

Supporting Information

Visible light-triggered selective C(sp²)-H/C(sp³)-H coupling of benzenes with aliphatic hydrocarbons

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1. General Information

General Remarks

Substrates **1zh–1zm**, **1zn**, **1zo**, **1zp** and **1zr–1zu**, **2z**, **2zl**, **82** were synthesized according to the published procedures.^[1–6] $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was purchased from Sigma-Aldrich (purity $\geq 99.99\%$). All others reagents were purchased from commercial suppliers (TCI, Sigma-Aldrich, Alfa Aesar, Macklin, Energy Chemical, Laajoo, Leyan, Bide Pharmatech, Adamas-beta® and *J&K* Scientific) and used without further purification. Synthesis of the substrates were carried out under an argon atmosphere with magnetic stirring unless stated otherwise. Visible-light photochemical reactions were performed in 10 mL Schlenk tubes at the indicated temperature under an argon atmosphere and under irradiation with a 50 W LED lamp ($\lambda_{\text{max}} = 395$ nm, $\lambda_{\text{max}} = 410$ nm, $\lambda_{\text{max}} = 425$ nm and $\lambda_{\text{max}} = 455$ nm; commercial supplier: Hong Chang Lighting Co. Ltd., website: <http://hongchang-led.taobao.com>) or a 40 W Kessil LED lamp (PR160L, $\lambda_{\text{max}} = 370$ nm; commercial supplier: Anhui Kemi Instrument Co. Ltd., website: <http://www.ahkemi.com>).

Purification Techniques

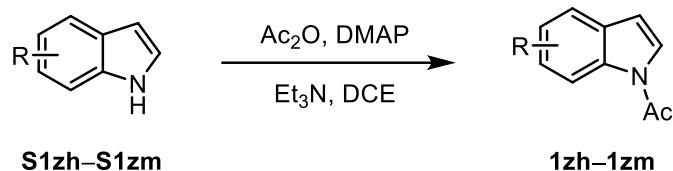
Flash column chromatography was performed with silica gel (300–400 mesh, pH = 6.7–7.0). Thin layer chromatography (TLC) were carried out on Leyan HPTLC Silica Gel 60 GF254, visualized with UV light (254 nm).

Analytical Techniques

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: $\text{CDCl}_3 = 7.26$ ppm (^1H NMR), 77.16 ppm (^{13}C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. High-resolution mass spectra were recorded on an Agilent 1290-G6545XT QTOF instrument using ESI technique. Power X-ray diffraction data were recorded on a XtaLAB Synergy four-circle diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184$ Å) at 100 K, 99.9 K and a Gemini S Ultra Synergy four-circle diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. Emission spectra were recorded on a Hitachi F-7000. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Qtac-100 LEIIS-XPS spectrometer with a hemispherical electron energy analyzer and a home-made reaction chamber. Monochromatic $\text{Al K}\alpha$ X-ray source (1486.6 eV, anode operating at 300 W) was used as the excitation source. The energy analysis error of the measurement was ± 0.2 eV for both binding energy and Auger energy. The binding energies in all the spectra were calibrated according to C 1s peak at 284.6 eV.

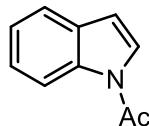
2. Synthesis of Substrates

According to the published procedure, ^[1] compounds **1zh–1zm** were prepared according to **general procedure A**.



General procedure A: To a solution of indole derivative (**S1zh–S1zm**, 10.0 mmol) in 1,2-dichloroethane (DCE) (20 mL), acetic anhydride (40.0 mmol), Et₃N (30.0 mmol) and 4-dimethylaminopyridine (DMAP) (3.8 mmol) were added, and the mixture was stirred at room temperature for 24 h. After completion of the reaction as monitored by TLC, the residue was washed with a saturated solution of NH₄Cl (30 mL) and extracted with CH₂Cl₂ (3×20 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated under vacuum. Purification using silica gel column chromatography (elution with petroleum ether (PE):ethyl acetate (EtOAc) = 9:1) afforded the pure product (**1zh–1zm**).

1-(1*H*-indol-1-yl)ethan-1-one (**1zh**)

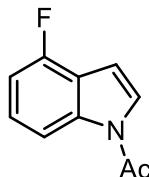


According to general procedure **A**, compound **1zh** was synthesized as a white solid (1.56 g, 9.80 mmol, 98% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.13 – 8.09 (m, 1H), 8.01 – 7.98 (m, 1H), 7.88 – 7.83 (m, 1H), 7.38 – 7.34 (m, 1H), 6.95 – 6.88 (m, 1H), 6.57 – 6.54 (m, 1H), 2.65 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.1, 135.8, 128.6, 127.4, 123.8, 122.7, 121.9, 116.5, 110.3, 24.5.

1-(4-fluoro-1*H*-indol-1-yl)ethan-1-one (**1zi**)

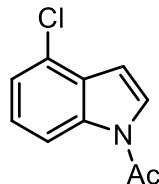


According to general procedure **A**, compound **1zi** was synthesized as a white solid (1.56 g, 8.80 mmol, 88% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.86 (m, 1H), 7.71 – 7.65 (m, 1H), 7.06 – 6.99 (m, 1H), 6.98 – 6.96 (m, 1H), 6.59 – 6.54 (m, 1H), 2.65 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.1, 156.5, 154.5, 136.8, 130.0, 124.5, 118.8, 111.8, 110.8, 24.5.

1-(4-chloro-1*H*-indol-1-yl)ethan-1-one (1zj)

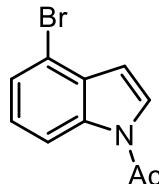


According to general procedure **A**, compound **1zj** was synthesized as a white solid (1.74 g, 8.98 mmol, 90% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.04 – 7.95 (m, 1H), 7.86 – 7.77 (m, 1H), 7.00 (d, *J* = 10.0 Hz, 2H), 6.60 – 6.52 (m, 1H), 2.67 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.2, 137.1, 130.1, 128.2, 126.8, 124.6, 121.6, 114.9, 112.3, 24.5.

1-(4-bromo-1*H*-indol-1-yl)ethan-1-one (1zk)

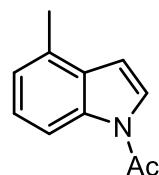


According to general procedure **A**, compound **1zk** was synthesized as a white solid (2.02 g, 8.48 mmol, 85% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.07 – 8.02 (m, 1H), 7.85 – 7.80 (m, 1H), 7.32 – 7.25 (m, 1H), 6.97 – 6.90 (m, 1H), 6.59 – 6.52 (m, 1H), 2.65 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.1, 138.8, 129.5, 128.5, 128.3, 123.2, 116.8, 115.6, 109.0, 24.5.

1-(4-methyl-1*H*-indol-1-yl)ethan-1-one (1zl)

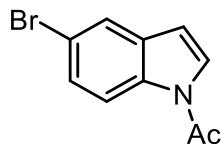


According to general procedure **A**, compound **1zl** was synthesized as a white solid (1.61 g, 9.29 mmol, 93% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.02 – 7.98 (m, 1H), 7.78 – 7.76 (m, 1H), 7.02 – 6.98 (m, 1H), 6.96 – 6.92 (m, 1H), 6.57 – 6.54 (m, 1H), 2.65 (s, 3H), 2.58 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.1, 136.3, 136.1, 125.2, 125.0, 122.5, 122.4, 113.7, 106.1, 24.5, 20.3.

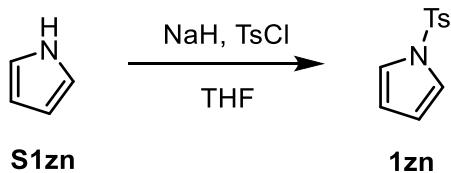
1-(5-bromo-1*H*-indol-1-yl)ethan-1-one (**1zm**)



According to general procedure **A**, compound **1zm** was synthesized as a white solid (2.00 g, 8.47 mmol, 85% yield).

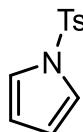
¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 15.5 Hz, 2H), 7.41 (d, *J* = 5.0 Hz, 2H), 6.58 – 6.54 (m, 1H), 2.65 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.1, 137.4, 127.8, 127.3, 125.8, 124.7, 122.1, 119.0, 111.1, 24.5.



According to the published procedure,^[2] compound **1zn** was synthesized. To a solution of pyrrole (**S1zn**, 10.0 mmol) in THF (15 mL), NaH (15.0 mmol) was added. The suspension was stirred for 30 min, then tosyl chloride (12.0 mmol) in THF (5.0 mL) was added. The mixture was stirred for additional 3 h, then quenched with water (30 mL), and extracted with EtOAc (3×20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Purification using silica gel column chromatography (elution with PE:EtOAc = 2:1) afforded the pure product **1zn** as a white solid (1.81 g, 8.18 mmol, 82% yield).

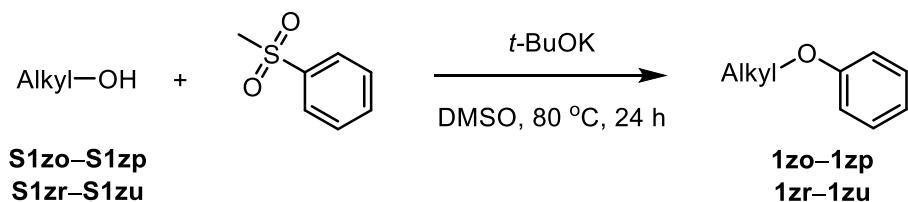
1-tosyl-1*H*-pyrrole (**1zn**)



¹H NMR (500 MHz, CDCl₃) δ 7.78 – 7.72 (m, 2H), 7.62 – 7.54 (m, 2H), 7.47 – 7.41 (m, 2H), 6.28 – 6.22 (m, 2H), 2.43 (s, 3H).

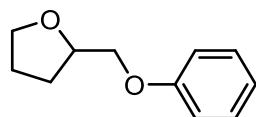
¹³C NMR (126 MHz, CDCl₃) δ 144.3, 136.9, 129.7, 127.2, 127.2, 101.7, 21.2.

According to the published procedure,^[3] compounds **1zo**, **1zp** and **1zr–1zu** were prepared according to **general procedure B**.



General procedure B: A Schlenk tube was added *t*-BuOK (4.0 mmol), (methylsulfonyl)benzene (2.0 mmol) under an argon atmosphere in a glove box. DMSO (2.0 mL) and alkyl alcohol (**S1zo–S1zp**, **S1zr–S1zu**, 4.0 mmol) were added *via* syringe under an argon atmosphere. The reaction mixture was heated to 80 °C in an oil bath and stirred for 24 h. Upon completion of the reaction, the sealed vial was cooled to room temperature. H₂O (20 mL) was added to quench the reaction. The mixture was extracted with dichloromethane (DCM) (3 × 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Purification using silica gel column chromatography (elution with hexane) afforded the compounds (**1zo–1zp** and **1zr–1zu**).

2-(phenoxy)methyltetrahydrofuran (1zo)

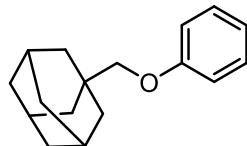


According to **general procedure B**, compound **1zo** was synthesized as a colorless oil (0.32 g, 1.80 mmol, 90% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.22 (m, 2H), 6.97 – 6.88 (m, 3H), 4.35 – 4.21 (m, 1H), 4.15 – 3.94 (m, 2H), 3.91 – 3.74 (m, 2H), 2.05 – 1.86 (m, 1H), 1.75 – 1.60 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 159.2, 129.8, 121.5, 115.8, 78.3, 70.3, 69.2, 30.3, 25.6.

1-(phenoxymethyl)adamantane (1zp)

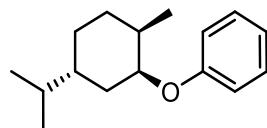


According to **general procedure B**, compound **1zp** was synthesized as a colorless oil (0.45 g, 1.86 mmol, 92% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.51 – 7.23 (m, 2H), 6.97 – 6.88 (m, 3H), 3.66 (s, 2H), 2.04 – 1.95 (m, 3H), 1.74 (d, *J* = 33.0 Hz, 6H), 1.70 (t, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 159.1, 129.5, 121.9, 115.9, 80.3, 39.3, 37.4, 33.2, 29.6.

((1*S*,2*R*,5*R*)-5-isopropyl-2-methylcyclohexyl)oxy)benzene (1zr)

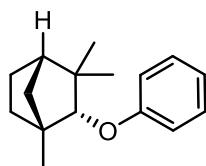


According to **general procedure B**, compound **1zr** was synthesized as a colorless oil (0.38 g, 1.64 mmol, 82% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.23 (m, 2H), 6.92 – 6.85 (m, 3H), 4.05 – 3.99 (m, 1H), 2.26 – 2.14 (m, 2H), 1.73 – 1.70 (m, 2H), 1.53 – 1.44 (m, 2H), 1.14 – 0.99 (m, 2H), 0.93 – 0.89 (m, 7H), 0.77 (d, *J* = 7.0 Hz, 3H)

¹³C NMR (126 MHz, CDCl₃) δ 158.4, 129.5, 120.4, 115.9, 48.1, 40.4, 34.6, 31.5, 26.1, 23.8, 22.2, 20.8, 16.6.

(1*R*,2*R*,4*S*)-1,3,3-trimethyl-2-phenoxybicyclo[2.2.1]heptane (1zs)



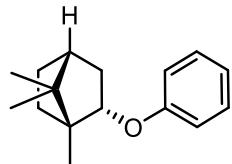
According to **general procedure B**, compound **1zs** was synthesized as a colorless oil (0.39 g, 1.69 mmol, 85% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.21 (m, 2H), 6.91 – 6.86 (m, 3H), 3.86 (d, *J* = 1.5 Hz, 1H), 2.05 – 2.02 (m, 1H), 1.77 – 1.72 (m, 2H), 1.60 – 1.47 (m, 1H), 1.51 – 1.43 (m, 1H), 1.21 – 1.17 (m, 4H), 1.12 – 1.05 (m, 4H), 0.86 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 160.3, 129.3, 120.1, 115.8, 90.0, 49.5, 49.1, 41.4, 40.0, 30.5,

26.4, 25.9, 20.4, 19.9.

(1*R*,2*S*,4*R*)-1,3,7,7-tetramethyl-2-phenoxybicyclo[2.2.1]heptane (1zt)

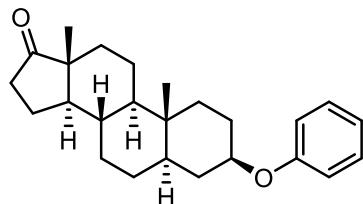


According to **general procedure B**, compound **1zt** was synthesized as a colorless oil (0.32 g, 1.39 mmol, 70% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.31 (t, *J* = 8.0 Hz, 2H), 6.98 – 6.84 (m, 3H), 4.40 – 4.35 (m, 1H), 2.42 (td, *J* = 9.3, 4.6 Hz, 1H), 2.30 (dt, *J* = 7.6, 4.7 Hz, 1H), 1.85 – 1.78 (m, 2H), 1.43 – 1.37 (m, 1H), 1.33 – 1.29 (m, 1H), 1.18 (dd, *J* = 13.3, 3.3 Hz, 1H), 1.00 (s, 3H), 0.97 (d, *J* = 5.0 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 159.2, 129.4, 120.1, 115.5, 82.7, 49.5, 47.6, 45.2, 36.9, 28.0, 26.8, 19.8, 19.0, 13.8.

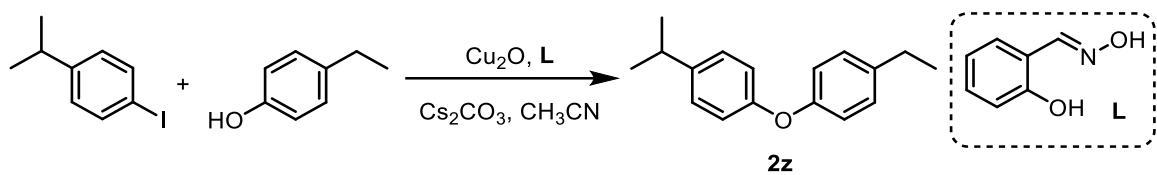
(3*R*,5*R*,8*S*,9*R*,10*R*,13*R*,14*R*)-10,13-dimethyl-3-phenoxyhexadecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (1zu)



According to **general procedure B**, compound **1zu** was synthesized as a colorless oil (0.44 g, 1.20 mmol, 60% yield).

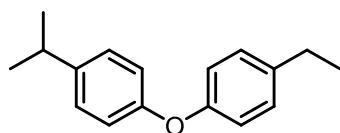
¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.24 (m, 2H), 7.01 – 6.86 (m, 3H), 3.66 – 3.52 (m, 1H), 2.37 – 2.12 (m, 2H), 1.94 – 1.77 (m, 4H), 1.72 – 1.46 (m, 6H), 1.45 – 1.26 (m, 5H), 1.23 – 1.13 (m, 2H), 1.11 – 0.99 (m, 2H), 0.86 (s, 3H), 0.82 (s, 3H), 0.80 – 0.68 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 219.9, 157.5, 130.1, 121.7, 117.1, 78.2, 54.4, 52.1, 48.6, 44.7, 37.7, 36.3, 36.2, 36.0, 33.6, 33.0, 31.2, 28.3, 26.3, 22.1, 22.0, 14.6, 13.4.



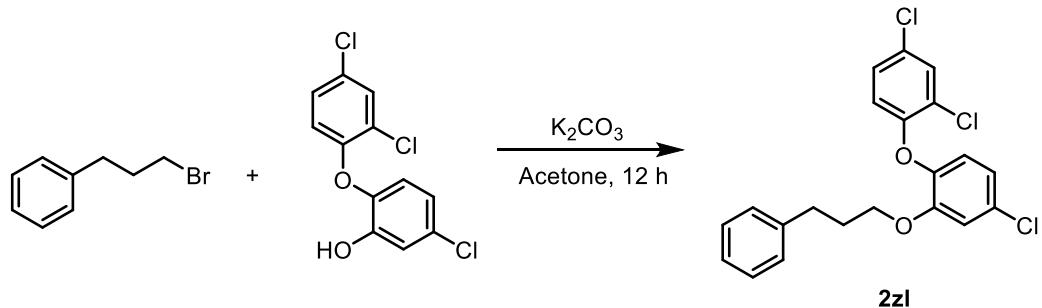
According to the published procedure,^[4] compound **2z** was synthesized. To a solution of Cu₂O (2.0 mmol) and ligand (2.0 mmol) in DMF (6.0 mL), 4-ethylphenol (10.0 mmol), 1-iodo-4-isopropylbenzene (15.0 mmol) and cesium carbonate (20.0 mmol) were added at 110 °C for 30 h. Purification using silica gel column chromatography (elution with hexane) afforded the compound **2z** as a colorless oil (1.56 g, 6.50 mmol, 65% yield).

1-ethyl-4-(4-isopropylphenoxy)benzene (**2z**)



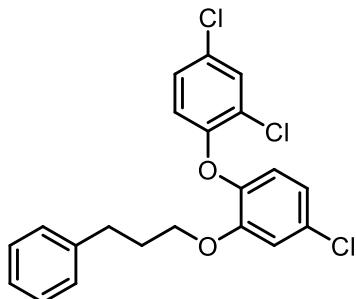
¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.33 (m, 5H), 7.32 – 7.30 (m, 1H), 7.17 – 7.11 (m, 2H), 2.95 – 2.80 (m, 1H), 2.72 (q, 2H), 1.21 (s, 3H), 1.19 (s, 3H), 1.18 (t, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.5, 153.6, 142.5, 139.6, 129.2, 128.5, 120.1, 119.4, 34.0, 27.8, 23.4, 13.2.



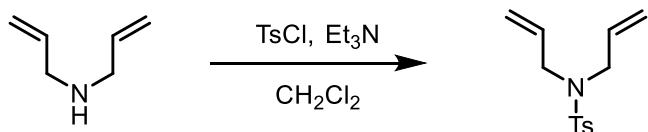
According to the published procedure,^[5] compound **2zl** was synthesized. The mixture of triclosan (7.5 mmol), (3-bromopropyl)benzene (5.0 mmol) and K₂CO₃ (10.0 mmol) in acetone (20 mL) was heated to reflux. Upon completion stirring for 12 h, the reaction mixture was cooled to room temperature and filtered. Purification using silica gel column chromatography (elution with PE:EtOAc = 10:1) afforded the compound **2zl** as a colorless oil (1.46 g, 3.60 mmol, 72% yield).

2,4-dichloro-1-(4-chloro-2-(3-phenylpropoxy)phenoxy)benzene (2zl)



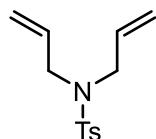
¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 2.5 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.19 – 7.16 (m, 1H), 7.10 – 7.06 (m, 3H), 7.00 – 6.97 (m, 1H), 6.93 – 6.91 (m, 2H), 6.65 (d, *J* = 8.8 Hz, 1H), 3.89 (d, *J* = 6.1 Hz, 2H), 2.55 (dd, *J* = 8.4, 6.7 Hz, 2H), 1.95 – 1.91 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 152.2, 148.6, 145.1, 142.0, 131.3, 130.5, 129.9, 128.5, 128.4, 128.4, 126.2, 124.2, 123.4, 120.5, 117.4, 116.1, 69.2, 32.7, 30.2.



According to the published procedure, ^[6] compound **82** was synthesized. In a round-bottom flask on ice, triethylamine (12.0 mmol) was added dropwise to a solution of diallylamine (**S82**, 12.0 mmol) in DCM (20 mL). The reaction was stirred at 0 °C for 30 min and 4-toluenesulfonyl chloride (10.0 mmol) was added slowly to the reaction. The reaction was slowly warmed to room temperature and stirred overnight. The reaction was washed with water and brine. The organic layer was dried over sodium sulfate and concentrated under reduced pressure afforded the compound **82** as a colorless oil (2.05 g, 8.20 mmol, 68% yield).

***N,N*-diallyl-4-methylbenzenesulfonamide (82)**



¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.64 – 5.56 (m, 2H), 5.15 (dd, *J* = 2.5, 1.2 Hz, 2H), 5.14 – 5.11 (m, 2H), 3.80 (d, *J* = 6.3 Hz, 4H), 2.42 (s, 3H).

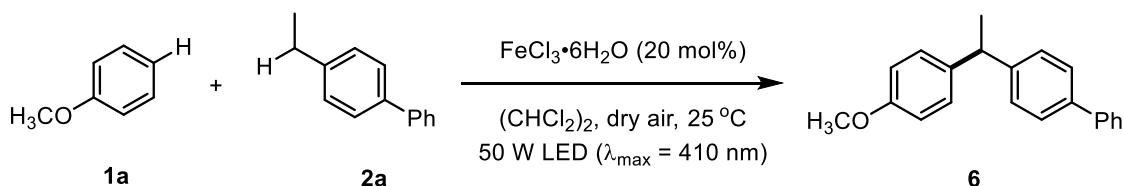
¹³C NMR (126 MHz, CDCl₃) δ 143.0, 137.3, 132.5, 129.5, 126.9, 118.7, 49.2, 21.2.

3. Photochemical C(sp²)-H/C(sp³)-H Coupling Reactions

3.1 Optimization of Reaction Conditions

A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410 \text{ nm}$). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with petroleum ether (PE): dichloromethane (DCM) = 5:1) gave the pure product.

Supplementary Table 1. Investigation of other conditions.^a

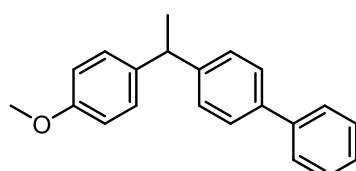


Entry	Deviation from standard conditions	Yield(%) ^b
1	O_2 instead of dry air	50
2	Ar instead of dry air	24
3	0.40 mmol H_2O as the additive	22
4	0.40 mmol K_2CO_3 as the additive	trace
5	0.40 mmol 2,2'-bipyridine as the additive	0

^a Reaction conditions: **1a** (0.30 mmol), **2a** (0.90 mmol), metal salt (0.060 mmol), indicated additive (0.40 mmol), $(\text{CHCl}_2)_2$ (0.75 mL), under dry air, irradiation with a 50 W LED lamp ($\lambda_{\text{max}} = 410 \text{ nm}$), 25 °C, 48 h. ^b Isolated yield.

3.2 Substrate Scope

4-(1-(4-methoxyphenyl)ethyl)-1,1'-biphenyl (3)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk

tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **3** as a white solid (65.7 mg, 0.228 mmol, 76% yield).

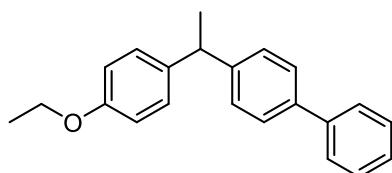
¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.61 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.92 – 6.89 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 1.70 (d, *J* = 7.3 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.0, 146.0, 141.1, 139.0, 138.6, 128.8, 128.7, 128.1, 127.2, 127.2, 127.1, 113.9, 55.4, 43.8, 22.2.

IR (film): ν (cm⁻¹) 3500, 2964, 2813, 1867, 1661, 1536, 1407, 1251, 1078, 831, 621.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₂₁O⁺ [M+H]⁺ 289.1587, found 289.1600.

4-(1-(4-ethoxyphenyl)ethyl)-1,1'-biphenyl (**4**)



A Schlenk tube (10 mL) was charged with ethoxybenzene (**1b**, 36.6 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **4** as a colorless oil (67.1 mg, 0.207 mmol, 74% yield).

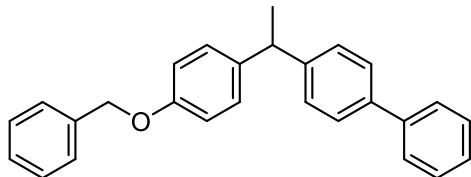
¹H NMR (500 MHz, CDCl₃) δ 7.62 – 7.60 (m, 2H), 7.57 – 7.54 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.90 – 6.87 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.69 (d, *J* = 7.2 Hz, 3H), 1.44 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.4, 146.1, 141.2, 139.0, 138.4, 128.8, 128.6, 128.1, 127.2, 127.1, 127.1, 114.5, 63.5, 43.8, 22.2, 15.0.

IR (film): ν (cm⁻¹) 3505, 2942, 2776, 2531, 1665, 1573, 1407, 1150, 1078, 895, 569.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₃O⁺ [M+H]⁺ 325.1563, found 325.1570.

4-(1-(4-(benzyloxy)phenyl)ethyl)-1,1'-biphenyl (5)



A Schlenk tube (10 mL) was charged with (benzyloxy)benzene (**1c**, 55.2 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **5** as a colorless oil (60.1 mg, 0.165 mmol, 55% yield).

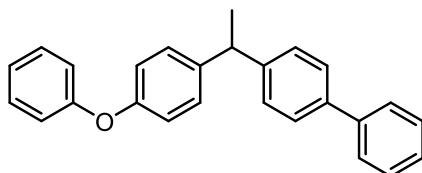
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 7.6$ Hz, 2H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.42 (m, 6H), 7.32 (m, 4H), 7.20 (d, $J = 8.6$ Hz, 2H), 6.95 (d, $J = 8.6$ Hz, 2H), 5.06 (s, 2H), 4.17 (q, $J = 7.2$ Hz, 1H), 1.67 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.3, 146.0, 141.2, 139.0, 138.9, 137.3, 128.8, 128.7, 128.7, 128.1, 128.1, 127.6, 127.2, 127.2, 127.2, 114.9, 70.2, 43.8, 22.2.

IR (film): ν (cm⁻¹) 3500, 3337, 2927, 1705, 1669, 1506, 1363, 1053, 825, 706, 672.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{27}\text{H}_{25}\text{O}^+$ [M+H]⁺ 365.1900, found 365.1907.

4-(1-(4-phenoxyphenyl)ethyl)-1,1'-biphenyl (6)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **6** as a white solid (78.8 mg, 0.225 mmol, 75% yield).

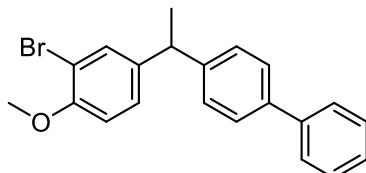
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 – 7.58 (m, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.36 – 7.30 (m, 5H), 7.23 (d, $J = 8.6$ Hz, 2H), 7.09 (t, $J = 7.4$ Hz, 1H), 7.04 – 6.95 (m, 4H), 4.20 (q, $J = 7.2$ Hz, 1H), 1.69 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.6, 155.5, 145.7, 141.3, 141.1, 139.1, 129.8, 129.0, 128.9, 128.1, 127.3, 127.2, 127.2, 123.2, 119.0, 118.9, 44.0, 22.2.

IR (film): ν (cm $^{-1}$) 3488, 3407, 2844, 1705, 1683, 1546, 1363, 1235, 1053, 825, 672.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{26}\text{H}_{23}\text{O}^+$ [M+H] $^+$ 351.1743, found 351.1749.

4-(1-(3-bromo-4-methoxyphenyl)ethyl)-1,1'-biphenyl (7)



A Schlenk tube (10 mL) was charged with 2-bromoanisole (**1e**, 56.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **7** as a white solid (74.7 mg, 0.204 mmol, 68% yield).

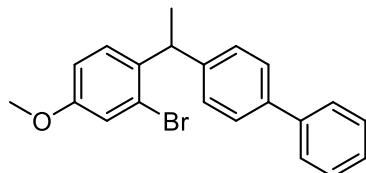
^1H NMR (500 MHz, CDCl_3) δ 7.60 – 7.57 (m, 2H), 7.55 – 7.52 (m, 2H), 7.46 (d, $J = 2.2$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.16 (m, 1H), 6.85 (d, $J = 8.5$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 1H), 3.88 (s, 3H), 1.65 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 145.2, 141.0, 140.2, 139.3, 132.5, 128.9, 128.0, 127.7, 127.3, 127.2, 127.1, 112.0, 111.7, 56.4, 43.5, 22.1.

IR (film): ν (cm $^{-1}$) 3500, 3337, 3147, 2927, 1681, 1669, 1506, 1363, 1323, 1053, 825, 706, 672, 493.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{19}\text{BrNaO}^+$ [M+Na] $^+$ 389.0511, found 389.0517.

4-(1-(2-bromo-4-methoxyphenyl)ethyl)-1,1'-biphenyl (8)



A Schlenk tube (10 mL) was charged with 3-bromoanisole (**1f**, 56.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp (λ_{max}

$\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **8** as a colorless oil (68.1 mg, 0.186 mmol, 62% yield).

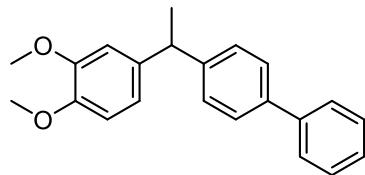
¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.62 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.37 (m, 3H), 7.22 – 7.19 (m, 2H), 6.89 (m, 1H), 4.68 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.4, 144.6, 141.1, 139.0, 137.4, 129.2, 128.8, 128.2, 127.2, 127.1, 127.1, 124.9, 118.0, 114.0, 55.6, 42.5, 21.6.

IR (film): ν (cm⁻¹) 3500, 3337, 3147, 2927, 1681, 1669, 1506, 1480, 1323, 1053, 988, 735, 672, 467.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₁₉BrNaO⁺ [M+Na]⁺ 389.0511, found 389.0521.

4-(1-(3,4-dimethoxyphenyl)ethyl)-1,1'-biphenyl (**9**)



A Schlenk tube (10 mL) was charged with 1,2-dimethoxybenzene (**1g**, 41.4 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 3:1) gave the pure product **9** as a white solid (66.8 mg, 0.210 mmol, 70% yield).

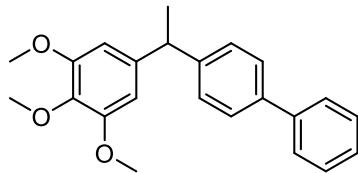
¹H NMR (500 MHz, CDCl₃) δ 7.60 – 7.57 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 11.5 Hz, 2H), 6.78 (d, *J* = 5.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.0, 147.5, 145.9, 141.1, 139.0, 139.0, 128.8, 128.0, 127.2, 127.2, 127.1, 119.5, 111.4, 111.2, 56.0, 56.0, 44.2, 22.2.

IR (film): ν (cm⁻¹) 3507, 2972, 2013, 1867, 1661, 1431, 1407, 1326, 1251, 1078, 831, 621, 597, 550.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₃O₂⁺ [M+H]⁺ 319.1693, found 319.1685.

4-(1-(3,4,5-trimethoxyphenyl)ethyl)-1,1'-biphenyl (**10**)



A Schlenk tube (10 mL) was charged with 1,2,3-trimethoxybenzene (**1h**, 50.5 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **10** as a white solid (70.0 mg, 0.201 mmol, 67% yield).

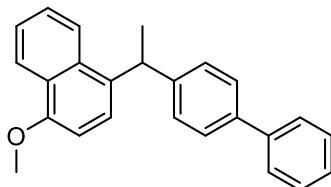
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 7.8$ Hz, 2H), 7.54 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 7.33 (t, $J = 8.1$ Hz, 3H), 6.95 (d, $J = 8.6$ Hz, 1H), 6.68 (d, $J = 8.6$ Hz, 1H), 4.52 (q, $J = 7.1$ Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.70 (s, 3H), 1.63 (d, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 152.2, 151.7, 146.2, 142.4, 141.2, 138.7, 132.5, 128.8, 128.1, 127.1, 127.1, 127.0, 122.0, 107.2, 60.9, 60.8, 56.1, 37.7, 21.8.

IR (film): ν (cm^{-1}) 3507, 2972, 1867, 1608, 1431, 1396, 1326, 1314, 1251, 1078, 831, 666, 585, 542.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{23}\text{H}_{25}\text{O}_3^+ [\text{M}+\text{H}]^+$ 349.1798, found 349.1803.

1-(1-([1,1'-biphenyl]-4-yl)ethyl)-4-methoxynaphthalene (**11**)



A Schlenk tube (10 mL) was charged with 1-methoxynaphthalene (**1i**, 47.5 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 4:1) gave the pure product **11** as a white solid (55.8 mg, 0.165 mmol, 55% yield).

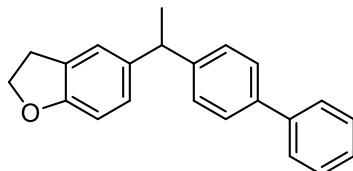
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 8.9$ Hz, 1H), 7.54 (d, $J = 7.6$ Hz, 2H), 7.46 – 7.44 (m, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 4H), 7.03 (m, 1H), 6.98 (d, $J = 2.2$ Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 1H), 3.76 (s, 3H), 1.63 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.5, 145.7, 141.5, 141.1, 139.1, 133.3, 129.3, 129.1, 128.8, 128.3, 127.4, 127.2, 127.2, 127.1, 127.0, 125.4, 118.8, 105.8, 55.4, 44.5, 22.0.

IR (film): ν (cm⁻¹) 3507, 3096, 1955, 1587, 1431, 1390, 1274, 1251, 1003, 845, 618, 497, 472.

HRMS (ESI-TOF, m/z) calculated for C₂₅H₂₃O⁺ [M+H]⁺ 339.1743, found 339.1744.

5-(1-([1,1'-biphenyl]-4-yl)ethyl)-2,3-dihydrobenzofuran (12)



A Schlenk tube (10 mL) was charged with 2,3-dihydrobenzofuran (**1j**, 36.0 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **12** as a colorless oil (51.3 mg, 0.171 mmol, 57% yield).

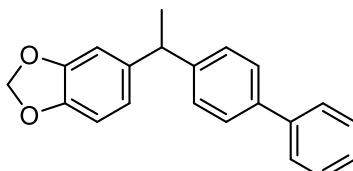
¹H NMR (500 MHz, CDCl₃) δ 7.60 (m, 2H), 7.56 – 7.54 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.36 – 7.32 (m, 3H), 7.10 (s, 1H), 7.06 – 7.04 (m, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 4.56 (t, $J = 8.7$ Hz, 2H), 4.17 (q, $J = 7.2$ Hz, 1H), 3.19 (t, $J = 8.7$ Hz, 2H), 1.68 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.5, 146.2, 141.1, 138.9, 138.6, 128.8, 128.0, 127.2, 127.2, 127.1, 124.2, 109.1, 71.3, 44.0, 30.0, 29.8, 22.3.

IR (film): ν (cm⁻¹) 3067, 3012, 2779, 1856, 1751, 1478, 1407, 1266, 1251, 1038, 851, 550.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₀NaO⁺ [M+Na]⁺ 323.1406, found 323.1412.

5-(1-([1,1'-biphenyl]-4-yl)ethyl)benzo[d][1,3]dioxole (13)



A Schlenk tube (10 mL) was charged with 1,3-benzodioxole (**1k**, 36.6 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to

dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **13** as a white solid (62.5 mg, 0.207 mmol, 69% yield).

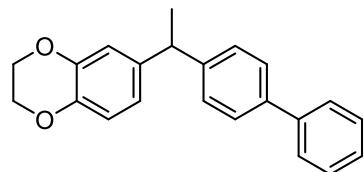
¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.78 – 6.74 (m, 3H), 5.93 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 147.8, 145.9, 145.7, 141.1, 140.5, 139.1, 128.8, 128.0, 127.3, 127.2, 127.2, 120.5, 108.3, 108.2, 101.0, 44.3, 22.2.

IR (film): ν (cm⁻¹) 3601, 3061, 3033, 2770, 1751, 1447, 1407, 1266, 1251, 1091, 851, 737, 550.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₁₉O₂⁺ [M+H]⁺ 303.1380, found 303.1383.

6-(1-([1,1'-biphenyl]-4-yl)ethyl)-2,3-dihydrobenzo[b][1,4]dioxine (14)



A Schlenk tube (10 mL) was charged with 1,4-benzodioxan (**11**, 58.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **14** as a colorless oil (65.4 mg, 0.207 mmol, 69% yield).

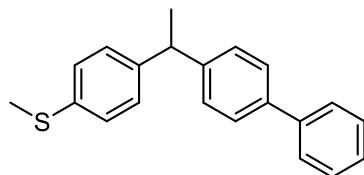
¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 (dd, *J* = 18.2, 7.7 Hz, 3H), 6.77 (m, 3H), 4.24 (s, 4H), 4.10 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.8, 143.4, 142.0, 141.2, 139.9, 139.1, 128.8, 128.0, 127.3, 127.2, 120.7, 117.2, 116.4, 64.6, 64.5, 44.0, 22.1.

IR (film): ν (cm⁻¹) 3450, 3057, 2995, 2762, 1798, 1502, 1478, 1427, 1212, 1176, 1008, 715, 535.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₁O₂⁺ [M+H]⁺ 317.1536, found 317.1543.

(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenyl)(methyl)sulfane (15)



A Schlenk tube (10 mL) was charged with thioanisole (**1m**, 37.3 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 3:1) gave the pure product **15** as a colorless oil (48.4 mg, 0.159 mmol, 53% yield).

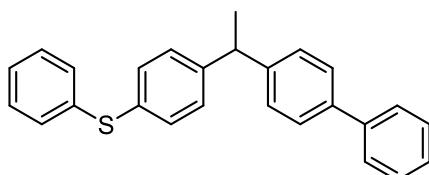
¹H NMR (500 MHz, CDCl_3) δ 7.57 – 7.53 (m, 2H), 7.51 – 7.48 (m, 2H), 7.42 – 7.38 (m, 2H), 7.32 – 7.28 (m, 1H), 7.26 (d, $J = 8.1$ Hz, 2H), 7.21 – 7.16 (m, 4H), 4.14 (q, $J = 7.2$ Hz, 1H), 2.43 (s, 3H), 1.64 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl_3) δ 145.5, 143.5, 141.1, 139.1, 135.9, 128.8, 128.3, 128.1, 127.3, 127.2, 127.1, 127.1, 44.1, 21.9, 16.3.

IR (film): ν (cm⁻¹) 3510, 3076, 3062, 2985, 1791, 1302, 1272, 1095, 1025, 691, 478, 435.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{21}\text{S}^+ [\text{M}+\text{H}]^+$ 305.1358, found 305.1355.

(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenyl)(phenyl)sulfane (16)



A Schlenk tube (10 mL) was charged with diphenylsulfane (**1n**, 55.8 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **16** as a white solid (54.9 mg, 0.150 mmol, 50% yield).

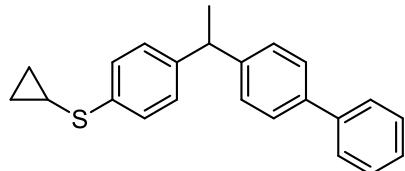
¹H NMR (500 MHz, CDCl_3) δ 7.57 – 7.54 (m, 2H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.40 (t, $J = 7.7$ Hz, 2H), 7.36 – 7.23 (m, 9H), 7.22 – 7.18 (m, 3H), 4.16 (q, $J = 7.2$ Hz, 1H), 1.65 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.7, 145.2, 141.0, 139.3, 136.3, 132.9, 131.6, 130.8, 129.3, 128.9, 128.7, 128.1, 127.3, 127.2, 127.1, 126.9, 44.3, 21.9.

IR (film): ν (cm⁻¹) 3503, 3019, 3004, 2856, 1723, 1685, 1483, 1075, 1027, 694, 478, 431.

HRMS (ESI-TOF, m/z) calculated for C₂₆H₂₃S⁺ [M+H]⁺ 367.1515, found 367.1506.

(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenyl)cyclopropylsulfane (17)



A Schlenk tube (10 mL) was charged with cyclopropyl(phenyl)sulfane (**1o**, 45.0 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **17** as a colorless oil (49.5 mg, 0.150 mmol, 50% yield).

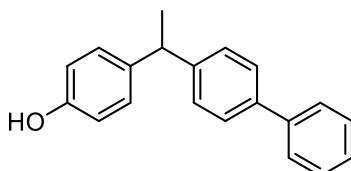
¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.60 (m, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.38 – 7.32 (m, 5H), 7.23 (d, $J = 8.3$ Hz, 2H), 4.20 (q, $J = 7.2$ Hz, 1H), 2.21 (tt, $J = 7.4, 4.4$ Hz, 1H), 1.71 (d, $J = 7.2$ Hz, 3H), 1.09 – 1.05 (m, 2H), 0.74 – 0.71 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 145.5, 143.4, 141.1, 139.1, 136.2, 128.8, 128.2, 128.1, 127.2, 127.2, 127.1, 126.9, 44.1, 22.0, 12.4, 8.6.

IR (film): ν (cm⁻¹) 3492, 3053, 3012, 2766, 1723, 1685, 1480, 1095, 1074, 691, 476, 467.

HRMS (ESI-TOF, m/z) calculated for C₂₃H₂₃S⁺ [M+H]⁺ 331.1515, found 331.1510.

4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenol (18)



A Schlenk tube (10 mL) was charged with phenol (**1p**, 28.2 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CHCl₃ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification

using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **18** as a colorless oil (45.2 mg, 0.164 mmol, 55% yield).

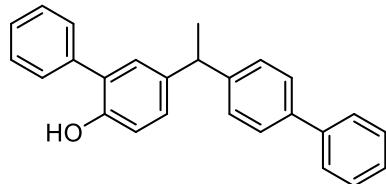
¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.00 (br, s, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 153.9, 146.0, 141.1, 139.0, 138.7, 128.9, 128.8, 128.0, 127.2, 127.1, 115.4, 43.8, 22.2.

IR (film): ν (cm⁻¹) 3226, 3219, 3204, 2956, 1723, 1632, 1473, 1295, 1237, 1118, 832, 694, 535, 478.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₈NaO⁺ [M+Na]⁺ 297.1250, found 297.1257.

5-(1-([1,1'-biphenyl]-4-yl)ethyl)-[1,1'-biphenyl]-2-ol (**19**)



A Schlenk tube (10 mL) was charged with [1,1'-biphenyl]-2-ol (**1q**, 51.0 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CHCl₃ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **19** as a white solid (47.3 mg, 0.135 mmol, 45% yield).

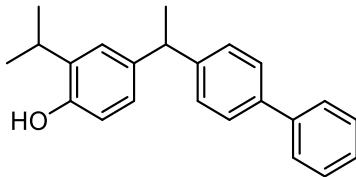
¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.41 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 1H), 5.14 (br, s, 1H), 4.14 (d, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 150.8, 145.9, 141.1, 139.0, 138.8, 137.4, 129.4, 129.3, 129.2, 128.8, 128.4, 128.0, 127.9, 127.2, 127.1, 115.9, 43.9, 22.2.

IR (film): ν (cm⁻¹) 3230, 3215, 3042, 2926, 1632, 1500, 1473, 1335, 1238, 881, 832, 691, 599, 551.

HRMS (ESI-TOF, m/z) calculated for C₂₆H₂₂NaO⁺ [M+Na]⁺ 373.1563, found 373.1555.

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-isopropylphenol (20)



A Schlenk tube (10 mL) was charged with 2-isopropylphenol (**1r**, 40.9 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 1:1) gave the pure product **20** as a white solid (58.8 mg, 0.186 mmol, 62% yield).

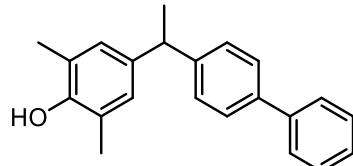
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 (d, $J = 7.4$ Hz, 2H), 7.54 (d, $J = 8.1$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.33 (m, 3H), 7.13 (d, $J = 2.3$ Hz, 1H), 6.95 (m, 1H), 6.70 (d, $J = 8.2$ Hz, 1H), 4.74 (br, s, 1H), 4.18 – 4.14 (m, 1H), 3.21 (p, $J = 6.9$ Hz, 1H), 1.67 (d, $J = 7.2$ Hz, 3H), 1.28 (m, 6H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.2, 146.2, 141.2, 138.9, 138.7, 134.3, 128.8, 128.0, 127.2, 127.1, 125.9, 125.7, 115.3, 44.1, 27.4, 22.7, 22.4.

IR (film): ν (cm⁻¹) 3575, 3026, 2964, 2856, 1632, 1592, 1505, 1473, 1365, 1237, 1108, 793, 802, 674, 585, 528.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{23}\text{H}_{24}\text{NaO}^+$ [M+Na]⁺ 339.1719, found 339.1724.

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-2,6-dimethylphenol (21)



A Schlenk tube (10 mL) was charged with 2,6-dimethylphenol (**1s**, 36.6 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 1:1) gave the pure product **21** as a white solid (65.3 mg, 0.216 mmol, 72% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58 (dd, $J = 8.2, 1.1$ Hz, 2H), 7.53 – 7.50 (m, 2H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.31 (dd, $J = 16.7, 7.8$ Hz, 3H), 6.88 (s, 2H), 4.50 (br, s, 1H), 4.07 (q, $J = 7.2$ Hz,

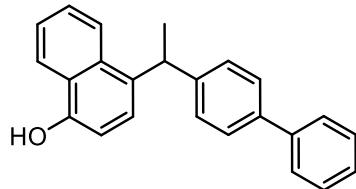
1H), 2.23 (s, 6H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 150.6, 146.2, 141.2, 138.9, 138.1, 128.8, 128.0, 127.8, 127.2, 127.1, 123.0, 43.9, 22.2, 16.2.

IR (film): ν (cm $^{-1}$) 3506, 3056, 2938, 2856, 1606, 1585, 1443, 1365, 1237, 1082, 789, 670, 58, 525.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{22}\text{NaO}^+$ [M+Na] $^+$ 325.1563, found 325.1572.

4-(1-([1,1'-biphenyl]-4-yl)ethyl)naphthalen-1-ol (22)



A Schlenk tube (10 mL) was charged with naphthalen-1-ol (**1t**, 43.3 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **22** as a white solid (41.9 mg, 0.129 mmol, 43% yield).

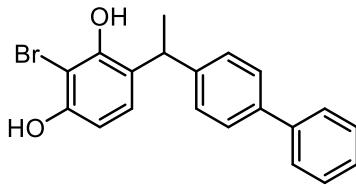
^1H NMR (500 MHz, CDCl_3) δ 8.12 – 8.10 (m, 1H), 7.83 – 7.81 (m, 1H), 7.57 (t, J = 8.6 Hz, 5H), 7.51 (s, 1H), 7.46 (d, J = 3.6 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 5.20 (br, s, 1H), 4.55 (q, J = 7.2 Hz, 1H), 1.79 (d, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 148.5, 144.0, 140.8, 139.9, 133.6, 129.0, 128.1, 127.8, 127.7, 127.4, 127.2, 126.0, 125.9, 125.5, 125.2, 125.1, 121.3, 120.7, 39.1, 21.2.

IR (film): ν (cm $^{-1}$) 3607, 3056, 1906, 1517, 1461, 1408, 1314, 1298, 1169, 1082, 1040, 958, 852, 712, 577, 520, 472.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{24}\text{H}_{21}\text{O}^+$ [M+H] $^+$ 325.1587, found 325.1580.

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-bromobenzene-1,3-diol (23)



A Schlenk tube (10 mL) was charged with 2-bromoresorcinol (**1u**, 56.7 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75

mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 1:1) gave the pure product **23** as a white solid (60.9 mg, 0.165 mmol, 55% yield).

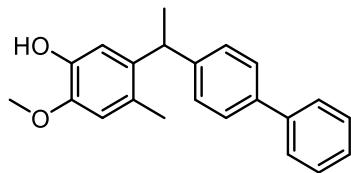
¹H NMR (500 MHz, CDCl₃) δ 7.59 – 7.57 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 3H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 5.47 (br, s, 1H), 5.35 (br, s, 1H), 4.49 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.3 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 151.1, 150.1, 144.8, 141.0, 139.1, 128.7, 127.9, 127.4, 127.2, 127.1, 127.1, 125.5, 107.7, 100.0, 38.2, 21.0.

IR (film): ν (cm⁻¹) 3500, 3074, 2639, 2488, 1909, 1777, 1352, 1248, 1184, 1166, 1042, 933, 847, 839, 555, 541, 488.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₈BrO₂⁺ [M+H]⁺ 369.0485, found 369.0493.

5-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-methoxy-4-methylphenol (24)



A Schlenk tube (10 mL) was charged with 2-methoxy-4-methylphenol (**1v**, 41.45 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CHCl₃ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 1:1) gave the pure product **24** as a white solid (64.9 mg, 0.204 mmol, 68% yield).

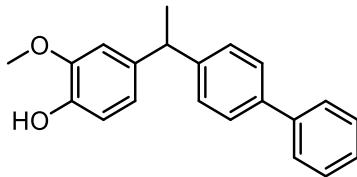
¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.96 (s, 1H), 6.69 (s, 1H), 5.51 (br, s, 1H), 4.30 (q, *J* = 7.1 Hz, 1H), 3.88 (s, 3H), 2.25 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.7, 144.6, 143.7, 141.2, 138.8, 136.9, 128.8, 128.1, 127.4, 127.2, 127.1, 113.5, 113.1, 56.1, 40.4, 22.3, 19.4.

IR (film): ν (cm⁻¹) 3662, 3490, 2961, 2939, 2843, 1514, 1466, 1367, 1272, 1123, 1040, 845, 681, 557.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₃O₂⁺ [M+H]⁺ 319.1693, found 319.1688.

5-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-methoxyphenol (25)



A Schlenk tube (10 mL) was charged with 2-methoxyphenol (**1w**, 37.2 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 1:1) gave the pure product **25** as a white solid (63.9 mg, 0.210 mmol, 70% yield).

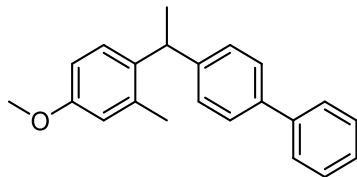
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 – 7.57 (m, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.34 (d, $J = 7.3$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1, 1.6$ Hz, 1H), 6.74 (d, $J = 1.7$ Hz, 1H), 5.51 (br, s, 1H), 4.14 (q, $J = 7.2$ Hz, 1H), 3.85 (s, 3H), 1.67 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 146.6, 146.0, 144.1, 141.1, 139.0, 138.4, 128.9, 128.0, 127.2, 127.2, 120.1, 114.3, 110.5, 56.0, 44.3, 22.3.

IR (film): ν (cm⁻¹) 3490, 2853, 1514, 1407, 1273, 1129, 1035, 838, 651, 595.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{21}\text{O}_2^+ [\text{M}+\text{H}]^+$ 305.1536, found 305.1544.

4-(1-(4-methoxy-2-methylphenyl)ethyl)-1,1'-biphenyl (26)



A Schlenk tube (10 mL) was charged with 1-methoxy-3-methylbenzene (**1x**, 36.7 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **26** as a white solid (59.8 mg, 0.198 mmol, 66% yield).

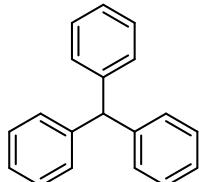
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 – 7.56 (m, 2H), 7.51 – 7.49 (m, 2H), 7.43 (d, $J = 5.6$ Hz, 2H), 7.33 (s, 1H), 7.23 (dd, $J = 8.4, 2.6$ Hz, 3H), 6.78 (dd, $J = 8.5, 2.7$ Hz, 1H), 6.74 (d, $J = 2.7$ Hz, 1H), 4.31 (d, $J = 7.2$ Hz, 1H), 3.80 (s, 3H), 2.26 (s, 3H), 1.64 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.9, 145.9, 141.2, 138.8, 137.6, 136.3, 128.8, 128.1, 127.8, 127.3, 127.1, 127.1, 116.3, 111.1, 55.3, 40.2, 22.5, 20.2.

IR (film): ν (cm⁻¹) 3473, 3452, 3031, 2953, 2858, 1513, 1465, 1435, 1298, 1176, 1125, 1110, 817, 646, 595.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₂NaO⁺ [M+Na]⁺ 325.1563, found 325.1556.

triphenylmethane (27)



A Schlenk tube (10 mL) was charged with benzene (**1y**, 69.6 mg, 0.30 mmol), diphenylmethane (**2n**, 164.8 mg, 0.90 mmol), FeBr₃ (17.7 mg, 0.11 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **27** as a yellow oil (34.2 mg, 0.140 mmol, 45% yield).

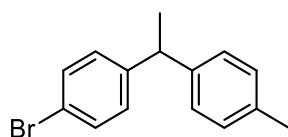
¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, $J = 7.5$ Hz, 6H), 7.23 (t, $J = 7.3$ Hz, 3H), 7.14 (d, $J = 7.5$ Hz, 6H), 5.57 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 144.0, 129.6, 128.4, 126.4, 57.0.

IR (film): ν (cm⁻¹) 3103, 3082, 3066, 3000, 1899, 1594, 1493, 1446, 1078, 1032, 1004, 977, 920, 857, 700, 620, 494, 466.

HRMS (ESI-TOF, m/z) calculated for C₁₉H₁₇⁺ [M+H]⁺ 245.1325, found 245.1327.

1-bromo-4-(1-(*p*-tolyl)ethyl)benzene (28)



A Schlenk tube (10 mL) was charged with toluene (**1z**, 27.6 mg, 0.30 mmol), 4-bromoethylbenzene (**2f**, 164.8 mg, 0.90 mmol), FeBr₃ (17.7 mg, 0.11 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product

28 as a light yellow oil (50.1 mg, 0.183 mmol, 61% yield).

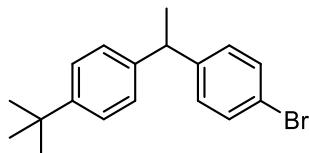
¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.06 (m, 6H), 4.08 (dd, *J* = 14.3, 7.1 Hz, 1H), 2.32 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.8, 142.9, 135.9, 131.5, 129.5, 129.3, 127.5, 119.9, 44.0, 21.9, 21.1.

IR (film): ν (cm⁻¹) 3079, 3040, 2943, 2874, 1774, 1593, 1488, 1453, 1375, 1317, 1234, 1205, 1011, 977, 705, 513.

HRMS (ESI-TOF, m/z) calculated for C₁₅H₁₆Br⁺ [M+H]⁺ 275.0430, found 275.0438.

1-bromo-4-(1-(4-(*tert*-butyl)phenyl)ethyl)benzene (29)



A Schlenk tube (10 mL) was charged with *tert*-butylbenzene (**1za**, 40.3 mg, 0.30 mmol), 4-bromoethylbenzene (**2f**, 164.8 mg, 0.90 mmol), FeBr₃ (17.7 mg, 0.11 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **29** as a light yellow oil (44.3 mg, 0.140 mmol, 47% yield).

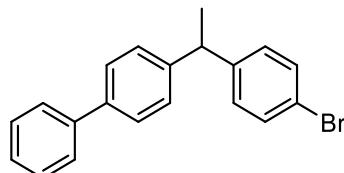
¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.12 (dd, *J* = 10.8, 6.1 Hz, 4H), 4.09 (dd, *J* = 14.9, 7.7 Hz, 1H), 1.62 (d, *J* = 7.0 Hz, 3H), 1.31 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 149.2, 145.8, 142.7, 131.5, 129.6, 127.2, 125.5, 119.9, 44.4, 43.9, 34.5, 31.5, 21.9.

IR (film): ν (cm⁻¹) 3079, 3040, 2943, 2874, 1942, 1787, 1488, 1453, 1375, 1317, 1205, 1119, 927, 845, 553.

HRMS (ESI-TOF, m/z) calculated for C₁₈H₂₂Br⁺ [M+H]⁺ 317.0899, found 317.0885.

4-(1-(4-bromophenyl)ethyl)-1,1'-biphenyl (30)



A Schlenk tube (10 mL) was charged with 1,1'-biphenyl (**1zb**, 46.3 mg, 0.30 mmol), 4-

bromoethylbenzene (**2f**, 164.8 mg, 0.90 mmol), FeBr_3 (17.7 mg, 0.11 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **30** as a light yellow oil (53.8 mg, 0.160 mmol, 53% yield).

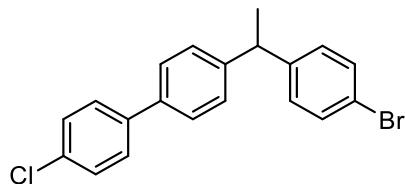
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.57 (t, $J = 6.5$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.44 – 7.41 (m, 4H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 4.16 (q, $J = 7.2$ Hz, 1H), 1.66 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.4, 144.9, 141.0, 139.3, 131.6, 129.6, 128.9, 128.1, 127.3, 127.3, 127.2, 120.0, 44.1, 21.9.

IR (film): ν (cm⁻¹) 3111, 3079, 3066, 2973, 2876, 1944, 1594, 1401, 1317, 1155, 1011, 917, 765, 613, 478.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{20}\text{H}_{18}\text{Br}^+ [\text{M}+\text{H}]^+$ 337.0586, found 337.0580.

4-(1-(4-bromophenyl)ethyl)-4'-chloro-1,1'-biphenyl (31)



A Schlenk tube (10 mL) was charged with 4-chloro-1,1'-biphenyl (**1zc**, 56.6 mg, 0.30 mmol), 4-bromoethylbenzene (**2f**, 164.8 mg, 0.90 mmol), FeBr_3 (17.7 mg, 0.11 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **31** as a light yellow oil (50.0 mg, 0.135 mmol, 45% yield).

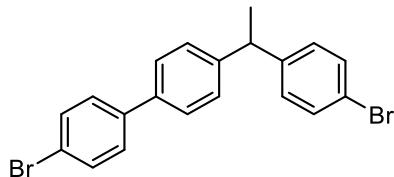
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.48 (dd, $J = 8.2, 5.8$ Hz, 4H), 7.40 (dd, $J = 16.5, 8.4$ Hz, 4H), 7.27 (s, 1H), 7.25 (s, 1H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.15 (q, $J = 7.2$ Hz, 1H), 1.65 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.4, 145.3, 139.4, 138.1, 133.4, 131.6, 129.5, 129.0, 128.4, 128.2, 127.2, 120.1, 44.1, 21.8.

IR (film): ν (cm⁻¹) 3088, 3035, 1969, 1902, 1597, 1566, 1479, 1400, 1388, 1312, 1123, 1099, 1005, 911, 833, 707, 687, 544, 498.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{20}\text{H}_{17}\text{BrCl}^+ [\text{M}+\text{H}]^+$ 371.0197, found 371.0191.

4-bromo-4'-(1-(4-bromophenyl)ethyl)-1,1'-biphenyl (32)



A Schlenk tube (10 mL) was charged with 4-bromo-1,1'-biphenyl (**1zd**, 69.9 mg, 0.30 mmol), 4-bromoethylbenzene (**2f**, 164.8 mg, 0.90 mmol), FeBr_3 (17.7 mg, 0.11 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **32** as a yellow oil (58.3 mg, 0.141 mmol, 47% yield).

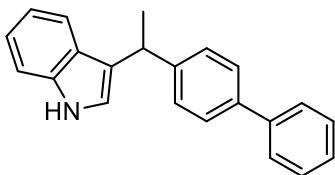
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.53 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 7.9$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 4H), 7.26 – 7.23 (m, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 4.14 (q, $J = 7.1$ Hz, 1H), 1.64 (d, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.4, 145.3, 139.9, 138.1, 132.0, 131.7, 129.5, 128.7, 128.2, 127.1, 121.5, 120.1, 44.1, 21.8.

IR (film): ν (cm⁻¹) 3128, 3031, 2066, 1908, 1587, 1551, 1449, 1388, 1309, 1019, 1007, 991, 830, 755, 691, 636, 544.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{20}\text{H}_{17}\text{Br}_2^+ [\text{M}+\text{H}]^+$ 414.9692, found 414.9698.

3-(1-([1,1'-biphenyl]-4-yl)ethyl)-1*H*-indole (33)



A Schlenk tube (10 mL) was charged with indole (**1ze**, 35.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **33** as a yellow oil (51.7 mg, 0.174 mmol, 58% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.59 (d, $J = 1.3$ Hz, 1H), 7.57 (d, $J = 0.9$ Hz, 1H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 7.9$ Hz, 3H), 7.38 (s, 1H), 7.37 – 7.35 (m, 2H), 7.33 (d, $J = 7.4$ Hz, 1H), 7.19 – 7.15 (m, 1H), 7.06 – 7.01 (m, 2H), 4.45 – 4.41 (m, 1H), 1.75 (d, $J = 7.2$ Hz, 3H).

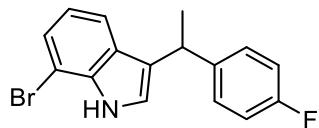
Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 146.1, 141.3, 138.9, 136.7, 128.8, 128.0, 127.2, 127.1, 127.1, 127.0, 122.2, 121.5, 121.2, 119.9, 119.4, 111.2, 36.7, 22.5 .

IR (film): ν (cm $^{-1}$) 3888, 3497, 3400, 3060, 2856, 1613, 1577, 1487, 1358, 1092, 1011, 933, 870, 775, 738, 612, 487.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{20}\text{N}^+$ $[\text{M}+\text{H}]^+$ 298.1590, found 298.1596.

7-bromo-3-(1-(4-fluorophenyl)ethyl)-1*H*-indole (34)



A Schlenk tube (10 mL) was charged with 7-bromo-1*H*-indole (**1zf**, 58.8 mg, 0.30 mmol), 1-bromo-4-isopropylbenzene (**2d**, 179.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **34** as a light yellow oil (47.7 mg, 0.149 mmol, 50% yield).

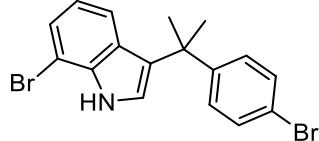
^1H NMR (500 MHz, CDCl_3) δ 8.18 (s, 1H), 7.31 (d, $J = 7.3$ Hz, 1H), 7.24 – 7.19 (m, 3H), 7.09 (dd, $J = 2.2, 0.8$ Hz, 1H), 6.95 (td, $J = 6.6, 3.3$ Hz, 2H), 6.89 (t, $J = 7.8$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 1H), 1.68 (d, $J = 7.1$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 161.4, 142.2, 135.5, 128.9, 128.1, 124.5, 122.6, 121.7, 120.6, 119.0, 115.2, 104.8, 36.5, 22.6.

IR (film): ν (cm $^{-1}$) 3870, 3512, 3411, 3123, 2907, 1663, 1607, 1423, 1366, 1083, 999, 941, 795, 765, 723, 506, 487.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{16}\text{H}_{14}\text{BrFN}^+$ $[\text{M}+\text{H}]^+$ 318.0288, found 318.0297.

7-bromo-3-(2-(4-bromophenyl)propan-2-yl)-1*H*-indole (35)



A Schlenk tube (10 mL) was charged with 7-bromo-1*H*-indole (**1zf**, 58.8 mg, 0.30 mmol), 1-bromo-4-isopropylbenzene (**2zk**, 179.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then

filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **35** as a light yellow oil (57.8 mg, 0.147 mmol, 49% yield).

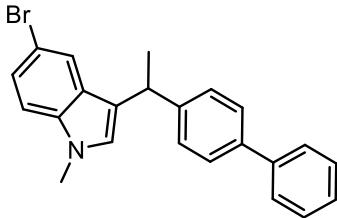
¹H NMR (500 MHz, CDCl₃) δ 8.17 (s, 1H), 7.42 – 7.39 (m, 2H), 7.34 – 7.32 (m, 1H), 7.25 – 7.22 (m, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 1.78 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 148.7, 135.8, 131.2, 128.4, 127.1, 126.8, 124.3, 121.3, 120.43, 120.4, 119.7, 104.9, 39.0, 30.6.

IR (film): ν (cm⁻¹) 3300, 3085, 2927, 2887, 1663, 1555, 1423, 1326, 1300, 10832, 921, 906, 533.

HRMS (ESI-TOF, m/z) calculated for C₁₇H₁₆Br₂N⁺ [M+H]⁺ 393.9624, found 393.9622.

3-(1-([1,1'-biphenyl]-4-yl)ethyl)-5-bromo-1-methyl-1*H*-indole (**36**)



A Schlenk tube (10 mL) was charged with 5-bromo-1-methyl-1*H*-indole (**1zg**, 63.0 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CH₂Cl₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **36** as a yellow oil (71.2 mg, 0.183 mmol, 61% yield).

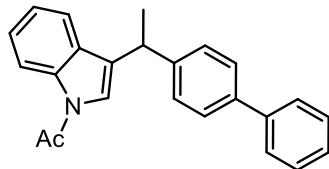
¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.59 (m, 3H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.33 (m, 1H), 7.29 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.89 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 1H), 3.74 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.6, 141.1, 139.0, 136.04 128.9, 128.8, 127.8, 127.2, 127.1, 124.5, 122.2, 119.6, 112.2, 110.7, 36.4, 32.9, 22.5.

IR (film): ν (cm⁻¹) 3436, 2907, 1632, 1503, 1334, 1250, 1197, 899, 854, 606.

HRMS (ESI-TOF, m/z) calculated for C₂₃H₂₁BrN⁺ [M+H]⁺ 390.0852, found 390.0859.

1-(3-(1-([1,1'-biphenyl]-4-yl)ethyl)-1*H*-indol-1-yl)ethan-1-one (37)



A Schlenk tube (10 mL) was charged with 1-(1*H*-indol-1-yl)ethan-1-one (**1zh**, 47.8 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **37** as a light yellow oil (71.3 mg, 0.210 mmol, 70% yield).

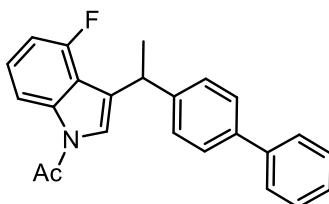
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.46 (s, 1H), 7.60 (d, $J = 7.5$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.39 – 7.29 (m, 6H), 7.21 (d, $J = 7.4$ Hz, 1H), 4.36 (q, $J = 7.0$ Hz, 1H), 2.66 (s, 3H), 1.77 (d, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.6, 144.2, 140.9, 139.4, 136.4, 130.2, 128.8, 127.8, 127.5, 127.4, 127.3, 127.1, 125.3, 123.5, 121.9, 120.0, 116.7, 36.5, 24.2, 22.0.

IR (film): ν (cm^{-1}) 3103, 1751, 1748, 1511, 1498, 1388, 1365, 1300, 1227, 1078, 993, 755, 739, 480.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{24}\text{H}_{22}\text{NO}^+$ [M+H]⁺ 340.1696, found 340.1703.

1-(3-(1-([1,1'-biphenyl]-4-yl)ethyl)-4-fluoro-1*H*-indol-1-yl)ethan-1-one (38)



A Schlenk tube (10 mL) was charged with 1-(4-fluoro-1*H*-indol-1-yl)ethan-1-one (**1zi**, 53.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **38** as a light yellow oil (68.6 mg, 0.192 mmol, 64% yield).

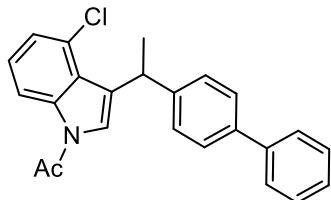
¹H NMR (500 MHz, CDCl₃) δ 8.30 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.19 (s, 1H), 6.94 (dd, *J* = 10.2, 8.5 Hz, 1H), 4.61 (q, *J* = 6.9 Hz, 1H), 2.65 (s, 3H), 1.78 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.6, 156.4, 144.3, 141.0, 139.3, 138.4 (d, *J*_{C-F} = 40.0 Hz), 128.8, 127.9, 127.2, 127.2, 127.1, 126.6, 126.2, 121.9, 118.5 (d, *J*_{C-F} = 75.0 Hz), 112.8, 109.6 (d, *J*_{C-F} = 75.0 Hz), 37.0, 24.2, 22.3.

IR (film): ν (cm⁻¹) 3133, 1762, 1750, 1563, 1505, 1383, 1375, 1290, 1287, 1118, 1074, 988, 753, 750, 741, 550.

HRMS (ESI-TOF, m/z) calculated for C₂₄H₂₁FNO⁺ [M+H]⁺ 358.1602, found 358.1599.

1-(3-(1-([1,1'-biphenyl]-4-yl)ethyl)-4-chloro-1*H*-indol-1-yl)ethan-1-one (39)



A Schlenk tube (10 mL) was charged with 1-(4-chloro-1*H*-indol-1-yl)ethan-1-one (**1zj**, 57.9 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CH₂Cl₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **39** as a light yellow oil (78.4 mg, 0.210 mmol, 70% yield).

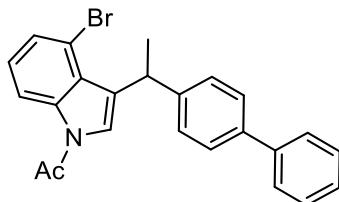
¹H NMR (500 MHz, CDCl₃) δ 8.46 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.25 – 7.19 (m, 3H), 5.01 (q, *J* = 7.0 Hz, 1H), 2.61 (s, 3H), 1.74 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.4, 144.9, 141.0, 139.1, 137.8, 128.8, 128.1, 127.7, 127.2, 127.1, 126.9, 126.5, 126.0, 125.1, 123.7, 115.4, 36.2, 24.2, 23.3.

IR (film): ν (cm⁻¹) 3133, 1762, 1750, 1563, 1505, 1383, 1375, 1290, 1287, 1118, 1074, 988, 753, 750, 741, 550.

HRMS (ESI-TOF, m/z) calculated for C₂₄H₂₁ClNO⁺ [M+H]⁺ 374.1306, found 374.1310.

1-(3-(1-([1,1'-biphenyl]-4-yl)ethyl)-4-bromo-1*H*-indol-1-yl)ethan-1-one (40)



A Schlenk tube (10 mL) was charged with 1-(4-bromo-1*H*-indol-1-yl)ethan-1-one (**1zk**, 71.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **40** as a light yellow oil (90.0 mg, 0.216 mmol, 72% yield).

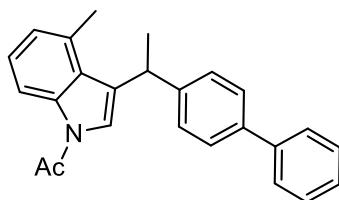
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.48 (d, $J = 8.3$ Hz, 1H), 7.54 (d, $J = 7.6$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.36 (dd, $J = 8.2, 7.4$ Hz, 3H), 7.28 (d, $J = 8.1$ Hz, 3H), 7.17 (s, 1H), 7.09 (t, $J = 8.1$ Hz, 1H), 5.06 (q, $J = 7.0$ Hz, 1H), 2.51 (s, 3H), 1.68 (d, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.3, 144.8, 140.9, 139.0, 137.7, 128.8, 128.6, 128.2, 128.1, 127.9, 127.2, 127.1, 127.0, 126.2, 124.1, 115.9, 114.2, 35.7, 24.1, 23.3.

IR (film): ν (cm⁻¹) 3099, 1801, 1766, 1569, 1522, 1381, 1352, 1287, 1279, 1101, 1032, 996, 773, 741, 670.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{24}\text{H}_{21}\text{BrNO}^+$ [M+H]⁺ 418.0801, found 418.0800.

1-(3-(1-([1,1'-biphenyl]-4-yl)ethyl)-4-methyl-1*H*-indol-1-yl)ethan-1-one (41)



A Schlenk tube (10 mL) was charged with 1-(5-methyl-1*H*-indol-1-yl)ethan-1-one (**1zl**, 51.9 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **41** as a light yellow oil (72.0 mg, 0.203 mmol, 68% yield).

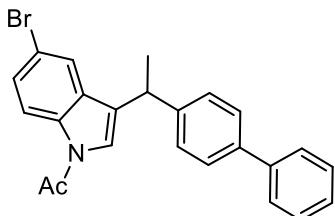
¹H NMR (500 MHz, CDCl₃) δ 8.42 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 6.7 Hz, 2H), 7.29 (dd, *J* = 10.7, 2.5 Hz, 3H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 2.71 (s, 3H), 2.45 (s, 3H), 1.76 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.6, 145.5, 140.9, 139.2, 137.0, 131.3, 128.9, 127.9, 127.7, 127.4, 127.3, 127.1, 125.9, 125.4, 122.8, 114.5, 37.4, 24.4, 24.0, 20.5.

IR (film): ν (cm⁻¹) 3406, 3104, 3034, 2903, 1771, 1584, 1436, 1411, 1356, 1238, 1081, 1033, 895, 721, 502.

HRMS (ESI-TOF, m/z) calculated for C₂₅H₂₄NO⁺ [M+H]⁺ 354.1852, found 354.1857.

1-(3-(1-([1,1'-biphenyl]-4-yl)ethyl)-5-bromo-1*H*-indol-1-yl)ethan-1-one (42)



A Schlenk tube (10 mL) was charged with 1-(5-bromo-1*H*-indol-1-yl)ethan-1-one (**1zm**, 71.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CH₂Cl₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **42** as a light yellow oil (91.3 mg, 0.219 mmol, 73% yield).

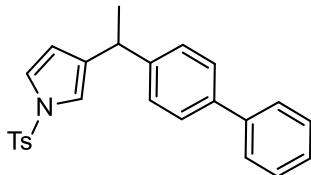
¹H NMR (500 MHz, CDCl₃) δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.9 Hz, 3H), 7.40 (d, *J* = 8.0 Hz, 3H), 7.29 (s, 1H), 7.22 (t, *J* = 8.1 Hz, 1H), 5.19 (q, *J* = 7.0 Hz, 1H), 2.63 (s, 3H), 1.80 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.3, 144.8, 140.9, 139.0, 137.7, 128.8, 128.6, 128.1, 128.1, 127.9, 127.2, 127.1, 127.0, 126.2, 124.1, 115.9, 114.2, 35.7, 24.1, 23.3.

IR (film): ν (cm⁻¹) 3413, 3108, 2923, 1571, 1569, 1436, 1463, 1642, 1109, 1081, 929, 883, 733, 506.

HRMS (ESI-TOF, m/z) calculated for C₂₄H₂₁BrNO⁺ [M+H]⁺ 418.0801, found 418.0817.

2-(1-([1,1'-biphenyl]-4-yl)ethyl)-1-tosyl-1*H*-pyrrole (43)



A Schlenk tube (10 mL) was charged with 1-tosyl-1*H*-pyrrole (**1zn**, 66.3 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CH_2Cl_2 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **43** as a yellow oil (54.1 mg, 0.135 mmol, 45% yield).

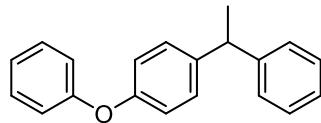
¹H NMR (500 MHz, CDCl_3) δ 7.54 – 7.51 (m, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.36 – 7.32 (m, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 6.97 (t, $J = 7.9$ Hz, 4H), 6.31 (t, $J = 3.4$ Hz, 1H), 6.27 (s, 1H), 4.72 (q, $J = 7.1$ Hz, 1H), 2.19 (s, 3H), 1.53 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl_3) δ 144.2, 144.2, 141.0, 139.1, 138.9, 136.3, 129.6, 128.9, 127.9, 127.2, 127.0, 126.9, 126.7, 123.1, 112.7, 111.2, 36.9, 23.9, 21.5.

IR (film): ν (cm⁻¹) 3111, 3097, 1750, 1662, 1500, 1342, 1286, 1084, 1072, 1002, 975, 959, 742, 662, 511.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{25}\text{H}_{24}\text{NO}_2\text{S}^+$ [M+H]⁺ 402.1522, found 402.1530.

1-phenoxy-4-(1-phenylethyl)benzene (44)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), ethylbenzene (**2b**, 95.6 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **44** as a colorless oil (57.5 mg, 0.209 mmol, 70% yield).

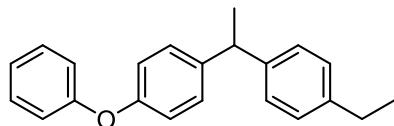
¹H NMR (500 MHz, CDCl_3) δ 7.36 (q, $J = 7.8$ Hz, 4H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 3H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 8.3$ Hz, 2H), 6.98 (d, $J = 8.4$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 1H), 1.69 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.6, 155.4, 146.6, 141.5, 129.8, 128.9, 128.5, 127.7, 126.2, 123.2, 119.0, 118.8, 44.3, 22.2.

IR (film): ν (cm⁻¹) 3110, 3084, 3074, 2963, 2877, 1981, 1496, 1488, 1336, 1321, 1240, 1076, 1031, 964, 881, 492, 480.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₉O⁺ [M+H]⁺ 275.1430, found 275.1434.

1-ethyl-4-(1-(4-phenoxyphenyl)ethyl)benzene (45)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1,4-diethylbenzene (**2c**, 120.8 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **45** as a colorless oil (67.0 mg, 0.222 mmol, 74% yield).

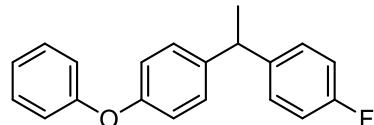
¹H NMR (500 MHz, CDCl₃) δ 7.28 (m, 2H), 7.16 (d, $J = 8.5$ Hz, 2H), 7.14 – 7.10 (m, 4H), 7.04 (t, $J = 7.4$ Hz, 1H), 6.97 (d, $J = 7.7$ Hz, 2H), 6.94 – 6.88 (m, 2H), 4.09 (q, $J = 7.2$ Hz, 1H), 2.60 (q, $J = 7.6$ Hz, 2H), 1.60 (d, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.6, 155.3, 143.8, 142.0, 141.7, 129.8, 128.9, 128.0, 127.6, 123.1, 118.9, 118.8, 43.9, 28.5, 22.2, 15.7.

IR (film): ν (cm⁻¹) 3134, 3091, 3078, 2929, 1790, 1673, 1516, 1312, 1234, 1022, 985, 971, 943, 800, 611, 547.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₃O⁺ [M+H]⁺ 303.1743, found 303.1737.

1-fluoro-4-(1-(4-phenoxyphenyl)ethyl)benzene (46)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-ethyl-4-fluorobenzene (**2d**, 111.7 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to

dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **46** as a colorless oil (60.4 mg, 0.207 mmol, 69% yield).

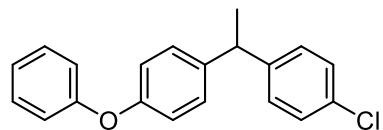
¹H NMR (500 MHz, CDCl₃) δ 7.34 (t, *J* = 7.9 Hz, 2H), 7.21 – 7.16 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.07 – 6.92 (m, 6H), 4.14 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 162.4, 160.4, 157.5, 155.6, 142.2, 141.2, 129.8 (d, *J*_{C-F} = 30.0 Hz), 129.1, 128.8, 123.2, 118.9 (d, *J*_{C-F} = 45.0 Hz), 115.3 (d, *J*_{C-F} = 85.0 Hz), 43.5, 22.3.

IR (film): ν (cm⁻¹) 3066, 3055, 1597, 1526, 1501, 1476, 1342, 1286, 1223, 1058, 1032, 1011, 975, 961, 899, 742, 519, 481.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₈FO⁺ [M+H]⁺ 293.1336, found 293.1344.

1-chloro-4-(1-(4-phenoxyphenyl)ethyl)benzene (**47**)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-chloro-4-ethylbenzene (**2e**, 126.5 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **47** as a colorless oil (62.9 mg, 0.204 mmol, 68% yield).

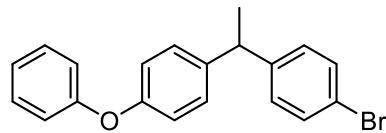
¹H NMR (500 MHz, CDCl₃) δ 7.34 (t, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.16 (m, 4H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.5, 155.6, 145.0, 140.8, 131.9, 129.8, 129.1, 128.9, 128.6, 123.3, 119.0, 118.9, 43.7, 22.1.

IR (film): ν (cm⁻¹) 3081, 3072, 3042, 3019, 1861, 1788, 1584, 1532, 1446, 1377, 1187, 1120, 1044, 1024, 1014, 935, 921, 702, 523, 469.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₈ClO⁺ [M+H]⁺ 309.1041, found 309.1038.

1-bromo-4-(1-(4-phenoxyphenyl)ethyl)benzene (48)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-bromoethylbenzene (**2f**, 166.6 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **48** as a colorless oil (73.9 mg, 0.210 mmol, 70% yield).

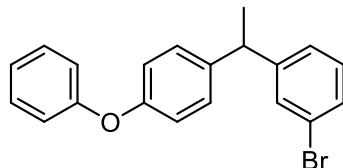
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41 – 7.38 (m, 2H), 7.30 (m, 2H), 7.15 – 7.12 (m, 2H), 7.10 – 7.07 (m, 3H), 7.01 – 6.97 (m, 2H), 6.94 – 6.91 (m, 2H), 4.08 (q, $J = 7.2$ Hz, 1H), 1.60 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.4, 155.6, 145.5, 140.7, 131.6, 129.8, 129.5, 128.8, 123.2, 120.0, 119.0, 118.9, 43.7, 22.0.

IR (film): ν (cm^{-1}) 3079, 3065, 3044, 3003, 1956, 1862, 1790, 1330, 1247, 1002, 866, 830, 683, 672, 544, 457.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{20}\text{H}_{18}\text{BrO}^+$ [M+H]⁺ 353.0536, found 353.0542.

1-bromo-3-(1-(4-phenoxyphenyl)ethyl)benzene (49)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-bromo-3-ethylbenzene (**2g**, 166.6 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **49** as a white solid (76.0 mg, 0.216 mmol, 72% yield).

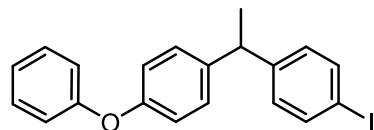
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.38 – 7.30 (m, 4H), 7.16 (d, $J = 7.9$ Hz, 4H), 7.09 (t, $J = 7.4$ Hz, 1H), 7.03 – 6.98 (m, 2H), 6.96 – 6.92 (m, 2H), 4.10 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.4, 155.7, 149.0, 140.5, 130.8, 130.1, 129.8, 129.4, 128.9, 126.4, 123.3, 122.7, 119.0, 118.9, 44.0, 22.0.

IR (film): ν (cm⁻¹) 3068, 3042, 3016, 2001, 1989, 1885, 1401, 1332, 1250, 980, 812, 695, 688, 651, 504, 403.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₈BrO⁺ [M+H]⁺ 353.0536, found 353.0539.

1-iodo-4-(1-(4-phenoxyphenyl)ethyl)benzene (50)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-ethyl-4-iodobenzene (**2h**, 208.9 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **50** as a yellow solid (72.0 mg, 0.180 mmol, 60% yield).

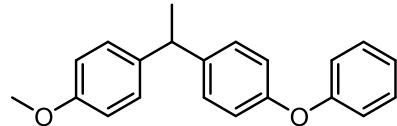
¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, $J = 8.2$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 2H), 7.15 (d, $J = 8.5$ Hz, 2H), 7.09 (t, $J = 7.3$ Hz, 1H), 6.99 (t, $J = 8.5$ Hz, 4H), 6.94 (d, $J = 8.4$ Hz, 2H), 4.09 (q, $J = 7.2$ Hz, 1H), 1.61 (d, $J = 7.2$ Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.5, 155.7, 146.3, 140.7, 137.6, 129.8, 128.9, 123.3, 119.0, 118.9, 91.4, 43.8, 22.0.

IR (film): ν (cm⁻¹) 3477, 3461, 3113, 3059, 2993, 1943, 1883, 1571, 1300, 1188, 1167, 1058, 1015, 996, 903, 835, 667, 614, 460.

HRMS (ESI-TOF, m/z) calculated for C₂₀H₁₈IO⁺ [M+H]⁺ 401.0397, found 401.0341.

1-methoxy-4-(1-(4-phenoxyphenyl)ethyl)benzene (51)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 1-ethyl-4-phenoxybenzene (**2i**, 178.3 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to

dryness. Purification using silica gel column chromatography (elution with PE:DCM = 6:1) gave the pure product **51** as a colorless oil (50.2 mg, 0.165 mmol, 55% yield).

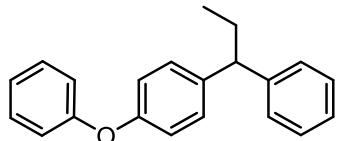
¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.29 (m, 2H), 7.19 – 7.14 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.0, 157.7, 155.4, 141.9, 138.75, 129.8, 128.9, 128.6, 123.13, 119.0, 118.8, 113.9, 55.4, 43.5, 22.4.

IR (film): ν (cm⁻¹) 3071, 3066, 3003, 2959, 2944, 2803, 1671, 1450, 1411, 1253, 1107, 1015, 882, 656, 556, 436.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₂₁O₂⁺ [M+H]⁺ 305.1536, found 305.1541.

1-phenoxy-4-(1-phenylpropyl)benzene (**52**)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), propylbenzene (**2j**, 108.2 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **52** as a colorless oil (61.4 mg, 0.213 mmol, 71% yield).

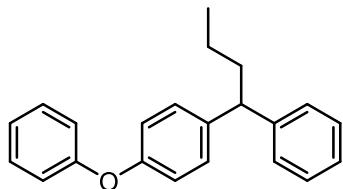
¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.25 (m, 4H), 7.24 – 7.21 (m, 2H), 7.20 – 7.16 (m, 3H), 7.13 – 6.85 (m, 5H), 3.77 (t, *J* = 7.8 Hz, 1H), 2.07 – 2.03 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.6, 155.4, 145.3, 140.3, 129.8, 129.2, 128.5, 128.0, 126.2, 123.1, 119.0, 118.8, 52.7, 28.9, 12.9.

IR (film): ν (cm⁻¹) 3108, 3066, 3028, 2978, 2898, 1583, 1445, 1341, 1178, 1111, 1083, 909, 619, 592, 585, 481.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₂₁O⁺ [M+H]⁺ 289.1587, found 289.1585.

1-phenoxy-4-(1-phenylbutyl)benzene (53)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), butylbenzene (**2k**, 120.8 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **53** as a white solid (63.4 mg, 0.210 mmol, 70% yield).

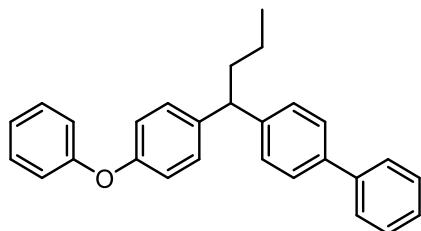
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 4H), 7.23 (d, $J = 7.2$ Hz, 2H), 7.20 – 7.16 (m, 3H), 7.06 (t, $J = 7.4$ Hz, 1H), 6.94 (m, 4H), 3.89 (t, $J = 7.8$ Hz, 1H), 2.00 (d, $J = 7.7$ Hz, 2H), 1.30 – 1.27 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.6, 155.4, 145.5, 140.5, 129.8, 129.2, 128.5, 128.0, 126.2, 123.1, 119.0, 118.8, 50.5, 38.2, 21.3, 14.2.

IR (film): ν (cm⁻¹) 3108, 3087, 3029, 3003, 2873, 2860, 1953, 1800, 1604, 1583, 1489, 1379, 1364, 1188, 1132, 955, 934, 779, 746, 661, 570, 503.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{23}\text{O}^+$ [M+H]⁺ 303.1743, found 303.1749.

4-(1-(4-phenoxyphenyl)butyl)-1,1'-biphenyl (54)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-butyl-1,1'-biphenyl (**2l**, 189.3 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **54** as a colorless oil (73.7 mg, 0.195 mmol, 65% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.57 – 7.54 (m, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.29 (m, 5H), 7.21 (d, $J = 8.7$ Hz, 2H), 7.05 (t, $J = 7.4$ Hz, 1H), 7.00 – 6.96 (m, 2H),

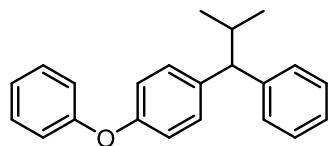
6.93 (d, $J = 8.6$ Hz, 2H), 3.92 (t, $J = 7.8$ Hz, 1H), 2.06 – 2.00 (m, 2H), 1.34 – 1.29 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.5, 155.5, 144.6, 141.1, 140.3, 139.1, 129.8, 129.2, 128.8, 128.3, 127.3, 127.2, 127.1, 123.2, 119.0, 118.9, 50.2, 38.2, 21.3, 14.2.

IR (film): ν (cm $^{-1}$) 3091, 3065, 3030, 2888, 2812, 1942, 1838, 1593, 1558, 1454, 1342, 1009, 1130, 935, 759, 733, 694, 510.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{28}\text{H}_{27}\text{O}^+$ [M+H] $^+$ 379.2056, found 379.2062.

1-(2-methyl-1-phenylpropyl)-4-phenoxybenzene (55)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), isobutylbenzene (**2m**, 120.8 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **55** as a white solid (59.8 mg, 0.198 mmol, 66% yield).

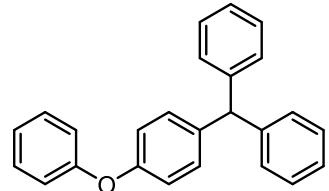
^1H NMR (500 MHz, CDCl_3) δ 7.29 (m, 2H), 7.27 (s, 2H), 7.26 (d, $J = 4.0$ Hz, 2H), 7.24 – 7.22 (m, 2H), 7.14 (m, 1H), 7.07 – 7.03 (m, 1H), 6.97 – 6.94 (m, 2H), 6.91 – 6.88 (m, 2H), 3.38 (d, $J = 10.8$ Hz, 1H), 2.44 (m, 1H), 0.89 (d, $J = 6.5$ Hz, 3H), 0.87 (d, $J = 6.5$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.6, 155.3, 145.1, 140.1, 129.8, 129.3, 128.6, 128.1, 126.1, 123.1, 119.0, 118.8, 60.3, 32.2, 22.0, 22.0.

IR (film): ν (cm $^{-1}$) 3086, 3065, 3028, 2924, 2849, 1665, 1375, 1324, 1178, 1168, 1122, 1058, 933, 922, 784, 737, 618, 591, 481.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{23}\text{O}^+$ [M+H] $^+$ 303.1743, found 303.1726.

((4-phenoxyphenyl)methylene)dibenzene (56)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), diphenylmethane (**2n**, 151.4 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and

(CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **56** as a white solid (72.6 mg, 0.216 mmol, 72% yield).

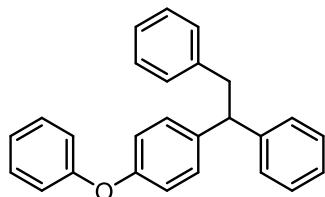
¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.31 (m, 3H), 7.30 (d, *J* = 7.7 Hz, 3H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 4H), 7.11 – 7.06 (m, 3H), 7.04 – 7.00 (m, 2H), 6.96 – 6.92 (m, 2H), 5.55 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 157.4, 155.8, 144.1, 138.9, 130.8, 129.8, 129.5, 128.5, 126.5, 123.3, 119.00 118.8, 56.3.

IR (film): ν (cm⁻¹) 3088, 3066, 3006, 2913, 1959, 1943, 1600, 1547, 1498, 1453, 1337, 1326, 1202, 1183, 1108, 1031, 1003, 933, 890, 632, 608, 464.

HRMS (ESI-TOF, m/z) calculated for C₂₅H₂₁O⁺ [M+H]⁺ 337.1592, found 337.1599.

(1-(4-phenoxyphenyl)ethane-1,2-diyl)dibenzene (57)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1,2-diphenylethane (**2o**, 164.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **57** as a white solid (69.3 mg, 0.198 mmol, 66% yield).

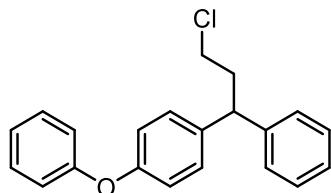
¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.18 (m, 6H), 7.15 – 7.09 (m, 6H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.92 (m, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.19 (t, *J* = 7.8 Hz, 1H), 3.32 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 157.5, 155.5, 144.6, 140.3, 139.6, 129.8, 129.4, 129.2, 128.5, 128.2, 128.1, 126.4, 126.0, 123.1, 119.0, 118.8, 52.6, 42.4.

IR (film): ν (cm⁻¹) 3120, 3083, 3058, 3027, 2943, 2918, 1953, 1946, 1751, 1146, 1065, 1003, 982, 959, 910, 841, 768, 752, 622, 528, 510.

HRMS (ESI-TOF, m/z) calculated for C₂₆H₂₃O⁺ [M+H]⁺ 351.1743, found 351.1752.

1-(3-chloro-1-phenylpropyl)-4-phenoxybenzene (58)



A Schlenk tube (10 mL) was charged diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), (3-chloropropyl)benzene (**2p**, 139.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 4:1) gave the pure product **58** as a light yellow oil (57.0 mg, 0.177 mmol, 59% yield).

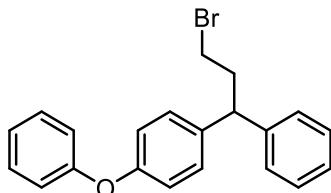
¹H NMR (500 MHz, CDCl_3) δ 7.33 – 7.28 (m, 4H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.21 (dd, $J = 11.8$, 4.9 Hz, 3H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.00 – 6.96 (m, 2H), 6.95 – 6.91 (m, 2H), 4.20 (t, $J = 7.8$ Hz, 1H), 3.45 (t, $J = 6.6$ Hz, 2H), 2.47 (q, $J = 5.0$ Hz, 2H).

¹³C NMR (126 MHz, CDCl_3) δ 157.3, 155.9, 143.7, 138.5, 129.8, 129.2, 128.8, 128.0, 126.7, 123.3, 119.1, 119.0, 47.3, 43.3, 38.4.

IR (film): ν (cm⁻¹) 3108, 3086, 3064, 2942, 2851, 1688, 1606, 1583, 1480, 1443, 1432, 1355, 1290, 1230, 1204, 1180, 1080, 1033, 914, 864, 745, 700, 658, 562.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{20}\text{ClO}^+$ [M+H]⁺ 323.1197, found 323.1201.

1-(3-bromo-1-phenylpropyl)-4-phenoxybenzene (59)



A Schlenk tube (10 mL) was charged diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), (3-bromopropyl)benzene (**2q**, 179.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 4:1) gave the pure product **59** as a light yellow oil (56.0 mg, 0.153 mmol, 51% yield).

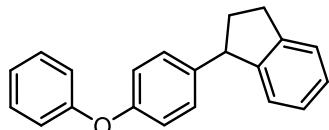
¹H NMR (500 MHz, CDCl_3) δ 7.33 – 7.29 (m, 4H), 7.25 (d, $J = 6.4$ Hz, 2H), 7.20 (t, $J = 8.3$ Hz, 3H), 7.10 – 7.06 (m, 1H), 7.00 – 6.91 (m, 4H), 4.18 (t, $J = 7.7$ Hz, 1H), 3.32 (t, $J = 6.7$ Hz, 2H), 2.55 (dd, $J = 14.3$, 6.9 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 157.3, 155.9, 143.6, 138.4, 129.9, 129.2, 128.8, 128.0, 126.7, 123.4, 119.1, 119.0, 48.6, 38.6, 32.1.

IR (film): ν (cm⁻¹) 3077, 3063, 3004, 2939, 2858, 1616, 1580, 1453, 1428, 1365, 1333, 1244, 1208, 1180, 1062, 1031, 910, 822, 745, 659, 651, 481.

MS (ESI) mass calculated for C₂₁H₂₀BrO⁺ [M+H]⁺ 367.0716, found 367.0717.

1-(4-phenoxyphenyl)-2,3-dihydro-1H-indene (60)



A Schlenk tube (10 mL) was charged diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), indan (**2r**, 106.4 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **60** as a colorless oil (42.9 mg, 0.150 mmol, 50% yield).

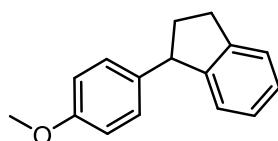
¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.27 (m, 3H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.20 – 7.16 (m, 3H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.12 – 6.91 (m, 5H), 4.36 (t, $J = 8.3$ Hz, 1H), 3.08 (m, 1H), 3.02 – 2.95 (m, 1H), 2.62 (m, 1H), 2.11 – 2.05 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 157.6, 155.7, 147.0, 144.4, 140.5, 129.8, 129.4, 126.7, 126.5, 125.0, 124.5, 123.2, 119.1, 118.8, 51.1, 36.8, 31.9.

IR (film): ν (cm⁻¹) 3363, 2922, 2849, 1588, 1488, 1408, 1237, 1166, 1022, 867, 751, 691, 535.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₁₉O⁺ [M+H]⁺ 287.1430, found 287.1438.

1-(4-methoxyphenyl)-2,3-dihydro-1H-indene (61)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), indan (**2r**, 106.4 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **61** as a

colorless oil (34.3 mg, 0.153 mmol, 51% yield).

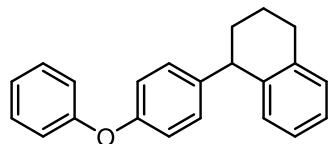
¹H NMR (500 MHz, CDCl₃) δ 7.31 (d, *J* = 7.4 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.15 – 7.13 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.90 – 6.87 (m, 2H), 4.32 (t, *J* = 8.3 Hz, 1H), 3.82 (s, 3H), 3.09 – 3.03 (m, 1H), 2.99 – 2.94 (m, 1H), 2.61 – 2.55 (m, 1H), 2.08 – 2.02 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 158.2, 147.3, 144.4, 137.6, 129.2, 126.6, 126.4, 125.0, 124.4, 114.0, 55.4, 51.0, 36.9, 31.9.

IR (film): ν (cm⁻¹) 3371, 2920, 2857, 1578, 1473, 1410, 1178, 1013, 865, 741, 676, 551.

MS (ESI) mass calculated for C₁₆H₁₇O⁺ [M+H]⁺ 225.1274, found 225.1278.

1-(4-phenoxyphenyl)-1,2,3,4-tetrahydronaphthalene (62)



A Schlenk tube (10 mL) was charged diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1,2,3,4-tetrahydronaphthalene (**2s**, 119.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **62** as a white solid (47.7 mg, 0.159 mmol, 53% yield).

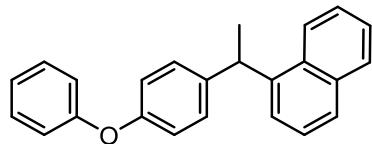
¹H NMR (500 MHz, CDCl₃) δ 7.36 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 5.5 Hz, 2H), 7.09 (m, 6H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 1H), 2.96 – 2.92 (m, 1H), 2.89 (q, *J* = 5.2, 4.5 Hz, 1H), 2.23 – 2.18 (m, 1H), 1.95 – 1.89 (m, 2H), 1.84 – 1.79 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 157.6, 155.4, 142.6, 139.5, 137.7, 130.3, 130.1, 129.8, 129.1, 126.1, 125.8, 123.1, 118.9, 118.8, 45.0, 33.4, 29.9, 21.0.

IR (film): ν (cm⁻¹) 3363, 2938, 2852, 2841, 1505, 1482, 1455, 1408, 1301, 1223, 1160, 1022, 751, 739, 691, 541.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₁O⁺ [M+H]⁺ 301.1587, found 301.1581.

1-(1-(4-phenoxyphenyl)ethyl)naphthalene (63)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-ethylnaphthalene (**2t**, 140.6 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **63** as a white solid (63.2 mg, 0.195 mmol, 65% yield).

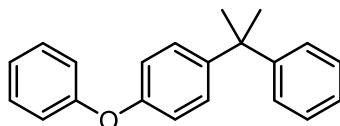
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.08 – 8.05 (m, 1H), 7.88 – 7.85 (m, 1H), 7.76 (d, $J = 7.9$ Hz, 1H), 7.49 – 7.44 (m, 4H), 7.31 (t, $J = 7.3$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 2H), 6.94 – 6.90 (m, 2H), 4.93 (q, $J = 7.0$ Hz, 1H), 1.78 (d, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.5, 155.4, 141.7, 141.7, 134.2, 131.8, 129.8, 129.0, 127.2, 126.0, 125.6, 125.5, 124.4, 124.1, 123.2, 119.0, 118.8, 40.0, 22.8.

IR (film): ν (cm^{-1}) 3502, 3054, 3027, 2965, 2919, 2849, 1662, 1485, 1392, 1181, 841, 766, 738, 697, 570.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{24}\text{H}_{21}\text{O}^+$ $[\text{M}+\text{H}]^+$ 325.1587, found 325.1592.

1-phenoxy-4-(2-phenylpropan-2-yl)benzene (64)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), cumene (**2u**, 108.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **64** as a white solid (42.3 mg, 0.147 mmol, 49% yield).

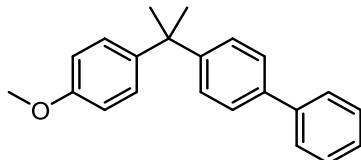
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35 – 7.30 (m, 3H), 7.28 (d, $J = 6.9$ Hz, 3H), 7.19 (d, $J = 8.6$ Hz, 3H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.93 – 6.89 (m, 2H), 1.69 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.5, 155.1, 150.8, 145.8, 129.8, 128.2, 128.2, 126.9, 125.8, 123.2, 118.9, 118.4, 42.7, 31.0.

IR (film): ν (cm $^{-1}$) 3085, 3068, 3029, 2927, 2871, 1944, 1867, 1801, 1702, 1632, 1550, 1494, 1466, 1458, 1364, 1323, 1282, 1108, 1050, 931, 906.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{21}\text{O}^+$ [M+H] $^+$ 289.1587, found 289.1595.

4-(2-(4-methoxyphenyl)propan-2-yl)-1,1'-biphenyl (65)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 4-isopropylbiphenyl (**2v**, 176.66 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **65** as a colorless oil (57.1 mg, 0.189 mmol, 63% yield).

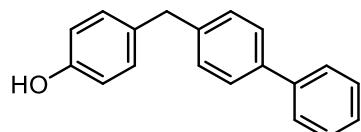
^1H NMR (500 MHz, CDCl_3) δ 7.58 (m, 2H), 7.52 – 7.49 (m, 2H), 7.44 – 7.40 (m, 2H), 7.34 – 7.29 (m, 3H), 7.22 – 7.18 (m, 2H), 6.86 – 6.82 (m, 2H), 3.80 (s, 3H), 1.71 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.6, 150.2, 142.9, 141.1, 138.5, 128.8, 128.0, 127.3, 127.2, 127.1, 126.8, 113.5, 55.4, 42.3, 31.1.

IR (film): ν (cm $^{-1}$) 3080, 3057, 2915, 2854, 1913, 1833, 1828, 1673, 1537, 1425, 1402, 1485, 1377, 1351, 1288, 1086, 913, 537.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{23}\text{O}^+$ [M+H] $^+$ 303.1743, found 303.1749.

4-([1,1'-biphenyl]-4-ylmethyl)phenol (66)



A Schlenk tube (10 mL) was charged with phenol (**1p**, 28.2 mg, 0.30 mmol), 4-methyl-1,1'-biphenyl (**2w**, 151.4 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness.

Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **66** as a colorless oil (41.4 mg, 0.159 mmol, 53% yield).

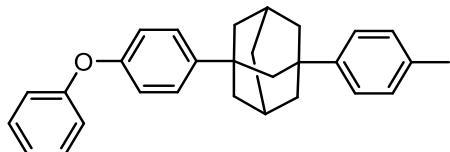
¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.59 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.98 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.1, 141.2, 140.8, 139.1, 133.4, 130.2, 129.3, 128.9, 127.3, 127.2, 127.2, 115.5, 40.8.

IR (film): ν (cm⁻¹) 3382, 3037, 2918, 2849, 1601, 1514, 1248, 1100, 819, 777, 689, 530.

HRMS (ESI-TOF, m/z) calculated for C₁₉H₁₆NaO⁺ [M+Na]⁺ 283.1093, found 283.1100.

1-(4-phenoxyphenyl)-3-(*p*-tolyl)adamantane (**67**)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-(*p*-tolyl)adamantane (**2x**, 678.5 mg, 3.0 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 80 °C for 60 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **67** as a colorless oil (61.5 mg, 0.156 mmol, 52% yield).

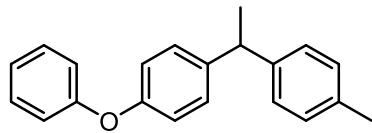
¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 8.7 Hz, 3H), 7.32 – 7.29 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00 (dd, *J* = 17.2, 8.3 Hz, 4H), 2.34 (s, 3H), 2.03 (s, 3H), 1.96 (d, *J* = 2.2 Hz, 10H), 1.80 (s, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 157.7, 155.0, 147.8, 145.9, 135.3, 129.8, 129.0, 126.3, 124.9, 123.1, 118.8, 188.7, 49.4, 42.6, 42.5, 37.1, 37.1, 36.1, 29.8, 21.0.

IR (film): ν (cm⁻¹) 3935, 3056, 2918, 2903, 2810, 2578, 2483, 1938, 1430, 1365, 1290, 1232, 978, 911, 859, 700.

HRMS (ESI-TOF, m/z) calculated for C₂₉H₃₀NaO⁺ [M+Na]⁺ 417.2189, found 417.2200.

1-methyl-4-(1-(4-phenoxyphenyl)ethyl)benzene (68)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-ethyl-4-methylbenzene (**2y**, 108.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **68** as a colorless oil (51.9 mg, 0.180 mmol, 60% yield).

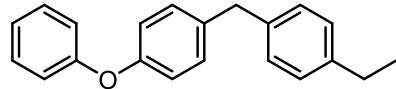
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.32 (t, $J = 7.9$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 1.4$ Hz, 4H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.02 – 6.98 (m, 2H), 6.93 (d, $J = 8.6$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 1H), 2.33 (s, 3H), 1.63 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.7, 155.4, 143.6, 141.7, 135.7, 129.8, 129.2, 128.9, 127.6, 123.1, 119.0, 118.8, 43.9, 22.2, 21.1.

IR (film): ν (cm⁻¹) 3135, 3094, 3005, 2929, 2873, 1893, 1791, 1516, 1377, 1234, 1118, 1022, 966, 816, 698, 468.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{21}\text{O}^+$ [M+H]⁺ 289.1587, found 289.1592.

1-ethyl-4-(4-phenoxybenzyl)benzene (68')



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-ethyl-4-methylbenzene (**2y**, 108.2 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **68'** as a colorless oil (10.4 mg, 0.036 mmol, 12% yield).

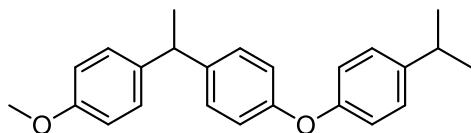
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 (t, $J = 7.9$ Hz, 2H), 7.20 – 7.12 (m, 6H), 7.10 (t, $J = 7.4$ Hz, 1H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.96 (d, $J = 8.5$ Hz, 2H), 3.96 (s, 2H), 2.65 (q, $J = 7.6$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.7, 155.5, 142.2, 138.5, 136.5, 130.2, 129.8, 128.9, 128.1, 123.1, 119.2, 118.7, 40.9, 28.6, 15.8.

IR (film): ν (cm⁻¹) 3135, 3094, 2966, 2929, 2731, 1893, 1649, 1516, 1377, 1234, 1118, 1022, 960, 816, 698, 468.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₂₁O⁺ [M+H]⁺ 289.1587, found 289.1592.

1-isopropyl-4-(4-(4-methoxyphenyl)ethyl)phenoxy)benzene (69)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 1-ethyl-4-(4-isopropylphenoxy)benzene (**2z**, 216.3 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 6:1) gave the pure product **69** as a colorless oil (73.7 mg, 0.213 mmol, 71% yield).

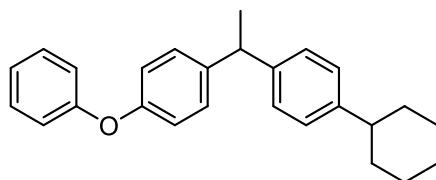
¹H NMR (500 MHz, CDCl₃) δ 7.20 (t, *J* = 6.0 Hz, 6H), 6.98 – 6.94 (m, 4H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 2.97 – 2.88 (m, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.28 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 158.0, 155.8, 155.4, 143.8, 141.5, 138.8, 128.7, 128.6, 127.6, 118.8, 118.6, 113.9, 55.3, 43.4, 33.6, 24.3, 22.4.

IR (film): ν (cm⁻¹) 3101, 3065, 3032, 2933, 2877, 1944, 1801, 1666, 1558, 1494, 1452, 1351, 1323, 1028, 906, 533, 518.

HRMS (ESI-TOF, m/z) calculated for C₂₄H₂₇O₂⁺ [M+H]⁺ 347.2006, found 347.2011.

1-cyclohexyl-4-(4-(4-phenoxyphenyl)ethyl)benzene (70)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-cyclohexyl-4-ethylbenzene (**2za**, 169.5 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **70** as a colorless oil (64.1 mg, 0.180 mmol, 60% yield).

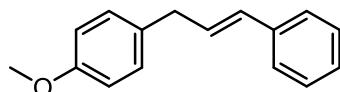
¹H NMR (500 MHz, CDCl₃) δ 7.32 (t, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.15 (s, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.11 (t, *J* = 7.2 Hz, 1H), 2.48 (dd, *J* = 10.9, 7.9 Hz, 1H), 1.89 – 1.82 (m, 5H), 1.75 (d, *J* = 12.6 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H), 1.48 – 1.32 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 157.6, 155.4, 145.9, 143.8, 141.8, 129.8, 129.0, 127.5, 126.9, 123.1, 118.9, 118.8, 44.2, 43.9, 34.6, 27.1, 26.3, 22.3.

IR (film): ν (cm⁻¹) 3080, 3066, 3001, 2777, 2669, 1939, 103, 1494, 1449, 1369, 1266, 1178, 1132, 1003, 986, 863, 765, 689, 526.

HRMS (ESI-TOF, m/z) calculated for C₂₆H₂₉O⁺ [M+H]⁺ 357.2213, found 357.2216.

1-cinnamyl-4-methoxybenzene (71)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), β -methylstyrene (**2zb**, 106.4 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **71** as a colorless oil (44.4 mg, 0.198 mmol, 66% yield).

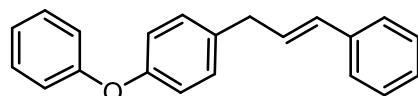
¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.35 (m, 1H), 3.81 (s, 3H), 3.50 (d, *J* = 6.6 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 158.2, 137.7, 132.3, 130.9, 129.8, 129.7, 128.6, 127.2, 126.2, 114.1, 55.4, 38.6.

IR (film): ν (cm⁻¹) 3103, 3083, 3061, 2934, 2915, 1663, 1644, 1578, 1443, 1408, 1379, 1105, 1081, 1069, 981, 964, 913, 806, 767, 613, 499.

HRMS (ESI-TOF, m/z) calculated for C₁₆H₁₇O⁺ [M+H]⁺ 225.1274, found 225.1279.

1-cinnamyl-4-phenoxybenzene (72)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), β -methylstyrene (**2zb**, 106.4 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air.

The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **72** as a colorless oil (58.4 mg, 0.204 mmol, 68% yield).

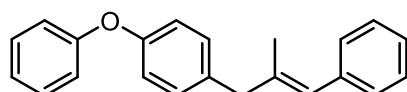
¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.20 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.92 (m, 4H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.35 (m, 1H), 3.53 (d, *J* = 6.7 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 157.7, 155.6, 137.6, 135.3, 131.2, 130.0, 129.8, 129.4, 128.7, 127.3, 126.3, 123.1, 119.3, 118.7, 38.8.

IR (film): ν (cm⁻¹) 3093, 3079, 3036, 2963, 2916, 1654, 1562, 1424, 1401, 1339, 1133, 1090, 1056, 963, 815, 735, 656, 513.

HRMS (ESI-TOF, m/z) calculated for C₂₁H₁₉O⁺ [M+H]⁺ 287.1430, found 287.1425.

(*E*)-1-(2-methyl-3-phenylallyl)-4-phenoxybenzene (**73**)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 2-methyl-1-phenylpropene (**2zc**, 119.0 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **73** as a white solid (52.2 mg, 0.174 mmol, 58% yield).

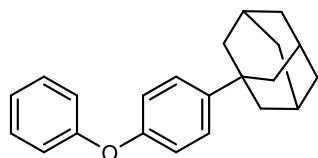
¹H NMR (500 MHz, CDCl₃) δ 7.32 (m, 5H), 7.28 (d, *J* = 2.8 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.38 (s, 1H), 3.46 (s, 2H), 1.82 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.7, 155.7, 138.4, 138.3, 134.9, 130.4, 129.8, 129.0, 128.2, 126.9, 126.3, 123.1, 119.1, 118.8, 46.5, 17.8.

IR (film): ν (cm⁻¹) 3016, 2978, 2881, 2750, 1694, 1612, 1566, 1477, 1259, 1142, 1067, 1053, 992, 926, 832, 756, 642, 557.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₁O⁺ [M+H]⁺ 301.1587, found 301.1588.

1-(4-phenoxyphenyl)adamantane (74)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), adamantane (**2zd**, 408.7 mg, 3.0 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 80 °C for 60 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **74** as a white solid (44.7 mg, 0.147 mmol, 49% yield).

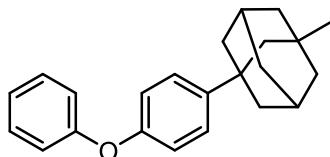
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35 – 7.30 (m, 4H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.01 (dd, $J = 8.6$, 0.9 Hz, 2H), 6.98 – 6.94 (m, 2H), 2.10 (s, 3H), 1.91 (d, $J = 2.5$ Hz, 6H), 1.77 (q, $J = 12.1$ Hz, 6H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.7, 154.9, 146.6, 129.8, 126.2, 123.0, 118.8, 118.6, 43.5, 36.9, 36.0, 29.1.

IR (film): ν (cm⁻¹) 3939, 3068, 3040, 2933, 2901, 2822, 2552, 1954, 1456, 1363, 1333, 1289, 1102, 988, 899, 792, 869, 693.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{25}\text{O}^+$ [M+H]⁺ 305.1900, found 305.1911.

1-methyl-3-(4-phenoxyphenyl)adamantane (75)



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 1-methyladamantane (**2ze**, 450.8 mg, 3.0 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 80 °C for 60 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE) gave the pure product **75** as a colorless oil (38.2 mg, 0.120 mmol, 40% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 – 7.30 (m, 4H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.01 (d, $J = 8.2$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 2H), 2.16 (s, 2H), 1.83 (dd, $J = 29.5$, 11.8 Hz, 5H), 1.70 – 1.66 (m, 2H), 1.50 (q, $J = 12.2$ Hz, 5H), 0.88 (s, 3H).

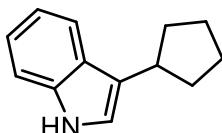
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.8, 154.9, 146.3, 129.8, 126.3, 123.0, 118.8, 118.7, 50.6,

43.9, 42.8, 36.9, 36.1, 31.3, 31.0, 29.7.

IR (film): ν (cm⁻¹) 3931, 3055, 2921, 2895, 2814, 2498, 1931, 1433, 1343, 1290, 1110, 976, 902, 869, 703.

HRMS (ESI-TOF, m/z) calculated for C₂₃H₂₇O⁺ [M+H]⁺ 319.2056, found 319.2060.

3-cyclopentyl-1*H*-indole (76)



A Schlenk tube (10 mL) was charged with indole (**1ze**, 35.1 mg, 0.30 mmol), cyclopentane (**2zf**, 0.75 mL) and FeBr₃ (32.5 mg, 0.11 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 25 °C for 120 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **76** as a white solid (23.9 mg, 0.129 mmol, 43% yield).

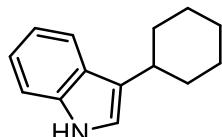
¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.72 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 3.42 – 3.35 (m, 1H), 2.30 – 2.24 (m, 2H), 1.96 – 1.89 (m, 2H), 1.87 – 1.79 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 136.7, 127.4, 121.9, 121.3, 119.8, 119.7, 119.1, 111.2, 37.1, 33.3, 25.4.

IR (film): ν (cm⁻¹) 3930, 3068, 3041, 2844, 2539, 1950, 1457, 1363, 1111, 983, 893, 788, 867, 663.

HRMS (ESI-TOF, m/z) calculated for C₁₃H₁₆N⁺ [M+H]⁺ 186.1277, found 186.1271.

3-cyclohexyl-1*H*-indole (77)



A Schlenk tube (10 mL) was charged with indole (**1ze**, 35.1 mg, 0.30 mmol), cyclohexane (**2zg**, 0.75 mL) and FeBr₃ (32.5 mg, 0.11 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 25 °C for 120 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **77** as a white solid (24.5

mg, 0.123 mmol, 41% yield).

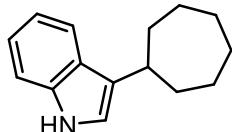
¹H NMR (500 MHz, CDCl₃) δ 7.85 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.15 (t, *J* = 9.6 Hz, 2H), 1.91 – 1.85 (m, 2H), 1.81 (d, *J* = 12.7 Hz, 1H), 1.50 (t, *J* = 9.9 Hz, 4H), 1.36 – 1.29 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 136.5, 126.9, 123.4, 121.9, 119.5, 119.4, 119.1, 111.2, 35.6, 34.2, 27.1, 26.7.

IR (film): ν (cm⁻¹) 3939, 3068, 3040, 2933, 2901, 2822, 2552, 1954, 1456, 1363, 1333, 1289, 1102, 988, 899, 792, 869, 693.

HRMS (ESI-TOF, m/z) calculated for C₁₄H₁₈N⁺ [M+H]⁺ 200.1434, found 200.1440.

3-cycloheptyl-1*H*-indole (78)



A Schlenk tube (10 mL) was charged with indole (**1ze**, 35.1 mg, 0.30 mmol), cycloheptane (**2zh**, 0.75 mL) and FeBr₃ (32.5 mg, 0.11 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 25 °C for 120 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **78** as a white solid (26.2 mg, 0.123 mmol, 41% yield).

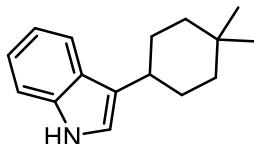
¹H NMR (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), 3.09 – 3.03 (m, 1H), 2.12 (ddd, *J* = 8.9, 6.6, 3.1 Hz, 2H), 1.84 – 1.78 (m, 2H), 1.78 – 1.70 (m, 4H), 1.66 – 1.59 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 136.6, 126.8, 124.6, 121.9, 119.5, 119.44, 119.1, 111.2, 37.4, 35.8, 28.5, 27.1.

IR (film): ν (cm⁻¹) 3944, 3077, 3053, 3046, 2941, 2801, 2664, 2553, 1936, 1476, 1338, 1323, 1269, 1024, 999, 876, 791, 866, 644, 593.

HRMS (ESI-TOF, m/z) calculated for C₁₅H₂₀N⁺ [M+H]⁺ 214.1590, found 214.1588.

3-(4,4-dimethylcyclohexyl)-1*H*-indole (79)



A Schlenk tube (10 mL) was charged with indole (**1ze**, 35.1 mg, 0.30 mmol), 1,1-dimethylcyclohexane (**2zi**, 0.75 mL) and FeBr_3 (32.5 mg, 0.11 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 25 °C for 120 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **79** as a white solid (29.3 mg, 0.129 mmol, 43% yield).

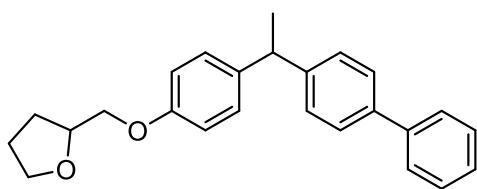
¹H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 7.9$ Hz, 1H), 7.78 (s, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.00 (d, $J = 2.1$ Hz, 1H), 2.89 (tt, $J = 12.0$, 3.5 Hz, 1H), 2.10 – 2.04 (m, 2H), 1.87 – 1.77 (m, 2H), 1.66 (d, $J = 12.8$ Hz, 2H), 1.60 – 1.52 (m, 2H), 1.15 (s, 3H), 1.14 (s, 3H).

¹³C NMR (126 MHz, CDCl_3) δ 136.5, 127.0, 122.8, 121.9, 119.6, 119.5, 119.1, 111.3, 39.9, 35.6, 33.3, 30.2, 29.8, 24.6.

IR (film): ν (cm⁻¹) 3943, 3066, 3061, 2912, 2844, 2738, 1976, 1456, 1444, 1384, 1365, 1343, 1217, 1175, 1062, 974, 954, 939, 857, 843.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{16}\text{H}_{22}\text{N}^+$ [M+H]⁺ 228.1747, found 228.1751.

2-((4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenoxy)methyl)tetrahydrofuran (92)



A Schlenk tube (10 mL) was charged with 2-(phenoxy)methyltetrahydrofuran (**1zo**, 53.4 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **92** as a white solid (64.5 mg, 0.180 mmol, 60% yield).

¹H NMR (500 MHz, CDCl_3) δ 7.58 – 7.55 (m, 2H), 7.53 – 7.49 (m, 2H), 7.42 (dd, $J = 10.5$, 4.8 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 8.6$ Hz, 2H), 6.89 – 6.86 (m, 2H), 4.29 – 4.24 (m, 1H), 4.15 (q, $J = 7.2$ Hz, 1H), 3.98 – 3.95 (m, 1H), 3.94 – 3.90 (m,

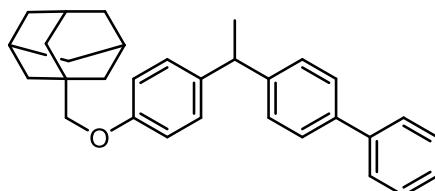
2H), 3.83 (dd, J = 14.4, 7.6 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.95 (dtd, J = 10.9, 8.3, 6.8 Hz, 2H), 1.79 – 1.73 (m, 1H), 1.65 (d, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.2, 145.9, 141.0, 138.9, 138.6, 128.7, 128.5, 127.9, 127.1, 127.0, 114.5, 77.1, 70.5, 68.6, 43.7, 28.3, 25.7, 22.1.

IR (film): ν (cm $^{-1}$) 3600, 344, 2977, 2874, 1460, 1445, 1356, 1434, 1285, 1203, 1197, 1098, 1042, 975, 932, 901, 867, 648, 489.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{25}\text{H}_{27}\text{O}_2^+$ [M+H] $^+$ 359.2006, found 359.2014.

1-((4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenoxy)methyl)adamantane (93)



A Schlenk tube (10 mL) was charged with 1-(phenoxyethyl)adamantane (**1zp**, 72.7 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **93** as a white solid (63.3 mg, 0.150 mmol, 50% yield).

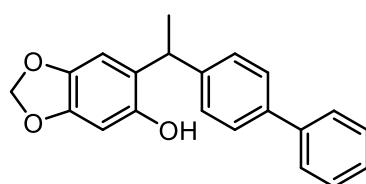
^1H NMR (500 MHz, CDCl_3) δ 7.62 – 7.59 (m, 1H), 7.55 (dd, J = 6.3, 2.0 Hz, 1H), 7.44 (d, J = 1.6 Hz, 1H), 7.34 (d, J = 14.6 Hz, 1H), 7.21 (s, 1H), 6.90 (s, 1H), 4.18 (d, J = 7.2 Hz, 1H), 3.51 (s, 1H), 2.05 (dd, J = 6.2, 3.2 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.70 – 1.68 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 158.2, 146.2, 141.2, 138.9, 138.1, 128.8, 128.6, 128.0, 127.2, 127.1, 114.5, 78.4, 43.8, 39.7, 37.3, 33.9, 28.4, 22.2.

IR (film): ν (cm $^{-1}$) 3229, 2913, 2845, 2674, 2655, 1471, 1434, 1367, 1346, 1316, 1221, 1172, 1104, 1042, 998, 975, 939, 912, 805, 699, 600, 488.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{31}\text{H}_{35}\text{O}^+$ [M+H] $^+$ 423.2682, found 423.2683.

6-(1-([1,1'-biphenyl]-4-yl)ethyl)benzo[d][1,3]dioxol-5-ol (94)



A Schlenk tube (10 mL) was charged with sesamol (**1zq**, 41.4 mg, 0.30 mmol), 4-ethylbiphenyl

(**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **94** as a white solid (59.2 mg, 0.186 mmol, 62% yield).

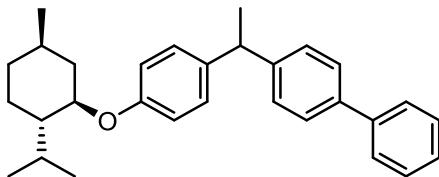
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 – 7.56 (m, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.35 – 7.32 (m, 3H), 6.78 (s, 1H), 6.40 (s, 1H), 5.90 (d, $J = 3.5$ Hz, 2H), 4.36 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 147.7, 146.3, 144.6, 141.7, 140.9, 139.4, 128.8, 127.8, 127.5, 127.2, 127.1, 124.2, 107.4, 101.1, 98.9, 38.1, 21.3.

IR (film): ν (cm⁻¹) 3474, 2964, 2927, 1503, 1485, 1436, 1169, 1037, 852, 766, 697, 590.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{21}\text{H}_{19}\text{O}_3^+ [\text{M}+\text{H}]^+$ 319.1329, found 319.1321.

4-(1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy)phenyl)ethyl)-1,1'-biphenyl (**95**)



A Schlenk tube (10 mL) was charged with ((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy)benzene (**1zr**, 69.7 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **95** as a colorless oil (90.2 mg, 0.219 mmol, 73% yield).

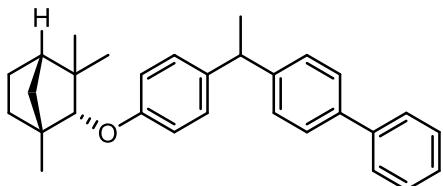
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 7.3$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.35 – 7.30 (m, 3H), 7.16 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 4.15 (q, $J = 7.2$ Hz, 1H), 4.01 (td, $J = 10.5, 4.1$ Hz, 1H), 2.23 (tt, $J = 9.1, 3.5$ Hz, 1H), 2.17 (d, $J = 12.5$ Hz, 1H), 1.75 – 1.70 (m, 2H), 1.67 (d, $J = 7.2$ Hz, 3H), 1.56 – 1.46 (m, 2H), 1.14 – 0.99 (m, 3H), 0.93 (dd, $J = 9.5, 6.9$ Hz, 6H), 0.79 (d, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 156.8, 146.1, 141.2, 139.0, 138.3, 128.8, 128.67, 128.1, 127.21, 127.2, 115.9, 77.6, 48.2, 43.8, 40.5, 34.7, 31.6, 26.2, 23.9, 22.3, 22.2, 20.9, 16.7.

IR (film): ν (cm⁻¹) 3344, 332, 2956, 2870, 2772, 1385, 1345, 1313, 1227, 1141, 1104, 1079, 1026, 994, 967, 845, 555, 541, 493.

HRMS (ESI-TOF, m/z) calculated for $C_{30}H_{37}O^+$ $[M+H]^+$ 413.2839, found 413.2848.

(1*S*,2*R*,4*S*)-2-(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenoxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (96)



A Schlenk tube (10 mL) was charged with (1*R*,2*R*,4*S*)-2-(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenoxy)-1,3,3-trimethylbicyclo[2.2.1]heptane (**1zs**, 68.8 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $FeCl_3 \cdot 6H_2O$ (16.2 mg, 0.060 mmol) and $(CHCl_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{max} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **96** as a colorless oil (68.9 mg, 0.168 mmol, 56% yield).

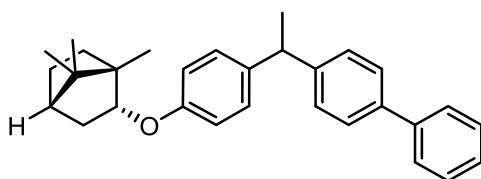
¹H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, $J = 8.2, 1.4$ Hz, 2H), 7.53 (s, 2H), 7.44 (dd, $J = 9.7, 4.1$ Hz, 2H), 7.33 (dd, $J = 12.8, 8.1$ Hz, 3H), 7.15 (dd, $J = 6.5, 2.2$ Hz, 2H), 6.86 (dd, $J = 6.6, 2.1$ Hz, 2H), 4.15 (dd, $J = 14.4, 7.2$ Hz, 1H), 3.85 – 3.83 (m, 1H), 2.07 – 2.02 (m, 1H), 1.79 (dd, $J = 9.4, 6.2$ Hz, 1H), 1.75 – 1.73 (m, 1H), 1.67 (d, $J = 7.2$ Hz, 3H), 1.59 (s, 1H), 1.48 (s, 1H), 1.22 – 1.20 (m, 1H), 1.18 (d, $J = 3.9$ Hz, 3H), 1.11 (s, 3H), 1.10 – 1.06 (m, 1H), 0.88 (s, 3H).

¹³C NMR (126 MHz, $CDCl_3$) δ 158.7, 146.1, 141.1, 138.9, 137.8, 128.7, 128.4, 128.0, 127.1, 127.0, 127.0, 115.7, 90.2, 49.6, 49.1, 43.7, 41.4, 40.0, 30.5, 26.4, 25.9, 22.1, 20.5, 20.0.

IR (film): ν (cm⁻¹) 3426, 3081, 3000, 2832, 1611, 1589, 1407, 1342, 1310, 1166, 1017, 988, 800, 761, 724, 494.

HRMS (ESI-TOF, m/z) calculated for $C_{30}H_{35}O^+$ $[M+H]^+$ 411.2682, found 411.2677.

(1*S*,2*R*,4*S*)-2-(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenoxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (97)



A Schlenk tube (10 mL) was charged with (1*S*,2*R*,4*S*)-1,7,7-trimethyl-2-phenoxybicyclo[2.2.1]heptane (**1zt**, 69.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90

mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **97** as a colorless oil (81.2 mg, 0.198 mmol, 66% yield).

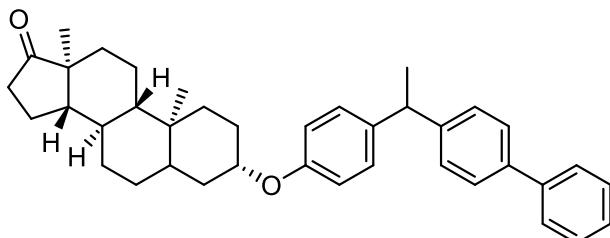
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 2H), 7.55 (d, $J = 7.9$ Hz, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.37 – 7.32 (m, 3H), 7.19 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 4.33 (d, $J = 9.1$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 1H), 2.41 – 2.36 (m, 1H), 2.30 – 2.26 (m, 1H), 1.81 – 1.76 (m, 2H), 1.69 (d, $J = 7.2$ Hz, 3H), 1.39 – 1.34 (m, 1H), 1.31 – 1.27 (m, 1H), 1.16 (dd, $J = 13.3$, 1.6 Hz, 1H), 0.97 (s, 3H), 0.95 (d, $J = 3.4$ Hz, 6H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.6, 146.2, 141.2, 139.0, 138.0, 128.8, 128.6, 128.1, 127.2, 127.1, 115.4, 82.9, 49.6, 47.7, 45.3, 43.8, 37.0, 28.1, 26.9, 22.2, 19.9, 19.1, 13.9.

IR (film): ν (cm⁻¹) 3426, 3081, 3000, 2832, 1611, 1589, 1407, 1342, 1310, 1166, 1017, 988, 800, 761, 724, 494.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{30}\text{H}_{35}\text{O}^+$ [M+H]⁺ 411.2682, found 411.2680.

(3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-3-(4-(1-([1,1'-biphenyl]-4-yl)ethyl)phenoxy)-10,13-dimethylhexadecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (98)



A Schlenk tube (10 mL) was charged with (3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-3-phenoxyhexadecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**1zu**, 109.9 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **98** as a colorless oil (57.4 mg, 0.105 mmol, 35% yield).

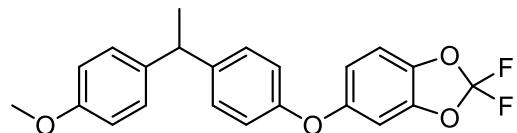
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58 – 7.56 (m, 2H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.34 – 7.31 (m, 1H), 7.30 – 7.28 (m, 2H), 7.17 – 7.14 (m, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 4.52 – 4.47 (m, 1H), 4.14 (d, $J = 7.2$ Hz, 1H), 2.44 (d, $J = 10.4$ Hz, 1H), 2.12 – 2.03 (m, 2H), 1.97 – 1.91 (m, 2H), 1.80 (ddd, $J = 13.8$, 7.1, 3.3 Hz, 3H), 1.65 (d, $J = 7.2$ Hz, 6H), 1.61 – 1.55 (m, 2H), 1.52 – 1.46 (m, 3H), 1.40 (d, $J = 9.6$ Hz, 1H), 1.27 (d, $J = 5.2$ Hz, 3H), 1.03 (d, $J = 18.6$ Hz, 2H), 0.87 (s, 3H), 0.85 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.1, 146.0, 141.0, 138.8, 138.1, 128.7, 128.5, 128.0, 127.1, 127.0, 127.0, 115.9, 71.90, 54.3, 51.5, 47.9, 43.7, 39.6, 36.0, 35.9, 35.1, 32.8, 32.7, 31.6, 30.8, 28.2, 25.7, 22.1, 21.8, 20.1, 13.9, 11.5.

IR (film): ν (cm⁻¹) 3470, 2976, 2950, 2916, 2891, 2837, 1728, 1469, 1451, 1387, 1373, 1305, 1293, 1132, 1099, 1060, 1024, 1010, 901, 888, 614, 589.

HRMS (ESI-TOF, m/z) calculated for C₃₉H₄₇O₂⁺ [M+H]⁺ 547.3571, found 547.3579.

2,2-difluoro-5-(4-(1-(4-methoxyphenyl)ethyl)phenoxy)benzo[d][1,3]dioxole (99)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 5-(4-ethylphenoxy)-2,2-difluorobenzo[d][1,3]dioxole (**2zj**, 250.4 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **99** as a colorless oil (80.7 mg, 0.210 mmol, 70% yield).

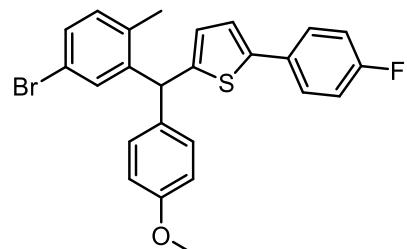
¹H NMR (500 MHz, CDCl₃) δ 7.18 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.81 – 6.63 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.1, 155.3, 153.9, 144.4, 142.5, 139.6, 138.5, 129.0 (d, *J*_{C-F} = 225.0 Hz), 118.7, 114.0, 113.4, 109.7, 102.0, 55.4, 43.5, 22.3.

IR (film): ν (cm⁻¹) 3065, 3007, 2954, 2944, 2779, 1750, 1628, 1498, 1484, 1405, 1334, 1304, 1266, 1152, 1093, 1023, 882, 691, 533.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₁₉F₂O₄⁺ [M+H]⁺ 385.1246, found 385.1244.

2-((5-bromo-2-methylphenyl)(4-methoxyphenyl)methyl)-5-(4-fluorophenyl)thiophene (100)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (**2zk**, 324.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **100** as a colorless oil (81.1 mg, 0.174 mmol, 58% yield).

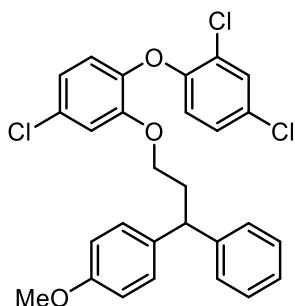
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.50 (dd, $J = 8.4, 5.4$ Hz, 2H), 7.31 – 7.29 (m, 1H), 7.18 (s, 1H), 7.09 (d, $J = 8.6$ Hz, 2H), 7.08 (d, $J = 3.7$ Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 3H), 6.87 (d, $J = 8.5$ Hz, 2H), 6.57 (d, $J = 3.5$ Hz, 1H), 5.70 (s, 1H), 3.81 (s, 3H), 2.23 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.3, 161.4, 158.7, 146.8, 144.6, 142.6, 135.4, 134.3, 131.9 (d, $J_{\text{C-F}} = 340.0$ Hz), 130.8 (d, $J_{\text{C-F}} = 10.0$ Hz), 130.1, 130.0, 127.8, 127.3 (d, $J_{\text{C-F}} = 30.0$ Hz), 122.71, 119.97, 115.9 (d, $J_{\text{C-F}} = 80.0$ Hz), 114.1, 55.4, 48.0, 19.4.

IR (film): ν (cm⁻¹) 3937, 3828, 3087, 3077, 3055, 2920, 1942, 1769, 1687, 1579, 1526, 1555, 1251, 1034, 1000, 988, 903, 871, 831, 714, 519, 457, 447.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{25}\text{H}_{20}\text{BrFNaOS}^+ [\text{M}+\text{Na}]^+$ 489.0294, found 489.0289.

2,4-dichloro-1-(4-chloro-2-(3-(4-methoxyphenyl)-3-phenylpropoxy)phenoxy)benzene (101)



A Schlenk tube (10 mL) was charged with anisole (**1a**, 32.4 mg, 0.30 mmol), 2,4-dichloro-1-(4-chloro-2-(3-phenylpropoxy)phenoxy)benzene (**2zl**, 366.3 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and DCE (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **101** as a colorless oil (61.4 mg, 0.120 mmol, 40% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.44 (d, $J = 2.5$ Hz, 1H), 7.24 (s, 1H), 7.17 (d, $J = 7.4$ Hz, 1H), 7.11 (dd, $J = 9.5, 6.4$ Hz, 4H), 7.02 (dd, $J = 10.3, 8.7$ Hz, 3H), 6.91 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.83 – 6.81 (m, 3H), 6.65 (d, $J = 8.8$ Hz, 1H), 3.86 (d, $J = 6.3$ Hz, 1H), 3.82 (t, $J = 6.0$ Hz, 2H),

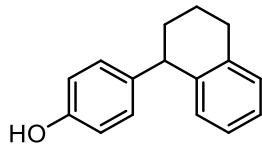
3.77 (s, 3H), 2.30 (dd, J = 12.7, 6.4 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 158.2, 153.0, 151.0, 144.4, 142.9, 136.1, 130.9, 130.4, 129.9, 128.9, 128.7, 127.9, 127.7, 126.4, 124.4, 122.7, 121.1, 117.6, 114.7, 114.0, 66.8, 55.4, 45.9, 35.0.

IR (film): ν (cm^{-1}) 3245, 3001, 2987, 1612, 1573, 1499, 1450, 1249, 1200, 1081, 1035, 996, 869, 677, 547.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{28}\text{H}_{23}\text{Cl}_3\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 535.0605, found 535.0611.

4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenol (102)



A Schlenk tube (10 mL) was charged phenol (**1p**, 28.2 mg, 0.30 mmol), 1,2,3,4-tetrahydronaphthalene (**2s**, 118.9 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and CHCl_3 (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **102** as a white solid (46.4 mg, 0.207 mmol, 69% yield).

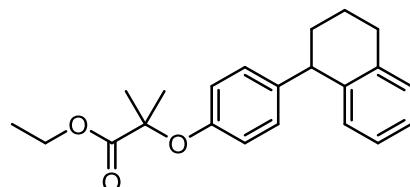
^1H NMR (500 MHz, CDCl_3) δ 7.14 (d, J = 6.1 Hz, 2H), 7.06 (dd, J = 9.7, 4.2 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 8.5 Hz, 2H), 4.87 (br, s, 1H), 4.08 (t, J = 6.5 Hz, 1H), 2.93 – 2.89 (m, 1H), 2.87 (t, J = 5.9 Hz, 1H), 2.17 – 2.13 (m, 1H), 1.91 – 1.85 (m, 2H), 1.80 – 1.76 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 153.8, 140.0, 139.8, 137.7, 130.2, 130.0, 129.1, 126.0, 125.7, 115.2, 44.9, 33.5, 29.9, 21.1.

IR (film): ν (cm^{-1}) 3101, 3075, 3044, 2853, 2838, 1579, 1557, 1431, 1341, 1238, 986, 824, 822, 690, 618.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{16}\text{H}_{17}\text{O}^+$ $[\text{M}+\text{H}]^+$ 225.1274, found 225.1268.

ethyl 2-methyl-2-(4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenoxy)propanoate (104)



According to the reference,^[7] a solution of 4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenol (**102**,

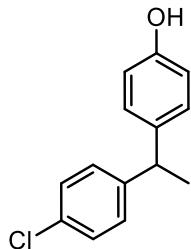
64.0 mg, 0.28 mmol) in DMF (2.0 mL), MgSO₄ (35.0 mg, 0.29 mmol), K₂CO₃ (157.0 mg, 1.12 mmol) and *tert*-butyl α -bromo isobutyrate (**103**, 266 μ L, 1.4 mmol) were added and the reaction was stirred at 100 °C for 24 h. After that time, the reaction was quenched with water (30 mL) and extracted three times with ethyl acetate (3 \times 20 mL). The combined organic layers were dried over MgSO₄, the solvent was removed under reduced pressure. Purification using silica gel column chromatography (elution with PE:EtOAc = 5:1) gave the pure product **104** as a colorless oil (92.9 mg, 0.275 mmol, 98% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.13 – 7.09 (m, 2H), 7.04 – 7.00 (m, 1H), 6.96 – 6.92 (m, 2H), 6.83 (d, J = 7.7 Hz, 1H), 6.77 – 6.73 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 4.05 (t, J = 6.7 Hz, 1H), 2.93 – 2.78 (m, 2H), 2.17 – 2.07 (m, 1H), 1.88 – 1.73 (m, 3H), 1.58 (s, 6H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.4, 152.5, 140.1, 138.6, 136.5, 129.1, 128.3, 127.9, 124.8, 124.5, 118.0, 78.0, 60.3, 43.8, 32.2, 28.7, 24.4, 19.9, 13.0.

HRMS (ESI-TOF, m/z) calculated for C₂₂H₂₆NaO₃⁺ [M+Na]⁺ 361.1774, found 361.1769.

4-(1-(4-chlorophenyl)ethyl)phenol (**105**)



A Schlenk tube (10 mL) was charged phenol (**1p**, 28.2 mg, 0.30 mmol), 1-chloro-4-ethylbenzene (**2e**, 126.5 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and CHCl₃ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **105** as a colorless oil (43.2 mg, 0.186 mmol, 62% yield).

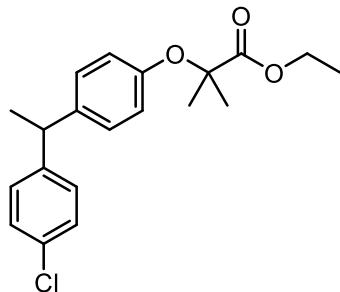
¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, J = 4.9 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.80 – 6.77 (m, 2H), 4.83 (br, s, 1H), 4.09 (q, J = 7.2 Hz, 1H), 1.61 (d, J = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 153.9, 145.3, 138.2, 131.7, 128.9, 128.7, 128.4, 115.3, 43.4, 22.0.

IR (film): ν (cm⁻¹) 3234, 3221, 3200, 2945, 2939, 1758, 1622, 1501, 1285, 1229, 1100, 832, 604, 535, 498, 478.

HRMS (ESI-TOF, m/z) calculated for C₁₄H₁₄ClO⁺ [M+H]⁺ 233.0728, found 233.0720.

ethyl 2-(4-(1-(4-chlorophenyl)ethyl)phenoxy)-2-methylpropanoate (106)



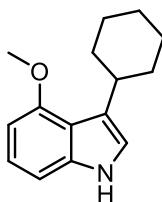
According to the published procedure,^[7] a solution of 4-(1-(4-chlorophenyl)ethyl)phenol (**103**, 65.0 mg, 0.28 mmol) in DMF (2.0 mL), MgSO₄ (35.0 mg, 0.29 mmol), K₂CO₃ (157.0 mg, 1.12 mmol) and *tert*-butyl α -bromoisobutyrate (**101**, 266 μ L, 1.4 mmol) were added and the reaction was stirred at 100 °C for 24 h. After that time, the reaction was quenched with water (30 mL) and extracted three times with ethyl acetate (3 \times 20 mL). The combined organic layers were dried over MgSO₄, the solvent was removed under reduced pressure. Purification using silica gel column chromatography (elution with PE:EtOAc = 5:1) gave the pure product **106** as a colorless oil (74.6 mg, 0.216 mmol, 77% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.21 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 6.78 – 6.74 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 4.05 (q, J = 7.2 Hz, 1H), 1.58 – 1.56 (m, 9H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 174.3, 153.7, 145.1, 139.4, 131.7, 128.9, 128.4, 128.1, 119.2, 79.1, 61.4, 43.4, 25.4, 25.4, 22.0, 14.1.

MS (ESI) mass calculated for C₂₀H₂₃ClNaO₃⁺ [M+Na]⁺ 369.1228, found 369.1232.

3-cyclohexyl-4-methoxy-1*H*-indole (107)



A Schlenk tube (10 mL) was charged with 4-methoxyindole (**1zv**, 44.2 mg, 0.30 mmol), cyclohexane (**2zg**, 0.75 mL) and FeBr₃ (32.5 mg, 0.11 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 25 °C for 120 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **107** as a white solid (26.1 mg, 0.114 mmol, 38% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.81 (s, 1H), 7.07 (t, J = 7.9 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H),

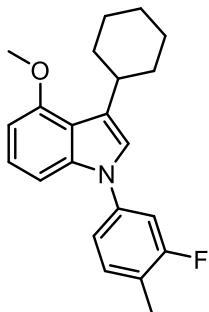
6.81 (d, $J = 2.1$ Hz, 1H), 6.48 (d, $J = 7.8$ Hz, 1H), 3.92 (s, 3H), 3.12 (tt, $J = 11.6, 3.1$ Hz, 1H), 2.17 – 2.12 (m, 2H), 1.84 (dd, $J = 9.7, 6.5$ Hz, 2H), 1.79 – 1.74 (m, 1H), 1.47 (qd, $J = 9.7, 6.4$ Hz, 2H), 1.38 – 1.32 (m, 2H), 1.27 (dt, $J = 12.8, 3.7$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 154.9, 138.0, 124.3, 122.5, 117.9, 116.9, 104.4, 99.4, 55.2, 36.3, 34.9, 27.1, 26.7.

IR (film): ν (cm $^{-1}$) 3924, 3101, 2061, 3056, 3001, 2900, 2886, 2812, 2566, 1958, 1950, 1403, 1397, 1343, 1303, 990, 876, 755, 693.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{15}\text{H}_{20}\text{NO}^+$ [M+H] $^+$ 230.1539, found 230.1541.

3-cyclohexyl-1-(3-fluoro-4-methylphenyl)-4-methoxy-1*H*-indole (**109**)



According to the published procedure, ^[8] an oven dried two-necked round bottom flask was charged with 2-fluoro-4-iodo-1-methylbenzene (**108**, 236.0 mg, 1.0 mmol), Cu-NP (101.7 mg, 1.6 mmol) and K_3PO_4 (424.5 mg, 2.0 mmol), evacuated and backfilled with an argon atmosphere. 3-cyclohexyl-4-methoxy-1*H*-indole (**107**, 229.2 mg, 1.0 mmol) and DMSO (2.0 mL) were added under argon. The flask was then immersed in a preheated oil bath at 80 °C until the conversion was completed. The cooled mixture was partitioned between EtOAc (10 mL) and saturated NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (2×10 mL), the organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. Purification using silica gel column chromatography (elution with PE:EtOAc = 1:1) gave the pure product **109** as a white solid (276.3 mg, 0.819 mmol, 82% yield).

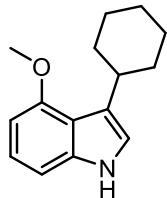
^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.27 (m, 1H), 7.24 (dd, $J = 7.9, 3.7$ Hz, 1H), 7.12 – 7.08 (m, 2H), 7.04 (d, $J = 8.2$ Hz, 1H), 6.90 (s, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 3.95 (s, 3H), 3.17 (tt, $J = 11.5, 2.9$ Hz, 1H), 2.34 (s, 3H), 2.18 (d, $J = 12.1$ Hz, 2H), 1.84 (d, $J = 13.0$ Hz, 2H), 1.77 (d, $J = 12.8$ Hz, 1H), 1.48 (tdd, $J = 12.8, 9.7, 3.1$ Hz, 2H), 1.41 – 1.34 (m, 2H), 1.30 – 1.26 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 155.1, 138.0, 136.1, 127.6 (d, $J_{\text{C-F}} = 25.0$ Hz), 126.3, 126.1, 125.2, 123.5 (d, $J_{\text{C-F}} = 35.0$ Hz), 123.0, 122.4, 118.2, 115.9 (d, $J_{\text{C-F}} = 95.0$ Hz), 103.6, 100.2, 55.4, 36.4, 35.0, 27.2, 26.8, 14.8.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{22}\text{H}_{25}\text{FNO}^+$ [M+H] $^+$ 338.1915, found 338.1919.

3.3 A Scale-up Reaction

3-cyclohexyl-4-methoxy-1*H*-indole (107)

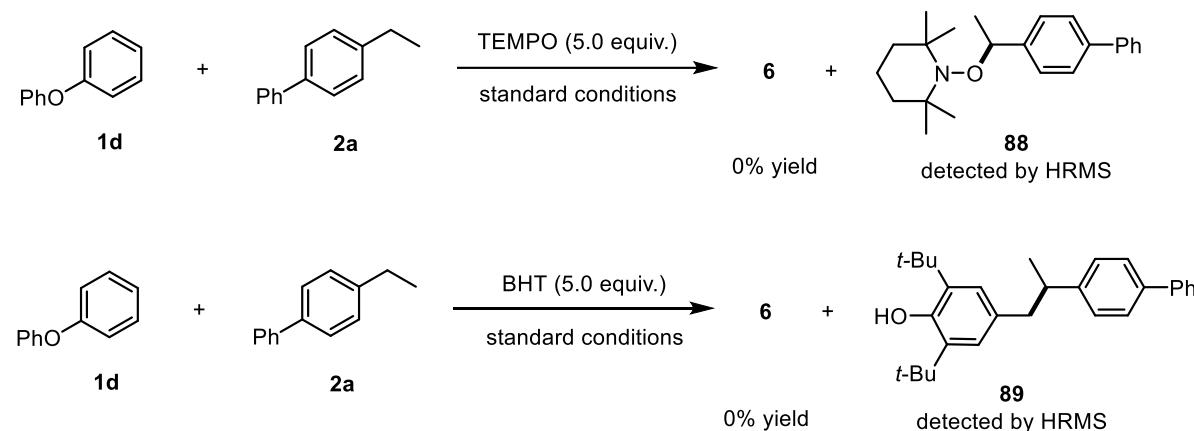


A Schlenk tube (10 mL) was charged with 4-methoxyindole (**1zv**, 839.8 mg, 5.7 mmol), cyclohexane (**2zg**, 20 mL) and FeBr_3 (591.0 mg, 0.11 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 40 W LED lamp ($\lambda_{\text{max}} = 370$ nm). After being stirred at 25 °C for 120 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 2:1) gave the pure product **107** as a white solid (444.1 mg, 1.938 mmol, 34% yield).

4. Mechanistic Investigations

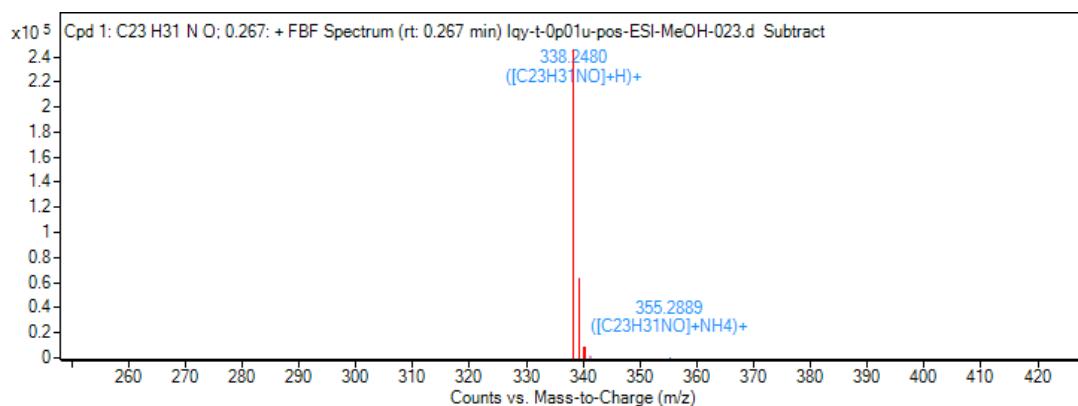
4.1 Radical Probing Experiments

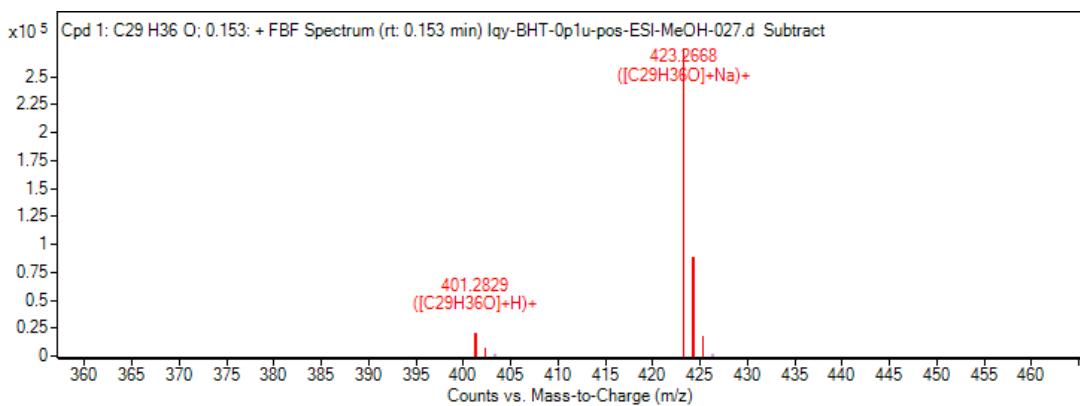
4.1.1 Probing Benzyl Radicals



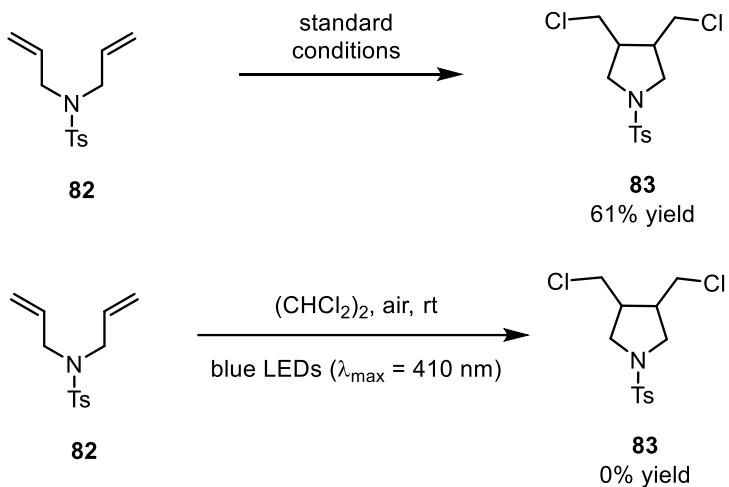
A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO, 234.5 mg, 1.50 mmol) or butylated hydroxytoluene (BHT, 330.5 mg, 1.50 mmol) was then added. The mixture was degassed *via* three freeze-pump-thaw cycles, and filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410 \text{ nm}$). After being stirred at 25 °C for 1 h, the reaction mixture was detected by HRMS.

For compound **88**, HRMS (ESI-TOF, m/z): calculated for $\text{C}_{23}\text{H}_{32}\text{NO}^+$ ($\text{M}+\text{H})^+$: 338.2478, found: 338.2480. For compound **89**, HRMS (ESI-TOF, m/z): calculated for $\text{C}_{29}\text{H}_{37}\text{O}^+$ ($\text{M}+\text{H})^+$: 401.2839, found: 401.2829.



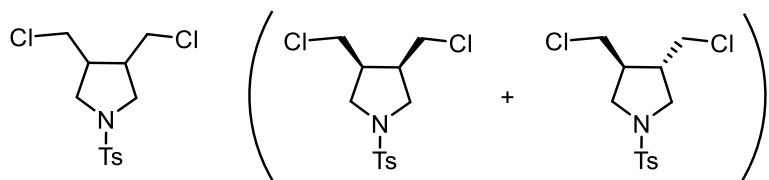


4.1.2 Probing Chlorine Radicals



A Schlenk tube (10 mL) was charged with *N,N*-diallyl-4-methylbenzenesulfonamide (**82**, 75.3 mg, 0.30 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410 \text{ nm}$). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:EtOAc = 3:1) gave the pure product **83** as a white solid (58.8 mg, 0.183 mmol, 61% yield).

3,4-bis(chloromethyl)-1-tosylpyrrolidine (**83**)

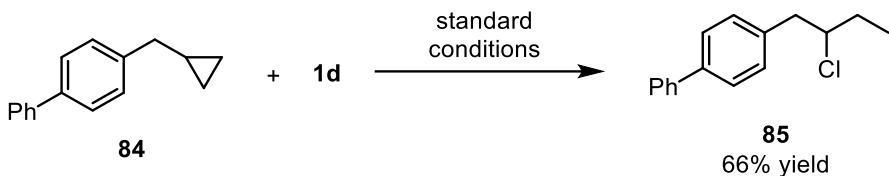


¹H NMR (500 MHz, CDCl₃) δ 7.71 (t, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.50 – 3.43 (m, 4H), 3.31 – 3.24 (m, 3H), 3.12 (dd, *J* = 10.3, 6.1 Hz, 1H), 2.64 – 2.60 (m, 1H), 2.43 (s, 3H), 2.42 – 2.34 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 144.1, 144.0, 133.5, 132.7, 129.9, 129.9, 127.9, 127.6, 51.2, 50.7, 45.3, 43.9, 43.3, 42.0, 21.7, 21.7.

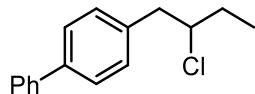
HRMS (ESI-TOF, m/z) calculated for C₁₃H₁₈Cl₂NO₂S⁺ [M+H]⁺ 322.0430, found 322.0433.

Remarks: In the absence of FeCl₃·6H₂O, compound **83** was not detected, indicating that chorine radicals derived from the iron salt rather than the solvent.



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-(cyclopropylmethyl)-1,1'-biphenyl (**84**, 187.5 mg, 0.90 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **85** as a white solid (48.3 mg, 0.198 mmol, 66% yield).

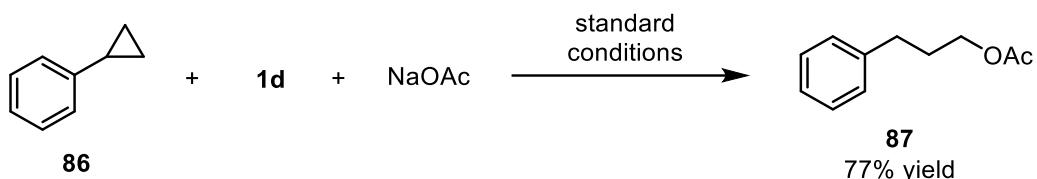
4-(2-chlorobutyl)-1,1'-biphenyl (**85**)



¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.58 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.27 (m, 3H), 4.16 – 4.04 (m, 1H), 3.10 (d, *J* = 6.9 Hz, 2H), 1.91 (td, *J* = 14.4, 7.2, 3.3 Hz, 1H), 1.74 (dt, *J* = 15.2, 7.6 Hz, 1H), 1.10 (t, *J* = 7.3 Hz, 3H).

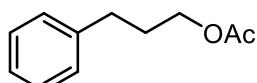
¹³C NMR (126 MHz, CDCl₃) δ 141.0, 139.8, 137.3, 129.9, 128.9, 127.3, 127.3, 127.2, 65.7, 44.41, 30.86, 11.08.

HRMS (ESI-TOF, m/z) calculated for C₁₆H₁₈Cl⁺ [M+H]⁺ 245.1092, found 245.1097.



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), cyclopropylbenzene (**86**, 106.3 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). NaOAc (204.1 mg, 1.5 mmol) was then added. The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410 \text{ nm}$). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 3:1) gave the pure product **87** as a colorless oil (41.1 mg, 0.231 mmol, 77% yield).

3-phenylpropyl acetate (**87**)

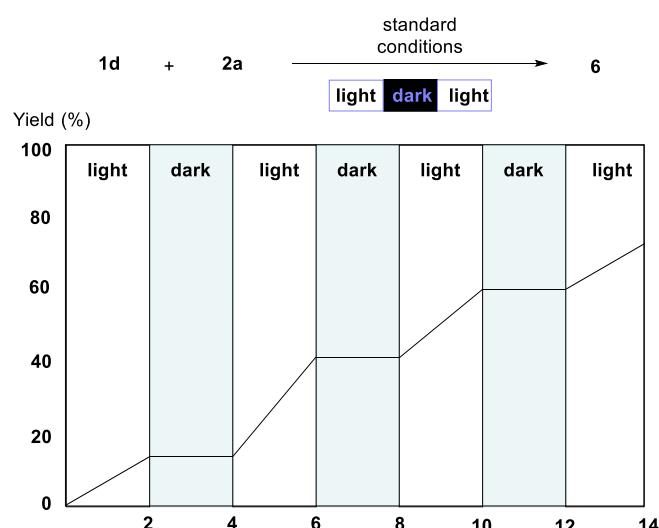


¹H NMR (500 MHz, CDCl_3) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 2H), 7.20 (s, 1H), 4.11 (t, $J = 6.6 \text{ Hz}$, 2H), 2.73 – 2.69 (m, 2H), 2.06 (s, 3H), 1.98 (ddt, $J = 13.1, 9.1, 6.5 \text{ Hz}$, 2H).

¹³C NMR (126 MHz, CDCl_3) δ 171.1, 141.2, 128.5, 128.4, 126.0, 63.9, 32.2, 30.2, 21.0.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{11}\text{H}_{15}\text{O}_2^+ [\text{M}+\text{H}]^+$ 179.2385, found 179.2389.

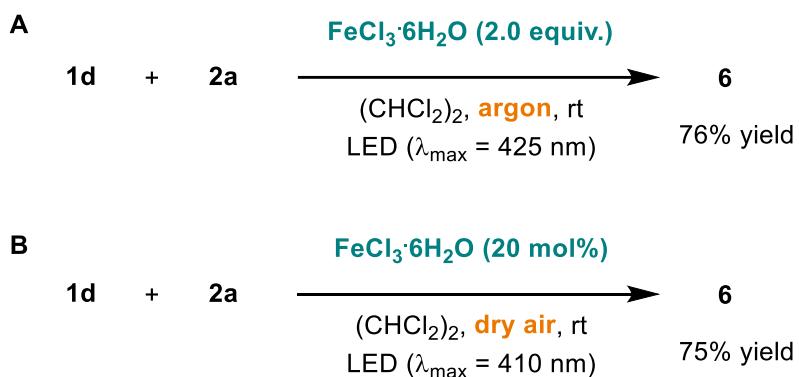
4.2 Light-Off/on Experiments



Supplementary Figure 1. Light-off/on experiments

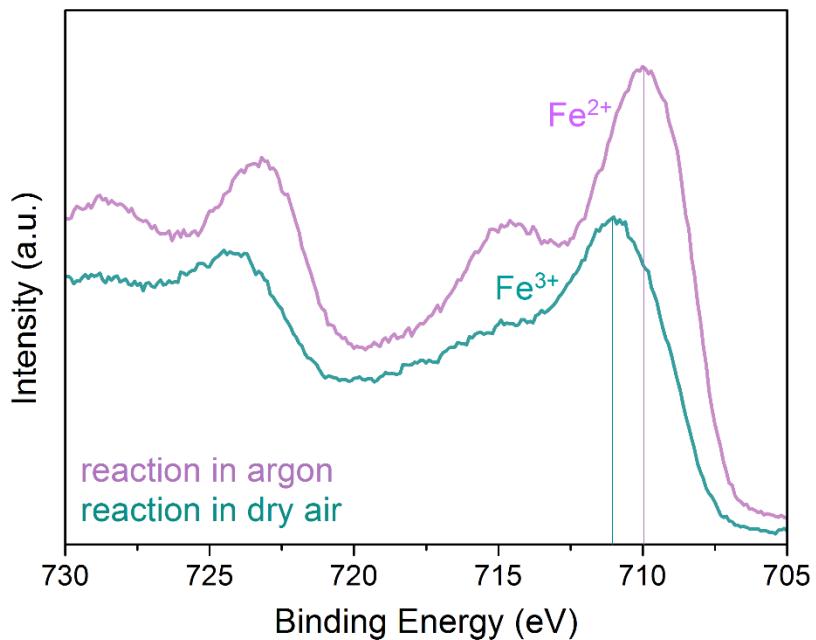
A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). The reaction was stirred at room temperature for the indicated time. A solution (0.10 mL) was taken from the reaction mixture, and the yields were determined by crude ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

4.3 XPS Spectroscopy



Sample A (a residue derived from the reaction in argon): A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (162.2 mg, 0.60 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with argon. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 425$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was filtered in argon and the residue was used for the X-ray photoelectron spectroscopy (XPS) analysis.

Sample B (a residue derived from the reaction in dry air): A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was filtered in argon and the residue was used for the XPS analysis.



Supplementary Figure 2. XPS analysis of reaction residues

4.4 UV/Vis-Absorption Spectra of the Reaction Components

Preparation of samples for the measurement of UV-Vis spectra:

2-Ethylbenzene **2a in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M):** 2-ethylbenzene **2a** was dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).

Diphenyl ether **1d in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M):** diphenyl ether **1d** was dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).

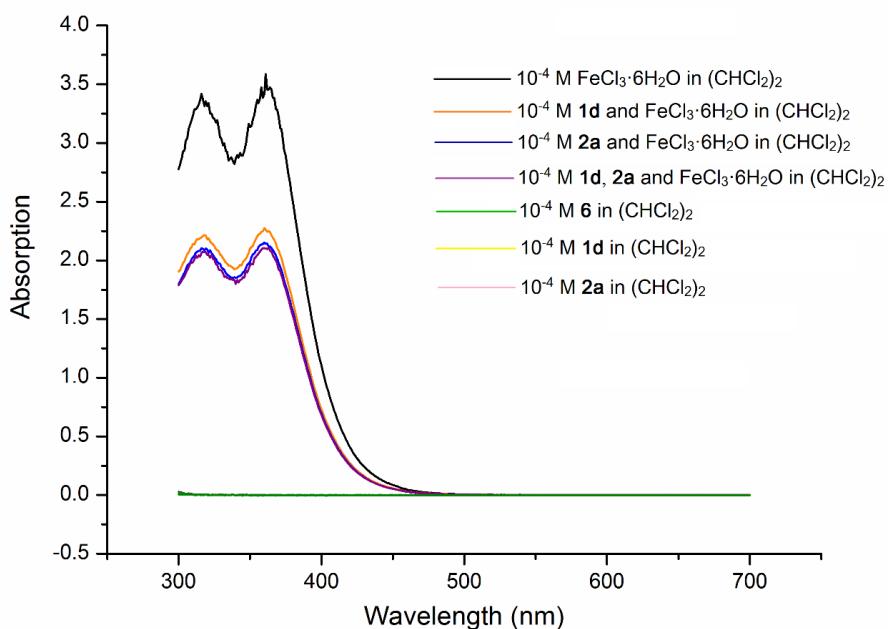
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M): $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).

2-Ethylbenzene **2a + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M):** 2-ethylbenzene **2a** and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).

Diphenyl ether **1d + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M):** diphenyl ether **1d** and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).

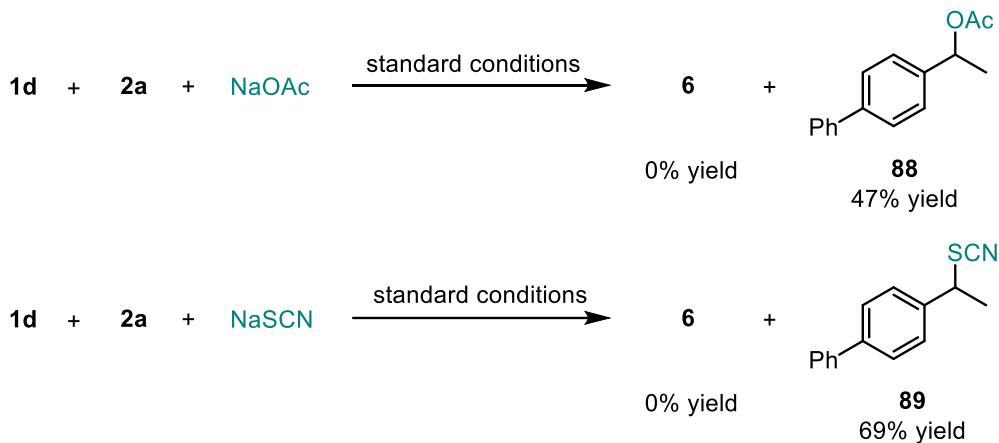
2-Ethylbenzene **2a + diphenyl ether **1d** + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M):** 2-ethylbenzene **2a**, diphenyl ether **1d** and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).

Product **6 in $(\text{CHCl}_2)_2$ (1.0×10^{-4} M):** product **6** was dissolved in distilled $(\text{CHCl}_2)_2$ (10 mL).



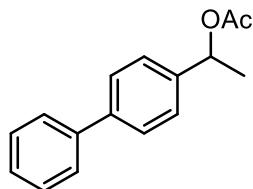
Supplementary Figure 3. UV-Vis spectra of the reaction components

4.5 Reaction Interfered with Competitive Nucleophiles



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), 4-ethylbiphenyl (**2a**, 164.0 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). Then NaOAc (204.1 mg, 1.5 mmol) or NaSCN (121.5 mg, 1.5 mmol) was added. The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 36 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:EtOAc = 5:1) gave the pure product **88** as a colorless oil (33.9 mg, 0.141 mmol, 47% yield), or **89** as a white solid (49.5 mg, 0.207 mmol, 69% yield).

1-([1,1'-biphenyl]-4-yl)ethyl acetate (88)

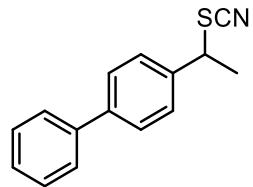


¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.9 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.93 (q, *J* = 6.6 Hz, 1H), 2.09 (s, 3H), 1.57 (d, *J* = 4.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.5, 141.3, 140.9, 140.8, 128.9, 1275, 127.4, 127.3, 126.7, 72.3, 22.3, 21.5.

HRMS (ESI-TOF, m/z) calculated for C₁₆H₁₆NaO₂⁺ [M+Na]⁺ 263.1043, found 263.1049.

4-(1-thiocyanatoethyl)-1,1'-biphenyl (89)

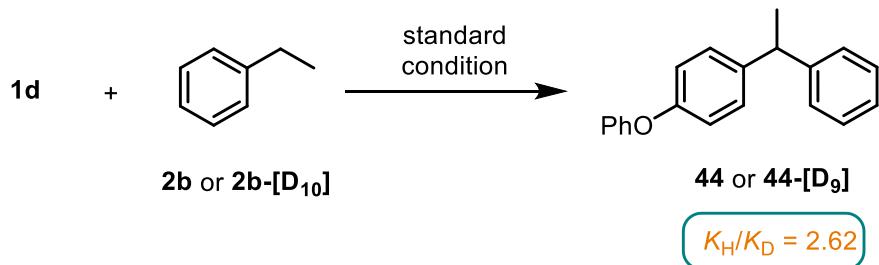


¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.56 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.34 (m, 3H), 4.95 (q, *J* = 6.8 Hz, 1H), 1.70 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 141.4, 140.5, 139.3, 129.0, 127.8, 127.7, 127.2, 126.0, 56.9, 25.1.

HRMS (ESI-TOF, m/z) calculated for C₁₅H₁₃NNaS⁺ [M+Na]⁺ 262.0661, found 262.0666.

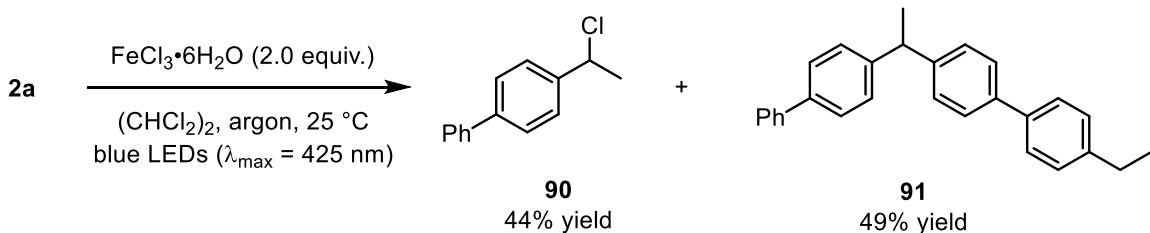
4.6 Kinetic Isotope Effect (KIE) Experiments



A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), ethylbenzene (**2b**, 95.6 mg, 1.0 mmol) or ethylbenzene-[D₁₀] (**2b-[D₁₀]**, 104.4 mg, 1.0 mmol), FeCl₃·6H₂O (16.2 mg, 0.060 mmol) and (CHCl₂)₂ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). The reaction was stirred at

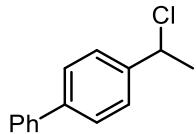
room temperature for the indicated time. The reaction mixture of hydrogen to deuterium in the product was determined as 2.62:1, thus the KIE value was $K_H/K_D = 2.62$.

4.7 Probing Other Intermediates



A Schlenk tube (10 mL) was charged with 4-ethylbiphenyl (**2a**, 54.6 mg, 0.30 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (162.2 mg, 0.60 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with an argon atmosphere. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 425 \text{ nm}$). After being stirred at 25 °C for 24 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **90** as a white solid (28.5 mg, 0.132 mmol, 44% yield) and **91** as a white solid (53.2 mg, 0.147 mmol, 49% yield).

4-(1-chloroethyl)-1,1'-biphenyl (**90**)

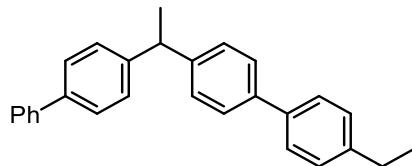


¹H NMR (500 MHz, CDCl_3) δ 7.77 – 7.74 (m, 2H), 7.62 – 7.50 (m, 2H), 7.54 – 7.41 (m, 4H), 7.40 – 7.36 (m, 1H), 5.26 (q, $J = 6.8 \text{ Hz}$, 1H), 1.97 (q, $J = 6.8 \text{ Hz}$, 3H).

¹³C NMR (126 MHz, CDCl_3) δ 144.7, 140.4, 139.1, 129.2, 128.9, 127.9, 127.4, 126.5, 60.0, 24.0.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{14}\text{H}_{14}\text{Cl}^+ [\text{M}+\text{H}]^+$ 217.0779, found 217.0780.

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-4'-ethyl-1,1'-biphenyl (**91**)

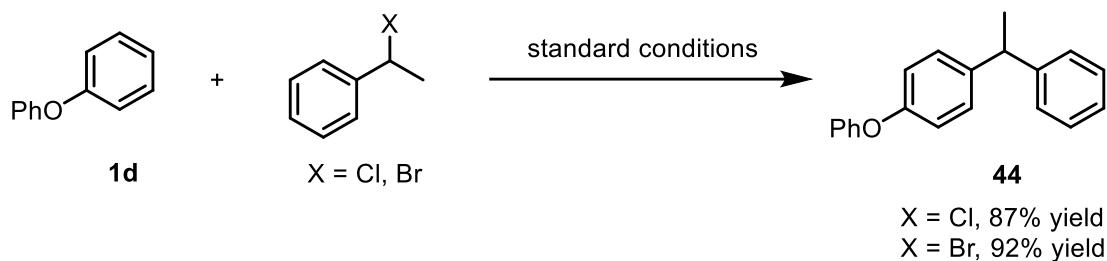


¹H NMR (500 MHz, CDCl_3) δ 7.62 (d, $J = 7.3 \text{ Hz}$, 2H), 7.58 – 7.53 (m, 6H), 7.45 (t, $J = 7.6$

Hz, 2H), 7.37 (t, J = 7.9 Hz, 5H), 7.29 (d, J = 8.0 Hz, 2H), 4.29 – 4.25 (m, 1H), 2.75 – 2.70 (m, 2H), 1.75 (d, J = 7.2 Hz, 3H), 1.32 (d, J = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 145.6, 145.2, 143.3, 141.1, 139.2, 138.5, 128.9, 128.4, 128.2, 128.1, 127.3, 127.2, 127.2, 127.1, 44.3, 28.6, 22.0, 15.7.

HRMS (ESI-TOF, m/z) calculated for $\text{C}_{28}\text{H}_{27}^+$ [M+H]⁺ 363.2107, found 363.2110.



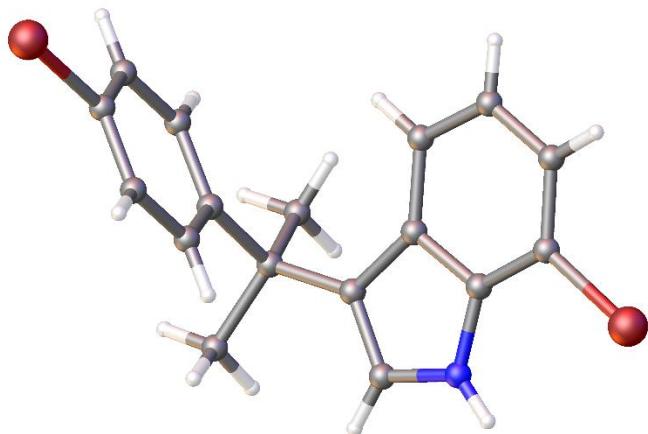
A Schlenk tube (10 mL) was charged with diphenyl ether (**1d**, 51.1 mg, 0.30 mmol), (1-chloroethyl)benzene (126.5 mg, 0.90 mmol) or (1-bromoethyl)benzene (166.6 mg, 0.90 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg, 0.060 mmol) and $(\text{CHCl}_2)_2$ (0.75 mL). The mixture was degassed *via* three freeze-pump-thaw cycles, then filled with dry air. The Schlenk tube was positioned approximately 5 cm away from a 50 W LED lamp ($\lambda_{\text{max}} = 410$ nm). After being stirred at 25 °C for 48 h, the reaction mixture was concentrated to dryness. Purification using silica gel column chromatography (elution with PE:DCM = 5:1) gave the pure product **44**. Obtained yields of 87% and 92%, respectively.

5. X-Ray Diffraction

5.1 Crystal Structure of Product 35

A procedure for crystallization. Compound **35** was dissolved in a mixture of CHCl_3 (0.5 mL) and hexane (1.0 mL). Single crystals were obtained after evaporation under ambient conditions for 4 days.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. Data reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on Supplementary Figure 4. Crystallographic data for complex **35** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2251704.

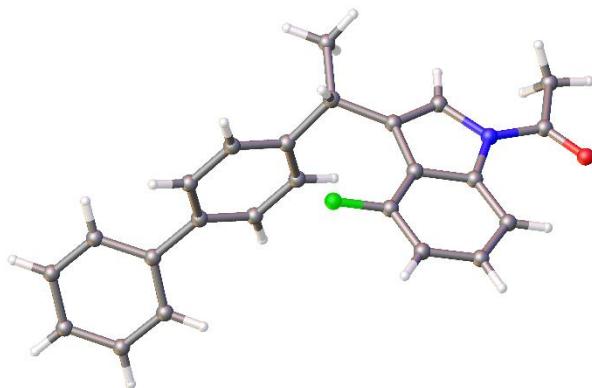


Supplementary Figure 4. Ortep drawing of compound **35**

5.2 Crystal Structure of Product 38

A procedure for crystallization. Compound **38** was dissolved in a mixture of CHCl_3 (0.5 mL) and hexane (1.0 mL). Single crystals were obtained after evaporation under ambient conditions for 5 days.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. Data reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on Supplementary Figure 5. Crystallographic data for complex **38** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2251707.



Supplementary Figure 5. Ortep drawing of compound **38**

Supplementary Table 2. Data collection and refinement statistics for the compounds **35** and **38**

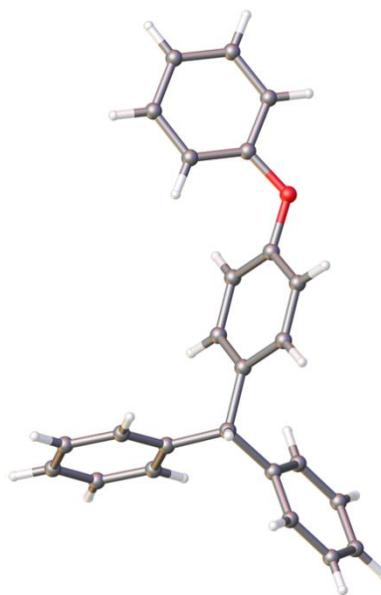
	35	38
CCDC	2251704	2251707
Empirical formula	C ₁₇ H ₁₅ Br ₂ N	C ₂₄ H ₂₀ FNO
Formula weight	357.41	357.41
Temperature (K)	265	272
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.3195, 17.5630, 19.6201	9.6287, 9.8951, 10.0269
α , β , γ (°)	68, 75, 89	100, 97, 95
Volume (Å ³)	3176.62	928.57
<i>Z</i>	2	2
Density (calculated, mg/m ³)	1.644	1.278
μ (mm ⁻¹)	6.374	0.678
<i>F</i> (000)	1552.0	376.0
Crystal size (mm ³)	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
2 θ range for data collection/°	5.042 to 177.252	9.134 to 150.266
Index ranges	-12 ≤ <i>h</i> ≤ 12, -21 ≤ <i>k</i> ≤ 22, -24 ≤ <i>l</i> ≤ 24	-12 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -9 ≤ <i>l</i> ≤ 12

Reflections collected	35049	9769
Independent reflections	12384 [$R_{\text{int}} = 0.0395$, $R_{\text{sigma}} = 0.0411$]	3616 [$R_{\text{int}} = 0.0244$, $R_{\text{sigma}} = 0.0288$]
Completeness	97.7%	99.4%
Absorption correction	multi-scan	multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12384/0/729	3616/0/247
Goodness-of-fit on F^2	1.071	1.058
Final R indices [$I >= 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.1242$	$R_1 = 0.0427$, $wR_2 = 0.1210$
R indices (all data)	$R_1 = 0.0605$, $wR_2 = 0.1384$	$R_1 = 0.0493$, $wR_2 = 0.1276$
Largest diff. peak/hole (e. \AA^{-3})	0.15/-0.98	0.17/-0.16

5.3 Crystal Structure of Product 56

A procedure for crystallization. Compound **56** was dissolved in a mixture of CHCl_3 (0.5 mL) and hexane (1.0 mL). Single crystals were obtained after evaporation under ambient conditions for 5 days.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. Data reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on Supplementary Figure 6. Crystallographic data for complex **56** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2098093.



Supplementary Figure 6. Ortep drawing of compound **56**

Supplementary Table 3. Data collection and refinement statistics for the compounds **56**

	56
CCDC	2098093
Empirical formula	C ₂₅ H ₂₀ O
Formula weight	336.41
Temperature (K)	100.15
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ /c
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.8428, 9.3075, 17.9231
α , β , γ (°)	90, 98, 90
Volume (Å ³)	1790.17
<i>Z</i>	4
Density (calculated, mg/m ³)	1.248
μ (mm ⁻¹)	0.573
<i>F</i> (000)	712.0
Crystal size (mm ³)	0.3 × 0.2 × 0.2
2 Θ range for data collection/°	8.24 to 124.464

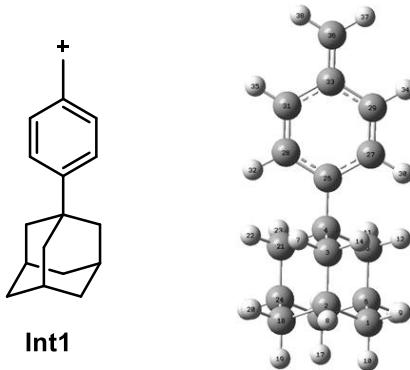
Index ranges	$-12 \leq h \leq 12, -10 \leq k \leq 10, -20 \leq l \leq 20$
Reflections collected	21892
Independent reflections	2798 [$R_{\text{int}} = 0.0472, R_{\text{sigma}} = 0.0224$]
Completeness	100%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2798/0/236
Goodness-of-fit on F^2	1.032
Final R indices [$I >= 2\sigma (I)$]	$R_1 = 0.0364,$ $wR_2 = 0.0952$
R indices (all data)	$R_1 = 0.0394,$ $wR_2 = 0.0991$
Largest diff. peak/hole (e. \AA^3)	0.16/-0.16

6. Computational Studies

6.1 General Information

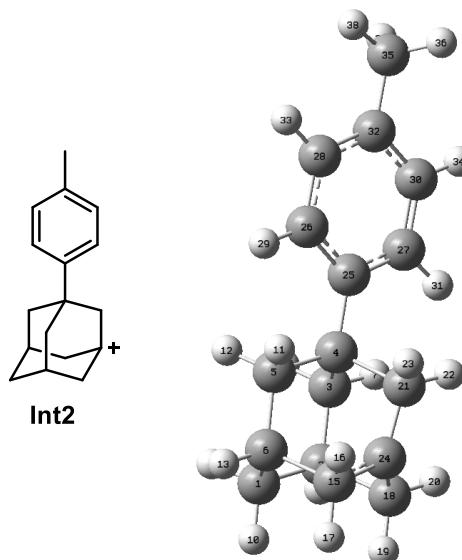
DFT calculations were performed with Gaussian 09. ^[9] Optimization of the geometries of key intermediates were conducted at M06-2X/def2-TZVP level of theory ^[10, 11] and solvation (dichloromethane) with SMD model. ^[12] All calculations are included semi-empirical dispersion correction (DFT-D3). ^[13] Hirshfeld charges were analyzed in Multiwfn. ^[14]

6.2 Hirshfeld Charge Analysis



Atom	Hirshfeld charges (a.u.)
Atom 1(C):	-0.05241841
Atom 2(C):	-0.01445658
Atom 3(C):	-0.04045956
Atom 4(C):	0.01908687
Atom 5(C):	-0.04747637
Atom 6(C):	-0.01630316
Atom 7(H):	0.03525841
Atom 8(H):	0.03681989
Atom 9(H):	0.03039333
Atom 10(H):	0.03243369
Atom 11(H):	0.03494354
Atom 12(H):	0.03696399
Atom 13(H):	0.03495487
Atom 14(H):	0.03525850
Atom 15(C):	-0.05378989
Atom 16(H):	0.03016640
Atom 17(H):	0.03170680
Atom 18(C):	-0.05241834
Atom 19(H):	0.03243370
Atom 20(H):	0.03039341

Atom	21(C):	-0.04747653
Atom	22(H):	0.03696425
Atom	23(H):	0.03494377
Atom	24(C):	-0.01630304
Atom	25(H):	0.03495478
Atom	26(C):	0.10527252
Atom	27(C):	-0.01590009
Atom	28(C):	-0.01590037
Atom	29(C):	0.04409792
Atom	30(H):	0.06911611
Atom	31(C):	0.04409826
Atom	32(H):	0.06911581
Atom	33(C):	0.01240613
Atom	34(H):	0.08631337
Atom	35(H):	0.08631347
Atom	36(C):	0.12308173
Atom	37(H):	0.10270518
Atom	38(H):	0.10270564

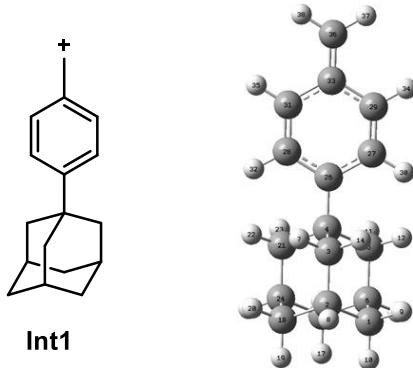


Atom	Hirshfeld charges (a.u.)	
Atom	1(C):	-0.04236664
Atom	2(C):	0.02210931
Atom	3(C):	-0.04440973
Atom	4(C):	0.04652892
Atom	5(C):	-0.04312083
Atom	6(C):	0.02317372
Atom	7(H):	0.04771333

Atom	8(H):	0.06552631
Atom	9(H):	0.05699887
Atom	10(H):	0.05078392
Atom	11(H):	0.04955060
Atom	12(H):	0.05570427
Atom	13(H):	0.06601865
Atom	14(H):	0.05454294
Atom	15(C):	-0.02178332
Atom	16(H):	0.07305742
Atom	17(H):	0.07236105
Atom	18(C):	-0.02212643
Atom	19(H):	0.07212646
Atom	20(H):	0.07255407
Atom	21(C):	-0.02716023
Atom	22(H):	0.06715372
Atom	23(H):	0.06849306
Atom	24(C):	0.18245679
Atom	25(C):	-0.00747487
Atom	26(C):	-0.04689384
Atom	27(C):	-0.04373245
Atom	28(C):	-0.05091855
Atom	29(H):	0.04933962
Atom	30(C):	-0.04803735
Atom	31(H):	0.05157090
Atom	32(C):	0.00267212
Atom	33(H):	0.04955513
Atom	34(H):	0.05126095
Atom	35(C):	-0.08303650
Atom	36(H):	0.04344916
Atom	37(H):	0.04378190
Atom	38(H):	0.04257756

Remarks: Hirshfeld charge analysis revealed that the positive charge density of the benzyl carbocation (**Int1**) was lower than that of the adamantly carbocation (**Int2**) (0.123 to 0.182 a.u.).

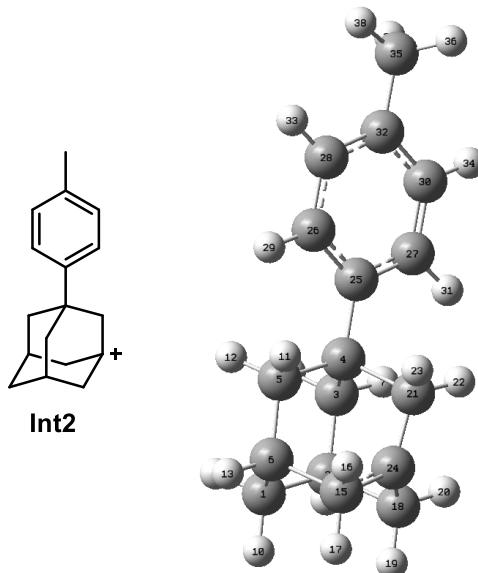
6.3 Geometry Optimization



Cartesian Coordinates for **Int1**

Atom	X	Y	Z
C	2.87586400	1.24946800	0.80334200
C	2.31225400	0.00007800	1.48756100
C	0.78142900	0.00007600	1.39159800
C	0.35217400	-0.00000400	-0.10818500
C	0.94898500	1.25412400	-0.78098100
C	2.47760700	1.24554300	-0.67674500
H	0.36889600	-0.88449200	1.88497700
H	2.58683700	0.00013500	2.54486400
H	2.49307800	2.15064900	1.29119200
H	3.96514800	1.26132800	0.89677400
H	0.63624600	1.28664100	-1.82893100
H	0.58470400	2.15993100	-0.29538900
H	2.86268400	2.14420300	-1.16314200
H	0.36889900	0.88469700	1.88488200
C	3.04168200	-0.00007500	-1.36194800
H	2.77145800	-0.00013200	-2.42194100
H	4.13340900	-0.00007400	-1.29953100
C	2.87585900	-1.24938600	0.80347600
H	3.96514400	-1.26124100	0.89691000
H	2.49307100	-2.15051400	1.29142200
C	0.94898100	-1.25420400	-0.78084800
H	0.58469600	-2.15995800	-0.29516000
H	0.63624200	-1.28683100	-1.82879500
C	2.47760300	-1.24561900	-0.67661200
H	2.86267700	-2.14433200	-1.16291200
C	-1.15277300	-0.00000200	-0.10469000
C	-1.87174400	1.22087700	-0.06606100

C	-1.87174400	-1.22088000	-0.06599700
C	-3.23242600	1.23046700	-0.01098000
H	-1.34212500	2.16034300	-0.08097400
C	-3.23242400	-1.23046700	-0.01089300
H	-1.34212500	-2.16034600	-0.08086700
C	-3.96322100	0.00000100	0.01353000
H	-3.78413900	2.16225300	0.01387800
H	-3.78413700	-2.16225200	0.01402300
C	-5.31940800	0.00000100	0.06989100
H	-5.87638700	0.92991300	0.09386000
H	-5.87646000	-0.92991000	0.09211200

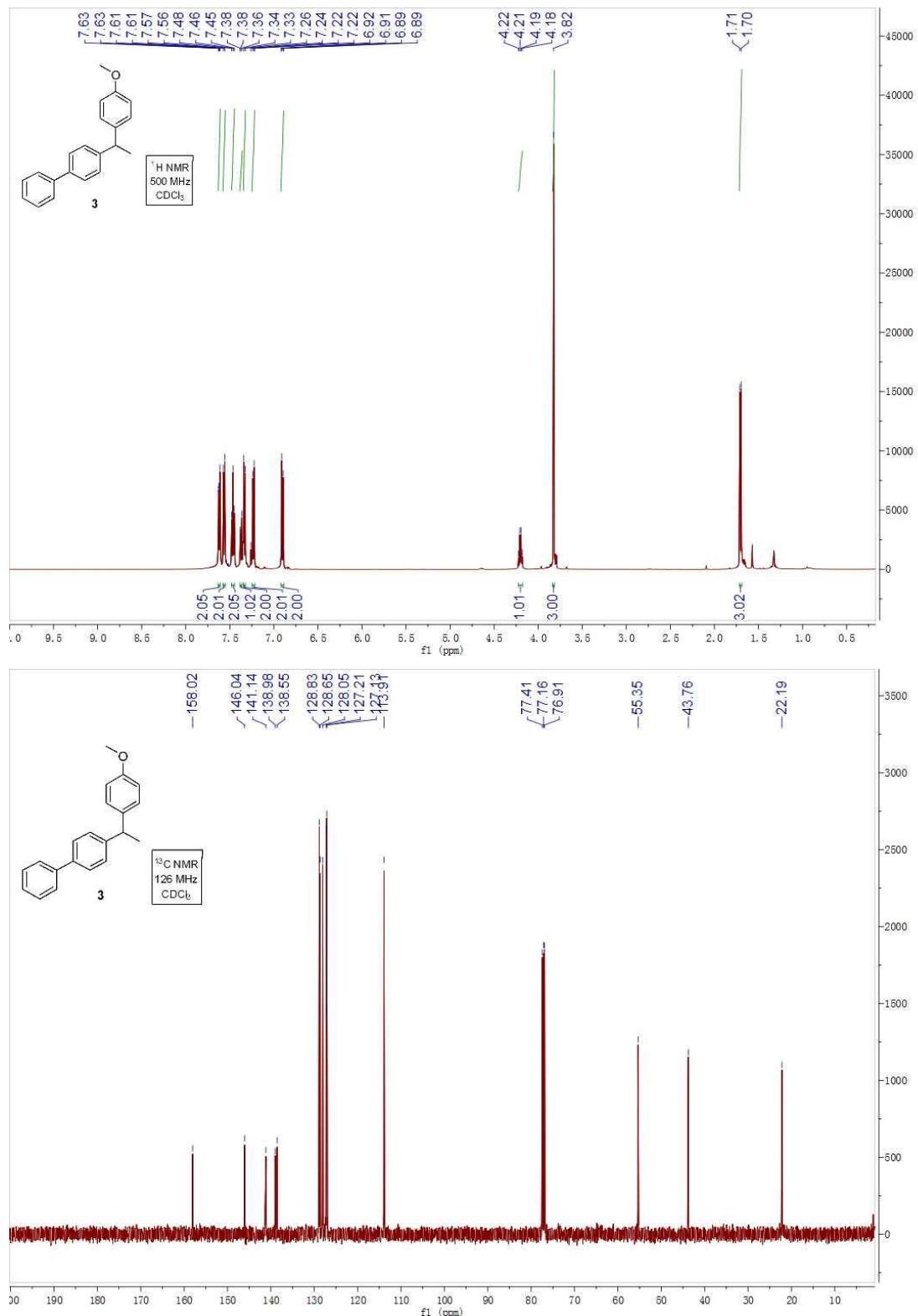


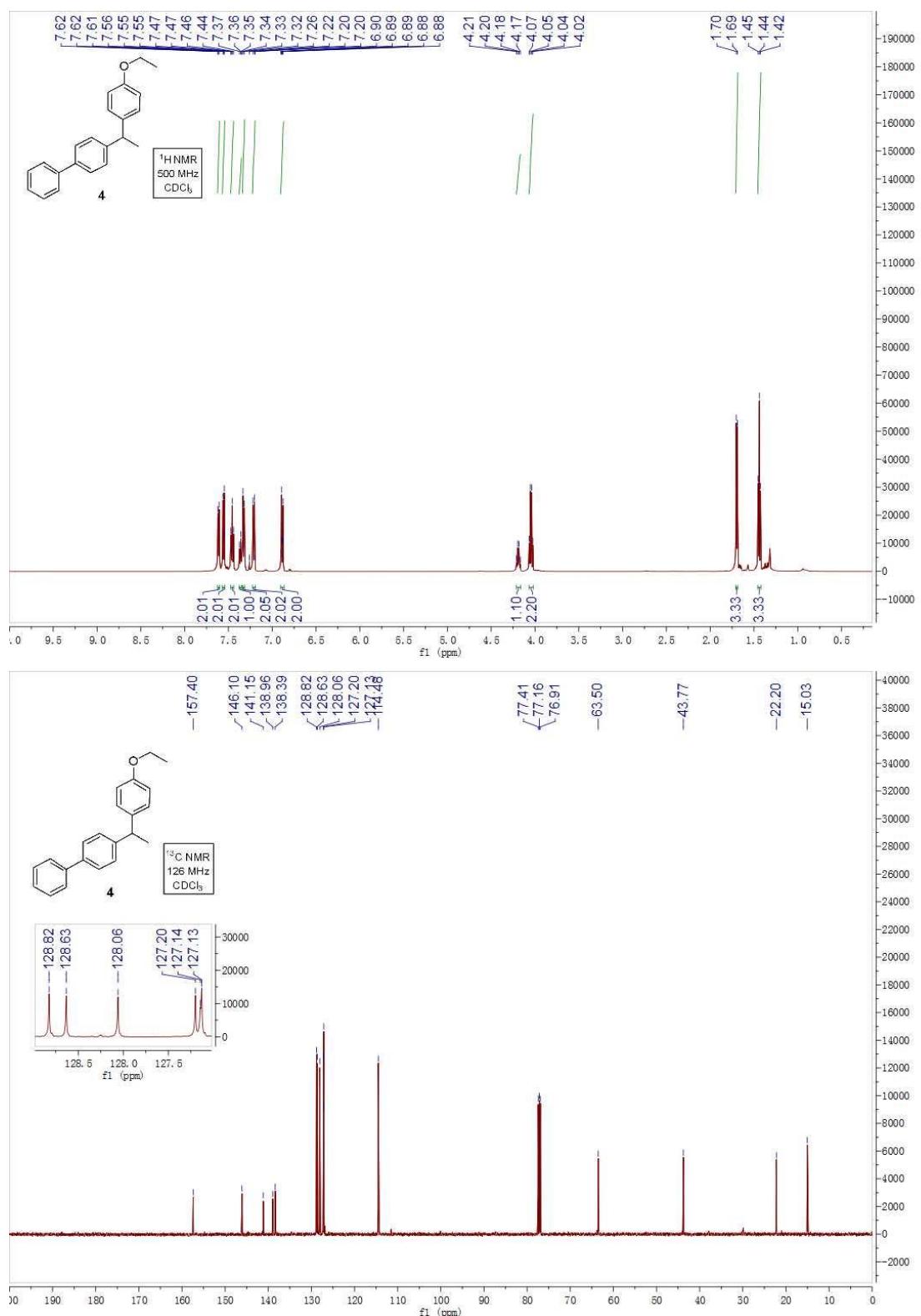
Cartesian Coordinates for **Int2**

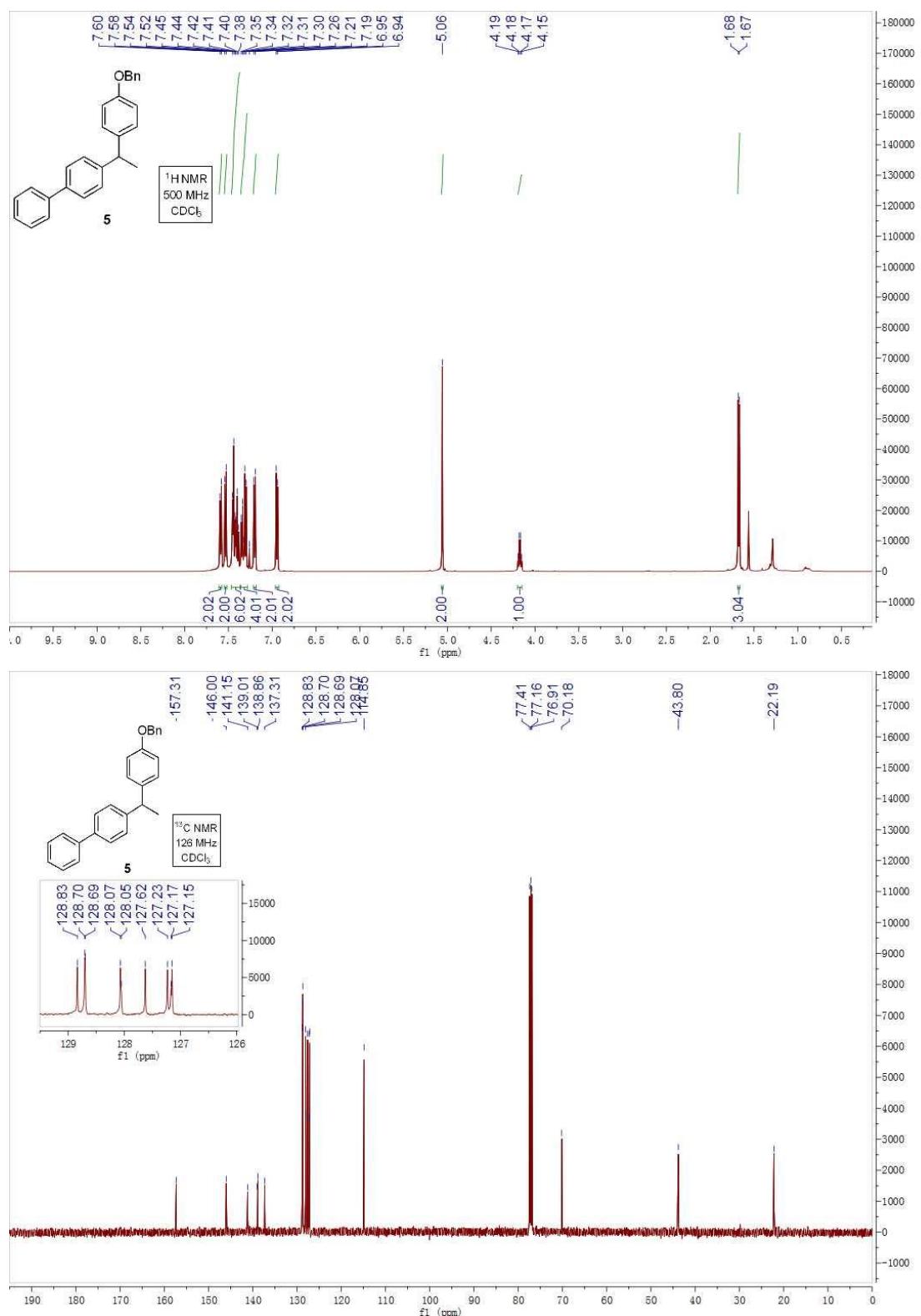
Atom	X	Y	Z
C	3.12205200	0.50083300	1.23103300
C	2.51779300	-0.89146100	1.10785700
C	0.99583200	-0.84340200	1.16110100
C	0.43117500	0.05875600	0.05342700
C	1.05250000	1.45475800	0.15876600
C	2.57435600	1.38341700	0.11784200
H	0.58959900	-1.85171500	1.07206500
H	2.91368600	-1.57503600	1.85770300
H	2.84845900	0.92870200	2.19809700
H	4.21109000	0.45438800	1.18408000
H	0.69173300	2.09069600	-0.65175800
H	0.74575300	1.91293300	1.10178000

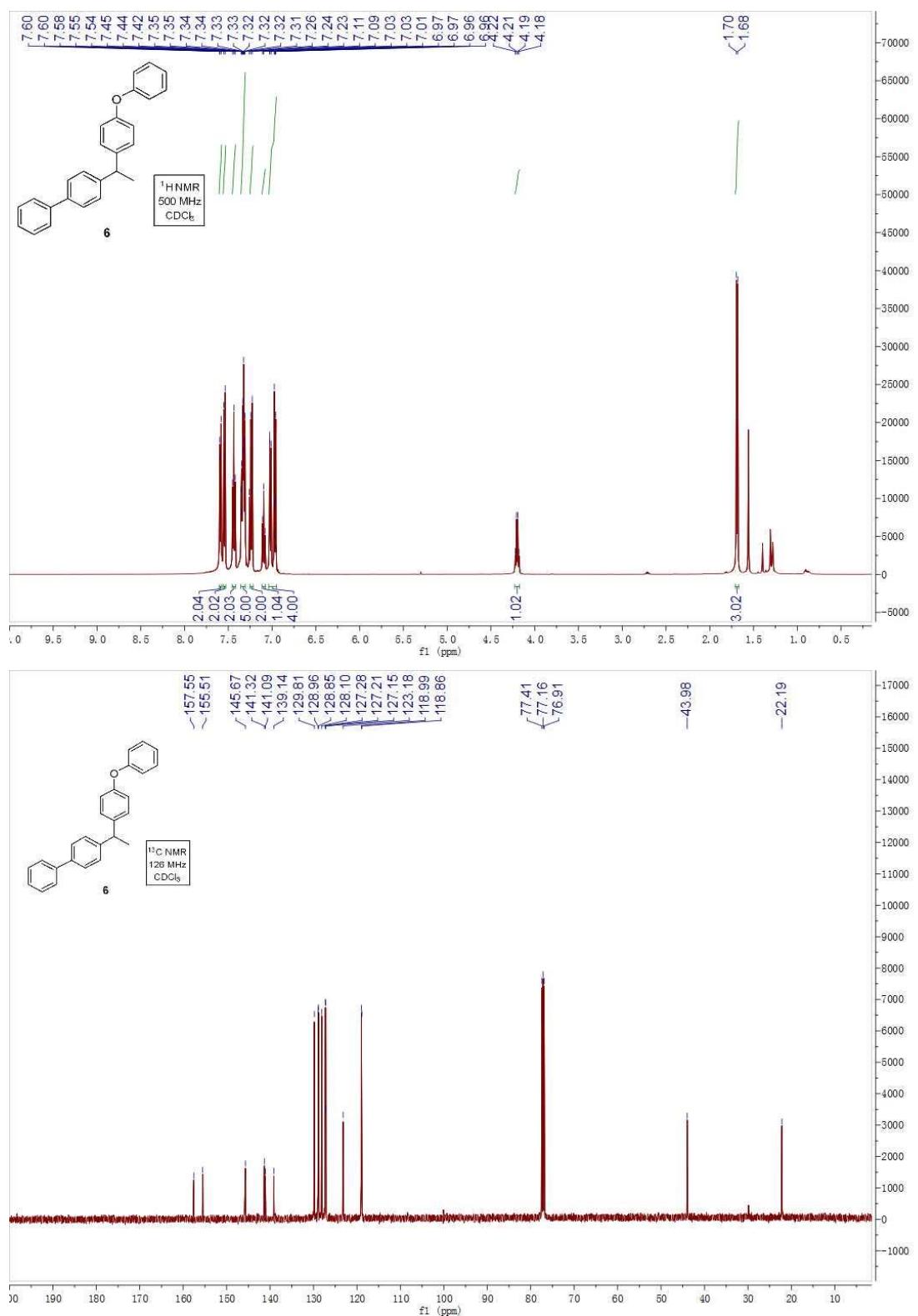
H	3.00986600	2.38155400	0.13935900
H	0.67827600	-0.44576300	2.12780600
C	3.02807000	0.76321900	-1.29608600
H	2.62982600	1.39068000	-2.08923800
H	4.11290000	0.70100300	-1.31335800
C	2.96370900	-1.51233600	-0.30705900
H	4.04959700	-1.53448700	-0.34801200
H	2.52111900	-2.50047100	-0.40359900
C	0.92983500	-0.56013700	-1.36411800
H	0.53774600	-1.57009700	-1.45118900
H	0.57273900	0.09418000	-2.15571700
C	2.36445100	-0.51527600	-1.16882300
C	-1.08753000	0.05686900	0.03380000
C	-1.83058600	1.23133200	0.09286600
C	-1.78492200	-1.15236600	-0.04391200
C	-3.22191300	1.19783700	0.07864000
H	-1.33915500	2.19259200	0.15668600
C	-3.16755300	-1.18133700	-0.05945400
H	-1.24273800	-2.08903300	-0.09904600
C	-3.91472500	-0.00329500	0.00166700
H	-3.77431100	2.12911700	0.12864000
H	-3.68124500	-2.13420600	-0.12241700
C	-5.41577500	-0.04916500	-0.01225100
H	-5.77998800	-0.59110300	-0.88703300
H	-5.79524400	-0.56729700	0.87106300
H	-5.84032300	0.95389300	-0.02768500

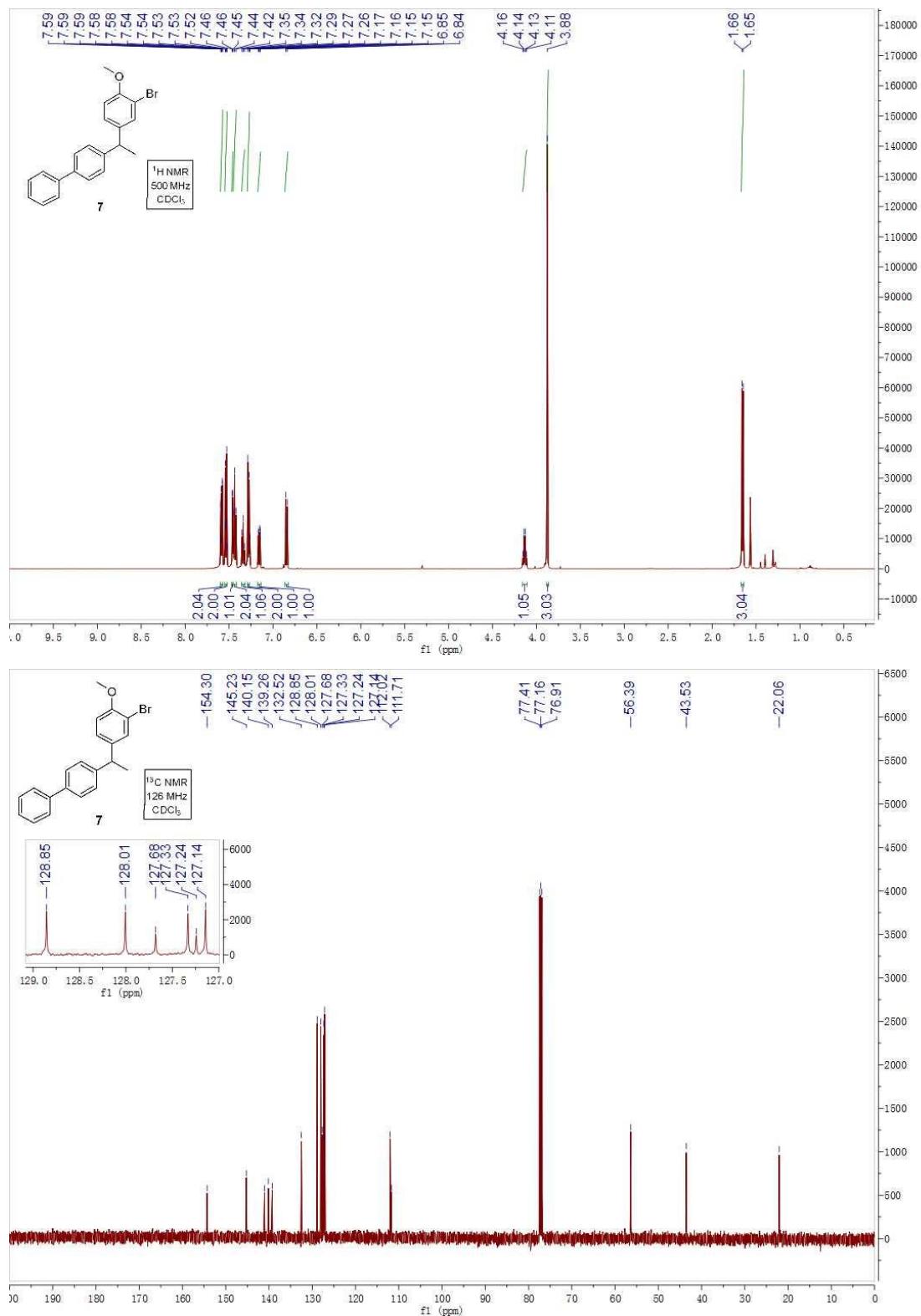
7. ^1H and ^{13}C NMR Spectrum

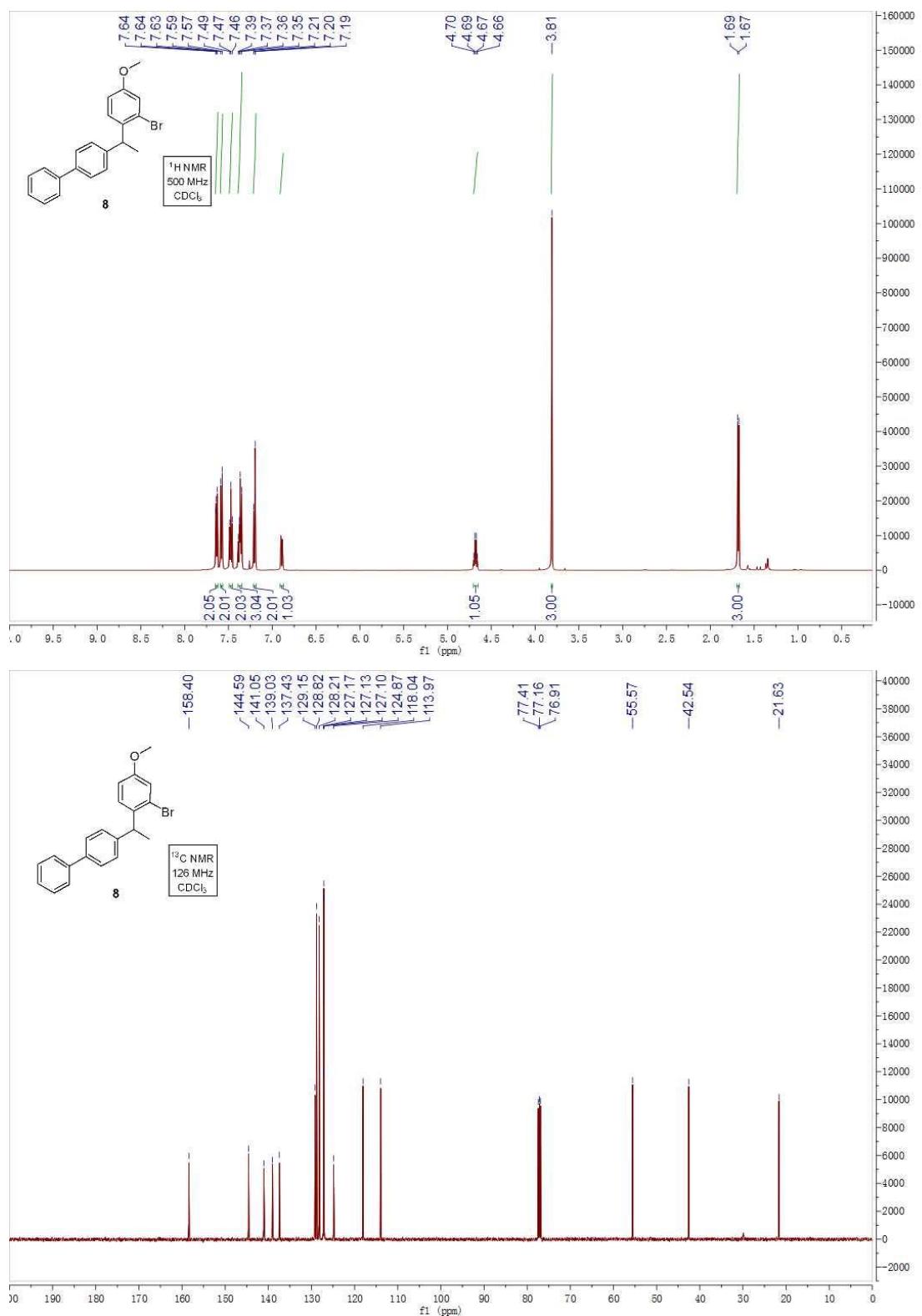


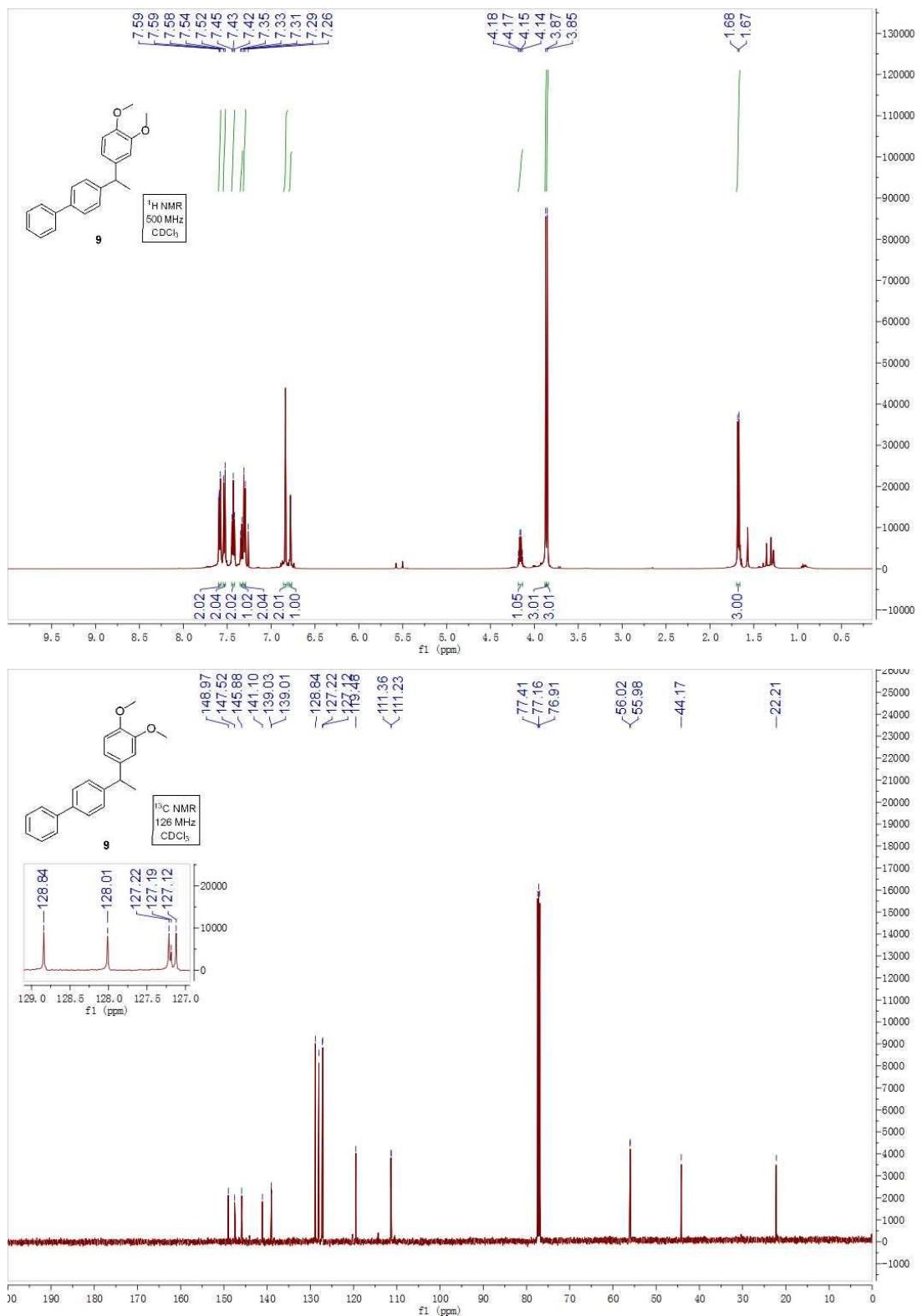


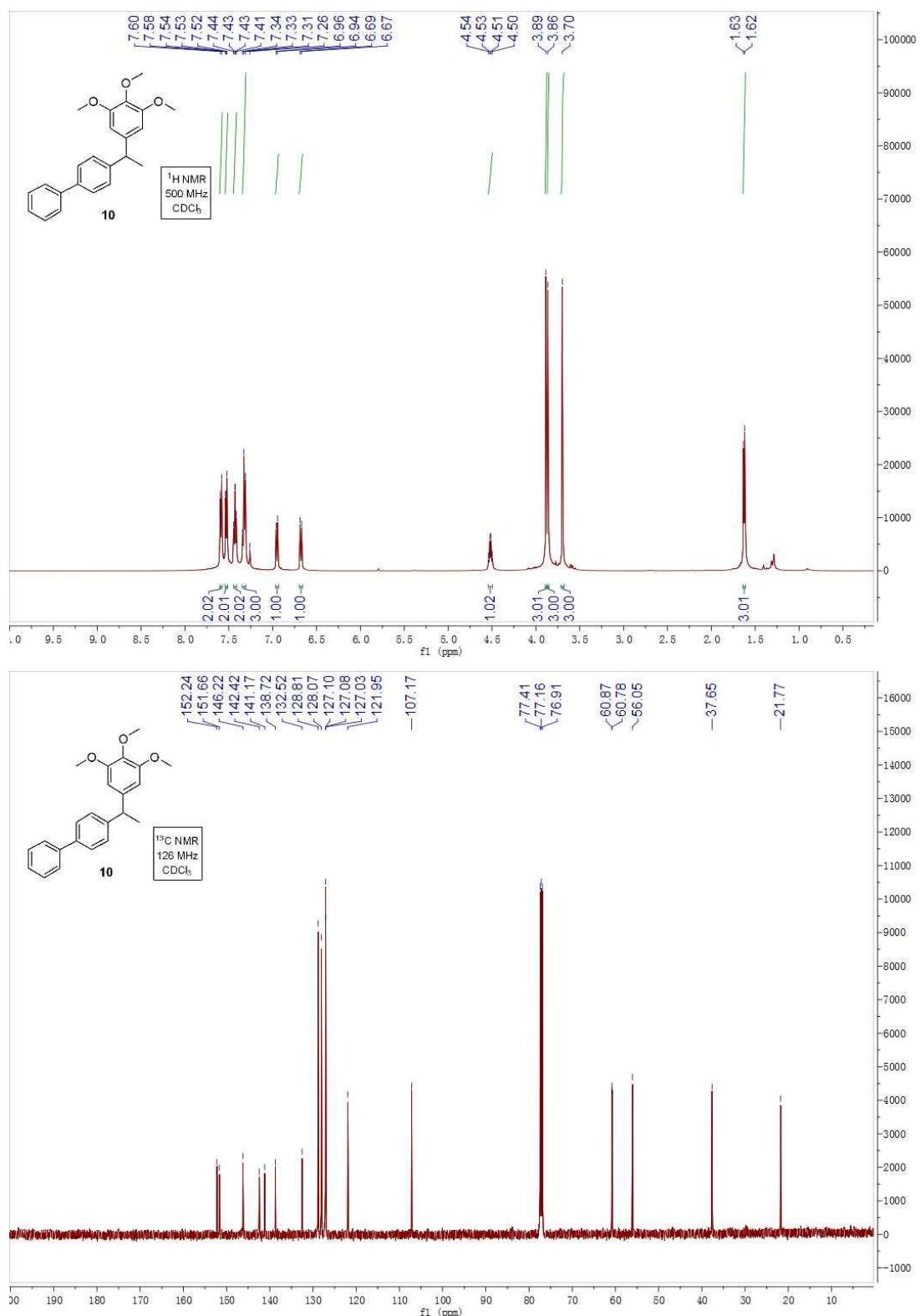


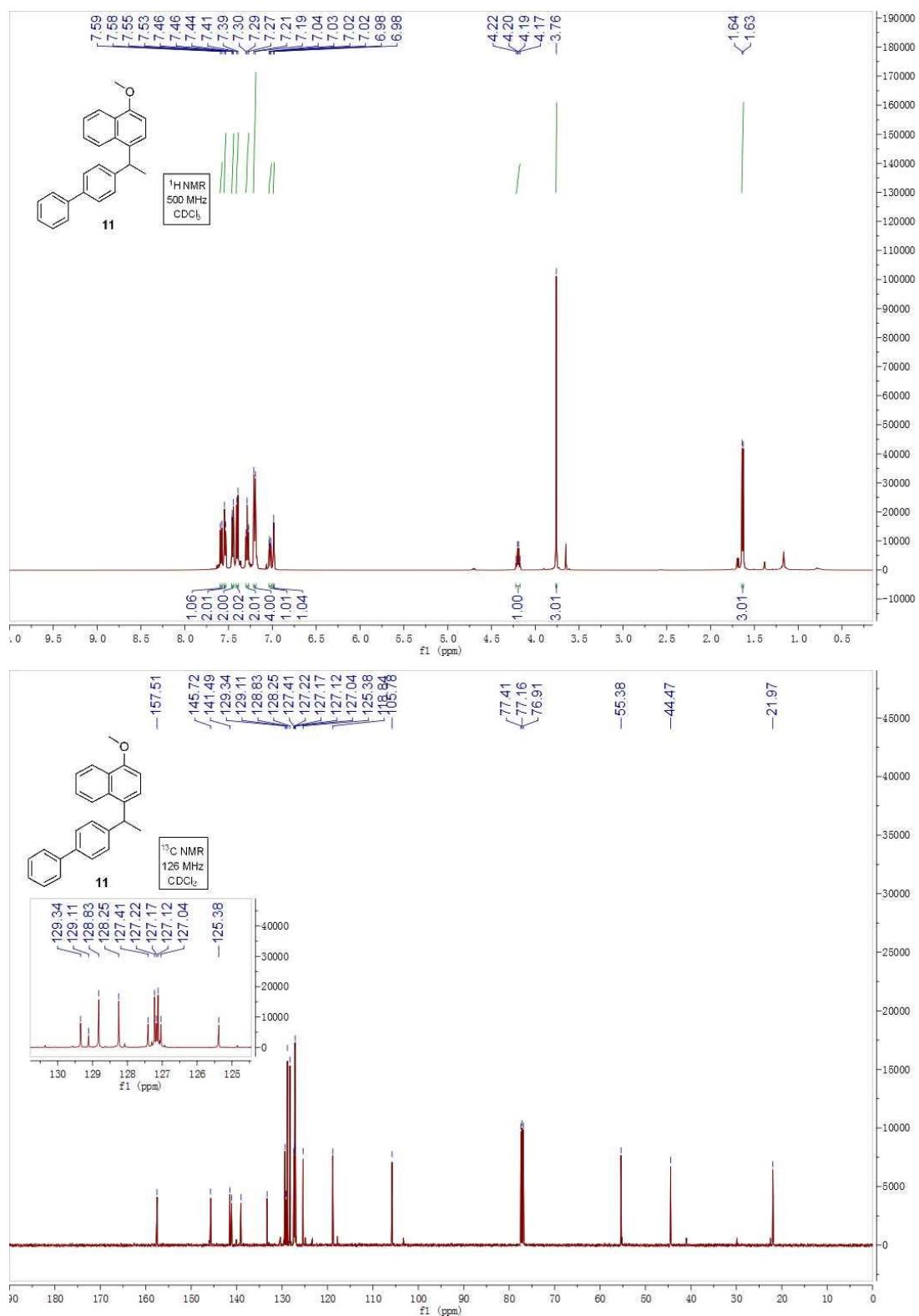


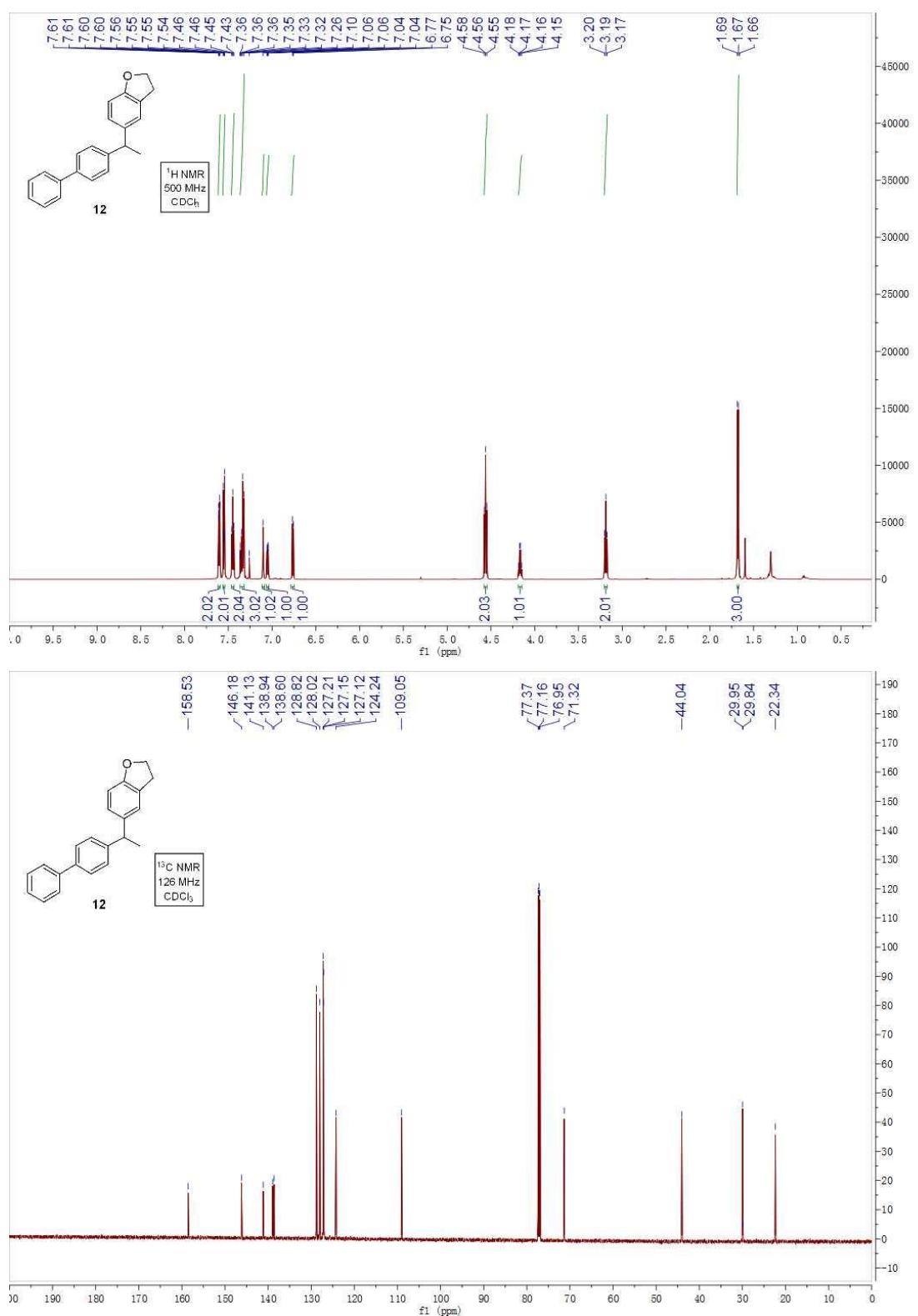


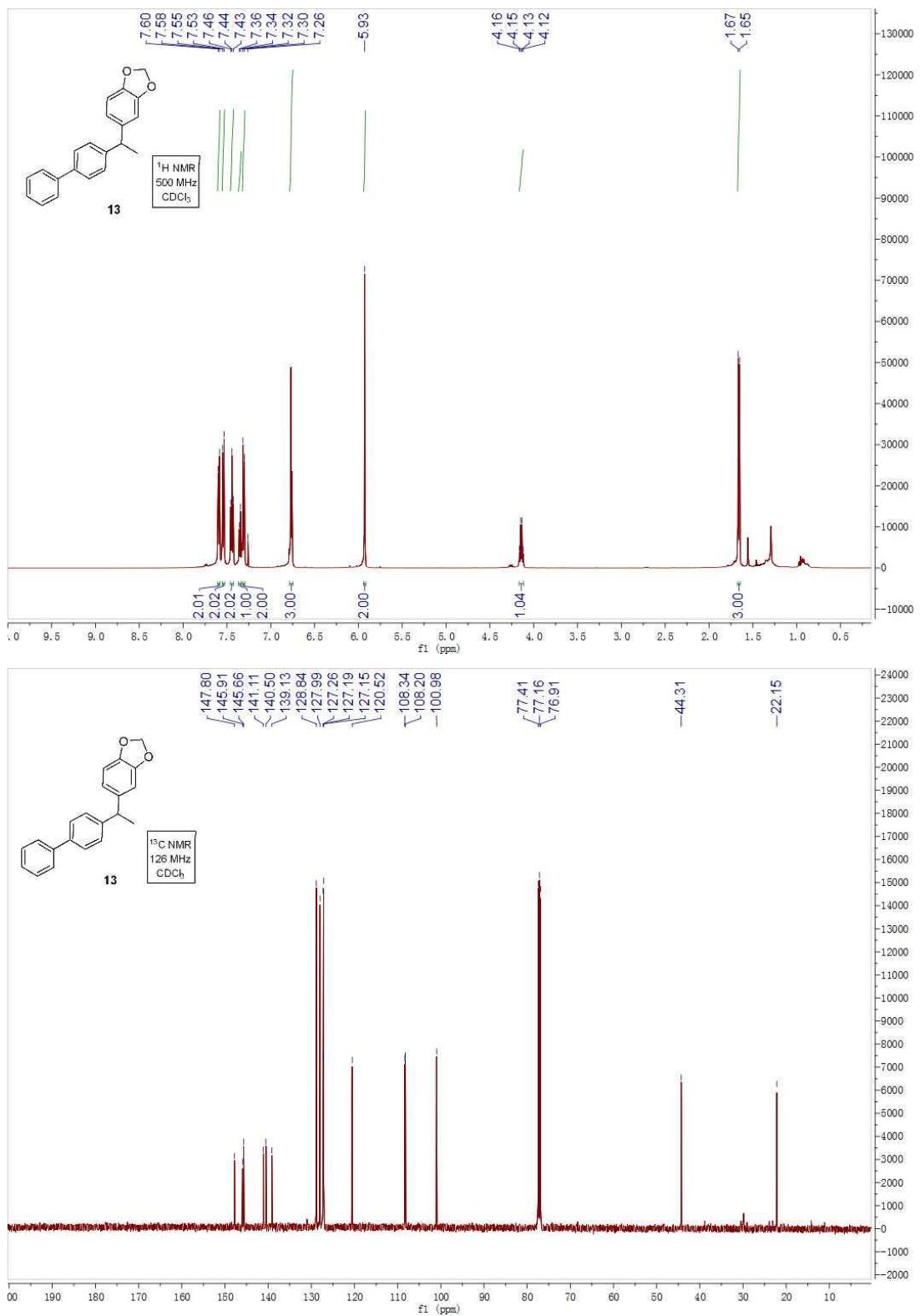


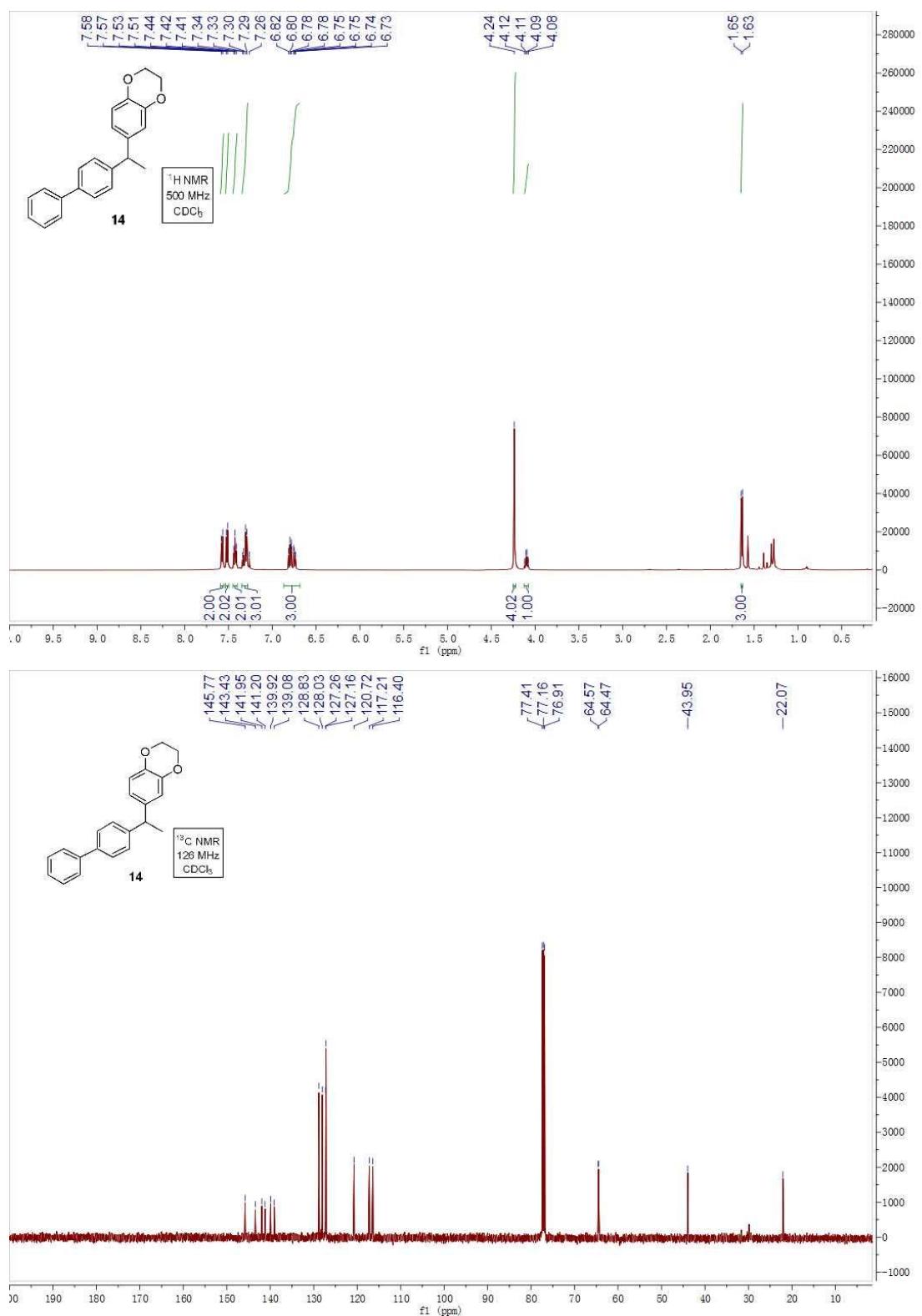


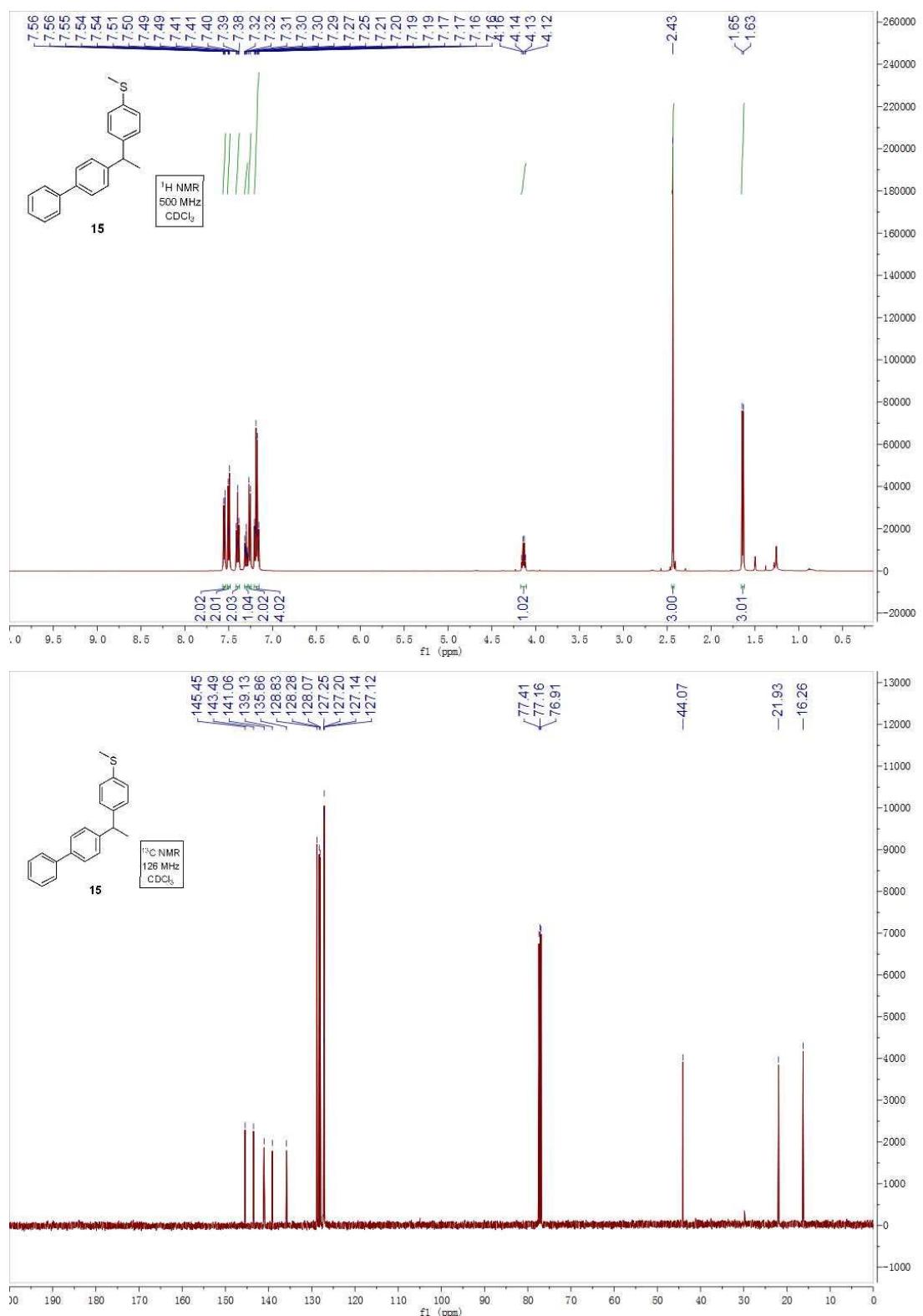


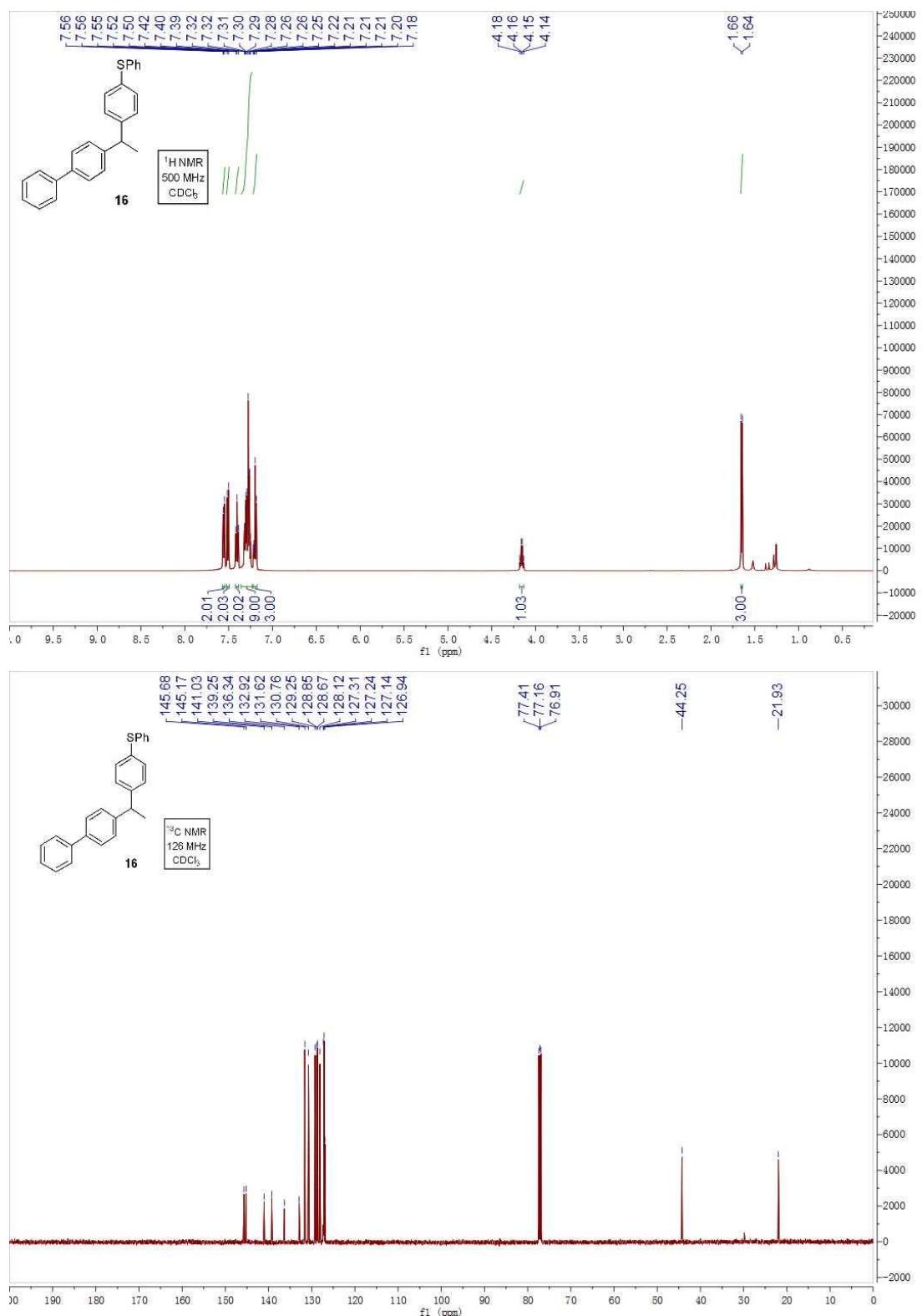


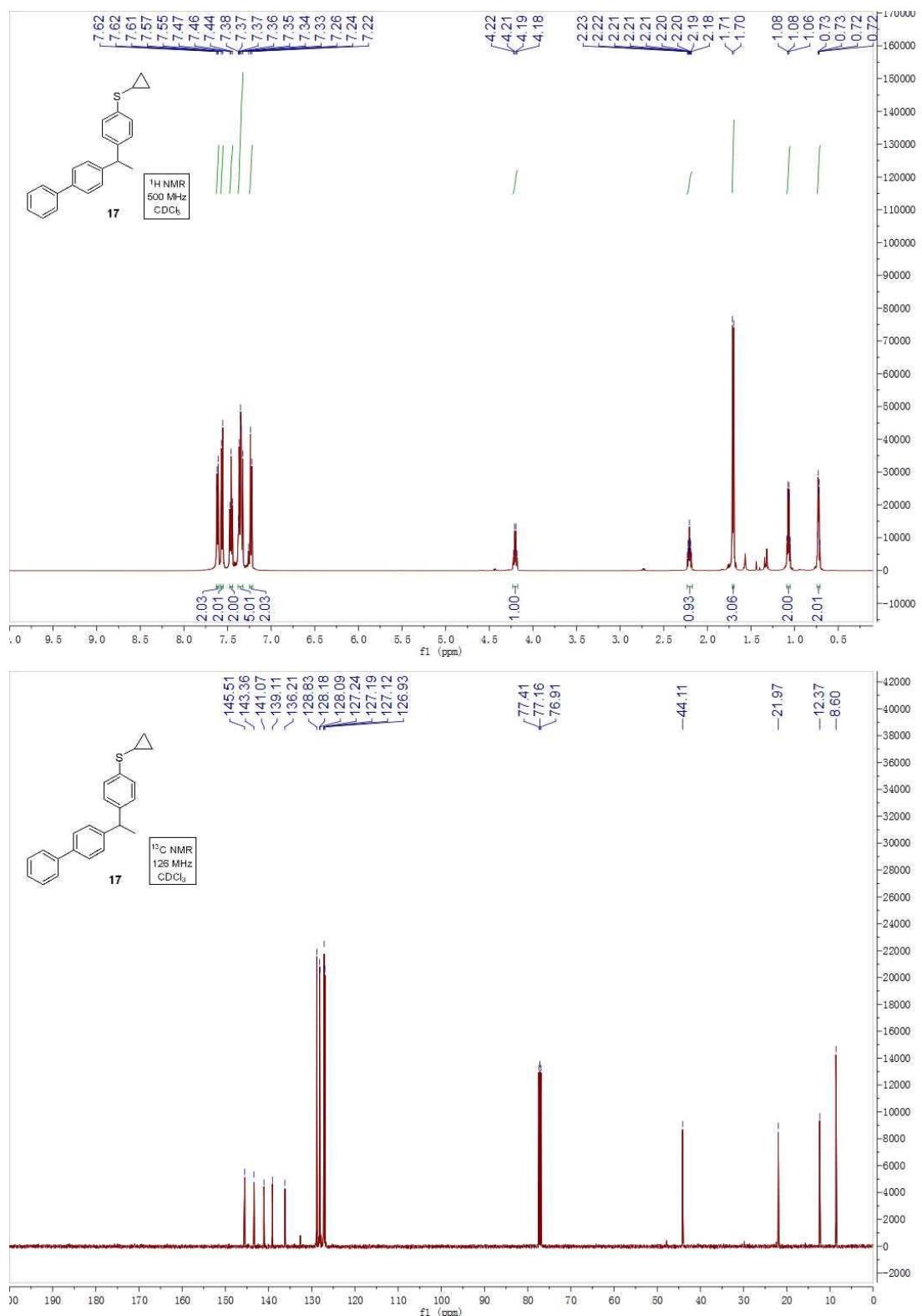


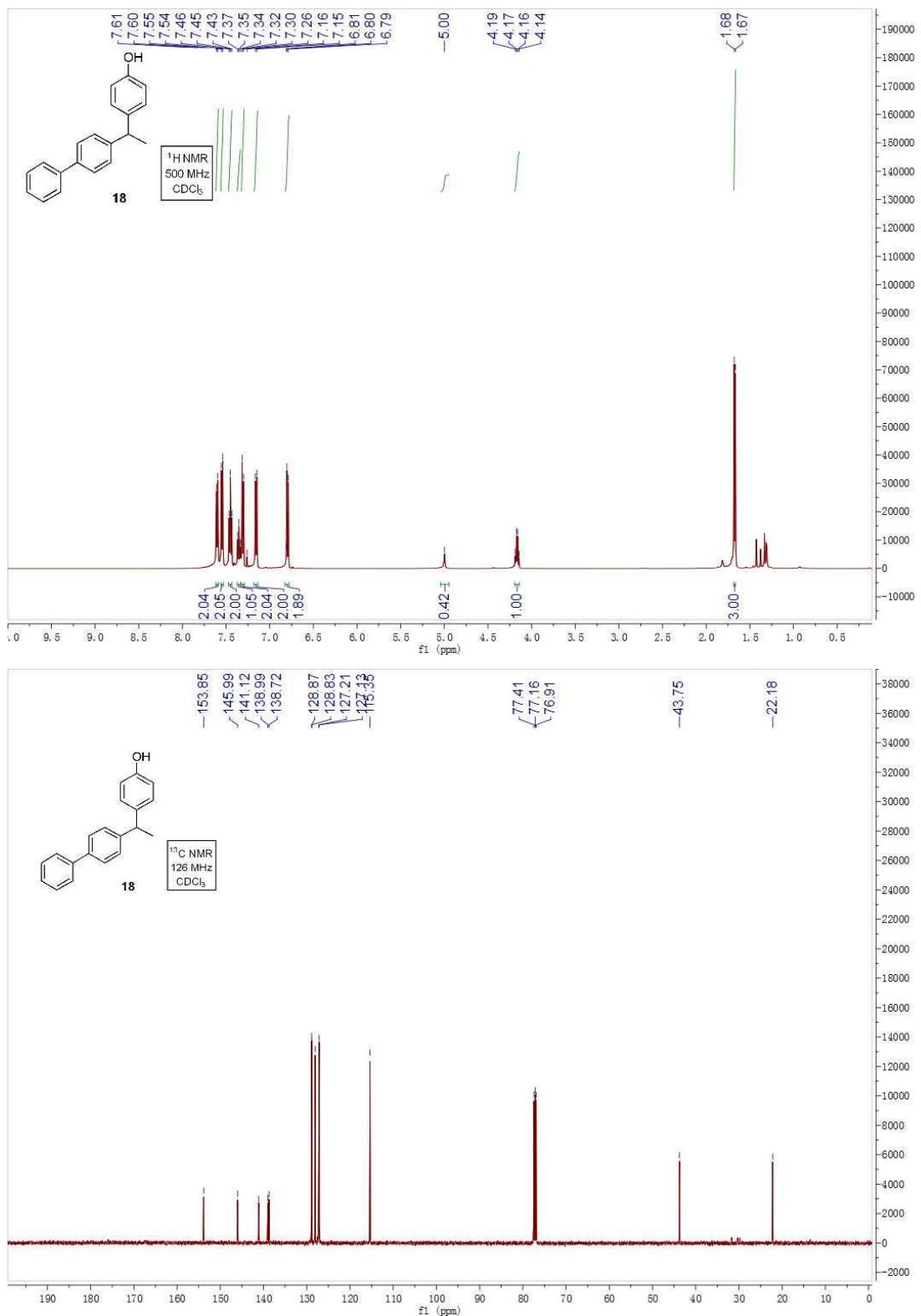


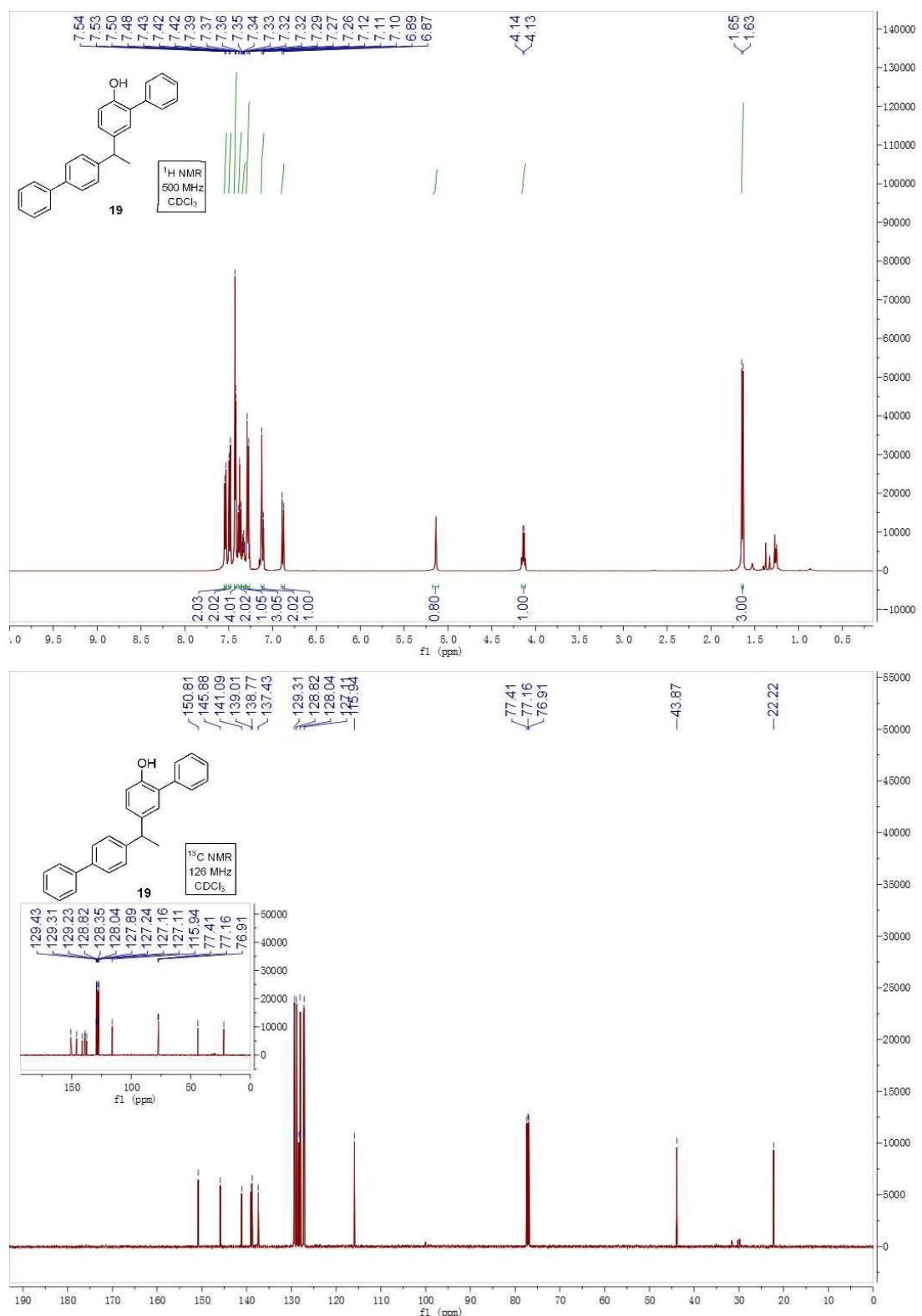


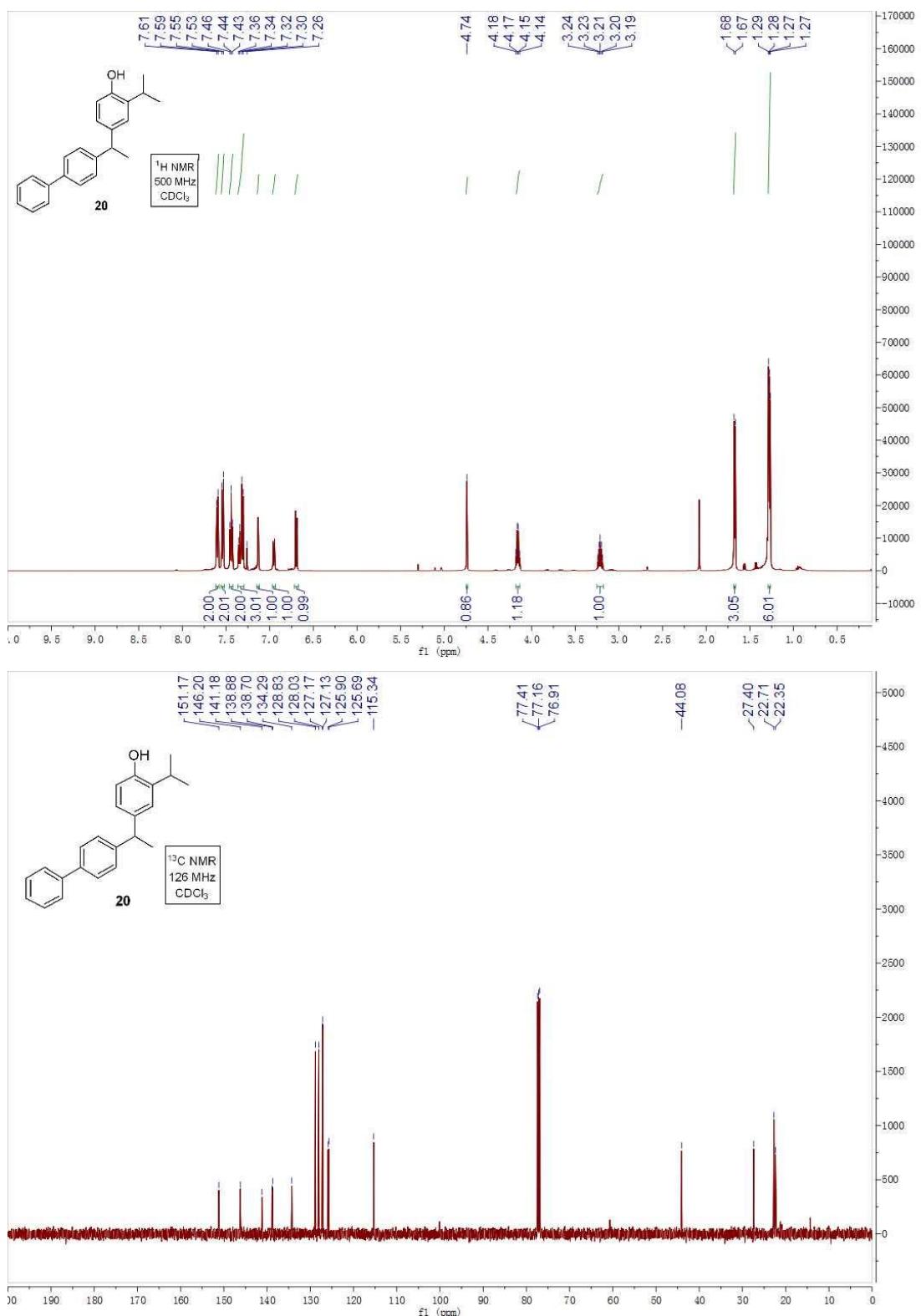


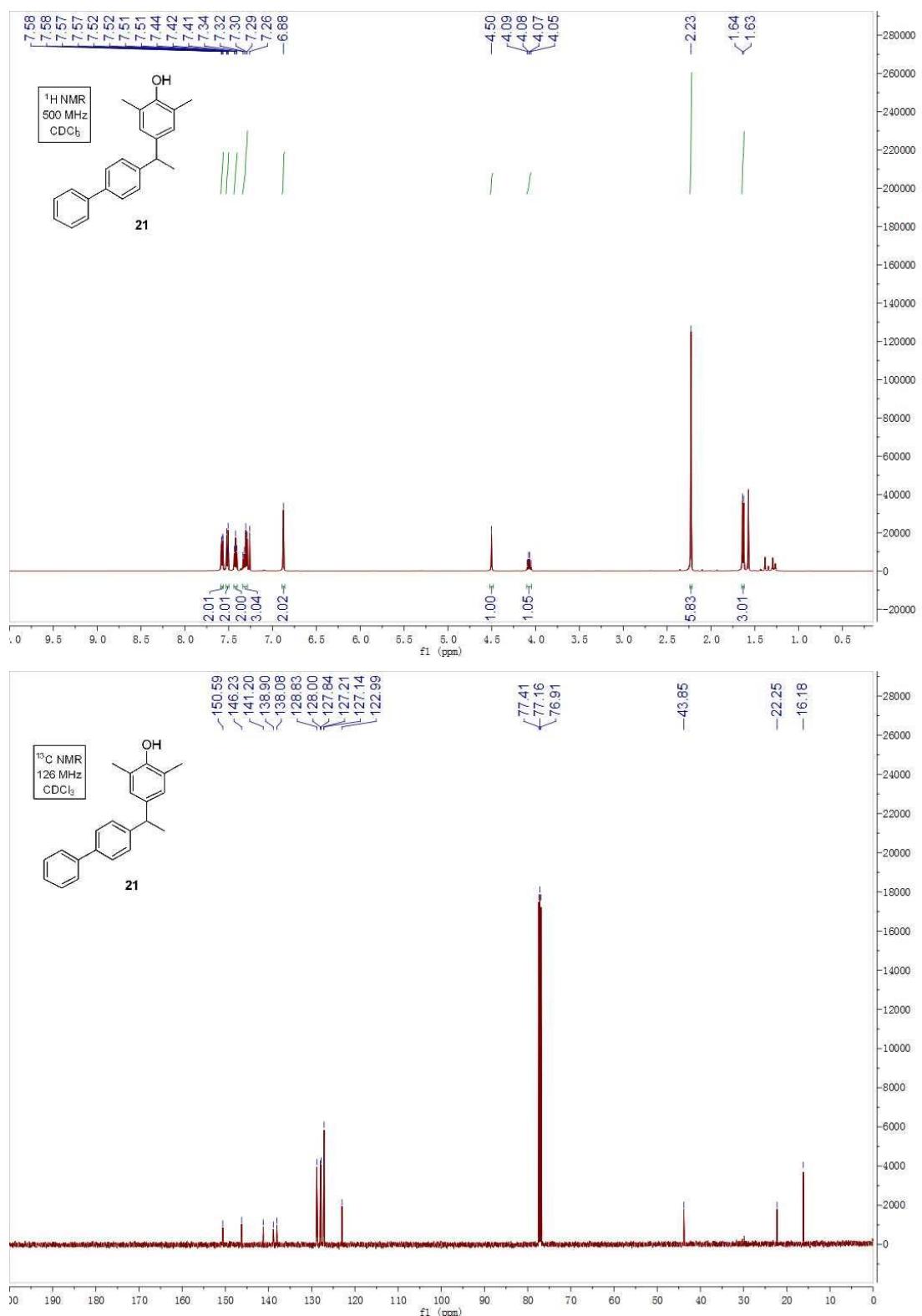


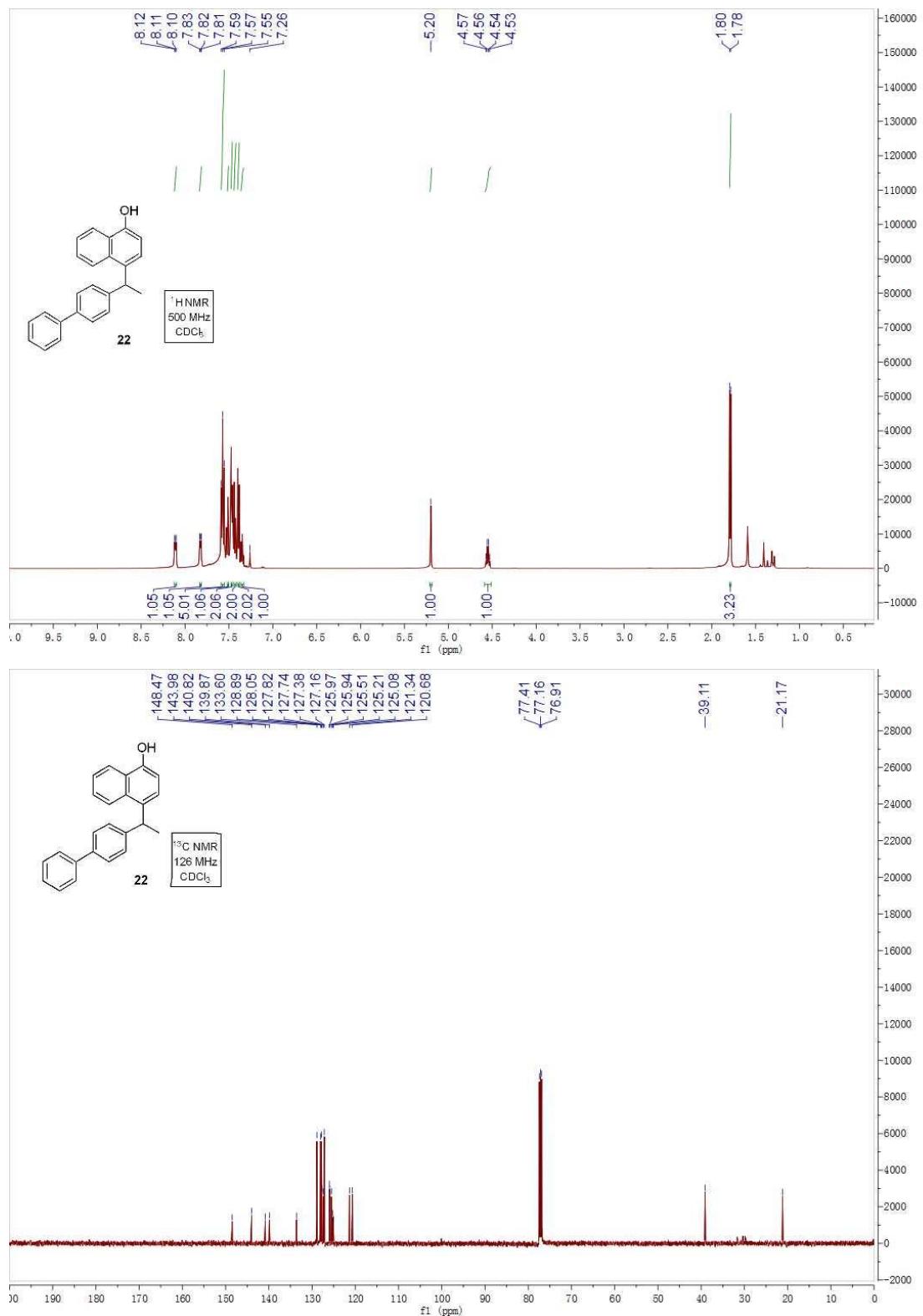


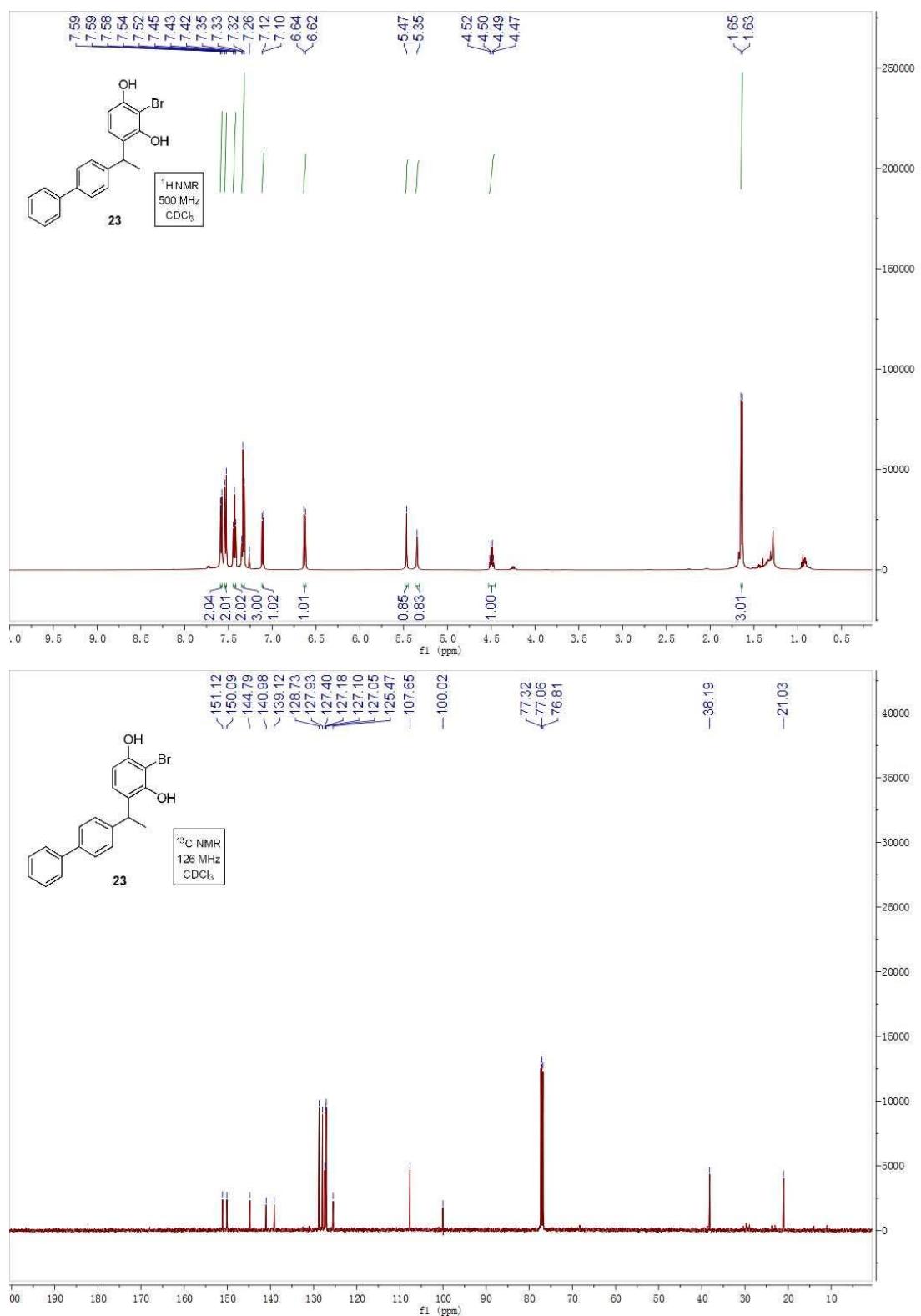


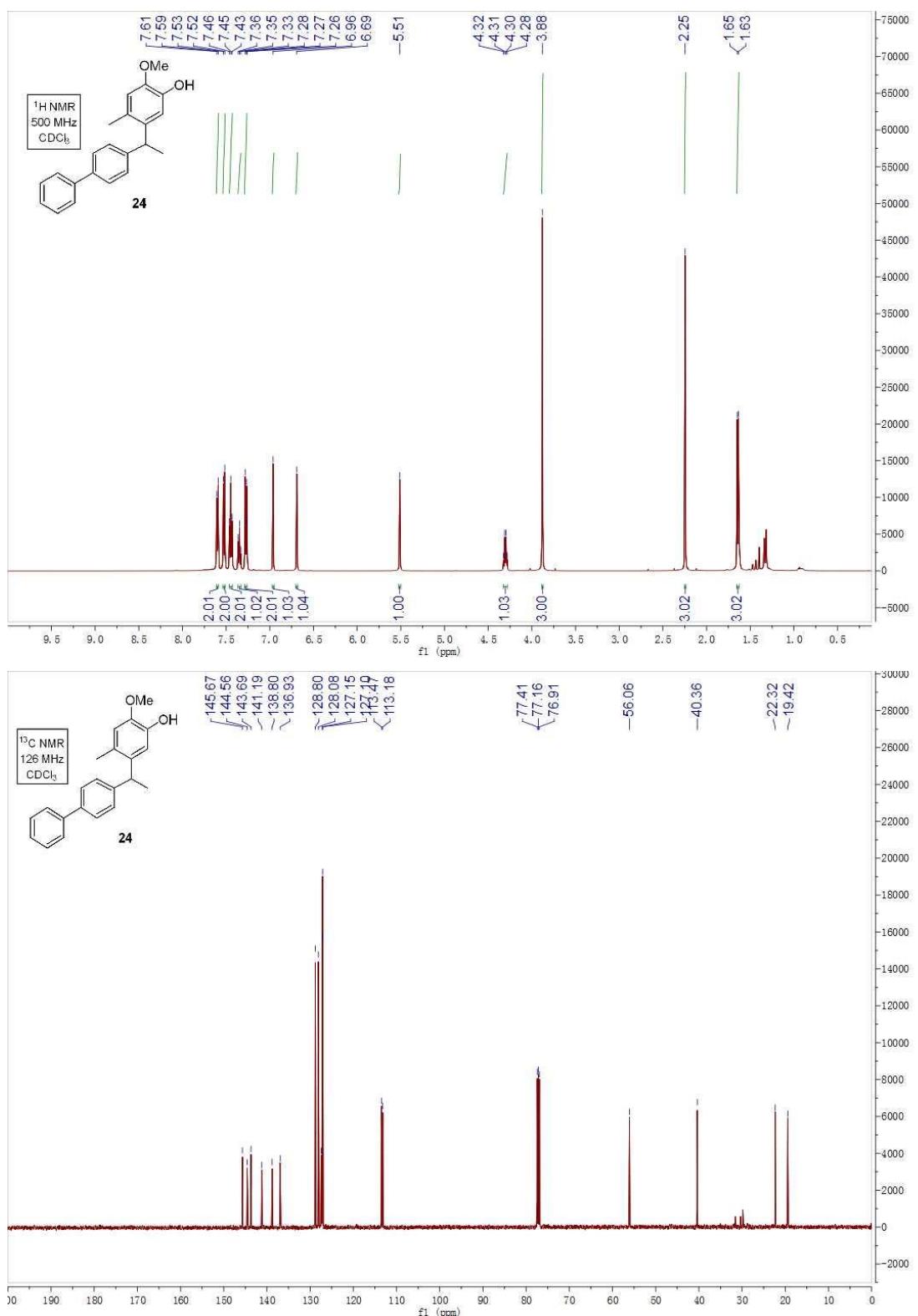


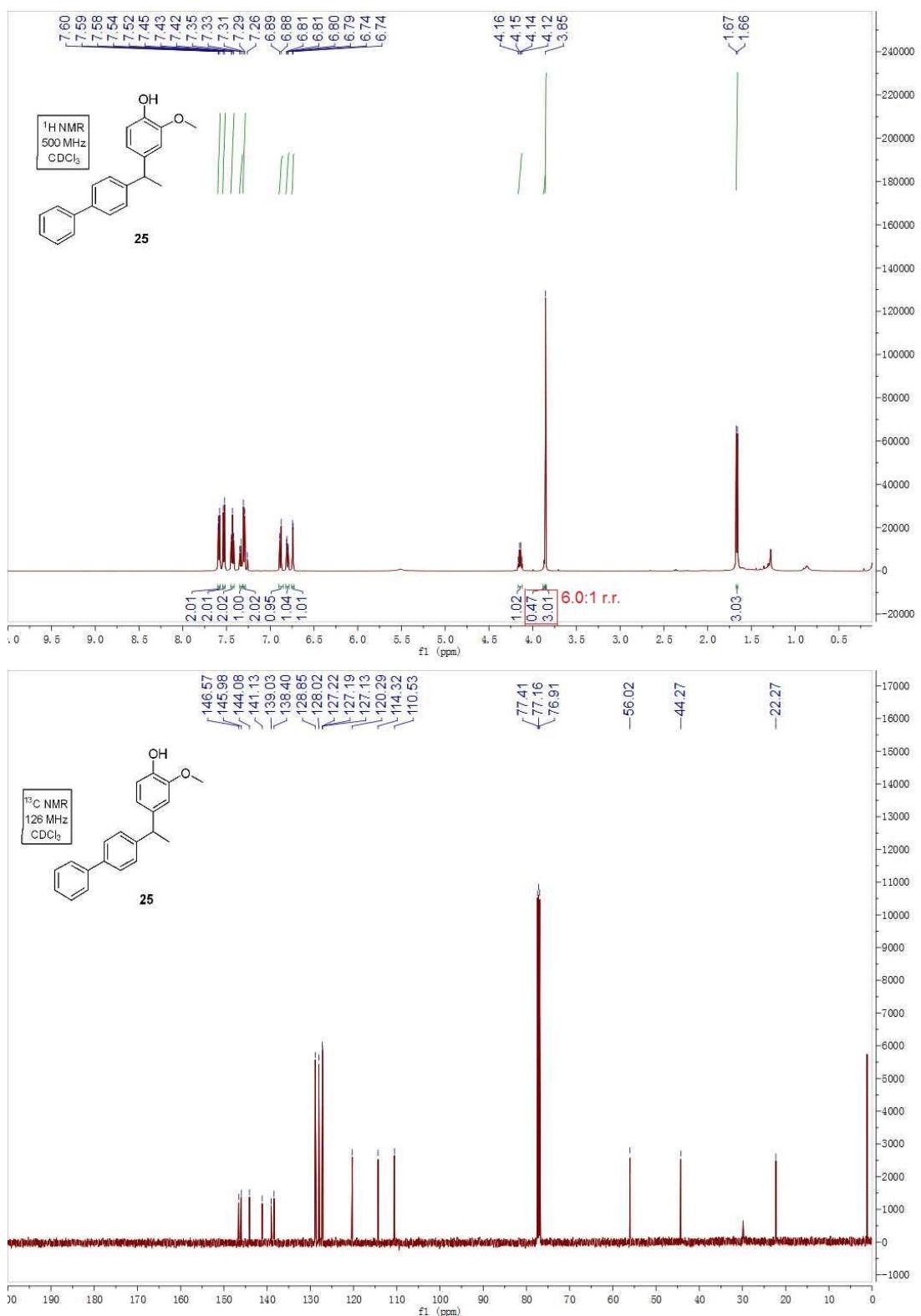


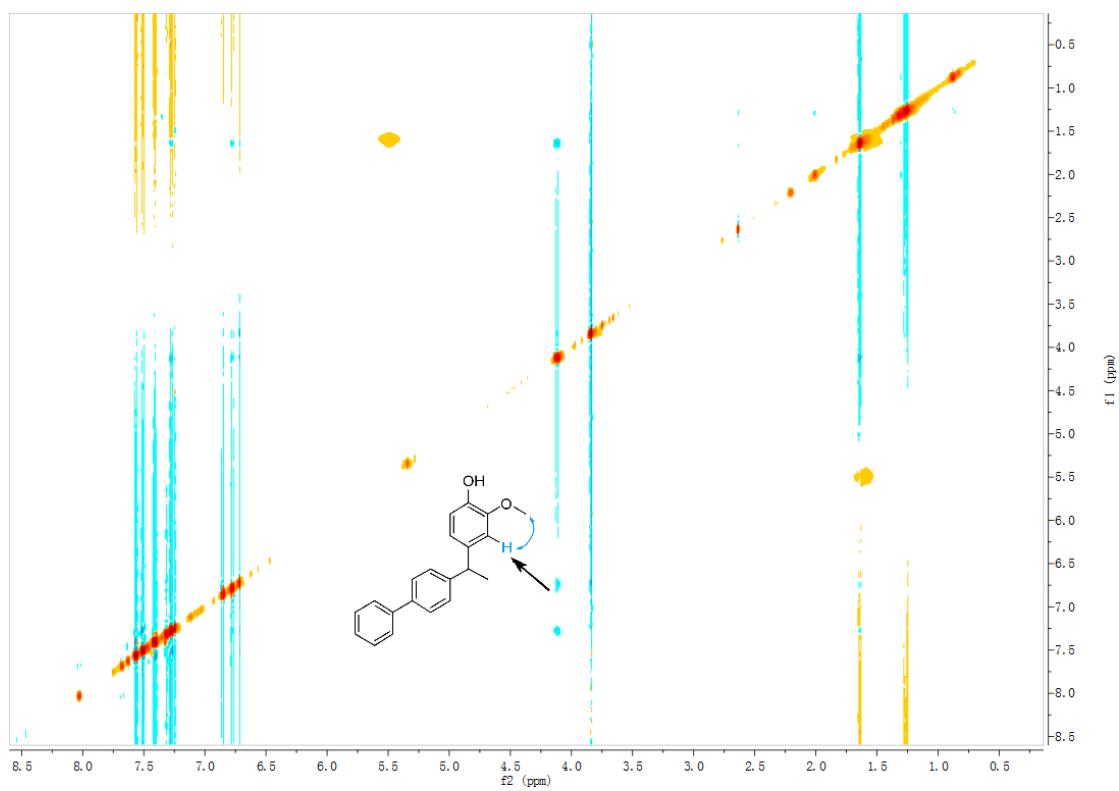


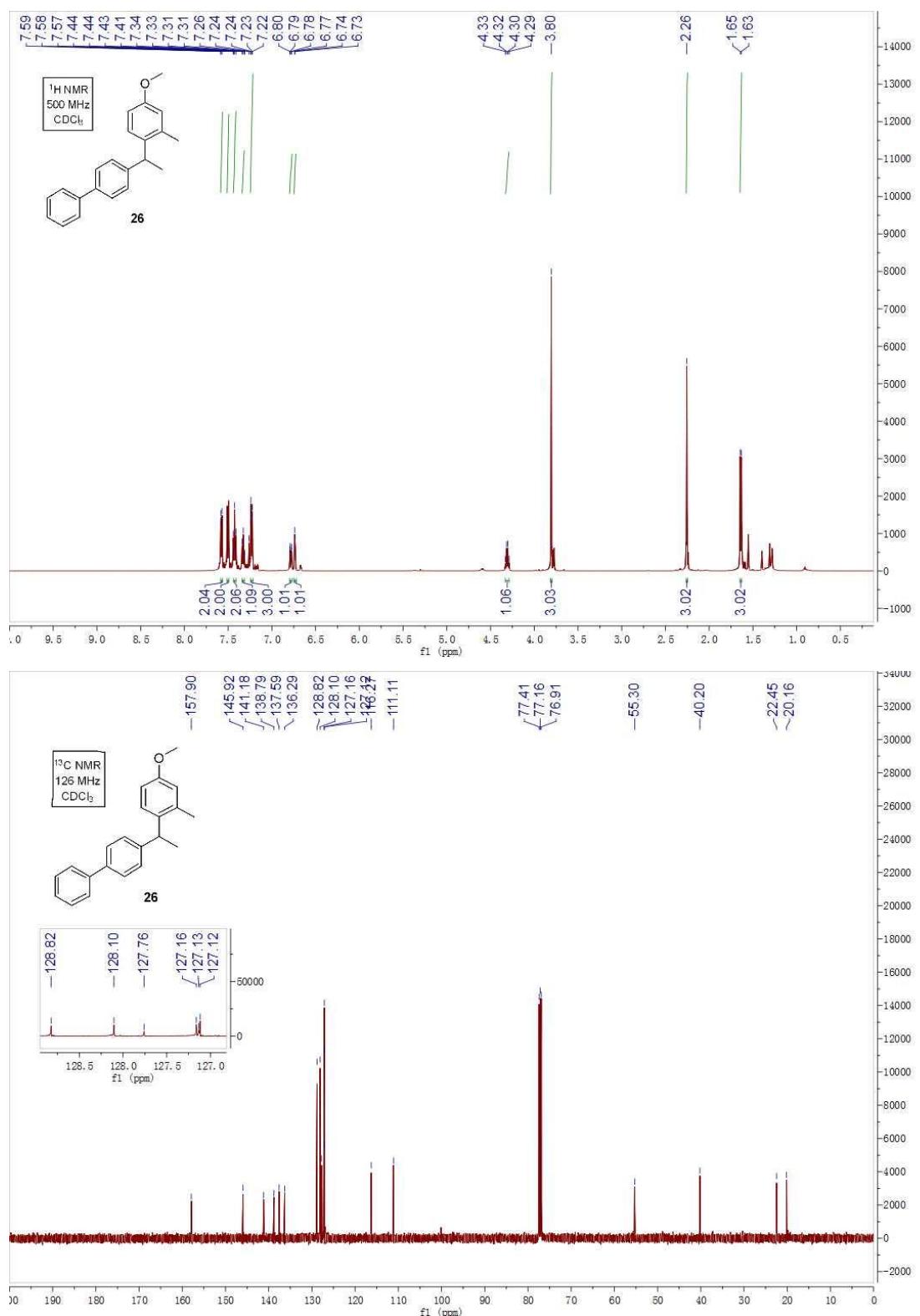


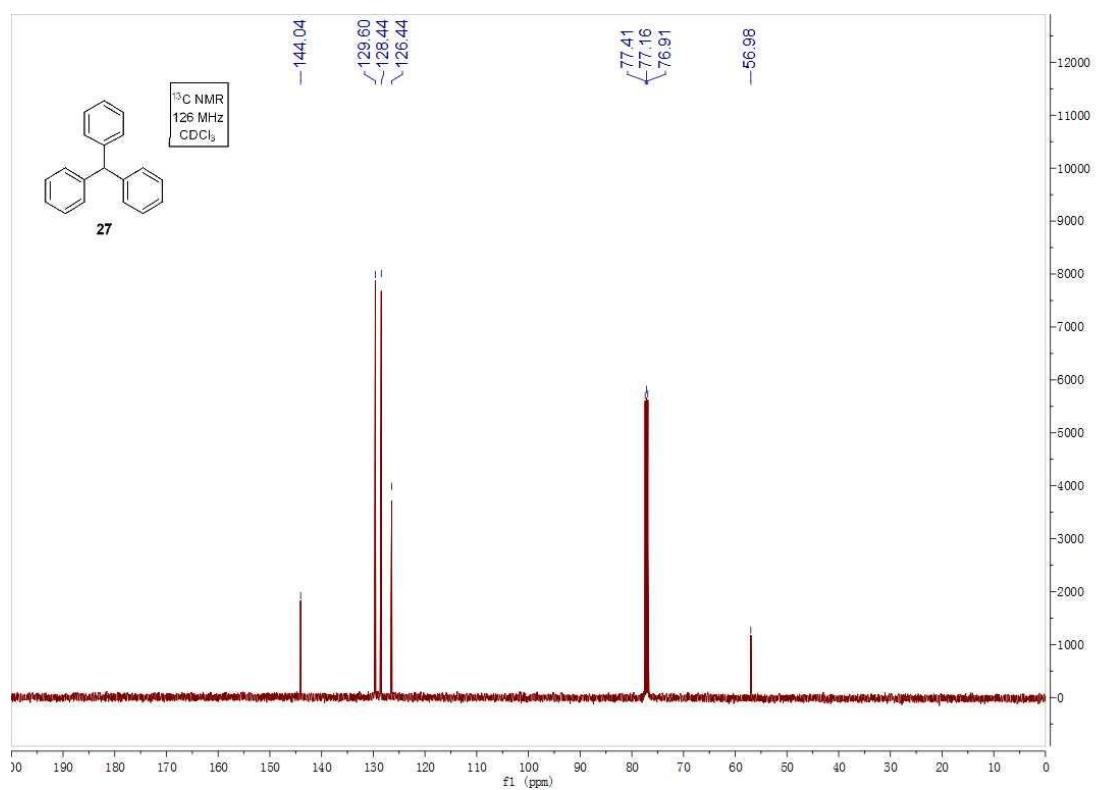
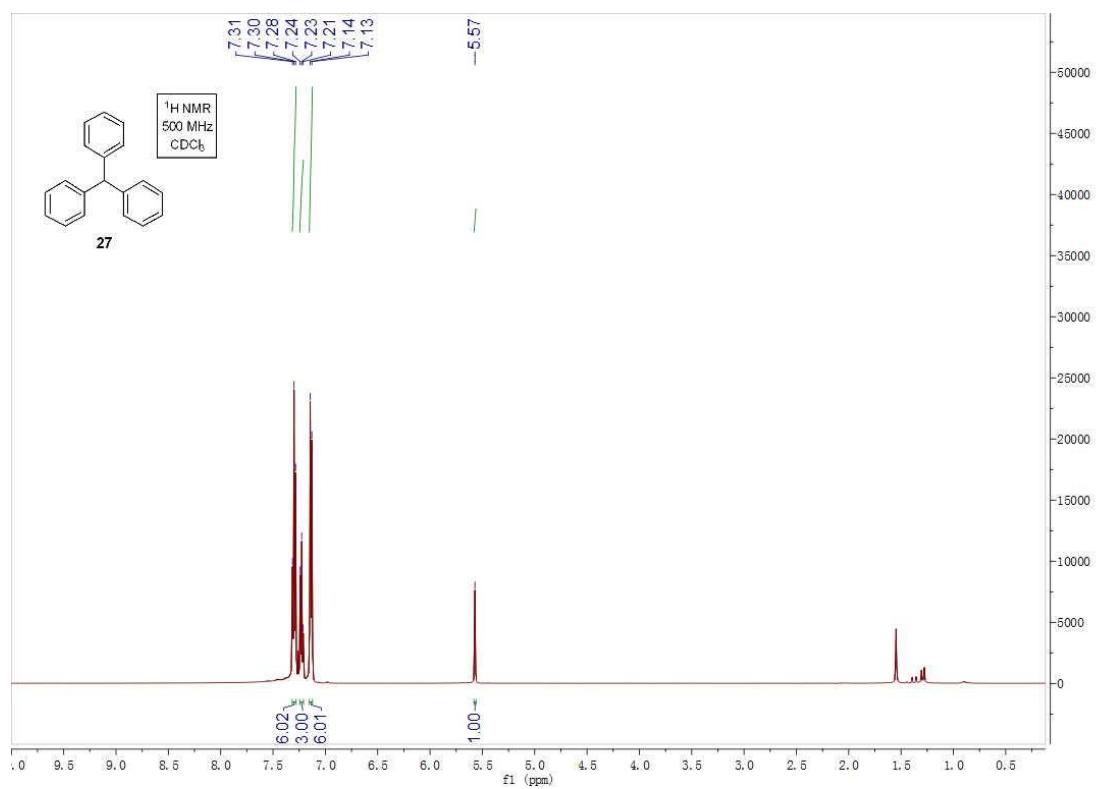


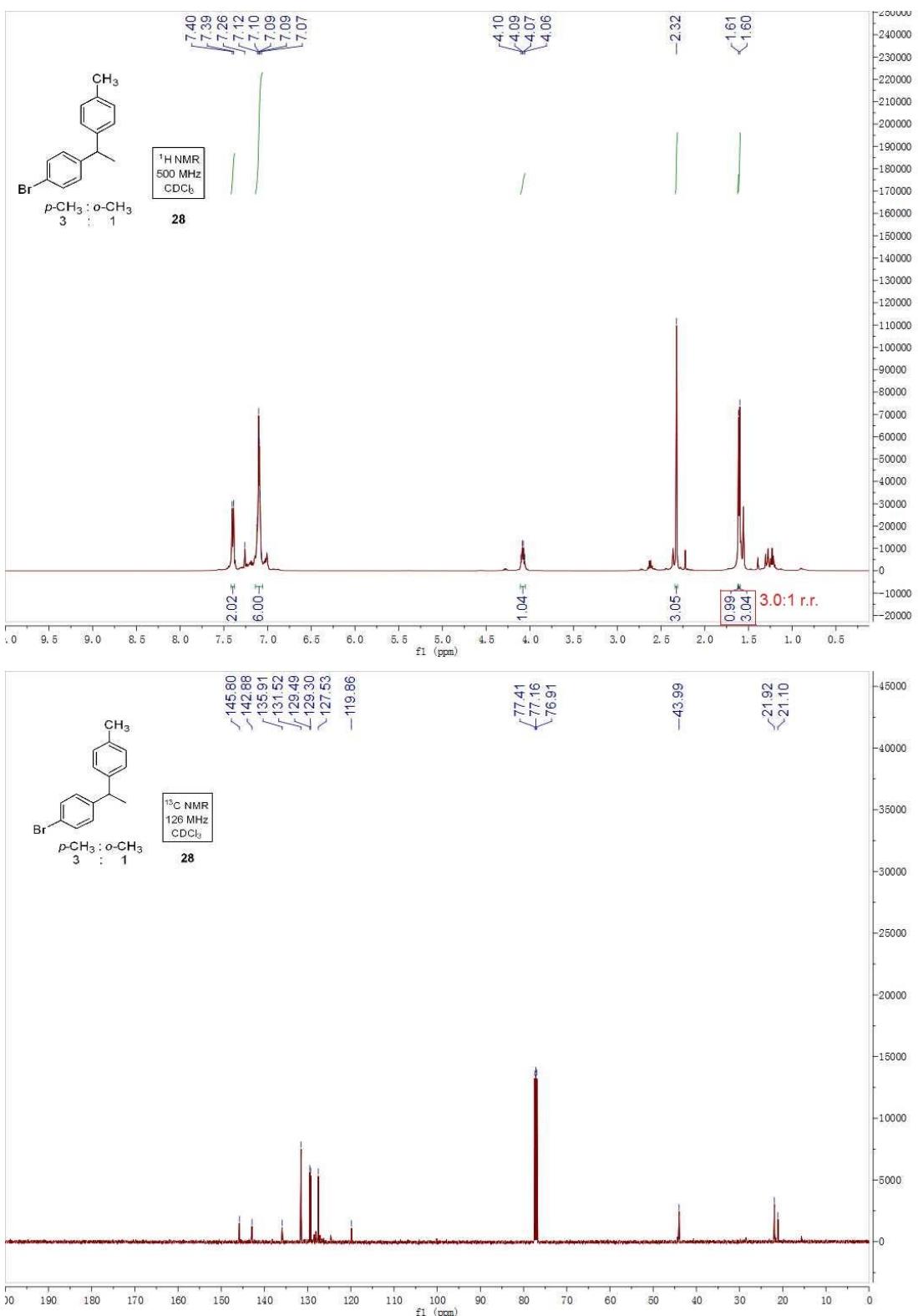


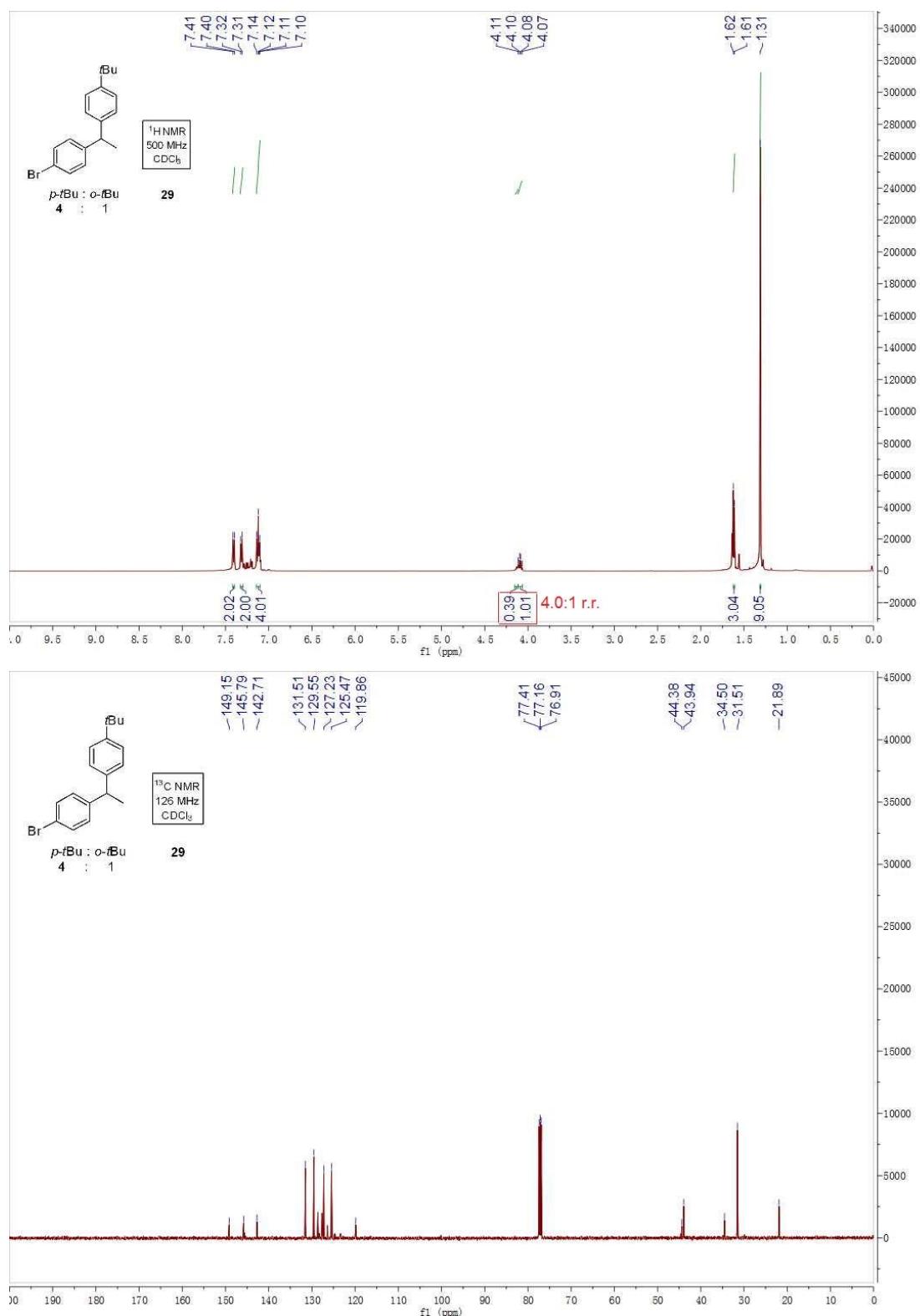


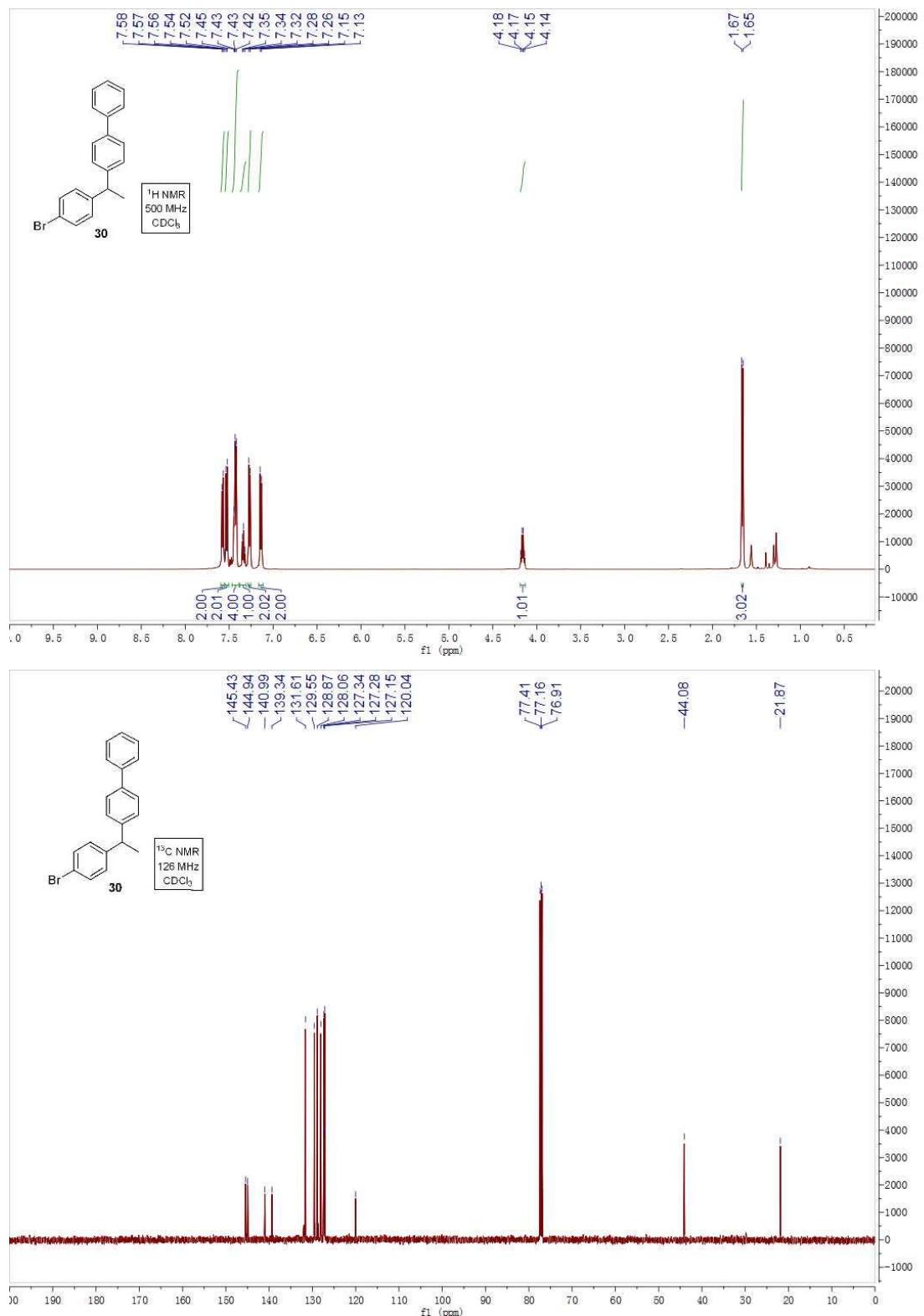


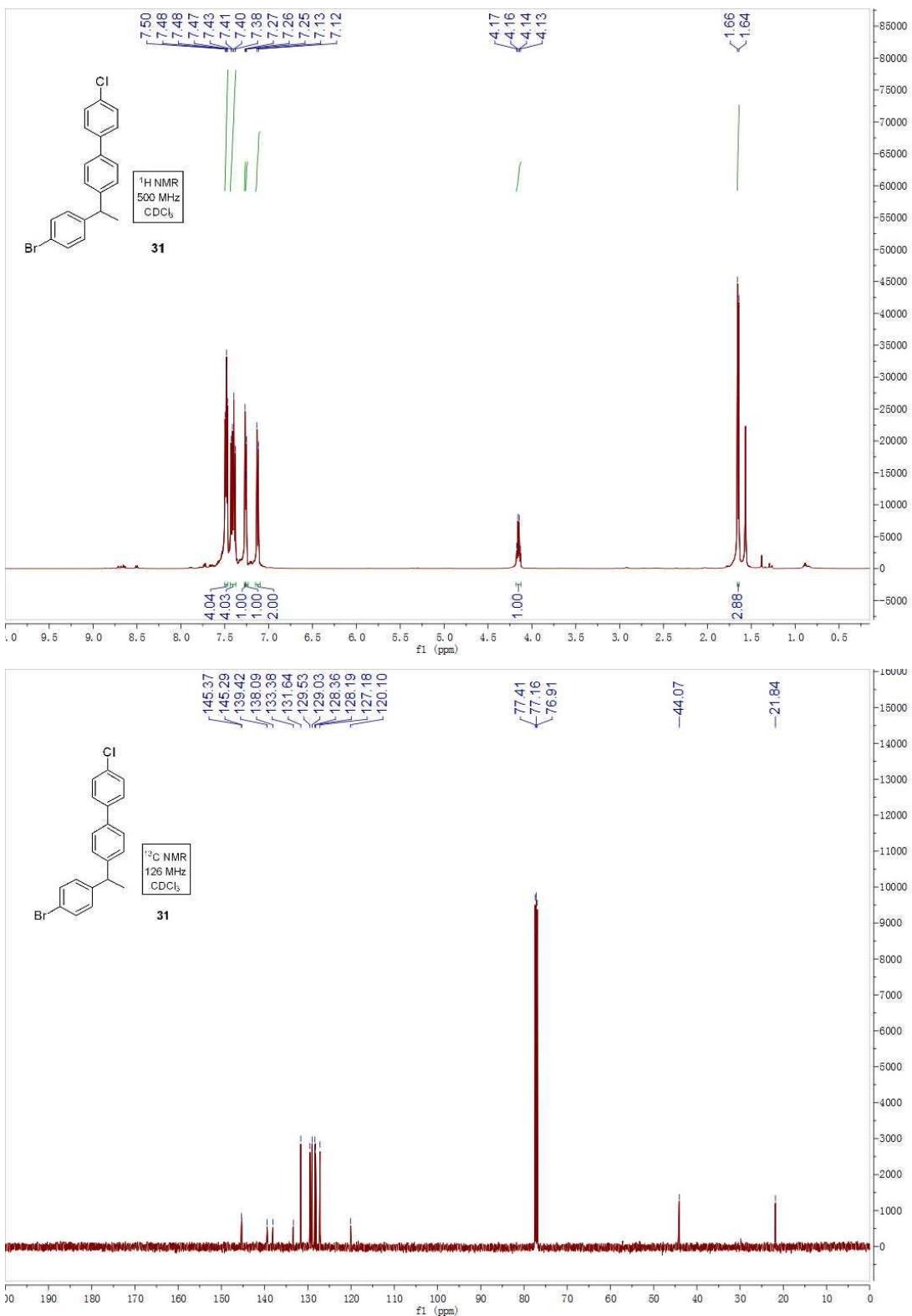


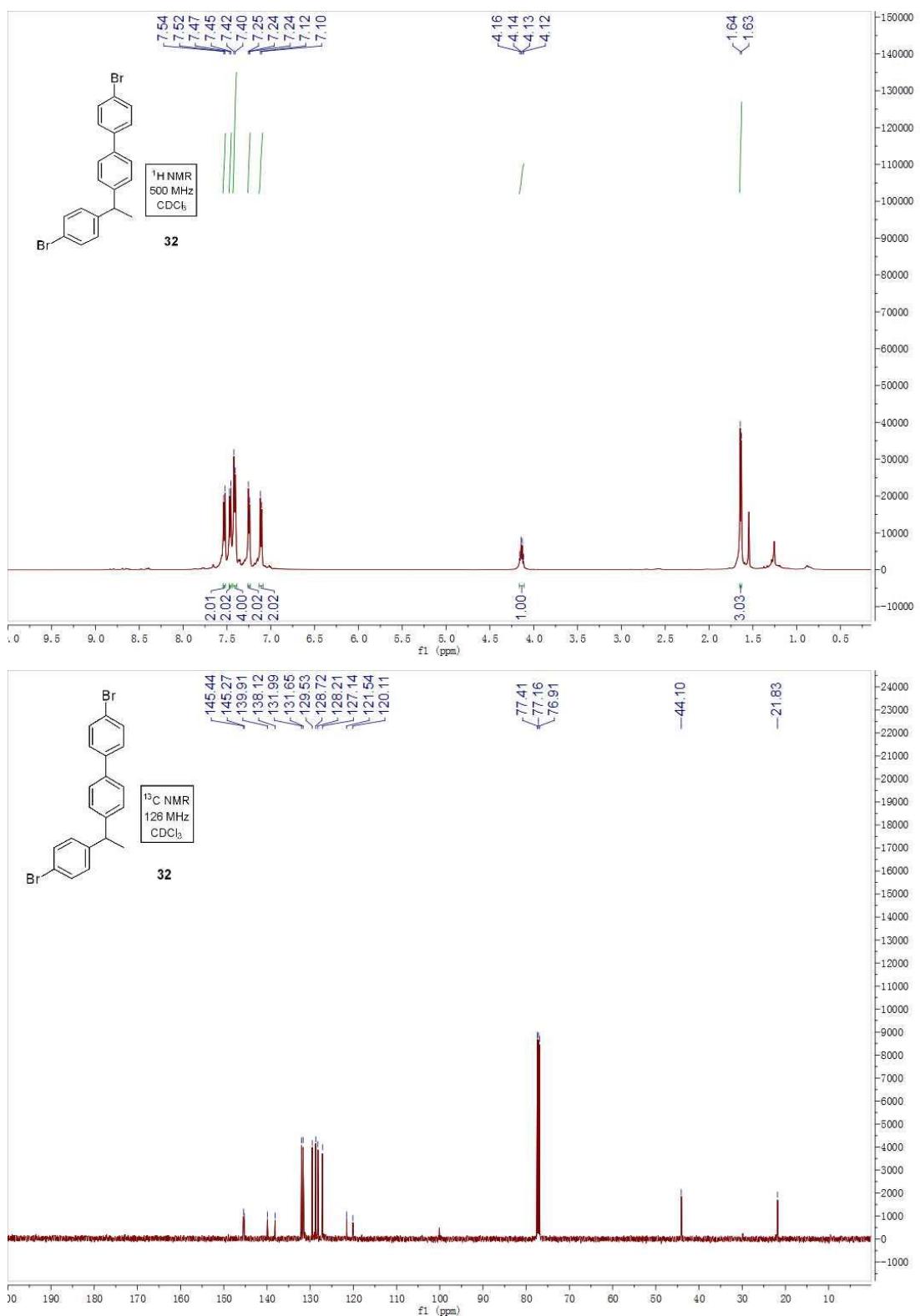


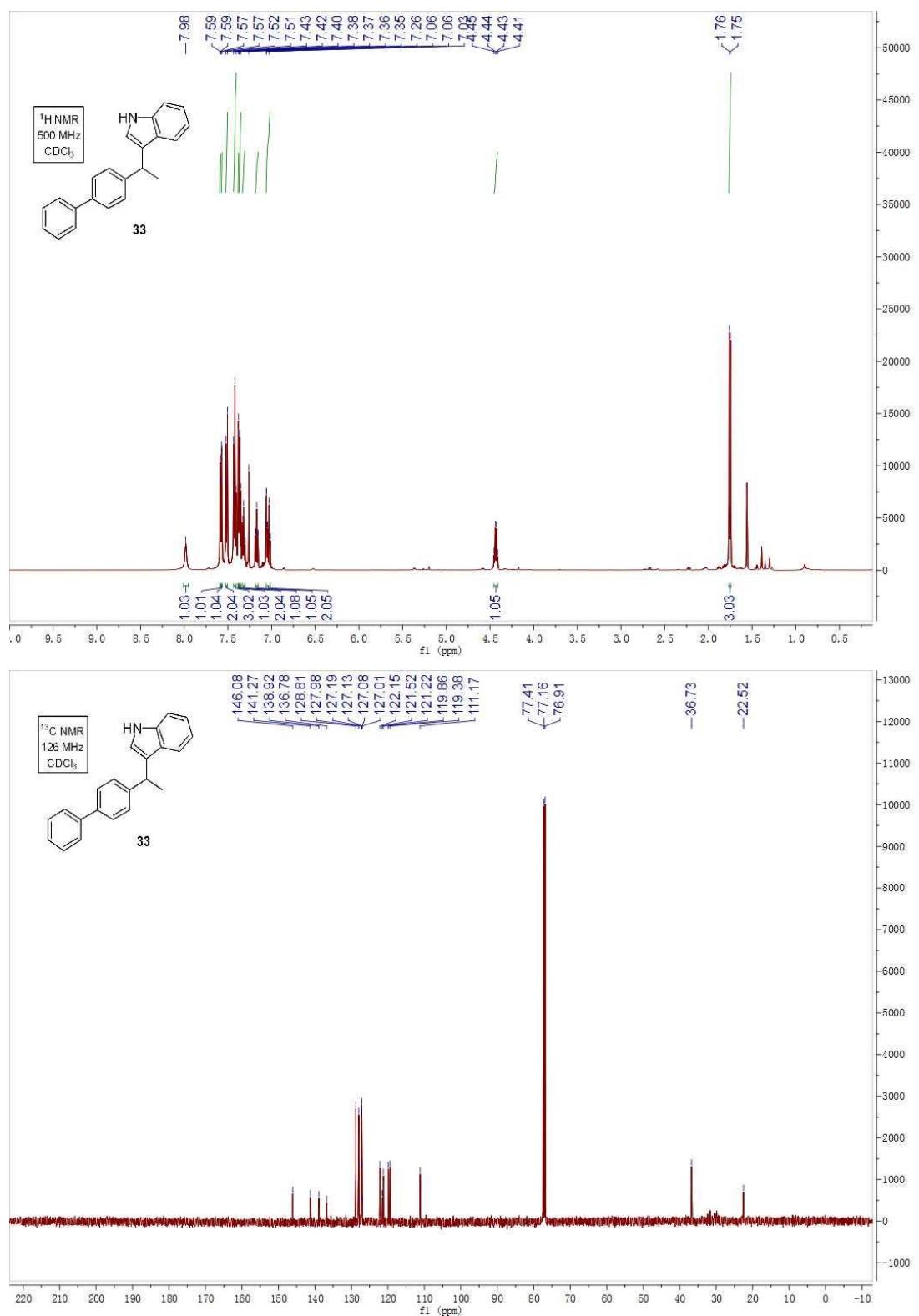


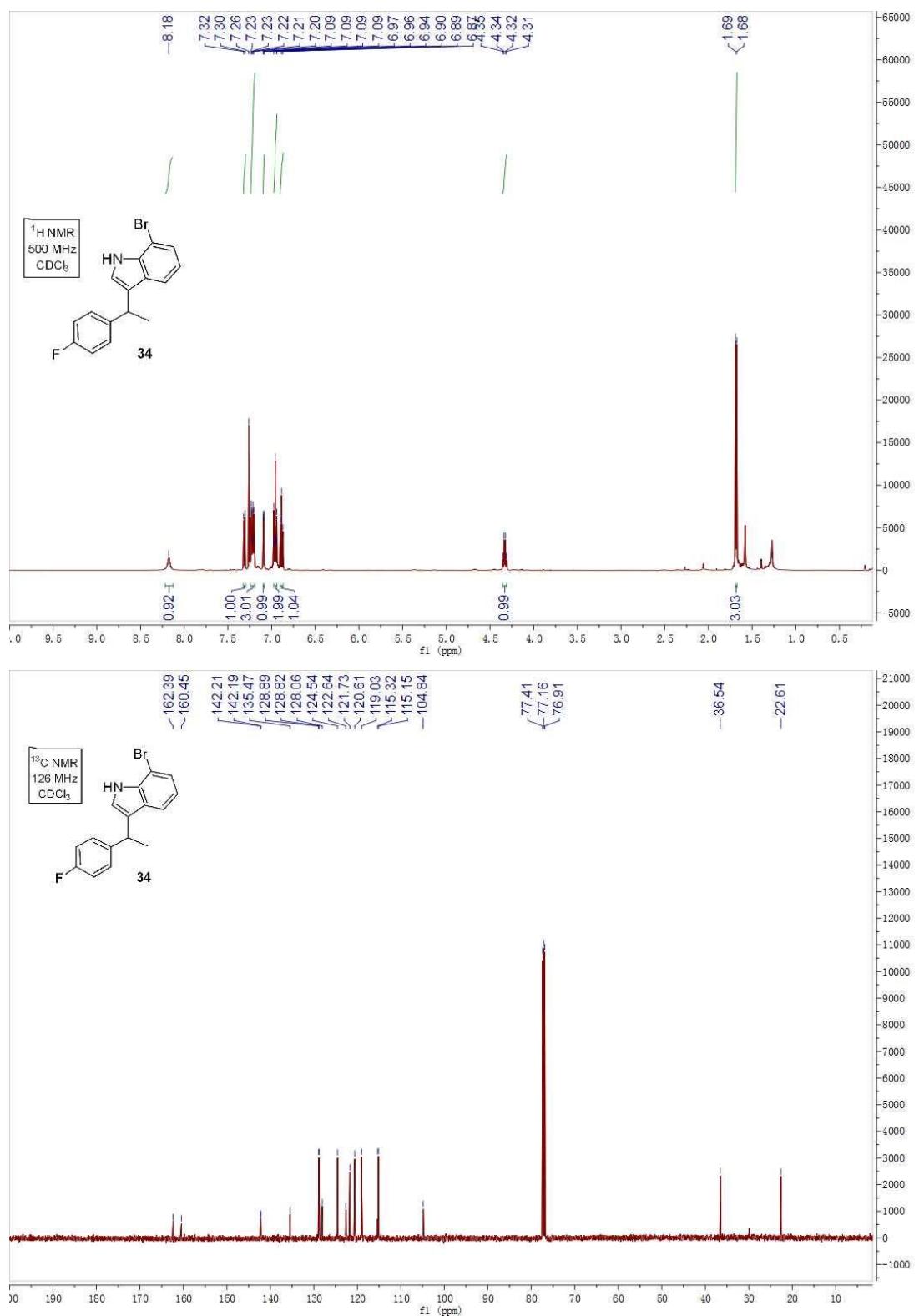


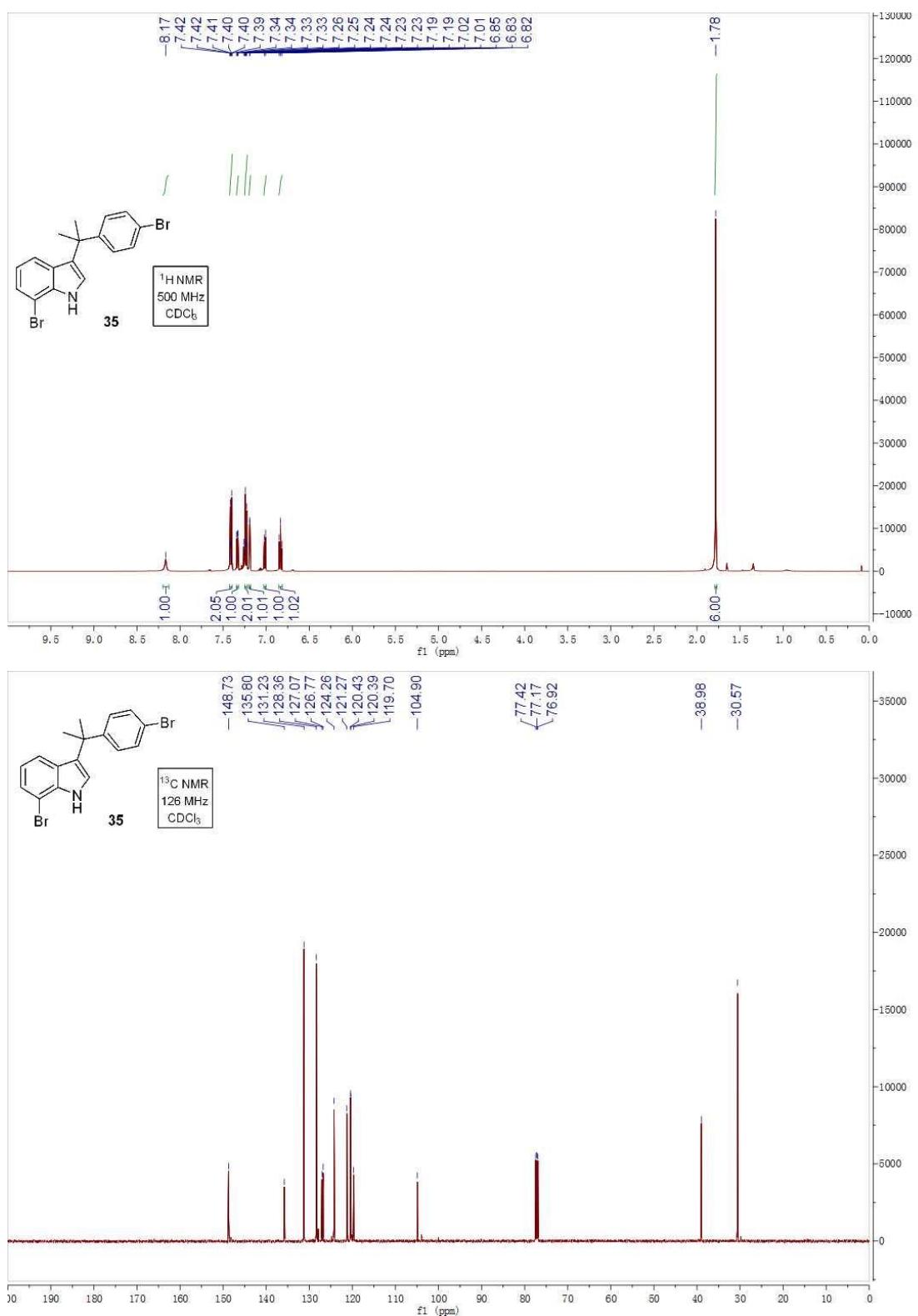


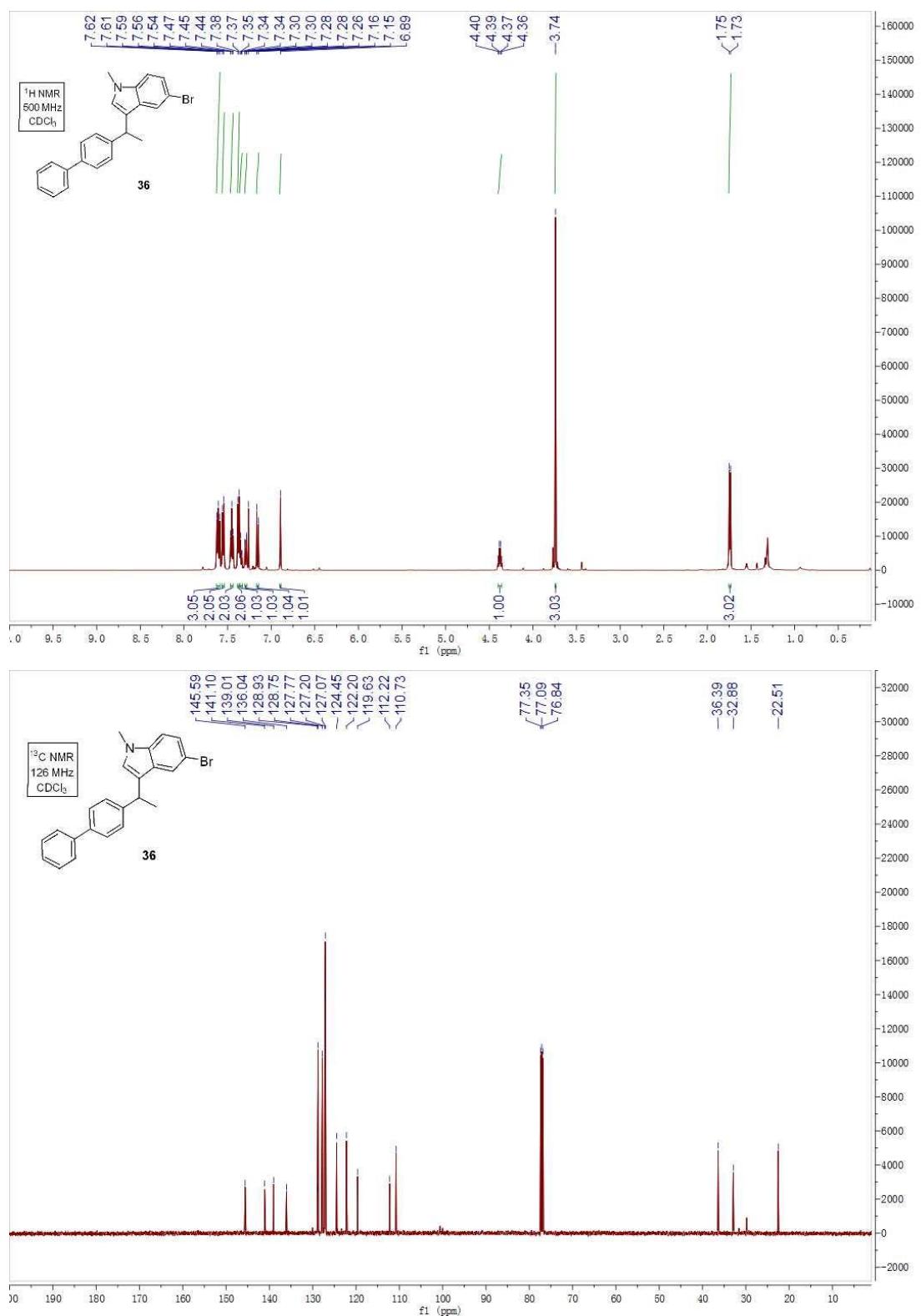


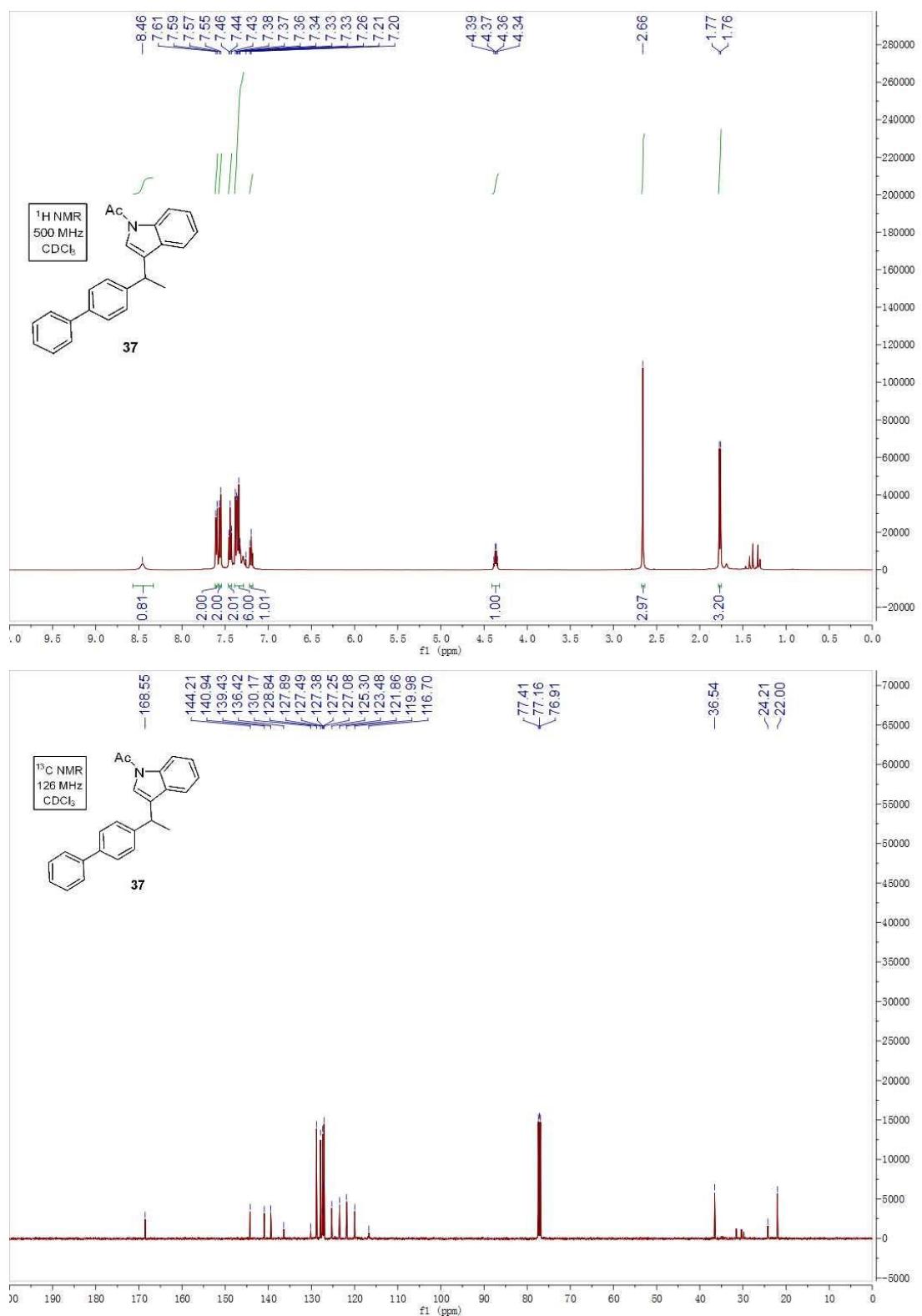


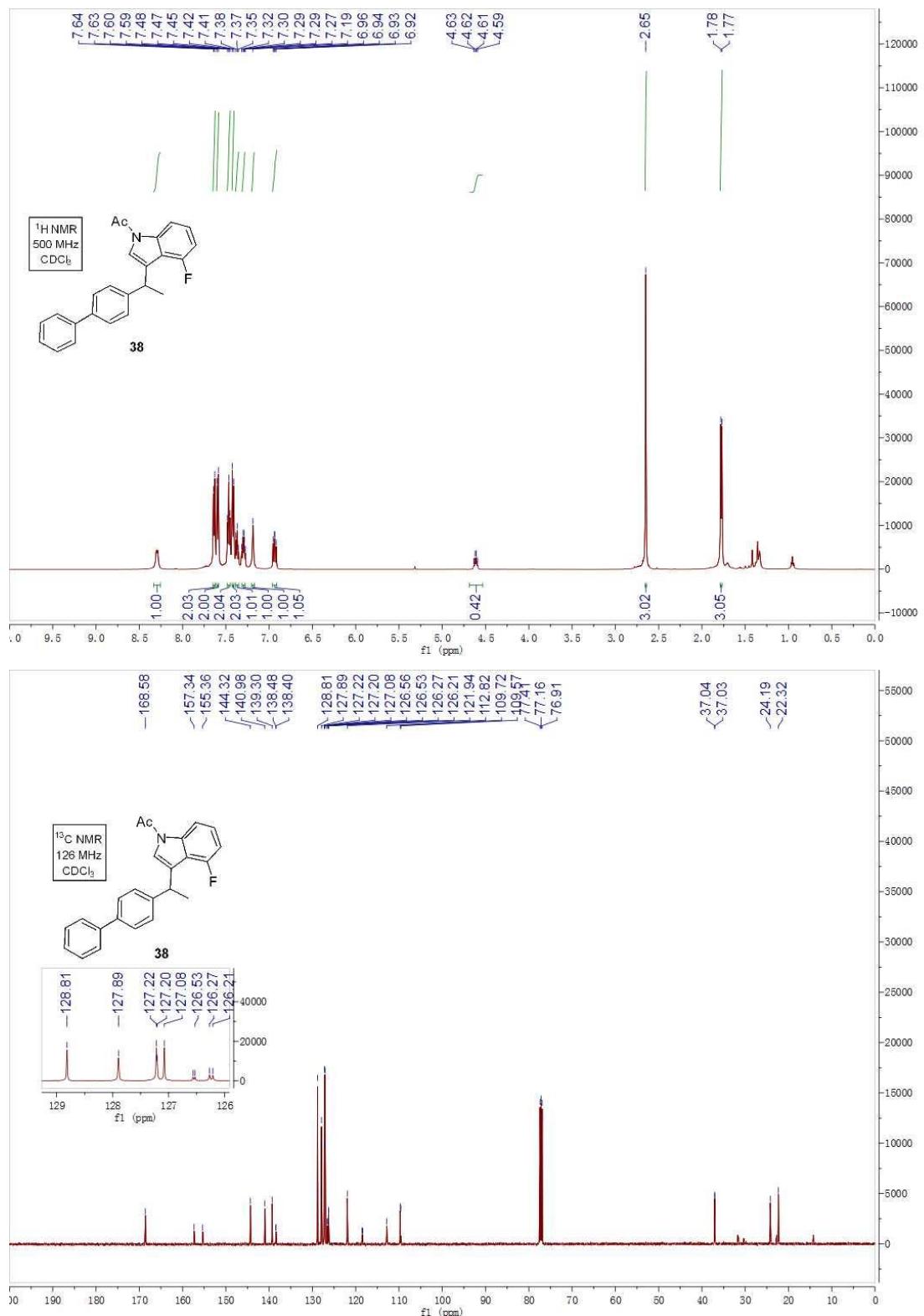


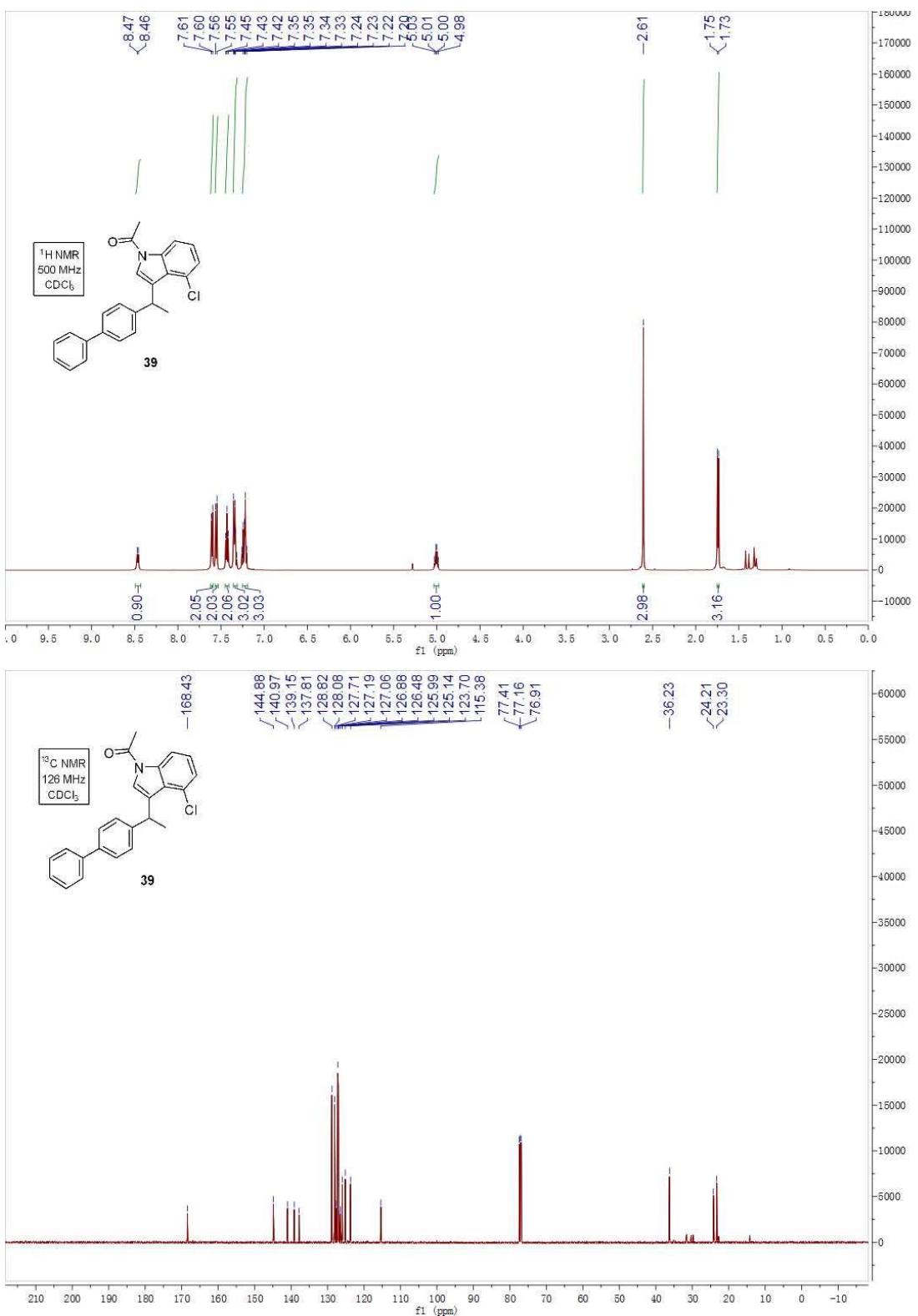


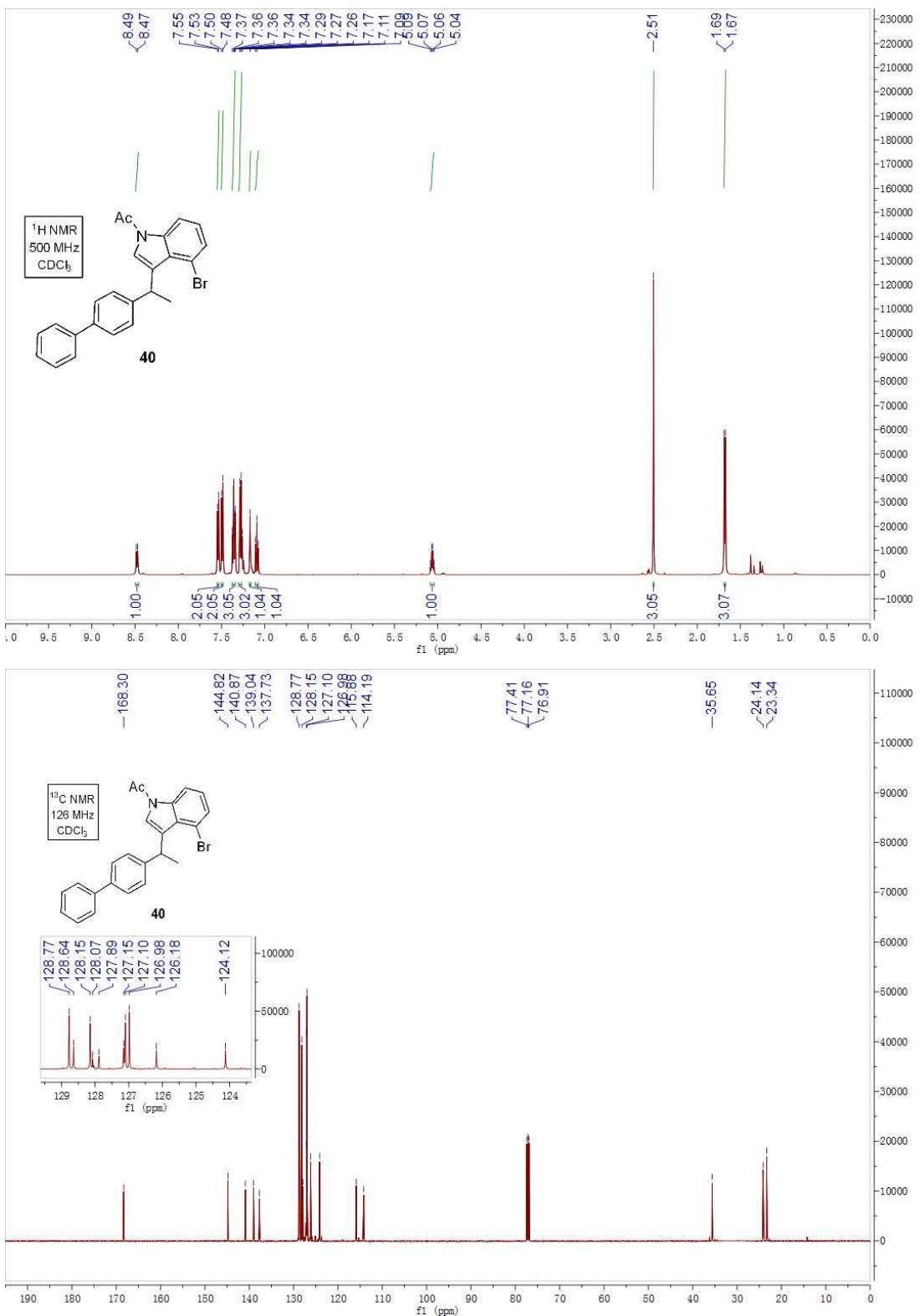


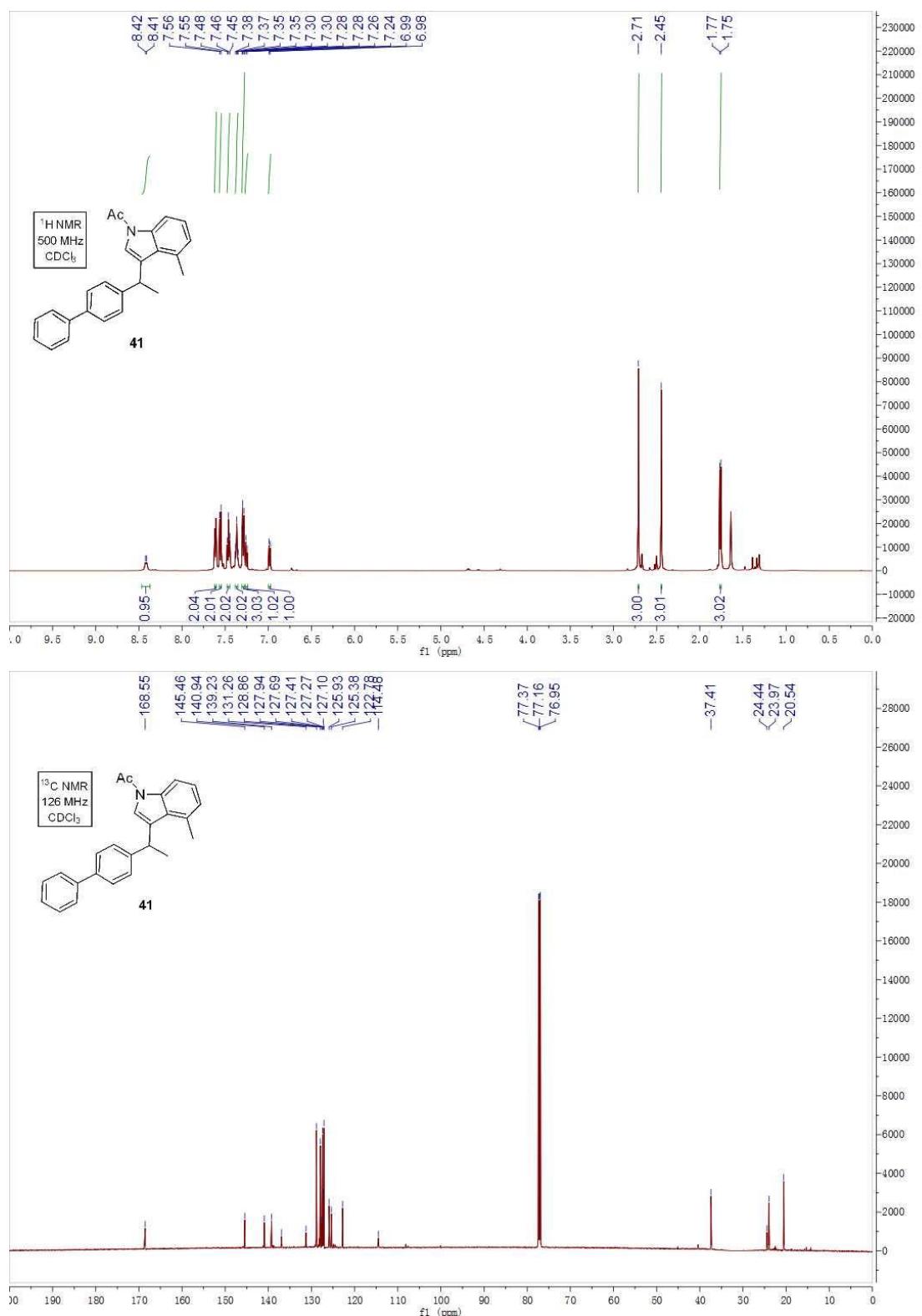


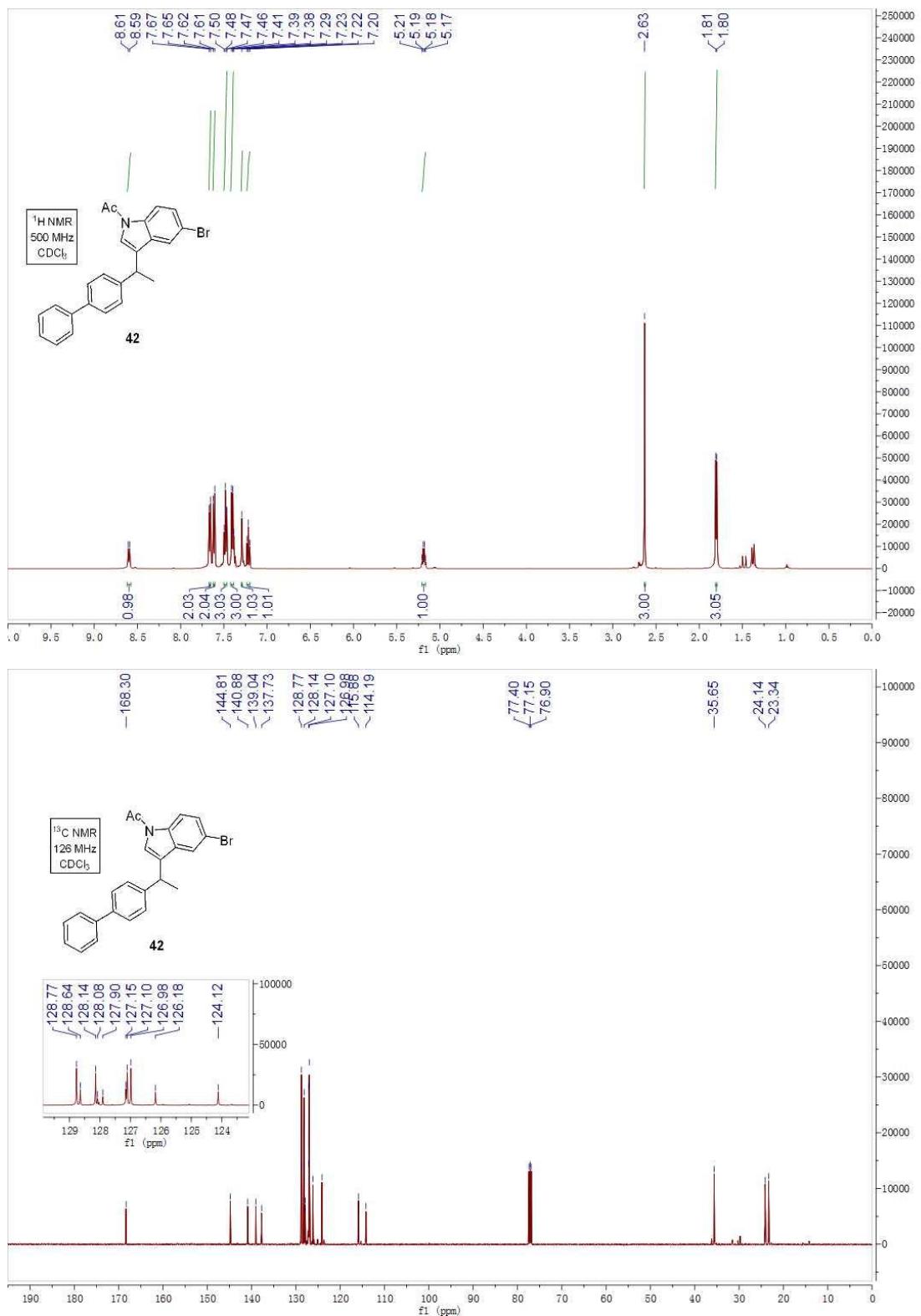


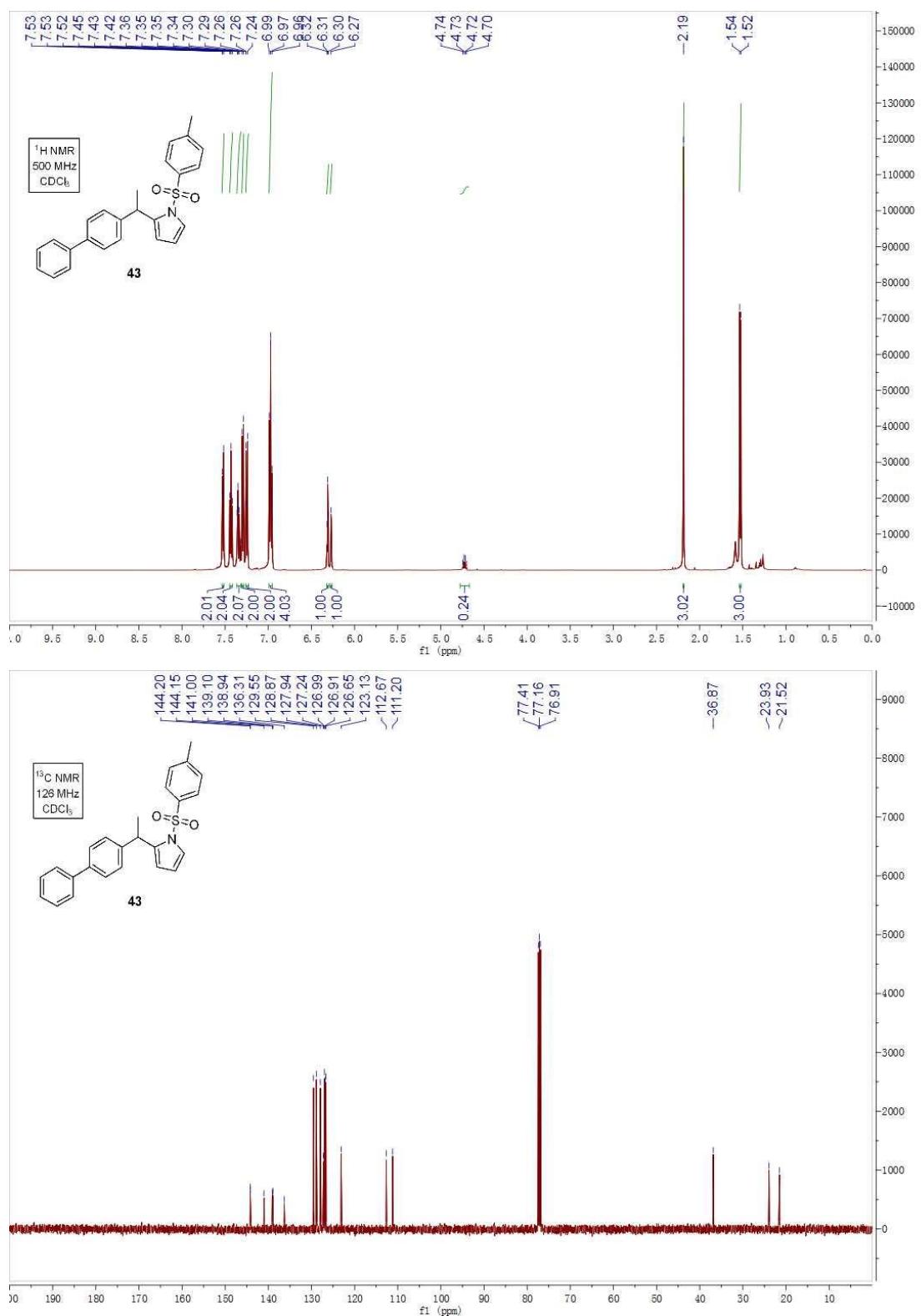


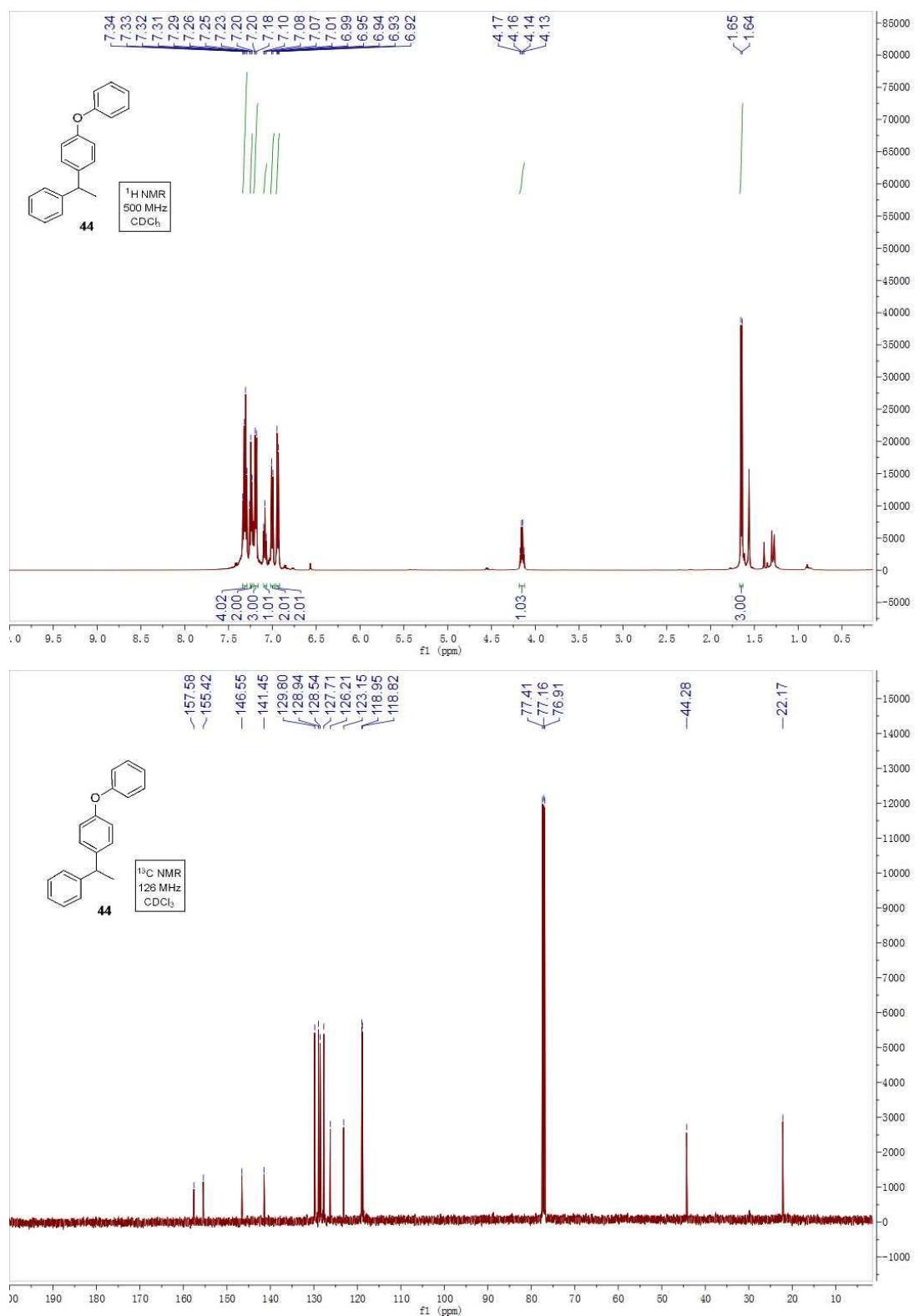


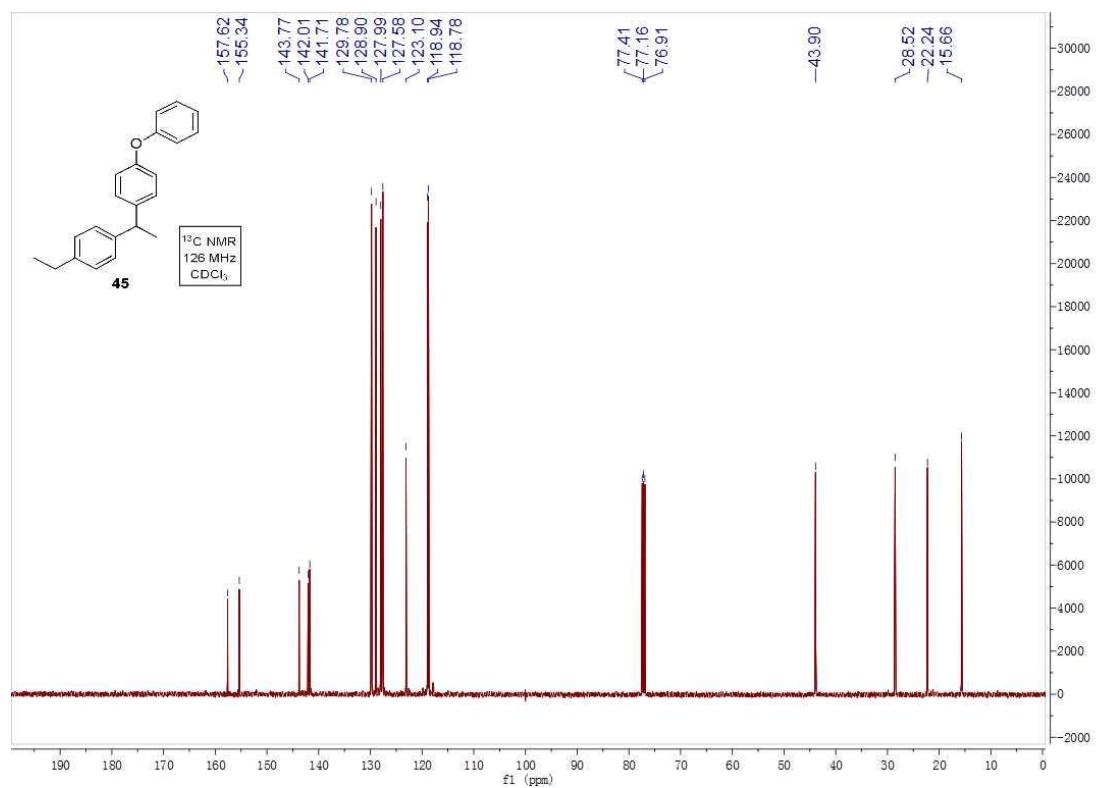
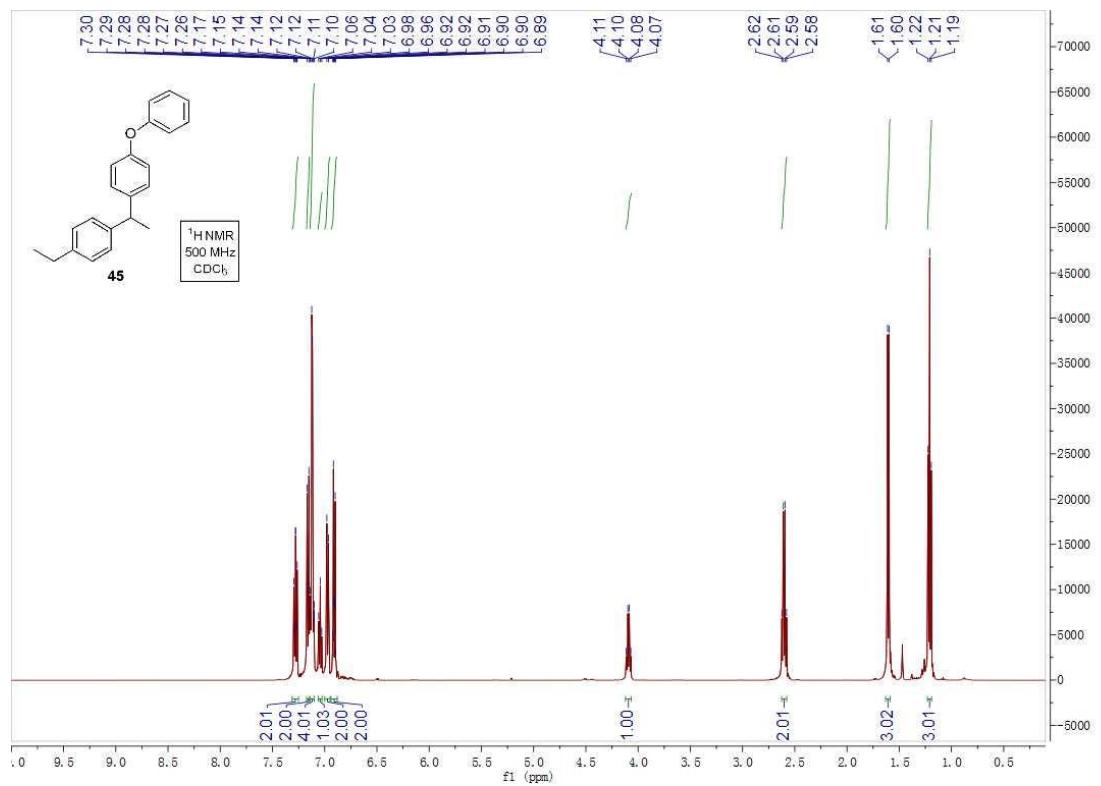


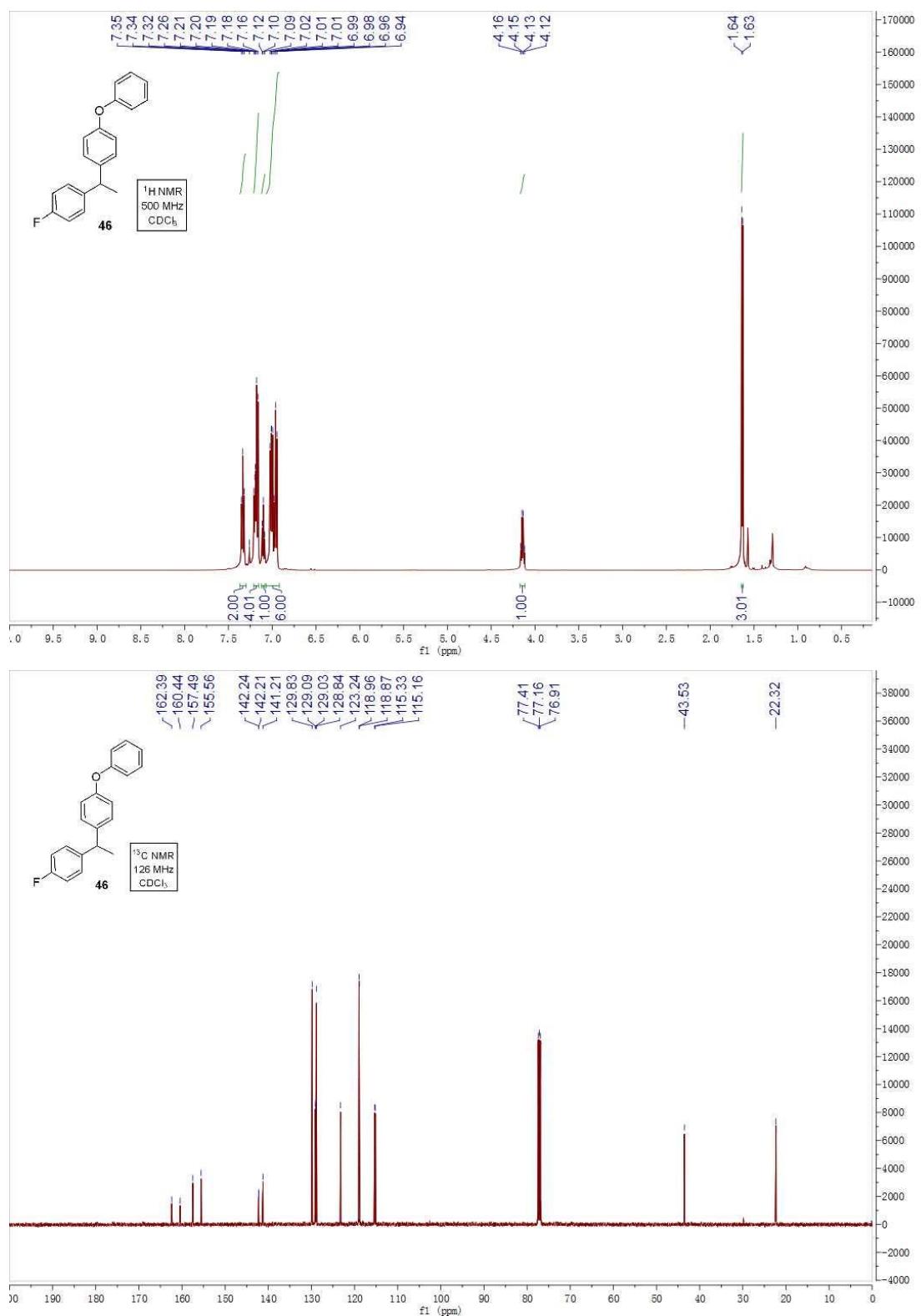


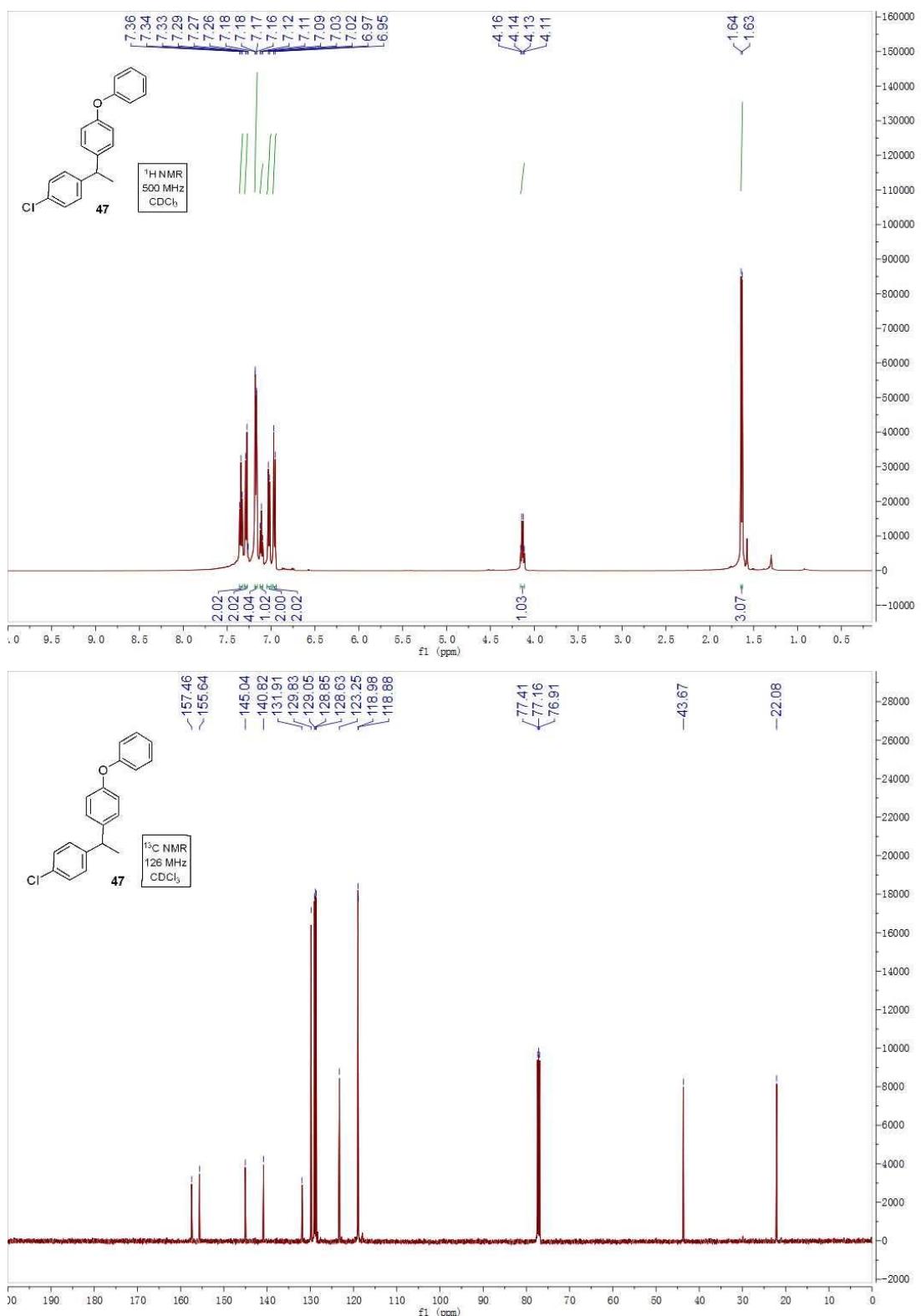


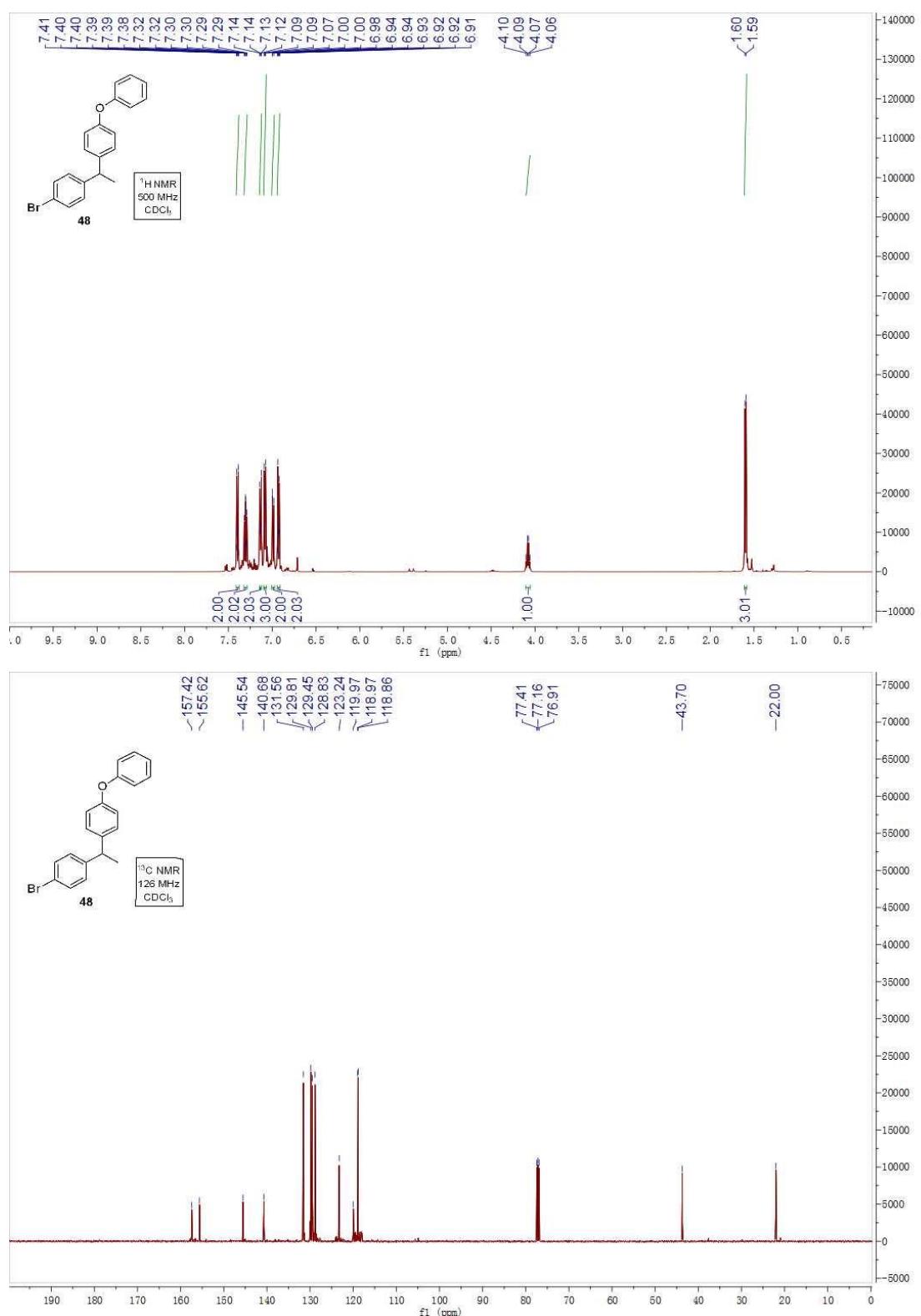


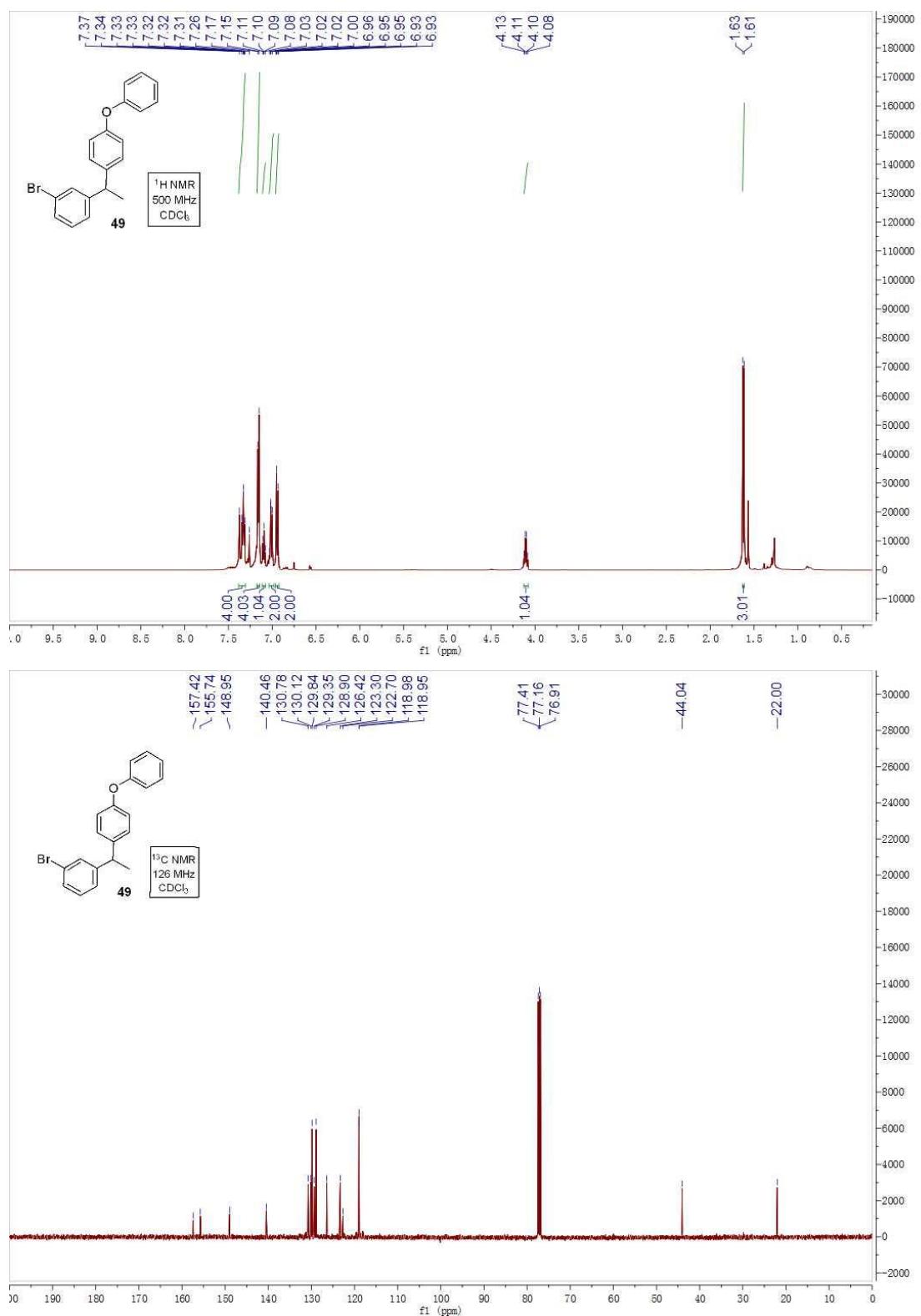


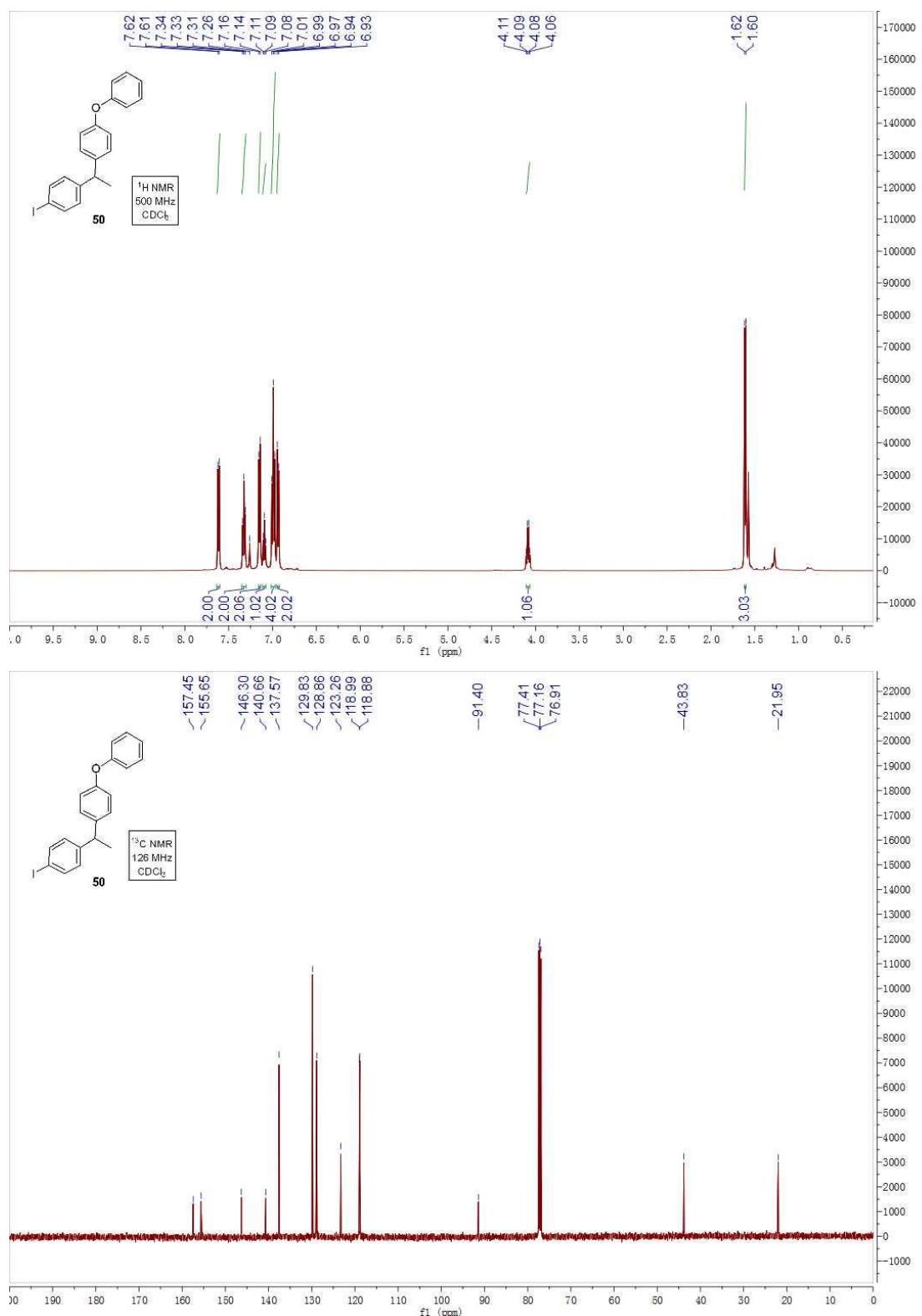


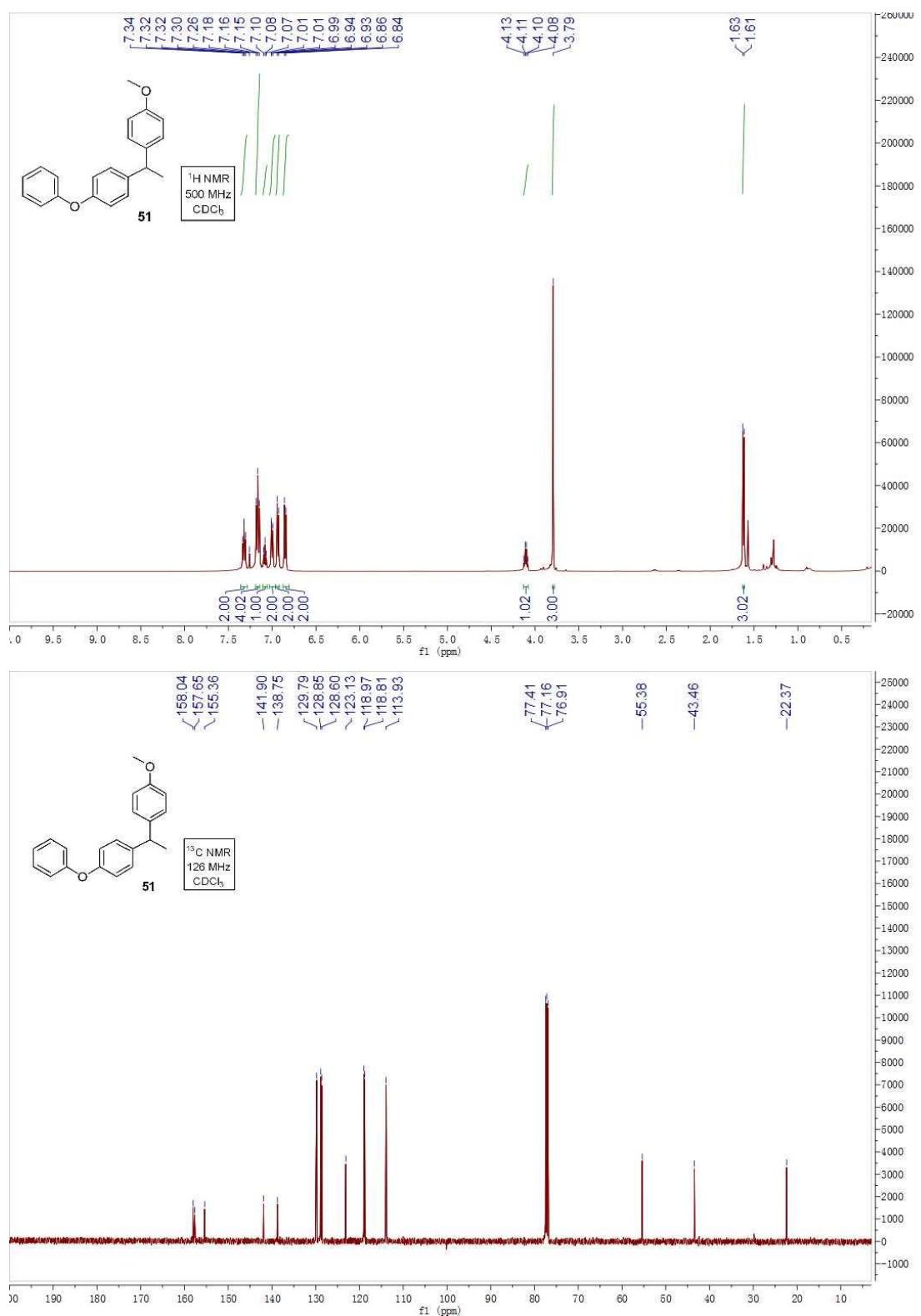


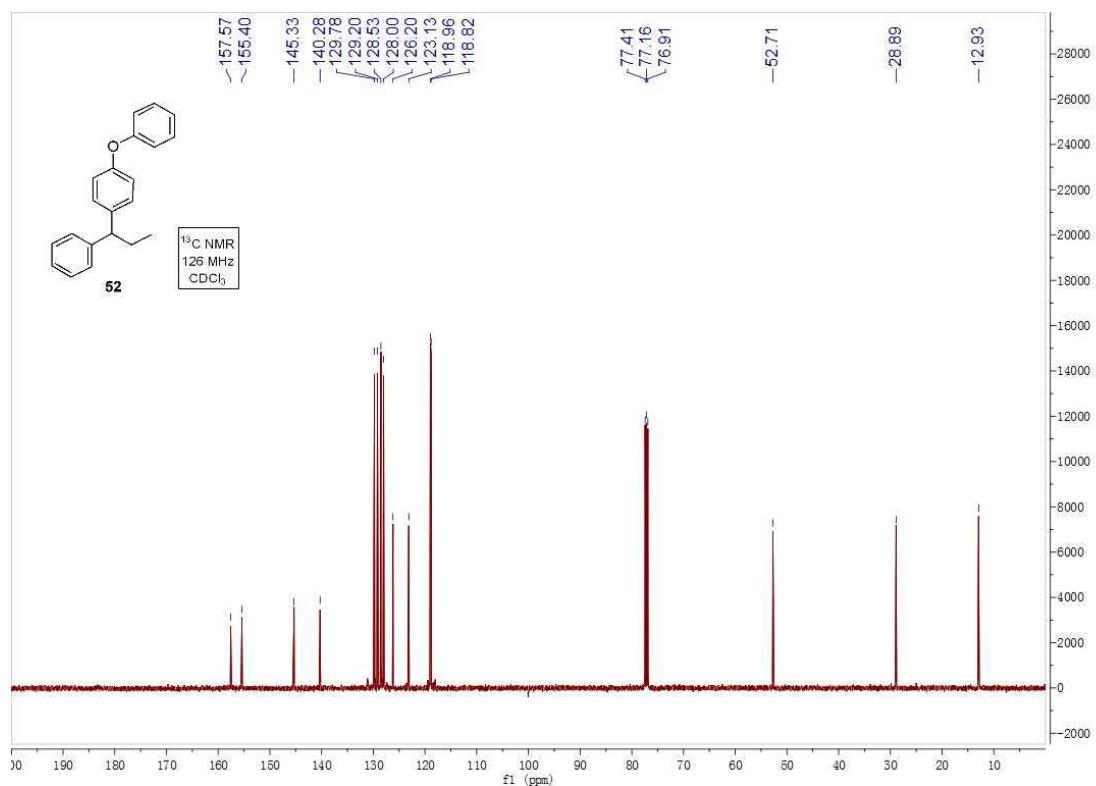
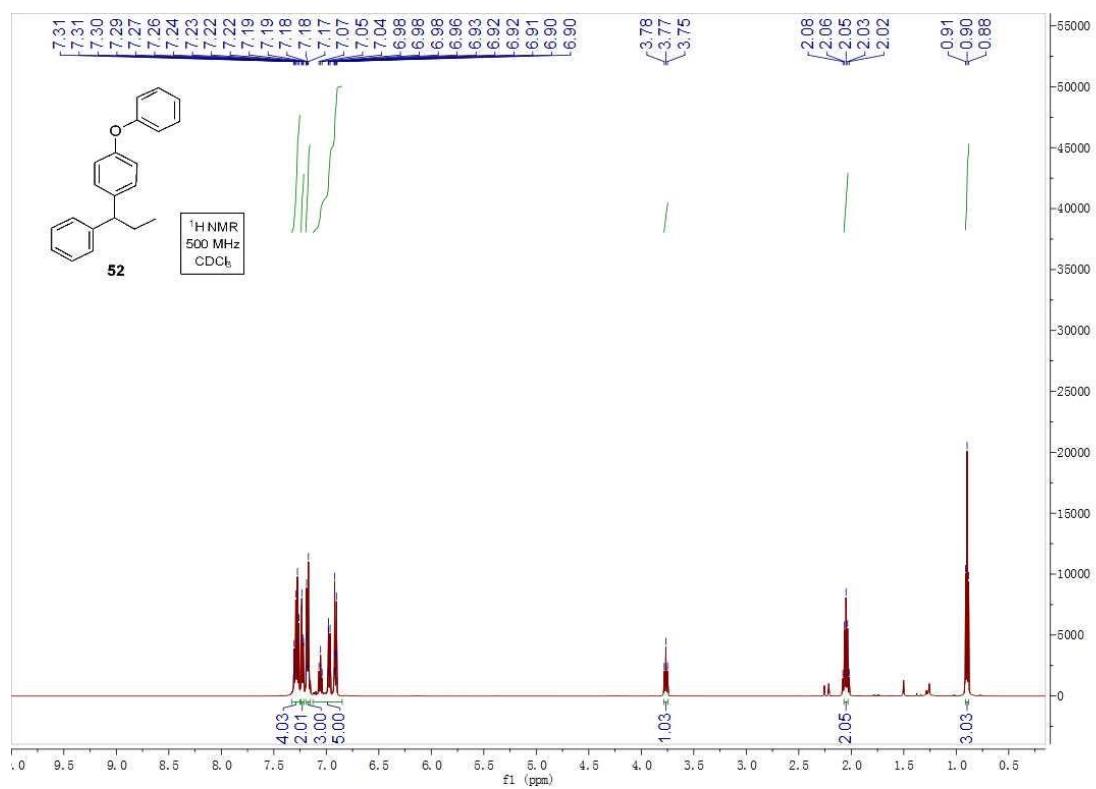


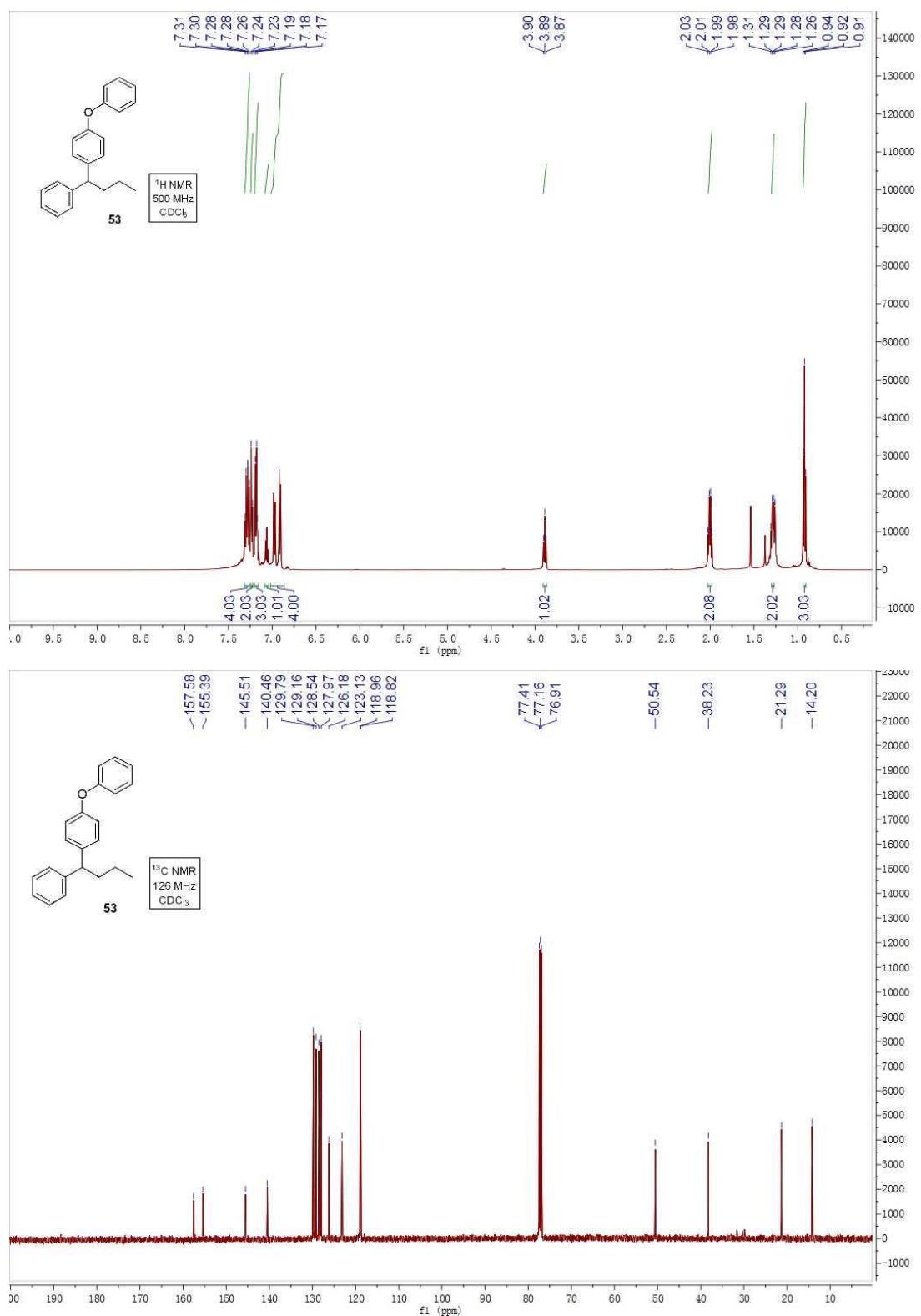


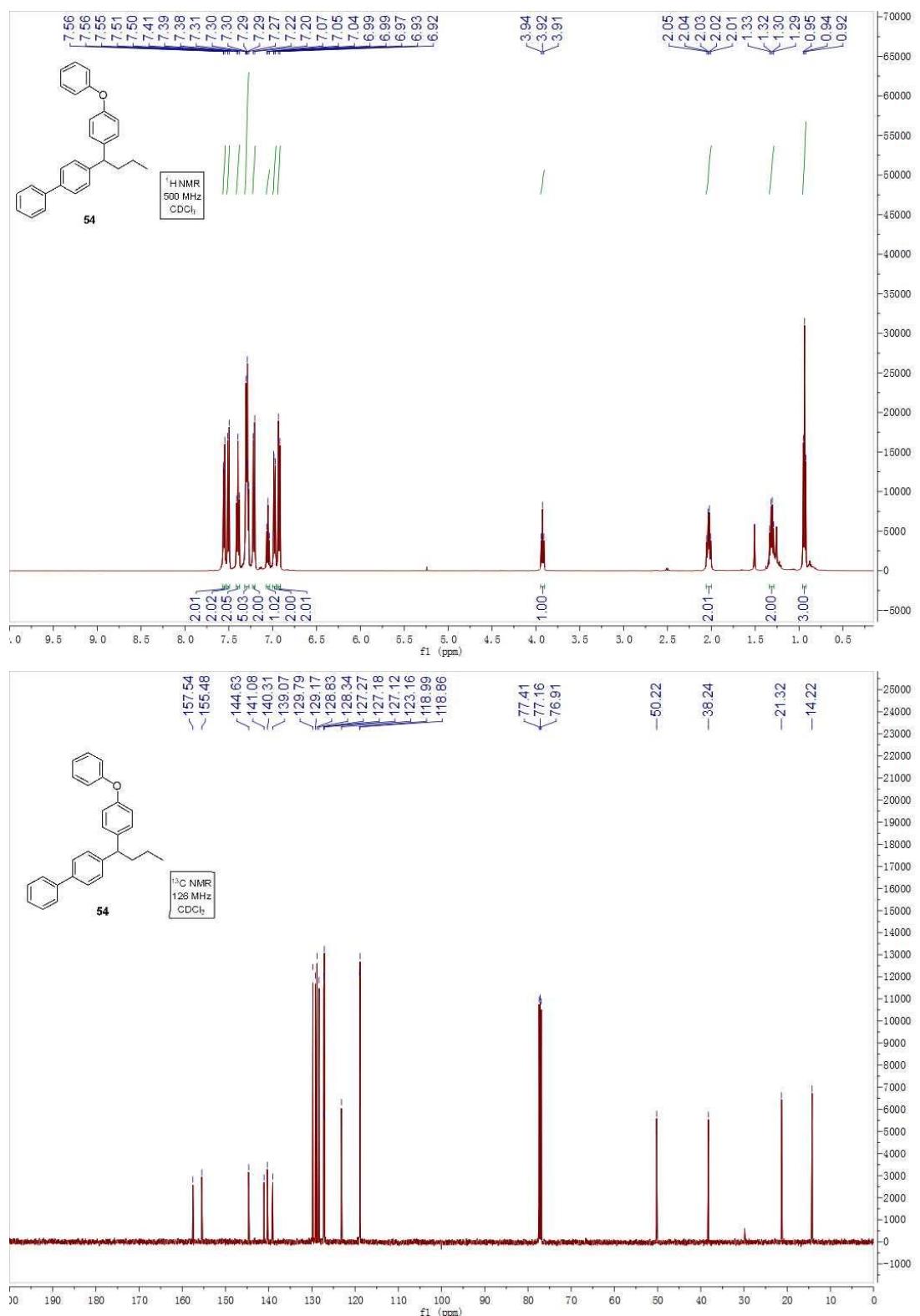


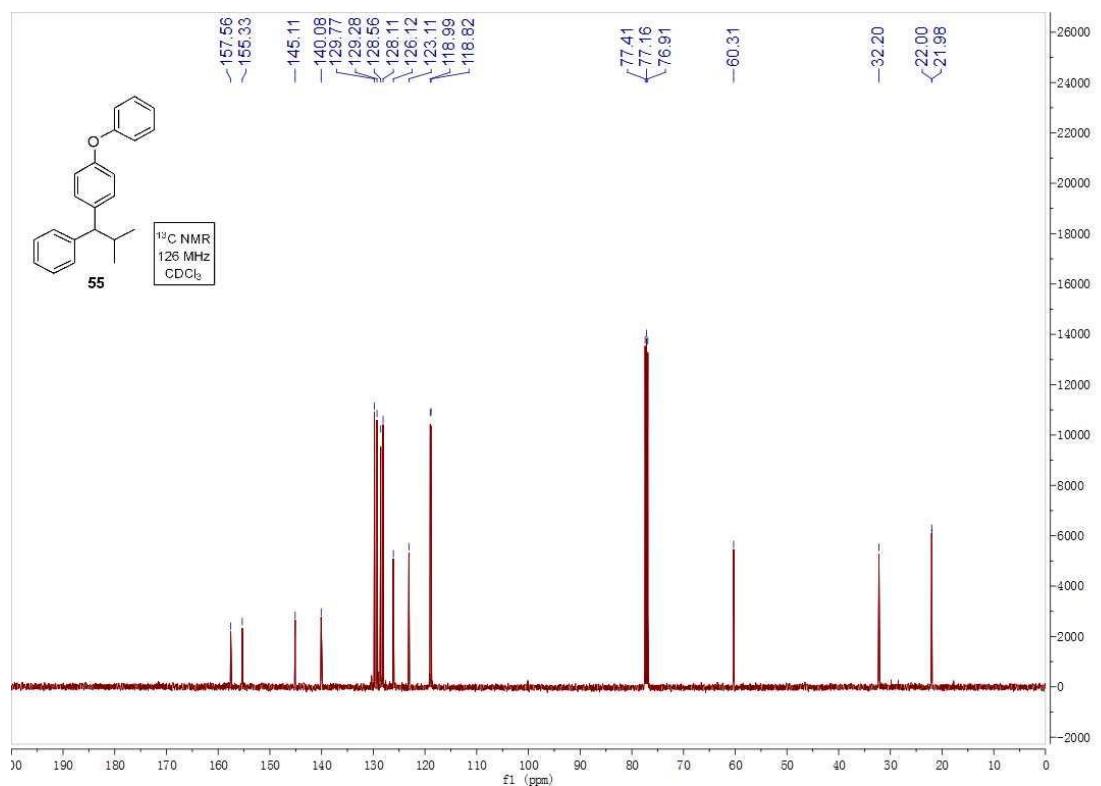
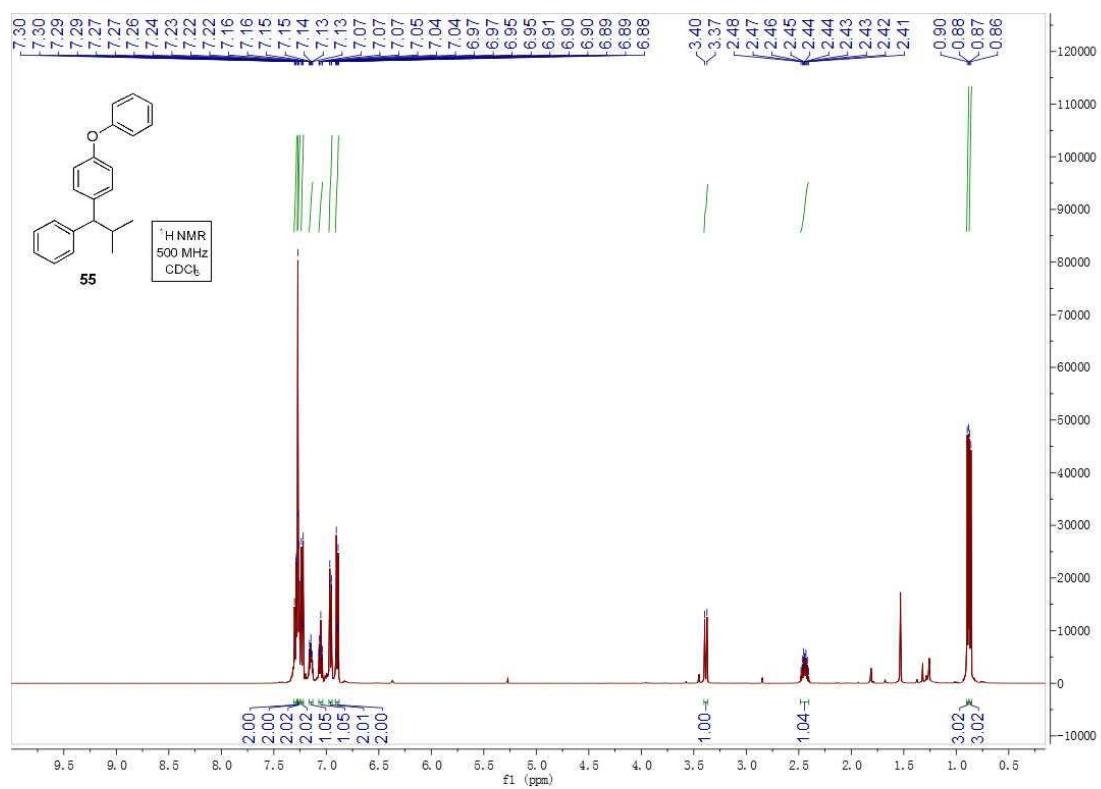


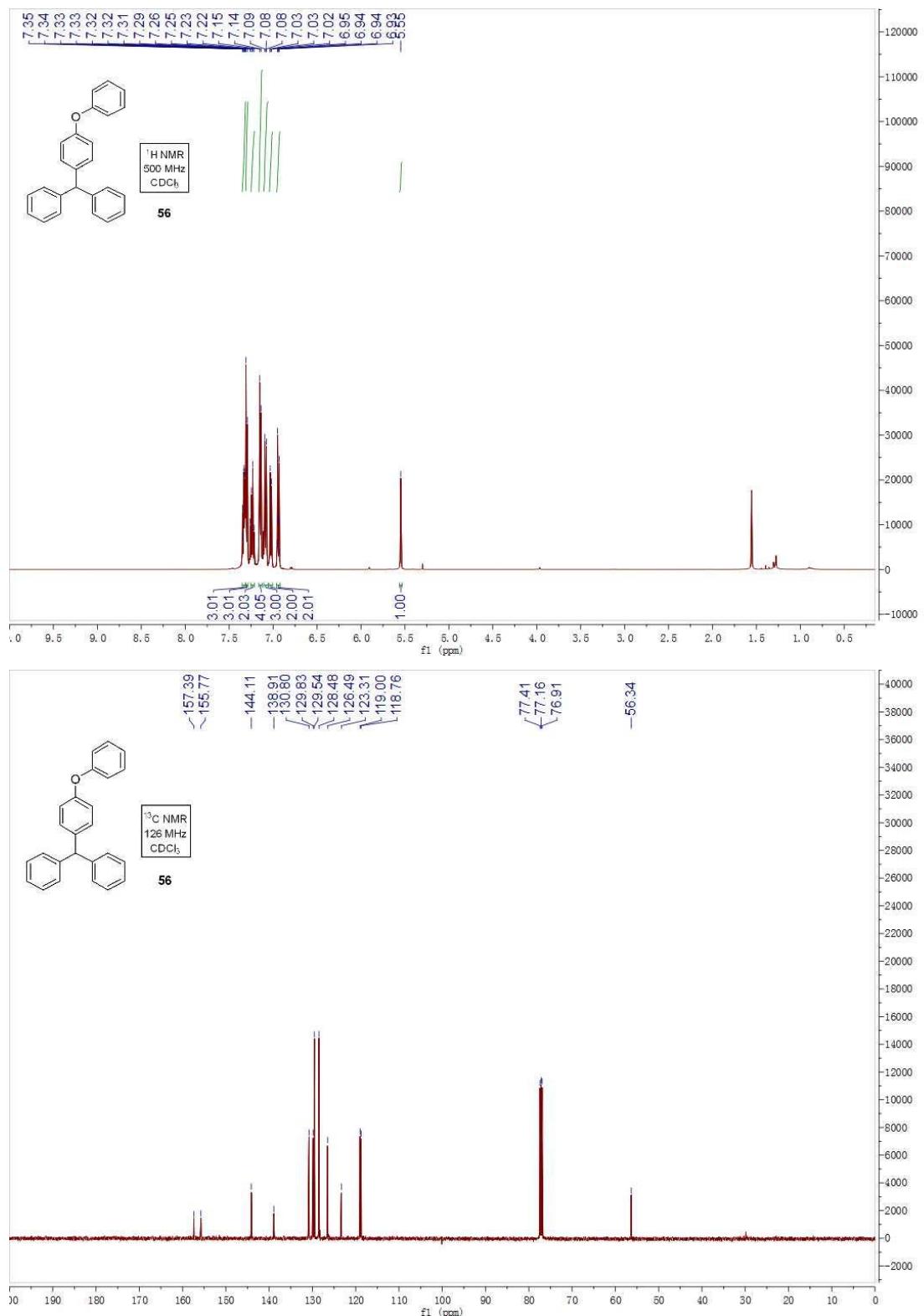


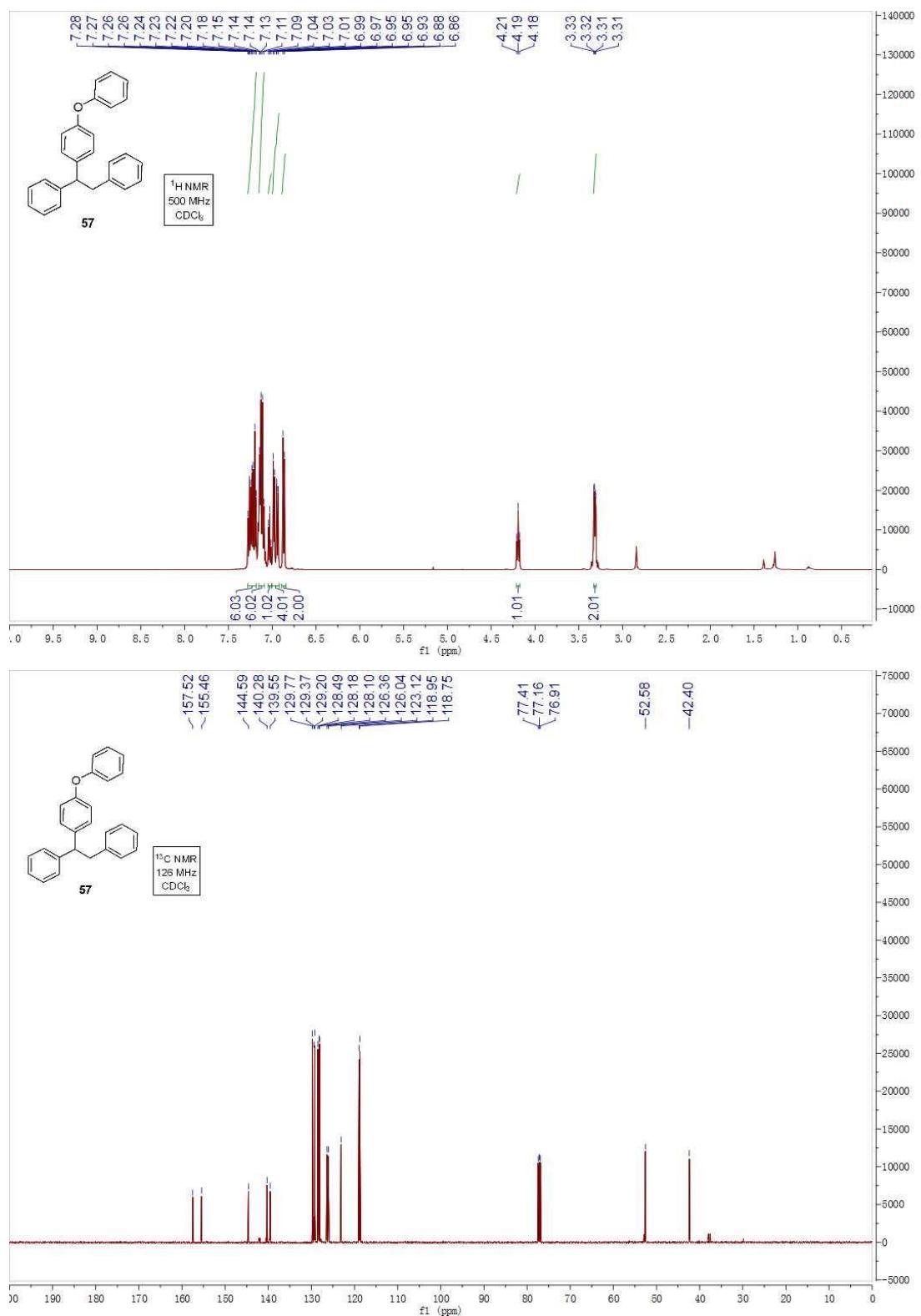


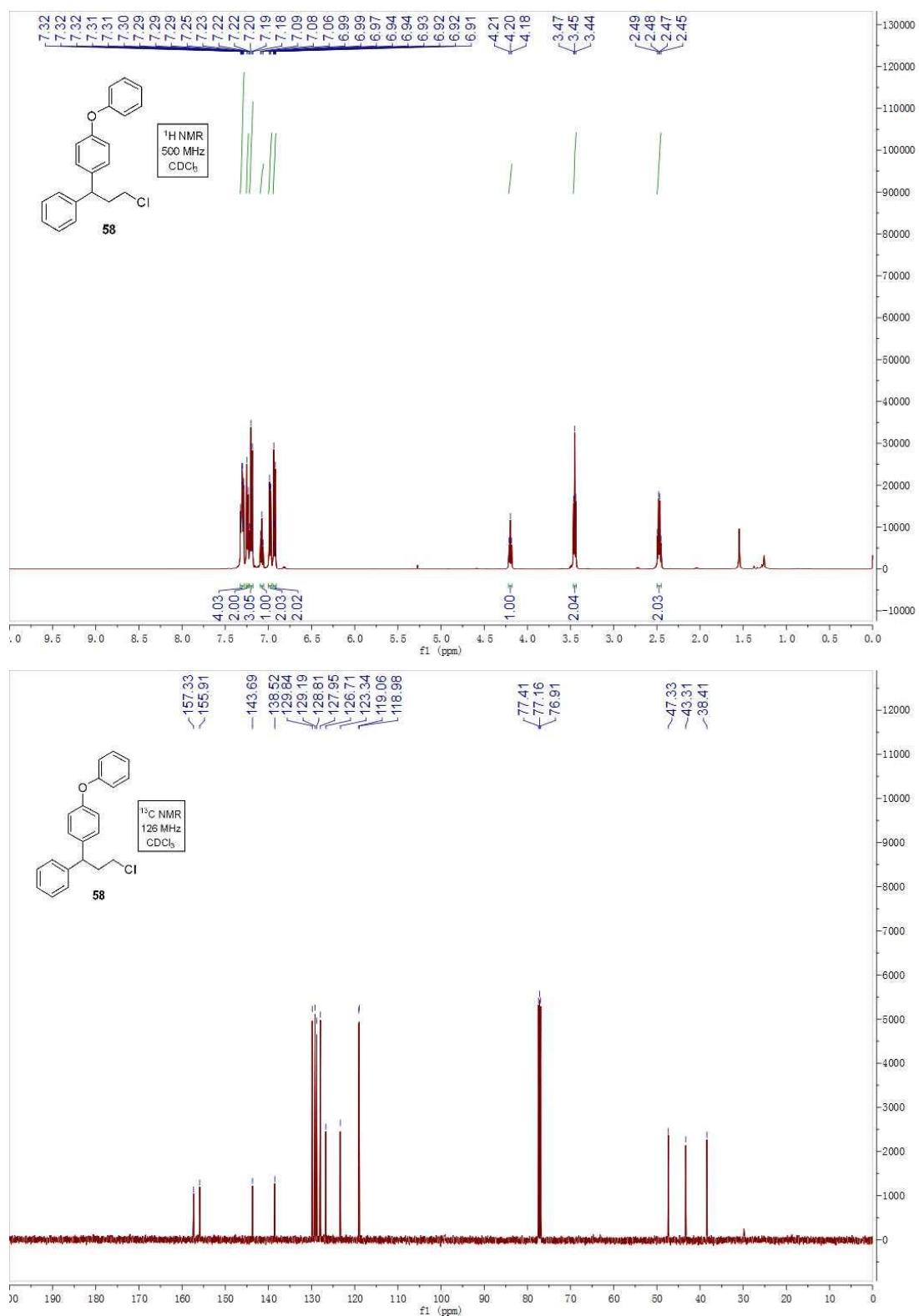


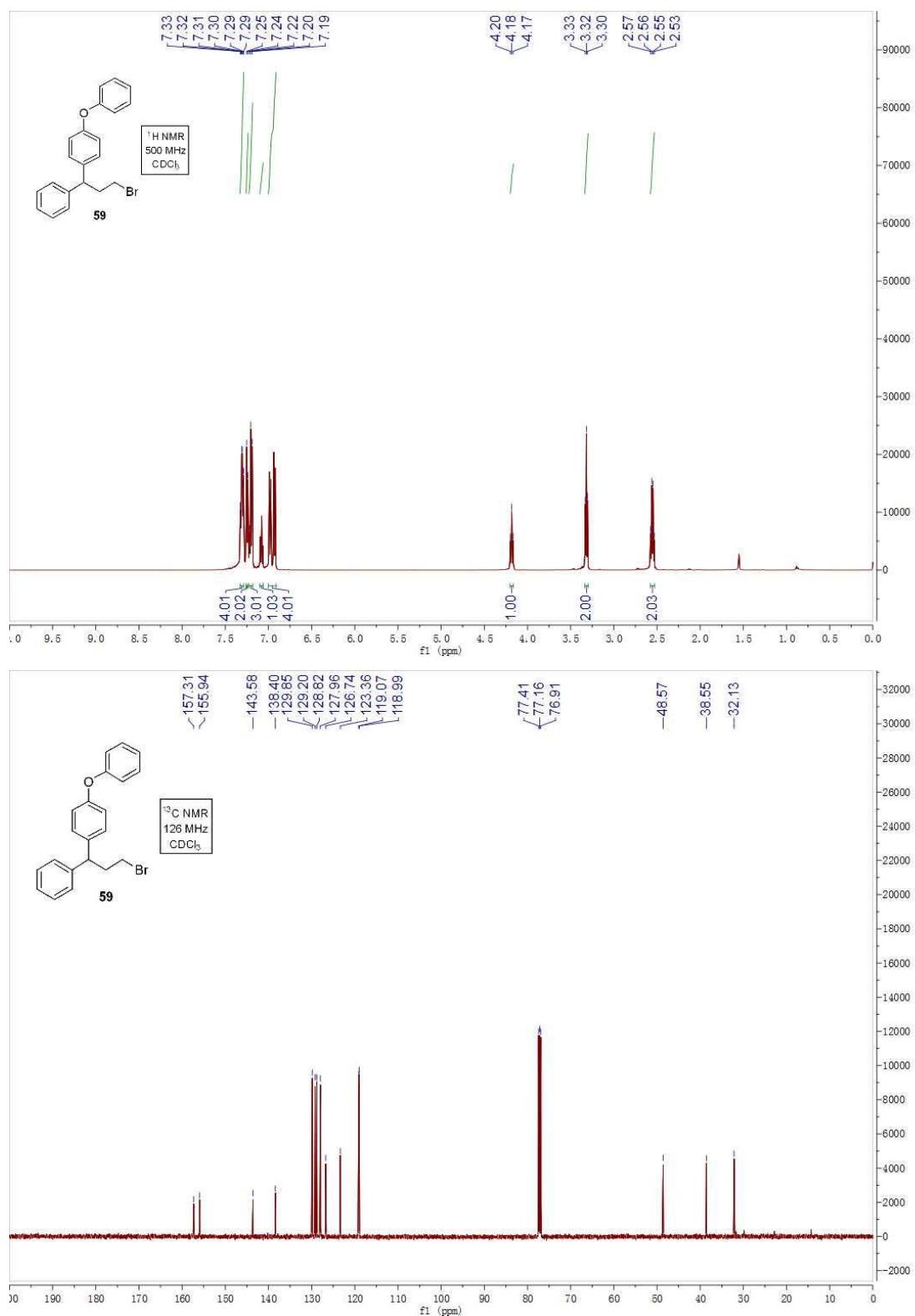


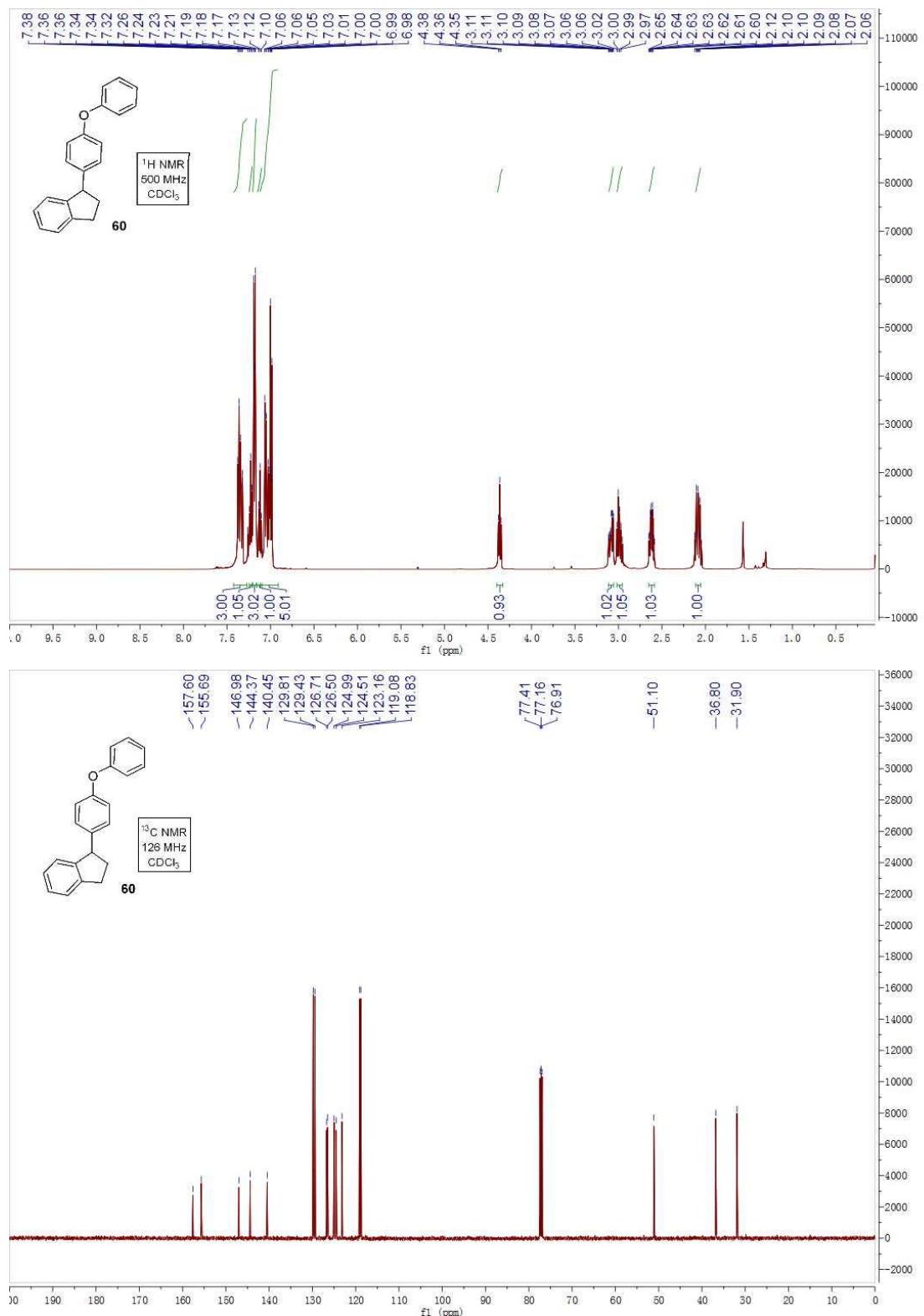


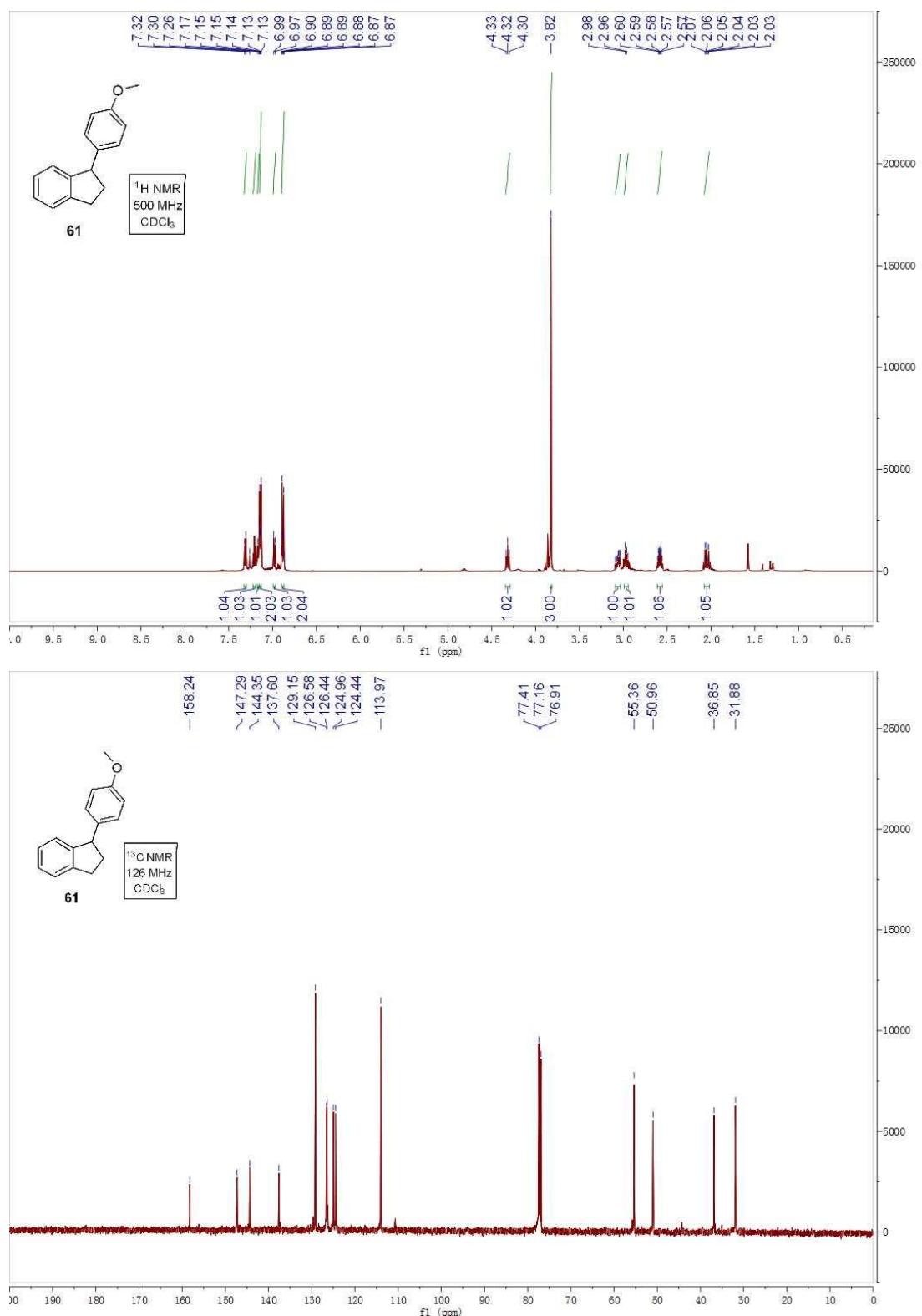


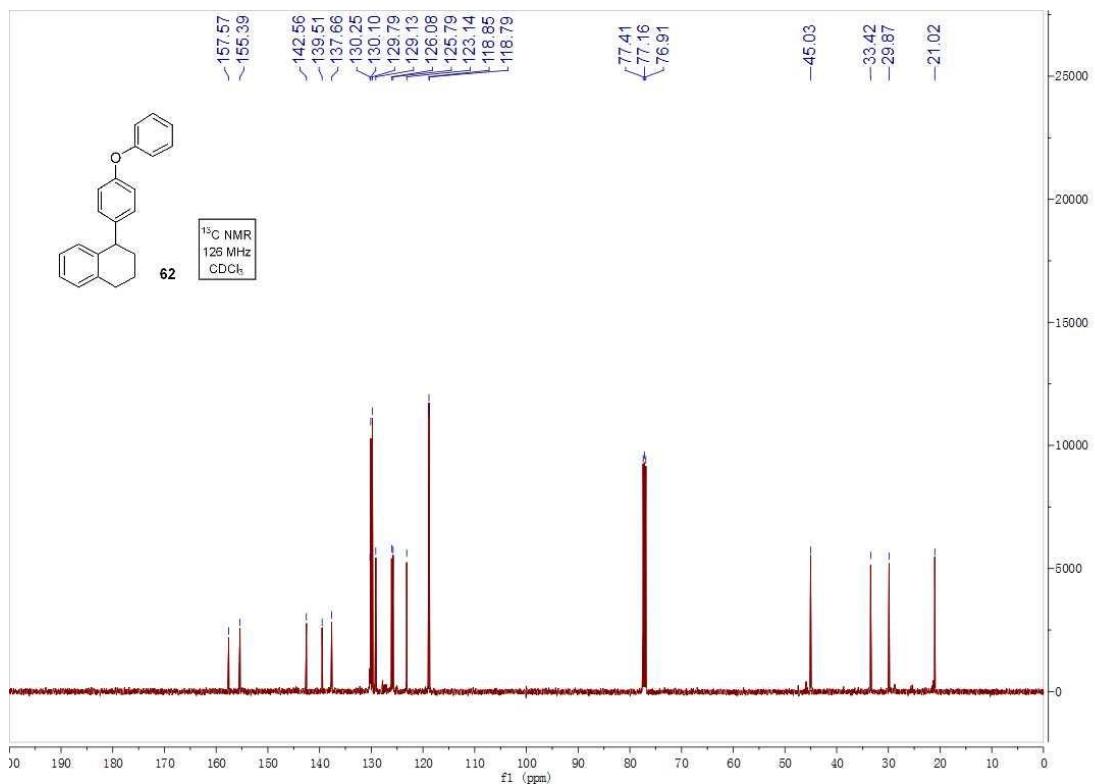
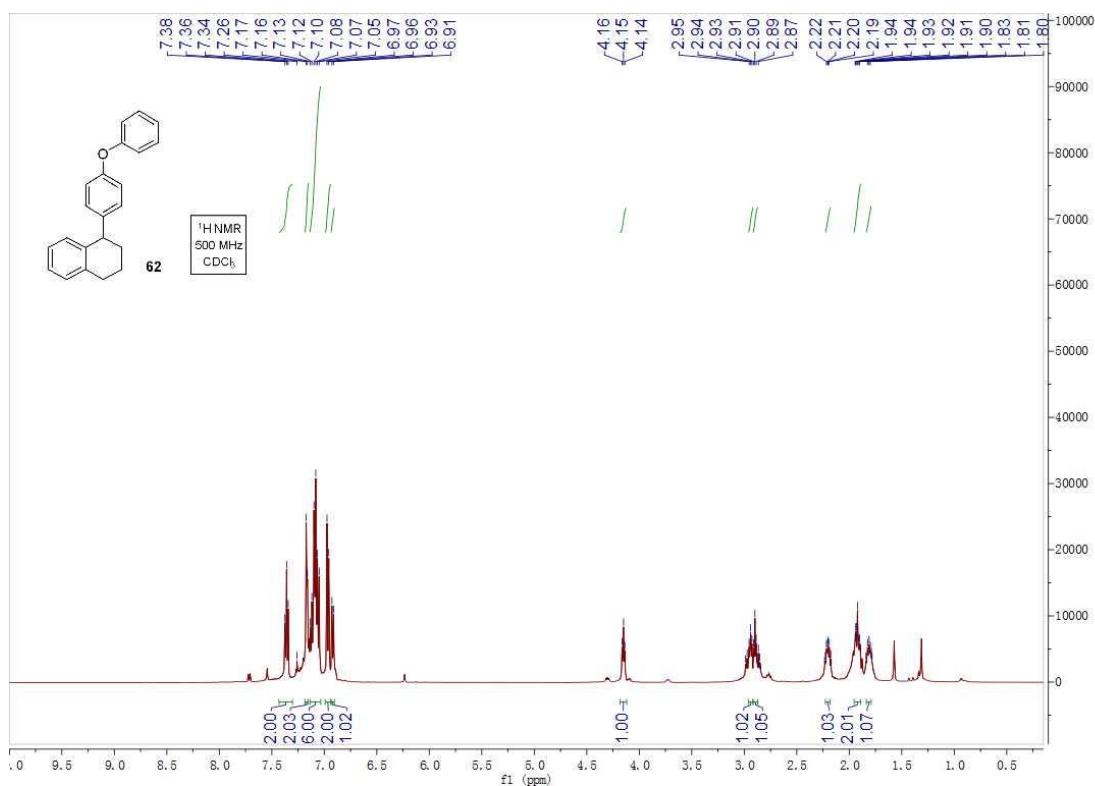


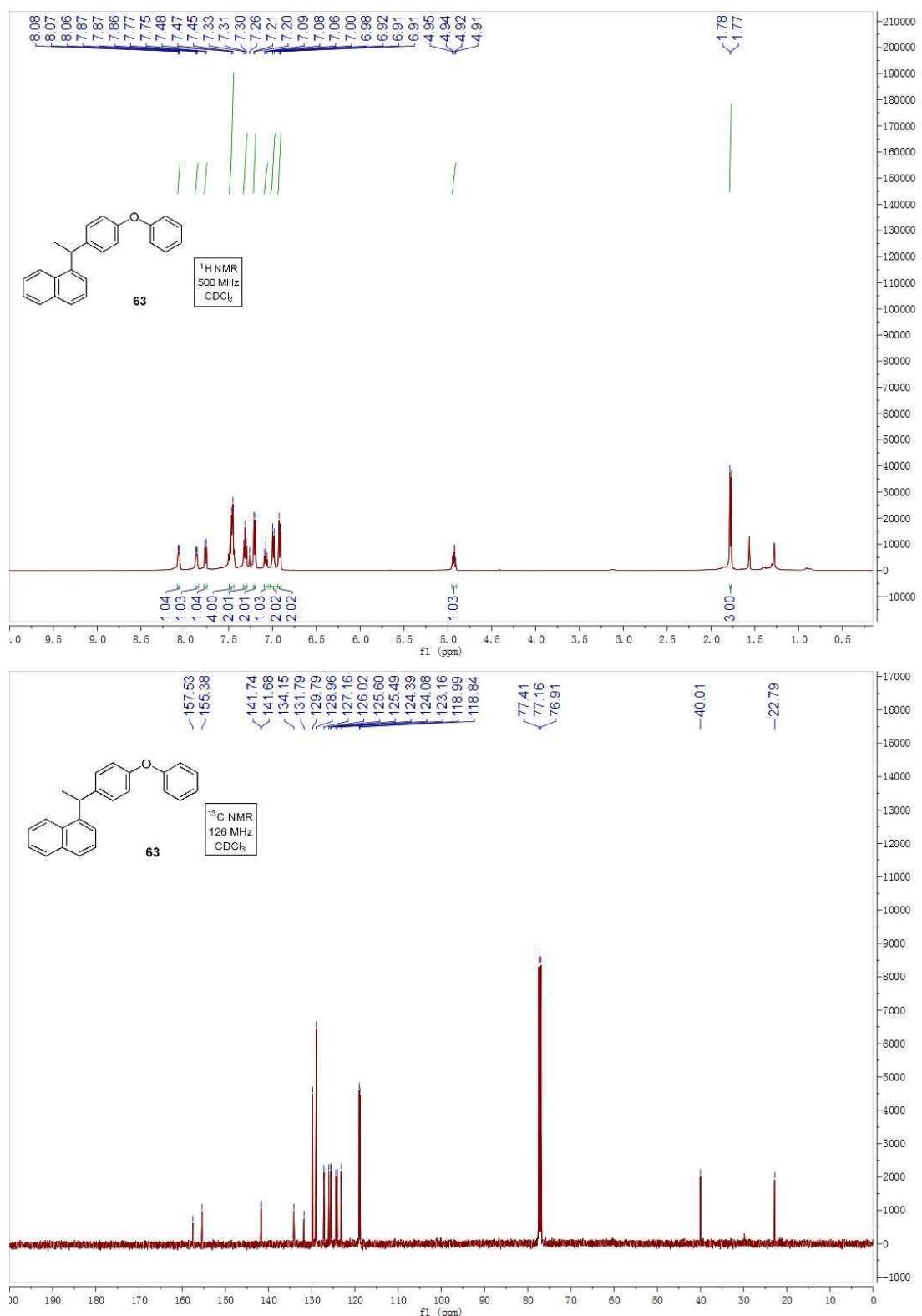


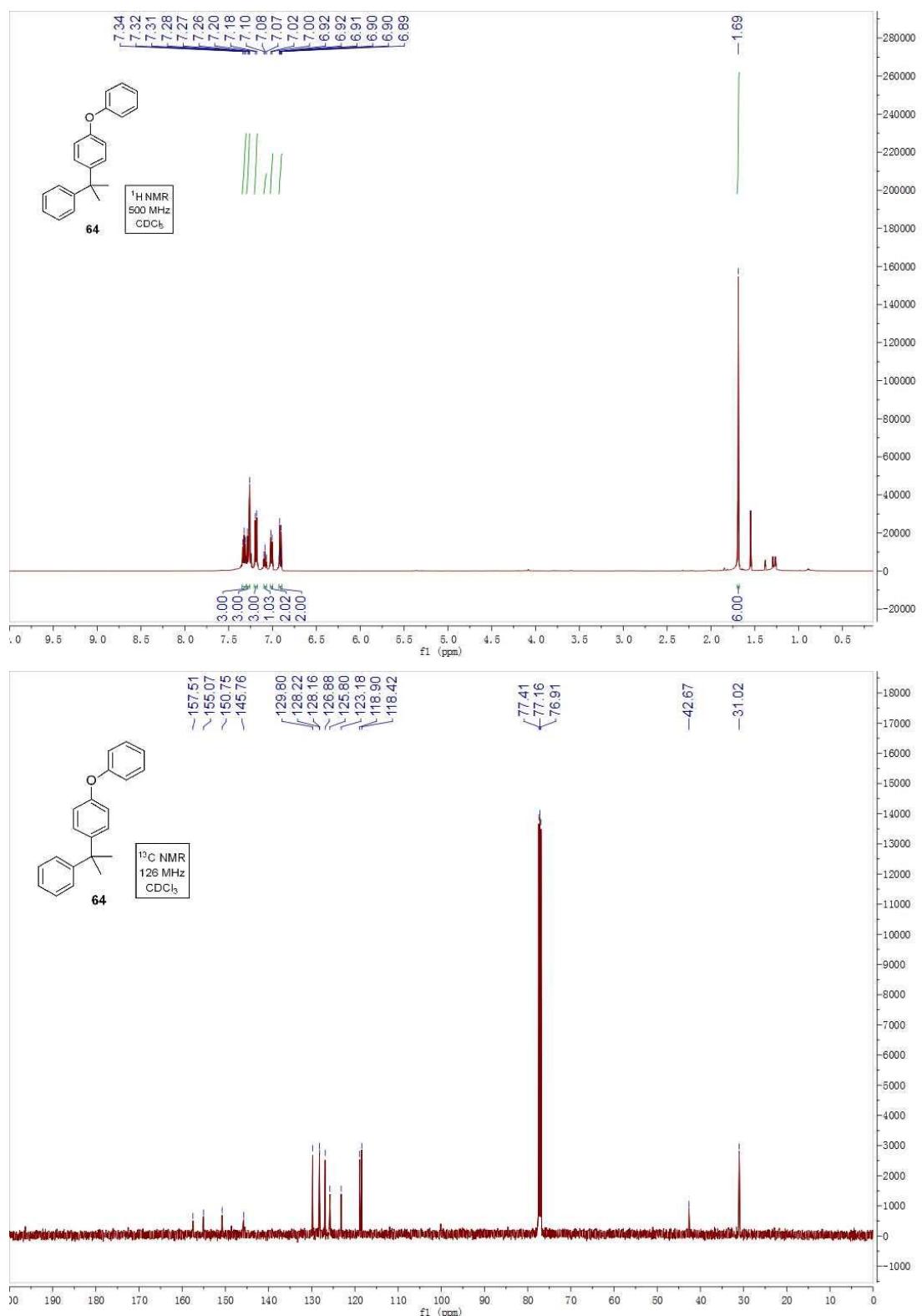


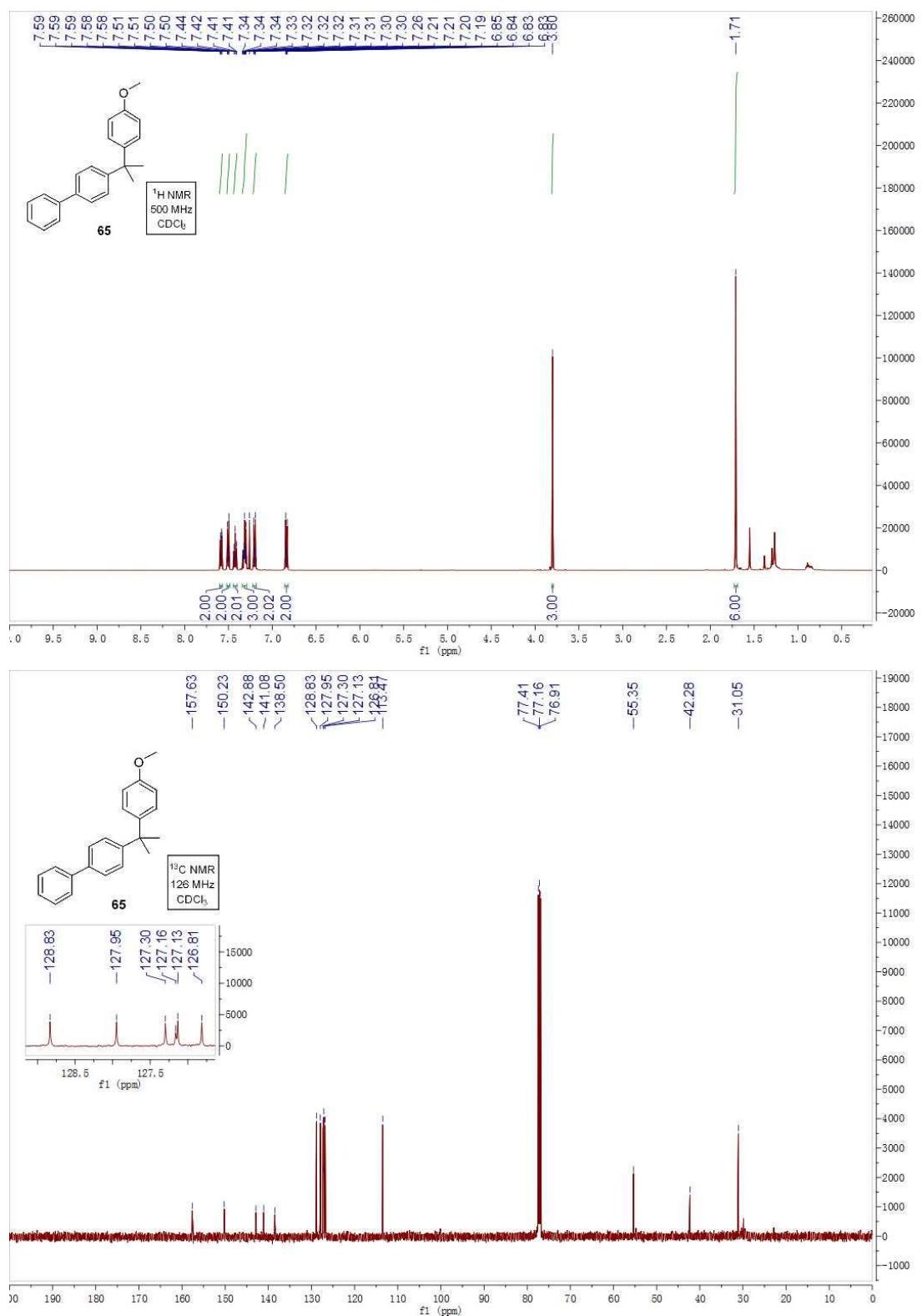


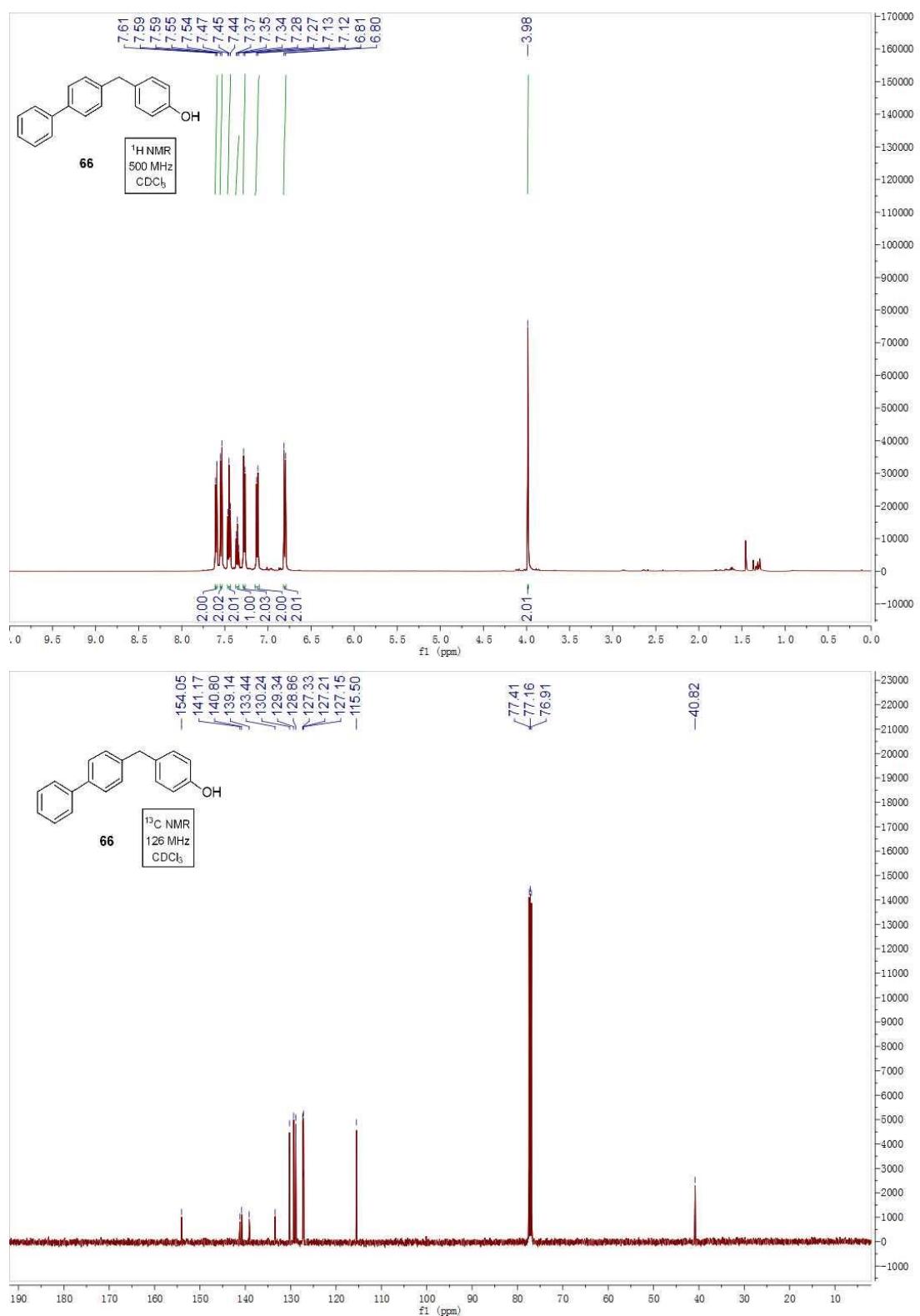


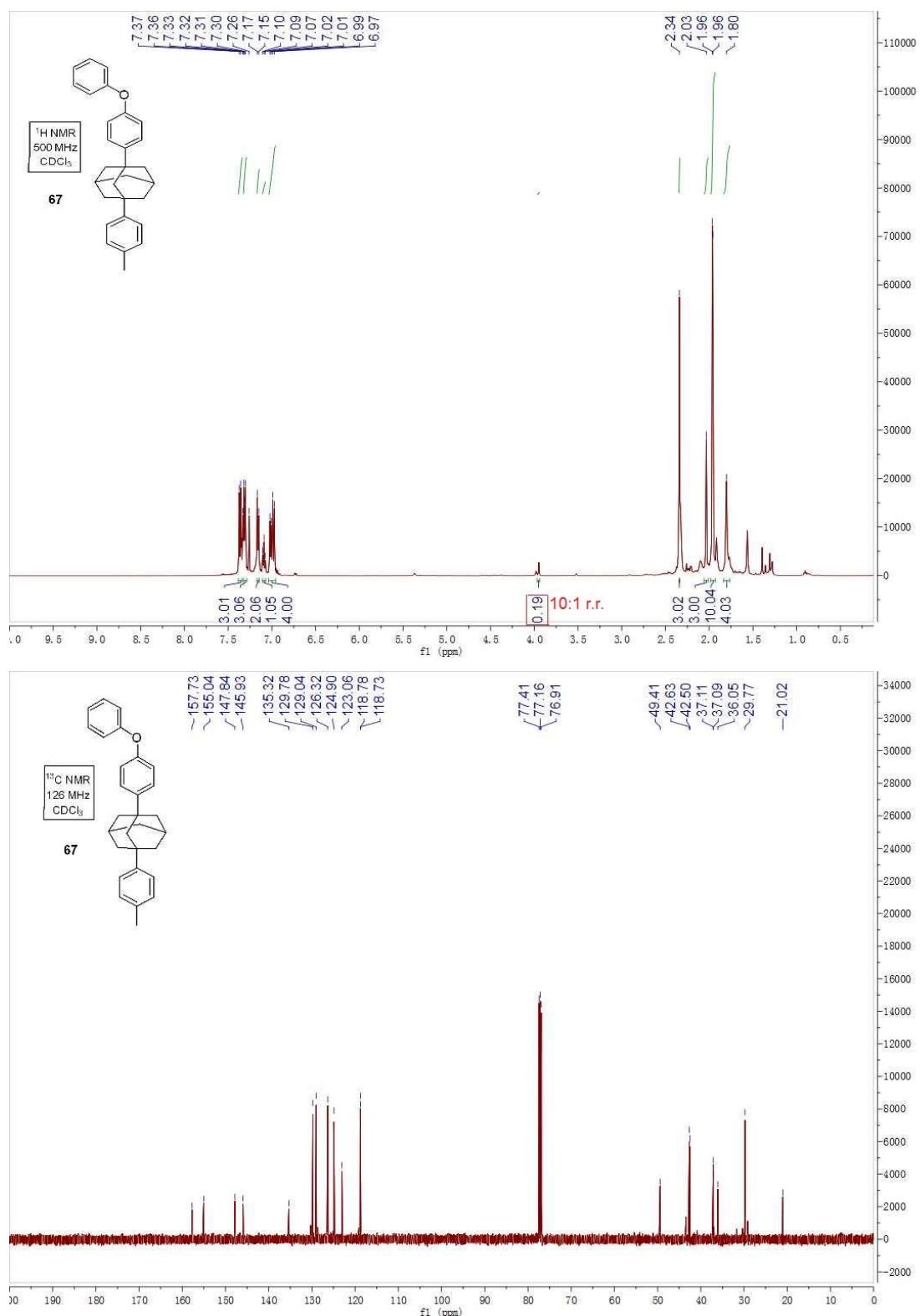


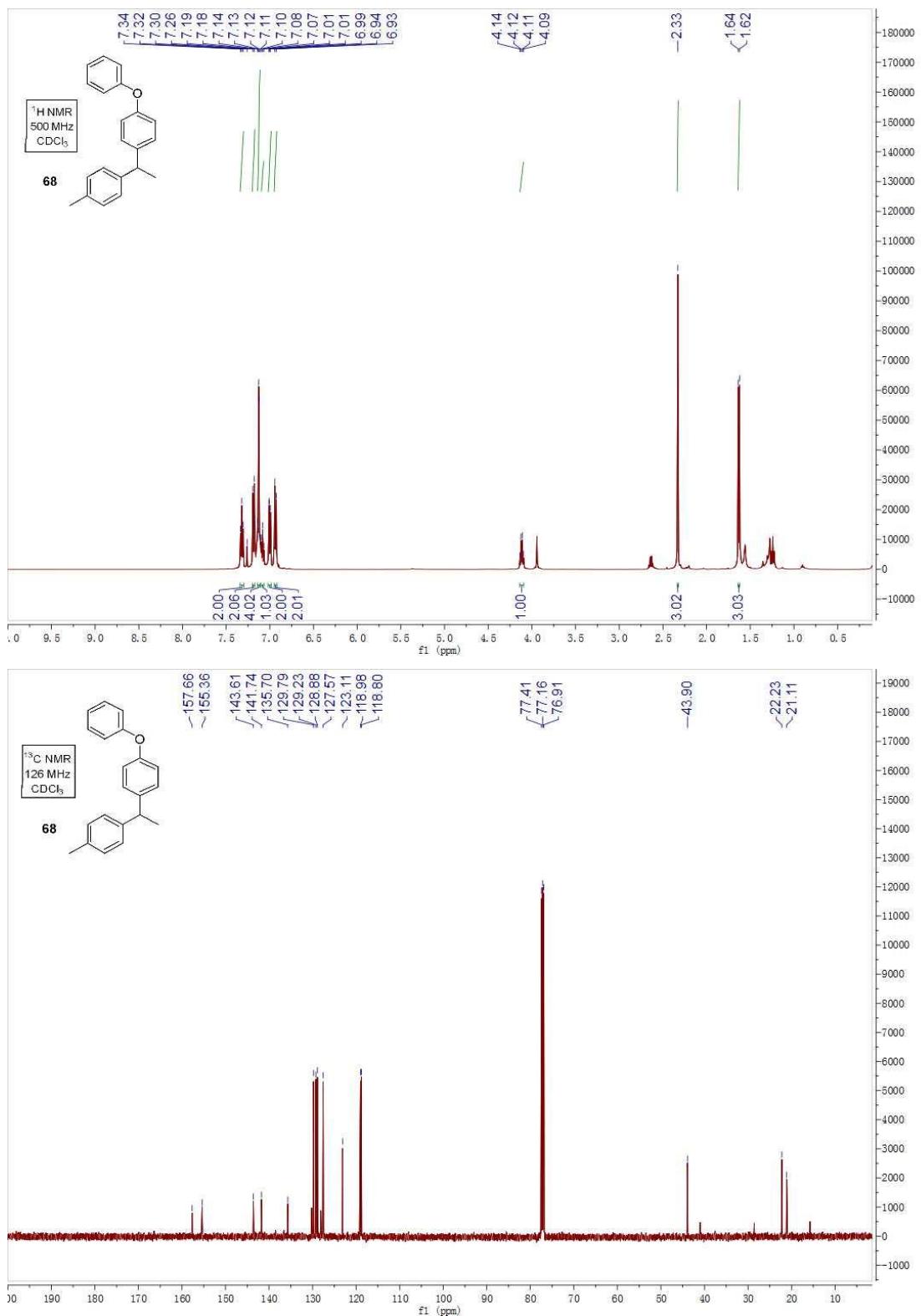


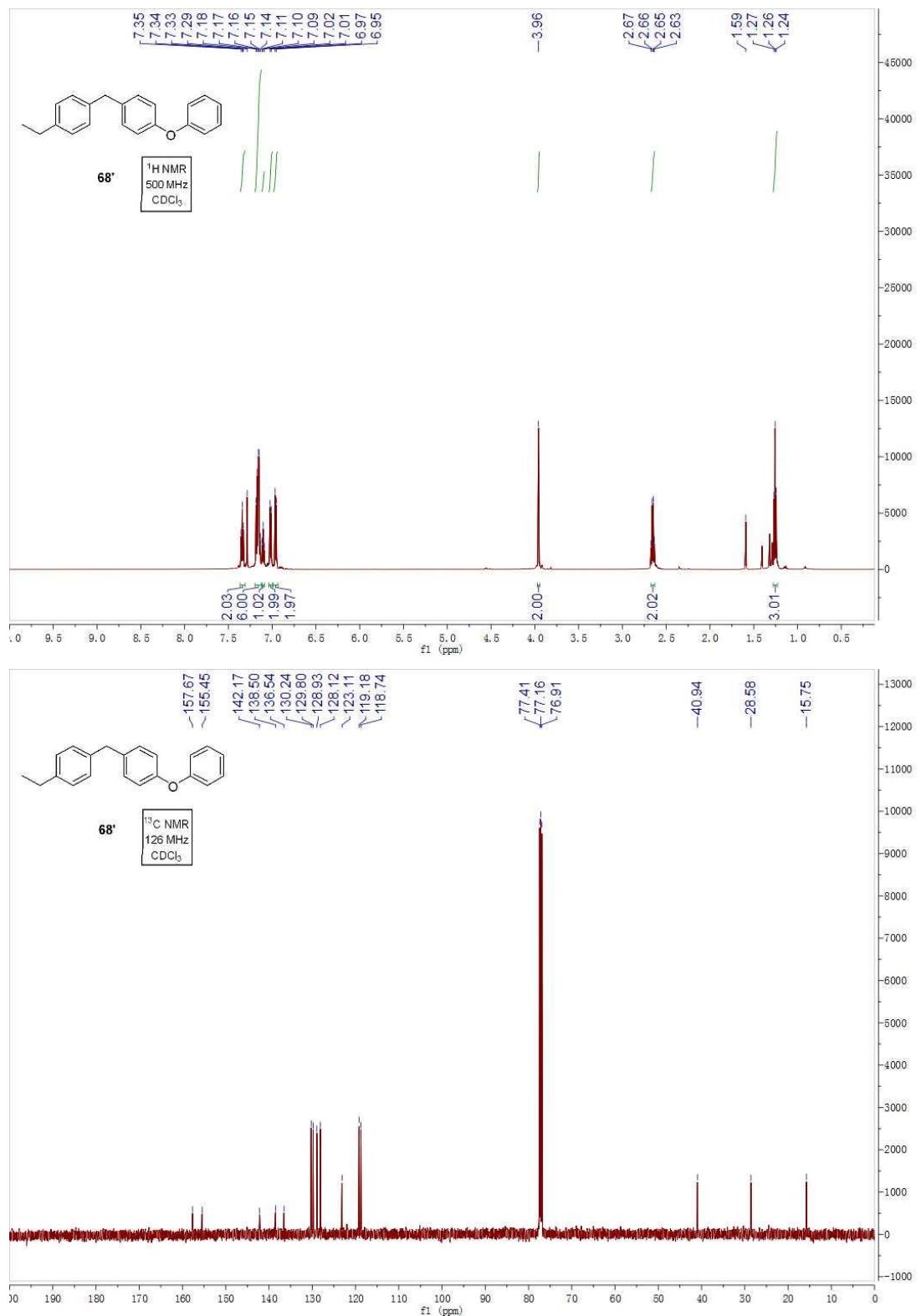


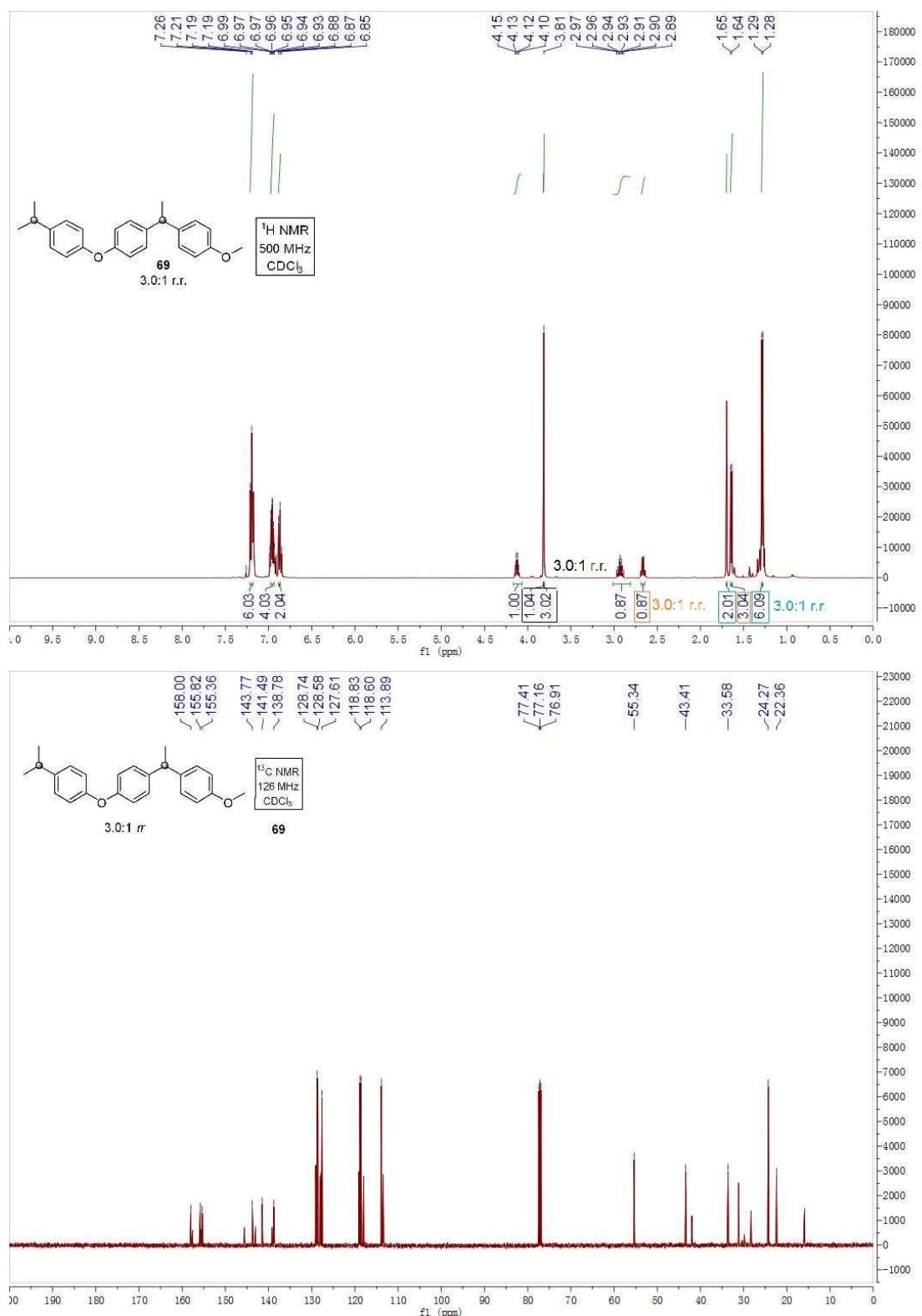


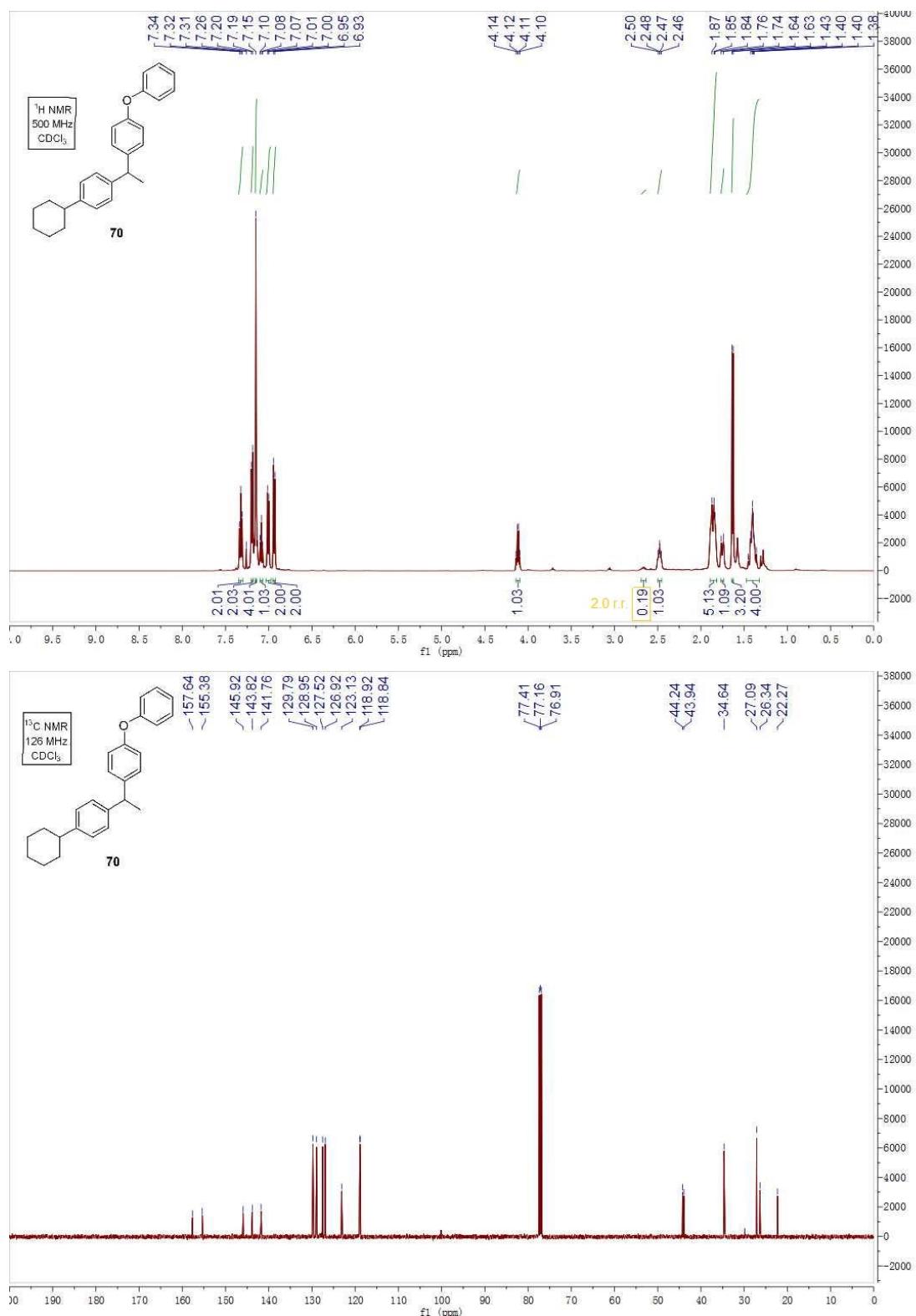


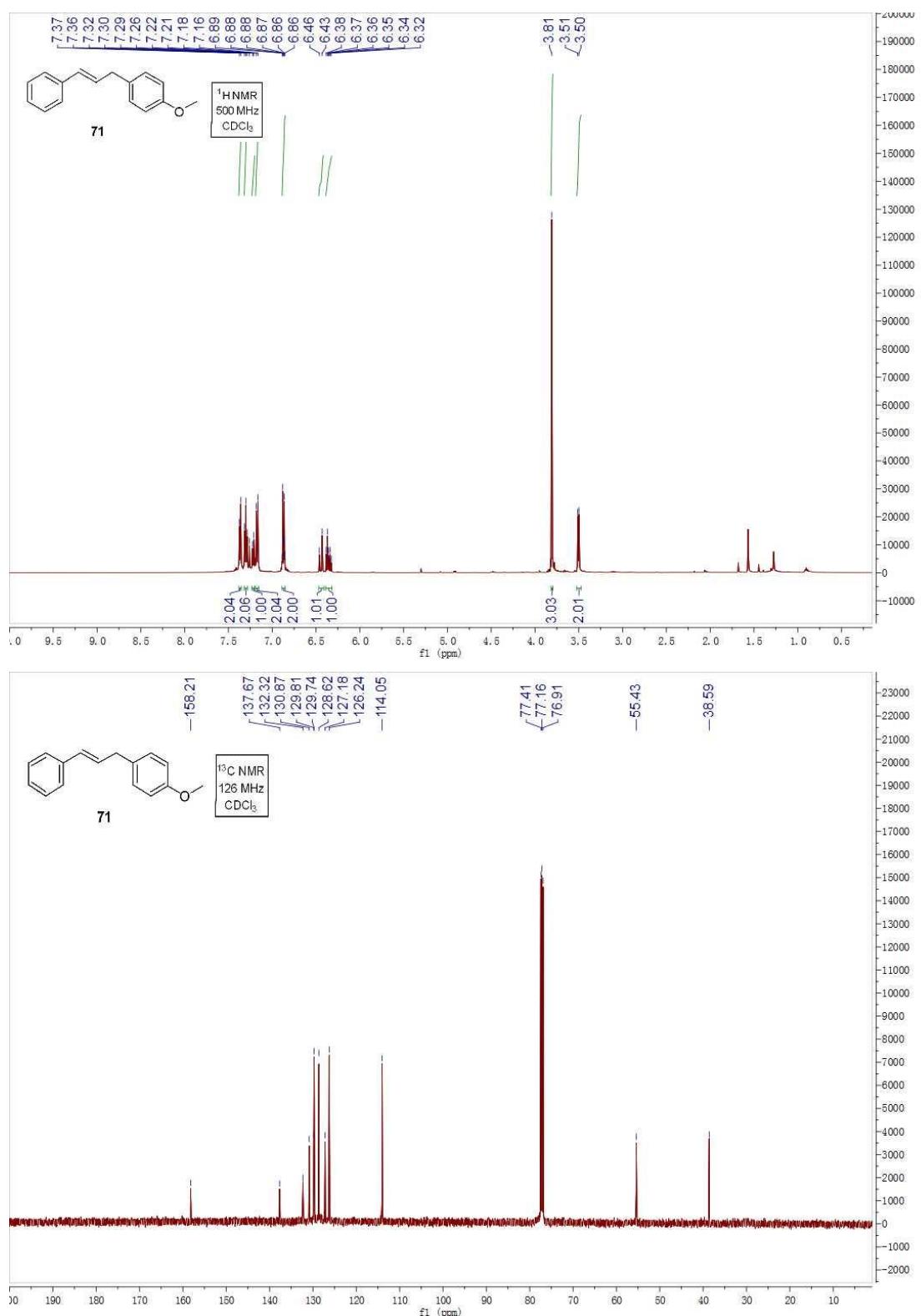


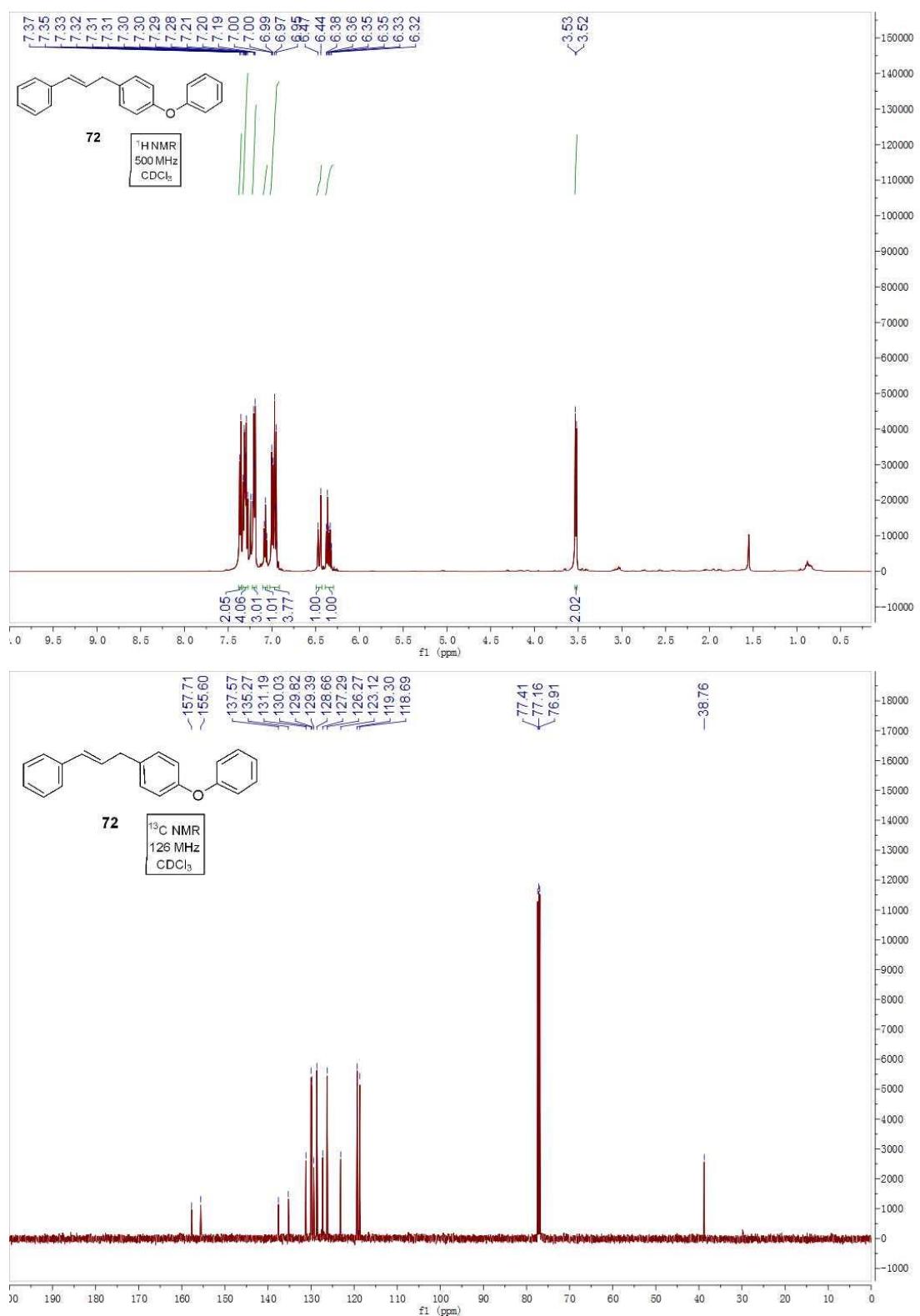


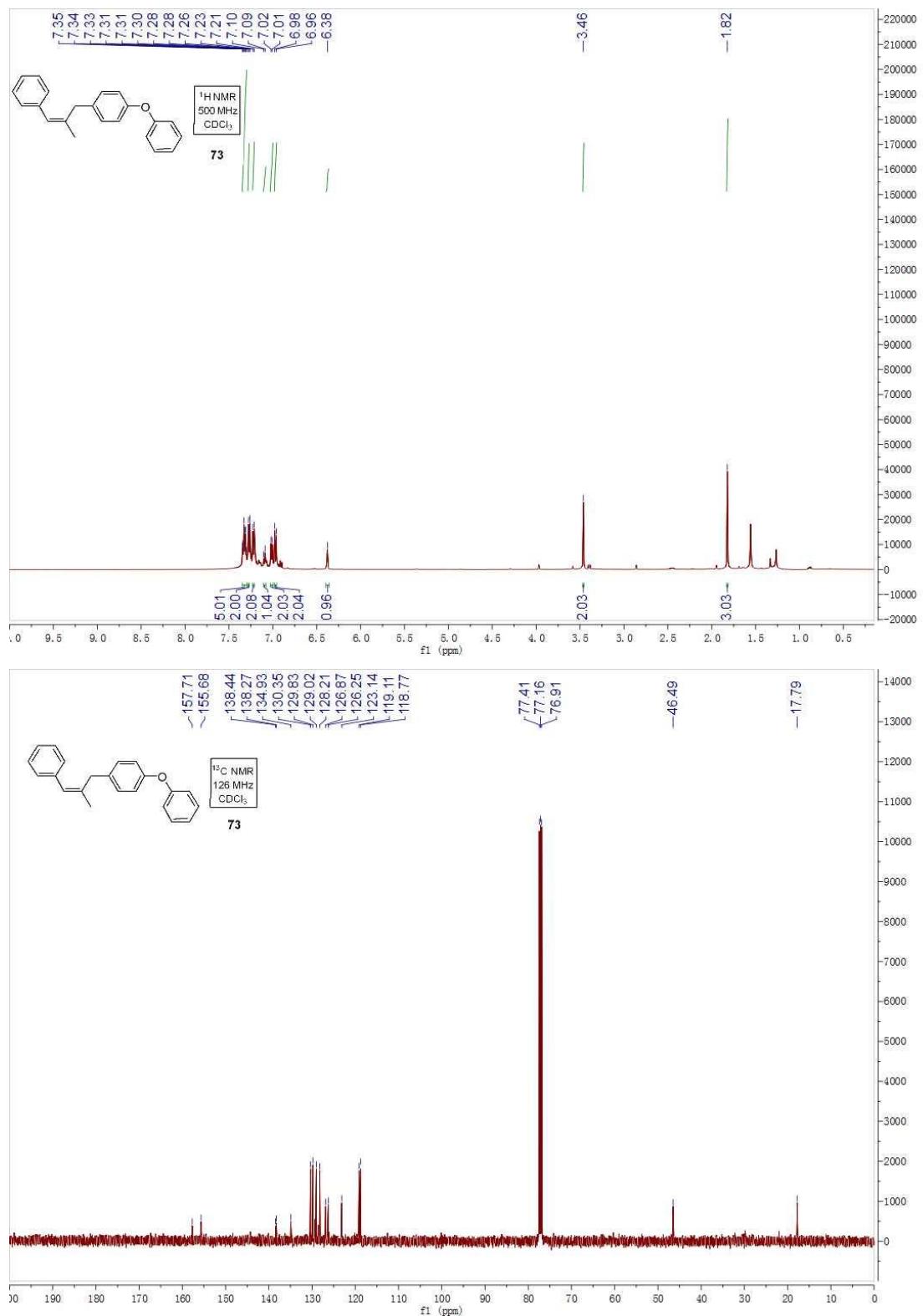


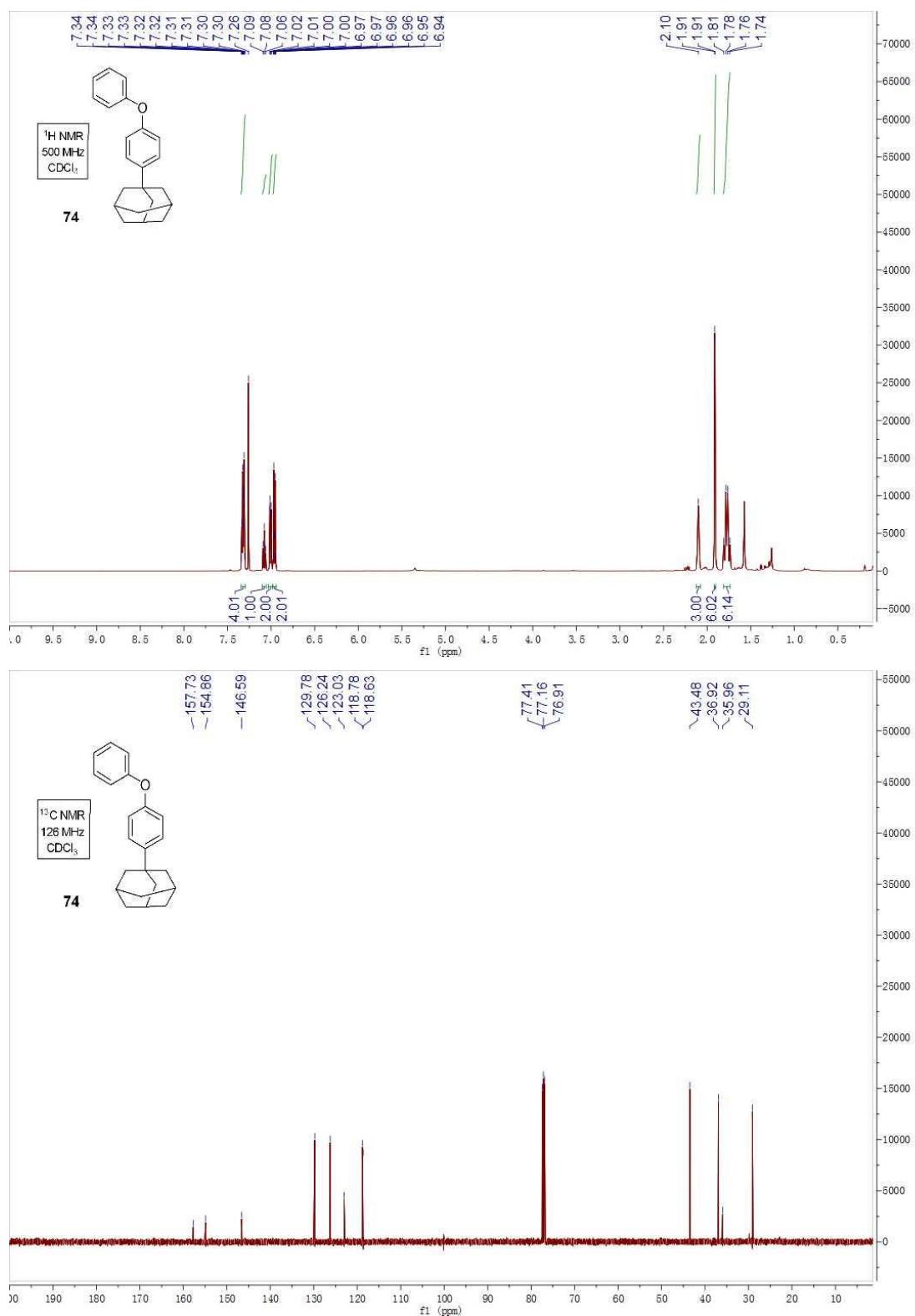


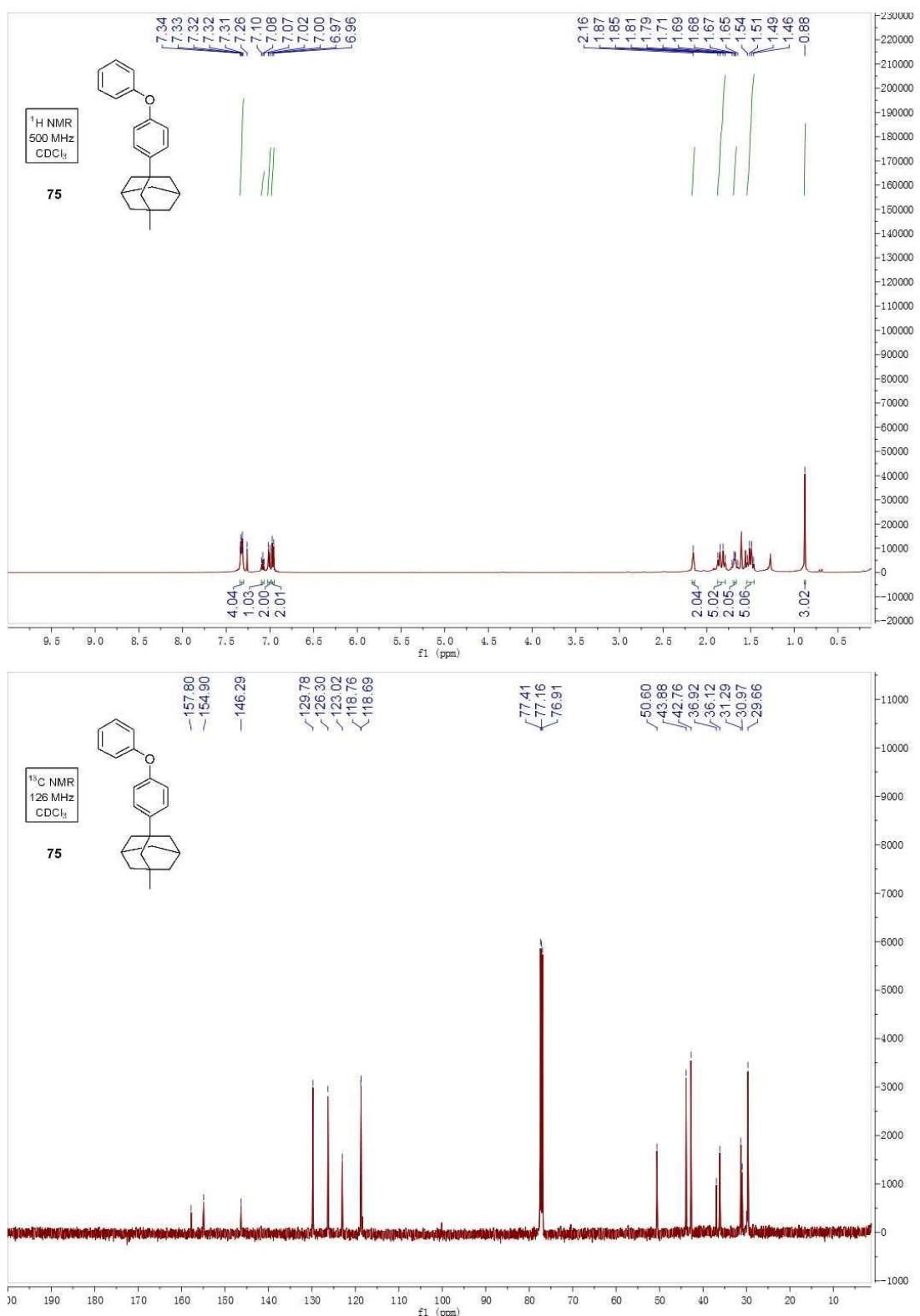


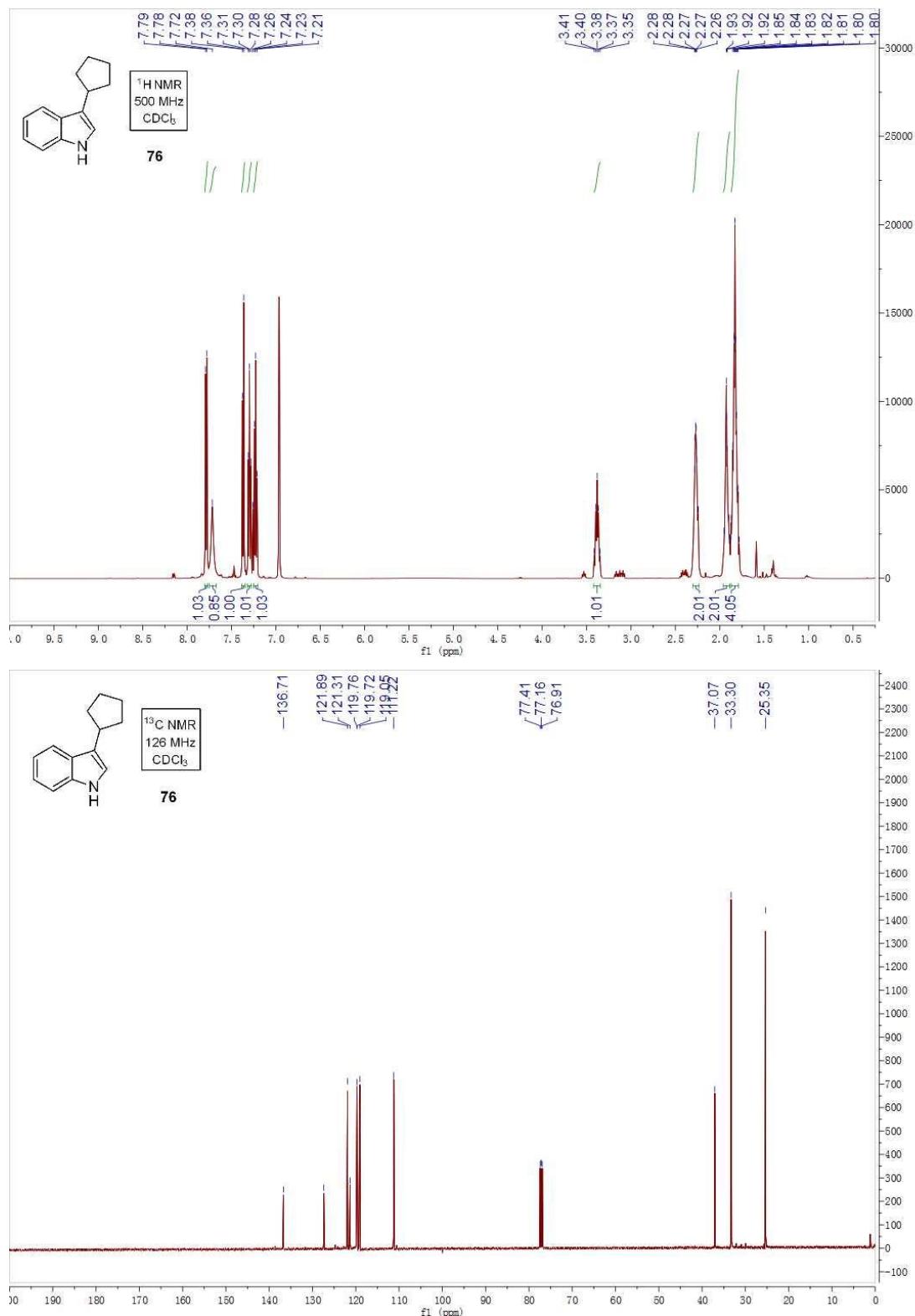


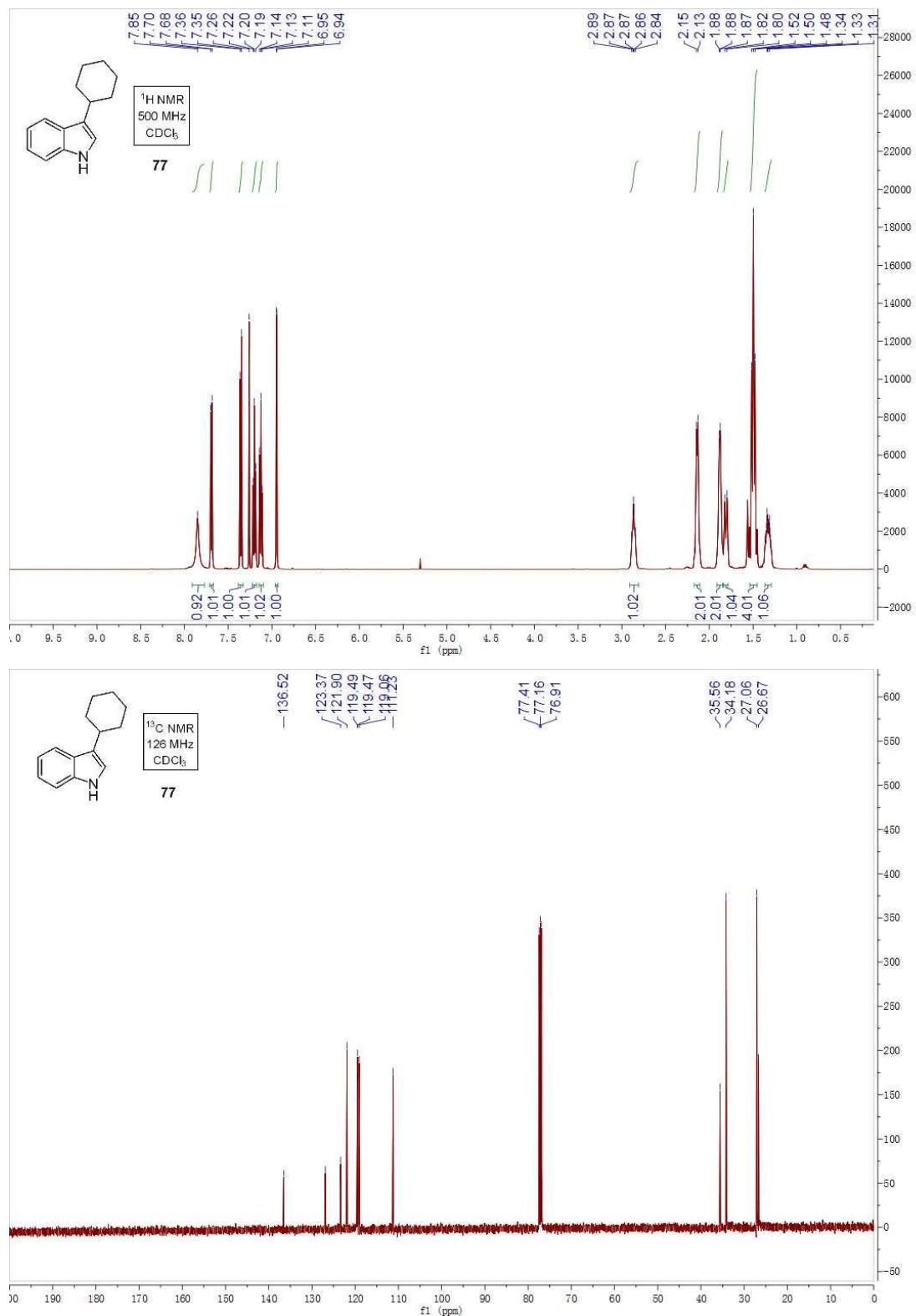


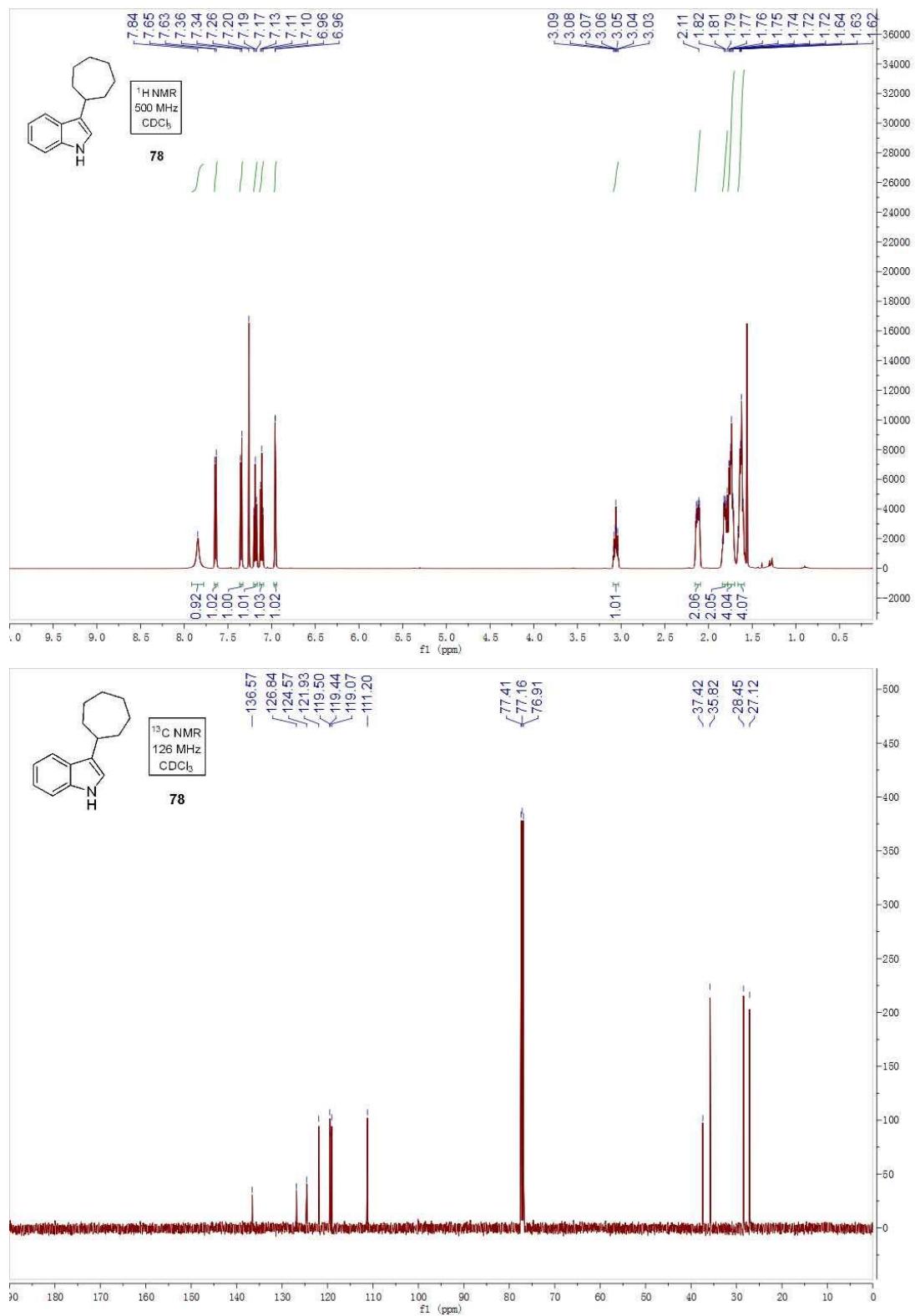


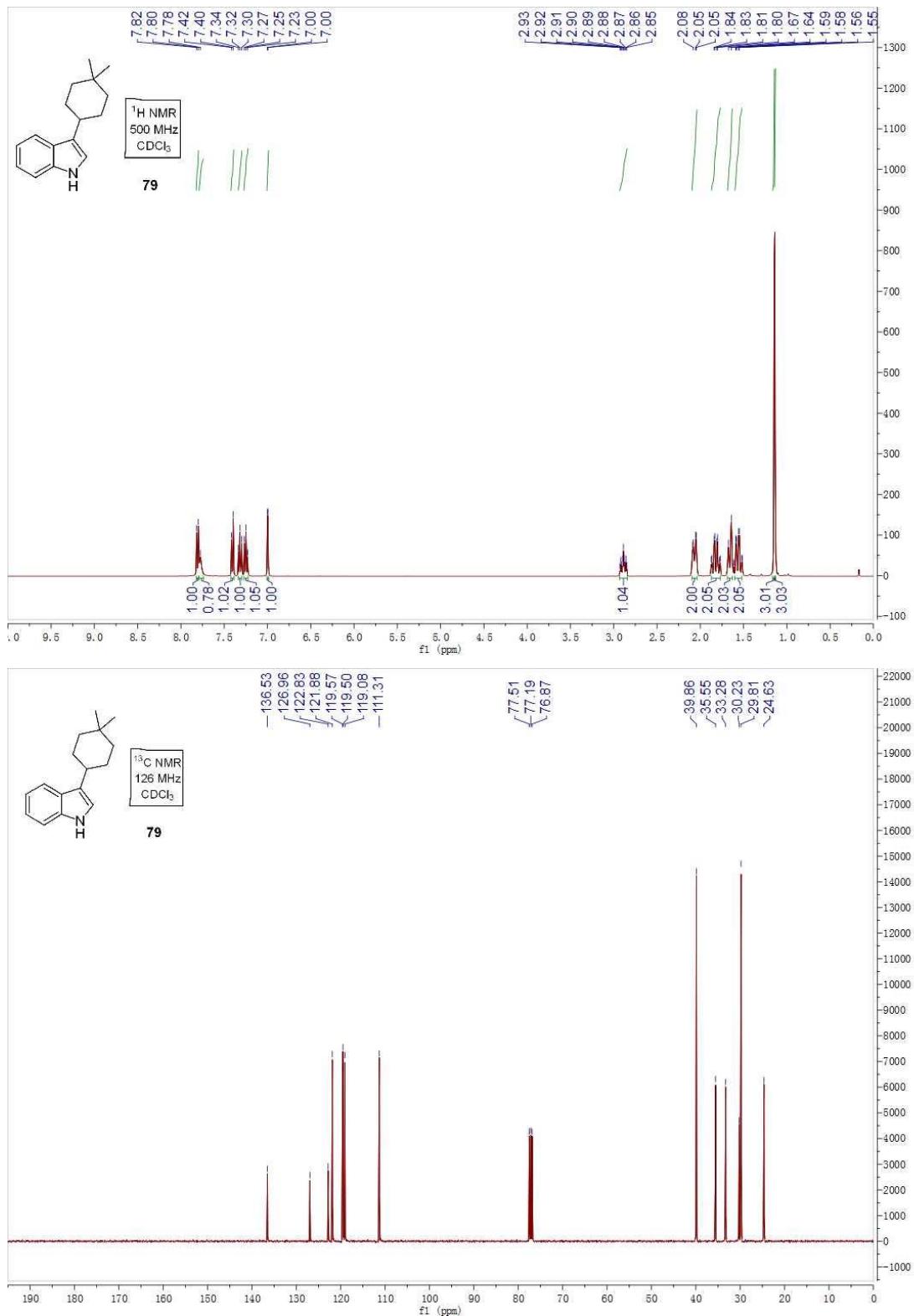


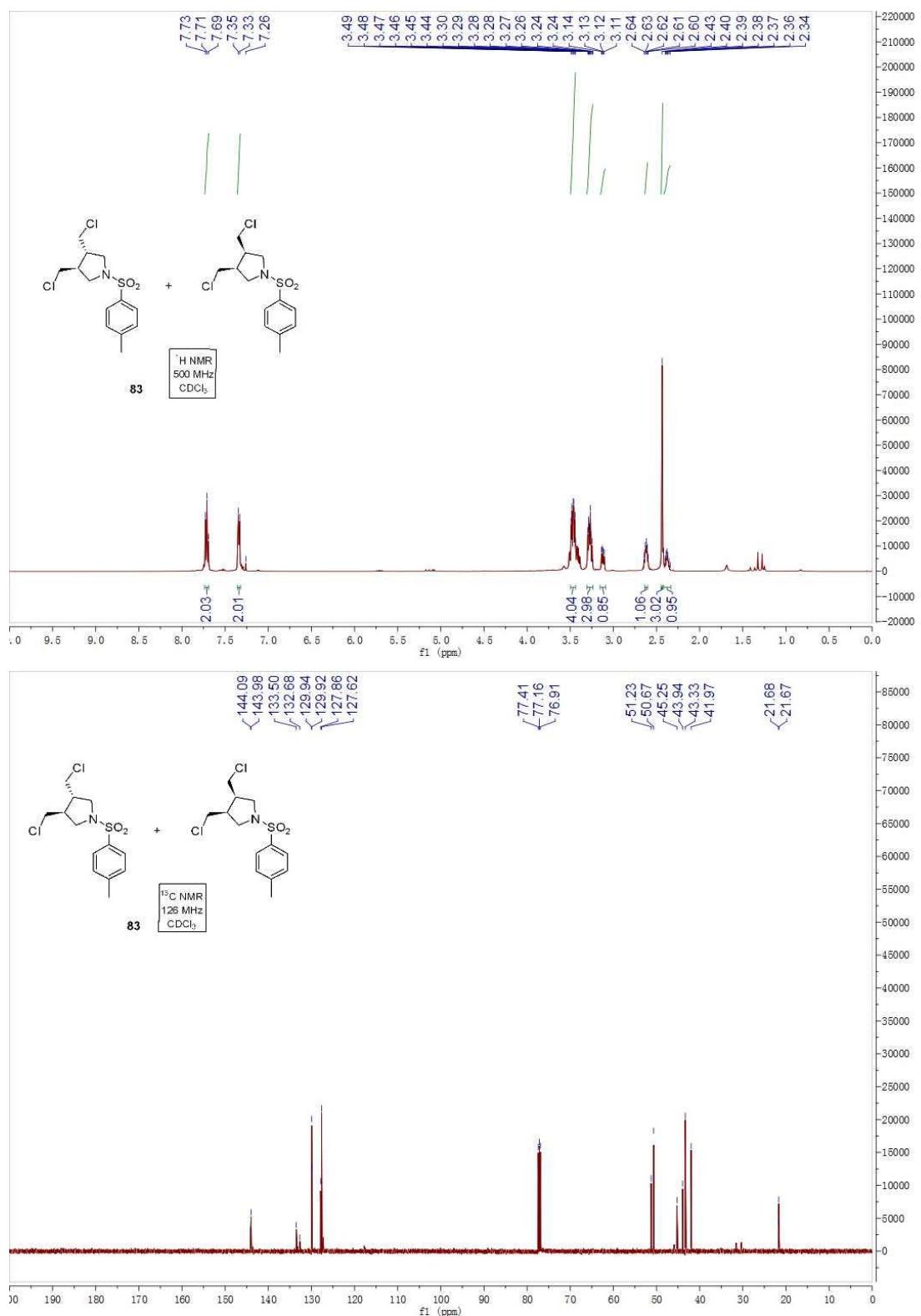


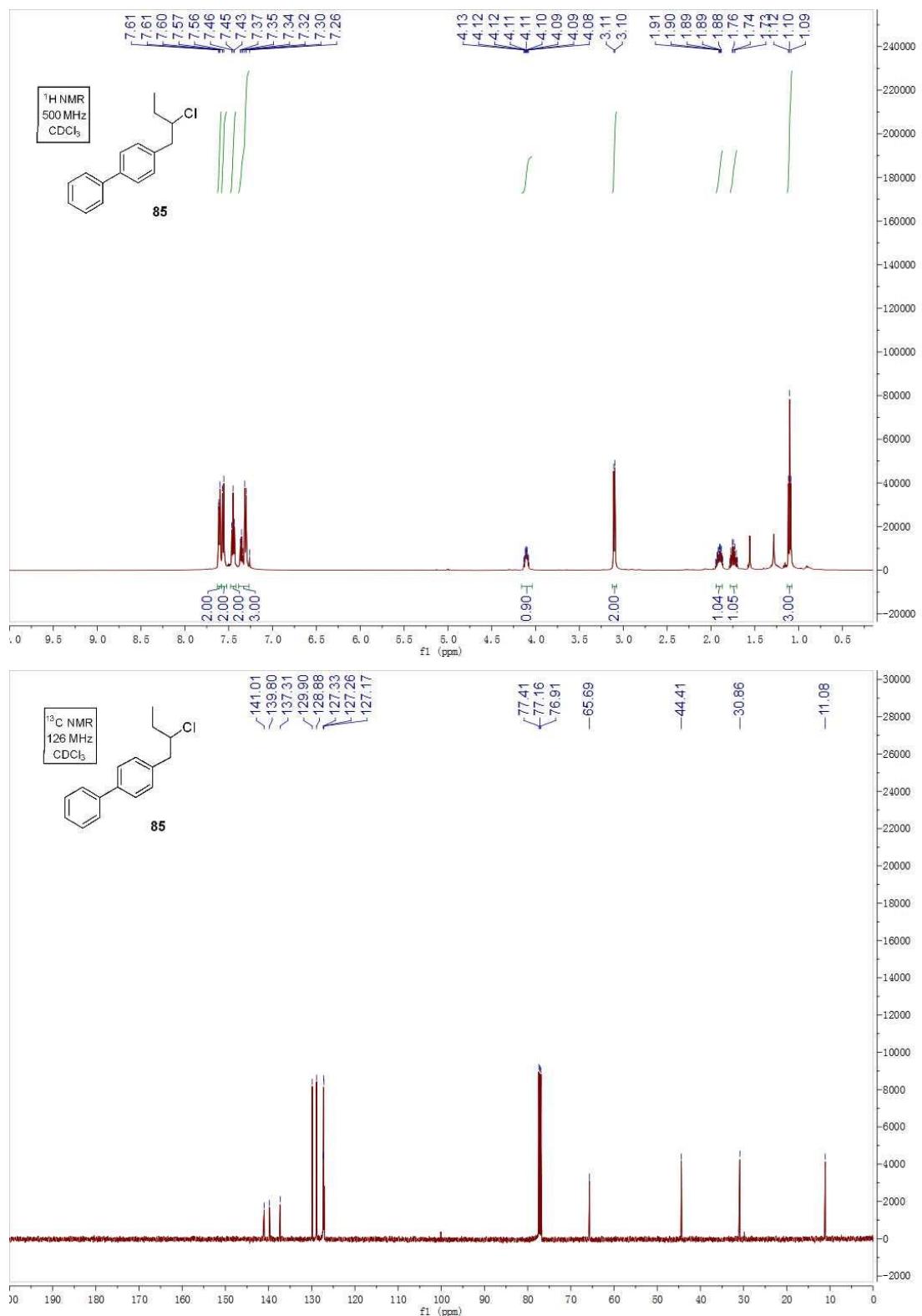


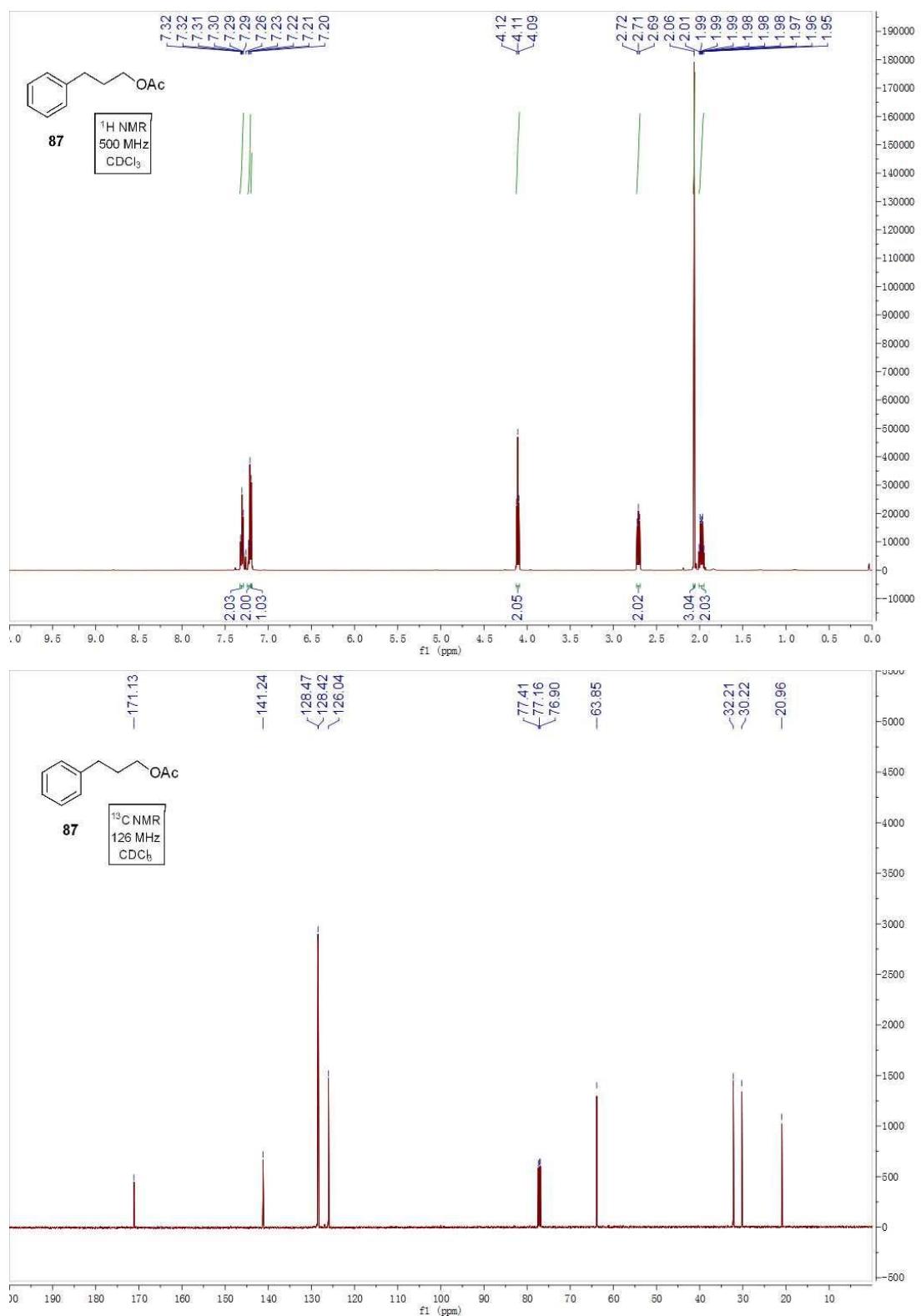


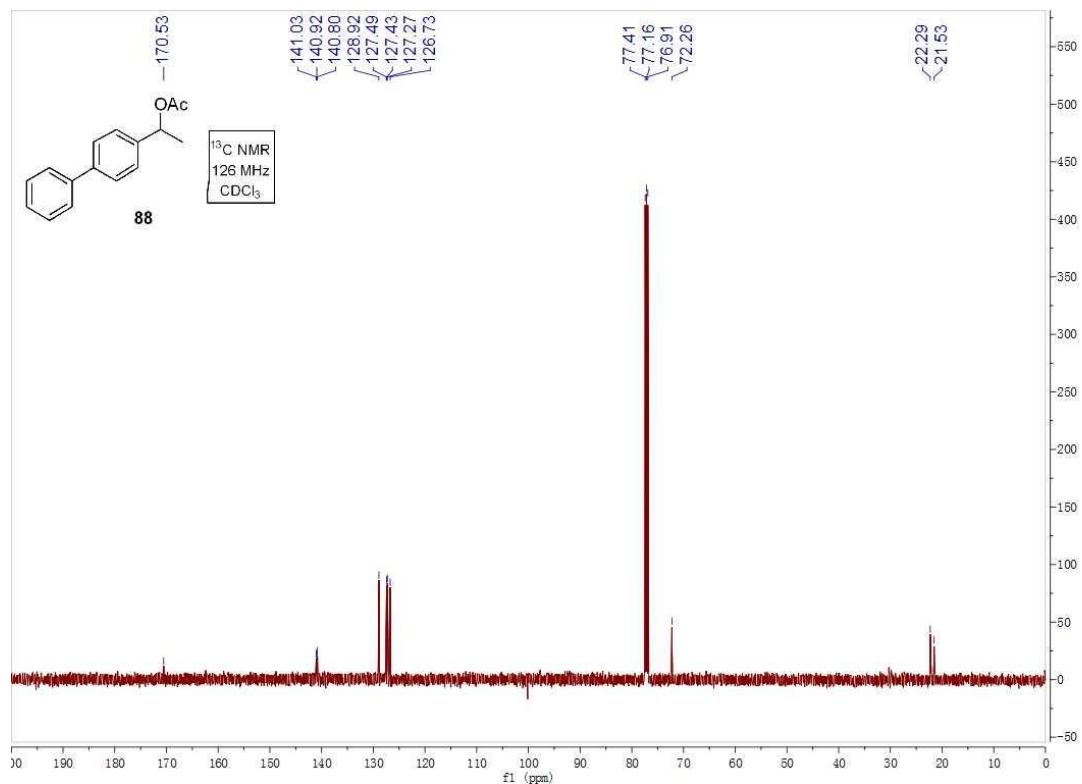
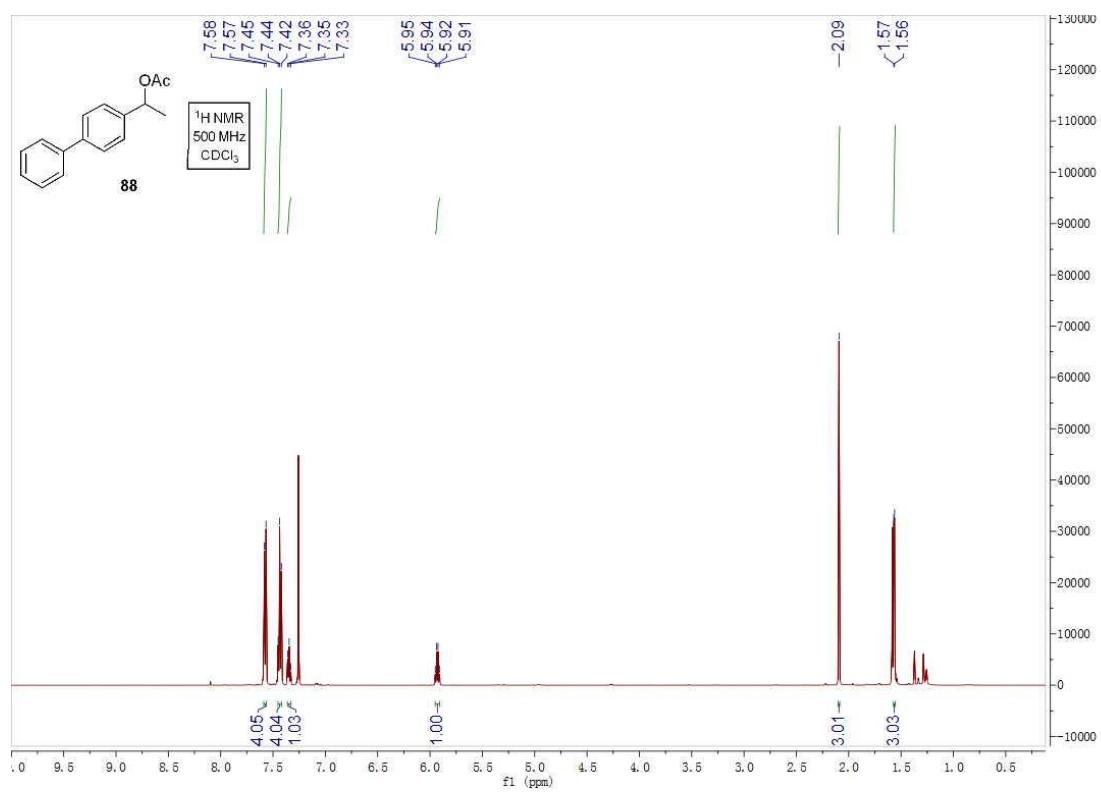


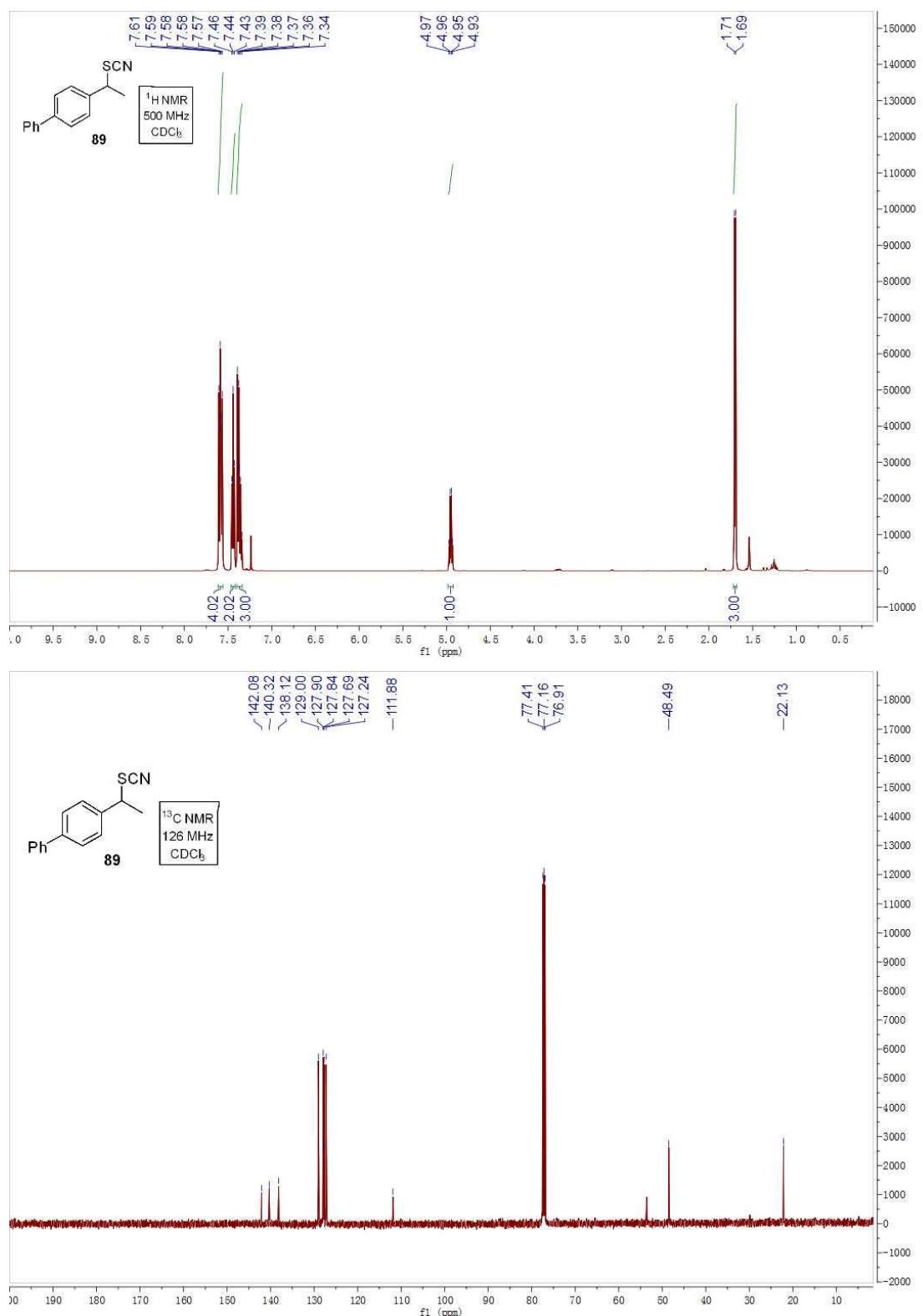


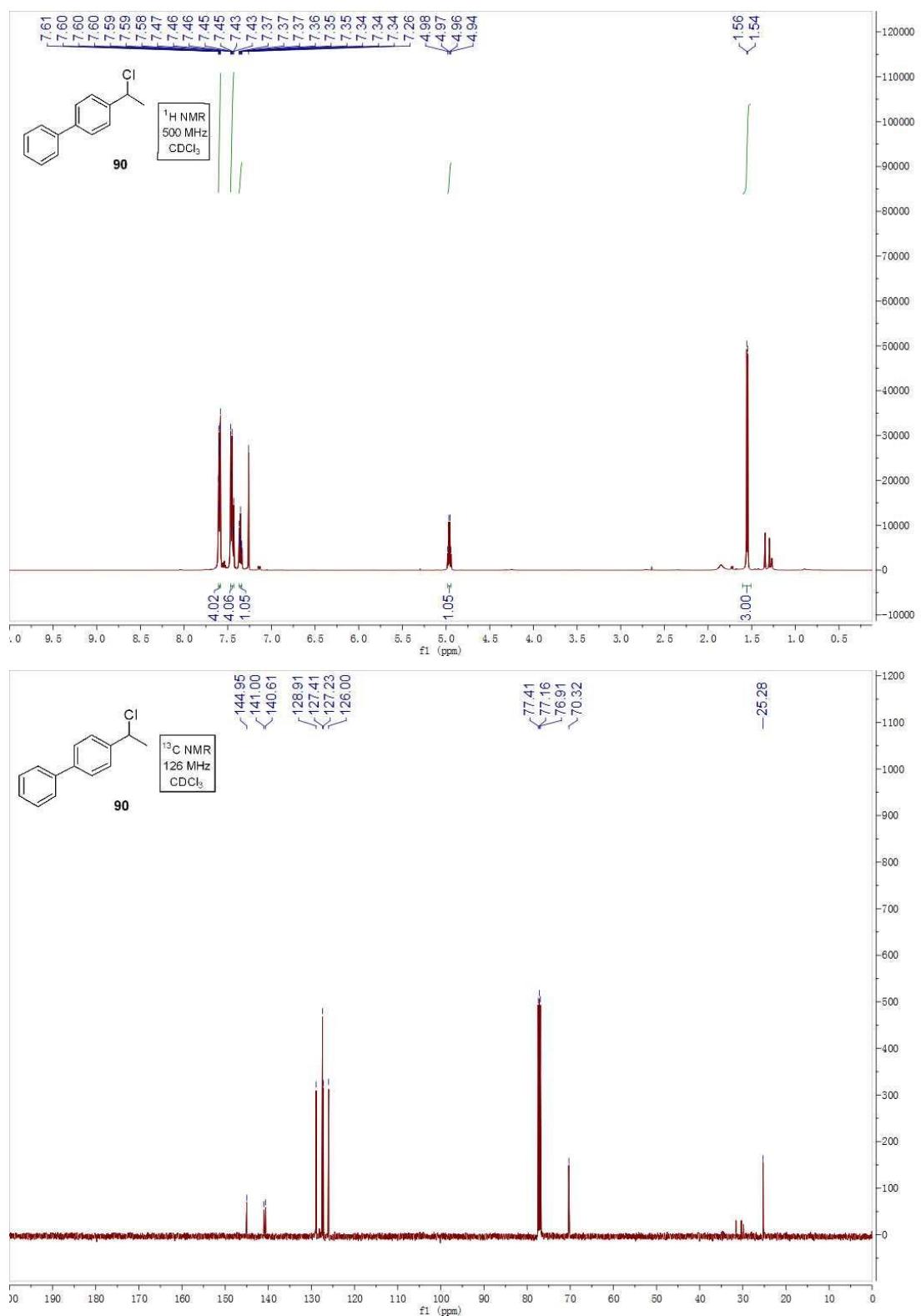


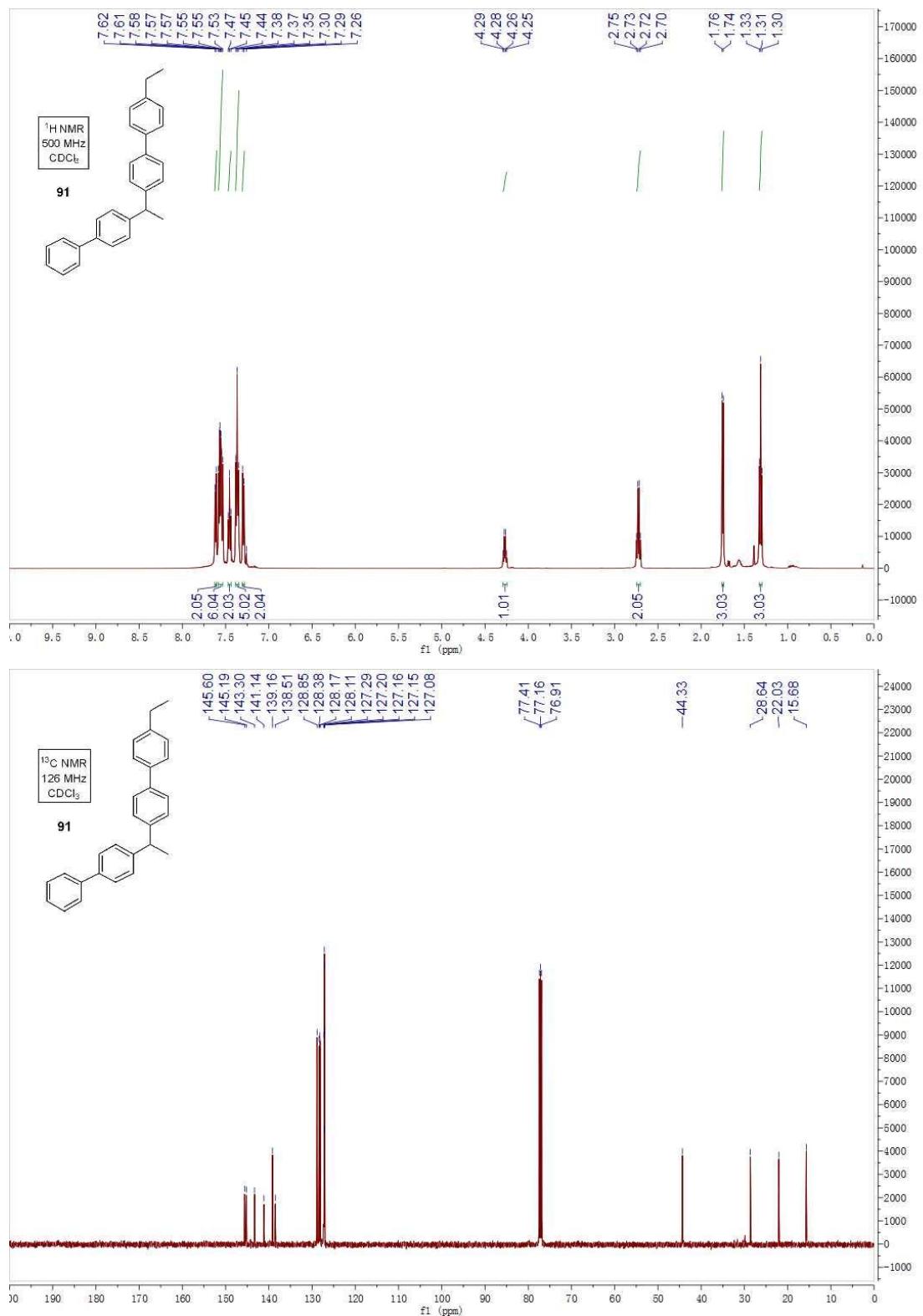


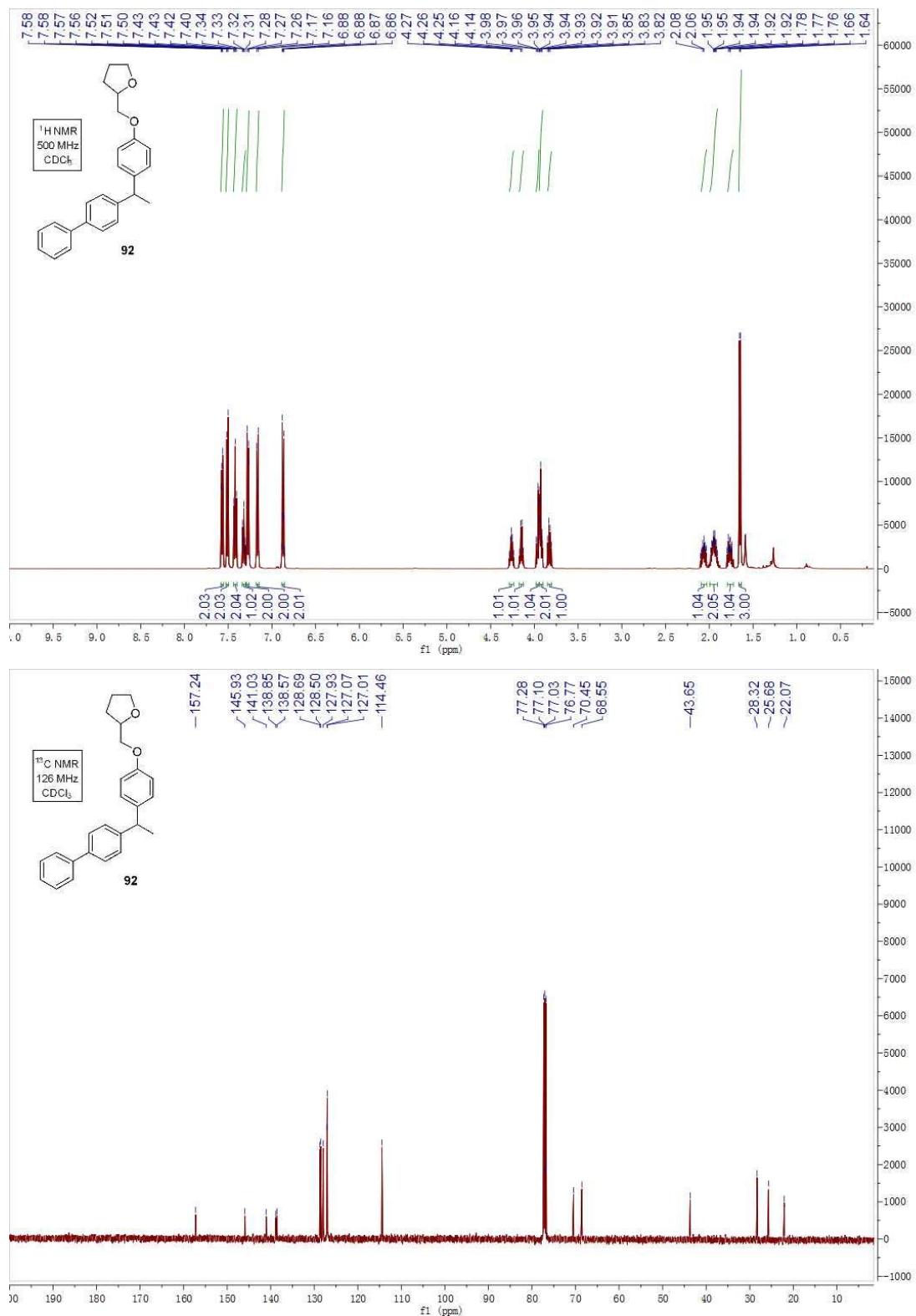


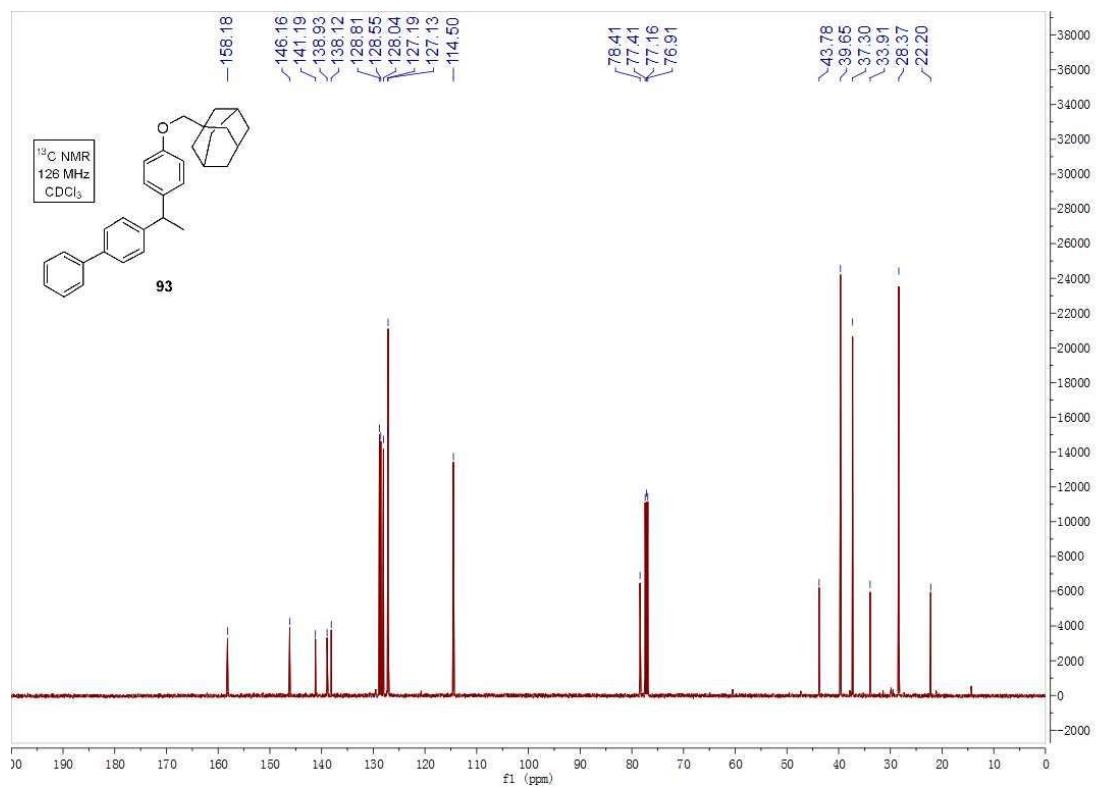
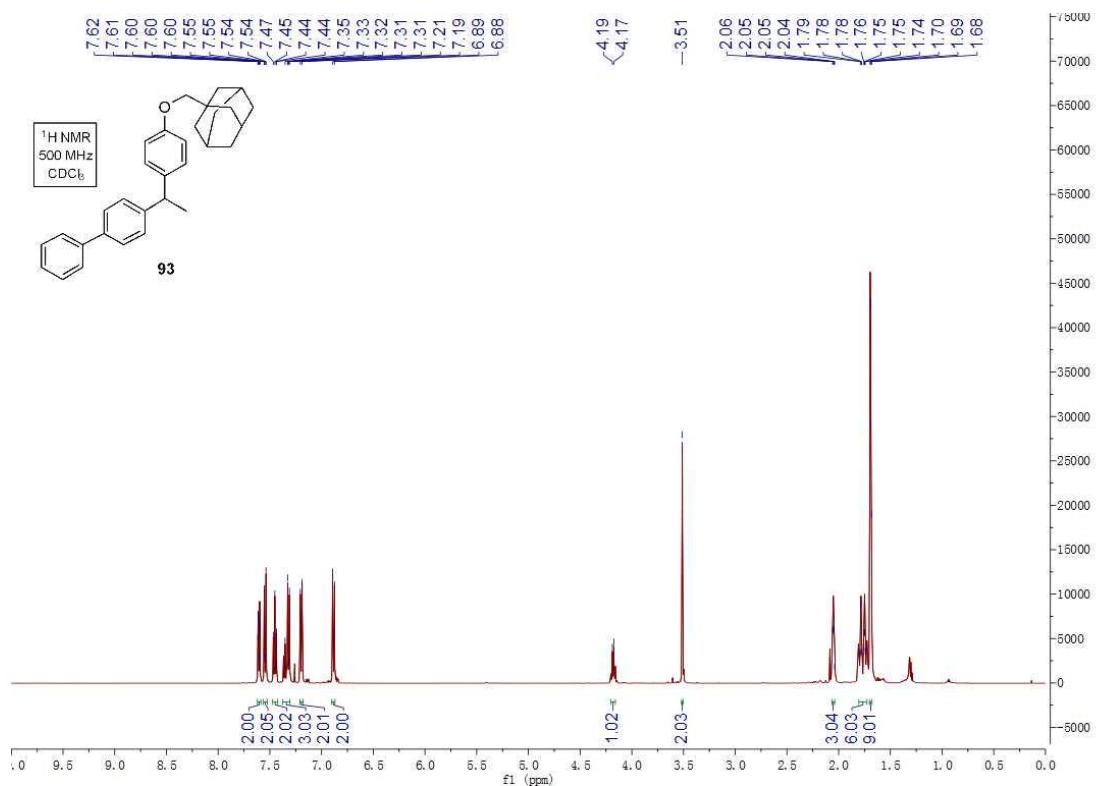


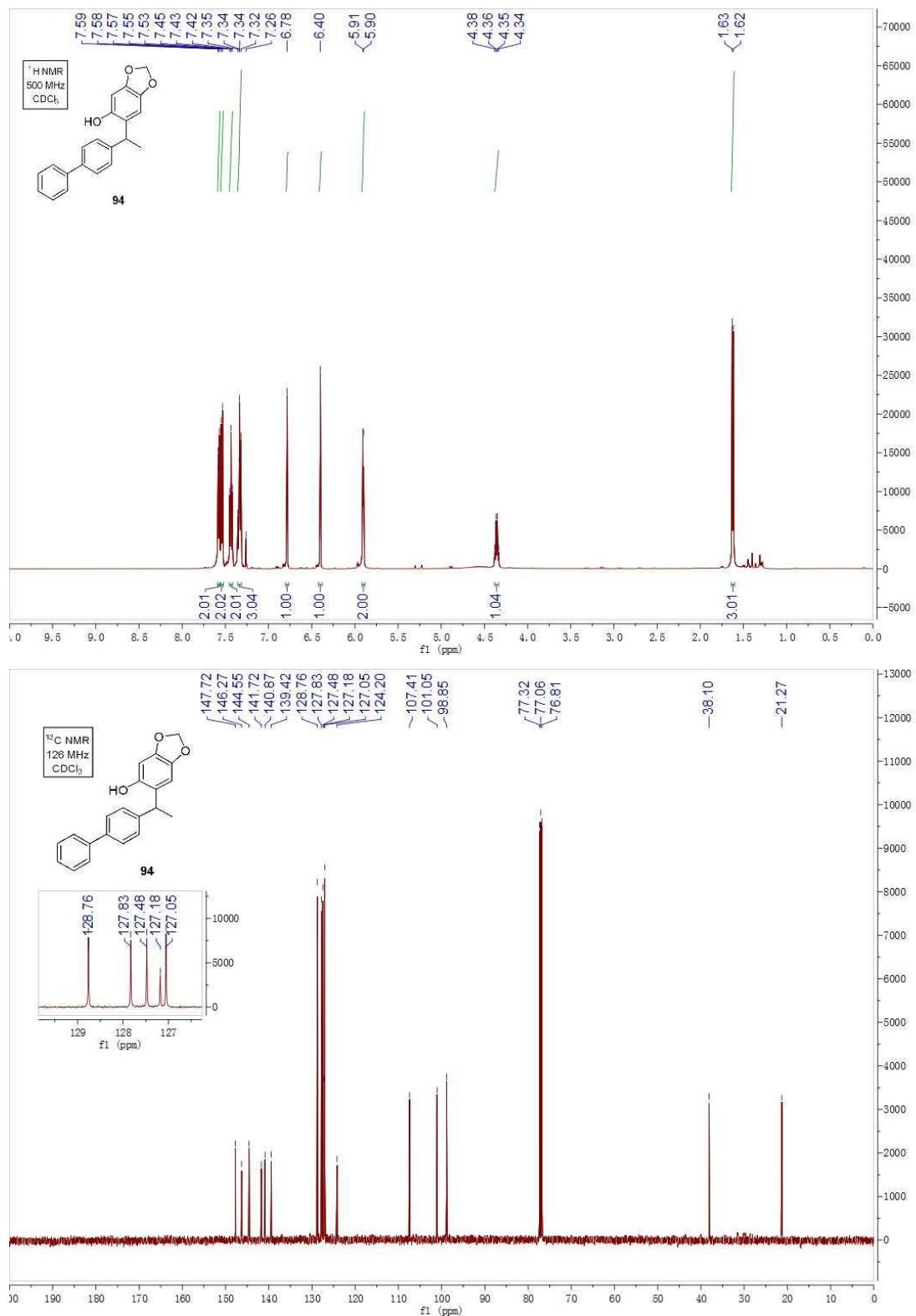


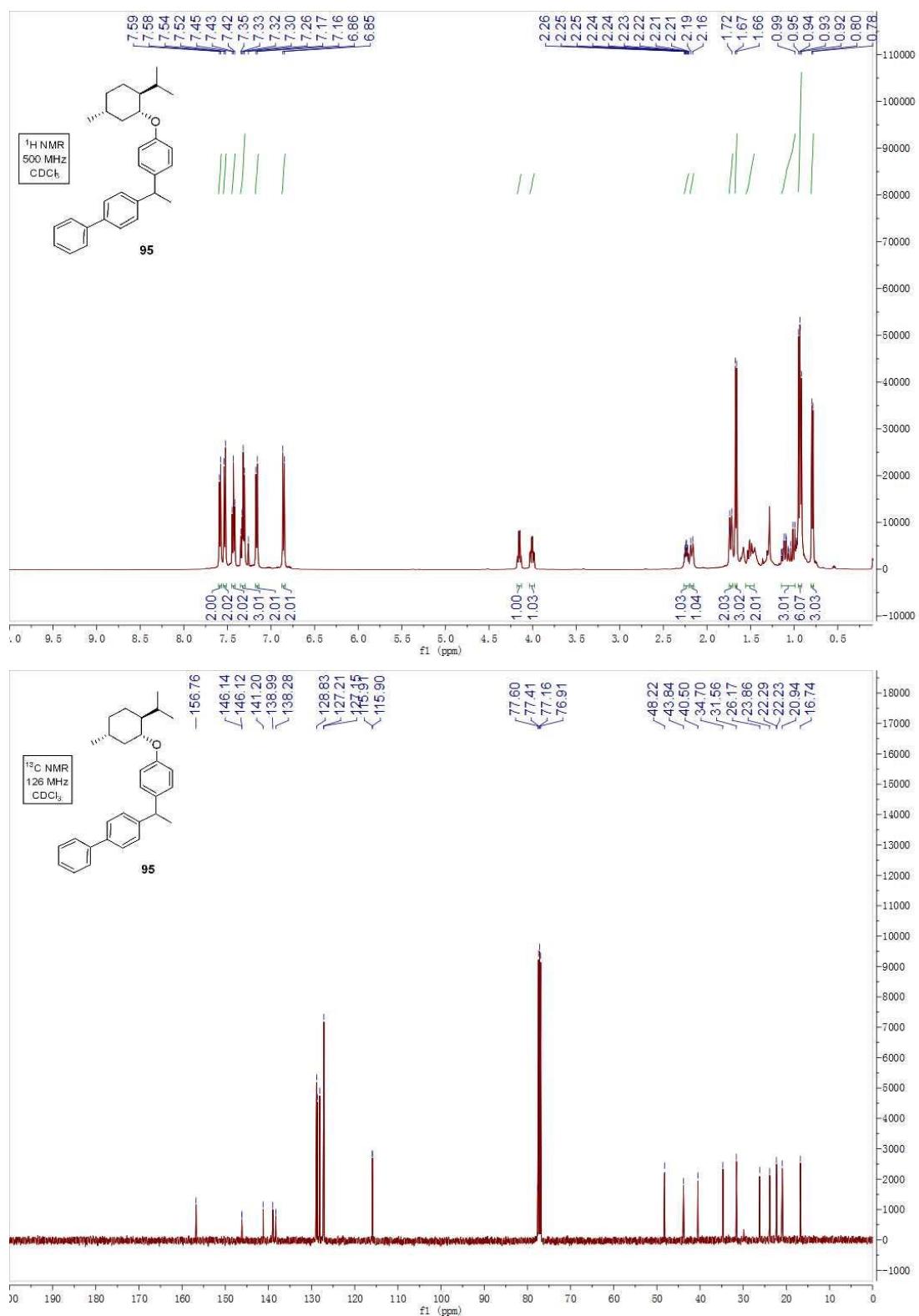


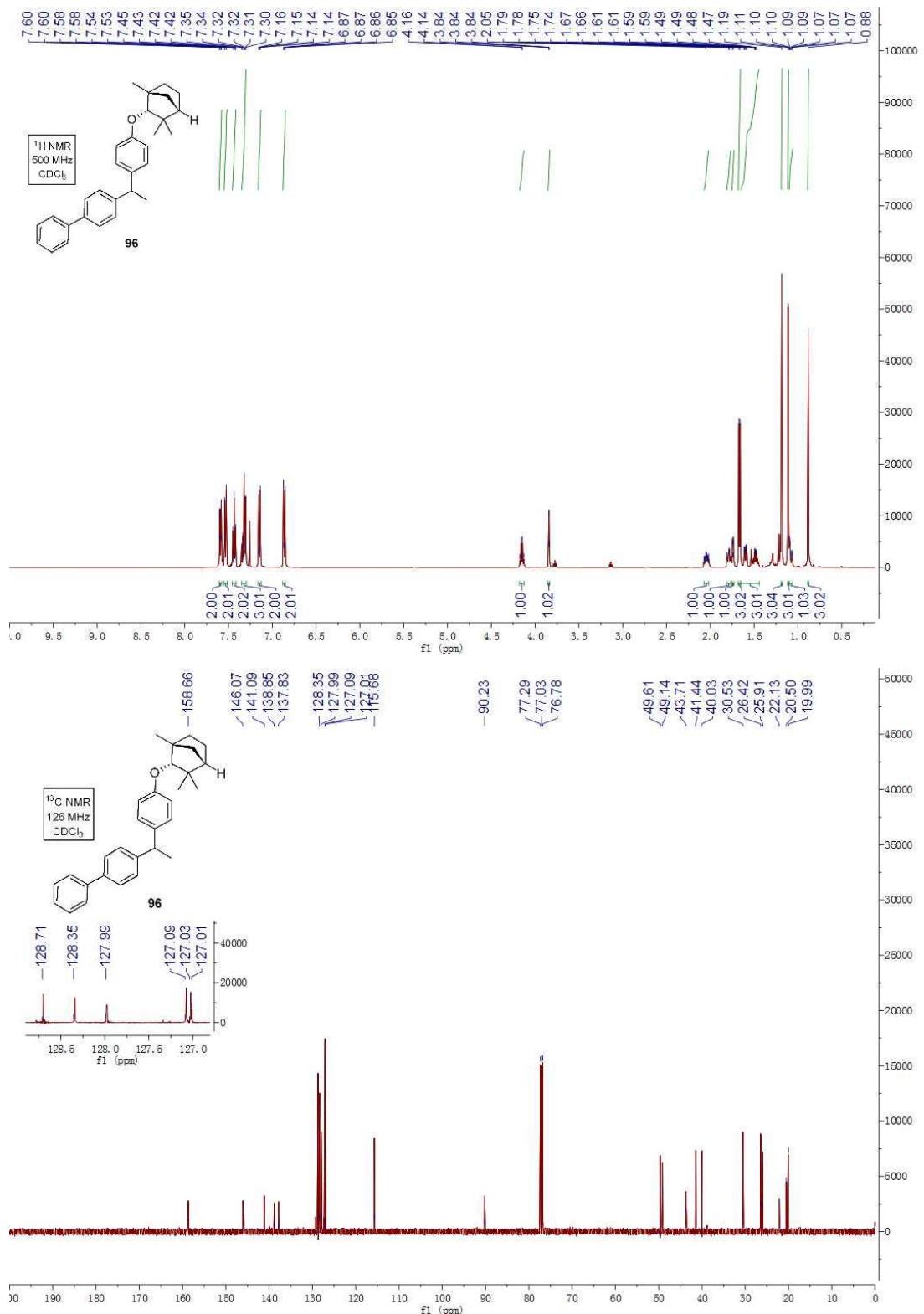


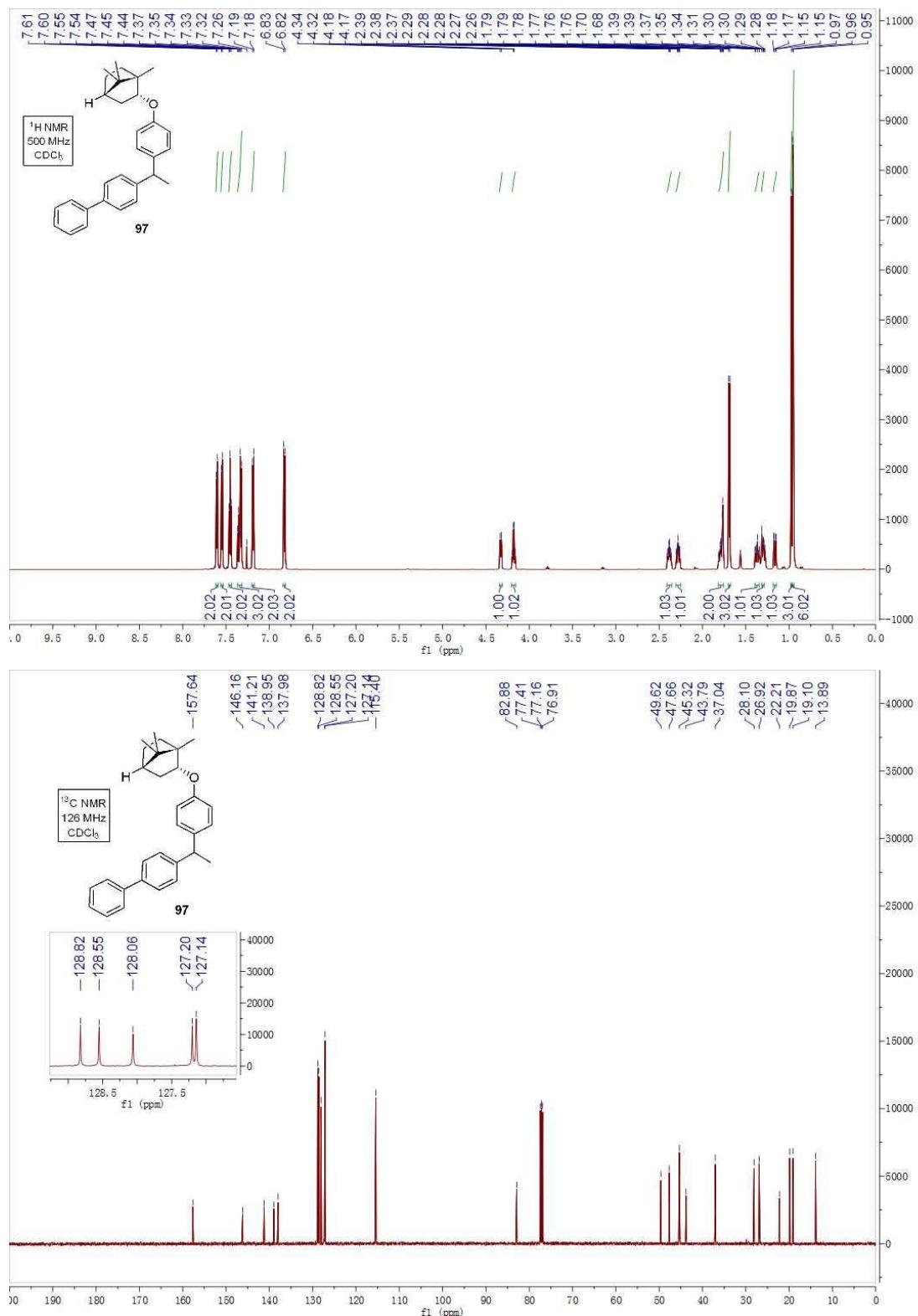


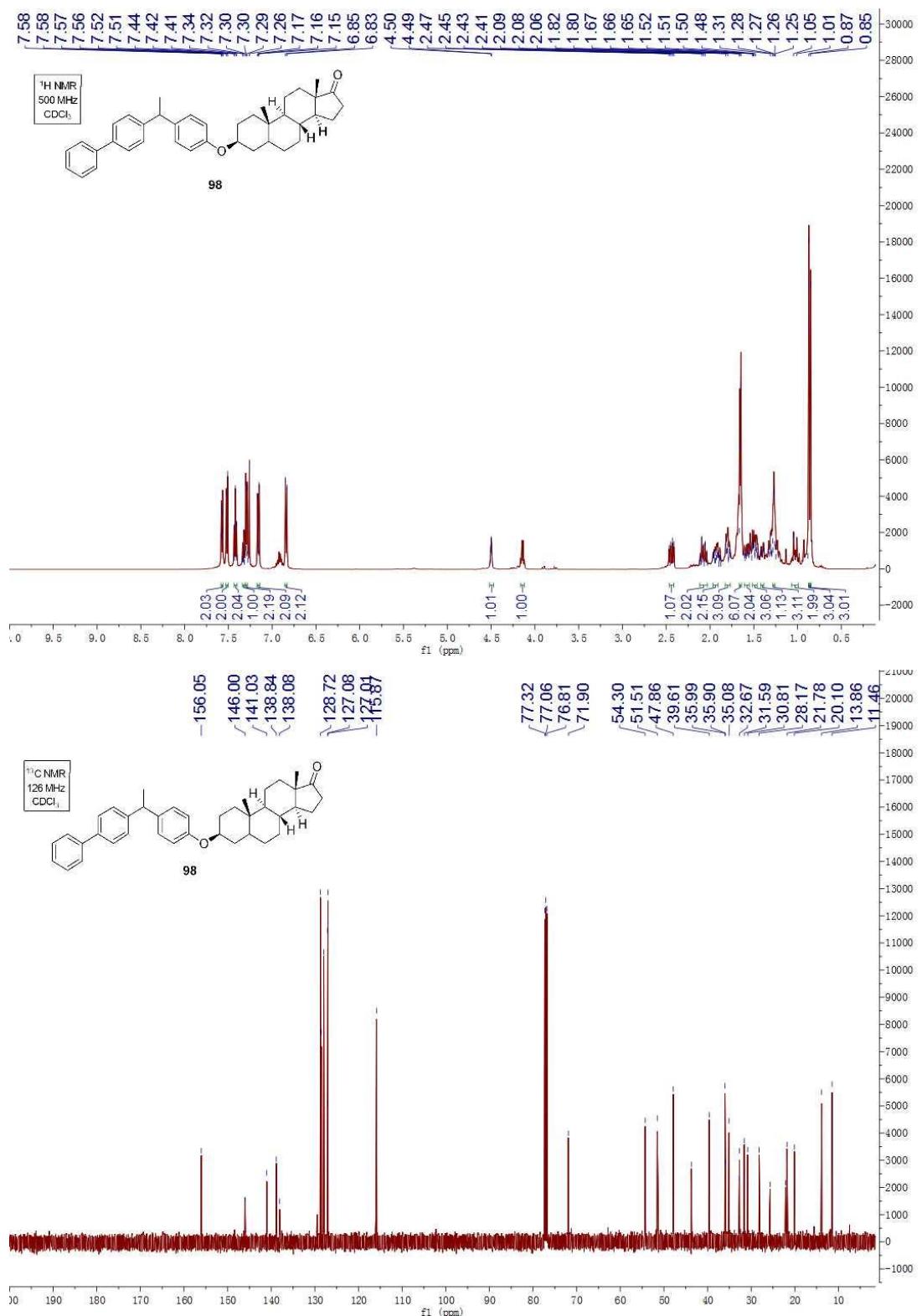


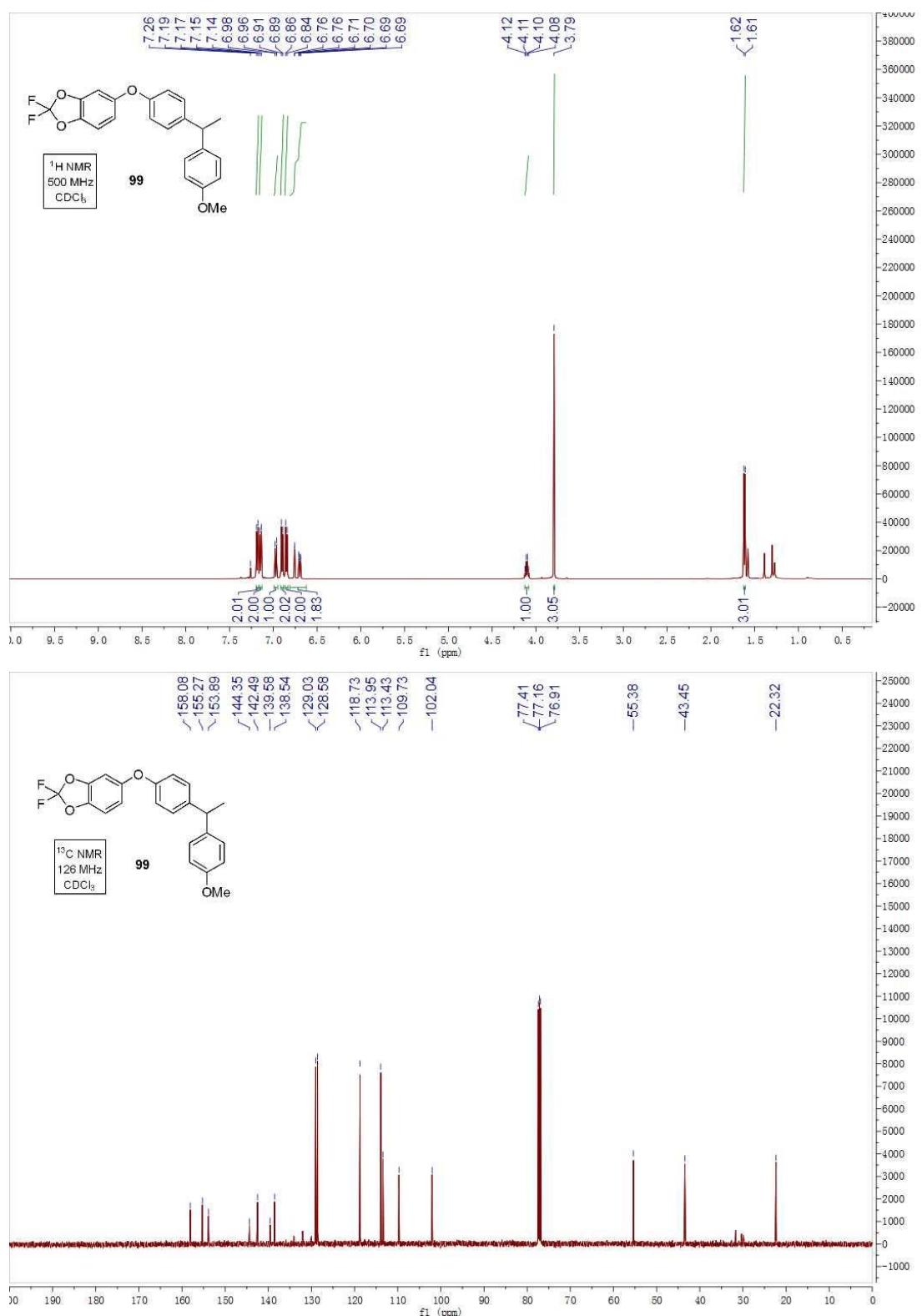


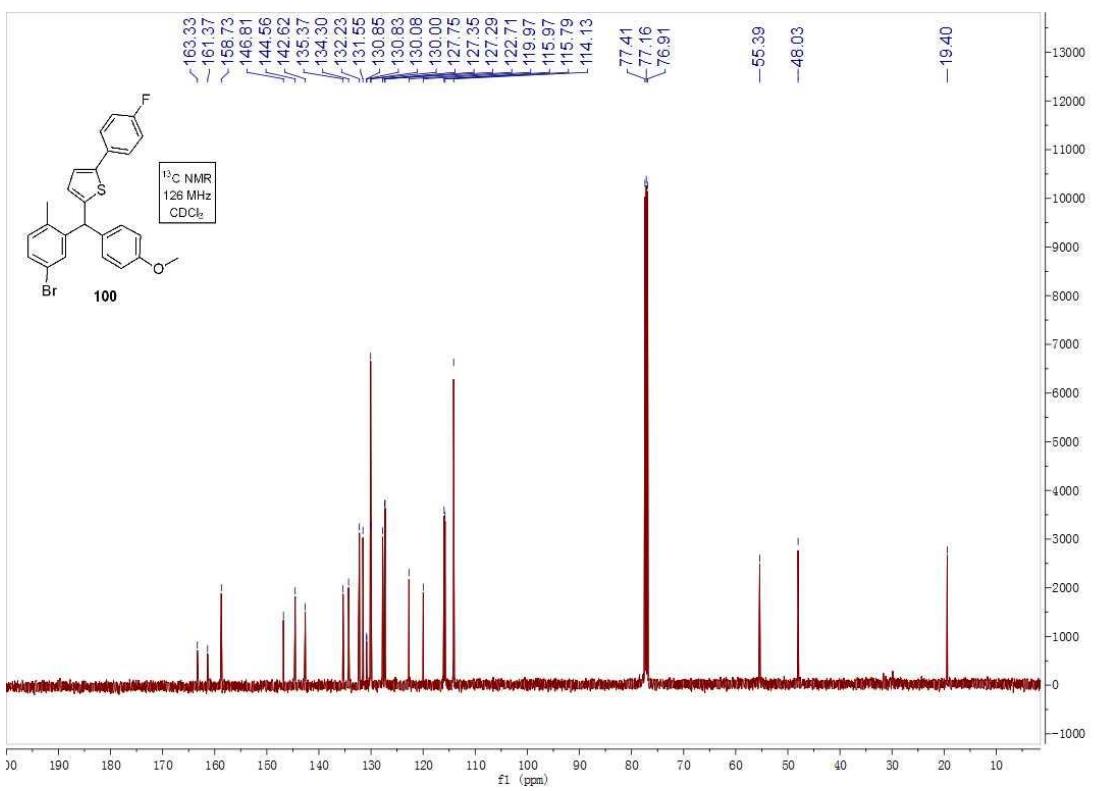
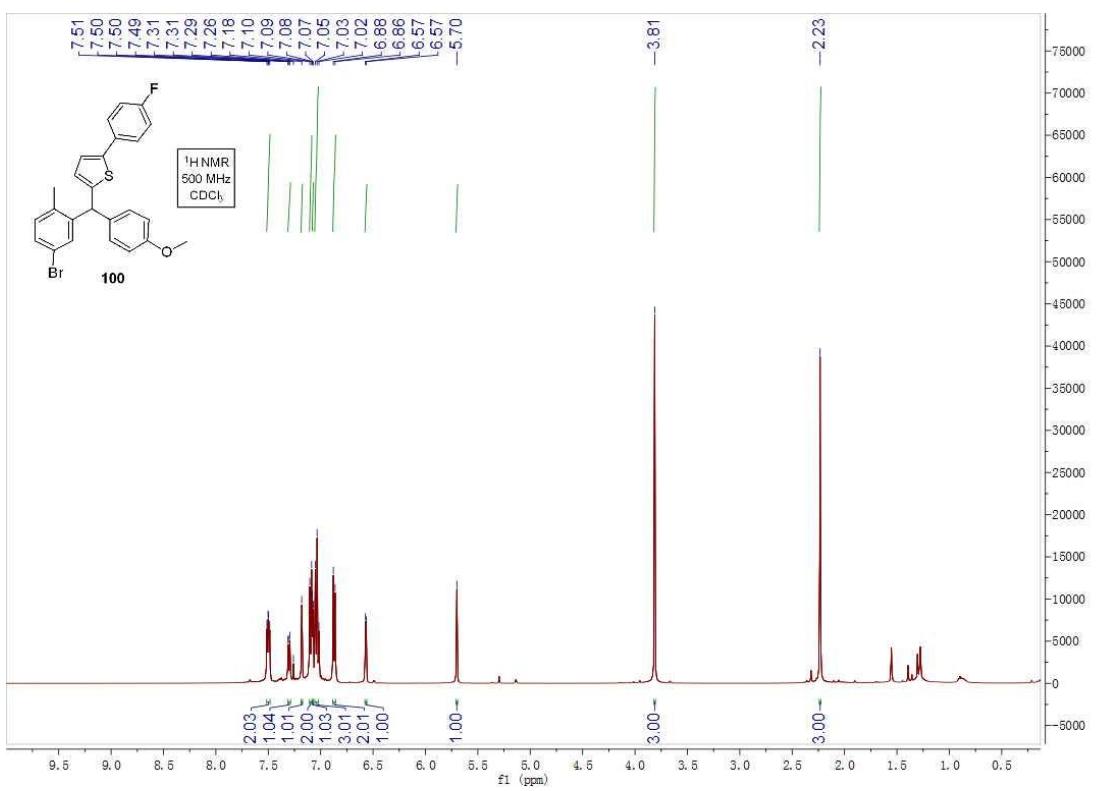


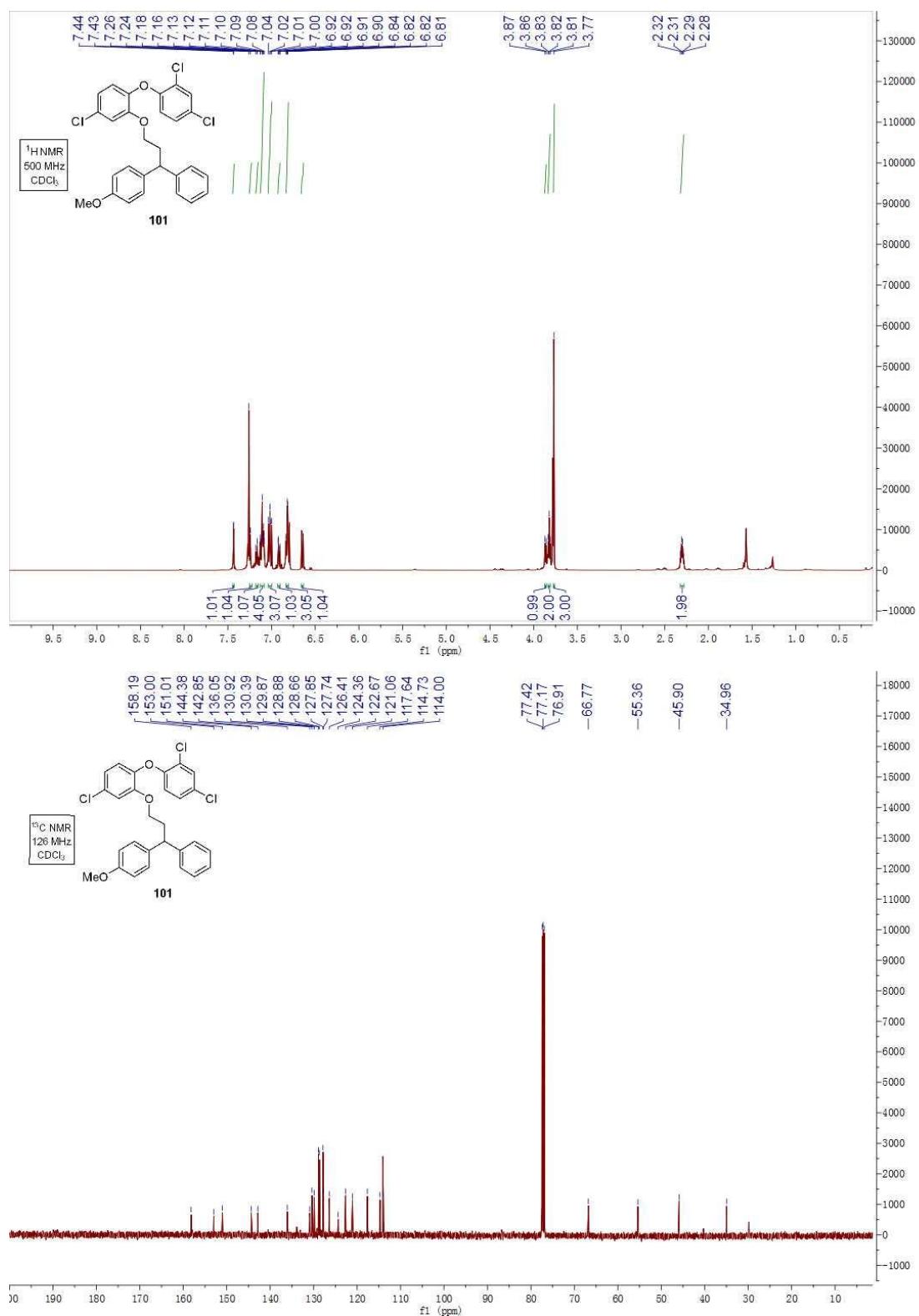


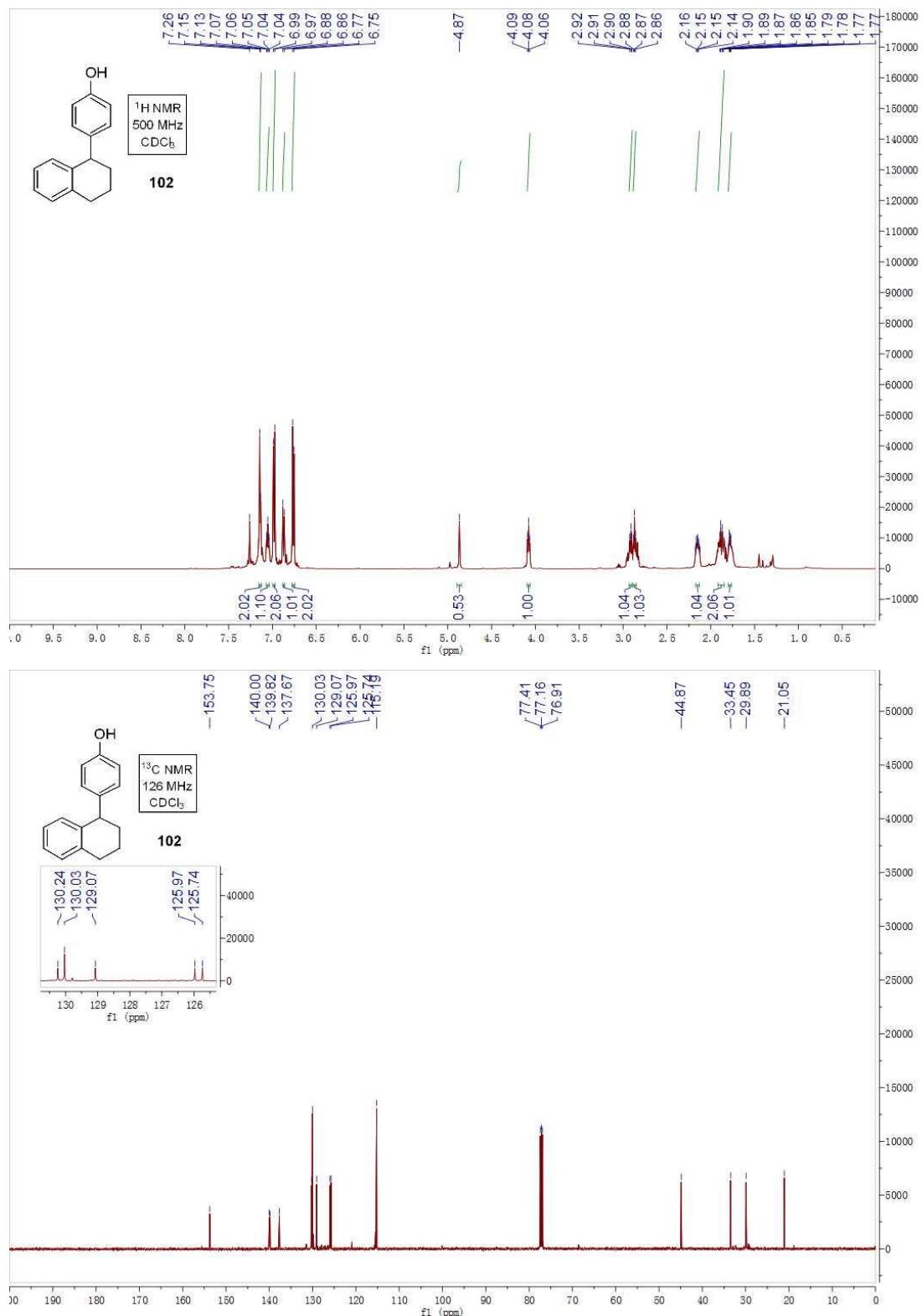


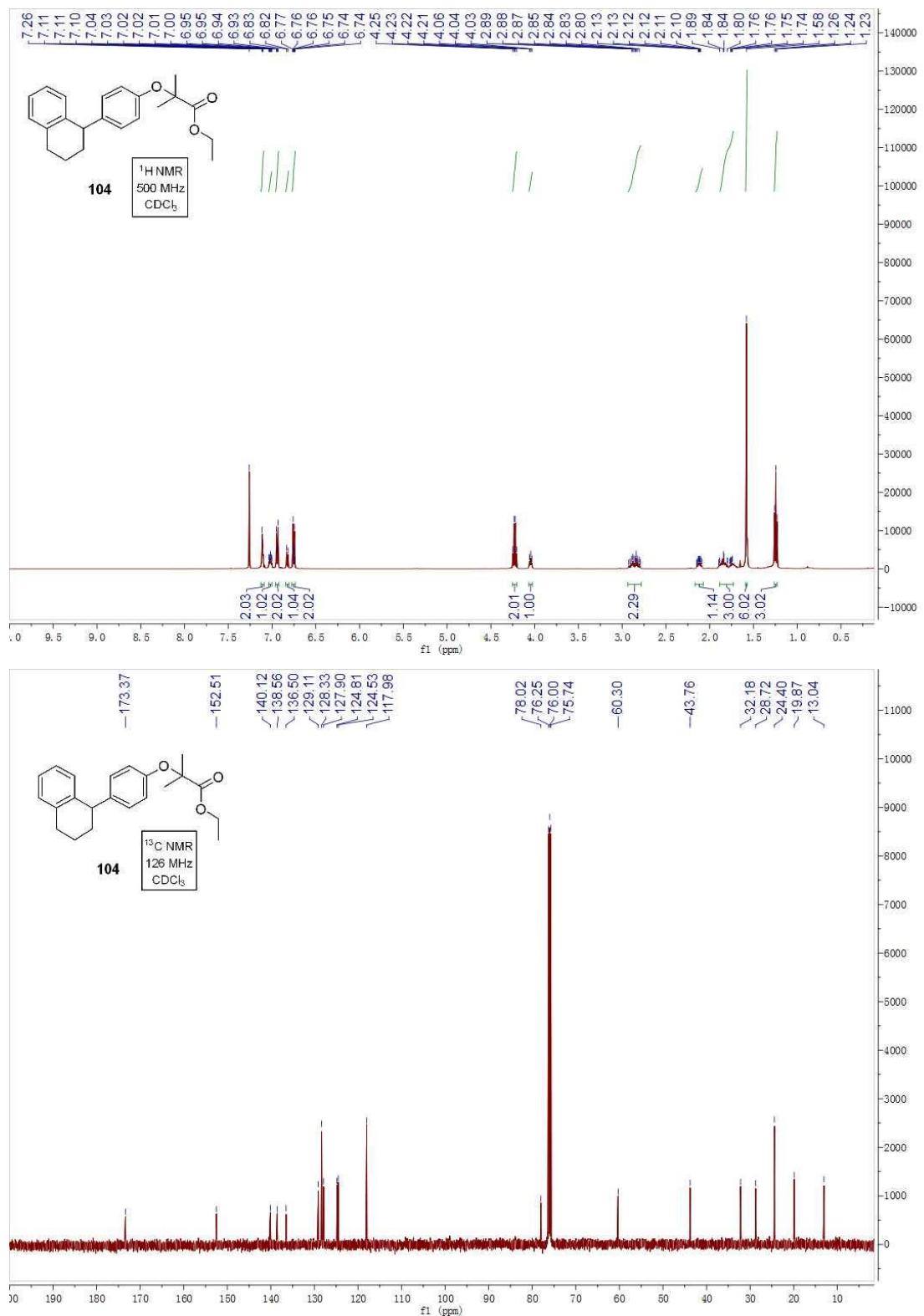


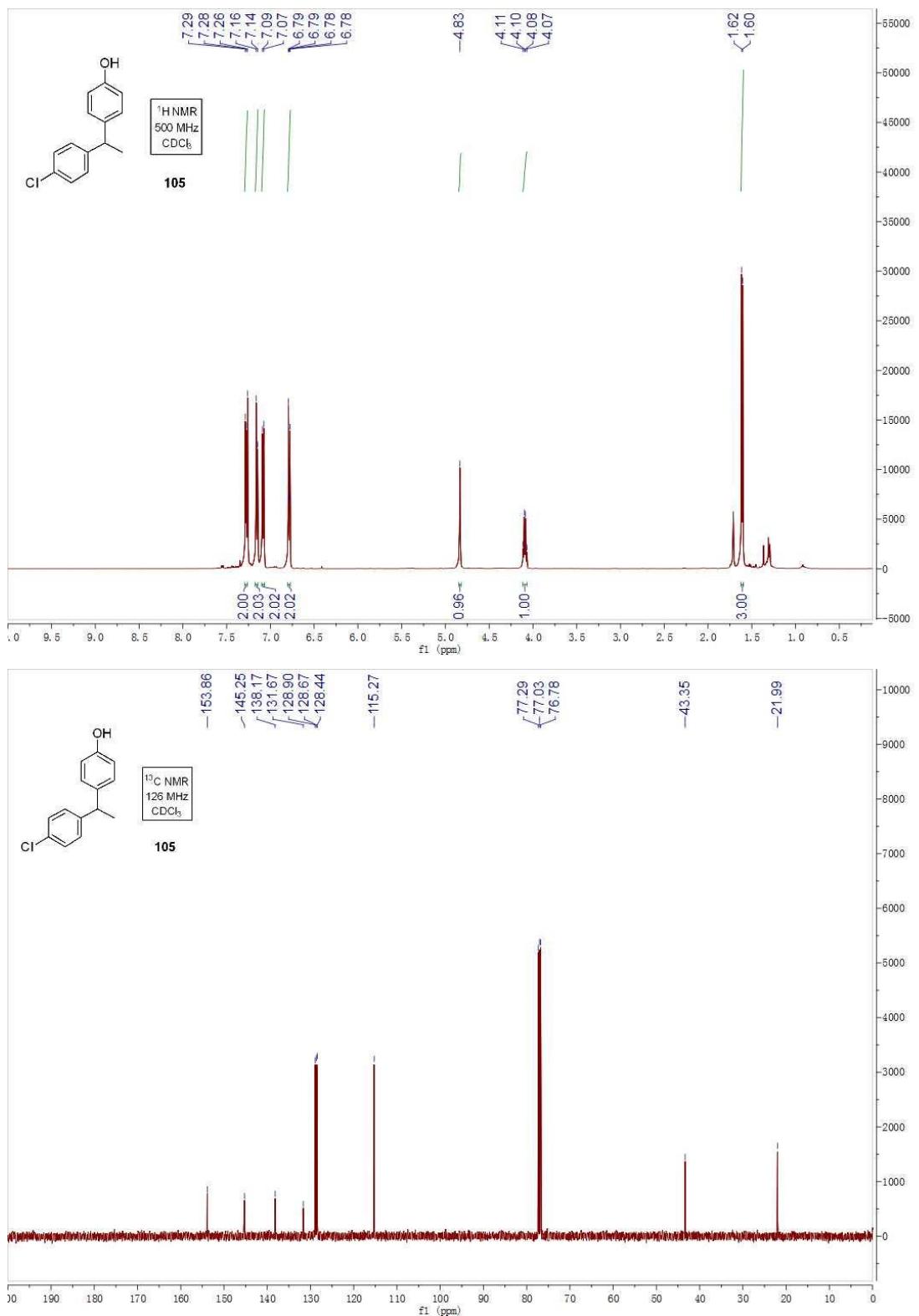


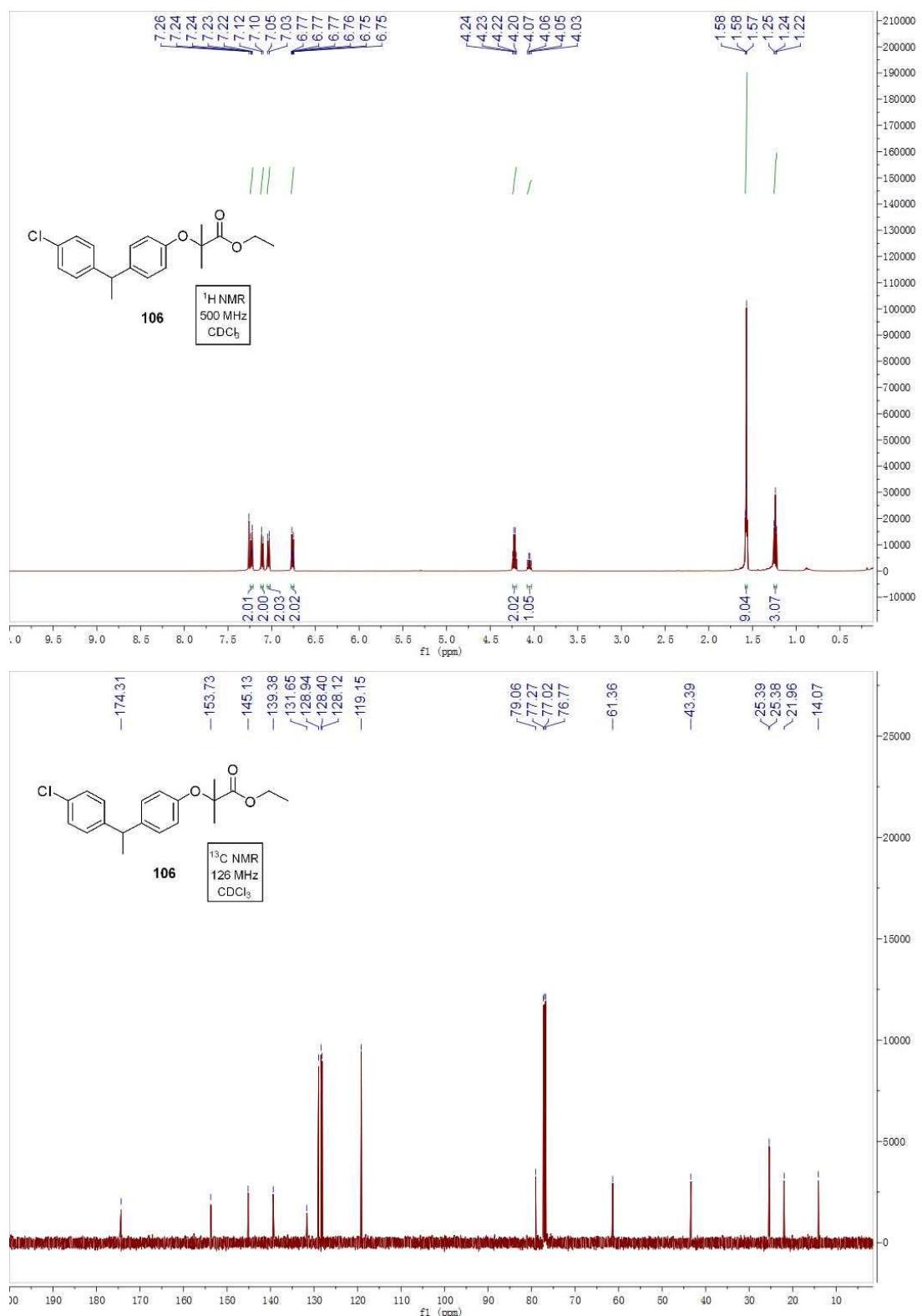


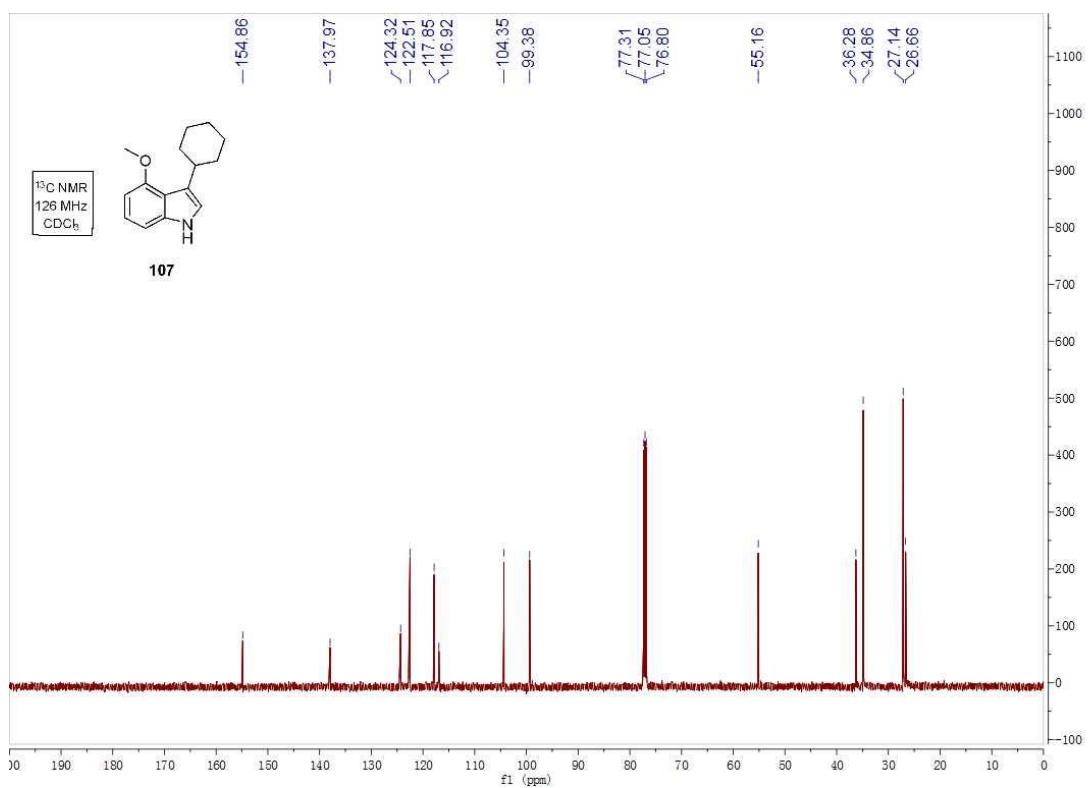
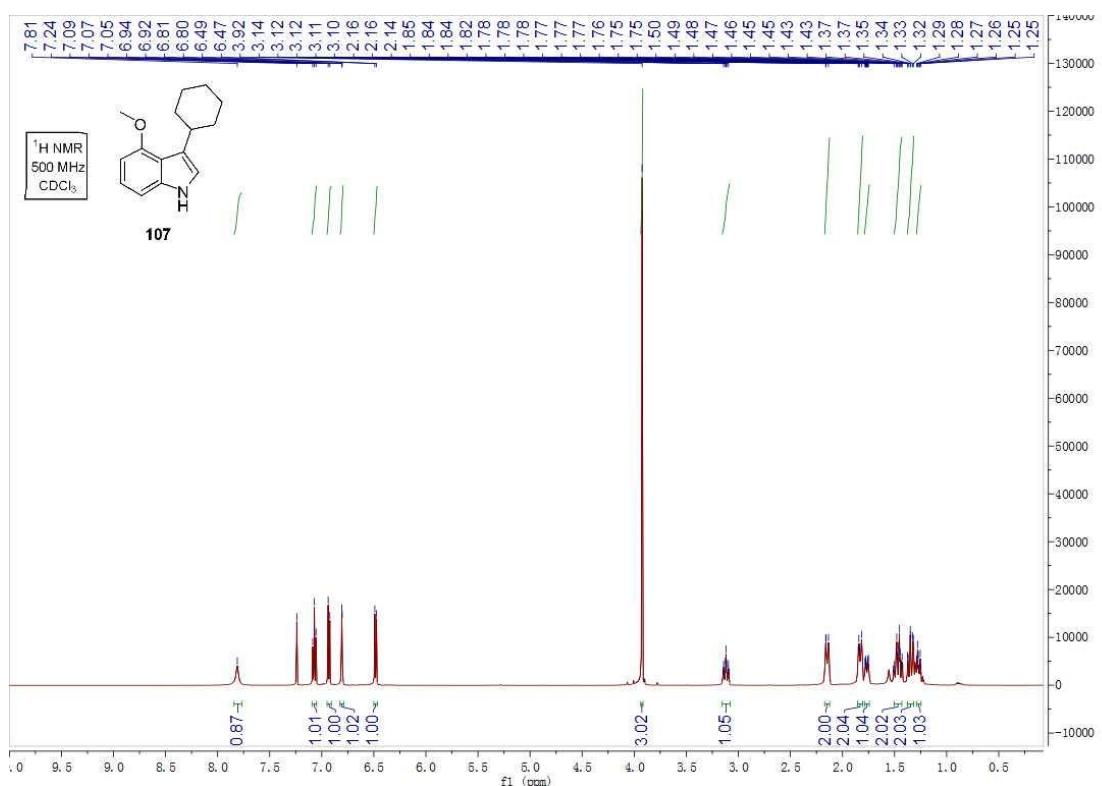


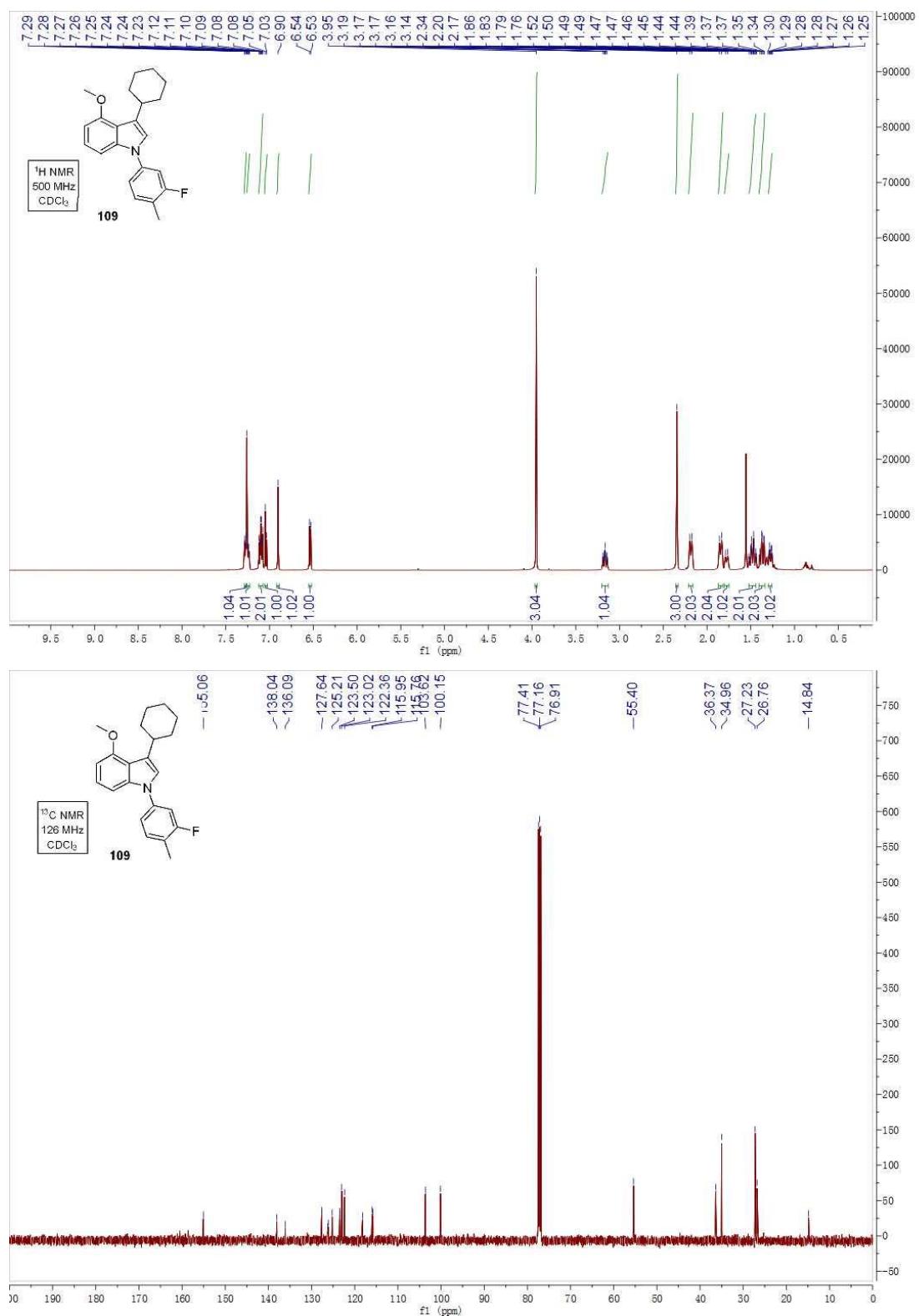












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