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SUPPLEMENTARY INFORMATION

Design, Synthesis and Optical Properties of a Green Fluorescent Photoswitchable Hexaarylbiimidazole (HABI) with Non-Conjugated Design.

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CONTENTS

1. **EXPERIMENTAL:**
   - (a) **GENERAL INFORMATION AND INSTRUMENTATION.**
   - (b) **SYNTHESIS.**
2. **^{1}HNMR SPECTRA.**
3. **MASS SPECTRA.**
4. **FIG. S1- UV-VIS Absorption Spectra of 2,4,5-triphenylimidazole (lophine) and HABI after UV-light irradiation (302 nm) and in darkness at room temperature.**
5. **FIG. S2- UV-VIS Absorption Spectra and the corresponding PL Spectra of NI-HABI before and after UV-light irradiation (302 nm).**
6. **CALCULATION OF FLUORESCENCE QUANTUM YIELDS (Φ_F).**
7. **FLUORESCENCE PHOTOS.**

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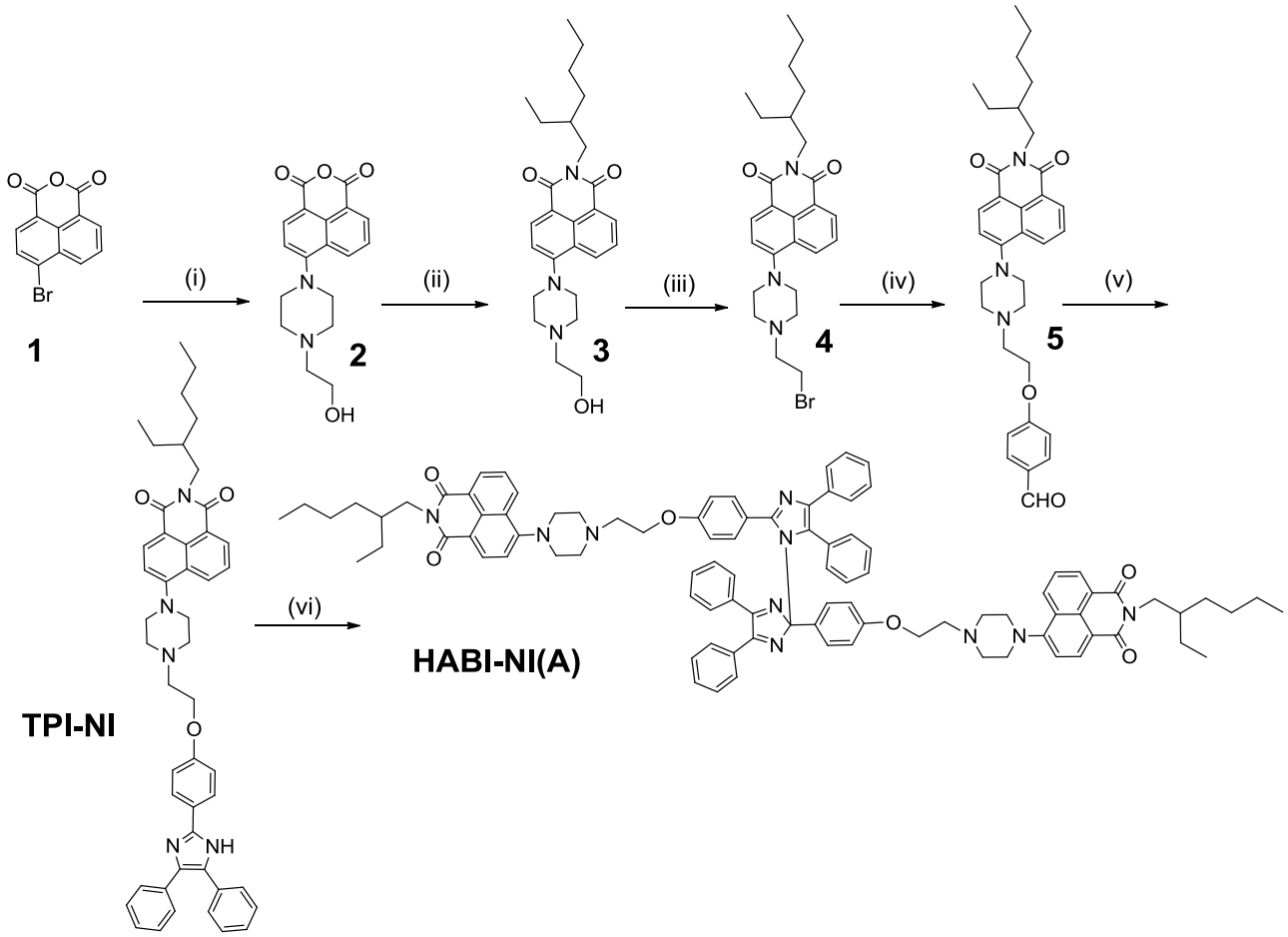
1. EXPERIMENTAL:

a) GENERAL INFORMATION AND INSTRUMENTATION.

Chemicals, reagents and solvents were purchased from Puyang Huicheng Chemical Co. Ltd, Alladin Chemicals, Energy Chemical and Sinopharm Chemical Reagent Co.,Ltd. and used without further purification, unless otherwise stated. Chloroform and DMF were dried over CaH_2 with stirring overnight followed by distillation. THF and toluene were dried and purified using sodium-benzophenone system followed by distillation.

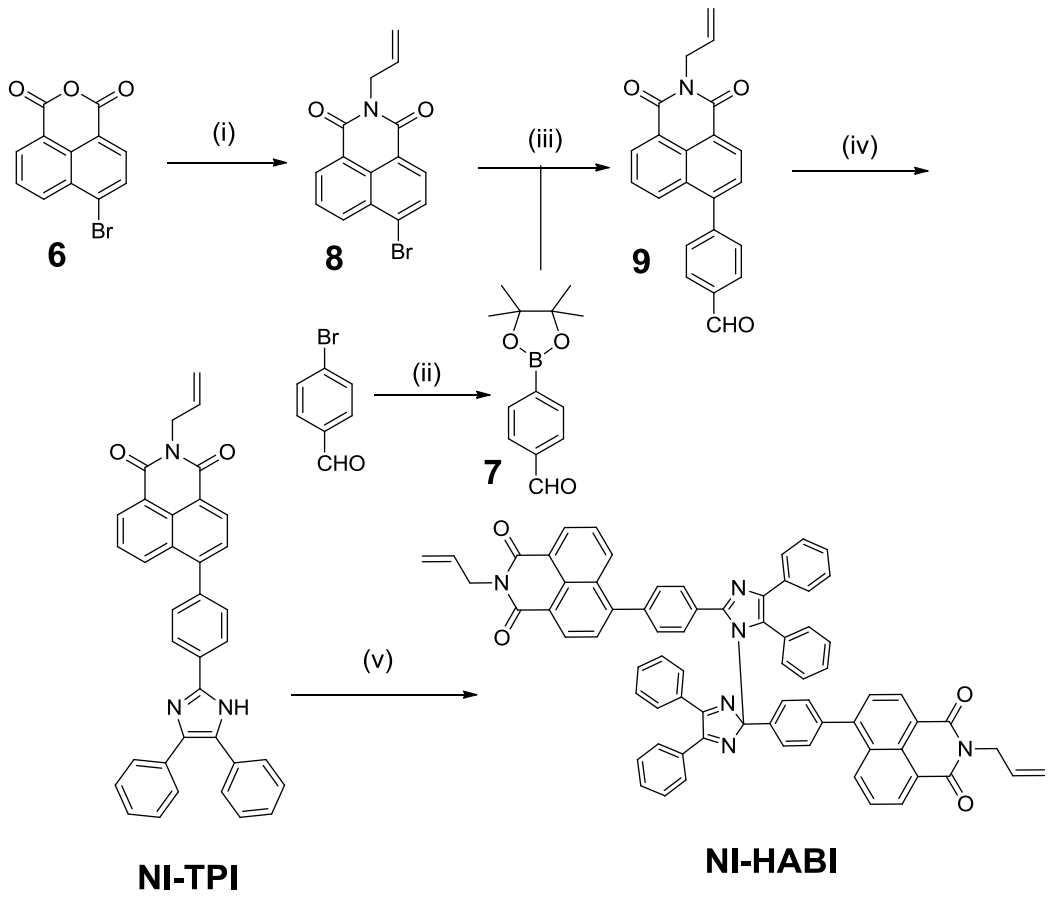
^{1}H-NMR and ^{13}C-NMR spectra were recorded using a 400M Bruker AV400 in $CDCl_3$ or CD_2Cl_2 and an internal standard of tetramethylsilane was used. Mass spectra were recorded using an Agilent 1100 LC/MSD Trap. Purification of intermediates and final products was accomplished mainly by gravity column chromatography, using silica gel (200-300 mesh). The purity of all final compounds was checked by elemental analysis (Elementar Vario Micro-cube). The UV-VIS spectra were recorded using a Shimadzu UV-vis-NIR Spectrophotometer (UV-3600). The PL spectra were recorded using Edinburgh instruments (FLSP920 spectrometers). The 302 nm/365 nm UV irradiation for the HABI cleavage reaction was performed using an ultraviolet transmission platform (UVP Transilluminator). Abbreviations; NI-TPI (naphthalene monoimide triphenyl imidazole), NI-HABI (naphthalene monoimide hexaarylbiimidazole), TPI (triphenyl imidazole), HABI (hexaarylbiimidazole).

b) SYNTHESIS (PART A, HABI-NI(A)) .



Scheme S1: Reagents and conditions: (i) *N*-(2-hydroxyethyl)-piperazine, 2-methoxyethanol, reflux, 12 h, (ii) 2-ethyl-1-hexylamine, ethanol, reflux, 10 h, (iii) PBr_3, chloroform, 0-5 ^oC (0.5 h) to reflux (5 h), (iv) 4-hydroxybenzaldehyde, DMF, 100 ^oC, 1 day (v) benzil, ammonium acetate, acetic acid, 90 ^oC, 12 h, (vi) potassium ferricyanide, KOH, benzene, r.t. 1day.

b) SYNTHESIS (PART B, NI-HABI) .



Scheme S2: Reagents and conditions: (i) 3-aminopropene, NMP, acetic acid, 90 ^{o}C, 8 h, (ii) bis (pinacolato)diboron, KOAc, Pd(dppf)Cl_2, DMF, 90 ^{o}C, 1 day, (iii) K_2CO_3, Pd(PPh_3)$_4$, tetrabutylammonium hydrogen sulfate, toluene, 90 ^{0}C, 12 h, (iv) benzil, ammonium acetate, acetic acid, 90 ^{o}C,1 day, (v) potassium ferricyanide, KOH, benzene, r.t. 1 day.

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SYNTHESIS PROCEDURES

Compound 2

6-Bromobenzo[de]isochromene-1,3-dione (**1**) (10.0 g, 36.1 mmol) and N-(2-hydroxyethyl)-piperazine (9.4 g, 72.2 mmol) were dissolved in 80 mL 2-methoxyethanol. The mixture was stirred and heated to reflux for 12 h. After the reaction was finished, the deep dark brown solution was cooled to room temperature and added to 500 mL distilled water dropwise and large amount of small yellow precipitate formed. The precipitate was collected by suction filtration, washed with a large amount of distilled water and dried to yield a yellow brown solid (9.5 g, 80.5 %). Since this yellow solid is very insoluble in normal organic solvent, it is used for the next step without further purification and characterisation.

Compound 3

2 (3.3 g, 10 mmol) and 2-ethyl-1-hexylamine (1.4 g, 11 mmol) was dissolved in 40 mL ethanol. The mixture was stirred and heated to reflux for 10 h. After the reaction was finished, the solvent ethanol was removed and directly purified by silica gel column chromatography using eluent: 5% methanol-95% dichloromethane (v/v) to yield a yellow solid (4.15 g, 94 %).
^{1}H-NMR ($CDCl_3$, 400MHz): δ8.58 (d, 1H, J=1.2Hz), δ8.56 (d, 1H, 1.2Hz), δ8.40 (m, 1H), δ7.70 (m, 1H), δ7.23 (d, 1H, J=8Hz), δ4.12 (m, 2H), δ3.73 (t, 2H, d=5.2Hz), δ3.33 (s, 4H), δ2.89 (s,4H), δ2.75 (t, 3H), δ1.90 (m, 1H), δ1.38 (m, 1H), δ0.94 (m, 6H).
MS m/z (APCI): calculated 437.57, found 438.3 [M+1]

Compound 4

3 (2.0 g, 4.6 mmol) was dissolved in 50 mL distilled chloroform and cooled in an ice-water bath (0-5℃). Phosphorus (Ⅲ) bromide (PBr_3) (0.65 mL, 6.9 mmol) was added dropwise into this solution over 10 mins period. The mixture was stirred at 0-5℃ for another 30 mins, then heated to reflux for 6 h. After the reaction was finished, silica gel was added and the chloroform removed under reduced pressure. The residue was purified by silica gel column chromatography using eluent: 6% methanol in dichloromethane (v/v) to yield a yellow solid (1.8 g, 78.3 %).
^{1}H-NMR ($CDCl_3$, 400MHz): δ8.60 (d, 1H, J=6.8Hz), δ8.54 (d, 1H, J=8Hz), δ8.35 (d, 1H, J=8.4Hz), δ7.74 (t, 1H, J=8Hz), δ7.30 (d, 1H, 7.6Hz), δ4.16 (m, 2H), δ3.20-3.70 (m, 12H), δ1.95 (m, 1H), δ1.40 (m, 1H), δ0.94 (m, 6H).
MS m/z (APCI): calculated 500.47, found 500.21 [M^+]

Compound 5

4 (1.0 g, 2 mmol), 4-hydroxybenzaldehyde (0.27g, 2.2mmol) and potassium carbonate (1.7g, 12mmol) were dissolved in 50 mL distilled *N*,*N*-dimethylformamide. The system was evacuated using vacuum and saturated with N_2 for few times and then stirred and heated to 100 ℃ for 1 day. After the reaction was finished, the solvent was removed by reduced pressure distillation and purified by silica gel column chromatography using eluent: 6% methanol in dichloromethane (v/v) to yield a light yellow oil (1.06 g, 95.4 %) and this oil is used for next step directly.

TPI-NI

5 (1.06 g, 2 mmol), benzil (0.84 g, 4 mmol) and ammonium acetate (3.1 g, 40 mmol) were dissolved in 40 mL acetic acid. The reaction mixture was stirred and heated to 90 ℃ for 1 day. After the reaction was finished, the mixture was dropped into saturated aqueous $NaHCO_3$ solution (100mL) and then extracted by dichloromethane (3 × 100mL). The organic phases were washed with water (3 × 100mL) and dried over $MgSO_4$. After the solvent was removed, the residue was purified using silica gel column chromatography using eluent: 10% acetone-90% dichloromethane (v/v) to yield a yellow orange powder (1.1 g, 76.9 %).
^{1}H-NMR ($^{d-}$DMSO, 400MHz): δ12.50 (s, 1H), δ8.48 (t, 2H), δ8.40 (d, 2H, J=8.08Hz), δ8.04 (d, 2H, J=8.84Hz), δ7.83 (m, 1H), δ7.56 (d, 2H, J=7.36Hz), δ7.51 (d, 2H, J=7.28Hz), δ7.46 (t, 2H, J=7.32Hz), δ7.28-7.38 (m, 4H), δ7.23 (t, 1H, J=7.28Hz), δ7.10 (d, 2H, J=8.92Hz), δ4.24 (t, 2H, J=5.56Hz), δ4.0 (m, 2H), δ3.27 (s, 4H), δ2.90 (m, 6H, overlap), δ1.85 (t, 1H, J=6.12Hz), δ1.30 (m, 8H), δ0.85 (m, 6H, CH_3).
MS m/z (APCI): calculated 731.92, found 732.7 [M+1]

HABI-NI(A)

TPI-NI (0.20 g, 0.27 mmol), potassium ferricyanide (3.8 g, 11.5mmol) and potassium hydroxide (1.9 g, 33.8 mmol) were dispersed in 40 mL benzene and 10 mL distilled water. The reaction flask was covered with aluminum foil and vigorously stirred at room temperature for 12 h. After the reaction was finished, the water layer was removed and the organic layer washed with a large amount of distilled water. The toluene was dried ($MgSO_4$), filtered and evaporated under reduced pressure to yield a yellow powder (0.15 g, 75 %).
^{1}H-NMR ($^{d-}$DMSO, 400MHz): δ8.47 (t, 4H), δ8.40 (d, 4H, J=8.08Hz), δ8.04 (d, 4H, J=8.84Hz), δ7.83 (m, 2H), δ7.56 (d, 4H, J=7.36Hz), δ7.51 (d, 4H, J=7.28Hz), δ7.46 (t, 4H, J=7.32Hz), δ7.28-7.38 (m, 4H), δ7.23 (t, 2H, J=7.28Hz), δ7.10 (d, 4H, J=8.92Hz), δ4.24 (t, 4H, J=5.56Hz), δ4.0 (m, 4H), δ3.27 (s, 8H), δ2.90 (m, 12H, overlap), δ1.85 (t, 2H, J=6.12Hz), δ1.30 (m, 16H), δ0.85 (m, 12H,CH_3).
^{13}C-NMR (100MHz, $^{d-}$DMSO): 164.4, 163.8, 159.1, 156.1, 146.1, 137.2, 135.8, 132.7, 131.7, 131.2, 131.0, 129.6, 129.1, 128.8, 128.6, 128.1, 127.5, 127.2, 126.9, 126.5, 125.8, 123.6, 123.0, 116.0, 115.5, 115.1, 66.1, 57.0, 53.5, 53.1, 43.5, 30.7, 28.6, 24.1,

22.9, 14.4, 11.0
MS m/z (APCI): calculated 1461.83, found 1462.2 [M+1].
Elemental analysis: (expected) C (77.23 %), H (6.62 %), N (9.58 %), O (6.57 %); (obtained) C (77.31 %), H (6.53 %), N (9.50 %), O (6.60 %);

Compound 7

6-Bromobenzo[de]isochromene-1,3-dione (**6**, 8.0 g, 28.9 mmol) and 3-aminopropene (1.81g, 31.8 mmol) were dispersed in 80 mL *N*-methyl-2-pyrrolidone and 15 mL acetic acid. The mixture was stirred and heated to 90 ℃ for 8 h. After the reaction was finished, the solution was poured into 250 mL saturated salt water and the grey precipitate collected by suction filtration and washed with distilled water (3×100 mL). After drying the crude product was purified by silica gel column chromatography using eluent: 50% chloroform-50% petroleum ether (v/v) to yield a white solid (7.8 g, 85.7 %).
^{1}H-NMR (400MHz, $CDCl_3$): δ8.65 (1H, dd, J=1.2Hz), δ8.55 (1H, dd, J=1.2Hz), δ8.40 (1H, d, J=8Hz), δ8.02 (1H, d, J=8Hz), δ7.85 (1H, m), δ6.0 (1H, m), δ5.3 (1H, m), δ5.2 (1H, m), δ4.80 (2H, m).
MS m/z (APCI): calculated 316.15, found 319.0 [M^+].(isotope of Br 79 and 81)

Compound 8

4-Bromobenzaldehyde (3.70 g, 20 mmol), bis(pinacolato)diboron (7.60 g, 30 mmol), potassium acetate (7.85 g, 80 mmol) and Pd(dppf)Cl_2 (0.82 g, 1 mmol) were added to a 250 mL round-bottomed flask with 100 mL dry DMF. Under a N_2 atmosphere, the solution was heated to 90℃ and stirred for 8 h. After the reaction was finished, the liquid was poured into saturated salt water (100 ml), and extracted into diethyl ether (200 ml × 3), dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography using eluent: 40 % DCM-60 % hexane (v/v) to yield a white sticky solid (3.51 g, 74 %).
^{1}H-NMR ($CDCl_3$, 400MHz): δ10.05 (s, 1H), δ7.97 (d, 2H, J=7.6Hz), δ7.87 (d, 2H, J=7.6Hz), δ1.26(s, 12H)
MS m/z (APCI): calculated 232.08, found 232.9 [M+1].

Compound 9

7 (0.5 g, 1.6 mmol), **8** (0.4 g, 1.7 mmol), potassium carbonate (1.3 g, 9.6 mmol), $Pd(PPh)_3)_4$ (0.05 g, 0.04 mmol) and tetrabutylammonium hydrogen sulfate (0.05 g, 0.15 mmol) were dispersed in 50 mL distilled toluene and 10 mL deionised water. The system was evacuated using vacuum and saturated with N_2 for few times and then the reaction mixture was heated to 90℃ and stirred for 12h. After the reaction was finished, the water layer was removed and the organic layer

washed with water, dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using eluent: 100% dichloromethane to yield a light yellow solid (0.40 g, 74 %).
^{1}H-NMR (400MHz, $CDCl_3$): δ10.16 (s, 1H), δ8.70 (t, 1H, J=7.2Hz), δ8.20 (d, 1H, J=8.4Hz), δ8.09 (1H, d, J=8Hz), δ7.76 (m, 4H), δ6.0 (m, 1H), δ5.38 (dd, 1H, J=1.2Hz), δ5.25 (dd, 1H, J=1.2Hz), δ4.85 (d, 2H, J=6Hz)
MS m/z (APCI): calculated 341.36, found 342.5 [M+1].

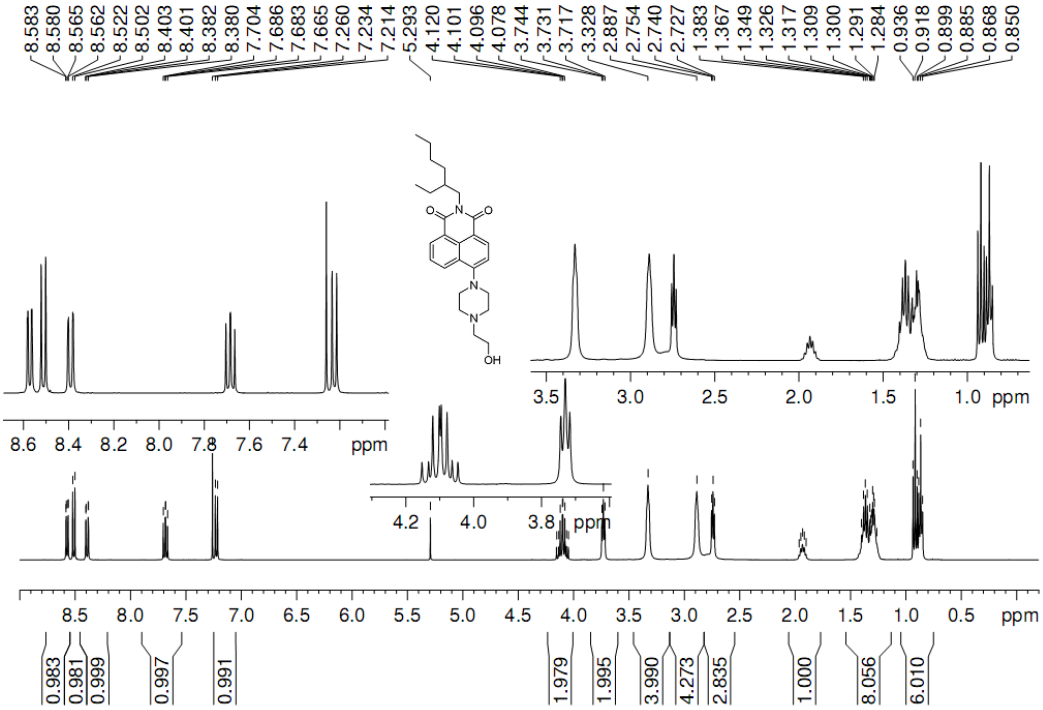
NI-TPI

9 (0.34 g, 1 mmol), benzil (0.25 g, 1.2 mmol) and ammonium acetate (1.54 g, 20 mmol) were dispersed in 25 mL acetic acid. The mixture was heated to 90℃ and stirred for 12 h. After the reaction was finished the solution was poured into 200 mL saturated aqueous $NaHCO_3$ solution and the large amount of yellow precipitate formed was collected by suction filtration and washed with distilled water (3×100 mL). This crude solid was purified by silica gel column chromatography using eluent: 5% acetone-95% dichloromethane (v/v) to yield a yellow solid (0.35 g, 66 %).
^{1}H-NMR (400MHz, $^{d-}$DMSO): δ12.89 (s, 1H), δ8.60 (s, 1H), δ8.40 (m, 3H), δ7.93 (d, 2H, J=7.12Hz), δ7.74 (d, 2H, J=7Hz), δ7.60 (m, 4H), δ7.49 (m, 2H), δ7.42 (m, 1H), δ7.35 (m, 2H), δ7.27 (m, 1H), δ5.99 (m, 1H), δ5.22 (m, 2H), δ4.72 (m, 2H).
MS m/z (APCI): calculated 531.6, found 532.5 [M+1].

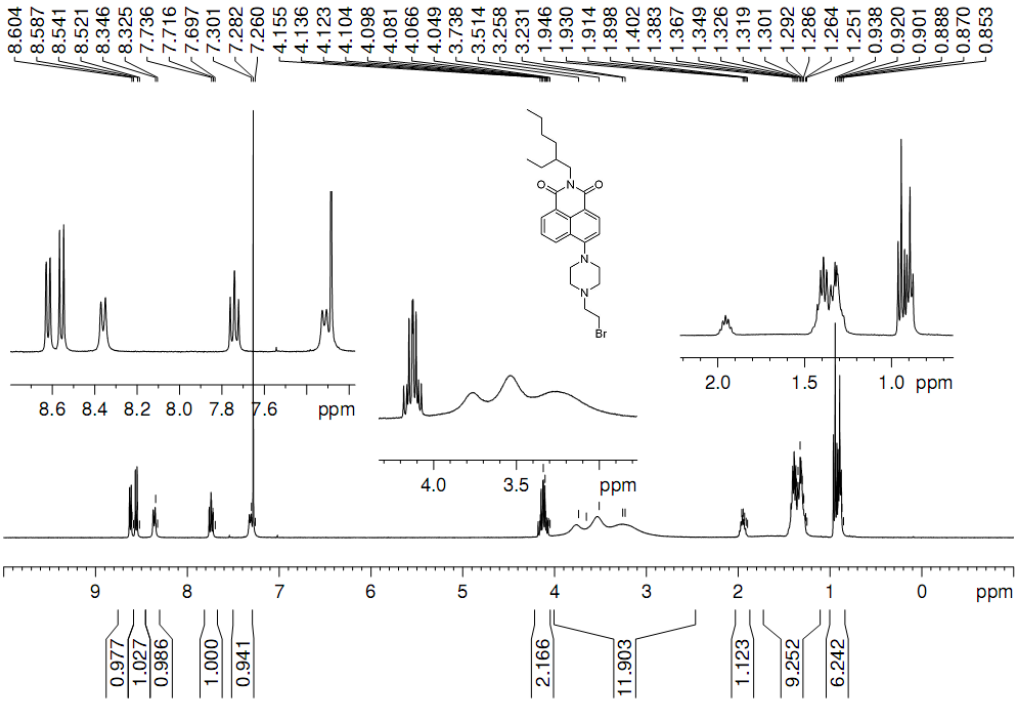
NI-HABI

NI-TPI (0.3 g, 0.56 mmol), potassium hydroxide (4.0 g, 70.6 mmol) and potassium ferricyanide (8.0 g, 24.3 mmol) were dispersed in 40 mL benzene and 10 mL distilled water. The reaction flask was covered using aluminum foil and vigorously stirred at room temperature for 12 h. After the reaction was finished the water layer was removed and the organic layer washed with a large amount of distilled water. The organic layer was dried ($MgSO_4$), filtered and removed under reduced pressure to yield a yellow-brown powder (0.23 g, 76.7 %).
^{1}H-NMR (400MHz, $^{d-}$DMSO): δ8.2-8.7 (m, 4H), δ7.7-8.2 (m, 4H), δ6.8-7.7 (m, 30H), δ5.92 (m, 2H), δ5.12 (m, 4H), δ4.63 (m, 4H)
MS m/z (APCI): calculated 1061.19, found 1062.2 [M+1].
Elemental analysis: (expected) C (81.49 %), H (4.56 %), N (7.92 %), O (6.03 %); (obtained) C (81.56 %), H (4.49 %), N (7.85 %), O (6.23 %);

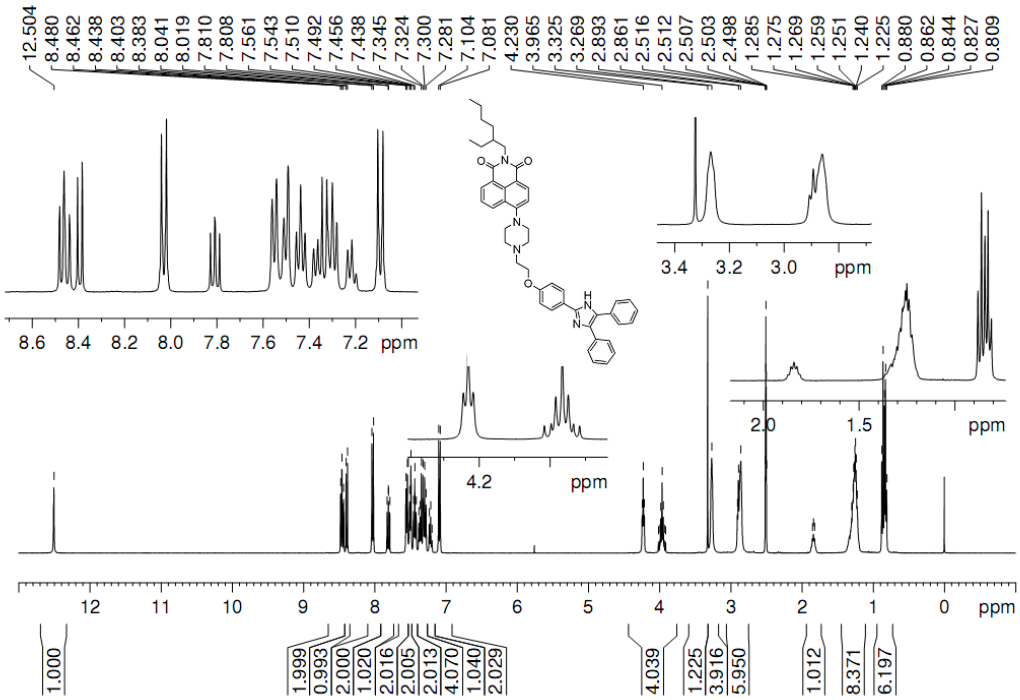
2. ^{1}H-NMR SPECTRA



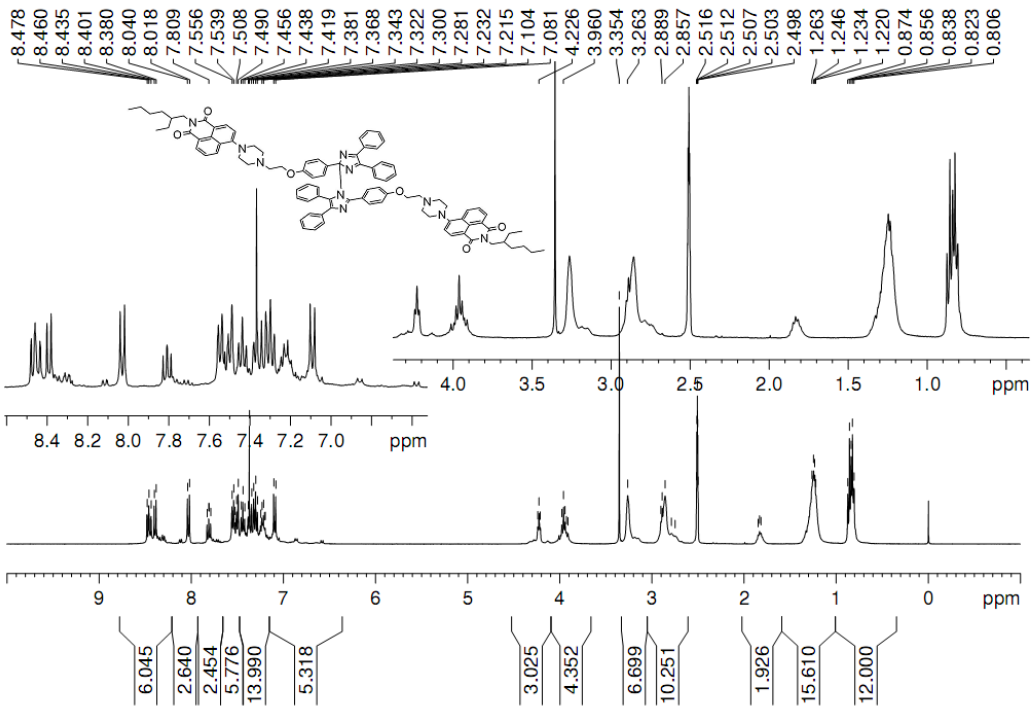
^{1}H-NMR spectrum of Compound 3 (solvent $CDCl_3$)



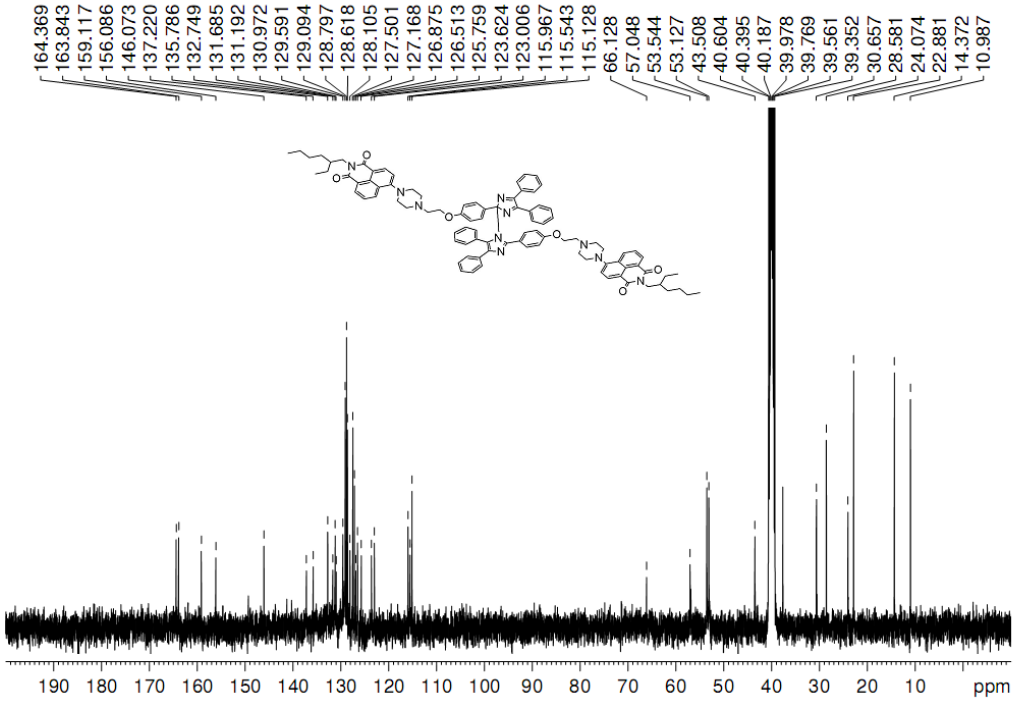
^{1}H-NMR spectrum of Compound 4 (solvent $CDCl_3$)



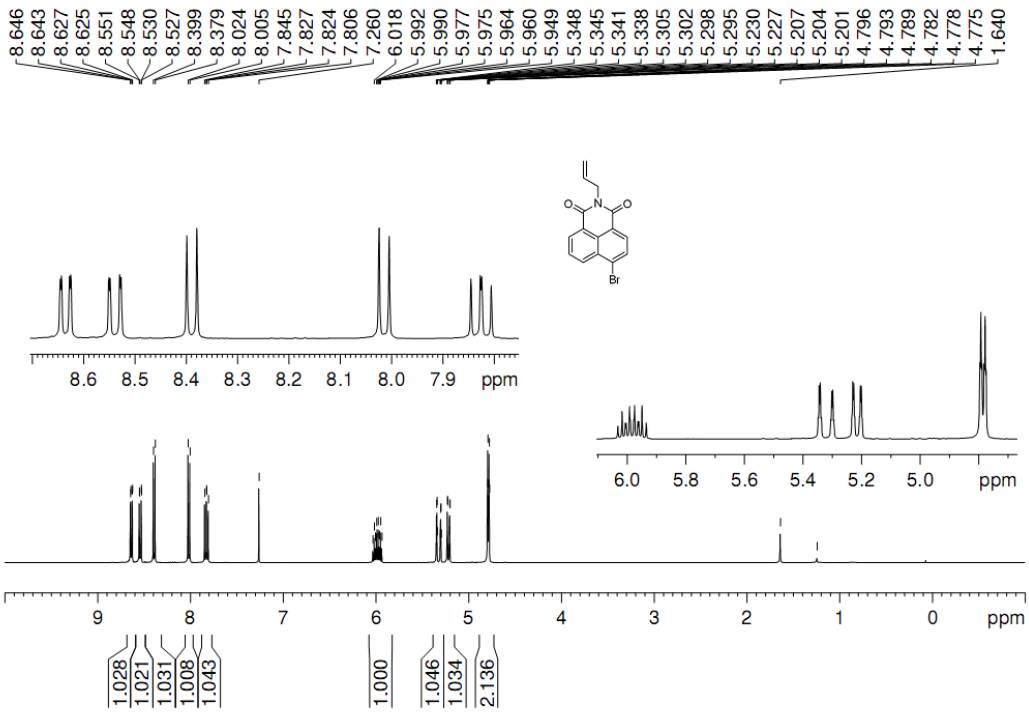
^{1}H-NMR spectrum of Imidazole-NI (solvent ^{d}-DMSO)



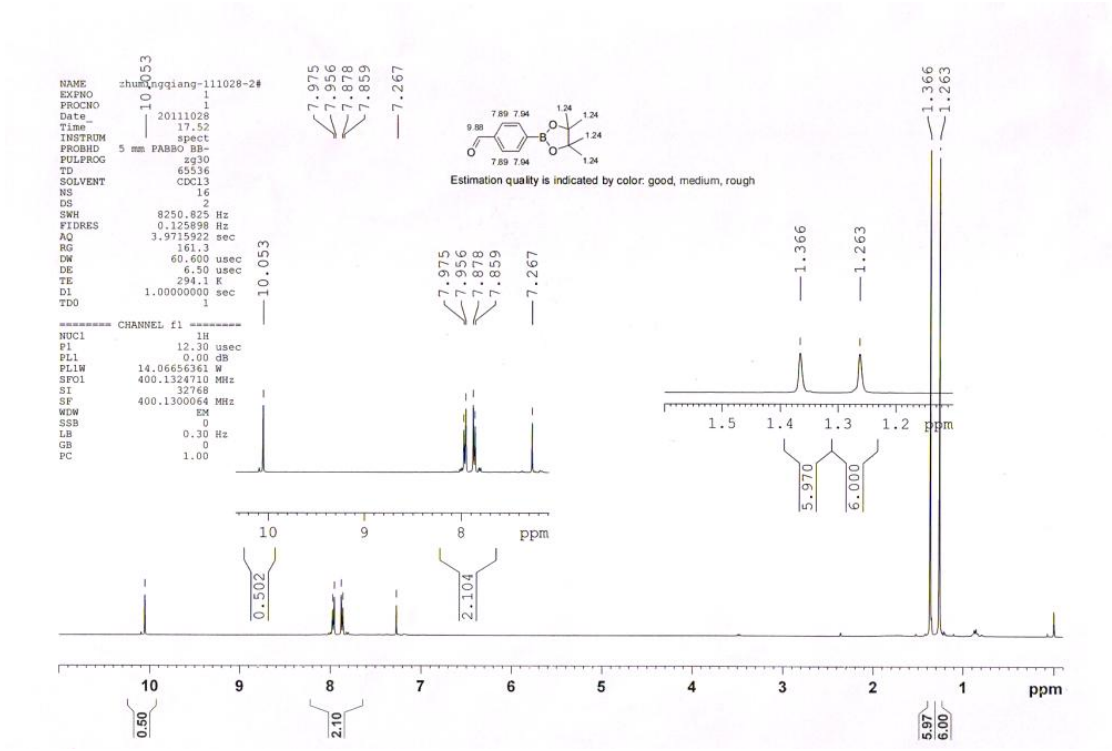
^{1}H-NMR spectrum of HABI-NI (A) (solvent ^{d}-DMSO)



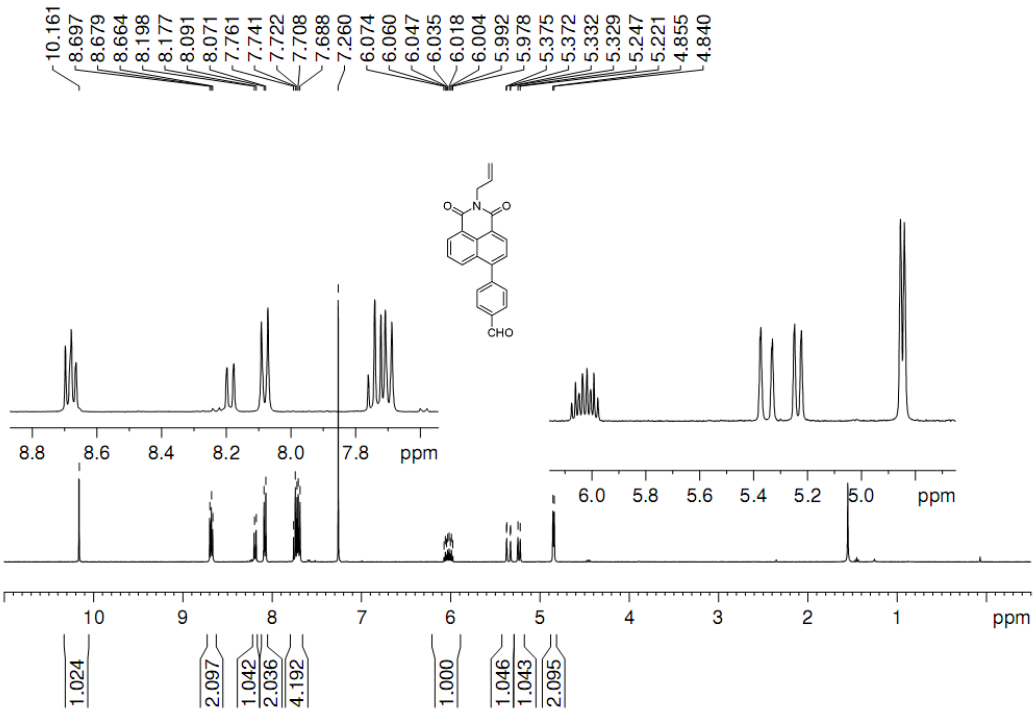
^{13}C-NMR spectrum of HABI-NI (A) (solvent ^{d}-DMSO)



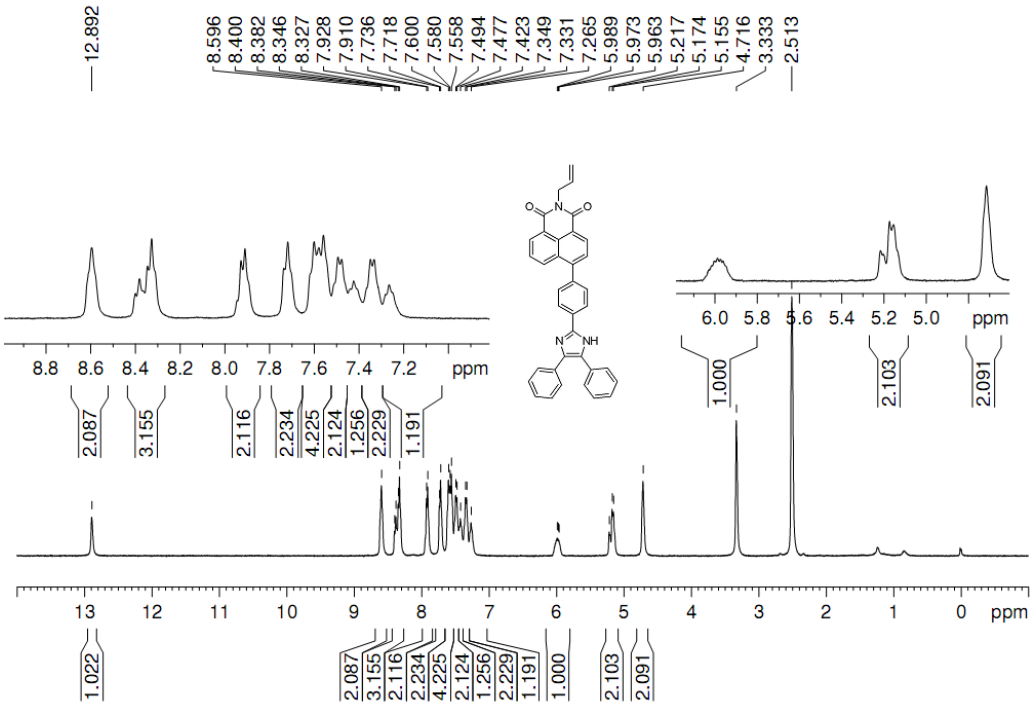
^{1}H-NMR spectrum of compound 7 (solvent $CDCl_3$)



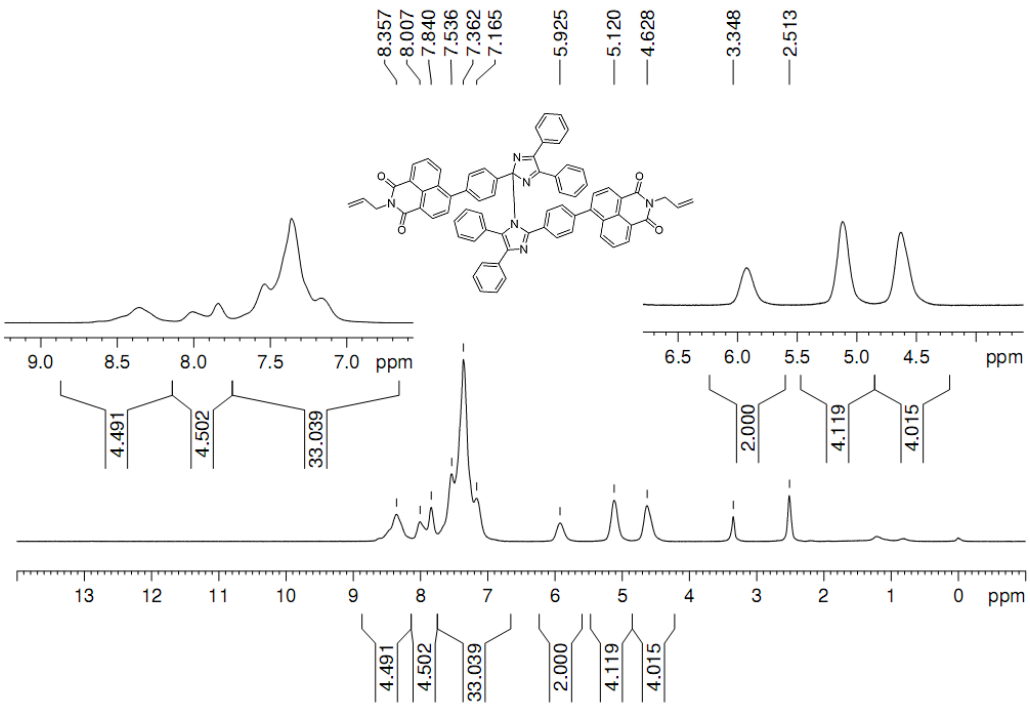
^{1}H-NMR spectrum of compound 8 (solvent $CDCl_3$)



^{1}H-NMR spectrum of compound 9 (solvent $CDCl_3$)

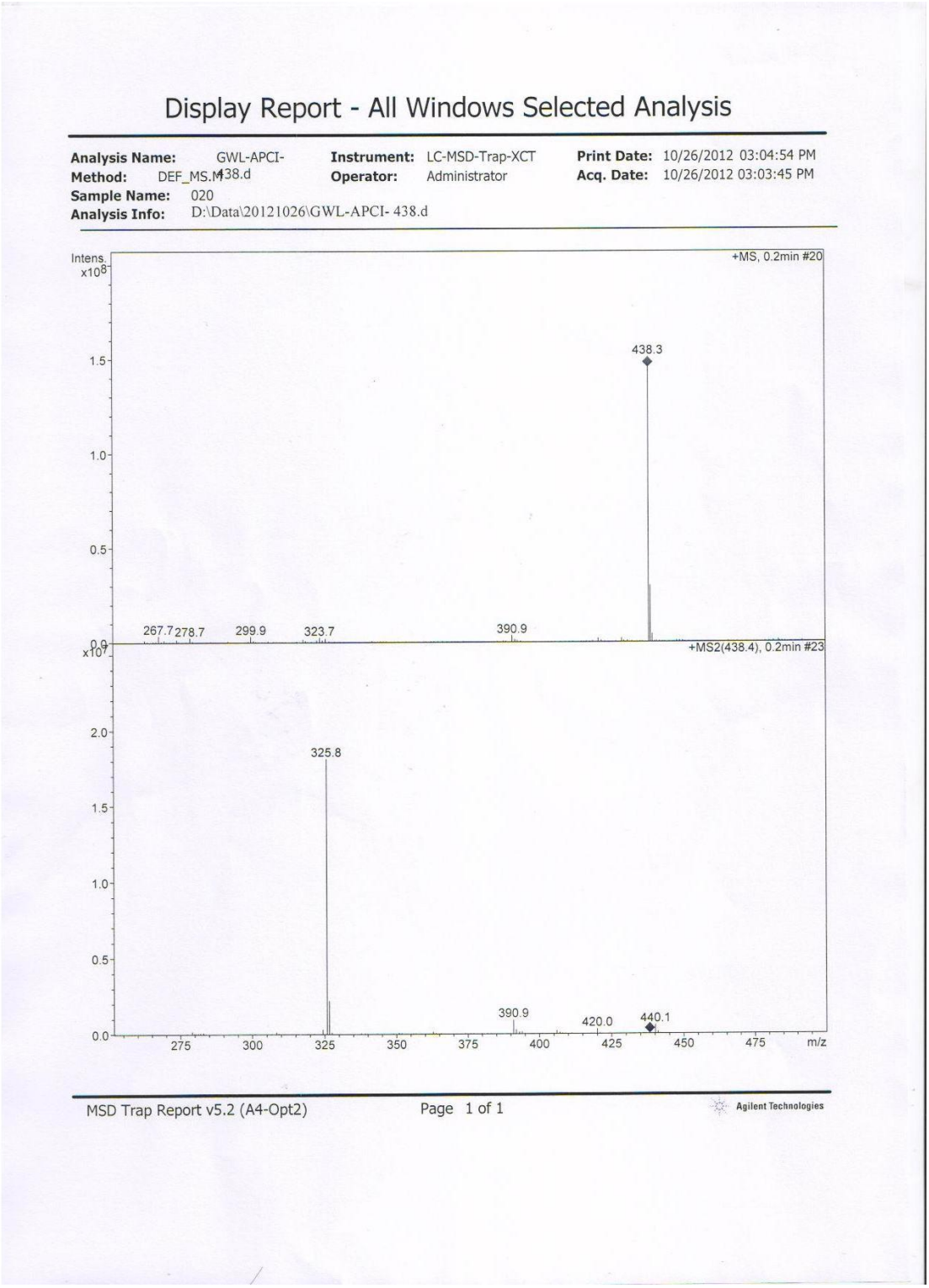


^{1}H-NMR spectrum of compound 10 (solvent ^{d}-DMSO)

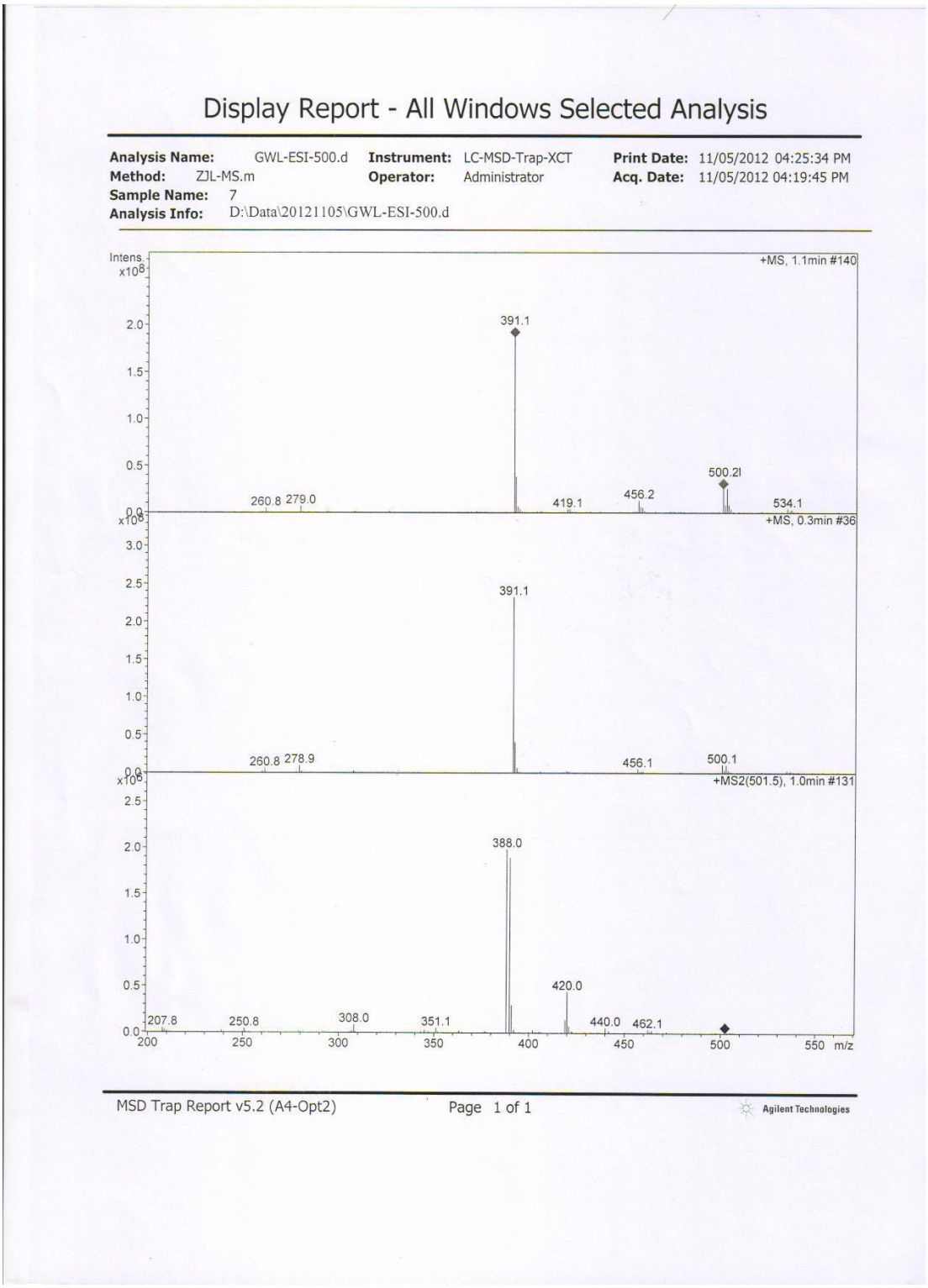


^{1}H-NMR spectrum of NI-HABI (solvent ^{d}-DMSO)

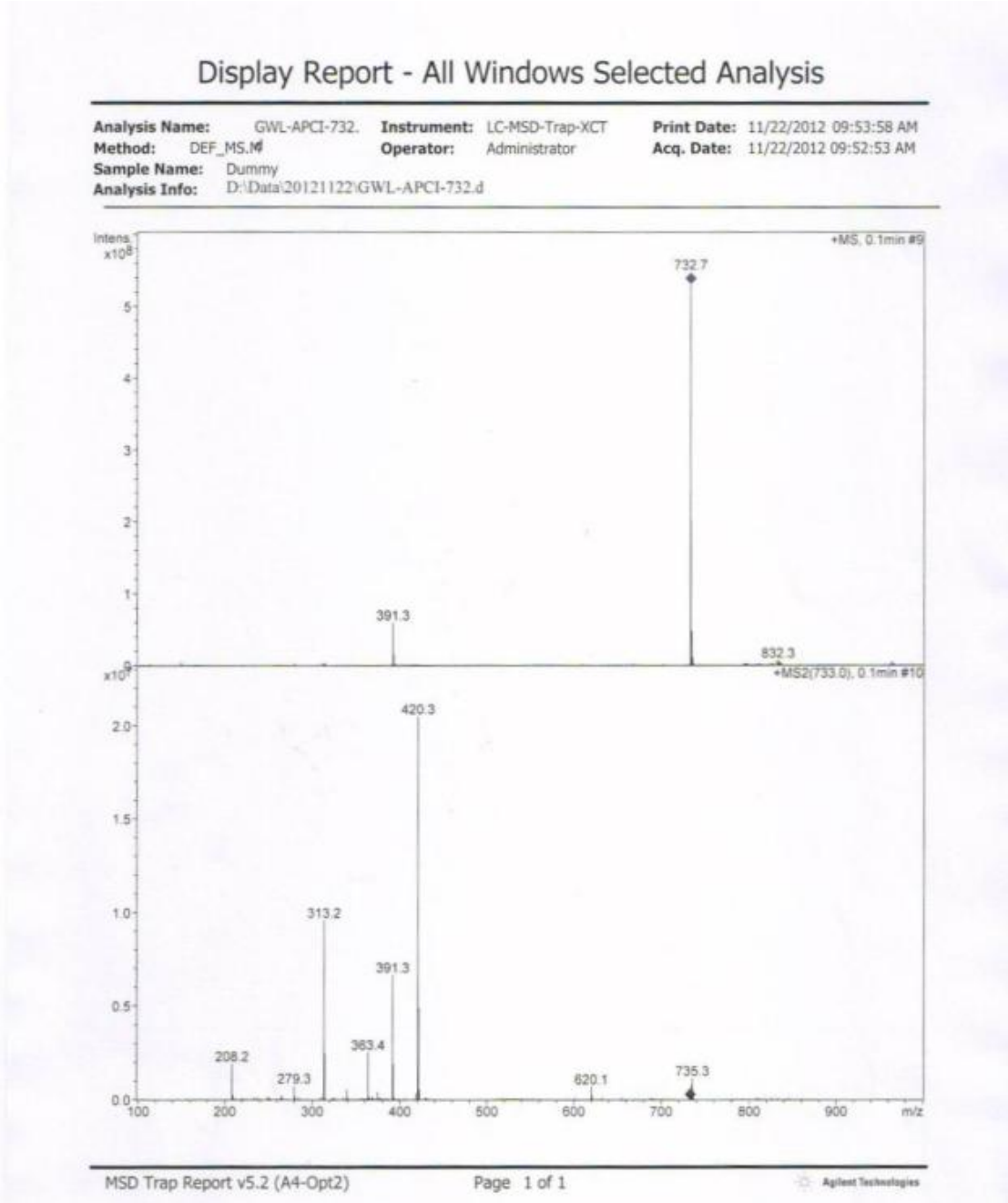
3. MASS SPECTRA



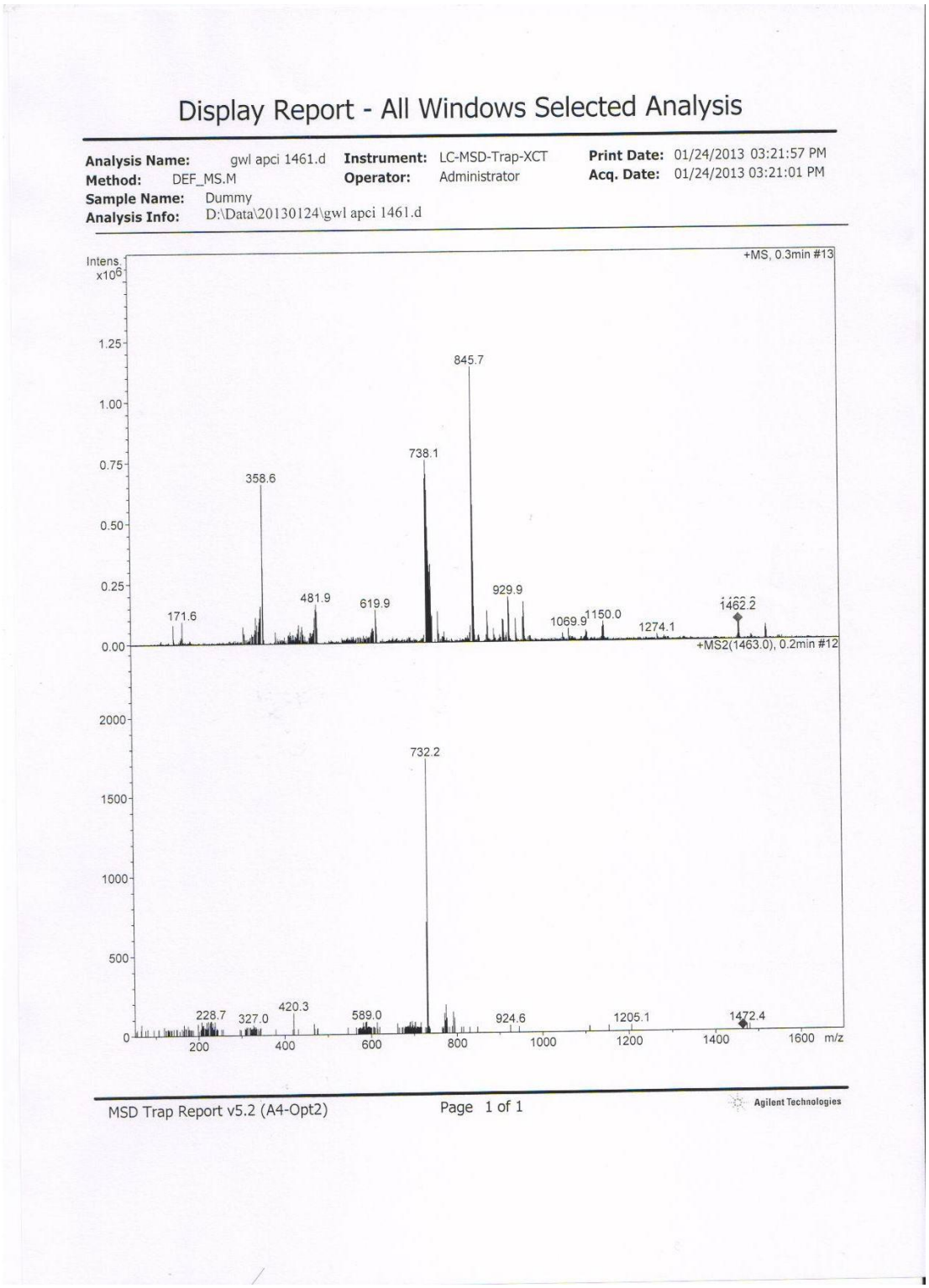
Mass spectrum of compound 3 (APCI, m/z)



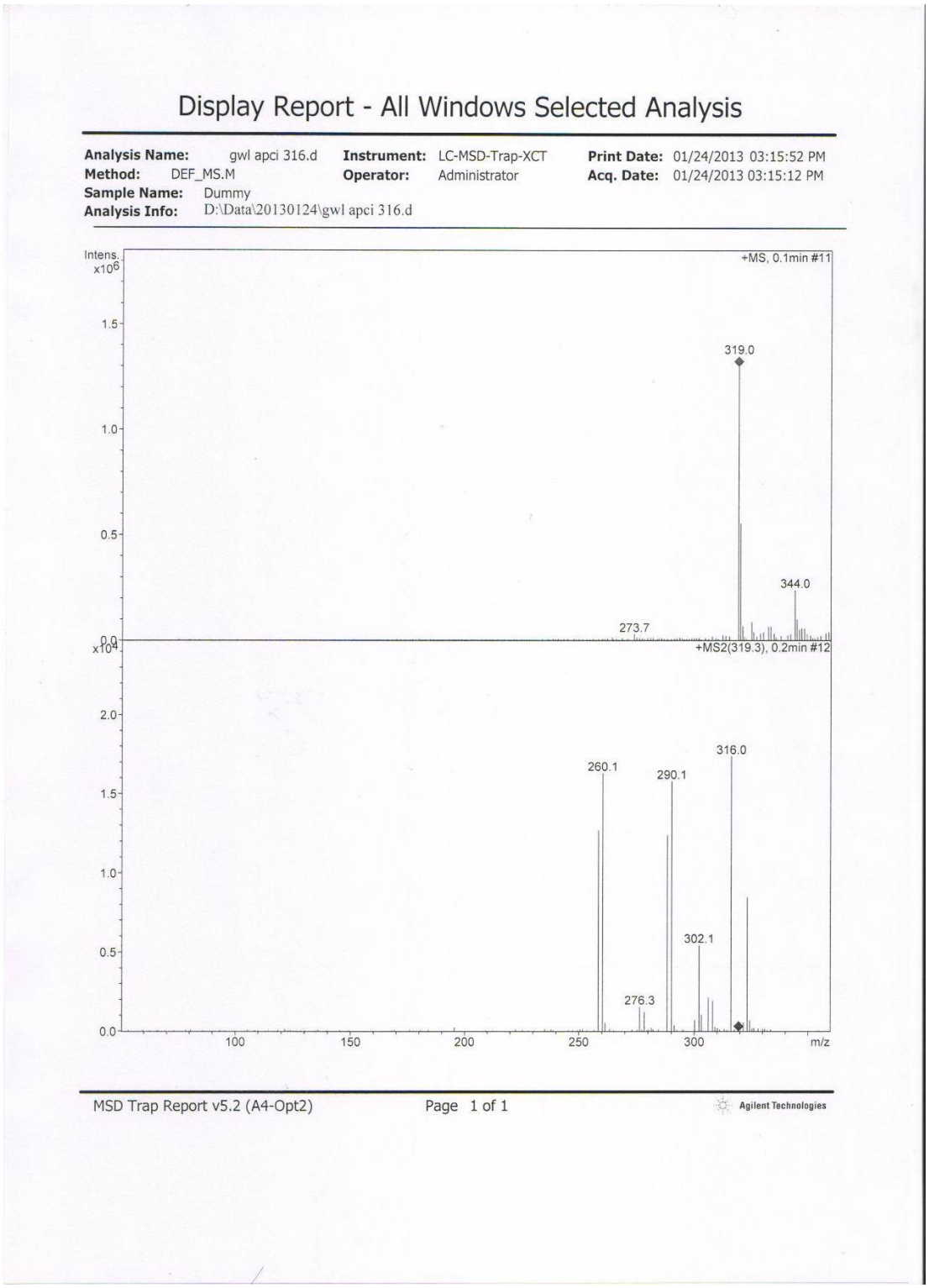
Mass spectrum of compound 4 (APCI, m/z)



Mass spectrum of Imidazole-NI (APCI, m/z)



Mass spectrum of HABI-NI (A)



Mass spectrum of compound 7 (APCI, m/z)

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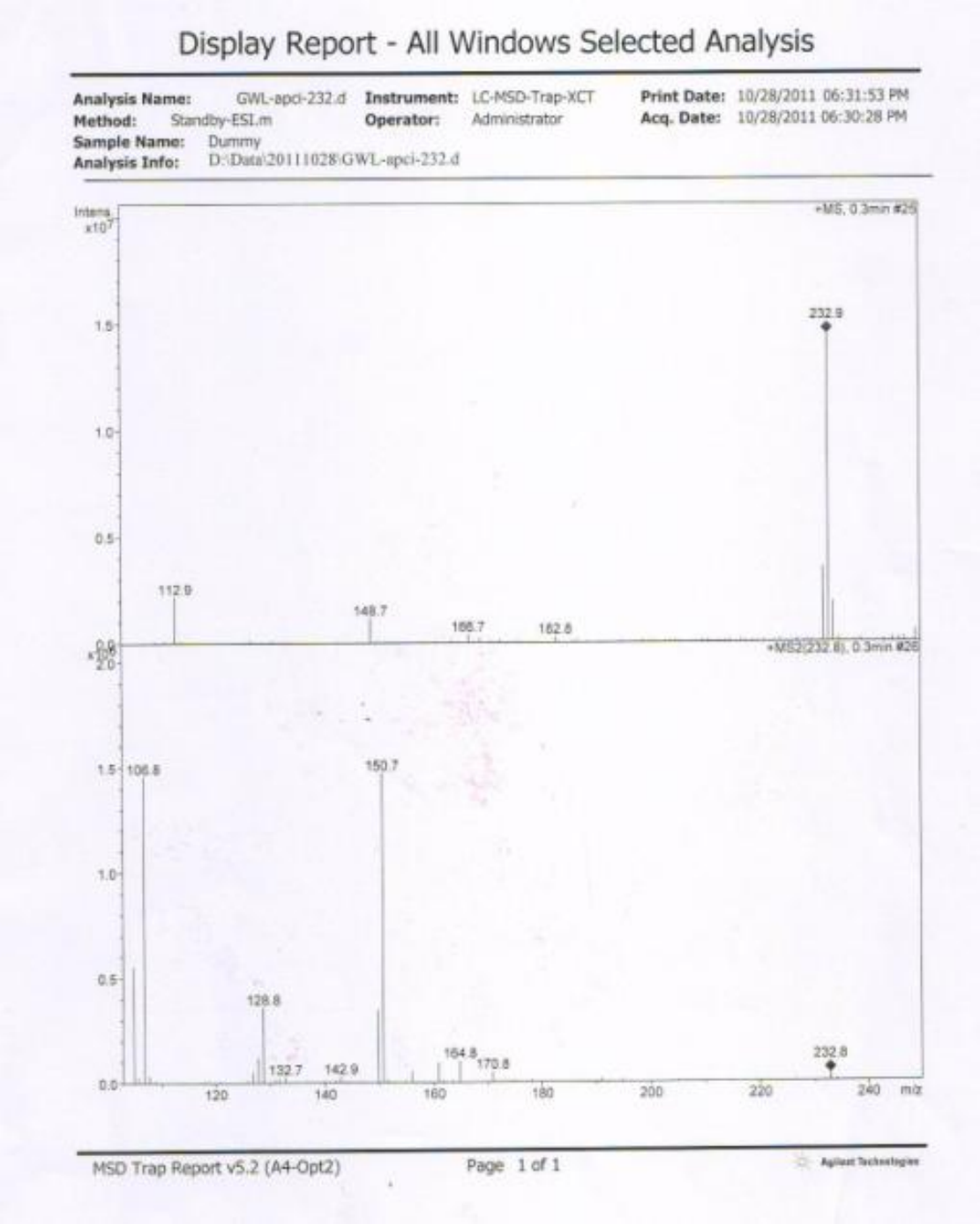
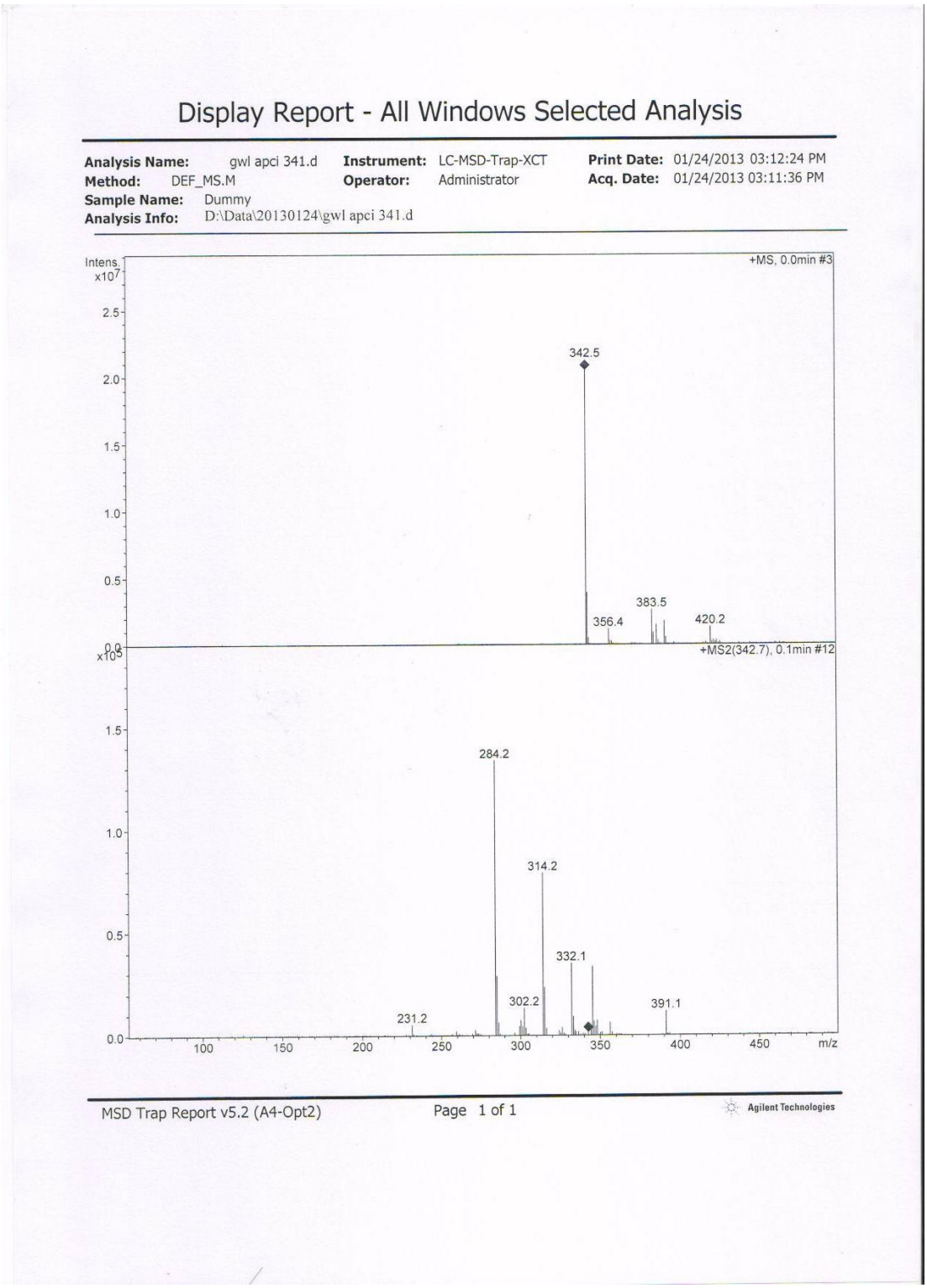
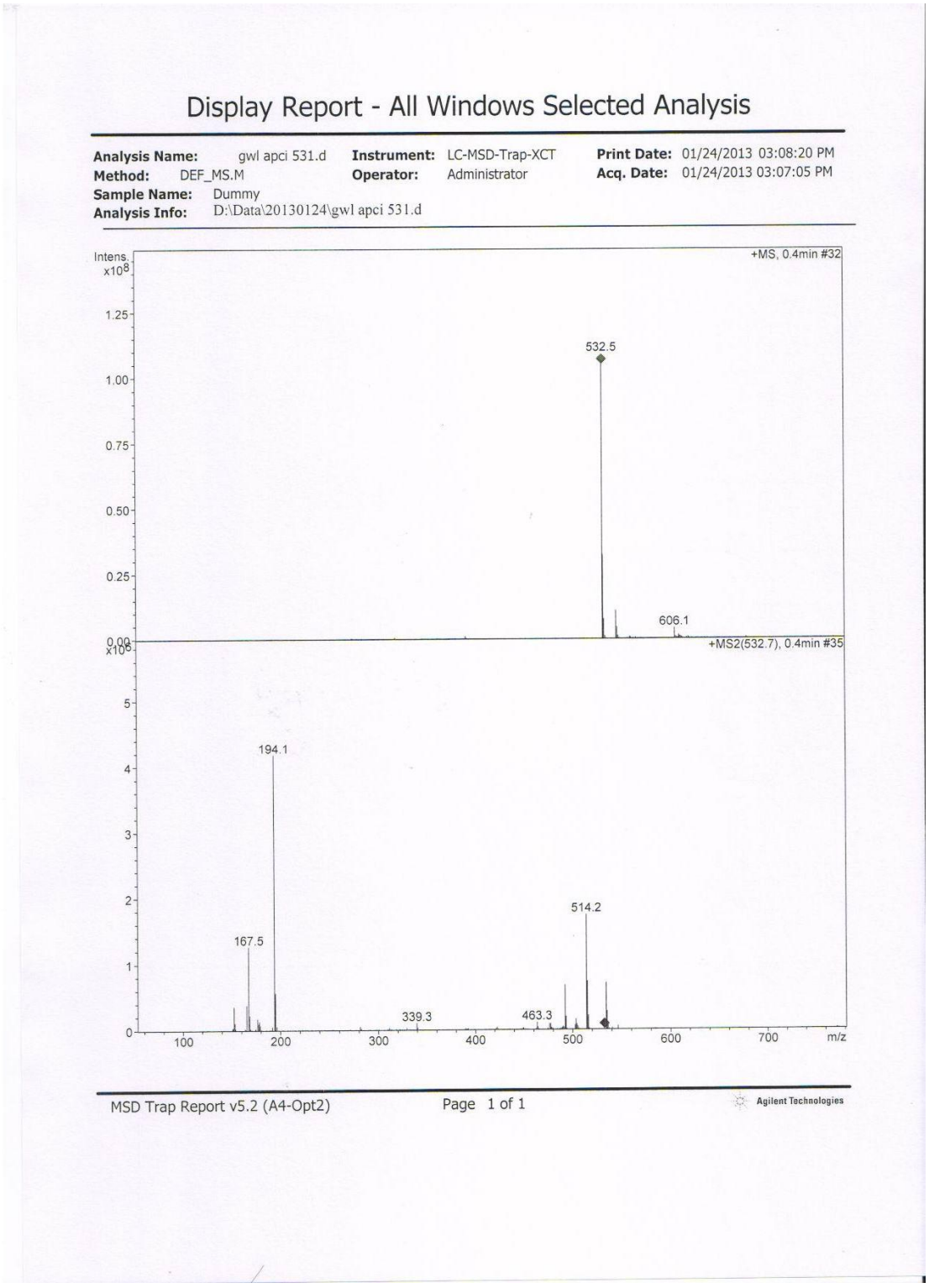


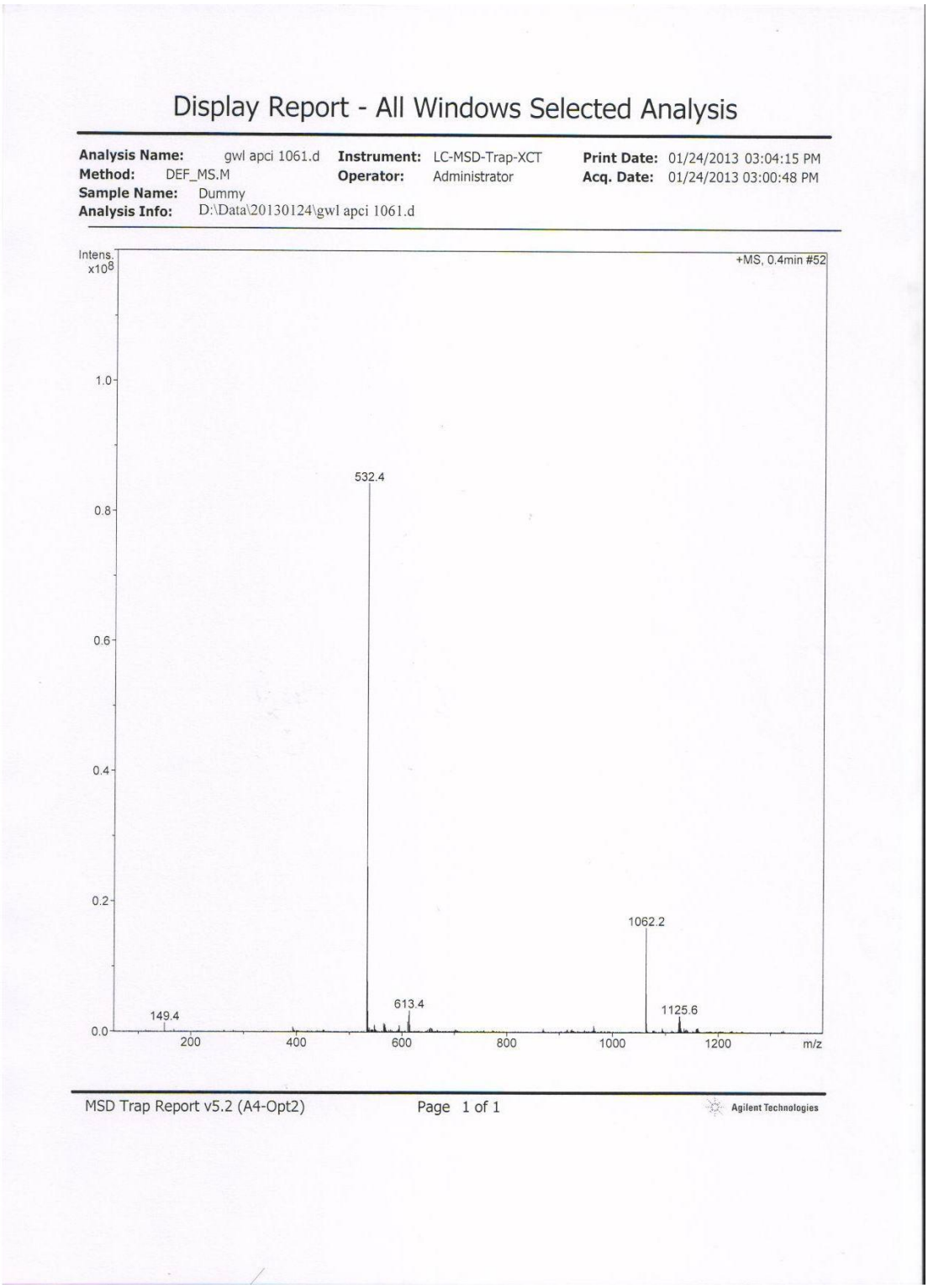
Mass spectrum of compound 8 (APCI, m/z)



Mass spectrum of compound 9 (APCI, m/z)

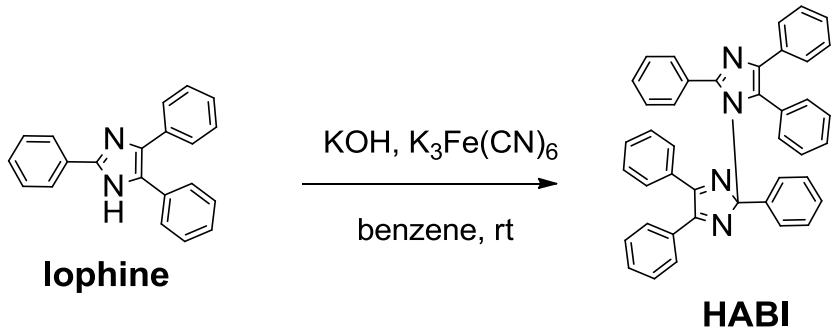


Mass spectrum of compound 10 (APCI, m/z)



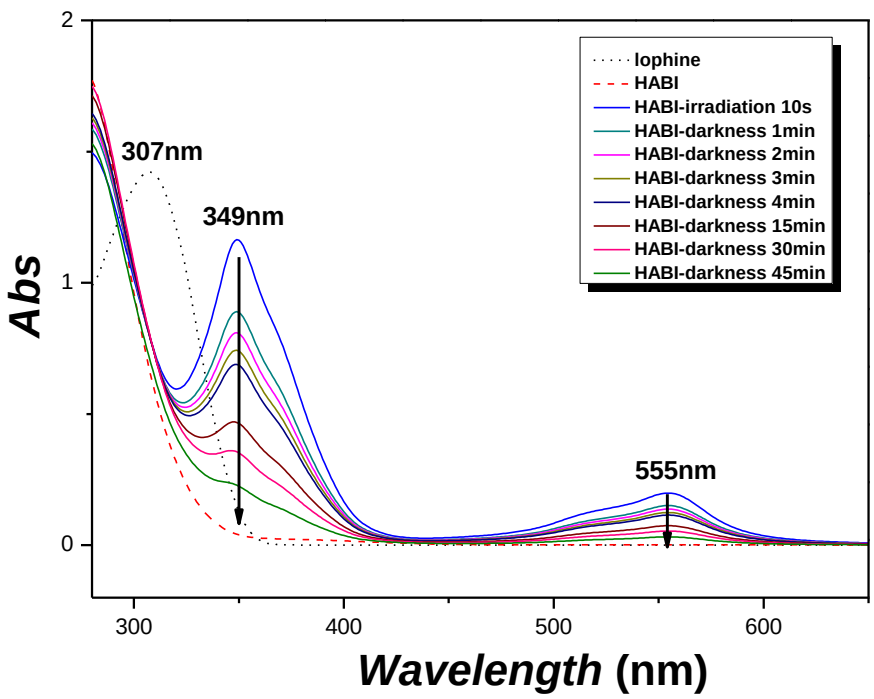
Mass spectrum of HABI-NI (APCI, m/z)

4. Synthesis of Hexaarylbiimidazole (HABI)

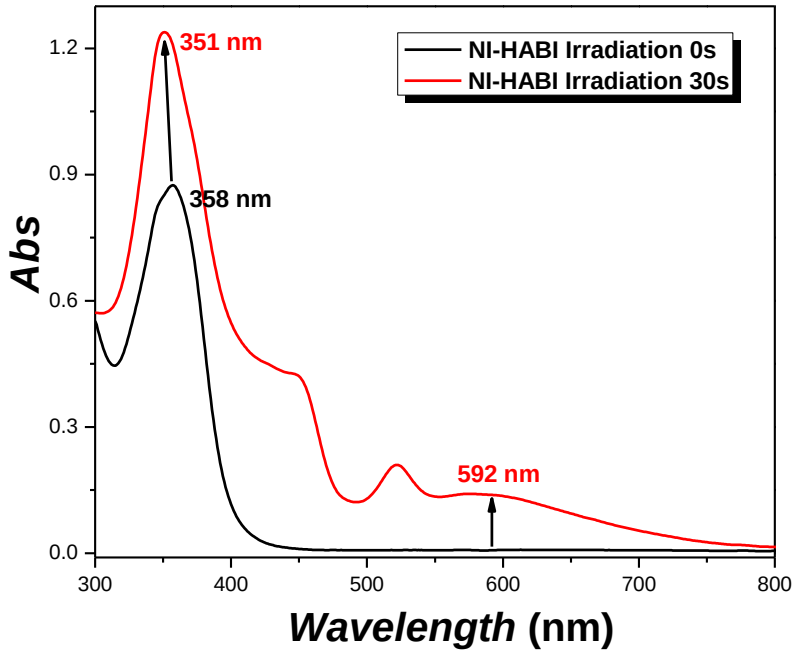


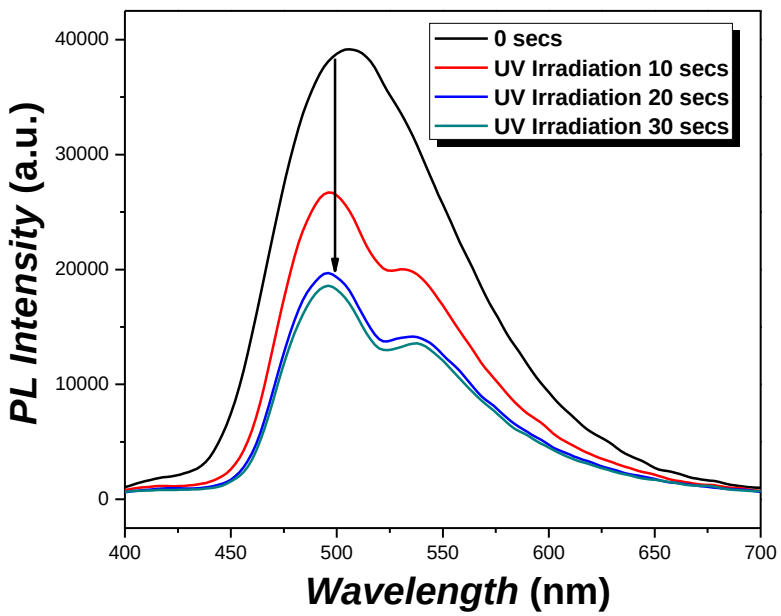
The preparation of HABI was synthesized following a previous literature procedure in good yield (85.1 %).

FIG. S1: UV-VIS Absorption of 2,4,5-triphenylimidazole (lophine) in benzene (concentration = 10^{-4} M) and HABI in benzene (concentration = 10^{-4} M) after UV-light irradiation (302 nm) and in darkness at room temperature.



5. FIG. S2: UV-VIS Absorption and the corresponding PL Spectra (excitation = 380 nm) of NI-HABI in benzene (concentration = 10^{-4} M) before and after UV-light irradiation (302 nm).



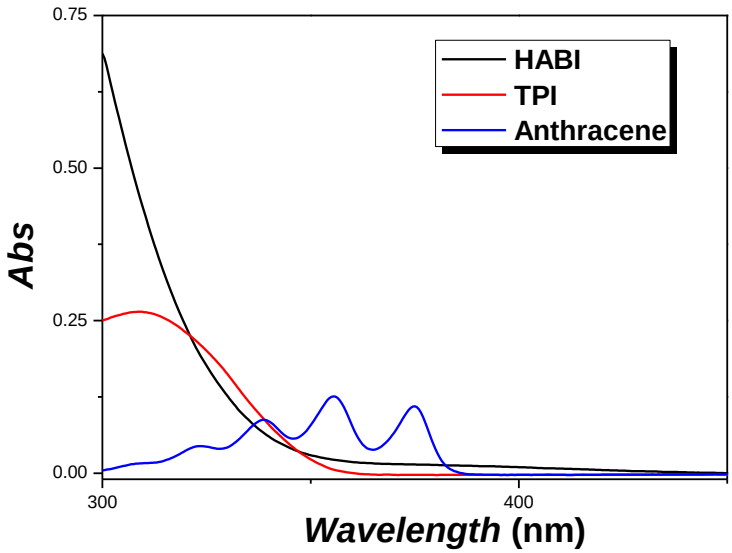


6. CALCULATION OF FLUORESCENCE QUANTUM YIELDS (Φ_F)

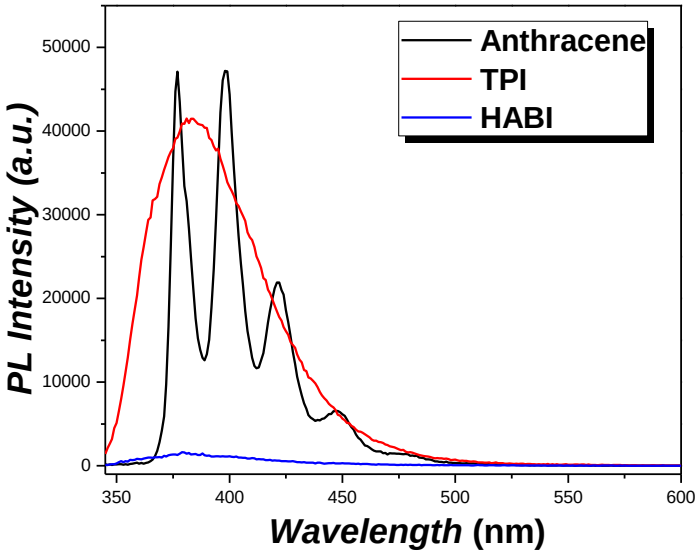
$$\Phi_X = \Phi_{ST}\left(\frac{PL \div Abs_X}{PL \div Abs_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

ST= standard sample, *X*= test sample, *PL*÷ *Abs* = integration of fluorescence intensity divided by absorbance at the excitation wavelength.η= the refractive index of the solvent.

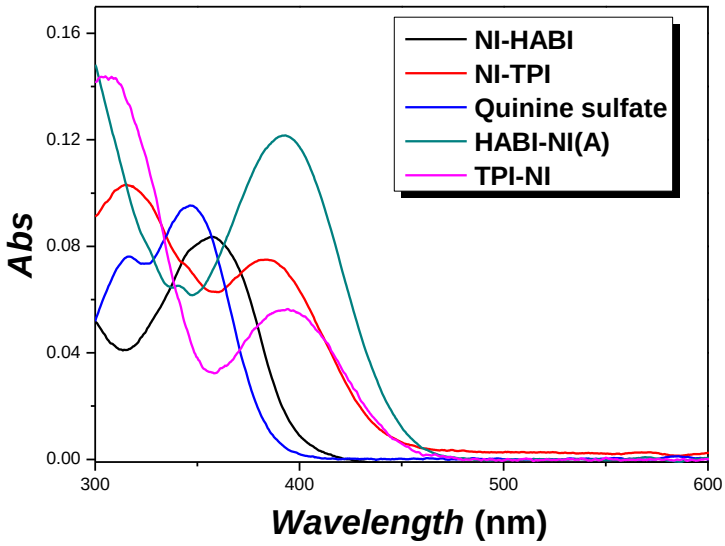
1. UV-Vis Absorption of HABI and TPI in benzene for quantum yield calculations using anthracene in ethanol as the standard. Anthracene (Φ_F = 27 % in ethanol) was used as the standard due to good overlap of its absorption and emission spectra with the test samples.



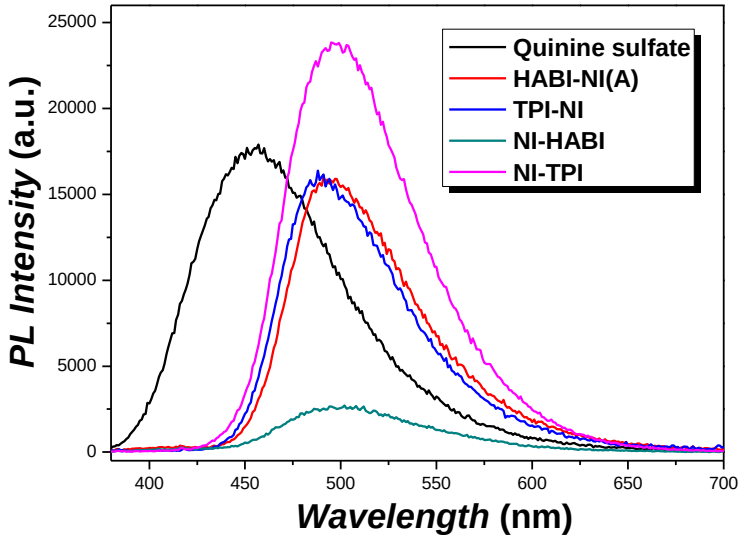
2. PL spectra of HABI, TPI and Anthracence for quantum yield calculation. Both HABI and TPI are dissolved in benzene, anthracence is dissolved in ethanol. ExBw and EmBw are 1 and 1, respectively, excitation wavelength: 340 nm



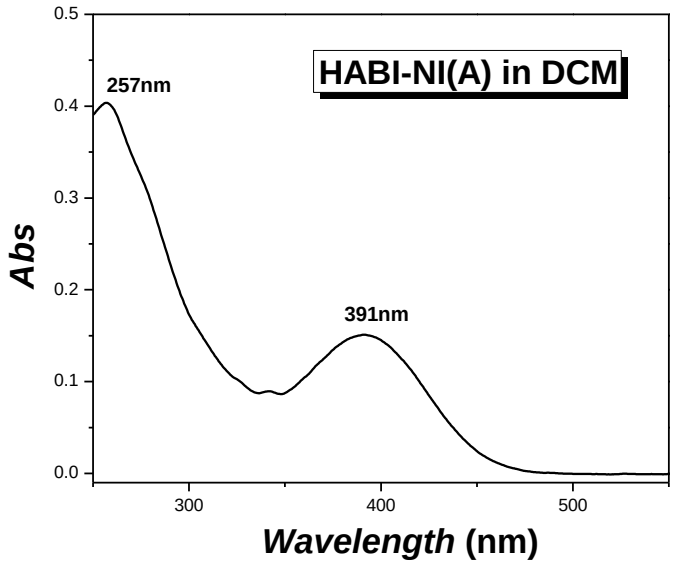
3. UV-Vis Absorption of NI-HABI, NI-TPI, HABI-NI(A) and TPI-NI in benzene for quantum yield calculation using quinine sulfate in 0.1M H_2SO_4 as the standard. Quinine sulfate (Φ_F = 54 % in 0.1M H_2SO_4) was used as the standard due to good overlap of its absorption and emission spectra with the test samples.



4. PL Spectra for all the corresponding materials (quinine sulfate is in 0.1M H_2SO_4, others in benzene). ExBw and EmBw are 1 and 1, respectively, and excitation wavelength: 375 nm



5. UV-VIS Absorption of HABI-NI(A) in DCM



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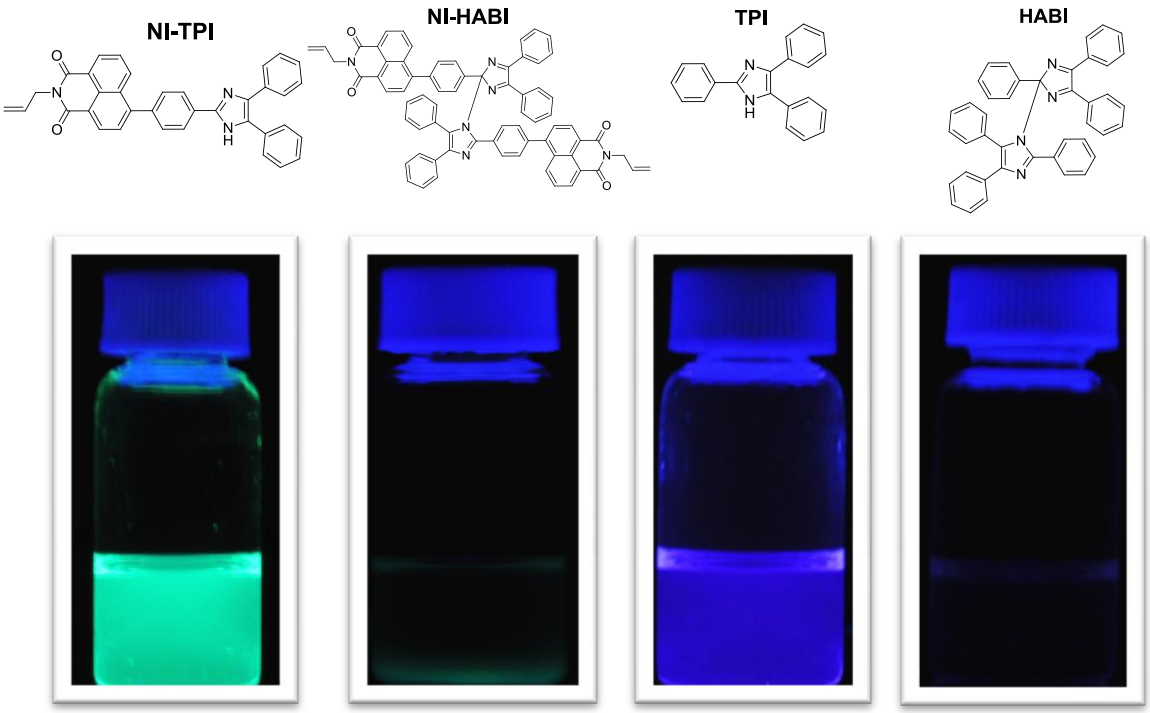
7. FLUORESCENCE PHOTOS



Photos in benzene solution (1 x 10^{-5} M) under UV illumination of 365 nm UV lamp (NI-TPI and NI-HABI) and 302 nm UV lamp (TPI and HABI).