

Supporting information

Encapsulation of $Ti_xFe_yLa_mO_z$ nanoparticle into NH_2 -MIL-125(Ti) to fabricate a promising photocatalyst for C-N coupling reaction

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Table S 1 The data for La@MOF with different loadings of $Ti_xFe_yLa_mO_z$ nanoparticle

Catalyst	Titanium butoxide (μmol)	2-amino terephthalic acid (mL)	Nanoparticle (μmol)
La(1)@MOF	10	15.8	10
La(1.05)@MOF	10	15.8	10.5
La(1.1)@MOF	10	15.8	11
La(1.15)@MOF	10	15.8	11.5



Figure S 1 The color of the different samples



Figure S 2 Photocatalytic Cross-coupling reaction

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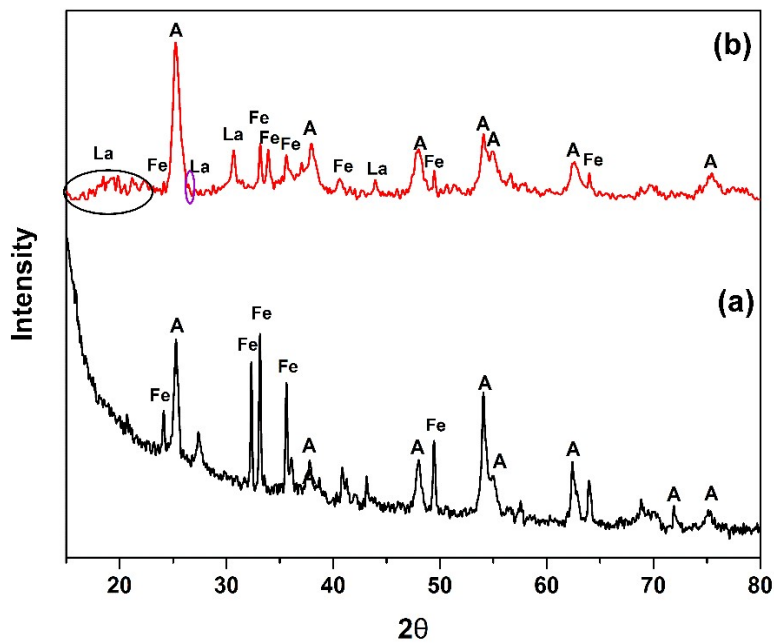


Figure S 3 PXRD pattern of (a) TixFeyOz , and (b) TixFeyLamOz

Table S 2 Chemical-Physical Features of the Samples

sample	JCPDS	crystal system	d value (anatase peak, 25.29Å) (nm)	crystallite size (nm)
TixFeyOz	96-152-0849	tetragonal	0.88	16.3
TixFeyLamOz	96-900-9087	tetragonal	0.75	14.36

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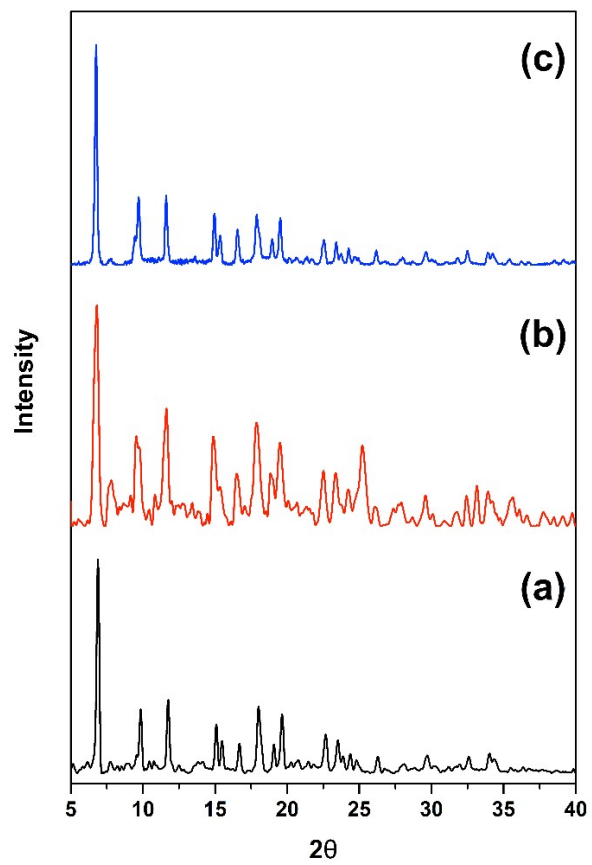


Figure S 4 PXR D pattern of (a) pristine MOF, (b) La@MOF and (c) Fe@MOF

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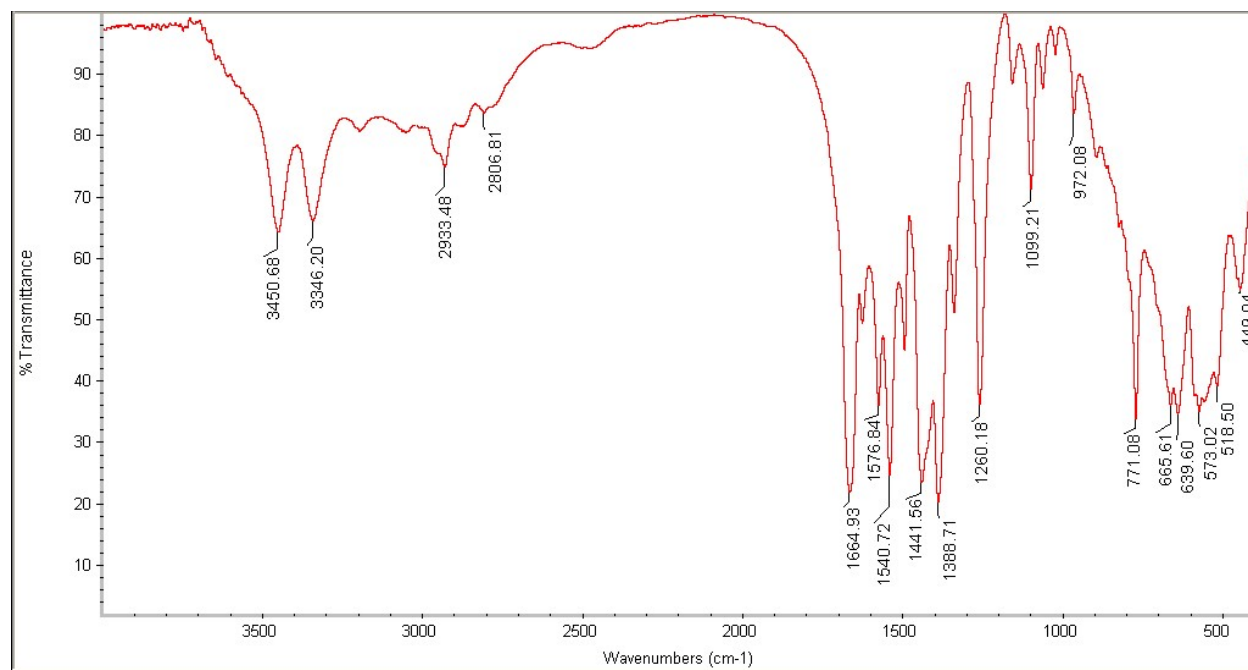


Figure S 5 FT-IR spectroscopy of Fe@MOF

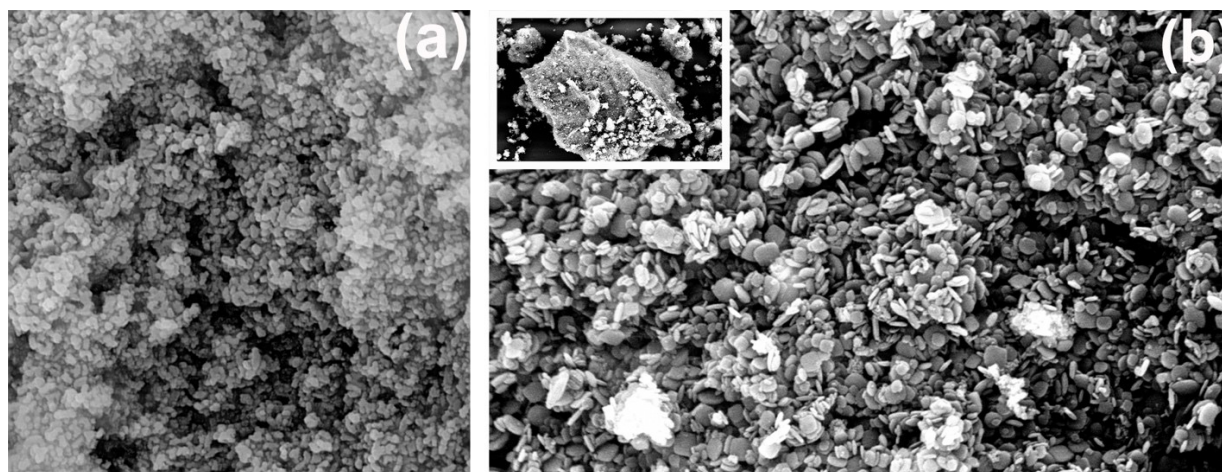


Figure S 6 FESEM image of (a) TixFeyOz, (b) Fe@MOF

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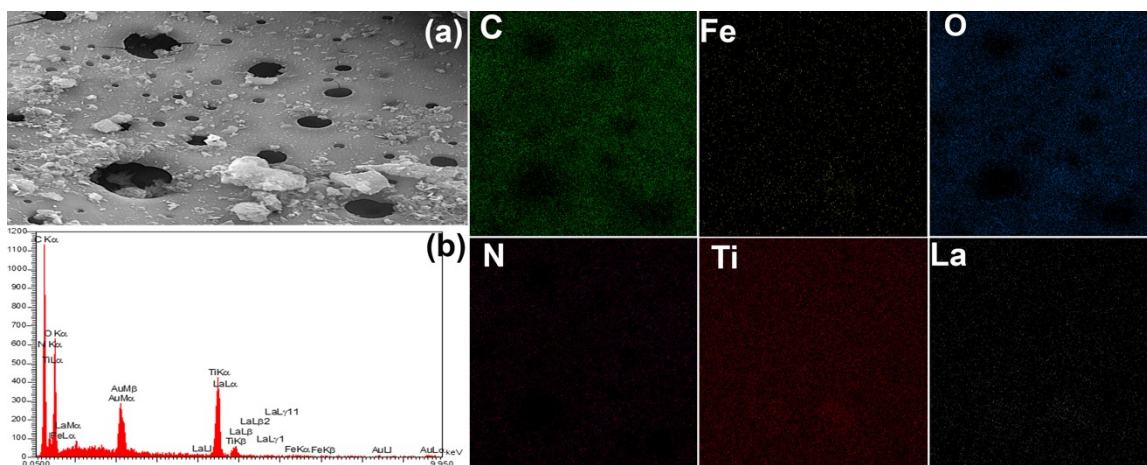


Figure S 7 EDX analysis of La(1)@MOF

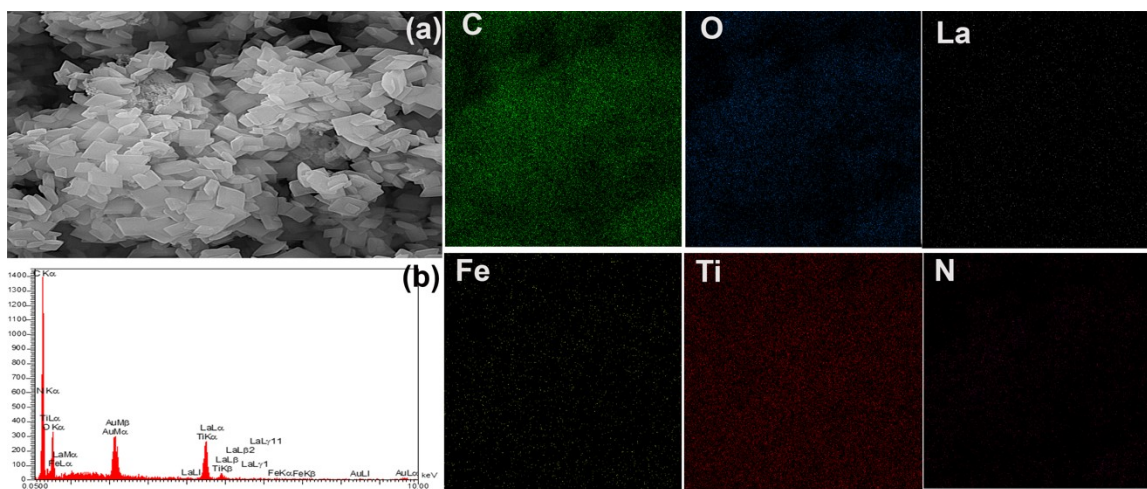


Figure S 8 EDX analysis of La(1.1)@MOF

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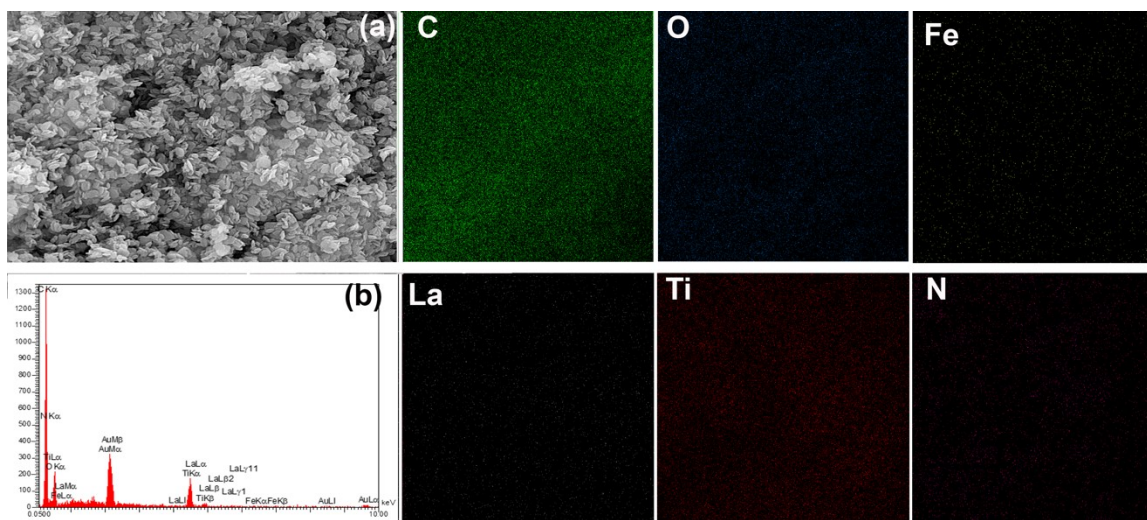


Figure S 9 EDX analysis of La(1.15)@MOF

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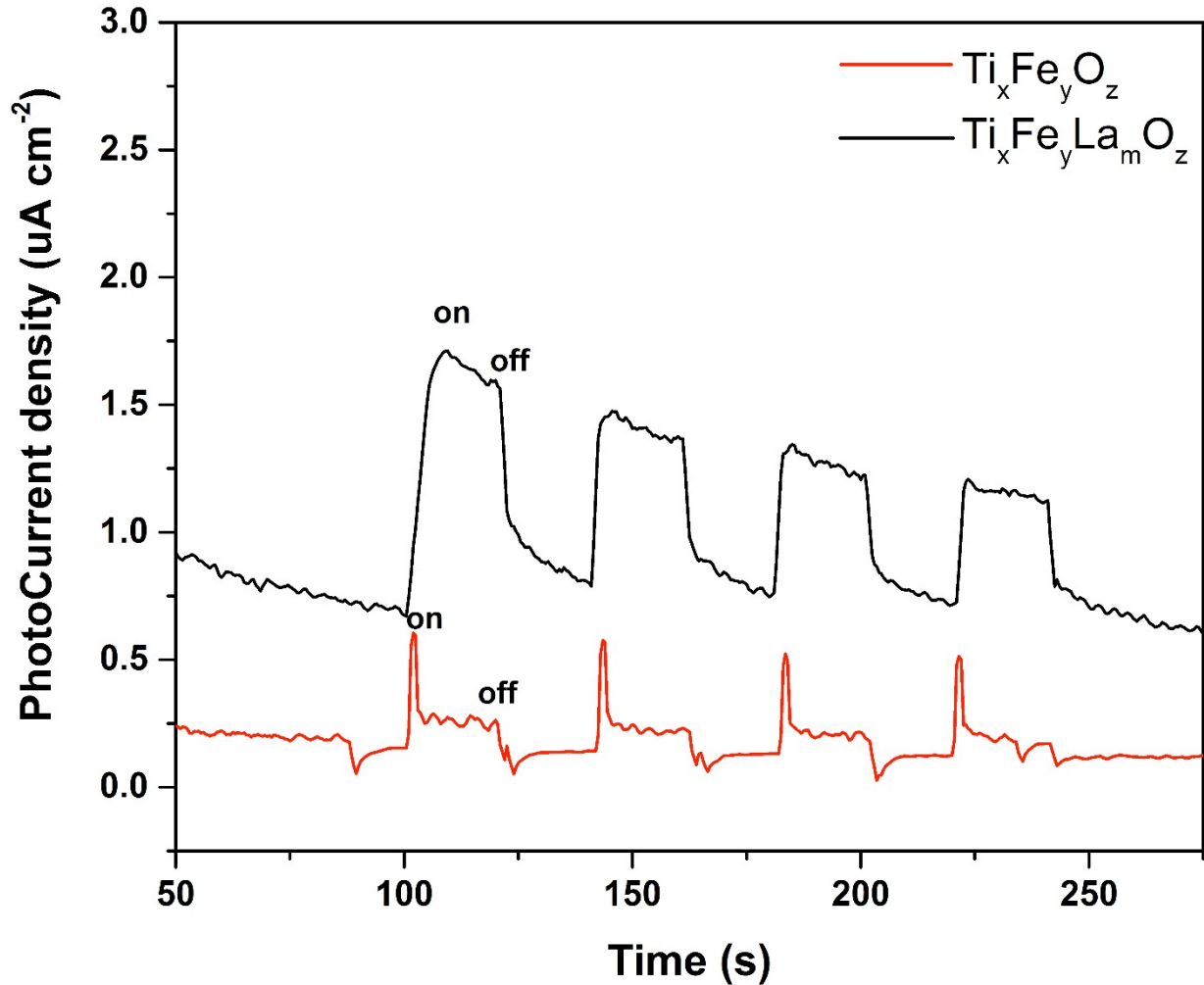


Figure S 10 Photocurrent transient response of Ti_xFe_yO_z, and Ti_xFe_yLa_mO_z nanoparticles under visible light irradiation

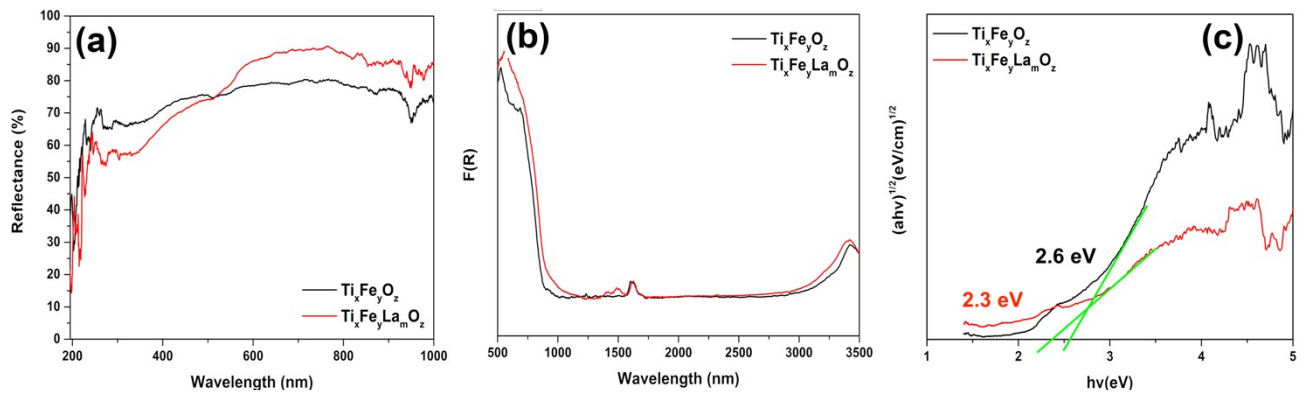


Figure S 11 (a) Diffuse reflectance spectra of Ti_xFe_yO_z, and Ti_xFe_yLa_mO_z nanoparticles; (b) UV-Vis Spectra of the Ti_xFe_yO_z, and Ti_xFe_yLa_mO_z nanoparticles; (c) the energy bandgap of the Ti_xFe_yO_z, and Ti_xFe_yLa_mO_z nanoparticles under the indirect transition assumption

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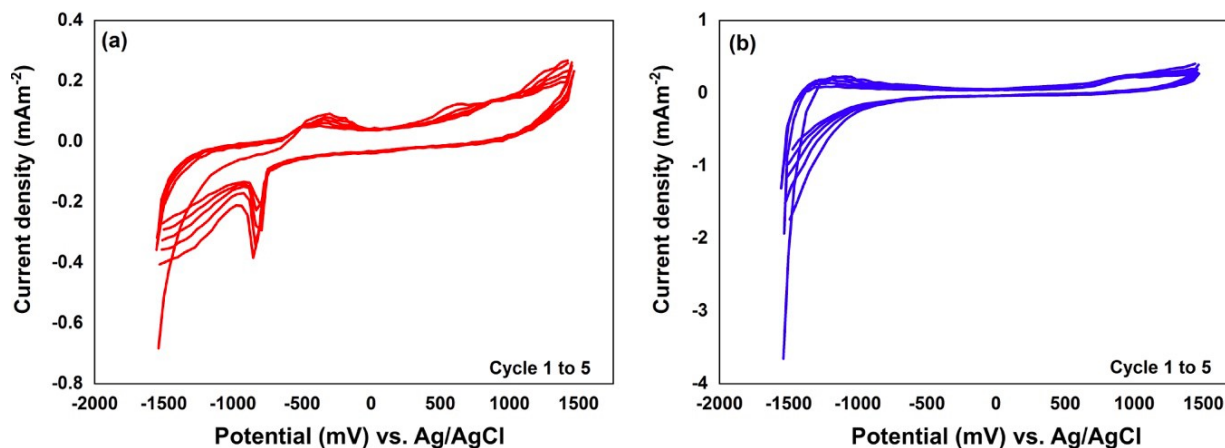


Figure S 12 (a) CV analysis of $Ti_xFe_yO_z$ nanoparticle and (b) $Ti_xFe_yLa_mO_z$ nanoparticle¹

- **Synthesis 2,4-dinitro-N-phenylaniline:** 0.25mmol of Aniline was dissolved in the mix of H_2O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight (Mashhad, Iran on oct18-2022, 22°C). The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature. M.P: 159 °C; FT-IR: 1620,1597,1583,1338,1270,1146,927,845; MS m/z: 259.06 ; 1H NMR (301 MHz, DMSO) δ 10.18 (s, 1H), 8.90 (d, $J = 2.8$ Hz, 1H), 8.24 (dd, $J = 9.6, 2.8$ Hz, 2H), 7.54 (dd, $J = 8.5, 7.0$ Hz, 2H), 7.45 – 7.33 (m, 3H), 7.12 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (76 MHz, DMSO) δ 147.1 (C8), 138.1 (C10), 136.8 (C6), 131.67(C11), 130.3 (C9), 130.3 (C2,4), 127.4 (C12), 126.2 (C1,5), 123.9 (C3), 117.3 (C13)..

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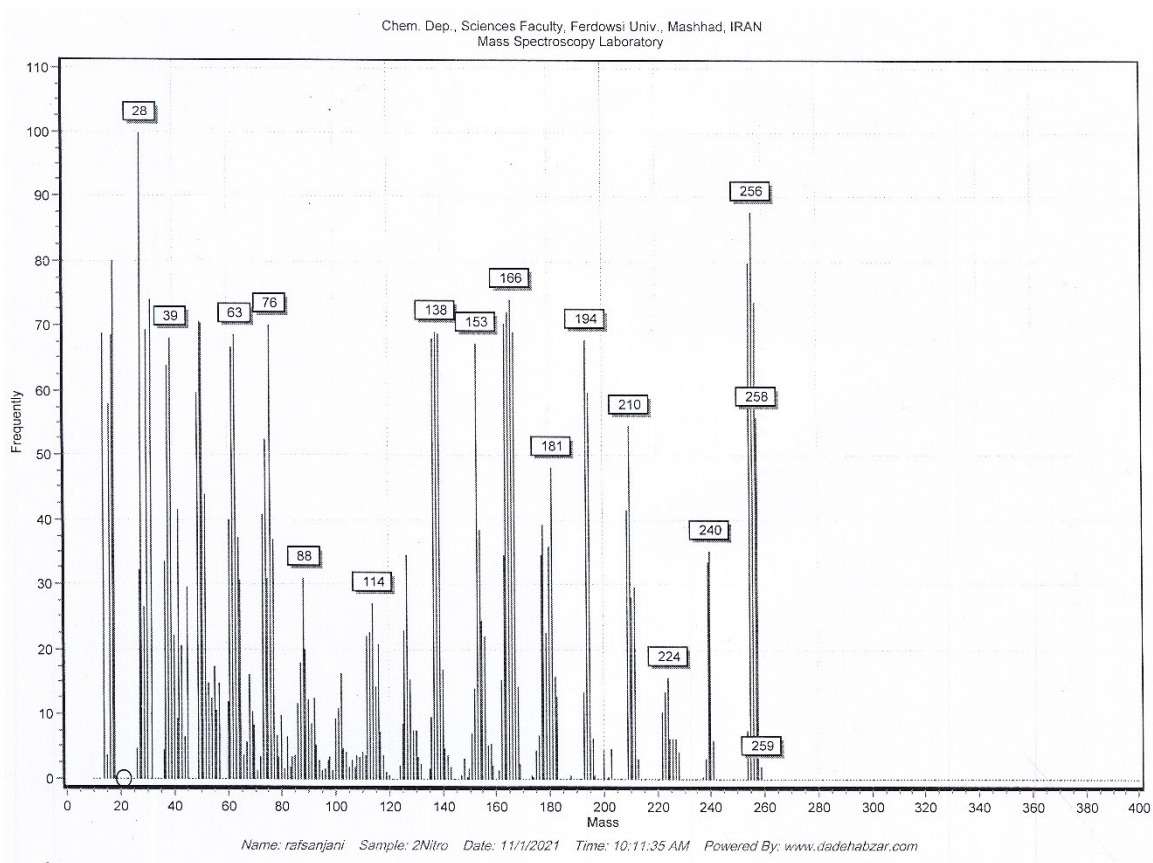


Figure S 13 Mass Spectroscopy of 2,4-dinitro-N-phenylaniline

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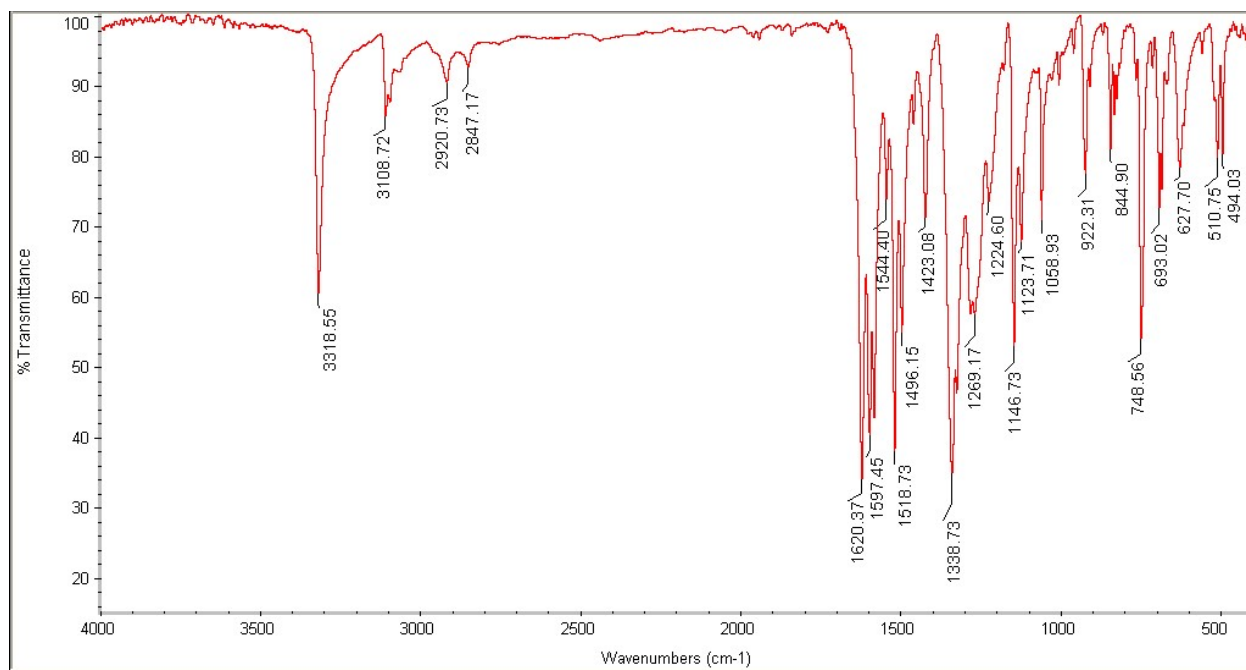


Figure S 14 FT-IR spectra of 2,4-dinitro-N-phenylaniline

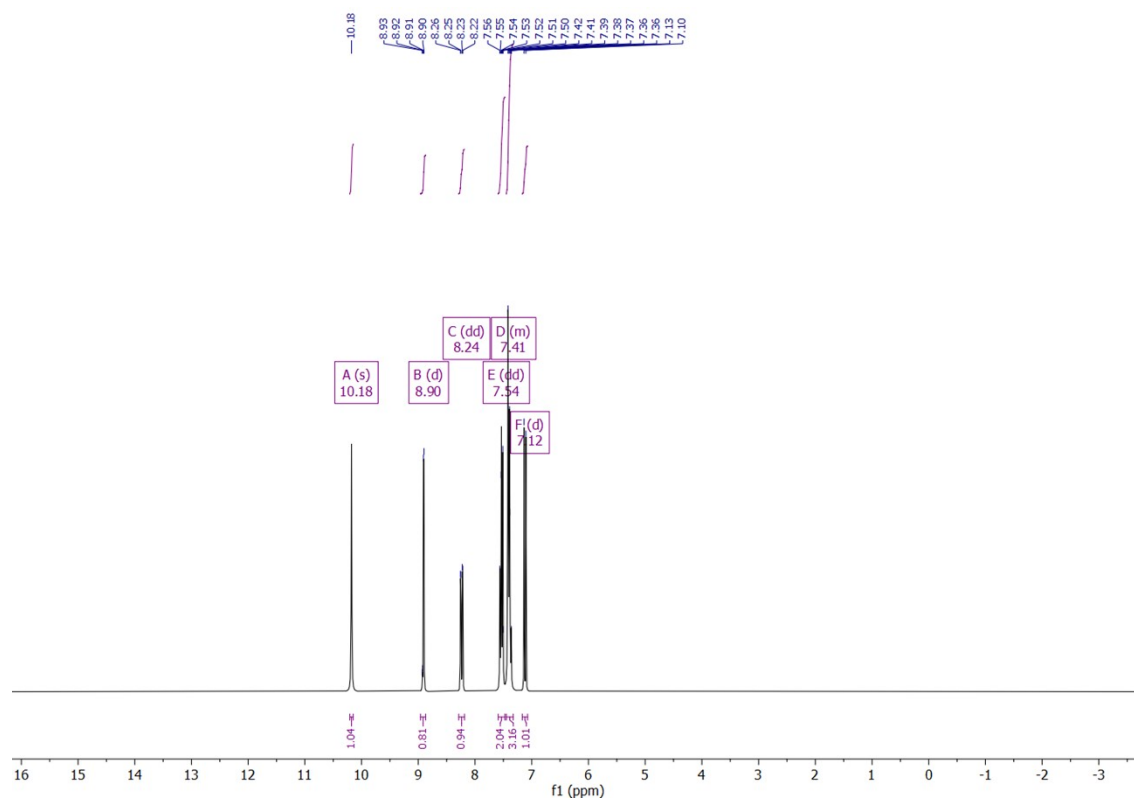


Figure S 15 ¹H-NMR spectra of 2,4-dinitro-N-phenylaniline

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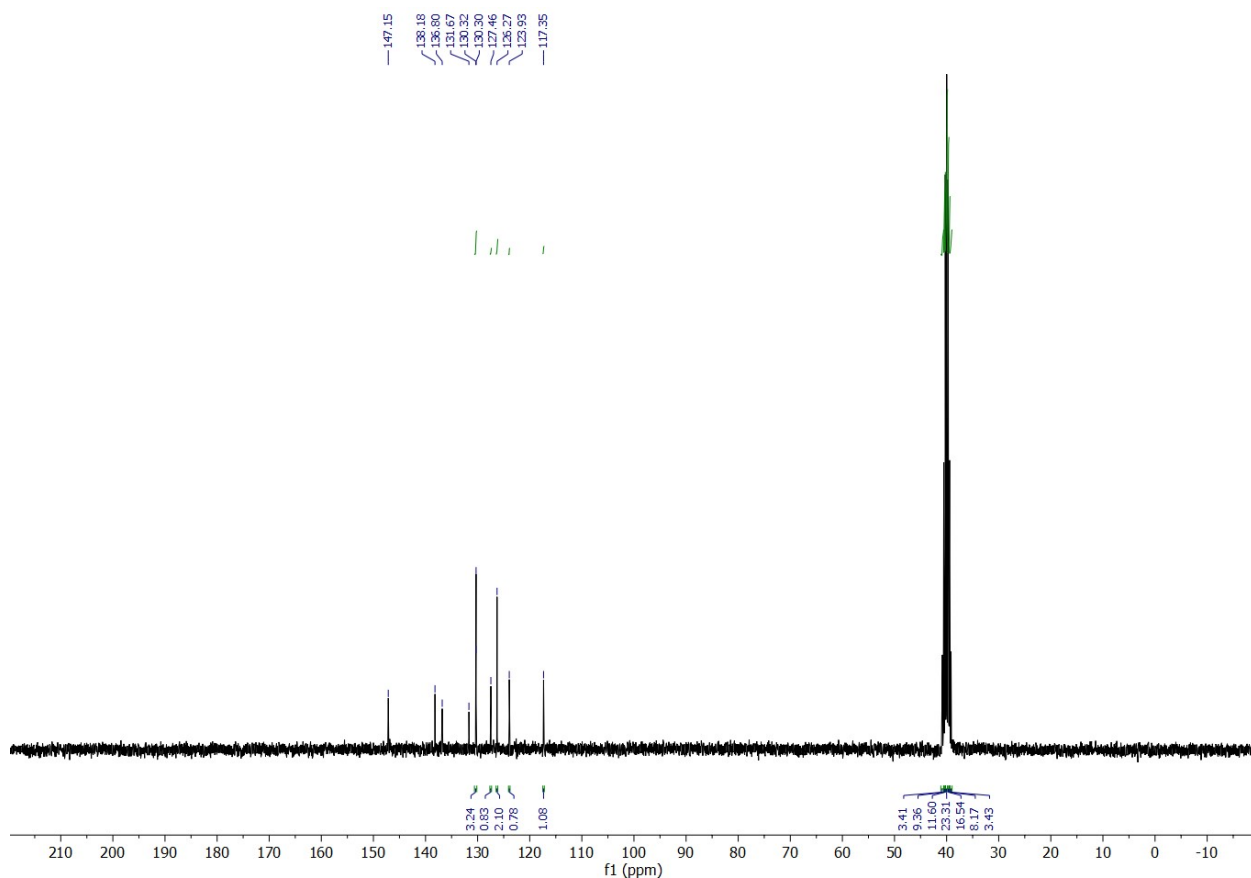


Figure S 16 ^{13}C -NMR spectra of 2,4-dinitro-N-phenylaniline

Synthesis N-(4-Bromophenyl)-2,4-dinitroaniline: 0.25mmol of 4-bromoaniline was dissolved in the mix of H_2O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature. M.P:158 $^\circ\text{C}$; Ft-IR : 1617, 1593, 1518, 1338, 1289, 1221, 926, 833, 637,498 ; MS m/z : 338 ; ^1H NMR (301 MHz, DMSO) δ 10.12 (s, 1H), 8.89 (d, J = 2.8 Hz, 1H), 8.23 (dd, J = 9.6, 2.8 Hz, 2H), 7.75 – 7.64 (m, 1H), 7.42 – 7.31 (m, 3H), 7.15 (d, J = 9.6 Hz, 1H). ^{13}C NMR (76 MHz, DMSO) δ 146.5 (C8), 137.3 (C6), 132.3 (C2,4), 132.0 (C11), 129.7 (C12), 128.7 (C9), 125.0 (C1,5), 121.5 (C10), 117.8 (C13), 116.0 (C3).

Supporting information

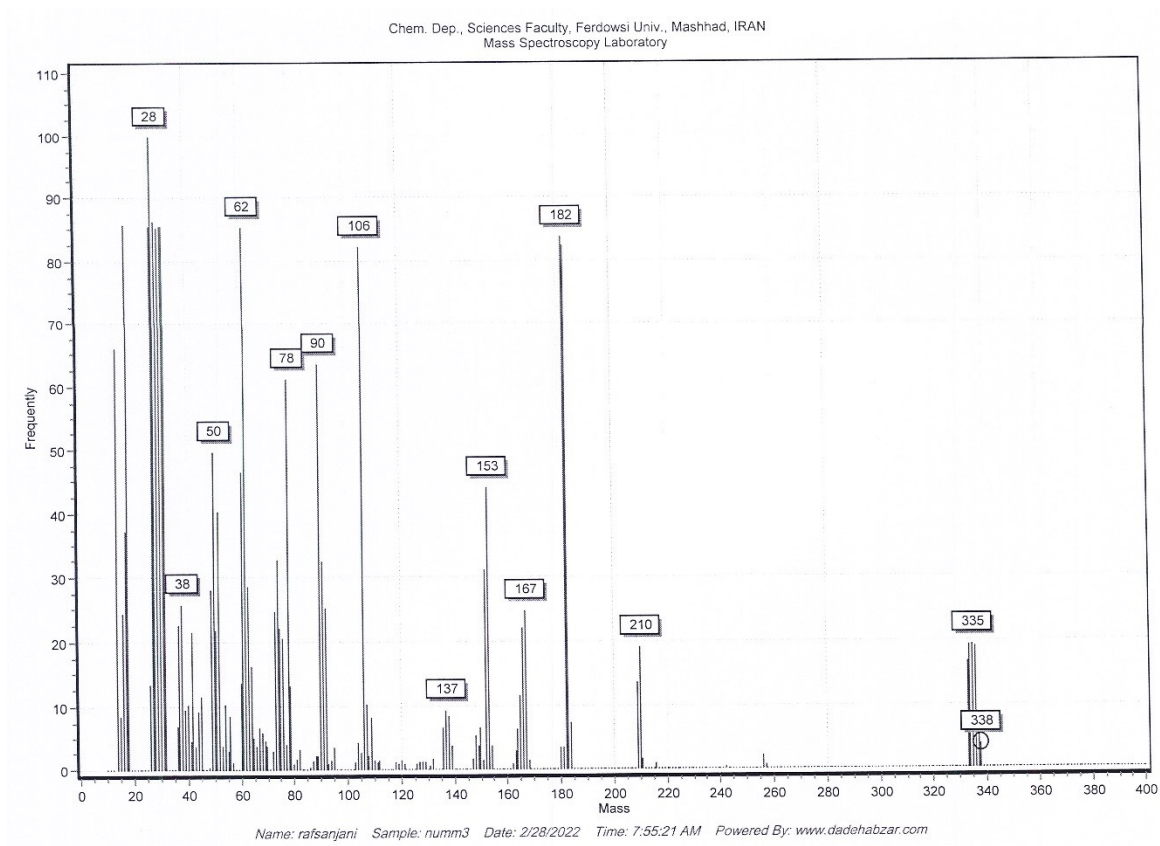


Figure S 17 Mass spectroscopy of *N*-(4-Bromophenyl)-2,4-dinitroaniline

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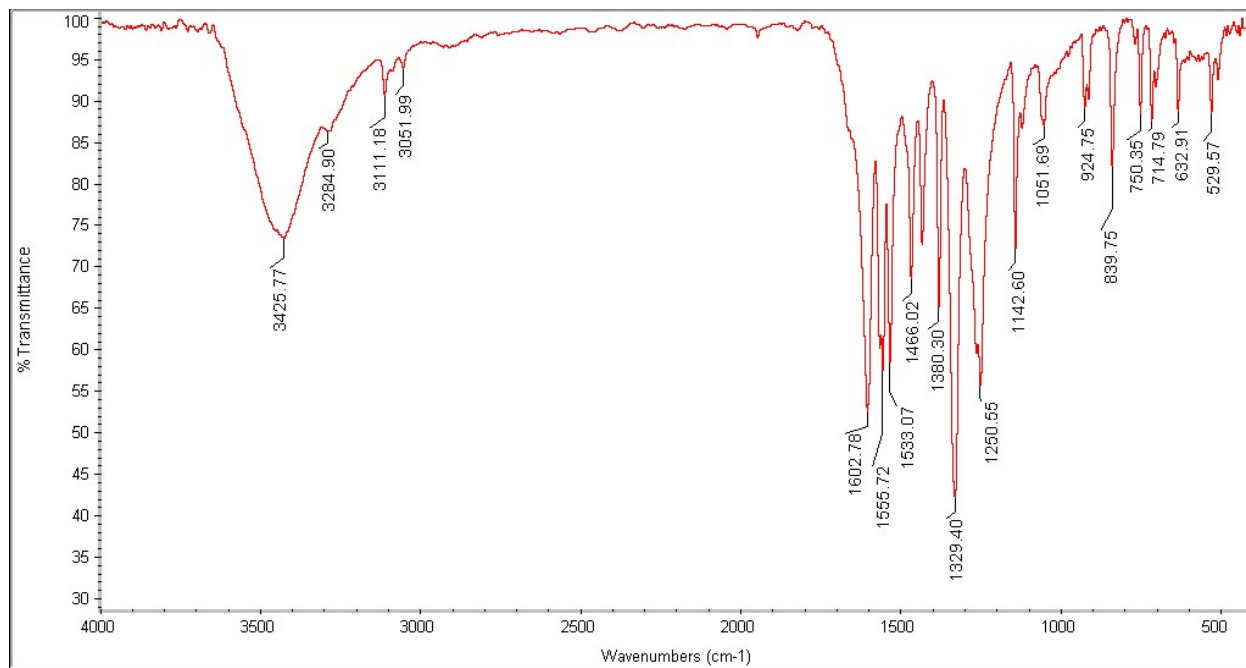


Figure S 18 FT-IR spectra of *N*-(4-Bromophenyl)-2,4-dinitroaniline

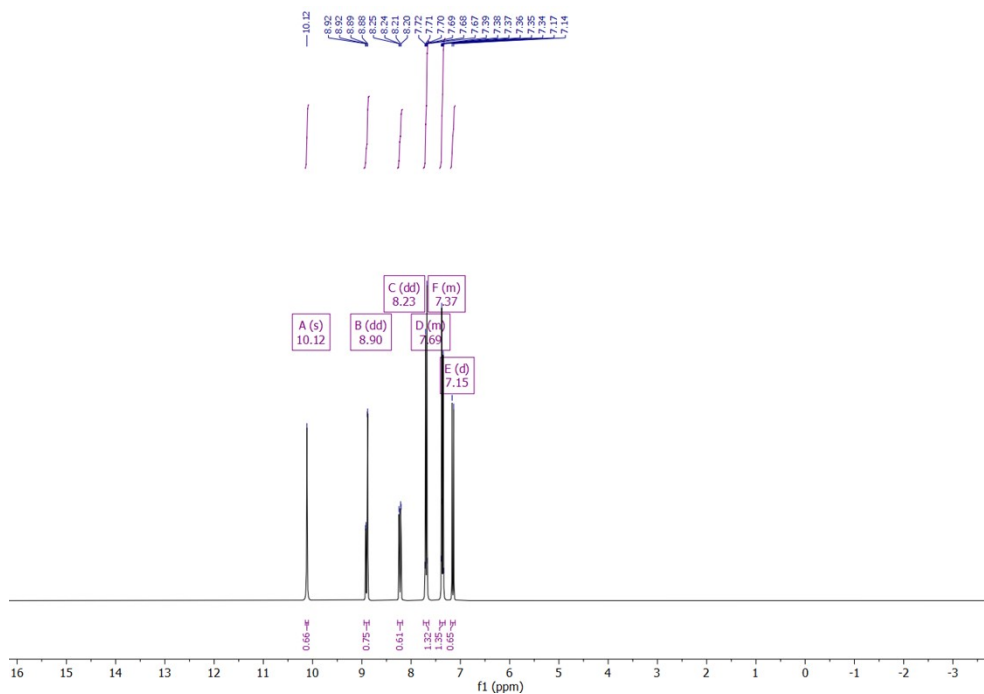


Figure S 19 ¹H-NMR spectra of *N*-(4-Bromophenyl)-2,4-dinitroaniline

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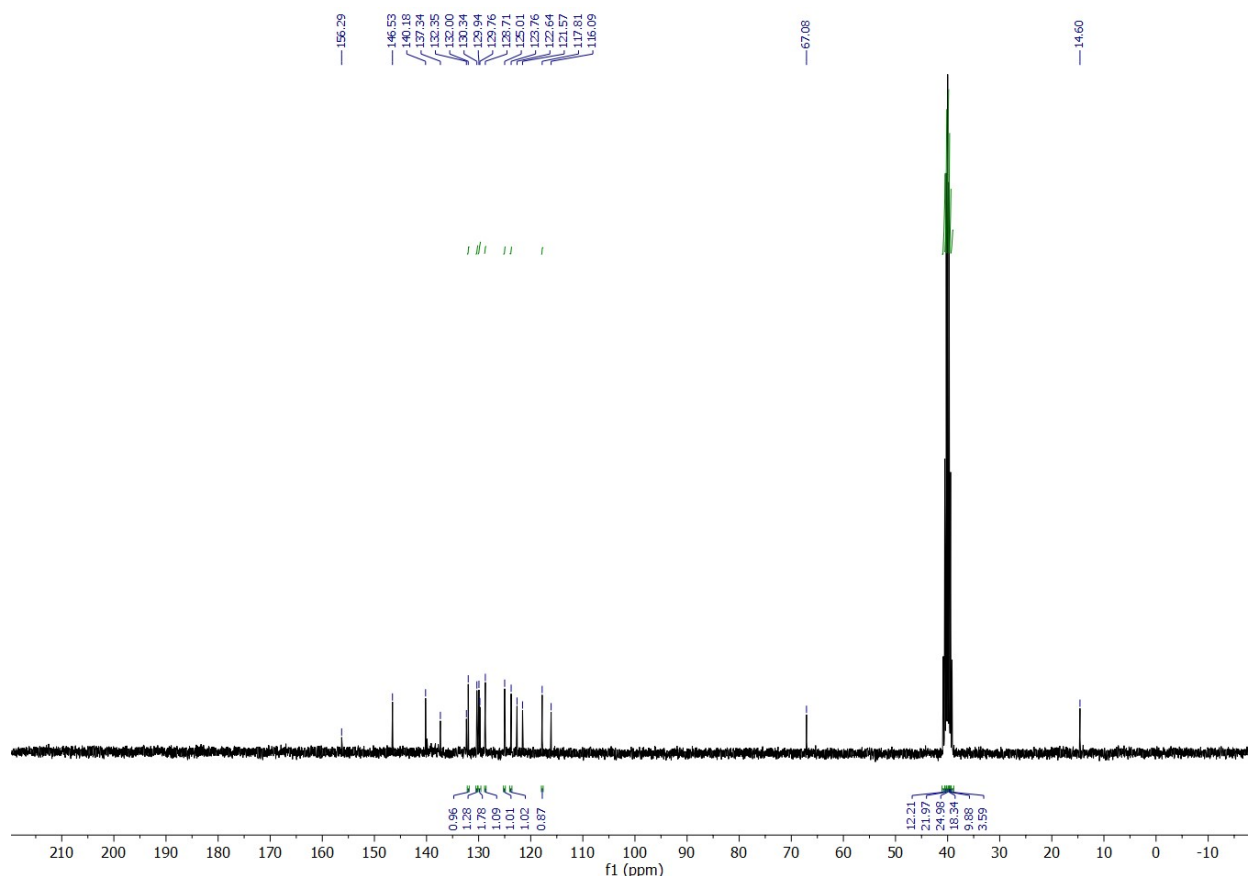


Figure S 20 C-NMR spectra of N-(4-Bromophenyl)-2,4-dinitroaniline

Synthesis N-(2-Bromophenyl)-2,4-dinitroaniline: 0.25mmol of 2-bromoaniline was dissolved in the mix of H₂O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature. M.P: 175-178°C; Ft-IR: 1607, 1538, 1395, 1289, 1154, 932, 834, 647, 528 ; MS m/z : 338 ; Hz, 2H), 8.22 (d, *J* = 2.8 Hz, 1H), 7.74 – 7.67 (m, 3H), 7.42 – 7.34 (m, 3H). ¹³C NMR (76 MHz, DMSO) δ 146.7 (C8), 137.8 (C6), 133.5 (C4), 133.1 (C9), 132.1 (C11), 130.2 (C12), 129.7 (C2), 128.2 (C3), 123.8 (C1), 121.5 (C10), 119.6 (C13), 117.6 (C5).

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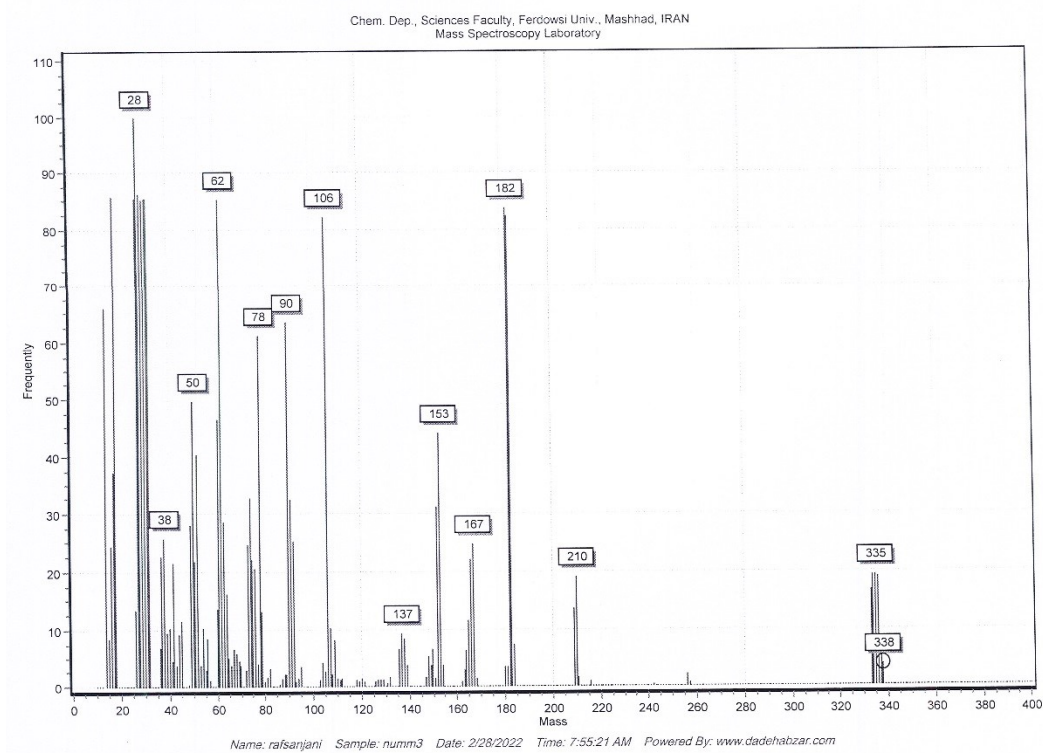


Figure S 21 Mass Spectroscopy of *N*-(2-Bromophenyl)-2,4-dinitroaniline

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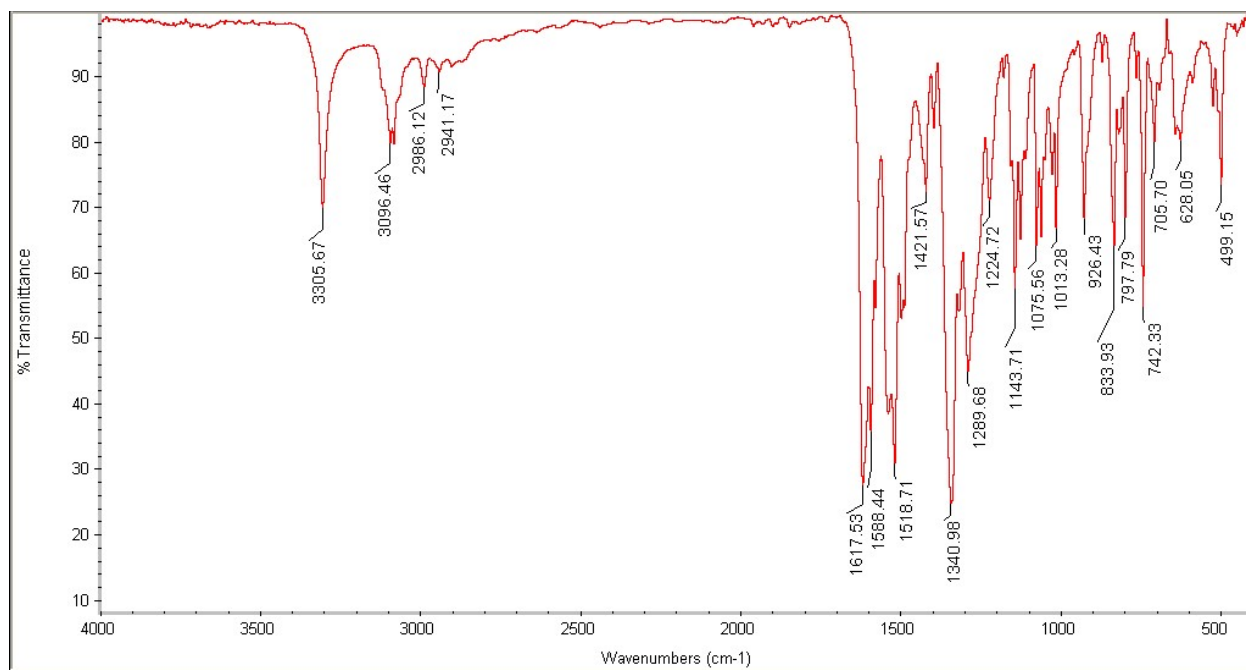


Figure S 22 FT-IR spectra of N-(2-Bromophenyl)-2,4-dinitroaniline

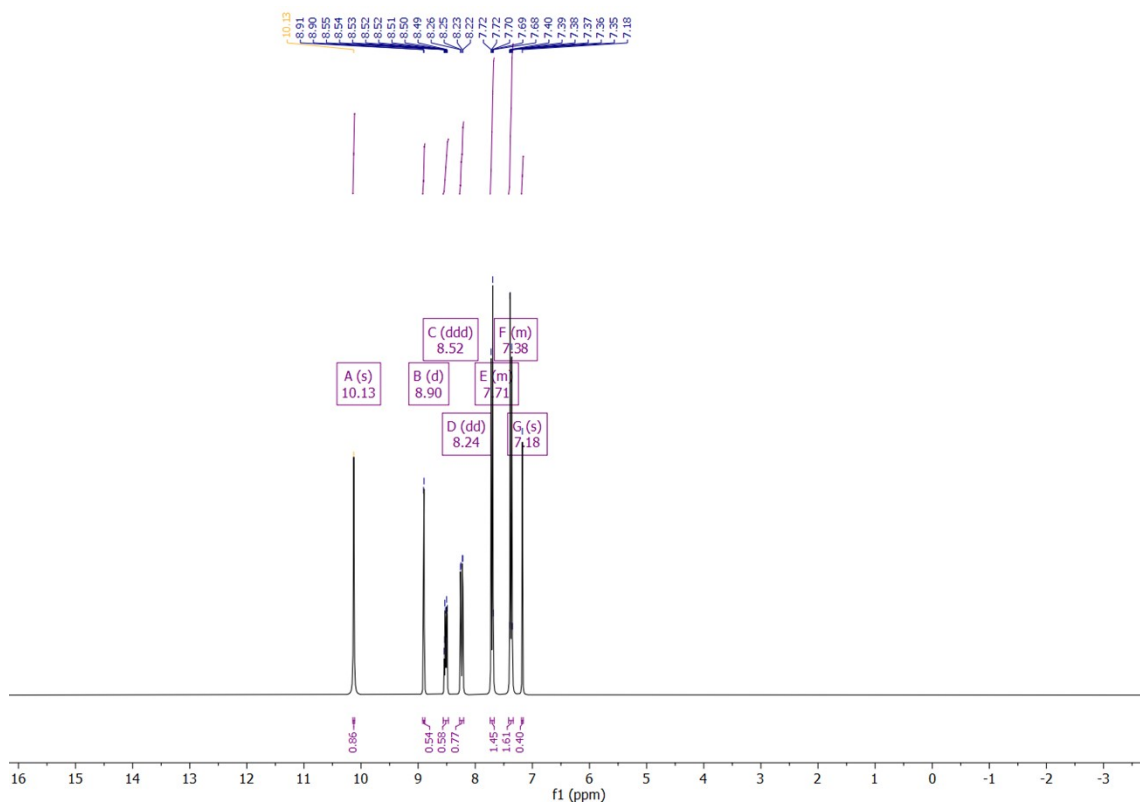


Figure S 23 ¹H-NMR spectra of N-(2-Bromophenyl)-2,4-dinitroaniline

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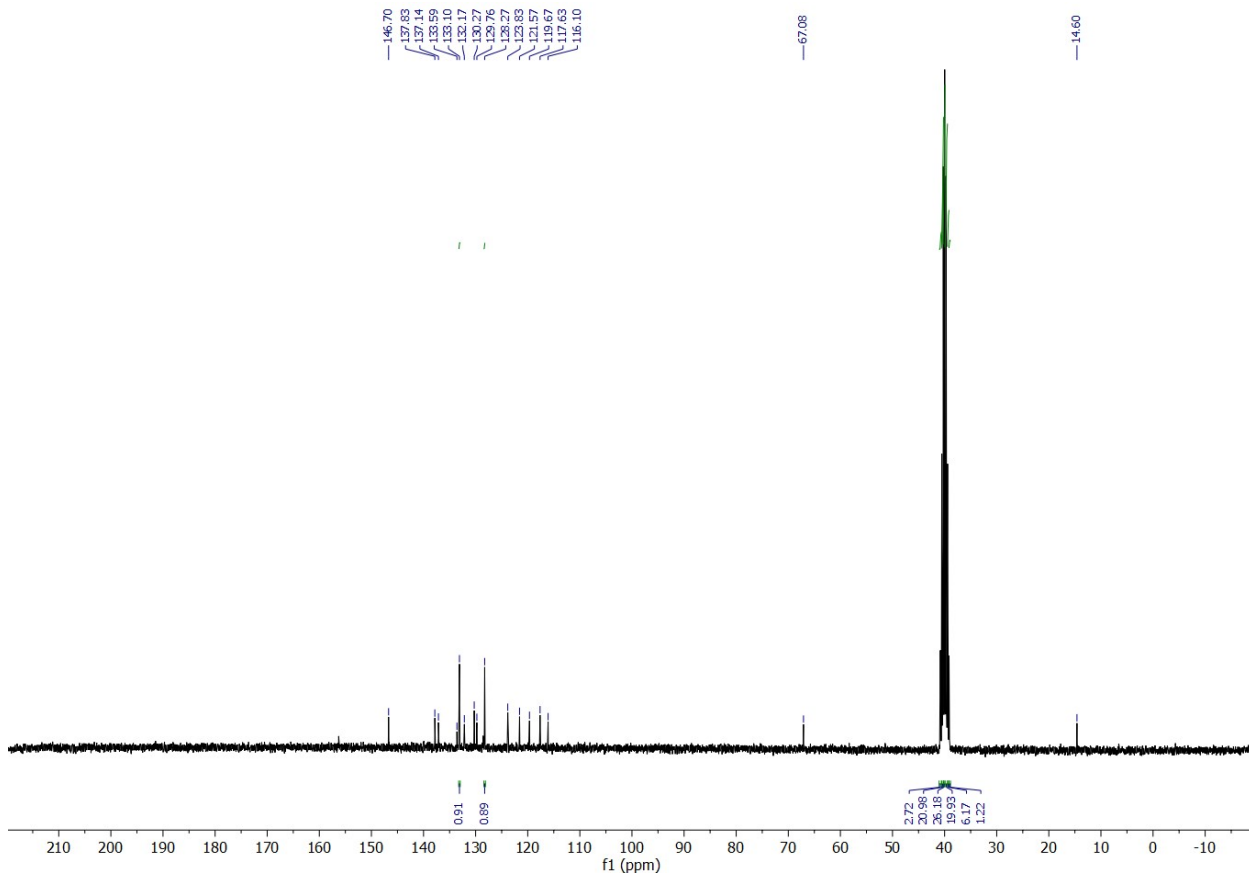


Figure S 24 C-NMR spectra of N-(2-Bromophenyl)-2,4-dinitroaniline

Synthesis N-(3-Bromophenyl)-2,4-dinitroaniline: 0.25mmol of 3-bromoaniline was dissolved in the mix of H₂O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature M.P: 174°C; Ft-IR: 1614, 1525, 1494, 1346, 1290, 1154, 933, 835, 649 ; MS m/z : 338 ; 1H NMR (301 MHz, DMSO) δ 10.14 (s, 1H), 8.89 (d, J = 2.7 Hz, 1H), 8.26 (dd, J = 9.5, 2.8 Hz, 2H), 7.68 – 7.36 (m, 3H), 7.19 (d, J = 9.5 Hz, 1H). 13C NMR (76 MHz, DMSO) δ 138.1 (C6), 136.8 (C8), 132.0 (C9), 130.3 (C2), 128.7

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(C12), 126.2 (C3), 125.0 (C5), 123.9 (C4), 121.5 (C1), 117.3 (C17), 116.1 (C13)

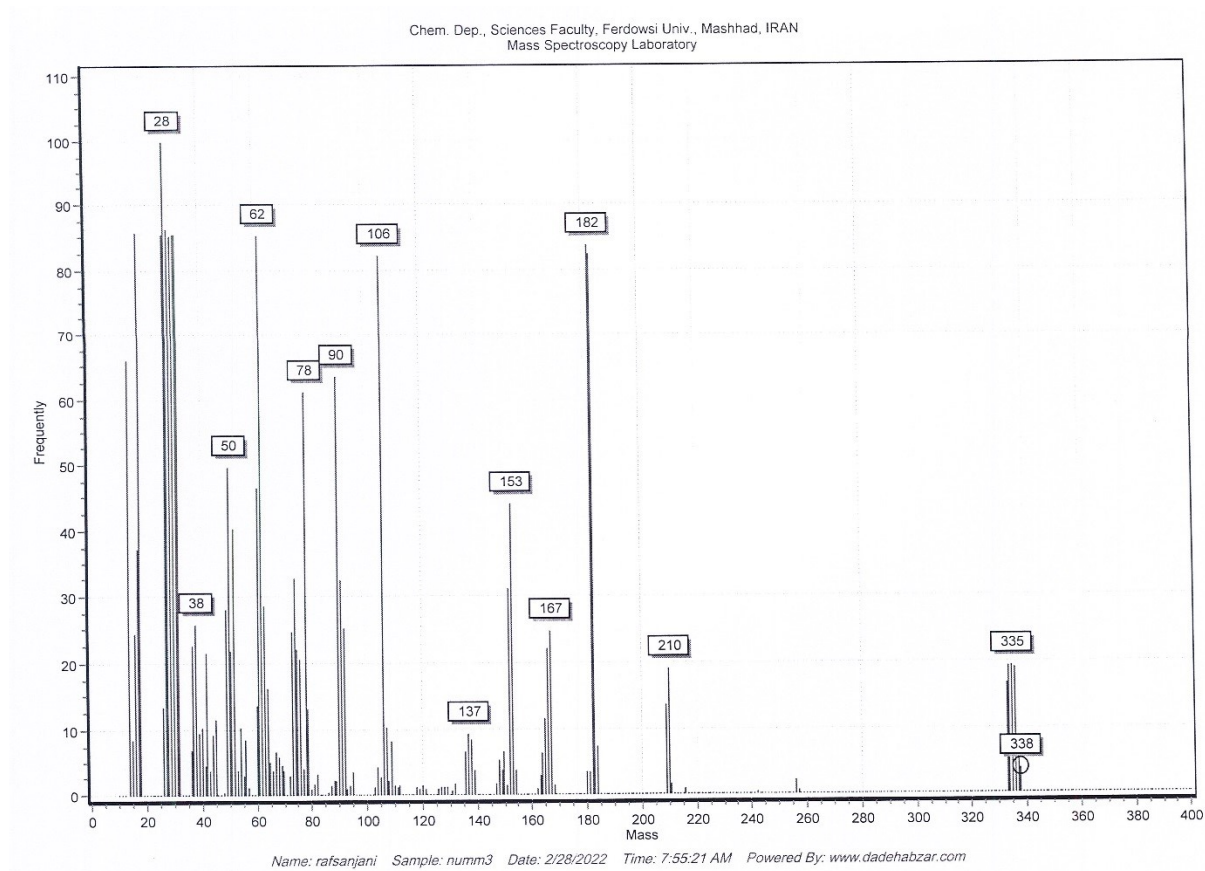


Figure S 25 Mass spectroscopy of N-(3-Bromophenyl)-2,4-dinitroaniline

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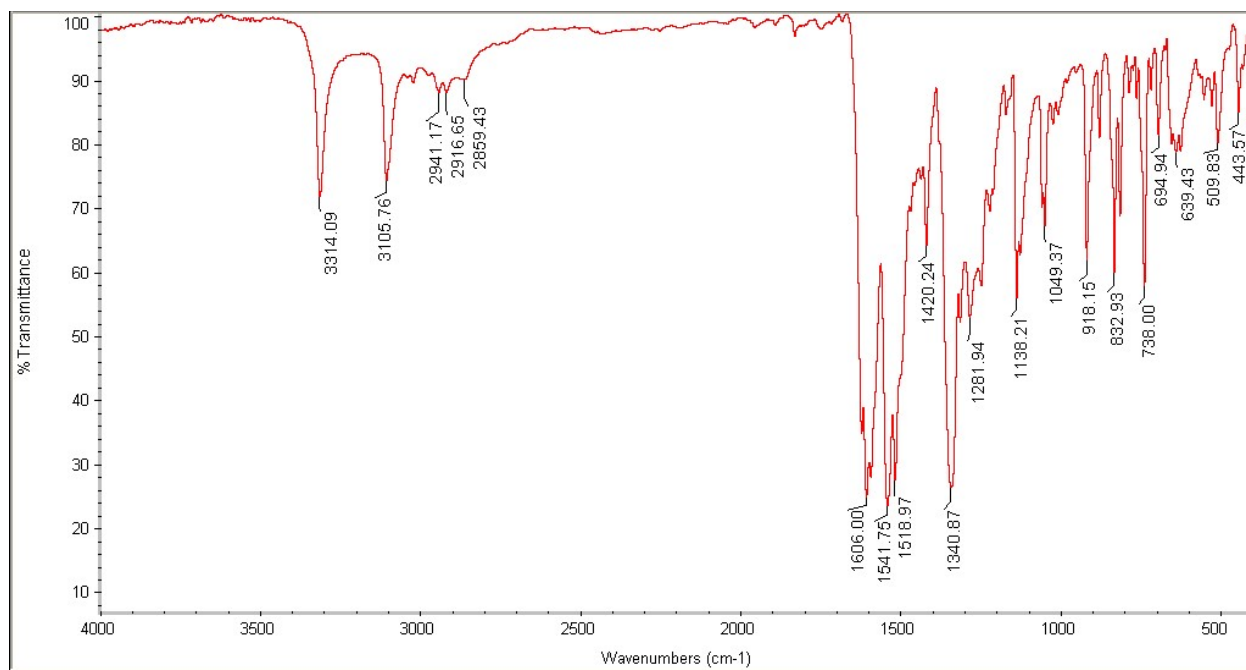


Figure S 26 FT-IR Spectra of *N*-(3-Bromophenyl)-2,4-dinitroaniline

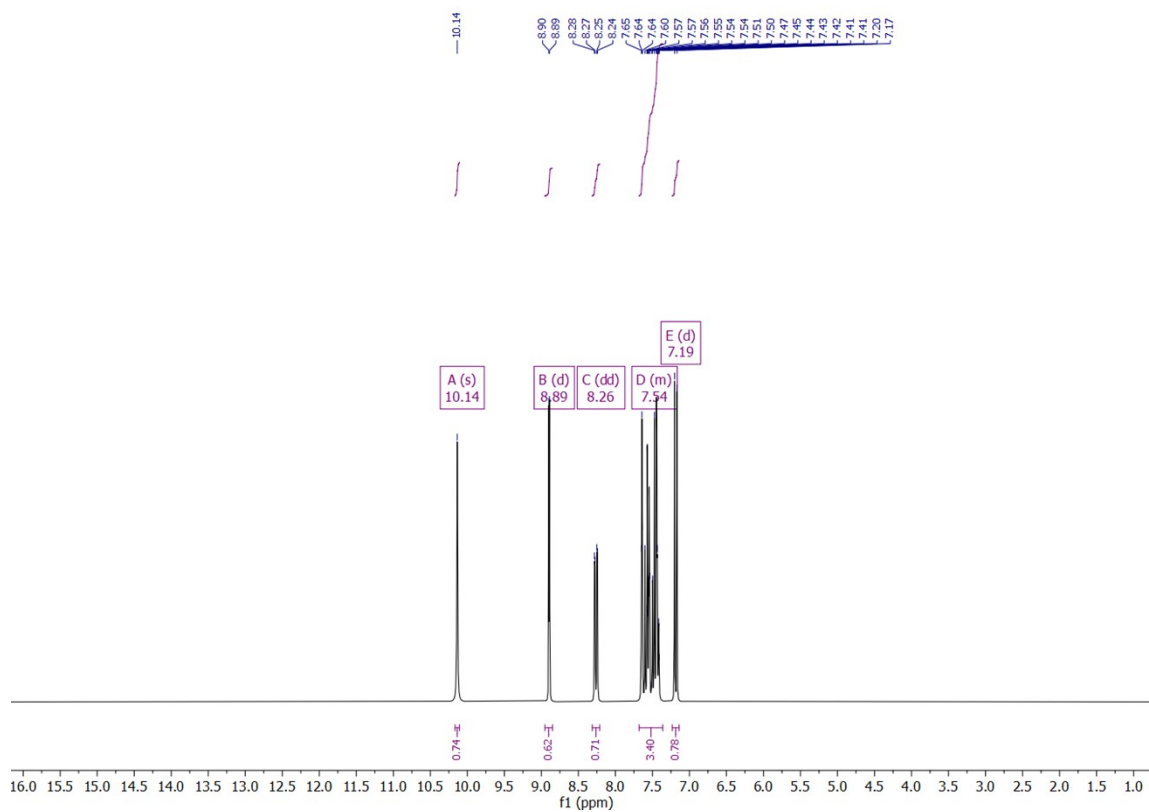


Figure S 27 ¹H-NMR spectra of *N*-(3-Bromophenyl)-2,4-dinitroaniline

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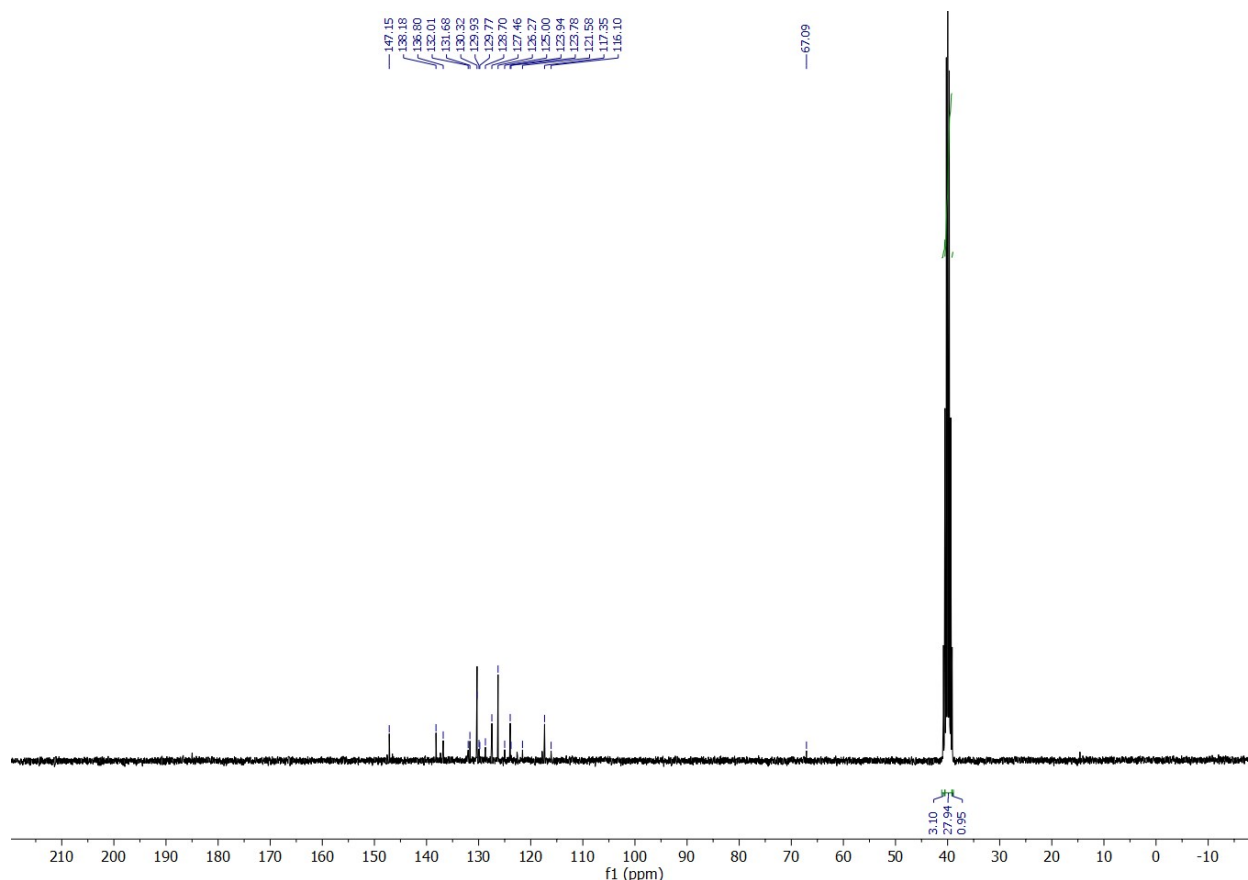


Figure S 28 ^{13}C -NMR spectra of *N*-(3-Bromophenyl)-2,4-dinitroaniline

Synthesis *N*-(3,4-dimethylphenyl)-2,4-dinitroaniline : 0.25mmol of 3,4-dimethylaniline was dissolved in the mix of H_2O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature. M.P: 154-155 $^\circ\text{C}$;FT-IR: 2945, 2920, 1609, 1542, 1516, 1338, 1287, 1138, 918, 832; MS $m/z(\text{M}^+)$: 289 ; ^1H NMR (301 MHz, DMSO) δ 10.10 (s, 1H), 8.88 (d, $J = 2.8$ Hz, 1H), 8.20 (dd, $J = 9.6, 3.4$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 2.3$ Hz, 1H), 7.13 – 7.02 (m, 3H), 2.27 (d, $J = 2.5$ Hz, 1H). ^{13}C NMR (76 MHz, DMSO) δ 147.5 (C8), 138.4 (C4), 135.8 (C6), 133.5 (C3), 131.2 (C9), 131.1 (C11), 130.2 (C2), 127.3 (s,C12), 123.7 (C5), 121.5 (C10), 117.3 (C13,1), 19.8 (C14), 19.4 (C15).

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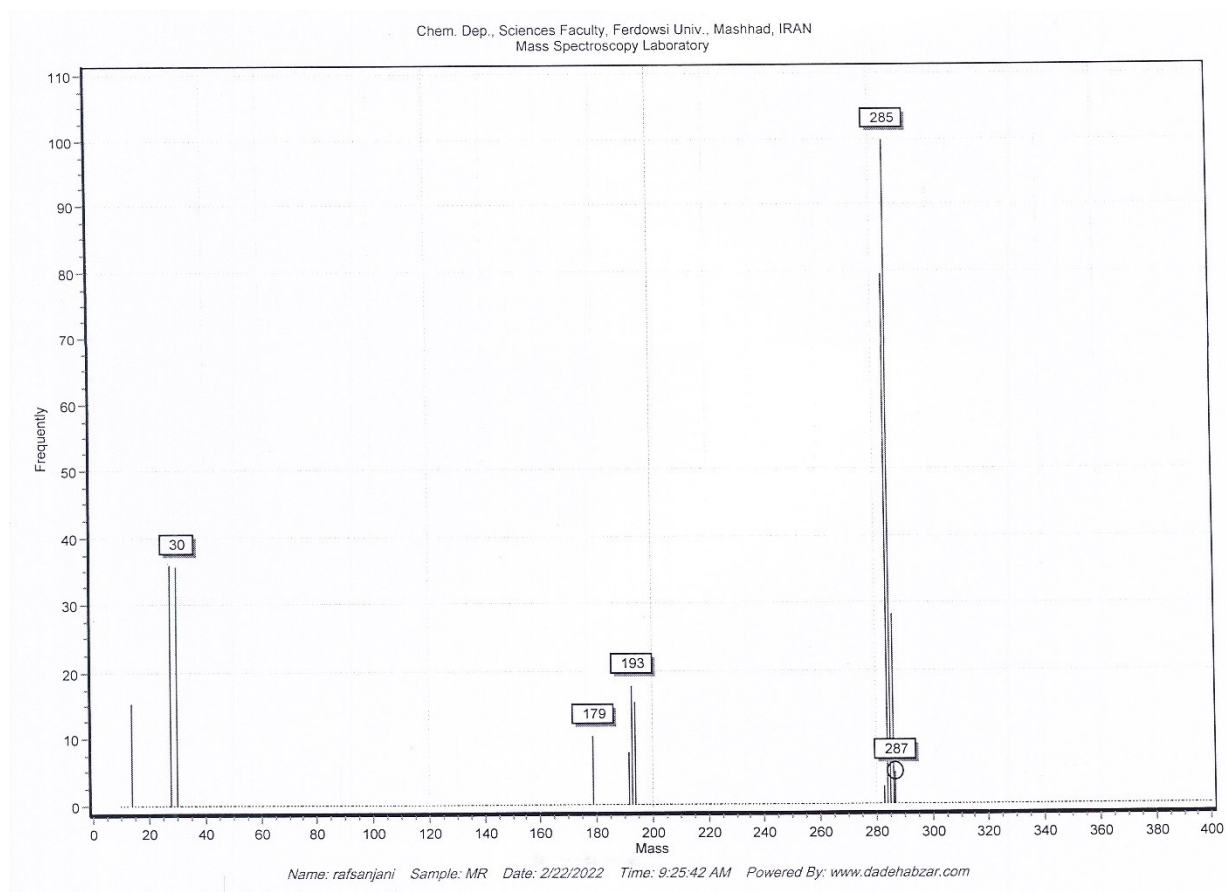


Figure S 29 Mass Spectroscopy of *N*-(3,4-dimethylphenyl)-2,4-dinitroaniline

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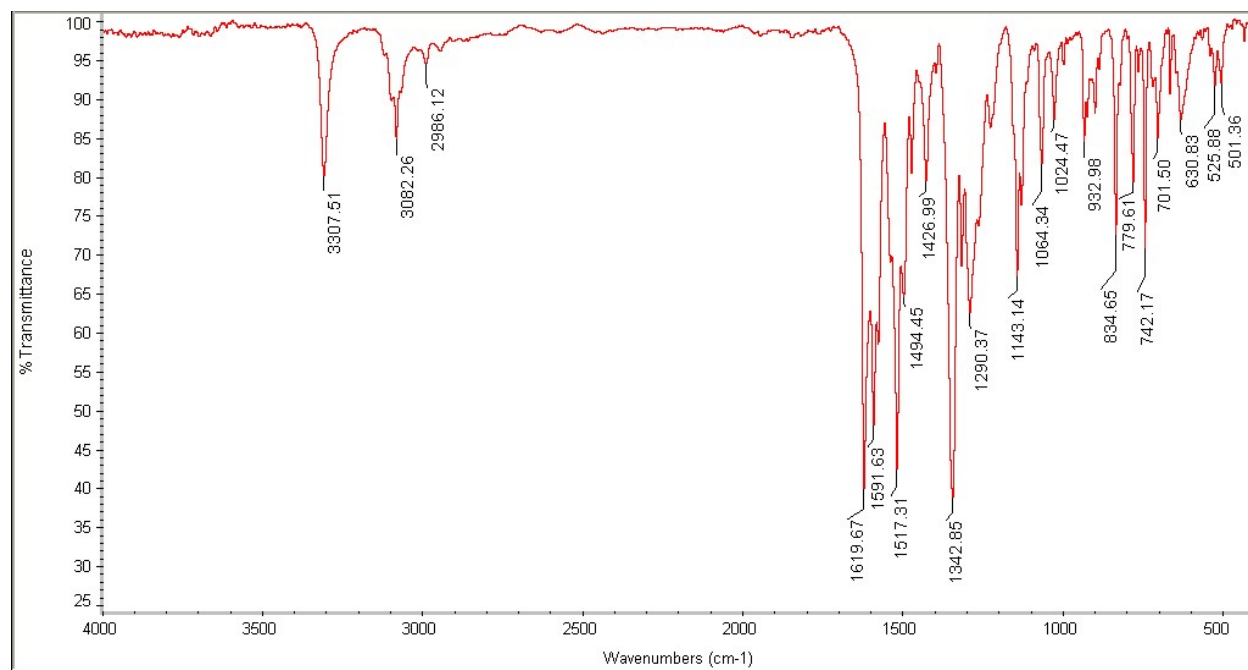


Figure S 30 FT-IR Spectra of *N*-(3,4-dimethylphenyl)-2,4-dinitroaniline

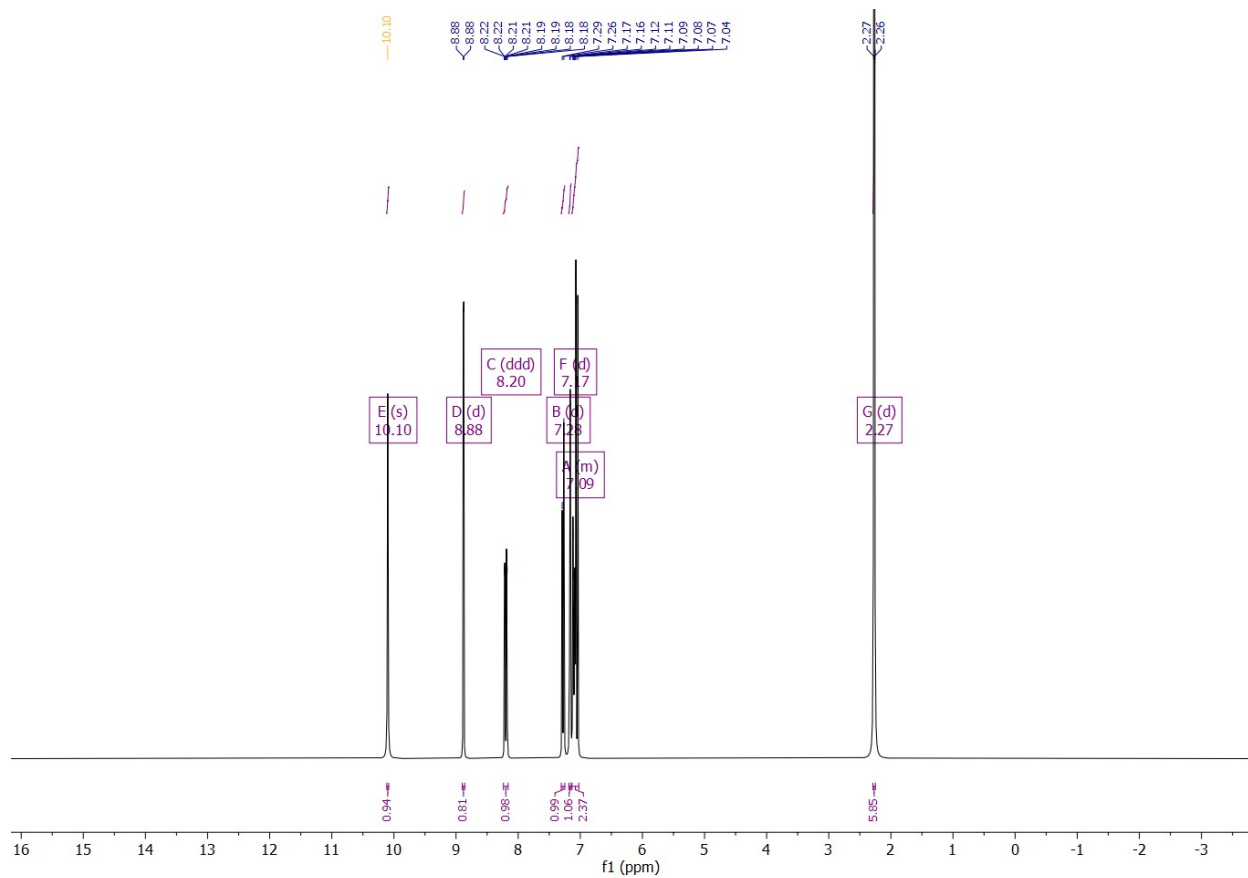


Figure S 31 ¹H-NMR Spectra of *N*-(3,4-dimethylphenyl)-2,4-dinitroaniline

Supporting information

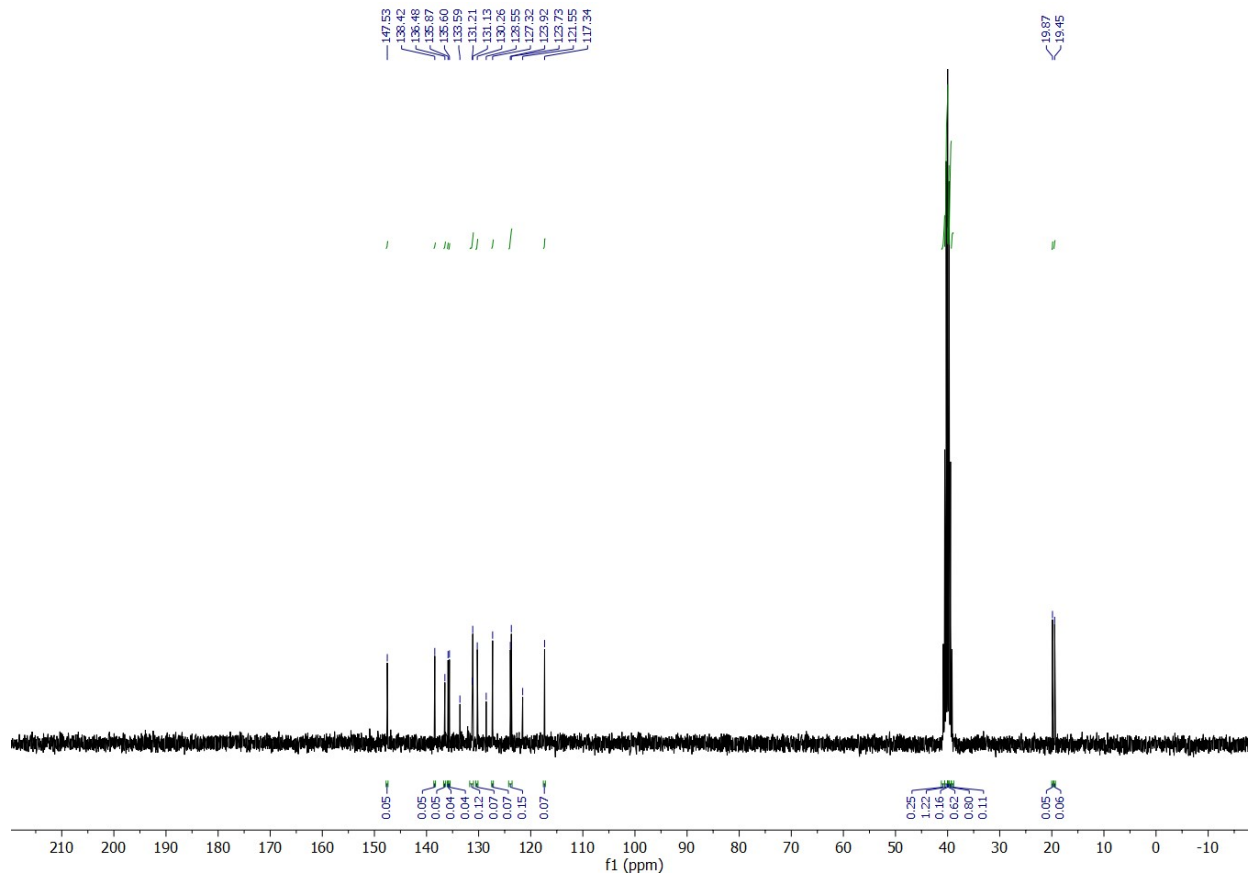


Figure S 32 C-NMR Spectra of N-(3,4-dimethylphenyl)-2,4-dinitroaniline

Synthesis 2,4-dinitro-N-(p-tolyl): 0.25mmol of p-tolyaniline was dissolved in the mix of H₂O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature M.P:141-142°C; Ft-IR: 2921, 1621, 1581, 1518, 1336, 1284, 1220, 1141, 918, 803; MS m/z(M⁺): 274; 1H NMR (301 MHz, DMSO) δ 10.11 (s, 1H), 8.90 (d, J = 2.8 Hz, 1H), 8.22 (dd, J = 9.6, 2.8 Hz, 2H), 8.11 (d, J = 8.9 Hz, 0H), 7.29 (d, J = 8.0 Hz, 1H), 7.21 – 7.01 (m, 3H), 2.27 (s, 1H). 13C NMR (76 MHz, DMSO) δ 148.0 (C8), 136.3 (C6), 133.5 (C3), 131.0 (C11), 130.6 (C2,4), 130.2 (C12), 128.2 (C9), 123.9 (C1,5), 121.5 (C10), 117.1 (C13), 55.8 (C14).

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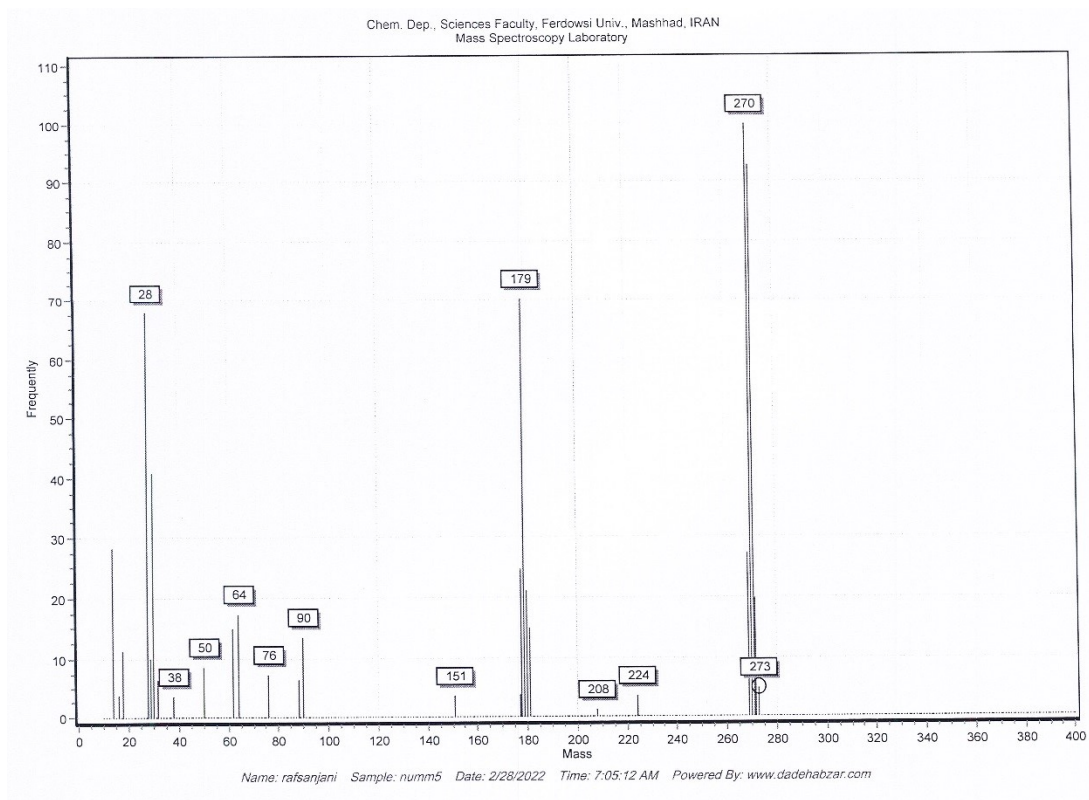


Figure S 33 Mass spectroscopy of 2,4-dinitro-N-(p-tolyl)

Supporting information

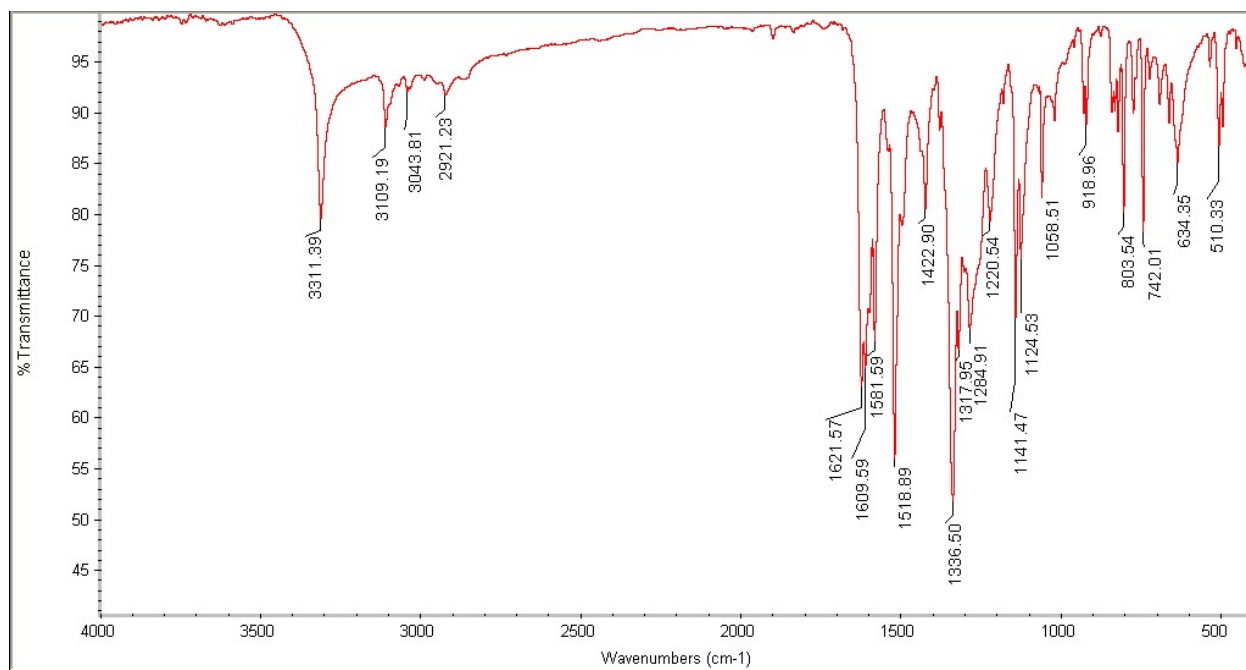


Figure S 34 FT-IR Spectroscopy of 2,4-dinitro-N-(p-tolyl)

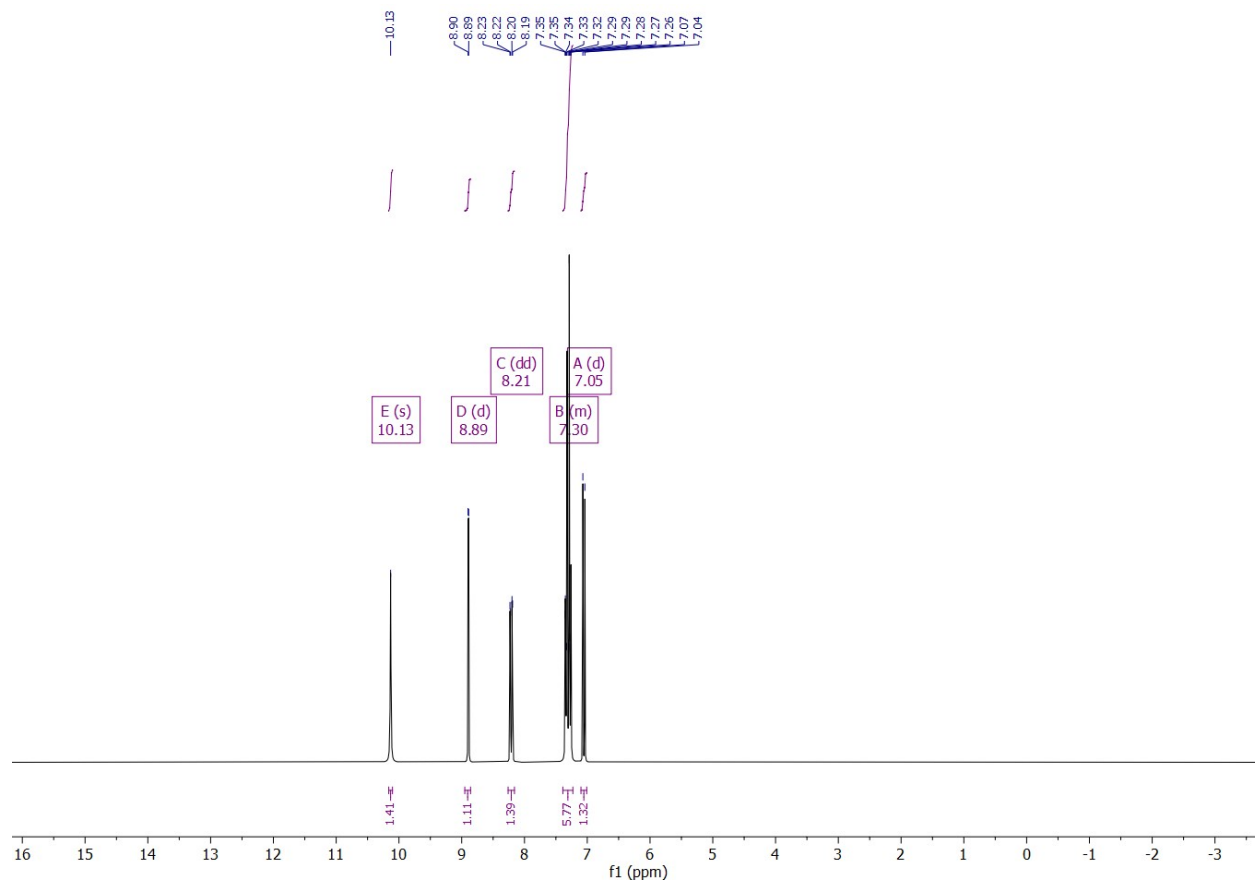


Figure S 35 ¹H-NMR Spectra 2,4-dinitro-N-(p-tolyl)

Supporting information

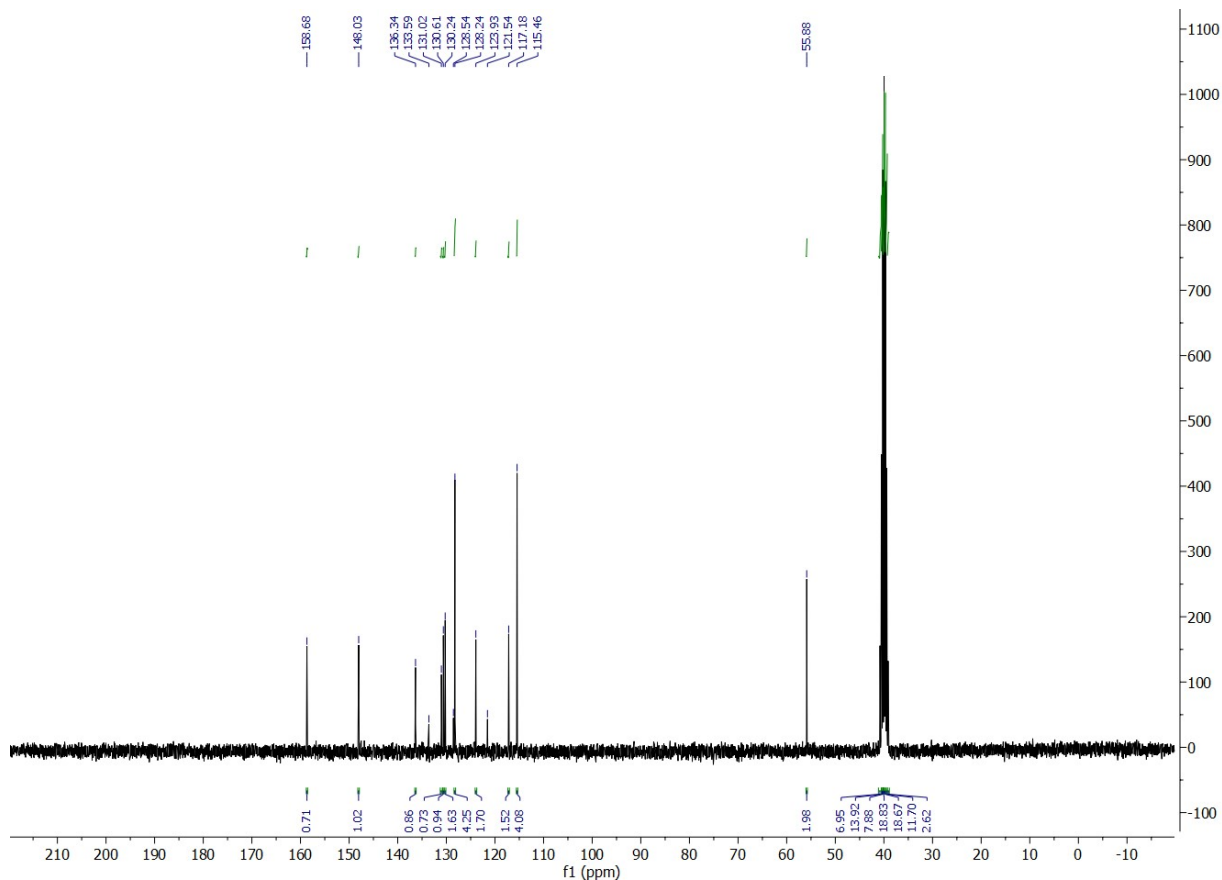


Figure S 36 C-NMR spectra of 2,4-dinitro-N-(p-tolyl)

- Synthesis N-(4-methoxyphenyl)-2,4-dinitroaniline:** 0.25mmol of 4-methoxyaniline was dissolved in the mix of H₂O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature M.P: 143-145°C : Ft-IR : 3329, 3309, 1619, 1593, 1512, 1336, 1247, 9278, 833; MS m/z: 289.25; ¹H NMR (301 MHz, DMSO) δ 10.12 (s, 1H), 8.89 (d, *J* = 2.7 Hz, 1H), 8.20 (dd, *J* = 9.6, 2.8 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.13 – 7.04 (m, 3H), 3.82 (s, 1H). ¹³C NMR (76 MHz, DMSO) δ 146.8 (C8), 131.4 (C11), 130.2 (C6), 130.1 (C9), 129.7 (C12), 128.5 (C3), 128.0 (C1,5), 121.5 (C10), 117.5 (C13), 116.0 (C2,4), 14.5 (C21).

Supporting information

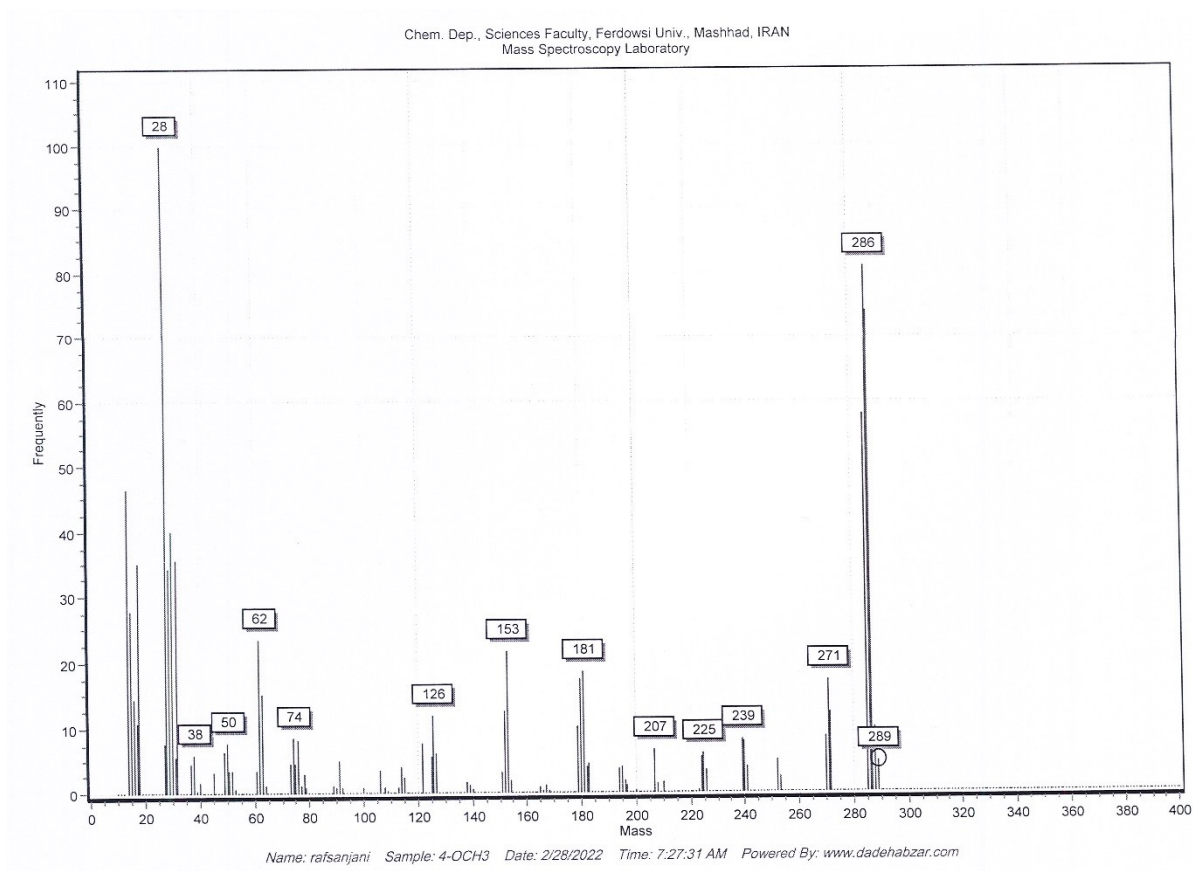


Figure S 37 Mass Spectroscopy of *N*-(4-methoxyphenyl)-2,4-dinitroaniline

Supporting information

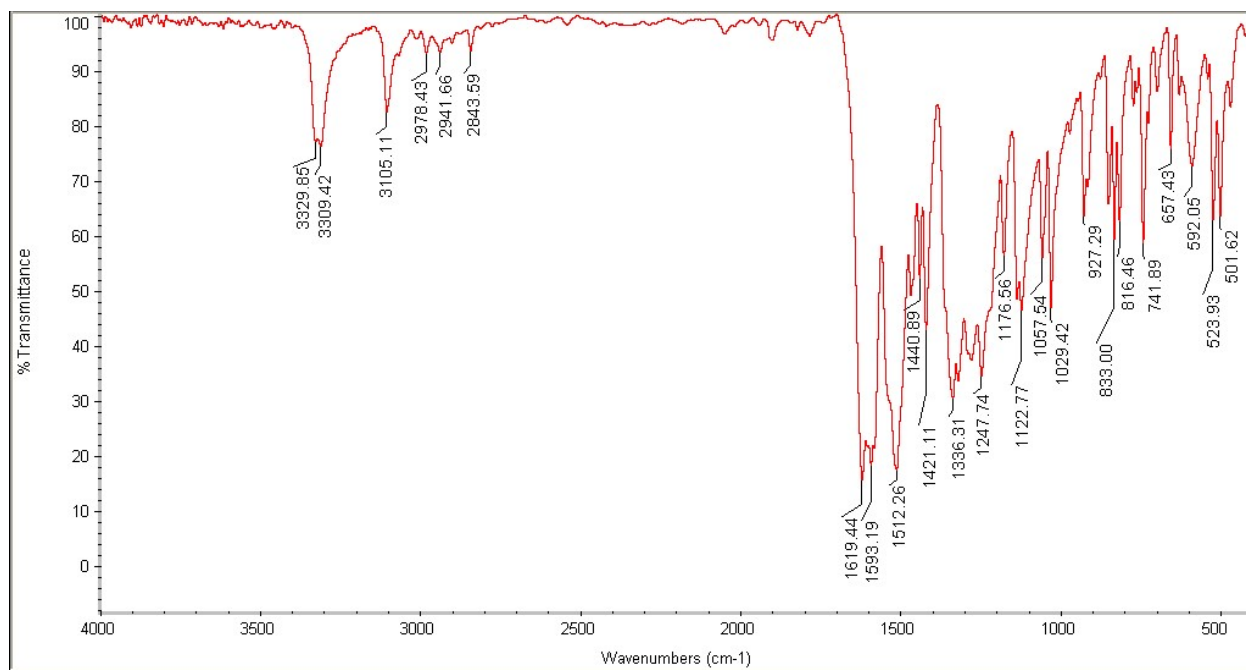


Figure S 38 FT-IR Spectroscopy of *N*-(4-methoxyphenyl)-2,4-dinitroaniline

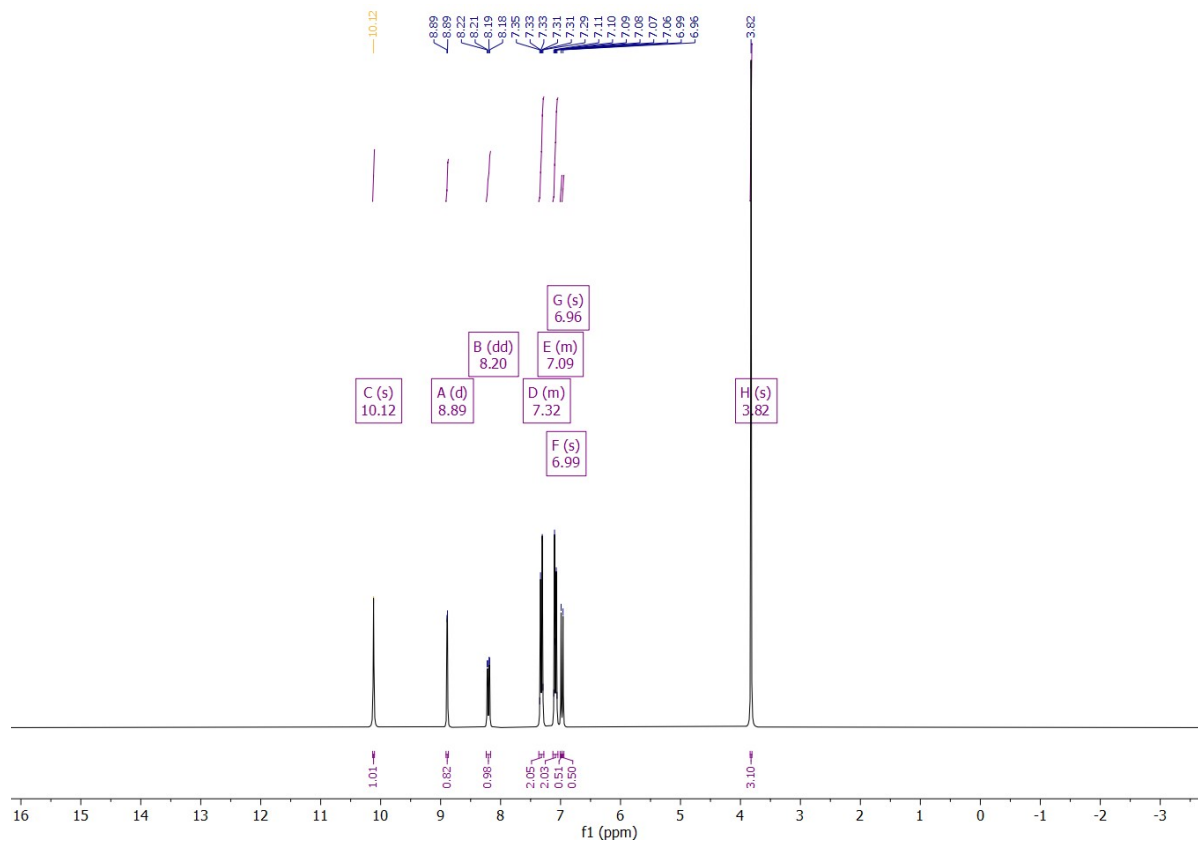


Figure S 39 ¹H-NMR Spectra of *N*-(4-methoxyphenyl)-2,4-dinitroaniline

Supporting information

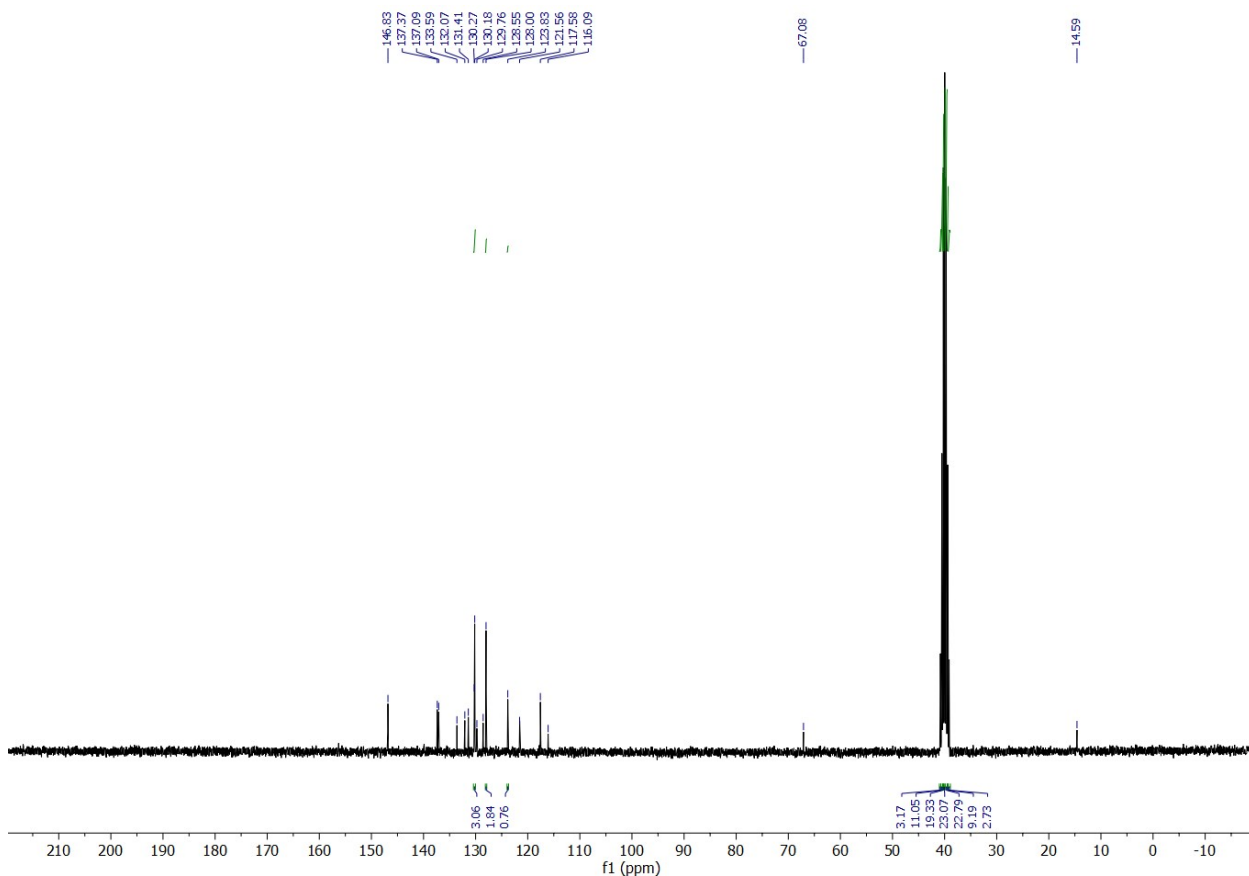


Figure S 40 ^{13}C -NMR spectra of *N*-(4-methoxyphenyl)-2,4-dinitroaniline

- Synthesis N-(4-chlorophenyl)-2,4-dinitroaniline:** 0.25mmol of 4-chloroaniline was dissolved in the mix of H_2O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature .M.P: 166-169 $^{\circ}\text{C}$; Ft-IR : 1619, 1608, 1519, 1341, 1286, 1141, 918, 833, 741; MS m/z :293.66; ^1H NMR (301 MHz, DMSO) δ 10.15 (s, 1H), 8.90 (d, J = 2.8 Hz, 1H), 8.53 (dd, J = 8.9, 2.7 Hz, 2H), 8.22 (d, J = 2.8 Hz, 1H), 7.64 – 7.53 (m, 3H), 7.44 (d, J = 8.7 Hz, 1H). ^{13}C NMR (76 MHz, DMSO) δ 146.8 (C8), 137.3 (C6), 131.4 (C11), 130.2 (C9), 130.1 (C2,4), 129.7 (C12), 128.5 (C3), 128.0 (C1,5), 121.5 (C10), 116.1 (C13).

Supporting information

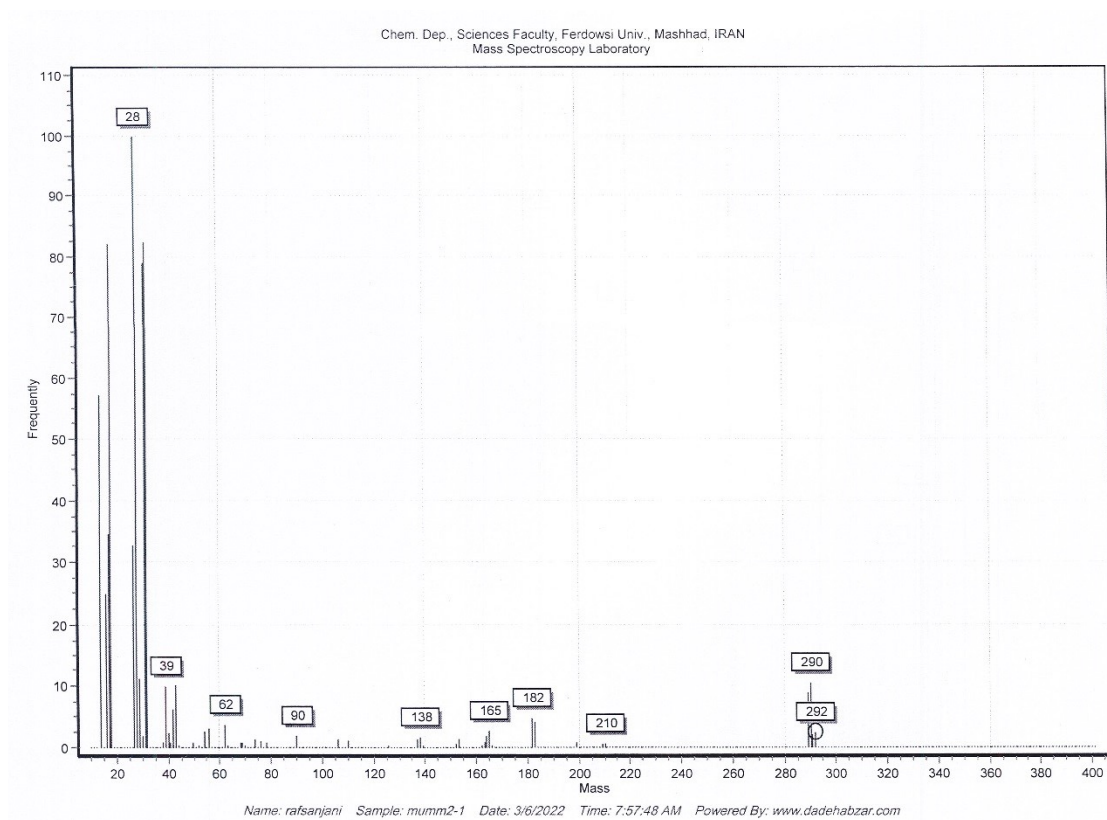


Figure S 41 Mass Spectroscopy of *N*-(4-chlorophenyl)-2,4-dinitroaniline

Supporting information

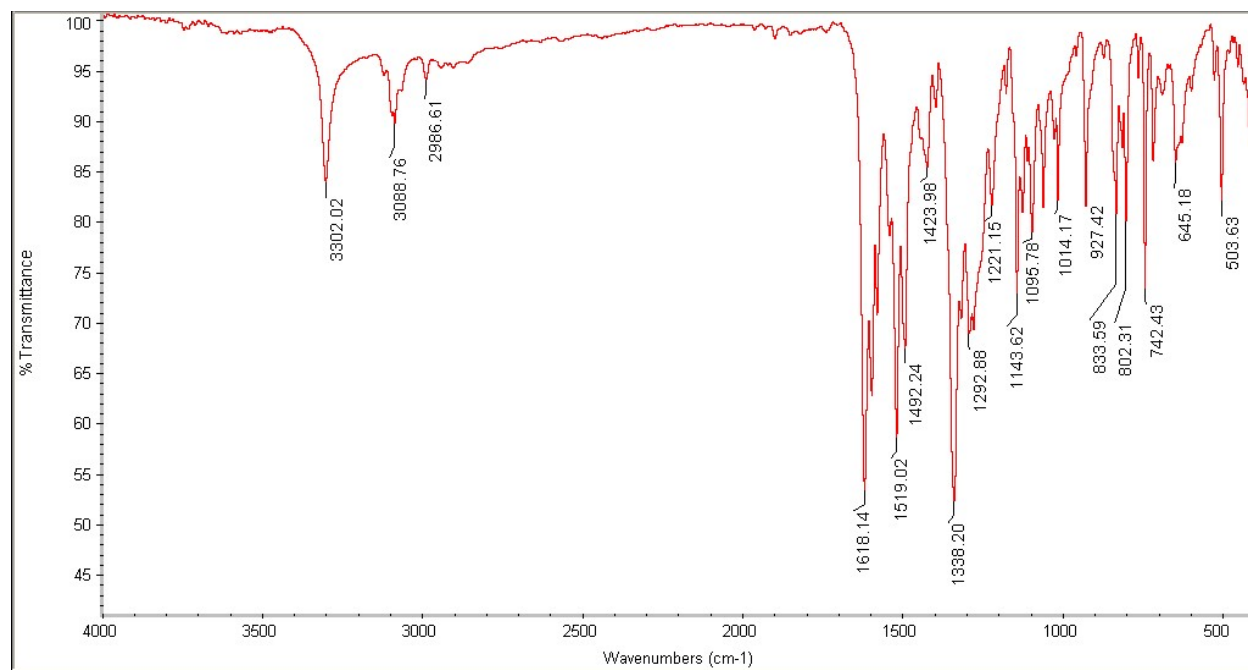


Figure S 42 FT-IR spectra of *N*-(4-chlorophenyl)-2,4-dinitroaniline

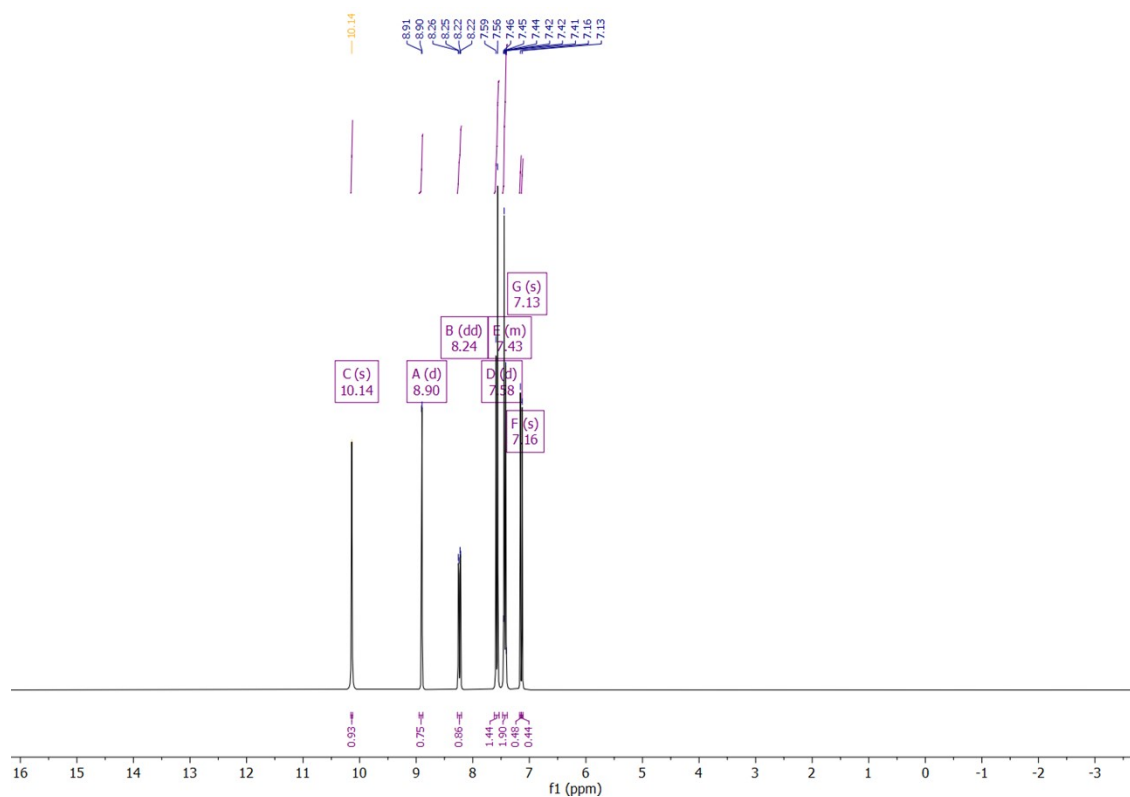


Figure S 43 ¹H-NMR Spectra of *N*-(4-chlorophenyl)-2,4-dinitroaniline

Supporting information

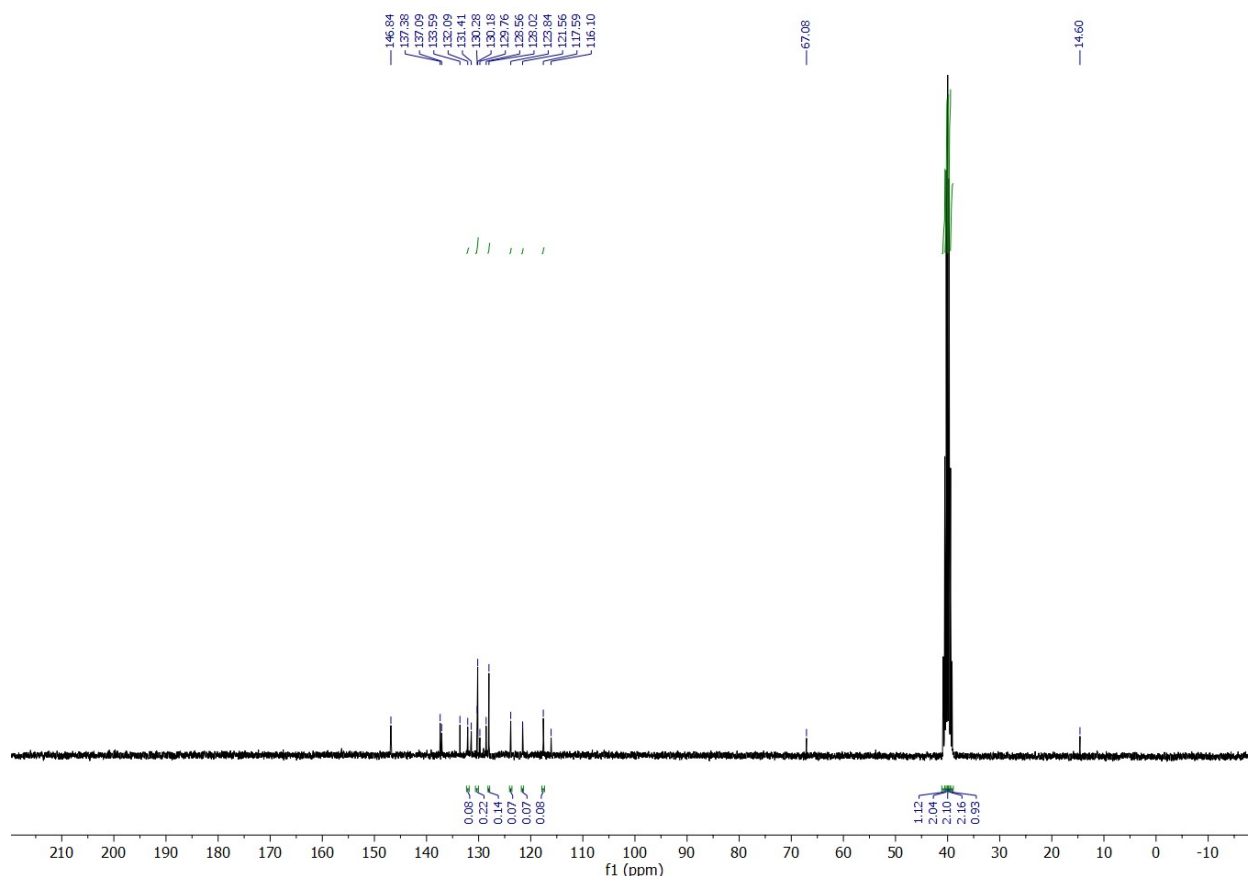


Figure S 44 ^{13}C -NMR Spectra of *N*-(4-chlorophenyl)-2,4-dinitroaniline

- Synthesis *N*-(3-chlorophenyl)-2,4-dinitroaniline** : 0.25mmol of 3-chloroaniline was dissolved in the mix of H_2O and ethanol (2cc / 1:1), after obtaining a uniform solution, 0.3mmol of 2,4-dinitrochlorobenzene was added and allowed them to be uniform. Finally, photocatalyst was added and the mixture was exposed to sunlight. The control of the reaction was carried out by TLC each 15 min. The reaction was carried out for 60 min. The product was filtered and the precipitate was washed with ethyl acetate. Then the liquid was kept under the hood to evaporate the solvent. Before full evaporation, the obtained precipitate was filtered again by filter paper and recrystallized by ethyl acetate and then it was dried at the room temperature M.P: 182-183°C; Ft-IR : 1618, 1519, 1492, 1338, 1292, 1143, 927, 802, 742; MS m/z :293.66; ^1H NMR (301 MHz, DMSO) δ 10.13 (s, 1H), 8.91 (dd, $J = 9.3, 2.7$ Hz, 2H), 8.52 (d, $J = 8.9, 2.7$ Hz, 1H), 8.26 (dd, $J = 9.5, 2.8$ Hz, 2H), 7.58 – 7.49 (m, 2H), 7.46 – 7.35 (m, 2H). ^{13}C NMR (76 MHz, DMSO) δ 138.4 (C6), 136.4 (C8), 135.8 (C4), 131.2 (C9), 131.1 (C11), 130.2 (C12), 128.5 (C2), 127.3 (C5), 123.7 (C3), 121.5 (C10), 117.3 (C1,13).

Supporting information

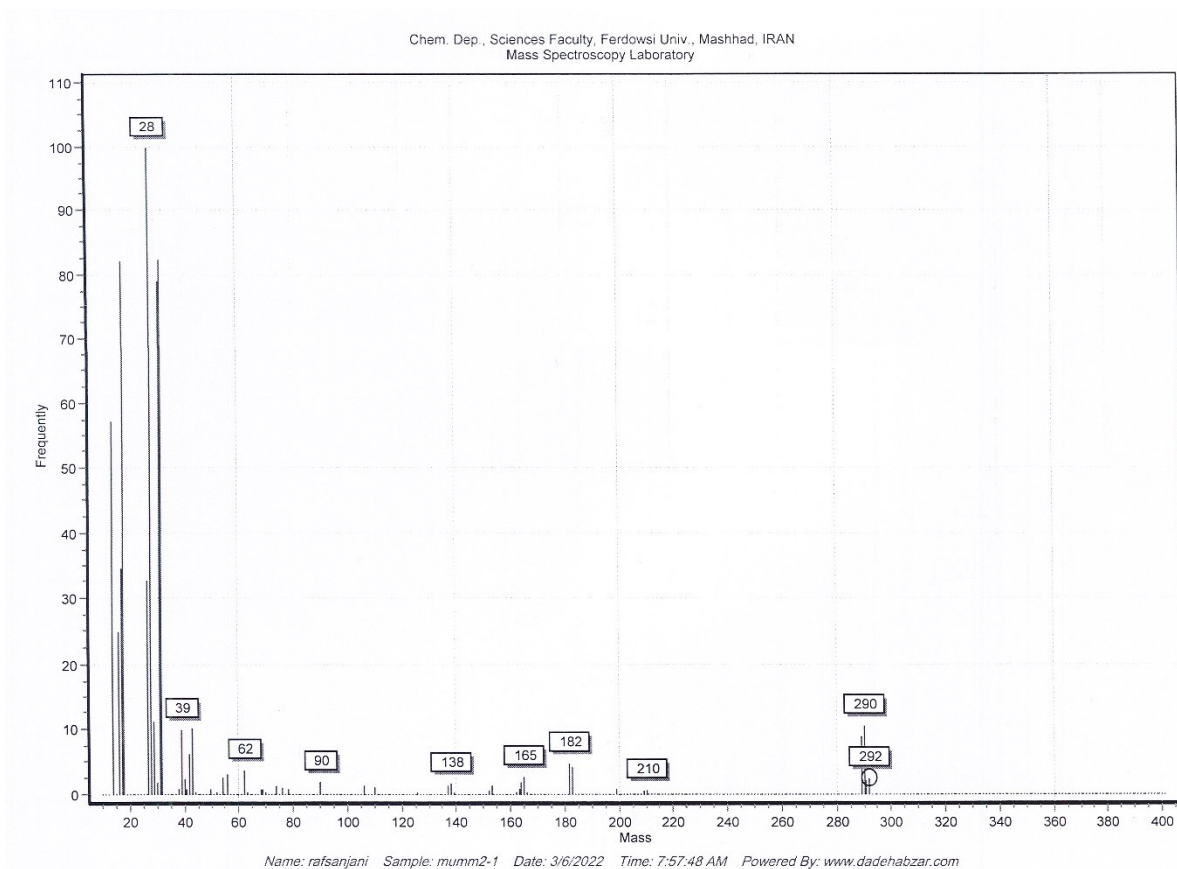


Figure S 45 Mass Spectroscopy of *N*-(3-chlorophenyl)-2,4-dinitroaniline

Supporting information

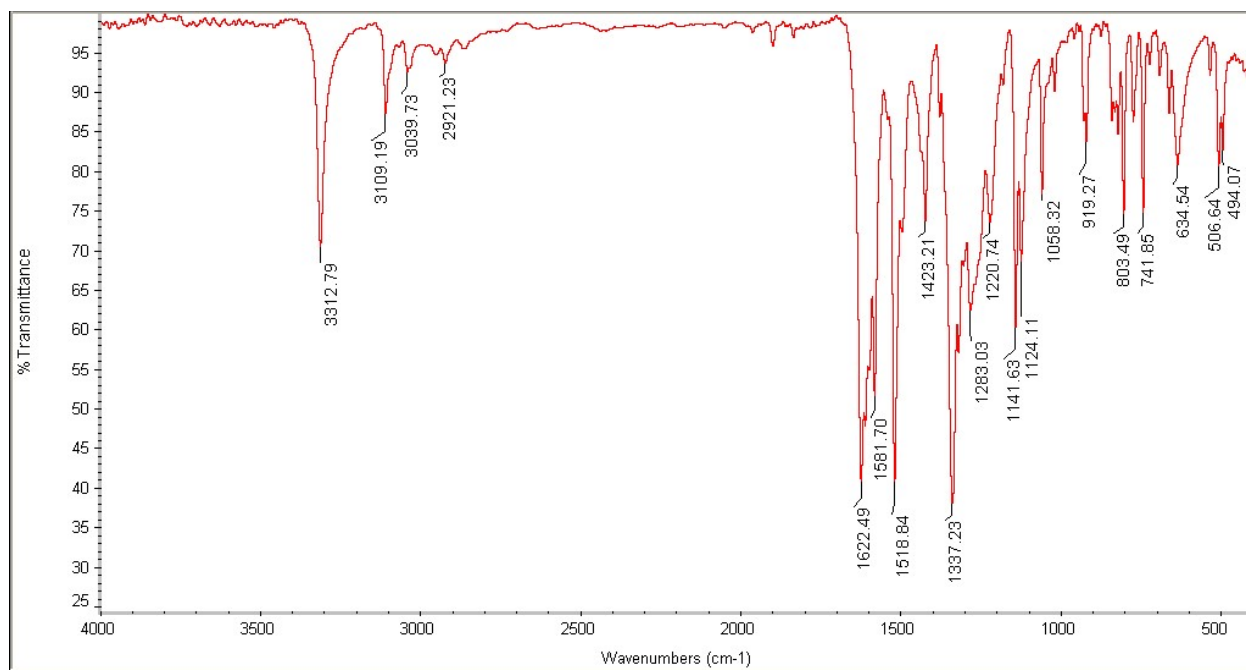


Figure S 46 FT-IR Spectra of *N*-(3-chlorophenyl)-2,4-dinitroaniline

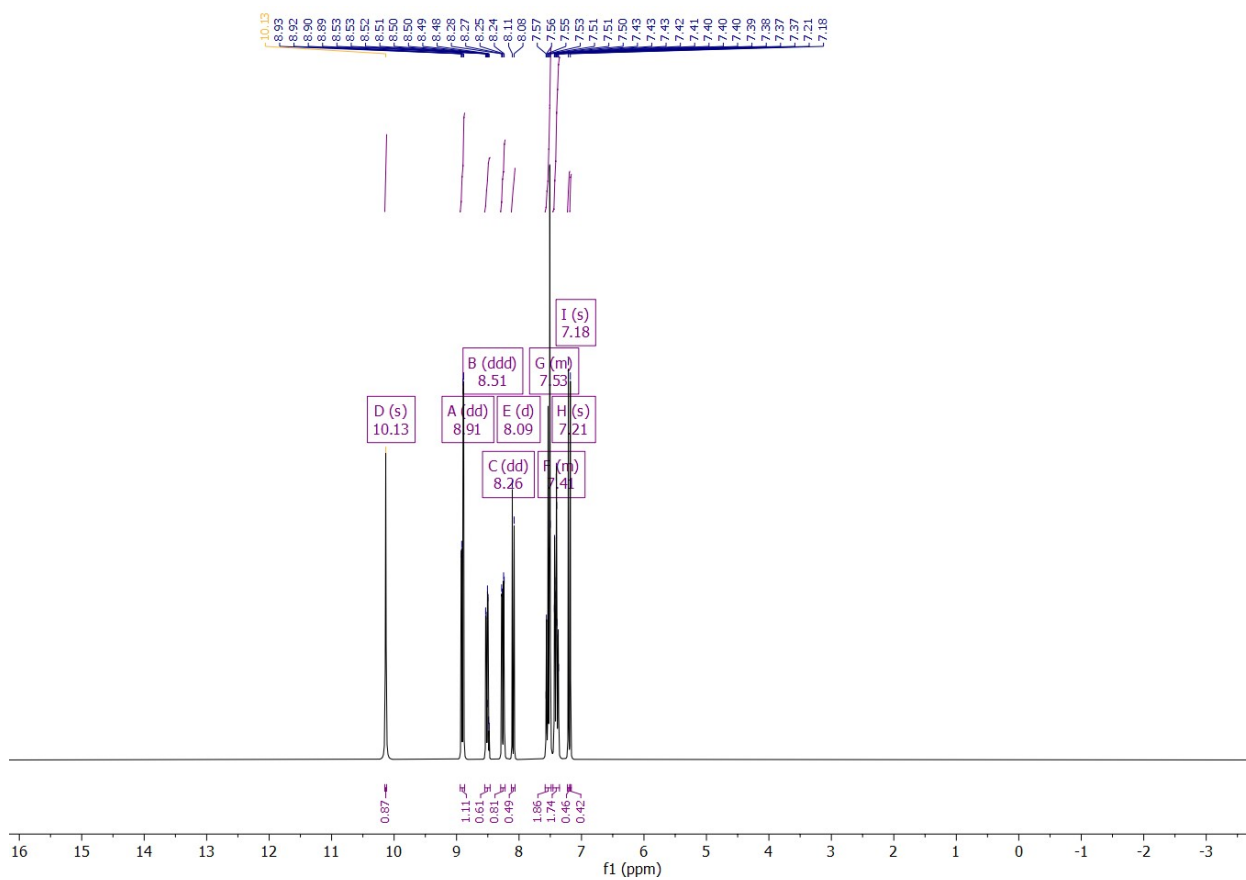


Figure S 47 ¹H-NMR Spectra of *N*-(3-chlorophenyl)-2,4-dinitroaniline

Supporting information

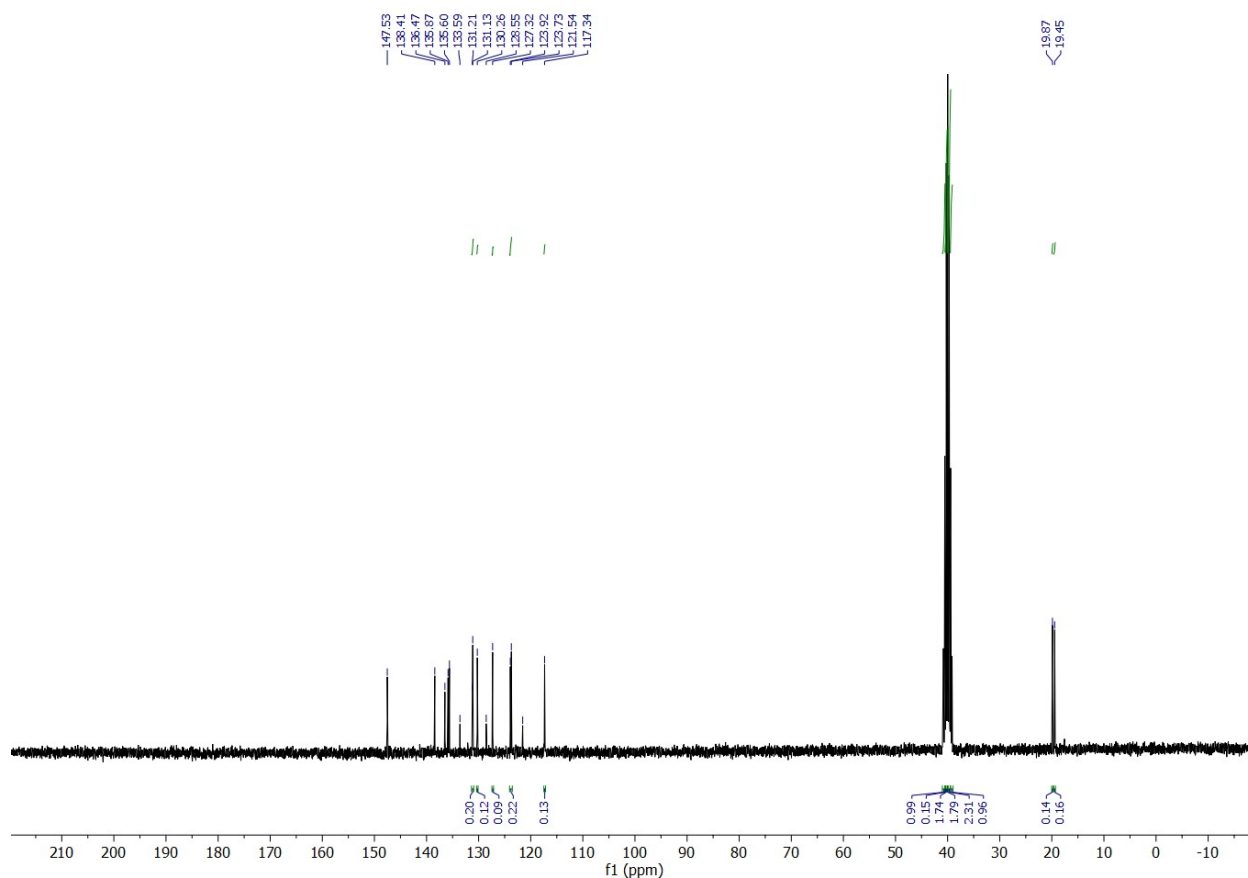


Figure S 48 C-NMR Spectra of N-(3-chlorophenyl)-2,4-dinitroaniline

- (1) Rafsanjani Dehghazi, M.; Absalan, Y.; Gholizadeh, M.; Razavi, M.; Souri, K. Noble-Free Nanophotocatalyst of $Ti_xFe_yLa_mO_z$ for Efficient Photocatalytic C–N Cross-Coupling Reactions under Visible Light. *ACS Appl. Nano Mater.* **2023**, *6* (2), 1106–1118. <https://doi.org/10.1021/acsanm.2c04617>.