Supporting information

Reductive deoxygenation of alcohols by PMHS assisted by iodide

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1.Materials

Acetonitrile, acetone, cyclohexane, n-hexane, 4-methyl-2-pentanone, furfuryl alcohol, 2-thiophenemethanol, 2-methylthiophene, benzyl alcohol, toluene, benzaldehyde, 4-methylbenzyl alcohol, xylenes, m-methylbenzyl alcohol, m-xylene, 2-methylbenzyl alcohol, ortho-xylene, 3,5-dimethoxybenzyl alcohol, 3,5-dimethoxytoluene, anisic alcohol, 4-methylanisole, 4-isopropylbenzyl alcohol, 4-isopropyltoluene, 4-cyanobenzyl alcohol, p-tolunitrile, terephthalyl alcohol, para-xylene, phenyl ethanol, ethylbenzene, styrene, cinnamic alcohol, 2-methylnaphthalene, 6-methylquinoline, hexane, 57.0 wt.% hydroiodic acid (HI), 47.0 wt.% hydrobromic acid (HBr) and 2,5-furandicarbaldehyde (DFF) were purchased from Aladdin; P-Hydroxybenzoic acid were purchased from Beijing Innochem Technology co., LTD; 2-methylfuran and 2,5-dimethylfuran were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd; 2-methyltetrahydrofuran (MTHF), tetrahydrofuran (THF), 5-methyl furfural (5-MF), p-toluic acid and 4-methylphenylene were purchased from MΛCKLIN; toluene and 37.0 wt.% hydrochloric acid (HCl) were purchased from Xilong Chemical; furan-2,5-diyldimethanol were purchased from Shanghai Adamas Reagent Co., Ltd; 2-naphthalenemethanol was purchased from Acros Organics; sulfuric acid (H_2SO_4) and acetic acid (CH_3COOH) were purchased from Tianjin Damao Chemical Reagent Factory; sodium iodide (NaI) was purchased from Chinese Medicine Group Chemical Reagent Co. Ltd. All solvents mentioned above do not contain BHT. All reagents were used without further purification, and solvents were not distilled unless specified.

2.Methods

Analytical procedures

The product was quantitatively analyzed using an Agilent 7820A gas chromatograph (GC) manufactured by Agilent, USA. The GC analysis conditions were as follows: chromatographic column HP-5 capillary column (30 m × 320 μm × 0.25 μm); hydrogen flame ionization detector (FID); initial oven temperature 40 °C, first increased at 3 °C min^{-1} to 100 °C, then increased at 10 °C min^{-1} to 200 °C, and finally maintained for 5 min; injection port temperature 280 °C; detector temperature 280 °C; high purity N_2 as the carrier gas, flowed at 1.5 mL min^{-1}; split ratio 20 : 1; the injection volume 1 μL.

The product was qualitatively analyzed using a Thermo Scientific TRACE 1310 GCMS. GCMS analysis conditions were as follows: chromatographic column HP-5 capillary column (30 m × 320 μm ×0.25 μm); initial oven temperature 40 °C, maintained for 5 min, and first increased at 5 °C min^{-1} to 100 °C, then increased at 10 °C min^{-1} to 150 °C, followed by increasing at 20 °C min^{-1} to 280 °C, and finally maintained for 5 min; ion source temperature 290 °C; the filament opened at 0 – 3.12 min and 4.0 – 35 min and closed at 3.12 – 4.0 min; high purity He as the carrier gas, at a flow rate of 1.0 ml min^{-1}; split ratio 20:1; the injection volume 0.2 μL.

Typical experiment

A high-pressure stainless-steel reactor, a temperature controller, and IKA magnetic stirring apparatus were supplied by Anhui Kemi Machinery Technology Co., ltd., China. In a typical reaction, 1 mmol substrate, 1 mmol HI, 2 mmol PMHS, 10 mL cyclohexane, were sequentially placed into a 50 mL quartz vial. Then, the vial was placed into a 50 mL stainless steel autoclave. And the stainless-steel autoclave was put on the IKA magnetic stirring apparatus. The autoclave was purged by three cycles of pressurization/venting with N_2 (400 psi N_2) before being pressurized with N_2 (200 psi N_2). For the standard reaction, the reaction temperature was set to 140 ℃ with a heating rate of 10 ℃/min and usually took 12 min to reach the desired temperature (not credited for reaction time). When the reaction was stopped, the reactor was cooled with a water bath. Then, the organic phase was collected for analysis and fractionated.

Synthesis separation method

First, the reaction solution was mixed with silica gel and spun dry. Then, the products were separated by silica gel column. Eluent was ethyl acetate: petroleum ether =1:100 mixed solvent. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm.

3. Table S1 Optimization of N_2 pressure and PMHS added amount

Entry	PMHS (mmol)	N_2 (psi)	Conv. (%)	Yield (%)	
				Toluene	Bn-I
1	2	14.7	99	46	48
2	2	100	99	99	N. D.
3	2	200	99	99	N. D.
4	2	300	99	99	N. D.
5	2	100	99	99	N. D.
6	1	100	99	99	N. D.

Reaction Condition: 1.0 mmol benzyl alcohol, 2.0 mmol PMHS, 1.0 mmol HI, 10 mL cyclohexane, 500 rpm，140 ℃, 2 h.

4. Liquid mass spectrometry data

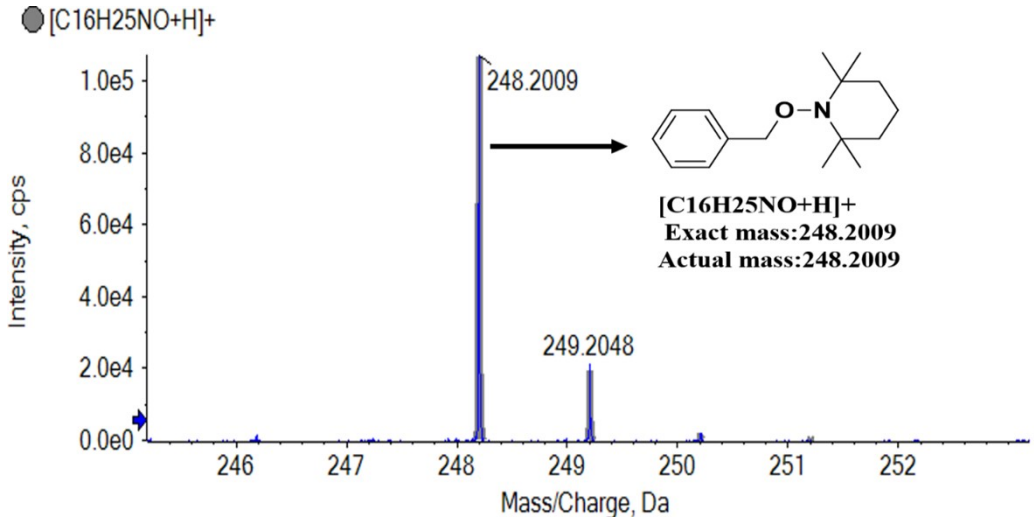


Figure S1 $C_{16}H_{25}NO$ (Tempo captured the toluene radical to form a new compound) liquid chromatography-mass spectrometry graph. $C_{16}H_{26}NO$ hydrogenation ($[C_{16}H_{25}NO+H]+$) prediction quality 248.2009 under Q-TOF positive ion scan, actual measurement quality 266.2009.

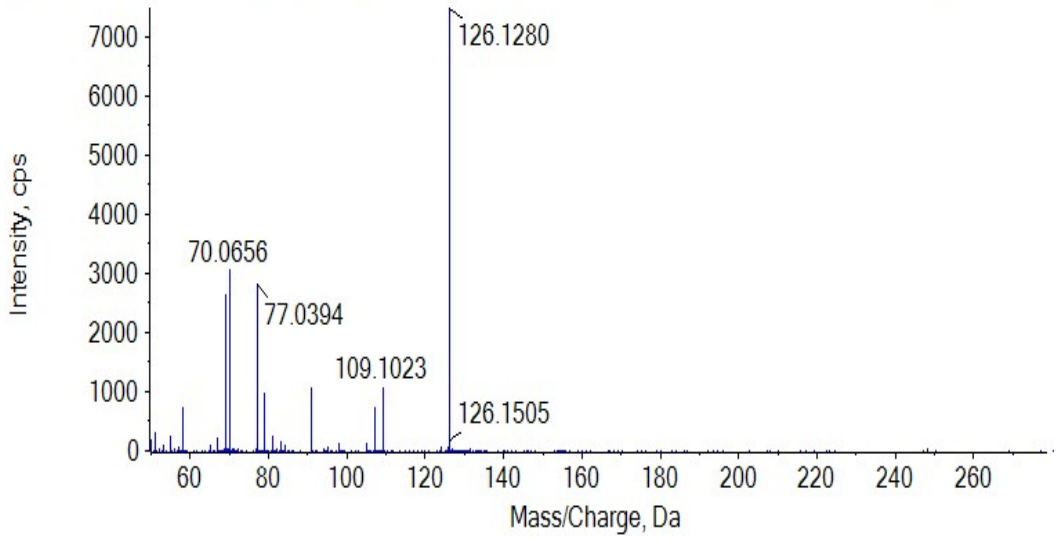
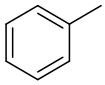


Figure S2 $C_{16}H_{25}NO$ (Tempo captured the toluene radical to form a new compound) liquid chromatography-mass spectrometry fragment peak graph.

5. 1H and 13C NMR Spectral data of all the compounds

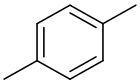
Toluene (P1)



P1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.8, 6.6 Hz, 2H), 7.88 (t, *J* = 7.2 Hz, 3H), 3.04 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.37, 129.77, 128.96, 126.08, 22.02.

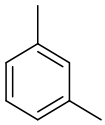
p-Xylene (P2, P11)



P2, P11

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 4H), 2.97 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.15, 129.58, 21.47.

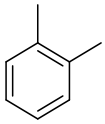
m-Xylene (P3)



P3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 9.0, 7.0 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 3H), 2.91 (d, *J* = 2.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.16, 130.47, 128.73, 126.67, 21.81.

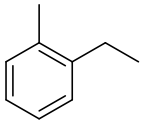
o-Xylene (P4)



P4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 4H), 2.97 (s, 6H).
^{13}C NMR (100MHz, $CDCl_3$) δ 136.98, 130.32, 126.58, 20.29.

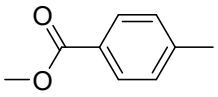
2-Ethyltoluene (P5)



P5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 4H), 3.34 (q, *J* = 7.6 Hz, 2H), 3.02 (s, 3H), 2.02 – 1.91 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.79, 136.17, 130.74, 128.55, 126.80, 126.49, 26.93, 19.72, 15.09.

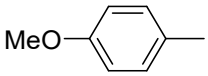
Methyl 4-methylbenzoate (P6)



P6

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dt, *J*=8.0, 2.4 Hz, 2H), 7.42-7.37 (m, 2H), 4.07 (s, 3H), 2.56 (s, 3H), 4.07 (d, 1H),
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 143.47, 129.56, 129.03, 127.40, 51.82, 21.53.

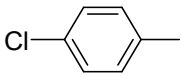
4-Methylanisole (P7)



P7

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 2H), 7.13 – 7.03 (m, 2H), 3.98 (s, 3H), 2.57 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.86, 130.16, 129.88, 113.93, 55.19, 20.62.

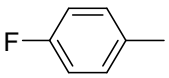
4-Chlorotoluene (P8)



P8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.36, 131.28, 130.56, 128.44, 20.91.

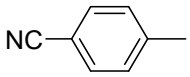
p-Fluorotoluene (P9)



P9

1H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 8.5, 5.6 Hz, 2H), 7.16 – 6.95 (m, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.41, 160.00, 133.46, 133.42, 130.44, 130.37, 115.10, 114.89, 20.59.

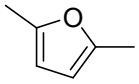
p-Tolunitrile (P10)



P10

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 2.46 – 2.29 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.71, 131.89, 129.83, 119.11, 109.11, 21.70.

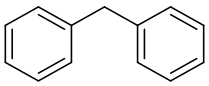
2,5-Dimethylfuran (P12)



P12

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (s, 2H), 2.43 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.13, 106.12, 13.28.

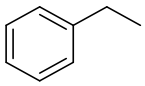
Diphenylmethane (P13)



P13

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.71 (m, 10H), 4.52 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.75, 129.62, 129.12, 126.73, 42.57.

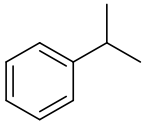
Ethylbenzene(P14)



P14

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.85 – 7.73 (m, 3H), 3.26 (q, *J* = 7.6 Hz, 2H), 1.92 – 1.84 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.70, 128.93, 128.45, 126.24, 29.57, 16.27.

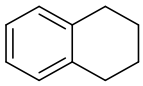
Cumene (P15)



P15

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.73 (m, 5H), 3.50 (hept, *J* = 6.9 Hz, 1H), 1.89 (d, *J* = 7.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.26, 128.93, 126.96, 126.39, 34.78, 24.62.

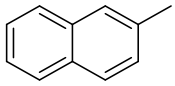
1,2,3,4-Tetrahydronaphthalene (P16)



P16

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.62 (m, 4H), 3.48 – 3.37 (m, 4H), 2.46 (dq, *J* = 6.9, 3.4 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.54, 129.77, 126.10, 30.11, 24.03.

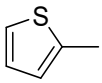
2-Methylnaphthalene (P17)



P17

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 3H), 7.76 (s, 1H), 7.65 – 7.54 (m, 2H), 7.46 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.66 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.58, 133.83, 131.87, 128.29, 127.87, 127.78, 127.42, 127.02, 126.04, 125.13, 21.89.

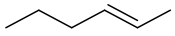
2-Methylthiophene (P18)



P18

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.2, 1.3 Hz, 1H), 7.26 (dd, *J* = 5.3, 3.4 Hz, 1H), 7.12 (dp, *J* = 3.5, 1.1 Hz, 1H), 2.85 (d, *J* = 1.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.82, 127.27, 125.57, 123.46, 15.32.

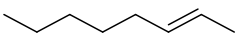
2-Hexene (P19)



P19

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.13 (m, 2H), 1.85 (q, *J* = 7.3 Hz, 2H), 1.52 – 1.38 (m, 3H), 1.22 (hept, *J* = 7.0 Hz, 2H), 0.74 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 130.46, 123.64, 28.89, 22.72, 13.56, 12.48.

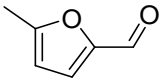
2-Octene (P20)



P20

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 – 5.09 (m, 2H), 1.98 – 1.77 (m, 2H), 1.54 (dt, *J* = 4.9, 1.5 Hz, 3H), 1.32 – 1.15 (m, 6H), 0.80 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.50, 124.32, 32.62, 31.48, 29.37, 22.59, 17.64, 13.86.

5-Methyl furfural(P21)

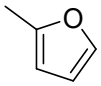


P21

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.12 (d, *J* = 3.7 Hz, 1H), 6.16 (dd, *J* = 3.6, 1.1 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.46, 159.42, 151.60, 124.01, 109.33, 13.52.

2-Methylfuran (P22)

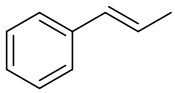


P22

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.2 Hz, 1H), 6.39 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.09 (dt, *J* = 3.1, 1.1 Hz, 1H), 2.41 (d, *J* = 1.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.10, 140.82, 110.36, 105.49, 13.25.

(E)- beta-Methylstyrene (P23)

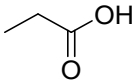


P23

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.78 – 7.61 (m, 3H), 5.87 – 5.81 (m, 1H), 5.53 (p, *J* = 1.5 Hz, 1H), 2.57 (d, *J* = 2.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65, 141.61, 128.66, 127.83, 125.93, 112.79, 22.17.

Propionic acid(P24)



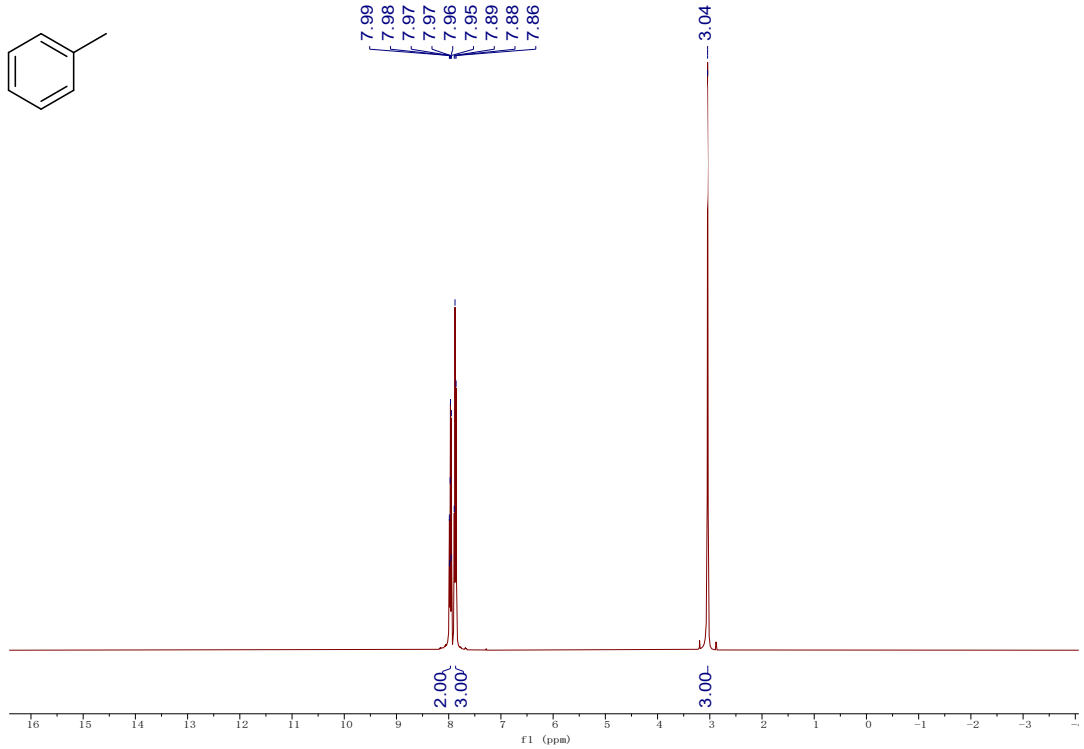
P24

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 2.02 (q, *J* = 7.6 Hz, 2H), 0.86 – 0.68 (m, 3H).

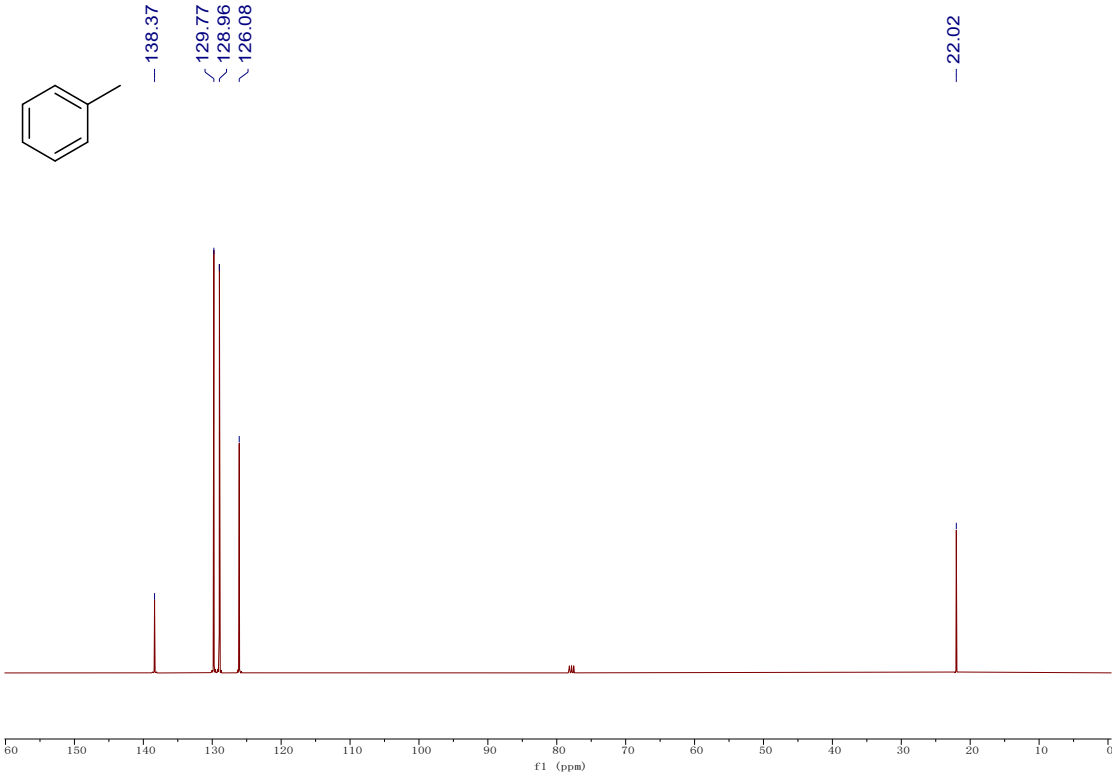
13C NMR (101 MHz, $CDCl_3$) δ 181.06, 27.11, 8.34.

6. Copies of 1 H NMR, and 13C NMR

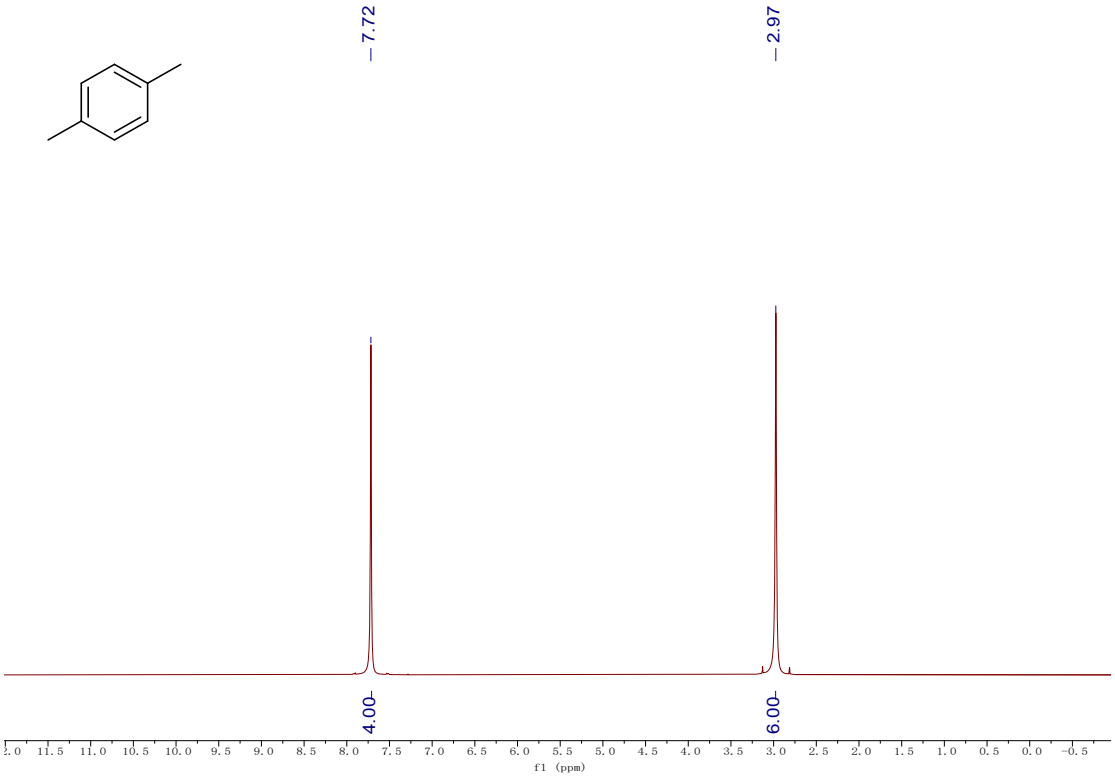
1H NMR (400 MHz, $CDCl_3$) of P1



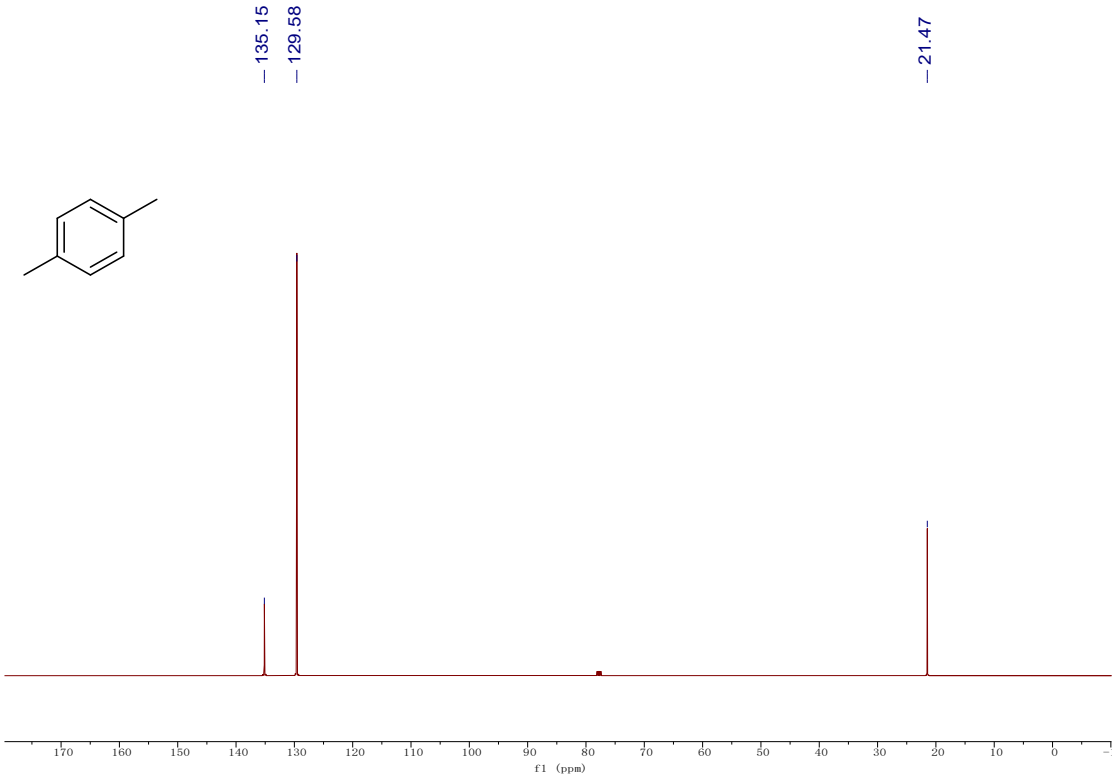
^{13}C NMR (101 MHz, $CDCl_3$) of P1



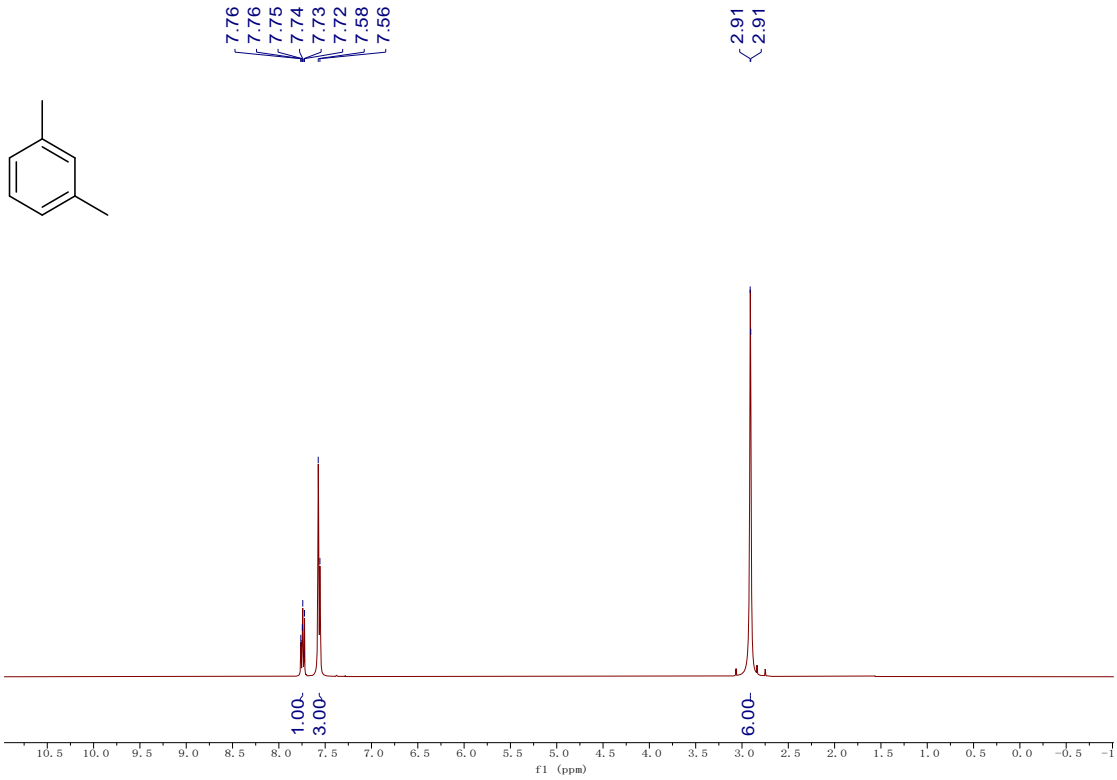
1H NMR (400 MHz, $CDCl_3$) of P2, P11



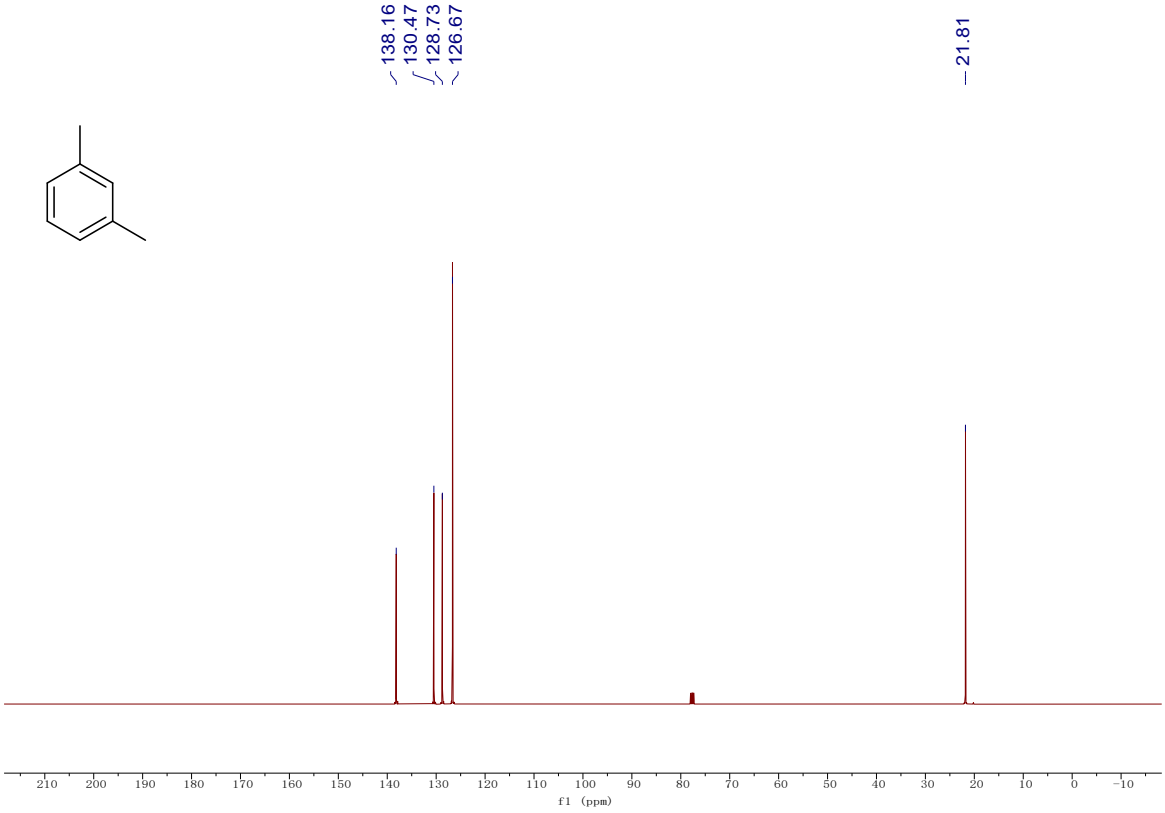
^{13}C NMR (101 MHz, $CDCl_3$) of P2, P11



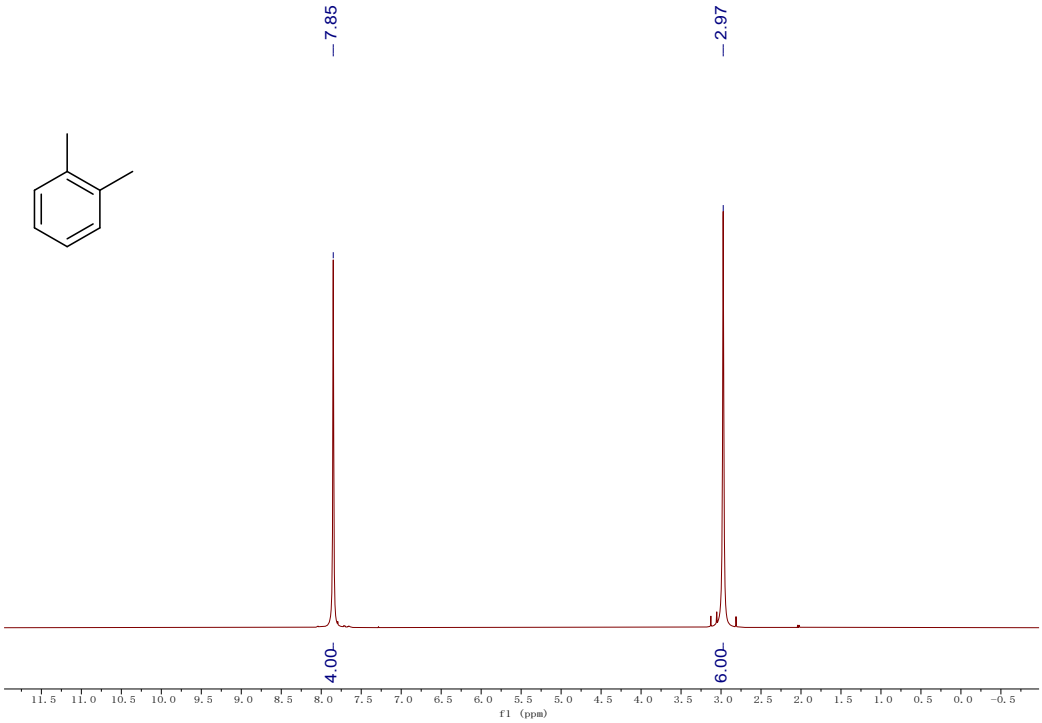
1H NMR (400 MHz, $CDCl_3$) of P3



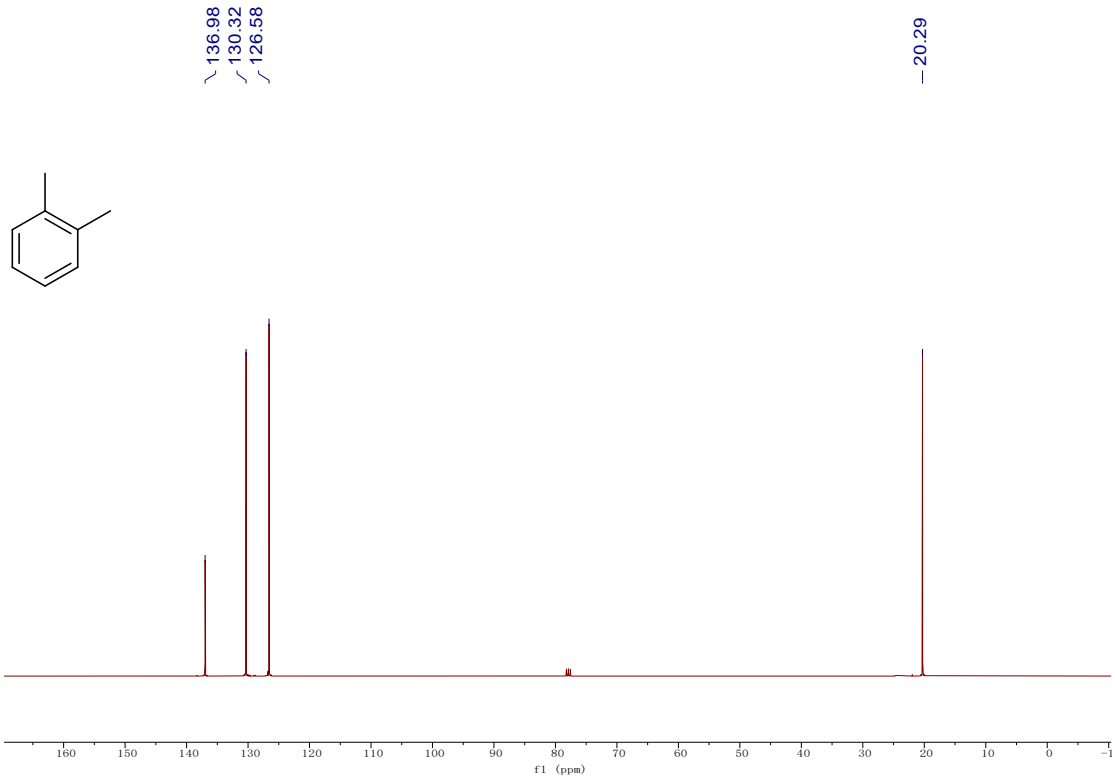
^{13}C NMR (101 MHz, $CDCl_3$) of P3



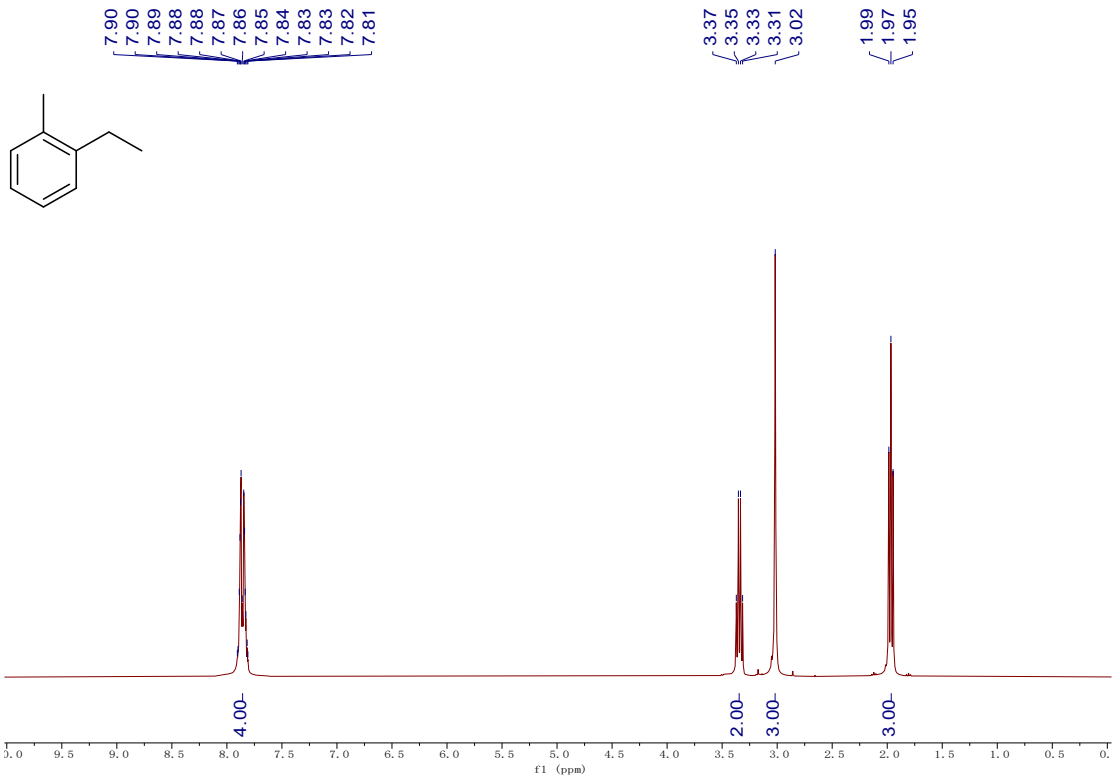
1H NMR (400 MHz, $CDCl_3$) of P4



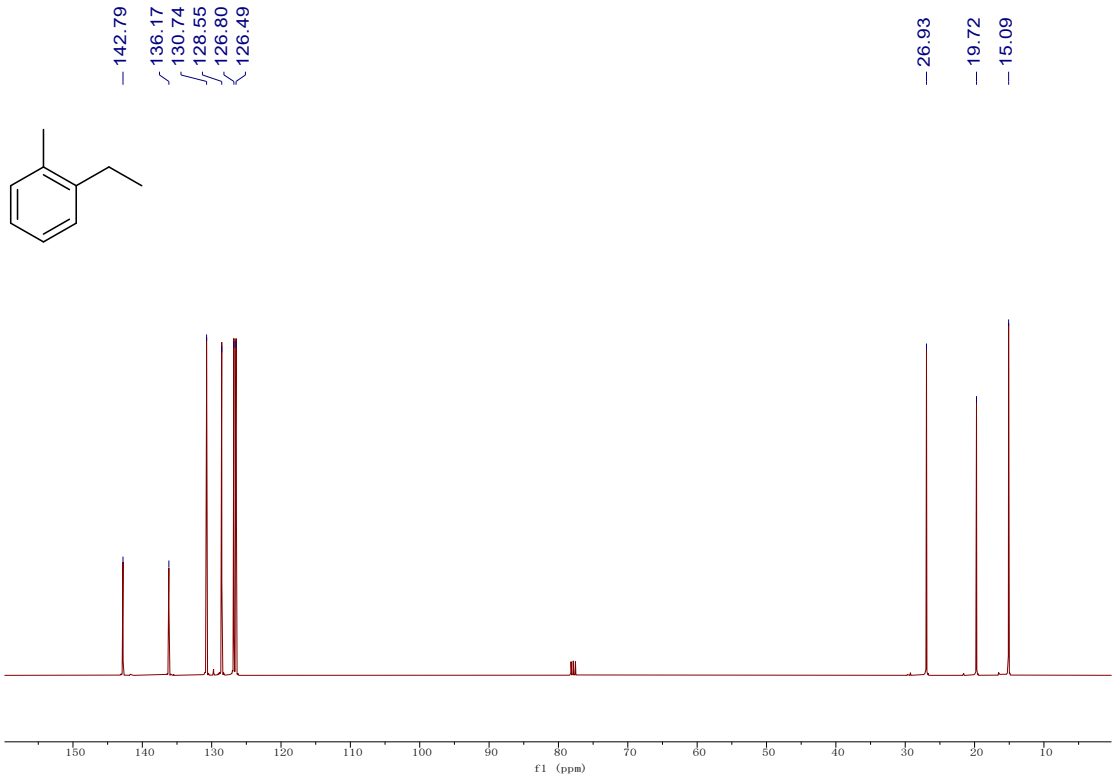
^{13}C NMR (101 MHz, $CDCl_3$) of P4



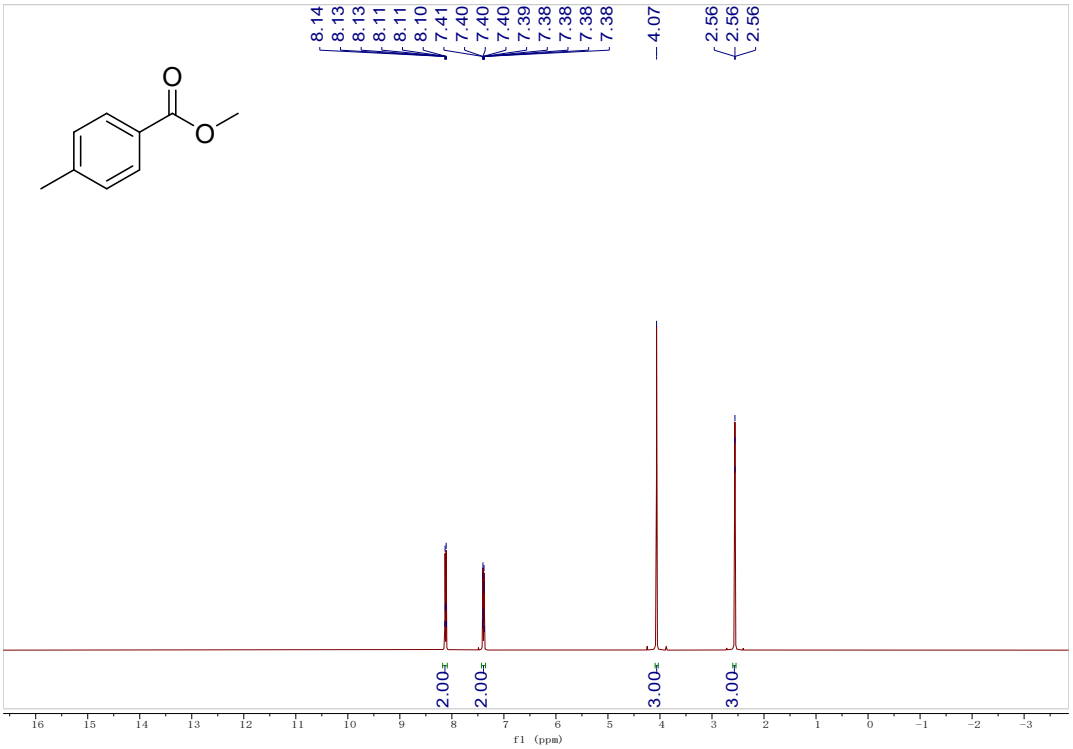
1H NMR (400 MHz, $CDCl_3$) of P5



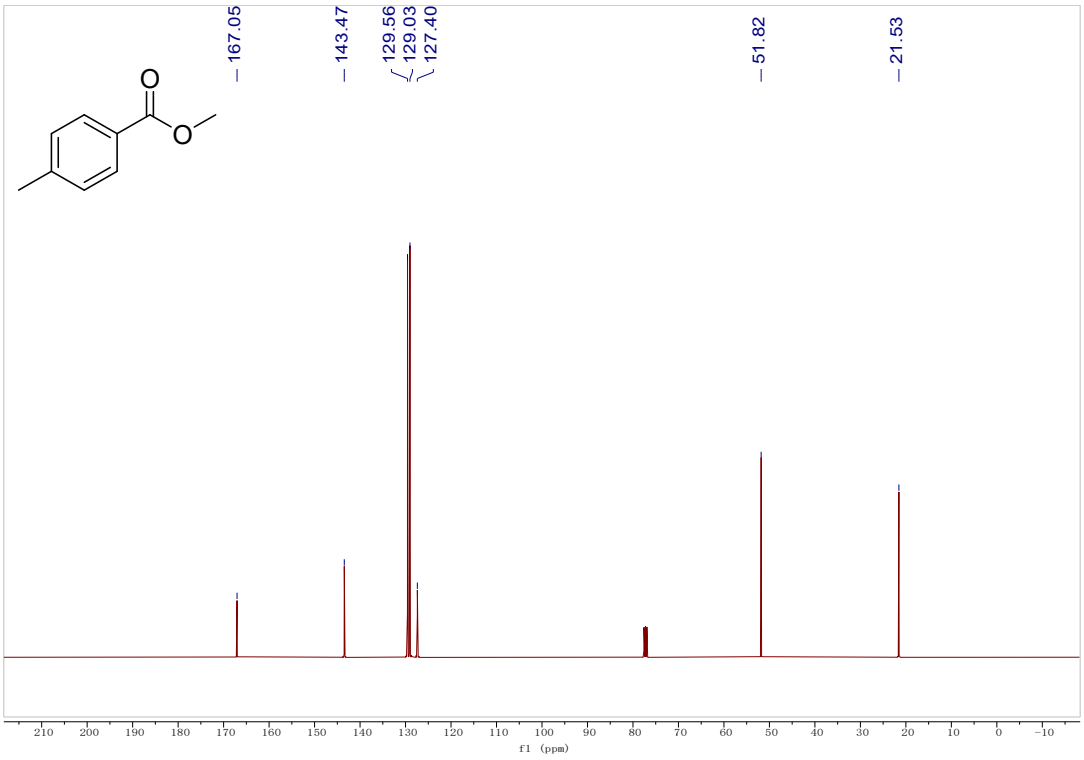
^{13}C NMR (101 MHz, $CDCl_3$) of P5



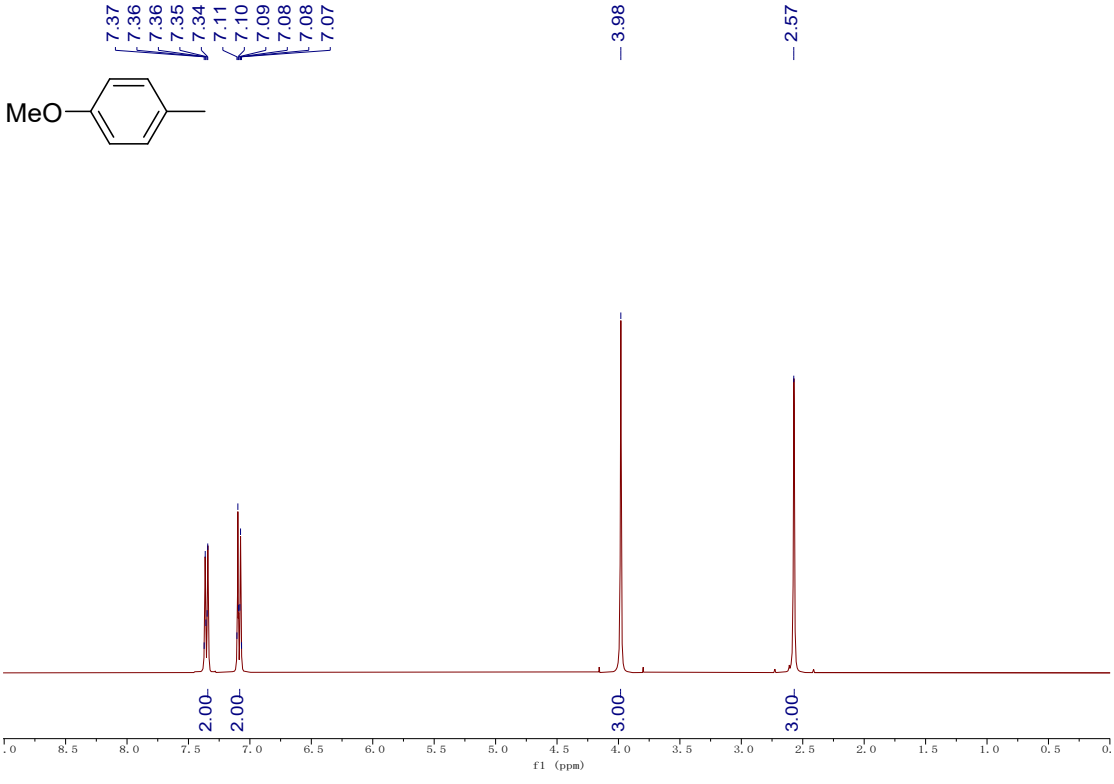
1H NMR (400 MHz, $CDCl_3$) of P6



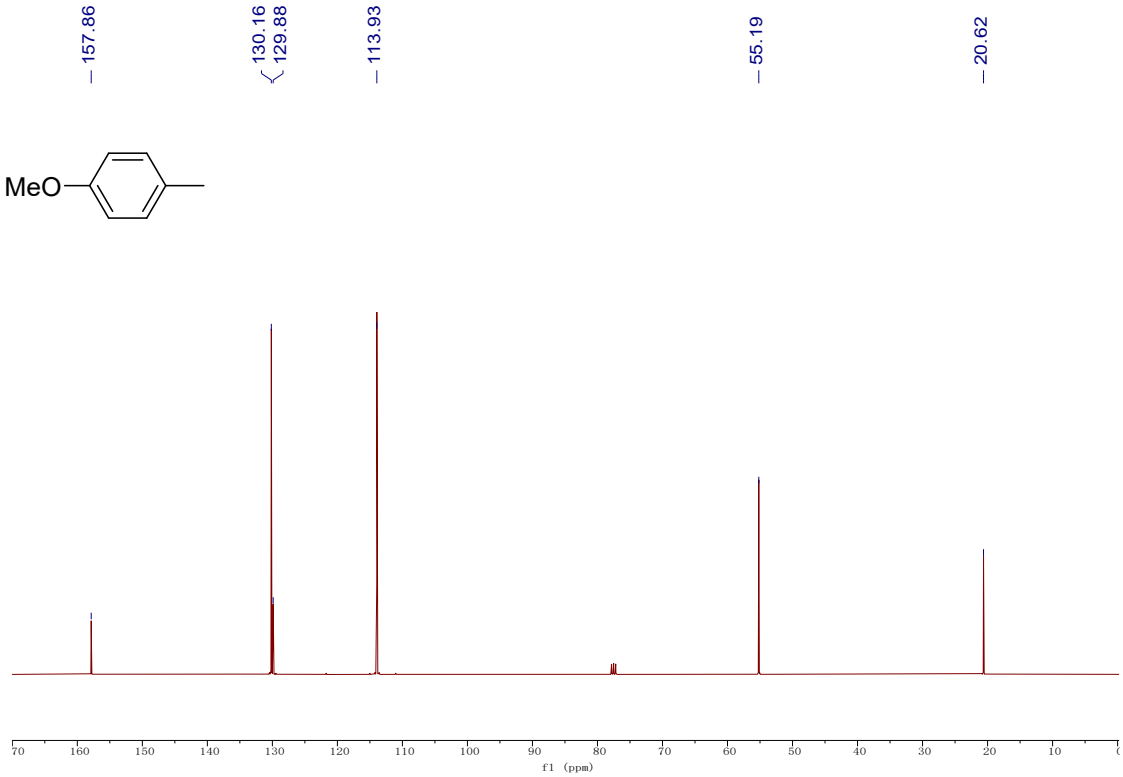
^{13}C NMR (101 MHz, $CDCl_3$) of P6



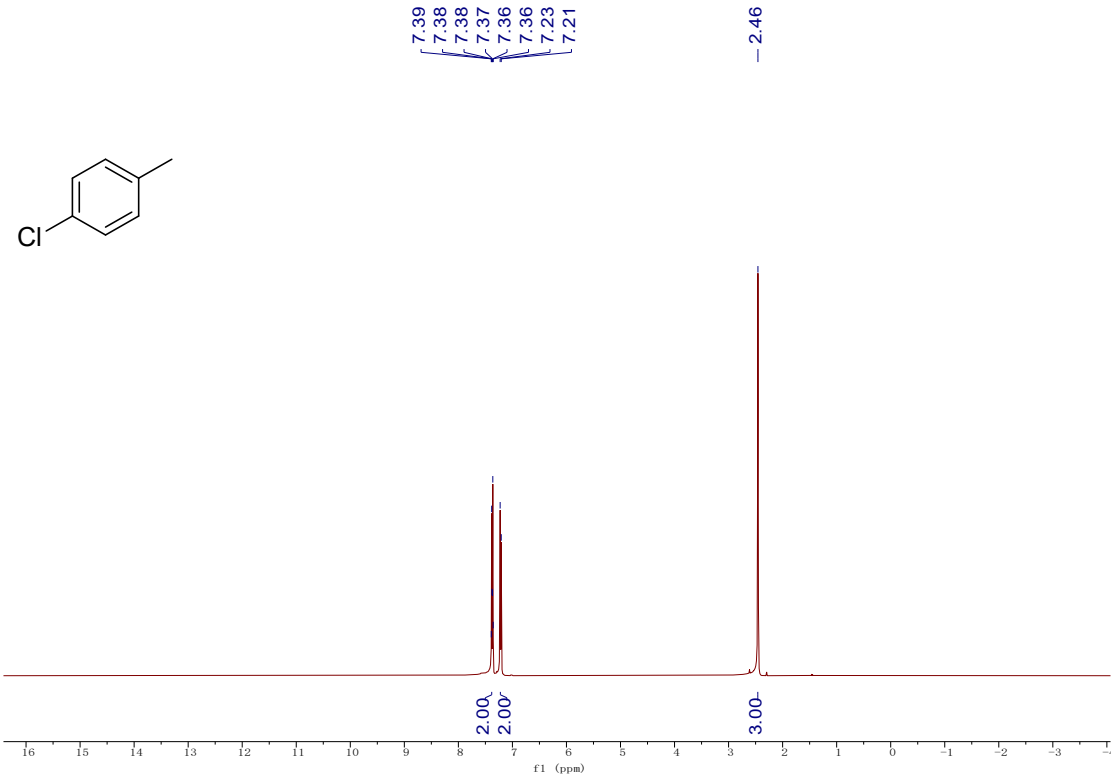
1H NMR (400 MHz, $CDCl_3$) of P7



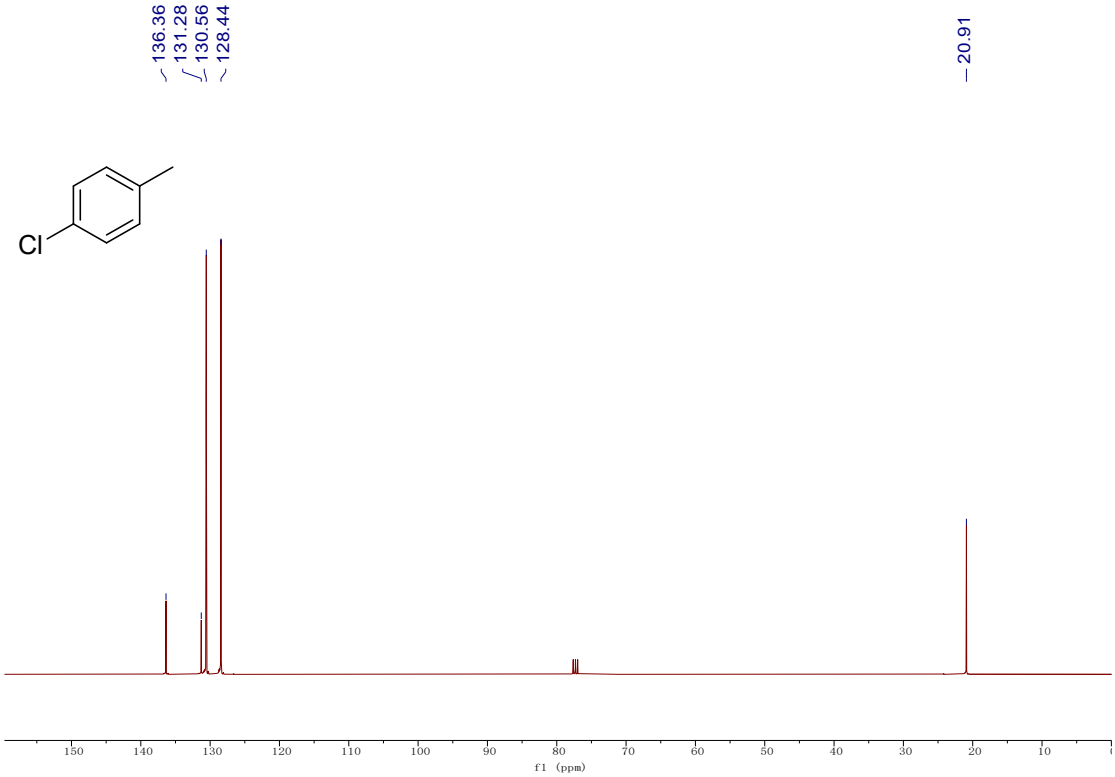
^{13}C NMR (101 MHz, $CDCl_3$) of P7



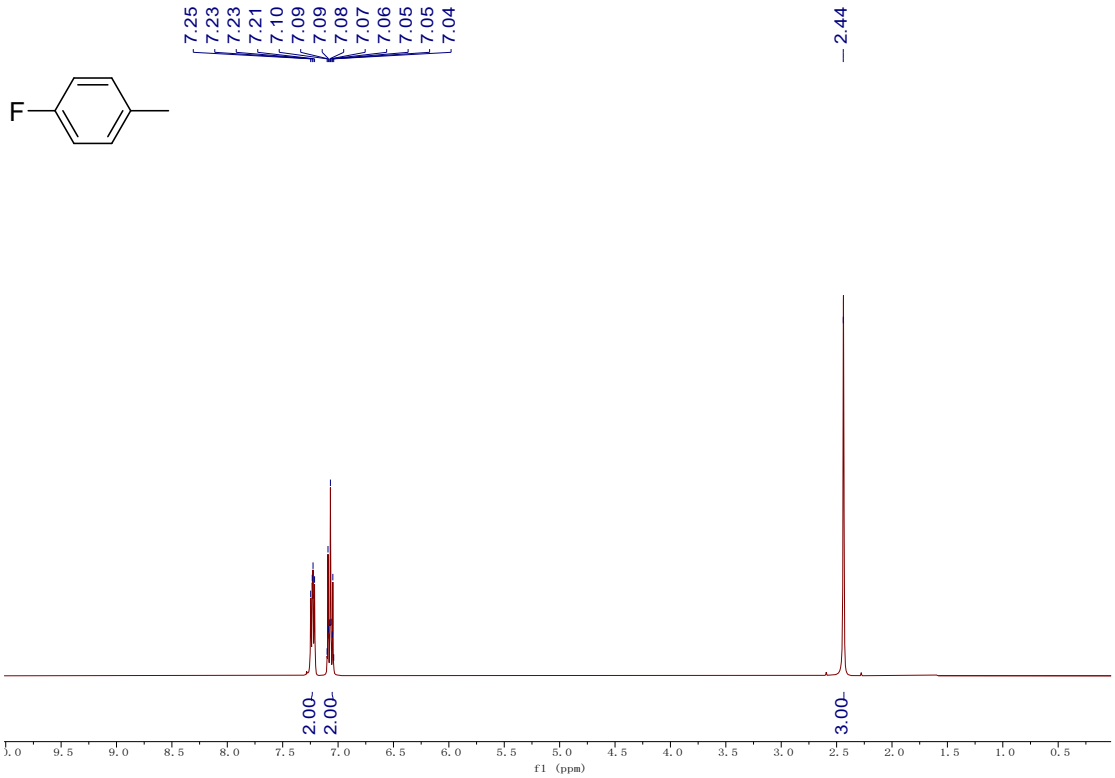
1H NMR (400 MHz, $CDCl_3$) of P8



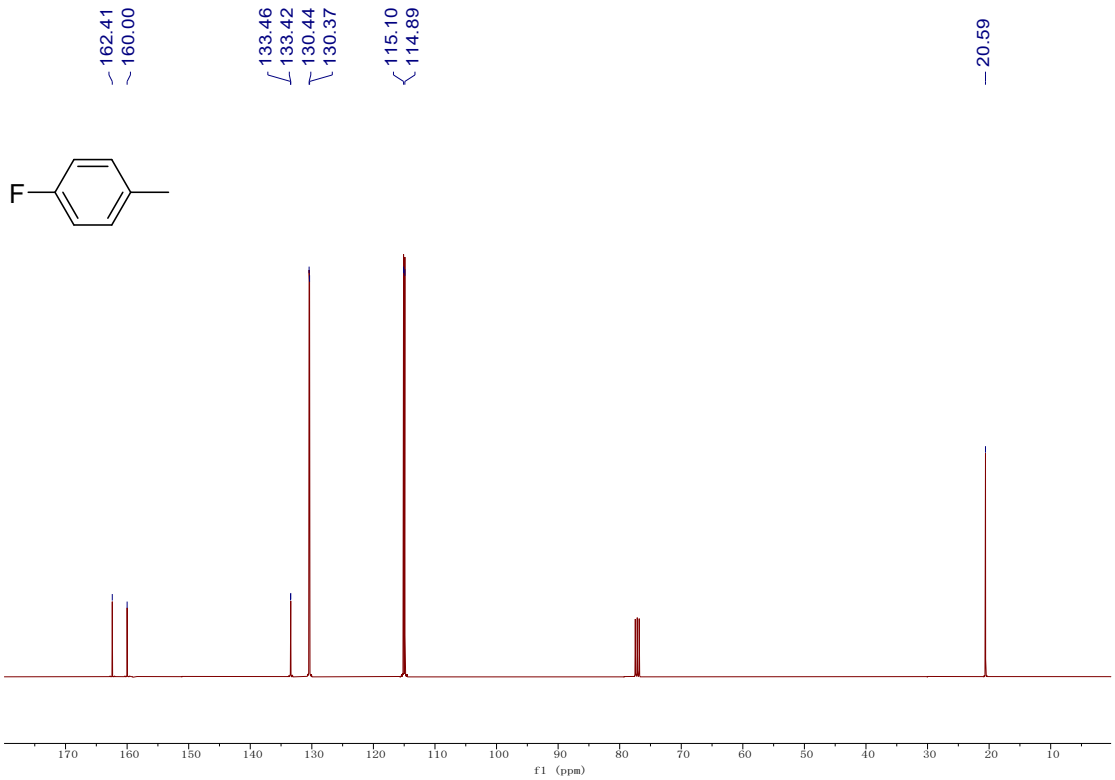
^{13}C NMR (101 MHz, $CDCl_3$) of P8



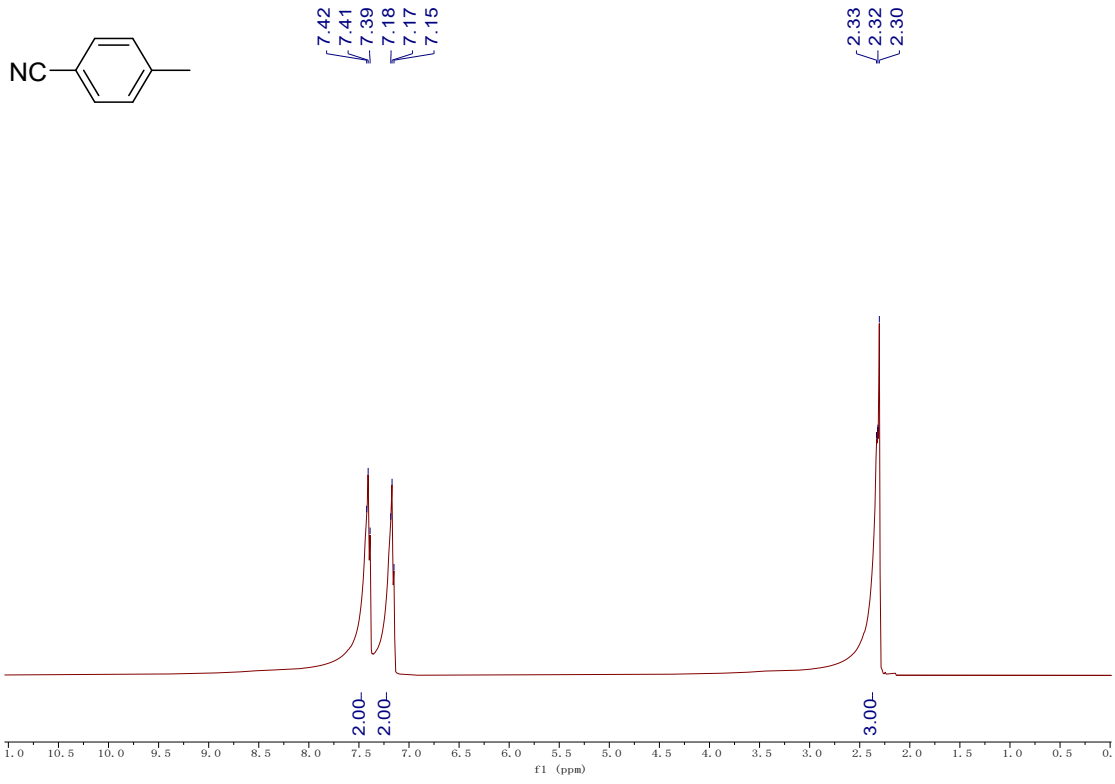
1H NMR (400 MHz, $CDCl_3$) of P9



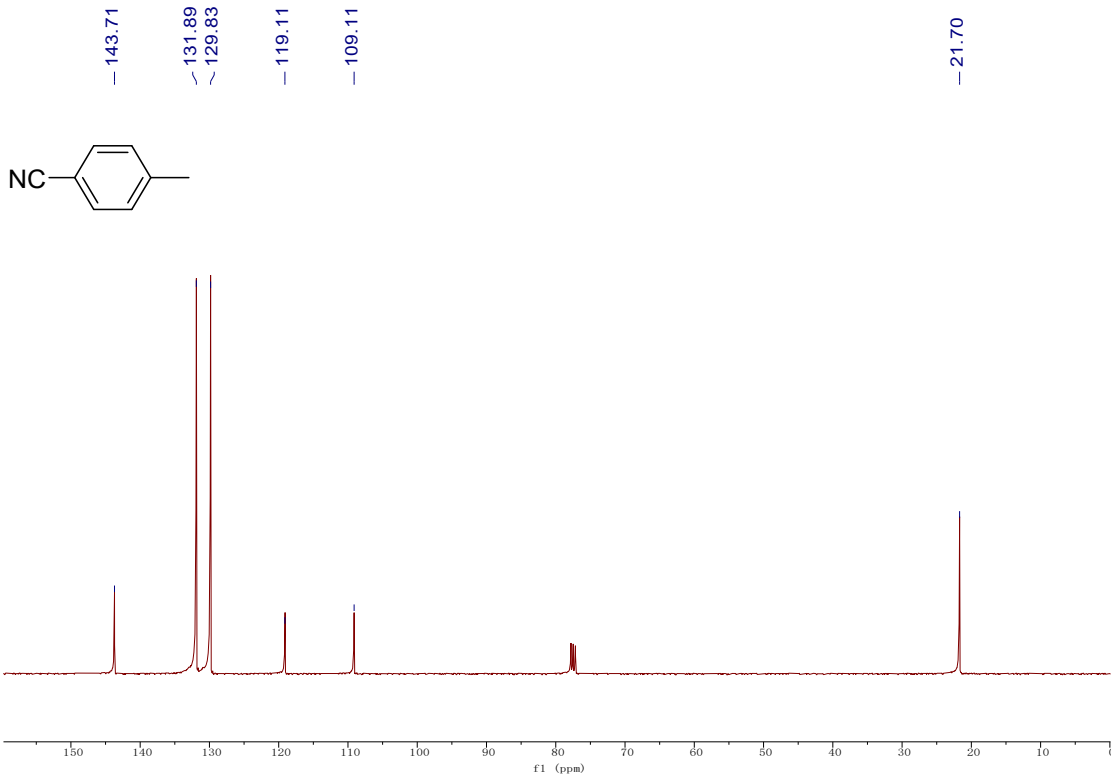
^{13}C NMR (101 MHz, $CDCl_3$) of P9



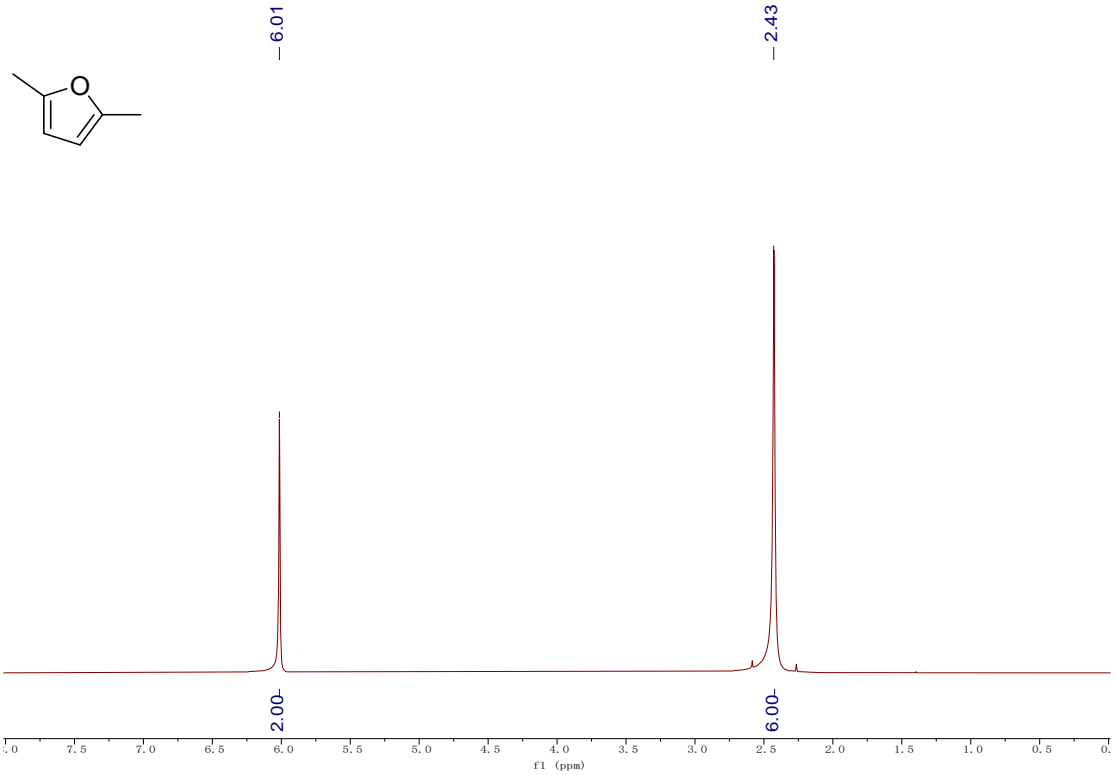
1H NMR (400 MHz, $CDCl_3$) of P10



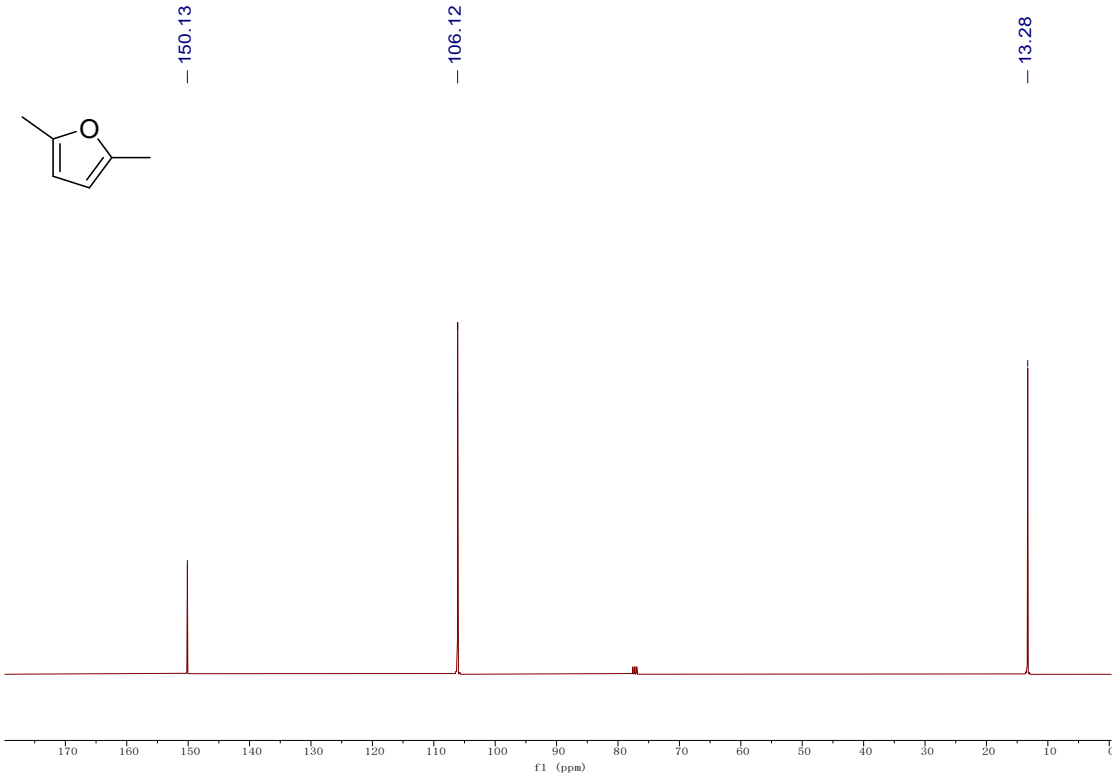
^{13}C NMR (101 MHz, $CDCl_3$) of P10



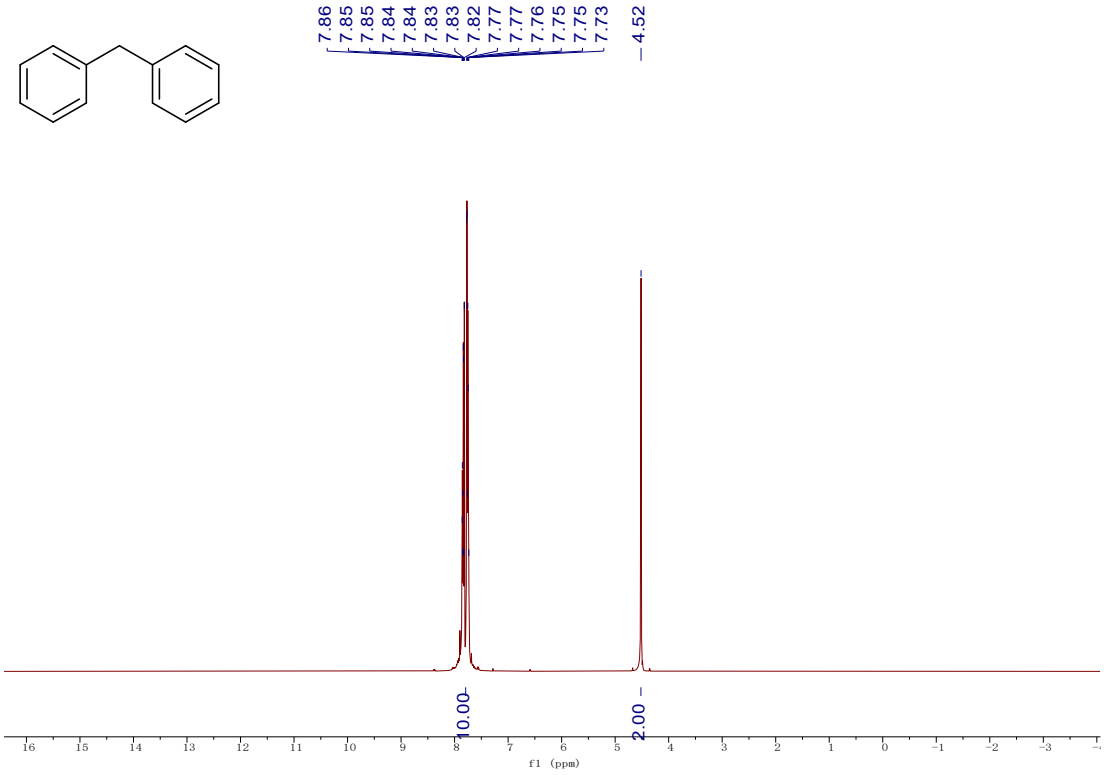
1H NMR (400 MHz, $CDCl_3$) of P12



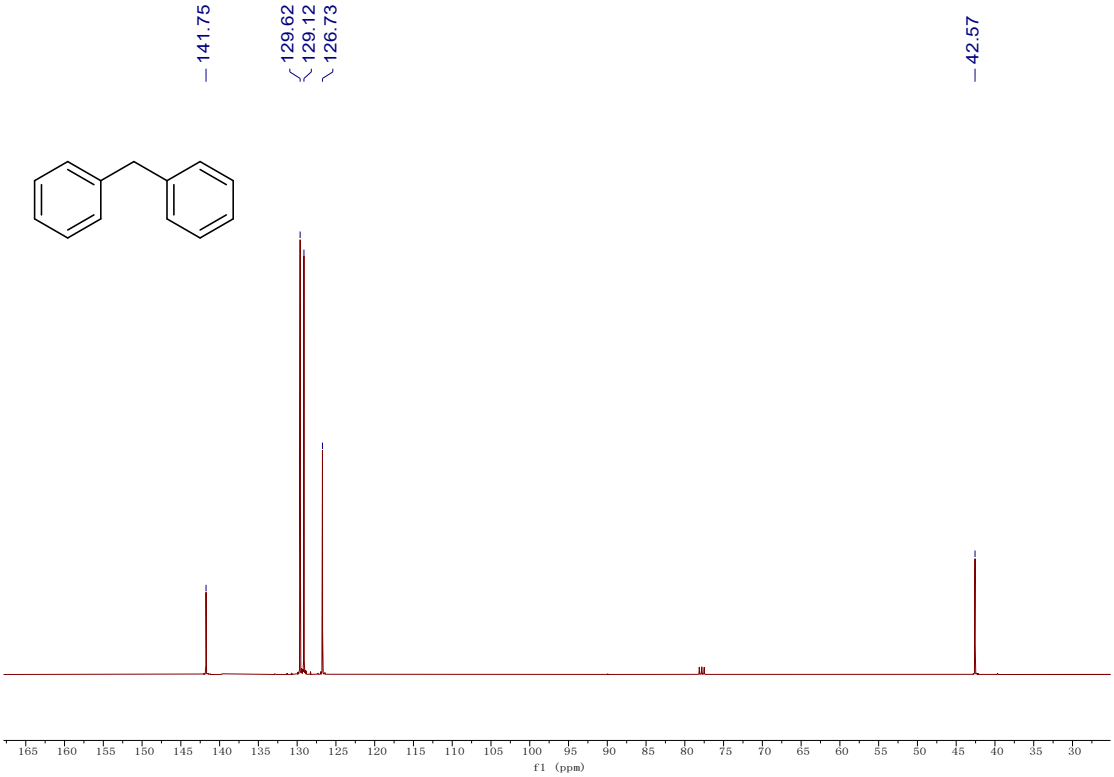
^{13}C NMR (101 MHz, $CDCl_3$) of P12



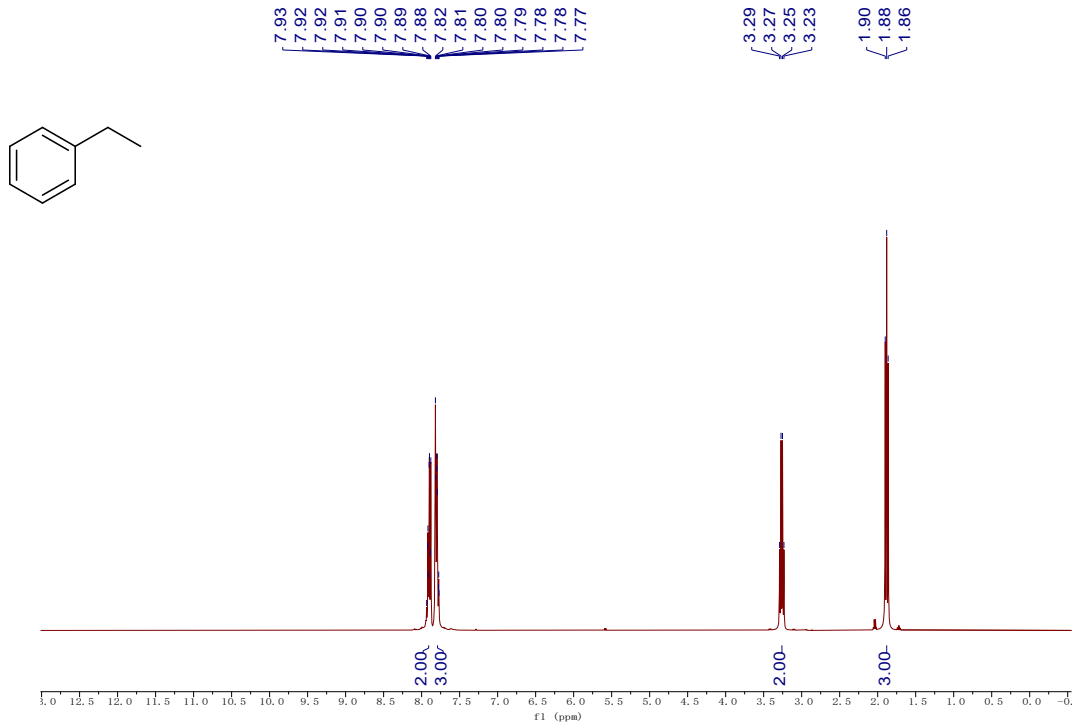
1H NMR (400 MHz, $CDCl_3$) of P13



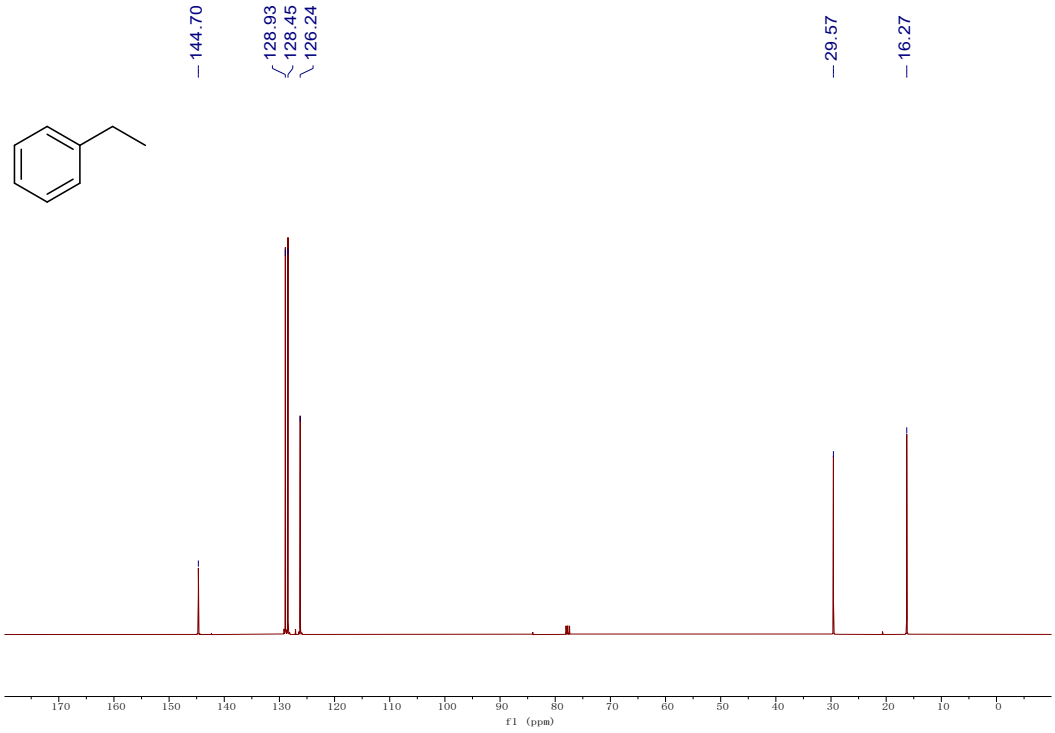
^{13}C NMR (101 MHz, $CDCl_3$) of P13



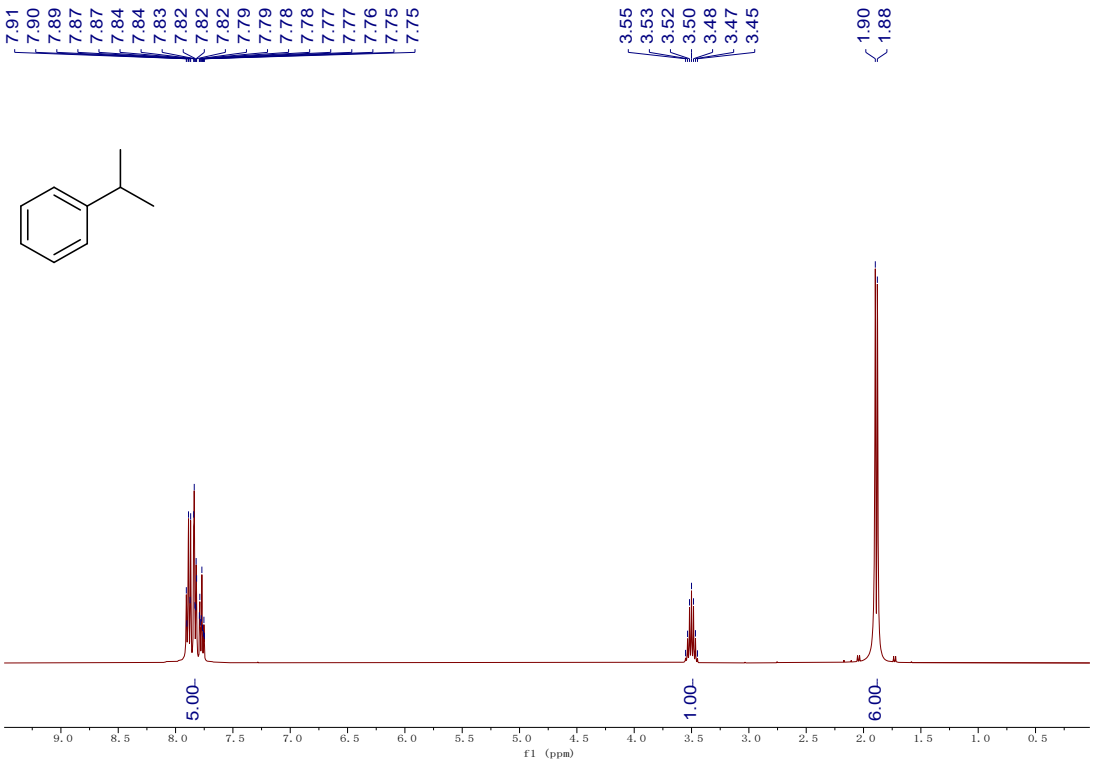
1H NMR (400 MHz, $CDCl_3$) of P14



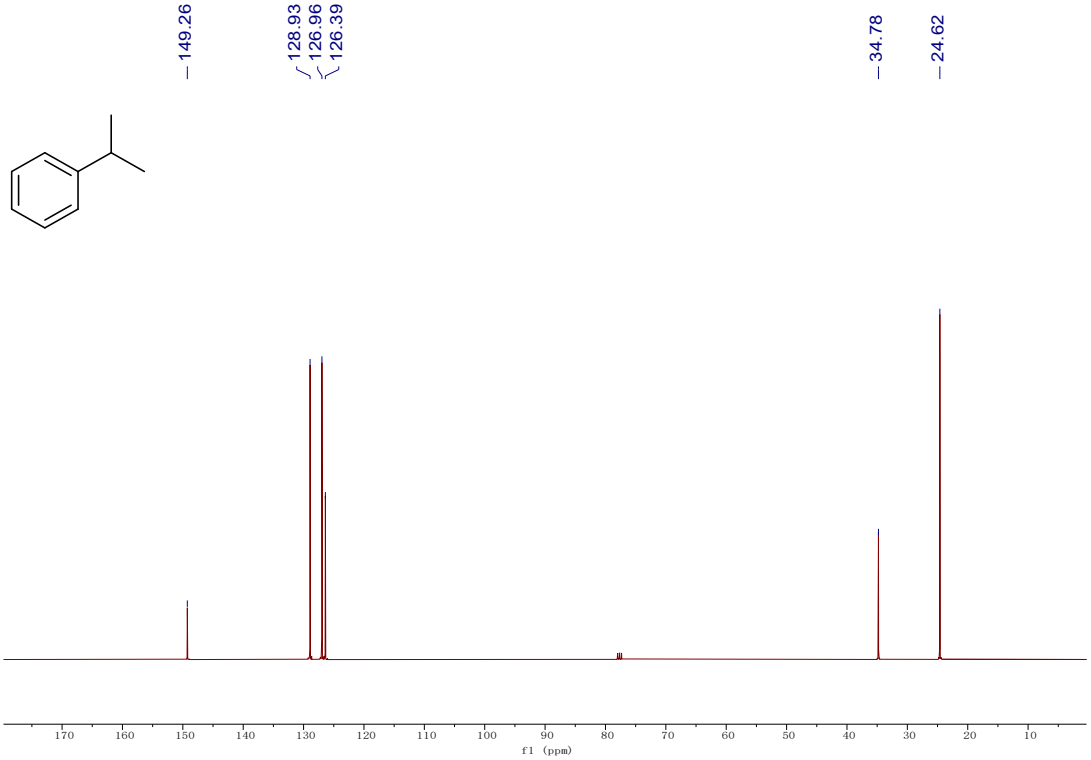
^{13}C NMR (101 MHz, $CDCl_3$) of P14



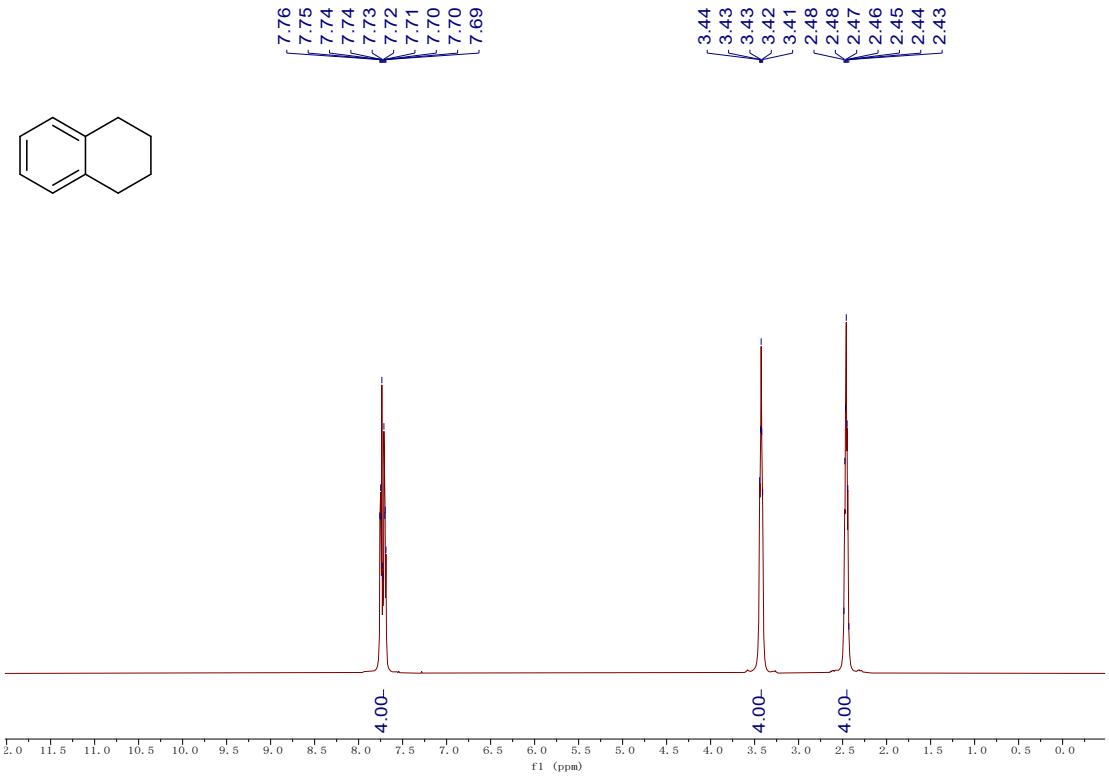
1H NMR (400 MHz, $CDCl_3$) of P15



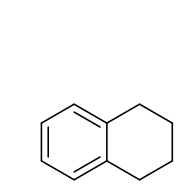
^{13}C NMR (101 MHz, $CDCl_3$) of P15



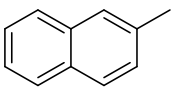
1H NMR (400 MHz, $CDCl_3$) of P16



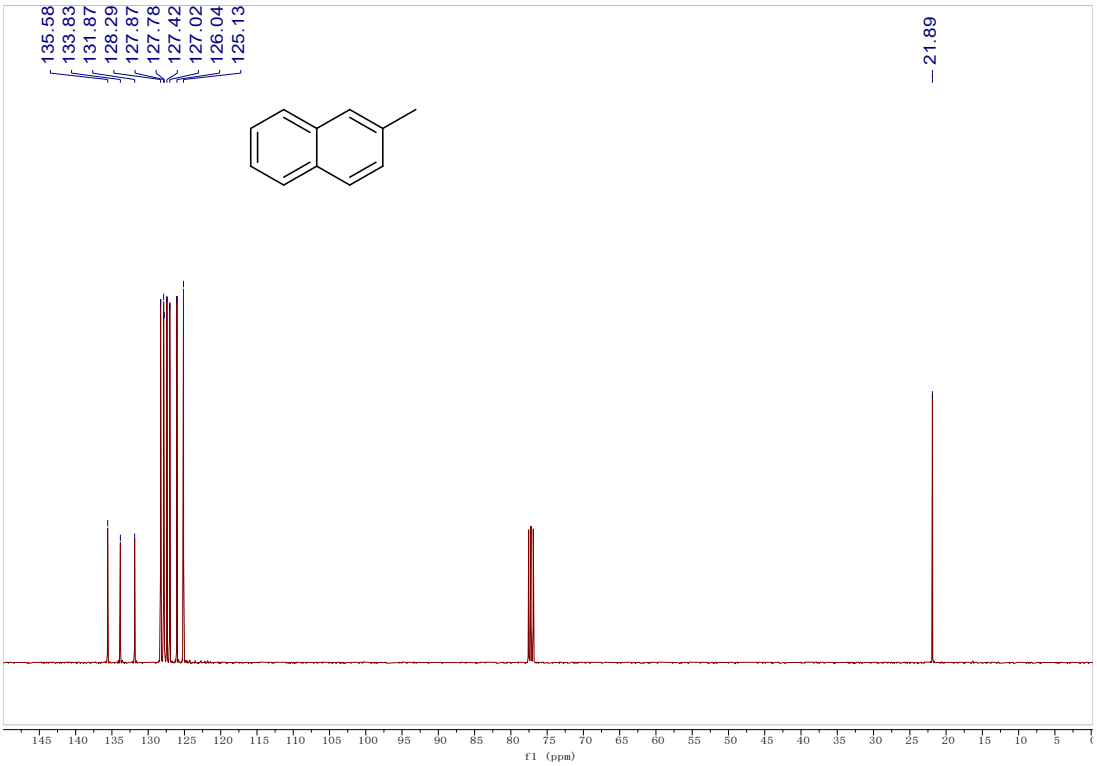
^{13}C NMR (101 MHz, $CDCl_3$) of P16



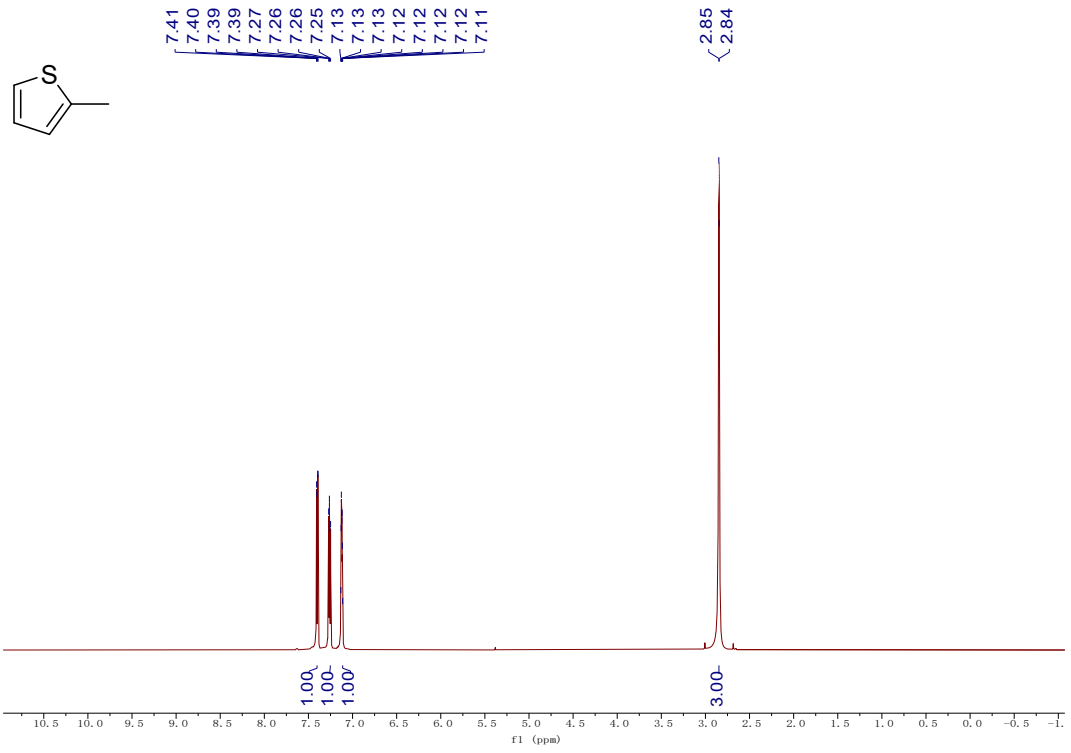
1H NMR (400 MHz, $CDCl_3$) of P17



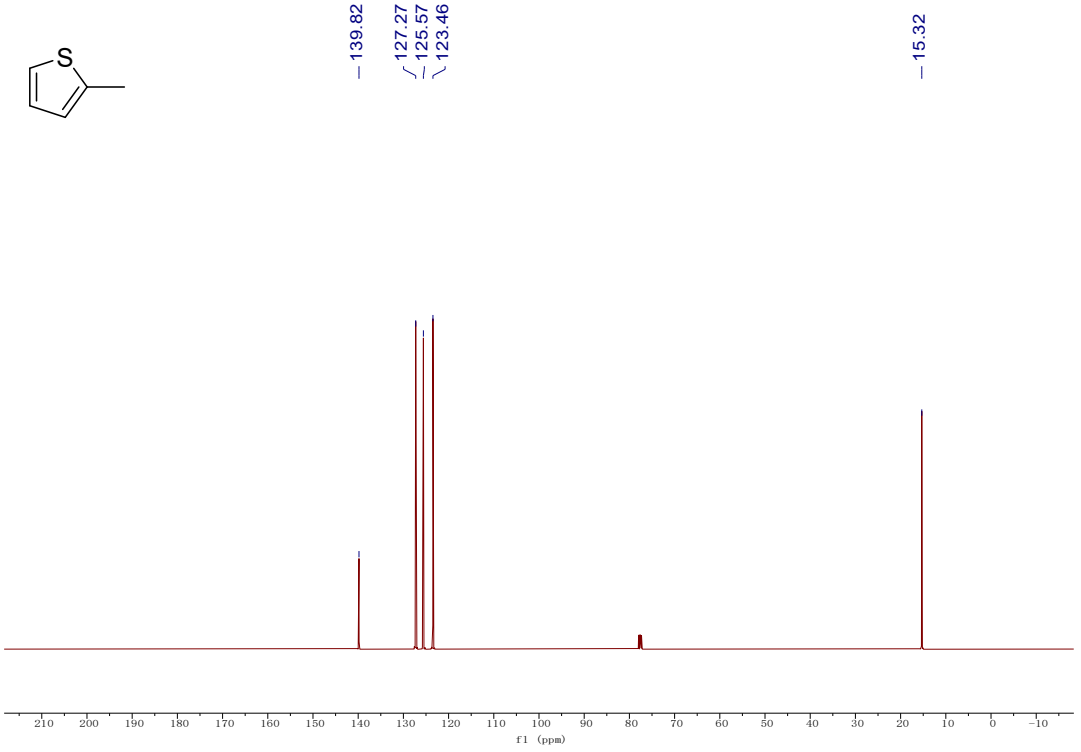
^{13}C NMR (101 MHz, $CDCl_3$) of P17



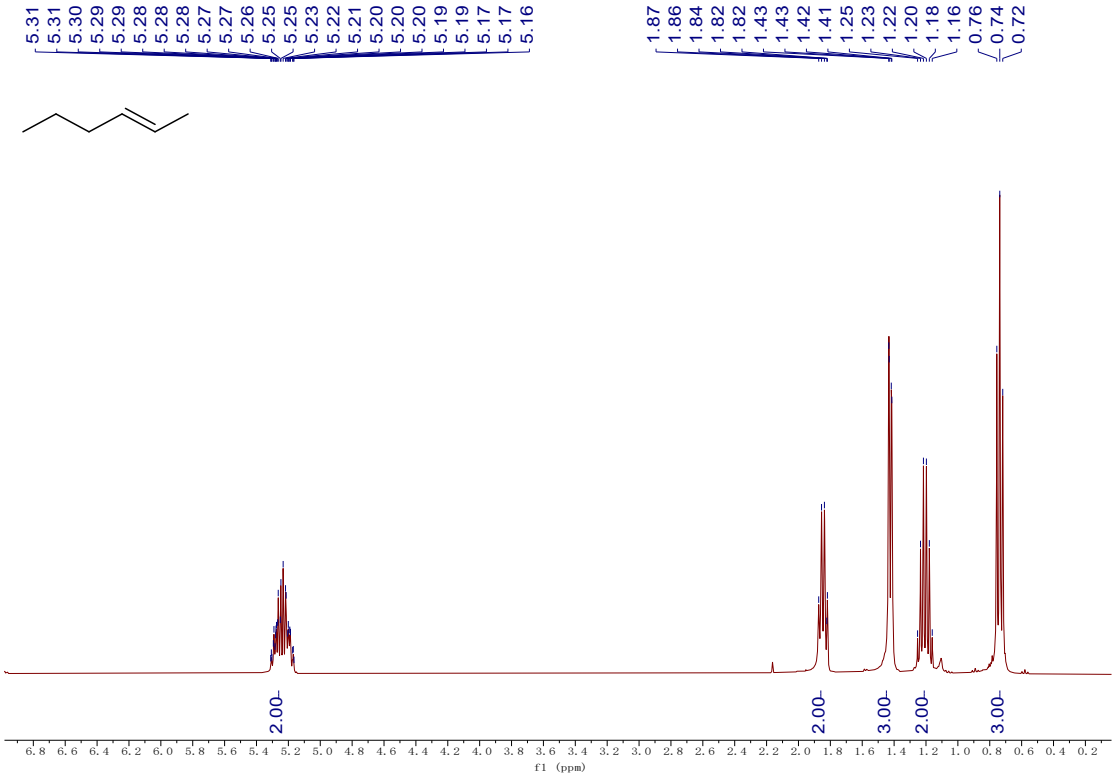
1H NMR (400 MHz, $CDCl_3$) of P18



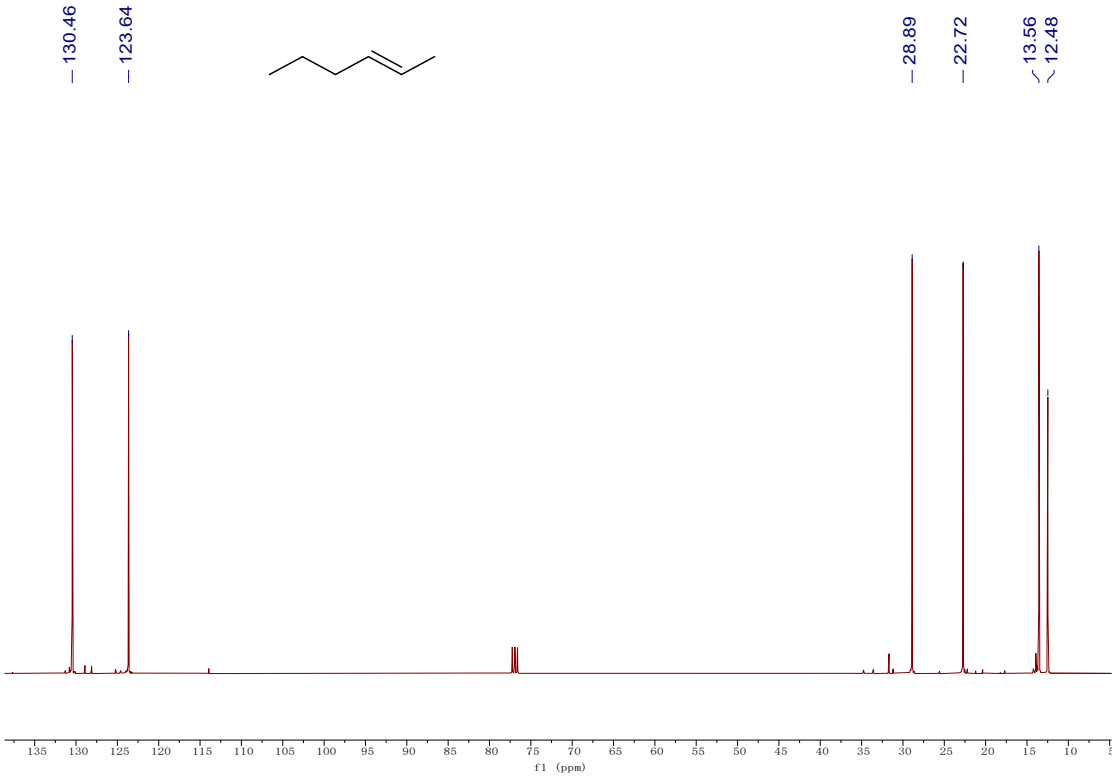
^{13}C NMR (101 MHz, $CDCl_3$) of P18



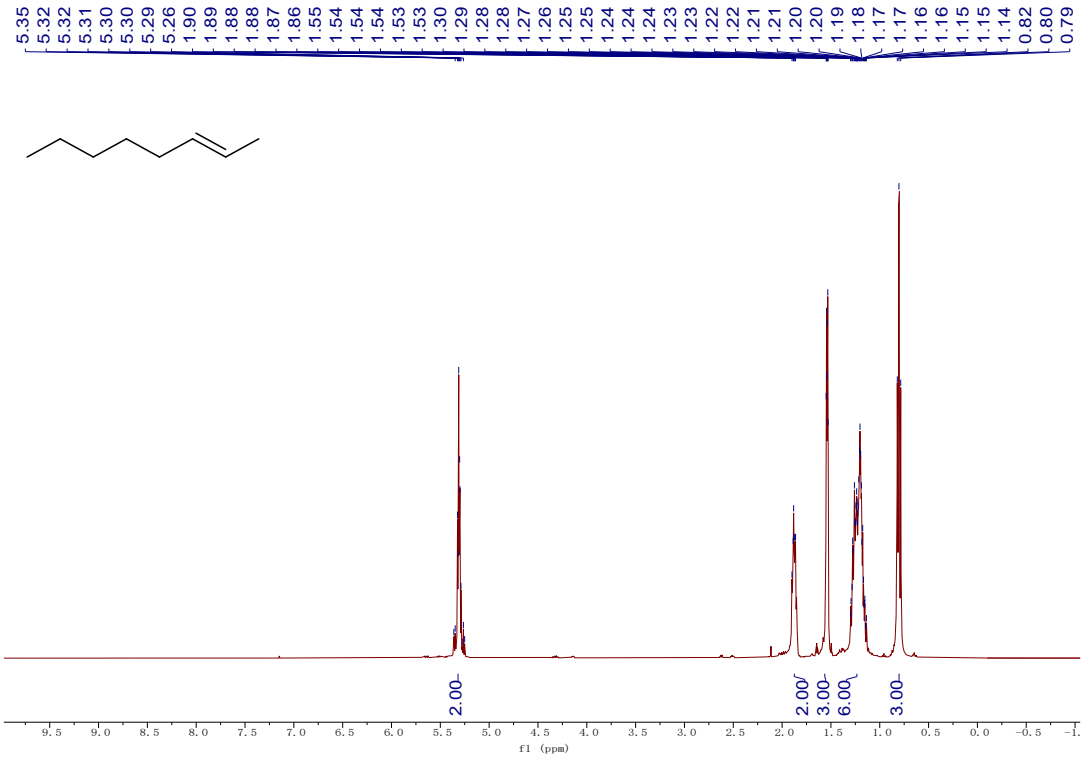
1H NMR (400 MHz, $CDCl_3$) of P19



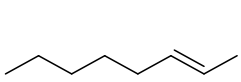
^{13}C NMR (101 MHz, $CDCl_3$) of P19



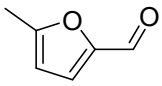
1H NMR (400 MHz, $CDCl_3$) of P20



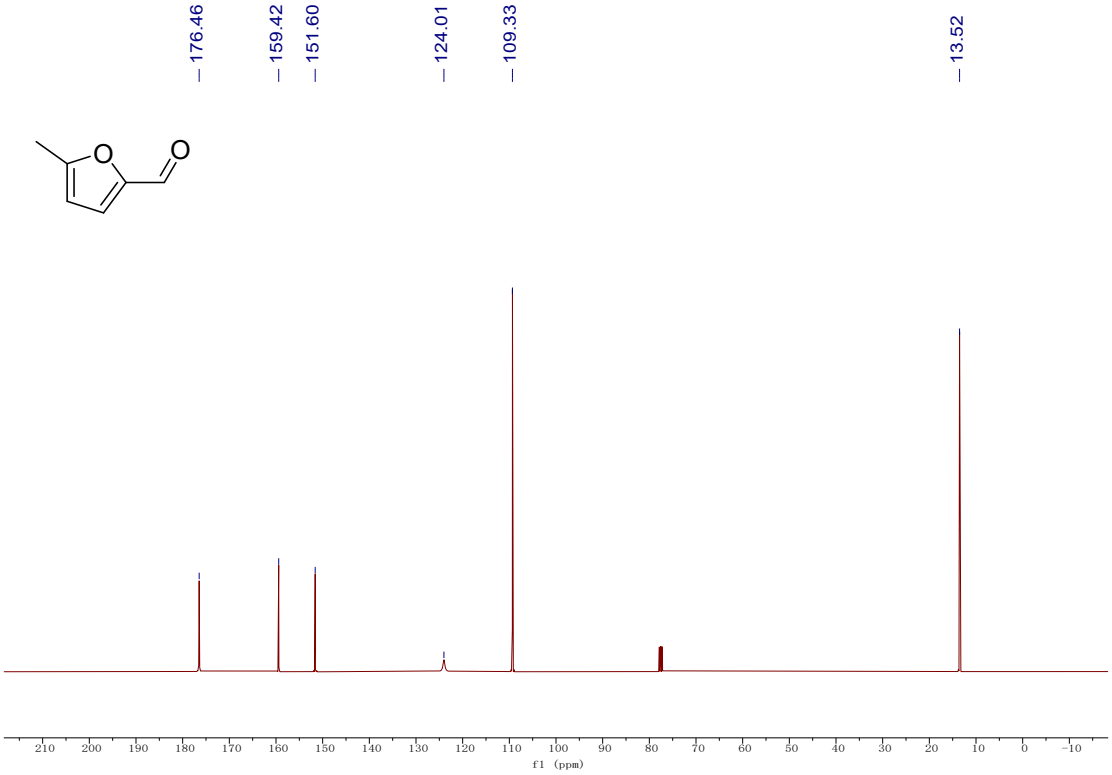
^{13}C NMR (101 MHz, $CDCl_3$) of P20



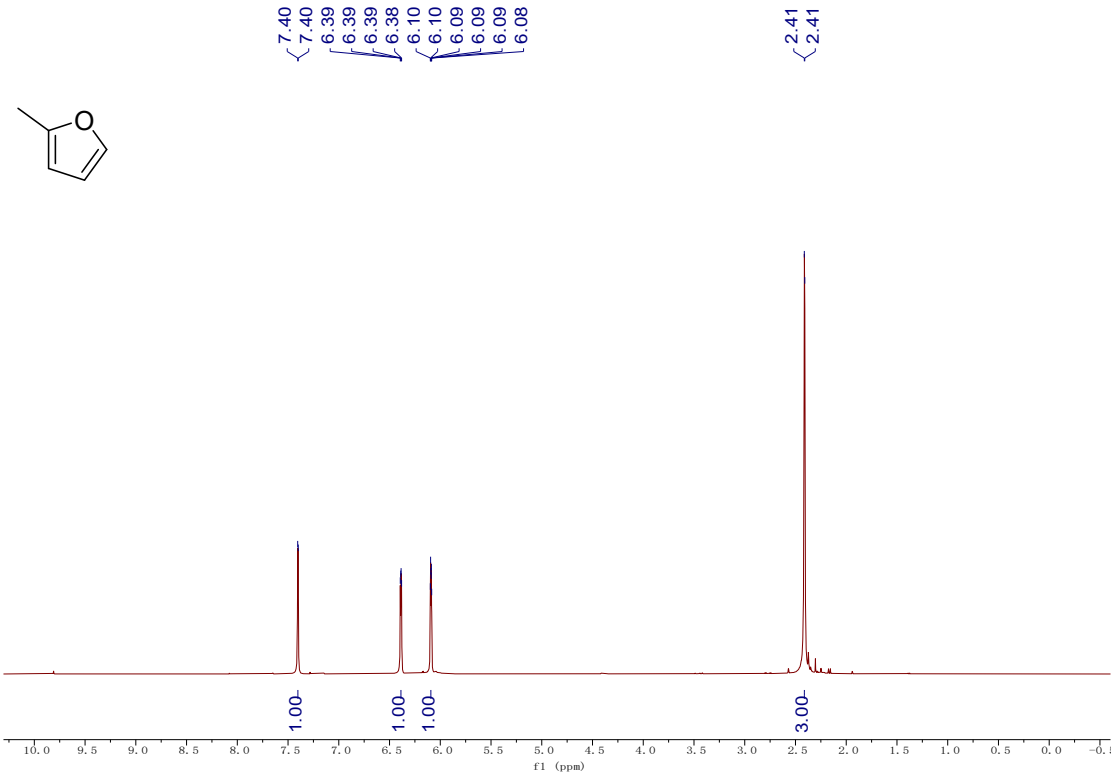
1H NMR (400 MHz, $CDCl_3$) of P21



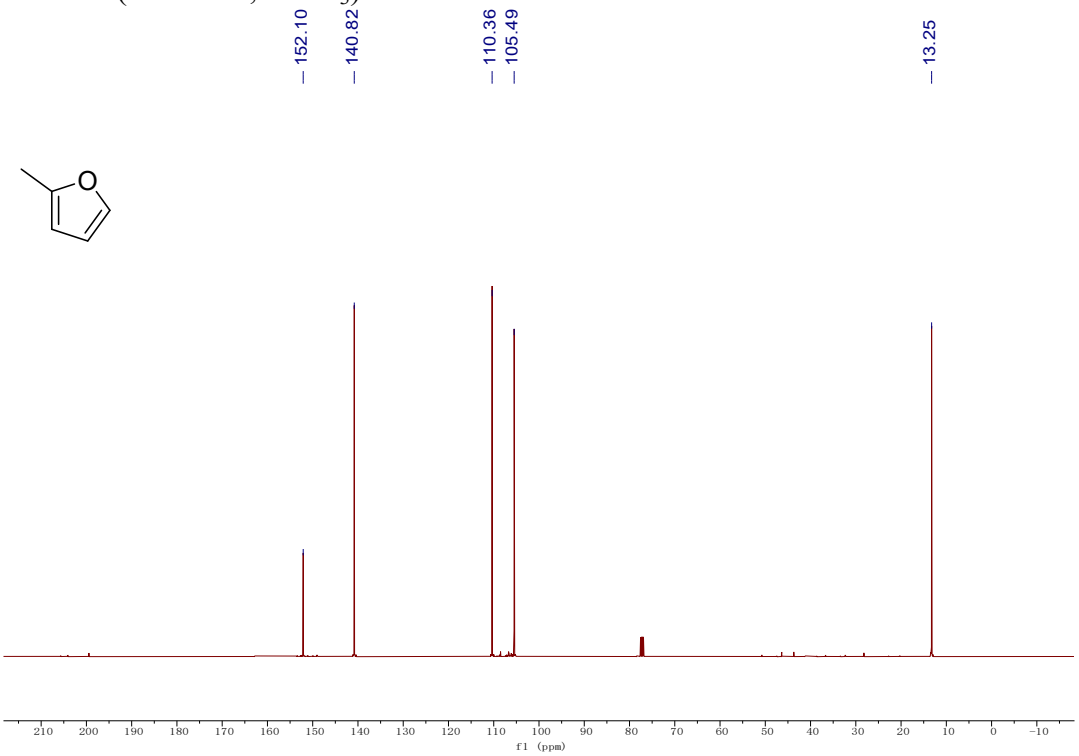
^{13}C NMR (101 MHz, $CDCl_3$) of P21



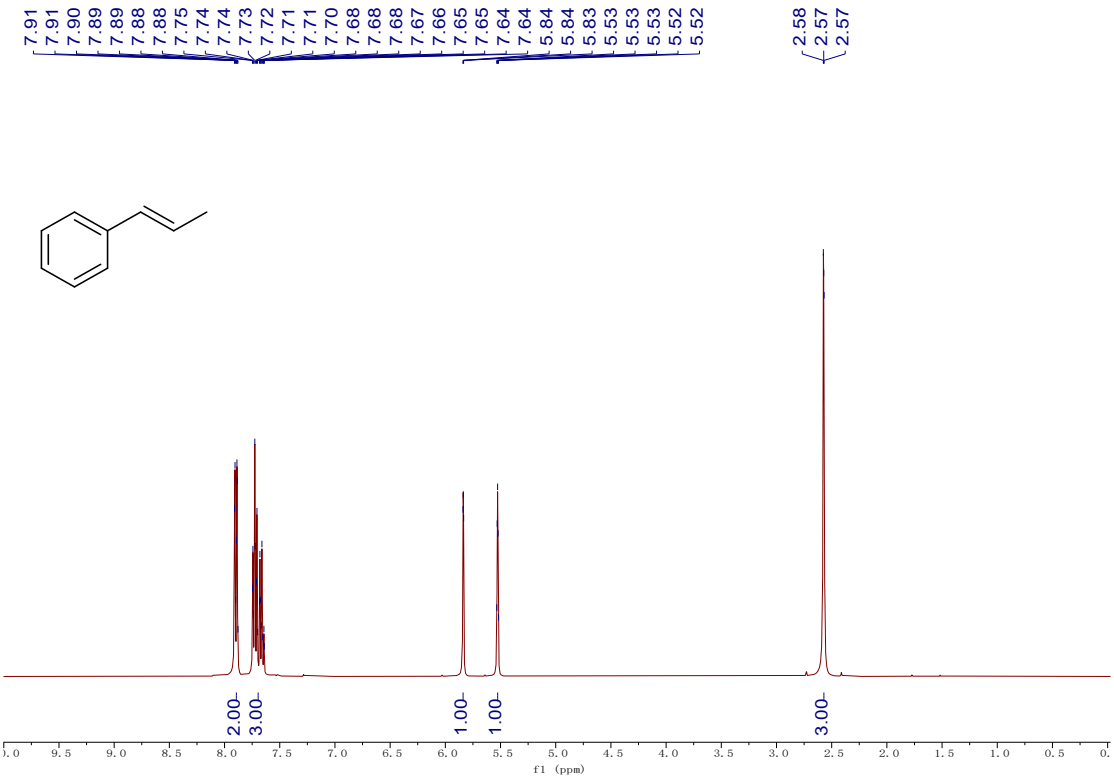
1H NMR (400 MHz, $CDCl_3$) of P22



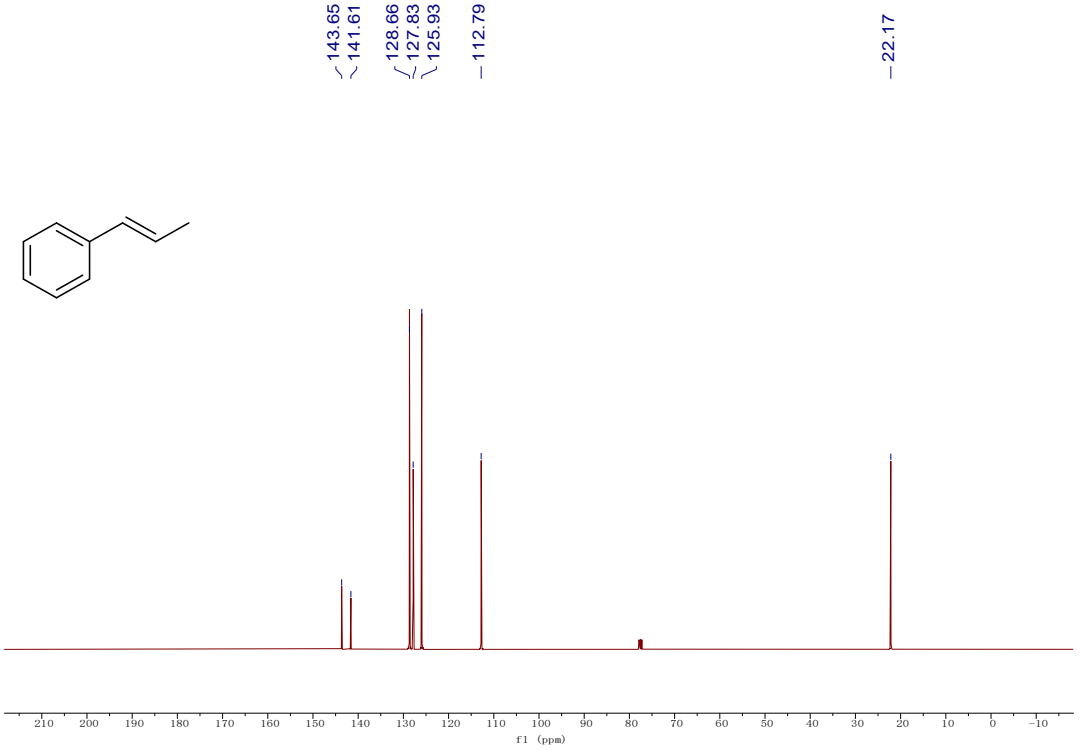
^{13}C NMR (101 MHz, $CDCl_3$) of P22



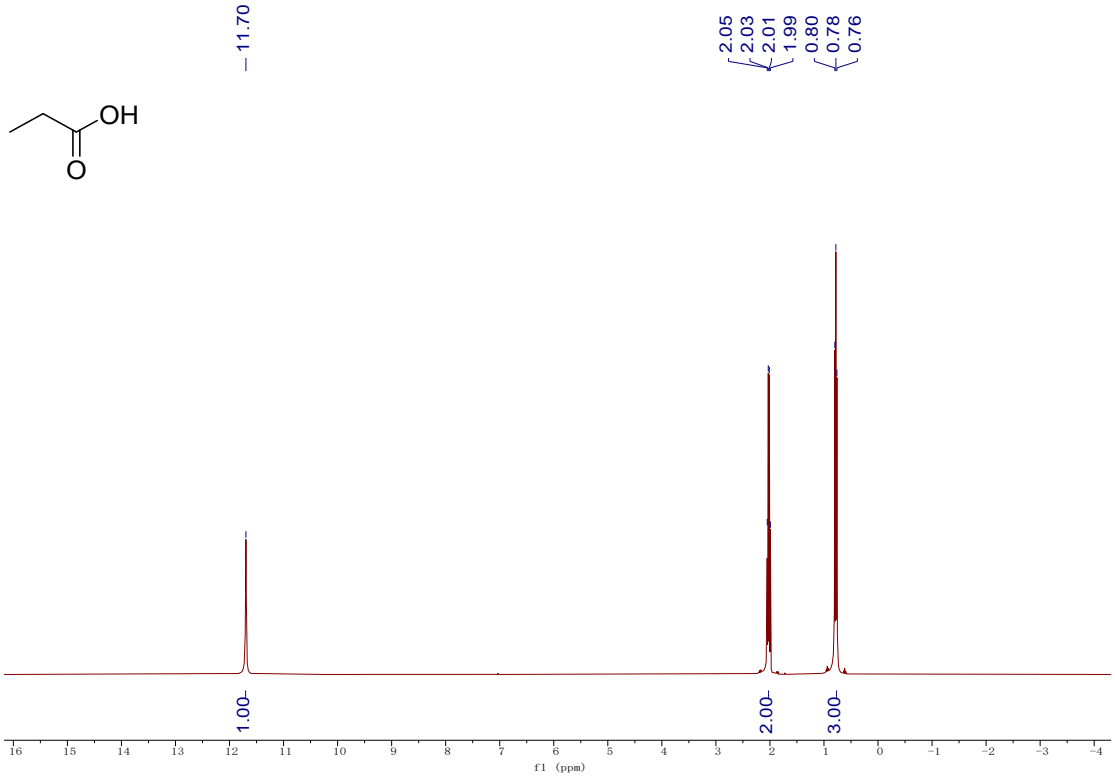
1H NMR (400 MHz, $CDCl_3$) of P23



^{13}C NMR (101 MHz, $CDCl_3$) of P23



1H NMR (400 MHz, $CDCl_3$) of P24



^{13}C NMR (101 MHz, $CDCl_3$) of P24