Supplementary Information

Iron-catalysed 1,2-aryl migration of tertiary azides

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1. General methods

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III-400 MHz spectrometer with $CDCl_3$ as the solvent. In $CDCl_3$, the chemical shifts in ^{1}H NMR spectra were determined with $Si(CH_3)_4$ as the internal standard (δ = 0.00 ppm); the chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.00 ppm). The coupling constants (*J* value) are reported in Hz (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad signal). Flash column chromatography (FCC) was conducted on silica gel (200-300 mesh). Thin layer chromatography (TLC) analyses were performed using Merck silica gel 60 F254 plates and visualized under UV, by phosphomolybdic acid or by iodine stain. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF QII by ESI. The Fourier transformation infrared spectra (FT-IR) were measured on a FT-IR spectrometer. Melting points (m.p.) were measured on an XT-4 melting point apparatus and are uncorrected.

Anhydrous $FeCl_2$ (beads, 10 mesh, 99.99%), anhydrous FeF_2 (98%) and anhydrous $Fe(OAc)_2$ (99.99%) was purchased from Sigma-Aldrich, anhydrous $FeBr_2$ (98.5%) was purchased from Alfa Aesar, anhydrous $Fe(acac)_2$ (99%), anhydrous $Fe(OTf)_2$ (97%) was purchased from adamas-beta. Anhydrous chlorobenzene, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), 1,2-dichloroethane (DCE), fluorobenzene were purchased from Energy Chemical and used without further treatment. Other solvents were treated before use following the standard procedures.

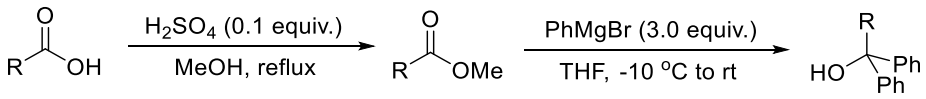
β-Diketiminates $\mathbf{L_1}$–$\mathbf{L_5}$ were prepared according to literature methods.[1] N-Heterocyclic carbenes $\mathbf{L_6}$–$\mathbf{L_{10}}$ were prepared according to literature methods.[2]

Unless otherwise noted, all other materials were obtained from commercial suppliers, and were used without further purification.

2. Experimental procedures

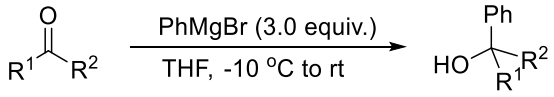
2.1 General procedure for the preparation of tertiary azides:

Preparation of diaryl alcohols[3]:



Method A: A carboxylic acid precursor (10.0 mmol) was dissolved in 30 mL methanol contained in a 100 mL round bottom flask equipped with a magnetic stirring bar. Into this solution was added dropwise 107 uL of *conc.* sulfuric acid (98%, 2.0 mmol,) over 5 min at room temperature. The resulting solution was stirred at reflux for 3 h. The reaction mixture was then cooled down to room temperature, and into the flask were added 1.0 M aqueous KOH solution (15 mL) and water (15 mL). The product was extracted three times with ethyl acetate (3×30 mL). The combined organic layers were washed twice with water (30 mL), dried with anhydrous $MgSO_4$ and concentrated with a rotary evaporator. The residual was purified by flash column chromatography on silica gel with the petroleum ether (PE) and ethyl acetate (EA) as eluent (PE/EA = 50:1) to give the ester product.

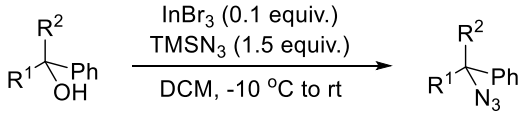
A THF solution of the prepared ester (10.0 mmol in 30 mL of anhydrous THF) was added into an oven-dried 100 mL Schlenk tube equipped with a stopper and a magnetic stirring bar, and was degassed with nitrogen three times. After that, PhMgBr (10.7 mL, 30.0 mmol, 2.8 mol/L in 2-methyl-THF) was added dropwise into the solution over 15 min at -10 ℃, which was then allowed to raise temperature gradually to 25 ℃. The reaction mixture was stirred at 25 ℃ for 6 h. It was then quenched with 1.0 M HCl (10 mL), and the product was extracted with EA (3×30 mL). The combined organic phases were washed with brine, and dried over anhydrous Na_2SO_4. The solution was concentrated with a rotary evaporator. Recrystallization of the residual from Et_2O afforded the corresponding diphenyl alcohol.



Method B: A solution of a ketone precursor (10.0 mmol) in 30 mL of anhydrous THF was added into a 100 mL oven-dried Schlenk tube equipped with a stopper and a magnetic stirring bar. The tube was degassed with nitrogen for three times. PhMgBr (10.7 mL, 30.0 mmol, 2.8mol/L in 2-methyl-THF) was added dropwise into the tube over 15 min at -10 ℃, and the temperature was then gradually raised to 25 ℃. This

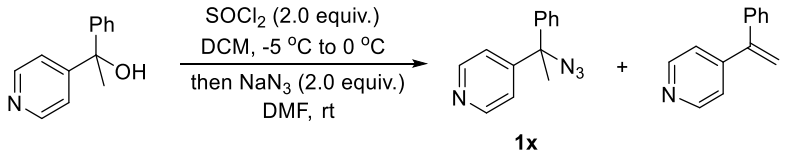
reaction mixture was stirred at 25 ℃ for 6 h. After that, it was quenched with the 1.0 M HCl (10 mL) and the product was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and was then concentrated *in vacuo*. Recrystallization of the residual from Et_2O afforded the corresponding α-aryl alcohol.

Procedure for the preparation of tertiary azides[4]:



A solution of alcohol (5.0 mmol) and $TMSN_3$ (0.986 mL, 7.5 mmol) in dry dichloromethane (DCM) 5 mL) were placed in a 100 mL Schlenk tube, the tube was degassed with nitrogen three times. $InBr_3$ (177 mg, 0.5 mmol) was added to this reaction mixture. The mixture was stirred at -10 ℃ for 10 min. Then the temperature gradually was raised to 25 ℃, and the stirring was continued until the reaction finished (a few min in general) as indicated by TLC analysis. The product was extracted with DCM (3×20 mL). The combined DCM phases were washed sequentially with 10% aqueous Na_2CO_3 solution (10 mL) and water (20 mL), and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure with a rotary evaporator. The resultant white oil was crystallized from Et_2O to afford the corresponding azide product.

Preparation of 4-(1-azido-1-phenylethyl)pyridine (1x):

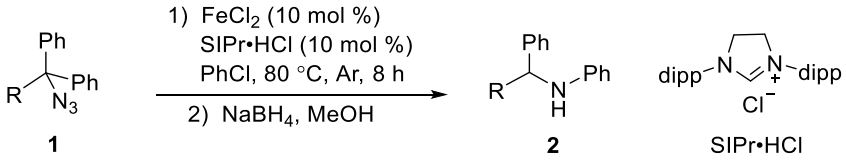


1x

To a solution of the alcohol (996 mg, 5.0 mmol.) in anhydrous DCM (10 mL) cooled at -5 ℃ was added dropwise $SOCl_2$ (0.72 mL, 10.0 mmol) over a period of 15 min under vigorous stirring. The resulting suspension was stirred at 0 ℃ for an additional 1 h. The reaction mixture was then concentrated and the residual was dissolved in DMF (10 mL). Sodium azide (0.650 g. 10.0 mmol) was then added into the DMF solution and the mixture was stirred at 25 °C for 12 h. The mixture was

diluted with water (50 mL) and extracted with EA (3×100 mL). The combined organic layers were washed with brine (3×100 mL), dried over $MgSO_4$, and concentrated to give the crude product, which was purified by flash chromatography (PE/EA = 10:1) to afford the 640 mg of product as a 1:1.2 mixture of **1x** with 4-(1-phenylvinyl)pyridine. This mixture was used to test the reaction of **1x** under the standard conditions as described below.

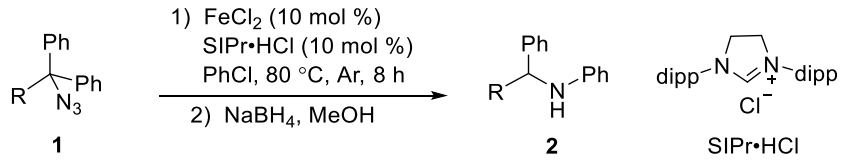
2.2. General procedure for the iron-catalysed 1,2-aryl migration of azides



1 **2** SIPr•HCl

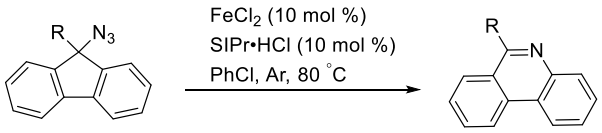
A 10 mL flame-dried tube equipped with a magnetic stirring bar and a rubber stopper was charged with azide **1** (0.3 mmol), $FeCl_2$ (3.8 mg, 0.03 mmol, 0.1 equiv.), SIPr·HCl (**L_6**) (12.8 mg, 0.03 mmol, 0.1 equiv.). The tube was evacuated and backfilled with argon (three times) at 0 ^oC (in ice-water bath). Anhydrous chlorobenzene (2.5 mL) was added with a syringe into the tube, and the mixture was stirred at 80 ^oC (in an alloy-bead heating bath) for 8 h. After the reaction mixture was cooled to room temperature, the tube was immersed in an ice-water bath. $NaBH_4$ (23 mg, 0.6 mmol, 2.0 equiv.) and methanol (3.0 mL) was then added into the tube, and the mixture was stirred under an argon atmosphere for 3 h. The reaction was then quenched with water, and the product was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed sequentially with 10% aqueous Na_2CO_3 solution (30 mL) and water (20 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure with a rotary evaporator to give the crude product, which was purified by flash chromatography (eluent PE and EA) to afford the aniline product.

The reactions of compounds **3** were carried out following the same procedure.



1 **2** SIPr•HCl

2.3 Procedure for the preparation of 7a and 7b



6 **7**

R = Me, **7a**; R = Et, **7b**

A 10 mL flame-dried tube equipped with a magnetic stirring bar and a rubber stopper was charged with azide **6** (0.3 mmol), $FeCl_2$ (3.8 mg, 0.03 mmol, 0.1 equiv.), SIPr·HCl (12.8 mg, 0.03 mmol, 0.1 equiv.). The tube was evacuated and backfilled with argon (three times) at 0 ^oC (in ice-water bath). Anhydrous chlorobenzene (2.5 mL) was added with a syringe into the tube, and the mixture was stirred at 80 ^oC (in an alloy-bead heating bath) for 8 h. The reaction was then quenched with water, and the product was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed sequentially with 10% aqueous Na_2CO_3 solution (30 mL) and water (20 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure with a rotary evaporator to give the crude product, which was purified by flash chromatography (eluent PE and EA) to afford phenanthridine **6a** or **6b**.

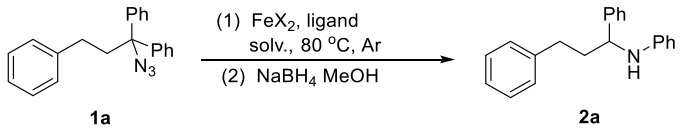
2.4 Gram scale preparation of compound 2a

A 50 mL flame-dried Schlenk tube equipped with a magnetic stirring bar and a rubber stopper was charged with azide **1** (5.0 mmol, 1.566 g), $FeCl_2$ (63.4 mg, 0.5 mmol, 0.1 equiv.), SIPr·HCl (213.5 mg, 0.5 mmol, 0.1 equiv.). The tube was evacuated and backfilled with argon (three times) at 0 ^oC (in ice-water bath). Anhydrous chlorobenzene (10 mL) was added with a syringe into the tube, and the mixture was stirred at 80 ^oC (in an alloy-bead heating bath) for 8 h. After the reaction mixture was cooled to room temperature, the tube was immersed in an ice-water bath. $NaBH_4$ (378.3 mg, 10.0 mmol, 2.0 equiv.) and methanol (3.0 mL) was then added into the tube, and the mixture was stirred under an argon atmosphere for 3 h. The reaction was then quenched with water, and the product was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed sequentially with 10% aqueous Na_2CO_3 solution (30 mL) and water (20 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure with a rotary evaporator to give the

crude product, which was purified by flash chromatography (PE/EA = 30:1) to afford 1.22 g of **2a**; yield: 85%.

3. Screening of reaction conditions

Table S1. Screening of ligands, solvents and ferrous salts



1a 2a

Entry	FeX_2 (mol %)	Ligand (mol %)	Solvent	Yields (%)[b]
1	$FeCl_2$ (10)	$\mathbf{L_1}$ (10)	PhCl	73
2	$FeCl_2$ (10)	$\mathbf{L_2}$ (10)	PhCl	77
3	$FeCl_2$ (10)	$\mathbf{L_3}$ (10)	PhCl	trace
4	$FeCl_2$ (10)	$\mathbf{L_4}$ (10)	PhCl	trace
5	$FeCl_2$ (10)	$\mathbf{L_5}$ (10)	PhCl	27
6	**$FeCl_2$** (10)	$\mathbf{L_6}$ (10)	**PhCl**	**87**
7	$FeCl_2$ (10)	$\mathbf{L_7}$ (10)	PhCl	trace
8	$FeCl_2$ (10)	$\mathbf{L_8}$ (10)	PhCl	trace
9	$FeCl_2$ (10)	$\mathbf{L_9}$ (10)	PhCl	86
10	$FeCl_2$ (10)	$\mathbf{L_{10}}$ (10)	PhCl	35
11	$FeBr_2$ (10)	$\mathbf{L_6}$ (10)	PhCl	39
12	FeF_2 (10)	$\mathbf{L_6}$ (10)	PhCl	trace
13	$Fe(acac)_2$ (10)	$\mathbf{L_6}$ (10)	PhCl	32
14	$Fe(OAc)_2$ (10)	$\mathbf{L_6}$ (10)	PhCl	46
15	$Fe(OTf)_2$ (10)	$\mathbf{L_6}$ (10)	PhCl	trace
16	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	DMSO	53
17	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	DMF	47
18	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	DCE	85
19	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	PhF	67
20	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	toluene	38
21	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	CH_3CN	41
22	$FeCl_2$ (5)	$\mathbf{L_4}$ (5)	PhCl	69
23	$FeCl_2$ (20)	$\mathbf{L_4}$ (20)	PhCl	89
24	none	$\mathbf{L_6}$ (10)	PhCl	N.R.
25	$FeCl_2$ (10)	none	PhCl	N.R.
26	$FeCl_2$ (10)	$\mathbf{L_6}$ (10)	PhCl	N.R.[c]

[a] The reaction was conducted on 0.3 mmol scale in 2.5 mL solvent at 80 °C under an argon atmosphere for 8 h. After the migration reaction finished, the reaction mixture was cooled to room temperature, and the vessel was immersed into an ice-water bath and then charged with 0.6 mmol of $NaBH_4$ and 3 mL of methanol. The reaction mixture was stirred for 3 h at 0 °C. [b] Isolated yield. [c] The reaction was conducted under the aerobic atmosphere.

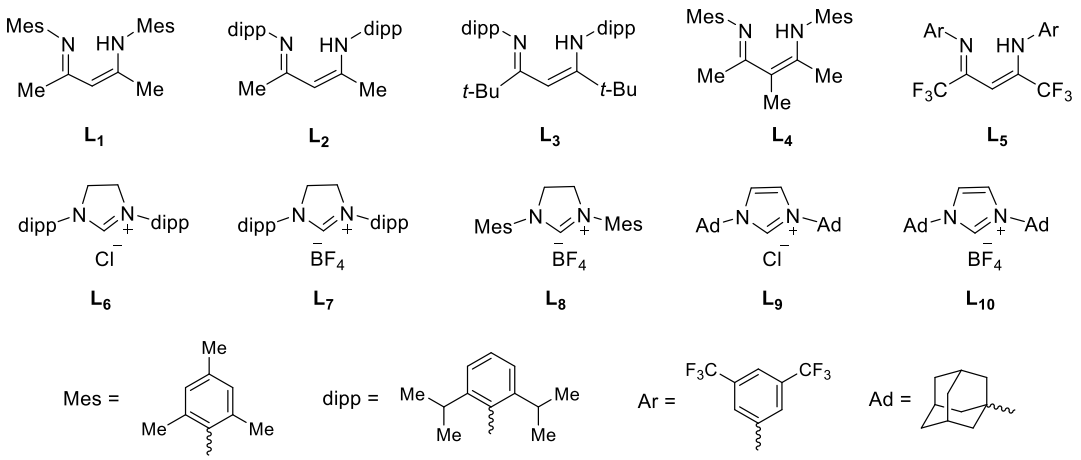
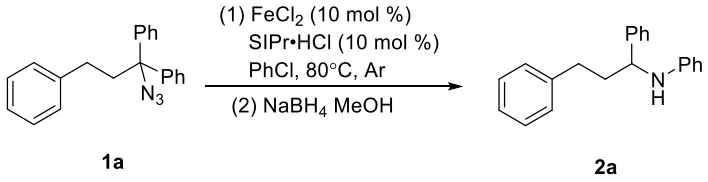
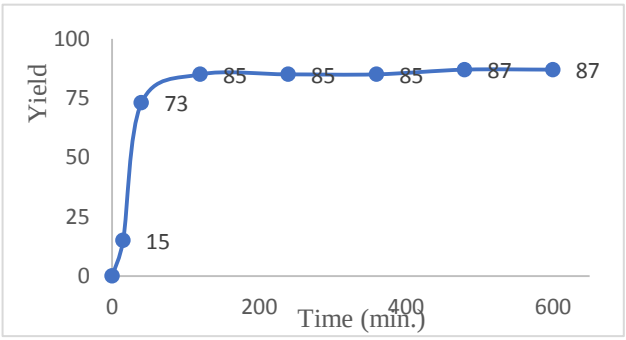


Figure S1 The structures of tested ligands.

Table S2. Screening of reaction time [a]



Entry	Time	Yields (%)[b]
1	15 min	15
2	40 min	73
3	2 h	85
4	4 h	85
5	6 h	85
6	8 h	87
7	10 h	87

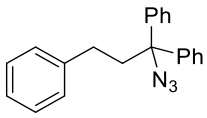


[a] The reaction was conducted on 0.3 mmol scale in 2.5 mL solvent. After the migration reaction finished, the reaction mixture was cooled to room temperature, and the vessel was immersed into an ice-water bath and then charged with 0.6 mmol of $NaBH_4$ and 3 mL of methanol. The reaction mixture was stirred for 3 h at 0 °C. [b] Isolated yield

Cautions

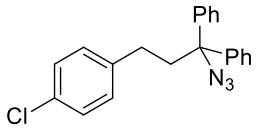
Azides are potentially explosive compounds. Although we haven't encountered any safety problem when handling them in our experiments, proper precautions must be taken to avoid strong mechanical shock or friction. The reactions and subsequent workup should be performed in a hood behind a blast shield. Plastic spatula or plastic pipettes are recommended for handling with $TMSN_3$ and NaN_3.

4. Characterization of starting materials



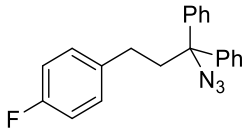
(1-Azidopropane-1,1,3-triyl)tribenzene (1a)

White crystals (recrystallization from Et_2O), 0.892 g, yield: 57%; m.p. 67–68 °C; R_f = 0.72 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50–7.02 (m, 15H), 2.82–2.60 (m, 2H), 2.58–2.39 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.8, 141.7, 128.5, 128.4, 128.4, 127.5, 127.0, 126.0, 72.4, 41.1, 30.7; FT-IR (KBr, cm^{-1}): 2100; HRMS: calcd for $C_{21}H_{20}N_3$ $[M + H]^+$ 314.1652, found 314.1658.



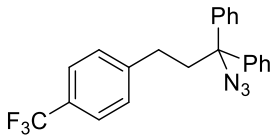
(1-Azido-3-(4-chlorophenyl)propane-1,1-diyl)dibenzene (1b)

White crystals (recrystallization from Et_2O), 0.854 g, yield: 49%; m.p. 79–80 °C; R_f = 0.72 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.26 (m, 10H), 7.26–7.18 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.73–2.56 (m, 2H), 2.52–2.38 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 140.2, 131.8, 129.8, 128.6, 128.5, 127.7, 127.0, 72.4, 41.0, 30.1; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{21}H_{19}ClN_3$ $[M + H]^+$ 348.1262, found 348.1262.



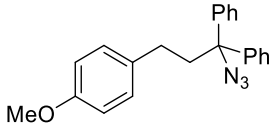
(1-Azido-3-(4-fluorophenyl)propane-1,1-diyl)dibenzene (1c)

White crystals (recrystallization from Et_2O), 1.027 g, yield: 62%; m.p. 72–73 °C; R_f = 0.68 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50–7.17 (m, 10H), 7.06 (t, *J* = 6.8 Hz, 2H), 6.94 (t, *J* = 8.8 Hz, 2H), 2.72–2.60 (m, 2H), 2.52–2.38 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5, 160.1, 142.7, 137.29, 137.3, 129.7, 129.7, 128.4, 127.6, 1267.0, 115.3, 115.1, 72.3, 41.2, 29.9; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{21}H_{19}FN_3$ $[M + H]^+$ 332.1387, found 332.1389.



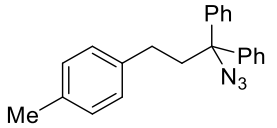
Azido-3-(4-(trifluoromethyl)phenyl)propane-1,1-diyl)dibenzene (1d)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 1.372 g, yield: 72%; R_f = 0.43 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.32–7.24 (m, 8H), 7.24–7.19 (m, 2H), 7.17–7.12 (m, 2H), 2.65–2.55 (m, 2H), 2.51–2.42 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 142.56 128.7, 128.5, 127.7, 127.0, 125.4, 125.4, 125.4, 125.3, 72.3, 40.8, 30.6; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{21}H_{18}F$ $[M - N_3]^+$ 289.1387, found 289.1389.



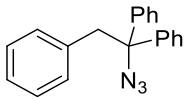
(1-Azido-3-(4-methoxyphenyl)propane-1,1-diyl)dibenzene (1e)

White crystals (recrystallization from Et_2O), 0.978 g, yield: 57%; m.p. 81–82 ^{o}C; R_f = 0.71 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46–7.22 (m, 10H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 2.65 (dt, *J* = 11.8, 3.8 Hz, 2H), 2.43 (dt, *J* = 12.1, 4.0 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.9, 142.9, 133.7, 129.3, 128.4, 127.5, 127.0, 113.9, 72.4, 55.3, 41.3, 29.7; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{22}H_{21}N_3OK$ $[M + K]^+$ 382.1316, found 382.1317.



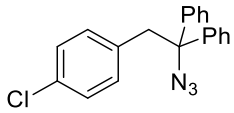
(1-Azido-3-(*p*-tolyl)propane-1,1-diyl)dibenzene (1f)

White crystals (recrystallization from Et_2O), 1.030 g, yields: 63%; m.p. 68–69 ^{o}C; R_f = 0.69 (PE/EA = 10:1); H NMR (400 MHz, Chloroform-*d*) δ 7.42–7.25 (m, 10H), 7.08 (d, *J* = 6.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.72–2.61 (m, 2H), 2.50–2.39 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9, 138.6, 135.5, 129.15, 128.4, 128.2, 127.5, 127.0, 72.4, 41.2, 30.2, 21.0; FT-IR (KBr, cm^{-1}): 2099; HRMS (ESI-TOF) calcd for $C_{22}H_{22}N_3$ $[M + H]^+$ 328.1808, found 328.1811.



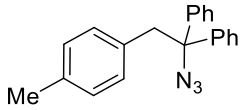
(1-Azidoethane-1,1,2-triyl)tribenzene) (1g)[4]

White crystals (recrystallization from Et_2O), 0.673 g, yields: 45%; m.p. 94–95 ^oC; R_f = 0.71 (PE/EA = 10:1); H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.20 (m, 10H), 7.18–7.04 (m, 3H), 6.73 (d, *J* = 8.3 Hz, 2H), 3.65 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 135.6, 130.5, 128.1, 127.6 127.5, 126.5, 73.2, 45.0; FT-IR (KBr, cm^{-1}): 2106; HRMS (ESI-TOF) calcd for $C_{20}H_{17}N_3K$ $[M + K]^+$ 338.1054, found 338.1056.



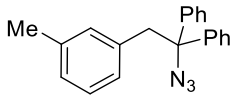
(1-Azido-2-(4-chlorophenyl)ethane-1,1-diyl)dibenzene (1h)

White crystals (recrystallization from Et_2O), 1.016 g, yields: 61%; m.p. 58–60 ^oC; R_f = 0.69 (PE/EA = 10:1); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32–7.13 (m, 10H), 7.09–6.97 (m, 2H), 6.77–6.50 (m, 2H), 3.58 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 134.0, 132.5, 131.8, 128.2, 127.7, 127.4, 73.0, 44.4; FT-IR (KBr, cm^{-1}): 2109; HRMS (ESI-TOF) calcd for $C_{20}H_{16}Cl$ $[M - N_3]^+$ 291.0935, found 291.0935.



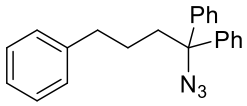
(1-Azido-2-(*p*-tolyl)ethane-1,1-diyl)dibenzene (1i)

White crystals (recrystallization from Et_2O), 1.017 g, yields: 65%; m.p. 97–98 ^oC; R_f = 0.71 (PE/EA = 10:1); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.20 (m, 10H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.61 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 136.1, 132.4, 130.34 128.3, 128.1, 127.5, 127.5, 73.2, 44.5, 21.0; FT-IR (KBr, cm^{-1}): 2107; HRMS (ESI-TOF) calcd for $C_{21}H_{19}N_3Na$ $[M + Na]^+$ 336.1471, found 336.1475.



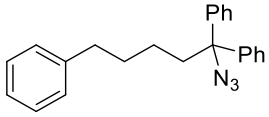
(1-Azido-2-(*m*-tolyl)ethane-1,1-diyl)dibenzene (1j)

White crystals (Recrystallization from Et_2O), 0.908 g, yields: 58%; m.p. 98–99 °C; R_f = 0.72 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.18 (m, 10H), 7.06–6.91 (m, 2H), 6.52 (dt, *J* = 12.6, 4.2 Hz, 2H), 3.62 (s, 2H), 2.18 (s, *J* = 3.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 137.0, 135.4, 131.4, 128.1, 127.5, 127.4, 127.2, 73.2, 45.0, 21.23; FT-IR (KBr, cm^{-1}): 2106; HRMS (ESI-TOF) calcd for $C_{21}H_{19}N_3Na$ $[M + Na]^+$ 336.1471, found 336.1472.



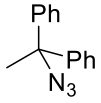
(1-Azidobutane-1,1,4-triyl)tribenzene (1k)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.981 g, yield: 60%; R_f = 0.48 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42–7.04 (m, 15H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.41 (dq, *J* = 8.0, 3.8 Hz, 2H), 1.57 (dq, *J* = 11.9, 7.9, 6.0 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.0, 141.7, 128.3, 128.3, 128.3, 127.4, 127.0, 125.8, 72.5, 38.2, 35.7, 25.6; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{22}H_{21}$ $[M - N_3]^+$ 285.1638, found 285.1637.



(1-Azidopentane-1,1,5-triyl)tribenzene (1l)

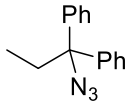
Colorless oil obtained by column chromatography (PE/EA = 100:1), 1.108 g, yield: 60%; R_f = 0.52 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42–7.18 (m, 12H), 7.11 (ddd, *J* = 19.9, 8.0, 3.2 Hz, 3H), 2.59–2.48 (m, 2H), 2.39 (dt, *J* = 11.7, 3.8 Hz, 2H), 1.70–1.53 (m, 2H), 1.28 (dq, *J* = 8.1, 3.8 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1, 142.3, 128.2, 128.2, 127.3, 127.0, 125.6, 72.5, 38.5, 35.7, 31.6, 23.8; FT-IR (KBr, cm^{-1}): 2102; HRMS (ESI-TOF) calcd for $C_{23}H_{23}$ $[M - N_3]^+$ 299.1794, found 299.1794.



(1-Azidoethane-1,1-diyl)dibenzene (1m)

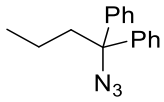
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.524 g, yield: 47%; R_f = 0.51 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65–7.02 (m,

10H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.2, 128.3, 127.5, 126.6, 69.4, 27.4; FT-IR (KBr, cm^{-1}): 2092; HRMS (ESI-TOF) calcd for $C_{14}H_{13}$ $[M - N_3]^+$ 181.1012, found 181.1013.



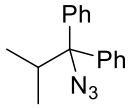
(1-Azidopropane-1,1-diyl)dibenzene (1n)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.747 g, yield: 63%; R_f = 0.45 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.26 (m, 8H), 7.26–7.18 (m, 2H), 2.50–2.32 (m, 2H), 0.88–0.77 (t, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.0, 128.3, 127.4, 127.2, 73.1, 31.6, 8.6; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{15}H_{15}$ $[M - N_3]^+$ 195.1168, found 195.1168.



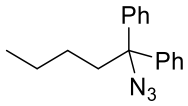
(1-Azidobutane-1,1-diyl)dibenzene (1o)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.703 g, yield: 56%; R_f = 0.51 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45–7.11 (m, 10H), 2.41–2.28 (m, 2H), 1.30–1.13 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 128.2, 127.3, 127.0, 72.6, 41.0, 17.5, 14.2; FT-IR (KBr, cm^{-1}): 2105; HRMS (ESI-TOF) calcd for $C_{16}H_{17}$ $[M - N_3]^+$ 209.1325, found 209.1325.



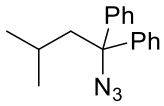
(1-Azido-2-methylpropane-1,1-diyl)dibenzene (1p)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.841 g, yield: 67%; R_f = 0.47 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49–7.17 (m, 10H), 2.95 (p, *J* = 6.7 Hz, 1H), 0.95 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.0, 128.1, 127.9, 127.3, 76.6, 34.8, 18.3; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{16}H_{17}N_3Na$ $[M + Na]^+$ 274.1315, found 274.1313.



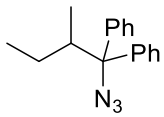
(1-Azidopentane-1,1-diyl)dibenzene (1q)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.636 g, yield: 48%; R_f = 0.49 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56–6.99 (m, 10H), 2.49–2.28 (m, 2H), 1.39–1.26 (m, 2H), 1.24–1.09 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 128.3, 127.4, 127.1, 72.6, 38.5, 26.3, 23.0, 14.0; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{17}H_{19}$ [M - N_3]$^+$ 223.1481, found 223.1481.



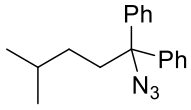
(1-Azido-3-methylbutane-1,1-diyl)dibenzene (1r)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.795 g, yield: 60%; R_f = 0.49 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.18 (m, 10H), 2.33 (d, *J* = 5.6 Hz, 2H), 1.54 (td, *J* = 12.3, 6.2 Hz, 1H), 0.84 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 128.2, 127.3, 127.0, 72.4, 46.5, 24.3, 24.0; FT-IR (KBr, cm^{-1}): 2107; HRMS (ESI-TOF) calcd for $C_{17}H_{19}$ [M - N_3]$^+$ 223.1481, found 223.1483.



(1-Azido-2-methylbutane-1,1-diyl)dibenzene (1s)

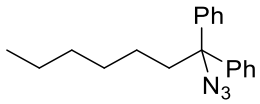
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.676 g, yield: 51%; R_f = 0.53 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.21 (m, 10H), 2.68–2.45 (m, 1H), 1.75 (dt, *J* = 14.7, 7.1 Hz, 1H), 1.03–0.90 (m, 6H), 0.90–0.81 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.5, 141.1, 128.1, 128.0, 127.8, 127.3, 127.3, 77.0, 42.2, 25.3, 14.7, 12.4; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{17}H_{19}$ [M - N_3]$^+$ 223.1481, found 223.1482.



(1-Azido-4-methylpentane-1,1-diyl)dibenzene (1t)

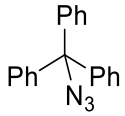
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.809 g, yield: 58%; R_f = 0.49 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40–7.16 (m, 10H), 2.48–2.31 (m, 2H), 1.63–1.45 (m, 1H), 1.17–1.00 (m, 2H), 0.86 (d, *J* = 6.6 Hz,

6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 128.2, 127.3, 127.0, 72.6, 36.5, 32.9, 28.2, 22.5; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{18}H_{21}$ [M - N_3]$^+$ 237.1638, found 237.1638.



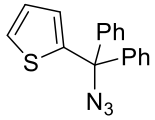
(1-Azidoheptane-1,1-diyl)dibenzene (1u)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.776 g, yield: 53%; R_f = 0.47 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51–7.00 (m, 10H), 2.47–2.28 (m, 2H), 1.37–1.09 (m, 8H), 0.84 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 128.2, 127.3, 127.0, 72.6, 38.7, 31.6, 29.5, 24.0, 22.6, 14.0; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{19}H_{23}N_3Na$ [M + Na]$^+$ 316.1784, found 316.1781.



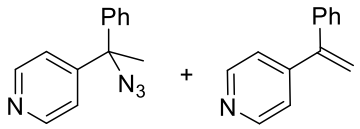
(Azidomethanetriyl)tribenzene (1v)[5]

White crystals (Recrystallization from Et_2O), 0.812 g, yields: 57%. m.p. 67–68 ^{o}C; R_f = 0.75 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.23 (m, 15H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1, 128.4, 128.2, 127.7; FT-IR (KBr, cm^{-1}): 2100; HRMS (ESI-TOF) calcd for $C_{19}H_{15}N_3K$ [M + K]$^+$ 324.0898, found 324.0899.



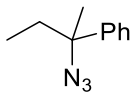
2-(Azidodiphenylmethyl)thiophene (1w)[5]

Colorless oil obtained by column chromatography (PE/EA = 50:1), 0.596 g, yield: 41%; R_f = 0.52 (PE/EA = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.25 (m, 11H), 6.98 (t, *J* = 4.4 Hz, 1H), 6.88 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9, 143.1, 128.2, 128.1, 127.9, 127.4, 126.7, 126.1, 74.6; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{17}H_{13}S$ [M - N_3]$^+$ 249.0732, found 249.0731.



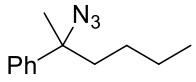
4-(1-Azido-1-phenylethyl)pyridine (1x) and 4-(1-Phenylvinyl)pyridine

Colorless oil obtained by column chromatography (PE/EA = 10:1), R_f = 0.18 (PE/EA = 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) for **1x** δ 8.56 (dt, *J* = 4.6, 1.7 Hz, 2H), 7.50–7.15 (m, 7H), 2.26 (s, 3H); ^{1}H NMR (400 MHz, Chloroform-*d*) for 4-(1-Phenylvinyl)pyridine δ 8.56 (dt, *J* = 4.6, 1.7 Hz, 2H), 7.50–7.15 (m, 7H), 5.57 (d, *J* = 2.8 2H); ^{13}C NMR (101 MHz, Chloroform-d) for **1x** and 4-(1-Phenylvinyl)pyridine δ 154.8, 149.9, 149.9, 148.8, 147.9, 144.5, 139.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.0, 122.8, 121.8, 117.0, 72.3, 33.3; FT-IR (KBr, cm^{-1}) for **1x** and 4-(1-Phenylvinyl)pyridine: 3057, 3025, 2983, 2927, 2850, 2095, 1595, 1542, 1491, 1445, 1409, 1377, 1336, 1241, 1219, 1065, 1027, 992, 911, 832, 778, 698, 669, 602, 591,574; HRMS (ESI-TOF) calcd for **1x** $C_{13}H_{13}N_4$ $[M + H]^+$ 225.1135, found 225.1157. HRMS (ESI-TOF) calcd for 4-(1-Phenylvinyl)pyridine $C_{13}H_{12}N$ $[M + H]^+$ 182.0967, found 182.0964.



(2-Azidobutan-2-yl)benzene (1y)

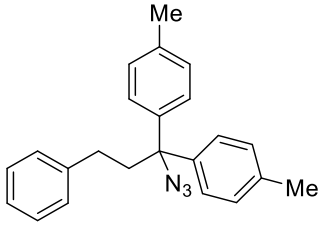
Colorless oil obtained by column chromatography (PE/EA = 50:1), 0.552 g, yield: 63%; R_f = 0.52 (PE/EA = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.31 (m, 4H), 7.30–7.20 (m, 1H), 1.87 (hept, *J* = 7.0 Hz, 2H), 1.65 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 128.4, 127.2, 125.7, 67.3, 35.0, 25.1, 8.7; FT-IR (KBr, cm^{-1}): 2098; HRMS (ESI-TOF) calcd for $C_{10}H_{13}$ $[M-N_3]^+$ 133.1012, found 280.1009.



(2-Azidohexan-2-yl)benzene (1z)

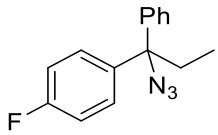
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.659 g, yield: 65%; R_f = 0.52 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.29–7.17 (m, 4H), 7.16–7.05 (m, 1H), 1.79–1.60 (m, 2H), 1.52 (s, 3H), 1.20–0.93 (m, 4H), 0.71 (t, J

= 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 143.74, 128.47, 127.20, 125.57, 66.97, 42.06, 26.45, 25.65, 22.86, 13.96; FT-IR (KBr, cm^{-1}): 2108; HRMS (ESI-TOF) calcd for $C_{12}H_{18}N$ $[M - N_2 + H]^+$ 176.1434, found 176.1433.



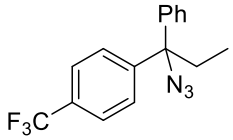
4,4'-(1-Azido-3-phenylpropane-1,1-diyl)bis(methylbenzene) (1aa)

White crystals (Recrystallization from Et_2O) 1.228 g, yields: 72%; m.p. 82–83 °C; R_f = 0.75 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34–7.06 (m, 13H), 2.70–2.56 (m, 2H), 2.56–2.42 (m, 2H), 2.33 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 140.049, 137.1, 129.0, 128.4, 128.4, 126.9, 125.9, 72.3, 41.2, 30.7, 21.0; FT-IR (KBr, cm^{-1}): 2102; HRMS (ESI-TOF) calcd for $C_{23}H_{24}N_3$ $[M+ H]^+$ 342.1965, found 342.1971.



1-(1-Azido-1-phenylpropyl)-4-fluorobenzene (3a)

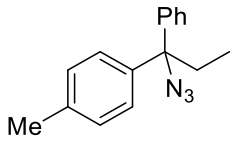
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.829 g, yield: 65%; R_f = 0.45 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.20 (m, 7H), 6.99 (t, *J* = 8.7 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1, 160.6, 142.7, 138.9, 138.8, 128.9, 128.8, 128.3, 127.5, 127.0, 115.1, 114.9, 72.5, 31.6, 8.5; FT-IR (KBr, cm^{-1}): 2104; HRMS (ESI-TOF) calcd for $C_{15}H_{14}F$ $[M - N_3]^+$ 213.1074, found 213.1079.



(S)-1-(1-Azido-1-phenylpropyl)-4-(trifluoromethyl)benzene (3b)

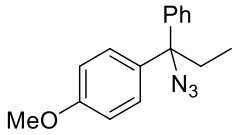
Colorless oil obtained by column chromatography (PE/EA = 100:1), 1.022 g, yield: 67%; R_f = 0.46 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* =

8.2 Hz, 2H), 7.48–7.39 (m, 2H), 7.38–7.23 (m, 5H), 2.44 (ddt, *J* = 18.1, 14.0, 7.0 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 147.1, 142.2, 129.6, 129.3, 128.5, 127.8, 127.4, 127.1, 125.4, 125.3, 125.2, 125.2, 125.1, 122.7, 72.6, 31.3, 8.4; FT-IR (KBr, cm^{-1}): 2104; HRMS: (ESI-TOF) calcd for $C_{16}H_{14}F_3$ $[M - N_3]^+$ 263.1042, found 263.1041.



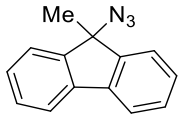
(S)-1-(1-Azido-1-phenylpropyl)-4-methylbenzene (3c)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.741 g, yield: 59%; R_f = 0.47 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 5.4 Hz, 4H), 7.26–7.15 (m, 3H), 7.15–7.06 (m, 2H), 2.40 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1, 140.0, 137.0, 128.9, 128.1, 127.2, 127.0, 72.9, 31.5, 21.0, 8.6; FT-IR (KBr, cm^{-1}): 2109; HRMS (ESI-TOF) calcd for $C_{16}H_{17}$ $[M - N_3]^+$ 209.1325, found 209.1322.



(S)-1-(1-Azido-1-phenylpropyl)-4-methoxybenzene (3d)

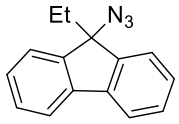
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.868 g, yield: 65%; R_f = 0.45 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.17 (m, 7H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 2.39 (qd, *J* = 7.1, 4.8 Hz, 2H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.7, 143.1, 135.1, 128.4, 128.2, 127.2, 127.0, 113.5, 72.80, 55.2, 31.7, 8.6; FT-IR (KBr, cm^{-1}): 2101; HRMS (ESI-TOF) calcd for $C_{16}H_{17}O$ $[M - N_3]^+$ 225.1274, found 225.1274.



9-Azido-9-methyl-9H-fluorene (6a)

Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.94 g, yield: 85%; R_f = 0.37 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.9 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.35 (dtd, *J* = 21.5, 7.4, 1.3 Hz, 4H), 1.69 (s,

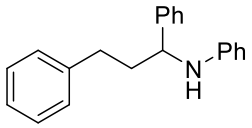
3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3, 139.4, 129.3, 128.1, 123.4, 120.2, 70.1, 24.6; FT-IR (KBr, cm^{-1}): 2085; HRMS (ESI-TOF) calcd for $C_{14}H_{11}$ $[M - N_3]^+$ 179.0855, found 179.0854.



9-Azido-9-ethyl-9H-fluorene (6b)

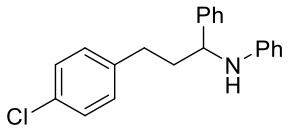
Colorless oil obtained by column chromatography (PE/EA = 100:1), 0.94 g, yield: 80%; R_f = 0.37 (PE/EA = 100:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 5.6 Hz, 2H), 7.35 (dt, *J* = 23.0, 7.1 Hz, 4H), 2.24–2.05 (m, 2H), 0.54 (dt, *J* = 10.5, 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 140.4, 129.2, 129.2, 128.0, 128.0, 123.6, 123.6, 120.1, 120.1, 77.3, 74.3, 31.2, 8.2; FT-IR (KBr, cm^{-1}): 2095; HRMS (ESI-TOF) calcd for $C_{15}H_{13}$ $[M - N_3]^+$ 193.1012, found 193.1011.

5. Characterization of products



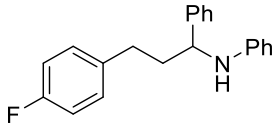
***N*-(1,3-Diphenylpropyl)aniline (2a)[6]**

Yellow oil obtained by column chromatography (PE/EA = 30:1), 75 mg, yield: 87%; R_f = 0.47 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32–7.21 (m, 6H), 7.17 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 1H), 3.99 (s, 1H), 2.77–2.53 (m, 2H), 2.06 (dtd, *J* = 8.7, 6.6, 4.0 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.2, 143.7, 141.4, 129.0, 128.5, 128.4, 128.3, 126.9, 126.3, 125.9, 117.1, 113.2, 57.5, 40.1, 32.5; FT-IR (KBr, cm^{-1}): 3410, 3056, 2921, 2853, 1601, 1503, 1317, 7489, 697; HRMS (ESI-TOF) calcd for $C_{21}H_{22}N$ $[M + H]^+$ 288.1747, found 288.1752.



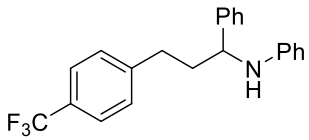
***N*-(3-(4-Chlorophenyl)-1-phenylpropyl)aniline (2b)**

Yellow oil obtained by column chromatography (PE/EA = 30:1), 91 mg, yield: 95%; R_f = 0.47 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33–7.09 (m, 7H), 7.01 (td, *J* = 8.3, 2.6 Hz, 4H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 7.4 Hz, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 3.96 (s, 1H), 2.59 (dt, *J* = 8.5, 6.2 Hz, 2H), 2.01 (hept, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 143.5, 139.8, 131.7, 129.7, 129.1, 128.6, 128.5, 127.1, 126.3, 117.3, 113.2, 57.3, 40.0, 31.9; FT-IR (KBr, cm^{-1}): 3415, 3054, 2923, , 1602, 1503, 1451, 1260, 750, 697; HRMS (ESI-TOF) calcd for $C_{21}H_{21}ClN$ $[M + H]^+$ 322.1357, found 322.1353.



***N*-(3-(4-Fluorophenyl)-1-phenylpropyl)aniline (2c)**

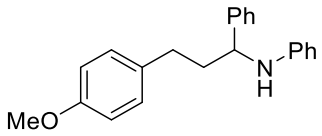
Colorless oil obtained by column chromatography (PE/EA = 30:1), 76 mg, yield: 83%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 4.4 Hz, 4H), 7.26–7.17 (m, 1H), 7.14–7.03 (m, 4H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.63 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.52–6.43 (m, 2H), 4.31 (t, *J* = 6.8 Hz, 1H), 4.03 (s, 1H), 2.82–2.54 (m, 2H), 2.21–1.88 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5, 160.1, 147.2, 143.6, 137.0, 137.0, 129.8, 129.7, 129.1, 128.6, 127.1, 126.4, 117.3, 115.3, 115.1, 113.2, 57.4, 40.3, 31.8; FT-IR (KBr, cm^{-1}): 3413, 3027, 2923, 1602, 1506, 1317, 1221, 829, 750, 698; HRMS (ESI-TOF) calcd for $C_{21}H_{21}FN$ $[M + H]^+$ 306.1653, found 306.1650.



***N*-(1-Phenyl-3-(4-(trifluoromethyl)phenyl)propyl)aniline (2d)**

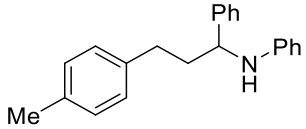
Light yellow oil obtained by column chromatography (PE/EA = 30:1), 80 mg, yield: 75%; R_f = 0.49 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0

Hz, 2H), 7.31 (d, *J* = 4.3 Hz, 4H), 7.27–7.18 (m, 3H), 7.14–7.02 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 1H), 4.02 (s, 1H), 2.91–2.59 (m, 2H), 2.28–1.96 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 145.6, 143.4, 129.1, 128.7, 128.7, 127.2, 126.4, 125.4, 125.4, 125.3, 125.3, 117.5, 113.3, 57.5, 39.8, 32.5; FT-IR (KBr, cm^{-1}): 3774, 3024, 2099, 1602, 1505, 1326, 1121, 750, 698; HRMS (ESI-TOF) calcd for $C_{22}H_{21}F_3N$ [M + H]$^+$ 356.1621, found 356.1621.



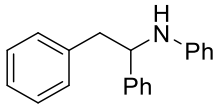
***N*-(3-(4-Methoxyphenyl)-1-phenylpropyl)aniline (2e)**

Light yellow oil obtained by column chromatography (PE/EA = 30:1), 79 mg, yield: 83%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.26 (m, 4H), 7.21 (td, *J* = 5.9, 2.7 Hz, 1H), 7.11–7.00 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.4 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 1H), 4.04 (s, 1H), 3.77 (s, 3H), 2.80–2.48 (m, 2H), 2.07 (tt, *J* = 7.2, 5.9 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.9, 147.3, 143.9, 133.4, 129.3, 129.1, 128.6, 127.0, 126.4, 117.2, 113.8, 113.2, 57.5, 55.2, 40.4, 31.7; FT-IR (KBr, cm^{-1}): 3409, 3054, 2930, 1604, 1509, 1246, 1074, 750, 698; HRMS (ESI-TOF) calcd for $C_{22}H_{24}NO$ [M + H]$^+$ 318.1852, found 318.1855.



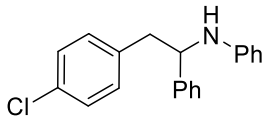
***N*-(1-Phenyl-3-(p-tolyl)propyl)aniline (2f)**

Yellow oil obtained by column chromatography (PE/EA = 30:1), 93 mg, yield: 96%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.23 (m, 4H), 7.19 (dd, *J* = 6.1, 2.9 Hz, 1H), 7.13–6.94 (m, 6H), 6.62 (d, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 7.9 Hz, 2H), 4.30 (q, *J* = 4.8, 2.6 Hz, 1H), 4.01 (s, 1H), 2.63 (d, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.06 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 143.8, 138.3, 135.4, 129.1, 129.0, 128.5, 128.3, 127.0, 126.4, 117.1, 113.2, 57.6, 40.3, 32.1, 21.0; FT-IR (KBr, cm^{-1}): 3412, 3023, 2922, 1602, 1508, 1260, 1180, 749, 697; HRMS (ESI-TOF) calcd for $C_{22}H_{24}N$ [M + H]$^+$ 322.1903, found 322.1902.



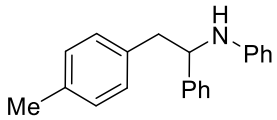
***N*-(1,2-Diphenylethyl)aniline (2g)[7]**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 64 mg, yield: 78%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.17 (m, 8H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 2H), 4.57 (dd, *J* = 8.3, 5.7 Hz, 1H), 4.10 (s, 1H), 3.12 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.00 (dd, *J* = 14.0, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.2, 143.4, 137.6, 129.2, 129.0, 128.5, 128.5, 127.0, 126.7, 126.4, 117.4, 113.6, 59.2, 45.1; FT-IR (KBr, cm^{-1}): 3410, 3026, 2921, 1602, 1503, 1452, 1356, 751, 697; HRMS (ESI-TOF) calcd for $C_{20}H_{20}N$ $[M + H]^+$ 274.1590, found 274.1589.



***N*-(2-(4-Chlorophenyl)-1-phenylethyl)aniline (2h)[6]**

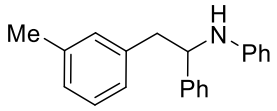
Colorless oil obtained by column chromatography (PE/EA = 30:1), 57 mg, yield: 62%; R_f = 0.42 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34–7.17 (m, 7H), 7.11–7.03 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.3 Hz, 2H), 4.62–4.49 (m, 1H), 4.06 (s, 1H), 3.17–2.92 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.0, 142.8, 136.1, 132.5, 130.6, 129.1, 128.6, 128.6, 127.2, 126.4, 117.6, 113.6, 59.1, 44.2; FT-IR (KBr, cm^{-1}): 3411, 2924, 1732, 1603, 1504, 1246, 1094, 813, 751; HRMS (ESI-TOF) calcd for $C_{20}H_{19}ClN$ $[M + H]^+$ 308.1201, found 308.1198.



***N*-(1-Phenyl-2-(p-tolyl)ethyl)aniline (2i)[6]**

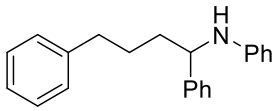
Light yellow oil obtained by column chromatography (PE/EA = 30:1), 32 mg, yield: 37%; R_f = 0.43 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.26 (m, 4H), 7.26–7.19 (m, 1H), 7.11–6.96 (m, 6H), 6.66–6.57 (m, 1H), 6.44 (d, *J* = 7.5 Hz, 2H), 4.55 (dd, *J* = 8.3, 5.5 Hz, 1H), 4.10 (s, 1H), 3.10 (dd, *J* = 14.0, 5.5 Hz, 1H), 2.95 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3,

143.6, 136.2, 134.5, 129.2, 129.0, 129.0, 128.5, 127.0, 126.4, 117.4, 113.6, 59.2, 44.8, 21.0; FT-IR (KBr, cm^{-1}): 3410, 3052, 3023, 1602, 1505, 1316, 750.0, 696, 510; HRMS (ESI-TOF) calcd for $C_{21}H_{22}N$ $[M + H]^+$ 288.1747, found 288.1747.



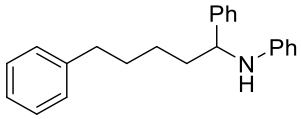
***N*-(1-Phenyl-2-(m-tolyl)ethyl)aniline (2j)[6]**

Light yellow oil obtained by column chromatography (PE/EA = 30:1), 30 mg, yield: 35%; R_f = 0.43 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.27 (m, 4H), 7.27–7.20 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 3H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 4.55 (dd, *J* = 8.6, 5.4 Hz, 1H), 4.11 (s, 1H), 3.10 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.93 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 143.6, 138.1, 137.6, 130.0, 128.9, 128.5, 128.4, 127.5, 127.0, 126.4, 126.1, 117.4, 113.6, 59.2, 45.2, 21.4; FT-IR (KBr, cm^{-1}): 3414, 2932, 2856, 1602, 1503, 1453, 1257, 749, 697; HRMS (ESI-TOF) calcd for $C_{21}H_{22}N$ $[M + H]^+$ 288.1747, found 288.1746.



***N*-(1,4-Diphenylbutyl)aniline (2k)[8]**

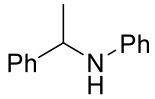
Colorless oil obtained by column chromatography (PE/EA = 30:1), 82 mg, yield: 91%; R_f = 0.47 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 6H), 7.24 – 7.10 (m, 4H), 7.10 – 7.01 (m, 2H), 6.61 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.53 – 6.40 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 1H), 3.99 (s, 1H), 2.62 (td, *J* = 7.4, 2.0 Hz, 2H), 1.94 – 1.57 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 144.0, 141.9, 129.1, 128.5, 128.4, 128.3, 126.9, 126.4, 125.8, 117.2, 113.2, 58.1, 38.3, 35.6, 28.0; FT-IR (KBr, cm^{-1}): 3412, 29245, 2854, 1601.6, 1504, 1453, 1317, 748, 698; HRMS (ESI-TOF) calcd for $C_{22}H_{24}N$ $[M + H]^+$ 302.1903, found 302.1901.



***N*-(1,5-Diphenylpentyl)aniline (2l)**

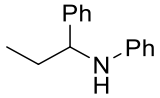
Light yellow oil obtained by column chromatography (PE/EA = 30:1), 88 mg, yield:

93%; R_f = 0.44 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.09 (m, 10H), 7.05 (t, *J* = 7.9 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 2H), 4.26 (t, *J* = 6.8 Hz, 1H), 3.98 (s, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.87–1.68 (m, 2H), 1.61 (p, *J* = 7.6 Hz, 2H), 1.51–1.28 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 144.1, 142.3, 129.0, 128.5, 128.3, 128.3, 126.8, 126.3, 125.7, 117.1, 113.2, 58.0, 38.7, 35.7, 31.2, 25.9; FT-IR (KBr, cm^{-1}): 3414, 2933, 2856, 1602, 1504, 1453, 1427, 1318, 749, 698; HRMS (ESI-TOF) calcd for $C_{23}H_{26}N$ $[M + H]^+$ 316.2060, found 316.2063.



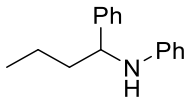
_N_-(1-Phenylethyl)aniline (2m)[9]

Colorless oil obtained by column chromatography (PE/EA = 30:1), 55 mg, yield: 93%; R_f = 0.47 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.25 (m, 4H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.46 (q, *J* = 6.7 Hz, 1H), 3.98 (s, 1H), 1.48 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.2, 145.2, 129.0, 128.6, 126.8, 125.8, 117.2, 113.2, 53.4, 25.0; FT-IR (KBr, cm^{-1}): 3411, 3024, 2967, 1602, 1504, 1318, 1206, 750, 697; HRMS (ESI-TOF) calcd for $C_{14}H_{16}N$ $[M + H]^+$ 198.1277, found 198.1277.



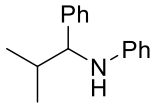
_N_-(1-Phenylpropyl)aniline (2n)[9]

Light yellow oil obtained by column chromatography (PE/EA = 30:1), 57 mg, yield: 90%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 7.9, 6.9, 4.3 Hz, 4H), 7.24–7.15 (m, 1H), 7.06 (td, *J* = 7.8, 7.3, 2.2 Hz, 2H), 6.68–6.57 (m, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 4.20 (t, *J* = 6.8 Hz, 1H), 4.03 (s, 1H), 2.03–1.62 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 143.9, 129.0, 128.4, 126.8, 126.4, 117.1, 113.2, 59.7, 31.6, 10.8; FT-IR (KBr, cm^{-1}): 3412, 2965, 2928, 1603, 1504, 1179, 749, 697; HRMS (ESI-TOF) calcd for $C_{15}H_{18}N$ $[M + H]^+$ 212.1434, found 212.1432.



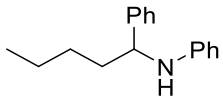
***N*-(1-Phenylbutyl)aniline (2o)[10]**

Light yellow oil obtained by column chromatography (PE/EA = 30:1), 55 mg, yield: 82%; R_f = 0.46 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.25 (m, 4H), 7.20 (ddt, *J* = 8.4, 6.1, 1.7 Hz, 1H), 7.12–7.01 (m, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.55–6.45 (m, 2H), 4.29 (t, *J* = 6.8 Hz, 1H), 4.04 (s, 1H), 1.88–1.63 (m, 2H), 1.56–1.22 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 144.3, 129.0, 128.5, 126.8, 126.3, 117.0, 113.2, 57.9, 41.1, 19.5, 13.9; FT-IR (KBr, cm^{-1}): 3414, 3054, 2869, 1602, 1504, 1317, 749, 697, 511; HRMS (ESI-TOF) calcd for $C_{16}H_{20}N$ $[M + H]^+$ 226.1590, found 226.1592.



***N*-(2-Methyl-1-phenylpropyl)aniline (2p)[11]**

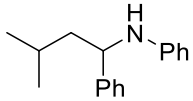
Light yellow oil obtained by column chromatography (PE/EA = 30:1), 57 mg, yield: 85%; R_f = 0.48 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 4.6 Hz, 4H), 7.25–7.18 (m, 1H), 7.10–7.01 (m, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.49 (dd, *J* = 8.7, 1.1 Hz, 2H), 4.12 (d, *J* = 6.0 Hz, 2H), 2.21–1.89 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.7, 142.6, 129.0, 128.2, 127.2, 126.7, 117.0, 113.2, 63.7, 34.9, 19.7, 18.6; FT-IR (KBr, cm^{-1}): 3057, 3026, 2965, 2100, 1601, 1504, 1448, 1250, 750, HRMS (ESI-TOF) calcd for $C_{16}H_{20}N$ $[M + H]^+$ 226.1590, found 226.1589.



***N*-(1-Phenylpentyl)aniline (2q)**

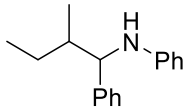
Colorless oil obtained by column chromatography (PE/EA = 30:1), 56 mg, yield: 78%; R_f = 0.48(PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.25 (m, 4H), 7.25–7.16 (m, 1H), 7.11–7.00 (m, 2H), 6.68–6.57 (m, 1H), 6.56–6.42 (m, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 4.04 (s, 1H), 1.89–1.66 (m, 2H), 1.33 (tdt, *J* = 13.7, 9.4, 6.6 Hz, 5H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 144.3, 129.0,

128.5, 126.8, 126.3, 117.0, 113.2, 58.2, 38.7, 28.5, 22.6, 14.0; FT-IR (KBr, cm^{-1}): 3414, 2930, 2858, 1602, 1504, 1317, 749, 697; HRMS (ESI-TOF) calcd for $C_{17}H_{22}N$ $[M + H]^+$ 240.1747, found 240.1745.



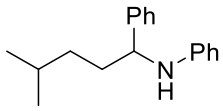
***N*-(3-Methyl-1-phenylbutyl)aniline (2r)[12]**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 57 mg, yield: 80%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.24 (m, 4H), 7.23–7.15 (m, 1H), 7.13–6.98 (m, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 4.36 (dd, *J* = 7.9, 5.8 Hz, 1H), 4.00 (s, 1H), 1.78–1.51 (m, 3H), 0.95 (dd, *J* = 19.4, 6.2 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 144.7, 129.1, 128.5, 126.8, 126.2, 117.0, 113.1, 56.1, 48.6, 25.0, 22.9, 22.4; FT-IR (KBr, cm^{-1}): 3416, 3055, 2957, 1602, 1504, 1365, 750, 697; HRMS (ESI-TOF) calcd for $C_{17}H_{22}N$ $[M + H]^+$ 240.1747, found 240.1749.



***N*-(2-Methyl-1-phenylbutyl)aniline (2s)[13]**

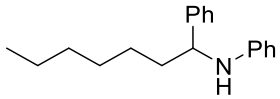
Colorless oil obtained by column chromatography (PE/EA = 30:1), 54 mg, yield: 75%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 3.5 Hz, 4H), 7.20 (ddt, *J* = 7.8, 4.3, 1.9 Hz, 1H), 7.05 (ddd, *J* = 8.6, 7.3, 2.3 Hz, 2H), 6.69–6.55 (m, 1H), 6.48 (d, *J* = 7.7 Hz, 2H), 4.07 (s, 1H), 1.88–1.72 (m, 1H), 1.67–1.41 (m, 1H), 1.29–1.17 (m, 1H), 1.01–0.80 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.8, 143.0, 142.4, 129.1, 129.1, 128.3, 128.2, 127.4, 127.0, 126.8, 126.7, 117.0, 117.0, 113.2, 113.2, 62.6, 61.5, 41.9, 41.6, 26.9, 25.4, 16.1, 14.5, 12.1, 11.8; FT-IR (KBr, cm^{-1}): 3057, 2964, 2875, 2100, 1601, 1502, 750, 701; HRMS (ESI-TOF) calcd for $C_{17}H_{22}N$ $[M + H]^+$ 240.1747, found 240.1747.



***N*-(4-Methyl-1-phenylpentyl)aniline (2t)[14]**

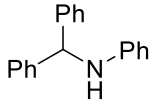
Colorless oil obtained by column chromatography (PE/EA = 30:1), 55 mg, yield: 73%;

R_f = 0.46 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.25 (m, 4H), 7.25–7.15 (m, 1H), 7.12–7.01 (m, 2H), 6.62 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.50 (dd, *J* = 8.7, 1.0 Hz, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.04 (s, 1H), 1.77 (dtd, *J* = 12.5, 6.2, 2.6 Hz, 2H), 1.53 (dq, *J* = 13.2, 6.5 Hz, 1H), 1.41–1.11 (m, 3H), 0.87 (dd, *J* = 6.6, 5.0 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 144.4, 129.1, 128.5, 126.8, 126.3, 117.1, 113.2, 58.5, 36.9, 35.5, 28.0, 22.6, 22.5; FT-IR (KBr, cm^{-1}): 3412, 3024, 2868, 1602, 1504, 1317; HRMS (ESI-TOF) calcd for $C_{18}H_{24}N$ $[M + H]^+$ 254.1903, found 254.1903.



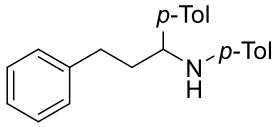
_N_-(1-Phenylheptyl)aniline (2u)[8]

Colorless oil obtained by column chromatography (PE/EA = 30:1), 55 mg, yield: 68%; R_f = 0.45 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.26 (m, 4H), 7.25–7.15 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 4.04 (s, 1H), 1.77 (td, *J* = 6.3, 2.7 Hz, 2H), 1.28 (dtt, *J* = 9.9, 7.1, 3.6 Hz, 8H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 144.3, 129.1, 128.5, 126.8, 126.3, 117.1, 113.2, 58.2, 39.0, 31.7, 29.2, 26.3, 22.6, 14.0; FT-IR (KBr, cm^{-1}): 3414, 2928, 2855, 1603, 1504, 1317, 749, 697; HRMS (ESI-TOF) calcd for HRMS (ESI-TOF) calcd for $C_{19}H_{26}N$ $[M + H]^+$ 268.2060, found 268.2058.



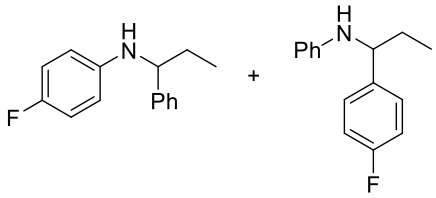
_N_-Benzhydrylaniline (2v)[15]

Colorless oil obtained by column chromatography (PE/EA = 30:1), 63 mg, yield: 81%; R_f = 0.46 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.16 (m, 10H), 7.15–7.03 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 2H), 5.48 (d, *J* = 3.0 Hz, 1H), 4.21 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 142.9, 129.1, 128.7, 127.4, 127.3, 117.6, 113.4, 63.0; FT-IR (KBr, cm^{-1}): 3411, 3056, 2925, 1601, 1500, 1182, 1101, 748, 698; HRMS (ESI-TOF) calcd for $C_{19}H_{18}N$ $[M + H]^+$ 260.1434, found 260.1430.



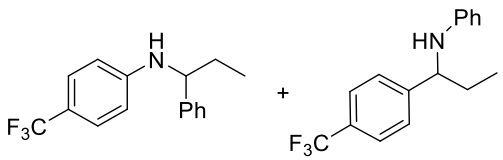
4-Methyl-*N*-(3-phenyl-1-(*p*-tolyl)propyl)aniline (2y)

Yellow oil obtained by column chromatography (PE/EA = 30:1), 91 mg, yield: 96%; R_f = 0.47 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34–7.02 (m, 9H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 8.1 Hz, 2H), 4.26 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 2.13–1.97 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.0, 141.6, 140.8, 136.4, 129.5, 129.2, 128.4, 128.4, 126.3, 126.2, 125.9, 113.4, 57.6, 40.1, 32.6, 21.0, 20.3; FT-IR (KBr, cm^{-1}): 3411, 3023, 2920, 1617, 1517, 1301, 1257, 809, 700; HRMS (ESI-TOF) calcd for $C_{23}H_{26}N$ $[M + H]^+$ 316.2060, found 316.2057.



4-Fluoro-*N*-(1-phenylpropyl)aniline (4a) and *N*-(1-(4-fluorophenyl)propyl)aniline (5a)[16,17]

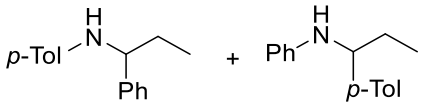
Colorless oil obtained by column chromatography (PE/EA = 30:1), 54 mg, yield: 75%; R_f = 0.23 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 4.3 Hz, 3H), 7.26–7.19 (m, 1H), 7.13–7.04 (m, 1H), 6.99 (t, *J* = 8.7 Hz, 1H), 6.77 (t, *J* = 8.8 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.42 (dd, *J* = 9.0, 4.4 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 1H), 3.99 (s, 1H), 1.96–1.68 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 143.8, 143.7, 139.5, 129.1, 128.5, 127.9, 127.8, 127.0, 126.4, 117.3, 115.6, 115.4, 115.3, 115.2, 114.0, 113.9, 113.2, 60.3, 59.1, 31.8, 31.7, 10.8, 10.7; FT-IR (KBr, cm^{-1}): 3418, 2966, 1603, 1509, 1316, 1219, 1156, 820, 749, 701, 510; HRMS (ESI-TOF) calcd for $C_{15}H_{17}FN$ $[M + H]^+$ 230.1340, found 230.1334



***N*-(1-Phenylpropyl)-4-(trifluoromethyl)aniline (4b) and**

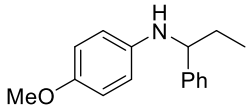
***N*-(1-(4-(trifluoromethyl)phenyl)propyl)aniline (5b)**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 61 mg, yield: 73%; R_f = 0.25 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36–7.26 (m, 2H), 7.13–7.02 (m, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.48 (dd, *J* = 11.2, 8.2 Hz, 2H), 4.25 (dt, *J* = 16.0, 6.5 Hz, 1H), 4.07 (s, 1H), 1.81 (hd, *J* = 7.0, 2.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 148.3, 147.0, 142.9, 129.3, 129.1, 129.0, 128.6, 127.2, 126.8, 126.4, 126.4, 126.3, 125.5, 125.5, 125.5, 125.4, 117.5, 113.2, 112.4, 59.4, 59.4, 31.6, 31.5, 10.7, 10.7; FT-IR (KBr, cm^{-1}): 3414, 2969, 1604, 1505, 1458 1326, 1163, 1108, 1067, 1017, 913, 825, 750, 694, 607, 509; HRMS (ESI-TOF) calcd for $C_{16}H_{17}F_3N$ $[M + H]^+$ 280.1308, found 280.1303



4-Methyl-*N*-(1-phenylpropyl)aniline and (4c) and *N*-(1-(*p*-tolyl)propyl)aniline (5c)[10, 18]

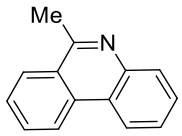
Colorless oil obtained by column chromatography (PE/EA = 30:1), 56 mg, yield: 83%; R_f = 0.23 (PE/EA = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.15 (m, 3H), 7.14 – 7.05 (m, 1H), 7.05 – 6.91 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 1H), 3.84 (s, 1H), 2.20 (s, 1H), 2.07 (s, 2H), 1.68 (ddt, *J* = 10.1, 7.3, 4.9 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 145.2, 144.0, 140.8, 136.3, 129.5, 129.1, 129.1, 129, 128.4, 126.7, 126.4, 126.3, 126.1, 116.9, 113.3, 113.1, 59.8, 59.3, 31.6, 31.6, 21.0, 20.3, 10.8, 10.8; FT-IR (KBr, cm^{-1}): 3412, 2965, 2734, 1866, 1618, 1519, 1405, 1380, 1200, 1181, 1107, 1052, 1005, 808, 750, 701, 510; HRMS (ESI-TOF) calcd for $C_{16}H_{20}N$ $[M + H]^+$ 226.1590, found 226.1585



4-Methoxy-*N*-(1-phenylpropyl)aniline (4d)[19]

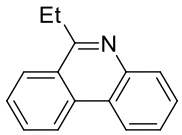
Colorless oil obtained by column chromatography (PE/EA = 50:1), 58 mg, yield: 81%; R_f = 0.23 (PE/EA = 30:1); 1H NMR (400 MHz, Chloroform-d) δ 7.36–7.25 (m, 4H),

7.24–7.15 (m, 1H), 6.67 (d, J = 8.9 Hz, 2H), 6.46 (d, J = 8.9 Hz, 2H), 4.14 (t, J = 6.7 Hz, 1H), 3.66 (s, 3H), 1.92–1.68 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); 13C NMR (101 MHz, Chloroform-d) δ 151.9, 144.2, 141.8, 128.5, 126.9, 126.6, 114.8, 114.6, 60.7, 55.8, 31.7, 10.9; FT-IR (KBr, cm^{-1}): 3403, 3027, 2963, 2832, 1733, 1513, 1454, 1241, 1039, 908, 819, 753, 702, 632, 520; HRMS (ESI-TOF) calcd for $C_{16}H_{20}NO$ $[M + H]^+$ 242.1539, found 242.1532.



6-Methylphenanthridine (7a)[20]

Colorless oil obtained by column chromatography (PE/EA = 20:1), 32 mg, yield: 55%; R_f = 0.19 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.0 Hz, 1H), 7.69 (dddd, *J* = 11.7, 8.2, 7.0, 1.3 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.8, 143.7, 132.5, 130.4, 129.3, 128.6, 127.3, 126.5, 126.3, 125.9, 123.7, 122.3, 121.9, 23.4; FT-IR (KBr, cm-1): 3384, 2953, 2852 1612, 1585, 1485, 1446, 1375, 1351, 1319; HRMS (ESI-TOF) calcd for $C_{14}H_{12}N$ $[M + H]^+$ 194.0964, found 194.0963.



6-Ethylphenanthridine (7b)[20]

Colorless oil obtained by column chromatography (PE/EA = 20:1), 37 mg, yield: 59%; R_f = 0.19 (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 7.9 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 9.3 Hz, 1H), 7.89–7.75 (m, 1H), 7.68 (dt, *J* = 14.7, 7.5 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 3.40 (q, *J* = 7.6 Hz, 2H), 1.51 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 143.8, 132.9, 130.2, 129.6, 128.5, 127.2, 126.2, 126.2, 125.0, 123.6, 122.5, 121.9, 29.3, 13.5; FT-IR (KBr, cm^{-1}): 3384, 2923, 1585, 1458, 1091, 749, 725; HRMS (ESI-TOF) calcd for $C_{15}H_{14}N$ $[M + H]^+$ 208.1121, found 208.1124.

6 References

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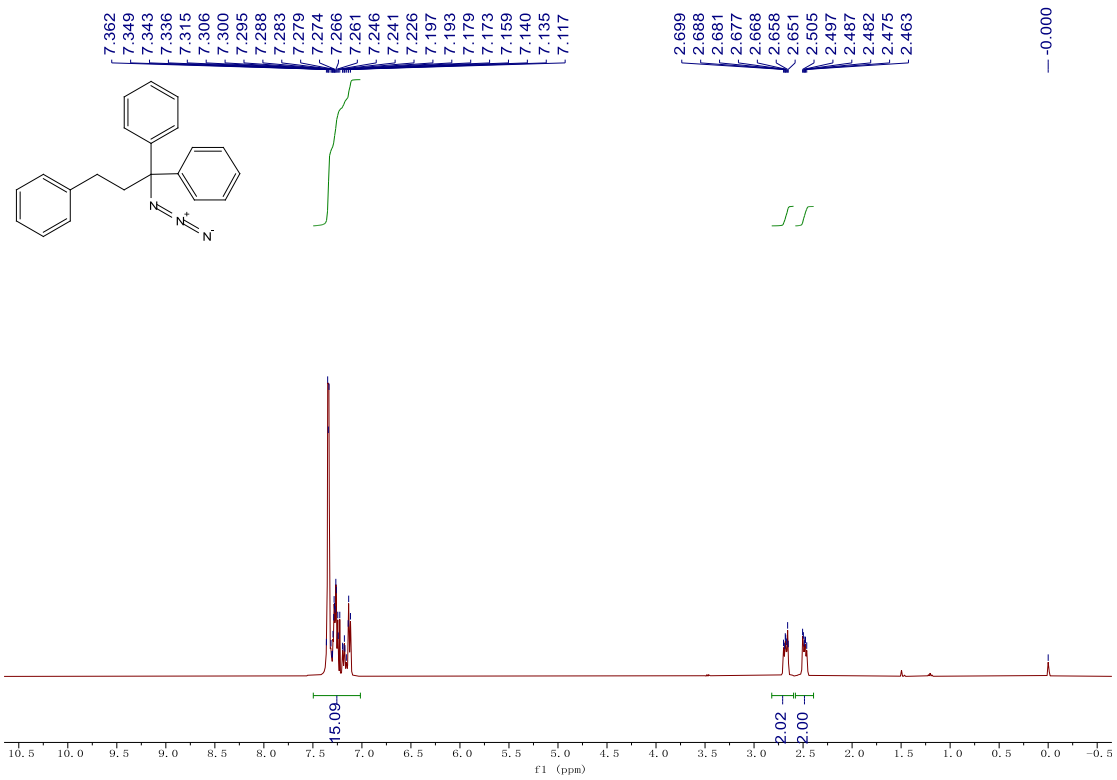
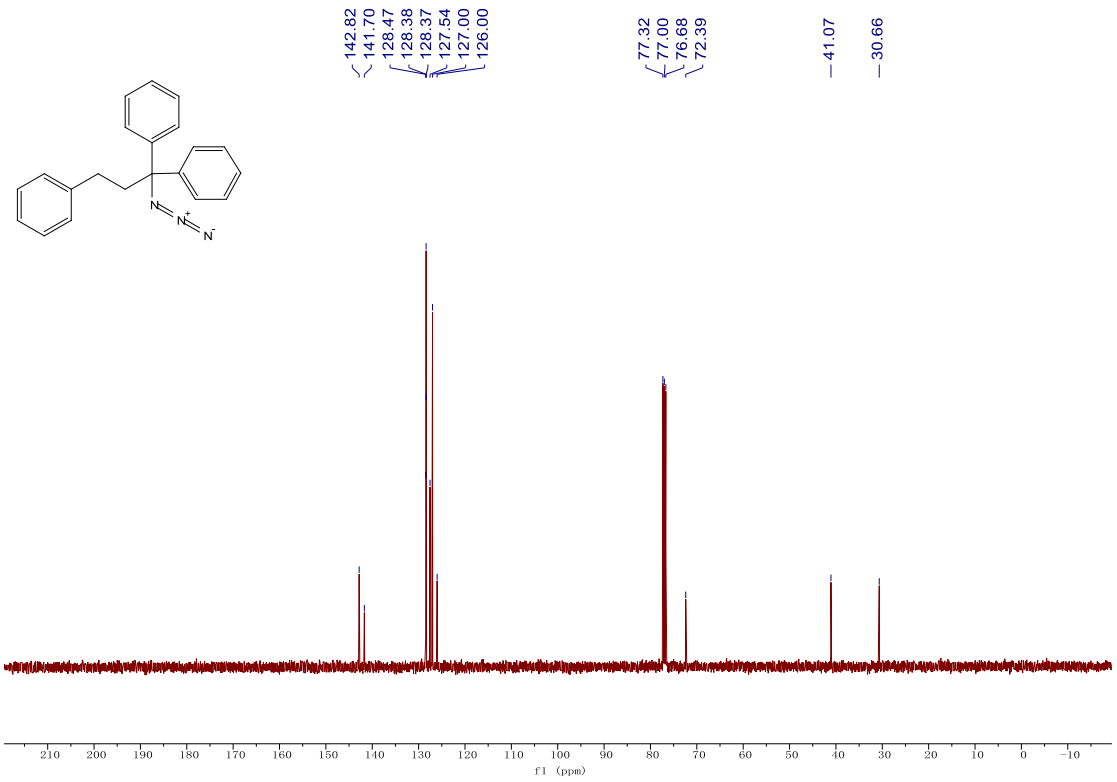
7. ^{1}H and ^{13}C NMR spectra

(1-Azidopropane-1,1,3-triyl)tribenzene (1a)





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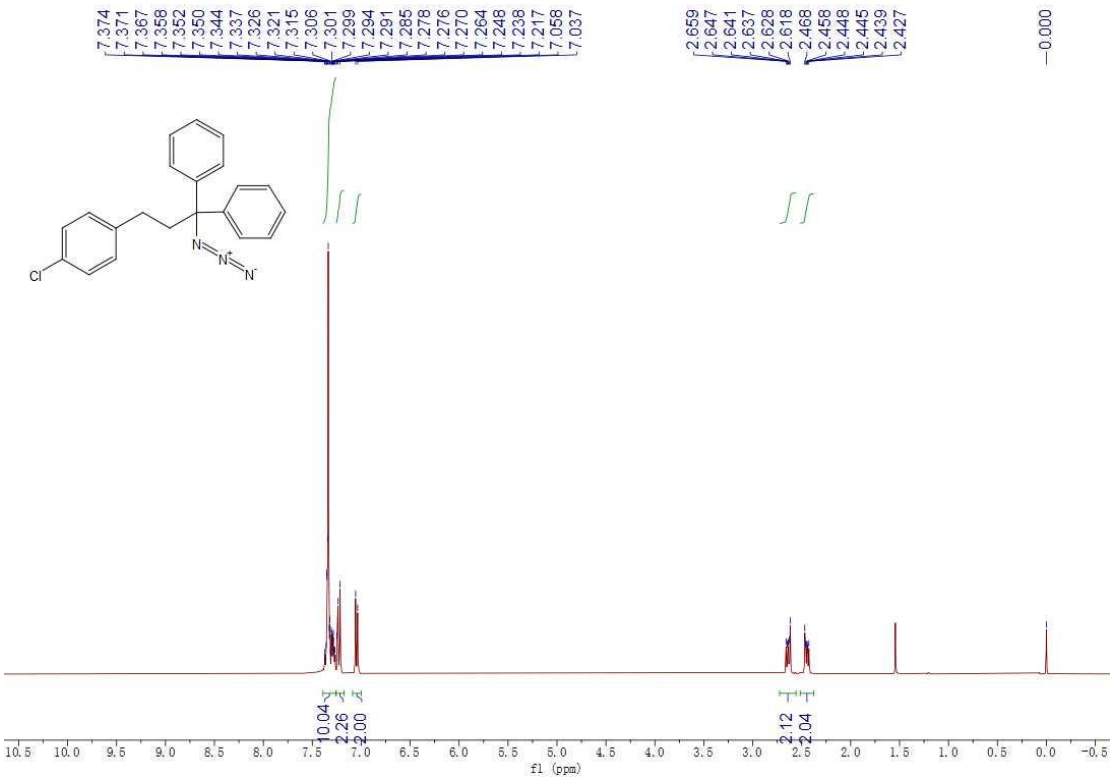

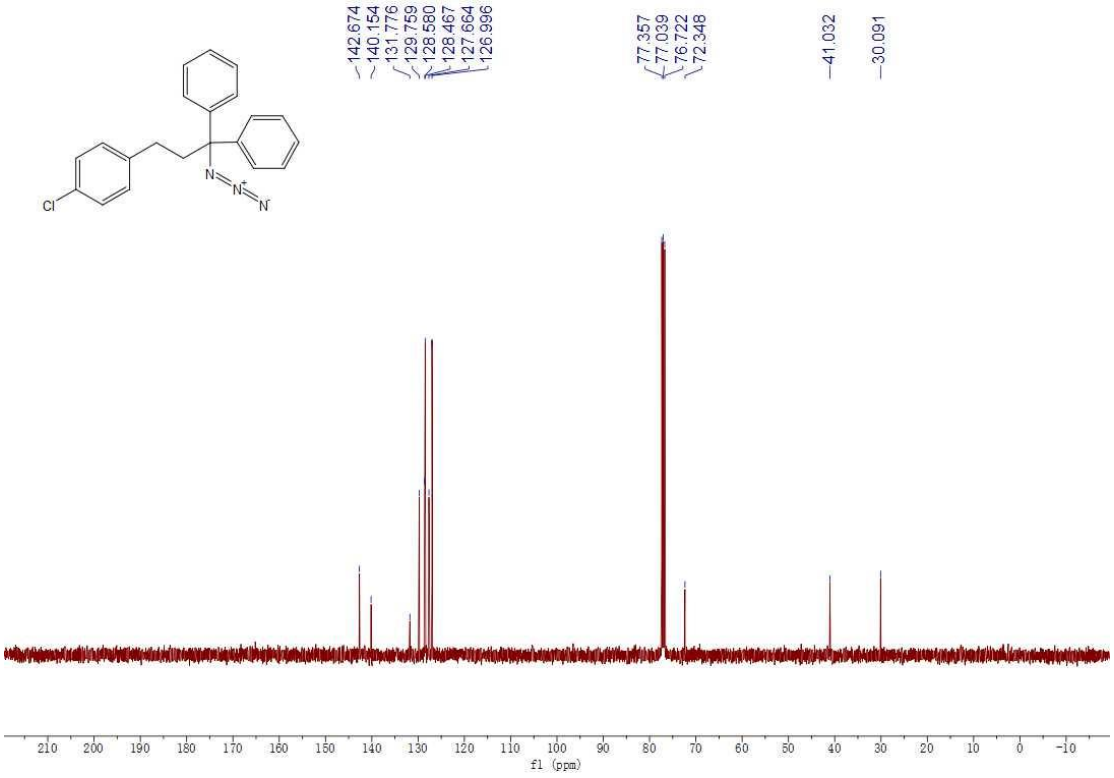

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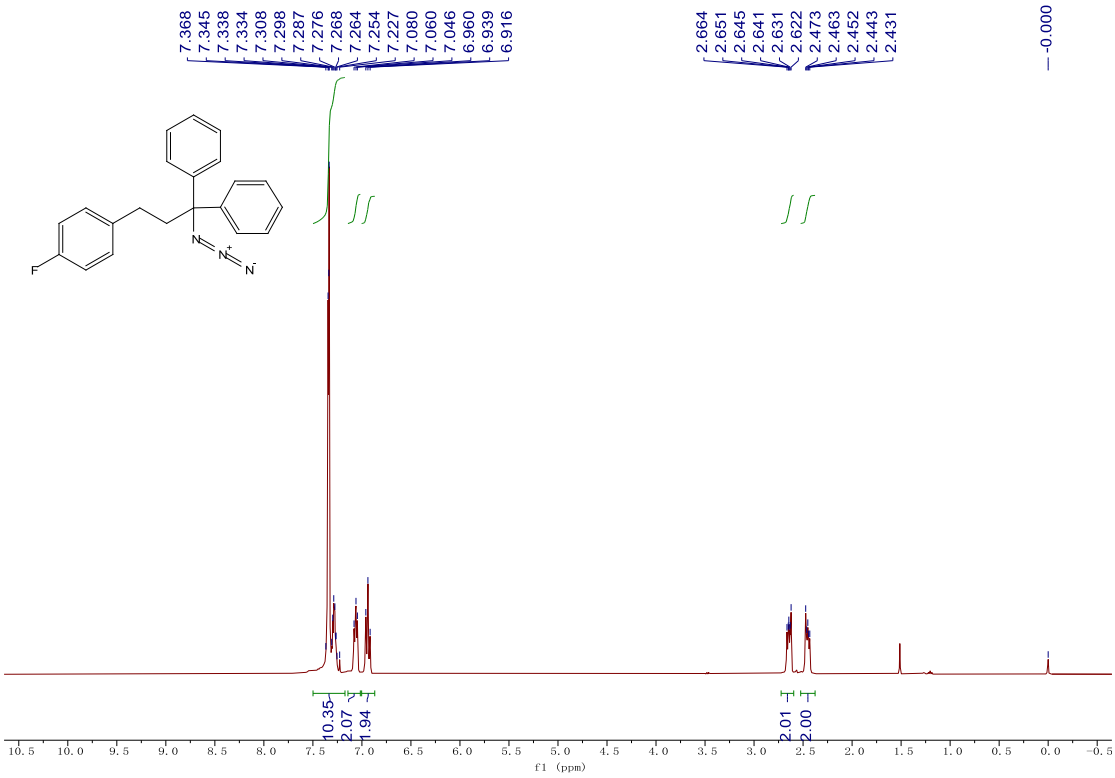

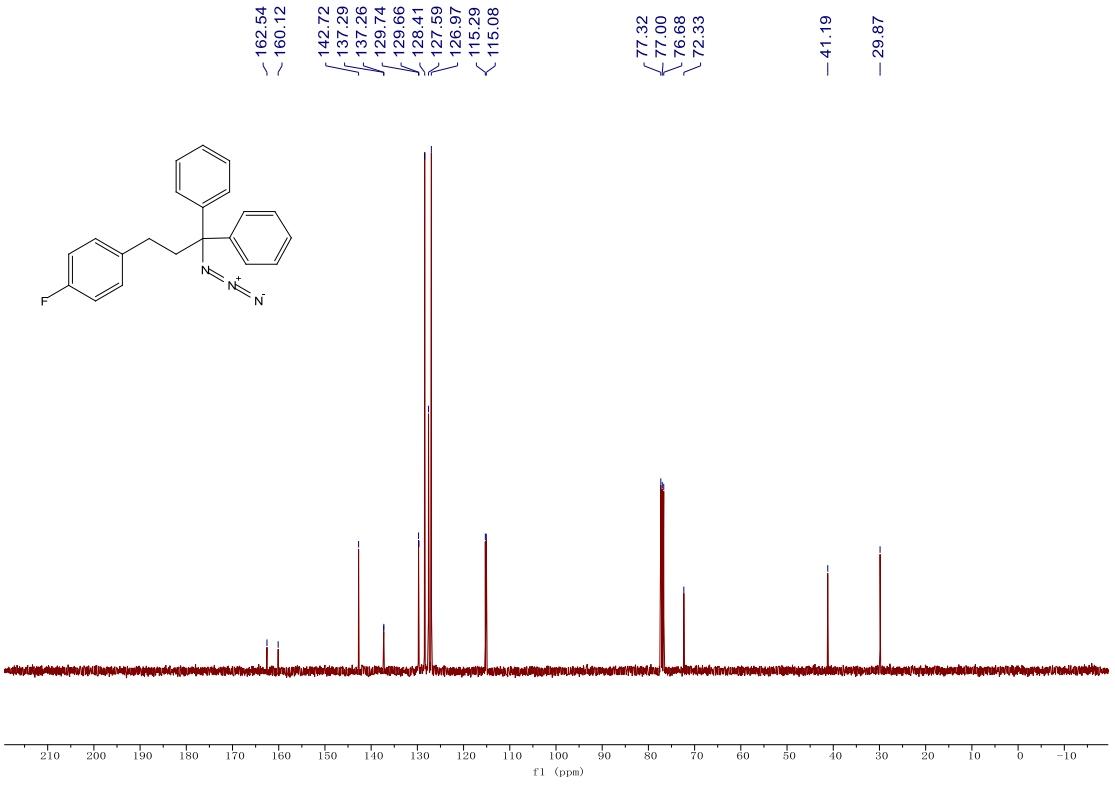

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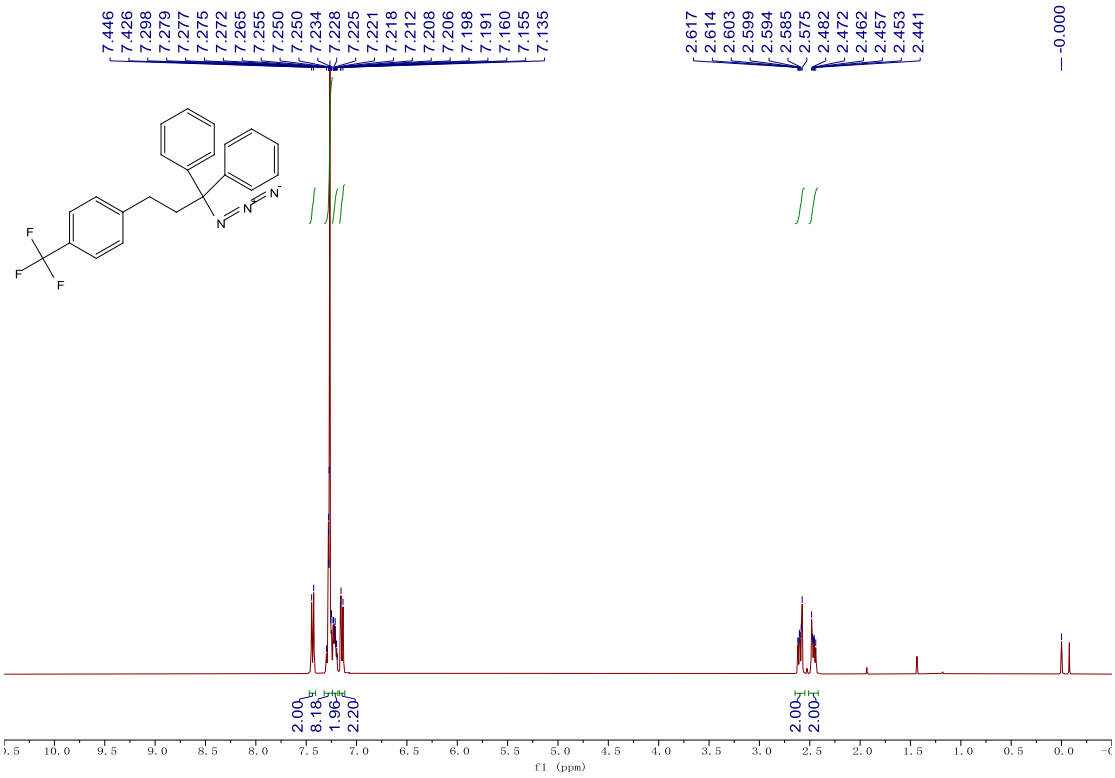

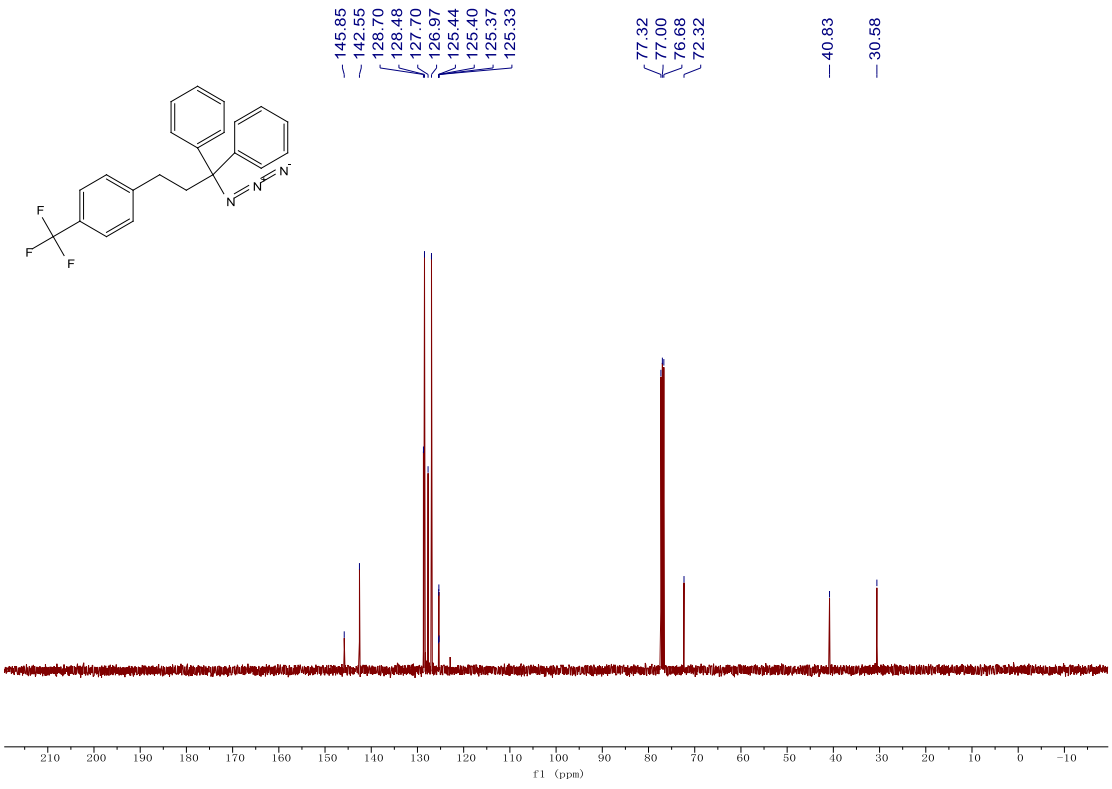

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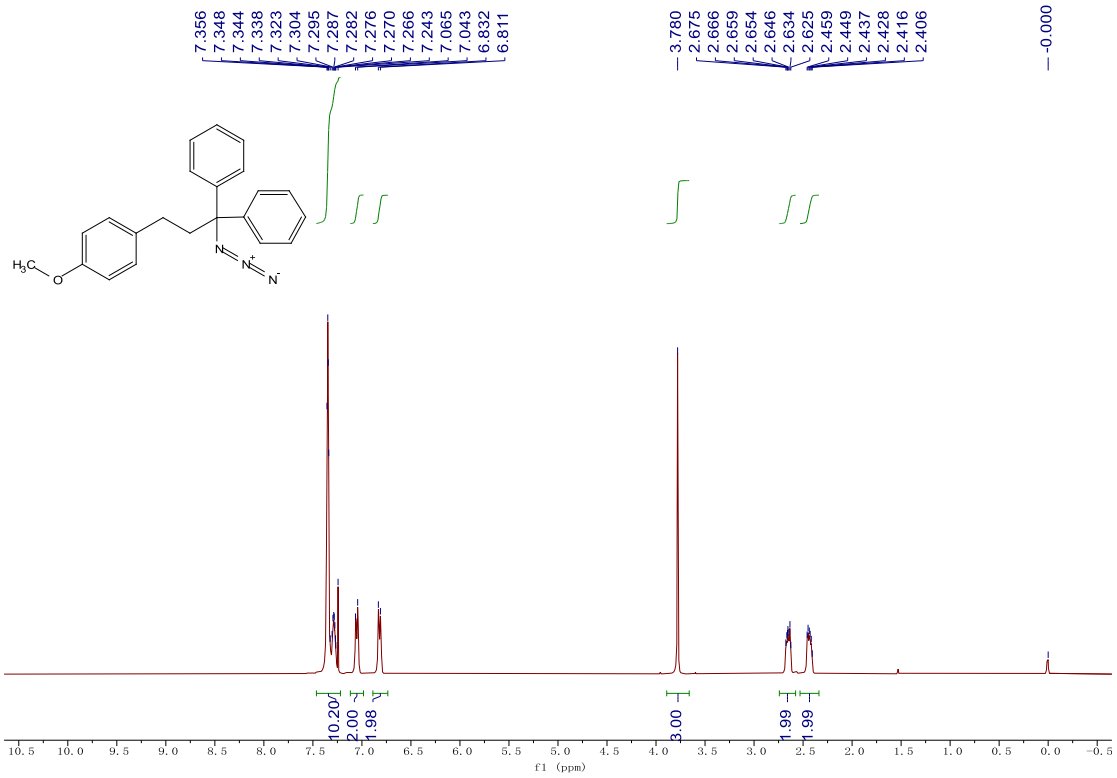

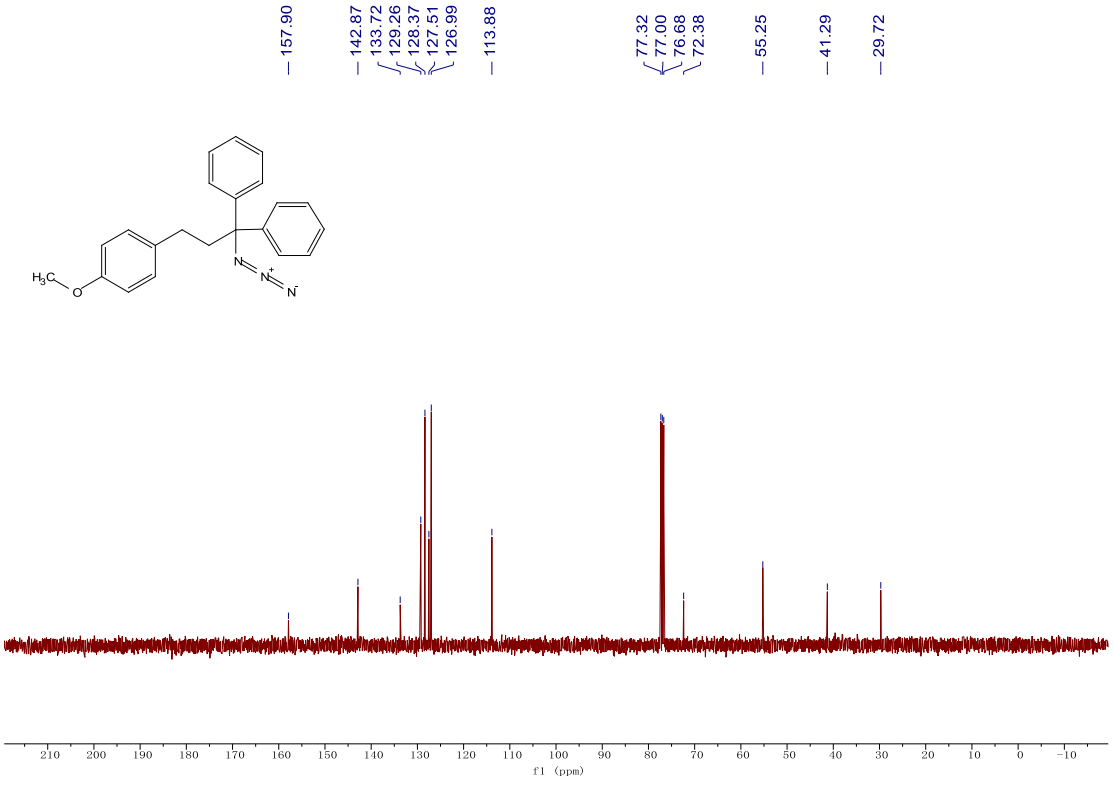

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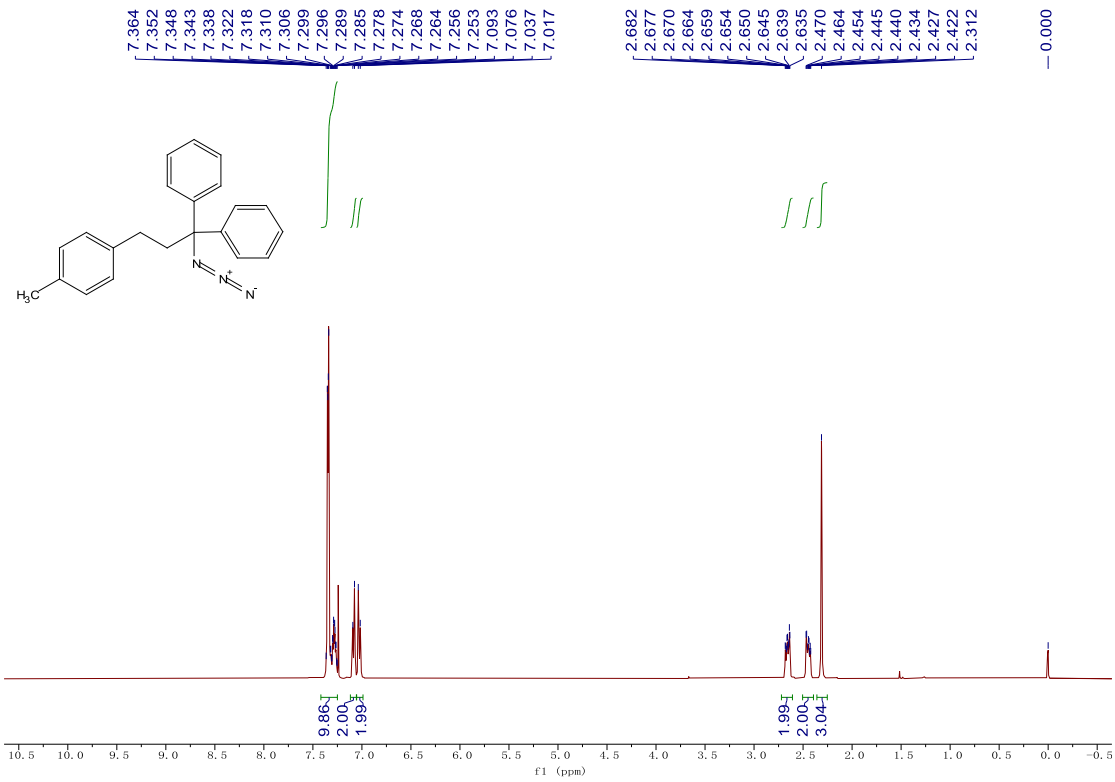
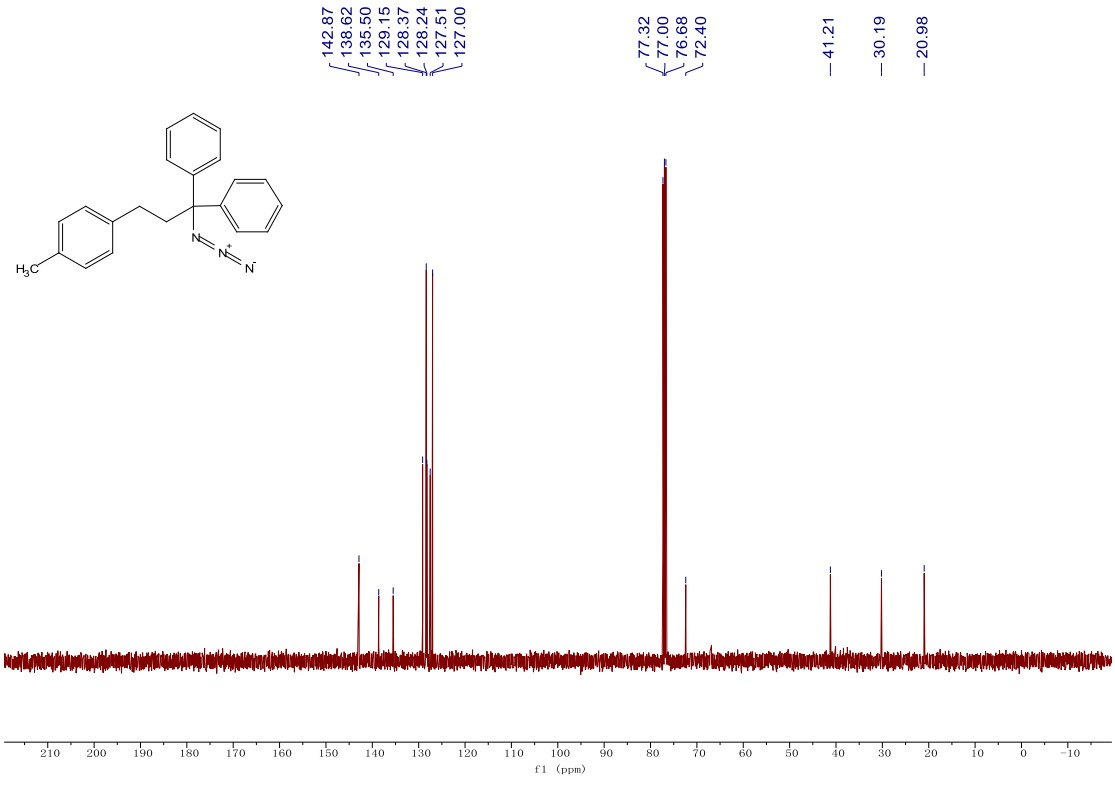
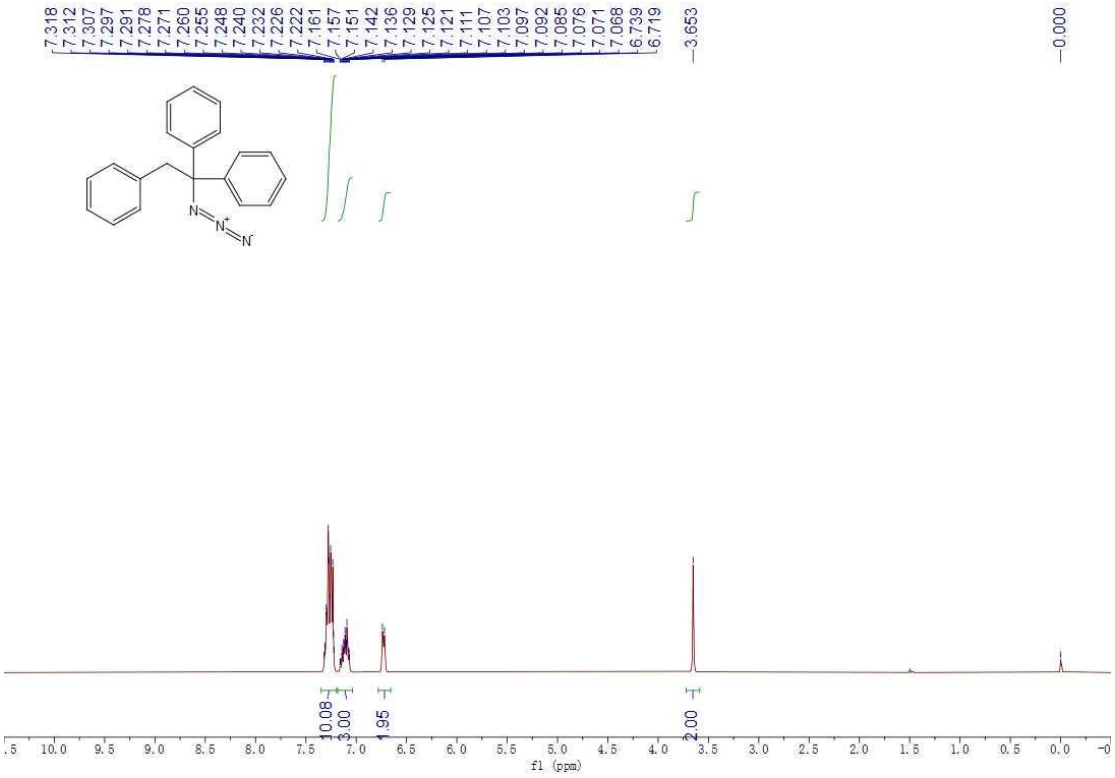
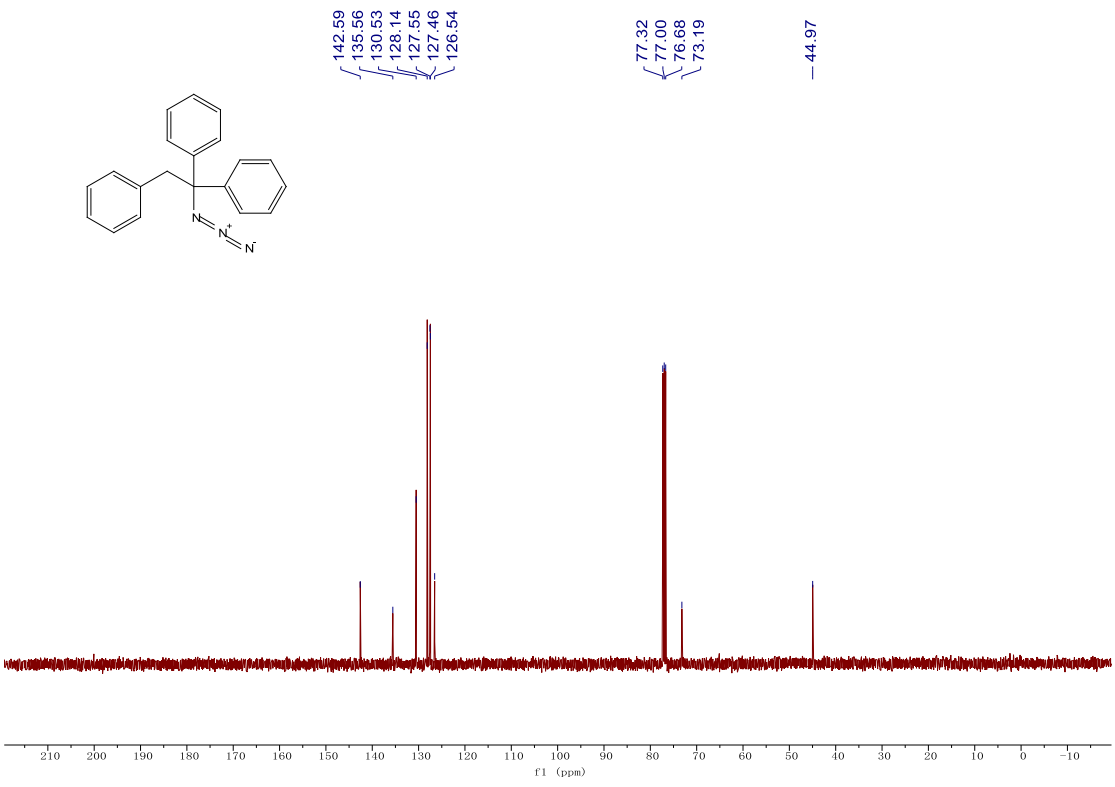




1-Azidoethane-1,1,2-triyl)tribenzene (1g)





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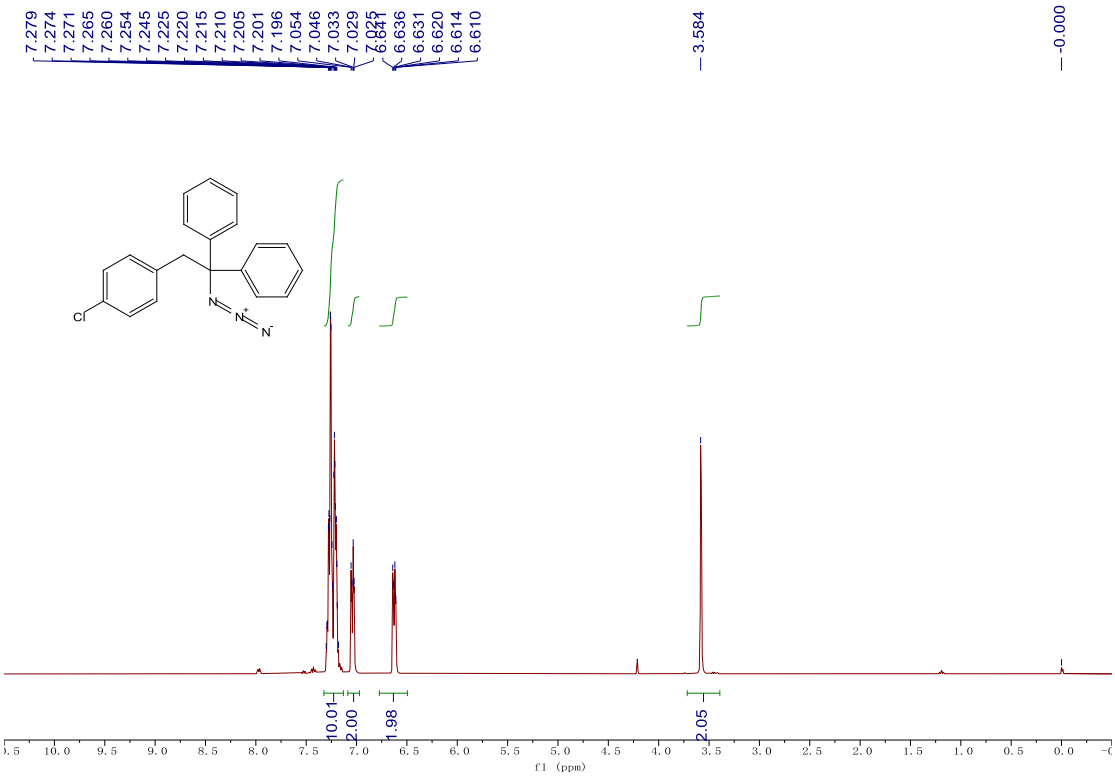

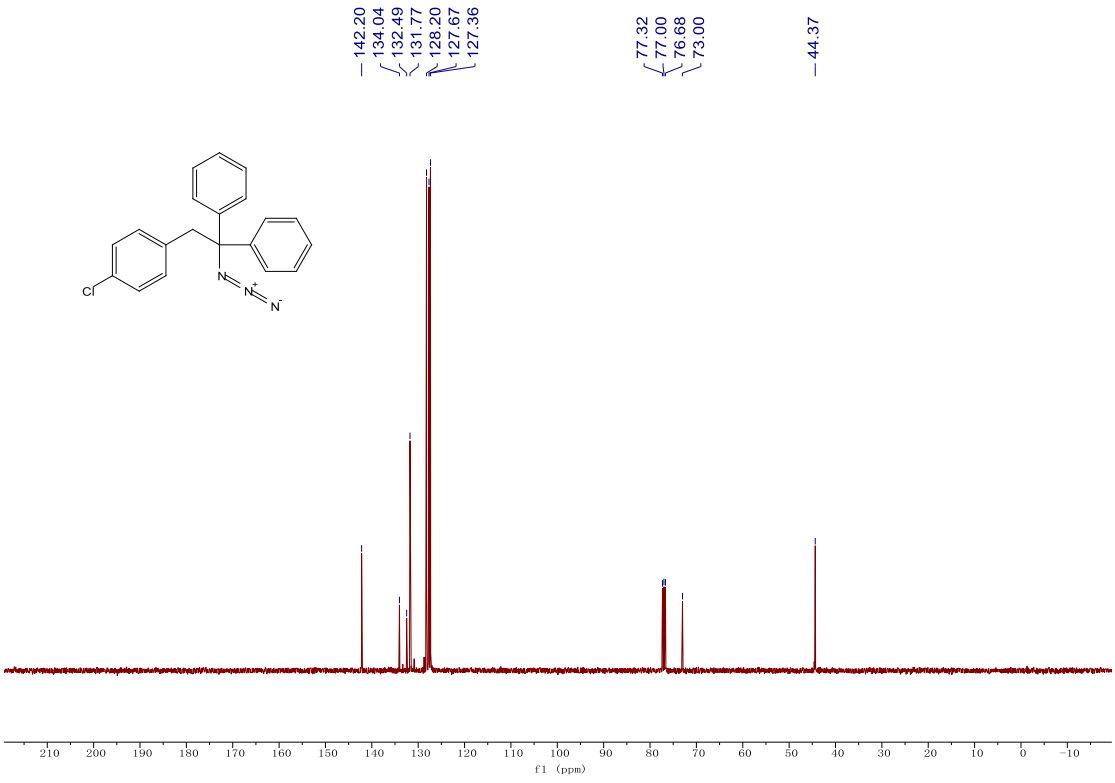

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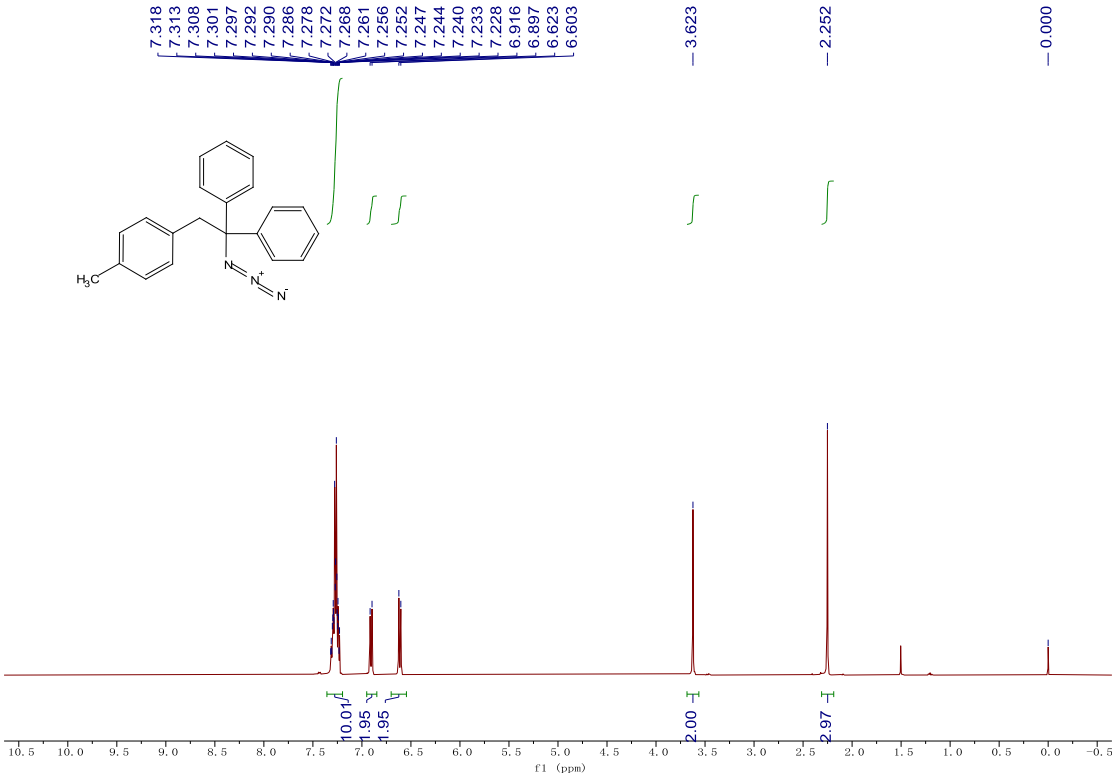

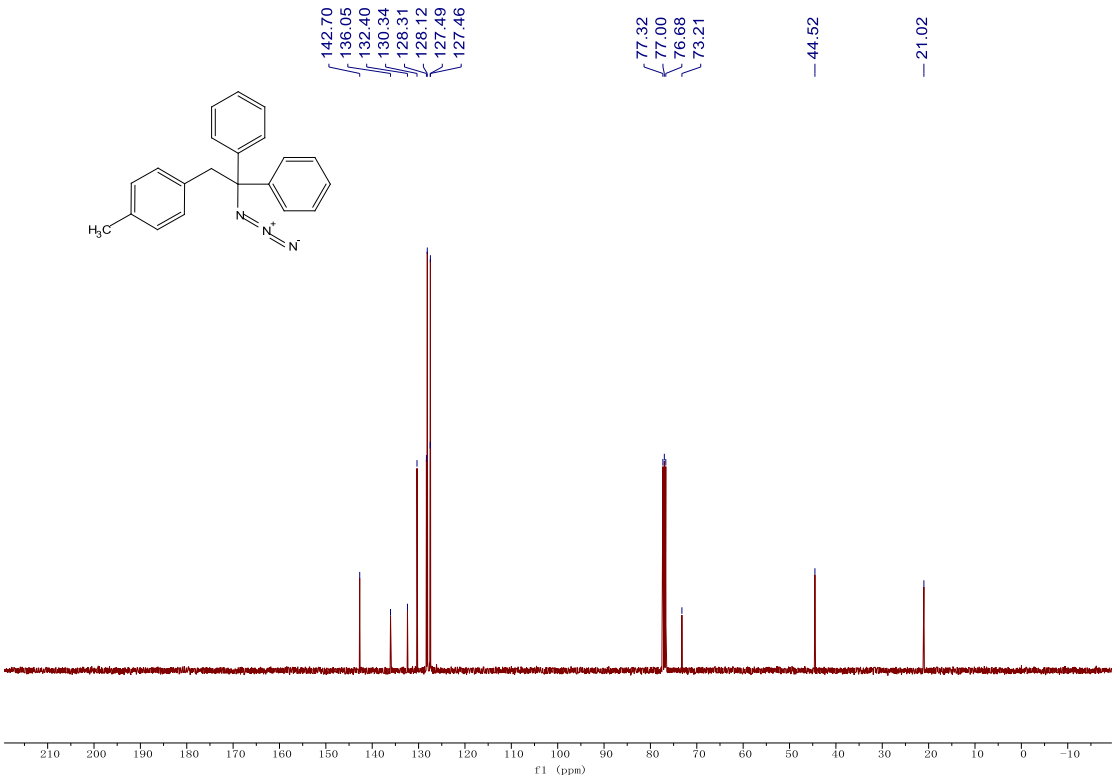

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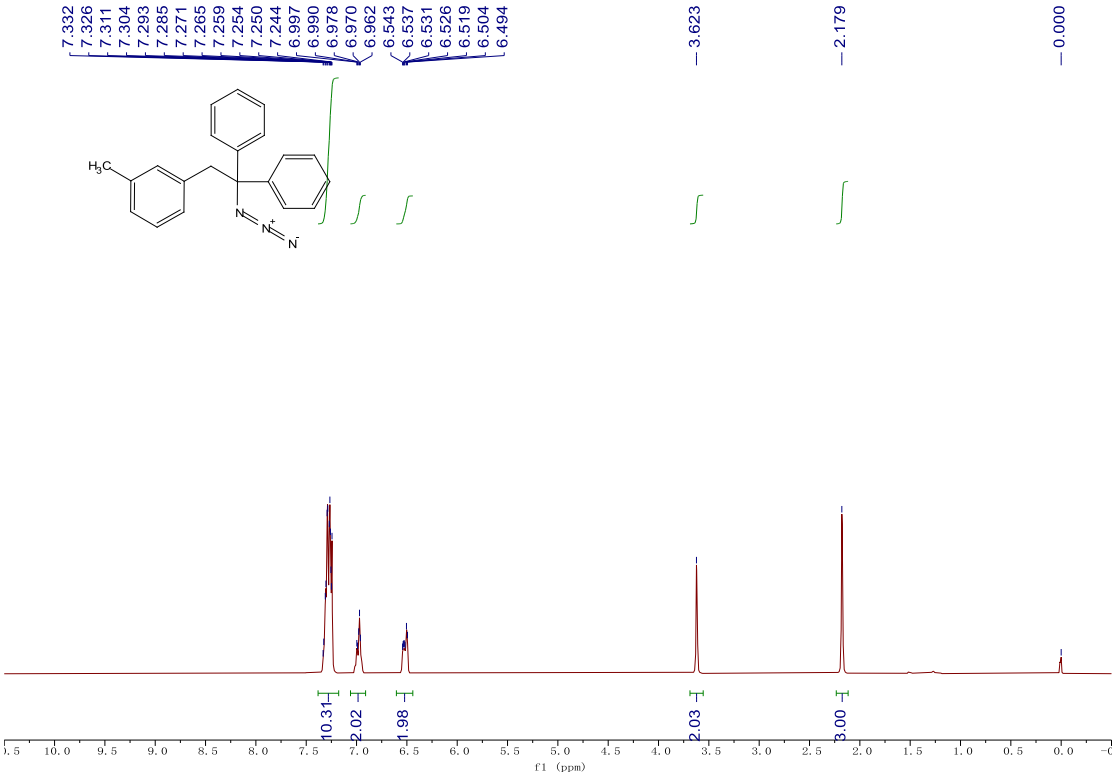

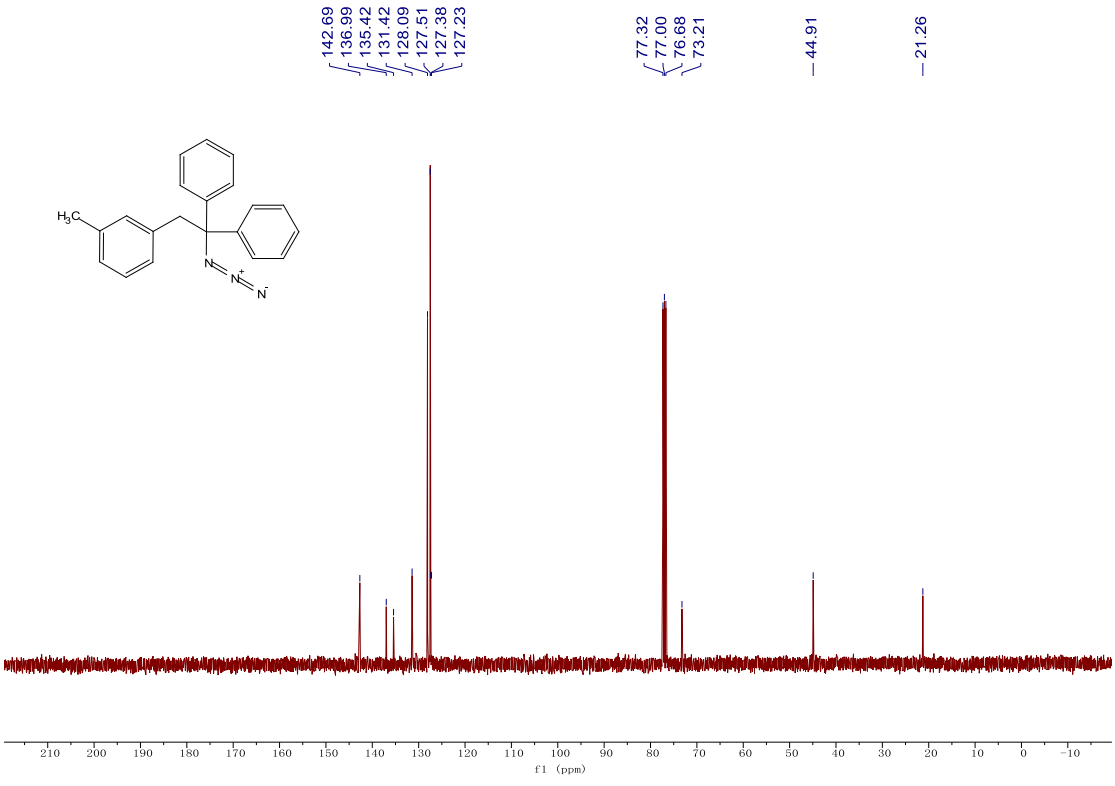

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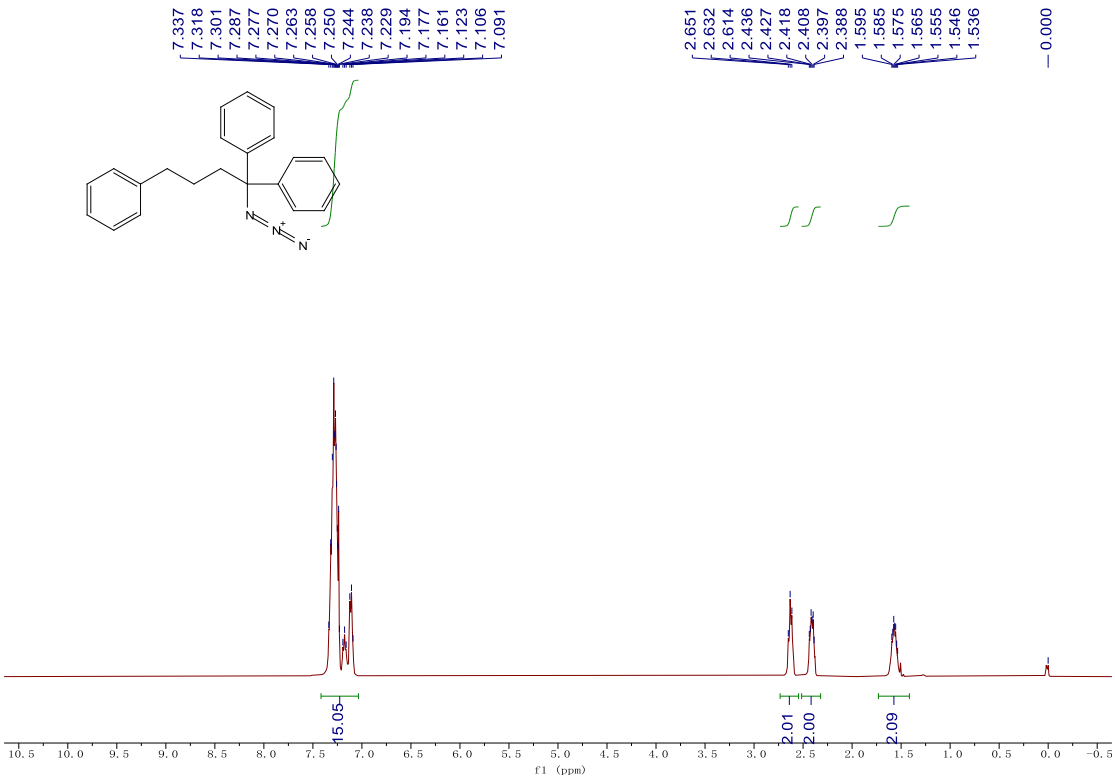

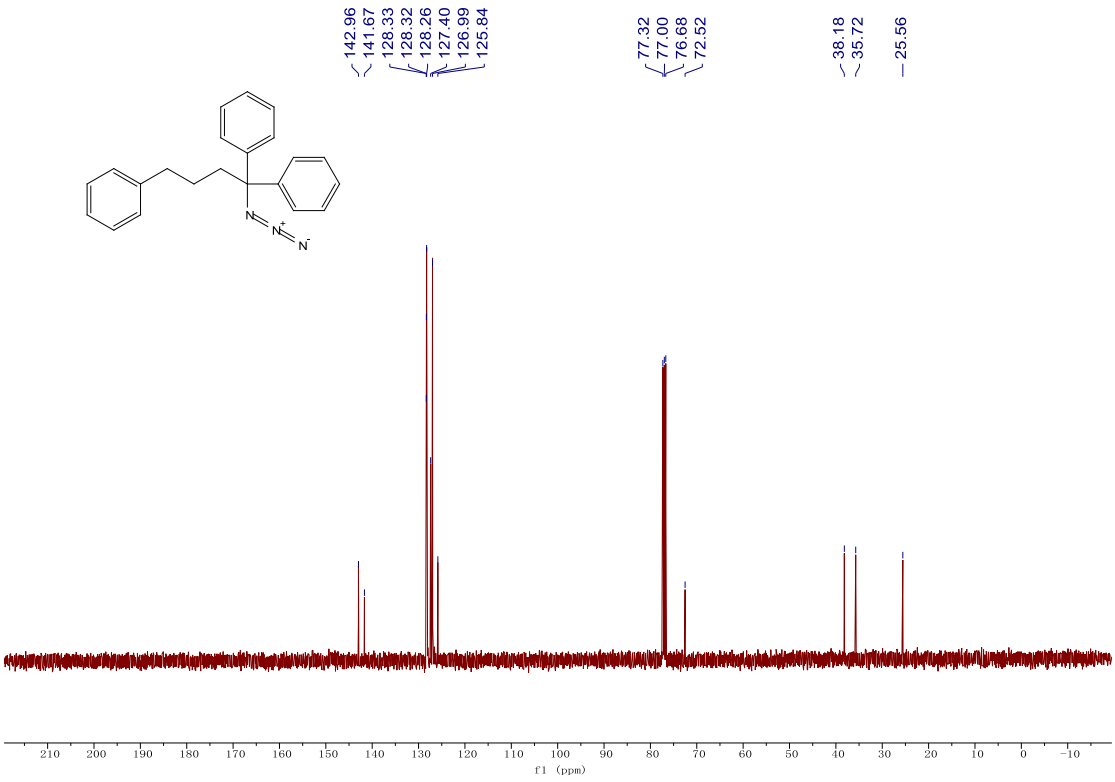

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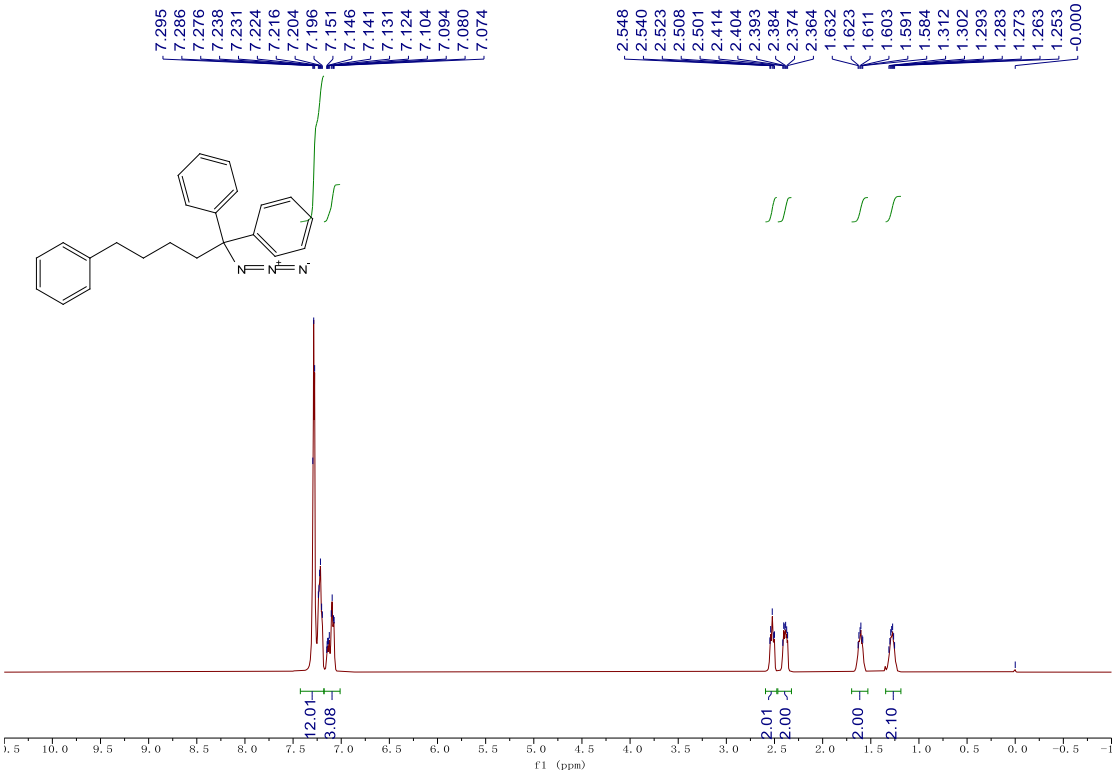
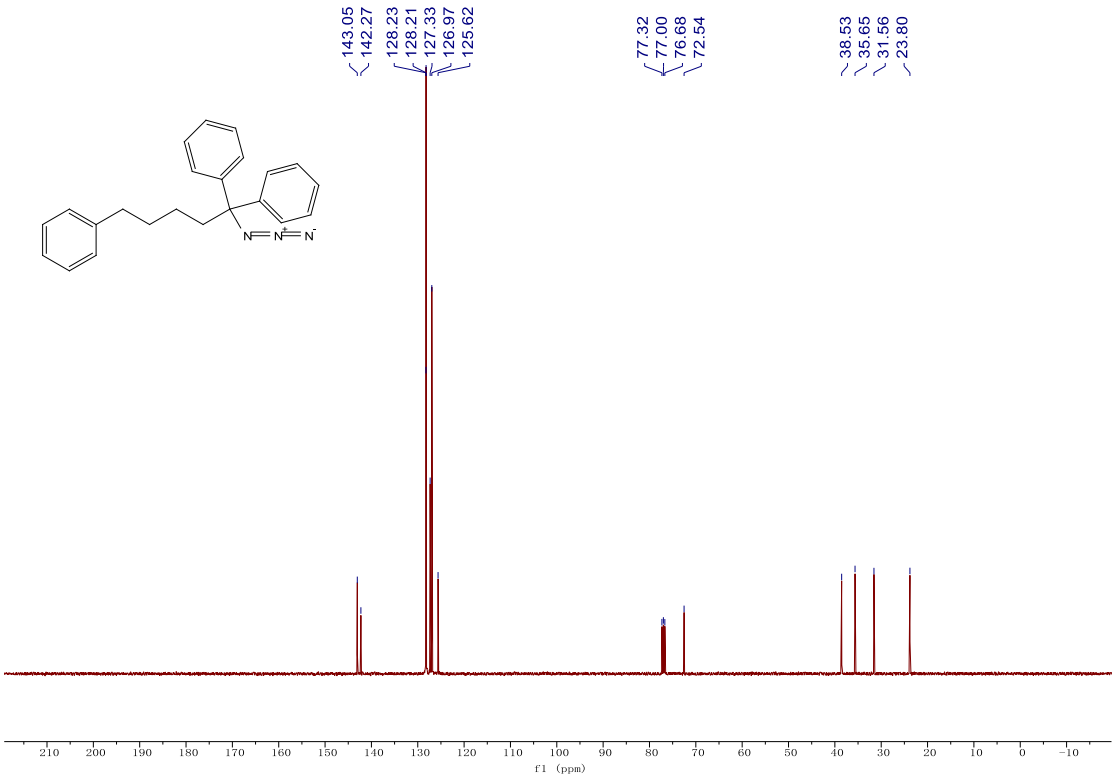
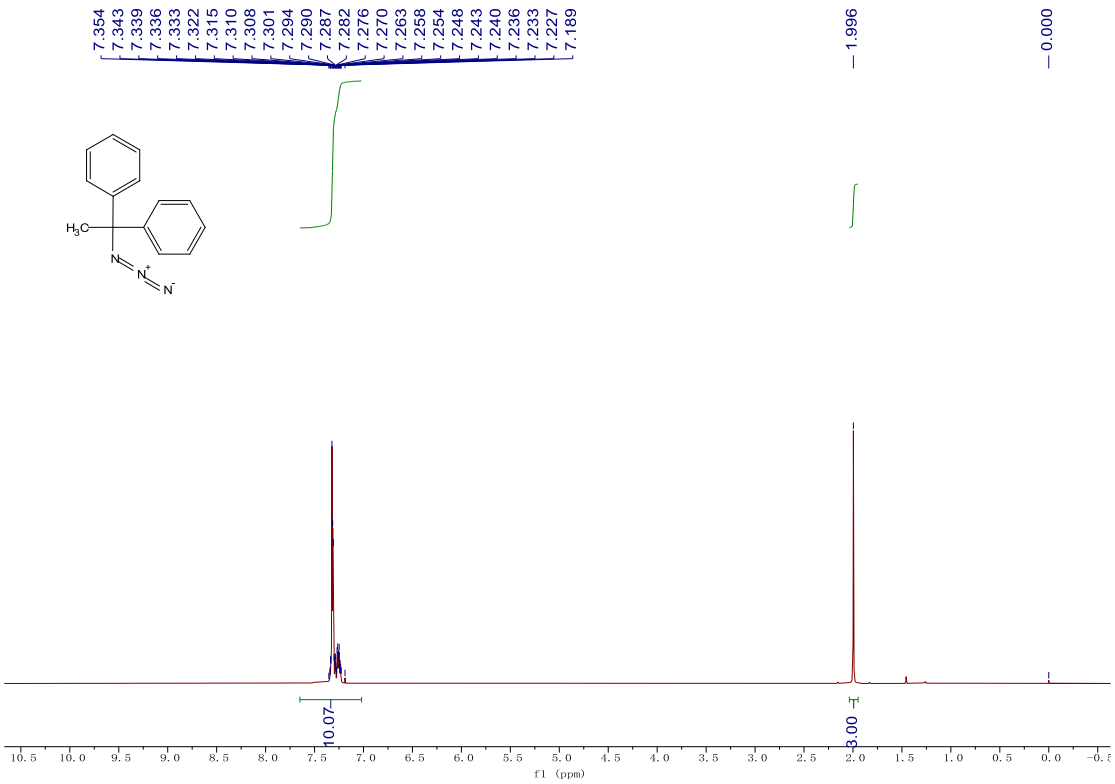
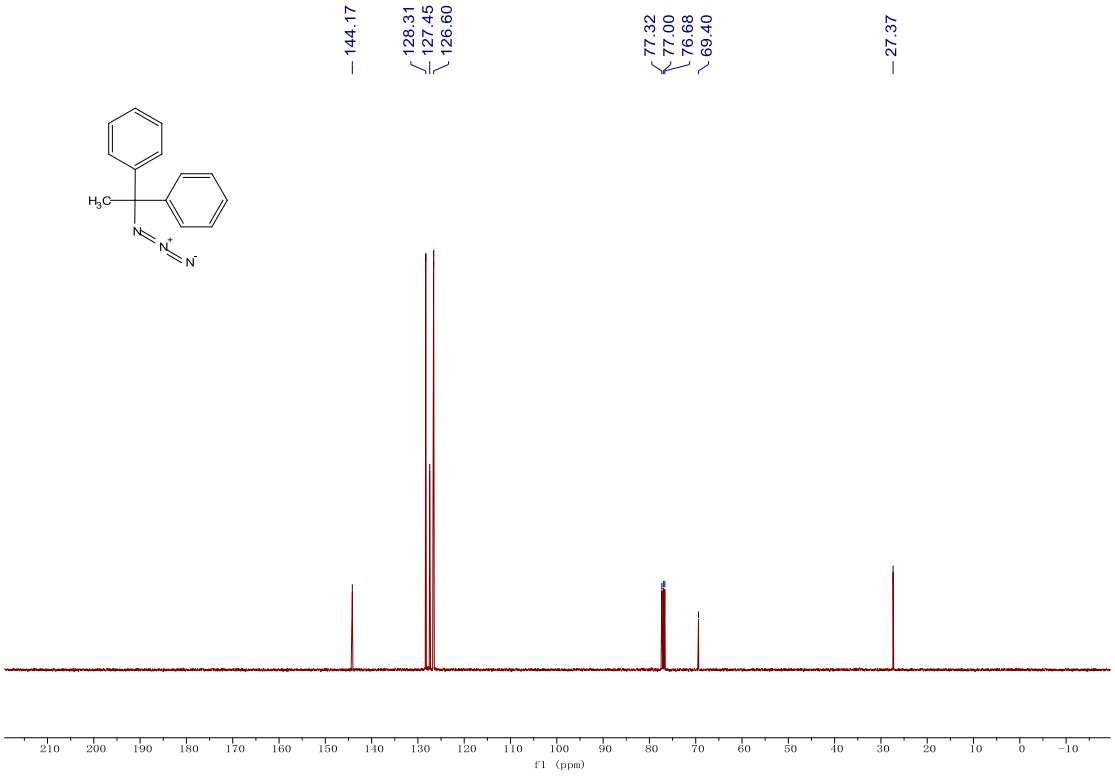


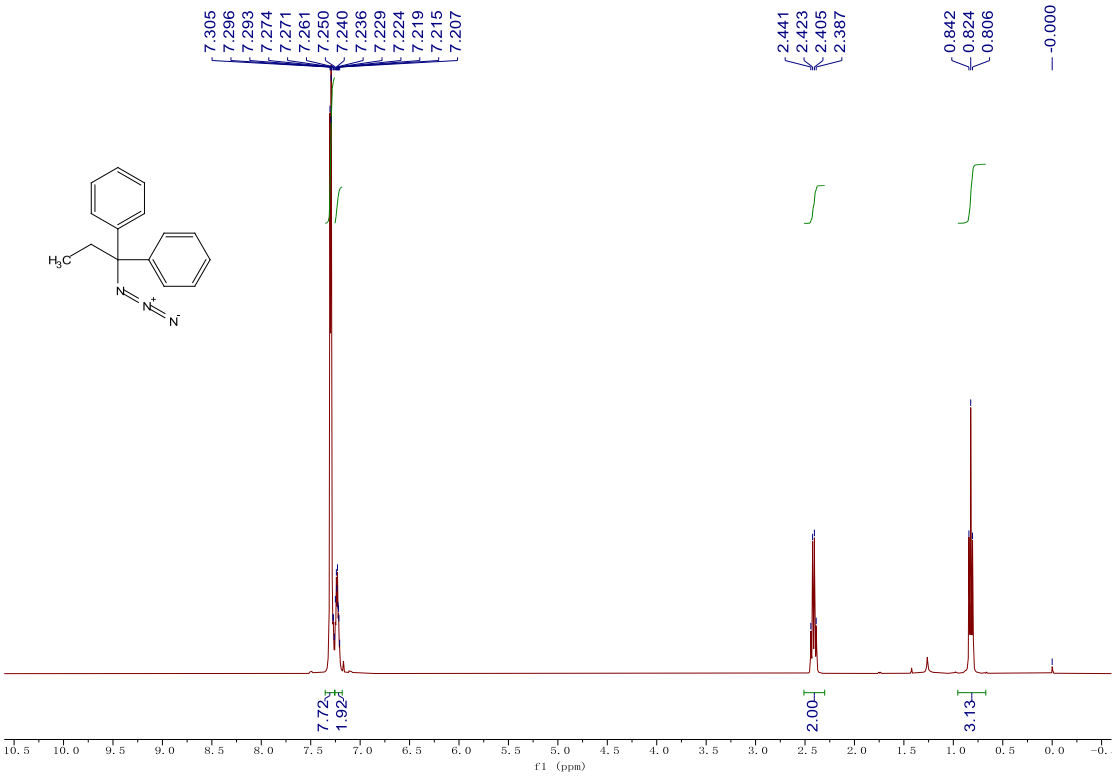


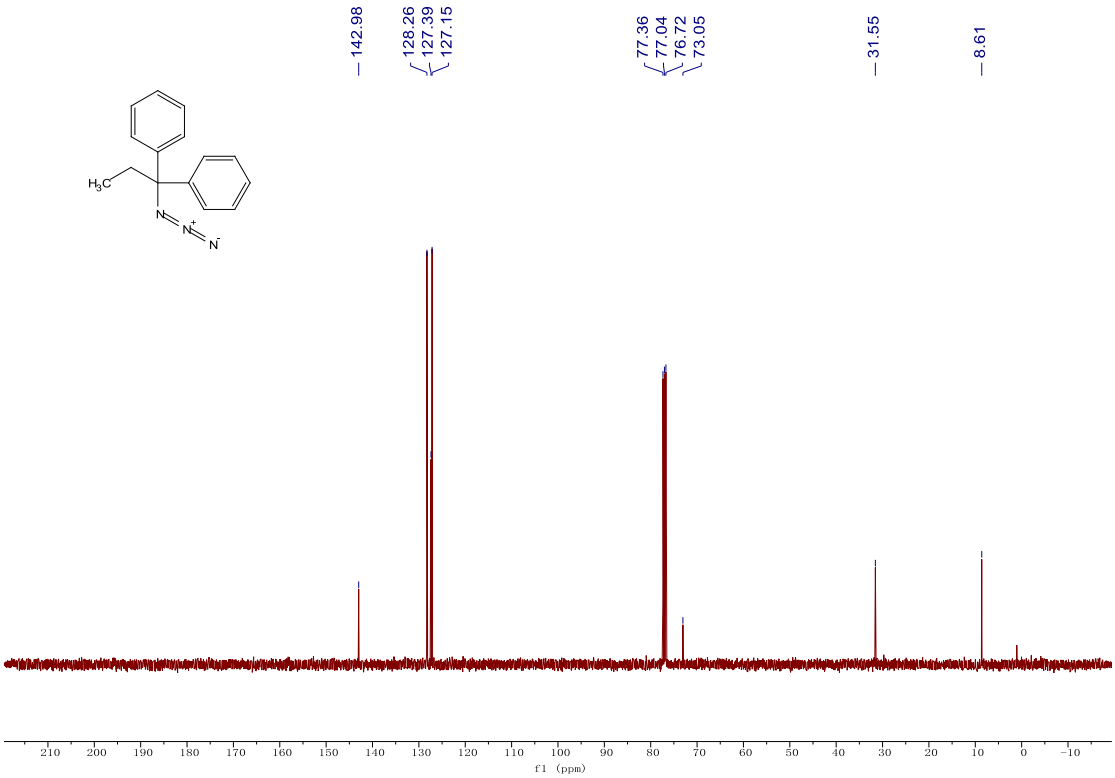
(1-Azidoethane-1,1-diyl)dibenzene (1m)





(1-Azidopropane-1,1-diyl)dibenzene (1n)





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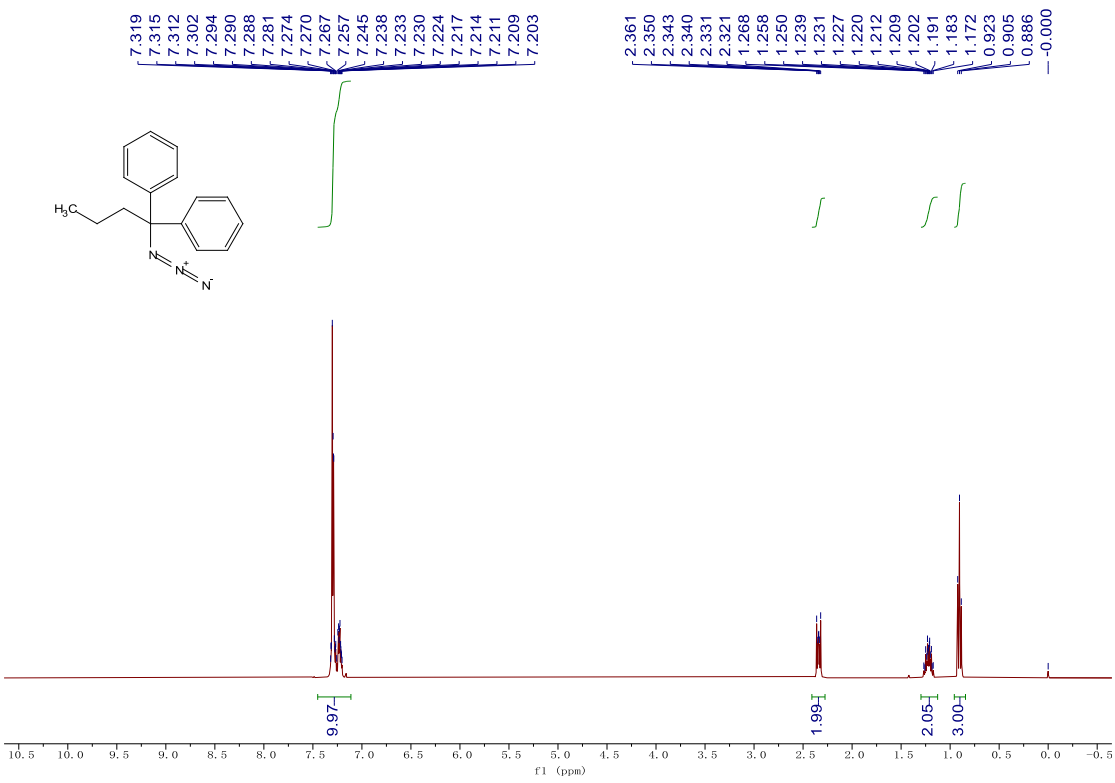
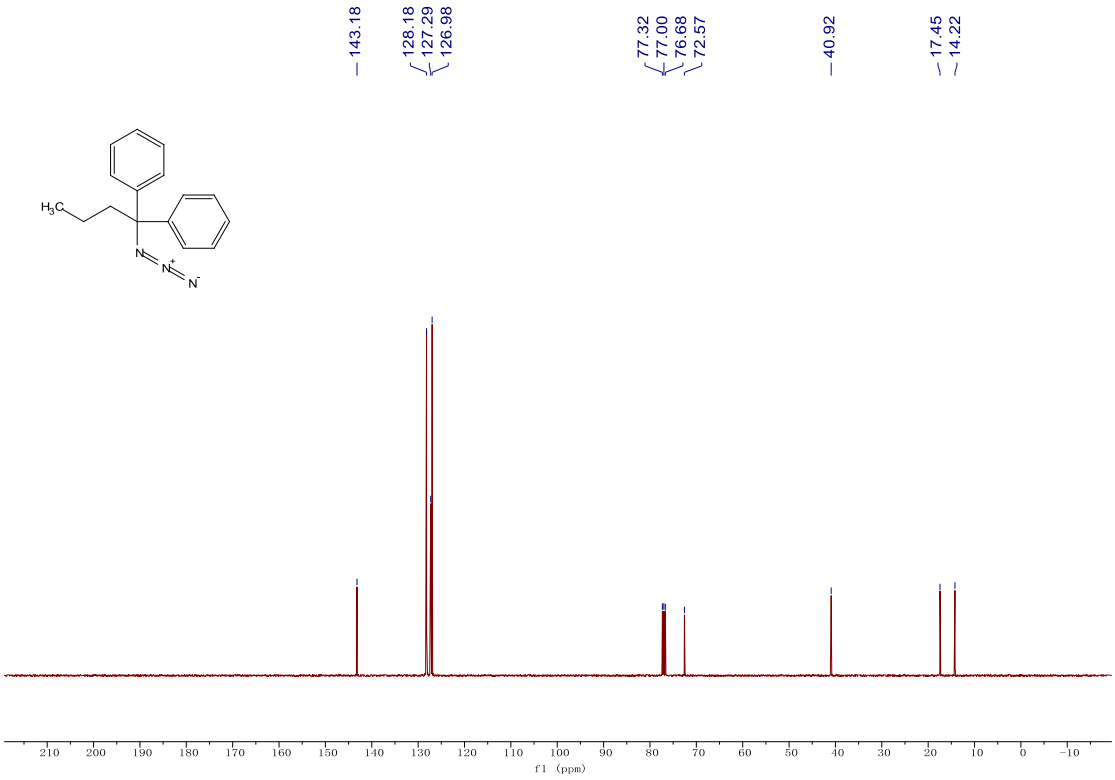
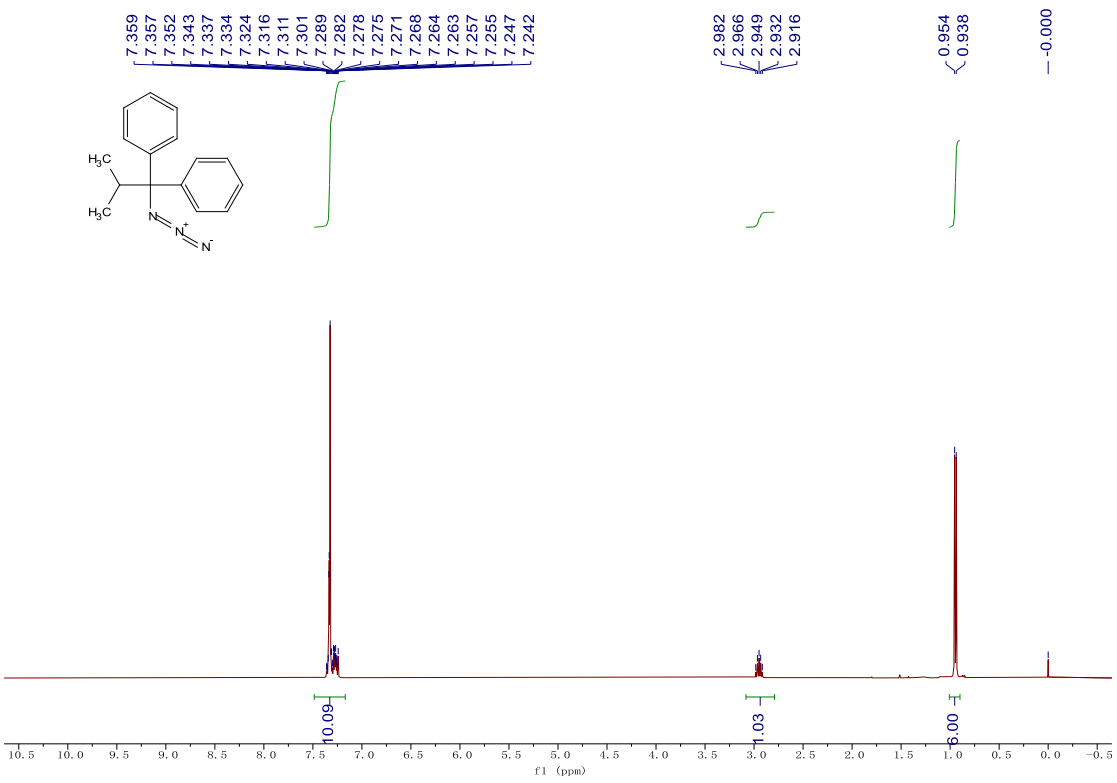
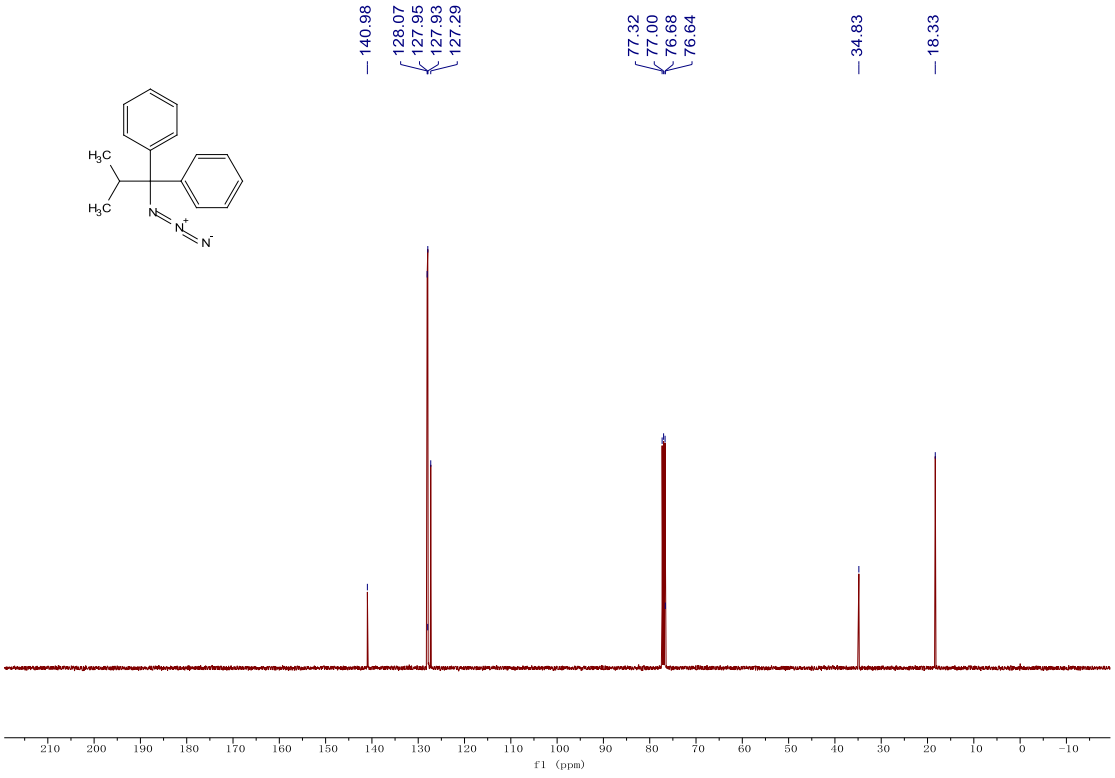


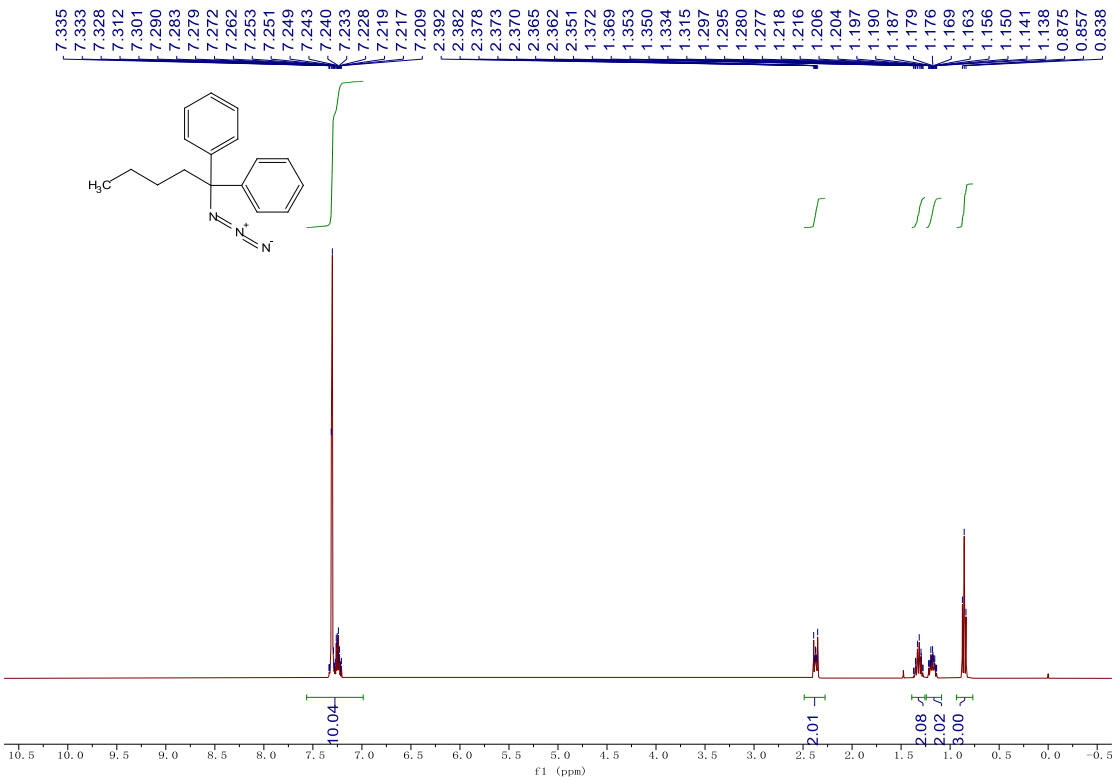


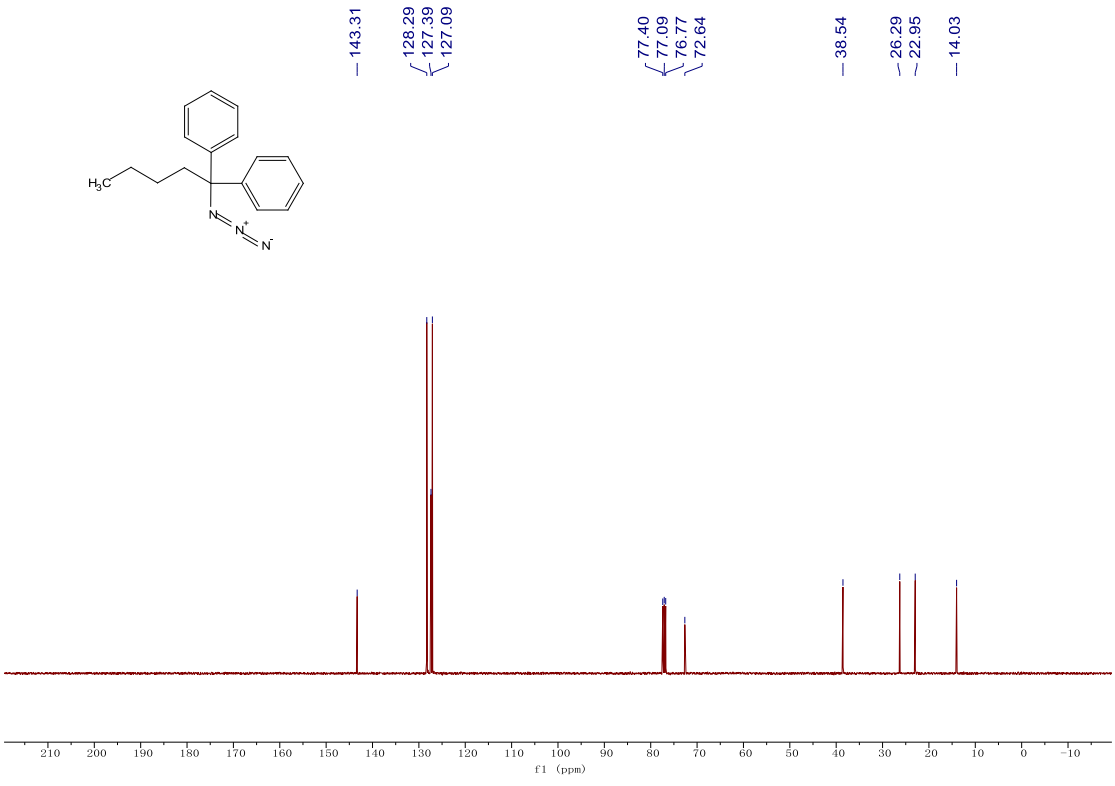
(1-Azido-2-methylpropane-1,1-diyl)dibenzene (1p)



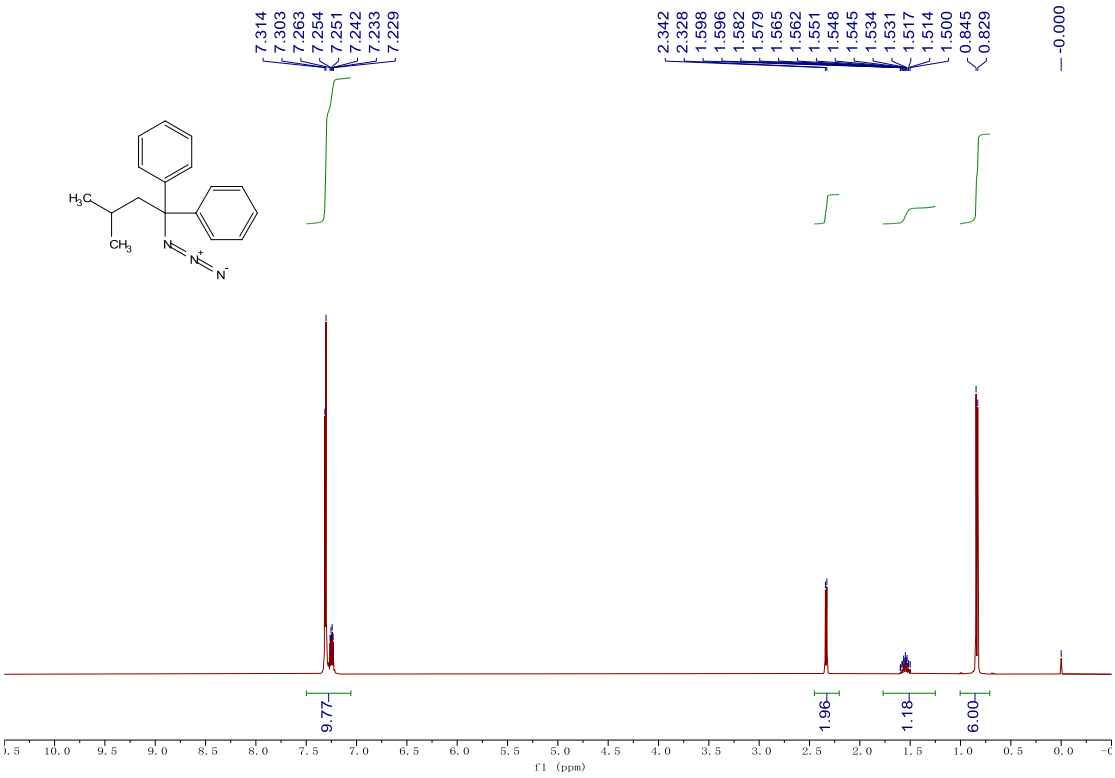


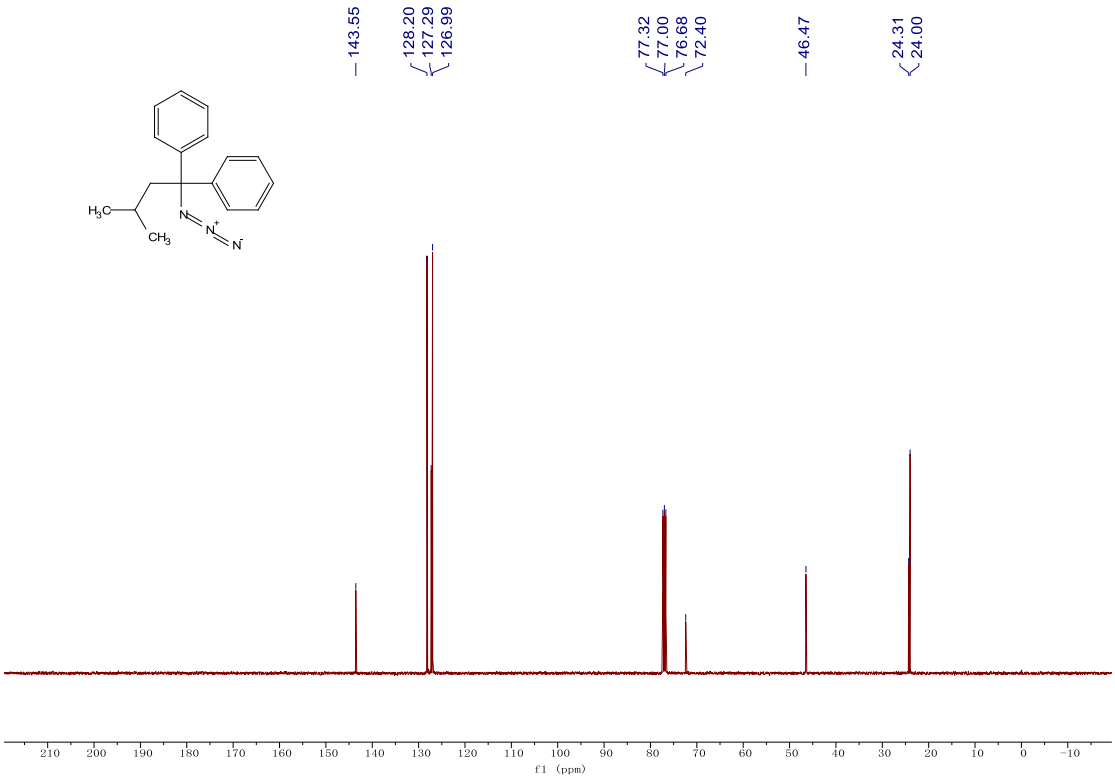
(1-Azidopentane-1,1-diyl)dibenzene (1q)



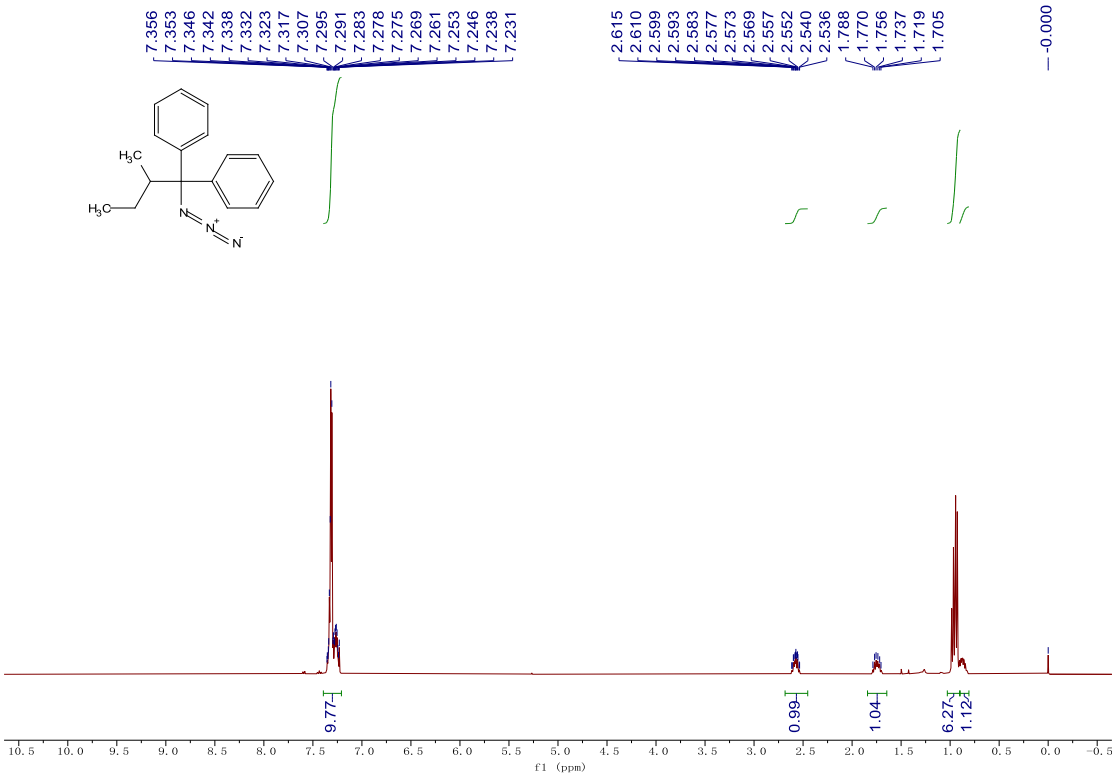


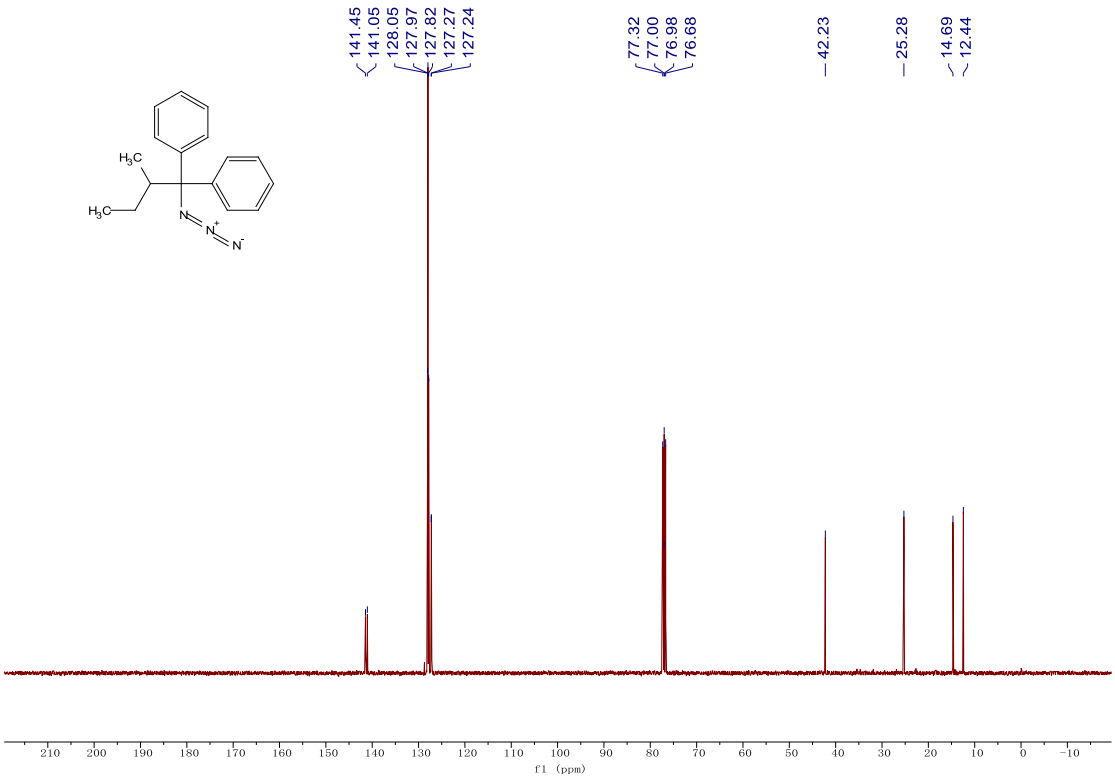
(1-Azido-3-methylbutane-1,1-diyl)dibenzene (1r)



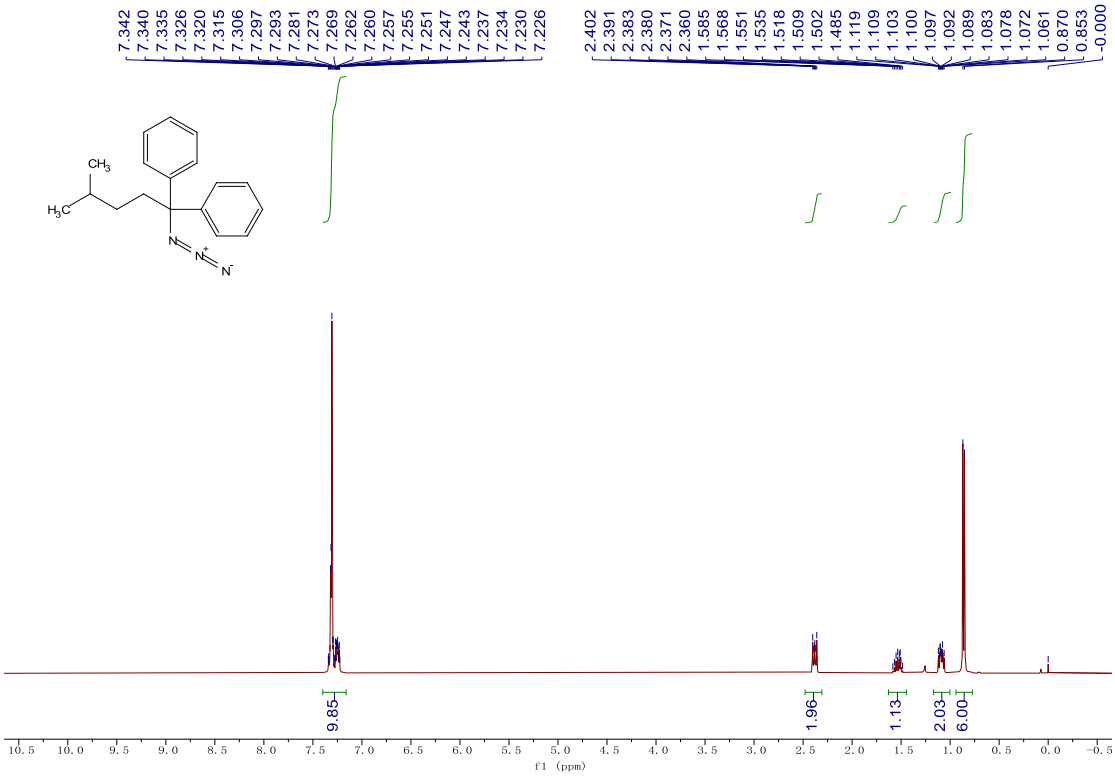


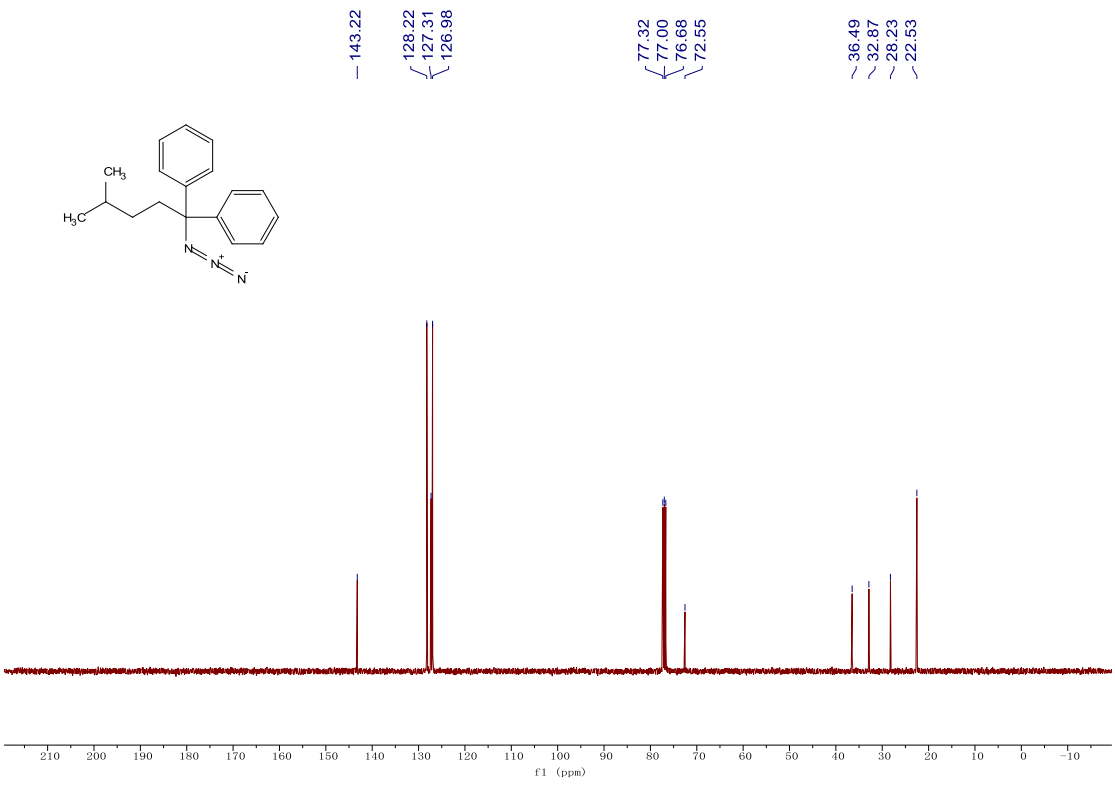
(1-Azido-2-methylbutane-1,1-diyl)dibenzene (1s)



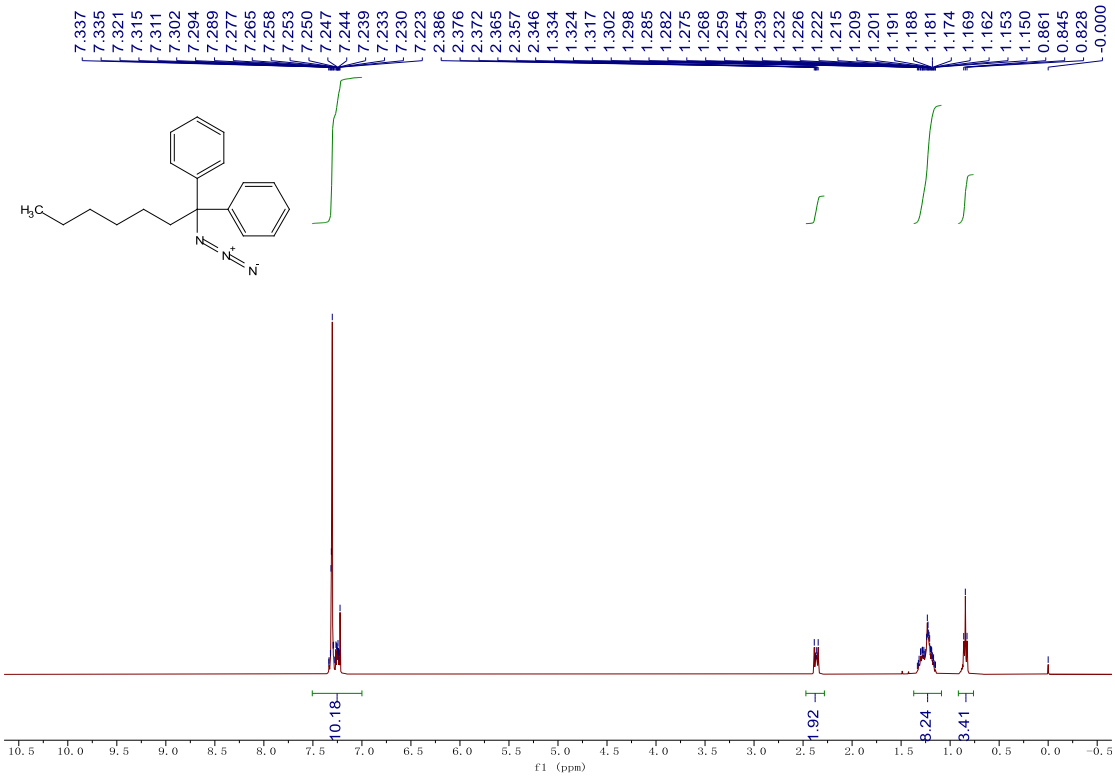


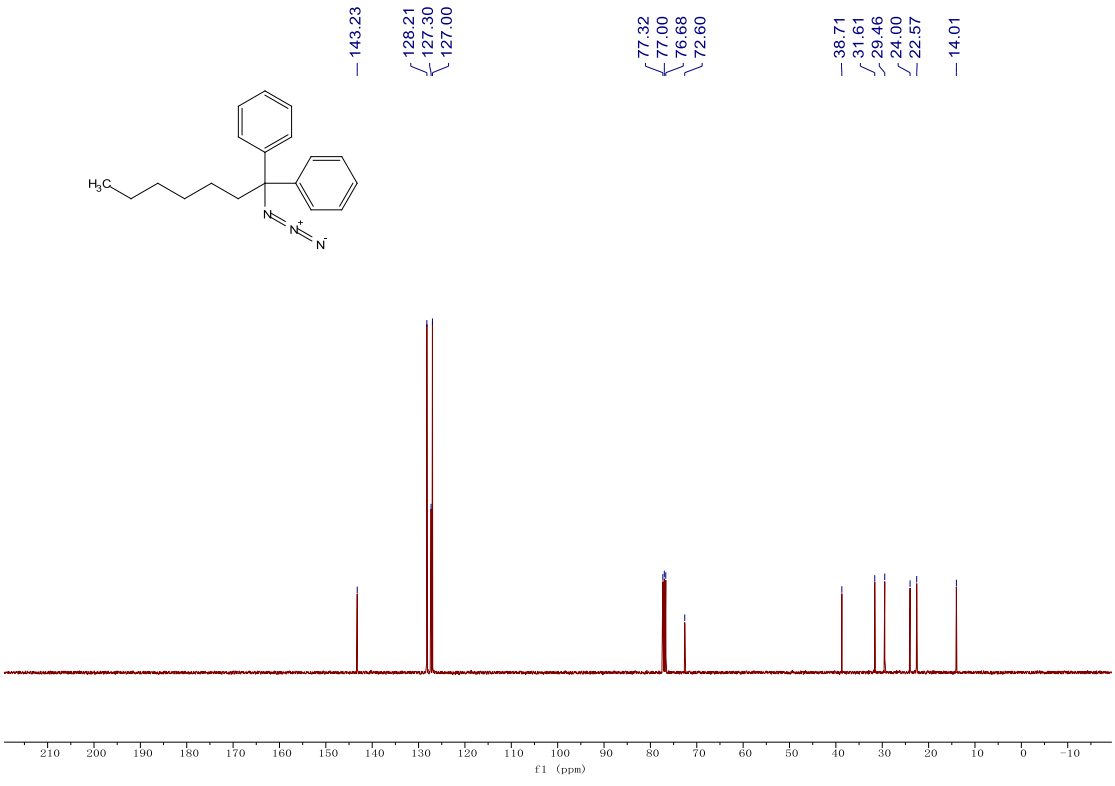
(1-Azido-4-methylpentane-1,1-diyl)dibenzene (1t)



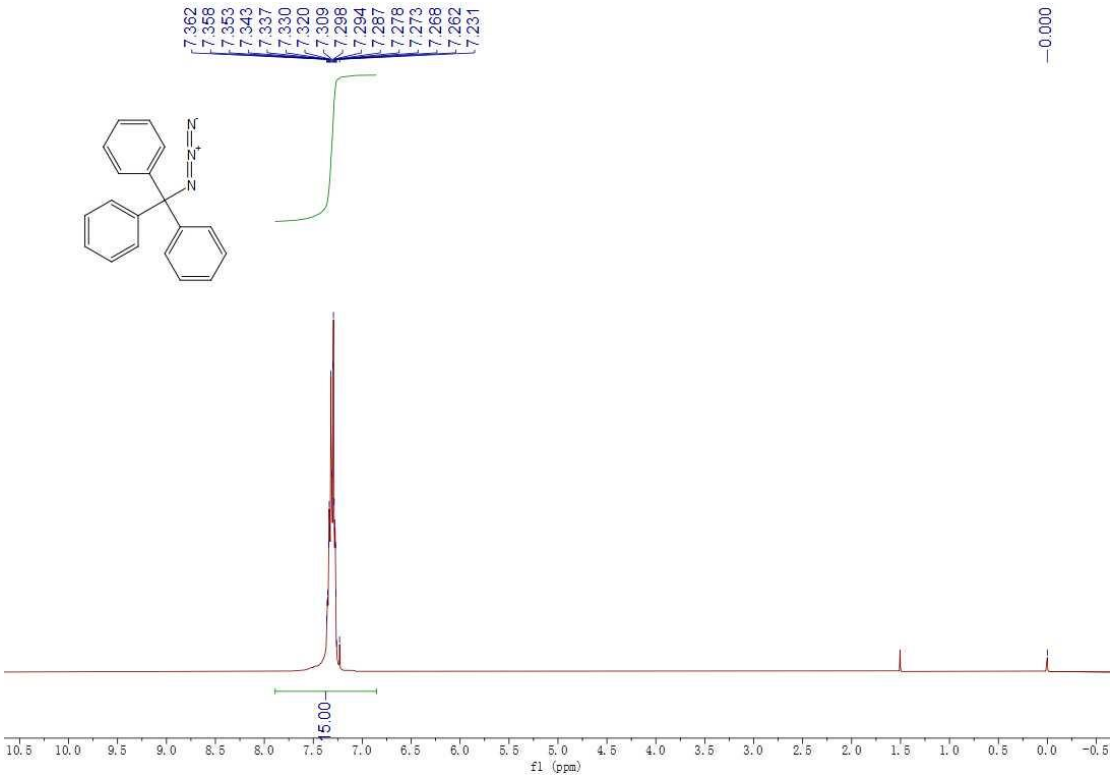


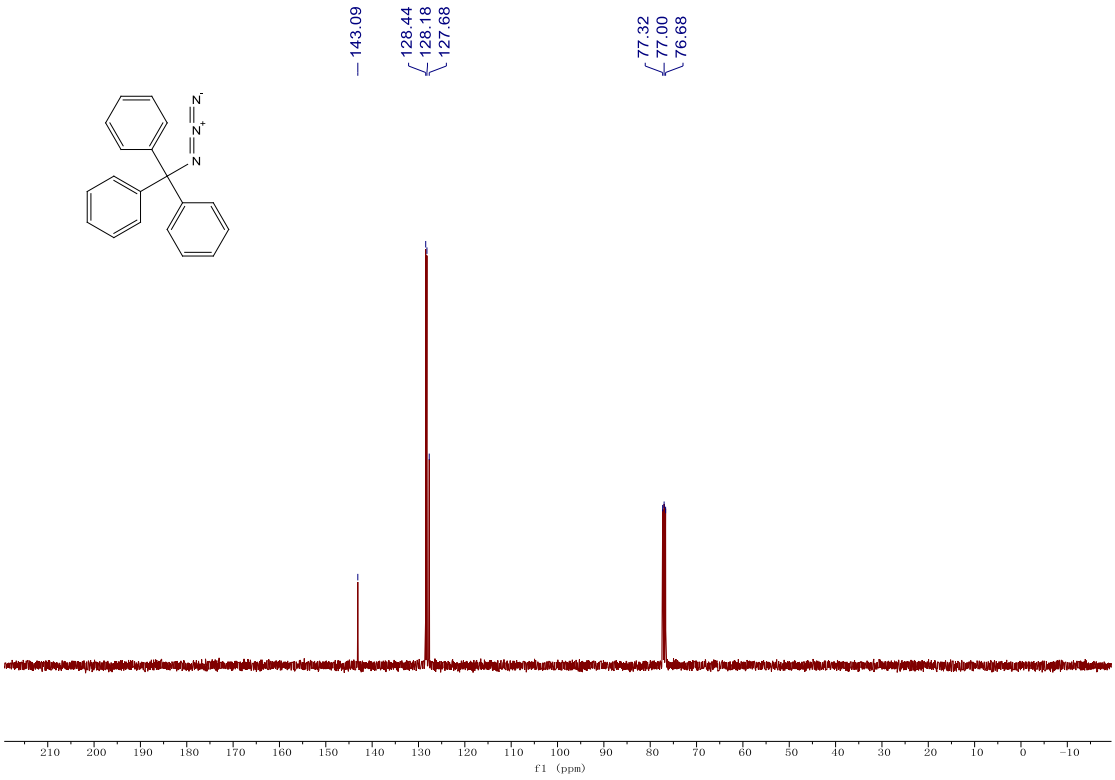
(1-Azidoheptane-1,1-diyl)dibenzene (1u)



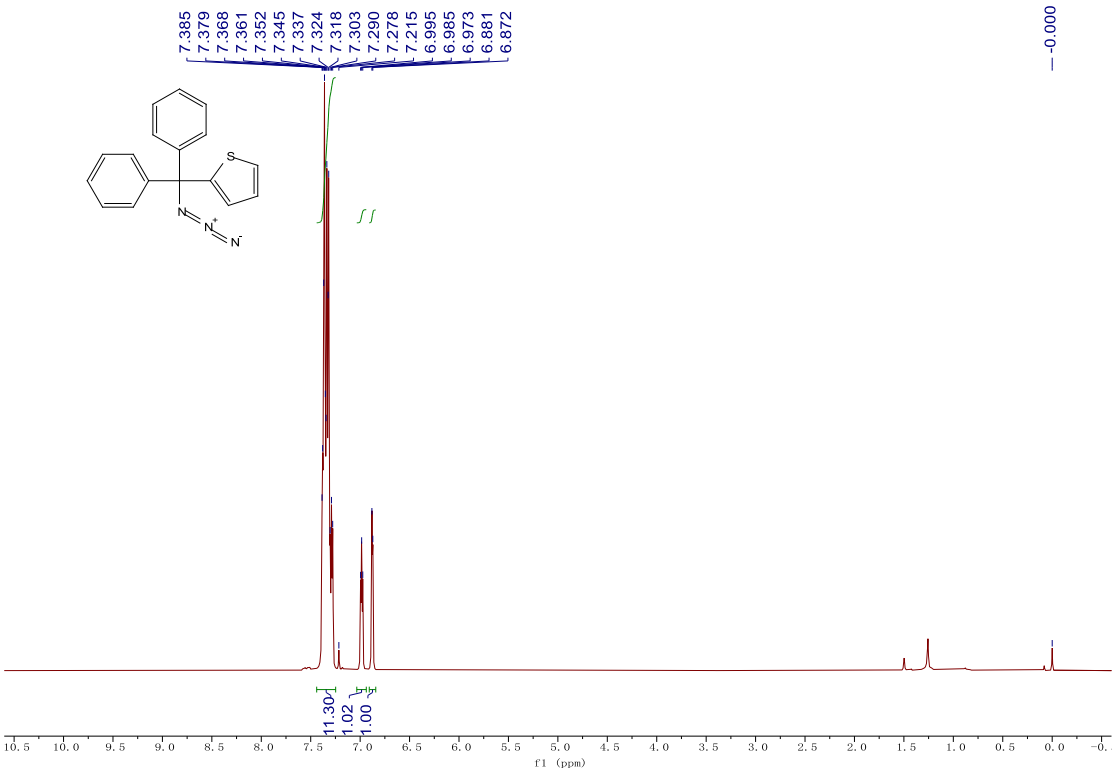


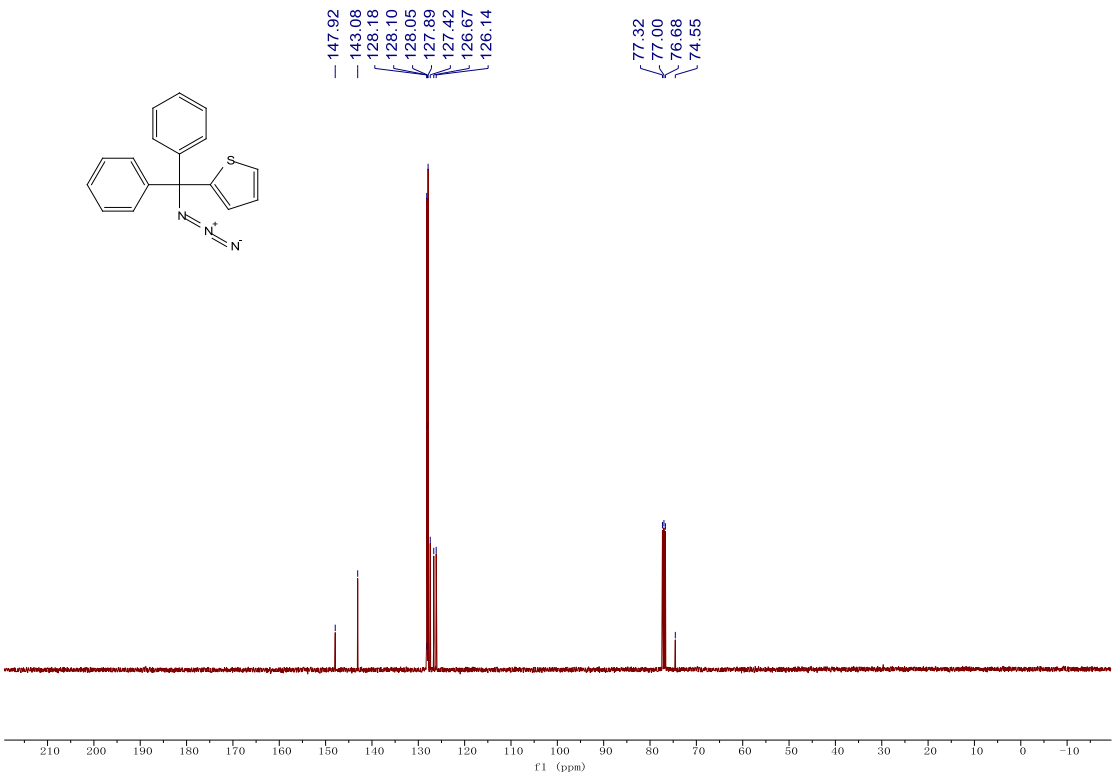
(Azidomethanetriyl)tribenzene (1v)



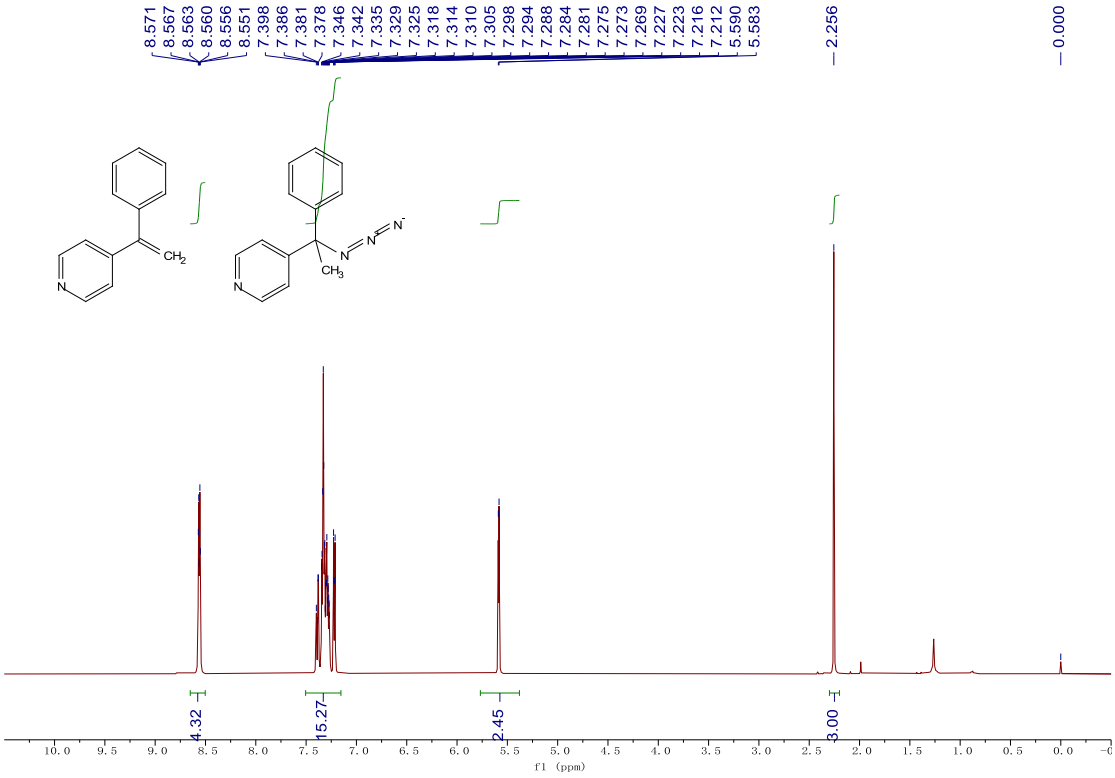


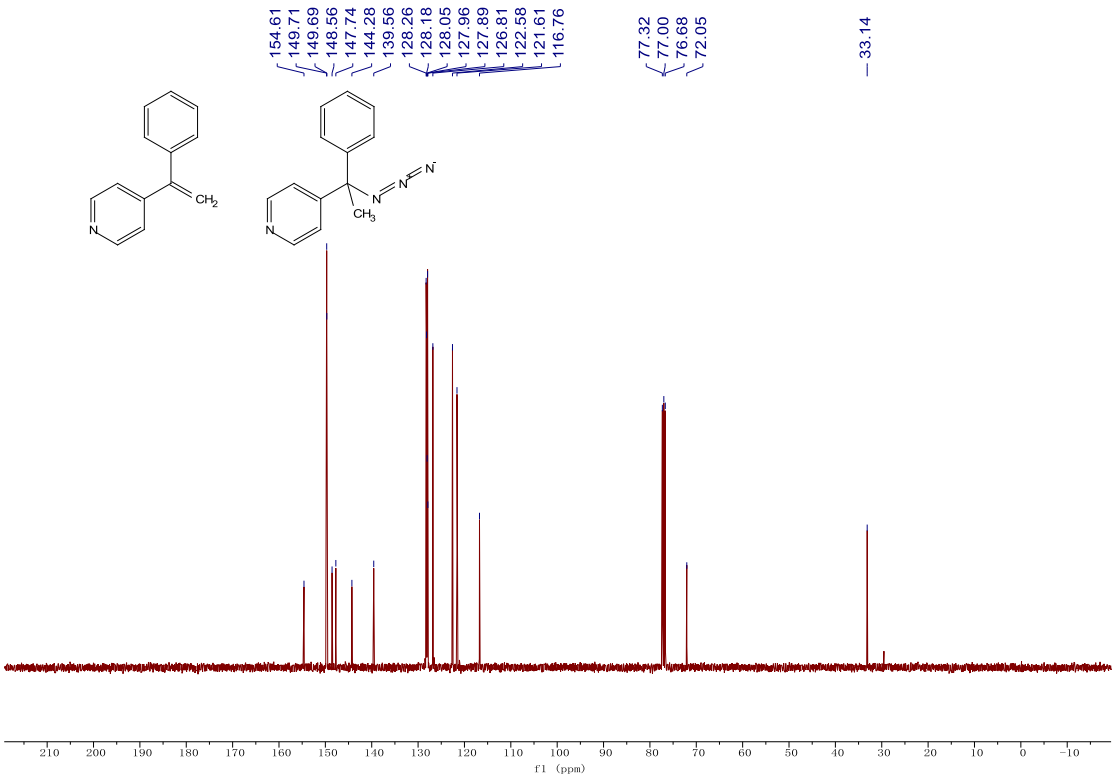
2-(Azidodiphenylmethyl)thiophene (1w)



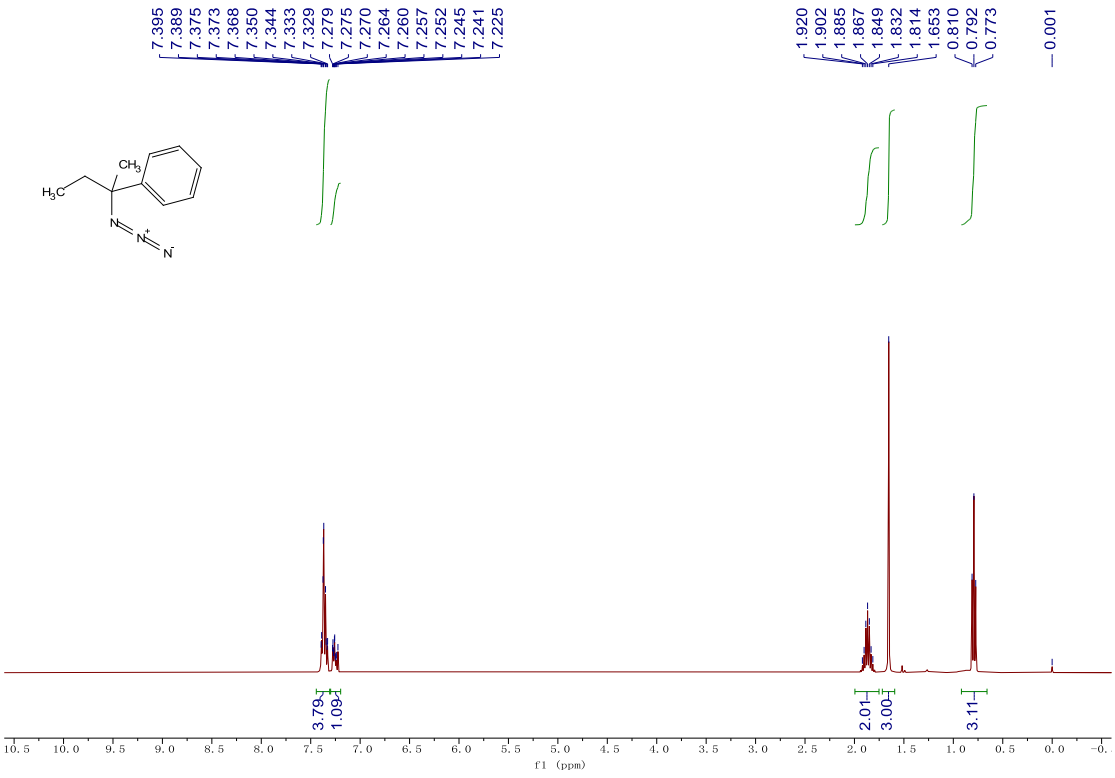


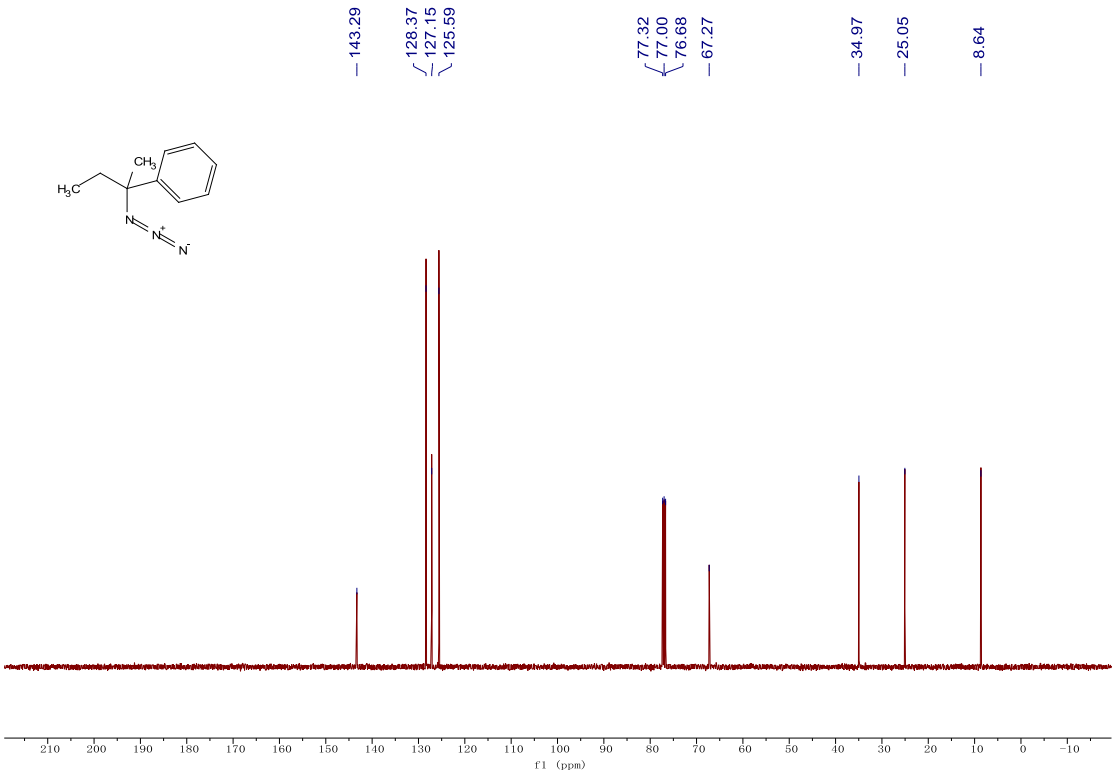
4-(1-Azido-1-phenylethyl)pyridine (1x)



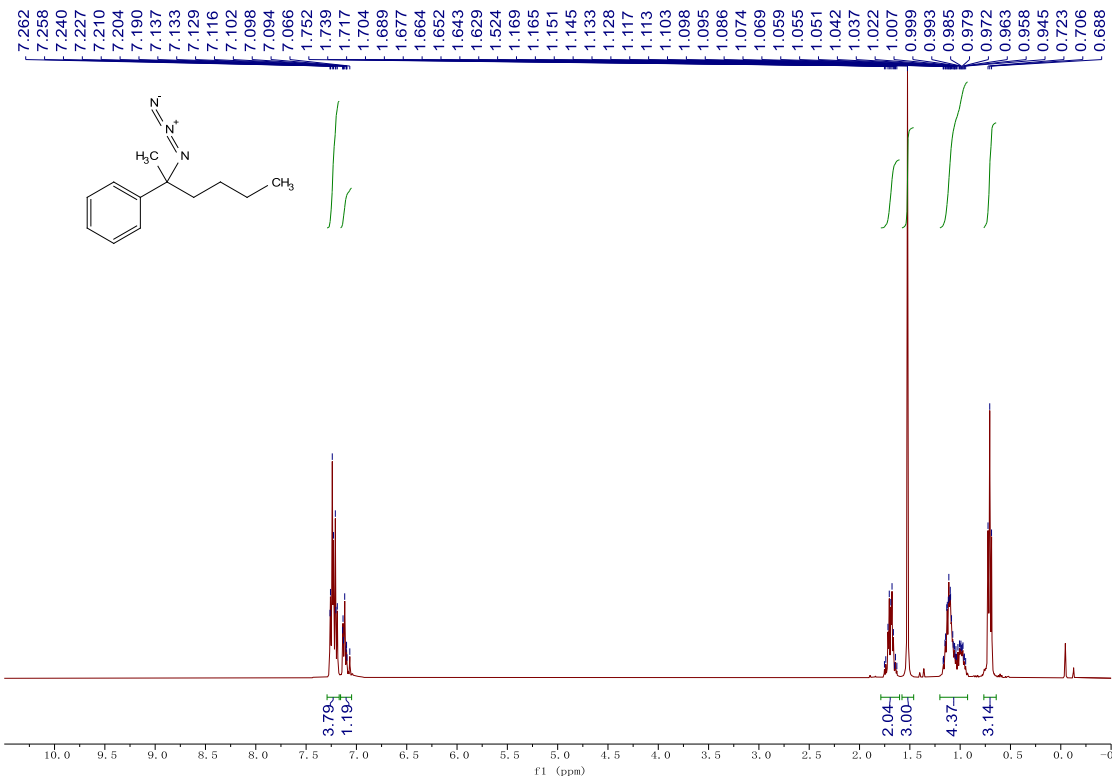


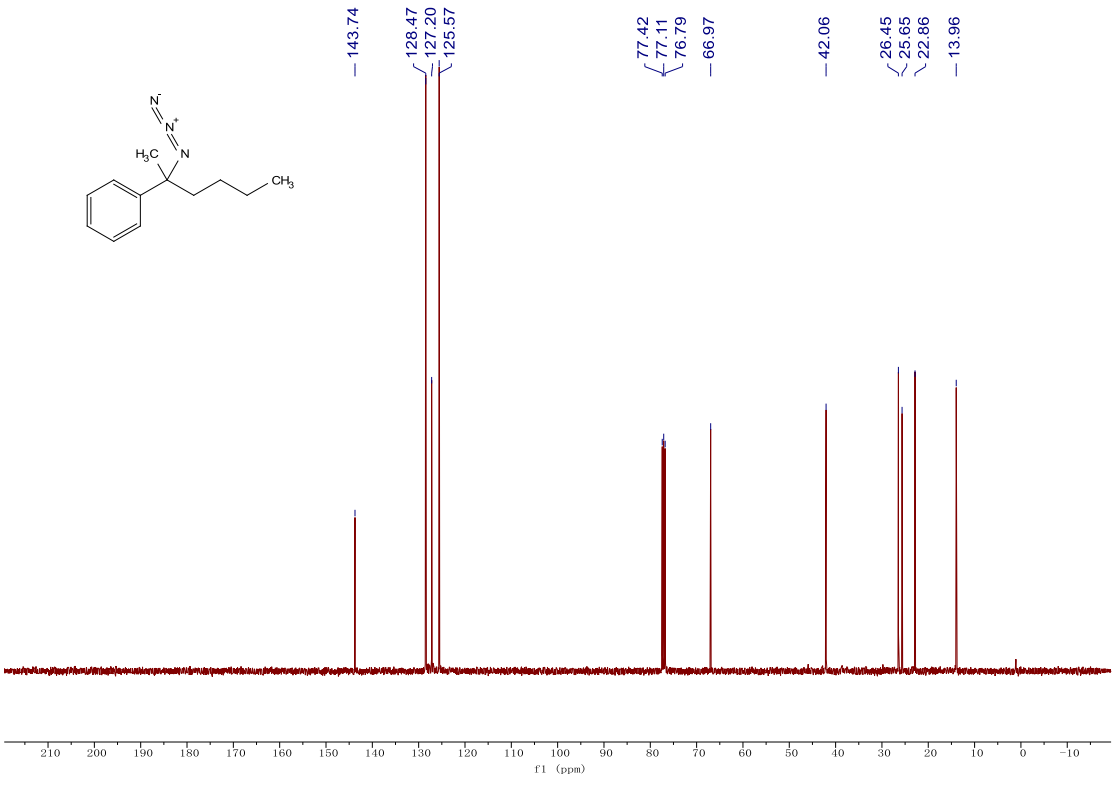
(2-Azidobutan-2-yl)benzene (1y)



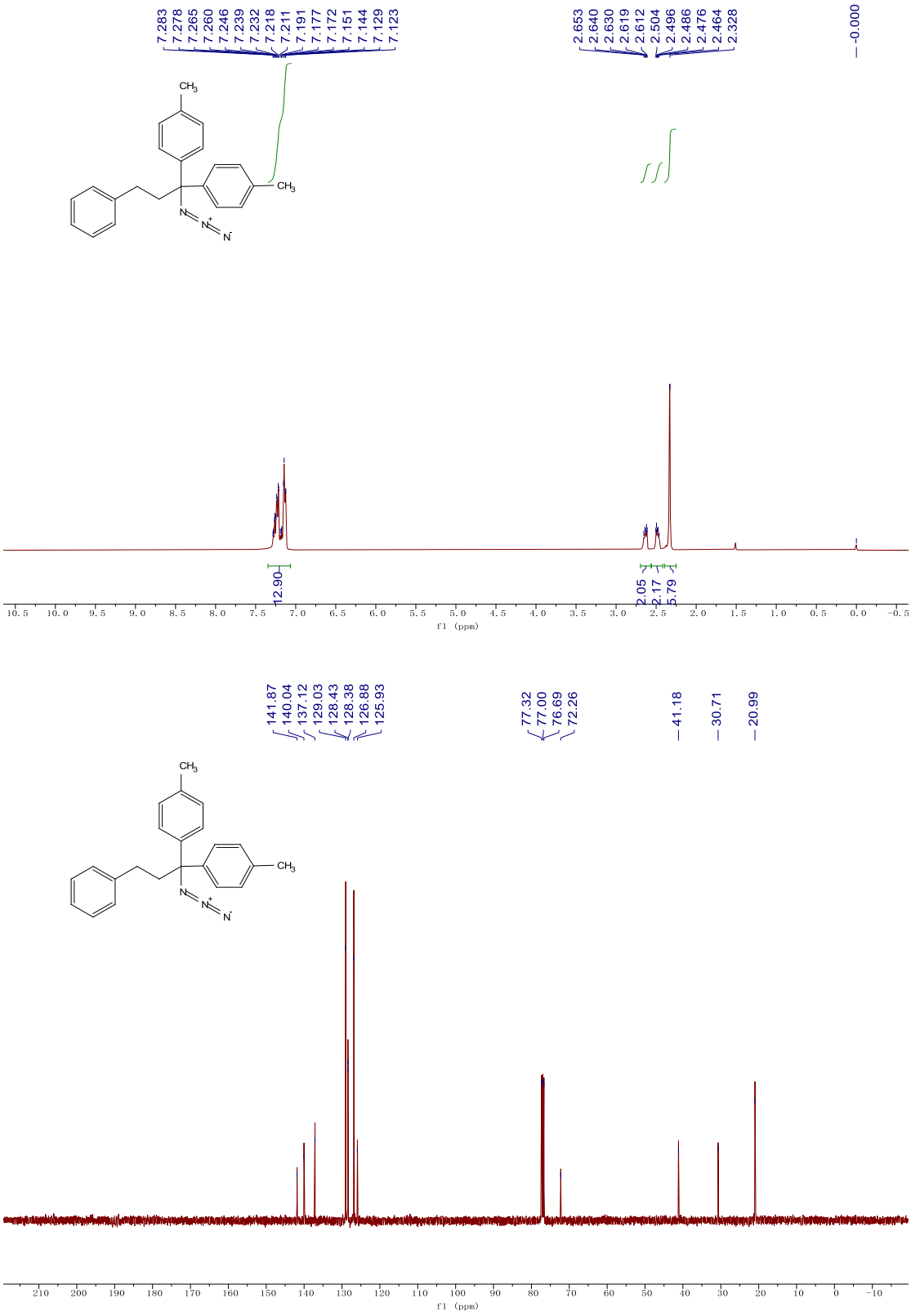


(2-Azidohexan-2-yl)benzene (1z)

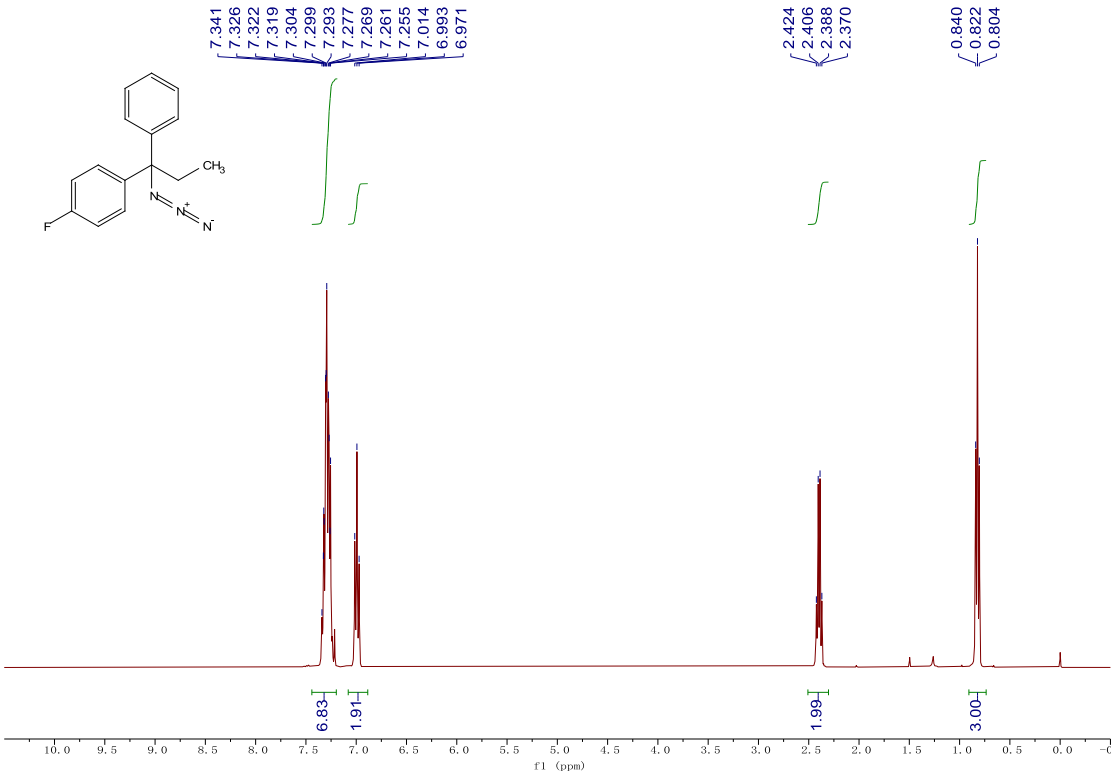


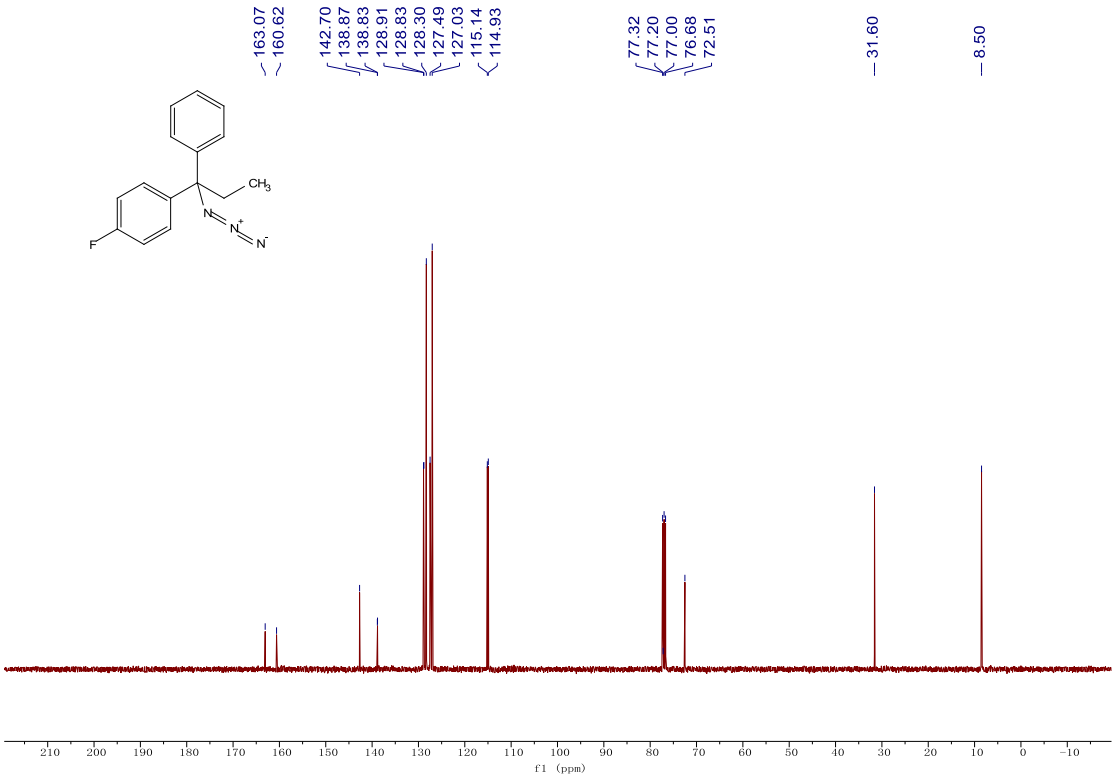


4,4'-(1-Azido-3-phenylpropane-1,1-diyl)bis(methylbenzene) (1aa)

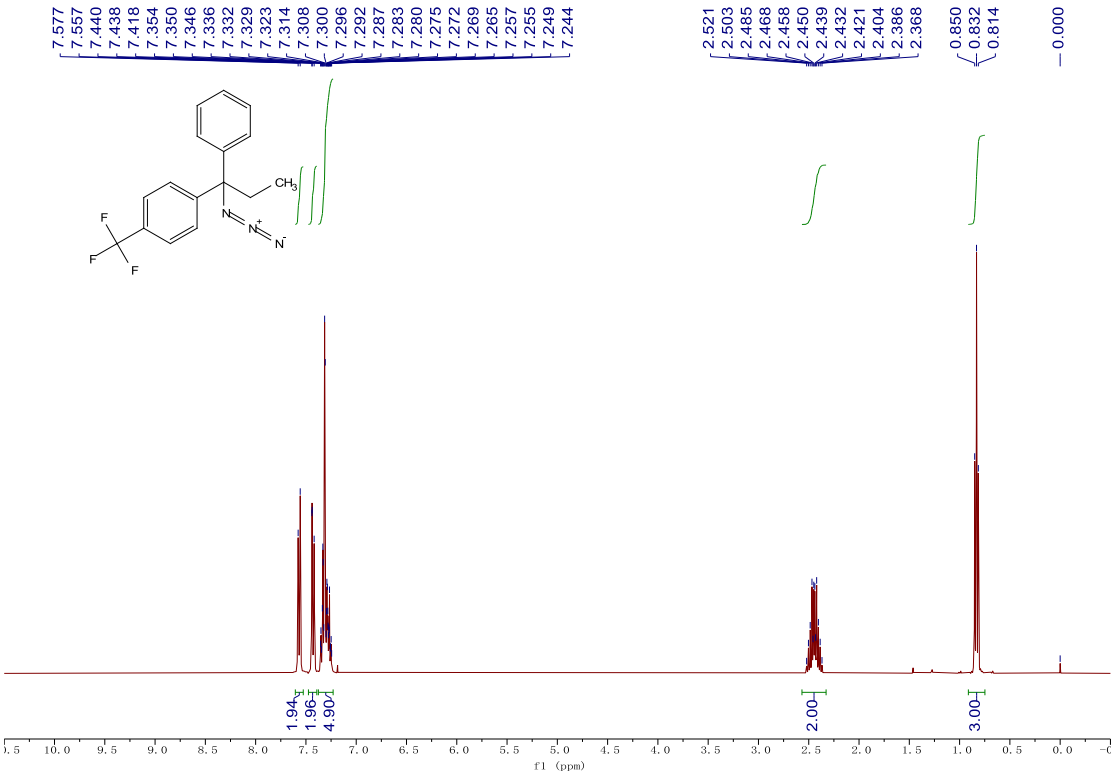


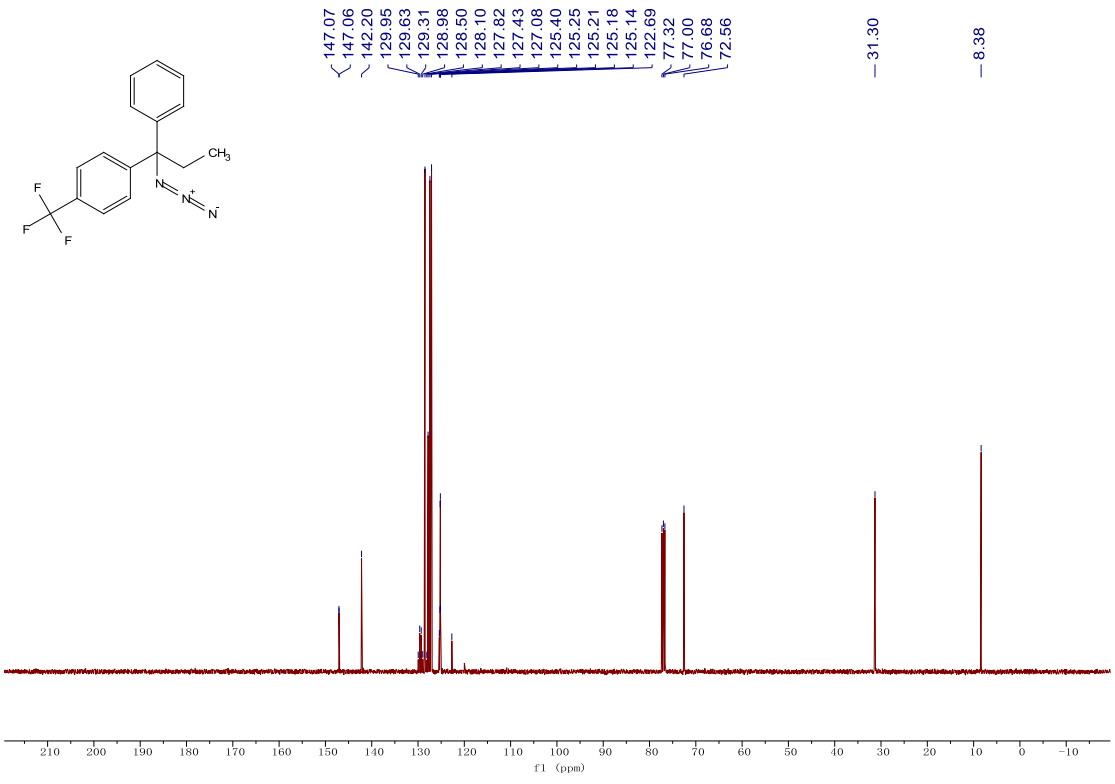
1-(1-Azido-1-phenylpropyl)-4-fluorobenzene (3a)



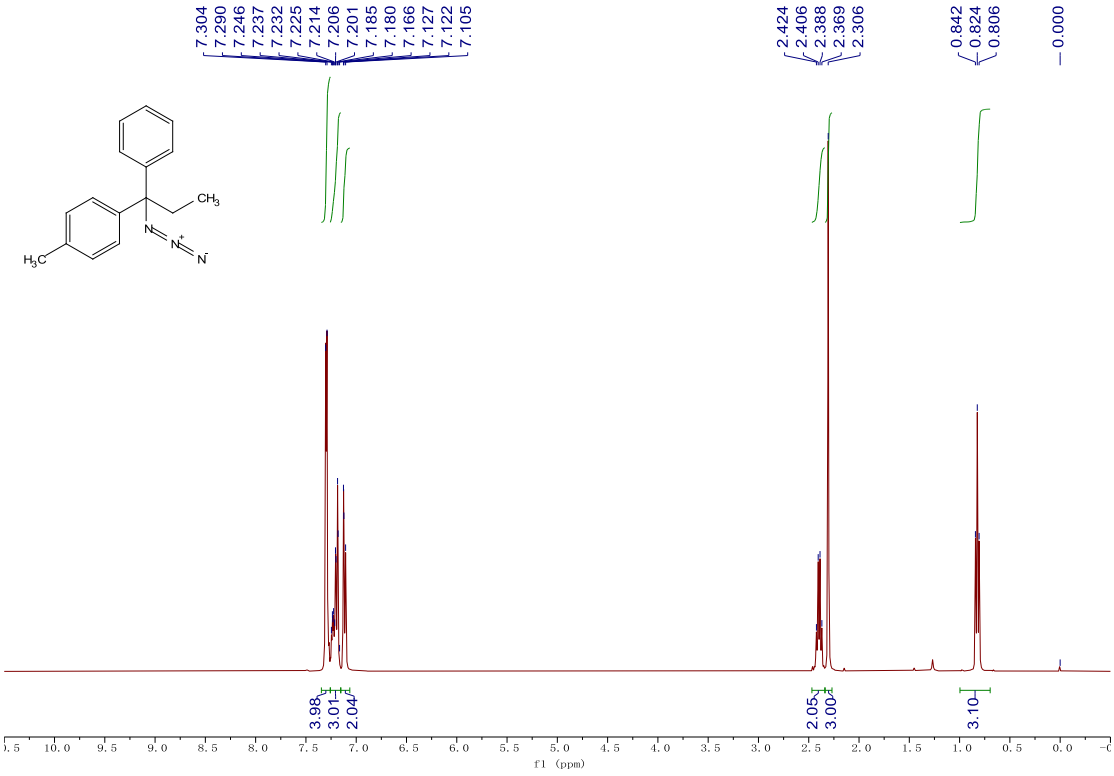


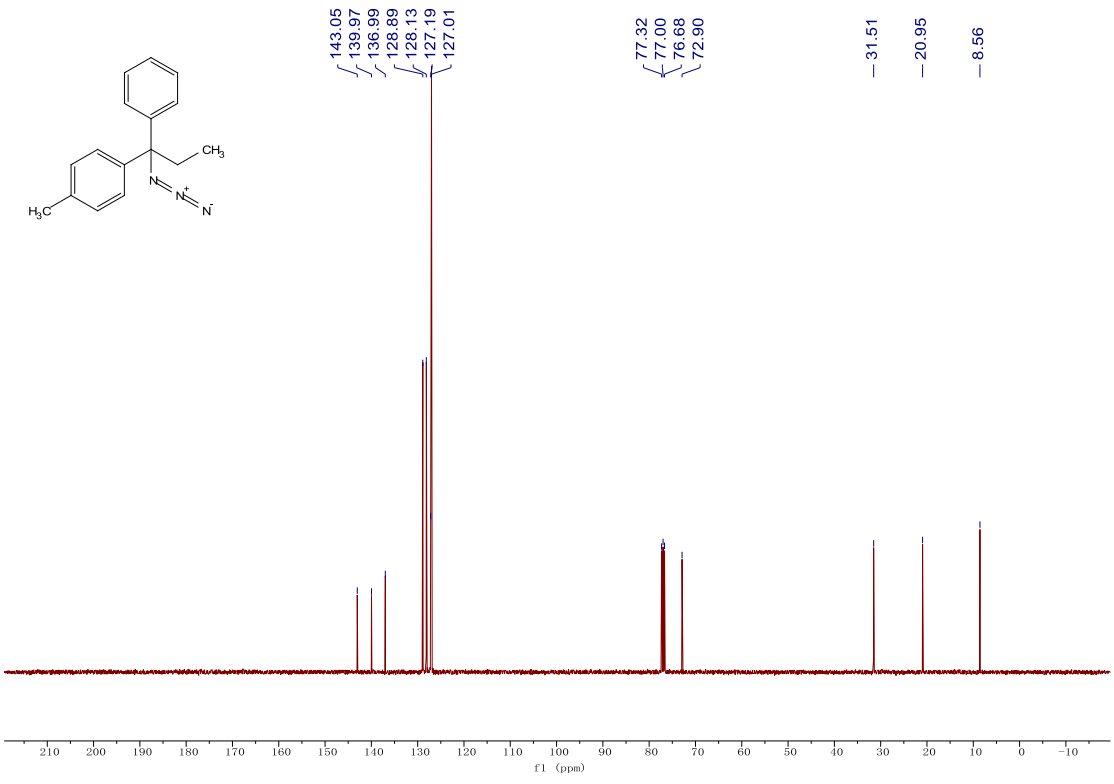
(S)-1-(1-Azido-1-phenylpropyl)-4-(trifluoromethyl)benzene (3b)



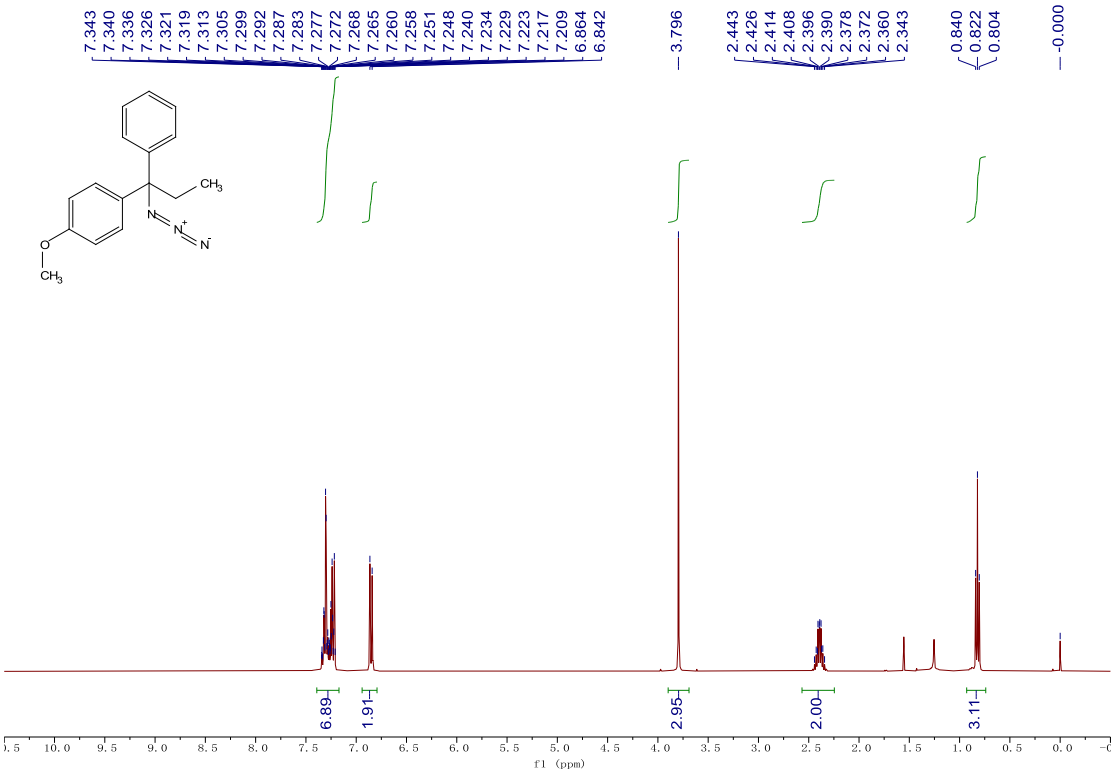


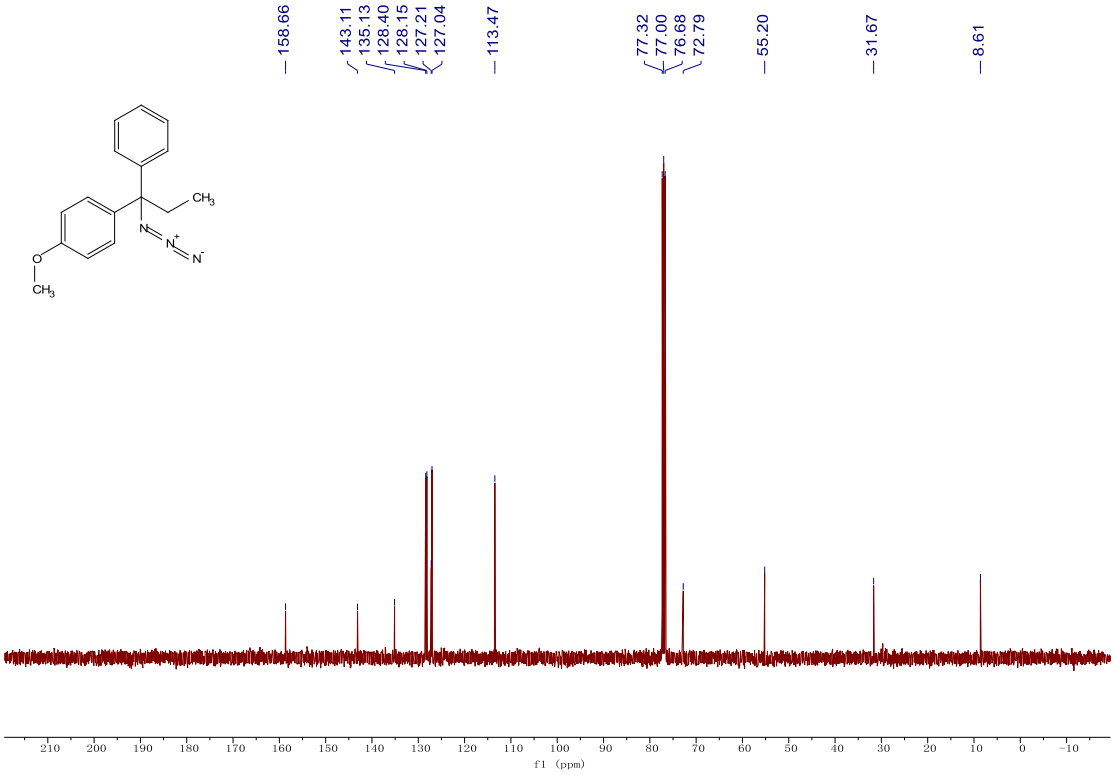
(S)-1-(1-Azido-1-phenylpropyl)-4-methylbenzene (3c)



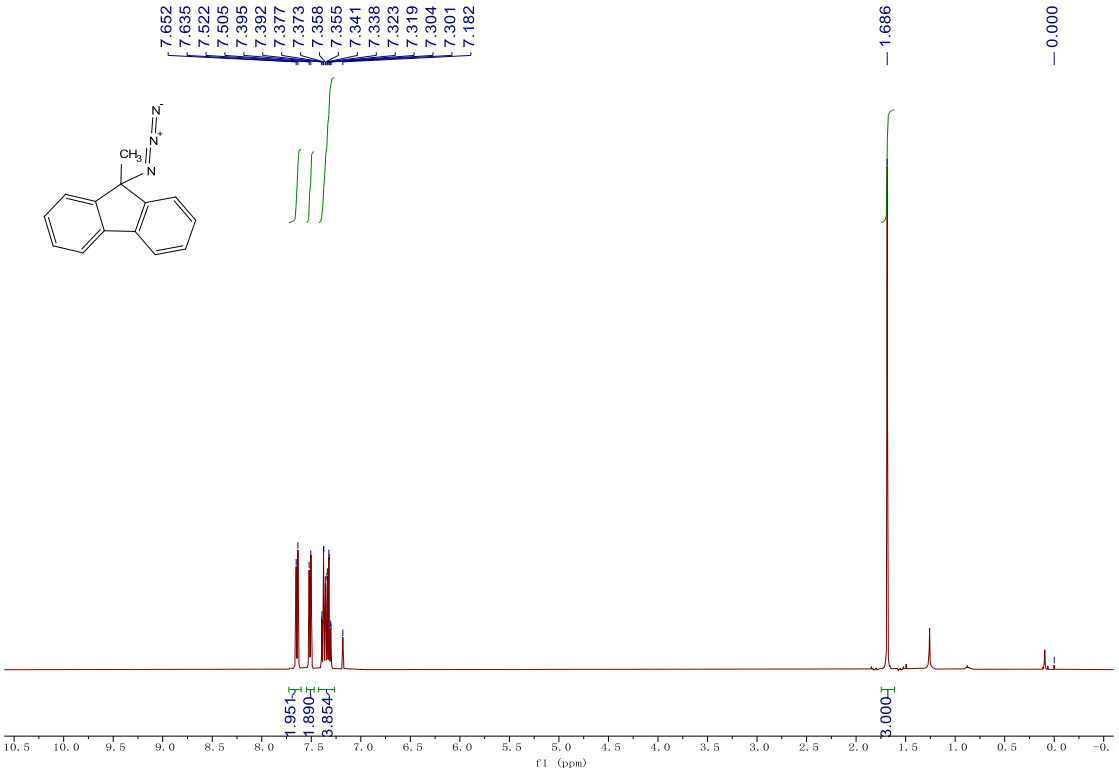


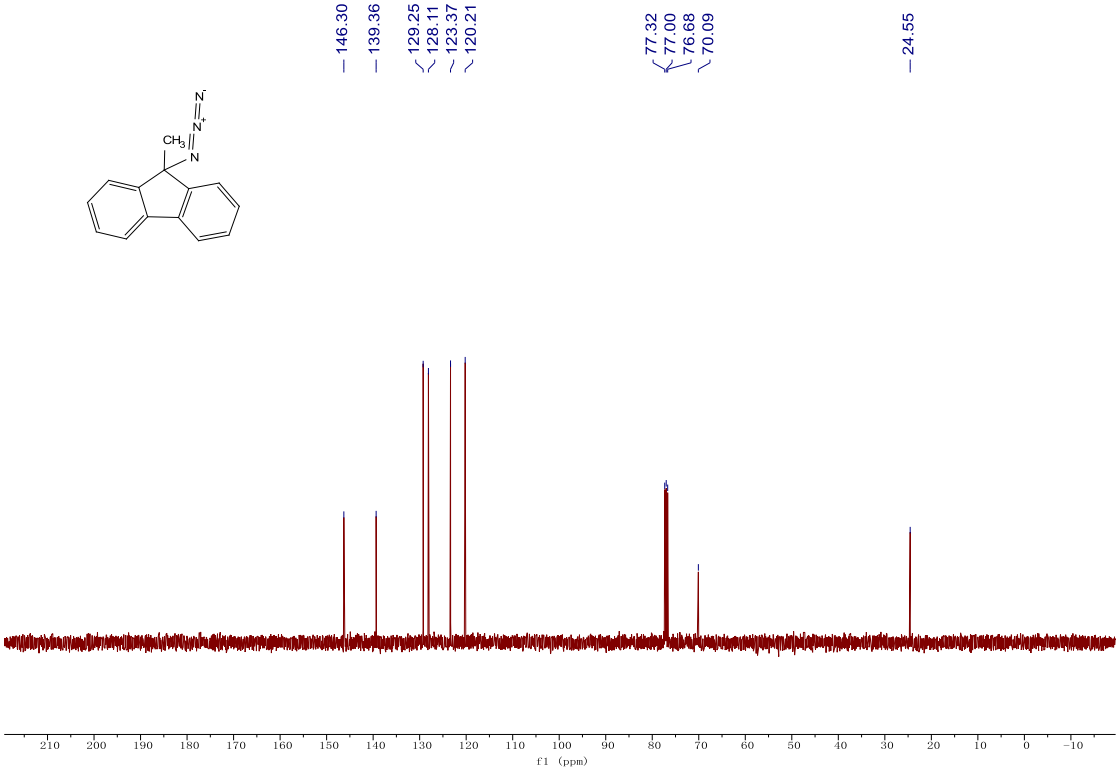
(S)-1-(1-Azido-1-phenylpropyl)-4-methoxybenzene (3d)



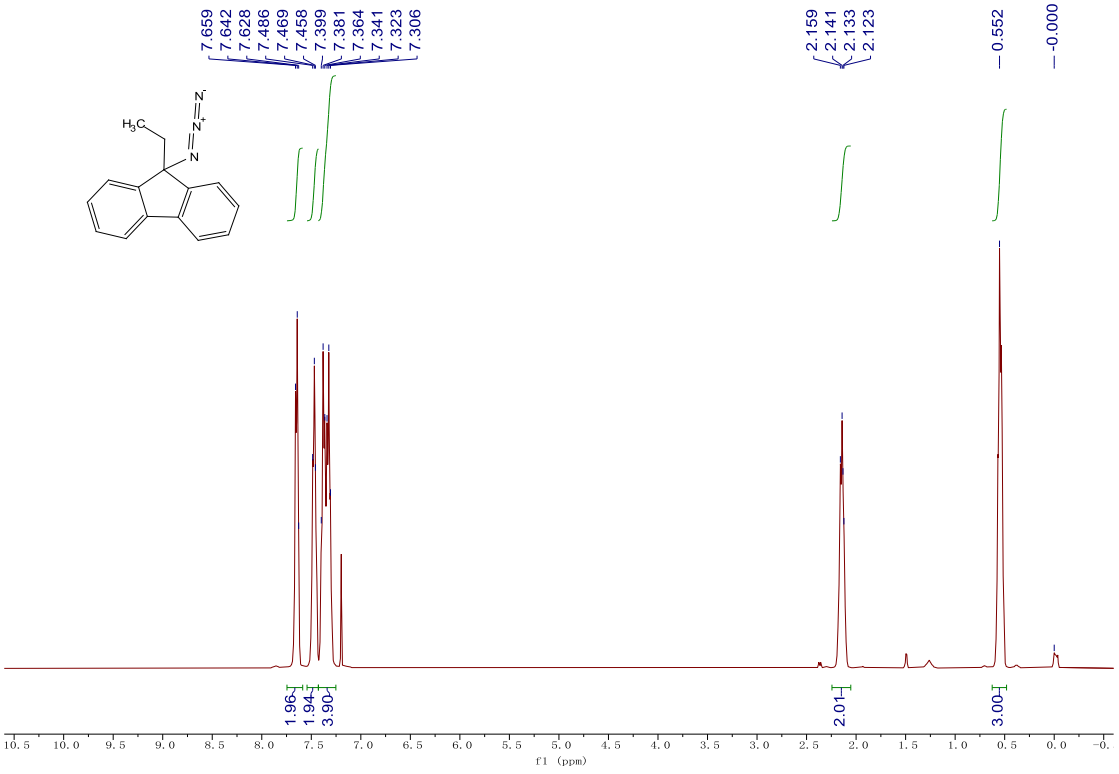


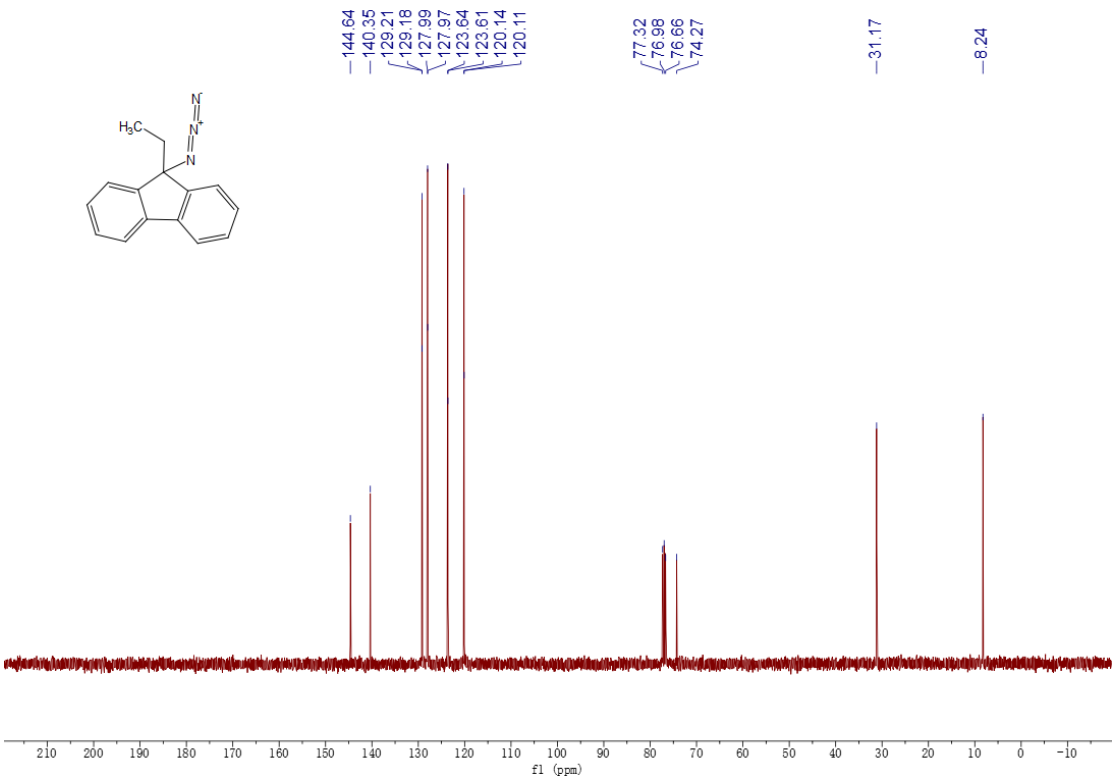
9-Azido-9-methyl-9H-fluorene (6a)



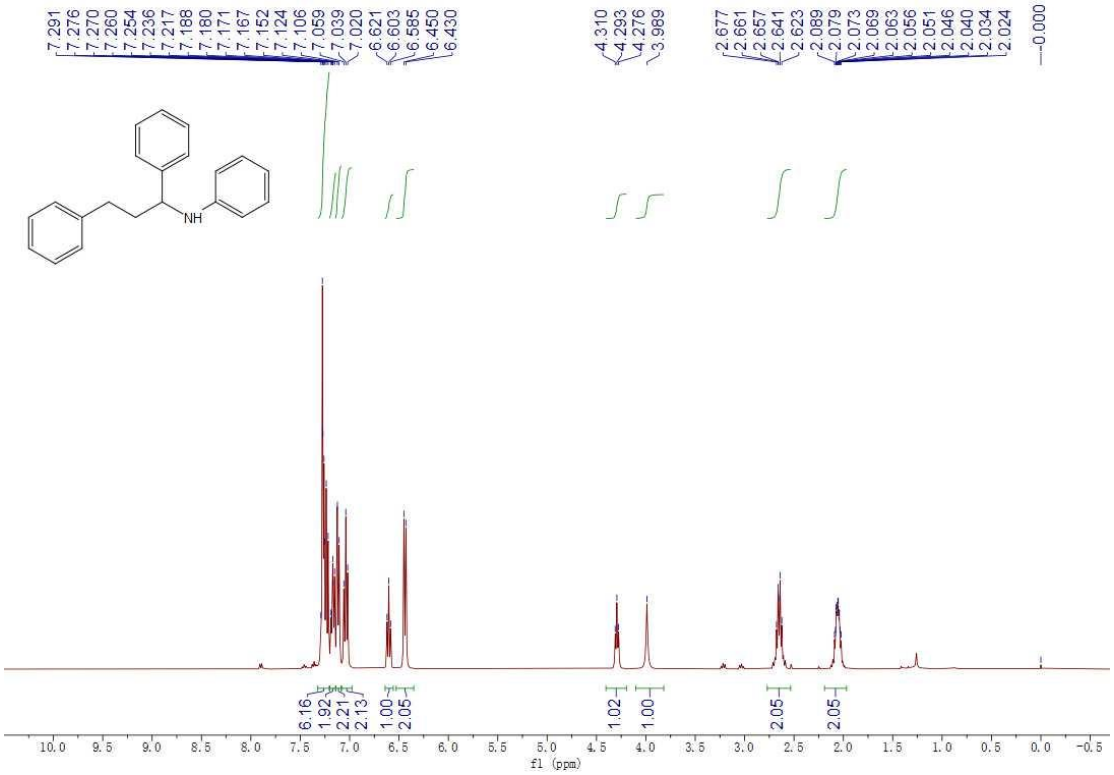


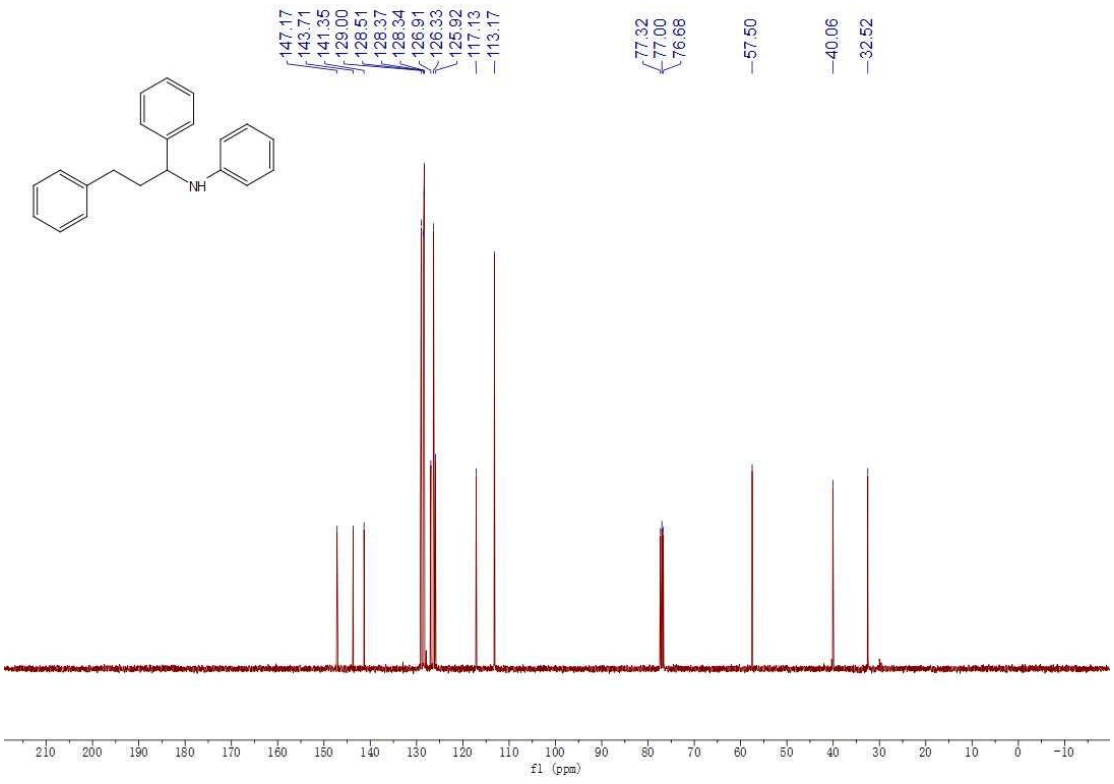
9-Azido-9-ethyl-9H-fluorene (6b)



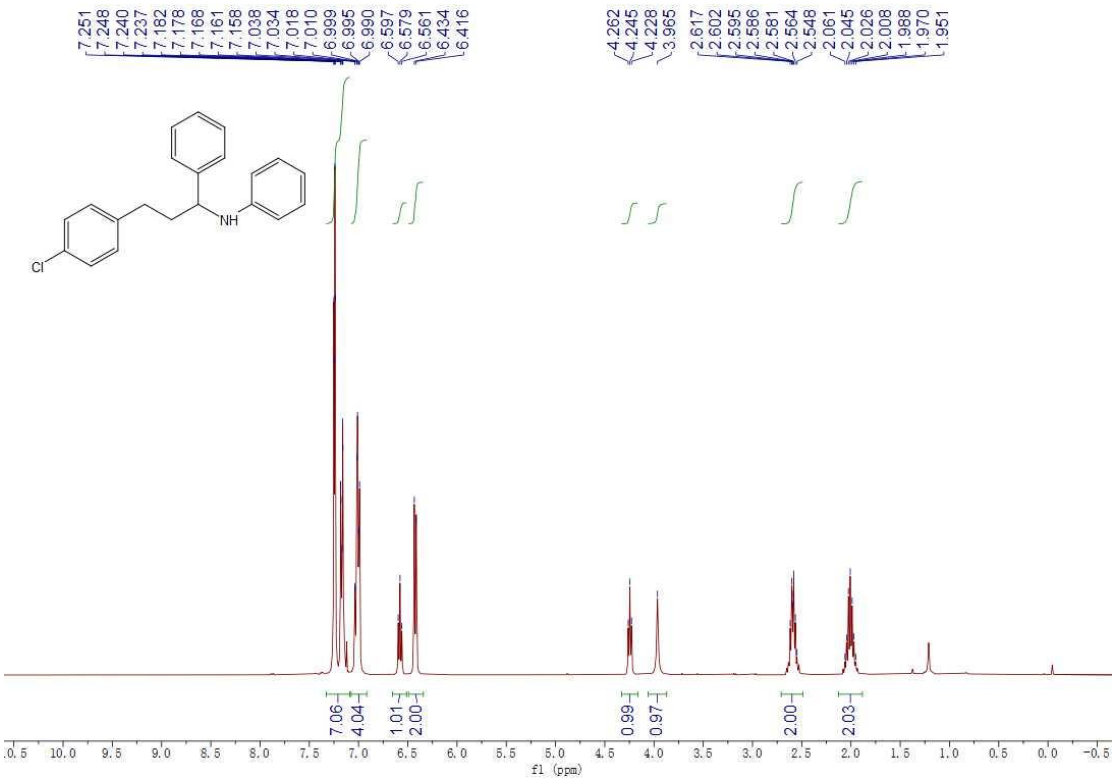


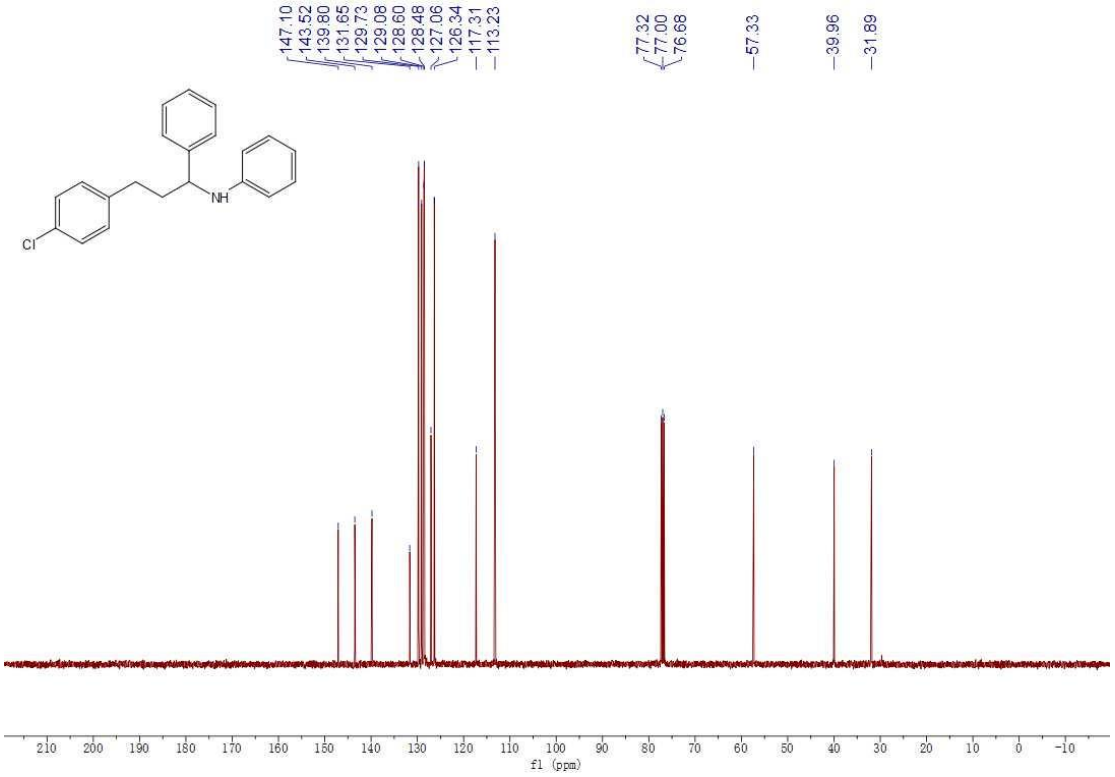
N-(1,3-Diphenylpropyl)aniline (2a)



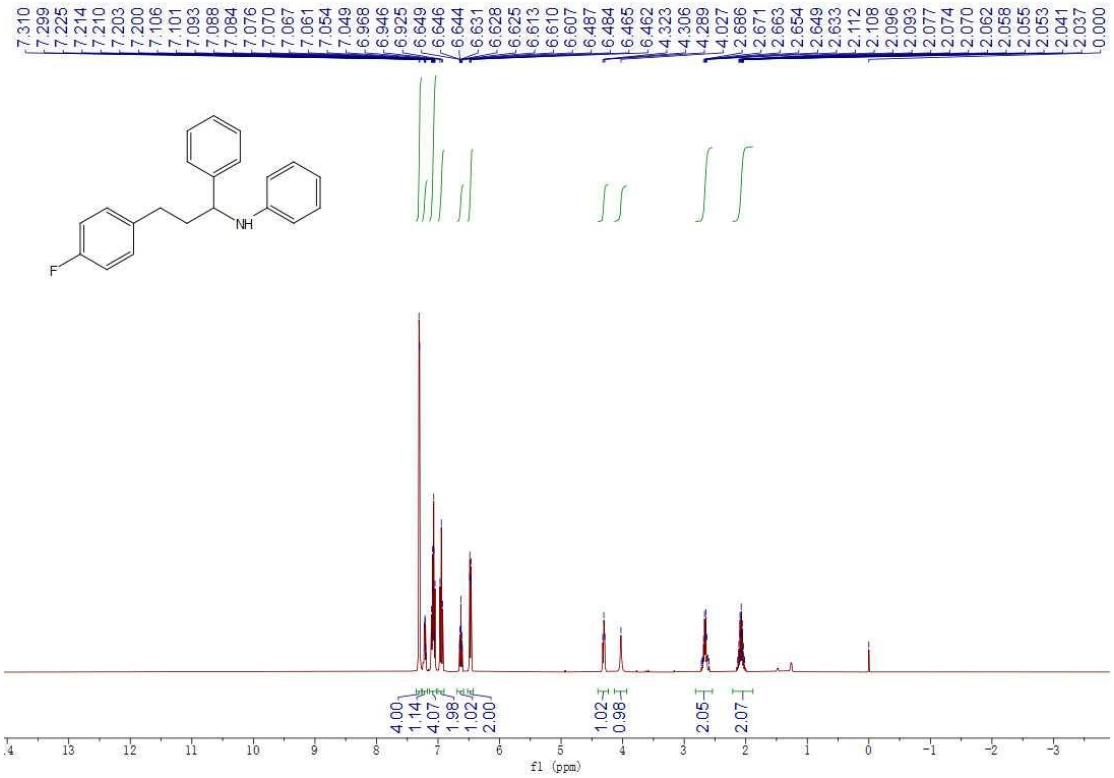


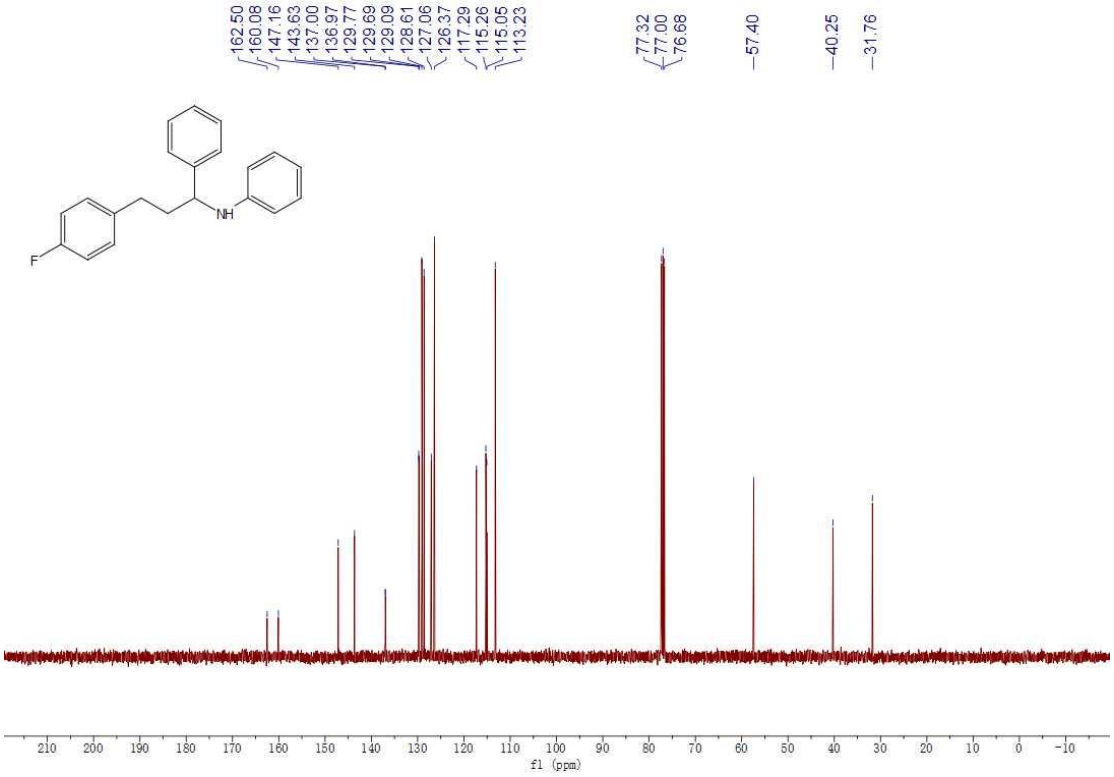
N-(3-(4-Chlorophenyl)-1-phenylpropyl)aniline (2b)



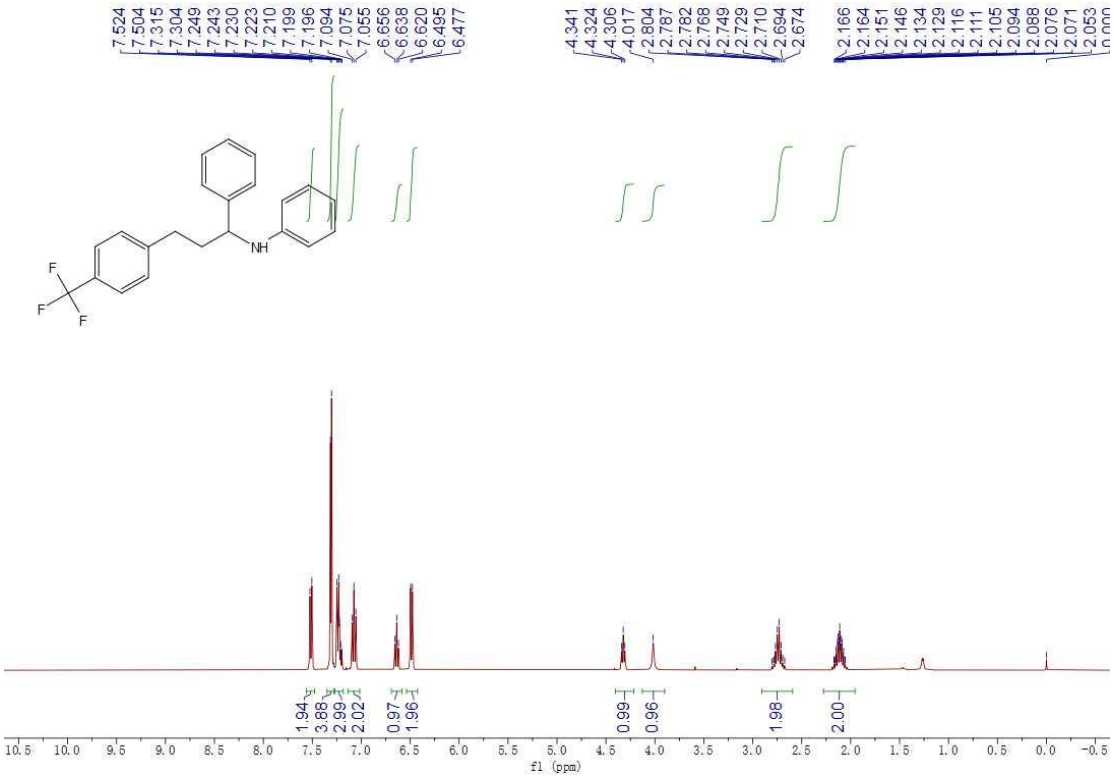


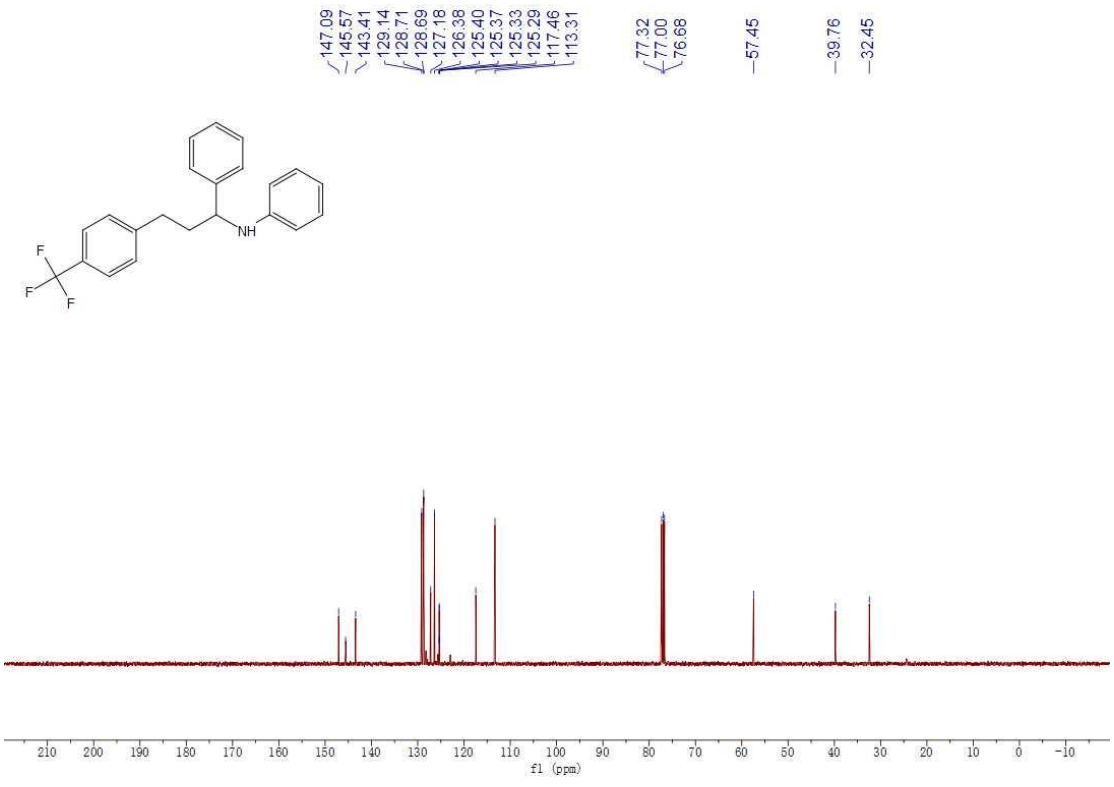
N-(3-(4-Fluorophenyl)-1-phenylpropyl)aniline (2c)



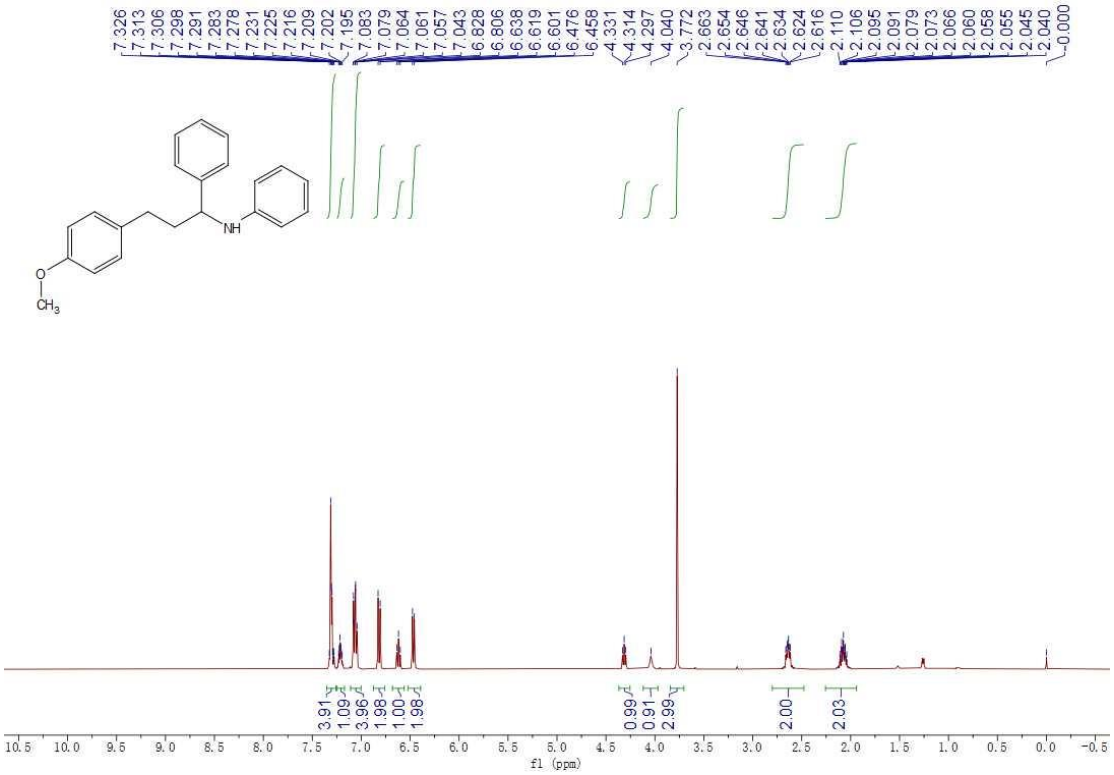


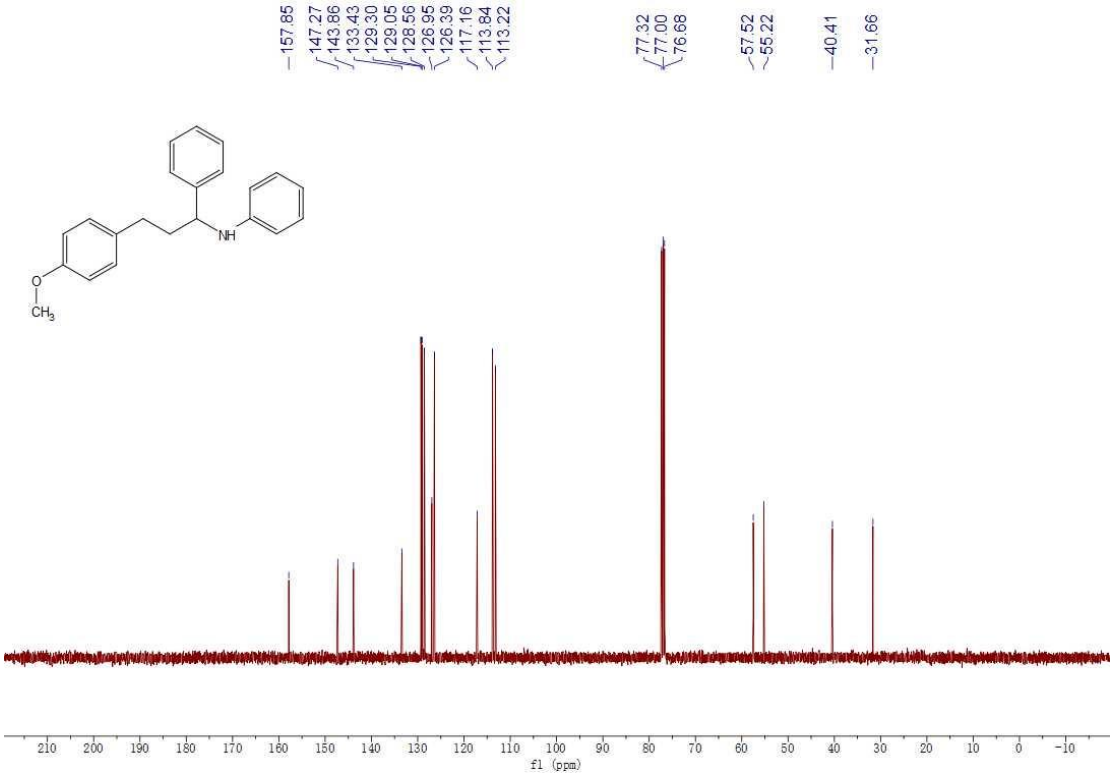
N-(1-Phenyl-3-(4-(trifluoromethyl)phenyl)propyl)aniline (2d)



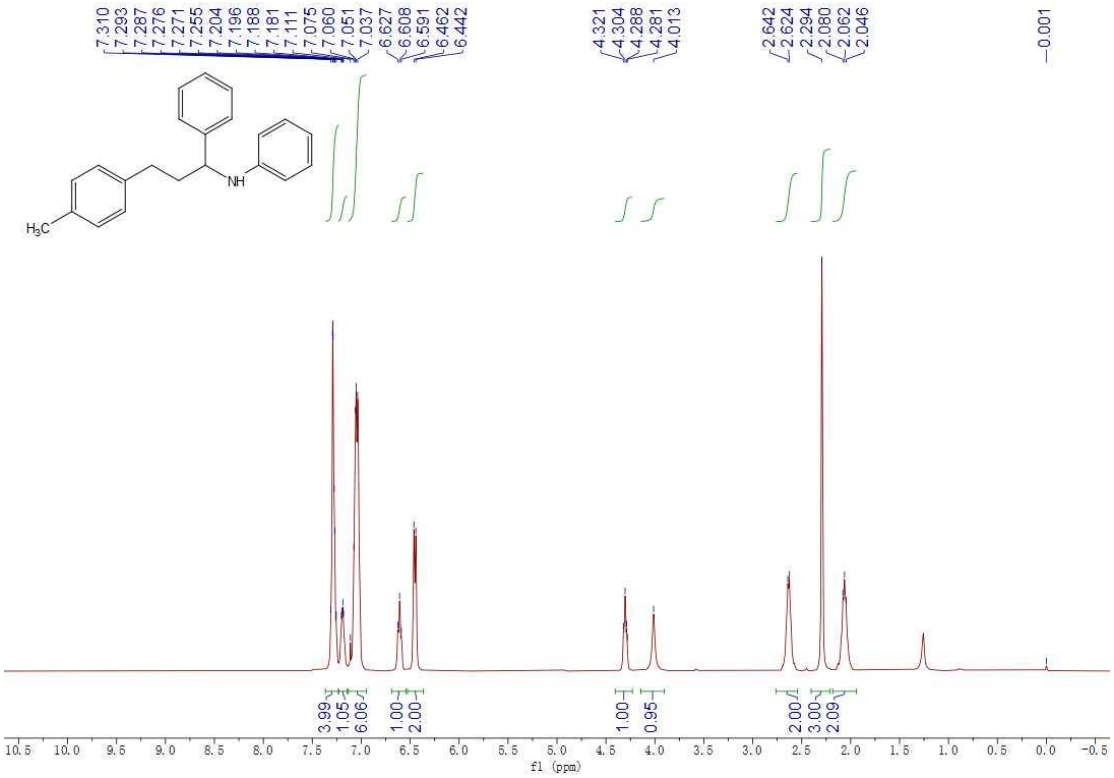


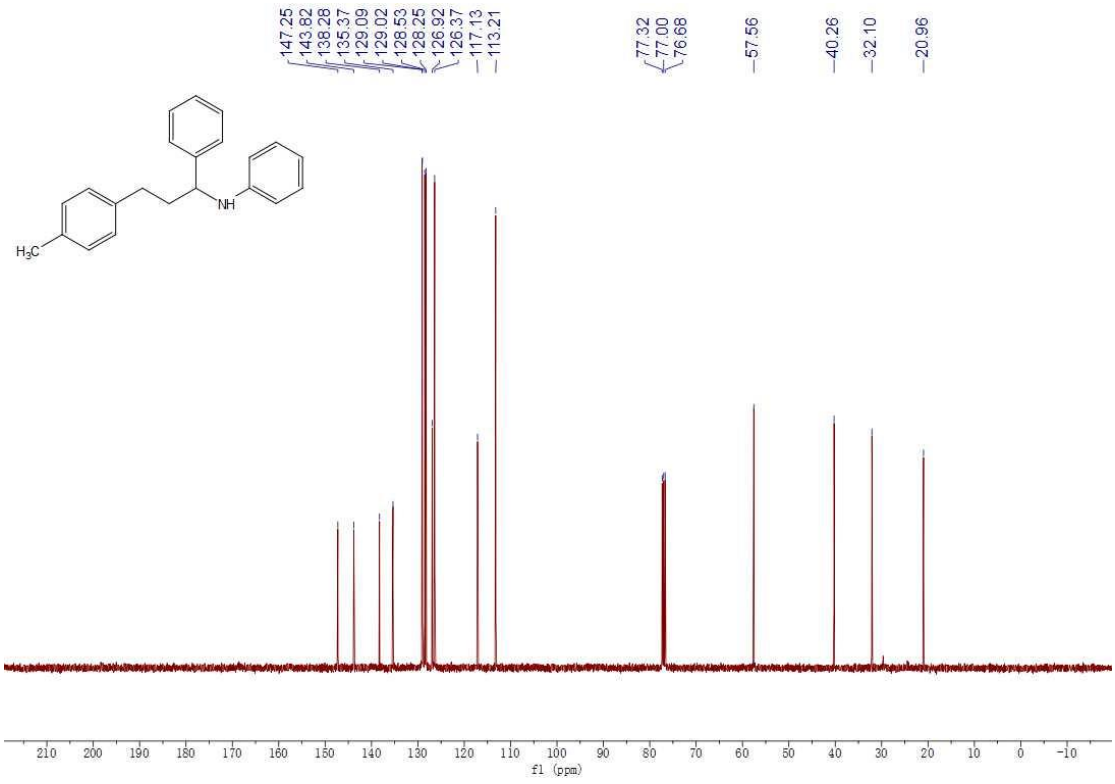
N-(3-(4-Methoxyphenyl)-1-phenylpropyl)aniline (2e)



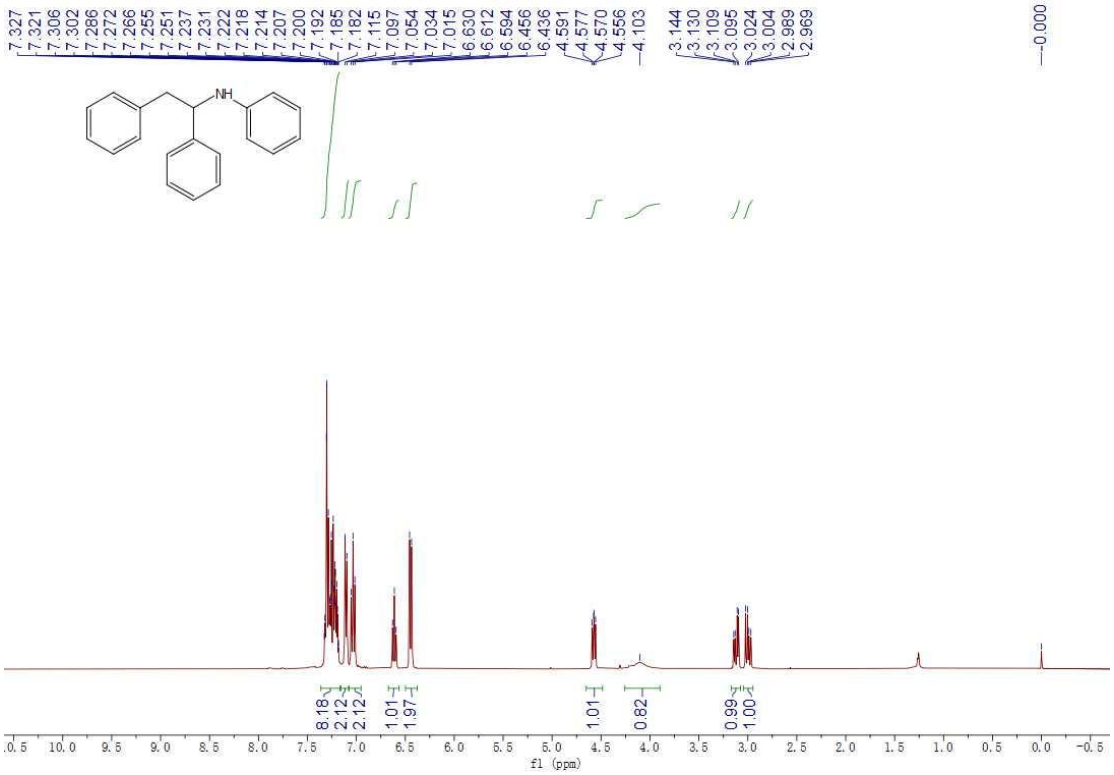


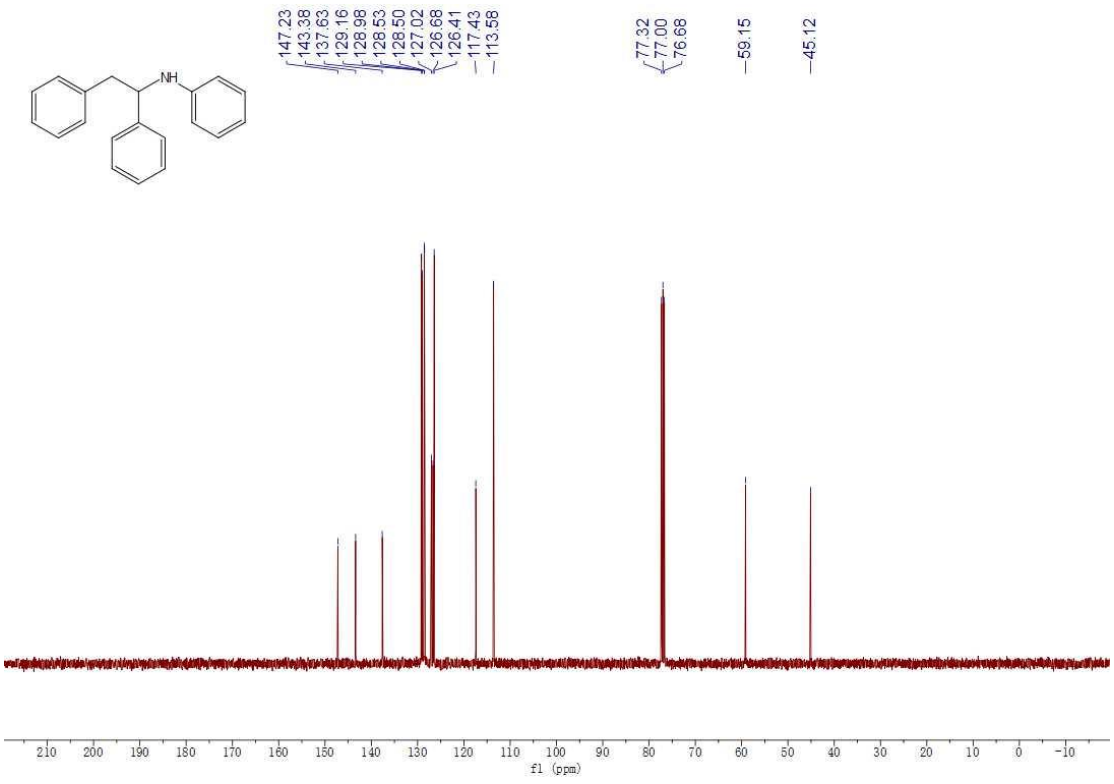
N-(1-Phenyl-3-(p-tolyl)propyl)aniline (2f)



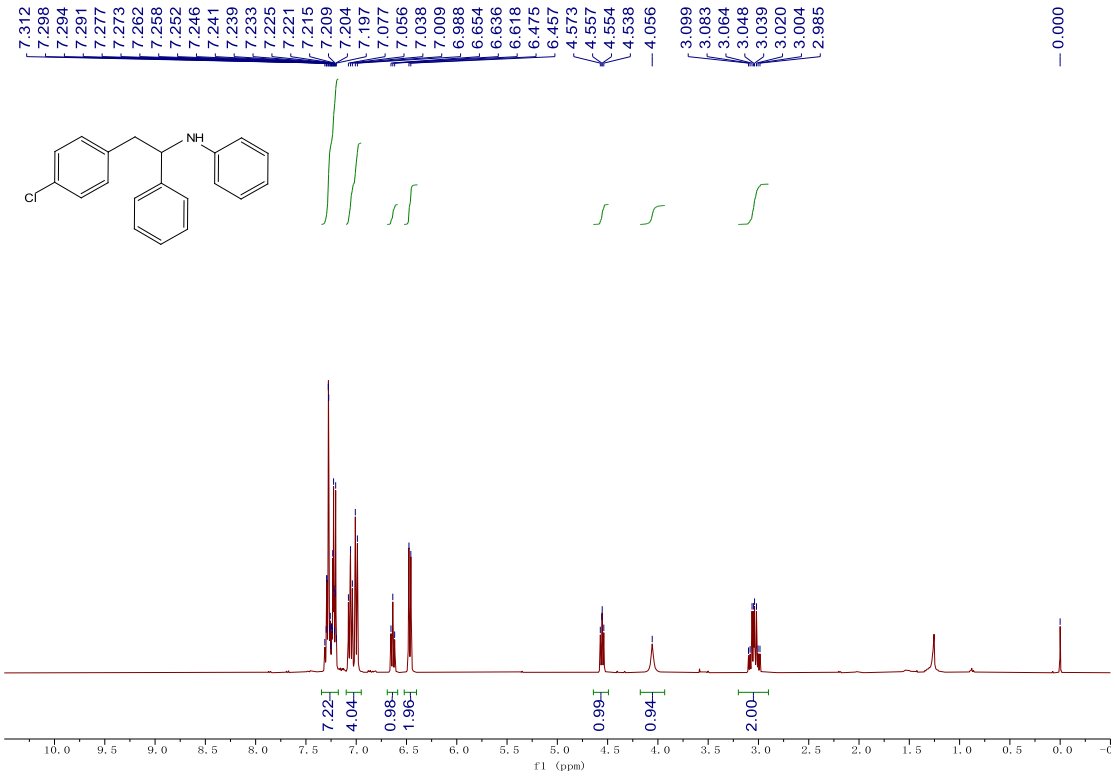


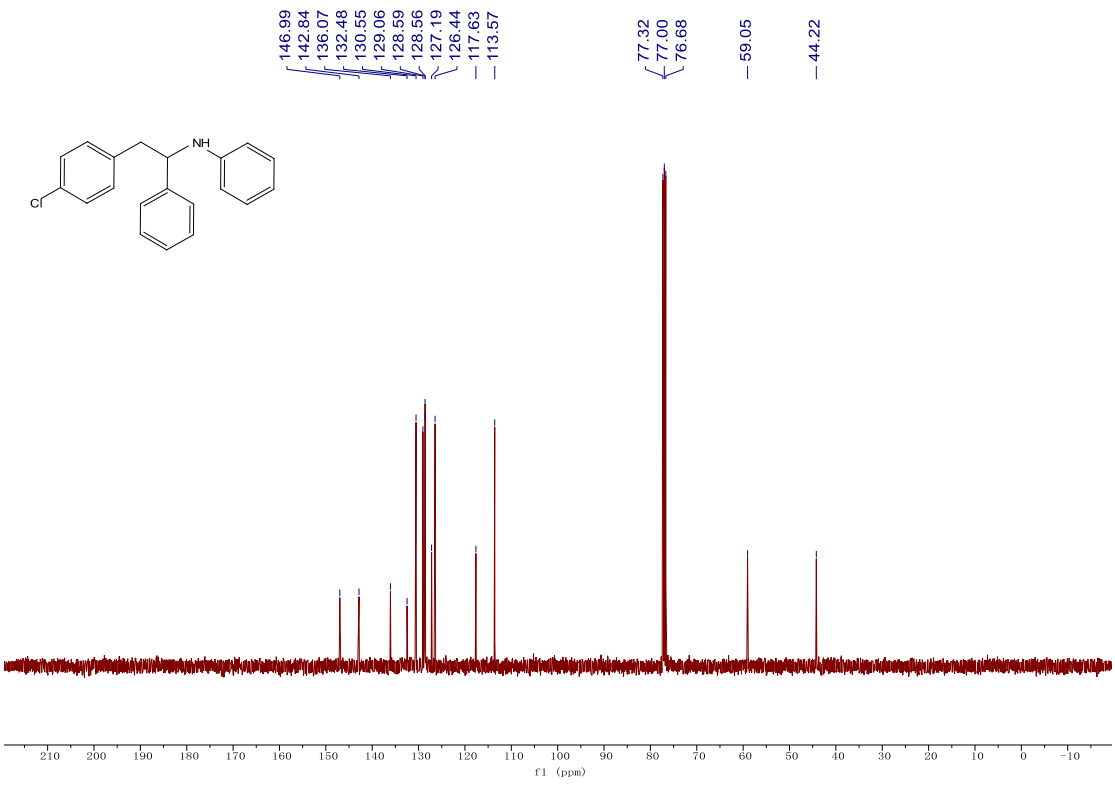
N-(1,2-Diphenylethyl)aniline (2g)



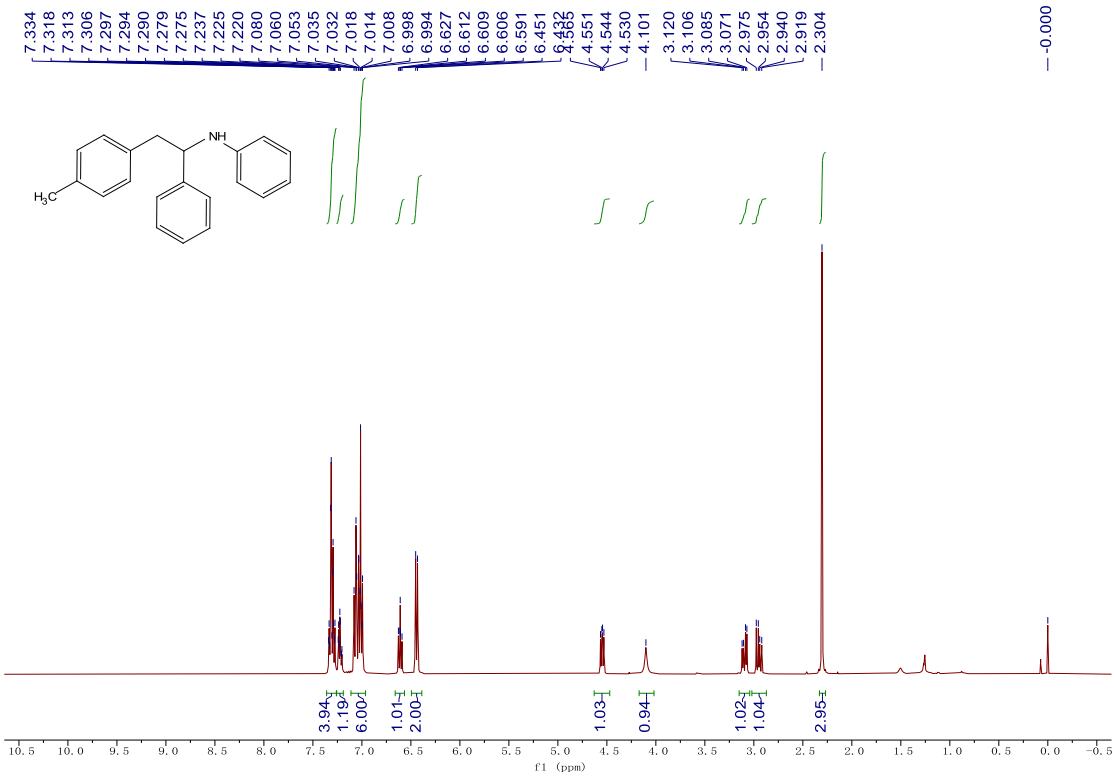


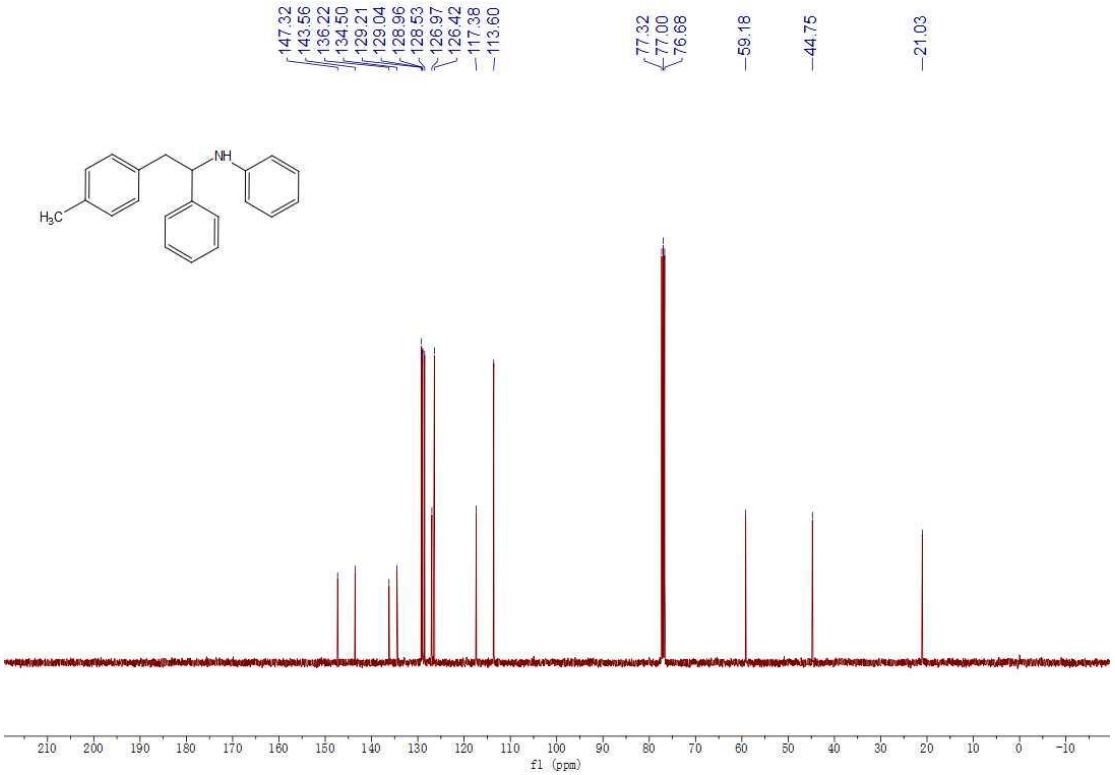
N-(2-(4-Chlorophenyl)-1-phenylethyl)aniline (2h)



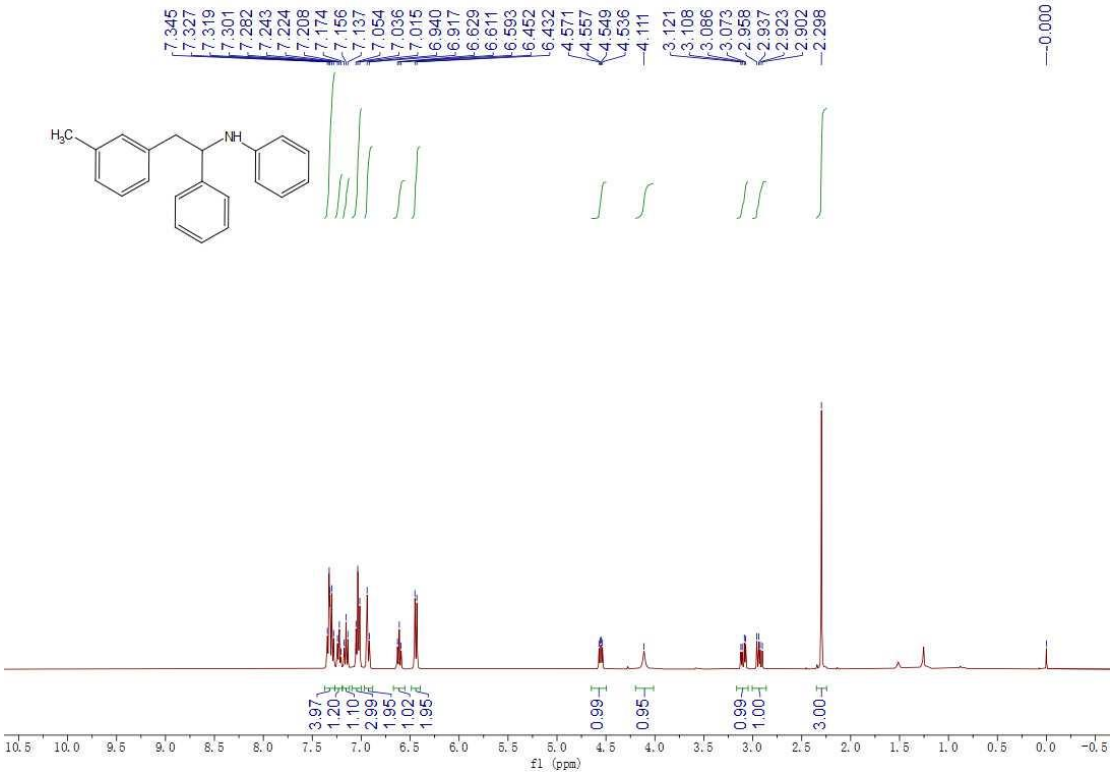


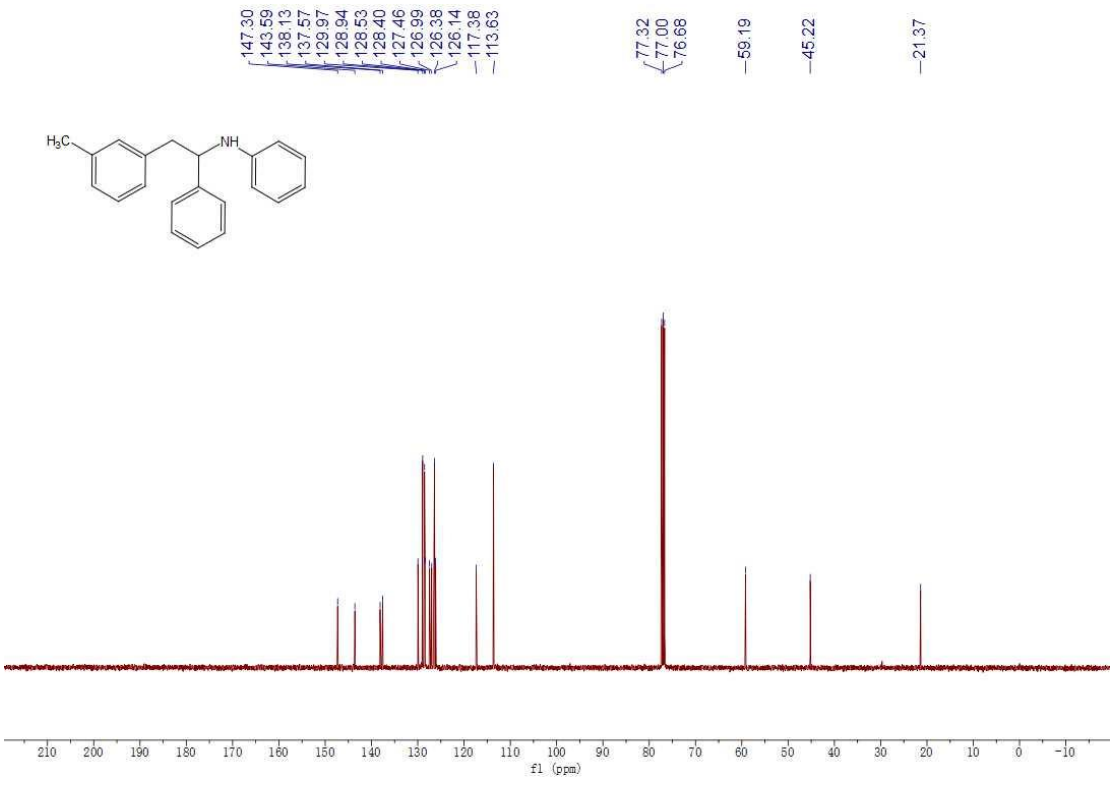
N-(1-Phenyl-2-(p-tolyl)ethyl)aniline (2i)



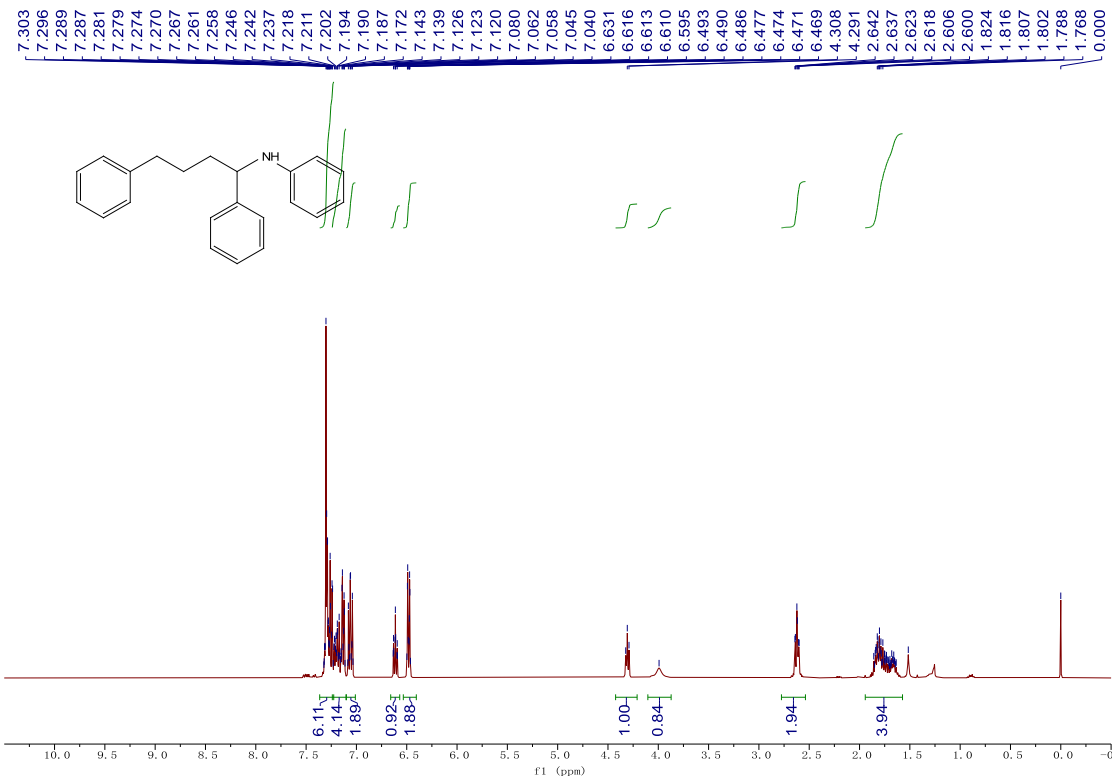


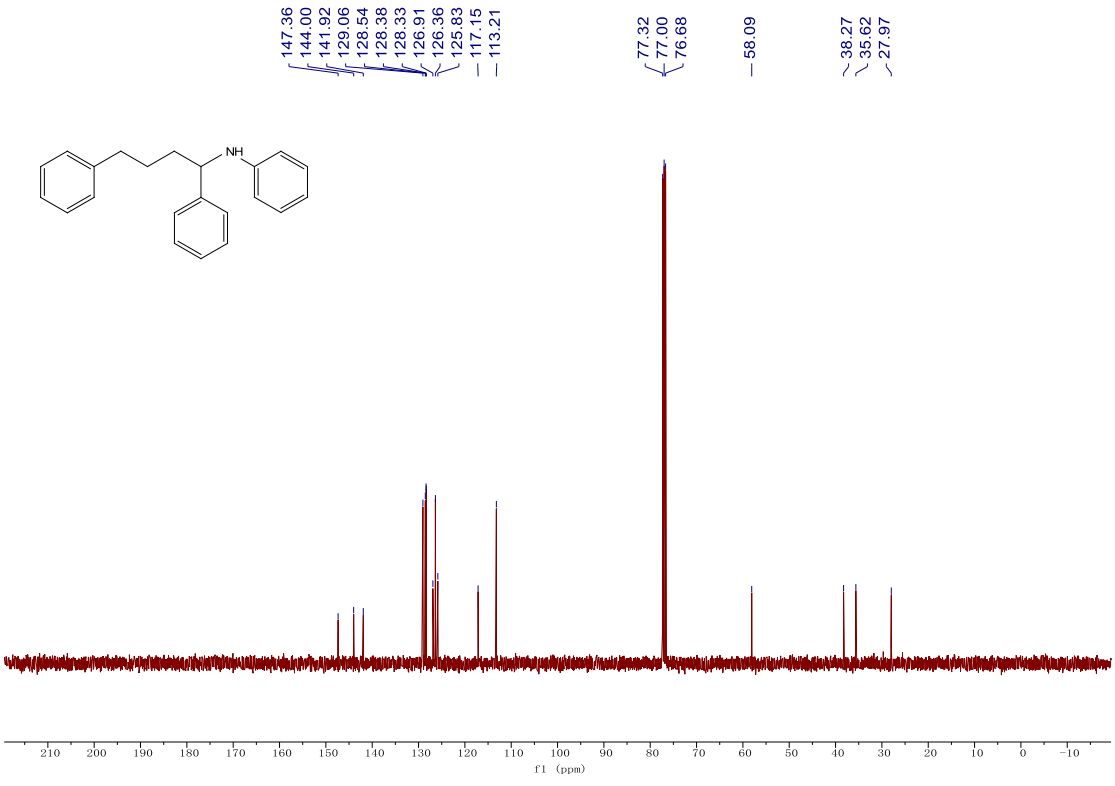
N-(1Phenyl-2-(m-tolyl)ethyl)aniline (2j)



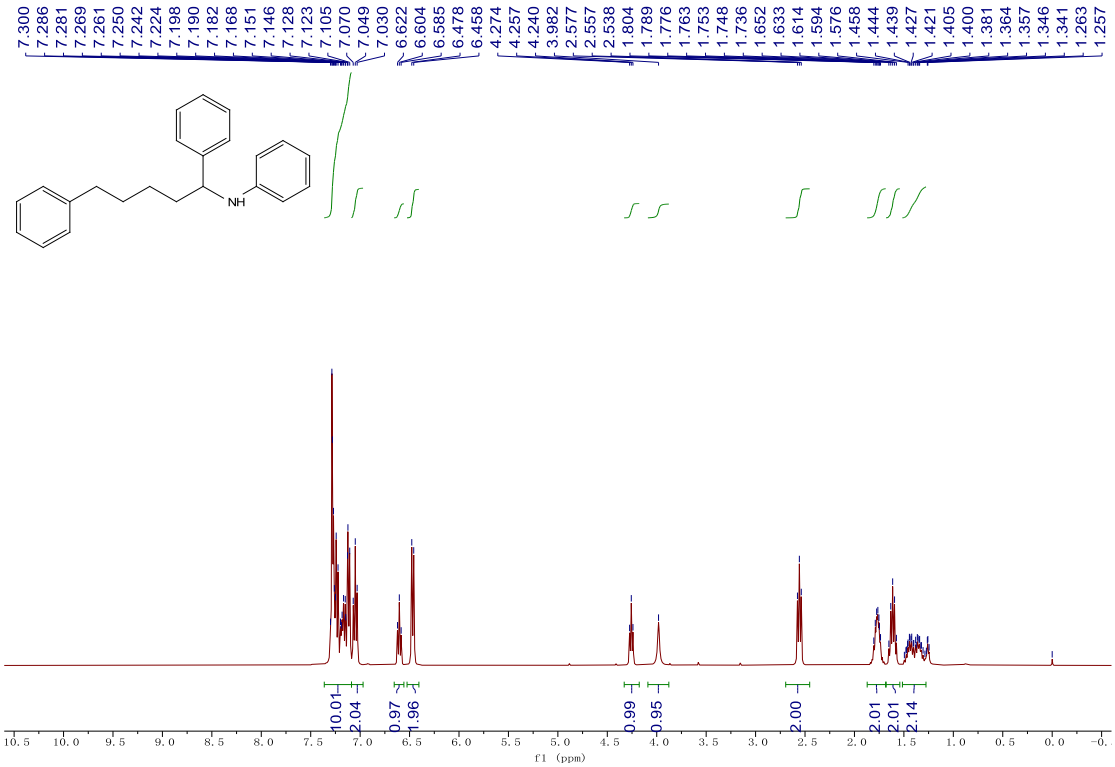


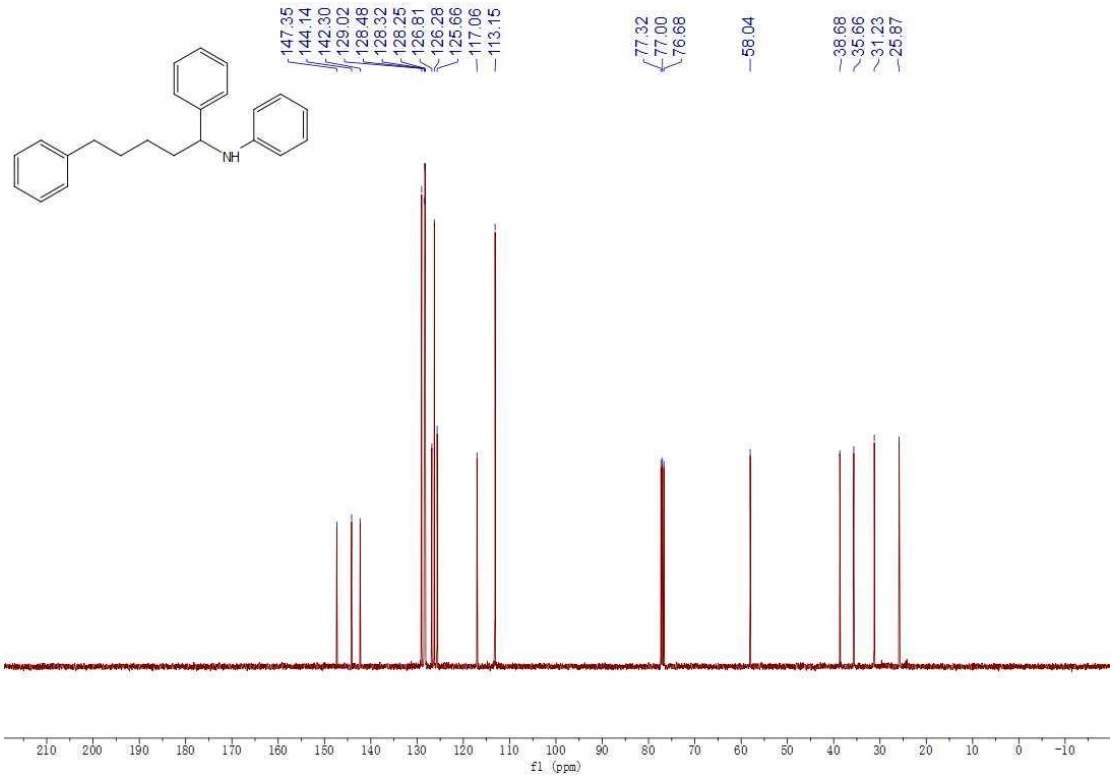
N-(1,4-Diphenylbutyl)aniline (2k)



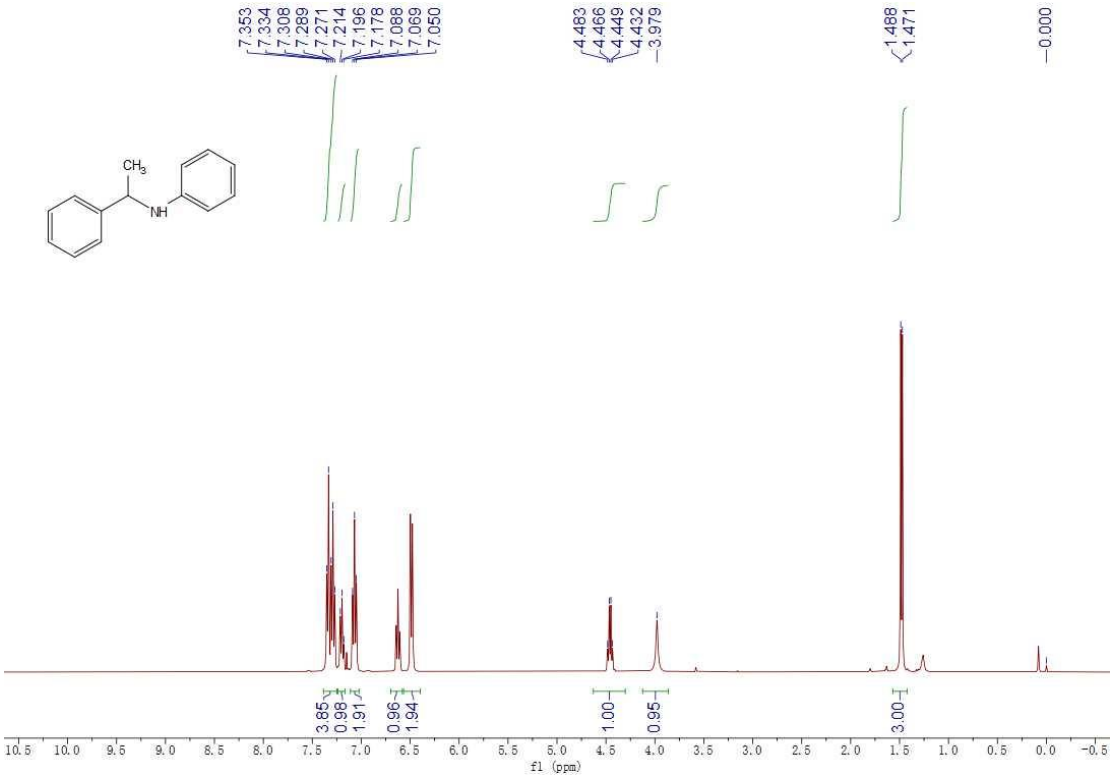


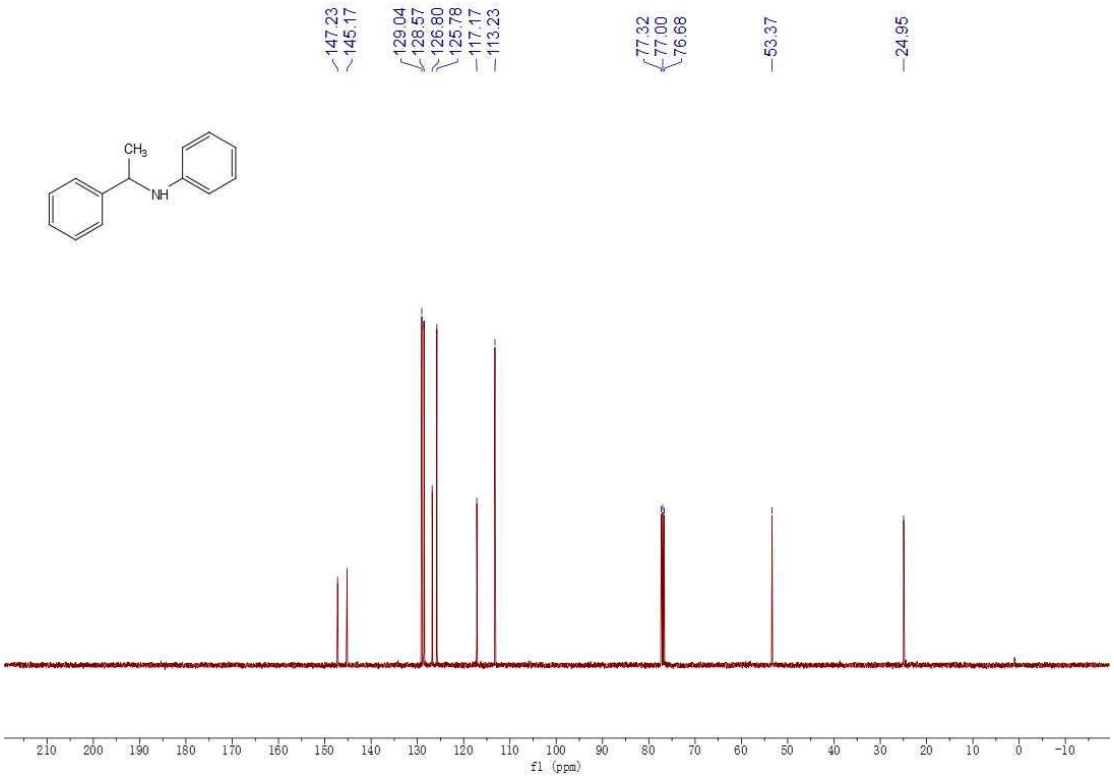
N-(1,5-Diphenylpentyl)aniline (2l)



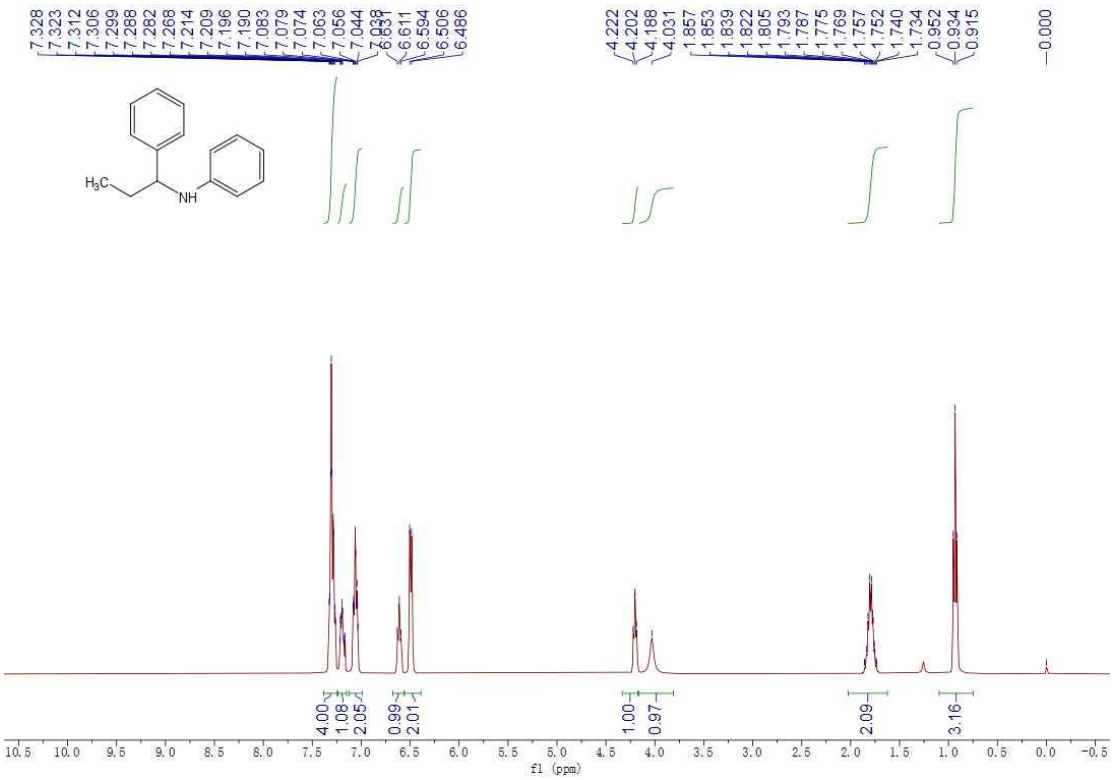


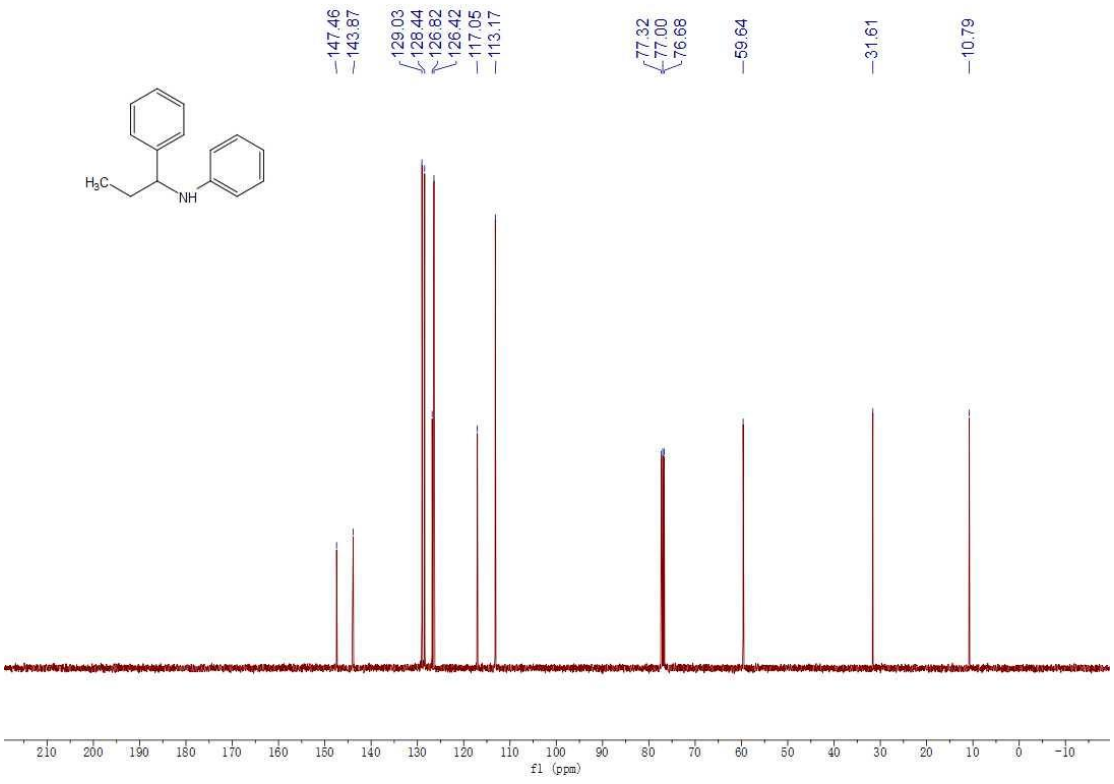
N-(1-Phenylethyl)aniline (2m)



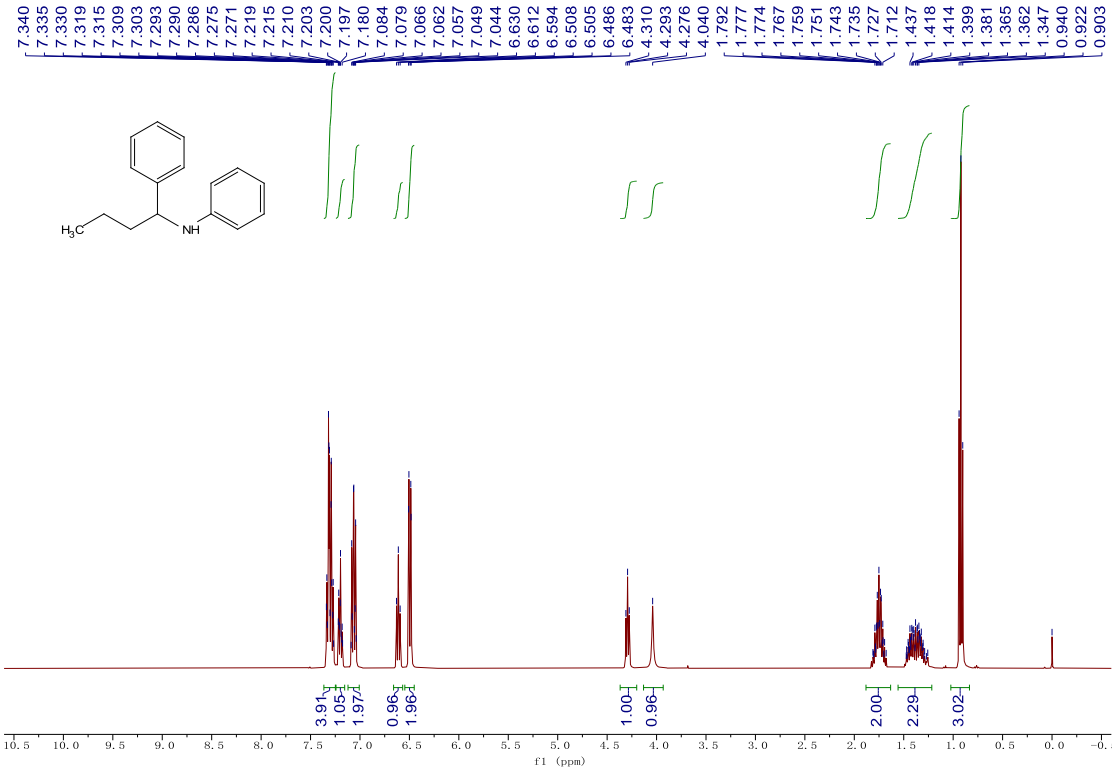


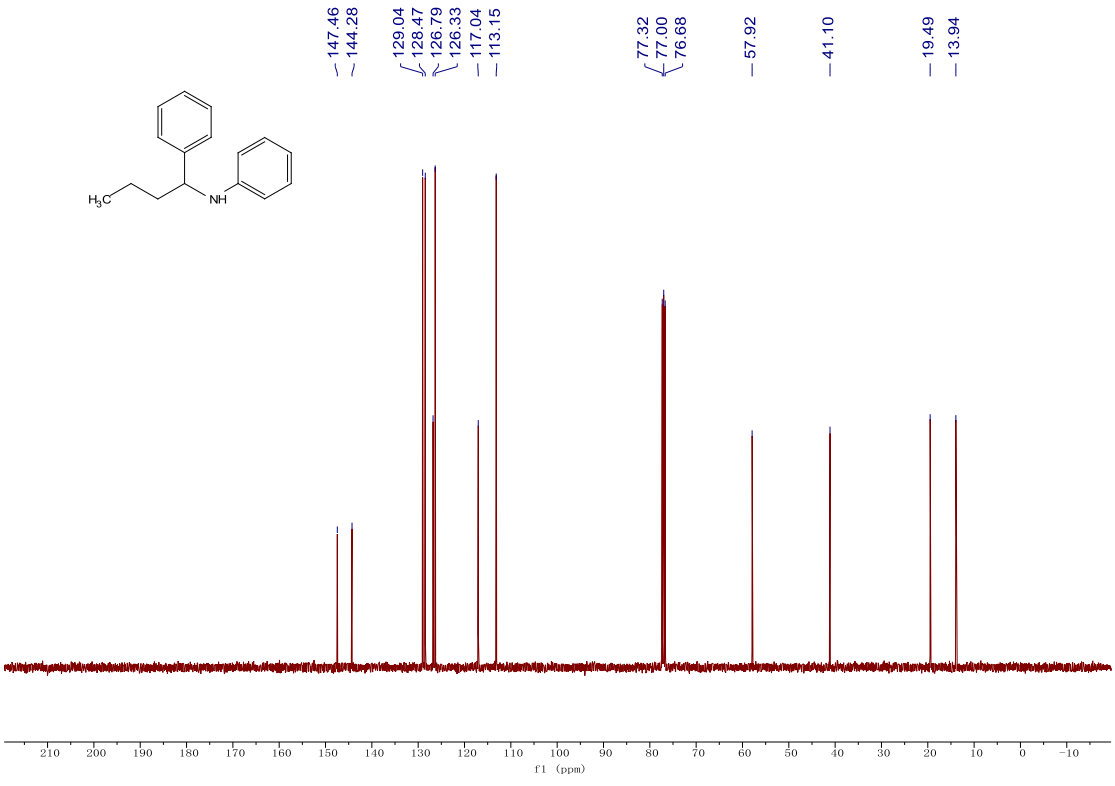
N-(1-Phenylpropyl)aniline (2n)



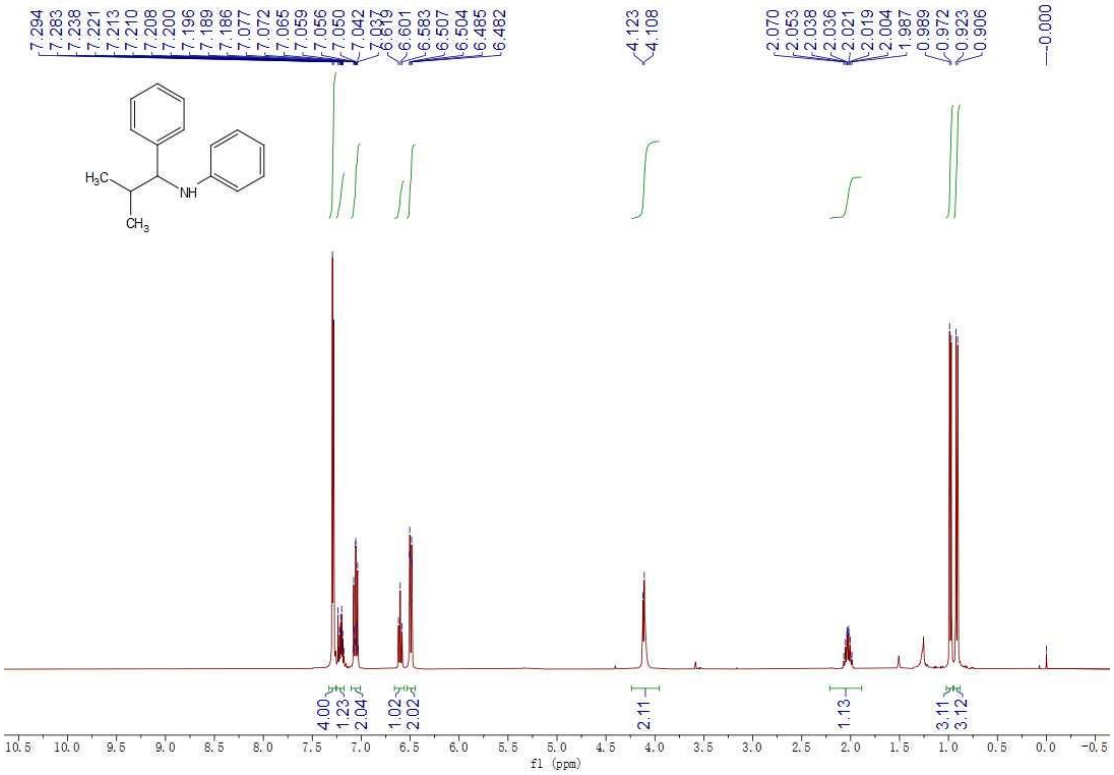


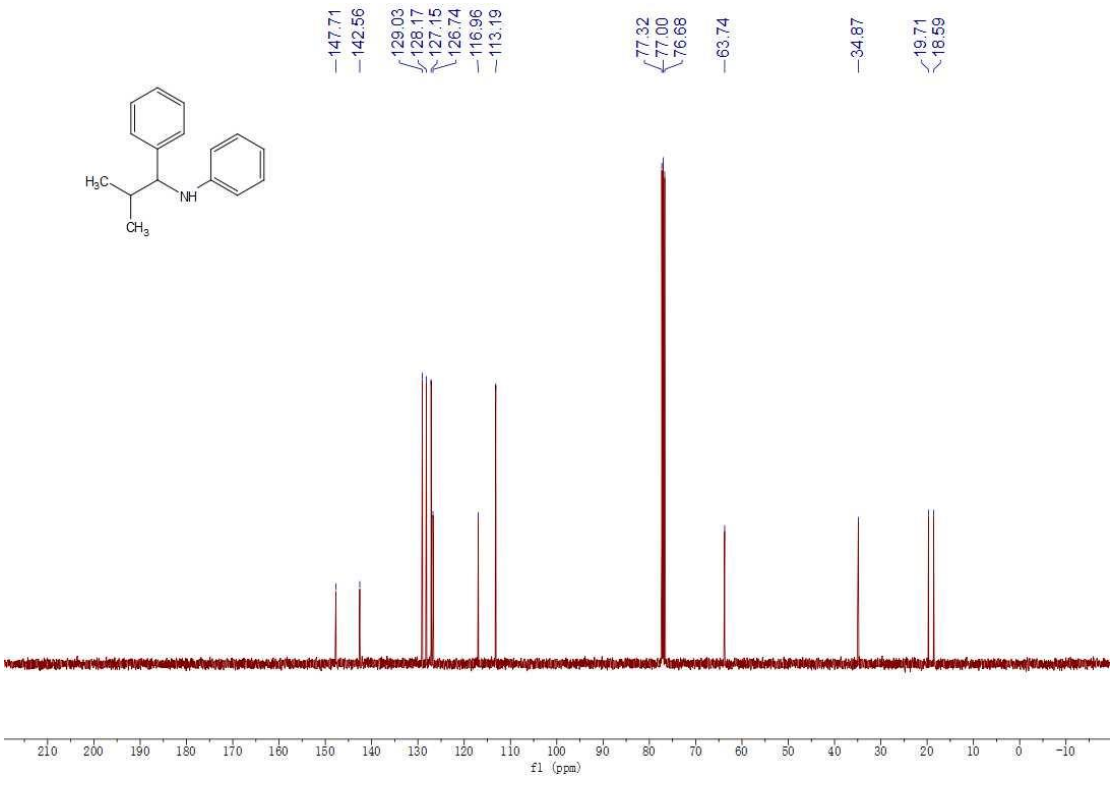
N-(1-Phenylbutyl)aniline (2o)



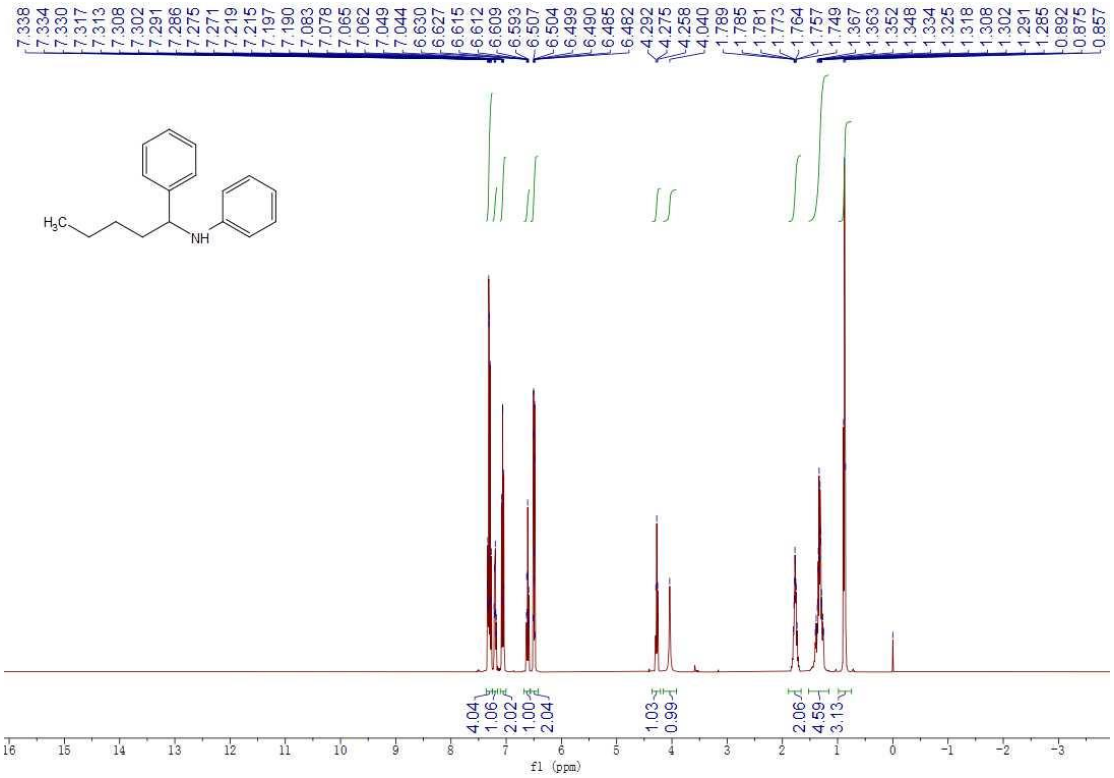


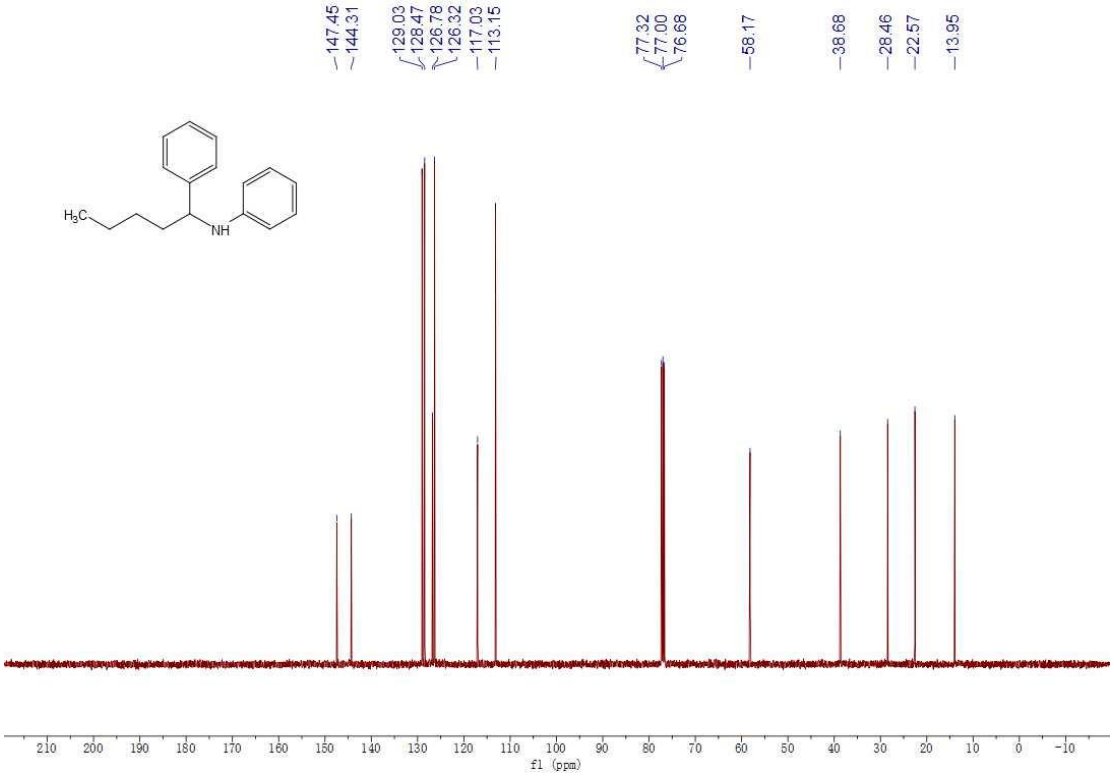
N-(2-Methyl-1-phenylpropyl)aniline (2p)



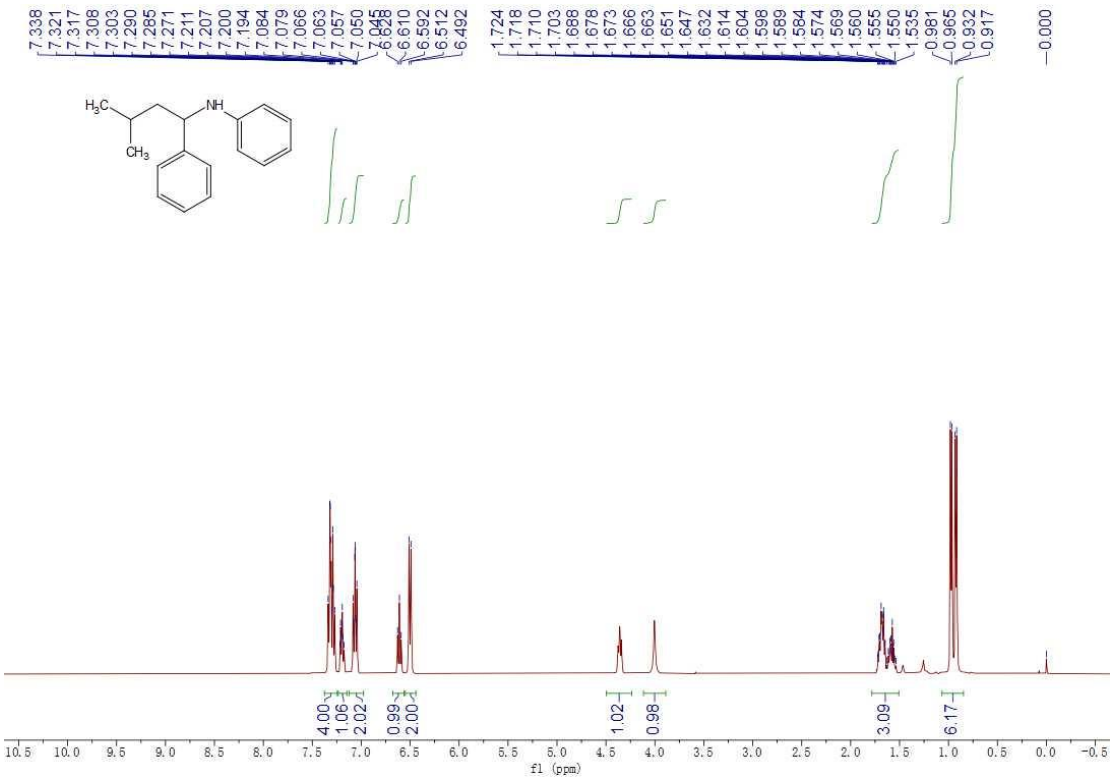


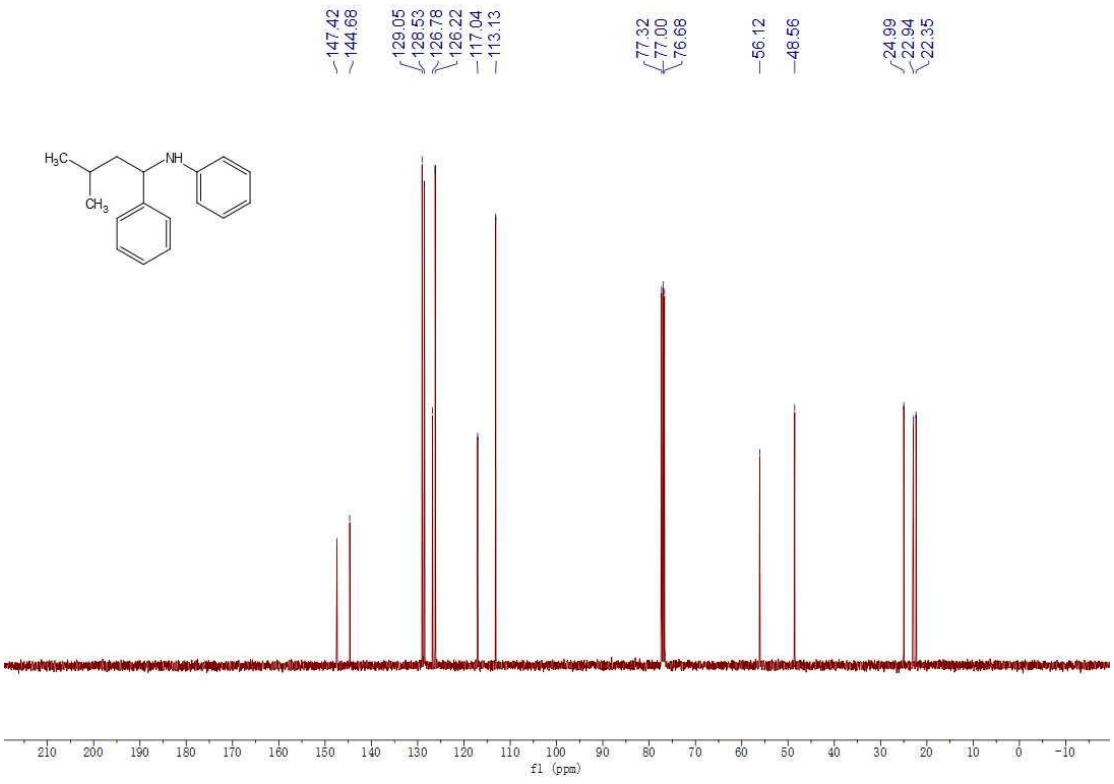
N-(1-Phenylpentyl)aniline (2q)



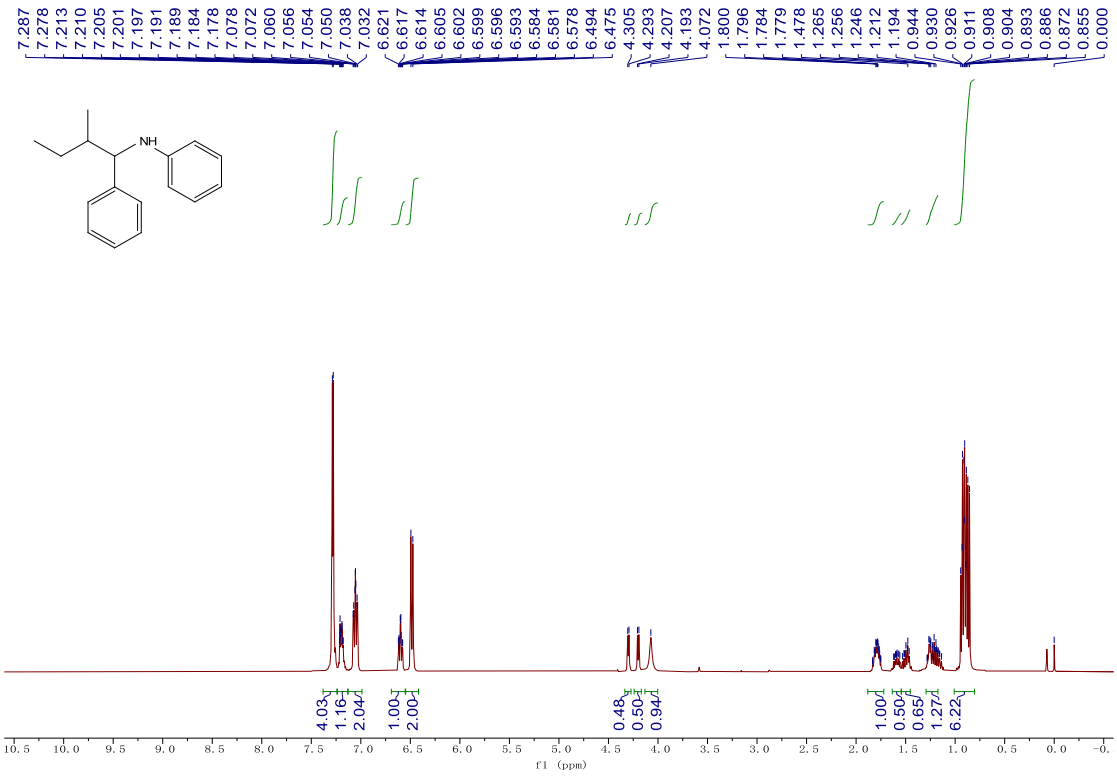


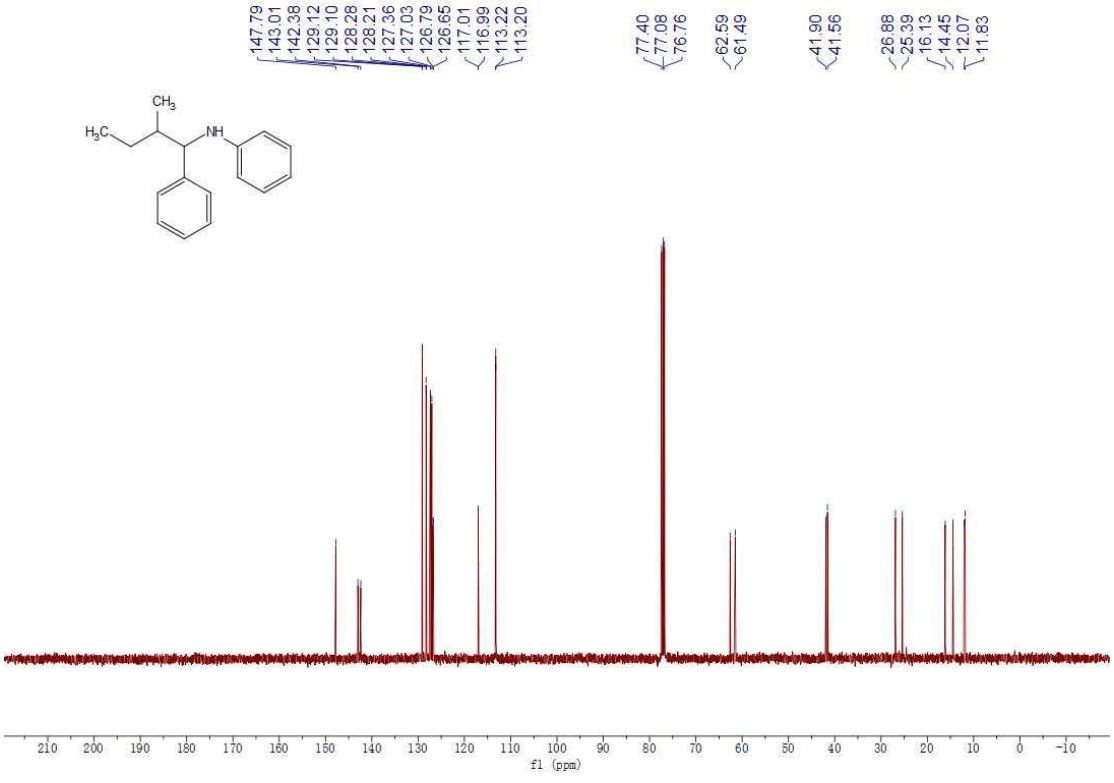
N-(3-Methyl-1-phenylbutyl)aniline (2r)



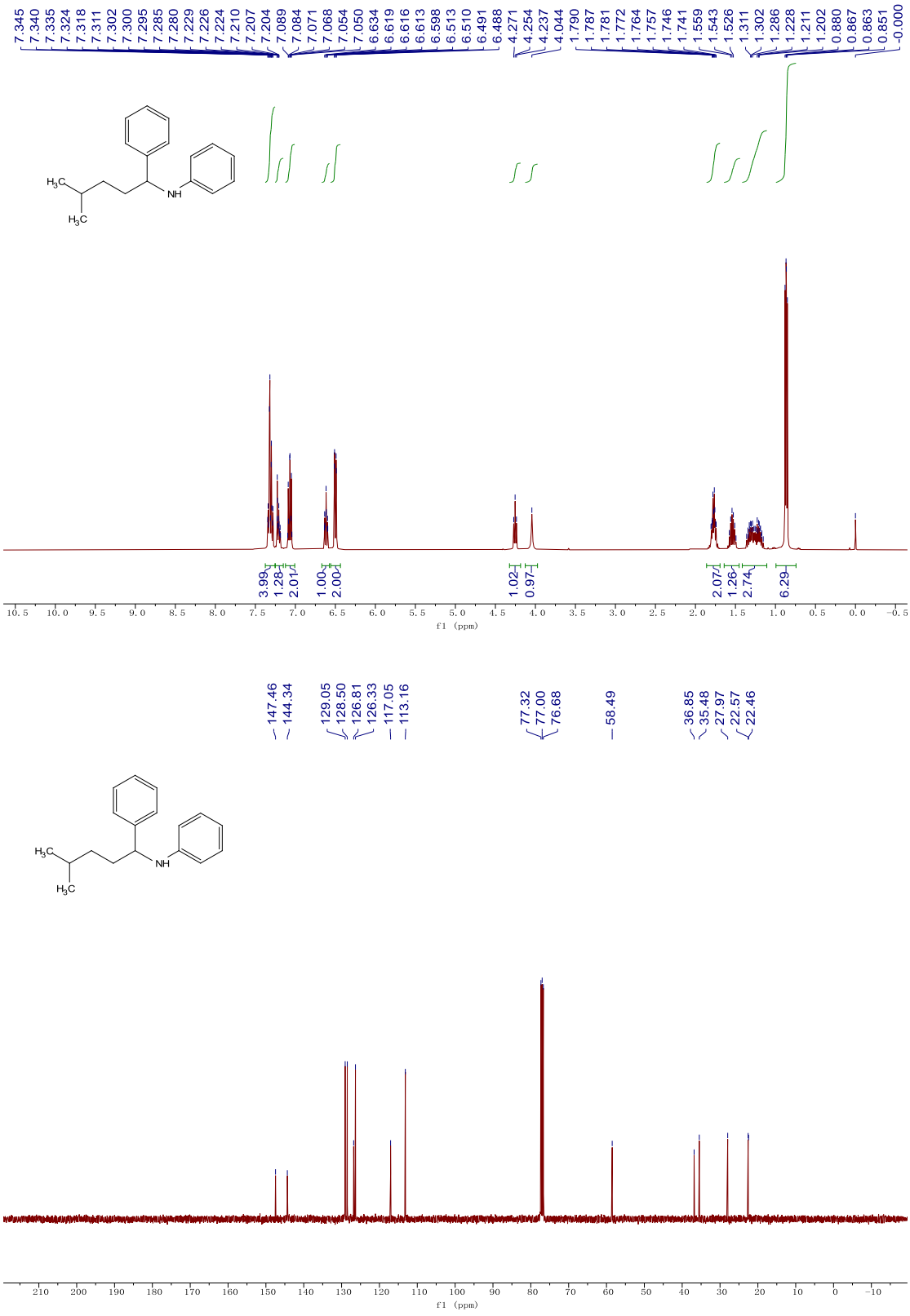


N-(2-Methyl-1-phenylbutyl)aniline (2s)

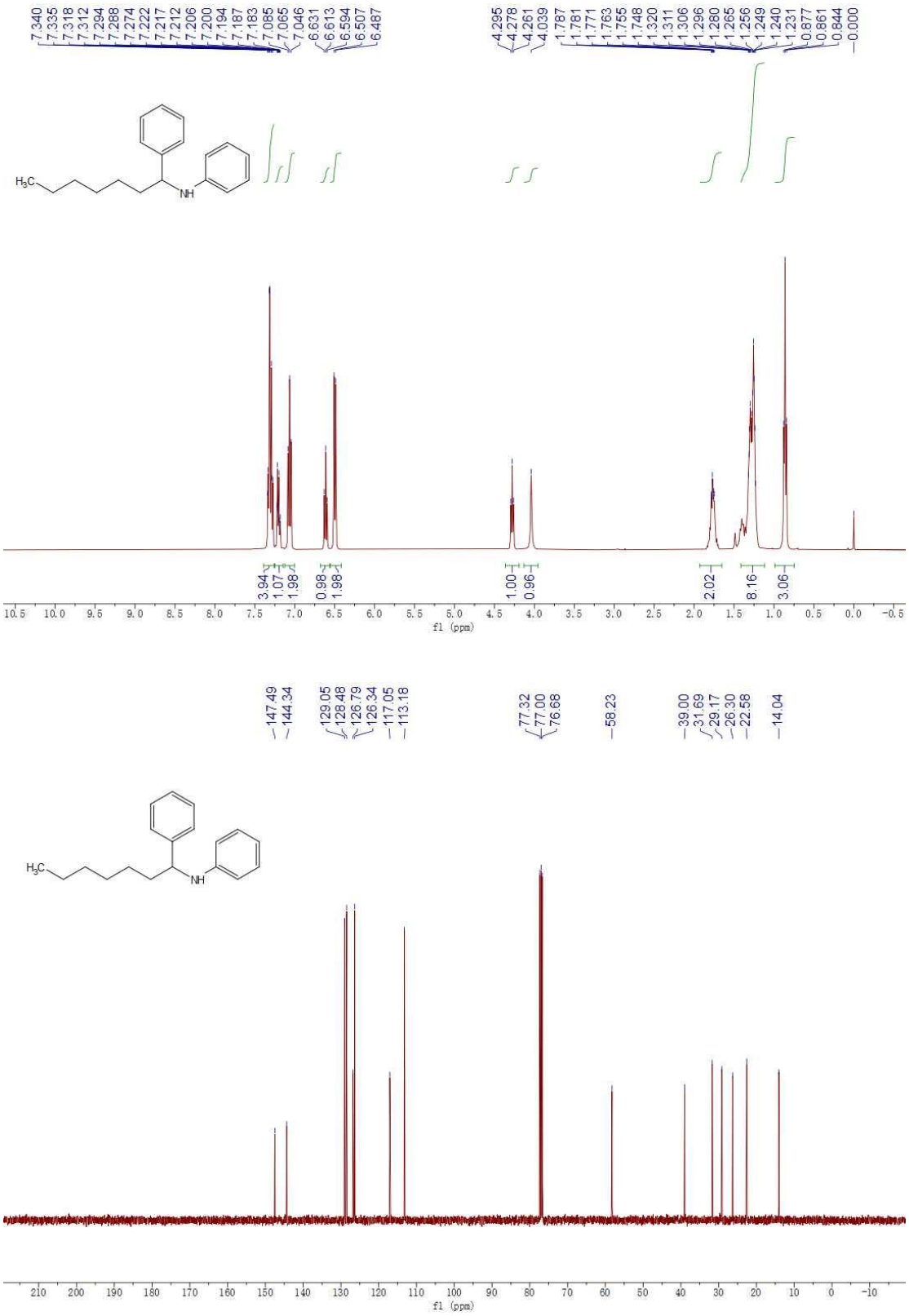




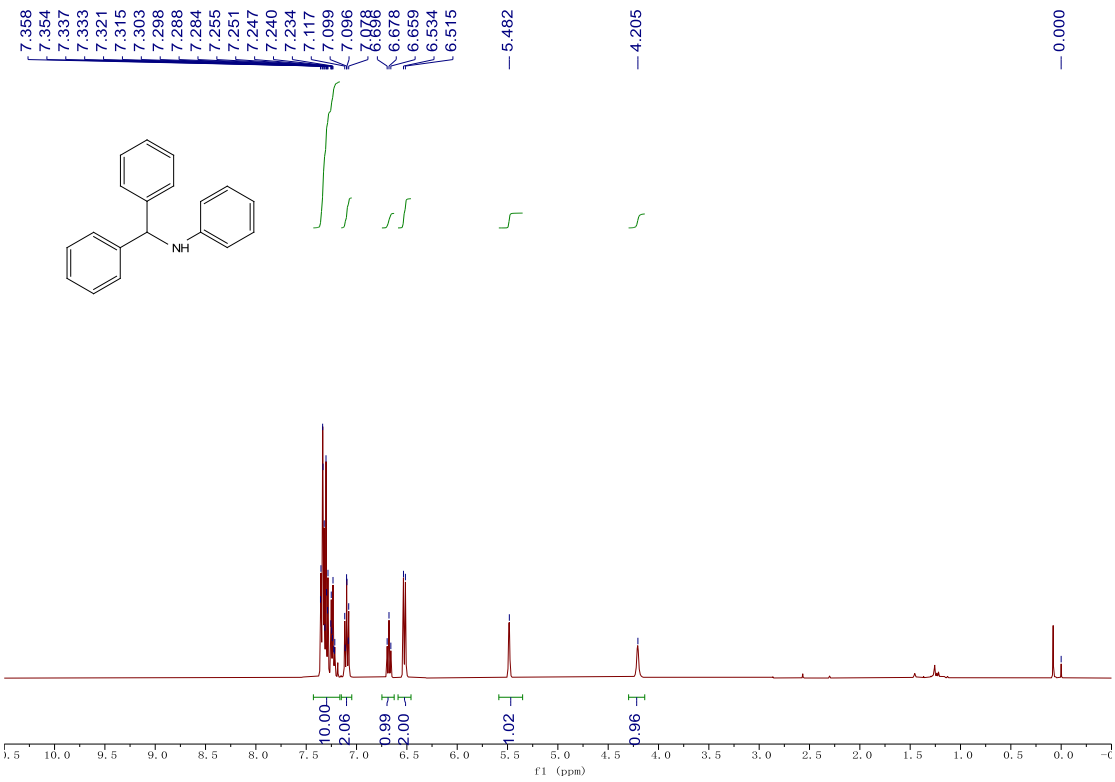
N-(4-Methyl-1-phenylpentyl)aniline (2t)

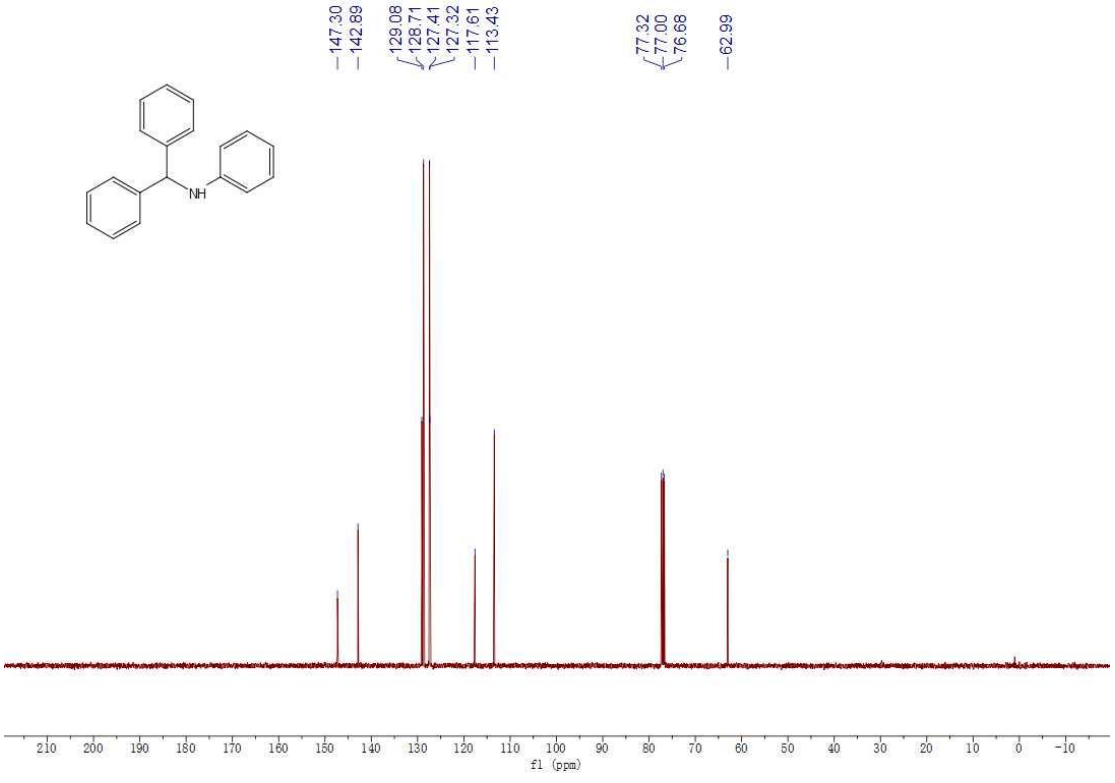


N-(1-Phenylheptyl)aniline (2u)

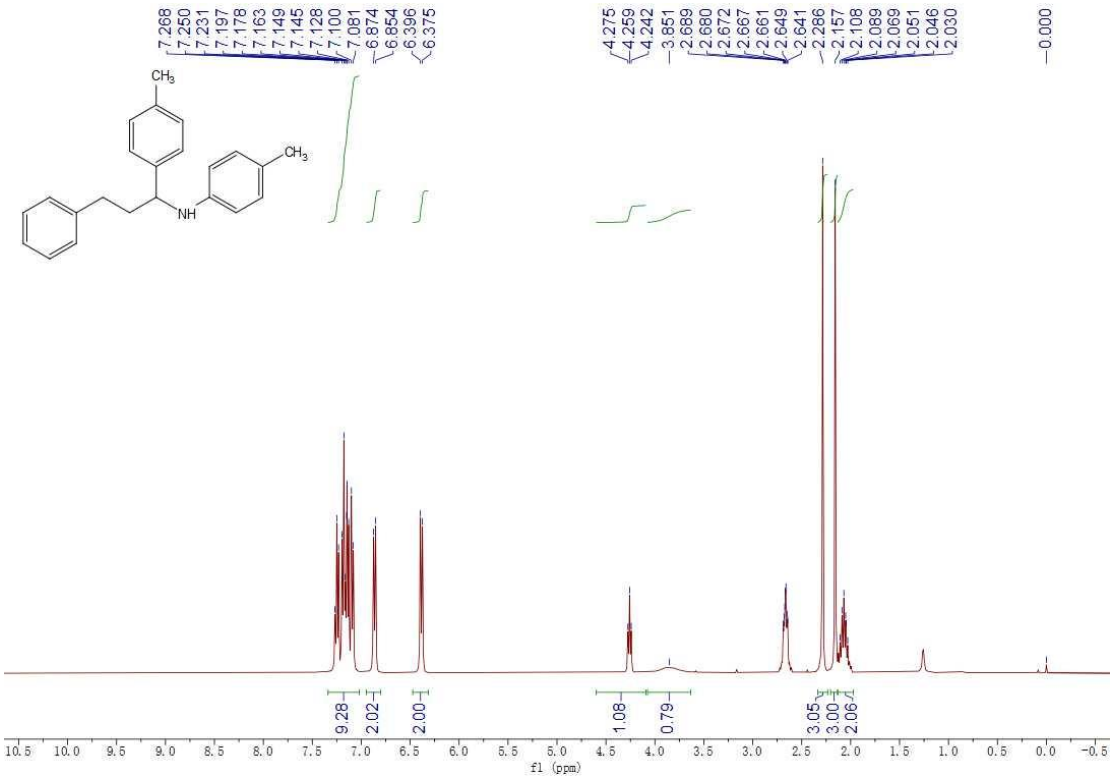


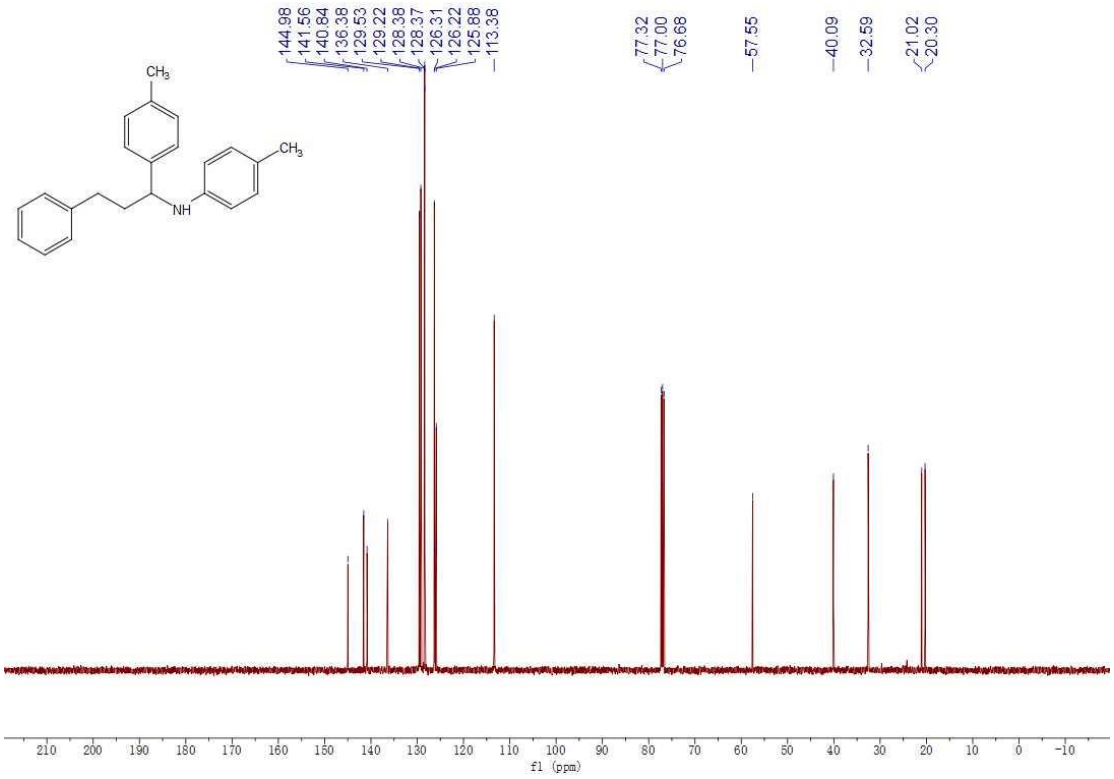
N-Benzhydrylaniline (2v)



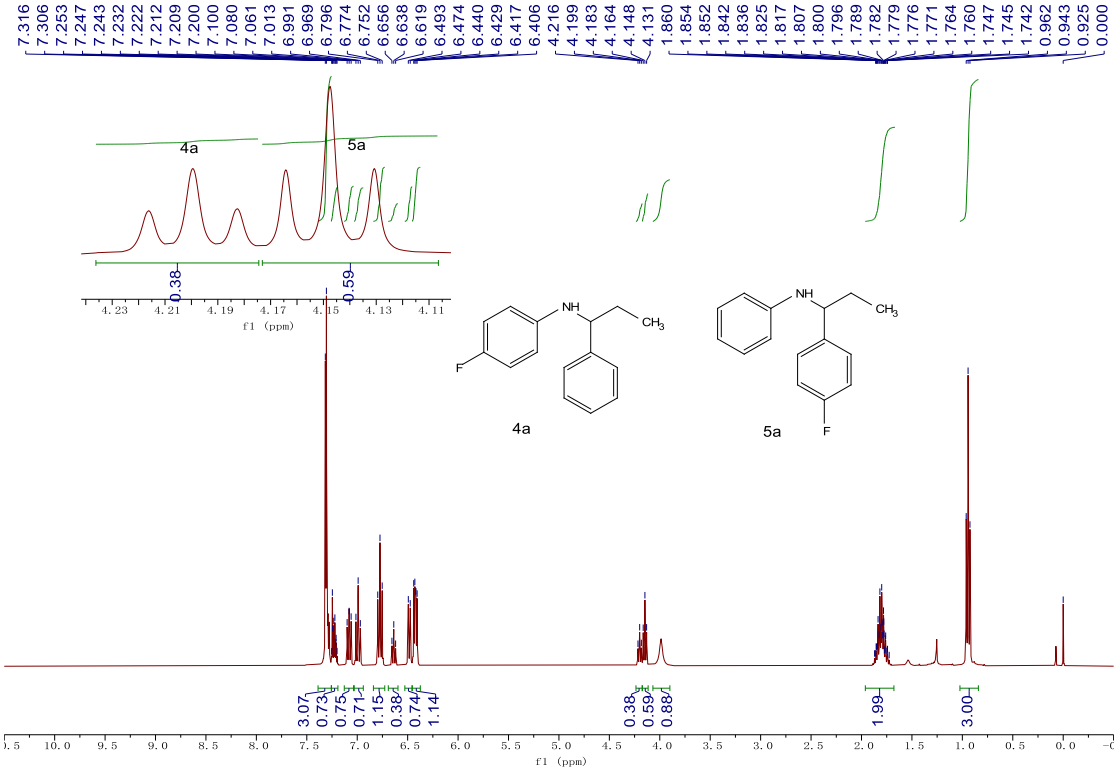


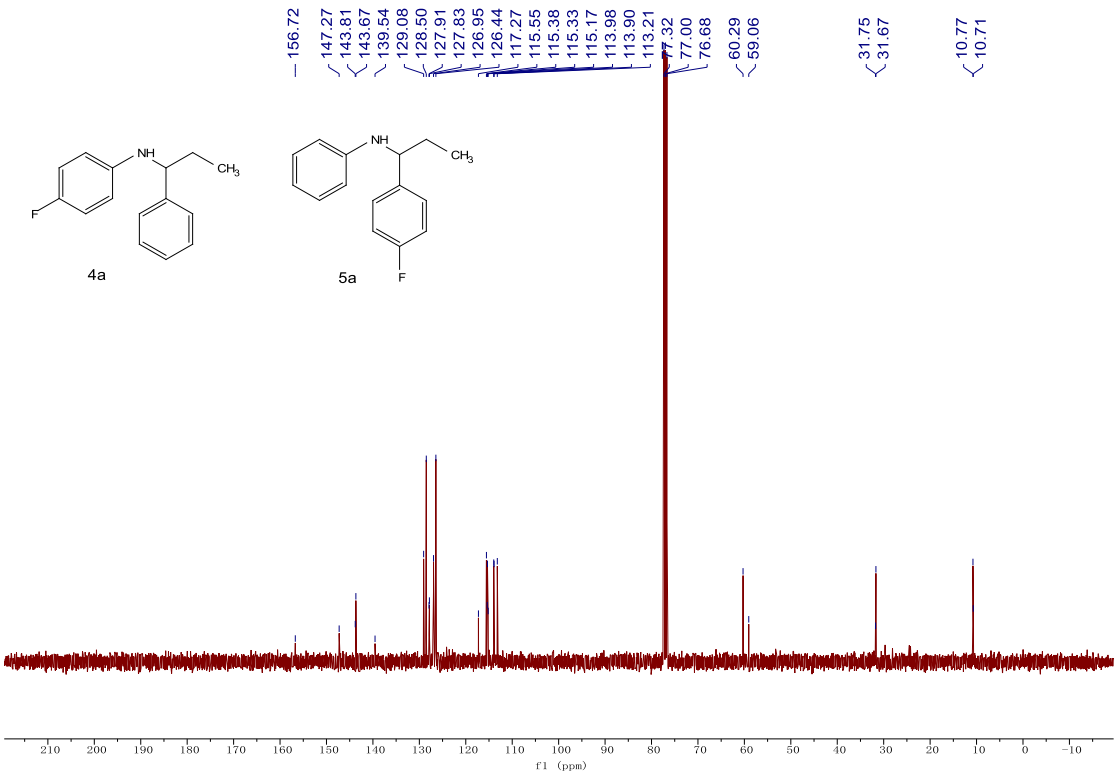
4-Methyl-*N*-(3-phenyl-1-(p-tolyl)propyl)aniline (2y)



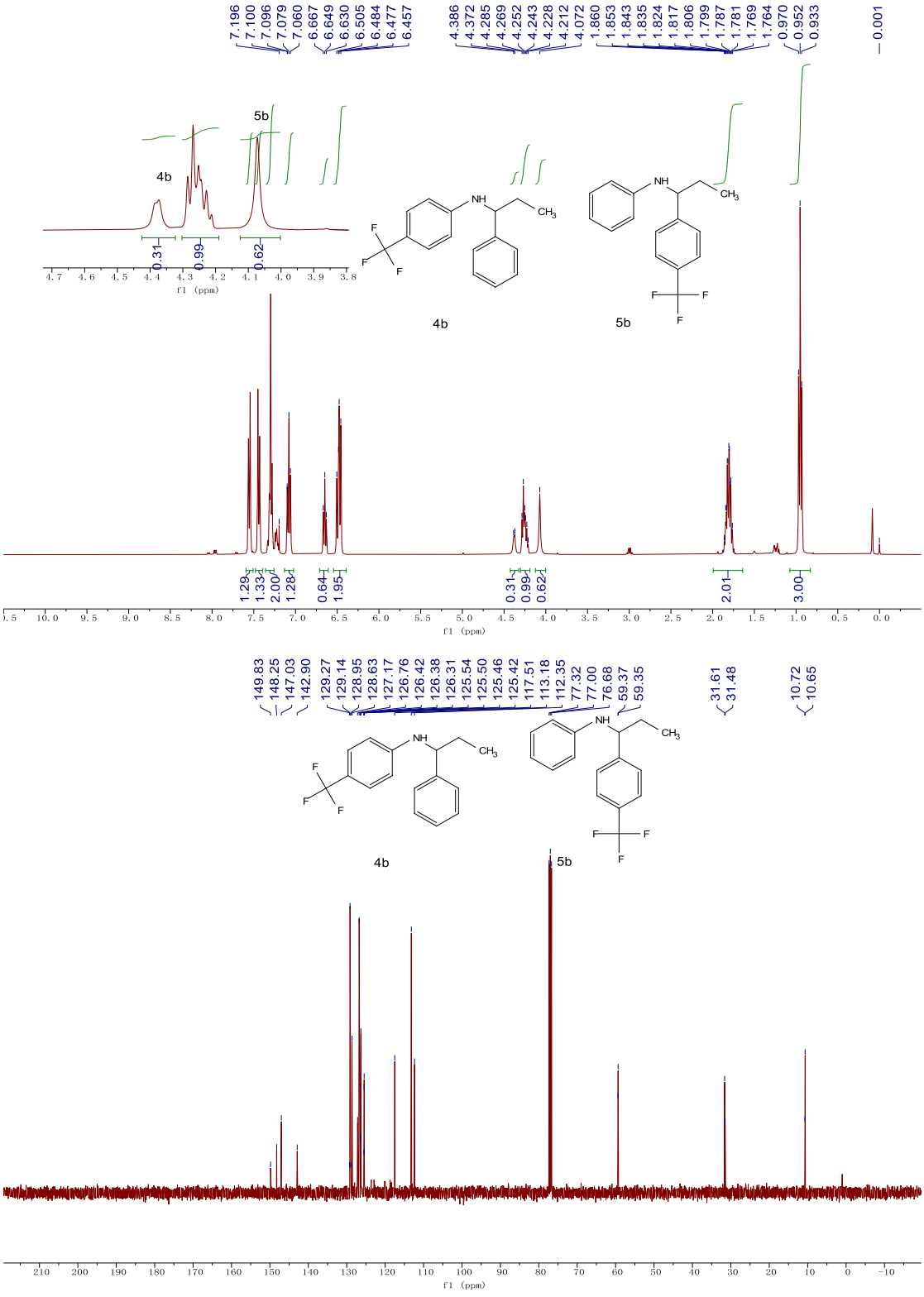


4-Fluoro-*N*-(1-phenylpropyl)aniline (4a) and *N*-(1-(4-fluorophenyl)propyl)aniline (5a)

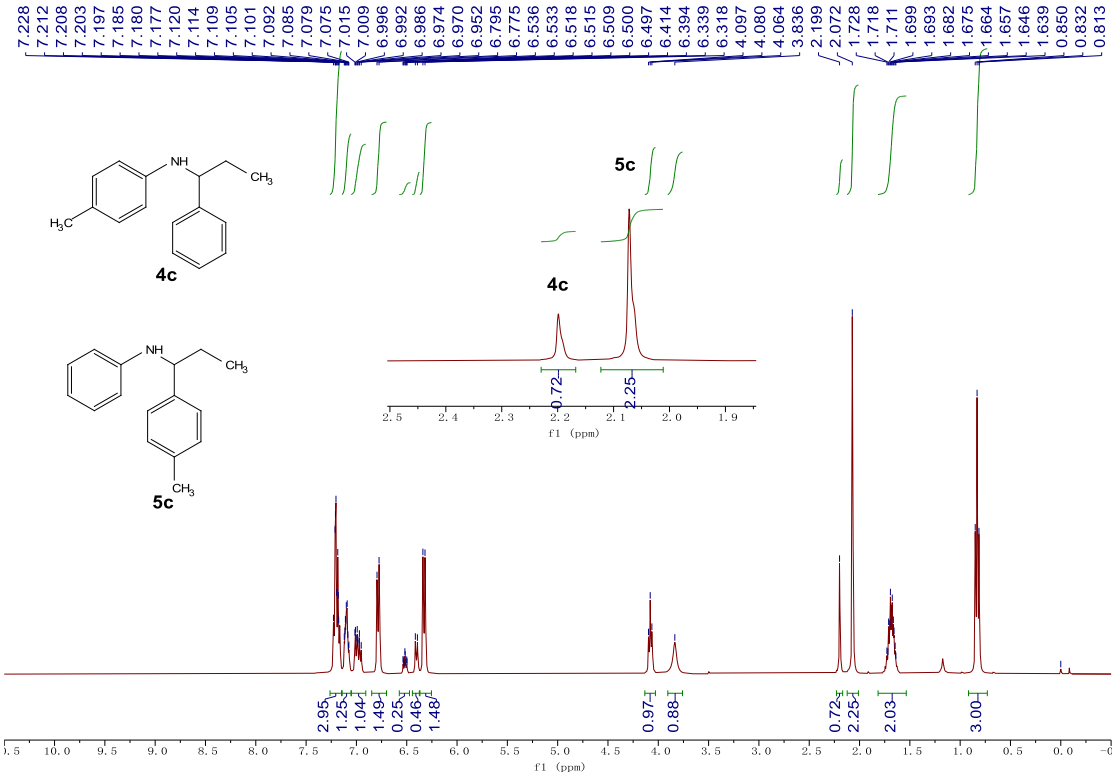


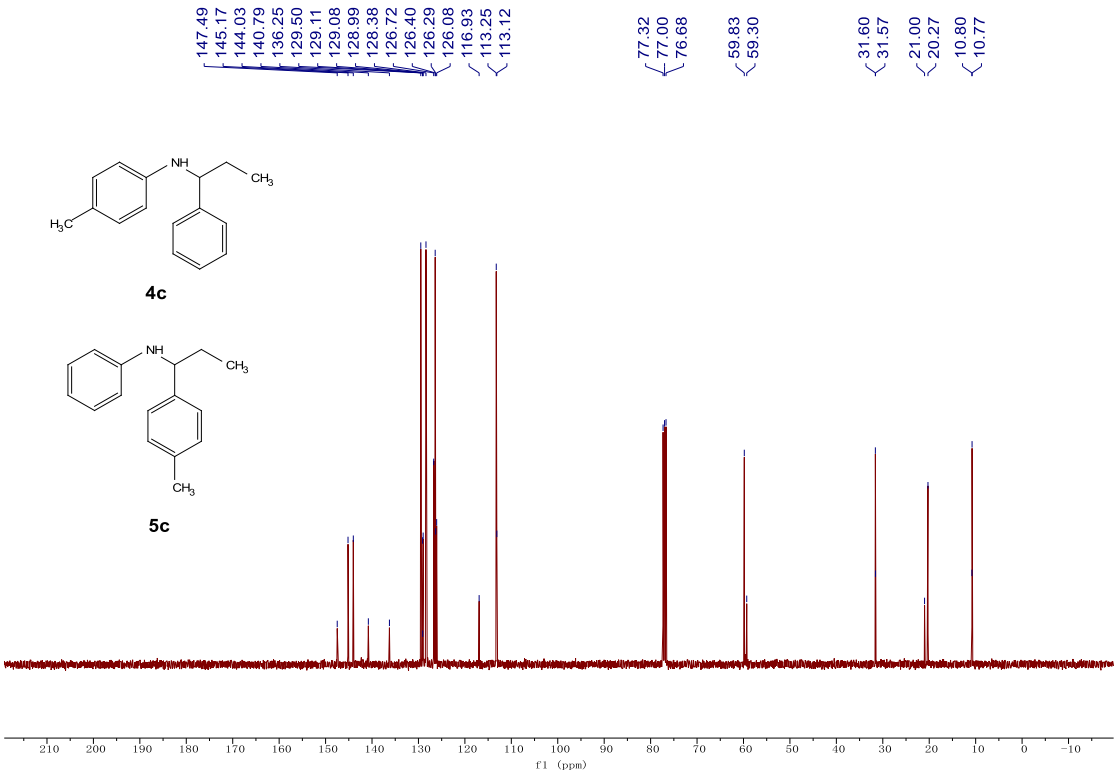


***N*-(1-Phenylpropyl)-4-(trifluoromethyl)aniline (4b) and *N*-(1-(4-(trifluoromethyl)phenyl)propyl)aniline (5b)**

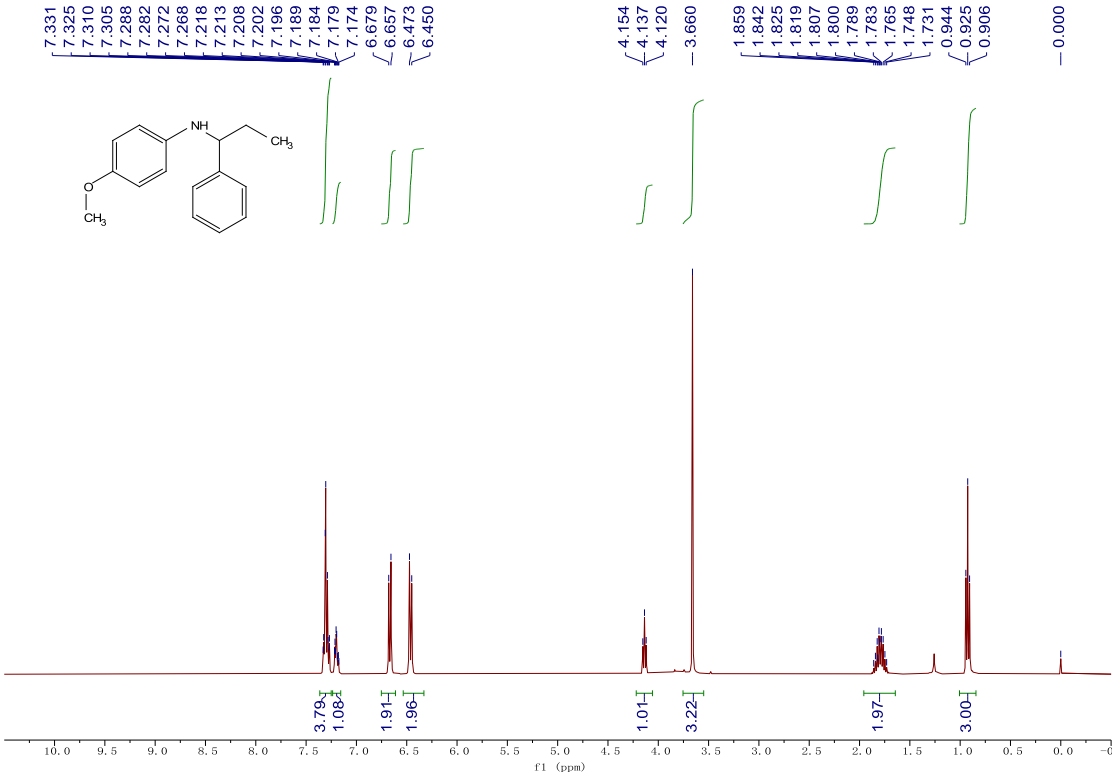


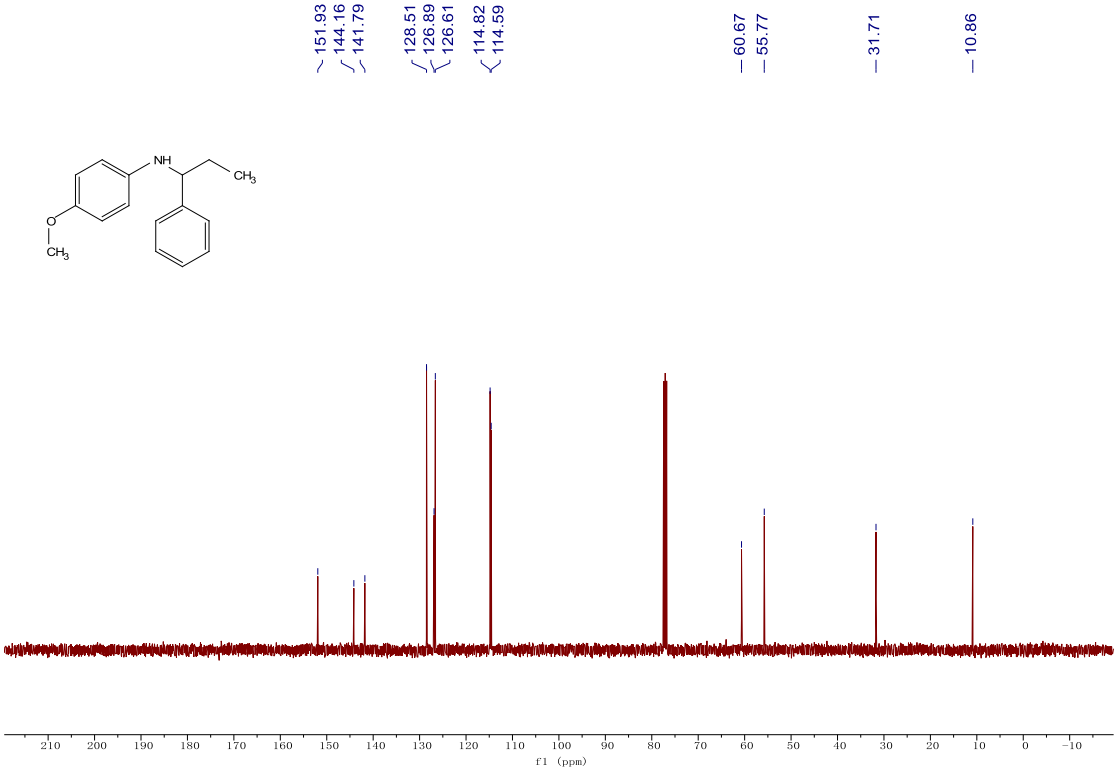
4-Methyl-*N*-(1-phenylpropyl)aniline (4c) and *N*-(1-(p-tolyl)propyl)aniline (5c)



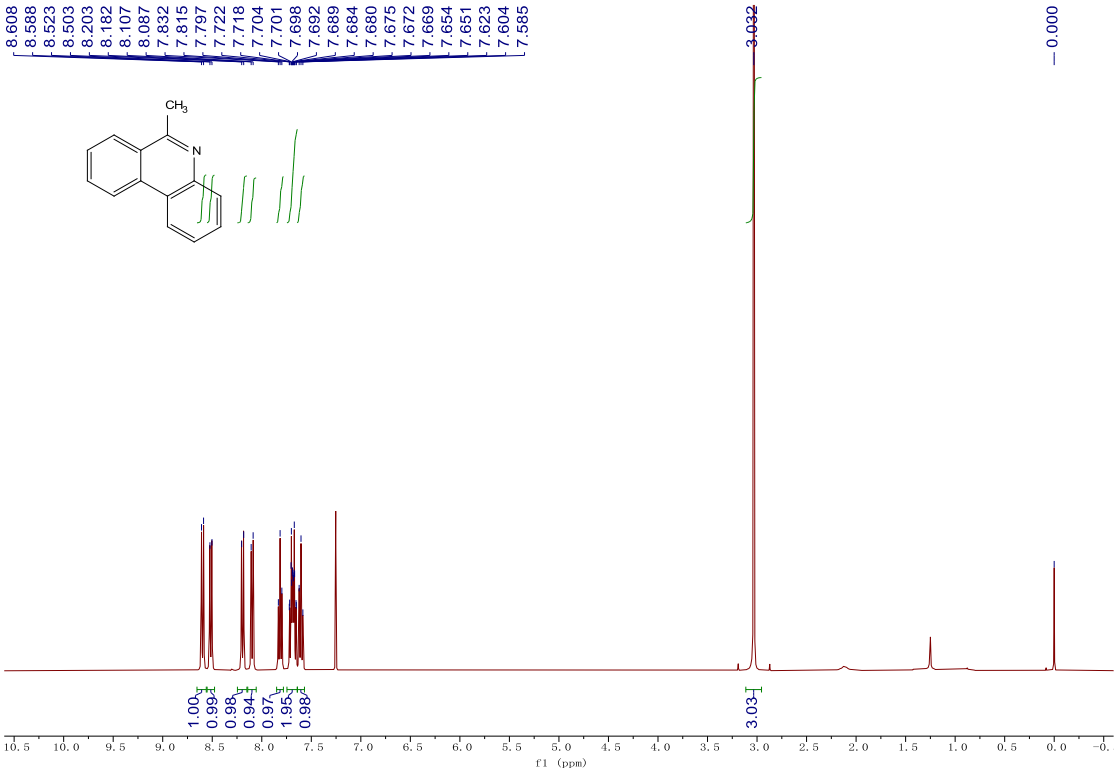


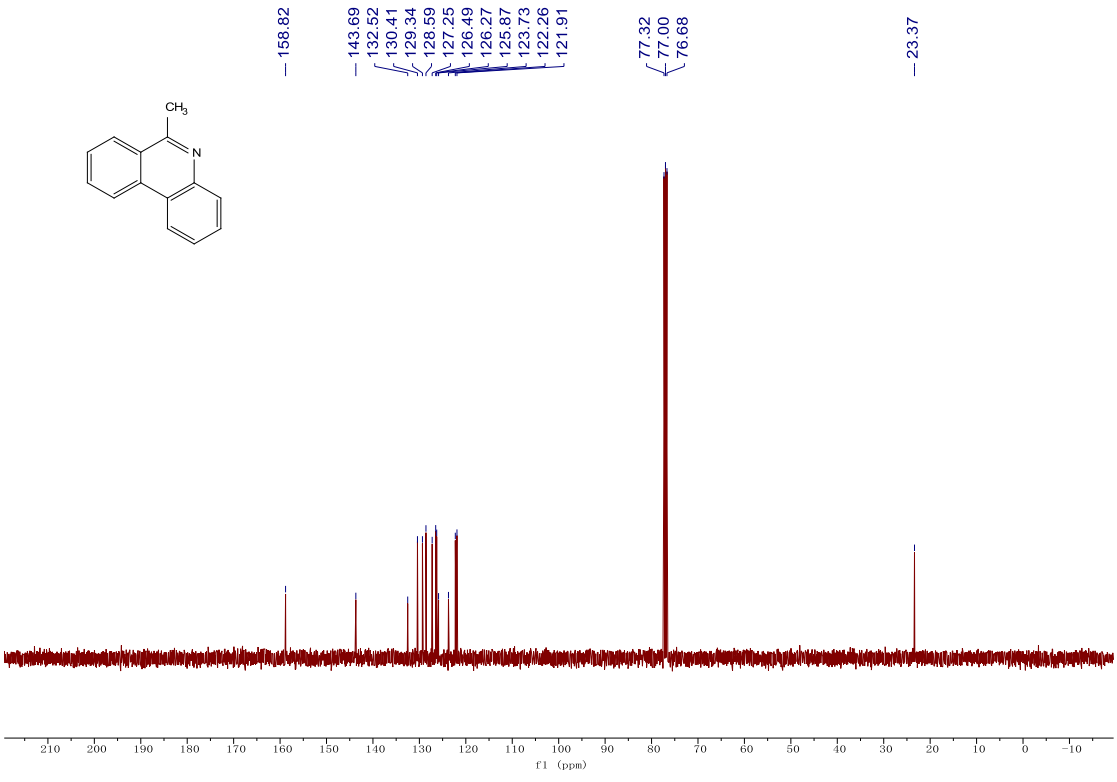
4-Methoxy-*N*-(1-phenylpropyl)aniline (4d)





6-Methylphenanthridine (7a)





6-Ethylphenanthridine (7b)