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Acid-Promoted Oxidative Methylenation of 1,3-Dicarbonyl Compounds with DMSO: Application to the Three-Component Synthesis of Hantzsch-Type Pyridines

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Context

General Information:

Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400 MHz, ^{13}C100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. HRMS-ESI spectra were obtained on Agilent 6450 spectrometer.

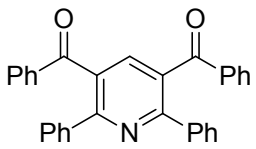
Typical Procedure for the Preparation of Polysubstituted Pyridines 4:

1,3-diones **1** (0.5 mmol), NH_4OAc (1.0 mmol), TFA (3.0 mmol), and 2 mL of DMSO were weighed in air and placed in a 5 mL Schlenk tube with magnetic stirring. The mixture was stirred at 120 ^{o}C under air atmosphere. After completing reaction, the mixture was diluted with dichlormethane (10 mL) and washed with water (3 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvents were evaporated, and the residue was purified by silica gel column chromatography with EA/petroleum ether (1:50) as the eluent to afford the products **4**.

Typical Procedure for the Preparation of methylene-bridged bis-1,3-dicarbonyl compounds 2:

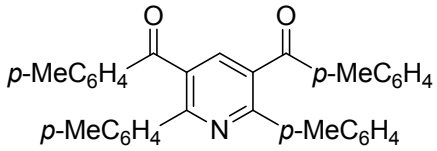
1,3-diones **1** (0.5 mmol), AcOH (1.50 mmol) and 2 mL of DMSO were weighed in air and placed in a 5 mL Schlenk tube with magnetic stirring. The mixture was stirred at 120 ^{o}C under air atmosphere. After completing reaction, the mixture was diluted with dichlormethane (10 mL) and washed with water (3 × 10 mL).The organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvents were evaporated, and the residue was purified by silica gel column chromatography with EA/petroleum ether (1:50) as the eluent to afford the products **2**.

Spectroscopic Data for Products



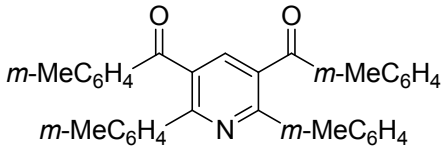
2,6-diphenylpyridine-3,5-diyl)bis(phenylmethanone (***4a***).

White solid (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.77 – 7.72 (m, 4H), 7.70–7.68 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.29 – 7.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 158.0, 138.8, 138.5, 136.3, 133.5, 131.8, 129.8, 129.5, 129.4, 128.4, 128.3.HRMS (ESI, *m/z*): calcd for $C_{31}H_{21}NO_2H^+$: 440.1645; found: 440.1652.



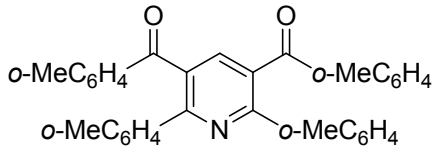
2,6-di-p-tolylpyridine-3,5-diyl)bis(p-tolylmethanone (***4b***).

White solid (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.60 (d, *J* = 7.9 Hz, 4H), 7.14 – 7.08 (m, 8H), 2.33 (s, 6H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 157.5, 144.4, 139.3, 138.2, 135.9, 133.9, 131.4, 130.1, 129.3, 129.2, 129.0, 21.6, 21.2. HRMS (ESI, *m/z*): calcd for $C_{35}H_{29}NO_2H^+$:496.2271; found: 496.2276.



2,6-di-m-tolylpyridine-3,5-diyl)bis(m-tolylmethanone (***4c***)

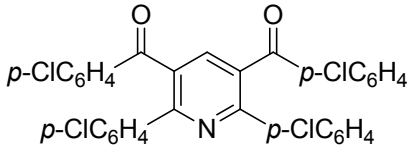
White solid (86% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.54 (s, 6H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.24 (s, 2H), 7.14 (t, *J* = 7.5 Hz, 4H), 7.06 (d, *J* = 7.1 Hz, 2H), 2.28 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 158.1, 138.6, 138.5, 138.1, 137.9, 136.3, 134.1, 131.8, 130.2, 130.1, 130.0, 128.2, 128.1, 127.0, 126.5, 21.2, 21.0. HRMS (ESI, *m/z*): calcd for $C_{35}H_{29}NO_2H^+$:496.2271; found: 496.2277.



2,6-di-o-tolylpyridine-3,5-diyl)bis(o-tolylmethanone (***4d***)

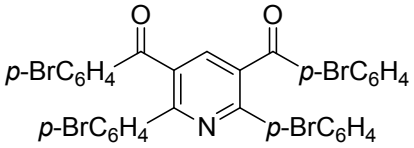
White solid (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.25 (d, *J* = 6.8 Hz, 4H), 7.14 – 6.98 (m, 12H), 2.36 (s, 6H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 159.7, 138.9, 138.4, 138.2, 137.0, 135.7, 134.6, 131.7, 131.5, 130.2, 130.0,

129.3, 128.6, 125.2, 124.8, 20.5, 19.9. HRMS (ESI, *m/z*): calcd for $C_{35}H_{29}NO_2H^+$:496.2271; found: 496.2279.



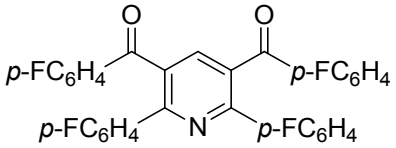
2,6-bis(4-chlorophenyl)pyridine-3,5-diyl)bis((4-chlorophenyl)methanone (***4e***)

White solid (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 4H), 7.60 (d, *J* = 7.9 Hz, 4H), 7.30 (dd, *J* = 12.1, 8.4 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 156.7, 140.5, 139.0, 136.5, 136.2, 134.3, 131.6, 131.1, 130.6, 129.0, 128.8. HRMS (ESI, *m/z*): calcd for $C_{31}H_{17}Cl_4NO_2H^+$:576.0086; found: 576.0093.



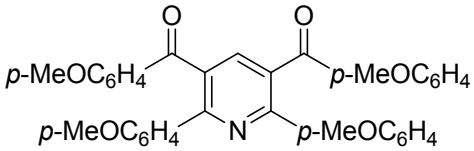
2,6-bis(4-bromophenyl)pyridine-3,5-diyl)bis((4-bromophenyl)methanone (***4f***).

White solid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 4H), 7.51 (dd, *J* = 11.9, 8.5 Hz, 8H), 7.45 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 156.8, 138.9, 136.9, 134.7, 132.1, 131.8, 131.5, 131.1, 130.9, 129.4, 124.6. HRMS (ESI, *m/z*): calcd for $C_{31}H_{17}Br_4NO_2H^+$:751.8066; found: 751.8073.



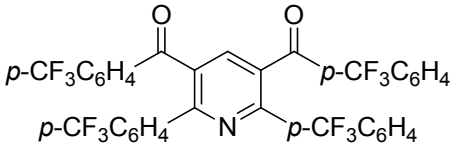
2,6-bis(4-fluorophenyl)pyridine-3,5-diyl)bis((4-fluorophenyl)methanone (***4g***)

White solid (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.74 (dd, *J* = 8.7, 5.4 Hz, 4H), 7.69 – 7.62 (m, 4H), 7.02-6.97 (m, 8H). ^{13}C NMR (100 MHz, CDCl3) δ 194.8, 166.0 (d, J = 238.5 Hz), 163.5 (d, J = 232.2 Hz), 156.7, 139.0, 134.4 (d, J = 3.2 Hz), 132.5 (d, J = 2.7 Hz,), 132.4 (d, J = 9.6 Hz), 131.5, 131.4 (d, J = 8.6 Hz), 115.8 (d, J = 22.3 Hz,), 115.6 (d, J = 21.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.9, -110.7. HRMS (ESI, *m/z*): calcd for $C_{31}H_{17}Cl_4NO_2H^+$:512.1268; found: 512.1274.



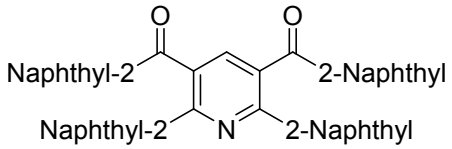
2,6-bis(4-methoxyphenyl)pyridine-3,5-diyl)bis((4-methoxyphenyl)methanone (*4h*)

White solid (37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 4H), 7.68 (d, *J* = 8.8 Hz, 4H), 6.81 (dd, *J* = 8.7, 6.6 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 163.7, 160.4, 156.6, 138.4, 132.3, 131.2, 130.9, 130.8, 129.3, 113.7, 113.7, 55.4, 55.2 HRMS (ESI, *m/z*): calcd for $C_{35}H_{29}NO_6H^+$:560.2068; found:560.2074.



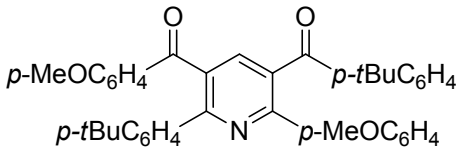
2,6-bis(4-(trifluoromethyl)phenyl)pyridine-3,5-diyl)bis((4-(trifluoromethyl)phenyl)methanone (*4i*)

White solid (94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 4H), 7.77 (d, *J* = 7.9 Hz, 4H), 7.60 (dd, *J* = 17.0, 8.0 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 157.37, 141.20, 139.35, 138.58, 135.1 (q, *J* = 32.9 Hz), 132.2, 131.7 (q, *J* = 32.8 Hz), 130.0, 129.8, 125.7 (q, *J* = 3.6 Hz), 125.5 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.4 Hz), 123.1 (q, *J* = 273.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0, -63.4. HRMS (ESI, *m/z*): calcd for $C_{35}H_{17}F_{12}NO_2H^+$:712.1140; found: 712.1148.



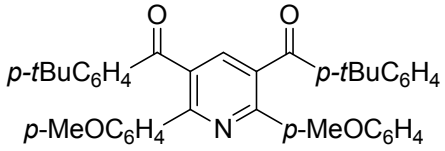
2,6-di(naphthalen-1-yl)pyridine-3,5-diyl)bis(naphthalen-1-ylmethanone (*4j*)

White solid (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 2H), 8.26 (s, 2H), 8.22 (s, 1H), 7.99 – 7.92 (m, 4H), 7.80 (dd, *J* = 14.2, 6.2 Hz, 5H), 7.78 – 7.69 (m, 7H), 7.52 (dd, *J* = 11.0, 4.0 Hz, 2H), 7.49 – 7.44 (m, 3H), 7.43 – 7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 157.9, 138.8, 136.0, 135.6, 133.7, 133.5, 132.9, 132.6, 132.2, 132.1, 129.7, 129.6, 128.8, 128.6, 128.3, 127.7, 127.5, 126.9, 126.8, 126.3, 126.3, 124.5. HRMS (ESI, *m/z*): calcd for $C_{47}H_{29}NO_2H^+$:640.2271; found: 640.2271.



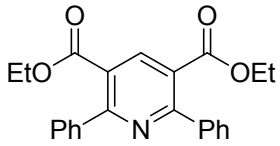
5-(4-(tert-butyl)benzoyl)-2-(4-(tert-butyl)phenyl)-6-(4-methoxyphenyl)pyridin-3-yl)(4-methoxyphenyl)methanone (***4k***)

White solid (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.73 (t, *J* = 8.8 Hz, 4H), 7.65 (dd, *J* = 12.2, 8.5 Hz, 4H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.86 – 6.77 (m, 4H), 3.80 (s, 3H), 3.76 (s, 3H), 1.29 (s, 11H), 1.26 (s, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 195.3, 163.7, 160.5, 157.4, 157.3, 157.1, 152.3, 138.2, 135.8, 133.9, 133.8, 132.4, 131.2, 131.1, 131.0, 130.9, 130.0, 129.6, 129.1, 125.4, 125.2, 113.8, 113.7, 55.4, 55.2, 35.1, 34.5, 31.1, 30.0. HRMS (ESI, *m/z*): calcd for $C_{41}H_{41}NO_4H^+$:612.3108; found: 612.3115.



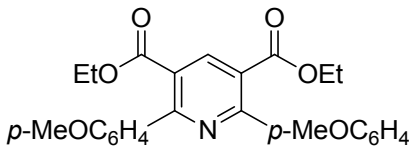
2,6-bis(4-methoxyphenyl)pyridine-3,5-diyl)bis((4-(tert-butyl)phenyl)methanone (***4k`***).

White solid (39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 4H), 7.64 (d, *J* = 8.4 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.9 Hz, 4H), 3.80 (s, 6H), 1.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 163.7, 157.4, 152.2, 138.03, 135.7, 132.4, 131.4, 129.5, 129.1, 125.2, 113.6, 55.4, 34.5, 31.0. HRMS (ESI, *m/z*): calcd for $C_{41}H_{41}NO_4H^+$:612.3108; found: 612.3115.



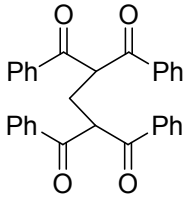
diethyl 2,6-diphenylpyridine-3,5-dicarboxylate (***4l***)

White solid (33% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.63 (dd, *J* = 6.6, 3.0 Hz, 5H), 7.44 (dd, *J* = 4.2, 2.2 Hz, 7H), 4.21 (q, *J* = 7.1 Hz, 5H), 1.10 (t, *J* = 7.1 Hz, 7H). ^{13}C NMR (100MHz, $CDCl_3$) δ 167.4, 159.7, 140.2, 139.3, 129.1, 128.9, 128.0, 124.7, 61.6, 13.6.



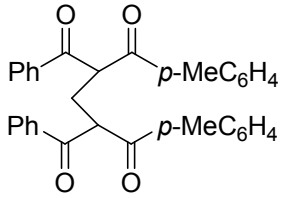
diethyl 2,6-bis(4-methoxyphenyl)pyridine-3,5-dicarboxylate (*4m*)

White solid (21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 4.24 (q, *J* = 7.1 Hz, 4H), 3.86 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 160.6, 158.9, 140.4, 131.7, 130.5, 123.4, 113.4, 61.5, 55.3, 13.8.



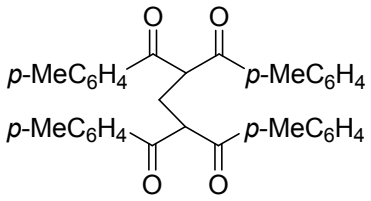
2,4-dibenzoyl-1,5-diphenylpentane-1,5-dione(***2a***)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 8H), 7.58 (t, *J* = 7.3 Hz, 4H), 7.48 (t, *J* = 7.7 Hz, 8H), 5.74 (t, *J* = 7.0 Hz, 2H), 2.76 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 135.4, 133.8, 129.0, 128.7, 53.9, 28.9.



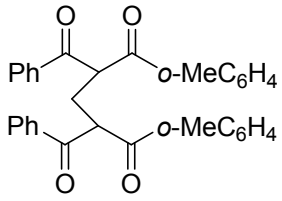
2,4-dibenzoyl-1,5-di-p-tolylpentane-1,5-dione(***2b***)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.09 (m, 4H), 8.05 (dd, *J* = 8.0, 6.5 Hz, 4H), 7.56 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.28 (dd, *J* = 8.0, 3.1 Hz, 4H), 5.71 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.0 Hz, 2H), 2.39 (d, *J* = 1.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 196.6, 196.2, 196.1, 144.8, 135.4, 135.4, 133.7, 132.9, 132.8, 129.7, 128.9, 128.9, 128.7, 128.7, 53.8, 28.9, 21.6.



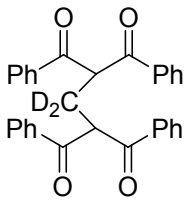
2,4-bis(4-methylbenzoyl)-1,5-di-p-tolylpentane-1,5-dione(***2c***).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 4H), 7.92 (t, *J* = 9.3 Hz, 4H), 7.42 – 7.32 (m, 4H), 7.31 – 7.24 (m, 4H), 5.69 (t, *J* = 6.7 Hz, 2H), 2.72 (t, *J* = 6.7 Hz, 2H), 2.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 196.8, 196.3, 196.2, 144.7, 138.7, 135.5, 135.4, 134.5, 133.0, 132.9, 129.6, 129.2, 128.9, 128.9, 128.9, 128.8, 125.9, 53.9, 28.9, 21.6, 21.3.



2,4-dibenzoyl-1,5-di-o-tolylpentane-1,5-dione(***2d).***

^{1}H NMR (400 MHz, $CDCl_3$)δ 8.01 – 7.92 (m, 1H), 7.86 – 7.77 (m, 2H), 7.51 – 7.42 (m, 2H), 7.35 (dd, *J* = 15.4, 7.7 Hz, 4H), 7.27 (dd, *J* = 14.7, 7.3 Hz, 2H), 7.30 – 7.19 (m, 4H), 5.60 (dd, *J* = 11.7, 6.9 Hz, 2H), 2.69 (dd, *J* = 13.0, 6.8 Hz, 2H), 2.36 (d, *J* = 16.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 199.4, 196.6, 196.4, 139.4, 136.6, 136.4, 135.7, 135.5, 133.7, 133.7, 132.2, 132.1, 132.0, 128.8, 128.8, 128.7, 128.6, 126.0, 56.1, 56.1, 29.0, 21.2.



2,4-dibenzoyl-3,3-deutero-1,5-diphenylpentane-1,5-dione (***2a-d$_2$***)

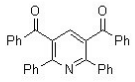
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.11 (m, 8H), 7.59 (dd, *J* = 10.5, 4.2 Hz, 4H), 7.49 (t, *J* = 7.6 Hz, 8H), 5.74 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 135.3, 133.8, 129.0, 128.7, 53.7, 28.7 – 28.2 (m).

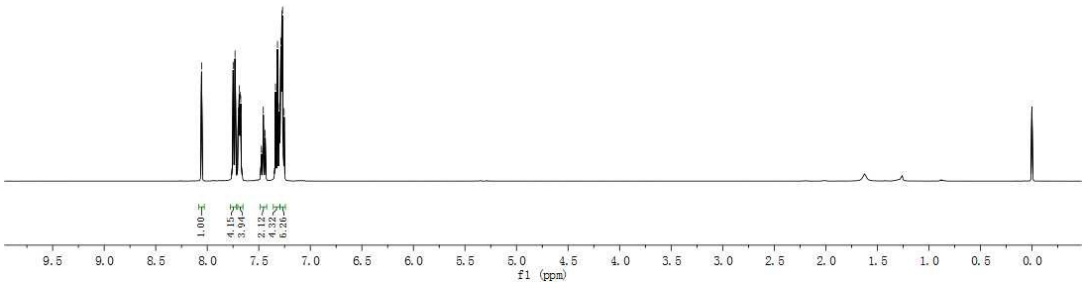
(5-benzoyl-2-(4-chlorophenyl)-6-phenylpyridin-3-yl)(4-chlorophenyl)methanone (***5***)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.75 – 7.70 (m, 2H), 7.70 – 7.64 (m, 4H), 7.64 – 7.60 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.26 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 195.2, 158.3, 156.5, 140.4, 138.9, 138.3, 136.9, 136.2, 136.0, 134.5, 133.7, 132.2, 131.3, 131.2, 130.7, 129.9, 129.6, 129.5, 129.0, 128.8, 128.5, 128.5; HRMS (ESI, *m/z*): calcd for $C_{31}H_{19}Cl_2NO_2H^+$: 508.0866; found: 508.0861.

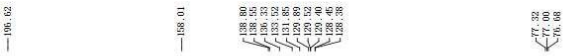
Copies of ^{1}H NMR, ^{13}C NMR spectra of products

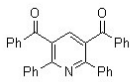
^{1}H NMR spectrum of product **4a**

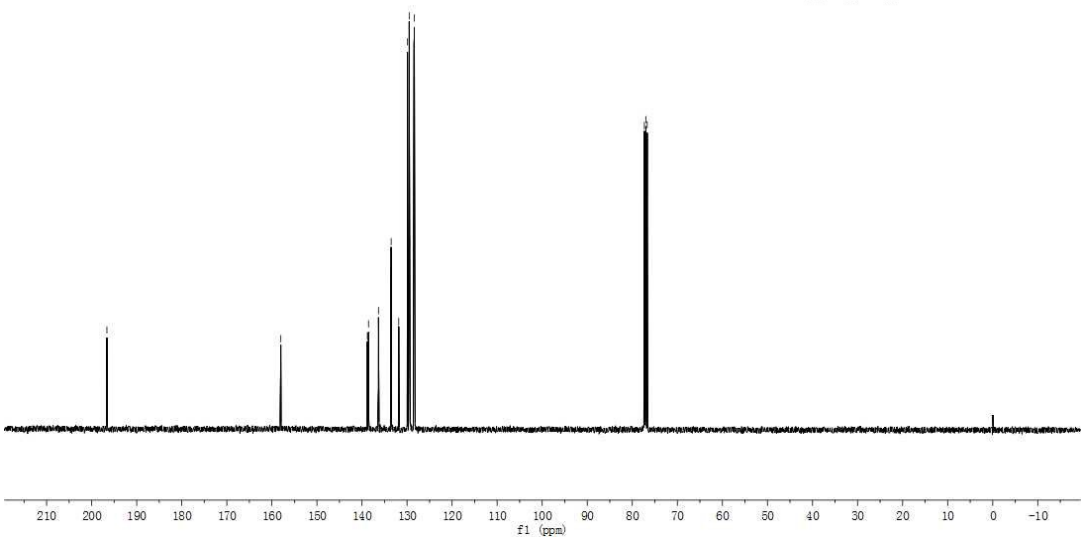




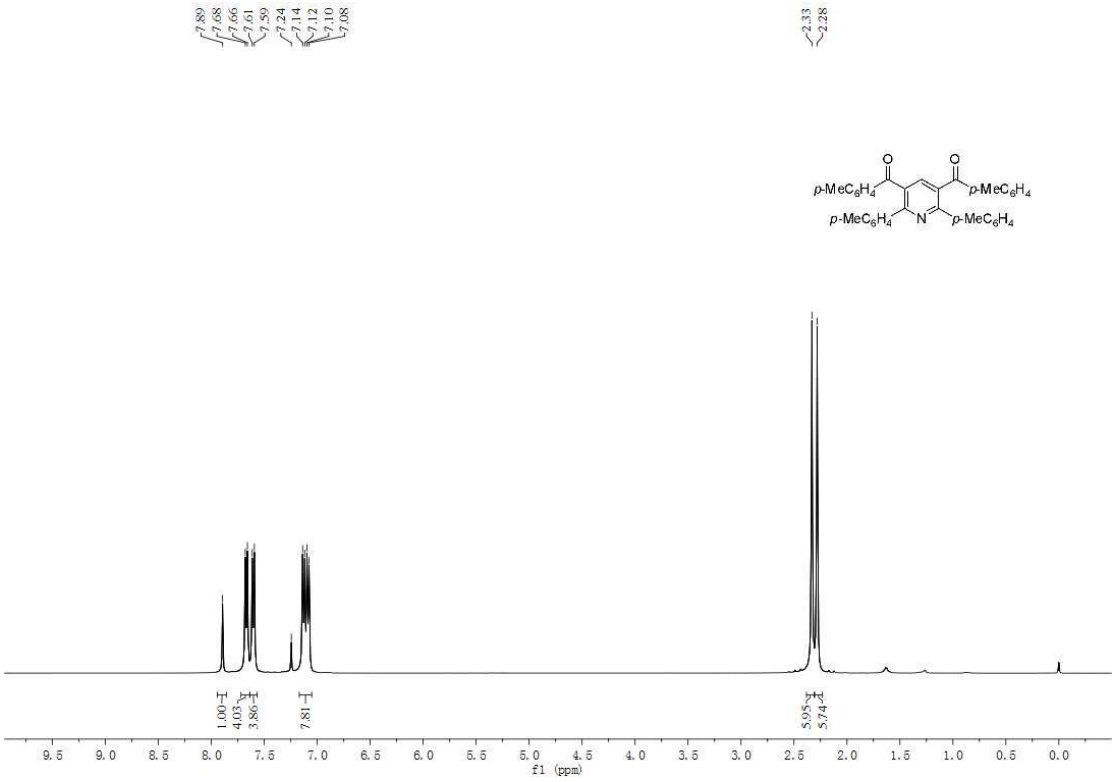
^{13}C NMR spectrum of product **4a**



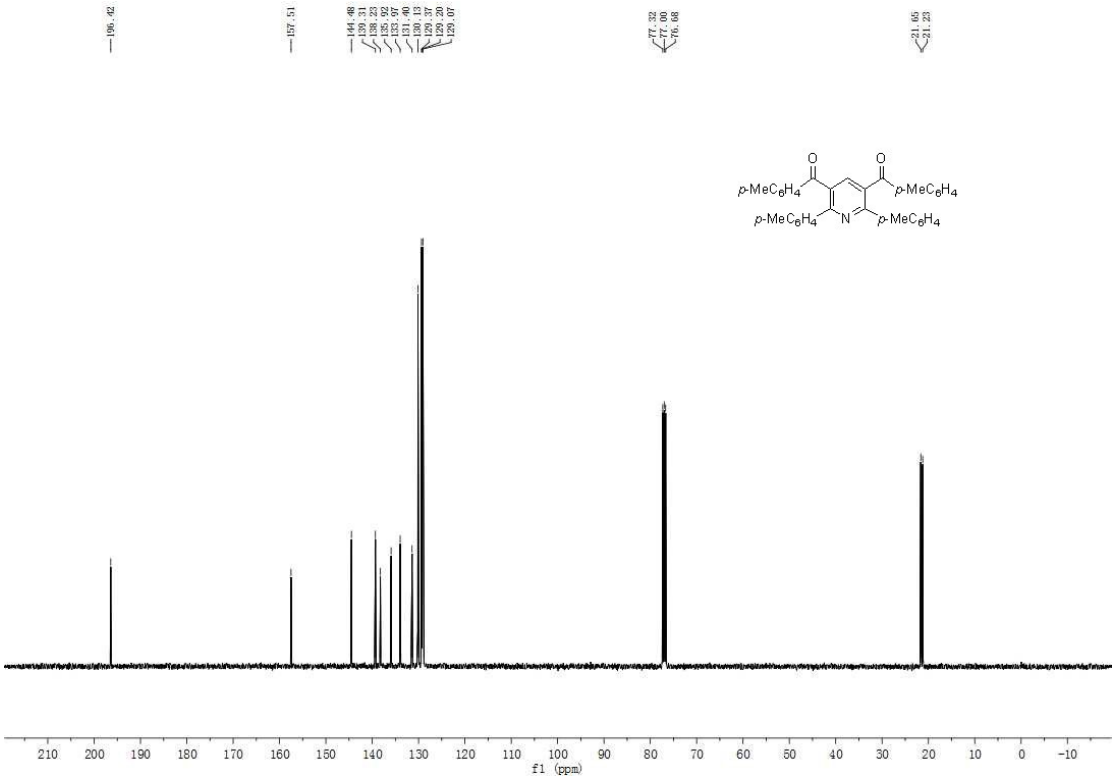




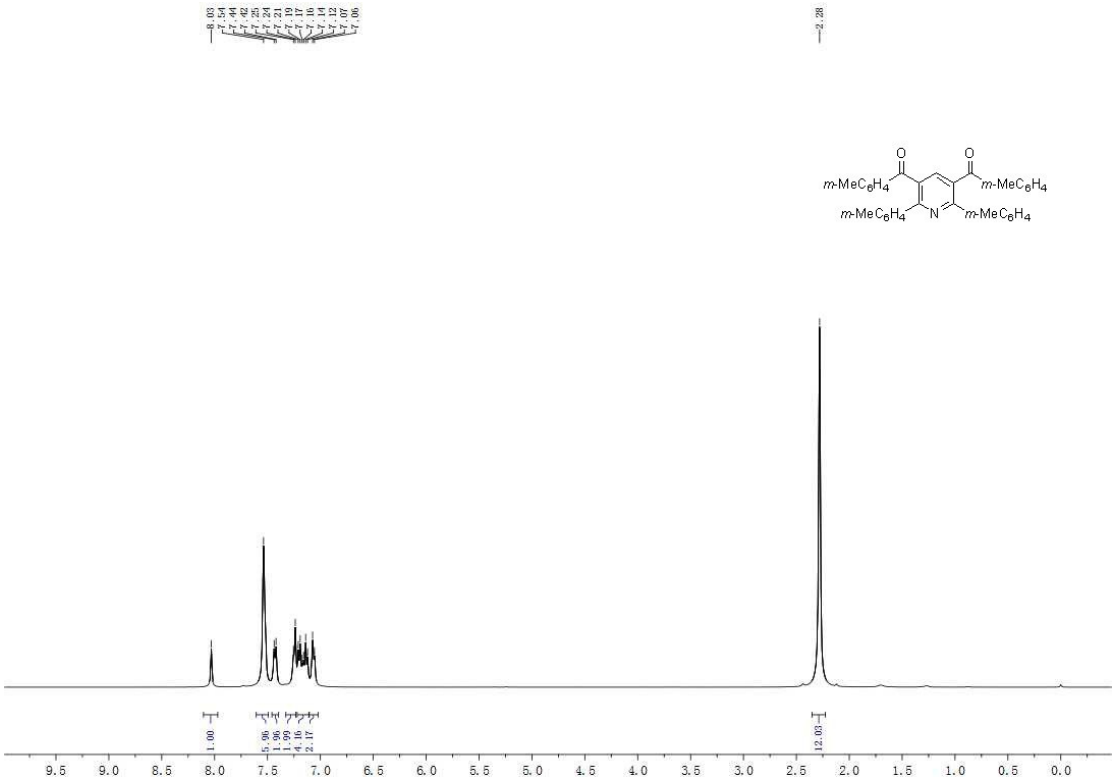
^{1}H NMR spectrum of product **4b**



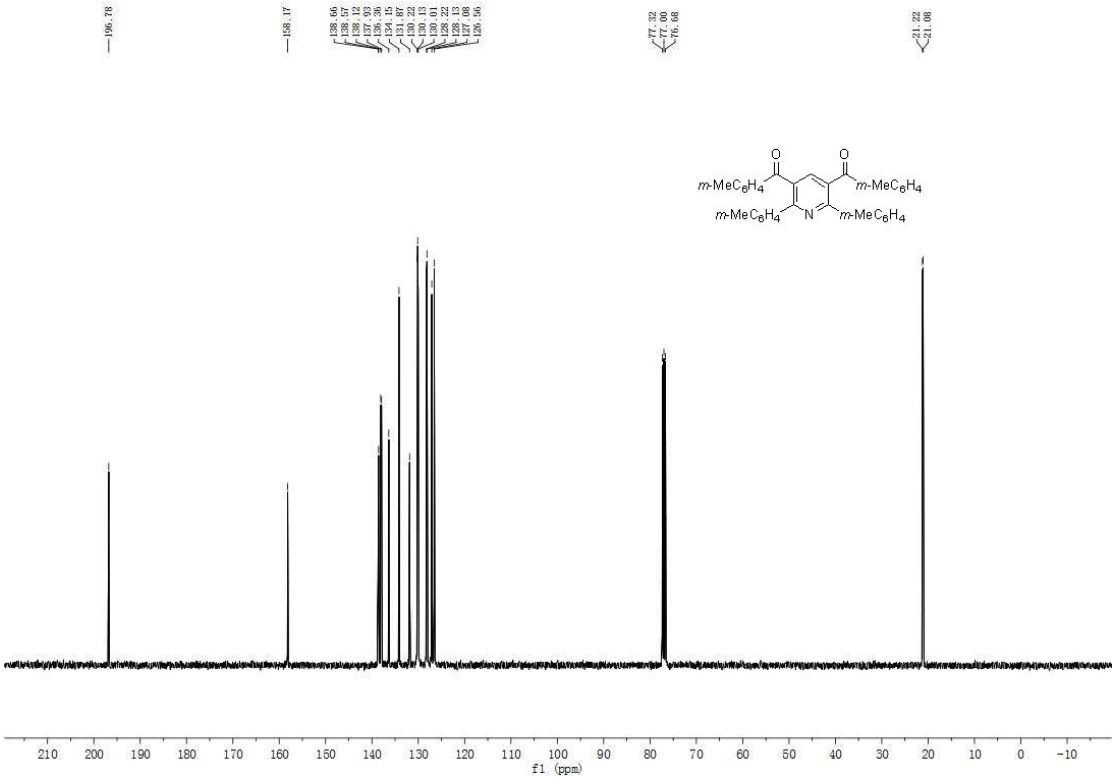
^{13}C NMR spectrum of product **4b**



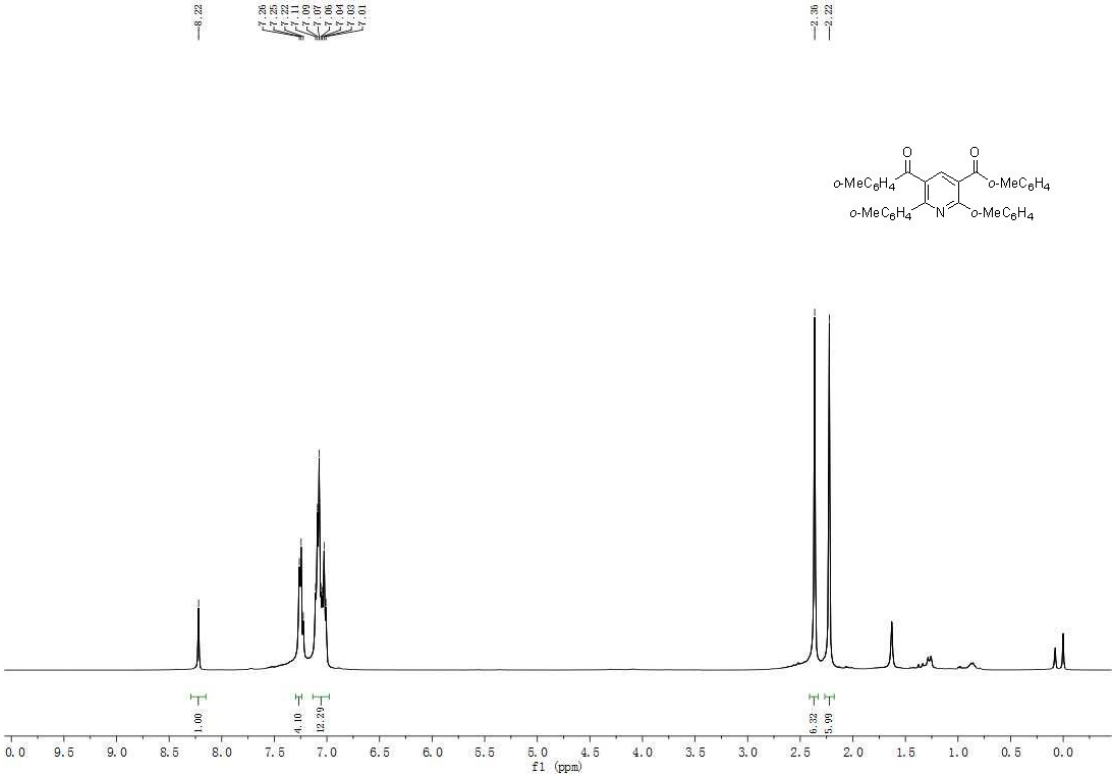
^{1}H NMR spectrum of product **4c**



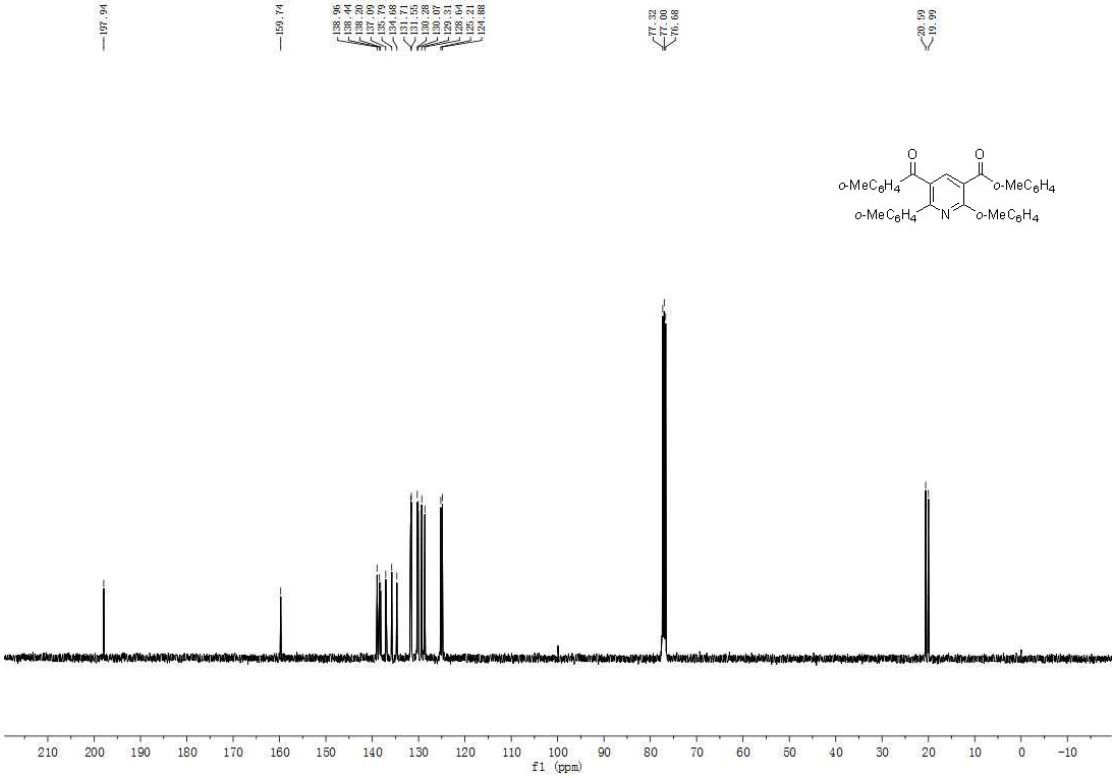
^{13}C NMR spectrum of product **4c**



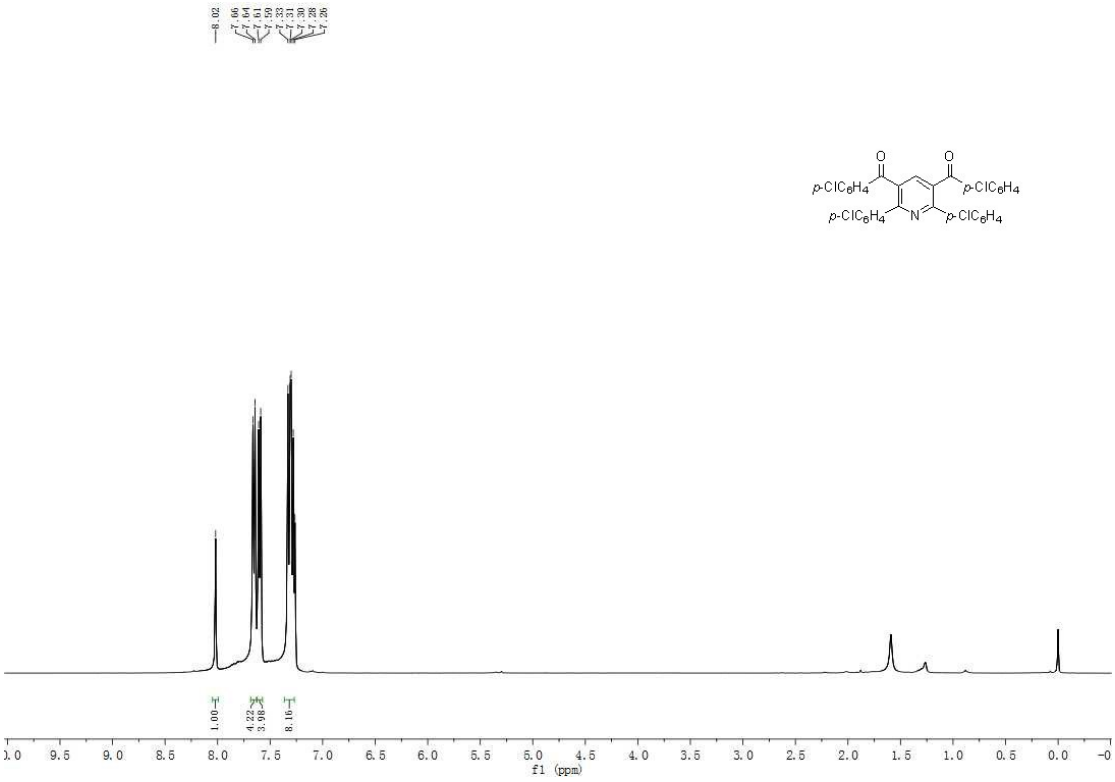
^{1}H NMR spectrum of product **4d**



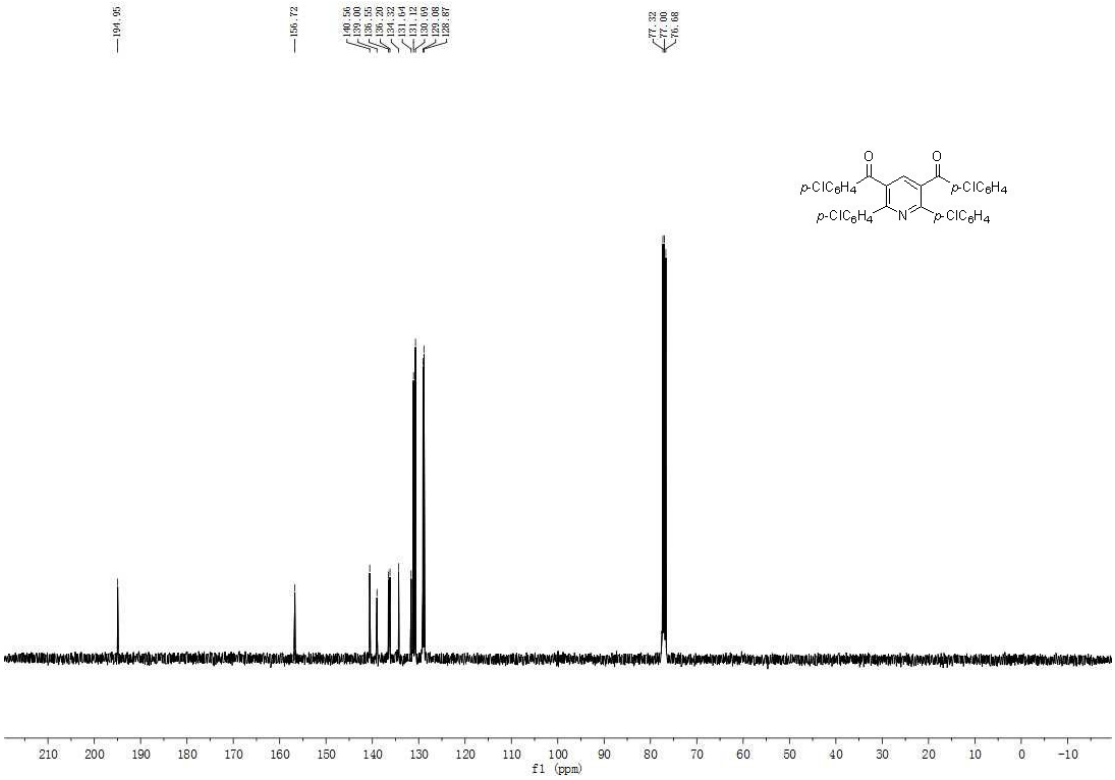
^{13}C NMR spectrum of product **4d**



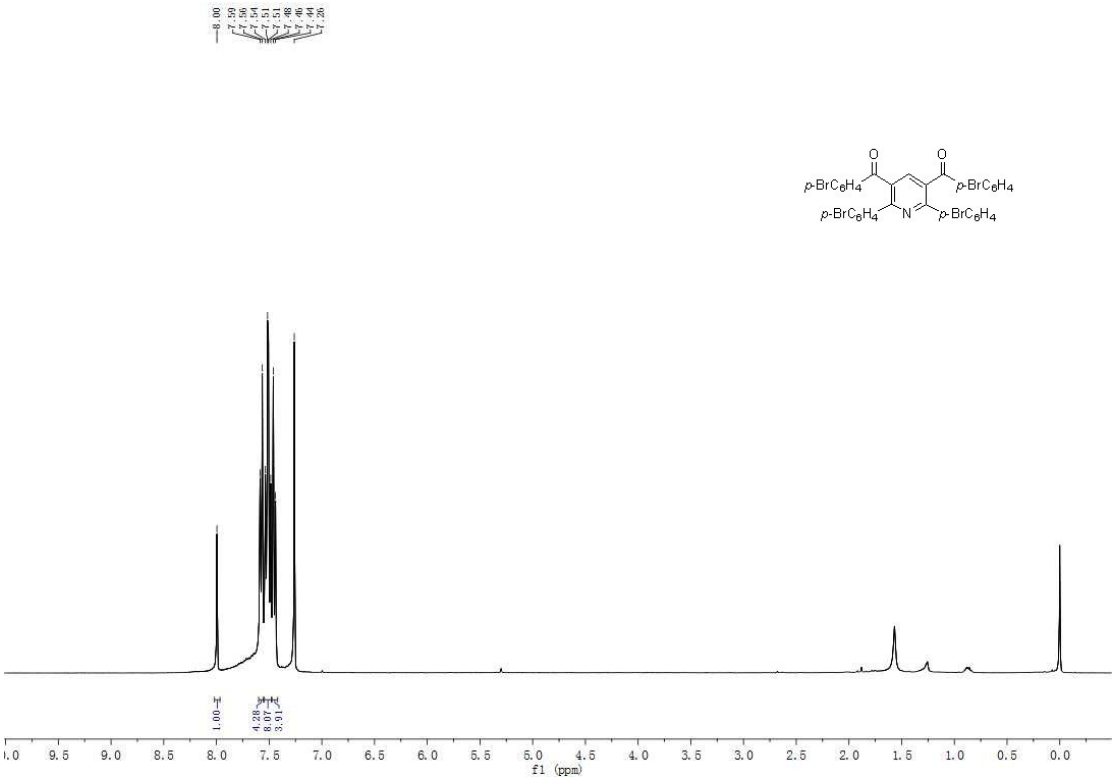
^{1}H NMR spectrum of product **4e**



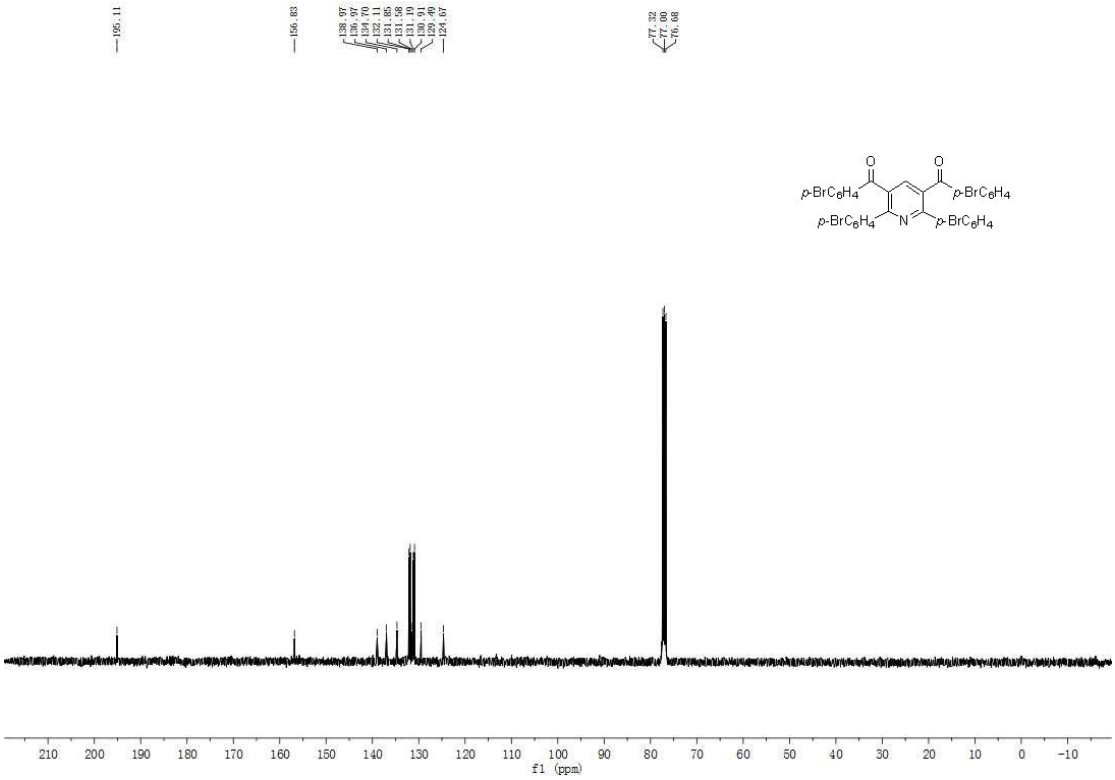
^{13}C NMR spectrum of product **4e**



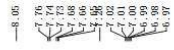
^{1}H NMR spectrum of product **4f**

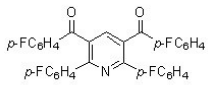


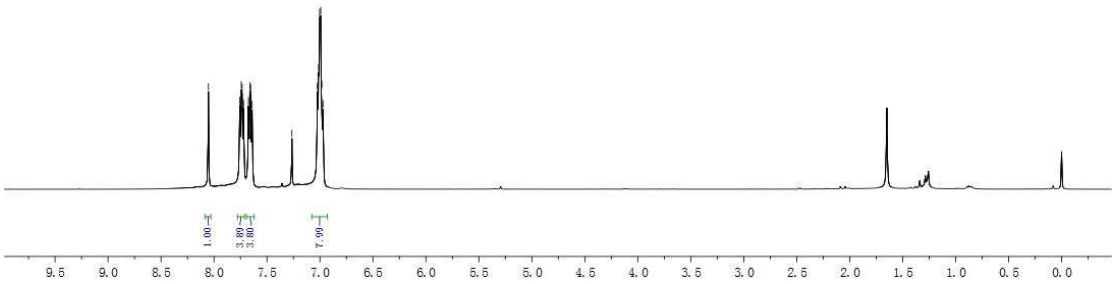
^{13}C NMR spectrum of product **4f**



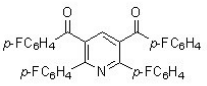
^{1}H NMR spectrum of product **4g**

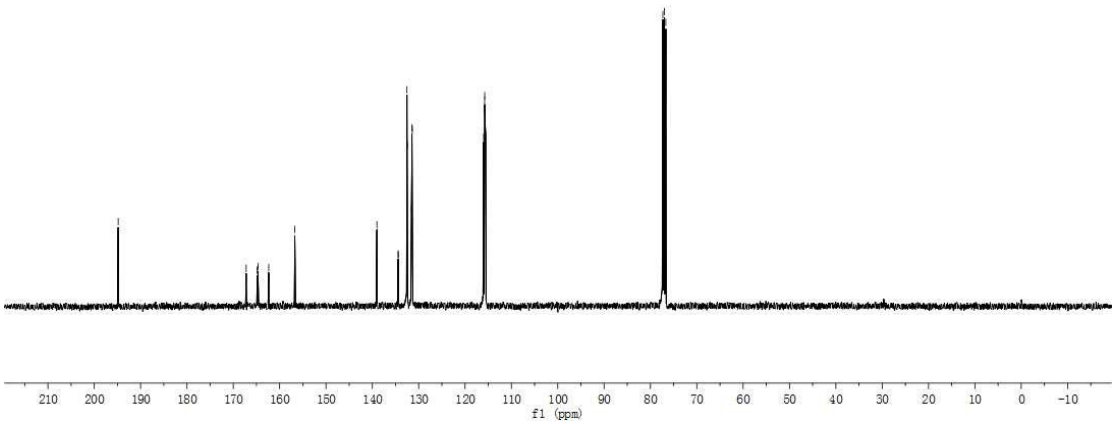




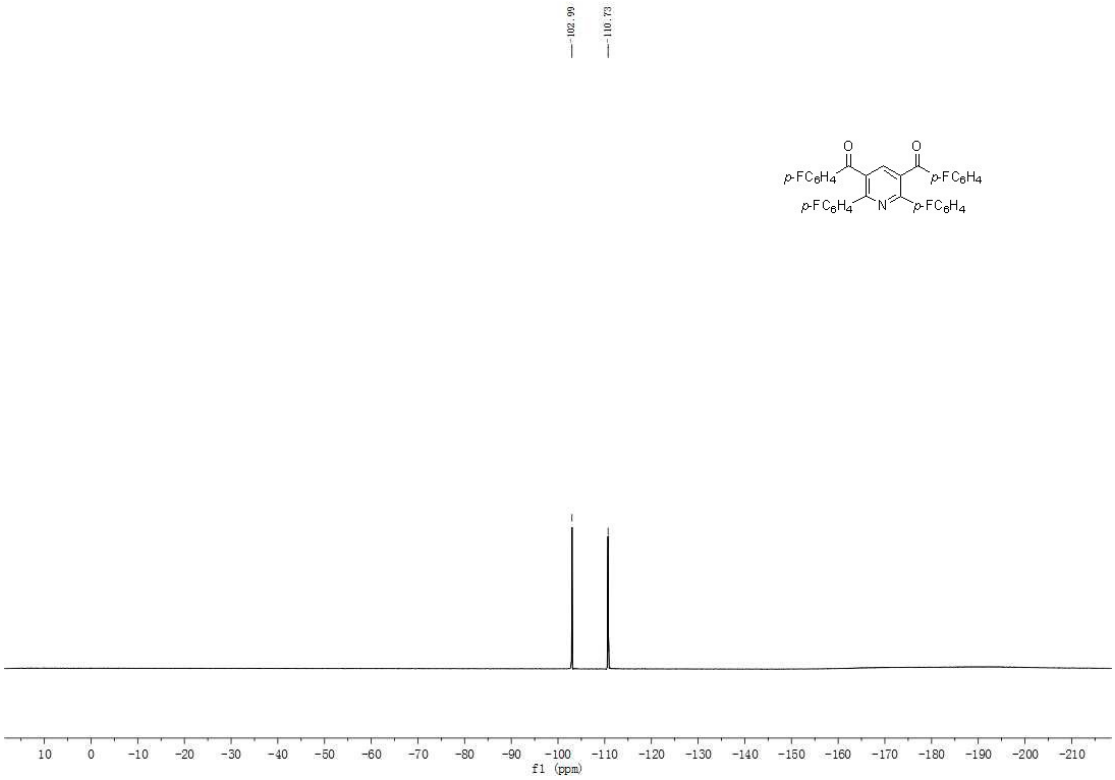


^{13}C NMR spectrum of product **4g**

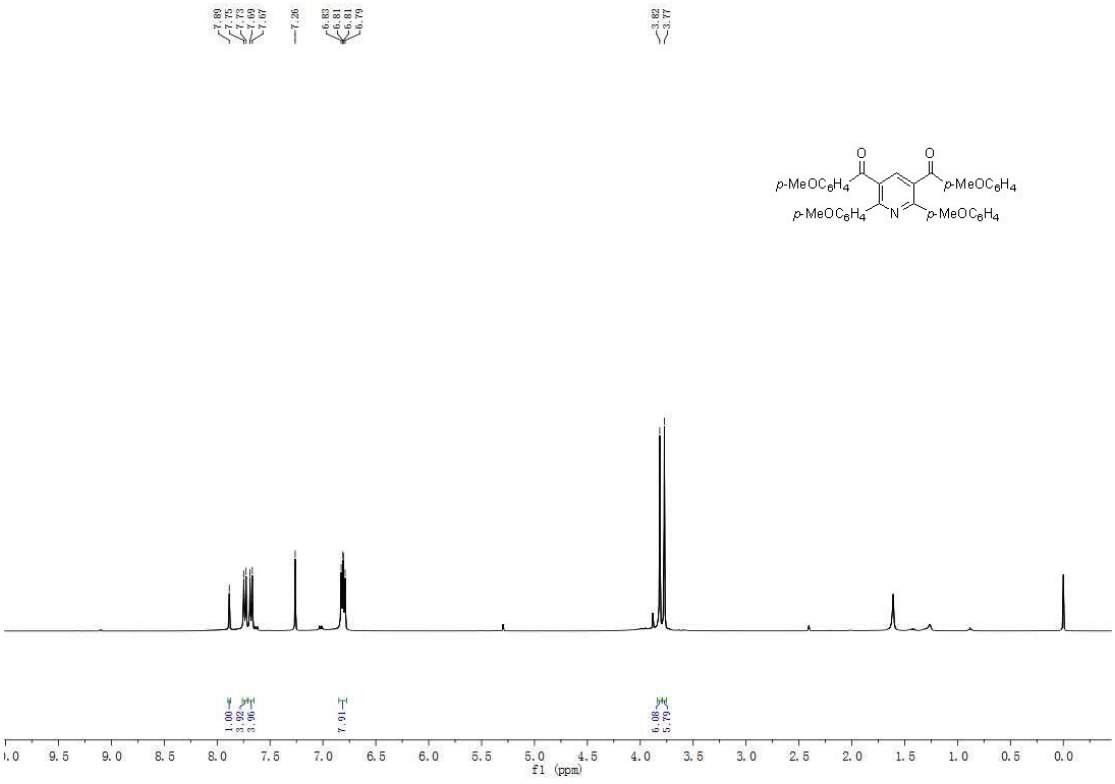




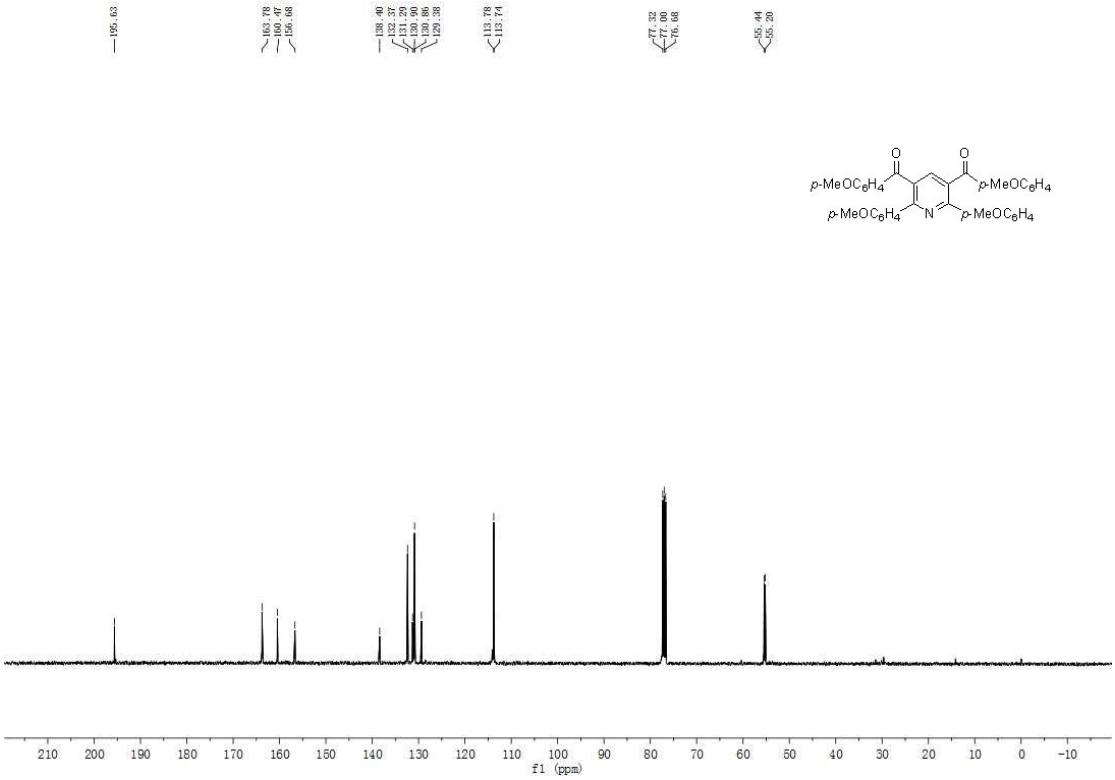
^{19}F NMR spectrum of product **4g**



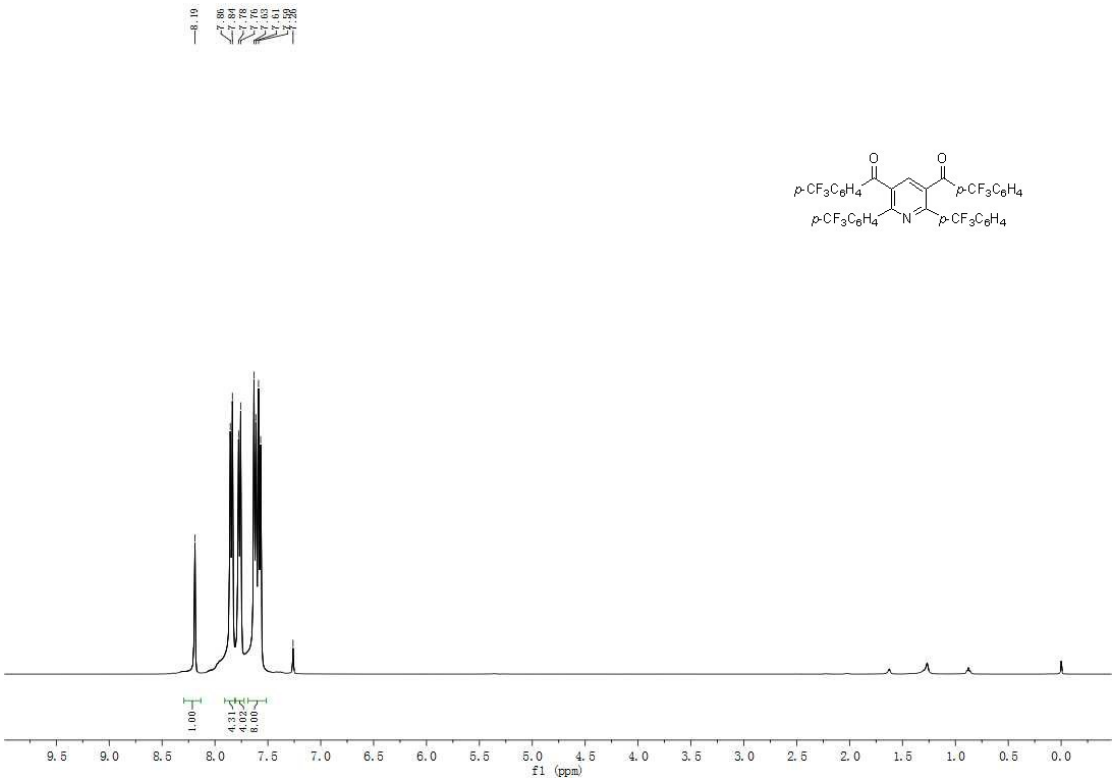
^{1}H NMR spectrum of product **4h**



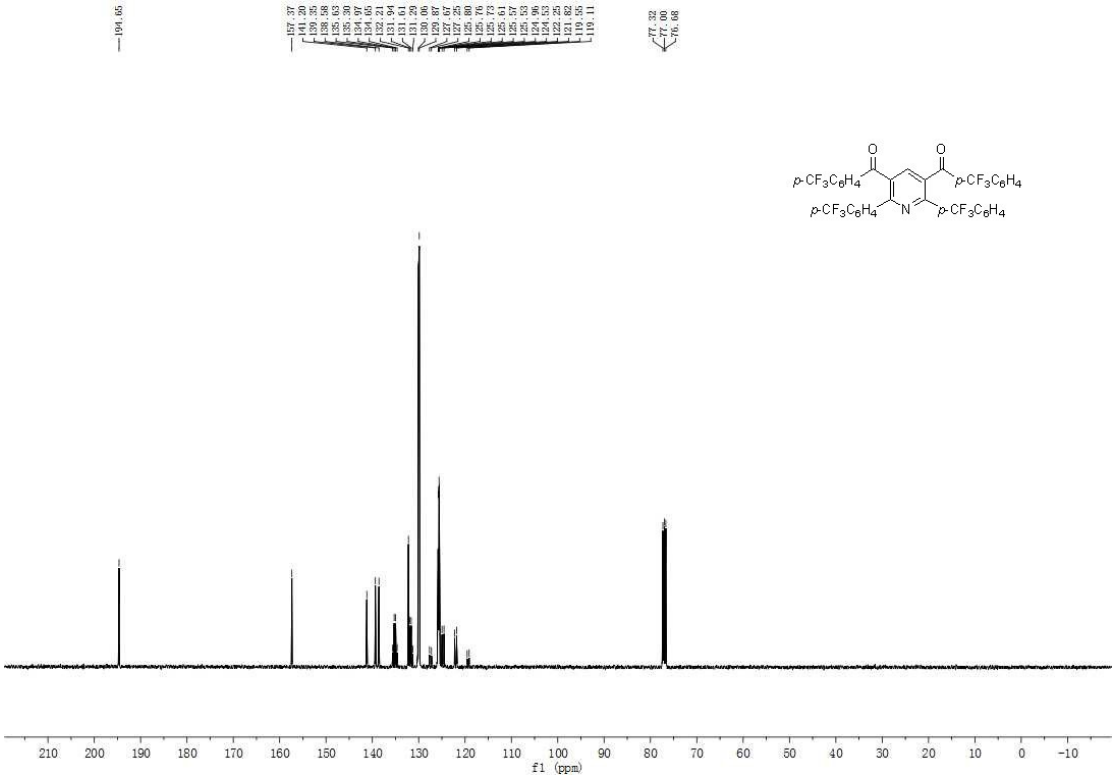
^{13}C NMR spectrum of product **4h**



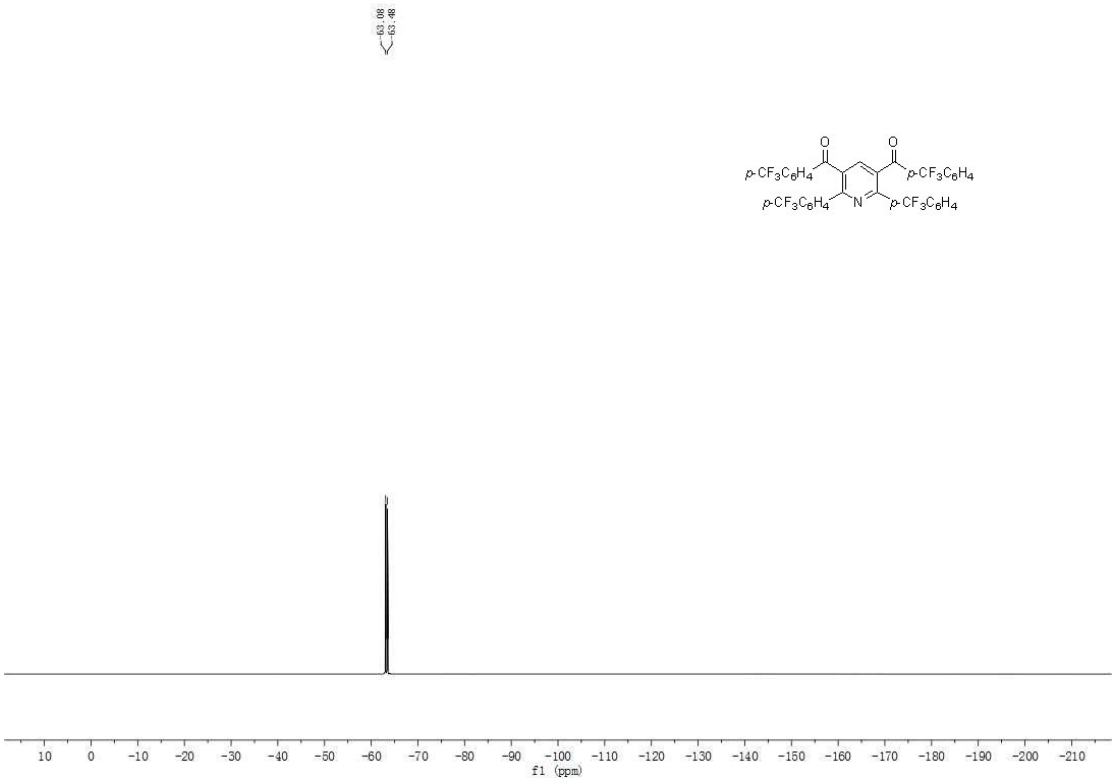
^{1}H NMR spectrum of product **4i**



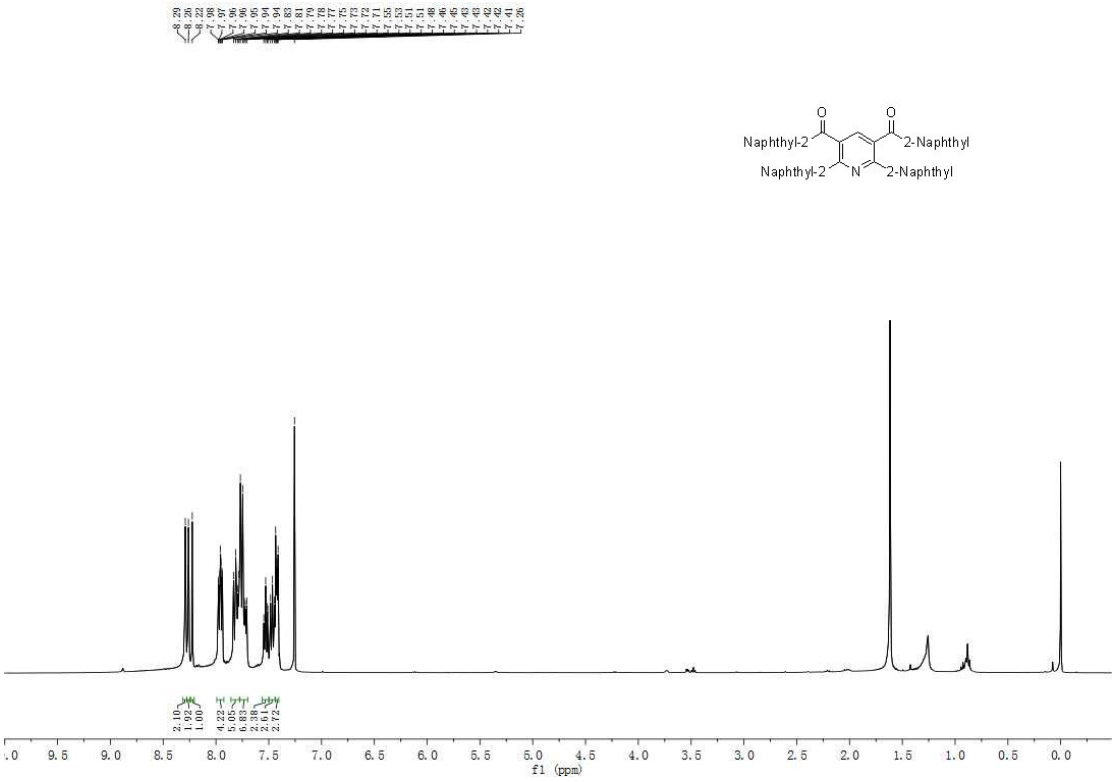
^{13}C NMR spectrum of product **4i**



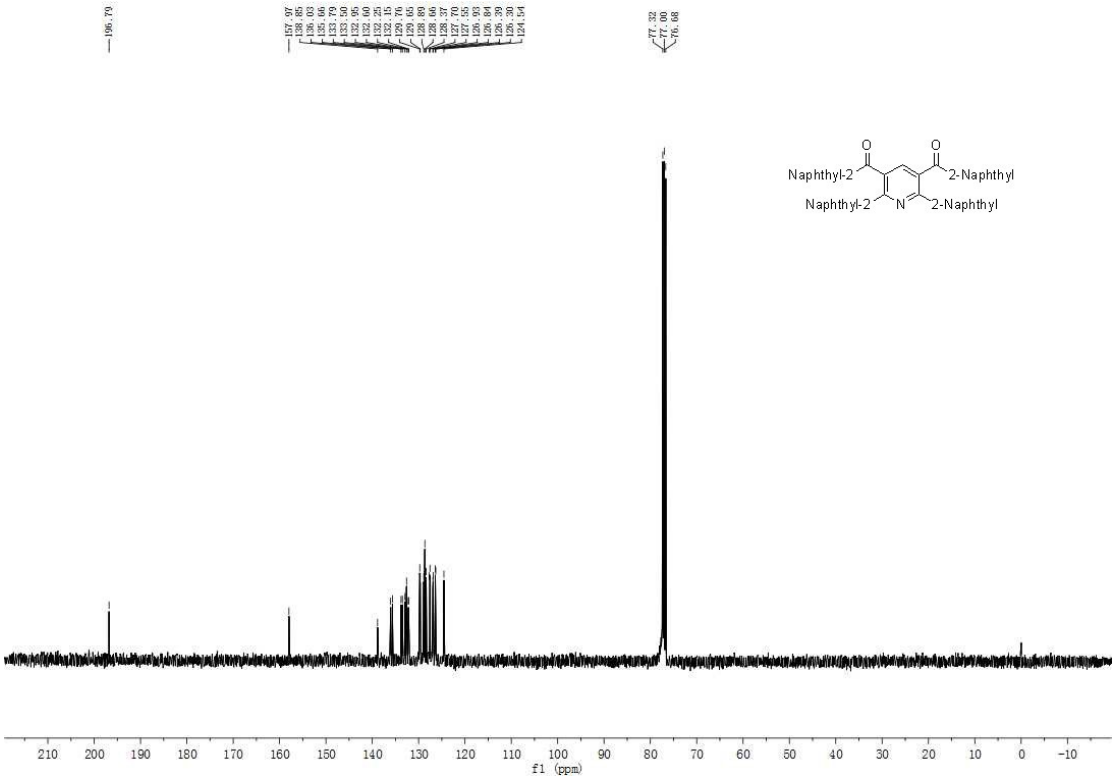
^{19}F NMR spectrum of product **4i**



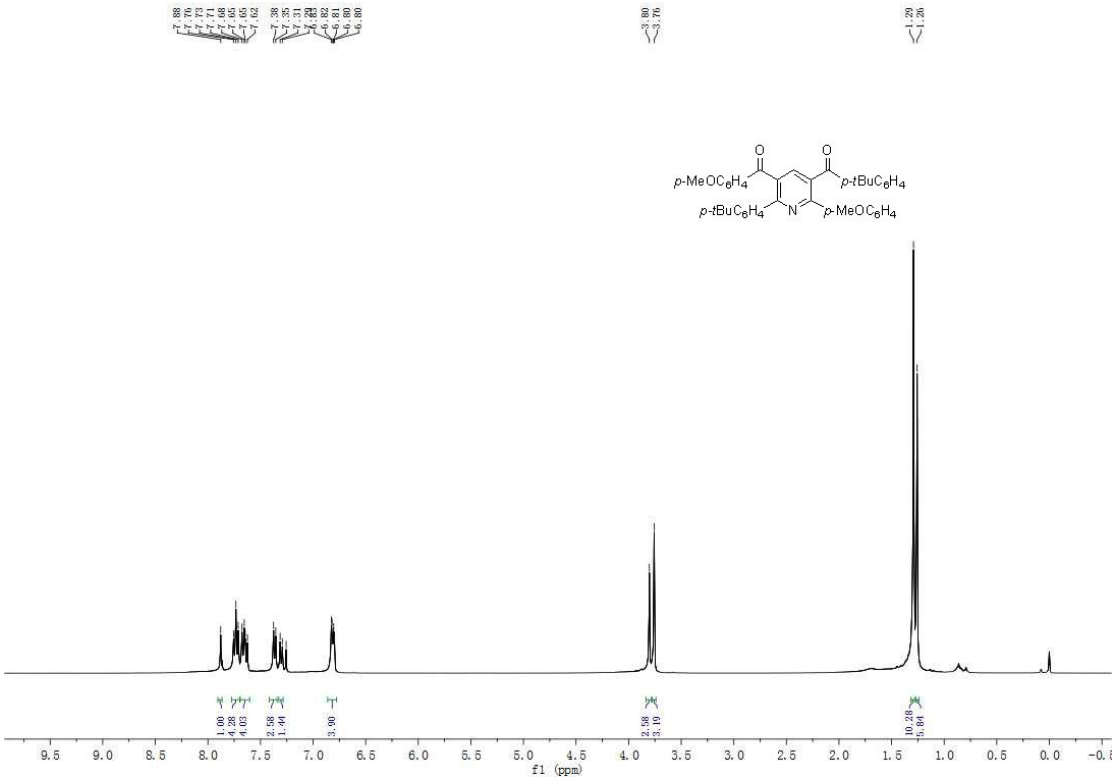
^{1}H NMR spectrum of product **4j**



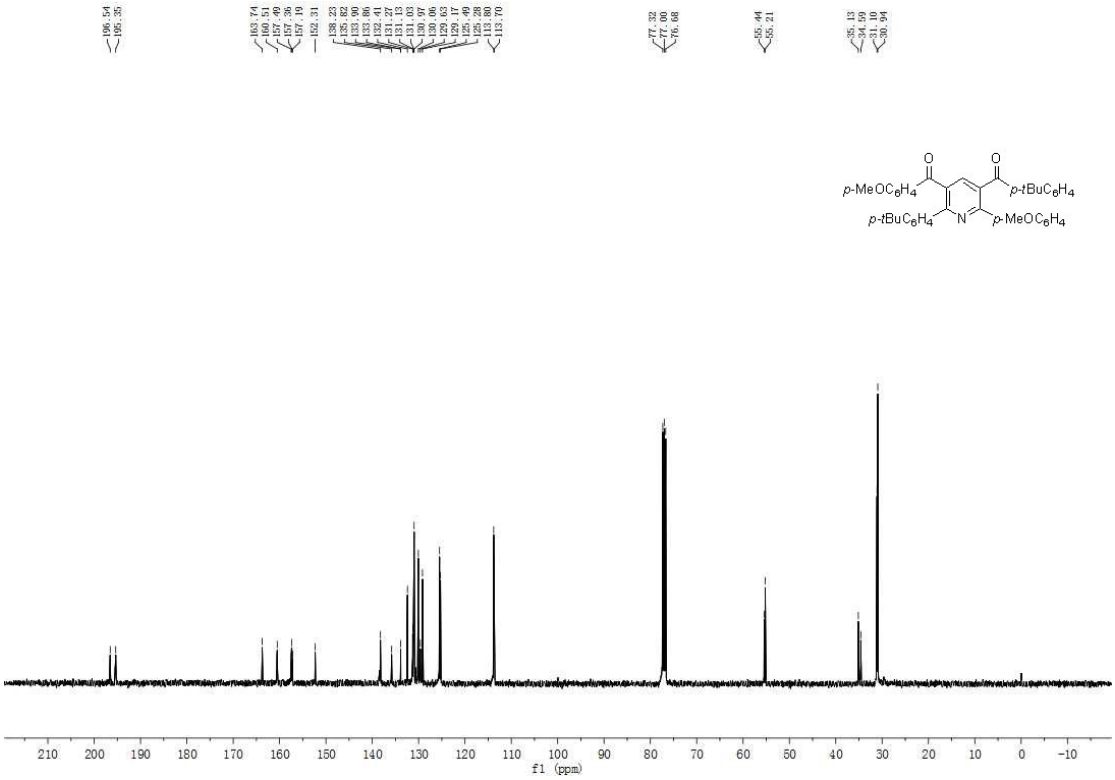
^{13}C NMR spectrum of product **4j**



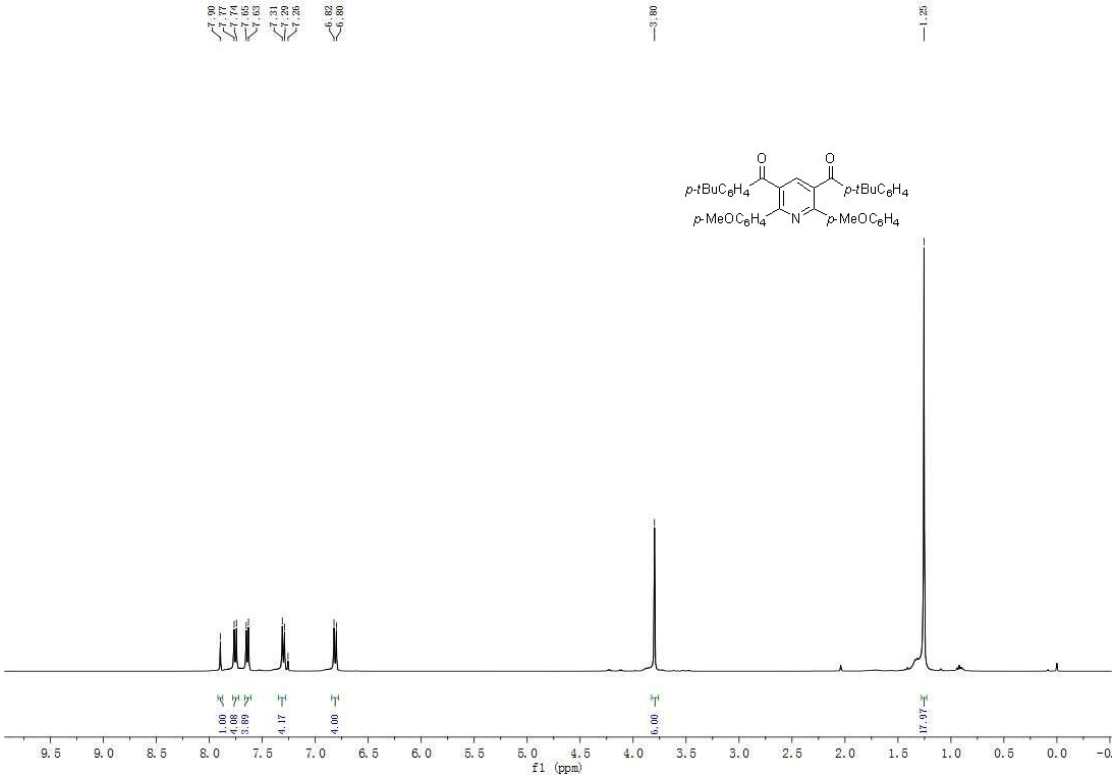
^{1}H NMR spectrum of product **4k**



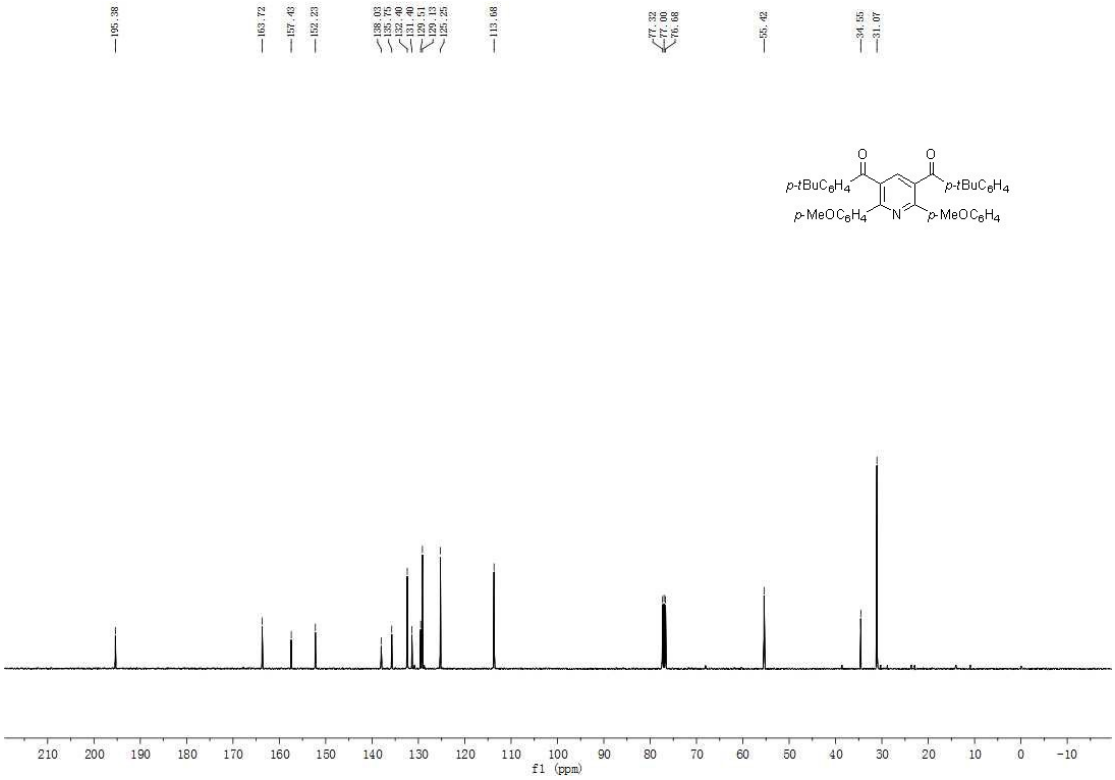
^{13}C NMR spectrum of product **4k**



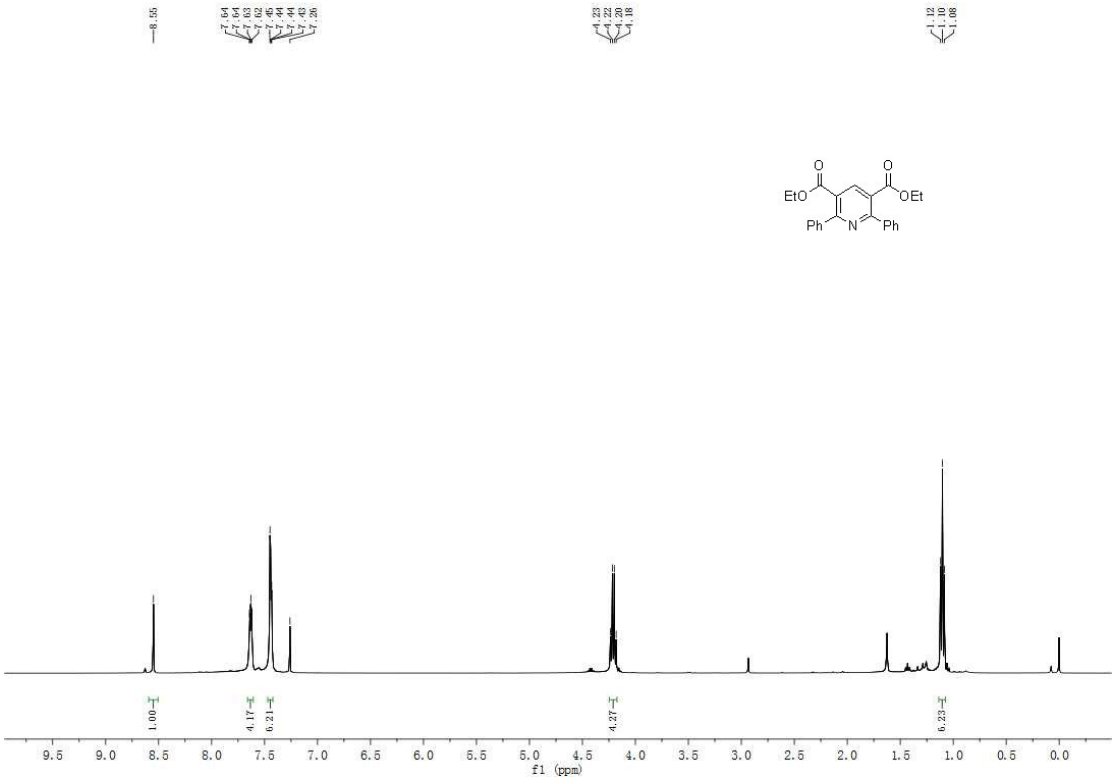
^{1}H NMR spectrum of product **4k`**



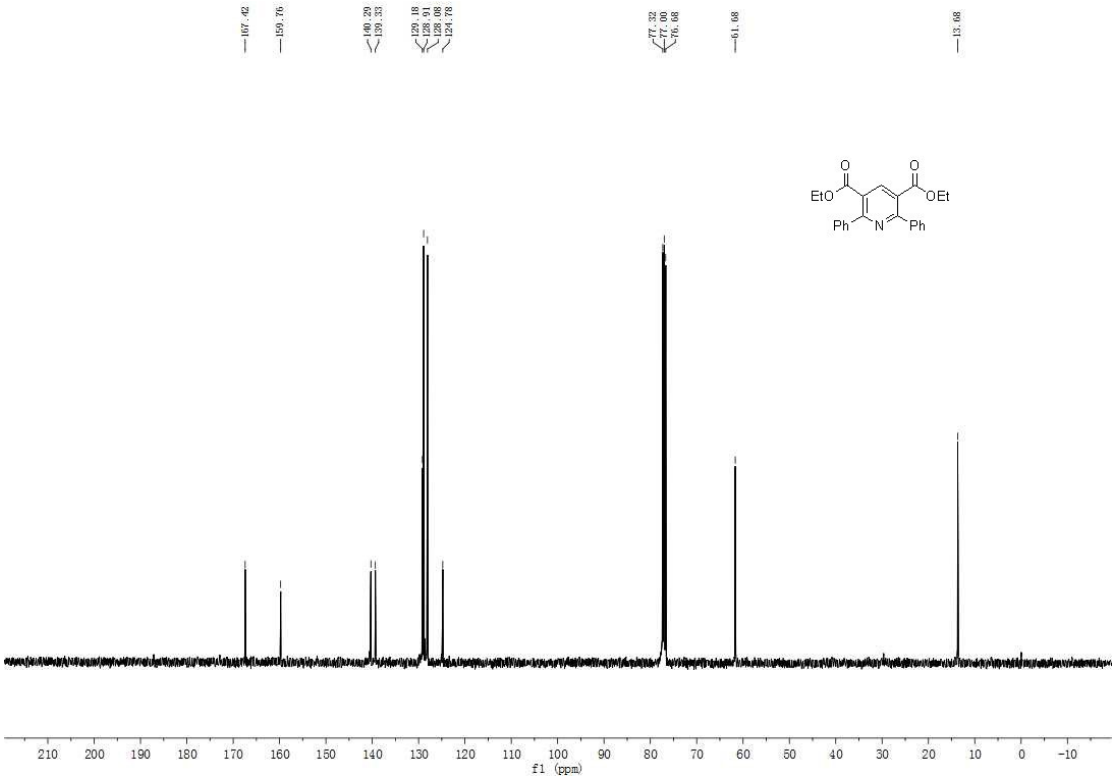
^{13}C NMR spectrum of product **4k`**



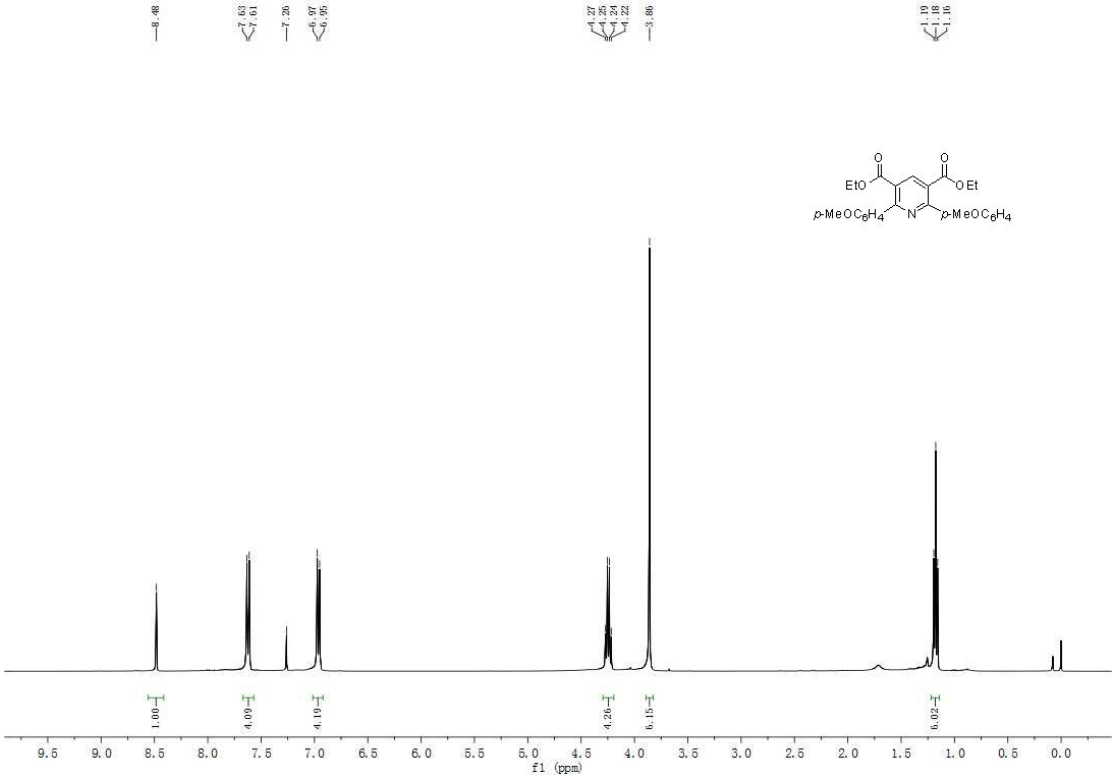
^{1}H NMR spectrum of product **4l**



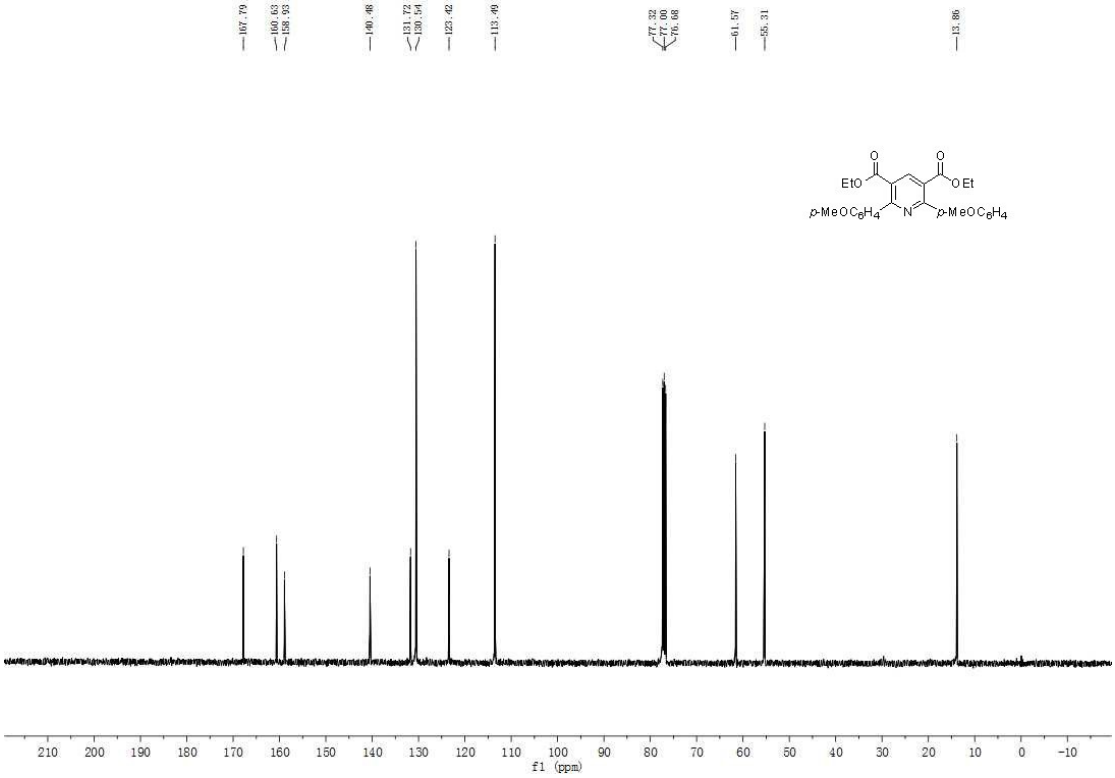
^{13}C NMR spectrum of product **4l**



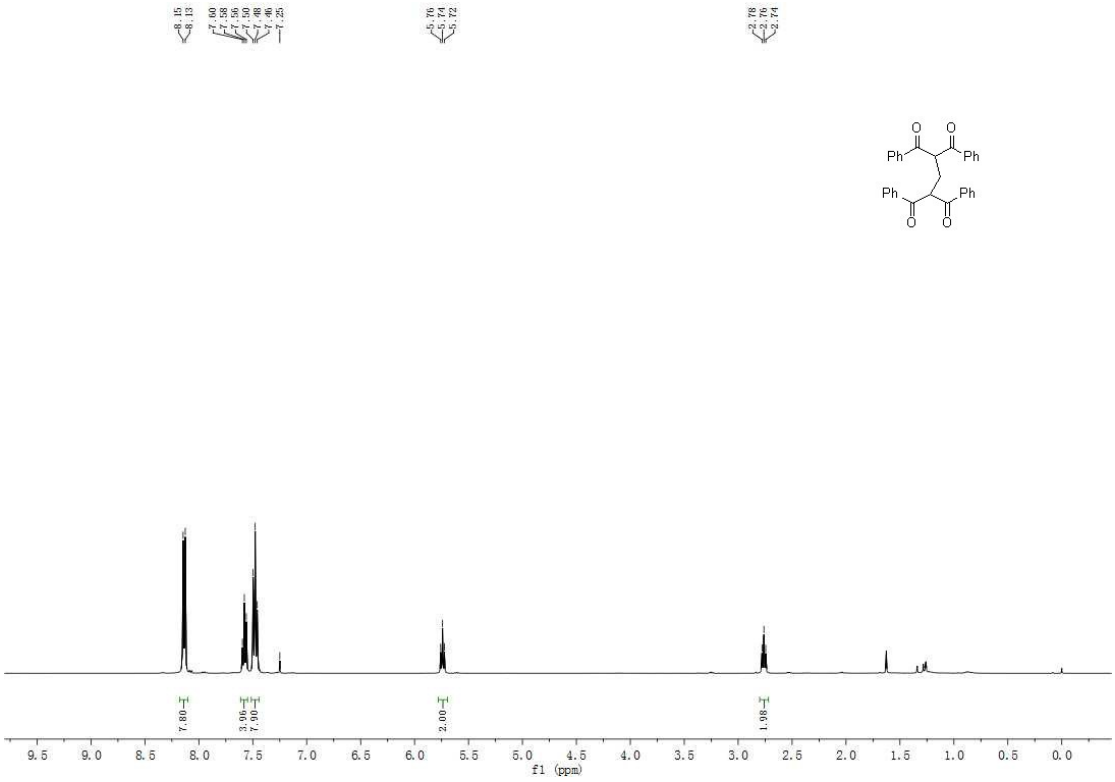
^{1}H NMR spectrum of product **4m**



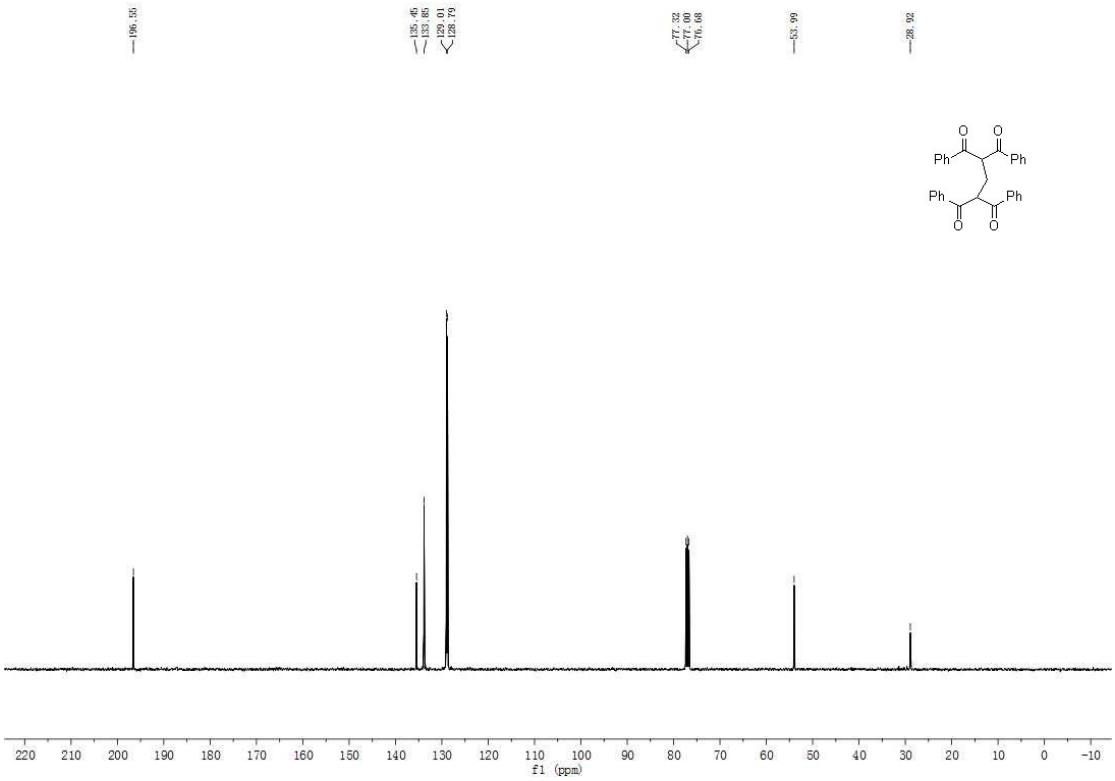
^{13}C NMR spectrum of product **4m**



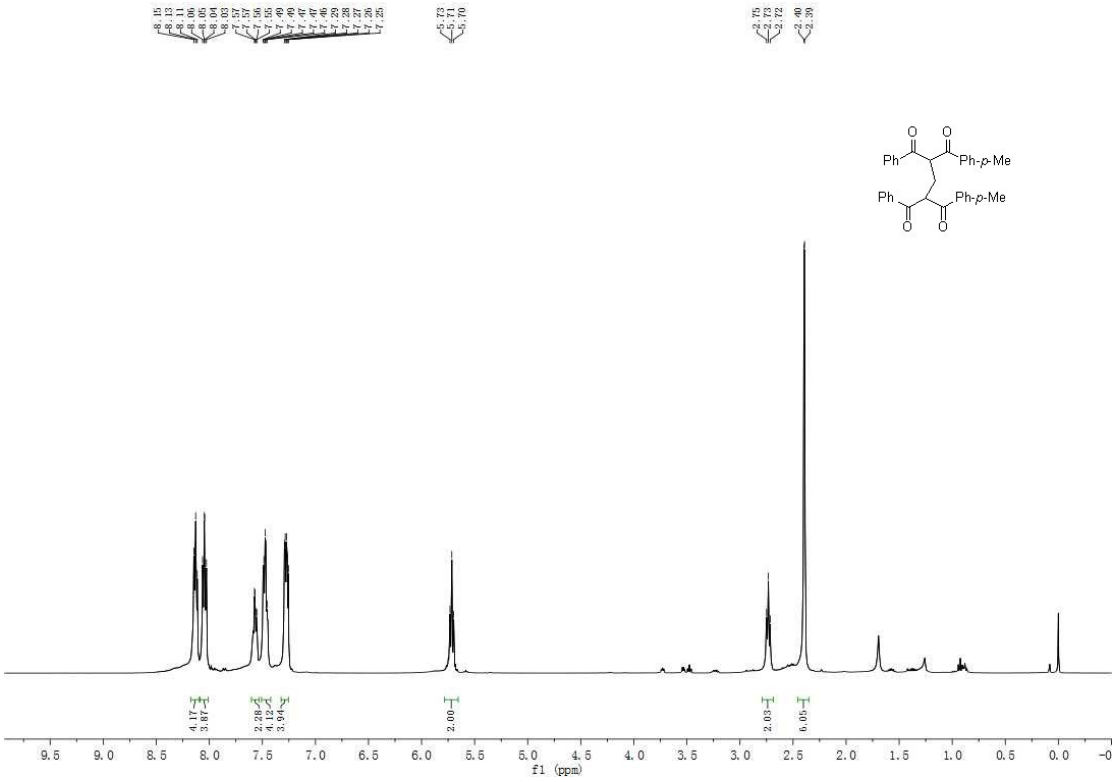
^{1}H NMR spectrum of product **2a**



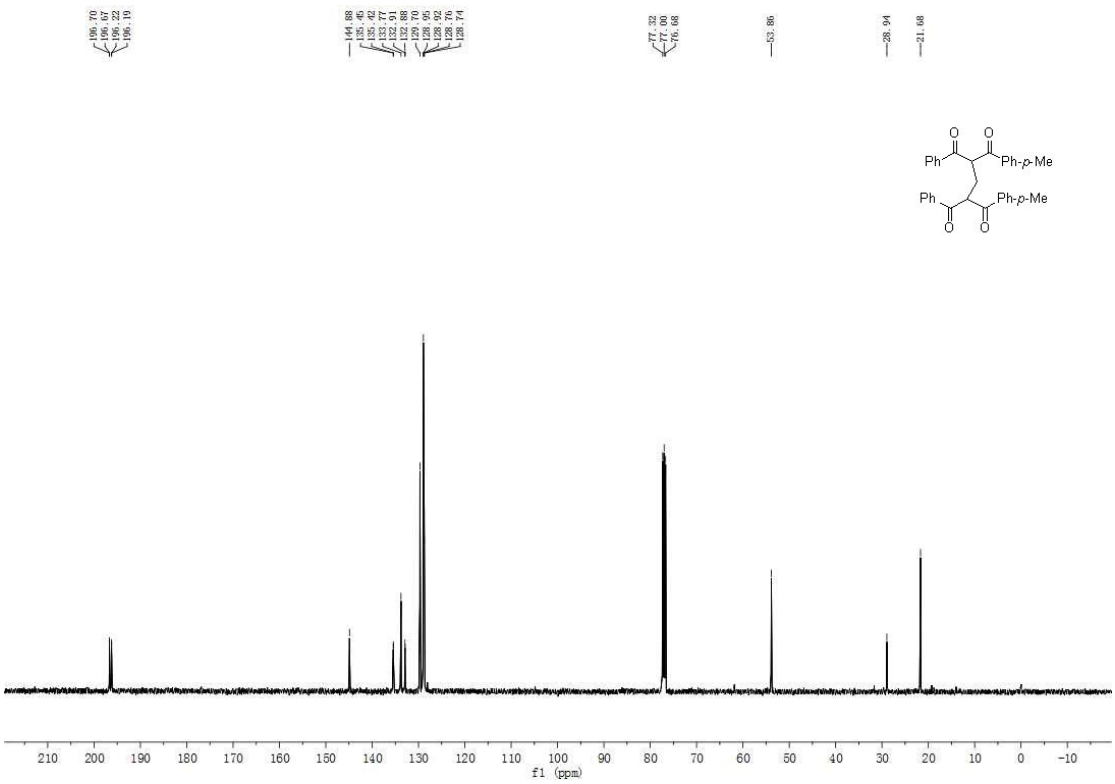
^{13}C NMR spectrum of product **2a**



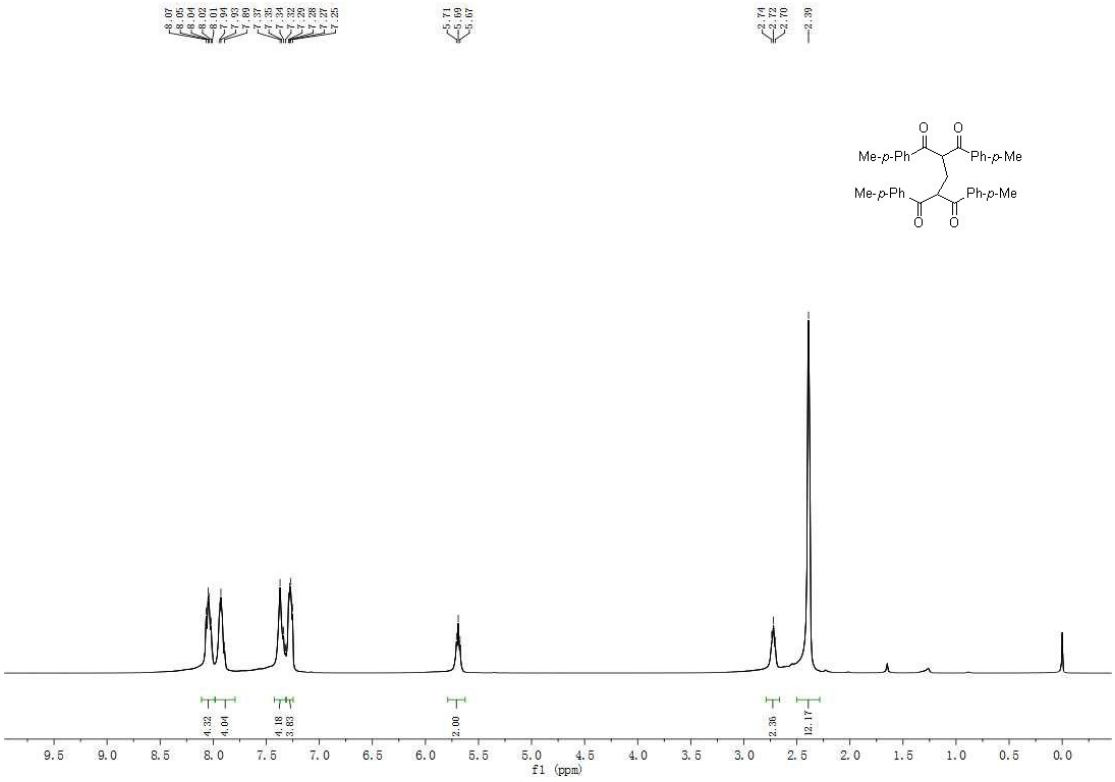
^{1}H NMR spectrum of product **2b**



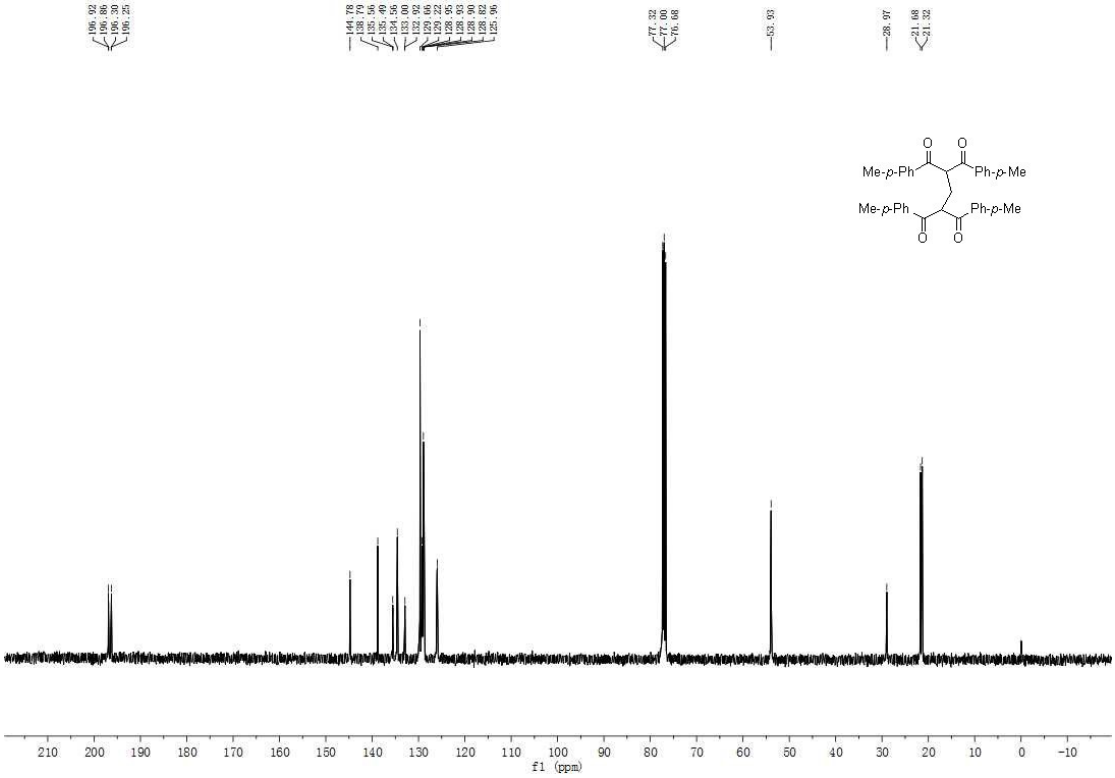
^{13}C NMR spectrum of product **2b**



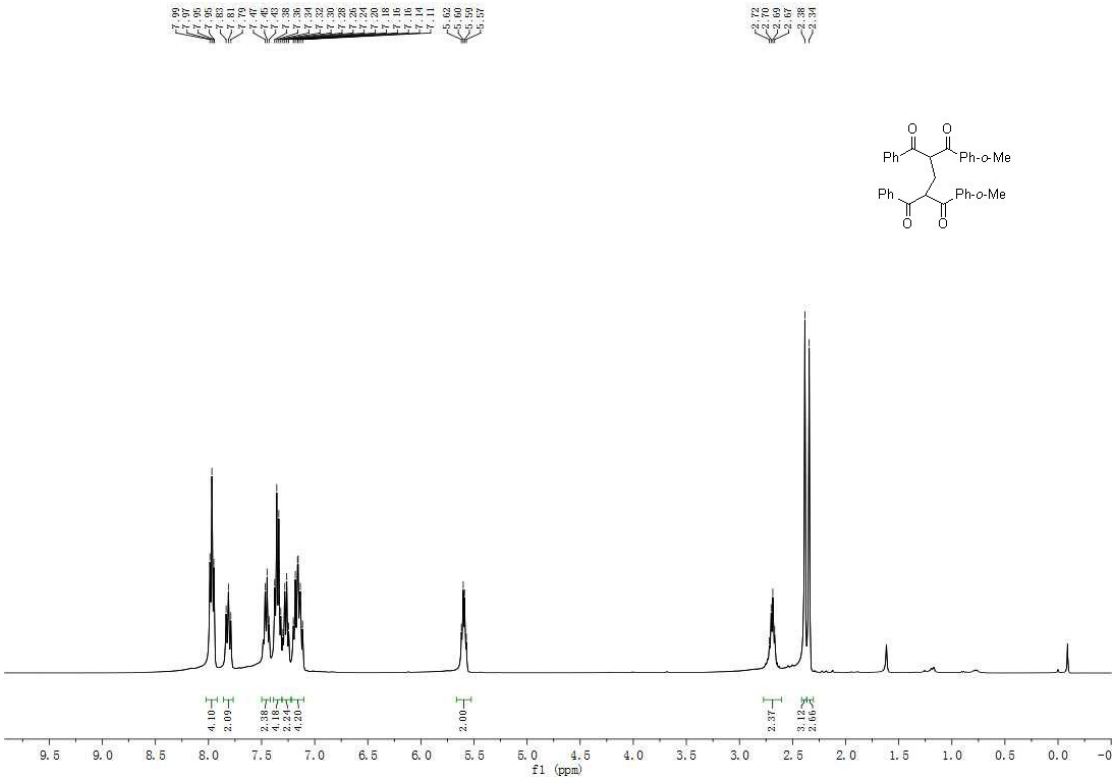
^{1}H NMR spectrum of product **2c**



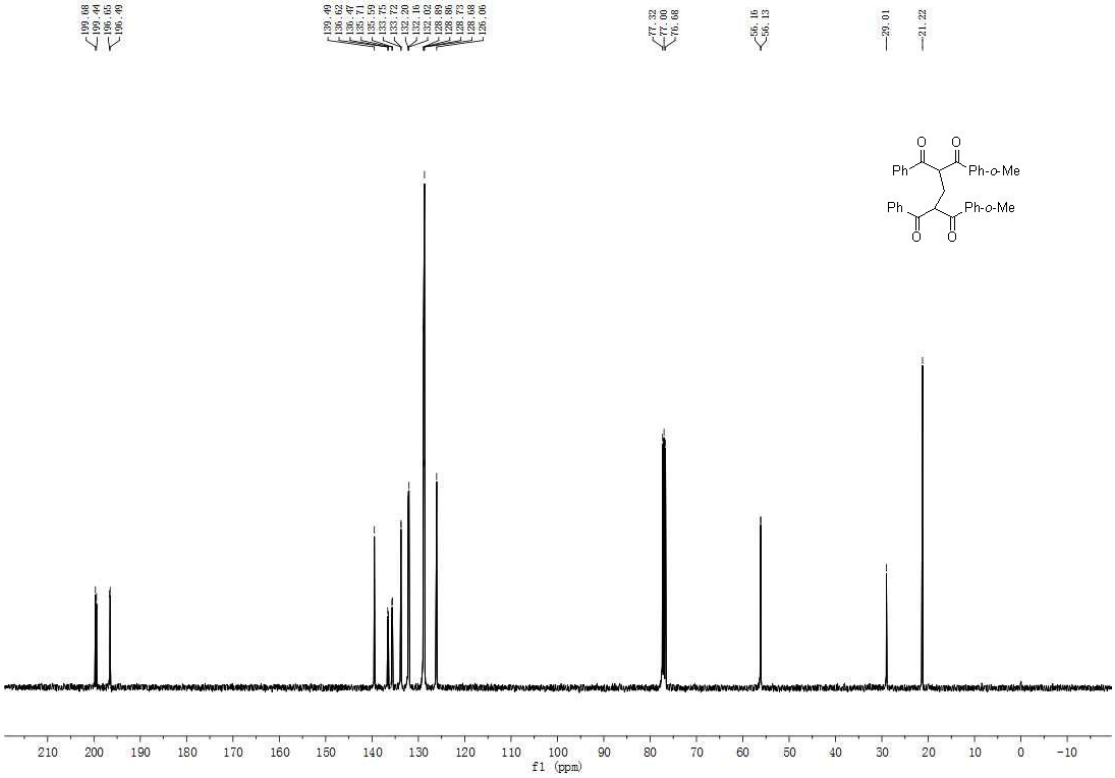
^{13}C NMR spectrum of product **2c**



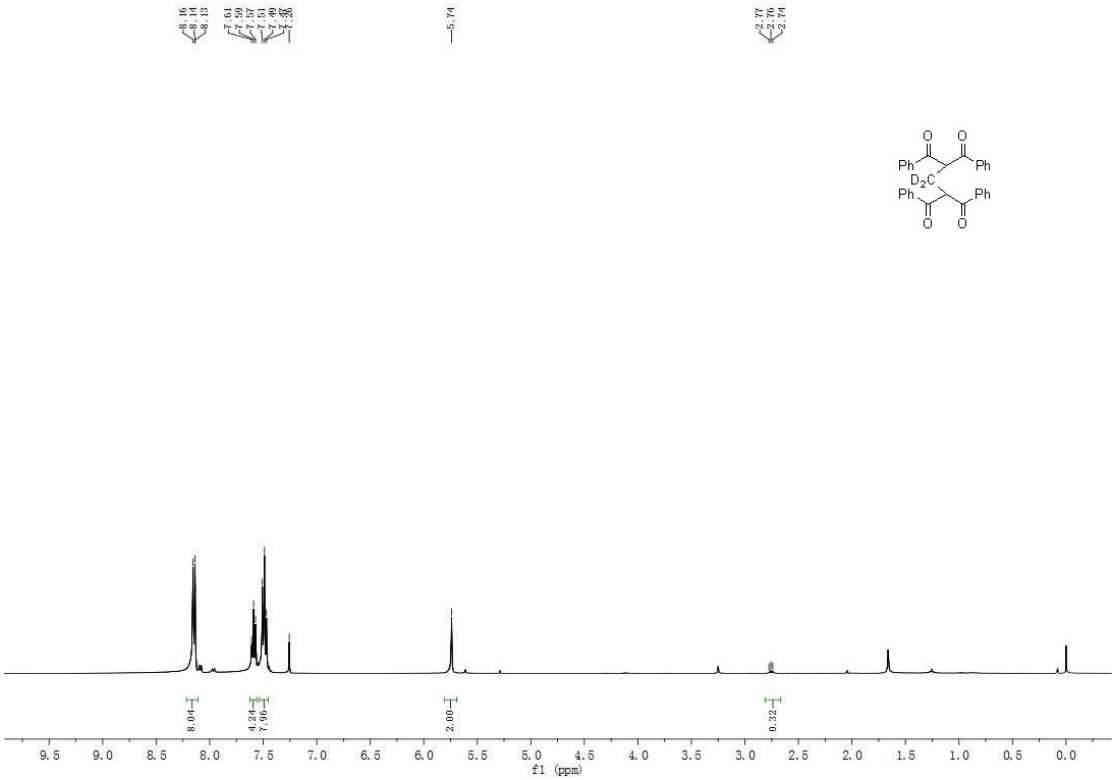
^{1}H NMR spectrum of product **2d**



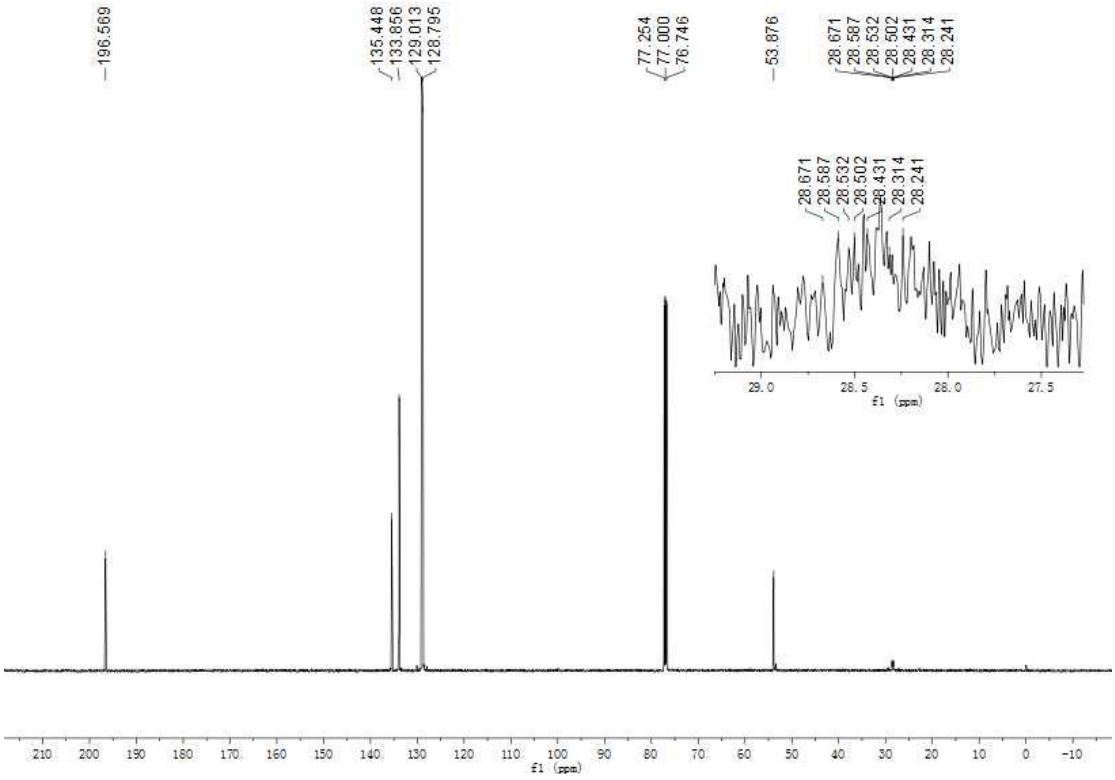
^{13}C NMR spectrum of product **2d**



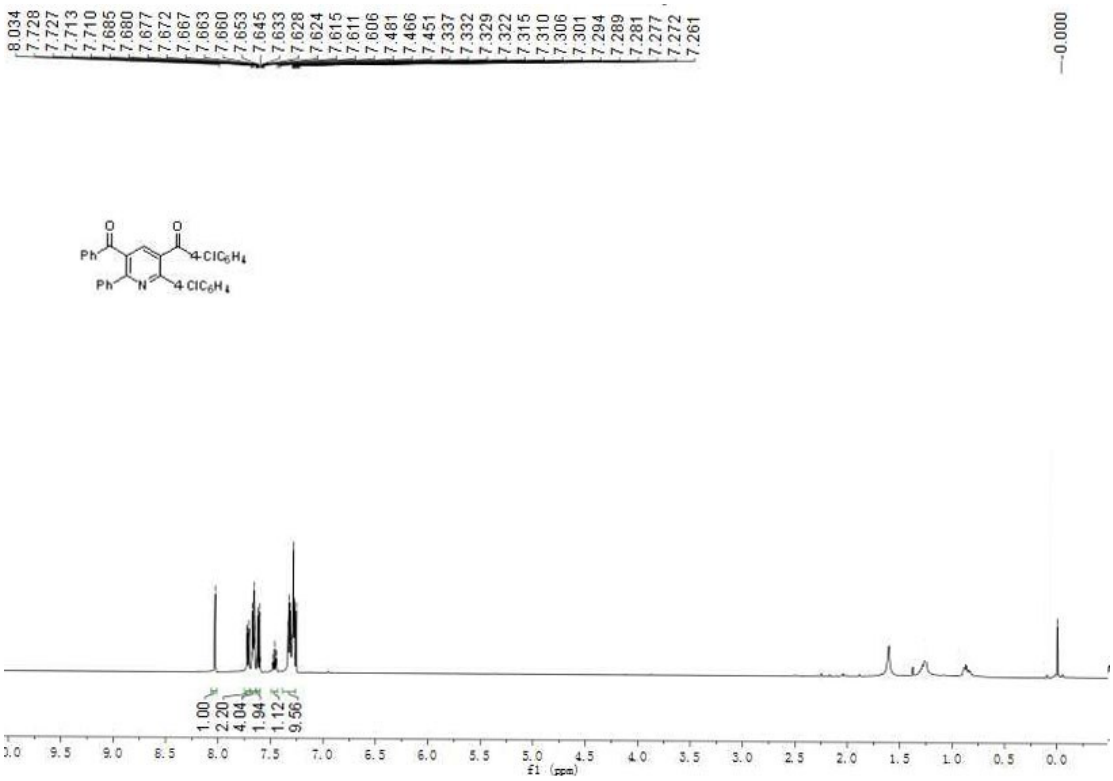
^{1}H NMR spectrum of product **2a-d_2**



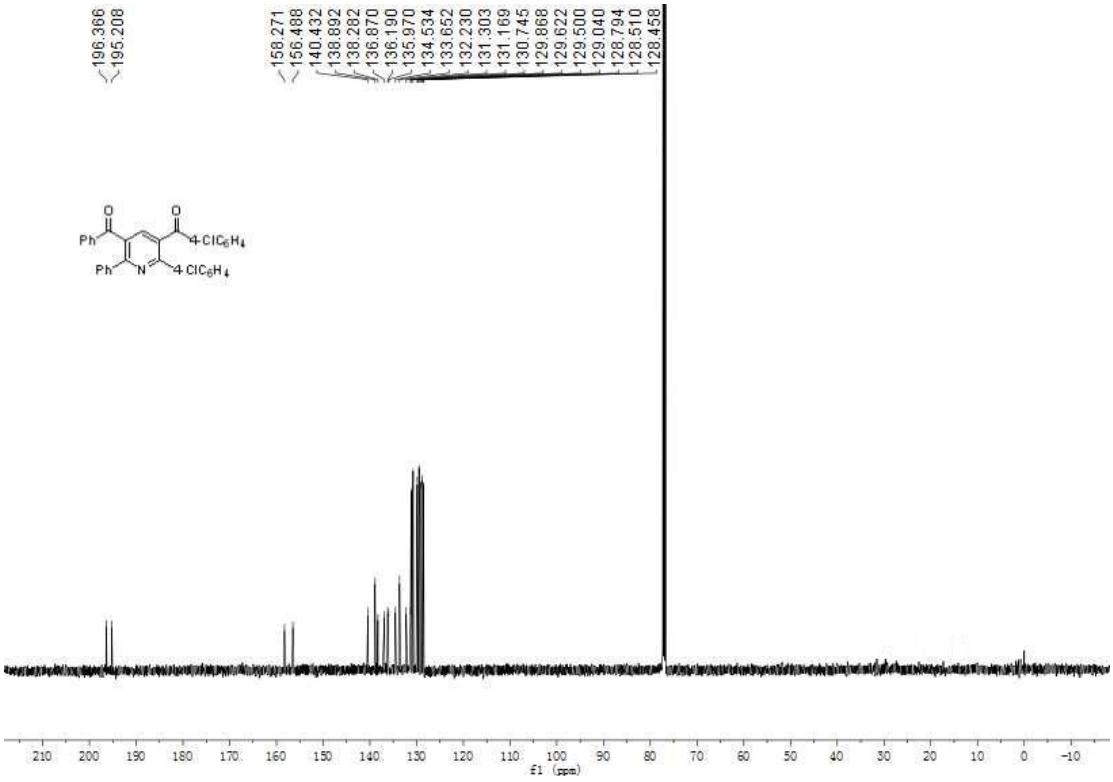
^{13}C NMR spectrum of product **2a-d_2**



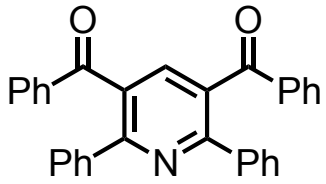
^{1}H NMR spectrum of product **5**



^{13}C NMR spectrum of product **5**



X-ray Crystallographic Data of 4a



4a

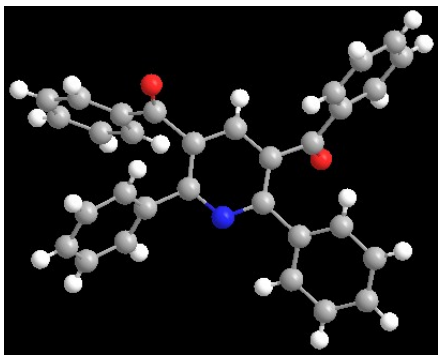


Table 1 Crystal data and structure refinement for 201209170.

Identification code	201209170
Empirical formula	$C_{31}H_{21}NO_2$
Formula weight	439.49
Temperature/K	291.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.03713(8)
b/Å	20.9196(3)
c/Å	18.2183(3)
α/°	90
β/°	96.0714(14)
γ/°	90
Volume/Å^3	2287.96(6)
Z	4
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.626
F(000)	920.0
Crystal size/mm^3	0.22 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.454 to 144.588
Index ranges	$-7 \leqslant h \leqslant 5$, $-25 \leqslant k \leqslant 25$, $-22 \leqslant l \leqslant 22$
Reflections collected	17209
Independent reflections	4491 [R_{int} = 0.0208, R_{sigma} = 0.0163]
Data/restraints/parameters	4491/0/307
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1066
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1125

Largest diff. peak/hole / e Å^{-3}	0.16/-0.22

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 201209170. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C_1	633(2)	6787.3(5)	8141.4(7)	37.6(3)
C_2	1953(2)	6803.7(6)	8822.3(7)	40.2(3)
C_3	3646(2)	6358.1(6)	8952.2(7)	44.6(3)
C_4	3928(2)	5890.3(6)	8430.7(7)	40.8(3)
C_5	2501(2)	5896.6(5)	7776.2(7)	38.9(3)
C_6	-1110(2)	7276.5(6)	7926.9(6)	38.8(3)
C_7	-3136(2)	7097.8(6)	7549.9(8)	46.5(3)
C_8	-4761(2)	7547.7(8)	7340.8(8)	54.3(3)
C_9	-4375(3)	8184.7(7)	7502.9(9)	56.1(4)
C_{10}	-2357(3)	8370.8(7)	7865.4(8)	52.5(3)
C_{11}	-728(2)	7922.2(6)	8077.9(7)	43.9(3)
C_{12}	1374(2)	7215.1(6)	9454.9(7)	42.9(3)
C_{13}	2998(2)	7693.1(6)	9789.0(7)	42.3(3)
C_{14}	2572(3)	7988.0(7)	10448.1(8)	55.8(4)
C_{15}	4051(3)	8429.2(9)	10776.1(9)	69.8(5)
C_{16}	5942(3)	8586.6(8)	10452.2(10)	68.6(5)
C_{17}	6376(3)	8302.6(7)	9802.3(9)	57.0(4)
C_{18}	4910(2)	7852.6(6)	9470.9(7)	46.8(3)
C_{19}	5676(2)	5381.2(6)	8591.6(7)	44.5(3)
C_{20}	4897(2)	4734.2(6)	8784.6(7)	42.4(3)
C_{21}	6256(3)	4212.4(7)	8692.9(8)	54.2(3)
C_{22}	5590(3)	3606.1(8)	8865.0(9)	64.9(4)
C_{23}	3605(3)	3516.8(8)	9156.3(9)	61.8(4)
C_{24}	2262(3)	4031.9(9)	9264.5(10)	66.9(4)
C_{25}	2879(2)	4640.2(8)	9066.5(9)	57.8(4)
C_{26}	2709(2)	5419.9(6)	7176.4(7)	41.0(3)
C_{27}	4649(2)	5370.1(7)	6839.2(9)	55.6(4)

C_{28}	4775(3)	4955.0(9)	6250.4(10)	65.6(4)
C_{29}	3006(3)	4574.1(8)	6014.9(10)	67.1(4)
C_{30}	1089(3)	4612.2(9)	6354.7(12)	74.9(5)
C_{31}	930(3)	5037.0(8)	6928.6(10)	60.5(4)
N_1	912.0(17)	6339.2(5)	7633.0(6)	39.2(2)
O_1	-407.8(18)	7125.9(5)	9692.5(6)	60.5(3)
O_2	7627.8(18)	5503.5(6)	8568.8(9)	74.9(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 201209170. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C_1	40.5(6)	33.2(5)	39.8(6)	1.6(4)	7.3(5)	-0.6(4)
C_2	44.7(6)	37.5(6)	38.8(6)	-0.6(5)	6.8(5)	0.9(5)
C_3	48.0(7)	47.7(7)	37.2(6)	-1.1(5)	0.8(5)	4.8(5)
C_4	42.0(6)	37.4(6)	43.5(6)	1.4(5)	6.2(5)	2.4(5)
C_5	41.3(6)	33.1(5)	42.6(6)	-0.3(5)	6.0(5)	-2.0(5)
C_6	43.1(6)	37.9(6)	36.3(6)	2.0(4)	8.1(5)	2.1(5)
C_7	46.1(7)	44.1(7)	49.6(7)	-0.7(5)	6.2(5)	-1.3(5)
C_8	43.1(7)	65.8(9)	53.5(8)	5.5(7)	2.7(6)	2.9(6)
C_9	58.6(8)	56.5(8)	53.7(8)	12.8(6)	8.7(6)	18.9(7)
C_{10}	67.7(9)	38.5(6)	51.6(8)	4.7(6)	8.3(6)	8.2(6)
C_{11}	50.6(7)	38.4(6)	42.6(6)	1.2(5)	4.2(5)	1.2(5)
C_{12}	51.1(7)	41.9(6)	36.4(6)	3.6(5)	7.6(5)	8.3(5)
C_{13}	54.2(7)	39.1(6)	33.1(6)	1.7(5)	1.6(5)	9.9(5)
C_{14}	71.6(9)	57.1(8)	39.7(7)	-4.6(6)	10.5(6)	8.1(7)
C_{15}	94.8(13)	68.7(10)	45.3(8)	-20.3(7)	5.1(8)	1.4(9)
C_{16}	82.7(12)	58.9(9)	60.6(10)	-14.2(7)	-9.2(8)	-5.7(8)
C_{17}	59.3(8)	53.1(8)	57.6(8)	-2.5(6)	0.9(7)	-0.5(6)
C_{18}	56.5(7)	44.4(7)	39.2(6)	-3.2(5)	3.5(5)	6.8(6)
C_{19}	40.6(6)	46.4(7)	46.4(7)	0.0(5)	4.5(5)	4.6(5)
C_{20}	40.8(6)	46.0(7)	39.4(6)	2.9(5)	0.0(5)	6.6(5)
C_{21}	58.8(8)	51.6(8)	54.1(8)	7.0(6)	14.5(6)	14.6(6)
C_{22}	88.3(12)	48.1(8)	59.7(9)	7.9(7)	14.2(8)	17.6(8)
C_{23}	76.7(10)	51.0(8)	54.4(8)	14.8(6)	-8.8(7)	-4.8(7)
C_{24}	48.4(8)	73(1)	78.5(11)	25.5(9)	3.7(7)	-3.1(7)
C_{25}	44.6(7)	56.7(8)	72.5(10)	14.2(7)	7.8(7)	10.3(6)
C_{26}	45.6(6)	32.9(6)	43.9(6)	-1.8(5)	1.0(5)	3.2(5)

C_{27}	49.1(7)	54.0(8)	64.2(9)	-16.7(7)	8.8(6)	-5.1(6)
C_{28}	59.5(9)	70.4(10)	68.7(10)	-21.0(8)	15.1(8)	6.5(8)
C_{29}	77.6(11)	56.6(9)	65.7(10)	-26.8(8)	0.8(8)	8.5(8)
C_{30}	69.6(11)	67.7(10)	86.5(12)	-34.4(9)	4.5(9)	-17.7(8)
C_{31}	53.3(8)	59.2(9)	69.7(10)	-18.6(7)	10.8(7)	-9.7(7)
N_1	42.4(5)	35.2(5)	39.8(5)	-0.9(4)	3.7(4)	0.8(4)
O_1	59.9(6)	67.0(7)	57.8(6)	-6.9(5)	21.7(5)	-1.3(5)
O_2	43.0(6)	62.4(7)	120.4(11)	16.0(7)	14.2(6)	2.7(5)

Table 4 Bond Lengths for 201209170.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C_1	C_2	1.4022(17)	C_{13}	C_{18}	1.386(2)
C_1	C_6	1.4902(16)	C_{14}	C_{15}	1.376(2)
C_1	N_1	1.3409(16)	C_{15}	C_{16}	1.379(3)
C_2	C_3	1.3850(18)	C_{16}	C_{17}	1.375(2)
C_2	C_{12}	1.5087(17)	C_{17}	C_{18}	1.386(2)
C_3	C_4	1.3870(18)	C_{19}	C_{20}	1.4870(18)
C_4	C_5	1.3952(18)	C_{19}	O_2	1.2110(17)
C_4	C_{19}	1.5060(17)	C_{20}	C_{21}	1.3860(18)
C_5	C_{26}	1.4944(17)	C_{20}	C_{25}	1.386(2)
C_5	N_1	1.3390(16)	C_{21}	C_{22}	1.377(2)
C_6	C_7	1.3891(18)	C_{22}	C_{23}	1.373(2)
C_6	C_{11}	1.3929(17)	C_{23}	C_{24}	1.375(3)
C_7	C_8	1.384(2)	C_{24}	C_{25}	1.384(2)
C_8	C_9	1.379(2)	C_{26}	C_{27}	1.383(2)
C_9	C_{10}	1.379(2)	C_{26}	C_{31}	1.3772(19)
C_{10}	C_{11}	1.3847(19)	C_{27}	C_{28}	1.388(2)
C_{12}	C_{13}	1.4852(19)	C_{28}	C_{29}	1.365(2)
C_{12}	O_1	1.2158(17)	C_{29}	C_{30}	1.372(3)
C_{13}	C_{14}	1.3978(18)	C_{30}	C_{31}	1.383(2)

Table 5 Bond Angles for 201209170.

Atom	Atom	Atom	Angle/	Atom	Atom	Atom	Angle/
C_2	C_1	C_6	122.33(11)	C_{18}	C_{13}	C_{14}	119.34(13)
N_1	C_1	C_2	121.79(11)	C_{15}	C_{14}	C_{13}	119.95(15)

N_1	C_1	C_6	115.85(11)	C_{14}	C_{15}	C_{16}	120.19(15)
C_1	C_2	C_{12}	122.27(11)	C_{17}	C_{16}	C_{15}	120.47(16)
C_3	C_2	C_1	118.35(11)	C_{16}	C_{17}	C_{18}	119.84(16)
C_3	C_2	C_{12}	118.67(11)	C_{13}	C_{18}	C_{17}	120.21(13)
C_2	C_3	C_4	119.98(12)	C_{20}	C_{19}	C_4	117.22(11)
C_3	C_4	C_5	118.00(11)	O_2	C_{19}	C_4	120.54(12)
C_3	C_4	C_{19}	119.99(12)	O_2	C_{19}	C_{20}	122.23(12)
C_5	C_4	C_{19}	121.97(11)	C_{21}	C_{20}	C_{19}	118.86(12)
C_4	C_5	C_{26}	121.78(11)	C_{25}	C_{20}	C_{19}	121.94(12)
N_1	C_5	C_4	122.53(11)	C_{25}	C_{20}	C_{21}	119.18(13)
N_1	C_5	C_{26}	115.65(11)	C_{22}	C_{21}	C_{20}	120.50(15)
C_7	C_6	C_1	120.35(11)	C_{23}	C_{22}	C_{21}	120.06(15)
C_7	C_6	C_{11}	118.52(12)	C_{22}	C_{23}	C_{24}	120.05(15)
C_{11}	C_6	C_1	121.10(11)	C_{23}	C_{24}	C_{25}	120.24(15)
C_8	C_7	C_6	120.98(13)	C_{24}	C_{25}	C_{20}	119.90(14)
C_9	C_8	C_7	119.95(14)	C_{27}	C_{26}	C_5	121.05(11)
C_{10}	C_9	C_8	119.75(13)	C_{31}	C_{26}	C_5	120.32(12)
C_9	C_{10}	C_{11}	120.52(13)	C_{31}	C_{26}	C_{27}	118.59(13)
C_{10}	C_{11}	C_6	120.27(13)	C_{26}	C_{27}	C_{28}	120.57(14)
C_{13}	C_{12}	C_2	120.06(11)	C_{29}	C_{28}	C_{27}	120.20(15)
O_1	C_{12}	C_2	118.01(12)	C_{28}	C_{29}	C_{30}	119.59(14)
O_1	C_{12}	C_{13}	121.88(12)	C_{29}	C_{30}	C_{31}	120.51(15)
C_{14}	C_{13}	C_{12}	118.41(13)	C_{26}	C_{31}	C_{30}	120.49(15)
C_{18}	C_{13}	C_{12}	122.25(11)	C_5	N_1	C_1	119.26(11)

Table 6 Torsion Angles for 201209170.

A	B	C	D	Angle/	A	B	C	D	Angle/
C_1	C_2	C_3	C_4	-3.29(19)	C_{12}	C_2	C_3	C_4	167.23(12)
C_1	C_2	C_{12}	C_{13}	-123.18(13)	C_{12}	C_{13}	C_{14}	C_{15}	179.46(14)
C_1	C_2	C_{12}	O_1	59.30(17)	C_{12}	C_{13}	C_{18}	C_{17}	179.88(12)
C_1	C_6	C_7	C_8	-179.36(12)	C_{13}	C_{14}	C_{15}	C_{16}	0.7(3)
C_1	C_6	C_{11}	C_{10}	179.13(12)	C_{14}	C_{13}	C_{18}	C_{17}	-0.32(19)
C_2	C_1	C_6	C_7	-140.44(13)	C_{14}	C_{15}	C_{16}	C_{17}	-0.4(3)
C_2	C_1	C_6	C_{11}	41.54(17)	C_{15}	C_{16}	C_{17}	C_{18}	-0.3(3)
C_2	C_1	N_1	C_5	-0.36(17)	C_{16}	C_{17}	C_{18}	C_{13}	0.6(2)
C_2	C_3	C_4	C_5	1.51(19)	C_{18}	C_{13}	C_{14}	C_{15}	-0.3(2)
C_2	C_3	C_4	C_{19}	-176.19(12)	C_{19}	C_4	C_5	C_{26}	-3.62(18)
C_2	C_{12}	C_{13}	C_{14}	-169.36(12)	C_{19}	C_4	C_5	N_1	178.63(11)

C_2	C_{12}	C_{13}	C_{18}	10.44(18)	C_{19}	C_{20}	C_{21}	C_{22}	-179.93(14)
C_3	C_2	C_{12}	C_{13}	66.69(16)	C_{19}	C_{20}	C_{25}	C_{24}	-177.55(15)
C_3	C_2	C_{12}	O_1	-110.82(15)	C_{20}	C_{21}	C_{22}	C_{23}	-2.5(3)
C_3	C_4	C_5	C_{26}	178.74(12)	C_{21}	C_{20}	C_{25}	C_{24}	1.1(2)
C_3	C_4	C_5	N_1	0.99(18)	C_{21}	C_{22}	C_{23}	C_{24}	1.1(3)
C_3	C_4	C_{19}	C_{20}	104.03(15)	C_{22}	C_{23}	C_{24}	C_{25}	1.4(3)
C_3	C_4	C_{19}	O_2	-75.31(19)	C_{23}	C_{24}	C_{25}	C_{20}	-2.5(3)
C_4	C_5	C_{26}	C_{27}	-59.66(18)	C_{25}	C_{20}	C_{21}	C_{22}	1.3(2)
C_4	C_5	C_{26}	C_{31}	122.88(15)	C_{26}	C_5	N_1	C_1	-179.44(11)
C_4	C_5	N_1	C_1	-1.57(18)	C_{26}	C_{27}	C_{28}	C_{29}	-2.3(3)
C_4	C_{19}	C_{20}	C_{21}	158.38(13)	C_{27}	C_{26}	C_{31}	C_{30}	0.0(3)
C_4	C_{19}	C_{20}	C_{25}	-22.92(19)	C_{27}	C_{28}	C_{29}	C_{30}	1.2(3)
C_5	C_4	C_{19}	C_{20}	-73.56(16)	C_{28}	C_{29}	C_{30}	C_{31}	0.6(3)
C_5	C_4	C_{19}	O_2	107.09(17)	C_{29}	C_{30}	C_{31}	C_{26}	-1.2(3)
C_5	C_{26}	C_{27}	C_{28}	-175.79(15)	C_{31}	C_{26}	C_{27}	C_{28}	1.7(2)
C_5	C_{26}	C_{31}	C_{30}	177.55(16)	N_1	C_1	C_2	C_3	2.77(18)
C_6	C_1	C_2	C_3	-175.14(11)	N_1	C_1	C_2	C_{12}	-167.39(11)
C_6	C_1	C_2	C_{12}	14.70(18)	N_1	C_1	C_6	C_7	41.53(16)
C_6	C_1	N_1	C_5	177.68(10)	N_1	C_1	C_6	C_{11}	-136.48(12)
C_6	C_7	C_8	C_9	0.4(2)	N_1	C_5	C_{26}	C_{27}	118.24(14)
C_7	C_6	C_{11}	C_{10}	1.08(19)	N_1	C_5	C_{26}	C_{31}	-59.22(17)
C_7	C_8	C_9	C_{10}	0.8(2)	O_1	C_{12}	C_{13}	C_{14}	8.06(19)
C_8	C_9	C_{10}	C_{11}	-1.0(2)	O_1	C_{12}	C_{13}	C_{18}	-172.15(13)
C_9	C_{10}	C_{11}	C_6	0.0(2)	O_2	C_{19}	C_{20}	C_{21}	-22.3(2)
C_{11}	C_6	C_7	C_8	-1.29(19)	O_2	C_{19}	C_{20}	C_{25}	156.41(16)

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 201209170.

Atom	*x*	*y*	*z*	U(eq)
H_3	4593	6373	9389	53
H_7	-3404	6669	7436	56
H_8	-6113	7421	7091	65
H_9	-5471	8488	7368	67
H_{10}	-2088	8801	7968	63
H_{11}	627	8053	8322	53
H_{14}	1290	7886	10665	67
H_{15}	3775	8622	11217	84
H_{16}	6931	8887	10675	82

H_{17}	7651	8412	9585	68
H_{18}	5210	7657	9034	56
H_{21}	7627	4272	8514	65
H_{22}	6484	3257	8784	78
H_{23}	3170	3108	9280	74
H_{24}	934	3971	9472	80
H_{25}	1940	4985	9123	69
H_{27}	5880	5617	7008	67
H_{28}	6069	4936	6016	79
H_{29}	3100	4290	5626	81
H_{30}	-114	4350	6198	90
H_{31}	-388	5064	7149	73