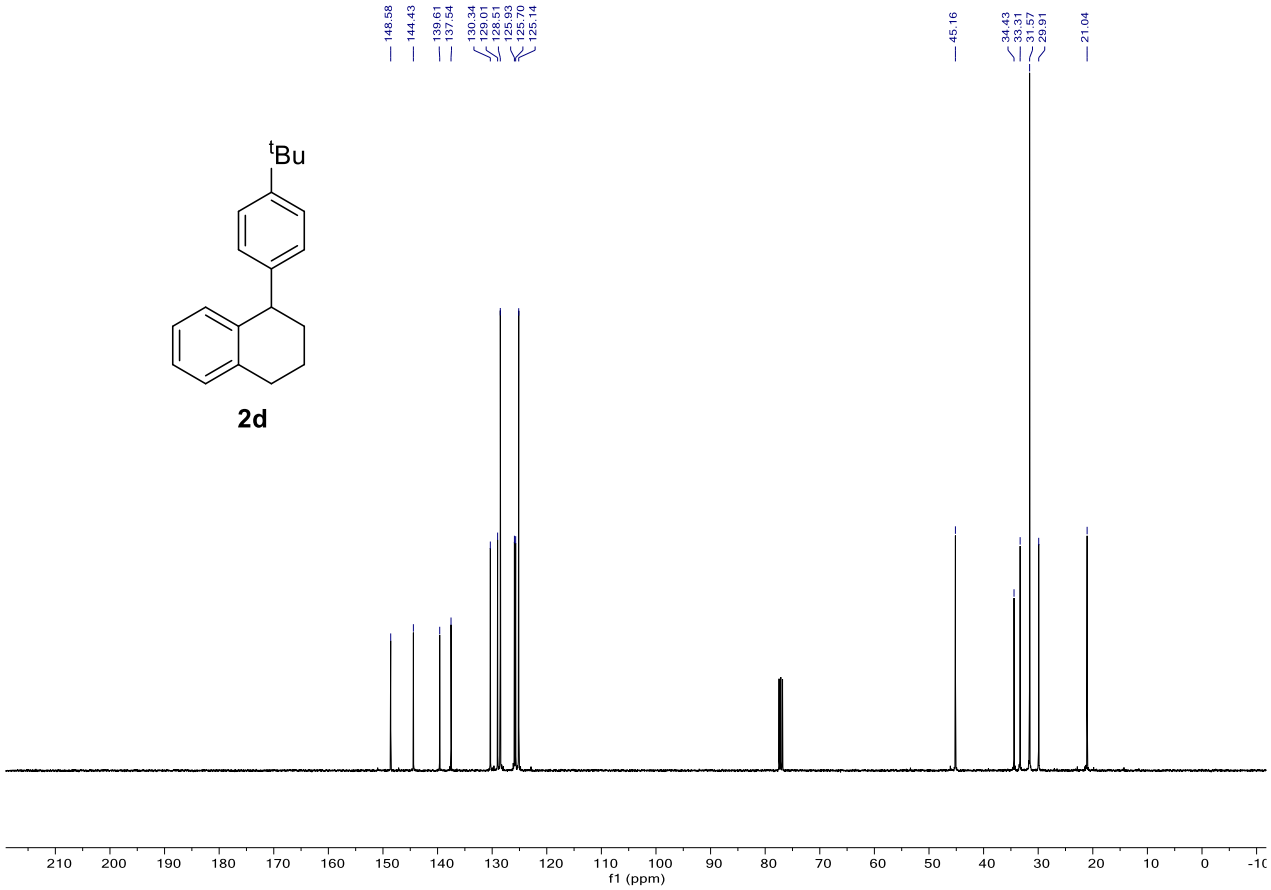

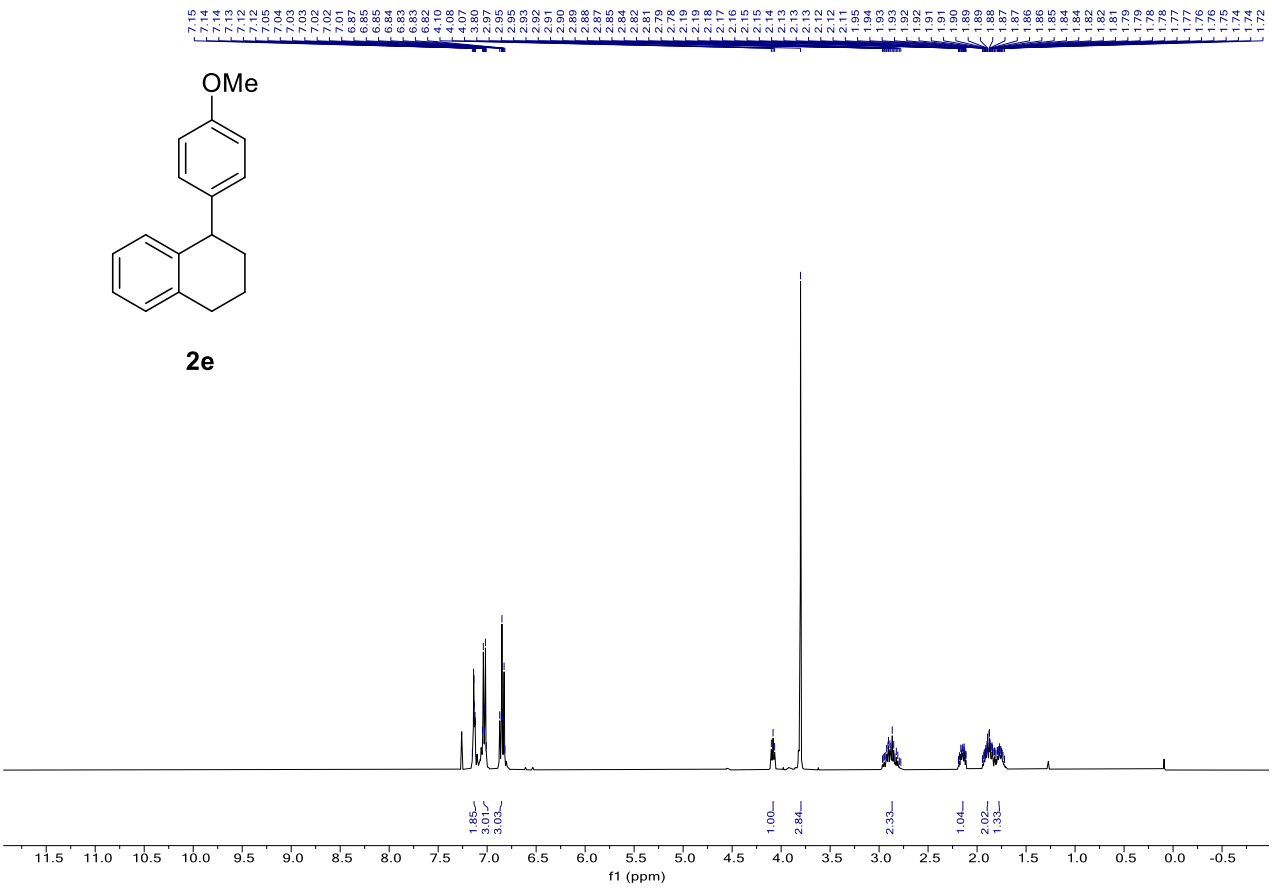

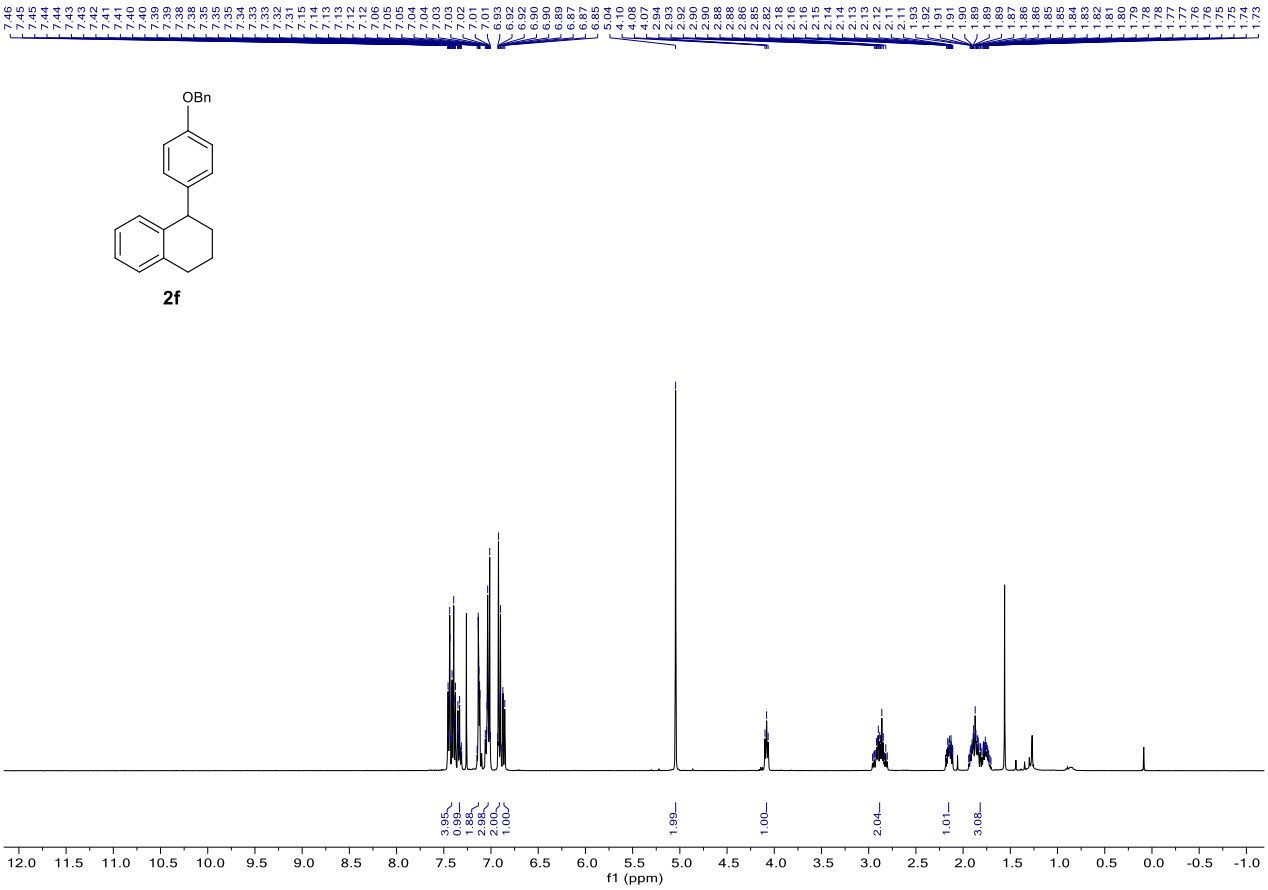

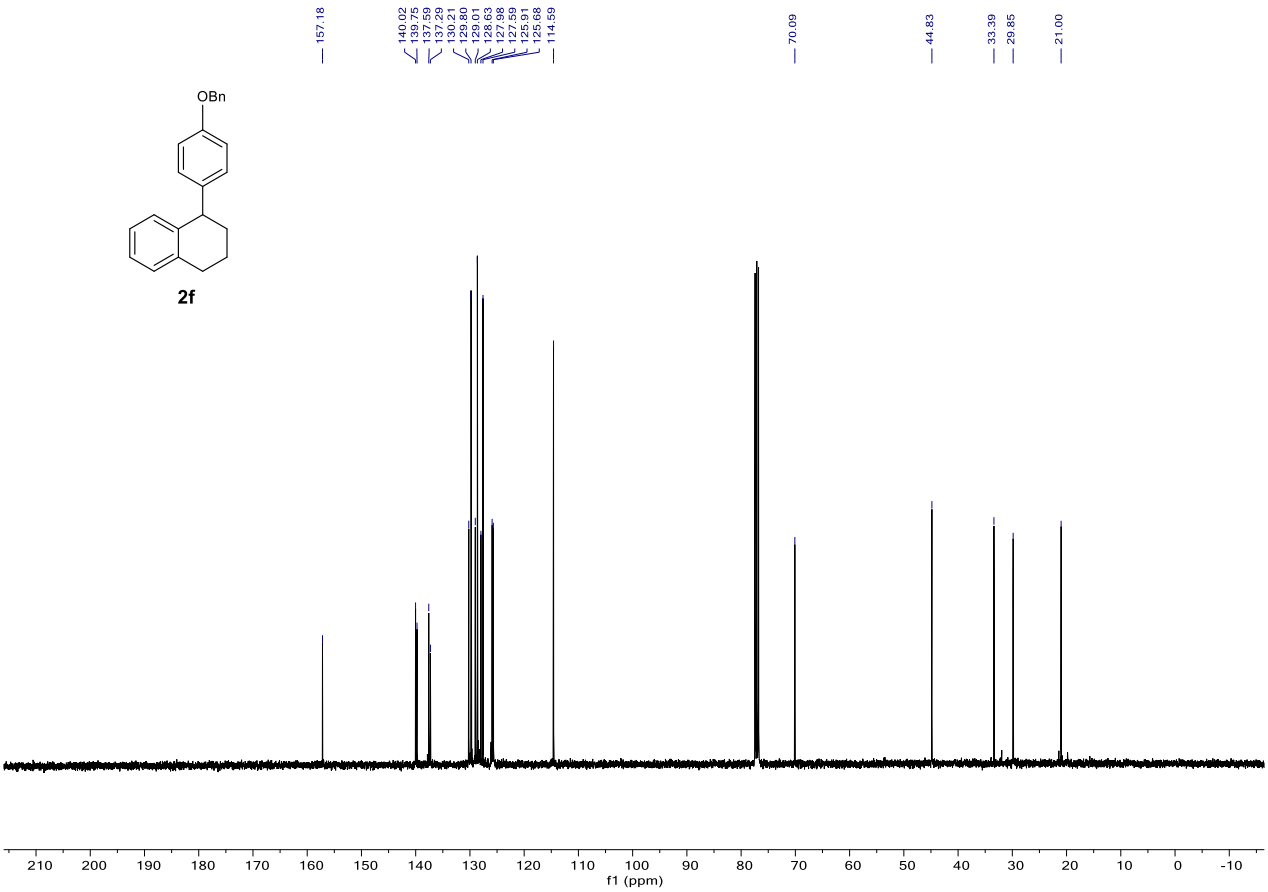

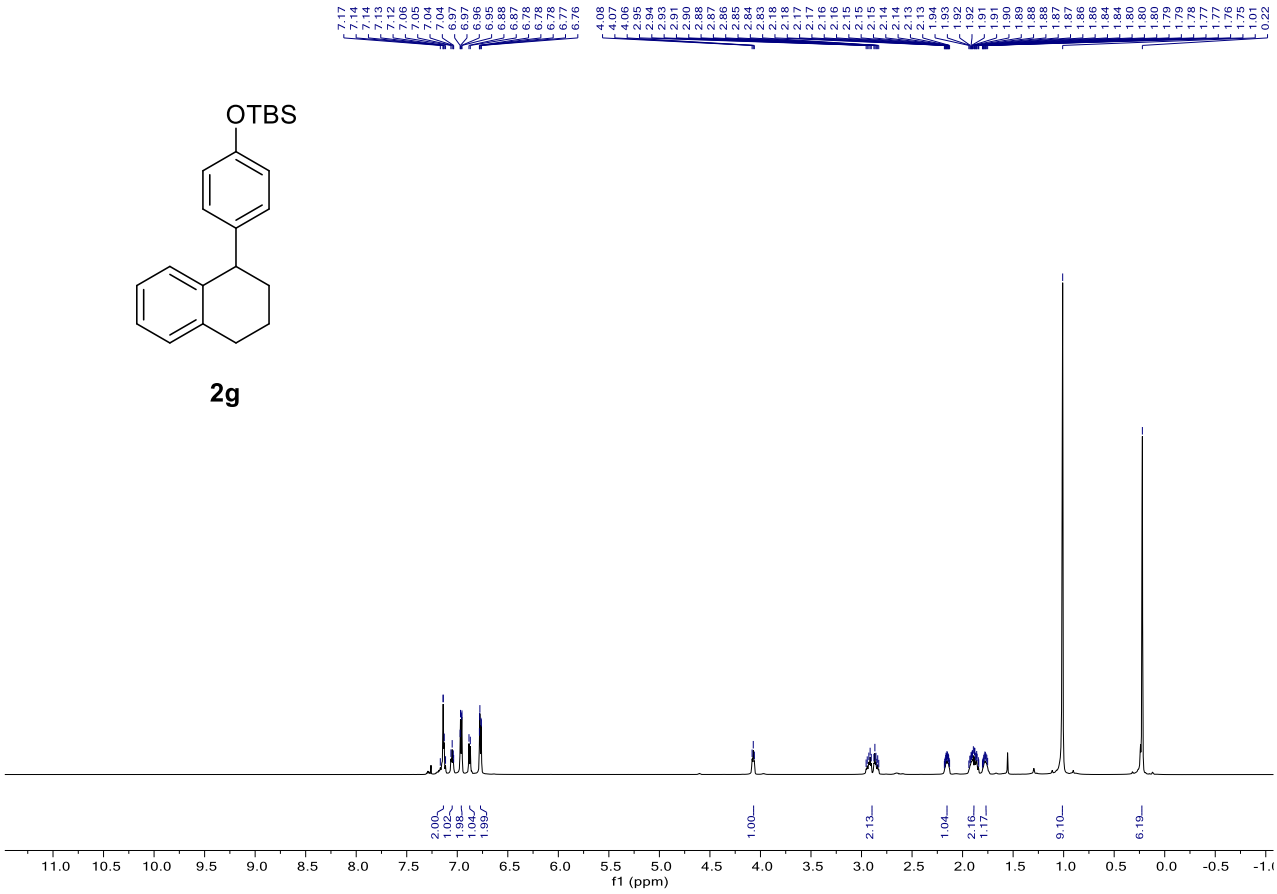

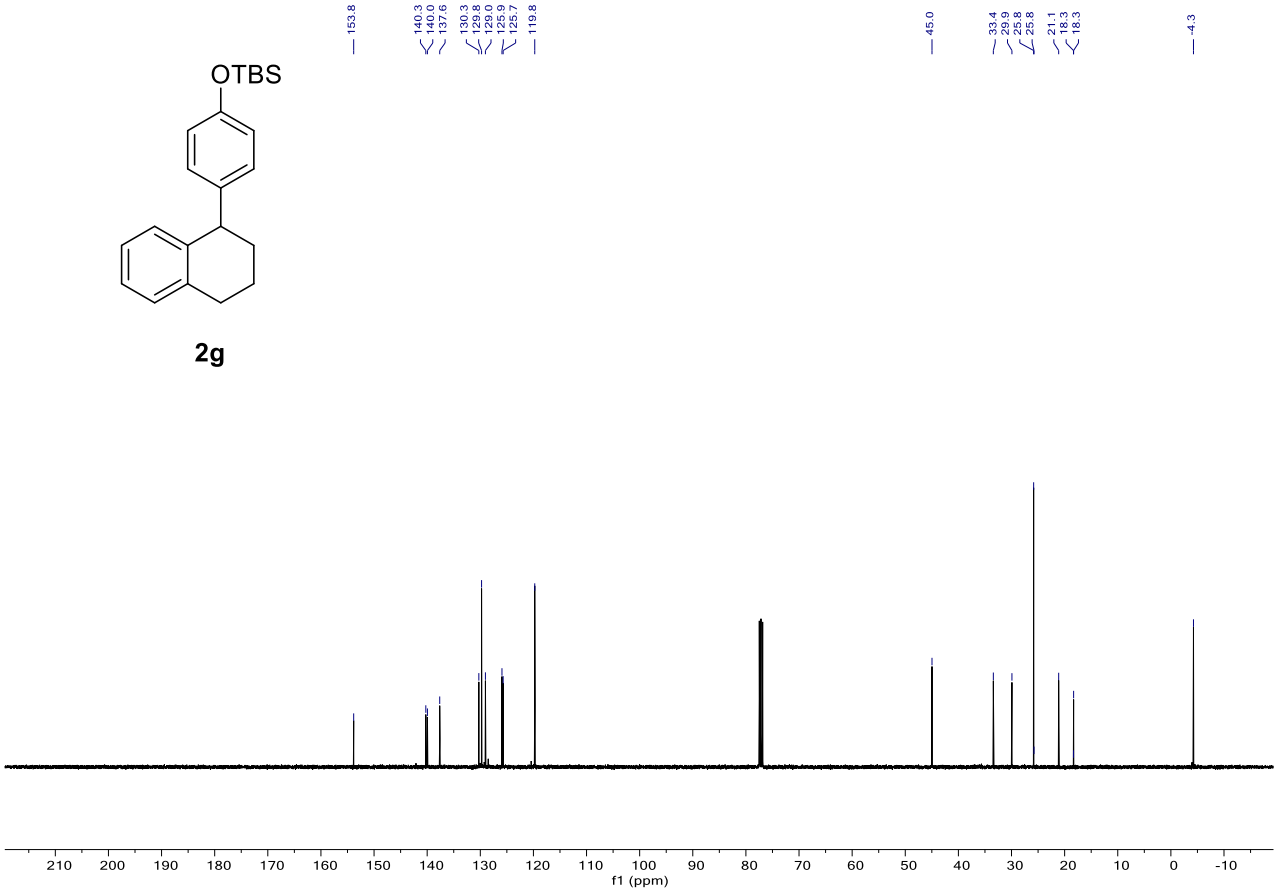

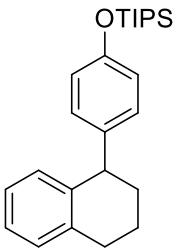

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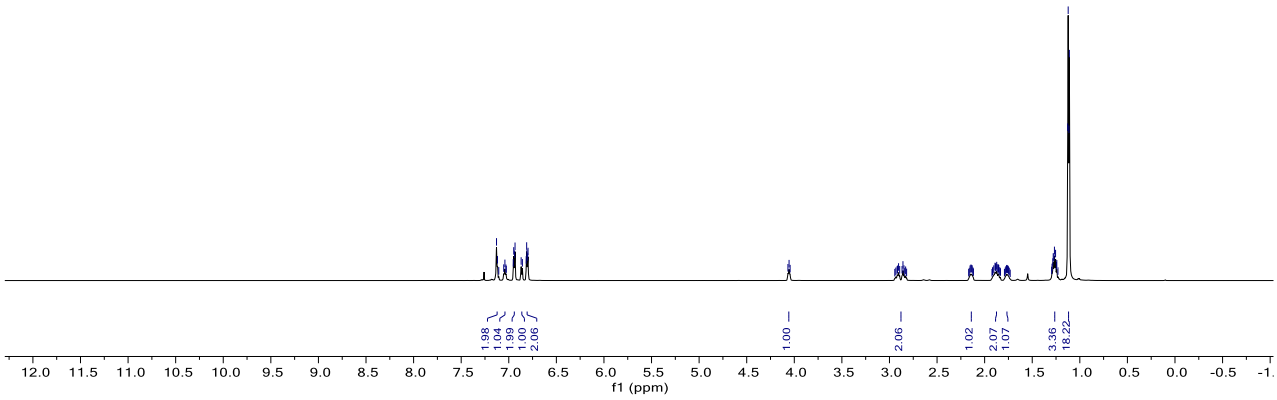

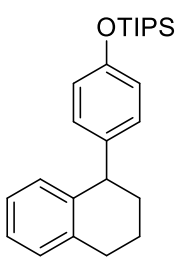

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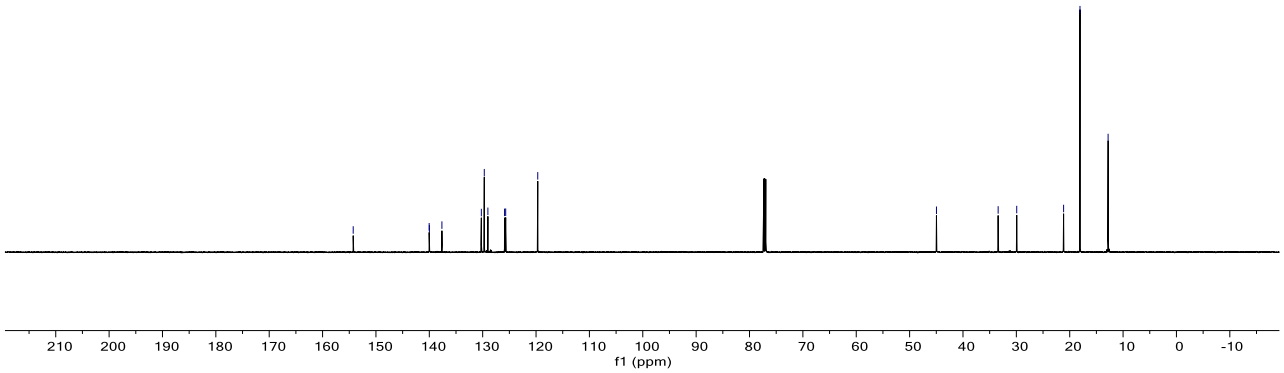

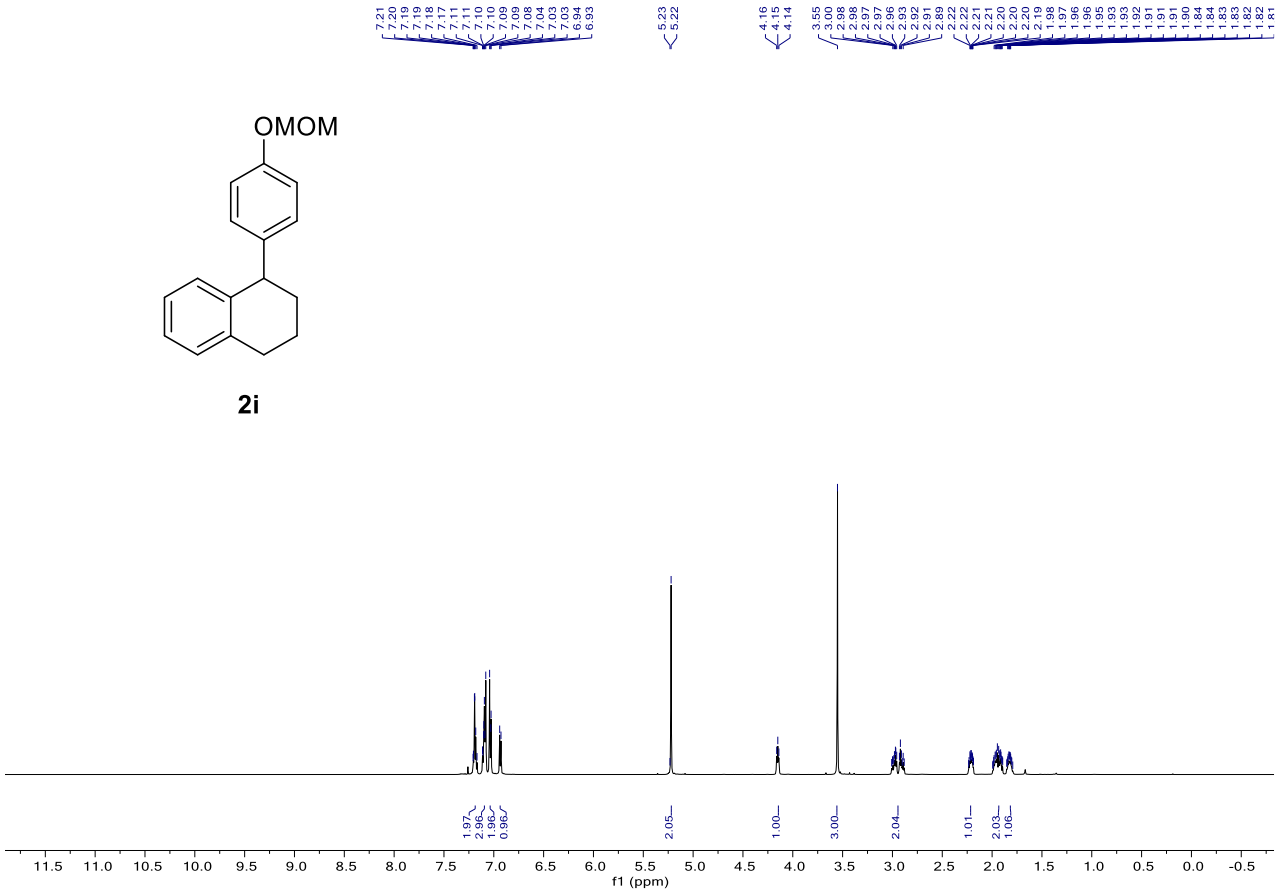

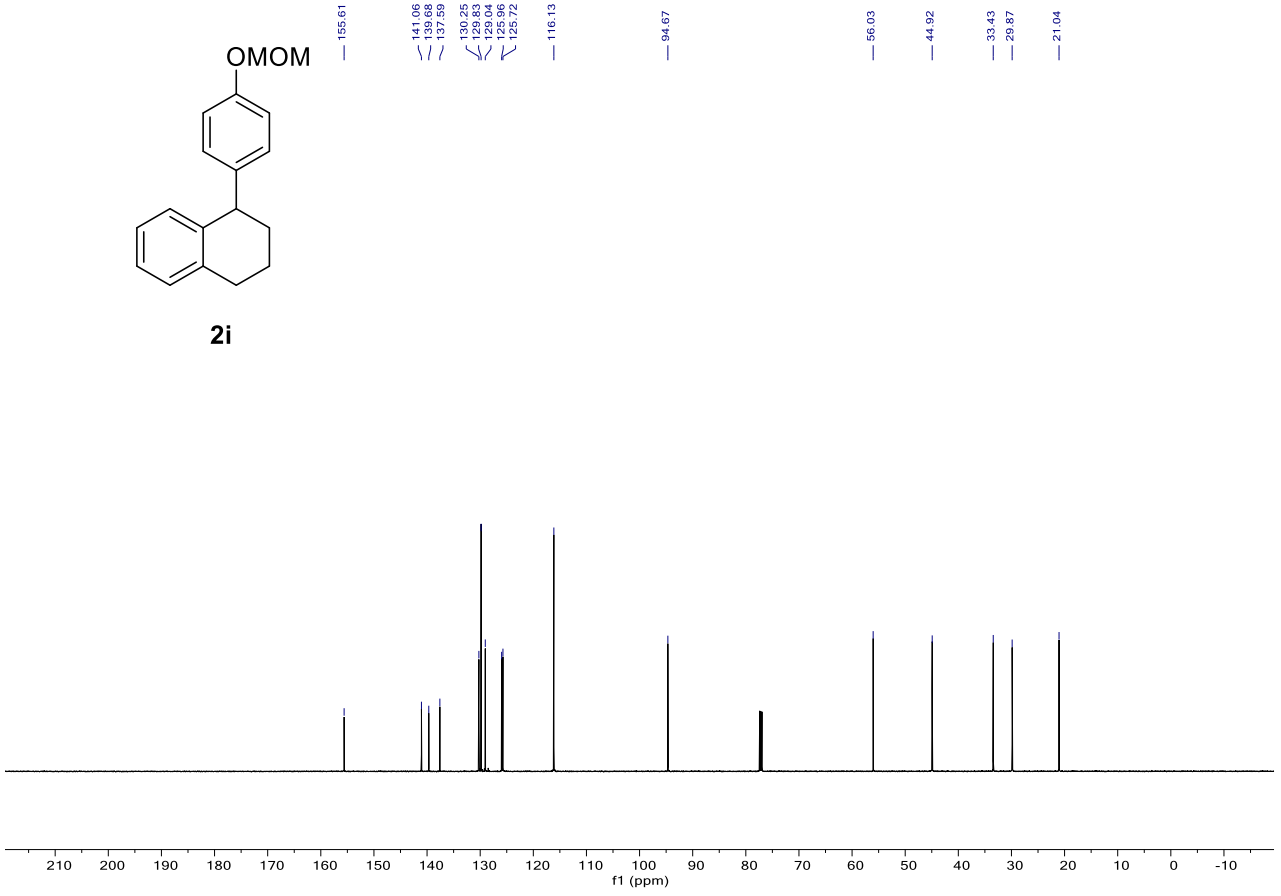

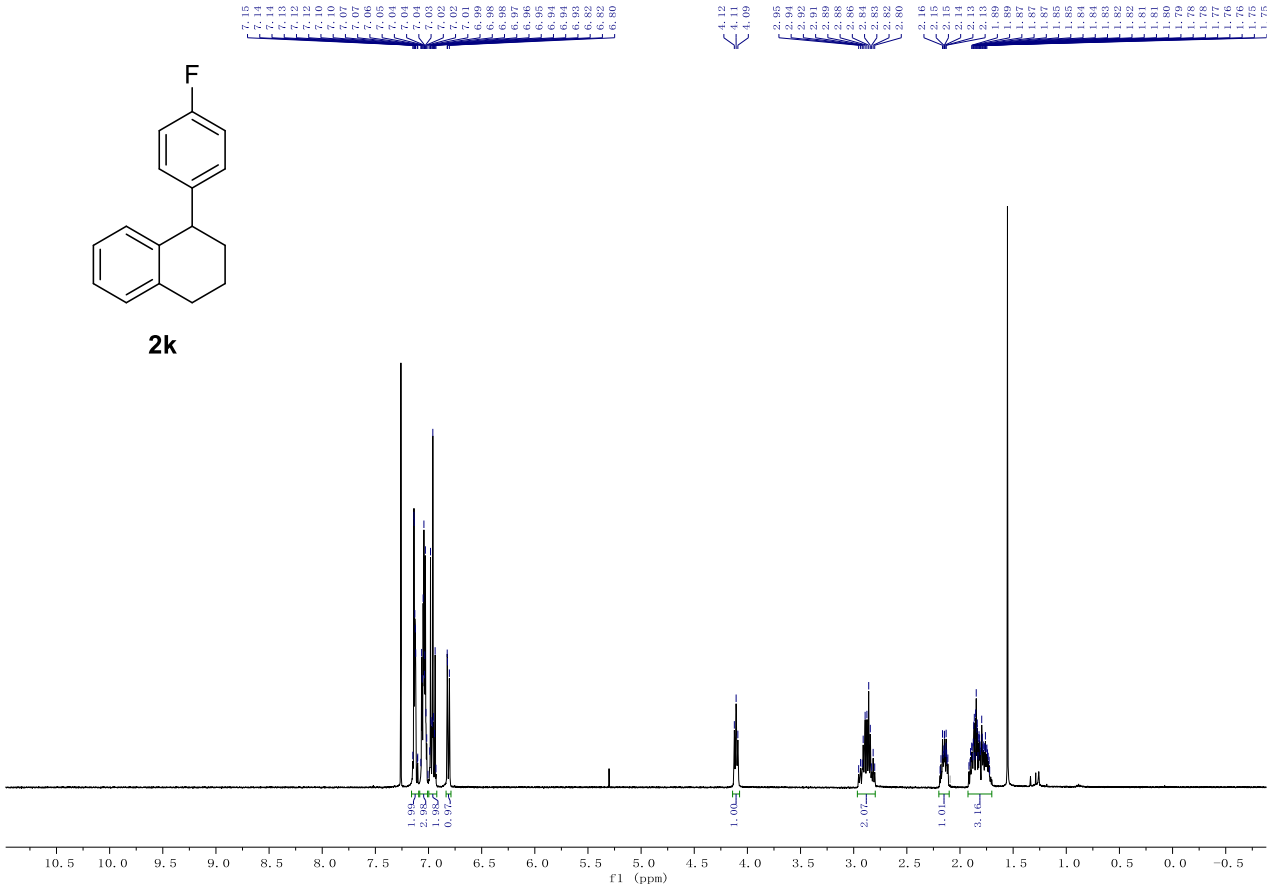

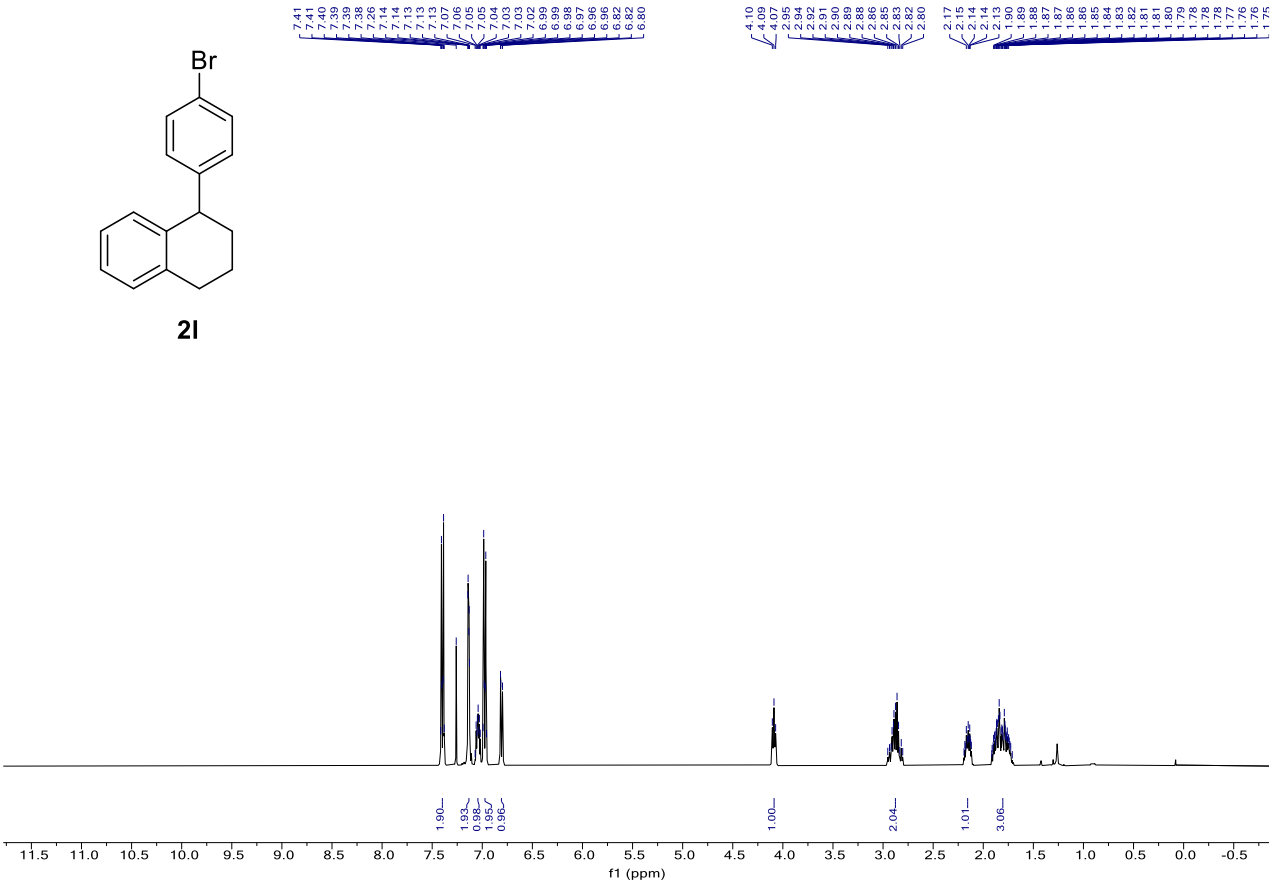

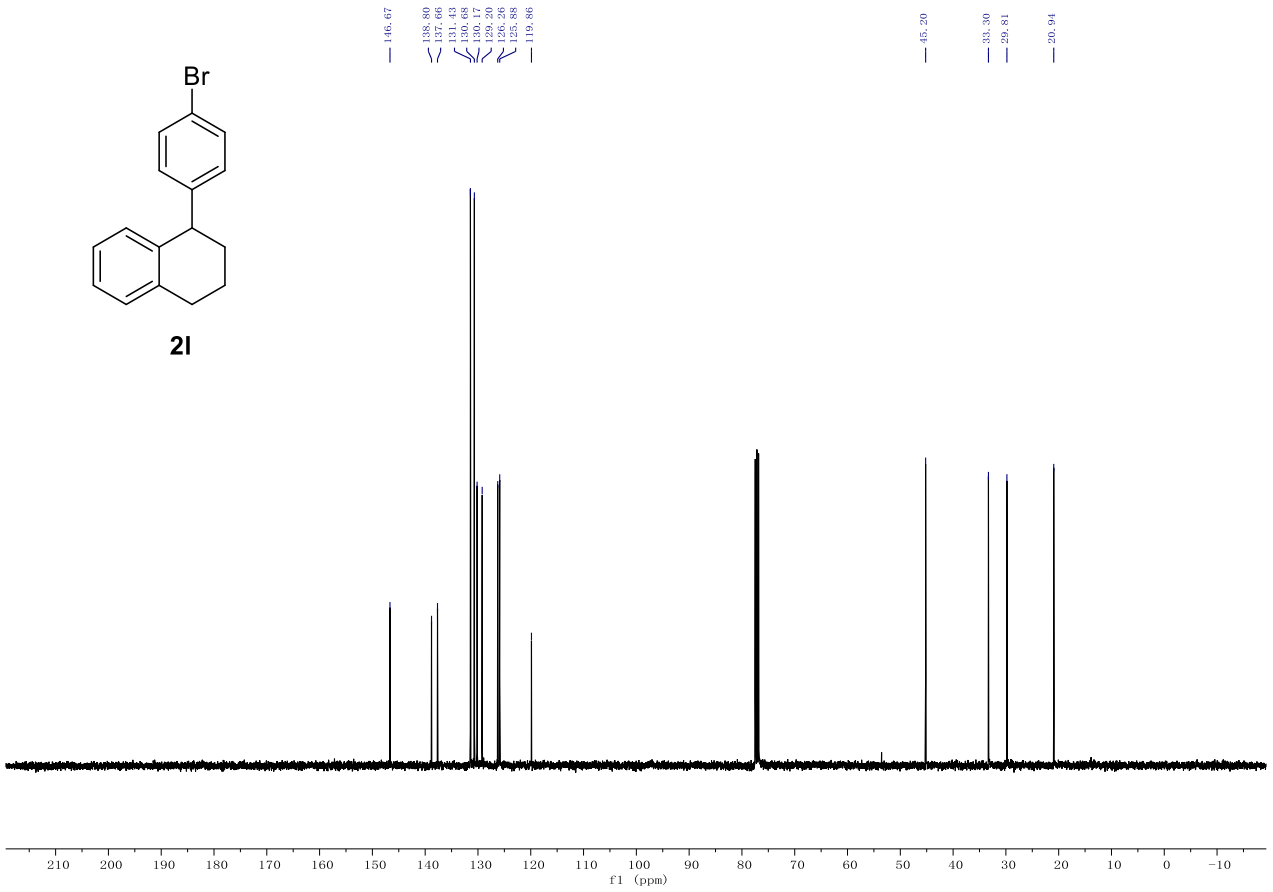

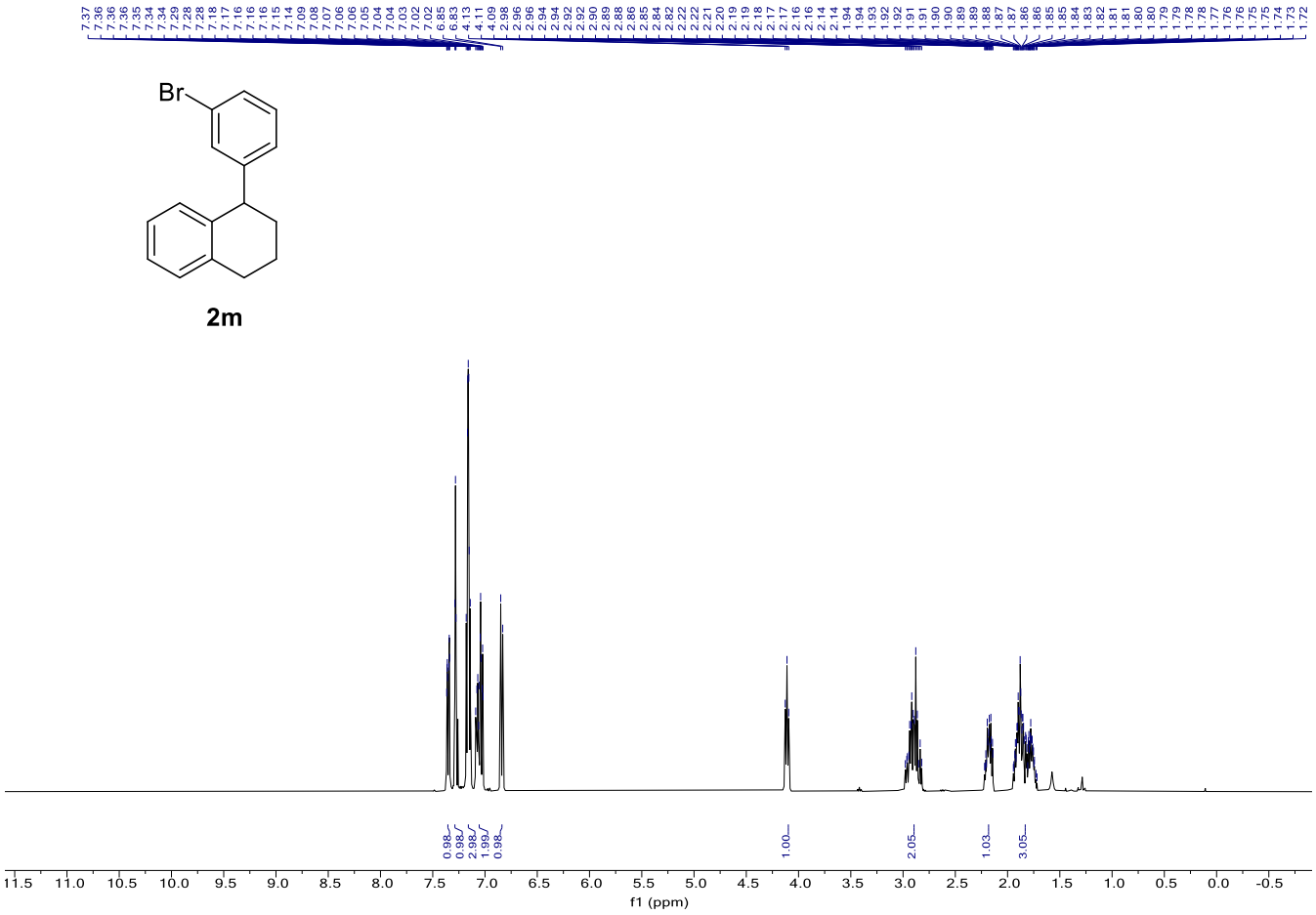

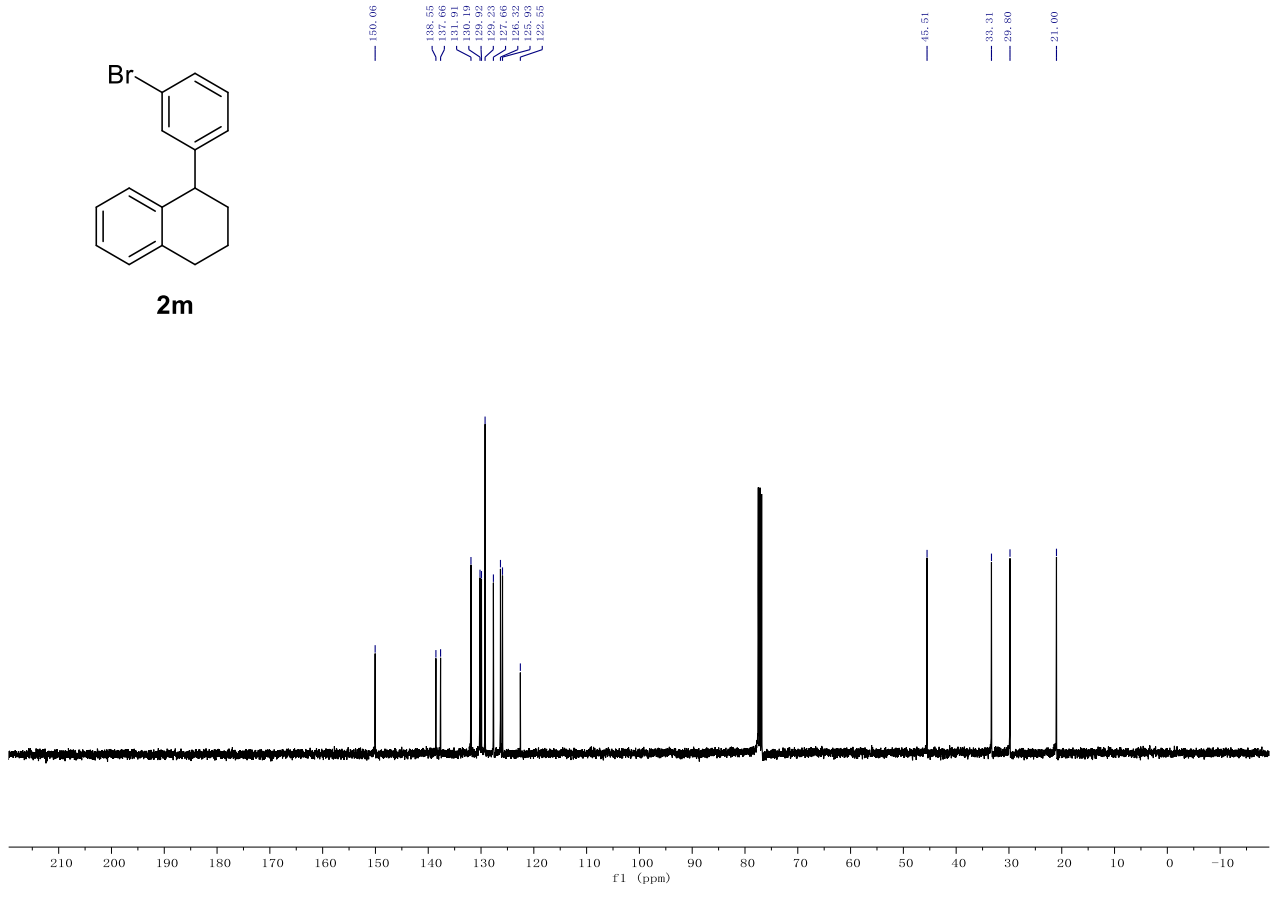

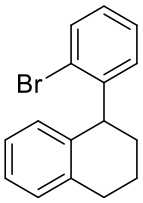

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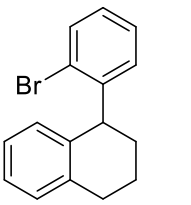

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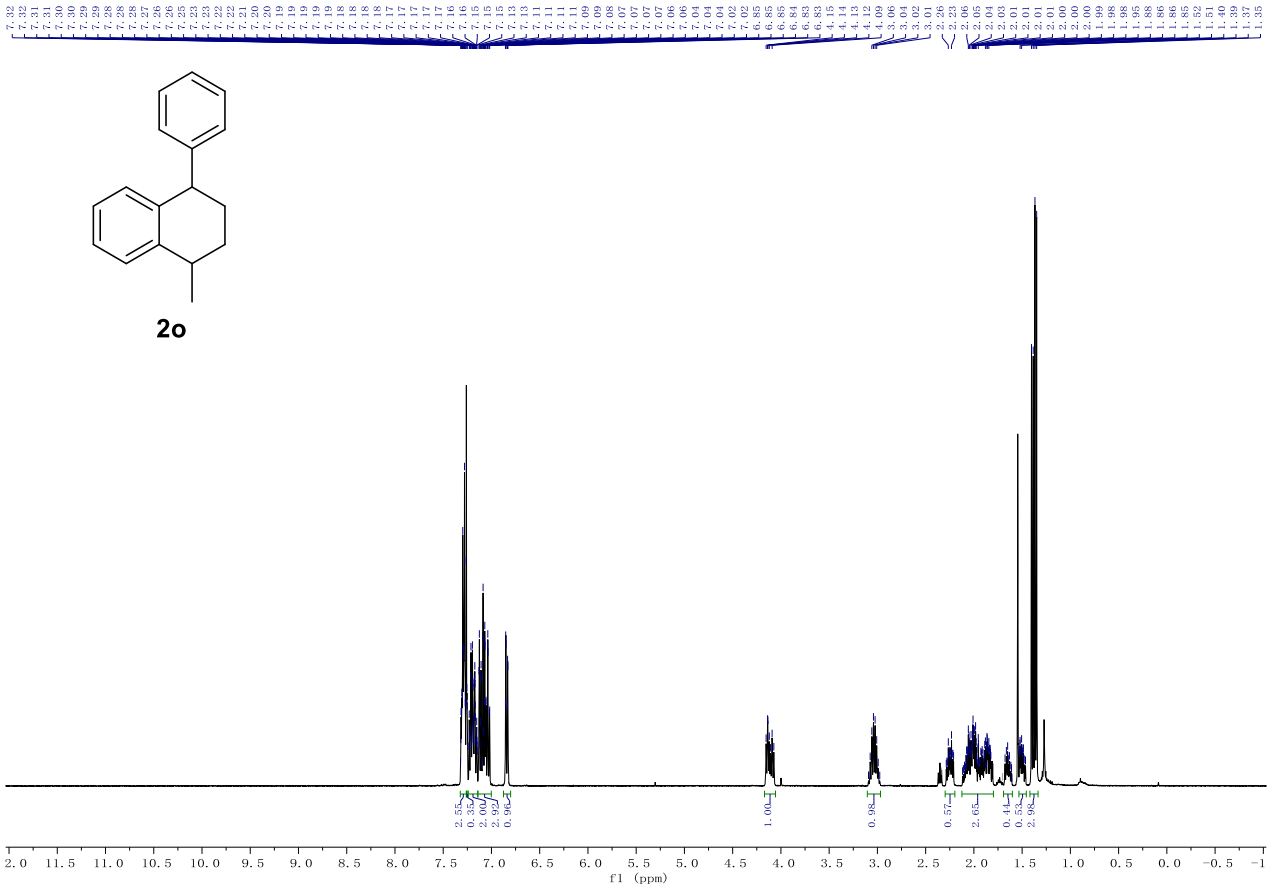

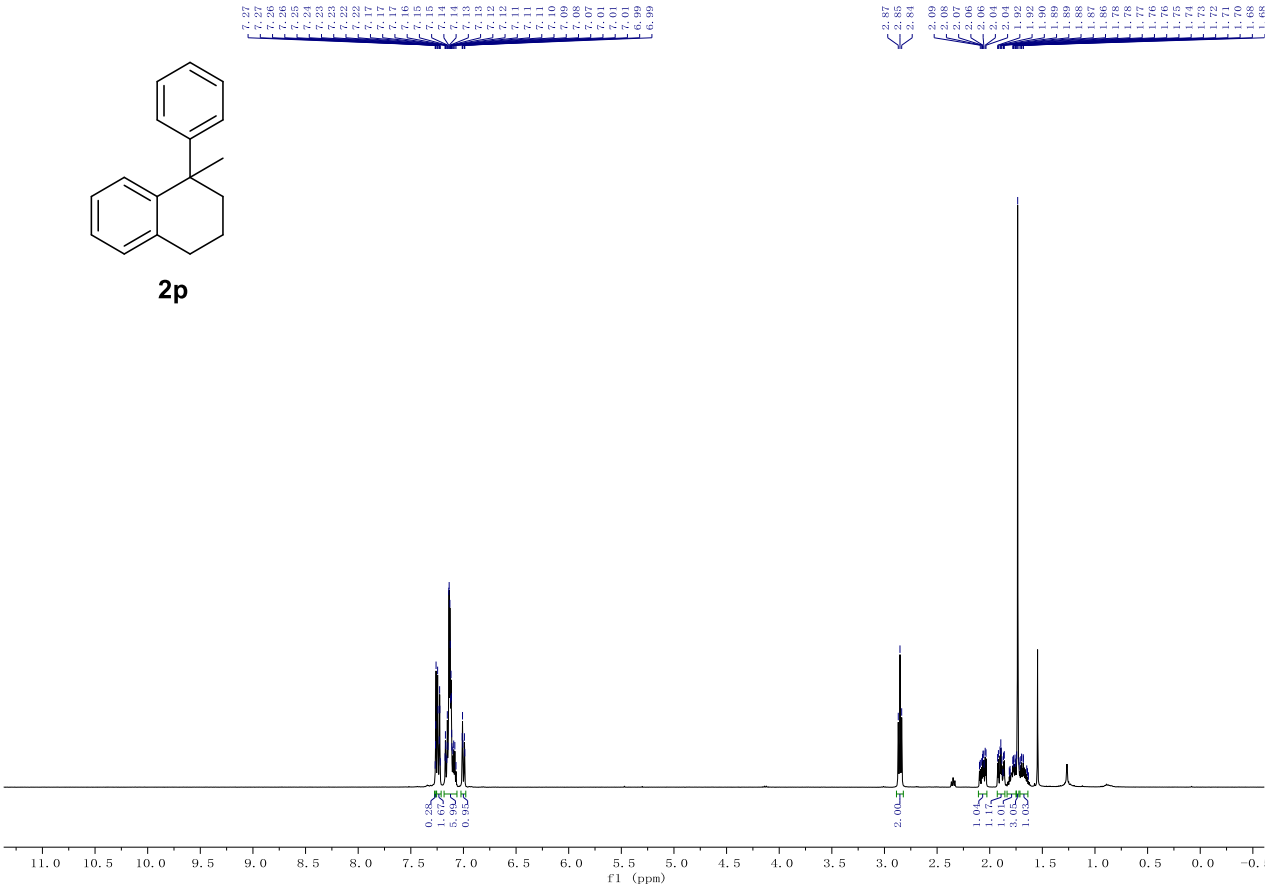

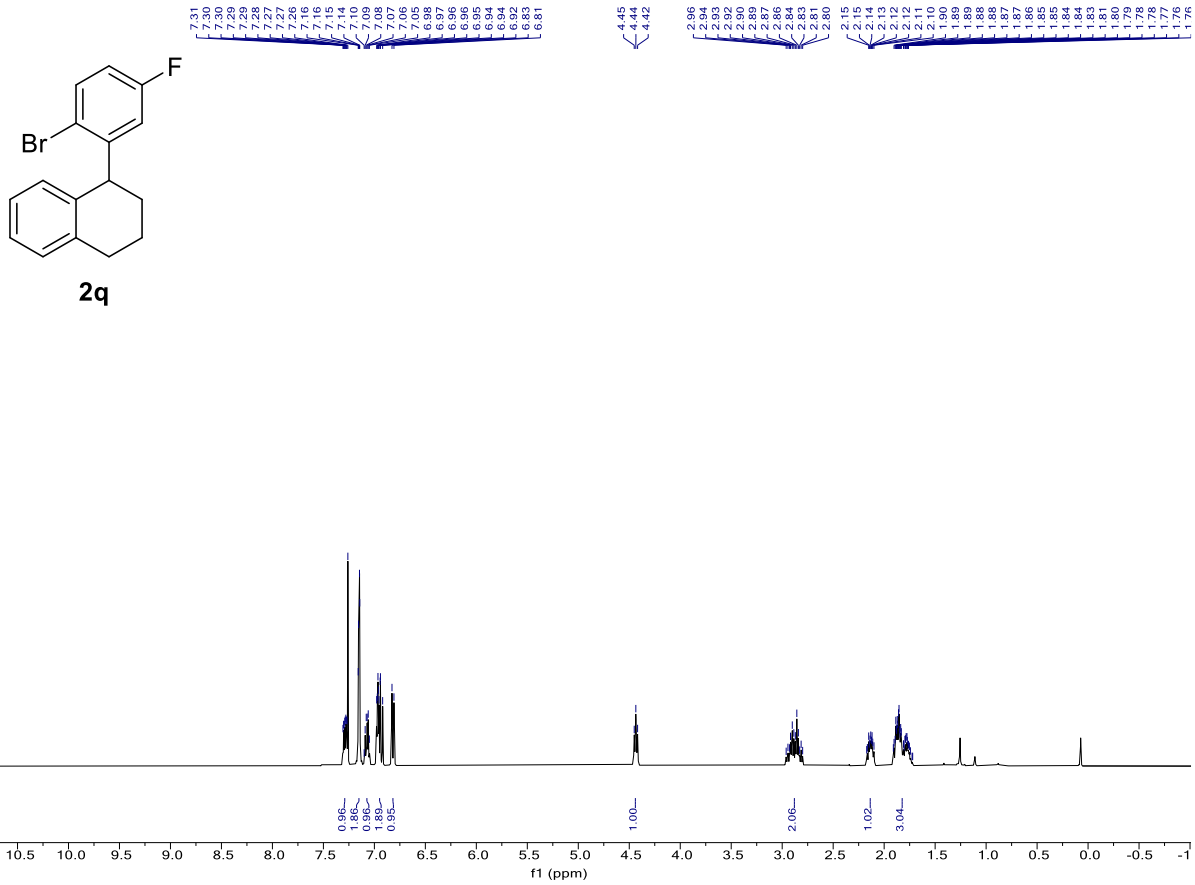

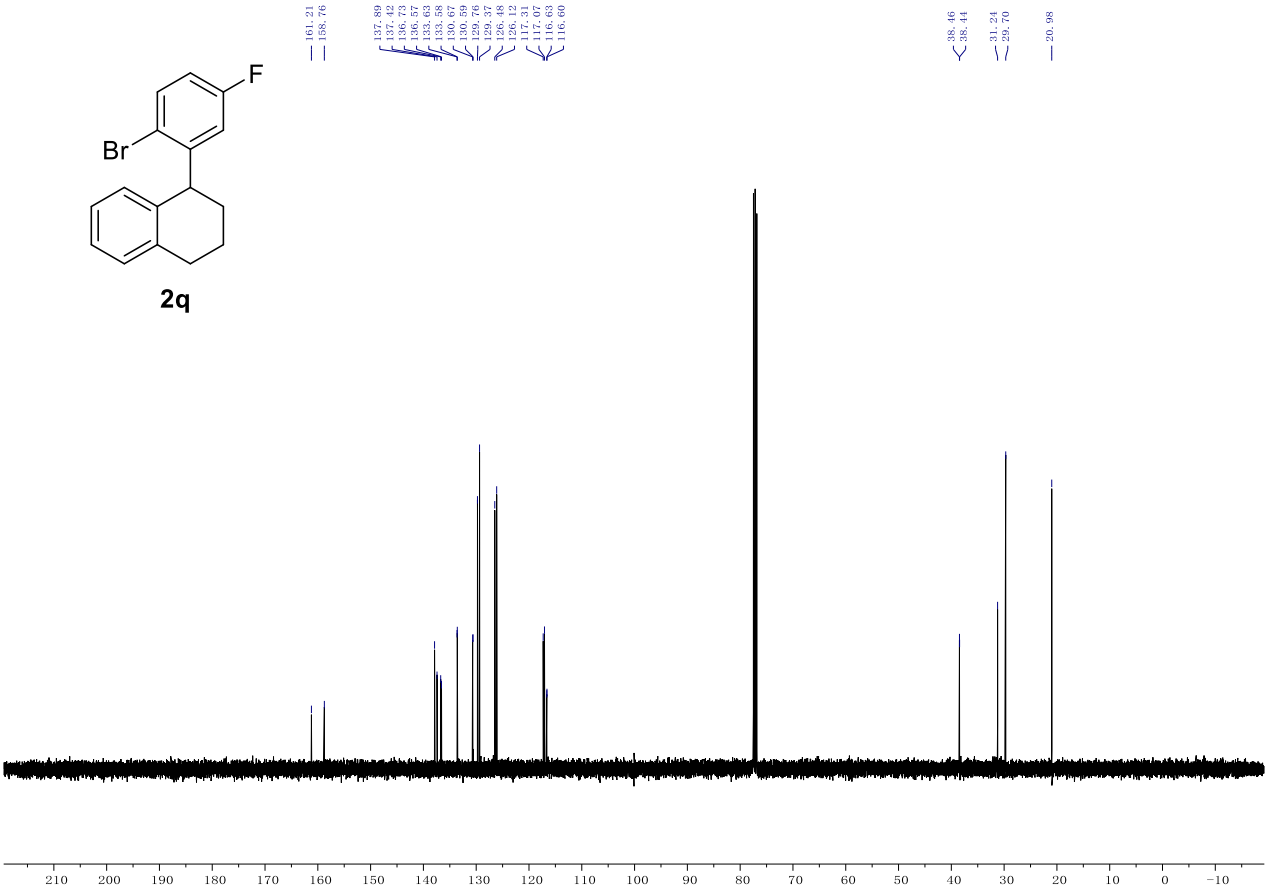

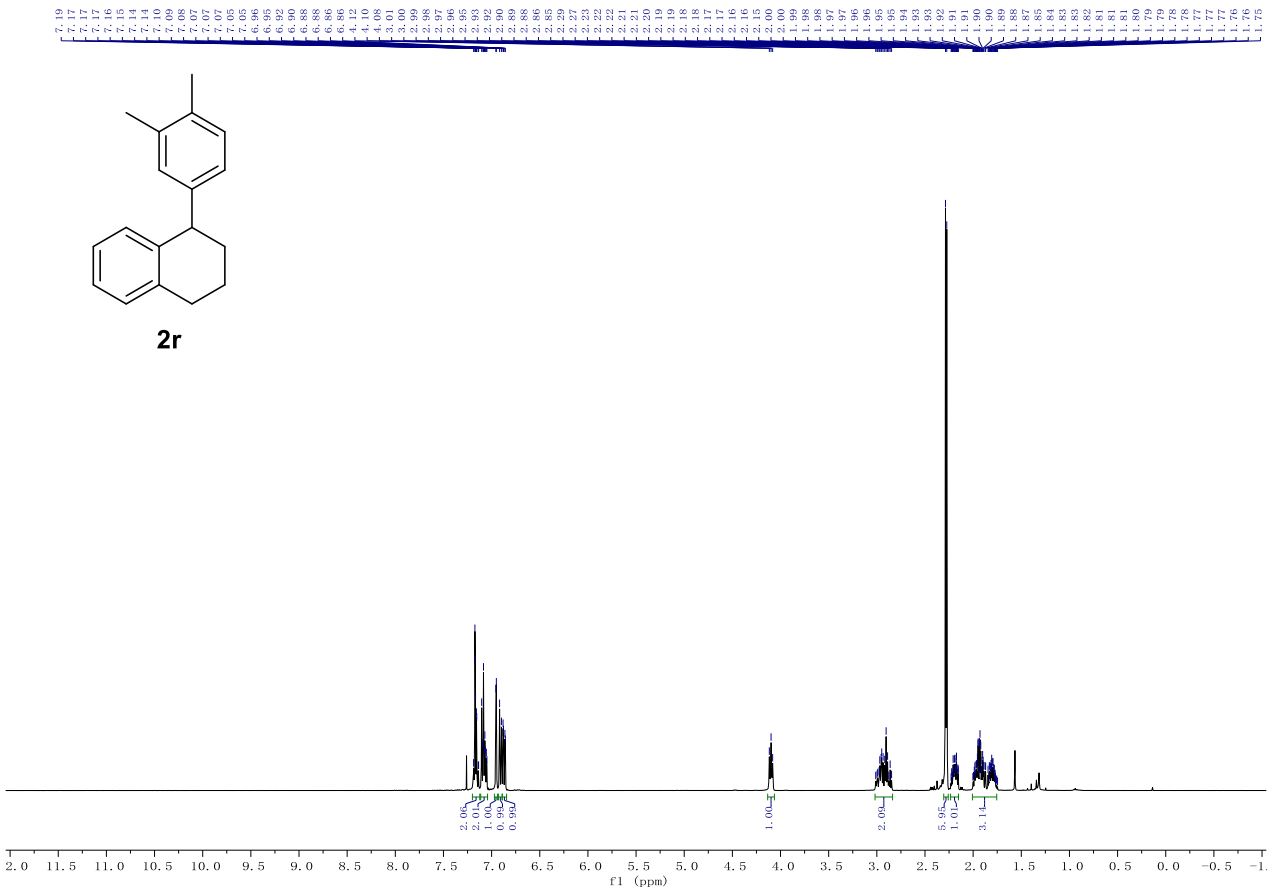

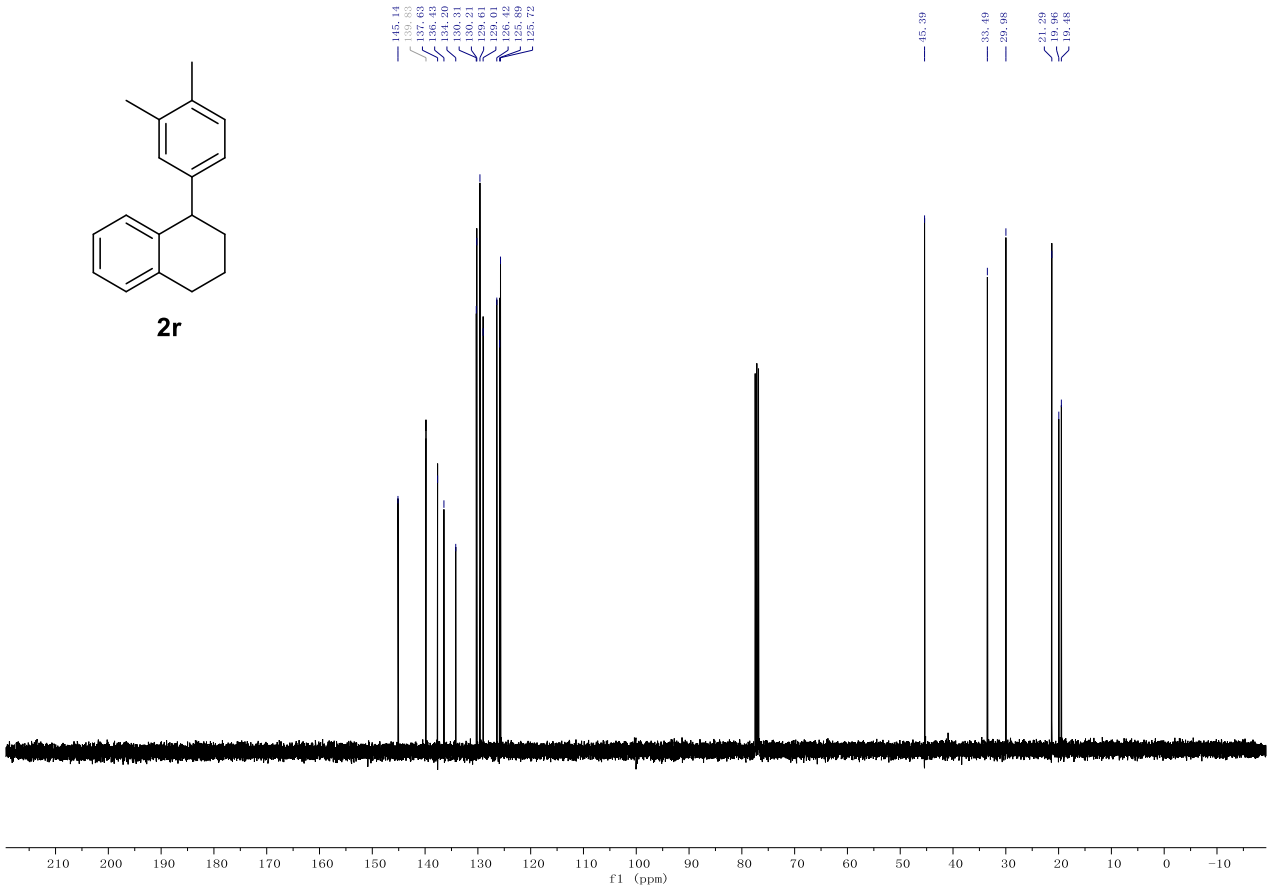

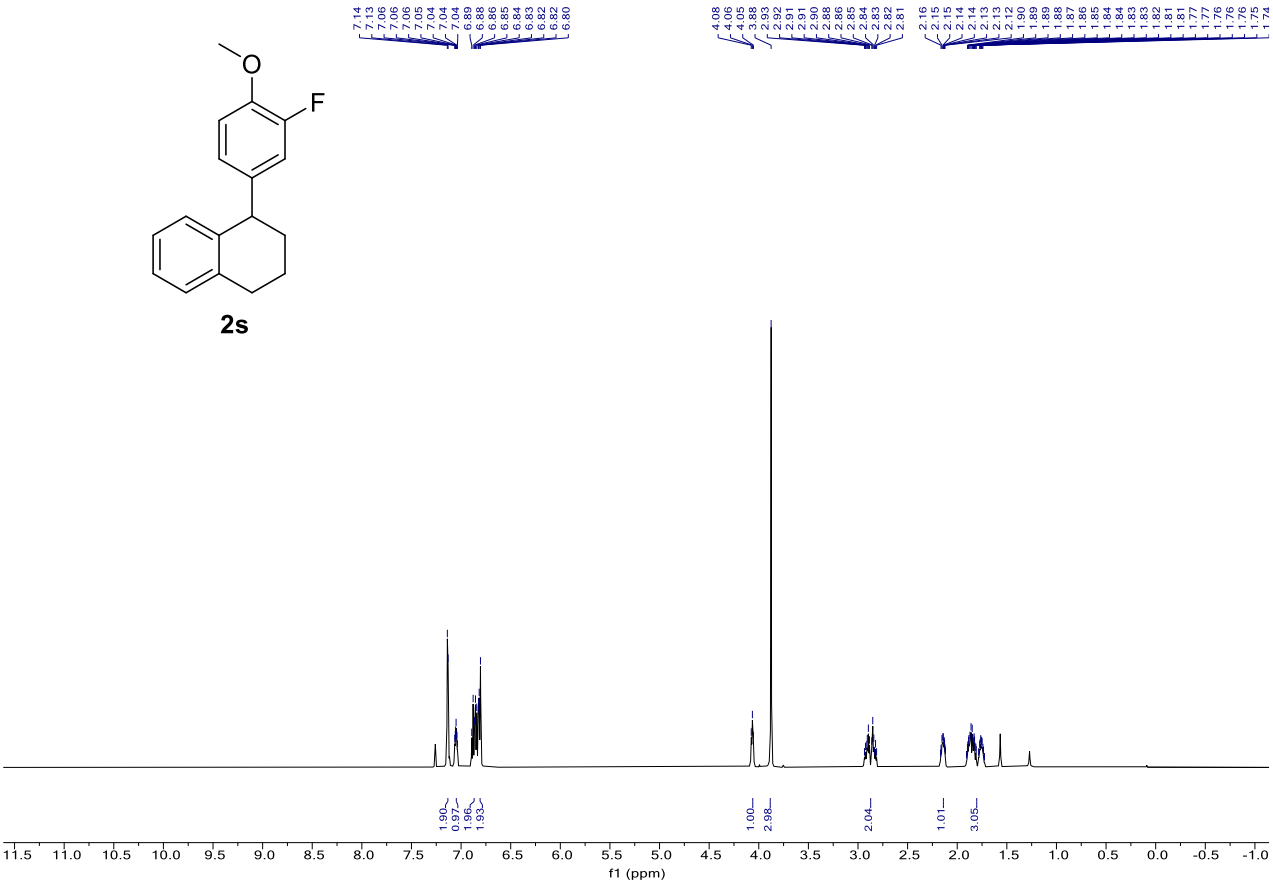

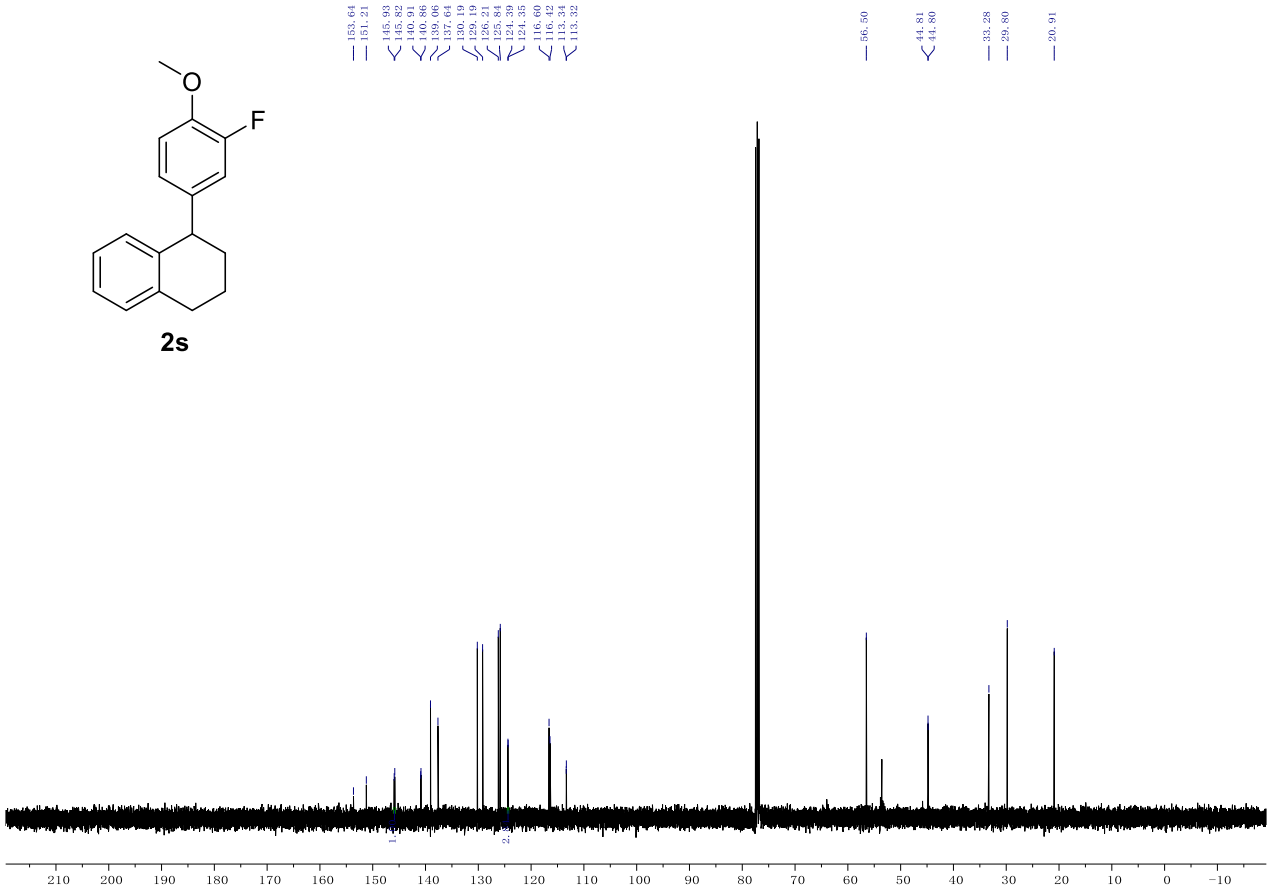

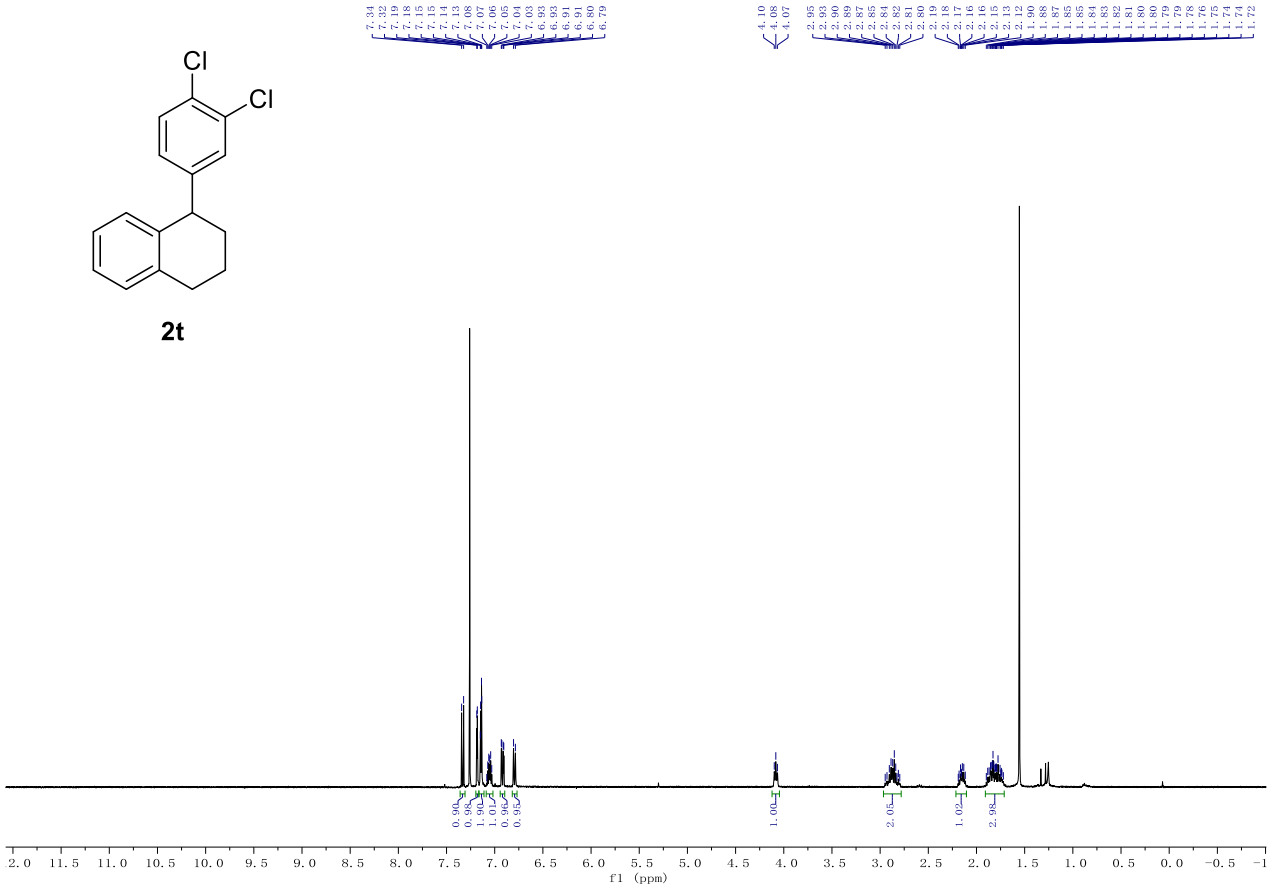

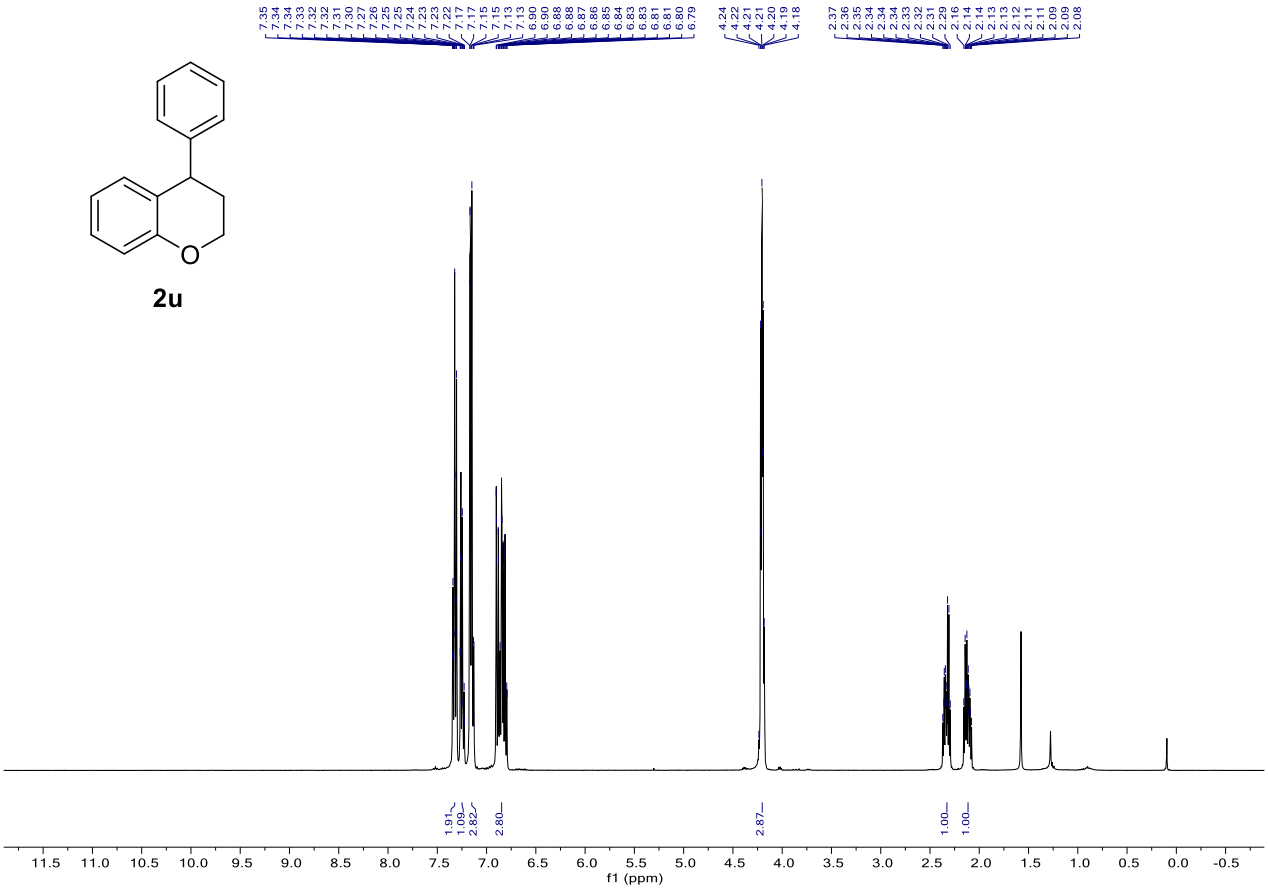

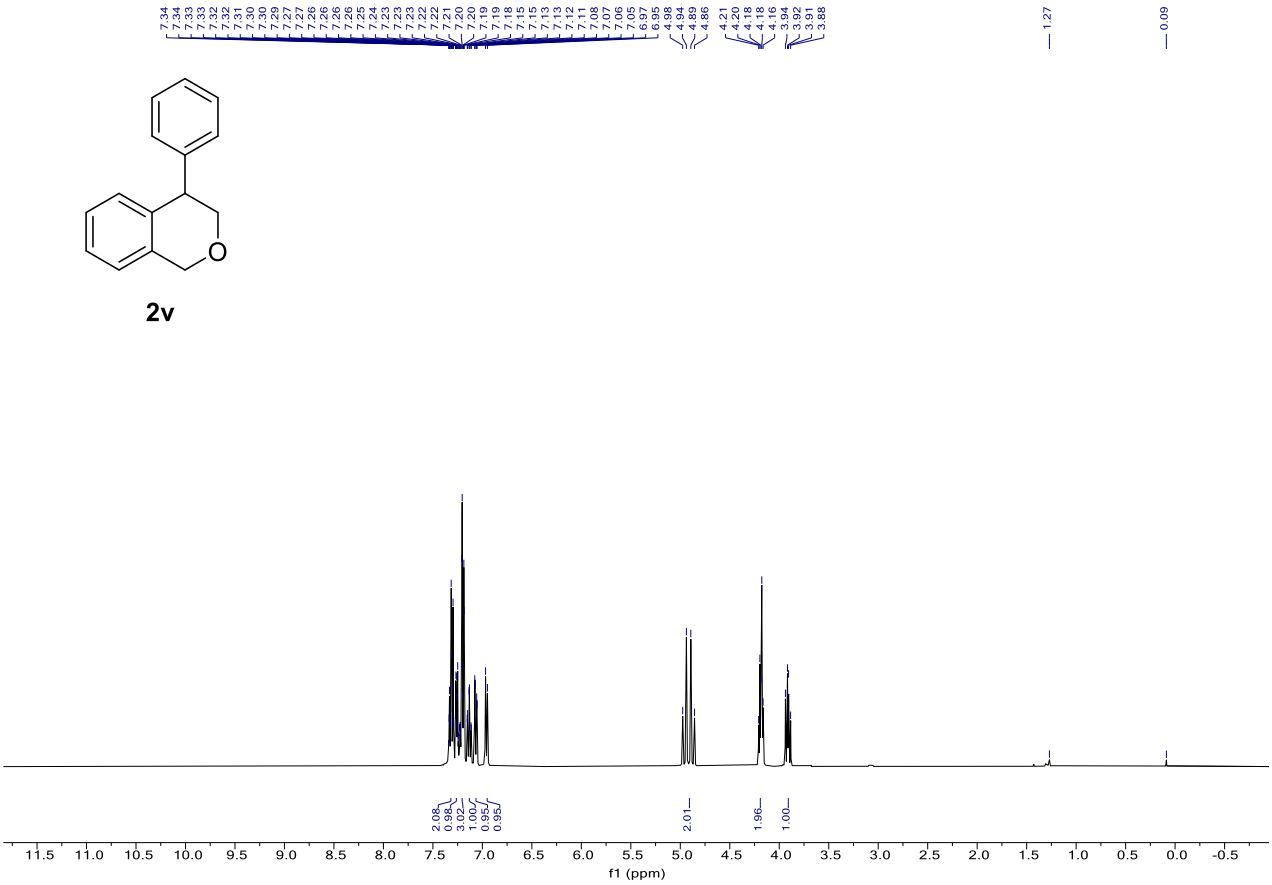

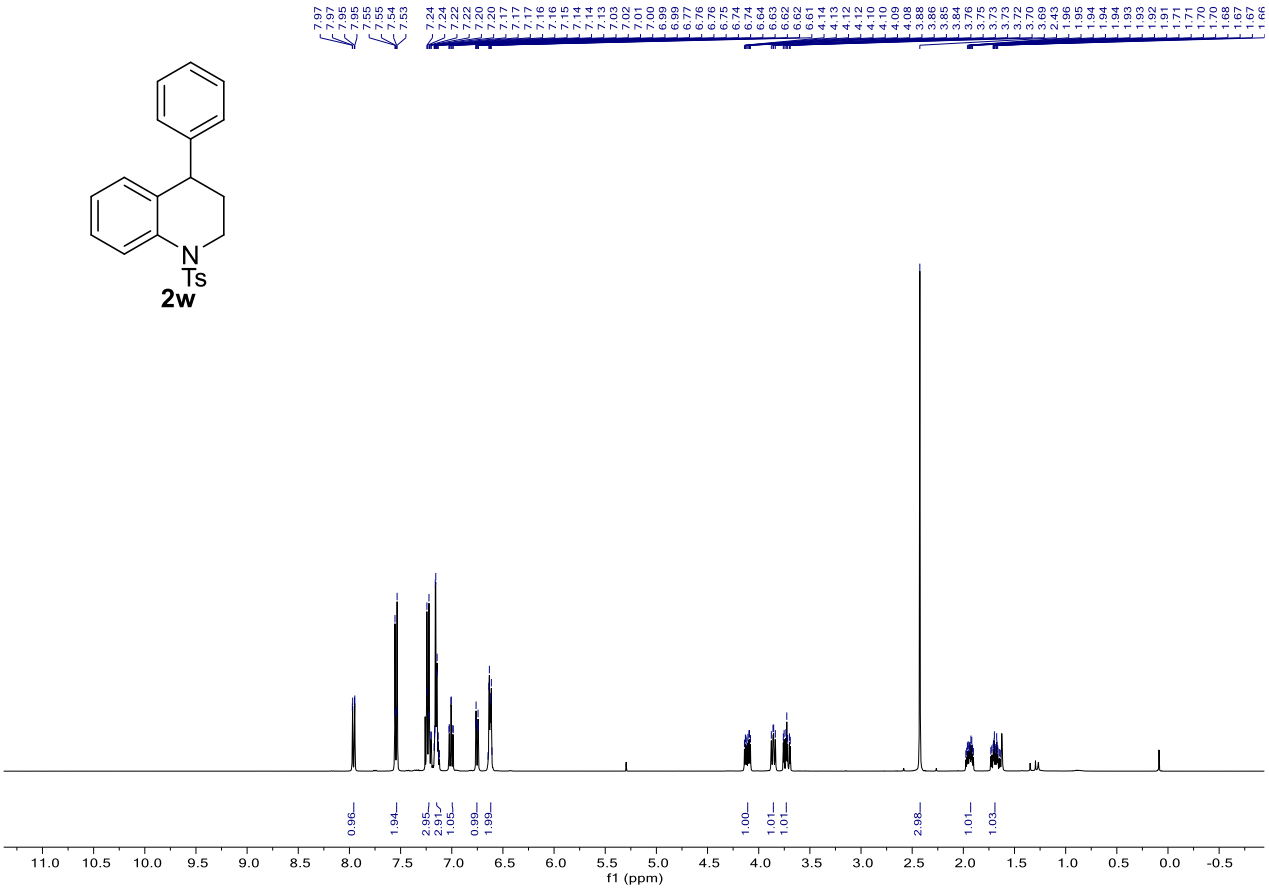

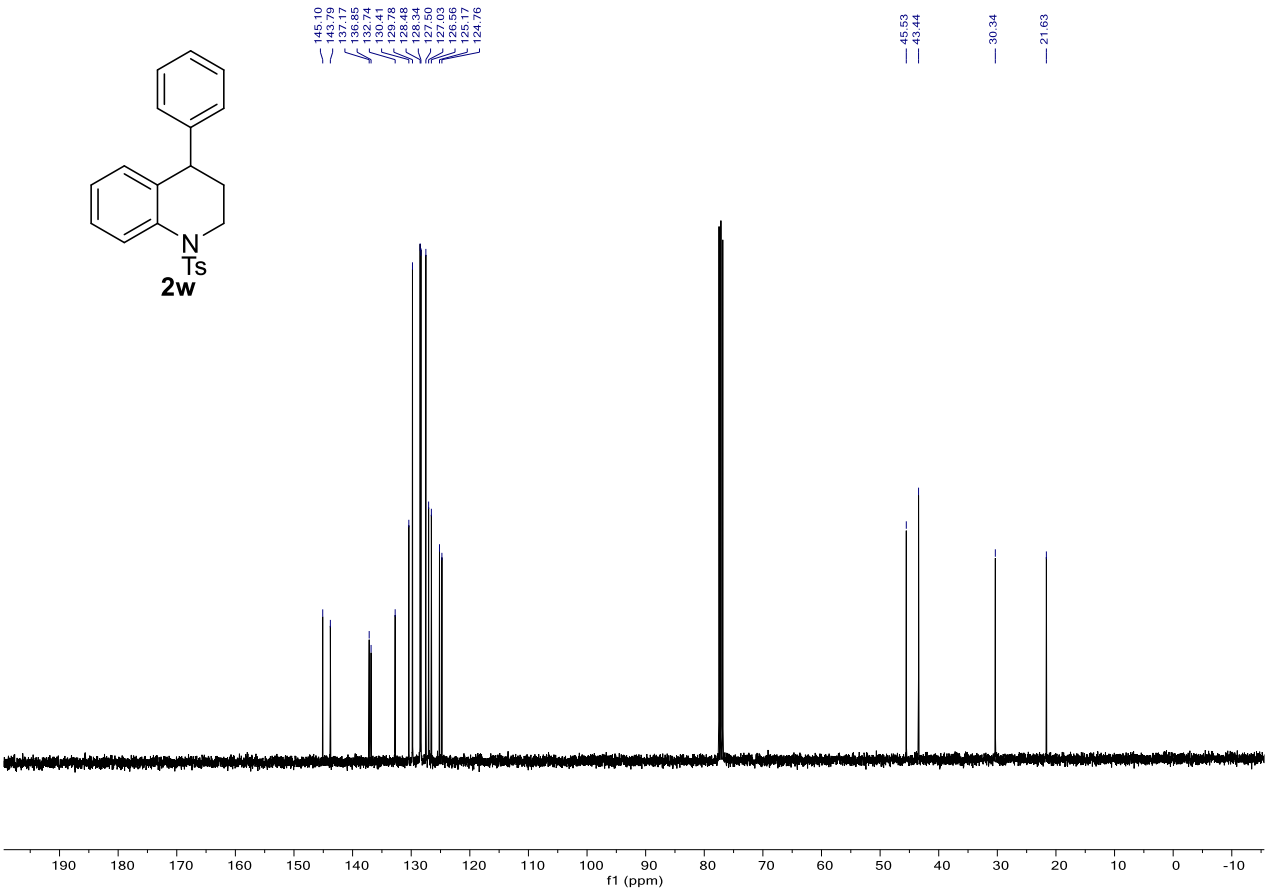

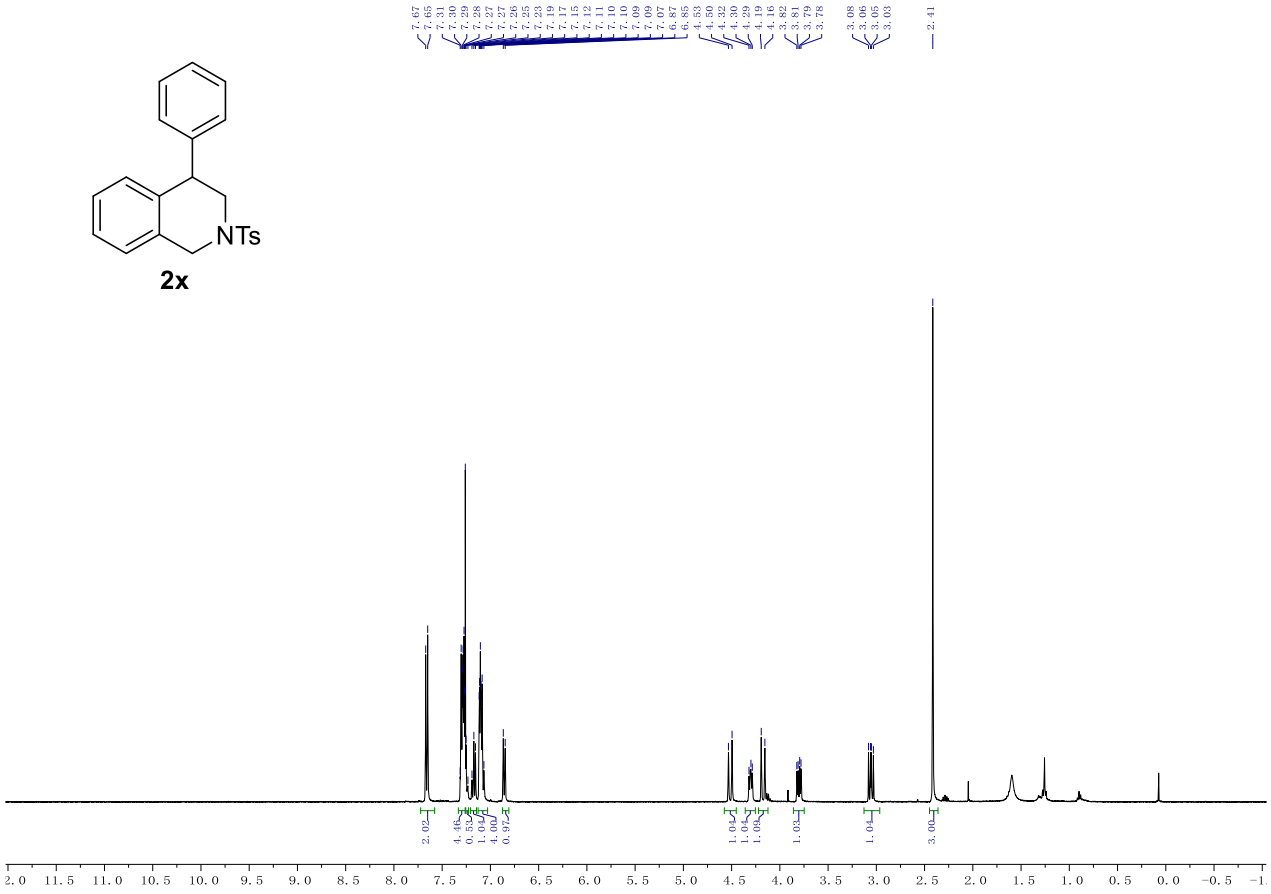

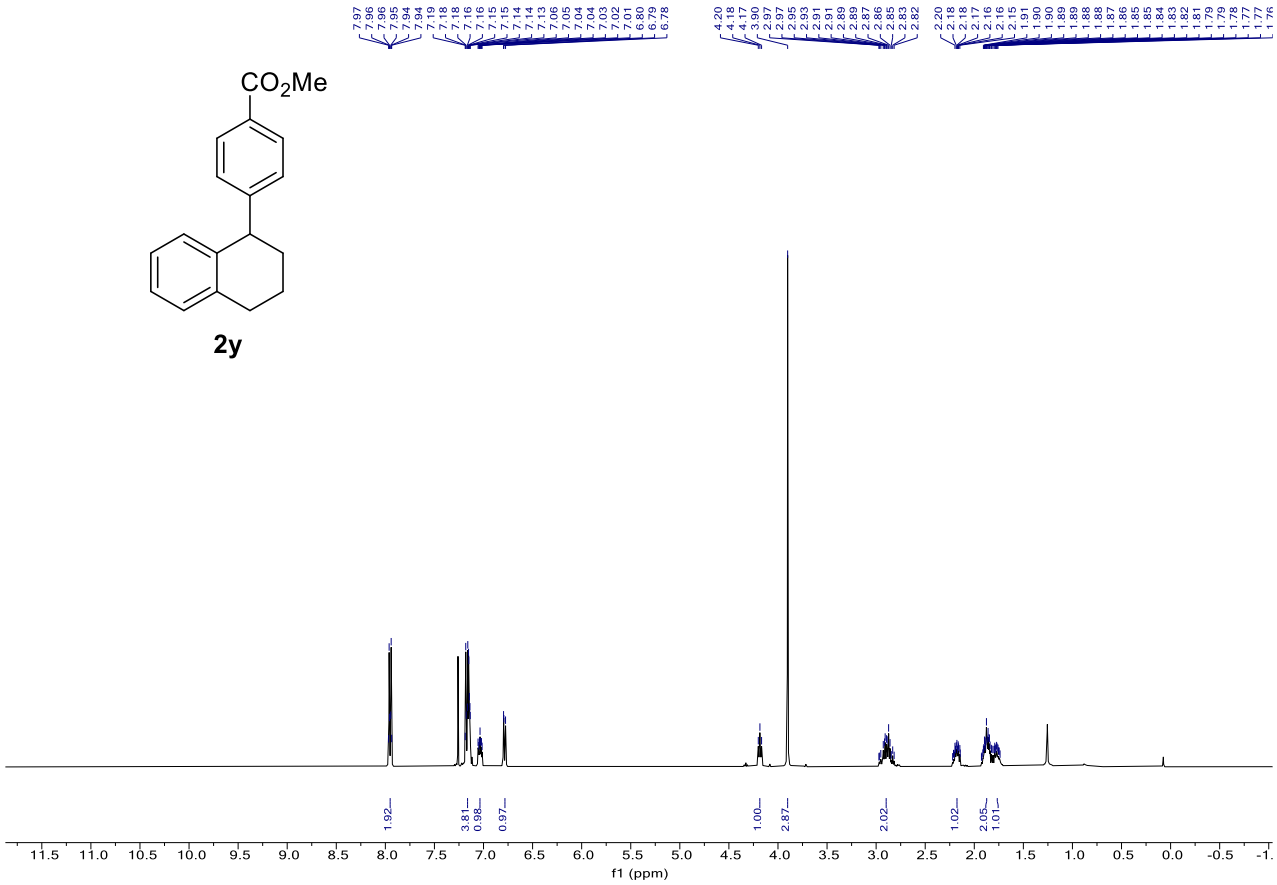

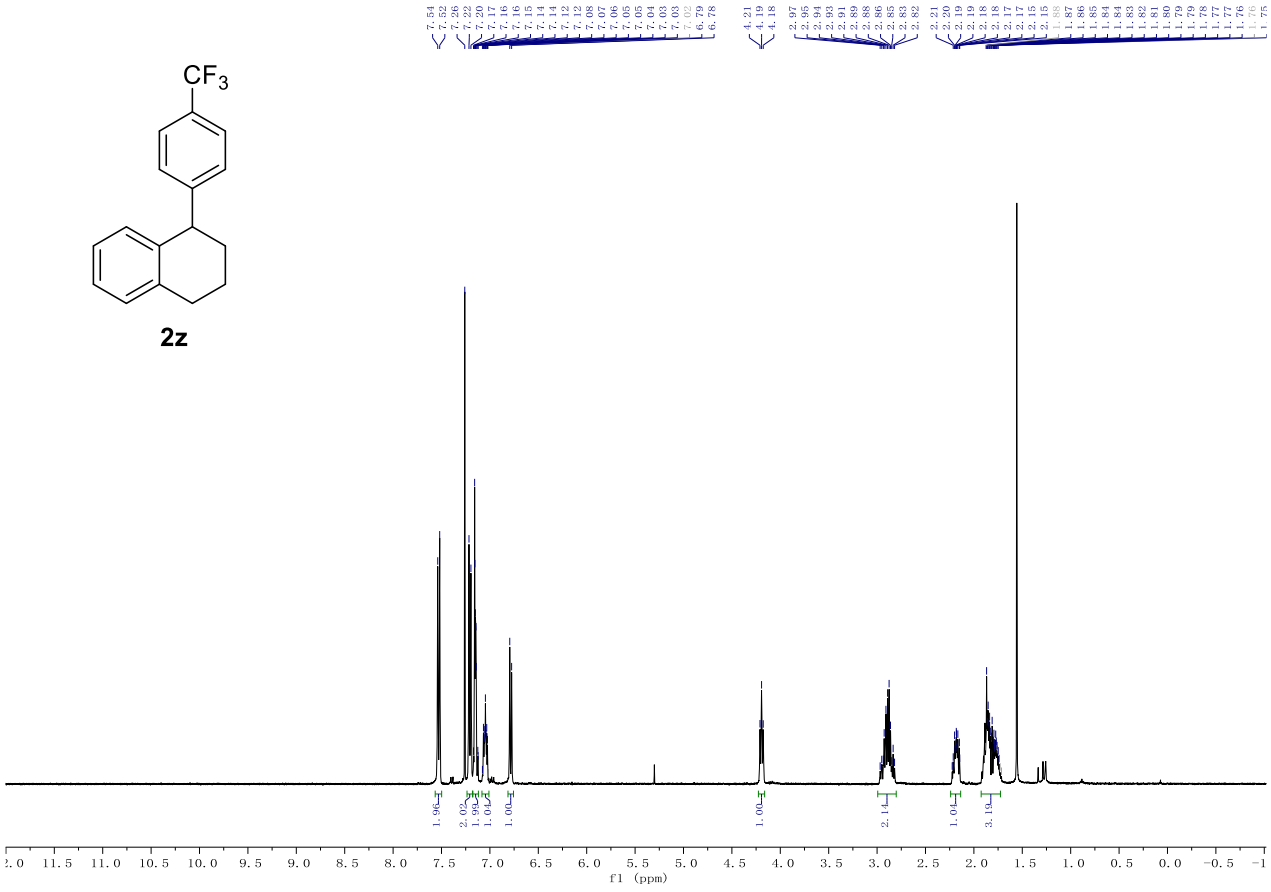

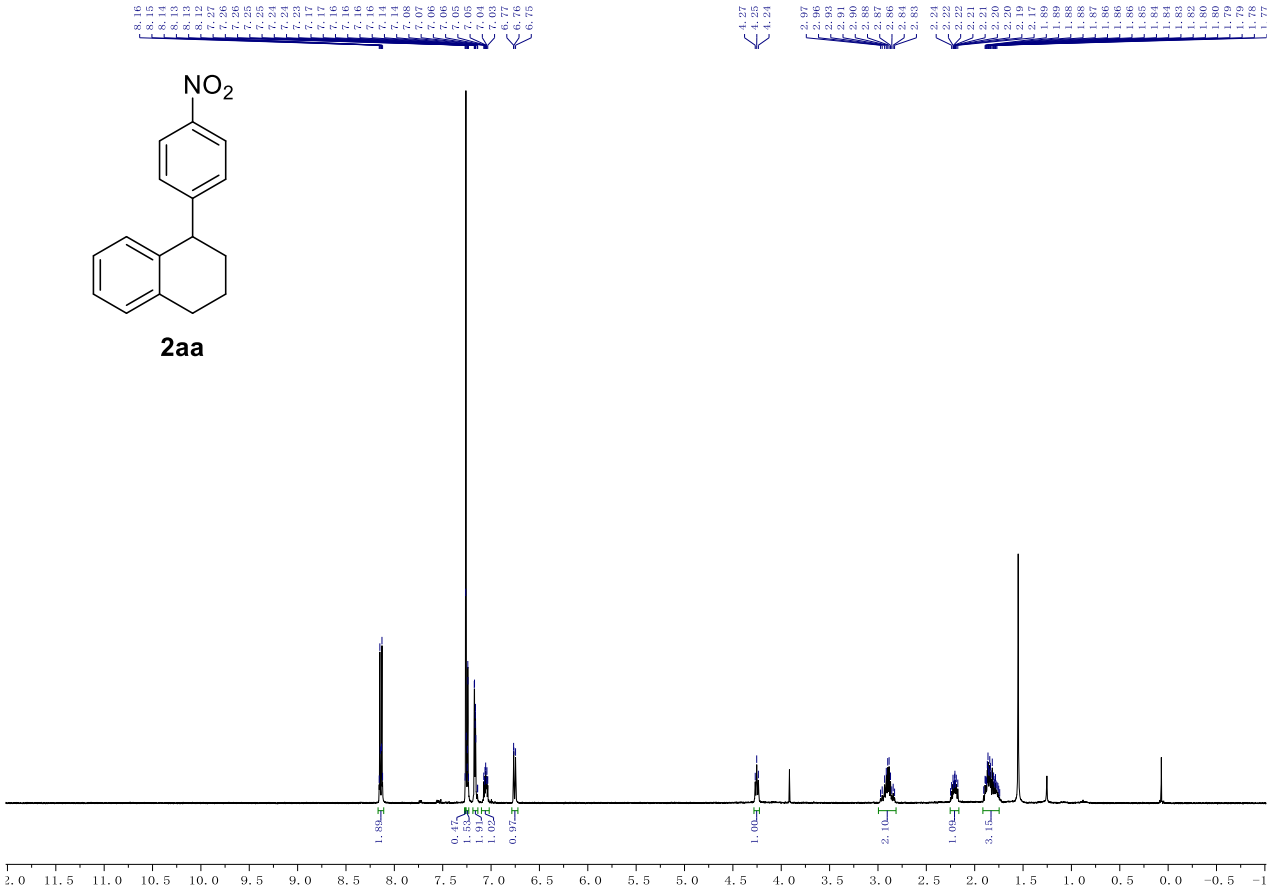

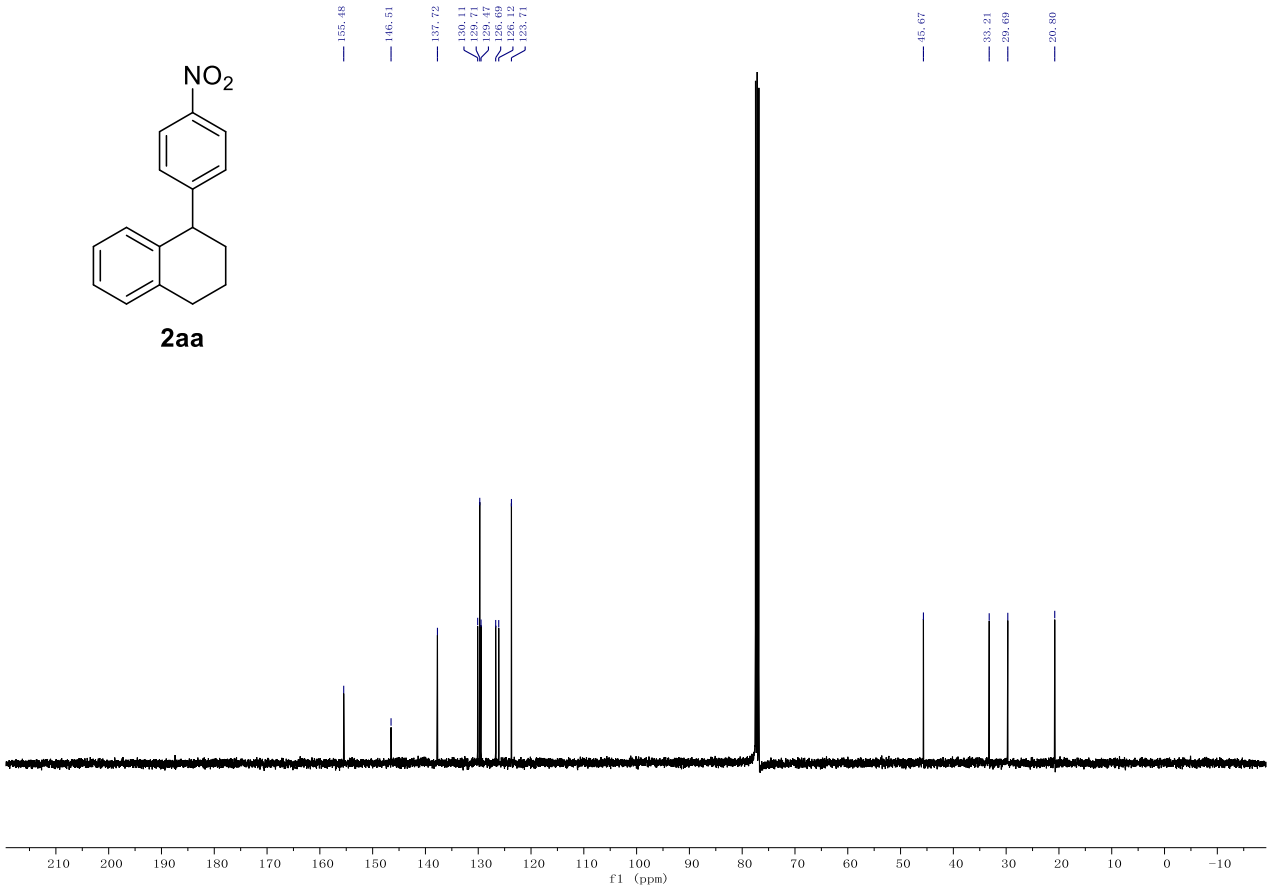

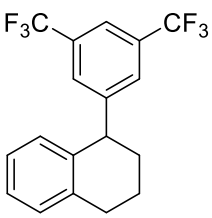

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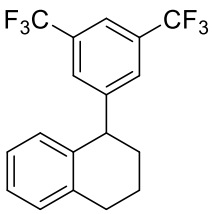

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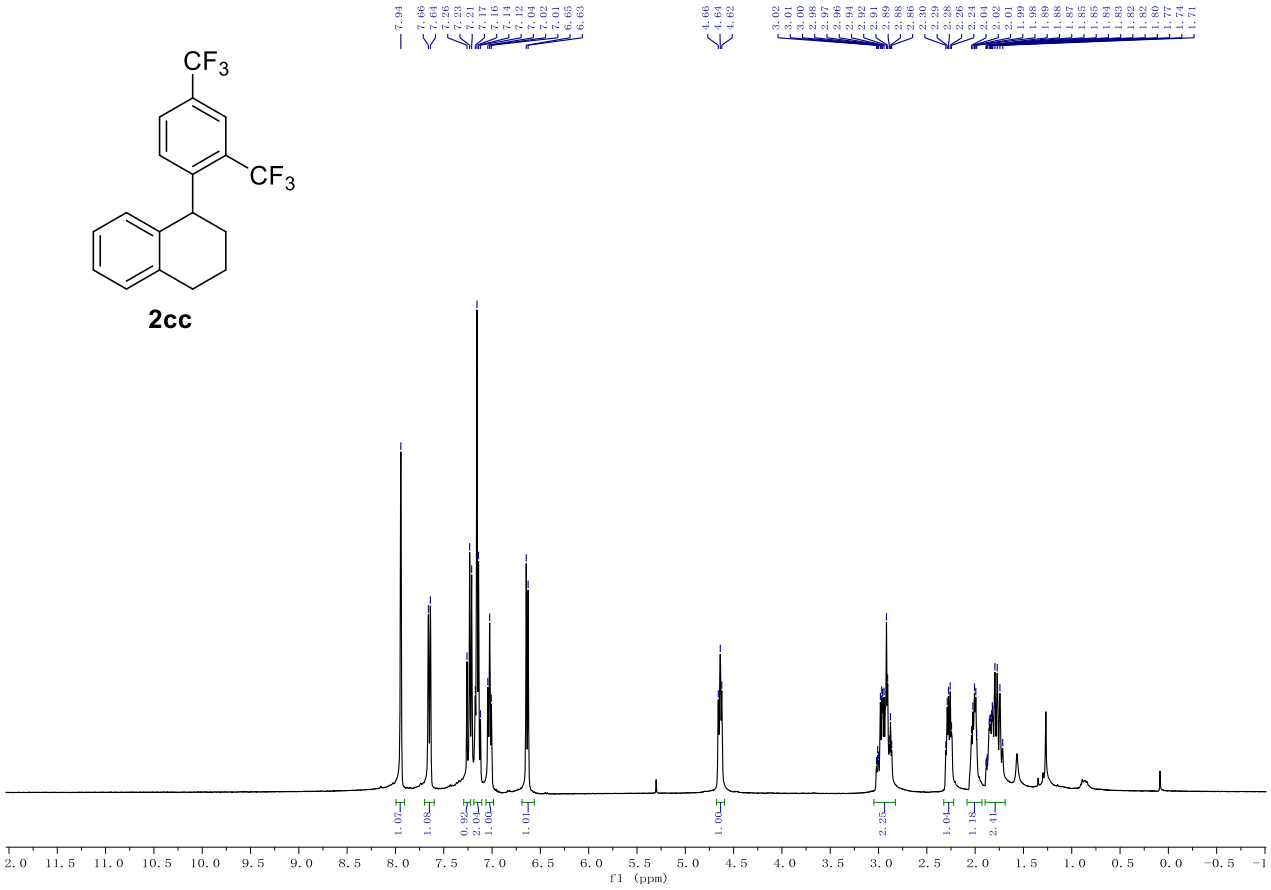

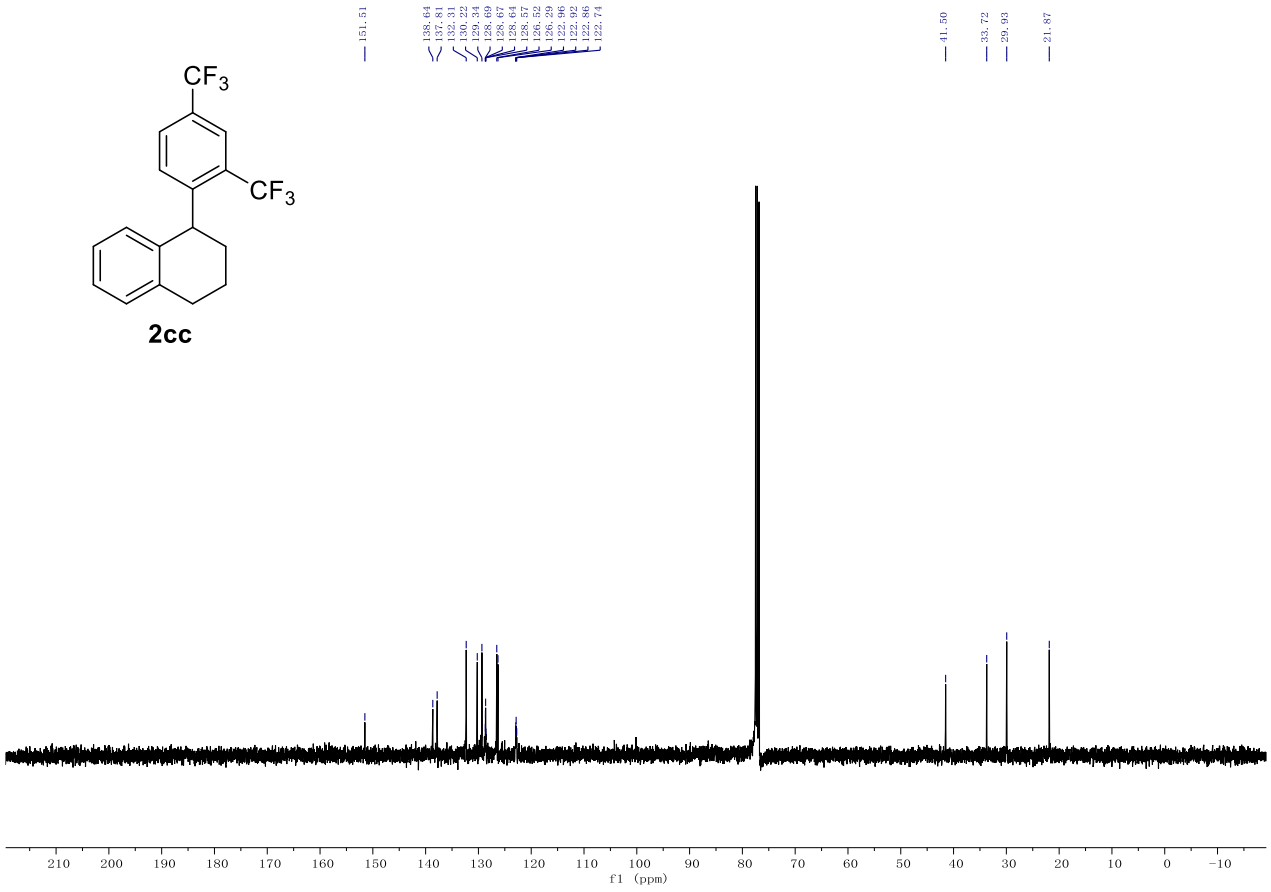

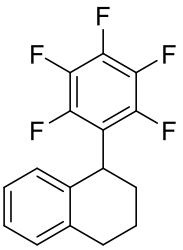

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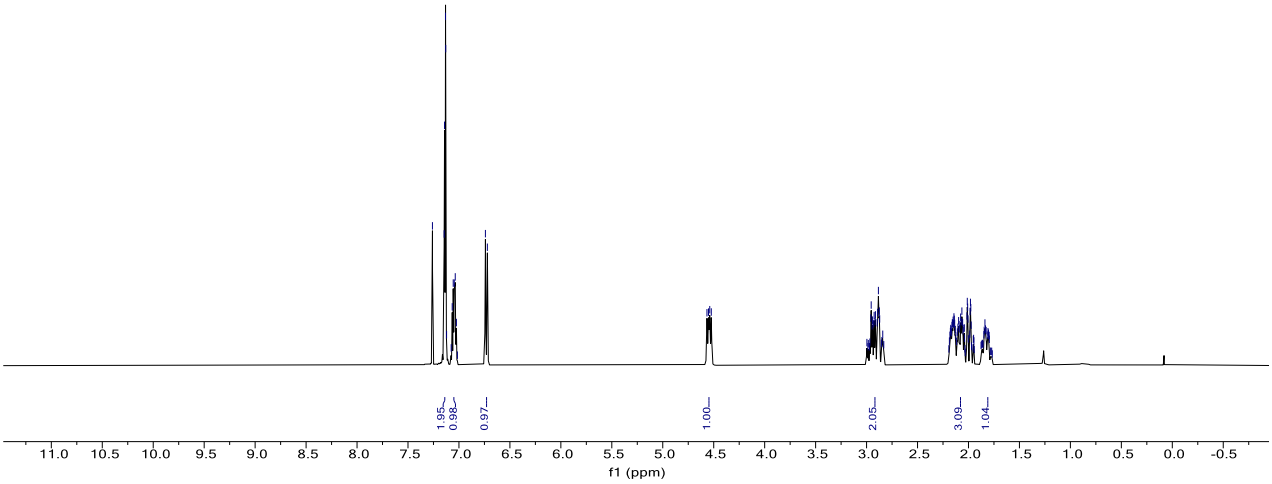

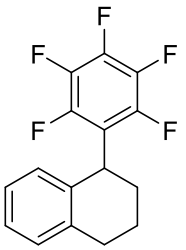

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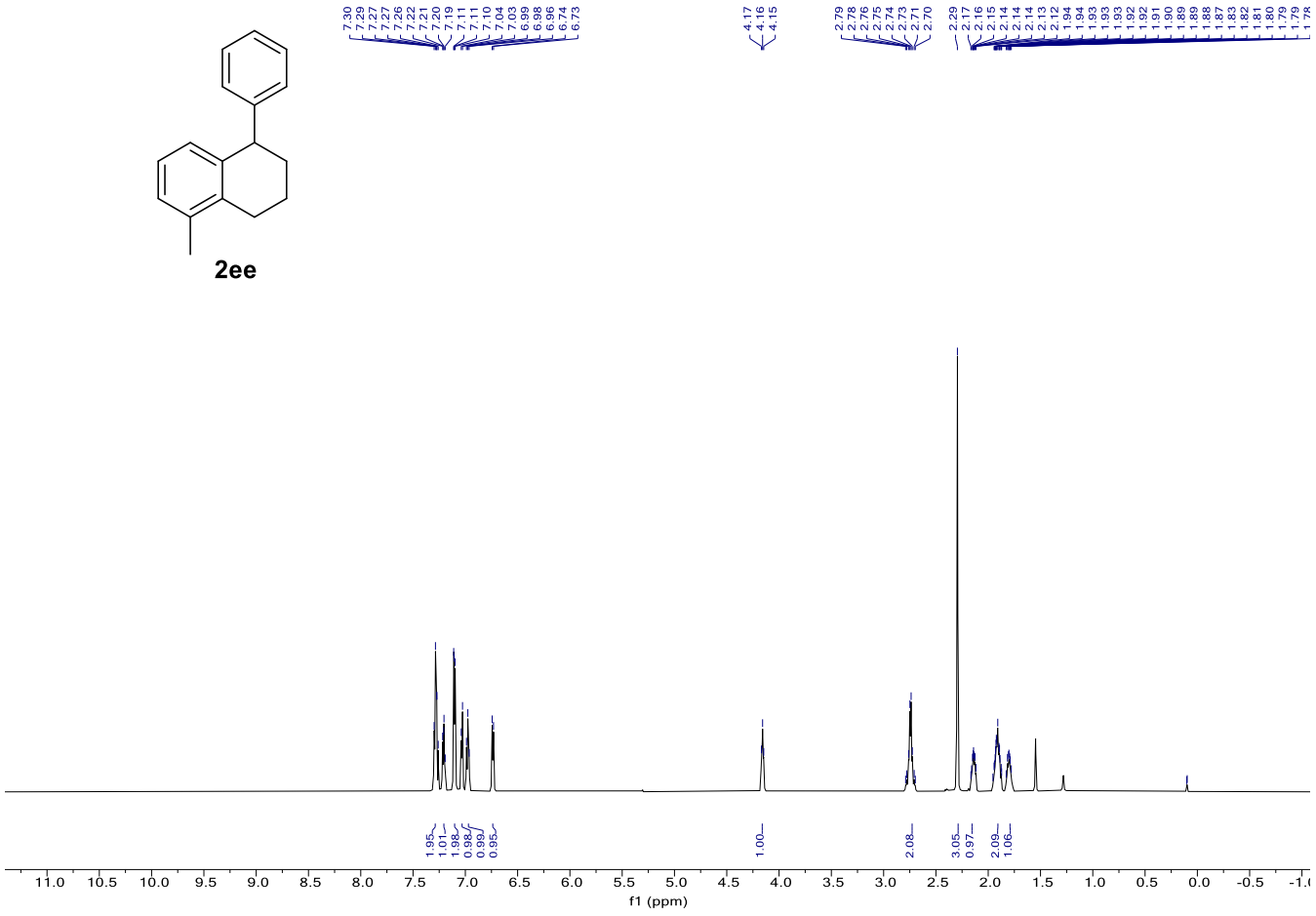

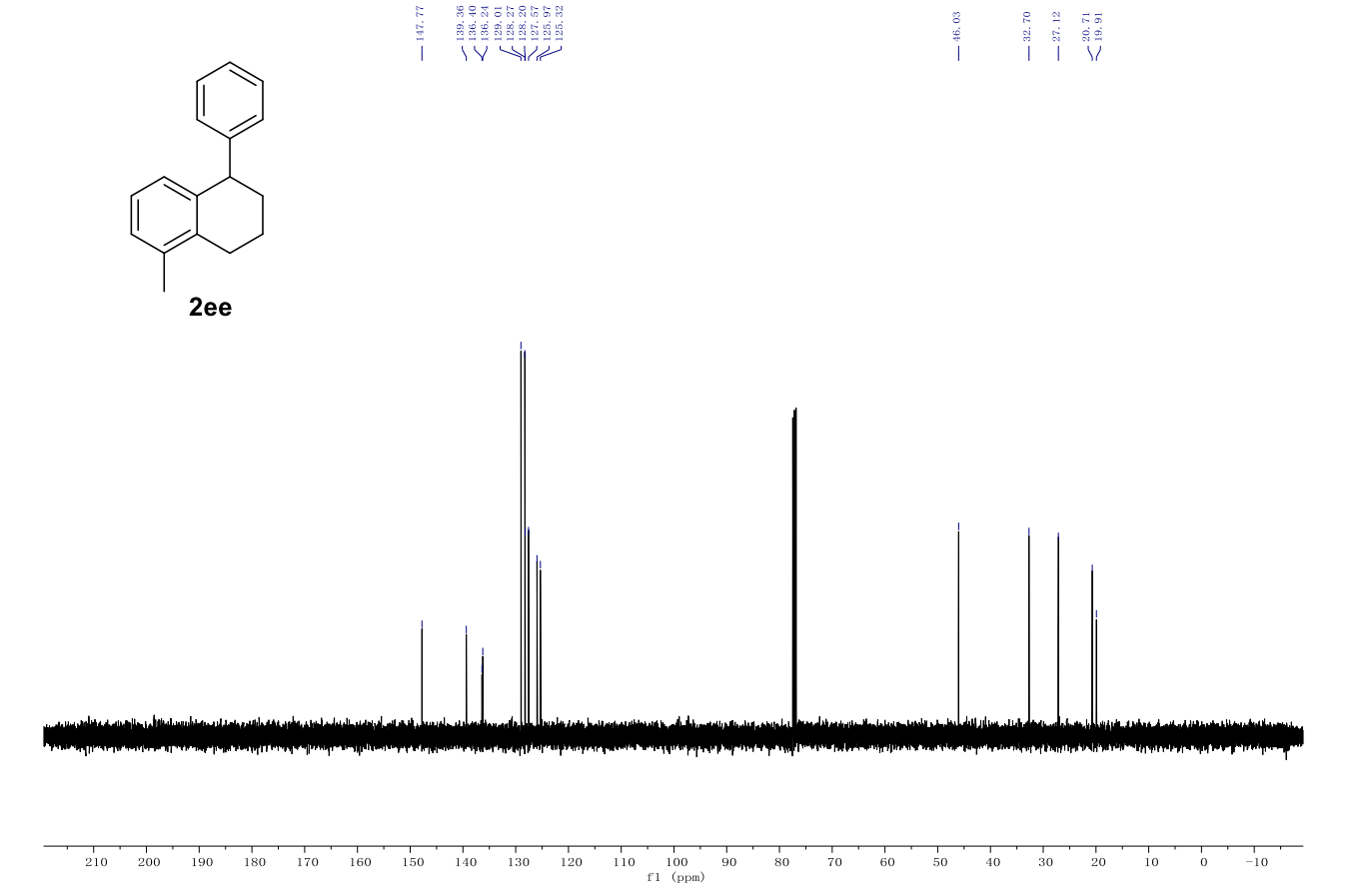

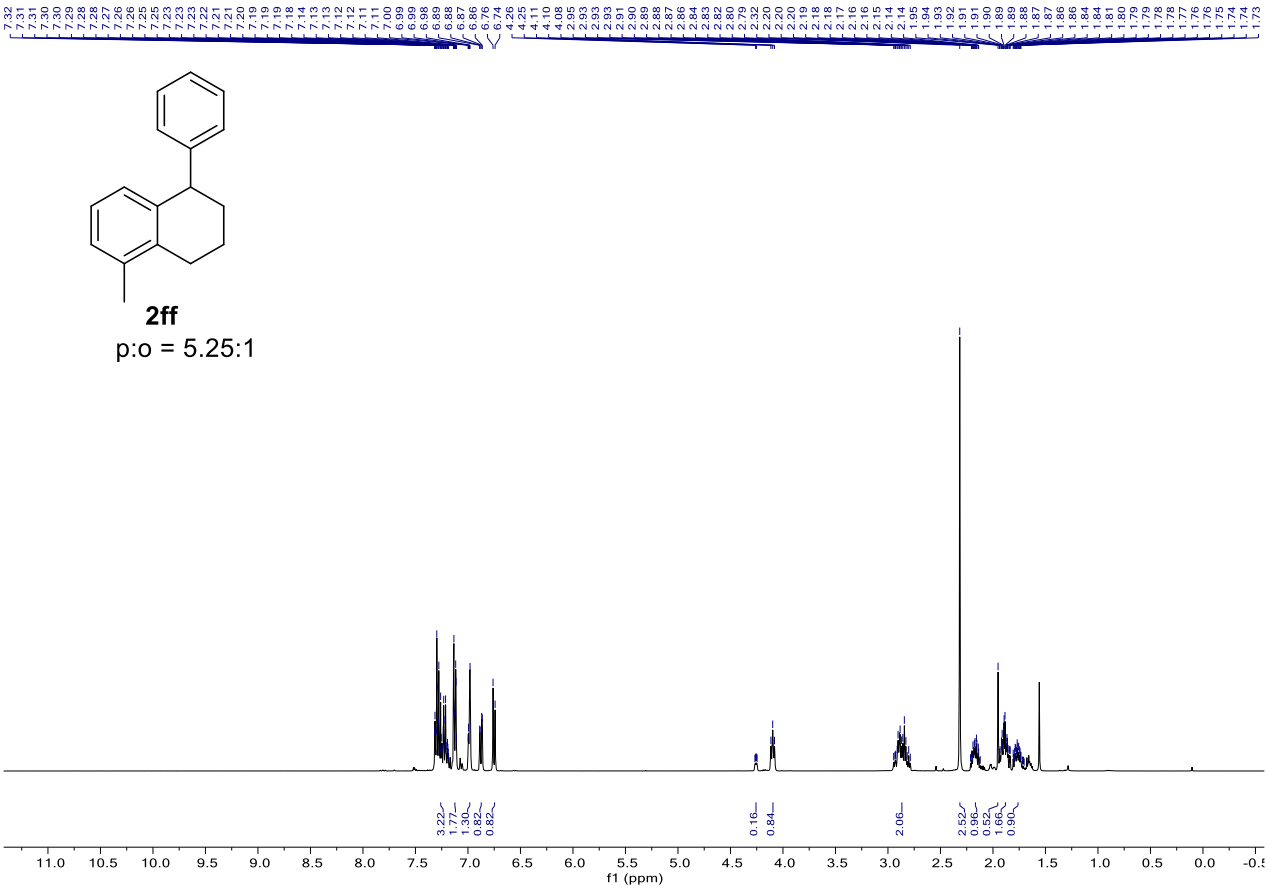

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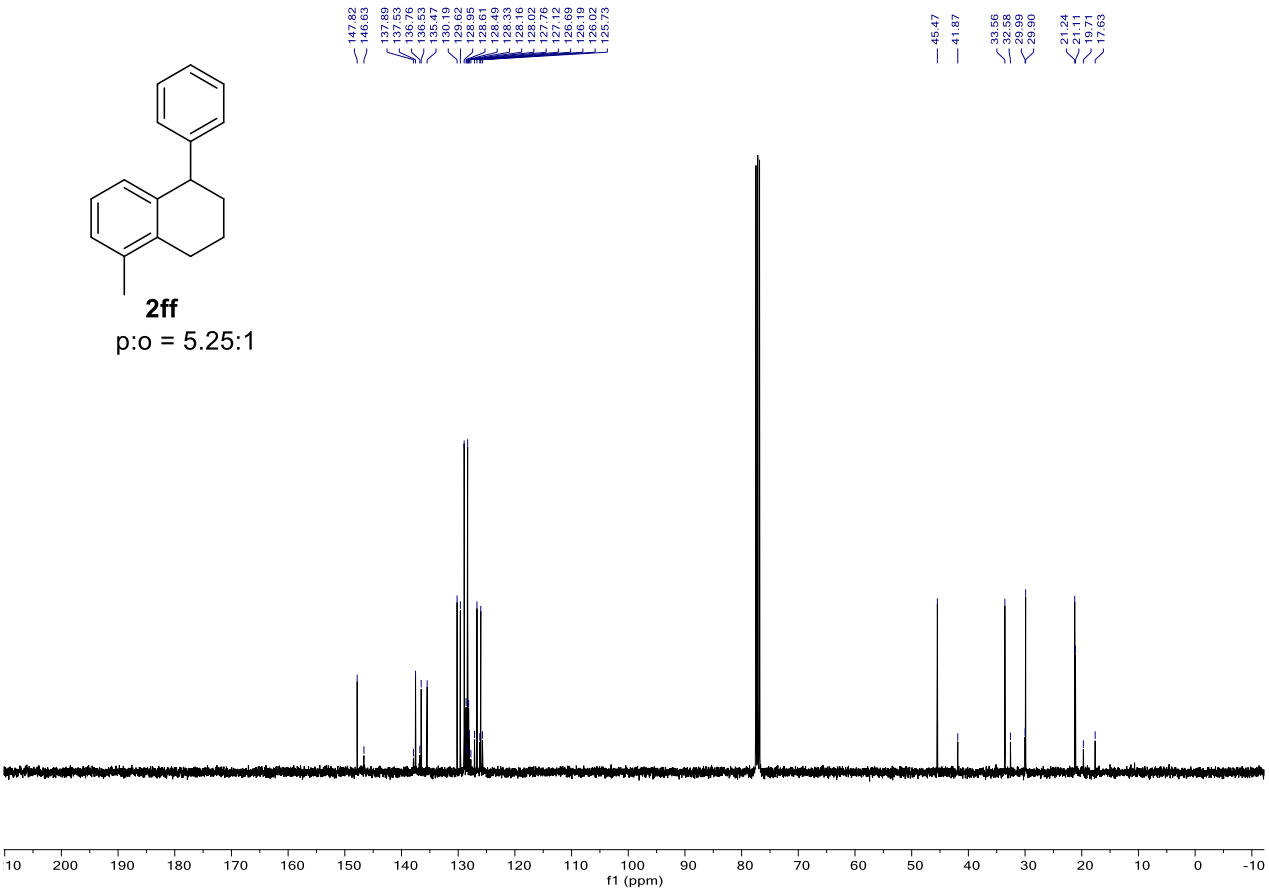

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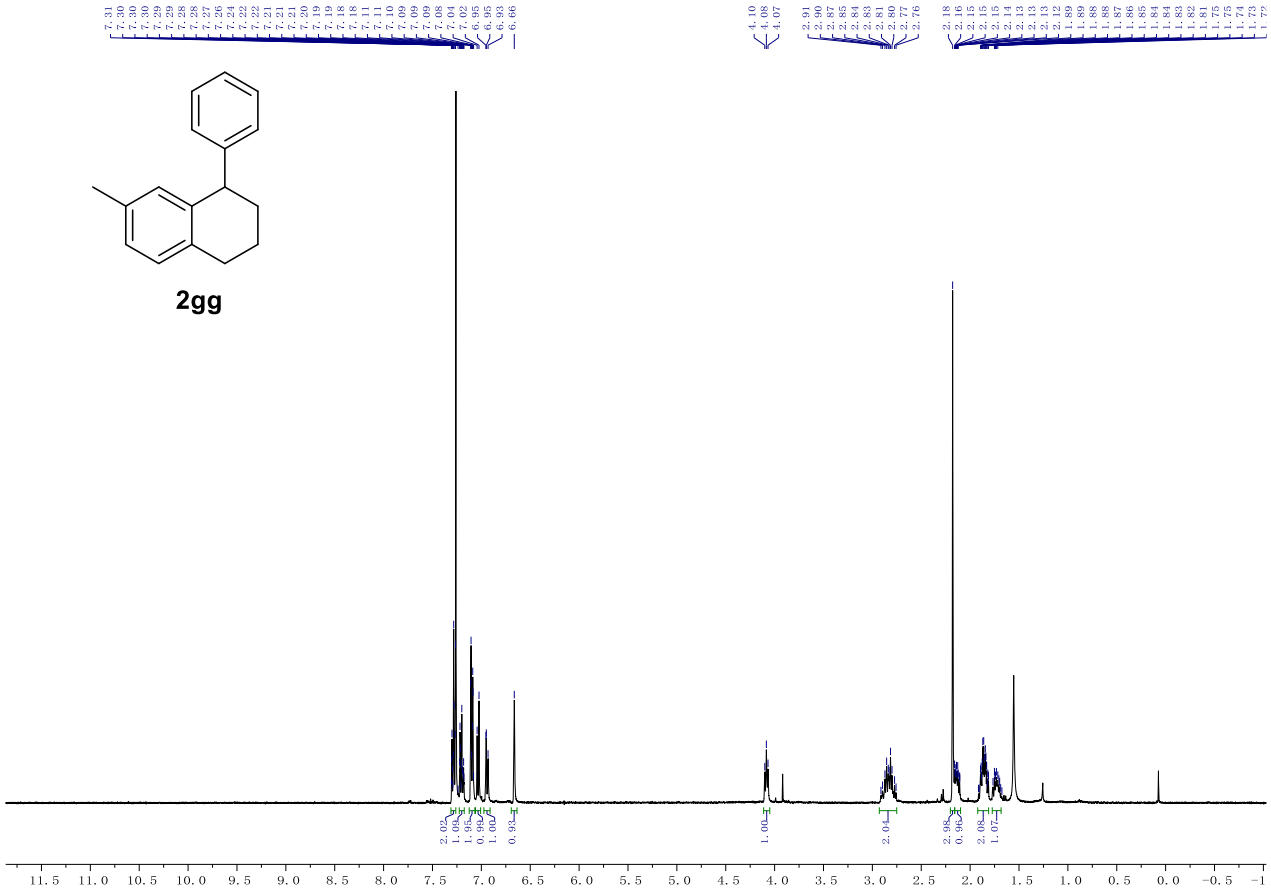

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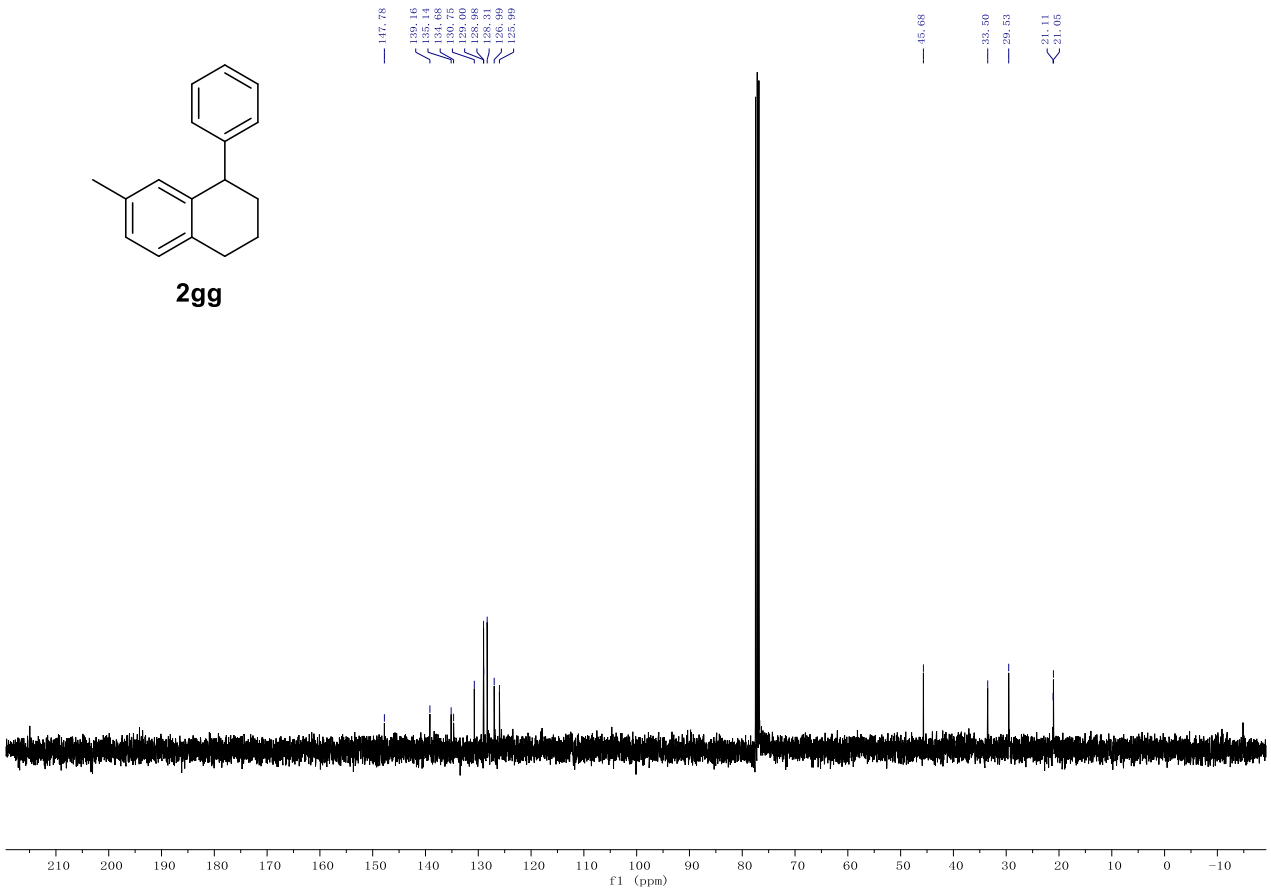

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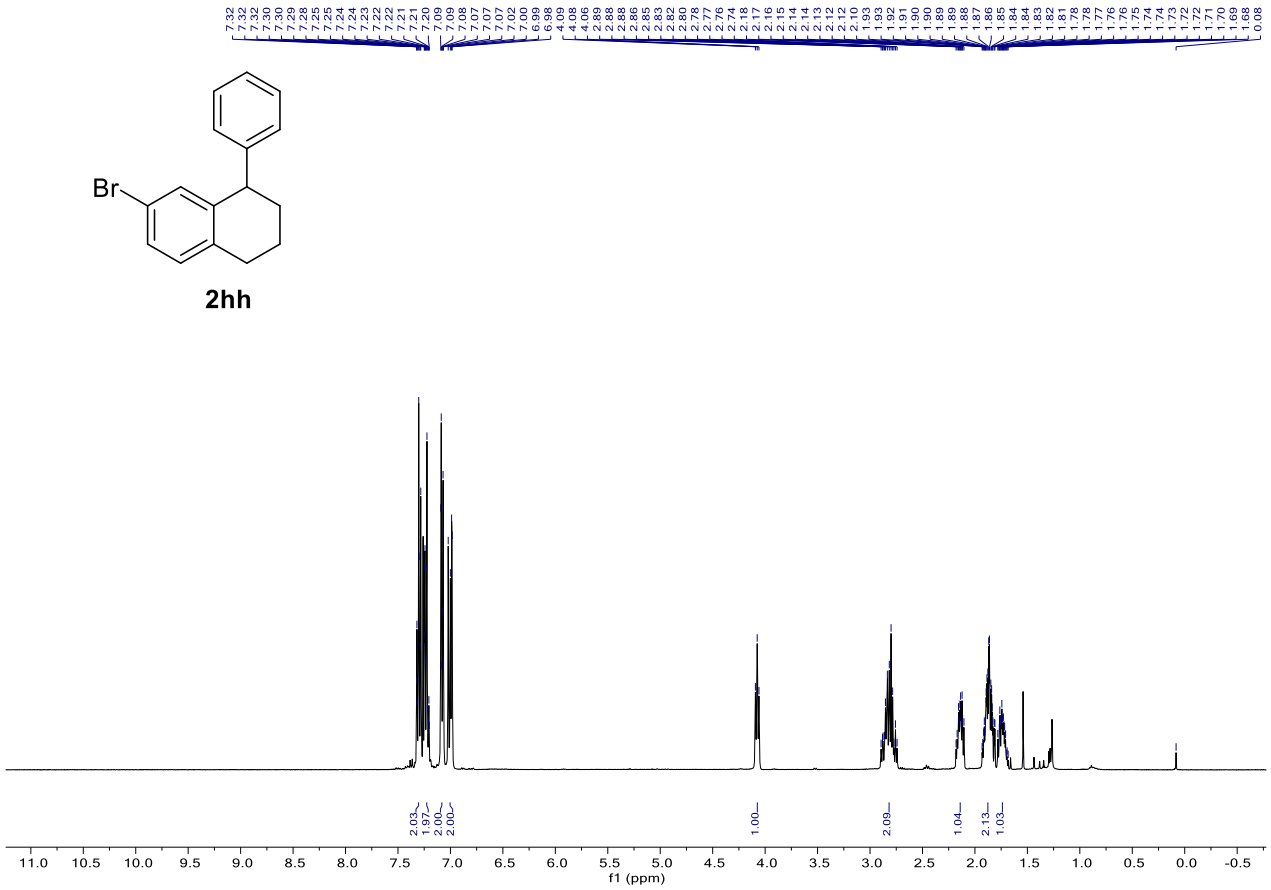

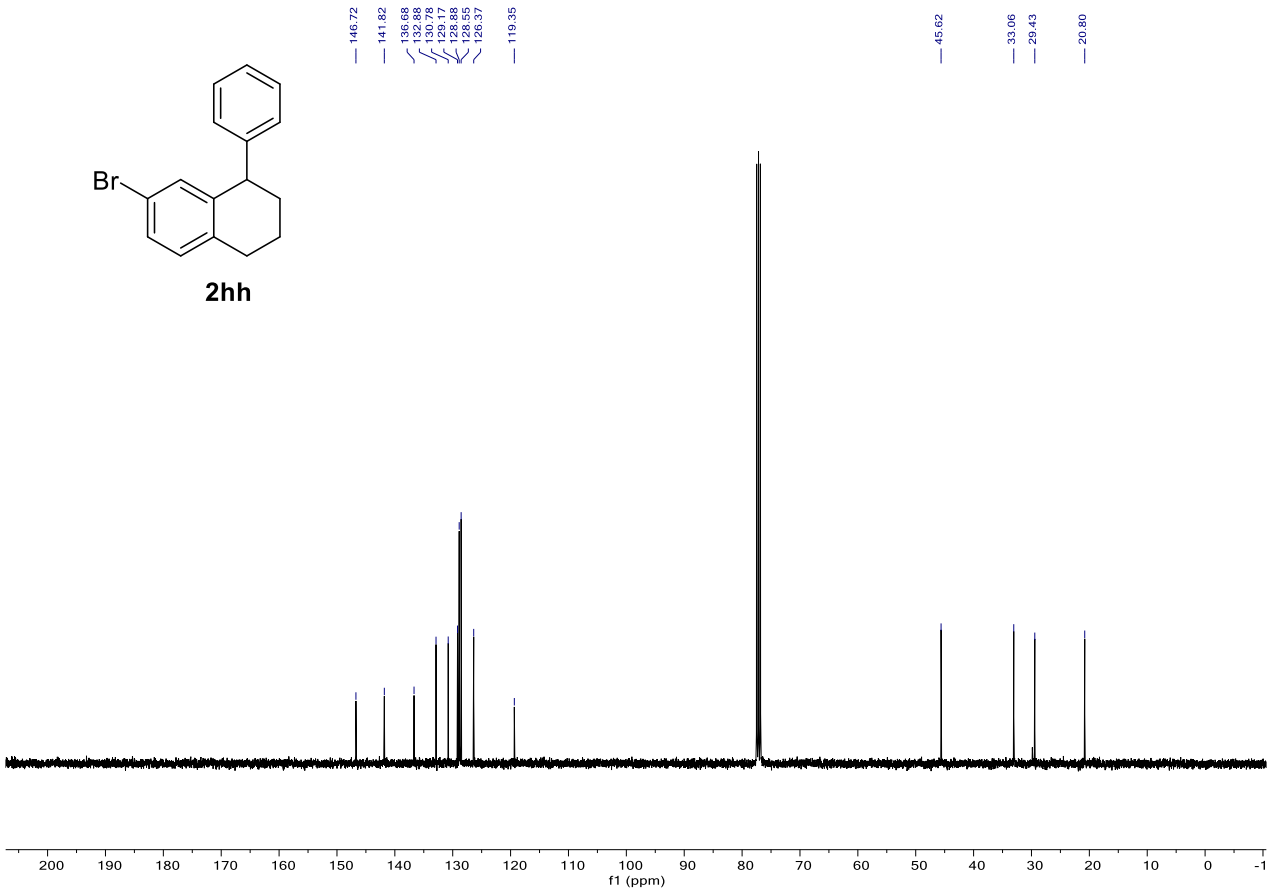

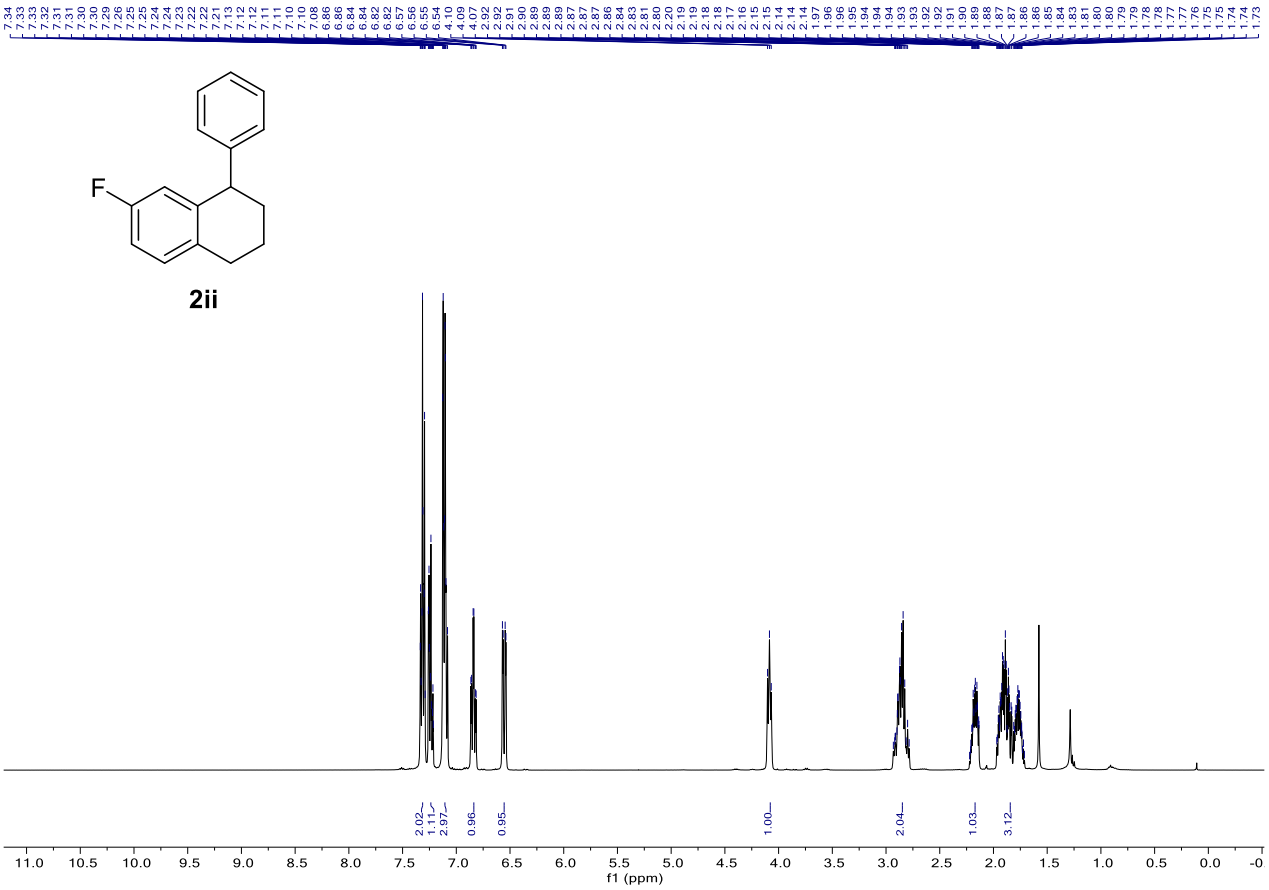

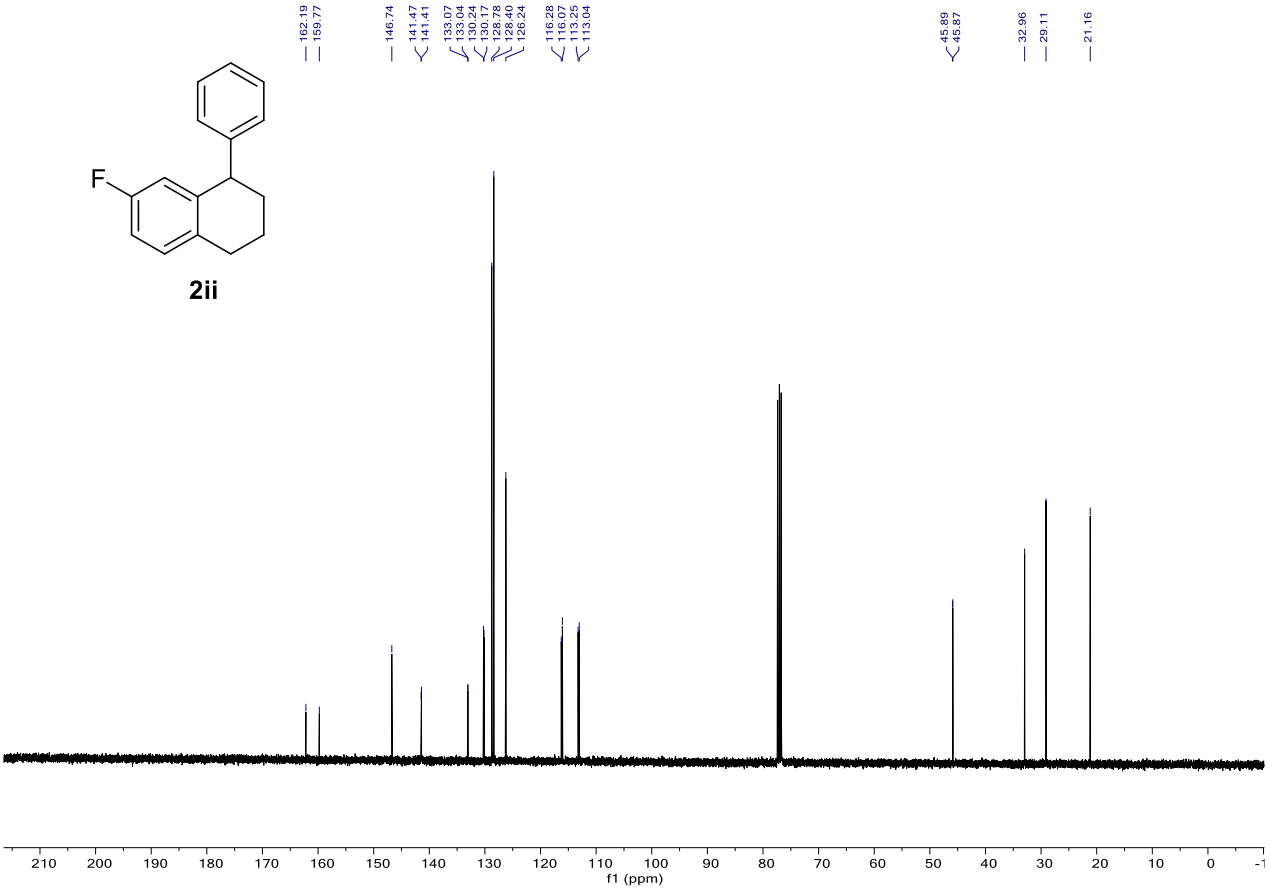

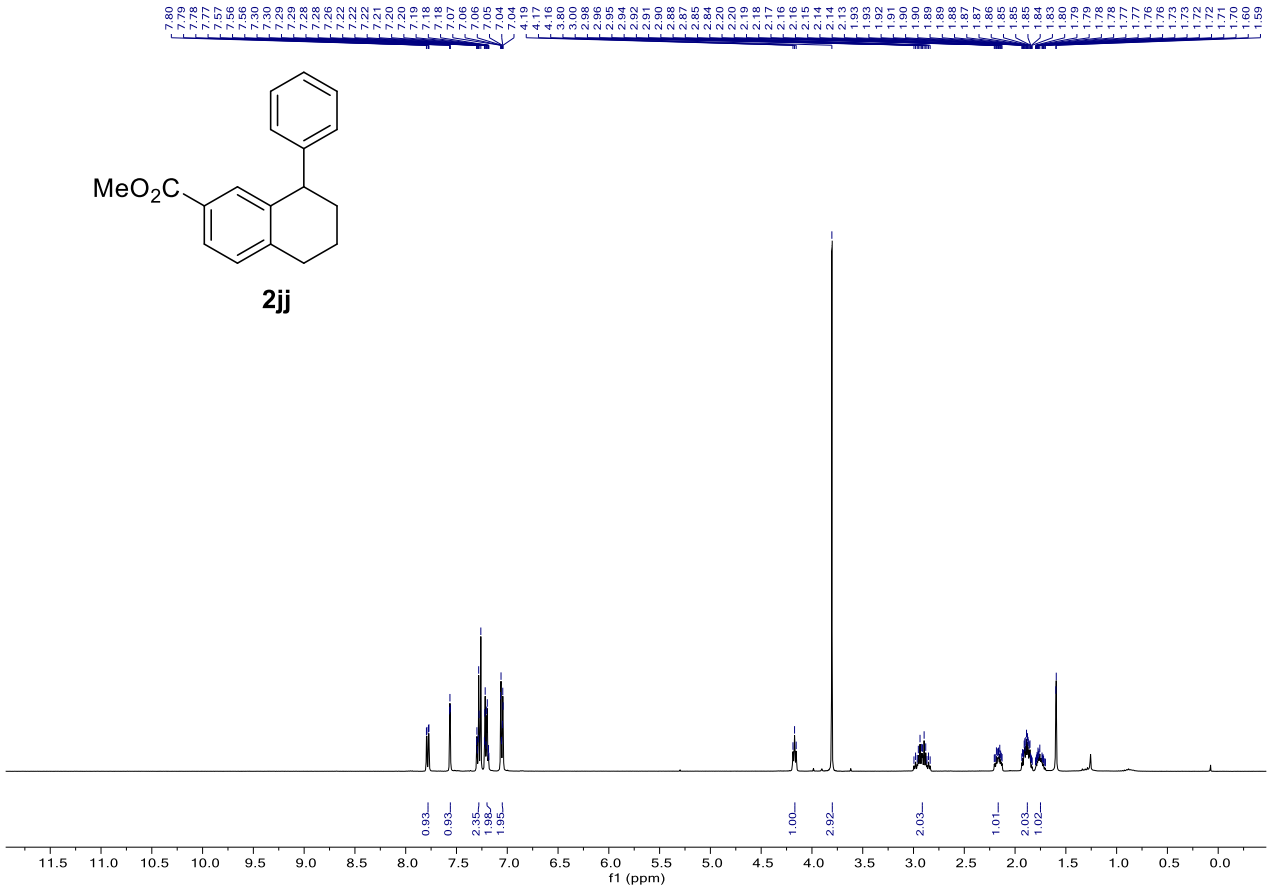

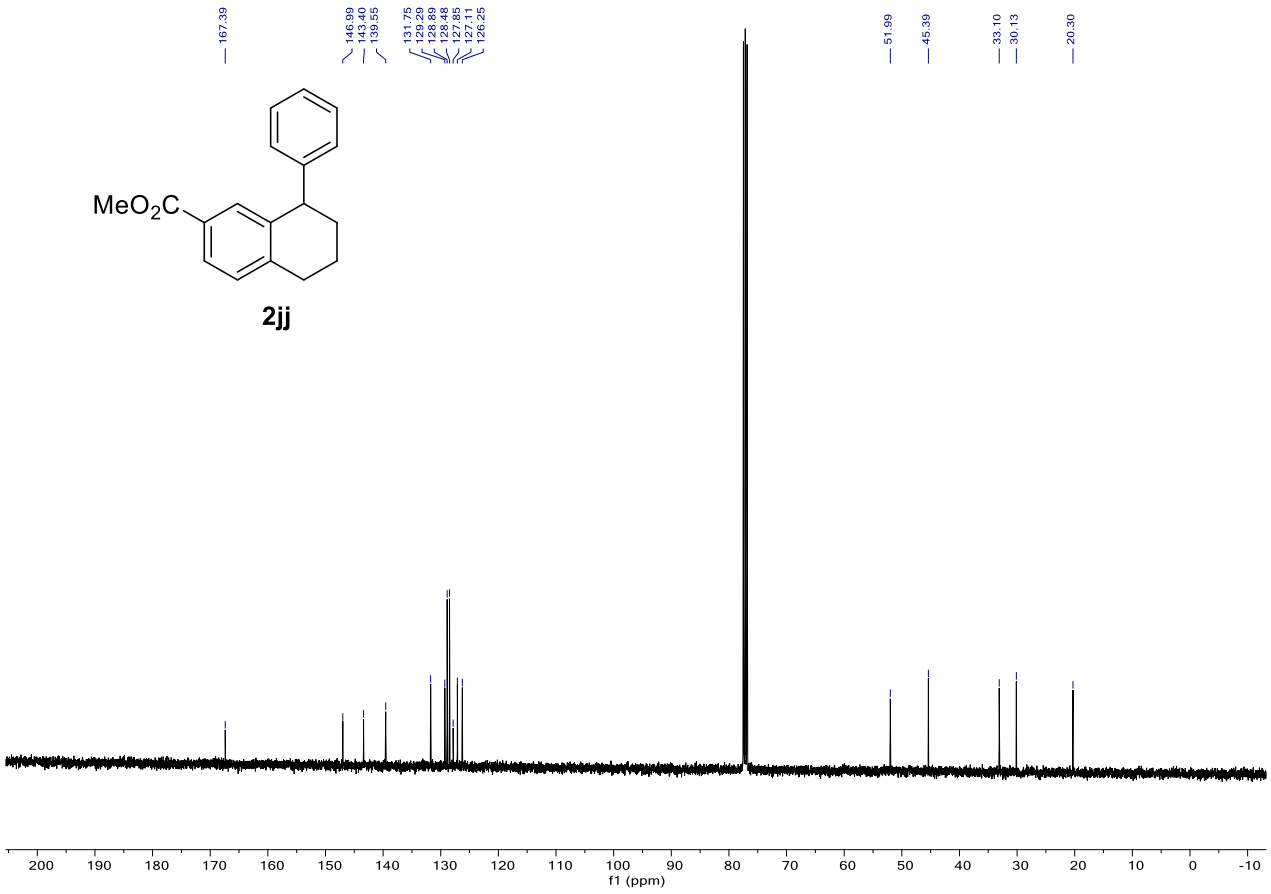

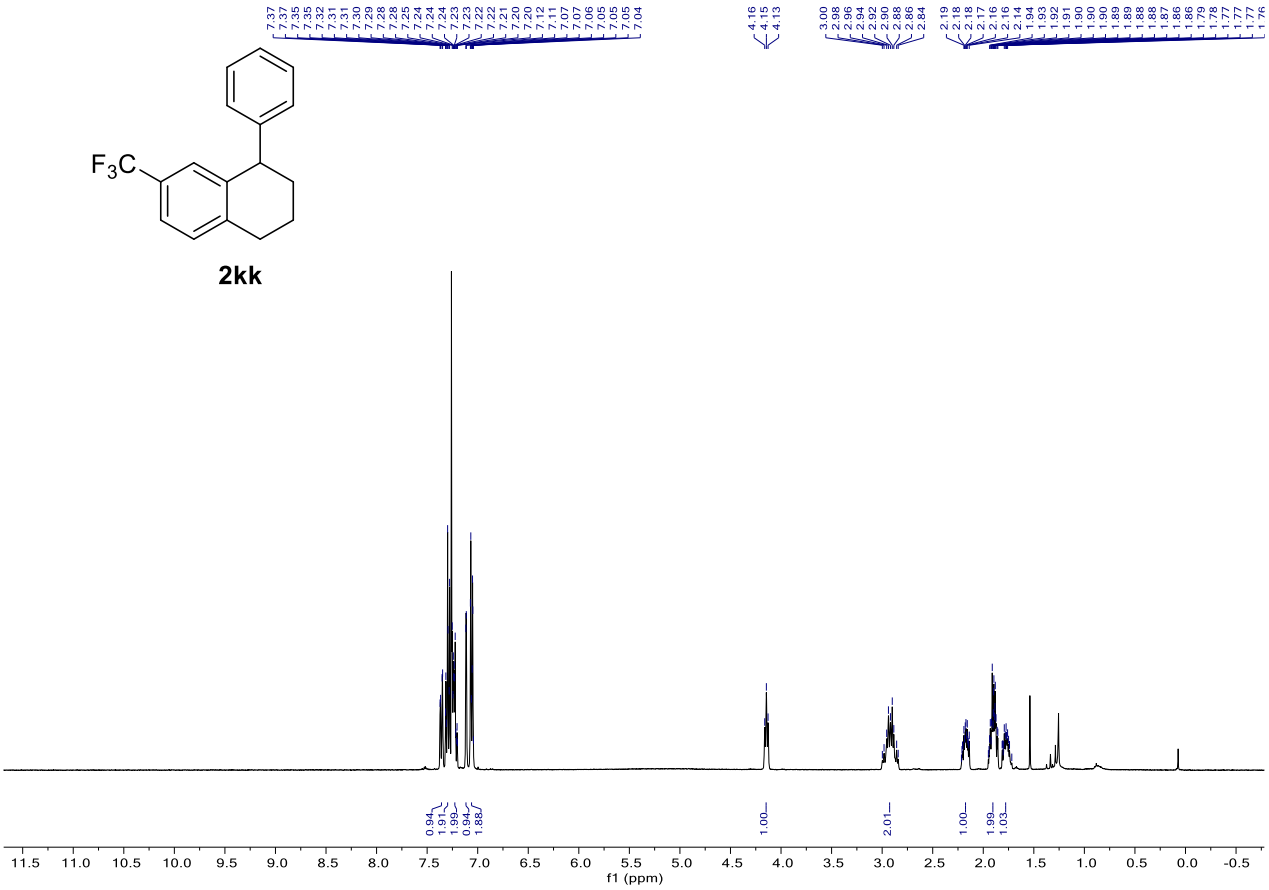

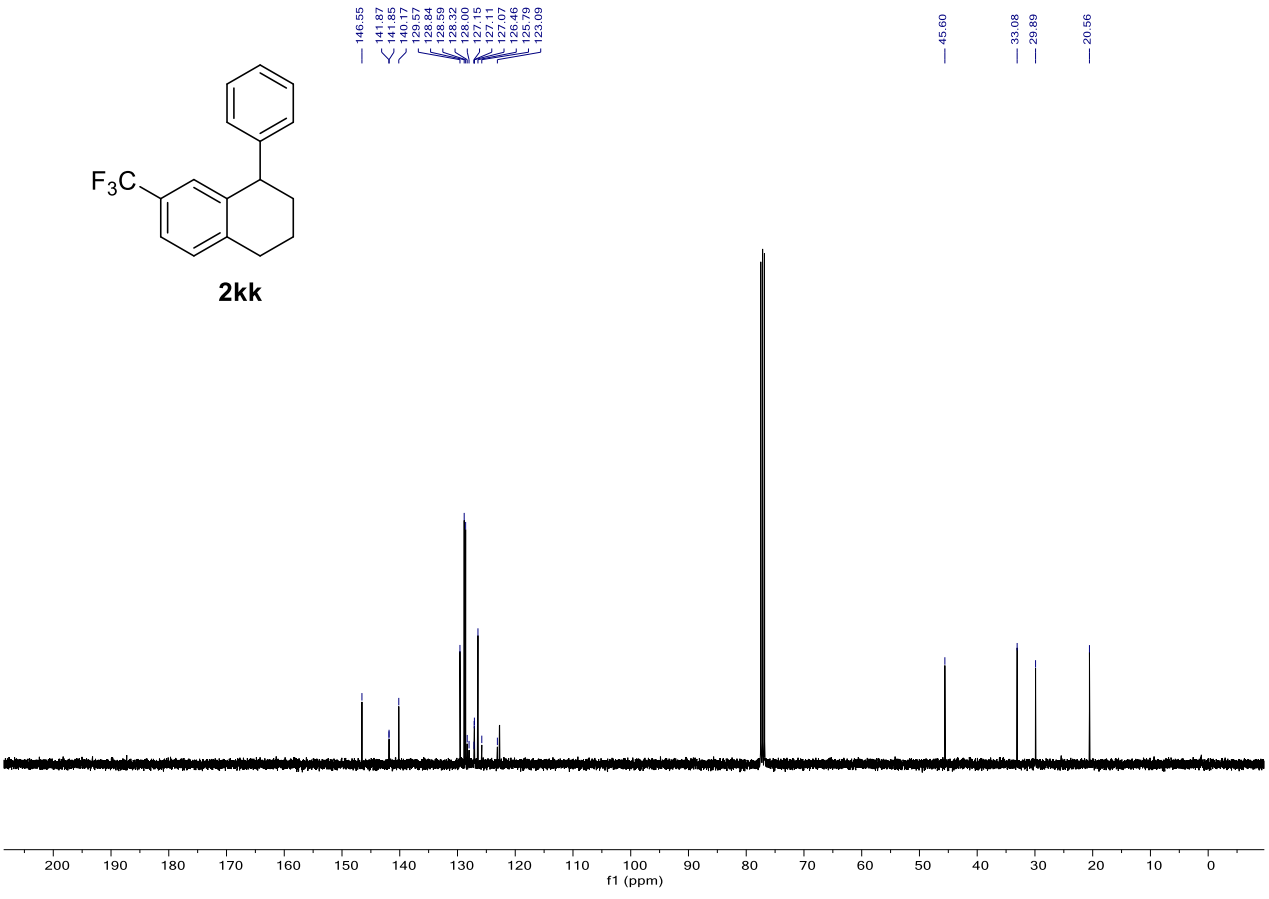

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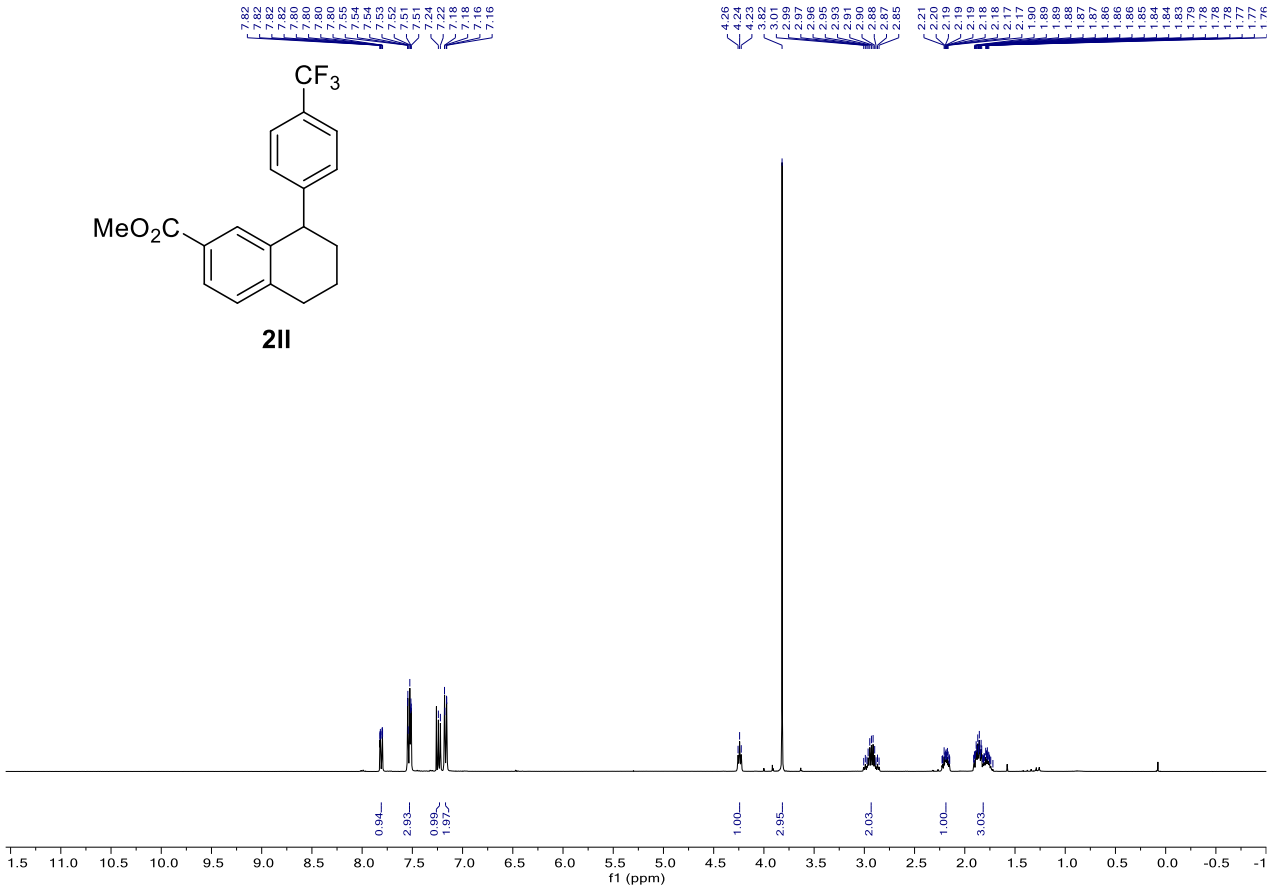

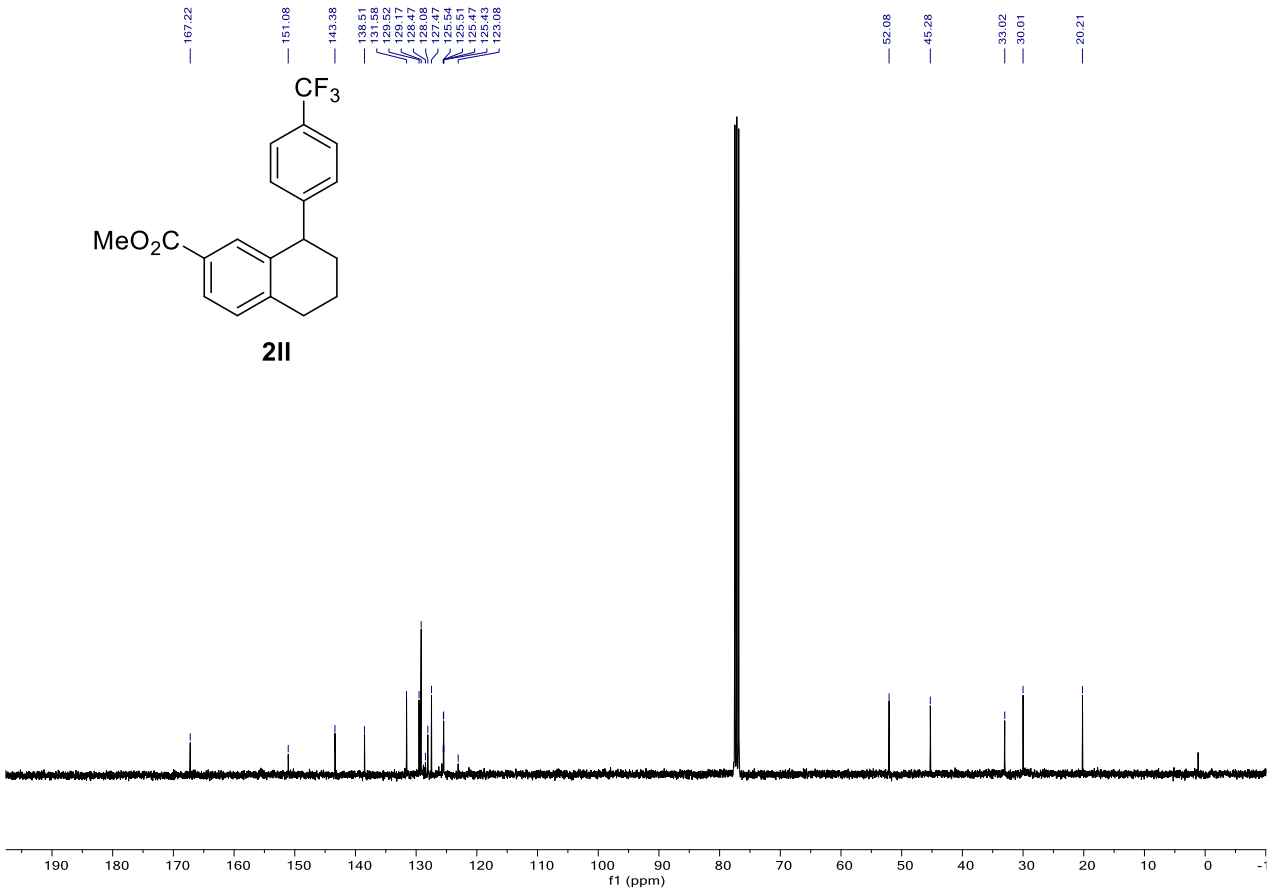

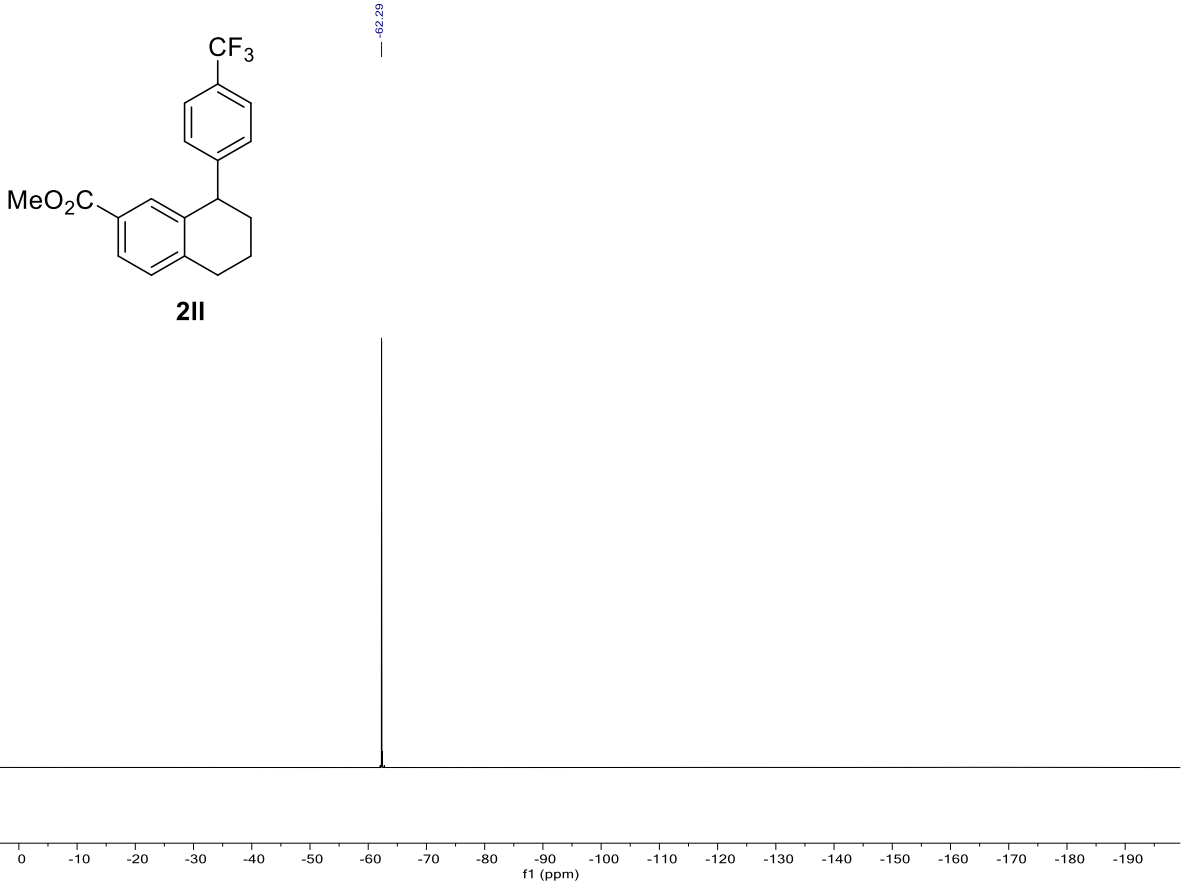

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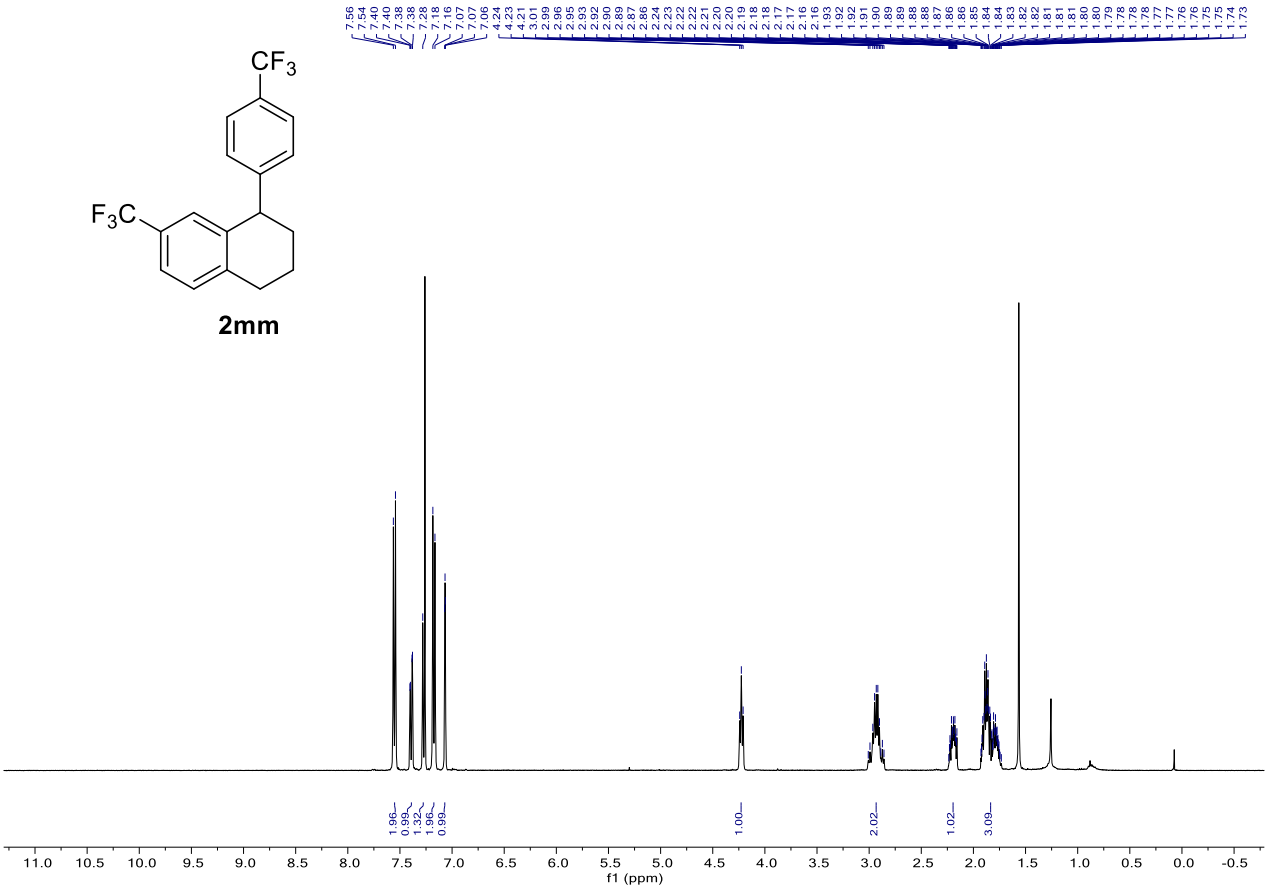

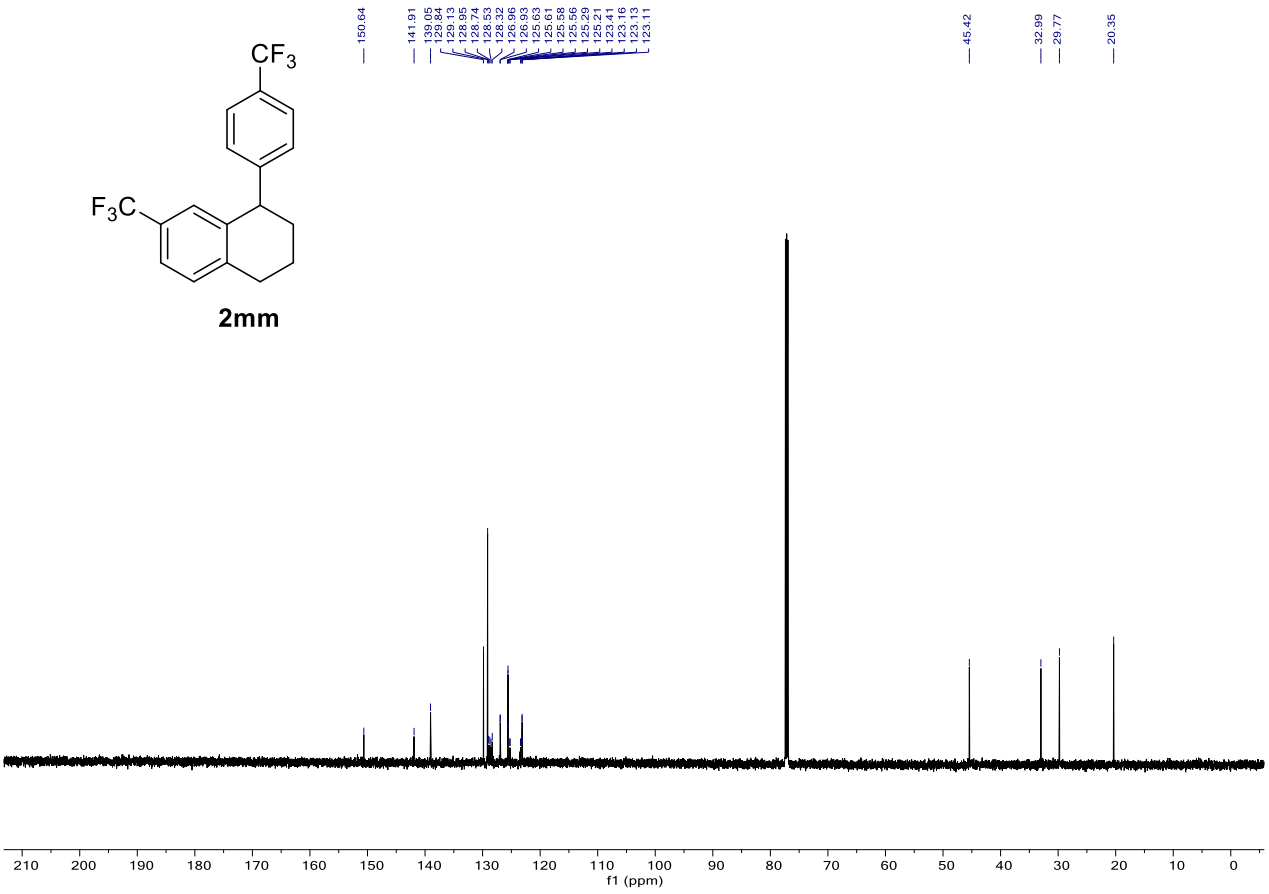

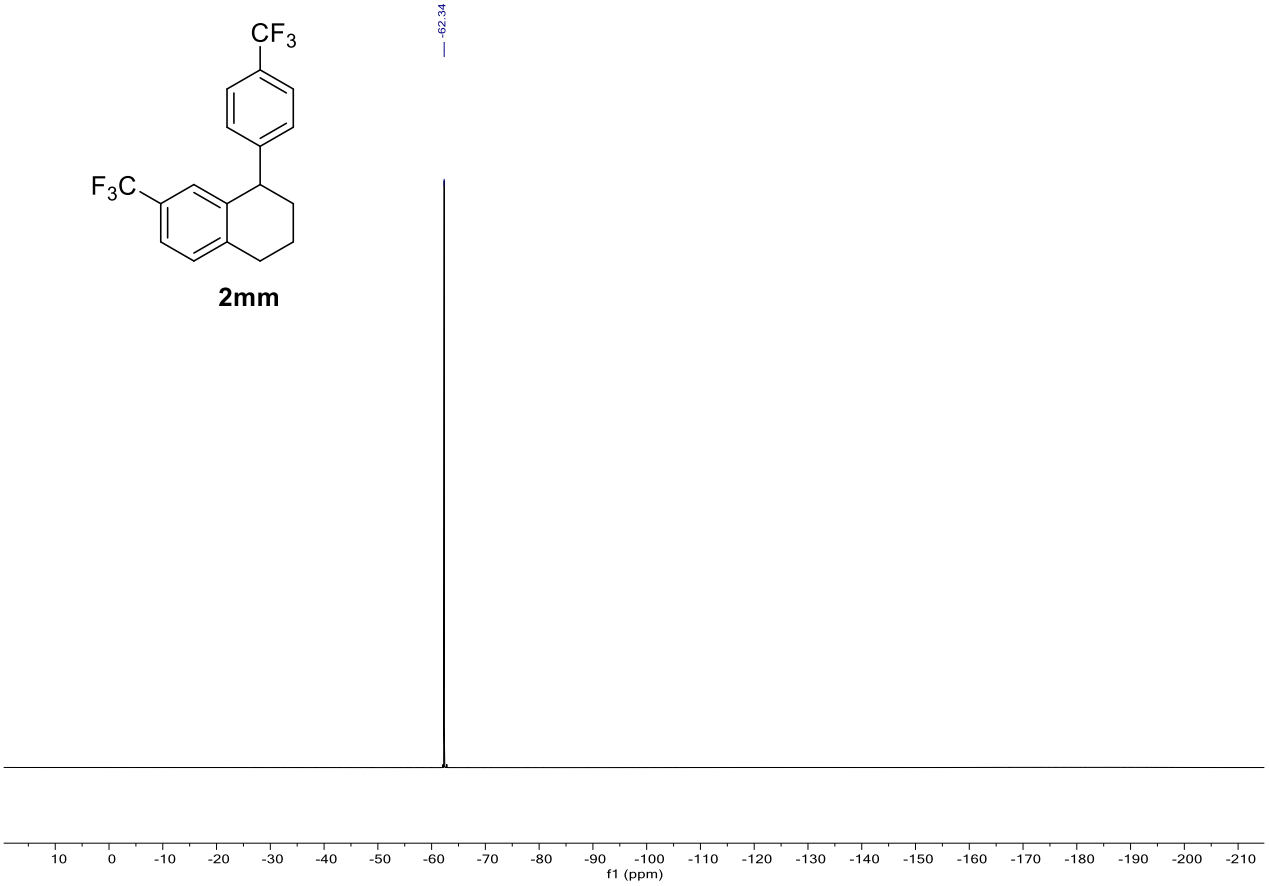

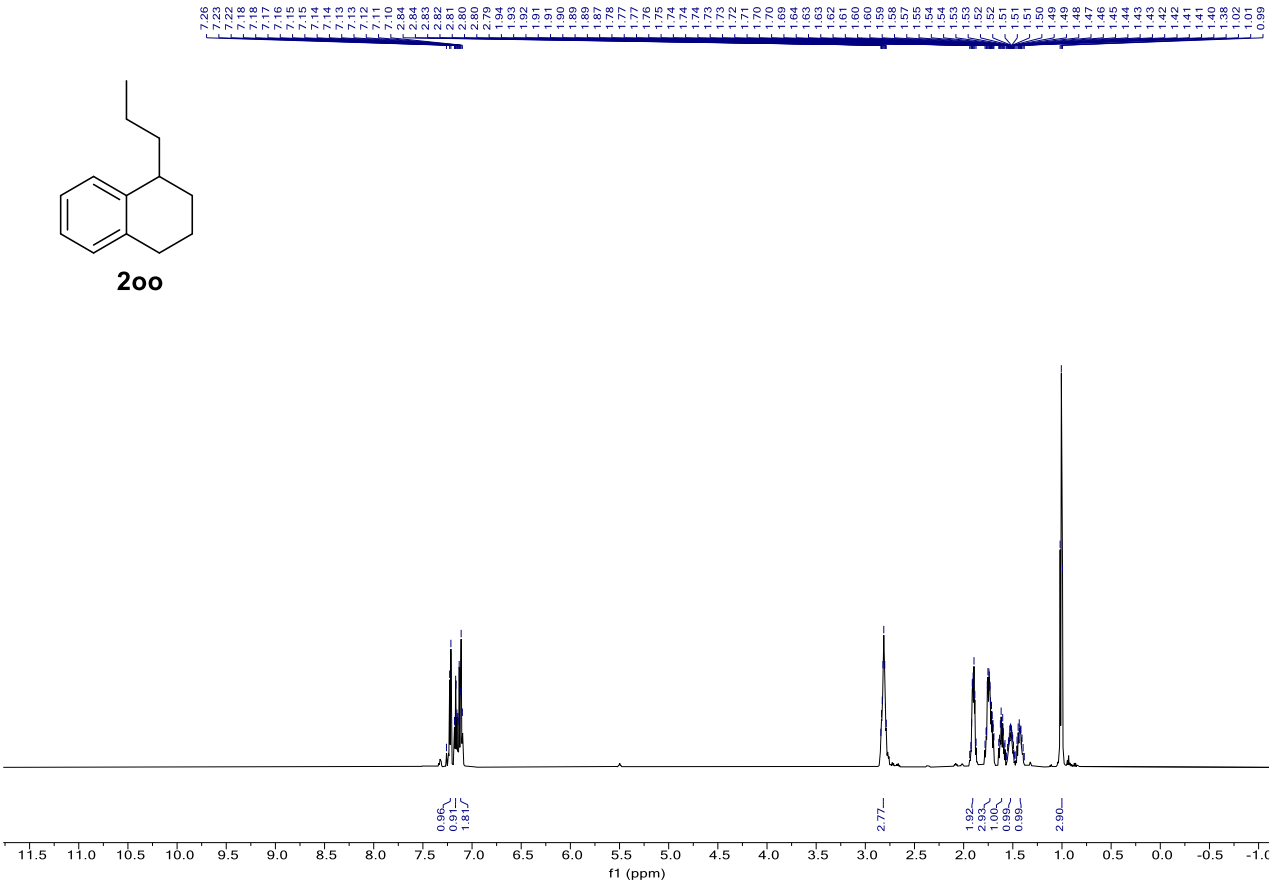

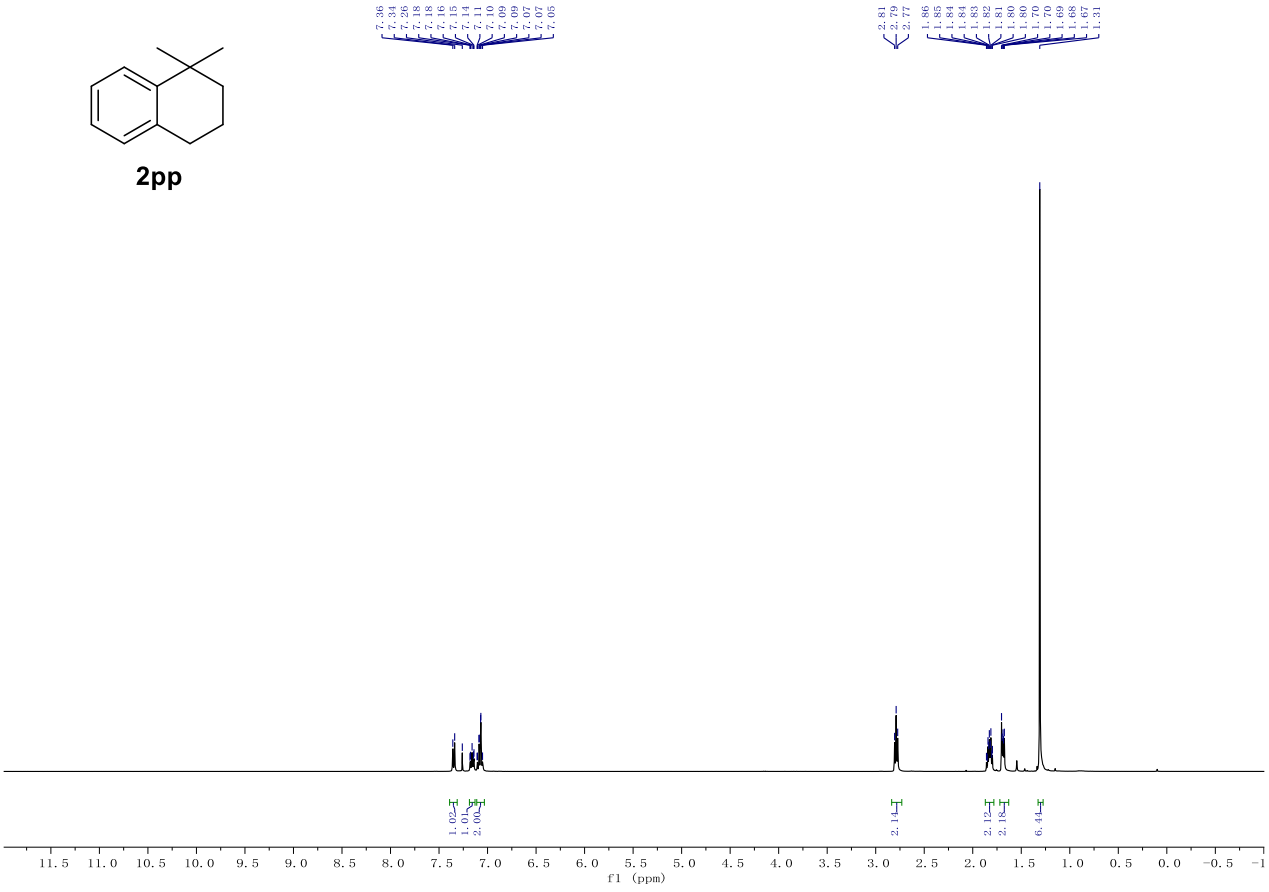

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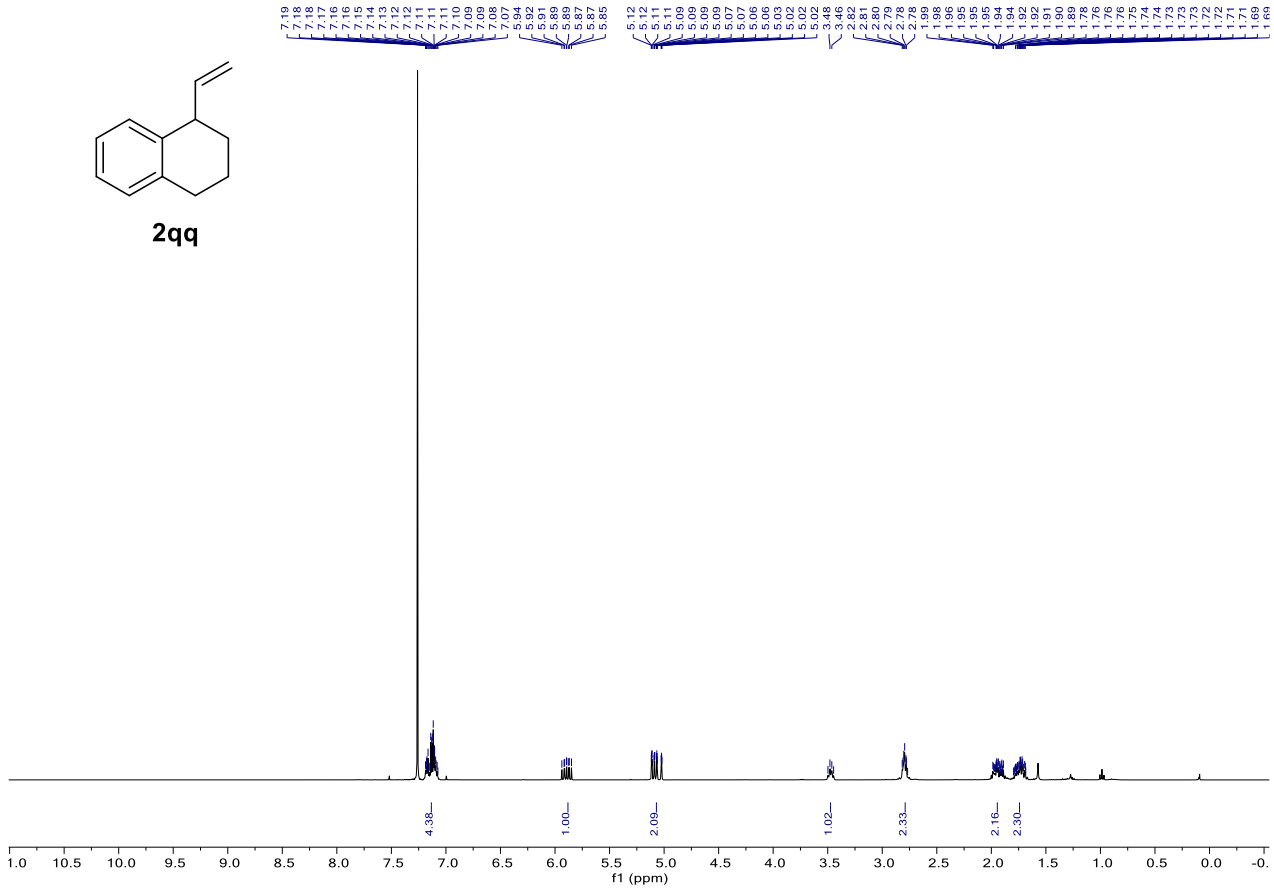

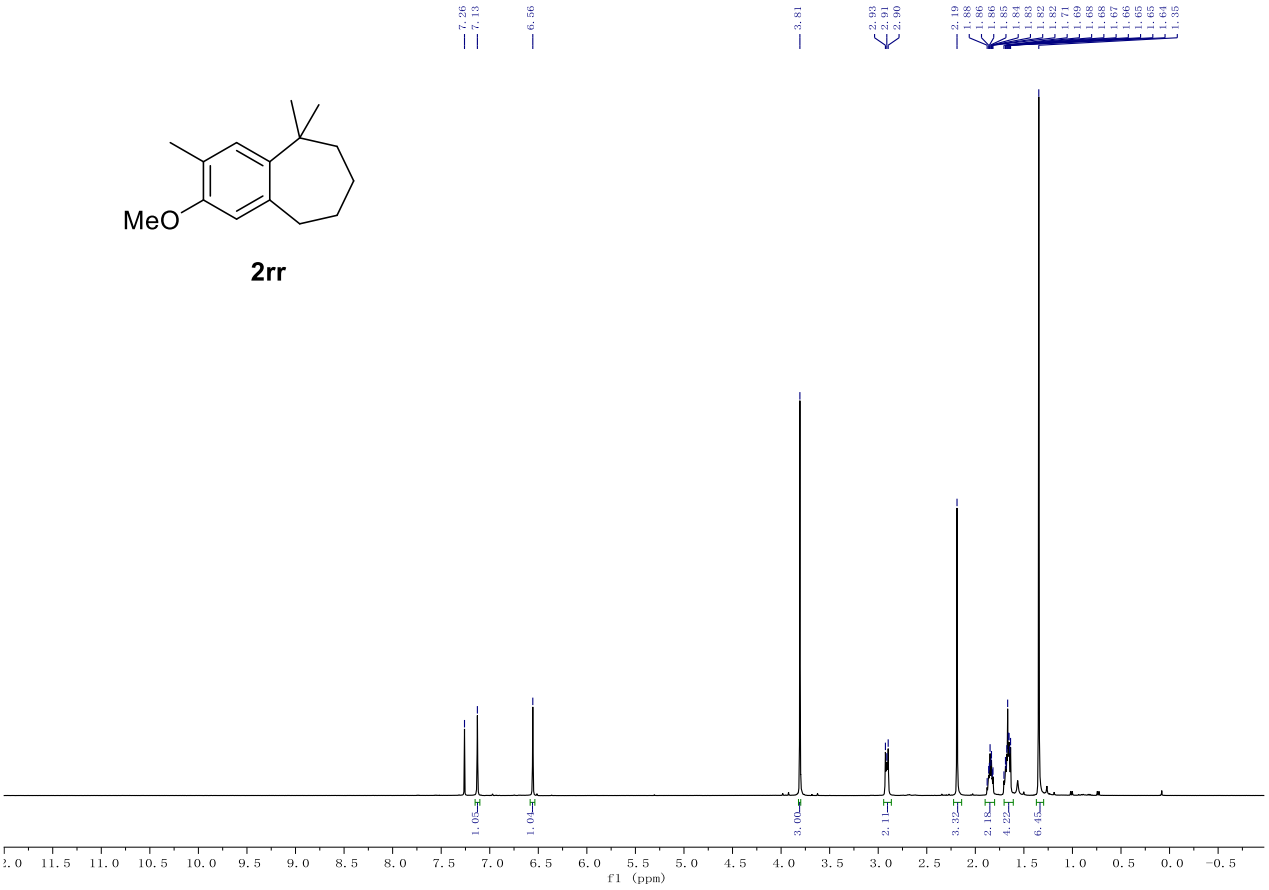

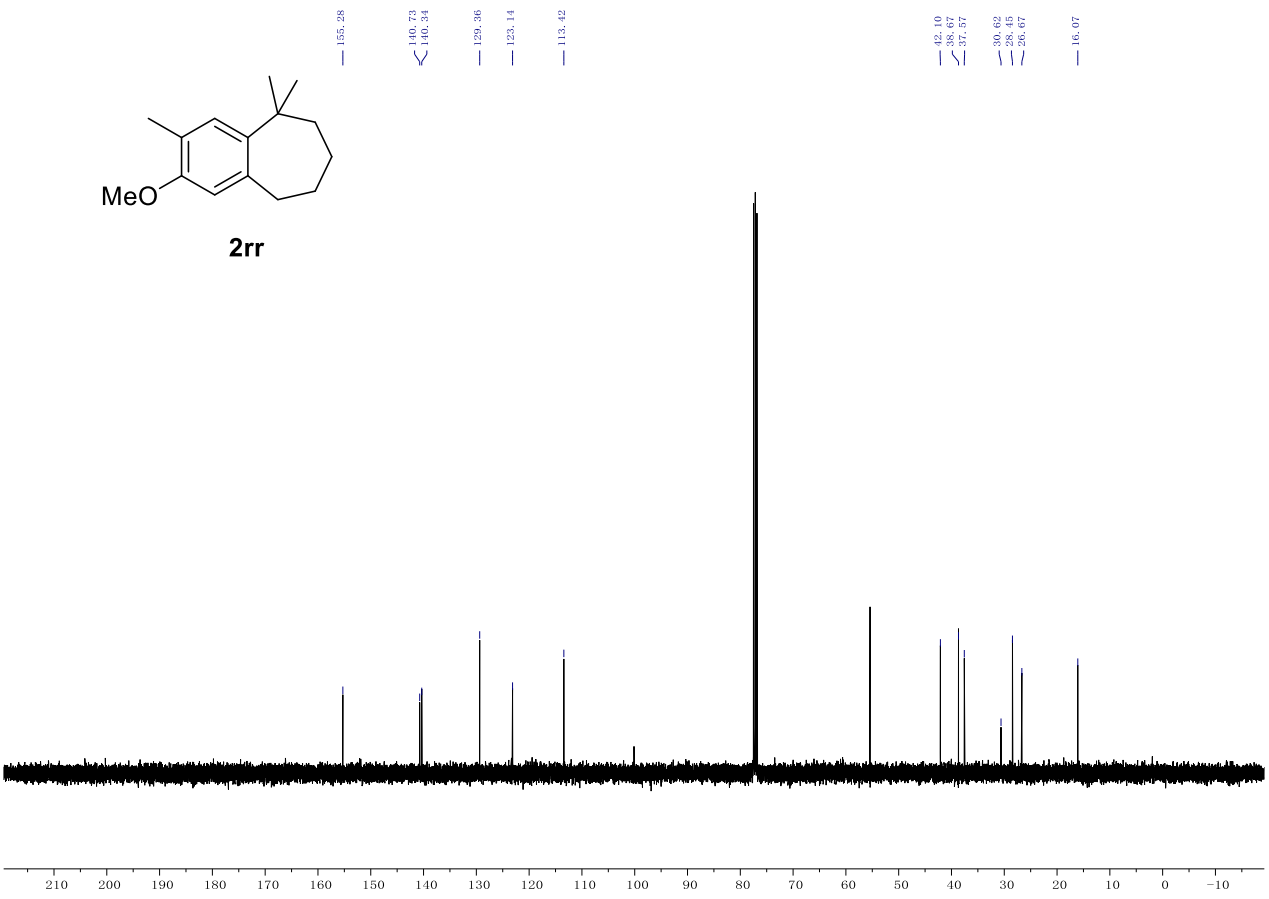

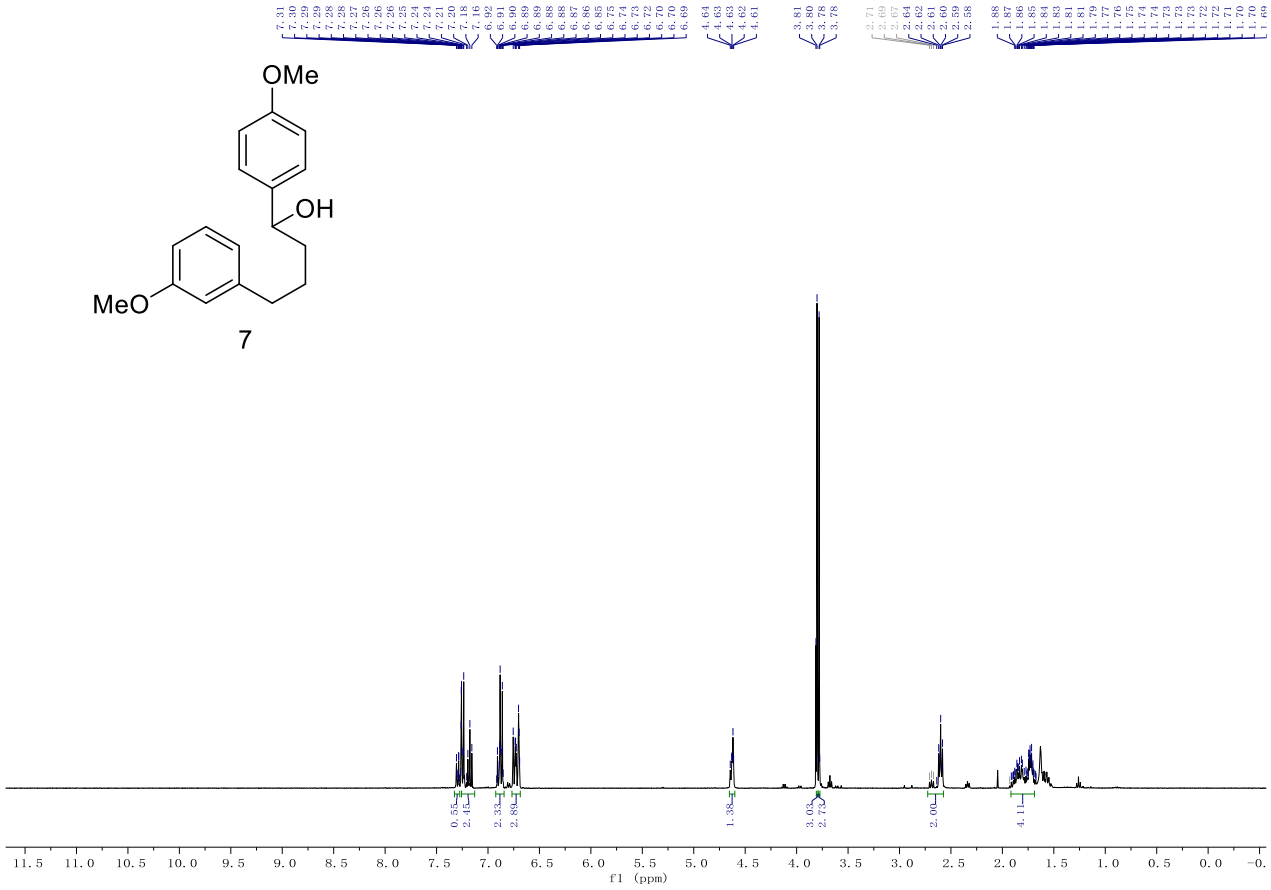

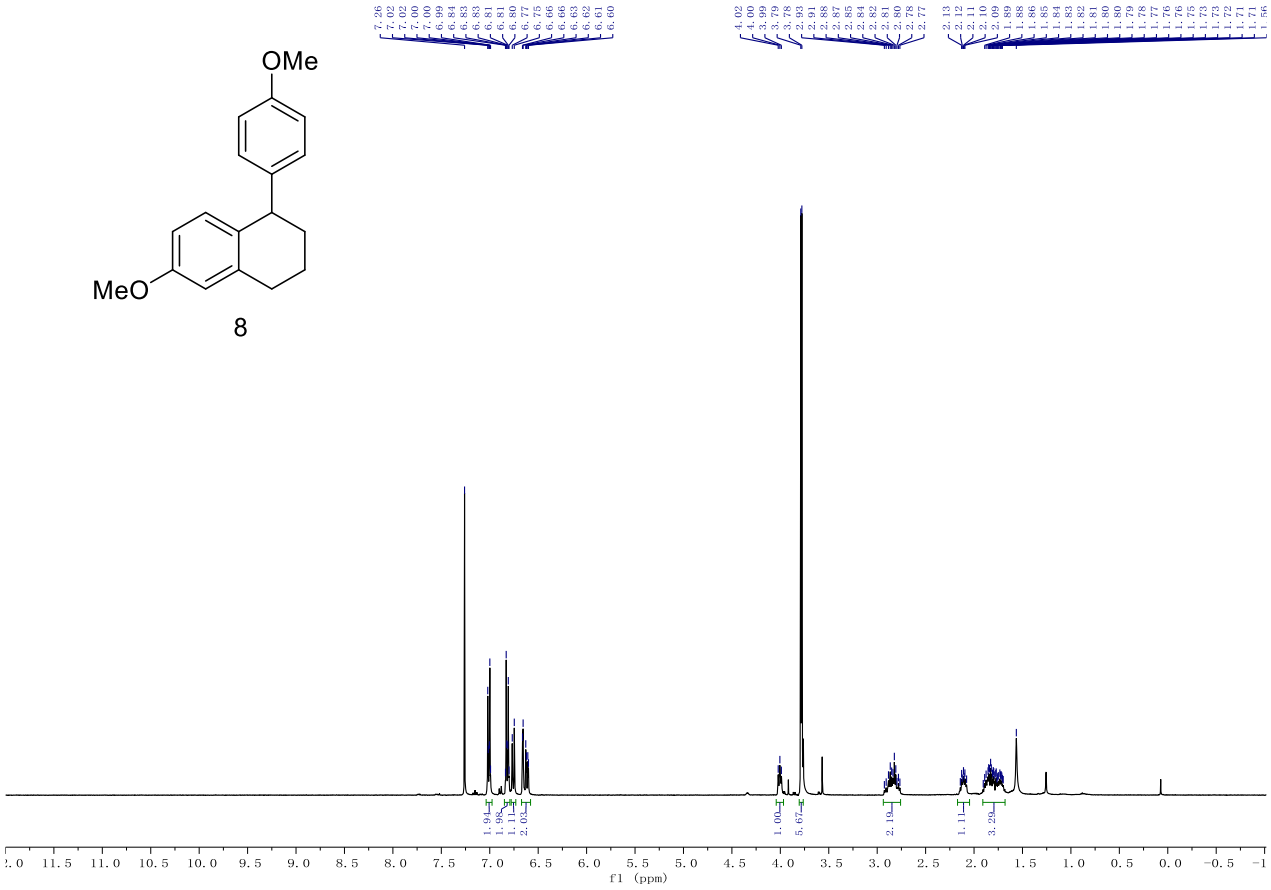

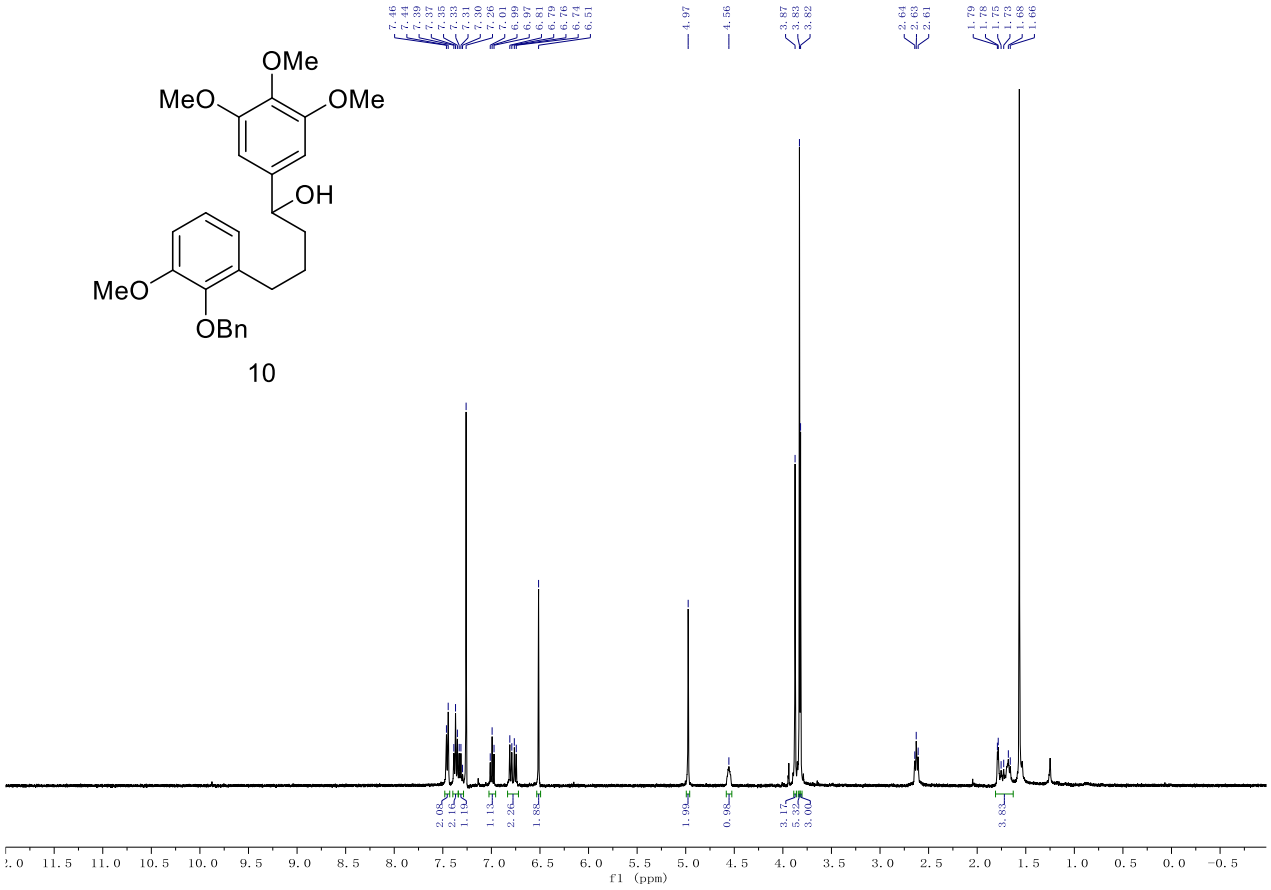

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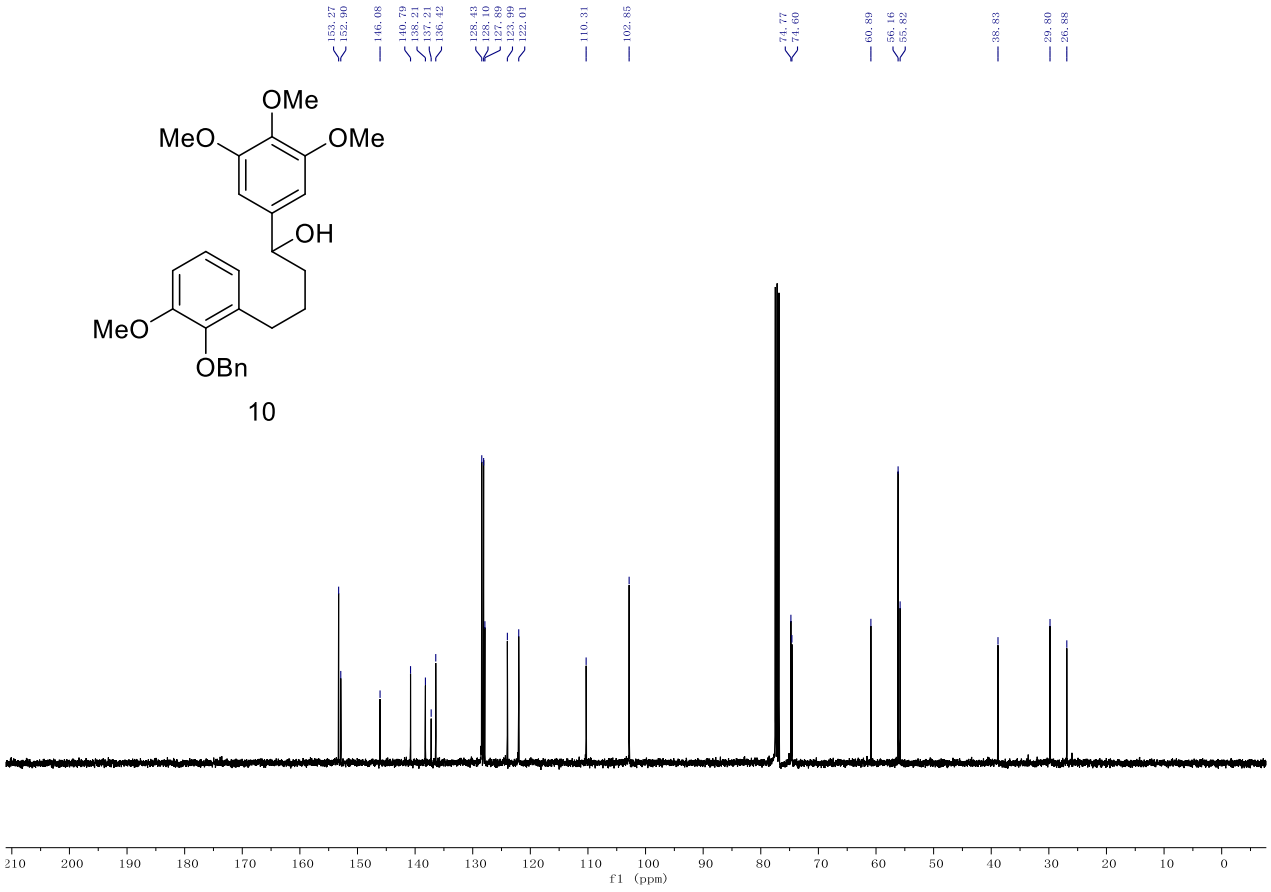

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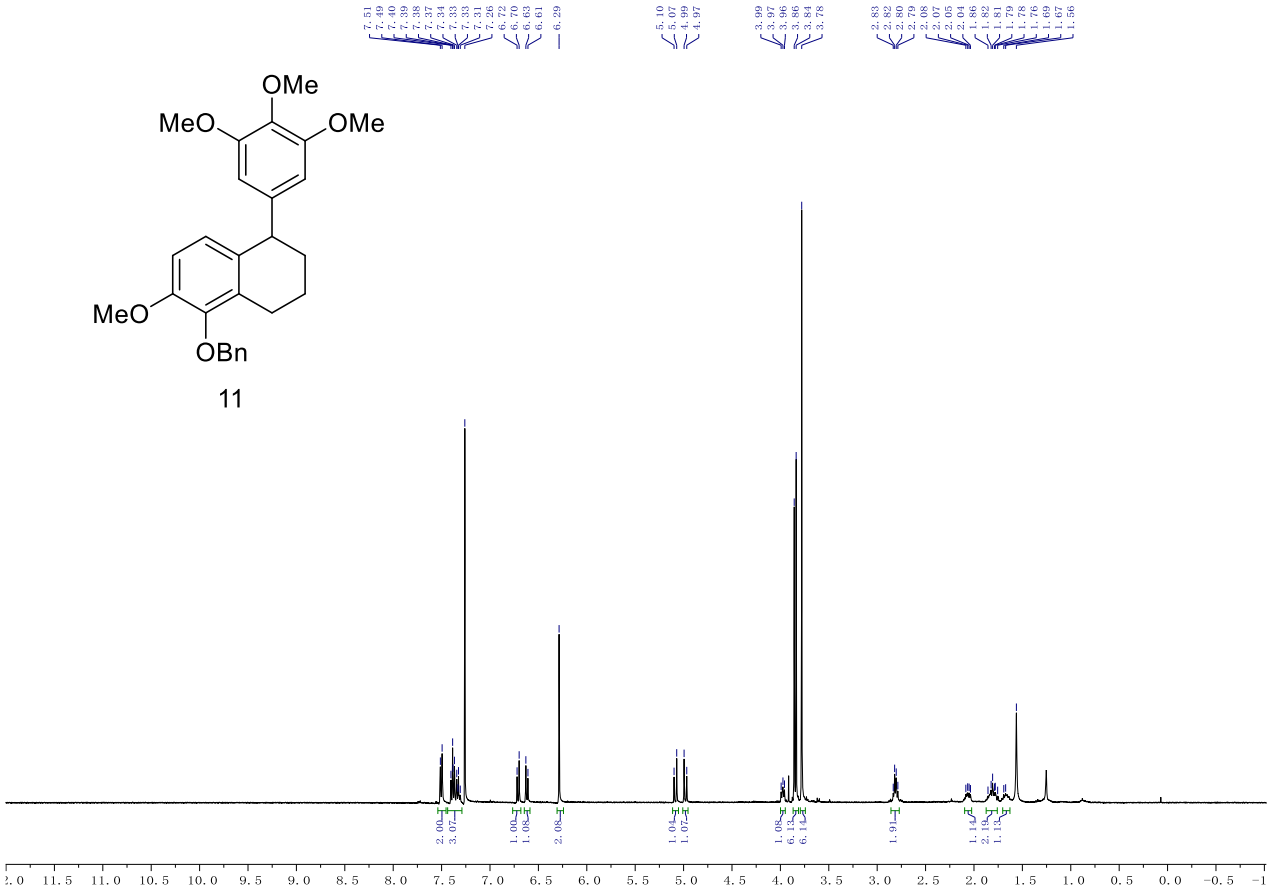

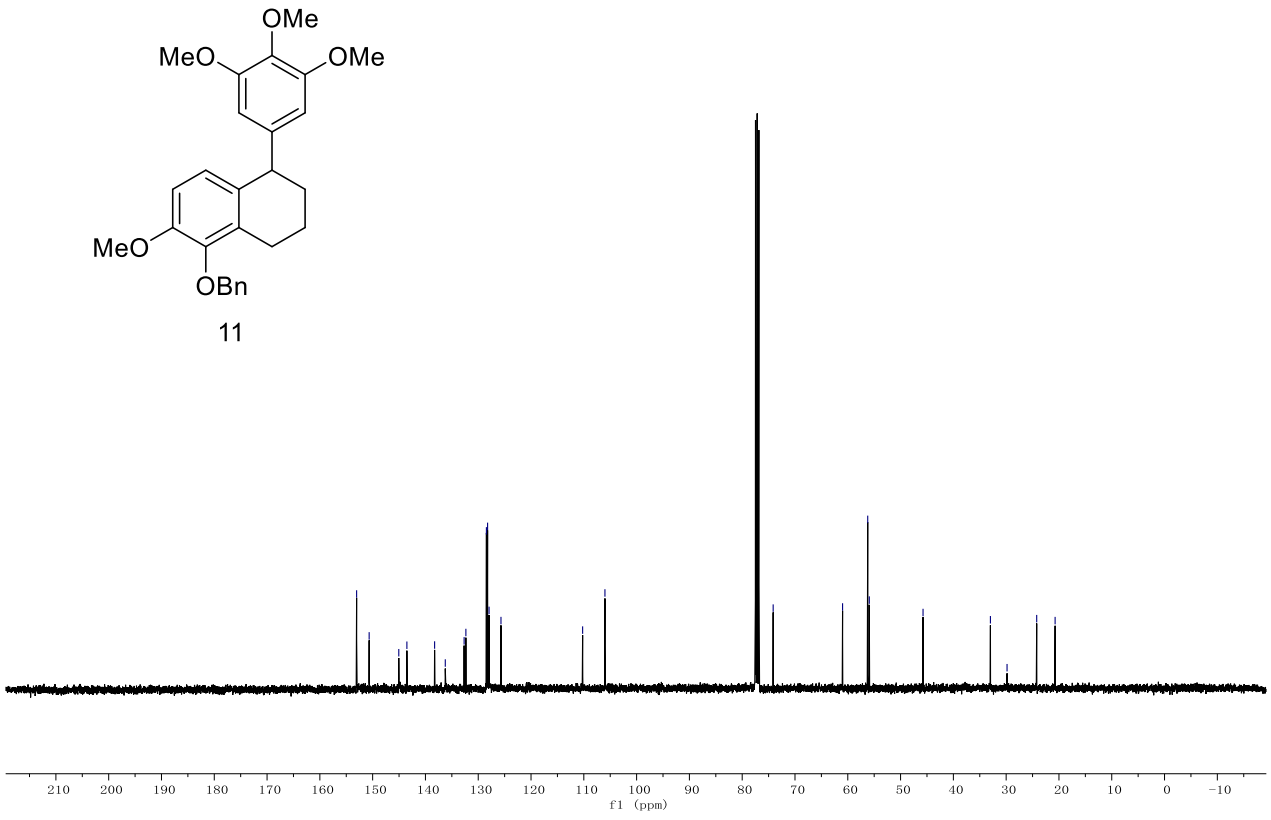

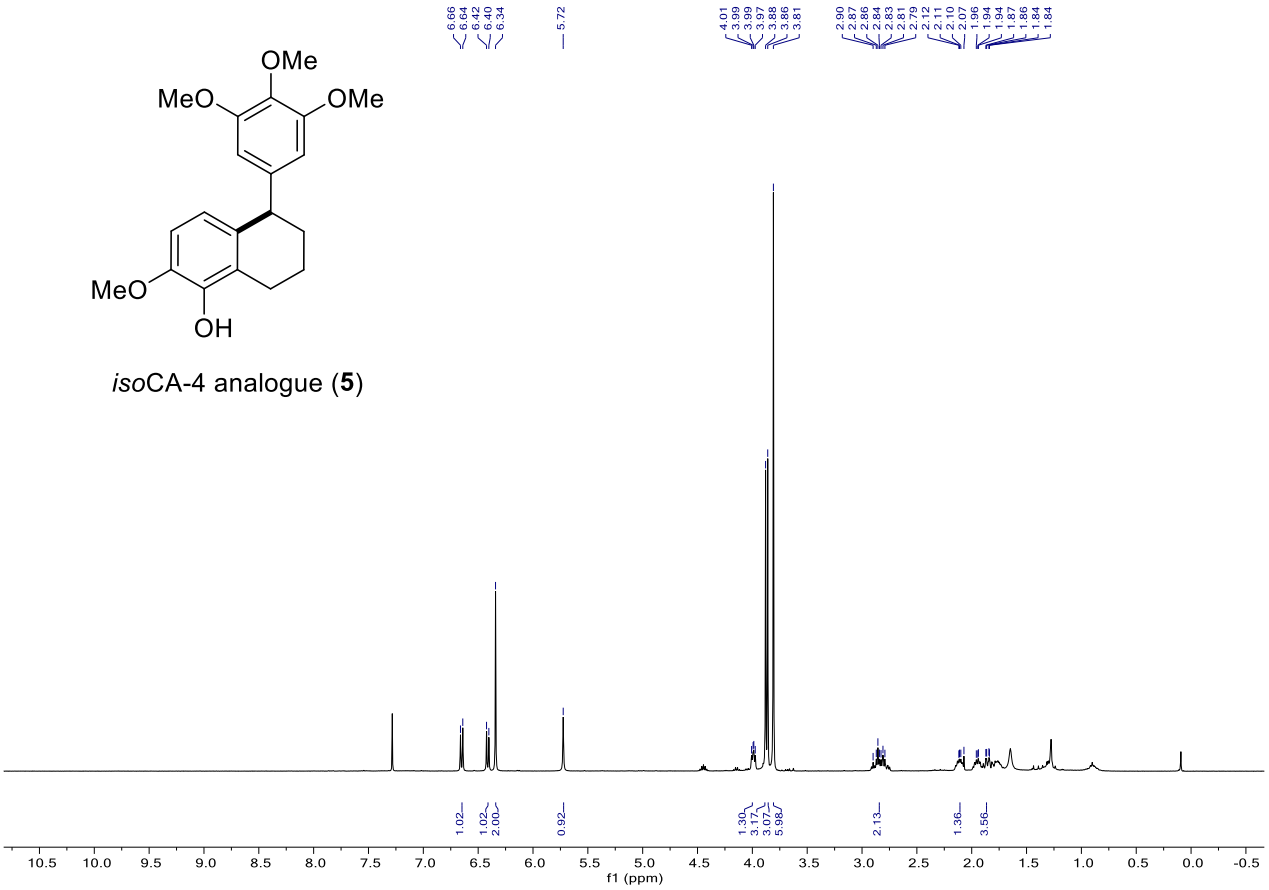

*iso*CA-4 analogue (**5**)