

Supporting Information to accompany...

Dibenzonaphthyridinones: Heterocycle-to-Heterocycle Synthetic Strategies and Photophysical Studies

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Experimental Methods and Data

All chemicals were purchase from standard chemical supply companies and used without further purification. Compounds **1a**, **1b**, **2a**, **2b**, and **2c** were made using literature methods.^[1] All melting points were collected on an Optimelt automated melting point system from Stanford research systems. All nuclear magnetic resonance (NMR) spectra were taken on a Varian 600MHz spectrometer and analyzed using MestReNova 10.0 (s: singlet, bs: broad singlet, d: doublet, dd: doublet of doublets, ddd: doublet of doublet of doublets, qd: quartet of doublets, t: triplet). All IR were collected and analyzed on a Bruker Alpha FT-IR with a Platinum ATR (with a diamond plate). All HRMS were collected and analyzed on a Bruker Thermo Electron LTQ-Orbitrap Hybrid MS.

General procedure for synthesis of isoxazoles **3a-3d** (Figure 1):

The alkyne moiety (**1a** or **1b**, 1eq) was placed in a flame dried round bottom flask containing stir bar and dissolved in anhydrous tetrahydrofuran (THF, ~0.5M) and cooled to 0 °C with an ice/water bath. To this solution was added NaH (60% dispersion in mineral oil, 3.2 eq) in portions. The chlorooxime (**2a/2b/2c**, 2.2 eq) was dissolved in a separate flame dried flask in anhydrous THF (enough to completely dissolve) and added to the reaction mixture drop-wise, via addition funnel (addition over the course of several hours). This reaction mixture was allowed to stir for 24 hours slowly warming from 0 °C to room temperature. The reaction mixture was then concentrated *in vacuo*, extracted with ethyl acetate (EtOAc, 3x, ~100mL), washed with water (2x, ~150mL), and finally washed with brine (2x, ~150mL). The combined organic fractions were dried over sodium sulfate, filtered, concentrated *in vacuo*, and purified via column chromatography (flash, Si gel, THF:hexanes mixtures) to yield the desired isoxazole as a light to dark beige solid (20-76% yield).

General procedures for synthesis of dibenzonaphthyridinones **5a-8**:

The isoxazole moiety (**3a-d**, 1eq.) was placed in a microwave vial containing stir bar and dissolved in neat acetic acid at 90 °C. This flask was removed from heat and Fe⁰ powder (20 eq.) was added. This mixture was sealed in the microwave vial and allowed to stir at 90 °C for 1 hour. At this time, the reaction mixture was neutralized using NaHCO₃ (sat., aq., until complete lack of effervescence with addition of more NaHCO₃), extracted with EtOAc (3x, ~100mL), washed with EDTA (sat., aq., 2x, ~100mL), and finally brine (2x, ~100mL). The combined organic fractions were dried over sodium sulfate, filtered and concentrated *in vacuo*. In the case of **5a-d**, this crude intermediate (**4aa-bc**) was then dissolved in neat acetone (~1M) with catalytic acetic acid in a microwave vial containing stir bar, sealed, and stirred at 90 °C for 24 hours. In the case of **6** and **7** this crude intermediate (**4aa**) was dissolved in ethanol (~1M) with catalytic acetic acid, the carbonyl species of choice was added (10 eq.), sealed, and stirred at 90 °C for 24 hours. In the case of **8** this crude intermediate (**4aa**) was dissolved in ethanol (4.0 eq., ~0.25M) at 90 °C in a 2-neck round bottom flask containing stir bar and outfitted with reflux condenser. To this mixture was added catalytic acetic acid, and 1,4-cyclohexanedione (1 eq., in ethanol to complete dissolution) drop-wise over the course of 2.5 hours, and stirred at 90 °C for 24 hours. In all cases, the crude reaction mixture was monitored by TLC to completion. At this time, the crude reaction mixture was concentrated *in vacuo*, re-dissolved in EtOAc and washed with NaHCO₃ (sat., aq., 1x, ~100mL) followed by brine (2x, ~100mL). The organic fraction was dried over sodium sulfate, filtered, concentrated *in vacuo* and purified via column chromatography (flash, Si gel, THF:hexanes or EtOAc: hexanes mixtures) to afford the desired dibenzonaphthyridinone as a bright yellow powder (16-92%).

1a (1-ethynyl-2-nitrobenzene) Prepared using literature methods. 24.1 mmol of the requisite aryl iodide were used to produce 2.29 g of the desired product as beige solid (64% over two steps). All experimental data matched literature data.

1b (1-ethynyl-4-methoxy-2-nitrobenzene) Prepared using literature methods. 14.3 mmol of the requisite aryl iodide was used to produce 1.24 g of the desired product as a beige solid (49%, MP 86.9-87.5 °C). IR (neat) ν_{max} 3278, 3084, 2952, 2972, 2849, 2571, 1519, and 1272 cm⁻¹. ¹H NMR (600MHz, CDCl₃) δ 7.60 (d, J=8.73 Hz, 1H), 7.52 (d, J=2.39 Hz, 1H), 7.09 (t, J=9.29, 2.53 Hz, 1H), and 3.9 (s, 3H) ppm. ¹³C NMR (150MHz, CDCl₃) δ 160.00, 151.21, 136.39, 119.64, 109.45, 83.24, 78.62, and 56.07 ppm. HRMS calculated for [C₉H₈NO₃]⁺ 178.0499 [M+H]⁺; found 178.0497.

2a (2-nitrobenzaldehyde oxime) Prepared using literature methods. 50.0 mmol of the requisite aryl iodide were used to produce 7.40 g of the desired product as a white solid (89%). All experimental data matched literature data.

2b (4-chloro-2-nitrobenzaldehyde oxime) Prepared using literature methods. 13.5 mmol of the requisite aryl aldehyde was used to produce 2.44 g of the desired product as an eggshell solid (90%, MP 174.2-175.5 °C) IR (neat) ν_{max} 3294, 3087, 3071, 3017, 1518, 1342, and 1153 cm⁻¹. ¹H NMR (600MHz, CDCl₃) δ 8.64 (s, 1H), 8.06 (s, 1H), 7.92 (d, J=9.59 Hz, 1H), 7.61 (d, J=9.59 Hz, 1H), and 2.17 (s, 1H) ppm. ¹³C NMR (150MHz, CDCl₃) δ 145.96, 136.33, 133.47, 129.64, 125.52, 124.87, and 109.92 ppm. HRMS calculated for [C₇H₆CIN₂O₃]⁺ 201.0061 [M+H]⁺; found 201.0060.

2c (5-chloro-2-nitrobenzaldehyde oxime) Prepared using literature methods. 21.5 mmol of the requisite aryl iodide was used to produce 4.07 g of the desired product as a pale yellow solid (94%, MP 98.2-99.3 °C). IR (neat) ν_{max} 3453, 3192, 3108, 3073, 3041, 2843, 1601, 1516, 1301, and 1194 cm⁻¹. ¹H NMR (600MHz, CDCl₃, mixture of E and Z isomers) δ 8.66 (s, 1H), 8.56 (bs, 1H), 8.09 (d, J=9.51 Hz, 0.3H), 8.03 (d, J=9.51 Hz, 1H), 7.88 (s, 1H), 7.84 (s, 0.3H), 7.73 (s, 0.3H), 7.52 (d, J=10.9 Hz, 0.3H), and 7.49 (d, J=9.16 Hz, 1H) ppm. ¹³C NMR (150MHz, CDCl₃, mixture of E and Z isomers) δ 146.11, 145.83, 145.57, 142.74, 140.20, 140.00, 130.97, 130.34, 130.30, 128.84, 128.59, 126.80, 126.40, and 126.01 ppm. HRMS calculated for [C₇H₆CIN₂O₃]⁺ 201.0061 [M+H]⁺; found 201.0061.

3a (3,5-bis(2-nitrophenyl)isoxazole) Prepared using the general synthetic procedure for isoxazoles described above. 20.4 mmol (1.0 eq) of **1a** and 44.9 mmol (2.2 eq) of **2a** were used to produce 3.83 g of the desired product as a tan solid (60%). All experimental data matched the literature data.

3b (3-(4-chloro-2-nitrophenyl)-5-(2-nitrophenyl)isoxazole) Prepared using the general synthetic procedure for isoxazoles described above. 2.04 mmol (1.0 eq.) of **1a** and 4.49 mmol (2.2 eq.) of **2b** were used to produce 281 mg of the desired product as a dark tan solid (40%, MP 195.5-196.7 °C). IR (neat) ν_{max} 3135, 3084, 3067, 2953, 2921, 2853, 1624, 1522, and 1354 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 8.30 (d, J=2.24 Hz, 1H), 8.11 (d, J=7.65 Hz, 1H), 7.97 (dd, J=8.97, 2.24 Hz, 1H), 7.90, (m, 4H), 7.82 (t, J=15.70, 7.65 Hz, 1H), and 7.34 (s, 1H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 166.41, 159.58, 149.19, 148.00, 136.22, 133.99, 133.69, 133.26, 132.87, 131.31, 125.20, 125.04, 120.98, and 120.16 ppm. HRMS calculated for [C₁₅H₉CIN₃O₅]⁺ 346.0225 [M+H]⁺; found 346.0226.

3c (5-(4-methoxy-2-nitrophenyl)-3-(2-nitrophenyl)isoxazole) Prepared using the general synthetic procedure for isoxazoles described above. 2.82 mmol (1eq.) of **1b** and 6.20 mmol (2.2 eq.) of **2a** were used to produce 417 mg of the desired product as a pale yellow solid (43%, MP159.1-159.9

°C). IR (neat) ν_{max} 3090, 2966, 2940, 2840, 1618, 1522, and 1345 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 8.10 (d, J=7.61 Hz, 1H), 7.84 (m, 4H), 7.89 (t, J=14.08, 7.42 Hz, 1H), 7.67 (d, J=3.43 Hz, 1H), 7.42 (dd, J=9.14, 3.43 Hz, 1H), 7.21 (s, 1H), and 3.90 (s, 3H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 166.07, 161.81, 160.38, 149.21, 148.70, 133.78, 132.35, 132.08, 131.83, 125.04, 122.55, 119.37, 112.00, 110.42, 103.55, and 56.80 ppm. HRMS calculated for [C₁₆H₁₂N₃O₆]⁺ 342.0721 [M+H]⁺; found 342.0726.

3d (3-(5-chloro-2-nitrophenyl)-5-(4-methoxy-2-nitrophenyl)isoxazole) Prepared using the general synthetic procedure for isoxazoles described above. 5.00 mmol (1 eq.) of **1b** and 11 mmol (2.2 eq.) of **2c** were used to produce 379 mg of the desired product as an off white solid (20%, MP 148.1-148.9 °C). IR (neat) ν_{max} 3079, 3039, 3001, 2849, 1625, 1522, and 1342 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 8.15 (d, J=8.41 Hz, 1H), 7.96 (s, 1H), 7.88 (t, J=8.41, 2.13 Hz, 1H), 7.84, (d, J=8.76 Hz, 1H), 7.67 (d, J=2.12 Hz, 1H), 7.42 (dd, J=8.85, 2.60 Hz, 1H), 7.28 (s, 1H), and 3.91 (s, 3H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 166.30, 161.80, 159.44, 149.14, 147.26, 138.30, 132.28, 131.81, 131.42, 126.93, 124.40, 119.25, 111.94, 110.52, 103.60, and 56.72 ppm. HRMS calculated for [C₁₆H₁₁CIN₃O₆]⁺ 376.0331 [M+H]⁺; found 376.0339.

5a (6,6-dimethyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridin-7(12H)-one) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 0.643 mmol (1 eq) of **3a** was used to produce 158 mg of bright yellow powder (89%, MP 276.7-277.8 °C [decomposition]). IR (neat) ν_{max} 3357, 3267, 3209, 3093, 3064, 2997, 2952, 2917, 1766, and 1624 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 10.94 (bs, 1H), 8.02 (d, J=8.77 Hz, 1H), 7.82 (d, J=8.77 Hz, 1H), 7.77 (d, J=8.77 Hz, 1H), 7.56 (t, J=15.63, 7.62 Hz, 1H), 7.21 (t, J=15.63, 7.82 Hz, 1H), 7.12 (t, J=15.44, 7.03 Hz, 1H), 6.60 (m, 2H), 6.14 (bs, 1H), and 1.61 (s, 6H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 174.71, 147.01, 140.82, 139.62, 132.32, 131.54, 125.15, 124.05, 122.84, 118.30, 115.87, 114.54, 112.46, 53.91, and 29.19 ppm. HRMS calculated for [C₁₈H₁₇N₂O]⁺ 277.1335 [M+H]⁺; found 277.1333.

5b (3-chloro-6,6-dimethyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridin-7(12H)-one) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 0.29 mmol (1 eq.) of **3b** was used to produce 72 mg of a bright yellow solid (80%, MP 293.5-294.3 °C). IR (neat) ν_{max} 3381, 3269, 3208, 3116, 3068, 2918, 2849, 1723, and 1627 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 10.88 (bs, 1H), 8.00 (d, J=8.05 Hz, 1H), 7.98 (d, J=8.62 Hz, 1H), 7.88 (d, J=8.62 Hz, 1H), 7.55 (t, J=14.44, 6.78 Hz, 1H), 7.21 (t, J=15.31, 7.87 Hz, 1H), 6.65, (d, J=1.73, 1H), 6.59 (dd, J=8.92, 1.73 Hz, 1H), 6.53 (s, 1H), and 1.61 (s, 6H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 174.75, 148.04, 140.06, 139.81, 136.86, 131.73, 126.29, 125.22, 125.16, 122.95, 118.51, 118.05, 115.44, 113.24, 111.41, 54.23, and 29.48 ppm. HRMS calculated for [C₁₈H₁₆CIN₂O]⁺ 311.0946 [M+H]⁺; found 311.0945.

5c (10-methoxy-6,6-dimethyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridin-7(12H)-one) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 0.29 mmol (1 eq.) of **3c** was used to produce 82 mg of a bright yellow powder (92%, MP 263.7-264.5 °C [decomposition]). IR (neat) ν_{max} 3364, 3271, 3214, 3116, 3078, 2962, 2920, 2851, 1735, and 1629 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 10.81 (bs, 1H), 7.90 (d, J=8.99 Hz, 1H), 7.77 (d, J=6.22 Hz, 1H), 7.23 (s, 1H), 7.10 (t, J=13.48, 7.60 Hz), 6.81 (d, J=8.99 Hz, 1H), 6.59 (m, 2H), 6.10 (bs, 1H), 3.81 (s, 3H), and 1.59 (2, 6H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 174.48, 162.06, 146.77, 141.34, 140.52, 132.20, 126.98, 123.69, 119.68, 117.84, 115.79, 114.34, 112.92, 112.50, 99.26, 55.71, 53.82, and 29.37 ppm. HRMS calculated for [C₁₉H₁₉N₂O₂]⁺ 307.1441 [M+H]⁺; found 307.1440.

5d (2-chloro-10-methoxy-6,6-dimethyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridin-7(12H)-one) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 0.266 mmol (1.0 eq.) of **3d** was used to produce 30 mg of the desired product as a bright yellow powder (33%, MP 299.4-300.2 °C [decomposition]). IR (neat) ν_{max} 3375, 3273, 3077, 2953, 2896, 2834, 1681, and 1629 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 10.82 (bs, 1H), 7.90 (d, J=9.70 Hz, 1H), 7.86 (s, 1H), 7.17 (d, J=3.16 Hz, 1H), 7.12 (dd, J=8.43, 2.28 Hz, 1H), 6.82 (dd, J=7.73, 2.99 Hz, 1H), 6.60 (d, J=8.60 Hz, 1H), 6.33 (bs, 1H), 3.82 (s, 3H), and 1.59 (s, 6H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 174.35, 162.13, 145.47, 141.36, 139.25, 131.84, 127.04, 122.93, 119.63, 119.28, 118.11, 115.86, 113.76, 113.17, 99.09, 55.74, 54.01, and 29.58 ppm. HRMS calculated for [C₁₉H₁₈ClN₂O₂]⁺ 341.1051 [M+H]⁺; found 341.1062.

6 (5'H-spiro[cyclohexane-1,6'-dibenzo[b,h][1,6]naphthyridin]-7'(12'H)-one) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 0.161 mmol (1.0 eq.) of **3a** and 1.61 mmol (10 eq.) of cyclohexane were used to produce 41 mg of the desired product as a bright yellow powder (80%, MP 251.7-252.4 °C [decomposition]). IR (neat) ν_{max} 3419, 3401, 3255, 3204, 3151, 3099, 3059, 2992, 2924, 2854, 1624, and 1611 cm⁻¹. ¹H NMR (600MHz, Acetone-d6) δ 10.18 (bs, 1H), 8.19 (dd, J=8.10, 1.55 Hz, 1H), 7.71 (d, J=7.56 Hz, 1H), 7.67 (d, J=8.34 Hz, 1H), 7.55 (ddd, J=15.45, 7.56, 1.42 Hz, 1H), 7.23 (ddd, J=14.84, 7.82, 0.95 Hz, 1H), 7.15 (ddd, J=15.32, 7.53, 1.25, 1H), 6.91 (dd, J=8.63, 1.21 Hz, 1H), 6.44 (ddd, J=15.10, 7.41, 1.21, 1H), 5.70 (bs, 1H), 3.04 (ddd, J=27.68, 14.07, 4.55 Hz, 2H), 1.80(dd, J=13.33, 1.70 Hz, 2H), 1.70 (m, 3H), 1.55 (m, 2H), and 1.36 (qdd, J=36.29, 14.13, 14.13, 3.51 Hz, 1H) ppm. ¹³C NMR (150MHz, Acetone-d6) δ 175.02, 146.23, 141.12, 139.38, 139.26, 131.83, 131.12, 125.51, 122.60, 122.31, 118.48, 117.40, 116.47, 115.02, 113.76, 55.91, 32.91, 24.88, and 20.55 ppm. HRMS calculated for [C₂₁H₂₁N₂O]⁺ 317.1648 [M+H]⁺; found 317.1650.

7 (*t*-butyl 7-oxo-7,12-dihydro-5H-spiro[dibenzo[b,h][1,6]naphthyridine-6,4'-piperidine]-1'-carboxylate) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 0.480 mmol (1 eq.) of **3a** and 4.80 mmol (10 eq.) of N-Boc piperidine were used to produce 86 mg of the desired product as a bright yellow powder (43%, MP 259.7-260.4 °C [decomposition]). IR (neat) ν_{max} 3419, 3402, 3262, 3201, 3063, 2918, 2858, 1674, 1627, and 1615 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 11.07 (bs, 1H), 8.01 (d, J=8.82 Hz, 1H), 7.84 (d, J=7.39, Hz, 1H), 7.79 (d, J=9.95, 1H), 7.57 (dd, J=15.07, 7.39 Hz, 1H), 7.22 (dd, J=16.21, 7.39 Hz, 1H), 7.16 (dd, J=13.65, 7.39 Hz, 1H), 6.95, (d, J=7.68 Hz, 1H), 6.66 (dd, J=15.07, 7.39 Hz, 1H), 6.37 (bs, 1H), 3.79 (m, 2H), 3.20 (m, 2H), 2.96 (m, 2H), 1.56 (d, J=12.5 Hz, 2H), 1.41, and (s, 9H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 174.74, 154.66, 146.23, 141.98, 139.51, 132.49, 131.80, 125.50, 125.34, 124.17, 123.06, 118.39, 116.81, 116.71, 115.44, 113.26, 78.83, 54.34, 32.94, 28.56, and 14.54 ppm. HRMS calculated for [C₂₅H₂₈N₃O₃]⁺ 418.2125 [M+H]⁺; found 418.2124.

8 (bis-6,6-spiro-diethyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridin-7(12H)-one) Prepared using the general synthetic procedure for dibenzonaphthyridinones given above. 1.8 mmol (4.0 eq.) of **3a** and 0.45 mmol (1.0 eq.) of 1,4-cyclohexanedione were used to produce 40 mg of the desired product as a bright yellow solid (16%, MP 340.1-341.5 °C [decomposition]). IR (neat) ν_{max} 3266, 3208, 3066, 2997, 2922, 1625, and 1611 cm⁻¹. ¹H NMR (600MHz, DMSO-d6) δ 11.18 (bs, 2H), 8.45 (d, J=8.91 Hz, 2H), 7.88 (d, J=8.02 Hz, 2H), 7.84 (d, J=8.91 Hz, 2H), 7.61 (dd, J=15.74, 6.53 Hz, 2H), 7.28 (dd, J=14.25, 6.53 Hz, 2H), 7.20 (dd, J=15.74, 7.72 Hz, 2H), 7.00 (d, J=7.72 Hz, 2H), 6.78 (bs, 2H), 6.67 (dd, J=13.06, 7.72 Hz, 2H), 3.07 (d, J=8.33 Hz, 4H), and 1.68 (d, J=7.86, 4H) ppm. ¹³C NMR (150MHz, DMSO-d6) δ 175.03, 146.74, 141.99, 139.54, 132.73, 125.39, 125.35, 124.20, 123.17,

118.51, 118.50, 118.05, 116.51, 115.49, 113.07, 79.59, 54.32, and 29.69 ppm. HRMS calculated for $[C_{36}H_{28}N_4O_2]^+$ 549.2285 $[M+H]^+$; found 549.2281.

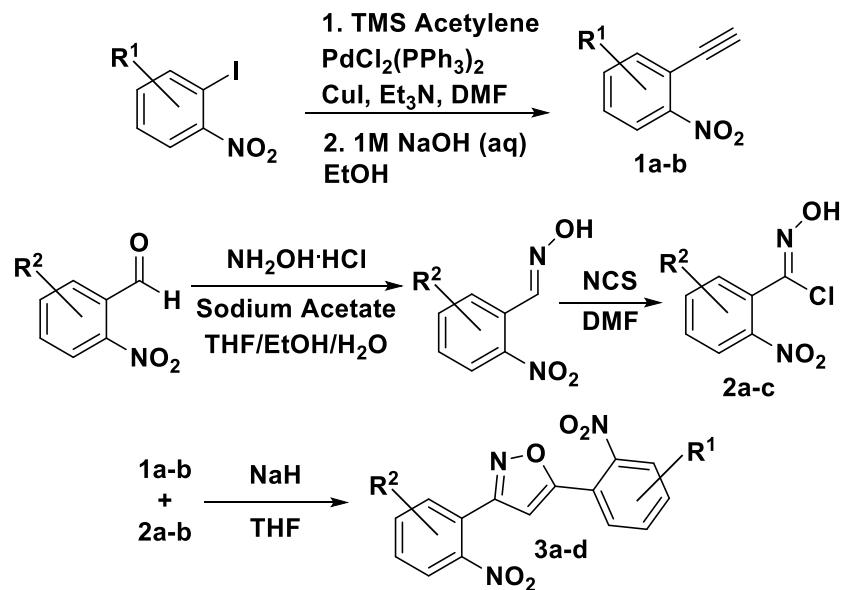
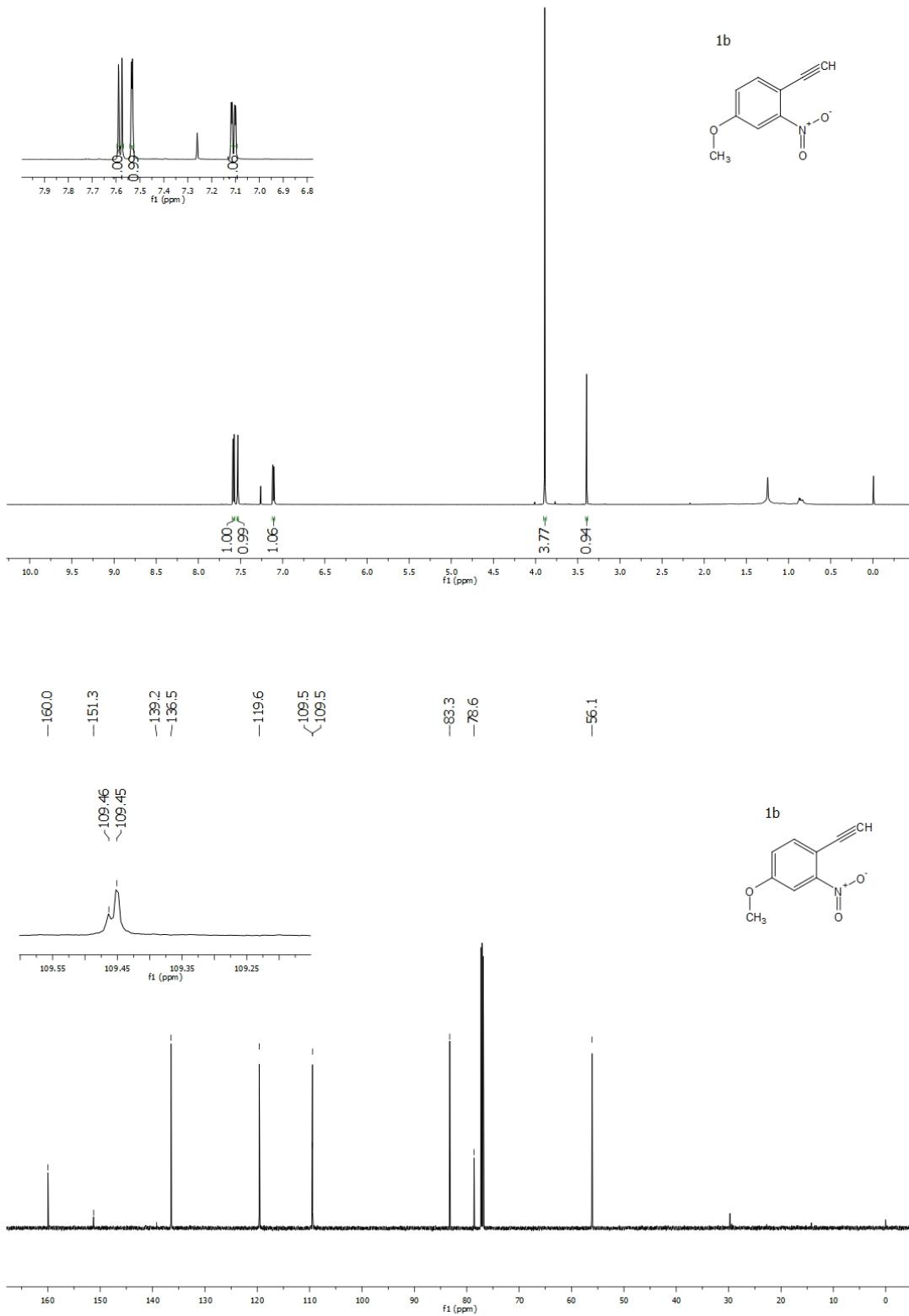


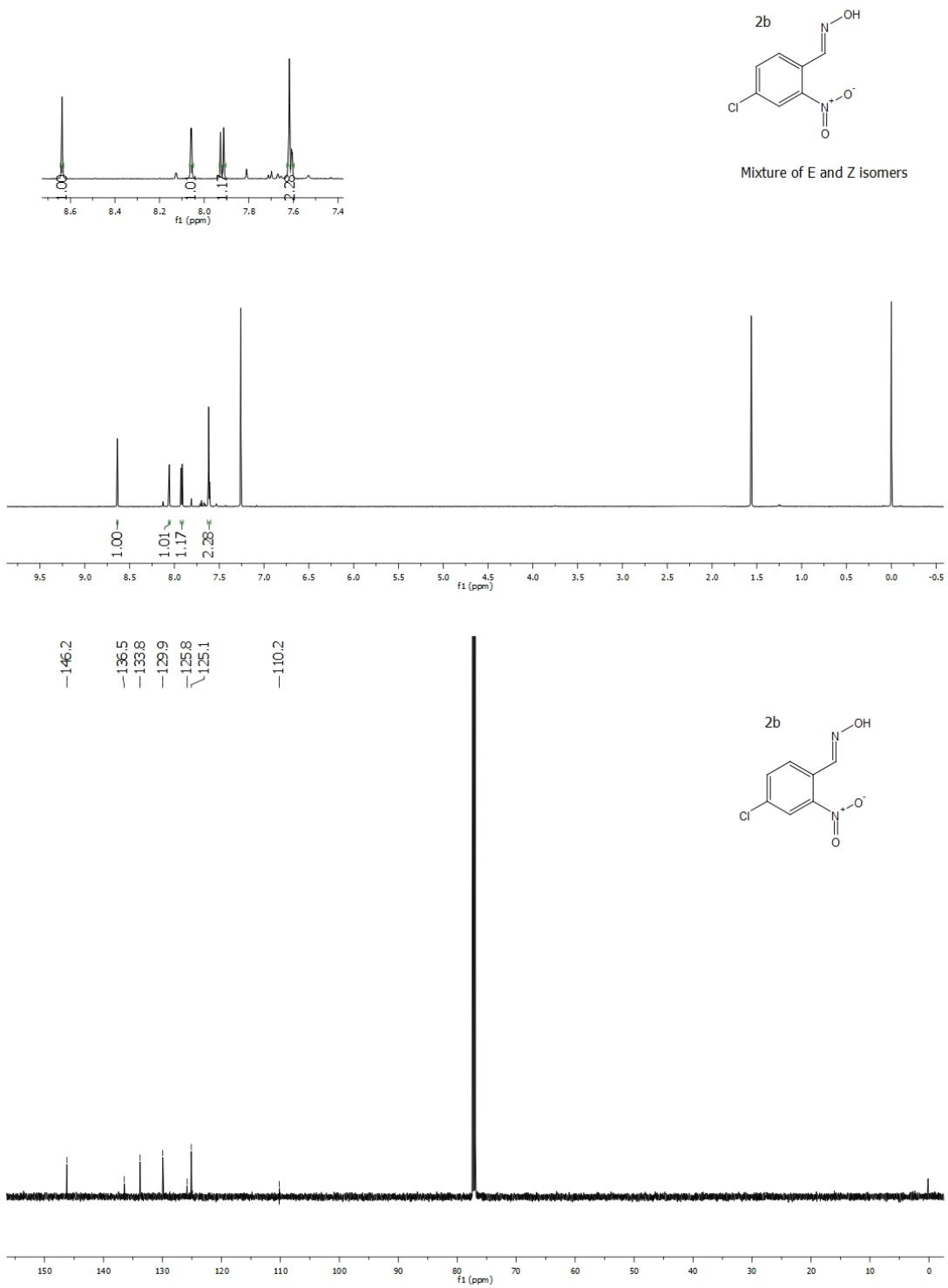
Figure 1. Synthesis of isoxazoles **3a-d**.

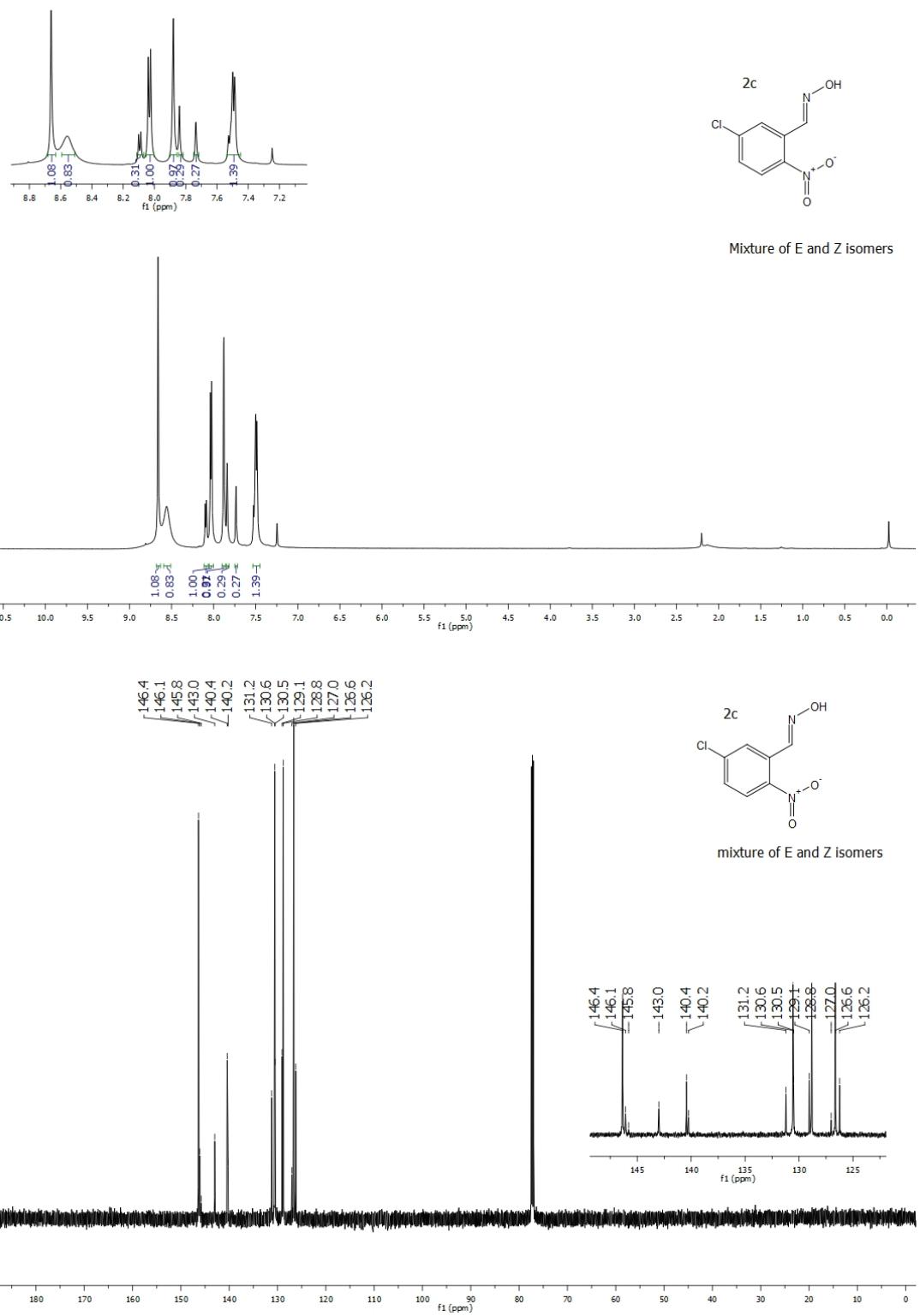
Table 1. Yields for isoxazoles **3a-d**.

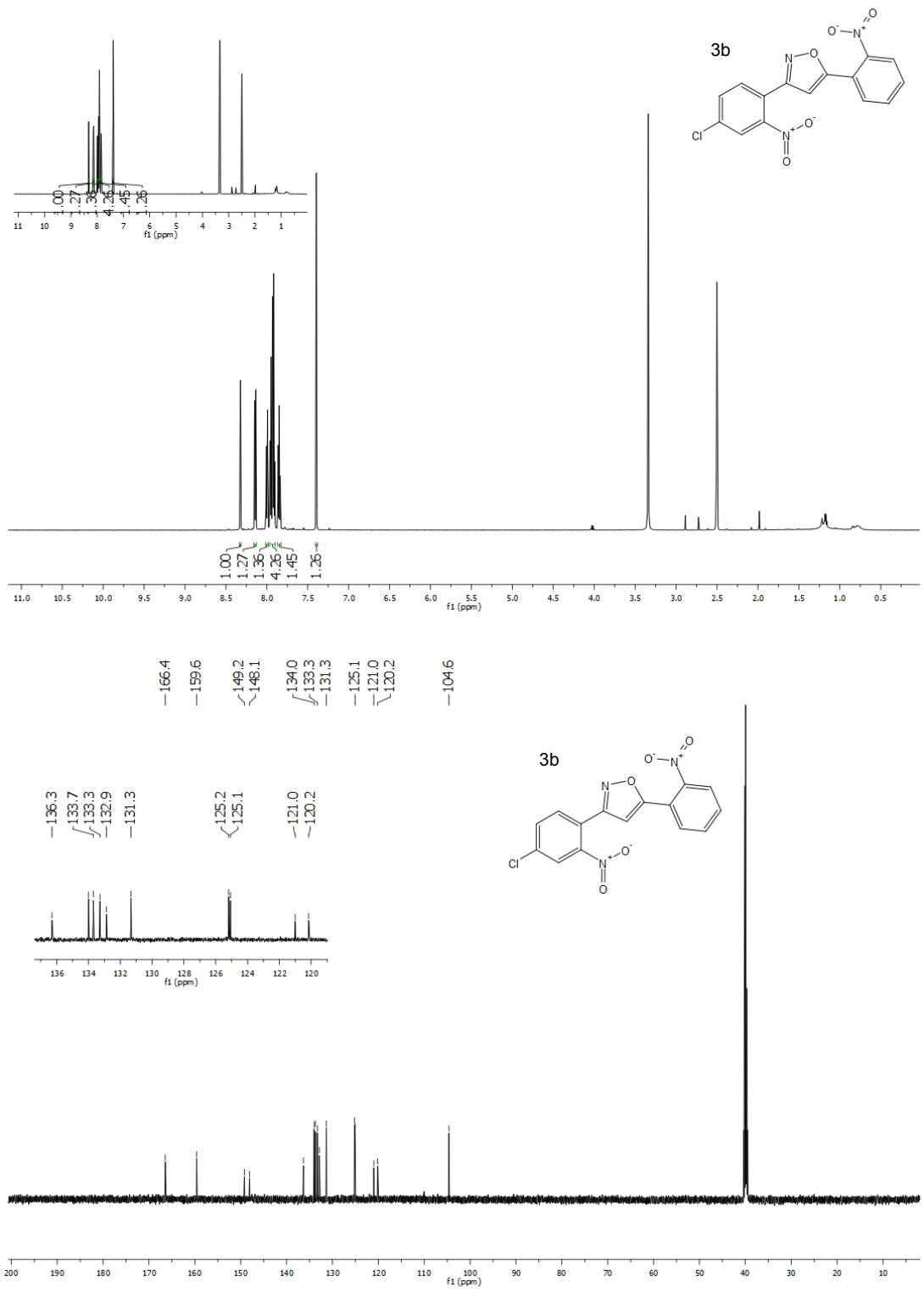
Compound	R ¹	R ²	% Yield
3a	H	H	76
3b	H	4-Cl	40
3c	4-OCH ₃	H	43
3d	4-OCH ₃	5-Cl	20

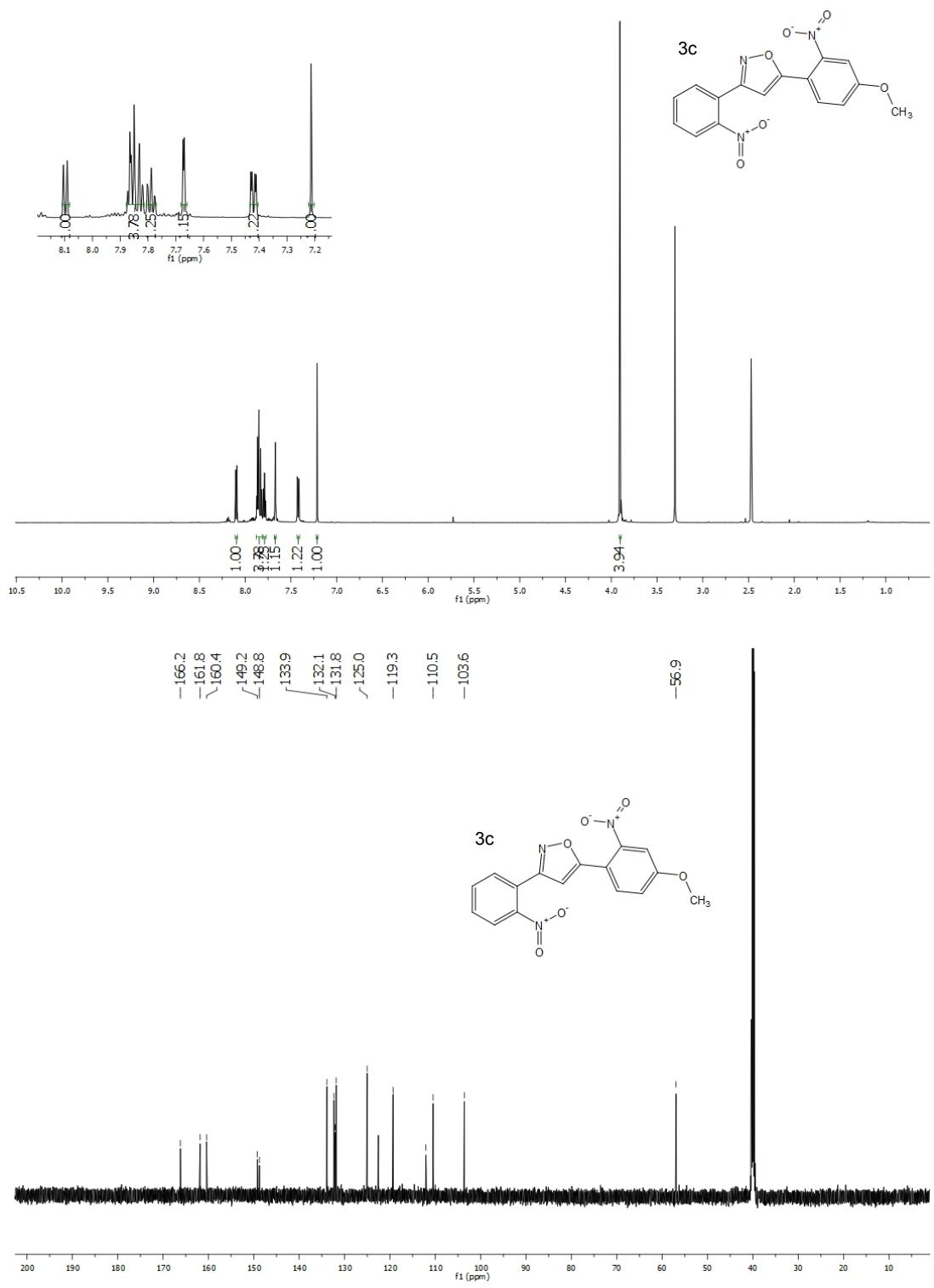
¹H and ¹³C NMR Spectra

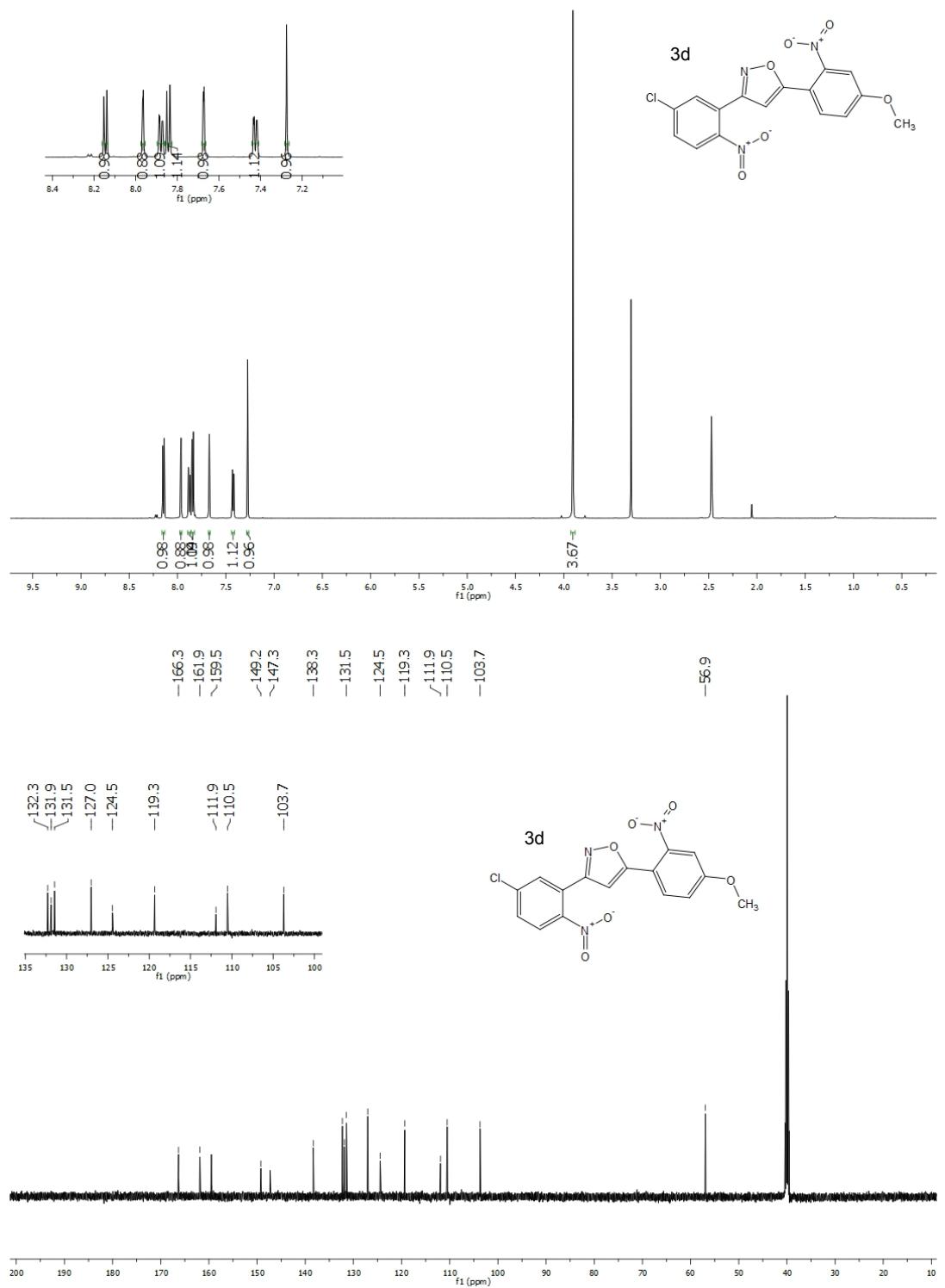


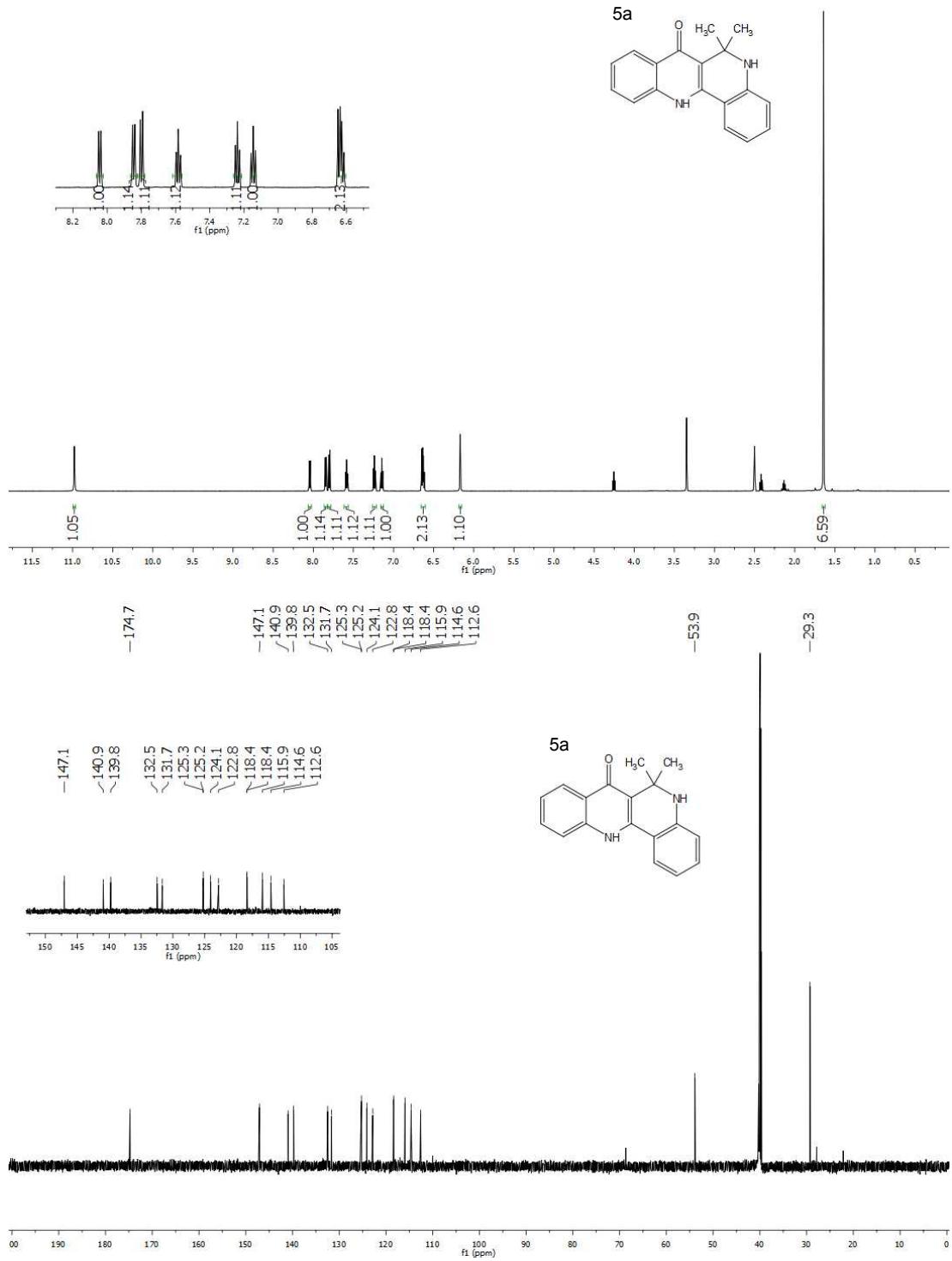


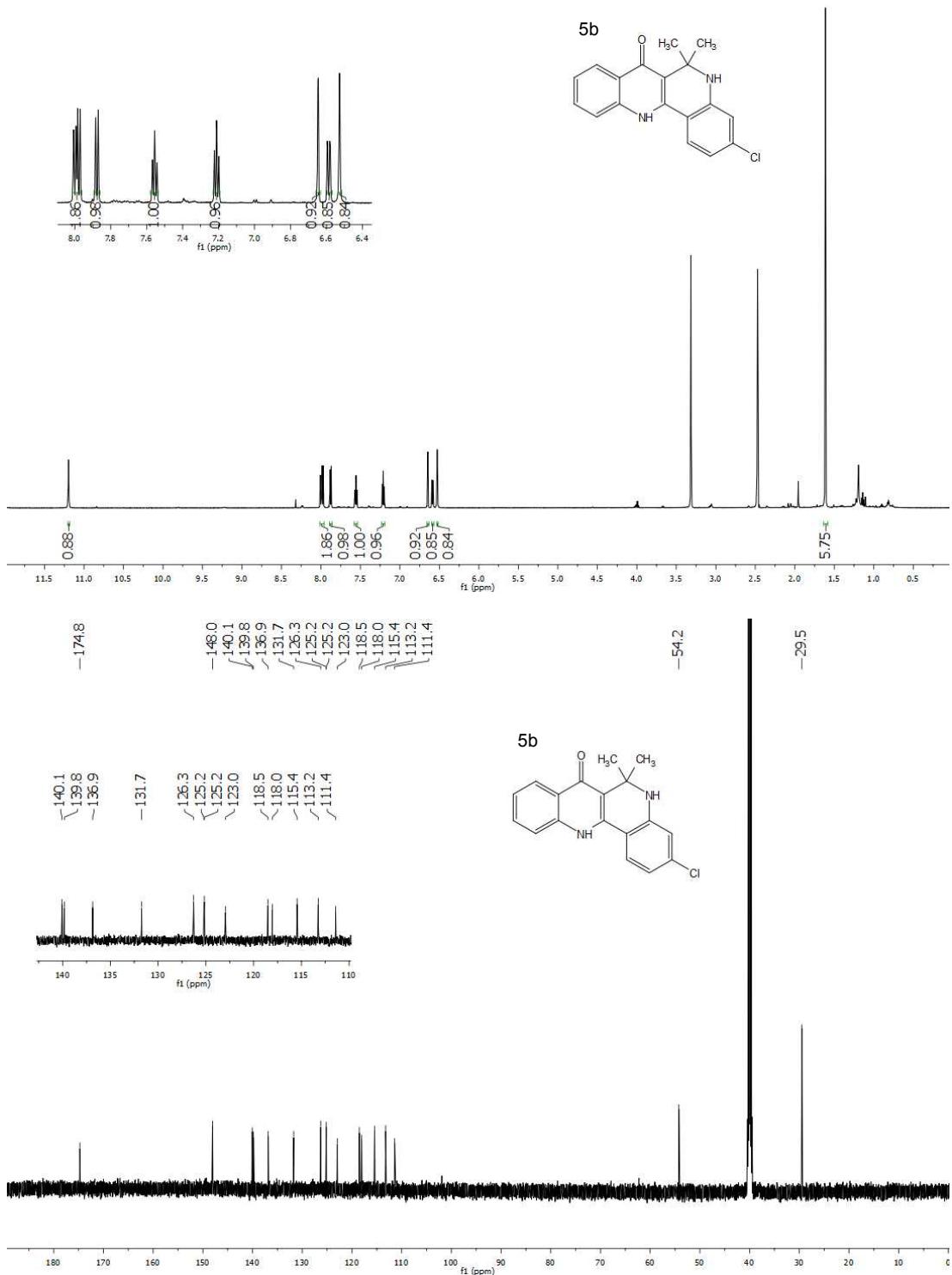


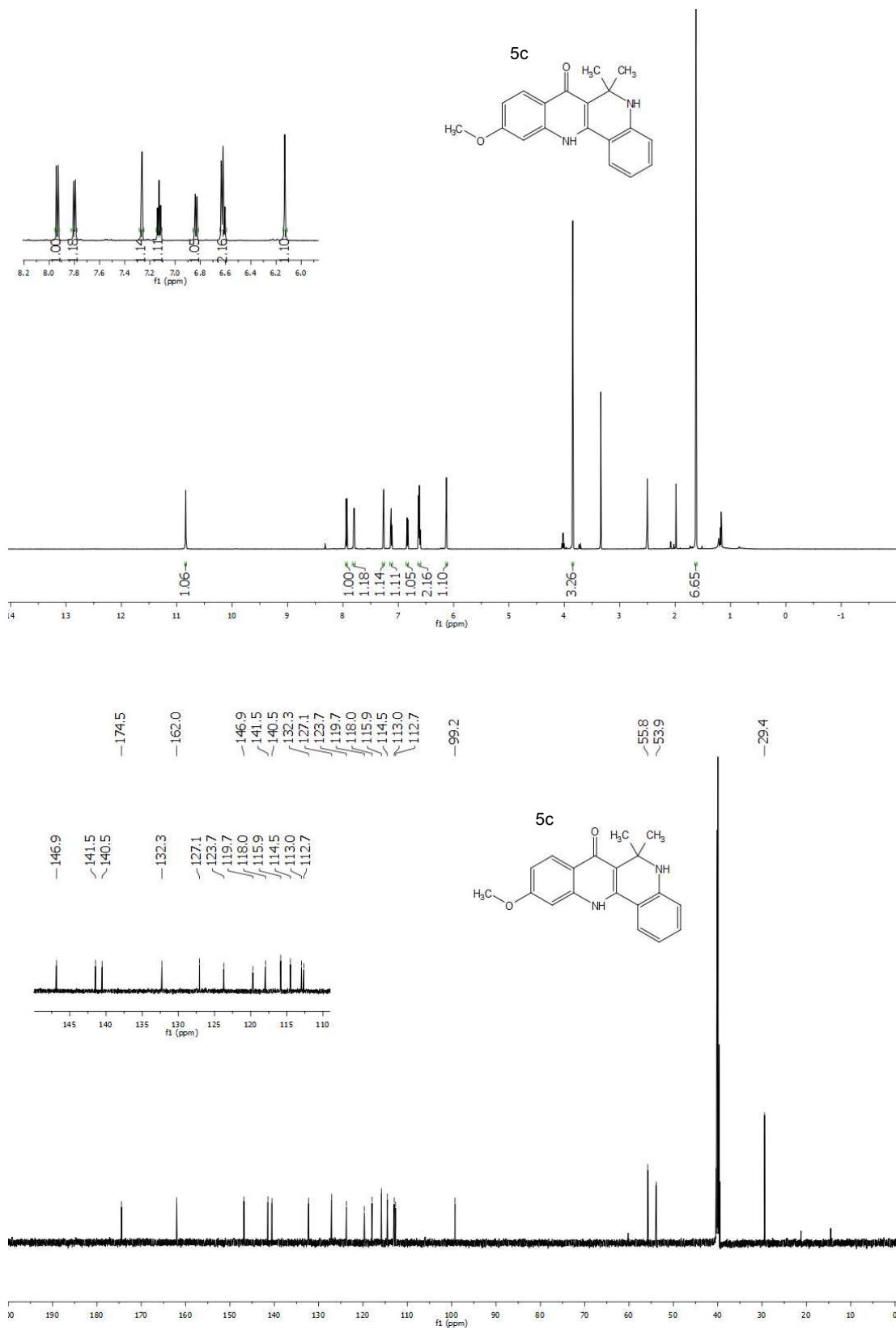


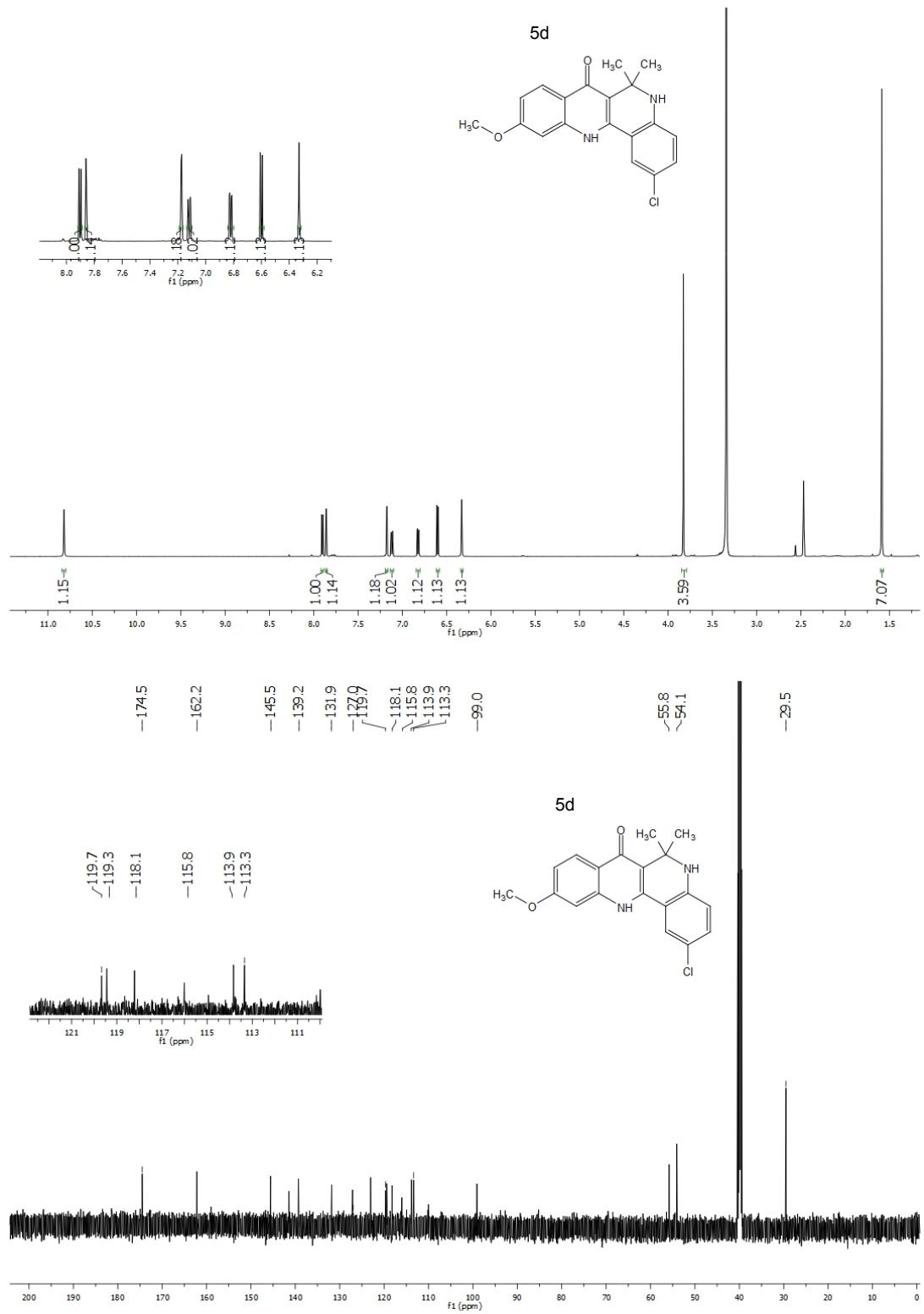


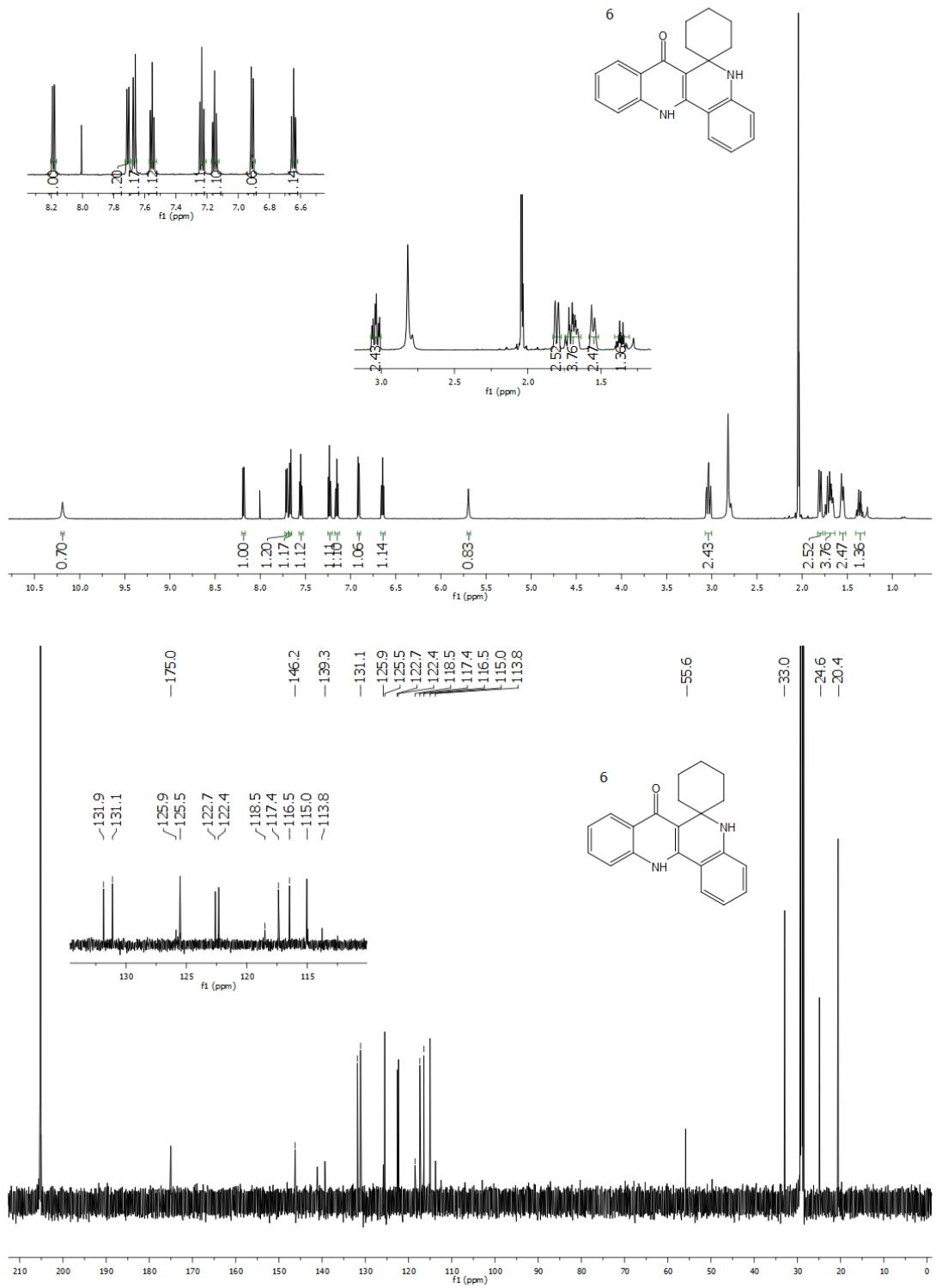


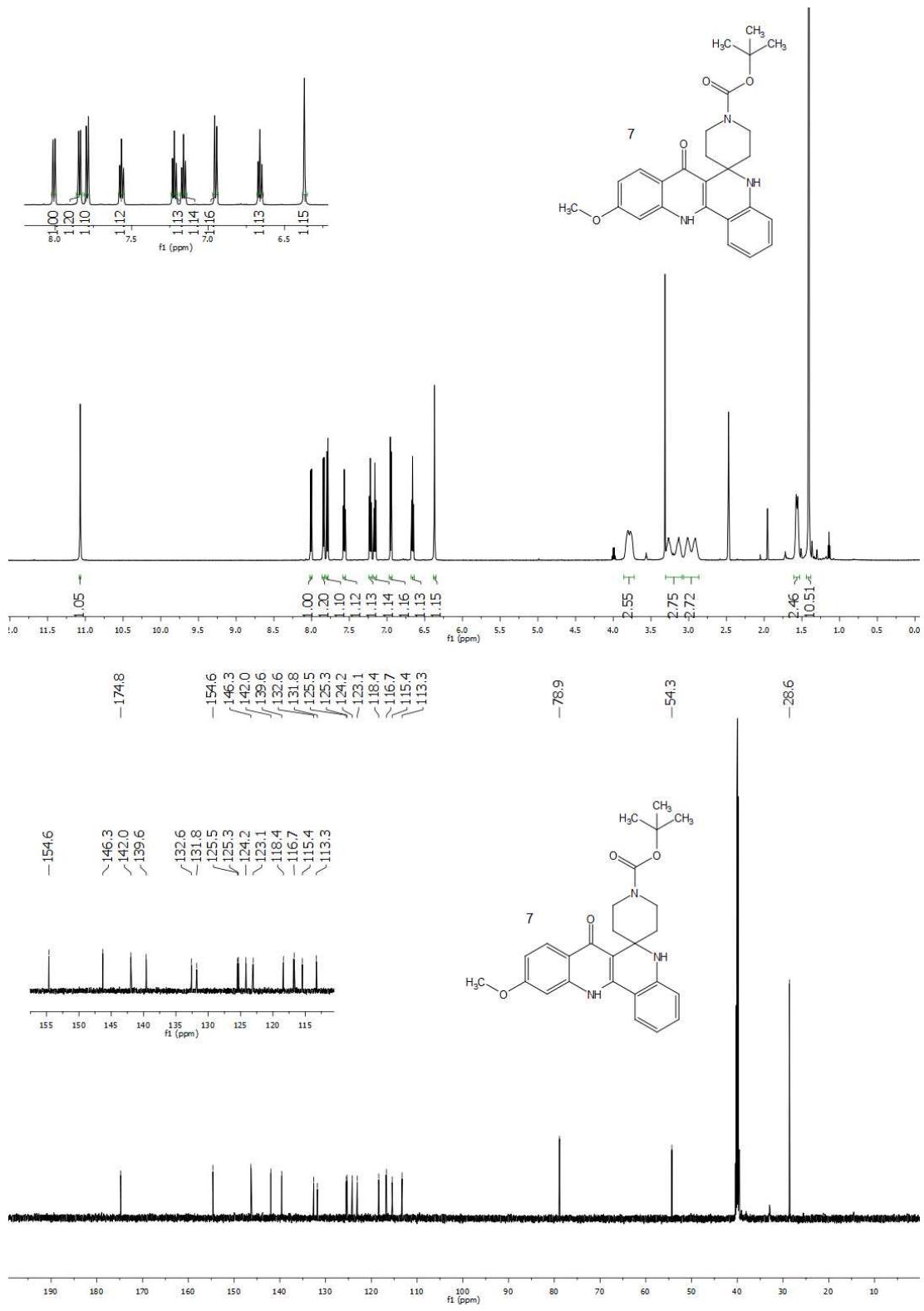


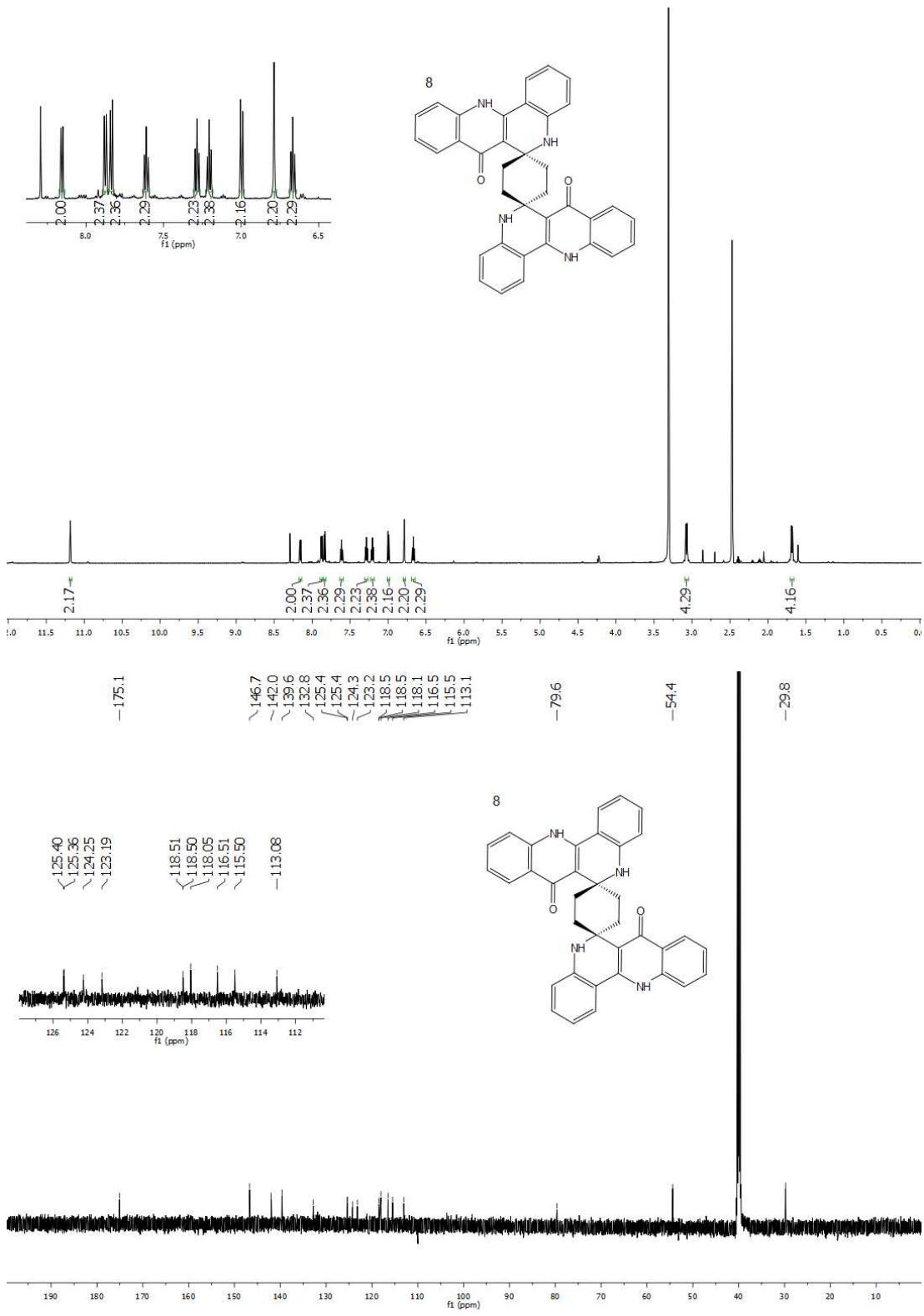












X-Ray Crystallographic Methods and Data

5a (TP2, CCDC 1403789)

An orange irregular crystal with approximate orthogonal dimensions $0.550 \times 0.390 \times 0.182 \text{ mm}^3$ was placed and optically centered on the Bruker Duo APEXII CCD system at -183°C (90K). Indexing of the unit cell used a random set of reflections collected from three series of 0.5° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Data were collected [$\text{CuK}\alpha$] with 0.5° wide scans, 4, 6, 8 or 12 seconds per frame dependent upon detector 2θ angle and varying φ and omega angles such that nearly all unique reflections were collected at least once. The crystal to detector distance was 4.96cm, thus providing a complete sphere of data to $2\theta_{\max}=136.53^\circ$.



Structural Refinement Data

All crystallographic calculations were performed on a Sony Vaio with 2.10GHz dual core processor and 4GB of extended memory. A total of 11852 reflections were collected and corrected for Lorentz and polarization effects with SAINT^[1] and absorption using crystal faces and Blessing's method as incorporated into the program SADABS^[2] with 6046 unique for point group 4. The SHELXTL^[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences, and intensity statistics indicated the centrosymmetric monoclinic space group P2₁ (no. 4). The structure was determined by direct methods with the successful location of a majority of the molecule using the program XT.^[4] The structure was refined with XL^[3] and Olex2.^[5] The data collected were merged for least squares refinement to 6046 unique data [$R(\text{int})=0.0212$]. A single least-squares difference-Fourier cycle was required to locate the remaining non-hydrogen atoms with a subsequent cycle required to locate the hydrogen atoms although all hydrogen atoms were initially idealized. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were allowed to refine freely throughout the final refinement stages. The final structure was refined to convergence with $R(F)=2.75\%$, $wR(F^2)=7.39\%$, $GOF=1.021$ for all 6046 unique reflections [$R(F)=2.76$, $wR(F^2)=7.40\%$ for those 6031 data with $F_o > 4\sigma(F_o)$]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

5a (TP2)

Table 1 Crystal data and structure refinement for TP2_final_2_a.

Identification code	TP2_final_2_a
Empirical formula	C ₁₉ H ₂₁ N ₂ O _{2.5}
Formula weight	317.38
Temperature/K	90.15
Crystal system	monoclinic
Space group	P2 ₁
a/Å	9.5219(3)
b/Å	17.2194(5)
c/Å	9.9584(3)
α/°	90
β/°	90.7800(10)
γ/°	90
Volume/Å ³	1632.64(9)
Z	4
ρ _{calc} g/cm ³	1.291
μ/mm ⁻¹	0.693
F(000)	676.0
Crystal size/mm ³	0.51 × 0.338 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.618 to 146.034
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -12 ≤ l ≤ 11
Reflections collected	11852
Independent reflections	6046 [R _{int} = 0.0212, R _{sigma} = 0.0290]
Data/restraints/parameters	6046/1/592
Goodness-of-fit on F ²	1.020
Final R indexes [I>=2σ (I)]	R ₁ = 0.0275, wR ₂ = 0.0739
Final R indexes [all data]	R ₁ = 0.0276, wR ₂ = 0.0740
Largest diff. peak/hole / e Å ⁻³	0.19/-0.17
Flack parameter	0.10(4)

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for TP2_final_2_a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	816.1(13)	6013.2(7)	2704.9(12)	21.3(3)
N1	-824.4(15)	7534.1(8)	5390.3(14)	17.0(3)
N2	-2289.2(18)	7699.9(10)	1469.0(16)	27.0(3)
C1	252.9(17)	6486.9(10)	3524.0(17)	17.6(3)
C2	735.8(17)	6483.8(10)	4917.1(17)	17.8(3)
C3	1760.1(17)	5951.1(10)	5378.6(17)	19.6(3)
C4	2224.1(18)	5969.3(10)	6693.6(18)	21.4(3)

C5	1695.3(19)	6530.7(11)	7576.0(17)	21.4(3)
C6	690.2(18)	7054.3(10)	7158.4(17)	19.6(3)
C7	194.3(17)	7025.4(10)	5819.8(17)	17.6(3)
C8	-1335.0(17)	7541.9(9)	4111.8(17)	16.7(3)
C9	-2429.0(17)	8110.3(9)	3780.4(17)	17.6(3)
C10	-3021.7(18)	8622(1)	4711.2(17)	19.9(3)
C11	-4016.3(19)	9162.8(11)	4331(2)	22.8(4)
C12	-4451.2(18)	9206.4(10)	2986.7(19)	22.5(4)
C13	-3886.6(19)	8716.9(11)	2048.8(18)	22.4(4)
C14	-2873.1(18)	8157.7(10)	2427.3(18)	19.9(3)
C15	-1407.3(17)	7019.2(10)	1718.8(16)	18.3(3)
C16	-807.1(18)	7033.8(10)	3153.3(17)	17.4(3)
C17	-2285(2)	6277.5(11)	1543.9(19)	23.6(4)
C18	-257(2)	7058.8(12)	651.7(18)	25.8(4)
O2	4175.5(12)	2922.0(7)	1096.9(12)	20.9(3)
N3	5774.0(15)	2362.0(8)	4780.0(14)	17.0(3)
N4	7993.5(15)	3970.9(9)	2664.7(15)	21.4(3)
C19	4758.6(17)	2724.4(10)	2192.5(17)	17.8(3)
C20	4215.1(17)	2063.3(10)	2950.9(17)	18.2(3)
C21	3142.2(18)	1587.4(11)	2405.8(18)	21.4(3)
C22	2648.6(19)	960.3(11)	3113(2)	23.7(4)
C23	3208.6(19)	791.8(10)	4394(2)	23.5(4)
C24	4247.1(18)	1248.5(11)	4951.8(19)	21.3(3)
C25	4752.9(17)	1890.1(9)	4230.0(18)	17.7(3)
C26	6346.5(17)	2961.3(9)	4097.6(17)	16.4(3)
C27	7404.4(17)	3431.9(10)	4801.3(17)	17.6(3)
C28	7653.5(18)	3393.5(10)	6192.2(18)	20.0(3)
C29	8718.6(19)	3822.5(10)	6791.6(18)	22.0(4)
C30	9563.1(18)	4297.4(10)	6002.6(19)	21.1(3)
C31	9320.7(18)	4357.8(10)	4637.8(19)	20.6(3)
C32	8229.1(17)	3935.6(10)	4016.9(17)	17.8(3)
C33	6637.9(18)	3786.4(10)	2013.1(17)	18.9(3)
C34	5935.2(17)	3125.1(9)	2780.2(17)	17.2(3)
C35	5667.2(19)	4500.2(11)	1989(2)	24.5(4)
C36	7012(2)	3549.7(11)	578.1(18)	24.4(4)
O3	3516.7(15)	6588.2(9)	2666.0(13)	27.6(3)
C37	3867(2)	6725.0(15)	1310(2)	35.2(5)
O4	427.5(14)	4743.9(8)	1205.6(13)	23.0(3)
C38	817(3)	4848.8(14)	-155(2)	36.9(5)
O5	1594.3(14)	3381.9(8)	2213.0(13)	24.4(3)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TP2_final_2_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + ...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	22.8(6)	20.3(6)	20.7(6)	-5.0(5)	0.2(4)	1.9(5)

N1	19.5(7)	16.0(7)	15.6(6)	-1.4(5)	1.0(5)	-1.2(5)
N2	38.0(9)	26.5(8)	16.4(7)	-0.8(6)	-4.5(6)	9.4(7)
C1	18.8(7)	15.6(8)	18.4(8)	-1.0(6)	2.1(6)	-4.8(6)
C2	18.2(8)	15.9(8)	19.3(8)	1.1(6)	0.9(6)	-4.9(6)
C3	19.6(8)	16.7(8)	22.5(8)	-0.2(7)	1.7(6)	-1.9(6)
C4	20.8(8)	18.7(8)	24.8(9)	4.4(7)	-1.0(6)	-0.7(7)
C5	23.8(8)	23.1(8)	17.2(8)	2.0(7)	-0.7(6)	-4.0(7)
C6	22.8(8)	19.0(8)	17.0(8)	-0.4(7)	1.9(6)	-2.4(6)
C7	18.2(8)	15.1(7)	19.4(8)	1.6(6)	2.0(6)	-3.6(6)
C8	18.0(7)	15.5(7)	16.5(7)	1.4(6)	1.3(6)	-4.3(6)
C9	16.5(7)	15.0(7)	21.3(8)	1.2(6)	2.1(6)	-3.3(6)
C10	20.3(8)	20.5(8)	18.8(8)	0.2(6)	1.8(6)	-1.7(6)
C11	21.9(8)	19.9(8)	26.7(9)	-2.5(7)	5.3(7)	0.2(6)
C12	19.0(8)	18.1(8)	30.4(10)	2.5(7)	-1.2(7)	0.5(6)
C13	22.5(8)	22.6(9)	22.0(8)	0.8(7)	-3.7(7)	-1.2(6)
C14	21.1(8)	17.0(8)	21.7(8)	-0.3(6)	1.1(6)	-2.6(6)
C15	20.9(8)	18.0(8)	15.8(7)	-0.7(6)	-0.2(6)	-0.5(6)
C16	19.4(7)	16.7(7)	16.1(7)	0.2(6)	0.9(6)	-2.9(6)
C17	25.5(8)	22.0(8)	23.2(8)	0.4(7)	-3.6(7)	-4.2(7)
C18	26.1(9)	33.8(10)	17.6(8)	1.8(7)	2.3(7)	-2.2(8)
O2	21.9(6)	22.9(6)	17.8(6)	1.3(5)	-0.9(4)	-2.0(5)
N3	17.4(6)	16.4(7)	17.2(7)	1.0(5)	-1.3(5)	0.4(5)
N4	20.2(7)	23.4(7)	20.5(7)	2.9(6)	1.6(6)	-6.9(6)
C19	17.5(8)	15.9(8)	20.0(8)	-1.3(6)	1.9(6)	1.7(6)
C20	16.5(7)	16.0(8)	22.2(8)	-1.9(7)	1.1(6)	0.2(6)
C21	19.9(8)	20.6(8)	23.5(8)	-1.9(7)	-2.0(6)	-0.6(6)
C22	20.1(8)	18.0(8)	33.0(9)	-2.1(7)	-2.7(7)	-2.8(6)
C23	21.4(8)	17.2(8)	31.9(10)	3.4(7)	2.0(7)	-0.5(6)
C24	20.0(8)	19.3(8)	24.6(9)	3.0(7)	0.1(7)	1.5(6)
C25	15.4(7)	15.0(8)	22.9(8)	-1.8(6)	1.7(6)	2.4(6)
C26	15.9(7)	14.1(7)	19.4(7)	-0.5(6)	2.4(6)	3.2(6)
C27	16.1(7)	14.4(7)	22.4(8)	-1.3(6)	1.1(6)	2.4(6)
C28	19.8(8)	17.4(8)	22.8(8)	0.2(6)	1.0(6)	1.7(6)
C29	24.1(8)	21.2(9)	20.8(8)	-2.8(7)	-1.9(6)	2.4(6)
C30	17.6(8)	17.4(8)	28.3(9)	-4.6(7)	-2.9(7)	1.7(6)
C31	17.9(8)	15.6(8)	28.2(9)	-2.7(7)	1.7(7)	0.9(6)
C32	17.0(7)	14.7(7)	21.8(8)	-1.7(6)	1.0(6)	2.9(6)
C33	19.9(8)	17.7(8)	19.2(8)	0.9(6)	0.1(6)	-1.0(6)
C34	16.9(7)	15.6(8)	19.3(8)	-0.4(6)	1.3(6)	1.3(6)
C35	24.4(9)	18.4(8)	30.6(9)	4.1(7)	2.0(7)	-0.1(7)
C36	24.2(9)	30.3(10)	18.7(8)	-0.1(7)	2.3(7)	-4.8(7)
O3	24.7(7)	33.7(7)	24.3(6)	-4.1(5)	0.4(5)	-5.3(5)
C37	29.2(10)	48.6(13)	27.8(10)	9.8(9)	-0.6(8)	-2.0(9)
O4	30.2(7)	18.0(6)	21.0(6)	-1.5(5)	2.8(5)	-2.1(5)
C38	57.6(15)	31.2(11)	22.2(9)	-0.2(8)	5.0(9)	-3.4(10)
O5	25.3(7)	25.8(7)	22.3(6)	5.8(5)	3.9(5)	5.7(5)

Table 4 Bond Lengths for TP2_final_2_a.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
O1	C1	1.277(2)	N3	C25	1.375(2)
N1	C7	1.371(2)	N3	C26	1.354(2)
N1	C8	1.357(2)	N4	C32	1.363(2)
N2	C14	1.362(2)	N4	C33	1.471(2)
N2	C15	1.461(2)	C19	C20	1.464(2)
C1	C2	1.456(2)	C19	C34	1.434(2)
C1	C16	1.425(2)	C20	C21	1.412(2)
C2	C3	1.411(2)	C20	C25	1.399(2)
C2	C7	1.399(2)	C21	C22	1.375(3)
C3	C4	1.377(2)	C22	C23	1.406(3)
C4	C5	1.404(3)	C23	C24	1.375(3)
C5	C6	1.375(3)	C24	C25	1.407(2)
C6	C7	1.409(2)	C26	C27	1.464(2)
C8	C9	1.464(2)	C26	C34	1.393(2)
C8	C16	1.394(2)	C27	C28	1.404(2)
C9	C10	1.403(2)	C27	C32	1.413(2)
C9	C14	1.409(2)	C28	C29	1.384(2)
C10	C11	1.377(3)	C29	C30	1.396(3)
C11	C12	1.398(3)	C30	C31	1.379(3)
C12	C13	1.373(3)	C31	C32	1.405(2)
C13	C14	1.411(2)	C33	C34	1.530(2)
C15	C16	1.532(2)	C33	C35	1.538(2)
C15	C17	1.535(2)	C33	C36	1.533(2)
C15	C18	1.538(2)	O3	C37	1.415(2)
O2	C19	1.264(2)	O4	C38	1.421(2)

Table 5 Bond Angles for TP2_final_2_a.

Atom	Atom	Atom	Angle/ $^{\circ}$	Atom	Atom	Atom	Angle/ $^{\circ}$
C8	N1	C7	122.82(14)	C26	N3	C25	122.52(14)
C14	N2	C15	125.73(15)	C32	N4	C33	123.88(14)
O1	C1	C2	118.46(15)	O2	C19	C20	120.02(15)
O1	C1	C16	123.97(15)	O2	C19	C34	123.67(15)
C16	C1	C2	117.56(15)	C34	C19	C20	116.30(15)
C3	C2	C1	121.38(15)	C21	C20	C19	120.77(15)
C7	C2	C1	119.71(15)	C25	C20	C19	120.52(14)
C7	C2	C3	118.90(15)	C25	C20	C21	118.71(15)
C4	C3	C2	120.42(16)	C22	C21	C20	120.62(16)
C3	C4	C5	119.85(16)	C21	C22	C23	119.89(16)
C6	C5	C4	121.07(16)	C24	C23	C22	120.70(17)
C5	C6	C7	119.07(16)	C23	C24	C25	119.48(16)
N1	C7	C2	119.40(15)	N3	C25	C20	119.01(15)

N1	C7	C6		119.94(15)	N3	C25	C24	120.38(16)
C2	C7	C6		120.65(15)	C20	C25	C24	120.61(15)
N1	C8	C9		117.57(15)	N3	C26	C27	117.43(15)
N1	C8	C16		120.57(15)	N3	C26	C34	121.13(15)
C16	C8	C9		121.84(15)	C34	C26	C27	121.44(15)
C10	C9	C8		124.23(15)	C28	C27	C26	123.52(15)
C10	C9	C14		118.51(15)	C28	C27	C32	119.13(15)
C14	C9	C8		117.23(15)	C32	C27	C26	117.34(15)
C11	C10	C9		121.63(16)	C29	C28	C27	120.91(16)
C10	C11	C12		119.53(16)	C28	C29	C30	119.62(16)
C13	C12	C11		120.32(16)	C31	C30	C29	120.58(16)
C12	C13	C14		120.66(16)	C30	C31	C32	120.50(17)
N2	C14	C9		121.09(15)	N4	C32	C27	119.22(15)
N2	C14	C13		119.47(16)	N4	C32	C31	121.49(15)
C9	C14	C13		119.35(16)	C31	C32	C27	119.20(16)
N2	C15	C16		110.60(14)	N4	C33	C34	109.11(14)
N2	C15	C17		109.71(14)	N4	C33	C35	110.97(15)
N2	C15	C18		105.06(14)	N4	C33	C36	104.77(14)
C16	C15	C17		108.37(13)	C34	C33	C35	109.62(14)
C16	C15	C18		112.55(14)	C34	C33	C36	112.11(14)
C17	C15	C18		110.52(15)	C36	C33	C35	110.19(15)
C1	C16	C15		118.99(14)	C19	C34	C33	119.92(14)
C8	C16	C1		119.87(15)	C26	C34	C19	119.68(15)
C8	C16	C15		121.04(15)	C26	C34	C33	120.10(14)

Table 6 Torsion Angles for TP2_final_2_a.

A	B	C	D	Angle/ [°]	A	B	C	D	Angle/ [°]
O1	C1	C2	C3	-2.6(2)	O2	C19	C20	C21	7.0(2)
O1	C1	C2	C7	176.44(15)	O2	C19	C20	C25	-173.11(15)
O1	C1	C16	C8	-178.36(15)	O2	C19	C34	C26	168.09(16)
O1	C1	C16	C15	5.2(2)	O2	C19	C34	C33	-5.7(2)
N1	C8	C9	C10	-2.9(2)	N3	C26	C27	C28	-12.8(2)
N1	C8	C9	C14	174.99(14)	N3	C26	C27	C32	165.79(14)
N1	C8	C16	C1	1.6(2)	N3	C26	C34	C19	8.5(2)
N1	C8	C16	C15	178.03(14)	N3	C26	C34	C33	-177.69(14)
N2	C15	C16	C1	-170.18(15)	N4	C33	C34	C19	-166.53(14)
N2	C15	C16	C8	13.4(2)	N4	C33	C34	C26	19.7(2)
C1	C2	C3	C4	178.59(15)	C19	C20	C21	C22	179.04(16)
C1	C2	C7	N1	2.4(2)	C19	C20	C25	N3	1.7(2)
C1	C2	C7	C6	-177.29(14)	C19	C20	C25	C24	-179.04(15)
C2	C1	C16	C8	0.3(2)	C20	C19	C34	C26	-10.5(2)
C2	C1	C16	C15	-176.15(13)	C20	C19	C34	C33	175.70(14)
C2	C3	C4	C5	-1.2(2)	C20	C21	C22	C23	0.4(3)
C3	C2	C7	N1	-178.52(14)	C21	C20	C25	N3	-178.46(15)
C3	C2	C7	C6	1.8(2)	C21	C20	C25	C24	0.8(2)

C3 C4 C5 C6	1.6(3)	C21 C22 C23 C24	0.1(3)
C4 C5 C6 C7	-0.3(2)	C22 C23 C24 C25	-0.1(3)
C5 C6 C7 N1	178.92(16)	C23 C24 C25 N3	178.87(15)
C5 C6 C7 C2	-1.4(2)	C23 C24 C25 C20	-0.4(2)
C7 N1 C8 C9	179.60(14)	C25 N3 C26 C27	178.75(14)
C7 N1 C8 C16	-1.6(2)	C25 N3 C26 C34	-0.8(2)
C7 C2 C3 C4	-0.5(2)	C25 C20 C21 C22	-0.8(2)
C8 N1 C7 C2	-0.4(2)	C26 N3 C25 C20	-4.3(2)
C8 N1 C7 C6	179.27(14)	C26 N3 C25 C24	176.42(15)
C8 C9 C10 C11	177.81(15)	C26 C27 C28 C29	176.53(15)
C8 C9 C14 N2	-1.0(2)	C26 C27 C32 N4	1.1(2)
C8 C9 C14 C13	-177.60(15)	C26 C27 C32 C31	-175.65(14)
C9 C8 C16 C1	-179.66(14)	C27 C26 C34 C19	-171.02(14)
C9 C8 C16 C15	-3.3(2)	C27 C26 C34 C33	2.8(2)
C9 C10 C11 C12	0.0(3)	C27 C28 C29 C30	-0.3(3)
C10 C9 C14 N2	177.02(16)	C28 C27 C32 N4	179.67(15)
C10 C9 C14 C13	0.4(2)	C28 C27 C32 C31	3.0(2)
C10 C11 C12 C13	-0.3(3)	C28 C29 C30 C31	1.7(3)
C11 C12 C13 C14	0.7(3)	C29 C30 C31 C32	-0.7(2)
C12 C13 C14 N2	-177.42(17)	C30 C31 C32 N4	-178.28(16)
C12 C13 C14 C9	-0.7(3)	C30 C31 C32 C27	-1.7(2)
C14 N2 C15 C16	-19.2(2)	C32 N4 C33 C34	-35.1(2)
C14 N2 C15 C17	100.3(2)	C32 N4 C33 C35	85.7(2)
C14 N2 C15 C18	-140.86(18)	C32 N4 C33 C36	-155.36(16)
C14 C9 C10 C11	0.0(2)	C32 C27 C28 C29	-2.0(2)
C15 N2 C14 C9	13.8(3)	C33 N4 C32 C27	25.9(2)
C15 N2 C14 C13	-169.55(17)	C33 N4 C32 C31	-157.47(16)
C16 C1 C2 C3	178.62(15)	C34 C19 C20 C21	-174.30(15)
C16 C1 C2 C7	-2.3(2)	C34 C19 C20 C25	5.5(2)
C16 C8 C9 C10	178.39(15)	C34 C26 C27 C28	166.81(15)
C16 C8 C9 C14	-3.8(2)	C34 C26 C27 C32	-14.6(2)
C17 C15 C16 C1	69.53(18)	C35 C33 C34 C19	71.77(19)
C17 C15 C16 C8	-106.90(17)	C35 C33 C34 C26	-102.00(18)
C18 C15 C16 C1	-53.0(2)	C36 C33 C34 C19	-50.9(2)
C18 C15 C16 C8	130.56(16)	C36 C33 C34 C26	135.30(16)

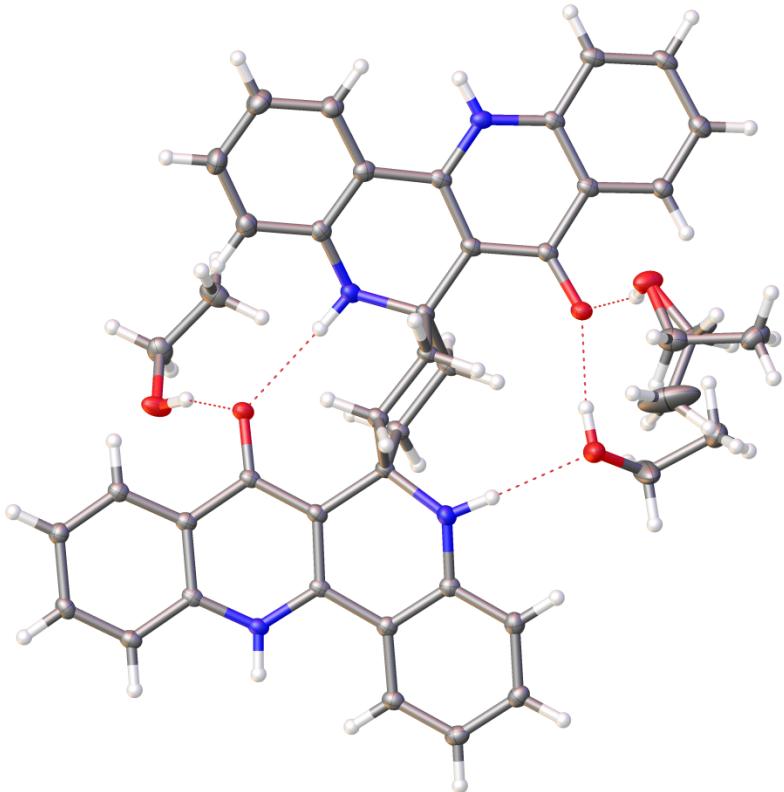
Table 7 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TP2_final_2_a.

Atom	x	y	z	U(eq)
H13	-4140(30)	8726(15)	1080(30)	27(6)
H5	2020(30)	6557(16)	8490(30)	28(6)
H29	8870(30)	3790(14)	7700(30)	26(6)
H28	7070(20)	3072(14)	6790(20)	22(5)
H18A	330(30)	7472(19)	840(30)	40(7)
H24	4630(20)	1147(14)	5770(20)	20(5)

H10	-2730(30)	8589(14)	5660(30)	29(6)
H36A	7640(30)	3077(17)	660(30)	41(7)
H31	9880(30)	4691(16)	4090(20)	27(6)
H18B	350(30)	6577(17)	660(30)	32(6)
H23	2900(20)	349(13)	4880(20)	18(5)
H4	2960(30)	5634(16)	6970(30)	29(6)
H17A	-2660(20)	6251(14)	590(20)	23(5)
H12	-5100(30)	9567(16)	2680(20)	28(6)
H11	-4370(30)	9497(16)	4930(30)	30(6)
H30	10260(30)	4590(15)	6430(20)	25(6)
H22	1890(30)	634(18)	2740(30)	39(7)
H35A	5540(20)	4698(14)	2940(20)	21(5)
H3	2110(20)	5561(15)	4760(20)	23(5)
H37A	4240(30)	6250(20)	890(30)	52(8)
H38A	1750(40)	5080(20)	-180(30)	55(9)
H21	2800(20)	1711(14)	1540(20)	23(5)
H3A	6060(30)	2215(15)	5580(30)	29(6)
H35B	4780(30)	4350(16)	1620(30)	34(6)
H6	320(30)	7457(15)	7690(20)	25(6)
H38B	150(40)	5210(20)	-610(30)	51(8)
H1	-1150(20)	7864(15)	6010(30)	23(5)
H17B	-3080(30)	6293(16)	2210(30)	36(7)
H36B	6150(30)	3443(16)	40(30)	32(6)
H4A	8540(20)	4270(14)	2220(20)	20(5)
H18C	-700(30)	7168(14)	-230(20)	26(6)
H37B	4690(30)	7112(19)	1290(30)	45(7)
H36C	7560(30)	3980(16)	200(30)	32(6)
H5A	2280(30)	3286(16)	1820(30)	29(6)
H17C	-1730(30)	5828(15)	1660(20)	23(5)
H3B	2700(30)	6342(17)	2690(30)	43(8)
H2	-2700(20)	7707(14)	680(30)	22(5)
H35C	6070(20)	4913(14)	1480(20)	23(5)
H5B	1320(30)	3832(17)	1850(30)	33(6)
H38C	860(40)	4340(20)	-590(30)	56(9)
H37C	3070(40)	7000(20)	810(30)	54(9)
H4B	560(30)	5130(17)	1650(30)	30(6)

8 (TP14_1, CCDC 1403790)

A yellow irregular plate crystal with approximate orthogonal dimensions $0.324 \times 0.137 \times 0.132$ mm³ was placed and optically centered on the Bruker Duo APEXII CCD system at -183°C (90K). Indexing of the unit cell used a random set of reflections collected from three series of 0.5° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Data were collected [CuK α] with 0.5° wide scans, 4, 6, 8 or 12 seconds per frame dependent upon detector 2 θ angle and varying φ and omega angles such that nearly all unique reflections were collected at least once. The crystal to detector distance was 4.96cm, thus providing a complete sphere of data to $2\theta_{\max}=136.53^\circ$.



Structural Refinement Data

All crystallographic calculations were performed on a Sony Vaio with 2.10GHz dual core processor and 4GB of extended memory. A total of 32252 reflections were collected and corrected for Lorentz and polarization effects with SAINT^[6] and absorption using crystal faces and Blessing's method as incorporated into the program SADABS^[2] with 6561 unique for point group 14. The SHELXTL^[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences, and intensity statistics indicated the centrosymmetric monoclinic space group $P2_1/c$ (no. 14). The structure was determined by direct methods with the successful location of a majority of the molecule using the program XT.^[4] The structure was refined with XL^[3] and Olex2.^[5] The data collected were merged for least squares refinement to 6561 unique data [$R(\text{int})=0.0309$]. A single least-squares difference-Fourier cycle was required to locate the remaining non-hydrogen atoms with a subsequent cycle required to locate the hydrogen atoms although all hydrogen atoms were initially idealized. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were allowed to refine freely throughout the final refinement stages. The final structure was refined to convergence with $R(F)=5.18\%$, $wR(F^2)=15.01\%$, $GOF=1.065$ for all 6561 unique reflections [$R(F)=5.88\%$, $wR(F^2)=16.43\%$ for those 5759 data with $F_o > 4\sigma(F_o)$]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

8 (TP14_1)

Table 1 Crystal data and structure refinement for TP14_final_1_a.

Identification code	TP14_final_1_a
Empirical formula	C ₃₆ H ₂₈ N ₄ O ₂
Formula weight	548.62
Temperature/K	90.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	21.8510(5)
b/Å	6.8018(2)
c/Å	25.1757(6)
α/°	90
β/°	113.2500(10)
γ/°	90
Volume/Å ³	3437.90(15)
Z	4
ρ _{calc} g/cm ³	1.060
μ/mm ⁻¹	0.530
F(000)	1152.0
Crystal size/mm ³	0.324 × 0.137 × 0.132
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.402 to 144.826
Index ranges	-26 ≤ h ≤ 25, -7 ≤ k ≤ 8, -29 ≤ l ≤ 30
Reflections collected	32252
Independent reflections	6561 [R _{int} = 0.0309, R _{sigma} = 0.0228]
Data/restraints/parameters	6561/0/630
Goodness-of-fit on F ²	1.065
Final R indexes [I>=2σ (I)]	R ₁ = 0.0518, wR ₂ = 0.1501
Final R indexes [all data]	R ₁ = 0.0588, wR ₂ = 0.1643
Largest diff. peak/hole / e Å ⁻³	0.49/-0.25

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for TP14_final_1_a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O001	6770.8(6)	8253.3(19)	5587.8(5)	28.8(3)
O002	8345.6(6)	6761(2)	3848.0(5)	30.1(3)
O003	6596.7(7)	11837(2)	6050.2(7)	41.5(6)
N004	4837.4(7)	7493(2)	4508.1(7)	23.5(3)
O005	8798.5(7)	3056(3)	3687.2(7)	43.9(4)
N007	6226.5(7)	6371(2)	3810.7(7)	29.1(3)
N008	9898.4(8)	7437(2)	5382.9(7)	27.2(3)
N009	8057.7(8)	8226(2)	5420.5(7)	28.7(3)

C00A	5311.0(8)	7333(2)	4282.7(8)	21.5(3)
C00B	4987.5(9)	7590(2)	5086.2(8)	22.3(4)
C00C	5577.1(8)	6567(2)	3450.3(7)	23.7(4)
C00D	10022.6(9)	7529(2)	4891.9(8)	24.0(4)
C00E	9277.5(9)	7416(2)	5380.0(8)	24.6(4)
C00F	6523.9(8)	7097(2)	4410.8(7)	22.2(4)
C00G	7687.8(8)	5451(3)	4728.7(8)	24.4(4)
C00H	6176.6(8)	7807(2)	5246.0(8)	23.0(4)
C00I	8809.7(9)	7186(3)	4332.0(8)	24.7(4)
C00J	5085.9(9)	7089(3)	3661.4(8)	25.1(4)
C00K	8017.9(9)	7493(2)	4854.9(8)	23.8(4)
C00L	5811.1(9)	7775(3)	6068.1(8)	25.6(4)
C00M	6873.0(8)	9102(3)	4427.5(8)	25.9(4)
C00N	4420.1(9)	7232(3)	3271.9(8)	26.4(4)
C00O	8715.9(9)	7433(3)	4856.7(8)	25.6(4)
C00P	5660.6(9)	7729(2)	5474.3(8)	23.7(4)
C00Q	7007.6(8)	5469(3)	4767.5(8)	25.5(4)
C00R	9603.3(9)	7550(3)	3846.6(9)	28.0(4)
C00S	4483.7(9)	7560(3)	5302.3(8)	25.8(4)
C00T	8574.1(9)	7739(3)	5928.2(8)	26.4(4)
C00U	5983.8(9)	7371(2)	4648.0(8)	24.2(4)
C00V	9480.8(9)	7425(3)	4353.4(8)	26.5(4)
C00W	4708.4(9)	6198(3)	2489.9(8)	29.5(4)
C00X	5367.5(9)	6099(3)	2860.2(8)	29.5(4)
C00Y	5319.9(9)	7691(3)	6276.9(8)	27.1(4)
C00Z	4649.1(9)	7600(3)	5886.1(8)	26.7(4)
C010	4222.4(9)	6803(3)	2694.2(8)	31.4(4)
C011	10673.6(9)	7721(3)	4916.3(9)	29.7(4)
C012	7560.6(8)	8951(3)	4401.9(8)	27.5(4)
C013	9742.9(10)	7005(3)	6465.9(9)	33.1(4)
C014	10774.3(9)	7860(3)	4414.4(9)	30.8(4)
C015	9210.9(9)	7362(3)	5933.0(8)	28.5(4)
C016	9026.0(12)	7446(3)	6968.7(9)	39.5(5)
C017	10238.8(10)	7791(3)	3872.7(9)	32.0(4)
C018	8489.7(11)	7777(3)	6453.3(9)	34.2(4)
C019	7095.0(11)	13266(3)	6232.7(10)	41.4(8)
C01A	9654.5(12)	7041(3)	6977.2(9)	41.7(5)
C01D	8327(3)	1776(10)	3282(3)	38.6(17)
C01F	8509.9(18)	1492(6)	2765.2(16)	44.3(15)
C10	7714.2(11)	12714(3)	6146.9(12)	40.5(9)
C4	7798(8)	1410(20)	3045(7)	65(7)
C1	7027(6)	7232(18)	2688(6)	49(3)
C13	7461.8(12)	6527(5)	2372.8(10)	57.3(7)
O15	7093.6(7)	5685(3)	3143.5(6)	40.2(6)
C1A	6948(6)	6571(18)	2614(5)	51(3)
C2	8473(16)	2230(40)	3092(18)	31(12)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TP14_final_1_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	21.6(6)	32.7(7)	31.6(7)	-6.9(5)	10.0(5)	-2.9(5)
O002	21.6(6)	37.6(7)	29.8(6)	-3.5(5)	8.6(5)	0.6(5)
O003	24.6(8)	36.3(10)	59.9(11)	-17.3(7)	12.9(7)	-2.9(6)
N004	18.8(7)	22.2(7)	28.9(8)	-0.9(6)	8.7(6)	-0.1(5)
O005	30.9(7)	42.6(9)	46.5(9)	-15.2(7)	2.7(6)	6.9(7)
N007	24.6(7)	35.3(9)	29.4(8)	-3.9(6)	12.8(6)	0.9(6)
N008	21.4(7)	23.8(8)	32.0(8)	-3.4(6)	6.0(7)	0.5(6)
N009	24.5(8)	30.4(8)	32.3(8)	-7.1(6)	12.5(6)	-1.6(6)
C00A	20.3(8)	14.0(7)	30.5(9)	-0.5(6)	10.1(7)	-0.5(6)
C00B	22.8(8)	14.2(8)	31.1(9)	1.3(6)	11.7(7)	0.8(6)
C00C	26.0(8)	17.6(8)	26.7(8)	0.6(6)	9.6(7)	0.5(6)
C00D	22.1(8)	16.4(8)	34(1)	-2.9(6)	11.6(7)	0.1(6)
C00E	23.1(8)	15.6(8)	34.6(10)	-3.7(6)	10.9(7)	-0.2(6)
C00F	19.0(8)	22.0(8)	25.5(8)	-2.1(7)	8.7(6)	-0.1(6)
C00G	19.9(8)	21.0(8)	31.0(9)	-1.1(7)	8.7(7)	2.0(7)
C00H	21.1(8)	17.8(8)	30.4(9)	-0.8(6)	10.5(7)	0.5(6)
C00I	21.9(8)	20.1(8)	32.8(9)	-1.2(7)	11.4(7)	1.0(6)
C00J	26.2(9)	19.4(8)	29.4(9)	-0.4(7)	10.7(7)	-1.6(7)
C00K	21.8(8)	23.2(9)	27.9(9)	-3.7(7)	11.5(7)	-2.1(6)
C00L	26.5(9)	20.1(8)	31.0(9)	-0.1(7)	12.3(7)	-0.4(7)
C00M	21.9(8)	21.4(8)	34.8(9)	2.8(7)	11.6(7)	1.0(7)
C00N	23.6(8)	23.8(9)	30.6(9)	2.0(7)	9.4(7)	-1.2(7)
C00O	21.8(9)	21.7(8)	32.6(9)	-1.8(7)	10.1(7)	-0.9(6)
C00P	22.6(8)	18.5(8)	29.8(9)	-0.7(6)	10.0(7)	-0.8(6)
C00Q	22.6(8)	21.0(9)	34.0(9)	-0.2(7)	12.3(7)	-1.0(7)
C00R	26.0(9)	25.4(9)	34.7(10)	-1.0(7)	14.1(8)	0.6(7)
C00S	22.1(8)	21.4(8)	33.5(9)	1.5(7)	10.7(7)	0.0(6)
C00T	29.7(9)	20.0(8)	30.7(9)	-4.7(7)	13.1(7)	-2.3(7)
C00U	22.2(8)	20.1(8)	31.8(9)	-1.2(7)	12.1(7)	-0.8(6)
C00V	22.9(9)	21.0(8)	35.4(10)	-2.1(7)	11.3(7)	0.4(6)
C00W	33.5(9)	27.1(9)	24.9(9)	-0.3(7)	8.4(7)	-3.9(7)
C00X	33.6(9)	26.3(9)	30.9(9)	-0.6(7)	15.4(8)	-1.8(7)
C00Y	29.4(9)	24.7(9)	27.9(9)	1.5(7)	11.9(7)	-0.8(7)
C00Z	28.3(9)	22.2(8)	34.4(9)	1.3(7)	17.5(8)	-1.0(7)
C010	29.1(9)	28.9(9)	31.6(9)	2.2(7)	7.2(8)	-3.5(8)
C011	23.3(9)	20.9(9)	42.0(11)	-2.9(7)	9.9(8)	-0.2(7)
C012	23.2(8)	22.7(9)	39.6(10)	1.2(7)	15.8(7)	0.6(7)
C013	30.8(10)	32(1)	34(1)	0.4(8)	10.2(8)	4.0(8)
C014	22.5(9)	23.2(9)	49.0(11)	-0.1(8)	16.8(8)	-0.3(7)
C015	29.3(9)	22.3(9)	31.7(10)	-3.3(7)	9.7(8)	-1.0(7)
C016	46.7(12)	42.7(12)	31.8(10)	-1.1(9)	18.2(9)	-1.4(9)
C017	29.0(9)	27.4(9)	43.1(11)	0.2(8)	17.9(8)	1.0(7)

C018	37.1(11)	32.6(10)	36.1(10)	-3.8(8)	17.9(9)	-3.0(8)
C019	44.9(13)	32.6(12)	50.0(14)	-5.7(9)	22.2(10)	-9.1(9)
C01A	44.0(12)	43.7(12)	32.4(10)	3.0(9)	9.7(9)	5.4(10)
C01D	28(2)	33(2)	44(3)	-2.0(19)	2.6(17)	-0.2(16)
C01F	43(2)	44(2)	33(2)	-11.8(17)	1.5(14)	2.6(15)
C10	33.1(13)	29.1(13)	62.9(17)	1.7(10)	22.7(11)	-3.6(9)
C4	54(11)	54(10)	59(10)	8(7)	-7(7)	-26(7)
C1	20(3)	76(7)	42(4)	-2(4)	0(3)	5(4)
C13	40.4(12)	97(2)	34.8(11)	0.5(13)	14.7(10)	-7.0(13)
O15	26.0(8)	68.4(12)	25.4(8)	-3.9(7)	9.3(6)	-4.6(7)
C1A	32(4)	86(8)	31(4)	12(4)	10(3)	-5(4)
C2	28(11)	15(10)	39(18)	-2(9)	0(10)	-1(7)

Table 4 Bond Lengths for TP14_final_1_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C00H	1.279(2)	C00I	C00O	1.424(3)
O002	C00I	1.273(2)	C00I	C00V	1.455(2)
O003	C019	1.395(3)	C00J	C00N	1.400(3)
N004	C00A	1.367(2)	C00K	C00O	1.524(2)
N004	C00B	1.361(2)	C00K	C012	1.543(2)
O005	C01D	1.425(4)	C00L	C00P	1.399(3)
O005	C2	1.49(3)	C00L	C00Y	1.370(3)
N007	C00C	1.356(2)	C00M	C012	1.533(2)
N007	C00F	1.474(2)	C00N	C010	1.375(3)
N008	C00D	1.368(3)	C00R	C00V	1.406(3)
N008	C00E	1.354(2)	C00R	C017	1.374(3)
N009	C00K	1.479(2)	C00S	C00Z	1.368(3)
N009	C00T	1.370(2)	C00T	C015	1.410(3)
C00A	C00J	1.452(2)	C00T	C018	1.405(3)
C00A	C00U	1.393(2)	C00W	C00X	1.374(3)
C00B	C00P	1.411(2)	C00W	C010	1.412(3)
C00B	C00S	1.408(2)	C00Y	C00Z	1.408(3)
C00C	C00J	1.418(2)	C011	C014	1.369(3)
C00C	C00X	1.408(2)	C013	C015	1.407(3)
C00D	C00V	1.406(3)	C013	C01A	1.375(3)
C00D	C011	1.405(3)	C014	C017	1.404(3)
C00E	C00O	1.402(3)	C016	C018	1.381(3)
C00E	C015	1.456(3)	C016	C01A	1.393(3)
C00F	C00M	1.555(2)	C019	C10	1.500(3)
C00F	C00Q	1.549(2)	C01D	C01F	1.515(11)
C00F	C00U	1.530(2)	C4	C2	1.54(5)
C00G	C00K	1.539(2)	C1	C13	1.535(15)
C00G	C00Q	1.527(2)	C1	O15	1.521(15)
C00H	C00P	1.455(2)	C13	C1A	1.473(14)
C00H	C00U	1.425(3)	O15	C1A	1.380(13)

Table 5 Bond Angles for TP14_final_1_a.

Atom	Atom	Atom	Angle/ $^{\circ}$	Atom	Atom	Atom	Angle/ $^{\circ}$
C00B	N004	C00A	123.05(16)	C012	C00M	C00F	114.73(14)
C00C	N007	C00F	125.05(15)	C010	C00N	C00J	122.13(18)
C00E	N008	C00D	123.47(17)	C00E	C00O	C00I	118.54(16)
C00T	N009	C00K	122.03(15)	C00E	C00O	C00K	120.44(16)
N004	C00A	C00J	117.79(15)	C00I	C00O	C00K	120.70(16)
N004	C00A	C00U	119.93(16)	C00B	C00P	C00H	119.16(16)
C00U	C00A	C00J	122.26(16)	C00L	C00P	C00B	118.86(16)
N004	C00B	C00P	119.27(16)	C00L	C00P	C00H	121.98(16)
N004	C00B	C00S	121.16(16)	C00G	C00Q	C00F	115.29(14)
C00S	C00B	C00P	119.58(16)	C017	C00R	C00V	120.98(18)
N007	C00C	C00J	121.39(16)	C00Z	C00S	C00B	119.97(17)
N007	C00C	C00X	120.18(16)	N009	C00T	C015	119.89(17)
C00X	C00C	C00J	118.24(16)	N009	C00T	C018	120.50(17)
N008	C00D	C00V	118.50(16)	C018	C00T	C015	119.39(18)
N008	C00D	C011	121.55(18)	C00A	C00U	C00F	121.05(16)
C011	C00D	C00V	119.95(17)	C00A	C00U	C00H	119.74(16)
N008	C00E	C00O	120.56(17)	C00H	C00U	C00F	119.07(15)
N008	C00E	C015	118.25(17)	C00D	C00V	C00I	119.60(17)
C00O	C00E	C015	121.19(16)	C00R	C00V	C00D	118.85(17)
N007	C00F	C00M	109.56(14)	C00R	C00V	C00I	121.55(17)
N007	C00F	C00Q	106.17(14)	C00X	C00W	C010	120.33(17)
N007	C00F	C00U	110.18(13)	C00W	C00X	C00C	121.48(17)
C00Q	C00F	C00M	113.32(14)	C00L	C00Y	C00Z	119.42(17)
C00U	C00F	C00M	109.17(13)	C00S	C00Z	C00Y	120.81(17)
C00U	C00F	C00Q	108.39(14)	C00N	C010	C00W	118.67(17)
C00Q	C00G	C00K	111.59(14)	C014	C011	C00D	119.66(18)
O001	C00H	C00P	118.82(16)	C00M	C012	C00K	111.81(14)
O001	C00H	C00U	123.94(16)	C01A	C013	C015	121.40(19)
C00U	C00H	C00P	117.25(15)	C011	C014	C017	121.21(17)
O002	C00I	C00O	124.22(16)	C00T	C015	C00E	117.25(17)
O002	C00I	C00V	118.11(16)	C013	C015	C00E	124.00(18)
C00O	C00I	C00V	117.66(16)	C013	C015	C00T	118.73(18)
C00C	C00J	C00A	116.59(15)	C018	C016	C01A	120.8(2)
C00N	C00J	C00A	124.27(16)	C00R	C017	C014	119.32(19)
C00N	C00J	C00C	119.05(16)	C016	C018	C00T	120.21(19)
N009	C00K	C00G	110.35(14)	O003	C019	C10	114.17(18)
N009	C00K	C00O	109.14(14)	C013	C01A	C016	119.4(2)
N009	C00K	C012	105.65(14)	O005	C01D	C01F	109.4(7)
C00G	C00K	C012	108.25(14)	O15	C1	C13	106.2(8)
C00O	C00K	C00G	111.30(14)	O15	C1A	C13	117.8(10)
C00O	C00K	C012	112.01(14)	O005	C2	C4	106(4)
C00Y	C00L	C00P	121.32(17)				

Table 6 Torsion Angles for TP14_final_1_a.

A	B	C	D	Angle/ [°]	A	B	C	D	Angle/ [°]
O001	C00H	C00P	C00B	168.72(15)	C00K	N009	C00T	C015	30.3(3)
O001	C00H	C00P	C00L	-11.7(2)	C00K	N009	C00T	C018	-155.23(17)
O001	C00H	C00U	C00A	-165.69(16)	C00K	C00G	C00Q	C00F	51.3(2)
O001	C00H	C00U	C00F	10.0(3)	C00L	C00Y	C00Z	C00S	1.1(3)
O002	C00I	C00O	C00E	164.48(17)	C00M	C00F	C00Q	C00G	-39.6(2)
O002	C00I	C00O	C00K	-9.1(3)	C00M	C00F	C00U	C00A	107.50(18)
O002	C00I	C00V	C00D	-168.21(16)	C00M	C00F	C00U	C00H	-68.08(19)
O002	C00I	C00V	C00R	11.6(3)	C00O	C00E	C015	C00T	-12.9(2)
N004	C00A	C00J	C00C	-168.76(15)	C00O	C00E	C015	C013	168.62(18)
N004	C00A	C00J	C00N	7.6(3)	C00O	C00I	C00V	C00D	11.4(2)
N004	C00A	C00U	C00F	177.09(15)	C00O	C00I	C00V	C00R	-168.73(16)
N004	C00A	C00U	C00H	-7.4(2)	C00O	C00K	C012	C00M	-176.43(15)
N004	C00B	C00P	C00H	1.2(2)	C00P	C00B	C00S	C00Z	-2.2(2)
N004	C00B	C00P	C00L	-178.32(15)	C00P	C00H	C00U	C00A	14.4(2)
N004	C00B	C00S	C00Z	178.07(16)	C00P	C00H	C00U	C00F	-169.92(15)
N007	C00C	C00J	C00A	-2.1(2)	C00P	C00L	C00Y	C00Z	-1.4(3)
N007	C00C	C00J	C00N	-178.66(16)	C00Q	C00F	C00M	C012	39.3(2)
N007	C00C	C00X	C00W	177.01(17)	C00Q	C00F	C00U	C00A	-128.63(16)
N007	C00F	C00M	C012	-79.03(18)	C00Q	C00F	C00U	C00H	55.78(19)
N007	C00F	C00Q	C00G	80.66(17)	C00Q	C00G	C00K	N009	54.72(19)
N007	C00F	C00U	C00A	-12.9(2)	C00Q	C00G	C00K	C00O	176.05(15)
N007	C00F	C00U	C00H	171.56(15)	C00Q	C00G	C00K	C012	-60.44(18)
N008	C00D	C00V	C00I	-1.2(2)	C00S	C00B	C00P	C00H	-178.52(15)
N008	C00D	C00V	C00R	178.98(15)	C00S	C00B	C00P	C00L	1.9(2)
N008	C00D	C011	C014	-178.26(16)	C00T	N009	C00K	C00G	85.38(19)
N008	C00E	C00O	C00I	8.9(2)	C00T	N009	C00K	C00O	-37.2(2)
N008	C00E	C00O	C00K	-177.52(15)	C00T	N009	C00K	C012	-157.82(16)
N008	C00E	C015	C00T	167.54(16)	C00U	C00A	C00J	C00C	10.1(2)
N008	C00E	C015	C013	-10.9(3)	C00U	C00A	C00J	C00N	-173.55(16)
N009	C00K	C00O	C00E	20.0(2)	C00U	C00F	C00M	C012	160.24(15)
N009	C00K	C00O	C00I	-166.60(15)	C00U	C00F	C00Q	C00G	-160.98(15)
N009	C00K	C012	C00M	-57.71(18)	C00U	C00H	C00P	C00B	-11.4(2)
N009	C00T	C015	C00E	-3.1(2)	C00U	C00H	C00P	C00L	168.15(16)
N009	C00T	C015	C013	175.47(17)	C00V	C00D	C011	C014	1.8(3)
N009	C00T	C018	C016	-174.53(19)	C00V	C00I	C00O	C00E	-15.1(2)
C00A	N004	C00B	C00P	6.5(2)	C00V	C00I	C00O	C00K	171.34(15)
C00A	N004	C00B	C00S	-173.71(15)	C00V	C00R	C017	C014	1.7(3)
C00A	C00J	C00N	C010	-173.54(17)	C00X	C00C	C00J	C00A	172.86(16)
C00B	N004	C00A	C00J	175.34(15)	C00X	C00C	C00J	C00N	-3.7(2)
C00B	N004	C00A	C00U	-3.6(2)	C00X	C00W	C010	C00N	-1.9(3)
C00B	C00S	C00Z	C00Y	0.6(3)	C00Y	C00L	C00P	C00B	-0.1(3)
C00C	N007	C00F	C00M	-98.36(19)	C00Y	C00L	C00P	C00H	-179.69(16)
C00C	N007	C00F	C00Q	138.93(17)	C010	C00W	C00X	C00C	0.8(3)

C00C N007 C00F C00U	21.8(2)	C011 C00D C00V C00I	178.77(16)
C00C C00J C00N C010	2.7(3)	C011 C00D C00V C00R	-1.1(2)
C00D N008 C00E C00O	1.9(2)	C011 C014 C017 C00R	-0.9(3)
C00D N008 C00E C015	-178.57(15)	C012 C00K C00O C00E	136.61(17)
C00D C011 C014 C017	-0.8(3)	C012 C00K C00O C00I	-50.0(2)
C00E N008 C00D C00V	-5.7(2)	C015 C00E C00O C00I	-170.63(16)
C00E N008 C00D C011	174.33(16)	C015 C00E C00O C00K	2.9(2)
C00F N007 C00C C00J	-15.2(3)	C015 C00T C018 C016	0.0(3)
C00F N007 C00C C00X	169.96(16)	C015 C013 C01A C016	-0.3(3)
C00F C00M C012 C00K	-51.0(2)	C017 C00R C00V C00D	-0.7(3)
C00G C00K C00O C00E	-102.05(18)	C017 C00R C00V C00I	179.48(17)
C00G C00K C00O C00I	71.4(2)	C018 C00T C015 C00E	-177.63(16)
C00G C00K C012 C00M	60.49(19)	C018 C00T C015 C013	0.9(3)
C00J C00A C00U C00F	-1.7(2)	C018 C016 C01A C013	1.2(3)
C00J C00A C00U C00H	173.81(16)	C01A C013 C015 C00E	177.66(19)
C00J C00C C00X C00W	2.0(3)	C01A C013 C015 C00T	-0.8(3)
C00J C00N C010 C00W	0.1(3)	C01A C016 C018 C00T	-1.0(3)

Table 7 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TP14_final_1_a.

Atom	x	y	z	U(eq)
H01I	7215	13529	6649	50
H01J	6915	14499	6019	50
H01D	7875	2348	3154	46
H01E	8326	490	3466	46
H01F	8186	613	2486	66
H01G	8956	912	2893	66
H01H	8506	2767	2583	66
H00C	6905(10)	9820(30)	4778(9)	26(5)
H00D	6588(10)	9900(30)	4118(9)	29(5)
H00A	7647(11)	4990(30)	4342(10)	35(6)
H01A	7504(10)	8460(30)	3995(9)	26(5)
H00E	6789(10)	4240(30)	4619(8)	23(5)
H00B	7957(10)	4520(30)	4974(9)	23(5)
H01B	7782(10)	10290(30)	4492(9)	29(5)
H00F	7068(11)	5620(30)	5182(10)	34(6)
H010	3736(10)	6810(30)	2363(9)	25(5)
H011	11015(12)	7770(30)	5280(11)	34(6)
H018	8035(12)	8030(30)	6444(10)	33(6)
H00Y	5401(11)	7630(30)	6674(10)	30(6)
H00L	6289(12)	7840(30)	6320(10)	35(6)
H004	4400(15)	7500(40)	4283(12)	48(7)
H00N	4096(13)	7660(40)	3436(11)	38(6)
H00R	9227(15)	7530(40)	3445(13)	54(8)
H013	10182(13)	6740(40)	6486(10)	42(6)

H00Z	4289(11)	7550(30)	6027(9)	27(5)
H00W	4544(11)	5890(40)	2094(10)	34(6)
H016	8964(12)	7480(30)	7320(11)	37(6)
H00S	4005(14)	7510(40)	5005(12)	50(7)
H017	10312(12)	7970(40)	3479(11)	43(6)
H00X	5721(11)	5630(30)	2716(10)	36(6)
H007	6484(14)	6200(40)	3598(12)	52(7)
H01C	10068(15)	6810(40)	7393(13)	57(8)
H014	11248(12)	8050(40)	4441(10)	39(6)
H008	10226(13)	7410(30)	5711(11)	33(6)
H009	7663(13)	8230(40)	5463(10)	38(6)
H10A	7910	11532	6373	61
H10B	8035	13797	6275	61
H10C	7602	12451	5736	61
H4A	7440	2032	2718	97
H4B	7737	1693	3402	97
H4C	7787	-15	2984	97
H1A	7182	8527	2871	59
H1B	6557	7357	2413	59
H13A	7933	6656	2630	86
H13B	7369	7329	2026	86
H13C	7361	5147	2261	86
H15	7378	6054	3464	60
H15A	7421	6253	3396	60
H005	8620(16)	4100(50)	3685(13)	66(9)
H003	6745(15)	10750(50)	5963(13)	64(9)
H1AA	6837	7964	2648	61
H1AB	6542	5942	2331	61
H2A	8750	1165	3032	37
H2B	8409	3261	2799	37

Table 8 Atomic Occupancy for TP14_final_1_a.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
O003	0.998(8)	C019	1.023(11)	H01I	0.78(5)
H01J	1.08(5)	C01D	0.75(3)	H01D	0.75
H01E	0.75	C01F	0.654(13)	H01F	0.73(6)
H01G	0.62(6)	H01H	0.71(6)	C10	0.947(11)
H10A	1.28(6)	H10B	1.15(5)	H10C	0.67(6)
C4	0.179(12)	H4A	0.16	H4B	0.16
H4C	0.16	C1	0.5	H1A	0.5
H1B	0.5	H13A	1.01(6)	H13B	1.02(6)
H13C	0.72(6)	O15	0.932(6)	H15	0.5
H15A	0.5	C1A	0.5	H1AA	0.5
H1AB	0.5	C2	0.13(3)	H2A	0.1458
H2B	0.15				

Photophysical Methods and Data

The absorption spectra were recorded at room temperature using a JASCO V-570 UV-VIS-NIR Spectrophotometer. The steady-state fluorescence (emission and excitation) measurements were also recorded with resolution increment 1 nm, slit 5 using Jobin-Yvon-Horiba Fluorolog III fluorometer and the FluorEssence program. The excitation source was a 100 W Xenon lamp, and the detector used was R-928 operating at a voltage of 950 V. The fluorescence lifetime measurements were done using the same instrument with a pulsed diode laser of 405 nm. The decay data was analyzed using Data Analysis Software. The fluorescence decay was acquired with a peak preset of 10,000 counts. The detector used was R-928 operating at a voltage of 950 V. The instrumental response function was collected using scatterer (colloidal silica). The best fit was with a χ^2 value in the range 0.9 to 1.5.

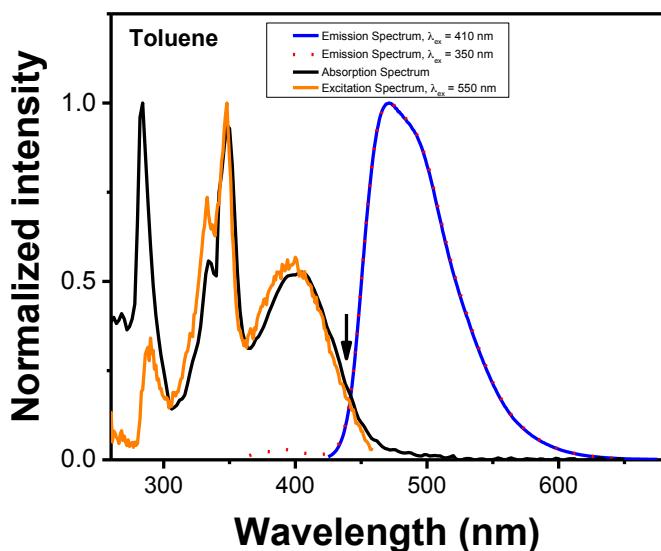
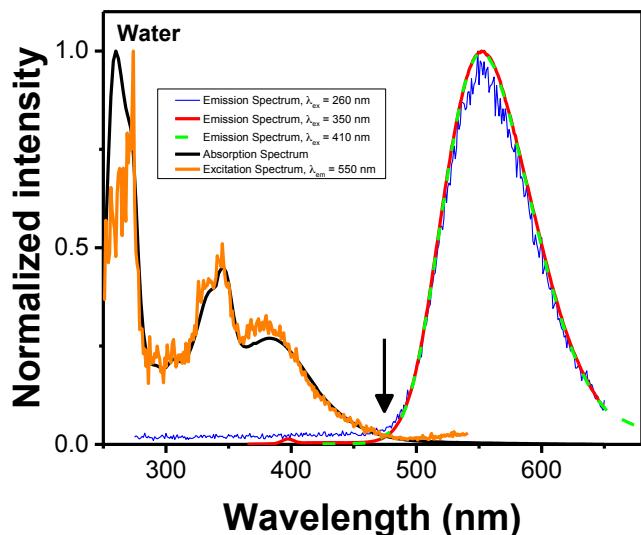


Figure S1. Absorption, fluorescence excitation and emission spectra of **5a** in water (top) and toluene (bottom). The fluorescence excitation spectra were recorded at emission wavelength 550 nm. The fluorescence emission spectra were recorded at excitation wavelength 260 nm, 350 nm and 410 nm.

The absorption spectrum of the compound showed three different absorption regions, 260-300 nm ($S_0 - S_3$ transition), 300-360 nm ($S_0 - S_2$ transition) and 370-460 nm ($S_0 - S_1$ transition). The chlorine substitutes (**5b**), methoxy substituted (**5c**) and both chlorine and methoxy substituted (**5d**) gave absorption spectra similar to the absorption of compound **5a** as given in Figure S2.

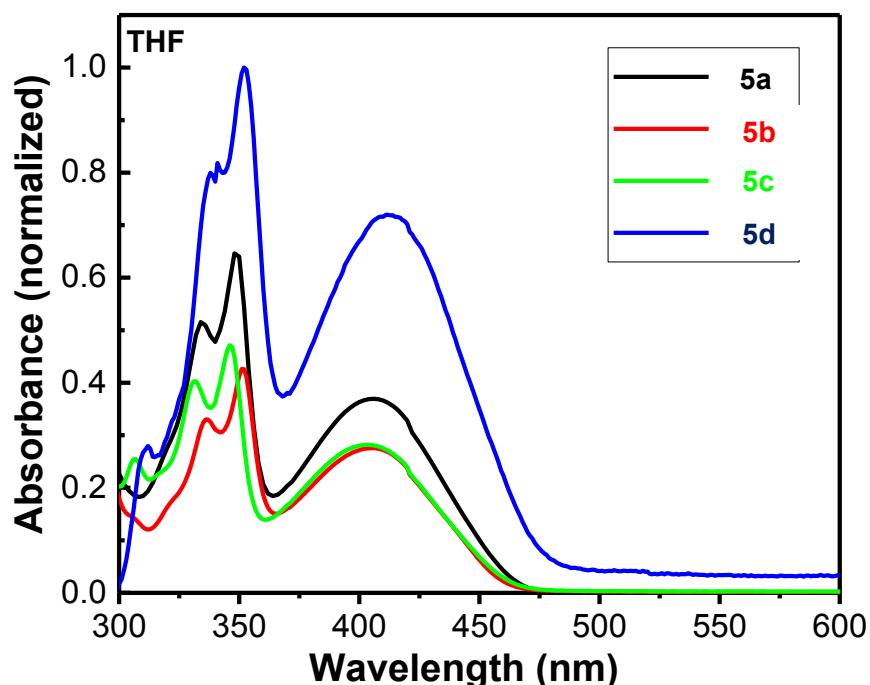


Figure S2. Absorption spectra of **5a**, **5b**, **5c**, and **5d** in THF.

Exciting the compound in any of these absorbing regions gave the same emission spectrum in both water and toluene. The absorption spectra in the region 300-360 nm ($S_0 - S_2$ transition) was found to be structured whereas the $S_0 - S_1$ transition was found to be broad in both the solvent environments. The fluorescence emission spectra were broad in the wavelength region 440 – 650 nm. However, the emission spectrum is slightly structured in toluene whereas in water this was broad. The crossing point of absorption and emission spectra at 475 nm in water confirmed that 0-0 transition is involved in both absorption and emission processes, which rules out any other photochemical transformation of the molecule during excitation process. The 0-0 transition of the molecule in toluene was found to be located at 441 nm. The cause of spectral shift due to solvent effect will be discussed later on. The excitation spectra recorded at emission wavelength 550 nm exactly matched with absorption spectra, which further reiterates that both the ground state absorbing species and excited state emissive species are the same. The mirror image symmetry between absorption/excitation spectrum and emission spectrum indicates the ground state (S_0) vibrational levels and excited state (S_1)

vibrational levels have similar structure. However, the Stokes shift, the difference between in absorption maximum and emission maximum in wave number scale, of the compound was found to substantially large in water (polar solvent) compared to that in toluene (non-polar solvent). To understand solvatochromism of the compound, the absorption (Figure S3) and fluorescence (Figure S4) spectra were measured in various other solvents having different polarity. Although these spectra displayed broad and intense absorptions and emission similar to observed for water, both the absorption and emission spectral positions were found to be susceptible to the nature of the solvent. The fluorescence spectrum in non-polar solvents such as CCl_4 , benzene, and toluene were found to be slightly structured. The fluorescence spectra of all the compounds **5a-d** were found to be sensitive to solvent environment as shown in Figure S4-S7.

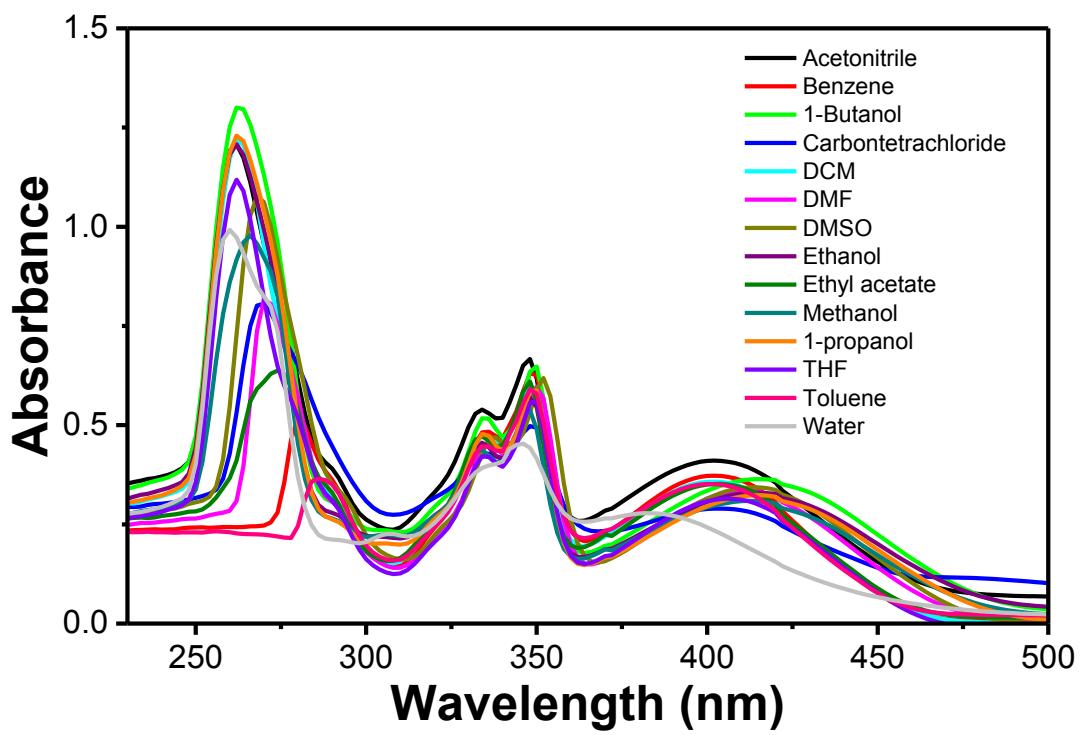


Figure S3. Absorption spectra of **5a** in various solvents.

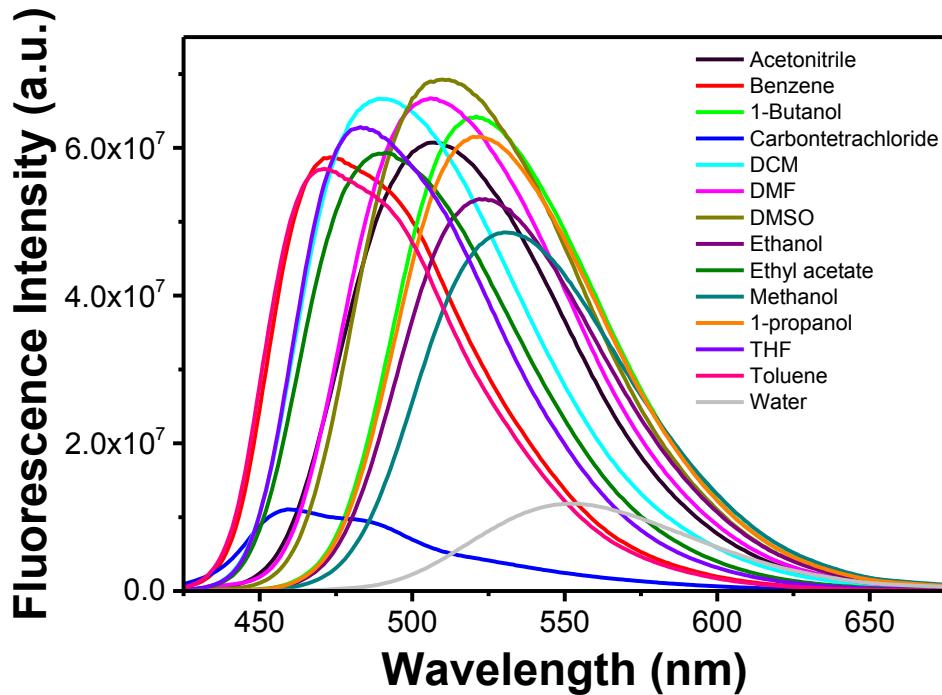


Figure S4. Fluorescence emission spectra of **5a** in various solvents. The fluorescence emission spectra were recorded at excitation wavelength 410 nm.

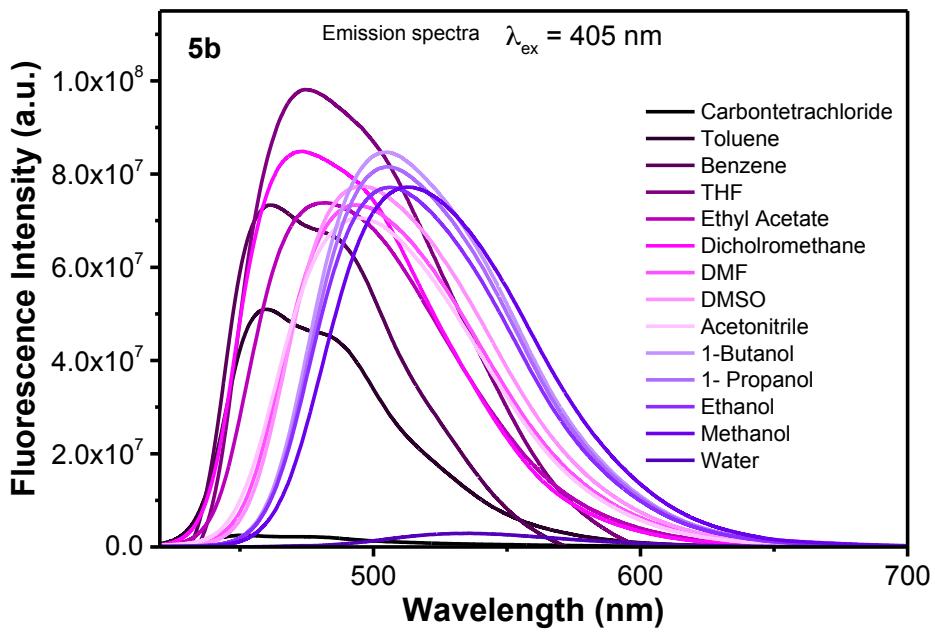


Figure S5. Fluorescence emission spectra of **5b** in various solvents.

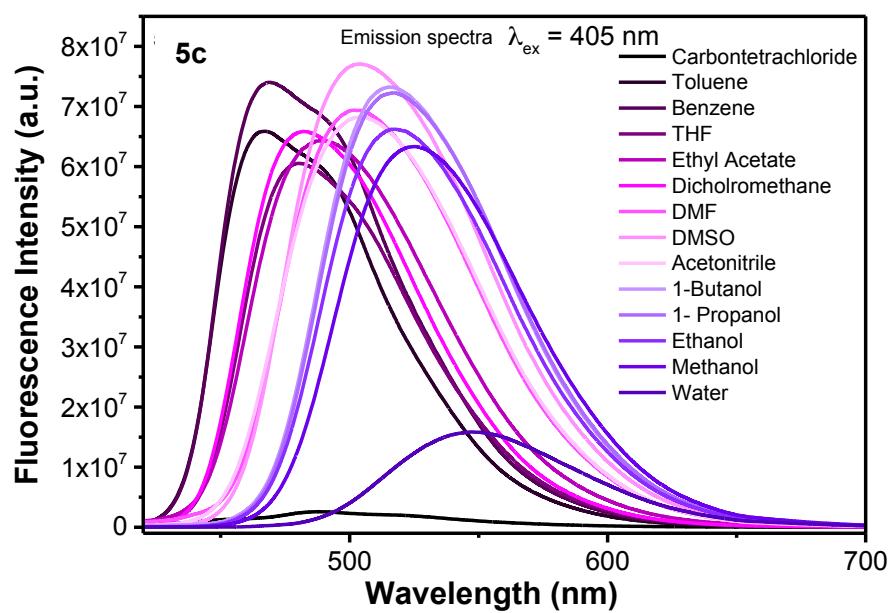


Figure S6. Fluorescence emission spectra of **5c** in various solvents.

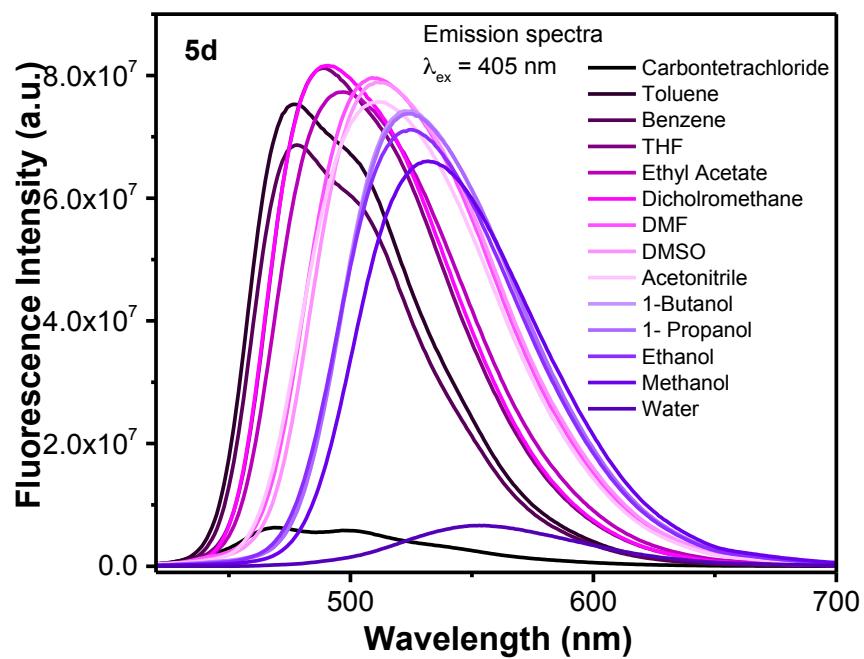


Figure S7. Fluorescence emission spectra of **5d** in various solvents.

Table 15-18 summarizes the absorption maxima along with corresponding extinction coefficients (ϵ), emission maximum and Stokes shift of the compound along with their relative solvent polarity.

Table S15. Absorption and fluorescence spectroscopic parameters of **5a** in various solvents.

Solvent	Relative Polarity	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Stokes shift (cm $^{-1}$)	RFE** (%)	τ (ns)
Carbon tetrachloride	0.052	270				
		348				
		402	460	3137	9	2.02
Toluene	0.099	256				
		348				
		400	471	3769	51	7.47
Benzene	0.111	280				
		348				
		402	474	3779	32	7.73
THF	0.207	262				
		350				
		406	483	3927	100	8.41
Ethyl acetate	0.228	274				
		348				
		404	491	4386	31	7.91
Dichloromethane	0.309	262				
		348				
		402	491	4509	34	10.40
DMF	0.386	270				
		348				
		410	506	4627	43	10.82
DMSO	0.444	268				
		352				
		414	510	4546	62	12.05
Acetonitrile	0.46	262				
		348				
		402	507	5152	19	9.39
1-Butanol	0.586	262				
		350				
		416	521	4845	43	10.7
1-Propanol	0.617	262				
		350				
		414	522	4998	32	10.51
Ethanol	0.654	262				
		348				
		414	523	5034	37	10.11
Methanol	0.761	266				
		348				
		412	531	5440	24	9.69
Water	1.0	260				
		346				
		382	552	8062	11	5.24

**RFE: Relative fluorescence efficiency. See text for calculation detail.

Table S16. Absorption and fluorescence spectroscopic parameters of **5b** in various solvents.

Solvent	Relative Polarity	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Stokes shift (cm ⁻¹)	RFE** (%)	τ (ns)
Carbon tetrachloride	0.052	342 395	451	3144	14	4.8
Toluene	0.099	350 404	460	3013	88	6.68
Benzene	0.111	351 404	462	3107	142	6.71
THF	0.207	351 407	474	3473	100	7.47
Ethyl acetate	0.228	350 403	482	4067	49	7.52
Dichloromethane	0.309	350 403	473	3672	88	8.06
DMF	0.386	342 421	493	3469	109	9.36
DMSO	0.444	345 424	494	3342	118	9.91
Acetonitrile	0.46	344 421	496	3592	141	8.72
1-Butanol	0.586	341 424	505	3783	97	9.26
1-Propanol	0.617	341 423	505	3839	88	9.2
Ethanol	0.654	341 424	506	3822	152	9.0
Methanol	0.761	344 424	513	4092	98	8.67
Water	1.0	350 404	536	6096	18	8.68

**RFE: Relative fluorescence efficiency. See text for calculation detail.

Table S17. Absorption and fluorescence spectroscopic parameters of **5c** in various solvents.

Solvent	Relative Polarity	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Stokes shift (cm ⁻¹)	RFE** (%)	τ (ns)
Carbon tetrachloride	0.052	347 404	488	4261	12	5.08
Toluene	0.099	346 397	467	3776	103	7.24
Benzene	0.111	347 402	469	3554	100	7.52
THF	0.207	346 404	480	3919	100	8.25
Ethyl acetate	0.228	344 395	489	4867	76	8.04
Dichloromethane	0.309	346 403	482	4067	126	9.46
DMF	0.386	342 421	504	3912	153	10.5
DMSO	0.444	345 424	504	3744	132	11.4
Acetonitrile	0.46	344 415	506	4334	136	9.16
1-Butanol	0.586	341 424	515	4167	121	10.2
1-Propanol	0.617	342 421	517	4411	102	10.1
Ethanol	0.654	342 424	516	4205	179	9.74
Methanol	0.761	343 424	526	4574	132	9.35
Water	1.0	341 383	547	7828	32	7.42

**RFE: Relative fluorescence efficiency. See text for calculation detail.

Table S18. Absorption and fluorescence spectroscopic parameters of **5d** in various solvents.

Solvent	Relative Polarity	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Stokes shift (cm ⁻¹)	RFE** (%)	τ (ns)
Carbon tetrachloride	0.052	355 419	469	2544	29	5.41
Toluene	0.099	352 405	477	3727	123	7.94
Benzene	0.111	357 420	478	2889	197	8.01
THF	0.207	352 411	489	3881	100	8.91
Ethyl acetate	0.228	355 417	497	3860	108	8.48
Dichloromethane	0.309	351 408	491	4143	109	9.85
DMF	0.386	344 425	509	3883	118	10.4
DMSO	0.444	345 426	511	3905	113	11.2
Acetonitrile	0.46	345 421	512	4222	95	9.32
1-Butanol	0.586	341 426	525	4427	92	9.93
1-Propanol	0.617	342 426	525	4427	85	9.91
Ethanol	0.654	341 426	525	4427	91	9.44
Methanol	0.761	344 428	532	4567	86	9.17
Water	1.0	344 405	555	6673	30	6.93

**RFE: Relative fluorescence efficiency. See text for calculation detail.

As can be observed the fluorescence emission maximum of the compounds (**5a-d**) correlates very well with the relative solvent polarity. Theory of general solvent effects^[7] describes that increase in refractive index results in a decrease in the energy difference between the ground and excited states. Together with it the ground and excited states are also stabilized due to an increase in dielectric constant. But the energy decrease of the excited state triggered by the dielectric constant occurs only after reorientation of the solvent dipoles as this process necessitates movement of entire solvent molecules, not just electrons. Taking this into account, dielectric continuum theory describes environmental effects for which it is assumed that a point dipole solute interacts with the solvent by virtue of the change in solute dipole moment. This change can be expressed by applying the Lippert-Mataga equation^[7,8]

$$\overline{\nu_A} - \overline{\nu_F} = \frac{2}{hc} \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{(\mu_E - \mu_G)^2}{a^3} + \text{Constant}$$

where $\overline{\nu_A}$ and $\overline{\nu_F}$ are the wave numbers (cm^{-1}) of the absorbance and fluorescence emission, respectively, h is Planck's constant, c is the speed of light in vacuum, a is the radius of the cavity in which the fluorophore resides, μ_E and μ_G are the dipole moments in the excited and ground states, respectively, and ϵ and n are the dielectric constant and the index of refraction of the solvents, respectively.^[8b] The Lippert-Mataga plot can be obtained by plotting the Stokes shift versus the term in parentheses in the above equation (referred to as the orientation polarizability (Δf) of the solvent), which is the result of both the mobility of the electrons in the solvent and the dipole moment of the solvent.

$$(\Delta f) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

The Lippert-Mataga plot of the compound in different solvents is presented in Figure S8.

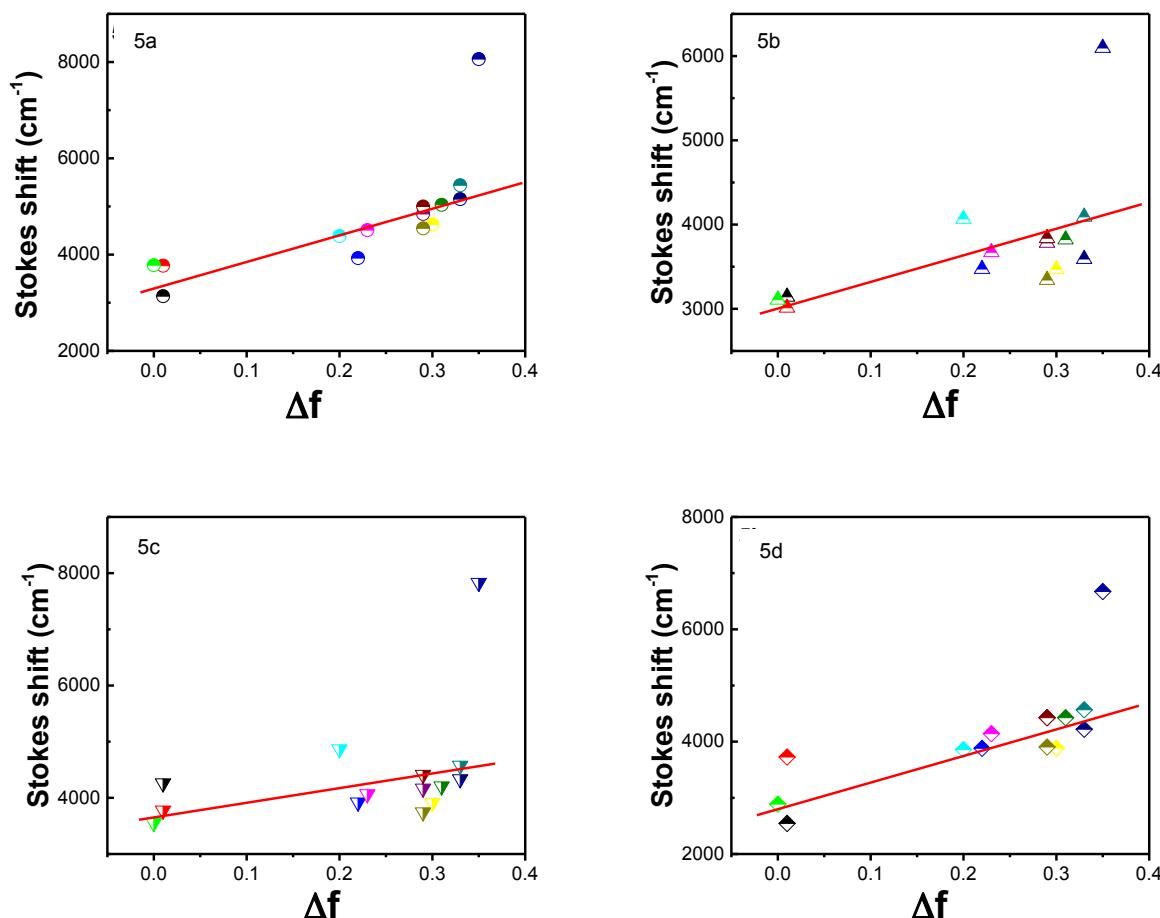


Figure S8. Lippert Mataga plot for **5a-d** in various solvents showing the variation of Stokes shift as a function of orientation polarizability (Δf) of the solvents. The lines are just to guide the eye.

The Stokes shift in water is exceptionally high and did not correlate with other solvent. Since the present compound has both N-H group and oxygen atom, it may interact with various solvents as H-donor as well as H-acceptor to form H-bond. The exceptional behavior in water may be due to special strong affinity of water as a solvent to have multiple H-bond with the compound as both H-

donor as well as H-acceptor. The gross solvent polarity indicator scale, E_{T30} , is more applicable in the case of charge transfer in a molecule.⁹ E_{T30} is defined as the molar electronic transition energies E_T of dissolved pyridinium N-phenolate betaine dye in kcal/mol at STP. As shown in Figure S9 plot of the Stokes shift versus the E_{T30} values of various solvents gives a better correlation.

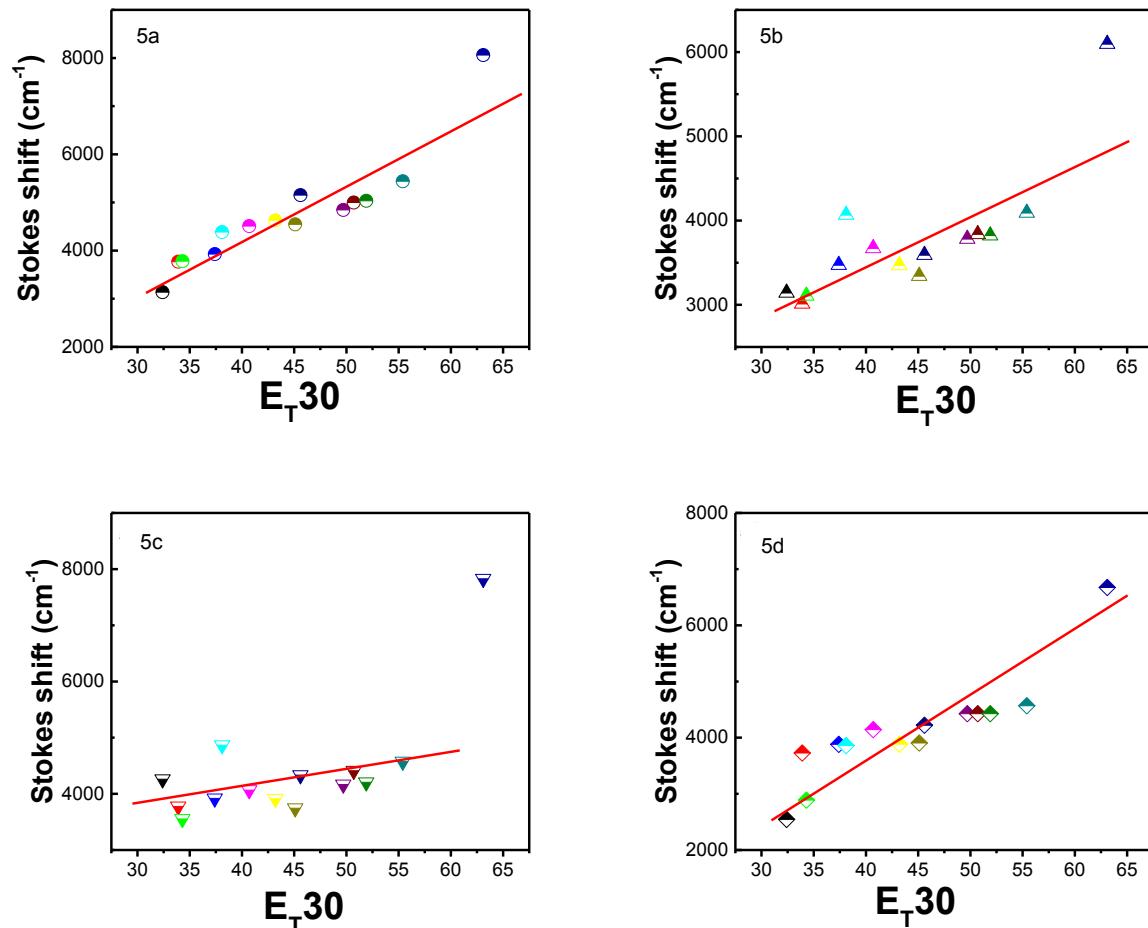


Figure S9. Correlation of Stokes shift of compounds **5a-d** with E_{T30} parameter in various solvents. The lines are just to guide the eye.

The fluorescence lifetime decay profile of the compound in various solvents is shown in Figure S10. Although in most of the cases the decay profile appeared mono-exponential and the data fit acceptably well to a mono-exponential decay except for CCl_4 and water, a bi-exponential decay gave a better chi-square (<1.5) in all cases, one of which was relative amplitude of less than 10 %.

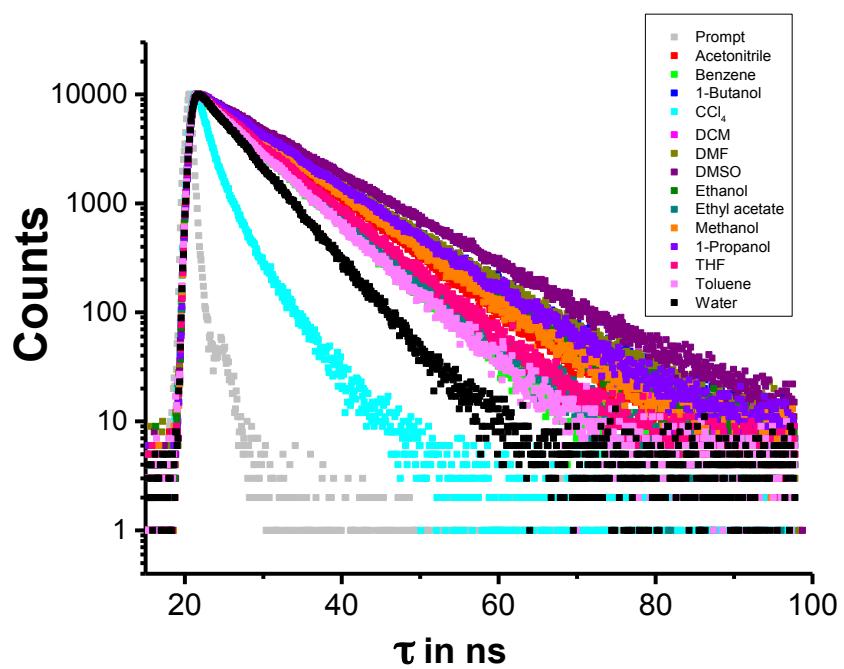
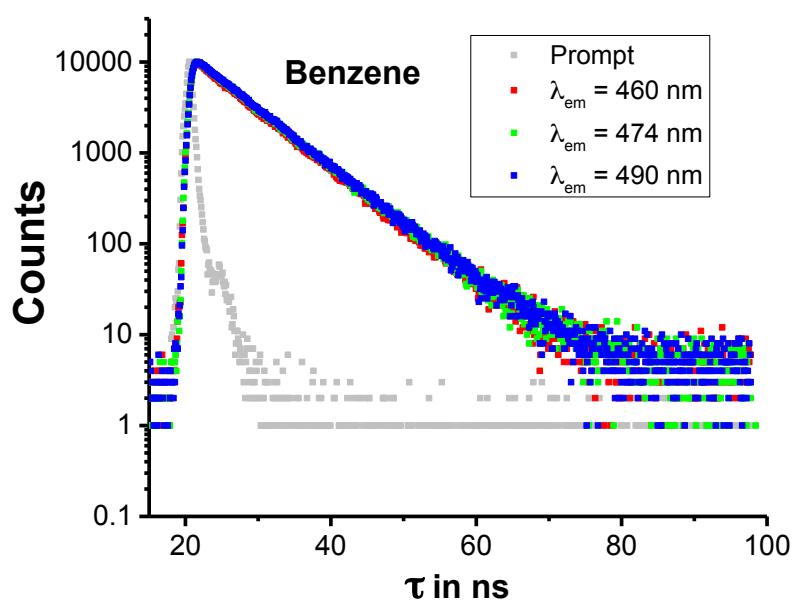


Figure S10. Fluorescence lifetime decay profile of **5a** in (top) benzene in different emission wavelengths and (bottom) various solvents. The excitation wavelength used was a 405 nm diode laser. The fluorescence emission maximum given in Table 1 was used for lifetime measurement in various solvents.

The average fluorescence lifetime was calculated as $\tau = \frac{\sum \alpha_i \tau_i}{100}$ where τ is the fluorescence lifetime and α is the percentage of relative amplitude. The average fluorescence lifetime obtained from bi-exponential decay were similar to that obtained from single exponential decay analysis; therefore, the average fluorescence lifetime was used for data interpretation. The fluorescence decay profile did not depend on emission wavelengths ruling out there is no formation of excimer and other excited state species. The excited state fluorescence lifetime values were in nanosecond time scale in the all solvents under studied and the value was highest in DMSO. It is thought that polar solvents stabilize the excited states, thereby increasing the fluorescence lifetimes. The decrease in fluorescence lifetime in water could be due to specific H-bonding interactions. The relatively short lifetimes of the compound in carbon tetrachloride can be attributed to decreased stabilization of the excited state in less polar solvents.

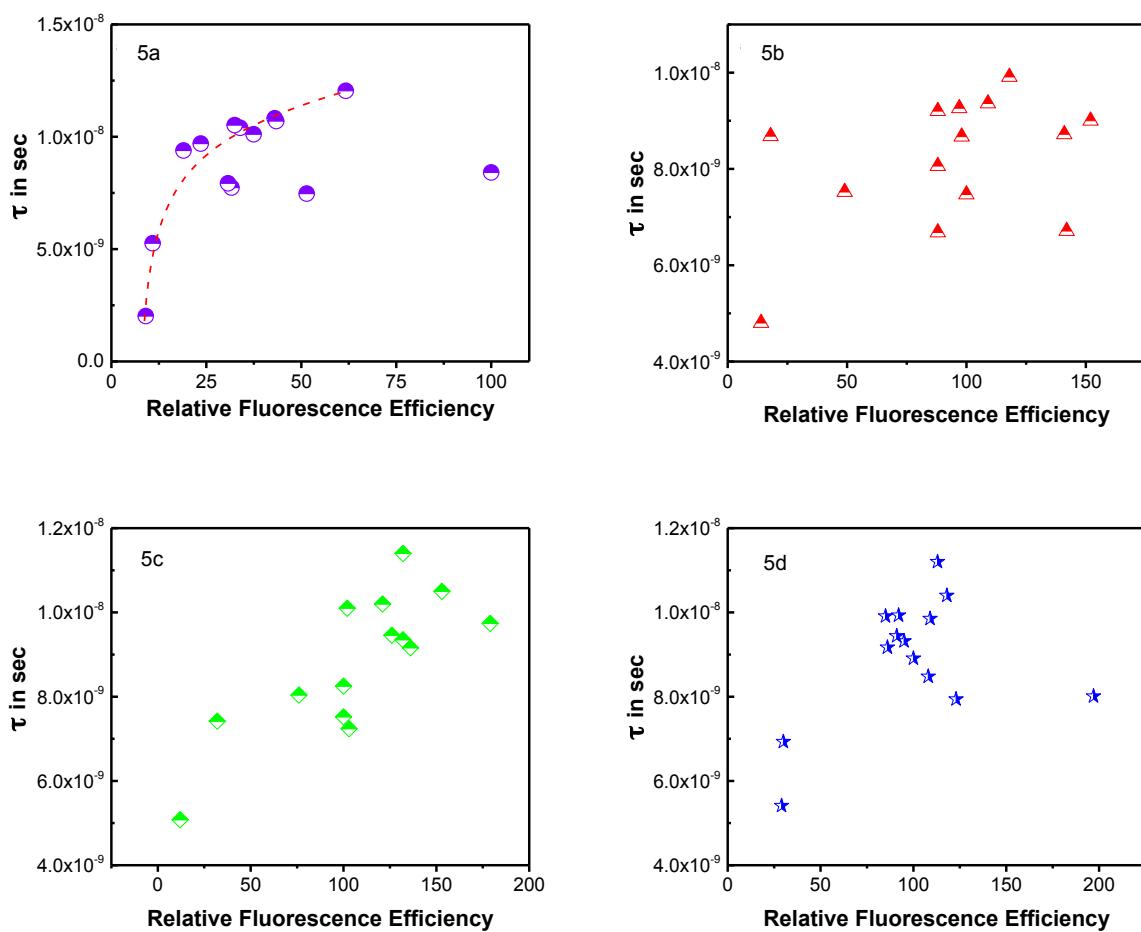


Figure S11. Correlation of fluorescence lifetime (τ) of **5a-d** and its derivatives with relative fluorescence efficiency in various solvents. The dotted line is just to guide the eye.

The relative fluorescence efficiency was calculated with respect to fluorescence emission of the compound in THF using the following equation:

$$\text{Relative fluorescence efficiency} = \frac{F_{\text{sol}}}{F_{\text{THF}}} \frac{A_{\text{THF}}}{A_{\text{sol}}} \frac{n_{\text{sol}}^2}{n_{\text{THF}}^2} \times 100$$

where F_{sol} and F_{THF} are the fluorescence intensity at the respective emission maximum in different solvents and THF, respectively, at excitation wavelength 410 nm; A_{sol} and A_{THF} are absorbance at 410 nm in different solvents and THF respectively; n_{sol} is the refractive index of various solvents used and n_{THF} is the refractive index of THF. The relative fluorescence efficiency of the compound is also given in Table 1. It is found that relative fluorescence efficiency is remarkably sensitive to solvent environment and it is maximum in THF (100%) and lowest in carbon tetrachloride and water. The trend is similar to as observed for excited state lifetime (see Figure S11) except for THF, benzene and toluene.

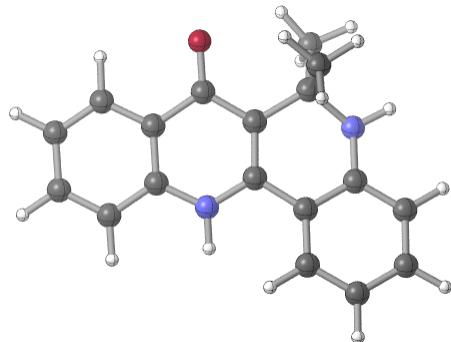
Full Gaussian09 Reference

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Computational Methods and Data

All geometries were built in *GaussView 5.0*, and optimized in *Gaussian09* using density functional theory (DFT) at the B3LYP^[10] level of theory with a 6-31+G(d,p)^[10] basis set in the gas phase. All structures were determined to be minima on the potential energy surface with the inclusion of a frequency calculation in which no imaginary frequencies were found. Single point time-dependent DFT ultraviolet and visible spectrum (TD-DFT, UV-Vis) calculations were performed on the optimized structures with the command td=(nstates=20,root=1) at the B3LYP level of theory with a 6-31+G(d,p) basis set using the SMD model of solvation^[11] in various solvents.

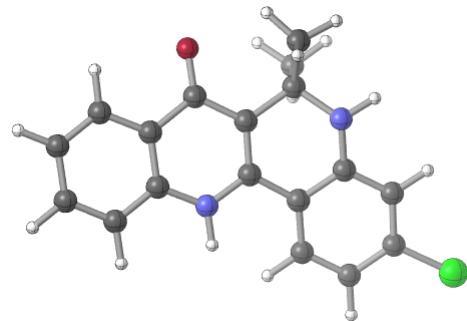
5a



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(Hartree/Particle)	
Thermal correction to Energy=	0.317352
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Thermal correction to Gibbs Free Energy=	0.257487
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Sum of electronic and thermal Energies=	-880.055226
Sum of electronic and thermal Enthalpies=	-880.054282
Sum of electronic and thermal Free Energies=	-880.115090

No imaginary frequencies found.

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5	6	0.000000667	0.000000287	-0.000006614
6	6	-0.000003236	-0.000003383	-0.000000295
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8	1	0.000002382	0.000002488	-0.000002136
9	1	0.000000710	-0.000001777	-0.000000175
10	1	-0.000000839	-0.000003089	-0.000000921
11	6	0.000000742	0.000007032	-0.000060265
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25	6	0.000002821	-0.000010044	-0.000003155
26	1	-0.000005330	-0.000006721	0.000002162
27	6	0.000029117	-0.000003708	-0.000013434
28	1	0.000013919	0.000000089	0.000003328
29	1	0.000007020	0.000003303	0.000014654
30	1	0.000007182	0.000006612	-0.000012569
31	6	0.000010312	0.000045233	-0.000021426
32	1	0.000001484	0.000005625	0.000011145
33	1	0.000011651	-0.000011616	0.000019602
34	1	-0.000003447	-0.000005170	0.000001092
35	7	-0.000051960	0.000029597	0.000015105
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37	1	-0.000008821	0.000002288	-0.000002404

5b

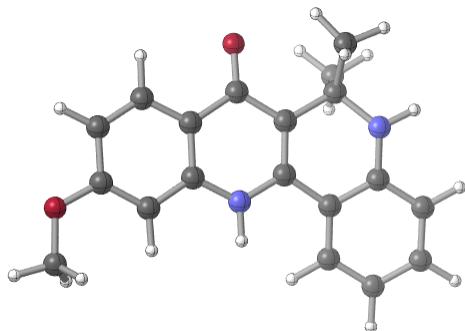
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No imaginary frequencies found.

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4	6	0.000003306	0.000007421	0.000002019
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6	6	0.000005667	0.000007657	-0.000000315
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8	1	-0.000002567	0.000001513	0.000002731
9	1	0.000000871	0.000000237	0.000000358
10	1	0.000000156	0.000000636	-0.000002495
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13	6	-0.000004570	0.000007165	0.000009665
14	8	-0.000007735	-0.000026564	-0.000003000
15	7	-0.000009729	-0.000006809	-0.000020859
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18	6	0.000016112	-0.000000115	0.000000741
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22	1	0.000000071	0.000000359	-0.000001766

23	6	0.000037426	-0.000012944	0.000000978
24	6	-0.000020842	-0.000008915	-0.000006028
25	1	-0.000005237	0.000001524	-0.000005708
26	6	-0.000008832	0.000005125	0.000007758
27	1	0.000001600	0.000001741	0.000005122
28	1	0.000001142	0.000000962	0.000002091
29	1	0.000004431	-0.000001601	0.000006705
30	6	-0.000004968	-0.000006335	0.000008966
31	1	0.000001583	-0.000003353	0.000000654
32	1	0.000001003	0.000001106	0.000002062
33	1	0.000000214	-0.000001827	0.000006557
34	7	-0.000013900	-0.000004811	-0.000003983
35	1	0.000002348	0.000003348	0.000003051
36	1	0.000004667	-0.000003023	-0.000004163
37	17	-0.000004428	-0.000004142	-0.000003903

5c

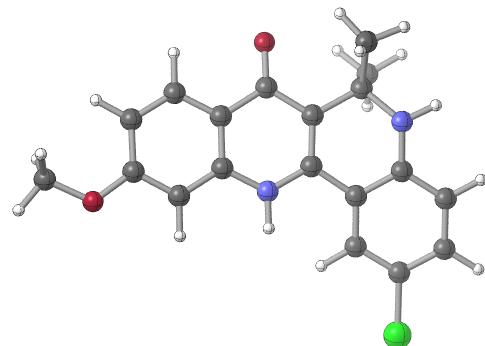


Zero-point correction=	0.333017
(Hartree/Particle)	
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Sum of electronic and thermal Energies=	-994.550084
Sum of electronic and thermal Enthalpies=	-994.549140
Sum of electronic and thermal Free Energies=	-994.616210

No imaginary frequencies found.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
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5	6	-0.000011659	-0.000004481	-0.000009861
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8	1	0.000005207	-0.000000267	-0.000000761
9	6	-0.000003771	-0.000000079	-0.000003842
10	6	-0.000002822	0.000000008	0.000000360
11	6	0.000004363	-0.000002103	0.000001868
12	8	-0.000000007	-0.000001390	0.000001544
13	7	-0.000004017	0.000006136	-0.000001857
14	1	0.000000408	-0.000000736	0.000001100
15	6	-0.000001307	-0.000000077	0.000000328
16	6	0.000003189	-0.000000298	0.000001489
17	6	0.000001840	0.000000248	0.000001917
18	6	-0.000001495	-0.000002547	0.000000939
19	6	-0.000000379	0.000001159	0.000000646
20	1	-0.000000109	-0.000000843	0.000000851
21	6	0.000002637	-0.000001439	0.000001493
22	6	-0.000001097	-0.000001312	0.000000142
23	1	0.000000662	-0.000000685	0.000001121
24	6	-0.000001581	-0.000000999	-0.000001591
25	1	-0.000001760	-0.000000605	0.000000769
26	1	-0.000001558	-0.000000720	0.000000071
27	1	-0.000001291	0.000000062	-0.000000058
28	6	-0.000000566	0.000000104	-0.000001021
29	1	-0.000000050	-0.000000388	0.000000641
30	1	-0.000000784	-0.000000179	-0.000000016
31	1	-0.000000812	-0.000000577	0.000000436
32	7	-0.000000998	0.000000724	-0.000000445
33	1	-0.000000997	-0.000000401	0.000001443
34	1	0.000000802	-0.000000322	0.000000569
35	1	0.000000439	-0.000001291	0.000001302
36	1	-0.000000303	-0.000002684	-0.000003355
37	8	-0.000023727	0.000004074	-0.000007753
38	6	0.000008455	0.000013447	-0.000005457
39	1	0.000005185	-0.000001154	0.000006247
40	1	0.000000396	-0.000004167	0.000003149
41	1	-0.000006422	0.000003465	-0.000005564

5d

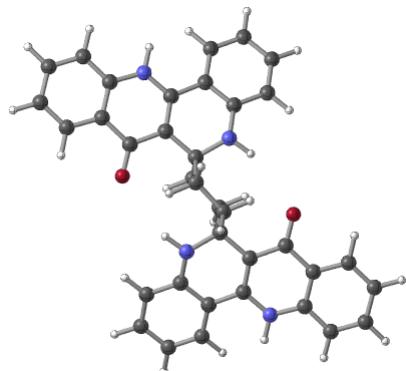
Zero-point correction= 0.323350
 (Hartree/Particle)
 Thermal correction to Energy= 0.344020
 Thermal correction to Enthalpy= 0.344964
 Thermal correction to Gibbs Free Energy= 0.274504
 Sum of electronic and zero-point Energies= -1454.171967
 Sum of electronic and thermal Energies= -1454.151297
 Sum of electronic and thermal Enthalpies= -1454.150353
 Sum of electronic and thermal Free Energies= -1454.220813

No imaginary frequencies found.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000020801	0.000016188	0.000002014
2	6	0.000014651	-0.000008115	-0.000010494
3	6	0.000003877	-0.000003195	0.000000770
4	6	-0.000005247	-0.000007976	-0.000000921
5	6	-0.000027425	0.000011835	-0.000003438
6	6	0.000007146	-0.000014083	0.000012581
7	1	0.000005218	-0.000003864	0.000001708
8	1	0.000001864	0.000000979	-0.000002684
9	6	0.000001614	0.000014868	-0.000006591
10	6	0.000001001	-0.000000178	0.000002710
11	6	-0.000001246	0.000003730	-0.000003561
12	8	-0.000000741	-0.000007794	-0.000001780
13	7	-0.000003715	-0.000006987	0.000024883
14	1	-0.000001511	0.000000717	-0.000011622
15	6	0.000000570	0.000008686	0.000001600
16	6	0.000015774	0.000005565	-0.000002643
17	6	0.000002937	0.000004499	-0.000014082
18	6	-0.000010505	-0.000010639	0.000001294
19	6	-0.000007387	0.000014472	-0.000000581
20	1	0.000000780	0.000000362	-0.000000123

21	6	0.000015427	-0.000001058	0.000003883
22	6	-0.000010381	-0.000009890	0.000001003
23	6	-0.000004981	-0.000002046	-0.000003918
24	1	-0.000001620	-0.000000118	-0.000000406
25	1	-0.000001101	-0.000003406	-0.000001926
26	1	0.000004329	-0.000000533	-0.000002427
27	6	-0.000004086	-0.000001949	0.000004270
28	1	0.000002051	0.000002256	-0.000001462
29	1	0.000002518	0.000004155	-0.000001327
30	1	0.000000712	0.000001460	-0.000000188
31	7	-0.000011038	-0.000009525	0.000007612
32	1	0.000001665	0.000001052	-0.000002473
33	1	0.000001277	0.000002376	0.000004015
34	1	0.000002544	-0.000001289	0.000002720
35	1	0.000023550	0.000001850	-0.000000827
36	8	-0.000002692	0.000006149	-0.000003418
37	6	0.000002969	-0.000012543	0.000000180
38	1	0.000001622	0.000002633	-0.000002015
39	1	0.000001138	0.000005451	-0.000001795
40	1	0.000001383	-0.000004176	0.000005483
41	17	-0.000002137	0.000000086	0.000003975

8 (*N,N-trans*)



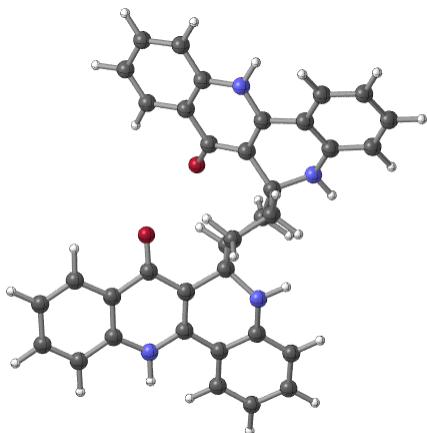
Zero-point correction=	0.564350
(Hartree/Particle)	
Thermal correction to Energy=	0.595588
Thermal correction to Enthalpy=	0.596532
Thermal correction to Gibbs Free Energy=	0.501162
Sum of electronic and zero-point Energies=	-1757.767600
Sum of electronic and thermal Energies=	-1757.736362
Sum of electronic and thermal Enthalpies=	-1757.735417
Sum of electronic and thermal Free Energies=	-1757.830788

No imaginary frequencies found.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-7.080331	-0.897388	0.169817
2	6	0	-5.699317	-0.618737	0.151729
3	6	0	-4.758581	-1.645084	0.356050
4	6	0	-5.222252	-2.957129	0.567128
5	6	0	-6.580462	-3.235962	0.586194
6	6	0	-7.510609	-2.197470	0.386487
7	1	0	-7.797279	-0.095555	0.010757
8	1	0	-4.478267	-3.732631	0.715227
9	1	0	-6.929007	-4.250156	0.754373
10	1	0	-8.575136	-2.412302	0.400215
11	6	0	-3.310498	-1.347074	0.345455
12	6	0	-2.937964	0.059532	0.207470
13	6	0	-3.909618	1.005333	-0.074966
14	8	0	-2.482211	-2.277389	0.435920
15	7	0	-5.238788	0.661330	-0.078662
16	1	0	-5.921499	1.392909	-0.203150
17	6	0	-3.577688	2.394898	-0.402998
18	6	0	-2.234416	2.801061	-0.196906
19	6	0	-1.457576	0.443505	0.236105
20	6	0	-1.874472	4.141696	-0.459544
21	6	0	-2.815725	5.046966	-0.928534
22	1	0	-0.846880	4.452507	-0.291277
23	6	0	-4.140160	4.647015	-1.163619
24	1	0	-2.515164	6.071774	-1.127340
25	6	0	-4.502807	3.330035	-0.900765
26	1	0	-4.870167	5.348370	-1.553216
27	6	0	-0.759563	-0.114742	1.507309
28	1	0	-0.990646	-1.176201	1.594528
29	1	0	-1.199349	0.380545	2.379872
30	6	0	-0.760380	-0.102366	-1.044849
31	1	0	-1.004575	-1.164937	-1.133475
32	1	0	-1.197198	0.396742	-1.918128
33	7	0	-1.325041	1.914072	0.304099
34	1	0	-0.372660	2.251078	0.371116
35	1	0	-5.525681	3.032612	-1.117346
36	6	0	0.760415	0.101976	-1.044834
37	6	0	1.457586	-0.443721	0.236216
38	1	0	1.004594	1.164538	-1.133601
39	1	0	1.197272	-0.397256	-1.918022
40	6	0	0.759476	0.114544	1.507363
41	1	0	1.199200	-0.380735	2.379960
42	1	0	0.990542	1.176003	1.594594
43	6	0	2.937937	-0.059604	0.207597
44	6	0	3.909676	-1.005322	-0.074851
45	6	0	3.577848	-2.394906	-0.402918
46	6	0	2.234620	-2.801184	-0.196804
47	6	0	3.310342	1.347038	0.345498
48	6	0	4.758394	1.645178	0.356104

49	6	0	5.699222	0.618915	0.151766
50	8	0	2.481970	2.277290	0.435898
51	6	0	7.080211	0.897692	0.169804
52	6	0	7.510376	2.197814	0.386456
53	1	0	7.797228	0.095923	0.010736
54	6	0	6.580139	3.236219	0.586203
55	1	0	8.574883	2.412746	0.400146
56	6	0	5.221953	2.957263	0.567175
57	1	0	6.928598	4.250441	0.754387
58	1	0	4.477903	3.732698	0.715292
59	7	0	5.238804	-0.661206	-0.078540
60	1	0	5.921583	-1.392630	-0.203555
61	6	0	4.503021	-3.329956	-0.900752
62	6	0	4.140457	-4.646943	-1.163676
63	1	0	5.525888	-3.032478	-1.117298
64	6	0	2.816054	-5.047000	-0.928596
65	1	0	4.870508	-5.348229	-1.553314
66	6	0	1.874756	-4.141820	-0.459523
67	1	0	2.515561	-6.071816	-1.127464
68	1	0	0.847188	-4.452706	-0.291245
69	7	0	1.325208	-1.914299	0.304344
70	1	0	0.372840	-2.251370	0.371233

8 (*N,N-cis*)



Zero-point correction=	0.563570
(Hartree/Particle)	
Thermal correction to Energy=	0.594771
Thermal correction to Enthalpy=	0.595715
Thermal correction to Gibbs Free Energy=	0.501948
Sum of electronic and zero-point Energies=	-1757.749447
Sum of electronic and thermal Energies=	-1757.718246
Sum of electronic and thermal Enthalpies=	-1757.717302
Sum of electronic and thermal Free Energies=	-1757.811069

No imaginary frequencies found.

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000003656	-0.000001853	-0.000003153
2	6	0.000004699	-0.000010392	0.000005867
3	6	0.000001057	-0.000001807	0.000004047
4	6	-0.000002901	-0.000000494	-0.000000917
5	6	0.000002358	-0.000003094	-0.000000670
6	6	0.000000440	-0.000004795	0.000000053
7	1	0.000000330	-0.000003315	-0.000001447
8	1	0.000002816	-0.000000919	-0.000000733
9	1	0.000002009	-0.000002394	-0.000000299
10	1	0.000002014	-0.000003719	-0.000000575
11	6	0.000006083	0.000004990	-0.000004413
12	6	-0.000021745	-0.000024551	0.000003048
13	6	-0.000006235	0.000018920	-0.000003988
14	8	-0.000001209	-0.000004508	0.000004390
15	7	-0.000007378	-0.000000389	-0.000018529
16	1	-0.000000239	-0.000001028	0.000011105
17	6	0.000014131	-0.000017223	0.000003075
18	6	0.000020672	-0.000011957	0.000005386
19	6	0.000034526	0.000014750	0.000007037
20	6	-0.000008615	0.000012430	-0.000005268
21	6	0.000004024	-0.000003867	0.000002219
22	1	-0.000002659	-0.000002560	-0.000000373
23	6	-0.000001864	-0.000003689	-0.000000057
24	1	-0.000003991	-0.000002252	-0.000000302
25	6	-0.000015758	0.000001079	-0.000004782
26	1	-0.000002273	-0.000003688	-0.000001296
27	6	-0.000030705	-0.000002174	0.000019177
28	1	0.000009229	-0.000003721	-0.000012256
29	1	-0.000003241	-0.000005318	-0.000001107
30	6	0.000001047	-0.000003501	-0.000006087
31	1	0.000000490	0.000005004	0.000001677
32	1	-0.000002950	-0.000001195	0.000000428
33	7	-0.000024855	0.000010644	-0.000008944
34	1	-0.000005563	-0.000005065	0.000008076
35	1	0.000002427	-0.000005259	-0.000000104
36	6	0.000005825	0.000002099	0.000013994
37	6	0.000017793	-0.000002488	0.000014903
38	1	0.000002962	-0.000004591	-0.000001646
39	1	-0.000001582	0.000005283	-0.000000302
40	6	-0.000003642	0.000014967	-0.000032712
41	1	0.000002867	-0.000000655	-0.000000480
42	1	0.000006145	0.000001515	-0.000001291
43	6	0.000005492	-0.000014022	0.000005558
44	6	-0.000000764	-0.000010036	0.000000535
45	6	0.000005663	0.000010834	0.000004899
46	6	0.000002709	0.000003179	-0.000000550

47	6	0.000000624	0.000002115	0.000000144
48	1	0.000001799	0.000003168	0.000000519
49	6	0.000004929	0.000002177	0.000001541
50	1	0.000003186	0.000002088	0.000000346
51	6	-0.000000246	-0.000001273	-0.000002919
52	1	0.000003333	0.000001218	-0.000000049
53	1	0.000003379	0.000000380	0.000001249
54	6	-0.000000423	0.000004425	0.000000433
55	6	0.000005193	0.000012476	0.000000579
56	6	0.000000803	-0.000004079	0.000003979
57	6	-0.000016390	0.000001345	-0.000011240
58	6	0.000006398	0.000003285	0.000005421
59	6	-0.000006473	0.000004282	-0.000003524
60	6	0.000013714	-0.000000726	0.000004358
61	8	-0.000008994	0.000002334	-0.000006890
62	7	0.000001560	0.000011295	-0.000002499
63	1	-0.000001773	0.000001369	0.000001503
64	6	-0.000015288	-0.000000347	-0.000013142
65	7	-0.000000363	0.000002781	0.000021080
66	1	0.000000360	-0.000000825	-0.000005399
67	1	-0.000001544	0.000002795	0.000000784
68	1	-0.000001989	0.000003998	0.000000757
69	1	-0.000003040	0.000003887	-0.000000121
70	1	-0.000002047	0.000002657	-0.000000105

Table S5. Computational and experimental $\lambda_{\max}^{\text{ex}}$ for **5a-d**.

Solvent	ϵ (dielectric constant)	5a $\lambda_{\max}^{\text{ex}}$ Comp.	5b $\lambda_{\max}^{\text{ex}}$ Comp.	5c $\lambda_{\max}^{\text{ex}}$ Comp.	5d $\lambda_{\max}^{\text{ex}}$ Comp.	5a $\lambda_{\max}^{\text{ex}}$ Exp.	5b $\lambda_{\max}^{\text{ex}}$ Exp.	5c $\lambda_{\max}^{\text{ex}}$ Exp.	5d $\lambda_{\max}^{\text{ex}}$ Exp.
CCl ₄	2.24	406	401	403	413	402	395	404	419
Benzene	2.28	406	402	401	414	402	404	402	420
CH ₃ Ph	2.38	406	402	401	414	400	404	397	405
EtOAc	6.02	408	403	402	414	404	403	395	417
THF	7.58	408	403	402	414	406	407	404	411
DCM	8.93	410	405	404	416	402	403	403	408
1-ButOH	17.26	415	409	409	421	416	424	424	426
1-PropOH	18.3	415	410	410	421	414	423	421	426
EtOH	24.6	415	410	410	421	414	424	424	426
CH ₃ OH	32.6	416	411	411	423	412	424	424	428
DMF	36.7	410	405	404	416	410	421	421	425
CH ₃ CN	37.5	410	405	404	416	402	421	415	421
DMSO	46.7	410	405	404	416	414	424	424	426
H ₂ O	78.54	417	412	412	423	382	404	383	405

Figure S12. Computational vs. Experimental correlation of $\lambda_{\max}^{\text{ex}}$ for **5a**. Each point represents a different solvent.

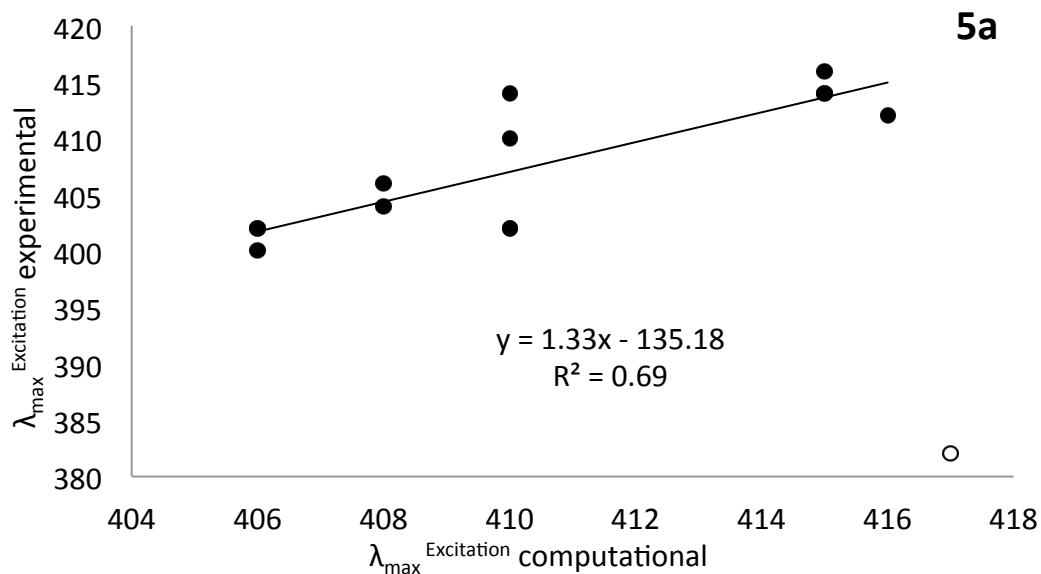


Figure S13. Computational vs. Experimental correlation of $\lambda_{\max}^{\text{ex}}$ for **5b**. Each point represents a different solvent.

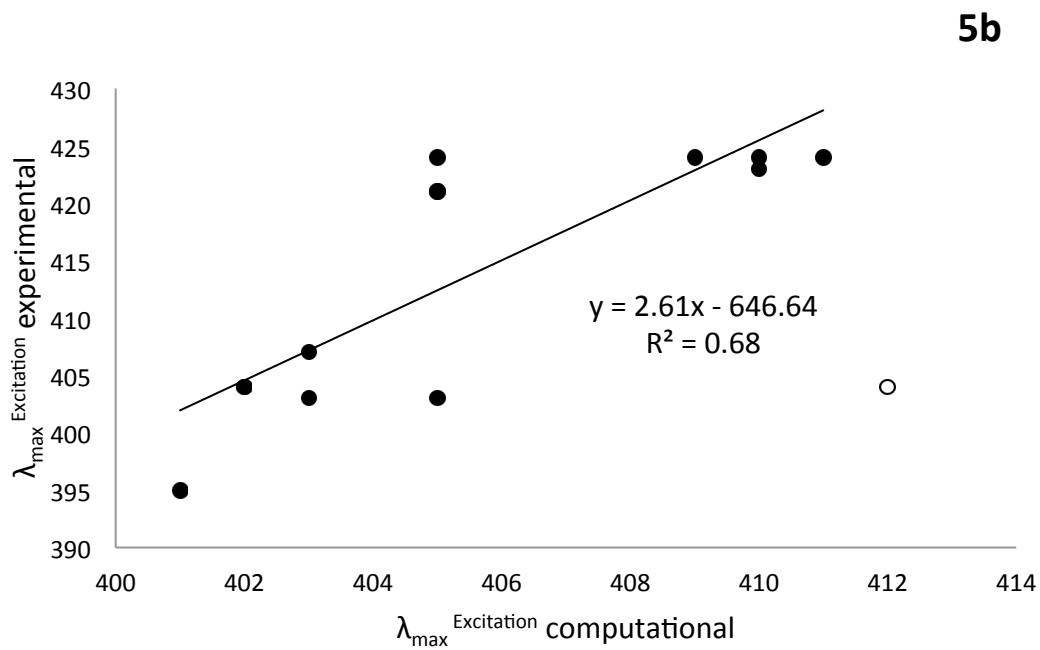


Figure S14. Computational vs. Experimental correlation of $\lambda_{\max}^{\text{ex}}$ for **5c**. Each point represents a different solvent.

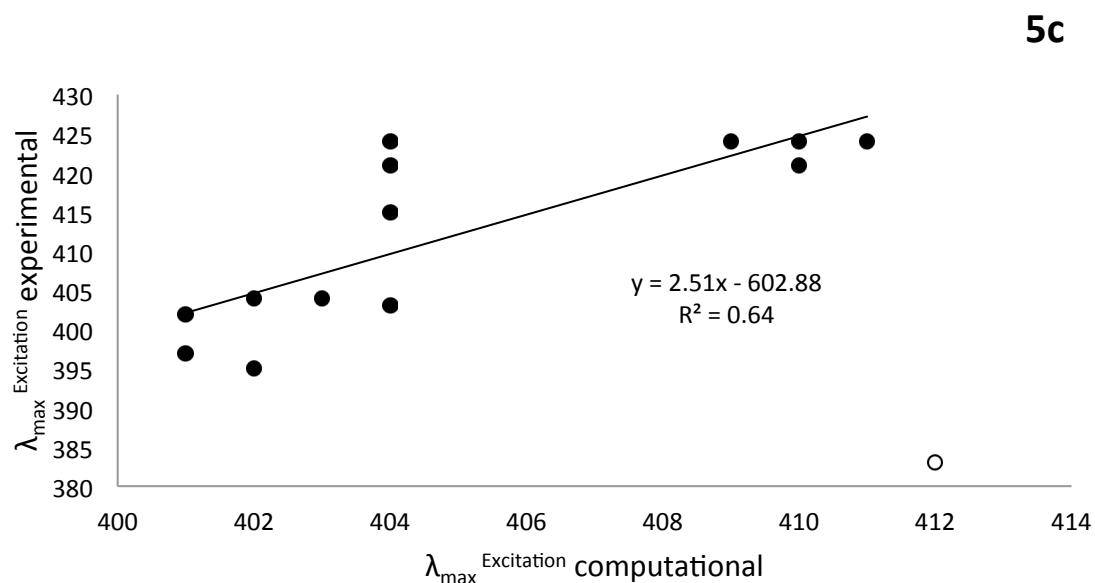
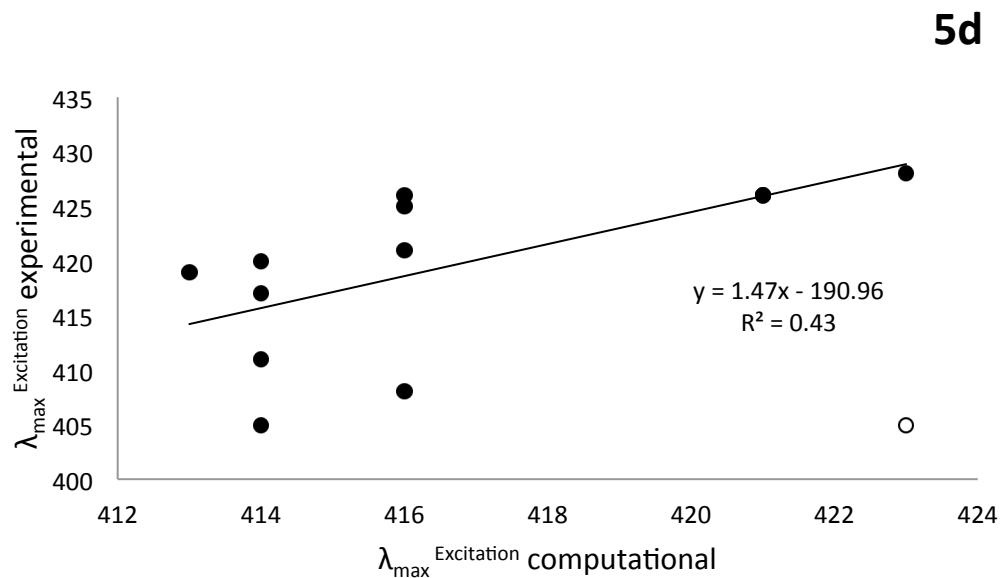
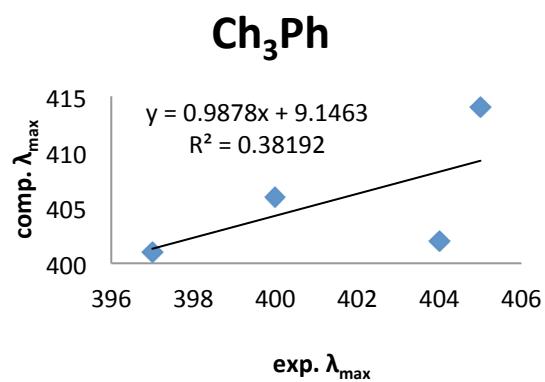
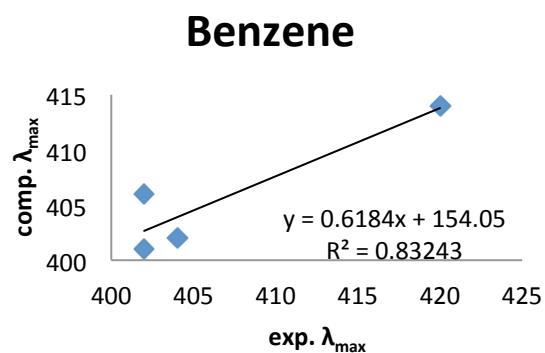
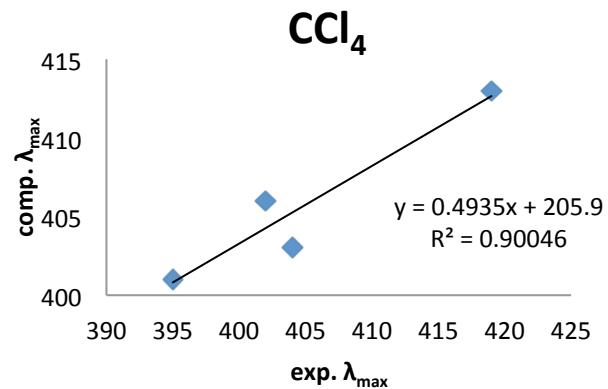
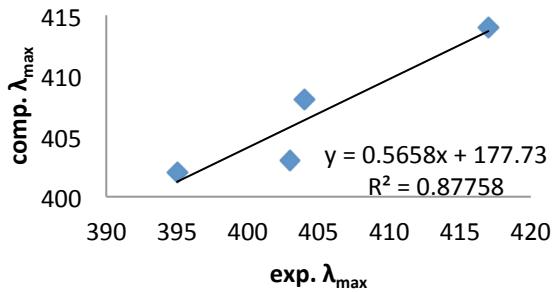


Figure S15. Computational vs. Experimental correlation of $\lambda_{\max}^{\text{ex}}$ for **5d**. Each point represents a different solvent.

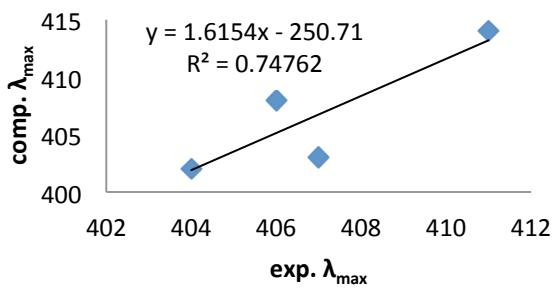




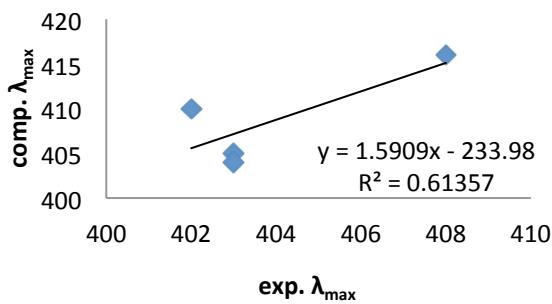
EtOAc



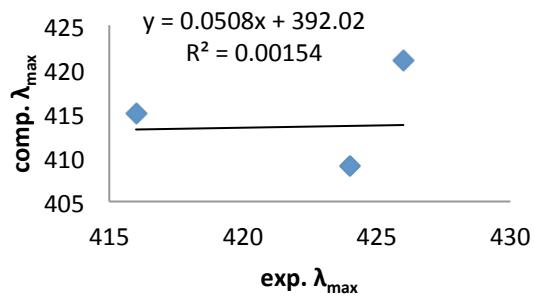
THF



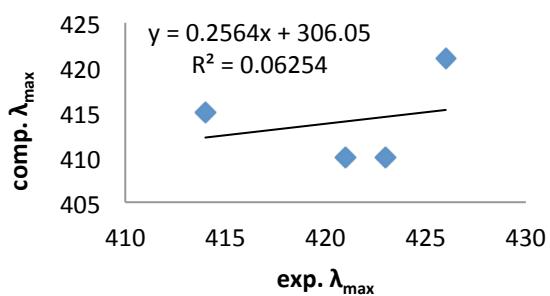
DCM



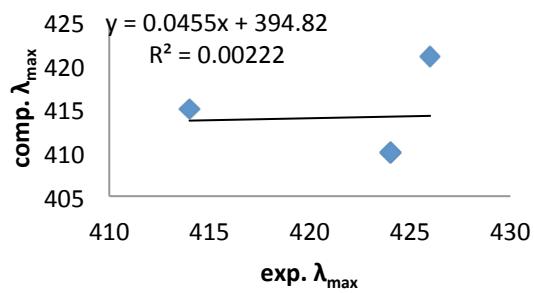
n-ButOH



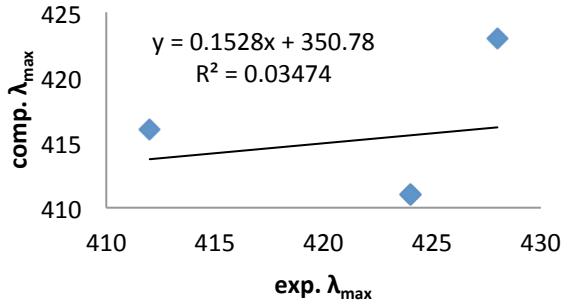
n-PropOH



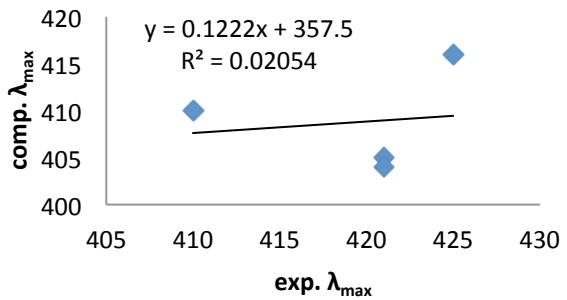
EtOH



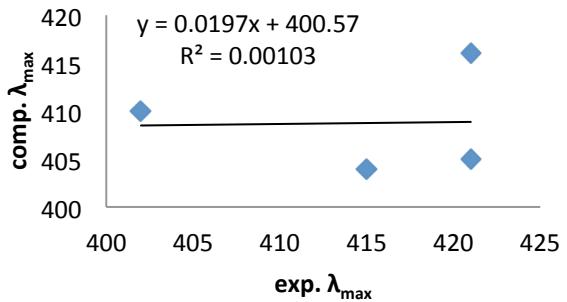
MeOH



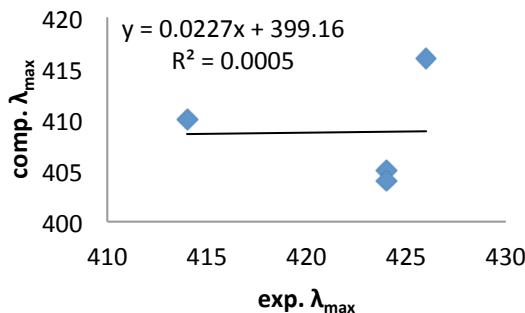
DMF



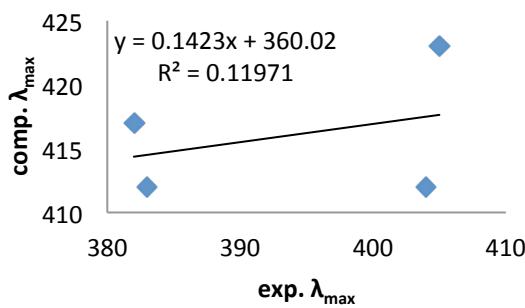
CH₃CN



DMSO



H₂O



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