Supplementary Materials

Catalyst-free decarboxylative alkylation: access to of quaternary center

Lulan Cai, Fang Li, Shuting Wang, Wentao Xu*

School of Chemistry and Chemical Engineering, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, Jiangxi, China. Email: wtxu@ncu.edu.cn

Table of Contents

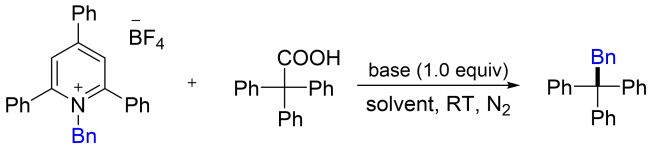
1. General information

All the reactions were conducted under nitrogen conditions unless otherwise noted. All solvents were obtained from commercial suppliers and used without further purification. Reagents were purchased from Energy Chemical, Adamas-beta, and etc. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ (δ H = 0.0 ppm, δ C = 77.02 ppm as standard). Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High-resolution mass spectra were obtained by APCI on a TOF mass analyzer.

2. Optimization of the reaction

Table S1. The optimization of reaction [a]



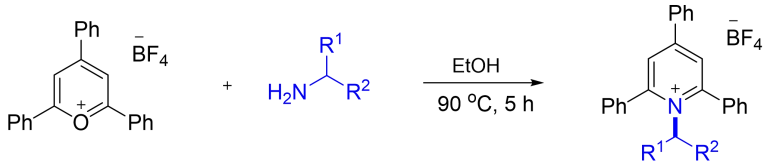
1a **2a** **3a**

Entry	Solvent	Base	Yield (%)[b]
1	CH_3CN	$KHCO_3$	43
2	toluene	$KHCO_3$	0
3	$CHCl_3$	$KHCO_3$	29
4	Acetone	$KHCO_3$	79
5	DMSO	$KHCO_3$	95
6[c]	**DMSO**	**$KHCO_3$**	**91 (84)**
7[c]	DMSO	K_2HPO_4	82
8[c]	DMSO	KH_2PO_4	13
9[c]	DMSO	2,4,6-Collidine	18
10[c, d]	DMSO	$KHCO_3$	21
11[c, e]	DMSO	$KHCO_3$	20
12[c]	DMSO	-	17
13 [c, f]	DMSO	$KHCO_3$	92
14[c]	Anhydrous DMSO	$KHCO_3$	94

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.1 mmol, 1.0 equiv), base (0.1 mmol, 1.0 equiv), DMSO (2.0 mL), room temperature, 6 h. [b] Determined by GC-MS using biphenyl as the internal standard. The number in parentheses is the isolated yield. [c] DMSO (0.5 mL). [d] $KHCO_3$ (0.02 mmol, 0.2 equiv). [e] air condition. [f] Dark conditions.

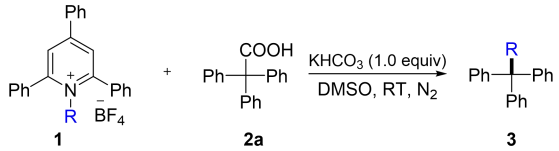
3. General procedure

3.1 General procedure for synthesis of pyridinium salts.



According to the procedure described by Watson and co-workers[1], 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv) and amine (1.2 equiv) were added to a Schlenk containing a stirring bar. This was followed by addition of dry EtOH (1.0 M), resulting in a colour change from yellow to black orange. The mixture was then stirred and heated at reflux in an oil bath at 90 ºC for 5 h. At that time, the mixture was allowed to cool to room temperature. Et_2O was then added (15 mL) and shaken vigorously, forming a solid precipitate. The solid thus obtained was filtered, washed with Et_2O (2 x 15 mL) and dried under high vacuum. If the pyridinium salt failed to precipitate, it was subjected to flash column chromatography, eluting with DCM/Acetone mixtures.

3.2 General procedure for decarboxylative alkylation.



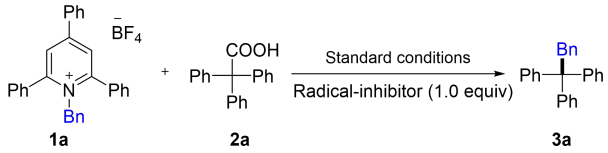
Pyridinium salt **1** (0.1 mmol), 2,2,2-triphenylacetic acid **2a** (28.8 mg, 0.1 mmol), $KHCO_3$ (10.0 mg, 0.1 mmol), replaced in a transparent Schlenk tube equipped with a stirring bar. The solvents DMSO (0.5 mL) were added under N_2 atmosphere. Next, the reaction mixture was replaced Magnetic Stirrer at room temperature for 6 h. When the reaction finished, the mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate).

Figure S1. Reaction set-up

4. Investigation of the reaction mechanism

4.1 Table S2. Radical-inhibiting experiments.

To clarify the possible reaction mechanism, radical inhibiting experiments were first conducted. Under the standard condition, three kinds of radical inhibitor were added. It is clearly that reductive inhibitors, like 2,6-di-tert-butyl-4-methylphenol (BHT) and N-tert-Butyl-α-phenylnitrone (PBN), makes no difference. When adding 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), the reaction was inhibited, probably due to the strong oxidation of TEMPO. Some byproducts were detected by GCMS, such as triphenyl methanol, and triphenylmethane.



Entry	Radical-inhibitor	Yield (%)[b]
1	TEMPO	19
2	BHT	88
3	PBN	89

Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.1 mmol, 1.0 equiv), $KHCO_3$ (0.1 mmol, 1.0 equiv), radical-inhibitor (0.1 mmol, 1.0 equiv), DMSO (0.5 mL), room temperature, 6 h. [b] Determined by GC-MS using biphenyl as the internal standard.

4.2 Deuterium Labeling Reaction.

Synthesis of potassium 2,2,2-triphenylacetate: 2,2,2-triphenylacetic acid （1.0 equiv，5 mmol），KOH（1.0 equiv），were replaced in a transparent Schlenk tube equipped with a stirring bar. The solvents MeOH (2.5 M) were added. Next, the reaction mixture was replaced Magnetic Stirrer at room temperature for 12 h. When the reaction finished, the mixture was extracted with ethyl acetate (3 x 10 mL). The water layer is evaporated to obtain potassium 2,2,2-triphenylacetate.

General procedure: Potassium 2,2,2-triphenylacetate (0.1 mmol) was replaced in a transparent Schlenk tube equipped with a stirring bar. Anhydrous DMSO (0.5 mL) was added under N_2 atmosphere, followed by adding D_2O (20.0 mg, 1 mmol). Next, the reaction mixture was replaced Magnetic Stirrer at room temperature for 6 h. When the reaction finished, determined by GC-MS using biphenyl as the internal standard.

In the presence of D_2O, we found that the prepared potassium 2,2,2-triphenylacetate directly proceeded decarboxylation and gave D-triphenylmethane in 98% yield. Next, anhydrous DMSO was used as the solvent. The desired decarboxylative alkylation product was afforded in a compatible yield (88%), accompanying a trace amount of triphenylmethane.

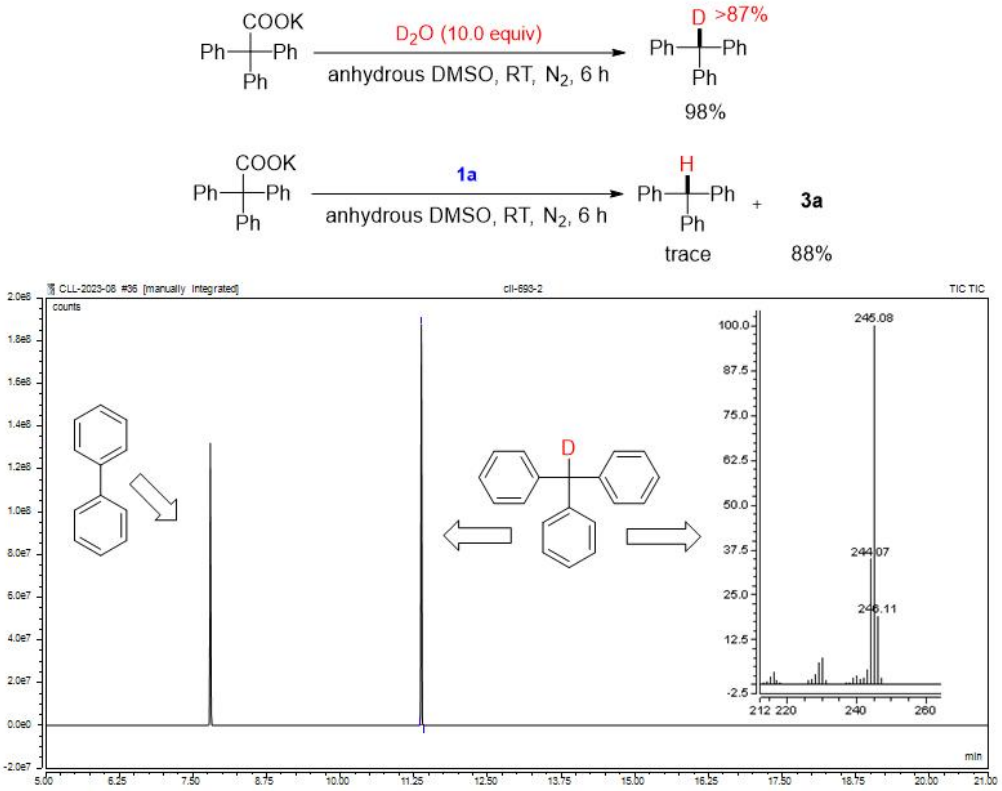
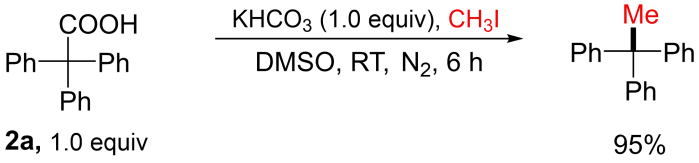
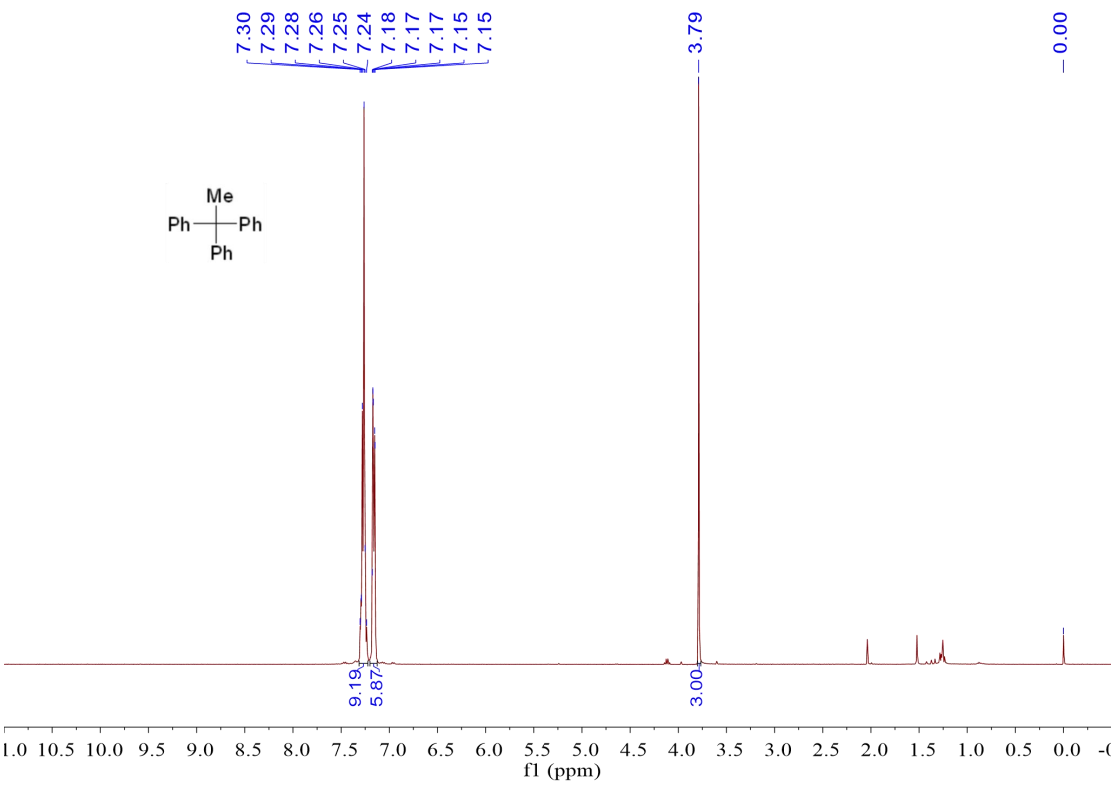


Figure S2. Deuterium Labeling Reaction.

4.3 Methyl Reaction.

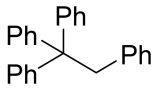
MeI is the most commonly used methyl reagent in organic synthesis and is an ideal substrate for SN_2 nucleophilic substitution reactions (*Sci Sin Chim.* **2020**, *50*, 526). When adding MeI, the desired methyl product was afforded in 95% isolated yield. Hence, it maybe polar process.



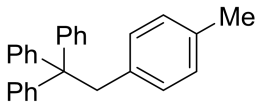


ethane-1,1,1-triyltribenzene ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (m, *J* = 7.1 Hz, 9H), 7.2 (m, *J* = 7.1, 1.6 Hz, 6H), 3.8 (s, 3H).

5. Characterization of products

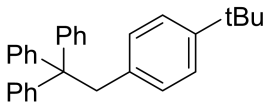


ethane-1,1,1,2-tetrayltetrabenzene (**3a**)[2]. According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature ; 28.2 mg, 84%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 – 7.1 (m, 15H), 7.0 (t, J = 7.4 Hz, 1H), 7.0 (t, J = 7.5 Hz, 2H), 6.6 (d, J = 7.6 Hz, 2H), 3.9 (s, 2H).

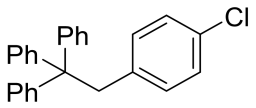


(2-(p-tolyl)ethane-1,1,1-triyl)tribenzene (**3b**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 25.8 mg, 74%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (dd, *J* = 4.4, 1.2 Hz, 11H), 7.2 – 7.1 (m, 3H), 7.2 – 7.1 (m, 1H), 6.8 (d, *J* = 7.7 Hz, 2H), 6.5 (d, *J* = 7.7 Hz, 2H), 3.9 (s, 2H), 2.2 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 135.4, 135.3, 131.0, 129.8, 128.0,

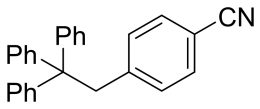
127.5, 125.9, 58.4, 45.9, 20.9; HRMS m/z (APCI) calcd for $C_{27}H_{25}^+$ $(M + H)^+$ 349.1951; found: 349.1957.



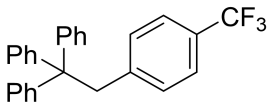
(2-(4-(tert-butyl)phenyl)ethane-1,1,1-triyl)tribenzene (**3c**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 27.3 mg, 70%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (s, 1H), 7.2 (d, *J* = 4.2 Hz, 12H), 7.2 – 7.1 (m, 2H), 7.0 (d, *J* = 8.0 Hz, 2H), 6.5 (d, *J* = 7.9 Hz, 2H), 3.9 (s, 2H), 1.2 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 146.8, 135.3, 130.7, 129.8, 127.5, 125.8, 124.2, 58.5, 45.8, 34.2, 31.3; HRMS m/z (APCI) calcd for $C_{30}H_{30}Na^+$ $(M + Na)^+$ 413.2240; found: 413.2237.



(2-(4-chlorophenyl)ethane-1,1,1-triyl)tribenzene (**3d**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 29.5 mg, 80%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 8.2 Hz, 3H), 7.2 (d, *J* = 6.8 Hz, 11H), 7.2 (t, 2H), 6.9 (d, *J* = 8.0 Hz, 1H), 6.5 (d, *J* = 8.0 Hz, 2H), 3.9 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 136.9, 132.4, 129.7, 129.6, 127.7, 127.4, 126.0, 58.4, 45.6; HRMS m/z (APCI) calcd for $C_{26}H_{22}Cl^+$ $(M + H)^+$ 369.1405; found: 369.1405.

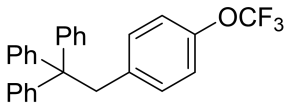


4-(2,2,2-triphenylethyl)benzonitrile (**3e**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 24 h at room temperature; 18.2 mg, 51%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.2 (m, 6H), 7.2 (m, *J* = 8.7 Hz, 11H), 6.7 (d, *J* = 7.9 Hz, 2H), 4.0 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 144.4, 131.6, 131.0, 129.5, 127.8, 126.2, 119.1, 109.8, 58.5, 46.3; HRMS m/z (APCI) calcd for $C_{27}H_{22}N^+$ $(M + H)^+$ 360.1747; found: 360.1739.

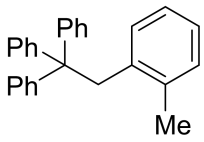


(2-(4-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tribenzene (**3f**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 23.8 mg, 59%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz,

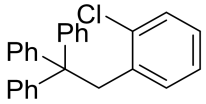
$CDCl_3$) δ 7.3 – 7.1 (m, 17H), 6.7 (d, *J* = 5.5 Hz, 2H), 4.0 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 142.8 (d, *J* = 1.01 Hz), 131.3, 130.2 (q, *J* = 25.25 Hz), 129.6, 127.7, 126.2, 124.1 (q, *J* = 4.04 Hz), 124.0 (q, *J* = 216.1 Hz), 58.5, 46.1; GCMS (EI) m/z 401 $(M)^+$.



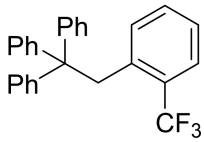
(2-(4-(trifluoromethoxy)phenyl)ethane-1,1,1-triyl)tribenzene (**3g**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 23.0 mg, 55%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.2 (m, 12H), 7.2 – 7.1 (m, 3H), 6.8 (d, *J* = 7.5 Hz, 2H), 6.6 (d, *J* = 8.6 Hz, 2H), 3.9 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6 (q, *J* = 2.02 Hz), 146.3, 137.3, 132.2, 129.7, 127.7, 126.1, 119.7, 118.2 (q, *J* = 216.1 Hz), 58.5, 45.5; HRMS m/z (APCI) calcd for $C_{27}H_{22}F_3O^+$ $(M + H)^+$ 419.1617; found: 419.1616.



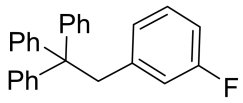
(2-(o-tolyl)ethane-1,1,1-triyl)tribenzene (**3h**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 20.2 mg, 58%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.1 (m, 15H), 7.0 (td, *J* = 7.3, 1.5 Hz, 1H), 6.9 (d, *J* = 7.4 Hz, 1H), 6.8 (dt, *J* = 14.7, 7.5 Hz, 2H), 3.9 (s, 2H), 1.5 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 138.8, 137.1, 130.2, 129.9, 129.7, 127.5, 126.0, 125.9, 125.0, 58.2, 41.6, 19.2; HRMS m/z (APCI) calcd for $C_{27}H_{24}$ Na^+ $(M + Na)^+$ 371.1770; found: 371.1765.



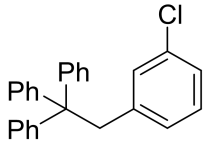
(2-(2-chlorophenyl)ethane-1,1,1-triyl)tribenzene (**3i**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 22.1 mg, 60%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 8.6 Hz, 3H), 7.2 (d, *J* = 6.6 Hz, 10H), 7.2 – 7.1 (m, 3H), 7.0 (q, *J* = 7.7, 7.1 Hz, 1H), 6.9 (d, *J* = 7.7 Hz, 1H), 6.8 (t, *J* = 7.5 Hz, 1H), 4.2 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 136.6, 136.5, 131.5, 129.8, 129.0, 127.7, 127.2, 126.0, 125.7, 57.9, 41.9; HRMS m/z (APCI) calcd for $C_{26}H_{22}Cl^+$ $(M + H)^+$ 369.1405; found: 369.1400.



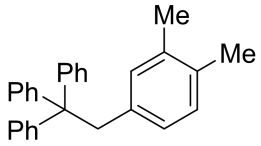
(2-(2-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tribenzene (**3j**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 22.5 mg, 56%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (d, *J* = 7.8 Hz, 1H), 7.3 – 7.1 (m, 15H), 7.1 (d, *J* = 7.6 Hz, 1H), 7.0 (q, *J* = 8.0 Hz, 2H), 4.3 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 137.9 (q, *J* = 1.01 Hz), 131.2 (d, *J* = 134.3 Hz), 130.5, 129.7, 127.8, 126.3 (q, *J* = 3.03 Hz), 126.1, 125.8 (q, *J* = 3.03 Hz), 125.6, 122.0 (q, *J* = 216.1 Hz), 57.4, 41.2 (d, *J* = 2.02 Hz); HRMS m/z (APCI) calcd for $C_{27}H_{22}F_3^+$ $(M + H)^+$ 403.1668; found: 403.1673.



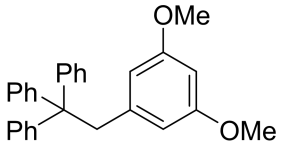
(2-(3-fluorophenyl)ethane-1,1,1-triyl)tribenzene (**3k**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 25.4 mg, 72%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 – 7.1 (m, 15H), 6.9 (q, *J* = 7.6 Hz, 1H), 6.7 (t, *J* = 7.2 Hz, 1H), 6.4 (d, *J* = 7.7 Hz, 1H), 6.3 (d, *J* = 10.7 Hz, 1H), 3.9 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.4 Hz), 146.3, 141.1 (d, *J* = 8.1 Hz), 129.6, 128.5 (d, *J* = 8.1 Hz), 127.7, 126.8 (d, *J* = 3.0 Hz), 126.1, 117.8 (d, *J* = 22.2 Hz), 112.9 (d, *J* = 21.2 Hz), 58.5, 46.0 (d, *J* = 2.02 Hz); HRMS m/z (APCI) calcd for $C_{26}H_{22}F^+$ $(M + H)^+$ 353.1700; found: 353.1708.



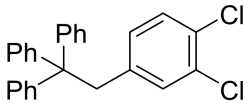
(2-(3-chlorophenyl)ethane-1,1,1-triyl)tribenzene (**3l**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 25.0 mg, 68%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.2 (m, 12H), 7.2 (m, 3H), 7.0 (d, *J* = 8.7 Hz, 1H), 6.9 (t, *J* = 7.8 Hz, 1H), 6.5 (d, *J* = 9.9 Hz, 2H), 3.9 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 140.5, 133.0, 131.2, 129.7, 129.2, 128.4, 127.7, 126.1, 126.1, 58.5, 45.9; HRMS m/z (APCI) calcd for $C_{26}H_{22}Cl^+$ $(M + H)^+$ 369.1405; found: 369.1407.



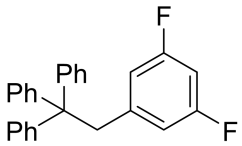
(2-(3,4-dimethylphenyl)ethane-1,1,1-triyl)tribenzene (**3m**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 20.3 mg, 56%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (s, 1H), 7.2 (d, *J* = 4.3 Hz, 11H), 7.2 (q, *J* = 3.9 Hz, 3H), 6.7 (d, *J* = 7.8 Hz, 1H), 6.4 (d, *J* = 6.8 Hz, 1H), 6.3 (s, 1H), 3.9 (s, 2H), 2.1 (s, 3H), 2.0 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 135.6, 135.1, 133.9, 132.8, 129.9, 128.5, 128.4, 127.5, 125.8, 58.4, 45.9, 19.5, 19.2; HRMS m/z (APCI) calcd for $C_{28}H_{27}^+$ $(M + H)^+$ 363.2107; found: 363.2100.



(2-(3,5-dimethoxyphenyl)ethane-1,1,1-triyl)tribenzene (**3n**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 25.2 mg, 64%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 4.1 Hz, 12H), 7.2 (h, *J* = 4.1 Hz, 3H), 6.2 (s, 1H), 5.8 (s, 2H), 3.9 (s, 2H), 3.5 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 146.6, 140.7, 129.8, 127.6, 125.9, 108.9, 99.0, 58.4, 55.0, 46.7; HRMS m/z (APCI) calcd for $C_{28}H_{27}O_2^+$ $(M + H)^+$ 395.2006; found: 395.1998.

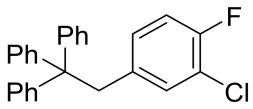


(2-(3,4-dichlorophenyl)ethane-1,1,1-triyl)tribenzene (**3o**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 27.7 mg, 69%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, *J* = 6.7 Hz, 15H), 7.1 – 7.0 (t, 1H), 6.6 (s, 1H), 6.5 (d, *J* = 8.3 Hz, 1H), 3.8 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 138.7, 133.0, 130.3, 129.6, 129.4, 129.1, 128.3, 127.8, 126.2, 58.4, 45.4; HRMS m/z (APCI) calcd for $C_{26}H_{21}Cl_2^+$ $(M + H)^+$ 403.1015; found: 403.1007.

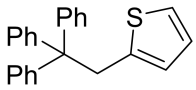


(2-(3,5-difluorophenyl)ethane-1,1,1-triyl)tribenzene (**3p**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 22.6 mg, 61%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.2 (m, 3H), 7.2 – 7.1 (m, 11H), 7.1 – 7.0 (m, 1H), 6.5 (t, *J* = 9.0 Hz, 1H), 6.1 (d, *J* = 6.6 Hz, 2H), 3.9 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ163.2 (d, *J* = 13.13 Hz), 160.7 (d, *J* = 1.01 Hz), 146.0, 142.5 (t, *J* = 13.9.09 Hz), 129.5, 127.8, 126.3, 113.9, 113.8 (d, *J* = 6.06 Hz), 113.7 (d, *J* = 7.07 Hz),

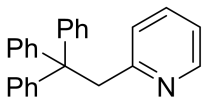
101.5 (t, J = 25.25 Hz), 58.5, 46.0 (t, J = 1.01 Hz); HRMS m/z (APCI) calcd for $C_{26}H_{21}F_2^+$ (M + H)$^+$ 371.1606; found: 371.1603.



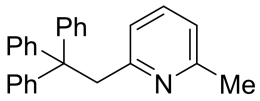
(2-(3-chloro-4-fluorophenyl)ethane-1,1,1-triyl)tribenzene (**3q**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 22.0 mg, 57%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.1 (m, 15H), 6.7 (t, J = 8.7 Hz, 1H), 6.6 – 6.5 (m, 2H), 3.8 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, (d, J = 46.5 Hz), 146.1, 135.4 (d, J = 4.0 Hz), 133.0, 130.5 (d, J = 7.07 Hz), 129.6, 128.8 (d, J = 10.1 Hz), 127.7, 126.2, 119.5 (d, J = 17.2 Hz), 115.2 (d, J = 21.2 Hz), 58.5, 45.2; GCMS (EI) m/z 385 (M)$^+$.



2-(2,2,2-triphenylethyl)thiophene (**3r**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 23.5 mg, 69%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, J = 7.7, 7.0 Hz, 15H), 6.9 (d, J = 5.1 Hz, 1H), 6.7 (t, J = 4.1 Hz, 1H), 6.3 (d, J = 3.4 Hz, 1H), 4.1 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 140.7, 129.6, 127.9, 127.7, 126.2, 125.7, 124.3, 58.1, 41.8; HRMS m/z (APCI) calcd for $C_{24}H_{21}S^+$ (M + H)$^+$ 341.1358; found: 341.1352.

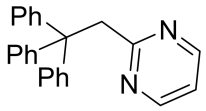


2-(2,2,2-triphenylethyl)pyridine (**3s**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 24.5 mg, 73%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.3 (d, J = 3.6 Hz, 1H), 7.3 (d, J = 7.7 Hz, 6H), 7.3 – 7.1 (m, 10H), 6.9 (dd, J = 7.5, 5.0 Hz, 1H), 6.3 (d, J = 7.9 Hz, 1H), 4.2 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 148.3, 146.7, 135.0, 129.7, 127.7, 126.0, 125.0, 121.0, 58.2, 49.0; HRMS m/z (APCI) calcd for $C_{25}H_{21}NNa^+$ (M + Na)$^+$ 358.1566; found: 358.1568.

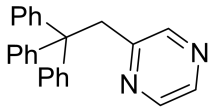


2-methyl-6-(2,2,2-triphenylethyl)pyridine (**3t**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 26.5 mg, 76%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (d, J = 7.8

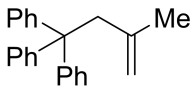
Hz, 6H), 7.2 (dd, *J* = 7.5 Hz, 6H), 7.2 (t, *J* = 7.3 Hz, 3H), 7.1 (t, *J* = 7.8 Hz, 1H), 6.8 (d, *J* = 7.6 Hz, 1H), 6.1 (d, *J* = 7.9 Hz, 1H), 4.2 (s, 2H), 2.4 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 156.7, 146.8, 135.3, 129.8, 127.6, 125.9, 121.7, 120.3, 58.1, 49.0, 24.3; HRMS m/z (APCI) calcd for $C_{26}H_{24}N^+$ $(M + H)^+$ 350.1903; found: 350.1907.



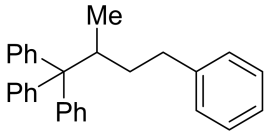
2-(2,2,2-triphenylethyl)pyrimidine (**3u**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 13.8 mg, 41%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.3 (d, *J* = 4.9 Hz, 2H), 7.3 (d, *J* = 8.0 Hz, 6H), 7.2 (t, *J* = 7.4 Hz, 6H), 7.1 (t, *J* = 7.2 Hz, 3H), 6.9 (t, *J* = 4.9 Hz, 1H), 4.4 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 155.9, 147.0, 129.6, 127.4, 125.8, 118.0, 58.2, 49.9; HRMS m/z (APCI) calcd for $C_{24}H_{21}N_2^+$ $(M + H)^+$ 337.1699; found: 337.1697.



2-(2,2,2-triphenylethyl)pyrazine (**3v**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 19.8 mg, 59%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.3 – 8.3 (m, 1H), 8.2 (d, *J* = 2.6 Hz, 1H), 7.5 (d, *J* = 1.6 Hz, 1H), 7.4 – 7.3 (m, 6H), 7.3 – 7.2 (m, 6H), 7.2 – 7.1 (m, 3H), 4.2 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 146.4, 146.2, 143.0, 141.6, 129.5, 127.8, 126.2, 58.4, 46.3; HRMS m/z (APCI) calcd for $C_{24}H_{21}N_2^+$ $(M + H)^+$ 337.1699; found: 337.1693.



(3-methylbut-3-ene-1,1,1-triyl)tribenzene (**3w**)[3]. According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent and 1.0 equiv 2,2,2-triphenylacetic acid reagent with reaction time of 6 h at room temperature; 25.3 mg, 85%, purified by flash chromatography, yellow oil; Rf = 0.5 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (dd, J = 13.7, 6.6 Hz, 12H), 7.2 – 7.1 (m, 3H), 4.7 (s, 1H), 4.3 (s, 1H), 3.4 (s, 2H), 1.4 (s, 3H); HRMS m/z (APCI) calcd for $C_{23}H_{23}^+$ $(M + H)^+$ 299.1794; found: 299.1790.

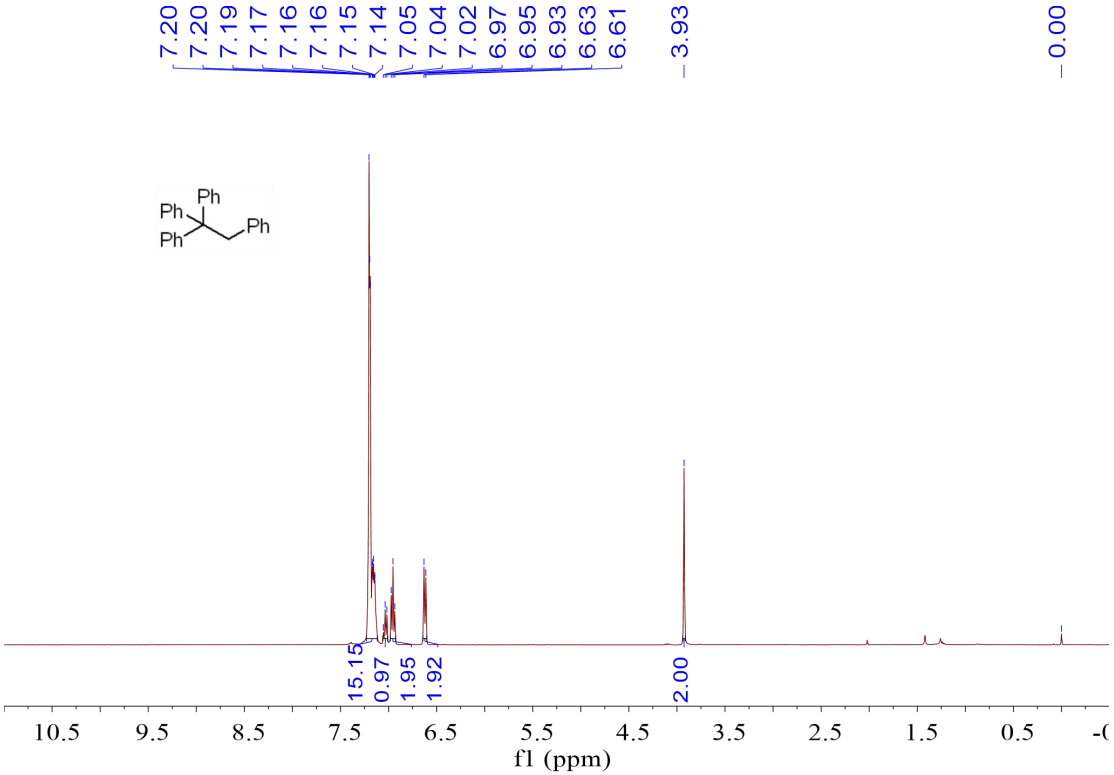


(2-methylbutane-1,1,1,4-tetrayl)tetrabenzene (**3x**). According to the general procedure in 0.1 mmol scale using 1.0 equiv $KHCO_3$ reagent, 1.0 equiv 2,2,2-triphenylacetic acid and 2.0 equiv **1x** in 2.0 mL DMSO with reaction time of 48 h at room temperature; 19.9 mg, 53%, purified by flash

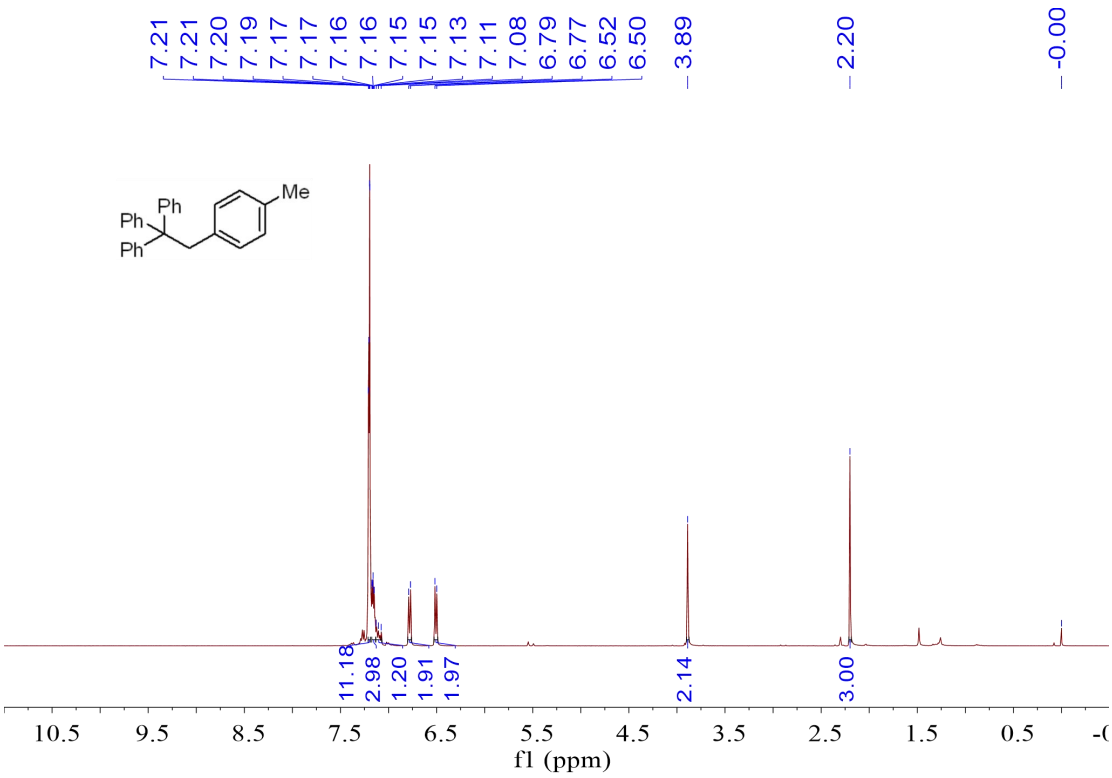
chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (t, *J* = 7.4 Hz, 5H), 7.2 (t, *J* = 6.4 Hz, 7H), 7.1 (d, *J* = 7.8 Hz, 6H), 7.1 – 6.9 (m, 2H), 3.3 (dt, *J* = 12.8, 6.5 Hz, 1H), 2.8 (ddd, *J* = 14.0, 9.4, 4.9 Hz, 1H), 2.7 – 2.6 (m, 1H), 2.1 – 1.9 (m, 1H), 1.0 (d, *J* = 6.4 Hz, 3H), 0.8 (dtd, *J* = 13.8, 9.3, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 129.4, 129.4, 128.7, 128.3, 126.9, 126.2, 125.8, 61.9, 35.3, 35.1, 34.2, 16.1; HRMS m/z (APCI) calcd for $C_{29}H_{29}^{+}$ $(M + H)^{+}$ 377.2264; found: 377.2267.

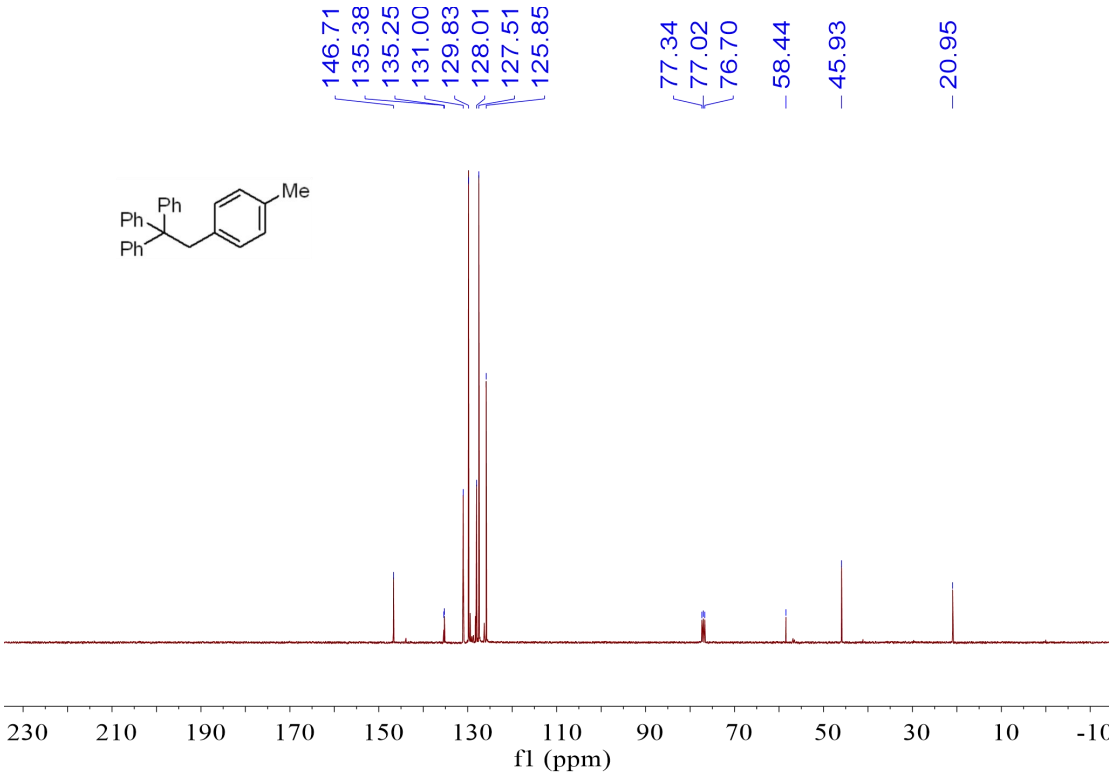
6. NMR spectra of products

ethane-1,1,1,2-tetrayltetrabenzene (**3a**)

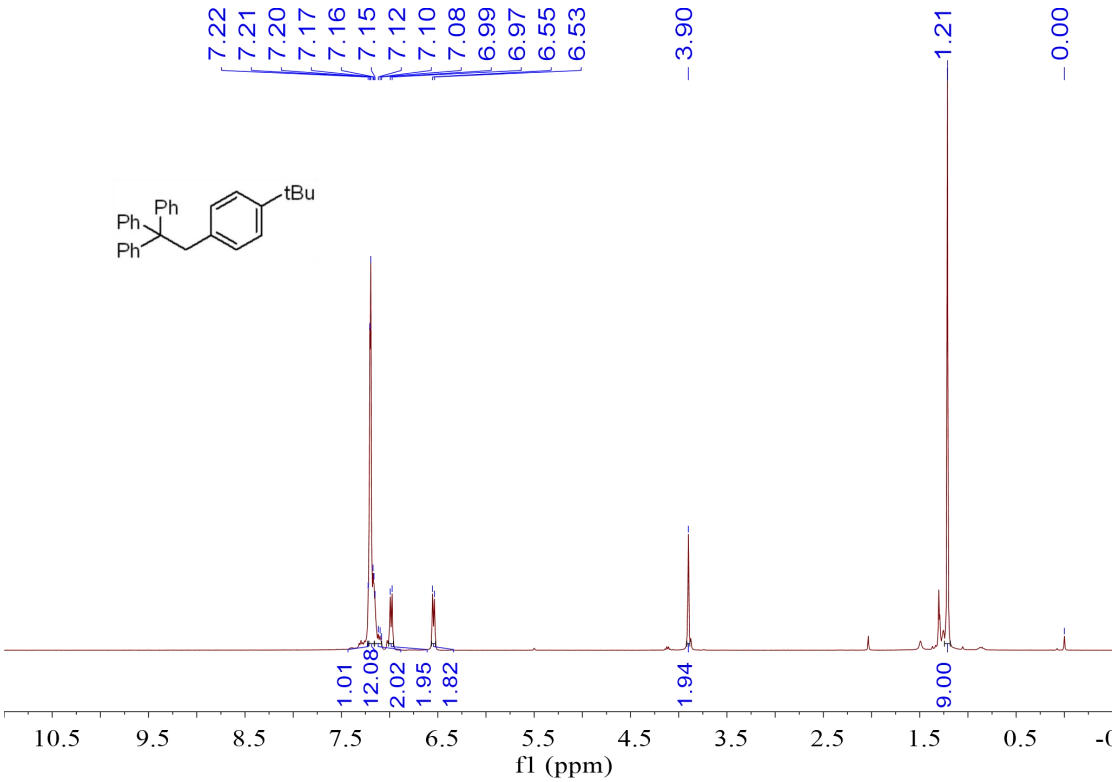


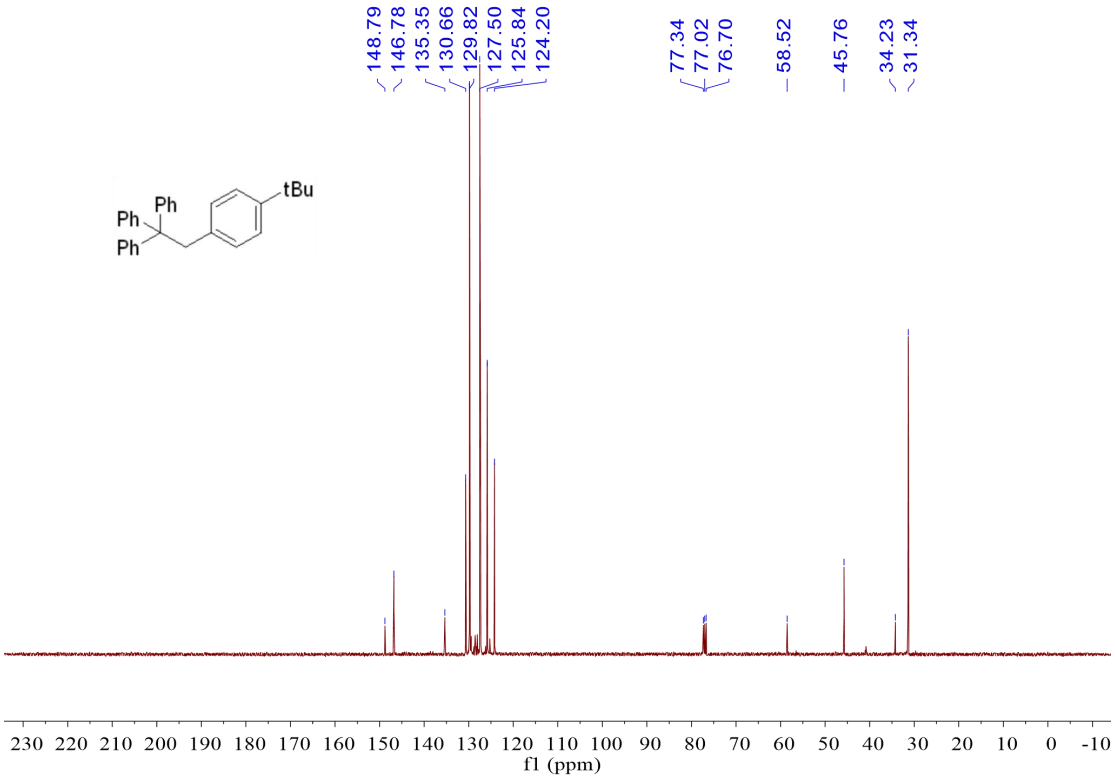
(2-(p-tolyl)ethane-1,1,1-triyl)tribenzene (**3b**)



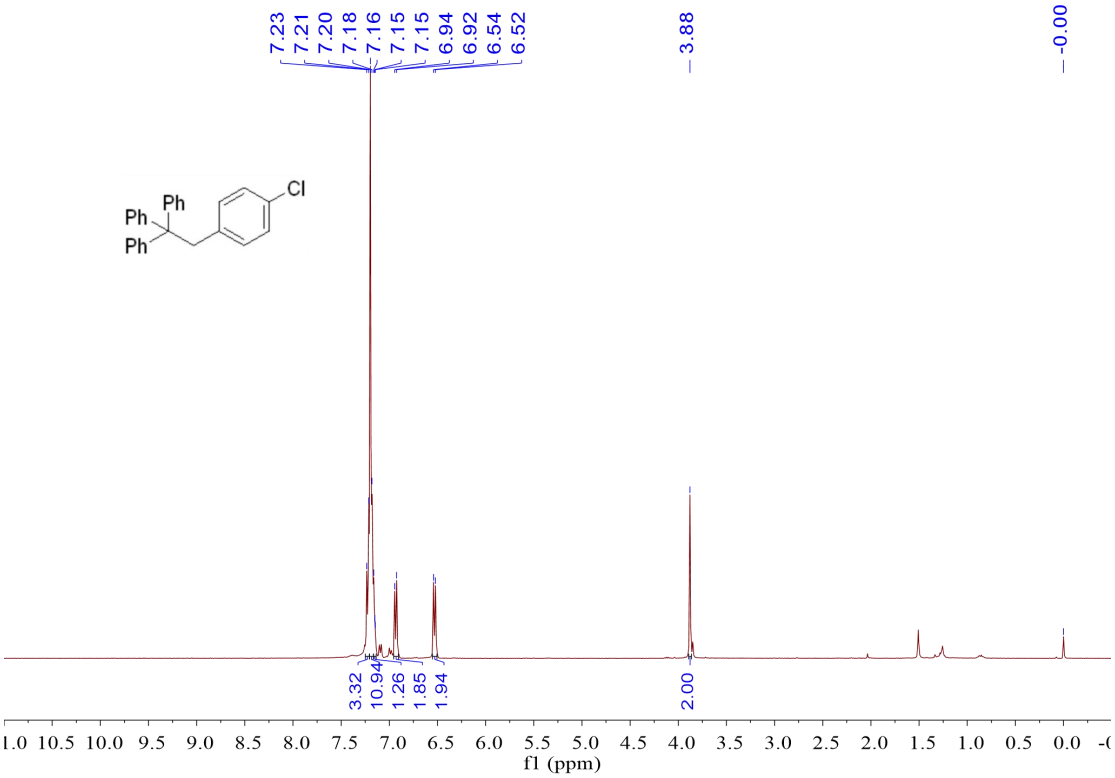


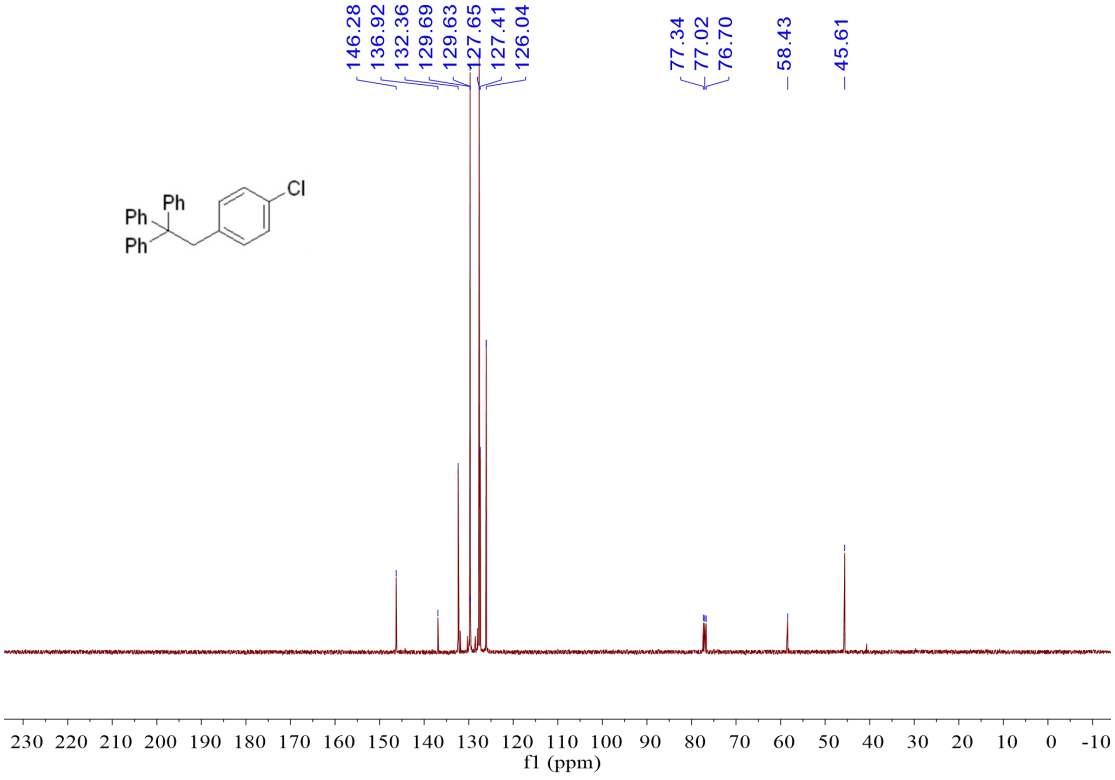
(2-(4-(tert-butyl)phenyl)ethane-1,1,1-triyl)tribenzene (**3c**)



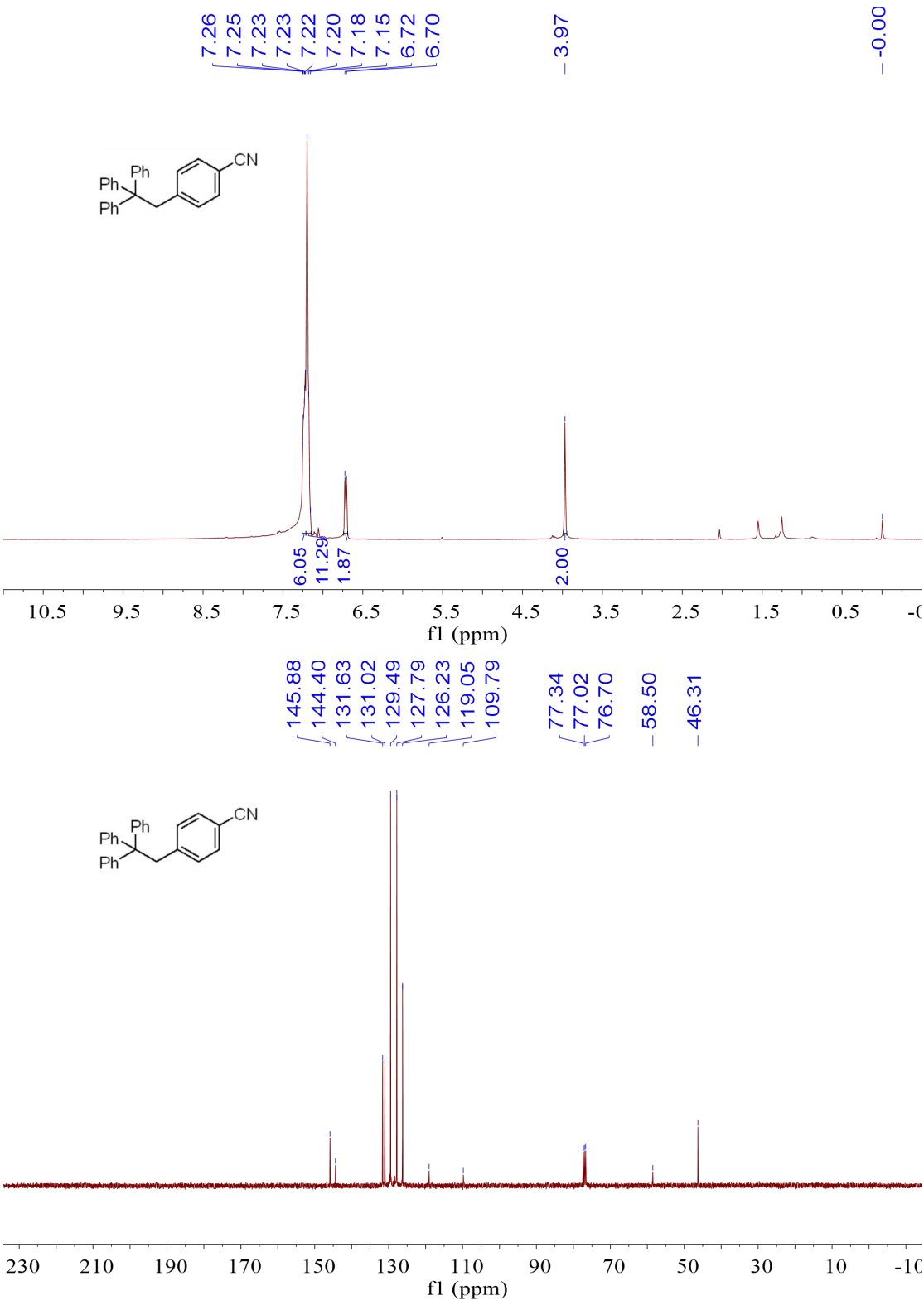


(2-(4-chlorophenyl)ethane-1,1,1-triyl)tribenzene (**3d**)

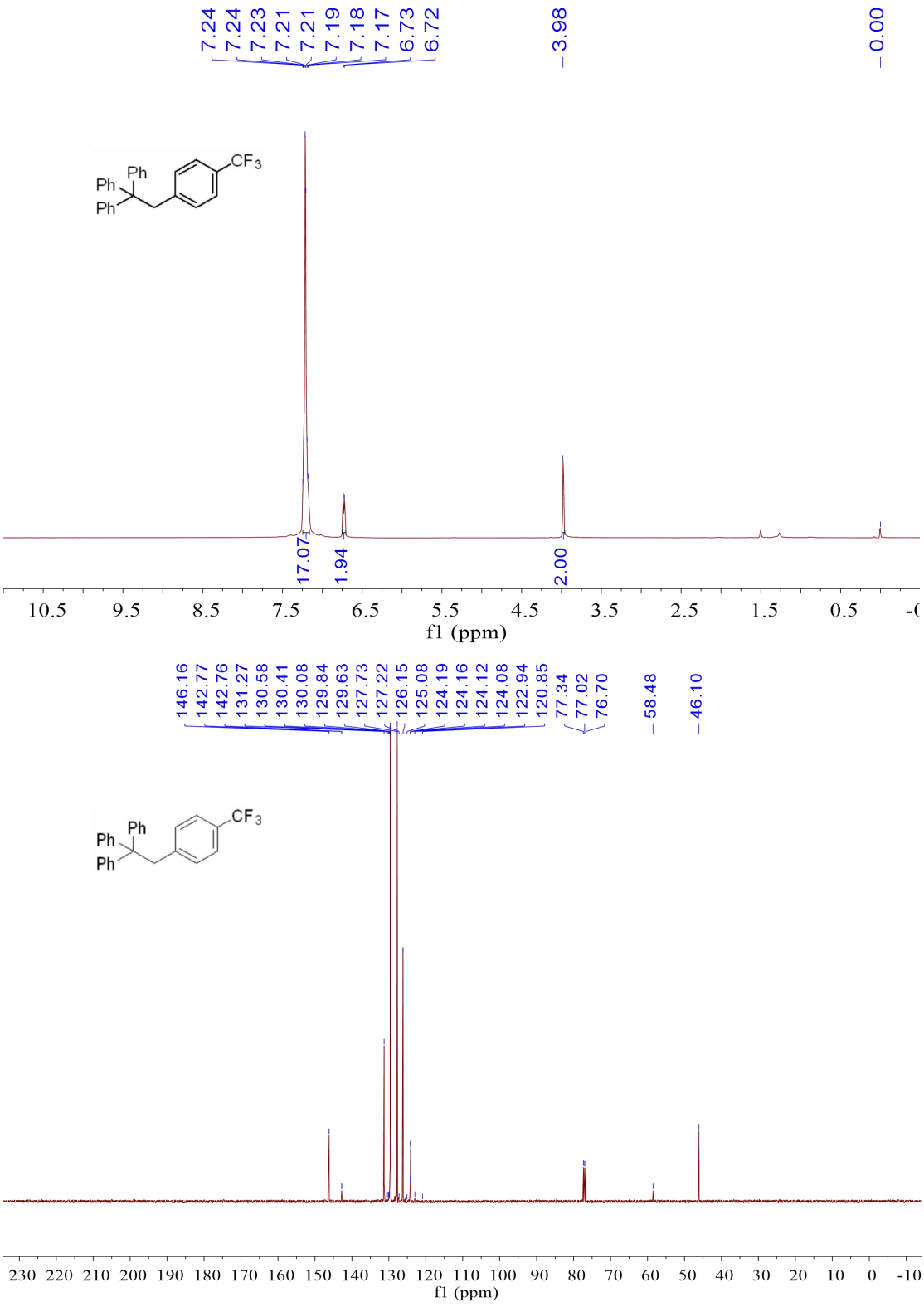




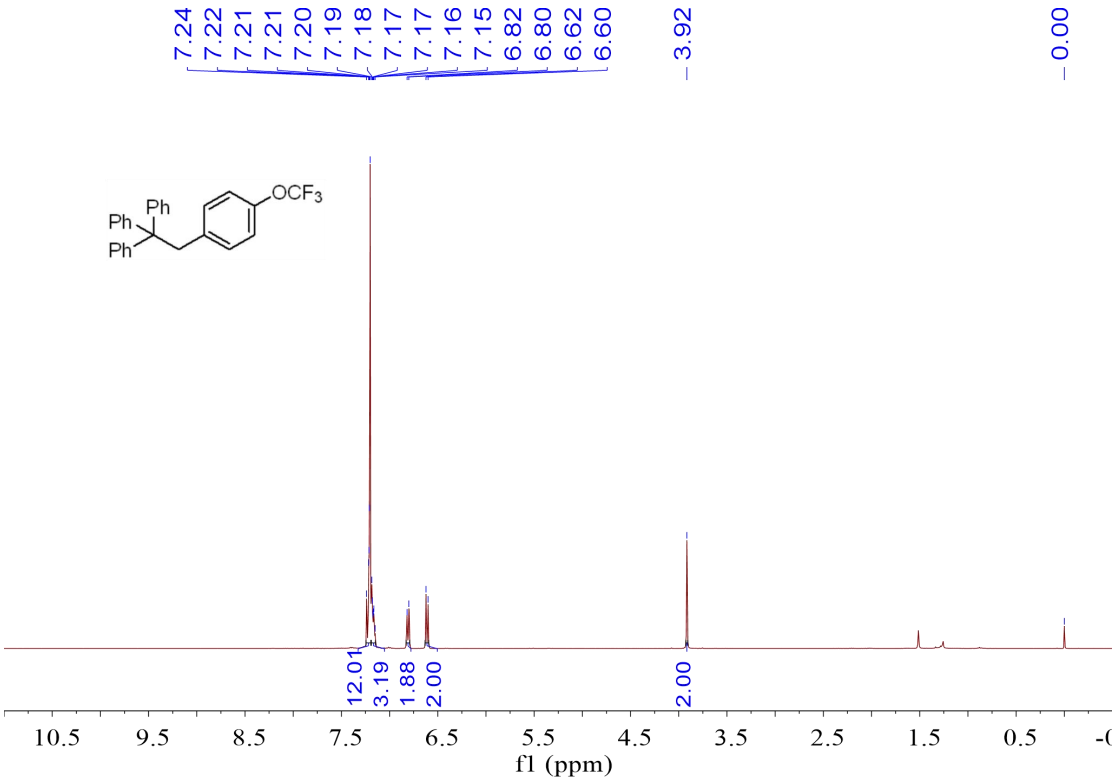
4-(2,2,2-triphenylethyl)benzonitrile (**3e**)

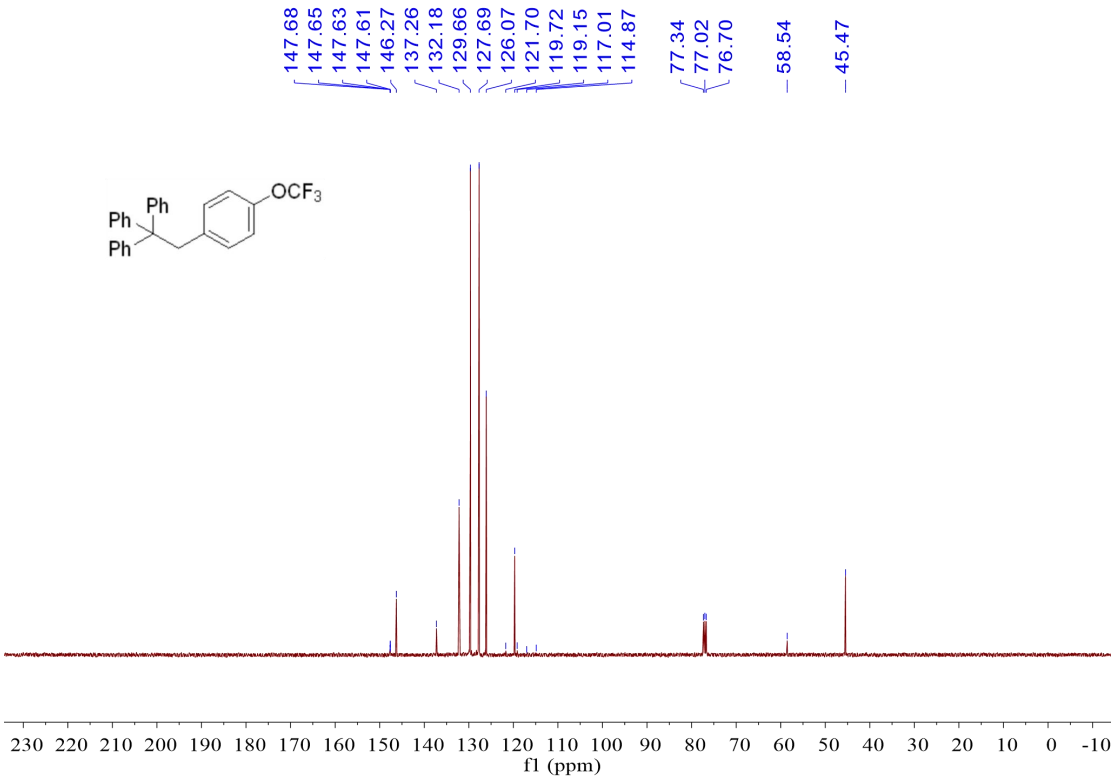


(2-(4-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tribenzene (**3f**)

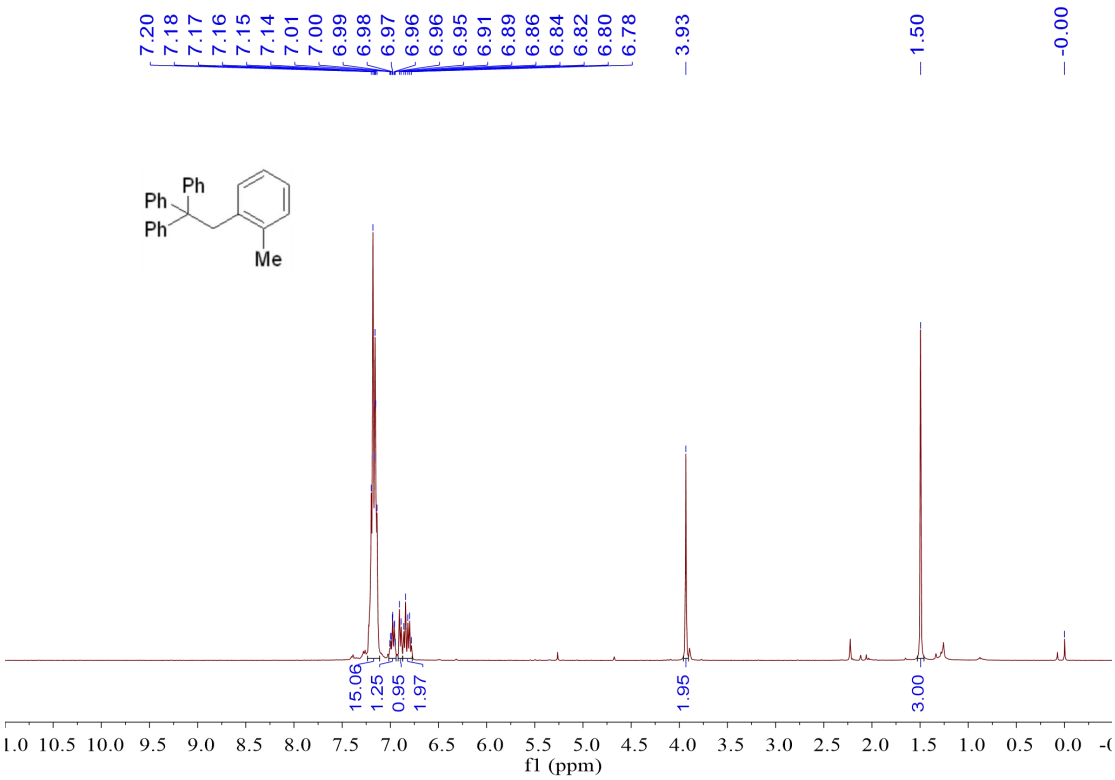


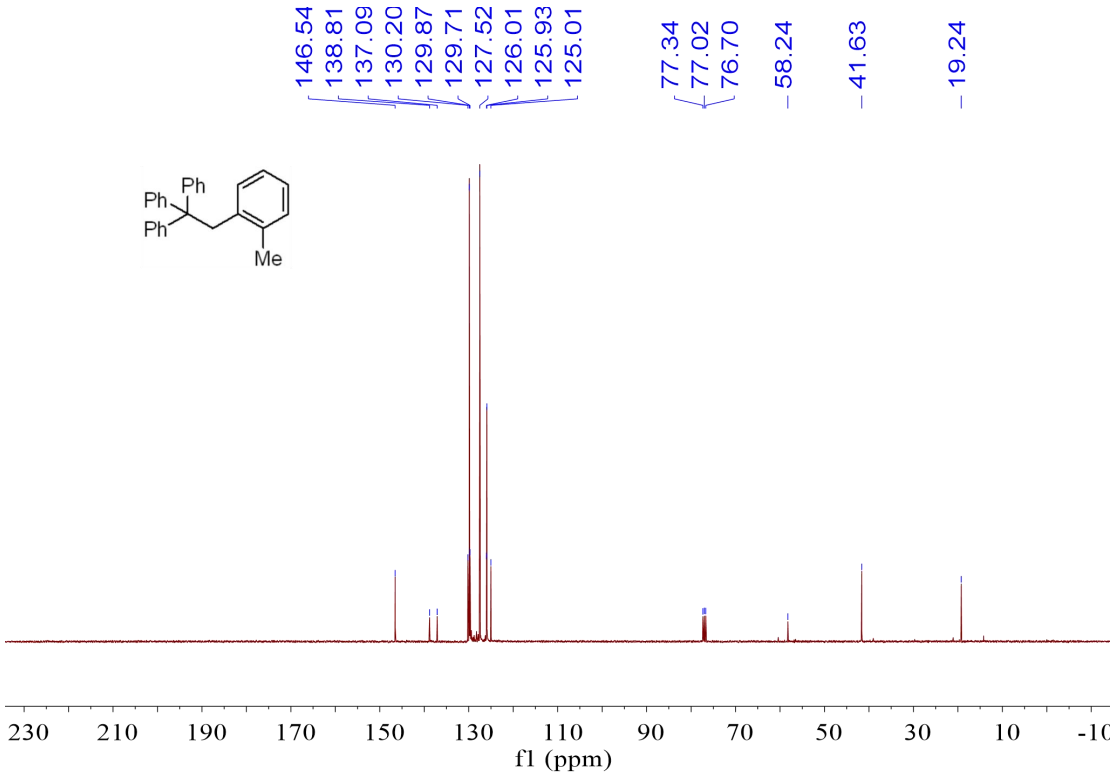
(2-(4-(trifluoromethoxy)phenyl)ethane-1,1,1-triyl)tribenzene (**3g**)



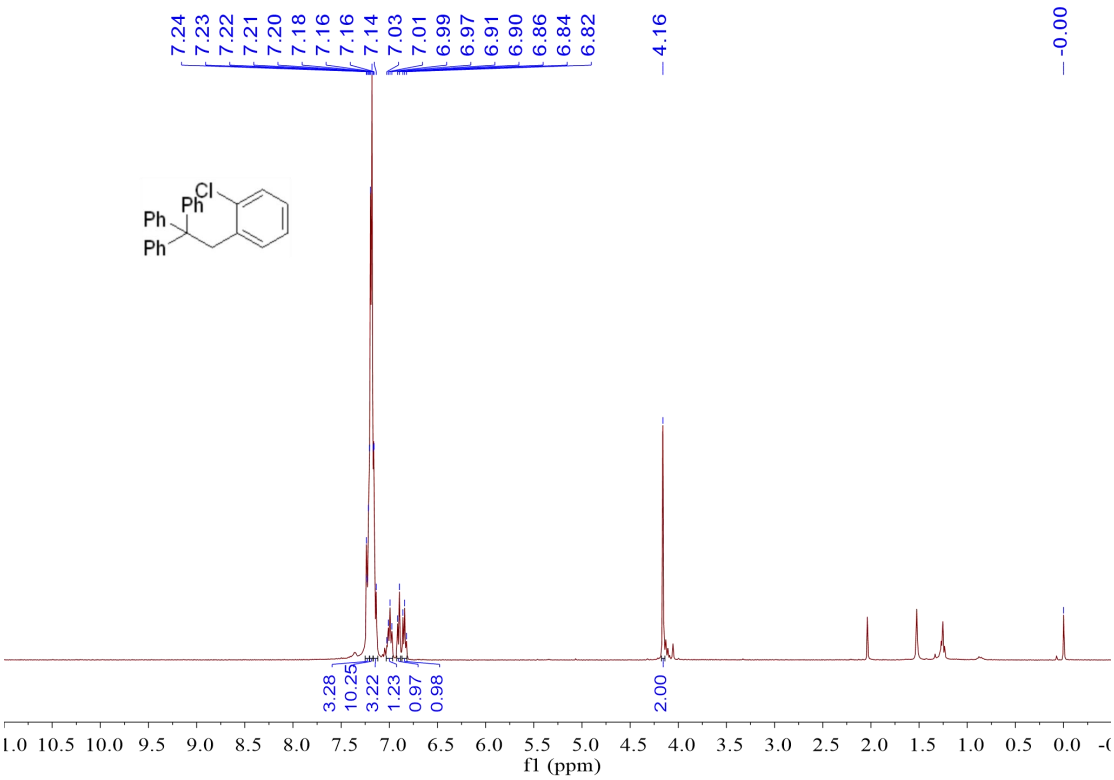


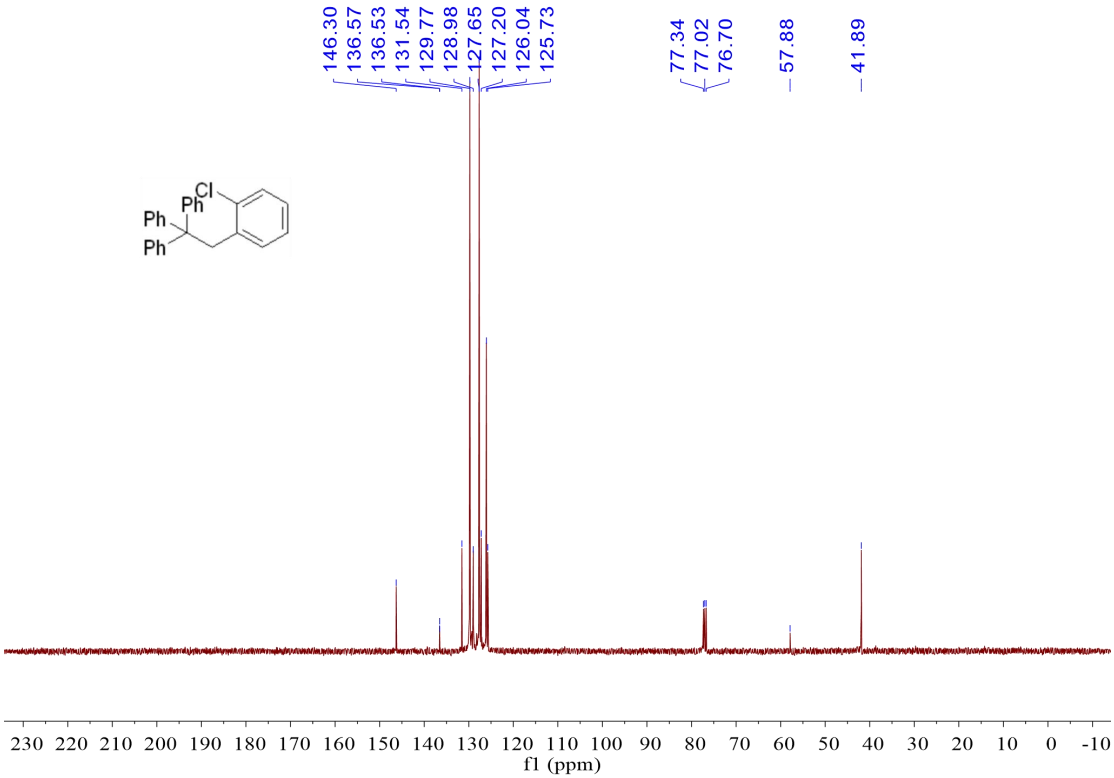
(2-(o-tolyl)ethane-1,1,1-triyl)tribenzene (**3h**)



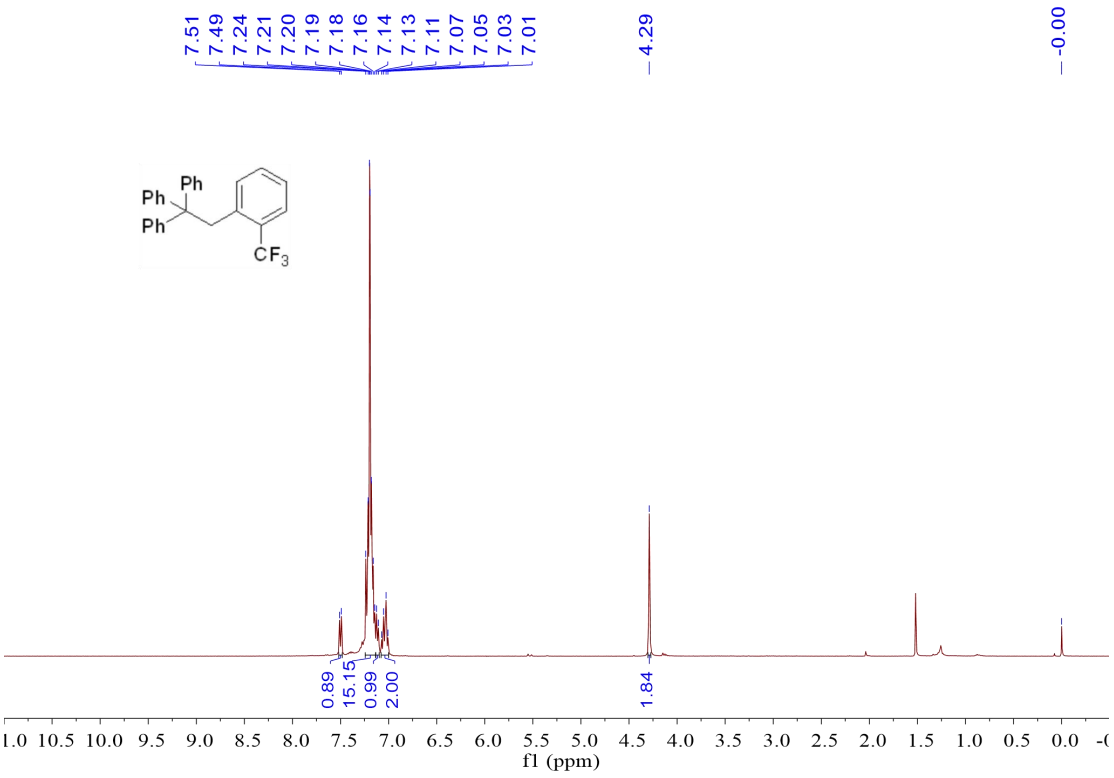


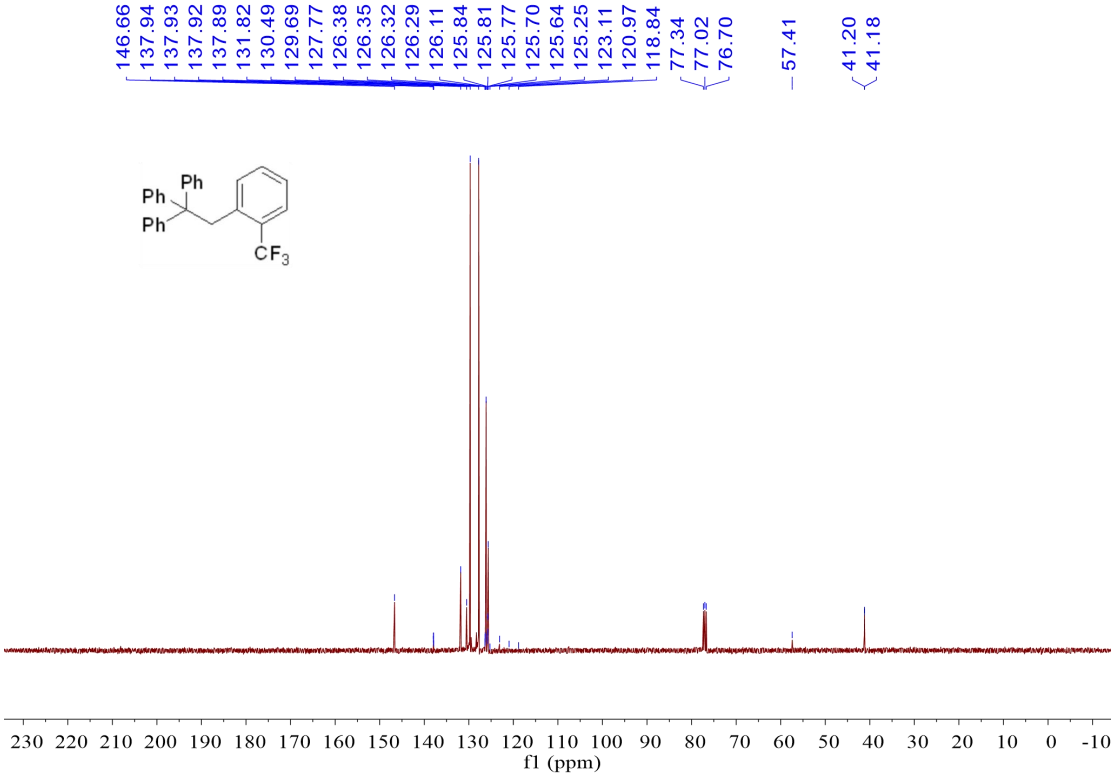
(2-(2-chlorophenyl)ethane-1,1,1-triyl)tribenzene (**3i**)



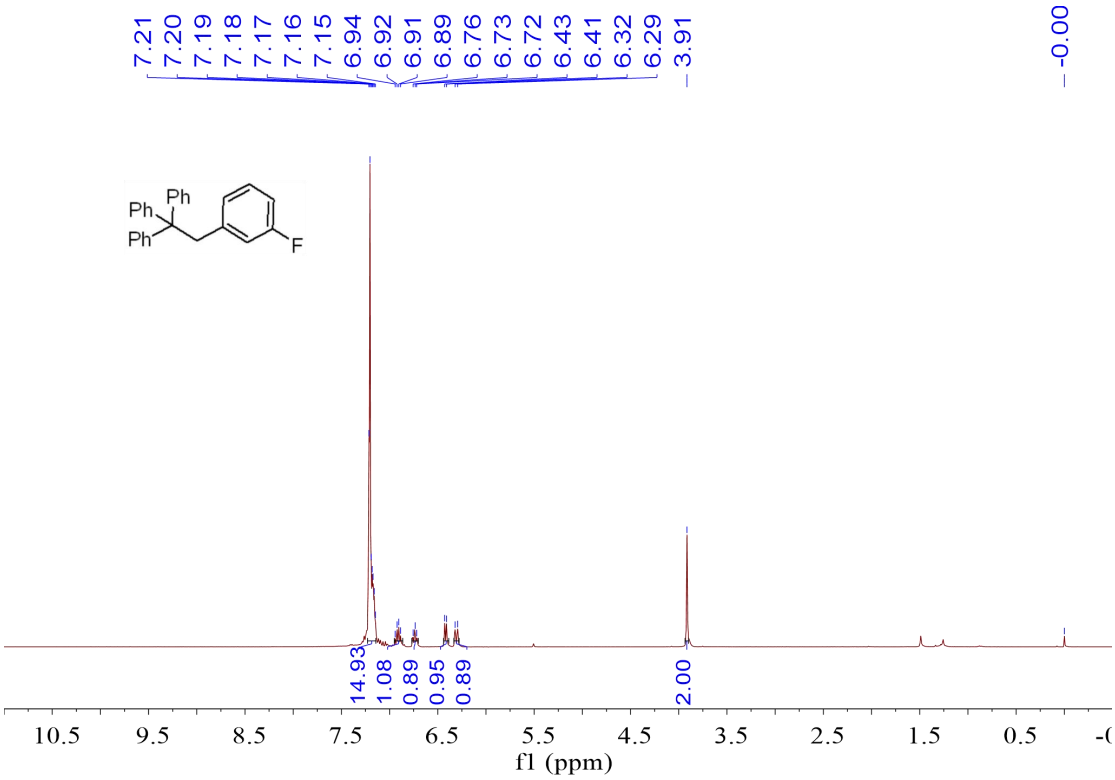


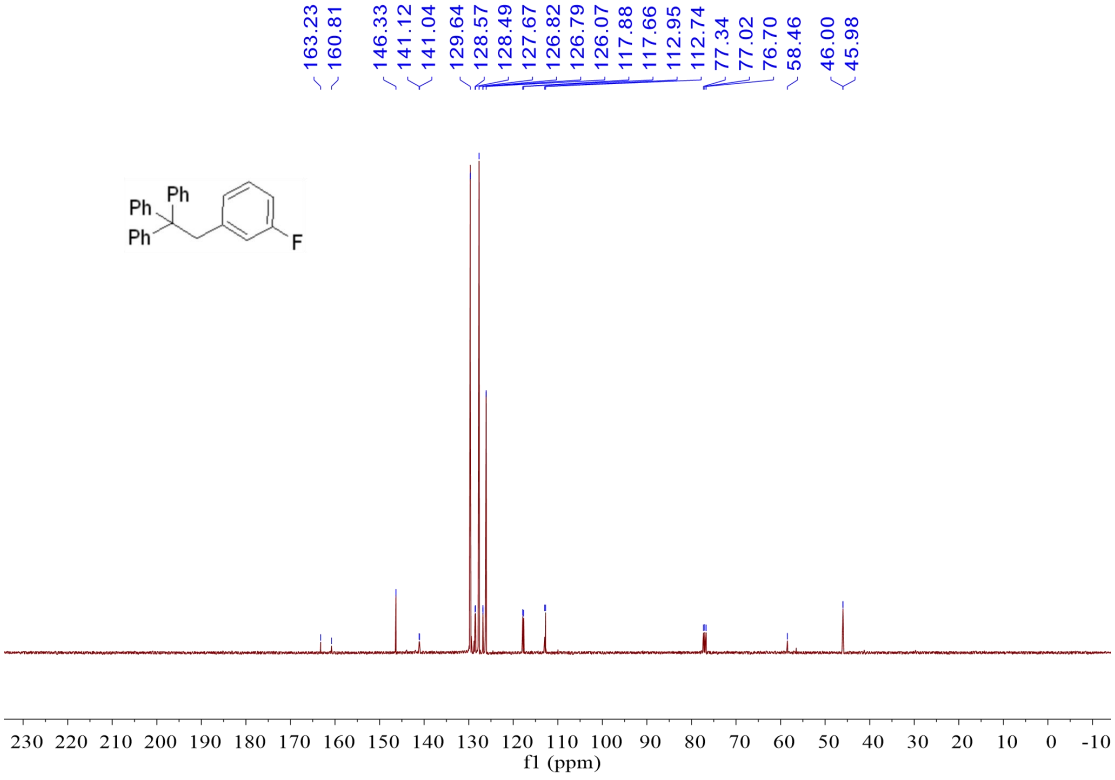
(2-(2-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tribenzene (**3j**)



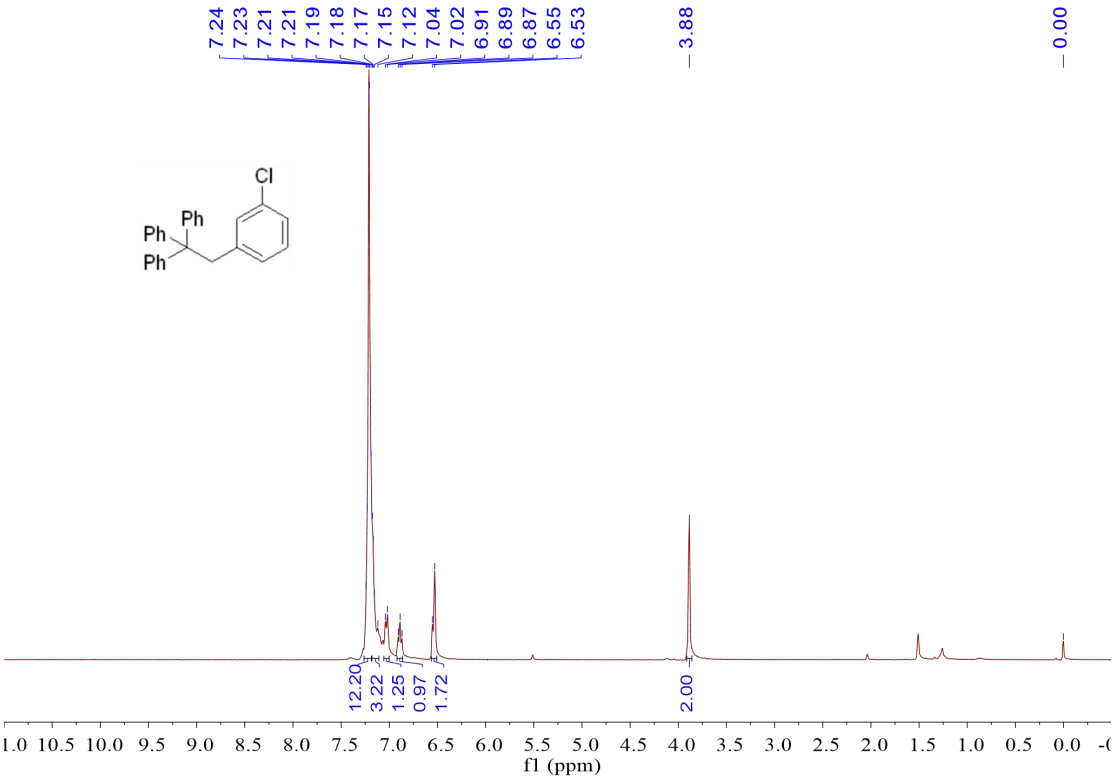


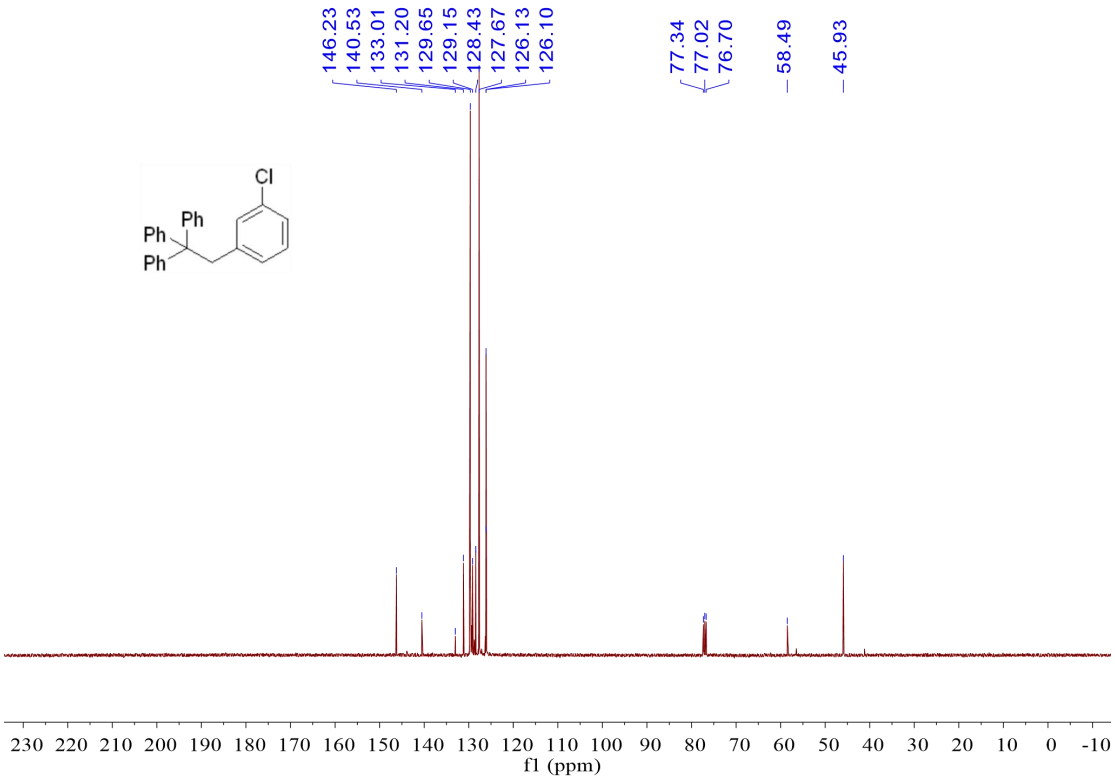
(2-(3-fluorophenyl)ethane-1,1,1-triyl)tribenzene (**3k**)



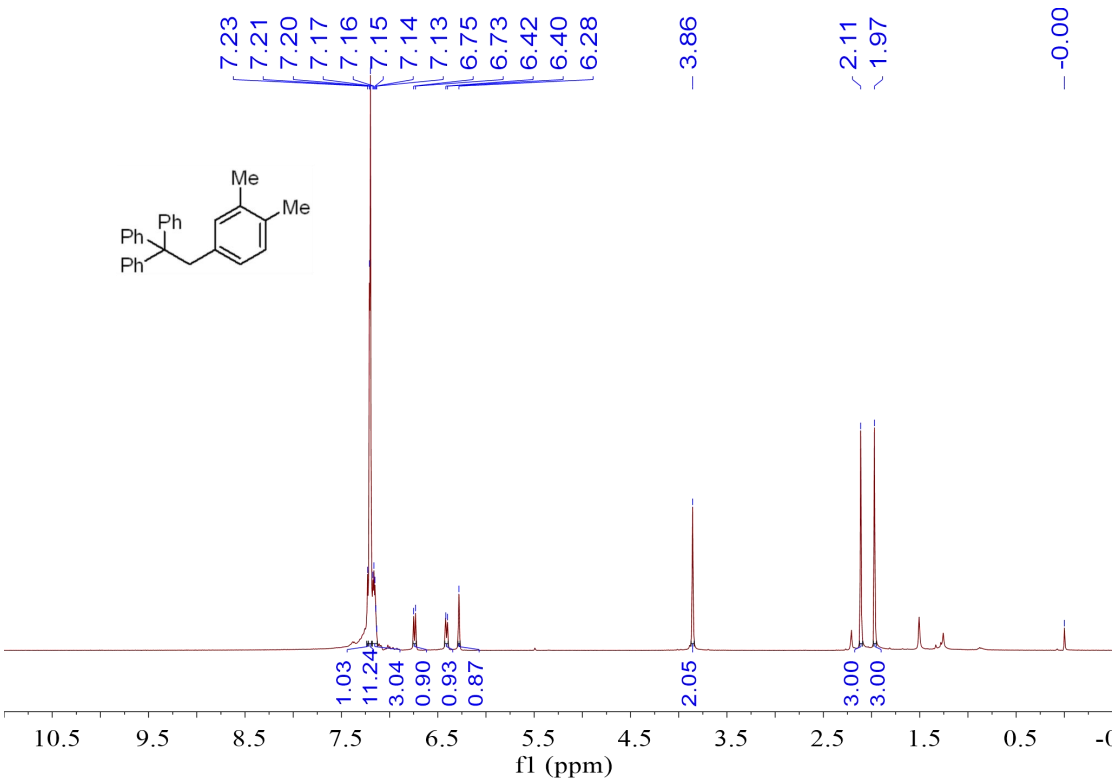


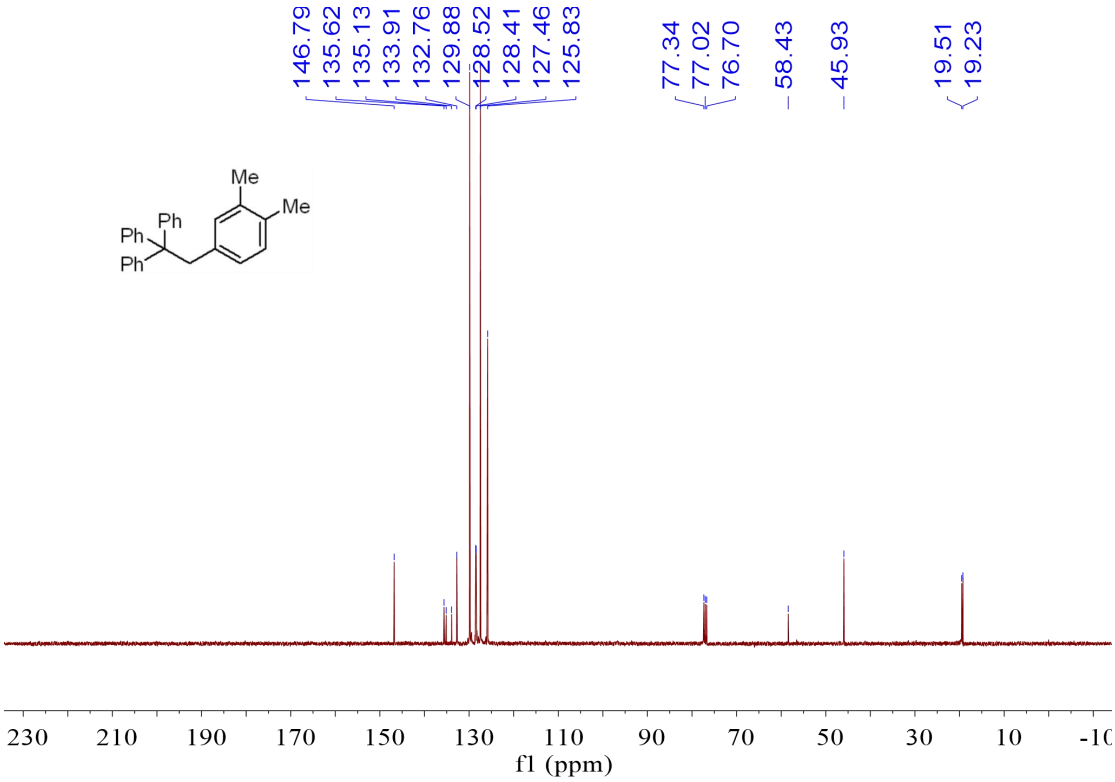
(2-(3-chlorophenyl)ethane-1,1,1-triyl)tribenzene (**3l**)



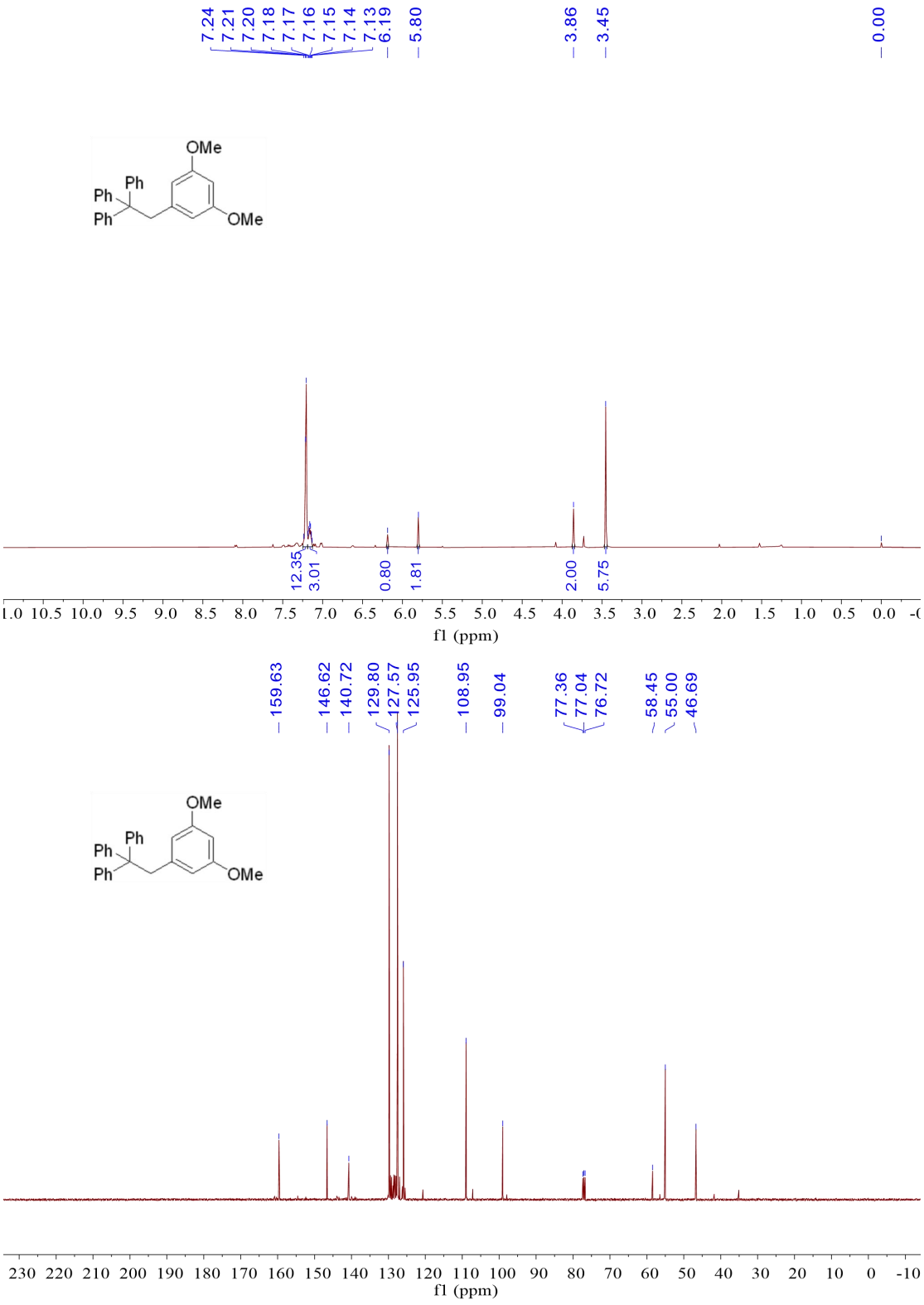


(2-(3,4-dimethylphenyl)ethane-1,1,1-triyl)tribenzene (**3m**)

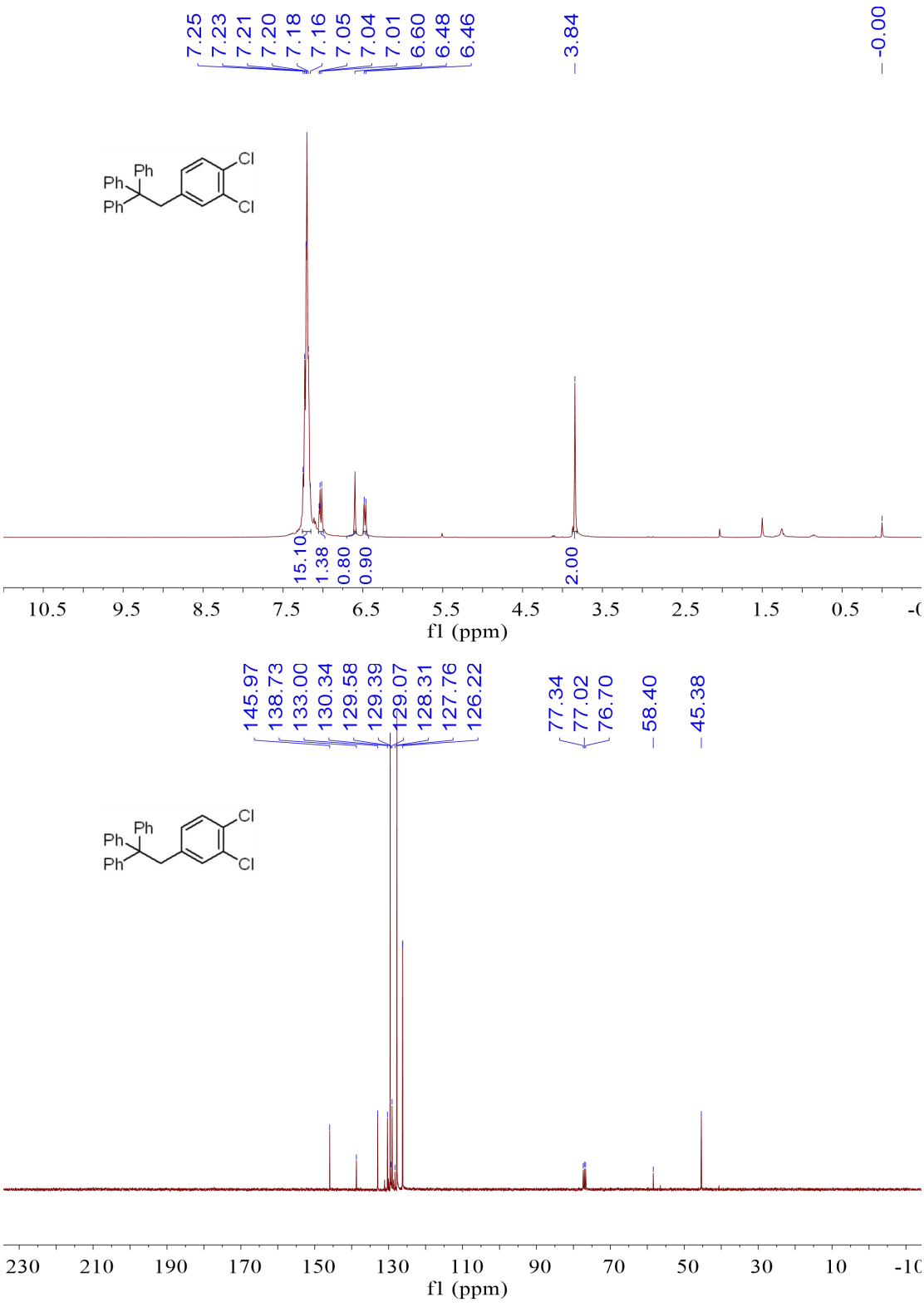




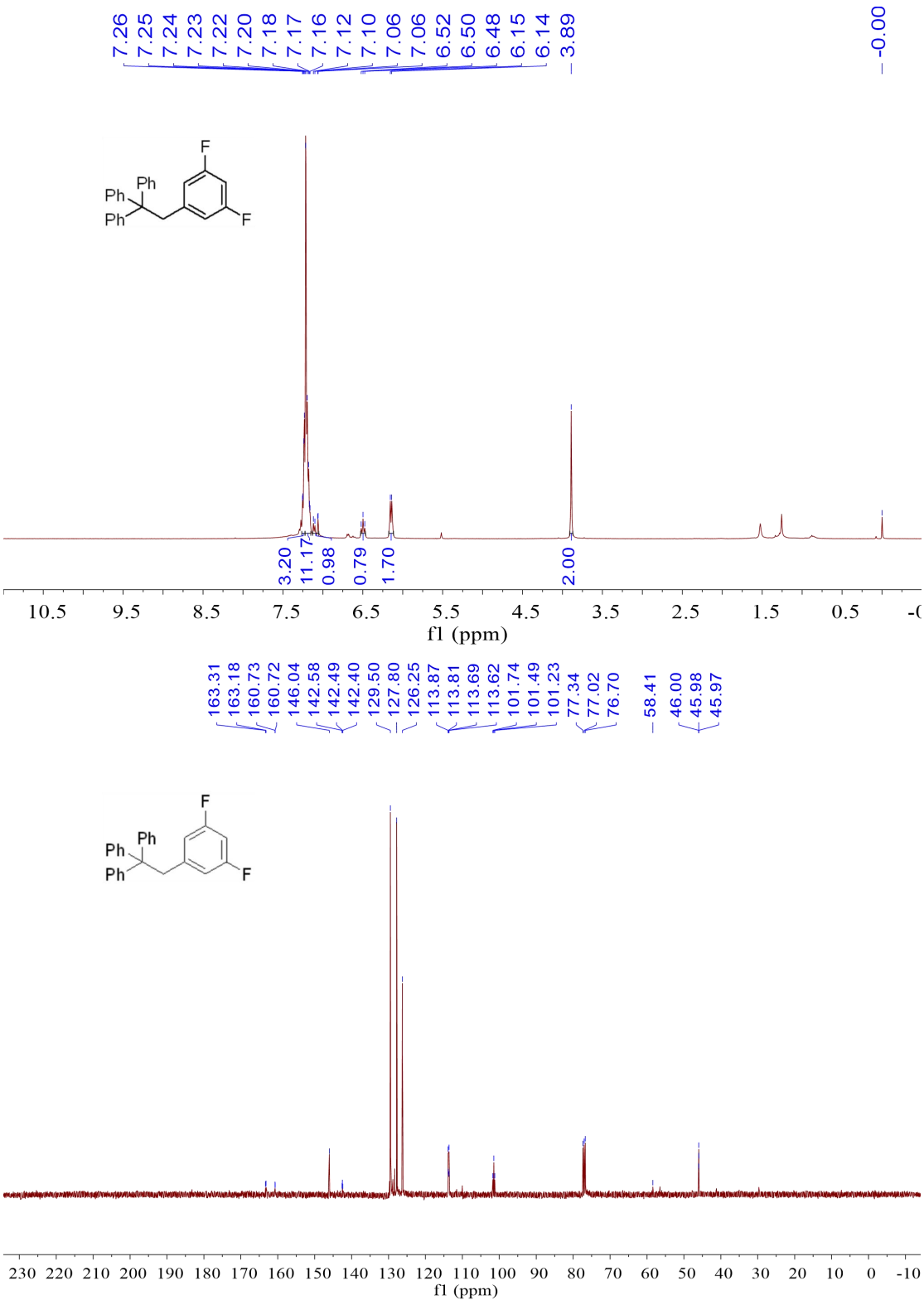
(2-(3,5-dimethoxyphenyl)ethane-1,1,1-triyl)tribenzene (**3n**)



(2-(3,4-dichlorophenyl)ethane-1,1,1-triyl)tribenzene (**3o**)

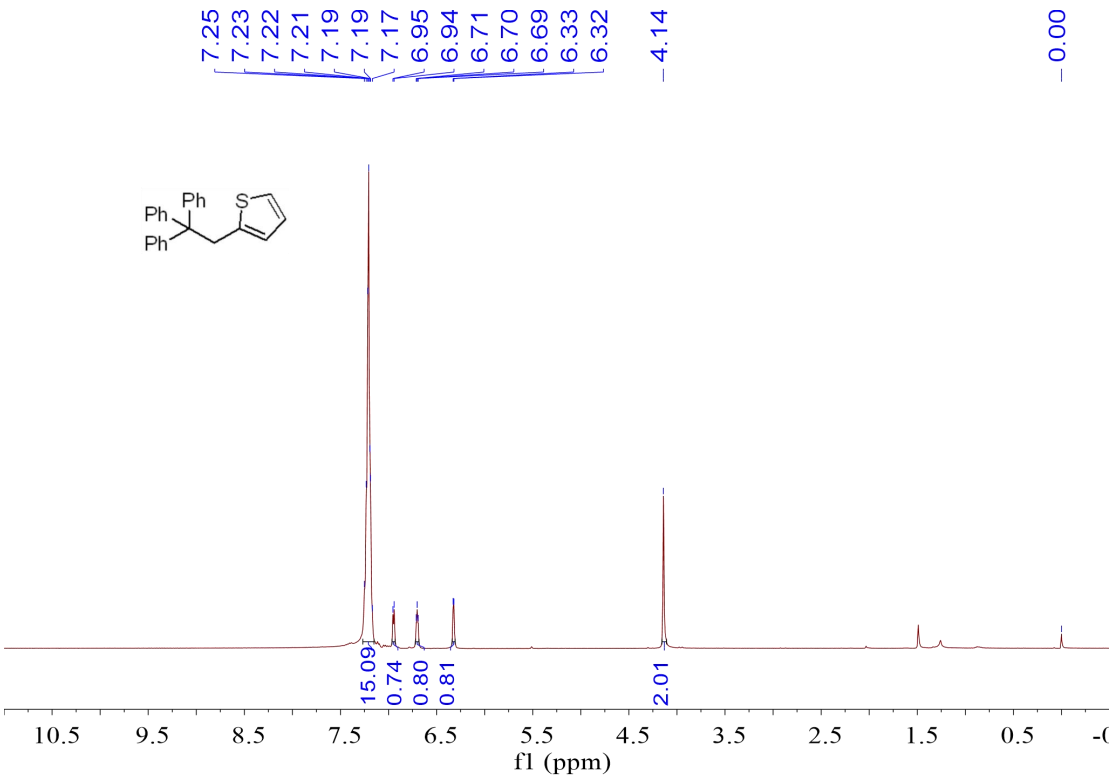


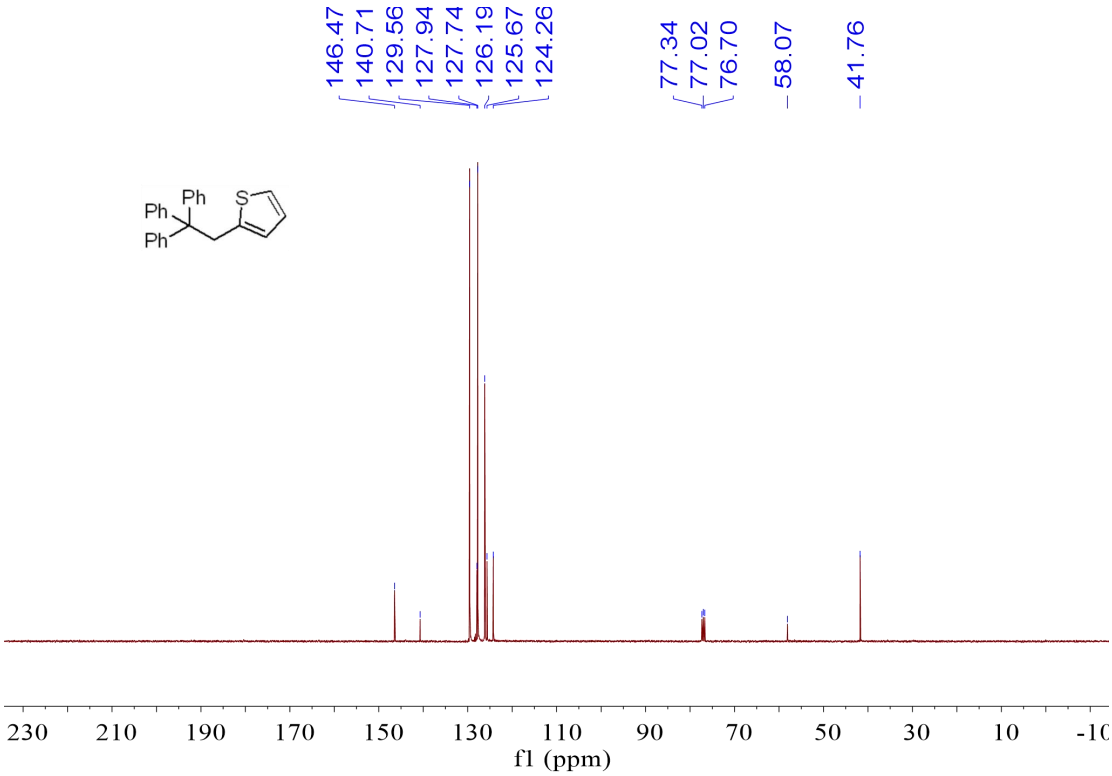
(2-(3,5-difluorophenyl)ethane-1,1,1-triyl)tribenzene (**3p**)



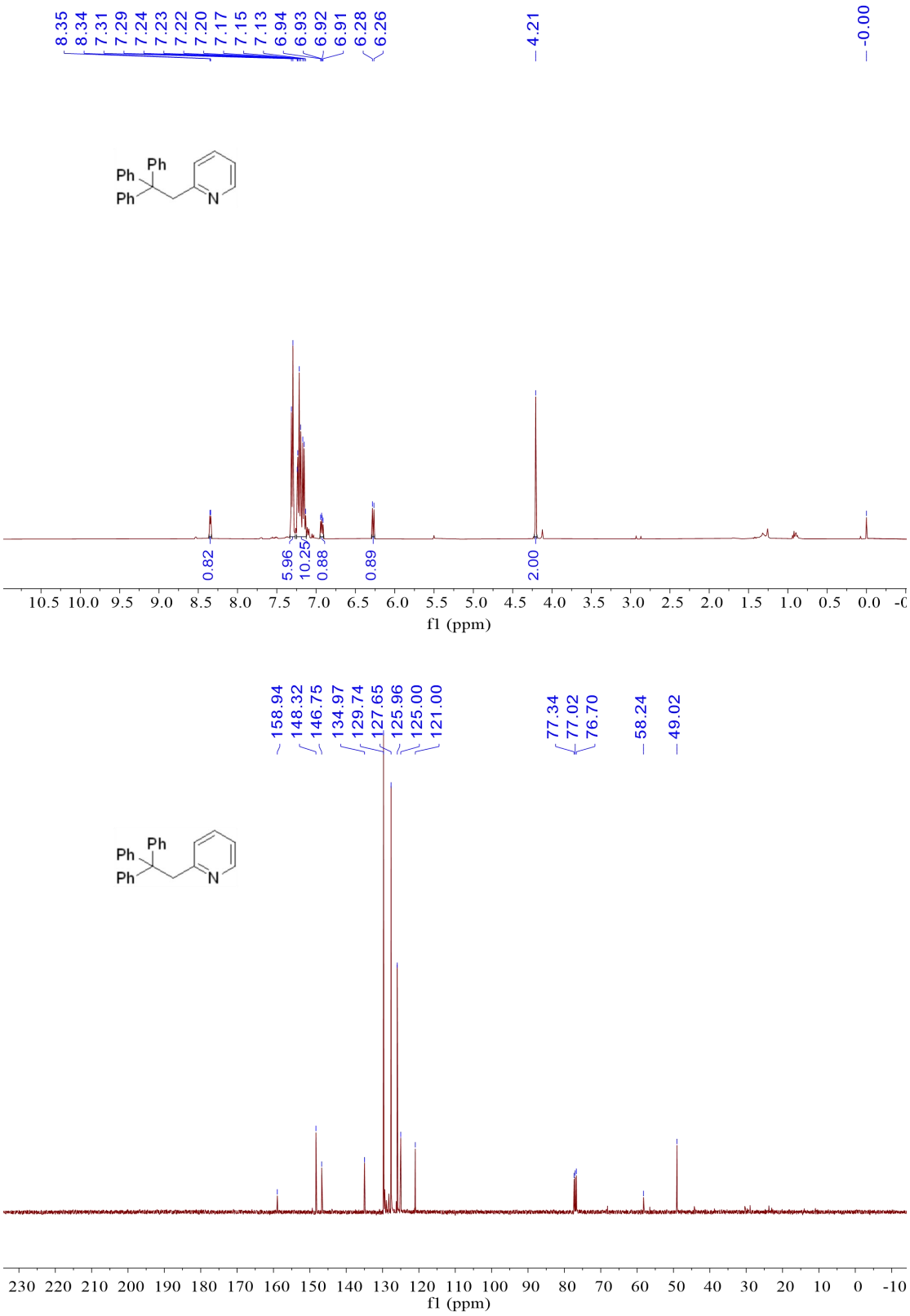
(**3q**) *(2-(3-chloro-4-fluorophenyl)ethane-1,1,1-triyl)tribenzene* (**3q**)

2-(2,2,2-triphenylethyl)thiophene (**3r**)

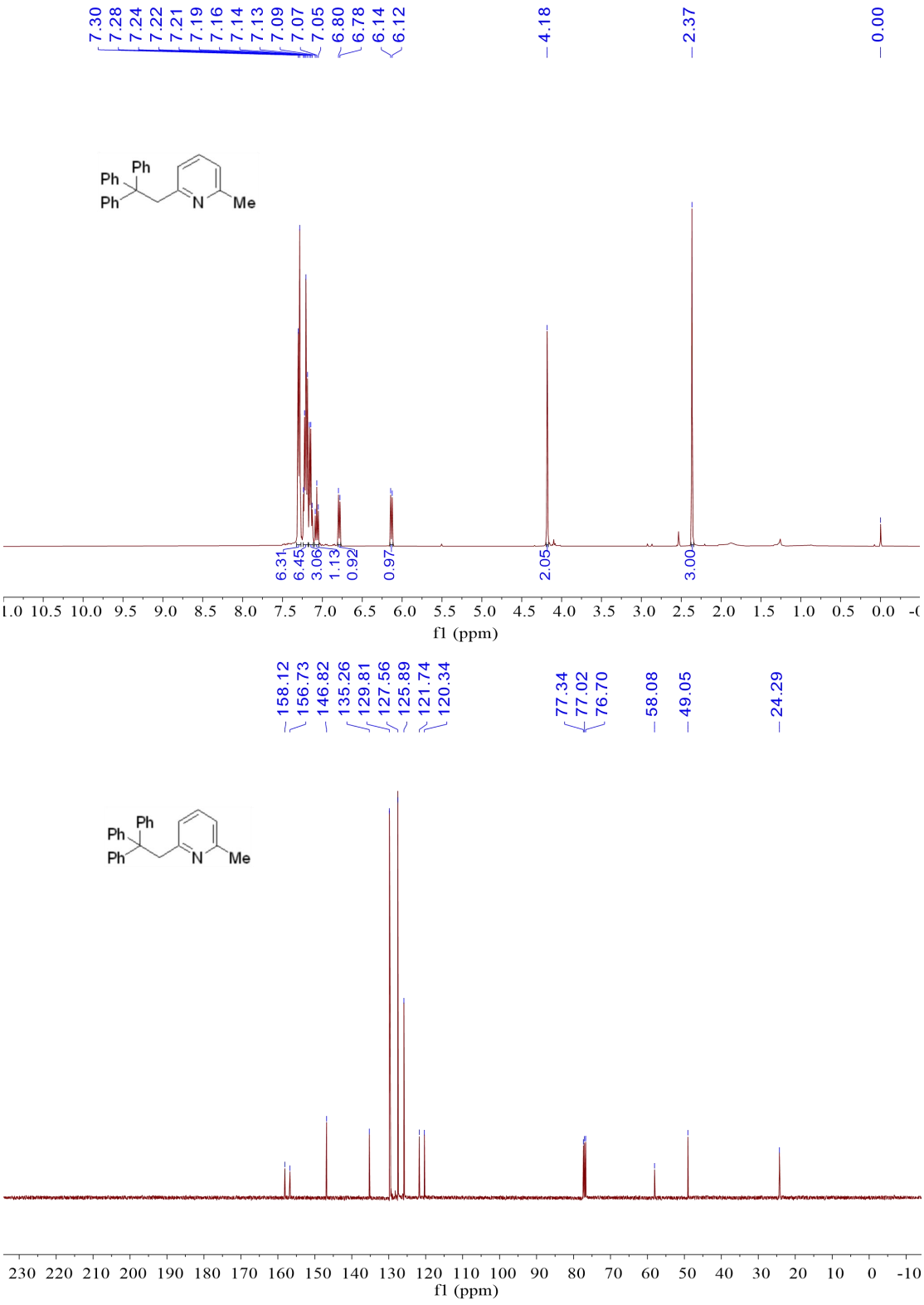




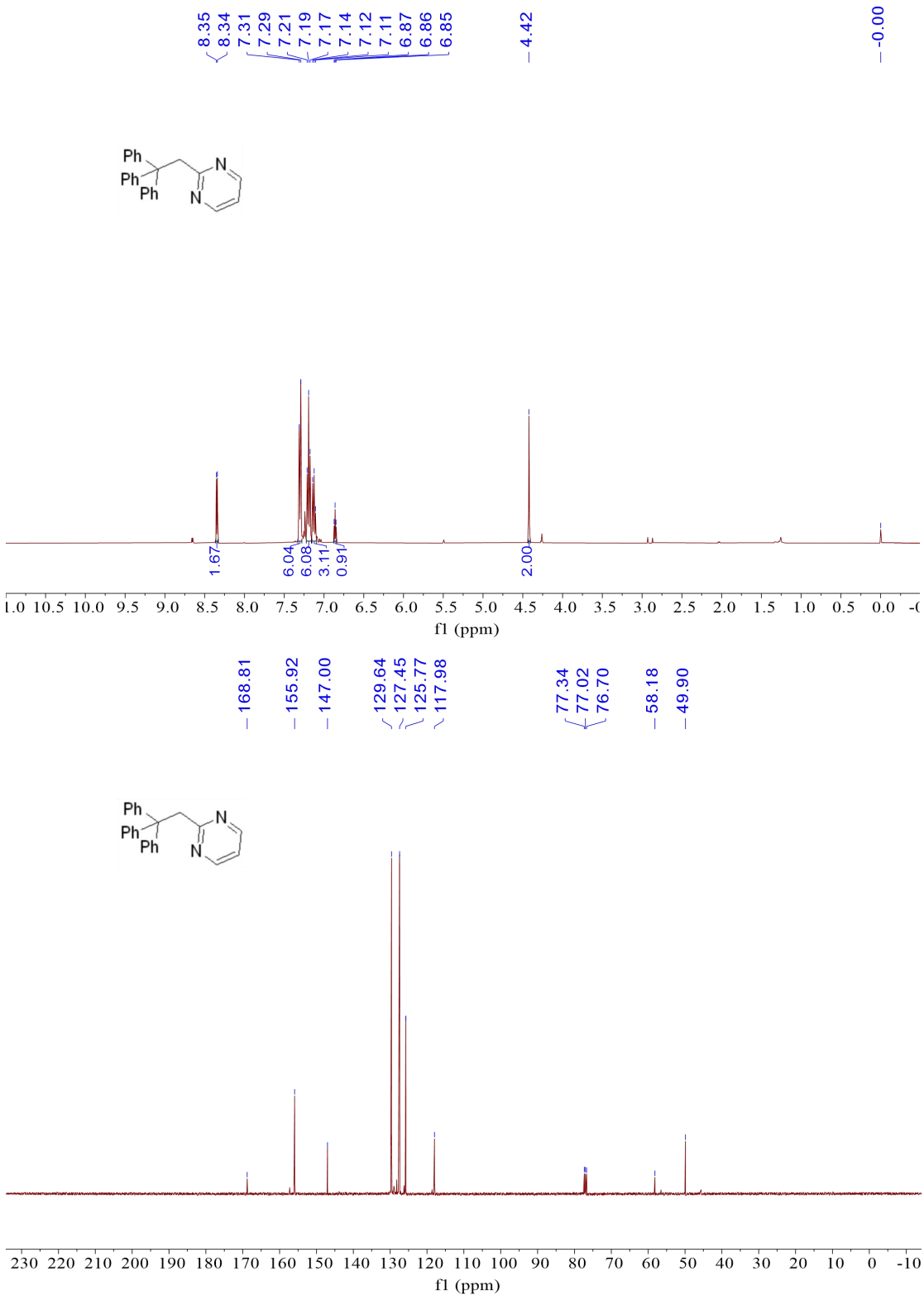
(**3s**) *2-(2,2,2-triphenylethyl)pyridine* (**3s**)



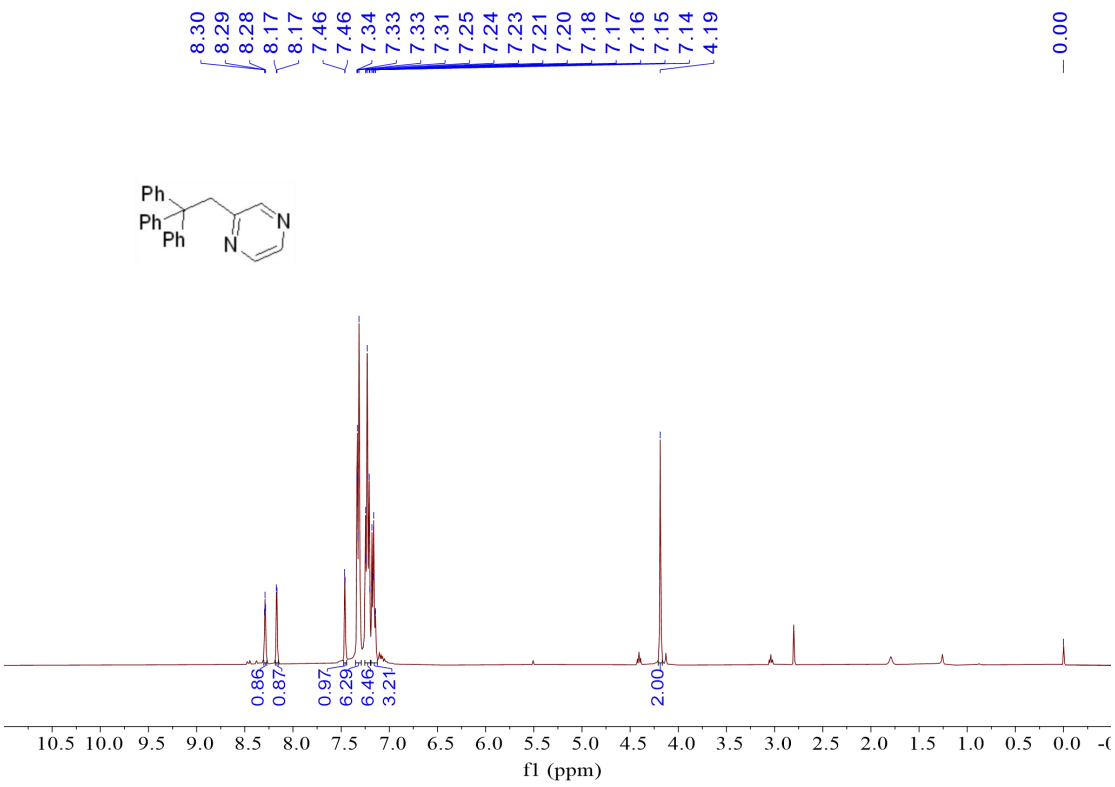
2-methyl-6-(2,2,2-triphenylethyl)pyridine (**3t**)



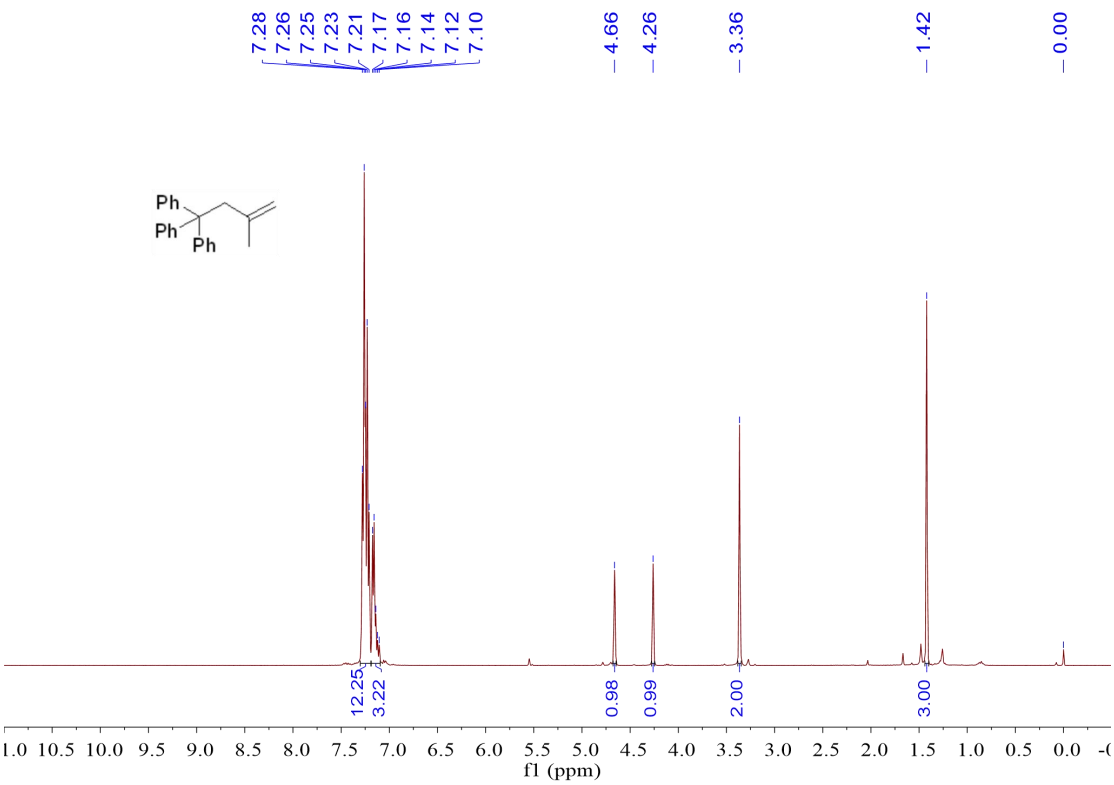
(**3u**) *2-(2,2,2-triphenylethyl)pyrimidine* (**3u**)



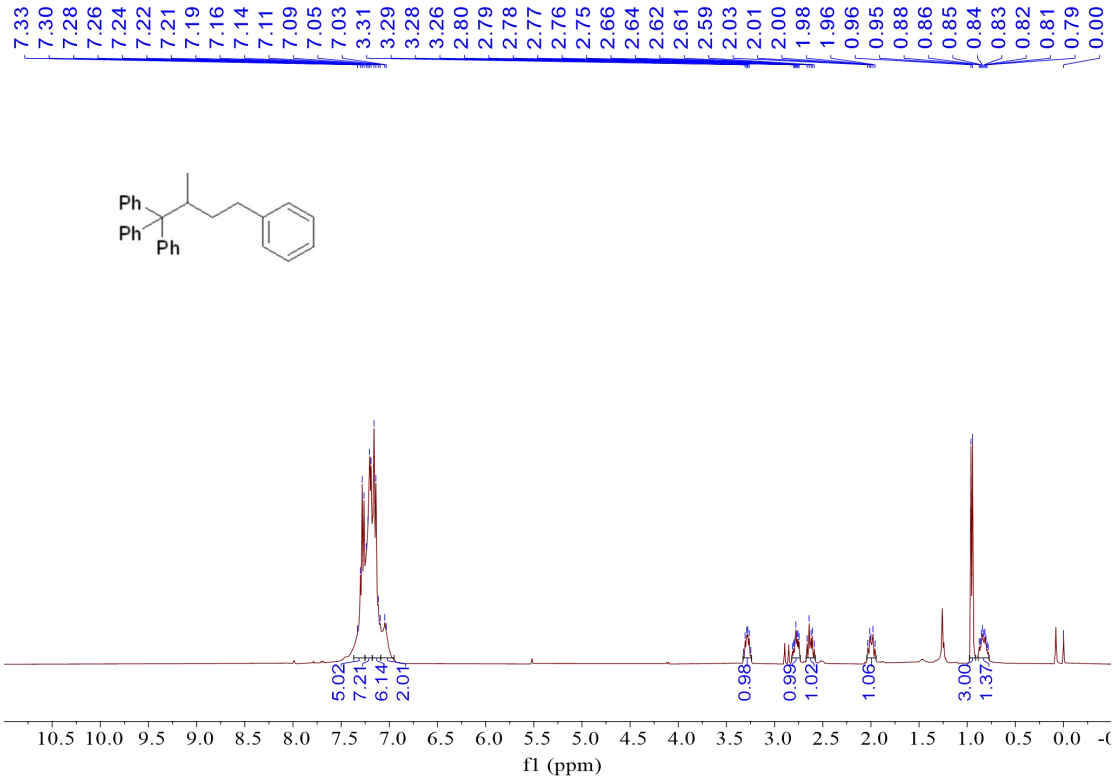
2-(2,2,2-triphenylethyl)pyrazine (**3v**)

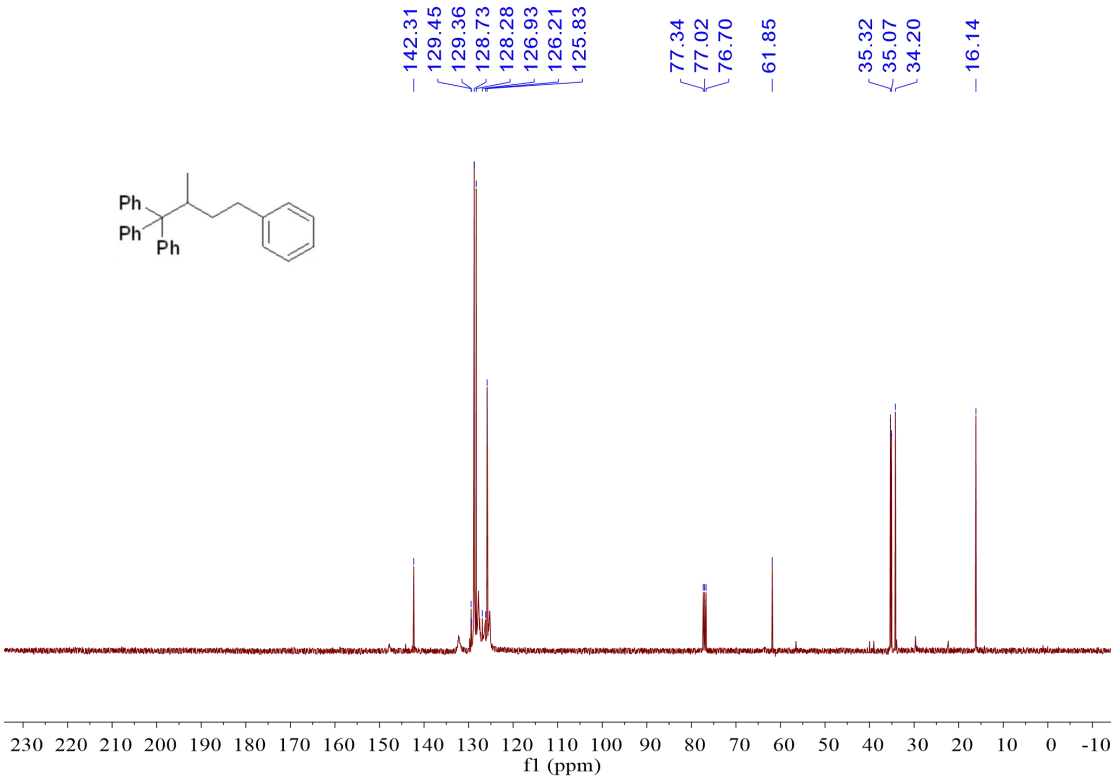


(3-methylbut-3-ene-1,1,1-triyl)tribenzene (**3w**)

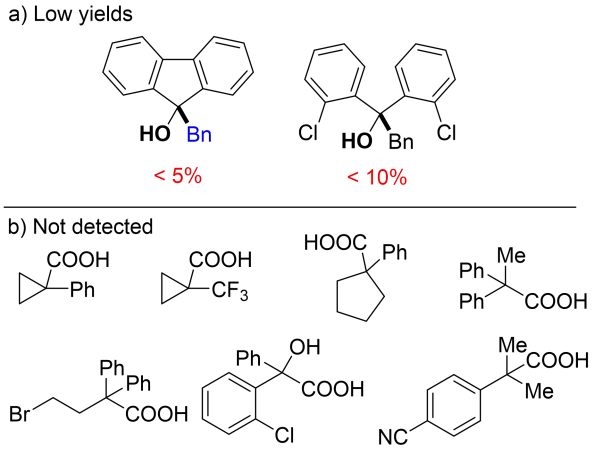


(2-methylbutane-1,1,1,4-tetrayl)tetrabenzene (**3x**)





7. Other failure examples of carboxylic acids



8. Reference

[1] Basch, C. H.; Liao, J.; Xu, J.; Piane, J. J.; Watson, M. P. *J. Am. Chem. Soc.,* **2017**, *139*, 5313.

[2] Kleeberg, C. *Dalton Trans* **2013**, *42*, 8276.

[3] Wang P.-D.; Yang N.-F.; Ling Y.; Li J.-C.; Cao J. *Chin. J. Org. Chem.,* **2007**, *27,* 885-889.