

IR Spectroscopy as a probe for C–H···X hydrogen bonded supramolecular synthons

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Supplementary information

Contents

S1	Synthesis of compounds	2
S2	PXRD	4
S3	Crystallographic information table	7
S4	Complete IR spectra of all the compounds	9
S5	References	24

S1: Synthesis of 6, 20, 21, 26 and 27

Synthesis of compound 6:

4-nitrobenzoyl chloride was obtained by refluxing 4-nitrobenzoic acid (200 mg) at ~ 75°C with excess of SOCl₂ for ~ 3 h. Excess SOCl₂ was removed under reduced pressure. Equimolar amount of benzylamine (0.13 mL) was then added into chloroform (~ 50 cm³) solution of 4-nitrobenzoyl chloride and the resulting mixture was refluxed for 1 h at ~ 75 °C. Product formation was confirmed by TLC. The mixture was then cooled and washed with 5% Na₂HCO₃ solution, 2N HCl, three times with water and finally with brine, and dried over Na₂SO₄. After cooling the mixture, the solvent was removed under reduced pressure. Slow evaporation of methanolic solution was allowed at room temperature to purify the product by crystallization. After IR analysis the product formation was confirmed by Single Crystal X-Ray Diffraction (SCXRD) study. Melting point: 123 °C

Synthesis of compound 20:

4-chlorobenzaldehyde (100 mg) and 3, 4-dimethoxyacetophenone (128.2 mg) were stirred in ethanol (~ 60 ml) at 0°C. Then 20% aqueous NaOH solution (~ 20 ml) was added and stirred for ~ 2 h. The resulting mixture was poured into crushed ice. The yellow precipitate formed was filtered off, washed with water and dried. The crude product was purified by crystallization from slow evaporation of acetone at room temperature. After IR analysis the product formation was confirmed by SCXRD study. Melting point: 125 °C

Synthesis of compound 21:

2,6-dichlorobenzaldehyde (100 mg) and 3,4-dimethoxyacetophenone (103 mg) were stirred in ethanol (~ 60 ml) at 0°C. After this, 20% aqueous NaOH solution (20 ml) was added and stirred for ~ 2 h. The resulting mixture was poured in to ice cold water. The precipitate formed was filtered off, washed with water and dried. The crude product was purified by crystallization from slow evaporation of acetone at room temperature. After IR analysis the product formation was confirmed by SCXRD study. Melting point: 110 °C

Synthesis of compound 26:

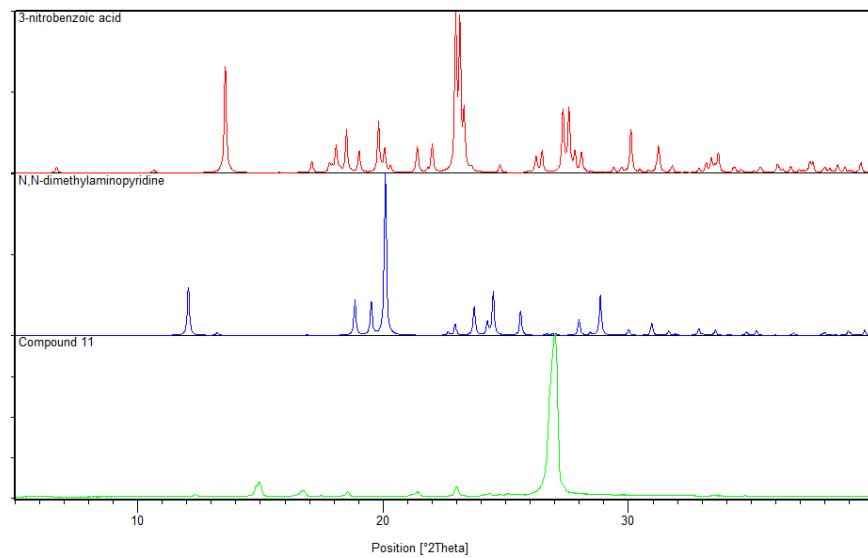
The compound **26** was prepared by solid state Schiff base reaction. 1:1 ratio of 4-cyanobenzaldehyde (100 mg) and 2-aminonaphthalene (109.2 mg) were ground for 15 min using mortar and pestle by solvent drop grinding method with methanol (see **S2**). After IR analysis the product formation was confirmed by Single Crystal X-Ray Diffraction (SCXRD) study.

Synthesis of compound 27:

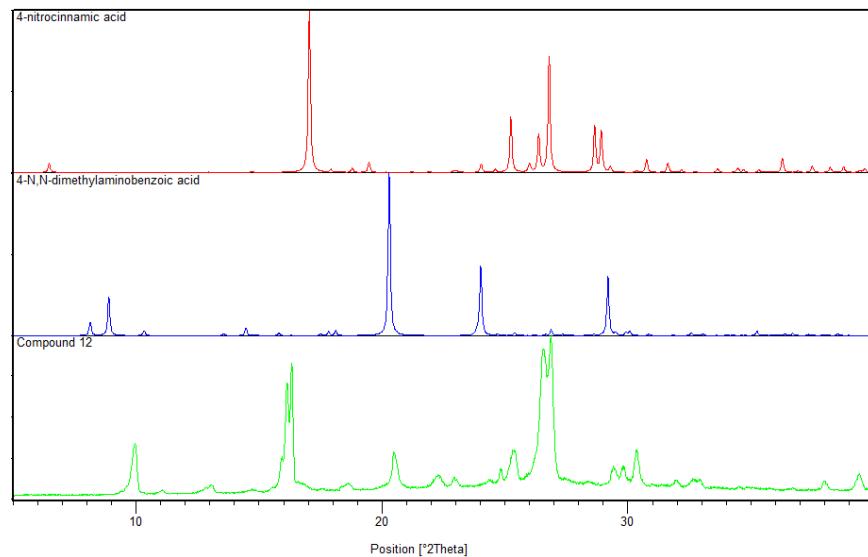
The compound **27** was prepared by solid state Schiff base reaction. 1:1 ratio of 4-cyanobenzaldehyde (100 mg) and 4-fluoro-3-nitroaniline (119.1 mg) were ground for 15 min using mortar and pestle by solvent drop grinding method with methanol (see **S2**). The resulting product was purified by crystallization from slow evaporation of MeOH at room temperature. After IR analysis the product formation was confirmed by Single Crystal X-Ray Diffraction (SCXRD) study. Melting point: 168 °C

S2: PXRD

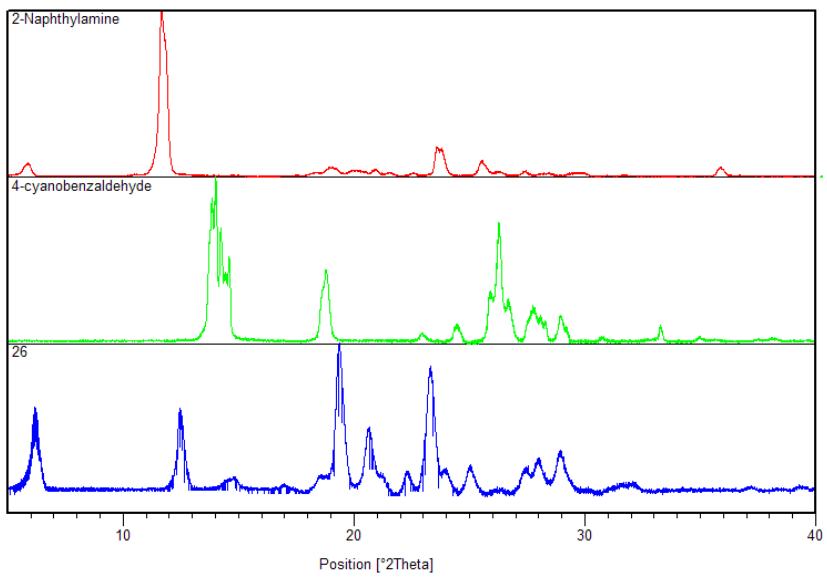
Compound 13



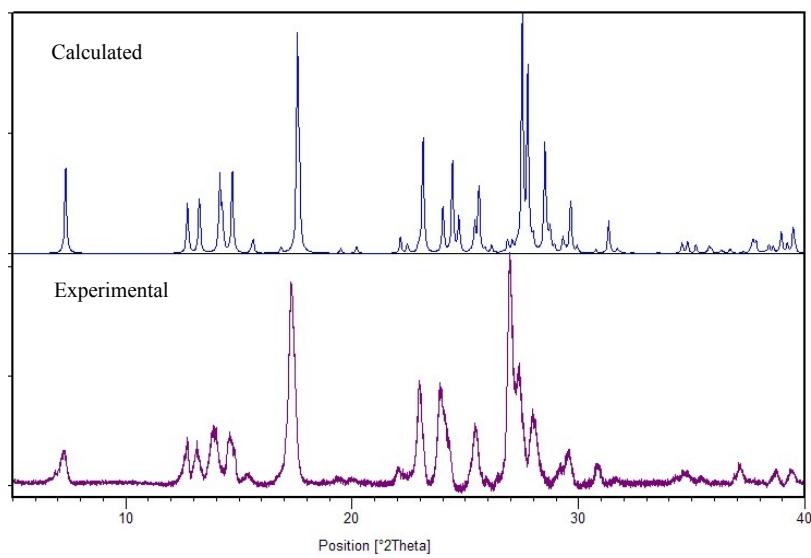
Compound 14



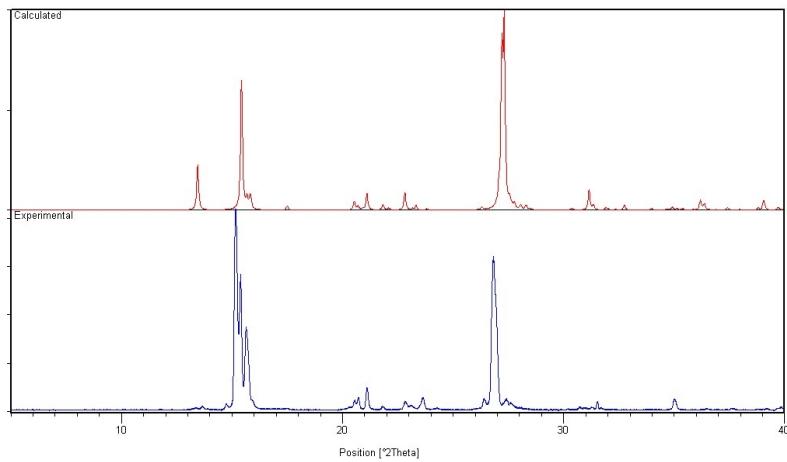
Compound 26



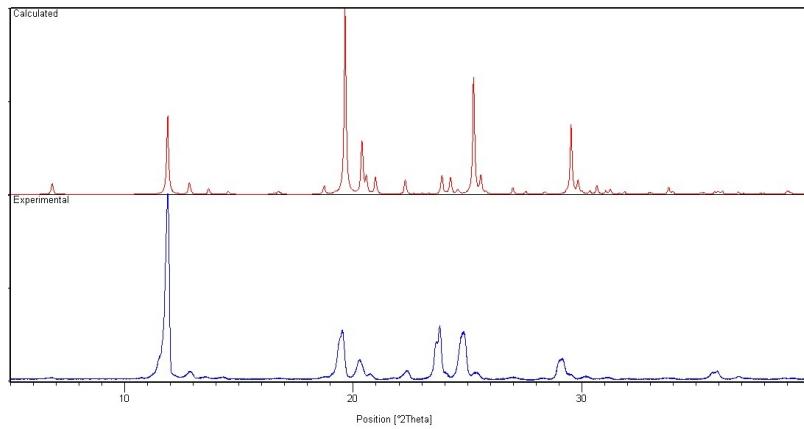
Compound 27



Compound 33



Compound 46

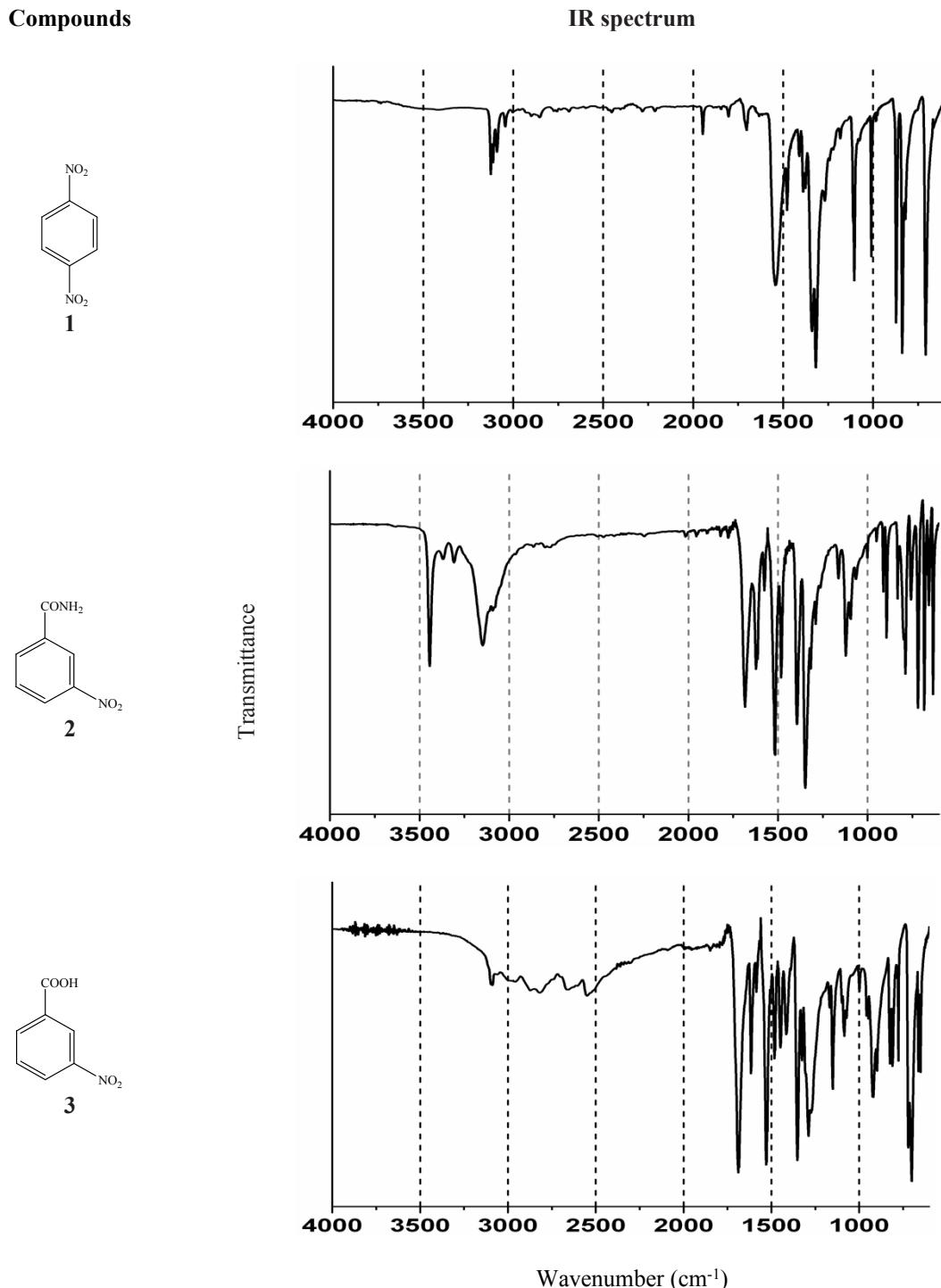


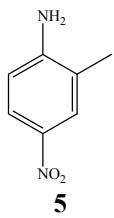
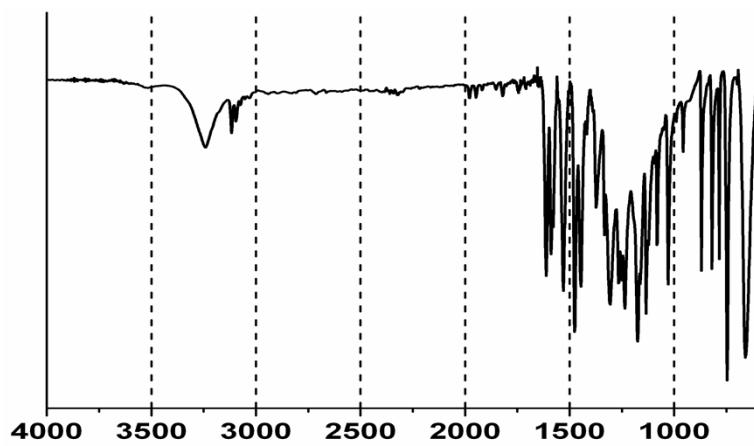
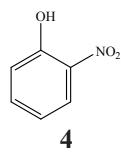
S3: Crystallographic parameters of compounds **6, **7**, **13**, **14**, **20**, **21**, **27**, **33**, and **46**.**

Compounds	6	7	13	14
Formula	C ₁₄ H ₁₂ N ₂ O ₃	C ₈ H ₇ N O ₄	C ₇ H ₄ N O ₄ , C ₇ H ₁₁ N ₂	C ₉ H ₇ N O ₄ , C ₉ H ₁₁ N
Molecular weight	256.26	181.15	289.29	358.34
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>P</i> 1
<i>a</i> (Å)	4.822(2)	7.463(2)	28.784(19)	8.781(8)
<i>b</i> (Å)	22.257(10)	7.747(1)	6.795(4)	9.080(10)
<i>c</i> (Å)	11.408(5)	15.435(5)	14.074(9)	11.641(12)
α (°)	90	94.522(3)	90	86.17(5)
β (°)	93.364(4)	97.041(2)	94.543(9)	69.02(4)
γ (°)	90	117.682(3)	90	73.38(4)
V (Å ³)	1222.3	774.8	2744	829.8
Z	4	4	8	2
ρ_{calc} (g/cm ³)	1.403	1.553	1.401	1.434
F(000)	528	330	1216	376
Temp. (K)	150	150	150	150
<i>R</i> _I	0.0527	0.0755	0.0474	0.0608
<i>wR</i> ₂	0.1799	0.2758	0.1479	0.1693
Goodness-of fit	0.872	0.974	1.100	1.085
CCDC No.	1023999	1024000	1024001	1027956

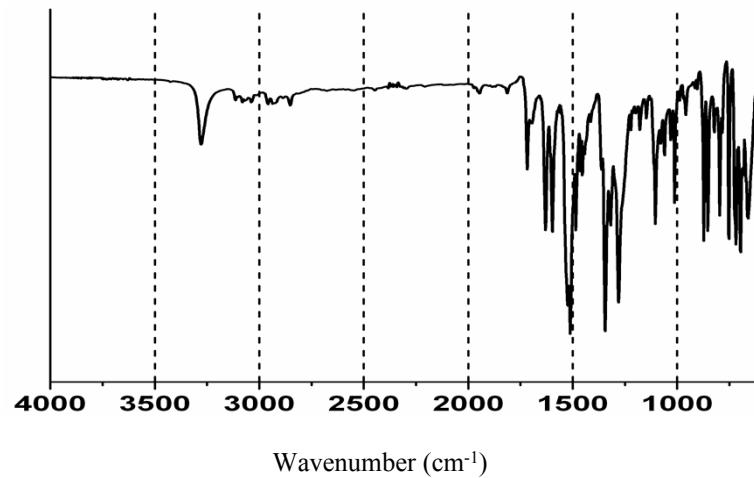
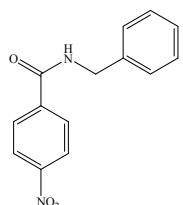
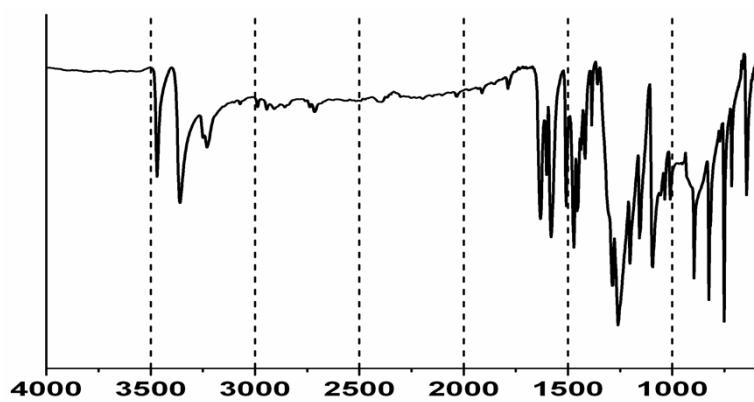
Compounds	20	21	27	33	46
Formula	C ₁₇ H ₁₅ ClO ₃	C ₁₅ H ₈ BrCl ₂ O	C ₁₄ H ₈ FN ₃ O ₂	C ₁₀ H ₈ N ₂ , 2(C ₇ H ₄ F ₂ O ₂)	C ₁₀ H ₈ N ₂ , 2(C ₁₀ H ₈ O)
Molecular weight	302.74	355.00	269.23	472.39	444.51
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.0137(18)	3.8793(7)	7.820(5)	6.916(4)	14.118(12)
<i>b</i> (Å)	5.7145(7)	15.208(3)	24.093(13)	6.922(4)	5.881(5)
<i>c</i> (Å)	17.311(2)	23.308(4)	7.286(4)	11.215(8)	15.040(13)
α (°)	90	90	90	88.869(17)	90
β (°)	105.671(7)	92.189(7)	117.167(6)	88.15(2)	113.629(10)
γ (°)	90	90	90	72.09(2)	90
V (Å ³)	1430.0	1374.1	1221.3	510.5	1144.0
Z	4	4	4	1	2
ρ_{calc} (g/cm ³)	1.406	1.716	1.464	1.537	1.290
F(000)	736	700	552	242	468
Temp. (K)	173	173	150	150	150
R_I	0.0302	0.051	0.0467	0.0513	0.0872
wR_2	0.0813	0.1030	0.1477	0.1501	0.2901
Goodness-of-fit	1.063	1.029	1.129	1.088	1.149
CCDC No.	1024002	1024003	1024004	1033507	1033508

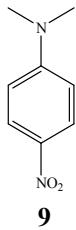
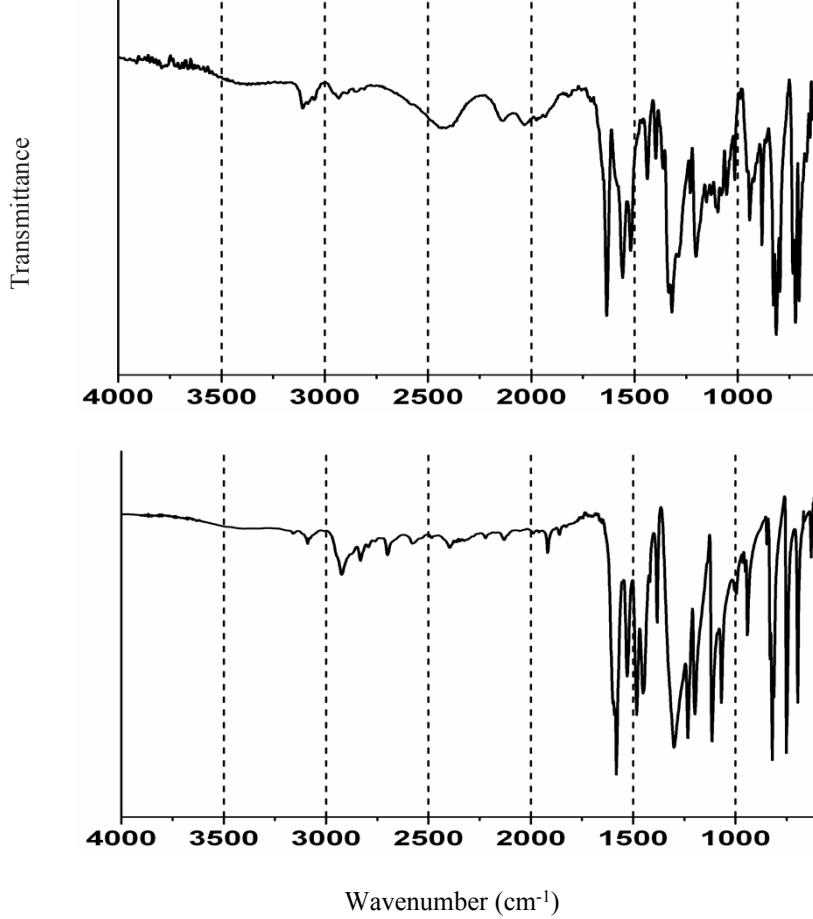
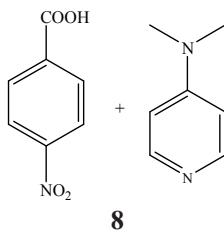
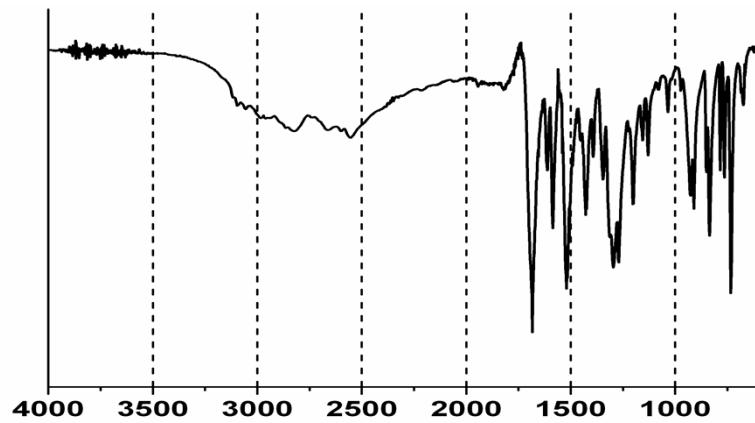
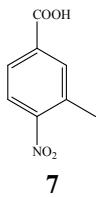
S4: Complete IR spectra of all compounds

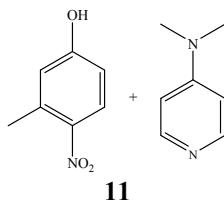
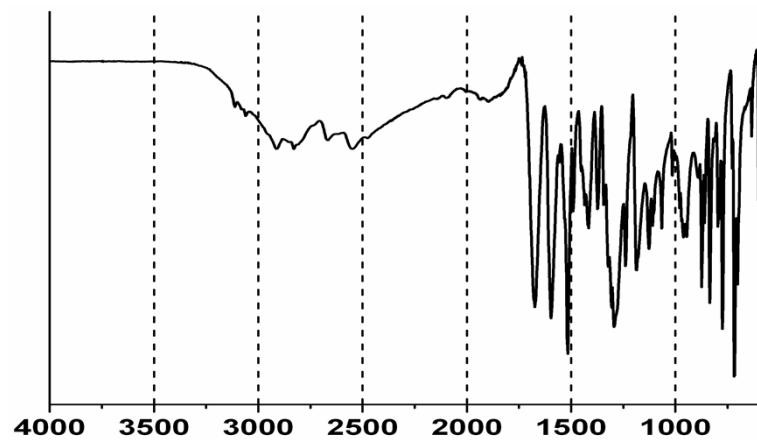
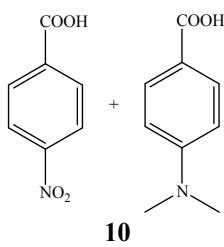




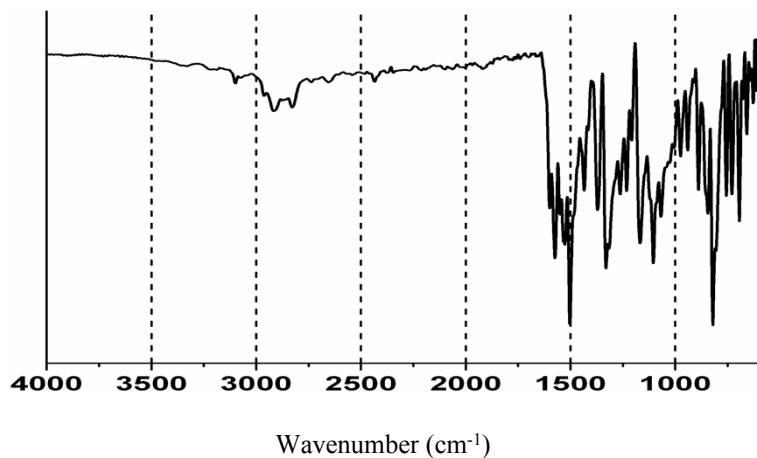
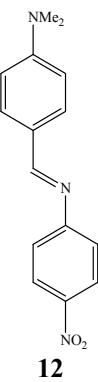
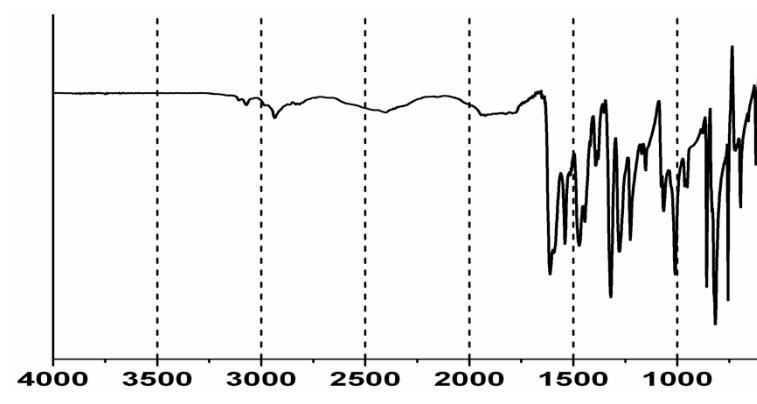
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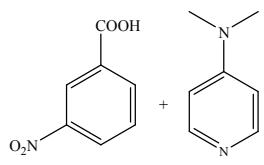




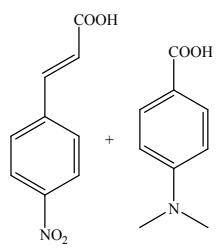
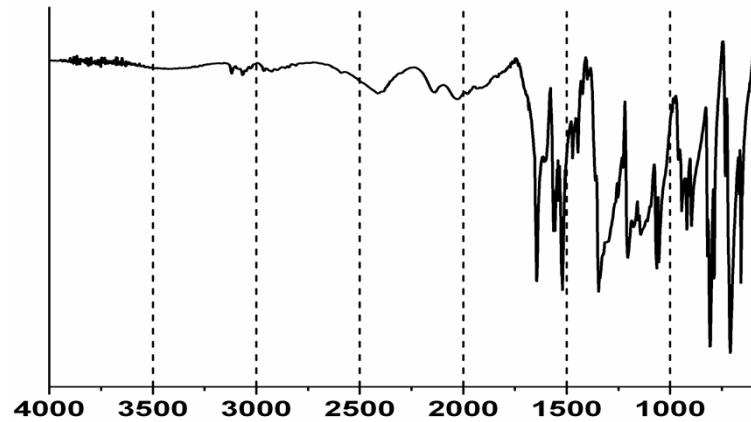


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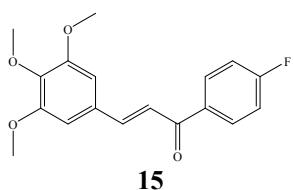
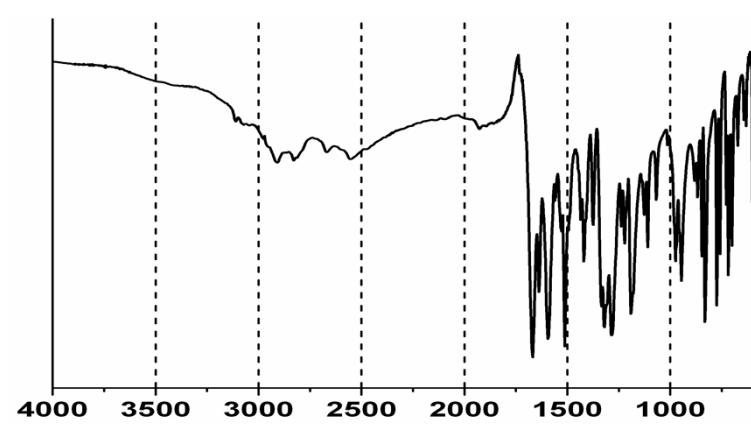


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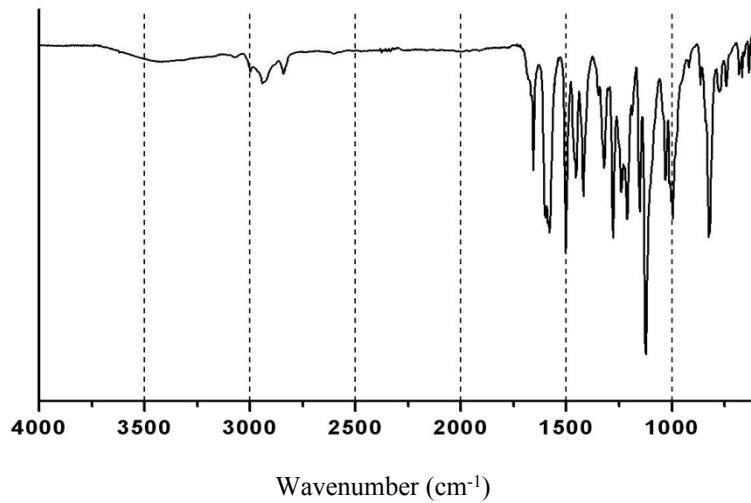


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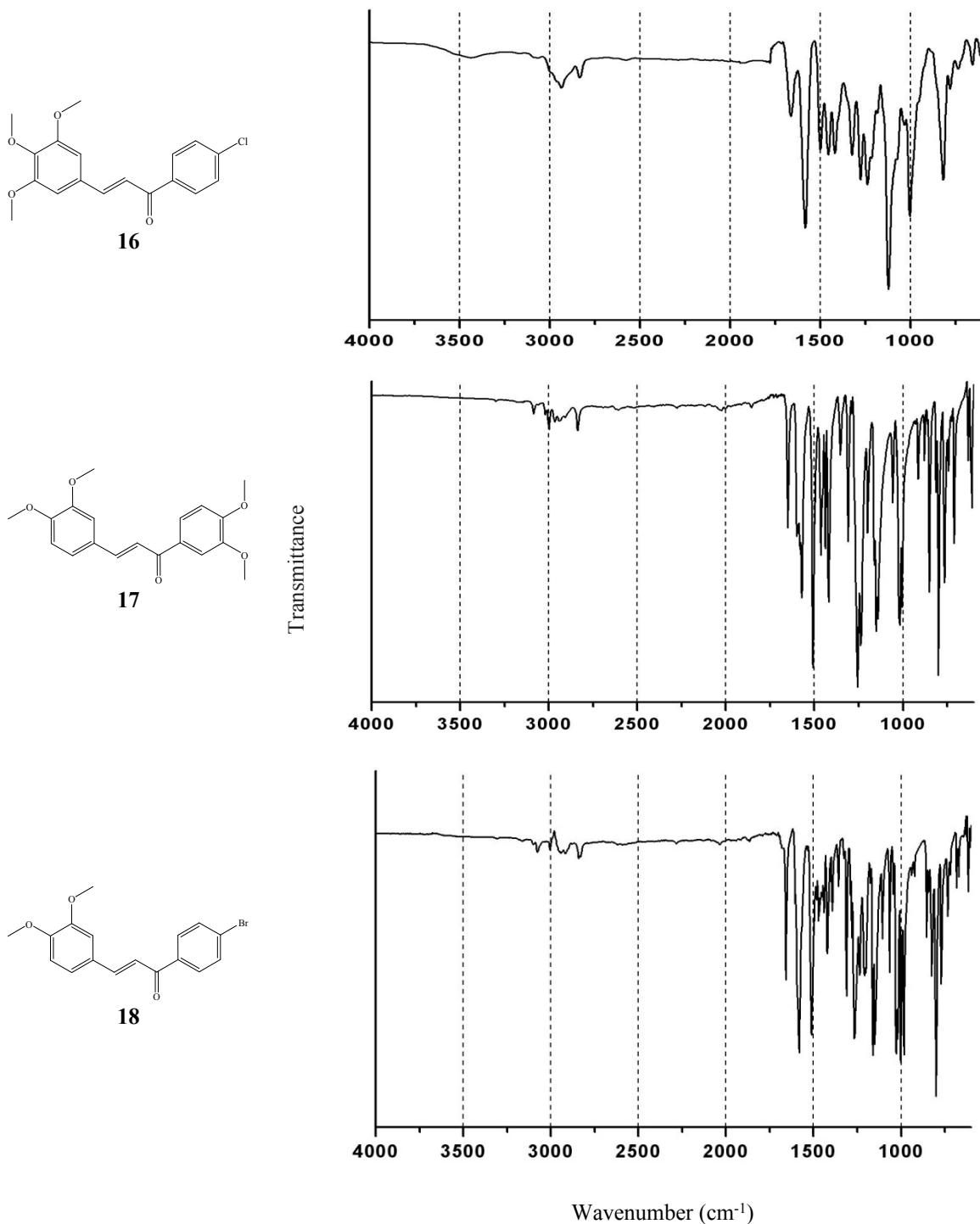
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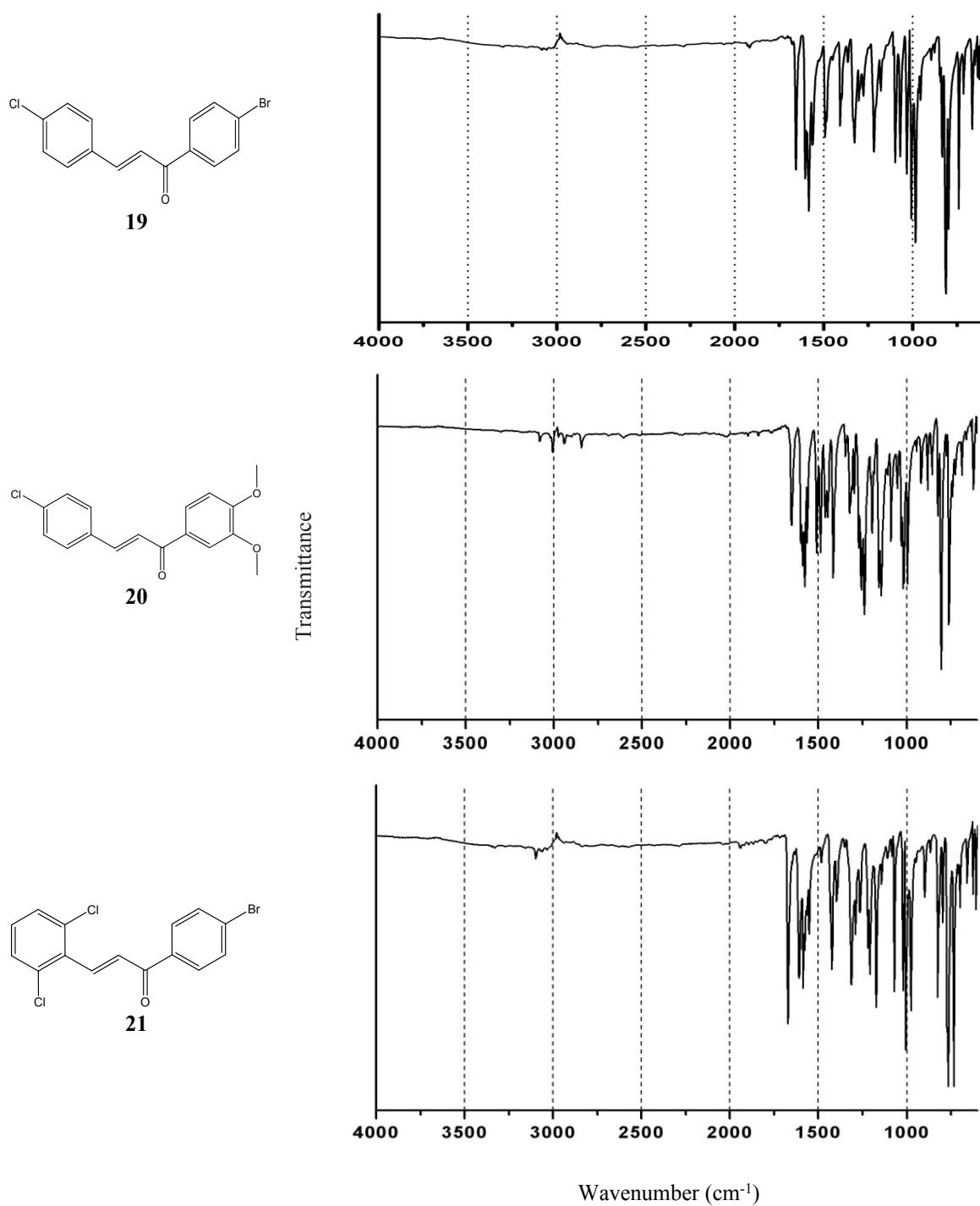


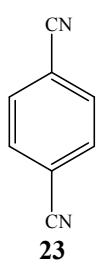
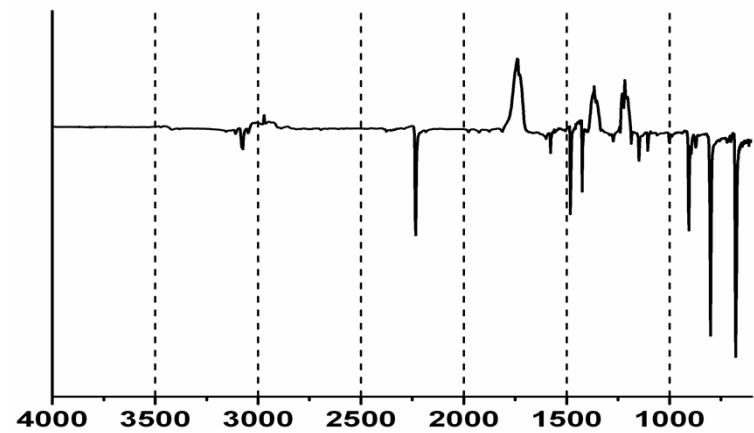
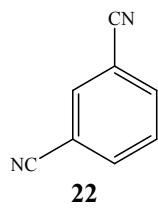
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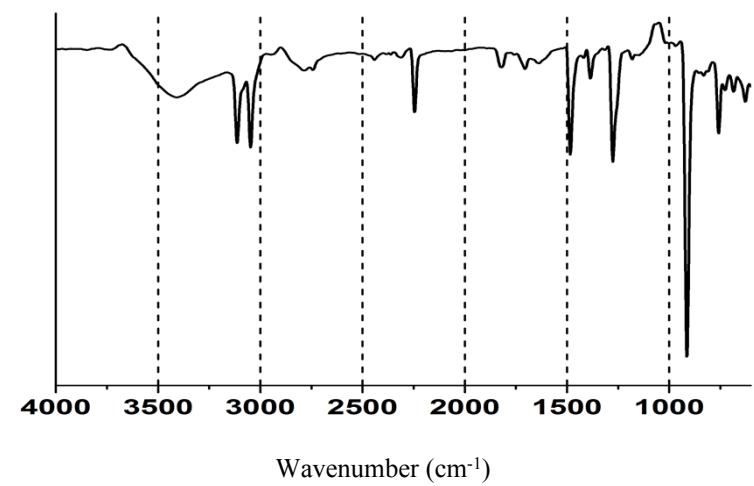
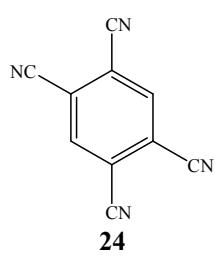
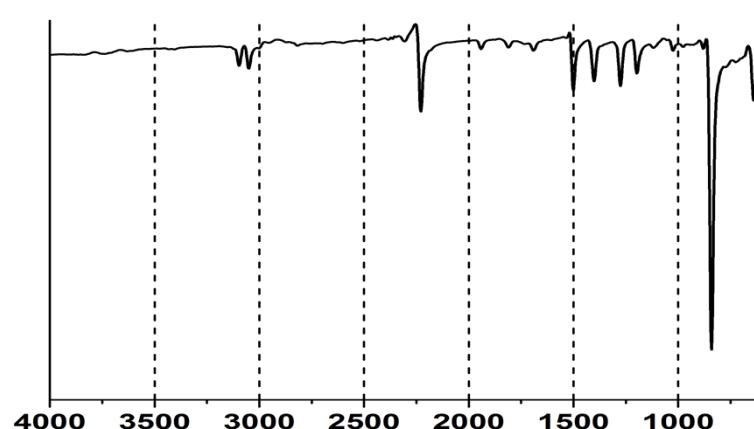
Wavenumber (cm⁻¹)



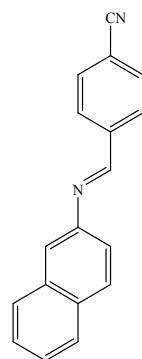
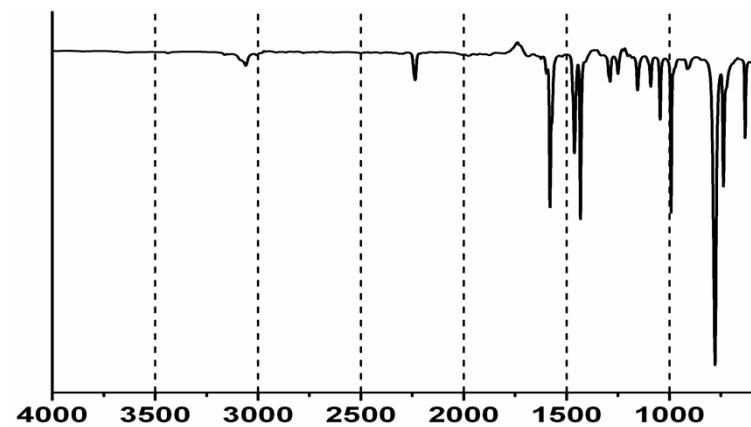
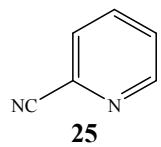




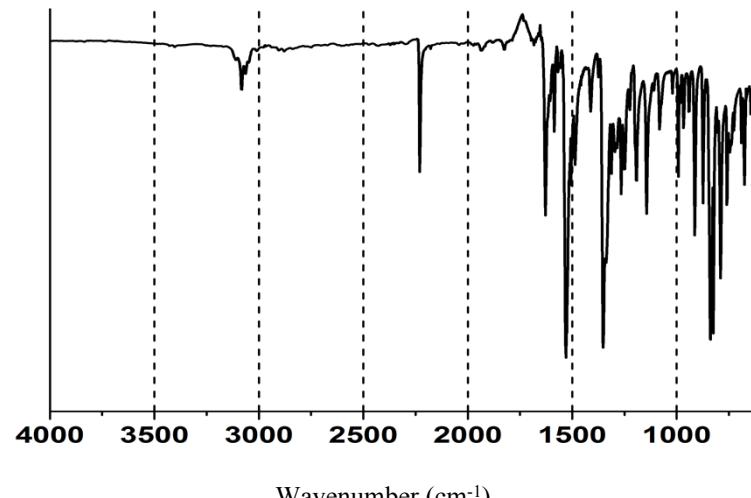
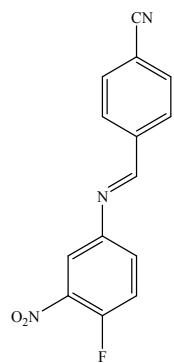
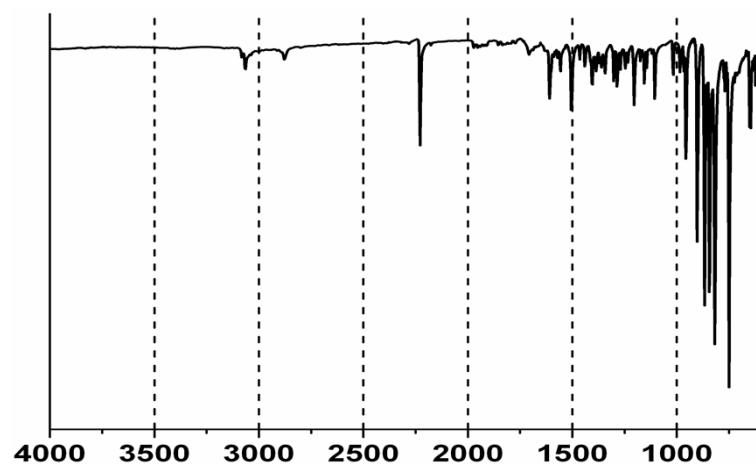
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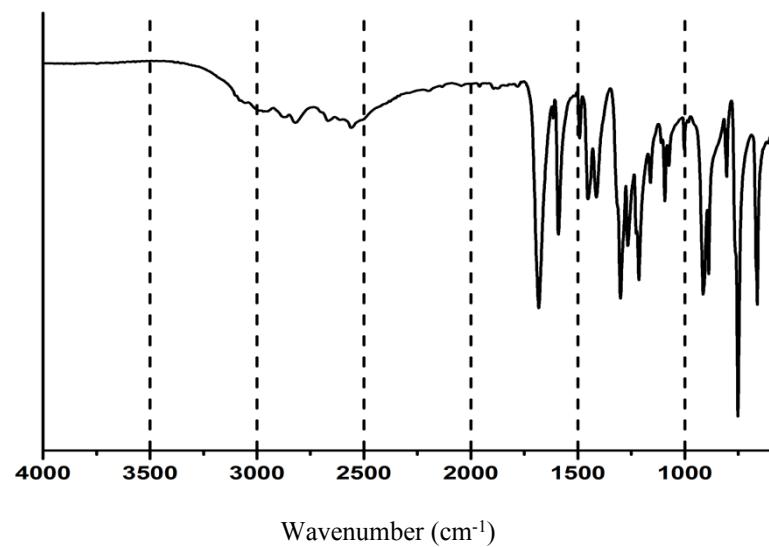
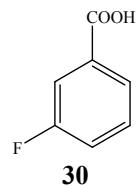
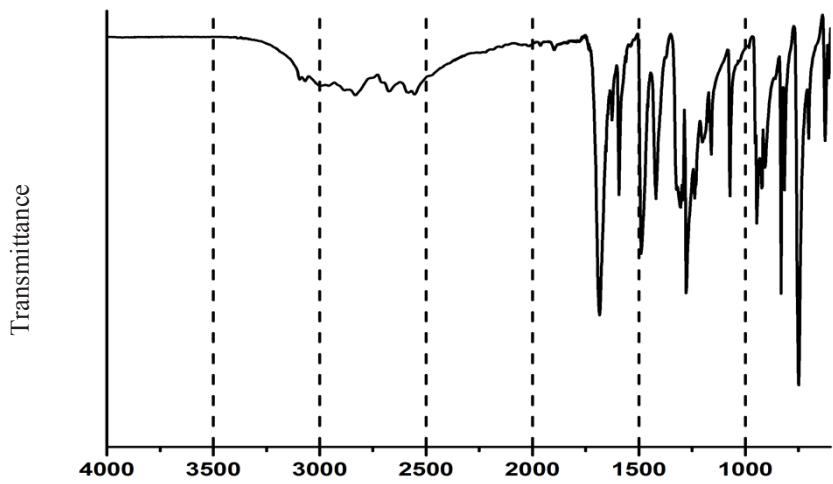
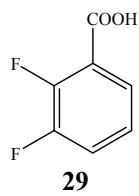
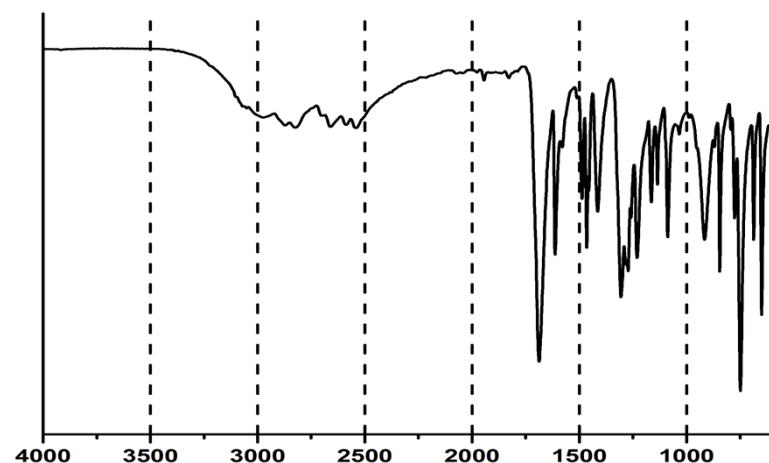
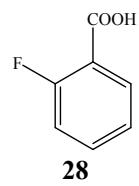


Wavenumber (cm⁻¹)

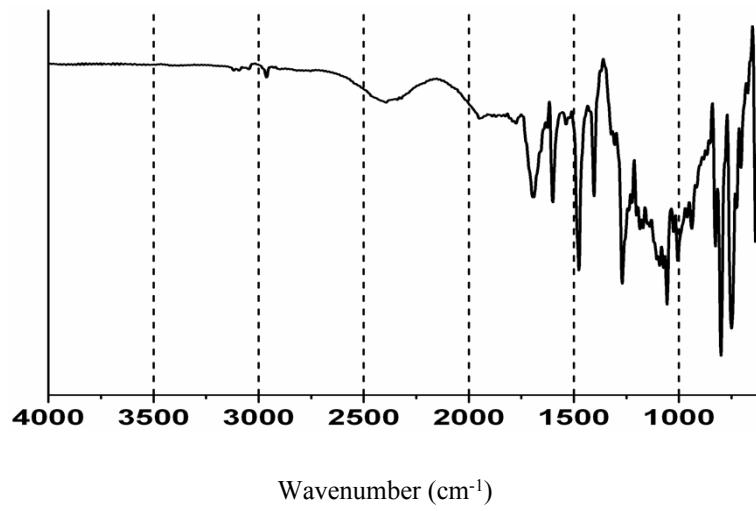
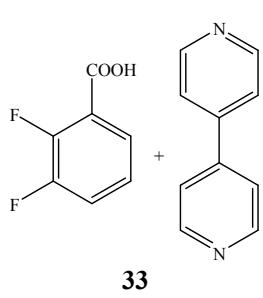
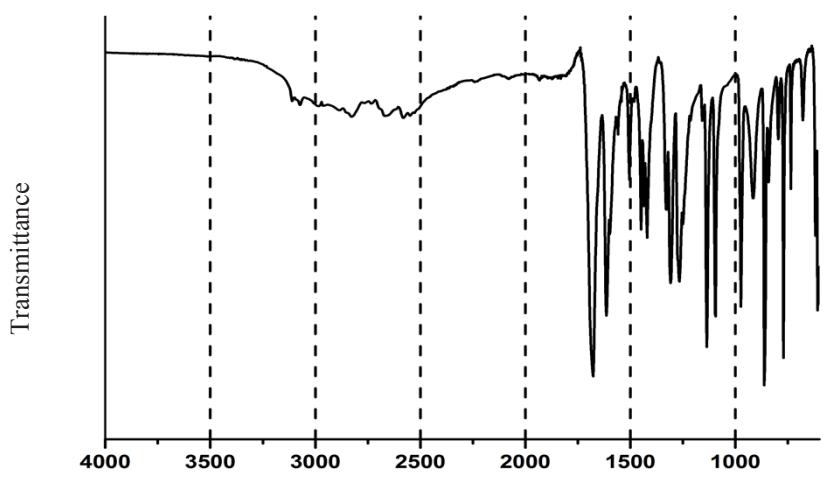
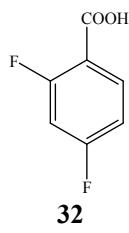
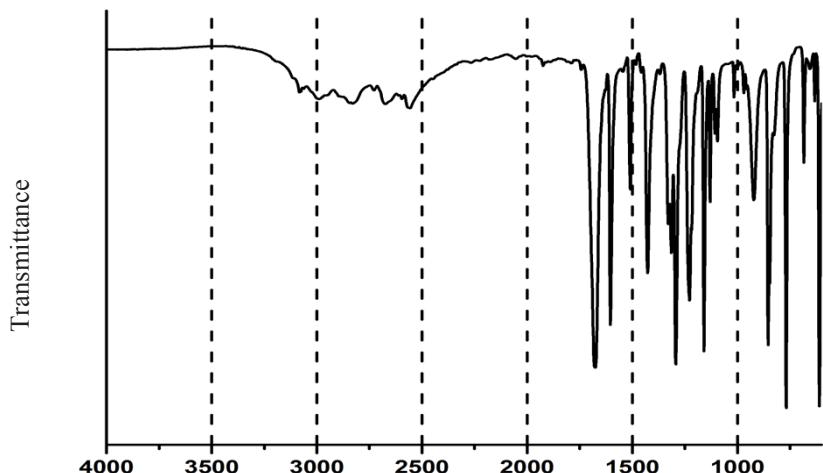
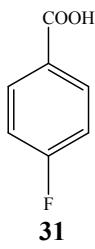


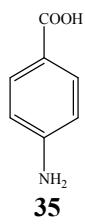
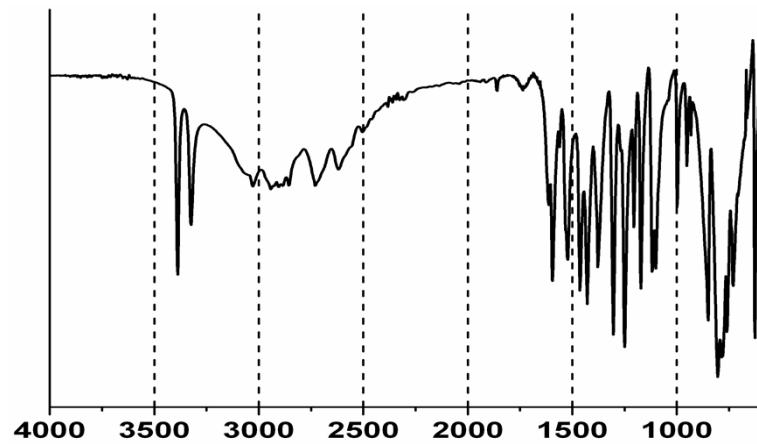
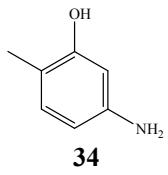
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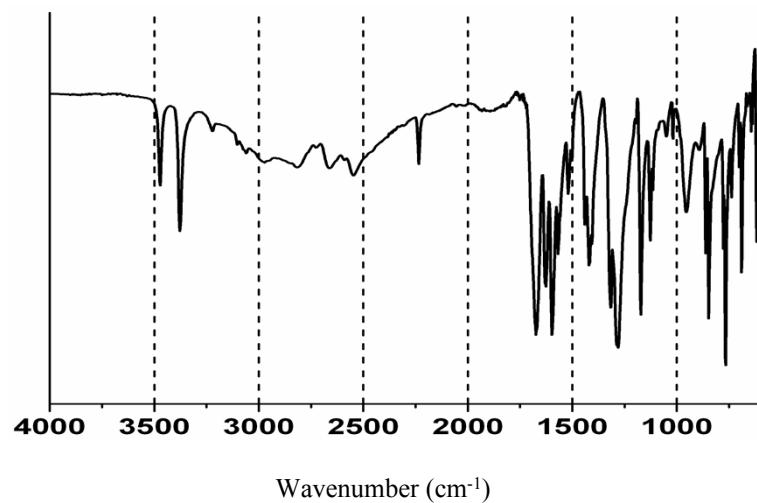
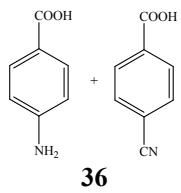
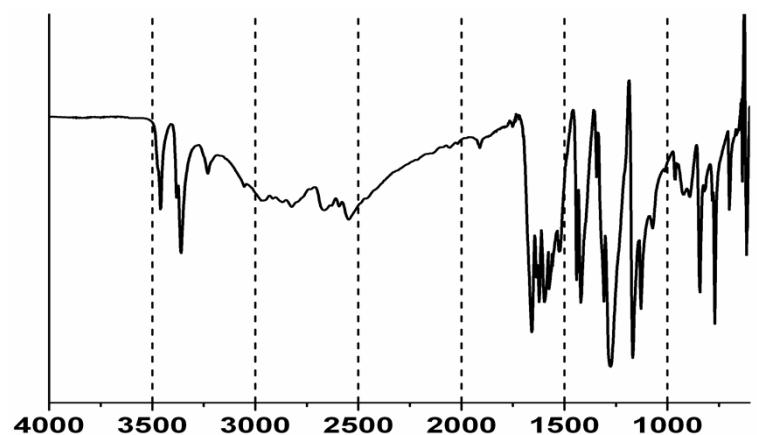


Wavenumber (cm^{-1})

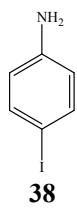
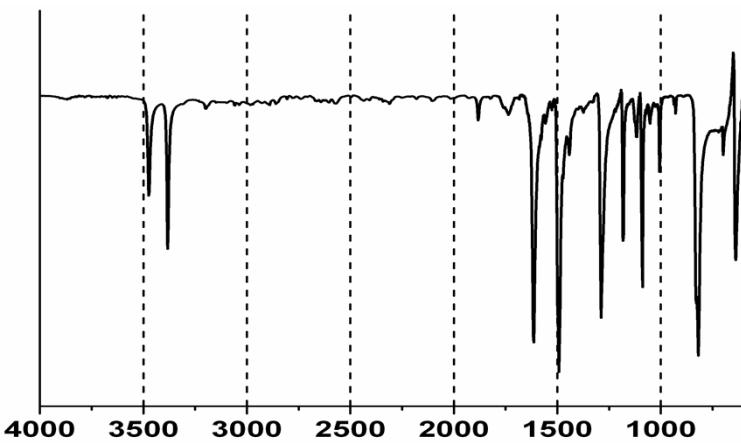
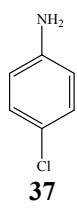




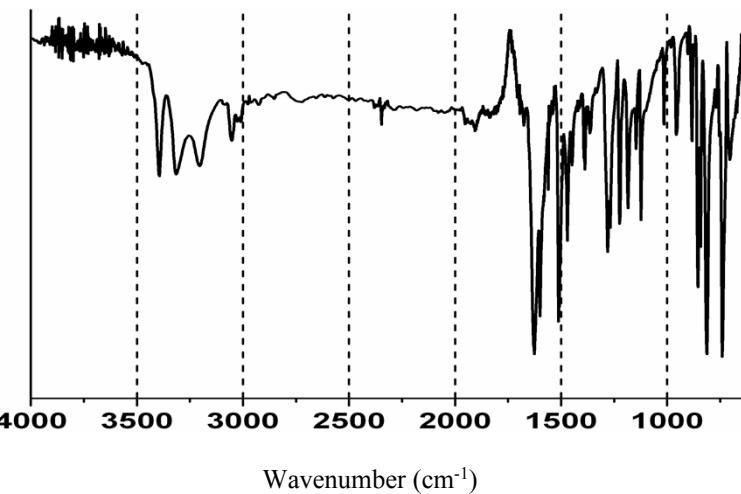
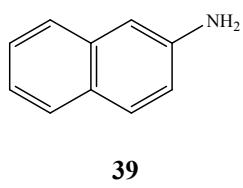
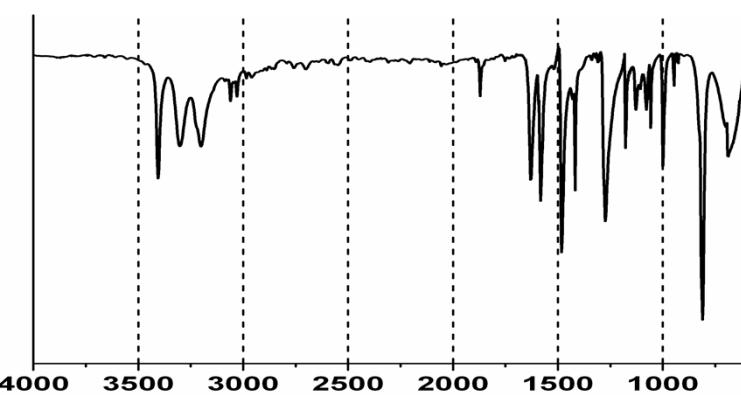
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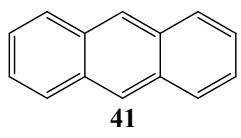
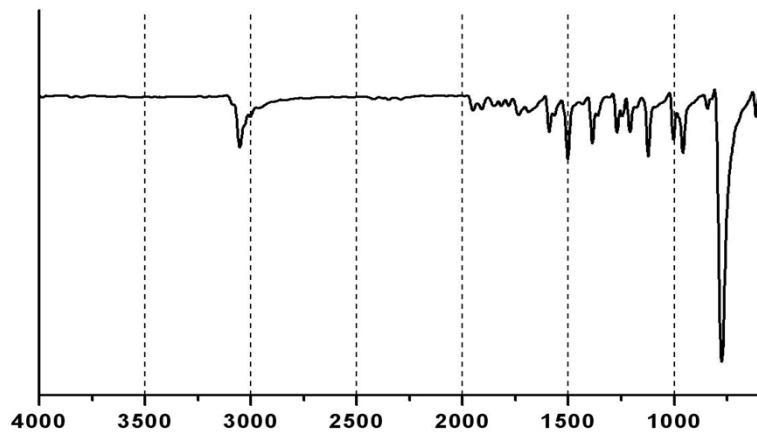
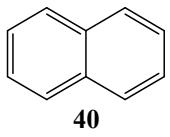


Wavenumber (cm⁻¹)

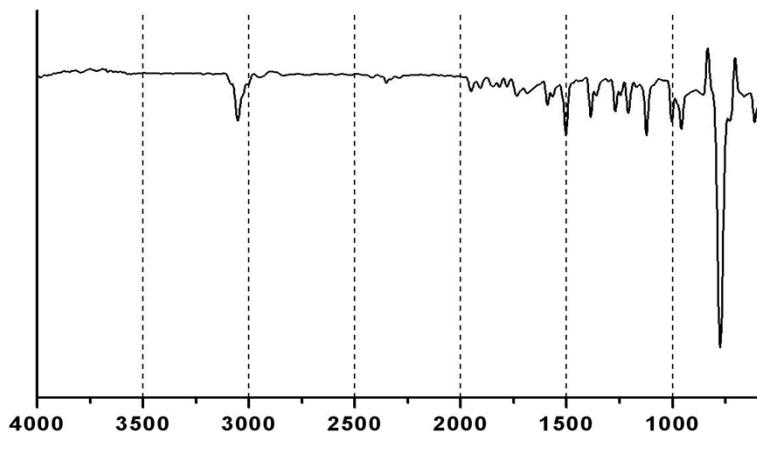
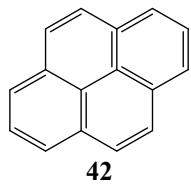
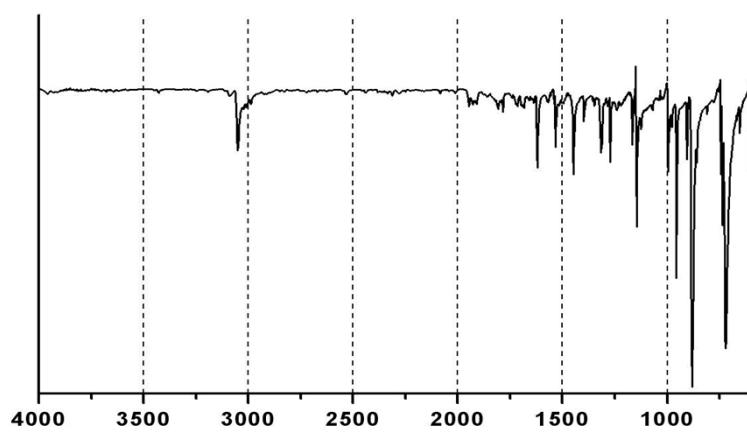


Transmittance

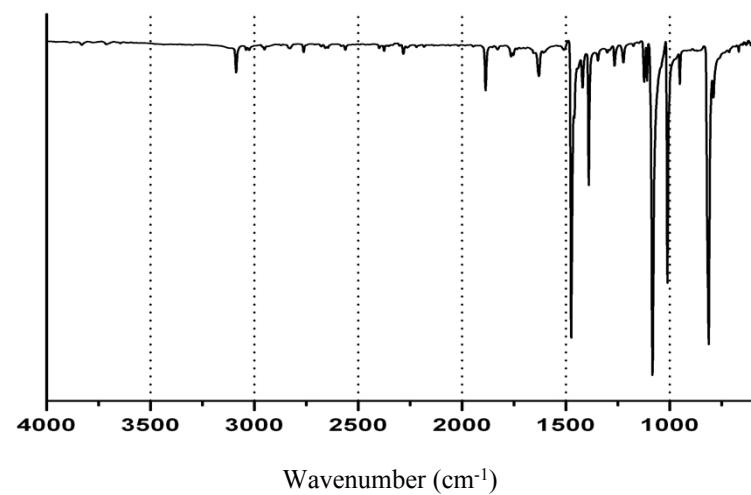
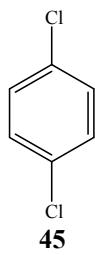
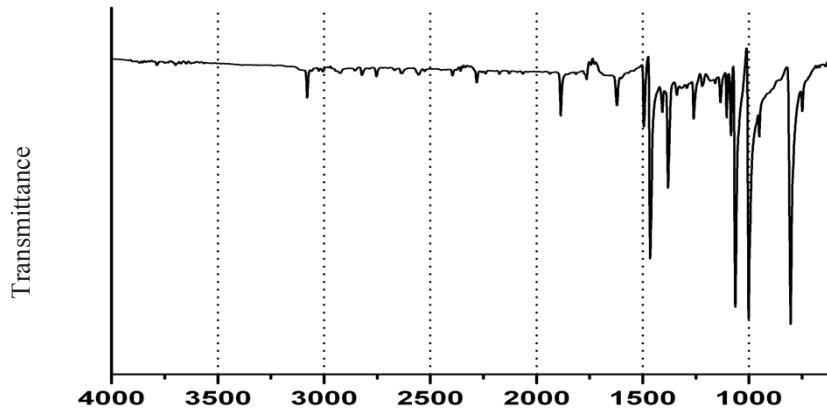
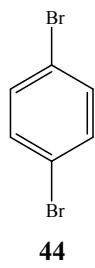
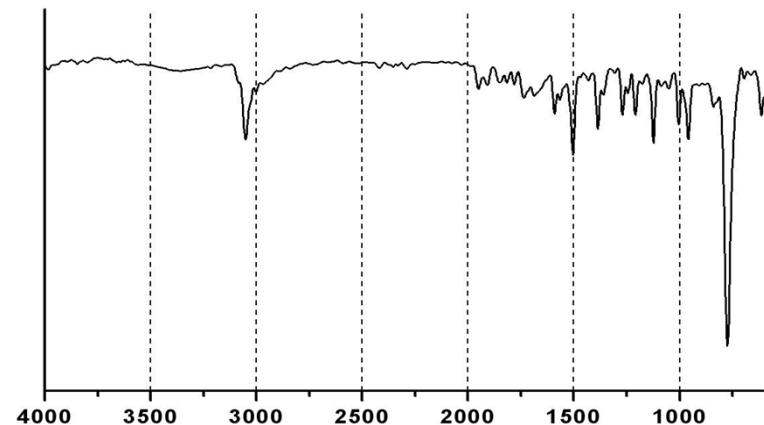
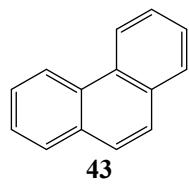


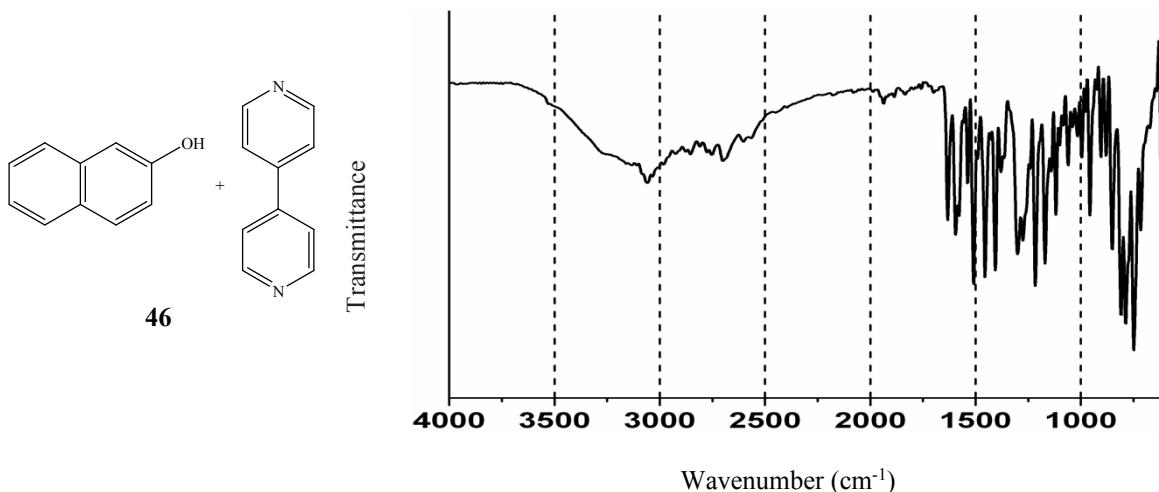


Transmittance



Wavenumber (cm⁻¹)





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