Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Nickel-Catalyzed Reductive Benzylation of Tertiary Alkyl Halides with Benzyl Chlorides and Chloroformates

Jiabao Wang,† Yuxin Gong,† Deli Sun,* and Hegui Gong*

Center for Supramolecular Chemistry and Catalysis and Department of Chemistry, 99 Shang-Da Road, Shanghai 200444, China

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I. Experimental Section

Part 1. General Information

1. Chemicals and Reagents

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glove box techniques. THF (99.5%, extra dry, with molecular sieves) was purchased and used directly. Deuterated solvents were used as received ($CDCl_3$ from J&K Co., China). $NiCl_2$ (Alfa Aesar), $NiBr_2$ (Alfa Aesar), NiI_2 (Alfa Aesar), $Ni(COD)_2$ (Strem), $Ni(ClO_4)_2{\cdot}6H_2O$ (Alfa Aesar), $Ni(acac)_2$ (Maclin Co., China) were used as received. Zinc powder (Aladdin) was activated with hydrochloric acid before use. DPPB (98%+, Adamas) and NaI (99%, TCI) were purchased, and used directly. Procedures for the synthesis of tertiary alkyl halides have been reported in our previous publications.[1-6] Benzyl chlorides and chloroformates were prepared according to the reported procedures.[7, 10] Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

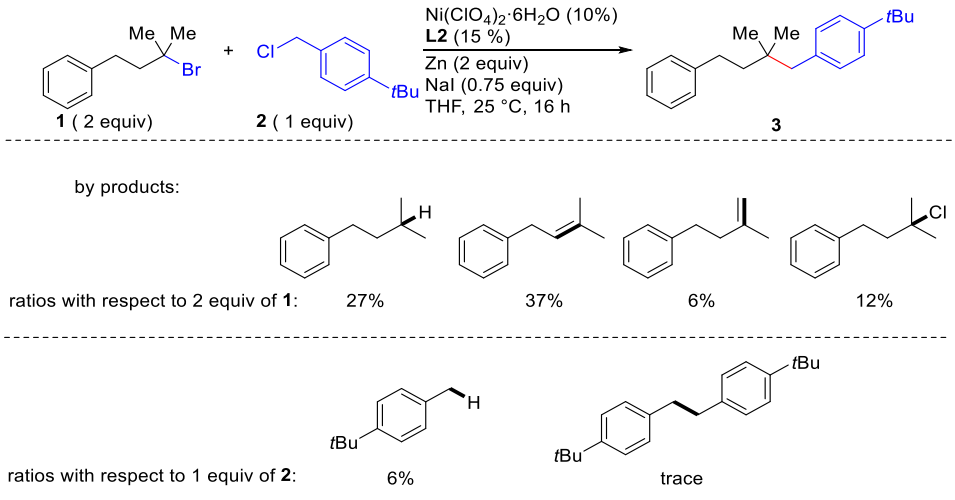
2. Physical method

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. Nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECZ400s/L or Bruker Avance 600 MHz. ^1H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^1H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS-ESI) were obtained using a Bruker APEXIII 7.0 Tesla Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and IonSpec 4.7 Tesla FT-MS instruments. High-resolution mass spectra (HRMS-EI) were obtained using a Thermo Fisher Scientific Thermo DFS double-focusing massassay. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Details of Optimization and Control Experiments

A typical procedure for optimization of the reaction conditions: To a flame-dried Schlenk tube equipped with a stir bar was added benzyl chloride (0.15 mmol, 100 mol %, if solid), alkyl bromide (0.3 mmol, 200 mol %, if solid), Zn (20 mg, 0.30 mmol, 200 mol %), ligand (0.0225 mmol, 15 mol %), Ni catalyst (0.015 mmol, 10 mol %), additive (0.1125 mmol, 75 mol %).The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, alkyl bromide (0.3 mmol, 200 mol %, if liquid) and benzyl chloride (0.15 mmol, 100 mol %, if liquid), was added via a syringe followed by addition of solvent (2 mL) via a syringe. The reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 25 ºC, and was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided the product as a solid or oil.

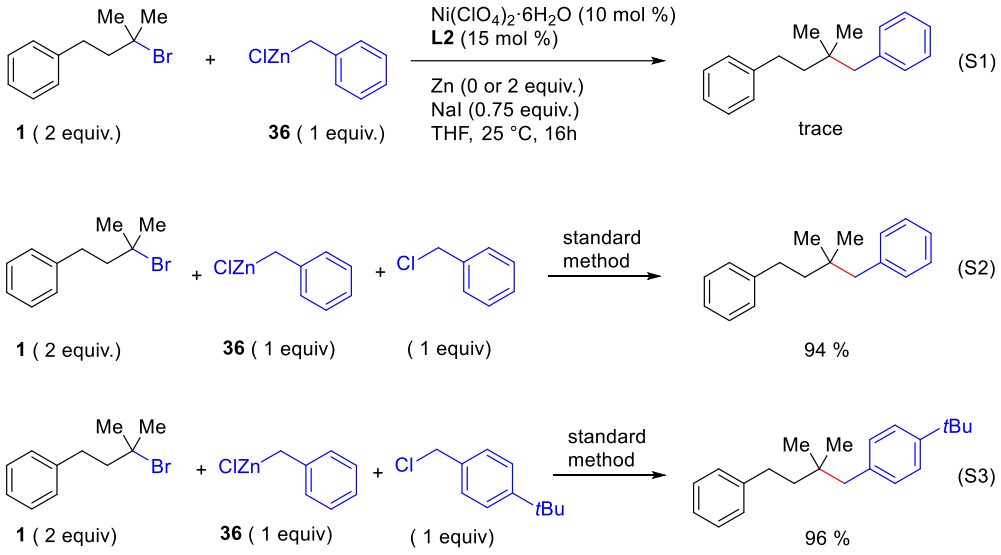
Scheme S1. Profile of byproducts for the reaction of **1** with **2**. [a]



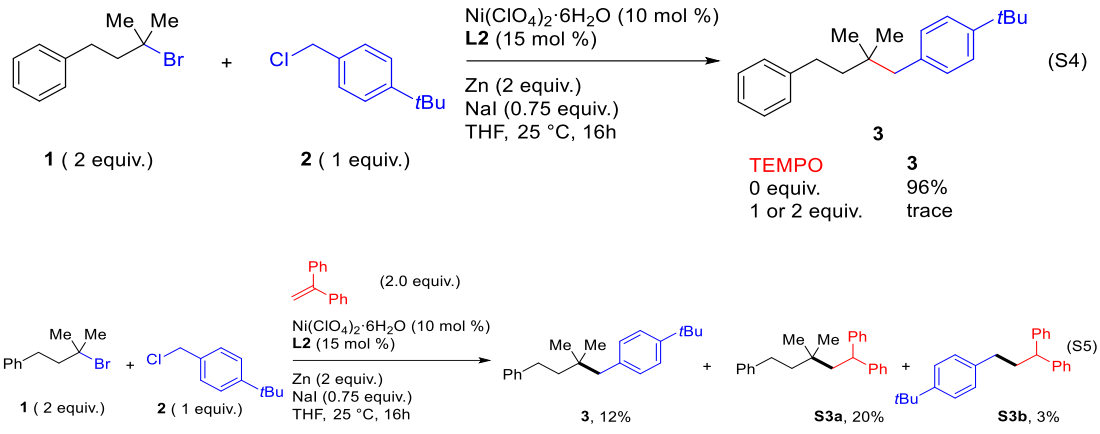
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.15 mmol), Ni (10 mol %), ligand (15 mol %), NaI (0.75 equiv), Zn (2 equiv), and THF (2 mL).[b] NMR yield using 2,5-dimethylfuran as the internal reference.

Part 3. Mechanistic Consideration

In order to exclude the possibility of an in situ Negishi mechanism, the reaction was performed using benzylzinc chloride **36** instead of benzyl chloride (eqn S1). Only trace amounts of product was detected under catalytic Ni conditions both with and without Zn. When benzylzinc chloride **36** and benzyl chloride (or 4-*tert*-butyl benzyl chloride) were subjected to the catalytic coupling reaction with **1** at the same time, the corresponding product can be obtained in excellent yields (eqn S2 & S3). These results indicate that the reaction should proceed via a non-Negishi process.



To further verify the reaction mechanism, one or two equivalents of TEMPO was added to the reaction under the standard coupling reaction (eqn S4), the reaction was significantly inhibited. In addition, two equivalents of 1,1- Diphenylethylene was added to the reaction under the standard coupling reaction (eqn S5), only 12% yield of product **3** was obtained, S**3a** (ms = 328) and/or S**3b** (ms = 328) were obtained in ~20% yield (using dodecane as internal standard, not calibrated), as evidenced by GCMS data (Figure S1 and Figure S2**)**. These results provide support for the presence of a C–centered radical in the reaction pathway.



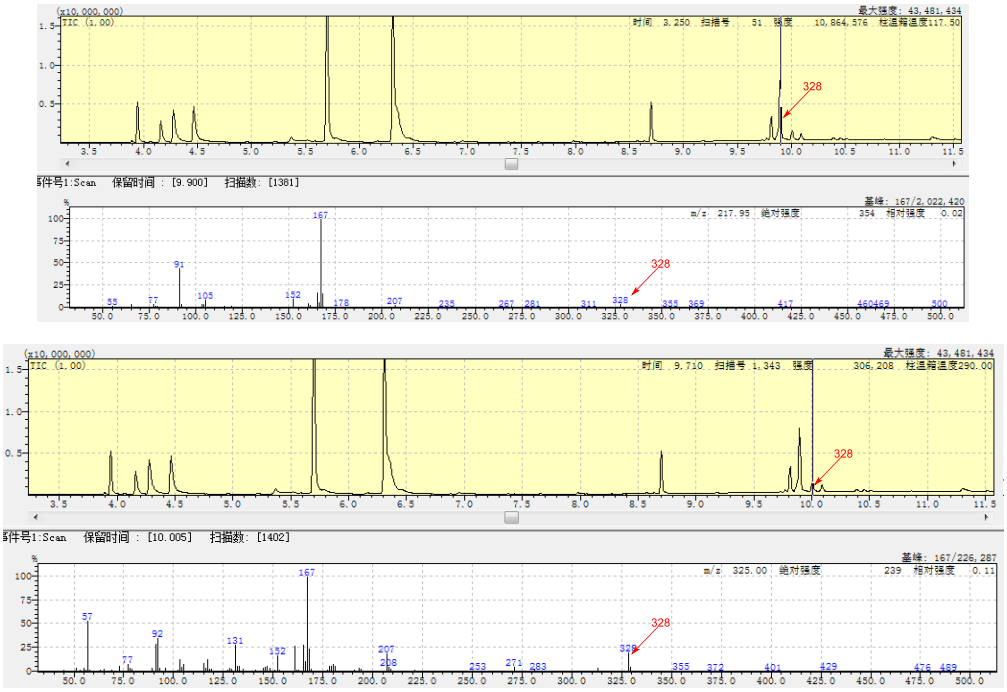
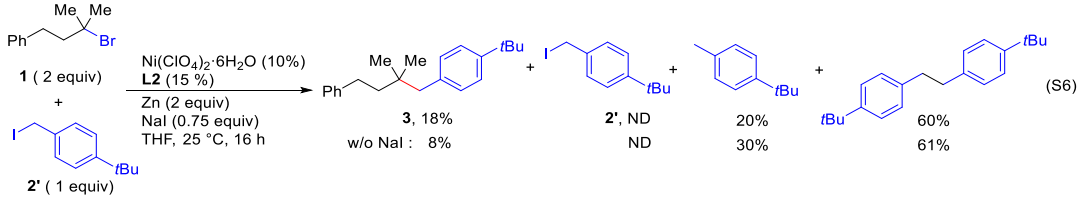


Figure S2. GCMS spectra of Compound **S3a** and/or **S3b**

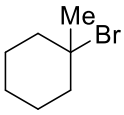
To verify if iodide is required for in situ halide exchange at the benzylic position (eq S6), we have tested benzyl iodide instead of the chloride analog. A low yield was observed due to substantial dimerization of benzyl iodide. We reason that slow Cl/I exchange under our standard conditions warrant low concentration of benzyl-I, so that the dimerization process can be prevented.



Part 4. Preparation of Tertiary Alkyl Bromides

A general procedure for the preparation of tertiary bromides: [1– 6] The tertiary alkyl bromides were prepared according to a literature procedure from the corresponding tertiary alcohol precursors. To a solution of alcohol (10 mmol, 100 mol %) in CH_2Cl_2 was added LiBr (1.80 g, 20 mmol, 200 mol %) in 48 wt % aqueous HBr at 0 ºC. The reaction mixture was allowed to warm to r.t. and stirred for overnight. The reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$. The organic layer was collected, washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography to afford the product.

1-Bromo-1-methylcyclohexane.[1]

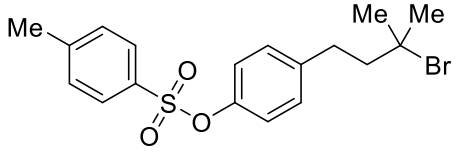


This compound was prepared according to the general procedure using 1-methylcyclohexan-1-ol (1.14 g, 10.0 mmol). The crude residue was purified by silica gel chromatography (SiO_2: 100% petroleum ether) to yield the product as a colorless liquid (1.17 g, 6.6 mmol, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.08 – 2.06 (m, 2H), 1.82 (s, 3H), 1.77 – 1.56 (m, 5H), 1.48 – 1.43 (m, 2H), 1.21 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 71.6, 43.0, 35.2, 25.2, 23.4.

4-(3-Bromo-3-methylbutyl)phenyl 4-methylbenzenesulfonate.



This compound was prepared according to the general procedure using 4-(3-hydroxy-3-methylbutyl)phenyl 4-methylbenzenesulfonate (3.34 g, 10.0 mmol). The crude residue was purified by silica gel chromatography (SiO_2: 10% ethyl acetate in petroleum ether) to yield the product as a yellow solid (3.14 g, 7.9 mmol, 79% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 2.84 – 2.78 (m, 2H), 2.45 (s, 3H), 2.05 – 1.99 (m, 2H), 1.80 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 145.2, 140.6, 132.5, 129.7, 129.5, 128.5, 122.3, 67.1, 49.1, 34.2, 32.3, 21.7.

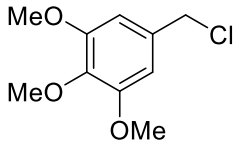
HRMS (ESI) calcd for $[M+Na^+]$ $(C_{18}H_{21}BrNaO_3S)^+$: m/z 419.0287, 421.0267; found: 419.0287, 421.0268.

M.p. 64–65 ºC.

Part 5. Preparation of Benzyl Chlorides

General procedure:[7] To a stirring solution of the corresponding benzyl alcohol (10 mmol), N,N-dimethylformamide (20 μL) and CH_2Cl_2 (20 mL) were added thionyl chloride (12 mmol) dropwise at 0 ºC. After addition, the mixture was allowed to stir at room temperature for 1 h. The complete consumption of the benzyl alcohol was verified by TLC or GC. Then the mixture was poured into saturated $NaHCO_3$ (20 mL), and extracted with dichloromethane (20 mL × 3). The combined organic layer was washed with water (20 mL), brine (20 mL), then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by silica gel chromatography.

5-(Chloromethyl)-1,2,3-trimethoxybenzene.[8]



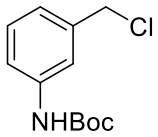
This compound was prepared according to the general procedure using (3,4,5-trimethoxyphenyl)methanol (1.98 g, 10.0 mmol). The crude residue was purified by silica gel chromatography (SiO_2: 10% ethyl acetate in petroleum ether) to yield the product as a white solid (1.41 g, 6.5 mmol, 65% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 (s, 2H), 4.54 (s, 2H), 3.88 (s, 6H), 3.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.3, 138.1, 132.9, 105.7, 60.8, 56.1, 46.8.

M.p. 55–56 ºC.

***tert*-Butyl (3-(chloromethyl)phenyl)carbamate.**[9]



This compound was prepared according to the general procedure using *tert*-butyl (3-(hydroxymethyl)phenyl)carbamate (2.23 g, 10.0 mmol). The crude residue was purified by silica gel chromatography (SiO_2: 10% ethyl acetate in petroleum ether) to yield the product as a white solid (1.69 g, 7.0 mmol, 70% yield).

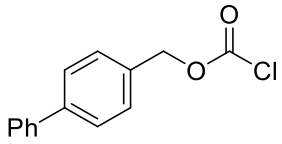
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.28–7.26 (m, 1H), 7.24–7.22 (m, 1H), 7.07–7.05 (m, 1H), 6.49 (dr, 1H), 4.55 (s, 2H), 1.52 (s, 9H).

M.p. 101–102 ºC.

Part 6. Preparation of Benzyl Chloroformates

A general procedure for the preparation of benzyl chloroformates:[10] To a stirred solution of the corresponding alcohol (1 equiv., 10 mmol) in dichloromethane (50 mL) at 0 °C was added triethylamine (2 equiv., 20 mmol) followed by triphosgene (1.2 equiv., 12 mmol). The resulting mixture was stirred at room temperature overnight, and then it was partially evaporated at reduced pressure and diluted with hexane (50 mL). The solid was removed by filtration and the filtrate was evaporated to afford the crude product. Then the crude oily liquid was purified by flash column chromatography, using a mixture of ethyl acetate in petroleum ether (1:99) as eluent. The filtrate was evaporated to afford the corresponding chloroformate in quantitative yield.

[1,1'-Biphenyl]-4-ylmethyl carbonochloridate.[10]



This compound was prepared according to the general procedure using 4-phenylbenzyl alcohol (1.84 g, 10.0 mmol). The crude residue was purified by silica gel chromatography (SiO_2: 1% ethyl acetate in petroleum ether) to yield the product as a white solid (2.37 g, 9.6 mmol, 96% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59–7.58 (m, 4H), 7.47–7.43 (m, 4H), 7.38–7.34 (m, 1H), 4.64 (s, 2H).

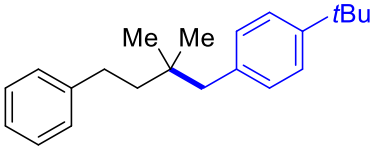
M.p. 69–70 ºC.

Part 7. Reductive Cross-Coupling Reactions

General Procedure for tertiary bromides with benzyl chlorides (Method A): To a flame-dried Schlenk tube equipped with a stir bar was charged with benzyl chloride (0.15 mmol, 100 mol %, if solid), Zn (20 mg, 0.30 mmol, 200 mol %), DPPB (9.6 mg, 0.0225 mmol, 15 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (5.5 mg, 0.015 mmol, 10 mol %), NaI (17.0 mg, 0.1125 mmol, 75 mol %).The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, alkyl bromide (0.3 mmol, 200 mol %) and benzyl chloride (0.15 mmol, 100 mol %, if liquid), were added via a syringe followed by addition of DME (2 mL) via a syringe. The reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 25 ºC, and was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided the product as a solid or oil.

General Procedure for tertiary bromides with benzyl chloromates (Method B): To a flame-dried Schlenk tube equipped with a stir bar was charged with benzyl chloride (0.15 mmol, 100 mol %, if solid), Zn (20 mg, 0.30 mmol, 200 mol %), DPPB (9.6 mg, 0.0225 mmol, 15 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (5.5 mg, 0.015 mmol, 10 mol %), NaI (17.0 mg, 0.1125 mmol, 75 mol %).The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, alkyl bromide (0.3 mmol, 200 mol %) and benzyl chloride (0.15 mmol, 100 mol %, if liquid), were added via a syringe followed by addition of DME (2 mL) via a syringe. The reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 25 ºC, and was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided the product as a solid or oil.

(2,2-Dimethylbutane-1,4-diyl)dibenzene (3).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate

in petroleum ether) provided this compound in 93% yield (41.1 mg, 0.140 mmol) as a white solid.

This compound was also prepared according to *Method B*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 93% yield (41.1 mg, 0.140 mmol) as a white solid.

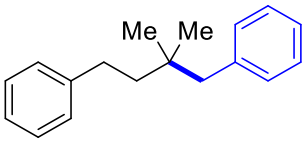
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 4H), 7.19 – 7.16 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.67 – 2.62 (m, 2H), 2.54 (s, 2H), 1.55 – 1.52 (m, 2H), 1.31 (s, 9H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 143.4, 136.1, 130.2, 128.3, 128.3, 125.5, 124.5, 47.8, 44.2, 34.4, 34.3, 31.4, 30.8, 26.8.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{22}H_{30}Na)^+$: m/z 317.2240; found: 317.2233.

M.p. 39–40 ° C.

(2,2-Dimethylbutane-1,4-diyl)dibenzene (4).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 92% yield (32.9 mg, 0.138 mmol) as a colorless oil.

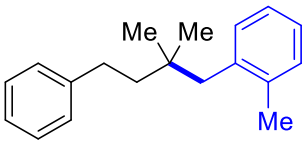
This compound was also prepared according to *Method B*, flash column chromatography (SiO2: 1% ethyl acetate in petroleum ether) provided this compound in 93% yield (33.3 mg, 0.140 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 4H), 7.22 – 7.15 (m, 6H), 2.66 – 2.63 (m, 2H), 2.58 (s, 2H), 1.55 – 1.52 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 139.2, 130.6, 128.3, 127.7, 125.8, 125.6, 48.4, 44.3, 34.4, 26.8.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{18}H_{22}Na)^+$: m/z 261.1614; found: 261.1617.

1-(2,2-Dimethyl-4-phenylbutyl)-2-methylbenzene (5).



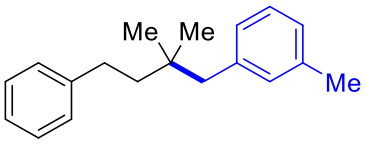
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 51% yield (19.3 mg, 0.077 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 4H), 7.22 – 7.15 (m, 6H), 2.67 - 2.61 (m, 2H), 2.58 (s, 2H), 1.55 - 1.51 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 137.7, 137.1, 131.6, 130.4, 128.3, 128.3, 125.9, 125.6, 125.0, 45.3, 44.2, 35.8, 30.8, 26.6.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{24}Na)^+$: m/z 275.1770; found: 275.1778.

1-(2,2-Dimethyl-4-phenylbutyl)-3-methylbenzene (6).



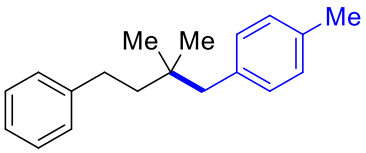
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 81% yield (30.7 mg, 0.122 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.19 – 7.16 (m, 4H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.97 – 6.95 (m, 2H), 2.67 – 2.62 (m, 2H), 2.54 (s, 2H), 2.33 (s, 3H), 1.54 – 1.50 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4 139.1, 137.1, 131.4, 128.3, 128.3, 127.6, 127.5, 126.5, 125.5, 48.2, 44.3, 34.4, 30.8, 26.8, 21.5.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{24}Na)^+$: m/z 275.1770; found: 275.1778.

1-(2,2-Dimethyl-4-phenylbutyl)-4-methylbenzene (7).



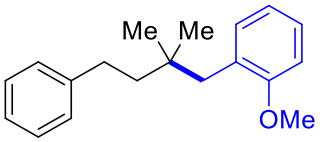
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 83% yield (31.4 mg, 0.125 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.66 – 2.61 (m, 2H), 2.54 (s, 2H), 2.32 (s, 3H), 1.54 – 1.51 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 136.1, 135.2, 130.5, 128.4, 128.3, 128.3, 125.5, 47.9, 44.2, 34.3, 30.8, 26.8, 21.0.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{24}Na)^+$: m/z 275.1770; found: 275.1778.

1-(2,2-Dimethyl-4-phenylbutyl)-2-methoxybenzene (8).



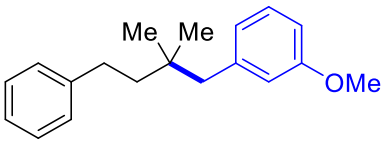
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 83% yield (33.4 mg, 0.125 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.19 – 7.15 (m, 4H), 7.11 – 7.10 (m, 1H), 6.88 – 6.84 (m, 2H), 3.77 (s, 3H), 2.67 – 2.65 (m, 2H), 2.64 (s, 2H), 1.58 – 1.55 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 143.7, 132.4, 128.3, 128.2, 128.0, 127.1, 125.4, 119.7, 110.3, 55.0, 44.6, 40.9, 35.1, 30.9, 26.7.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{24}NaO)^+$: m/z 291.1719; found: 291.1714.

1-(2,2-Dimethyl-4-phenylbutyl)-3-methoxybenzene (9).



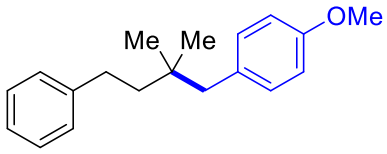
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 91% yield (36.6 mg, 0.137 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.22 – 7.10 (m, 4H), 6.76 – 6.74 (m, 2H), 6.70 (s, 1H), 3.78 (s, 3H), 2.67 – 2.60 (m, 2H), 2.56 (s, 2H), 1.56 – 1.52 (m, 2H), 0.95 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 143.3, 140.8, 128.5, 128.3, 125.6, 123.22, 116.5, 110.9, 55.1, 48.4, 44.3, 34.4, 30.8, 26.9.

HRMS (ESI) calcd for [M+Na^+] $(C_{19}H_{24}NaO)^+$: m/z 291.1719; found: 291.1714.

1-(2,2-Dimethyl-4-phenylbutyl)-4-methoxybenzene (10).



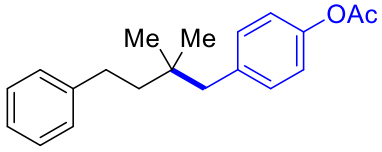
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 89% yield (34.0 mg, 0.137 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 2H), 7.18 – 7.15 (m, 3H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.66 – 2.60 (m, 2H), 2.52 (s, 2H), 1.54 – 1.48 (m, 2H), 0.92 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 143.3, 131.4, 131.2, 128.3, 128.3, 125.5, 113.1, 55.1, 47.5, 44.2, 34.3, 30.8, 26.7.

HRMS (ESI) calcd for [M+Na^+] $(C_{19}H_{24}NaO)^+$: m/z 291.1719; found: 291.1714.

4-(2,2-Dimethyl-4-phenylbutyl)phenyl acetate (11).



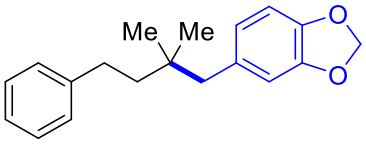
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 74% yield (32.9 mg, 0.111 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.18 – 716 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 2.66 – 2.61 (m, 2H), 2.56 (s, 2H), 2.28 (s, 3H), 1.55 – 1.51 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 148.9, 143.2, 136.8, 131.4, 128.3, 125.6, 120.7, 47.8, 44.2, 34.4, 30.8, 26.6, 21.2.

HRMS (ESI) calcd for [M+Na^+] $(C_{20}H_{24}NaO_2)^+$: m/z 319.1669; found: 319.1668.

5-(2,2-Dimethyl-4-phenylbutyl)benzo[d][1,3]dioxole (12).



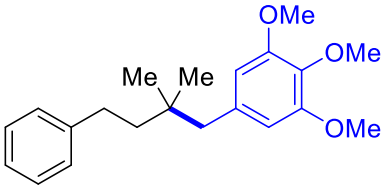
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 63% yield (26.7 mg, 0.095 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.18 – 7.16 (m, 3H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.64 (s, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 2H), 2.65 – 2.59 (m, 2H), 2.50 (s, 2H), 1.54 – 1.49 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 145.7, 143.3, 132.9, 128.3, 128.3, 125.6, 123.4 110.9, 107.6, 100.7, 48.2, 44.3, 34.4, 30.8, 26.7.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{22}NaO_2)^+$: m/z 305.1512; found: 305.1514.

5-(2,2-Dimethyl-4-phenylbutyl)-1,2,3-trimethoxybenzene (13).



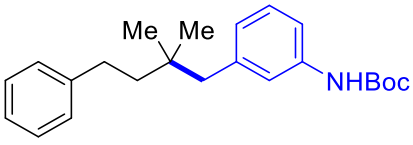
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether) provided this compound in 70% yield (34.5 mg, 0.105 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.19 – 7.16 (m, 3H), 6.35 (s, 2H), 3.84 (s, 3H), 3.82 (s, 6H), 2.68 – 2.62 (m, 2H), 2.53 (s, 2H), 1.58 – 1.54 (m, 2H), 0.97 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 143.2, 136.3, 135.0, 128.4, 128.3, 125.7, 107.7, 60.9, 56.1, 48.6, 44.1, 34.5, 30.8, 27.1.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{21}H_{28}NaO_3)^+$: m/z 351.1931; found: 351.1931.

***tert*-Butyl (3-(2,2-dimethyl-4-phenylbutyl)phenyl)carbamate (14).**



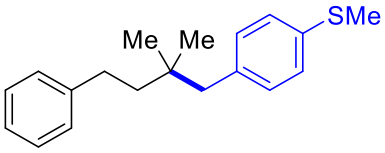
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 86% yield (45.6 mg, 0.129 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.28 –7.26 (m, 2H), 7.21 – 7.15 (m, 4H), 7.13 (s, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.41 (dr, 1H), 2.66 – 2.61 (m, 2H), 2.55 (s, 2H), 1.54 – 1.52 (m, 11H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 143.3, 140.2, 137.8, 128.4, 128.3, 128.2, 125.5, 125.4, 48.3, 44.4, 34.4, 30.8, 28.4, 26.9.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{23}H_{31}NNaO_2)^+$: m/z 376.2247; found: 376.2246.

(4-(2,2-Dimethyl-4-phenylbutyl)phenyl)(methyl)sulfane (15).



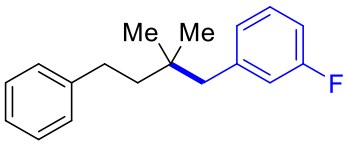
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 73% yield (31.2 mg, 0.110 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.18 – 7.16 (m, 5H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.66 – 2.60 (m, 2H), 2.53 (s, 2H), 2.47 (s, 3H), 1.53 – 1.50 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 136.3, 135.3, 131.1, 128.3, 128.3, 126.3, 125.6, 47.9, 44.2, 34.4, 30.8, 26.7, 16.1.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{24}NaS)^+$: m/z 307.1491; found: 307.1496.

1-(2,2-Dimethyl-4-phenylbutyl)-3-fluorobenzene (16).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 82% yield (31.5 mg, 0.123 mmol) as a colorless oil.

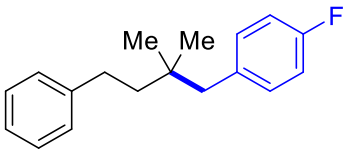
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.28 (m, 2H), 7.24 – 7.20 (m, 1H), 7.20 – 7.13 (m, 3H), 6.96 – 6.88 (m, 2H),6.87 – 6.85(m, 1H), 2.67 – 2.60 (m, 2H), 2.57 (s, 2H), 1.55 – 1.49 (m, 2H), 0.95 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (d, *J* = 244.9 Hz), 143.1, 141.8 (d, *J* = 7.1 Hz), 129.0 (d, *J* = 8.3 Hz), 128.4, 128.3, 126.2 (d, *J* = 2.7 Hz), 125.6, 117.3 (d, *J* = 21.3 Hz), 112.7 (d, *J* = 20.9 Hz), 48.2, 44.3, 34.4, 30.8, 26.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.47, -114.49, -114.49, -114.50, -114.51, -114.52.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{18}H_{21}FNa)^+$: m/z 279.1520; found: 279.1517.

1-(2,2-Dimethyl-4-phenylbutyl)-4-fluorobenzene (17).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 96% yield (36.9 mg, 0.144 mmol) as a colorless oil.

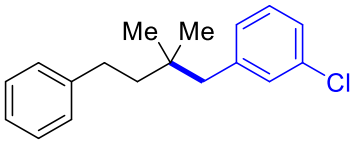
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.18 – 7.17 (m, 3H), 7.10 – 7.08 (m, 2H), 6.96 –6.93 (m, 2H), 2.67 – 2.59 (m, 2H), 2.55 (s, 2H), 1.53 – 1.48 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.4 Hz), 143.2, 134.8 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 7.7 Hz), 128.4, 128.3, 125.6, 114.4 (d, *J* = 20.9 Hz),47.6, 44.2, 34.3, 30.8, 26.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.82, -117.83, -117.83, -117.84, -117.85, -117.86, -117.87.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{18}H_{21}FNa^+)$: m/z 279.1520; found: 279.1525.

1-Chloro-3-(2,2-dimethyl-4-phenylbutyl)benzene (18).



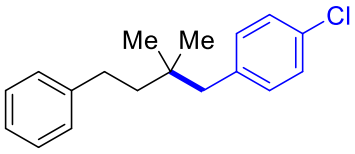
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 69% yield (28.2 mg, 0.104 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.16 (m, 5H), 7.15 (s, 1H), 7.04 – 7.01 (m, 1H), 2.67 – 2.60 (m, 2H), 2.55 (s, 2H), 1.54 – 1.51 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 141.3, 133.5, 130.5, 128.9, 128.7, 128.4, 128.3, 126.0, 125.6, 48.0, 44.3, 34.4, 30.8, 26.7.

HRMS (ESI) calcd for [M+Na^+] $(C_{18}H_{21}ClNa)^+$: m/z 295.1224, 297.1195; found: 295.1223, 297.1192.

1-Chloro-4-(2,2-dimethyl-4-phenylbutyl)benzene (19).



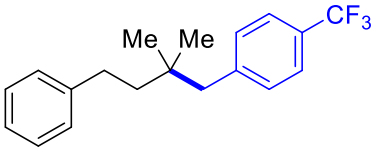
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 78% yield (31.9 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 7.18 – 7.16 (m, 3H), 7.07 (d, *J* = 8.3 Hz, 2H), 2.66 – 2.59 (m, 2H), 2.54 (s, 2H), 1.53 – 1.49 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 137.6, 131.8, 128.4, 128.3, 127.8, 125.6, 47.8, 44.2, 34.4, 30.8, 26.6.

HRMS (ESI) calcd for [M+Na^+] $(C_{18}H_{21}ClNa)^+$: m/z 295.1224, 297.1195; found: 295.1230, 297.1200.

1-(2,2-Dimethyl-4-phenylbutyl)-4-(trifluoromethyl)benzene (20).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 56% yield (25.7 mg, 0.084 mmol) as a colorless oil.

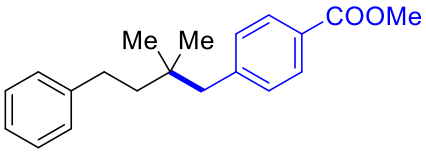
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.17 (m, 3H), 2.66 – 2.63 (m, 4H), 1.55 – 1.52 (m, 2H), 0.95 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4 (q, *J* = 243.6 Hz), 143.2, 134.8 (q, *J* = 3.1 Hz), 131.8 (q, *J* = 7.7 Hz), 128.4, 128.3, 125.6, 114.4 (d, *J* = 20.9 Hz), 47.6, 44.2, 34.3, 30.8, 26.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.25.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{21}F_3Na)^+$: m/z 329.1488; found: 329.1487.

Methyl 4-(2,2-dimethyl-4-phenylbutyl)benzoate (21).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 40% yield (17.8 mg, 0.060 mmol) as a white solid.

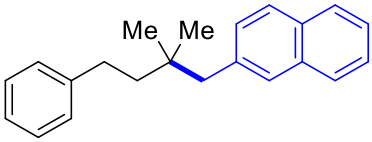
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.66 – 2.61 (m, 2H), 2.54 (s, 2H), 2.32 (s, 3H), 1.54 – 1.49 (m, 2H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4 136.1, 135.2, 130.5, 128.4, 128.3, 128.3, 125.5, 47.9, 44.2, 34.3, 30.8, 26.8.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{20}H_{24}NaO_2)^+$: m/z 319.1669; found: 319.1668.

M.p. 54–55 º C.

2-(2,2-Dimethyl-4-phenylbutyl)naphthalene (22).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 68% yield (29.4 mg, 0.102 mmol) as a white solid.

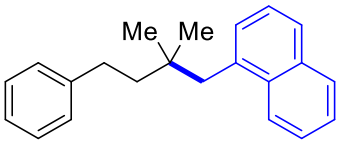
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.47 – 7.39 (m, 2H), 7.31 – 7.30 (m, 1H), 7.29 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 2.75 (s, 2H), 2.71 – 2.65 (m, 2H), 1.60 – 1.56 (m, 2H), 0.99 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 136.9, 133.2, 132.0, 129.5, 128.8, 128.3, 127.5, 127.0, 125.7, 125.6, 125.1, 48.5, 44.4, 34.8, 30.9, 26.9.

HRMS (ESI) calcd for [M+Na$^+$] $(C_{22}H_{24}Na)^+$: m/z 311.1770; found: 311.1773.

M.p. 64–65 ° C.

1-(2,2-Dimethyl-4-phenylbutyl)naphthalene (23).



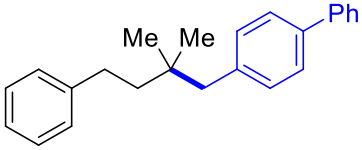
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 52% yield (22.5 mg, 0.078 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.42(m, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.20 – 7.16 (m, 3H), 3.10 (s, 2H), 2.73 – 2.66 (m, 2H), 1.73 – 1.68 (m, 2H), 0.97 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 135.8, 133.9, 133.4, 128.9, 128.6, 128.3, 126.7, 125.6, 125.3, 125.1, 125.1, 124.9, 45.6, 43.3, 35.7, 30.9, 27.1.

HRMS (ESI) calcd for [M+Na$^+$] $(C_{22}H_{24}Na)^+$: m/z 311.1770; found: 311.1773.

4-(2,2-Dimethyl-4-phenylbutyl)-1,1'-biphenyl (24).



This compound was prepared according to *Method B*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 86% yield (40.6 mg, 0.129 mmol) as a white solid.

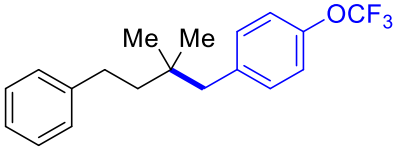
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 –7.41 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.23 – 7.16 (m, 5H), 2.69 – 2.63 (m, 2H), 2.62 (s, 2H), 1.59 – 1.54 (m, 2H), 0.98 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 141.0, 138.6, 138.3, 131.0, 128.7, 128.31, 127.0, 126.9, 126.4, 125.6, 48.0, 44.3, 34.5, 30.8, 26.8.

HRMS (ESI) calcd for [M+Na$^+$] $(C_{24}H_{26}Na)^+$: m/z 337.1927; found: 337.1925.

M.p. 71–72 ° C.

1-(2,2-Dimethyl-4-phenylbutyl)-4-(trifluoromethoxy)benzene (25).



This compound was prepared according to *Method B*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 84% yield (40.6 mg, 0.126 mmol) as a colorless oil.

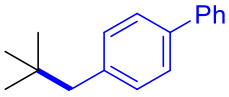
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 2H), 7.19 – 7.17 (m, 3H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.67 – 2.61 (m, 2H), 2.58 (s, 2H), 1.54 – 1.51 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6 (q, *J* = 1.6 Hz), 143.1, 137.9, 131.7, 128.4, 128.3, 125.7, 120.2, 47.7, 44.3, 34.4, 30.8, 26.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.86.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{21}F_3NaO)^+$: m/z 345.1437; found: 345.1433.

1-(*tert*-Butyl)-4-neopentylbenzene (26).[11]



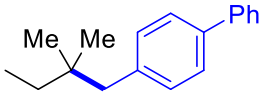
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (20.5 mg, 0.092mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.53 (s, 2H), 0.94 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 138.9, 138.6, 130.9, 128.7, 127.0, 126.9, 126.3, 31.8, 29.4.

HRMS (EI) calcd for $[M^+]$ $(C_{17}H_{20})^+$: m/z 224.1560; found: 224.1560.

1-(*tert*-Butyl)-4-(2,2-dimethylbutyl)benzene (27).[12]



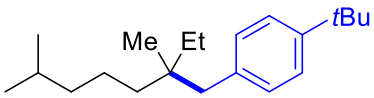
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum

ether) provided this compound in 61% yield (21.8 mg, 0.092 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.53 (s, 2H), 1.31 – 1.27 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.87 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 138.8, 138.5, 131.0, 128.7, 127.0, 126.9, 126.3, 47.7, 34.3, 26.3, 8.6.

1-(*tert*-Butyl)-4-(2-ethyl-2,6-dimethylheptyl)benzene (28).



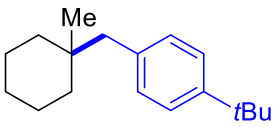
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 78% yield (33.8 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 2.46 (s, 2H), 1.56 – 1.53 (m, 1H), 1.31 (s, 9H), 1.27 – 1.07 (m, 8H), 0.89 – 0.88 (m, 6H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.77 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 136.4, 130.2, 124.4, 45.0, 40.0, 38.6, 36.6, 34.3, 31.0, 31.0, 28.0, 24.4, 22.7, 21.4, 8.2.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{21}H_{36}Na)^+$: m/z 311.2709; found: 311.2707.

1-(*tert*-Butyl)-4-((1-methylcyclohexyl)methyl)benzene (29).



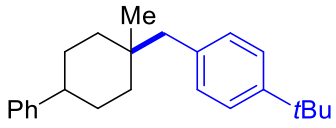
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 73% yield (26.8 mg, 0.110 mmol) as a colorless oil

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 2.49 (s, 2H), 1.55 – 1.50 (m, 2H), 1.48 – 1.36 (m, 4H), 1.33 – 1.28 (m, 13H), 0.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 136.1, 130.3, 124.4, 37.7, 34.3, 34.0, 33.3, 31.4, 28.2, 26.5, 22.2.

HRMS (EI) calcd for $[M+H^+]$ $(C_{18}H_{29})^+$: m/z 245.2264; found: 245.2191.

1-(*tert*-Butyl)-4-((1-methyl-4-phenylcyclohexyl)methyl)benzene (30).



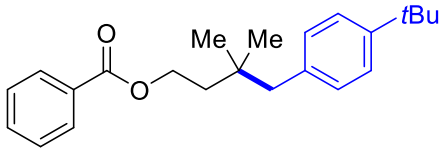
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 76% yield (36.5 mg, 0.114 mmol) as a colorless oil with a dr value of 4.6:1. The dr value was determined by the characteristic ^1H NMR peaks of the methyl groups attached to the cyclohexane rings of the two isomers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 6H), 7.24 – 7.22 (m, 1H), 7.11 – 7.10 (m, 2H), 2.71 (s, 2H), 2.55 – 2.51 (m, 1H), 1.92 – 1.84 (m, 2H), 1.80 – 1.77 (m, 2H), 1.67 – 1.65 (m, 2H), 1.33 – 1.30 (m, 11H), 0.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 147.6, 136.3, 130.2, 128.3, 126.9, 125.9, 124.6, 44.4, 41.3, 37.8, 34.3, 33.4, 31.4, 29.9, 29.7.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{24}H_{32}Na)^+$: m/z 343.2396; found: 343.2396.

4-(4-(*tert*-Butyl)phenyl)-3,3-dimethylbutyl benzoate (31).



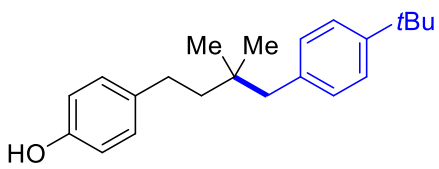
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% diethyl ether in petroleum ether) provided this compound in 68% yield (34.5 mg, 0.102 mmol) as a colorless oil

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 4.45 (t, J = 7.3 Hz, 2H), 2.57 (s, 2H), 1.75 (t, J = 7.3 Hz, 2H), 1.32 (s, 9H), 0.99 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 148.7, 135.5, 132.8, 130.5, 130.3, 129.5, 128.3, 124.7, 62.4, 48.4, 39.9, 34.3, 33.7, 31.4, 27.0.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{23}H_{30}NaO_2)^+$: m/z 361.21138; found: 361.2136.

4-(4-(4-(*tert*-Butyl)phenyl)-3,3-dimethylbutyl)phenol (32).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether) provided this compound in 92% yield (42.9 mg, 0.138 mmol) as a white solid.

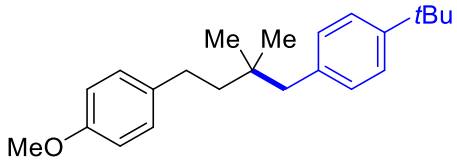
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.04(m, 4H), 6.75 (d, *J* = 6.5 Hz, 2H), 4.67 (dr, 1H), 2.59 – 2.55 (m, 2H), 2.53 (s, 2H), 1.52 – 1.47 (m, 2H), 1.31 (s, 9H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4, 148.5, 136.1, 135.6, 130.2, 129.4, 124.5, 115.1, 47.8, 44.4, 34.4, 31.4, 29.9, 26.8.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{22}H_{30}NaO)^+$: m/z 333.2189; found: 333.2180.

M.p. 98–99 ° C.

1-(*tert*-Butyl)-4-(4-(4-methoxyphenyl)-2,2-dimethylbutyl)benzene (33).



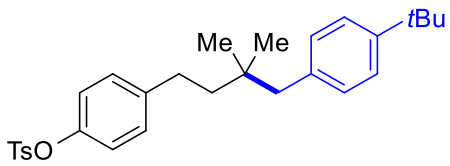
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 94% yield (45.8 mg, 0.141 mmol) as a colorless oil

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.07 (m, 4H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.61 – 2.56 (m, 2H), 2.53 (s, 2H), 1.52 – 1.48 (m, 2H), 1.31 (s, 9H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, CDCl3) δ 157.6, 148.5, 136.1, 135.4, 130.2, 129.2, 124.5, 113.7, 55.3, 47.8, 44.4, 34.4, 34.3, 31.4, 29.9, 26.8.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{19}H_{24}NaO)^+$: m/z 347.2345; found: 347.2344.

4-(4-(4-(*tert*-Butyl)phenyl)-3,3-dimethylbutyl)phenyl 4-methylbenzenesulfonate (34).



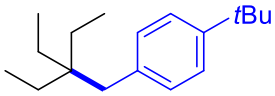
This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% diethyl ether in petroleum ether) provided this compound in 92% yield (64.1 mg, 0.138 mmol) as a colorless oil

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.07 (m, 4H), 6.87 (d, J = 8.4 Hz, 2H), 2.62 – 2.57 (m, 2H), 2.52 (s, 2H), 2.45 (s, 3H), 1.50 – 1.46 (m, 2H), 1.31 (s, 9H), 0.92 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 147.5, 145.2, 142.4, 135.9, 132.6, 130.2, 129.7, 129.3, 128.5, 124.6, 122.1, 47.8, 43.9, 34.3, 31.4, 30.2, 26.8, 21.7.

HRMS (ESI) calcd for $[M+Na^+]$ $(C_{29}H_{36}NaO_3S)^+$: m/z 487.2277; found: 487.2279.

1-(*tert*-Butyl)-4-(2,2-diethylbutyl)benzene (35).



This compound was prepared according to *Method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 40% yield (14.8 mg, 0.060 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 2.44 (s, 2H), 1.30 (s, 9H), 1.17 (q, *J* = 7.5 Hz, 6H), 0.85 (t, *J* = 7.5 Hz, 9H).

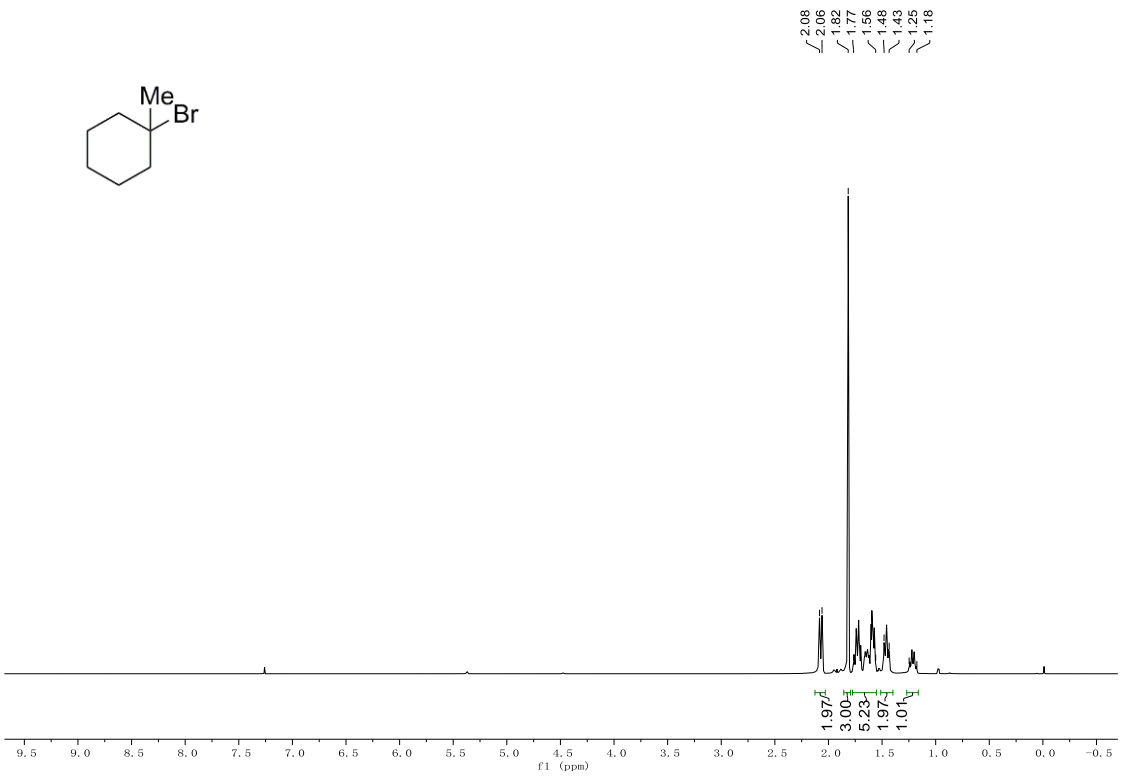
^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 136.4, 130.0, 124.5, 40.1, 39.1, 34.3, 31.4, 27.1, 7.7.

HRMS (EI) calcd for $[M+H^+]$ $(C_{18}H_{31})^+$: m/z 247.2420; found: 247.2471.

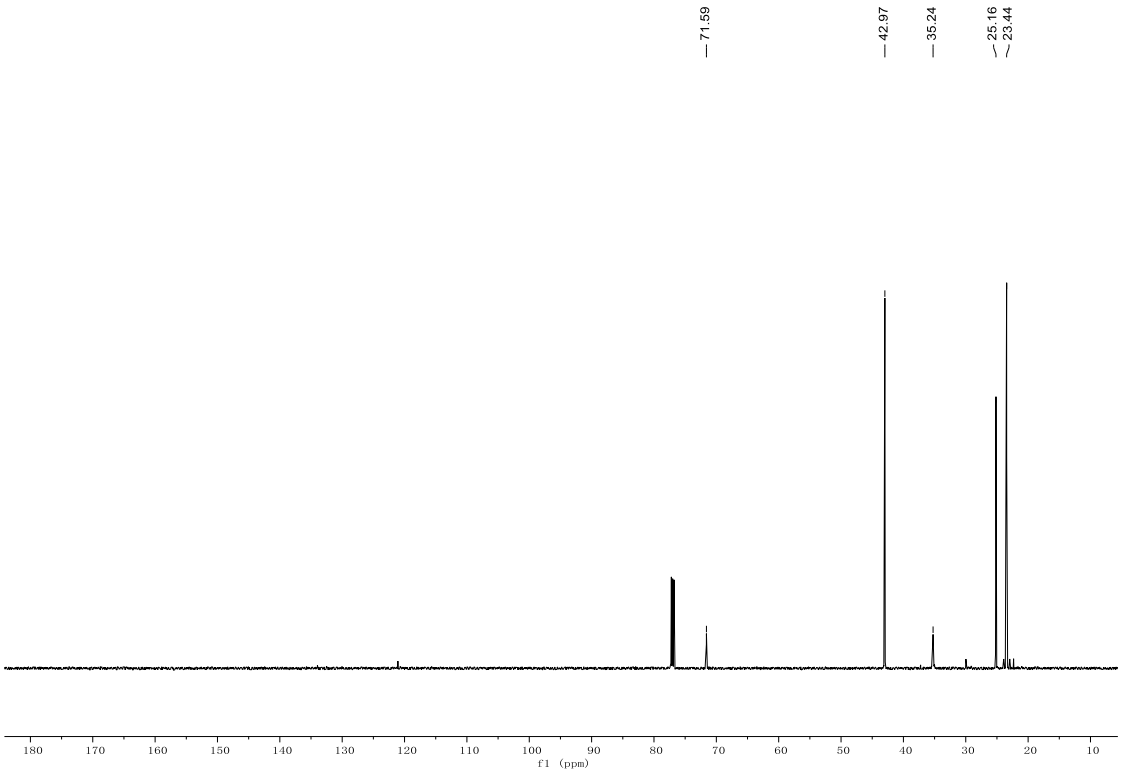
II. Spectral Data for Compounds

1-Bromo-1-methylcyclohexane:

^{1}H NMR (600 MHz, $CDCl_3$)

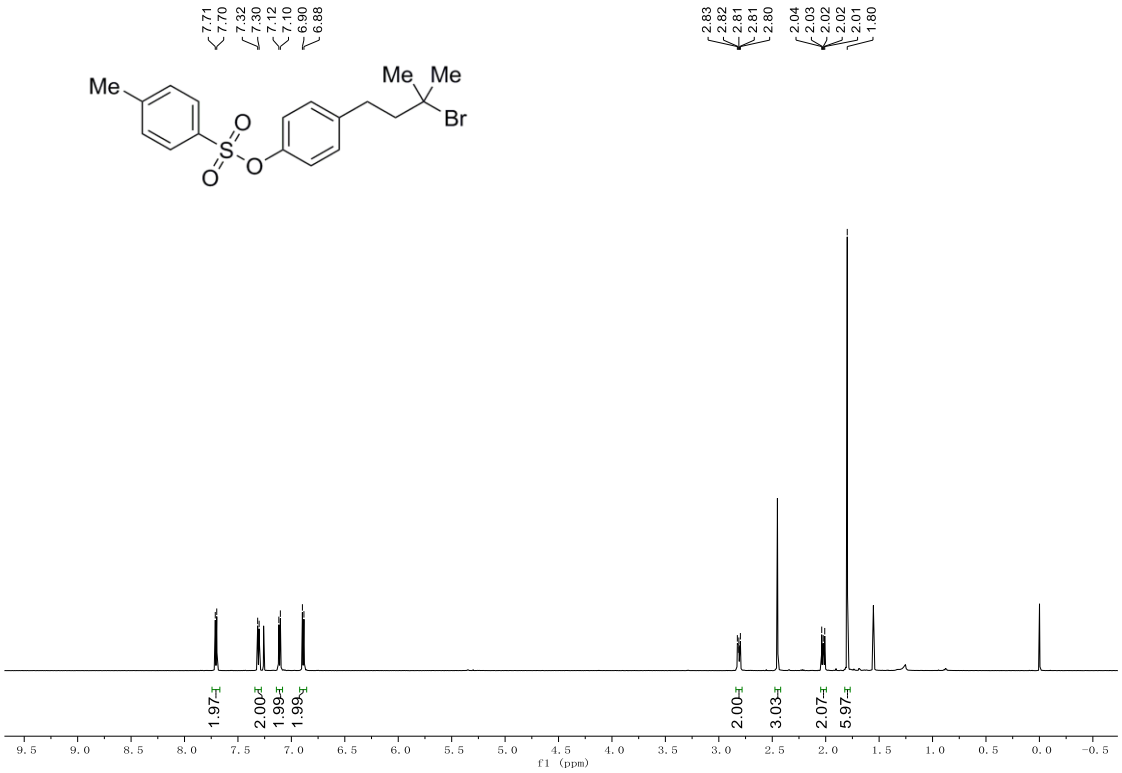


^{13}C NMR (151 MHz, $CDCl_3$)

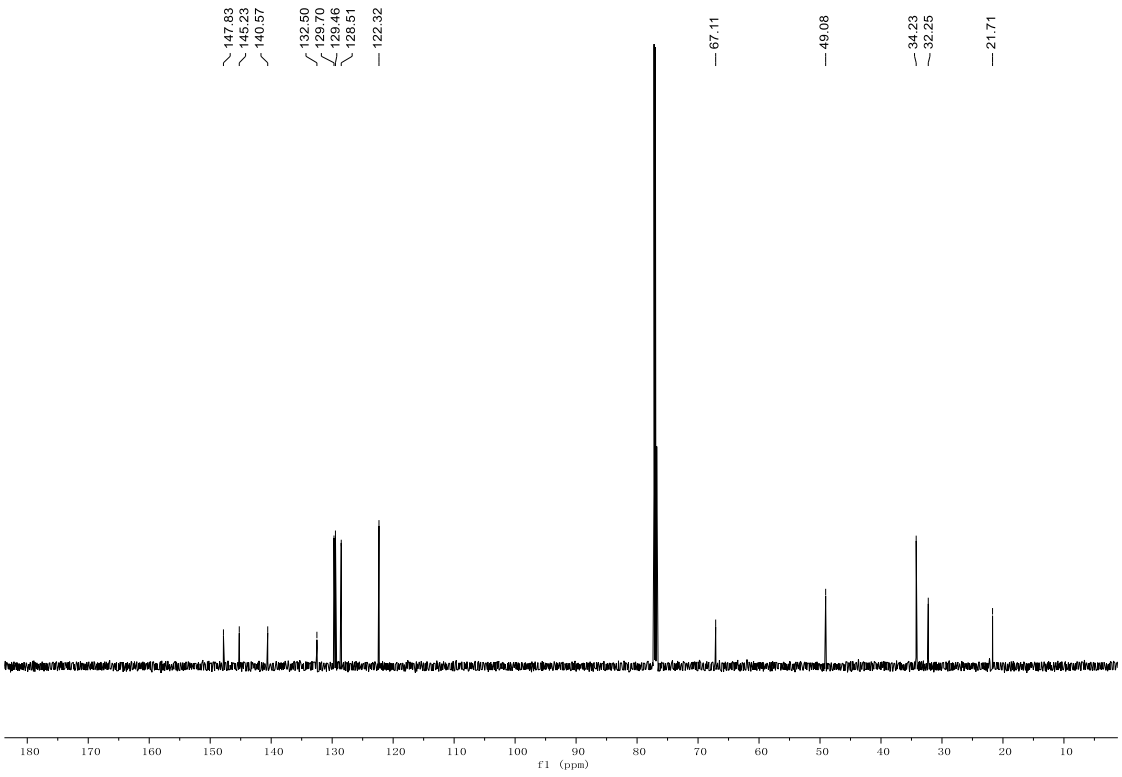


4-(3-Bromo-3-methylbutyl)phenyl 4-methylbenzenesulfonate:

^{1}H NMR (600 MHz, $CDCl_3$)

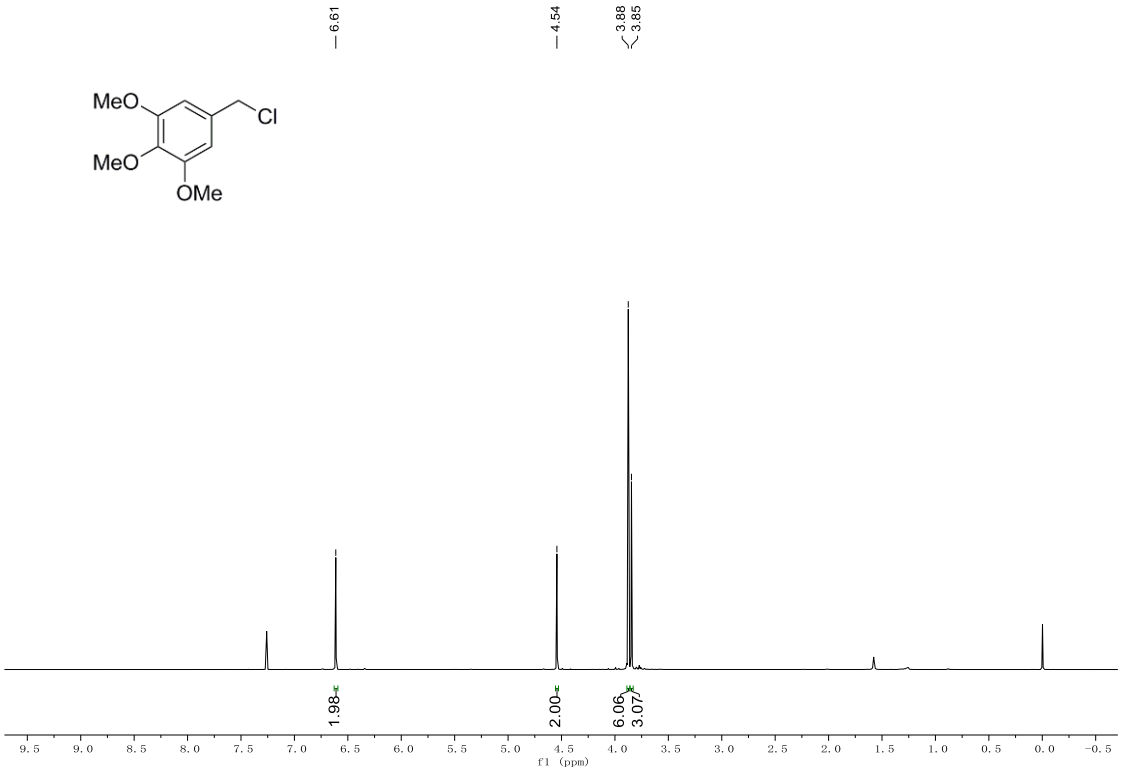


^{13}C NMR (151 MHz, $CDCl_3$)

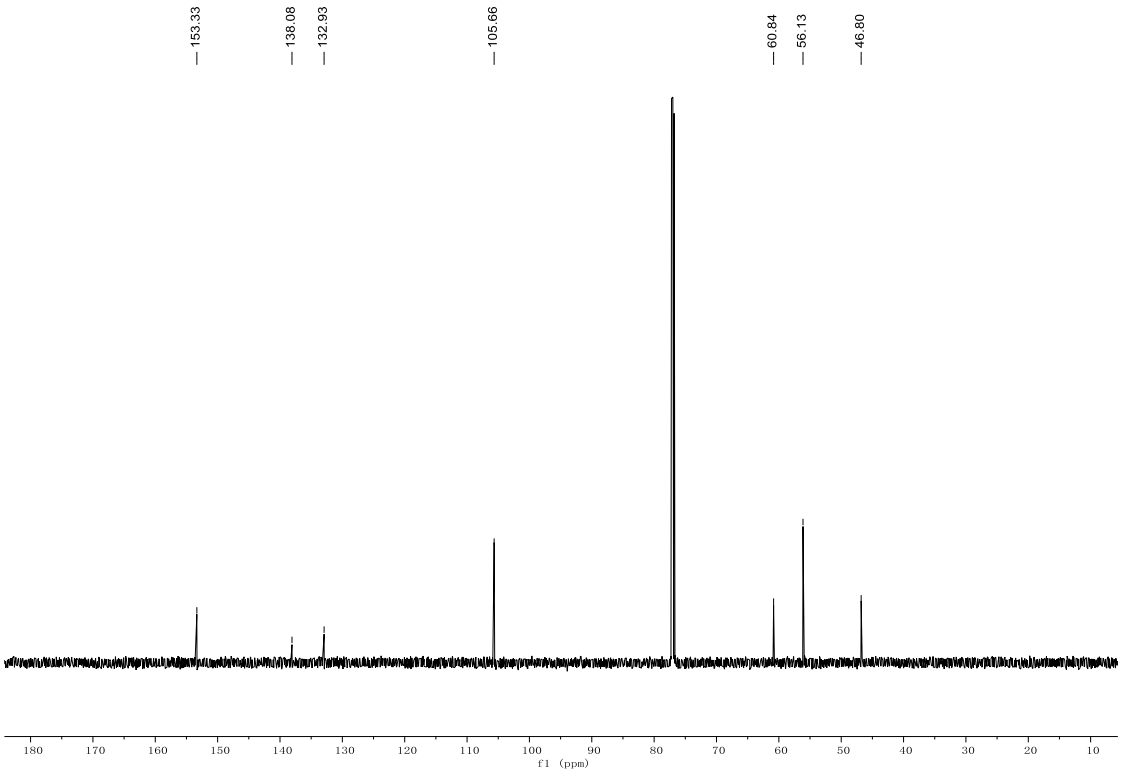


5-(Chloromethyl)-1,2,3-trimethoxybenzene:

^{1}H NMR (600 MHz, $CDCl_3$)

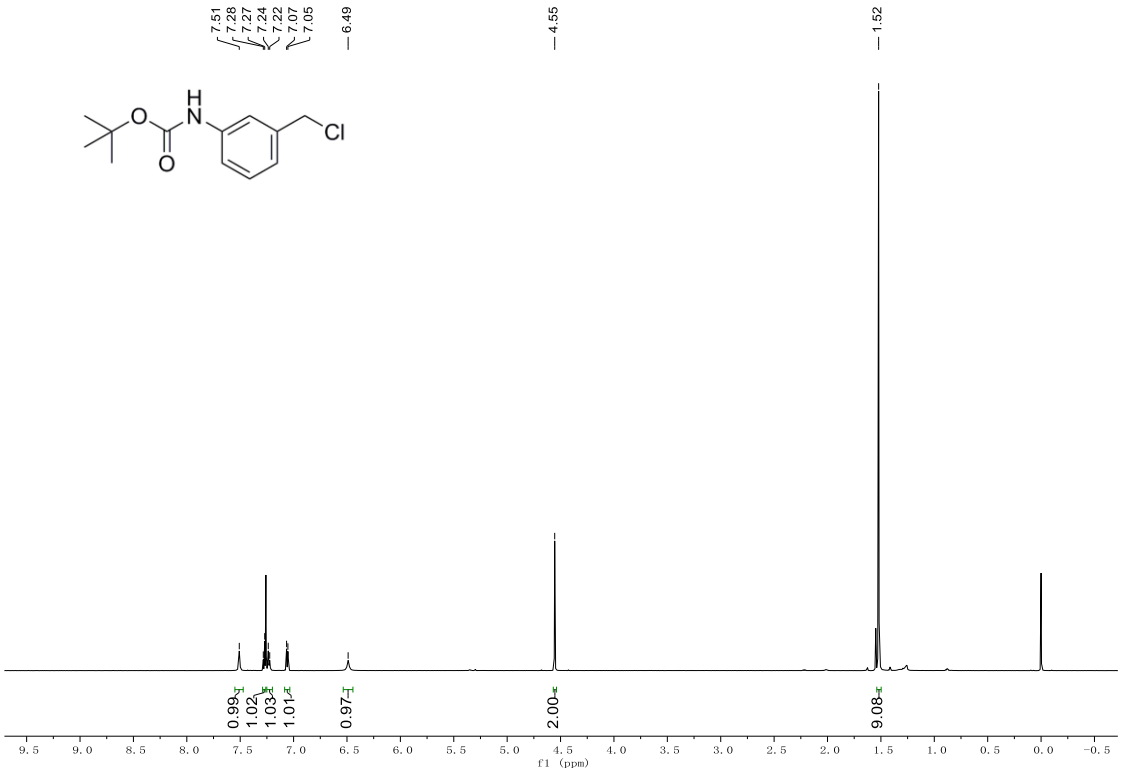


^{13}C NMR (151 MHz, $CDCl_3$)



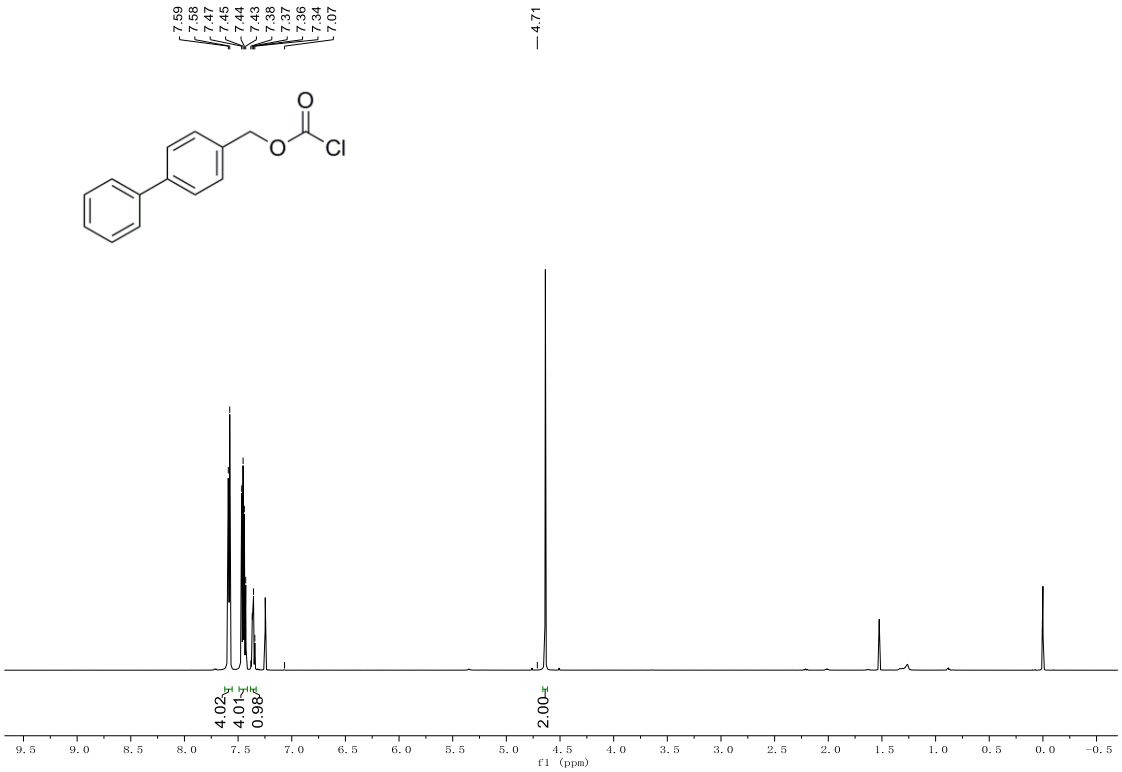
***tert*-Butyl (3-(chloromethyl)phenyl)carbamate.**

^{1}H NMR (600 MHz, $CDCl_3$)

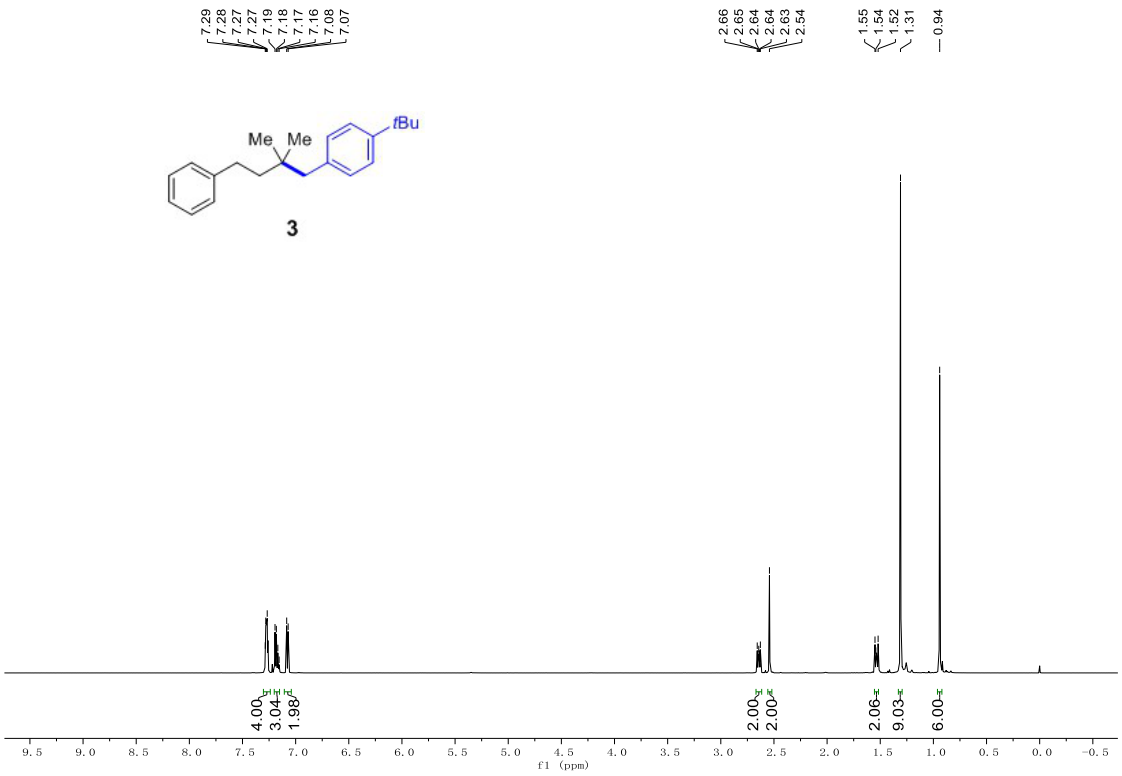


[1,1'-Biphenyl]-4-ylmethyl carbonochloridate:

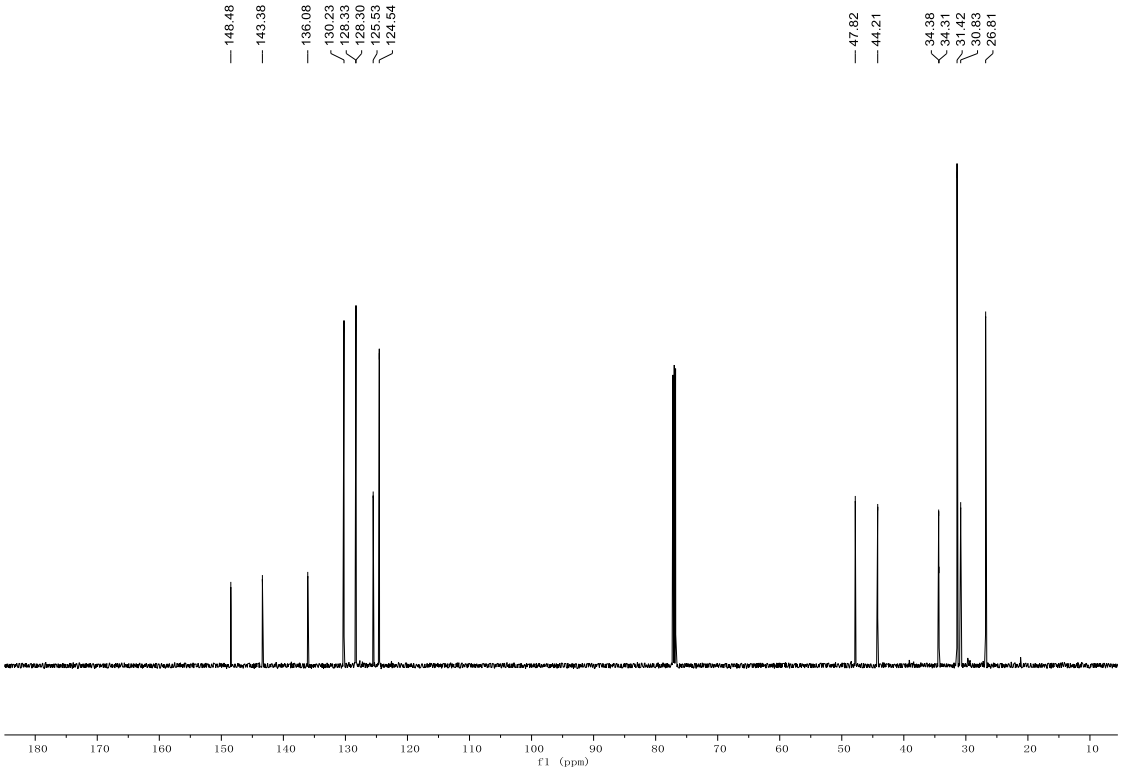
^{1}H NMR (600 MHz, $CDCl_3$)



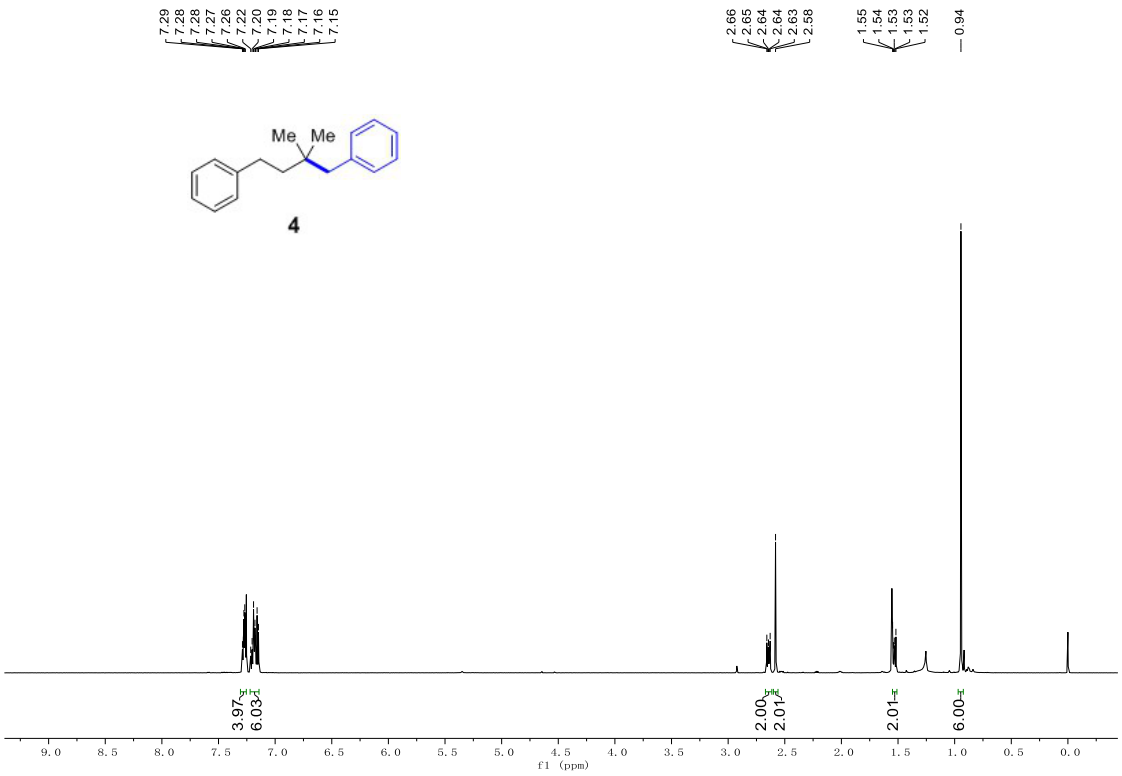
^{1}H NMR (600 MHz, $CDCl_3$) of **3**:



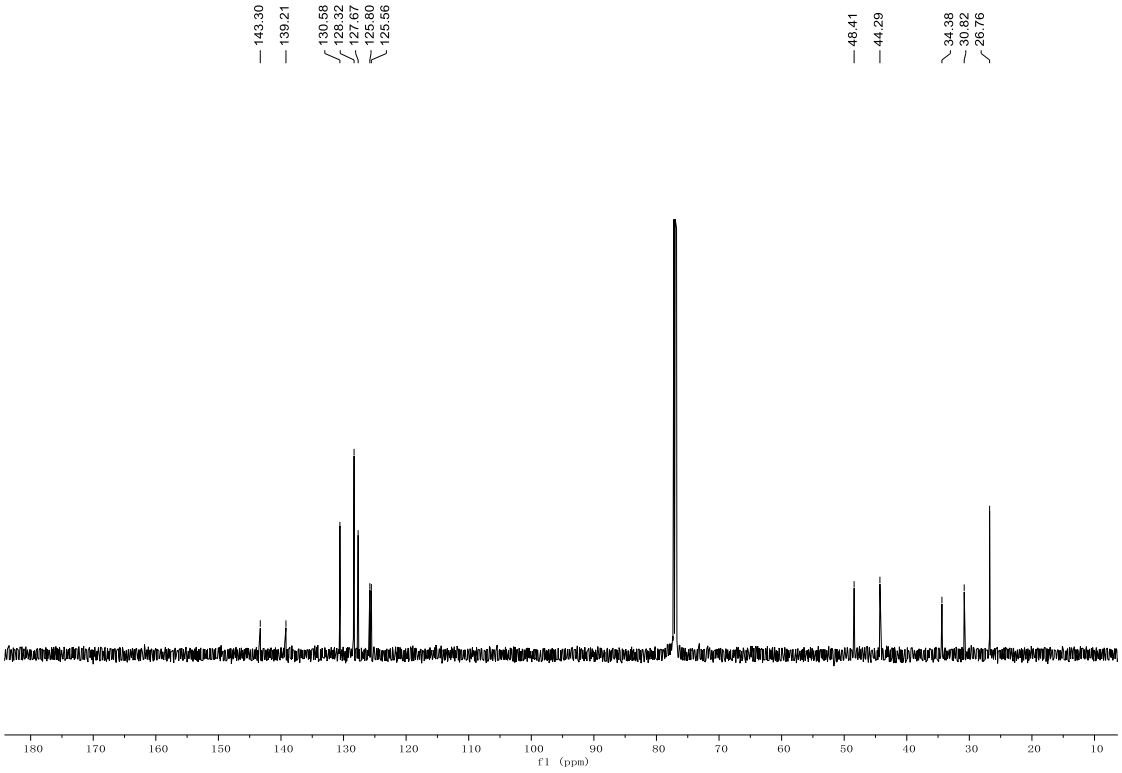
^{13}C NMR (151 MHz, $CDCl_3$) of **3**:



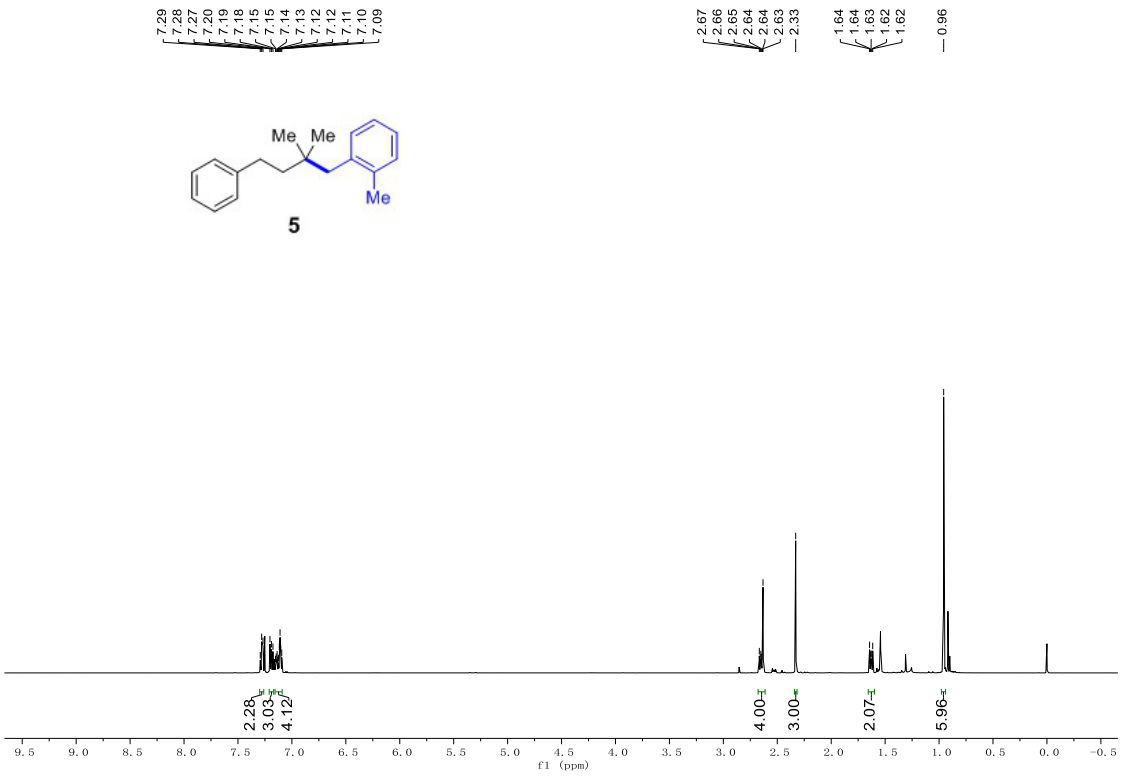
^{1}H NMR (600 MHz, $CDCl_3$) of **4**:



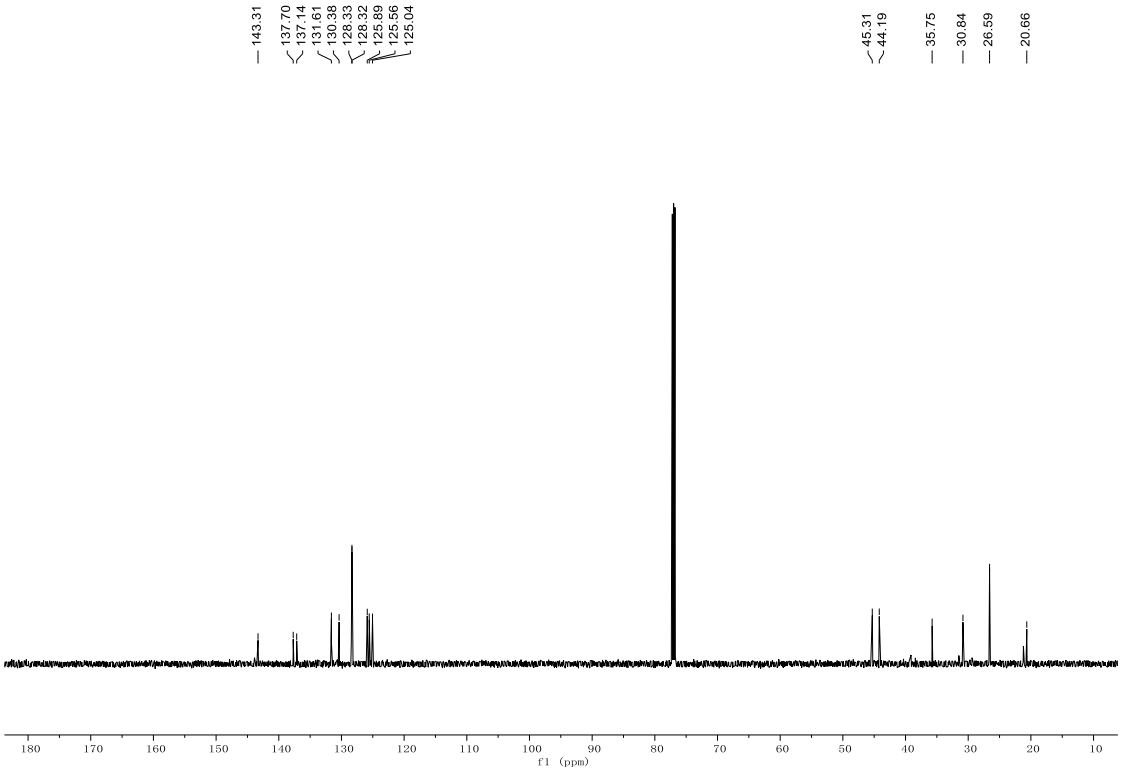
^{13}C NMR (151 MHz, $CDCl_3$) of **4**:



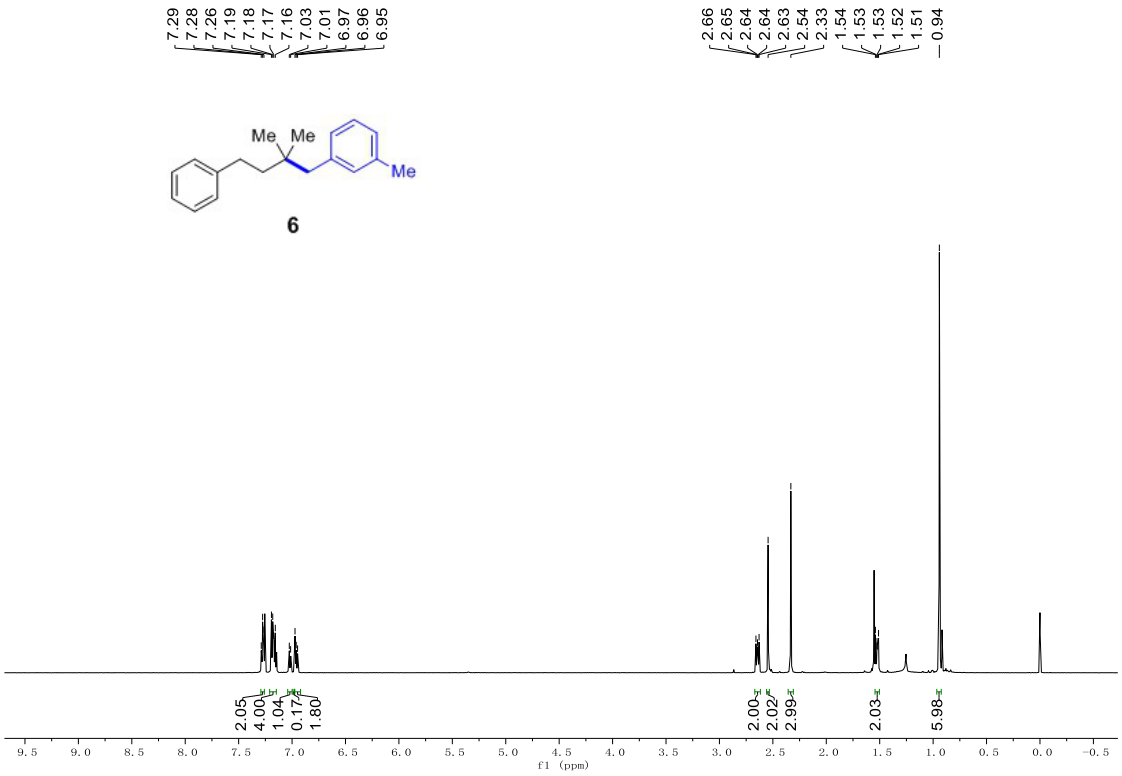
^{1}H NMR (600 MHz, $CDCl_3$) of **5**:



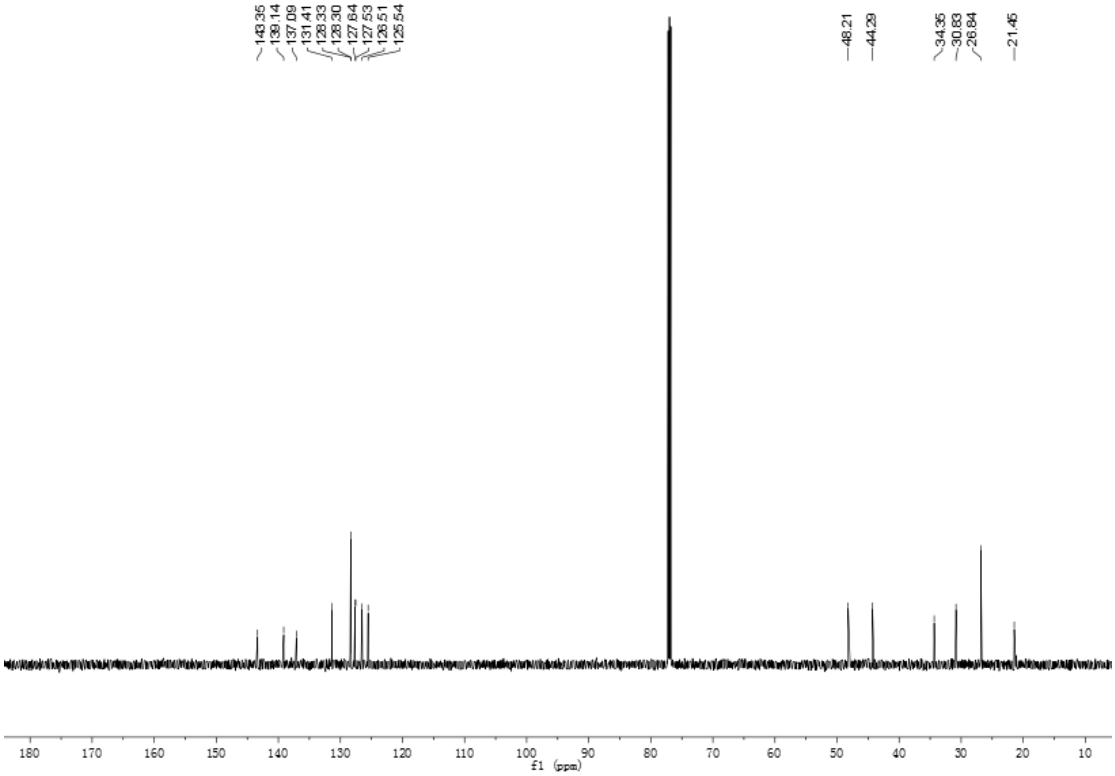
^{13}C NMR (151 MHz, $CDCl_3$) of **5**:



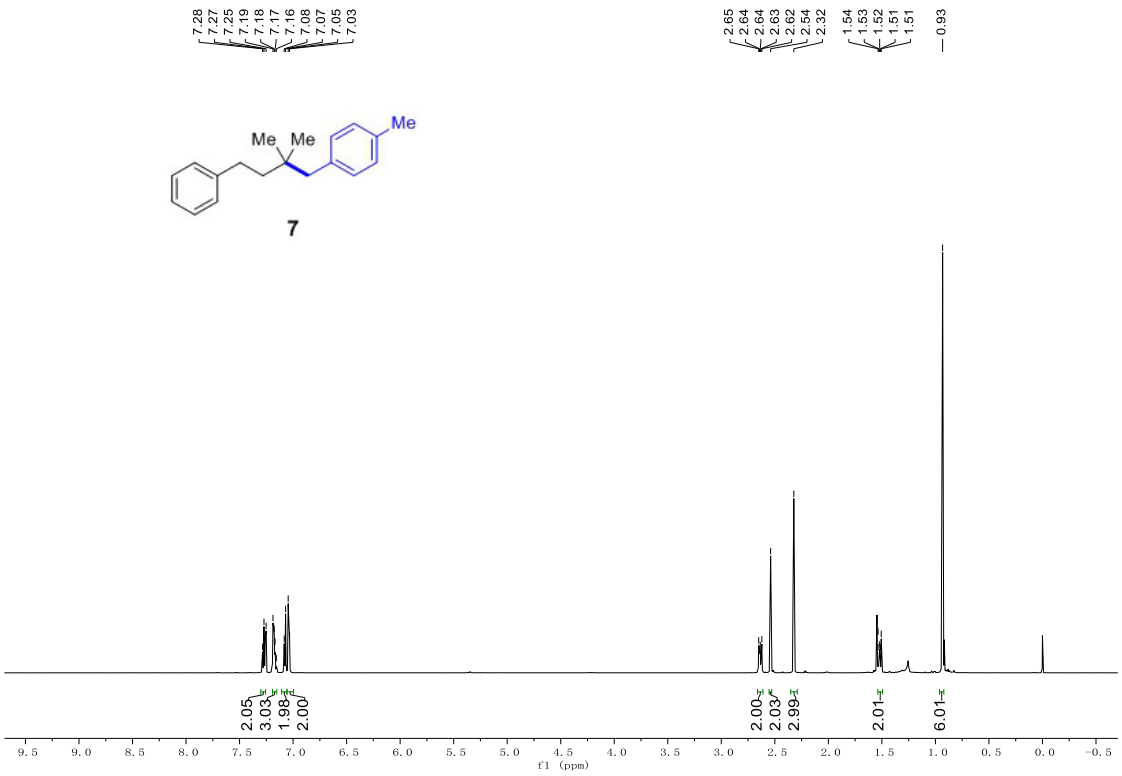
^{1}H NMR (600 MHz, $CDCl_3$) of **6**:



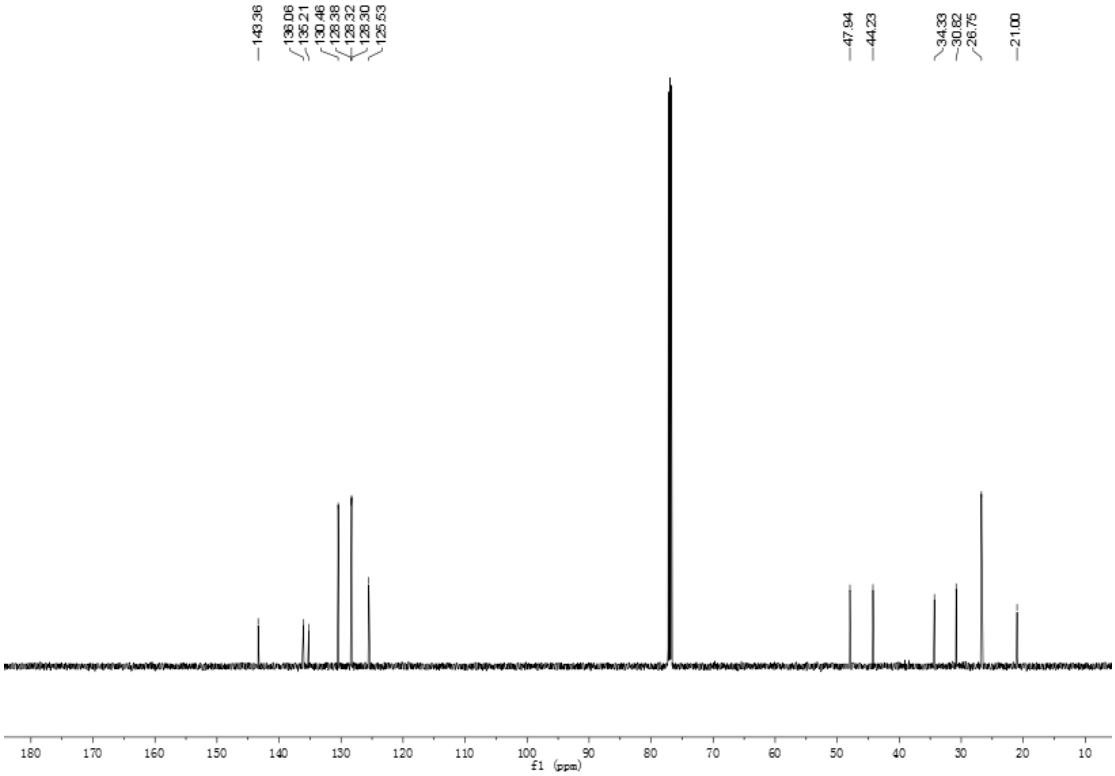
^{13}C NMR (151 MHz, $CDCl_3$) of **6**:



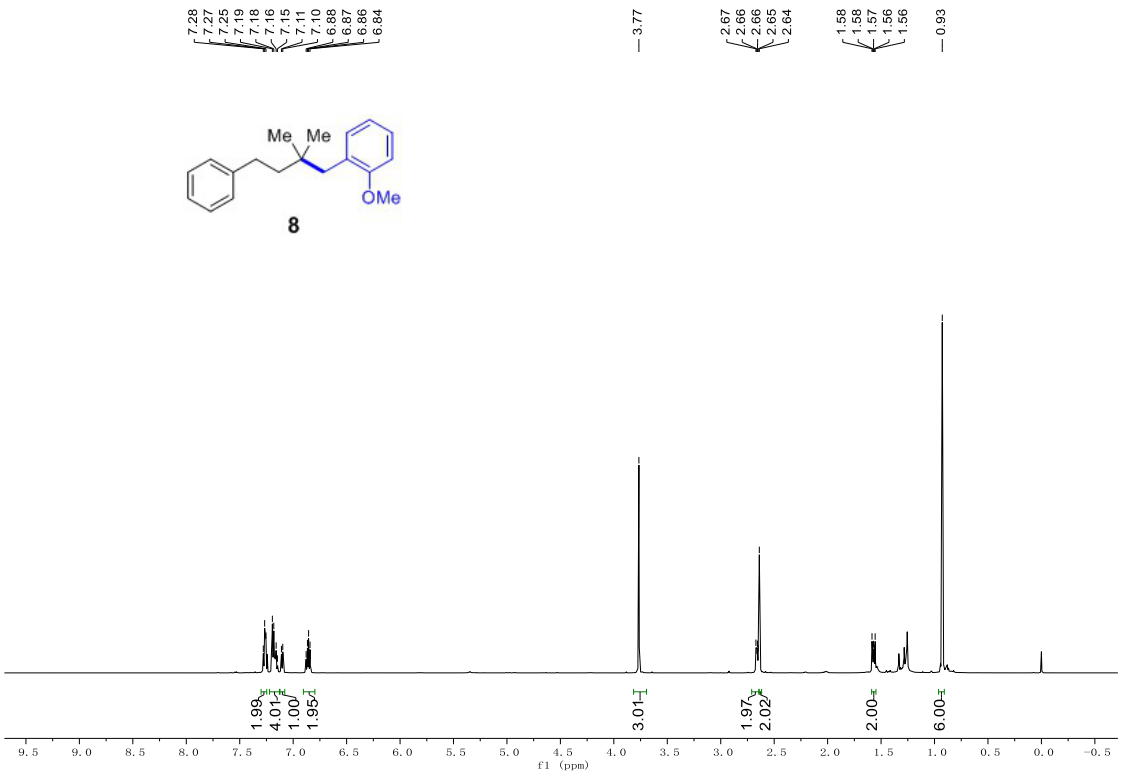
^{1}H NMR (600 MHz, $CDCl_3$) of **7**:



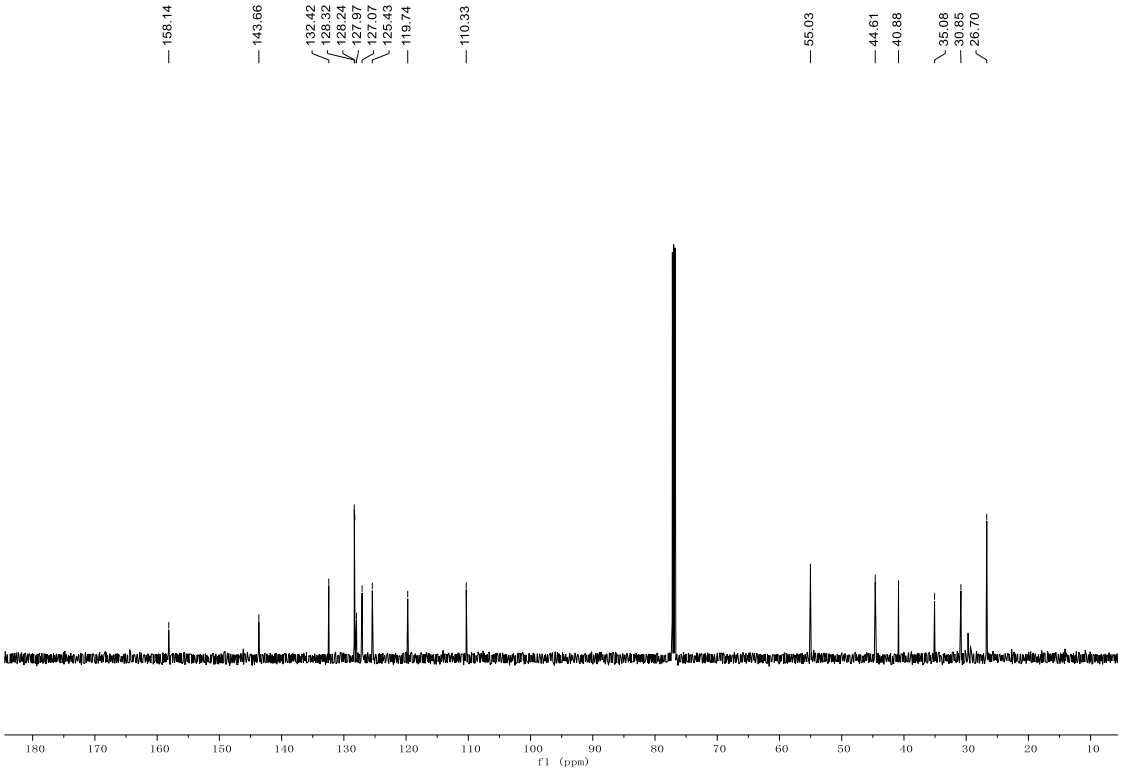
^{13}C NMR (151 MHz, $CDCl_3$) of **7**:



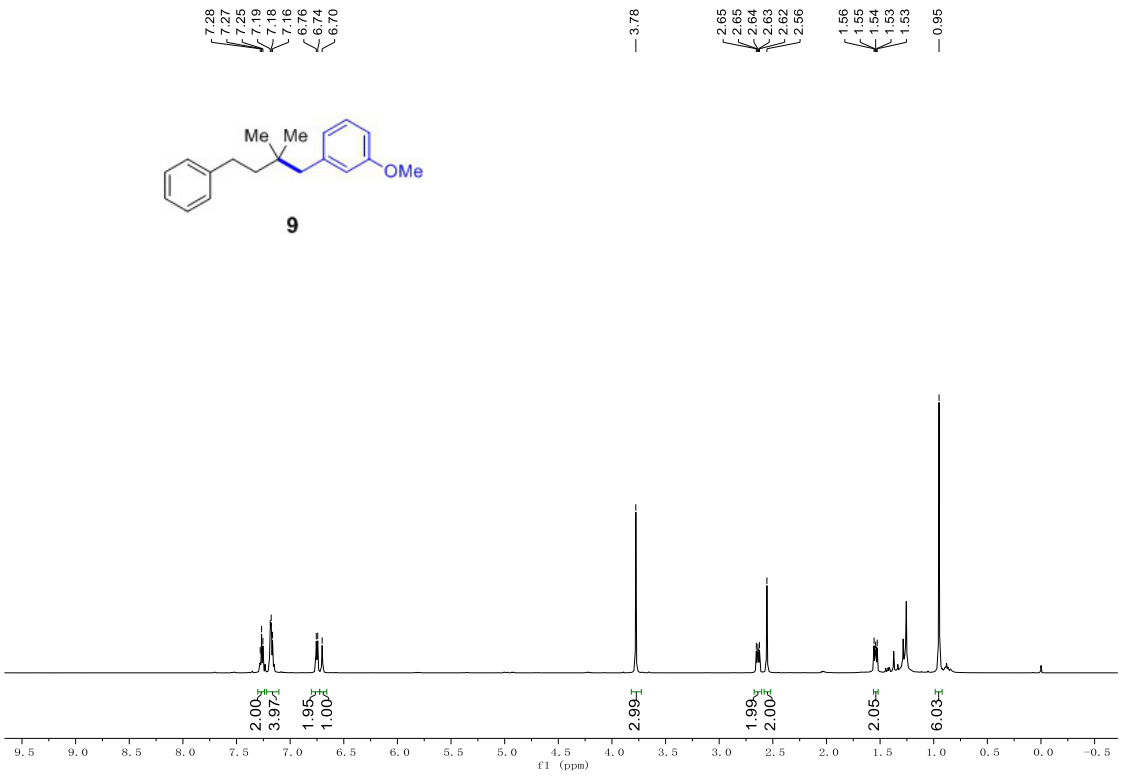
^{1}H NMR (600 MHz, $CDCl_3$) of **8**:



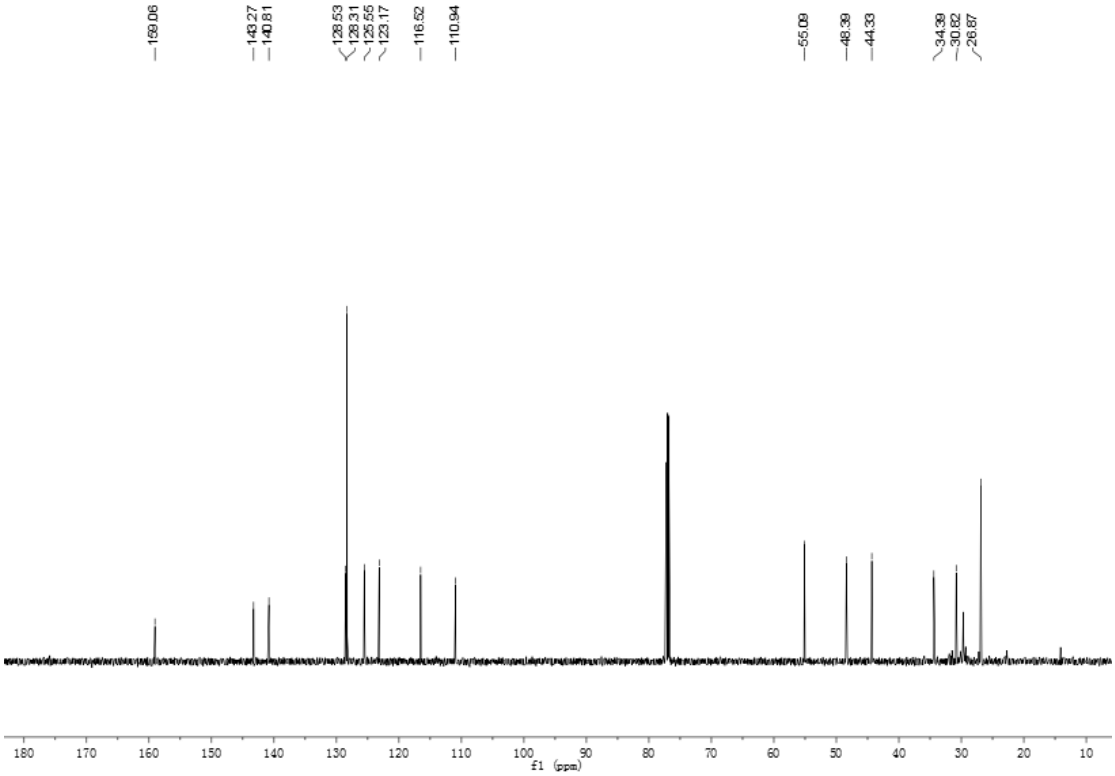
^{13}C NMR (151 MHz, $CDCl_3$) of **8**:



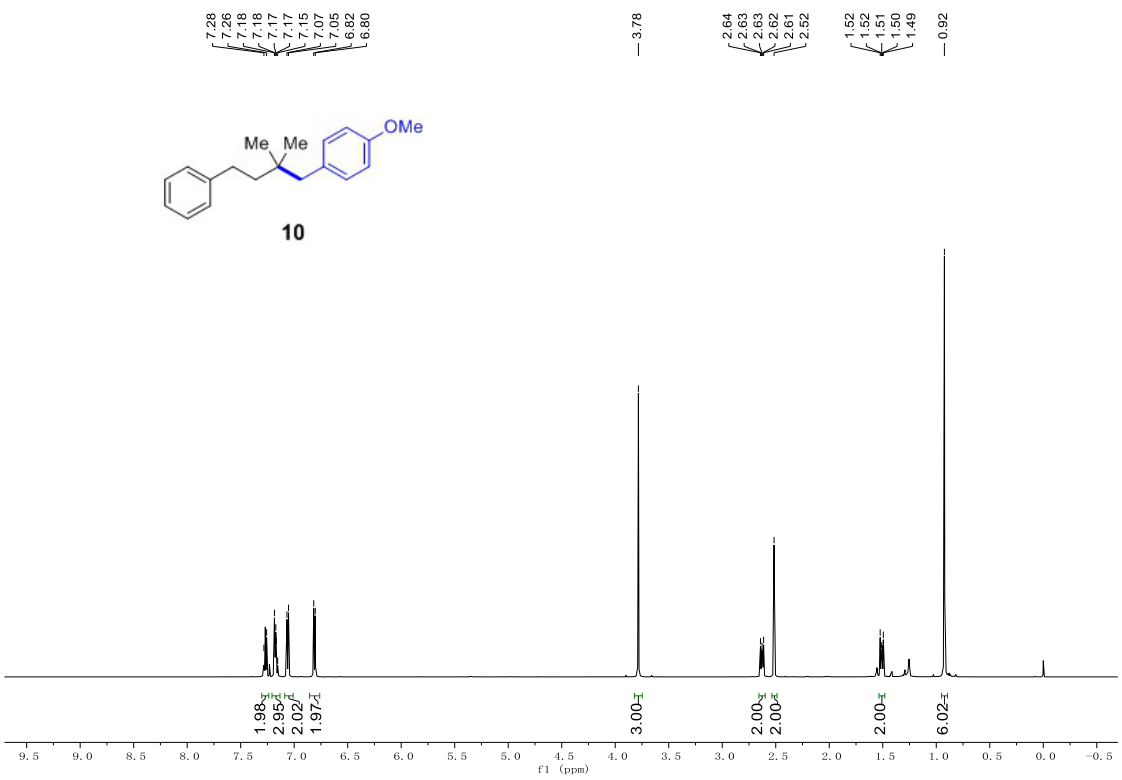
^{1}H NMR (600 MHz, $CDCl_3$) of **9**:



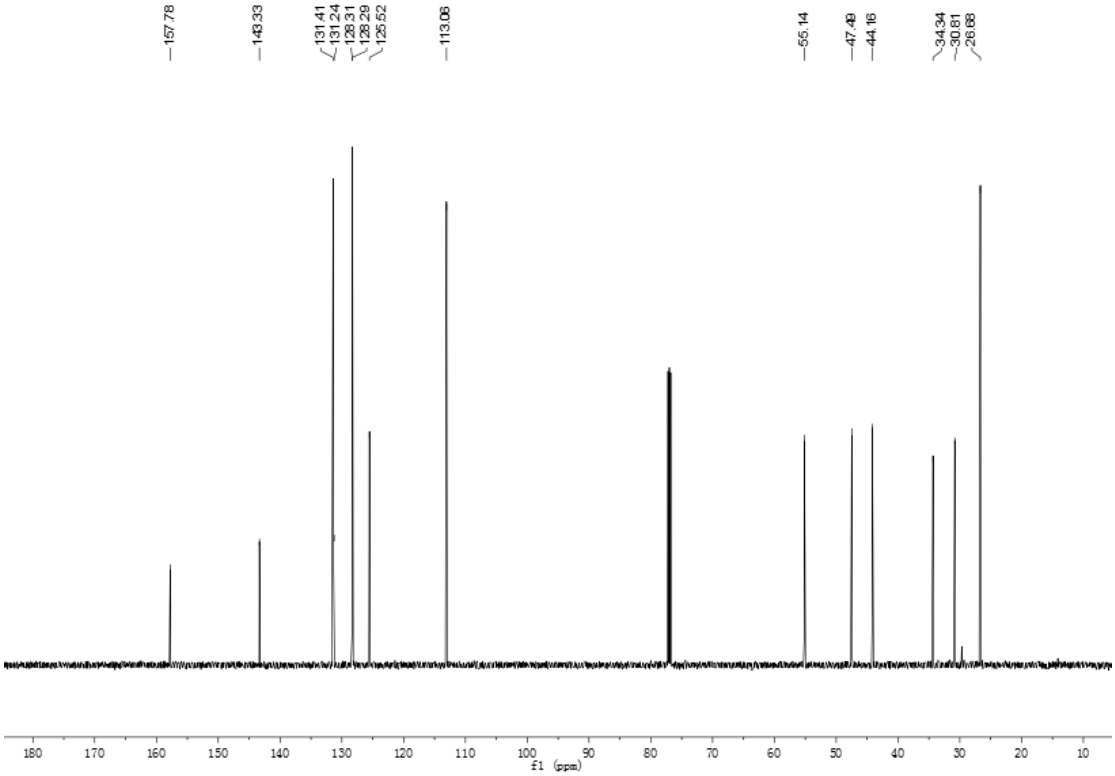
^{13}C NMR (151 MHz, $CDCl_3$) of **9**:



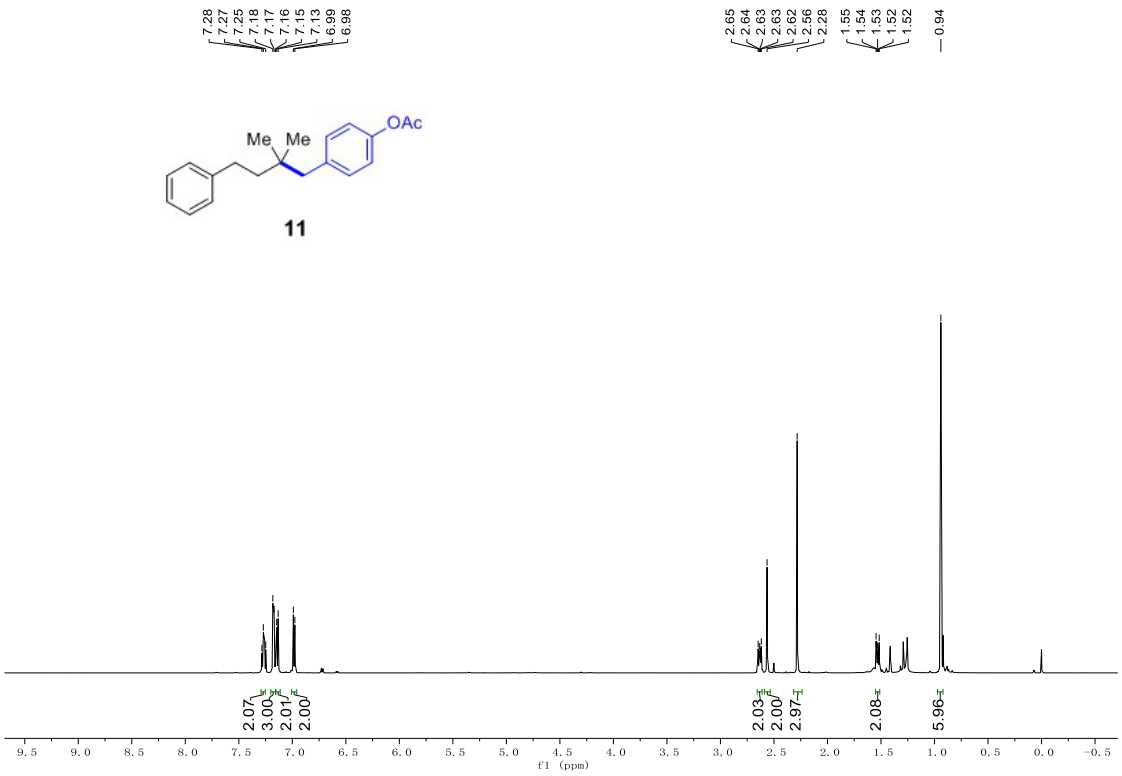
^{1}H NMR (600 MHz, $CDCl_3$) of **10**:



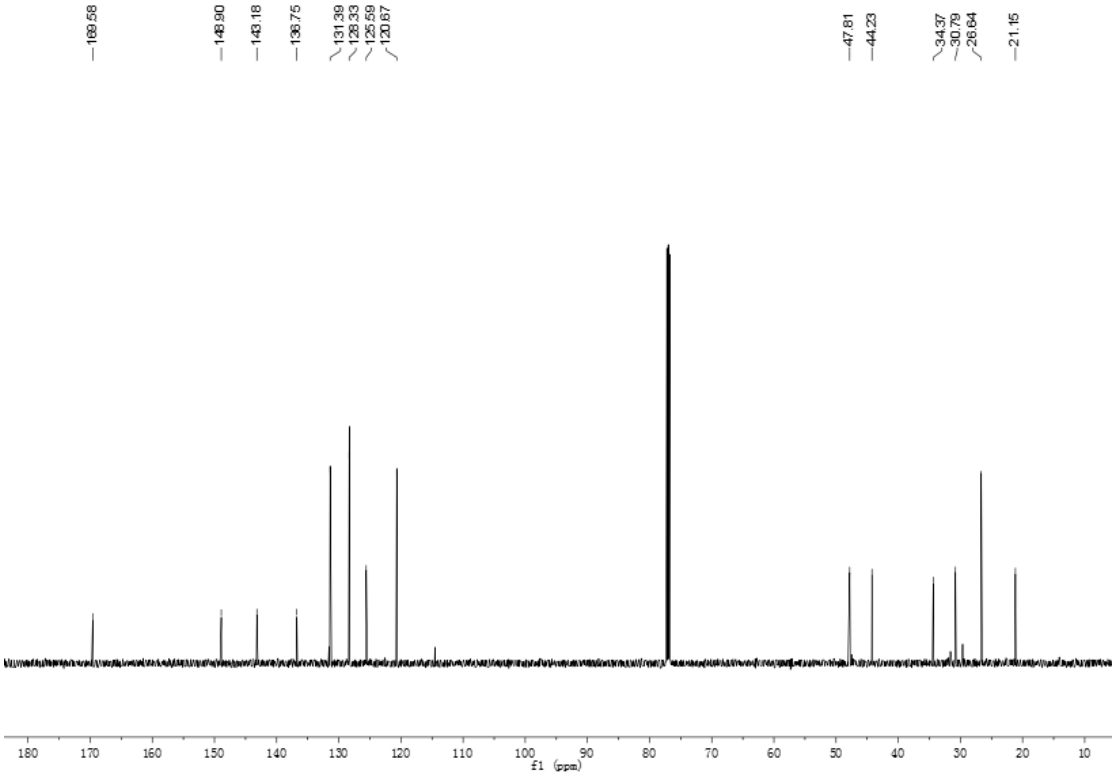
^{13}C NMR (151 MHz, $CDCl_3$) of **10**:



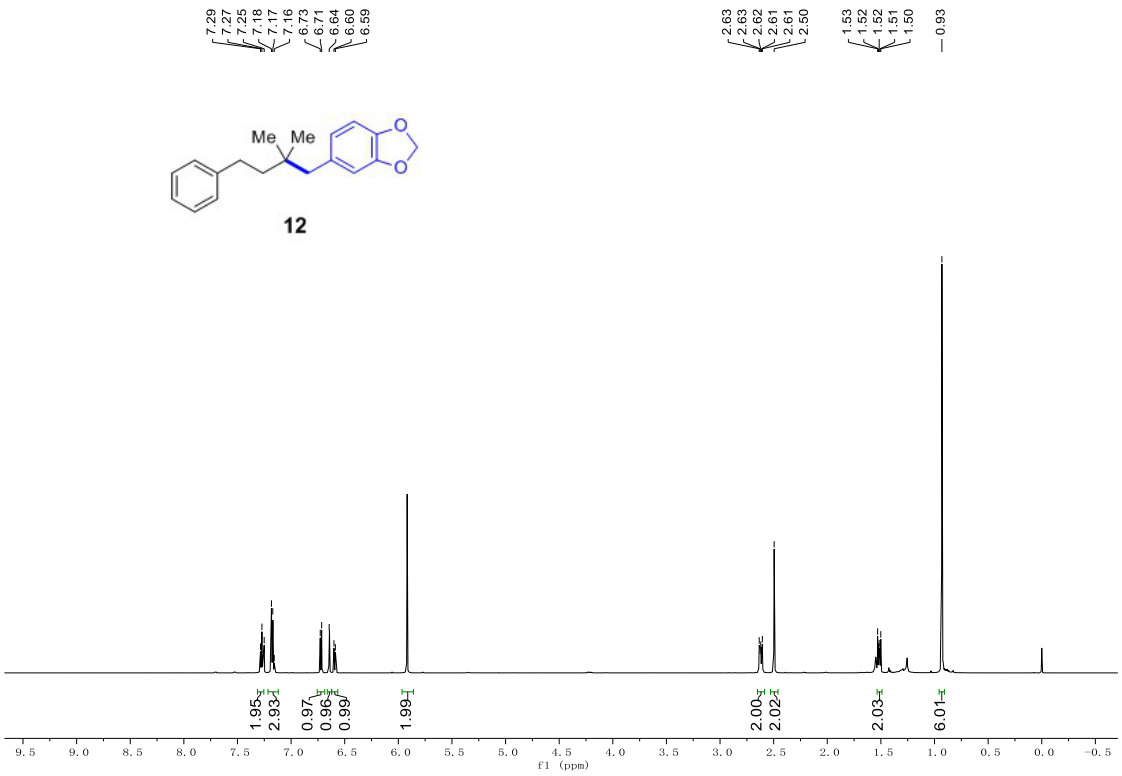
^{1}H NMR (600 MHz, $CDCl_3$) of **11**:



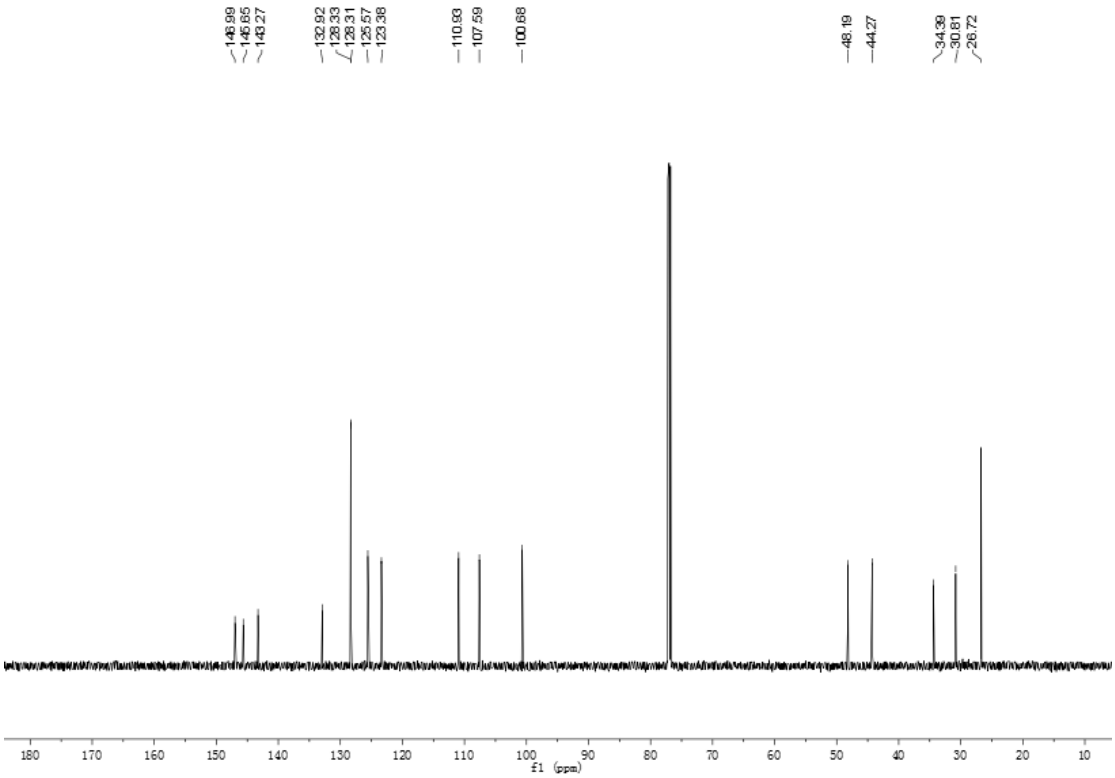
^{13}C NMR (151 MHz, $CDCl_3$) of **11**:



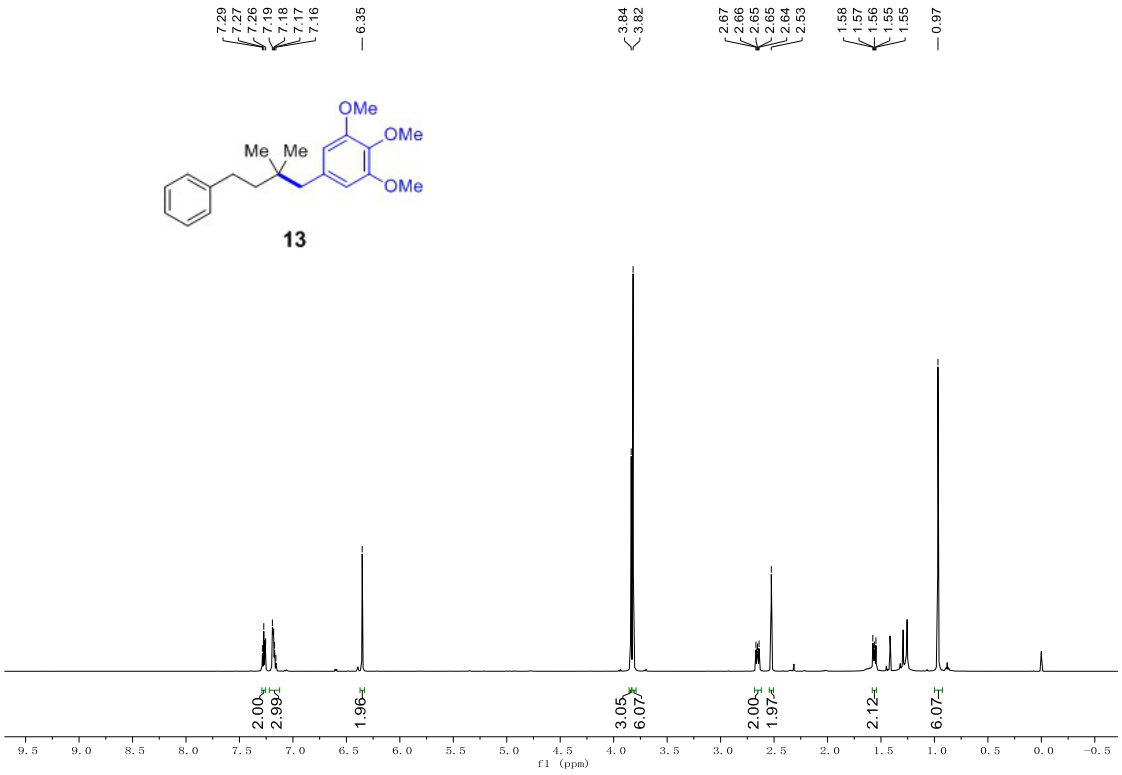
^{1}H NMR (600 MHz, $CDCl_3$) of **12**:



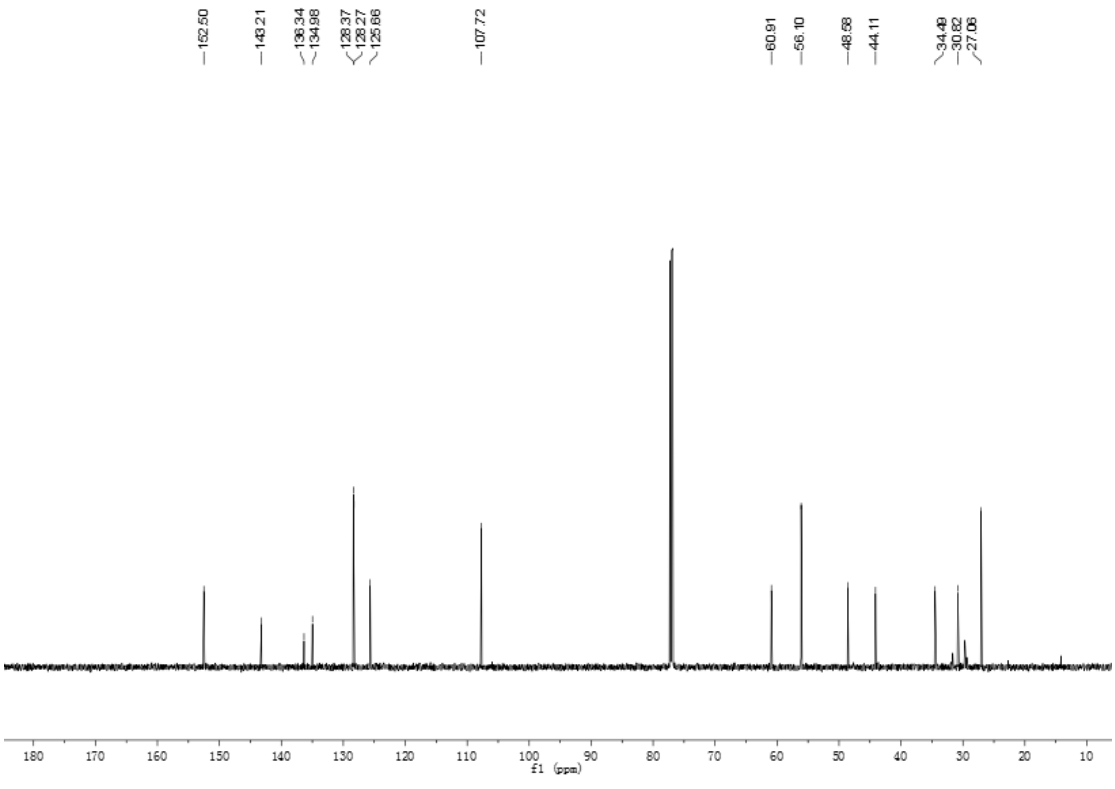
^{13}C NMR (151 MHz, $CDCl_3$) of **12**:



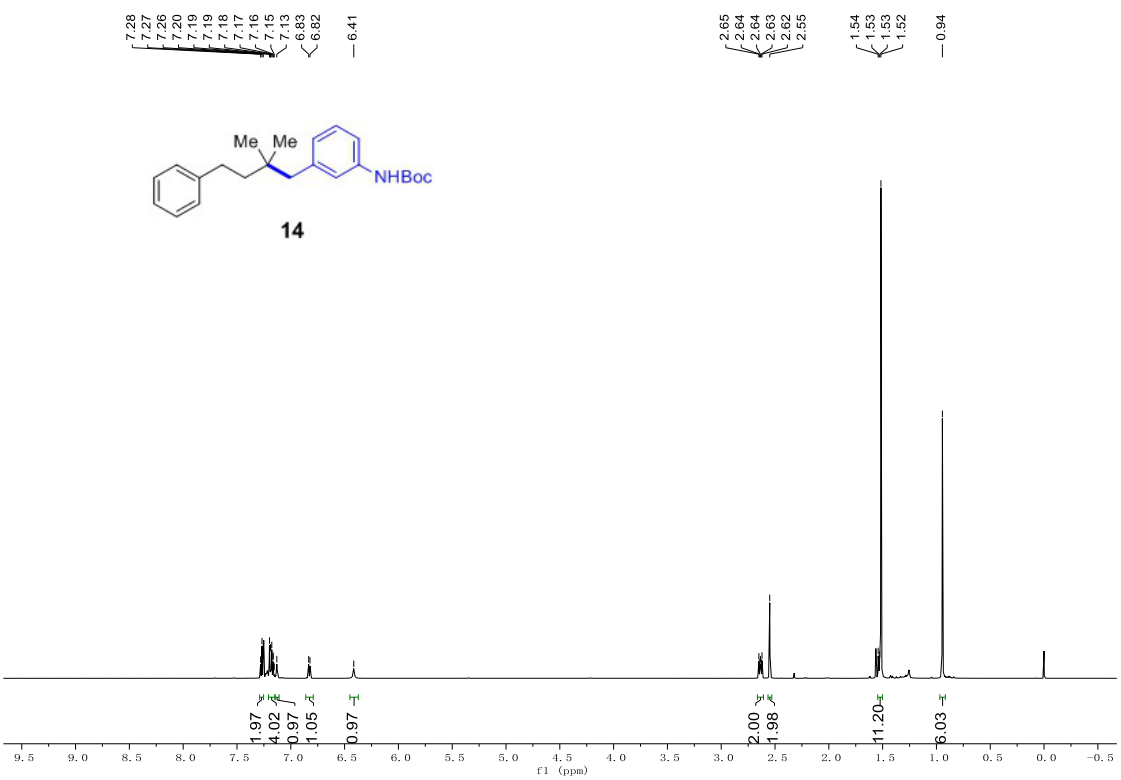
^{1}H NMR (600 MHz, $CDCl_3$) of **13**:



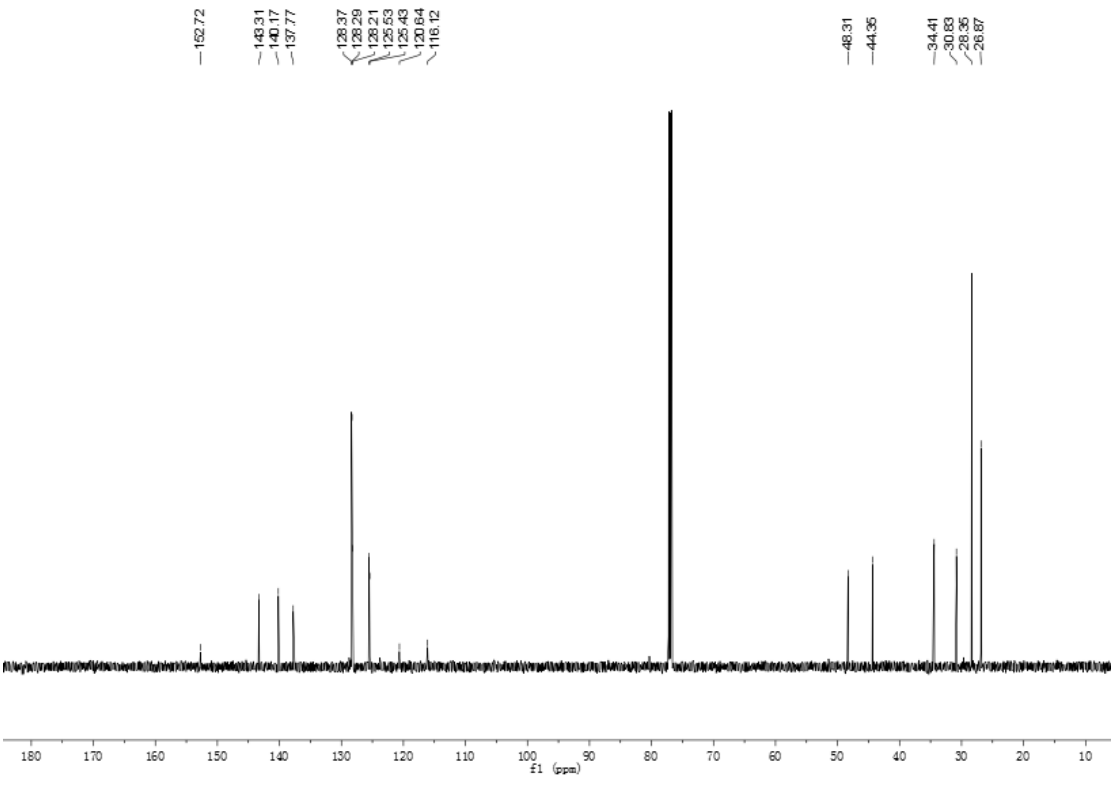
^{13}C NMR (151 MHz, $CDCl_3$) of **13**:



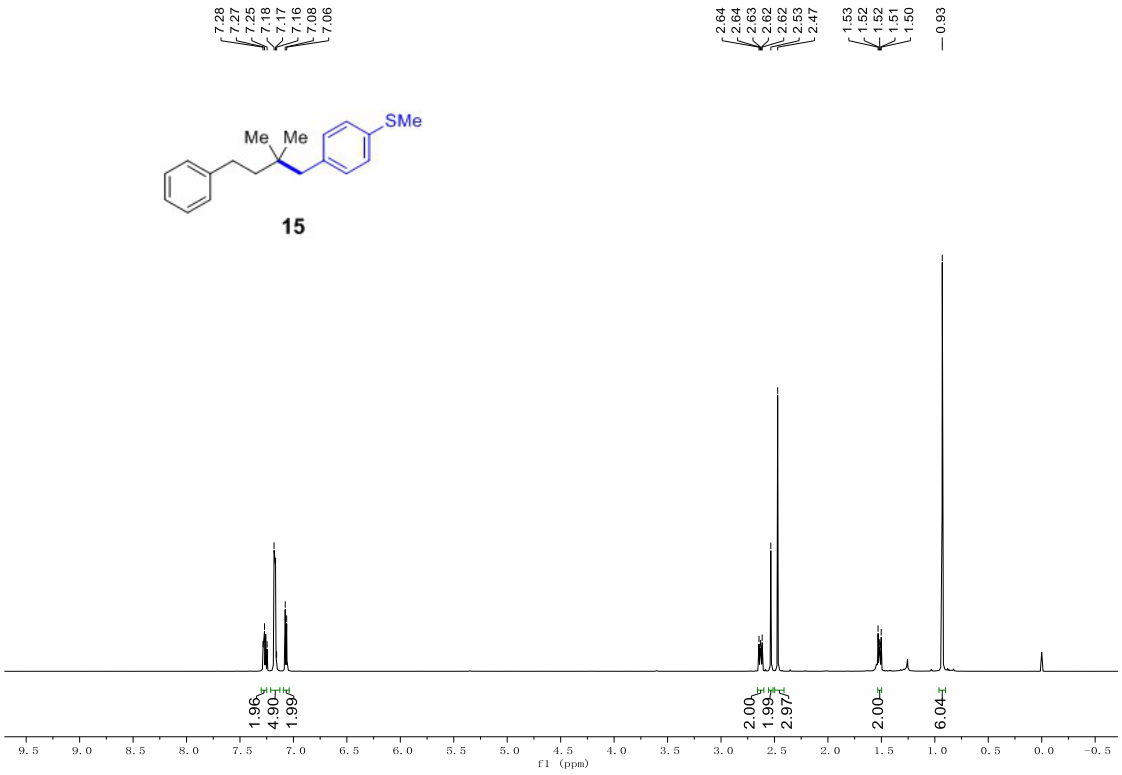
^{1}H NMR (600 MHz, $CDCl_3$) of **14**:



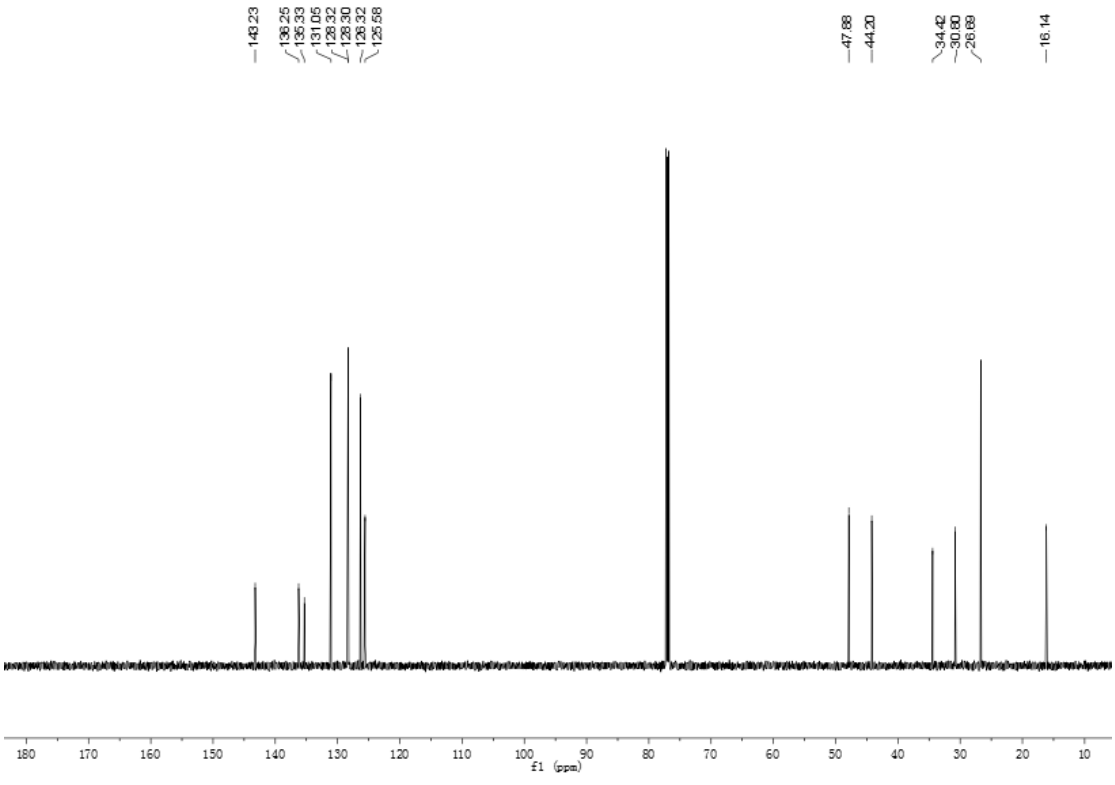
^{13}C NMR (151 MHz, $CDCl_3$) of **14**:



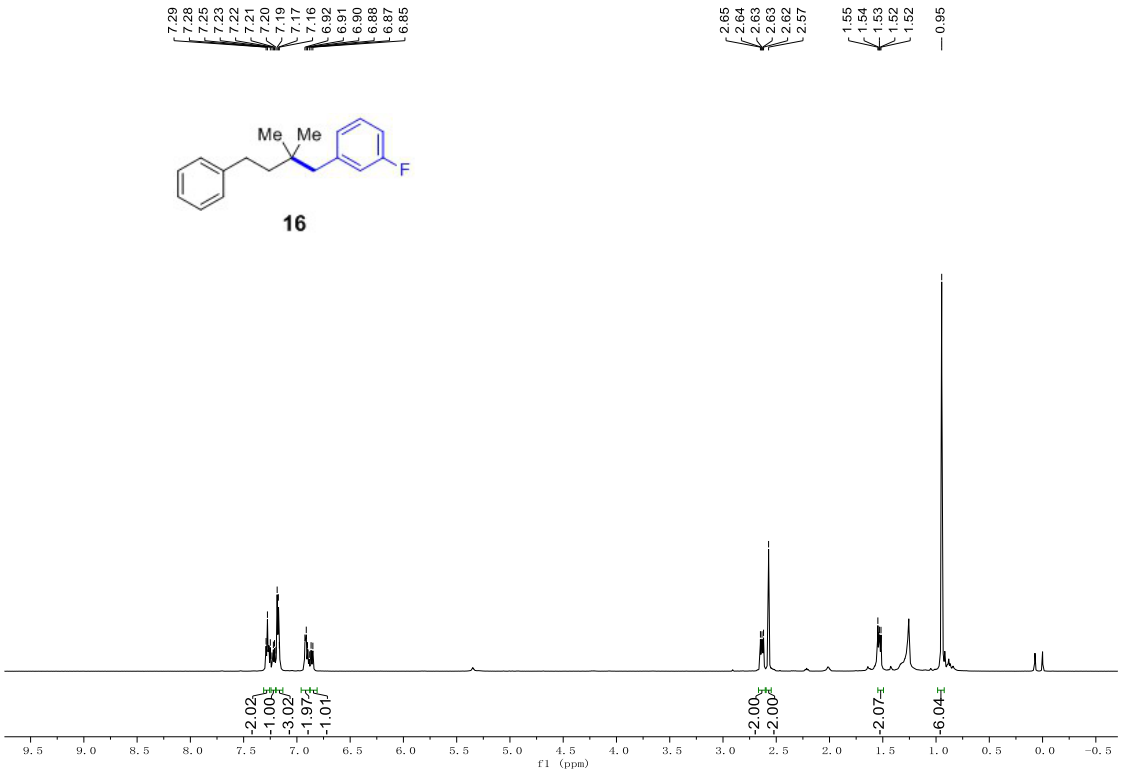
^{1}H NMR (600 MHz, $CDCl_3$) of **15**:



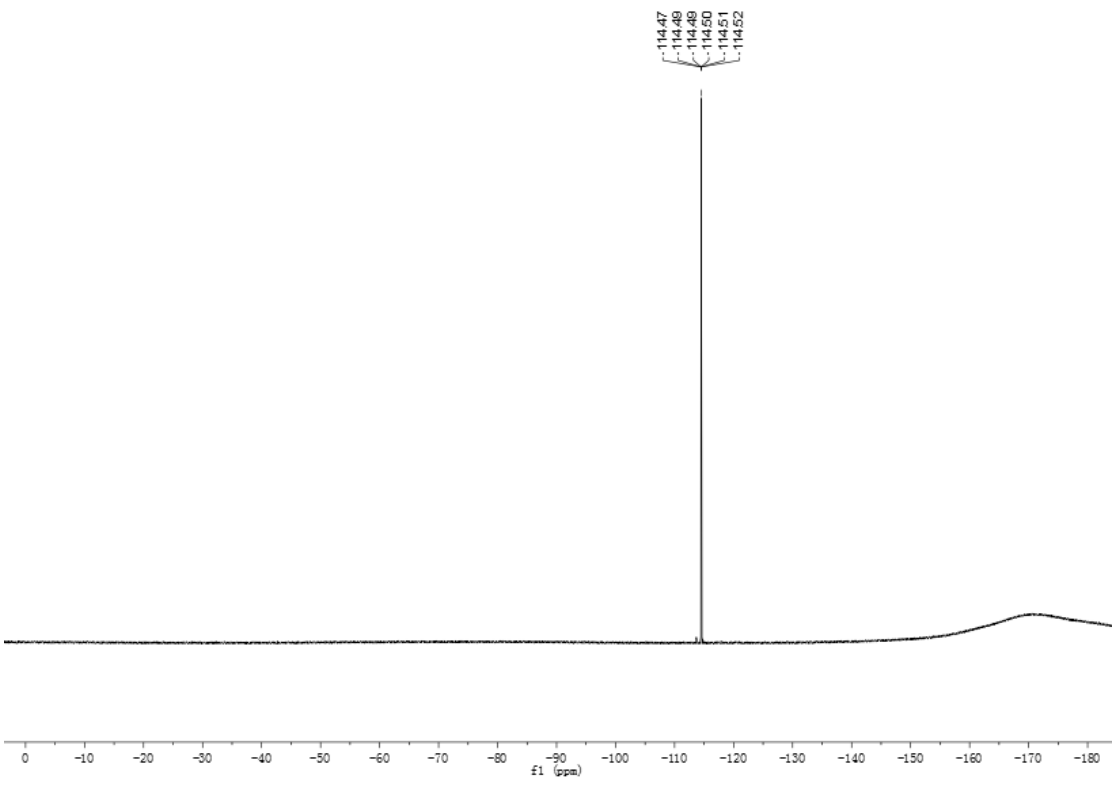
^{13}C NMR (151 MHz, $CDCl_3$) of **15**:



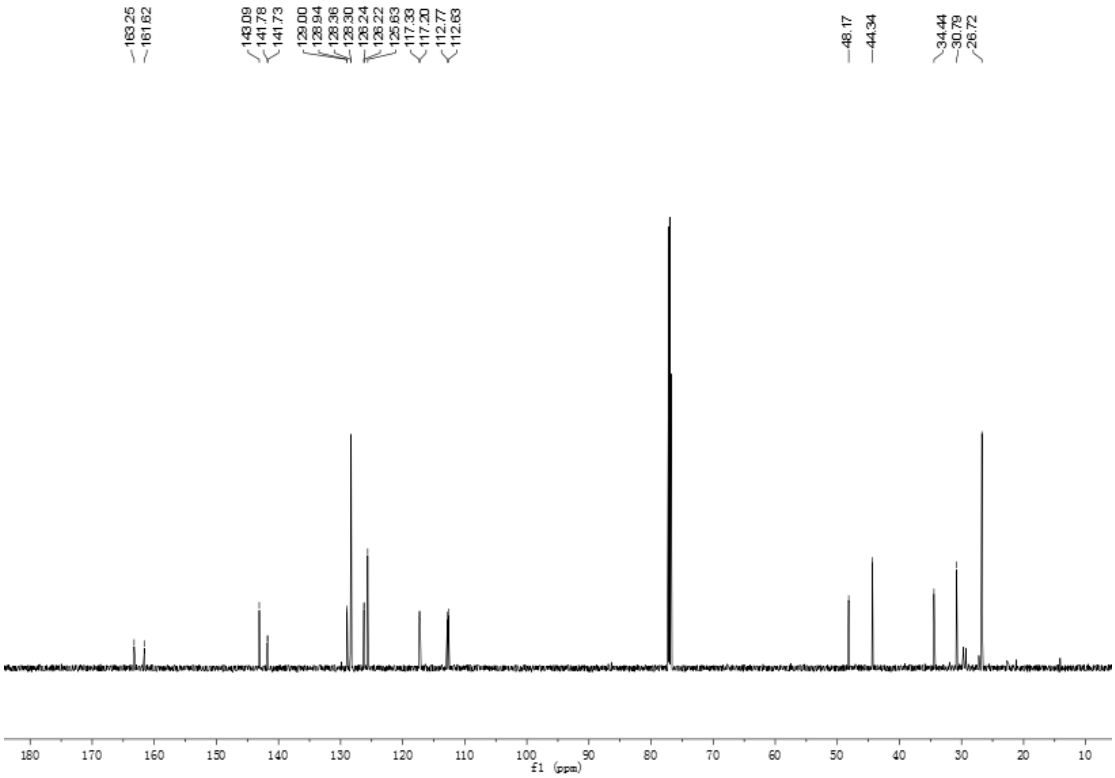
^{1}H NMR (600 MHz, $CDCl_3$) of **16**:



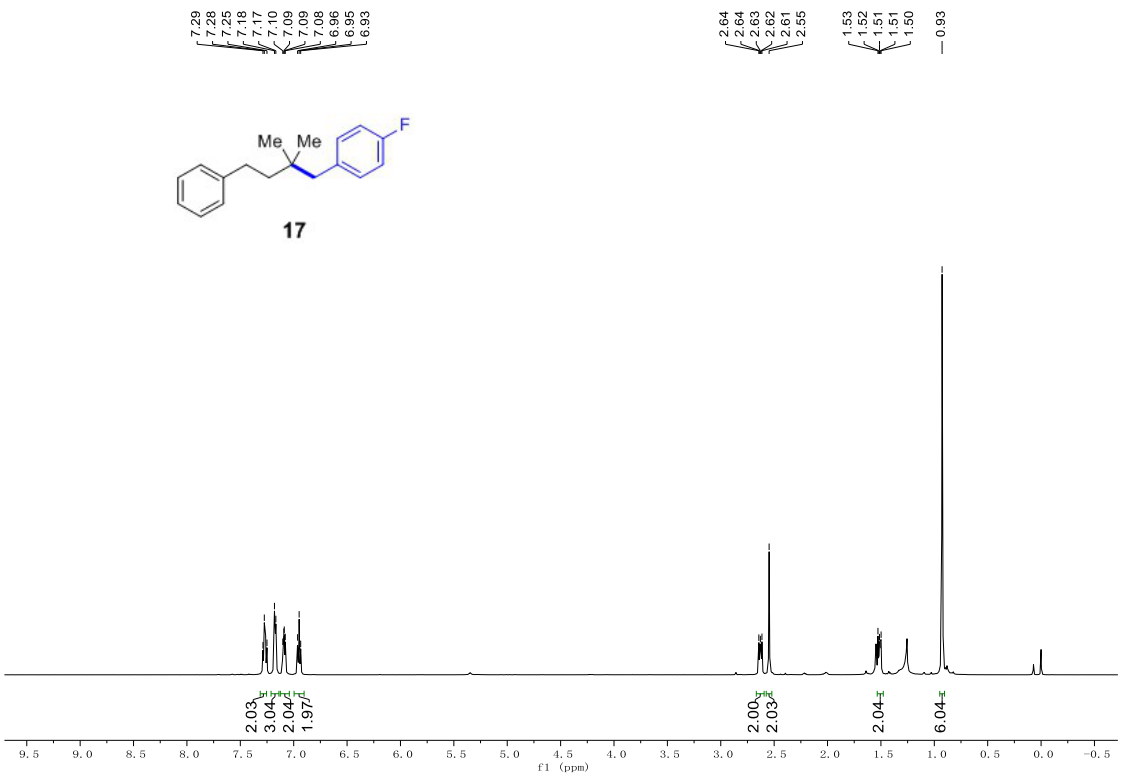
^{19}F NMR (565 MHz, $CDCl_3$) of **16**:



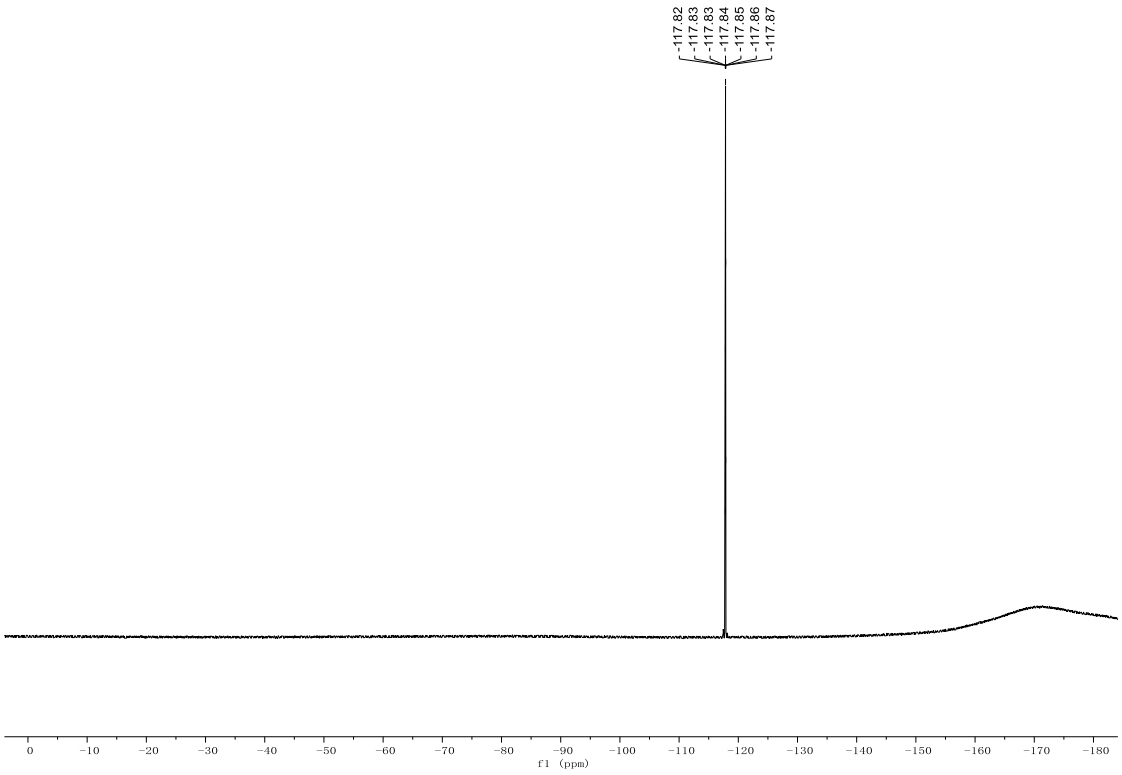
^{13}C NMR (151 MHz, $CDCl_3$) of **16**:



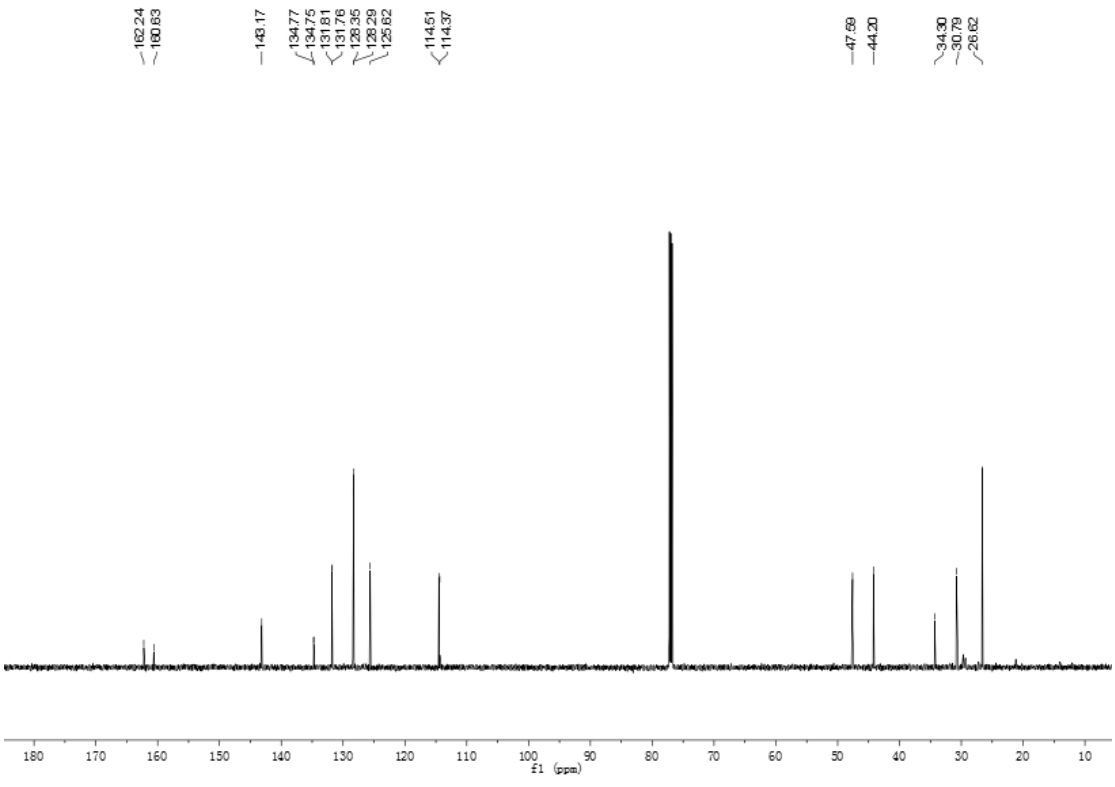
^{1}H NMR (600 MHz, $CDCl_3$) of **17**:



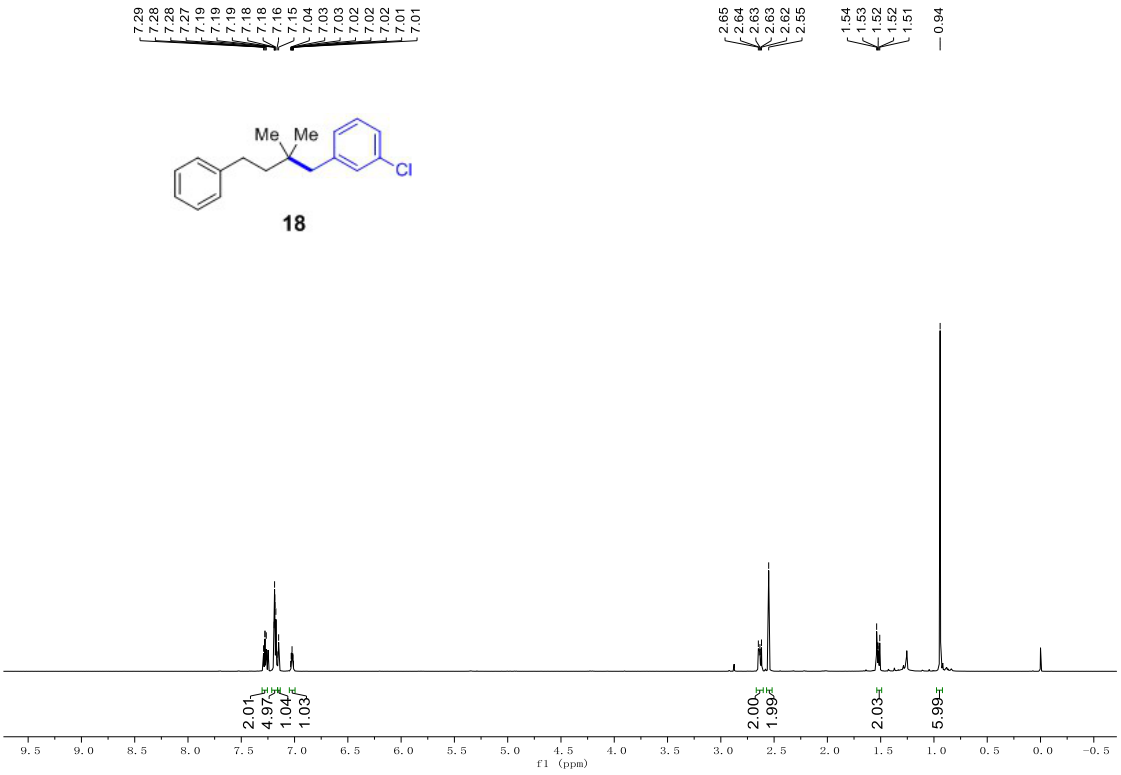
^{19}F NMR (565 MHz, $CDCl_3$) of **17**:



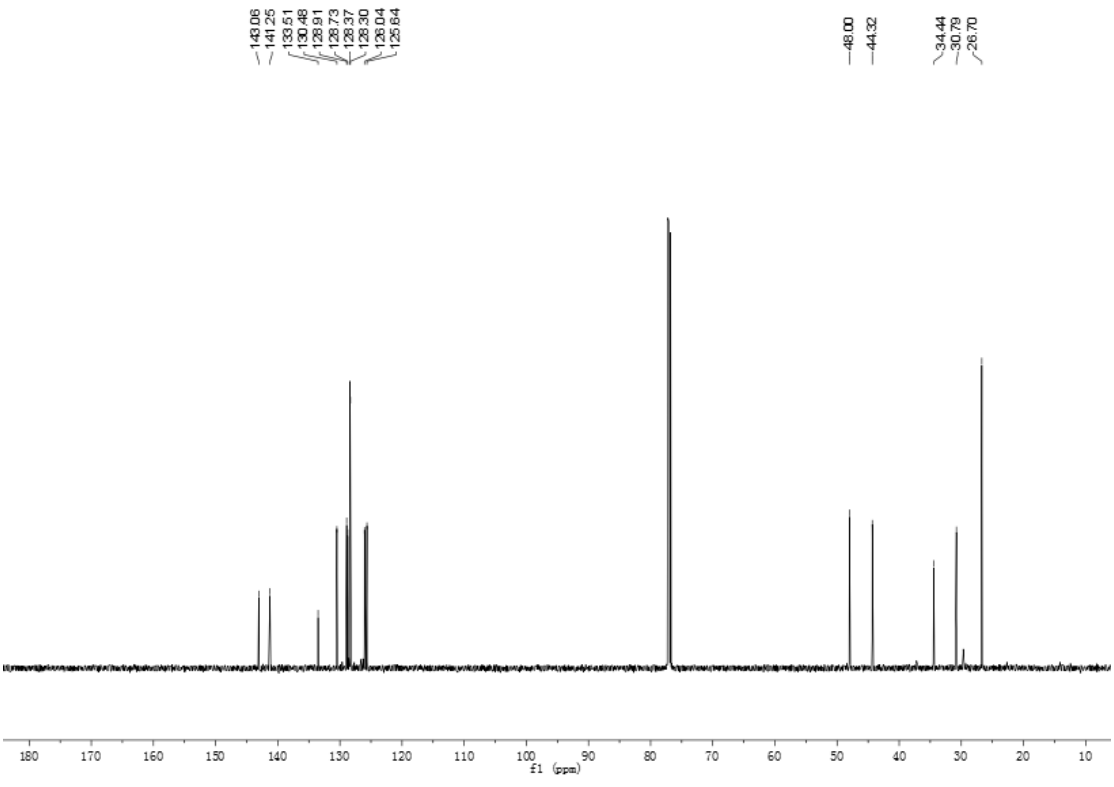
^{13}C NMR (151 MHz, $CDCl_3$) of **17**:



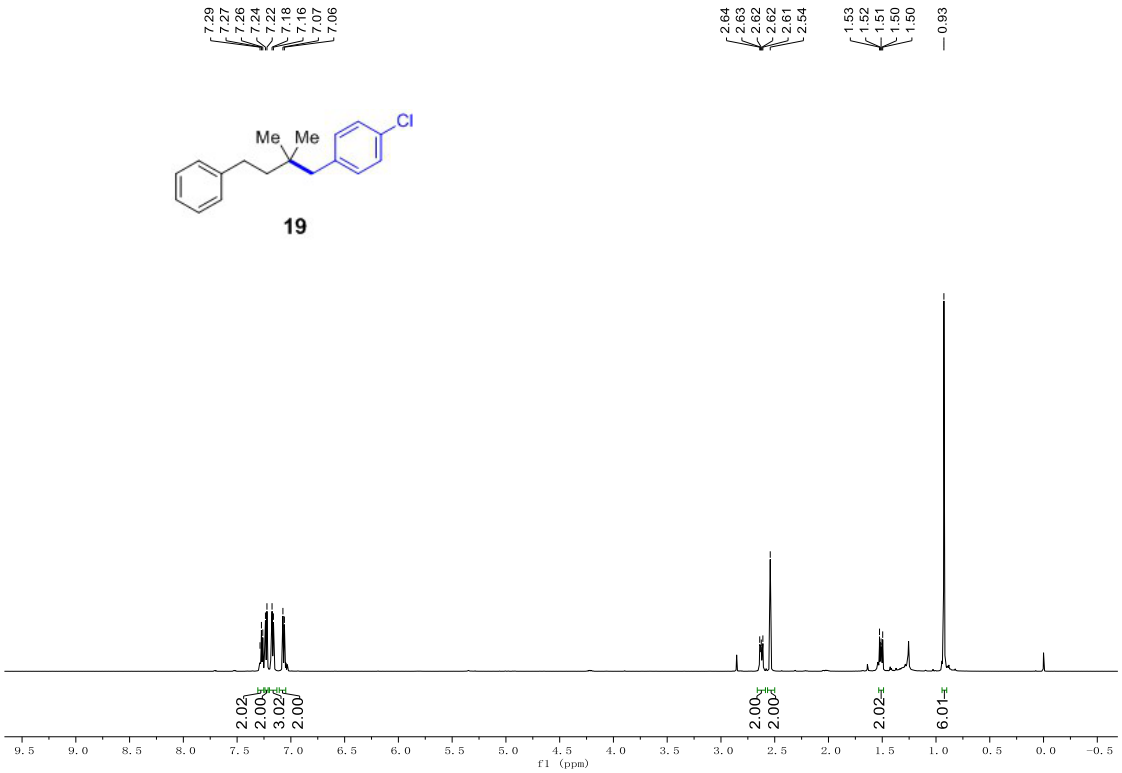
^{1}H NMR (600 MHz, $CDCl_3$) of **18**:



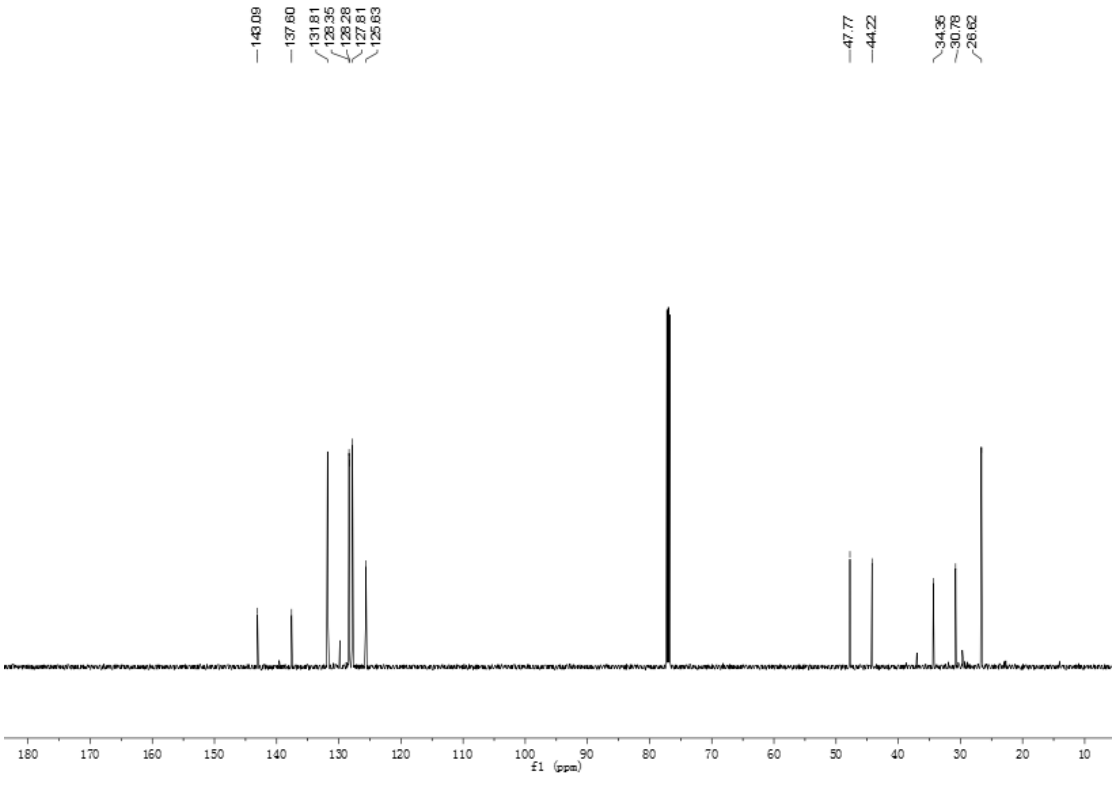
^{13}C NMR (151 MHz, $CDCl_3$) of **18**:



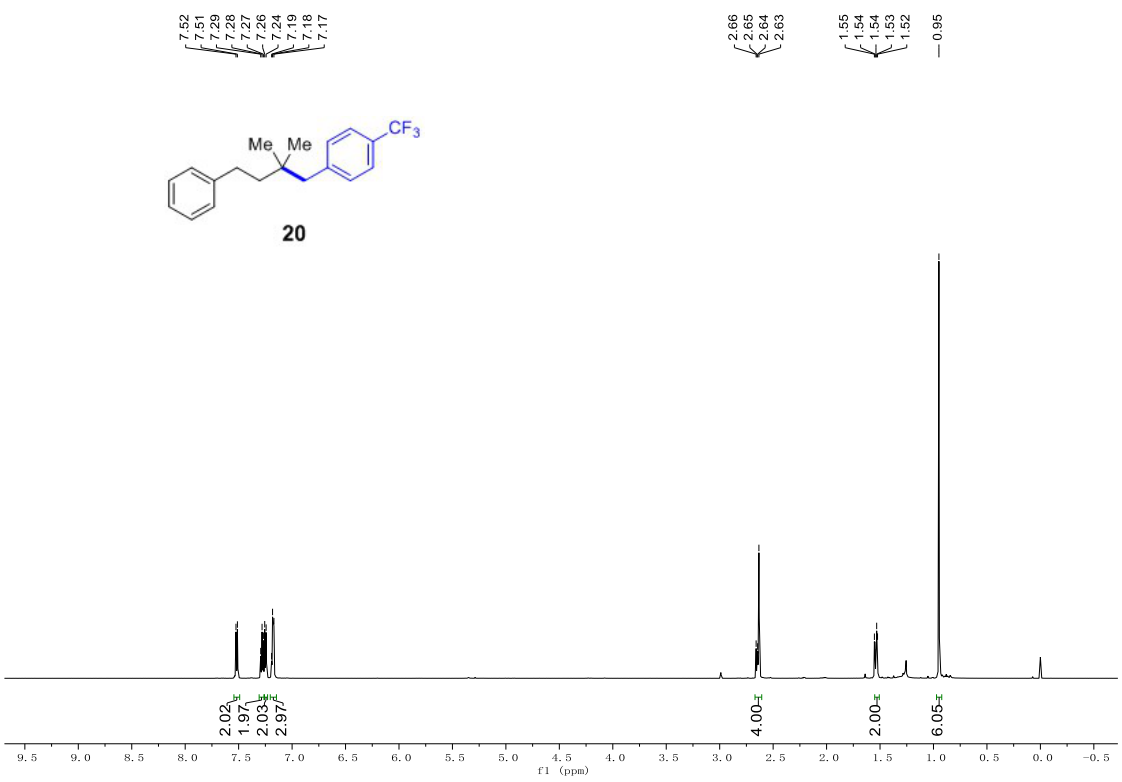
^{1}H NMR (600 MHz, $CDCl_3$) of **19**:



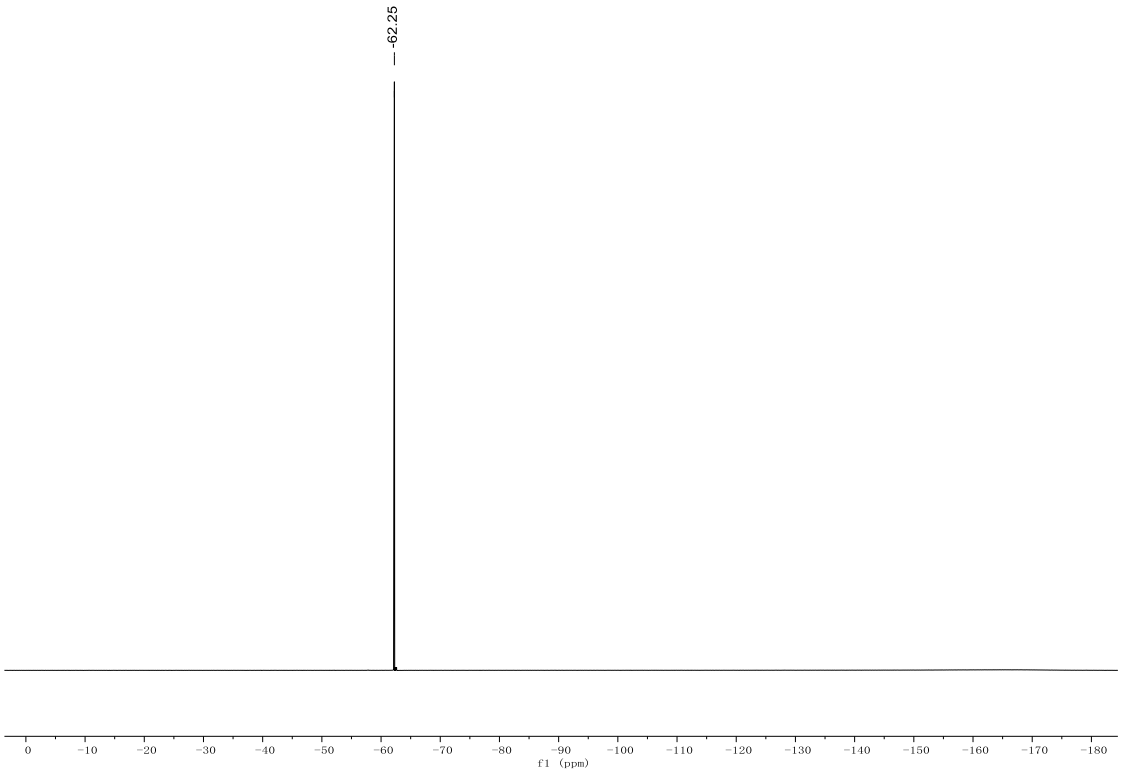
^{13}C NMR (151 MHz, $CDCl_3$) of **19**:



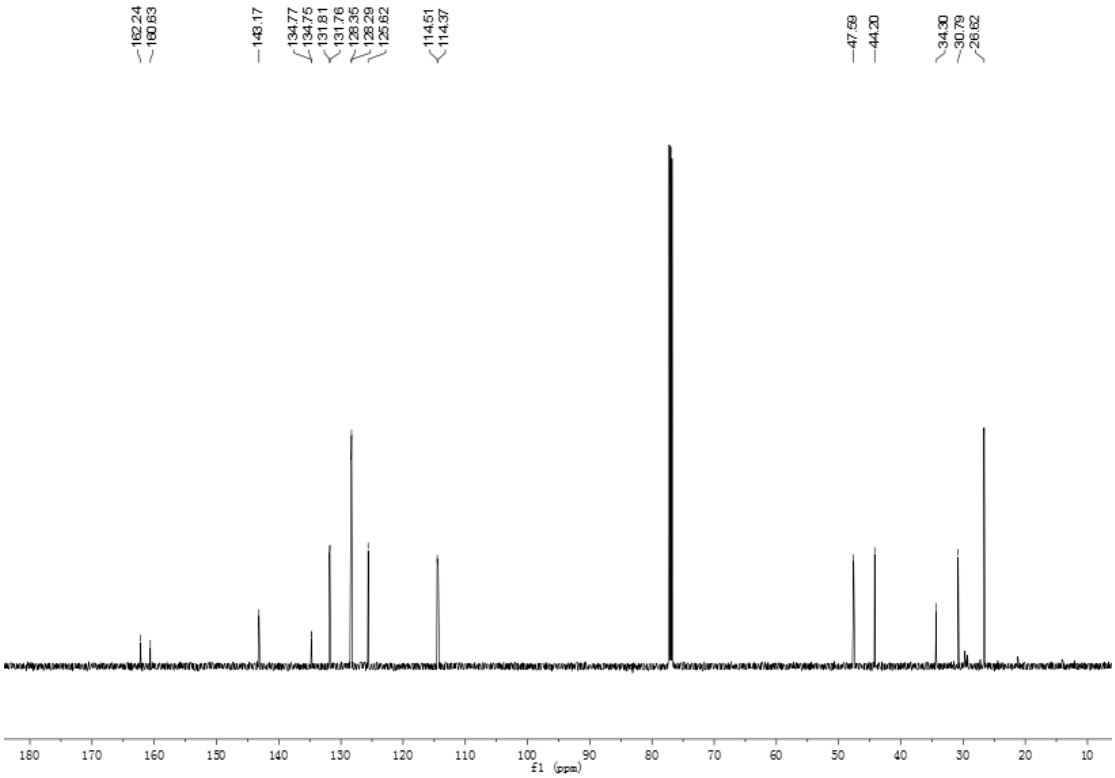
^{1}H NMR (600 MHz, $CDCl_3$) of **20**:



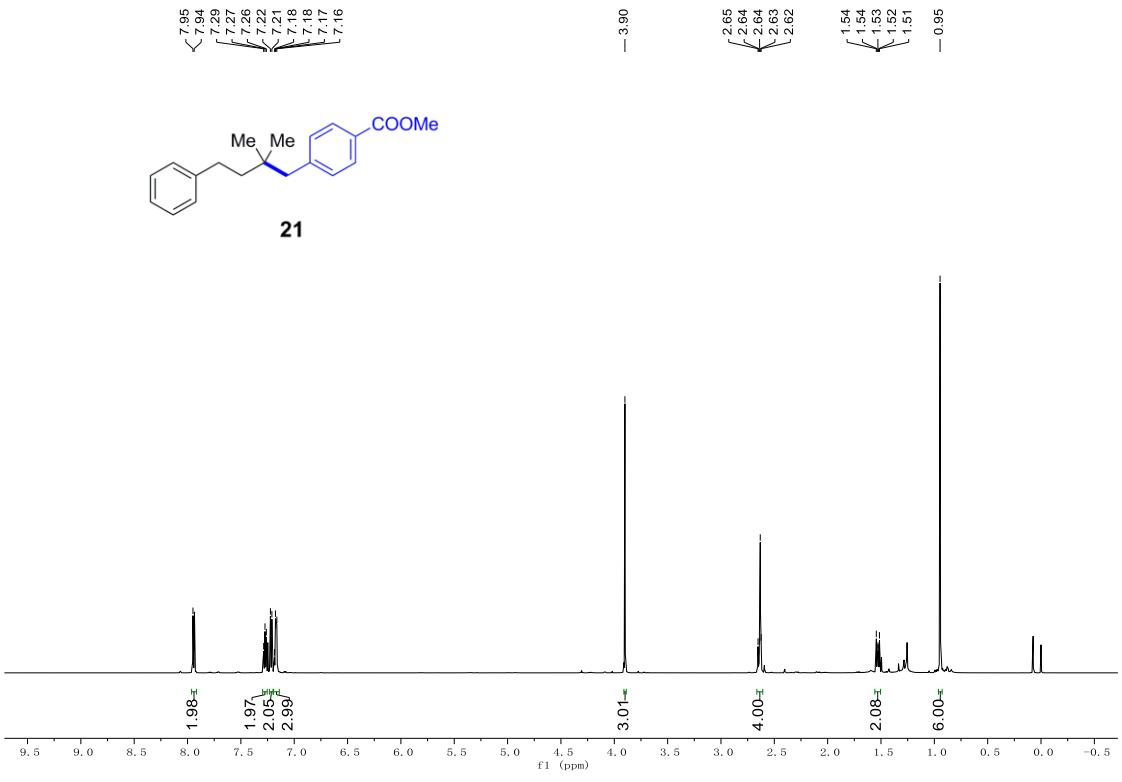
^{19}F NMR (565 MHz, $CDCl_3$) of **20**:



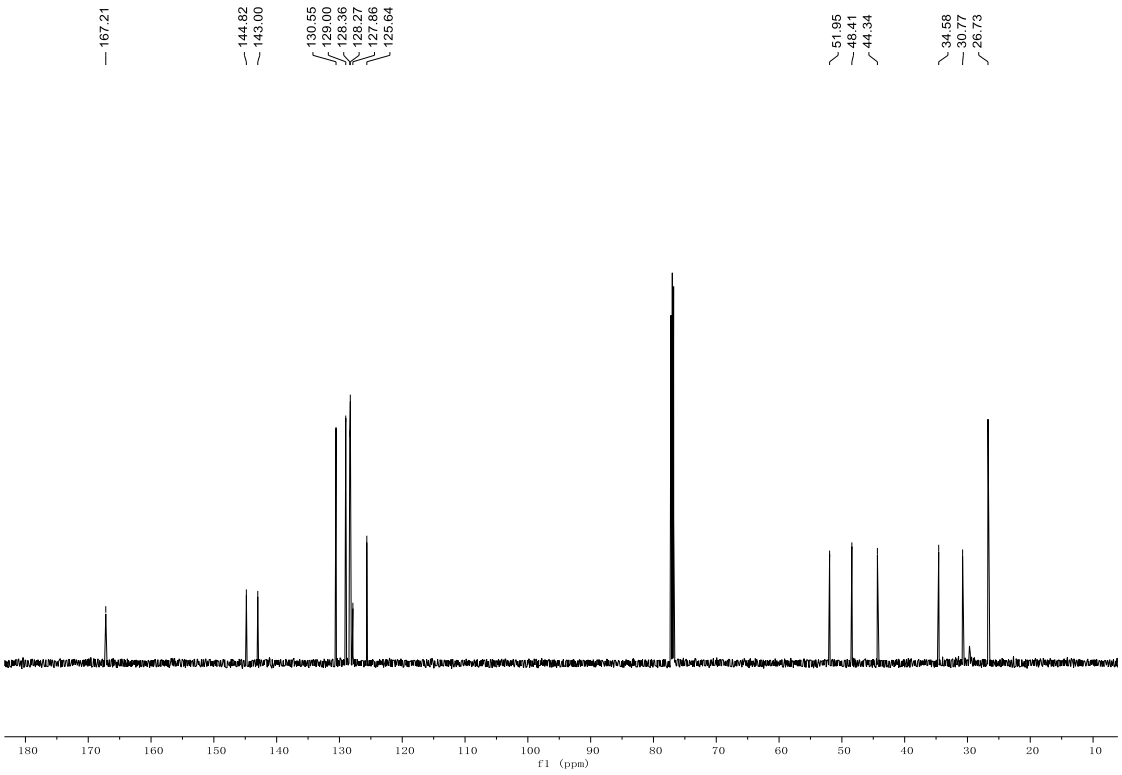
^{13}C NMR (151 MHz, $CDCl_3$) of **20**:



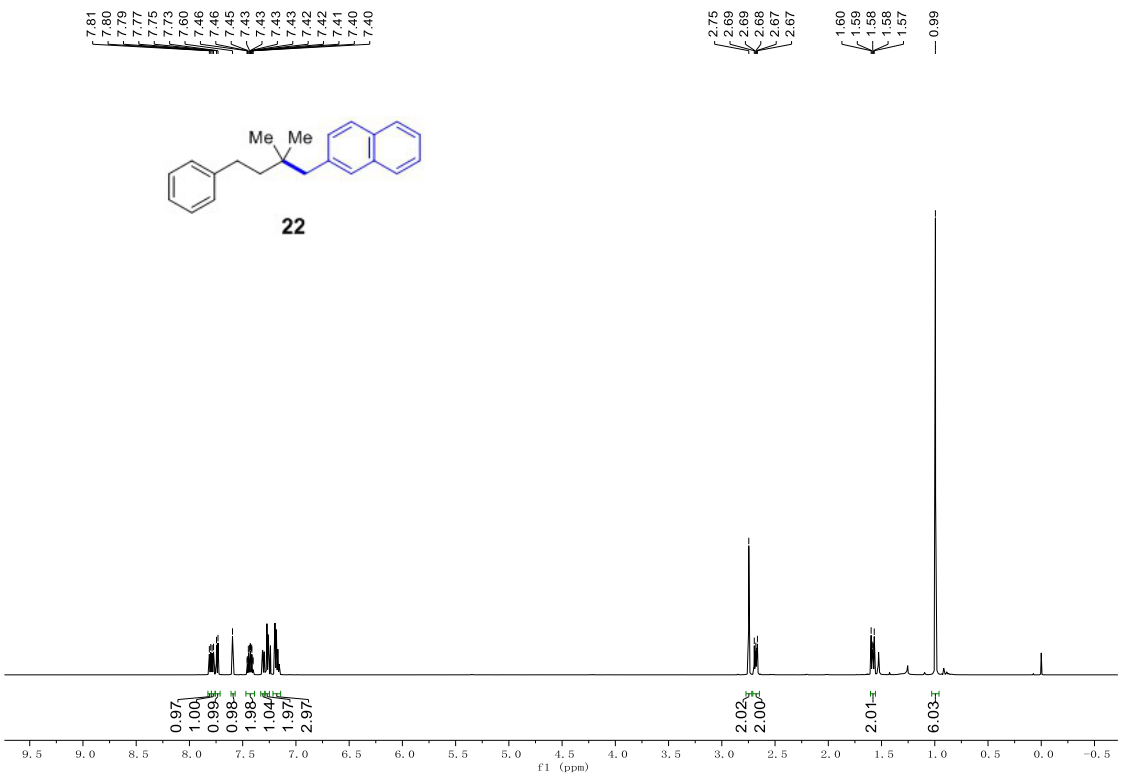
^{1}H NMR (600 MHz, $CDCl_3$) of **21**:



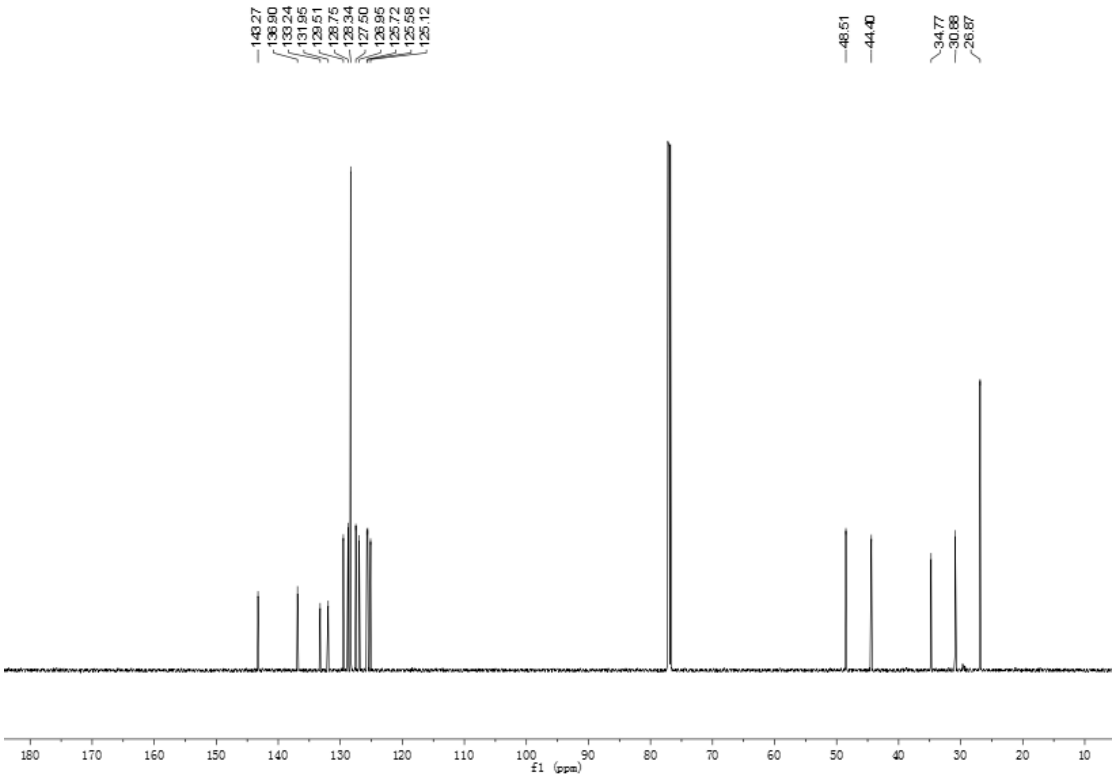
^{13}C NMR (151 MHz, $CDCl_3$) of **21**:



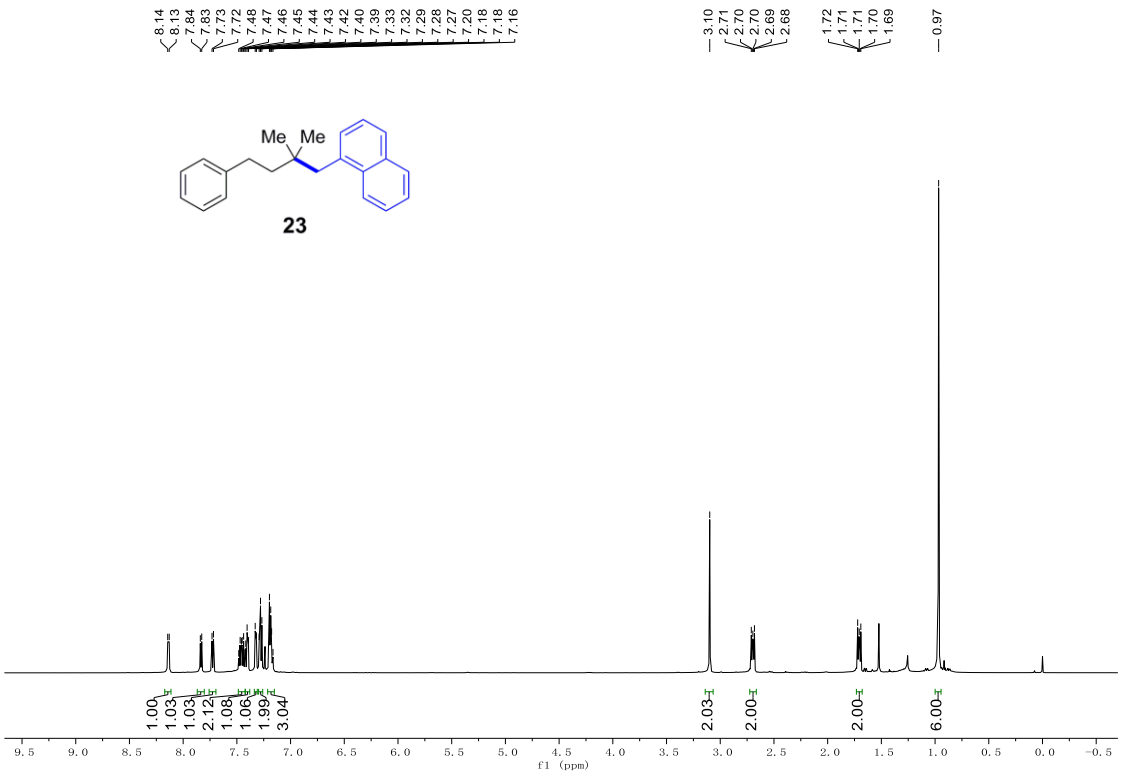
^{1}H NMR (600 MHz, $CDCl_3$) of **22**:



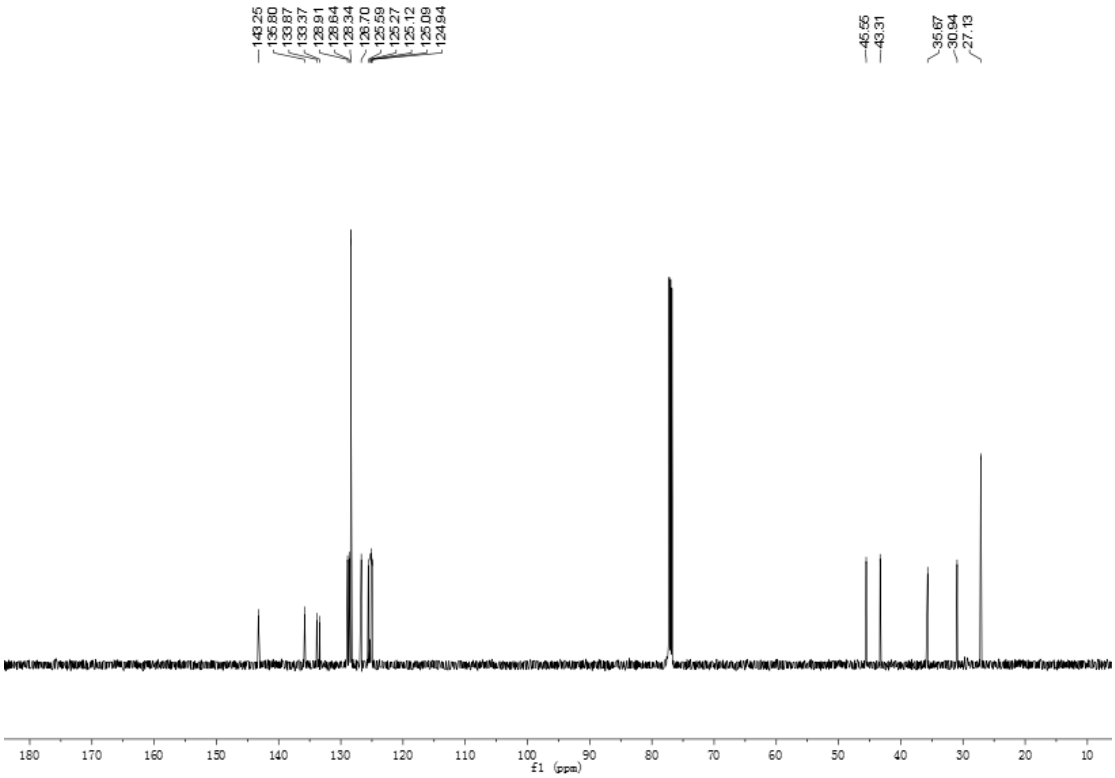
^{13}C NMR (151 MHz, $CDCl_3$) of **22**:



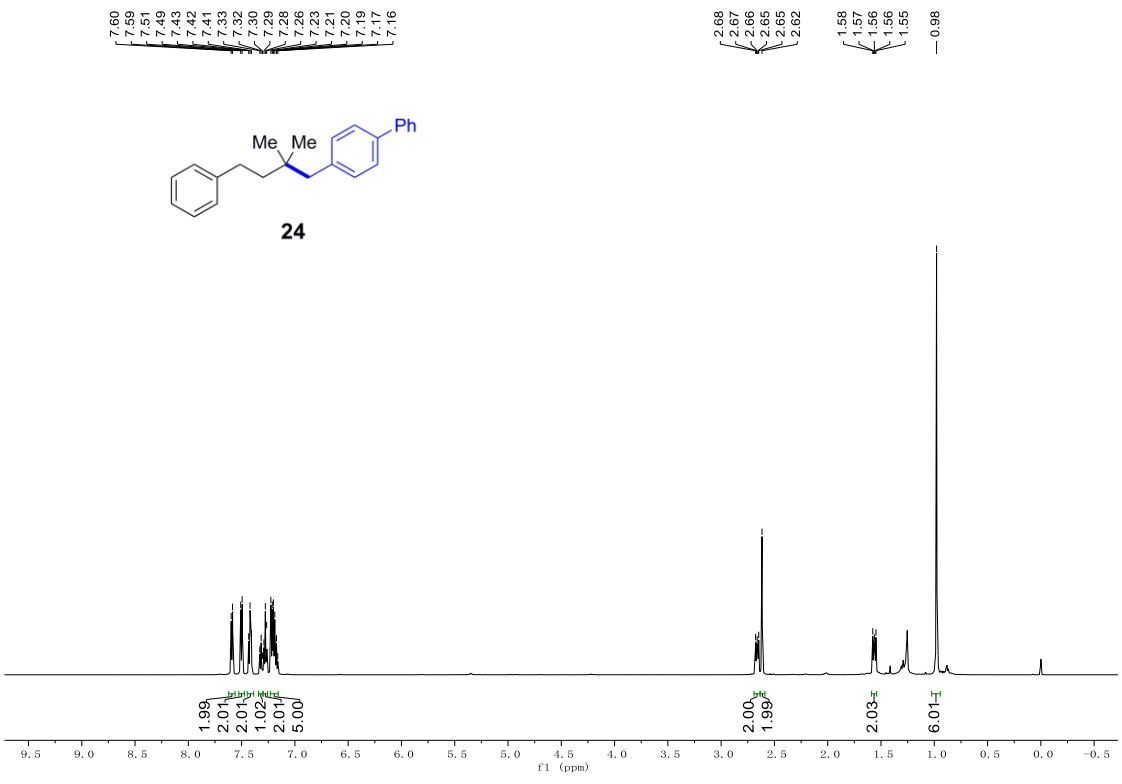
^{1}H NMR (600 MHz, $CDCl_3$) of **23**:



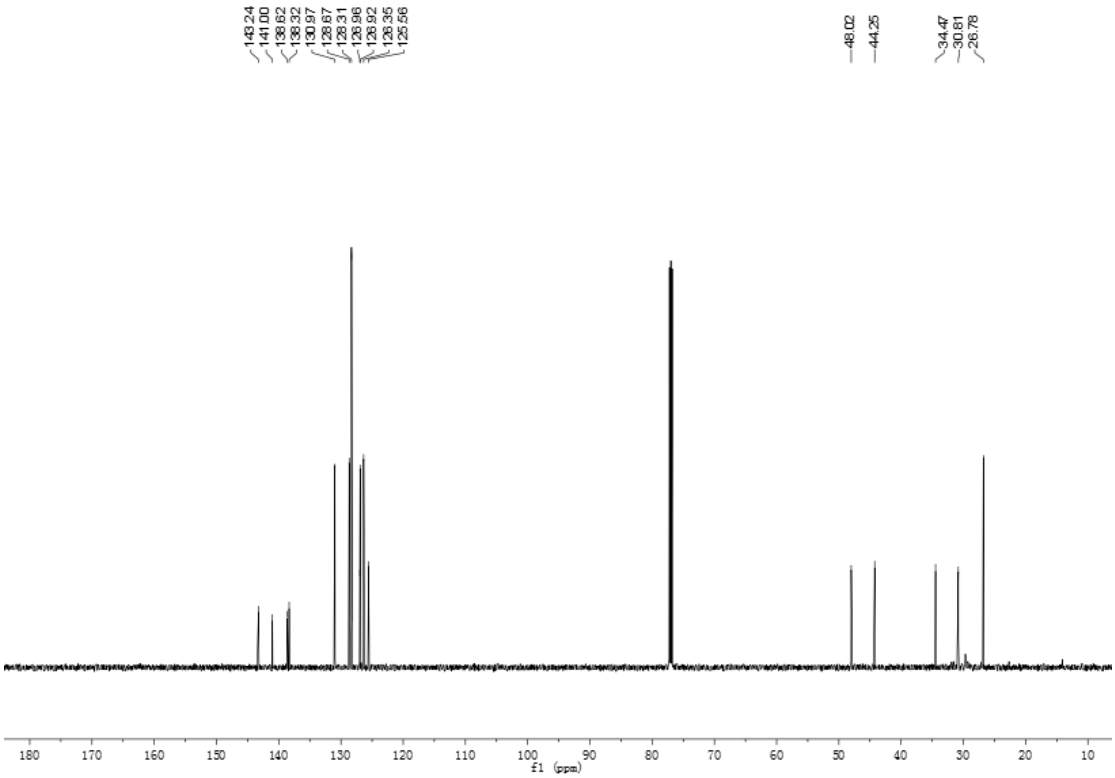
^{13}C NMR (151 MHz, $CDCl_3$) of **23**:



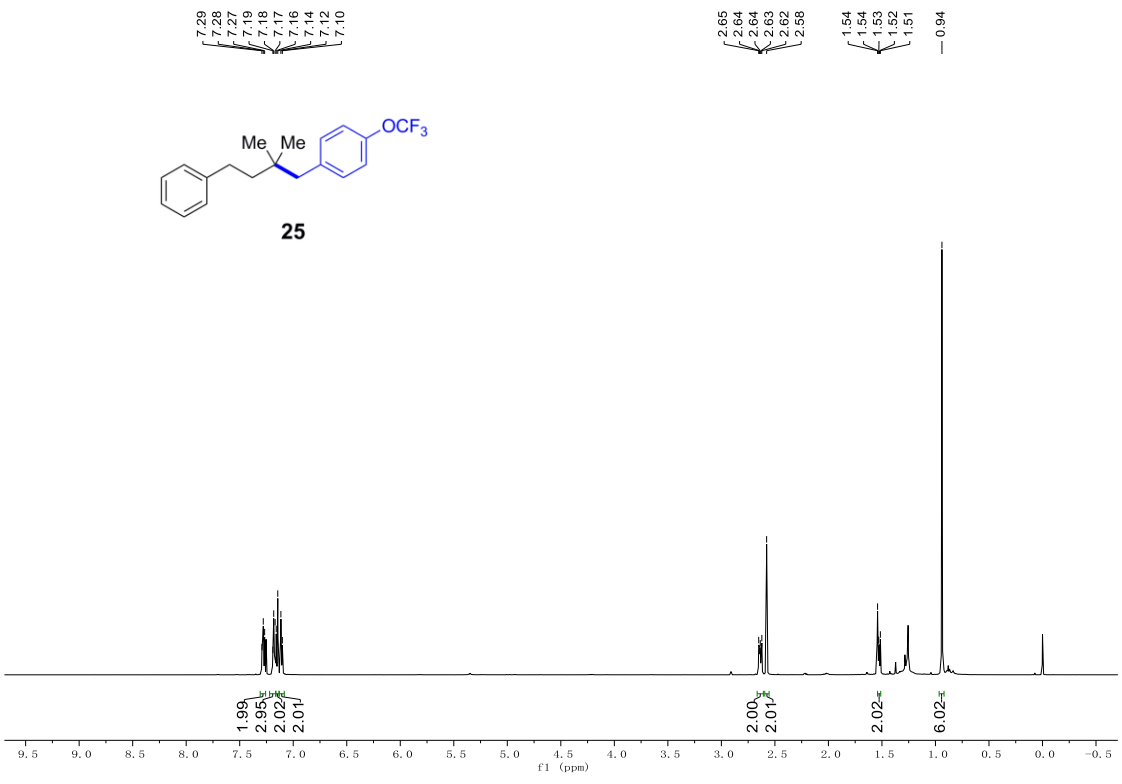
^{1}H NMR (600 MHz, $CDCl_3$) of **24**:



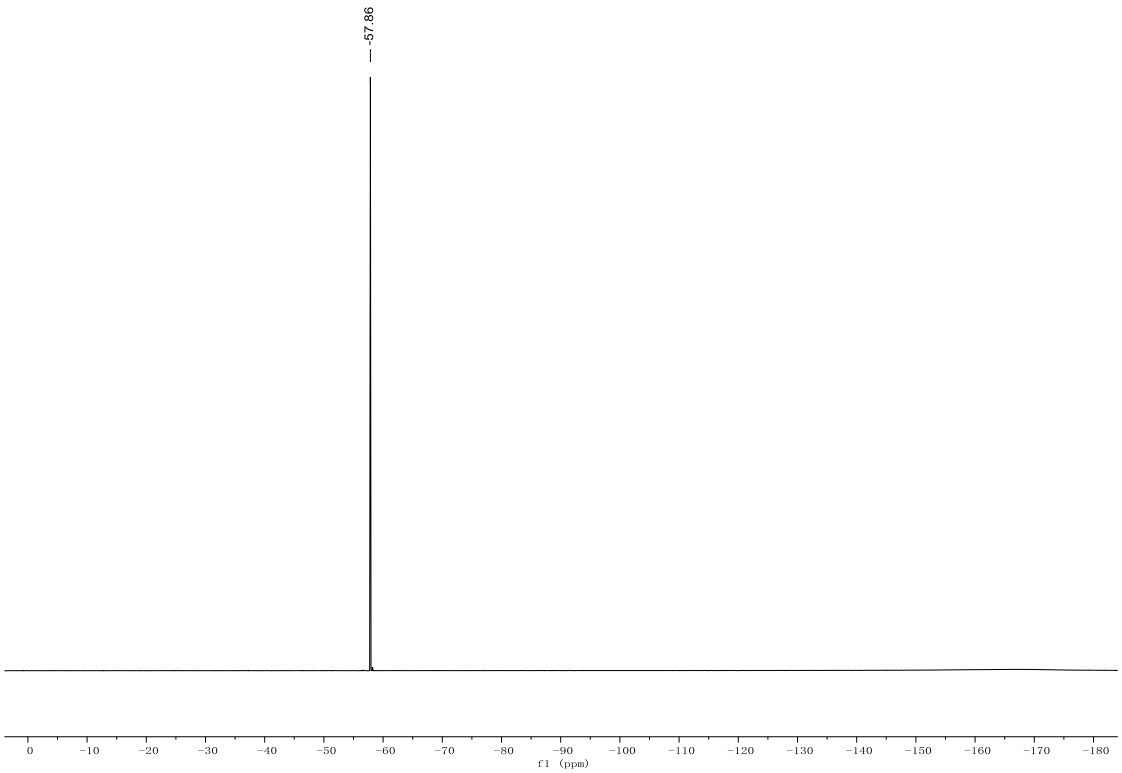
^{13}C NMR (151 MHz, $CDCl_3$) of **24**:



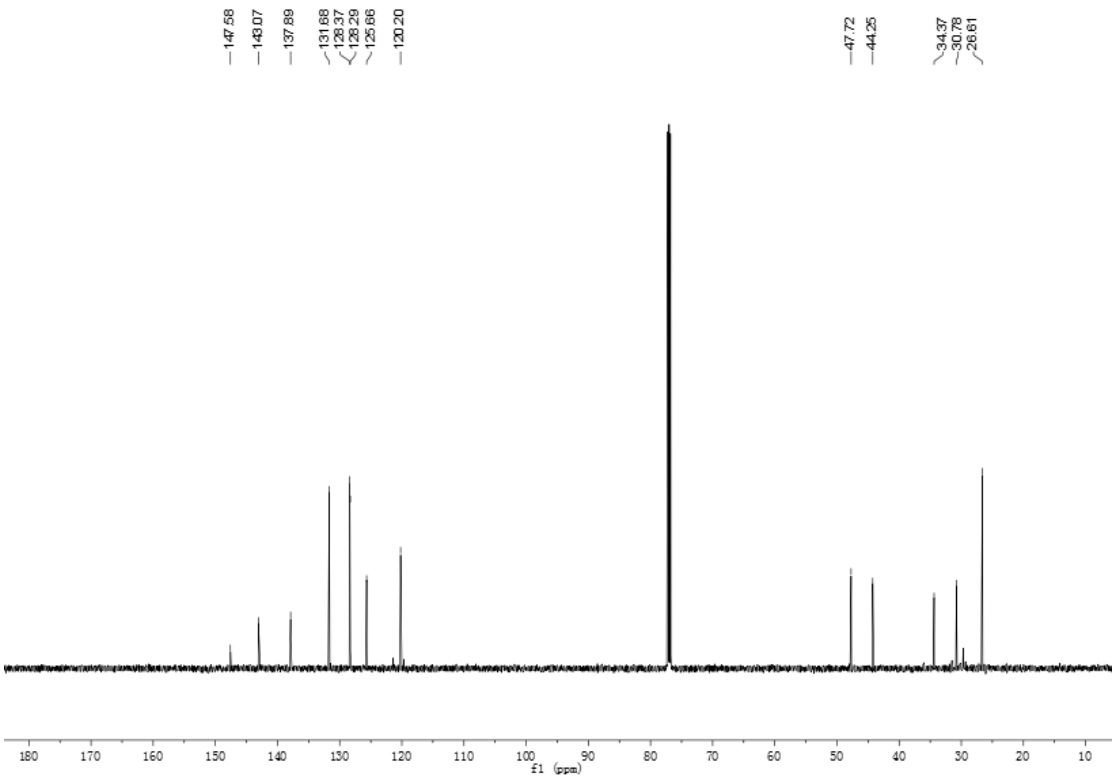
^{1}H NMR (600 MHz, $CDCl_3$) of **25**:



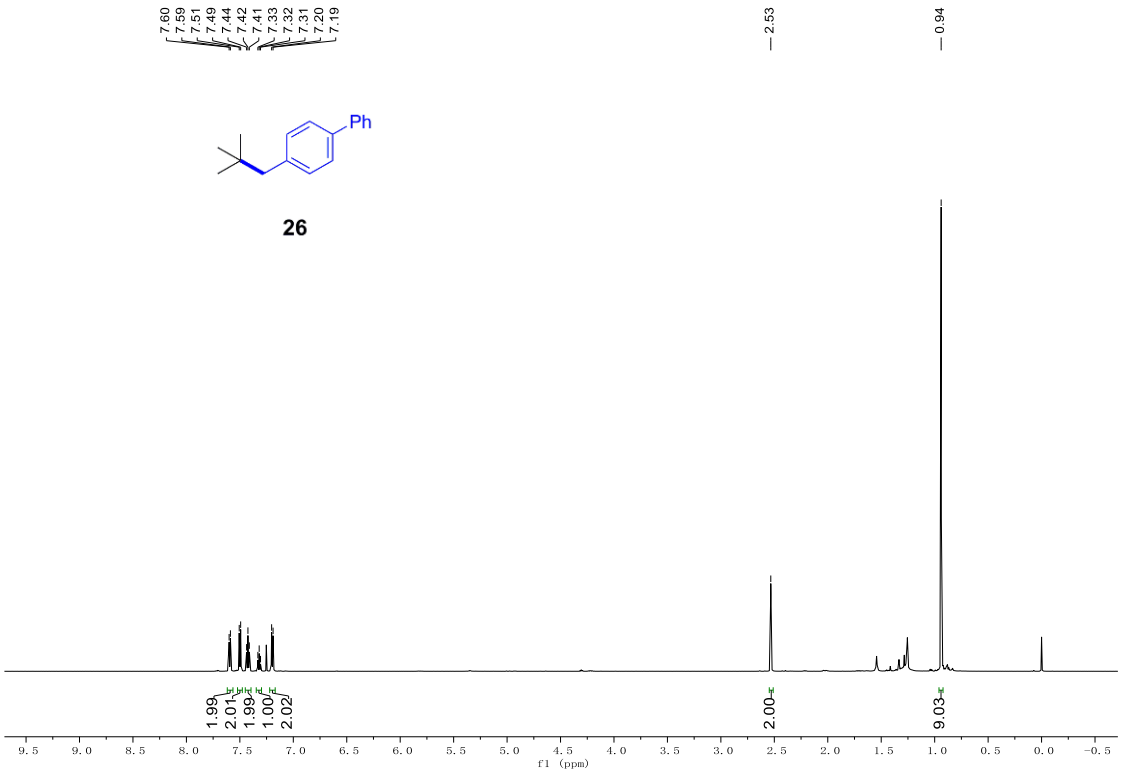
^{19}F NMR (565 MHz, $CDCl_3$) of **25**:



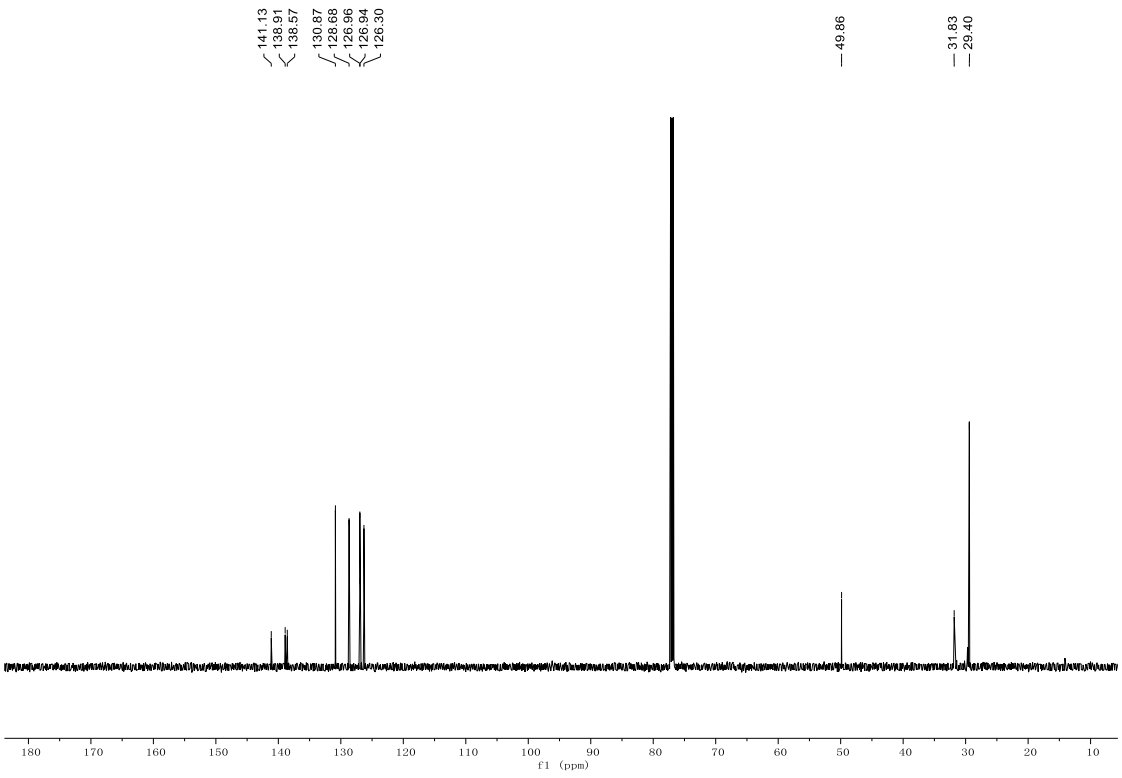
^{13}C NMR (151 MHz, $CDCl_3$) of **25**:



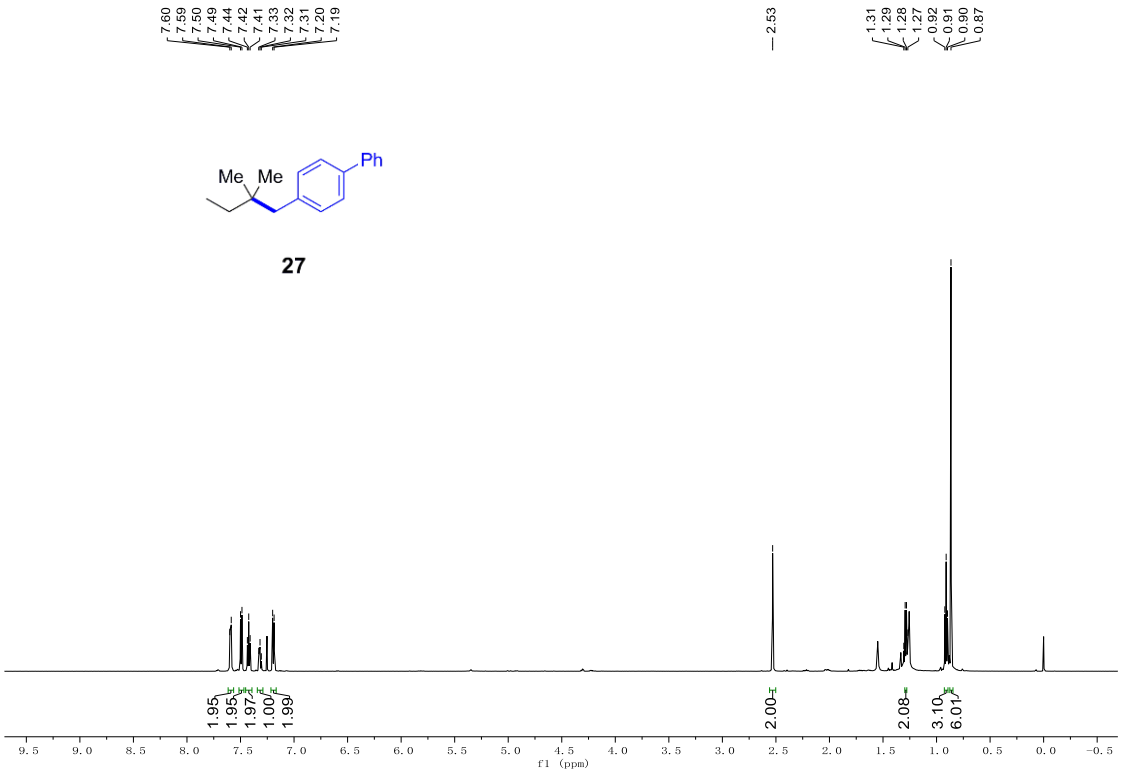
^{1}H NMR (600 MHz, $CDCl_3$) of **26**:



^{13}C NMR (151 MHz, $CDCl_3$) of **26**:

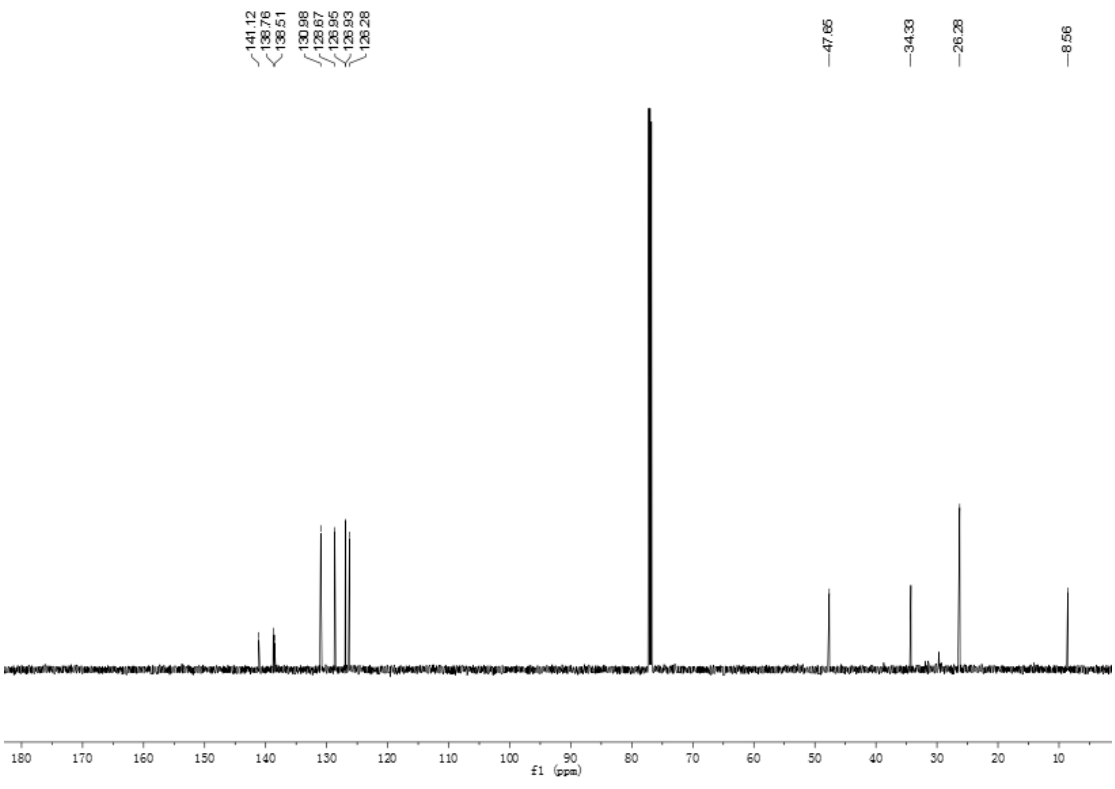


^{1}H NMR (600 MHz, $CDCl_3$) of **27**:

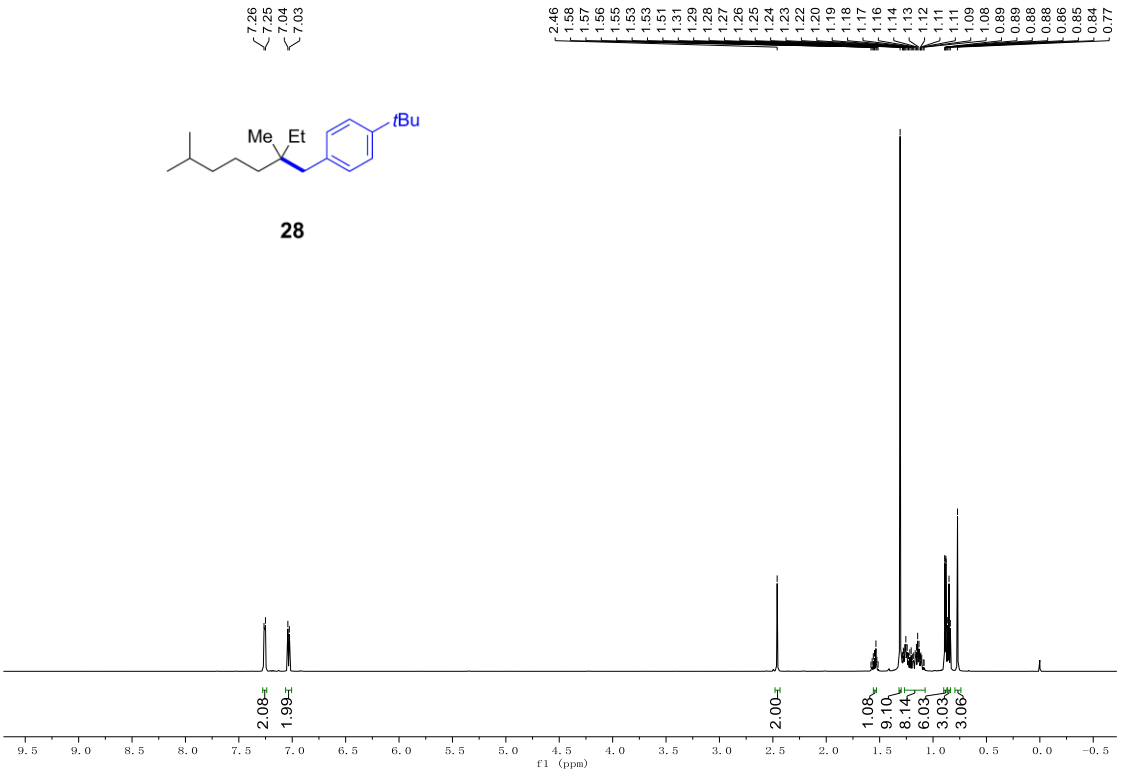


27

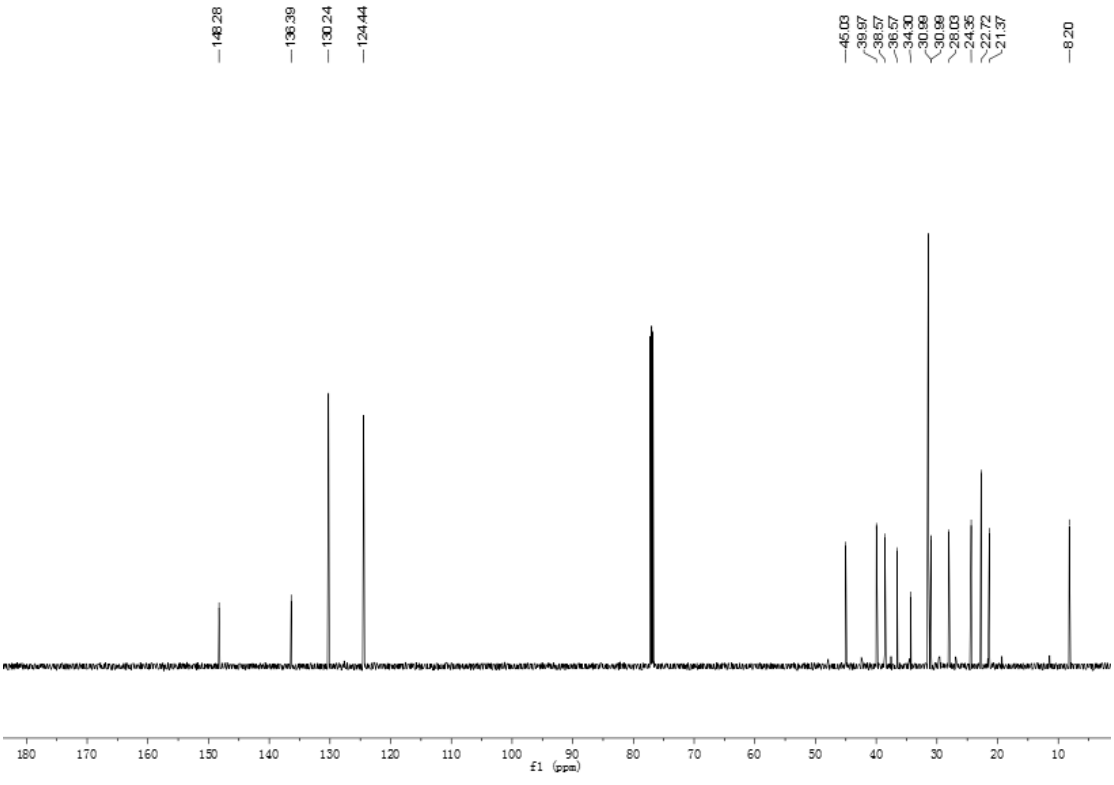
^{13}C NMR (151 MHz, $CDCl_3$) of **27**:



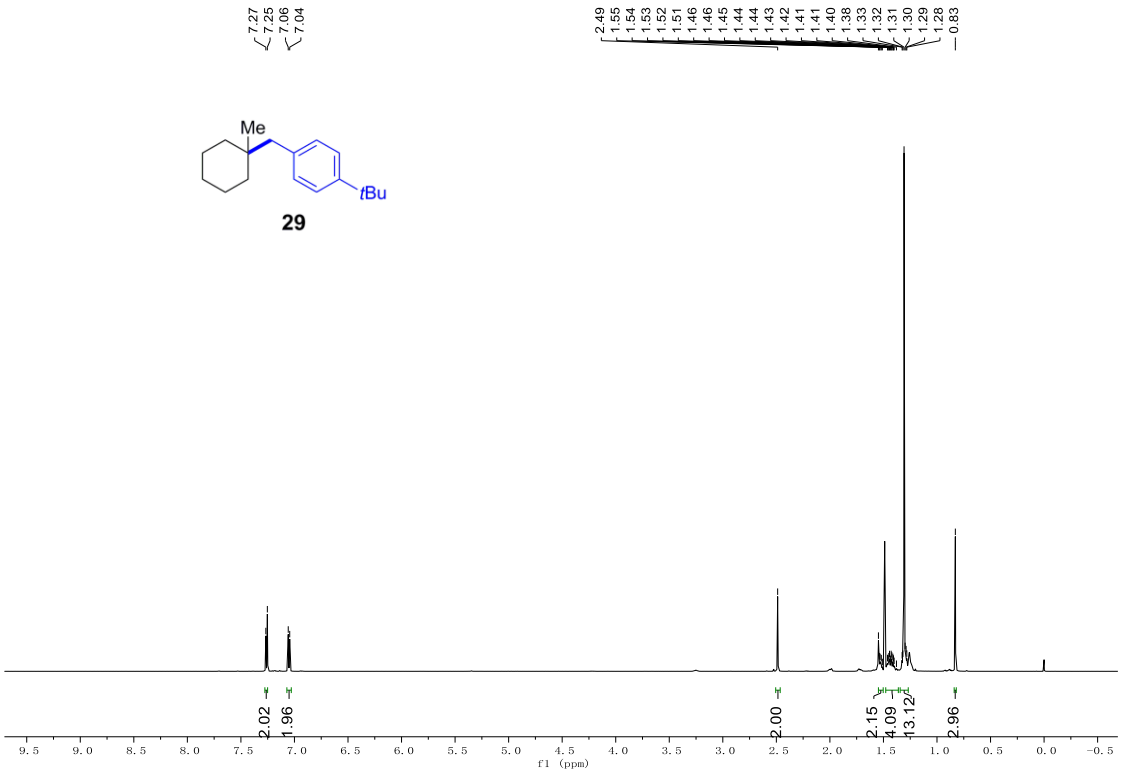
^{1}H NMR (600 MHz, $CDCl_3$) of **28**:



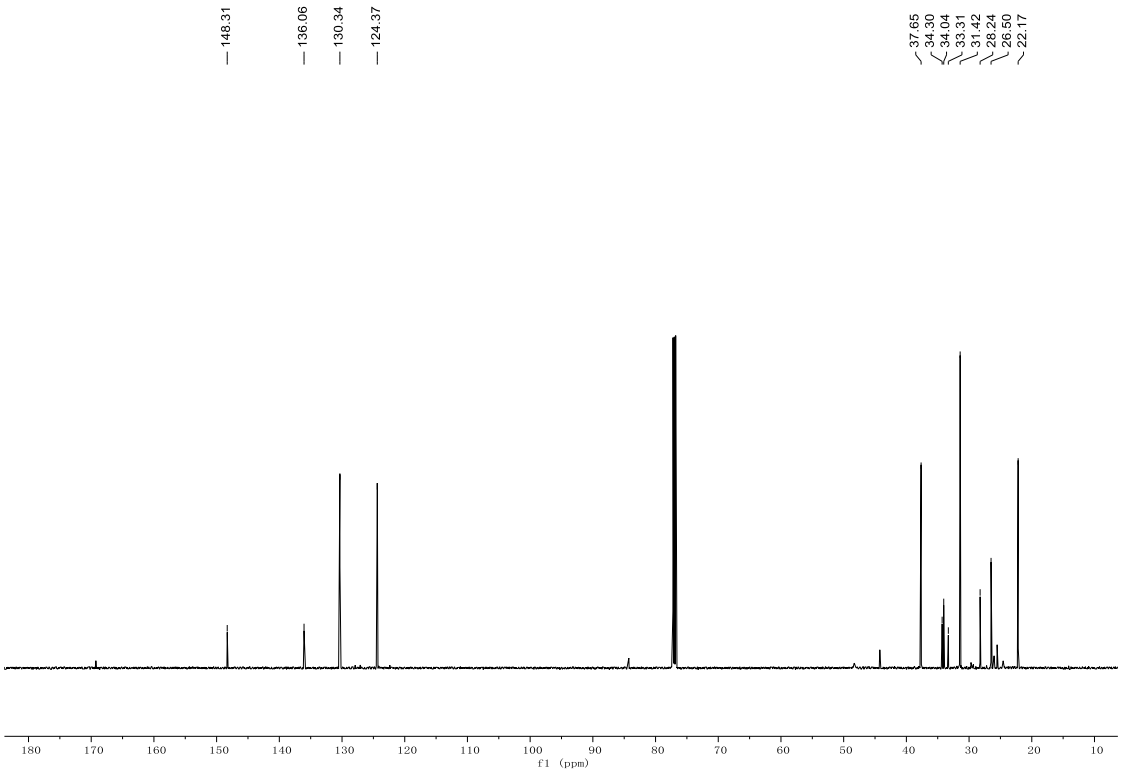
^{13}C NMR (151 MHz, $CDCl_3$) of **28**:



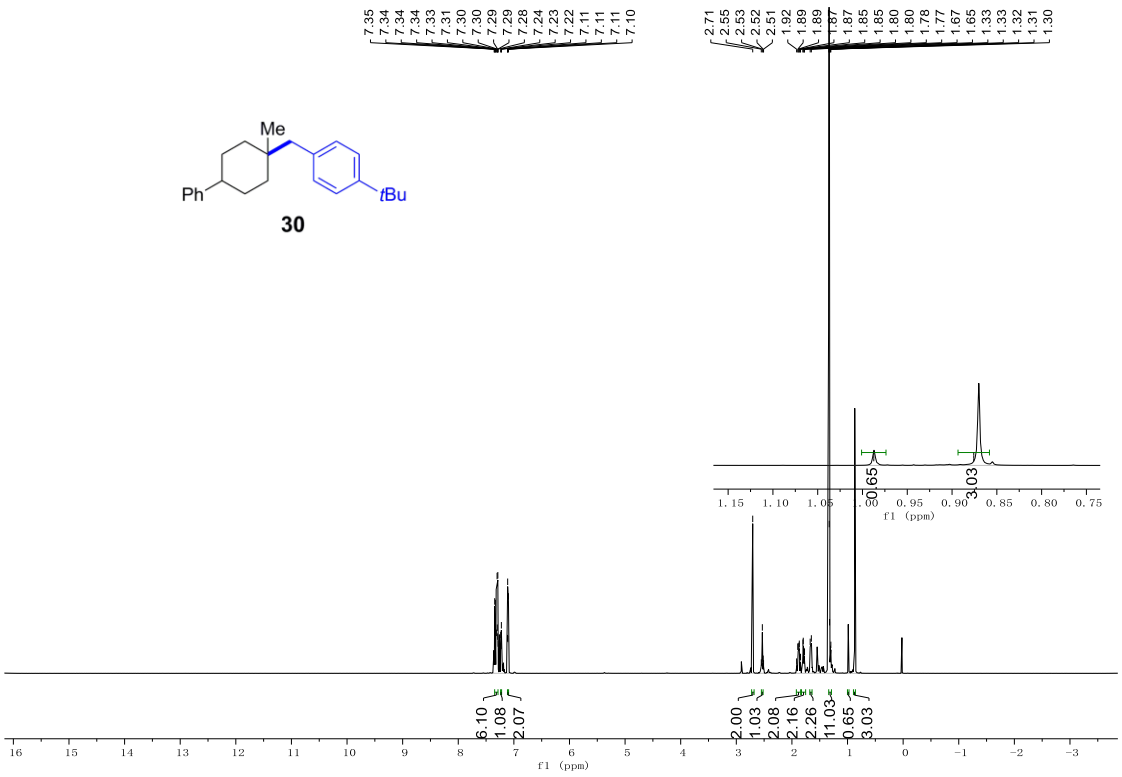
^{1}H NMR (600 MHz, $CDCl_3$) of **29**:



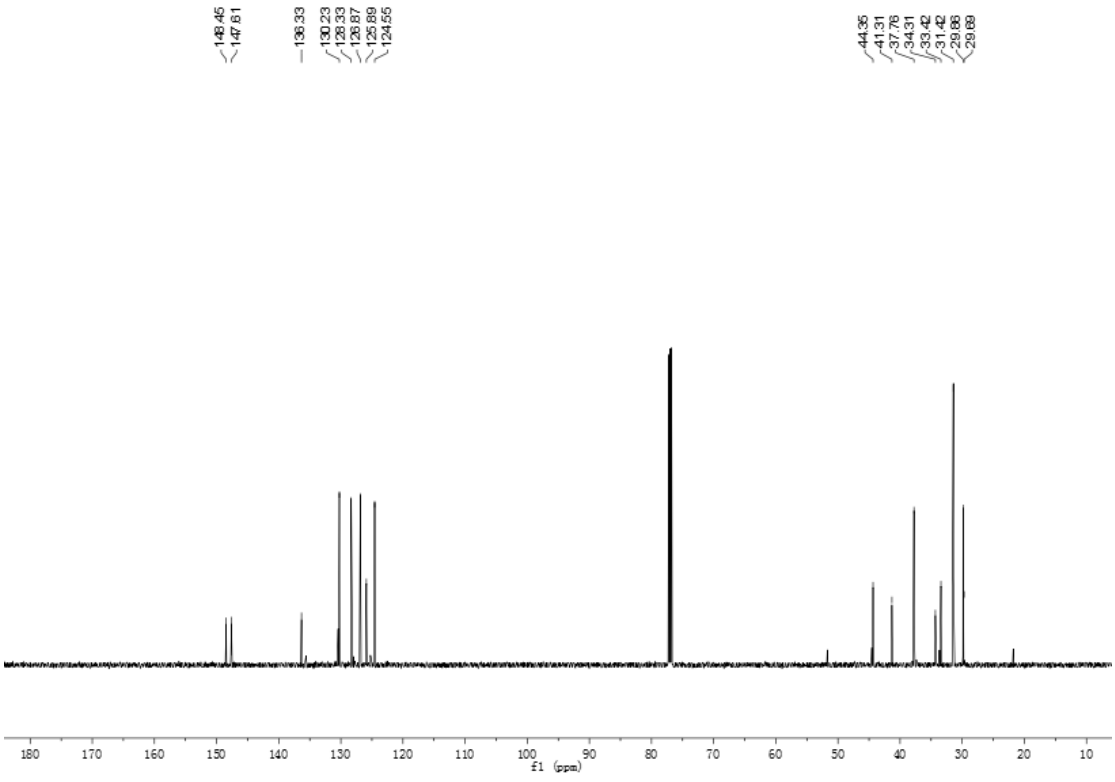
^{13}C NMR (151 MHz, $CDCl_3$) of **29**:



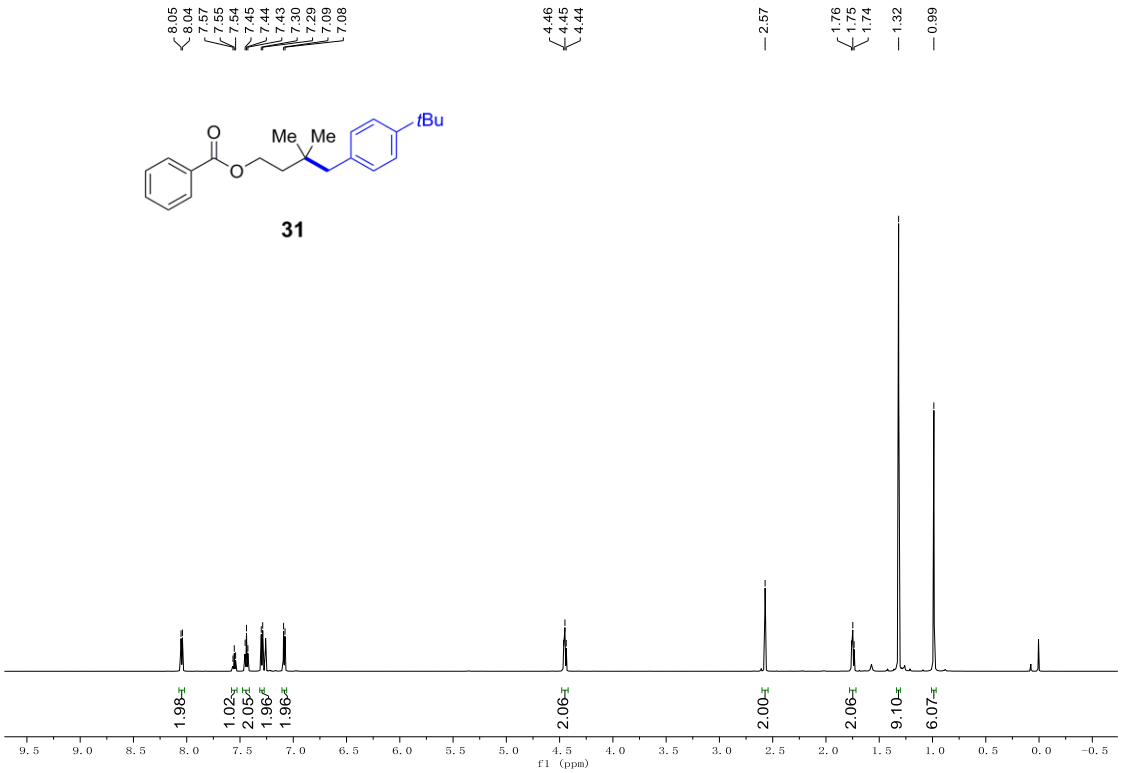
^{1}H NMR (600 MHz, $CDCl_3$) of **30**:



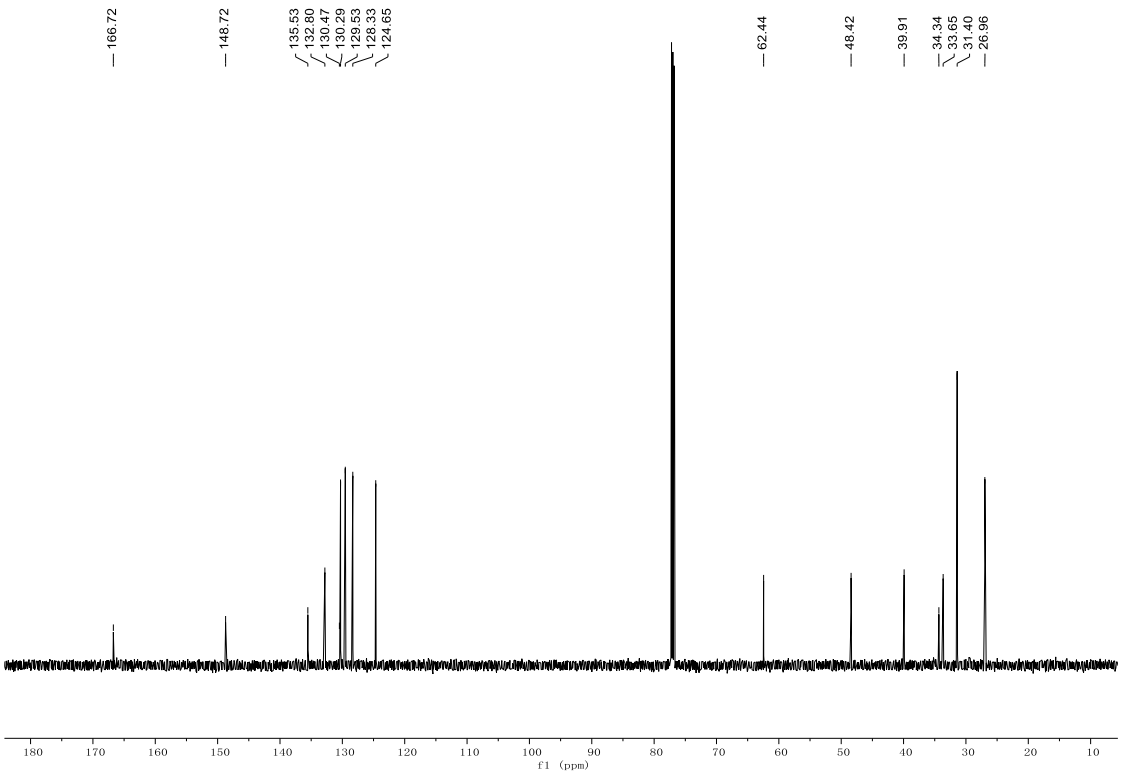
^{13}C NMR (151 MHz, $CDCl_3$) of **30**:



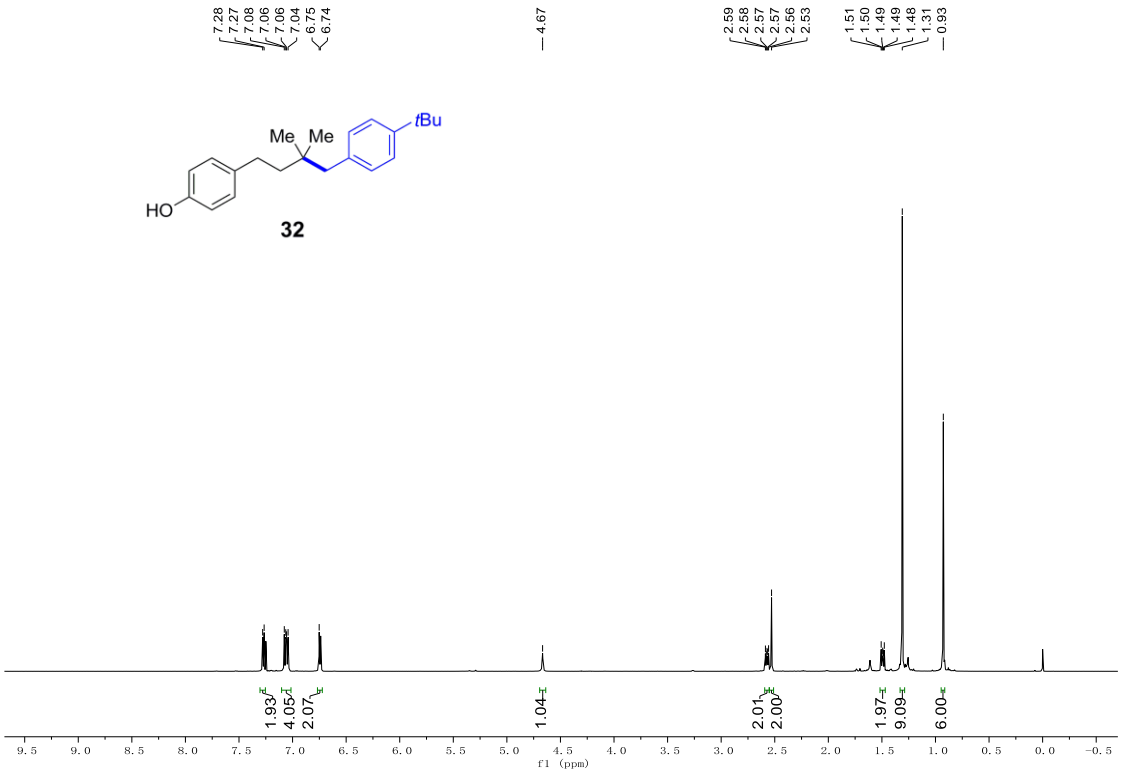
^{1}H NMR (600 MHz, $CDCl_3$) of **31**:



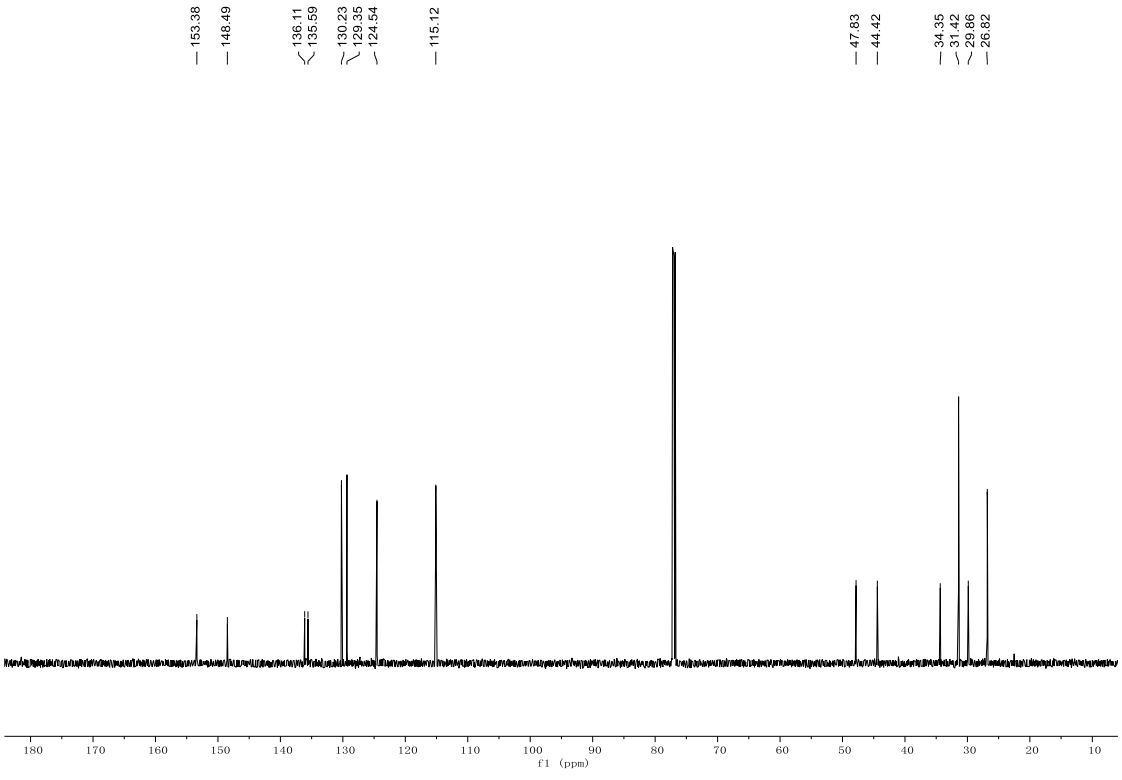
^{13}C NMR (151 MHz, $CDCl_3$) of **31**:



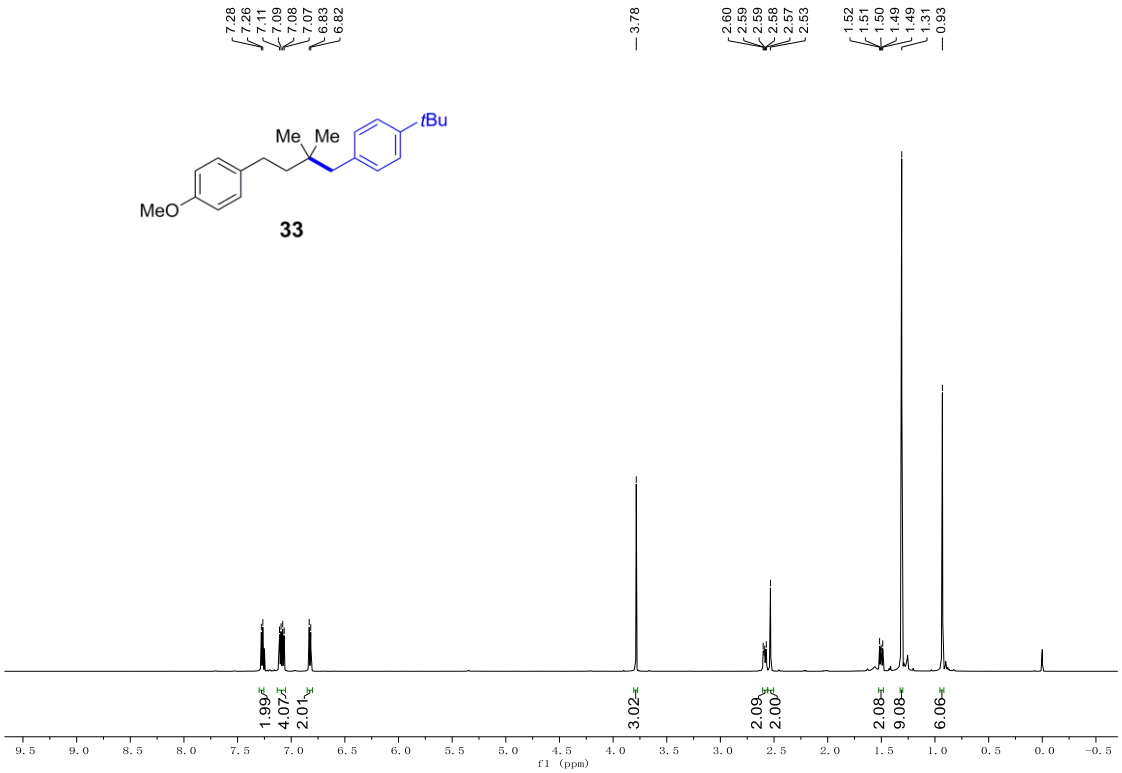
^{1}H NMR (600 MHz, $CDCl_3$) of **32**:



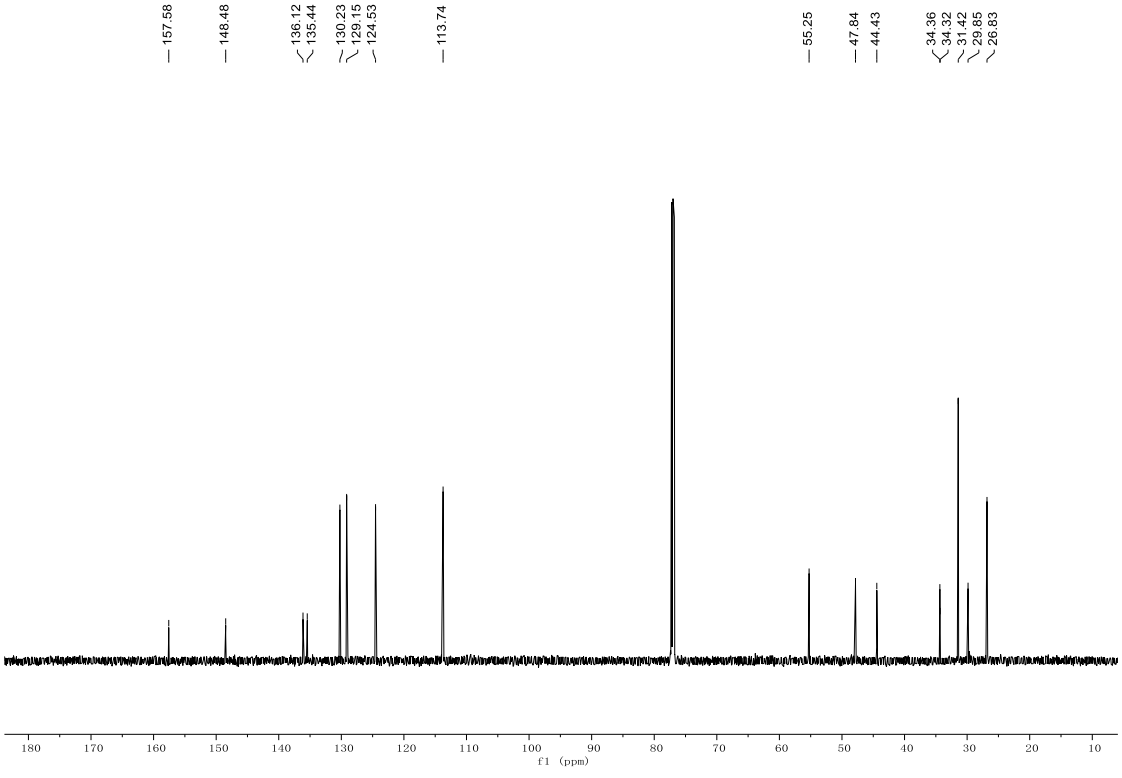
^{13}C NMR (151 MHz, $CDCl_3$) of **32**:



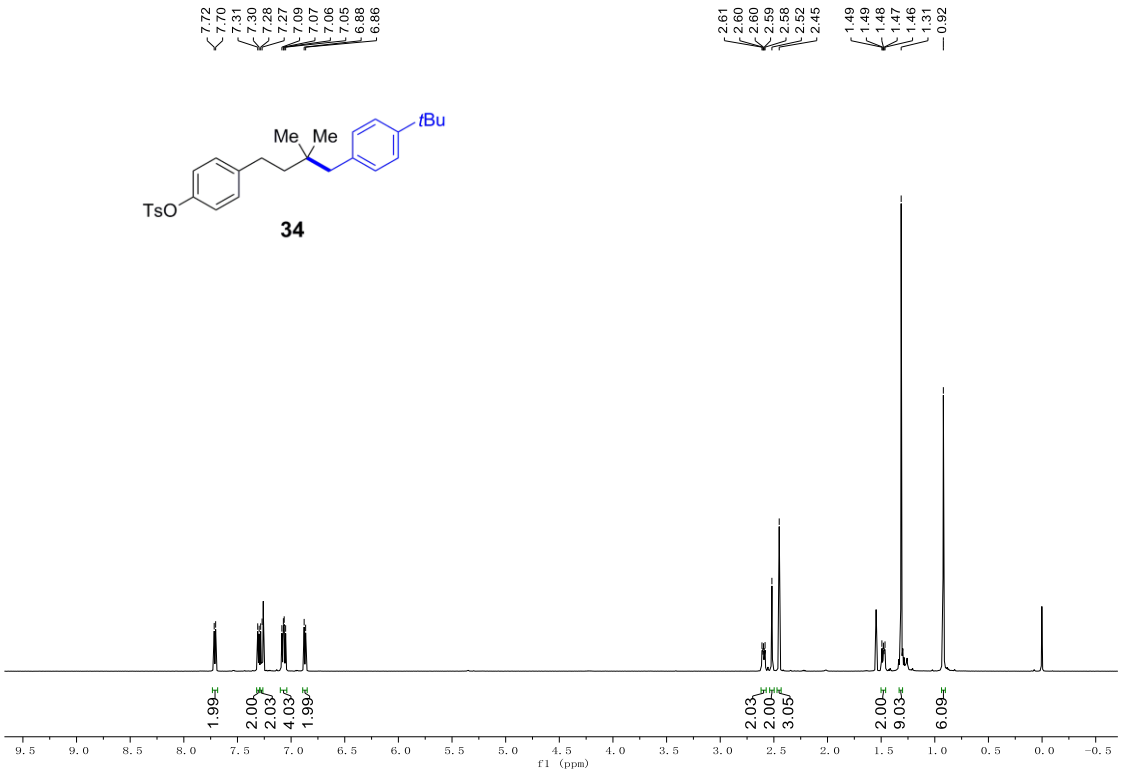
^{1}H NMR (600 MHz, $CDCl_3$) of **33**:



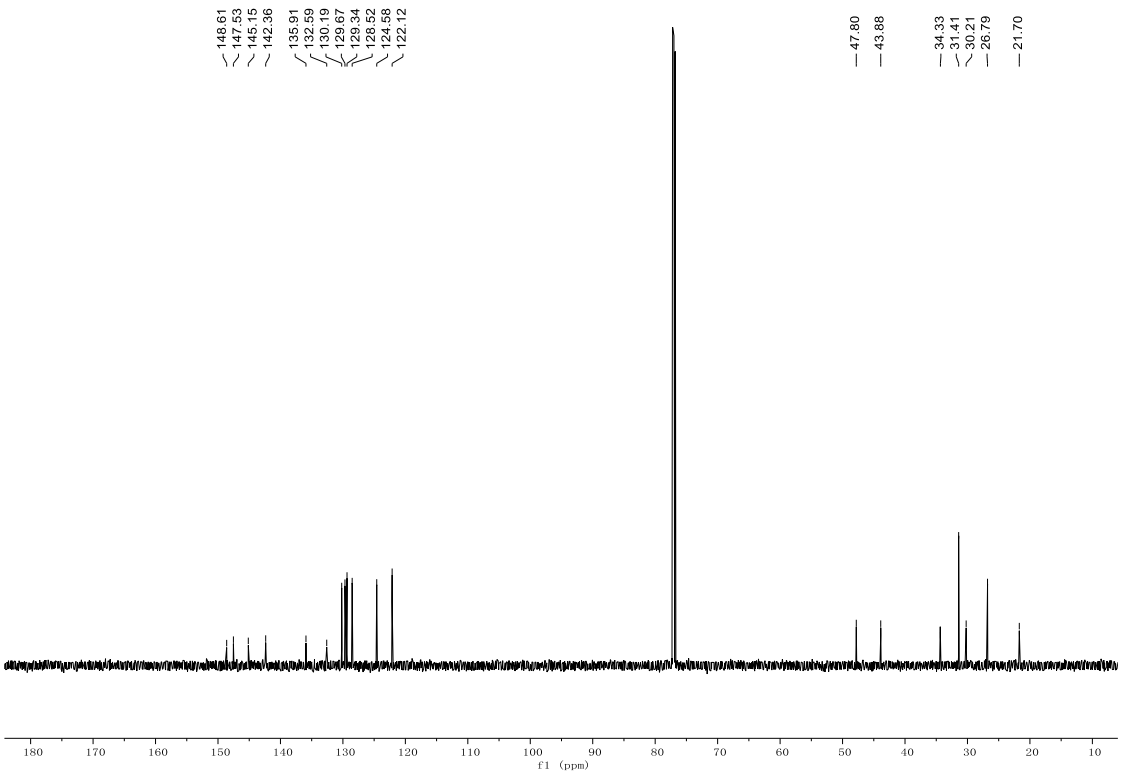
^{13}C NMR (151 MHz, $CDCl_3$) of **33**:



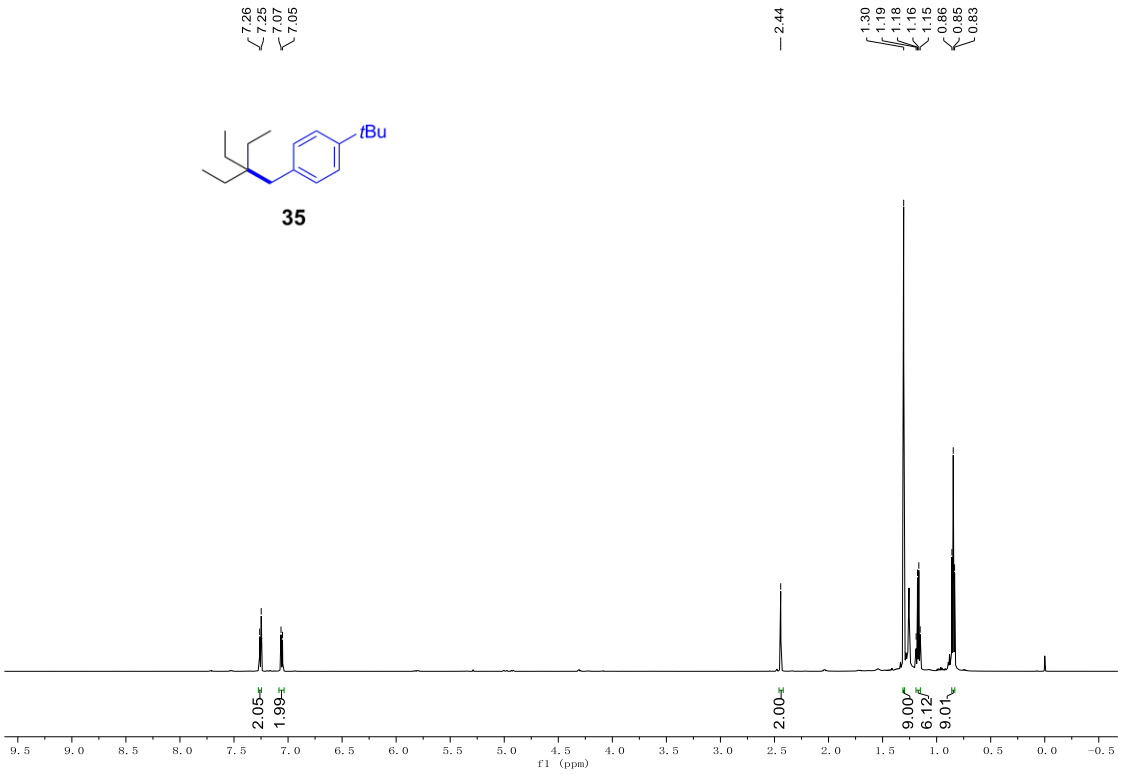
^{1}H NMR (600 MHz, $CDCl_3$) of **34**:



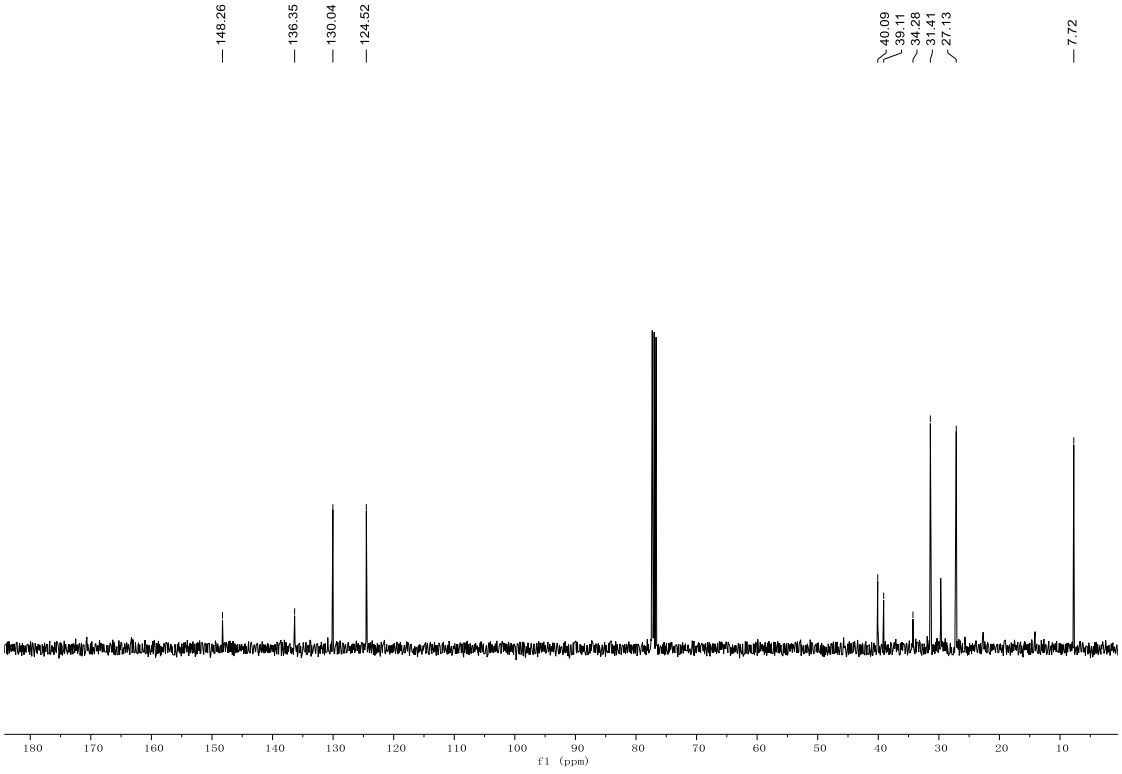
^{13}C NMR (151 MHz, $CDCl_3$) of **34**:



^{1}H NMR (600 MHz, $CDCl_3$) of **35**:



^{13}C NMR (151 MHz, $CDCl_3$) of **35**:



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