**Montmorillonite K-10 catalyzed Mannich reaction - Synthesis of aminonaphthoquinone derivatives from Lawsone**

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**Synthetic Procedure for various aminonaphthoquinones**

**Synthetic procedure for the preparation of 2-hydroxy-3-(phenyl(phenylamino)methyl)naphthalene-1,4-dione (4a)**

A mixture of benzaldehyde(1 mmol), aniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-(phenyl(phenylamino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-(phenyl(*p-*tolylamino)methyl)naphthalene-1,4-dione (4b)**

A mixture of benzaldehyde(1 mmol), 4-methylaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-(phenyl(*p-*tolylamino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-(*p*-tolyl(*p*-tolylamino)methyl)naphthalene-1,4-dione (4c)**

A mixture of 4-methylbenzaldehyde(1 mmol), 4-methylaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-(*p*-tolyl(*p*-tolylamino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((4-chlorophenyl)(*p*-tolylamino)methyl-3-hydroxy)naphthalene-1,4-dione (4d):**

A mixture of 4-chlorobenzaldehyde(1 mmol), 4-methylaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((4-chlorophenyl)(*p*-tolylamino)methyl-3-hydroxy)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-(4-bromophenyl(*p*-tolylamino)methyl)naphthalene-1,4-dione (4e)**

A mixture of 4-bromobenzaldehyde(1 mmol), 4-methylaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-(4-bromophenyl(*p*-tolylamino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-(((4-nitrophenyl)(*p*-tolyl)amino)methyl)naphthalene-1,4-dione (4f)**

A mixture of 4-methylbenzaldehyde(1 mmol), 4-nitroaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-(((4-nitrophenyl)(*p*-tolyl)amino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-((4-nitrophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione (4g)**

A mixture of 4-nitrobenzaldehyde(1 mmol), 4-nitroaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-((4-nitrophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-((4-chlorophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione (4h)**

A mixture of 4-chlorobenzaldehyde(1 mmol), 4-nitroaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-((4-chlorophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-((4-chlorophenyl)((4-methoxyphenyl)amino)methyl)naphthalene-1,4-dione (4i)**

A mixture of 4-chlorobenzaldehyde(1 mmol), 4-methoxyaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-((4-chlorophenyl)((4-methoxyphenyl)amino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-((4-methoxyphenyl)amino((4-nitrophenyl)methyl)naphthalene-1,4-dione (4j)**

A mixture of 4-nitrobenzaldehyde(1 mmol), 4-methoxyaniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-((4-methoxyphenyl)amino((4-nitrophenyl)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-((2-nitrophenyl(phenylamino)methyl)naphthalene-1,4-dione (4k)**

A mixture of 2-nitrobenzaldehyde(1 mmol), aniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-((2-nitrophenyl(phenylamino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((2,6-dimethylphenyl)(phenylamino)methyl)-3-hydroxynaphthalene-1,4-dione (4l)**

A mixture of 2,6-dimethylbenzaldehyde(1 mmol), aniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((2,6-dimethylphenyl)(phenylamino)methyl)-3-hydroxynaphthalene-1,4-dione.

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**Synthetic procedure for the preparation of 2-hydroxy-3-((phenylamino)(3,4,5-trimethoxyphenyl)methyl)naphthalene-1,4-dione (4m)**

A mixture of 3,4,5-trimethoxybenzaldehyde(1 mmol), aniline (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-(phenylamino)(3,4,5-trimethoxyphenyl)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-hydroxy-3-((4-nitrophenyl)pyridin-2-ylamino)methyl)naphthalene-1,4-dione (4n)**

A mixture of 4-nitrobenzaldehyde(1 mmol), 2-aminopyridine (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-hydroxy-3-((4-nitrophenyl)pyridin-2-ylamino)methyl)naphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-(((1*H*-benzo[*d*]imidazol-2-yl)amino(4-nitrophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4o)**

A mixture of 4-nitrobenzaldehyde(1 mmol), 2-aminobenzimidazole (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-(((1*H*-benzo[*d*]imidazol-2-yl)amino(4-nitrophenyl)methyl)-3-hydroxynaphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((benzo[*d*]thiazol-2-yl)amino(phenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4p)**

A mixture of benzaldehyde(1 mmol), 2-aminobenzothiazole (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((benzo[*d*]thiazol-2-yl)amino(phenyl)methyl)-3-hydroxynaphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((benzo[*d*]thiazol-2-yl)amino(4-nitrophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4q)**

A mixture of 4-nitrobenzaldehyde(1 mmol), 2-aminobenzothiazole (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((benzo[*d*]thiazol-2-yl)amino(4-nitrophenyl)methyl)-3-hydroxynaphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((benzo[*d*]thiazol-2-ylamino)(4-hydroxyphenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4r)**

A mixture of 4-hydroxybenzaldehyde(1 mmol), 2-aminobenzothiazole (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((benzo[*d*]thiazol-2-ylamino)(4-hydroxyphenyl)methyl)-3-hydroxynaphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((benzo[*d*]thiazol-2-ylamino)(4-bromophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4s)**

A mixture of 4-bromobenzaldehyde(1 mmol), 2-aminobenzothiazole (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((benzo[*d*]thiazol-2-ylamino)(4-bromophenyl)methyl)-3-hydroxynaphthalene-1,4-dione.

**Synthetic procedure for the preparation of 2-((benzo[*d*]thiazol-2-ylamino)(*p*-tolyl)methyl)-3-hydroxynaphthalene-1,4-dione (4t)**

A mixture of 4-methylbenzaldehyde(1 mmol), 2-aminobenzothiazole (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and montmorillonite K-10 (10 mol%) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH2Cl2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol to get 2-((benzo[*d*]thiazol-2-ylamino)(*p*-tolyl)methyl)-3-hydroxynaphthalene-1,4-dione.

**SPECTRAL DETAILS**

**2-Hydroxy-3-(phenyl(phenylamino)methyl)naphthalene-1,4-dione (4a)** (Lit. 28)

Yield 93%; An orange solid; mp: 143-145 oC**;** IR (ATR cm-1): 3420 (OH), 3321 (NH), 1660 (C=O), 1636 (C=O); 1H NMR(400 MHz, DMSO-*d6*): *δ* 11.18 (s, 1H, OH), 10.12 (s, 1H, NH), 7.94-6.82 (m, 14H, Ar-H), 6.01 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 182.4, 180.6, 153.1, 145.2, 143.8, 135.7 (2C), 131.2, 130.9, 129.4 (2C), 128.8 (2C), 127.7, 126.9 (2C), 125.7 (2C), 120.1, 117.3, 113.2 (2C), 52.3 ppm.

**2-Hydroxy-3-(phenyl(*p-*tolylamino)methyl)naphthalene-1,4-dione (4b)** (Lit. 28)

Yield 85%; A yellow solid; mp: 147-149 oC**;** IR(ATR cm-1): 3391 (OH), 3324 (NH), 1665 (C=O), 1634 (C=O)**;** 1H NMR(400 MHz, DMSO-*d6*): *δ* 11.08 (s, 1H, OH), 10.04 (s, 1H, NH), 7.9-6.51 (m, 13H, Ar-H), 6.13 (s, 1H, CH), 2.37 (s, 3H, CH3) ppm;13C NMR (100 MHz, DMSO-*d6*): *δ* 183.9, 181.8, 153.8, 144.5, 142.2, 135.8 (2C), 131.1, 130.2, 129.9 (2C), 128.4, 127.2 (2C), 126.5 (2C), 125.7, 124.7 (2C), 116.0, 113.0 (2C), 52.1, 21.8 ppm.

**2-Hydroxy-3-(*p*-tolyl(*p*-tolylamino)methyl)naphthalene-1,4-dione (4c)** (Lit. 28)

Yield 88%; A dark red solid; mp: 146-148 oC**;** IR (ATR cm-1): 3427 (OH), 3332 (NH), 1675 (C=O), 1645 (C=O)**;** 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.21 (s, 1H, OH), 9.92 (s, 1H, NH), 7.94-6.47 (m, 12H, Ar-H), 6.18 (s, 1H, CH), 2.35 (s, 6H, two CH3 gps) ppm;13C NMR (100 MHz, DMSO-*d6*): *δ* 183.1, 181.5, 153.1, 142.2, 140.4, 136.2, 135.5 (2C), 131.7, 130.4, 129.8 (2C), 129.1, 128.2 (2C), 126.9 (4C), 117.8, 113.8 (2C), 52.7, 21.6 (2C) ppm.

**2- ((4-Chlorophenyl)(*p*-tolylamino)methyl-3-hydroxy)naphthalene-1,4-dione (4d):** (Lit. 33)

Yield 83%; An orange solid; mp: 151-153 oC; IR (ATR cm-1): 3397 (OH), 3325 (NH), 1681 (C=O), 1653 (C=O);1H NMR(400 MHz, DMSO-*d6*): *δ* 11.17 (s, 1H, OH), 10.18 (s, 1H, NH), 7.93-6.47 (m, 12H, Ar-H), 6.12 (s, 1H, CH), 2.34 (s, 3H, CH3) ppm;13C NMR (100 MHz, DMSO-*d6*): *δ* 183.4, 181.1, 152.4, 143.6, 142.6, 135.3 (2C), 132.8, 131.5, 130.0, 129.8 (2C), 129.3, 128.0 (2C), 126.6 (2C), 126.3 (2C), 117.5, 113.4 (2C), 52.0, 21.8 ppm.

**2-Hydroxy-3-(4-bromophenyl(*p*-tolylamino)methyl)naphthalene-1,4-dione (4e)** (Lit. 28)

Yield 90%; An orange solid; mp: 148-150 oC. IR (ATR cm-1): 3393 (OH), 3318 (NH), 1672 (C=O), 1649 (C=O); 1H NMR(400 MHz, DMSO-*d6*): *δ* 11.31 (s, 1H, OH), 9.97 (s, 1H, NH), 7.98-6.45 (m, 12H, Ar-H), 6.13 (s, 1H, CH), 2.24 (s, 3H, CH3) ppm;13C NMR (100 MHz, DMSO-*d6*): *δ* 183.4, 181.8, 153.4, 143.0, 142.9, 135.8 (2C), 132.8 (2C), 131.6, 130.1, 129.8 (2C), 129.2, 128.8 (2C), 126.5 (2C), 121.5, 117.8, 113.6 (2C), 52.2, 21.9 ppm.

**2-Hydroxy-3-(((4-nitrophenyl)(*p*-tolyl)amino)methyl)naphthalene-1,4-dione (4f)** (Lit. 33)

Yield 81%; An orange solid; mp: 145-147 oC. IR (ATR cm-1): 3419 (OH), 3321 (NH), 1679 (C=O), 1650 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.31 (s, 1H, OH), 10.07 (s, 1H, NH), 8.05-6.76 (m, 12H, Ar-H), 6.18 (s, 1H, CH), 2.39 (s, 3H, CH3) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.3, 181.1, 153.6, 151.9, 140.3, 137.2, 136.1, 135.7 (2C), 131.2, 130.8, 128.7 (2C), 127.3 (2C), 126.6 (4C), 117.9, 114.8 (2C), 52.4, 21.6 ppm.

**2-Hydroxy-3-((4-nitrophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione (4g)**

(Lit. 33)

Yield 93%; A yellow solid; mp: 134-136 oC. IR (ATR cm-1): 3408 (OH), 3334 (NH), 1685 (C=O), 1656 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.23 (s, 1H, OH), 10.13 (s, 1H, NH), 8.15-6.79 (m, 12H, Ar-H), 6.08 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.1, 181.3, 153.4, 151.2, 149.2, 146.7, 136.2, 135.0 (2C), 131.4, 130.2, 128.4 (2C), 127.0 (2C), 126.7 (2C), 125.2 (2C), 117.1, 114.5 (2C), 52.3 ppm.

**2-Hydroxy-3-((4-chlorophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione (4h)** (Lit. 33)

Yield 90%; An orange solid; mp: 132-134 oC. IR (ATR cm-1): 3429 (OH), 3317 (NH), 1673 (C=O), 1643 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 10.21 (s, 1H, OH), 9.24 (s, 1H, NH), 8.04-6.77 (m, 12H, Ar-H), 6.11 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.9, 181.0, 153.7, 152.2, 149.6, 136.4, 135.9 (2C), 132.1, 131.0, 130.4, 128.1 (2C), 127.8 (2C), 126.6 (2C), 125.1 (2C), 117.8, 114.1 (2C), 52.1 ppm.

**2-Hydroxy-3-((4-chlorophenyl)((4-methoxyphenyl)amino)methyl)naphthalene-1,4-dione (4i)** (Lit. 33)

Yield 85%; A yellow solid; mp: 127-128 oC. IR (ATR cm-1): 3433 (OH), 3319 (NH), 1677 (C=O), 1647 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 10.04 (s, 1H, OH), 9.33 (s, 1H, NH), 7.94-6.76 (m, 12H, Ar-H), 6.10 (s, 1H, CH), 3.84 (s, 3H, OCH3) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.3, 181.1, 153.0, 151.7, 149.7, 138.0, 135.0 (2C), 132.5, 131.4, 130.2, 128.8 (2C), 126.6 (2C), 125.2 (2C), 117.0, 115.6 (2C), 115.1 (2C), 56.2, 52.1 ppm.

**2-Hydroxy-3-((4-methoxyphenyl)amino((4-nitrophenyl)methyl)naphthalene-1,4-dione (4j)** (Lit. 33)

Yield 83%; A yellow solid; mp: 139-140 oC. IR (ATR cm-1): 3421 (OH), 3338 (NH), 1680 (C=O), 1651 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.34 (s, 1H, OH), 9.97 (s, 1H, NH), 8.15-6.74 (m, 12H, Ar-H), 6.08 (s, 1H, CH), 3.85 (s, 3H, OCH3) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.3, 181.5, 153.4, 152.0, 149.5, 145.2, 138.0, 135.5 (2C), 131.6, 130.1, 128.0 (2C), 126.1 (2C), 125.4 (2C), 117.0, 115.8 (2C), 115.1 (2C), 55.0, 52.2 ppm.

**2-Hydroxy-3-((2-nitrophenyl(phenylamino)methyl)naphthalene-1,4-dione (4k)**

Yield 90%; An orange solid; mp: 143-145 oC; IR (ATR cm-1): 3425 (OH), 3317 (NH), 1672 (C=O), 1647 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.02 (s, 1H, OH), 9.92 (s, 1H, NH), 8.15-6.29 (m, 13H, Ar-H), 6.09 (s, 1H, CH) ppm;  13C NMR (100 MHz, DMSO-*d6*): *δ* 183.7, 181.0, 154.9, 148.1, 145.2, 140.4, 135.2 (2C), 132.1, 131.5, 130.7, 129.4 (2C), 128.1, 126.8, 125.7 (2C), 124.1, 120.9, 117.8, 112.5 (2C), 48.7 ppm. HRMS:*m/z* Calculated: 401.1137, Found: 401.1135 [M + H] +

**2-((2,6-Dimethylphenyl)(phenylamino)methyl)-3-hydroxynaphthalene-1,4-dione (4l)**

Yield 81%; A red solid; mp: 145-147 oC. IR (ATR cm-1): 3431 (OH), 3331 (NH), 1678 (C=O), 1651 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.69 (s, 1H, OH), 9.83 (s, 1H, NH), 7.98-6.69 (m, 12H, Ar-H), 6.45 (s, 1H, CH), 2.76 (s, 6H, two CH3 gps) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 182.2, 180.5, 153.1, 145.6, 143.4, 136.3 (2C), 134.2 (2C), 131.1, 130.8, 129.2 (2C), 128.7 (2C), 127.4 (2C), 126.8, 120.6, 117.7, 112.2 (2C), 49.6, 20.9 (2C) ppm; HRMS:*m/z* Calculated: 384.1599, Found: 384.1596 [M + H] +

**2-Hydroxy-3-((phenylamino)(3,4,5-trimethoxyphenyl)methyl)naphthalene-1,4-dione (4m)**

Yield 83%; A red solid; mp: 160-162 oC. IR (ATR cm-1): 3427 (OH), 3326 (NH), 1675 (C=O), 1649 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.01 (s, 1H, OH), 10.57 (s, 1H, NH), 7.92-6.19 (m, 11H, Ar-H), 6.06 (s, 1H, CH), 3.84 (s, 9H, OCH3 ) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 182.7, 181.6, 154.0, 152.2 (2C), 146.9, 137.3, 136.6, 135.1 (2C), 131.3, 130.4, 129.9 (2C), 127.0 (2C), 120.2, 118.1, 113.9 (2C), 103.3 (2C), 60.1, 55.9 (2C), 53.6 ppm; HRMS:*m/z* Calculated: 445.1603, Found: 446.1605 [M + H]+

**2-Hydroxy-3-((4-nitrophenyl)pyridin-2-ylamino)methyl)naphthalene-1,4-dione (4n)** (Lit. 33)

Yield 91%; An orange solid; mp: 150-152 oC. IR (ATR cm-1): 3431 (OH), 3327 (NH), 1681 (C=O), 1654 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.27 (s, 1H, OH), 9.82 (s, 1H, NH), 8.27-6.64 (m, 12H, Ar-H), 6.11 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 182.8, 181.5, 154.2, 153.8, 149.5, 148.1, 145.8, 138.5, 135.8 (2C), 131.5, 130.4, 128.1 (2C), 126.3 (2C), 125.8 (2C), 118.4, 117.9, 106.5, 52.7 ppm.

**2-(((1*H*-Benzo[*d*]imidazol-2-yl)amino(4-nitrophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4o)** (Lit. 33)

Yield 93%; An orange solid; mp: 151-153 oC. IR (ATRcm-1): 3435 (OH), 3332 (NH), 3327 (NH), 1682 (C=O); 1663 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.18 (s, 1H, OH), 10.25 (s, 1H, NH), 9.87 (s, 1H, NH), 8.19-7.17 (m, 12H, Ar-H), 6.10 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*,): *δ* 183.7, 181.2, 153.7, 149.1, 145.7, 141.0, 136.7 (2C), 135.7 (2C), 131.1, 130.3, 128.3 (2C), 126.3 (2C), 125.7 (2C), 123.4 (2C), 117.1, 115.4 (2C), 51.8 ppm.

**2-((Benzo[*d*]thiazol-2-yl)amino(phenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4p)**

Yield 89%; An orange solid; mp: 151-153 oC; IR (ATR cm-1): 3421 (OH), 3339 (NH), 1672 (C=O), 1647 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.74 (s, 1H, OH), 10.08 (s, 1H, NH), 8.24-7.16 (m, 13H, Ar-H), 6.04 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.8, 181.0, 173.1, 155.3 153.3, 148.6, 135.5 (2C), 131.4, 130.8, 129.5, 128.8 (2C), 127.1 (2C), 126.7, 125.2, 124.6, 123.0 (2C), 121.0, 117.4, 116.6, 50.8 ppm; HRMS:*m/z* Calculated: 413.0960, Found: 413.0963 [M + H] +

**2-((Benzo[*d*]thiazol-2-yl)amino(4-nitrophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4q)**

Yield 92%; A red solid; mp: 149-151 oC; IR (ATR cm-1): 3410 (OH), 3314 (NH), 1670 (C=O), 1645 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.04 (s, 1H, OH), 10.03 (s, 1H, NH), 8.54-7.49 (m, 12H, Ar-H), 6.08 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 181.0, 180.1, 170.8, 165.5, 152.9, 149.3, 148.2, 135.0 (2C), 131.2, 130.5 (2C), 129.2, 128.2 (2C), 125.9 (2C), 125.6 (2C), 123.4, 120.2, 112.5, 111.9, 49.2 ppm; HRMS:*m/z* Calculated: 458.0810, Found: 458.0812 [M + H] +

**2-((Benzo[*d*]thiazol-2-ylamino)(4-hydroxyphenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4r)**

Yield 90%; A red solid; mp: 150-152 oC; IR (ATR cm-1): 3392 (OH), 3325 (NH), 1680 (C=O), 1653 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 10.15 (s, 1H, OH), 9.48 (s, 1H, NH), 8.15-6.66 (m, 12H, Ar-H), 6.07 (s, 1H, CH), 5.07 (s, 1H, OH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 183.1, 181.6, 175.4, 156.5, 153.9, 152.1, 136.4, 135.0 (2C), 132.8, 130.6 (2C), 127.3 (2C), 126.3 (2C), 125.5, 124.9, 121.8, 117.4, 116.1, 115.8 (2C), 52.0 ppm; HRMS: *m/z* Calculated: 429.0909, Found: 429.0912 [M + H] +

**2-((Benzo[*d*]thiazol-2-ylamino)(4-bromophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (4s)**

Yield 93%; A red solid; mp: 152-154 oC; IR (ATR cm-1): 3423 (OH), 3318 (NH), 1673 (C=O), 1649 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.28 (s, 1H, OH), 10.58 (s, 1H, NH), 8.25-7.20 (m, 12H, Ar-H), 6.01 (s, 1H, CH) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 181.7, 180.8, 172.2, 156.2, 154.2, 141.1, 135.7 (2C), 132.4 (2C), 131.1, 130.4 (2C), 128.7 (2C), 126.8, 125.4 (2C), 123.0, 121.9, 120.5, 118.5, 116.0, 51.1 ppm; HRMS**:** *m/z* Calculated: 491.0065, Found: 491.0061 [M + H]+

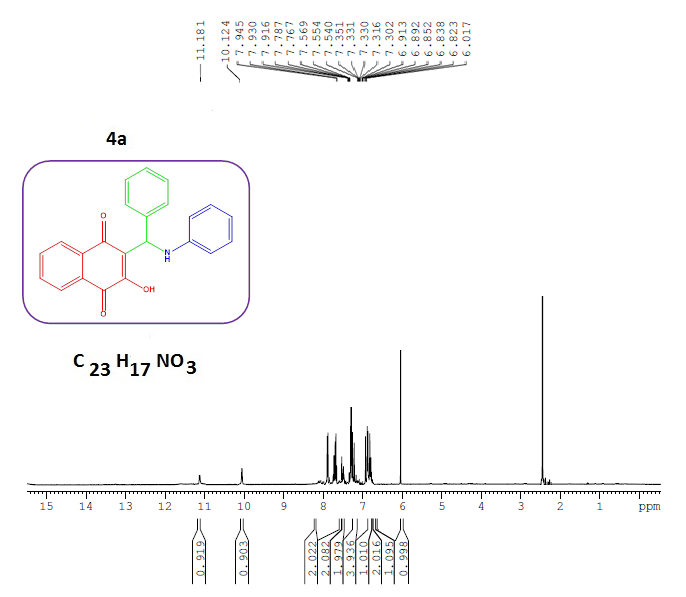
**2-((Benzo[*d*]thiazol-2-ylamino)(*p*-tolyl)methyl)-3-hydroxynaphthalene-1,4-dione (4t)**

Yield 87%; An orange solid; mp: 157-159 oC; IR (ATR cm-1): 3419 (OH), 3324 (NH), 1683 (C=O), 1650 (C=O); 1H NMR (400 MHz, DMSO-*d6*): *δ* 11.07 (s, 1H, OH), 10.18 (s, 1H, NH), 8.22-7.23 (m, 12H, Ar-H), 5.97 (s, 1H, CH), 2.38 (s, 3H, CH3) ppm; 13C NMR (100 MHz, DMSO-*d6*): *δ* 182.7, 181.8, 173.2, 154.8, 152.2, 141.9, 137.7, 136.8 (2C), 132.4, 131.8 (2C), 129.9 (2C), 126.6 (2C), 125.5 (2C), 125.0, 123.9, 120.7, 119.8, 117.0, 50.8, 22.3 ppm; HRMS:*m/z* Calculated: 427.1116, Found: 427.1119 [M + H] +

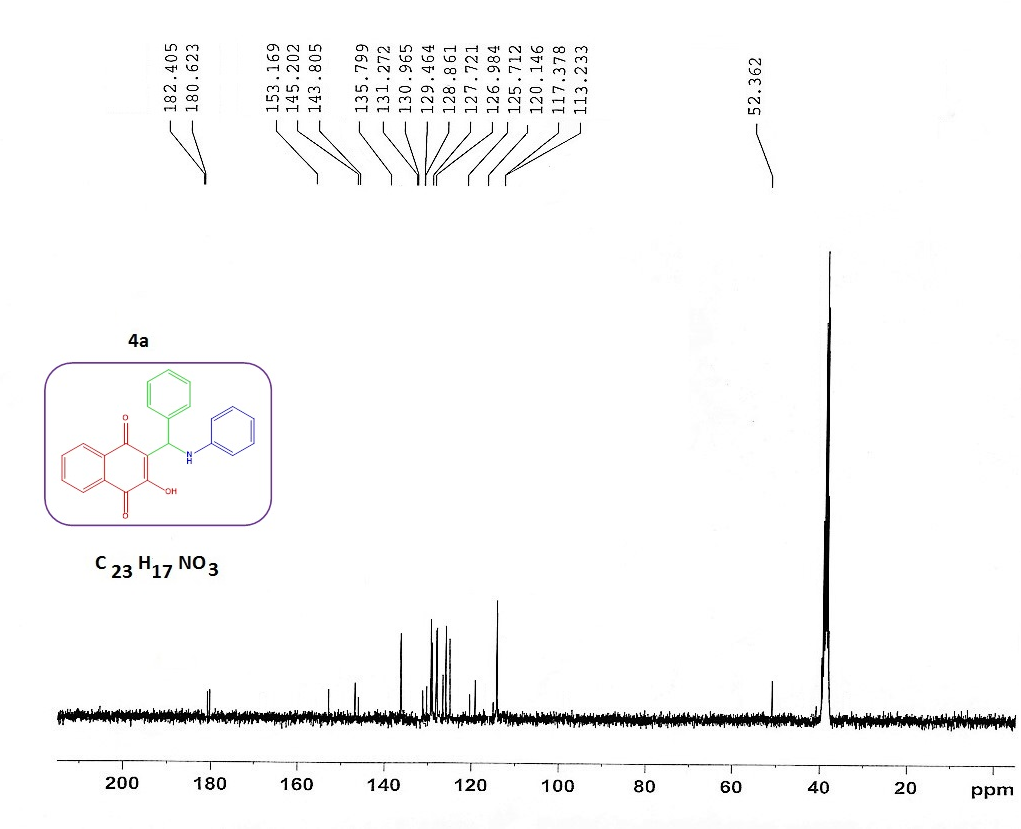
**Supporting Information:**

**Contents**

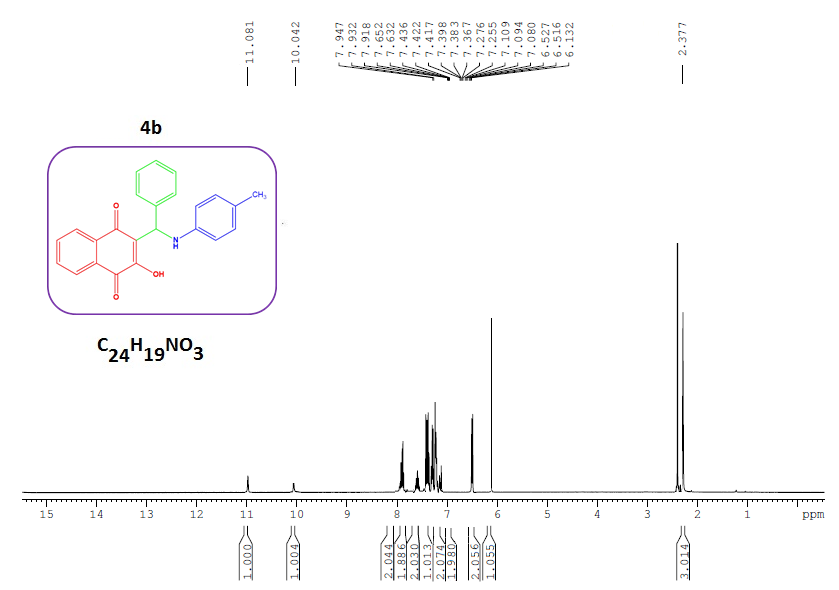
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| --- |
| 1H NMR and 13C NMR spectra of 4a……………….......................................S14 - S15  1H NMR and 13C NMR spectra of 4b………………......................................S16 - S17  1H NMR and 13C NMR spectra of 4c………………...................................... S18 – S19  1H NMR and 13C NMR spectra of 4d……………………………………….. S20 – S21  1H NMR and 13C NMR spectra of 4e……………………………………….. S22 – S23  1H NMR and 13C NMR spectra of 4f………………………………………... S24 – S25  1H NMR and 13C NMR spectra of 4g……………………………………….. S26 – S27  1H NMR and 13C NMR spectra of 4h………………………………………... S28 – S29  1H NMR and 13C NMR spectra of 4i………………………………………… S30 – S31  1H NMR and 13C NMR spectra of 4j………………………………………… S32 – S33  1H NMR and 13C NMR spectra of 4k………………………………………… S34 – S35  HRMS spectra of 4k……………………………………………………………...S35  1H NMR and 13C NMR spectra of 4l…………………………………………. S36 – S37  HRMS spectra of 4l……………………………………………………………...S37  1H NMR and 13C NMR spectra of 4m………………………………………… S38 – S39  HRMS spectra of 4m……………………………………………………………...S39  1H NMR and 13C NMR spectra of 4n……………………………………………. S40 – S41  1H NMR and 13C NMR spectra of 4o…………………………………………… S42 – S43  1H NMR and 13C NMR spectra of 4p…………………………………………… S44 – S45  HRMS spectra of 4p……………………………………………………………...S45  1H NMR and 13C NMR spectra of 4q……………………………………………. S46 – S47  HRMS spectra of 4q……………………………………………………………...S47  1H NMR and 13C NMR spectra of 4r…………………………………………….. S48 – S49  HRMS spectra of 4r……………………………………………………………...S49  1H NMR and 13C NMR spectra of 4s………………………………………………S50 – S51  HRMS spectra of 4s……………………………………………………………...S51  1H NMR and 13C NMR spectra of 4t……………………………………………….S52 – S53  HRMS spectra of 4t……………………………………………………………...S53 |



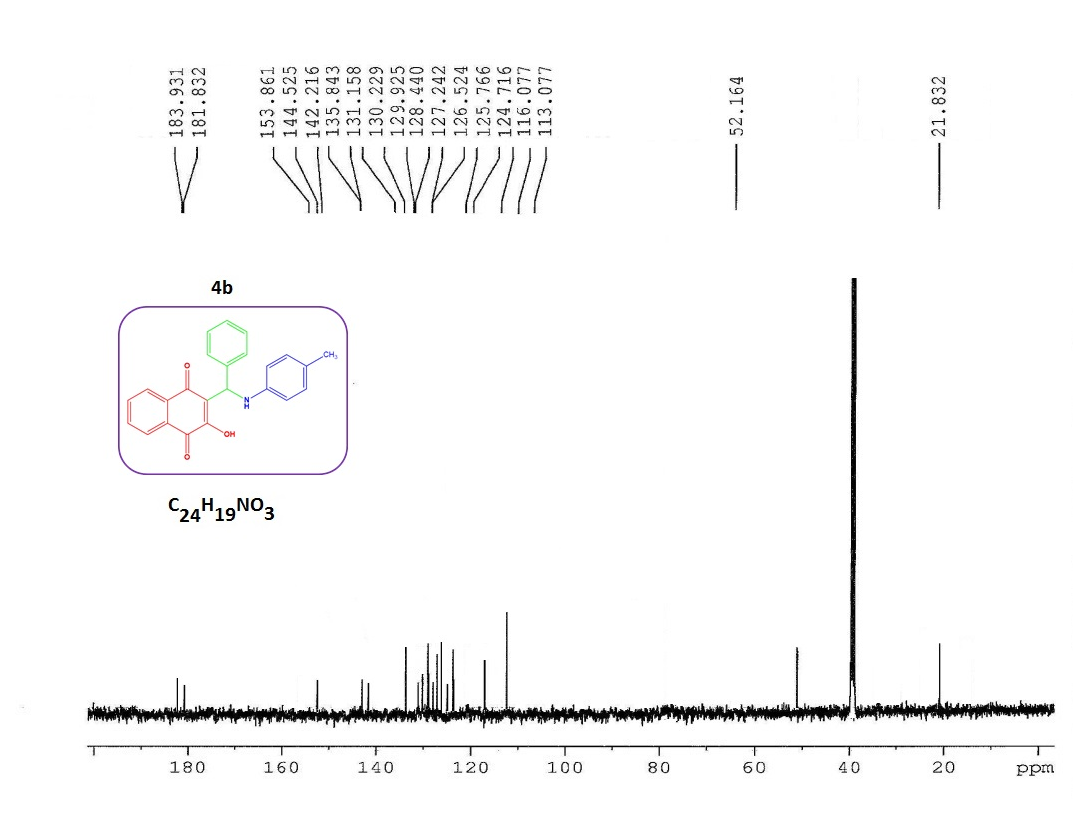
**1H NMR of 4a**

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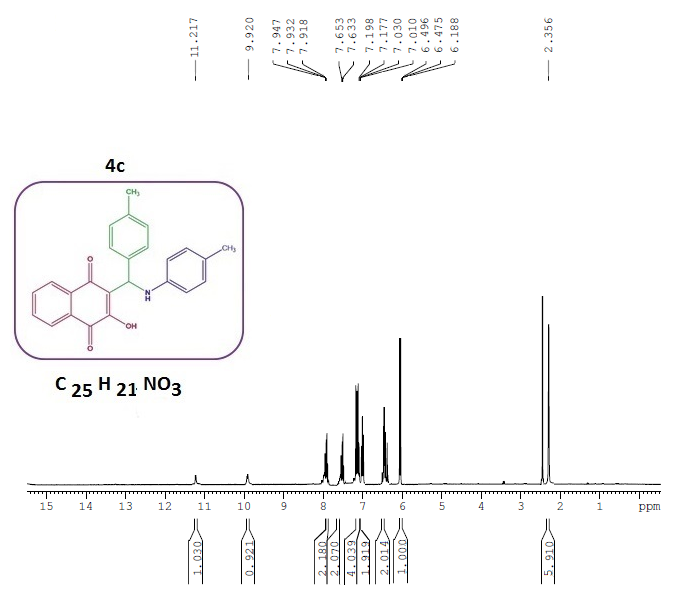
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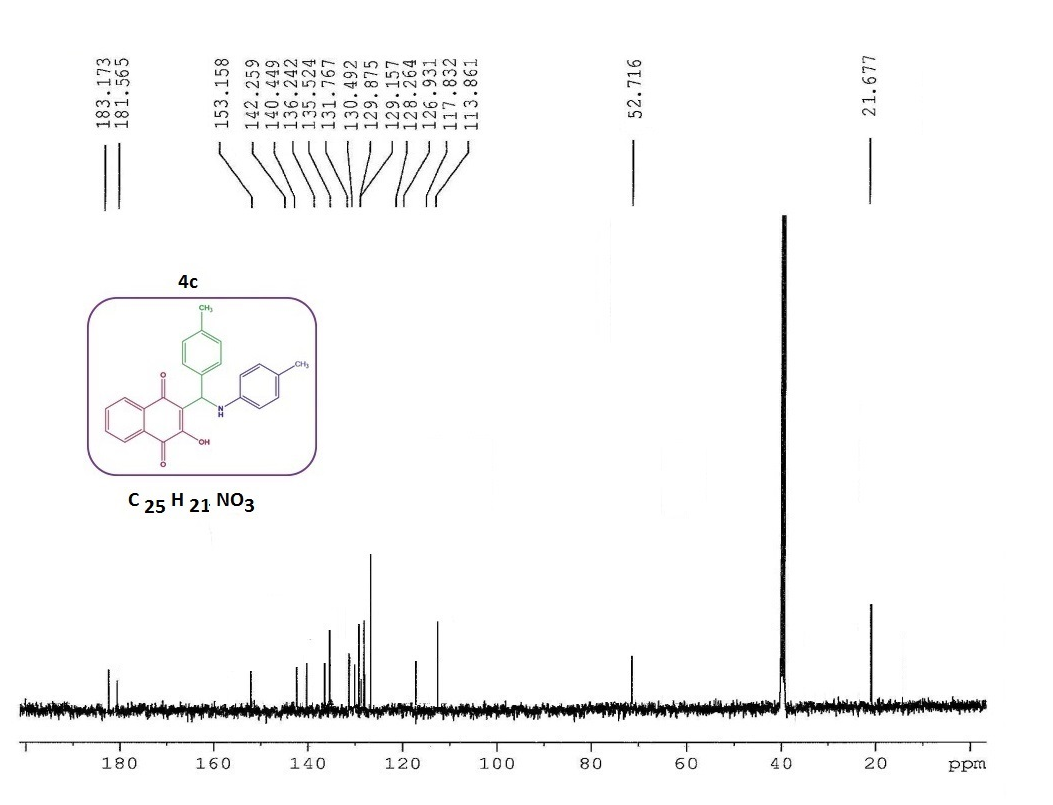
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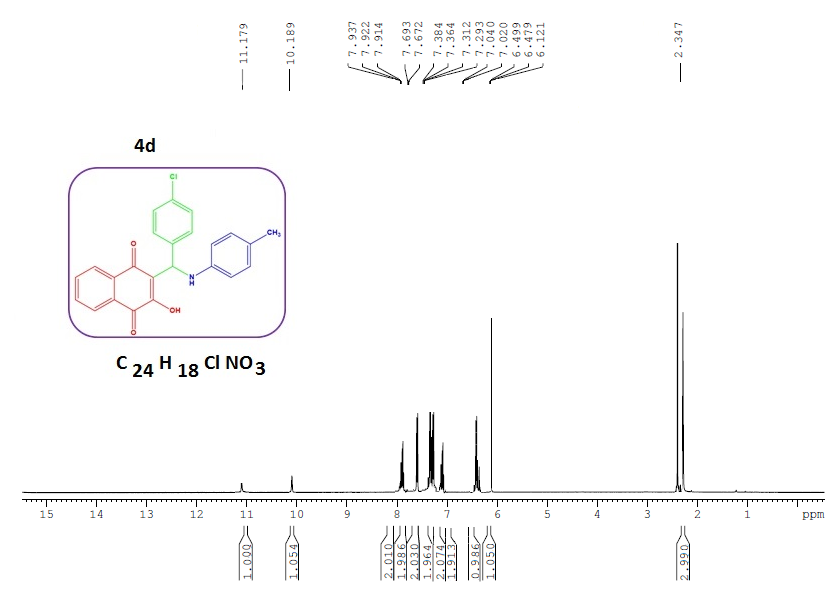
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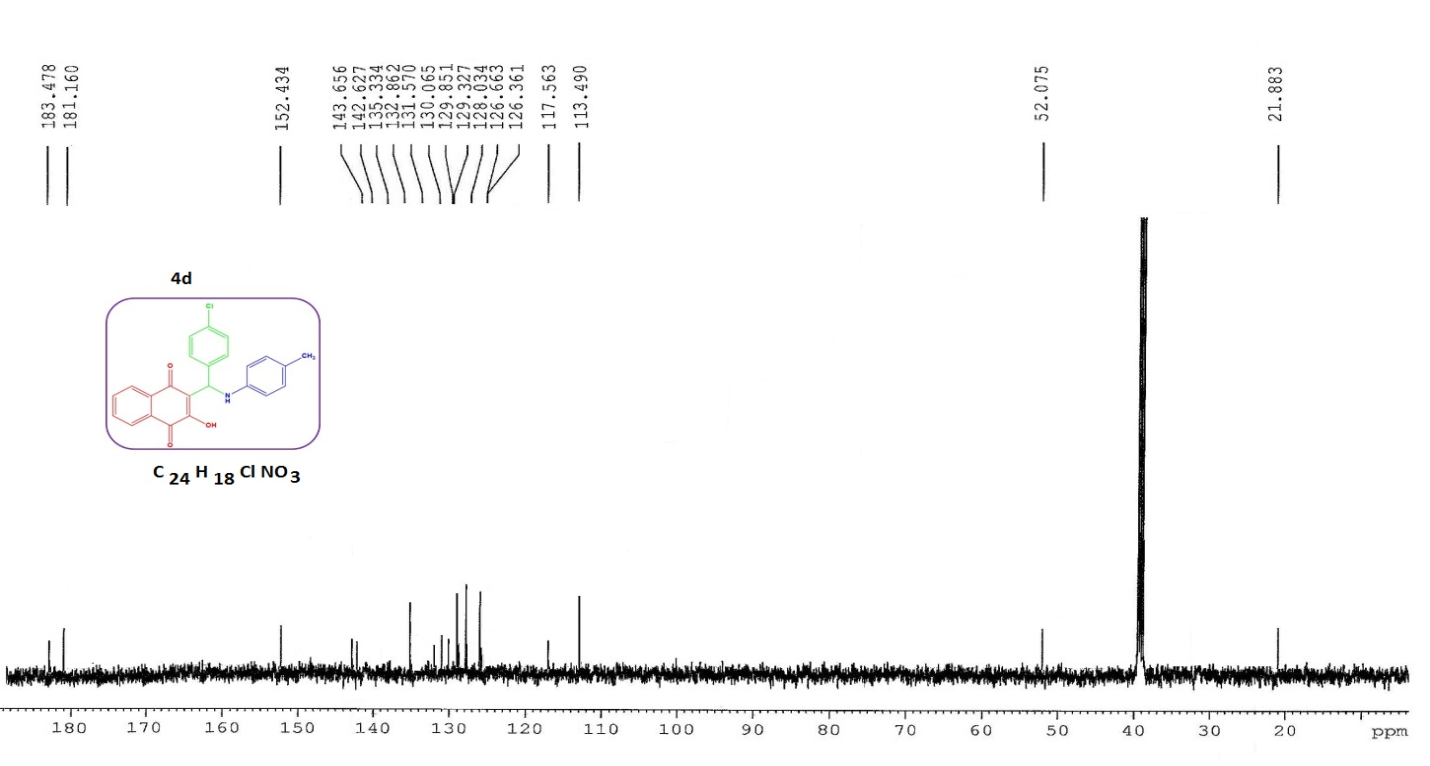
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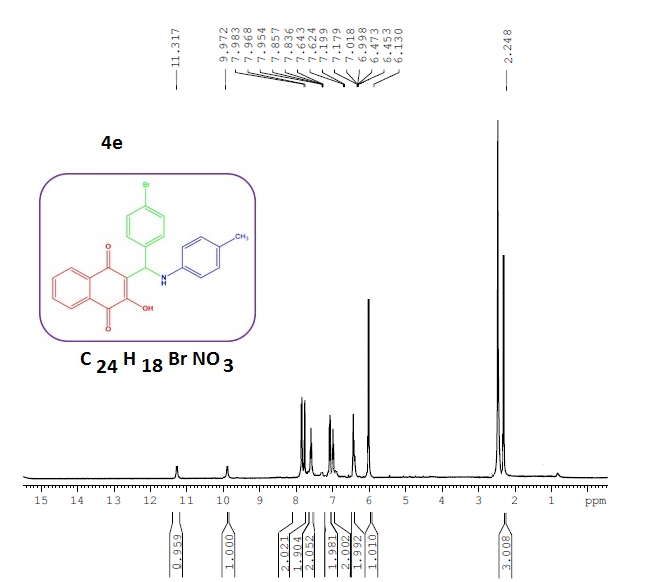
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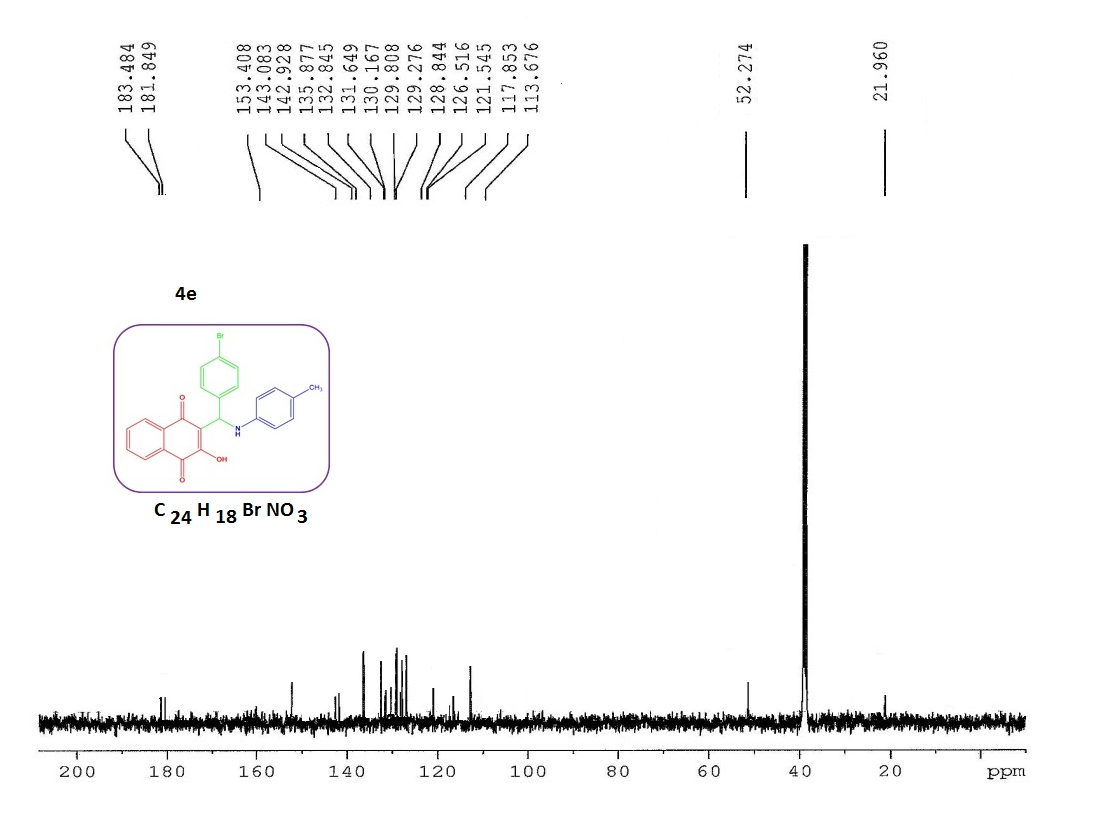
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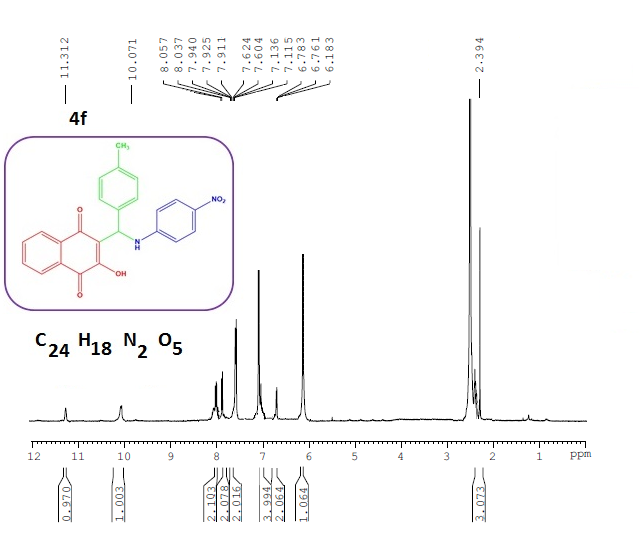
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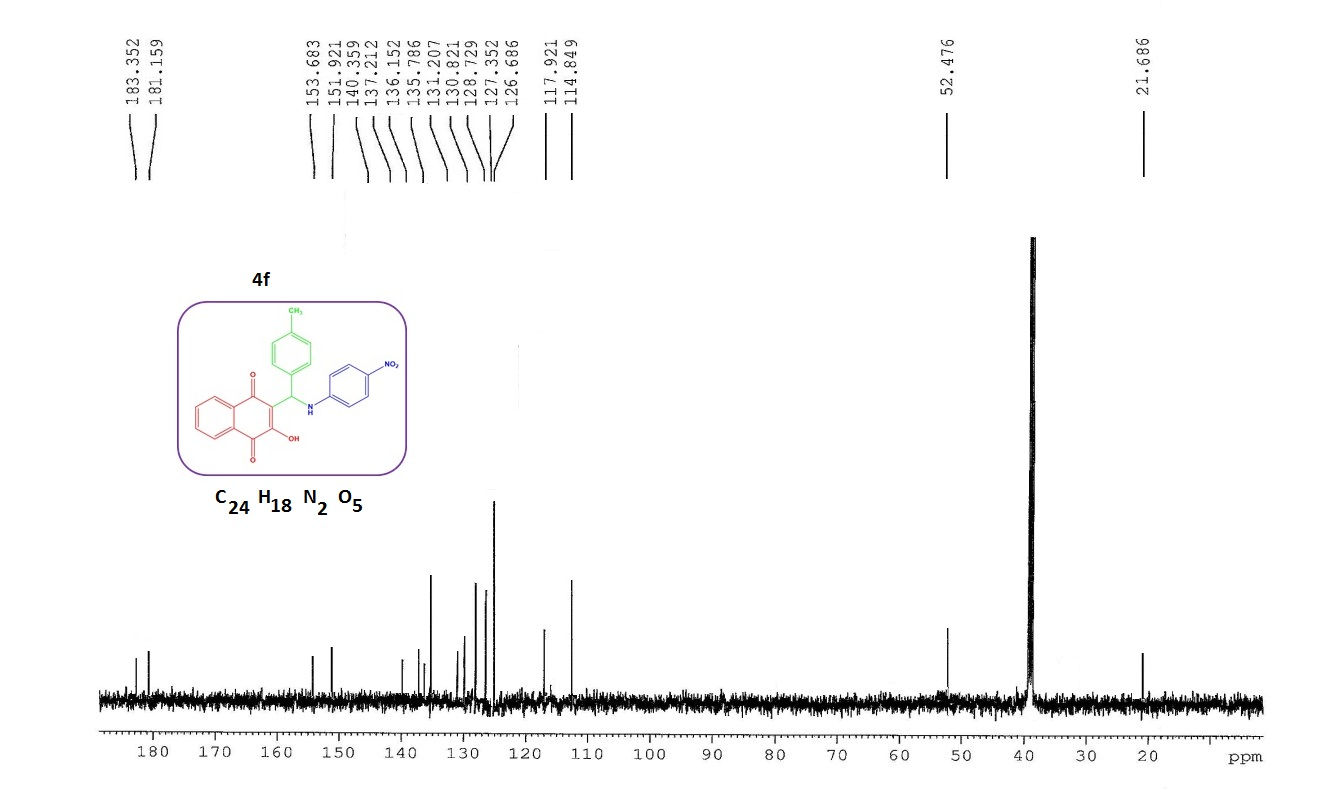
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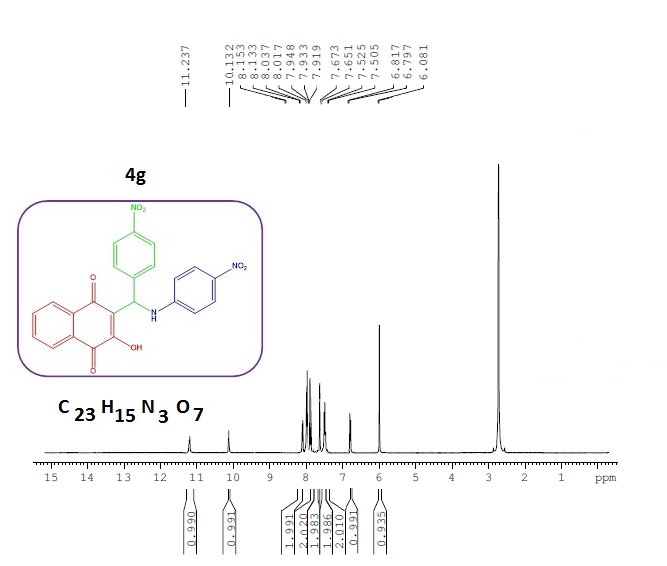
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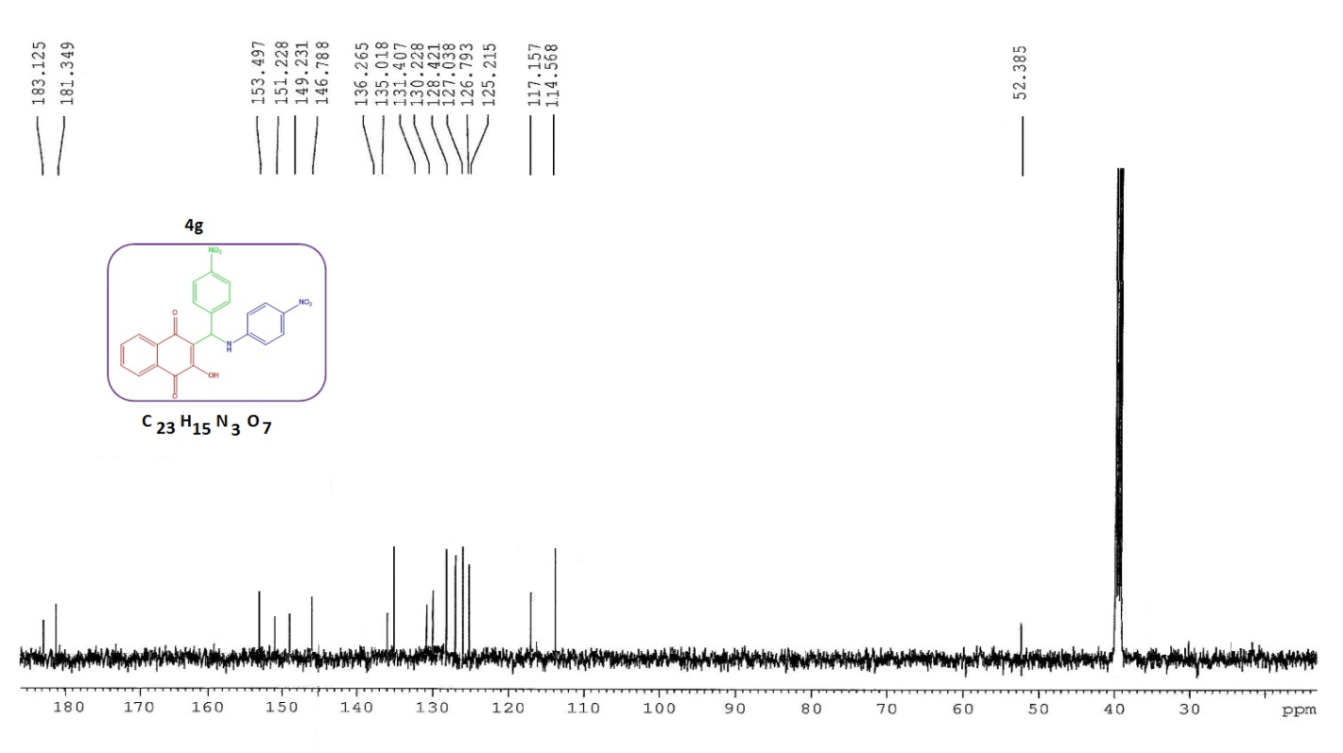
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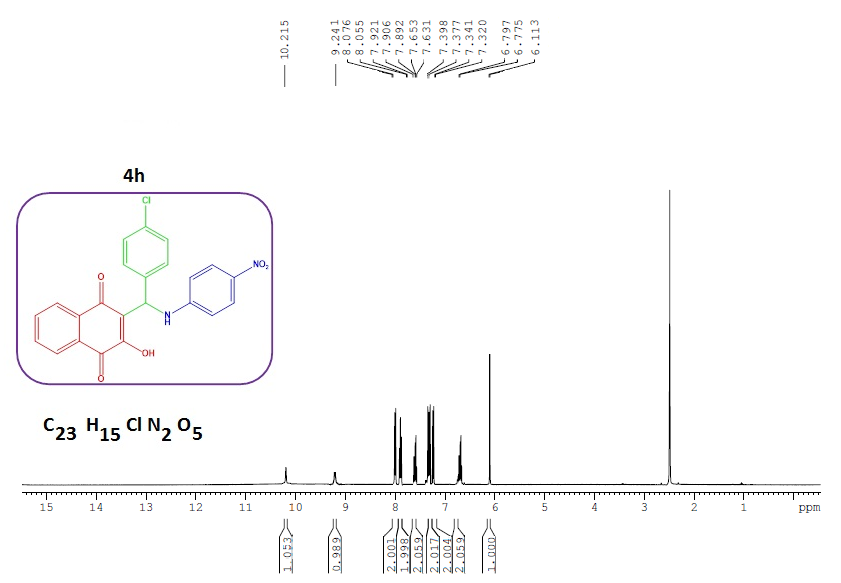
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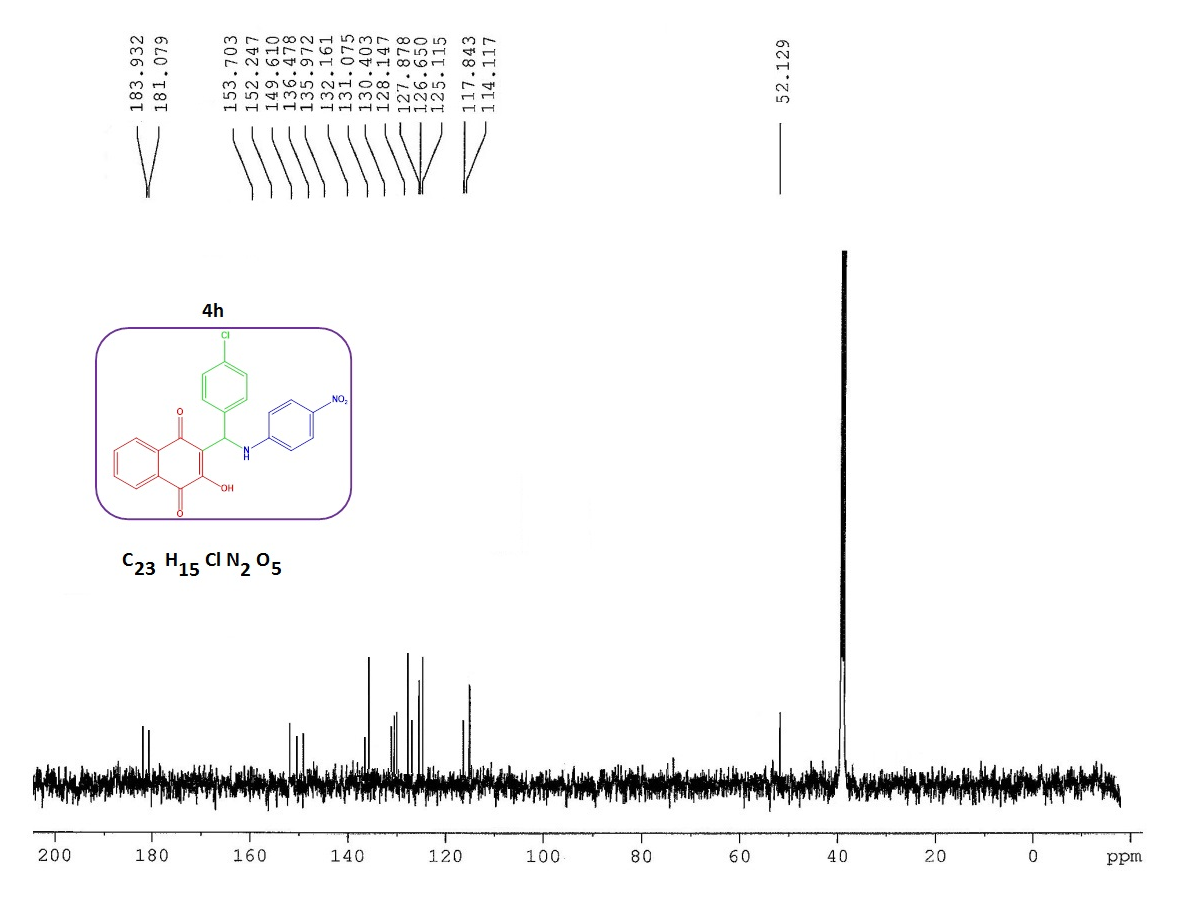
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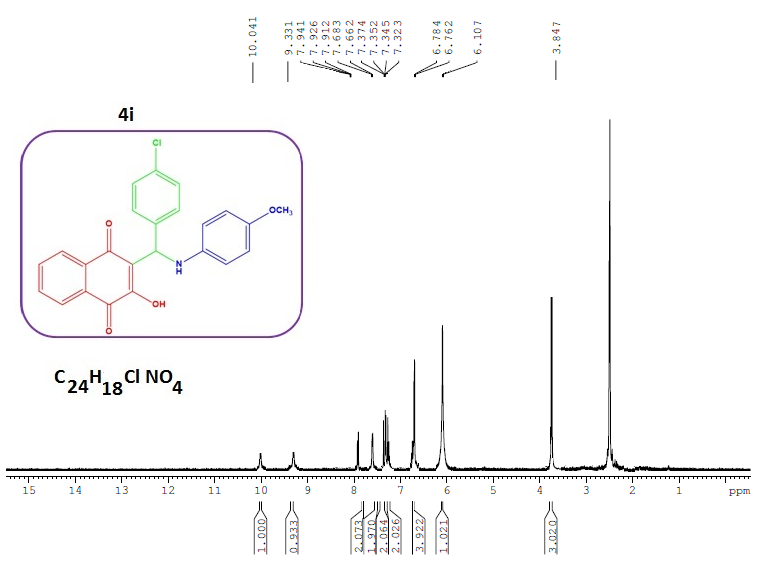
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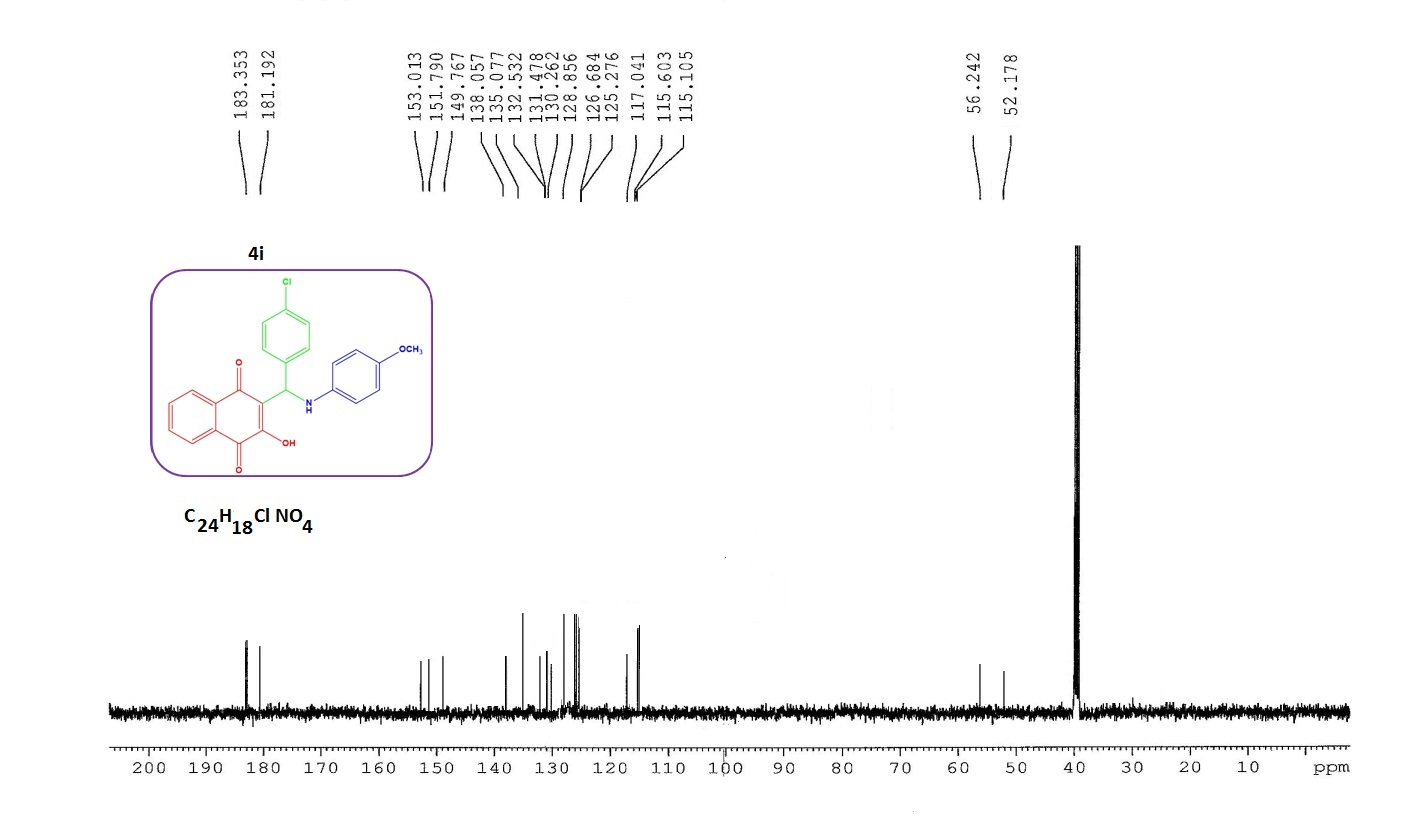
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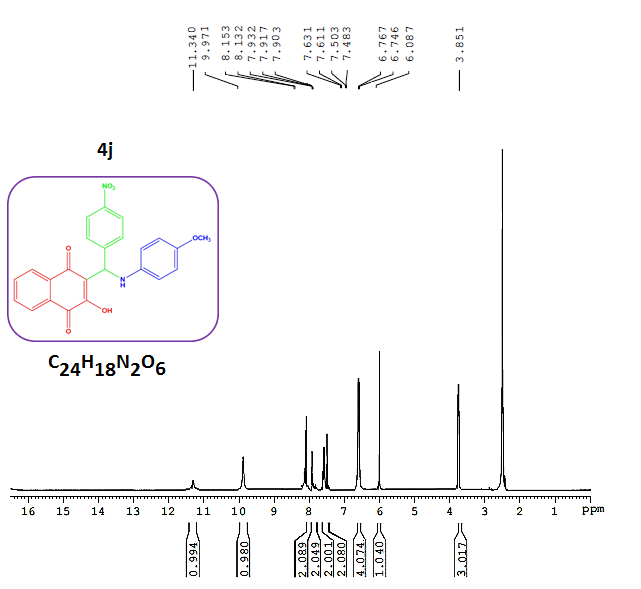
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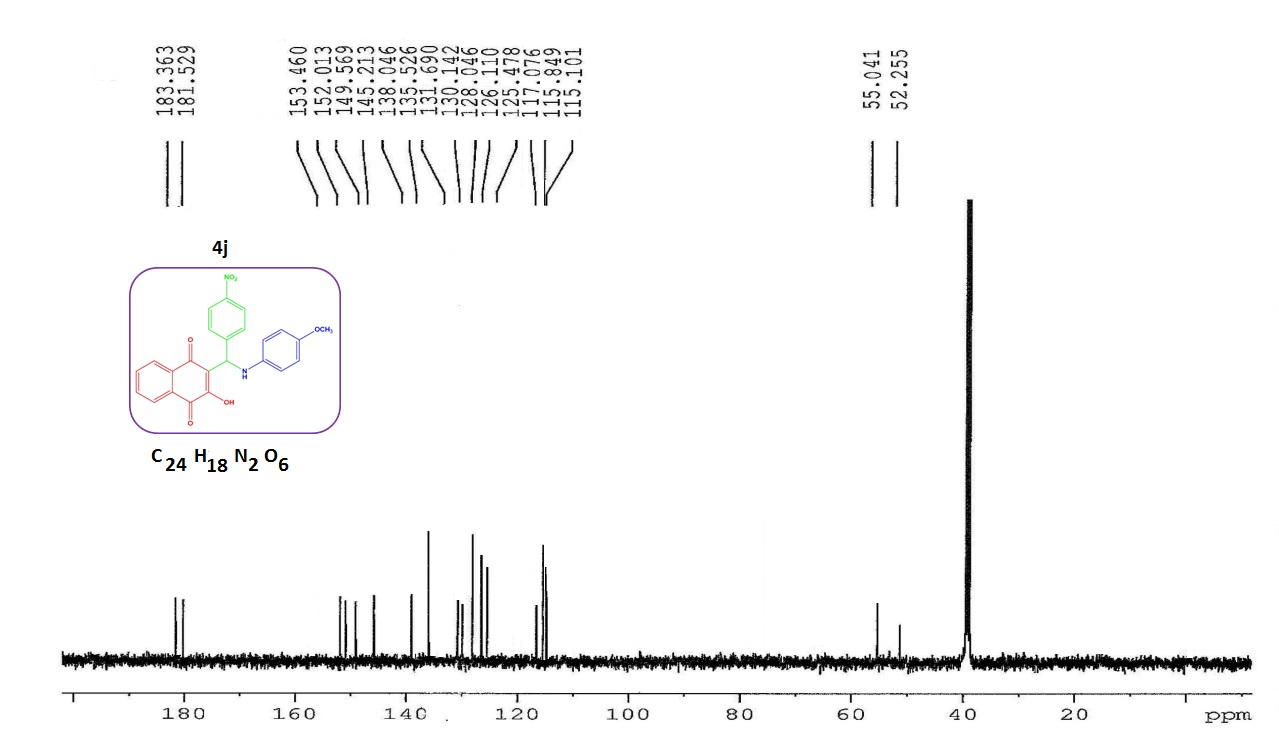
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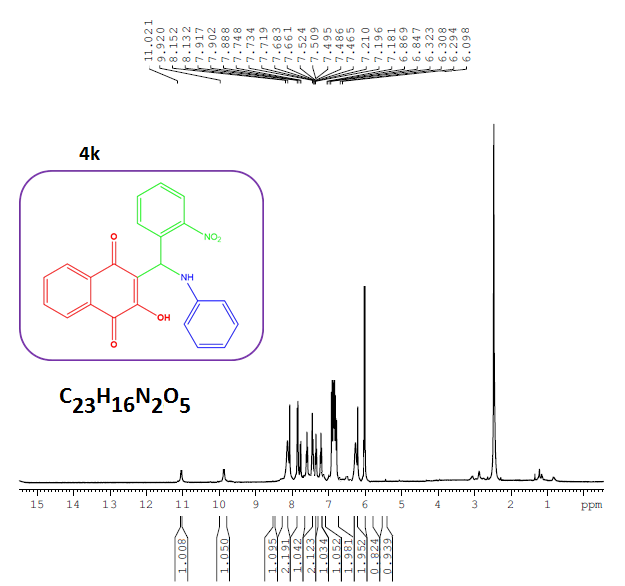
**13C NMR of 4i**

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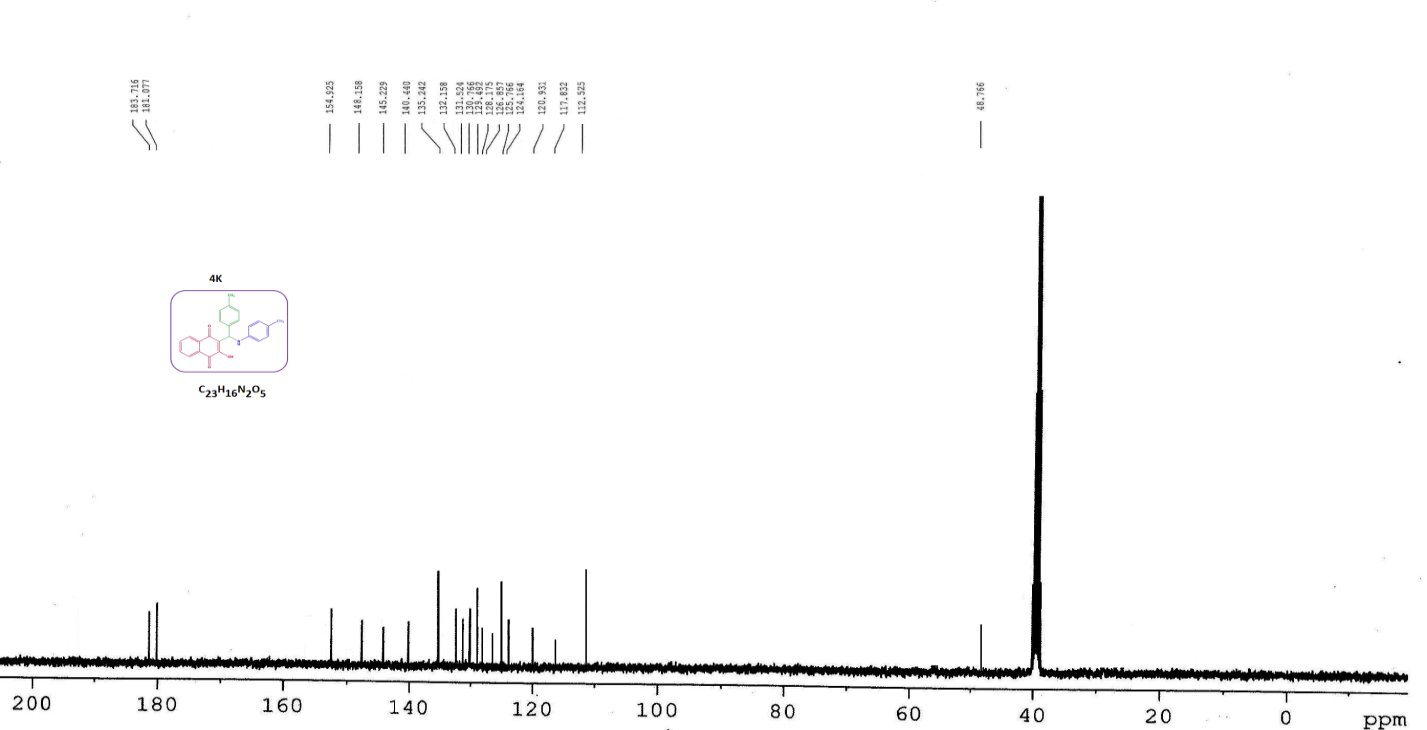
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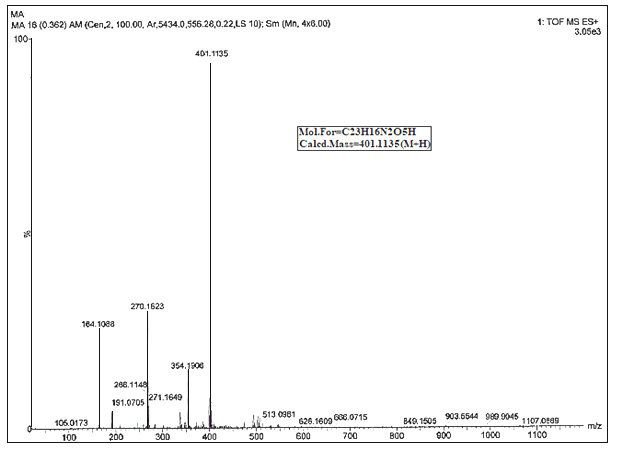
**13C NMR of 4j**

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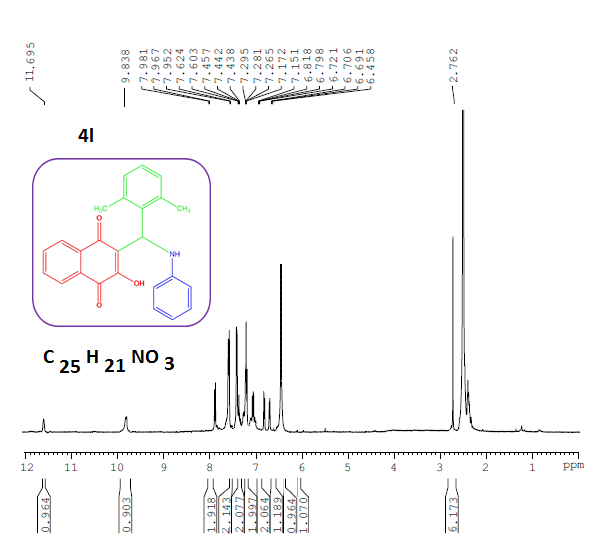
**1H NMR of 4k**

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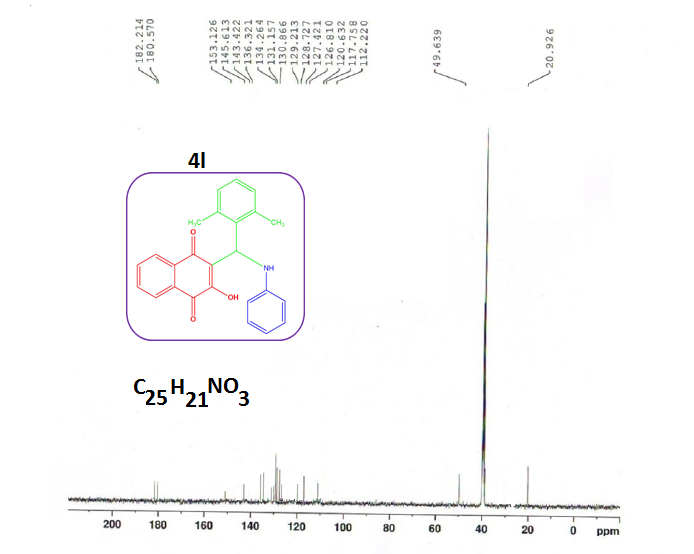
**13C NMR of 4k**

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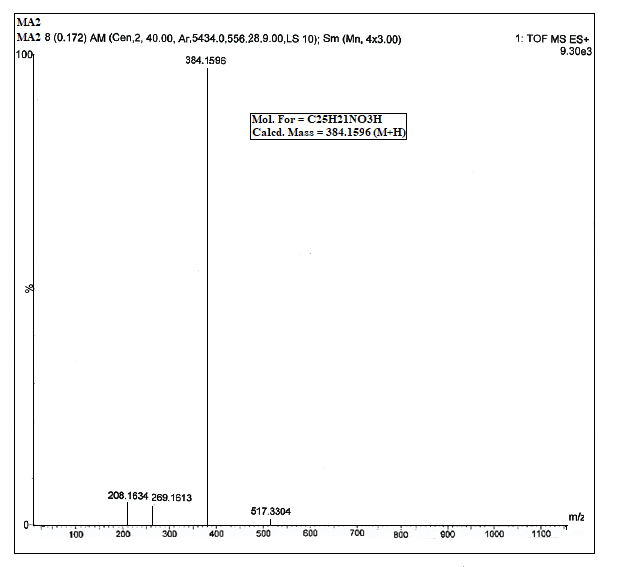
**HRMS of 4k**

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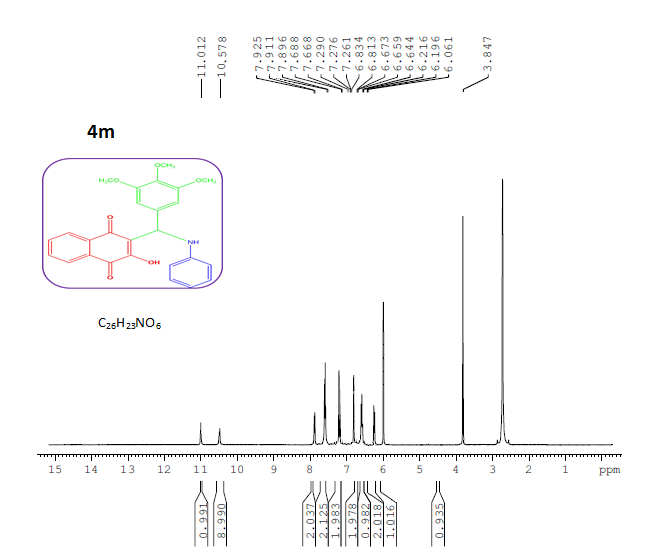
**1H NMR of 4l**

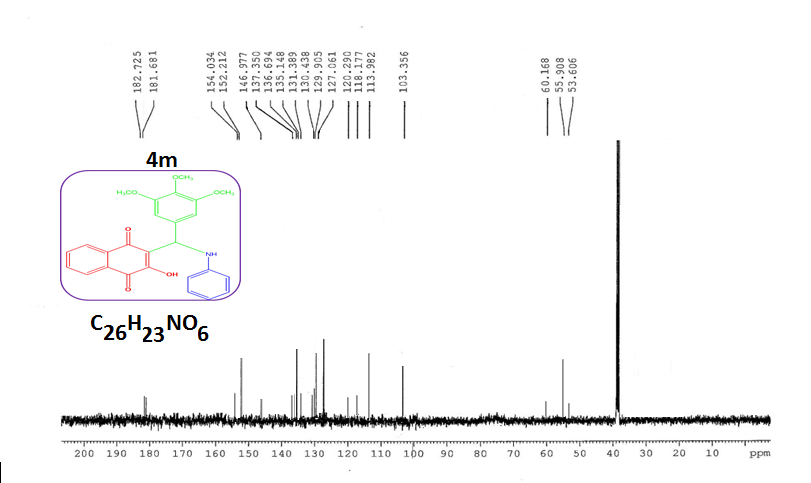
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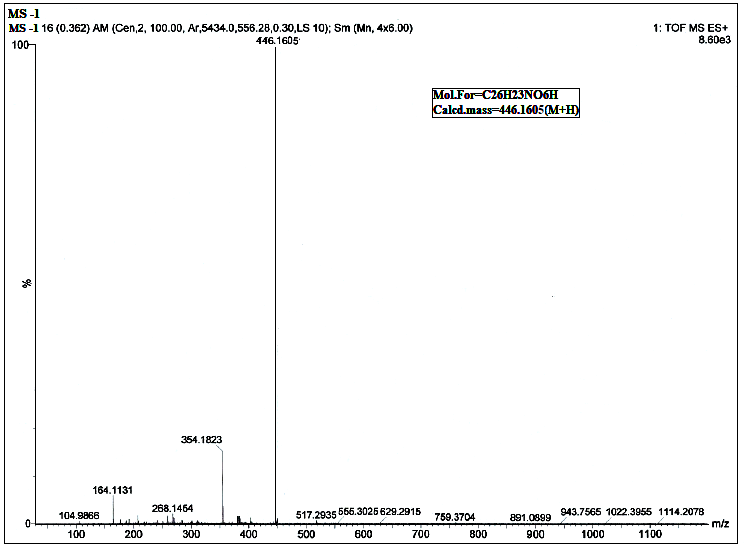
**13C NMR of 4l**

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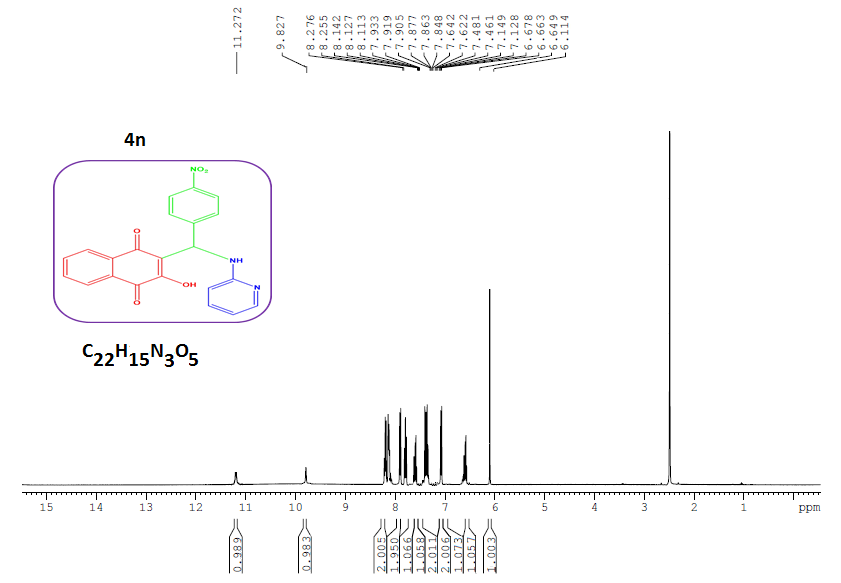
**HRMS of 4l**

**1H NMR of 4m**

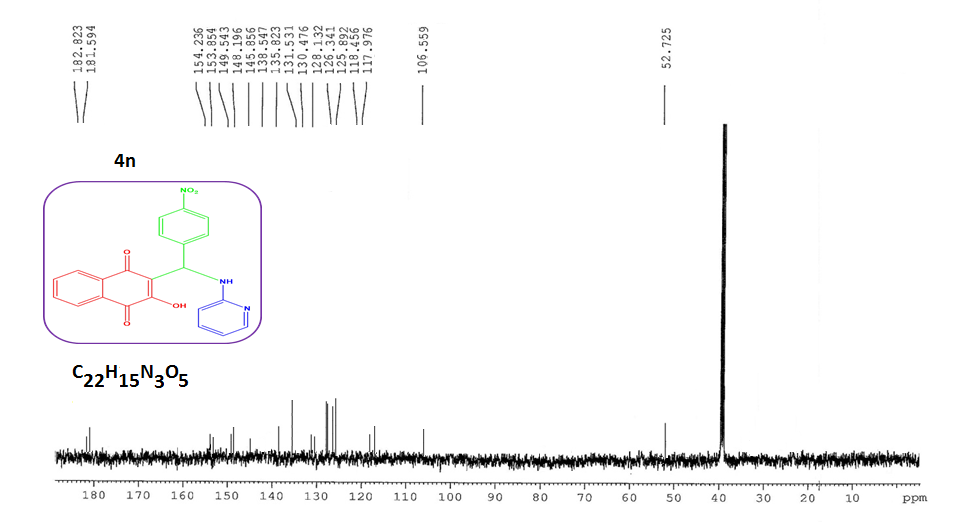
**13C NMR of 4m**

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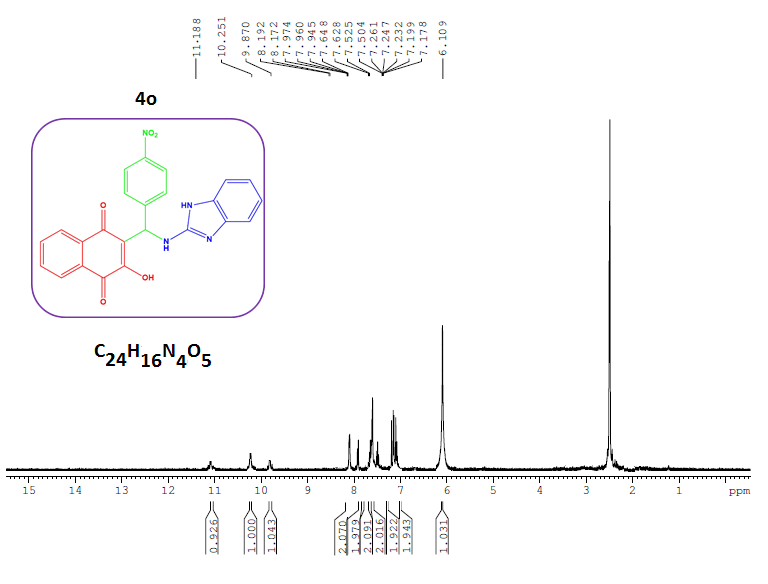
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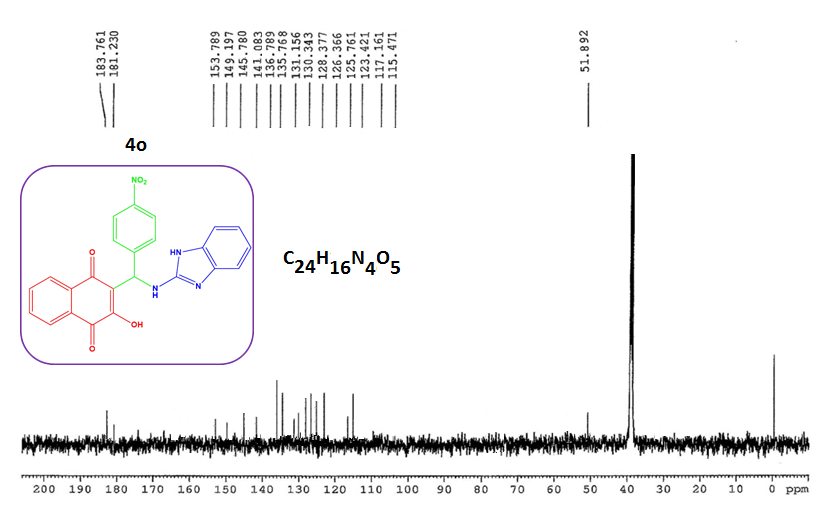
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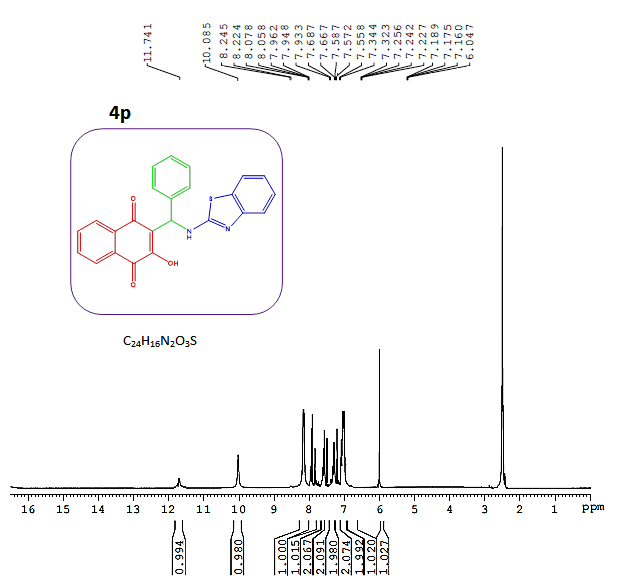
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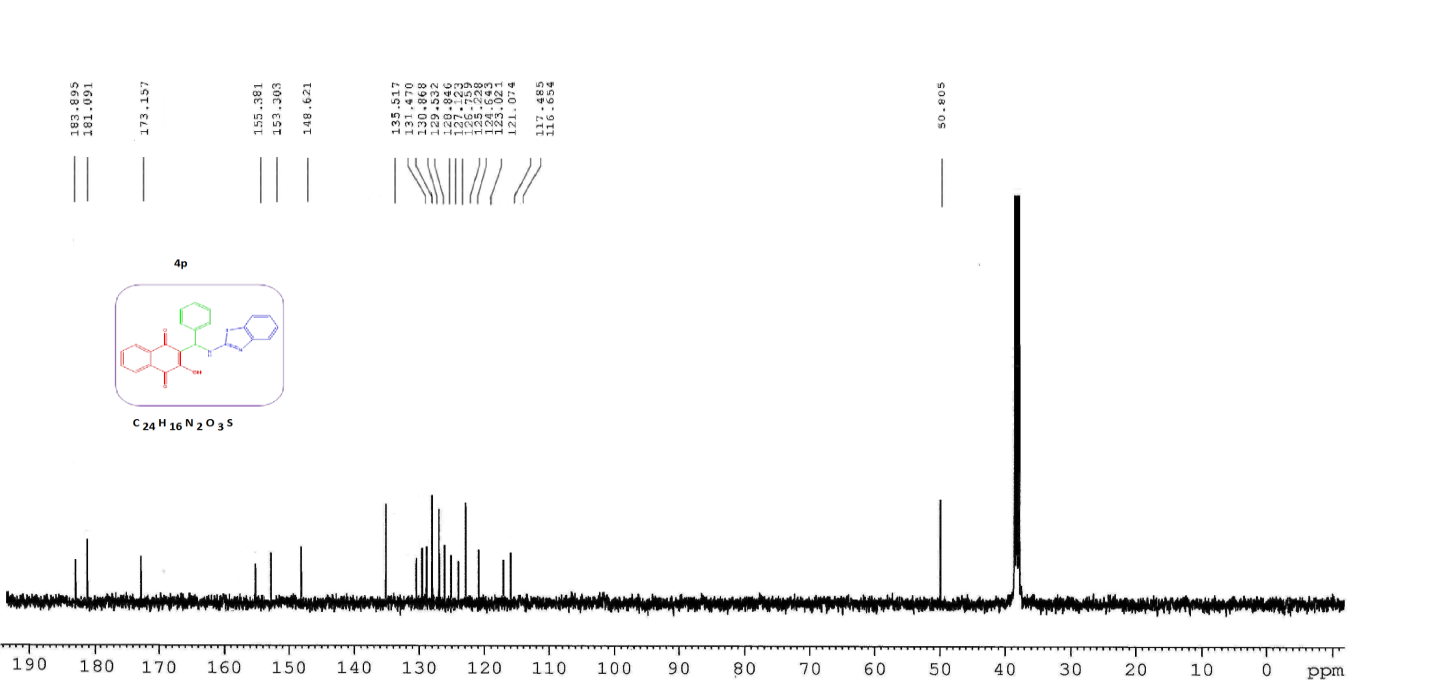
**1H NMR of 4o**

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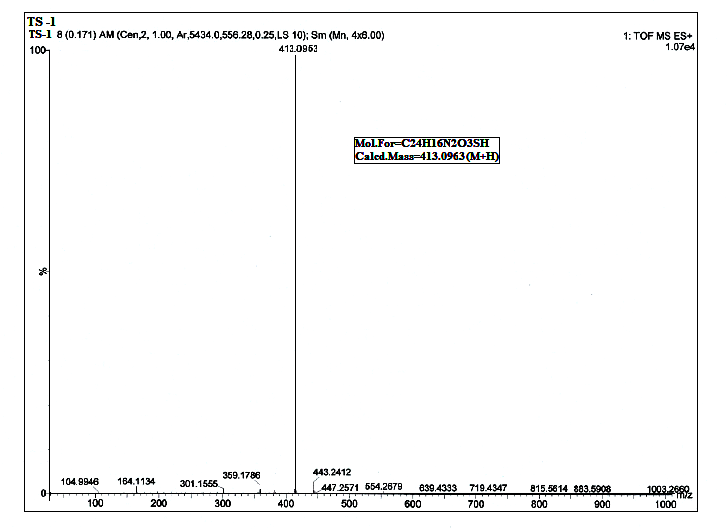
**13C NMR of 4o**

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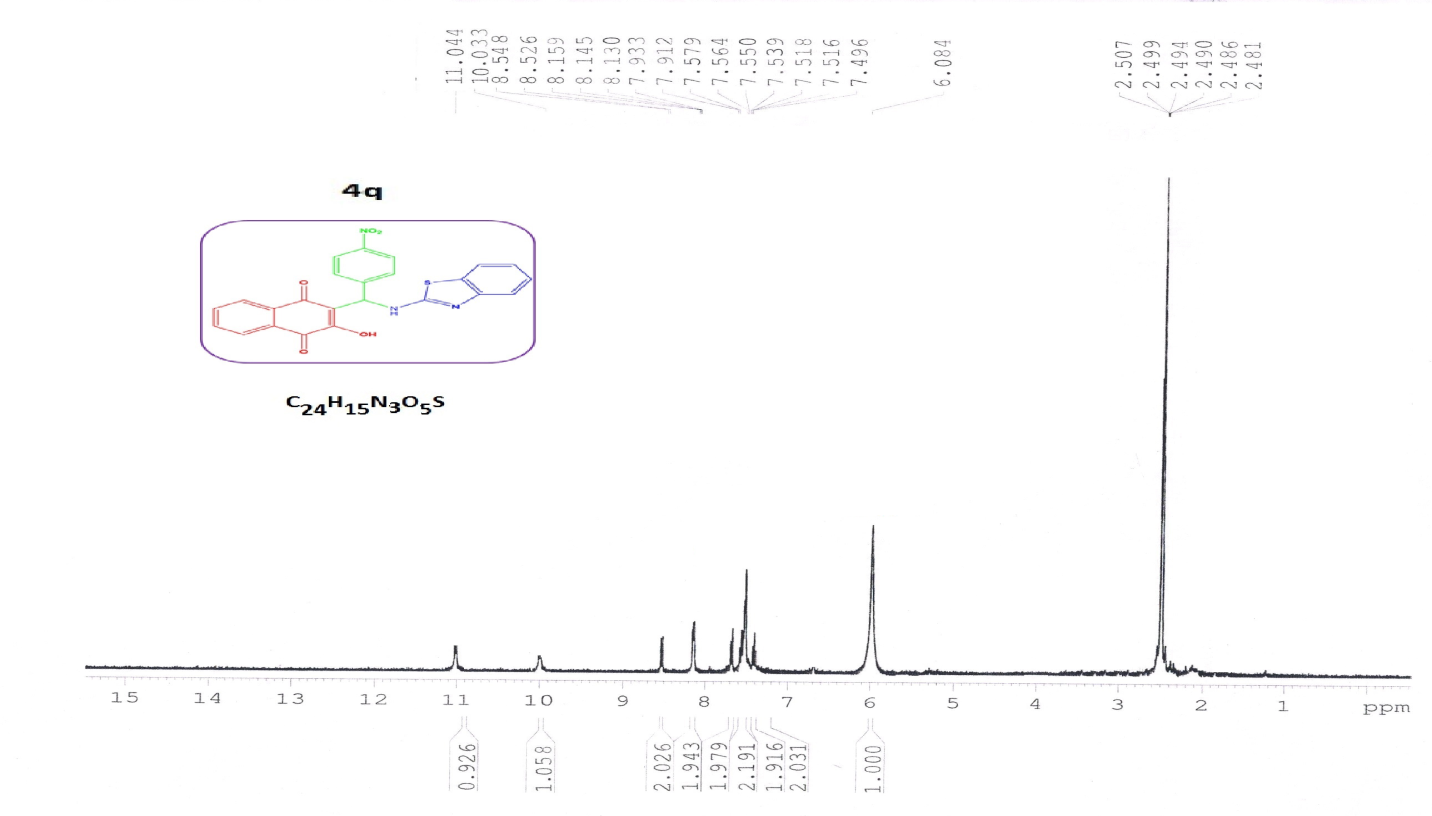
**1H NMR of 4p**

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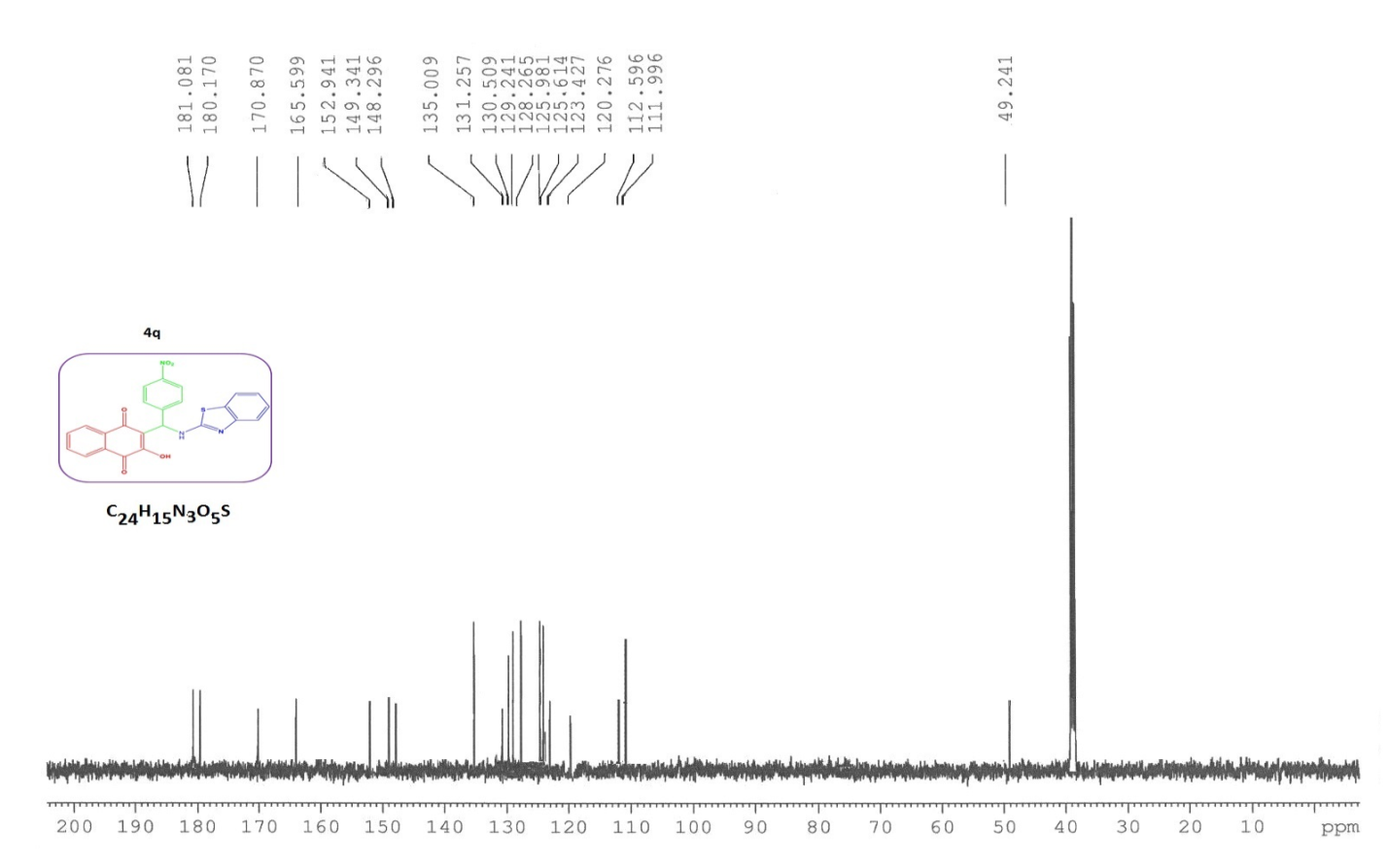
**13C NMR of 4p**

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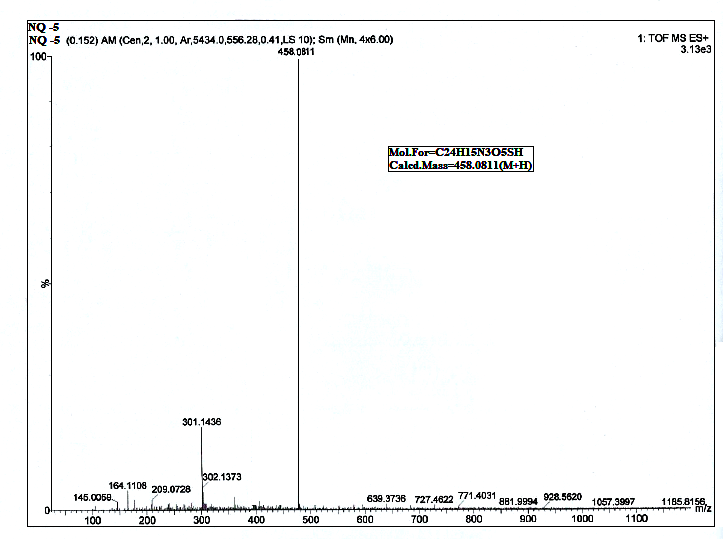
**HRMS of 4p**

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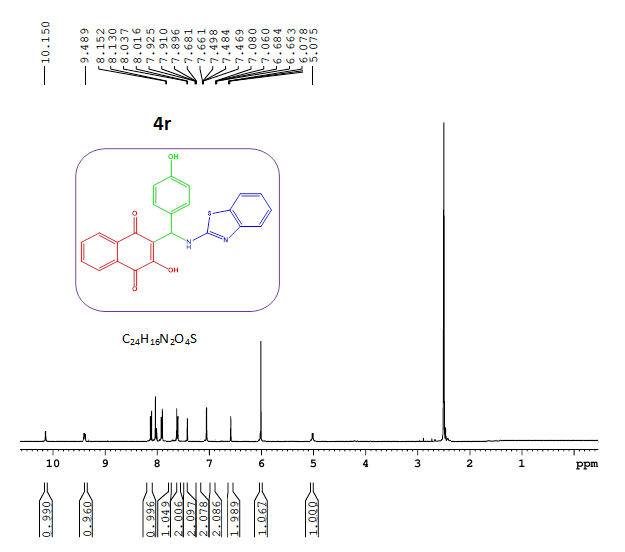
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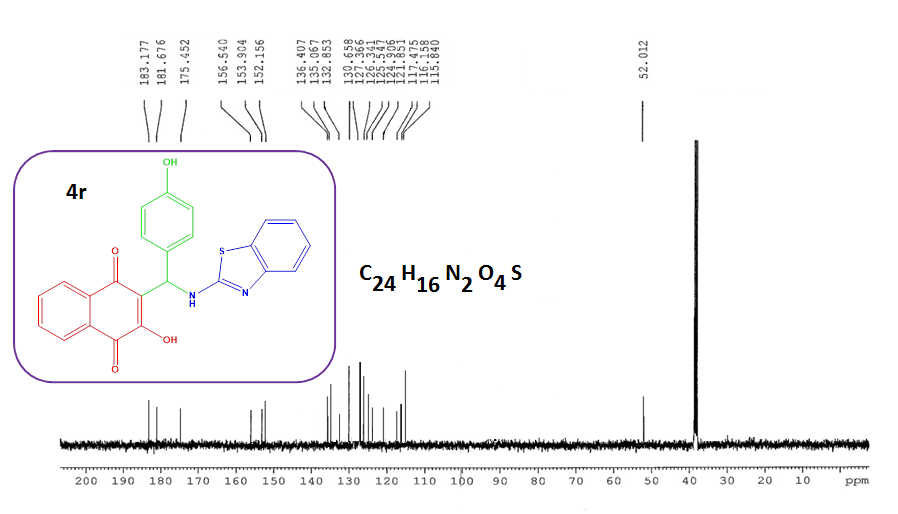
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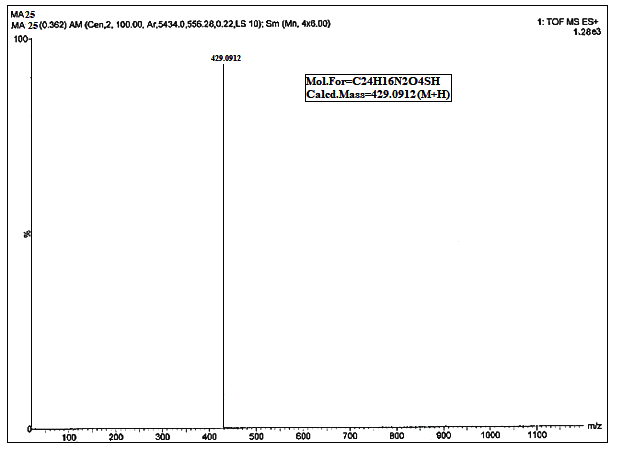
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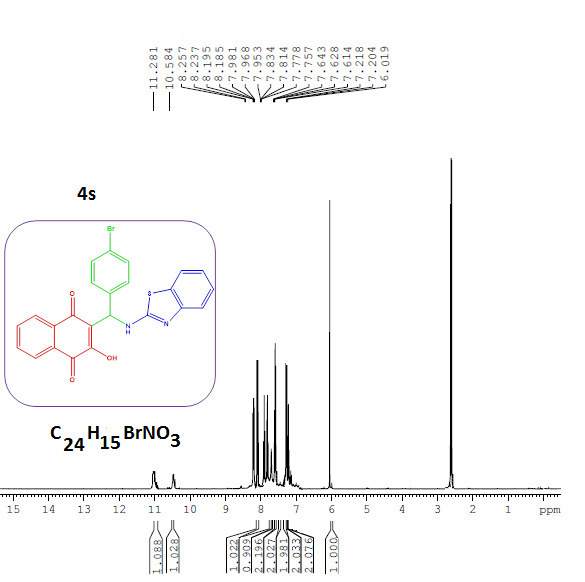
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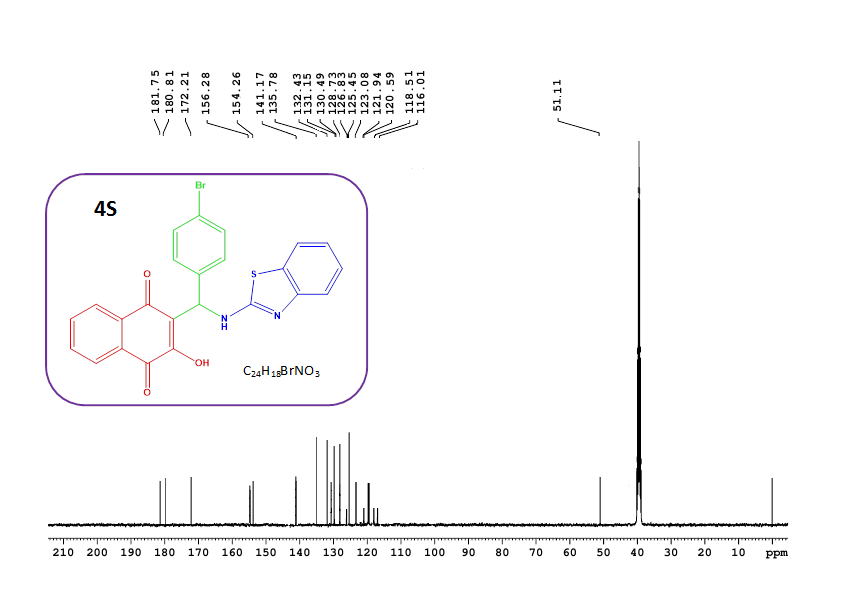
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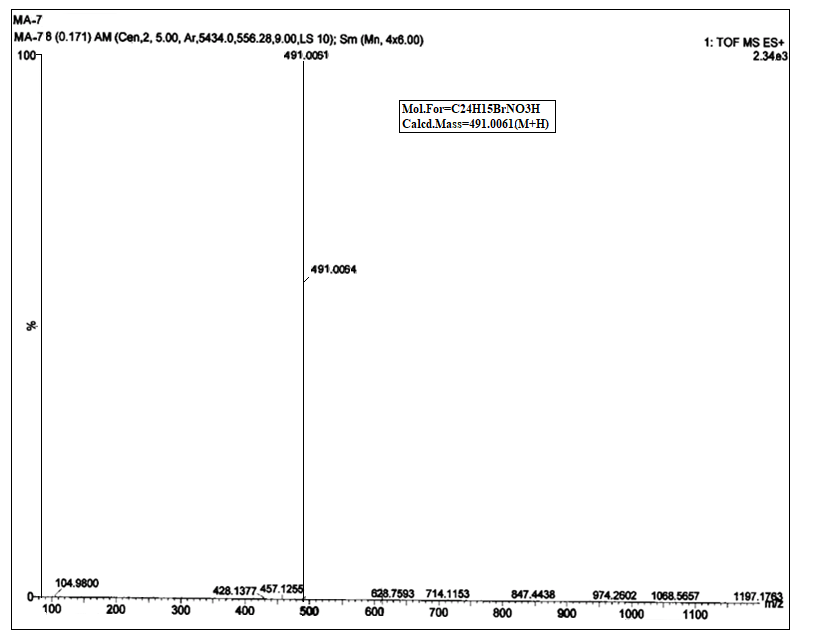
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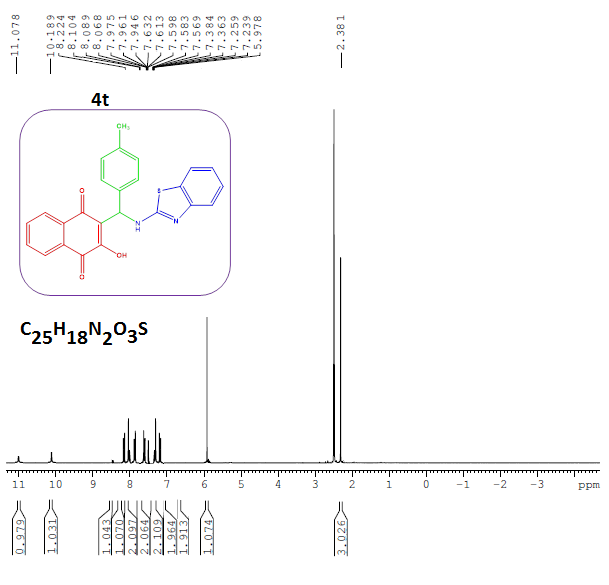
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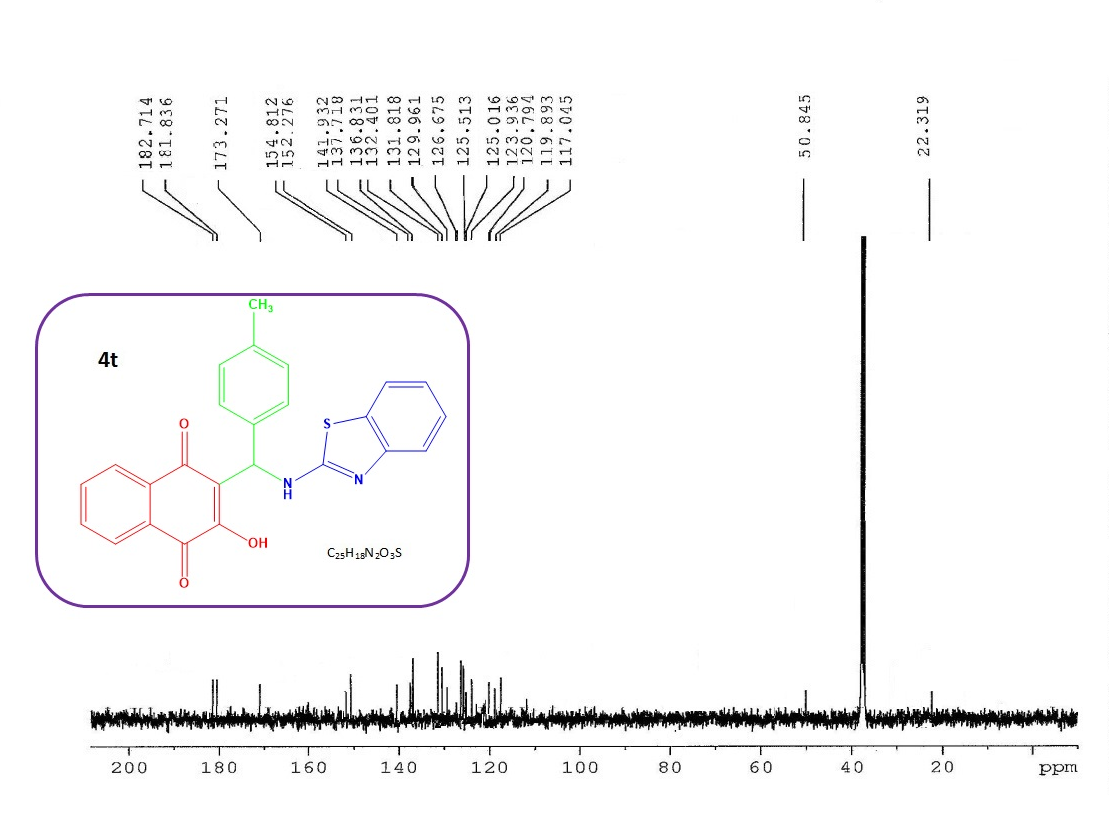
**13C NMR of 4s**

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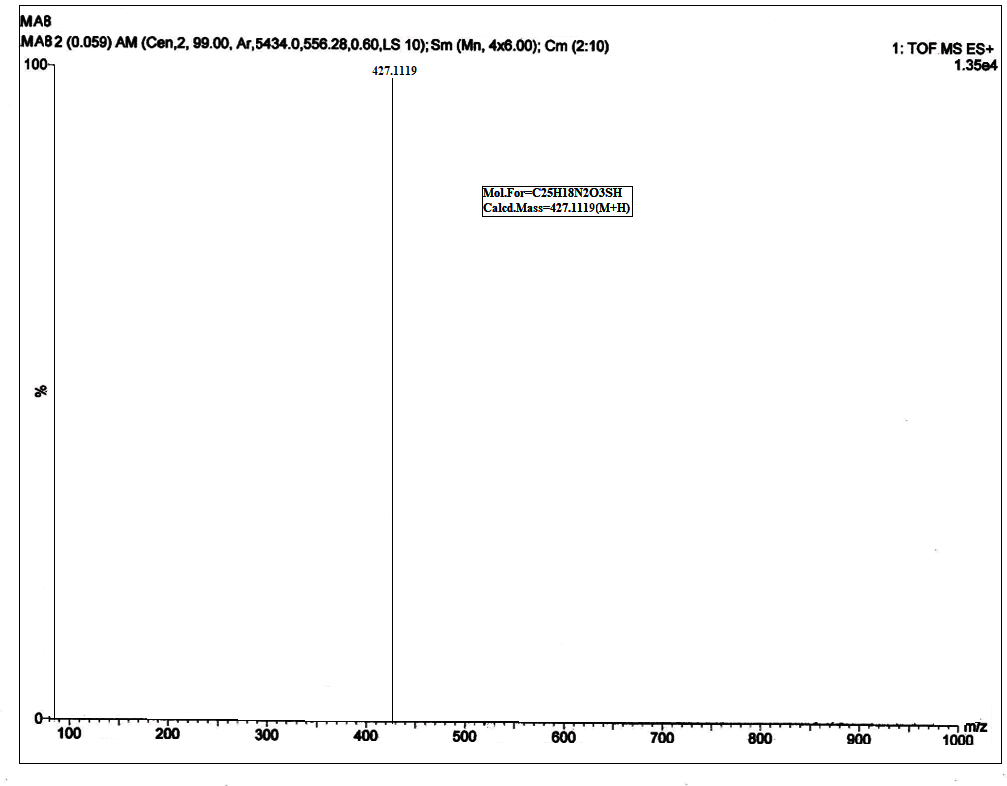
**HRMS of 4s**

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**1H NMR of 4t**

****

**13C NMR of 4t**



**HRMS of 4t**