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Graded IR-filters: Distinguishing between single and multipoint $NO_2\cdots I$ halogen bonded supramolecular synthons (P, Q, R synthons)

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SUPPLEMENTARY MATERIAL

Table of Contents

S1: Synthesis of compounds 9-14.

Synthesis of compound 9:

First, 3-methyl-4-nitrobenzoic acid was refluxed at ~ 75˚C with excess of $SOCl_2$ for ~ 3 h to get 3-methyl-4-nitrobenzoyl chloride. After this, the excess of $SOCl_2$ was removed under reduced pressure. Then equimolar amounts of the 3-methyl-4-nitrobenzoyl chloride and 4-iodoaniline (2 mmol of each component) were dissolved in chloroform (~ 50 cm^3), and the resulting mixture was refluxed for 1 h at ~ 75˚C. New product formation was followed by TLC. The mixture was then cooled and washed first with 5% Na_2HCO_3 solution, 2(N) HCl, three times with water, finally with brine, respectively and dried over Na_2SO_4. After cooling the mixture, the solvent was removed under reduced pressure, and the resulting product was purified by crystallization from THF, the melting point (205˚C) was then checked. After IR analysis the product formation was confirmed by Single Crystal X-Ray Diffraction (SCXRD) study.

Synthesis of compound 10:

After the synthesis of 4-iodobenzoyl chloride from 4-iodobenzoic acid following above process for **9**, equimolar amounts (2 mmol of each) of 4-iodobenzoyl chloride and 3-nitrophenol in chloroform (~ 50 cm^3) were refluxed for 1 h at ~ 75˚C. New product formation was followed by TLC. The mixture was then cooled and washed first with 5% Na_2HCO_3 solution, then three times with water, finally with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude was crystallized from ethanol, the melting point (146˚C) was then checked. After IR analysis the product formation was confirmed by SCXRD study.

Synthesis of compound 11:

Equimolar amounts (2 mmol of each) of 4-iodobenzoyl chloride and 3-fluoro-4-nitrophenol in chloroform (~ 50 cm^3) were refluxed for 1 h at ~ 75˚C. New product formation was followed by TLC. The mixture was then cooled and washed first with 5% Na_2HCO_3 solution, then three times with water, finally with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude was crystallized from THF, the melting point (147˚C) was then checked. After IR analysis the product formation was confirmed by SCXRD study.

Synthesis of compound 12:

Equimolar amounts (2 mmol of each) of 4-iodobenzoyl chloride and 4-nitrophenol in chloroform (~ 50 cm^3) were refluxed for 1 h at ~ 75˚C. New product formation was followed by TLC. The mixture was then cooled and washed first with 5% Na_2HCO_3 solution, then three times with water, finally with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude was crystallized from $CHCl_3$, the melting point (168˚C) was then checked. After IR analysis the product formation was confirmed by SCXRD study.

Synthesis of compound 13:

After the synthesis of 3-iodobenzoyl chloride from 3-iodobenzoic acid following above process for **9**, equimolar amounts (2 mmol of each) of 4-iodobenzoyl chloride and 3-nitrophenol in chloroform (~ 50 cm^3) were refluxed for 1 h at ~ 75˚C. New product formation was followed by TLC. The mixture was then cooled and washed first with 5% Na_2HCO_3 solution, then three times with water, finally with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude was crystallized from methanol, the melting point

(121˚C) was then checked. After IR analysis the product formation was confirmed by SCXRD study.

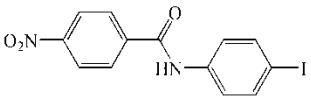
Synthesis of compound 14:

Equimolar amounts (2 mmol of each) of 3-iodobenzoyl chloride and 2-nitrophenol in chloroform (~ 50 cm^3) were refluxed for 1 h at ~ 75˚C. New product formation was followed by TLC. The mixture was then cooled and washed first with 5% Na_2HCO_3 solution, then three times with water, finally with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude was crystallized from $CHCl_3$, the melting point (123˚C) was then checked. After IR analysis the product formation was confirmed by SCXRD study.

S2: Melting points of compounds 9-14.

Compound	Melting point (˚C)
9	205
10	146
11	147
12	168
13	121
14	123

S3: Full solid state IR spectra of Step 1 compounds



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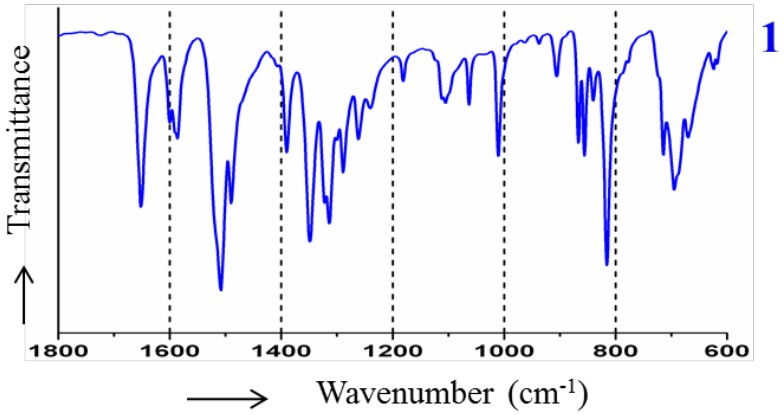
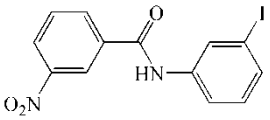


Solid state IR spectrum of **1**.



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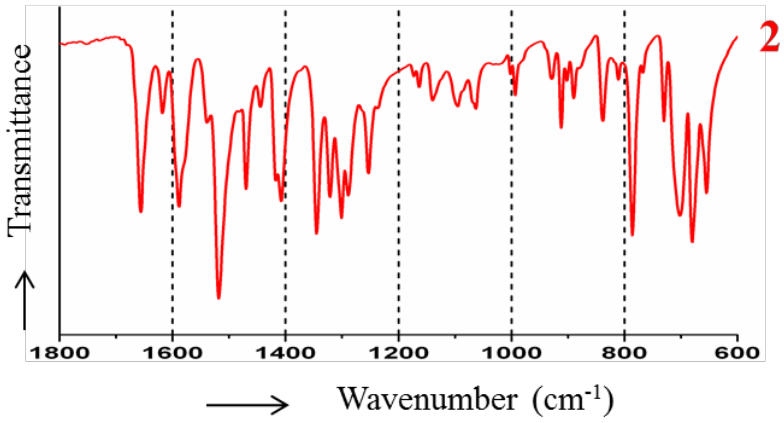
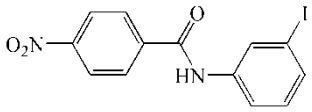


Solid state IR spectrum of **2**.



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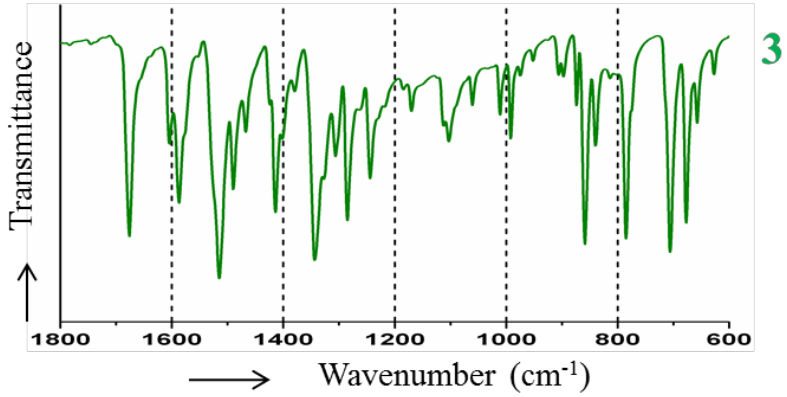
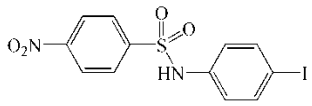


Solid state IR spectrum of **3**.

S4: Full solid state IR spectra of Step 2 compounds



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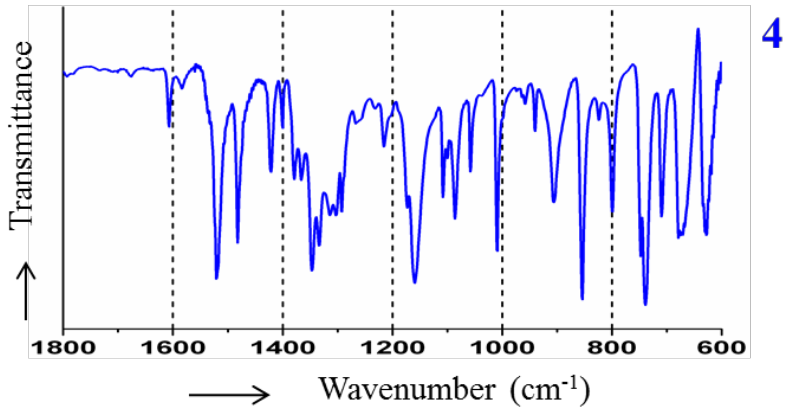
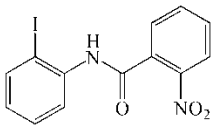


Solid state IR spectrum of **4**.

The absorption of the sulfonamide group appears at ~ 1345 cm^{-1} (L. J. Bellamy, *Advances in Infrared Group Frequencies*, **1968**, Methuen) and is close to the symmetric stretch of the nitro group in compound **4**. However, the symmetric nitro stretch lies at a frequency that is lower than the sulfonamide absorption thereby allowing clear identification of a split symmetric stretch.



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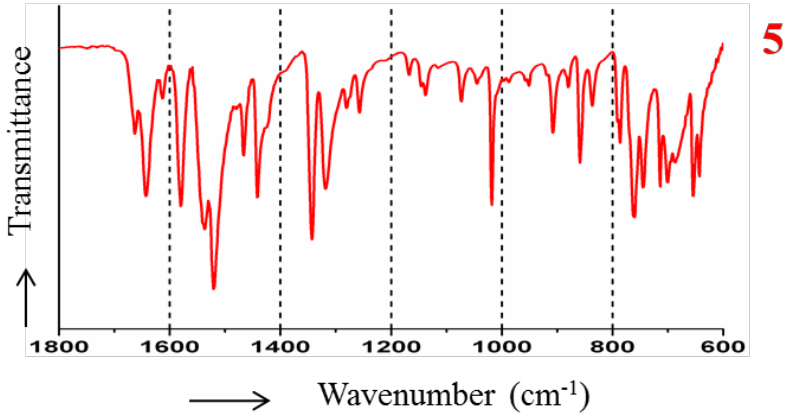
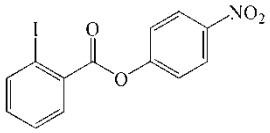


Solid state IR spectrum of **5**.



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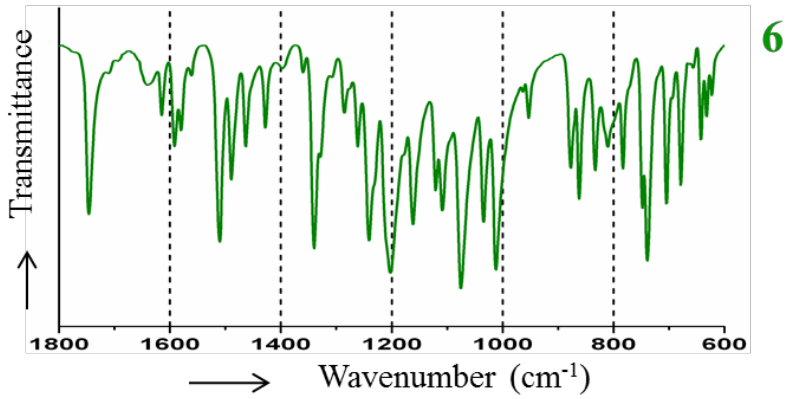
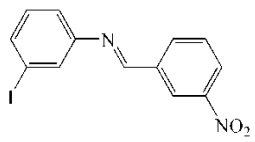


Solid state IR spectrum of **6**.

S5: Full solid state IR spectra of Step 4 compounds



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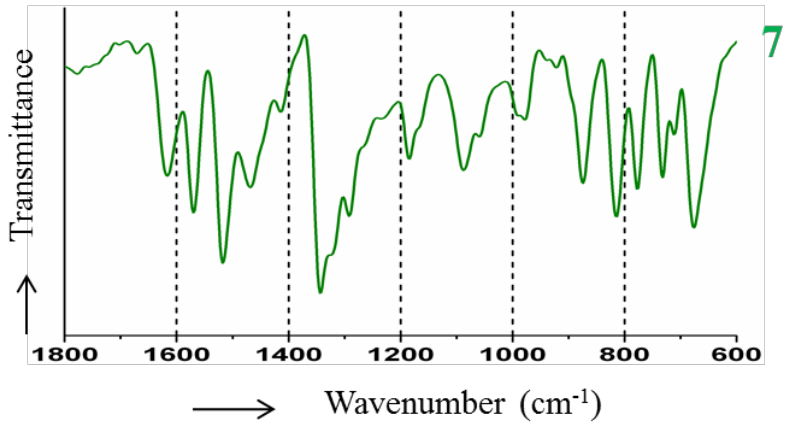
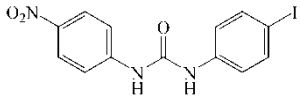


Solid state IR spectrum of **7**.



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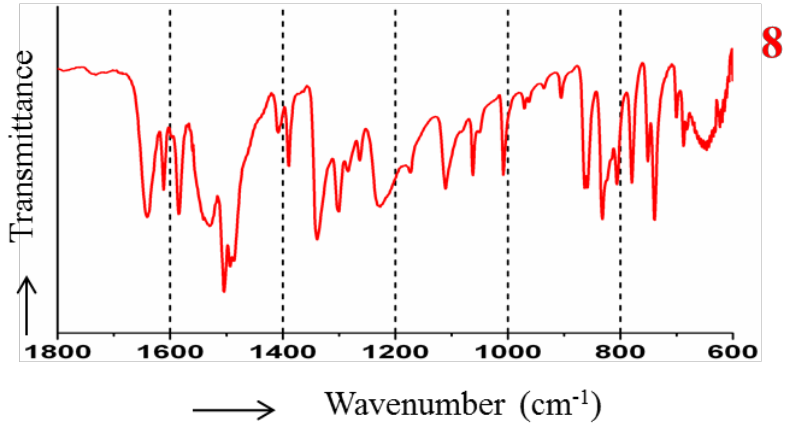
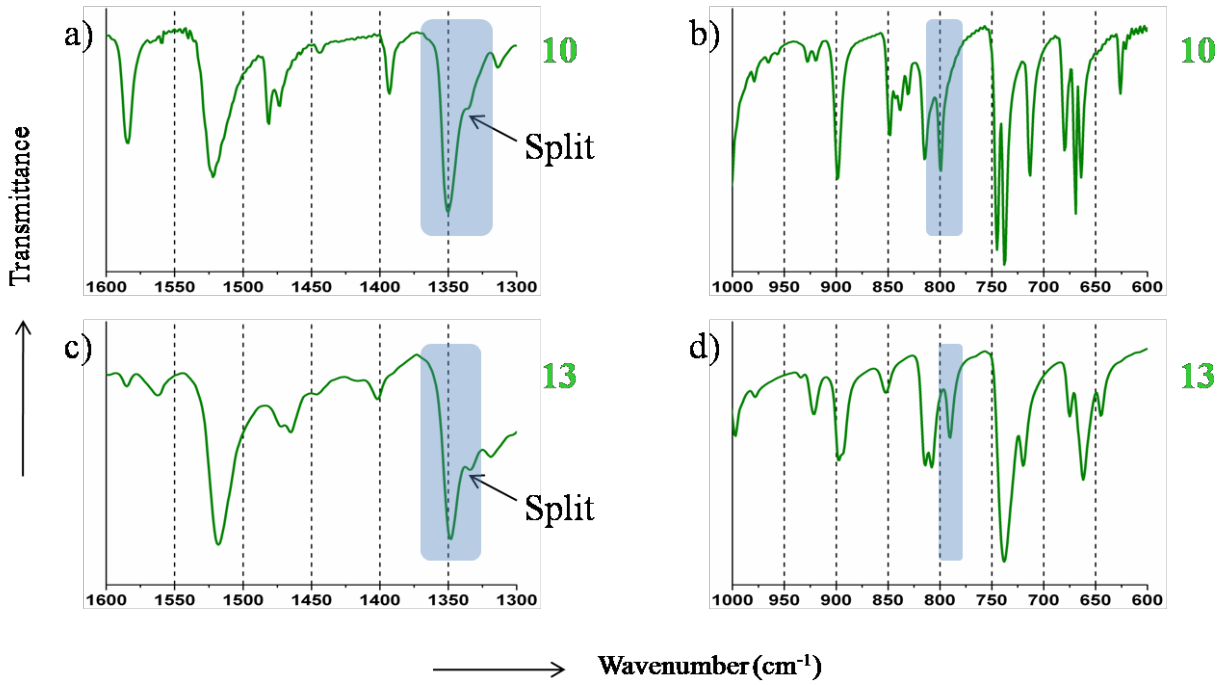
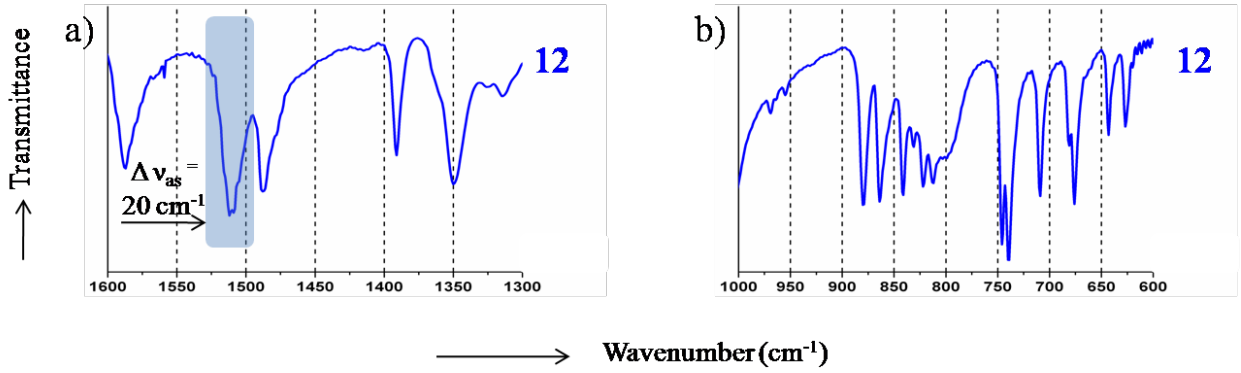


Solid state IR spectrum of **8**.

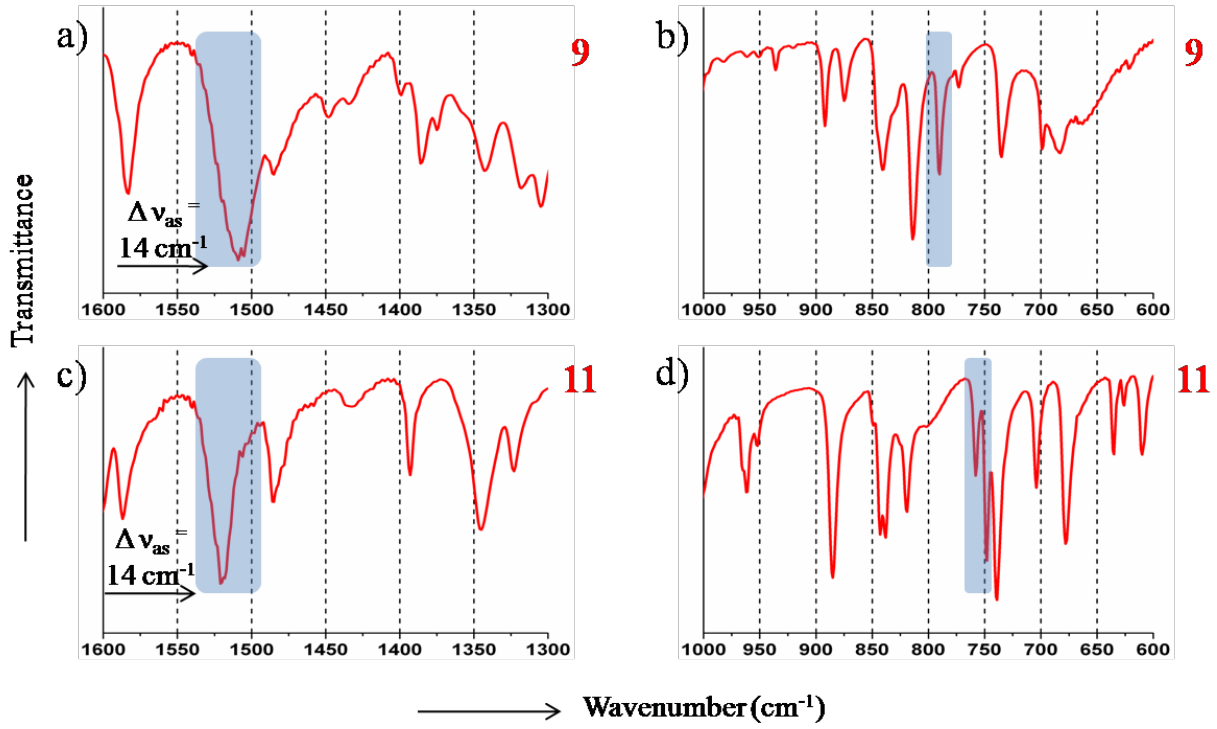
S6: Solid state IR spectra of Step 5 compounds in different regions



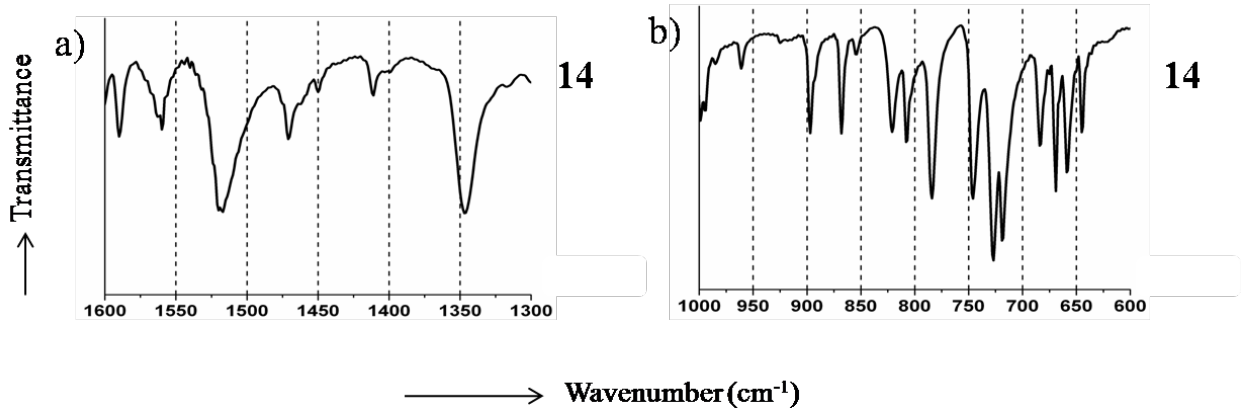
Solid state IR spectra of compounds **10** and **13**. Full spectra are given in supplementary S7.



Solid state IR spectra of compound **12**. Complete spectra are given in supplementary S7.

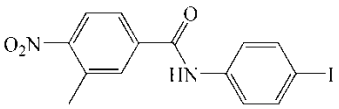


Solid state IR spectra of compounds **9** and **11**. Full spectra are given in supplementary S7.



Solid state IR spectra of compound **14**. Complete spectra are given in supplementary S7.

S7: Full Solid state IR spectra of Step 5 compounds



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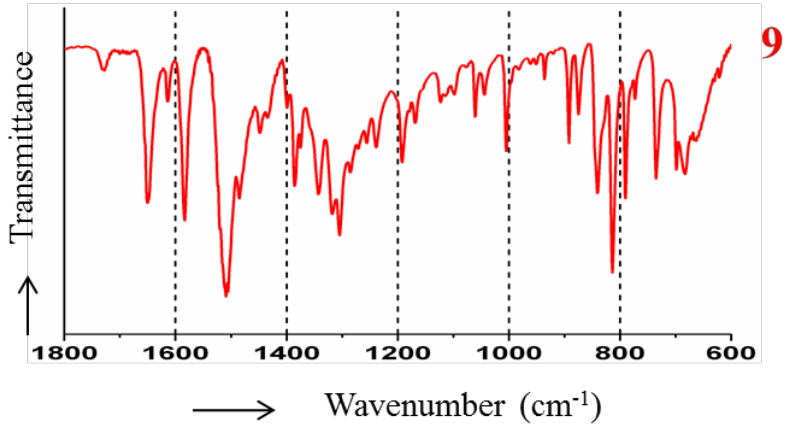
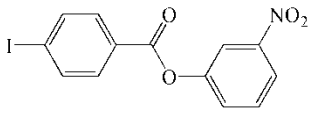


Solid state IR spectrum of **9**.



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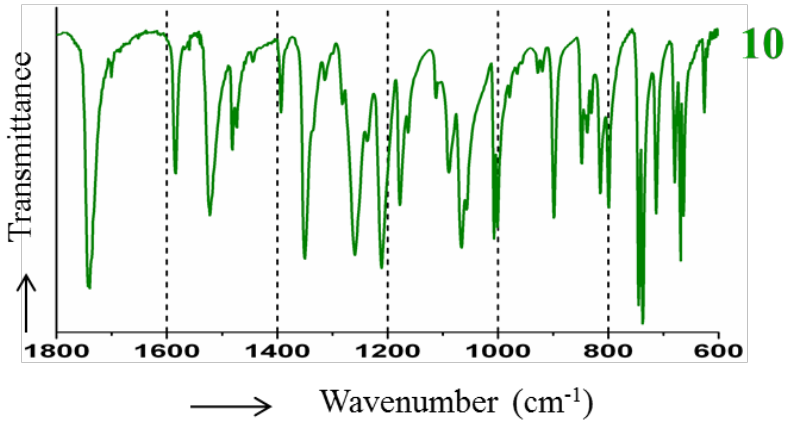
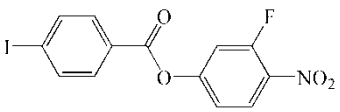


Solid state IR spectrum of **10**.



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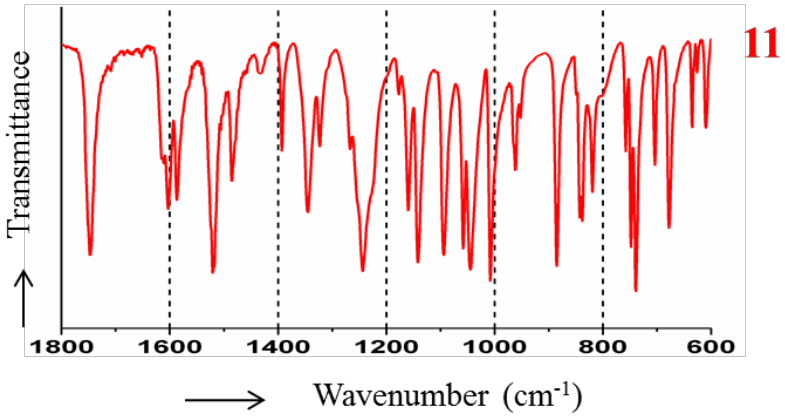
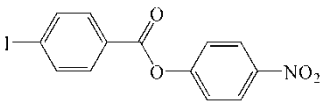


Solid state IR spectrum of **11**.



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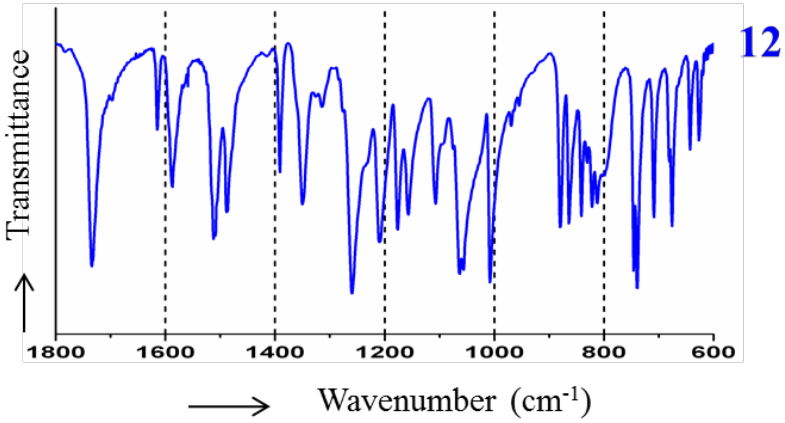
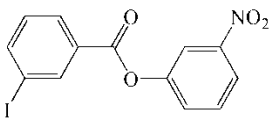


Solid state IR spectrum of **12**.



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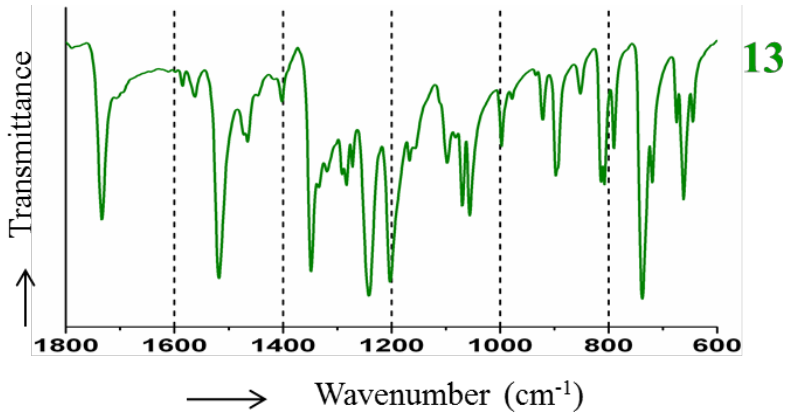
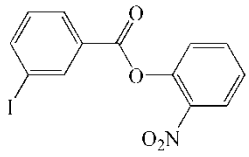


Solid state IR spectrum of **13**.



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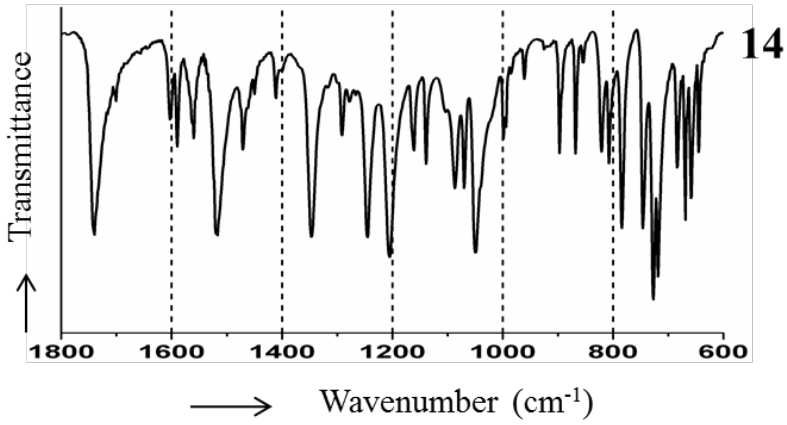
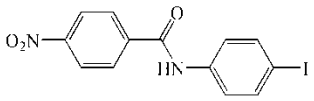


Solid state IR spectrum of **14**.

S8: Solution IR spectra of Step 1 compounds



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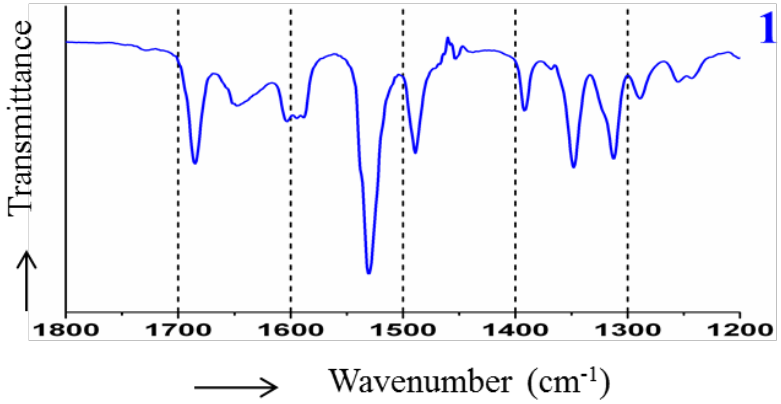
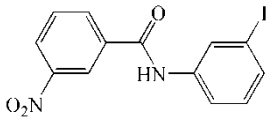


Solution IR spectrum of **1**.



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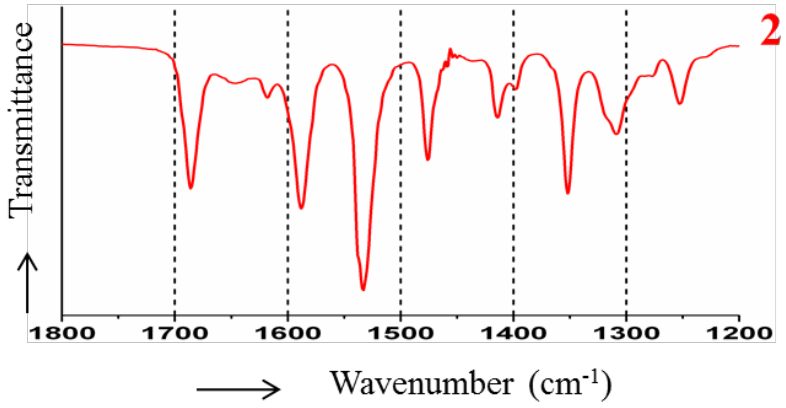
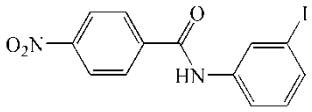


Solution IR spectrum of **2**.



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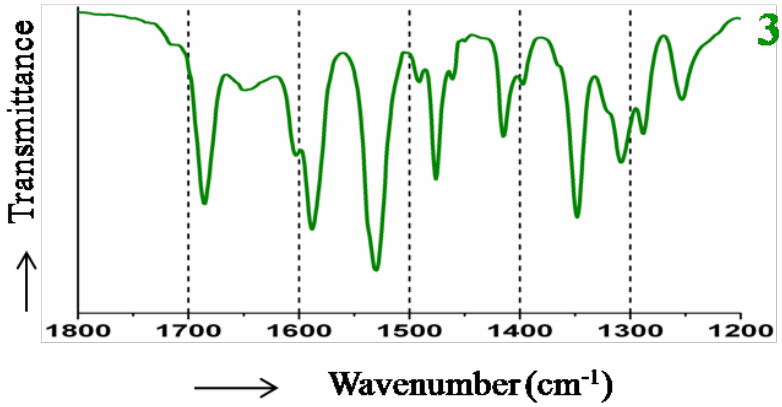
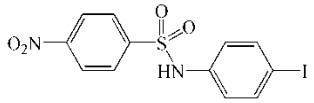


Solution IR spectrum of **3**.

S9: Solution IR spectra of Step 2 compounds



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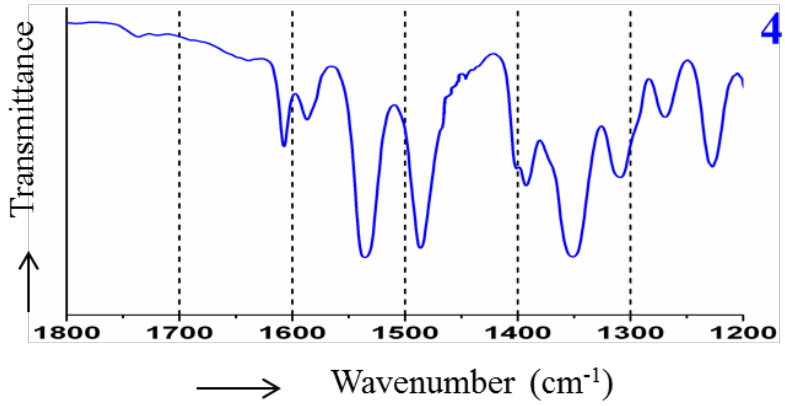
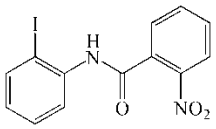


Solution IR spectrum of **4**.



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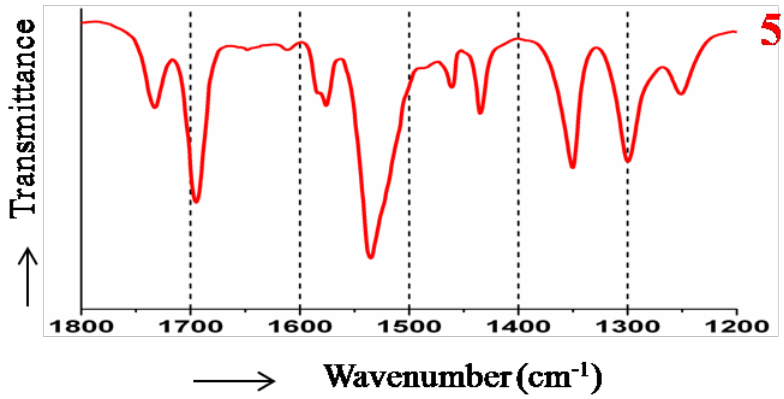
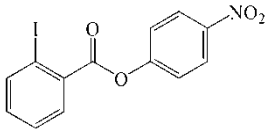


Solution IR spectrum of **5**.



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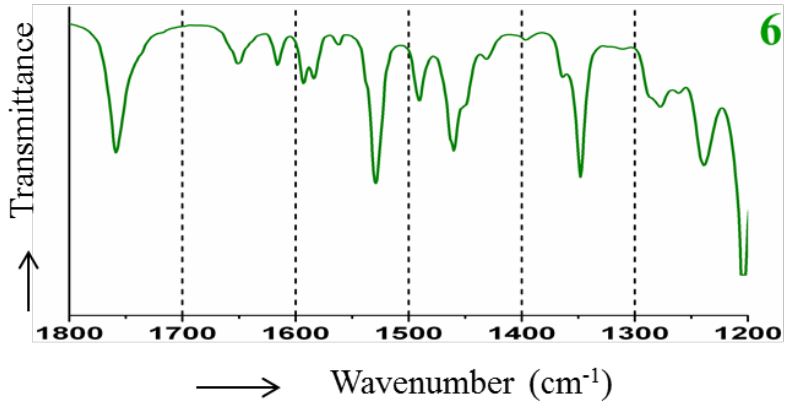
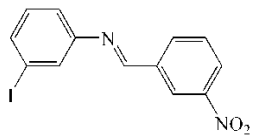


Solution IR spectrum of **6**.

S10: Solution IR spectra of Step 4 compounds



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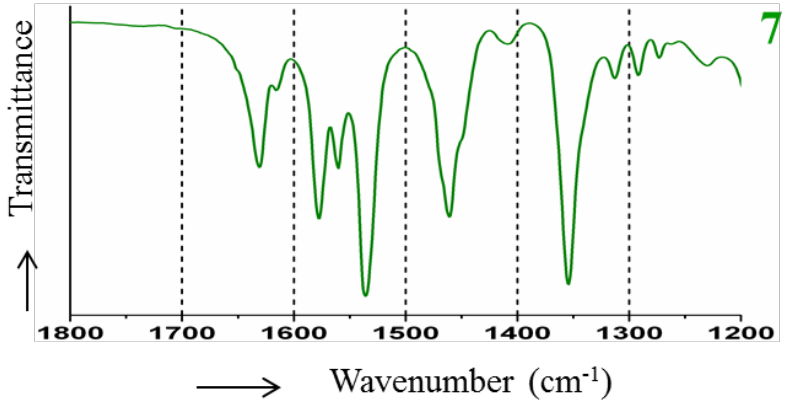
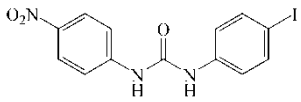


Solution IR spectrum of **7**.



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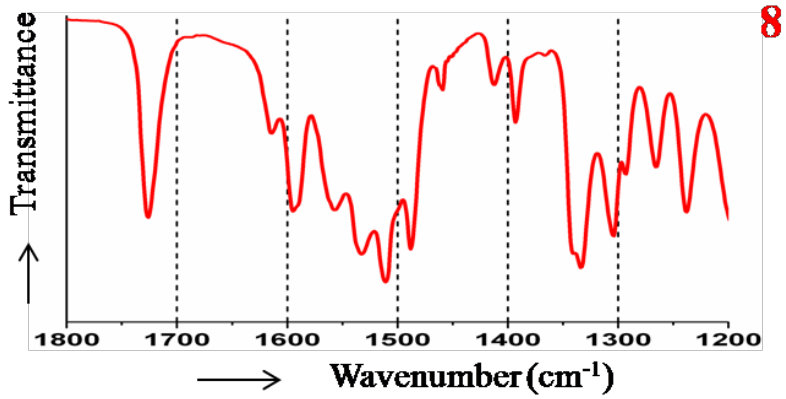
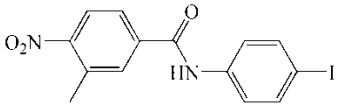
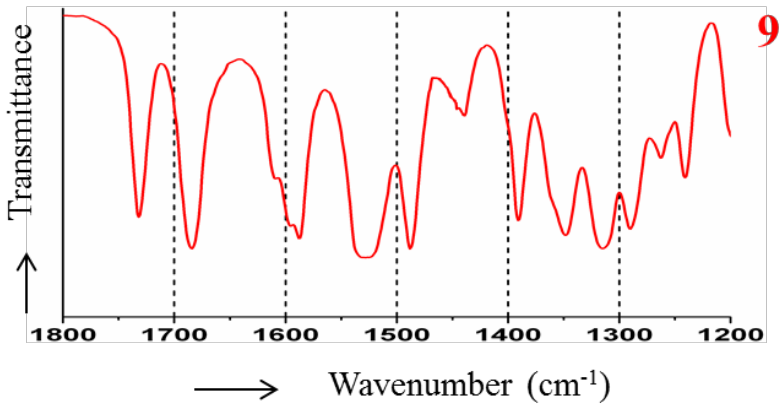


Solution IR spectrum of **8**.

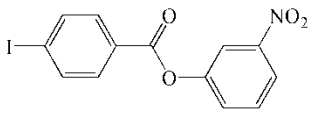
S11: Solution IR spectra of Step 5 compounds



9



Solution IR spectrum of **9**.



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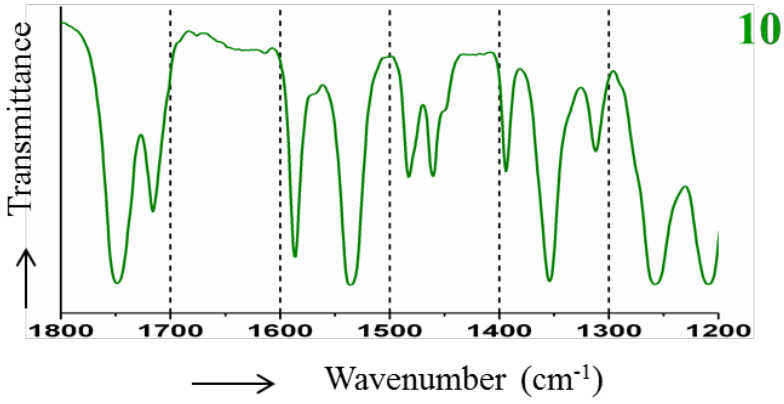
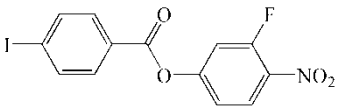
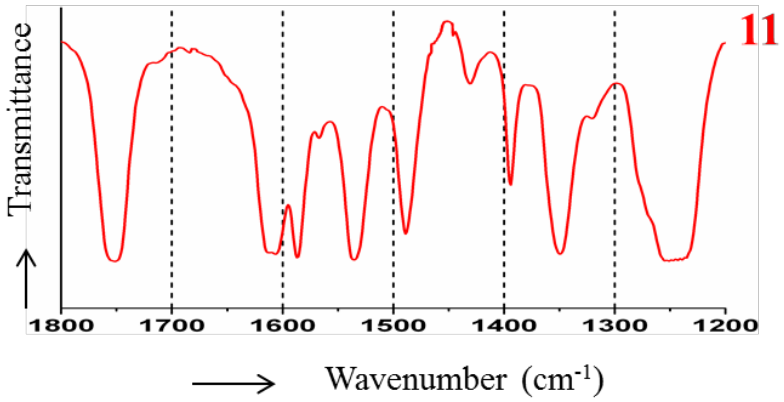


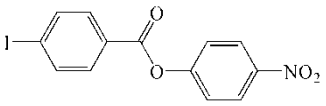
Solution IR spectrum of **10**.



11



Solution IR spectrum of **11**.



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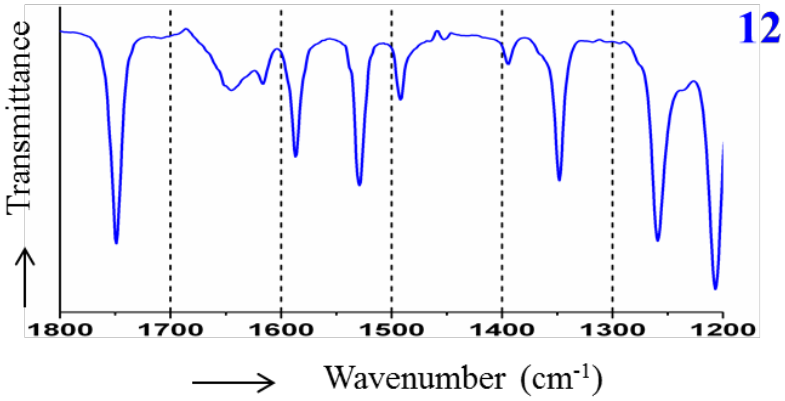
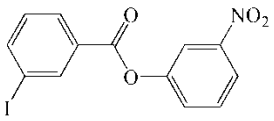


Solution IR spectrum of **12**.



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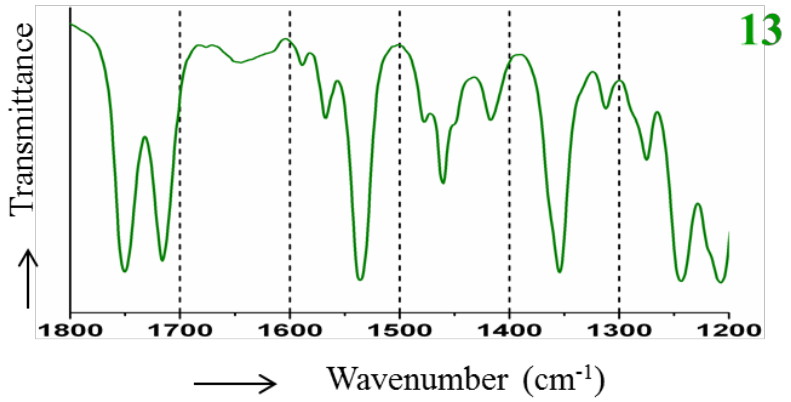
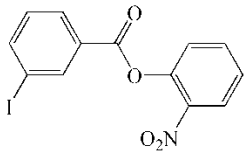
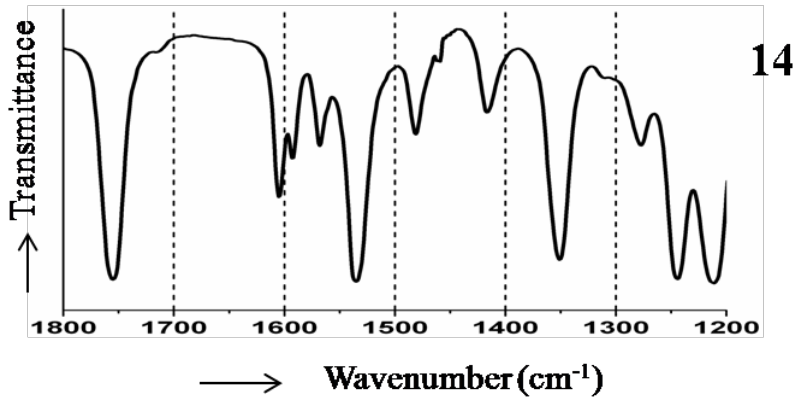


Solution IR spectrum of **13**.



14

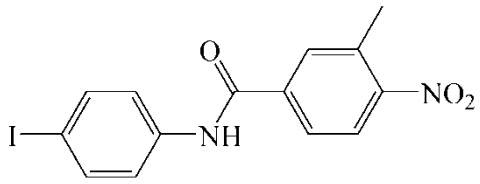


Solution IR spectrum of **14**.

S12: Crystallographic information table

	9	**10**	**11**	**12**	**13**	**14**
Formula	$C_{14}H_{11}IN_2O_3$	$C_{13}H_8INO_4$	$C_{13}H_7FINO_4$	$C_{13}H_8INO_4$	$C_{13}H_8INO_4$	$C_{13}H_8INO_4$
Molecular weight	382.15	369.10	387.10	369.10	369.10	369.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1	$P2_1/c$	P-1
a (Å)	16.732(12)	13.942(8)	9.175(5)	3.978(2)	14.269(6)	7.822(4)
b (Å)	5.122(3)	4.128(2)	9.354(5)	12.694(6)	12.159(5)	9.204(6)
c (Å)	16.293(12)	22.012(12)	15.009(8)	12.733(6)	7.271(3)	9.696(6)
α (°)	90	90	90	100.39(2)	90	89.12(3)
β (°)	102.440(10)	95.060(7)	98.793(7)	94.530(19)	95.714(6)	75.68(3)
γ (°)	90	90	90	97.448(15)	90	70.702(14)
Volume ($Å^3$)	1363.55	1261.91	1272.98	623.633	1255.23	636.675
Z/Z′	4/1	4/1	4/1	2/1	4/1	2/1
ρ_{calc} (g/cm^3)	1.862	1.943	2.020	1.966	1.953	1.925
F(000)	744.0	712.0	744.0	356.0	712.0	356.0
Temp. (K)	150	150	150	150	150	150
R_1	0.0335	0.0333	0.0301	0.0315	0.0288	0.0291
wR_2	0.1220	0.1357	0.1092	0.1207	0.1068	0.1021
Goodness-of fit	1.239	1.227	0.777	1.248	1.204	0.786
CCDC No.	1006583	1006584	1006585	1006586	1006587	1006588

S13: ORTEP Diagrams



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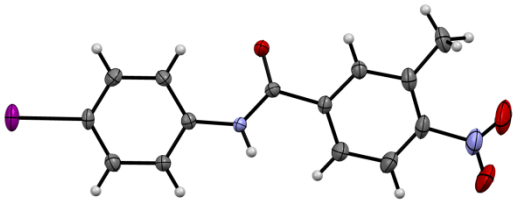

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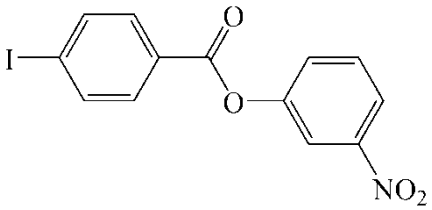

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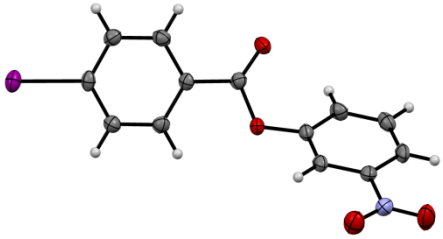

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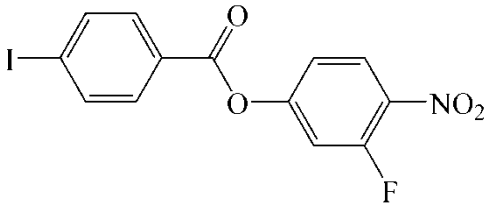

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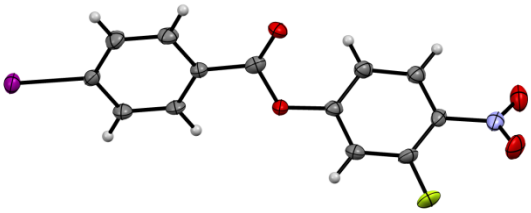

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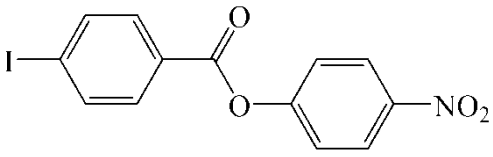

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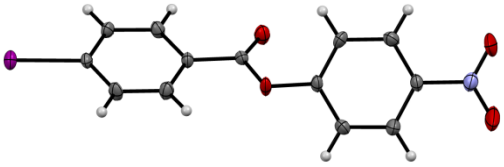

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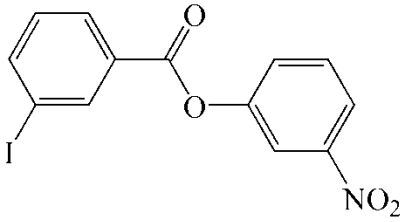

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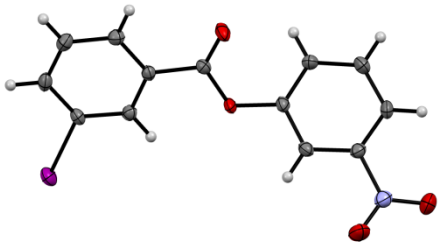

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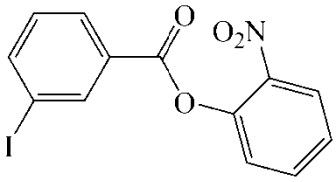

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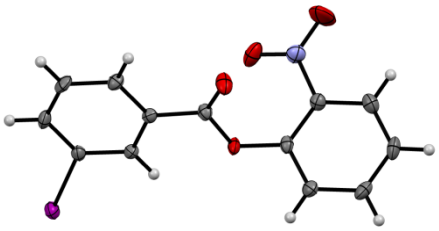

14