Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Novel crabby biological-based glycoluril with alkane sulfonic acid pendings as a reusable nanostructured catalyst: Application for synthesis of new mono and bis-spiropyrans under mild and green conditions and *in vitro* biological performance

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[b]Department of Biology, Faculty of Science, Bu-Ali Sina University, P. O. Box 65175/4161, Hamedan, Iran.

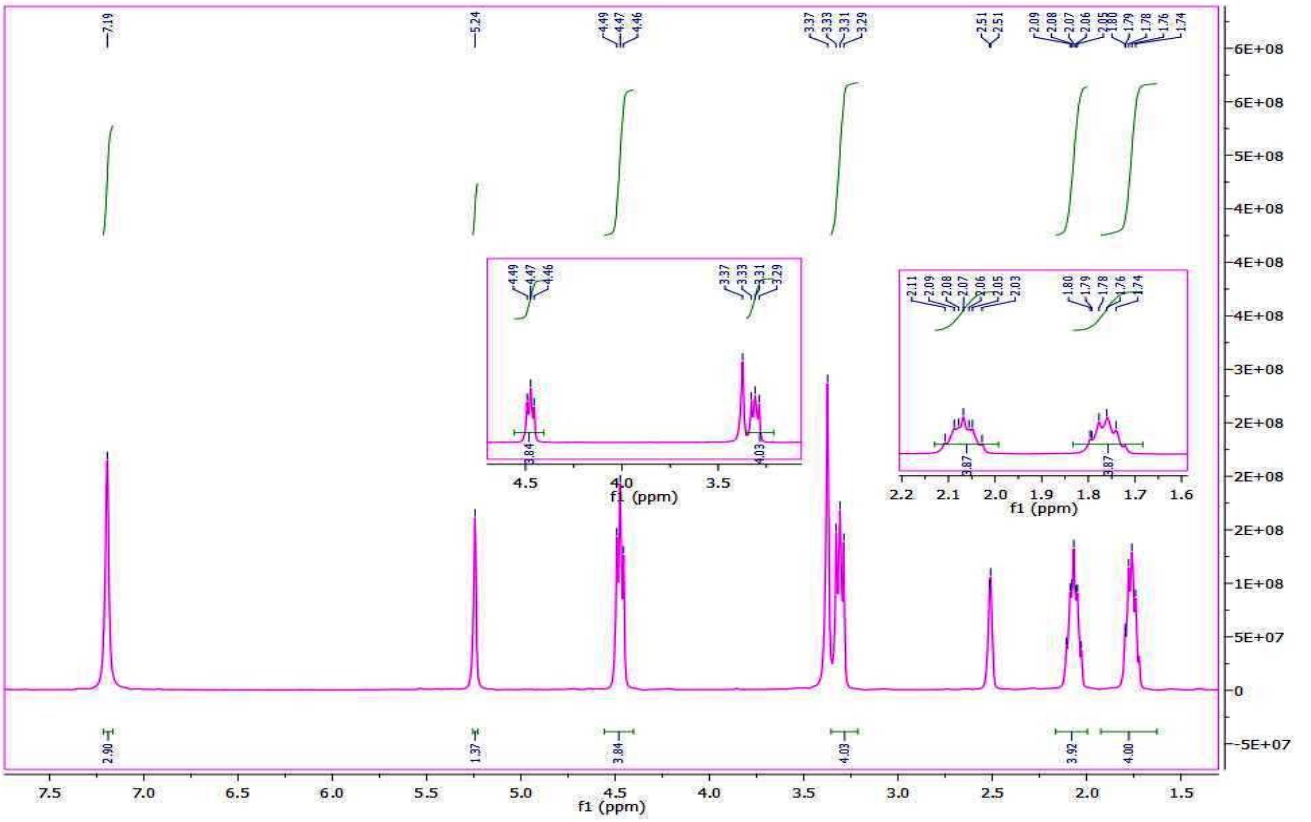


Fig. S1: ^{1}H NMR of glycoluril tetrakis (butane-1-sulfonic acid) (GTBSA)

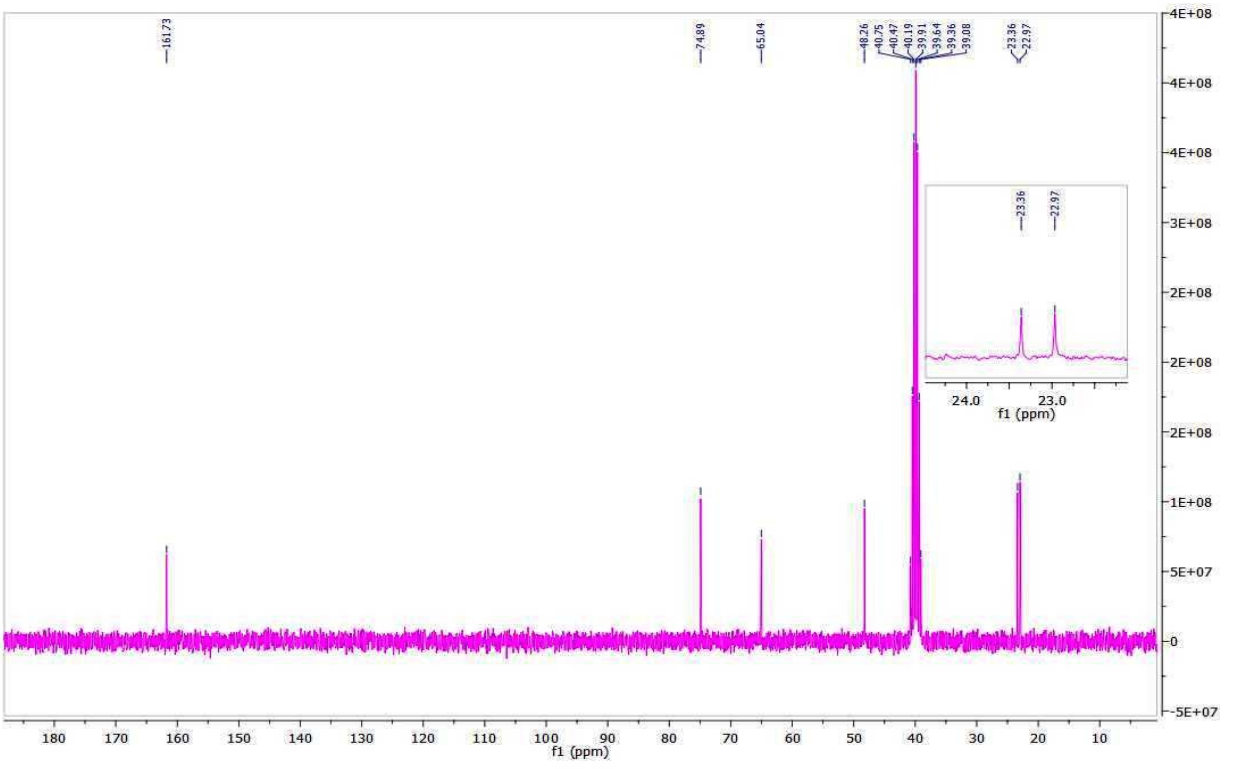


Fig. S2: ^{13}C NMR of glycoluril tetrakis (butane-1-sulfonic acid) (GTBSA)

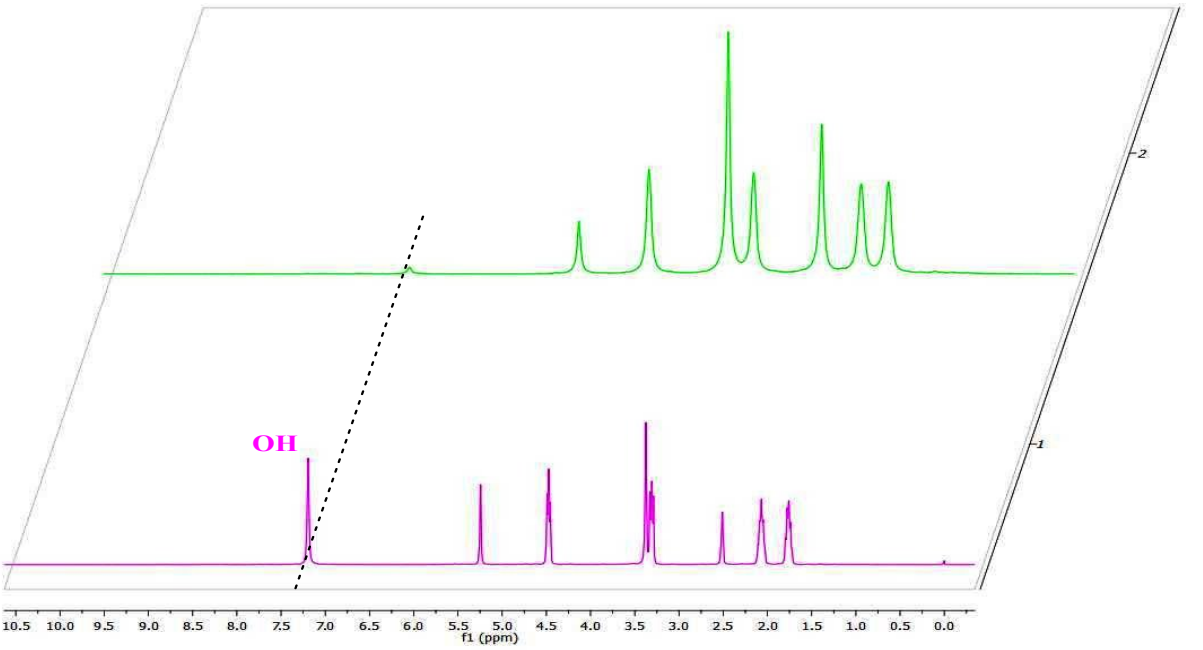
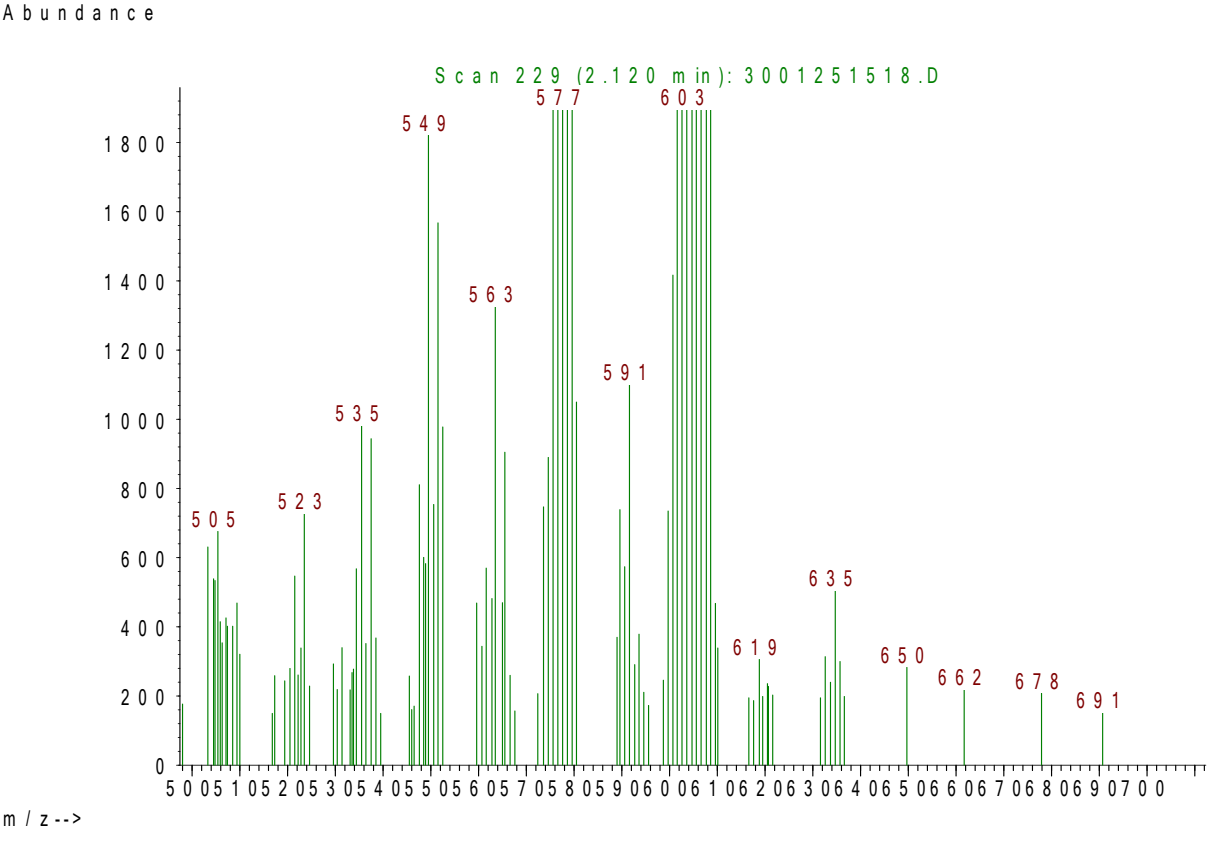


Fig. S3: ^{1}H NMR of glycoluril tetrakis (butane-1-sulfonic acid) (GTBSA) a) in DMSO-D2O b) in DMSO



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g. S4: Mass spectra of glycoluril tetrakis (butane-1-sulfonic acid) (GTBSA)

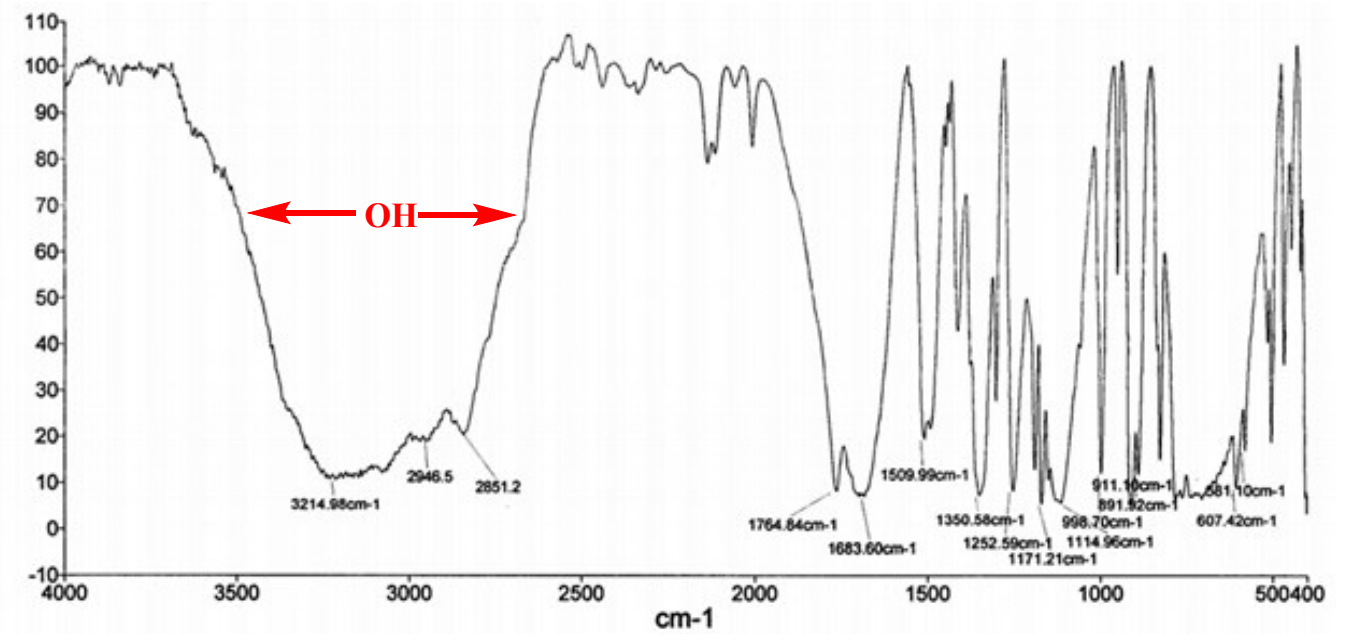


Fig. S5: FT-IR of glycoluril tetrakis (butane-1-sulfonic acid) (GTBSA)

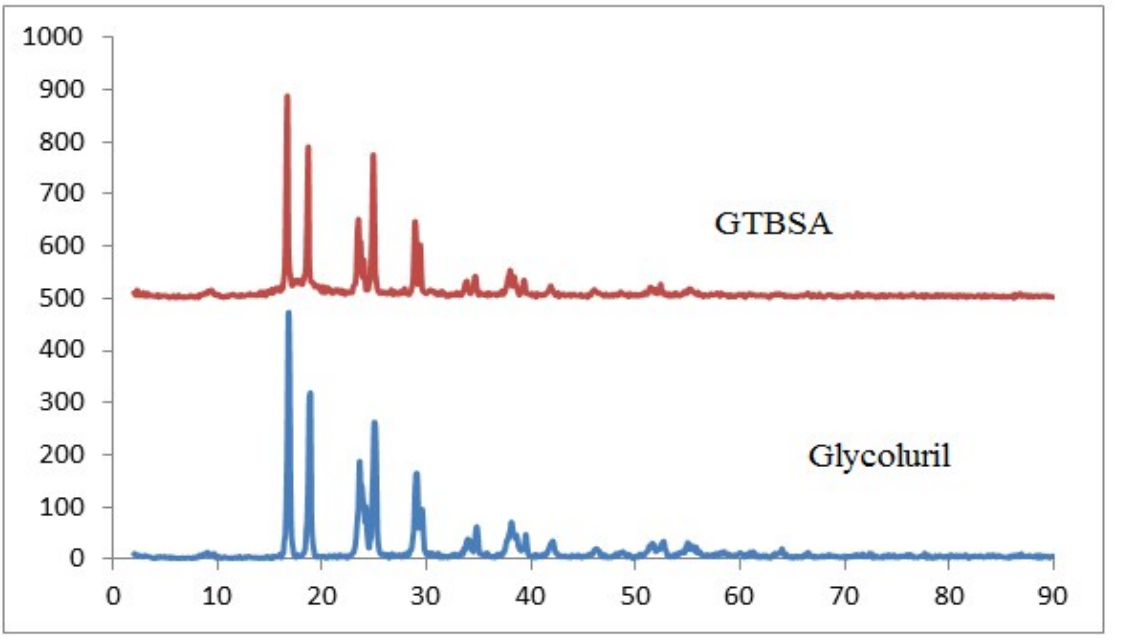


Fig. S6: XRD pattern of glycoluril tetrakis (butane-1-sulfonic acid) (GTBSA) and glycoluril

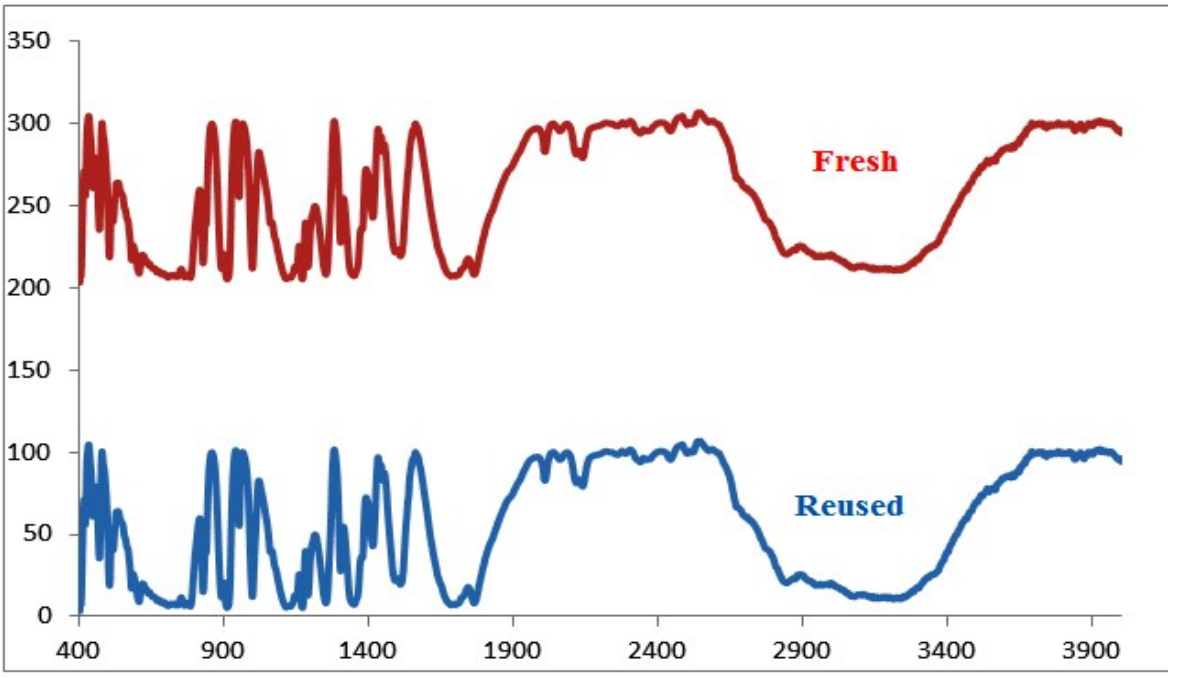
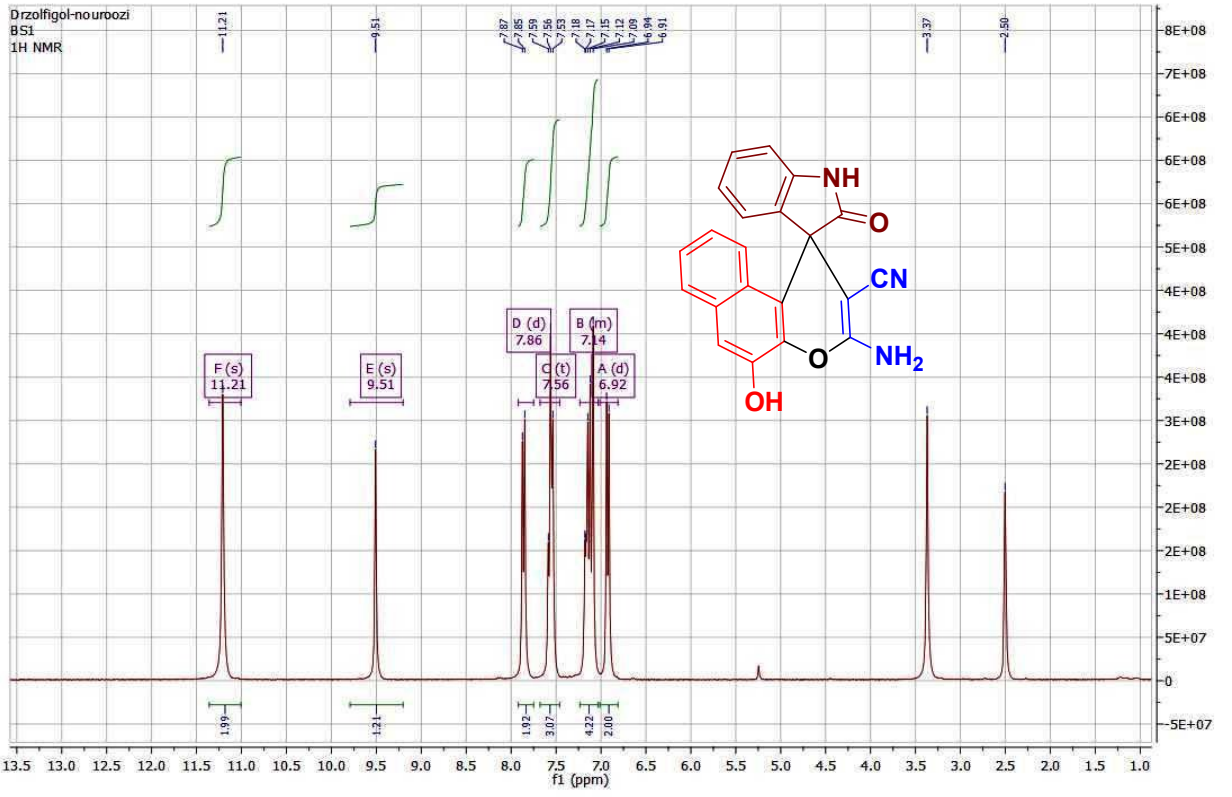


Fig. S7: Compration FT-IR of GTBSA fresh and reused

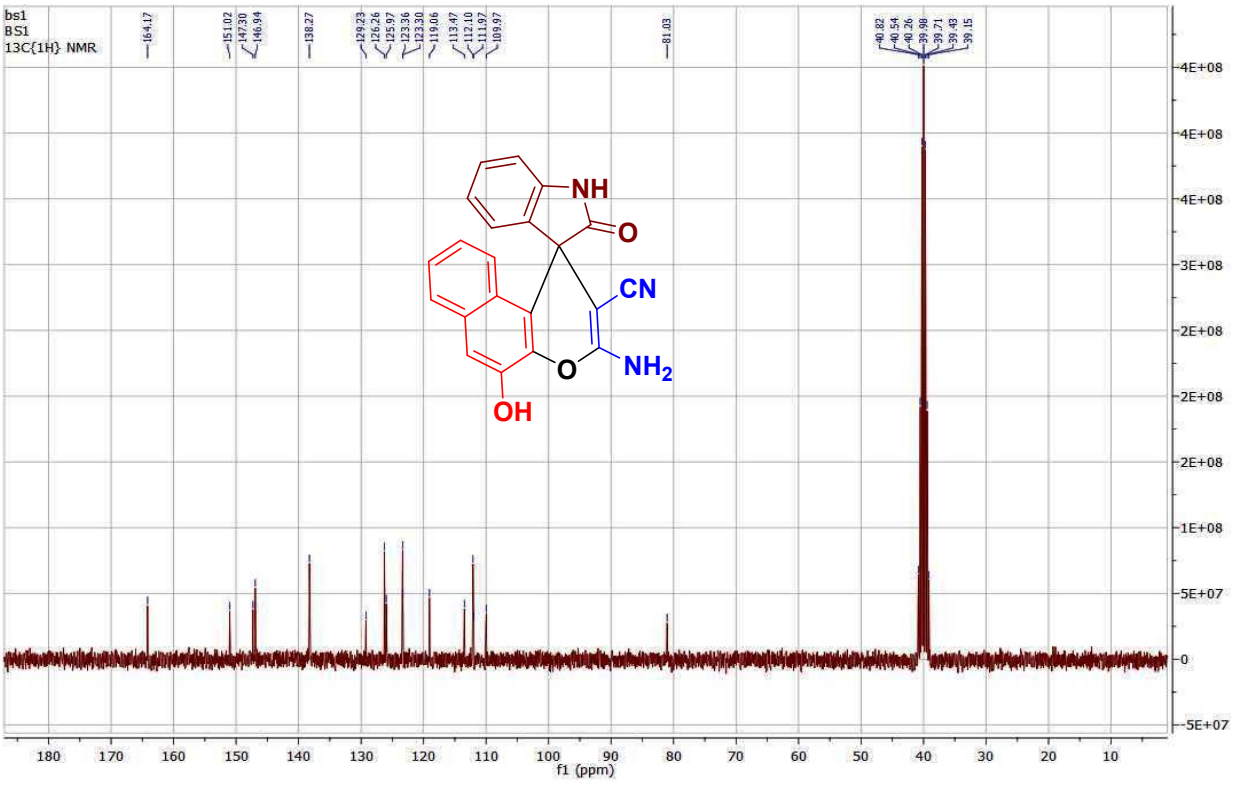
Table S1: Scavenging activity (%) of the synthesized compounds at different concentrations (mg ml^{-1}), quercetin and ascorbic acid as standard antioxidants

Compound	Concentration (mg ml^{-1})					Average
	0.2	0.4	0.6	0.8	1	
13s	61.50±0.95^{a}	66.38±1.11^{a}	71.39±1.48^{a}	74.52±1.19^{cd}	77.22±1.43^{cd}	70.20
14s	33.53±0.71^{e}	42.35±1.29^{g}	46.20±0.78^{g}	54.09±1.24^{h}	59.52±1.10^{g}	47.14
8S	55.58±3.31^{b}	58.62±0.98^{b-d}	70.74±2.84^{ab}	81.62±0.37^{a}	89.54±1.55^{a}	71.22
15S	48.84±1.63^{c}	60.72±1.24^{b}	73.35±0.51^{a}	80.27±1.29^{ab}	82.17±1.23^{b}	69.07
7S	52.76±0.74^{b}	61.06±2.05^{b}	64.78±0.90^{cd}	70.08±0.35^{e}	74.17±0.97^{d}	64.57
16S	47.52±0.80^{bc}	56.78±0.83^{c-e}	63.08±2.15^{de}	70.66±1.79^{de}	77.54±1.93^{c}	63.11
11S	53.02±2.74^{b}	53.78±0.58^{ef}	62.08±0.74^{de}	68.16±1.08^{e}	71.04±1.22^{e}	61.61
10S	46.87±0.43^{bc}	51.95±1.29^{ef}	53.69±0.35^{f}	56.20±0.40^{gh}	58.71±1.58^{g}	53.48
12S	46.79±0.43^{bc}	55.16±0.62^{d-f}	59.82±2.28^{e}	63.98±0.34^{f}	76.25±0.31^{cd}	60.40
9S	54.12±1.17^{b}	61.58±0.64^{b}	70.32±1.15^{bc}	76.48±1.10^{bc}	84.37±1.32^{b}	69.37
2S	44.45±1.80^{d}	55.32±1.27^{d-f}	55.43±1.52^{f}	59.40±1.77^{g}	64.10±1.66^{f}	55.47
3S	54.45±0.25^{b}	59.17±0.60^{bc}	66.57±1.03^{c}	71.45±1.22^{de}	77.43±1.27^{c}	65.81
4S	54.89±1.60^{b}	62.42±1.87^{b}	67.77±1.04^{bc}	72.21±0.98^{de}	77.56±1.51^{c}	66.97
Ascorbic acid	71.47±1.00^{a}	73.75±0.99^{a}	77.07±1.51^{a}	78.86±1.53^{a}	80.89±1.09^{a}	76.41
Quercetin	76.11±0.69^{a}	81.13±1.01^{a}	86.85±1.81^{a}	88.13±0.92^{a}	91.85±1.32^{a}	84.81

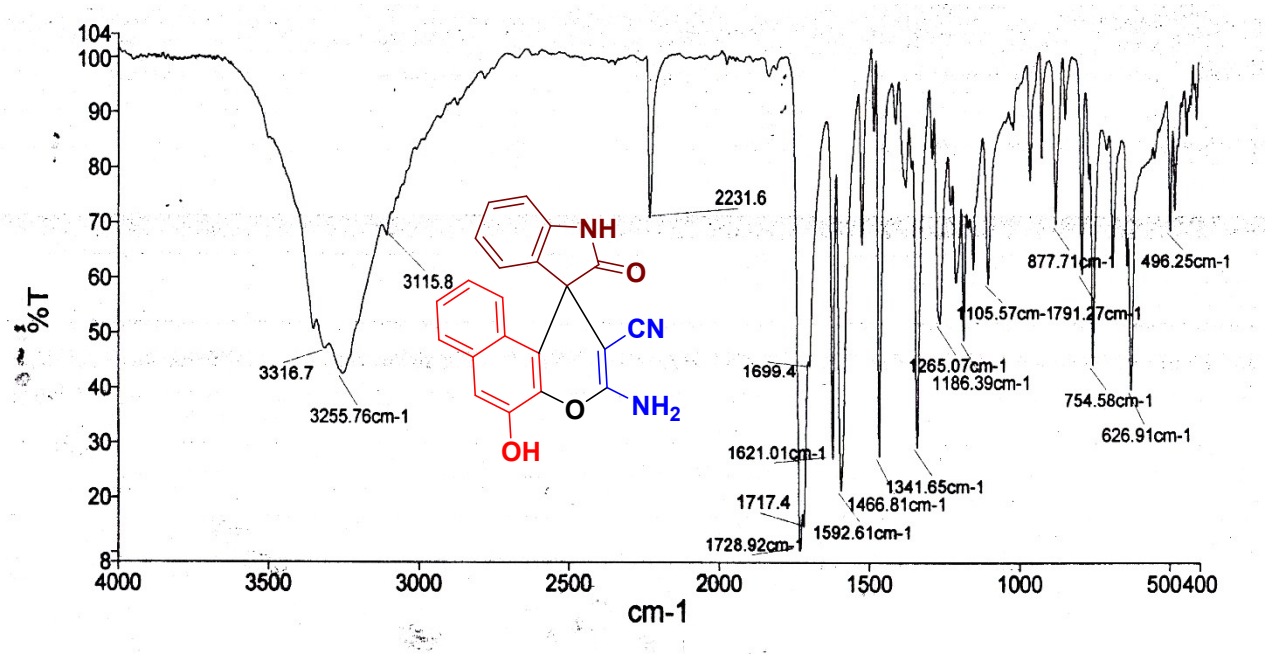
Experiment was performed in triplicate and expressed as mean ± SD. Values along each column with different superscripts are significantly different ($P< 0.05$).



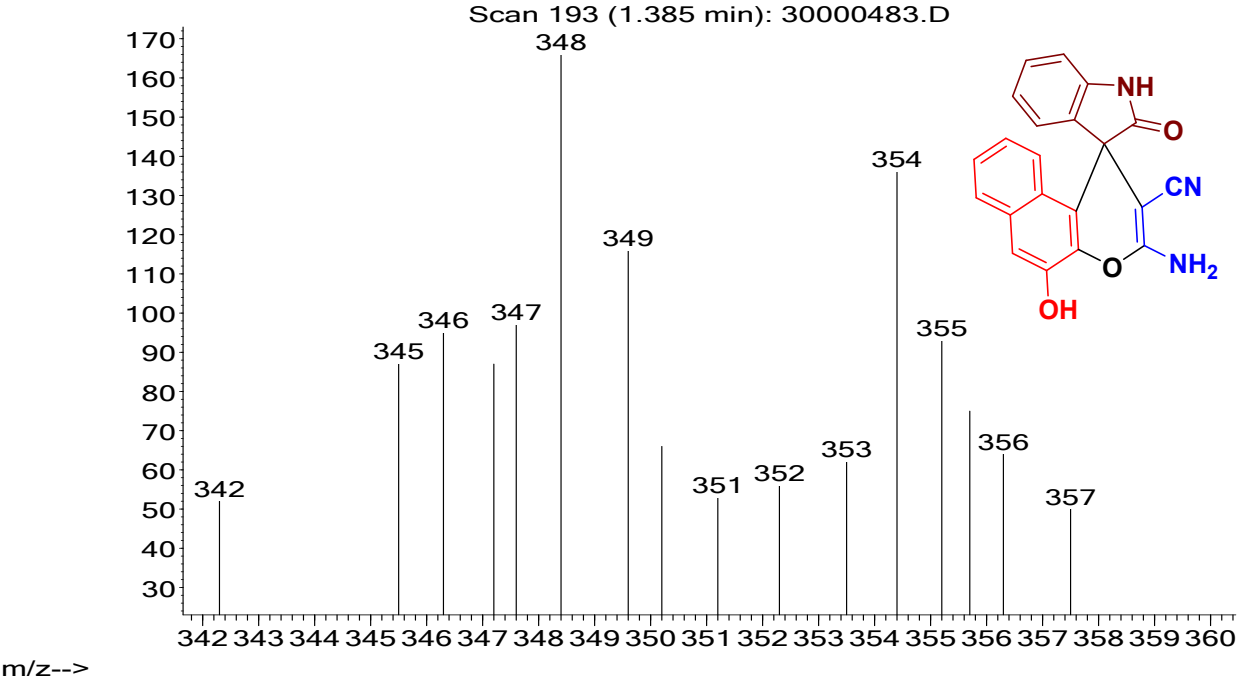
[1]HNMR spectrum of 3-amino-5-hydroxy-2'-oxospiro[benzo[f]chromene-1,3'-indoline]-2-carbonitrile (1S)



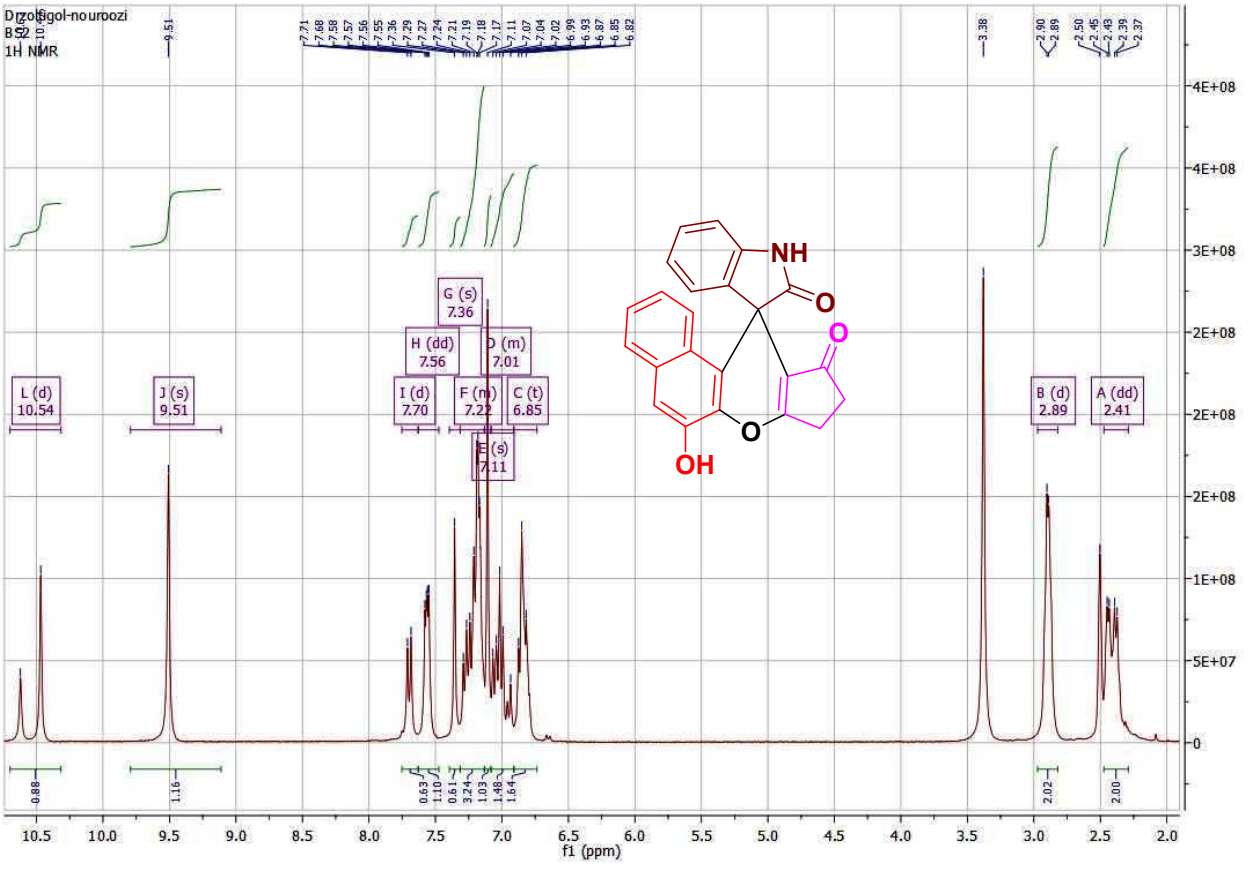
[13]CNMR spectrum of 3-amino-5-hydroxy-2'-oxospiro[benzo[f]chromene-1,3'-indoline]-2-carbonitrile (1S)



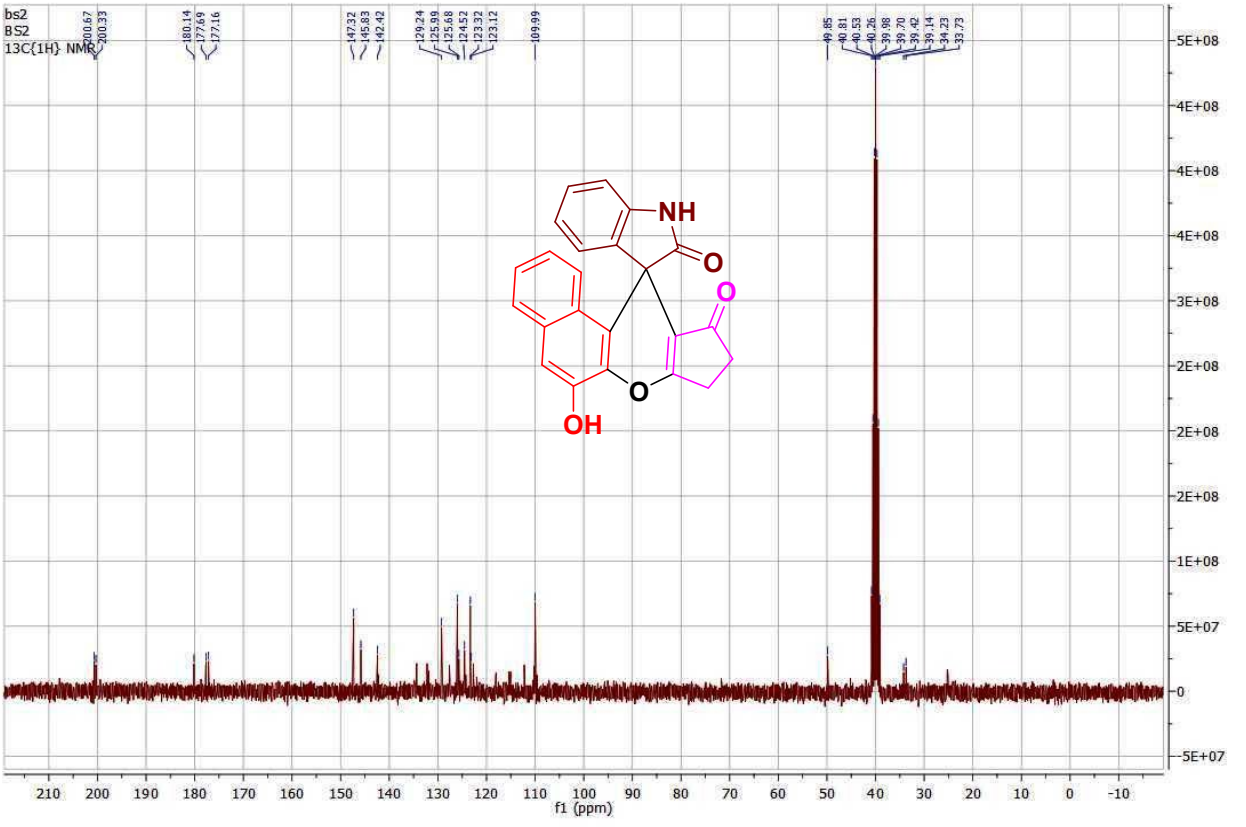
FT-IR spectrum of 3-amino-5-hydroxy-2'-oxospiro[benzo[f]chromene-1,3'-indoline]-2-carbonitrile (1S)



Mass spectrum of 3-amino-5-hydroxy-2'-oxospiro[benzo[f]chromene-1,3'-indoline]-2-carbonitrile (1S)



[1]HNMR spectrum of 6-hydroxy-8,9-dihydro-10H-spiro[benzo[f]cyclopenta[b]chromene-11,3'-indoline]-2',10-dione (2S)



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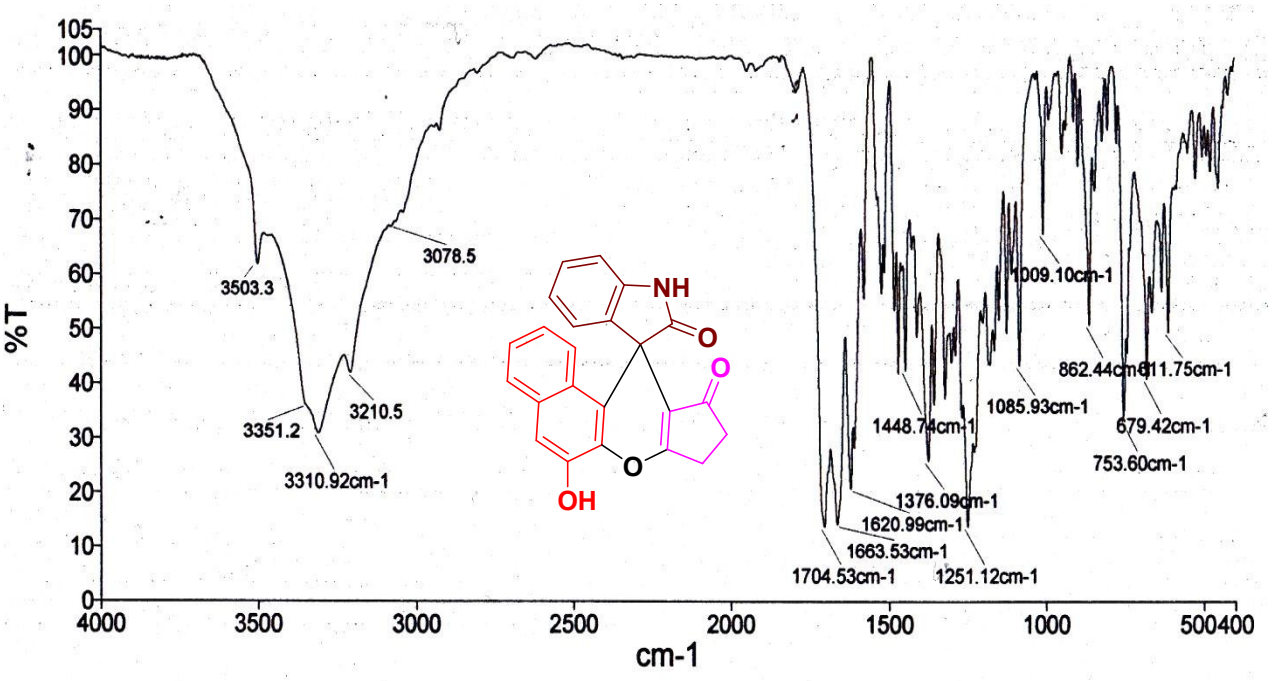

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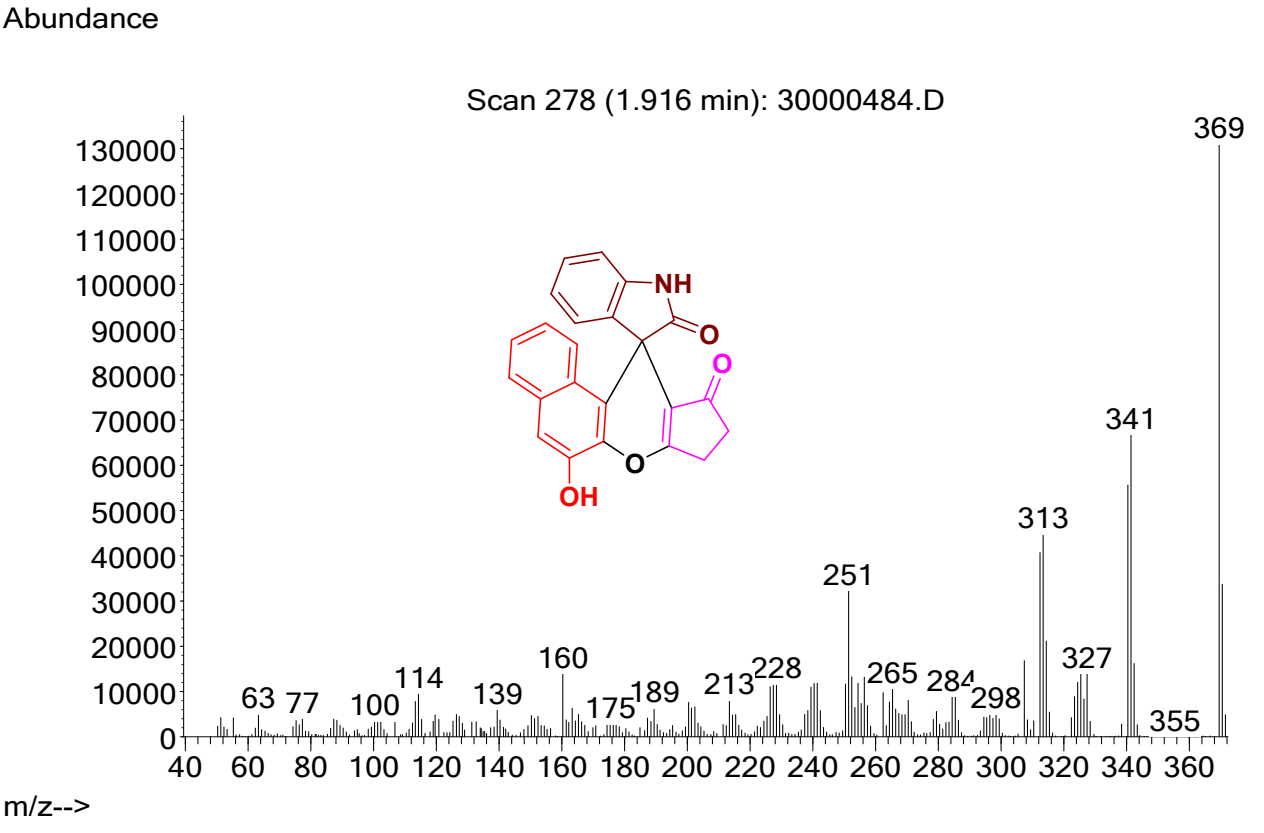

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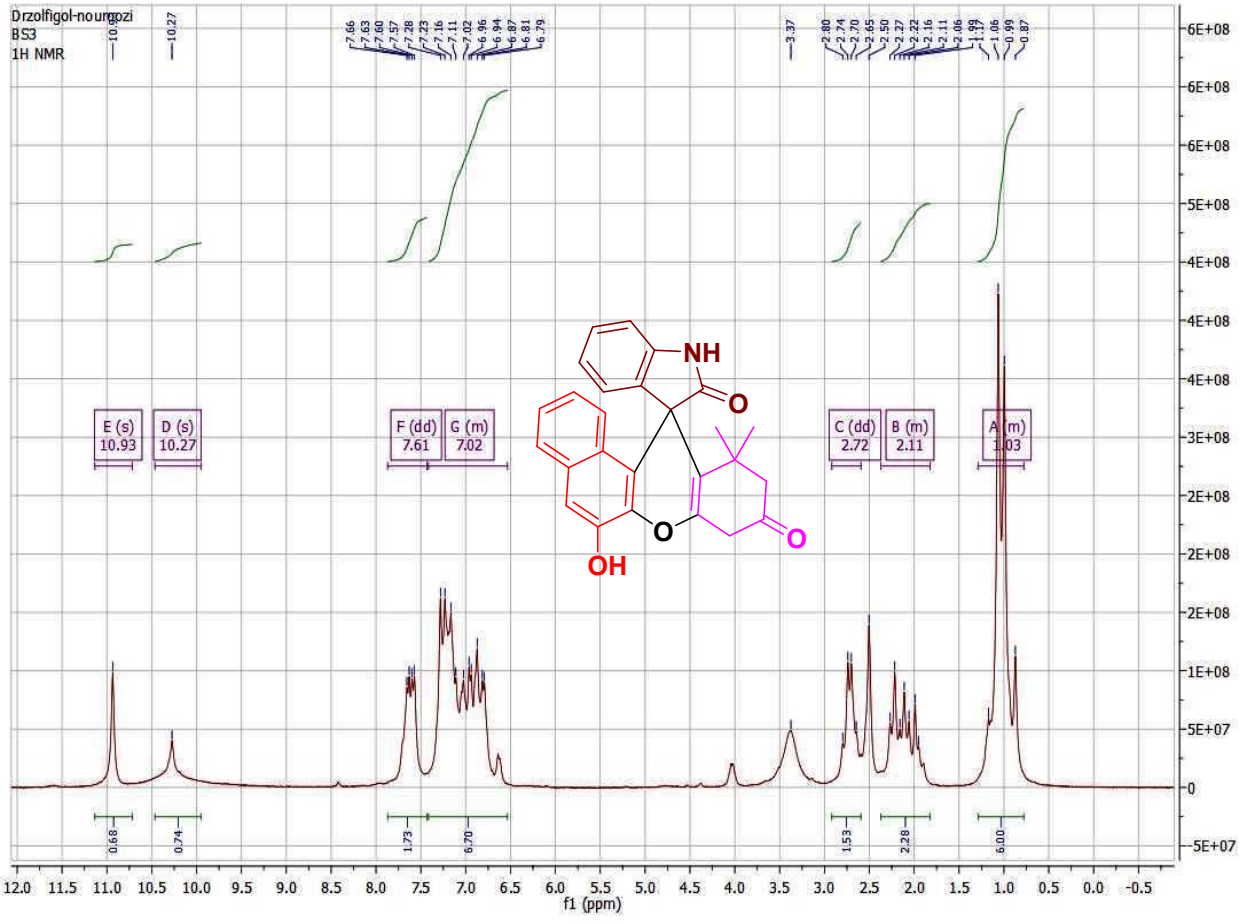
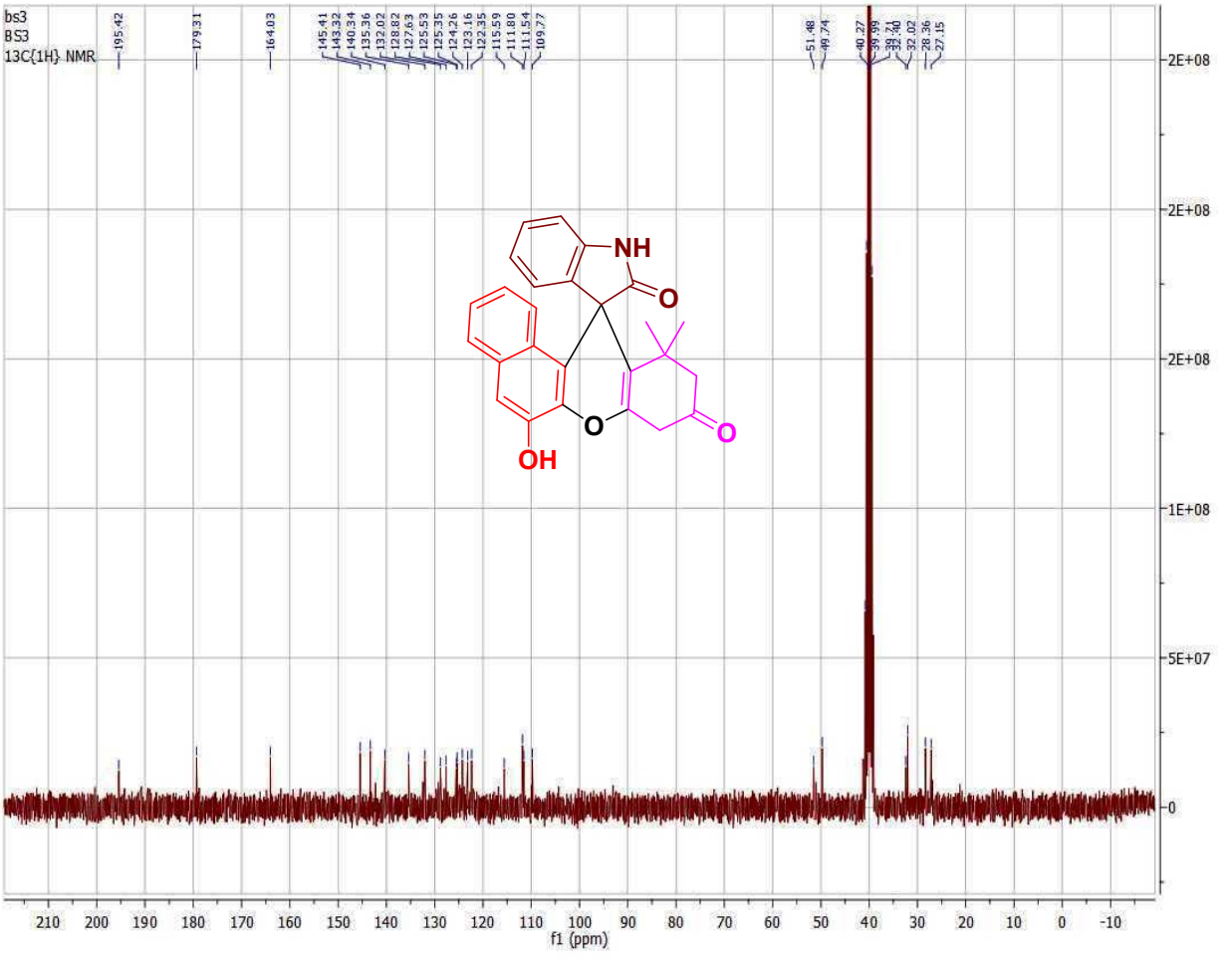


[1]HNMR spectrum of 6-hydroxy-9,9-dimethyl-9,10-dihydrospiro[benzo[a]xanthene-12,3'-indoline]-2',11(8H)-dione (3S)



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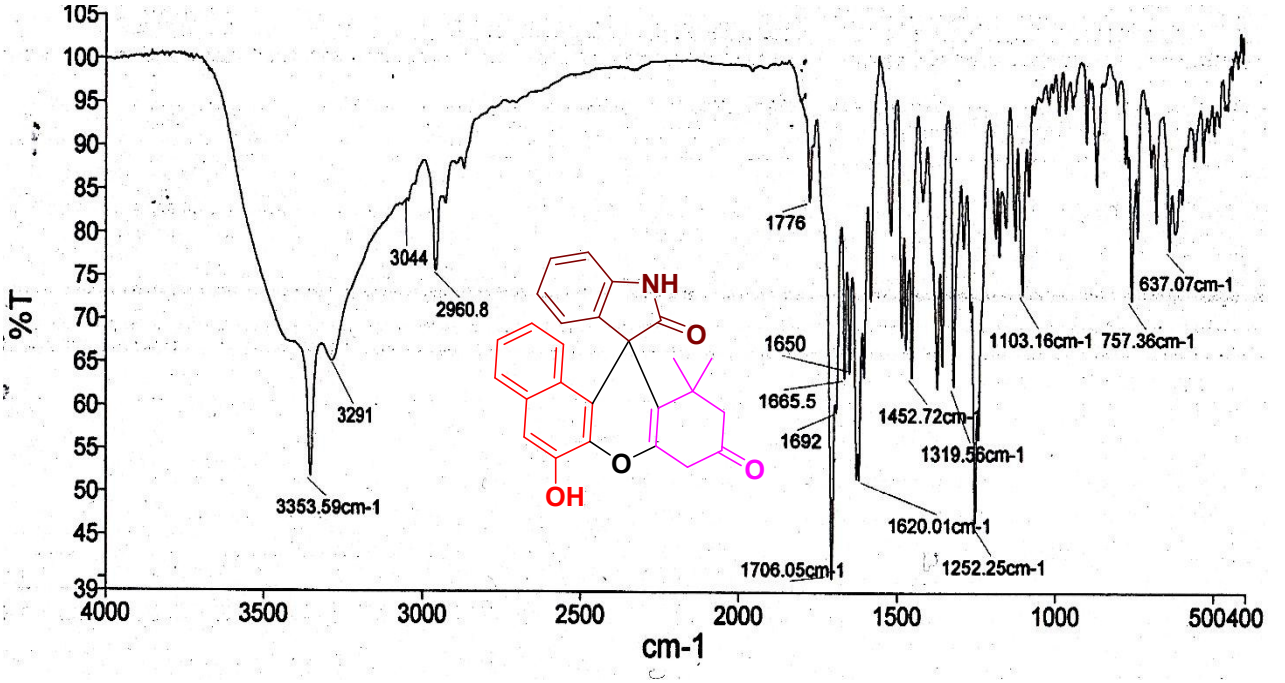

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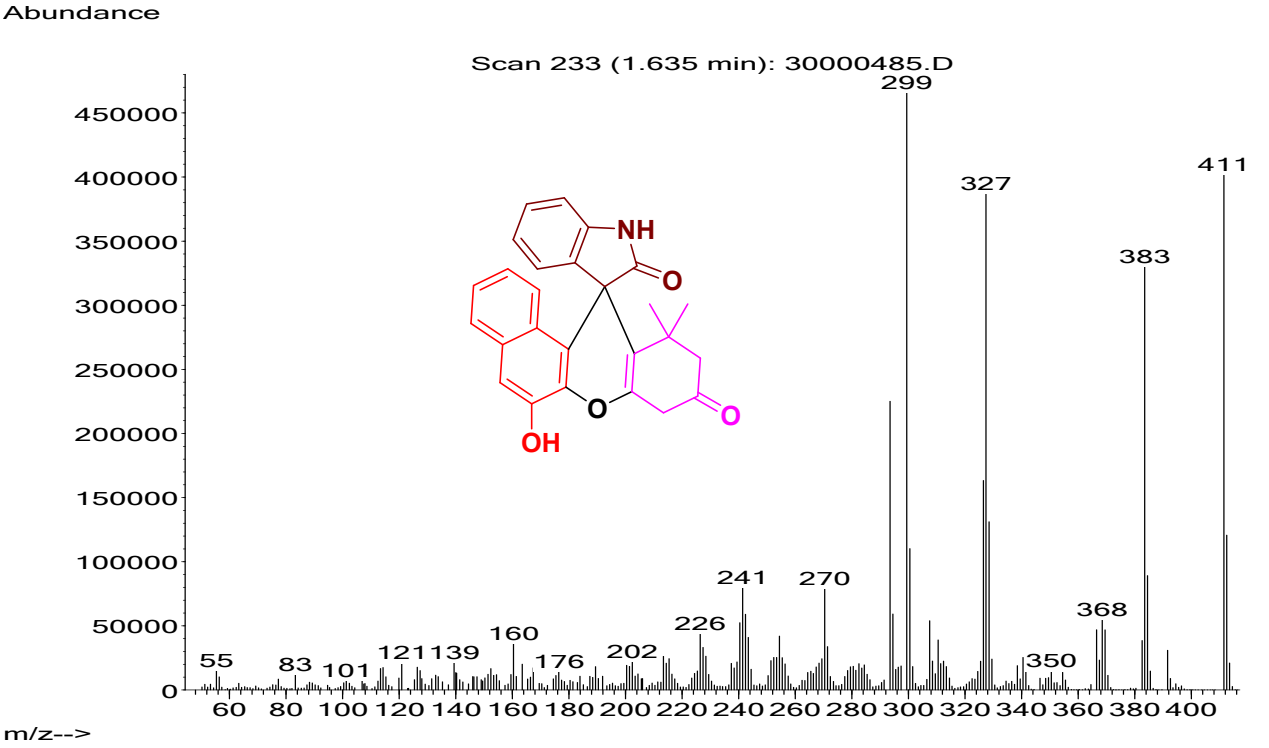

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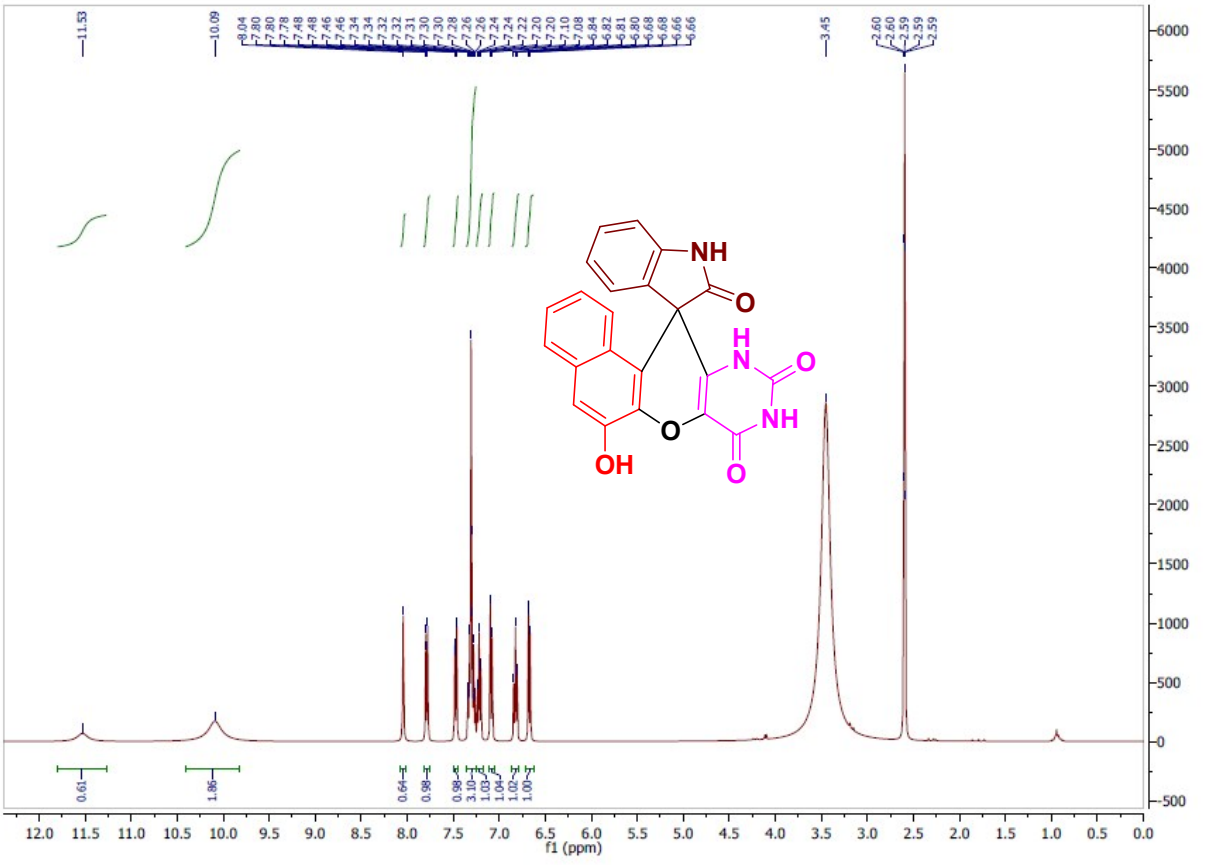
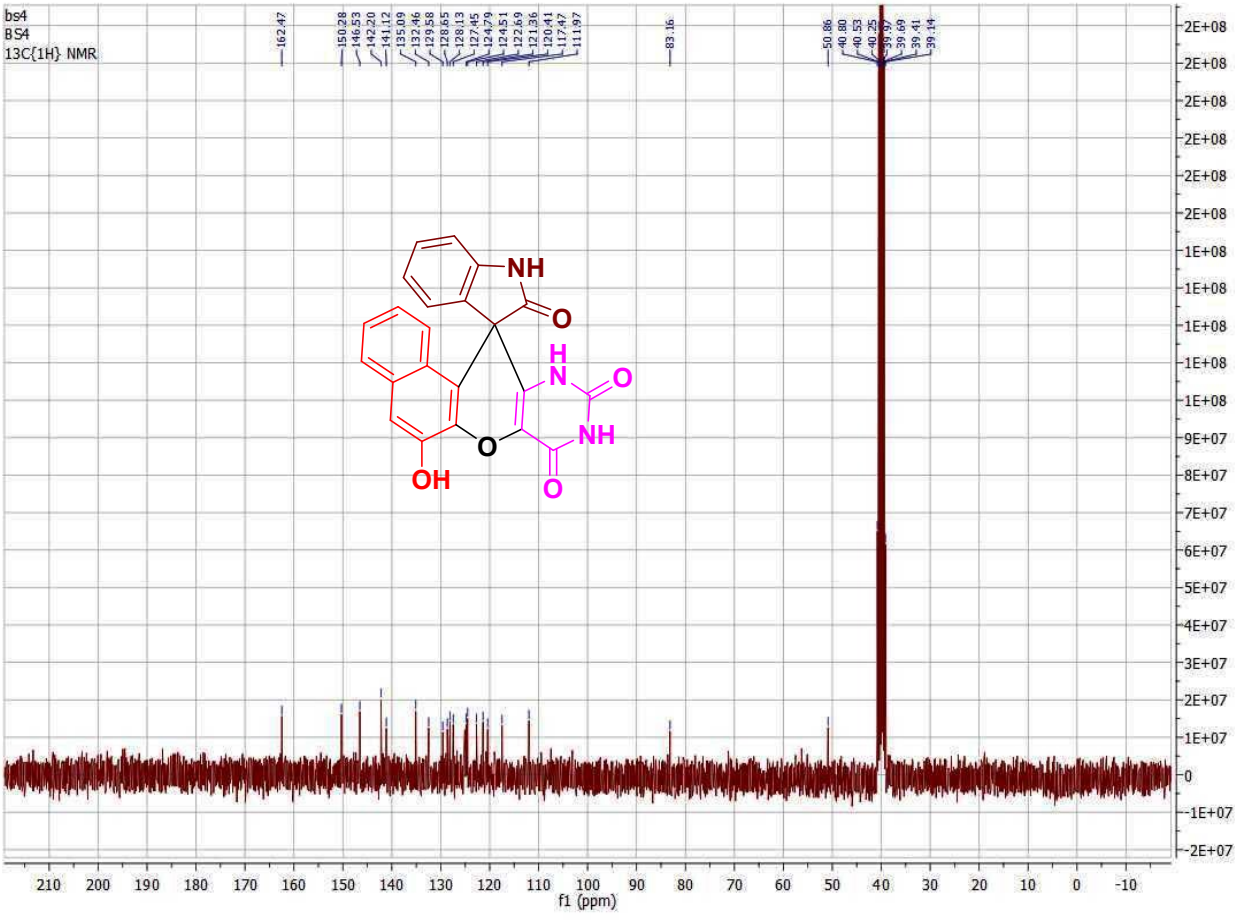


[1]HNMR spectrum of 6-hydroxyspiro[benzo[5,6]chromeno[2,3-d]pyrimidine-12,3'-indoline]-2',9,11(8H,10H)-trione (4S)



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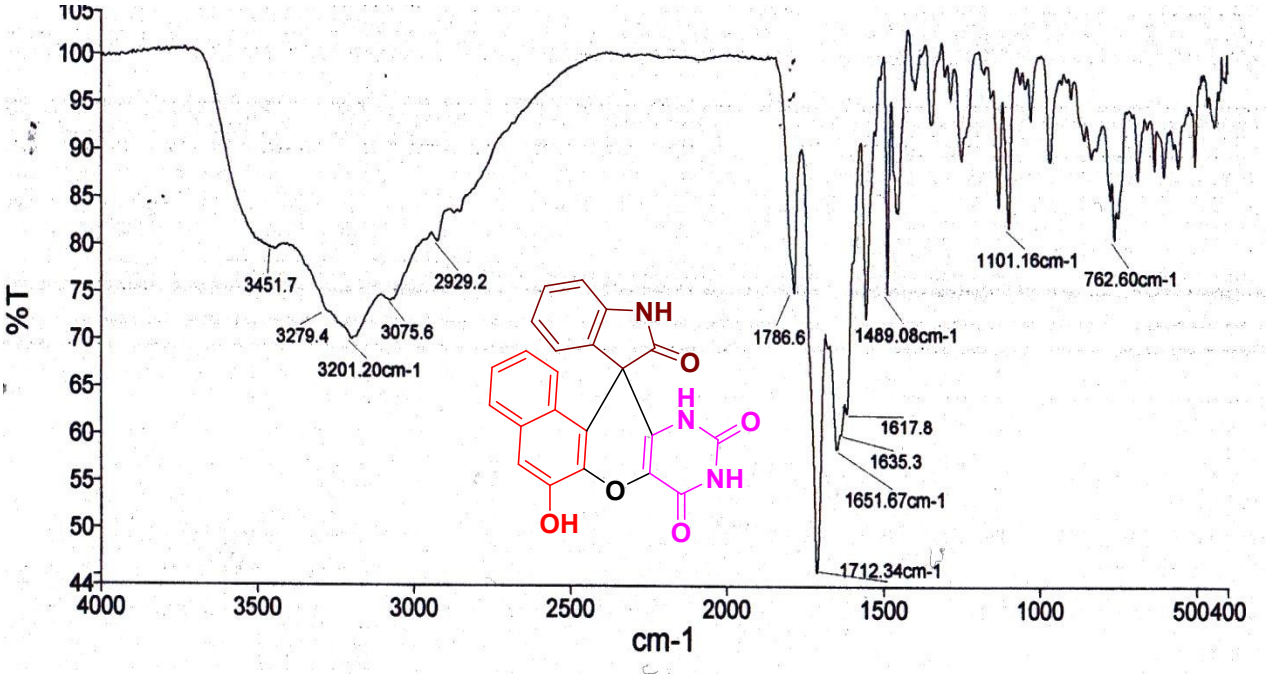

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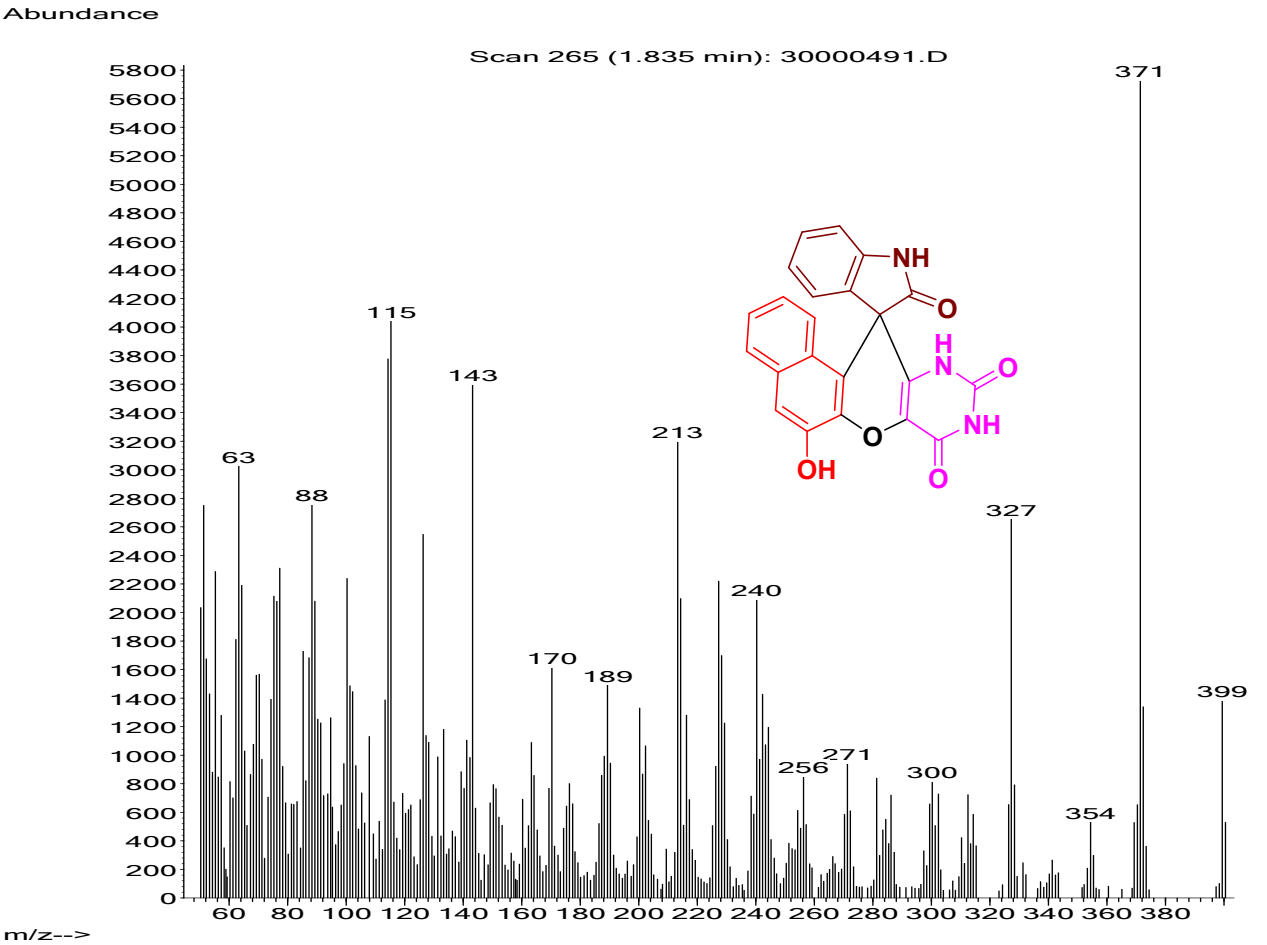

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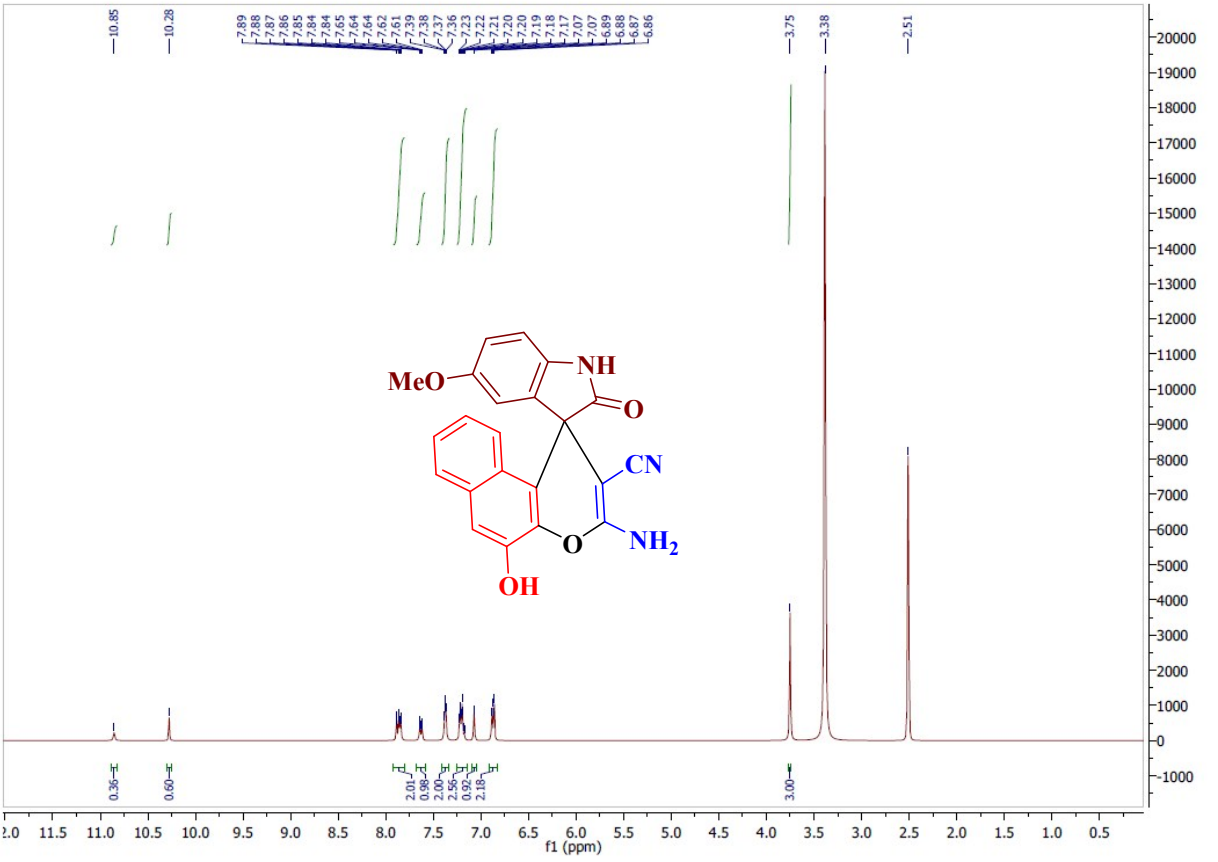

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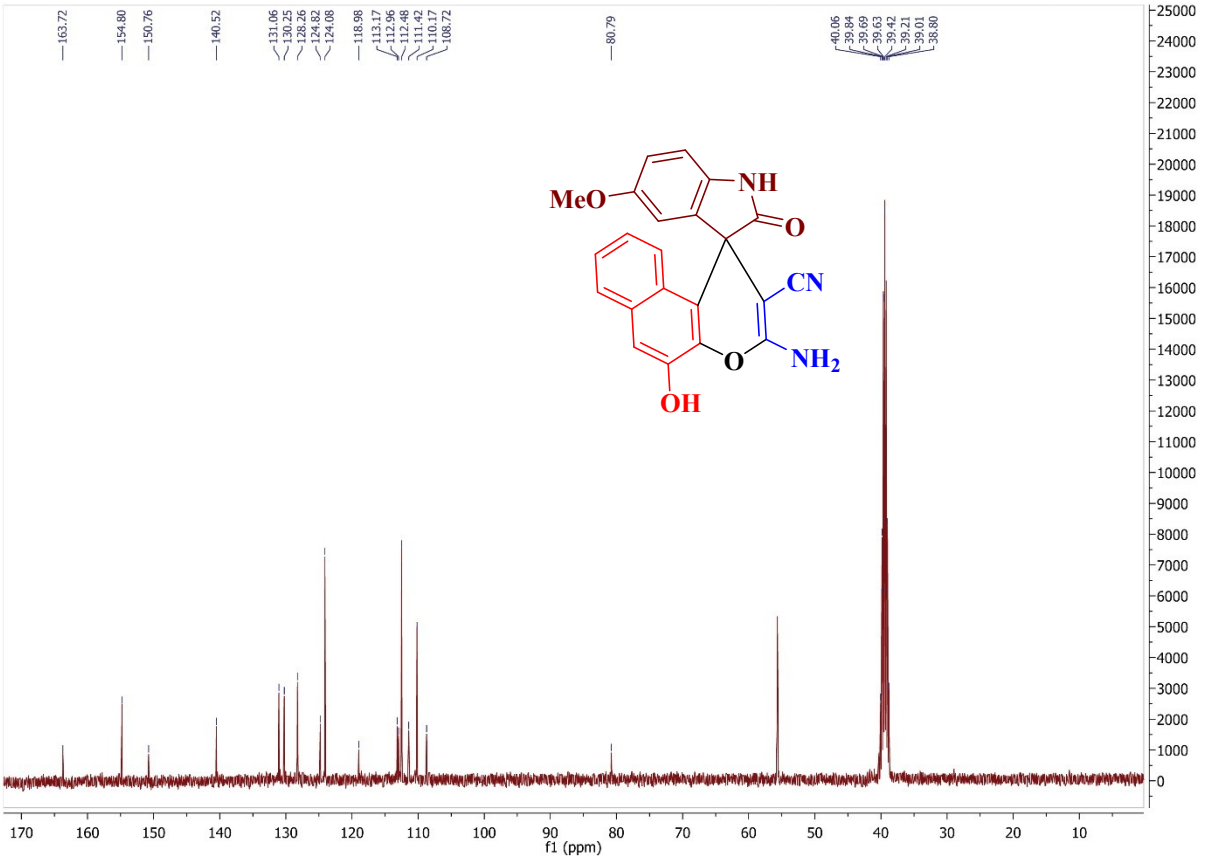

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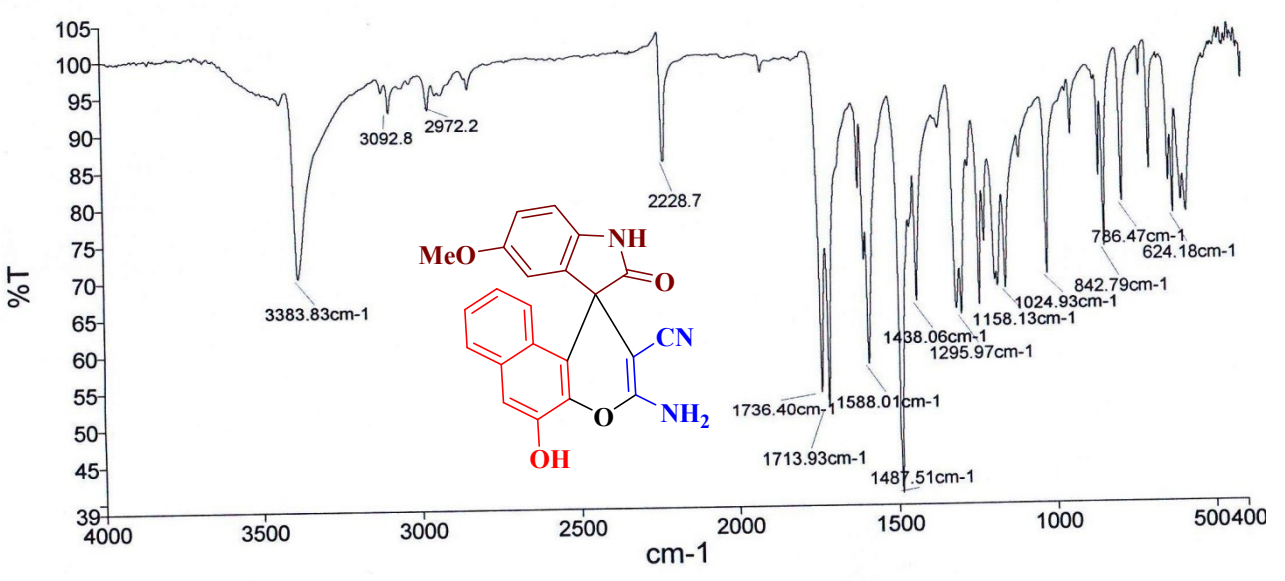

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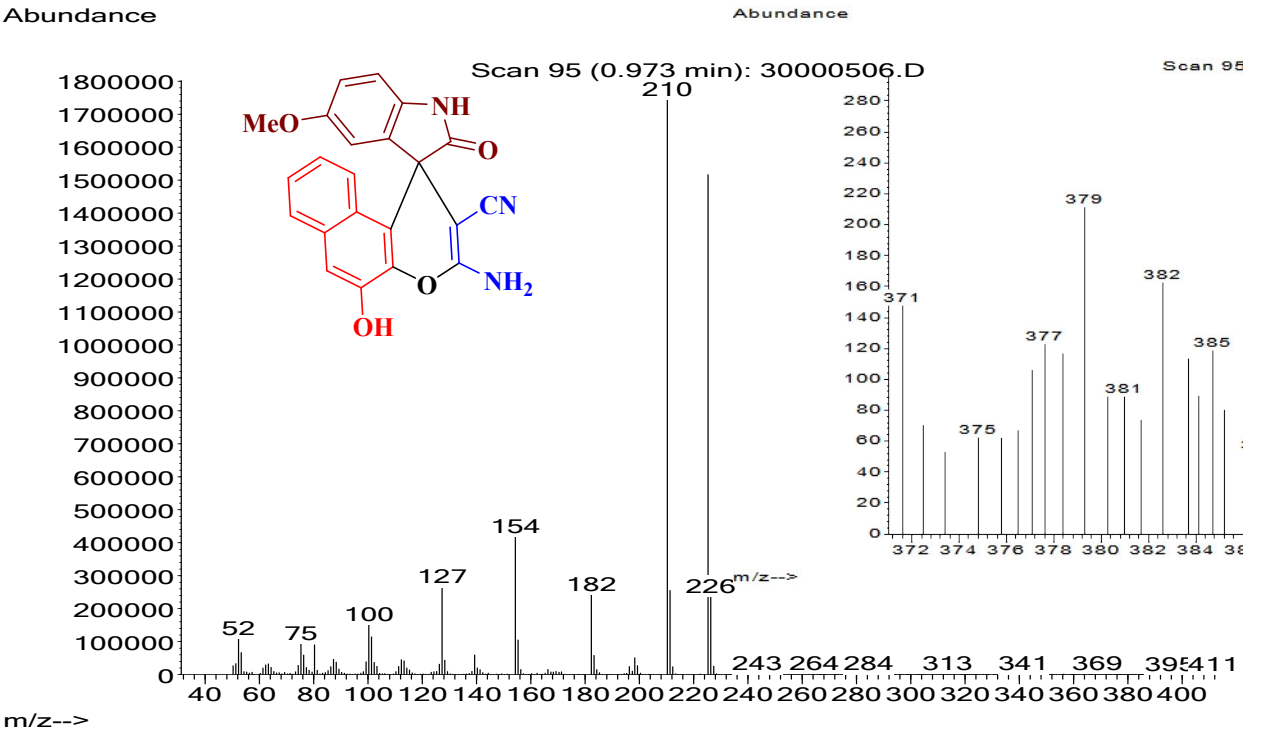

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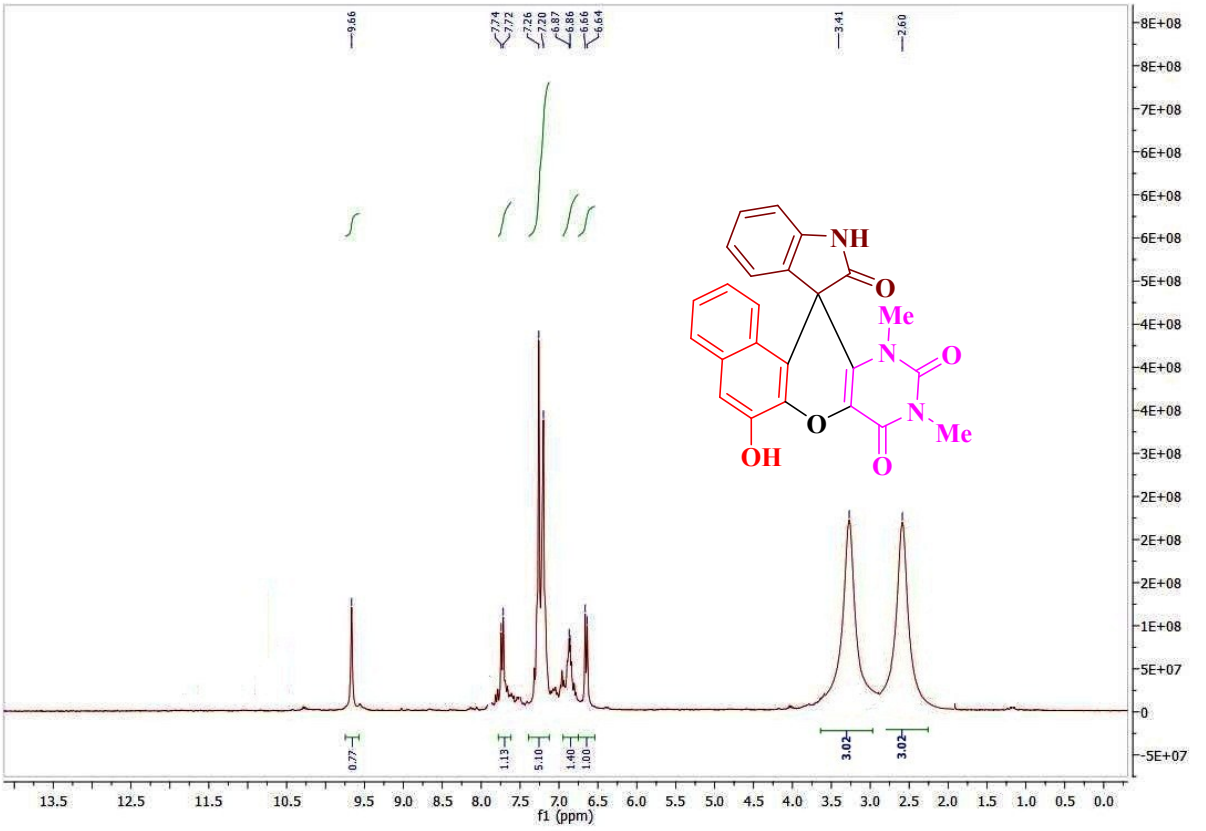

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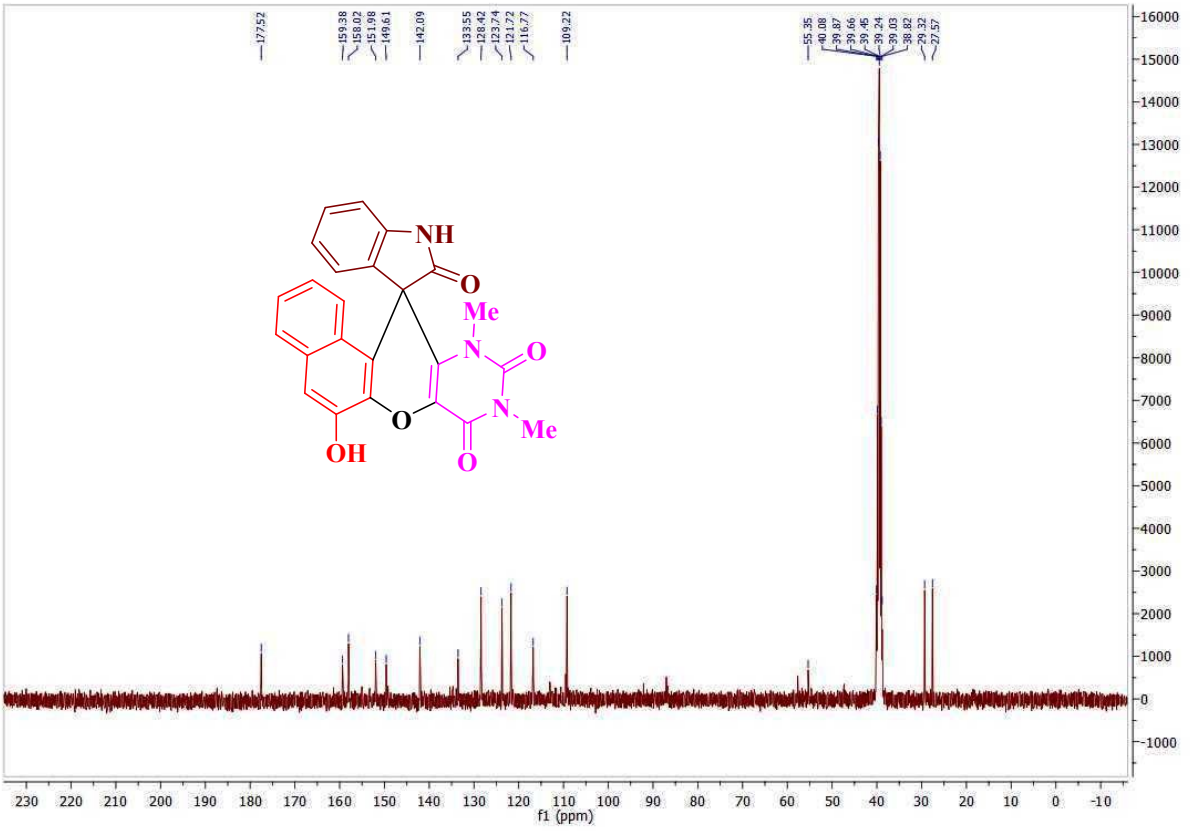

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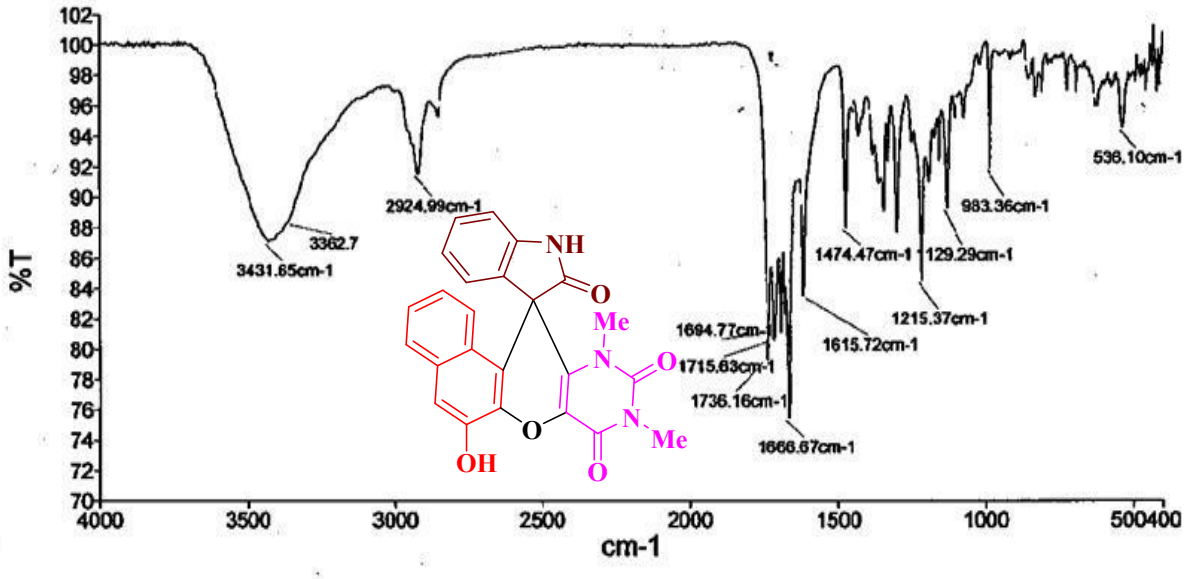

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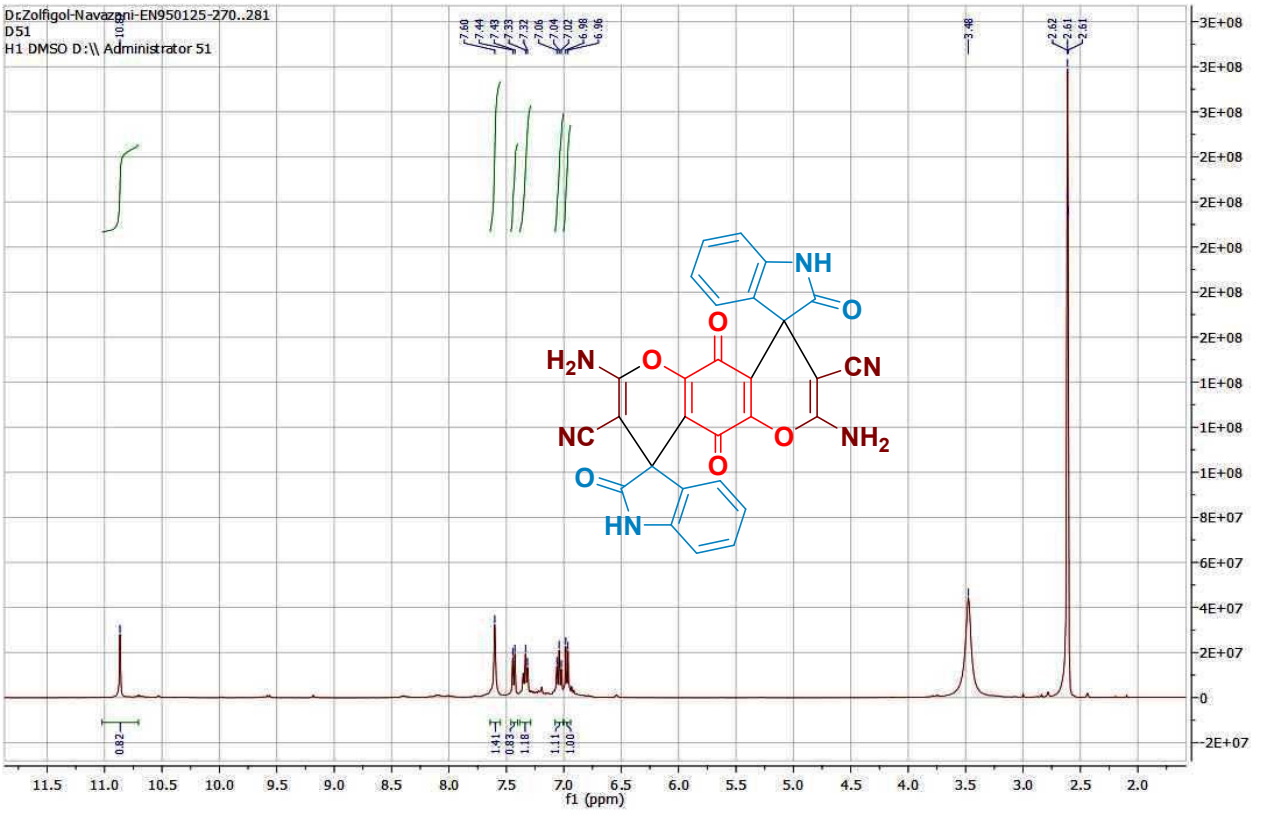

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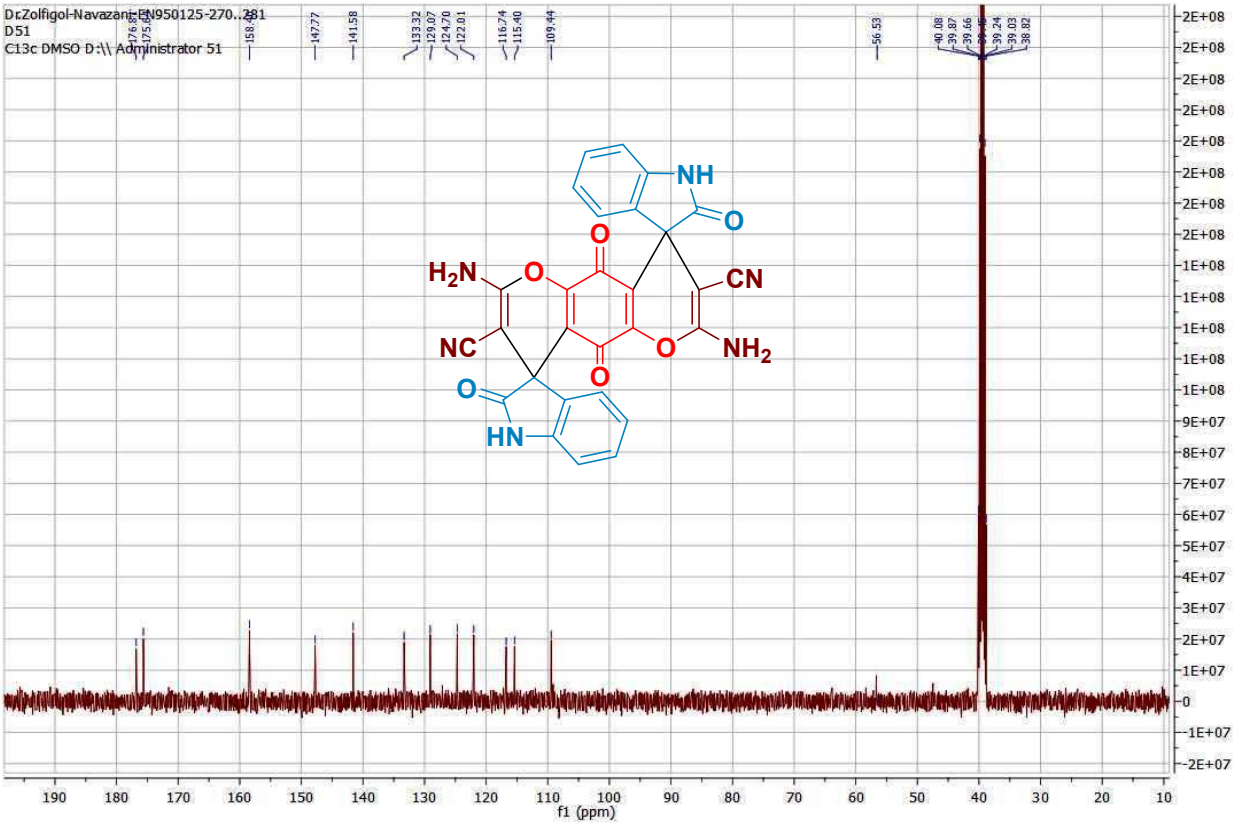

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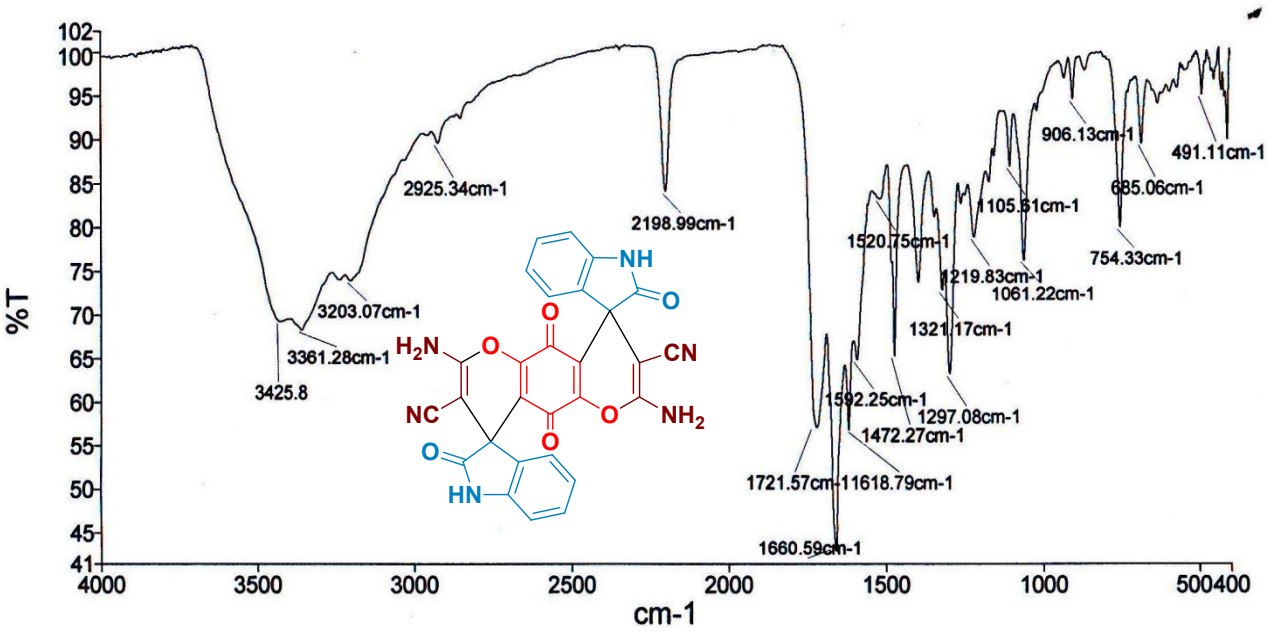

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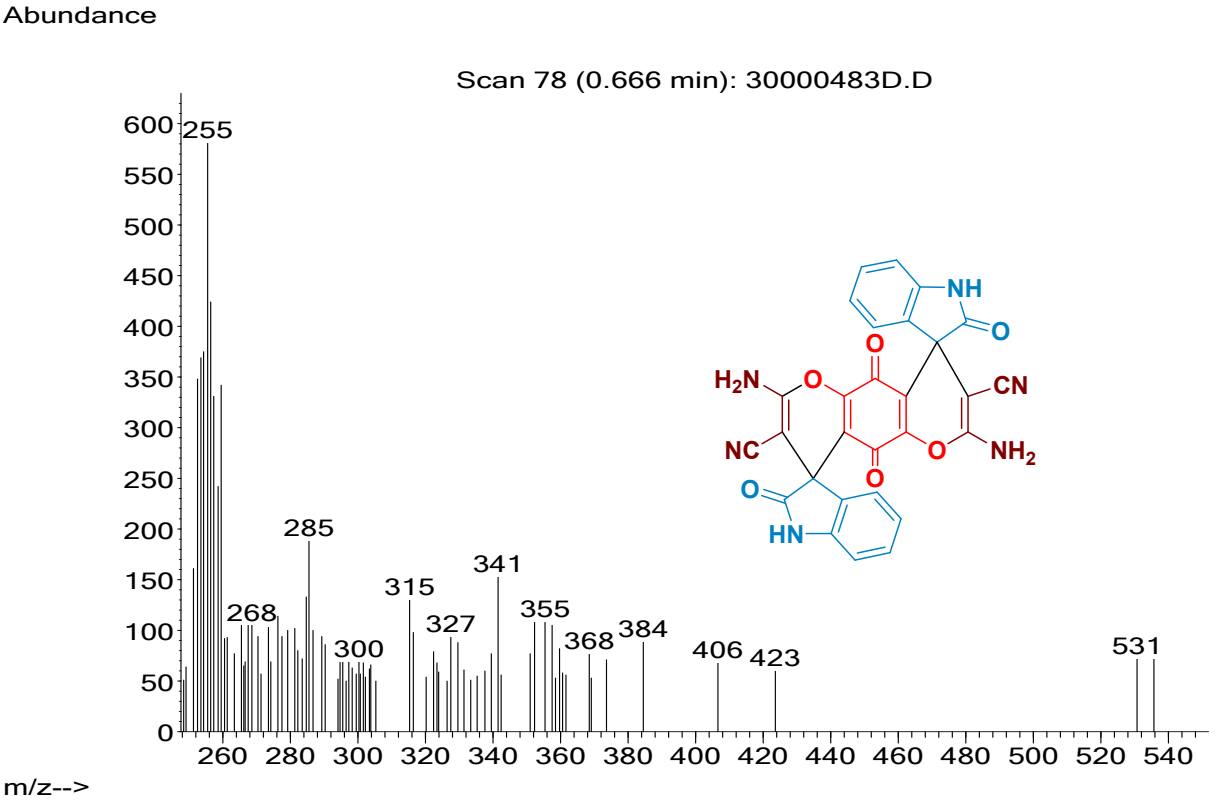

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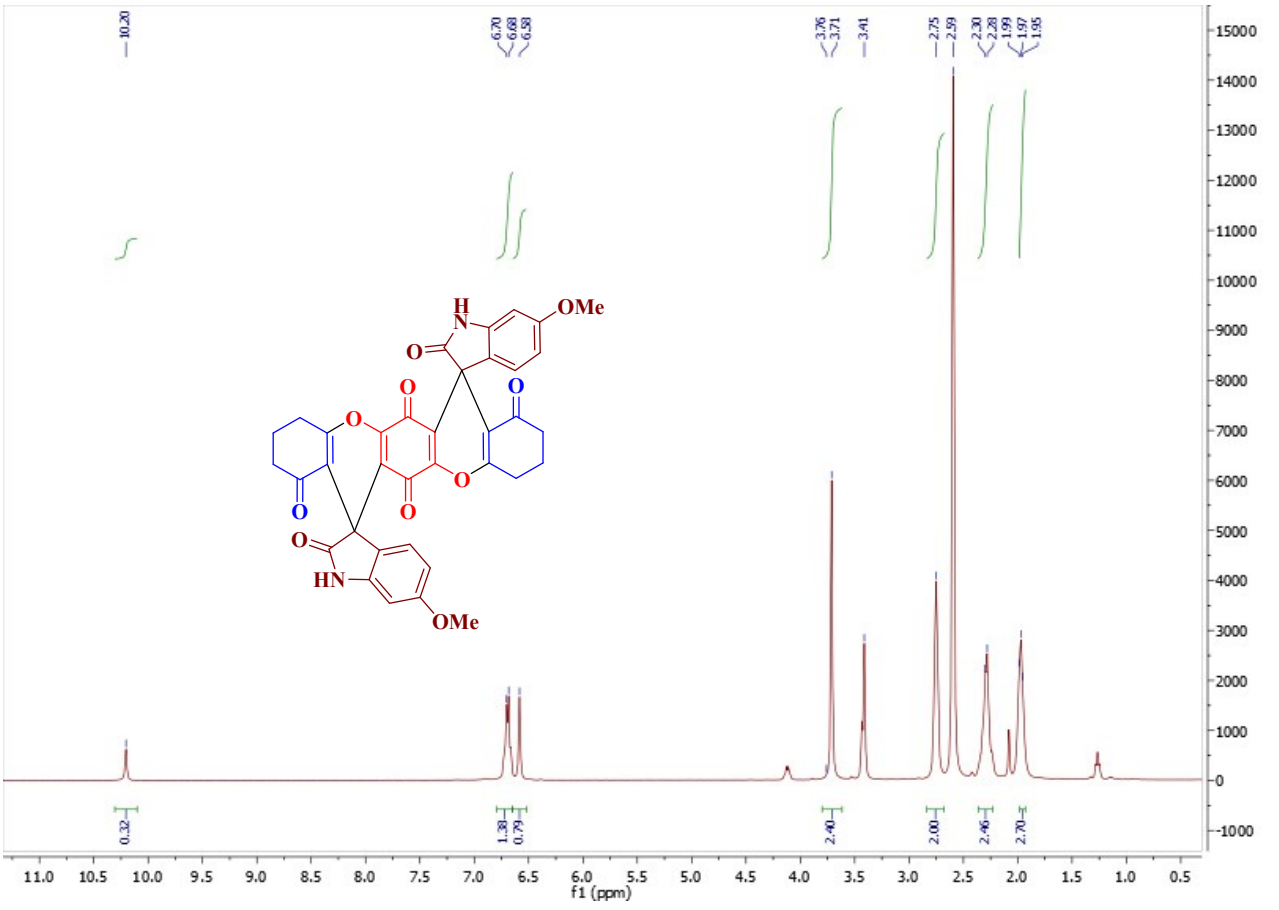

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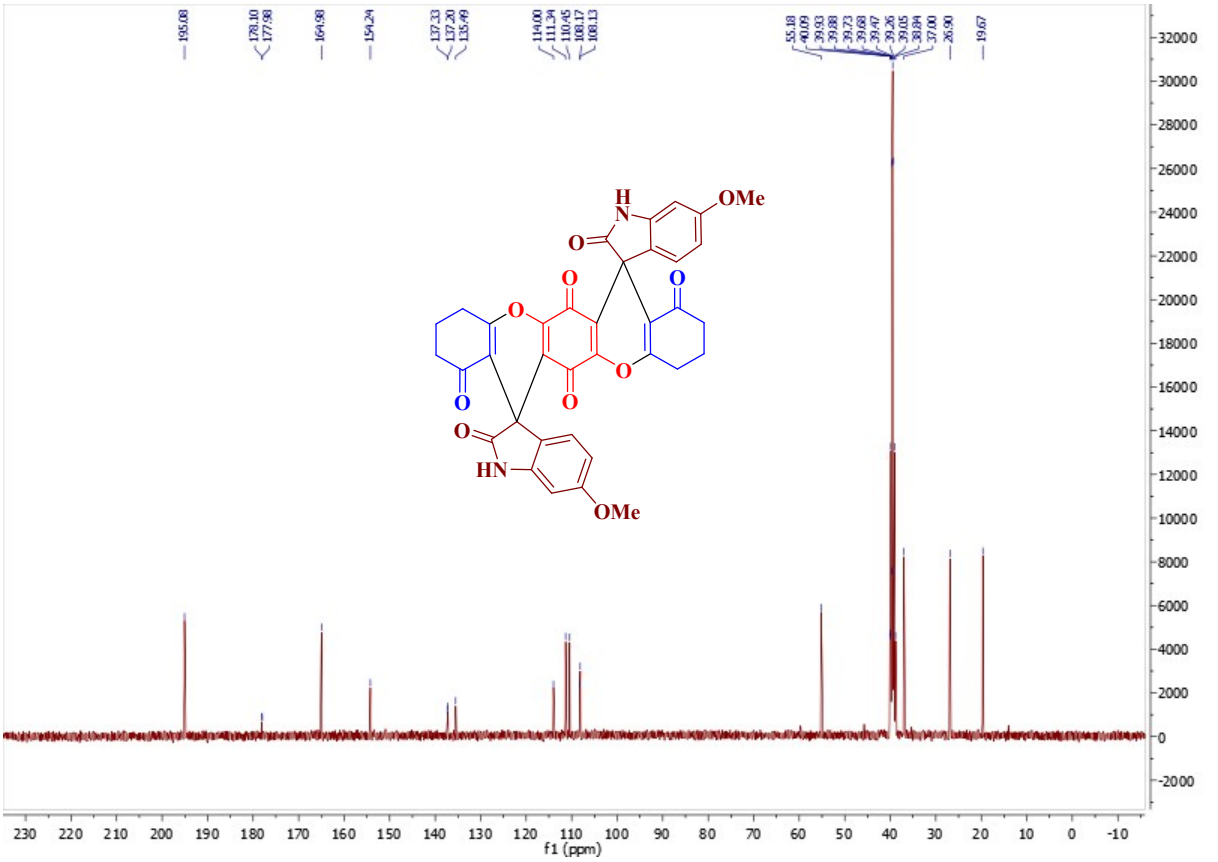
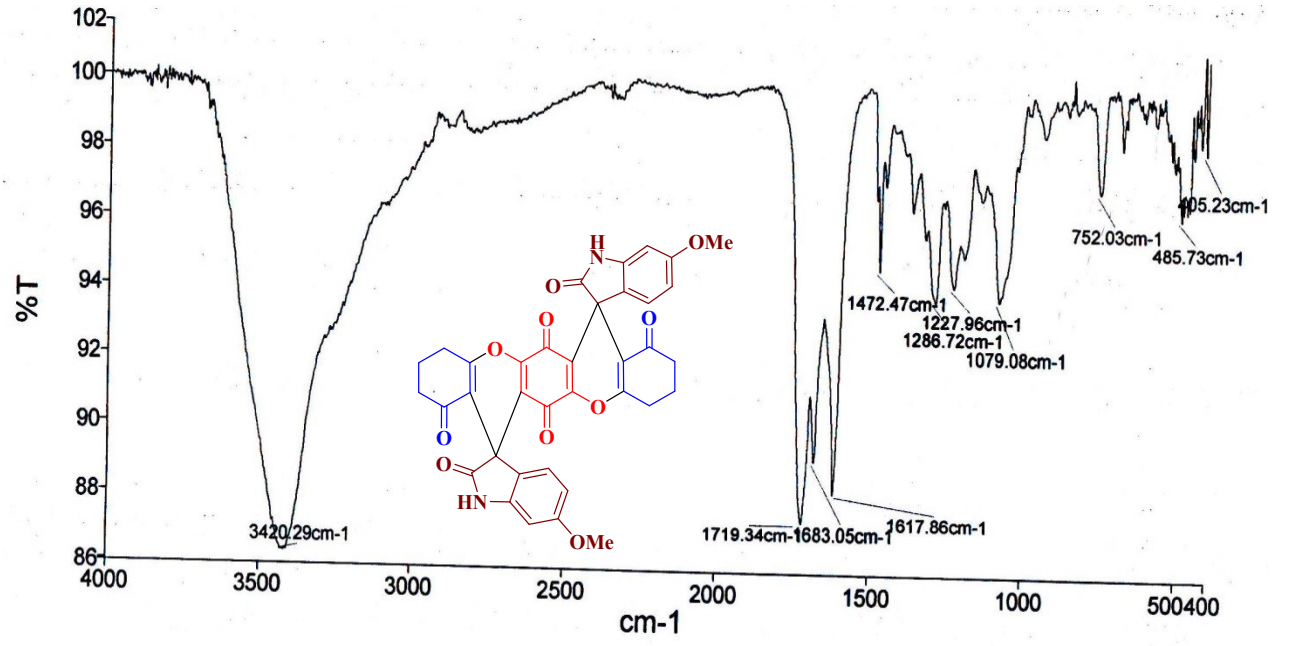
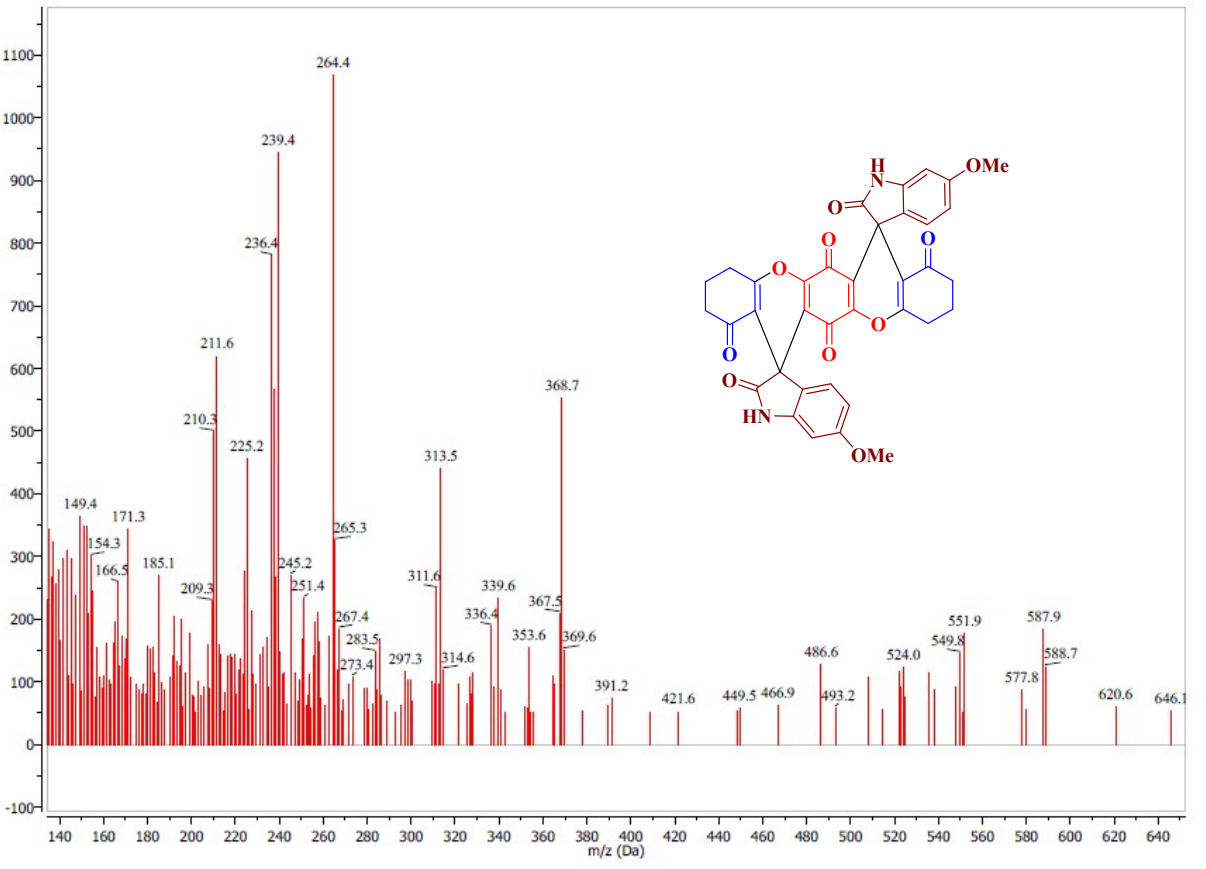


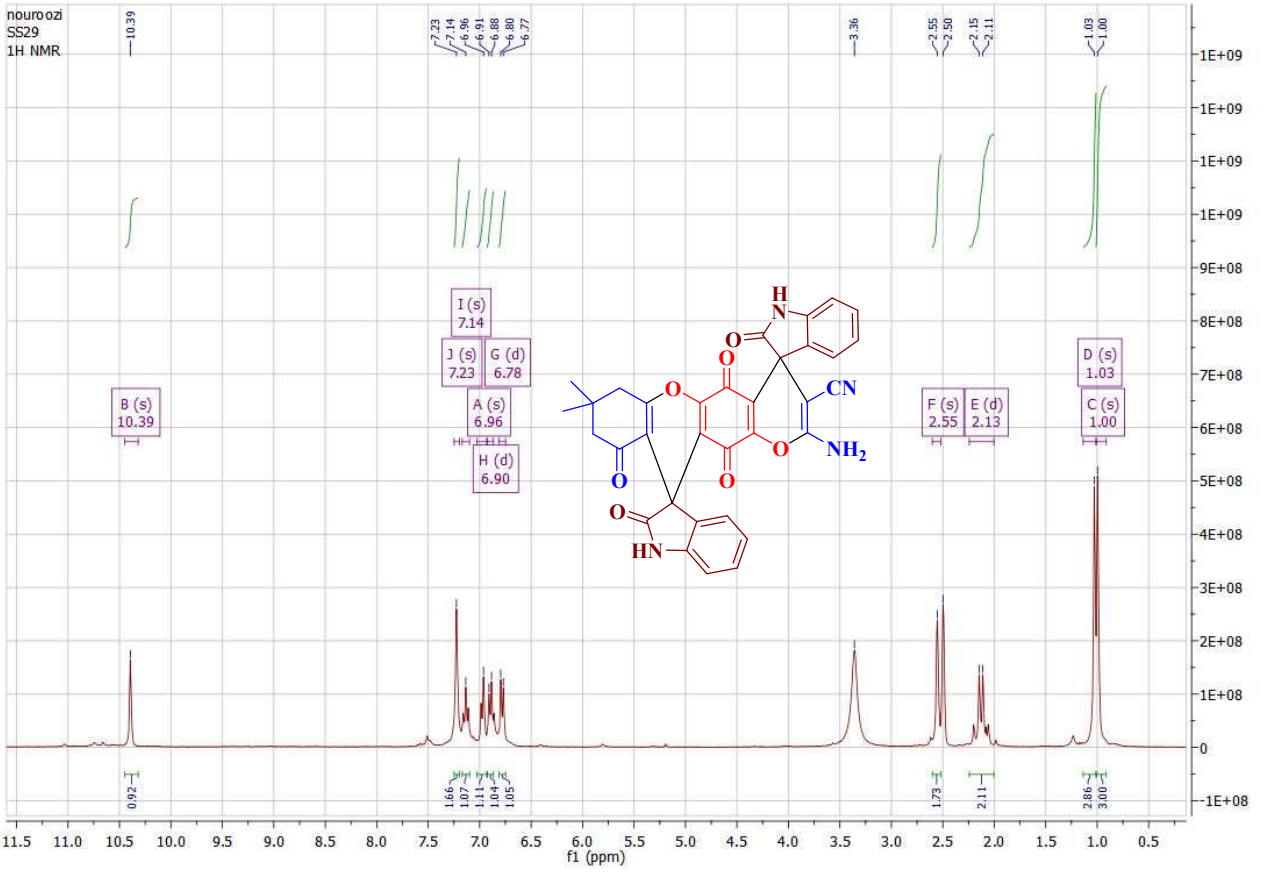
^{13}CNMR spectrum of (3R)-6,6''-dimethoxy-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (8S)



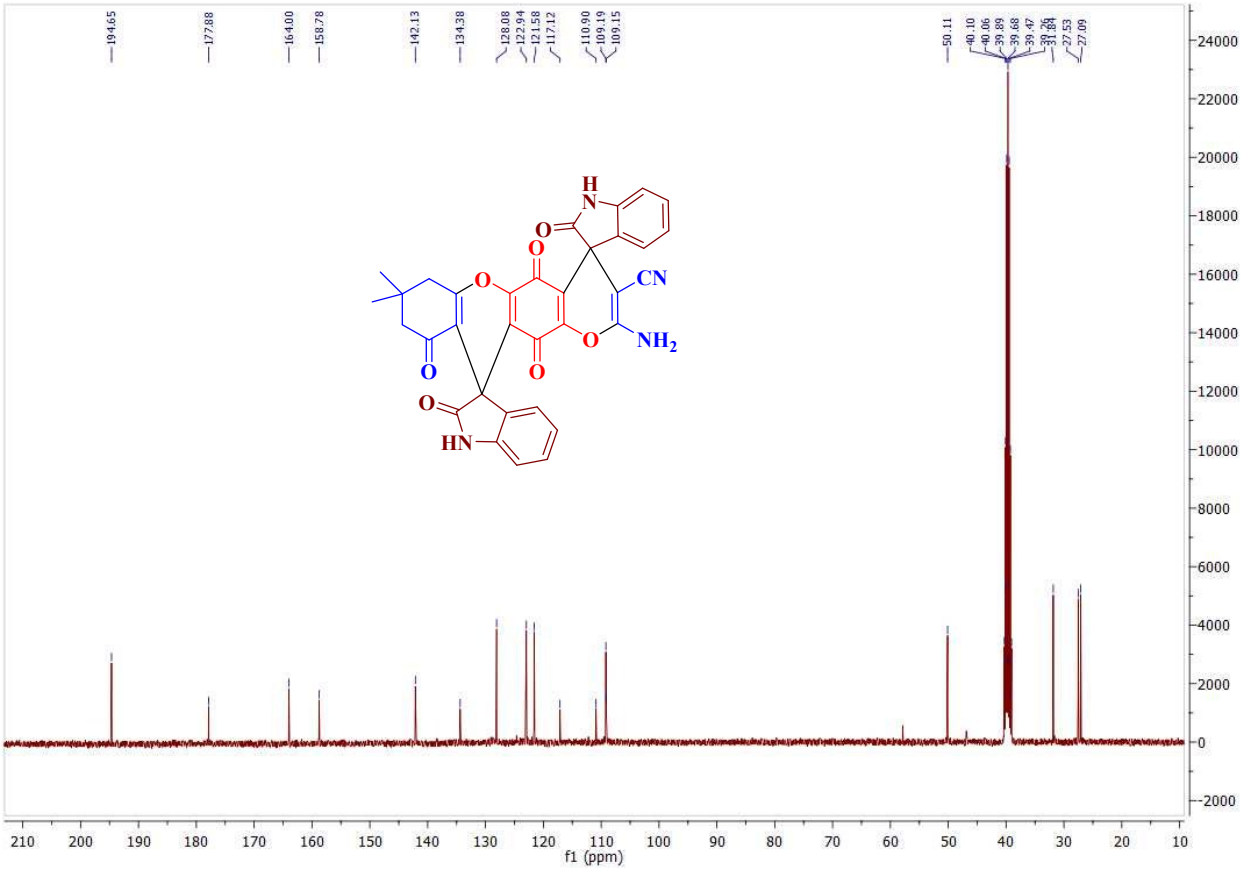
FT-IR spectrum of (3R)-6,6''-dimethoxy-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (8S)



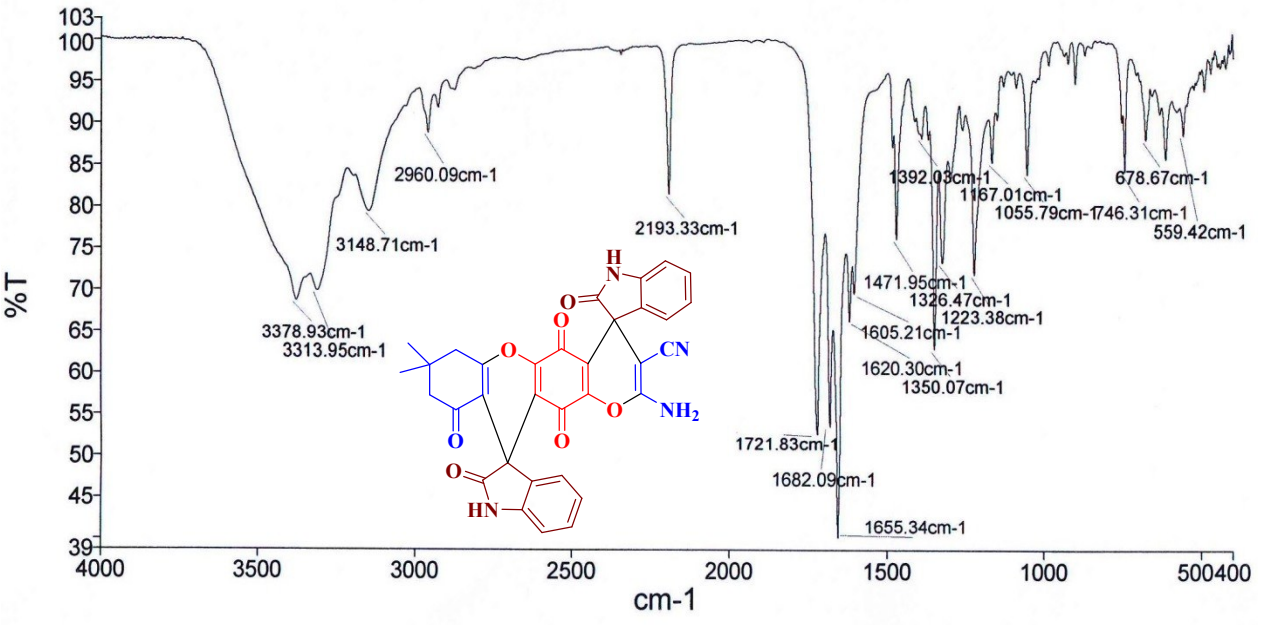
Mass spectrum of (3R)-6,6''-dimethoxy-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (8S)



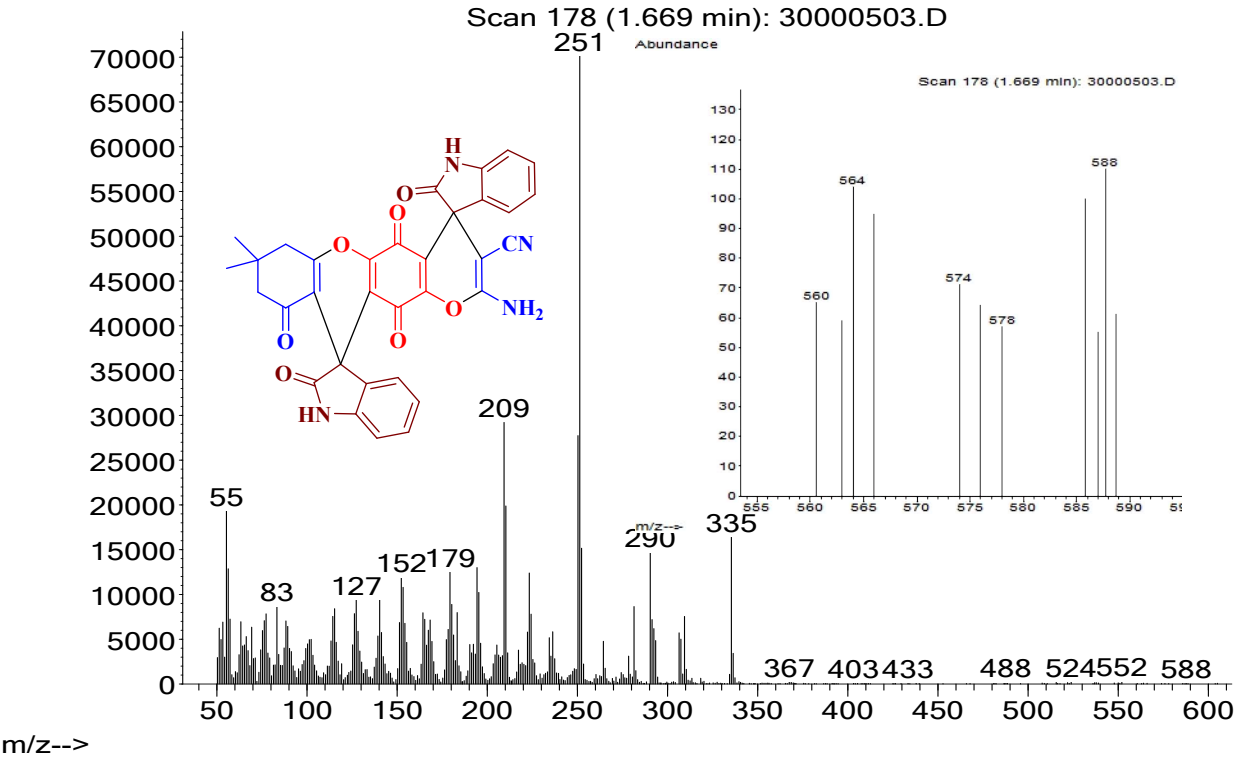
[1]HNMR spectrum of (3R)-2'-amino-8',8'-dimethyl-2,2'',5',10',12'-pentaoxo-5',7',8',9',10',12'-hexahydrodispiro[indoline-3,4'-pyrano[2,3-b]xanthene-11',3''-indoline]-3'-carbonitrile (9S)



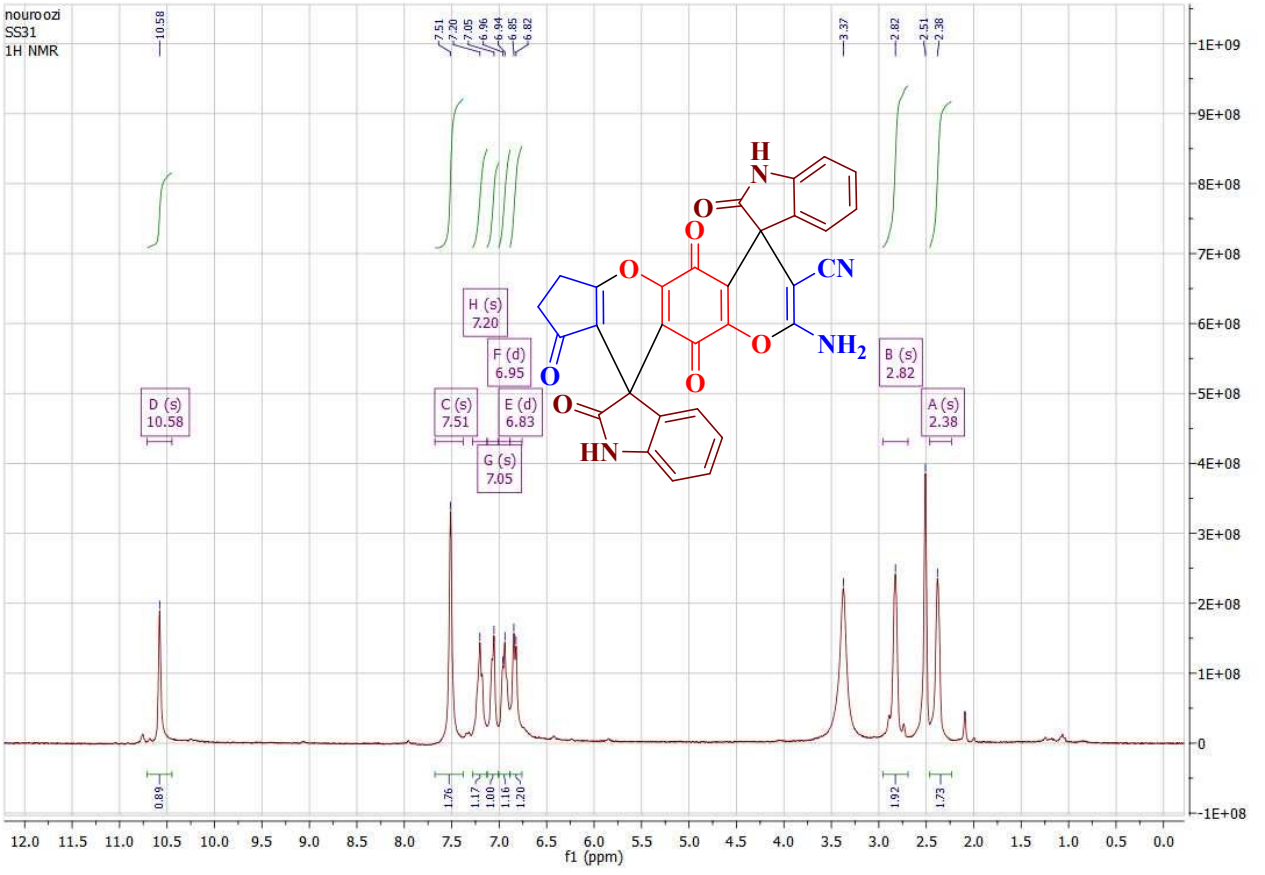
^{13}CNMR spectrum of (3R)-2'-amino-8',8'-dimethyl-2,2'',5',10',12'-pentaoxo-5',7',8',9',10',12'-hexahydrodispiro[indoline-3,4'-pyrano[2,3-b]xanthene-11',3''-indoline]-3'-carbonitrile (9S)



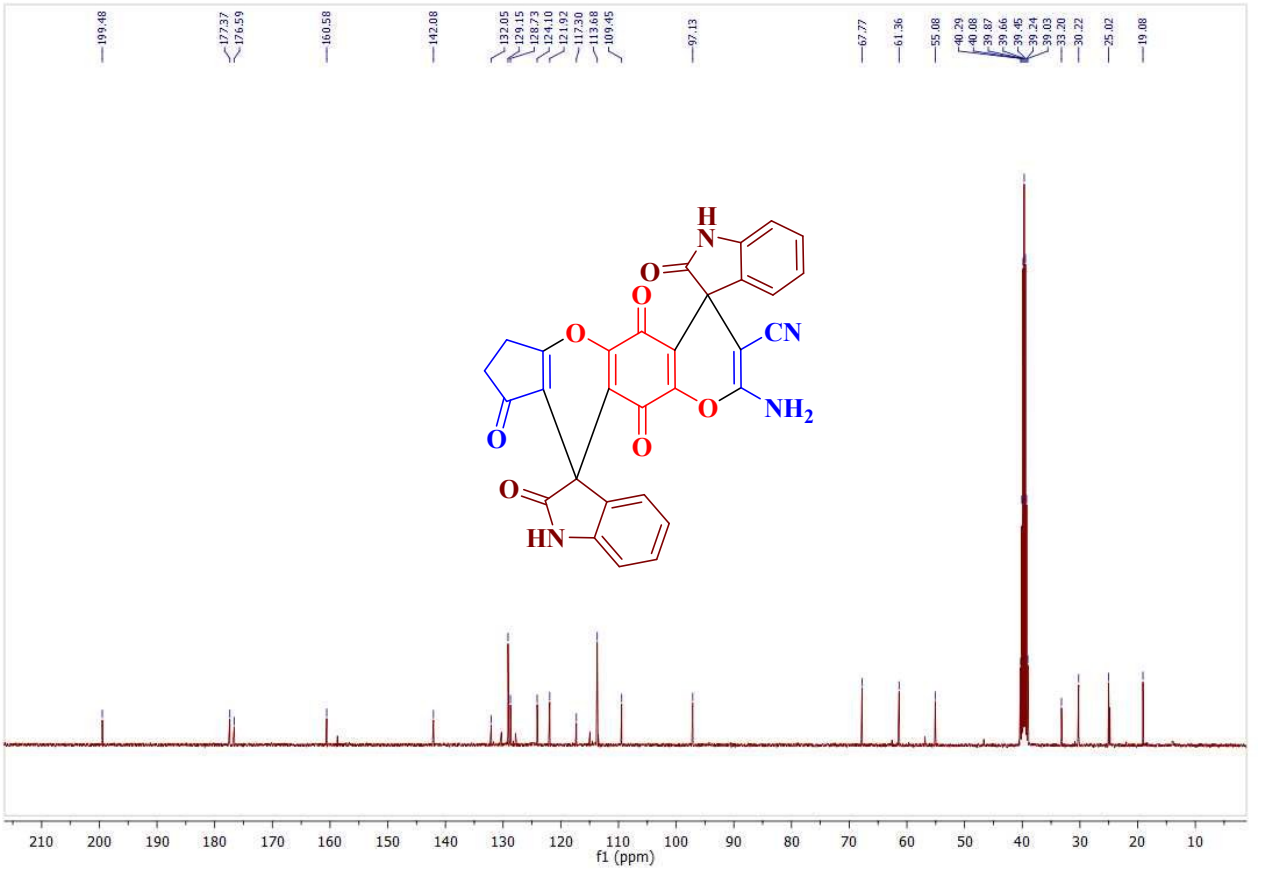
FT-IR spectrum of (3R)-2'-amino-8',8'-dimethyl-2,2'',5',10',12'-pentaoxo-5',7',8',9',10',12'-hexahydrodispiro[indoline-3,4'-pyrano[2,3-b]xanthene-11',3''-indoline]-3'-carbonitrile (9S)



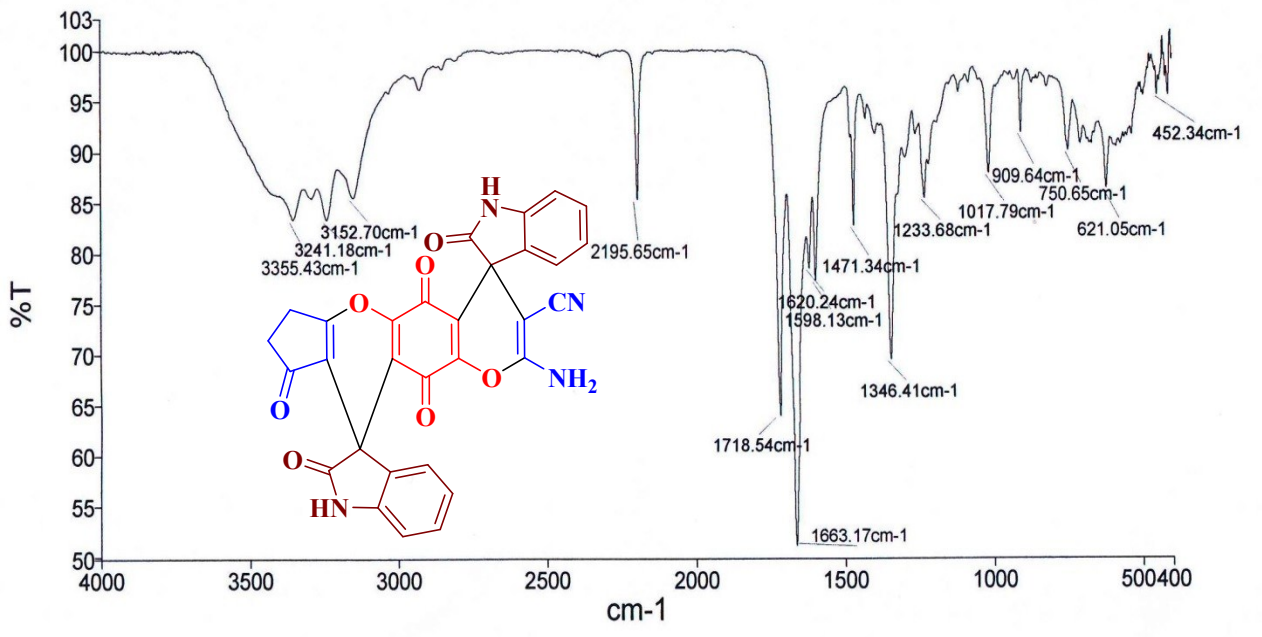
Mass spectrum of (3R)-2'-amino-8',8'-dimethyl-2,2'',5',10',12'-pentaoxo-5',7',8',9',10',12'-hexahydrodispiro[indoline-3,4'-pyrano[2,3-b]xanthene-11',3''-indoline]-3'-carbonitrile (9S)



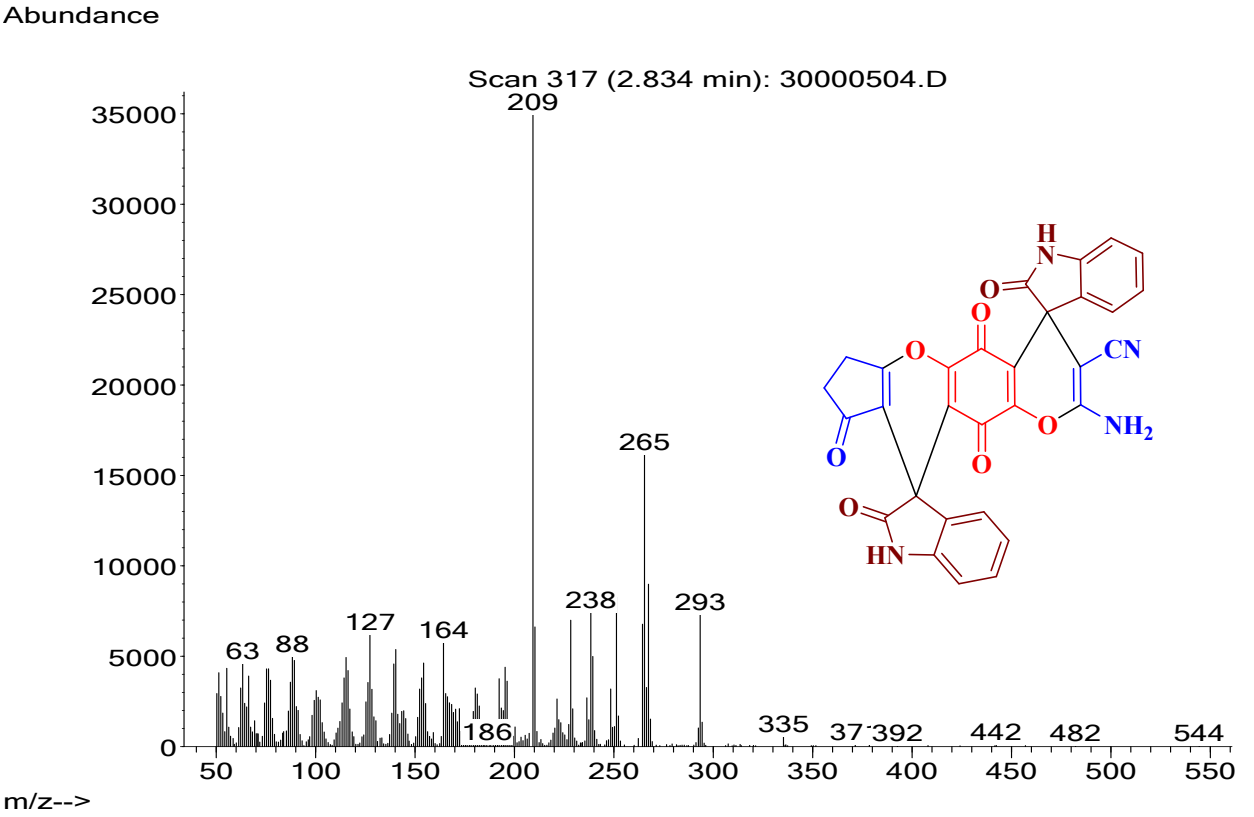
[1]HNMR spectrum of 2'-amino-2,2'',5',9',11'-pentaoxo-5',8',9',11'-tetrahydro-7'H-dispiro[indoline-3,4'-cyclopenta[b]pyrano[2,3-g]chromene-10',3''-indoline]-3'-carbonitrile (10S)



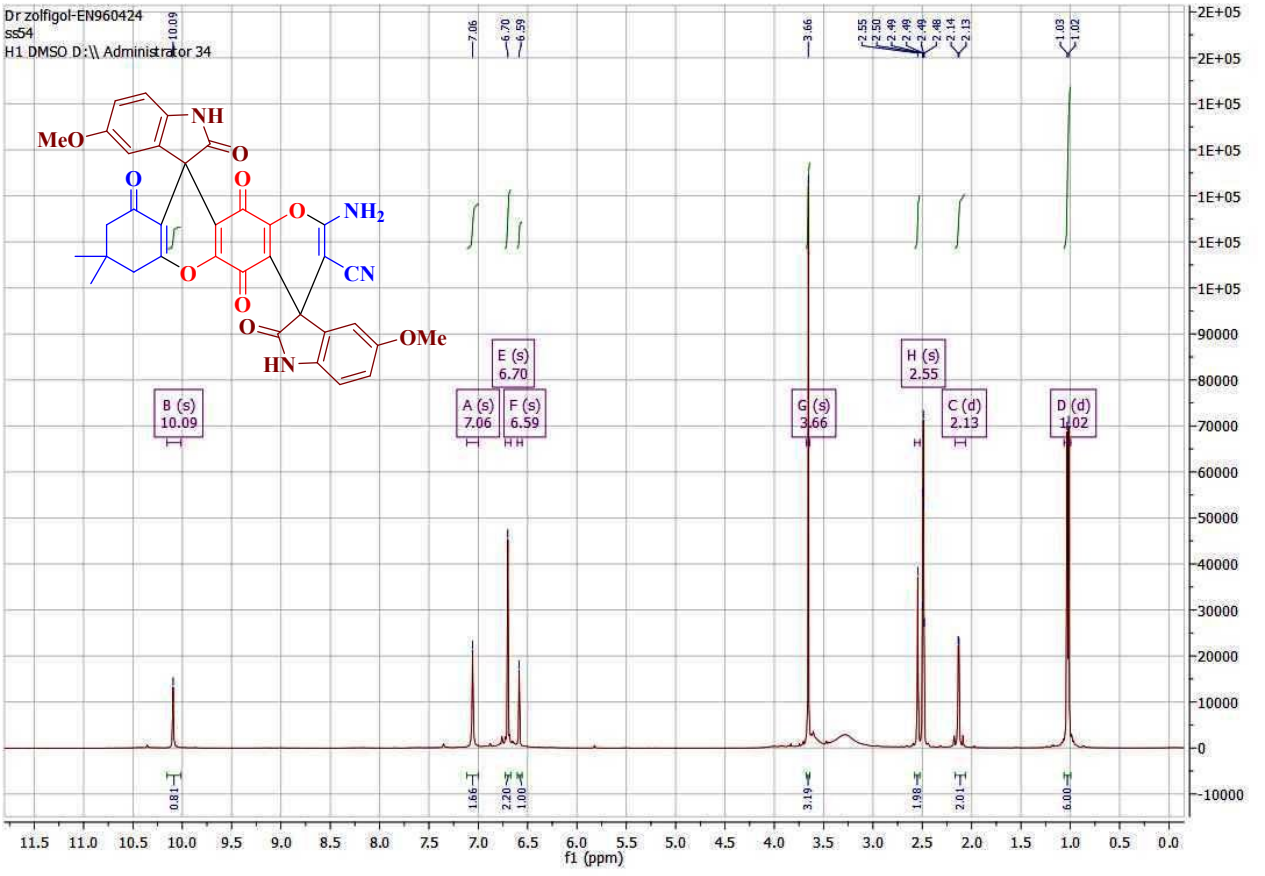
^{13}CNMR spectrum of 2'-amino-2,2'',5',9',11'-pentaoxo-5',8',9',11'-tetrahydro-7'H-dispiro[indoline-3,4'-cyclopenta[b]pyrano[2,3-g]chromene-10',3''-indoline]-3'-carbonitrile (10S)



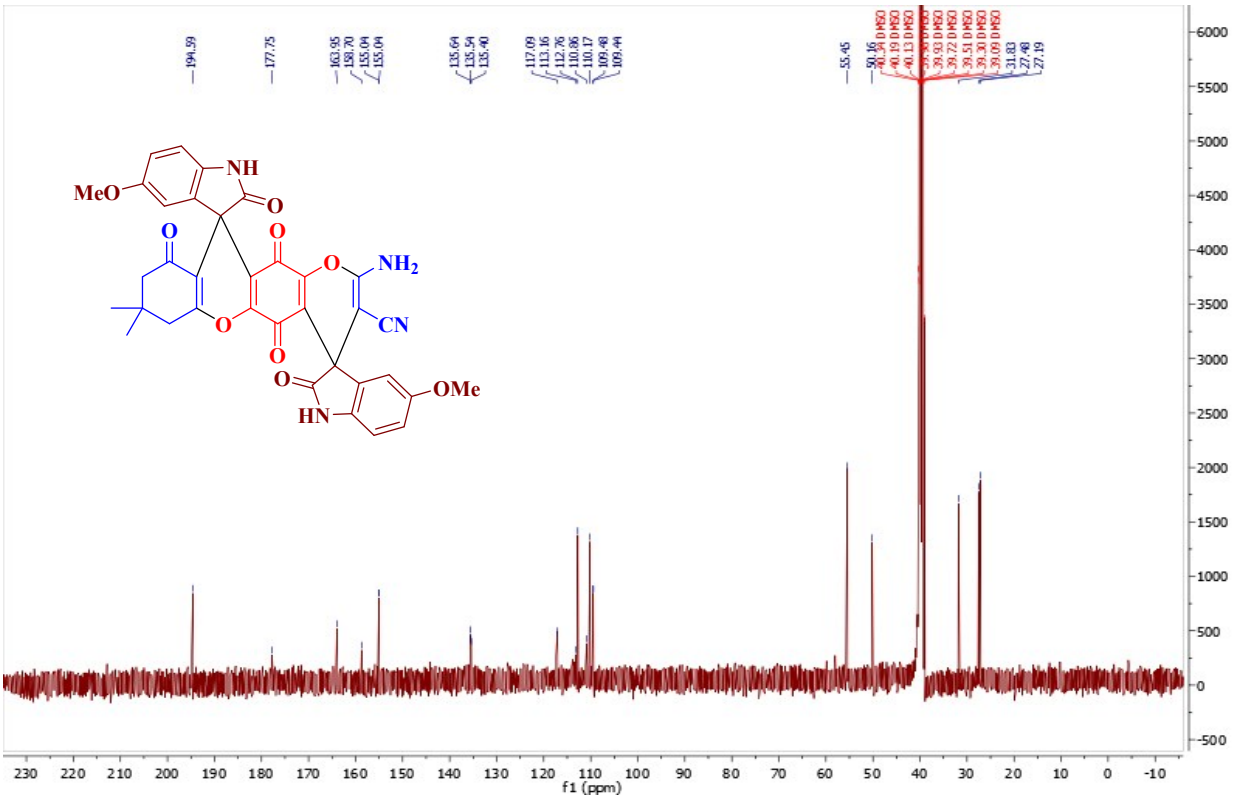
FT-IR spectrum of 2'-amino-2,2'',5',9',11'-pentaoxo-5',8',9',11'-tetrahydro-7'H-dispiro[indoline-3,4'-cyclopenta[b]pyrano[2,3-g]chromene-10',3''-indoline]-3'-carbonitrile (10S)



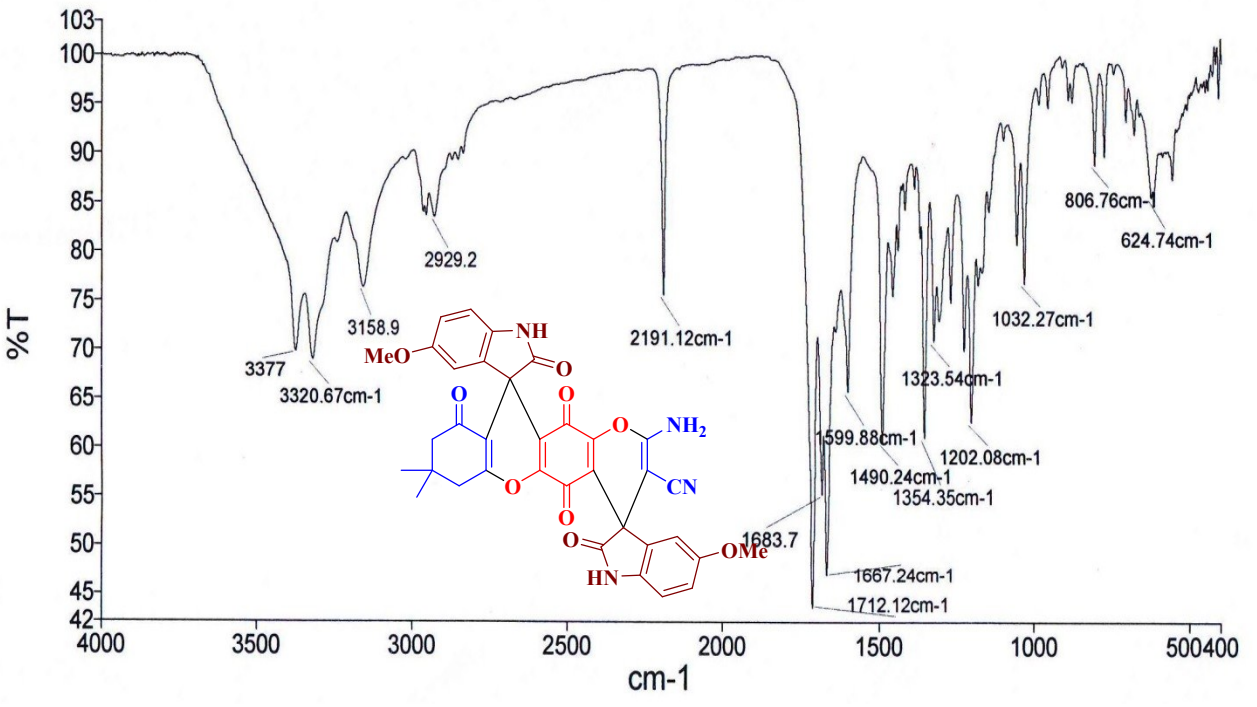
Mass spectrum of 2'-amino-2,2'',5',9',11'-pentaoxo-5',8',9',11'-tetrahydro-7'H-dispiro[indoline-3,4'-cyclopenta[b]pyrano[2,3-g]chromene-10',3''-indoline]-3'-carbonitrile (10S)



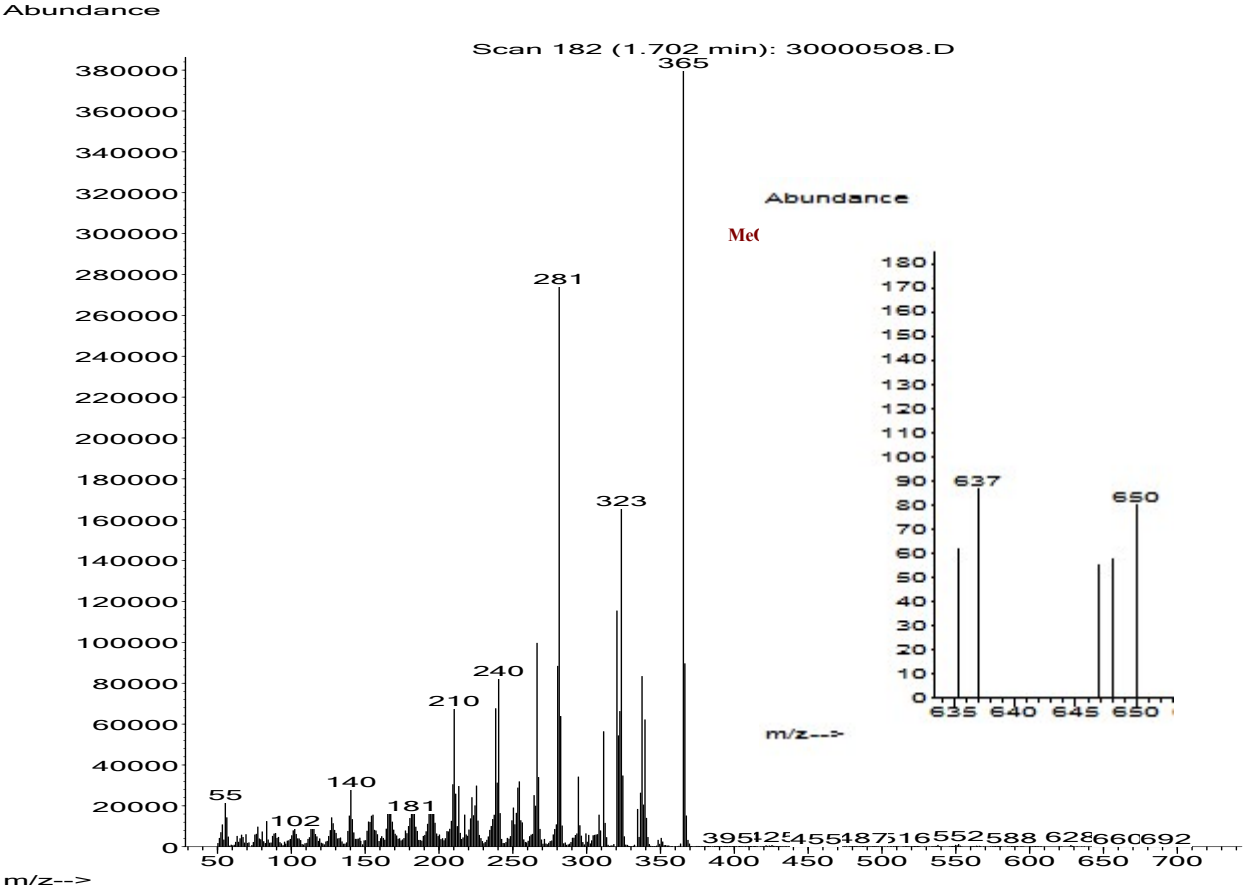
[1]HNMR spectrum of 5,5''-dimethoxy-3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone *(11S)*



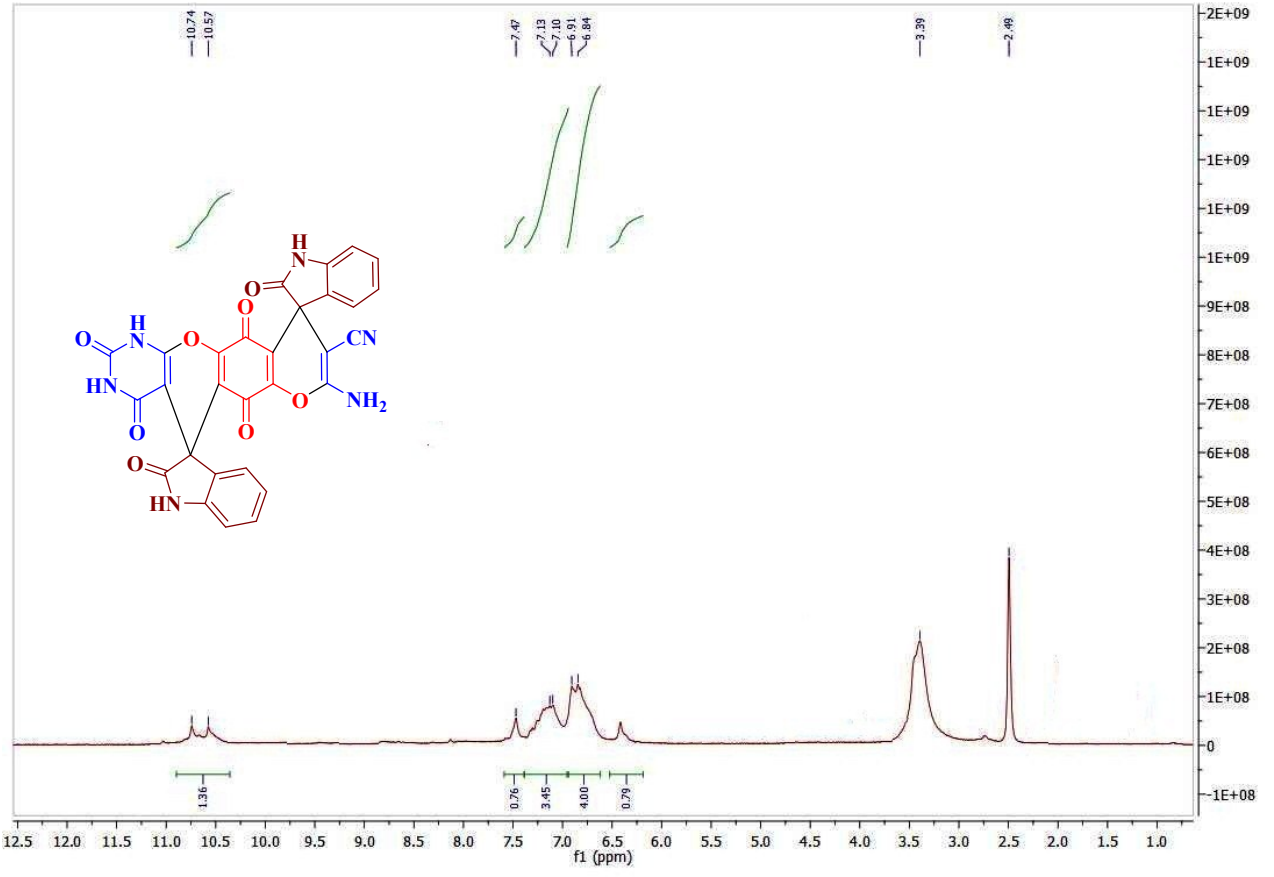
[13]CNMR spectrum of 5,5''-dimethoxy-3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone *(11S)*



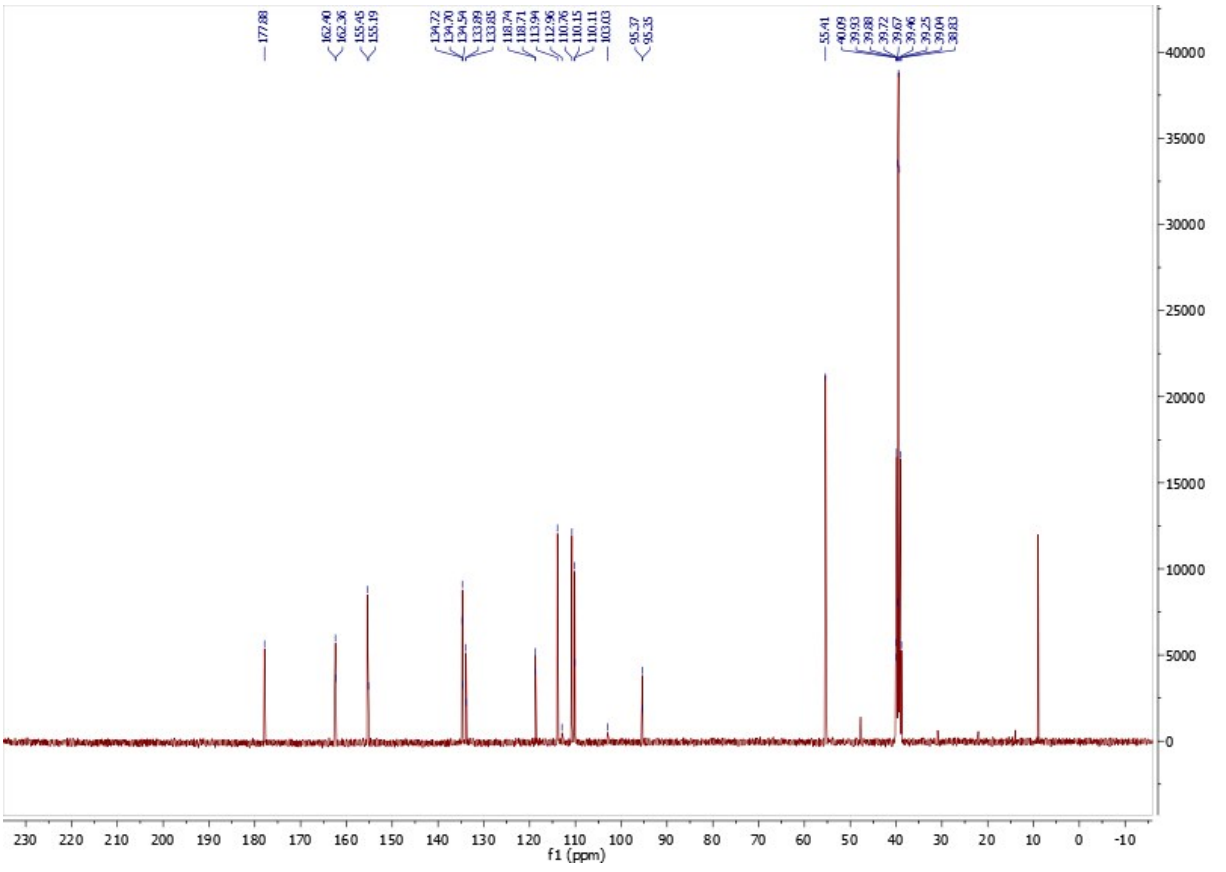
FT-IR spectrum of 5,5''-dimethoxy-3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone *(11S)*



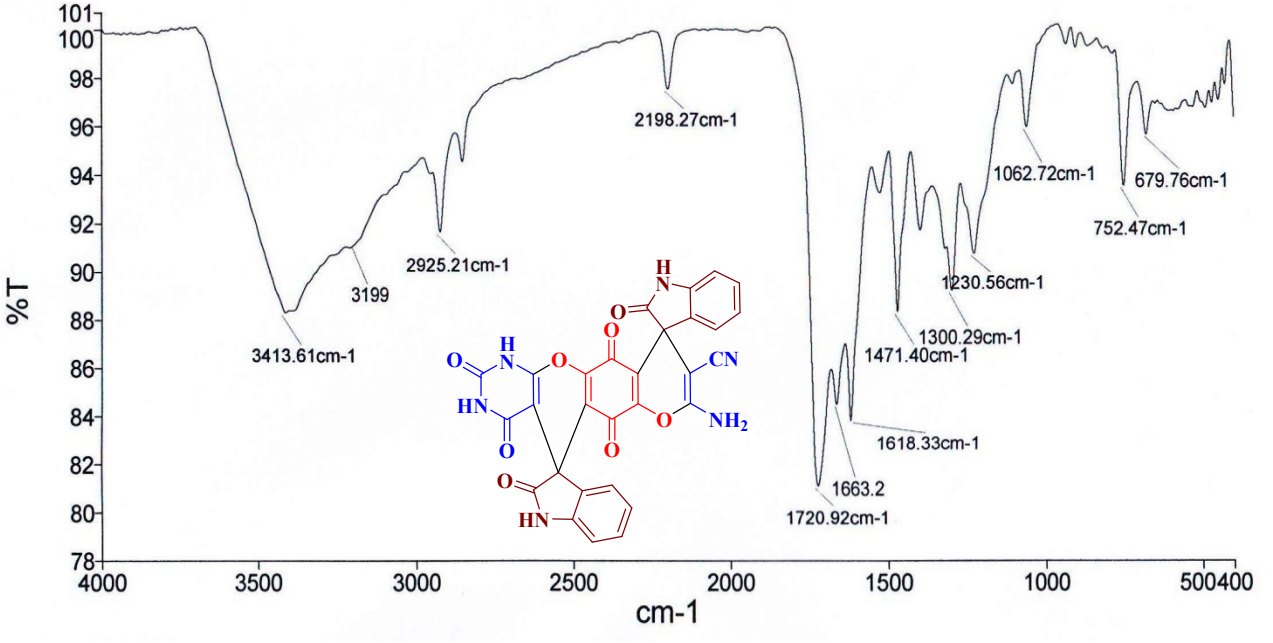
Mass spectrum of 5,5''-dimethoxy-3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (11S)



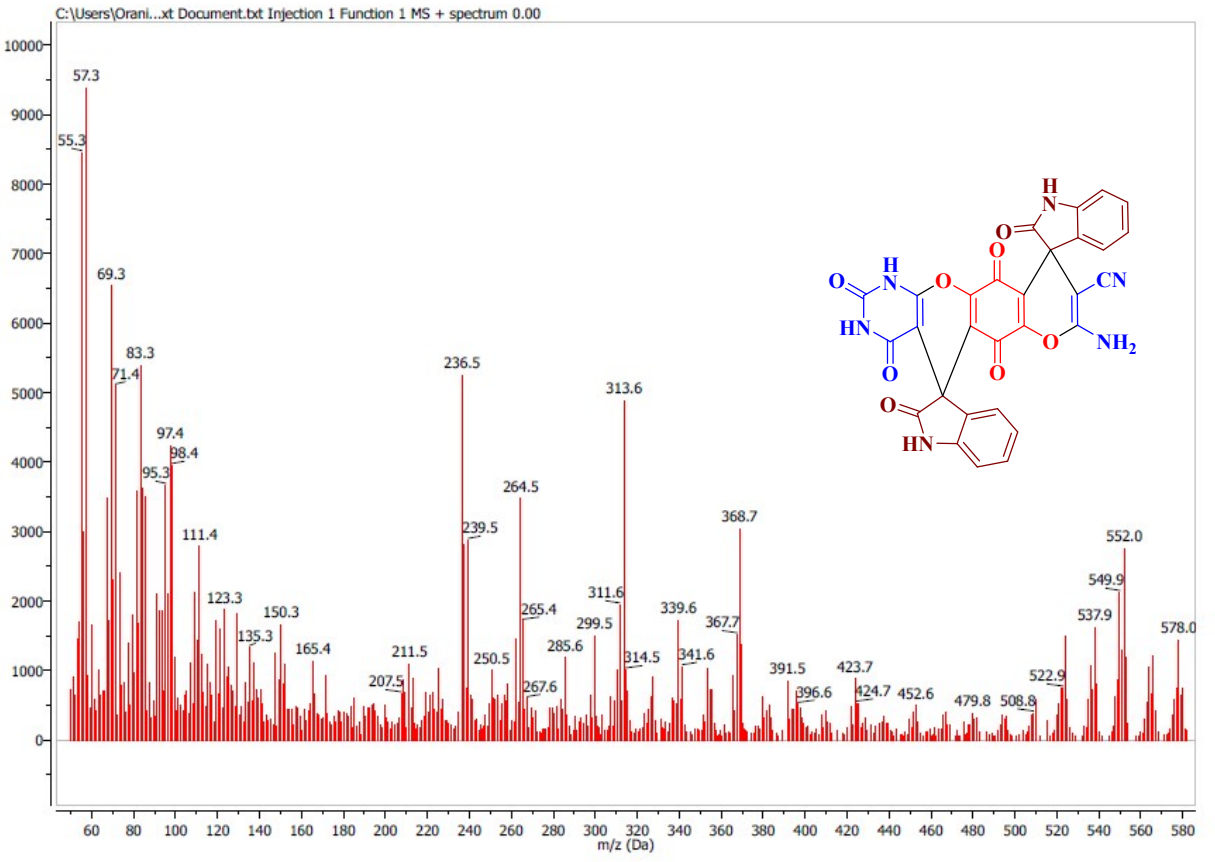
[1]HNMR spectrum of (10'R)-8'-amino-2,2',2'',4',6',11'-hexaoxo-1',2',3',4',6',11'-hexahydrodispiro[indoline-3,5'-pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-10',3''-indoline]-9'-carbonitrile (12S)



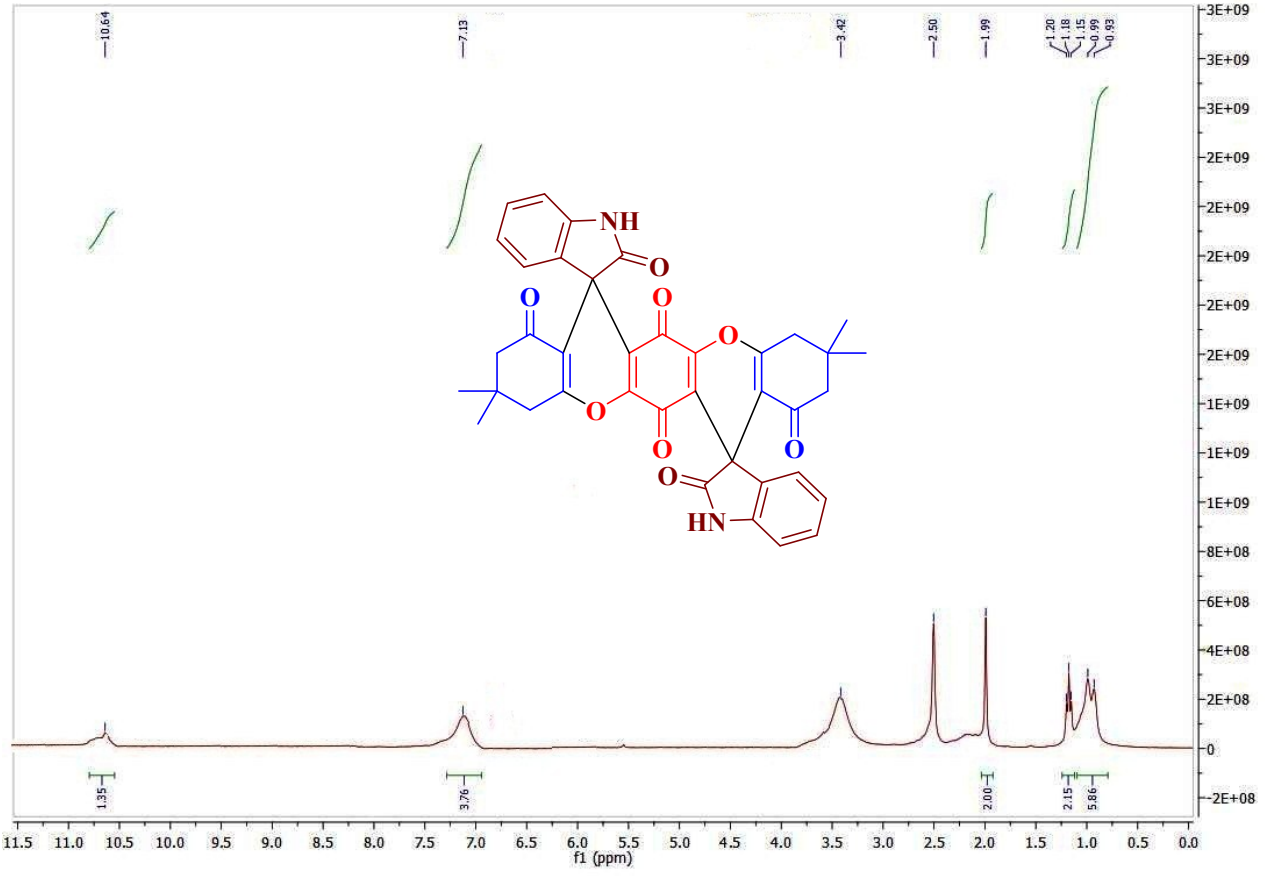
^{13}CNMR spectrum of (10'R)-8'-amino-2,2',2'',4',6',11'-hexaoxo-1',2',3',4',6',11'-hexahydrodispiro[indoline-3,5'-pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-10',3''-indoline]-9'-carbonitrile (12S)



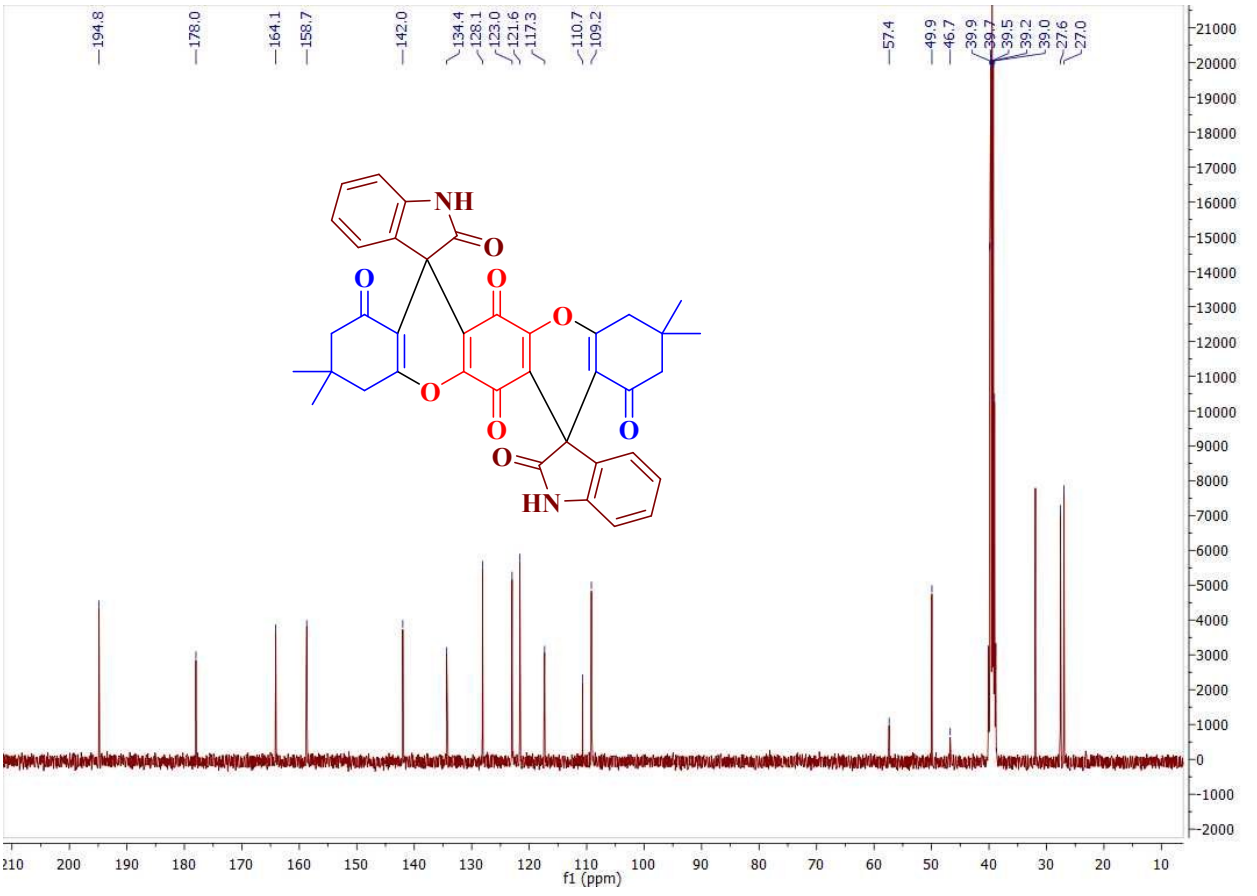
FT-IR spectrum of (10'R)-8'-amino-2,2',2'',4',6',11'-hexaoxo-1',2',3',4',6',11'-hexahydrodispiro[indoline-3,5'-pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-10',3''-indoline]-9'-carbonitrile (12S)



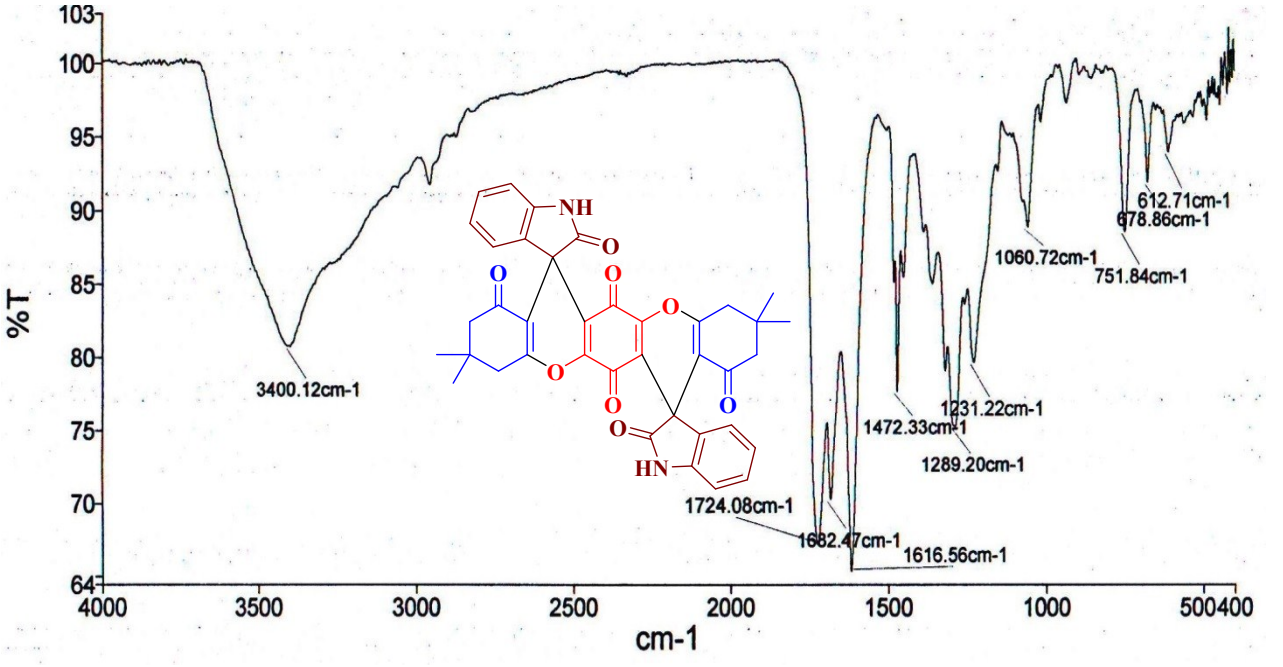
Mass spectrum of (10'R)-8'-amino-2,2',2'',4',6',11'-hexaoxo-1',2',3',4',6',11'-hexahydrodispiro[indoline-3,5'-pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-10',3''-indoline]-9'-carbonitrile (12S)



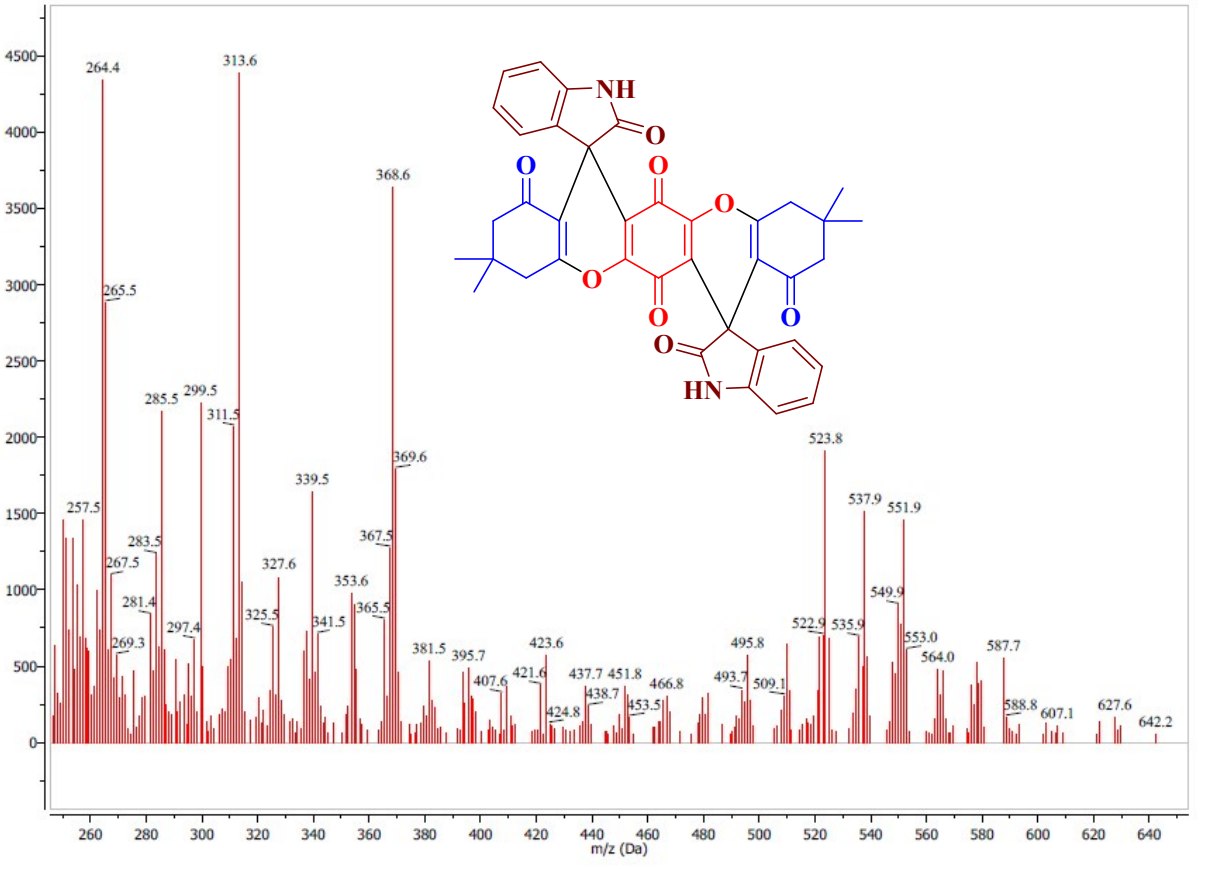
[1]HNMR spectrum of 3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (13S)



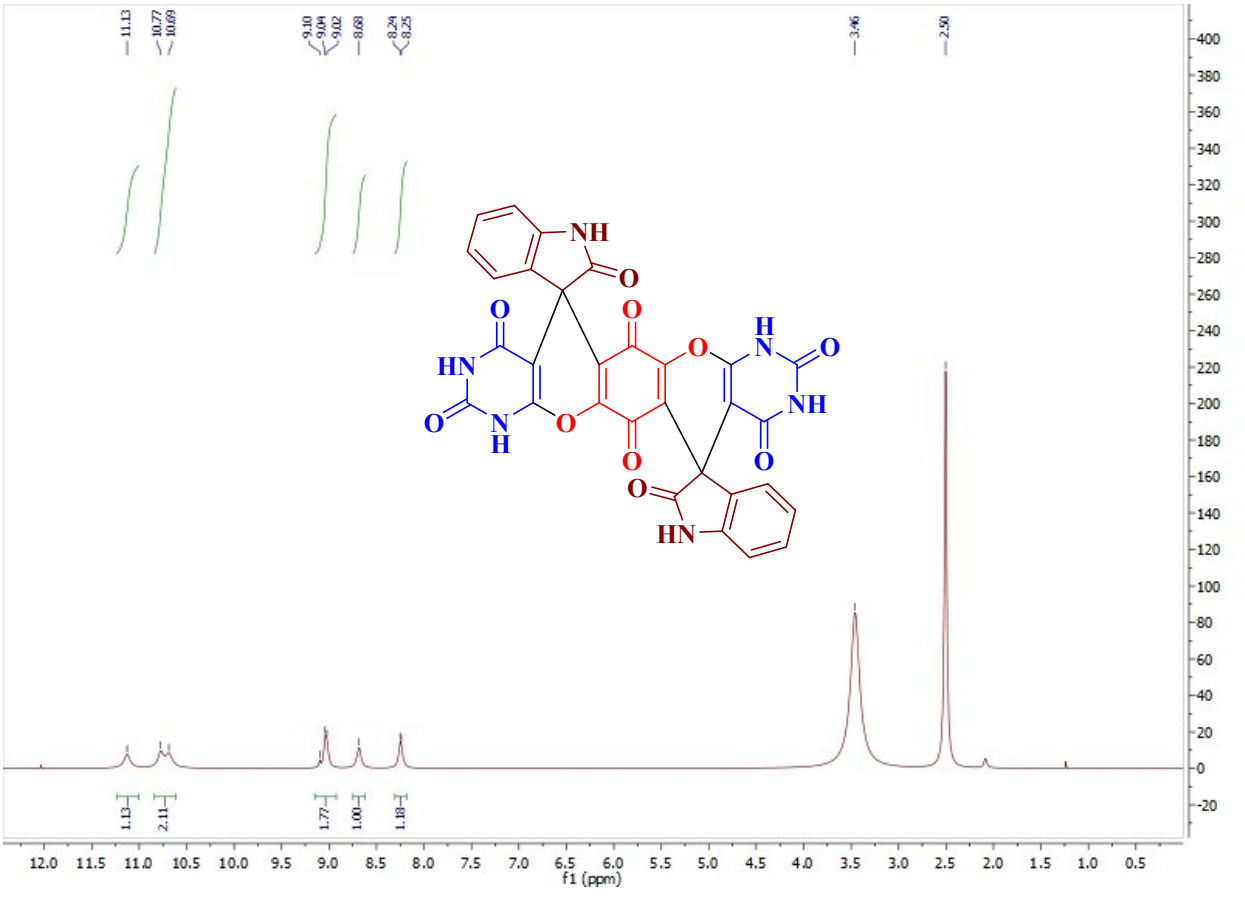
^{13}CNMR spectrum of 3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (13S)



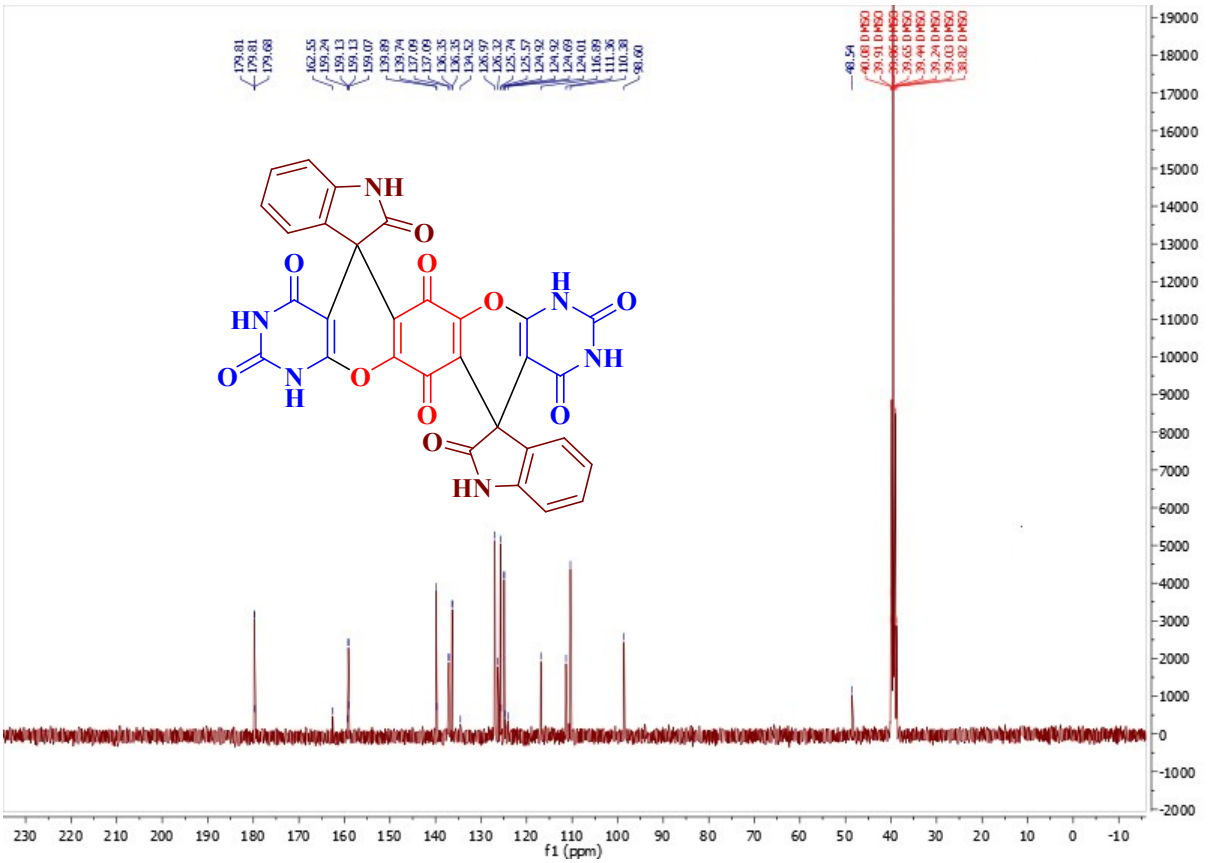
FT-IR spectrum of 3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (13S)



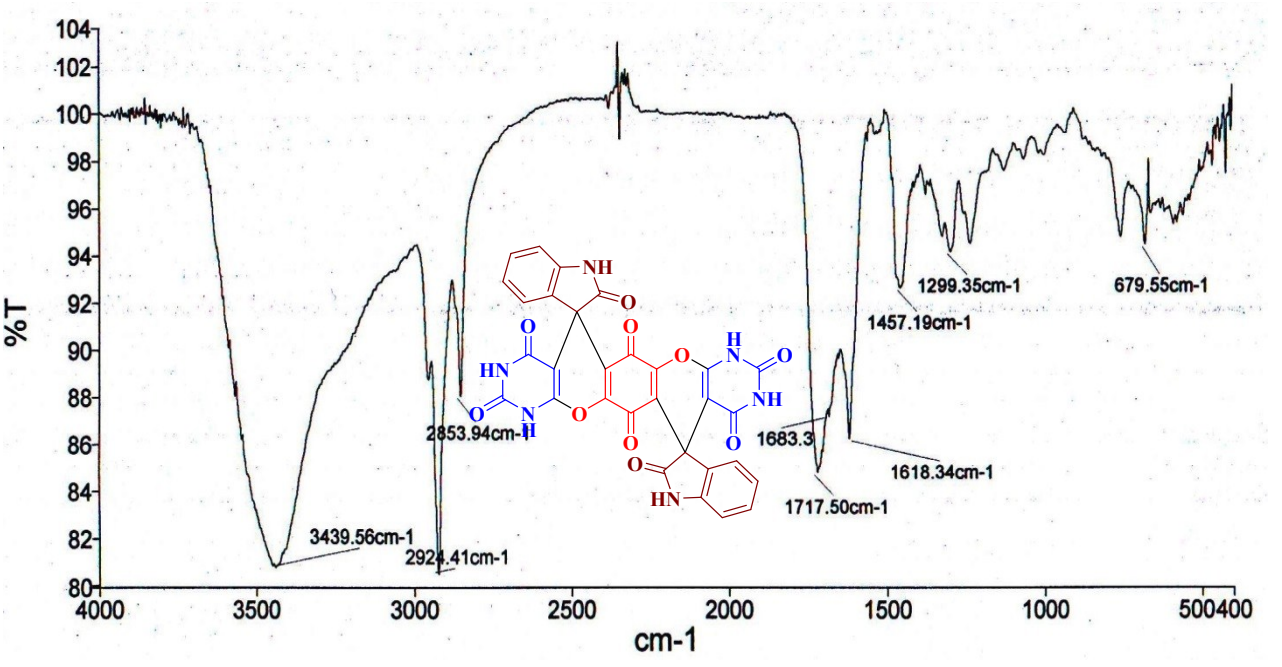
Mass spectrum of 3',3',10',10'-tetramethyl-3',4',10',11'-tetrahydrodispiro[indoline-3,7'-chromeno[2,3-b]xanthene-14',3''-indoline]-1',2,2'',6',8',13'(2'H,9'H)-hexaone (13S)



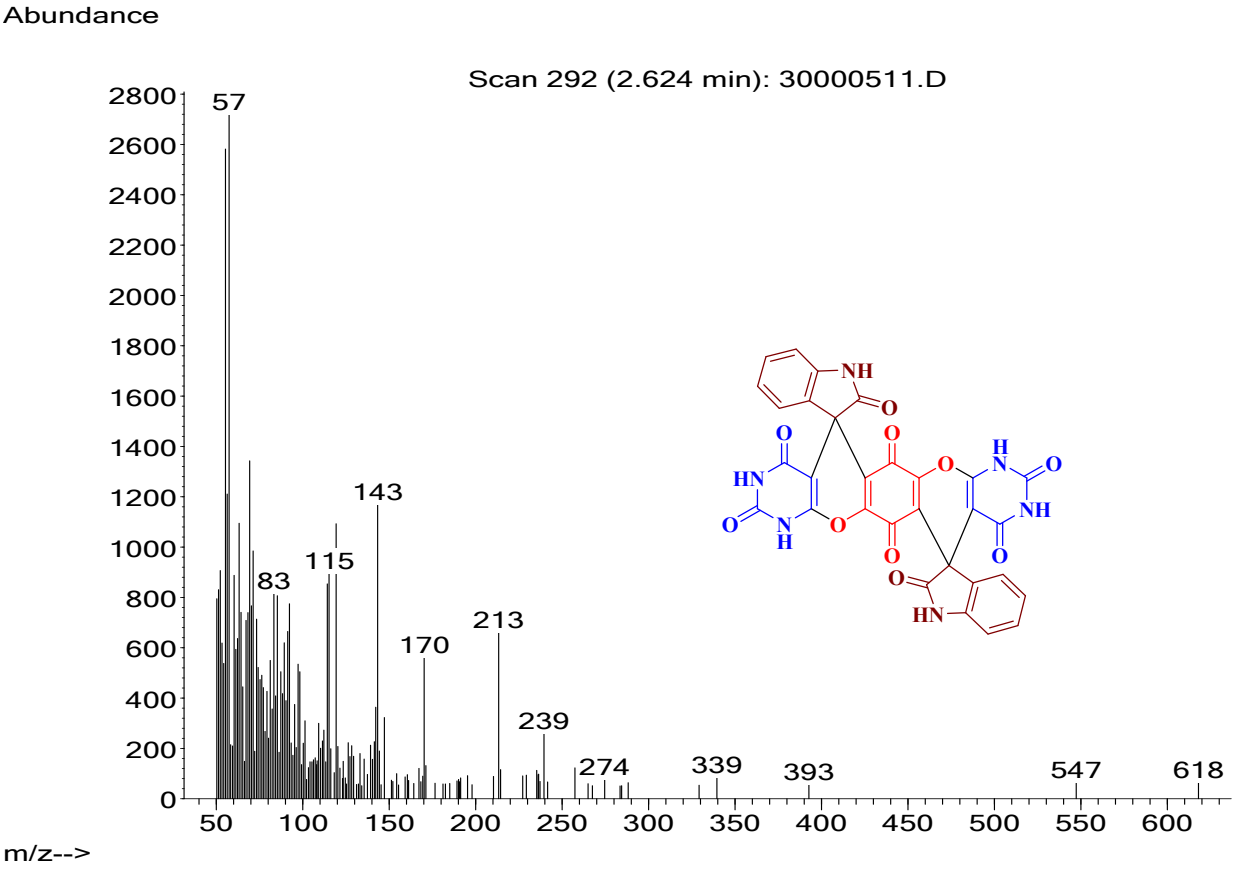
[1]HNMR spectrum of dispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (14S)



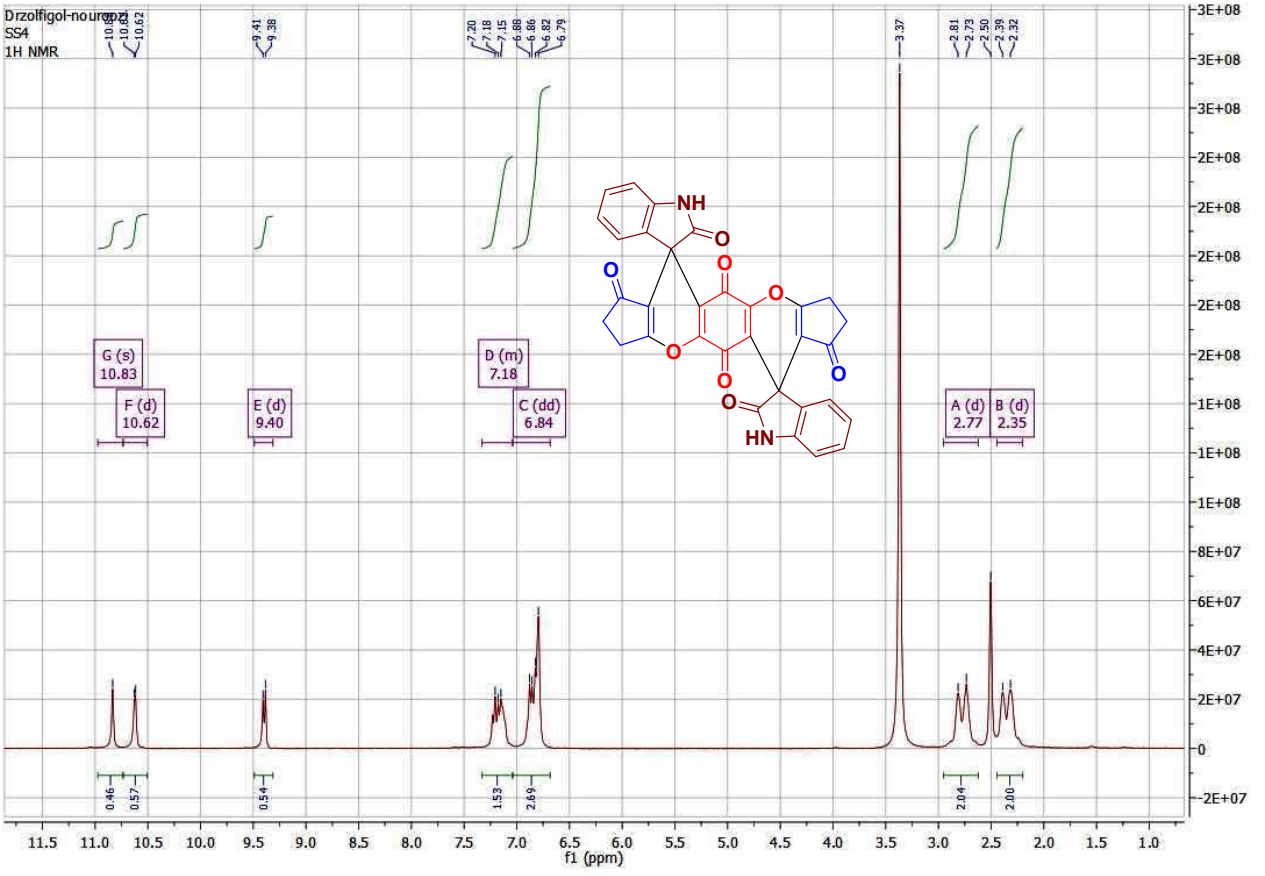
^{13}CNMR spectrum of dispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (14S)



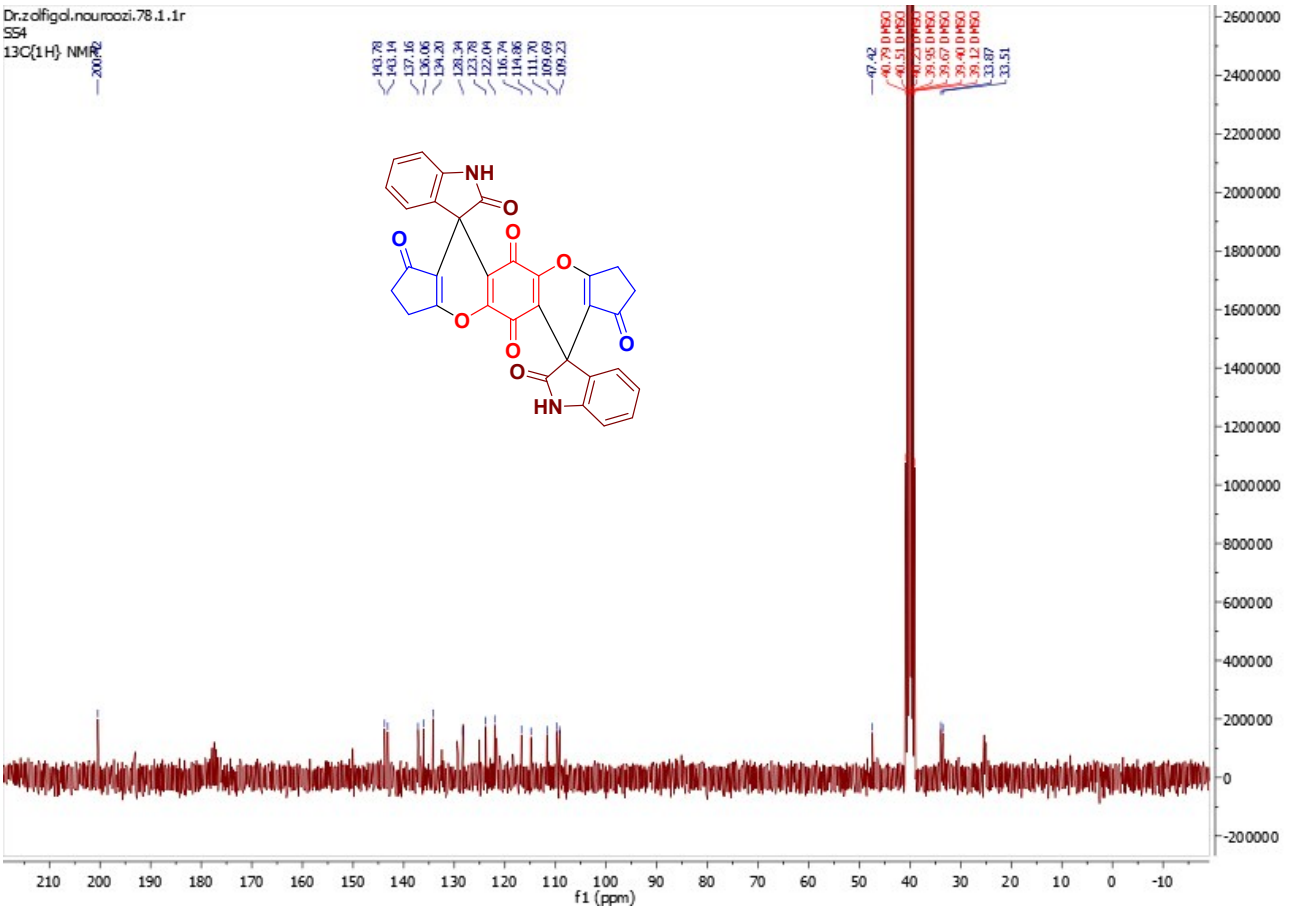
FT-IR spectrum of dispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (14S)



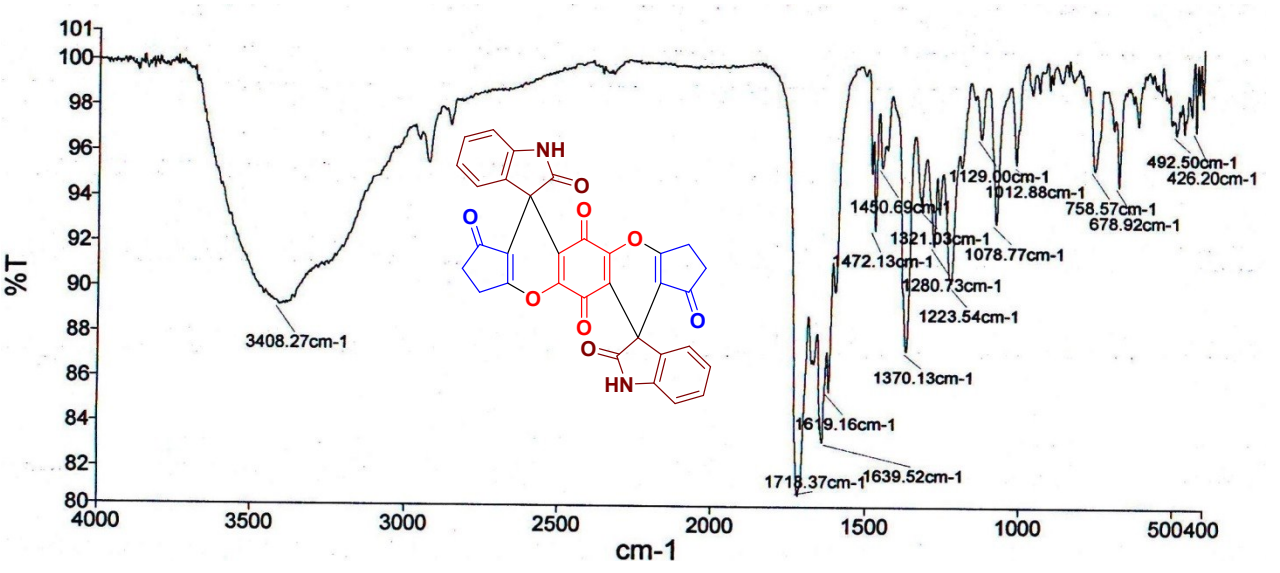
Mass spectrum of dispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (14S)



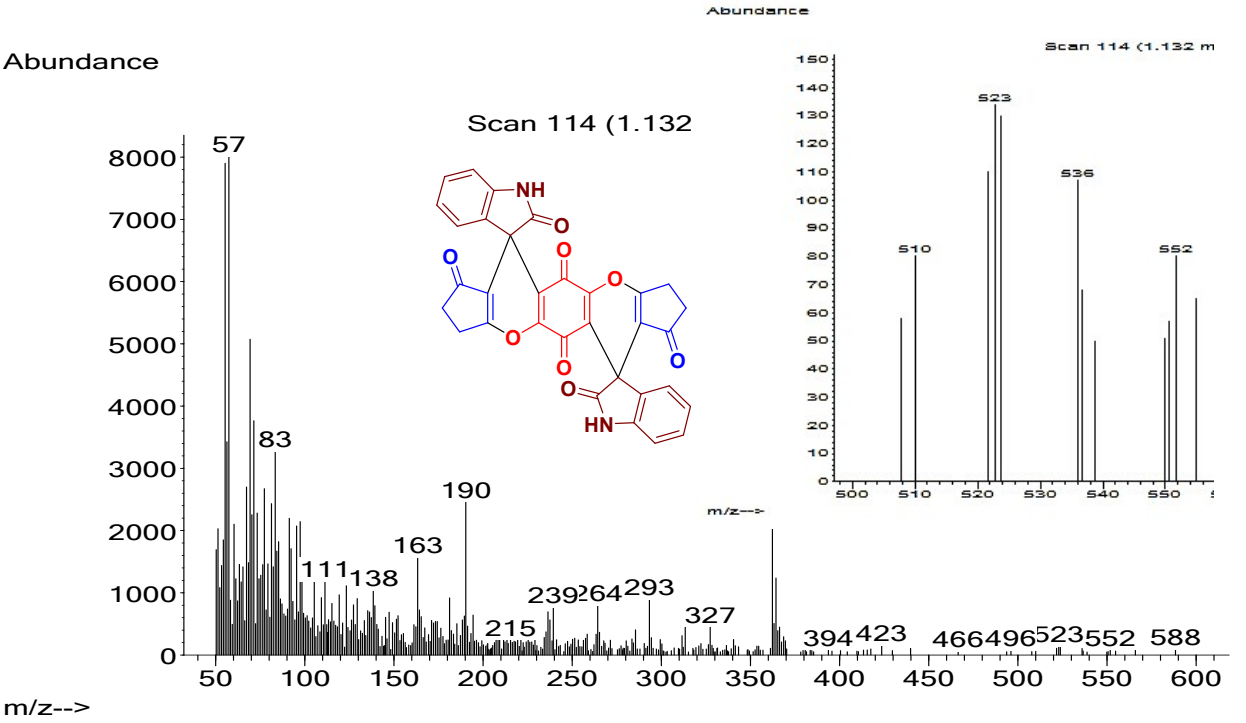
[1]HNMR spectrum of 2',3',8',9'-tetrahydro-1'H,7'H-dispiro[indoline-3,6'-cyclopenta[5,6]pyrano[2,3-g]cyclopenta[b]chromene-12',3''-indoline]-1',2,2'',5',7',11'-hexaone (15S)



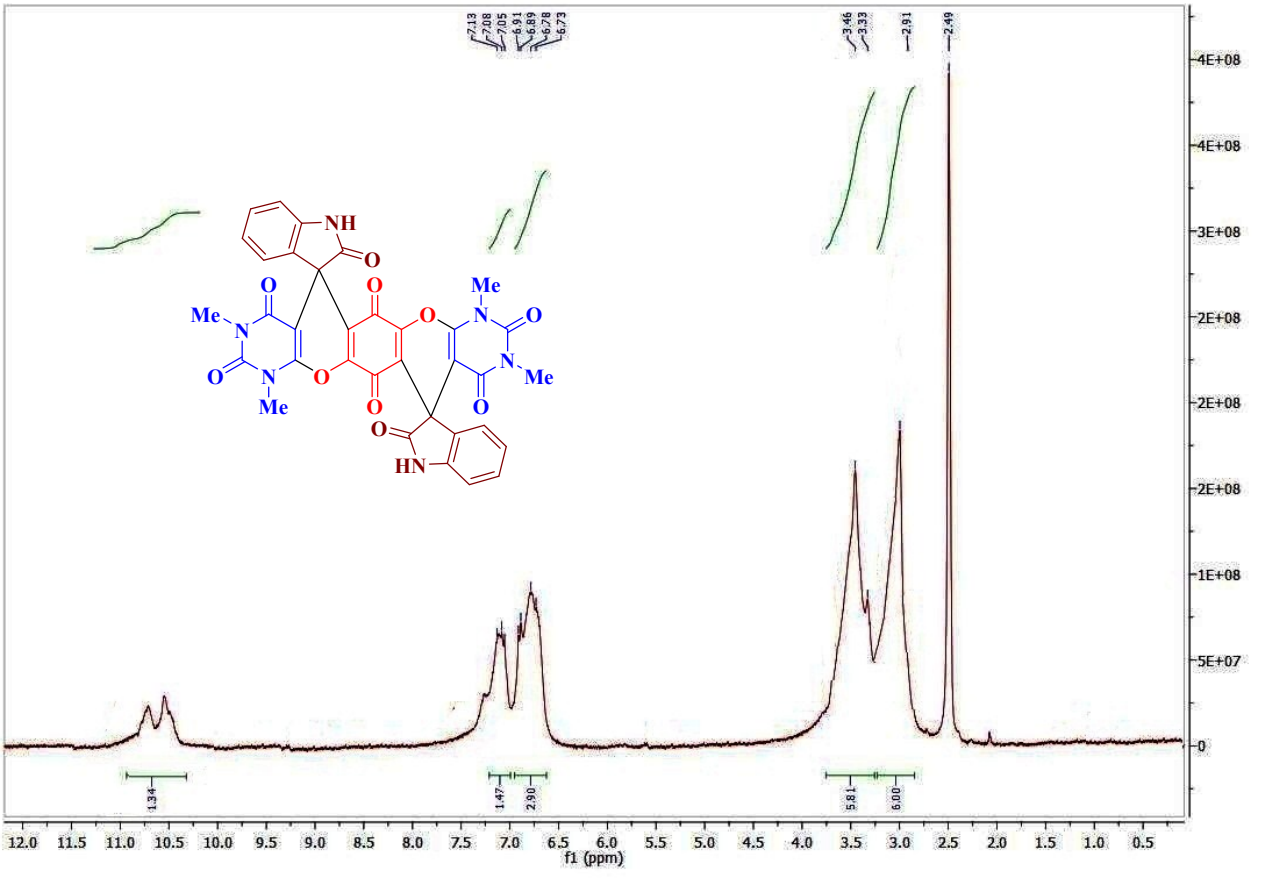
^{13}CNMR spectrum of 2',3',8',9'-tetrahydro-1'H,7'H-dispiro[indoline-3,6'-cyclopenta[5,6]pyrano[2,3-g]cyclopenta[b]chromene-12',3''-indoline]-1',2,2'',5',7',11'-hexaone (15S)



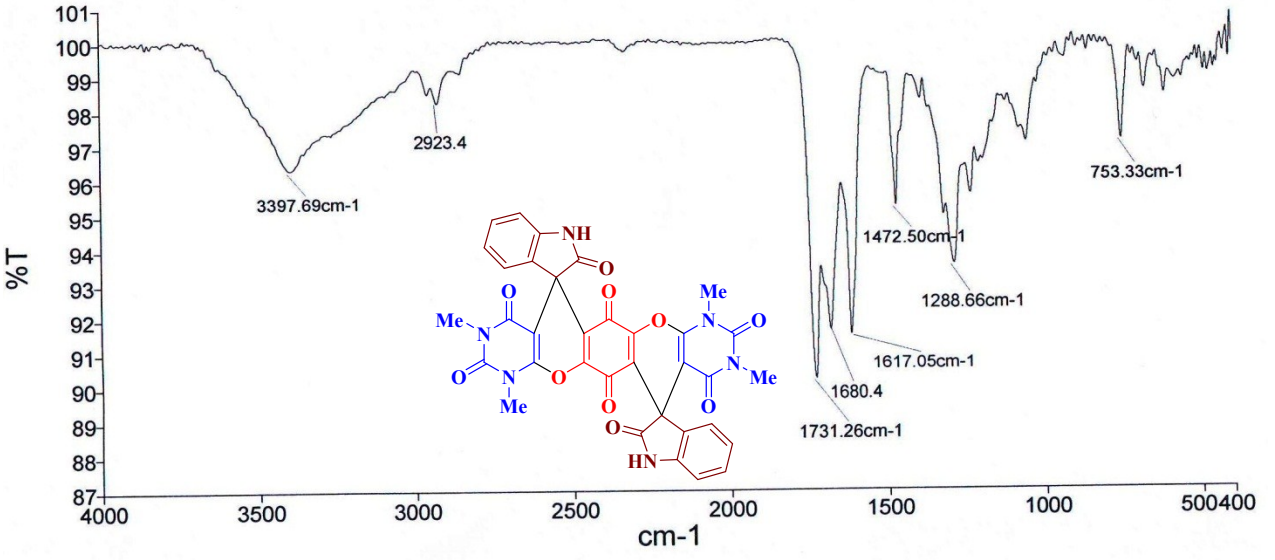
FT-IR spectrum of 2',3',8',9'-tetrahydro-1'H,7'H-dispiro[indoline-3,6'-cyclopenta[5,6]pyrano[2,3-g]cyclopenta[b]chromene-12',3''-indoline]-1',2,2'',5',7',11'-hexaone (15S)



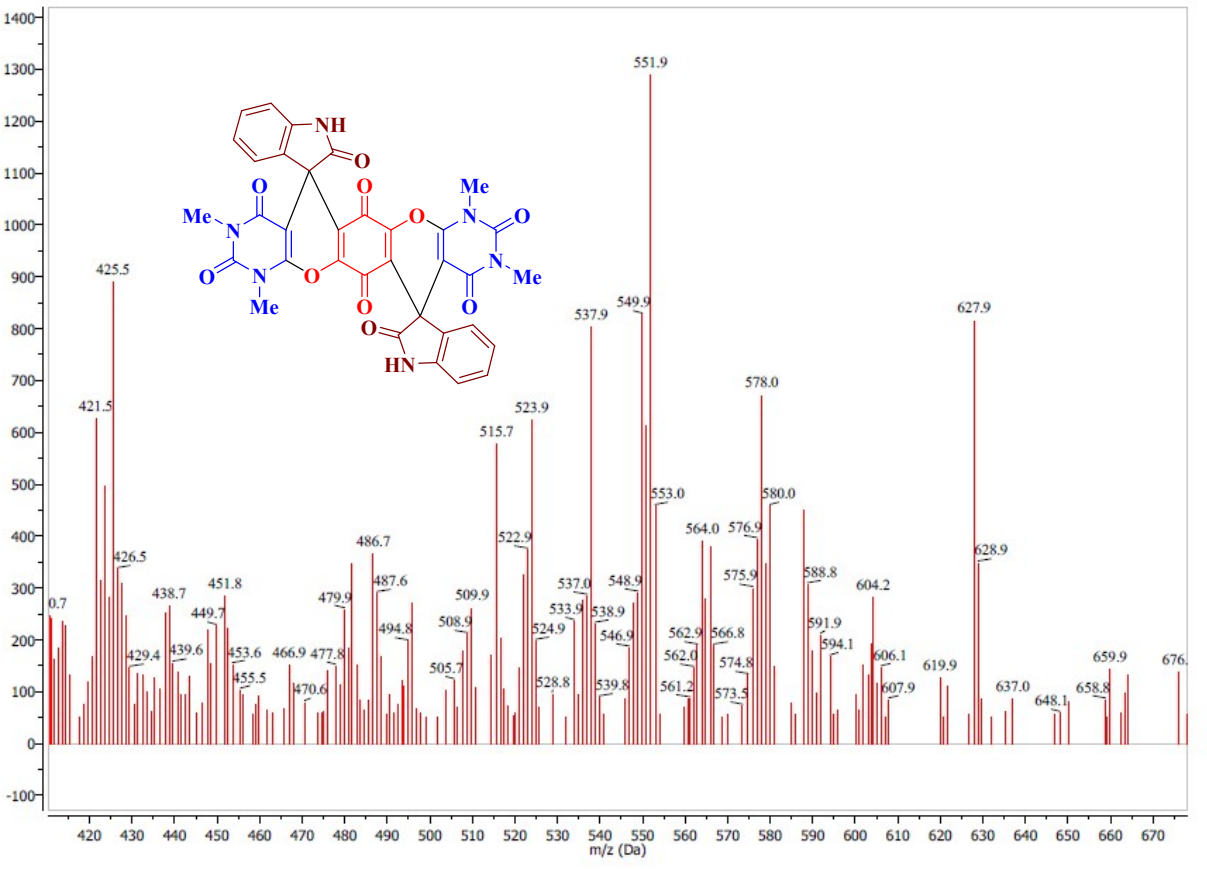
Mass spectrum of 2',3',8',9'-tetrahydro-1'H,7'H-dispiro[indoline-3,6'-cyclopenta[5,6]pyrano[2,3-g]cyclopenta[b]chromene-12',3''-indoline]-1',2,2'',5',7',11'-hexaone (15S)



[1]HNMR spectrum of 1',3',8',10'-tetramethyldispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (16S)



FT-IR spectrum of 1',3',8',10'-tetramethyldispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (16S)



Mass spectrum of 1',3',8',10'-tetramethyldispiro[indoline-3,5'-pyrido[3'',4'':5',6']pyrano[2',3':6,7]chromeno[2,3-d]pyrimidine-12',3''-indolin]-2,2',2'',4',6',9',11',13'(1'H,3'H,8'H,10'H)-octaone (16S)