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EXPERIMENTAL SECTION

Materials and Methods

Isatin, isatin derivatives, acenaphthenequinone, ethyl cyanoacetate, 3-methyl-1-phenyl-5-pyrazolone, diketones, 1-methyl imidazole, and 2-chloro acetic acid were purchased from Sigma-Aldrich, and all organic solvents were acquired from commercial suppliers and were utilized without any additional purification. Analytical thin-layer chromatography (TLC) was performed on 0.25-mm silica gel-coated Kieselgel 60 F254 plates. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and DEPT-135 NMR (100 MHz) spectra were obtained through a Bruker AVANCE III 400 MHz spectrometer. Chemical shifts and coupling constants are explained in parts per million (ppm) and Hertz (Hz), respectively, using tetramethyl silane (TMS) as an internal standard and the solvent resonance at (DMSO-d_6: ^{1}H NMR 400 MHz and ^{13}C NMR 100 MHz): δ 2.5 and 39.5 ppm; (D_2O: ^{1}H NMR 400 MHz): 4.65 ppm. The peak multiplicities are written as s (singlet), d (doublet), dd (doublet of doublet), m (multiplet), and t (triplet). The FT-IR spectra were collected employing the Perkin-Elmer RX-I FTIR spectrometer in ATR mode.

General Procedure for the Synthesis of 1-carboxymethyl 3-methyl imidazolium tetrafluoroborate 4.

In a 250 mL round-bottom flask, 2.0 g (1.0 equiv, 2.43 mmol) of 1-methylimidazole **1** was incorporated with 2.5 g (1.1 equiv, 2.68 mmol) of chloroacetic acid **2**. The mixture was stirred for 2 hours at 80 ^{o}C. Then, the reaction mixture was left to cool, and the pale-yellow viscous liquid was washed several times with ether and then dried under vacuum. The resulting [BMMIM][Cl] ionic-liquid **3** was mixed with $NaBF_4$ (2.94 g, 1.1 equiv, 2.68 mmol), diluted in 20 mL of dry acetonitrile, and stirred for 36 h at room temperature. The resultant white precipitate (NaCl) was filtered and washed frequently with acetonitrile (3 X 30 mL). The concentration of the cumulative filtrates yields 1-carboxymethyl-3-methyl imidazolium tetrafluoroborate [CMMIM][BF_4] **4** as a pale-yellow liquid in 97% yield. The product was characterized by ^{1}H NMR, ^{13}C NMR, DEPT-135, and FT-IR spectra and was discovered to be the same as those mentioned in the literature.

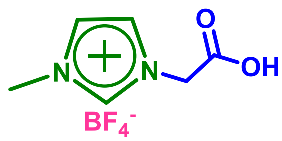
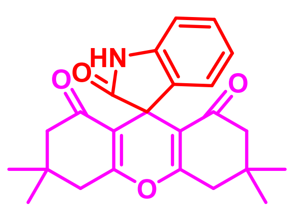
General Procedure for the Synthesis of 3',3',6',6'-tetramethyl-3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-trione 8a.

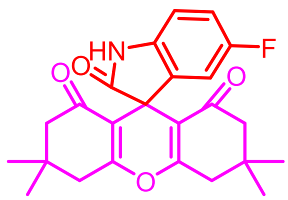
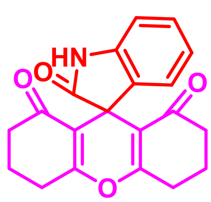
To a dry 25-mL round-bottom flask, isatin **5a** (1 equiv), and dimedone **6a** (2 equiv) and 6 mol% of [CMMIM][BF_4] ionic liquid **4** were successively added to 6 mL of ethanol: water (1:1 v/v 6 mL) and refluxed at 80 ^{o}C for 3 h. The progress of the reaction was monitored using TLC. After the completion of the reaction, the resulting solid precipitate was filtered out and then washed with 30% of ethyl acetate (10 mL X 3) and ether without any column chromatography to achieve the desired product **8a** with 95% yield. The given products were analyzed using ^{1}H NMR, ^{13}C NMR, and FT-IR spectra and were found to resemble those published previously in the literature.

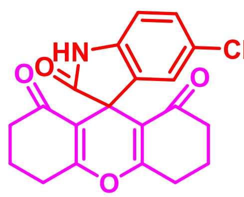
General Procedure for the Synthesis of ethyl 2-amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9a.

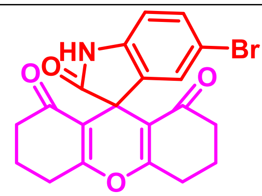
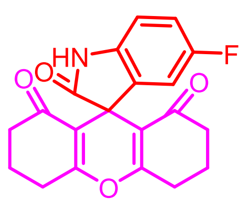
To a dry 25 mL round-bottom flask, isatin **5a** (1 equiv), dimedone **6a** (1 equiv), ethyl cyanoacetate **7** (1 equiv) and 5 mol% of [CMMIM][BF_4] ionic liquid **4** were successively added to 6 mL of ethanol: water (1:1 v/v 6mL) and refluxed at 80 ^{o}C for 3 h. The progress of the reaction was monitored using TLC. After the completion of the reaction, the resulting solid precipitate was filtered out and then washed with 30% of ethyl acetate (10 mL X 3) and ether without column chromatography to achieve the desired product **9a** with 97% yield. The given products were analyzed using ^{1}H NMR, ^{13}C NMR, and FT-IR spectra and were found to resemble those published previously in the literature.

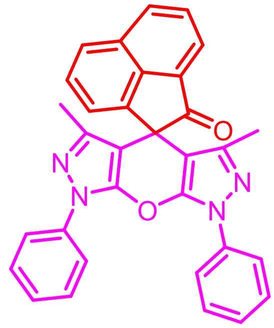
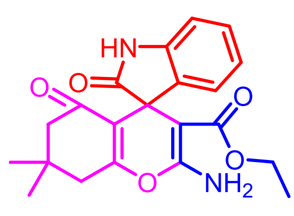
Table S1. Spectral characterization data

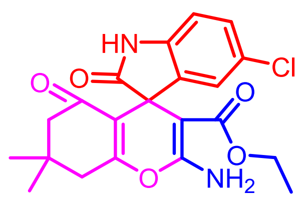
S. No	Name of Compounds	Structures	Characterization
1.	**1-carboxymethyl 3-methyl imidazolium tetrafluoroborate [CMMIM][BF4] 4**		Pale yellow liquid, 97% yield **FT-IR (ATR mode, cm^{-1})**: 3330, 1760, 1030, 759, 625, 523. **^{1}H NMR (400 MHz, D_2O, ppm) δ** 8.66 (s, 1H), 7.42 (s, 1H), 7.41 (s, 1H), 5.03 (s, 2H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, D_2O, ppm)** δ 172.41, 139.83, 125.96, 52.28, 38.34. **^{19}F NMR (400 MHz, D_2O, ppm)** δ −150.36, −150.41. **^{11}B NMR (128MHz, D_2O, ppm)** δ −1.43.
2.	**3',3',6',6'-tetramethyl-3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-trione 8a.**		White Solid, 95% yield, Mp (°C): >300 **FT-IR (ATR mode, cm^{-1}):** 3363, 2966, 1712, 1666, 1616, 1469, 1307, 1170, 1126, 1018, 748, 524. **^{1}H NMR (400 MHz, DMSO-d_6, ppm)** δ 10.28 (s, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.0 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 2.64 (d, J = 17.6 Hz, 2H), 2.57 – 2.48 (m, 2H), 2.19 (d, J = 15.9 Hz, 2H), 2.03 (d, J = 15.9 Hz, 2H), 1.03 (s, 6H), 0.95 (s, 6H). **^{13}C NMR (100 MHz, DMSO-d_6, ppm)** δ 195.45, 178.69, 163.92, 144.30,

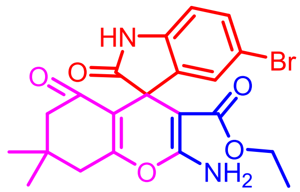
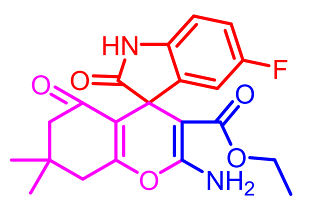
			134.51, 128.19, 122.67, 121.13, 113.46, 108.93, 51.00, 45.67, 32.12, 28.40, 27.06. **DEPT-135 (100 MHz, DMSO-d$_6$, ppm)** δ 128.19, 122.67, 121.13, 108.93, 51.00, 40.59, 28.40, 27.06.
3.	**5-fluoro-3',3',6',6'-tetramethyl-3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-trione 8b.**		White Solid, 92% yield; Mp (°C):289-291 **FT-IR (ATR mode, cm^{-1}):** 3370, 2972, 1728, 1666, 1620, 1485, 1340, 1172, 1114, 1033, 817, 582. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.34 (s, 1H), 6.88 (t, J = 8.9 Hz, 1H), 6.78 (d, J = 6.4 Hz, 1H), 6.68 (dd, J = 8.1, 4.2 Hz, 1H), 2.62 (d, J = 17.6 Hz, 2H), 2.54 (d, J = 18.1 Hz, 2H), 2.19 (d, J = 15.9 Hz, 2H), 2.07 (d, J = 15.9 Hz, 2H), 1.02 (s, 6H), 0.97 (s, 6H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 195.11, 178.16, 163.74, 156.51, 140.22, 135.61, 135.54, 113.80, 113.57, 112.48, 110.27, 110.03, 108.77, 50.46, 45.69, 31.62, 27.70, 26.86.
4.	**3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-trione 8c.**		Pale Yellow Solid, 90% yield; Mp (°C): >300 **FT-IR (ATR mode, cm^{-1}):** 3360, 2951, 1732, 1674, 1620, 1477, 1303, 1207, 1130, 983, 748, 621, 532.

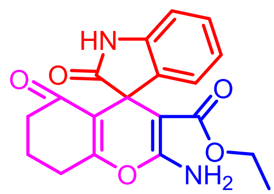
			^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ 10.28 (s, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.0 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 1H), 2.66 (d, *J* = 5.4 Hz, 4H), 2.27 – 2.09 (m, 4H), 1.88 (d, *J* = 5.5 Hz, 4H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 195.26, 178.50, 165.19, 143.82, 134.34, 127.70, 122.71, 120.73, 114.15, 108.32, 45.41, 37.05, 26.95, 19.77.
5.	**5-chloro-3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-trione 8d.**		Pale Yellow Solid, 88% yield; Mp (^{o}C): >300 **FT-IR (ATR mode, cm^{-1}):** 3359, 2958, 1724, 1670, 1620, 1481, 1303, 1219, 1126, 979, 837, 736, 628, 540. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.44 (s, 1H), 7.10 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 2.67 (t, *J* = 6.1 Hz, 4H), 2.22 (dd, *J* = 11.0, 6.2 Hz, 4H), 1.92 – 1.87 (m, 4H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 19.78, 27.08, 29.13, 37.07, 45.79, 109.73, 113.64, 123.01, 124.78, 127.66, 136.40, 142.99, 165.87, 178.48, 195.68.
6.	**5-bromo-3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-**		Pale Yellow Solid, 89% yield; Mp (^{o}C): >300

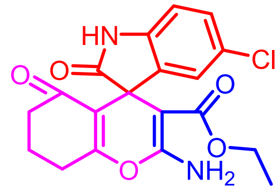
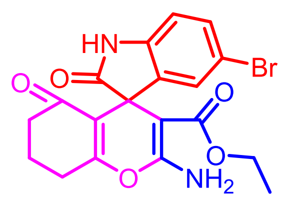
	trione 8e.		**FT-IR (ATR mode, cm^{-1}):** 3356, 2958, 1735, 1658, 1608, 1469, 1350, 1303, 1207, 1134, 987, 833, 617, 540. **^{1}H NMR (400 MHz, DMSO-d_6, ppm)** δ 10.45 (s, 1H), 7.23 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.08 (d, *J* = 1.8 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 2.67 (t, *J* = 6.1 Hz, 4H), 2.26 – 2.18 (m, 4H), 1.91 (dd, *J* = 12.5, 6.2 Hz, 4H). **^{13}C NMR (100 MHz, DMSO-d_6, ppm)** δ 19.79, 27.09, 29.14, 37.08, 45.76, 110.36, 112.53, 113.65, 125.64, 130.55, 136.81, 143.41, 165.92, 178.40, 195.73.
7.	**5-fluoro-3',4',6',7'-tetrahydrospiro[indoline-3,9'-xanthene]-1',2,8'(2'H,5'H)-trione 8f.**		White Solid, 93% yield; Mp (°C): >300 **FT-IR (ATR mode, cm^{-1}):** 3359, 2958, 1724, 1689, 1666, 1485, 1300, 1219, 1130, 979, 794, 601, 532. **^{1}H NMR (400 MHz, DMSO-d_6, ppm)** δ 10.39 (s, 1H), 6.93 (t, *J* = 9.1 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.73 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.72 (t, *J* = 5.9 Hz, 4H), 2.34 – 2.20 (m, 4H), 2.01 – 1.88 (m, 4H). **^{13}C NMR (100 MHz, DMSO-d_6, ppm)** δ 195.48, 178.59, 165.61, 158.99, 156.65, 140.24, 135.94, 113.84, 113.69, 113.61, 110.92, 110.68, 108.74, 108.66, 45.98, 37.05, 27.04, 19.75.

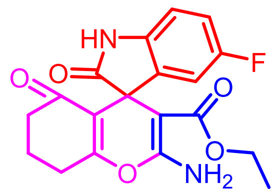
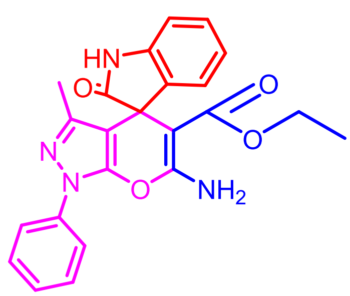
8.	**3',5'-dimethyl-1',7'-diphenyl-1'H,2H,7'H-spiro[acenaphthylene-1,4'-pyrano[2,3-c:6,5-c']dipyrazol]-2-one 8g.**		Yellow solid, 95% yield; Mp (°C): 202-204 **FT-IR (ATR mode, cm^{-1}):** 3050, 2796, 1728, 1624, 1566,1492, 1396, 1361, 1303, 1215, 1118, 995, 783, 732, 690, 582, 543. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 8.29 (d, *J* = 8.0 Hz, 1H), 8.12 – 7.93 (m, 2H), 7.88 (dt, *J* = 14.9, 7.5 Hz, 1H), 7.78 – 7.46 (m, 6H), 7.51 – 7.25 (m, 4H), 7.19 (dd, *J* = 24.0, 17.1 Hz, 2H), 2.00 (d, *J* = 25.9 Hz, 6H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 13.34, 53.31, 118.30, 119.21, 121.48, 122.14, 123.83, 124.84, 128.14, 128.68, 128.90, 129.12, 130.39, 131.39, 133.19, 137.44, 140.26, 141.94, 147.85, 203.07.
9.	**Ethyl 2-amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9a.**		Ivory Solid, 95% yield; Mp (°C): 255-257 **FT-IR (ATR mode, cm^{-1}):** 3375, 3186, 1696, 1681, 1639, 1527, 1469, 1342, 1292, 1222, 1138, 1029, 748, 675, 601. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.15 (s, 1H), 7.86 (s, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.1 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 3.70 (td, *J* = 6.9, 4.2 Hz, 2H), 2.59 (d, *J* = 17.5 Hz, 1H), 2.49 (d, *J* =

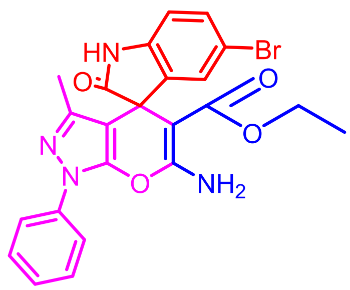
			17.1 Hz, 1H), 2.16 (d, *J* = 15.8 Hz, 1H), 2.02 (d, *J* = 15.8 Hz, 1H), 1.02 (s, 3H), 0.95 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 194.64, 179.77, 167.63, 162.39, 159.09, 144.03, 135.97, 127.15, 122.21, 120.51, 113.08, 108.10, 76.30, 58.82, 50.63, 46.59, 31.53, 27.77, 26.66, 13.08. **DEPT-135 (100 MHz, DMSO-d$_6$, ppm)** δ 127.15, 122.21, 120.51, 108.09, 58.81, 50.62, 40.10, 27.77, 26.65, 13.08.
10.	**Ethyl 2-amino-5'-chloro-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9b.**		Ivory Solid, 97% yield; Mp (°C): 250-251 **FT-IR (ATR mode, cm^{-1}):** 3387, 3285, 1724, 1678, 1651, 1516, 1481, 1300, 1222, 1168, 1041, 636, 551. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.31 (s, 1H), 7.94 (s, 2H), 7.10 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.91 (d, *J* = 1.8 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 3.76 – 3.71 (m, 2H), 2.53 (d, *J* = 14.2 Hz, 2H), 2.11 (q, *J* = 15.8 Hz, 2H), 1.01 (s, 3H), 0.97 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 194.84, 179.52, 167.43, 162.88, 159.18, 143.13, 138.12, 126.98, 124.38, 122.37, 112.47, 109.36, 75.66, 58.95, 50.56, 46.89, 27.42, 27.08, 13.12.

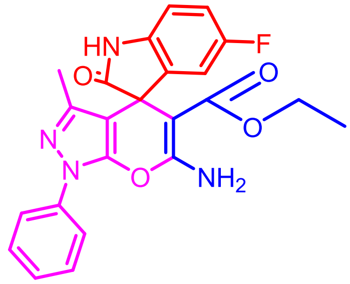
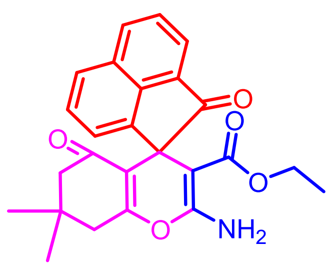
11.	**Ethyl 2-amino-5'-bromo-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9c.**		White Solid, 95% yield; Mp (°C): 295-298 **FT-IR (ATR mode, cm⁻¹):** 3390, 3282, 1720, 1685, 1616, 1516, 1477, 1350, 1296, 1211, 1165, 1053, 1018, 821, 632, 536. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.32 (s, 1H), 7.94 (s, 2H), 7.23 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.66 (t, *J* = 11.2 Hz, 1H), 3.82 – 3.66 (m, 2H), 2.51 (s, 2H), 2.11 (q, *J* = 15.8 Hz, 2H), 0.99 (d, *J* = 15.5 Hz, 6H), 0.83 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 194.86, 179.39, 167.42, 162.90, 159.18, 143.53, 138.50, 129.84, 125.05, 112.48, 112.04, 109.99, 75.66, 58.97, 50.55, 46.84, 31.56, 27.40, 27.09, 13.12.
12.	**Ethyl 2-amino-5'-fluoro-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9d.**		White Solid, 97% yield; Mp (°C): 291-292 **FT-IR (ATR mode, cm⁻¹):** 3383, 3275, 1724, 1689, 1647, 1481, 1354, 1296, 1165, 1053, 802, 536. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.18 (s, 1H), 7.91 (s, 2H), 6.90 – 6.83 (m, 1H), 6.77 (dd, *J* = 8.1, 2.5 Hz, 1H), 6.64 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.82 – 3.65 (m, 2H), 2.54 (dd, *J* = 21.1, 11.6

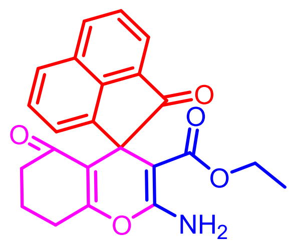
			Hz, 2H), 2.19 – 2.01 (m, 2H), 1.02 (s, 3H), 0.97 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 194.74, 179.75, 167.51, 162.73, 159.15, 140.41, 113.18, 112.95, 112.57, 110.26, 110.02, 108.33, 75.79, 58.89, 50.60, 47.15, 31.53, 27.58, 26.93, 13.12.
13.	**Ethyl 2-amino-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9e.**		White Solid, 93% yield; Mp (°C): 252-254 **FT-IR (ATR mode, cm^{-1}):** 3363, 3248, 1685, 1651, 1612, 1516, 1469, 1292, 1226, 1076, 1029, 929, 740, 621, 605, 500. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.21 (s, 1H), 7.92 (s, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.1 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 3.87 – 3.68 (m, 2H), 2.70 (t, *J* = 5.8 Hz, 2H), 2.36 – 2.15 (m, 2H), 2.08 – 1.78 (m, 2H), 0.94 – 0.76 (m, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 194.81, 179.88, 167.66, 164.20, 158.98, 144.02, 136.10, 127.12, 122.43, 120.51, 114.22, 108.02, 76.36, 58.82, 46.71, 37.09, 26.93, 19.65, 13.09.
14.	**Ethyl 2-amino-5'-chloro-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-**		White Solid, 95% yield; Mp (°C): 280-282

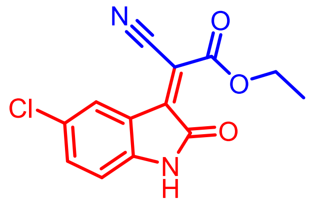
	4,3'-indoline]-3-carboxylate 9f.		**FT-IR (ATR mode, cm^{-1}):** 3348, 3178, 1700, 1651, 1527, 1477, 1300, 1219, 1141, 1033, 806, 586, 532. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.31 (s, 1H), 7.93 (s, 2H), 7.09 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 3.82 – 3.65 (m, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.29 – 2.12 (m, 2H), 1.95 – 1.84 (m, 2H), 0.82 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 195.01, 179.63, 167.46, 164.78, 159.06, 143.10, 138.22, 126.94, 124.37, 122.62, 113.57, 109.28, 75.73, 58.96, 46.98, 36.99, 26.96, 19.57, 13.12.
15.	**Ethyl 2-amino-5'-bromo-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9g.**		White Solid, 96% yield; Mp (^{o}C): 261-263 **FT-IR (ATR mode, cm^{-1}):** 3359, 3190, 1685, 1651, 1527, 1480, 1300, 1222, 1134, 1029, 813, 578. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.32 (s, 1H), 7.93 (s, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 3.85 – 3.58 (m, 2H), 2.64 (t, *J* = 5.7 Hz, 2H), 2.35 – 2.08 (m, 2H), 2.02 – 1.77 (m, 2H), 0.83 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 195.03, 179.51, 167.45, 164.82, 159.06, 143.50, 138.62, 129.81, 125.27,

			113.58, 112.08, 109.91, 75.75, 58.98, 46.94, 37.00, 26.96, 19.57, 13.13.
16.	**Ethyl 2-amino-5'-fluoro-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate 9h.**		White Solid, 97% yield; Mp (°C): 223-224 **FT-IR (ATR mode, cm^{-1}):** 3375, 3192, 1689, 1662, 1527, 1477, 1350, 1296, 1188, 1083, 1029, 806, 682, 597, 505. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.18 (s, 1H), 7.91 (s, 2H), 6.91 – 6.82 (m, 1H), 6.78 (dd, J = 8.2, 2.4 Hz, 1H), 6.63 (dd, J = 8.3, 4.3 Hz, 1H), 3.80 – 3.63 (m, 2H), 2.64 (t, J = 6.0 Hz, 2H), 2.36 – 2.11 (m, 2H), 1.89 (dd, J = 12.3, 6.1 Hz, 2H), 0.90 – 0.74 (m, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 194.95, 179.90, 167.55, 164.63, 159.05, 156.55, 140.40, 137.91, 113.68, 113.16, 110.52, 108.36, 75.89, 58.92, 47.28, 37.06, 27.00, 19.61, 13.14.
17.	**Ethyl 6'-amino-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate 9i.**		White Solid, 96% yield; Mp (°C): 208-210 **FT-IR (ATR mode, cm^{-1}):** 3356, 3217, 1689, 1639, 1508, 1377, 1284, 1222, 1134, 1045, 929, 744, 675, 601. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.52 (s, 1H), 8.22 (s, 2H), 7.82 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.9 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.88

			(dd, J = 16.7, 7.7 Hz, 2H), 3.93 – 3.64 (m, 2H), 1.59 (s, 3H), 0.91 – 0.57 (m, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 179.25, 167.87, 161.32, 144.20, 143.94, 142.18, 137.35, 135.78, 129.41, 127.75, 126.32, 123.17, 121.74, 119.93, 108.82, 98.19, 74.57, 58.99, 47.47, 13.09, 11.71.
18.	**Ethyl 6'-amino-5-bromo-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate 9j.**		White Solid, 96% yield; Mp (^{o}C): 254-256 **FT-IR (ATR mode, cm^{-1}):** 3344, 3190, 1698, 1643, 1516, 1400, 1284, 1134, 1041, 810, 744, 690, 543. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.67 (s, 1H), 8.27 (s, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.23 (s, 1H), 6.83 (d, J = 8.2 Hz, 1H), 3.90 – 3.65 (m, 2H), 1.63 (s, 3H), 0.92 – 0.69 (m, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 178.91, 167.67, 161.43, 144.08, 143.97, 141.50, 138.24, 137.31, 130.51, 126.40, 126.20, 120.10, 113.42, 110.80, 97.51, 74.04, 59.11, 47.68, 13.16, 11.78.
19.	**Ethyl 6'-amino-5-fluoro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-**		White Solid, 90% yield; Mp (^{o}C): 199-200

	c]pyrazole]-5'-carboxylate 9k.		**FT-IR (ATR mode, cm^{-1}):** 3387, 3190, 1720, 1685, 1635, 1485, 1384, 1276, 1122, 1033, 802, 694, 586. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 10.55 (s, 1H), 8.26 (s, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.08 – 6.91 (m, 2H), 6.85 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.91 – 3.64 (m, 2H), 1.62 (s, 3H), 0.81 (m, *J* = 14.1, 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 179.29, 167.73, 161.40, 157.14, 144.07, 138.37, 137.33, 129.40, 126.38, 120.00, 114.03, 111.25, 111.01, 109.52, 97.64, 74.15, 59.05, 48.01, 13.14, 11.73.
20.	**Ethyl 2'-amino-7',7'-dimethyl-2,5'-dioxo-5',6',7',8'-tetrahydro-2H-spiro[acenaphthylene-1,4'-chromene]-3'-carboxylate 9l.**		White Solid, 95% yield; Mp (°C): 244-246 **FT-IR (ATR mode, cm^{-1}):** 3387, 3278, 2966, 1720, 1654, 1523, 1338, 1303, 1219, 1080, 771, 597, 509. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 8.18 (d, *J* = 7.8 Hz, 1H), 8.03 (s, 2H), 7.85 (m, *J* = 21.2, 13.6, 7.7 Hz, 3H), 7.68 – 7.57 (m, 1H), 7.33 (d, *J* = 6.8 Hz, 1H), 3.42 – 3.35 (m, 2H), 2.69 (dd, *J* = 41.4, 17.6 Hz, 2H), 2.09 (dd, *J* = 60.2, 16.0 Hz, 2H), 1.10 (s, 3H), 1.03 (s, 3H), 0.04 (t, *J* = 7.1 Hz, 3H).

			^{13}C NMR (100 MHz, DMSO-d$_6$, ppm) δ 205.17, 195.24, 167.43, 162.93, 159.37, 145.28, 140.61, 135.97, 129.41, 129.23, 128.20, 127.69, 123.75, 119.11, 118.99, 114.84, 77.19, 58.38, 50.68, 50.00, 31.68, 27.76, 26.69, 12.18.
21.	**Ethyl 2'-amino-7',7'-dimethyl-2,5'-dioxo-5',6',7',8'-tetrahydro-2H-spiro[acenaphthylene-1,4'-chromene]-3'-carboxylate 9m.**		White Solid, 94% yield; Mp (°C): 261-263 **FT-IR (ATR mode, cm^{-1}):** 3390, 3302, 1716, 1678, 1604, 1519, 1342, 1292, 1249, 1195, 1080,1018, 887, 786, 536, 500. **^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 8.19 (d, J = 7.7 Hz, 1H), 8.02 (s, 2H), 7.95 – 7.75 (m, 3H), 7.63 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 6.8 Hz, 1H), 3.46 – 3.24 (m, 3H), 2.79 (t, J = 5.7 Hz, 2H), 2.33 – 2.07 (m, 2H), 1.98 (dd, J = 11.6, 5.9 Hz, 2H), 0.04 (t, J = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 205.45, 195.63, 167.61, 164.97, 159.39, 145.55, 140.70, 136.11, 129.54, 129.30, 128.38, 127.83, 123.85, 119.35, 119.21, 116.08, 77.40, 58.55, 50.91, 36.56, 26.90, 19.81, 12.30.
22.	**Ethyl (Z)-2-(5-chloro-2-oxoindolin-3-ylidene)-2-cyanoacetate**		Red Solid, **FT-IR (ATR mode, cm^{-1}):** 3356, 3250, 2218, 1720, 1581, 1438, 1249, 1168, 1018, 844, 763, 605, 555.

			**^{1}H NMR (400 MHz, DMSO-d$_6$, ppm)** δ 11.23 (s, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$, ppm)** δ 164.98, 161.14, 144.81, 144.67, 135.26, 128.96, 125.79, 120.12, 113.95, 112.25, 106.17, 63.27, 13.73,13.50. **DEPT-135 NMR (100 MHz, DMSO-d$_6$, ppm)** δ 135.02, 128.72, 112.59, 112.01, 63.04, 13.50. **HRMS (ESI, +ve mode):** Calculated for $C_{13}H_9ClN_2O_3$ $[M+H]^+$ m/z: 277.0380; Found $[M+H]^+$: 277.0421.

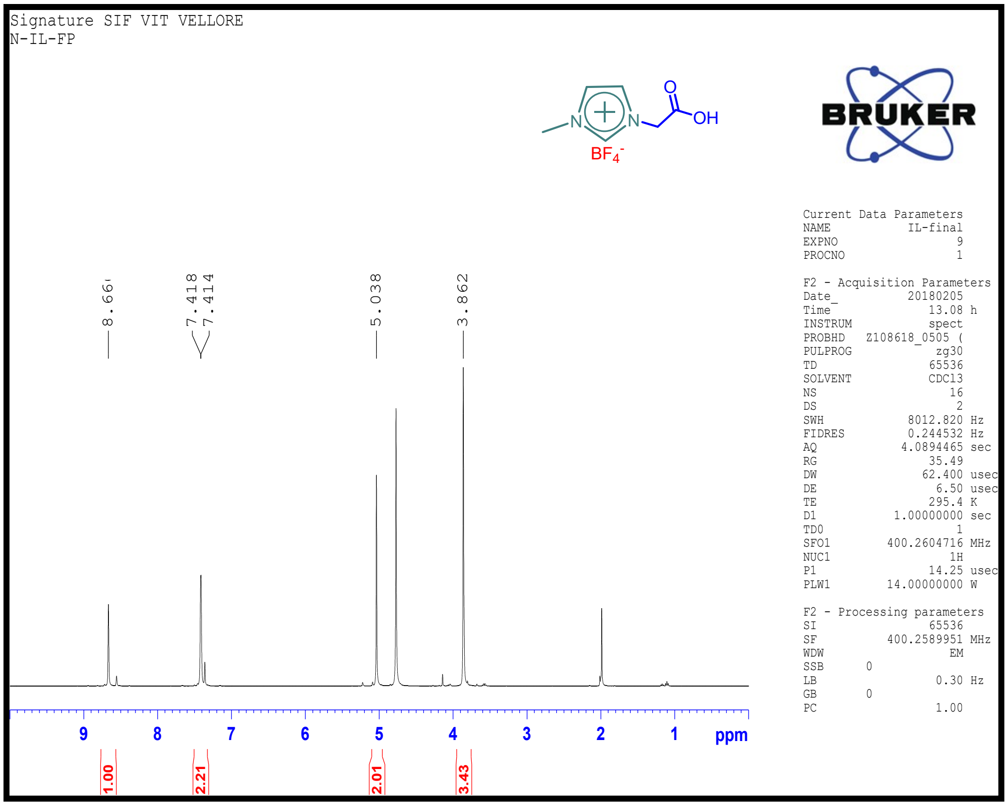


Figure S1. ^{1}H NMR spectrum (400 MHz) of **4** in D_2O

.

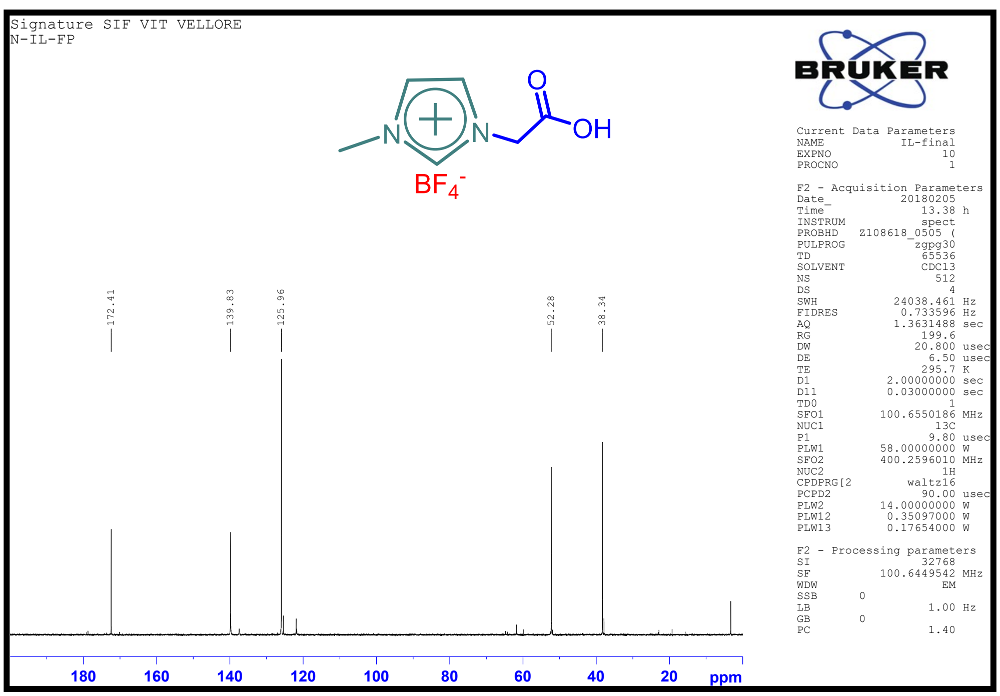


Figure S2. ^{13}C NMR spectrum (100 MHz) of **4** in D_2O

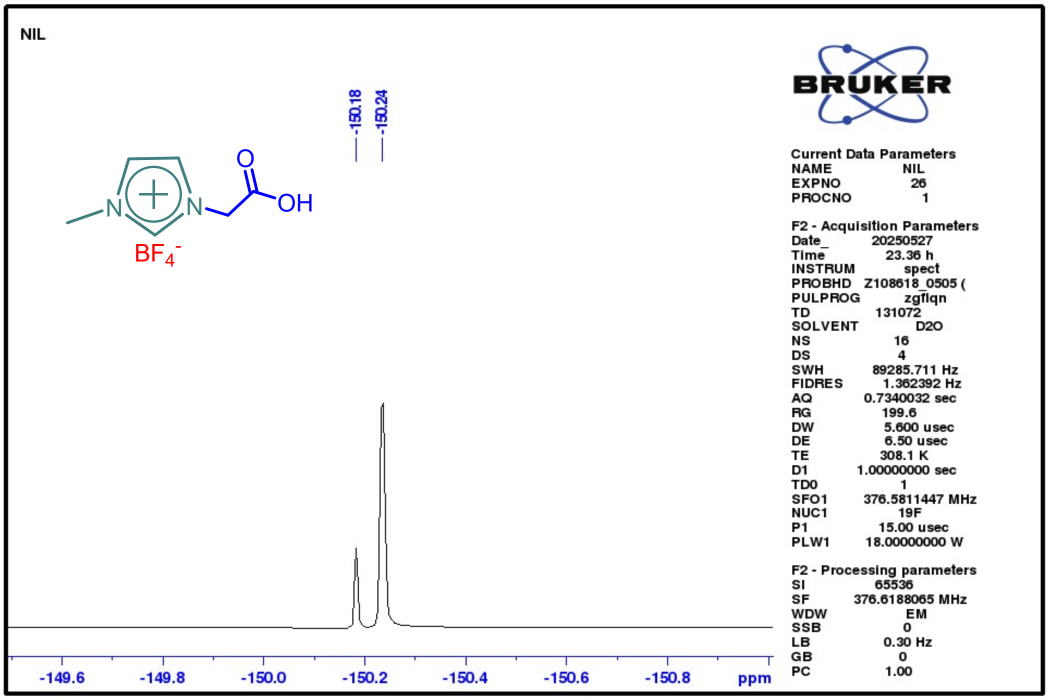


Figure S3. ^{19}F NMR spectrum (400 MHz) of **4** in D_2O **(**an isotopic chemical shift of the BF_4^- peak can be seen, which is due to the two boron isotopes ^{10}B and ^{11}B).

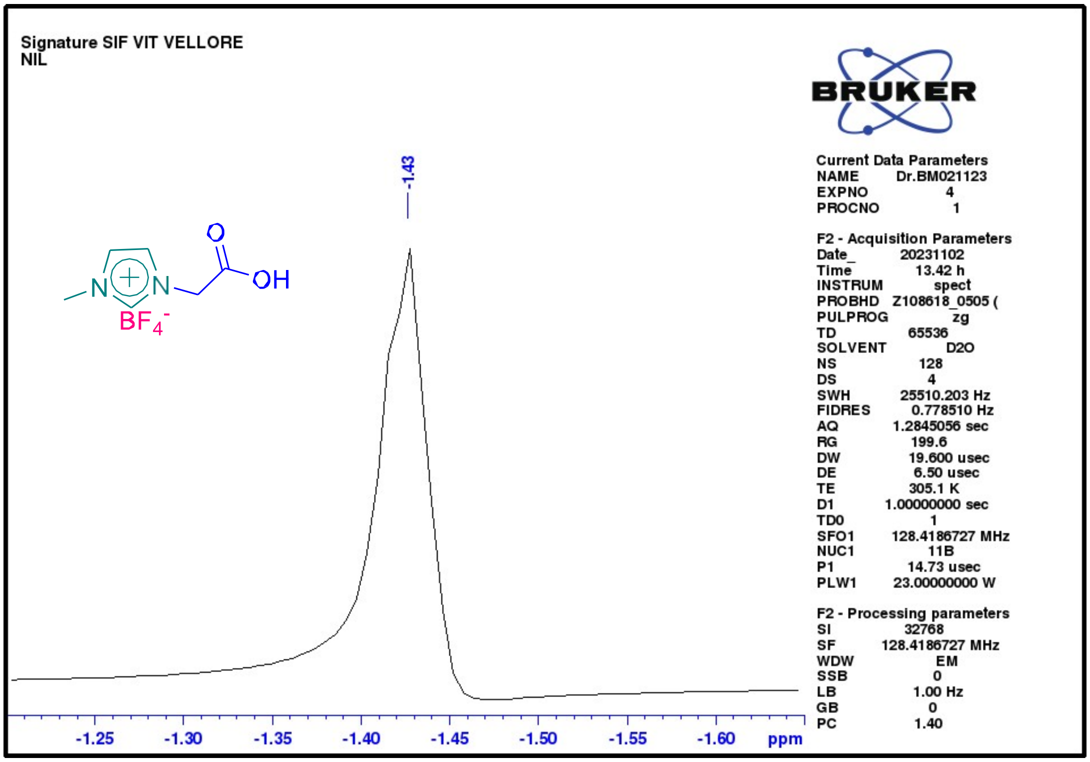


Figure S4. ^{11}B NMR spectrum (128 MHz) of **4** in D_2O.

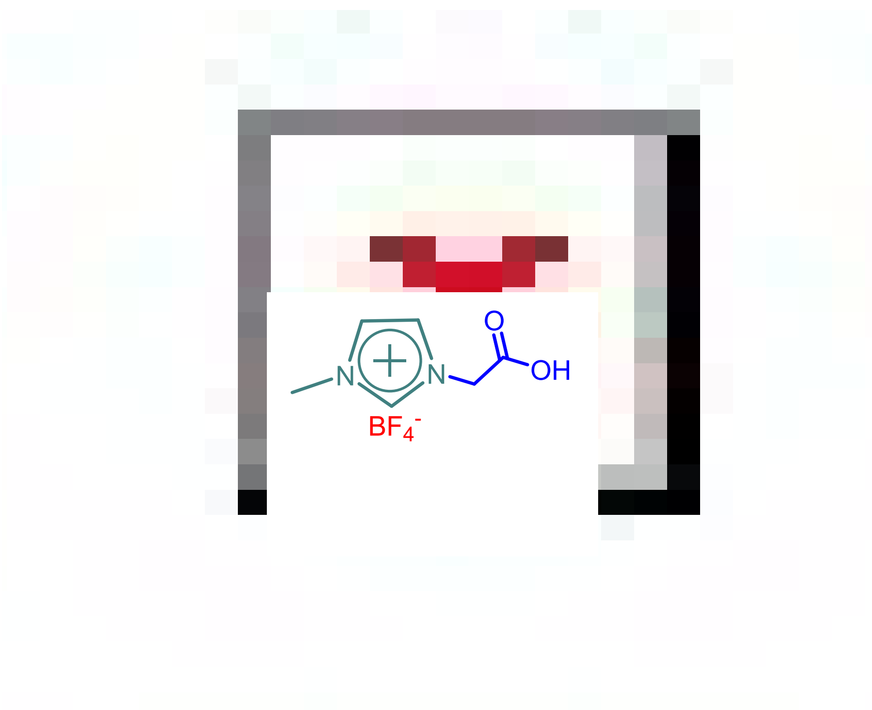


Figure S5. FT-IR spectrum of **4**

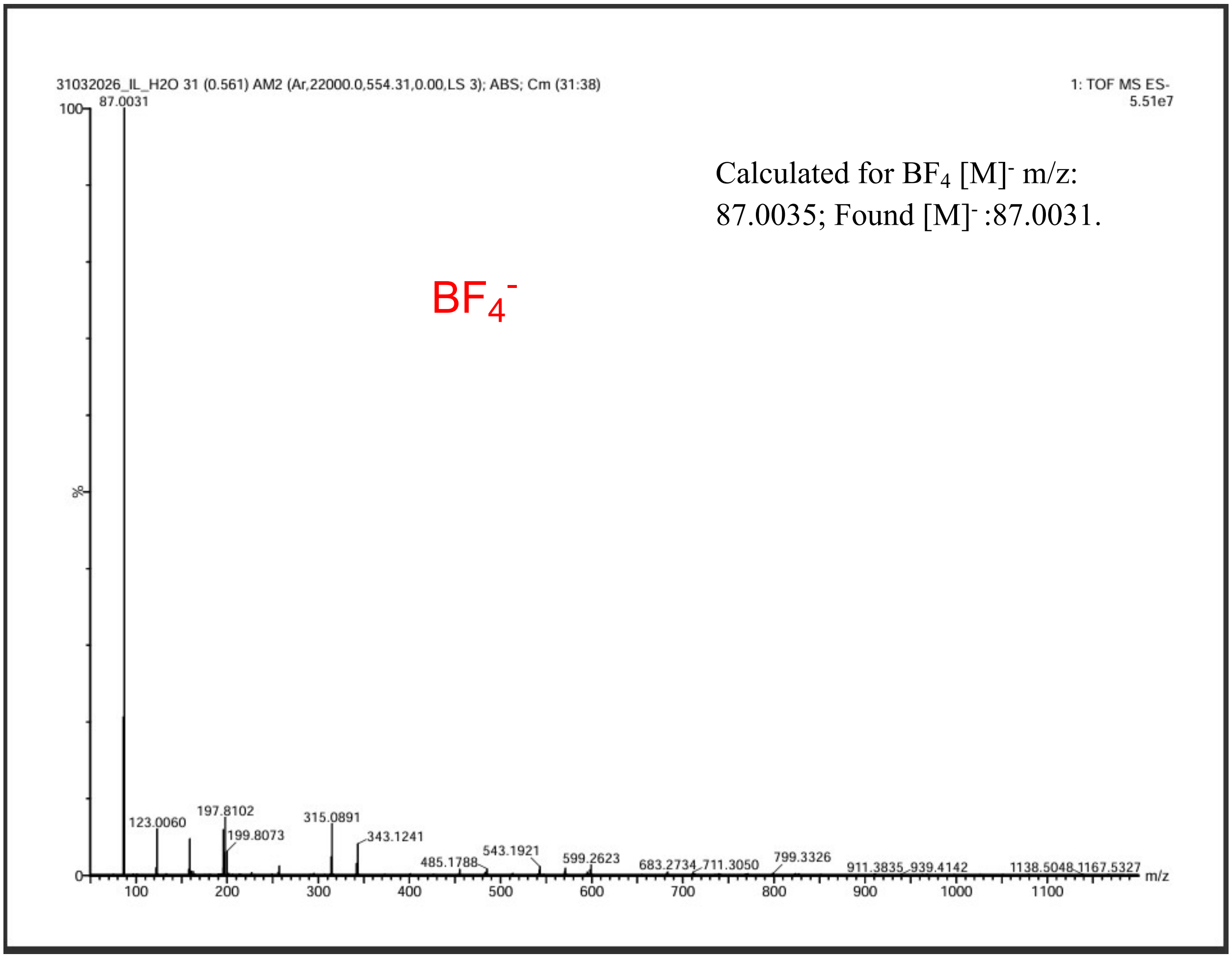


Figure S6. HRMS (-ve mode) of recycled ionic liquid.

Symmetric Compounds **8a-8g**

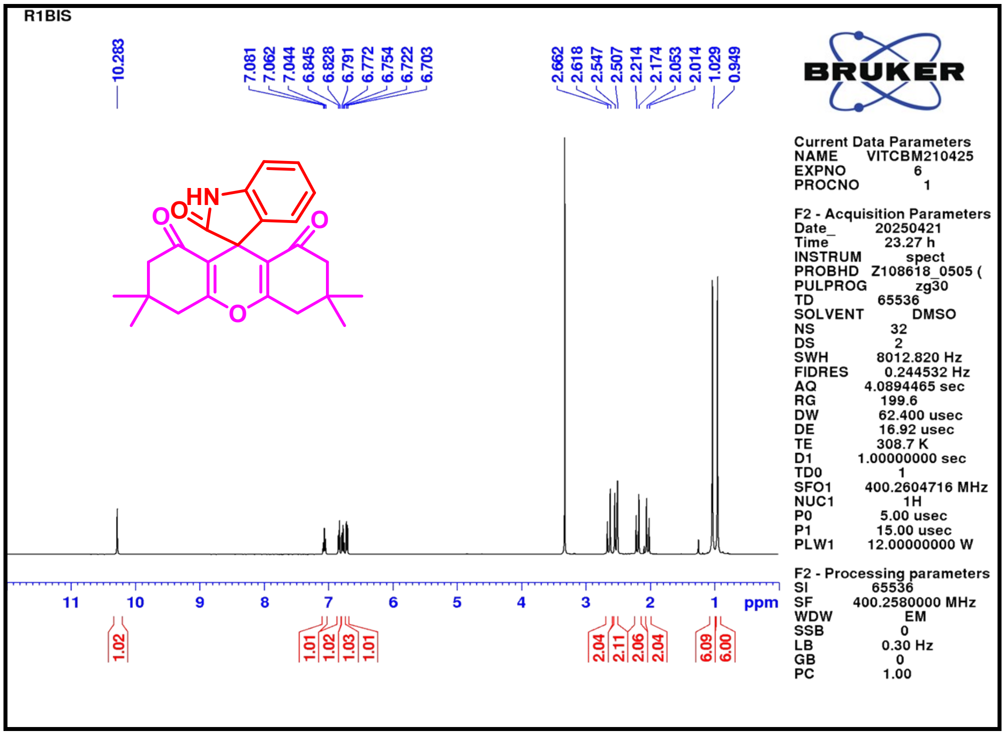


Figure S7. ^{1}H NMR spectrum (400 MHz) of **8a** in DMSO-d$_6$.

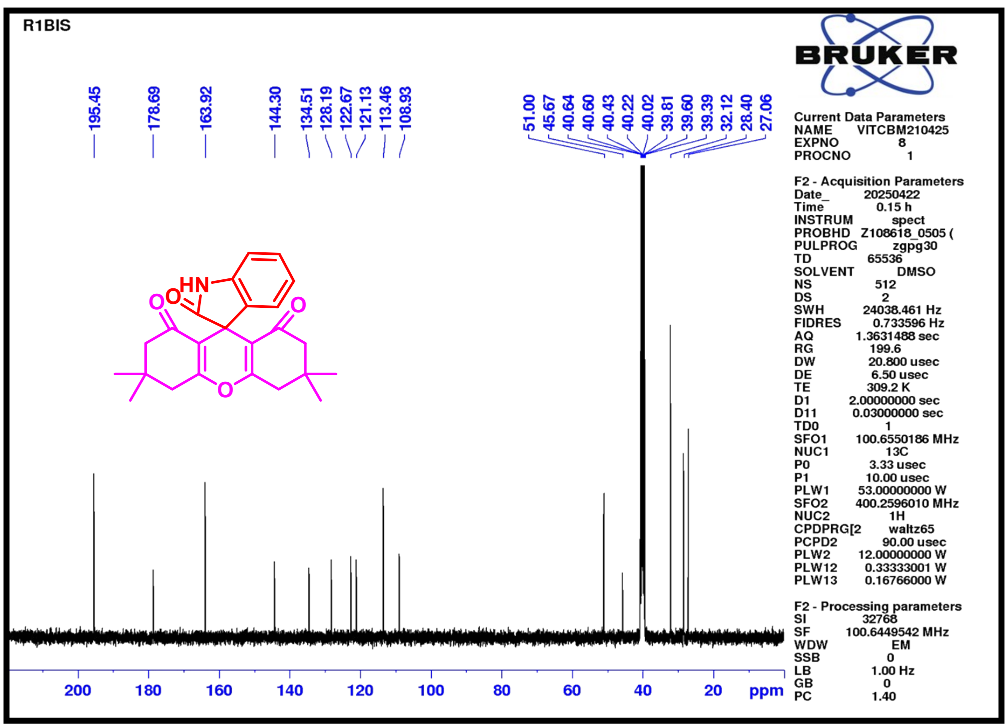


Figure S8. ^{13}C NMR spectrum (100 MHz) of **8a** in DMSO-d$_6$.

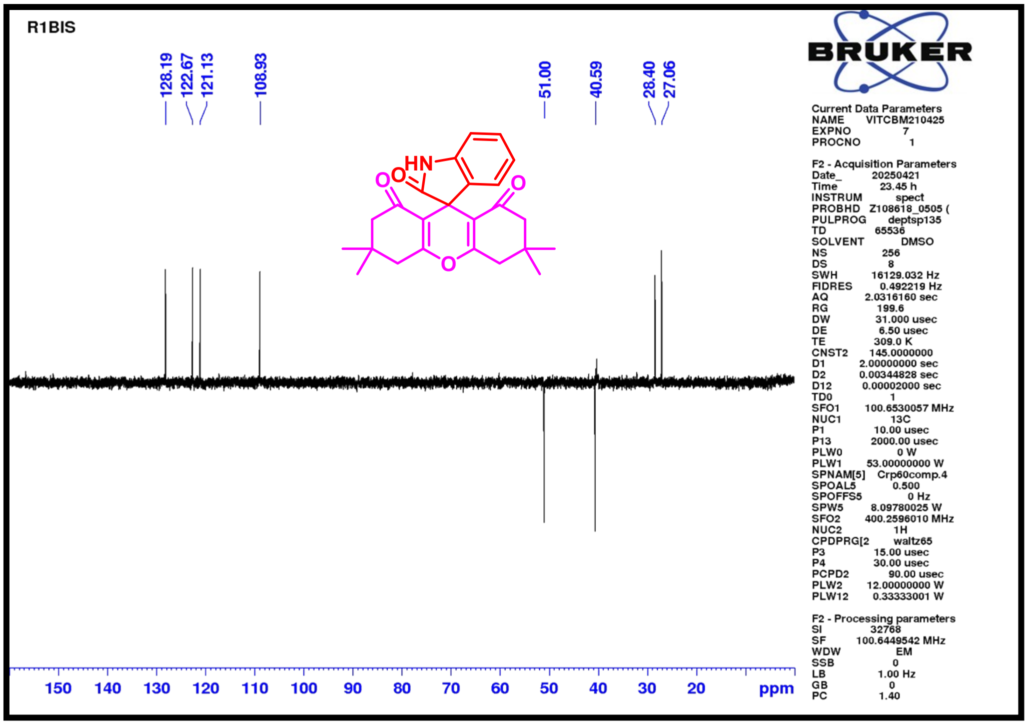


Figure S9. DEPT-135 spectrum (100 MHz) of **8a** in DMSO-d6.

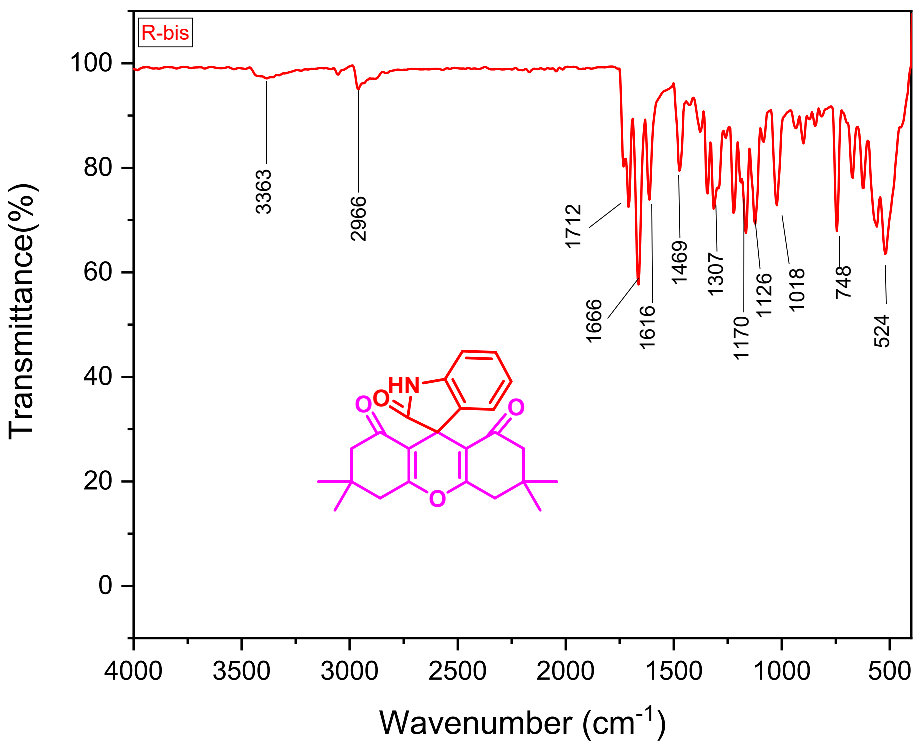


Figure S10. FT-IR spectrum of **8a**.

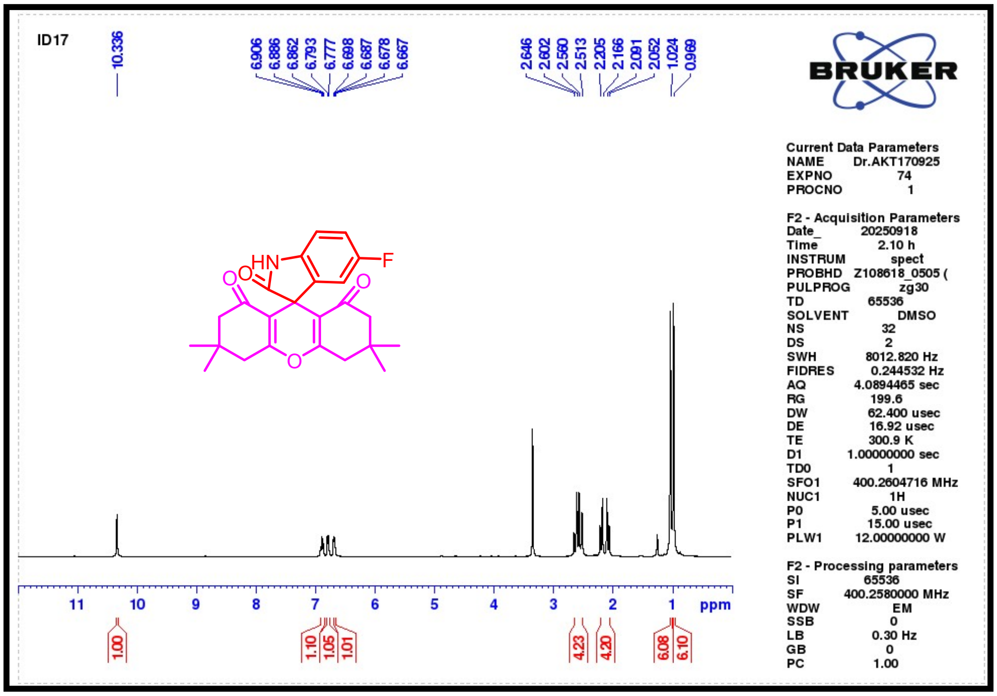


Figure S11. ^{1}H NMR spectrum (400 MHz) of **8b** in DMSO-d$_6$.

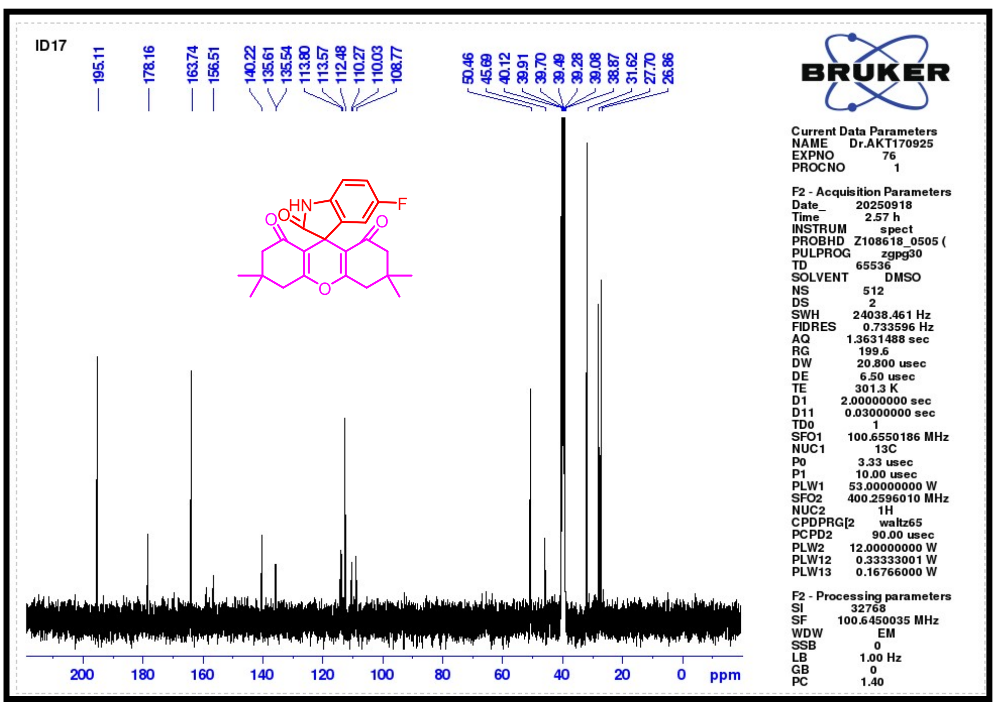


Figure S12. ^{13}C NMR spectrum (100 MHz) of **8b** in DMSO-d$_6$.

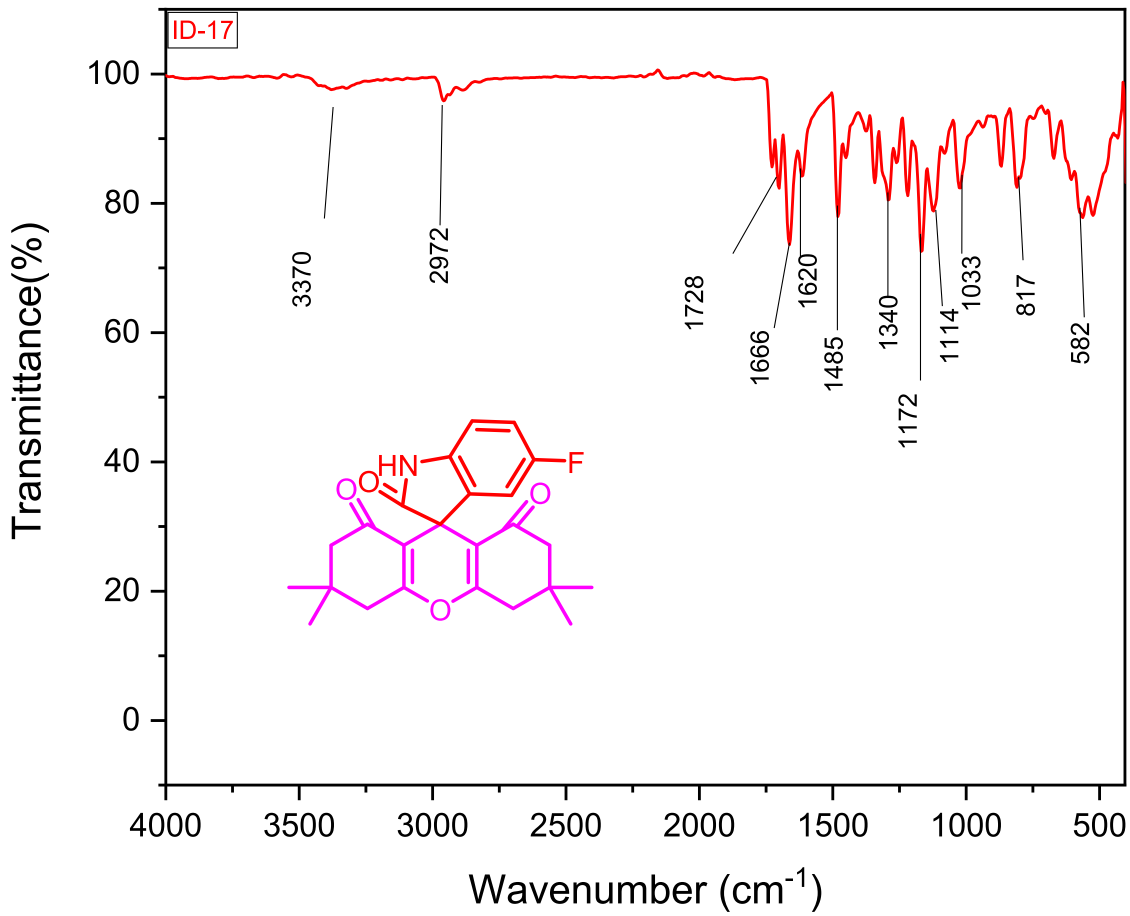


Figure S13. FT-IR spectrum of **8b**.

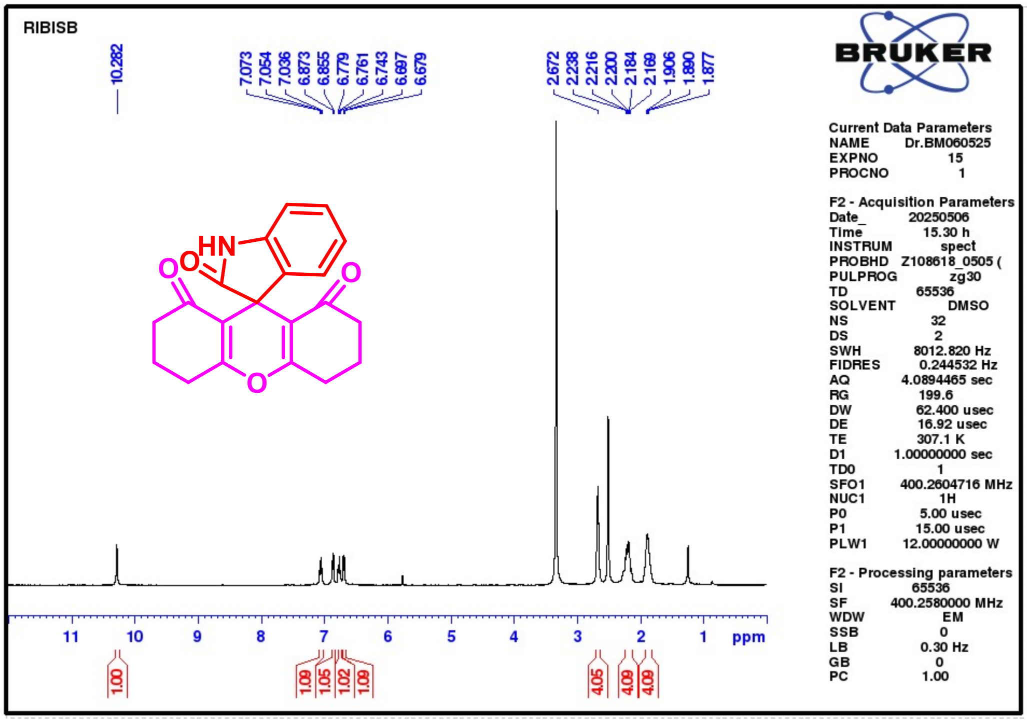


Figure S14. [1]H NMR spectrum (400 MHz) of **8c** in DMSO-d6.

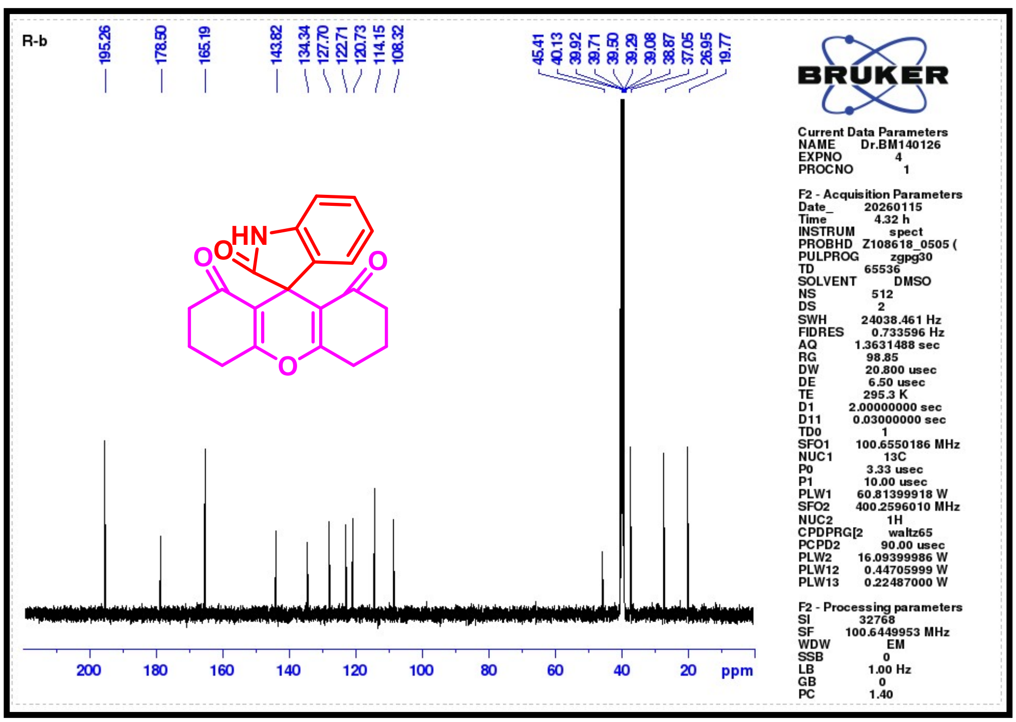


Figure S15. [13]C NMR spectrum (100 MHz) of **8c** in DMSO-d6.

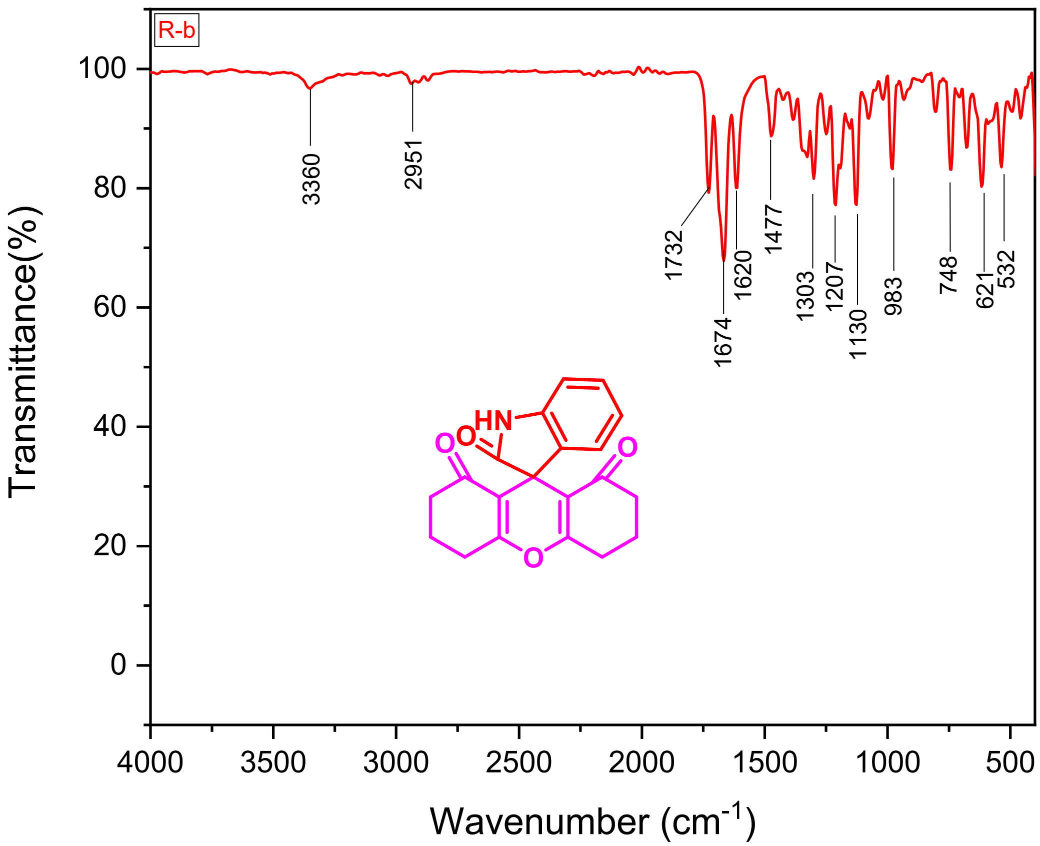


Figure S16. FT-IR spectrum of **8c.**

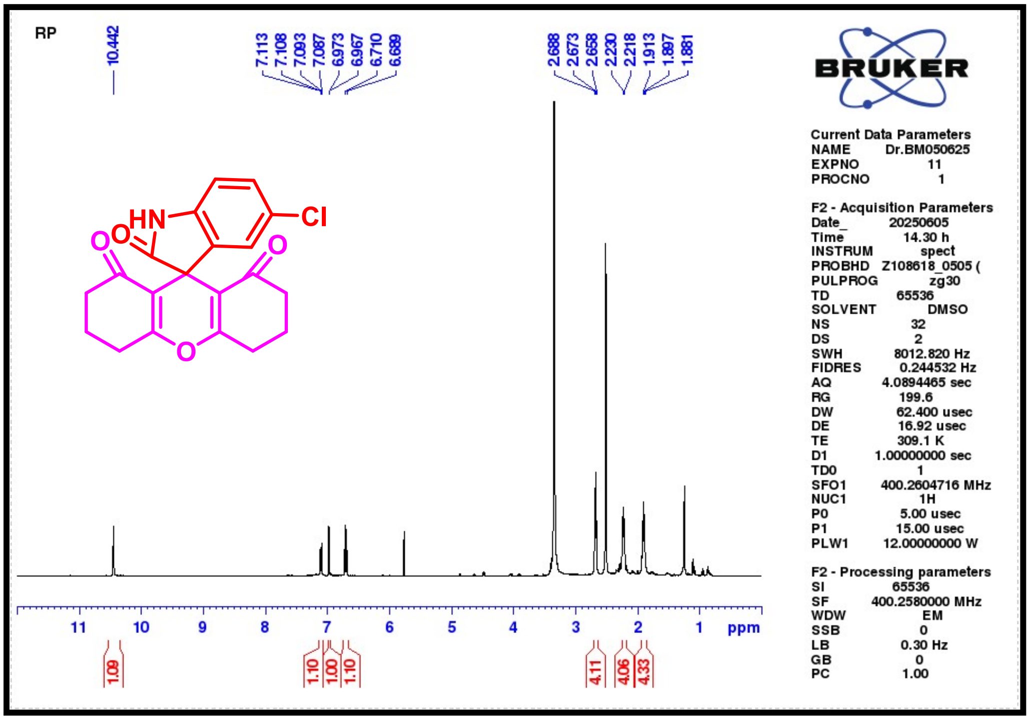


Figure S17. ^{1}H NMR spectrum (400 MHz) of **8d** in DMSO-d_6.

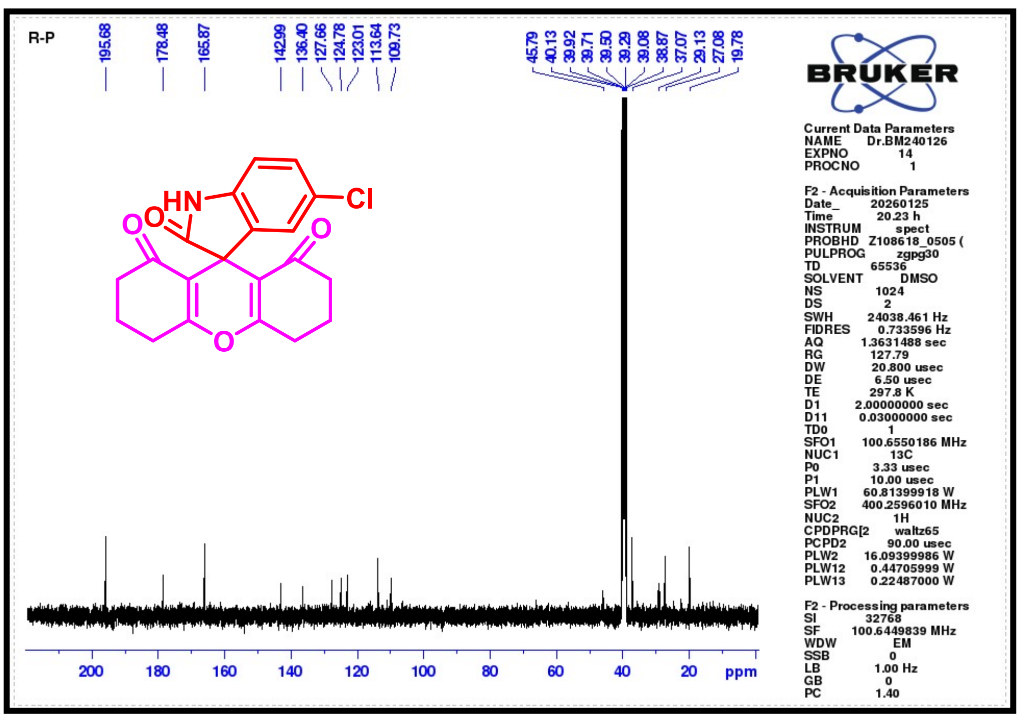


Figure S18. ^{13}C NMR spectrum (100 MHz) of **8d** in DMSO-d_6.

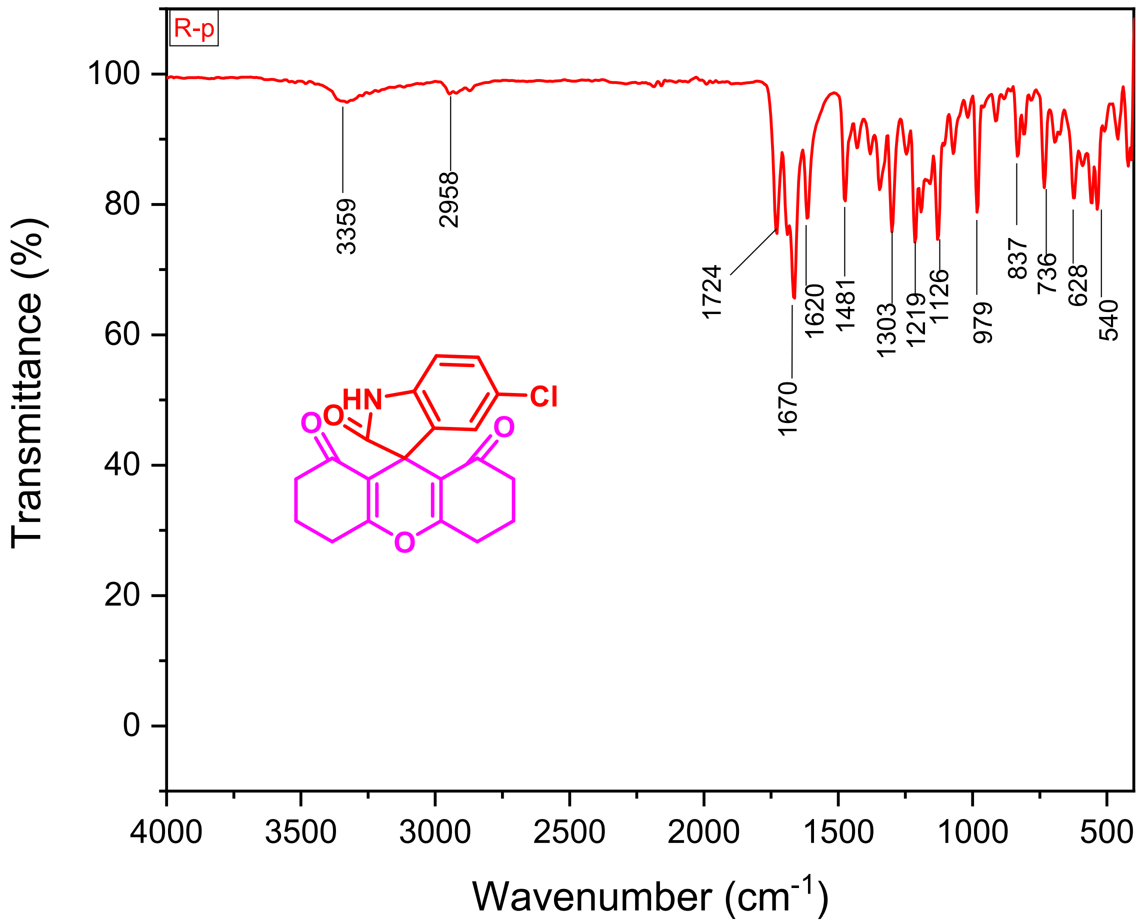


Figure S19. FT-IR spectrum of **8d**.

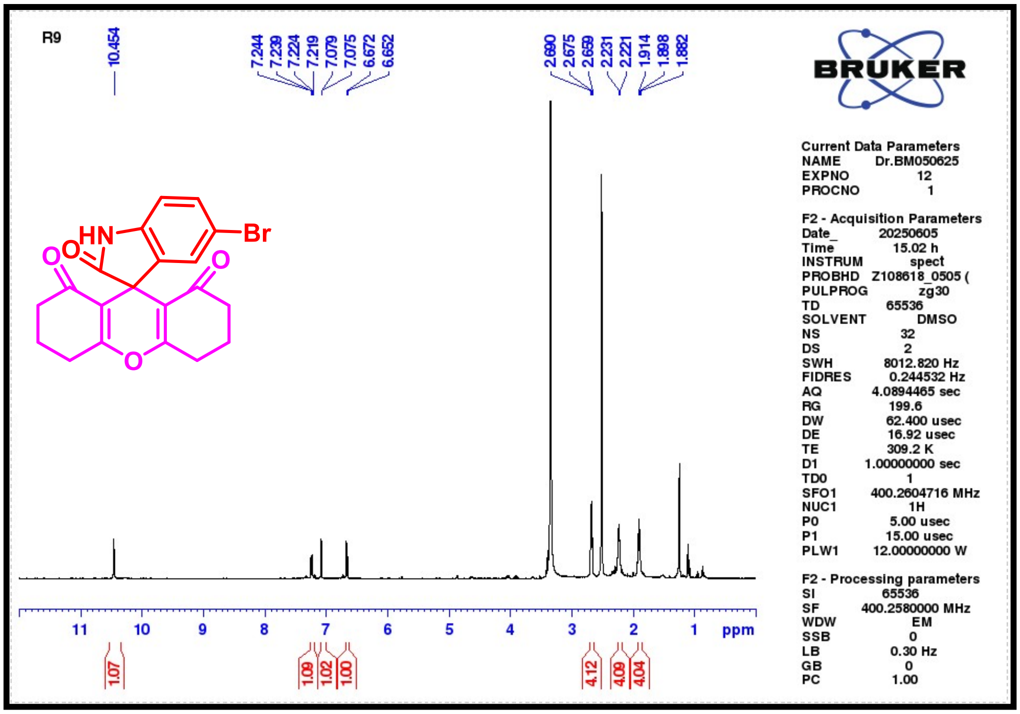


Figure S20. ^{1}H NMR spectrum (400 MHz) of **8e** in DMSO-d_6.

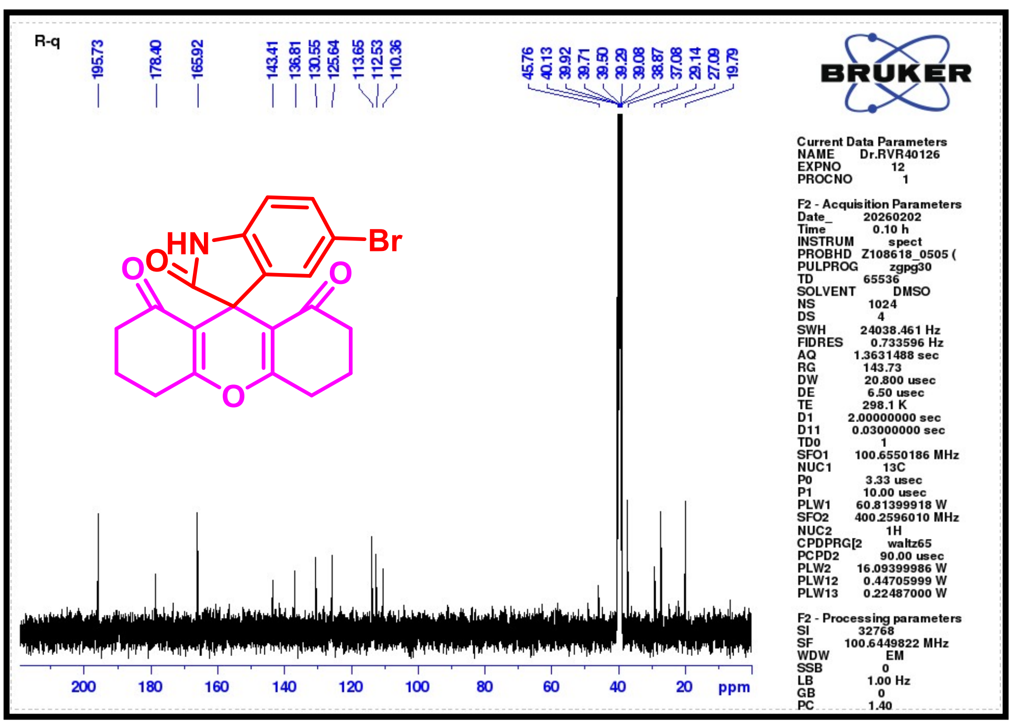


Figure S21. ^{13}C NMR spectrum (100 MHz) of **8e** in DMSO-d_6.

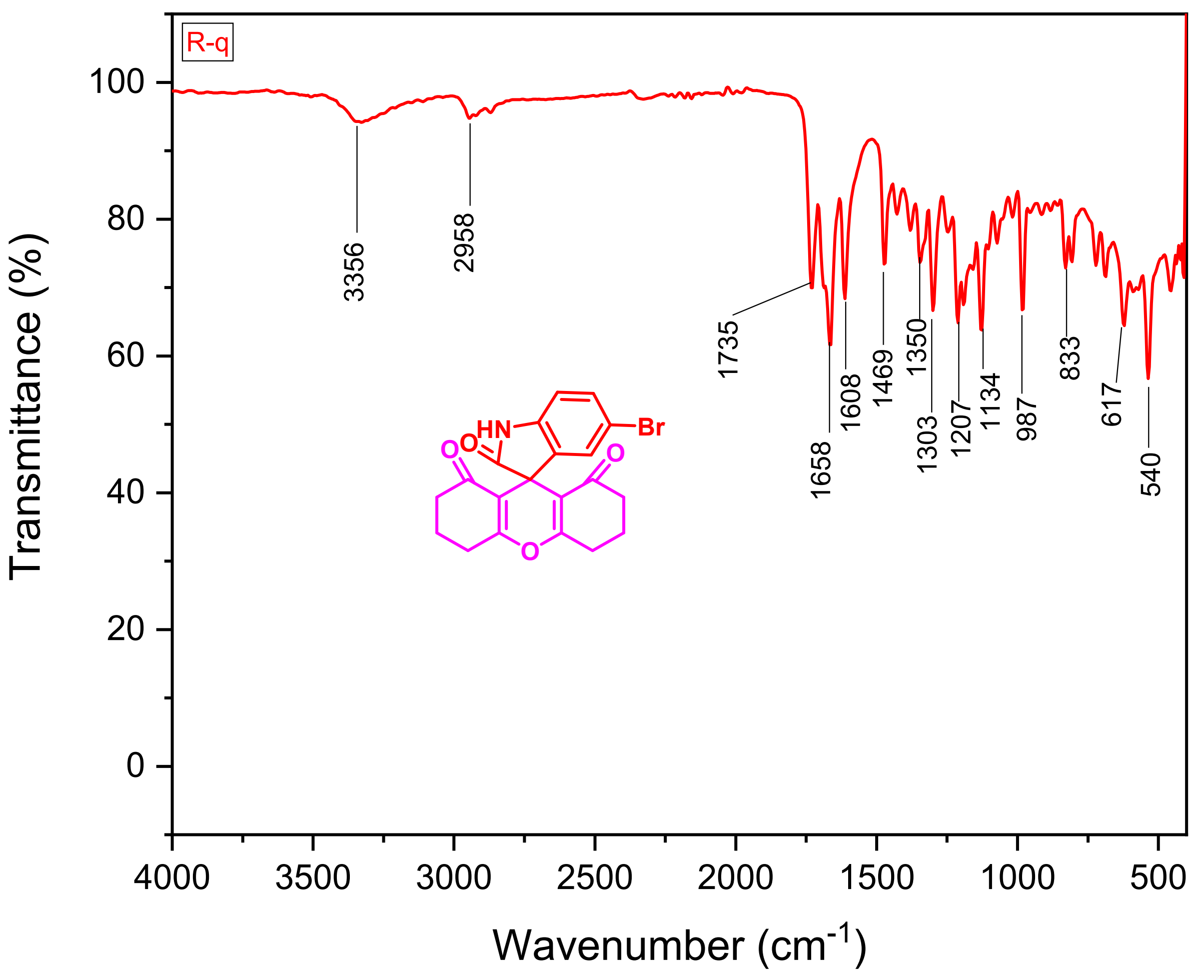


Figure S22. FT-IR spectrum of **8e.**

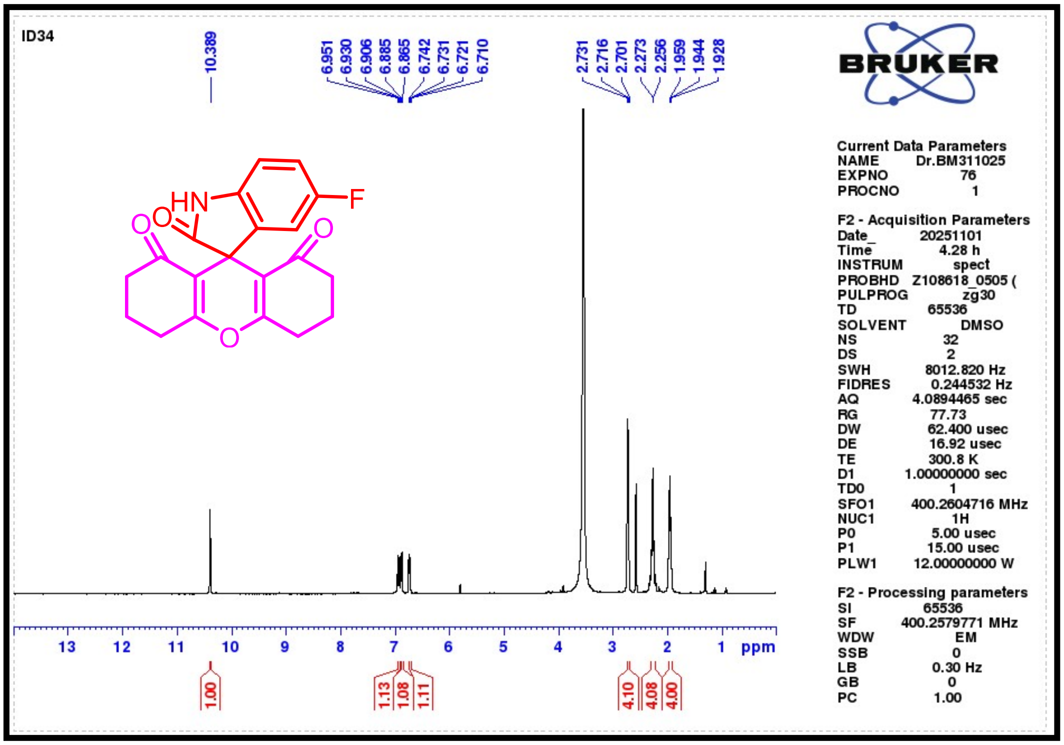


Figure S23. ^{1}H NMR spectrum (400 MHz) of **8f** in DMSO-d6.

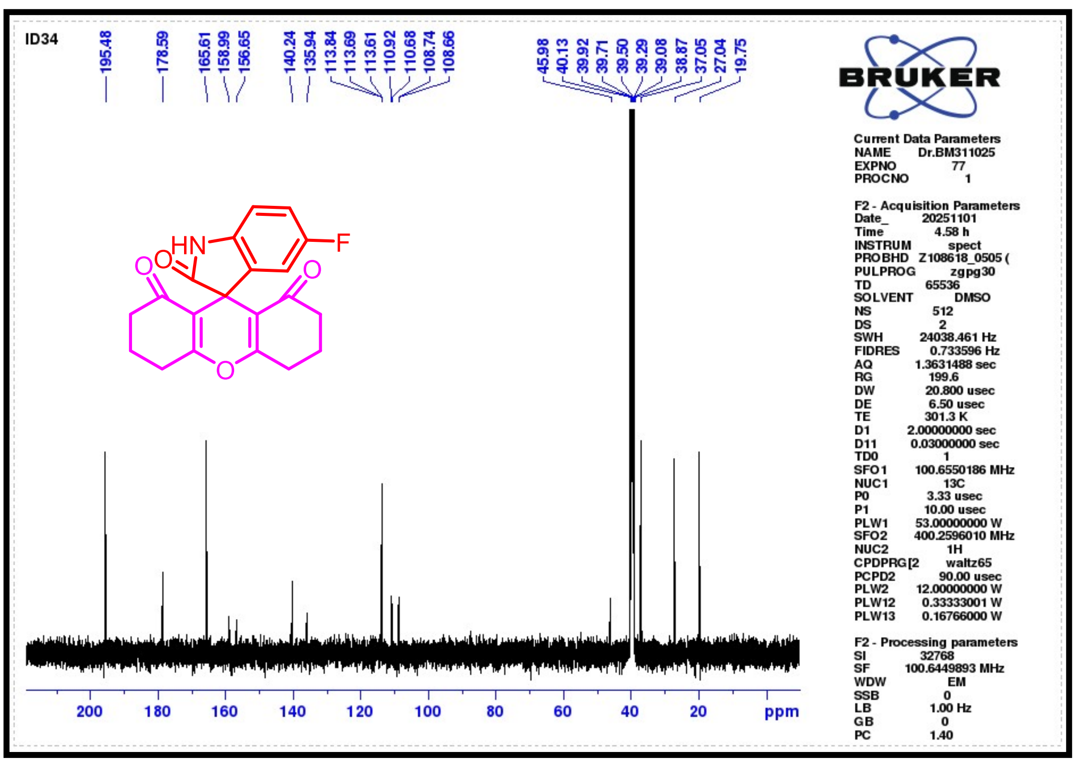


Figure S24. ^{13}C NMR spectrum (100 MHz) of **8f** in DMSO-d6.

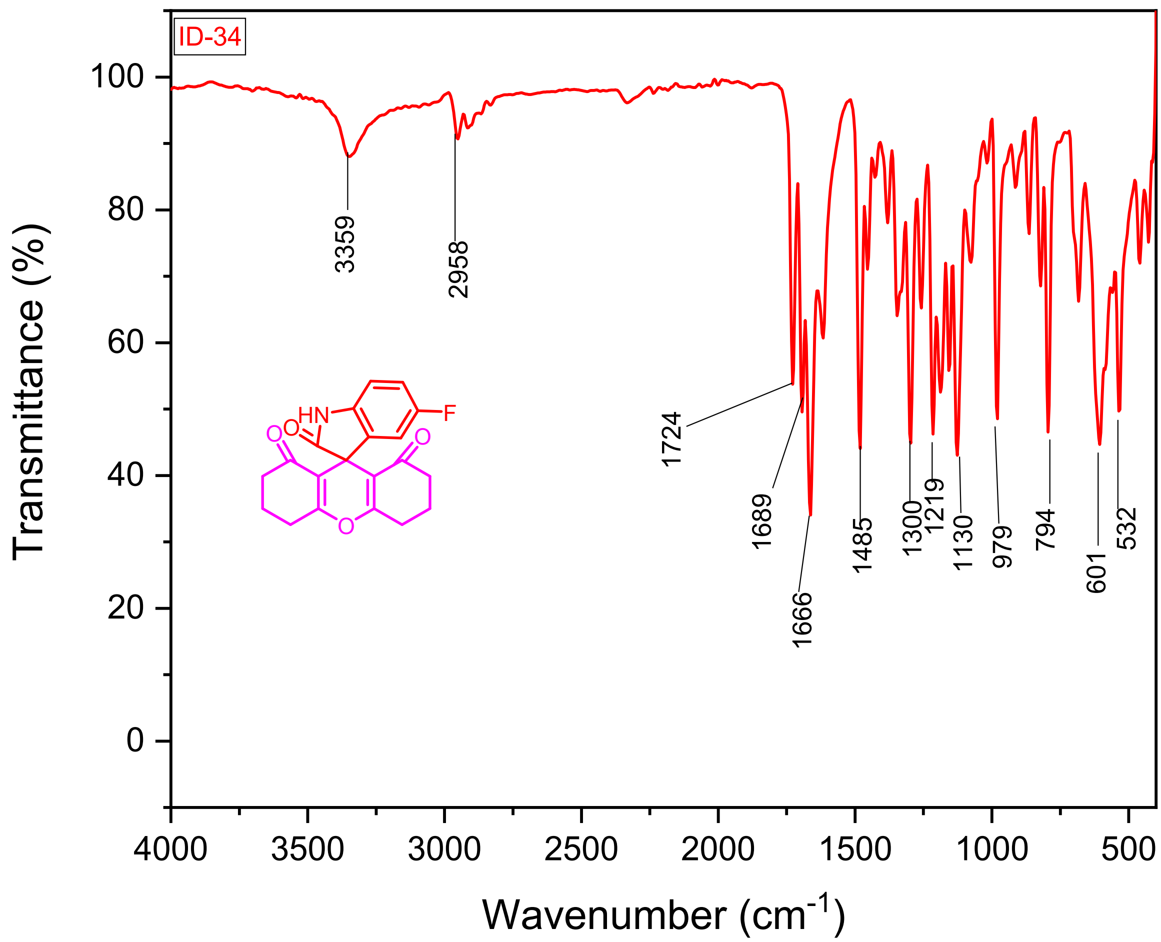


Figure S25. FT-IR spectrum of **8f**.

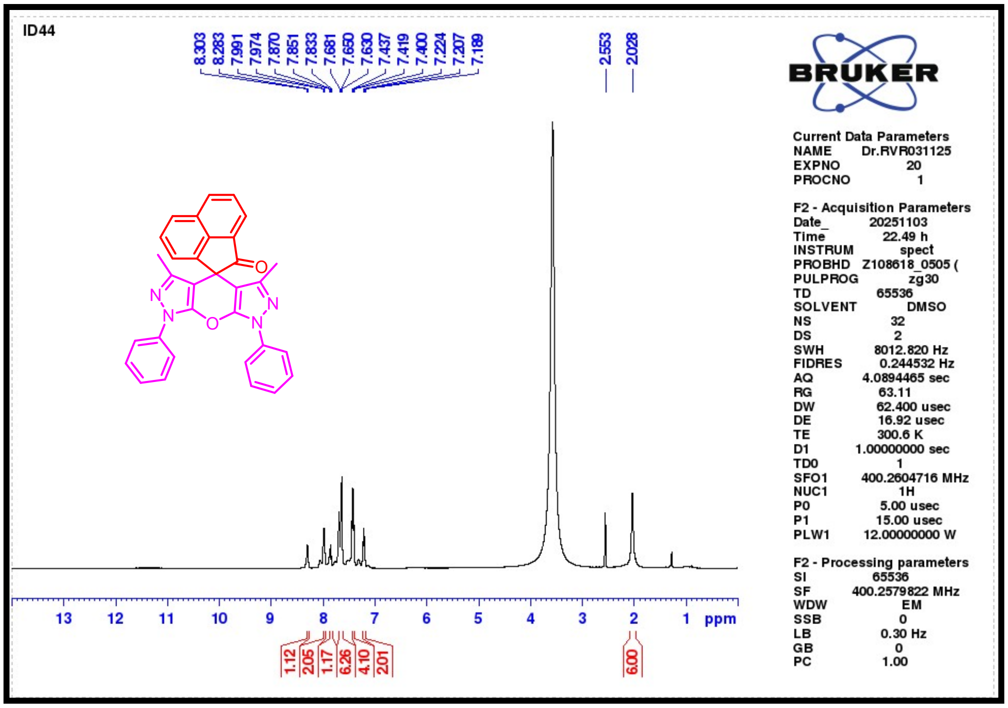


Figure S26. ^{1}H NMR spectrum (400 MHz) of **8g** in DMSO-d$_6$.

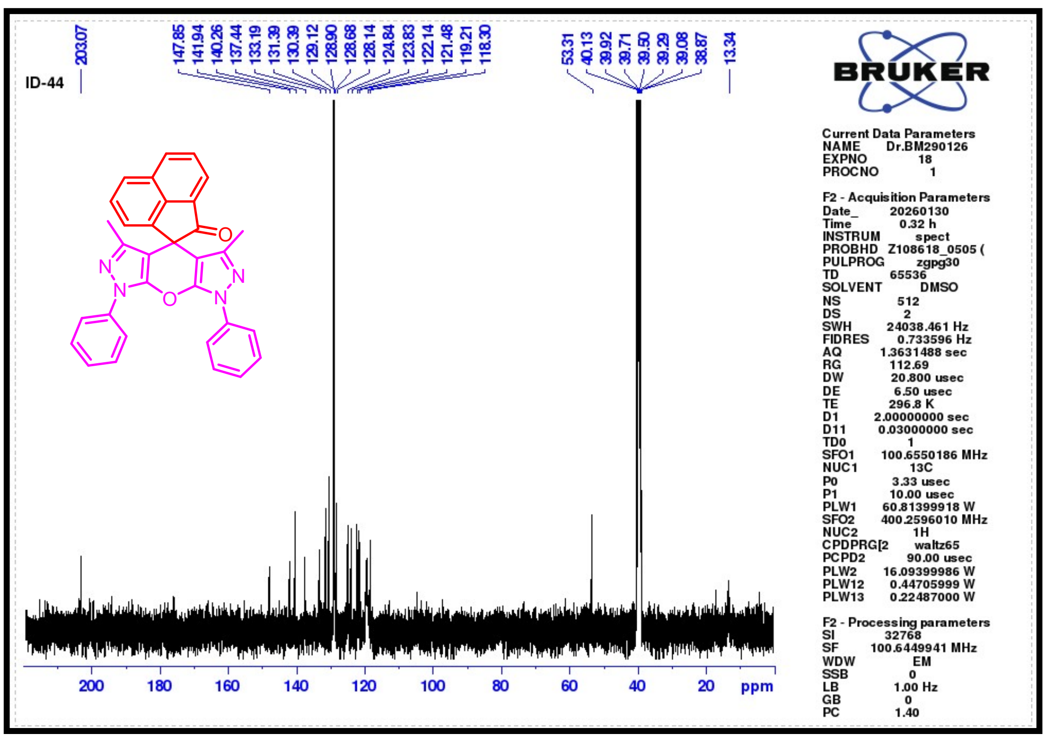


Figure S27. ^{13}C NMR spectrum (100 MHz) of **8g** in DMSO-d$_6$.

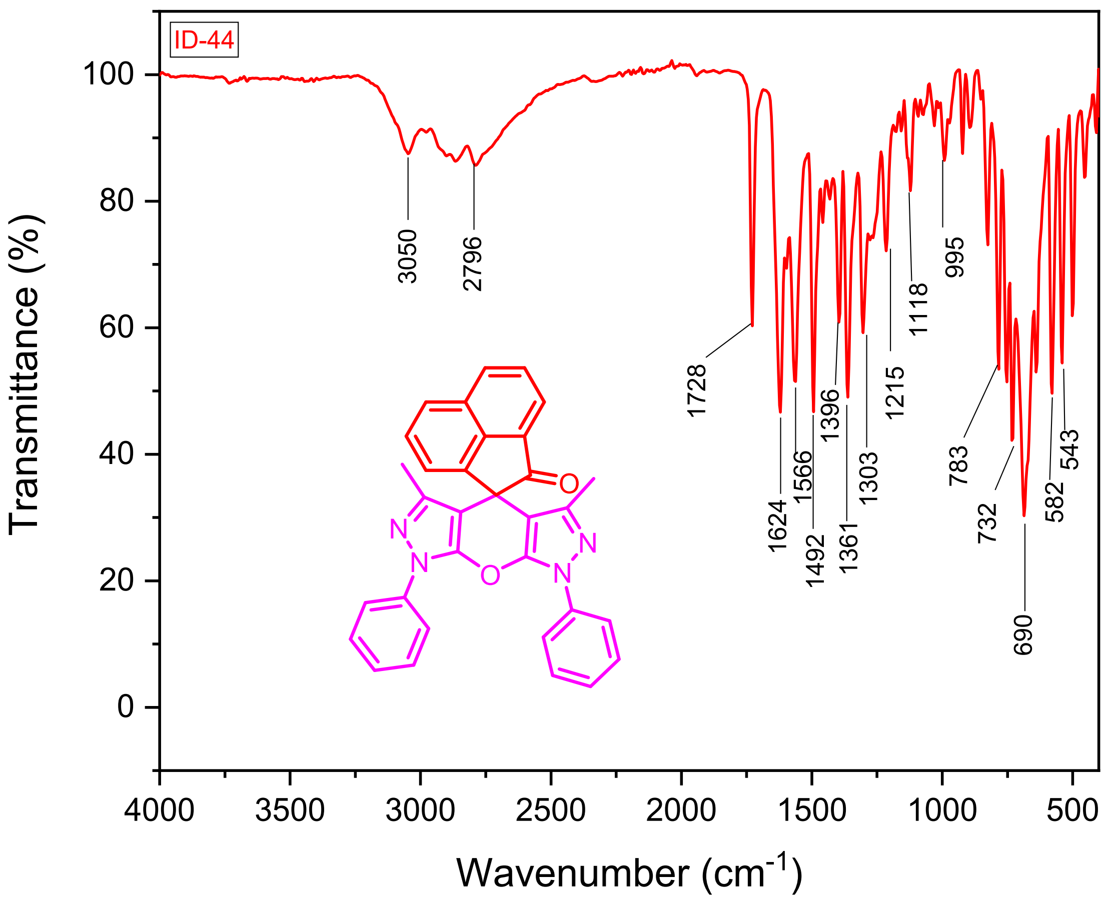


Figure S28. FT-IR spectrum of **8g**.

Unsymmetric Compounds **9a-9m**

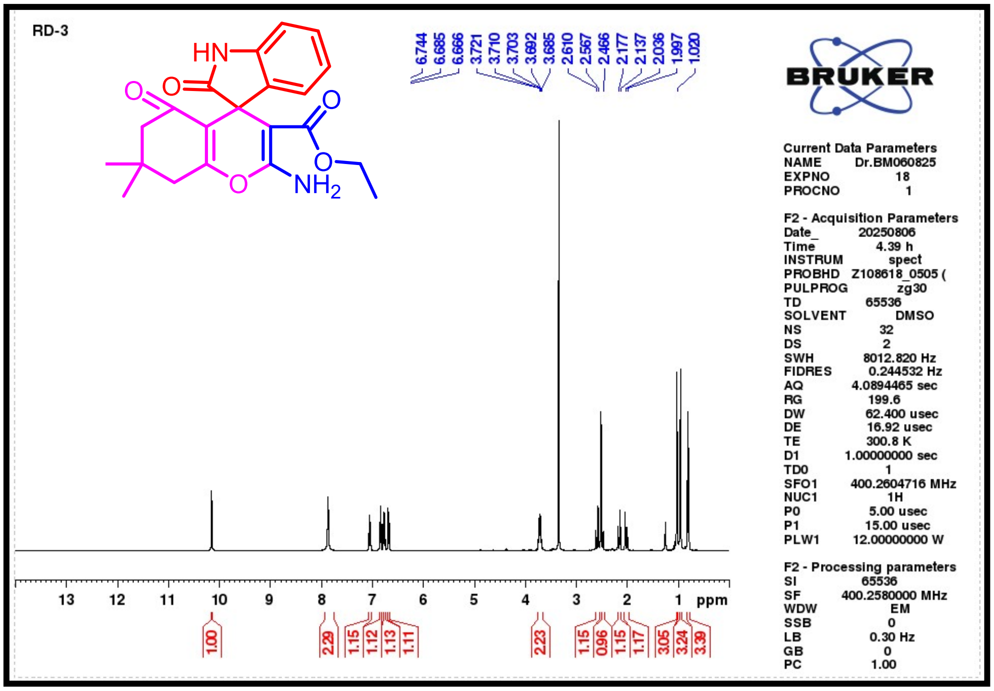


Figure S29. ^{1}H NMR spectrum (400 MHz) of **9a** in DMSO-d6.

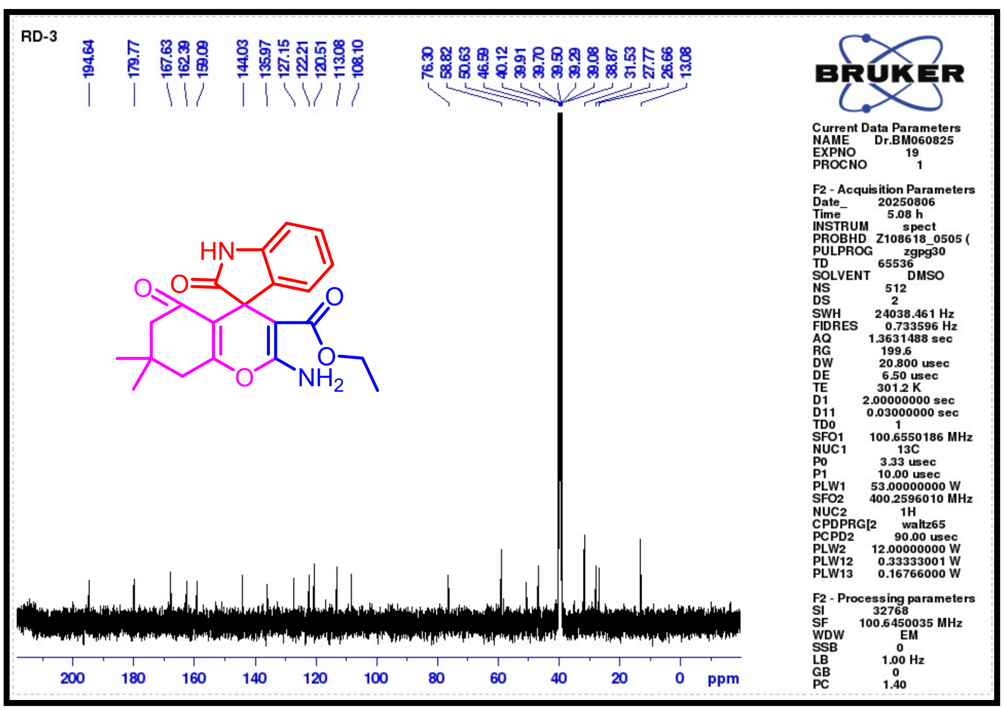


Figure S30. ^{13}C NMR spectrum (100 MHz) of **9a** in DMSO-d6.

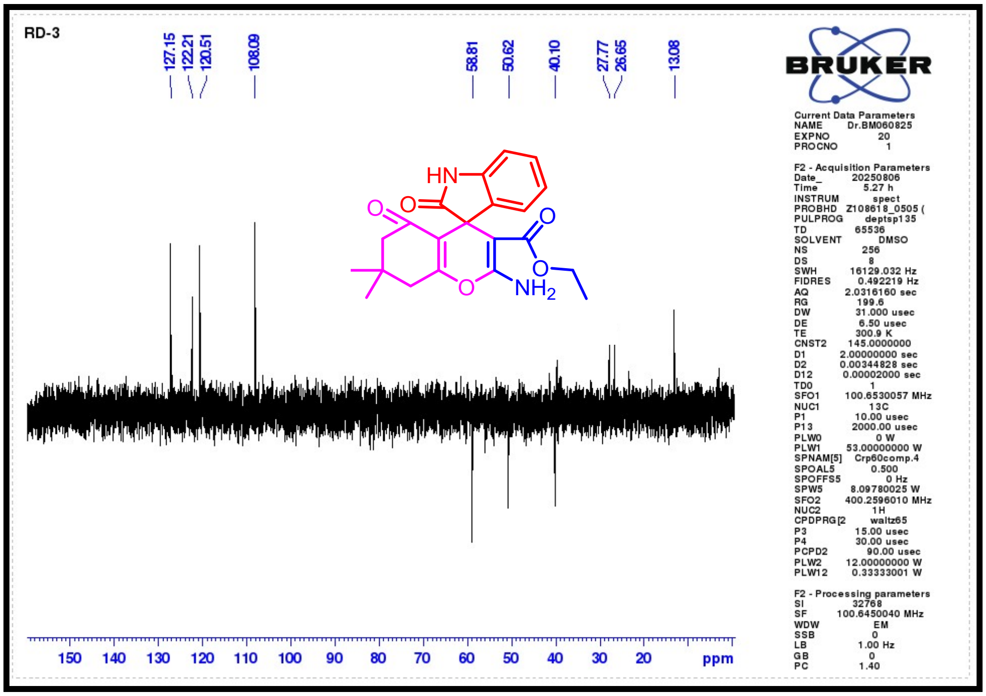


Figure S31. DEPT-135 spectrum (100 MHz) of **9a** in DMSO-d6.

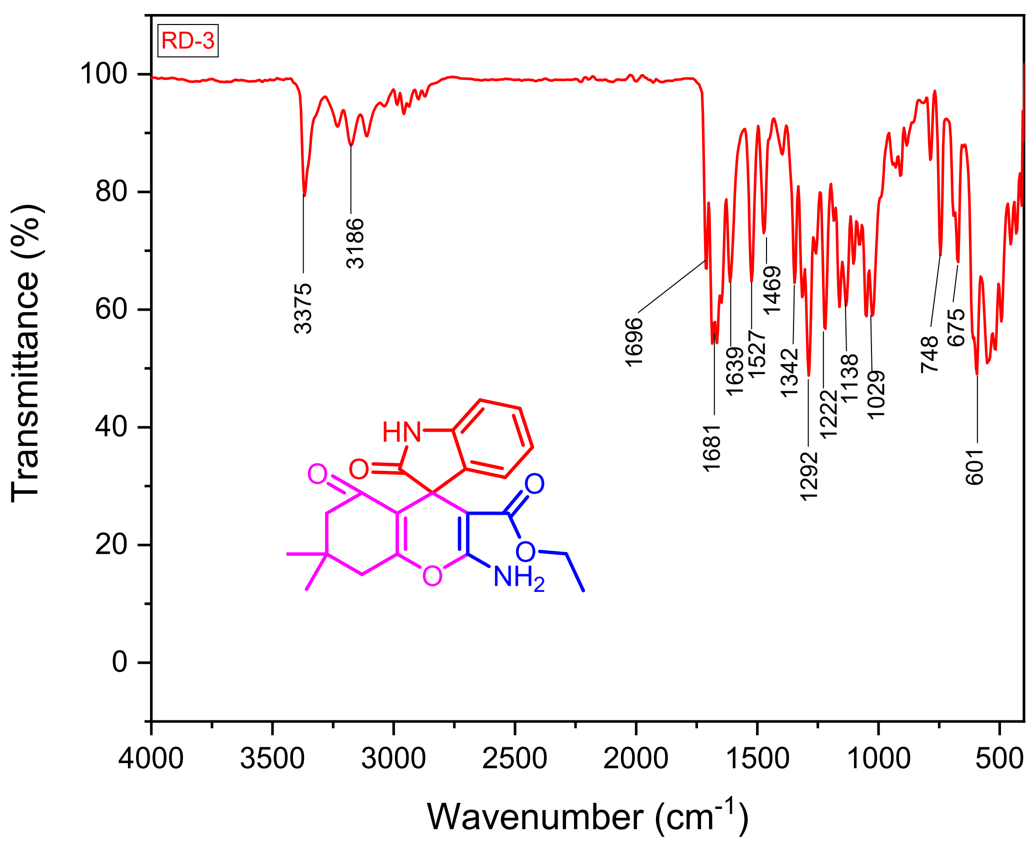


Figure S32. FT-IR spectrum of **9a**.

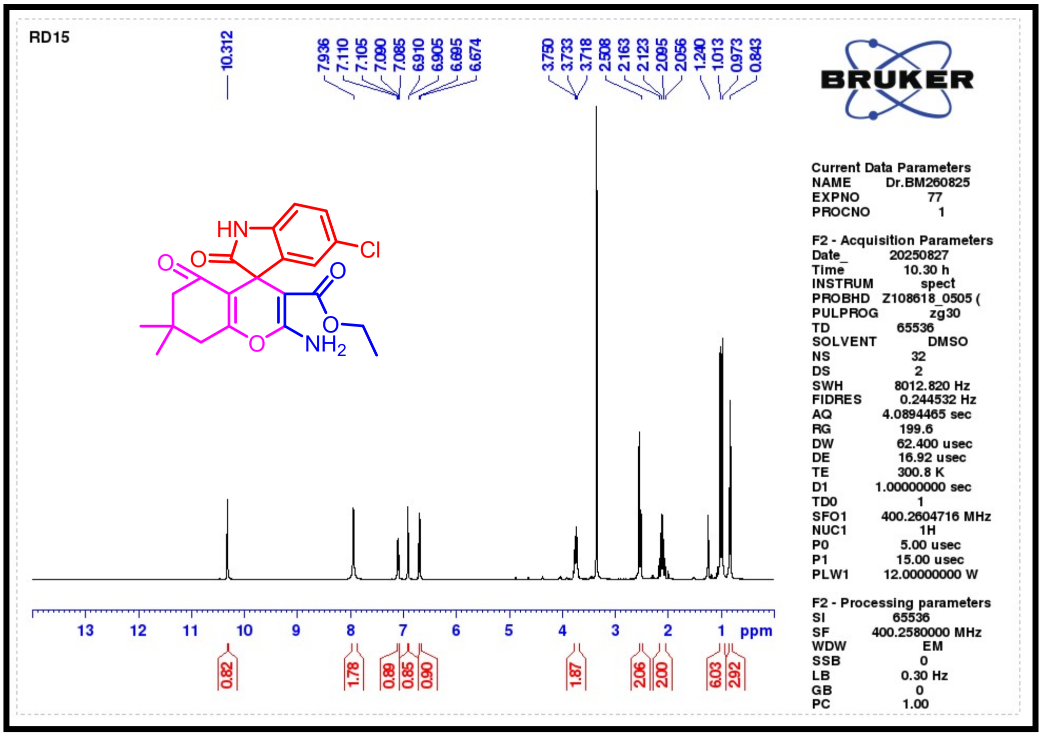


Figure S33. ^{1}H NMR spectrum (400 MHz) of **9b** in DMSO-d6.

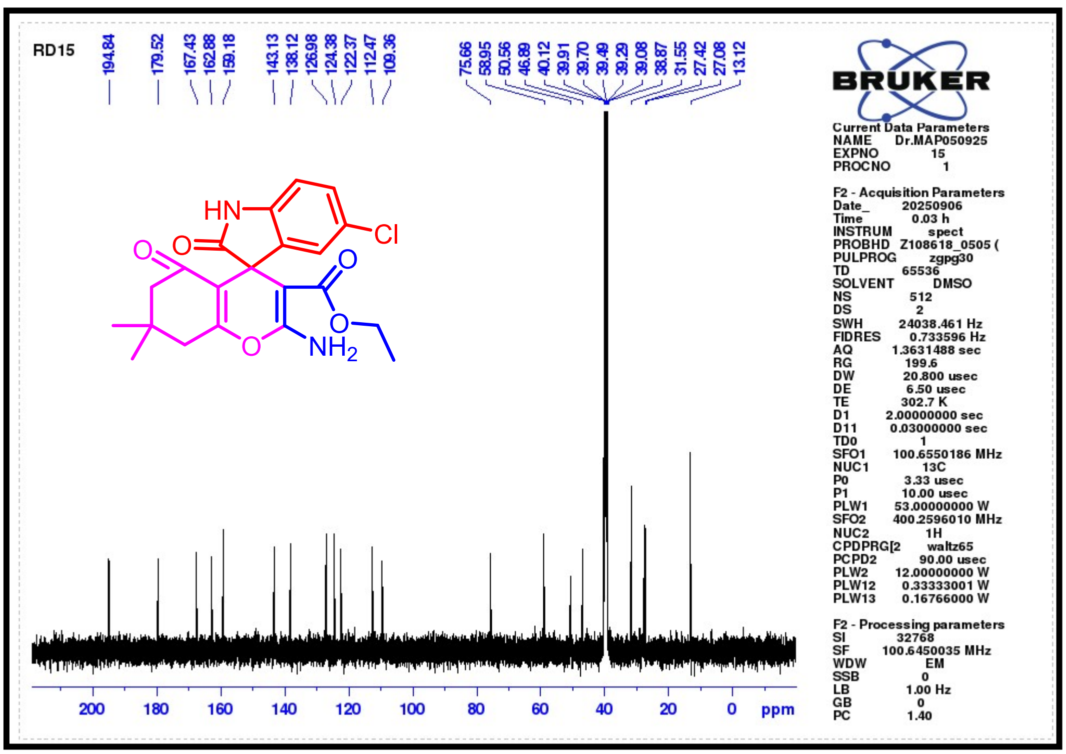


Figure S34. ^{13}C NMR spectrum (100 MHz) of **9b** in DMSO-d6.

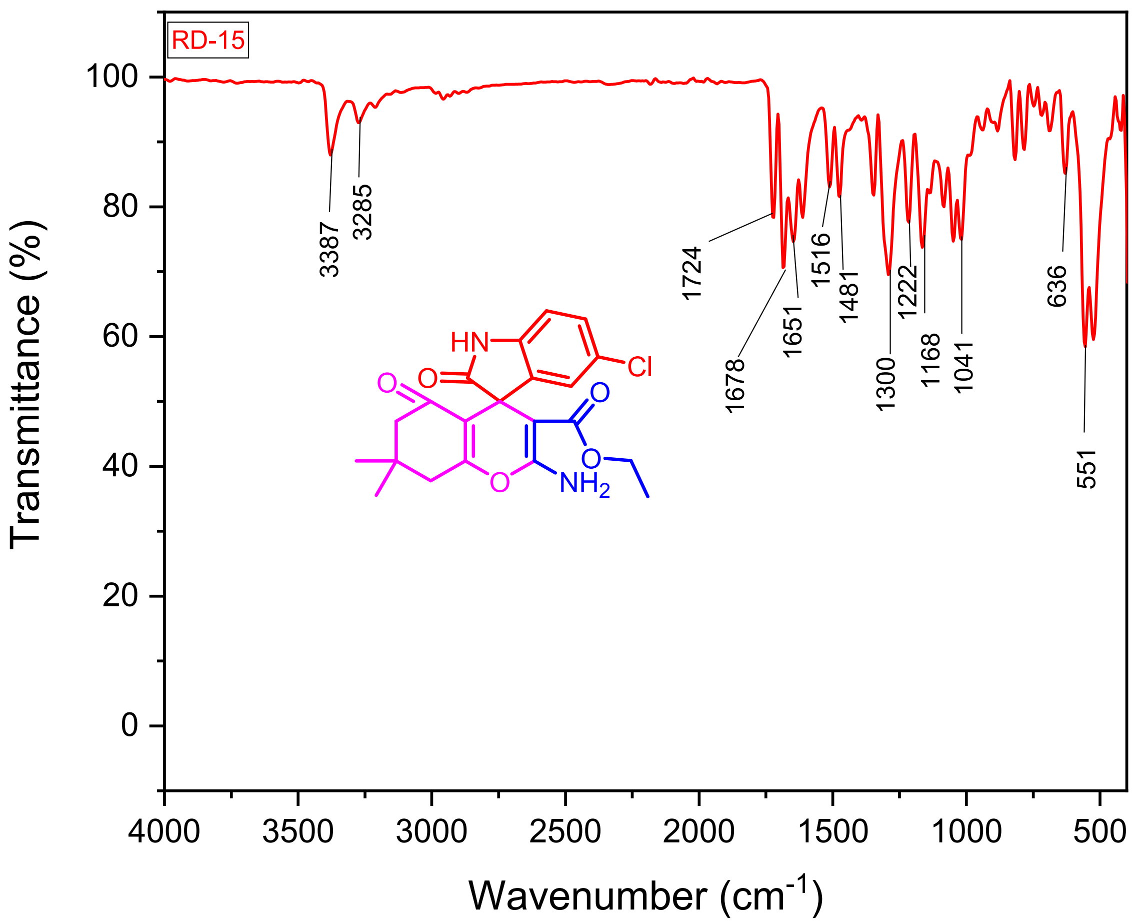


Figure S35. FT-IR spectrum of **9b**.

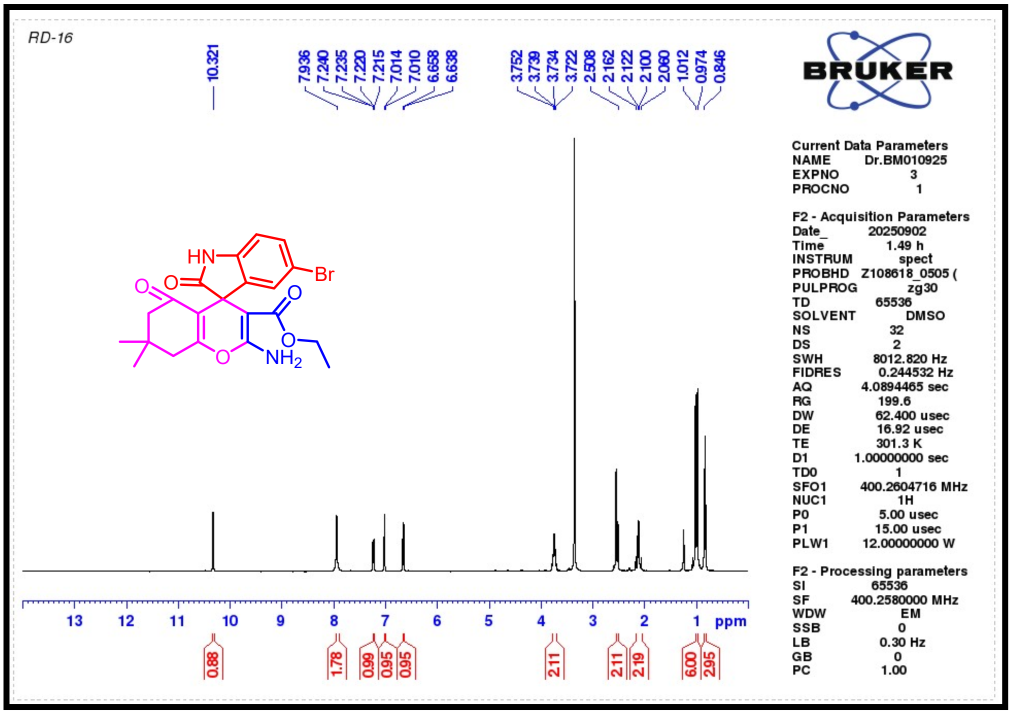


Figure S36. ^{1}H NMR spectrum (400 MHz) of **9c** in DMSO-d$_6$.

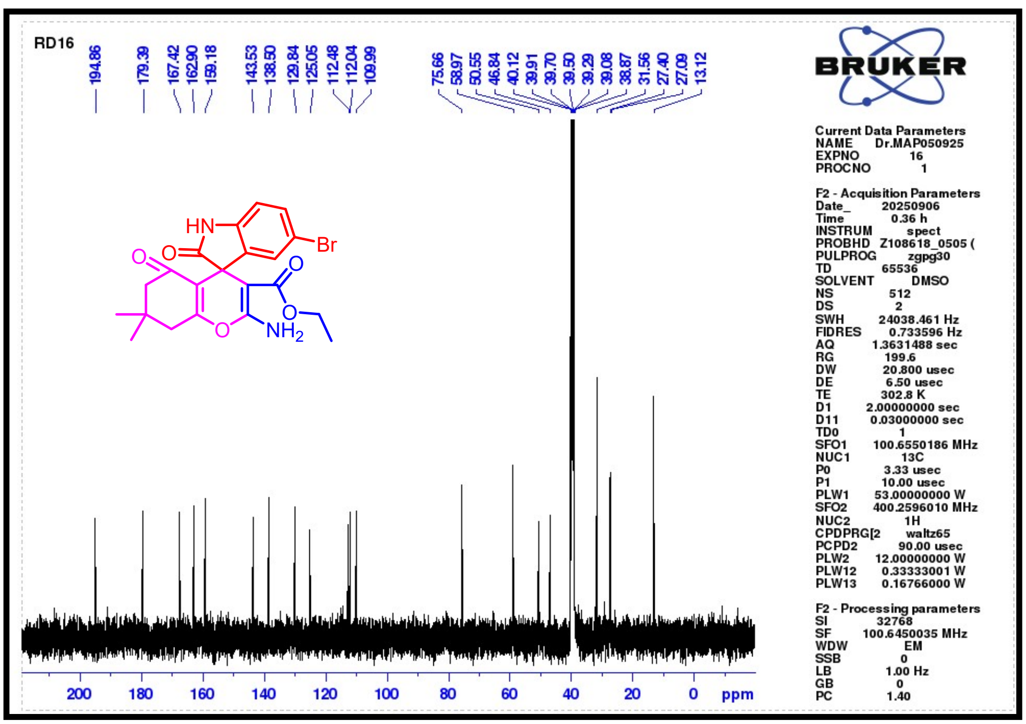


Figure S37. ^{13}C NMR spectrum (100 MHz) of **9c** in DMSO-d$_6$.

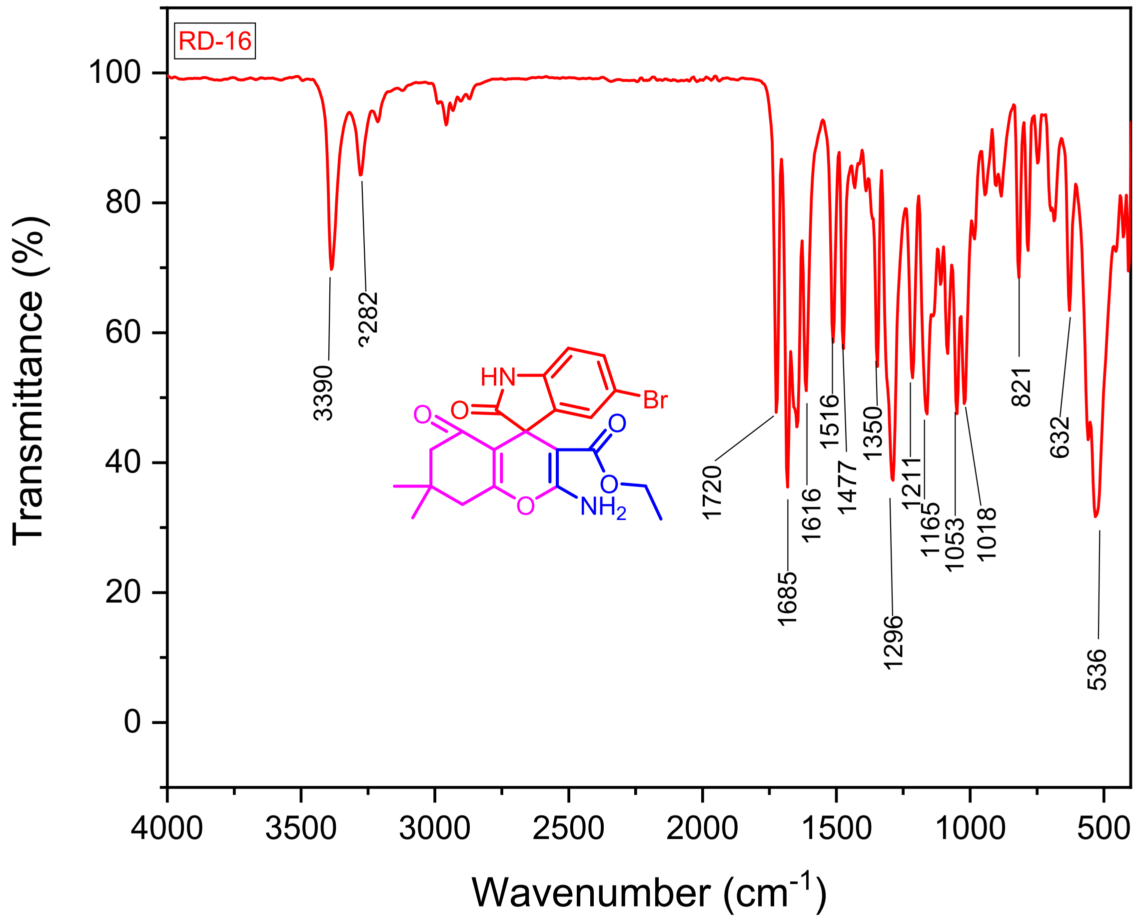


Figure S38. FT-IR spectrum of **9c.**

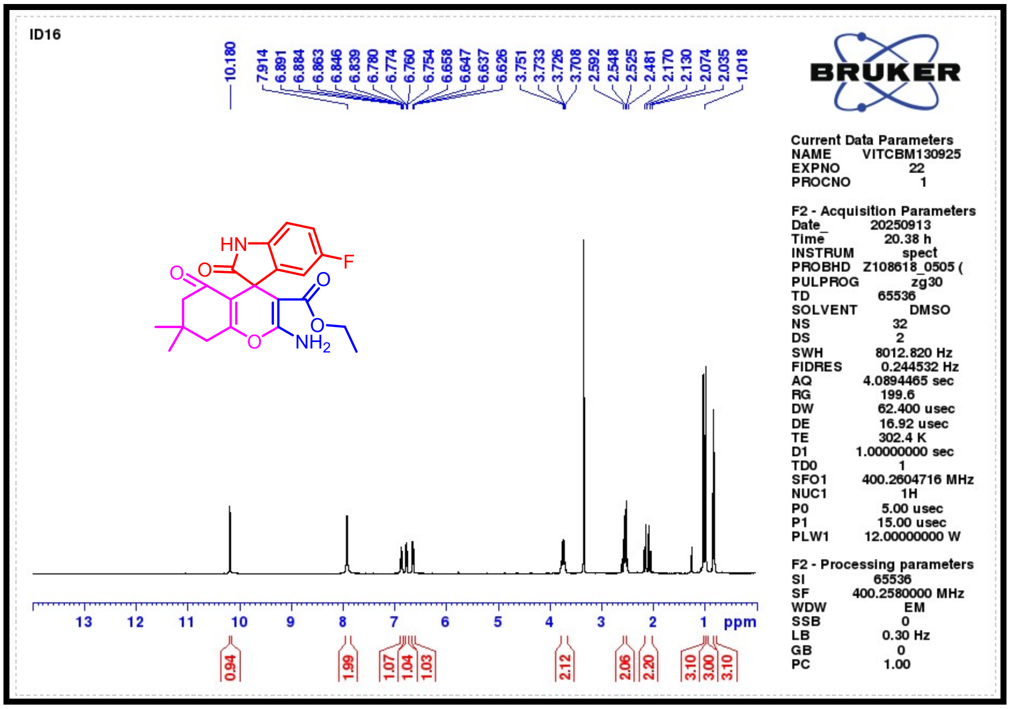


Figure S39. ^{1}H NMR spectrum (400 MHz) of **9d** in DMSO-d6.

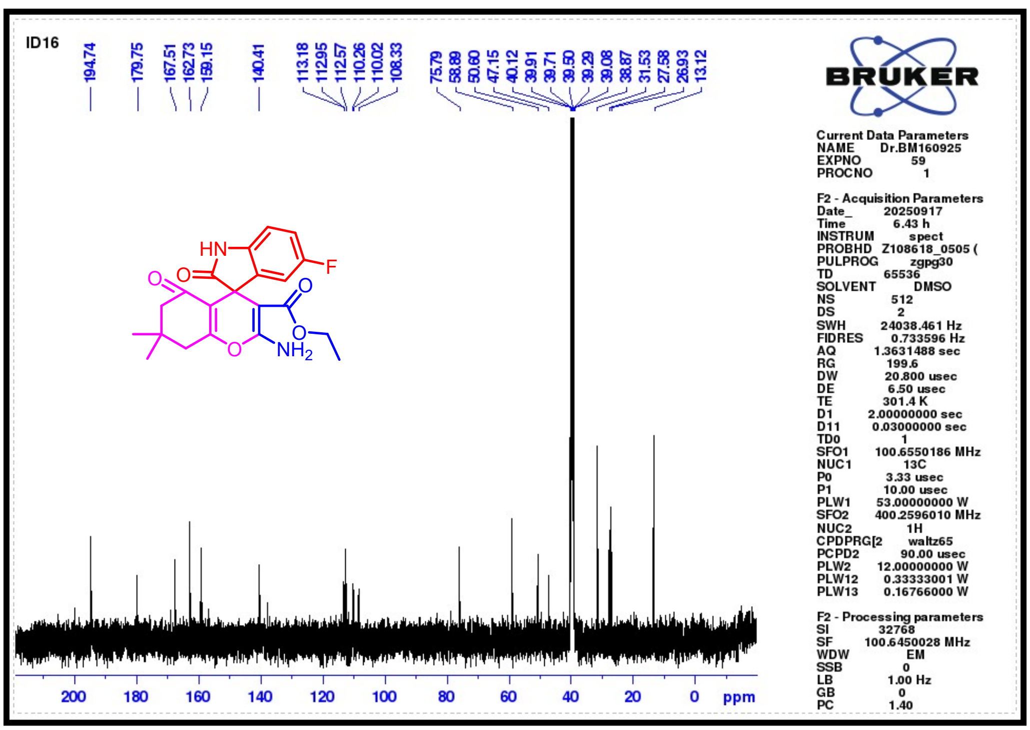


Figure S40. ^{13}C NMR spectrum (100 MHz) of **9d** in DMSO-d6.

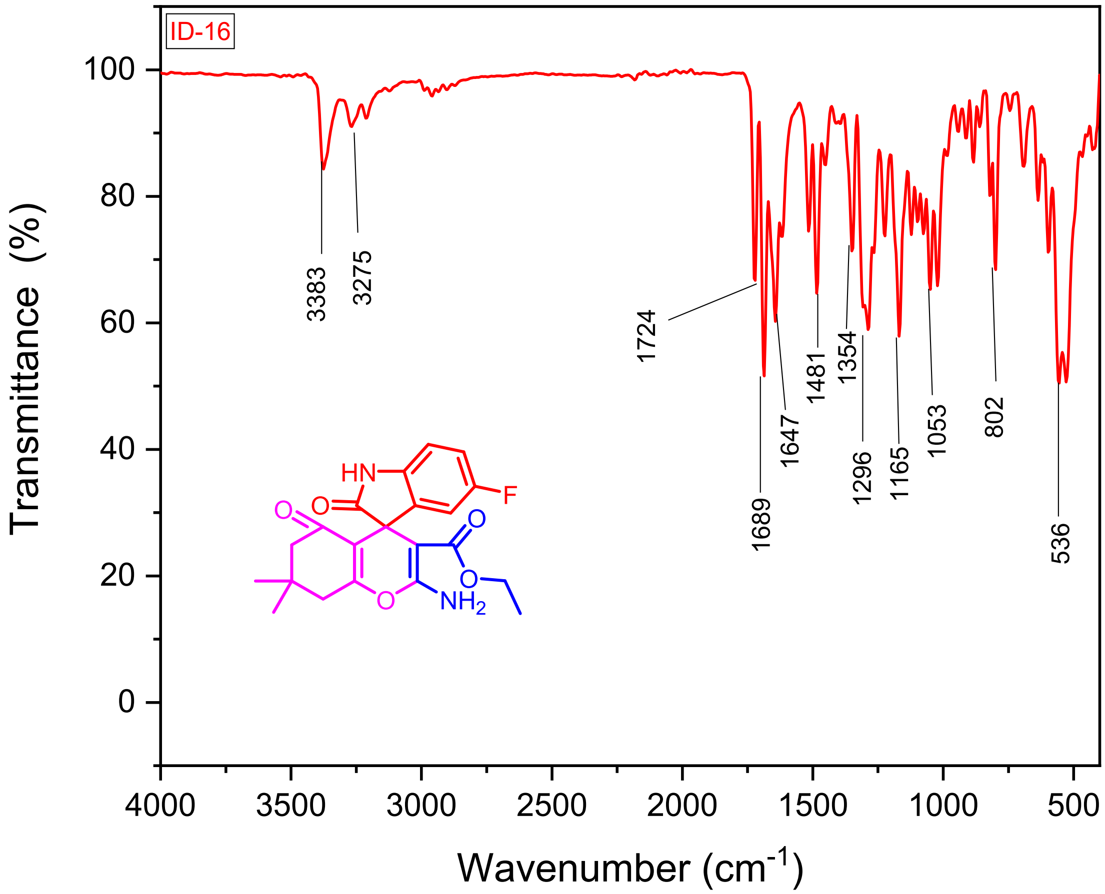


Figure S41. FT-IR spectrum of **9d.**

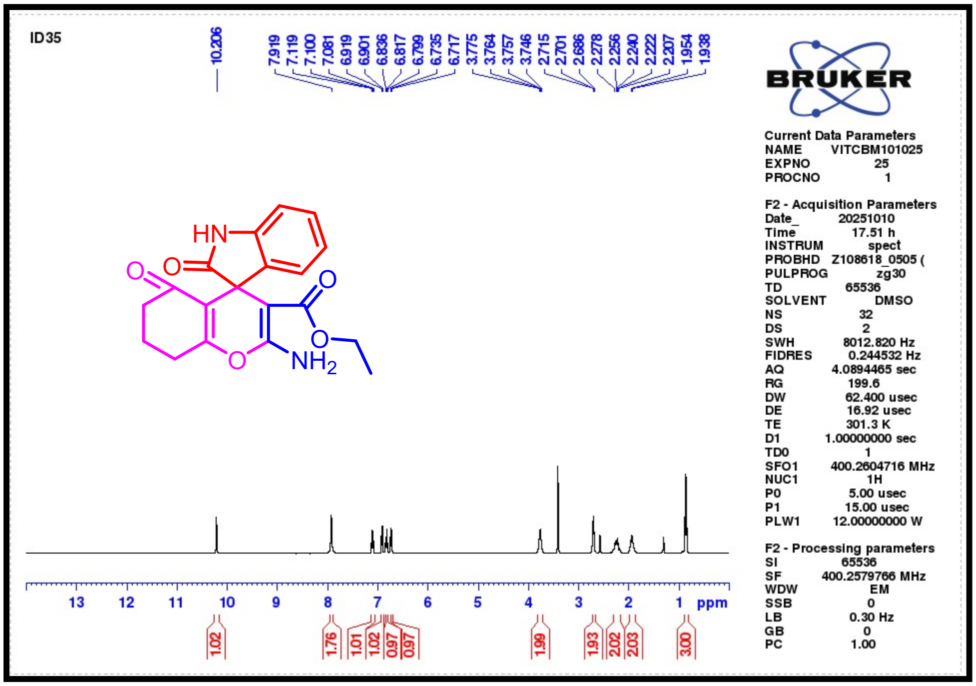


Figure S42. ^{1}H NMR spectrum (400 MHz) of **9e** in DMSO-d$_6$.

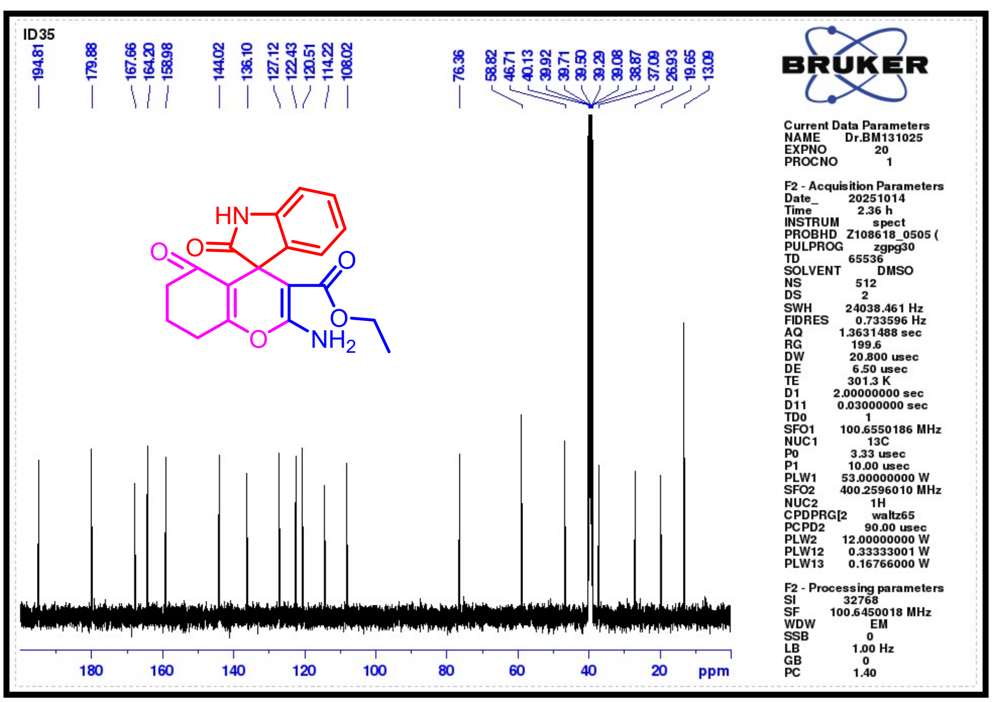


Figure S43. ^{13}C NMR spectrum (100 MHz) of **9e** in DMSO-d$_6$.

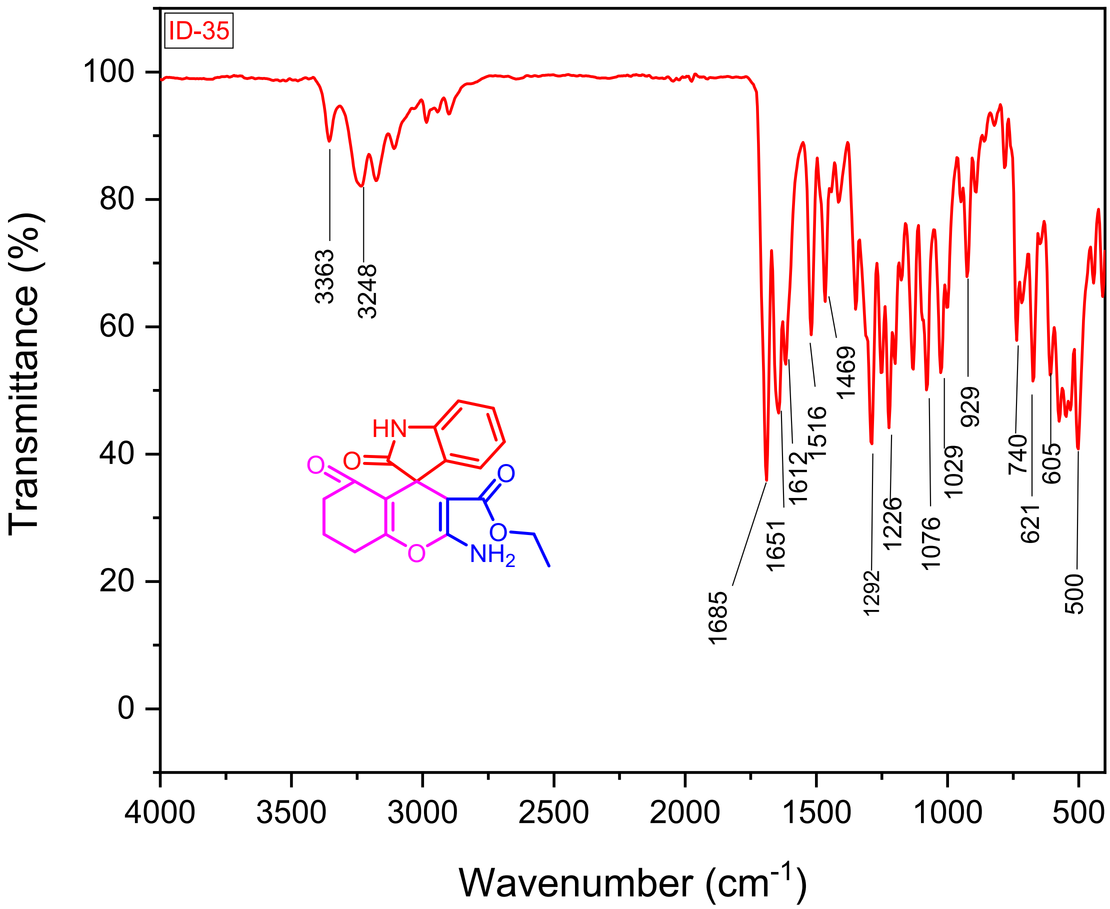


Figure S44. FT-IR spectrum of **9e**.

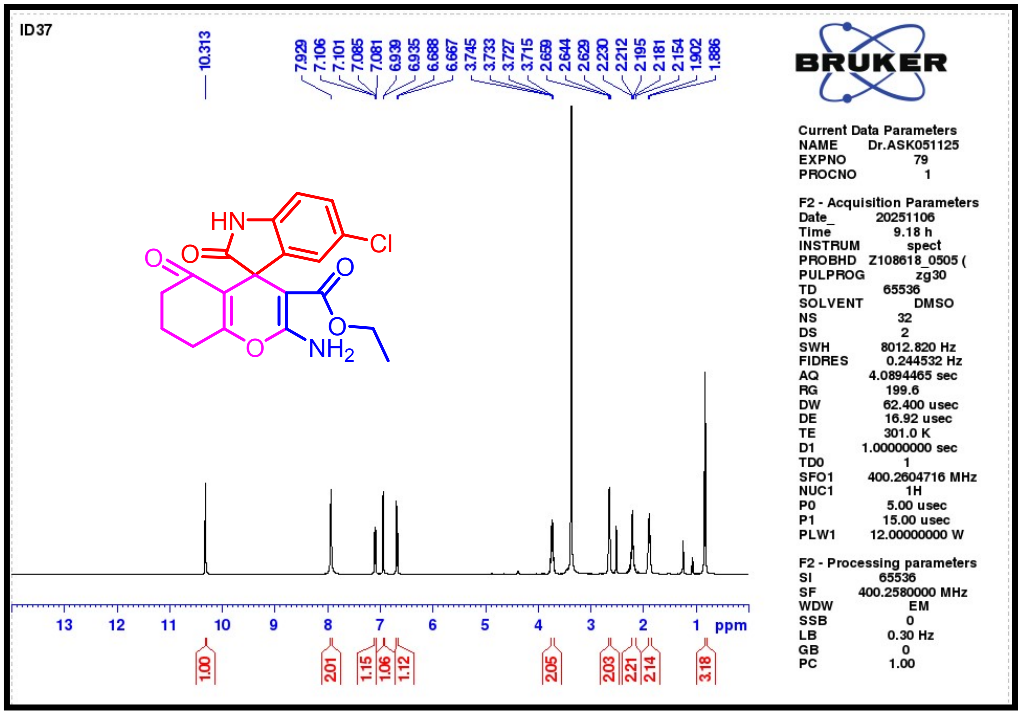


Figure S45. ^{1}H NMR spectrum (400 MHz) of **9f** in DMSO-d_6.

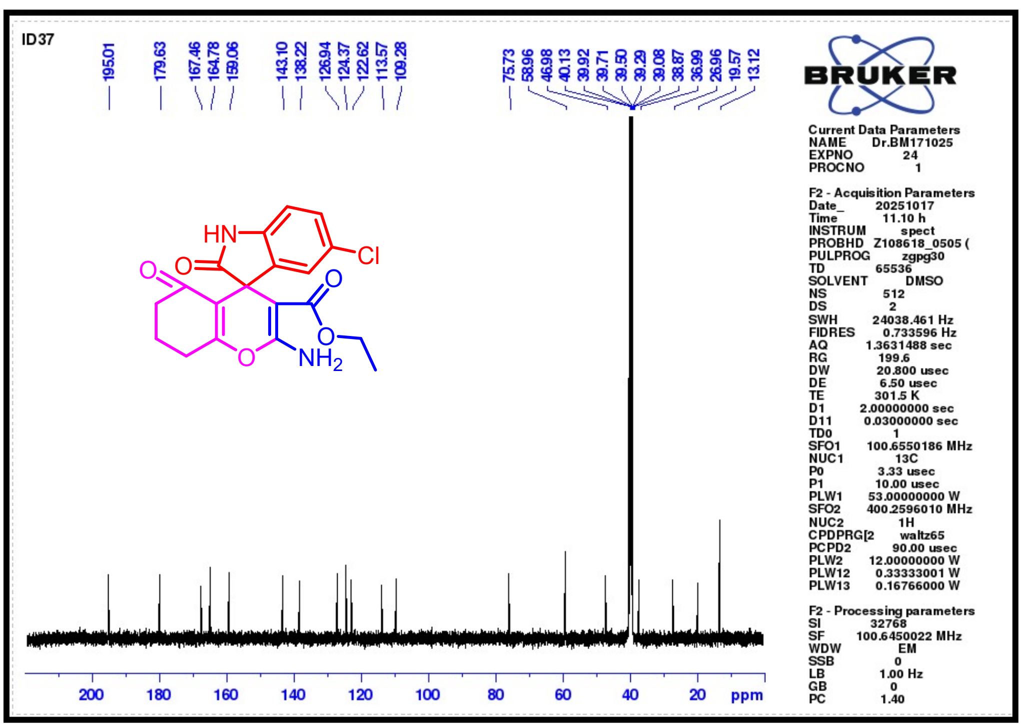


Figure S46. ^{13}C NMR spectrum (100 MHz) of **9f** in DMSO-d_6.

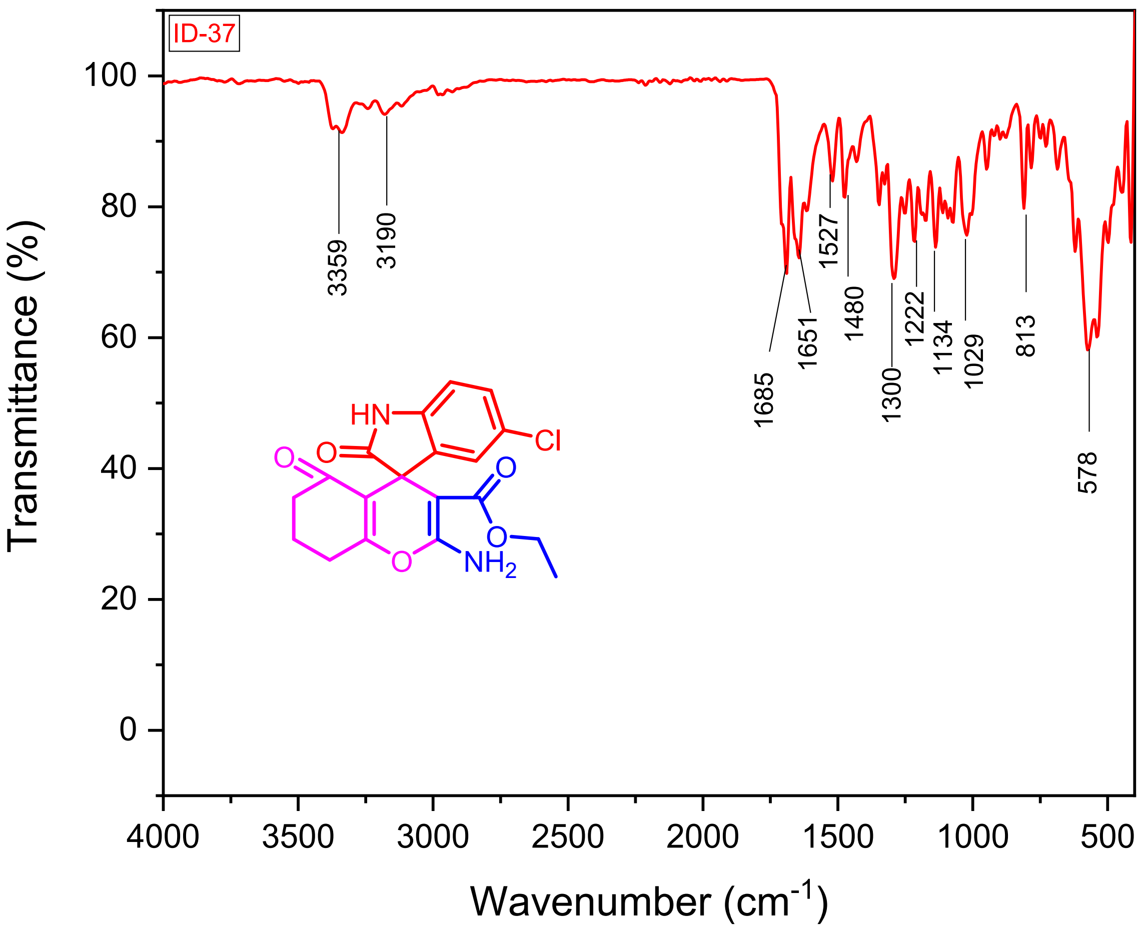


Figure S47. FT-IR spectrum of **9f**.

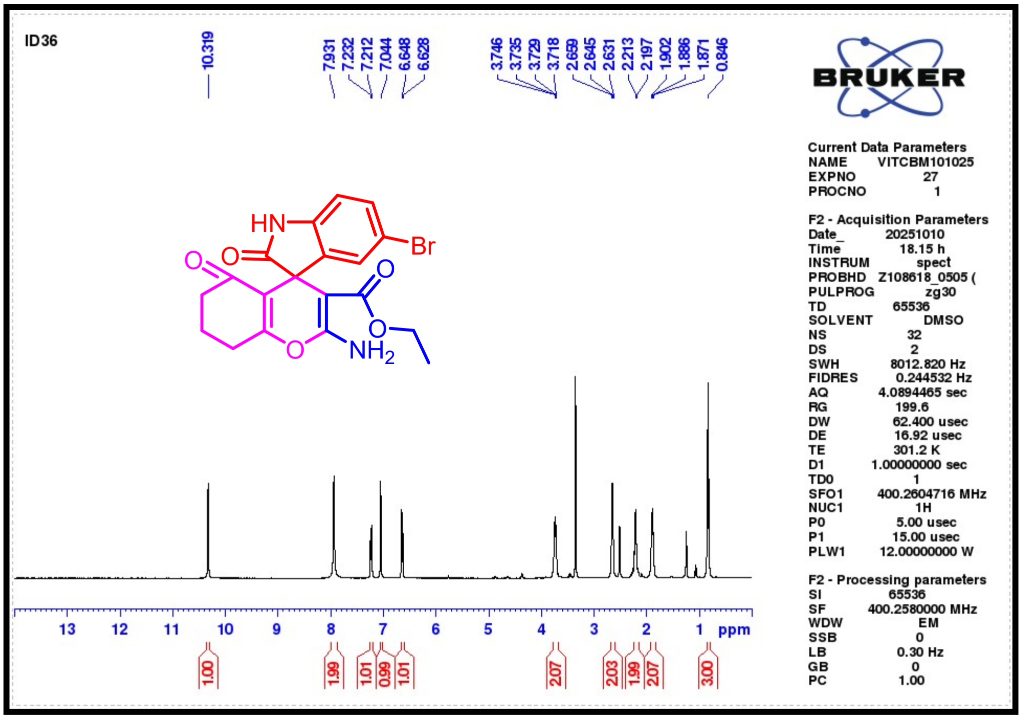


Figure S48. ^{1}H NMR spectrum (400 MHz) of **9g** in DMSO-d_6.

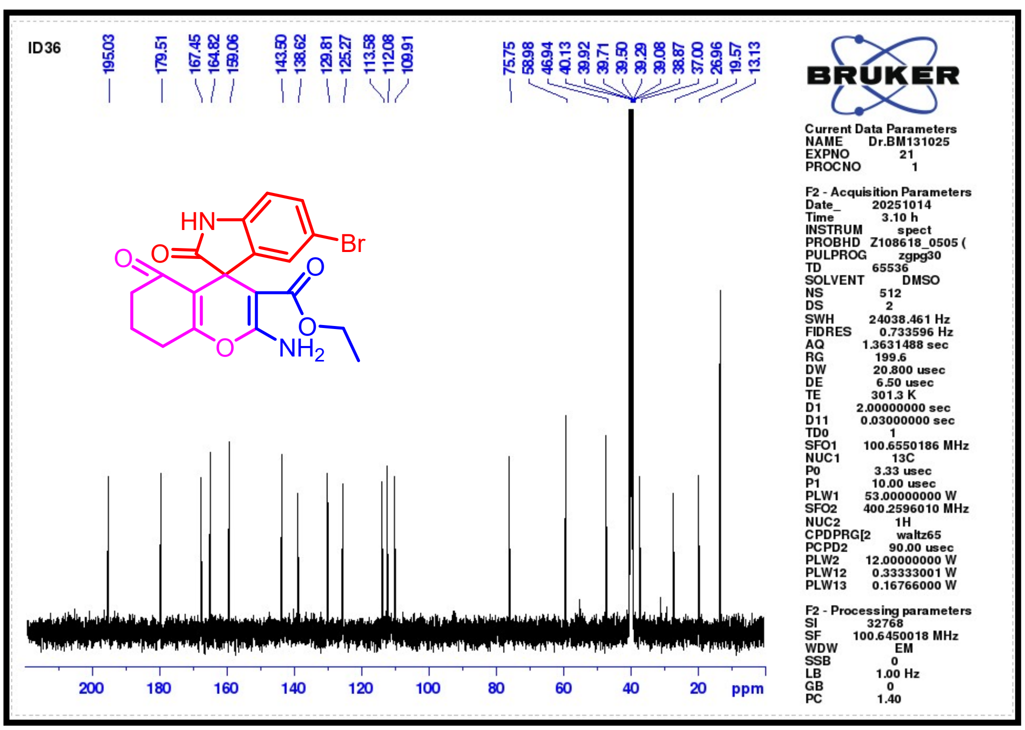


Figure S49. ^{13}C NMR spectrum (100 MHz) of **9g** in DMSO-d_6.

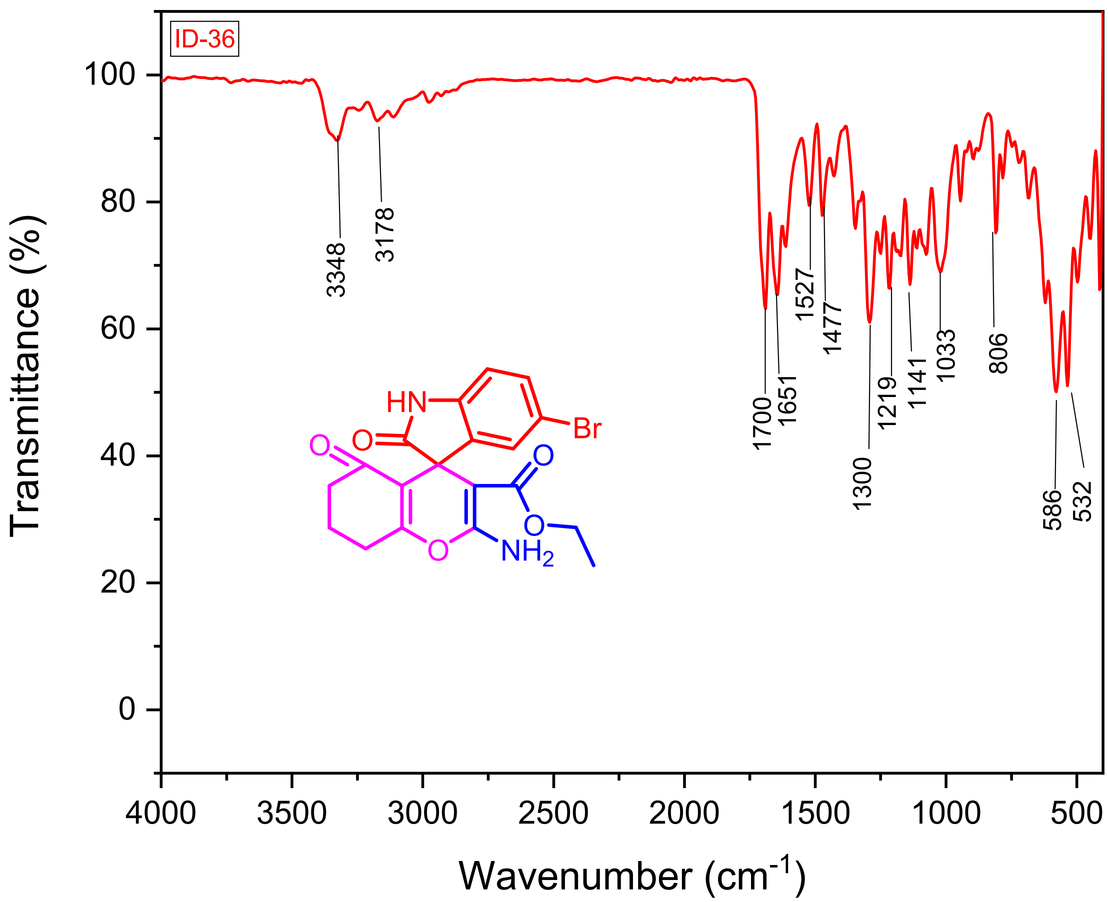


Figure S50. FT-IR spectrum of **9g**.

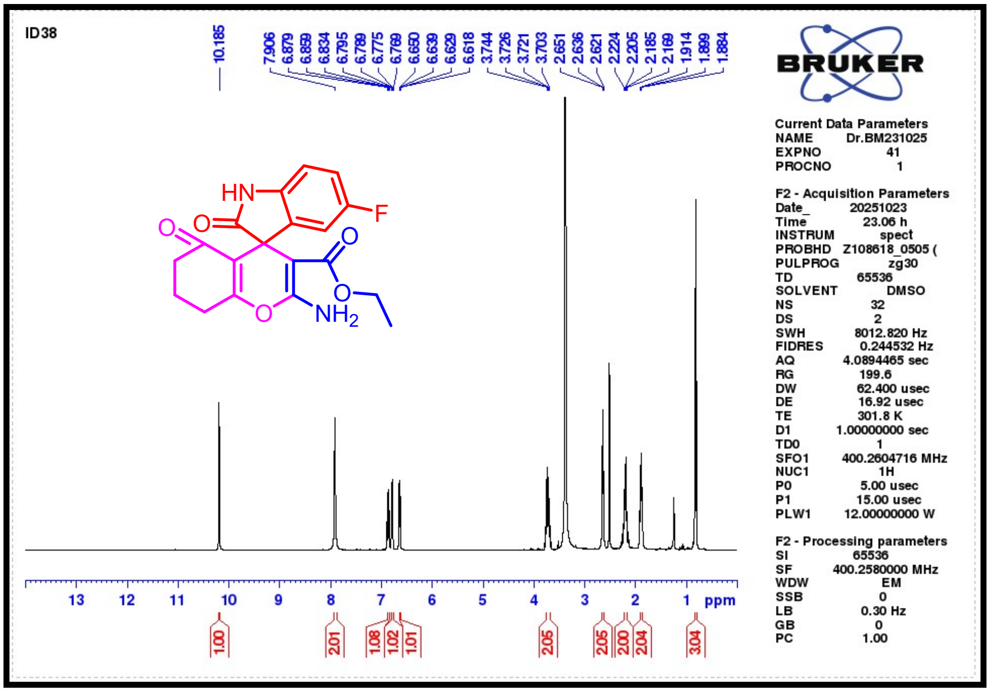


Figure S51. ^{1}H NMR spectrum (400 MHz) of **9h** in DMSO-d_6.

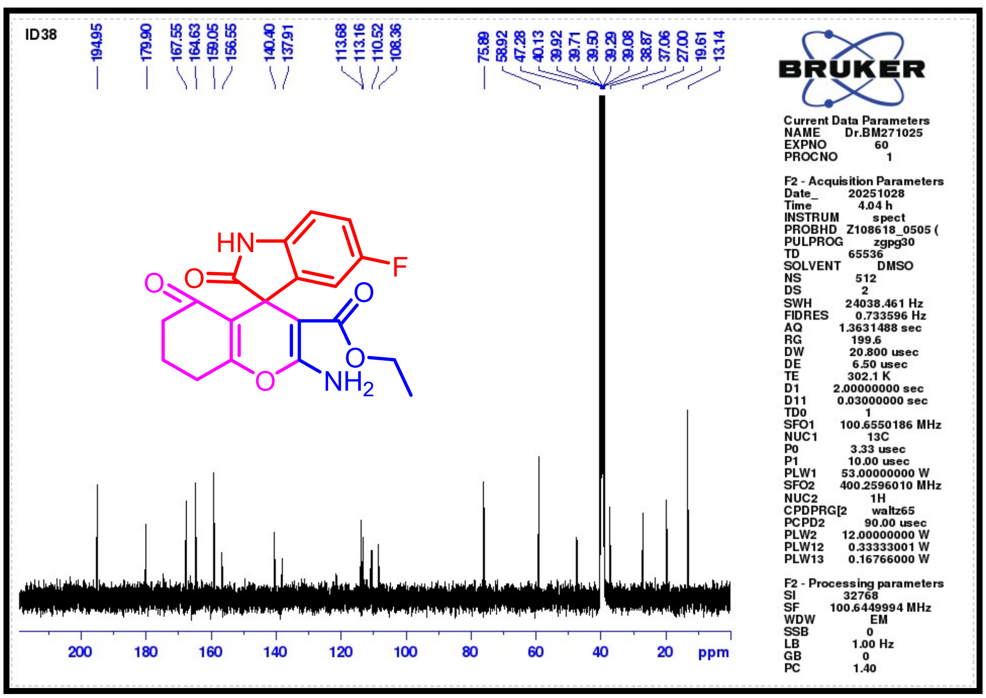


Figure S52. ^{13}C NMR spectrum (100 MHz) of **9h** in DMSO-d_6.

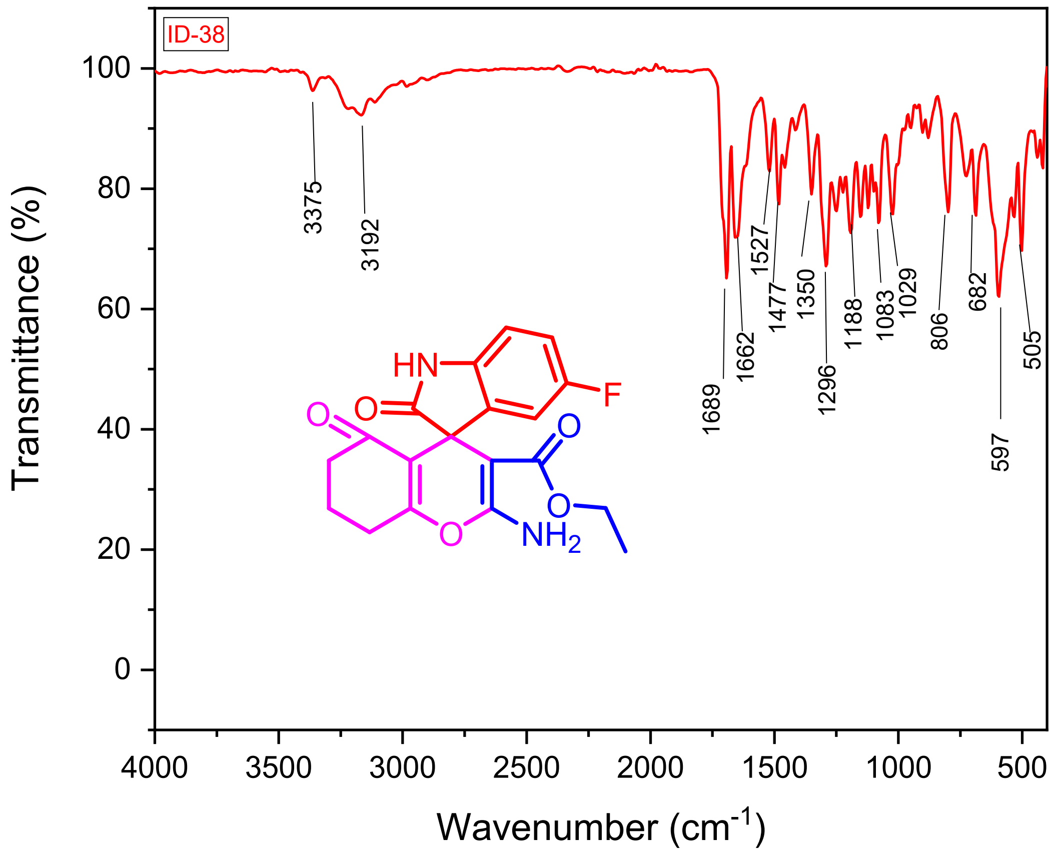


Figure S53. FT-IR spectrum of **9h**.

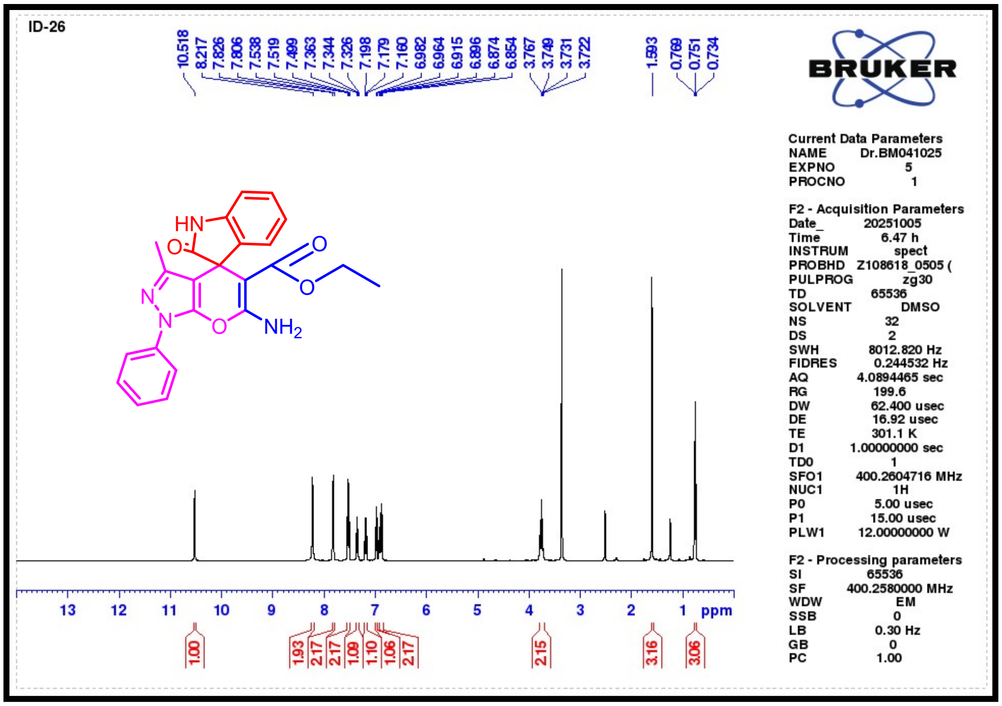


Figure S54. ^{1}H NMR spectrum (400 MHz) of **9i** in DMSO-d$_6$.

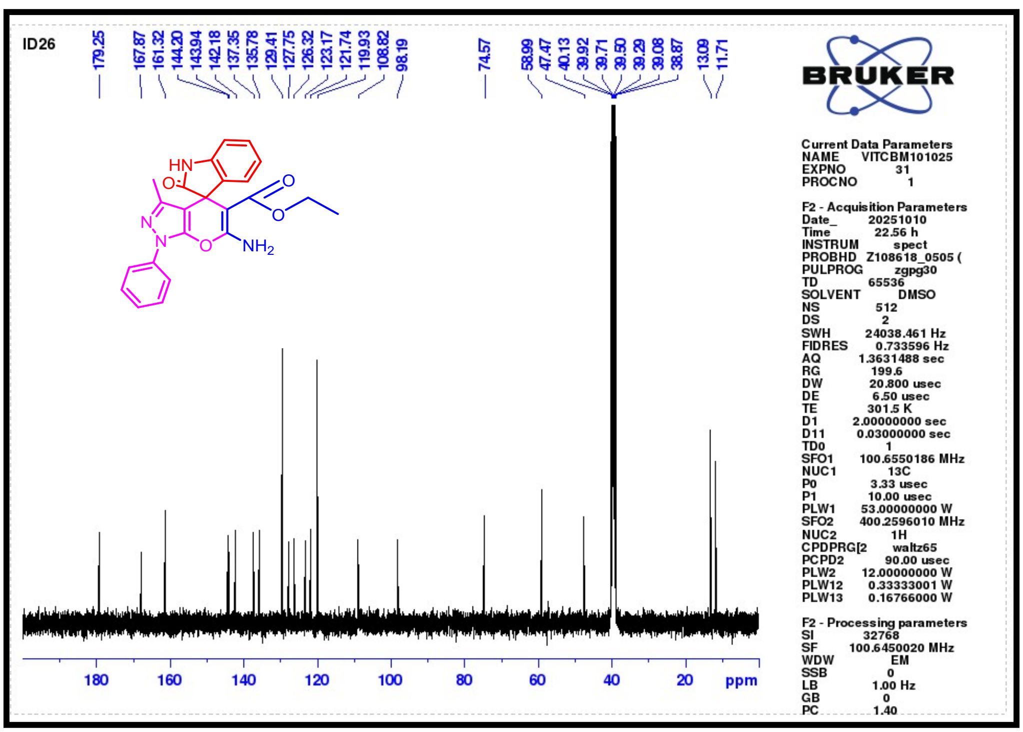


Figure S55. ^{13}C NMR spectrum (100 MHz) of **9i** in DMSO-d$_6$.

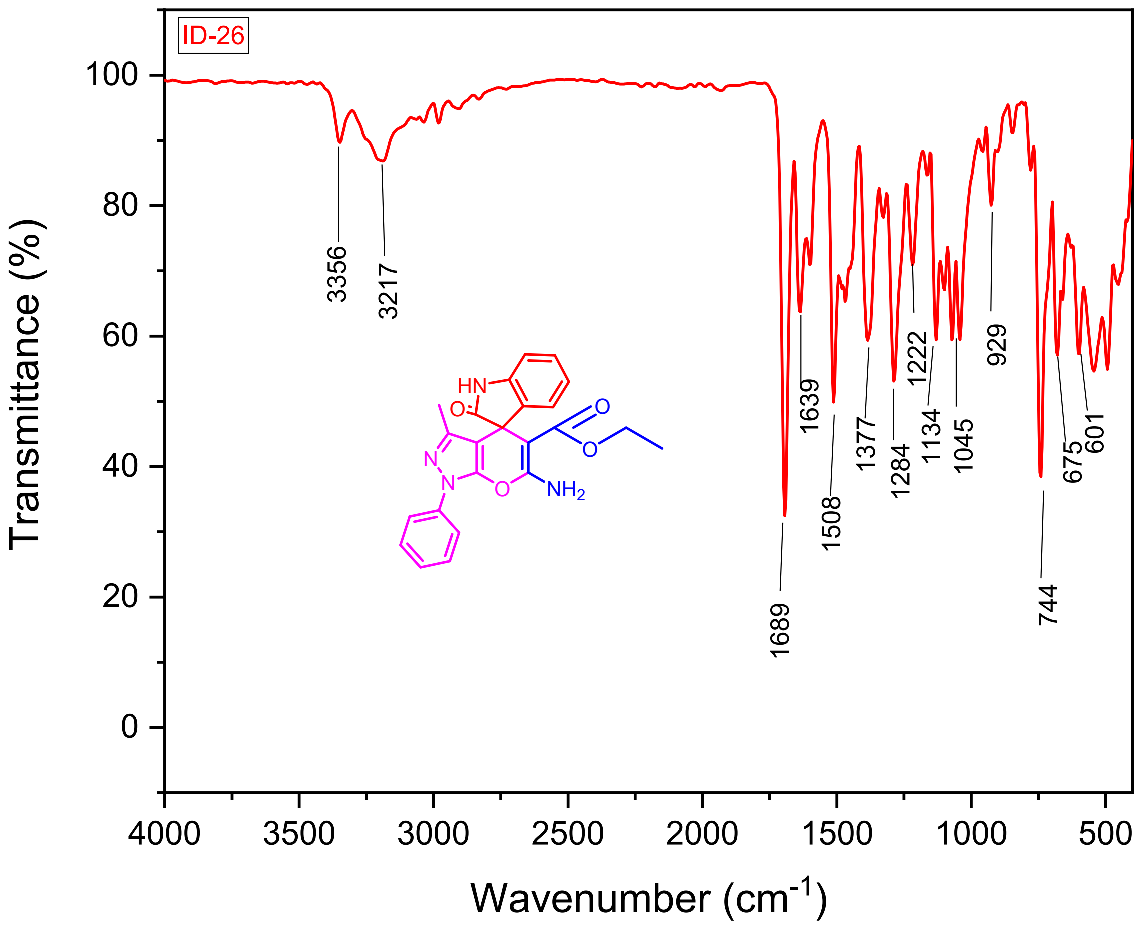


Figure S56. FT-IR spectrum of **9i.**

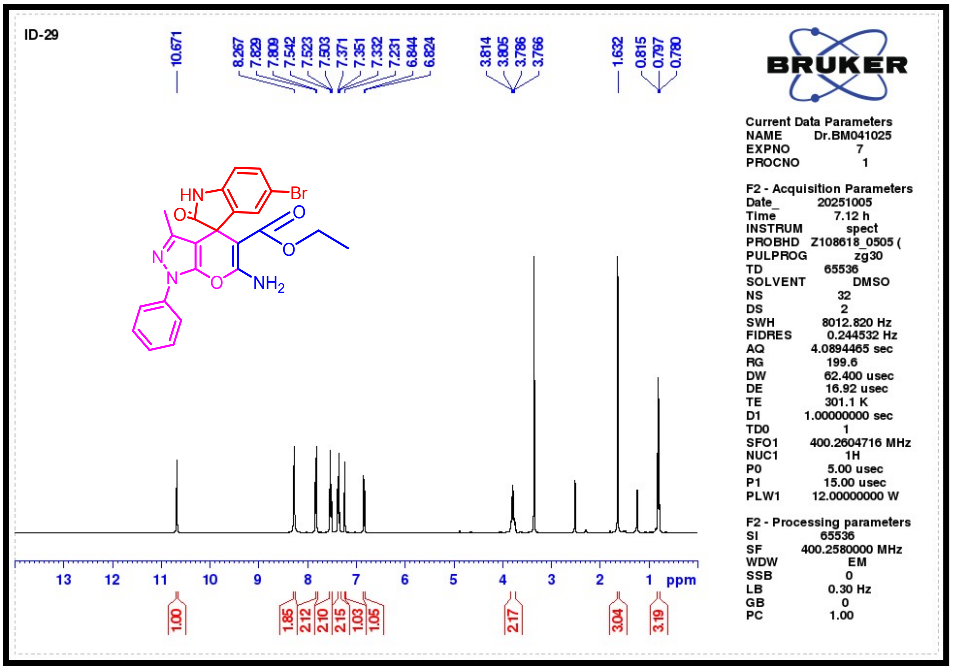


Figure S57. ^{1}H NMR spectrum (400 MHz) of **9j** in DMSO-d$_6$.

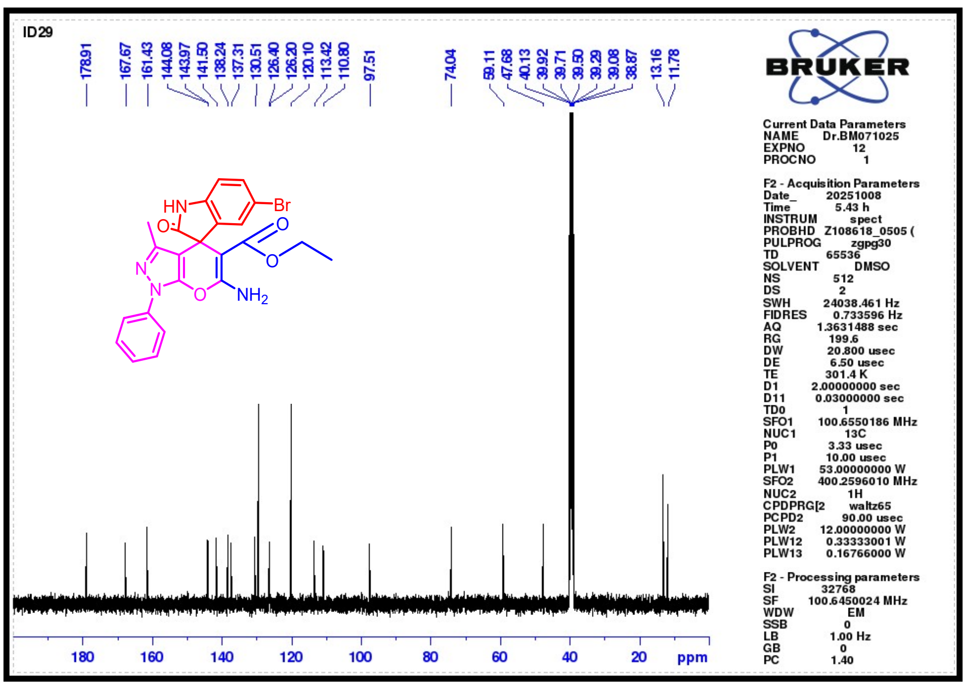


Figure S58. ^{13}C NMR spectrum (100 MHz) of **9j** in DMSO-d$_6$.

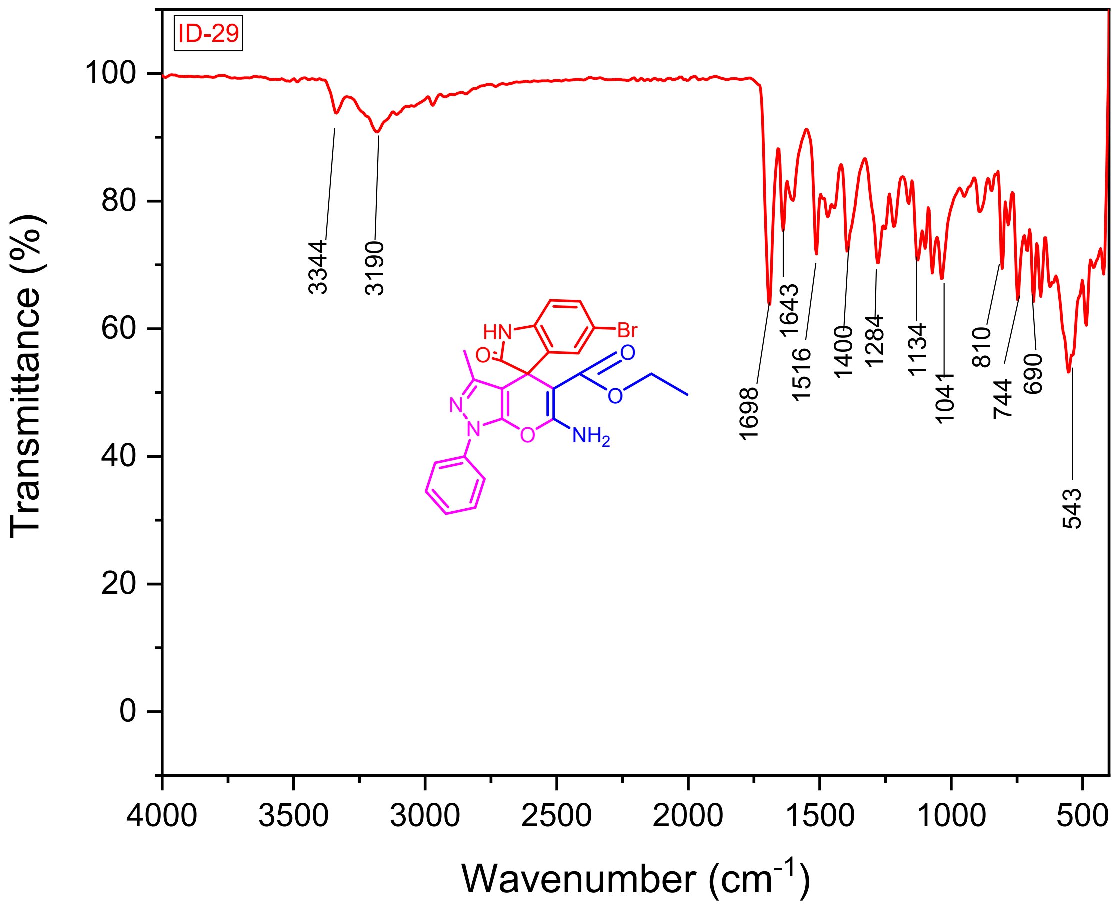


Figure S59. FT-IR spectrum of **9j**.

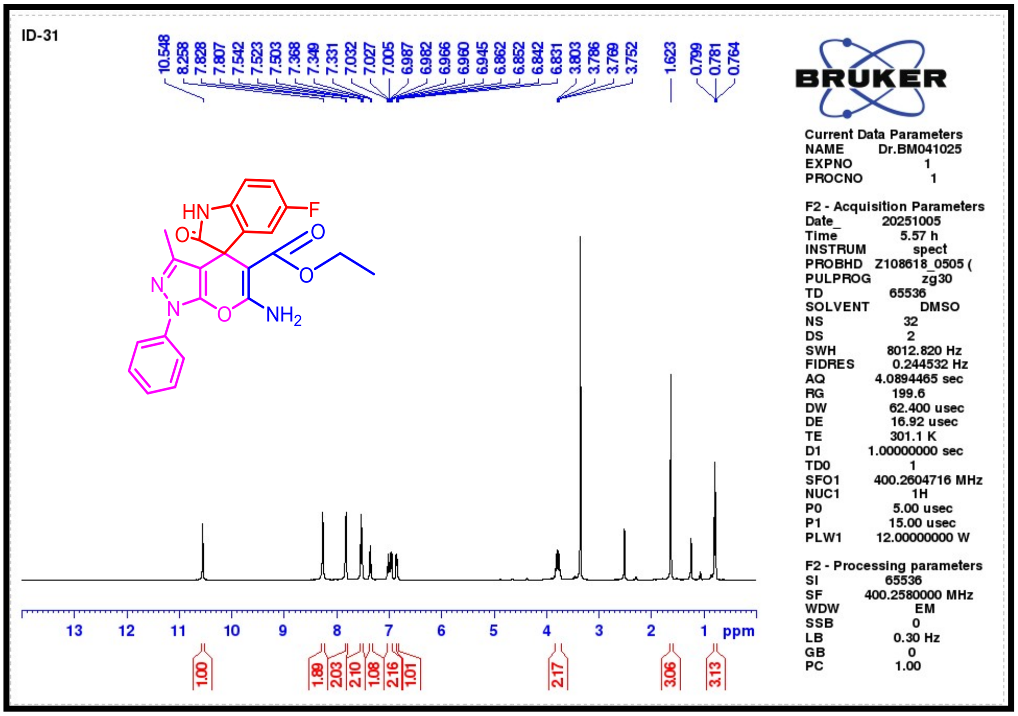


Figure S60. ^{1}H NMR spectrum (400 MHz) of **9k** in DMSO-d$_6$.

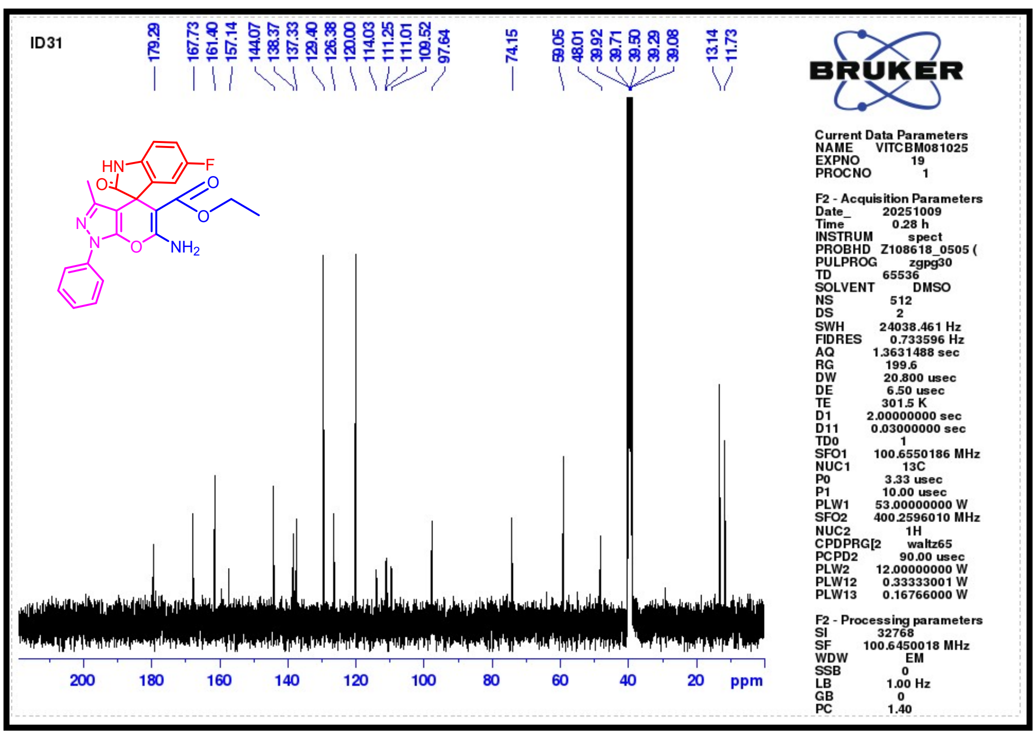


Figure S61. ^{13}C NMR spectrum (100 MHz) of **9k** in DMSO-d$_6$.

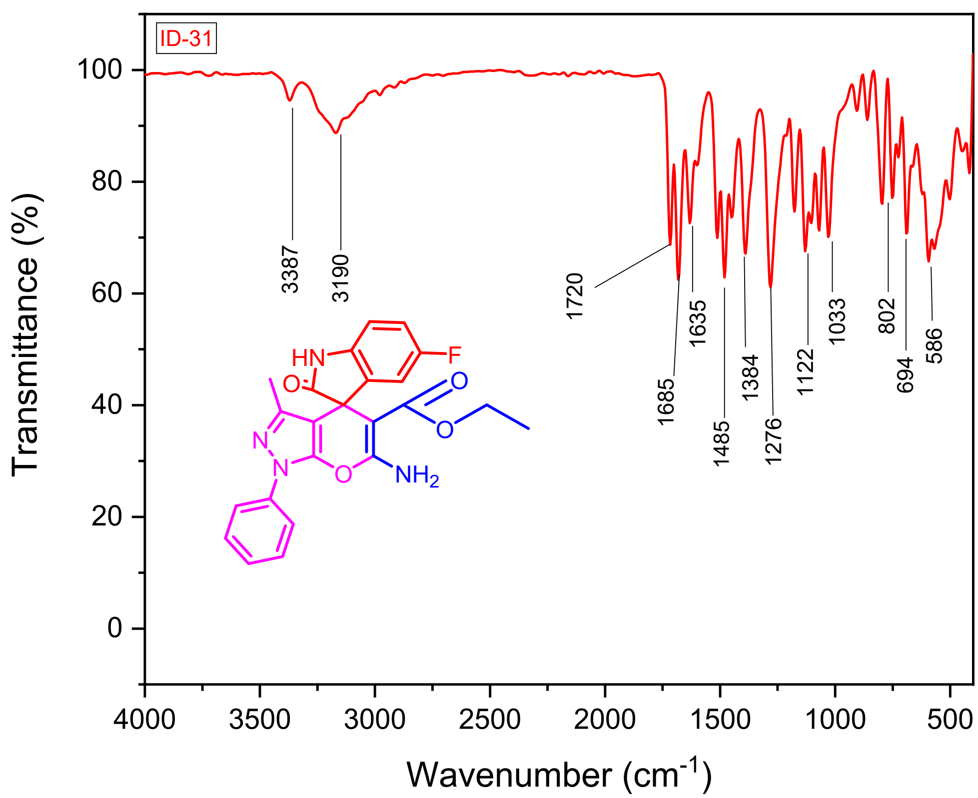


Figure S62. FT-IR spectrum of **9k**.

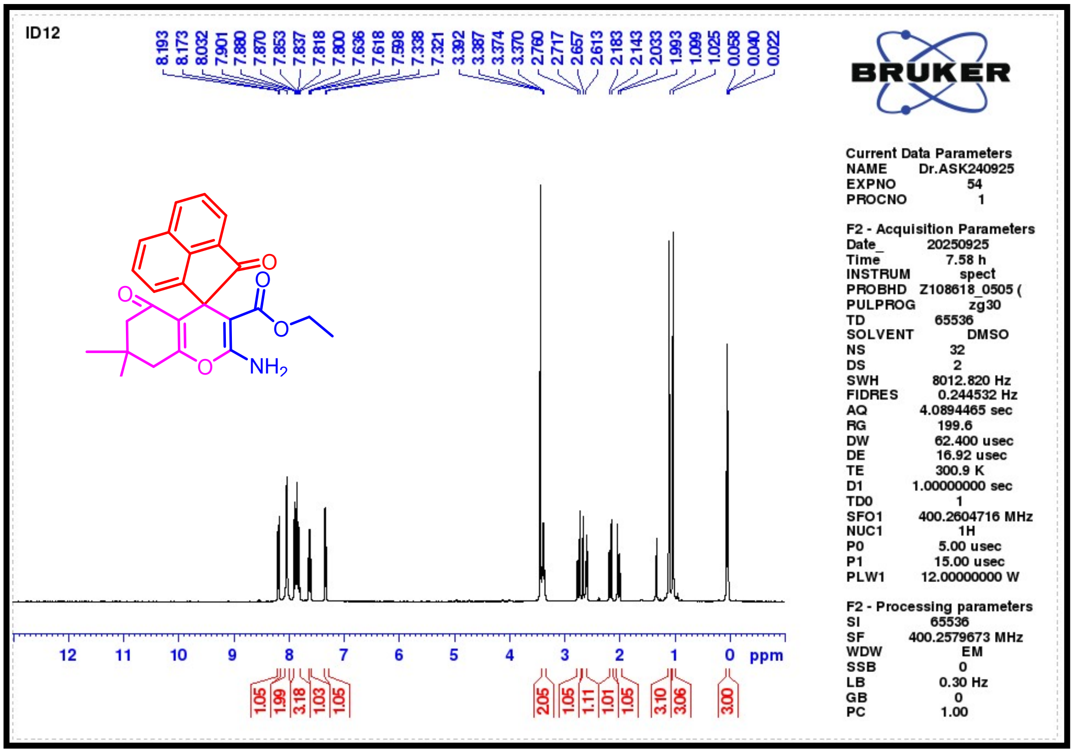


Figure S63. [1]H NMR spectrum (400 MHz) of **9l** in DMSO-d6.

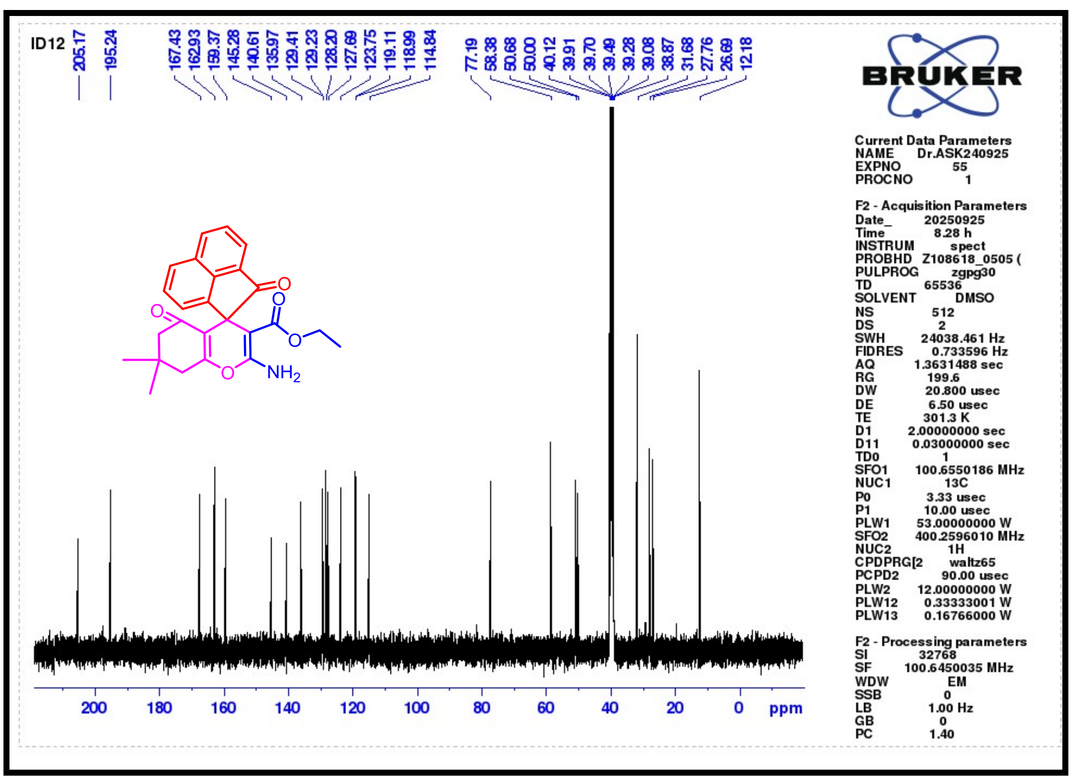


Figure S64. [13]C NMR spectrum (100 MHz) of **9l** in DMSO-d6.

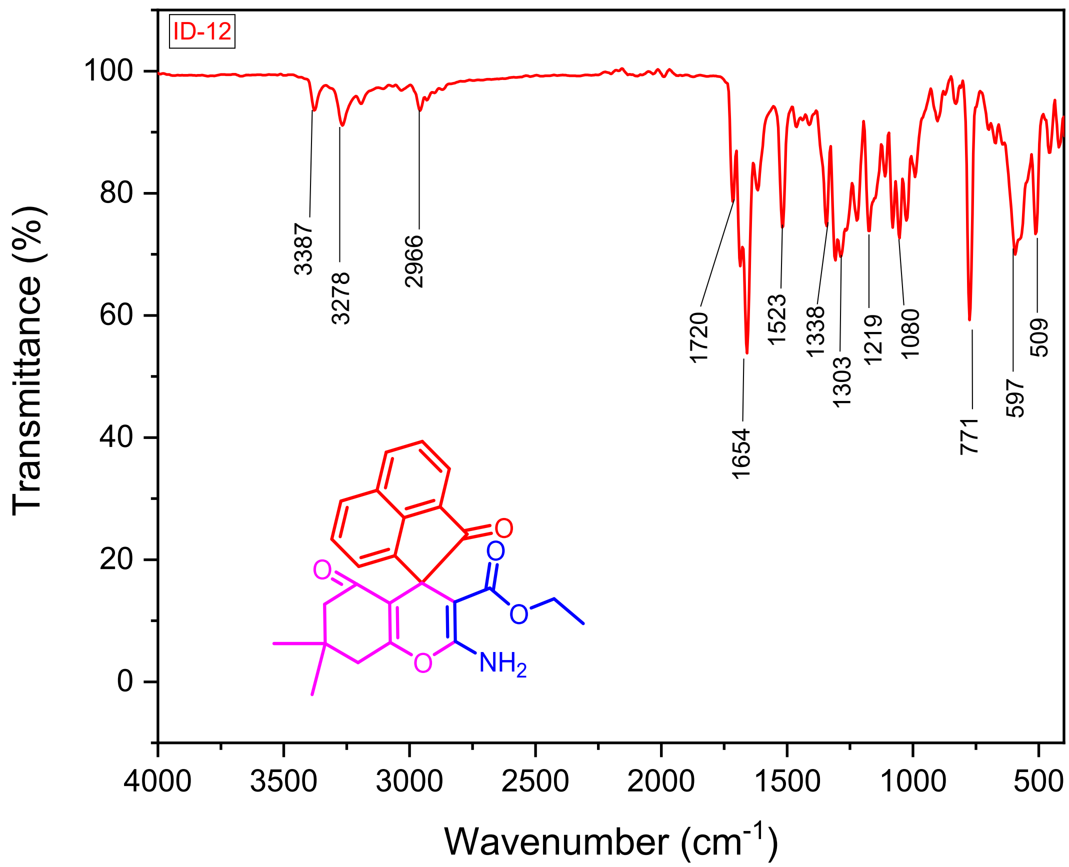


Figure S65. FT-IR spectrum of **9l.**

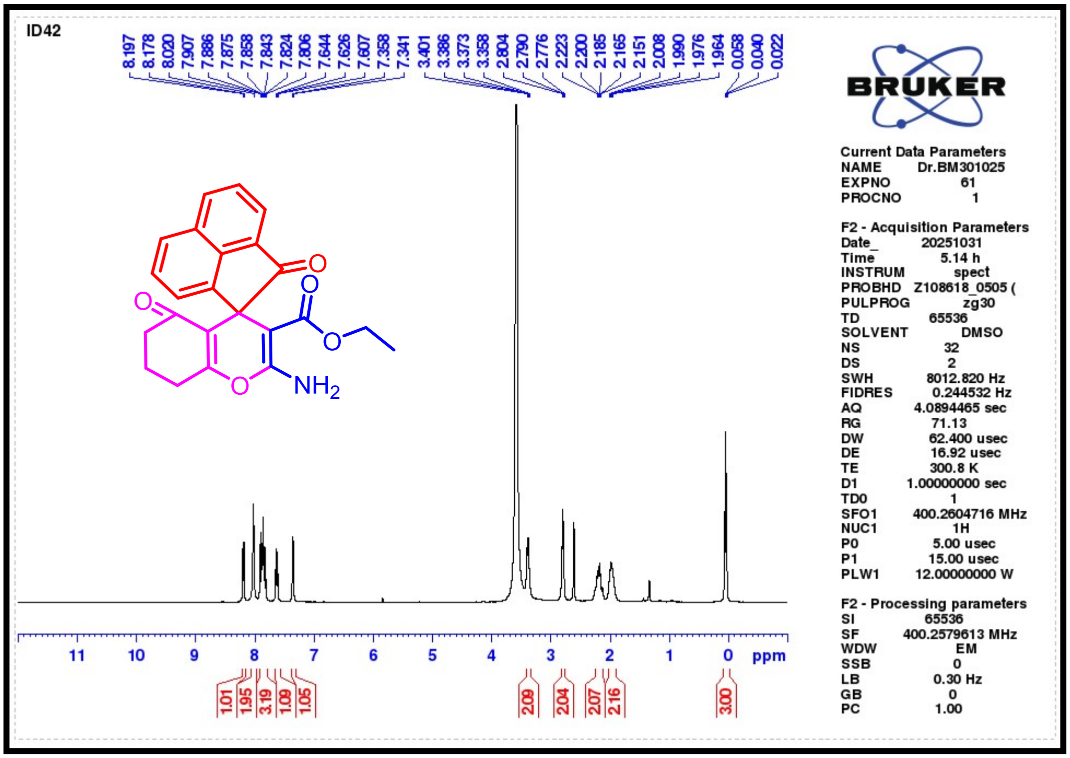


Figure S66. ^{1}H NMR spectrum (400 MHz) of **9m** in DMSO-d_6.

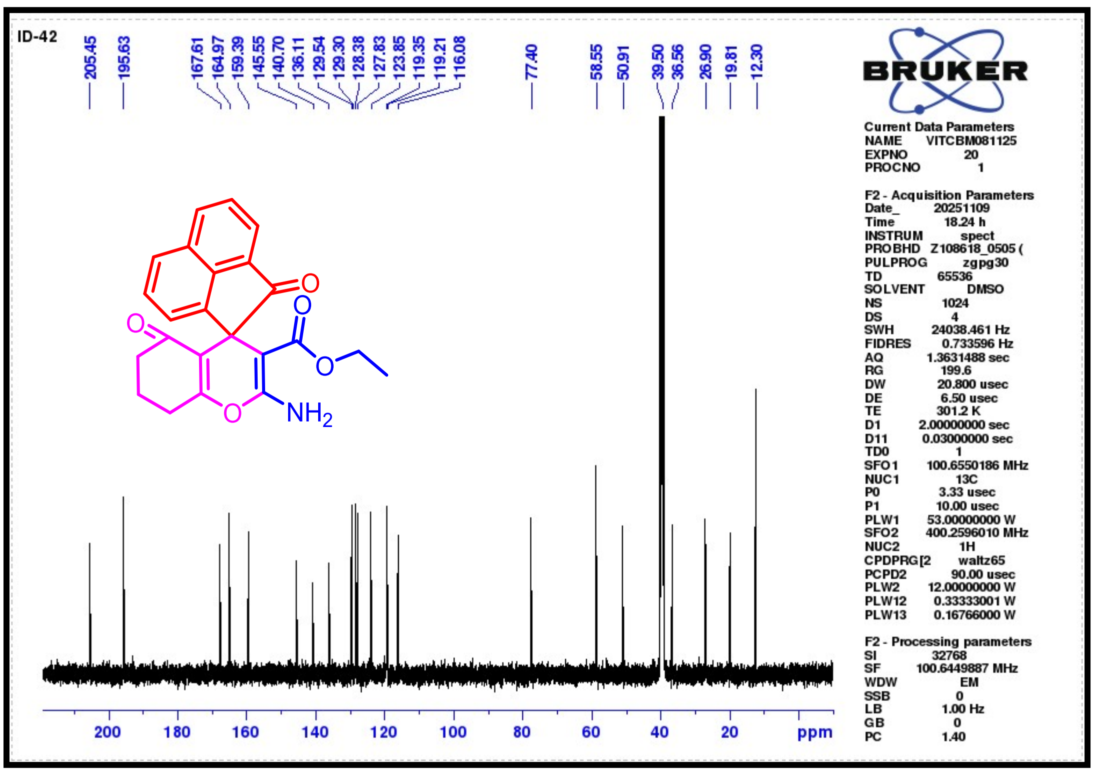


Figure S67. ^{13}C NMR spectrum (100 MHz) of **9m** in DMSO-d_6.

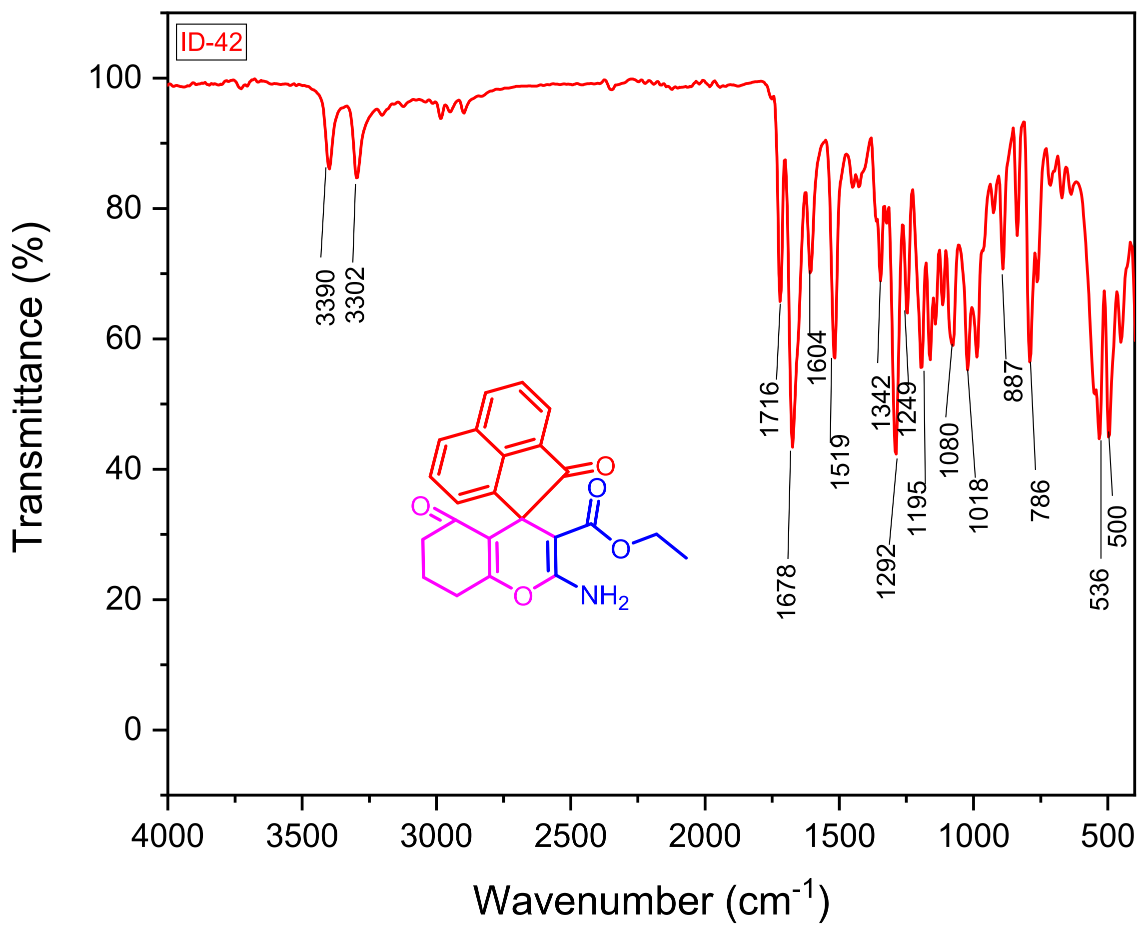


Figure S68. FT-IR spectrum of **9m**.

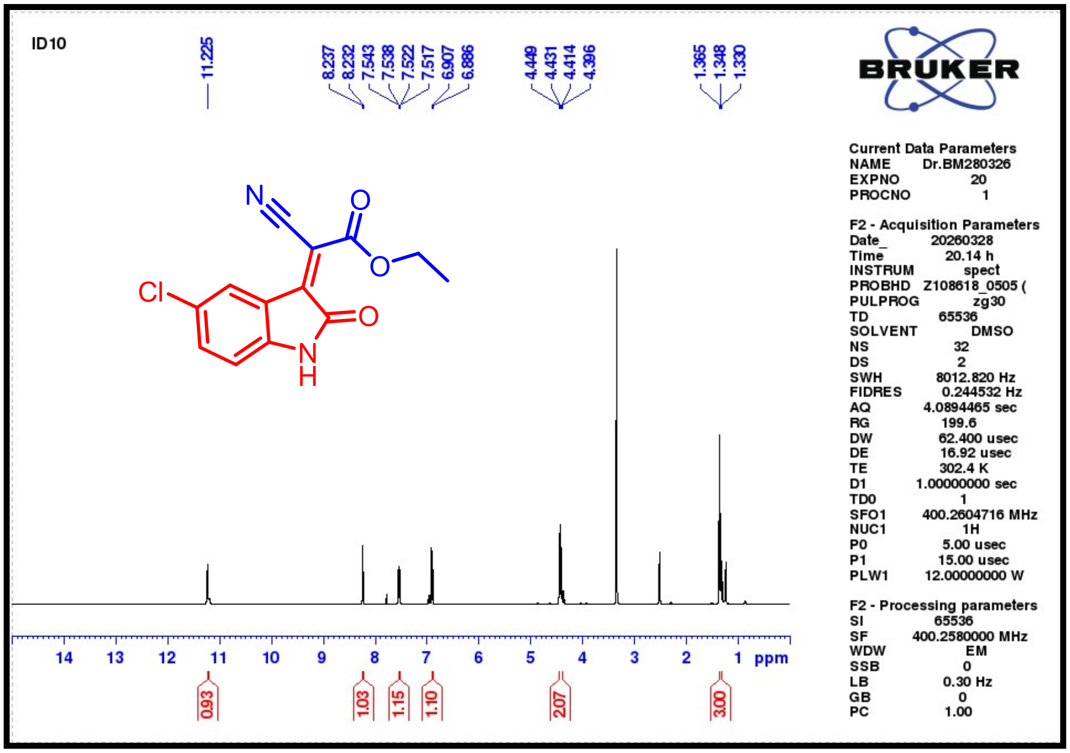


Figure S69. ^{1}H NMR spectrum (400 MHz) of **intermediate C** in DMSO-d$_6$.

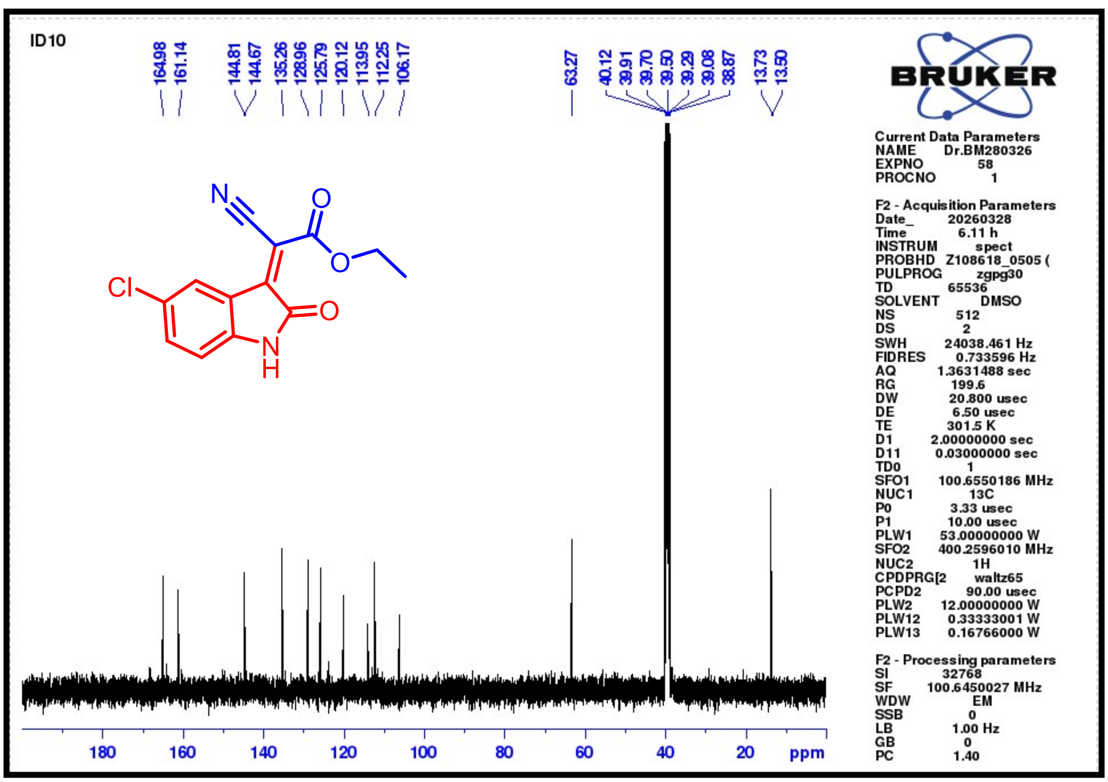


Figure S70. ^{13}C NMR spectrum (100 MHz) of **intermediate C** in DMSO-d$_6$.

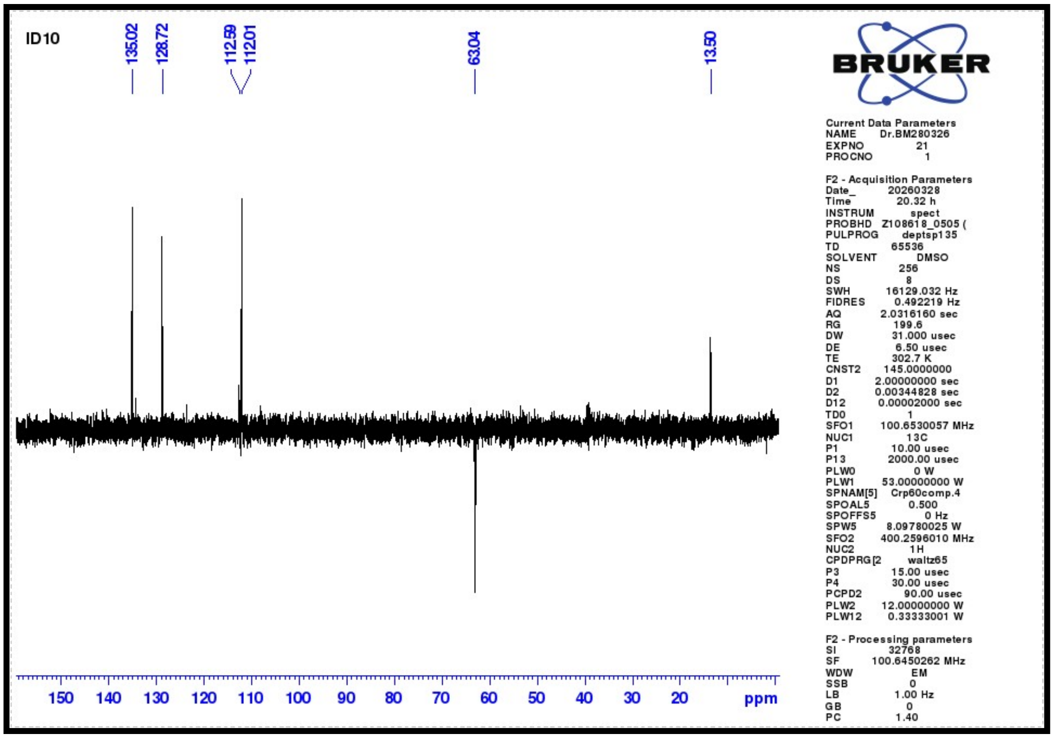


Figure S71. DEPT-135 spectrum (100 MHz) of **intermediate C** in DMSO-d6.

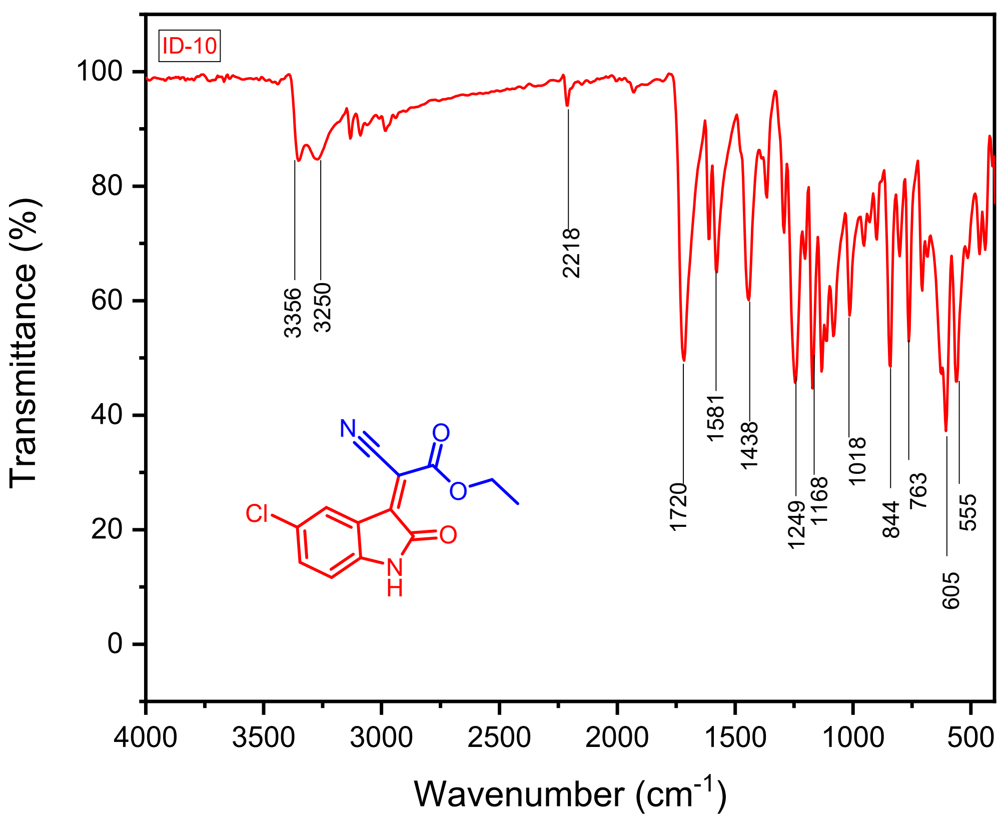


Figure S72. FT-IR spectrum of **intermediate C.**

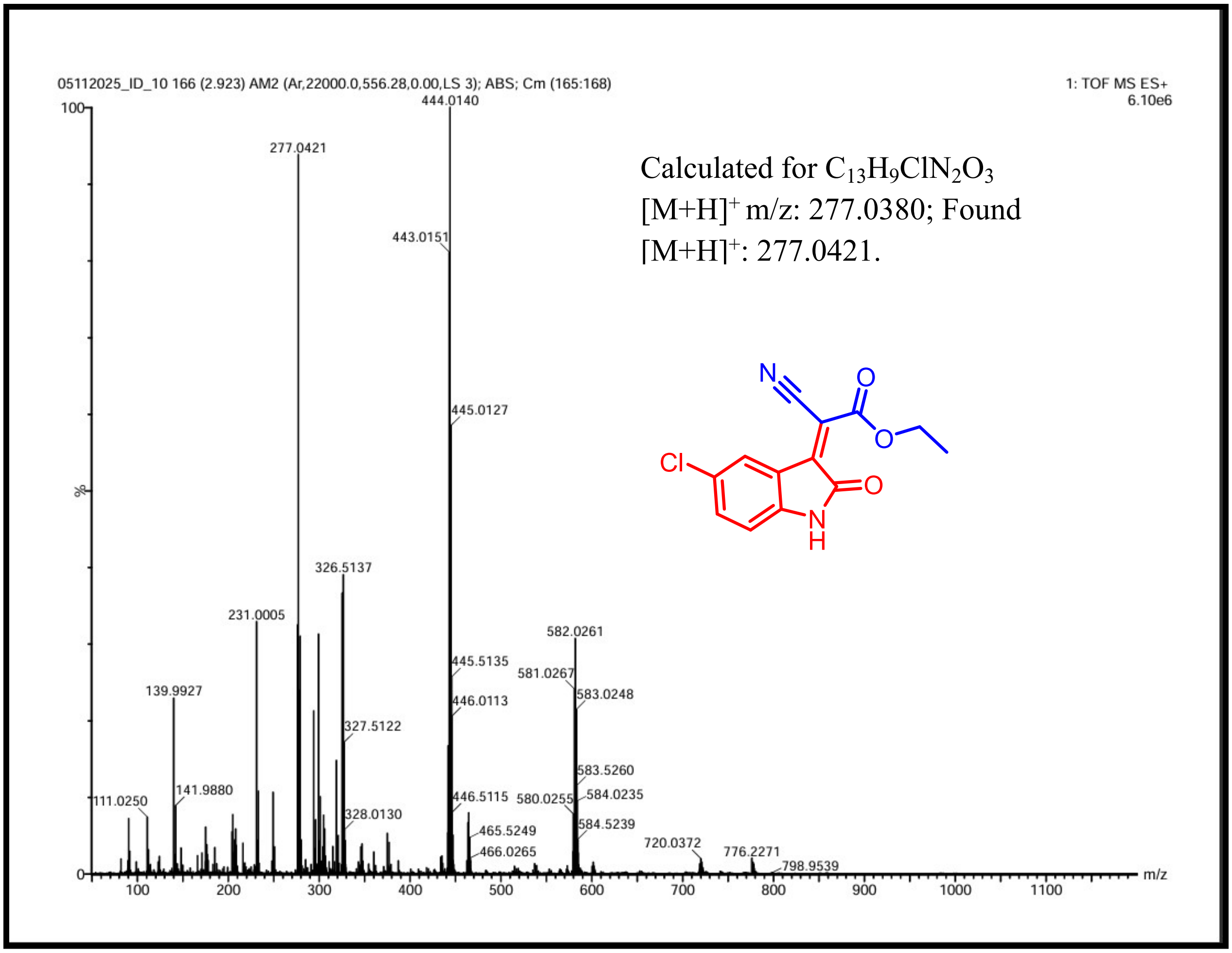


Figure S73. HRMS of **intermediate C.**

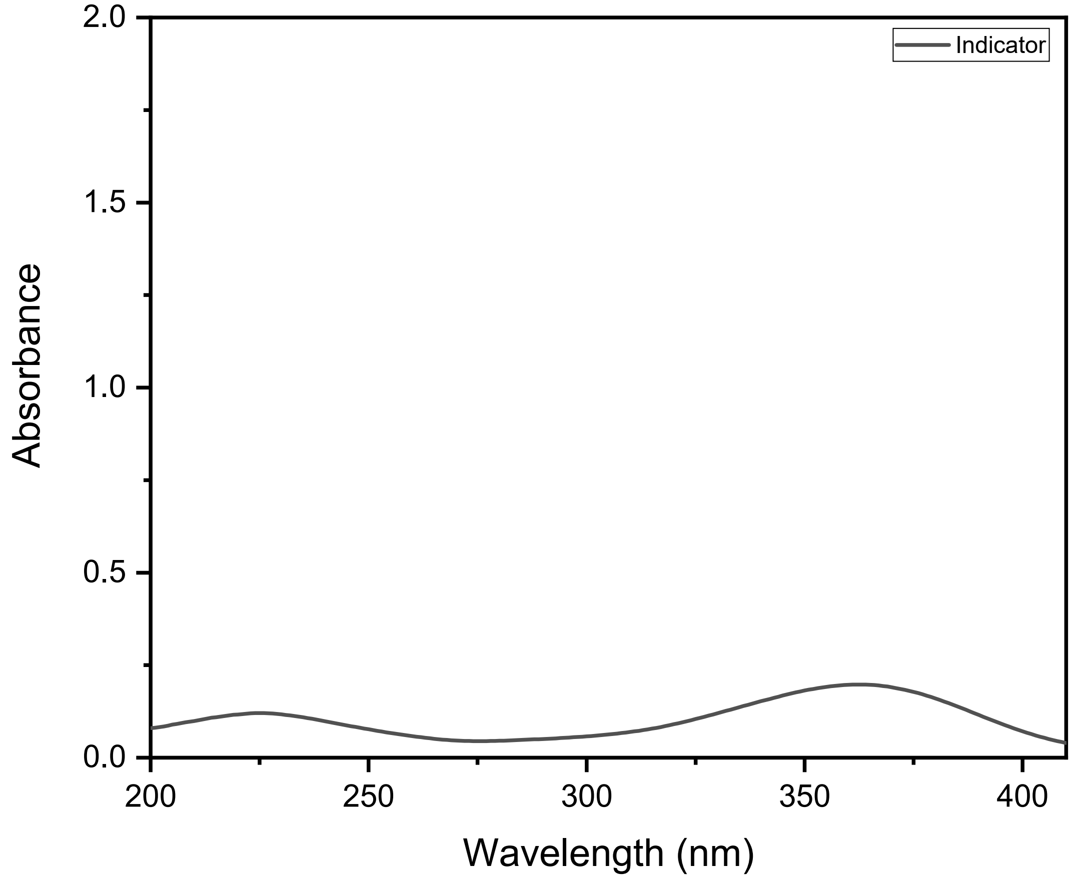


Fig. S74. UV-Vis spectra of 10^{-5} M concentration of 4-nitroaniline in acetonitrile solution.

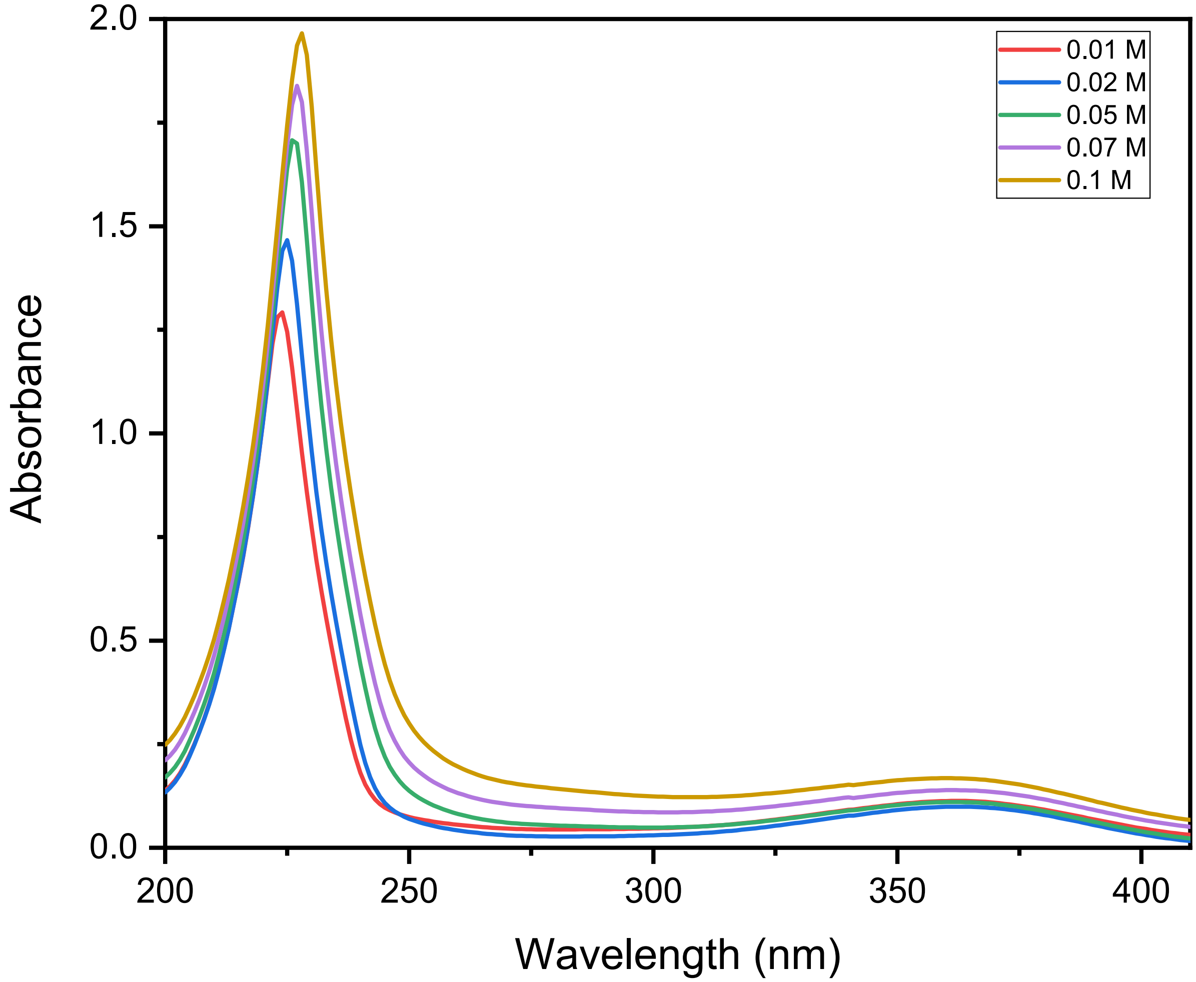


Fig. S75. UV-Vis spectra of 4 nitroaniline in different concentration of [CMMIM] [BF_4] ionic liquid (10^{-5} M 4-nitroaniline)

Table S2. Single Crystal data and structure refinement for 8c.

A specimen of $C_{20}H_{17}NO_4$, approximate dimensions 0.050 mm x 0.126 mm x 0.176 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å) The integration of the data using a monoclinic unit cell yielded a total of 30266 reflections to a maximum θ angle of 28.27° (0.75 Å resolution), of which 3934 were independent (average redundancy 7.693, completeness = 99.9%, R_{int}= 4.69%, R_{sig} = 3.21%) and 2836 (72.09%) were greater than 2σ(F^2). The final cell constants of a = 8.6939(15) Å, b = 20.983(4) Å, c = 9.7236(17) Å, β = 116.045(5)°, volume = 1593.7(5) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9830 and 0.9950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{20}H_{17}NO_4$. The final anisotropic full-matrix least-squares refinement on F^2 with226 variables converged at R1 = 4.82%, for the observed data and wR2 = 12.17% for all data. The goodness-of-fit was 1.066. The largest peak in the final difference electron density synthesis was 0.282 $e^-/Å^3$ and the largest hole was -0.192 $e^-/Å^3$ with an RMS deviation of 0.042 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.398 g/cm^3 and F (000), 704 e^-.

Table S2a. Sample and crystal data for 8c.

Identification code	8c	
CCDC NO	2498521	
Chemical formula	$C_{20}H_{17}NO_4$	
Formula weight	335.35 g/mol	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.126 x 0.176 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.6939(15) Å	α = 90°
	b = 20.983(4) Å	β = 116.045(5)°
	c = 9.7236(17) Å	γ = 90°
Volume	1593.7(5) $Å^3$	
Z	4	

Density (calculated)	1.398 g/cm^3
Absorption coefficient	0.098 mm^{-1}
F (000)	70

Table S2b. Data collection and structure refinement for 8c.

Theta range for data collection	2.52 to 28.27°	
Index ranges	-11<=h<=11, -27<=k<=27, -12<=l<=11	
Reflections collected	30266	
Independent reflections	3934 [R(int) = 0.0469]	
Max. and min. transmission	0.9950 and 0.9830	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	Σ w $(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3934 / 0 / 226	
Goodness-of-fit on F^2	1.066	
Final R indices	2836 data; I>2σ(I)	R1 = 0.0482, wR2 = 0.1021
	all data	R1 = 0.0768, wR2 = 0.1217
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0373P)^2+0.8191P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.282 and -0.192 eÅ^{-3}	
R.M.S. deviation from mean	0.042 eÅ^{-3}	

Table S2c. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 8c.

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.06681(15)	0.60588(6)	0.40829(1	
O2	0.18923(18)	0.63634(8)	0.92678(1	
O3	0.59220(17)	0.71227(7)	0.67615(1	
O4	0.28314(18)	0.75870(6)	0.76591(1	
N2	0.50612(19)	0.69838(7)	0.93879(1	
C1	0.1439(2)	0.62384(8)	0.67279(1	
C2	0.0900(2)	0.62222(9)	0.7969(2)	
C3	0.9075(3)	0.60470(12)	0.7564(2)	
C4	0.8314(3)	0.55853(12)	0.6255(3)	
C5	0.8557(2)	0.58084(11)	0.4886(2)	
C6	0.0324(2)	0.60495(9)	0.53302(1	
C7	0.2127(2)	0.63644(8)	0.42260(1	
C8	0.3309(2)	0.65859(8)	0.55609(1	
C9	0.3234(2)	0.64714(8)	0.70782(1	
C10	0.2174(2)	0.64032(10)	0.2713(2)	
C11	0.3959(3)	0.65557(13)	0.2908(2)	
C12	0.4731(3)	0.70940(11)	0.4039(2)	
C13	0.4763(2)	0.69461(8)	0.5562(2)	
C14	0.4646(2)	0.60321(8)	0.81333(1	
C15	0.3651(2)	0.70939(8)	0.80545(1	
C16	0.5683(2)	0.63632(8)	0.94638(1	
C17	0.7090(2)	0.60822(9)	0.0621(2)	
C18	0.7432(2)	0.54514(10)	0.0428(2)	
C19	0.6417(2)	0.51163(9)	0.9120(2)	
C20	0.5018(2)	0.54095(8)	0.7952(2)	

Table S2d. Bond lengths (Å) for 8c.

O1-C6	1.371(2)	O1-C7	1.373(2)
O2-C2	1.212(2)	O3-C13	1.217(2)
O4-C15	1.219(2)	N2-C15	1.357(2)
N2-C16	1.399(2)	C1-C6	1.337(2)
C1-C2	1.475(2)	C1-C9	1.524(2)
C2-C3	1.502(3)	C3-C4	1.502(3)
C4-C5	1.510(3)	C5-C6	1.490(2)
C7-C8	1.336(2)	C7-C10	1.491(2)
C8-C13	1.473(2)	C8-C9	1.524(2)
C9-C14	1.518(2)	C9-C15	1.561(2)
C10-C11	1.513(3)	C11-C12	1.512(3)
C12-C13	1.501(3)	C14-C20	1.376(2)
C14-C16	1.395(2)	C16-C17	1.379(2)
C17-C18	1.387(3)	C18-C19	1.380(3)

Table S2e. Bond angles (°) for 8c.

C6-O1-C7	117.90(13)	C15-N2-C16	112.01(14)
C6-C1-C2	118.42(15)	C6-C1-C9	122.46(15)
C2-C1-C9	119.12(14)	O2-C2-C1	120.67(16)
O2-C2-C3	121.34(17)	C1-C2-C3	117.97(16)
C2-C3-C4	113.72(17)	C3-C4-C5	111.48(18)
C6-C5-C4	112.06(16)	C1-C6-O1	123.53(15)
C1-C6-C5	126.19(16)	O1-C6-C5	110.27(14)
C8-C7-O1	122.89(15)	C8-C7-C10	126.64(16)
O1-C7-C10	110.47(14)	C7-C8-C13	118.22(15)
C7-C8-C9	122.97(15)	C13-C8-C9	118.80(14)
C14-C9-C8	112.61(13)	C14-C9-C1	113.65(13)
C8-C9-C1	107.99(12)	C14-C9-C15	101.18(12)

C8-C9-C15	111.07(13)	C1-C9-C15	110.26(13)
C7-C10-C11	111.03(15)	C12-C11-C10	110.61(18)
C13-C12-C11	111.90(17)	O3-C13-C8	120.42(16)
O3-C13-C12	122.10(17)	C8-C13-C12	117.47(15)
C20-C14-C16	119.96(15)	C20-C14-C9	131.00(15)
C16-C14-C9	109.04(14)	O4-C15-N2	127.13(16)
O4-C15-C9	124.81(15)	N2-C15-C9	108.06(14)
C17-C16-C14	121.63(16)	C17-C16-N2	128.67(16)
C14-C16-N2	109.70(14)	C16-C17-C18	117.65(17)
C19-C18-C17	121.47(17)	C18-C19-C20	120.21(17)
C14-C20-C19	119.07(16)		

Table S2f. Anisotropic atomic displacement parameters (Å^2) for 8c.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0319(6)	0.0581(8)	0.0288(6)	-0.0064(5)	0.0101(5)	-0.0104(6)
O2	0.0522(8)	0.0799(10)	0.0332(7)	-0.0044(7)	0.0199(7)	-0.0060(7)
O3	0.0432(8)	0.0658(9)	0.0429(8)	-0.0063(7)	0.0125(6)	-0.0208(7)
O4	0.0571(8)	0.0358(7)	0.0478(8)	0.0037(6)	0.0198(7)	0.0115(6)
N2	0.0415(8)	0.0342(8)	0.0299(7)	-0.0081(6)	0.0073(6)	-0.0039(6)
C1	0.0270(8)	0.0359(9)	0.0298(8)	0.0021(7)	0.0105(7)	0.0024(7)
C2	0.0369(9)	0.0446(10)	0.0358(10)	0.0014(8)	0.0165(8)	0.0026(8)
C3	0.0455(12)	0.0836(16)	0.0537(13)	-0.0078(11)	0.0307(10)	-0.0084(11)
C4	0.0431(11)	0.0795(16)	0.0593(13)	-0.0038(12)	0.0250(10)	-0.0167(11)
C5	0.0316(10)	0.0724(14)	0.0438(11)	-0.0063(10)	0.0126(8)	-0.0126(9)
C6	0.0282(8)	0.0441(10)	0.0325(9)	0.0008(7)	0.0124(7)	-0.0009(7)
C7	0.0285(8)	0.0382(9)	0.0288(8)	0.0022(7)	0.0098(7)	0.0006(7)
C8	0.0280(8)	0.0343(8)	0.0268(8)	0.0027(6)	0.0093(7)	0.0014(6)
C9	0.0271(8)	0.0333(8)	0.0246(8)	-0.0011(6)	0.0084(6)	-0.0006(6)
C10	0.0408(10)	0.0581(12)	0.0286(9)	-0.0001(8)	0.0127(8)	-0.0028(9)
C11	0.0497(12)	0.0944(18)	0.0355(10)	-0.0046(11)	0.0225(9)	-0.0117(12)
C12	0.0464(11)	0.0680(14)	0.0430(11)	0.0084(10)	0.0199(9)	-0.0130(10)
C13	0.0338(9)	0.0387(9)	0.0373(9)	0.0016(7)	0.0139(8)	-0.0022(7)
C14	0.0261(8)	0.0339(8)	0.0258(8)	0.0017(6)	0.0091(6)	-0.0010(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	0.0379(9)	0.0342(9)	0.0320(9)	0.0010(7)	0.0149(7)	-0.0004(7)
C16	0.0312(8)	0.0362(9)	0.0260(8)	0.0003(6)	0.0088(7)	-0.0016(7)
C17	0.0347(9)	0.0549(12)	0.0282(9)	0.0013(8)	0.0052(7)	-0.0012(8)
C18	0.0382(10)	0.0568(12)	0.0389(10)	0.0129(9)	0.0093(8)	0.0123(9)
C19	0.0449(11)	0.0381(10)	0.0493(11)	0.0087(8)	0.0220(9)	0.0106(8)
C20	0.0349(9)	0.0361(9)	0.0350(9)	-0.0027(7)	0.0143(7)	-0.0019(7)

Table S2g. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 8c.

	x/a	y/b	z/c	U(eq)
H2	0.5519	0.7262	1.0102	0.046000
H3A	-0.1612	0.6432	0.7301	0.069000
H3B	-0.0978	0.5862	0.8455	0.069000
H4A	-0.2900	0.5538	0.5965	0.072000
H4B	-0.1150	0.5172	0.6579	0.072000
H5A	-0.1675	0.5457	0.4173	0.061000
H5B	-0.2258	0.6145	0.4370	0.061000
H10A	0.1388	0.6731	0.2095	0.052000
H10B	0.1804	0.6000	0.2181	0.052000
H11A	0.4676	0.6180	0.3269	0.070000
H11B	0.3912	0.6676	0.1927	0.070000
H12A	0.5889	0.7172	0.4177	0.063000
H12B	0.4070	0.7479	0.3628	0.063000
H17	0.7784	0.6307	1.1499	0.051000
H18	0.8367	0.5250	1.1198	0.057000
H19	0.6670	0.4693	0.9019	0.052000
H20	0.4343	0.5188	0.7061	0.043000

Table S3. Single Crystal data and structure refinement for 9a

A specimen of $C_{21}H_{22}N_2O_5$, approximate dimensions 0.085 mm x 0.181 mm x 0.188 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å). The integration of the data using a monoclinic unit cell yielded a total of 36347 reflections to a maximum θ angle of 28.29° (0.75 Å resolution), of which 4724 were independent (average redundancy 7.694, completeness = 100.0%, R_{int} = 4.57%, R_{sig} = 3.04%) and 3480 (73.67%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.5244(4) Å, b = 11.6767(5) Å, c = 19.3306(8) Å, β = 99.0810(10) °, volume = 1899.99(14) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9820 and 0. 9920.The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{21}H_{22}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 256 variables converged at R1 = 5.11%, for the observed data and wR2 = 12.90% for all data. The goodness-of-fit was 1.082. The largest peak in the final difference electron density synthesis was 0.221 e^-/Å^3 and the largest hole was -0.248 e^-/Å^3 with an RMS deviation of 0.048 e^-/Å^3. On the basis of the final model, the calculated density was 1.337 g/cm^3 and F (000), 808 e^-.

Table S3a. Sample and crystal data for work 9a.

Identification code	9a
CCDC NO	2500027
Chemical formula	$C_{21}H_{22}N_2O_5$
Formula weight	382.40 g/mol
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal size	0.085 x 0.181 x 0.188 mm
Crystal system	monoclinic
Space group	P 1 21/n 1

Unit cell dimensions	a = 8.5244(4) Å	α = 90°
	b = 11.6767(5) Å	β = 99.0810(10) °
	c = 19.3306(8) Å	γ = 90°
Volume	1899.99(14) $Å^3$	
Z	4	
Density (calculated)	1.337 g/cm^3	
Absorption coefficient	0.096 mm^{-1}	
F (000)	808	

Table S3b. Data collection and structure refinement for 9a

Theta range for data collection	2.04 to 28.29°	
Index ranges	-11<=h<=11, -15<=k<=15, -25<=l<=25	
Reflections collected	36347	
Independent reflections	4724 [R(int) = 0.0457]	
Max. and min. transmission	0.9920 and 0.9820	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	Σ w $(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4724 / 0 / 256	
Goodness-of-fit on F^2	1.082	
Final R indices	3480 data; I>2σ(I)	R1 = 0.0511, wR2 = 0.1106
	all data	R1 = 0.0767, wR2

	= 0.1290
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0411P)^2+0.9465P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.221 and -0.248 eÅ^{-3}
R.M.S. deviation from mean	0.048 eÅ^{-3}

Table S3c. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 9a.

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.24223(16)	0.45141(11)	0.37135(7)	0.0456(3)
O2	0.41612(15)	0.17444(11)	0.24676(6)	0.0430(3)
O3	0.65229(17)	0.45539(12)	0.40465(7)	0.0549(4)
O4	0.15650(15)	0.21641(12)	0.44228(7)	0.0487(3)
O5	0.07285(15)	0.07460(11)	0.36743(7)	0.0465(3)
N2	0.37986(17)	0.39946(12)	0.47815(7)	0.0357(3)
N3	0.2201(2)	0.05471(15)	0.25666(9)	0.0571(5)
C1	0.51799(19)	0.31623(14)	0.33017(8)	0.0306(3)
C2	0.51209(19)	0.26572(14)	0.26785(8)	0.0326(3)
C3	0.6029(2)	0.30022(16)	0.21112(9)	0.0402(4)
C4	0.7538(2)	0.36830(15)	0.23724(9)	0.0375(4)
C5	0.7131(2)	0.45760(15)	0.28913(10)	0.0414(4)
C6	0.6299(2)	0.41171(15)	0.34656(9)	0.0361(4)

	x/a	y/b	z/c	U(eq)
C7	0.41397(18)	0.27907(13)	0.38358(8)	0.0289(3)
C8	0.29402(18)	0.19116(14)	0.35002(8)	0.0314(3)
C9	0.3071(2)	0.14055(15)	0.28783(9)	0.0369(4)
C10	0.8092(3)	0.42865(19)	0.17502(11)	0.0555(5)
C11	0.8838(2)	0.28905(19)	0.27256(12)	0.0565(5)
C12	0.50683(18)	0.23685(14)	0.45255(8)	0.0315(3)
C13	0.33206(19)	0.38768(14)	0.40855(8)	0.0320(3)
C14	0.48112(19)	0.31107(15)	0.50608(8)	0.0341(4)
C15	0.5475(2)	0.29227(18)	0.57475(9)	0.0468(5)
C16	0.6399(2)	0.1953(2)	0.58933(11)	0.0570(6)
C17	0.6643(2)	0.11969(19)	0.53710(12)	0.0555(6)
C18	0.5971(2)	0.14020(16)	0.46761(10)	0.0423(4)
C19	0.1655(2)	0.15279(15)	0.38558(9)	0.0360(4)
C20	0.0235(3)	0.2007(2)	0.47959(12)	0.0626(6)
C21	0.0022(4)	0.3092(3)	0.51629(16)	0.0889(9)

Table S3d. Bond lengths (Å) for 9a.

O1-C13	1.218(2)	O2-C2	1.366(2)
O2-C9	1.372(2)	O3-C6	1.221(2)
O4-C19	1.336(2)	O4-C20	1.448(2)
O5-C19	1.222(2)	N2-C13	1.350(2)
N2-C14	1.398(2)	N3-C9	1.333(2)
C1-C2	1.335(2)	C1-C6	1.469(2)

C1-C7	1.526(2)	C2-C3	1.494(2)
C3-C4	1.529(3)	C4-C11	1.520(3)
C4-C5	1.524(2)	C4-C10	1.532(2)
C5-C6	1.507(2)	C7-C8	1.520(2)
C7-C12	1.521(2)	C7-C13	1.561(2)
C8-C9	1.360(2)	C8-C19	1.453(2)
C12-C18	1.371(2)	C12-C14	1.393(2)
C14-C15	1.376(2)	C15-C16	1.383(3)
C16-C17	1.381(3)	C17-C18	1.395(3)
C20-C21	1.478(3)		

Table S3e. Bond angles (°) for 9a.

C2-O2-C9	118.72(13)	C19-O4-C20	119.27(15)
C13-N2-C14	112.37(14)	C2-C1-C6	117.41(14)
C2-C1-C7	122.80(14)	C6-C1-C7	119.79(13)
C1-C2-O2	123.33(15)	C1-C2-C3	126.38(15)
O2-C2-C3	110.27(13)	C2-C3-C4	113.85(14)
C11-C4-C5	110.26(16)	C11-C4-C3	110.34(16)
C5-C4-C3	107.83(14)	C11-C4-C10	109.83(16)
C5-C4-C10	109.42(15)	C3-C4-C10	109.13(15)
C6-C5-C4	115.08(14)	O3-C6-C1	121.15(15)
O3-C6-C5	120.37(16)	C1-C6-C5	118.44(14)
C8-C7-C12	112.16(13)	C8-C7-C1	109.07(12)
C12-C7-C1	114.05(13)	C8-C7-C13	112.16(13)

C12-C7-C13	100.87(12)	C1-C7-C13	108.32(12)
C9-C8-C19	117.23(15)	C9-C8-C7	121.81(14)
C19-C8-C7	120.86(14)	N3-C9-C8	127.50(16)
N3-C9-O2	109.55(15)	C8-C9-O2	122.94(15)
C18-C12-C14	120.21(16)	C18-C12-C7	130.53(16)
C14-C12-C7	109.16(14)	O1-C13-N2	126.09(15)
O1-C13-C7	125.75(14)	N2-C13-C7	108.16(13)
C15-C14-C12	121.89(17)	C15-C14-N2	128.68(17)
C12-C14-N2	109.41(14)	C14-C15-C16	117.48(19)
C17-C16-C15	121.39(18)	C16-C17-C18	120.52(19)
C12-C18-C17	118.48(19)	O5-C19-O4	122.18(16)
O5-C19-C8	126.59(16)	O4-C19-C8	111.22(14)
O4-C20-C21	107.22(18)		

Table S3f. Anisotropic atomic displacement parameters (Å^2) for 9a.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0522(8)	0.0421(7)	0.0437(7)	0.0086(6)	0.0111(6)	0.0124(6)
O2	0.0451(7)	0.0497(8)	0.0363(6)	-0.0152(6)	0.0123(5)	-0.0125(6)
O3	0.0647(9)	0.0569(9)	0.0481(8)	-0.0240(7)	0.0243(7)	-0.0258(7)
O4	0.0443(7)	0.0616(9)	0.0441(7)	-0.0107(6)	0.0193(6)	-0.0192(6)
O5	0.0404(7)	0.0450(8)	0.0535(8)	-0.0003(6)	0.0057(6)	-0.0142(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	0.0443(8)	0.0332(7)	0.0313(7)	-0.0067(6)	0.0118(6)	-0.0026(6)
N3	0.0583(11)	0.0631(11)	0.0517(10)	-0.0267(9)	0.0144(8)	-0.0266(9)
C1	0.0330(8)	0.0309(8)	0.0289(8)	-0.0025(6)	0.0080(6)	-0.0021(6)
C2	0.0332(8)	0.0330(8)	0.0322(8)	-0.0026(7)	0.0065(6)	-0.0005(7)
C3	0.0431(10)	0.0476(11)	0.0320(8)	-0.0022(7)	0.0129(7)	0.0017(8)
C4	0.0359(9)	0.0396(10)	0.0393(9)	0.0040(7)	0.0133(7)	0.0038(7)
C5	0.0454(10)	0.0342(9)	0.0478(10)	0.0010(8)	0.0170(8)	-0.0024(8)
C6	0.0373(9)	0.0327(9)	0.0403(9)	-0.0051(7)	0.0125(7)	-0.0017(7)
C7	0.0302(8)	0.0284(8)	0.0282(7)	-0.0018(6)	0.0053(6)	-0.0025(6)
C8	0.0308(8)	0.0318(8)	0.0309(8)	-0.0018(6)	0.0025(6)	-0.0034(6)
C9	0.0339(8)	0.0380(9)	0.0378(9)	-0.0060(7)	0.0029(7)	-0.0051(7)
C10	0.0566(12)	0.0633(13)	0.0527(12)	0.0073(10)	0.0276(10)	-0.0010(10)
C11	0.0446(11)	0.0565(13)	0.0684(14)	0.0064(11)	0.0092(10)	0.0133(10)
C12	0.0289(8)	0.0334(8)	0.0319(8)	0.0011(6)	0.0040(6)	-0.0062(6)
C13	0.0353(8)	0.0302(8)	0.0322(8)	0.0011(7)	0.0111(6)	-0.0023(7)
C14	0.0349(8)	0.0392(9)	0.0286(8)	-0.0001(7)	0.0061(6)	-0.0092(7)
C15	0.0489(11)	0.0613(13)	0.0295(9)	0.0020(8)	0.0041(8)	-0.0128(9)
C16	0.0490(12)	0.0792(16)	0.0390(10)	0.0197(11)	-0.0050(9)	-0.0100(11)
C17	0.0422(11)	0.0556(13)	0.0652(13)	0.0246(11)	-0.0022(9)	0.0009(9)
C18	0.0362(9)	0.0394(10)	0.0512(11)	0.0043(8)	0.0064(8)	-0.0001(8)
C19	0.0331(8)	0.0379(9)	0.0355(8)	0.0052(7)	0.0010(7)	-0.0024(7)
C20	0.0539(13)	0.0844(17)	0.0561(13)	-0.0052(12)	0.0288(10)	-0.0212(12)
C21	0.0814(18)	0.106(2)	0.092(2)	-0.0231(17)	0.0528(16)	-0.0154(17)

Table S3g. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 9a.

	x/a	y/b	z/c	U(eq)
H2	0.3513	0.4550	0.5026	0.043000
H3A	0.1457	0.0252	0.2762	0.068000
H3B	0.2384	0.0289	0.2170	0.068000
H3C	0.5344	0.3461	0.1770	0.048000
H3D	0.6316	0.2319	0.1875	0.048000
H5A	0.8106	0.4948	0.3105	0.050000
H5B	0.6462	0.5156	0.2635	0.050000
H10A	0.8298	0.3727	0.1412	0.083000
H10B	0.9047	0.4709	0.1911	0.083000
H10C	0.7280	0.4803	0.1538	0.083000
H11A	0.9111	0.2350	0.2390	0.085000
H11B	0.8466	0.2487	0.3101	0.085000
H11C	0.9759	0.3334	0.2909	0.085000
H15	0.5308	0.3429	0.6100	0.056000
H16	0.6866	0.1806	0.6353	0.068000
H17	0.7259	0.0546	0.5483	0.067000
H18	0.6132	0.0895	0.4323	0.051000
H20A	0.0450	0.1385	0.5130	0.075000
H20B	-0.0718	0.1824	0.4470	0.075000
H21A	-0.0241	0.3693	0.4825	0.133000
H21B	0.0988	0.3282	0.5467	0.133000

	x/a	y/b	z/c	U(eq)
H21C	-0.0822	0.3007	0.5435	0.133000

Table S4. Single Crystal data and structure refinement for 9i.

A specimen of $C_{23}H_{20}N_4O_4$, approximate dimensions 0.070 mm x 0.256 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The integration of the data using a triclinic unit cell yielded a total of 39163 reflections to a maximum θ angle of 28.33° (0.75 Å resolution), of which 4995 were independent (average redundancy 7.840, completeness = 99.7%, R_{int} =5.49%, R_{sig} = 3.39%) and 3244 (64.94%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.1800(7) Å, b = 10.8402(8) Å, c = 11.1726(9) Å, α = 71.138(3) °, β = 89.122(3) °, γ = 73.437(3)°, volume = 1004.83(14) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9720 and 0.9930.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{23}H_{20}N_4O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 282variables converged at R1 = 6.26%, for the observed data and wR2 = 19.63% for all data. The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was 0.234 e^-/Å^3 and the largest hole was-0.276 e^-/Å^3 with an RMS deviation of 0.056 e^-/Å^3. On the basis of the final model, the calculated density was 1.376 g/cm^3 and F (000), 436 e^-.

Table S4a. Sample and crystal data for 9i.

Identification code	9i
CCDC NO	2515684
Chemical formula	$C_{23}H_{20}N_4O_4$
Formula weight	416.43 g/mol
Temperature	302(2) K
Wavelength	0.71073 Å
Crystal size	0.070 x 0.256 x 0.300 mm
Crystal system	triclinic

Space group	P -1	
Unit cell dimensions	a = 9.1800(7) Å	α = 71.138(3) °
	b = 10.8402(8) Å	β = 89.122(3) °
	c = 11.1726(9) Å	γ = 73.437(3) °
Volume	1004.83(14) $Å^3$	
Z	2	
Density (calculated)	1.376 g/cm^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	436	

Table S4b. Data collection and structure refinement for 9i

Theta range for data collection	1.93 to 28.33°	
Index ranges	-12<=h<=12, -14<=k<=14, -14<=l<=14	
Reflections collected	39163	
Independent reflections	4995 [R(int) = 0.0549]	
Max. and min. transmission	0.9930 and 0.9720	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	Σ w $(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4995 / 0 / 282	
Goodness-of-fit on F^2	1.072	
Final R indices	3244 data; I>2σ(I)	R1 = 0.0626, wR2 = 0.1519
	all data	R1 = 0.1059, wR2 = 0.1963
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0715P)^2+0.8525P]$ where $P=(F_o^2+2F_c^2)/3$	

Largest diff. peak and hole 0.234 and -0.276 eÅ^{-3}

R.M.S. deviation from mean 0.056 eÅ^{-3}

Table S4c. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 9i.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.57927(19)	0.48989(16)	0.33857(16)	0.0452(4)
O2	0.8095(2)	0.70515(18)	0.55453(17)	0.0535(5)
O3	0.4454(2)	0.83839(17)	0.49194(17)	0.0484(4)
O4	0.8637(2)	0.4779(2)	0.63352(19)	0.0658(6)
N2	0.4003(2)	0.63394(19)	0.16484(19)	0.0409(4)
N3	0.3390(2)	0.7719(2)	0.1018(2)	0.0462(5)
N4	0.5922(2)	0.9632(2)	0.3711(2)	0.0449(5)
N5	0.7323(3)	0.3596(2)	0.5109(2)	0.0516(5)
C1	0.3596(3)	0.5391(2)	0.1188(2)	0.0423(5)
C2	0.4309(4)	0.4022(3)	0.1688(3)	0.0676(9)
C3	0.3917(4)	0.3133(3)	0.1185(3)	0.0741(9)
C4	0.2820(4)	0.3596(3)	0.0216(3)	0.0650(8)
C5	0.2106(4)	0.4958(4)	0.9738(3)	0.0778(10)
C6	0.2473(4)	0.5877(3)	0.0213(3)	0.0676(8)
C7	0.4063(3)	0.8333(2)	0.1596(2)	0.0420(5)
C8	0.5142(2)	0.7370(2)	0.2599(2)	0.0364(5)
C9	0.5040(2)	0.6156(2)	0.2586(2)	0.0369(5)

C10	0.3610(3)	0.9851(3)	0.1171(3)	0.0573(7)
C11	0.6257(2)	0.7464(2)	0.3514(2)	0.0357(5)
C12	0.6946(2)	0.6039(2)	0.4462(2)	0.0382(5)
C13	0.6716(3)	0.4888(2)	0.4351(2)	0.0391(5)
C14	0.5426(3)	0.8518(2)	0.4157(2)	0.0393(5)
C15	0.7137(3)	0.9422(2)	0.2950(2)	0.0416(5)
C16	0.7417(2)	0.8144(2)	0.2829(2)	0.0387(5)
C17	0.7964(3)	0.5859(2)	0.5523(2)	0.0447(5)
C18	0.9130(4)	0.6995(4)	0.6527(3)	0.0683(8)
C19	0.9147(6)	0.8414(5)	0.6305(5)	0.1238(19)
C20	0.7999(3)	0.0278(3)	0.2421(3)	0.0544(6)
C21	0.9206(3)	0.9808(3)	0.1763(3)	0.0603(7)
C22	0.9535(3)	0.8527(3)	0.1668(3)	0.0555(7)
C23	0.8633(3)	0.7675(3)	0.2193(2)	0.0459(5)

Table S4d. Bond lengths (Å) for 9i

O1-C9	1.352(3)	O1-C13	1.377(3)
O2-C17	1.340(3)	O2-C18	1.437(3)
O3-C14	1.230(3)	O4-C17	1.222(3)
N2-C9	1.354(3)	N2-N3	1.379(3)
N2-C1	1.423(3)	N3-C7	1.329(3)
N4-C14	1.353(3)	N4-C15	1.403(3)
N5-C13	1.339(3)	C1-C2	1.365(4)
C1-C6	1.371(4)	C2-C3	1.389(4)
C3-C4	1.353(4)	C4-C5	1.357(4)
C5-C6	1.389(4)	C7-C8	1.420(3)
C7-C10	1.488(3)	C8-C9	1.351(3)

C8-C11	1.504(3)	C11-C12	1.521(3)
C11-C16	1.523(3)	C11-C14	1.555(3)
C12-C13	1.367(3)	C12-C17	1.448(3)
C15-C20	1.373(3)	C15-C16	1.386(3)
C16-C23	1.376(3)	C18-C19	1.482(5)
C20-C21	1.387(4)	C21-C22	1.374(4)
C22-C23	1.398(4)		

Table S4e. Bond angles (°) for 9i

C9-O1-C13	114.72(17)	C17-O2-C18	116.9(2)
C9-N2-N3	108.77(17)	C9-N2-C1	131.5(2)
N3-N2-C1	119.48(18)	C7-N3-N2	105.80(18)
C14-N4-C15	111.72(19)	C2-C1-C6	119.8(2)
C2-C1-N2	121.4(2)	C6-C1-N2	118.7(2)
C1-C2-C3	119.8(3)	C4-C3-C2	121.1(3)
C3-C4-C5	118.6(3)	C4-C5-C6	121.9(3)
C1-C6-C5	118.8(3)	N3-C7-C8	111.4(2)
N3-C7-C10	119.5(2)	C8-C7-C10	129.1(2)
C9-C8-C7	103.49(19)	C9-C8-C11	121.75(19)
C7-C8-C11	134.73(19)	C8-C9-O1	127.7(2)
C8-C9-N2	110.54(19)	O1-C9-N2	121.69(19)
C8-C11-C12	107.57(17)	C8-C11-C16	111.79(18)
C12-C11-C16	114.69(18)	C8-C11-C14	109.50(17)
C12-C11-C14	112.85(18)	C16-C11-C14	100.35(17)
C13-C12-C17	117.0(2)	C13-C12-C11	123.96(19)
C17-C12-C11	119.01(19)	N5-C13-C12	127.8(2)
N5-C13-O1	108.69(19)	C12-C13-O1	123.5(2)
O3-C14-N4	125.4(2)	O3-C14-C11	126.1(2)
N4-C14-C11	108.45(19)	C20-C15-C16	122.6(2)
C20-C15-N4	128.0(2)	C16-C15-N4	109.33(19)

C23-C16-C15	119.7(2)	C23-C16-C11	130.8(2)
C15-C16-C11	109.49(19)	O4-C17-O2	121.6(2)
O4-C17-C12	126.5(2)	O2-C17-C12	111.9(2)
O2-C18-C19	106.7(3)	C15-C20-C21	117.3(3)
C22-C21-C20	121.0(3)	C21-C22-C23	121.1(3)
C16-C23-C22	118.3(2)		

Table S4f. Anisotropic atomic displacement parameters (Å²) for 9i

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0525(10)	0.0350(8)	0.0484(9)	-0.0132(7)	-0.0066(7)	-0.0136(7)
O2	0.0571(11)	0.0557(11)	0.0531(10)	-0.0208(8)	-0.0117(8)	-0.0209(9)
O3	0.0505(10)	0.0482(10)	0.0568(10)	-0.0263(8)	0.0151(8)	-0.0209(8)
O4	0.0699(13)	0.0537(11)	0.0611(12)	-0.0079(9)	-0.0236(10)	-0.0102(10)
N2	0.0395(10)	0.0371(10)	0.0488(11)	-0.0163(8)	-0.0034(8)	-0.0125(8)
N3	0.0423(10)	0.0393(10)	0.0559(12)	-0.0160(9)	-0.0079(9)	-0.0097(8)
N4	0.0489(11)	0.0374(10)	0.0572(12)	-0.0232(9)	0.0104(9)	-0.0178(9)
N5	0.0572(13)	0.0357(10)	0.0548(13)	-0.0076(9)	-0.0068(10)	-0.0108(9)
C1	0.0445(12)	0.0454(12)	0.0474(13)	-0.0230(10)	0.0048(10)	-0.0204(10)
C2	0.0722(19)	0.0474(15)	0.087(2)	-0.0278(15)	-0.0261(16)	-0.0153(14)
C3	0.089(2)	0.0490(16)	0.091(2)	-0.0307(16)	-0.0192(19)	-0.0204(15)
C4	0.080(2)	0.0639(18)	0.0682(18)	-0.0333(15)	-0.0050(15)	-0.0329(16)
C5	0.087(2)	0.077(2)	0.077(2)	-0.0304(17)	-0.0293(18)	-0.0279(18)
C6	0.075(2)	0.0570(17)	0.0730(19)	-0.0263(15)	-0.0230(16)	-0.0163(14)

C7	0.0406(12)	0.0387(11)	0.0469(13)	-0.0158(10)	-0.0005(10)	-0.0102(9)
C8	0.0356(10)	0.0356(11)	0.0421(11)	-0.0167(9)	0.0028(9)	-0.0122(8)
C9	0.0353(10)	0.0352(11)	0.0417(11)	-0.0144(9)	0.0015(9)	-0.0107(8)
C10	0.0582(16)	0.0392(13)	0.0706(18)	-0.0166(12)	-0.0124(13)	-0.0092(11)
C11	0.0344(10)	0.0347(10)	0.0418(11)	-0.0170(9)	0.0001(9)	-0.0110(8)
C12	0.0383(11)	0.0366(11)	0.0404(12)	-0.0142(9)	0.0002(9)	-0.0102(9)
C13	0.0395(11)	0.0376(11)	0.0402(11)	-0.0137(9)	0.0036(9)	-0.0107(9)
C14	0.0386(11)	0.0387(11)	0.0441(12)	-0.0170(9)	0.0014(9)	-0.0127(9)
C15	0.0411(12)	0.0427(12)	0.0449(12)	-0.0146(10)	0.0024(10)	-0.0185(10)
C16	0.0351(11)	0.0424(12)	0.0405(11)	-0.0146(9)	-0.0008(9)	-0.0130(9)
C17	0.0435(12)	0.0439(13)	0.0467(13)	-0.0149(10)	-0.0017(10)	-0.0129(10)
C18	0.0572(17)	0.095(2)	0.0646(18)	-0.0369(17)	-0.0103(14)	-0.0275(16)
C19	0.120(4)	0.116(4)	0.167(5)	-0.078(3)	-0.042(3)	-0.044(3)
C20	0.0571(15)	0.0532(15)	0.0611(16)	-0.0173(12)	0.0056(13)	-0.0309(13)
C21	0.0534(15)	0.0737(19)	0.0624(17)	-0.0194(14)	0.0093(13)	-0.0358(14)
C22	0.0390(13)	0.0734(18)	0.0540(15)	-0.0191(13)	0.0057(11)	-0.0192(12)
C23	0.0383(12)	0.0501(13)	0.0467(13)	-0.0167(11)	-0.0013(10)	-0.0084(10)

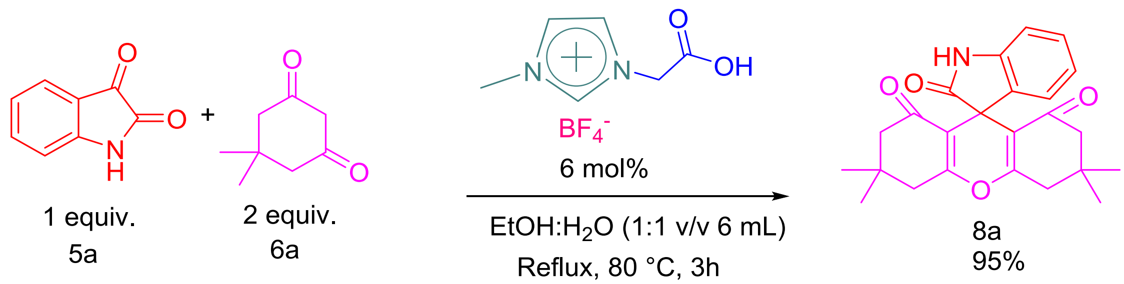
Table S4g. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 9i

	x/a	y/b	z/c	U(eq)
H4	0.5540	1.0376	0.3874	0.054000
H5A	0.7939	0.3417	0.5756	0.062000
H5B	0.7098	0.2945	0.4948	0.062000
H2	0.5054	0.3686	0.2362	0.081000
H3	0.4417	0.2203	0.1520	0.089000
H4A	0.2561	0.2995	-0.0114	0.078000
H5	0.1350	0.5284	-0.0928	0.093000
H6	0.1967	0.6806	-0.0124	0.081000
H10A	0.4505	1.0151	0.1029	0.086000
H10B	0.3073	1.0162	0.1812	0.086000
H10C	0.2960	1.0218	0.0396	0.086000
H18A	1.0144	0.6422	0.6488	0.082000

	x/a	y/b	z/c	U(eq)
H18B	0.8788	0.6623	0.7356	0.082000
H19A	0.9833	0.8423	0.6941	0.186000
H19B	0.8139	0.8969	0.6350	0.186000
H19C	0.9482	0.8771	0.5480	0.186000
H20	0.7783	1.1138	0.2501	0.065000
H21	0.9802	1.0369	0.1380	0.072000
H22	1.0372	0.8221	0.1248	0.067000
H23	0.8848	0.6814	0.2115	0.055000

Green Chemistry Metrics:

Green Chemistry Metrics for 8a (symmetric derivative)



Mass: 0.2g	0.381g		0.505g
Moles: 1.36 mmol	2.72 mmol		1.36 mmol
GMW: 147.13	140.18		391.1784

1. Percentage Yield (%) = (0.505÷0.532) ×100 = 95%

2. Atom Economy = (391.18÷427.49) ×100 = 91.5%

3. Atom Efficiency (%) = 0.95×91.5 = 86.9%

4. Carbon Economy = (24÷24) ×100= 100%

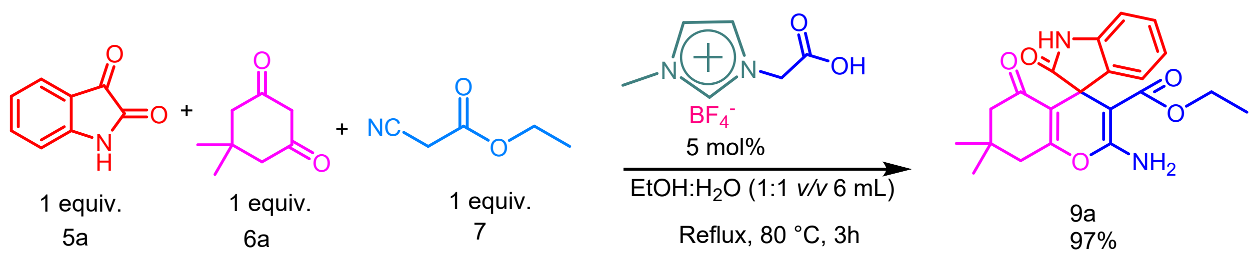
5. Reaction Mass Efficiency (%) = (0.505÷0.581) ×100= 86.92 %

6. E-Factor = (0.076÷0.505) = 0.15

7.TON (Turn over number) = 15.86

8. TOF (Turn over frequency) = 5.287 h^{-1}

Green Chemistry Metrics for 9a (unsymmetric derivative)



Mass: 0.2g 0.191g 0.154g 0.504g

Moles: 1.36 mmol 1.36 mmol 1.36 mmol 1.36 mmol

GMW: 147.13 140.18 113.11 382.1529

1. Percentage Yield (%) = (0.504÷0.52) ×100 = 97%

2. Atom Economy = (382.15÷400.42) ×100 = 95%

3. Atom Efficiency (%) = 0.97×95 = 92.15%

4. Carbon Economy = (21÷21) ×100= 100%

5. Reaction Mass Efficiency (%) = (0.504÷0.545) ×100= 92.5 %

6. E-Factor = (0.041÷0.504) = 0.08

7.TON (Turn over number) = 19.40

8. TOF (Turn over frequency) = 6.47 h^{-1}

Summarized Green Chemistry Metrics for 8a and 9a

Name of Compounds	Percentage Yield (%)	Atom Economy	Atom Efficiency (%)	Carbon Economy	Reaction mass efficiency (%)	E-factor	TON	TOF
8a	95%	91.5%	86.9%	100%	86.92 %	0.15	15.86	5.287 h^{-1}
9a	97%	95%	92.15%	100%	92.5 %	0.08	19.40	6.47 h^{-1}