Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2021

Crystal-packing modes determine solid-state ESIPT fluorescence in highly dipolar 2'-hydroxychalcones.

Alix Tordo[†], *Erwann Jeanneau*[‡], *Mathieu Bordy*[†], *Yann Bretonnière*[†], *Jens Hasserodt*[†]*.

[†]Univ. Lyon, ENS Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie, UMR 5182, 46 Allée d'Italie, 69364 Lyon, France.

[‡] Univ. Lyon 1, Centre de Diffractométrie Henri Longchambon, 5 rue de la Doua, 69100 Villeurbanne, France.

jens.hasserodt@ens-lyon.fr

Table of Contents

1. Organic synthesis

a. General

b. Synthesis of **1a-e**, **2a-e**, **3a-e**

2. Spectroscopy

a. General

b. Crystal-state fluorescence emission spectra of **1a-e**, **2a-e**, **3a-e**

3. Single-crystal X-ray crystallography

a. General

b. Intramolecular parameters

c. Data for compounds **1a-e**, **2a-e**, **3a-e**

d. Additional data for compound **2a, 2b, 2e, 2c, 2d, 3e**

4. NMR Spectra

5. References

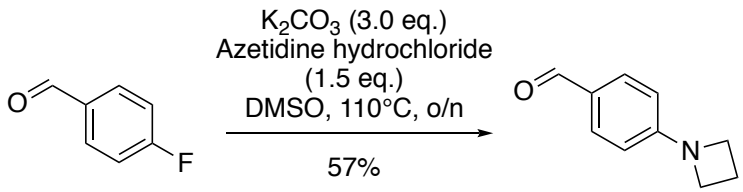
1. Organic synthesis

a. General

Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. Column chromatography was performed using Merck silica gel Si-60 (40-63 µm). All mixed solvent eluents are reported as v/v solutions. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired at 297 K on a Bruker AVANCE 400 (400 MHz and 100 MHz for ^{1}H and ^{13}C, respectively) as indicated. Data are reported as follows: chemical shift (reported in ppm and referenced to solvent peaks as internal standards), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublets, etc.), NMR coupling constants J (reported in Hertz and referring to (H, H) coupling), integration.

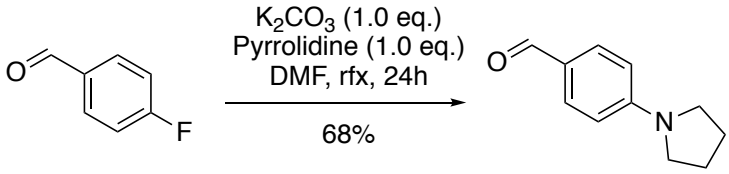
b. Synthesis of intermediates **4** and **5**, and of 2'-hydroxychalcones **1a-e**, **2a-e**, **3a-e.**

Synthesis of 4-(azetidin-1-yl)benzaldehyde (**4**)



To a solution of 4-fluorobenzaldehyde (2.0 mL, 19 mmol, 1.0 eq.) in DMSO (40 mL) was added anhydrous K_2CO_3 (7.9 g, 57 mmol, 3.0 eq.) followed by the addition of azetidine hydrochloride (2.63 g, 27 mmol, 1.5 eq.) with stirring at 110 °C overnight. The mixture was then cooled to room temperature, diluted with water (200 mL), and extracted with ethyl acetate (3 × 100 mL). The organic layer was washed with brine (50 mL) and dried over Na_2SO_4, then concentrated *in vacuo*. The product was then purified by flash column chromatography (20 % EtOAc/hexanes) affording **4** as a pale yellow solid (1.76 g, 11 mmol, 57 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 6.36 (d, *J* = 8.3 Hz, 2H), 4.01 (t, *J* = 7.4 Hz, 4H), 2.42 (p, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 155.2, 132.0, 125.8, 109.8, 51.5, 16.52.

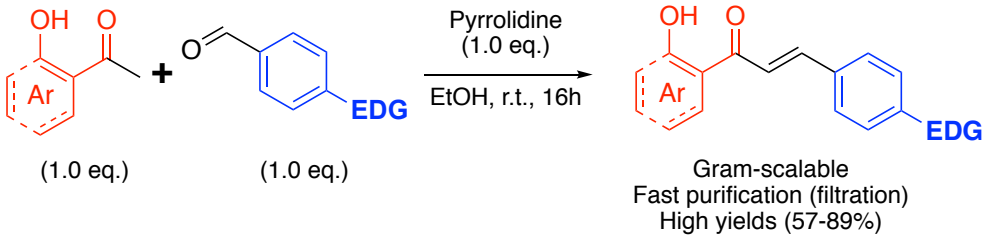
Synthesis of 4-(1-pyrrolidinyl)benzaldehyde (**5**)



4-Fluoro benzaldehyde (4.07 mL, 38.0 mmol, 1.0 eq.), pyrrolidine (3,17 mL, 38.0 mmol, 1.0 eq.), and K_2CO_3 (5.25 g, 38.0 mmol, 1.0 eq.) were refluxed in DMF (40 mL) for 24 h. After completion of the reaction, the mixture was poured into ice-water (50 mL). The precipitated product was filtered, washed with water, dried, and recrystallized from EtOH to give a beige powder (4.52 g, 25.8 mmol, 68 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.39 (q, *J* = 4.9, 3.1 Hz, 4H), 2.05 (p, *J* = 3.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 152.1, 132.3, 125.0, 111.3, 47.8, 25.6.

General protocol A for the synthesis of 2'-hydroxychalcone derivatives (**1a-e, 2a-e, 3a-e**):

To a solution of methylketone (1.0 eq.) in EtOH was added the benzaldehyde (1.0 eq) and pyrrolidine (1.0 eq). The resulting mixture was stirred at room temperature overnight (16h). The precipitated solid was filtered and washed with cold EtOH and PE to obtain the desired condensed product.



1a- According to general procedure **A** and using 2'-hydroxyacetophenone (602 µL, 5.00 mmol, 1.0 eq.), dimethylaminobenzaldehyde (748 mg, 5.00 mmol, 1.0 eq.) and pyrrolidine (441 µL, 5.00 mmol, 1.0 eq.) in EtOH (15 mL), the fluorophore **1a** (1176 mg, 4.40 mmol, 88 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.85 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.52 – 7.38 (m, 2H), 7.01 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.98 – 6.86 (m, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.06 (d, *J* = 1.2 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 163.6, 152.5, 146.7, 135.8, 131.0, 129.5, 122.5, 120.5, 118.7, 114.4, 111.9, 40.2.

1b - According to general procedure **A** and using 2'-hydroxyacetophenone (602 µL, 5.00 mmol, 1.0 eq.), diethylaminobenzaldehyde (886 mg, 5.00 mmol, 1.0 eq.) and pyr- rolidine (441 µL, 5.00 mmol, 1.0 eq.) in EtOH (15 mL), the fluorophore **1b** (1.24 g, 4.18 mmol, 84 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.85 (m, 2H), 7.61 – 7.51 (m, 2H), 7.50 – 7.39 (m, 2H), 7.01 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.92 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 6.72 – 6.62 (m, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 163.6, 150.2, 146.8, 135.7, 131.4, 129.5, 121.8, 120.6, 118.7, 113.8, 111.5, 44.7, 12.8.

1c - According to general procedure **A** and using 2'-hydroxyacetophenone (120 µL, 1.00 mmol, 1.0 eq.), 4-(azetidin-1-yl)benzaldehyde **1** (161 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **1c** (158 mg, 0.57 mmol, 57 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.78 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 2H), 4.00 (t, *J* = 7.2 Hz, 4H), 2.43 (p, *J* = 7.3 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 163.6, 153.6, 146.8, 135.8, 130.8, 129.5, 123.2, 120.5, 118.7, 114.6, 110.8, 51.9, 16.7.

1d - According to general procedure **A** and using 2'-hydroxyacetophenone (120 µL, 1.00 mmol, 1.0 eq.), 4-(1-pyrrolidinyl)benzaldehyde **2** (175 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **1d** (249 mg, 0.85 mmol, 85 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.88 (m, 2H), 7.57 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.01 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.97 – 6.88 (m, 1H), 6.63 – 6.51 (m, 2H), 3.50 – 3.24 (m, 4H), 2.15 – 1.93 (m, *J* = 6.2, 5.4 Hz, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 163.6, 150.1, 147.0, 135.7, 131.2, 129.5, 122.0, 120.6, 118.7, 113.7, 112.0, 47.8.

1e - According to general procedure **A** and using 2'-hydroxyacetophenone (120 µL, 1.00 mmol, 1.0 eq.), 4-methoxybenzaldehyde (121 µL, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), the fluorophore **1e** (159 mg, 0.63 mmol, 63 %) was obtained as a yellow powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.87 (m, 2H), 7.68 – 7.59 (m, 2H), 7.55 (d, *J* = 15.4 Hz, 1H), 7.49 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.99 – 6.90 (m, 3H), 3.87 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 163.7, 162.2, 145.5, 136.3, 130.7, 129.7, 127.5, 120.3, 118.9, 118.75, 117.8, 114.7, 55.6.

2a - According to general procedure **A** and using 1'-hydroxy-2'-acetonaphtone (136 mg, 1.00 mmol, 1.0 eq.), dimethylaminobenzaldehyde (149 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3

mL), fluorophore **3a** (273 mg, 0.86 mmol, 86 %) was obtained as an orange powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 – 8.46 (m, 1H), 7.98 (d, *J* = 15.1 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.82 – 7.72 (m, 1H), 7.67 – 7.46 (m, 4H), 7.29 (d, *J* = 8.9 Hz, 1H), 6.81 – 6.58 (m, 2H), 3.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 164.2, 152.4, 146.3, 137.3, 131.0, 129.9, 127.5, 125.8, 124.5, 124.2, 122.7, 118.0, 114.8, 113.9, 112.0, 40.2.

2b - According to general procedure **A** and using 1'-hydroxy-2'-acetonaphtone (136 mg, 1.00 mmol, 1.0 eq.), diethylaminobenzaldehyde (177 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **3b** (259 mg, 0.75 mmol, 75 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 – 8.42 (m, 1H), 7.98 (d, *J* = 15.1 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.42 (m, 5H), 7.29 (d, *J* = 8.9 Hz, 1H), 6.77 – 6.59 (m, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 164.1, 150.2, 146.4, 137.2, 131.4, 129.8, 127.5, 125.8, 124.5, 124.2, 121.9, 117.9, 114.1, 113.9, 111.5, 44.7, 12.8.

2c - According to general procedure **A** and using 1'-hydroxy-2'-acetonaphtone (136 mg, 1.00 mmol, 1.0 eq.), 4-(azetidin-1-yl)benzaldehyde **1** (161 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **3c** (211 mg, 0.64 mmol, 64 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.96 (d, *J* = 15.2 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.77 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.67 – 7.47 (m, 5H), 7.33 – 7.27 (m, 1H), 6.47 – 6.32 (m, 2H), 3.99 (t, *J* = 7.3 Hz, 4H), 2.49 – 2.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 164.2, 153.5, 146.4, 137.3, 130.8, 129.9, 127.5, 125.8, 124.5, 124.2, 123.4, 118.0, 114.9, 113.8, 110.9, 51.9, 16.7.

2d - According to general procedure **A** and using 1'-hydroxy-2'-acetonaphtone (136 mg, 1.00 mmol, 1.0 eq.), 4-(1-pyrrolidinyl)benzaldehyde **2** (175 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **3d** (271 mg, 0.79 mmol, 79 %) was obtained as a purple powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.99 (d, *J* = 15.1 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.57 – 7.47 (m, 2H), 7.29 (d, *J* = 8.9 Hz, 1H), 6.63 – 6.53 (m, 2H), 3.49 – 3.18 (m, 4H), 2.10 – 1.96 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 164.1, 150.1, 146.7, 137.3, 131.2, 129.8, 127.5, 125.8, 124.5, 124.3, 122.2, 117.9, 114.1, 112.0, 47.7, 25.6.

2e - According to general procedure **A** and using 1'-hydroxy-2'-acetonaphtone (186 mg, 1.00 mmol, 1.0 eq.), 4-methoxybenzaldehyde (121 µL, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), the fluorophore **3e** (232 mg, 0.76 mmol, 76 %) was obtained as an orange powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.97 (d, *J* = 15.4 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.59 (m, 4H), 7.54 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.02 – 6.92 (m, 2H), 3.88 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 164.4, 162.1, 145.1, 137.5, 130.7, 130.2, 127.5, 126.0, 124.6, 118.3, 114.7, 113.7, 55.6.

3a - According to general procedure **A** and using 2'-hydroxy-4-methoxy-acetophenone (166 mg, 1.00 mmol, 1.0 eq.), dimethylaminobenzaldehyde (149 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **2a** (265 mg, 0.89 mmol, 89 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.79 (m, 2H), 7.60 – 7.52 (m, 2H), 7.38 (d, *J* = 15.2 Hz, 1H), 6.74 – 6.67 (m, 2H), 6.53 – 6.41 (m, 2H), 3.85 (s, 3H), 3.05 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 166.6, 165.8, 152.3, 145.6, 130.8, 122.7, 114.7, 112.0, 107.5, 101.2, 55.7, 40.3.

3b – According to general procedure **A** and using 2'-hydroxy-4-methoxy-acetophenone (166 mg, 1.00 mmol, 1.0 eq.), diethylaminobenzaldehyde (177 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (15 mL), the fluorophore **2b** (225 mg, 0.69 mmol, 69 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.74 (m, 2H), 7.60 – 7.45 (m, 2H), 7.34 (d, *J* = 15.2 Hz, 1H), 6.73 – 6.54 (m, 2H), 6.54 – 6.38 (m, 2H), 3.82 (s, 3H), 3.38 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 166.4, 165.6, 149.9, 145.6, 131.0, 121.7, 114.4, 113.8, 111.3, 107.2, 101.1, 55.5, 44.5, 12.6.

3c – According to general procedure **A** and using 2'-hydroxy-4-methoxy-acetophenone (166 mg, 1.00 mmol, 1.0 eq.), .), 4-(azetidin-1-yl)benzaldehyde **1** (161 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (15 mL), the fluorophore **2c** (118 mg, 0.73 mmol, 73 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.75 (m, 2H), 7.57 – 7.47 (m, 2H), 7.36 (d, *J* = 15.2 Hz, 1H), 6.47 (dd, *J* = 7.1, 2.5 Hz, 2H), 6.44 – 6.35 (m, 2H), 3.98 (t, *J* = 7.3 Hz, 4H), 3.85 (s, 3H), 2.48 – 2.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 166.6, 165.8, 153.4, 145.7, 131.1, 130.6, 123.4, 114.9, 114.5, 110.9, 107.5, 101.2, 55.7, 51.9, 16.7.

3d - According to general procedure **A** and using 2'-hydroxy-4-methoxy-acetophenone (231 mg, 1.39 mmol, 1.0 eq.), 4-(1-pyrrolidinyl)benzaldehyde **2** (244 mg, 1.39 mmol, 1.0 eq.) and pyrrolidine (114 µL, 1.39 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **2d** (312 mg, 0.96 mmol, 70 %) was obtained as a red powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 15.2 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.60 – 7.50 (m, 2H), 7.35 (d, *J* = 15.1 Hz, 1H), 6.61 – 6.51 (m, 2H), 6.50 – 6.41 (m, 2H), 3.85 (s, 3H), 3.42 – 3.31 (m, 4H), 2.09 – 1.96 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 166.6, 165.7, 149.9, 145.9, 131.0, 122.1, 114.5, 114.0, 111.9, 107.4, 101.2, 55.7, 47.7, 25.6.

3e – According to general procedure **A** and using 2'-hydroxy-4-methoxy-acetophenone (166 mg, 1.00 mmol, 1.0 eq.), 4-methoxybenzaldehyde (136 mg, 1.00 mmol, 1.0 eq.) and pyrrolidine (88 µL, 1.00 mmol, 1.0 eq.) in EtOH (3 mL), fluorophore **2e** (199 mg, 0.70 mmol, 70 %) was obtained as a yellow powder. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.75 (m, 2H), 7.66 – 7.53 (m, 2H), 7.46 (d, *J* = 15.4 Hz, 1H), 7.01 – 6.83 (m, 2H), 6.48 (d, *J* = 7.8 Hz, 2H), 3.86 (d, *J* = 2.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.5, 165.9, 161.6, 144.1, 130.9, 130.2, 127.4, 117.7, 114.3, 114.0, 107.4, 100.9, 55.4, 55.3.

2. Spectroscopy

a. General

Fluorescence spectra were recorded on a Horiba Jobin-Yvon Fluorolog-3® spectrofluorimeter equipped with Hamamatsu R928 or water cooled R2658 photomuliplier tubes. Spectra were reference corrected for both the intensity variations of the excitation source light (lamp and grating) and the emission spectral response (detector and grating).

Absolute fluorescence quantum yields in crystal Φs were measured using a calibrated integrative sphere collecting all the emission (2π steradians covered with spectralon®), model G8 from GMP (Renens, Swiss) as described by de Mello *et al*. and Porrès *et al*.[1,2] For each sample, four measurements were made using the same excitation and emission monochromatic band pass (slits opening) to give four integrated intensities. Quantum yield are therefore given by equation (1):

$$\Phi_S = \frac{E_{in} - E_{empty}}{ND \times (L_{empty} - L_{in})}$$

where E_{in} and E_{empty} are the integrated fluorescence resulting of a direct excitation of the sample and the integrated fluorescence without any sample (the background of the sphere), L_{empty} is the integrated excitation profile with the empty sphere, and L_{in} is the integrated excitation profile with the sample inside the sphere. For the determination of L_{empty} and L_{in}, a neutral density filter (ND = 0.5 %) was used to reduce the intensity without changing the excitation profile.

b. <u>Crystal-state fluorescence emission spectra of **1a-e**, **2a-e**, **3a-e.**</u>

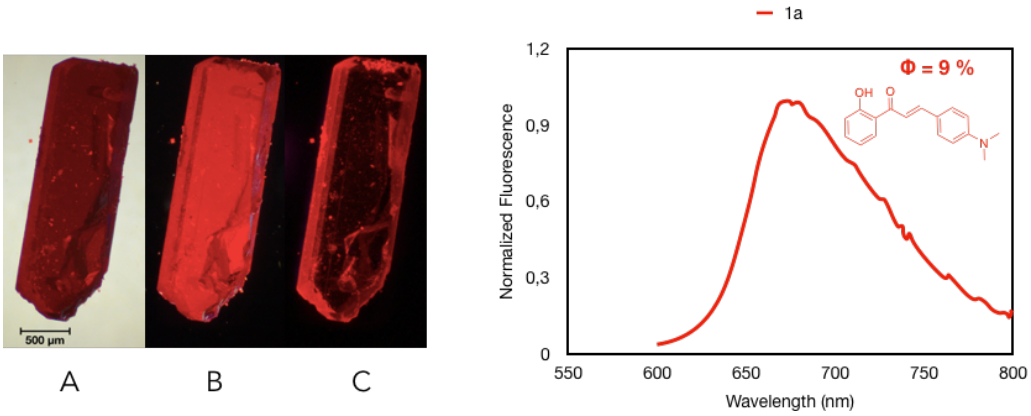


Figure SI 1 – **Left**: Crystal **1a** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **1a** measured with an integration sphere, λ_{exc} = 450 nm.

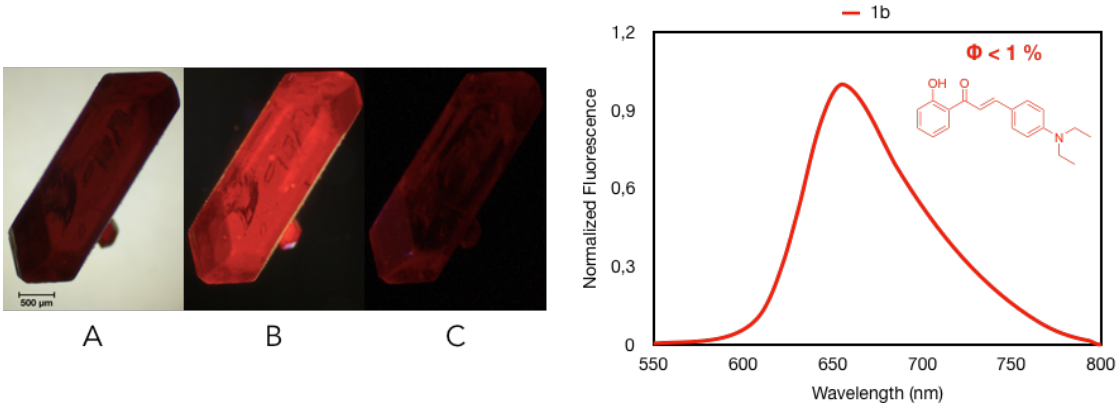


Figure SI 2 – **Left**: Crystal **1b** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **1b** measured with an integration sphere, λ_{exc} = 450 nm.

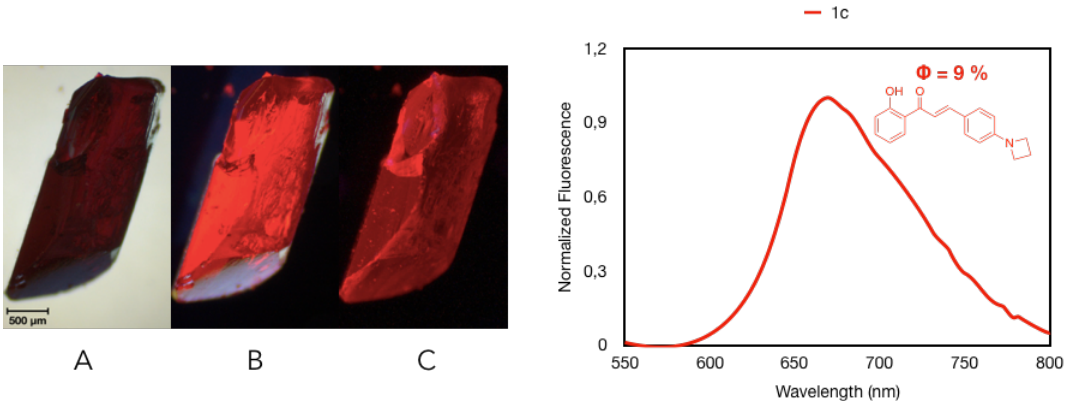


Figure SI 3 – **Left**: Crystal **1c** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **1c** measured with an integration sphere, λ_{exc} = 450 nm.

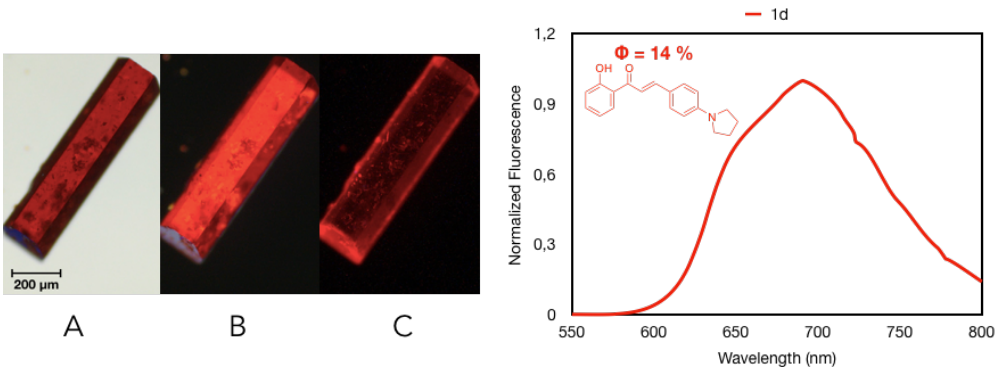


Figure SI 4 – **Left**: Crystal **1d** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **1d** measured with an integration sphere, λ_{exc} = 450 nm.

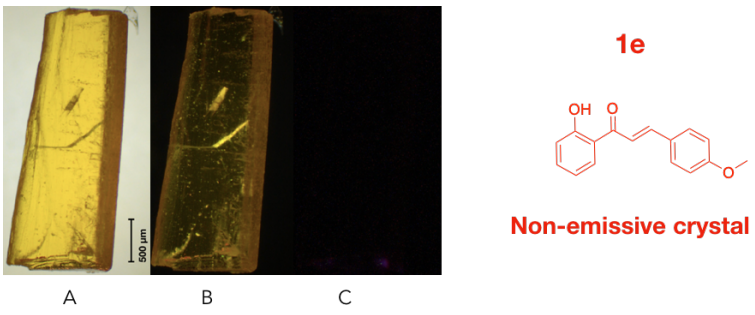


Figure SI 5 – **Left**: Crystal **1e** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Molecular structure of crystal **1e** (not emissive enough to measure a fluorescence emission spectrum).

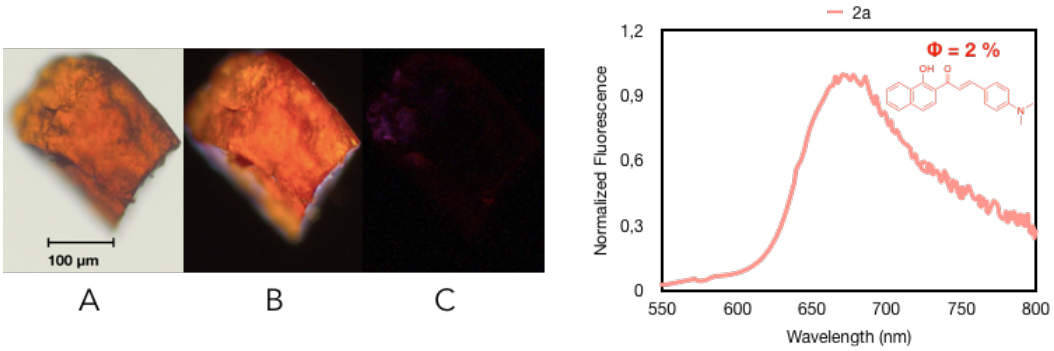


Figure SI 6 – **Left**: Crystal **2a** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **2a** measured with an integration sphere, λ_{exc} = 450 nm.

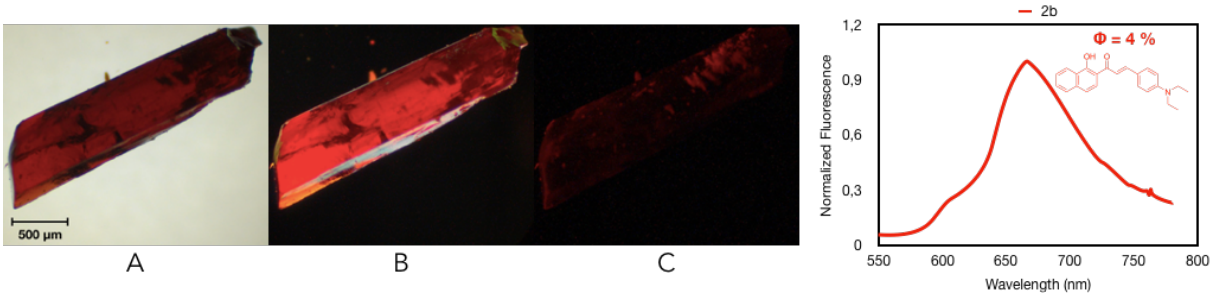


Figure SI 7 – **Left**: Crystal **2b** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **2b** measured with an integration sphere, λ_{exc} = 450 nm.

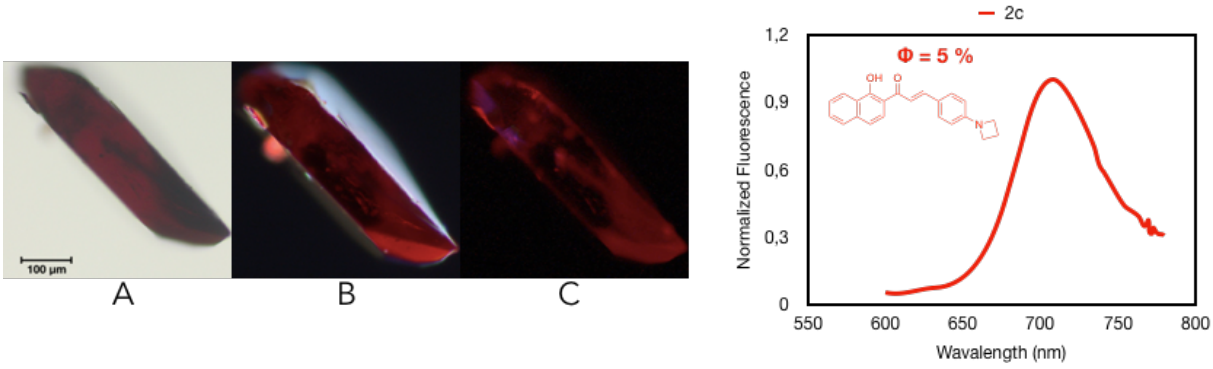


Figure SI 8 – **Left**: Crystal **2c** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **2c** measured with an integration sphere, λ_{exc} = 450 nm.

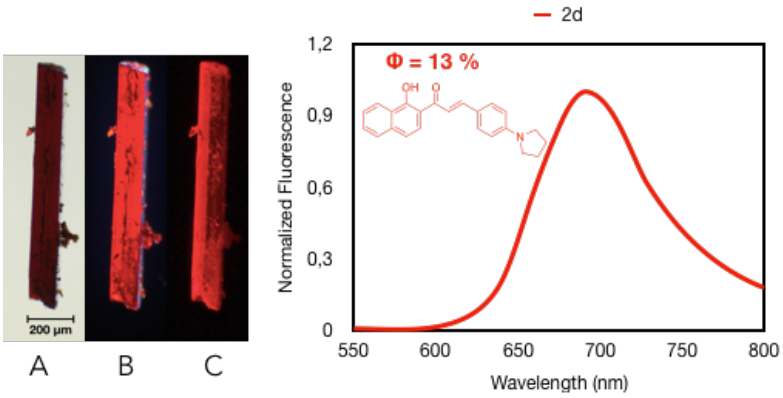


Figure SI 9 – **Left**: Crystal **2d** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **2d** measured with an integration sphere, λ_{exc} = 450 nm.

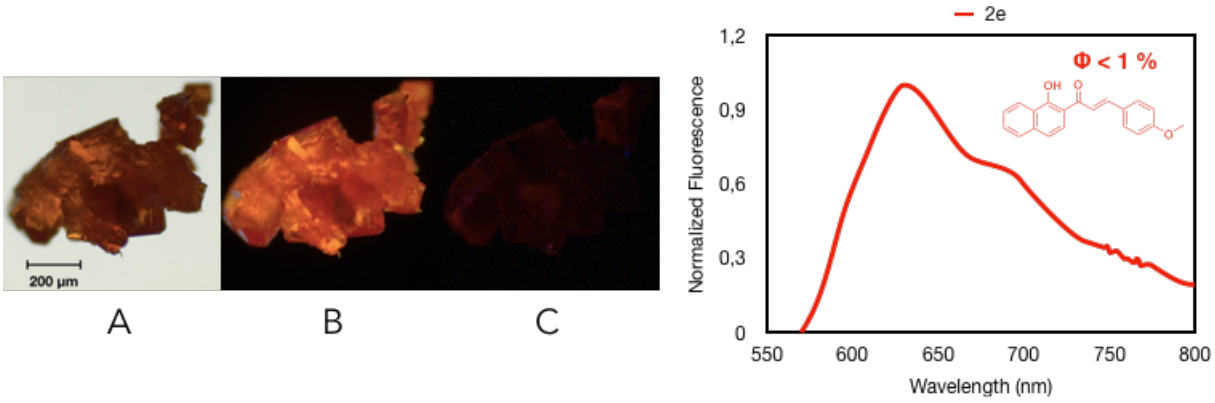


Figure SI 10 – **Left**: Crystal **2e** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **2e** measured with an integration sphere, λ_{exc} = 450 nm.

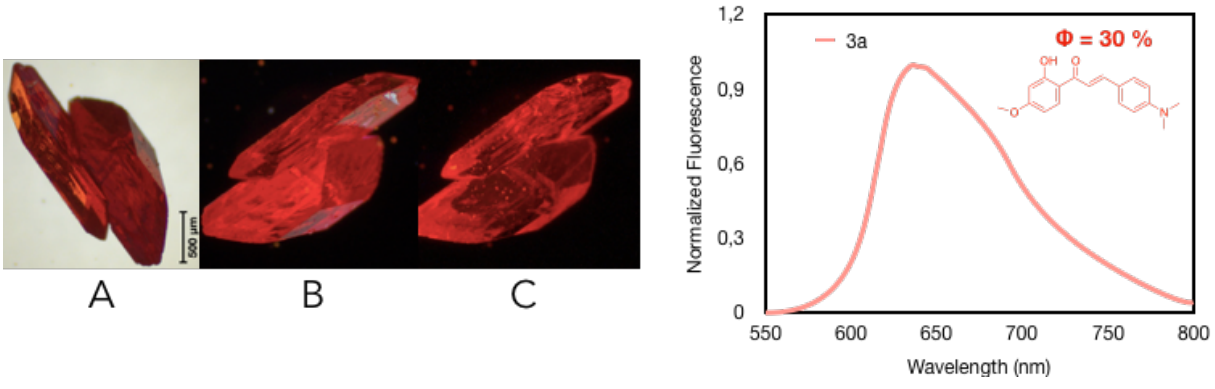


Figure SI 11 – **Left**: Crystal **3a** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **3a** measured with an integration sphere, λ_{exc} = 450 nm.

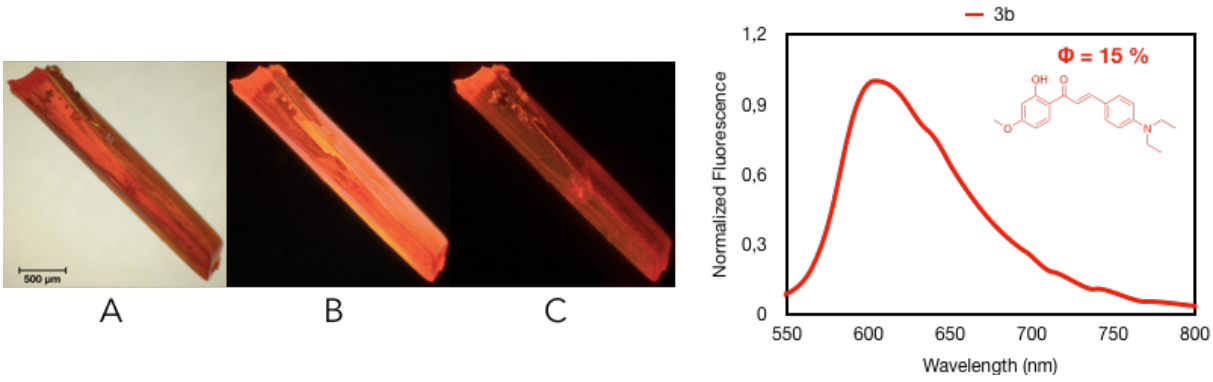


Figure SI 12 – **Left**: Crystal **3b** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **3b** measured with an integration sphere, λ_{exc} = 450 nm.

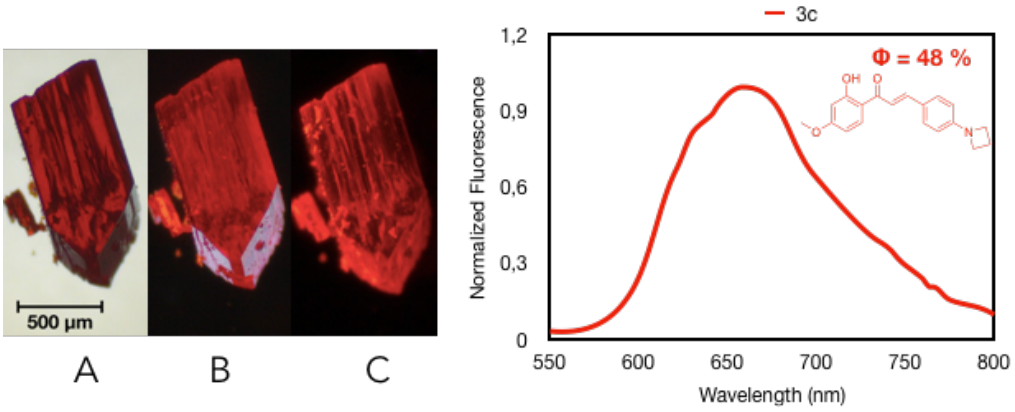


Figure SI 13 – **Left**: Crystal **3c** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **3c** measured with an integration sphere, λ_{exc} = 450 nm.

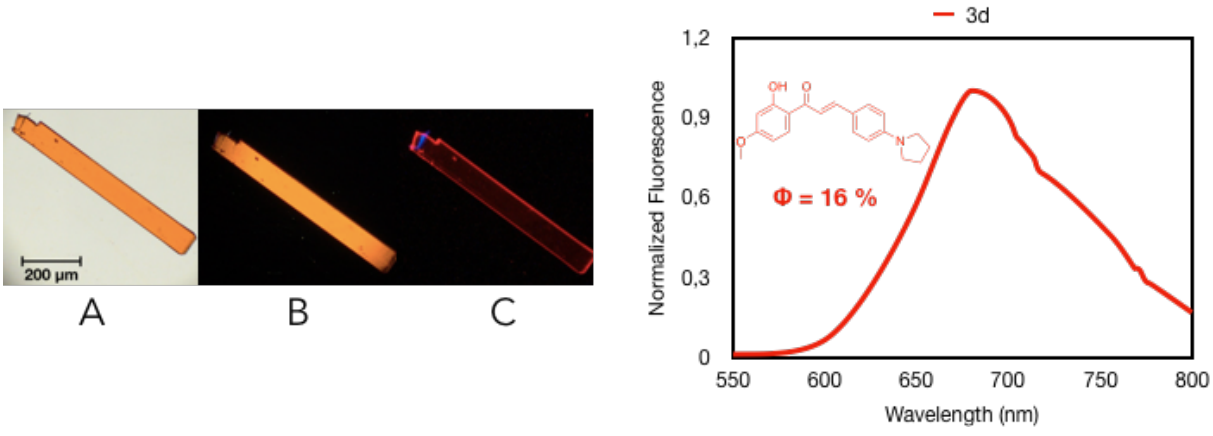
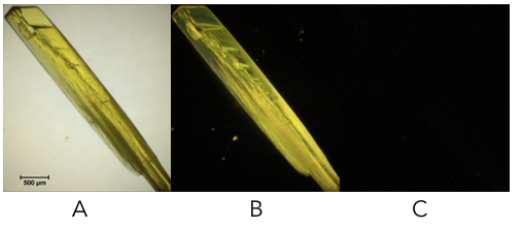


Figure SI 14 – **Left**: Crystal **3d** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Fluorescence emission spectrum of crystal **3d** measured with an integration sphere, λ_{exc} = 450 nm.



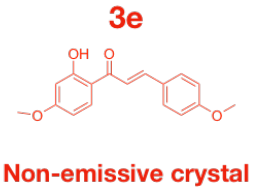


Figure SI 15 – **Left**: Crystal **3e** under sunlight (**A**), polarized light (**B**), UV irradiation (**C**). **Right**: Molecular structure of crystal **3e** (not emissive enough to measure a fluorescence emission spectrum).

3. Single-crystal X-ray crystallography

a. General

Suitable crystals were of molecular complexes **1a-3e** were obtained by slow liquid/liquid diffusion of MeOH in concentrated solution in $CHCl_3$. Crystals structure were determined on an Xcalibur Gemini kappa-geometry diffractometer equipped with an Atlas CCD and a Copper X-ray source (λ = 1.54184Å). Intensities were collected by means of the CrysalisPro software[3]. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software [1]. An analytical absorption correction was applied using the modeled faces of the crystals.[4] The resulting sets of *hkl* was used for structure solution and refinement. The structures were solved with the ShelXT [5] structure solution program using the intrinsic phasing solution method and by using Olex2 [6]as the graphical interface. The model was refined with version 2018/3 of ShelXL [7] using least-squares minimization.

CCDC 2089012-2089026 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Date Centre via www.ccdc.cam.ac.uk/data_request/cif.

b. Intramolecular parameters

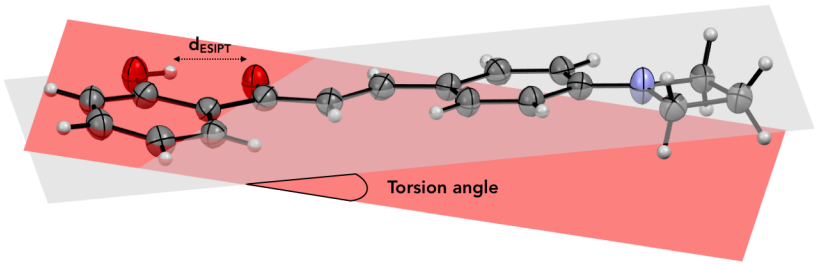


Figure SI 16 – Definition of parameters from XRD datas.

c. Data for compounds **1a-e**, **2a-e**, **3a-e.**

Table SI 1. Crystallographic Data Collection and Refinement Statistics

Compound	**1a**	**1b**	**1c**	**1d**	**1e**
Formula	$C_{17}H_{17}NO_2$	$C_{19}H_{21}NO_2$	$C_{18}H_{17}NO_2$	$C_{19}H_{19}NO_2$	$C_{16}H_{14}O_3$
$D_{calc.}$/ g cm^{-3}	1.309	1.281	1.306	1.296	1.350
□/mm^{-1}	0.684	0.654	0.085	0.084	0.755
Formula Weight	267.31	295.37	279.32	293.35	254.27
Colour	red	red	dark violet	dark violet	yellow
Shape	block	block	block	block	block
Size/mm^3	0.57×0.35×0.30	0.42×0.30×0.09	0.60×0.47×0.23	0.45×0.30×0.29	0.49×0.36×0.26
T/K	150.01(10)	150.01(10)	150.01(10)	150.00(10)	150.00(10)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Flack Parameter	*N.A.*	*N.A.*	*N.A.*	*N.A.*	0.03(17)
Hooft Parameter	*N.A.*	*N.A.*	*N.A.*	*N.A.*	-0.08(7)
Space Group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$Pca2_1$
a/Å	12.0443(8)	8.7822(7)	8.8738(10)	13.1158(17)	25.3047(16)
b/Å	10.1586(5)	16.9997(13)	15.8093(19)	9.9987(11)	3.9444(2)
c/Å	12.3923(9)	10.4535(8)	10.3070(12)	12.9251(19)	12.5302(9)
□/°	90	90	90	90	90
□/°	116.530(9)	101.025(7)	100.799(11)	117.486(18)	90
□/°	90	90	90	90	90
V/Å^3	1356.58(18)	1531.9(2)	1420.3(3)	1503.7(4)	1250.66(14)
Z	4	4	4	4	4
Z'	1	1	1	1	1
Wavelength/Å	1.54184	1.54184	0.71073	0.71073	1.54184
Radiation type	Cu K□	Cu K□	Mo K□	Mo K□	Cu K□
□$_{min}$/°	4.102	5.035	2.668	2.739	4.967
□$_{max}$/°	66.982	67.078	29.666	29.480	66.879
Measured Refl's.	14375	16326	12533	10749	10990
Indep't Refl's	2410	2721	3455	3708	2198
Refl's I≥2 □(I)	2285	2356	2494	2947	2146
R_{int}	0.0383	0.0564	0.0407	0.0320	0.0499
Parameters	185	203	192	201	175
Restraints	0	0	0	0	1
Largest Peak	0.190	0.205	0.350	0.314	0.149
Deepest Hole	-0.220	-0.238	-0.261	-0.264	-0.152
GooF	1.027	1.055	1.068	1.109	1.065
wR_2 (all data)	0.1049	0.1112	0.1765	0.1711	0.1035
wR_2	0.1030	0.1035	0.1462	0.1518	0.1008
R_1 (all data)	0.0396	0.0473	0.0841	0.0700	0.0389
R_1	0.0381	0.0405	0.0595	0.0564	0.0362

Compound	**2a**	2b	**2c**	**2d**	**2e**
Formula	$C_{21}H_{19}NO_2$	$C_{23}H_{23}NO_2$	$C_{22}H_{19}NO_2$	$C_{23}H_{21}NO_2$	$C_{20}H_{16}O_3$
$D_{calc.}$/ g cm^{-3}	1.317	1.255	1.324	1.306	1.367
□/mm^{-1}	0.670	0.627	0.671	0.656	0.736
Formula Weight	317.37	345.42	329.38	343.41	304.33
Colour	red	dark red	dark violet	violet	yellow
Shape	block	plate	block	block	block
Size/mm^3	0.19×0.17×0.12	0.35×0.26×0.10	0.40×0.19×0.18	0.33×0.21×0.13	0.15×0.15×0.09
T/K	150.00(10)	150.00(10)	150.00(10)	150.01(10)	150.02(11)
Crystal System	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Flack Parameter	*N.A.*	*N.A.*	*N.A.*	*N.A.*	*N.A.*
Hooft Parameter	*N.A.*	*N.A.*	*N.A.*	*N.A.*	*N.A.*
Space Group	*P*-1	$P2_1/n$	*C*2/*c*	*C*2/*c*	*Pbca*
a/Å	8.9885(12)	8.2451(5)	14.0991(17)	14.2455(10)	15.1108(17)
b/Å	11.7602(11)	9.5049(6)	15.5571(19)	15.1719(12)	9.3204(8)
c/Å	16.0667(12)	23.4203(15)	15.216(2)	16.1994(15)	21.004(2)
□/°	77.958(7)	90	90	90	90
□/°	85.456(9)	95.132(5)	97.917(11)	94.197(8)	90
□/°	74.512(10)	90	90	90	90
V/Å^3	1600.2(3)	1828.1(2)	3305.7(7)	3491.8(5)	2958.1(5)
Z	4	4	8	8	8
Z'	2	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K□	Cu K□	Cu K□	Cu K□	Cu K□
□$_{min}$/°	3.977	3.790	4.254	4.263	4.210
□$_{max}$/°	67.282	66.886	66.942	67.041	67.011
Measured Refl's.	16841	19766	9835	18525	16672
Indep't Refl's	5629	3230	2921	3092	2616
Refl's I≥2 □(I)	4434	2668	2543	2643	2264
R_{int}	0.0379	0.0557	0.0481	0.0463	0.0560
Parameters	439	238	228	236	210
Restraints	0	0	0	0	0
Largest Peak	0.230	0.174	0.253	0.157	0.209
Deepest Hole	-0.307	-0.187	-0.224	-0.242	-0.190
GooF	1.032	1.037	1.066	1.028	1.053
wR_2 (all data)	0.1587	0.1320	0.1532	0.1330	0.1328
wR_2	0.1426	0.1206	0.1460	0.1248	0.1231
R_1 (all data)	0.0651	0.0543	0.0575	0.0534	0.0518
R_1	0.0525	0.0448	0.0519	0.0467	0.0457

Compound	**3a**	**3b**	**3c**	**3d**	**3e**
Formula	$C_{18}H_{19}NO_3$	$C_{20}H_{23}NO_3$	$C_{19}H_{19}NO_3$	$C_{20}H_{21}NO_3$	$C_{17}H_{16}O_4$
$D_{calc.}$/ g cm^{-3}	1.287	1.282	1.285	1.292	1.344
□/mm^{-1}	0.088	0.688	0.702	0.087	0.784
Formula Weight	297.34	325.39	309.35	323.38	284.30
Colour	dark violet	yellow	red	red	yellow
Shape	block	block	block	plate	plate
Size/mm^3	0.79×0.45×0.36	0.69×0.36×0.28	0.29×0.24×0.18	0.40×0.33×0.10	0.57×0.25×0.15
T/K	150.00(10)	150.00(10)	150.00(10)	150.00(10)	150.01(10)
Crystal System	triclinic	monoclinic	monoclinic	monoclinic	triclinic
Flack Parameter	*N.A.*	-0.02(17)	*N.A.*	*N.A.*	*N.A.*
Hooft Parameter	*N.A.*	0.09(6)	*N.A.*	*N.A.*	*N.A.*
Space Group	*P*-1	$P2_1$	$P2_1/n$	$P2_1/c$	*P*-1
a/Å	10.2227(7)	5.1591(2)	11.0731(10)	13.6857(16)	9.1891(6)
b/Å	12.1794(8)	22.5328(10)	12.6166(9)	10.0690(9)	9.2697(6)
c/Å	13.3210(8)	14.6030(7)	12.3419(10)	13.1089(13)	17.1760(7)
□/°	91.336(5)	90	90	90	101.119(4)
□/°	91.101(5)	96.692(4)	112.002(10)	113.007(13)	91.071(4)
□/°	112.224(6)	90	90	90	101.323(5)
V/Å^3	1534.22(18)	1686.03(13)	1598.6(3)	1662.7(3)	1405.22(14)
Z	4	4	4	4	4
Z'	2	2	1	1	2
Wavelength/Å	0.71073	1.54184	1.54184	0.71073	1.54184
Radiation type	Mo K□	Cu K□	Cu K□	Mo K□	Cu K□
□$_{min}$/°	3.061	3.624	4.584	3.122	4.917
□$_{max}$/°	29.661	67.059	66.974	29.644	67.104
Measured Refl's.	40547	17423	17200	22942	37745
Indep't Refl's	7773	5359	2829	4211	4938
Refl's I≥2 □(I)	5878	5237	2466	3171	4177
R_{int}	0.0464	0.0411	0.0552	0.0440	0.0527
Parameters	406	442	210	220	386
Restraints	0	1	0	0	0
Largest Peak	0.294	0.244	0.165	0.318	0.183
Deepest Hole	-0.313	-0.253	-0.205	-0.271	-0.255
GooF	1.091	1.092	1.053	1.106	1.035
wR_2 (all data)	0.2039	0.1233	0.1167	0.1748	0.1175
wR_2	0.1844	0.1214	0.1109	0.1507	0.1091
R_1 (all data)	0.0839	0.0446	0.0475	0.0779	0.0477
R_1	0.0643	0.0424	0.0413	0.0583	0.0401

d. Additional data for compounds **1a-e**, **2a-e**, **3a-e.**

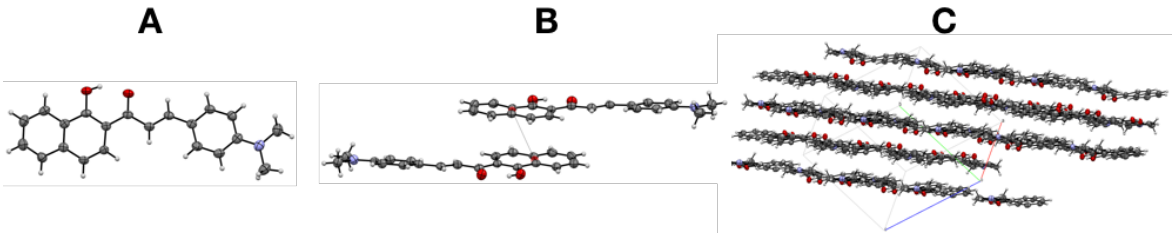


Figure SI 17 – ORTEP structure (**A**), type of dimer (**B**) and 3D arrangements (**C**) of crystal **2a**.

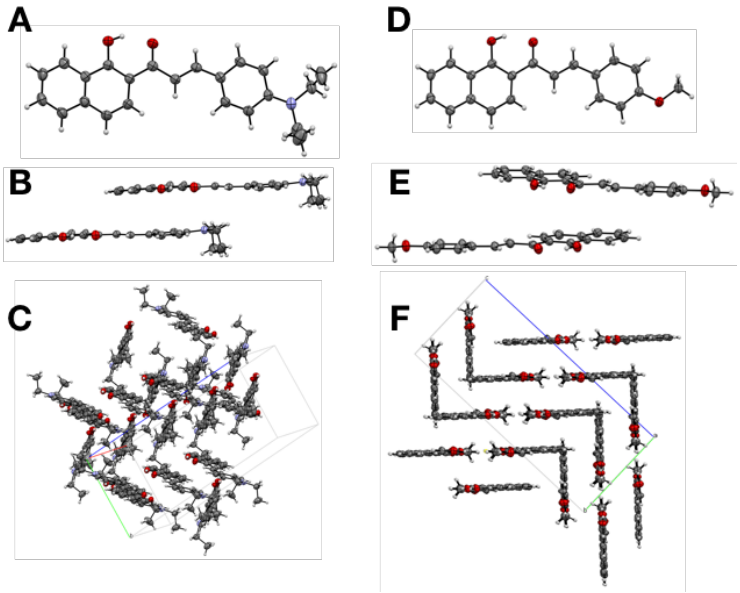


Figure SI 18 – ORTEP structure (**A, D**), type of dimer (**B, E**) and 3D arrangements (**D, F**) of crystal **2b** and **2e** respectively.

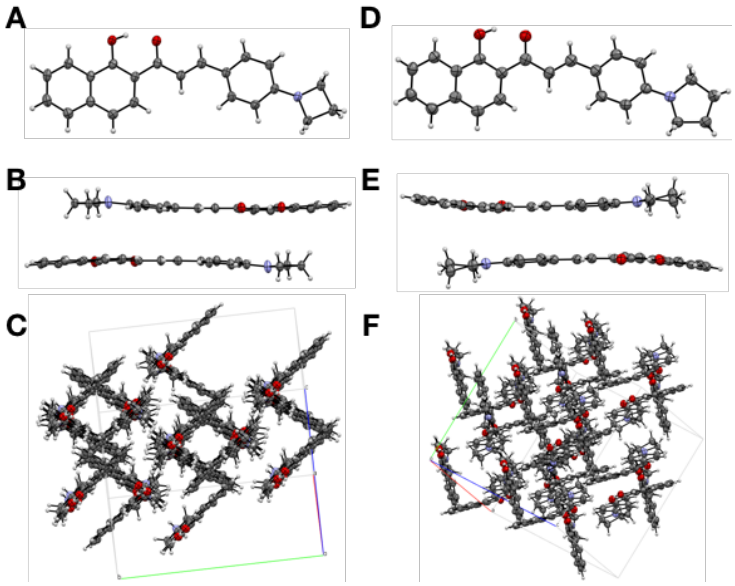


Figure SI 19 – ORTEP structure (**A, D**), type of dimer (**B, E**) and 3D arrangements (**D, F**) of crystal **2c** and **2d** respectively.

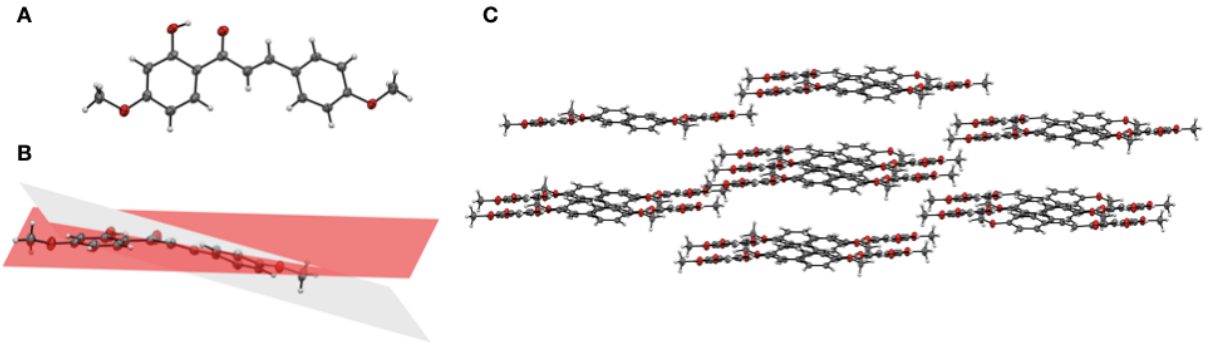


Figure SI 20 – ORTEP structure (**A**), intramolecular torsion (**B**) and 3D arrangements (**C**)of crystal **3e**.

4. NMR Spectra

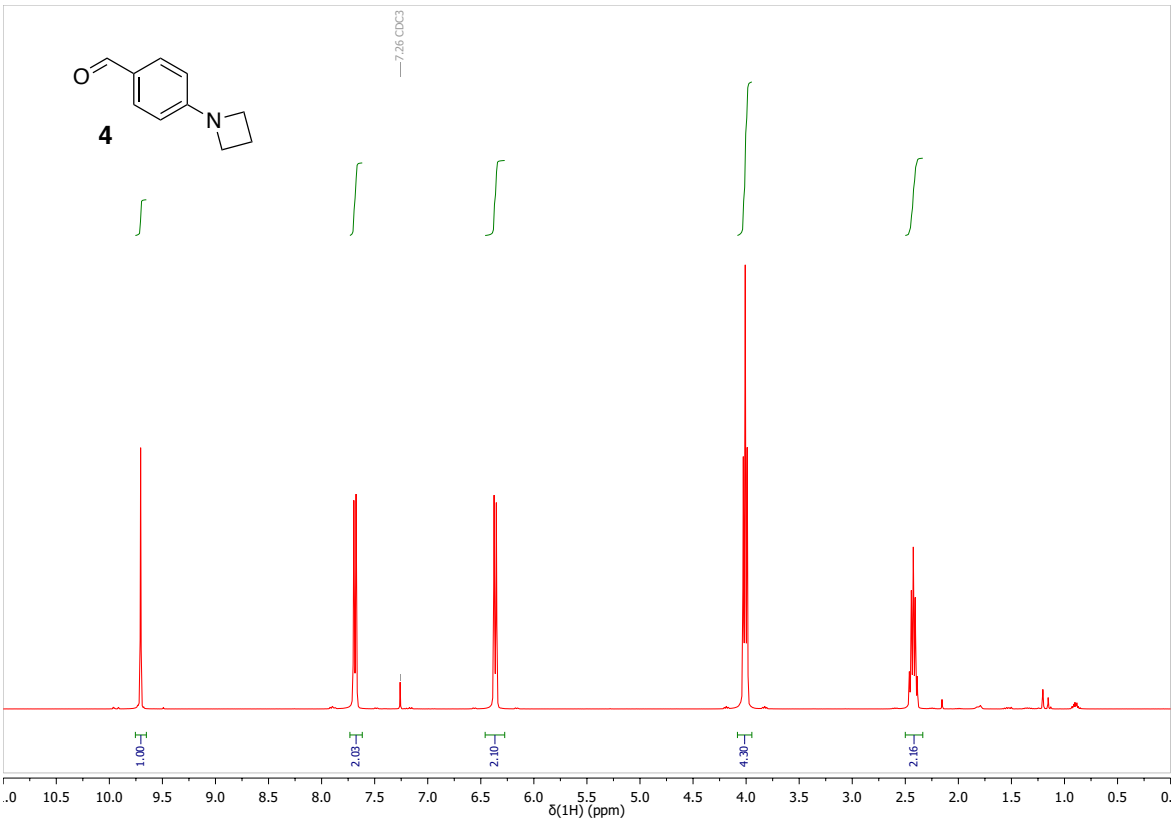


Fig. SI 21. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

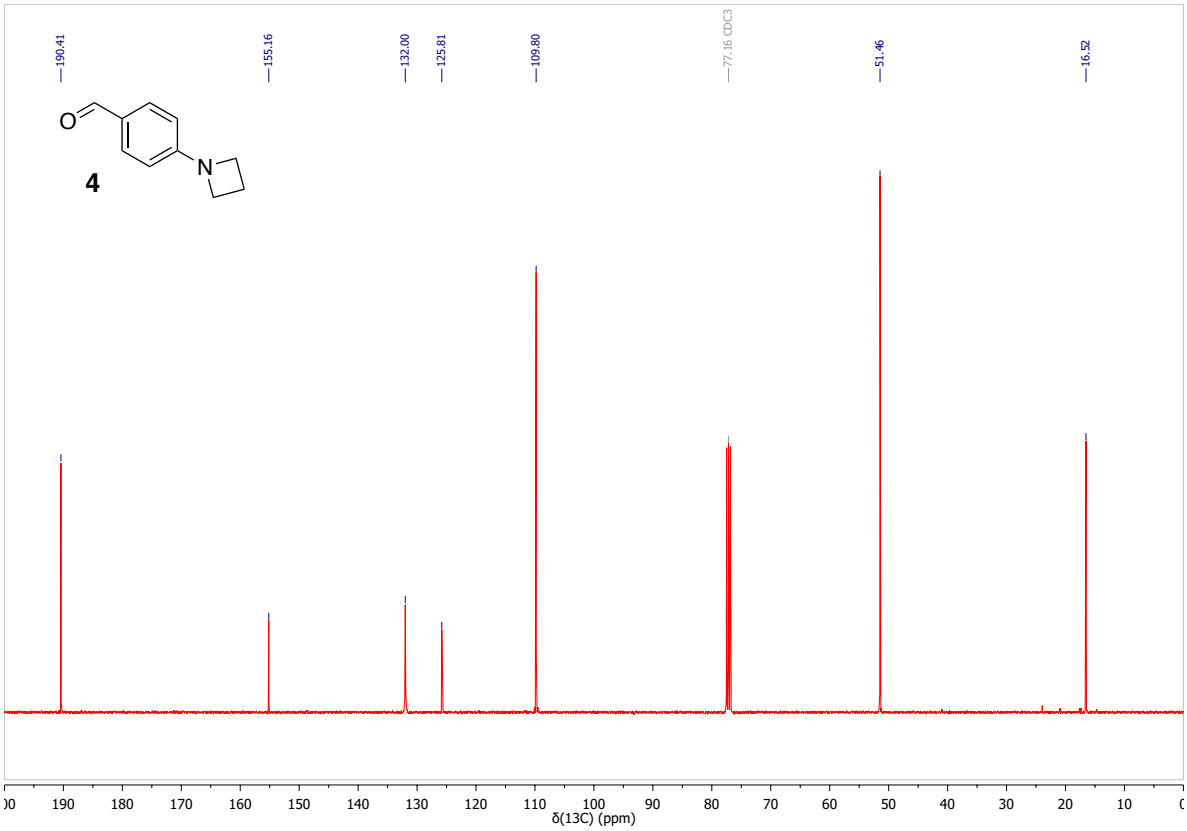


Fig. SI 22. ^{13}C NMR spectrum of **4** (101 MHz, $CDCl_3$).

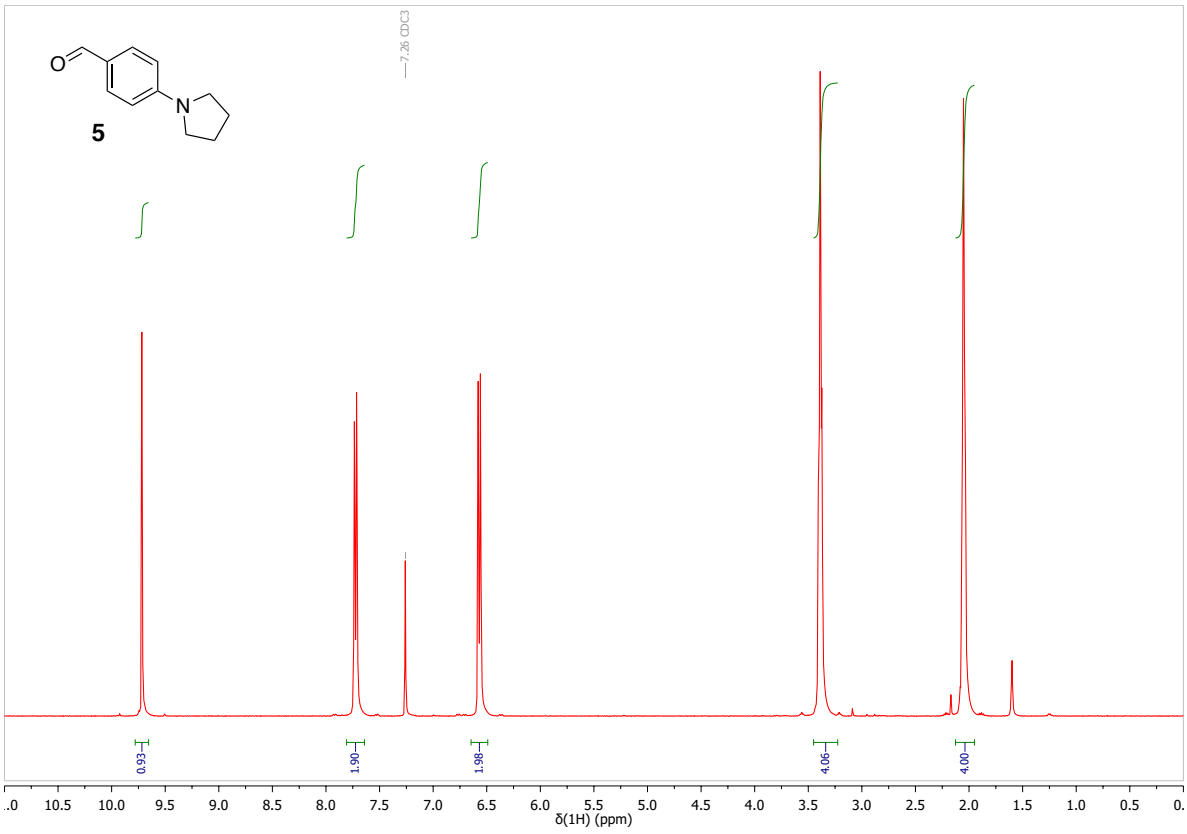


Fig. SI 23. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

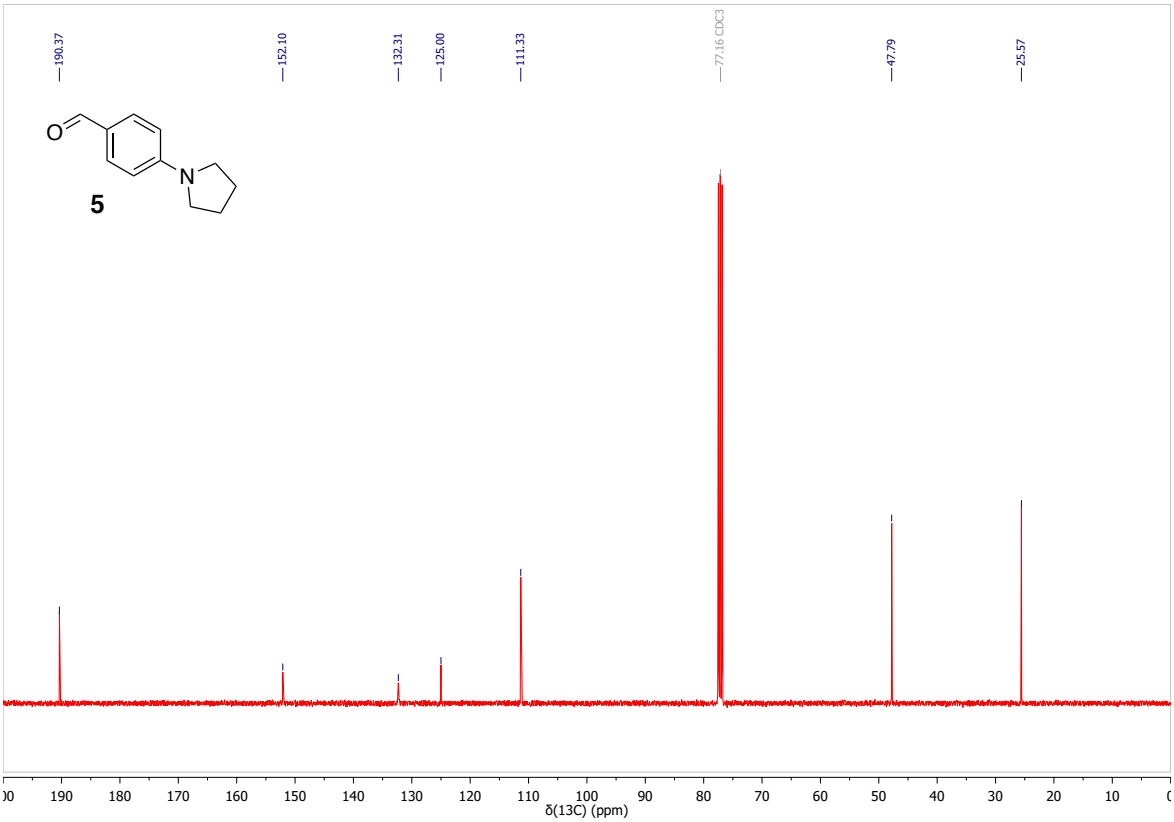


Fig. SI 24. ^{13}C NMR spectrum of **5** (101 MHz, $CDCl_3$).

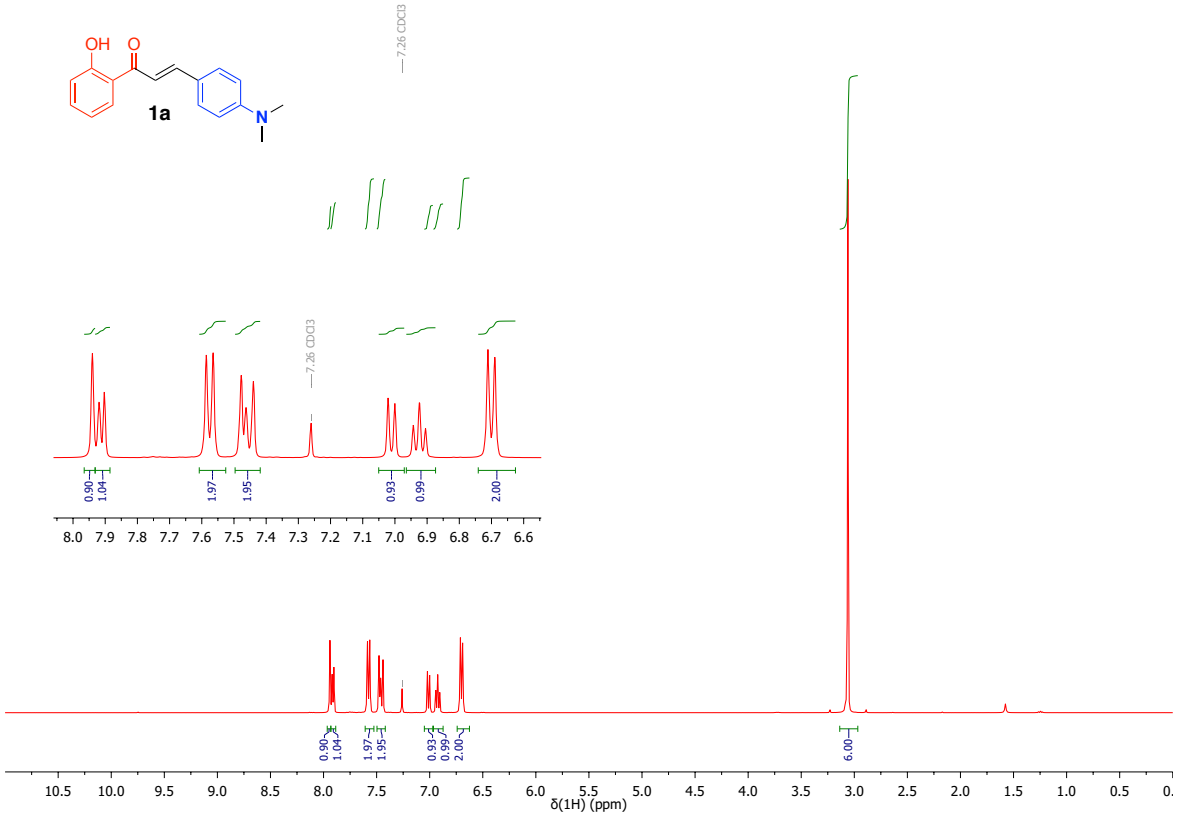


Fig. SI 25. ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$).

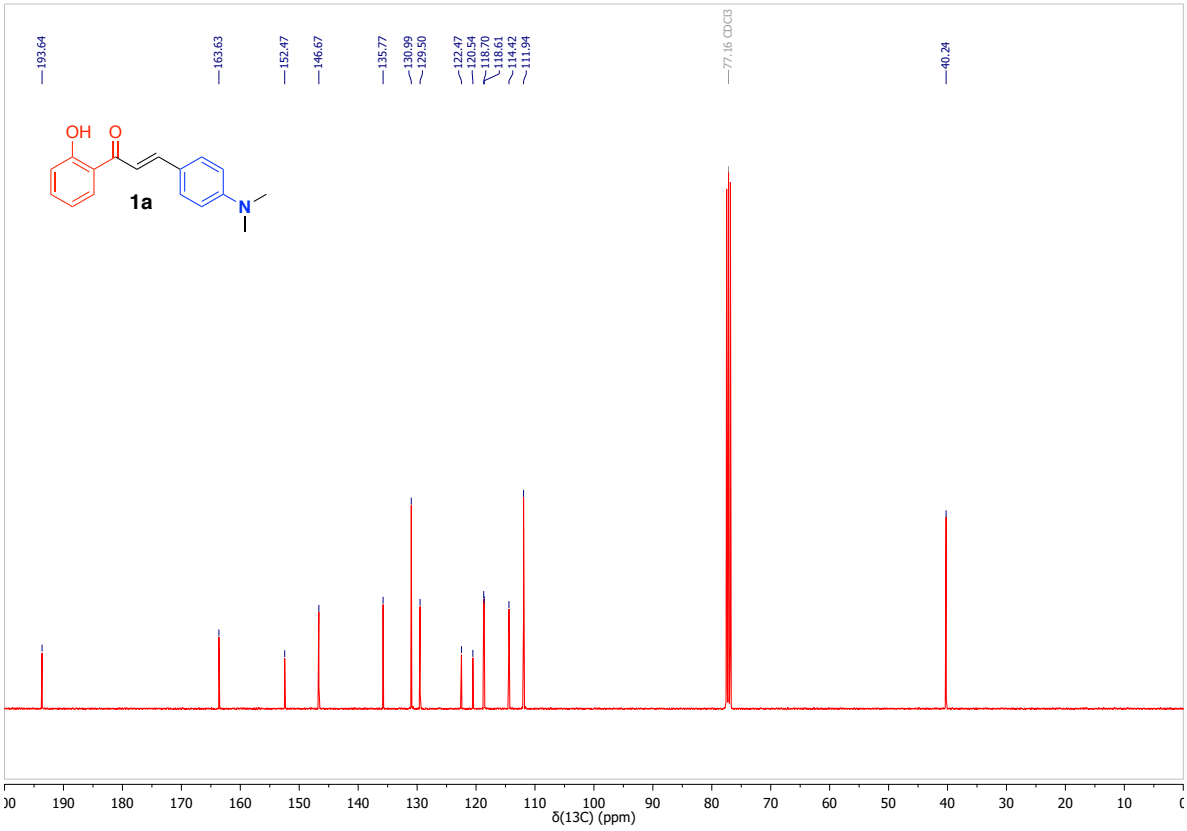


Fig. SI 26. ^{13}C NMR spectrum of **1a** (101 MHz, $CDCl_3$).

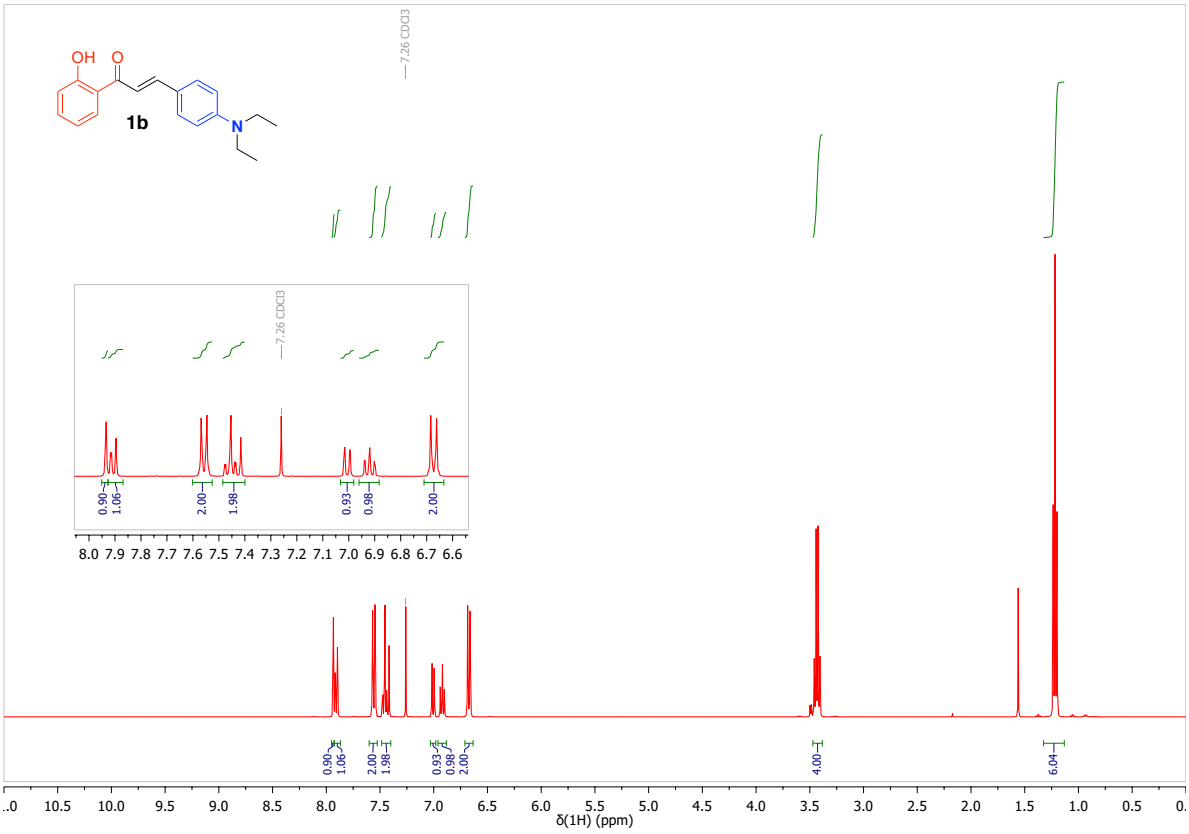


Fig. SI 27. ^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$).

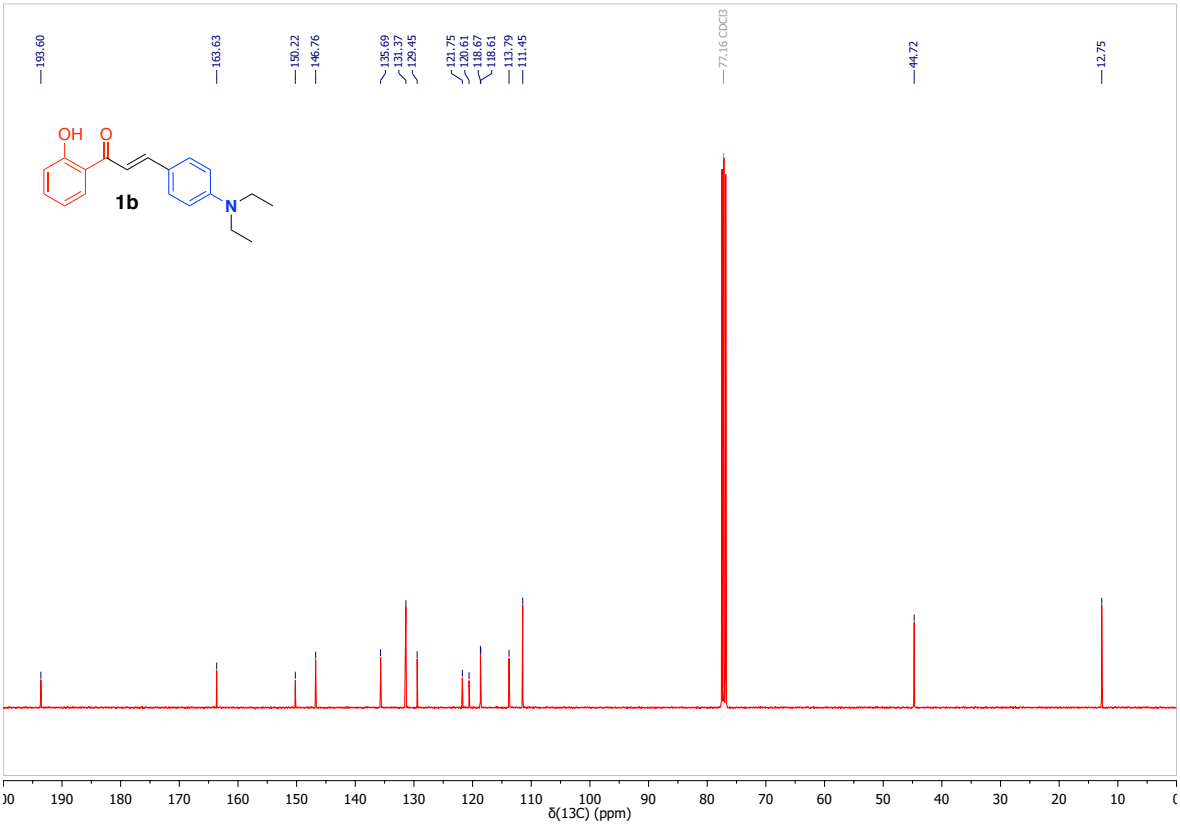


Fig. SI 28. ^{13}C NMR spectrum of **1b** (101 MHz, $CDCl_3$).

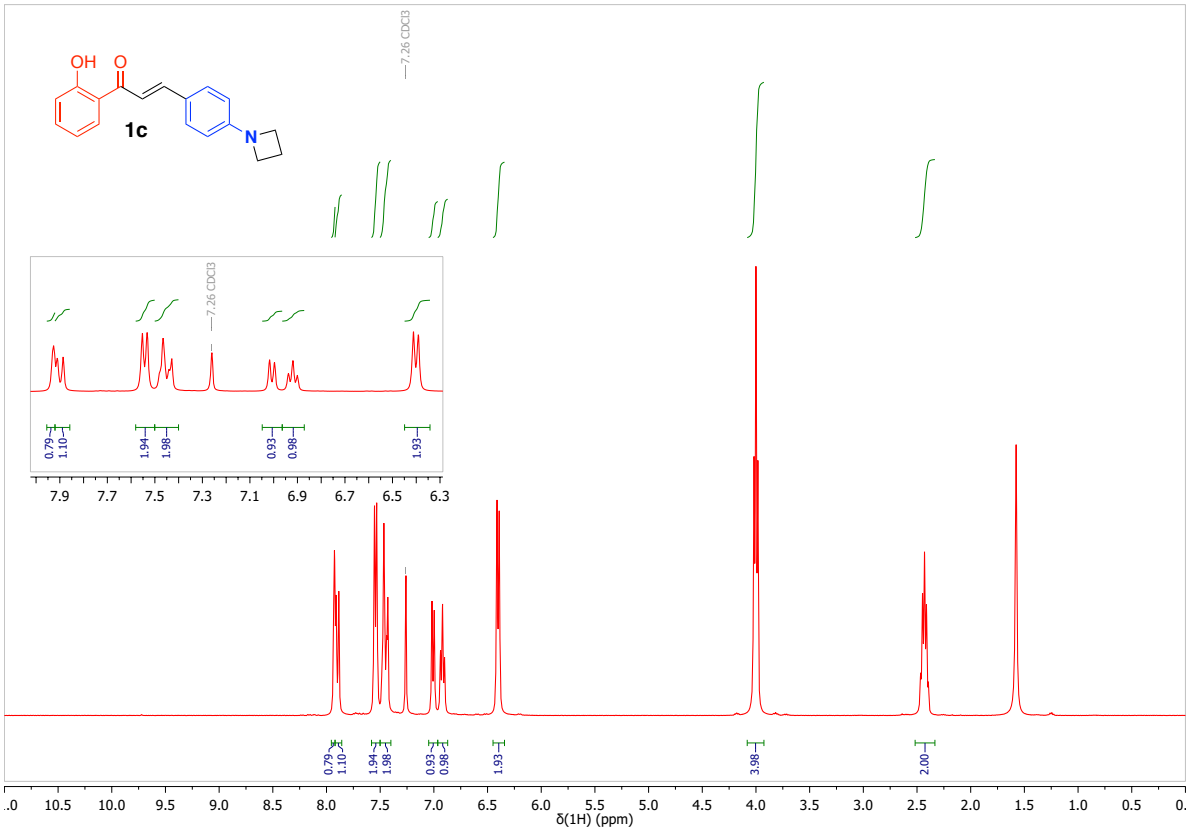


Fig. SI 29. ^{1}H NMR spectrum of **1c** (400 MHz, CDCl3).

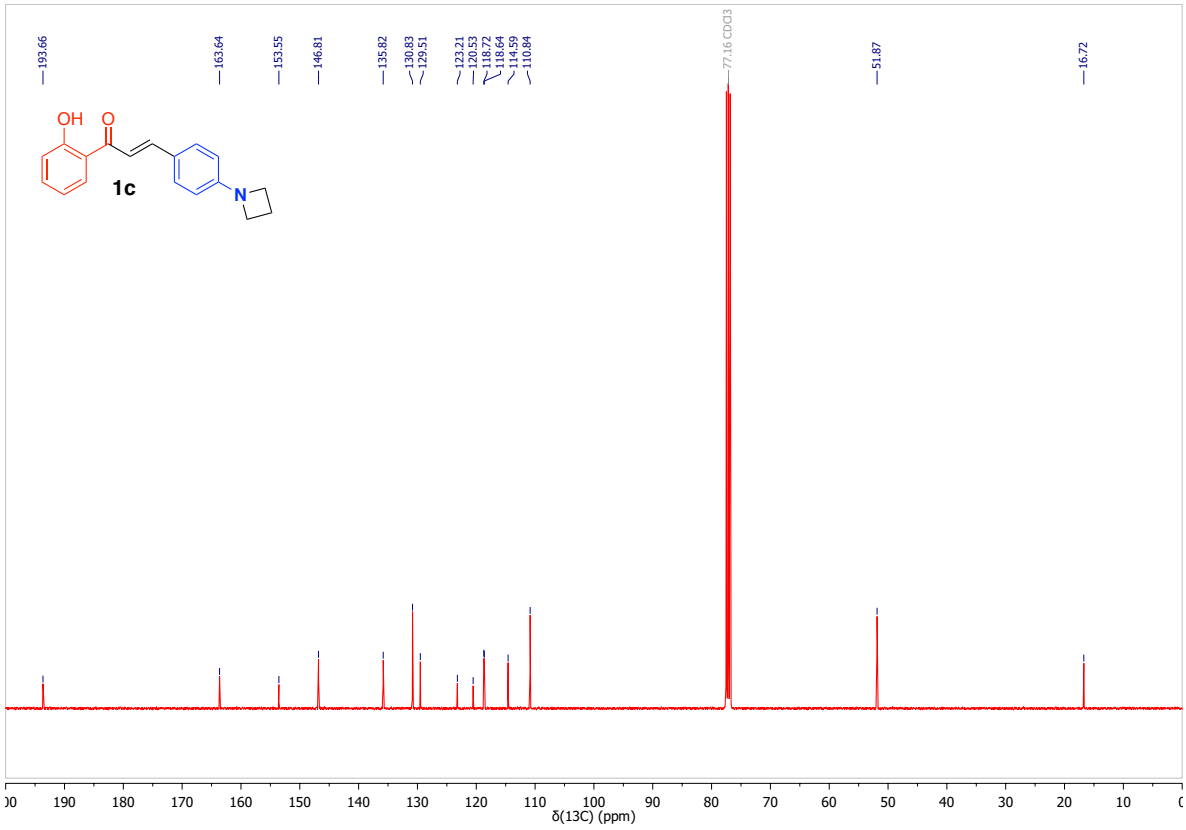


Fig. SI 30. ^{13}C NMR spectrum of **1c** (101 MHz, CDCl3).

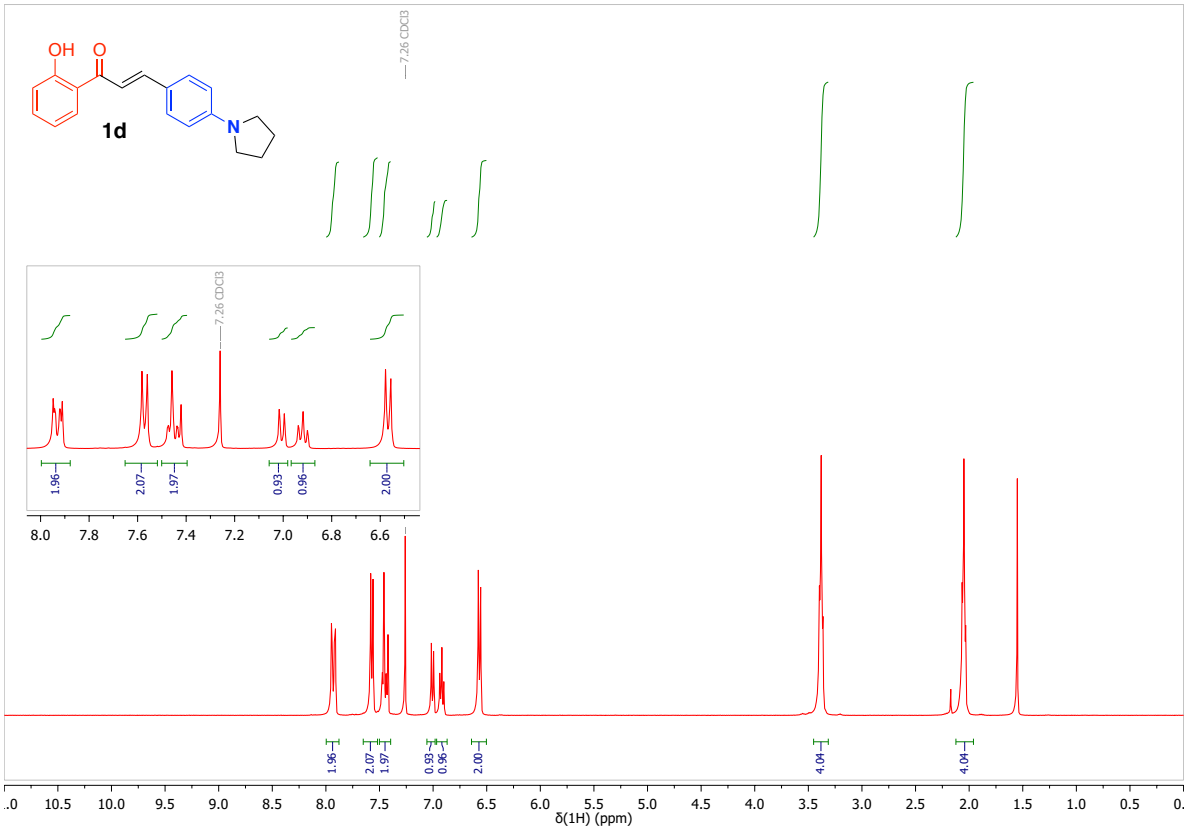


Fig. SI 31. ^{1}H NMR spectrum of **1d** (400 MHz, $CDCl_3$).

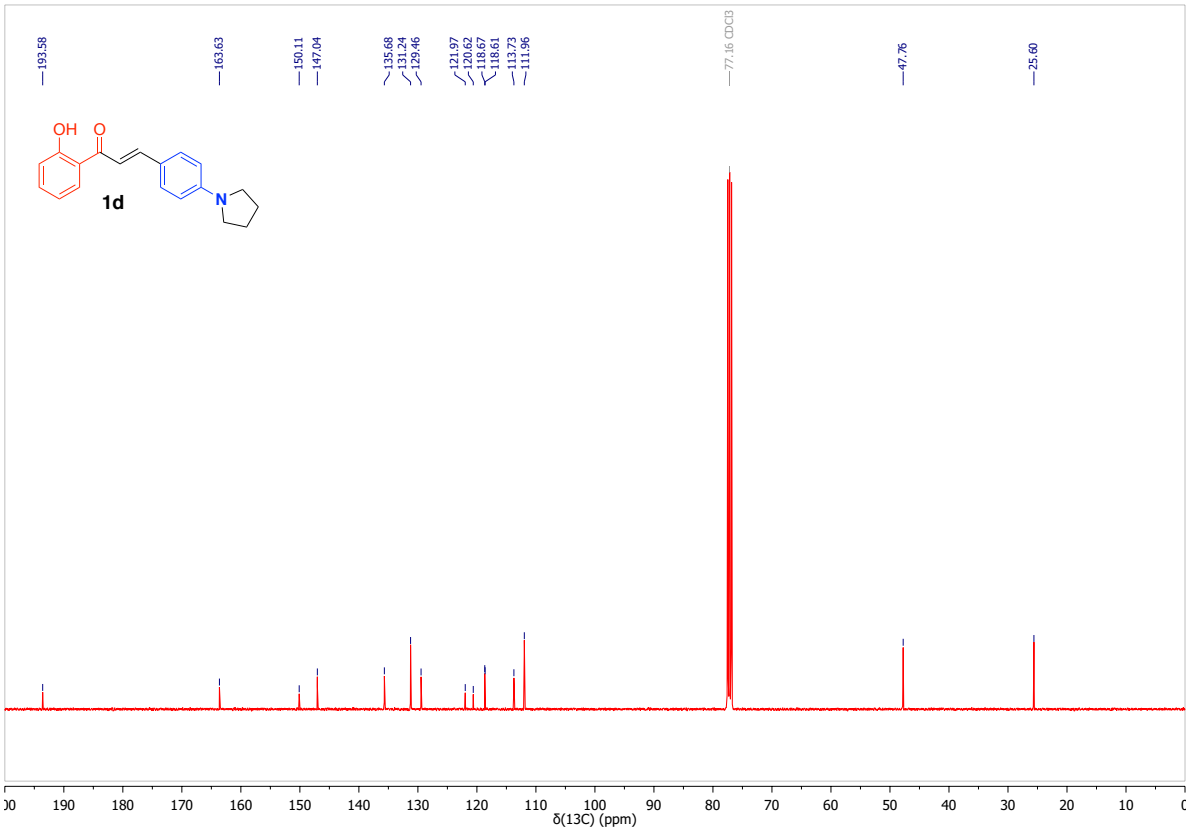


Fig. SI 32. ^{13}C NMR spectrum of **1d** (101 MHz, $CDCl_3$).

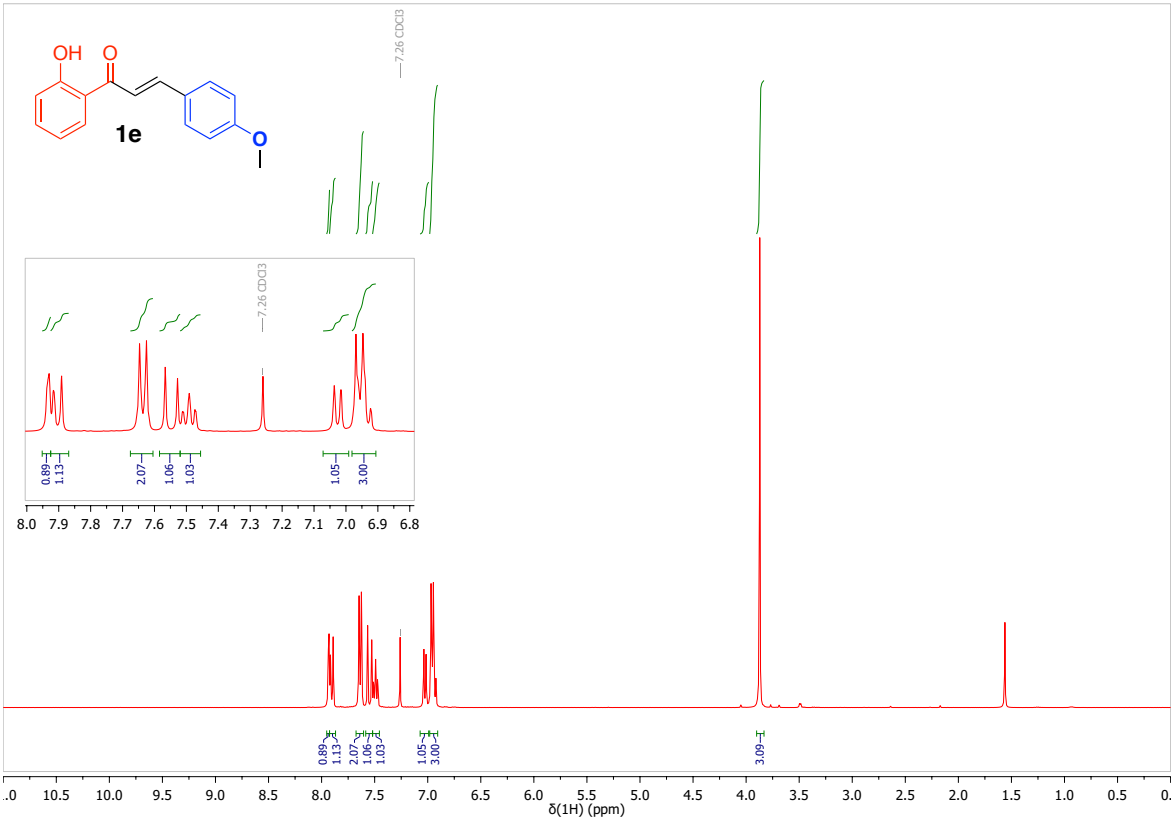


Fig. SI 33. ^{1}H NMR spectrum of **1e** (400 MHz, $CDCl_3$).

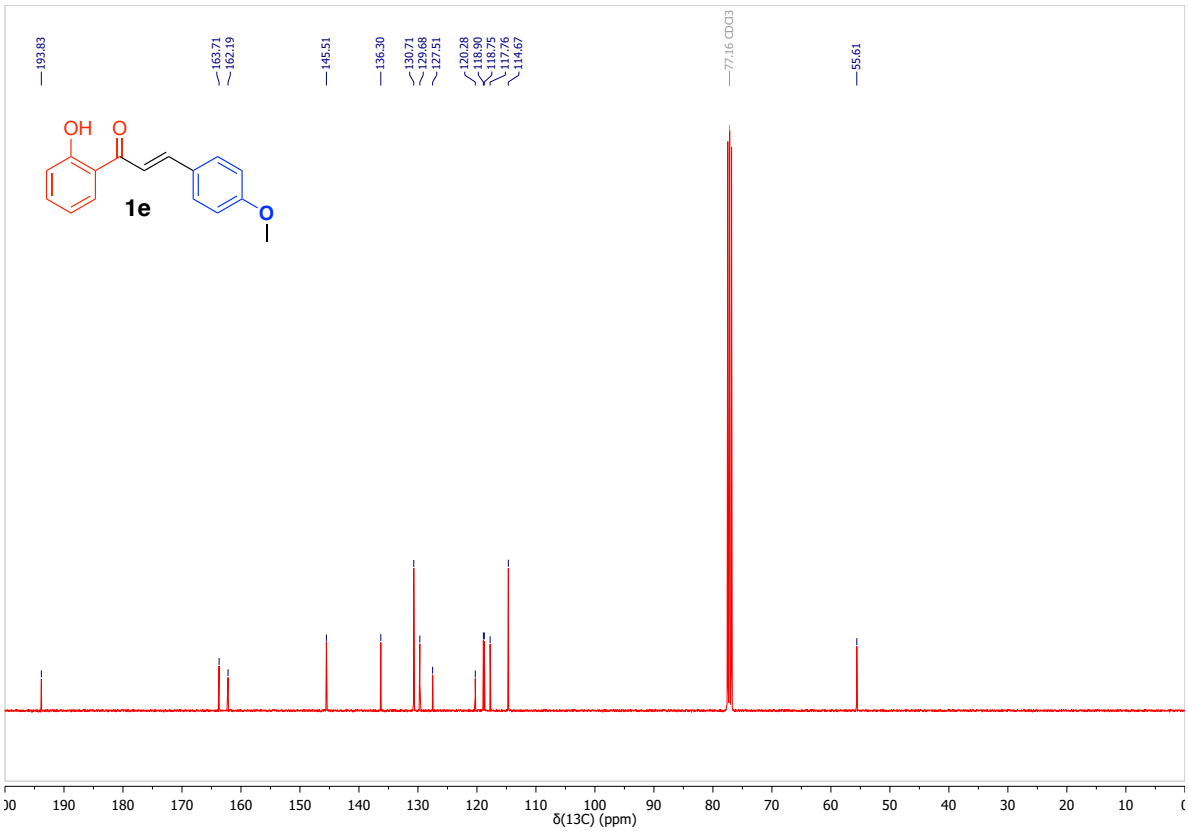


Fig. SI 34. ^{13}C NMR spectrum of **1e** (101 MHz, CDCl3).

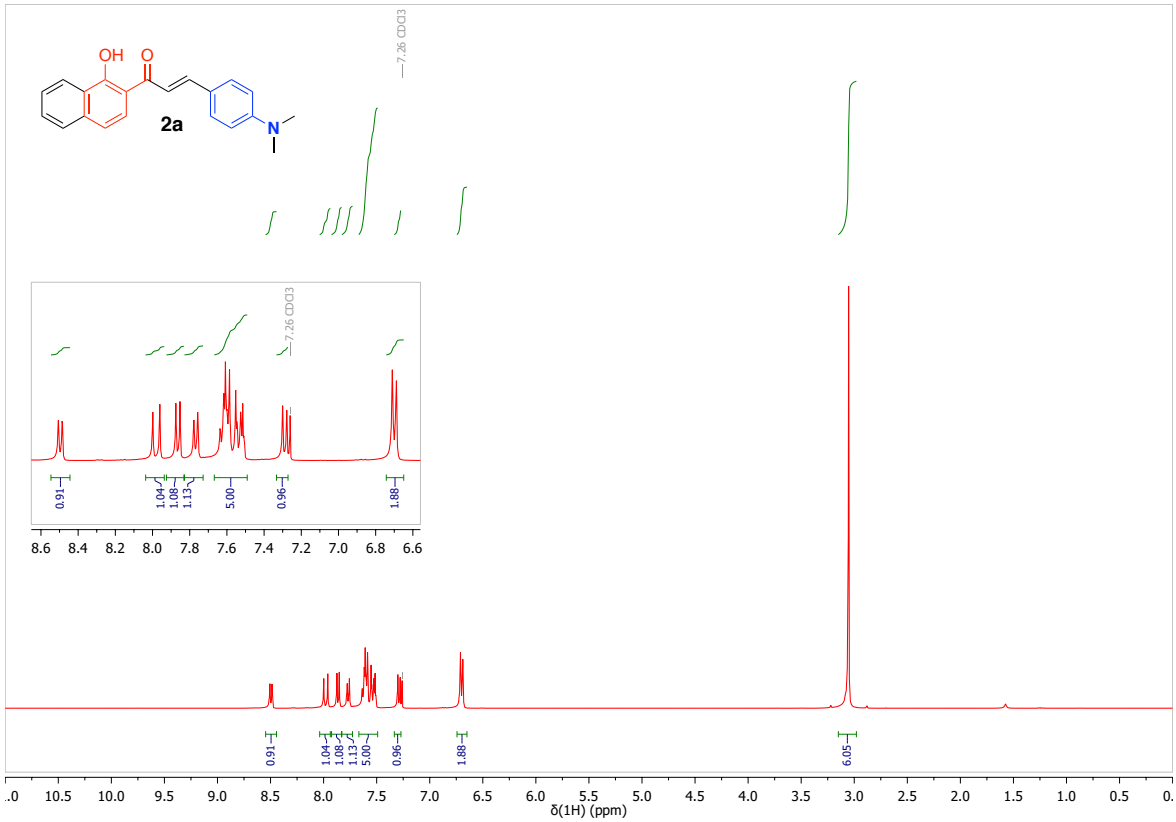


Fig. SI 35. ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$).

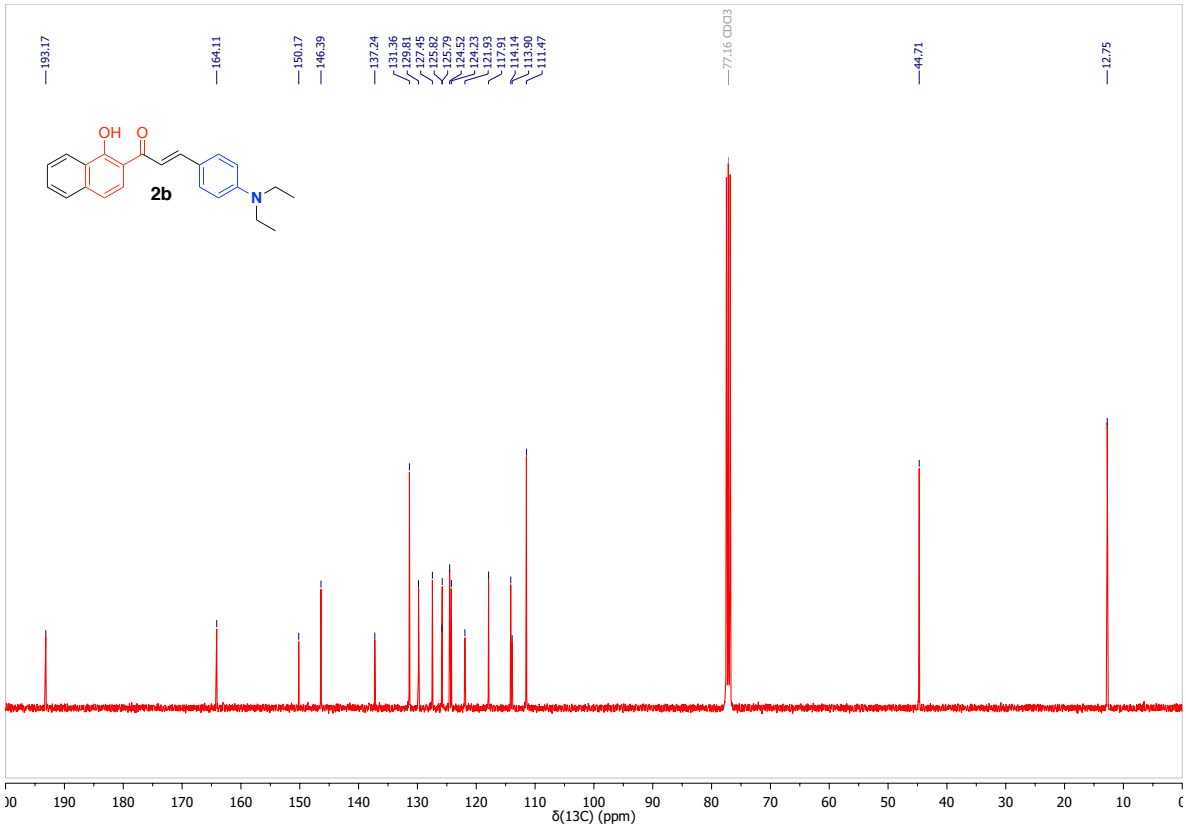


Fig. SI 36. ^{13}C NMR spectrum of **2a** (101 MHz, CDCl3).

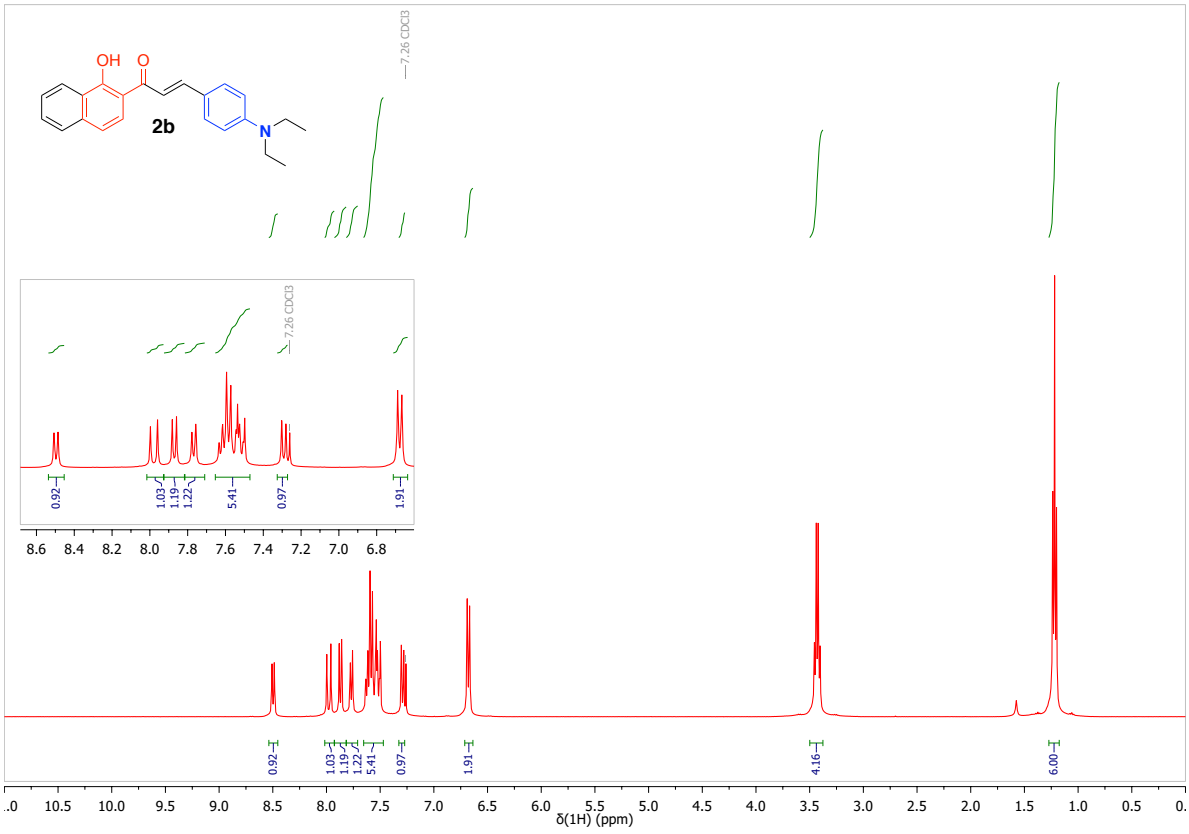


Fig. SI 37. ^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$).

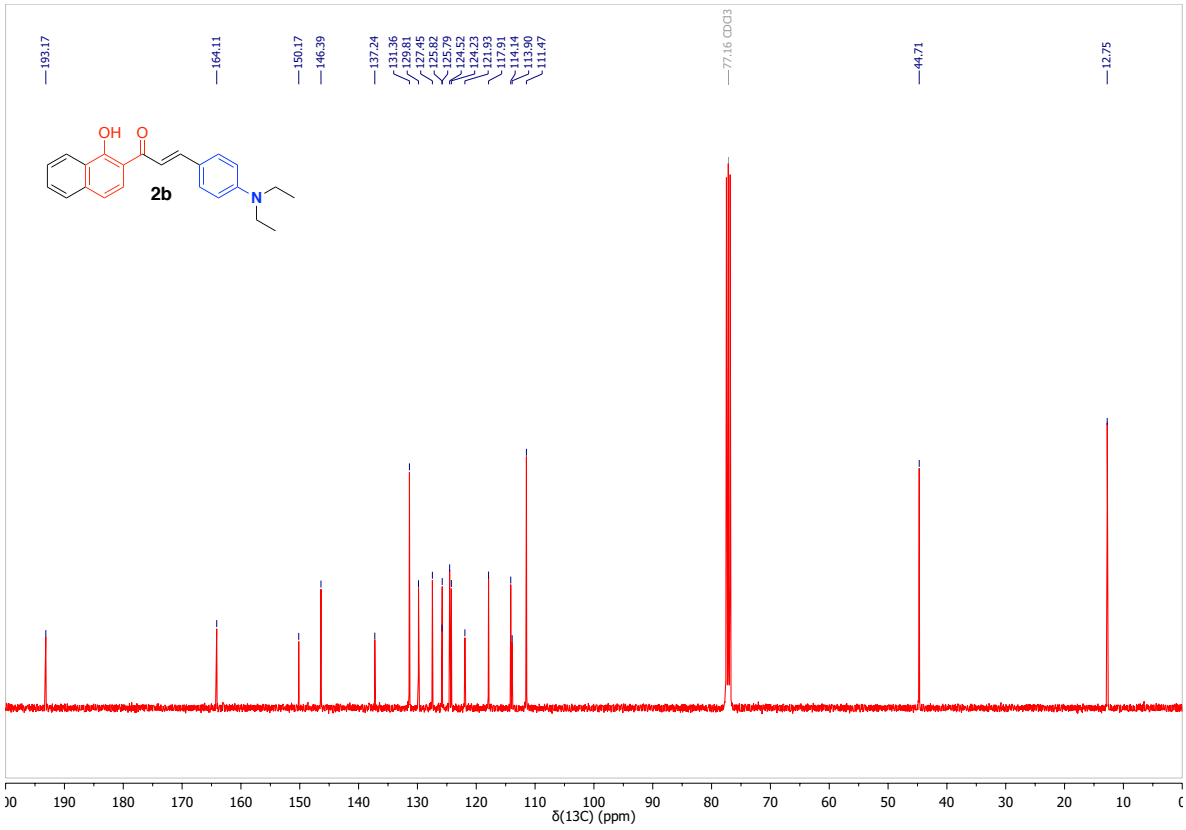


Fig. SI 38. ^{13}C NMR spectrum of **2b** (101 MHz, CDCl3).

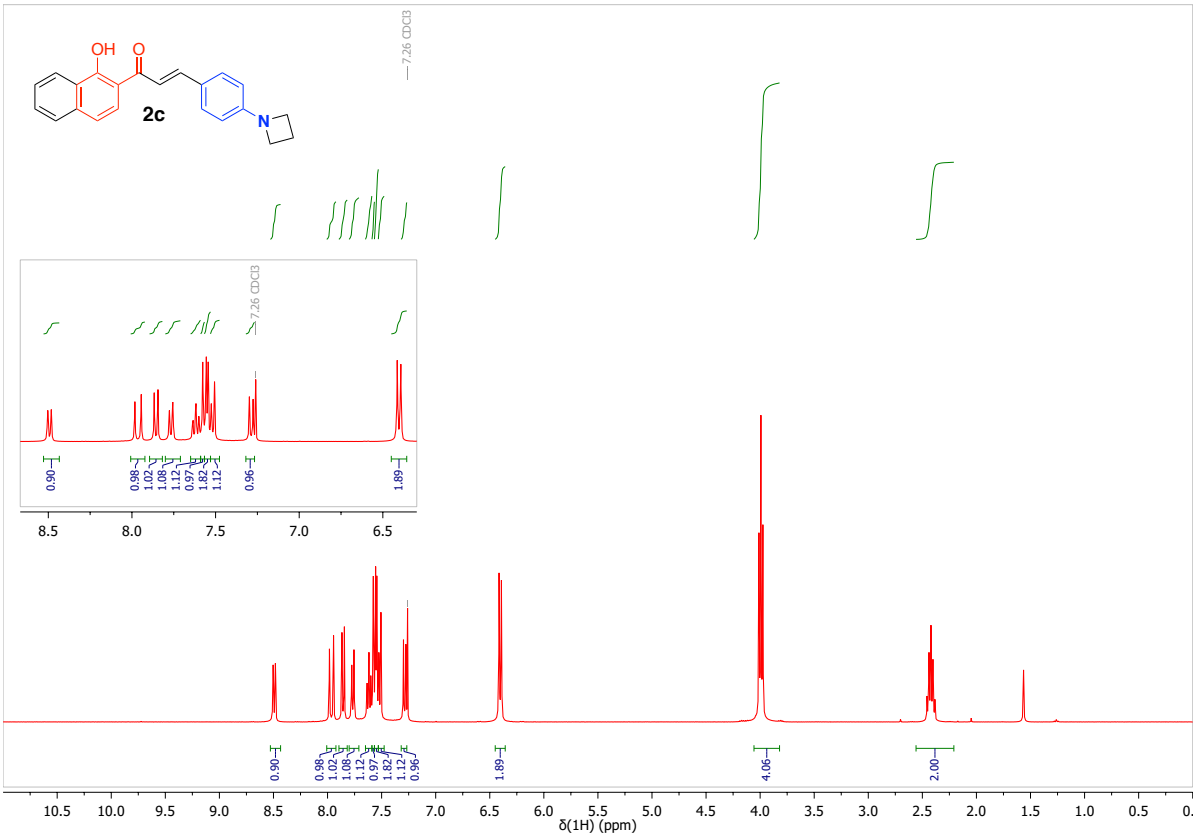


Fig. SI 39. ^{1}H NMR spectrum of **2c** (400 MHz, CDCl3).

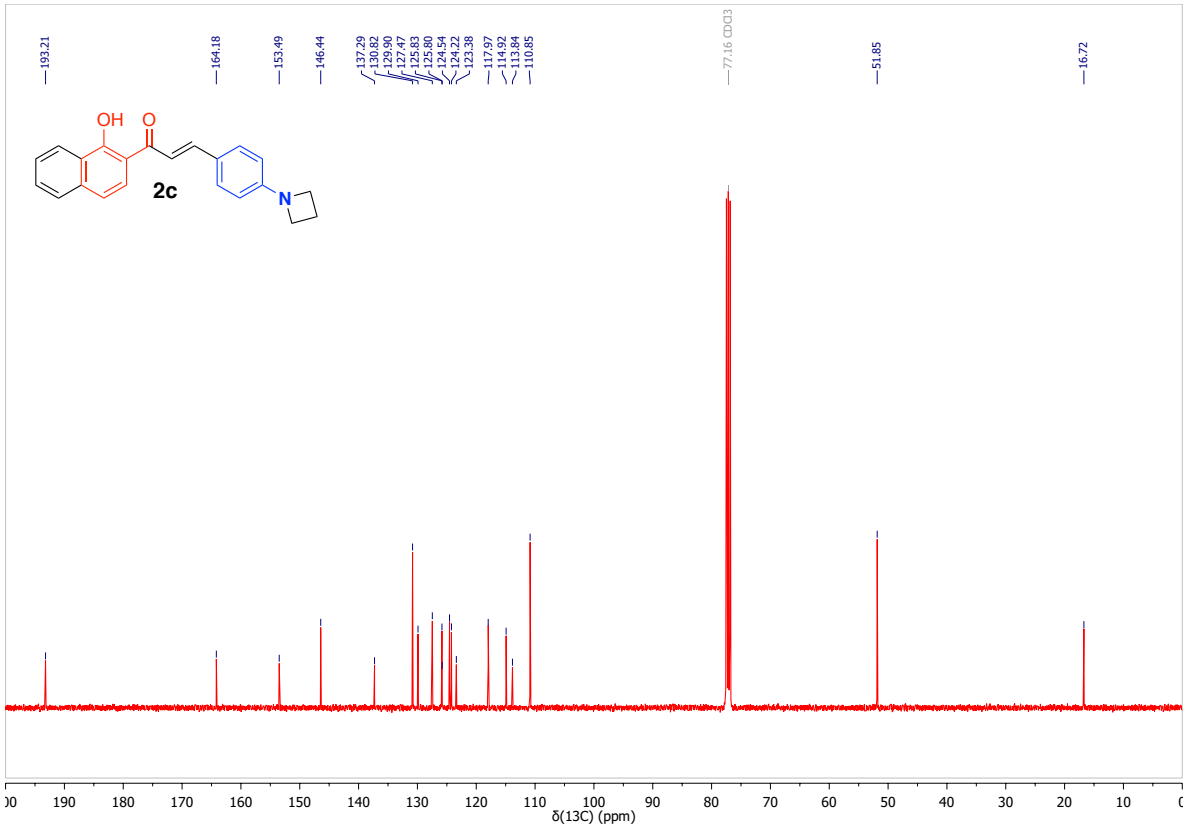


Fig. SI 40. ^{13}C NMR spectrum of **2c** (101 MHz, CDCl3).

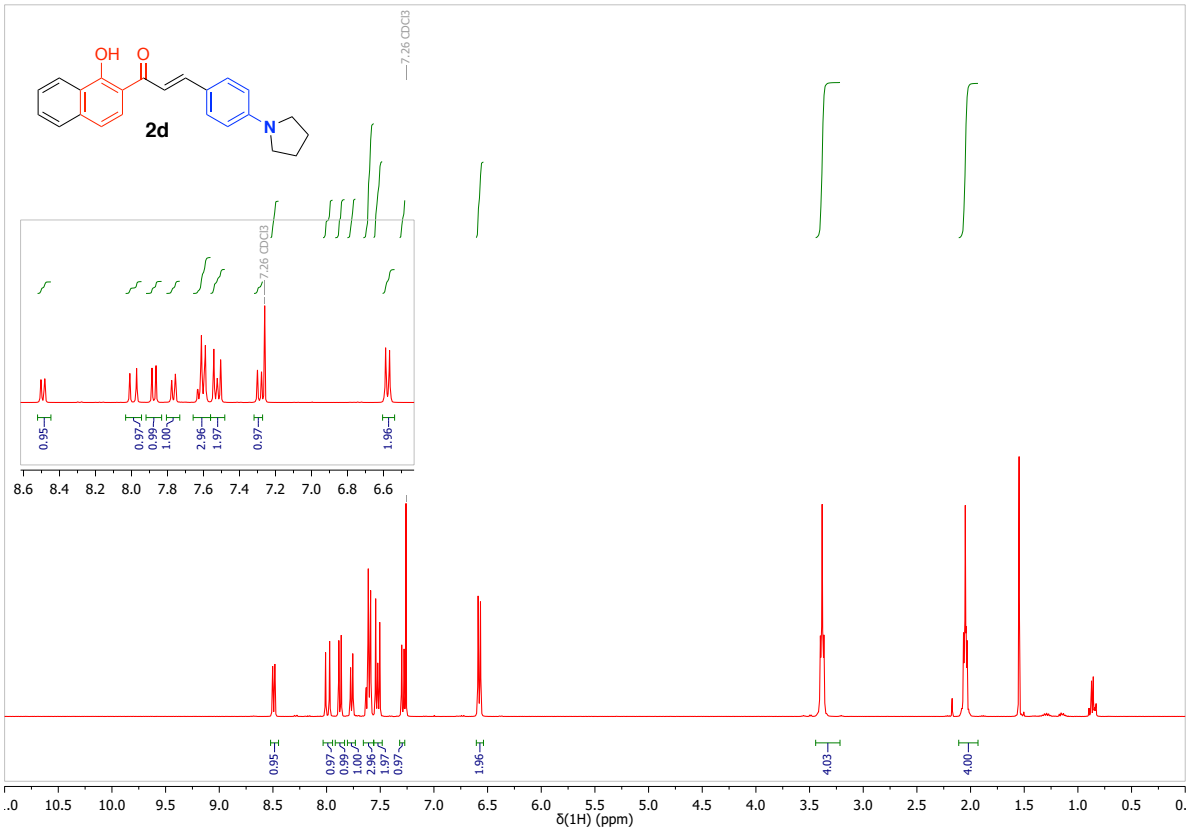


Fig. SI 41. ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$).

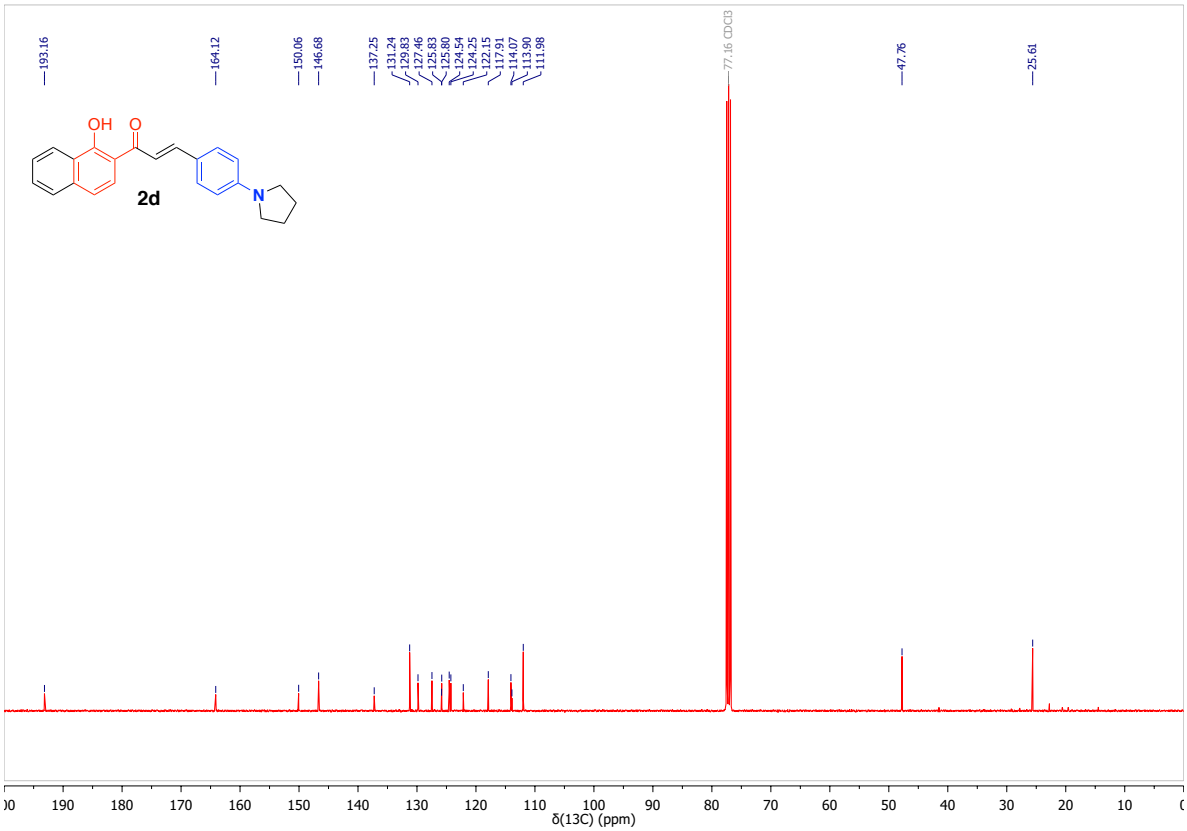


Fig. SI 42. ^{13}C NMR spectrum of **2d** (101 MHz, $CDCl_3$).

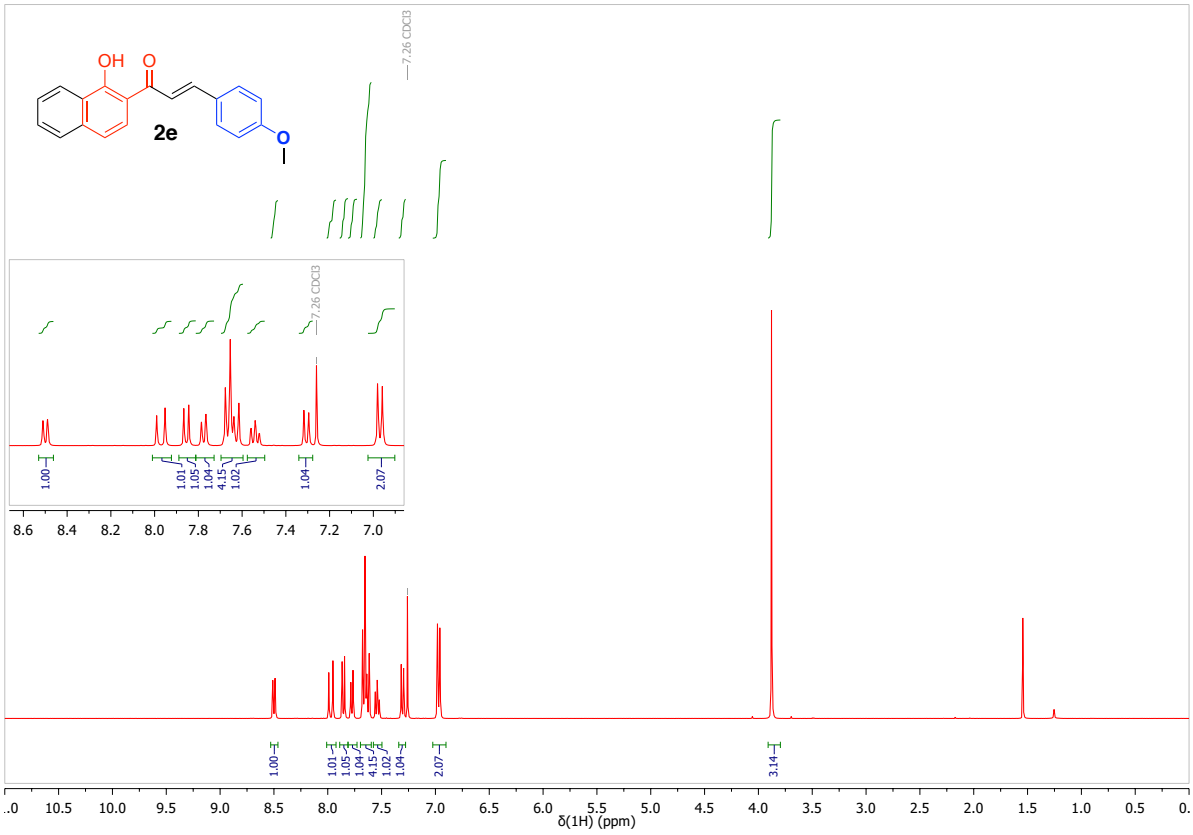


Fig. SI 43. ^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$).

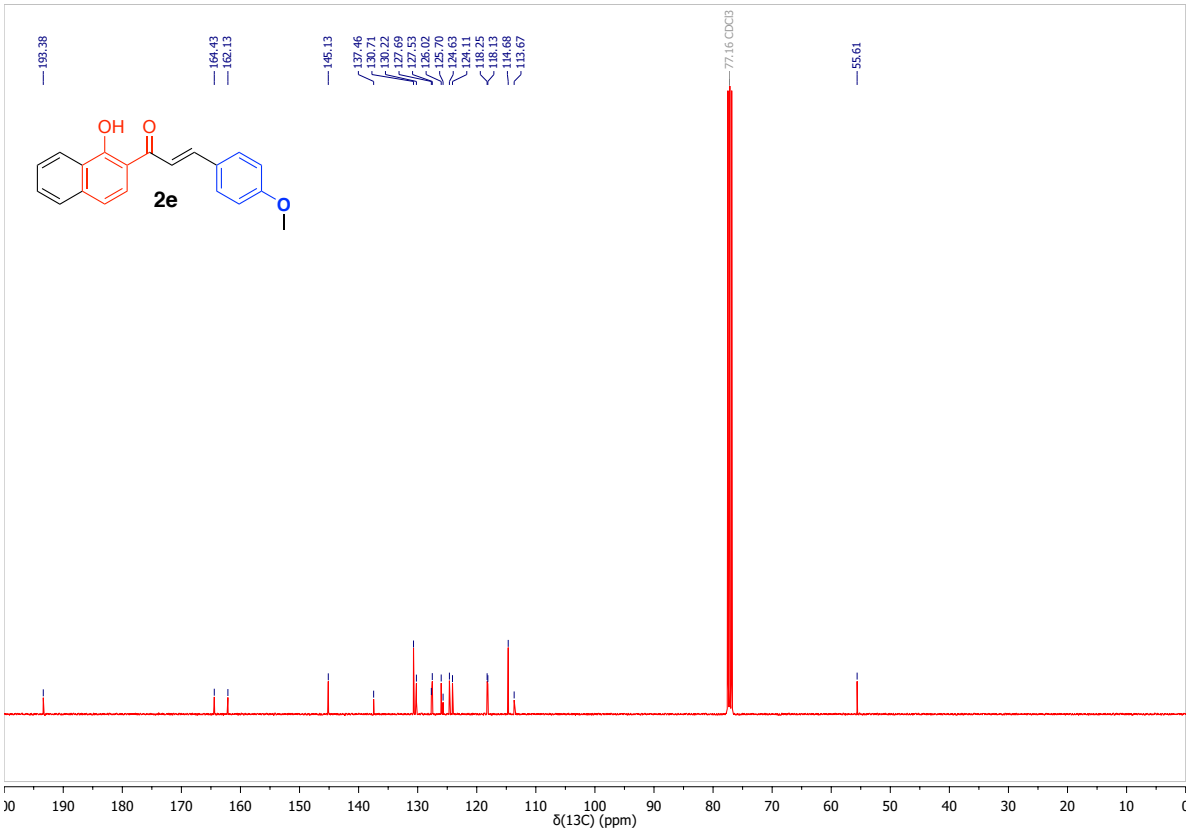


Fig. SI 44. ^{13}C NMR spectrum of **2e** (101 MHz, CDCl3).

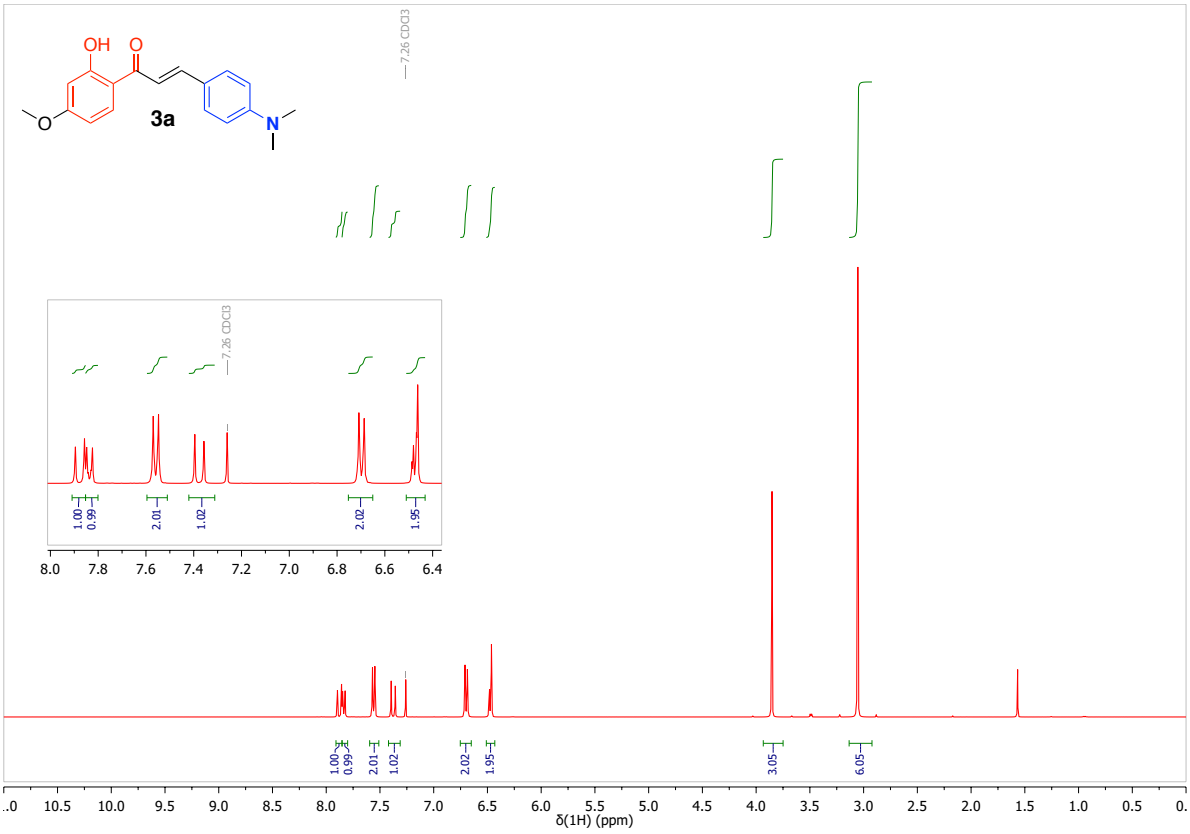


Fig. SI 45. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$).

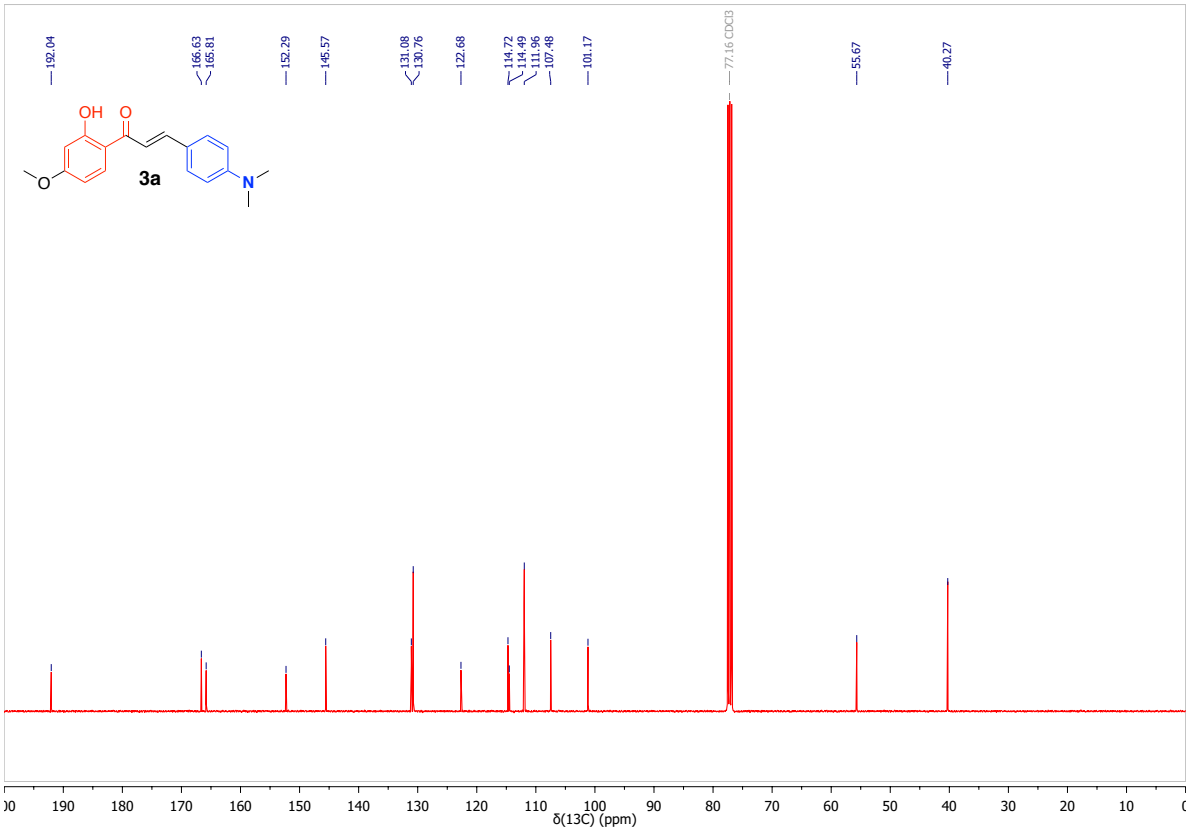


Fig. SI 46. ^{13}C NMR spectrum of **3a** (101 MHz, CDCl3).

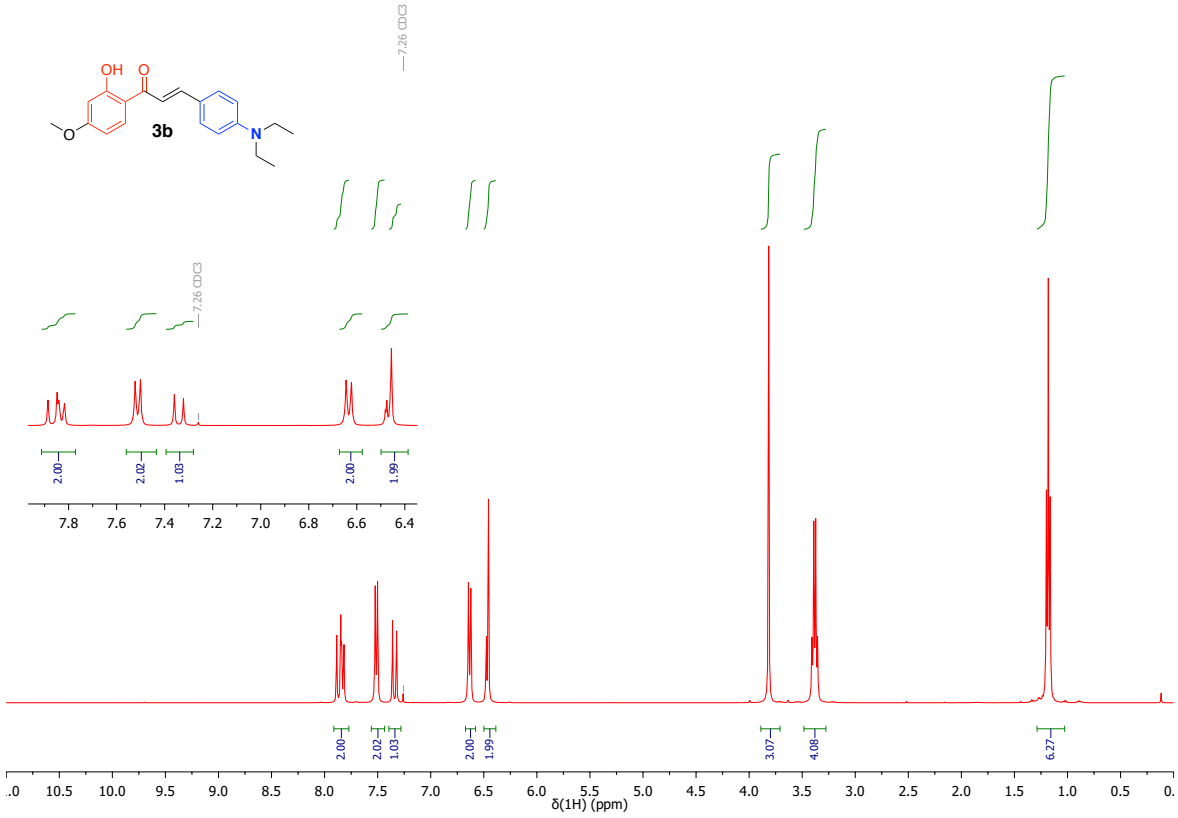


Fig. SI 47. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$).

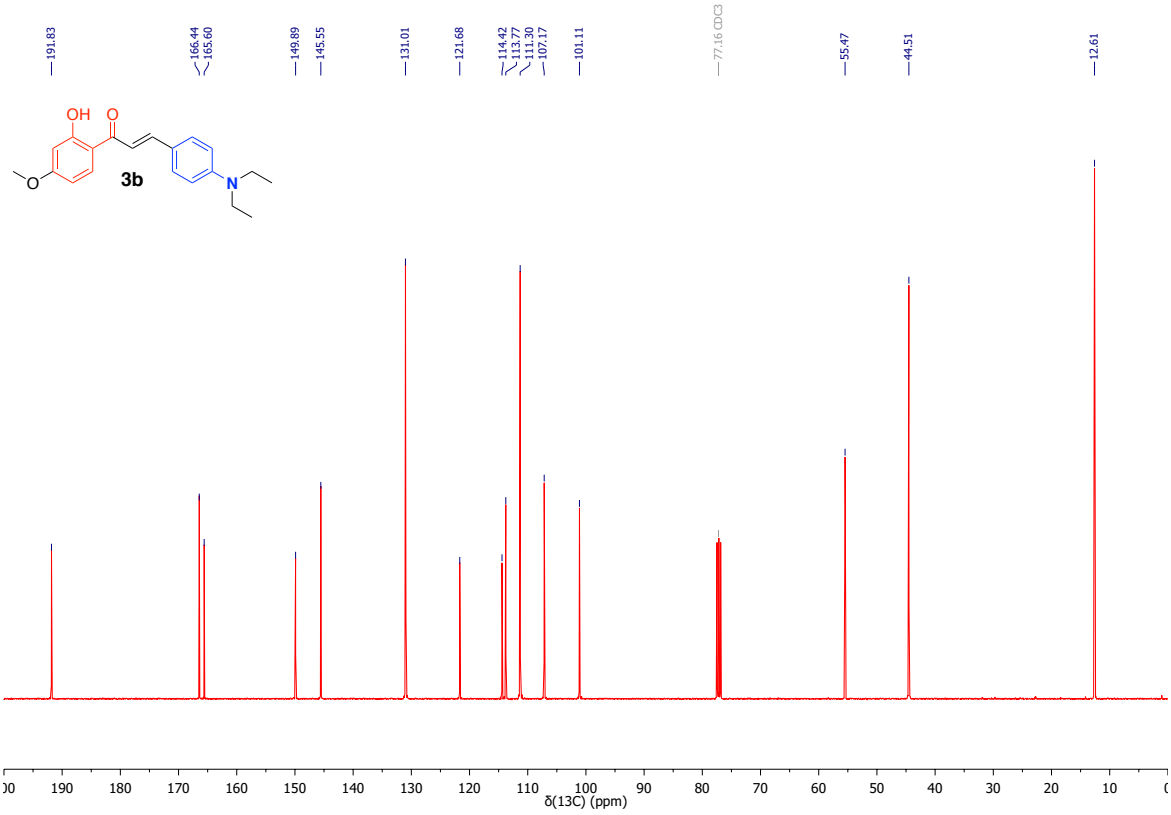


Fig. SI 48. ^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$).

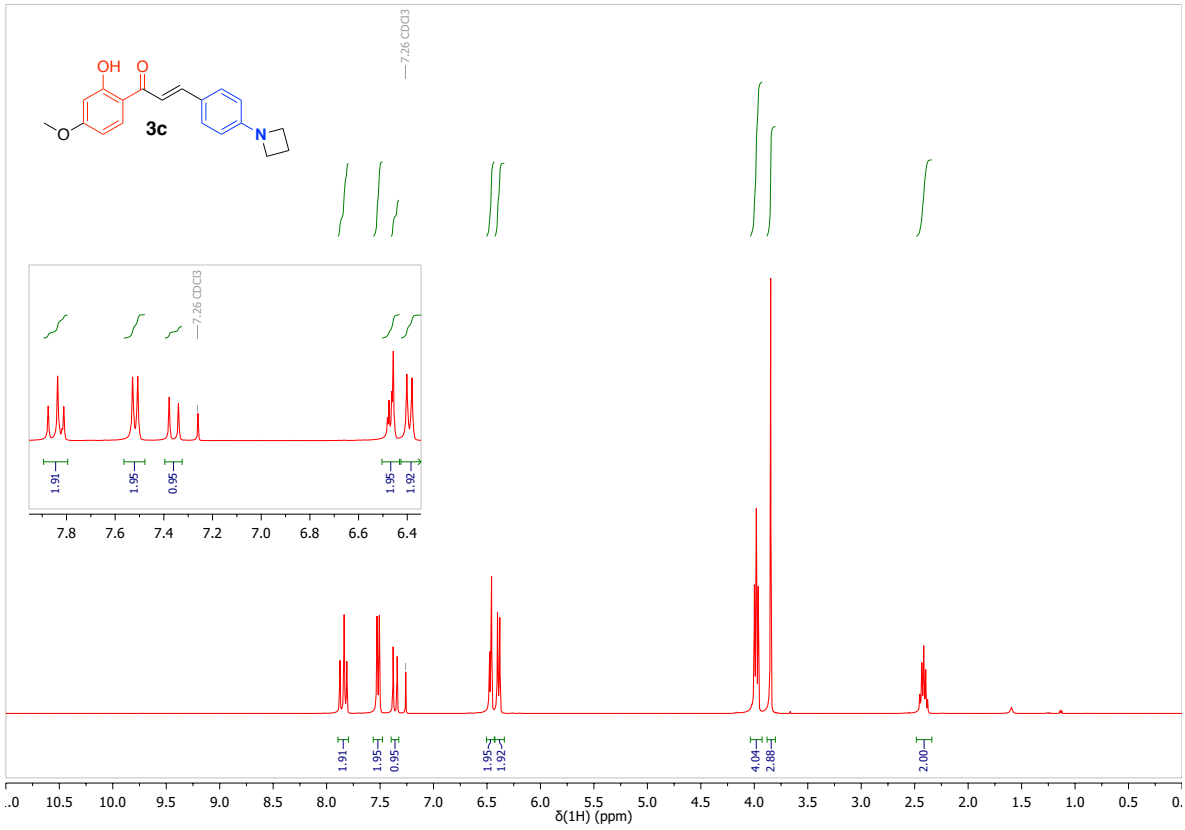


Fig. SI 49. ^{1}H NMR spectrum of **3c** (400 MHz, CDCl3).

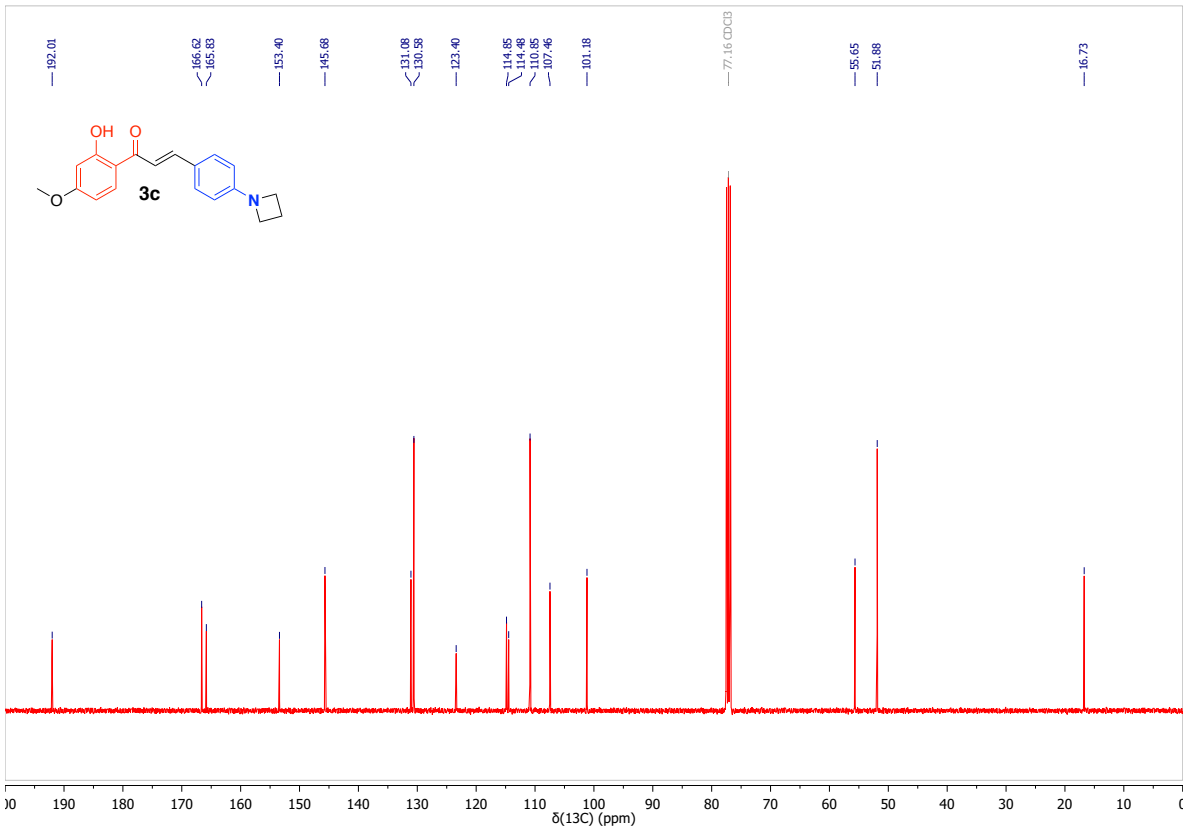


Fig. SI 50. ^{13}C NMR spectrum of **3c** (101 MHz, CDCl3). `

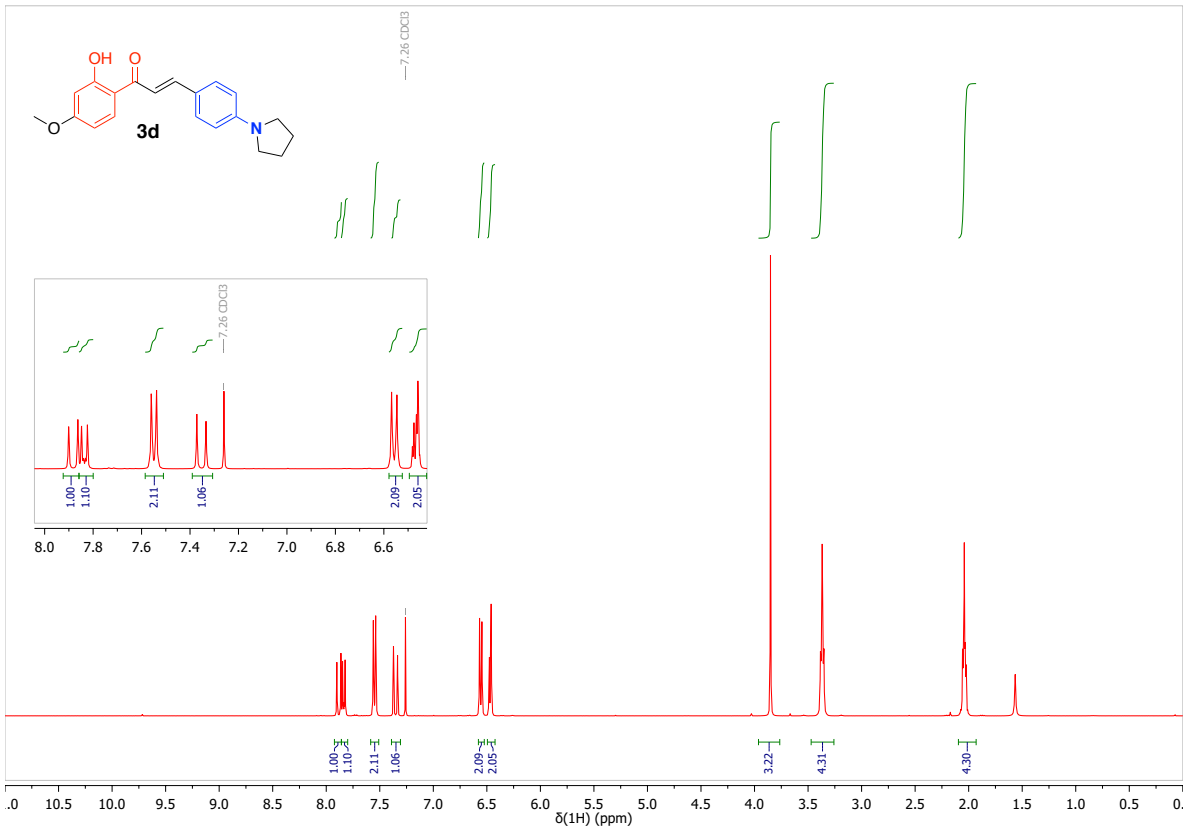


Fig. SI 51. ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$).

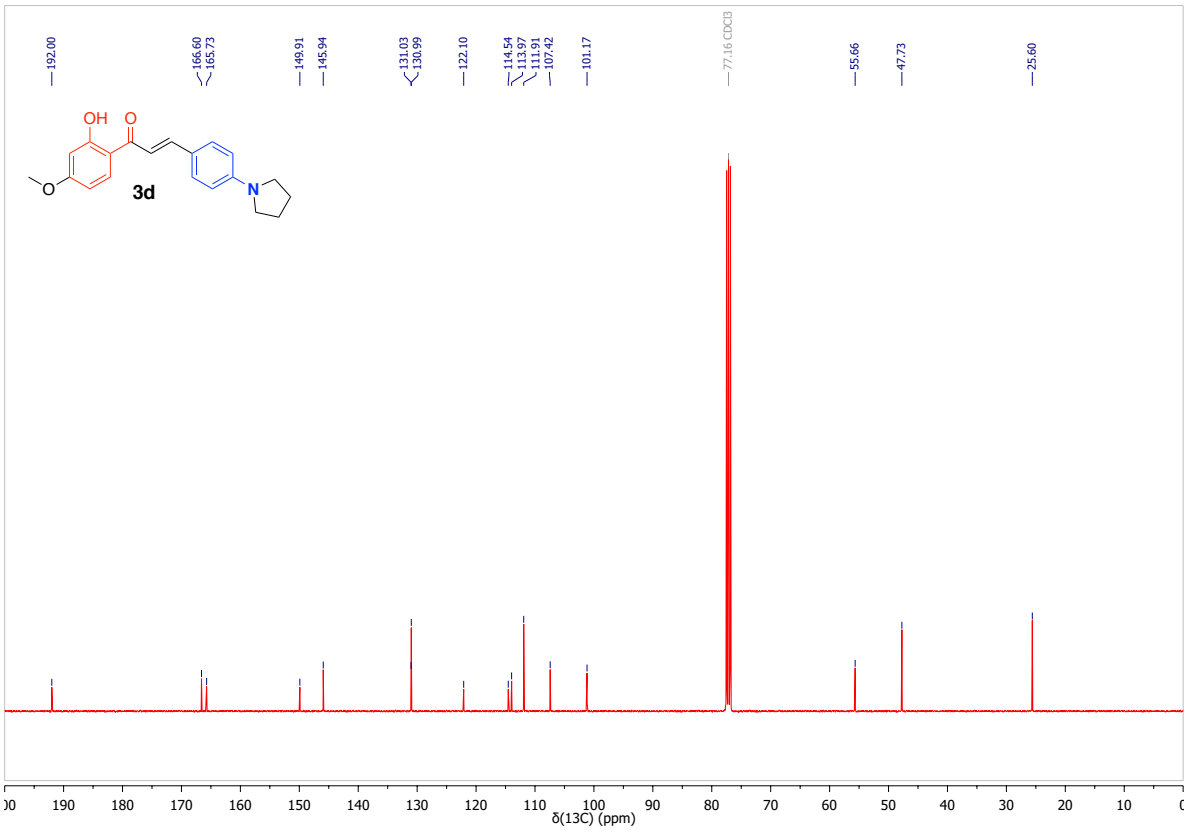


Fig. SI 52. ^{13}C NMR spectrum of **3d** (101 MHz, CDCl3).

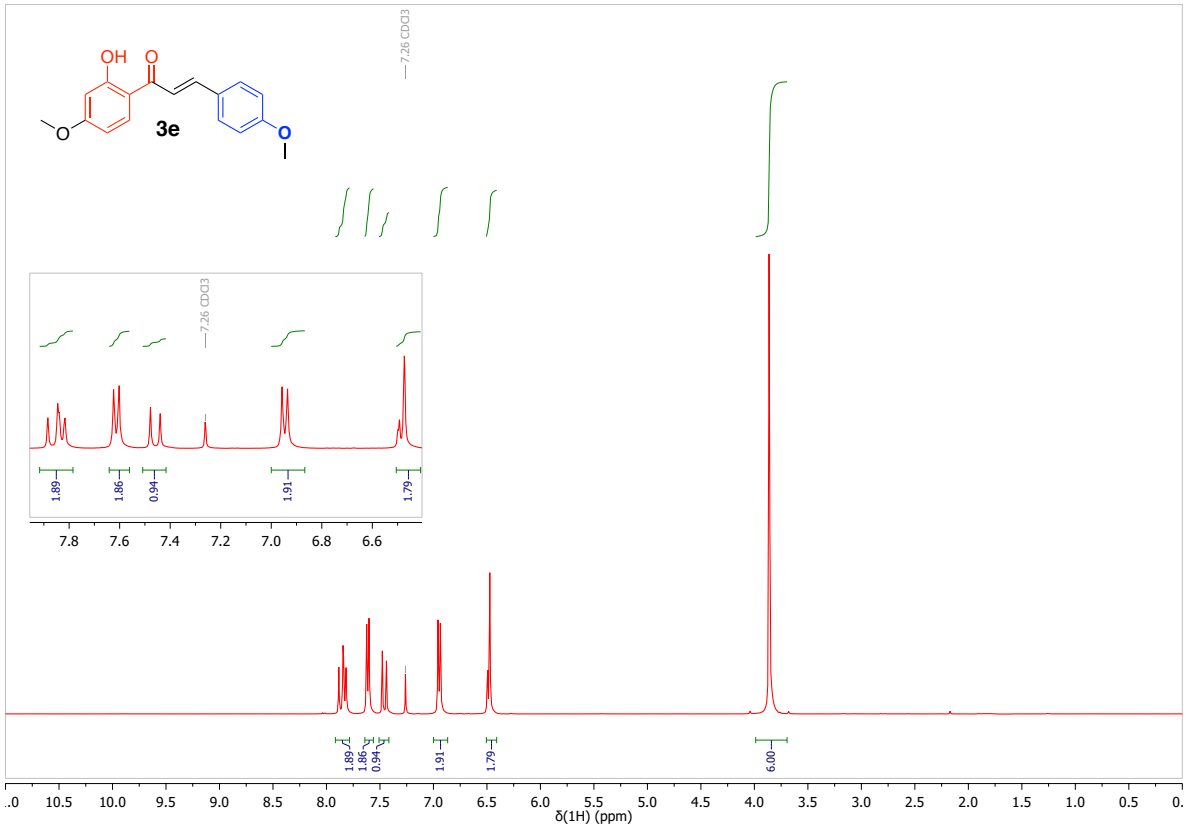


Fig. SI 53. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$).

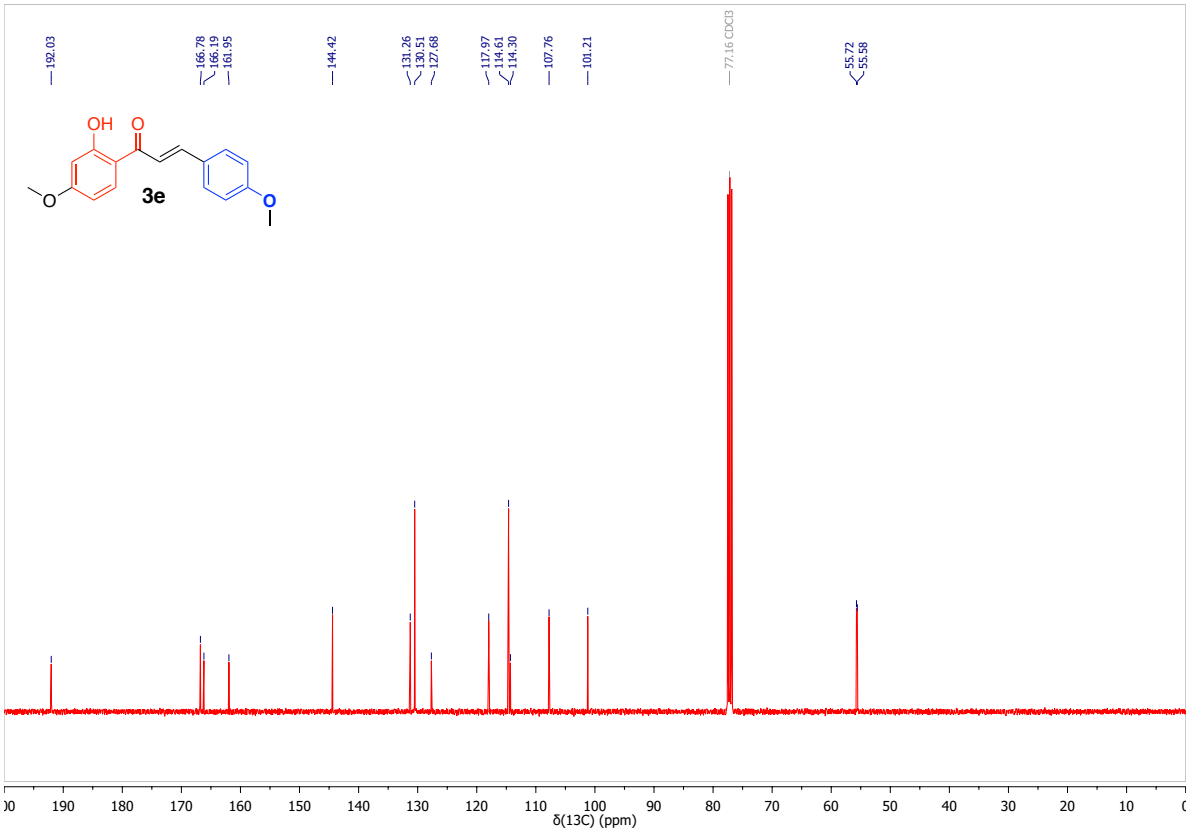


Fig. SI 54. ^{13}C NMR spectrum of **3e** (101 MHz, CDCl3).

5. References

(1) de Mello, J. C.; Wittmann, H. F.; Friend, R. H. An Improved Experimental Determination of External Photoluminescence Quantum Efficiency. *Adv. Mater.* 1997. https://doi.org/10.1002/adma.19970090308.

(2) Porrès, L.; Holland, A.; Pålsson, L.-O.; Monkman, A. P.; Kemp, C.; Beeby, A. Absolute Measurements of Photoluminescence Quantum Yields of Solutions Using an Integrating Sphere. *J. Fluoresc.* 2006, *16* (2), 267–272. https://doi.org/10.1007/s10895-005-0054-8.

(3) *Rigaku Oxford Diffraction, (2019), CrysAlisPro Software System, Version 1.171.40.67a, Rigaku Corporation, Oxford, UK.*

(4) Clark, R. C.; Reid, J. S. The Analytical Calculation of Absorption in Multifaceted Crystals. *Acta. Cryst. A* 1995, *51* (6), 887–897. https://doi.org/10.1107/S0108767395007367.

(5) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta. Cryst. C* 2015, *71* (1), 3–8. https://doi.org/10.1107/S2053229614024218.

(6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. a. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* 2009, *42* (2), 339–341. https://doi.org/10.1107/S0021889808042726.

(7) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta. Cryst. A* 2015, *71* (1), 3–8. https://doi.org/10.1107/S2053273314026370.