

Supporting Information

Cross-Coupling of Aryltrimethylammonium Iodides with Arylzinc Reagents Catalyzed by Amido Pincer Nickel Complexes

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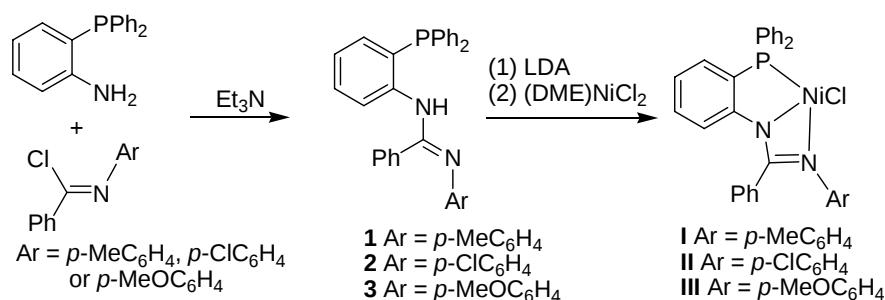
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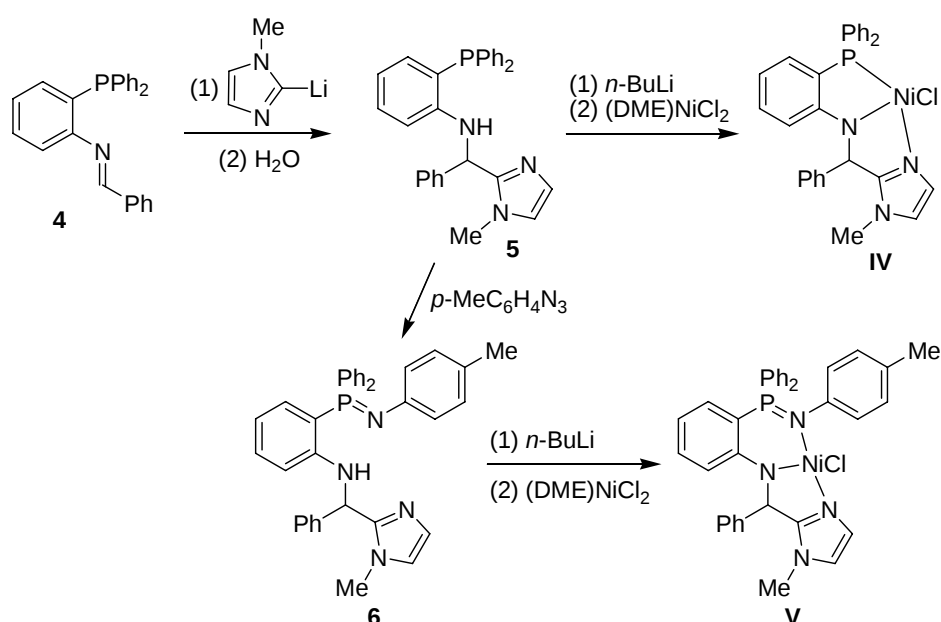
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Scheme S1. Synthesis of complexes I-III



Scheme S2. Synthesis of complexes IV and V



Crystal Structure Determination: Single crystals of **I** were obtained from a mixed solvent of toluene and benzene. Single crystals of **V** were obtained by recrystallization of complex **V** from a mixed solvent of CH₂Cl₂ and toluene. The single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 298(2) K using a area detector with graphite-monochromated Mo-*K*_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97¹ and refined against F^2 by full-matrix least squares using SHELXL-97.² Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table S1.

Table S1. Details of the X-ray structure determinations of complexes I and V

	I·0.5C₆H₆	V·0.5C₇H₈
Empirical formula	C ₃₅ H ₂₉ ClN ₂ NiP	C ₇₉ H ₇₂ Cl ₂ N ₈ Ni ₂ P ₂
Formula mass	602.73	1383.71
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	10.4293(11)	9.8520(9)
<i>b</i> (Å)	11.1260(14)	13.7371(14)
<i>c</i> (Å)	14.4551(17)	14.6279(16)
α (deg)	75.9010(10)	111.060(2)
β (deg)	87.844(2)	93.1010(10)
γ (deg)	70.9890(10)	106.5450(10)
<i>V</i> (Å ³)	1536.5(3)	1743.7(3)
<i>Z</i>	2	1
<i>D</i> _{calcd} (g/cm ³)	1.303	1.318
<i>F</i> (000)	626	722
μ (mm ⁻¹)	0.796	0.713
θ range for data collec (deg)	1.45 to 25.02	1.52 to 25.02
No. of reflns collected	8096	9276
No. of indep reflns (<i>R</i> _{int})	5331 (<i>R</i> _{int} = 0.0268)	6089 (<i>R</i> _{int} = 0.0921)
No. of data/restraints/params	5331 / 0 / 362	6089 / 0 / 427
Goodness of fit on <i>F</i> ²	1.080	1.044
Final <i>R</i> indices ^a [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0498 w <i>R</i> 2 = 0.1163	<i>R</i> 1 = 0.0863 w <i>R</i> 2 = 0.1811
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0842 w <i>R</i> 2 = 0.1266	<i>R</i> 1 = 0.2567 w <i>R</i> 2 = 0.2110
Largest diff peak and hole [e·Å ⁻³]	1.122 and -0.586	0.488 and -0.428

$$^a \quad R1 = \frac{\sum \|F_o\| - \|F_c\|}{\sum \|F_o\|}; \quad wR2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^4)} \right]^{1/2}$$

References

- (1) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467
- (2) Sheldrick, G. M. *SHELXL97, Programs for structure refinement*, Universität Göttingen, **1997**.

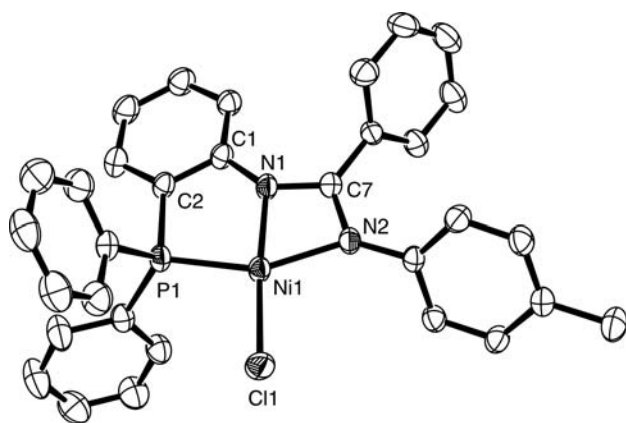


Figure S1. ORTEP drawing of complex I (30% probability. C₆H₆ molecule is omitted).

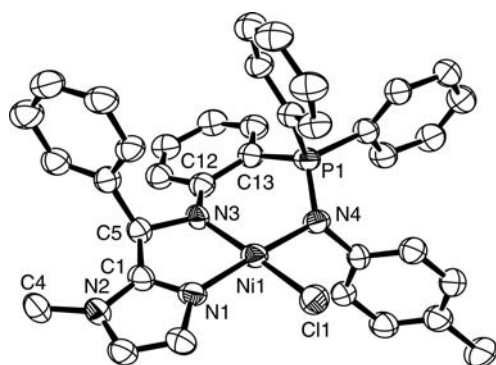
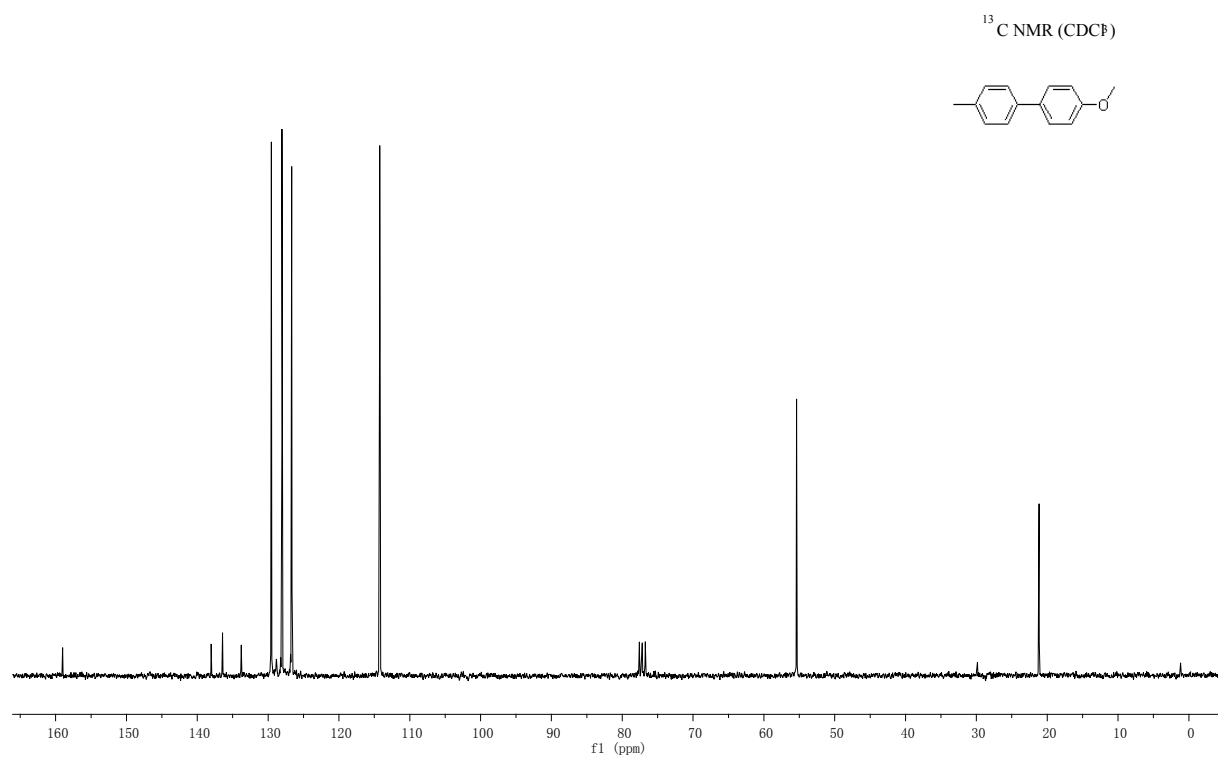
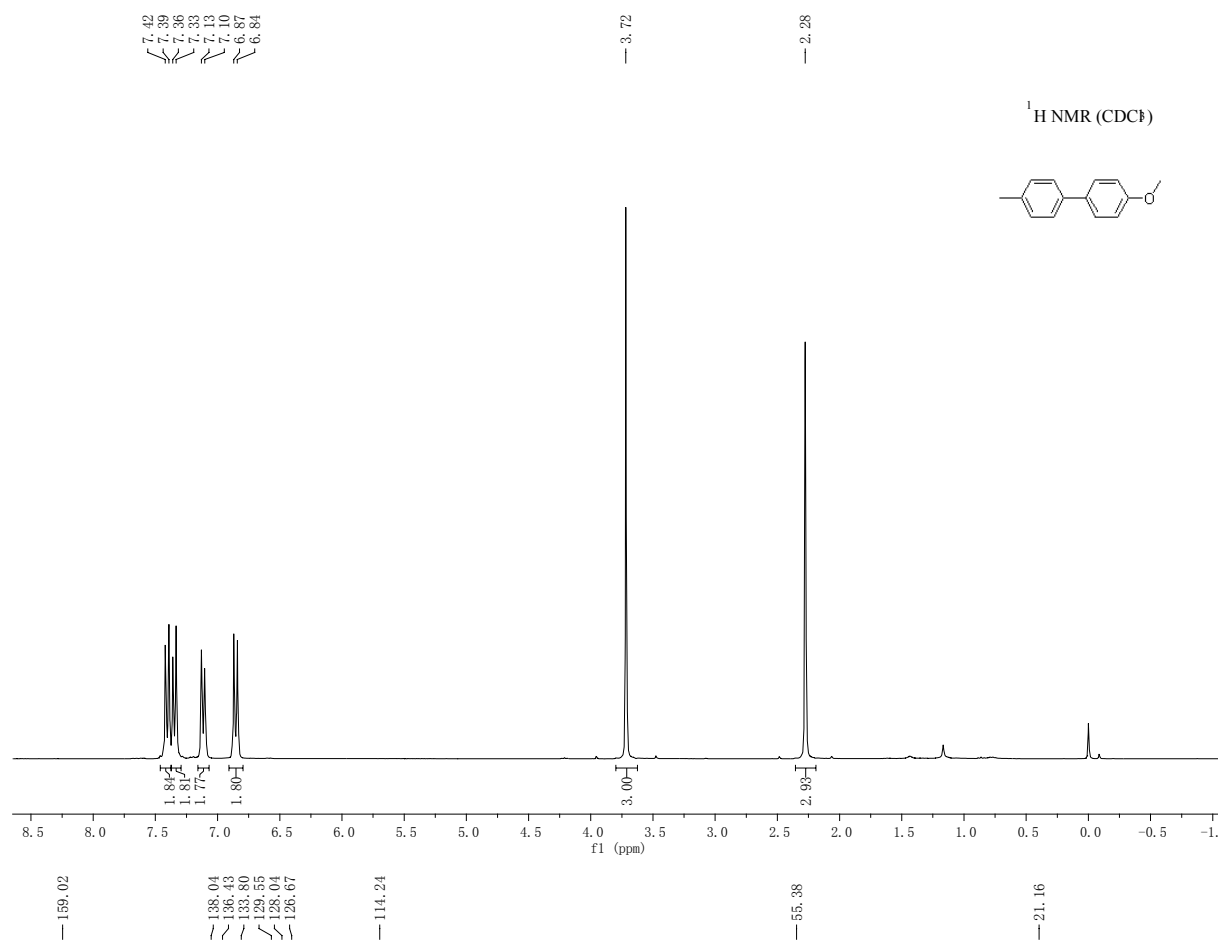


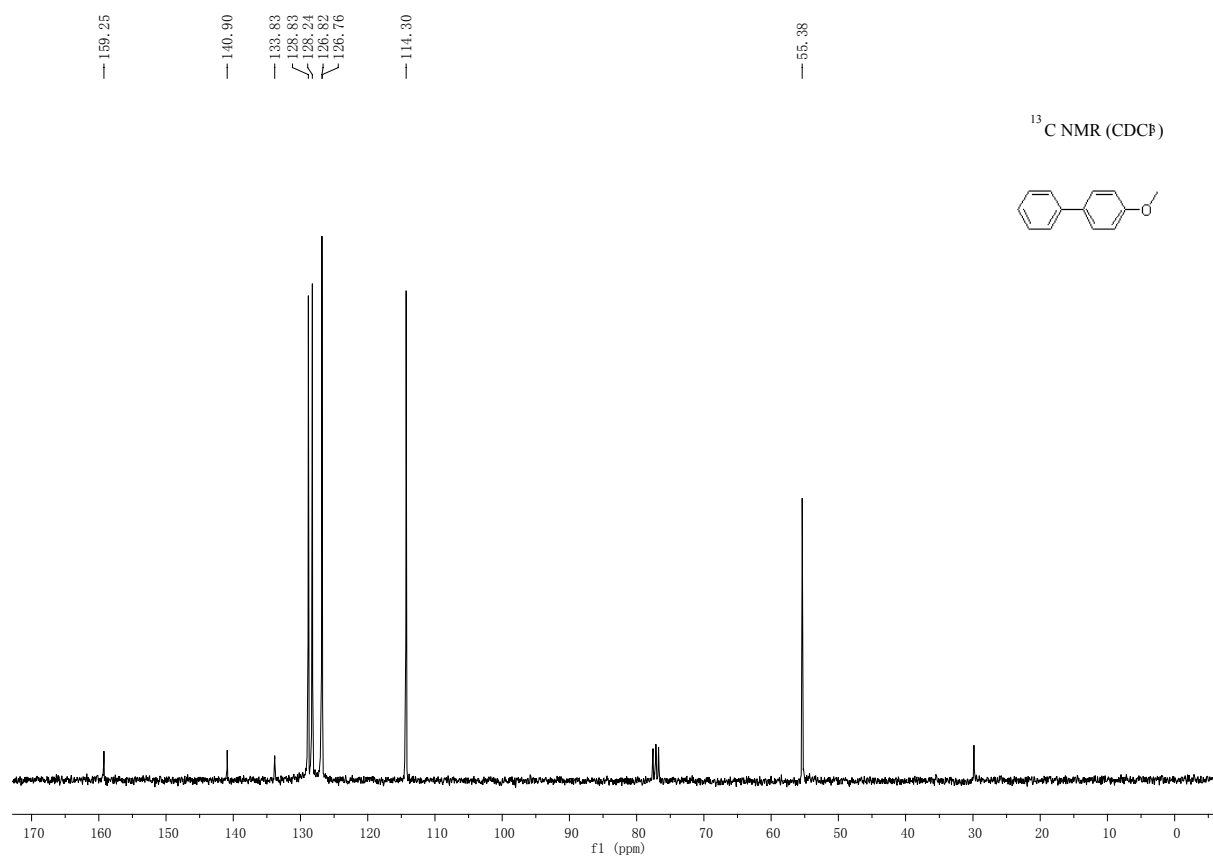
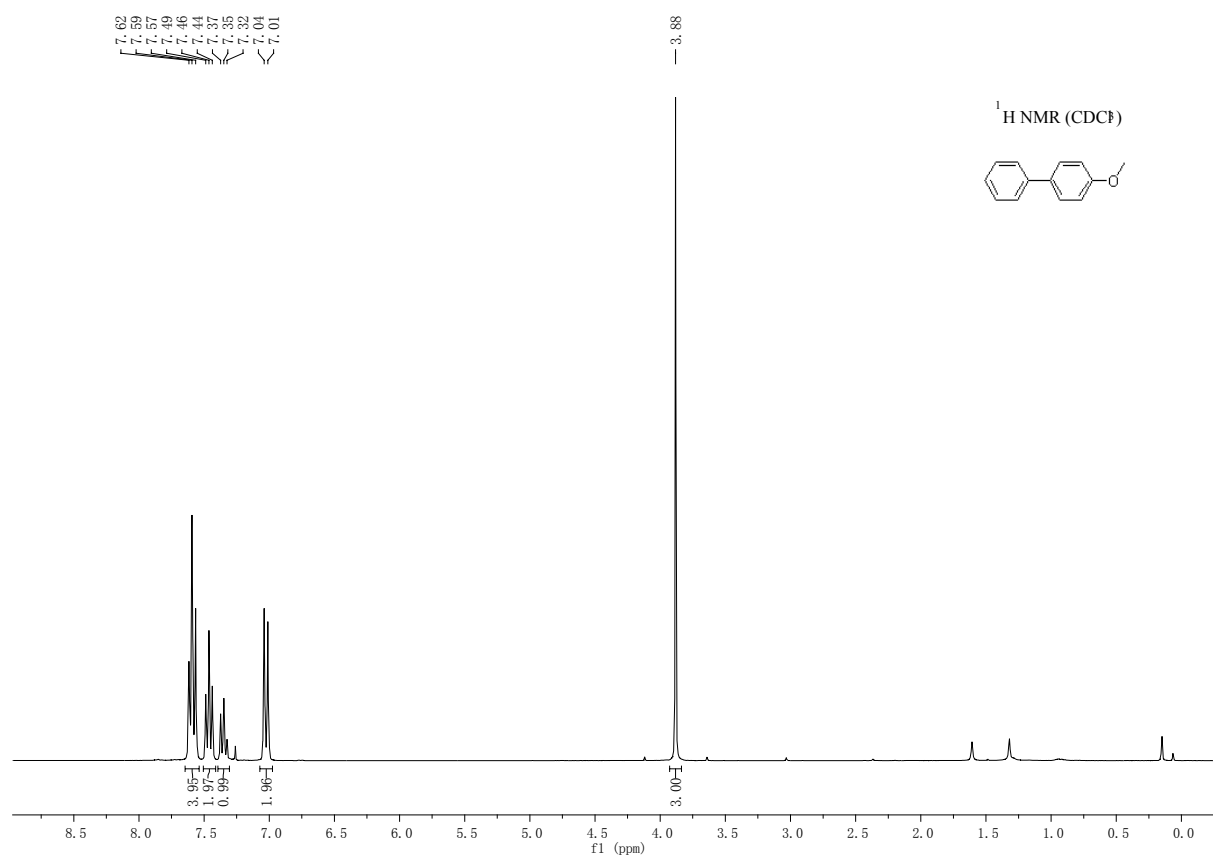
Figure S2. ORTEP drawing of complex V (30% probability. Toluene molecule is omitted).

NMR spectra

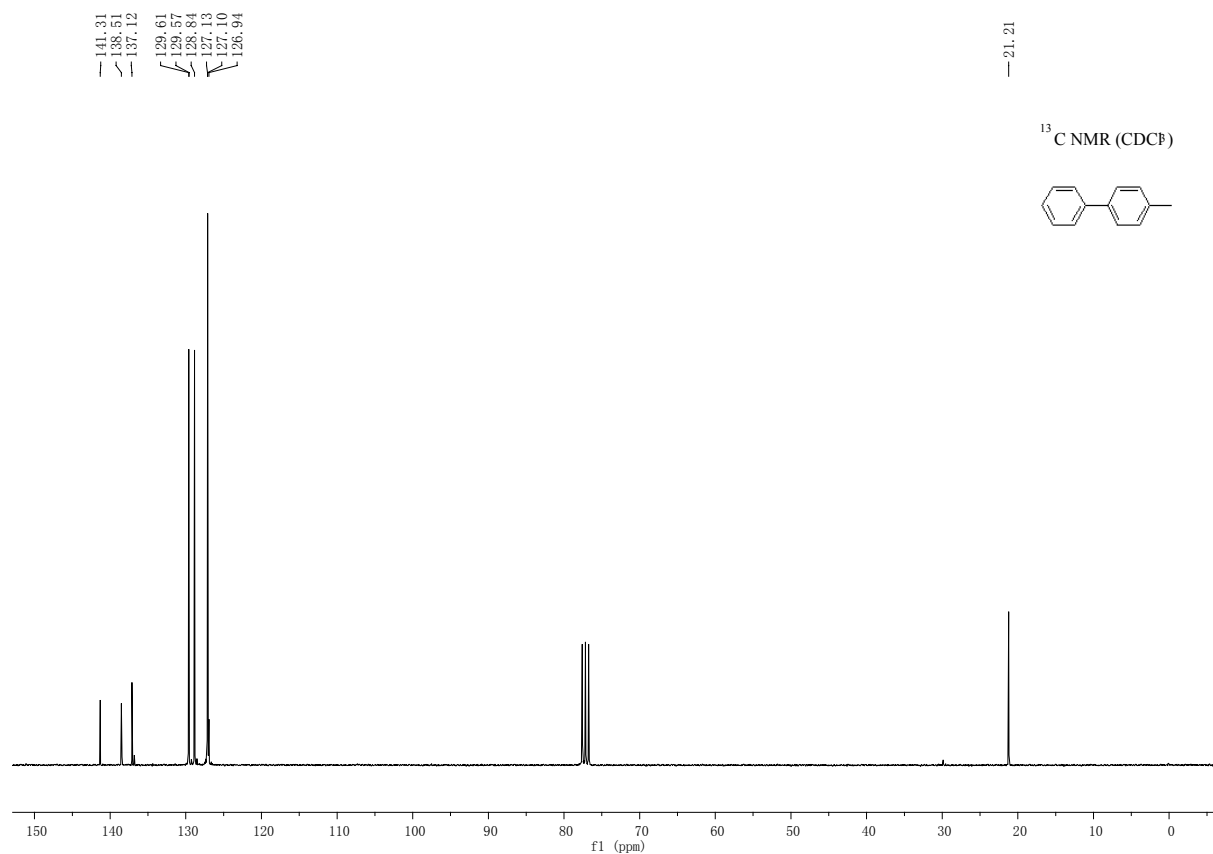
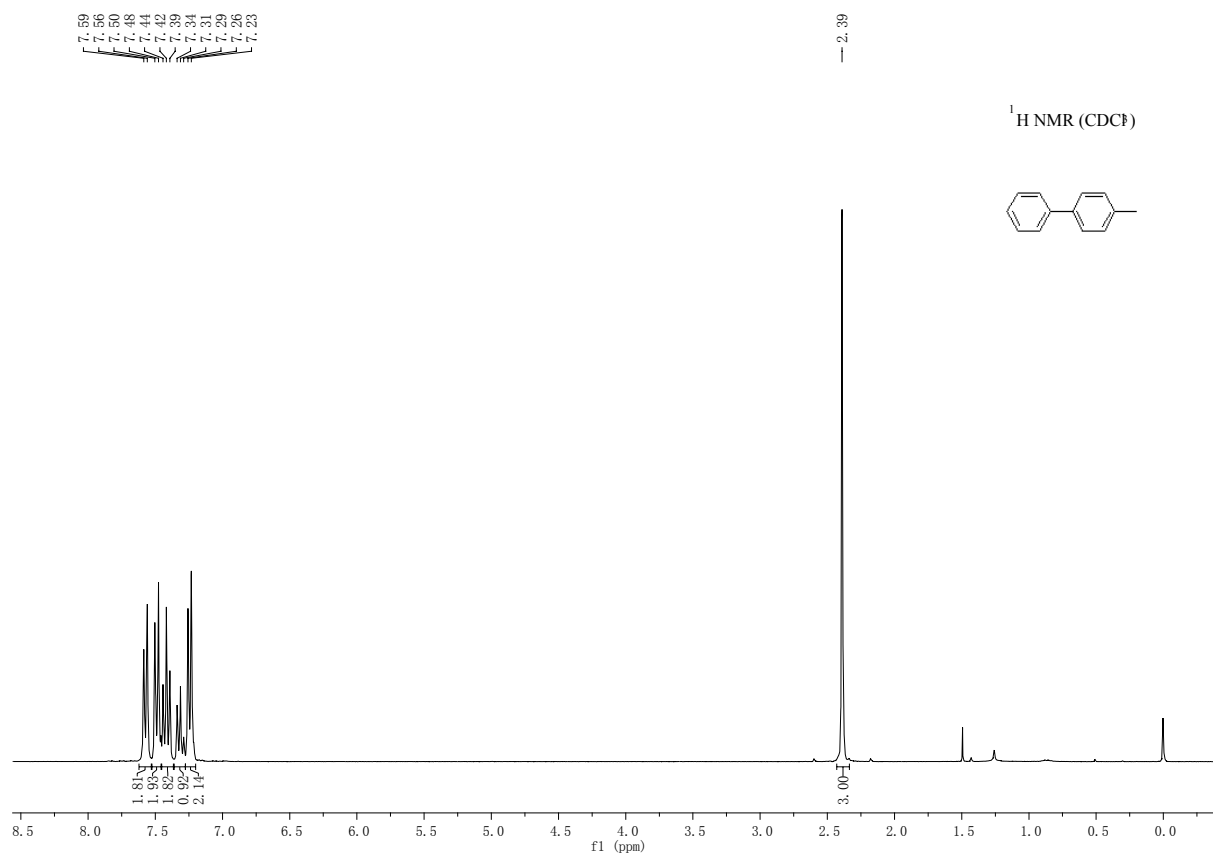
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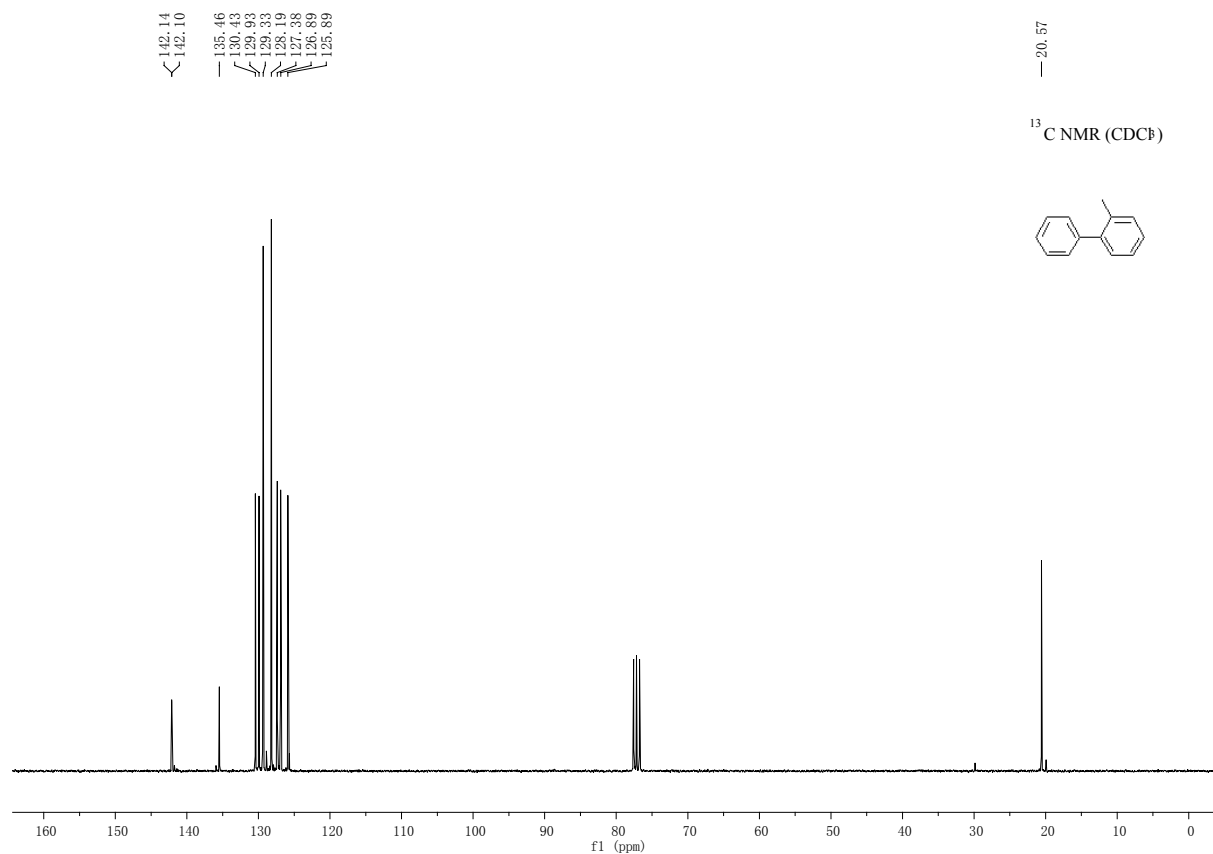
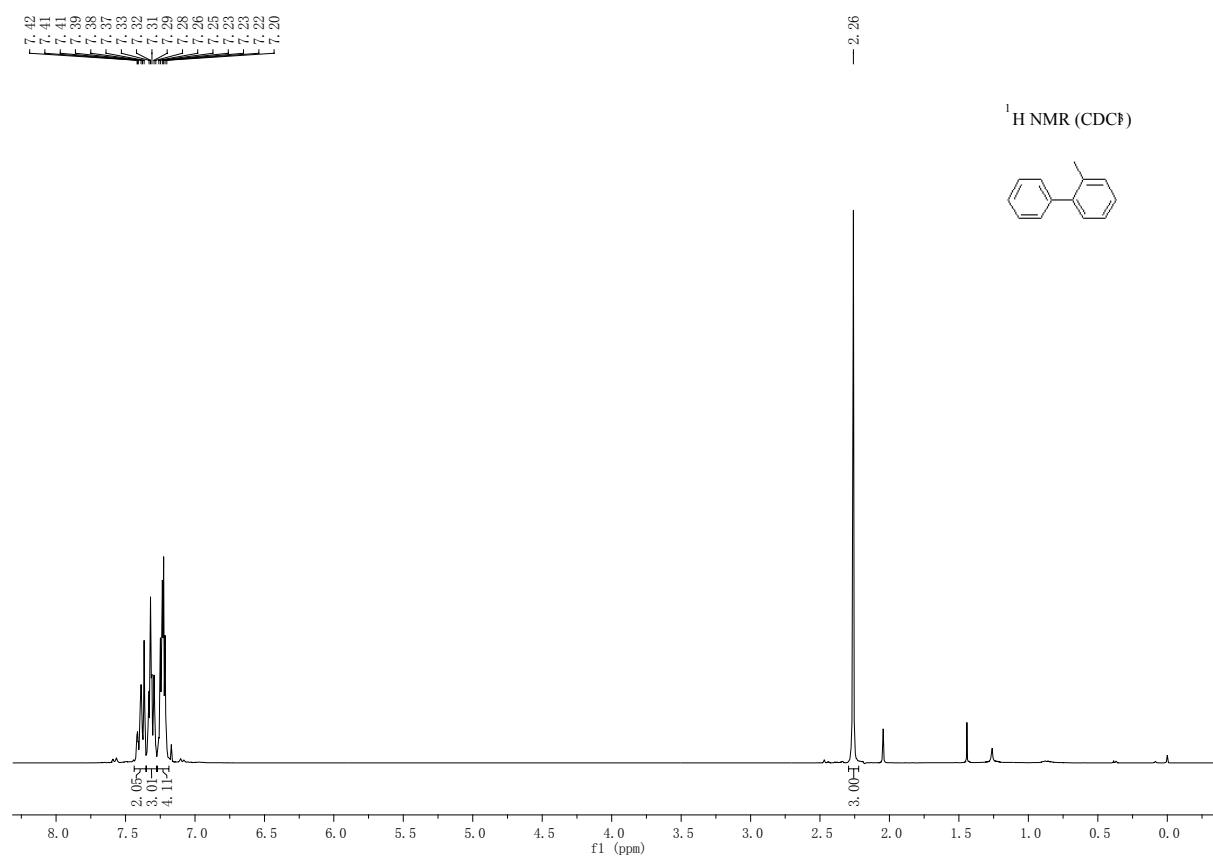
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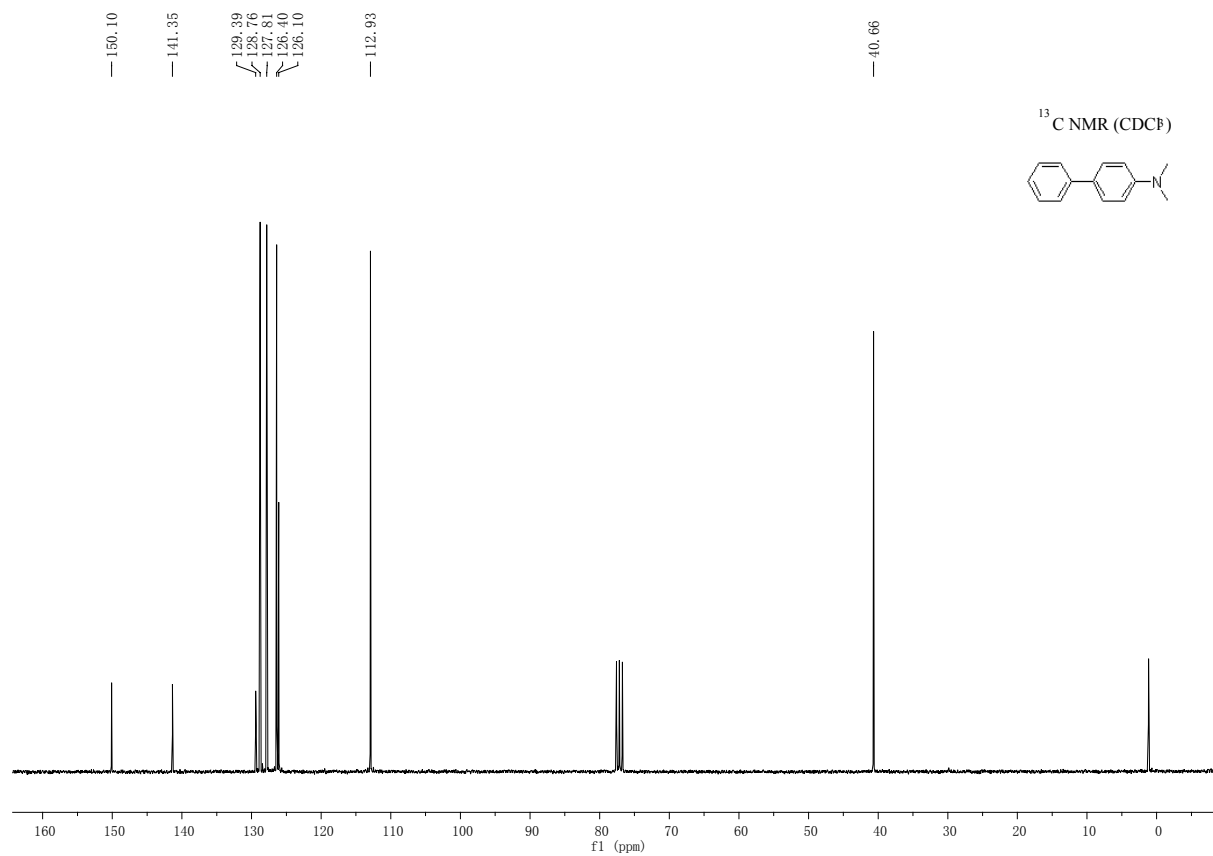
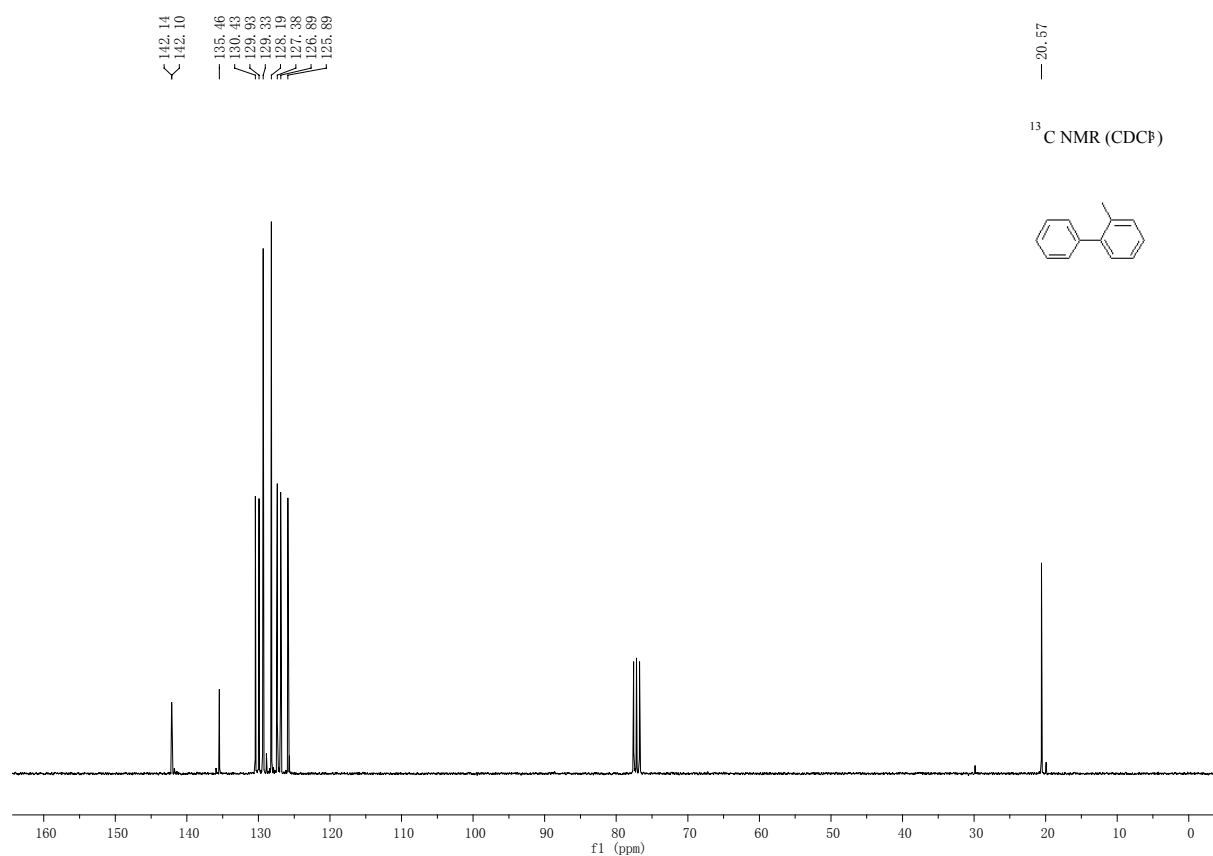
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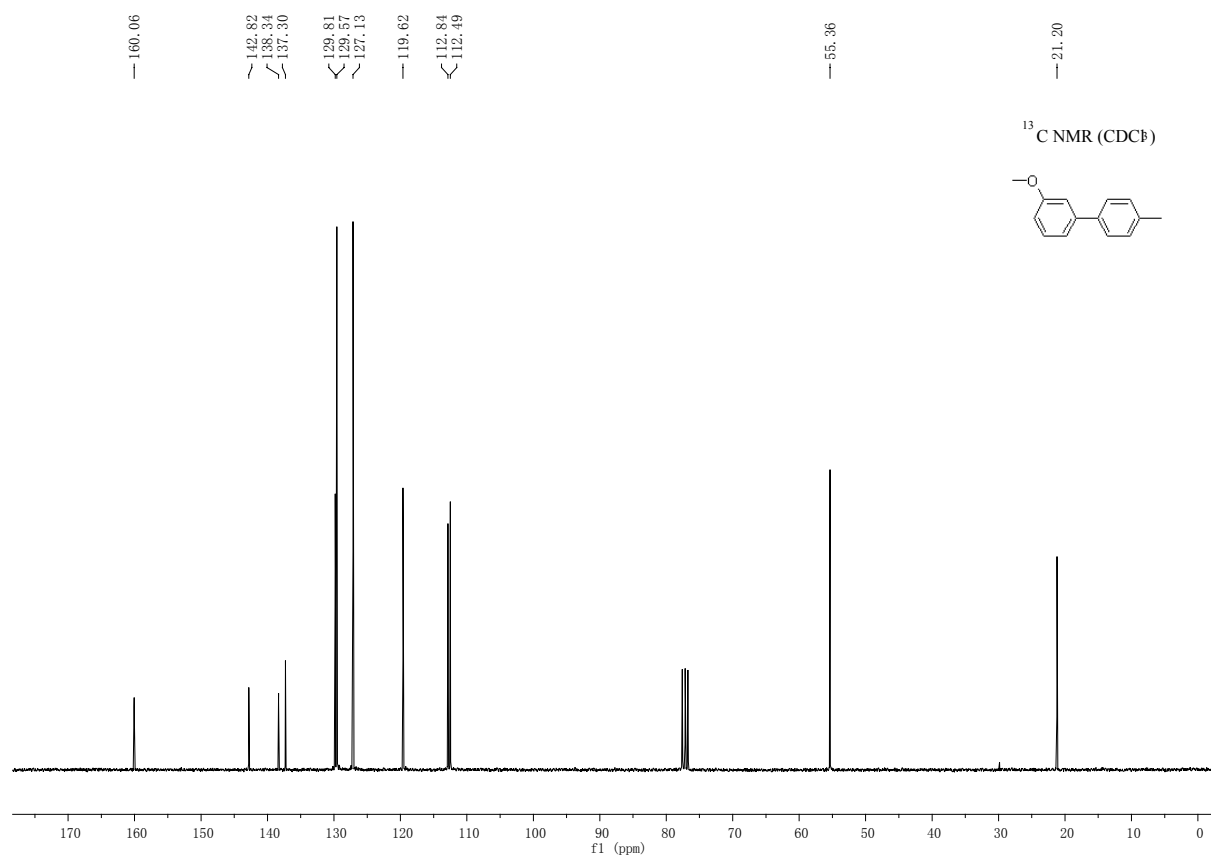
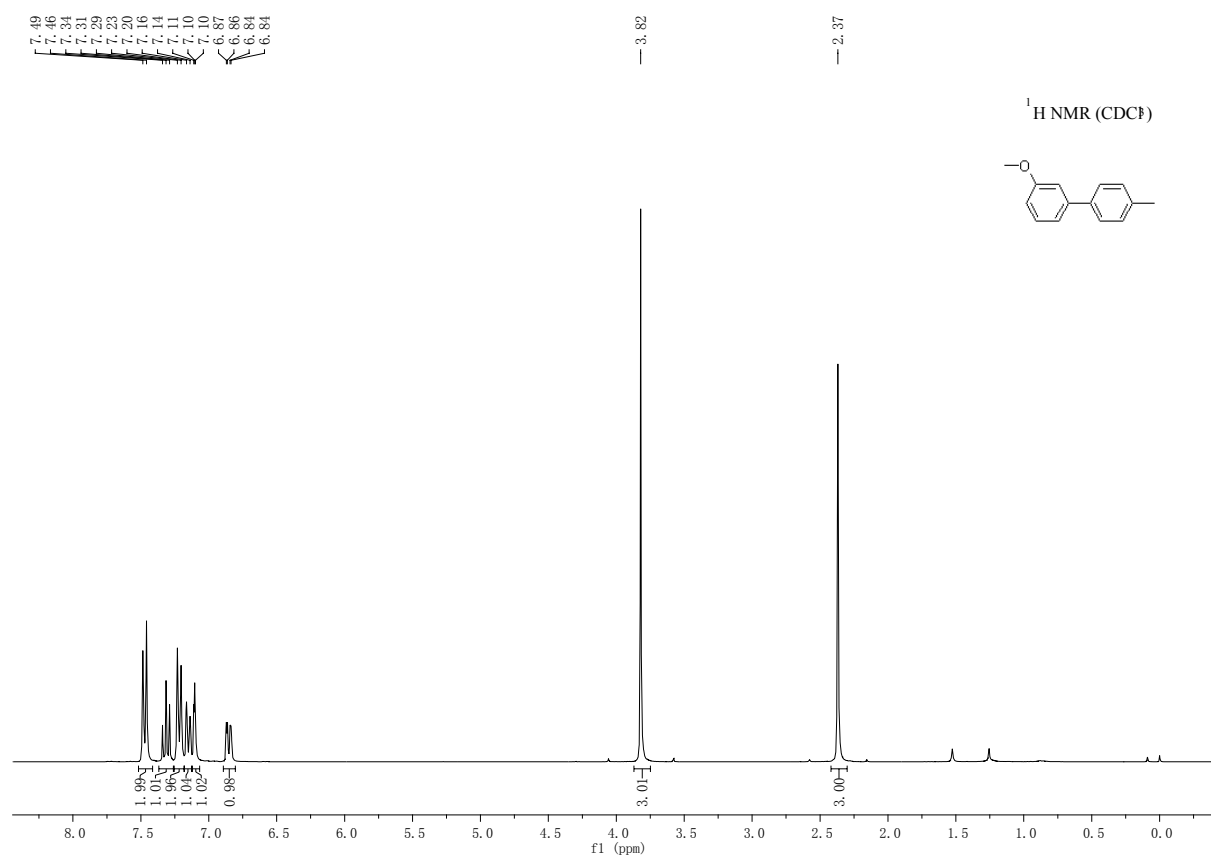
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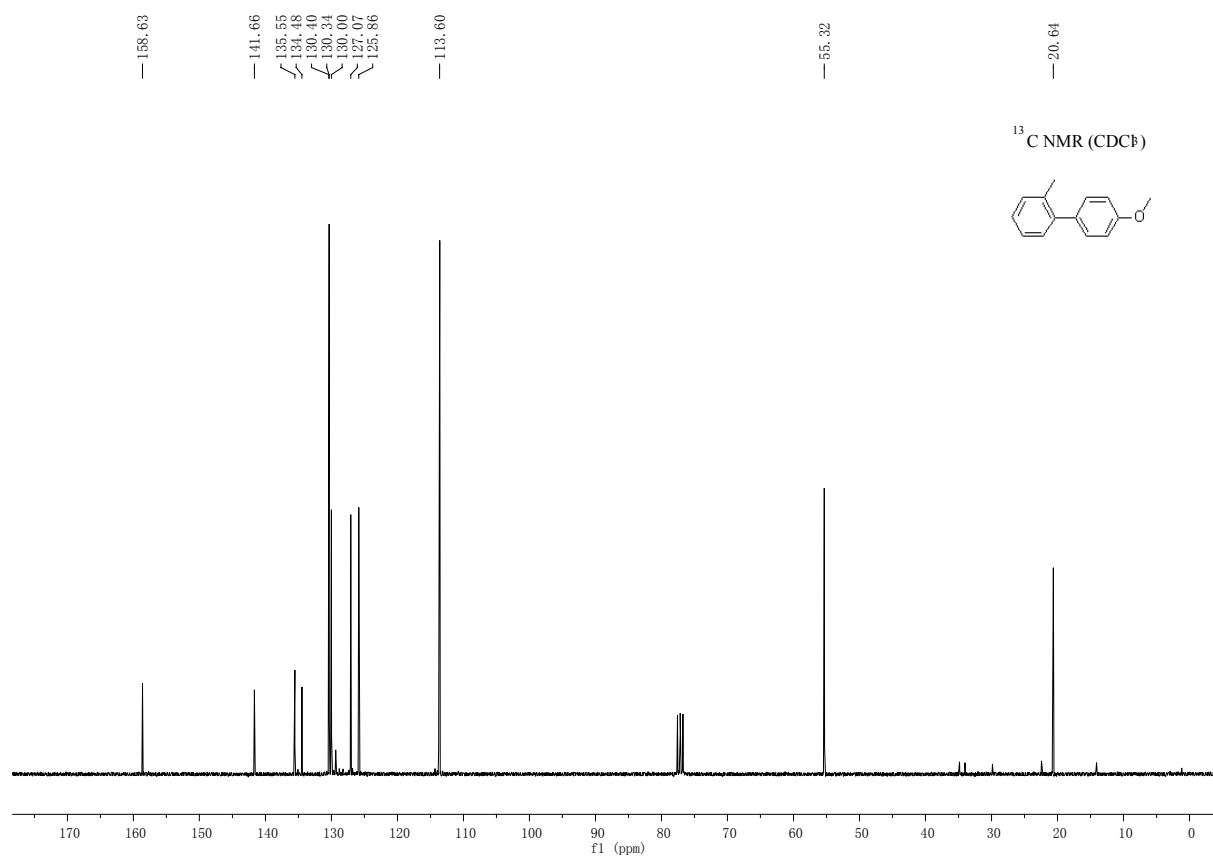
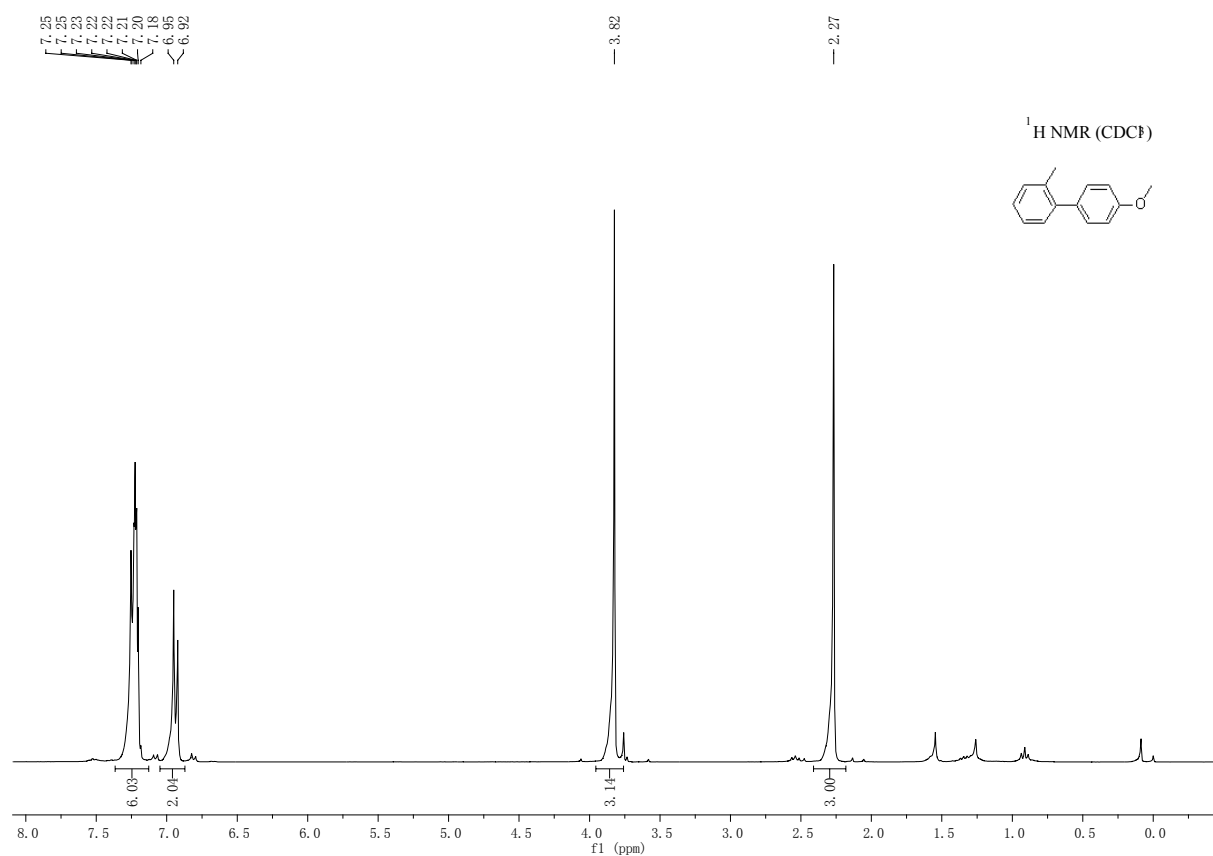
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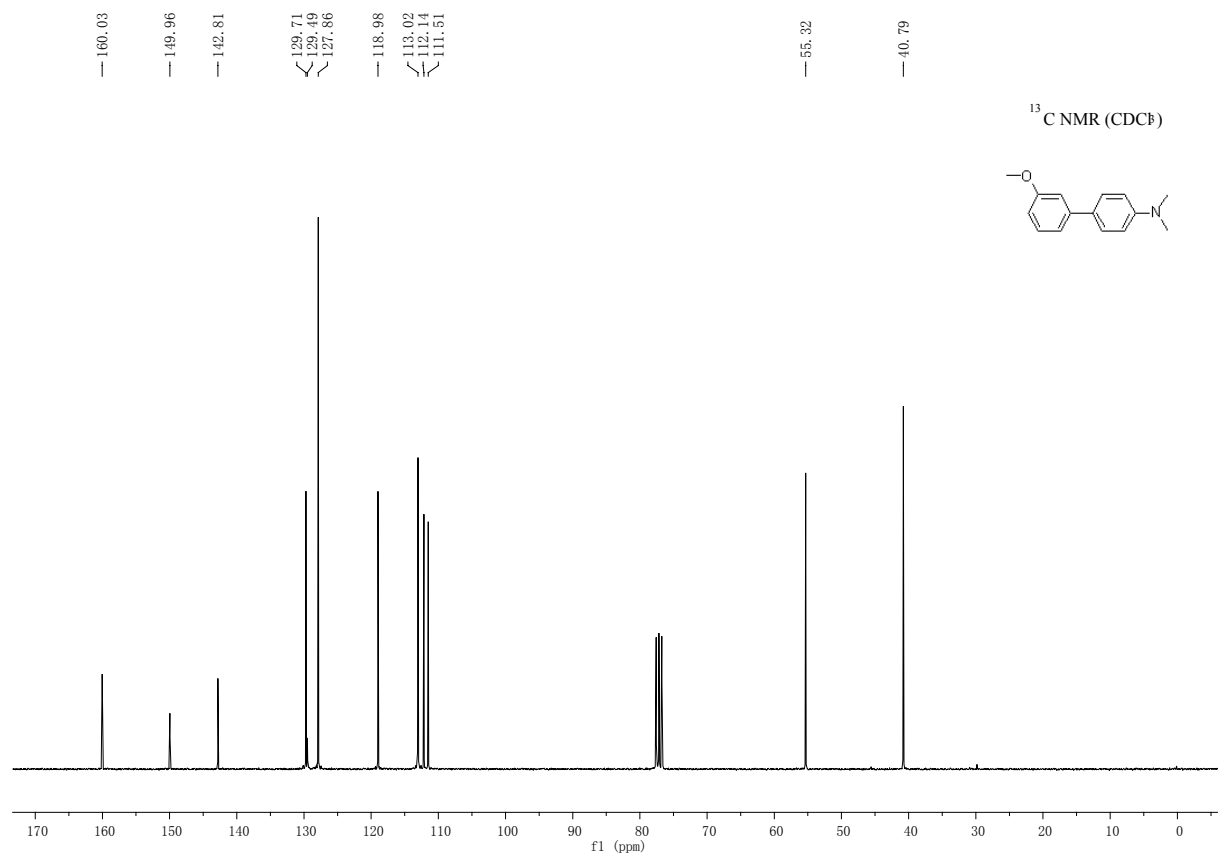
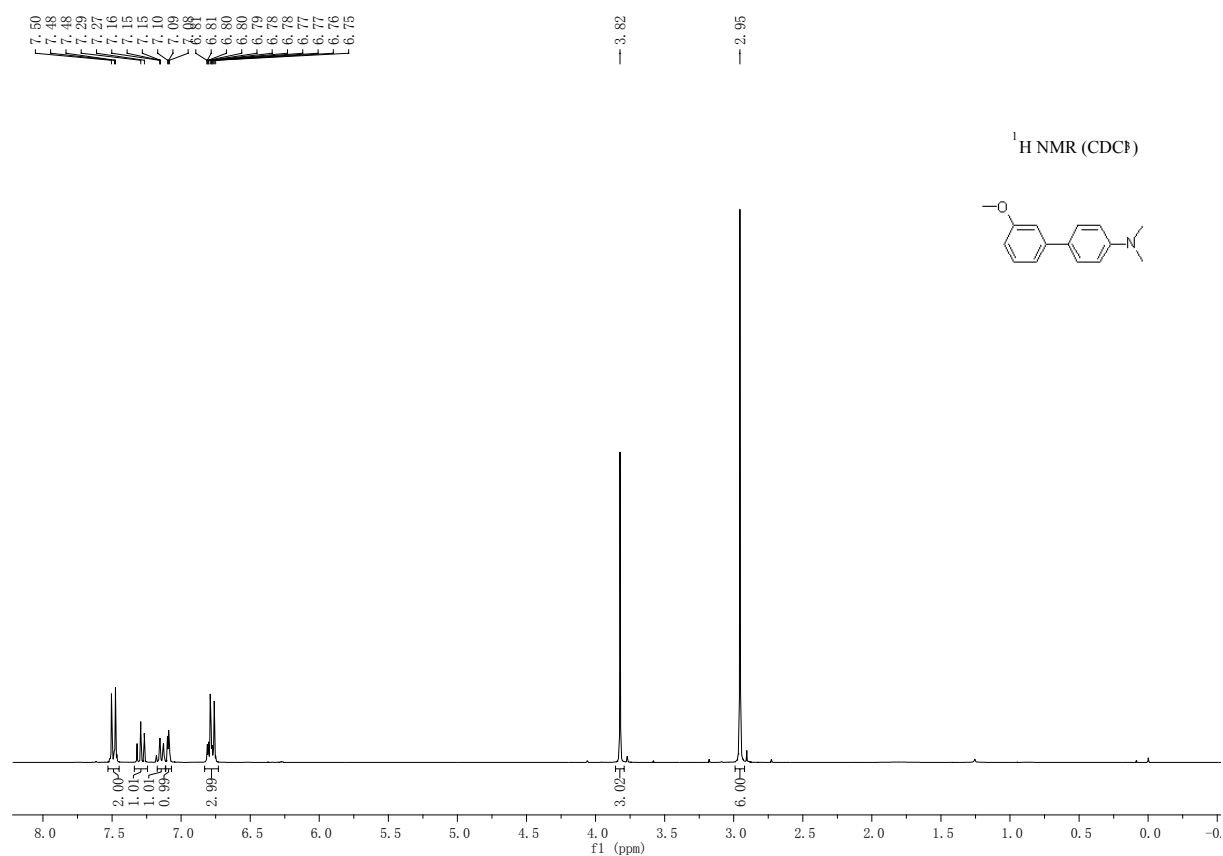
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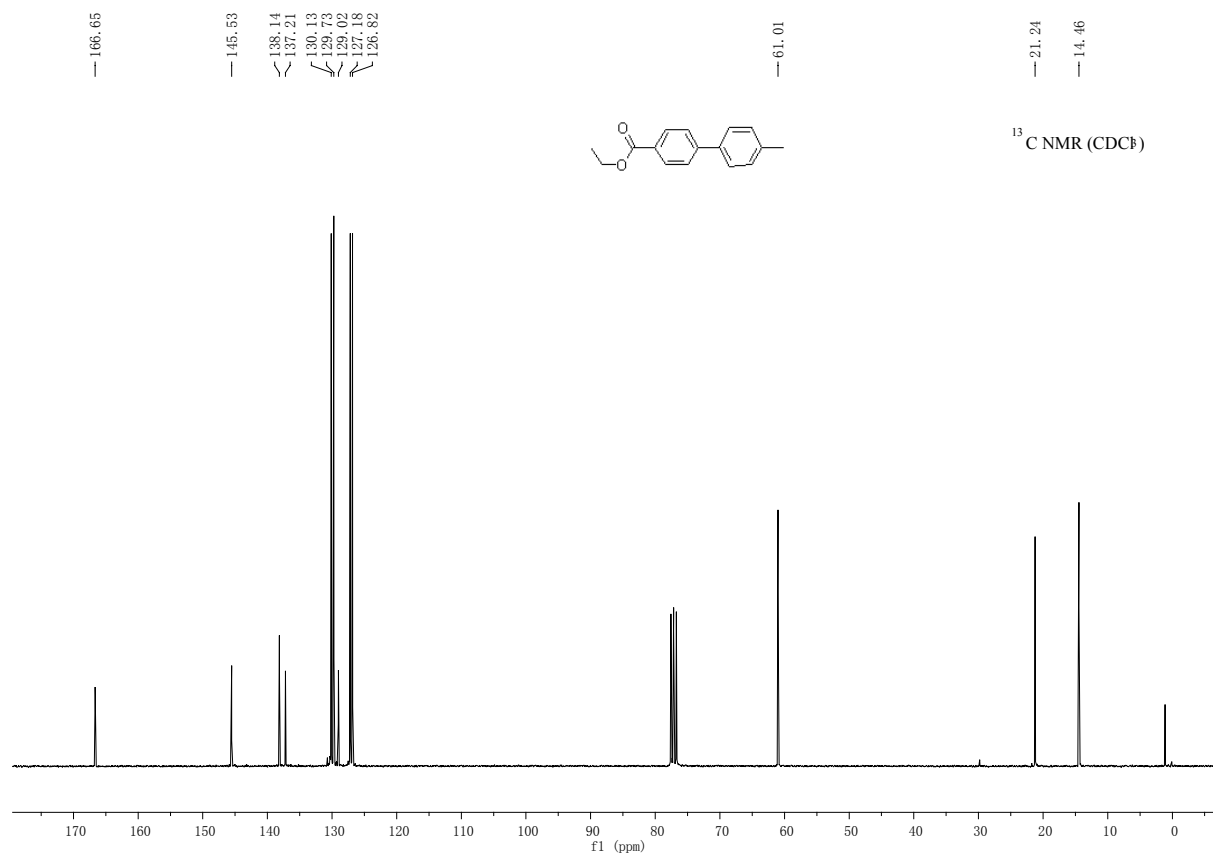
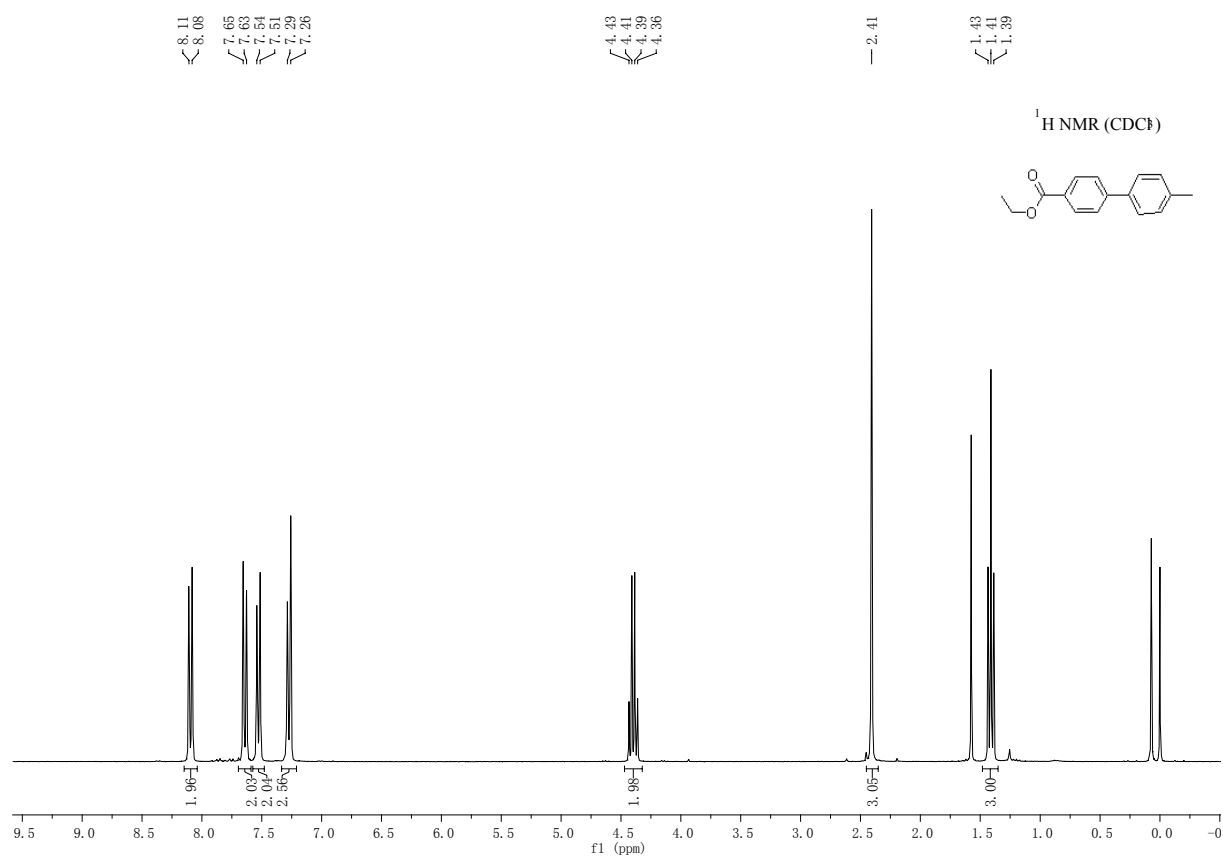
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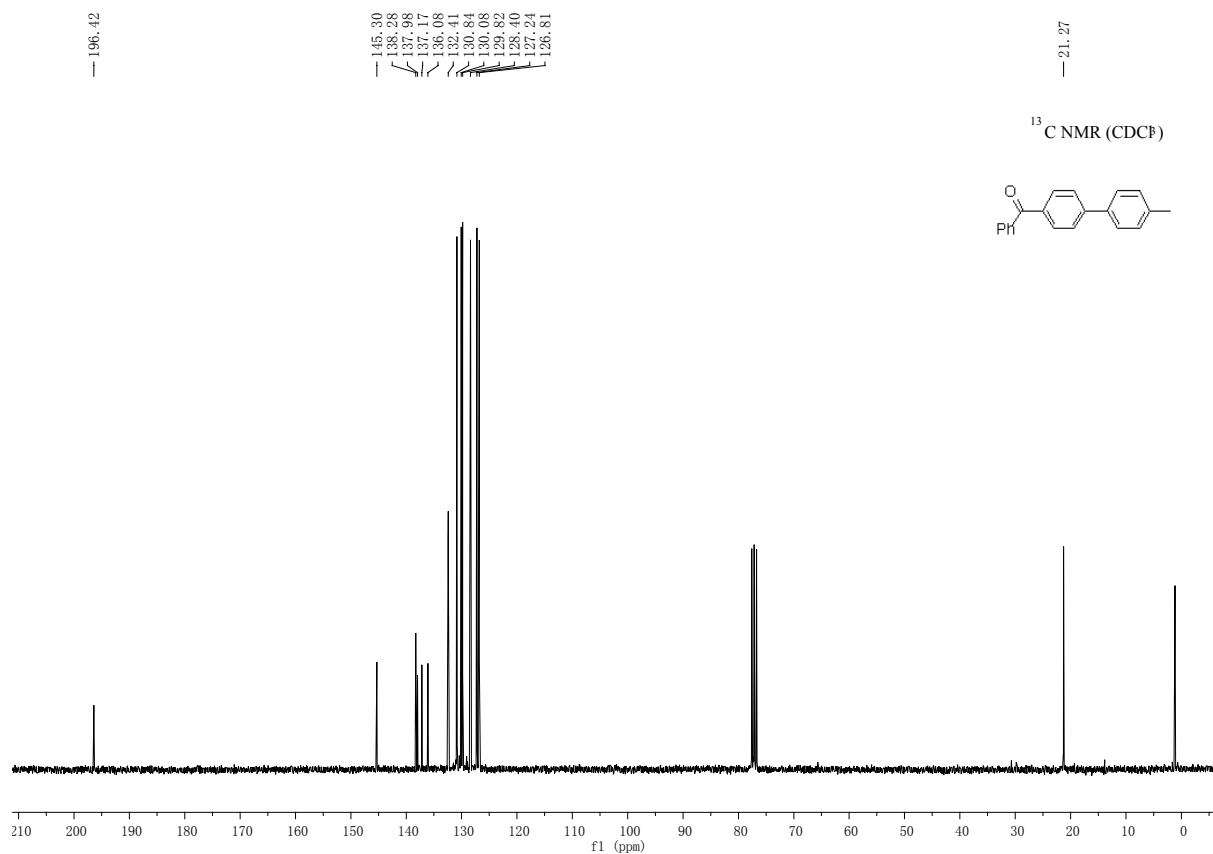
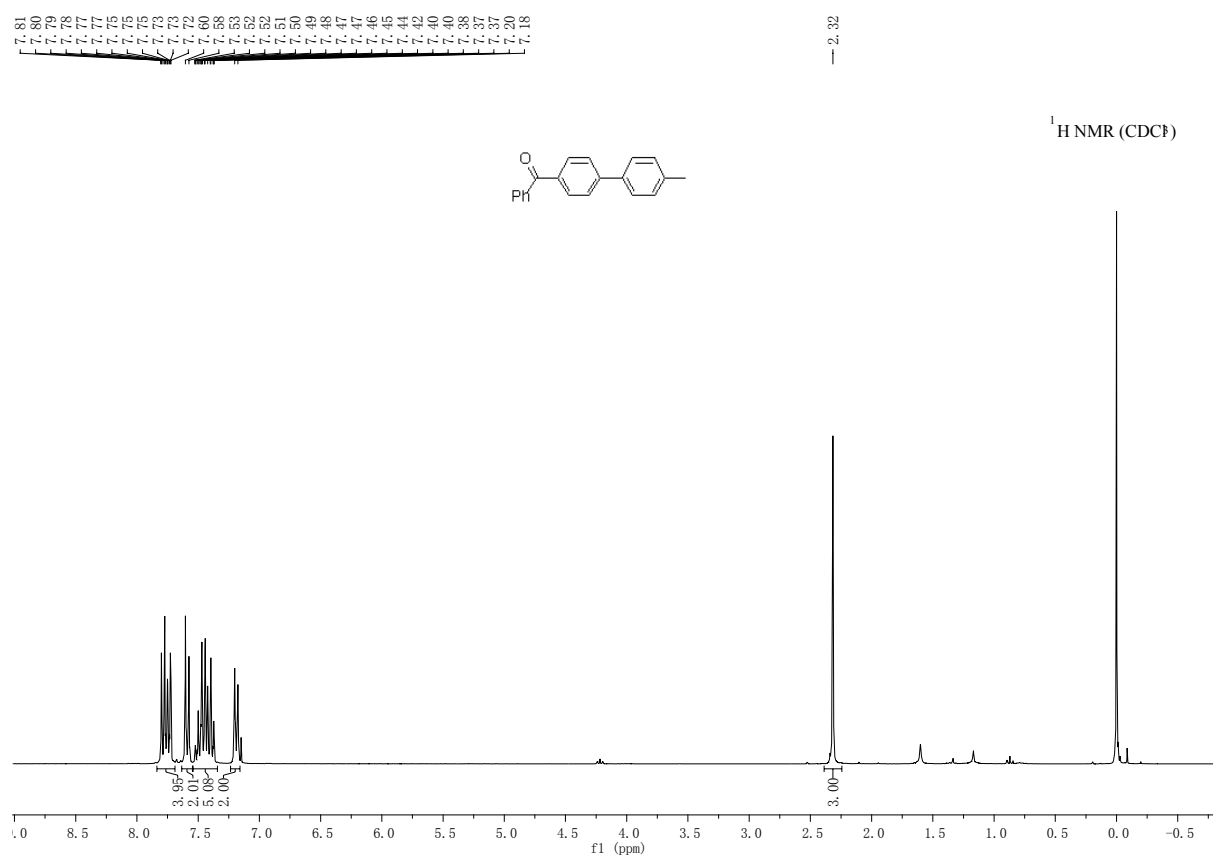
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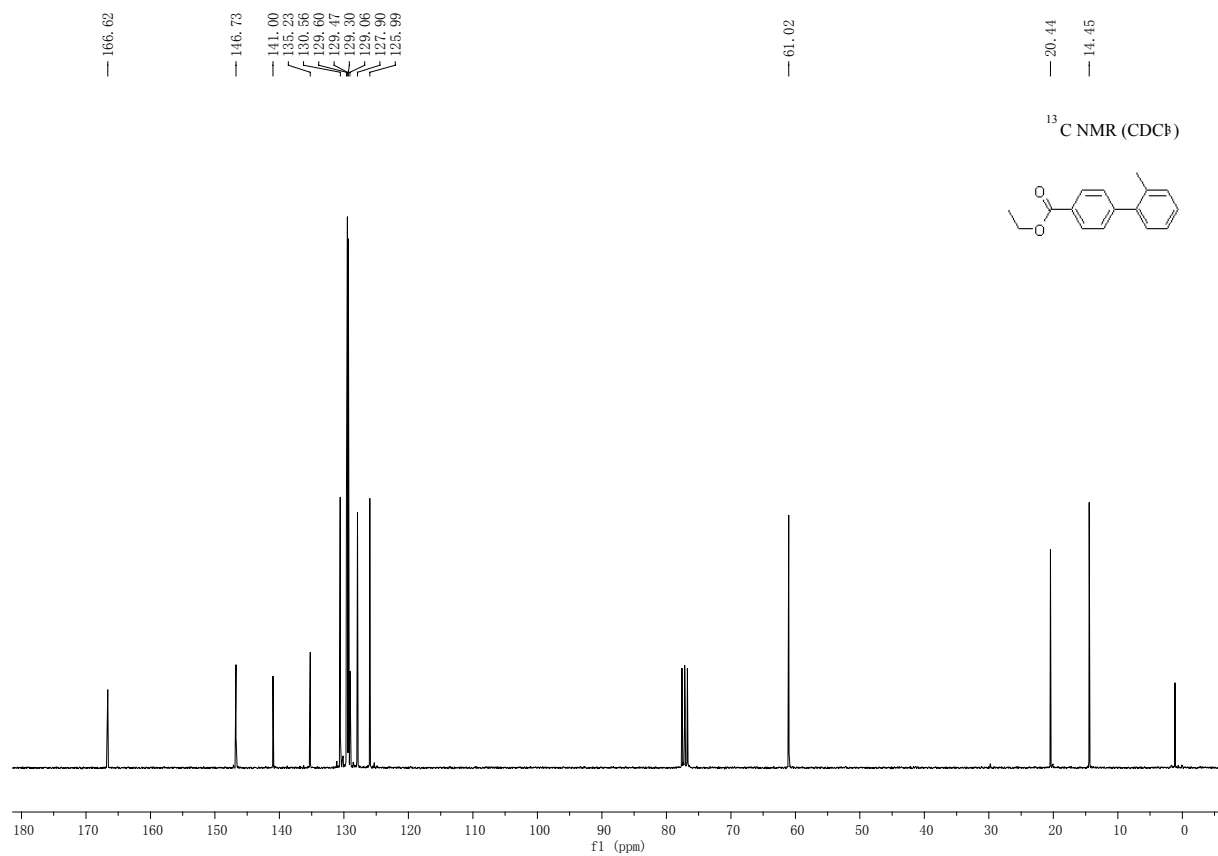
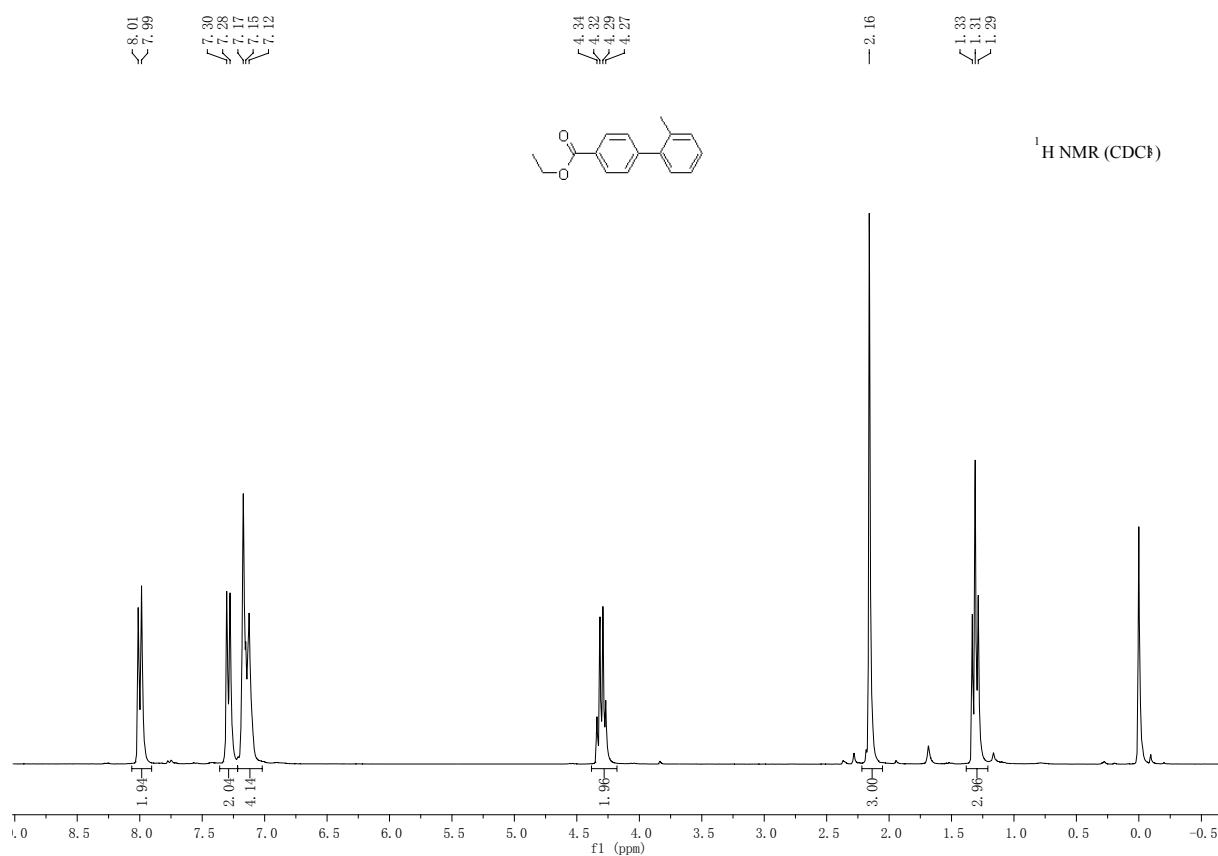
(9) Ethyl 4'-methylbiphenyl-4-carboxylate



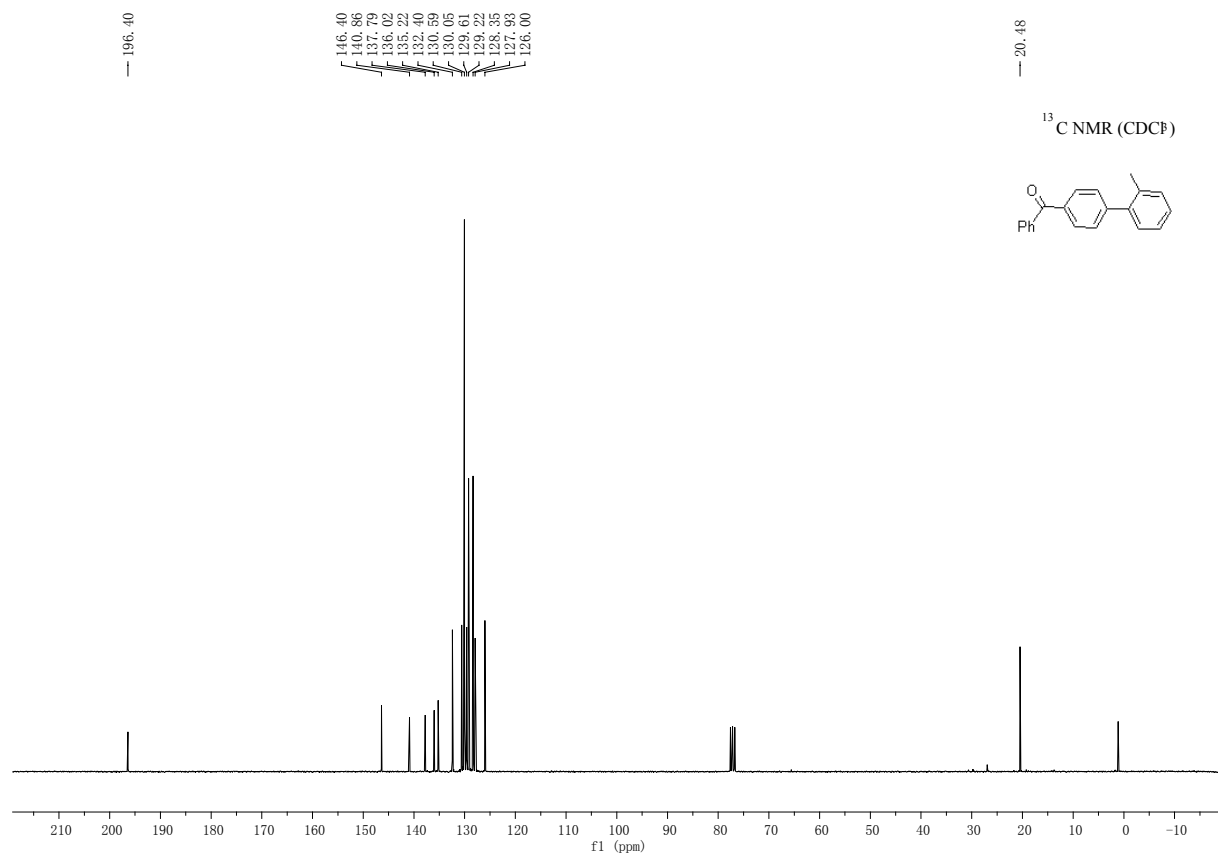
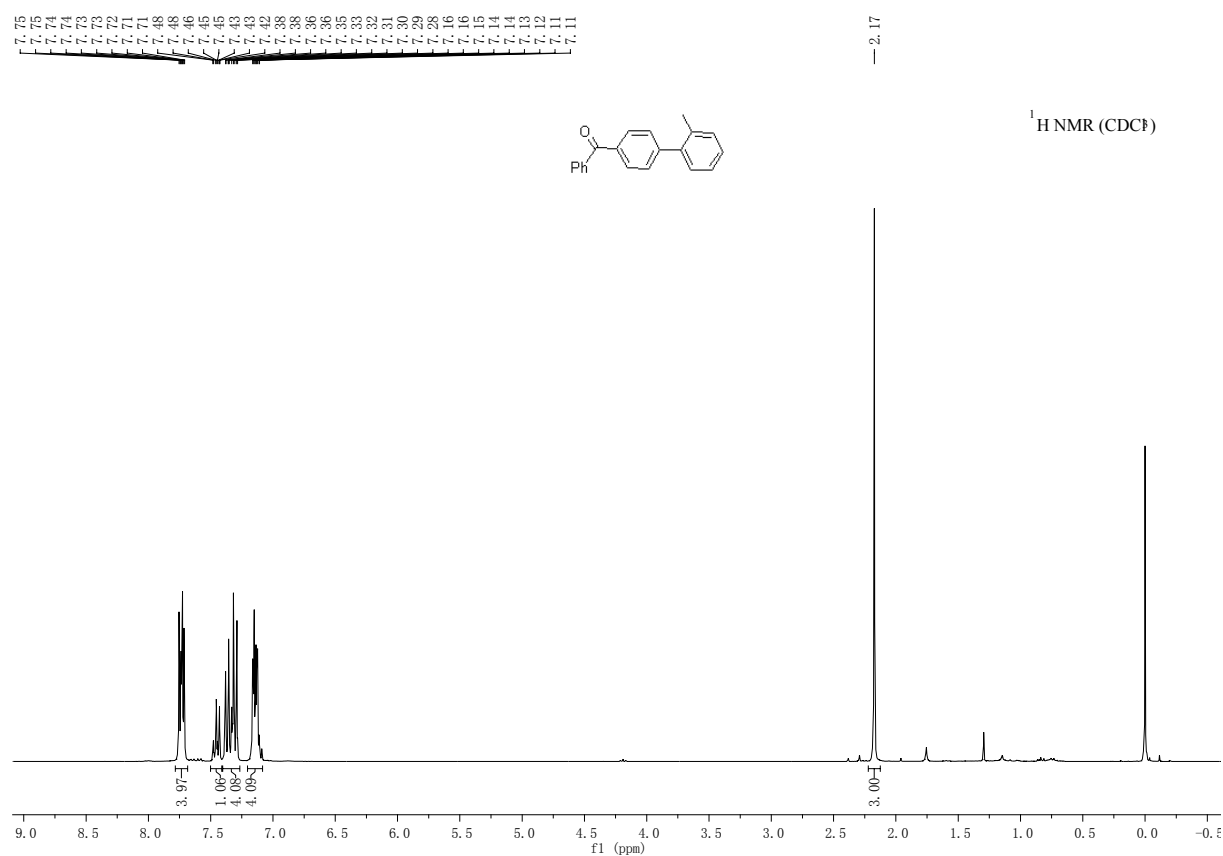
(10) Phenyl(*p*-tolyl)methanone



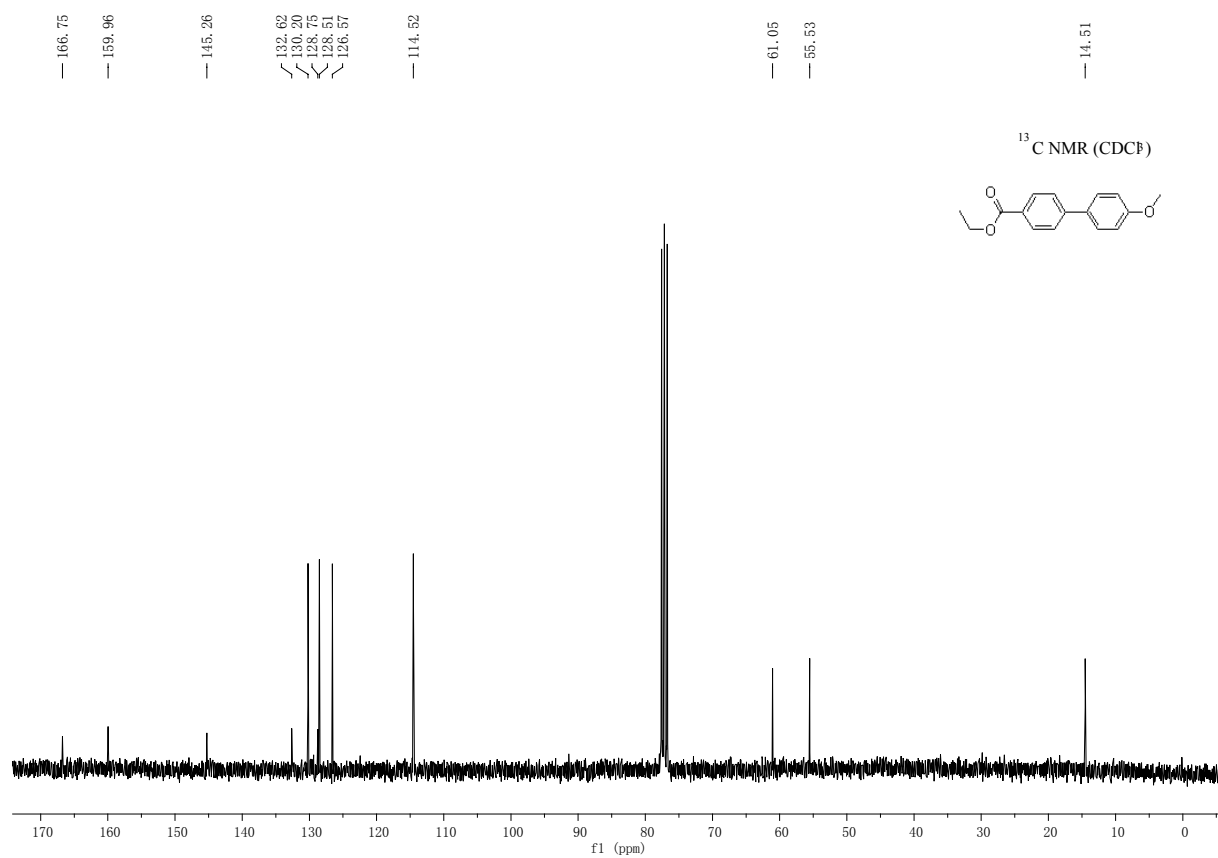
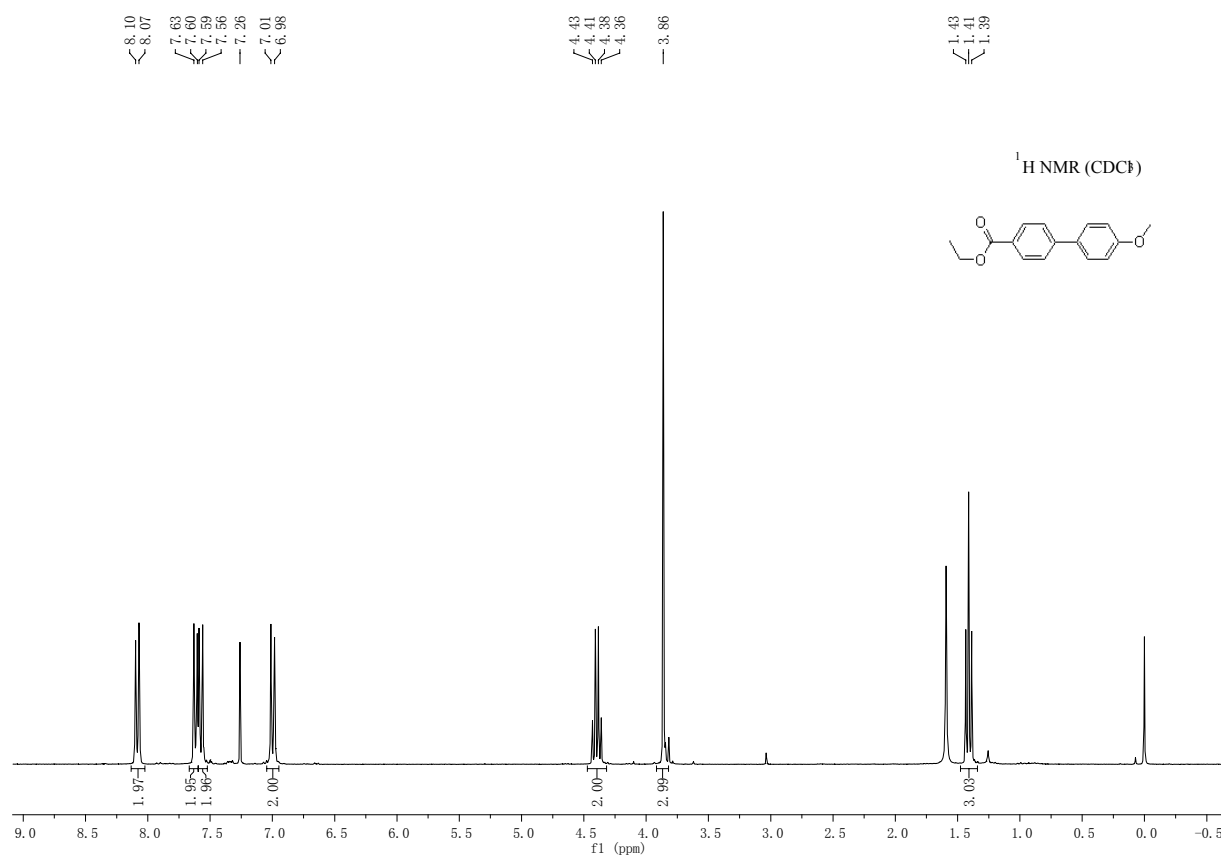
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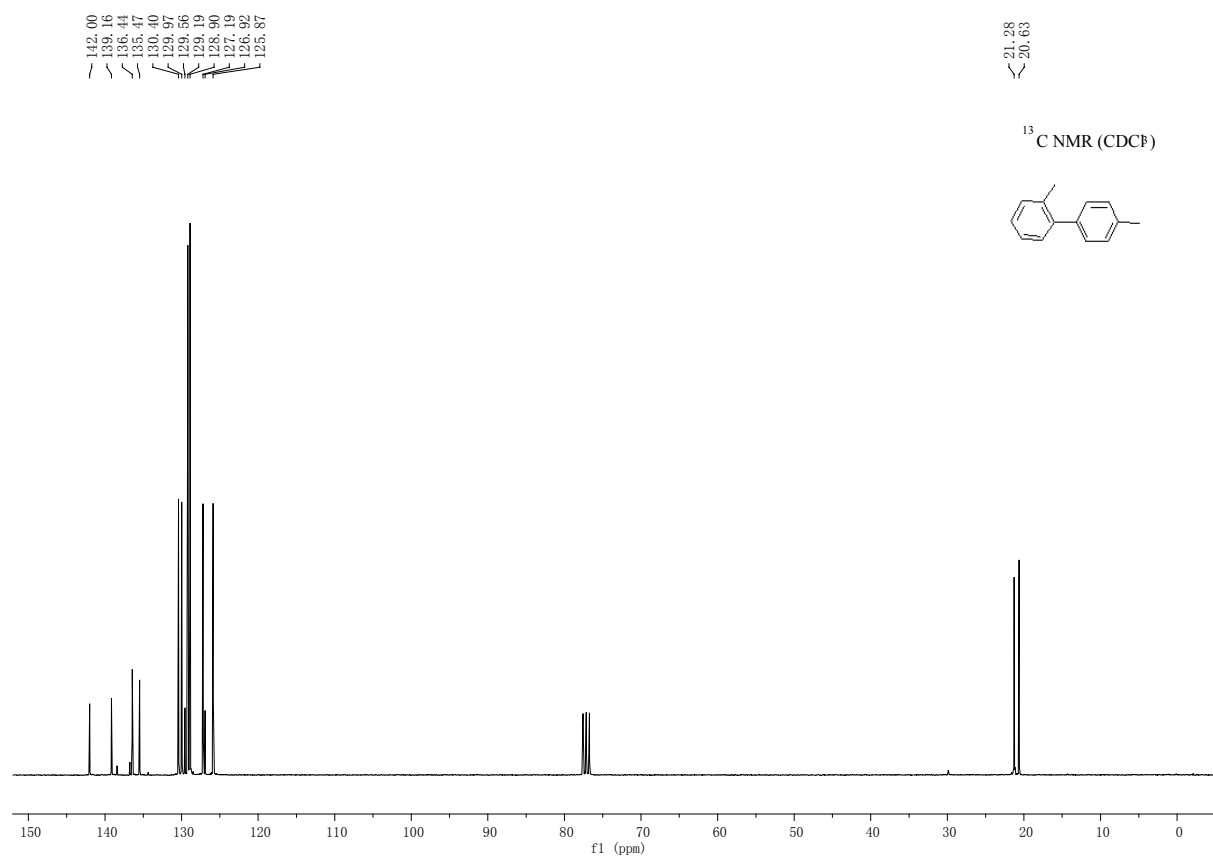
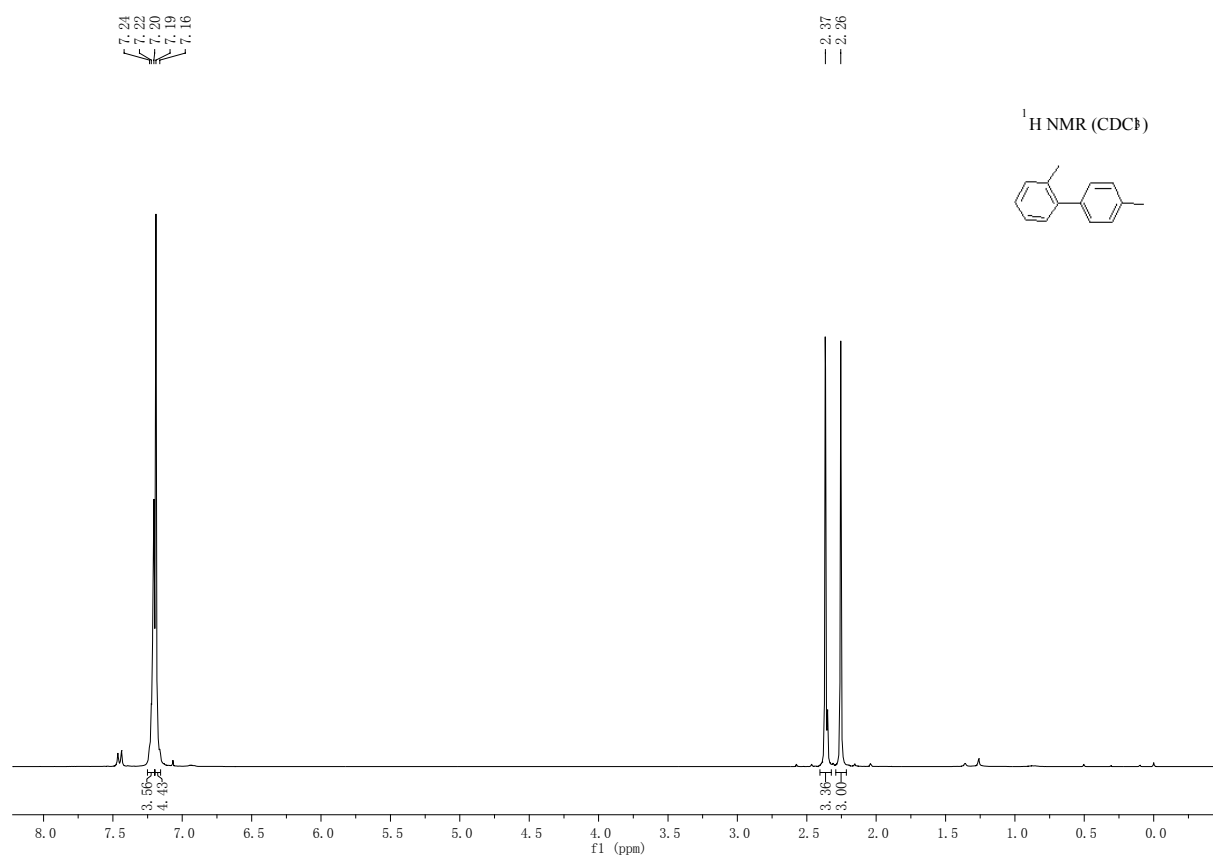
(12) (2'-Methylbiphenyl-4-yl)(phenyl)methanone



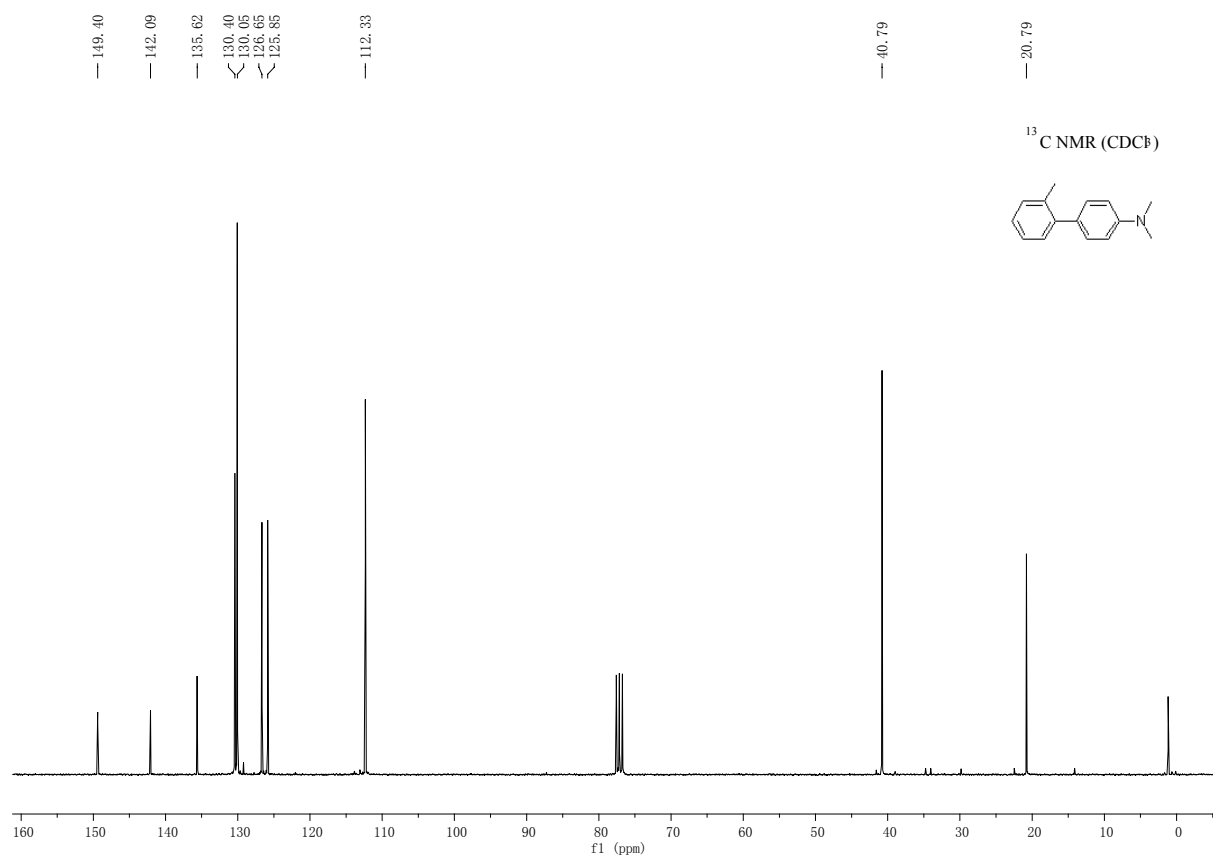
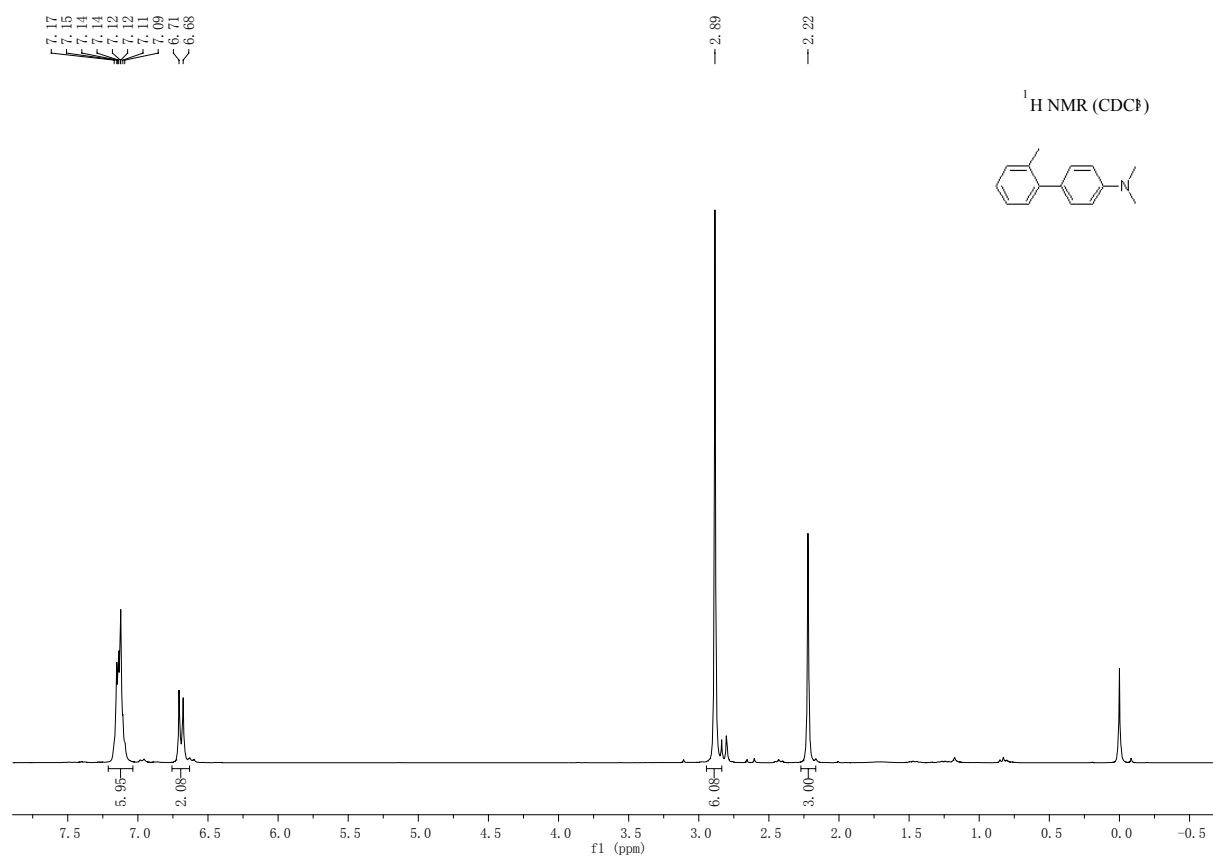
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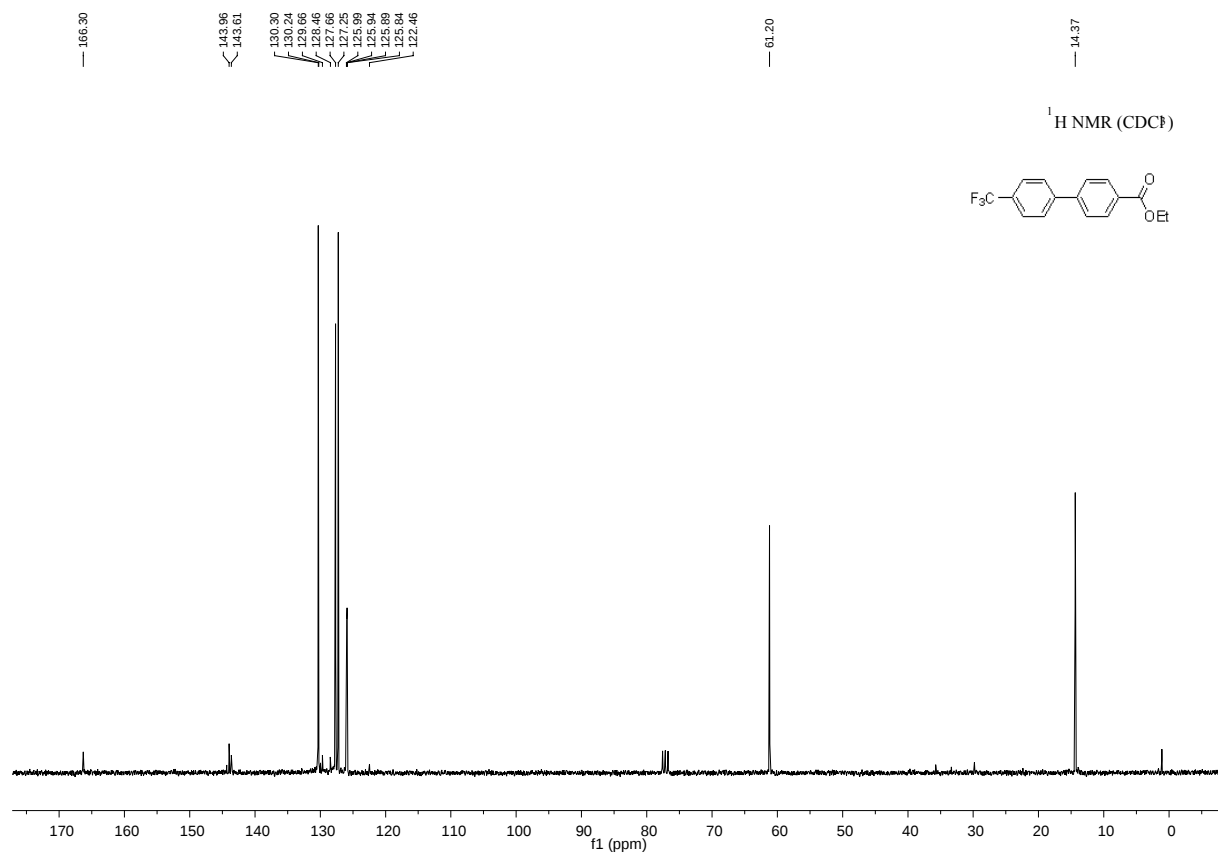
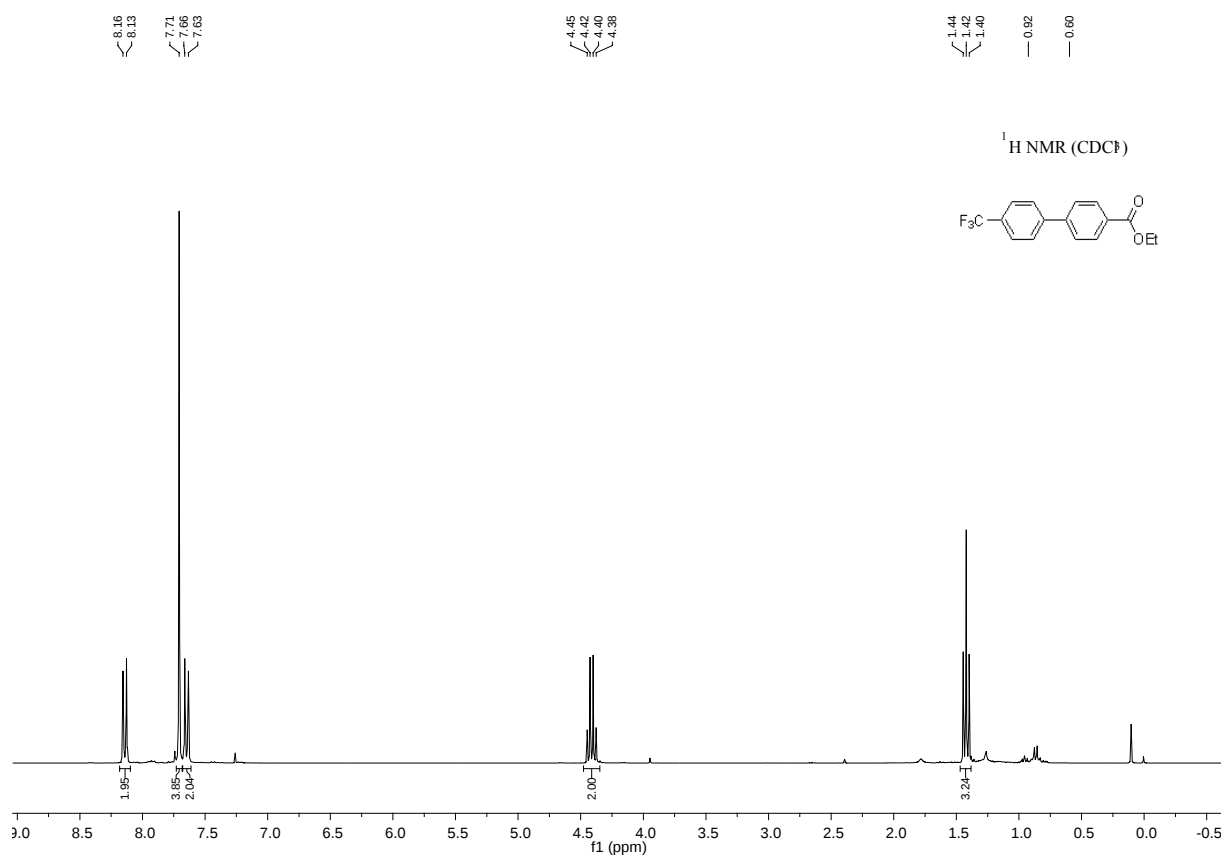
(14) 2,4'-Dimethylbiphenyl



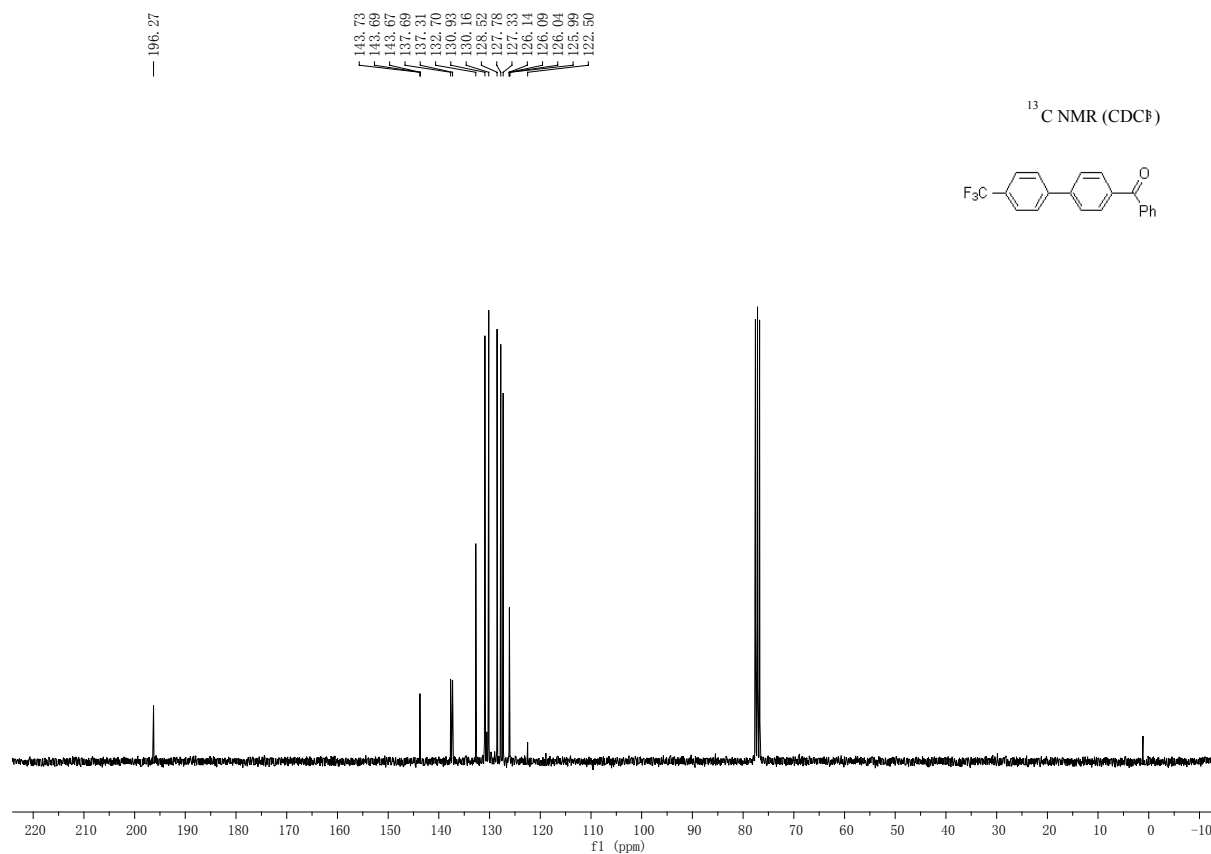
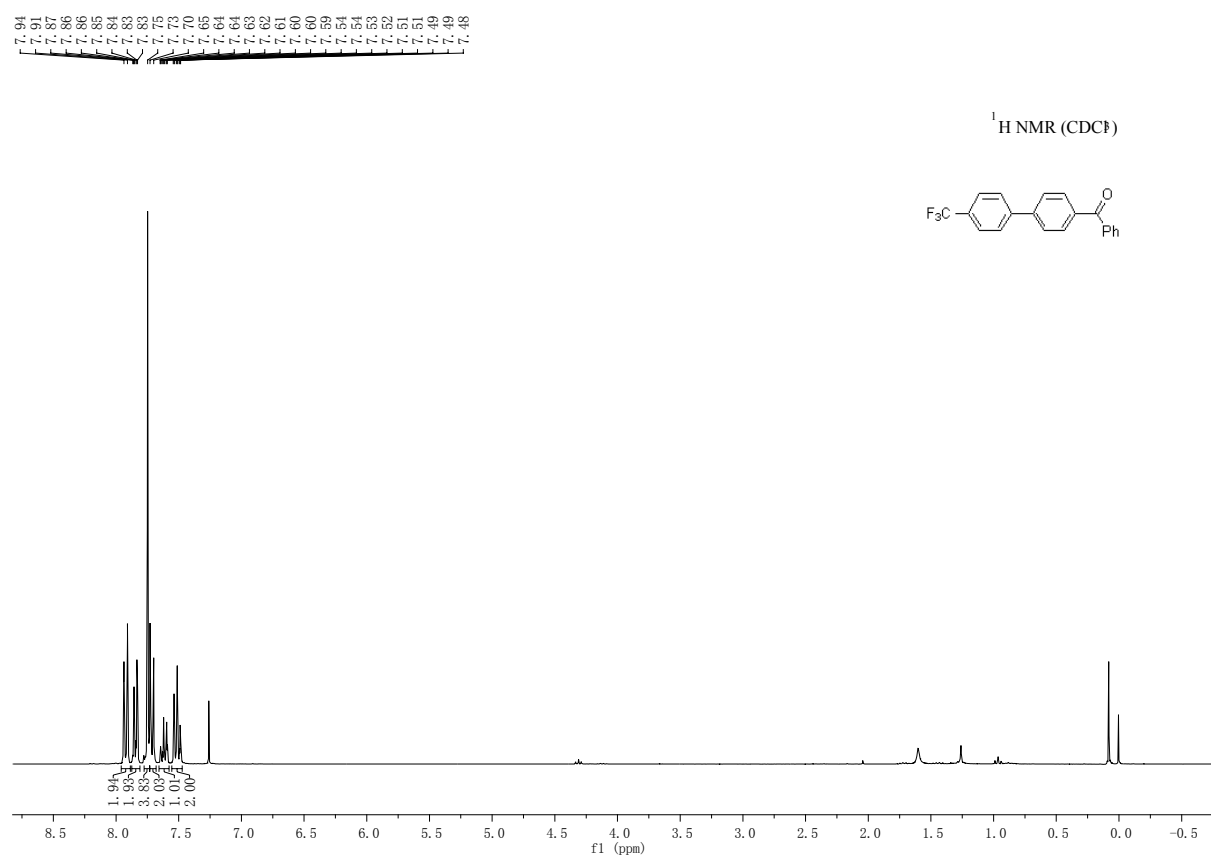
(15) 2'-Methyl-*N,N*-dimethylbiphenyl-4-amine



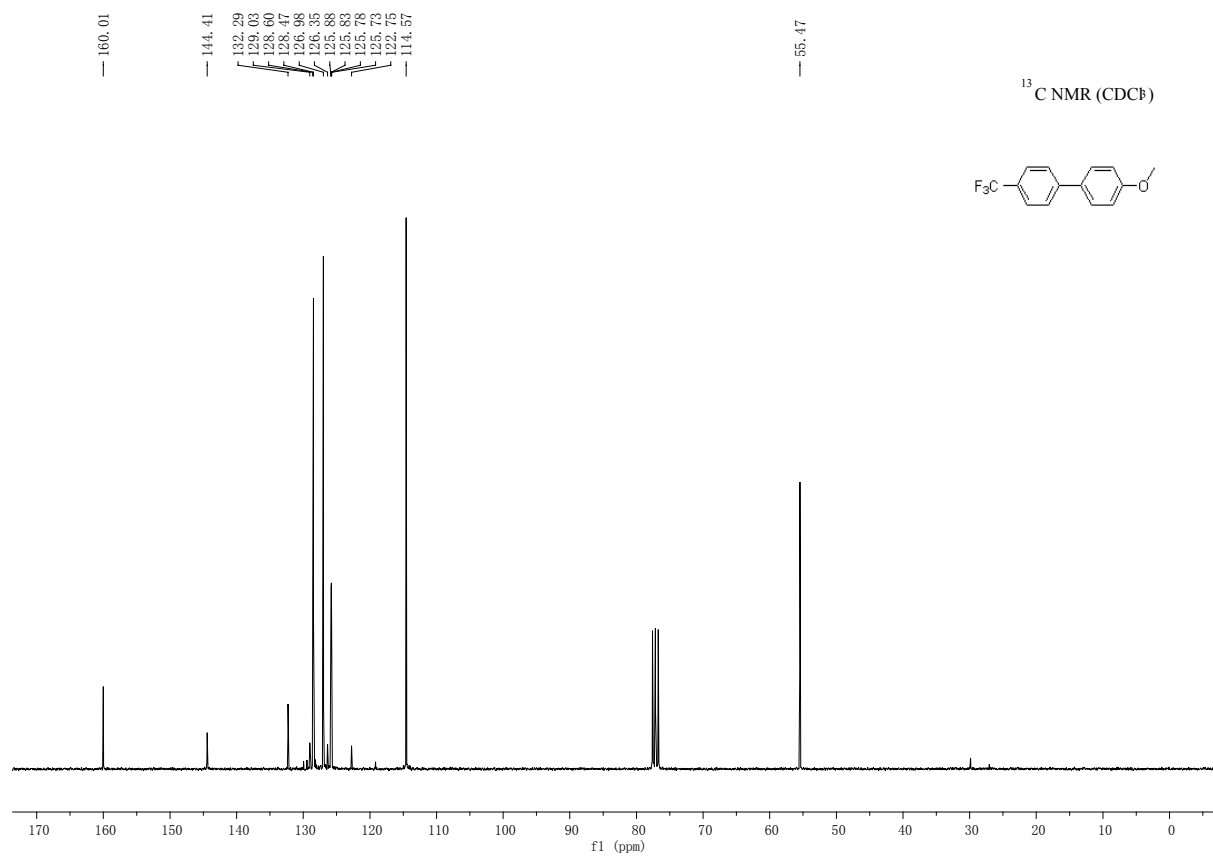
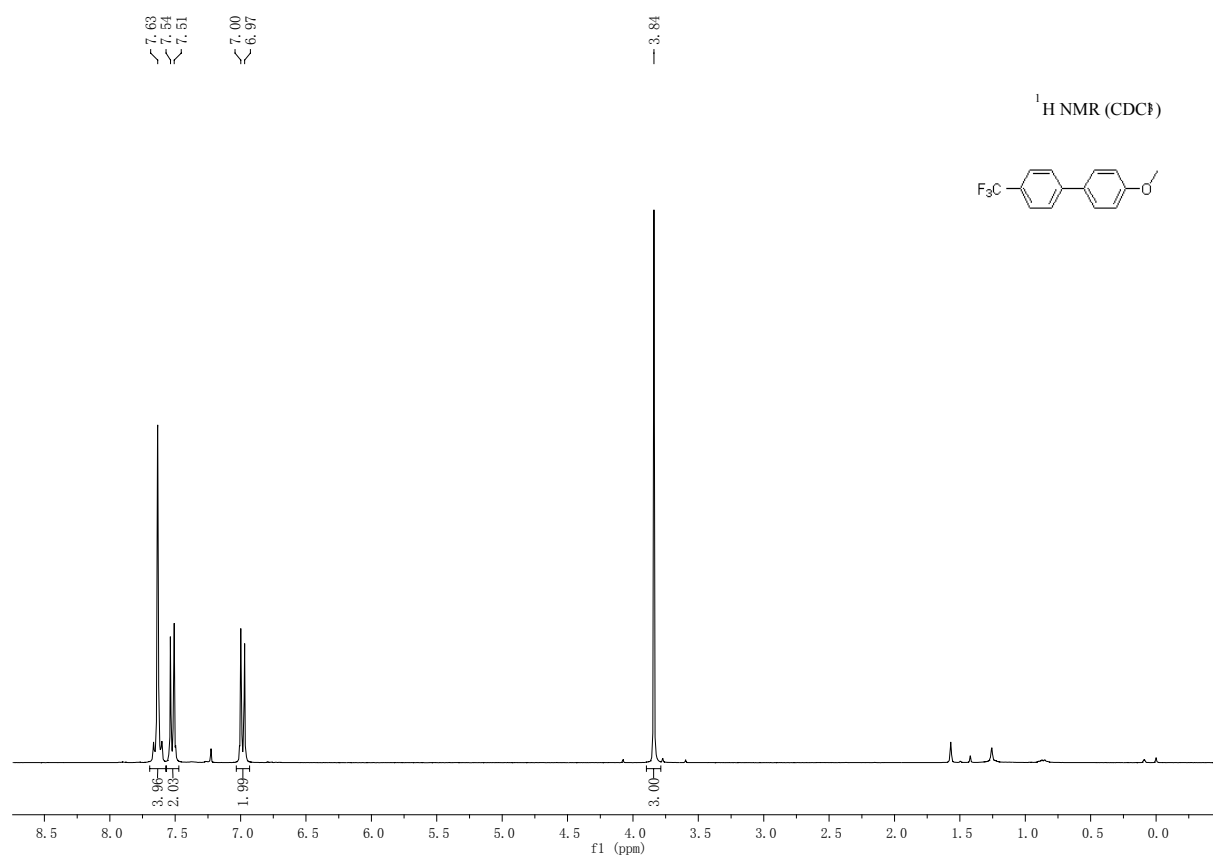
(16) Ethyl 4-[4-(trifluoromethyl)phenyl]benzoate



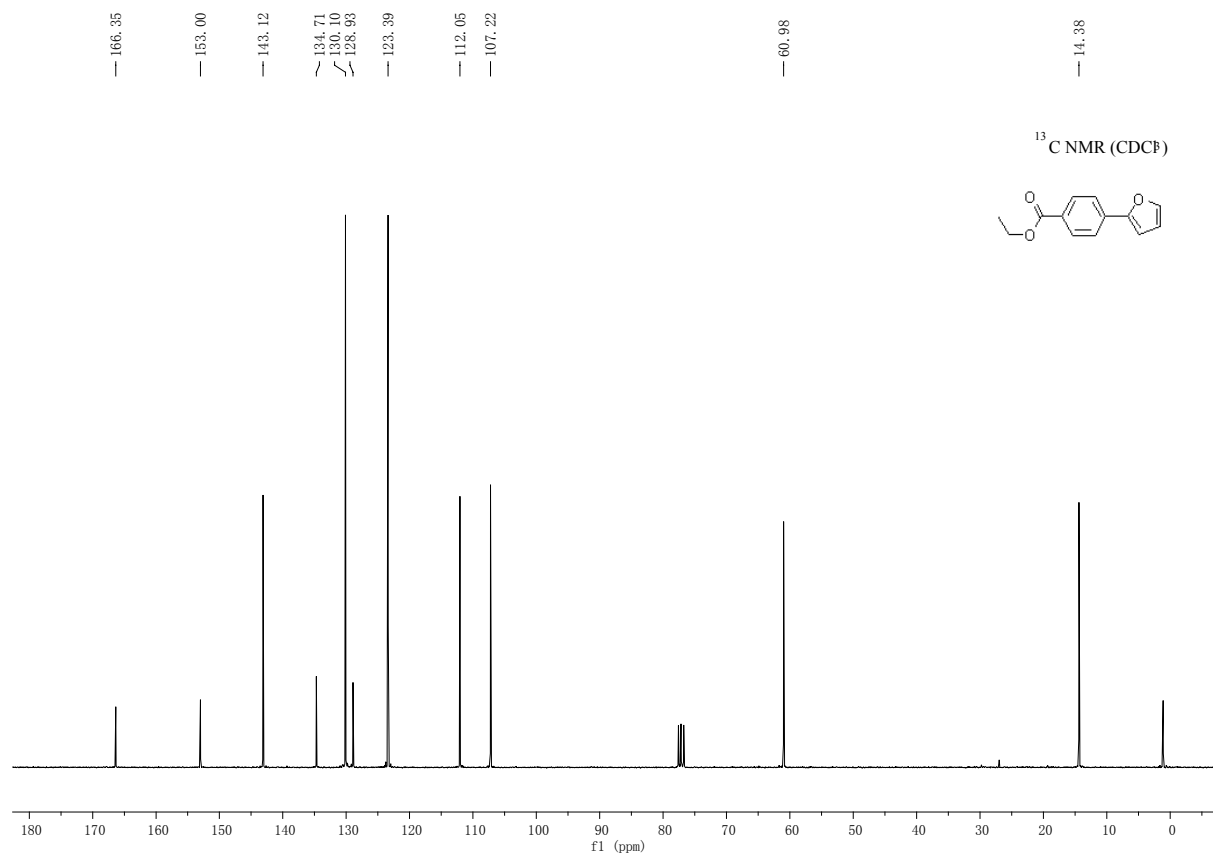
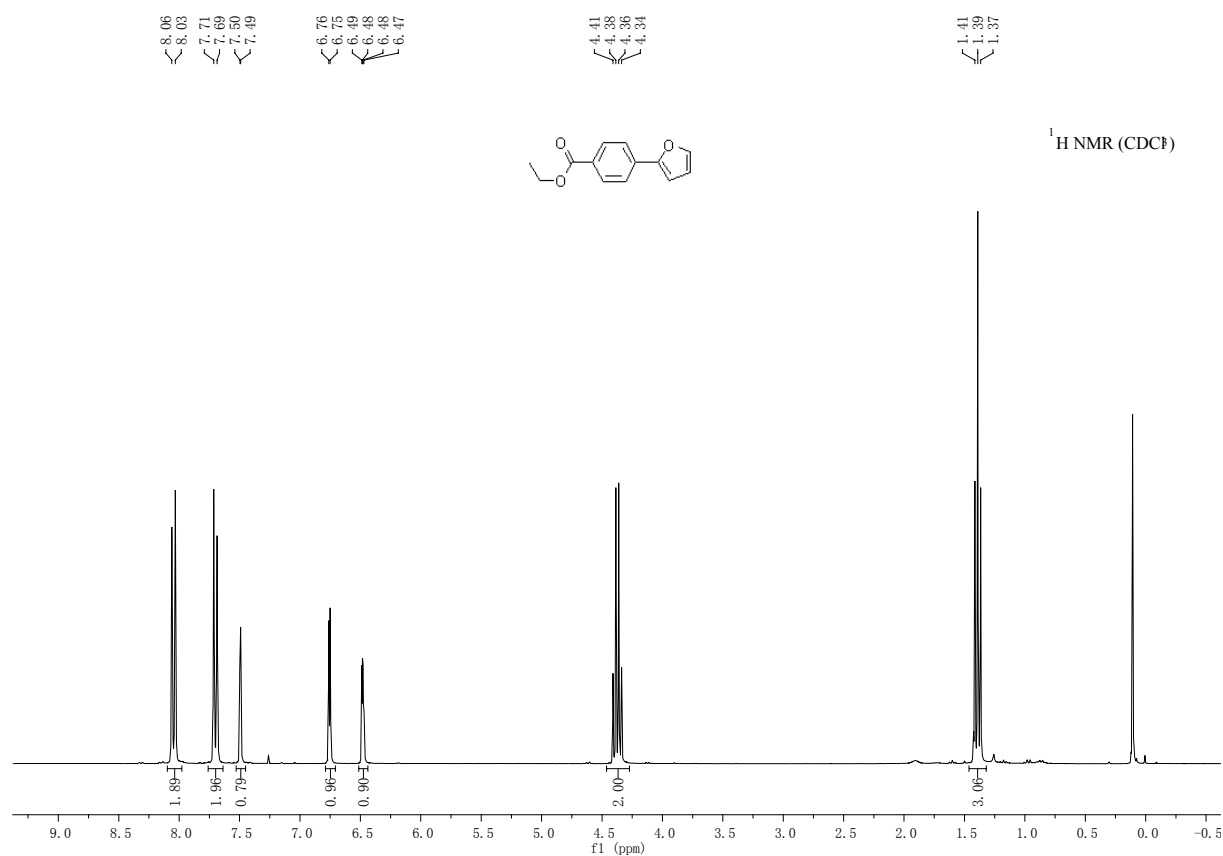
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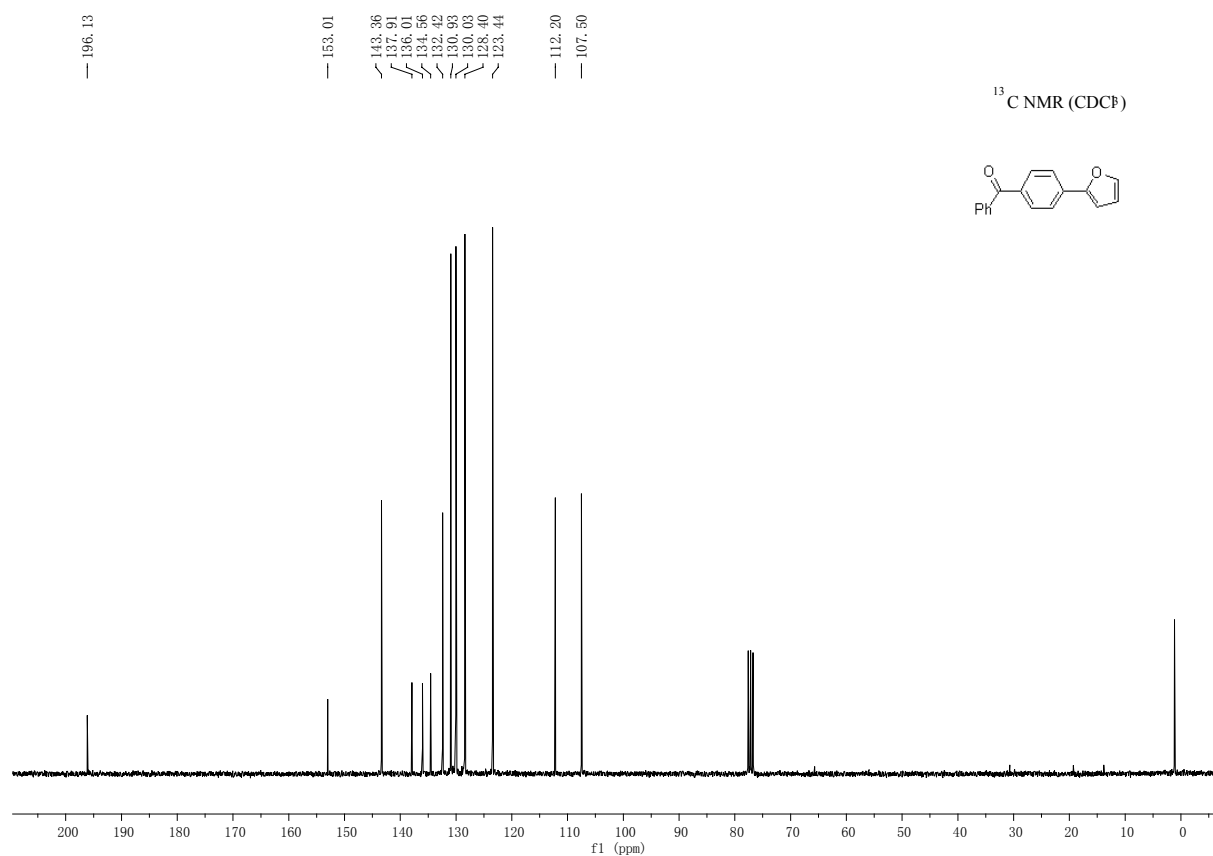
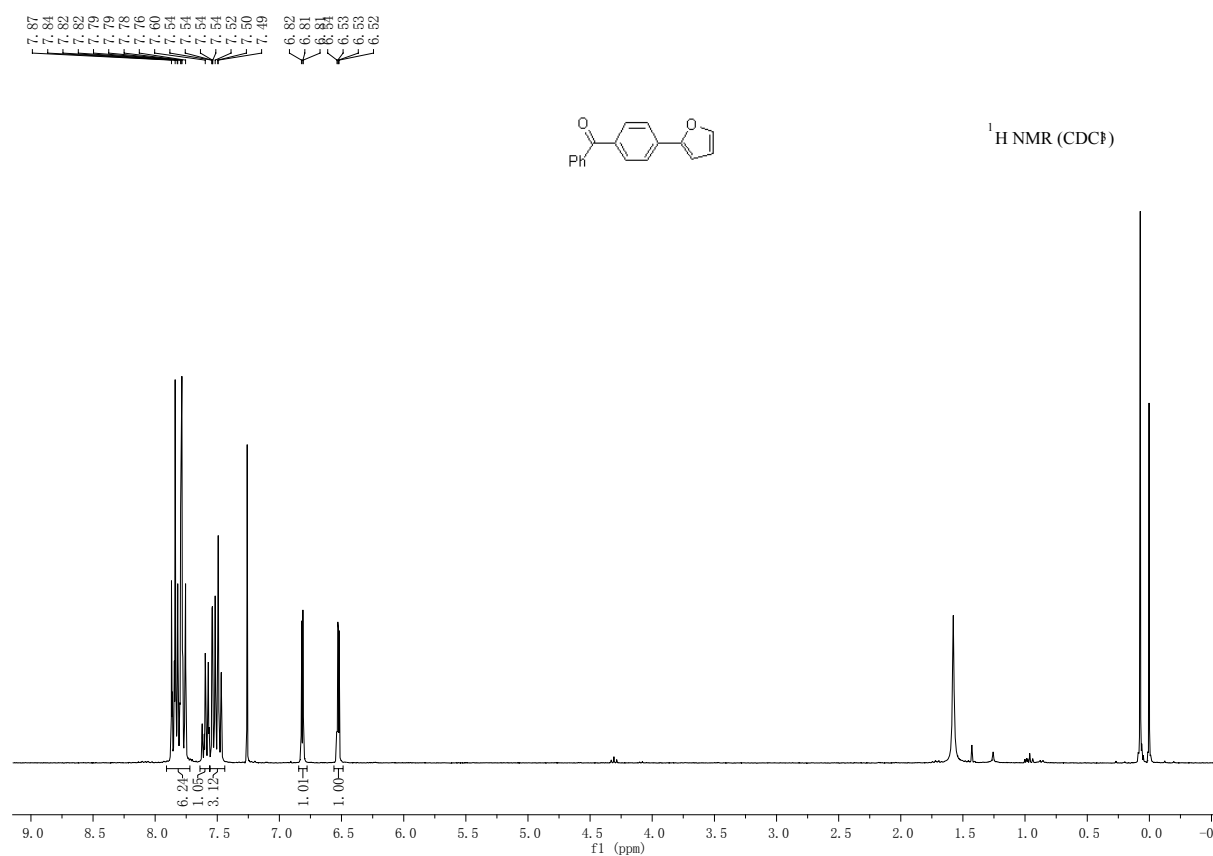
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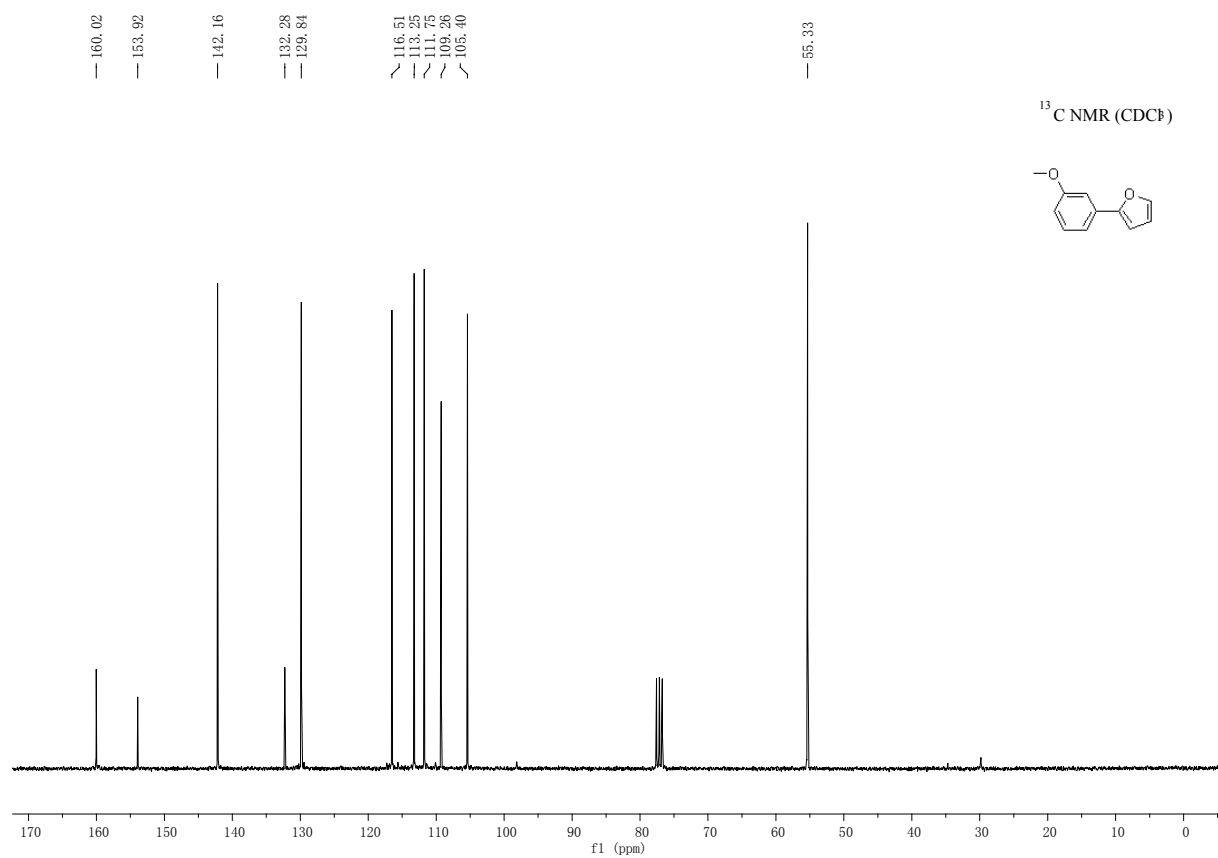
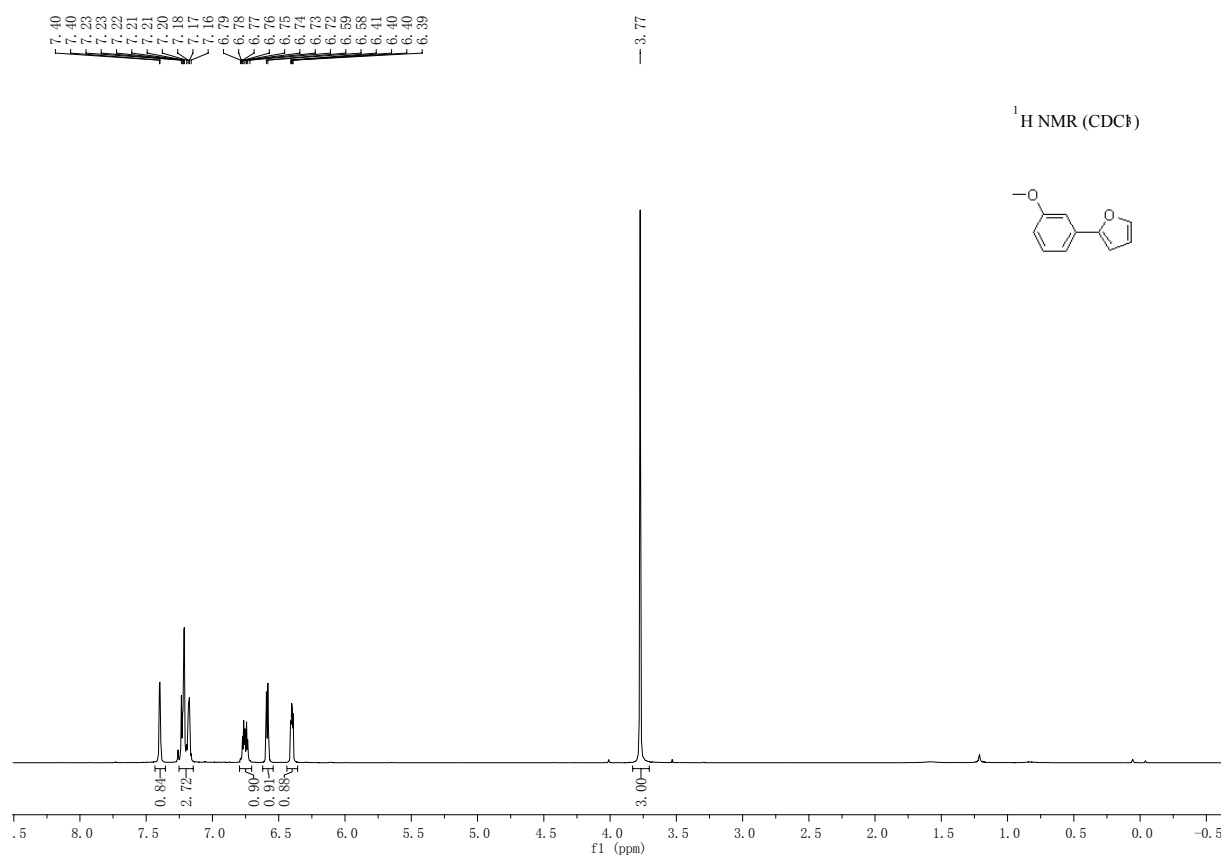
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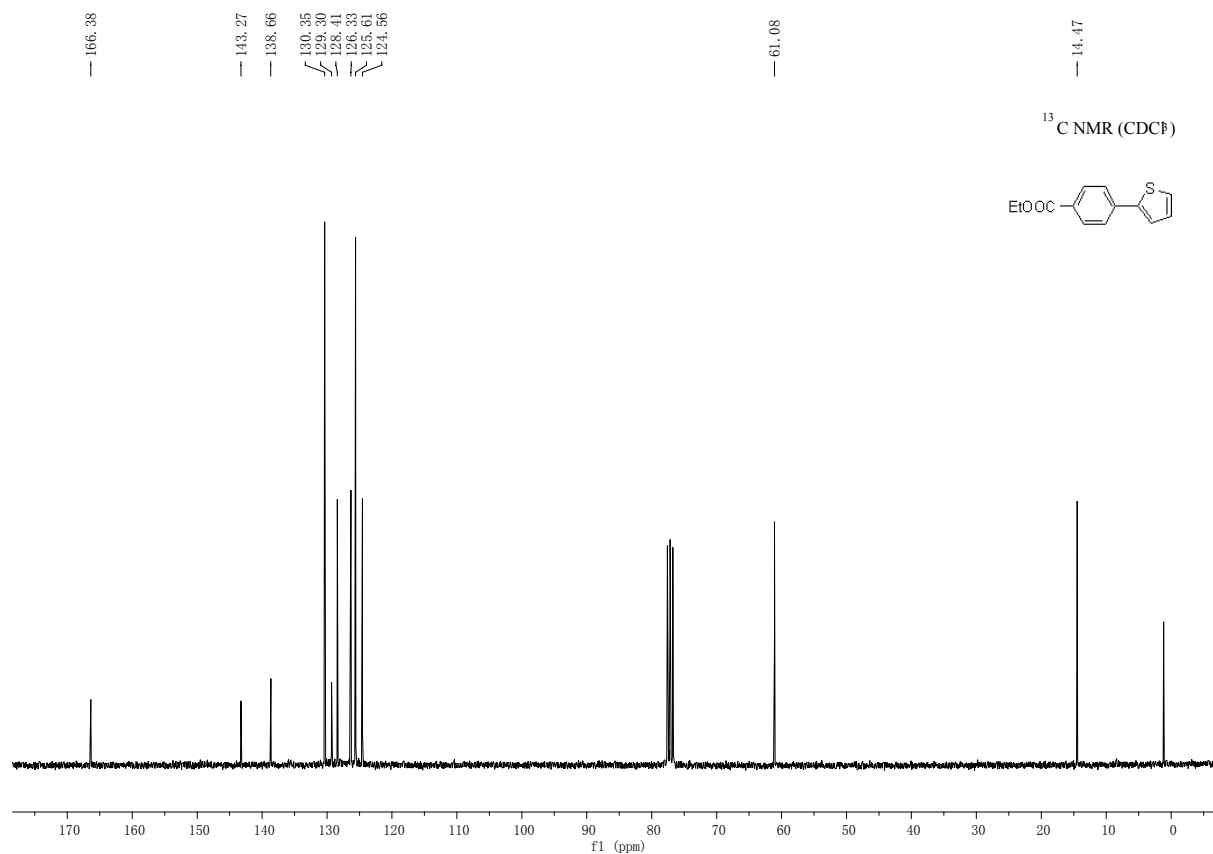
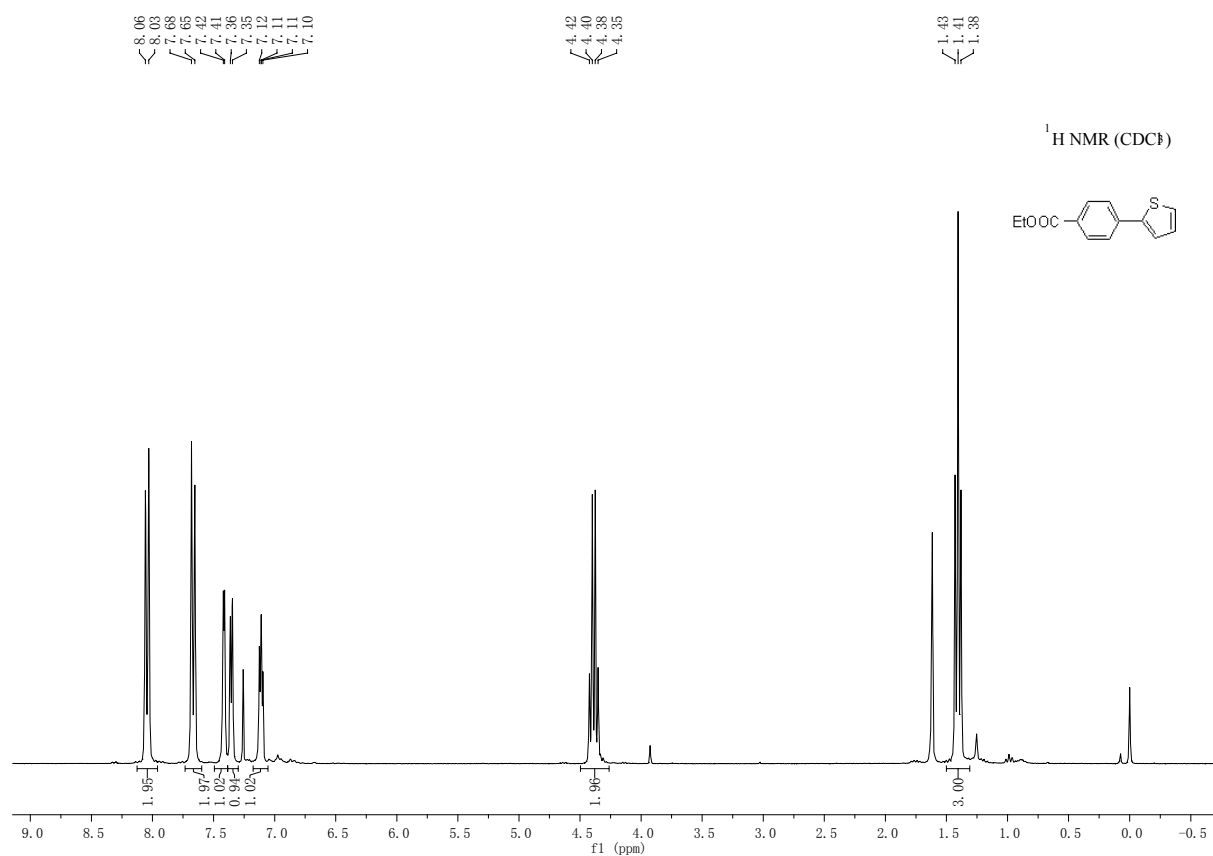
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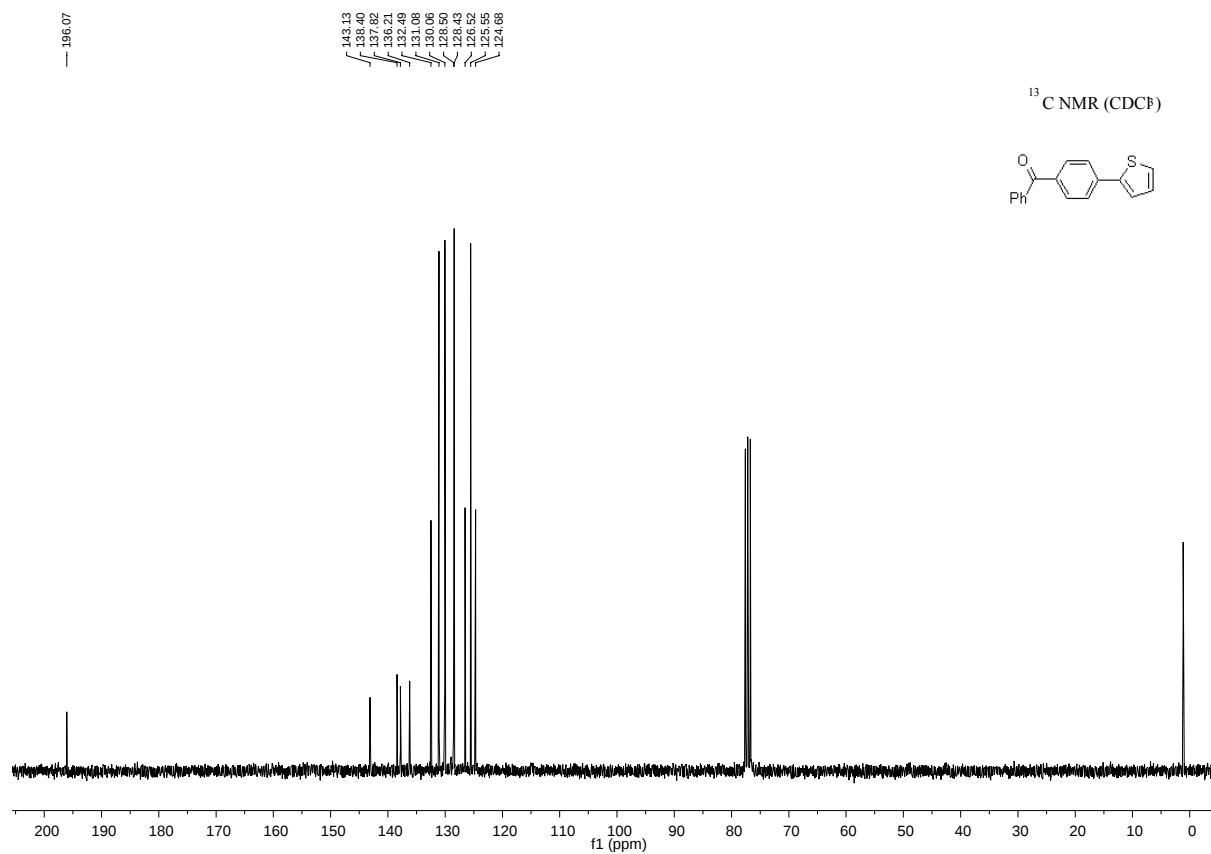
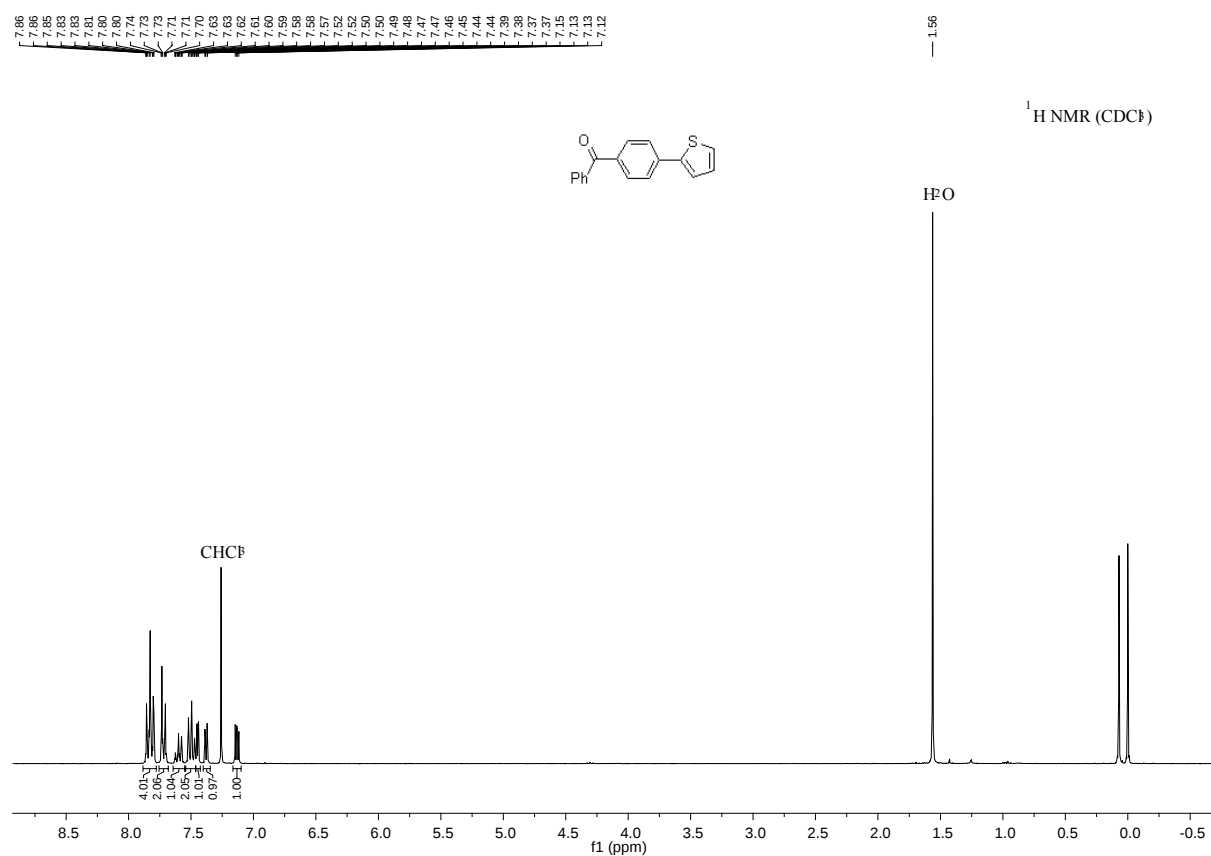
(21) 2-(3-Methoxyphenyl)furan



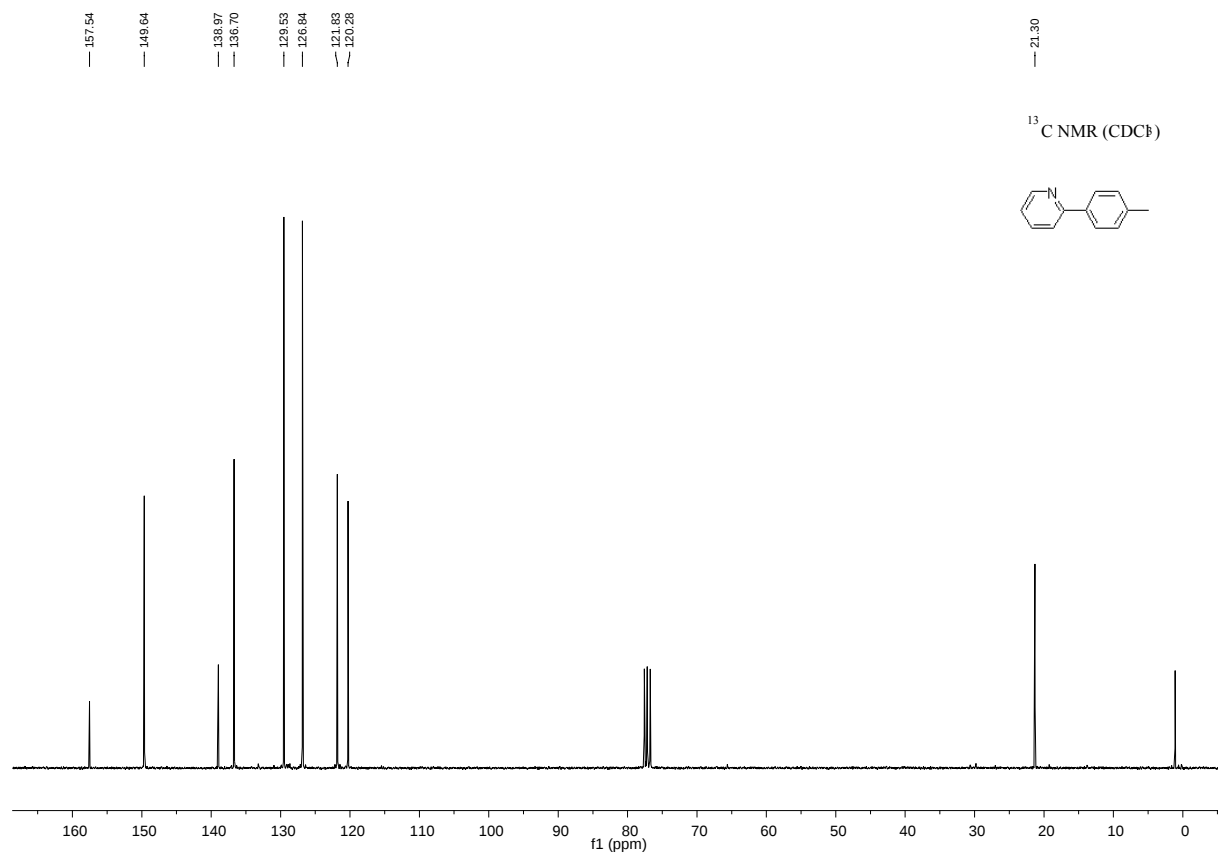
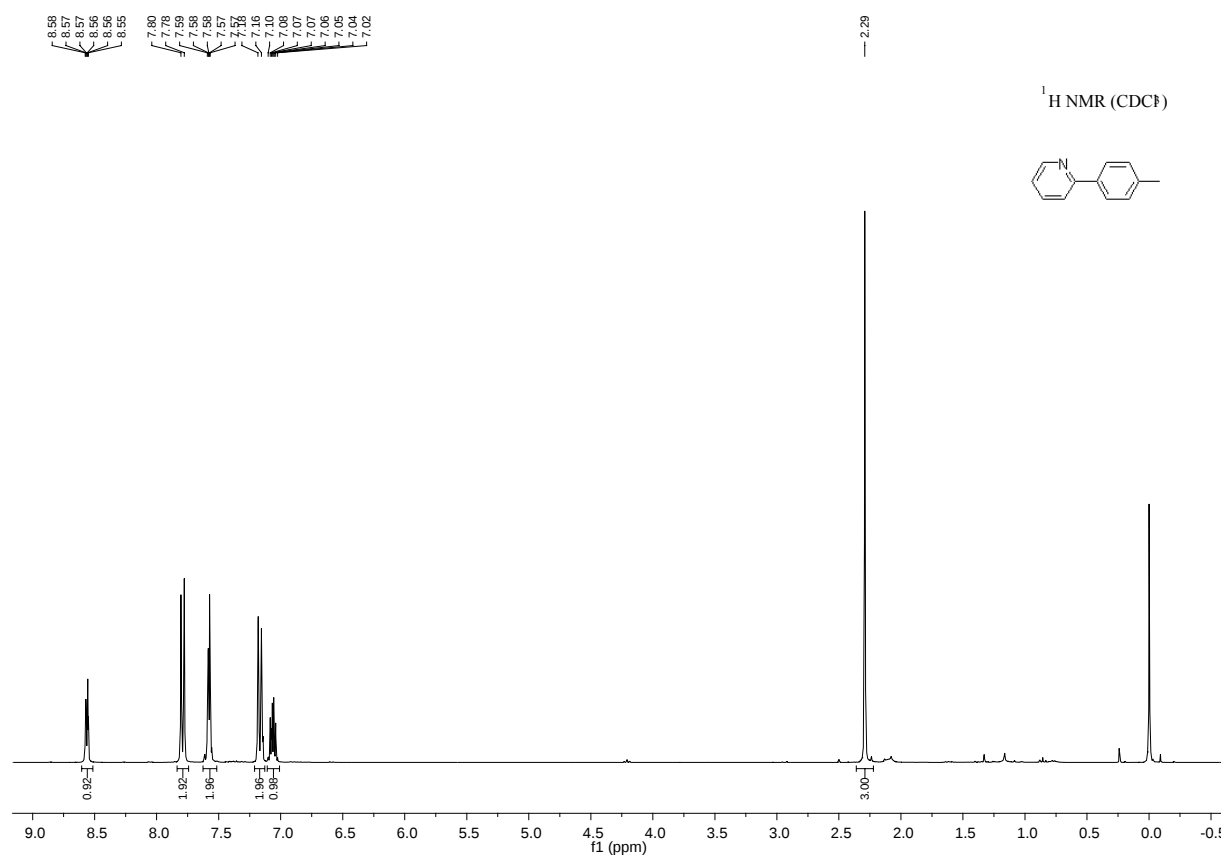
(22) 2-(4-Ethoxycarbonylphenyl)thiophene



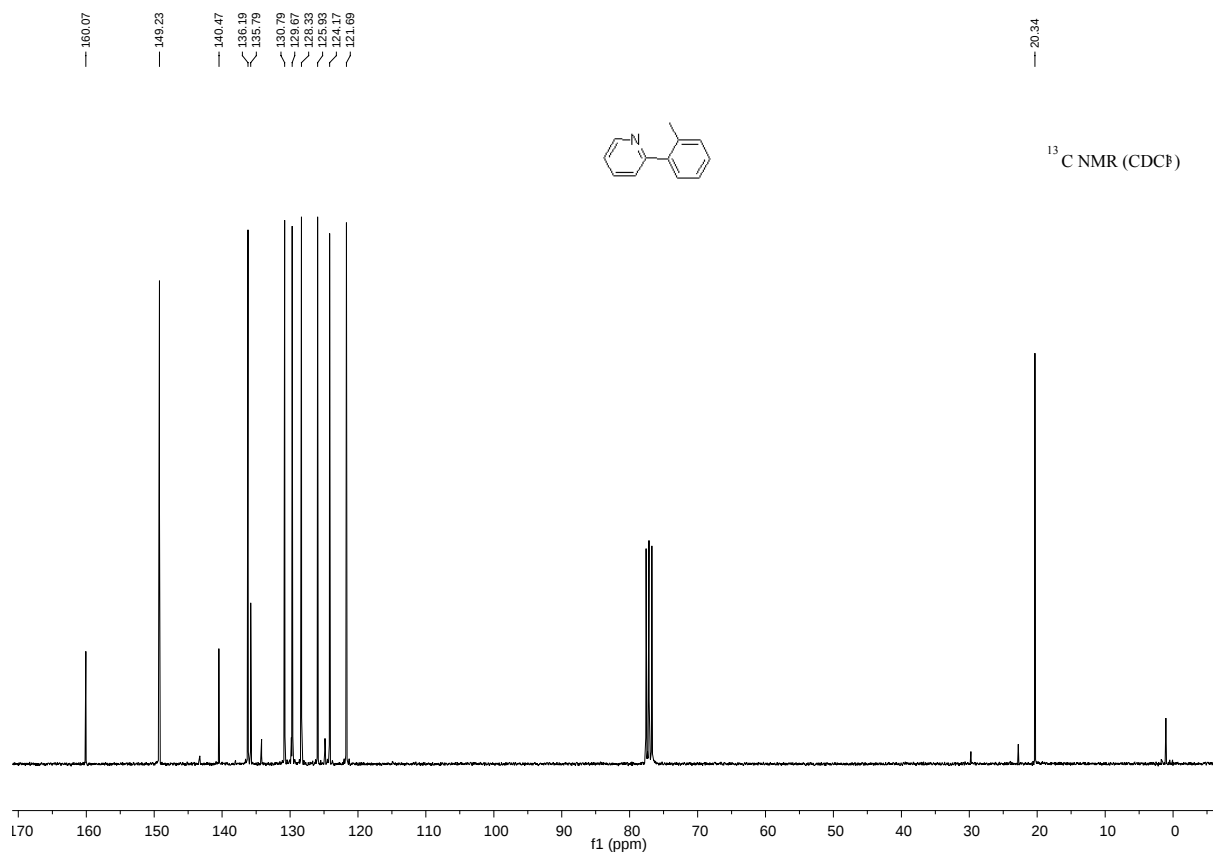
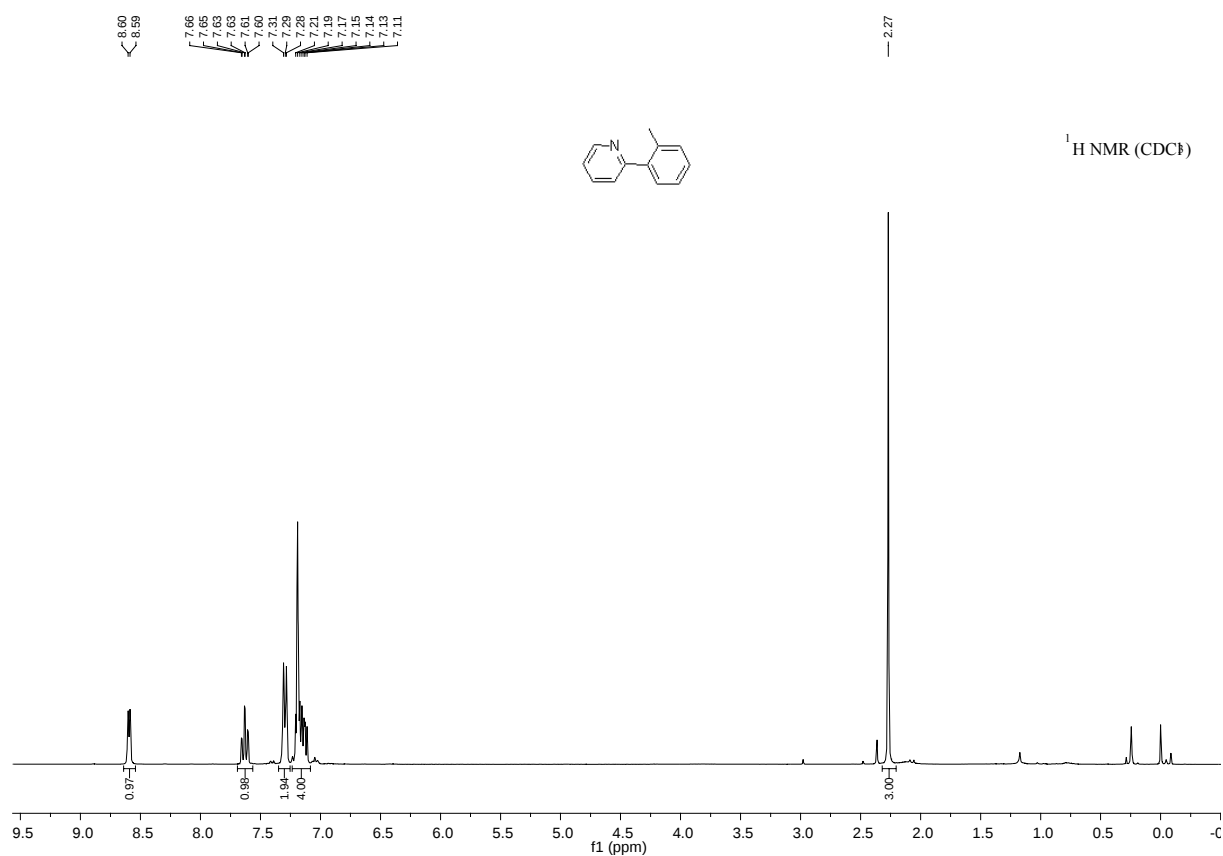
(23) Phenyl(4-(thiophen-2-yl)phenyl)methanone



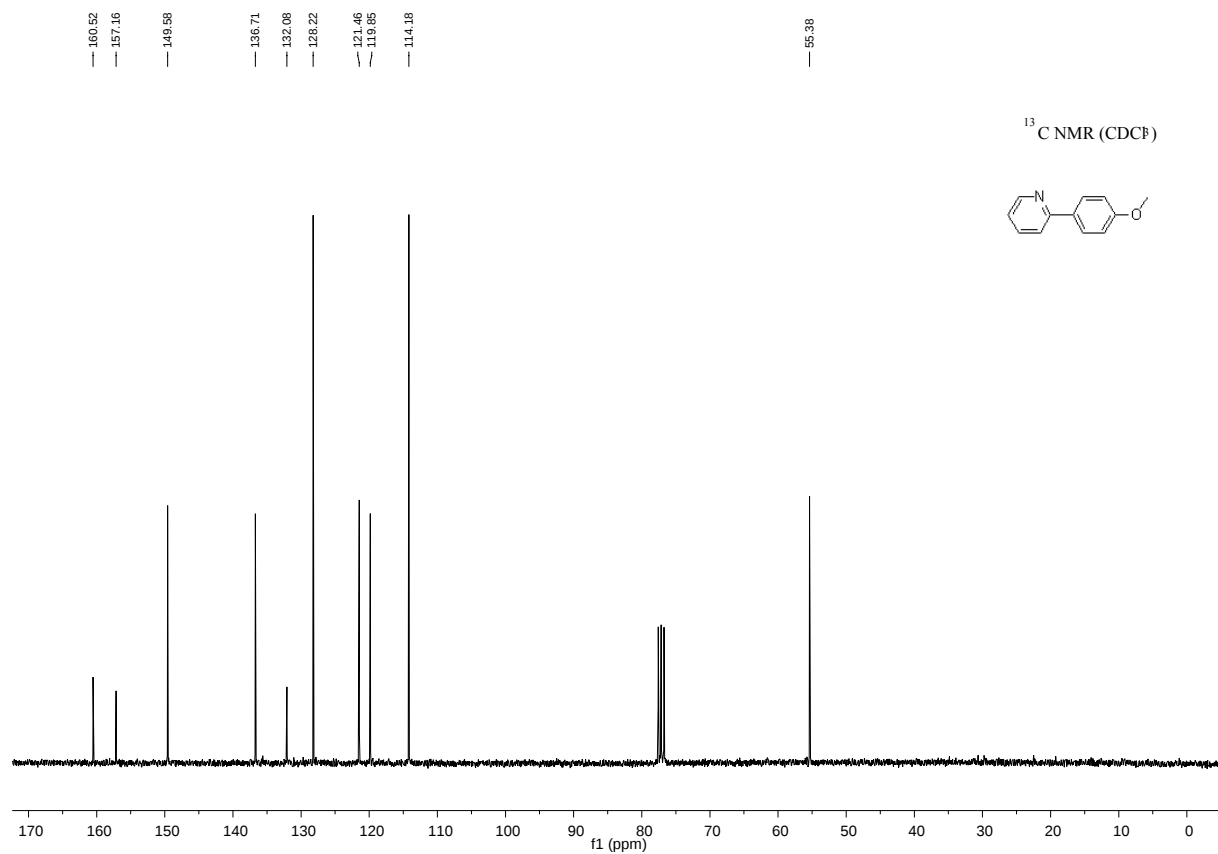
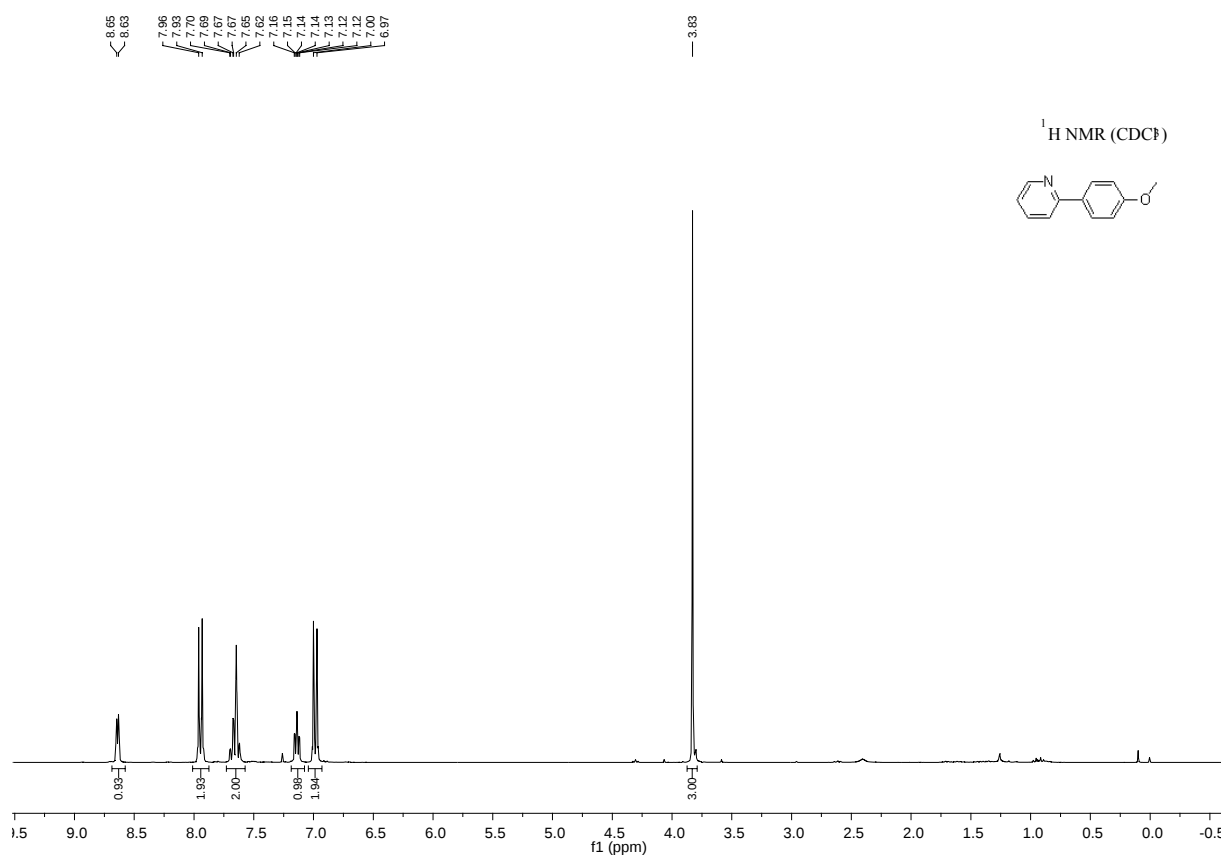
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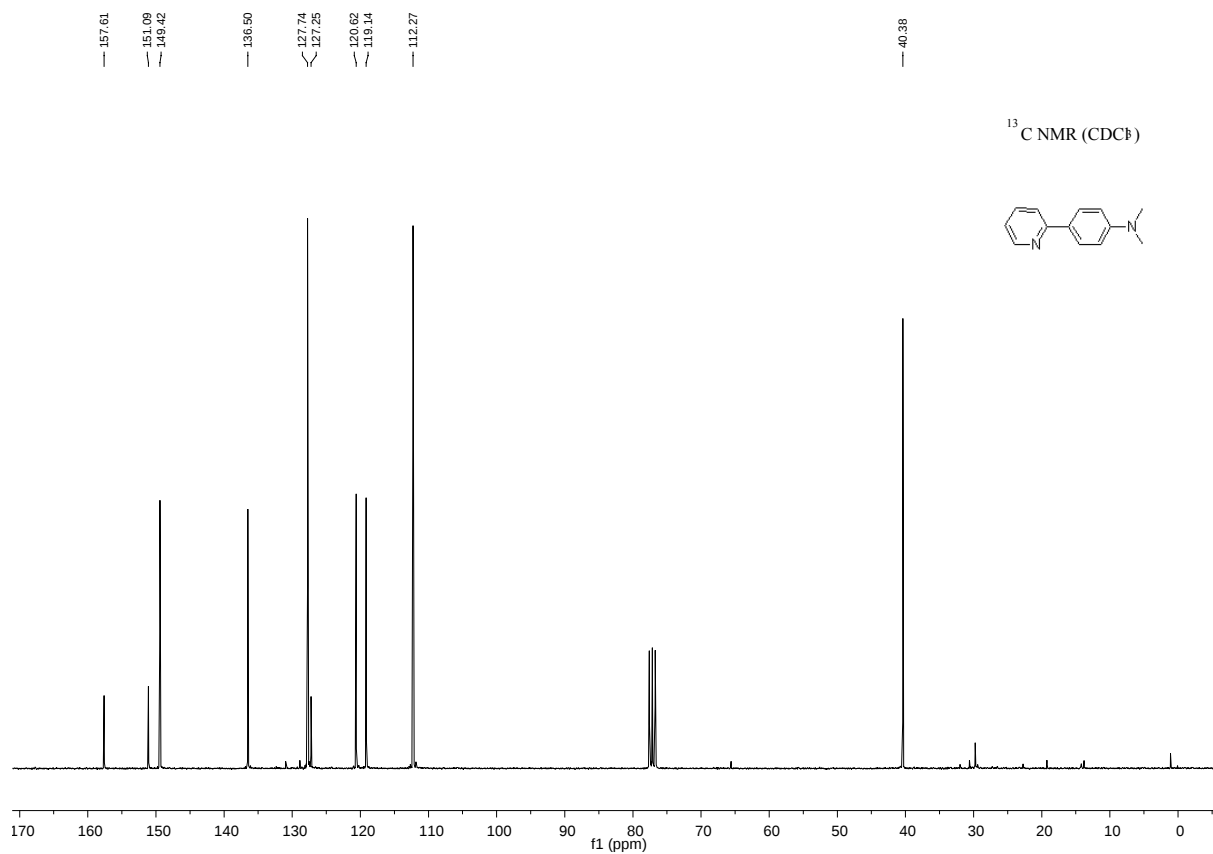
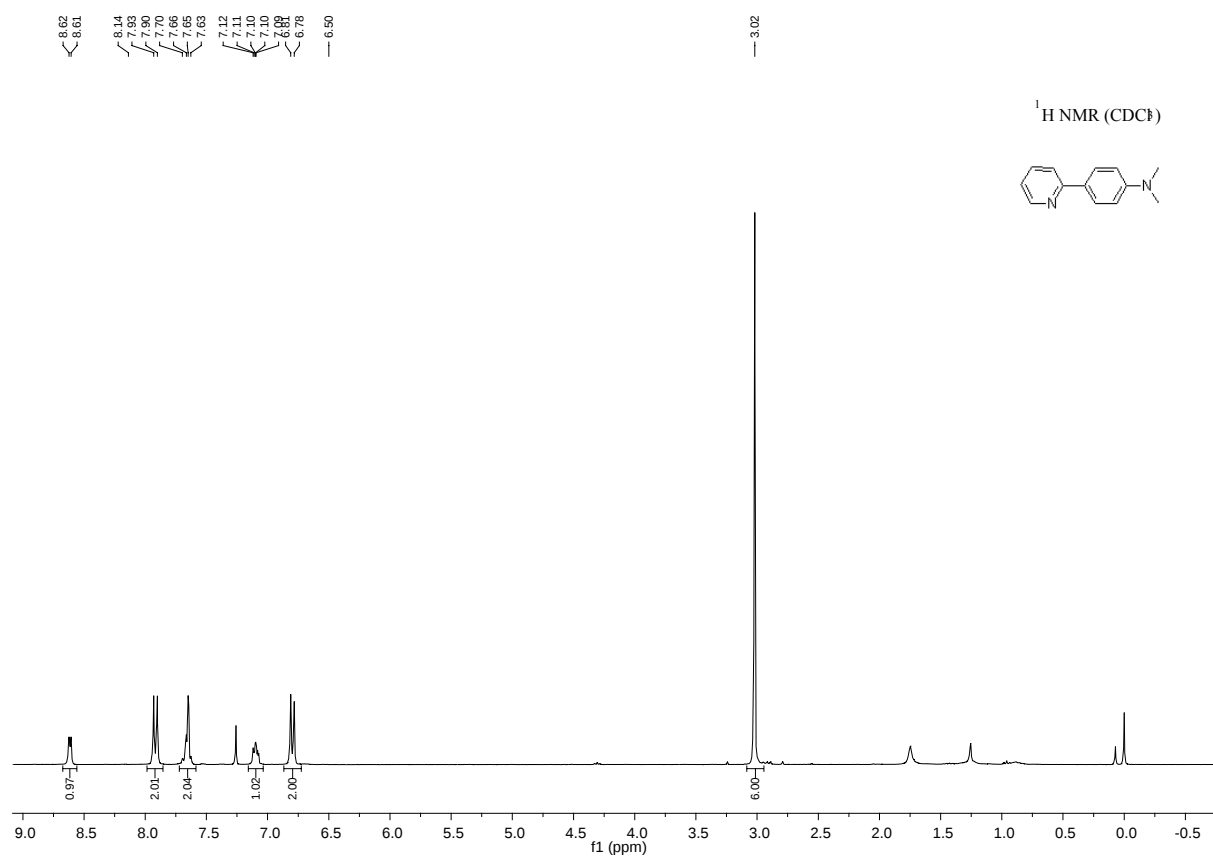
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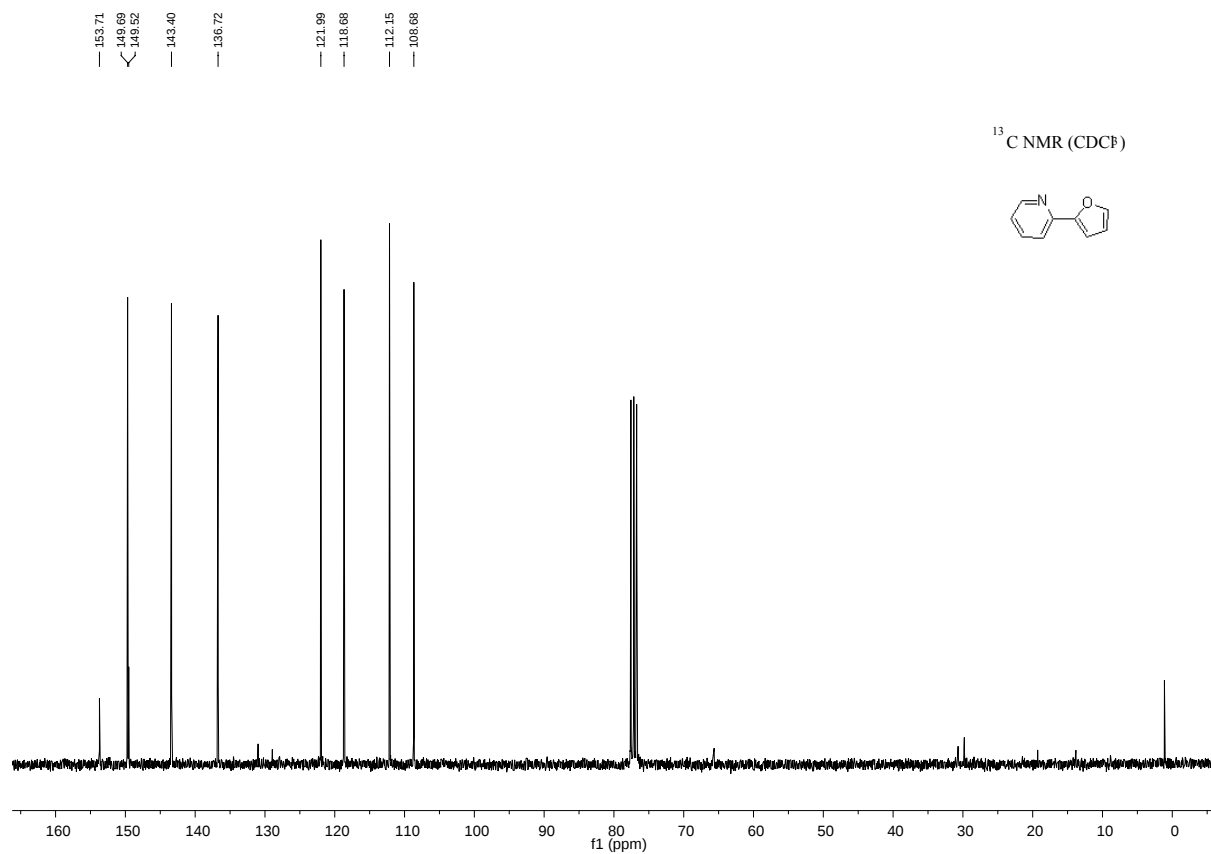
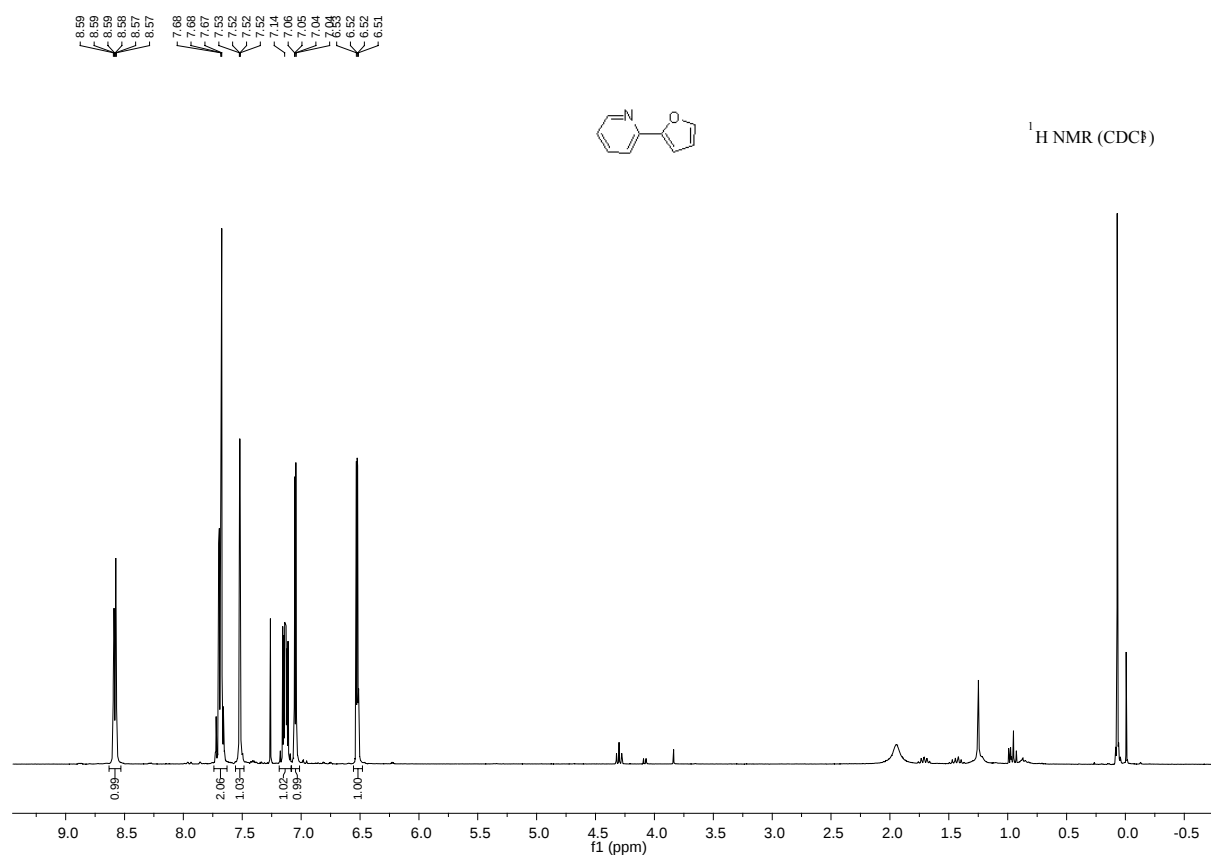
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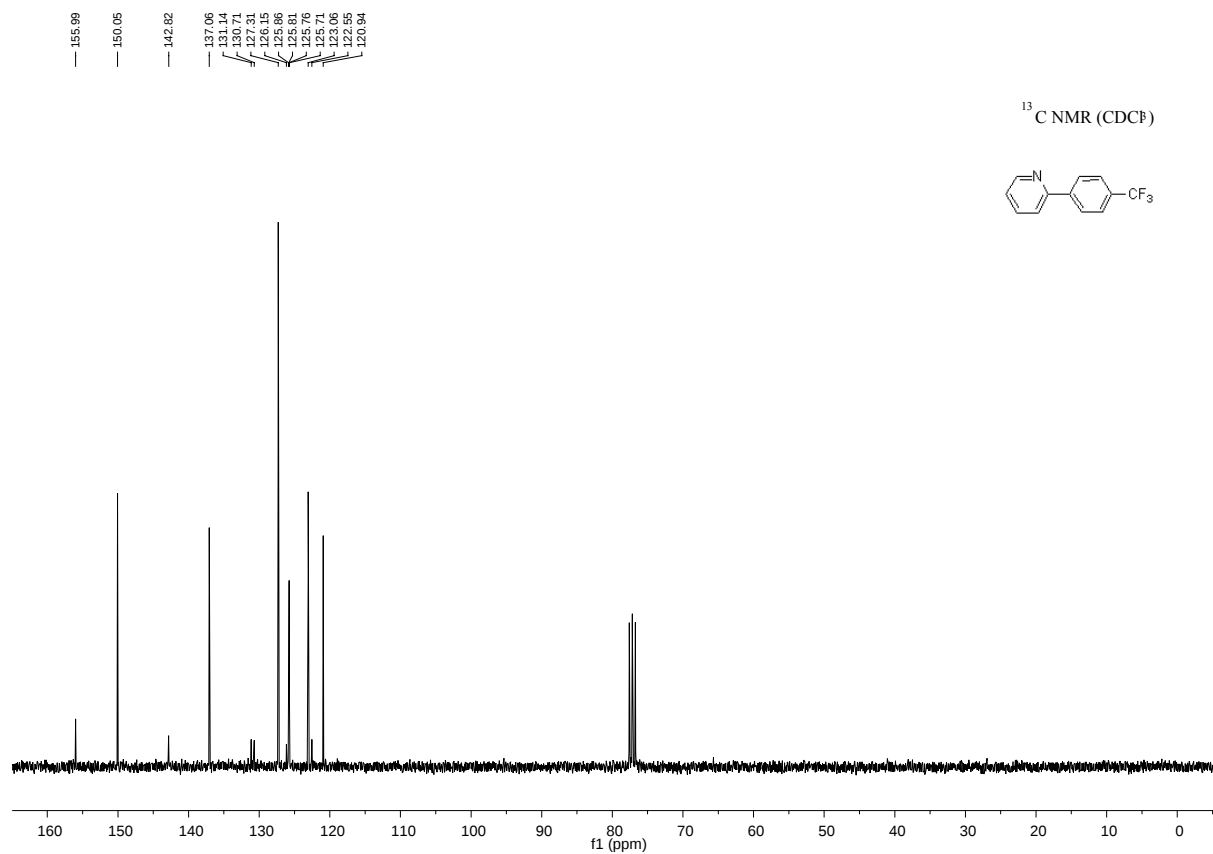
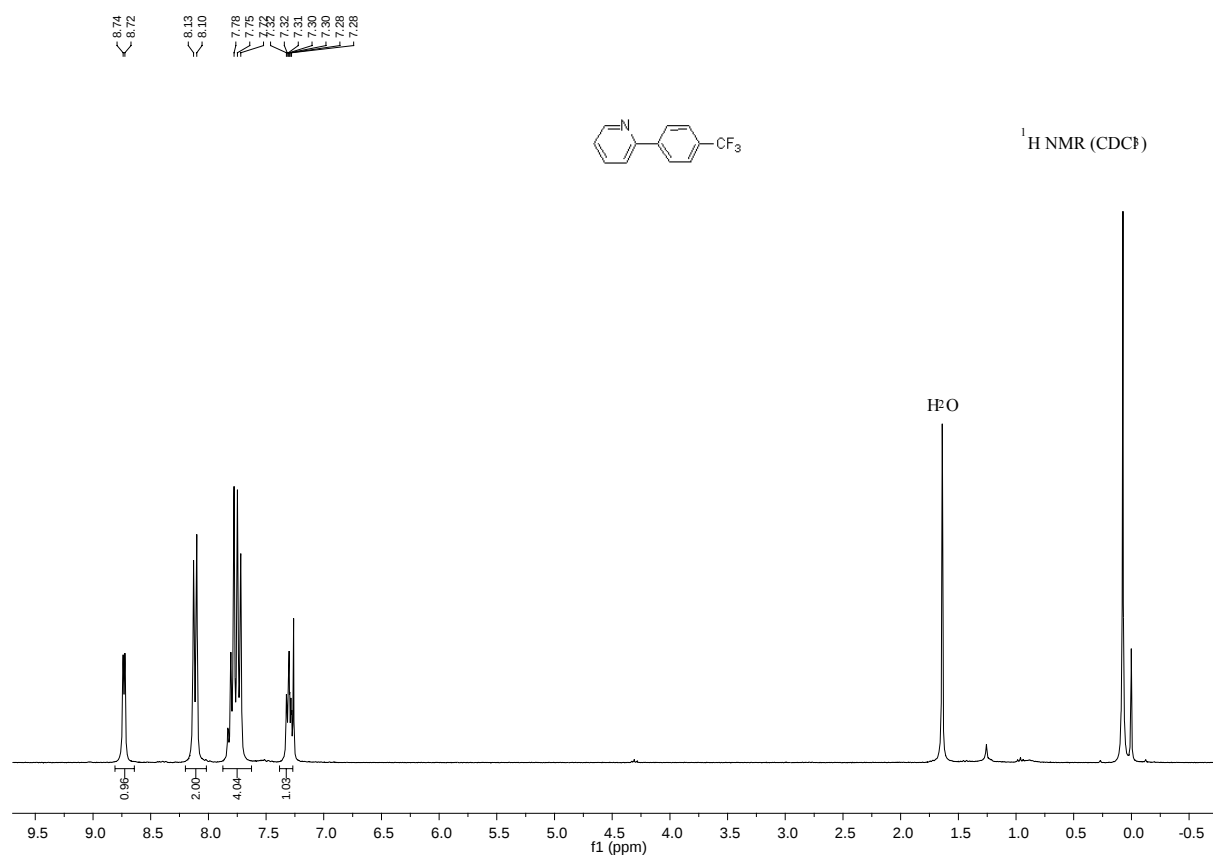
(27) *N,N*-Dimethyl-4-(pyridin-2-yl)benzenamine



(28) 2-(Furan-2-yl)pyridine



(29) 2-(4-(Trifluoromethyl)phenyl)pyridine



2-P(Ph)⁵H⁴NHC(Ph)=N⁶-MeC⁶H⁴)

¹H NMR (CDCl₃)

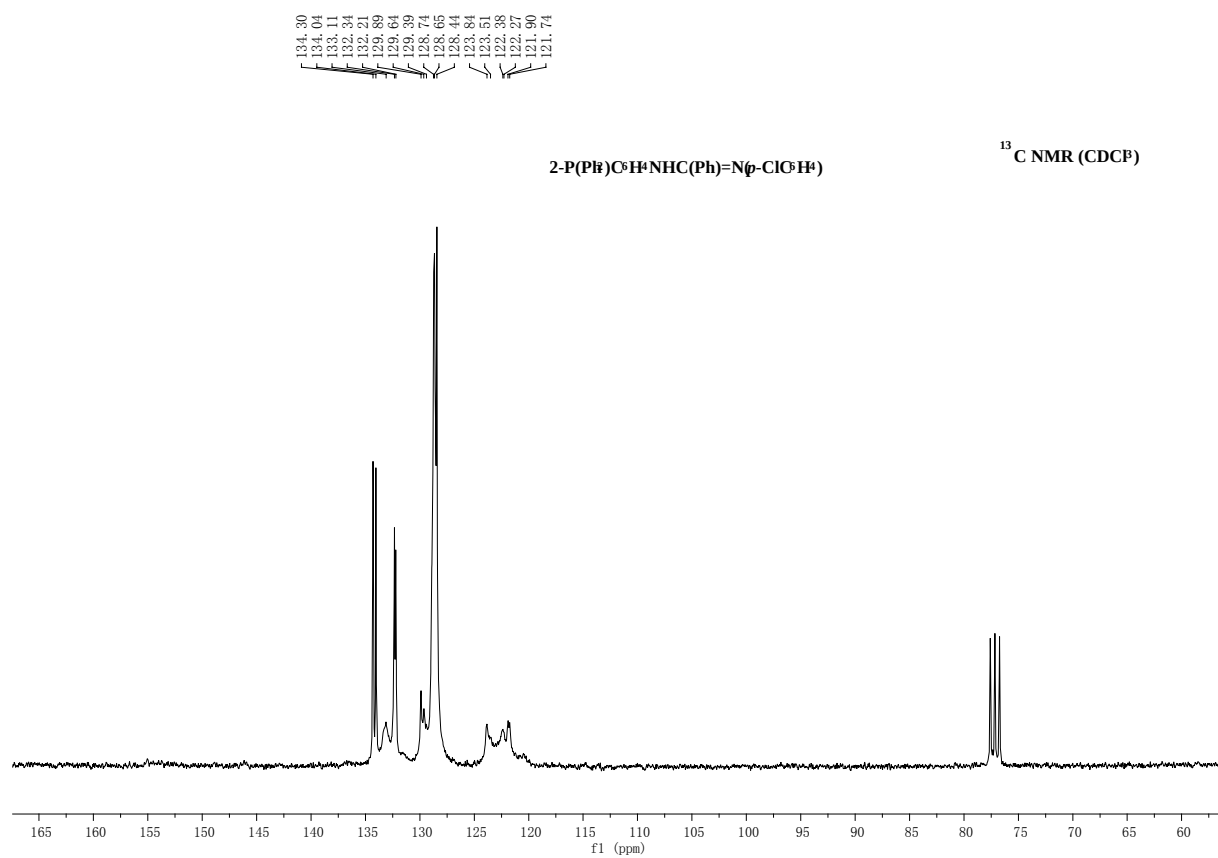
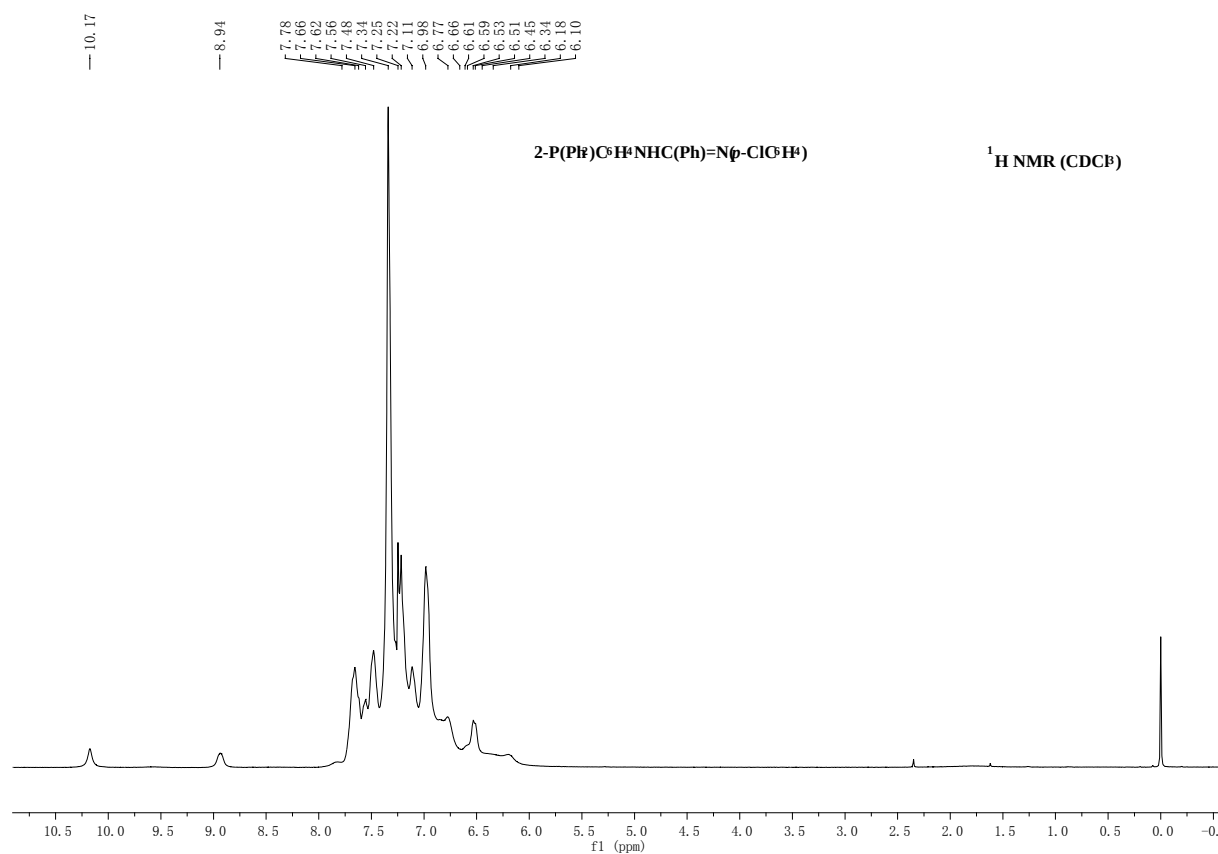
Chemical structure: Cc1ccc(cc1)/N=C(c2ccccc2)Nc3ccccc3P(c4ccccc4)c5ccccc5

¹H NMR (CDCl₃) spectrum showing chemical shifts (ppm) and integration values:

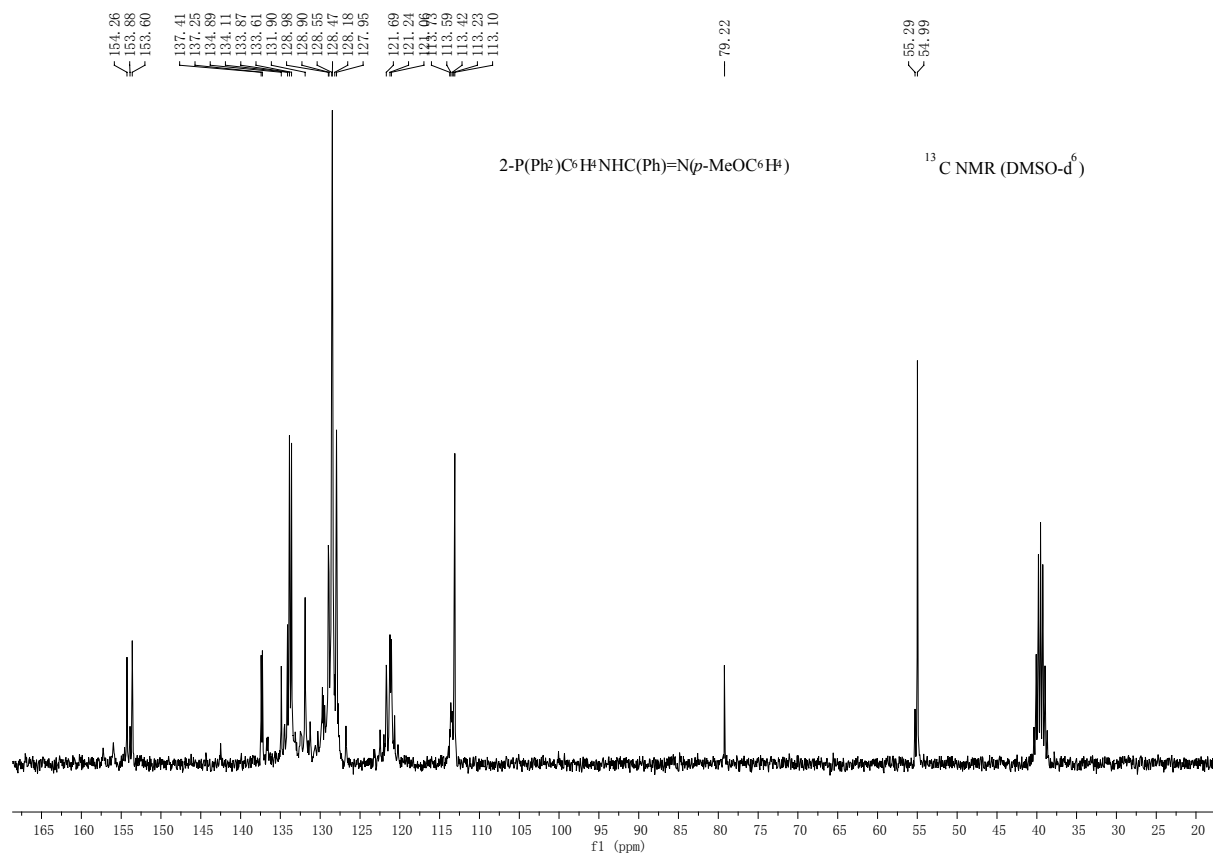
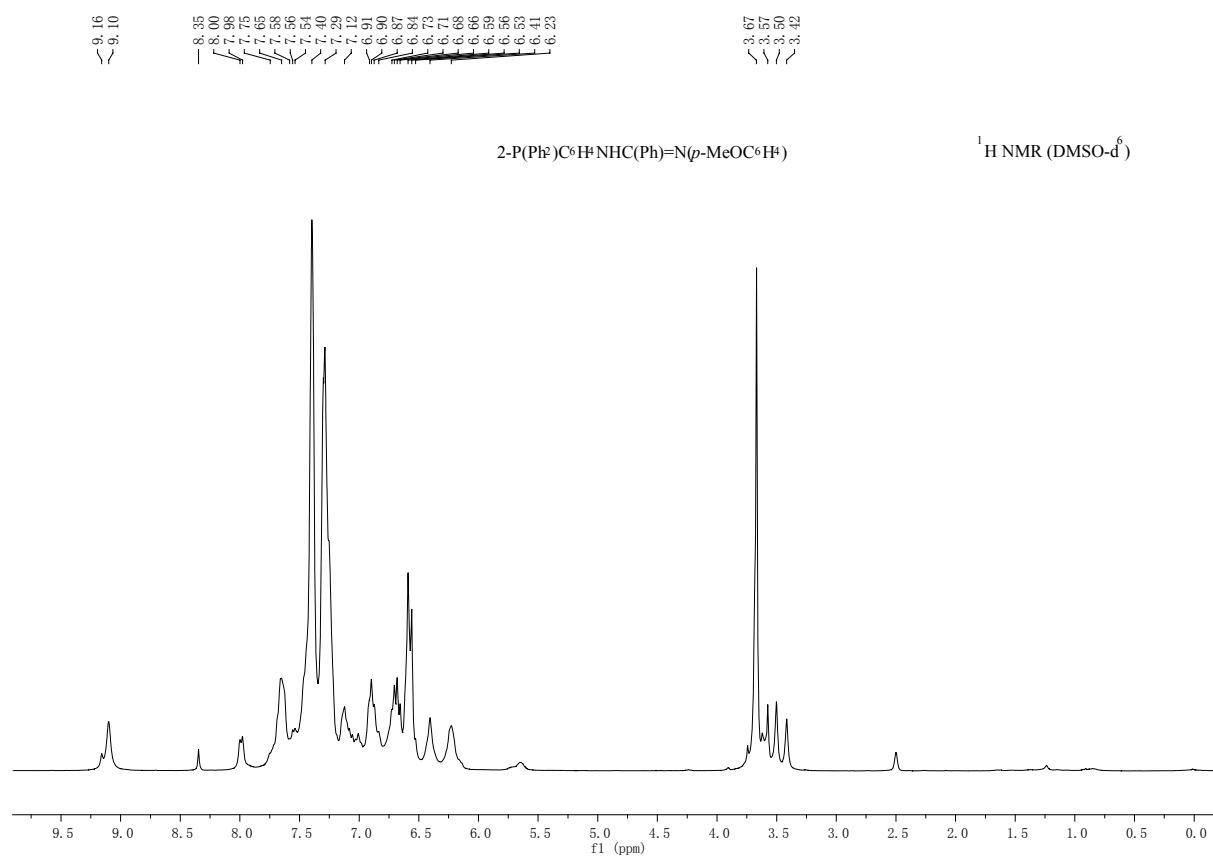
Chemical Shift (ppm)	Integration
7.88	0.88
7.87	0.87
7.31	0.31
7.25	0.25
7.05	0.05
7.03	0.03
6.98	0.98
6.96	0.96
6.92	0.92
6.89	0.89
6.75	0.75
6.73	0.73
6.67	0.67
6.65	0.65
6.60	0.60
6.58	0.58
2.35	0.35
2.23	0.23
2.15	0.15
2.06	0.06

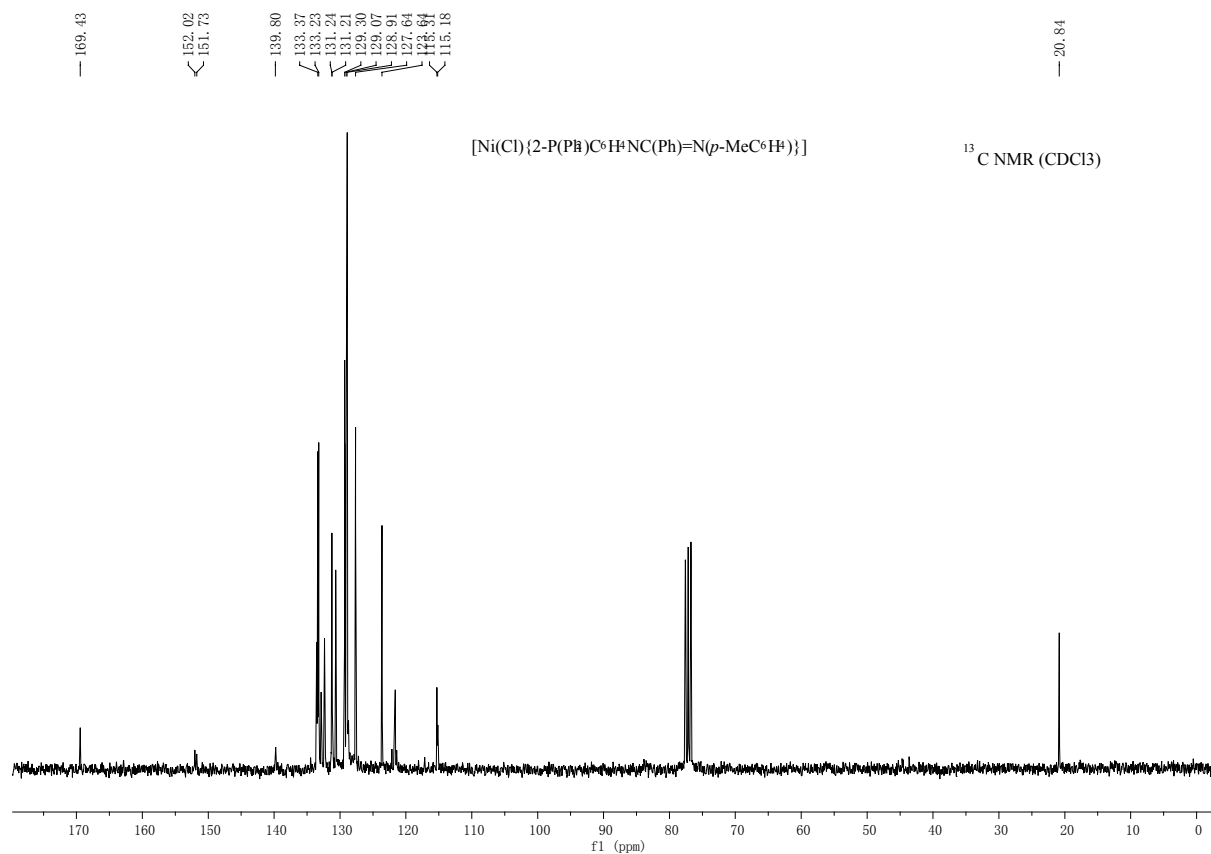
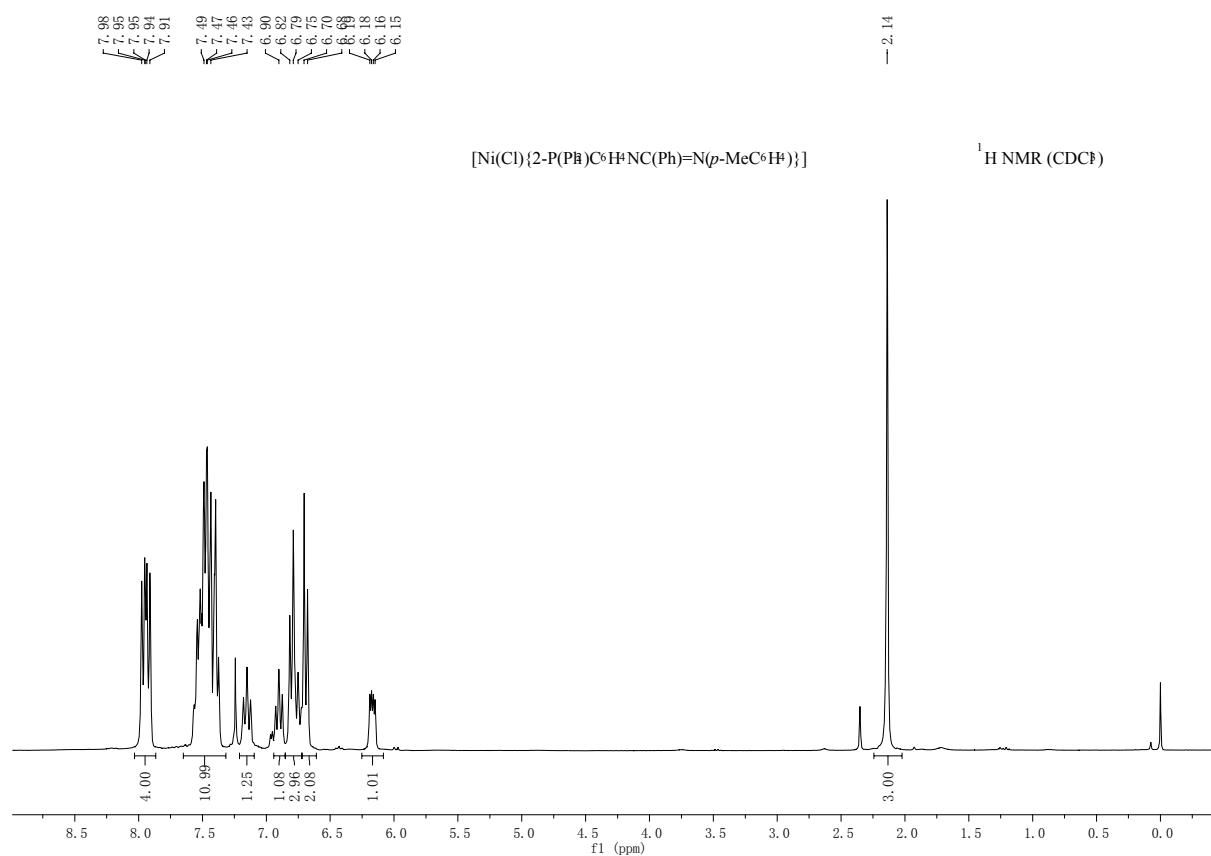


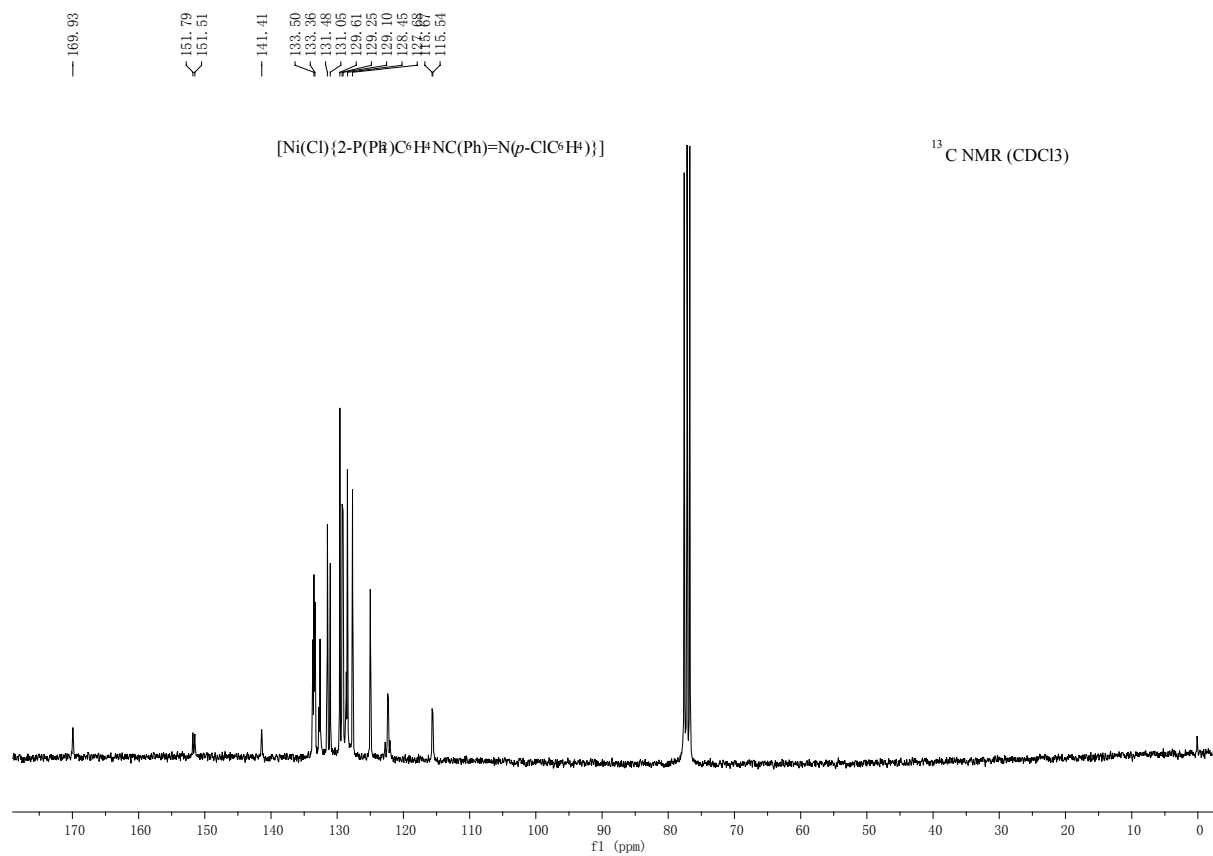
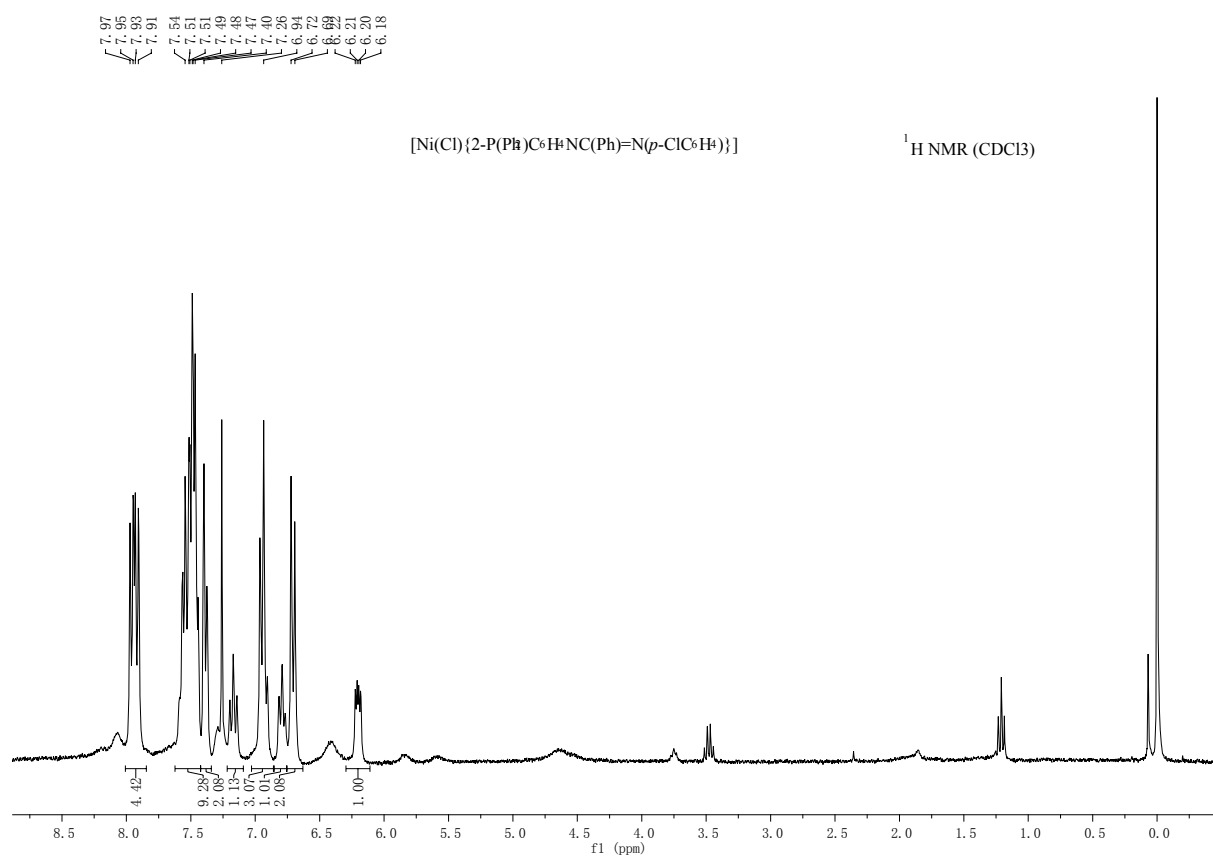
2-P(Ph₂)C₆H₄NHC(Ph)=N(*p*-ClC₆H₄) (2)

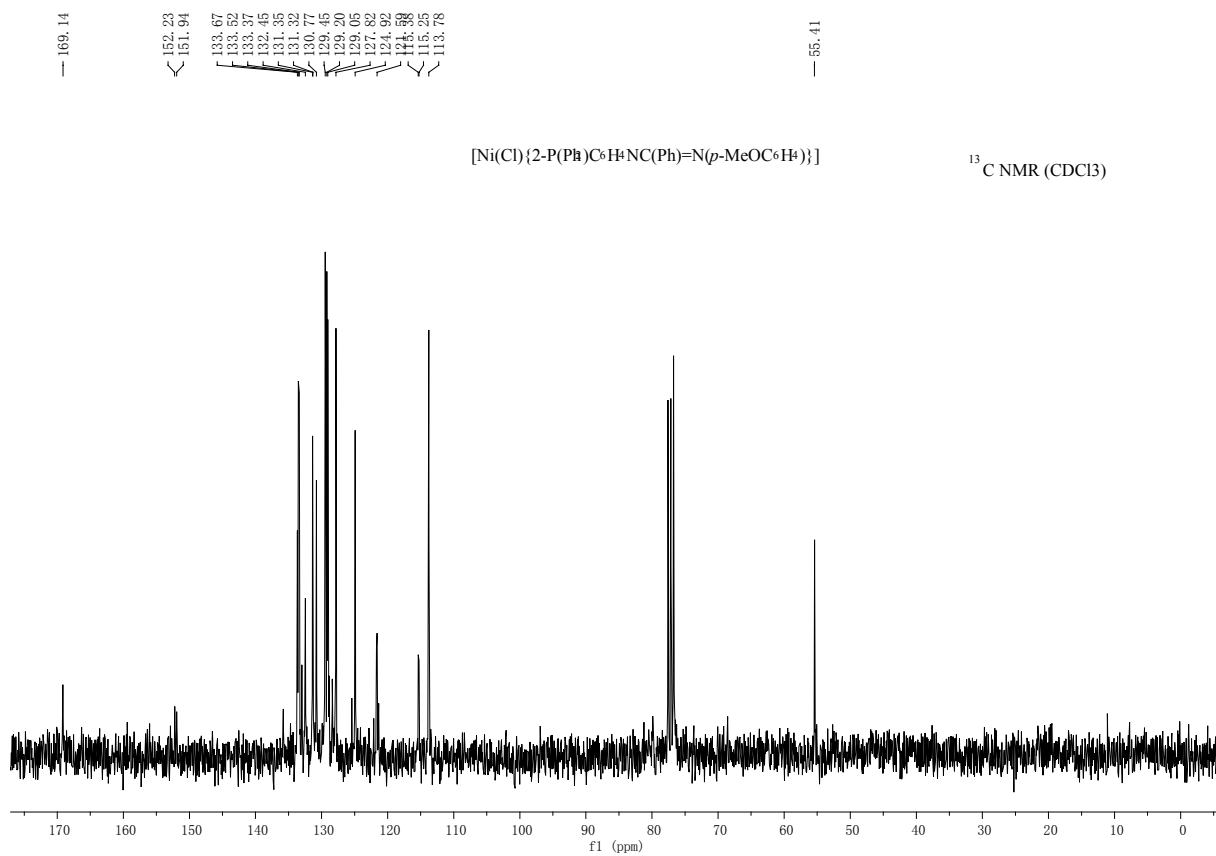
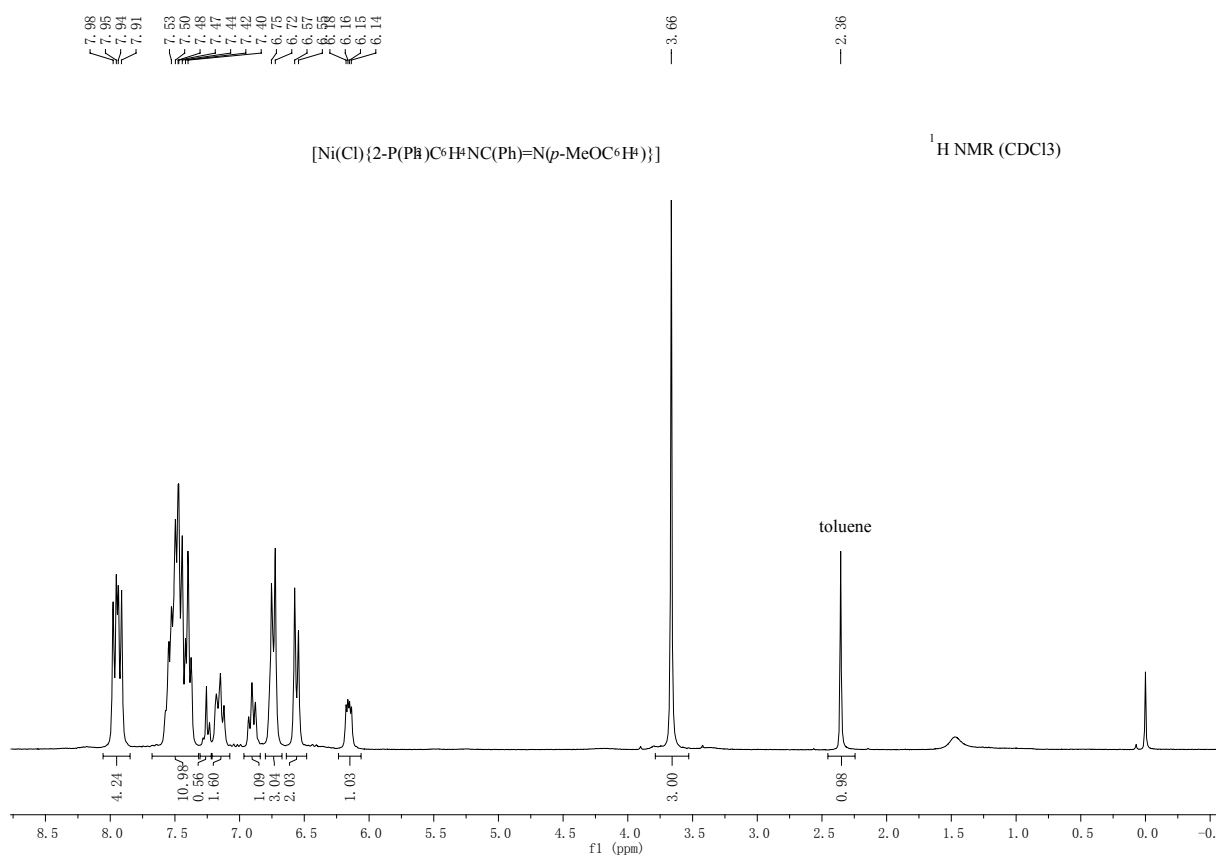
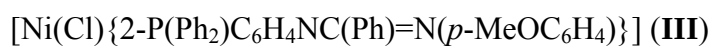


2-P(Ph₂)C₆H₄NHC(Ph)=N(*p*-MeOC₆H₄) (**3**)

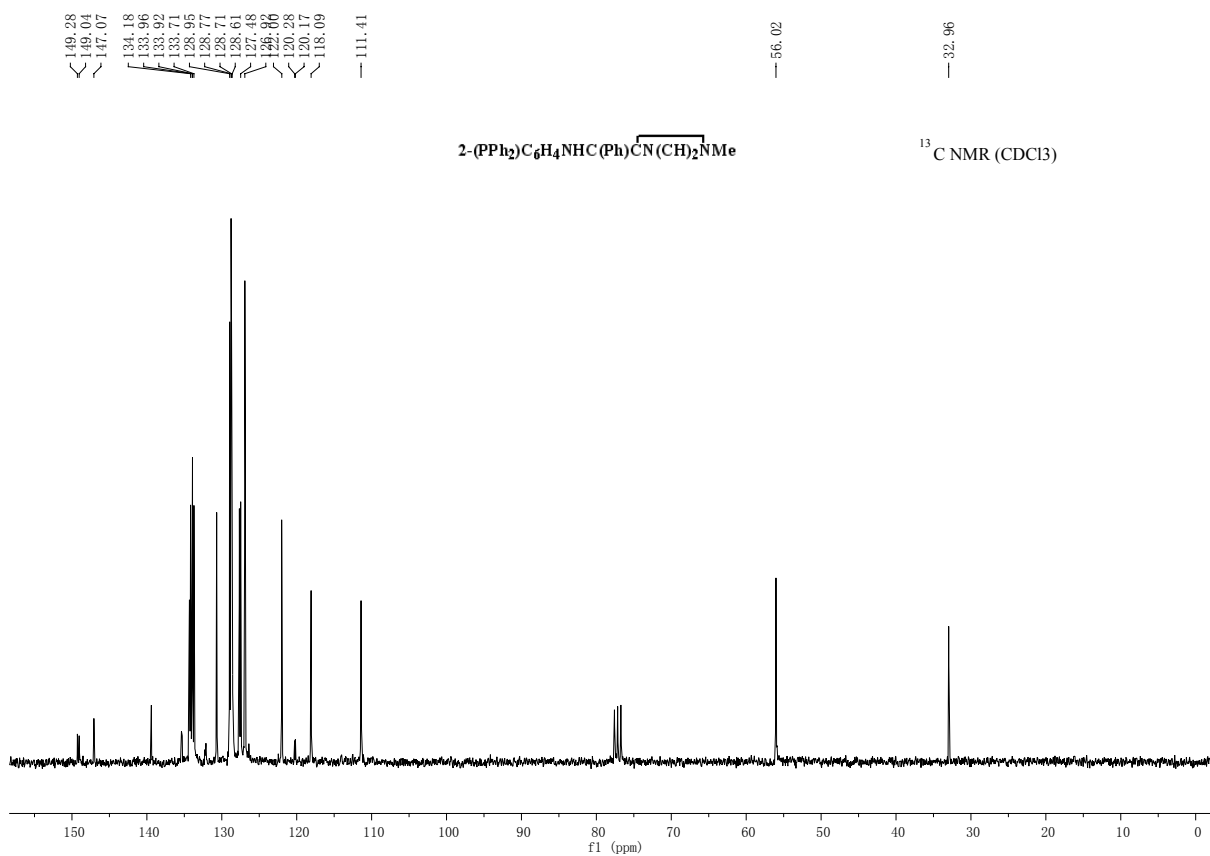
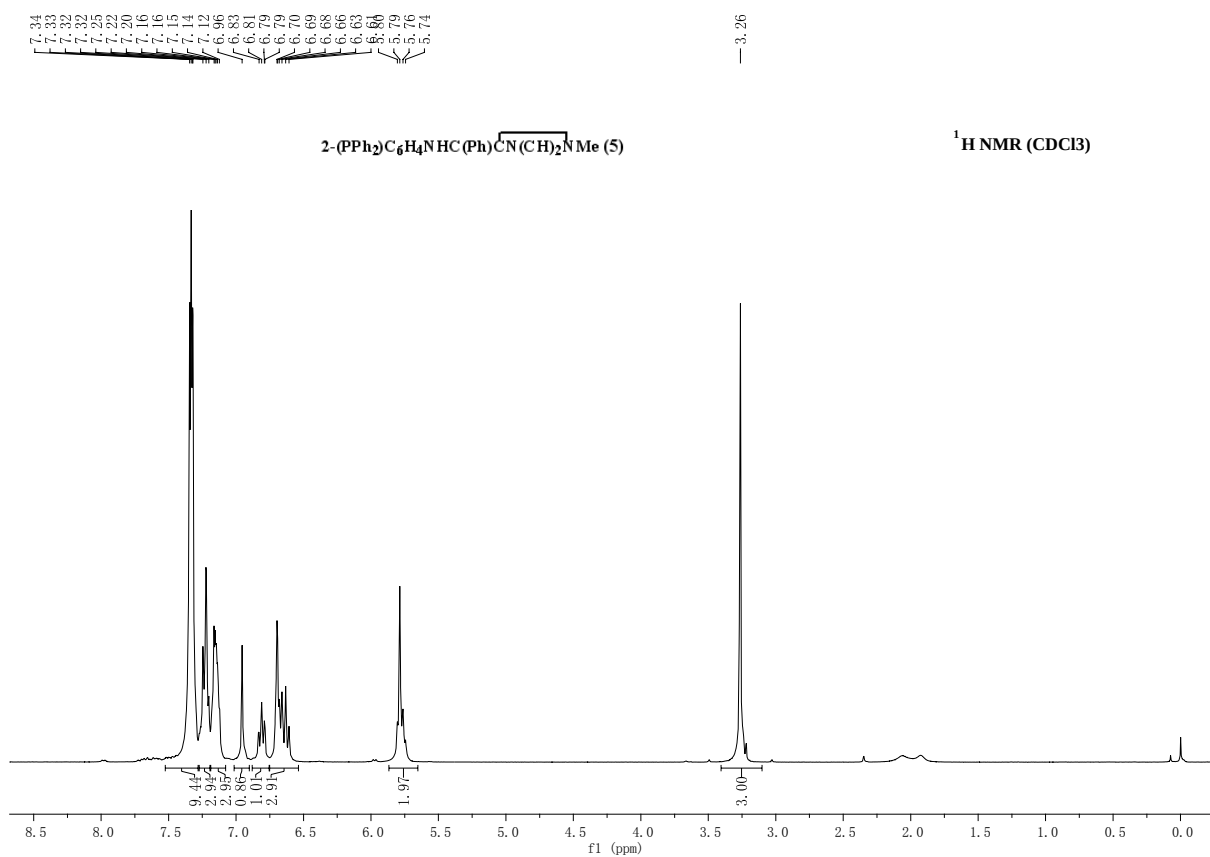




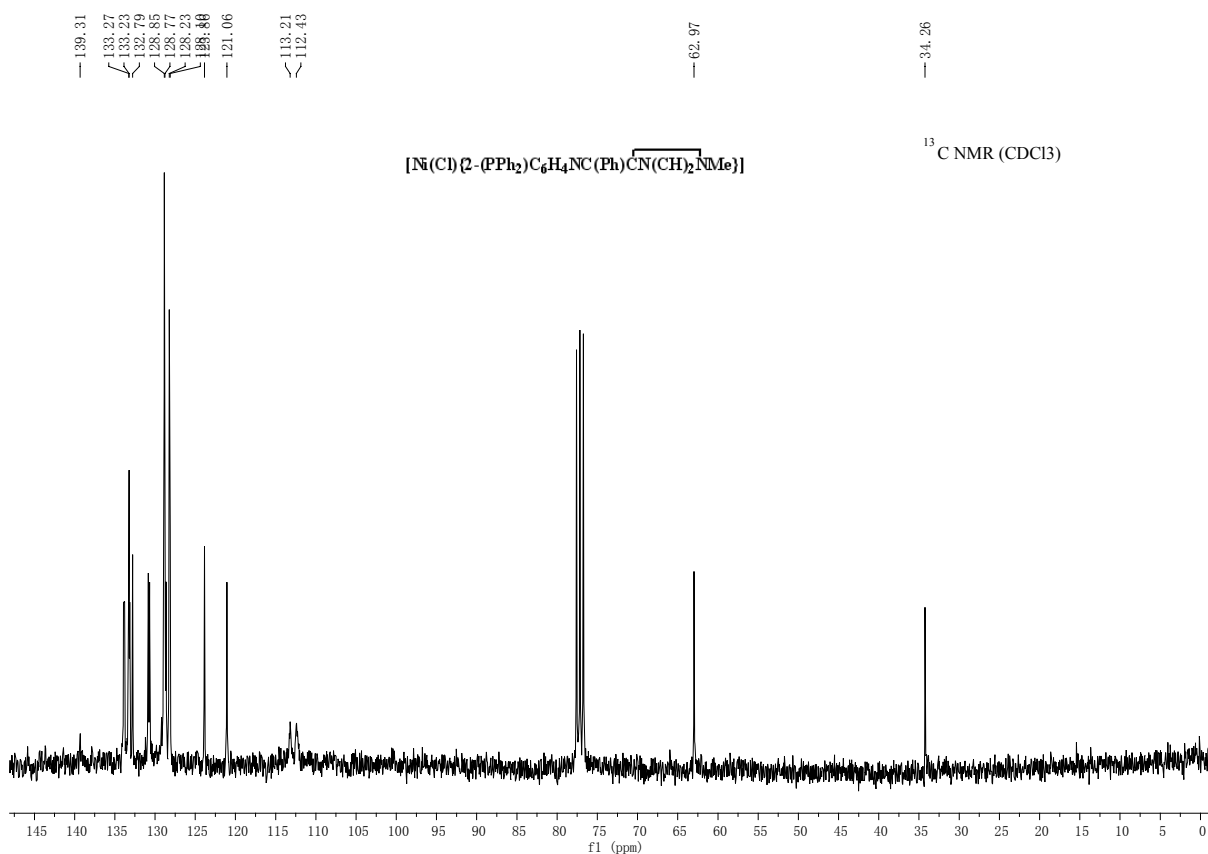
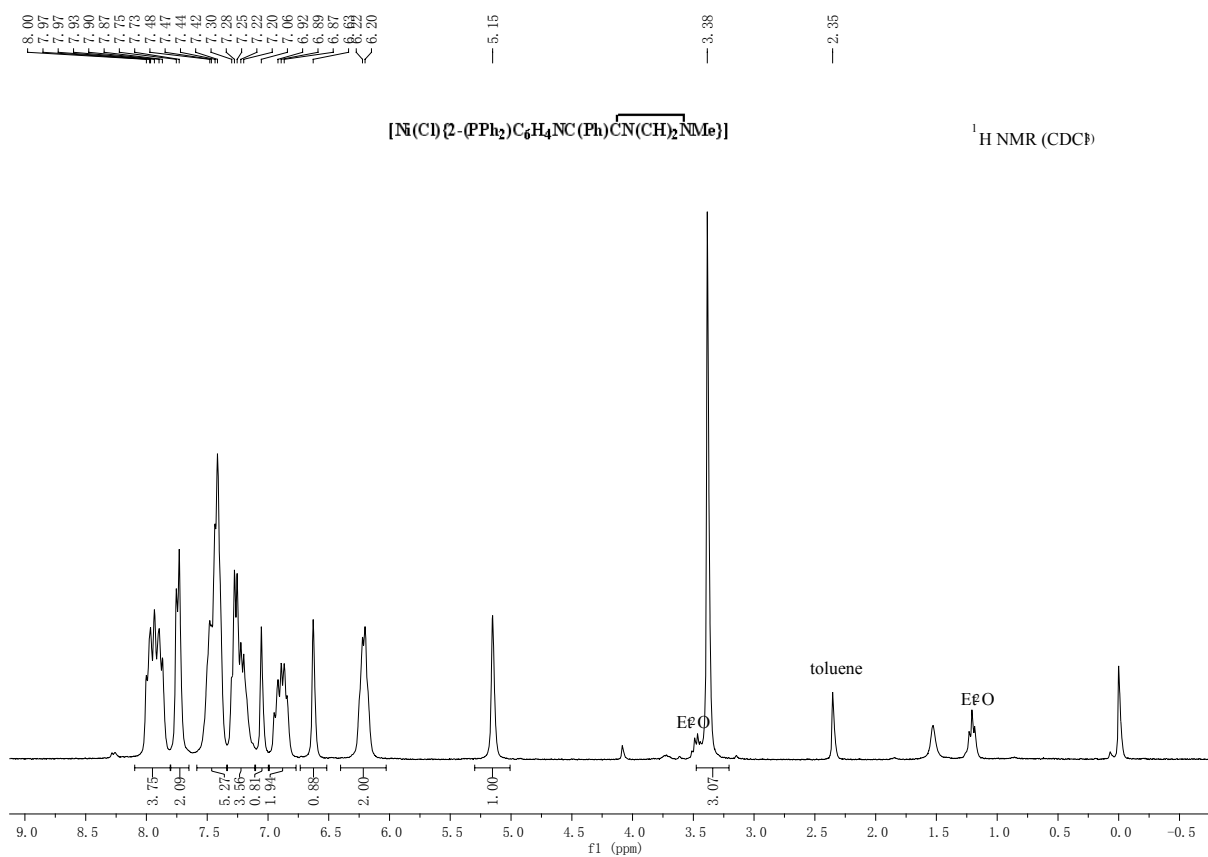




2-(PPh₂)C₆H₄NHC(Ph)CN(CH₂)₂NMe (5)



[Ni(Cl){2-(PPh₂)C₆H₄NC(Ph)CN(CH₂)₂NMe}] (IV)



2-(*p*-MeC₆H₄N=PPh₂)C₆H₄NHC(Ph)CN(CH₂)₂NMe (6)

