Supporting Information for

Bridged eosin Y: A visible and near-infrared photoredox catalyst

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1. Instrumentation and Materials

Instruments

^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL ECZ-400S spectrometer (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR). ^{1}H- and ^{13}C- spectra were referenced to $CHCl_3$ (δ: 7.26 and 77.16 ppm for ^{1}H- and ^{13}C-NMR, respectively), trifluoroacetic acid (δ: 11.50 and 164.2 ppm for ^{1}H- and ^{13}C-NMR, respectively), MeOH (δ: 3.31 and 49.0 ppm for ^{1}H- and ^{13}C-NMR, respectively) and DMSO (δ: 2.50 and 39.52 ppm for ^{1}H- and ^{13}C-NMR, respectively) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet. HRMS (ESI) spectra were recorded on Agilent 6230 Accurate-Mass TOF LC/MS system using electrospray ionization. UV/Vis spectra were recorded on a HITACHI UH-5700 spectrophotometer and fluorescence spectra on a HITACHI F-7100 spectrophotometer. Crystal structures were determined by the single-crystal X-ray diffraction method at T = 103 K. These diffraction data were collected using Rigaku XtaLAB Synergy-i diffractometer (Cu-Kα radiation). Cyclic voltammetry measurements were carried out with a Hokuto Denko HZ-7000 voltammetric analyzer.

Photoreactions

Photoreactions were performed in a Schlenck tube using a LED light (Techno Sigma PER-AMP series for 521 nm and 631 nm, ASAHI SPECTRA CL series for 730 nm, 830 nm and 940 nm). See experimental procedure for details of the photoreaction.

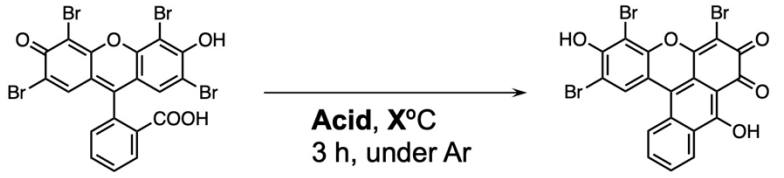
Materials

Reagents were purchased from Wako Pure Chemical Industries, Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd. All solvents were used without further purification.

2. Experimental Procedure

2-1. Synthesis of BEY (2)

Scheme S1. Examination of reaction condition of **2**.

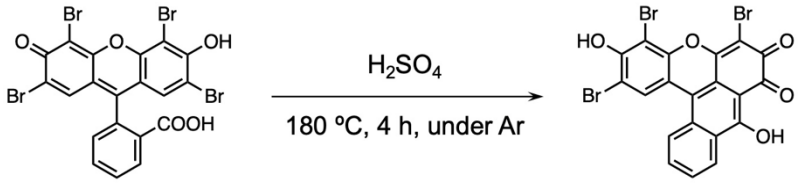


EY (1) **BEY (2)**

Entry	Acid	X (°C)	Yield (%)
1	H_2SO_4	120	<1
2	H_2SO_4	140	7
3	H_2SO_4	160	57
4	H_2SO_4	180	95
5	H_3PO_4	160	–
6	CH_3SO_3H	160	–

Synthesis of 2: **1** (200 mg, 0.308 mmol) was dissolved in concentrated H_2SO_4 (10 ml). The resulting mixture was stirred for 3 h at 180°C. The reaction mixture was allowed to cool and slowly added to ice. The precipitated solid was collected with a Büchner funnel under reduced pressure, and washed 3 times with 50 ml of water. The collected solid was dried under reduced pressure. CH_2Cl_2 was added to silica gel (50 g) to form a slurry, and the collected dried solid was added and stirred for 10 min. This silica gel mixture was filled in a chromatographic column and **2** was isolated using CH_2Cl_2/MeOH (10:1 → 4:1 (with 0.5% methanesulfonic acid)). The solution containing **2** was washed with water to remove methanesulfonic acid, and then hexane was added. The precipitated **2** crystals were collected with a Kiriyama funnel and dried under reduced pressure. **2** was obtained as reddish brown needle-like crystalline powder (167 mg, 95%).

2: **^{1}H-NMR** (400 MHz, trifluoroacetic acid-d): δ 9.25-9.10 (m, 1H), 8.95-8.65 (m, 2H), 8.30-8.05 (m, 2H); **^{13}C-NMR** (100 MHz, trifluoroacetic acid-d): δ 182.5, 158.0, 155.9, 147.5, 138.8, 138.1, 135.6, 134.4, 133.6, 133.3, 131.8; **HRMS** (ESI, positive) *m*/*z* calcd. for $C_{20}H_8O_5Br_3$ ($M+H^+$): 564.7922, found: 568.7896.



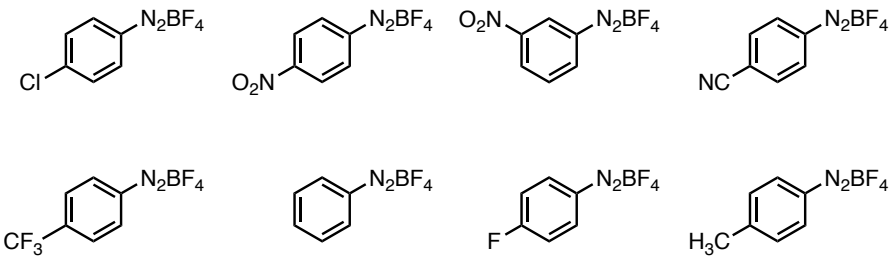
1 **2**

Synthesis of 2 (gram scale): **1** (5.0 g, 7.72 mmol) was dissolved in concentrated H_2SO_4 (100 ml). The resulting mixture was stirred for 4 h at 180°C. The reaction mixture was allowed to cool and slowly added to ice. The precipitated solid was collected with a Büchner funnel under reduced pressure, and washed 3 times with 50 ml of water. The collected solid was suspended in methanol (100 ml) and collected with a Kiriyama funnel. CH_2Cl_2 was added to silica gel (300 g) to form a slurry, and the collected solid was added and stirred for 1 h. This silica gel mixture was filled in a chromatographic column and **2** was isolated using CH_2Cl_2/MeOH (10:1 → 4:1 (with 0.5% methanesulfonic acid)). The solution containing **2** was washed with water to remove methanesulfonic acid, and then hexane was added. The precipitated **2** crystals were collected with a Kiriyama funnel and dried under reduced pressure. **2** was obtained as reddish brown needle-like crystalline powder (3.7 g, 85%).

2-2. Preparation of aryl diazonium tetrafluoroborate[1]

Aryldiazonium tetrafluoroborates were synthesized from the corresponding anilines according to the reported procedure[1]. The aniline derivatives (4.5 mmol) were dissolved in glacial acetic acid (3 mL) at room temperature. Then, 48 % aqueous tetrafluoroboric acid (1.3 mL) and a solution of iso-amylnitrite (1 mL) in glacial acetic acid (2 mL) were slowly added at room temperature. After 5 minutes, diethylether (15 mL) was added and the reaction mixture was cooled down to –30 °C (dry ice/EtOH). The precipitated crystals were filtered off in vacuo, washed with diethylether (2 x 10 mL) and dried under reduced pressure.

Chart S1 Aryldiazonium tetrafluoroborate used in this study



2-3. Photoredox catalysis

2-3-1 LED light source in this work

521 nm: PER-521 (Techno Sigma), output power 226 mW/cm^2

631 nm: PER-631(Techno Sigma), output power 249 mW/cm^2

730 nm: CL-H1-730-9-1 (ASAHI SPECTRA), output power 148 mW/cm^2 (WD = 20mm)

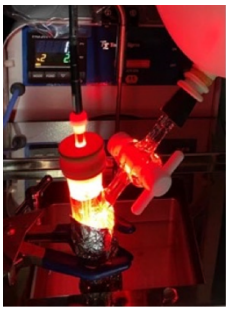
830 nm: CL-H1-830-9-1(ASAHI SPECTRA), output power 158 mW/cm^2 (WD = 20mm)

940 nm: CL-H1-940-9-1(ASAHI SPECTRA), output power 281 mW/cm^2 (WD = 20mm)

2-3-2 Set up

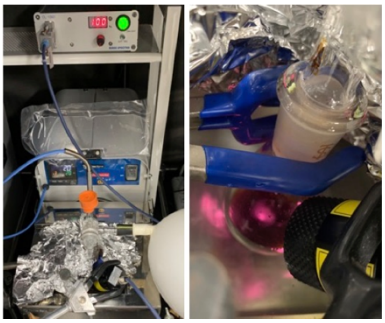
Photoreaction using PER-521 and PER-631

The reactions were carried in a Schlenk tube equipped with a magnetic stirrer. The LEDs were plugged directly into the Schlenk tube. The Schlenk tube was fully covered by alminium foil to remove the external visible light. All reactions were performed under argon atmosphere in the darkroom.



Photoreaction using CL series

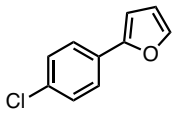
The reactions were carried in a round bottom flask equipped with a magnetic stirrer. One near-infrared LED was placed at about 3 cm away from the light source. The Schlenk tube was fully covered by alminium foil to remove the external visible light. All reactions were performed under argon atmosphere in the darkroom.



General procedure for the reaction of aryl diazonium tetrafluoroborates with furan[2]

The photoreactions were performed with reference to the condition of König *et al*.[2] In a 20 mL dried Schlenk tube equipped with magnetic stirring bar, the **2** (0.01 eq.), aryl diazonium tetrafluoroborate (1 eq.) and furan (10 eq.) were dissolved in dehydrated DMSO (0.23 mmol/mL). Then, LED was attached to the Schlenk tube. After 2 h of irradiation the reaction mixture was transferred to separating funnel, diluted with ethyl acetate and washed twice with 100 mL of water. The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate (100:0 to 10:1) as eluent.

2-(4-chlorophenyl)-furan (3a)

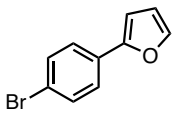


3a

3a was obtained as a white powder. ^{1}H and ^{13}C NMR of **3a** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 153.1, 142.5, 133.1, 129.5, 129.0, 125.1, 111.9, 105.6.

2-(4-bromophenyl)-furan (3b)

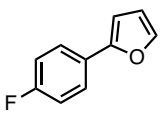


3b

3b was obtained as a white powder. ^{1}H and ^{13}C NMR of **3b** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.57-7.51 (m, 4H), 7.50-7.48 (m, 1H), 6.66 (d, *J* = 2.8 Hz, 1H), 6.49 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 153.0, 142.5, 131.9, 129.8, 125.4, 121.1, 111.9, 105.6.

2-(4-fluorophenyl)-furan (3c)

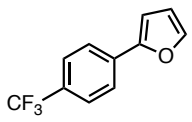


3c

3c was obtained as a colorless powder. ^{1}H and ^{13}C NMR of **3c** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.66-7.62 (m, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.10-7.05 (m, 2H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.47 (dd, *J* = 3.6 Hz, 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 161.0, 153.3, 142.2, 127.4, 125.6, 115.8, 111.8, 104.8.

2-(4-trifluoromethyl-phenyl)-furan (3d)

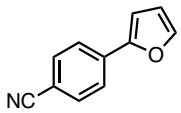


3d

3d was obtained as a white powder. ^{1}H and ^{13}C NMR of **3d** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.76 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 1.2 Hz, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.52 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 152.6, 143.2, 134.1, 129.0, 125.8, 123.9, 123.0, 112.1, 107.1.

2-(4-cyanophenyl)-furan (3e)

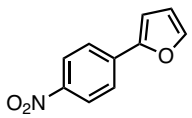


3e

3e was obtained as a white powder. ^{1}H and ^{13}C NMR of **3e** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.72 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 2.8 Hz, 1H), 6.80 (d, *J* = 3.6 Hz, 1H), 6.52 (dd, *J* = 3.2 Hz, 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 152.0, 143.2, 134.7, 132.6, 124.0, 119.1, 112.3, 110.3, 108.3.

2-(4-nitrophenyl)-furan (3f)

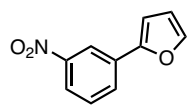


3f

3f was obtained as a yellow powder. ^{1}H and ^{13}C NMR of **3f** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.27-8.23 (m, 2H), 7.81-7.78 (m, 2H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.38 (d, *J* = 3.2 Hz, 1H), 6.56 (dd, *J* = 3.2 Hz, 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 151.9, 146.5, 144.3, 136.6, 124.5, 124.1, 112.6, 109.1.

2-(3-nitrophenyl)-furan (3g)

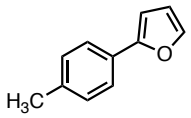


3g

3g was obtained as a yellow powder. ^{1}H and ^{13}C NMR of **3g** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.50-8.49 (m, 1H), 8.10-8.07 (m, 1H), 7.97-7.95 (m, 1H), 7.57-7.53 (m, 2H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.53 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 151.6, 148.8, 143.4, 132.5, 129.8, 129.4, 121.8, 118.6, 112.2, 107.4.

2-(4-methylphenyl)-furan (3h)

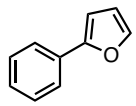


3h

3h was obtained as a pale brown liquid. ^{1}H and ^{13}C NMR of **3h** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 4.0 Hz, 1H), 6.47 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 154.3, 141.8, 137.3, 129.5, 128.3, 123.9, 111.7, 104.3, 21.4.

2-phenyl-furan (3i)

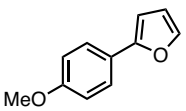


3i

3i was obtained as a pale brown liquid. ^{1}H and ^{13}C NMR of **3i** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.68 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.28-7.24 (m, 1H), 6.66 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 2.8 Hz, 2.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 154.1, 142.2, 131.0, 128.8, 127.4, 123.9, 111.8, 105.1.

2-(4-methoxyphenyl)-furan (3j)

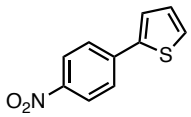


3j

3j was obtained as a white powder. ^{1}H and ^{13}C NMR of **3j** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 9.2 Hz, 2H), 6.52 (d, *J* = 3.2 Hz, 1H), 6.46-6.44 (m, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 159.1, 154.1, 141.5, 128.9, 124.7, 112.9, 111.7, 103.5, 55.4.

2-(4-nitrophenyl)-thiophene (3k)

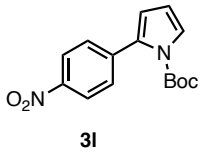


3k

3k was obtained as a yellow powder. ^{1}H and ^{13}C NMR of **3k** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.24 (d, *J* = 9.2 Hz, 2H) , 7.74 (d, *J* = 7.2 Hz, 2H), 7.48 (dd, *J* = 3.6 Hz, 1H), 7.50-7.40 (m, 1H), 7.16 (dd, *J* = 5.2 Hz, 3.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 141.6, 141.7, 140.7, 128.8, 127.6, 126.1, 125.9, 124.5.

2-(4-nitrophenyl)-pyrrole-1-carboxylic acid *tert*-butyl ester (3l)



3l

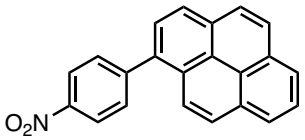
3l was obtained as a yellow powder. ^{1}H and ^{13}C NMR of **3l** were in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.21 (d, *J* = 8.8 Hz, 2H) , 7.51 (d, *J* = 6.8 Hz, 2H), 7.41 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H), 6.33 (dd, *J* = 3.6 Hz, 1.6 Hz, 1H), 6.27 (t, *J* = 4.0 Hz, 1H) 1.44 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 149.0, 146.6, 140.8, 132.9, 129.6, 124.4, 123.0, 116.7, 111.3, 84.6, 27.9.

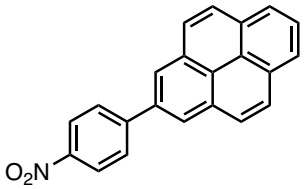
Procedure for the reaction of 4-nitrophenyl diazonium tetrafluoroborates with PAHs

In a 20 mL dried Schlenk tube equipped with magnetic stirring bar, the **2** (0.01 eq.), 4-nitrophenyl diazonium tetrafluoroborate (1 eq.) and PAHs (2 eq.) were suspended in dehydrated DMSO (0.23 mmol/mL). Then, LEDs was attached to the Schlenk tube. After 2 h of irradiation the reaction mixture was transferred to separating funnel, diluted with $CHCl_3$ and washed twice with 100 mL of water. The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using hexane/ $CHCl_3$ (100:1 to 10:1) as eluent.

4-nitrophenyl-pyrene (3m)



3mA



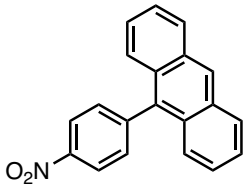
3mB

3m was obtained as an orange powder. ^{1}H and ^{13}C NMR of **3m** were in agreement with the literature[3]. There were two isomers (**3mA** and **3mB**) in **3m**. **3mA** and **3mB** could not be separated by silica gel column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.43-8.40 (m, 2H), 8.23 (dd, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 6.4 Hz, 1H), 8.16-7.98 (m, 5H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.85-7.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.2, 147.1, 131.5, 131.0, 128.5, 128.3, 127.4, 127.3, 126.4, 125.8, 125.4, 124.8, 124.3, 123.7; **HRMS** (APCI, positive) *m*/*z* calcd. for $C_{22}H_{13}NO_2$ ($M+H^+$): 324.1024, found: 324.1017.

9-(4-nitrophenyl)-anthracene (3n)

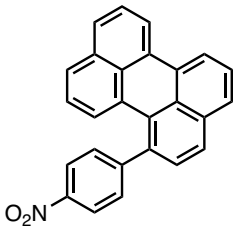


3n

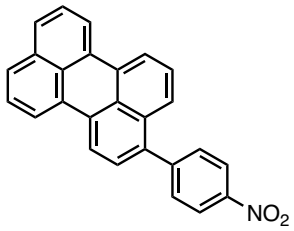
3n was obtained as a yellow powder. ^{1}H and ^{13}C NMR of **3n** were in agreement with the literature[4].

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.57 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.54-7.46 (m, 4H), 7.40 (t, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 147.6, 146.4, 134.1, 132.5, 131.2, 129.8, 128.3, 127.9, 126.3, 125.9, 125.5, 123.8; **HRMS** (APCI, positive) *m*/*z* calcd. for $C_{20}H_{13}NO_2$ ($M+H^+$): 300.1024, found: 300.1013.

4-nitrophenyl-perylene (3o)



3oA



3oB

3o (**3oA** +**3oB**) was obtained as a red powder.

1-(4-nitrophenyl)-perylene (3oA)

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.29 (d, *J* = 8.4 Hz, 2H), 8.23 (t, *J* = 6.8 Hz, 2H), 7.77-7.70 (m, 3H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.60-7.52 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 152.2, 146.9, 131.7, 130.9, 130.7, 130.4, 129.7, 128.1, 128.0, 127.7, 127.6, 127.2, 126.7, 125.6, 125.1, 121.5, 120.7; **HRMS** (APCI, positive) *m*/*z* calcd. for $C_{26}H_{15}NO_2$ ($M+H^+$): 374.1181, found: 374.1178.

3-(4-nitrophenyl)-perylene (3oA)

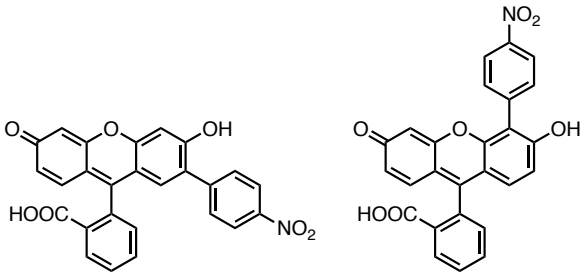
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.42-8.35 (m, 2H), 8.29-8.20 (m, 4H), 7.78-7.68 (m, 4H), 7.65 (dd, *J* = 8.6 Hz, 2.4 Hz, 2H), 7.57-7.40 (m, 4H), 7.29-7.24 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 147.9, 147.3, 137.4, 134.8, 132.5, 131.2, 131.0, 128.5, 128.3, 128.1, 127.3, 126.9, 126.8, 125.2, 123.9, 120.9, 120.8, 119.9; **HRMS** (APCI, positive)

m/*z* calcd. for $C_{26}H_{15}NO_2$ ($M+H^+$): 374.1181, found: 374.1178.

Procedure for the reaction of 4-nitrophenyl diazonium tetrafluoroborates with xanthene dyes

In a dried round-bottom flask equipped with magnetic stirring bar, the xanthene dyes, **2** (0.02 eq.), 4-nitrophenyl diazonium tetrafluoroborate (2 eq.) were dissolved in dehydrated DMSO (4 mL). After irradiation the reaction mixture was transferred to separating funnel, diluted with CH_2Cl_2 and washed twice with 100 mL of water. The organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuum. Purification of the crude product was achieved by preparative layer chromatography using $CHCl_3$ / MeOH (10:1).

4-nitrophenyl-fluorescein (4)



4 (**4A**+**4B**) was obtained as a red foam solid.

2-(4-nitrophenyl)-fluorescein (4A)

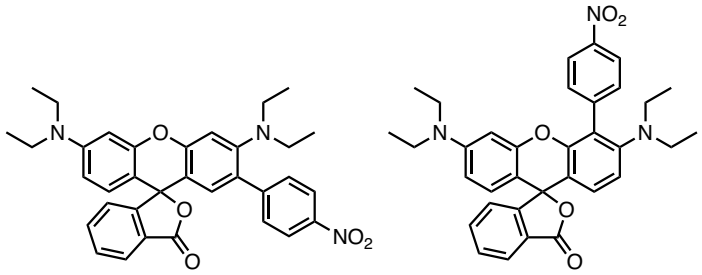
^{1}H NMR (400 MHz, DMSO-d6) δ ppm 8.12 (d, *J* = 8.4 Hz, 2H), 8.00 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.70-7.60 (m, 4H), 7.29 (d, *J* = 6.8 Hz, 1H), 6.74 (s, 1H), 6.67 (s, 1H), 6.59 (d, *J* = 8.8 Hz, 1H), 6.56 (s, 1H), 8.00 (dd, *J* = 9.0 Hz, 2.2 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d6) δ ppm 169.1, 154.0, 153.6, 145.6, 145.1,132.3, 129.7, 129.5, 129.4, 126.5, 125.9, 123.1, 122.9, 110.1, 103.5, 102.5; **HRMS** (ESI, positive) *m*/*z* calcd. for $C_{26}H_{15}NO_7$ ($M+H^+$): 454.0926, found: 454.0919.

4-(4-nitrophenyl)-fluorescein (4B)

^{1}H NMR (400 MHz, DMSO-d6) δ ppm 8.32 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 6.80-6.63 (m, 2H), 6.63-6.50 (m, 2H), 6.43 (d, *J* = 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d6) δ ppm 168.9, 167.8, 161.4, 159.8, 152.3, 151.9, 149.7, 147.4, 146.2, 143.2, 140.9, 134.7, 132.5, 130.0, 129.2, 125.6, 125.0, 123.0, 122.8, 113.8, 113.7,

110.3, 109.9, 109.4, 102.3; **HRMS** (ESI, positive) *m*/*z* calcd. for $C_{26}H_{15}NO_7$ ($M+H^+$): 454.0926, found: 454.0916.

4-nitrophenyl-rhodamine B (5)



5 (5A+5B) was obtained as a purple foam solid.

2-(4-nitrophenyl)-rhodamine B (5A)

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.13 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.65 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.59 (td, *J* = 7.2 Hz, 1.0 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.53 (s, 1H), 6.48 (s, 1H), 6.38 (d, *J* = 7.2 Hz, 1H), 3.37 (q, *J* = 7.2 Hz, 4H), 2.90 (q, *J* = 7.2 Hz, 4H), 1.18 (t, *J* = 7.2 Hz, 6H), 0.95 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 169.7, 153.1, 152.6, 151.2, 149.9, 147.8, 145.5, 134.9, 130.8, 129.7, 129.5, 129.1, 127.5, 125.2, 124.3, 123.7, 113.1, 108.9, 108.7, 97.6, 46.1, 44.7, 12.6, 11.8; **HRMS** (ESI, positive) *m*/*z* calcd. for $C_{34}H_{34}N_3O_5$ ($M+H^+$): 564.2498, found: 564.2493.

4-(4-nitrophenyl)-rhodamine B (5B)

^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 8.37 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.90-7.65 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.55-6.35 (m, 2H), 6.08 (d, *J* = 2.0 Hz, 1H), 3.30-3.32 (m, 4H), 2.78 (q, *J* = 7.0 Hz, 4H), 1.03 (t, *J* = 6.8 Hz, 6H), 0.79 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ ppm 168.7, 152.3, 152.0, 151.1, 149.3, 148.8, 146.3, 142.9, 135.5, 132.4, 130.1, 128.5, 127.8, 126.6, 124.6, 124.3, 123.2, 121.6, 117.1, 113.4, 108.8, 104.6, 96.8, 83.9, 45.8, 43.5, 12.3, 12.0; **HRMS** (ESI, positive) *m*/*z* calcd. for $C_{34}H_{34}N_3O_5$ ($M+H^+$): 564.2498, found: 564.2493.

3. Single X-ray Structure Analysis

Single crystals of **2** were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of **2** at 10ºC. Single crystals of **3mA, 3n,** and **3oA** were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **3mA, 3n,** and **3oA** at 10ºC. These crystal structures were determined by the single-crystal X-ray diffraction method at T = 103 K. The diffraction data were collected using Rigaku XtaLAB Synergy-i diffractometer (Cu-Kα radiation). The structure was solved using the SHELXT[5] and refined with SHELXL-2018/3[6] via OLEX2[7]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were put on calculated geometrically, and were refined by applying riding models. Crystal data and structure refinement were summarized in **Table S1-S4**. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 2165148 (**2**); 2165150 (**3mA**); 2165151 (**3n**); and 2165152 (**3oA**).

Table S1. Crystal data and structure refinement for **2**.

	2
Chemical formula	$C_{20}H_7O_5Br_3$
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	–
Crystal system	Triclinic
Space group [No.]	*P*-1 [2]
Crystal color, habit	Metallic black, plate
Crystal size, mm	0.129 × 0.099 × 0.033
a, Å	7.9825(4)
b, Å	9.6307(5)
c, Å	12.1546(6)
α, °	68.286(5)
β, °	76.020(4)
γ, °	83.671(4)
Volume, Å^3	842.17(8)
Z	2
D_{calcd}, g/cm^3	2.236
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	9.196
$2\theta_{max}$ °	68.0090
F(000)	544
Reflns collected	3051
Unique reflns	2788
No. of parameters	255
R1 ($I > 2.00\sigma(i)$)	0.0376
R (all reflection)	0.0401
GOF	1.105

Table S2. Crystal data and structure refinement for **3mA**

	3mA
Chemical formula	$C_{22}H_{13}NO_2$
Recrystallization solvent	$CHCl_3$ / Hexane
Included solvent	–
Crystal system	Monoclinic
Space group [No.]	$P\,2_1/c$ [14]
Crystal color, habit	Clear yellow, block
Crystal size, mm	0.216 × 0.099 × 0.071
a, Å	9.6037(4)
b, Å	11.9960(5)
c, Å	13.4769(5)
α, °	90
β, °	97.696(4)
γ, °	90
Volume, Å^3	1538.63(11)
Z	4
D_{calcd}, g/cm^3	1.396
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	0.719
$2\theta_{max}$ °	68.2740
F(000)	672
Reflns collected	2792
Unique reflns	2356
No. of parameters	226
R1 ($I > 2.00\sigma(i)$)	0.0499
R (all reflection)	0.0566
GOF	1.068

Table S3. Crystal data and structure refinement for **3n**.

	3n
Chemical formula	$C_{20}H_{13}NO_2$
Recrystallization solvent	$CHCl_3$ / Hexane
Included solvent	–
Crystal system	Monoclinic
Space group [No.]	*C* 2/*c* [15]
Crystal color, habit	Clear yellow, block
Crystal size, mm	0.886 × 0.383 × 0.351
a, Å	16.1681(5)
b, Å	8.0980(2)
c, Å	22.3810(7)
α, °	90
β, °	98.728(3)
γ, °	90
Volume, Å^3	2896.39(15)
Z	8
D_{calcd}, g/cm^3	1.373
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	0.715
$2\theta_{max}$ °	68.0800
F(000)	1248
Reflns collected	2635
Unique reflns	2515
No. of parameters	209
R1 ($I > 2.00\sigma(i)$)	0.0332
R (all reflection)	0.0347
GOF	1.068

Table S4. Crystal data and structure refinement for **3oA**.

	3oA
Chemical formula	$C_{26}H_{15}NO_2$
Recrystallization solvent	$CHCl_3$ / Hexane
Included solvent	–
Crystal system	Orthorhombic
Space group [no.]	*P b c a* [61]
Crystal color, habit	Clear orange, block
Crystal size, mm	0.275 × 0.189 × 0.041
a, Å	12.1091(2)
b, Å	13.4501(2)
c, Å	43.2055(9)
α, °	90
β, °	90
γ, °	90
Volume, Å^3	7036.8(2)
Z	8
D_{calcd}, g/cm^3	1.410
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	0.711
$2\theta_{max}$ °	67.8910
F(000)	3104
Reflns collected	6425
Unique reflns	5840
No. of parameters	524
R1 ($I > 2.00\sigma(i)$)	0.0583
R (all reflection)	0.0639
GOF	1.156

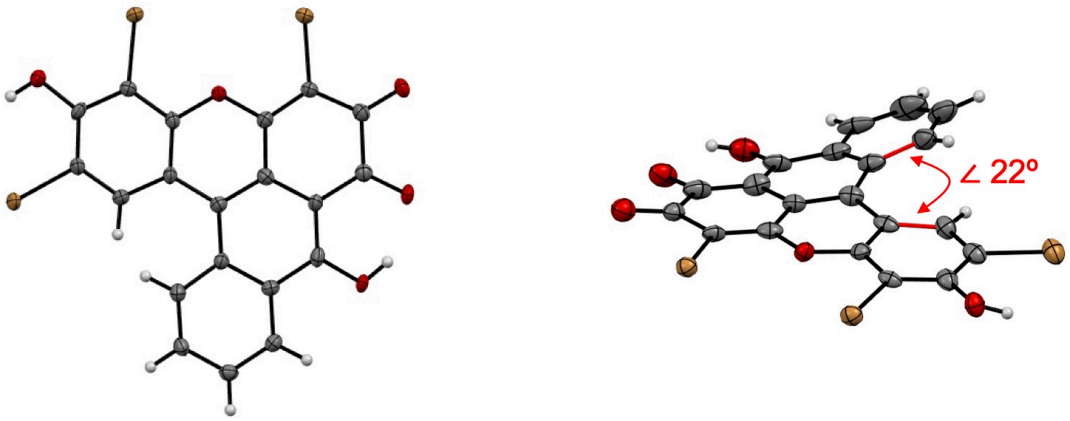


Fig. S1 Top and side views of the X-ray crystal structure for **2**. The thermal ellipsoids are scaled to the 50% probability level.

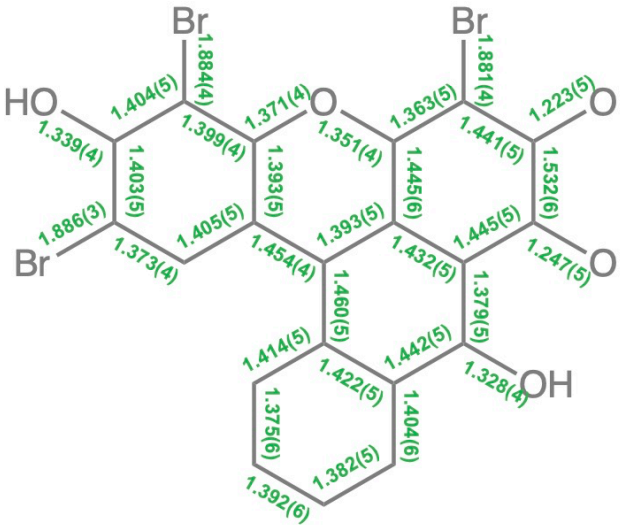


Fig. S2 Bond length (Å) obtained from X-ray crystallographic analysis of **2**.

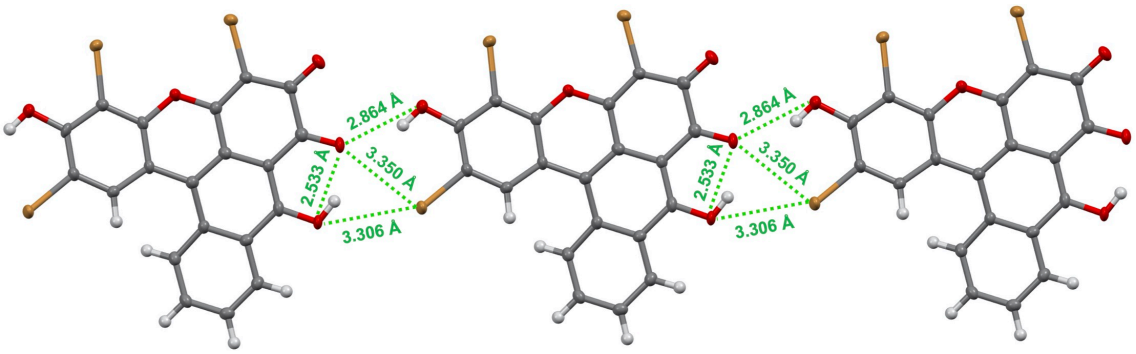


Fig. S3 Intramolecular and intermolecular hydrogen bonding of **2**.

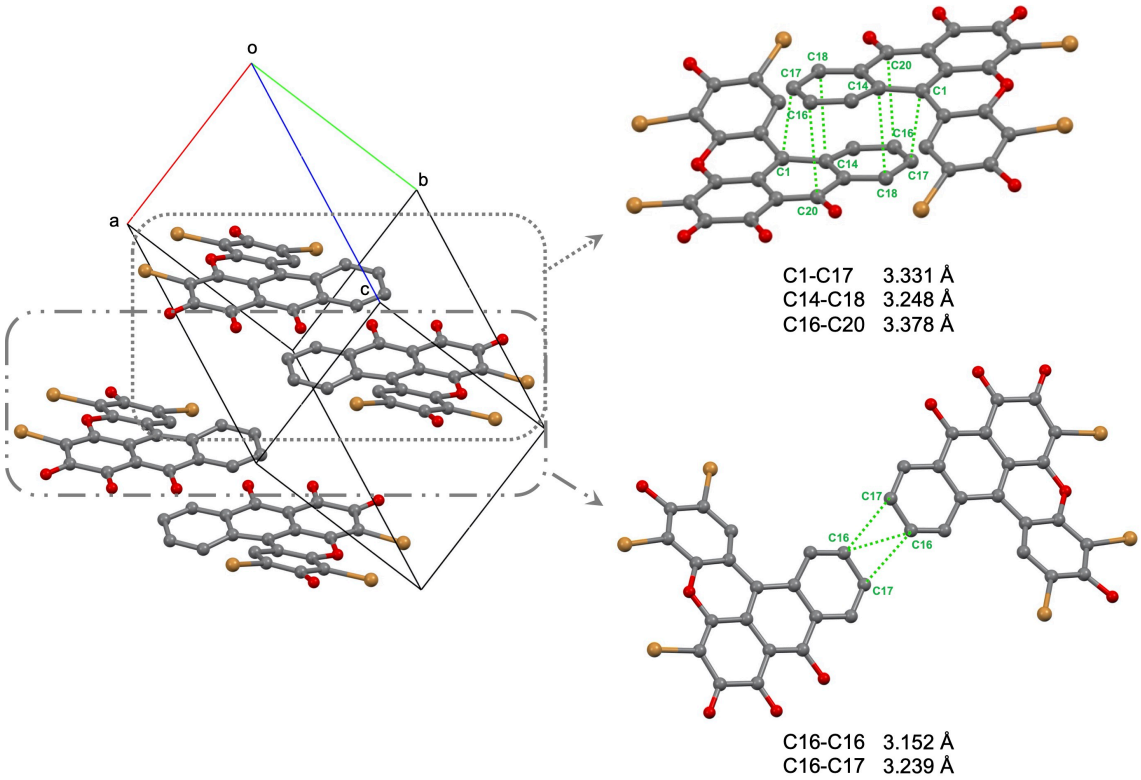


Fig. S4 Short contact of **2** in the X-ray structure. Intermolecular distances less than the van der Waals distance (3.4 Å) are shown in Å.

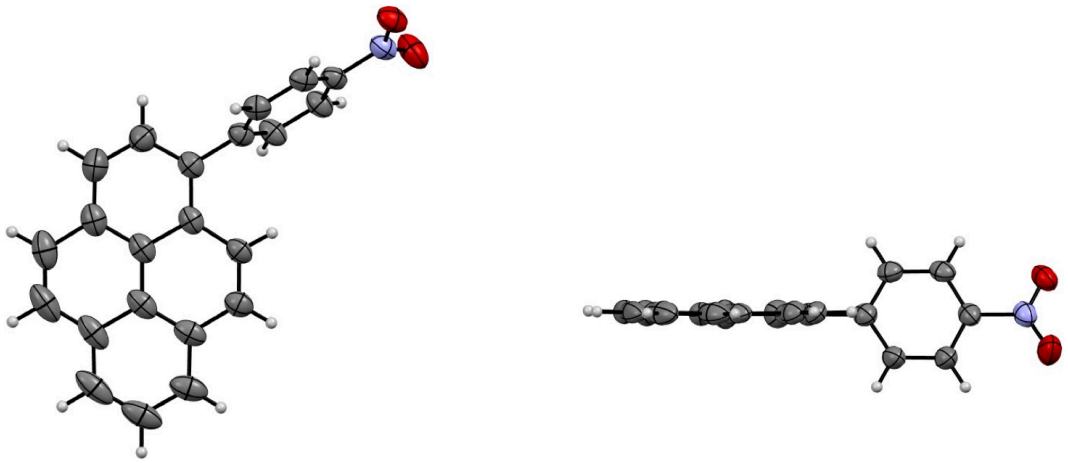


Fig. S5 Top and side views of the X-ray crystal structure for **3mA**. The thermal ellipsoids are scaled to the 50% probability level.

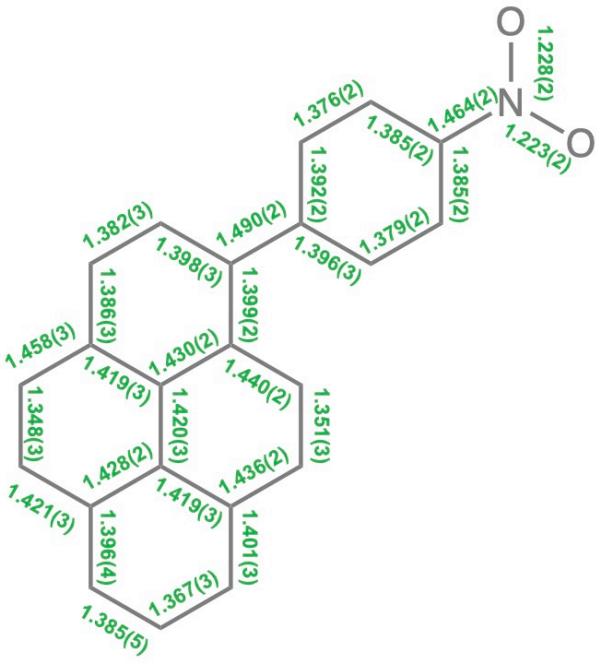


Fig. S6 Bond length (Å) obtained from X-ray crystallographic analysis of **3mA**.

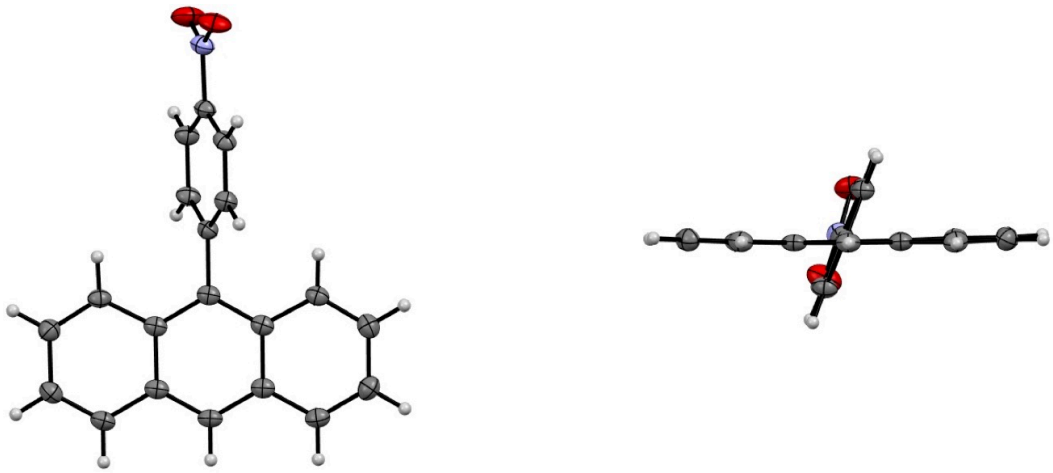


Fig. S7 Top and side views of the X-ray crystal structure for **3n**. The thermal ellipsoids are scaled to the 50% probability level.

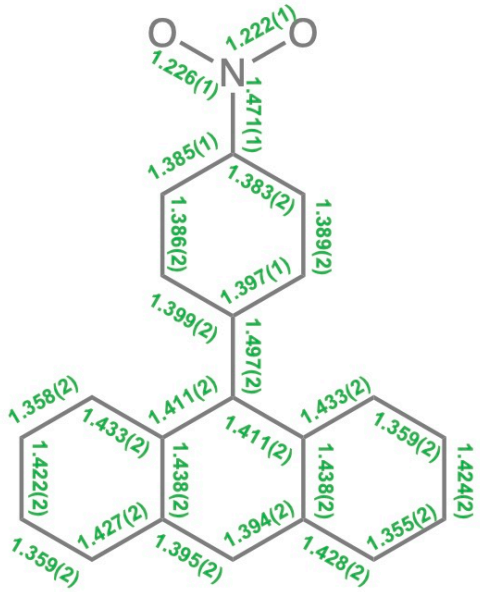


Fig. S8 Bond length (Å) obtained from X-ray crystallographic analysis of **3n**.

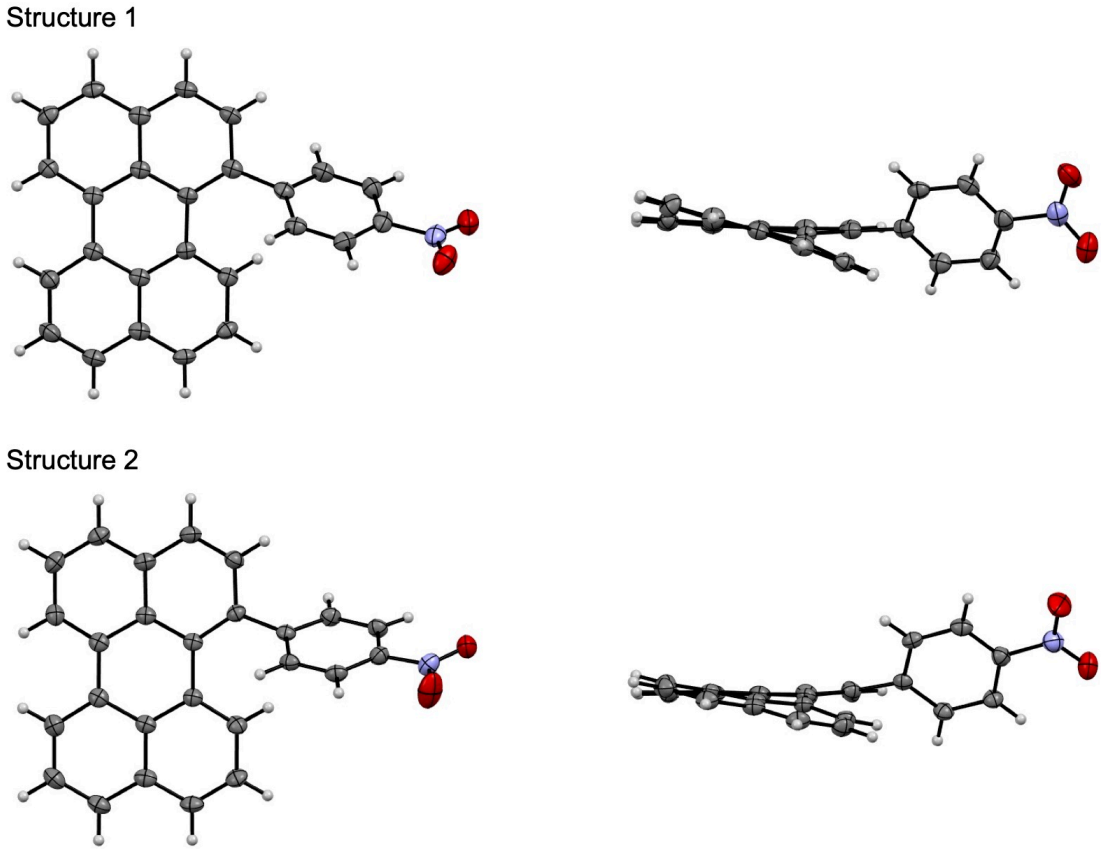


Fig. S9 Top and side views of the X-ray crystal structure for **3oA**. The thermal ellipsoids are scaled to the 50% probability level.

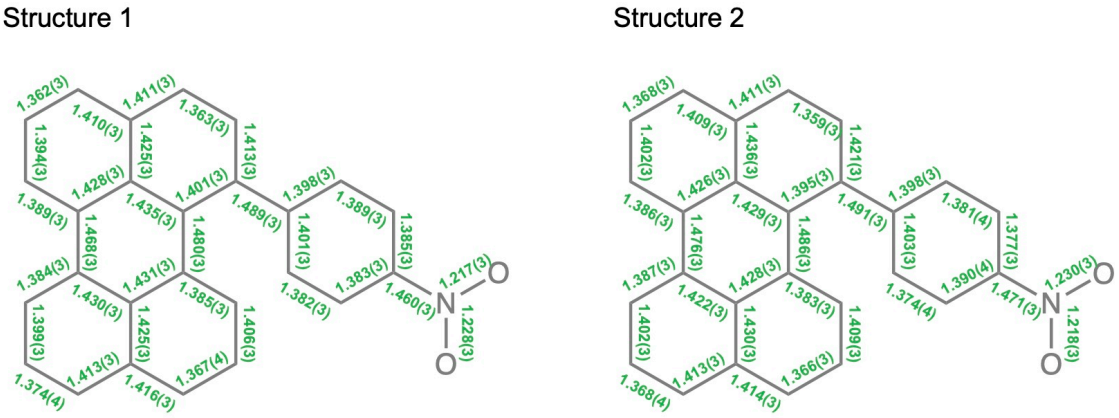


Fig. S10 Bond length (Å) obtained from X-ray crystallographic analysis of **3oA**.

4. Optical Properties of BEY

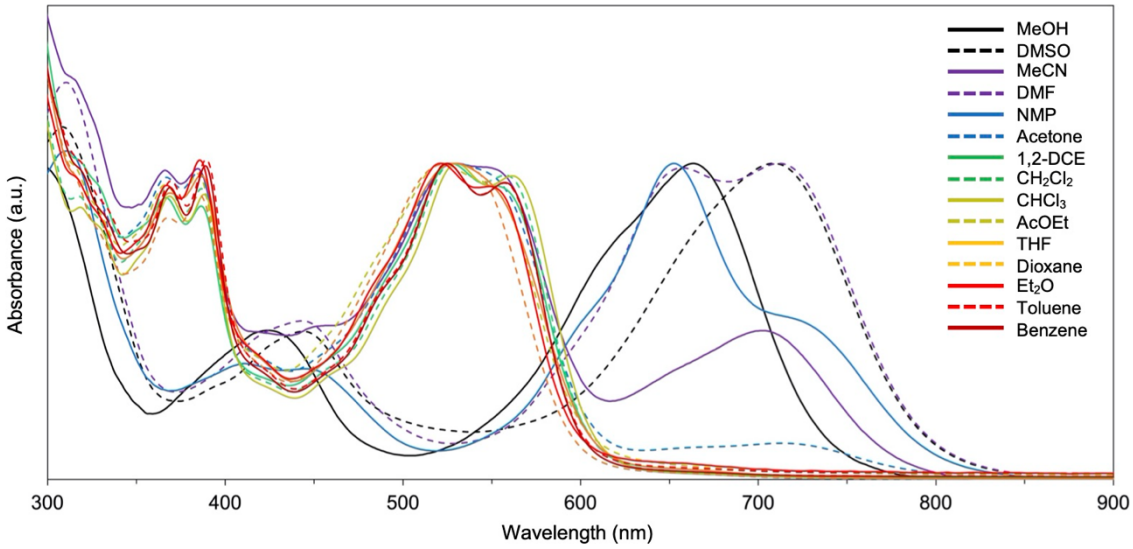


Fig. S11 Absorption spectra of **2** in various organic solvent.

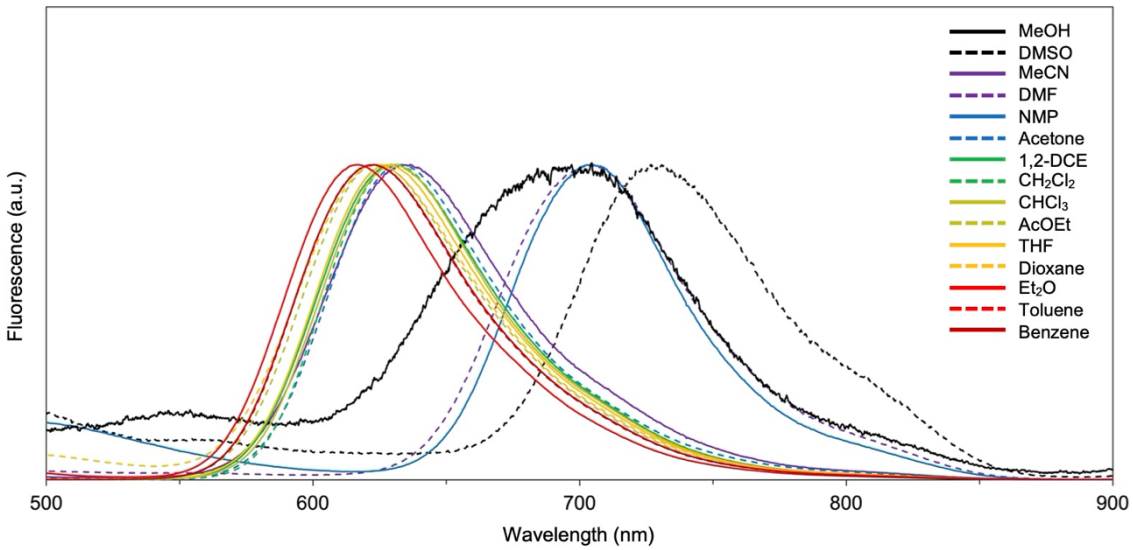
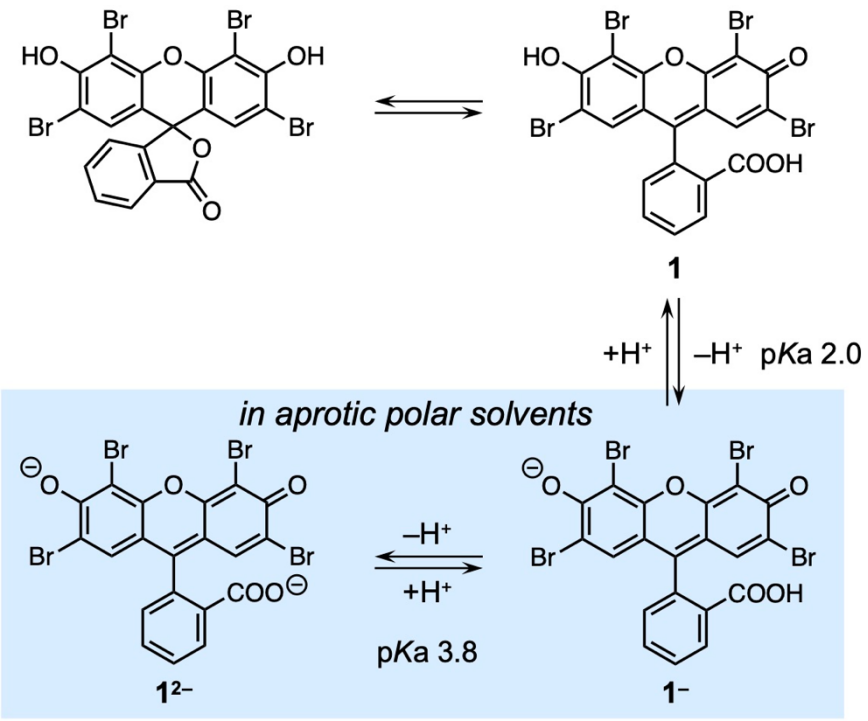


Fig. S12 Emission spectra of **2** in various organic solvent.



Scheme S2. Molecular species formed by **1** in organic solvents.

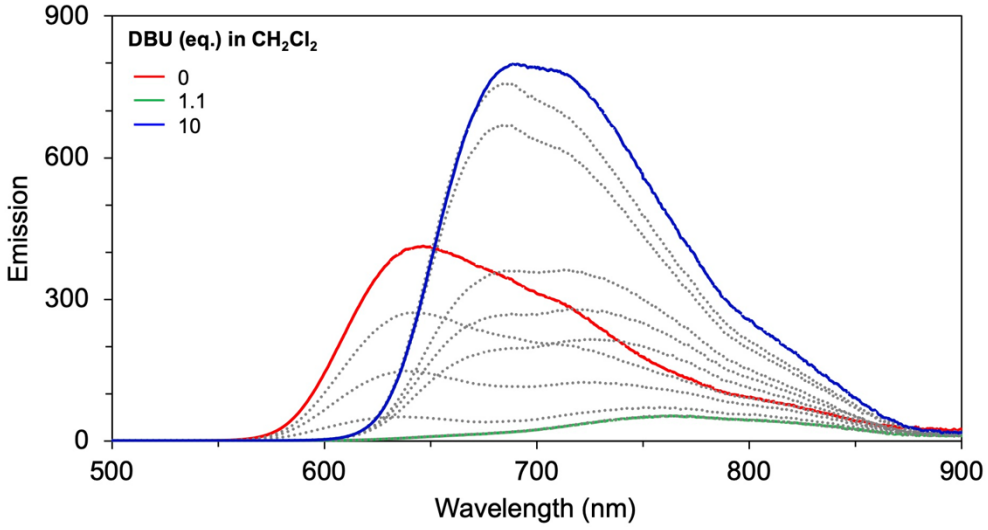


Fig. S13 Emission spectra of **2** in CH_2Cl_2 containing DBU. Concentration of **2** was 50 μM.

Table S5. Optical properties of each molecular species of **BEY** in CH_2Cl_2.

	λ_{abs} (nm)	λ_{fl} (nm)	ε (cm^{-1} M^{-1})	Φ[*1] (%)
2	529	644	13000	6
$\mathbf{2}^{-}$	678	763	21000	–[*2]
$\mathbf{2}^{2-}$	603	690	28000	19

[*1]Relative fluorescence quantum yields (Φ) were calculated by using rhodamine 101 (Φ = 91.3% in ethanol) as the standard. [*2]Difficult to generate a single molecular species.

5. Computational Details

All calculations were performed at the Density Functional Theory (DFT), by means of B3LYP functional level as implemented in Gaussian 09[8]. The 6-31+G(d,p) basis set was used for all atoms. Excitation wavelengths and oscillator strengths were obtained at the density functional level using time-dependent perturbation theory (TDDFT) approach. Vibrational frequency computations verified the nature of the stationary points.

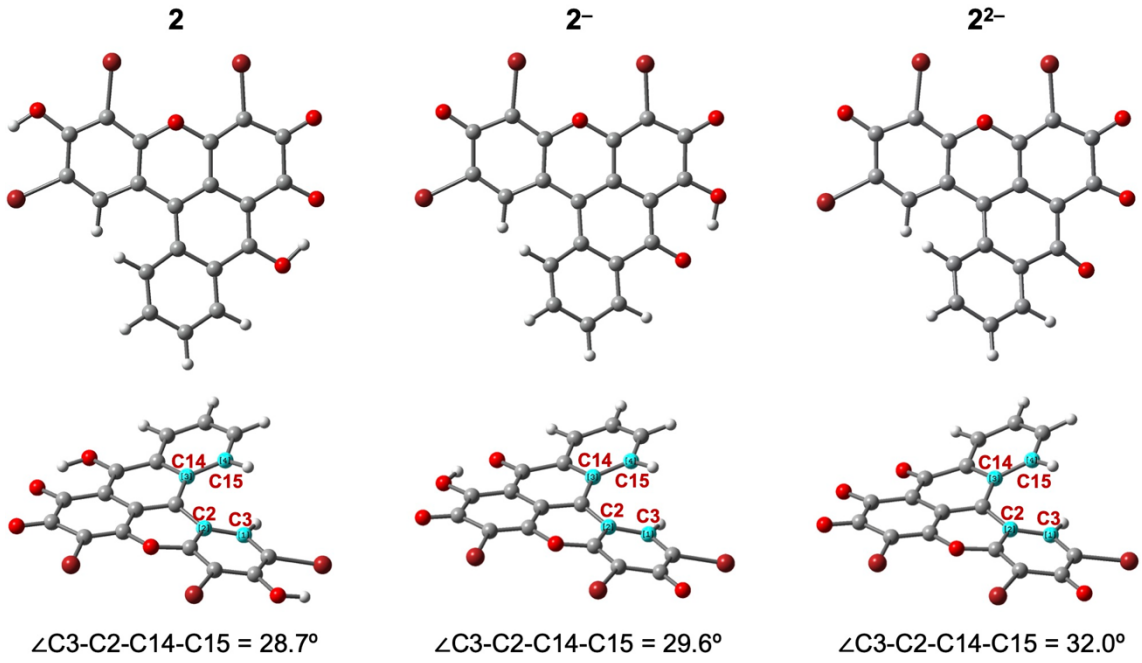
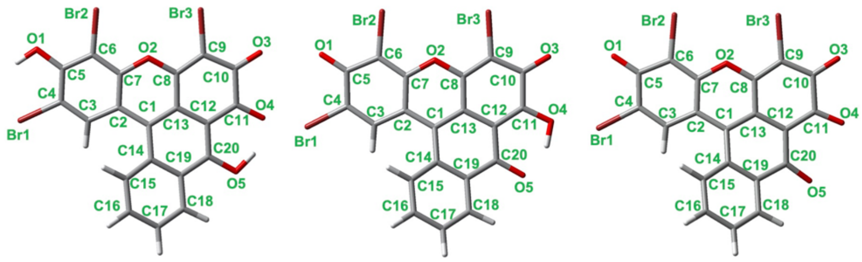


Fig. S14 Calculated optimized structures of **2**, **2**$^{-}$ and **2**$^{2-}$.

Table S6. Selected bond length of optimized structures of **2**, **2**⁻, and **2**²⁻.



2		**2^-**		**2^{2-}**	
Atom	Length [Å]	Atom	Length [Å]	Atom	Length [Å]
C1-C2	1.446	C1-C2	1.428	C1-C2	1.451
C1-C13	1.394	C1-C13	1.408	C1-C13	1.409
C1-C14	1.458	C1-C14	1.477	C1-C14	1.459
C2-C3	1.408	C2-C3	1.426	C2-C3	1.418
C2-C7	1.411	C2-C7	1.433	C2-C7	1.415
C3-C4	1.384	C3-C4	1.366	C3-C4	1.376
C4-C5	1.406	C4-C5	1.466	C4-C5	1.453
C5-C6	1.399	C5-C6	1.454	C5-C6	1.447
C6-C7	1.398	C6-C7	1.379	C6-C7	1.390
C8-C9	1.371	C8-C9	1.385	C8-C9	1.377
C8-C13	1.450	C8-C13	1.424	C8-C13	1.449
C9-C10	1.455	C9-C10	1.444	C9-C10	1.441
C10-C11	1.537	C10-C11	1.488	C10-C11	1.556
C11-C12	1.453	C11-C12	1.401	C11-C12	1.456
C12-C13	1.431	C12-C13	1.438	C12-C13	1.441
C12-C20	1.399	C12-C20	1.445	C12-C20	1.451
C14-C15	1.417	C14-C15	1.412	C14-C15	1.420
C14-C19	1.430	C14-C19	1.421	C14-C19	1.420
C15-C16	1.386	C15-C16	1.392	C15-C16	1.388
C16-C17	1.406	C16-C17	1.400	C16-C17	1.406
C17-C18	1.383	C17-C18	1.389	C17-C18	1.388
C18-C19	1.411	C18-C19	1.403	C18-C19	1.406
C19-C20	1.440	C19-C20	1.478	C19-C20	1.498
C4-Br1	1.907	C4-Br1	1.907	C4-Br1	1.924
C5-O1	1.347	C5-O1	1.242	C5-O1	1.255
C6-Br2	1.882	C6-Br2	1.893	C6-Br2	1.903
C7-O2	1.360	C7-O2	1.368	C7-O2	1.370
C8-O2	1.357	C8-O2	1.357	C8-O2	1.357
C9-Br3	1.883	C9-Br3	1.890	C9-Br3	1.911
C10-O3	1.222	C10-O3	1.240	C10-O3	1.235
C11-O4	1.242	C11-O4	1.324	C11-O4	1.235
C20-O5	1.325	C20-O5	1.261	C20-O5	1.248

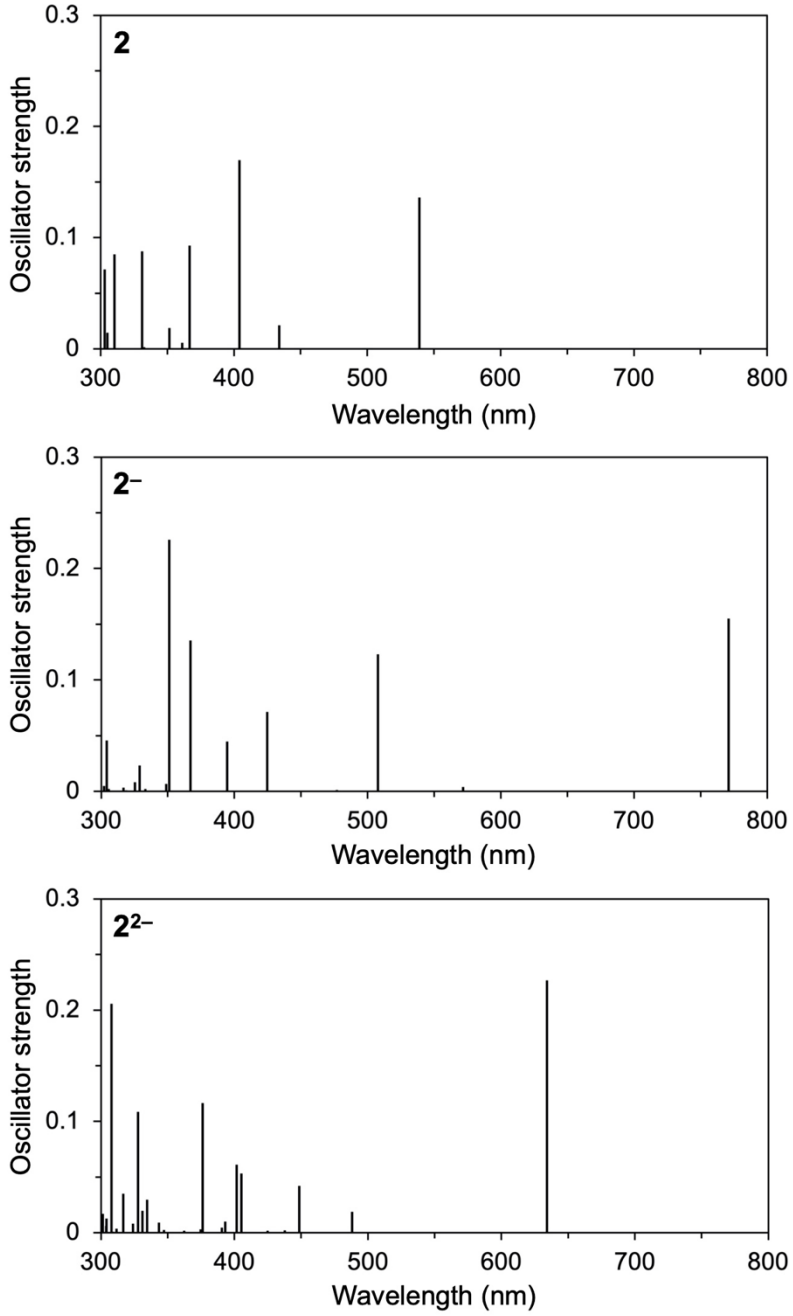
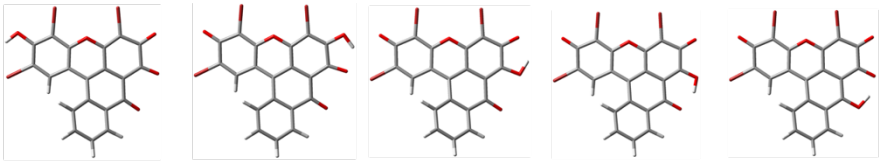


Fig. S15 Calculated absorption spectra of **2**, $\mathbf{2}^{-}$, and $\mathbf{2}^{2-}$. Calculations were performed at TDB3LYP/6-31+G(d,p) level.

Table S7. Energy differences between 2^- isomers (**A**~**E**). 2^- has 5 isomers (**A**~**E**) depending on the position and orientation of the hydroxyl group. The structure of **D** showed the lowest energy in all calculations.



	A	B	C	D	E
Computational level	**[hartree]**	**[hartree]**	**[hartree]**	**[hartree]**	**[hartree]**
B3LYP/6-31+G(d,p)	-8857.190941	-8857.206145	-8857.211425	-8857.213850	-8857.210809
ωB97XD/6-31+G(d,p)	-8856.880502	-8856.892474	-8856.897980	-8856.898956	-8856.896724
M06-2X/6-31+G(d,p)	-8856.982844	-8856.992165	-8856.998379	-8856.998858	-8856.996852

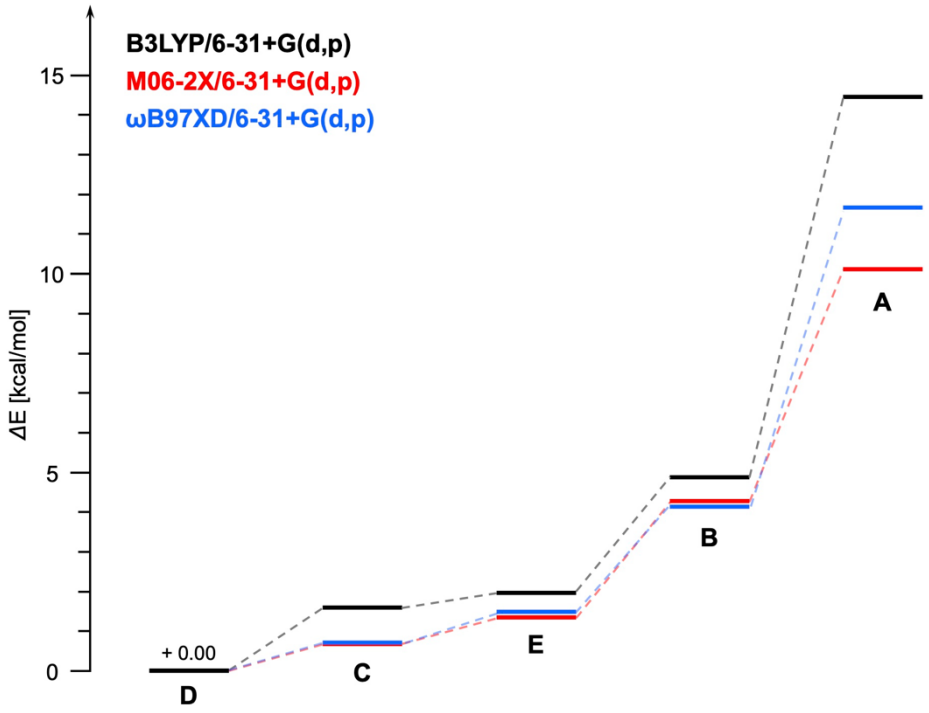


Fig. S16 Energy differences between 2^- isomers. The energy of the most stable isomer **D** was set to 0 kcal/mol.

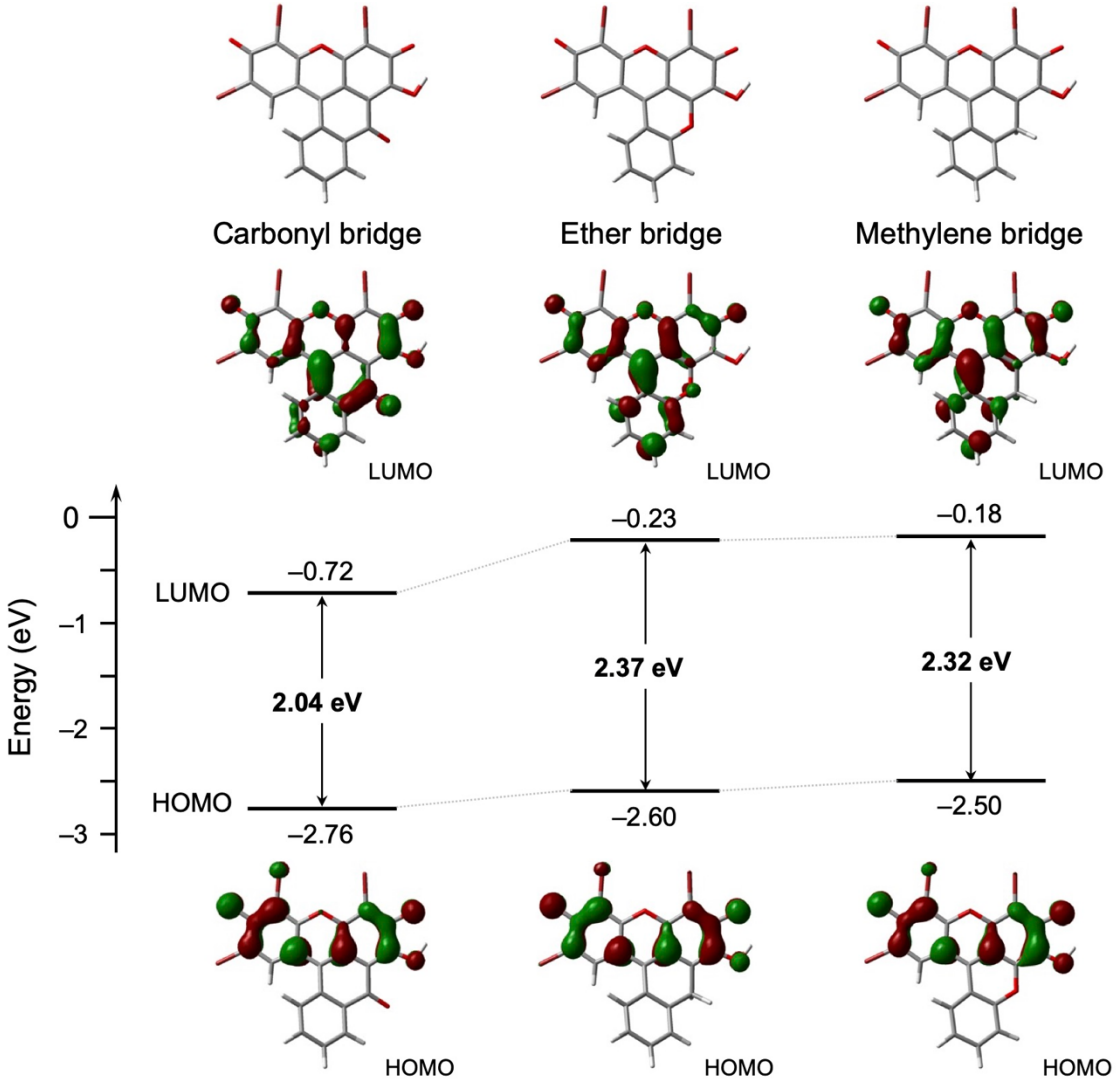
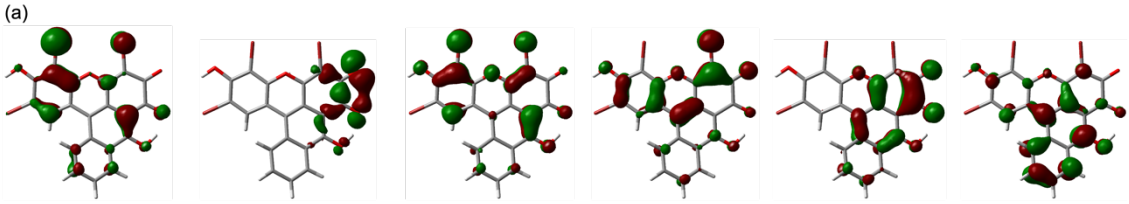


Fig. S17 Relationship between intramolecular bridged structures and molecular orbitals.

(a)



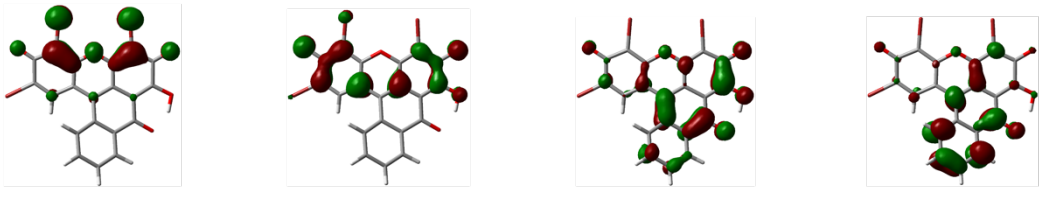
HOMO-3 –7.47 eV | HOMO-2 –7.23 eV | HOMO-1 –6.95 eV | HOMO –6.21 eV | LUMO –3.57 eV | LUMO+1 –2.73 eV

(b)

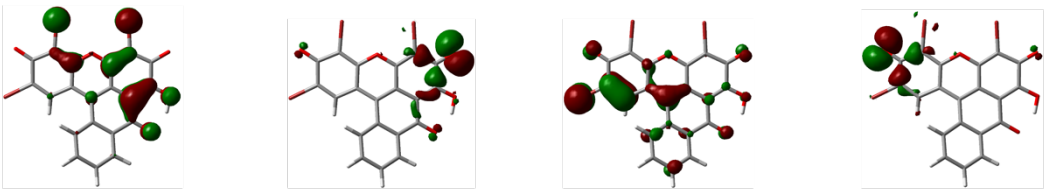
Excited state	Wavelength [nm]	*f*	Contribution
1	539.20	0.1360	HOMO → LUMO (91%) HOMO → LUMO+1 (3%) HOMO–1 → LUMO (3%)
2	501.33	0.0006	HOMO–2 → LUMO (97%)
3	433.88	0.0212	HOMO–1 → LUMO (92%) HOMO → LUMO+1 (4%)
4	404.14	0.1697	HOMO → LUMO+1 (87%) HOMO–3 → LUMO (5%) HOMO → LUMO (3%) HOMO–1 → LUMO (3%)

Fig. S18 (a) Frontier molecular orbitals of **2** (isovalue = 0.04). (b) Calculated absorption wavelength, oscillator strength (*f*), and major contribution for **2**. Absorption wavelength of more than 400 nm are shown.

(a)



HOMO-1 –3.58 eV | HOMO –2.65 eV | LUMO –0.87 eV | LUMO+1 0.21 eV



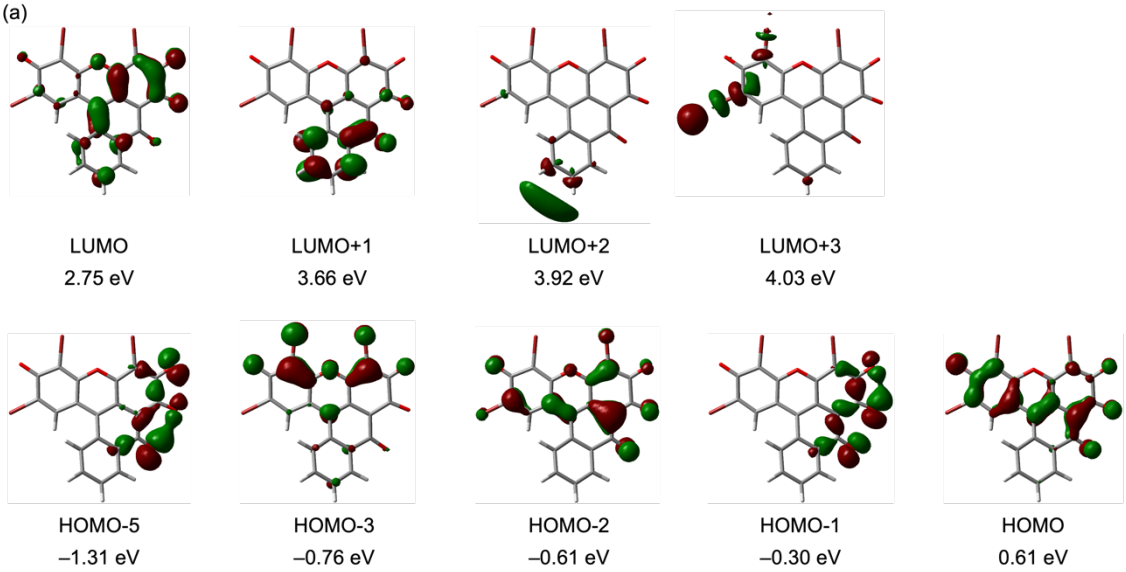
LUMO-5 –4.50 eV | LUMO-4 –4.31 eV | HOMO-3 –4.26 eV | HOMO-2 –4.02 eV

(b)

Excited state	Wavelength [nm]	*f*	Contribution
1	770.93	0.1552	HOMO → LUMO (97%) HOMO → LUMO+1 (3%) LUMO → HOMO (2%)
2	571.68	0.0040	HOMO–1 → LUMO (98%)
3	507.74	0.1231	HOMO → LUMO+1 (94%) HOMO → LUMO (3%)
4	491.38	0.0007	HOMO–4 → LUMO (68%) HOMO–2 → LUMO (29%)
5	476.93	0.0013	HOMO–2 → LUMO (68%) HOMO–4 → LUMO (29%)
6	424.79	0.0713	HOMO–5 → LUMO (59%) HOMO–3 → LUMO (6%) HOMO–1 → LUMO+1 (4%)

Fig. S19 (a) Frontier molecular orbitals of $\mathbf{2}^-$ (isovalue = 0.04). (b) Calculated absorption wavelength, oscillator strength (*f*), and major contribution for $\mathbf{2}^-$. Absorption wavelength of more than 400 nm are shown.

(a)



(b)

Excited state	Wavelength [nm]	*f*	Contribution
1	634.22	0.2268	HOMO → LUMO (95%)
2	488.10	0.0186	HOMO → LUMO+1 (94%) HOMO–2 → LUMO (4%)
3	448.72	0.0420	HOMO–2 → LUMO (91%) HOMO → LUMO+1 (3%)
4	437.77	0.0021	HOMO → LUMO+2 (50%) HOMO → LUMO+3 (46%)
5	424.96	0.0017	HOMO → LUMO+2 (49%) HOMO → LUMO+3 (48%)
6	405.15	0.0531	HOMO–3 → LUMO (41%) HOMO–1 → LUMO+1 (27%) HOMO–5 → LUMO (15%) HOMO–5 → LUMO+1 (2%)
7	401.63	0.0610	HOMO–1 → LUMO+1 (44%) HOMO–3 → LUMO (41%) HOMO–5 → LUMO (4%) HOMO–5 → LUMO+1 (2%)

Fig. S20 (a) Frontier molecular orbitals of $\mathbf{2}^{2-}$ (isovalue = 0.04). (b) Calculated absorption wavelength, oscillator strength (*f*), and major contribution for $\mathbf{2}^{2-}$. Absorption wavelength of more than 400 nm are shown.

6. Photoredox catalysis of BEY

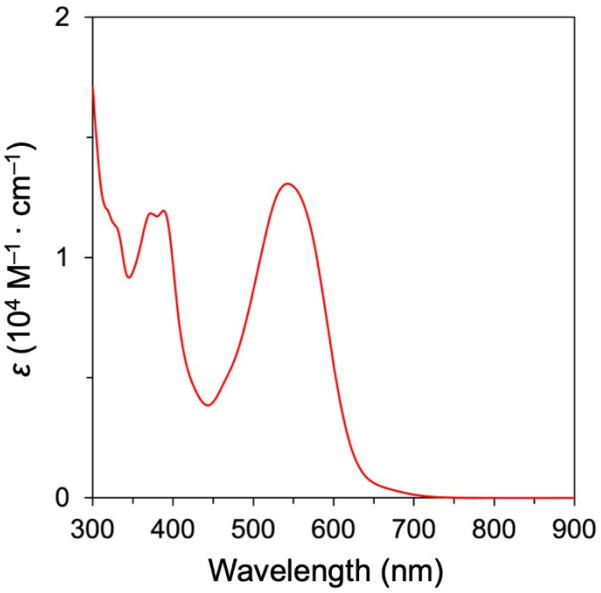
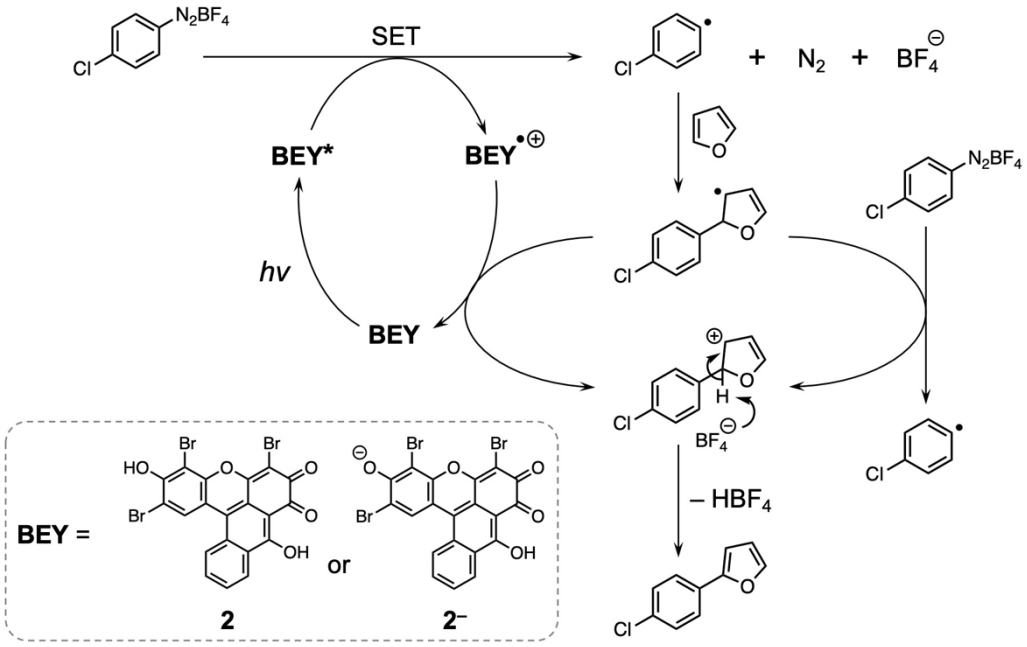


Fig. S21 Absorption spectrum of **2** in DMSO containing TFA.

Scheme S3. Estimated mechanism for photocatalytic direct C–H arylation of heteroarenes.[2]



7. Electrochemical Properties

Cyclic voltammetry measurements were carried out with a Hokuto Denko HZ-7000 voltammetric analyzer. The cell contained inlets for a glassy carbon disk working electrode of 3.0 mm diameter and a platinum-wire counter electrode. The reference electrode was $Ag/AgNO_3$ (0.1 M in MeCN). The scan rate was 100 mV/s. Ferrocene (Fc) was used as an internal standard and potentials were referenced to Fc/Fc^+. The referenced value was converted to SCE by adding 0.40 V. The redox potentials of **BEY** in the ground state ($E_{ox}^{1/2}$, $E_{red}^{1/2}$) and the singlet excited states (E_{ox}^{S1}, E_{red}^{S1}) are collected in **Table S9**. The excited state redox potentials were calculated using equations 1 and 2.

$$E_{ox}^{S1} = E_{ox}^{1/2} - E_{0,0}^{S1} \quad \text{eq. 1}$$

$$E_{red}^{S1} = E_{red}^{1/2} + E_{0,0}^{S1} \quad \text{eq. 2}$$

$E_{0,0}^{S1}$ is the excited state energy of **BEY**, which is determined by using maximum wavelength of emission.

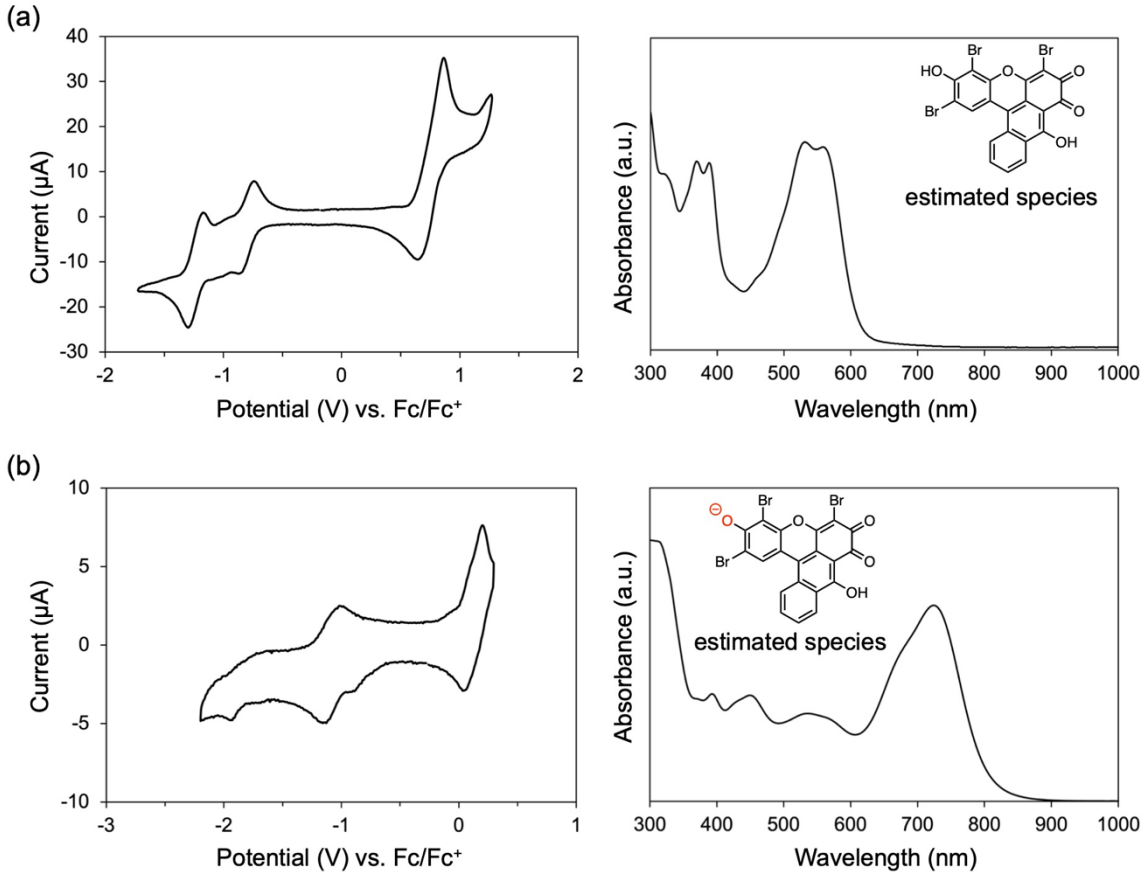


Fig. S22 Cyclic voltammogram of **BEY** in (a) 0.1 M n-Bu_4NClO_4/CH_2Cl_2, and (b) 0.1 M n-Bu_4NClO_4/NMP solution under Ar. The right panels showed the absorption spectra of the measured solutions. From these absorption spectra, it is estimated that **BEY** exists as **2** in (a) and $\mathbf{2}^-$ in (b).

Table S8. Ground state redox potentials of **2** and $\mathbf{2}^-$ estimated from Fig. S21

	ground state redox potentials (V vs Fc/Fc+)		measurement conditions
	$E_{ox}^{1/2}$	$E_{red}^{1/2}$	
2 *1	0.76	–0.74, –1.17	0.1 M n-Bu_4NClO_4 /CH_2Cl_2
$\mathbf{2}^-$ *1	0.11	–1.09	0.1 M n-Bu_4NClO_4 /NMP

*1The molecular species of **BEY** were estimated from the absorption spectra of the measurement solutions.

Table S9. Electrochemical properties of **2** and **2**$^{-}$

	excited state energies[*1] (eV)	ground state redox potentials (V vs SCE)		excited state redox potentials[*2] (V vs SCE)	
	$E_{0,0}^{S1}$	$E_{ox}^{1/2}$	$E_{red}^{1/2}$	E_{ox}^{S1}	E_{red}^{S1}
2	1.97	1.16	–0.34	–0.81	+1.63
2^{-}	1.71	0.51	–0.69	–1.20	+1.02

[*1]Determined by using the maximum wavelength of emission. [*2]Calculated using the excited state energies and ground state redox potentials.

8. Optical Properties of arylated fluorescent dyes

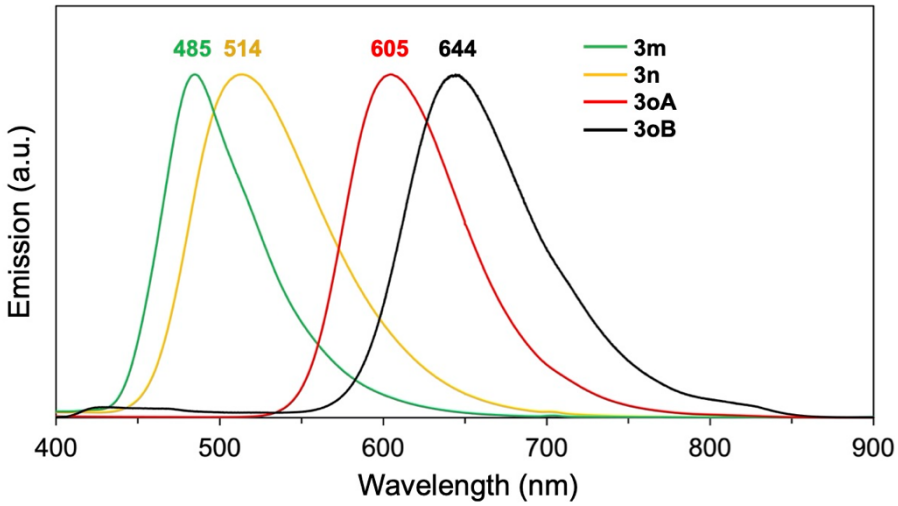


Fig. S23 Solid state fluorescence of **3m**, **3n** and **3o**.

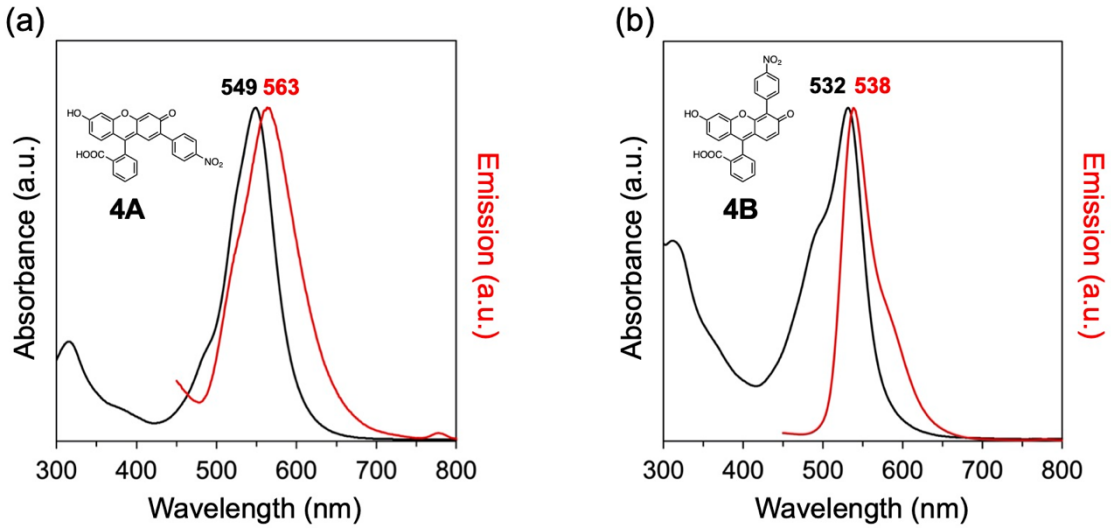


Fig. S24 Absorption and emission spectra of (a) **4A** and (b) **4B** in DMSO.

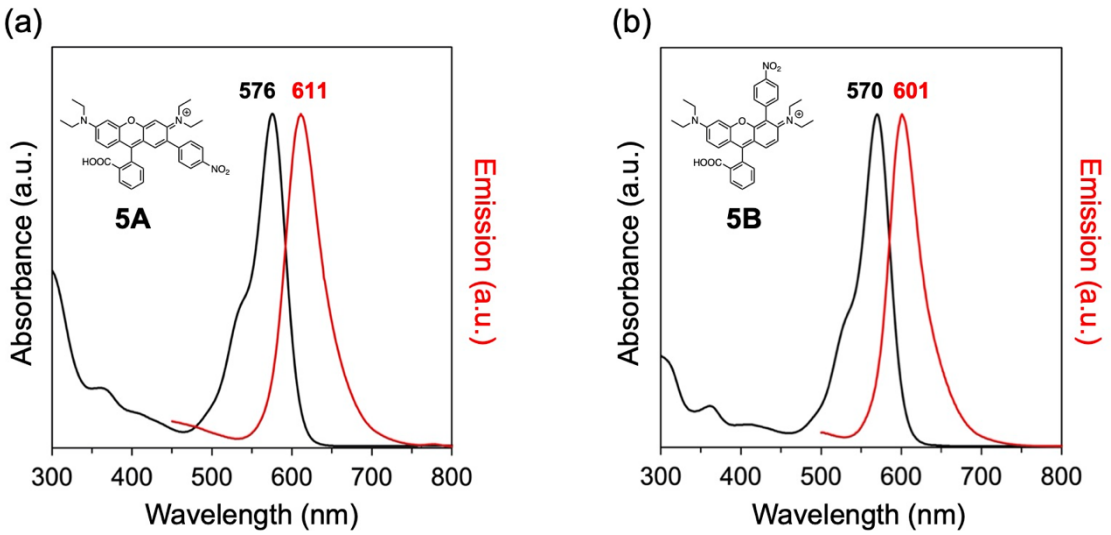
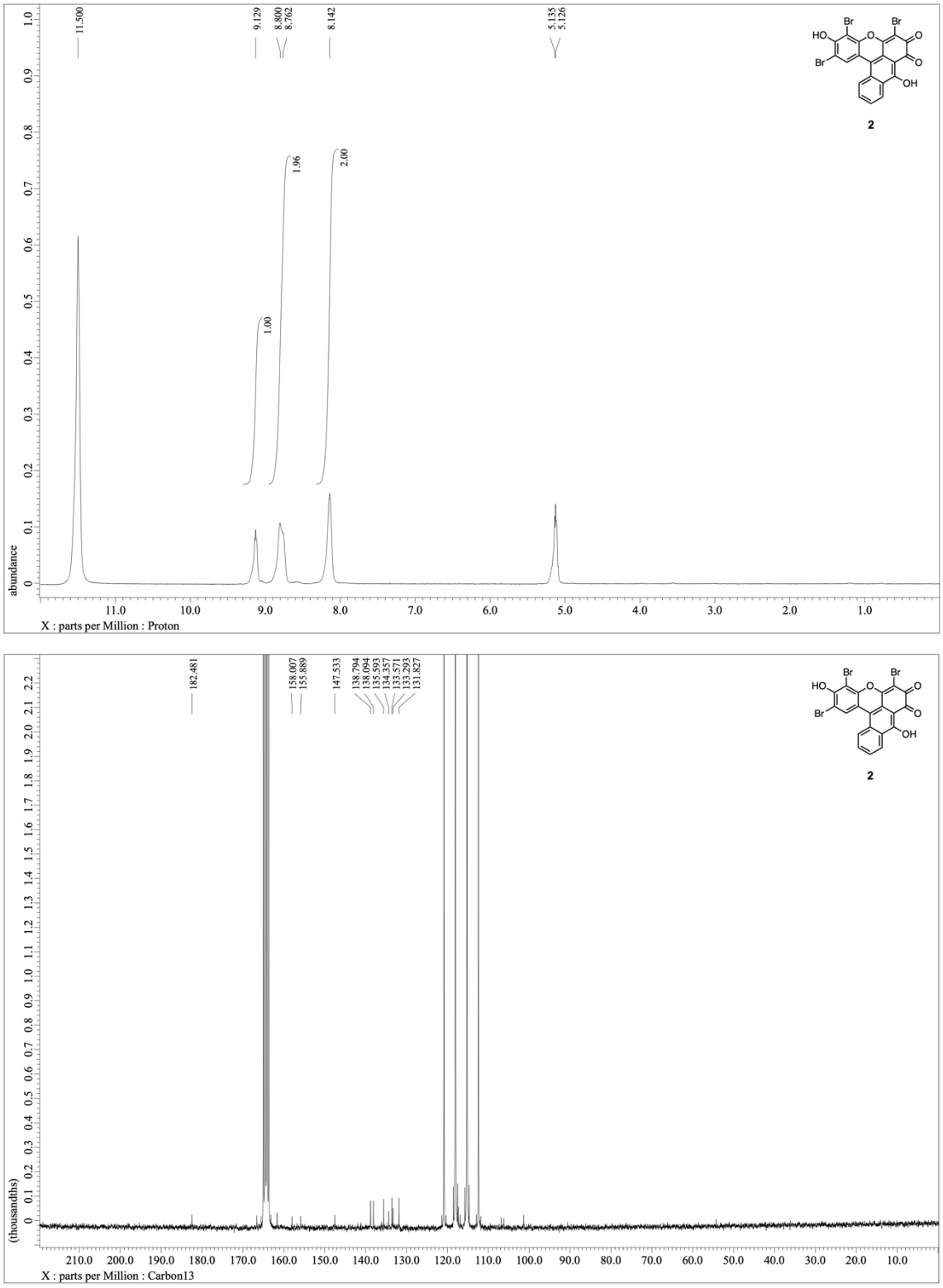
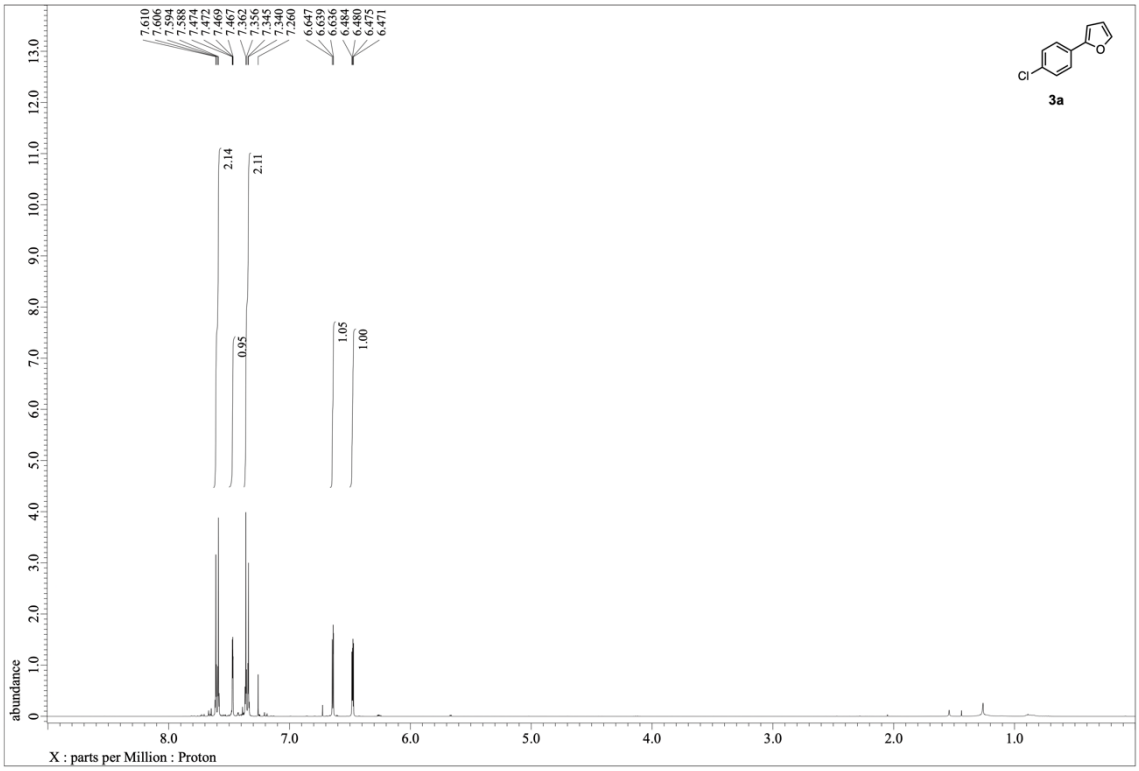


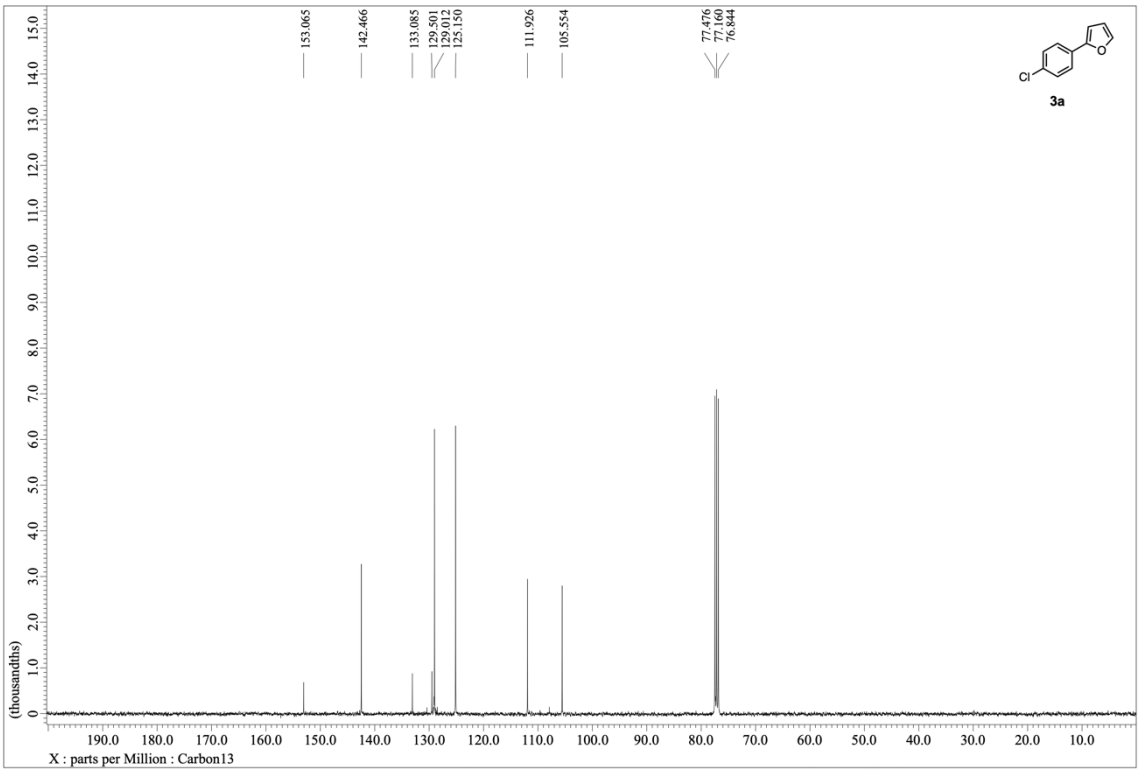
Fig. S25 Absorption and emission spectra of (a) **5A** and (b) **5B** in DMSO containing 1% TFA.

9. NMR Spectra of Compounds

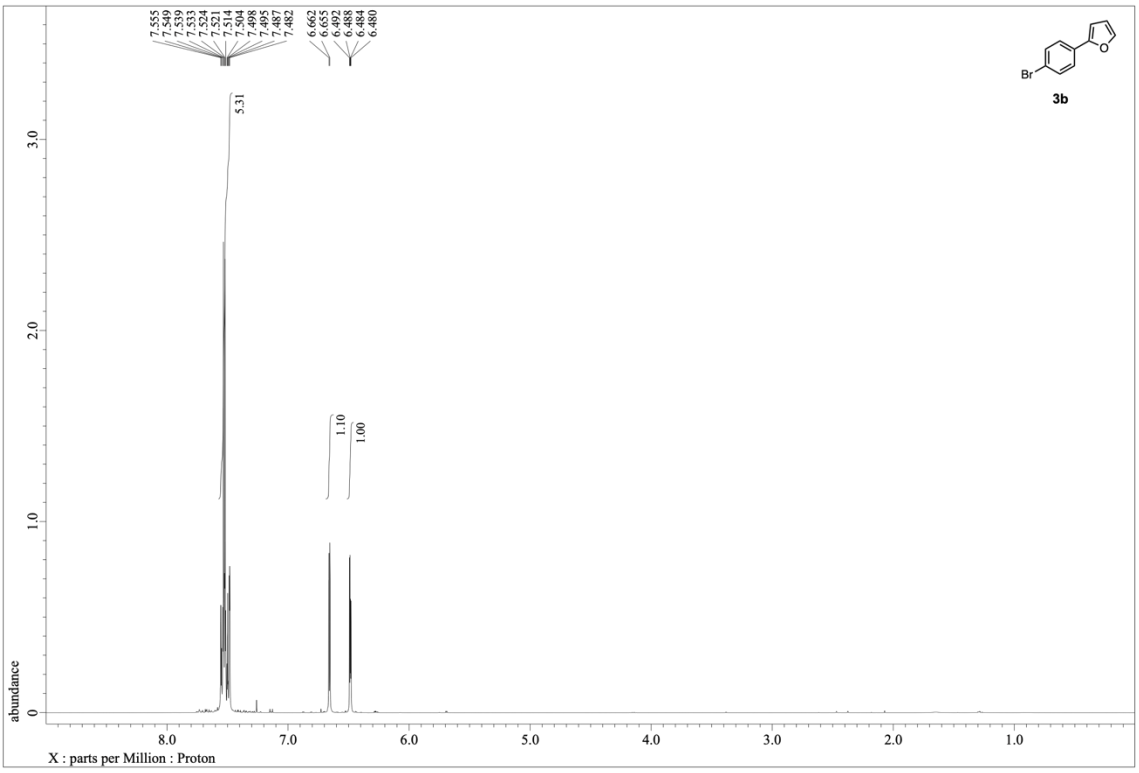


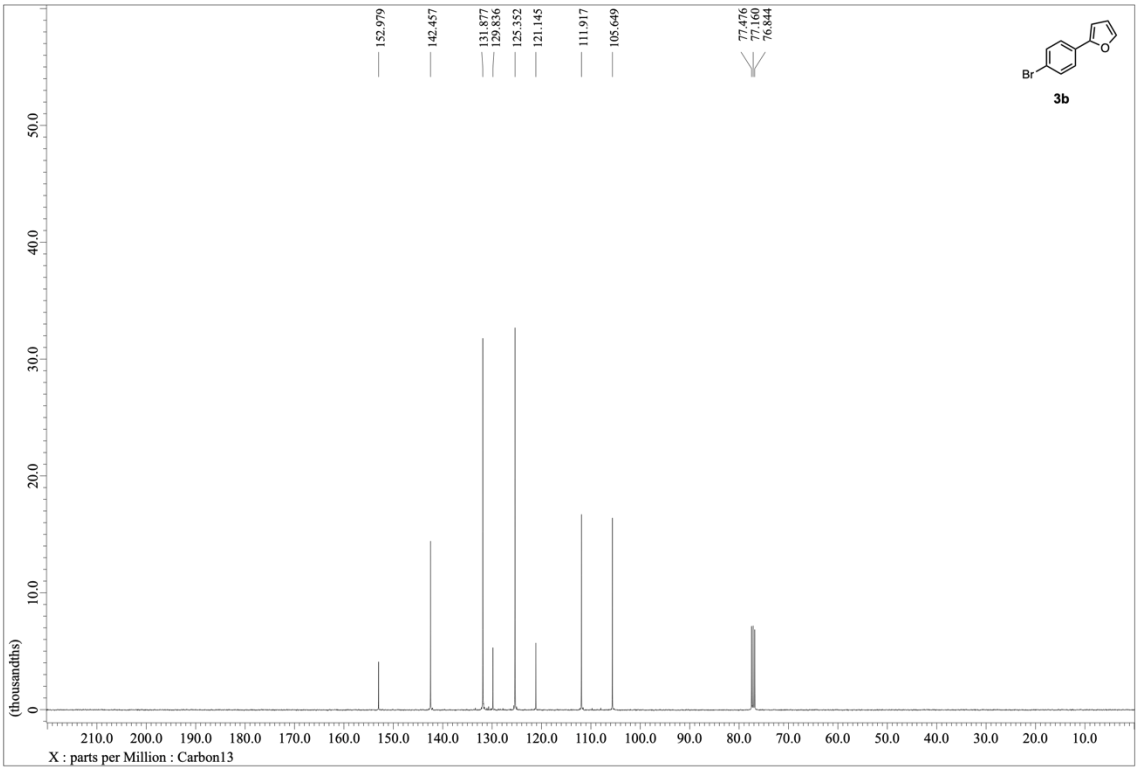
^{1}H (top) and ^{13}C (bottom) NMR spectra of **2** at 25°C in trifluoroacetic acid-d.



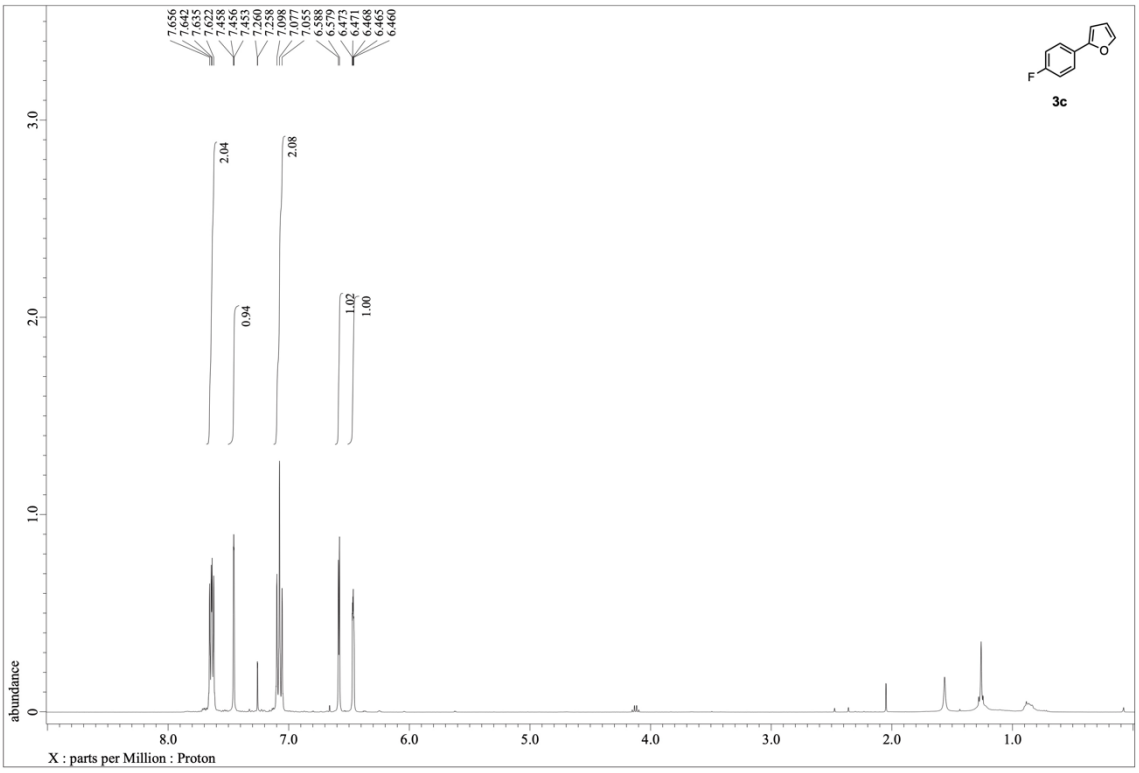


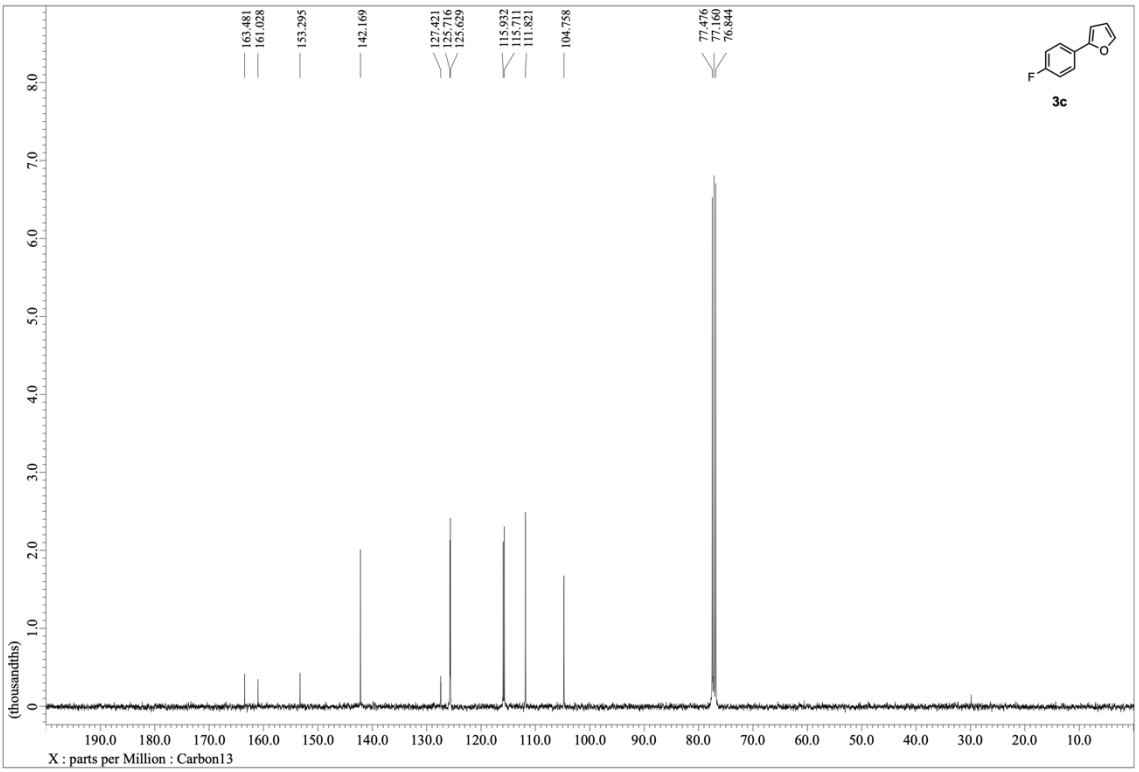
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3a** at 25°C in $CDCl_3$.



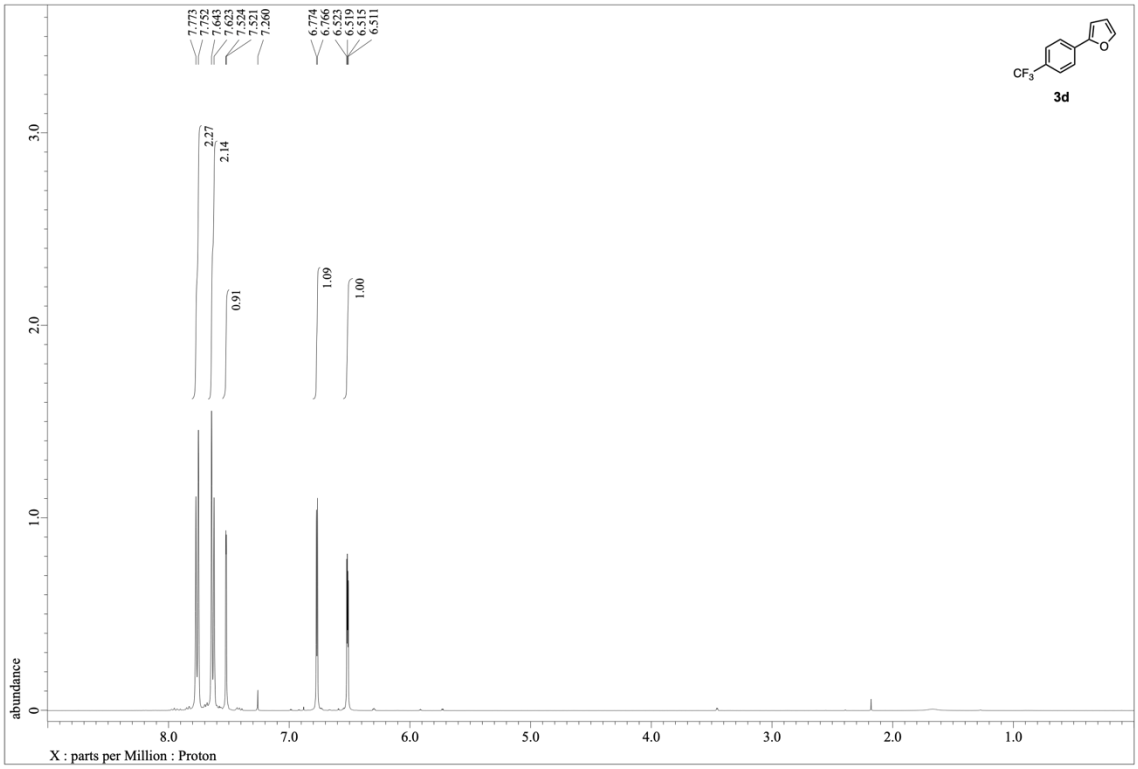


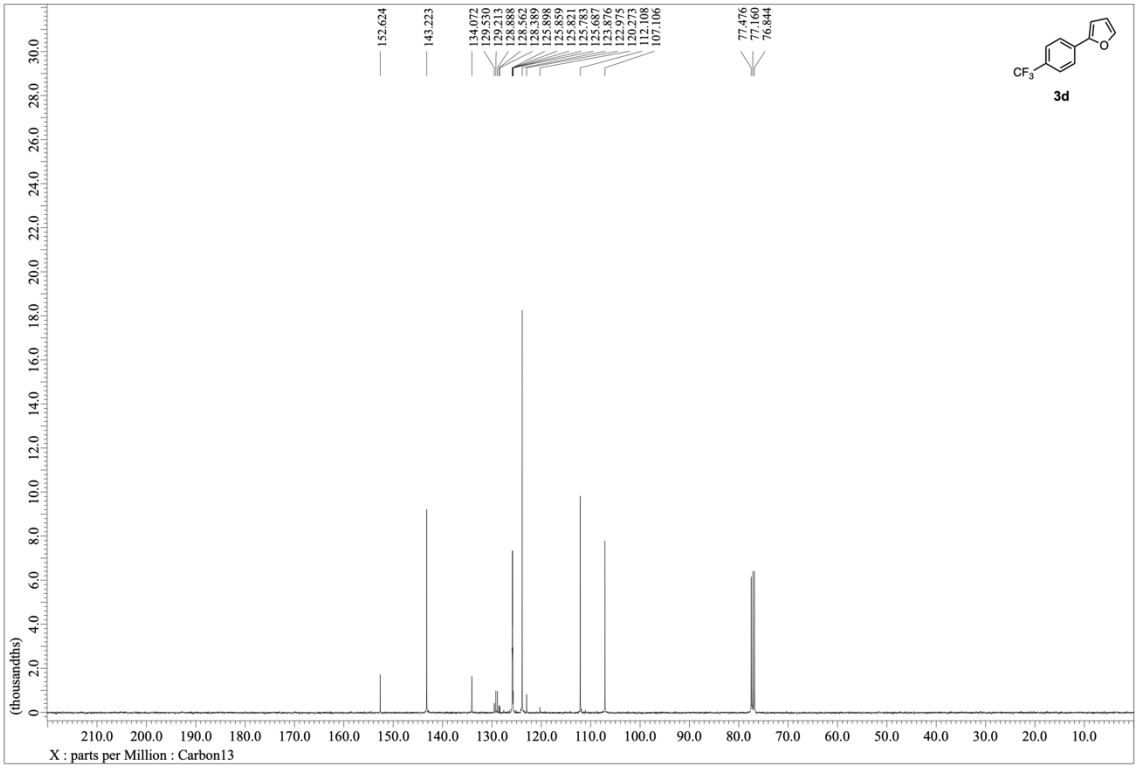
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3b** at 25°C in $CDCl_3$.



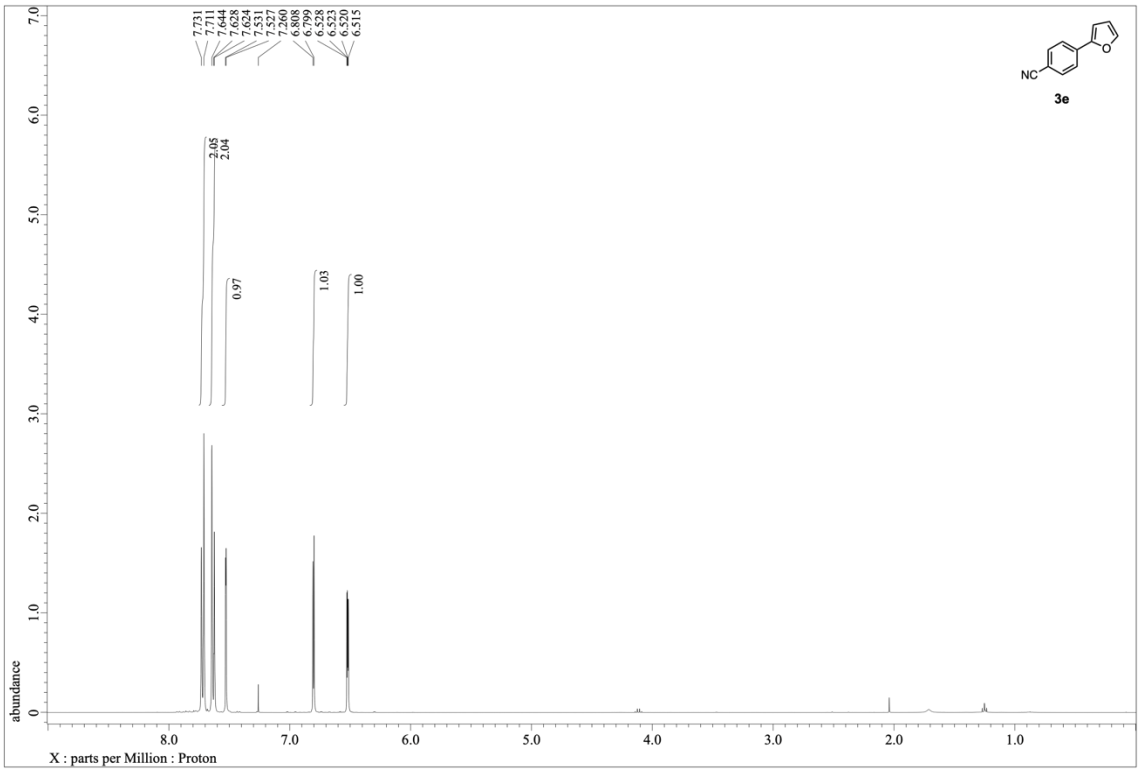


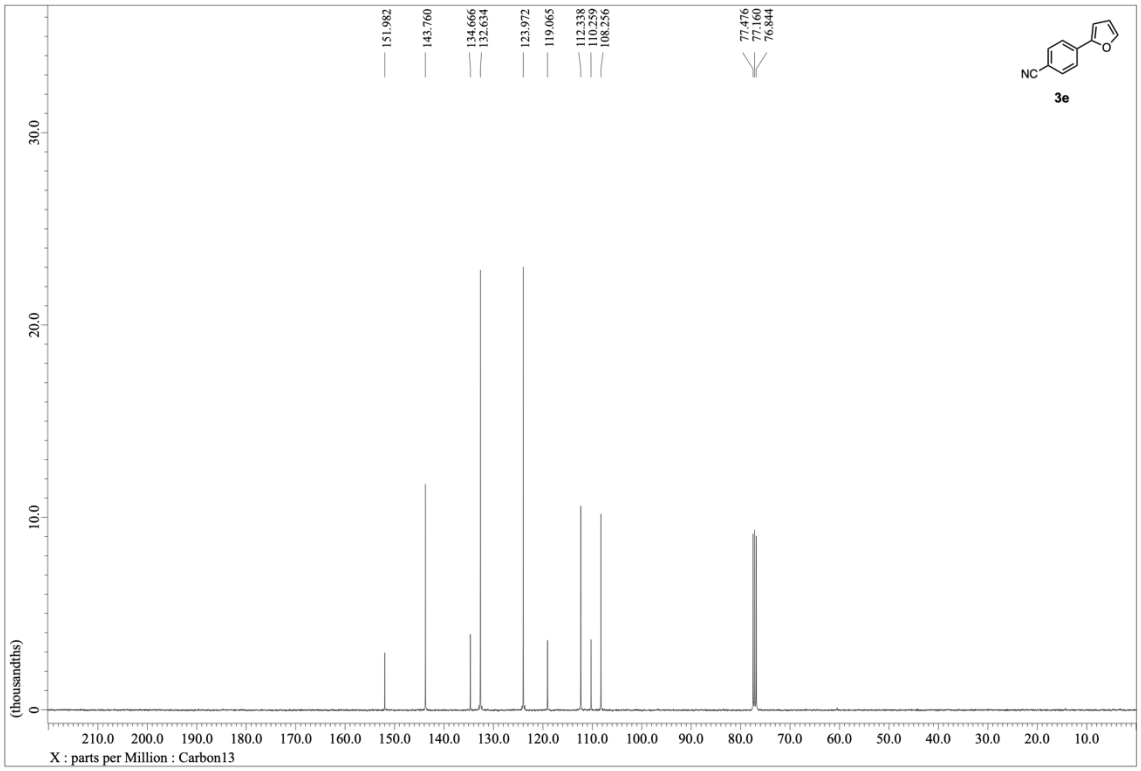
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3c** at 25°C in $CDCl_3$.



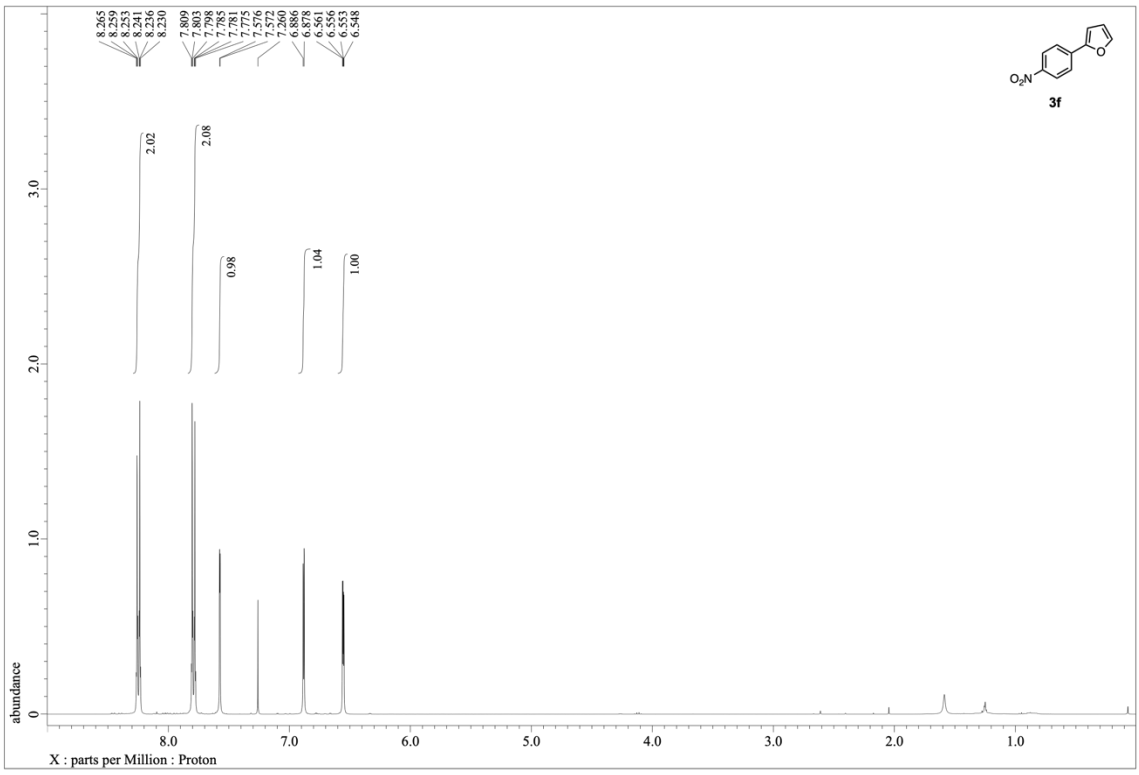


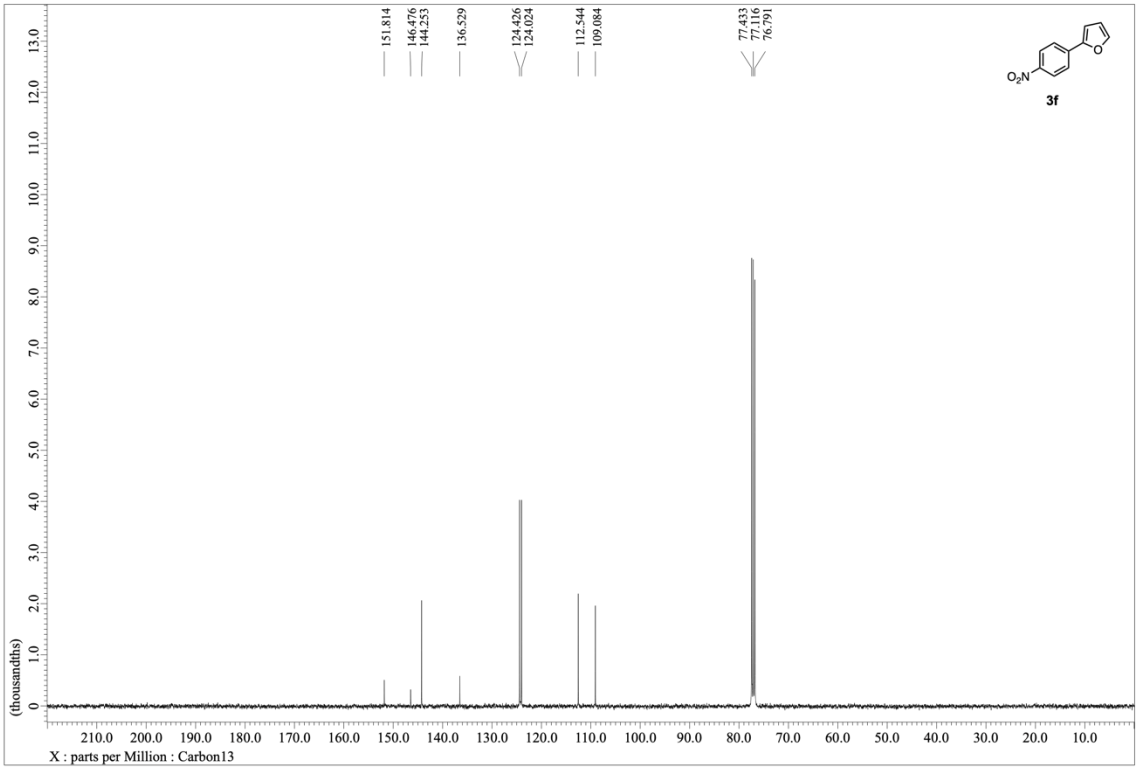
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3d** at 25°C in $CDCl_3$.



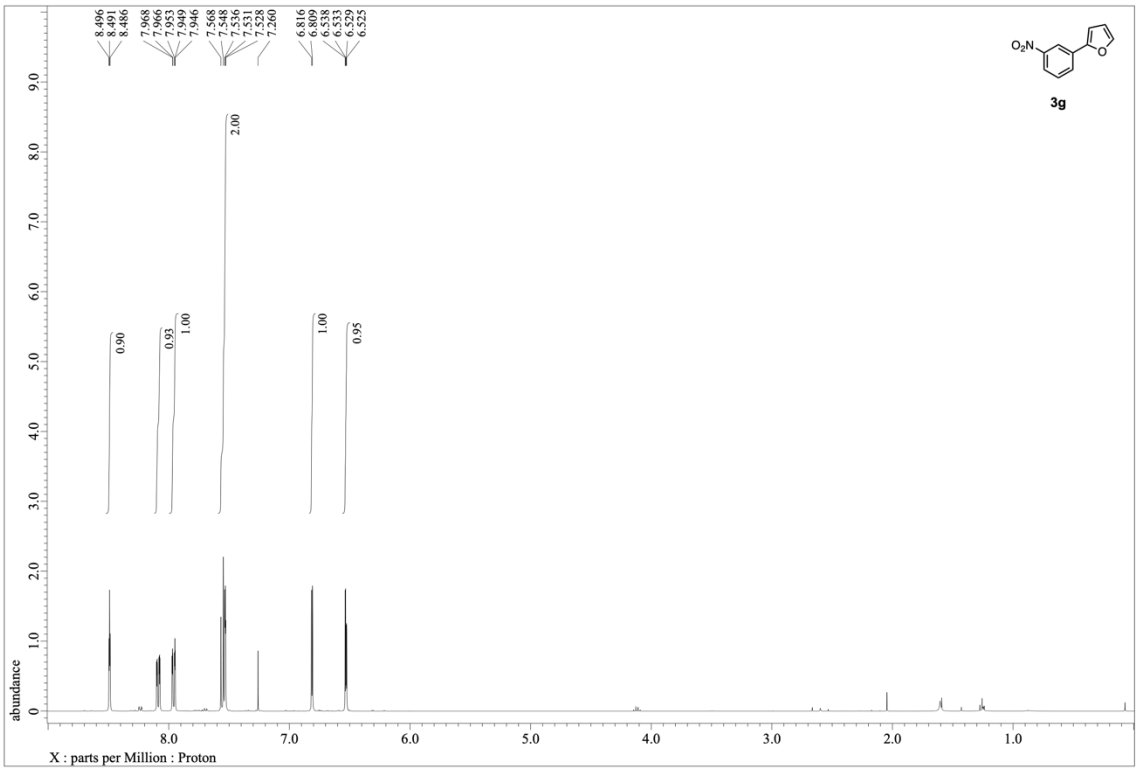


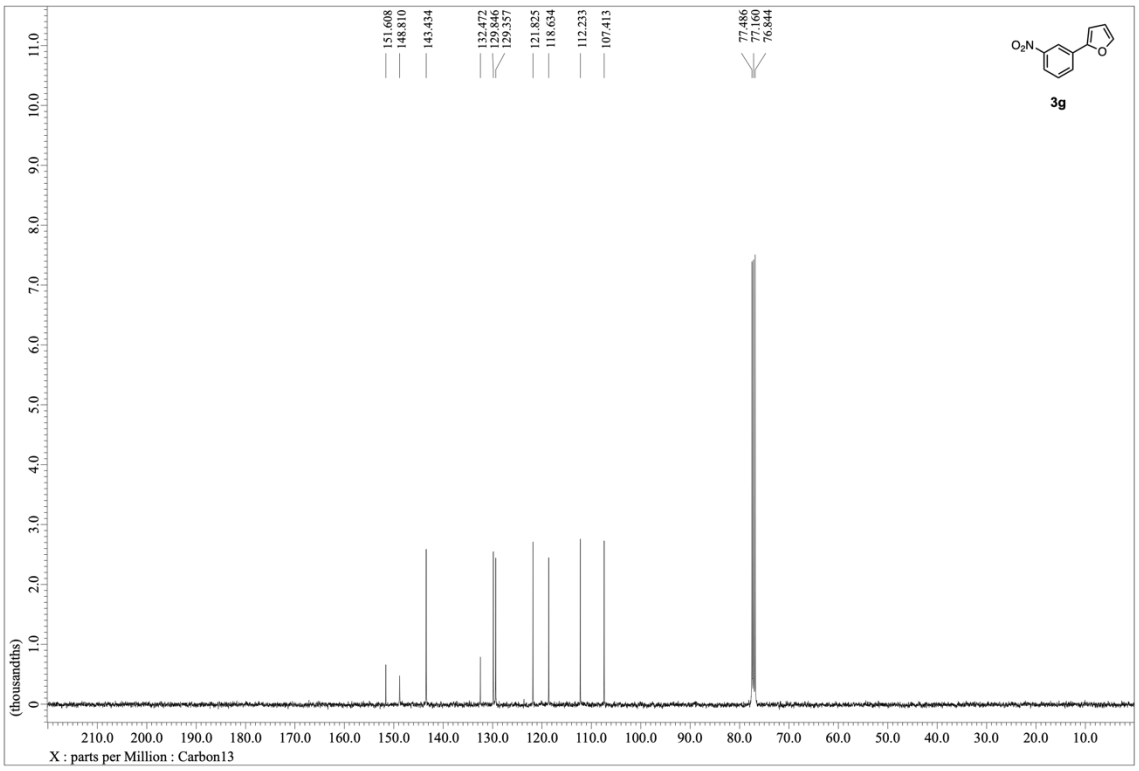
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3e** at 25°C in $CDCl_3$.



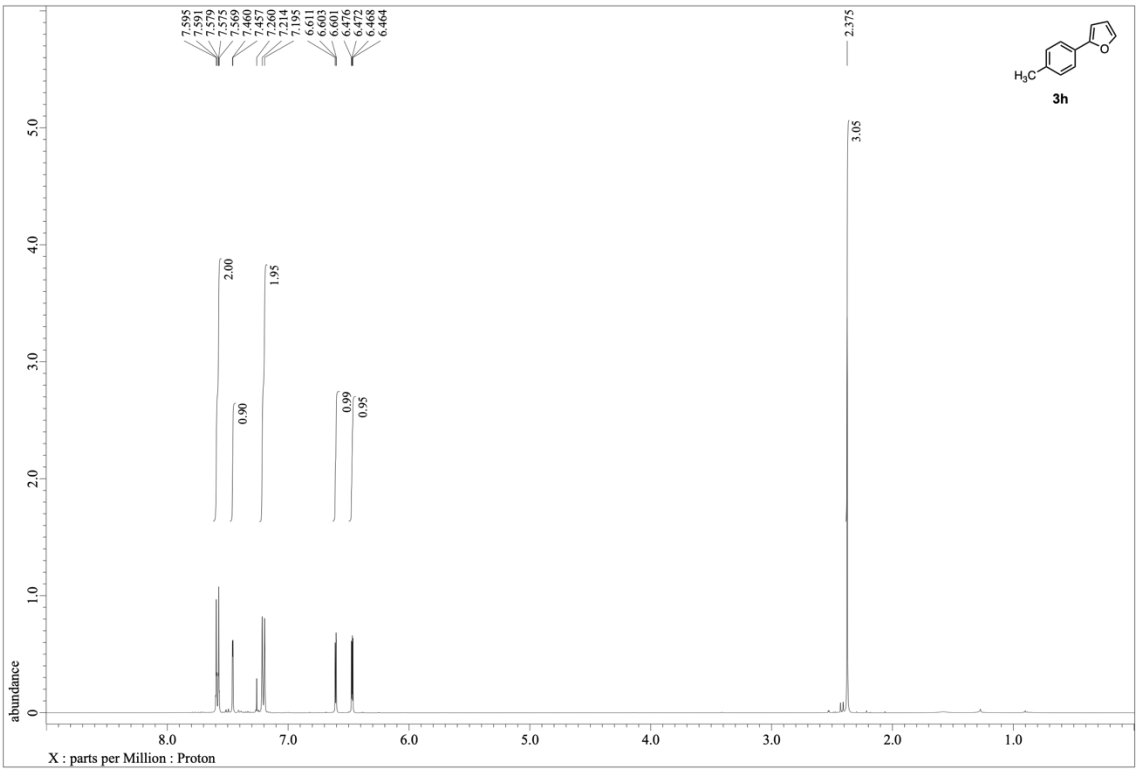


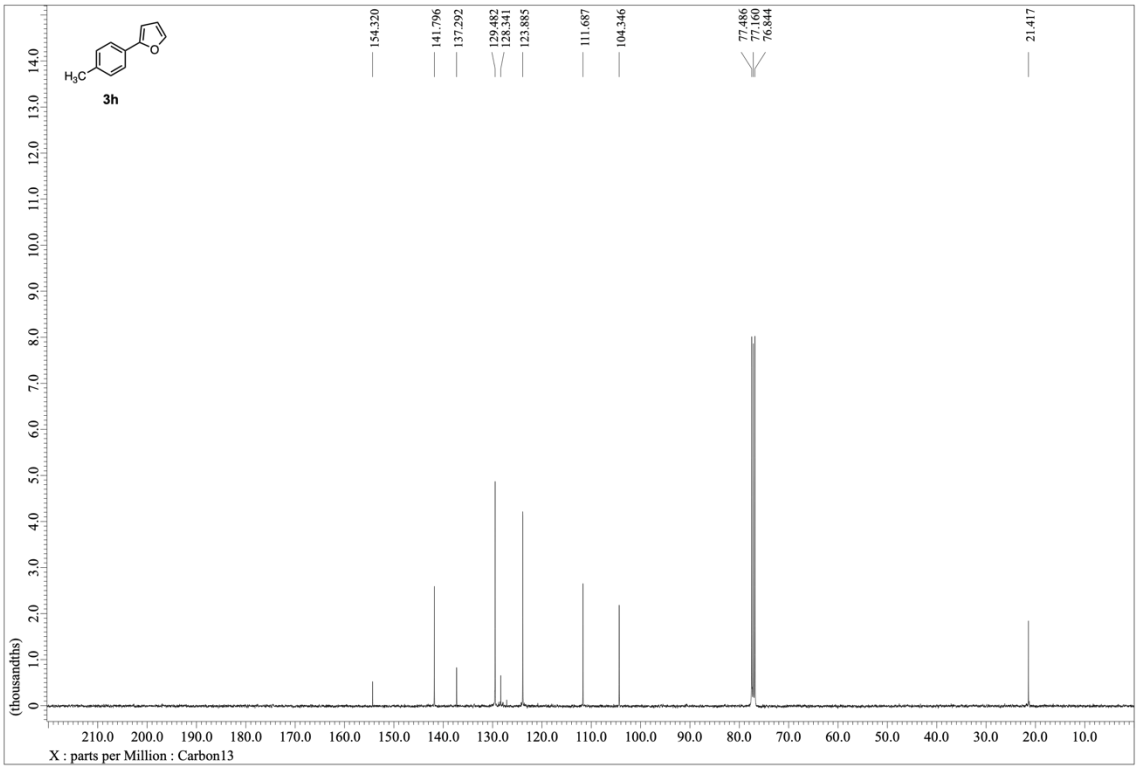
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3f** at 25°C in $CDCl_3$.



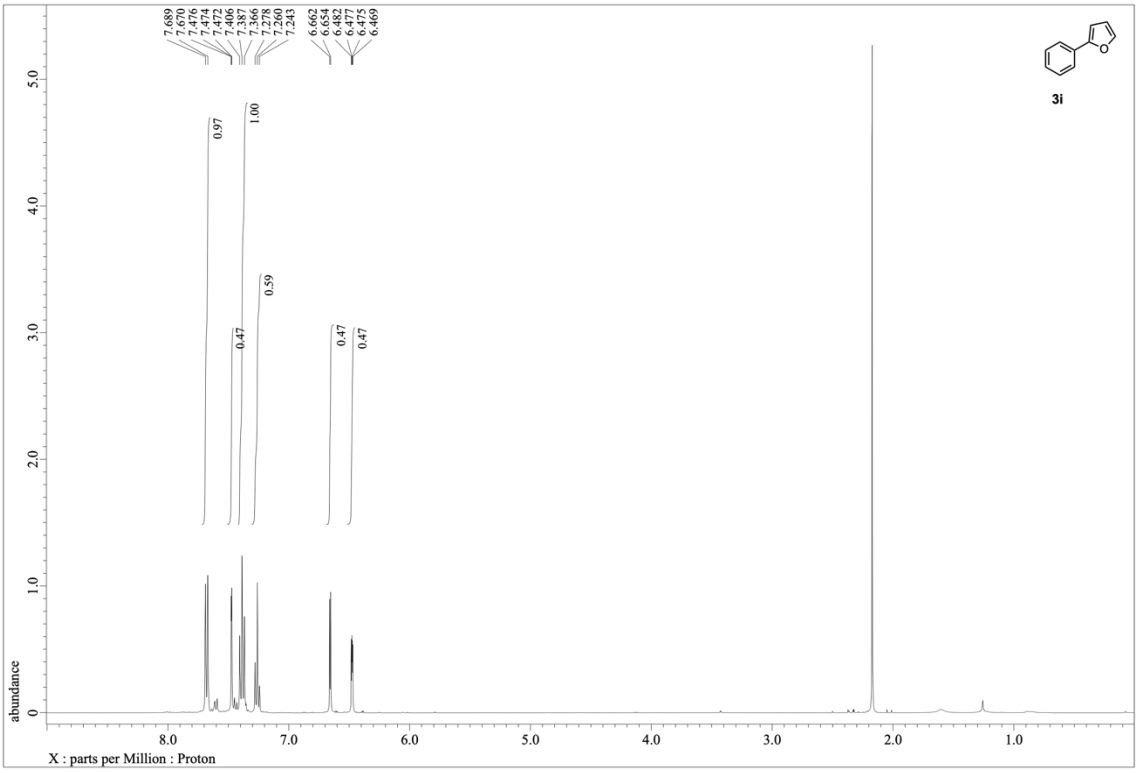


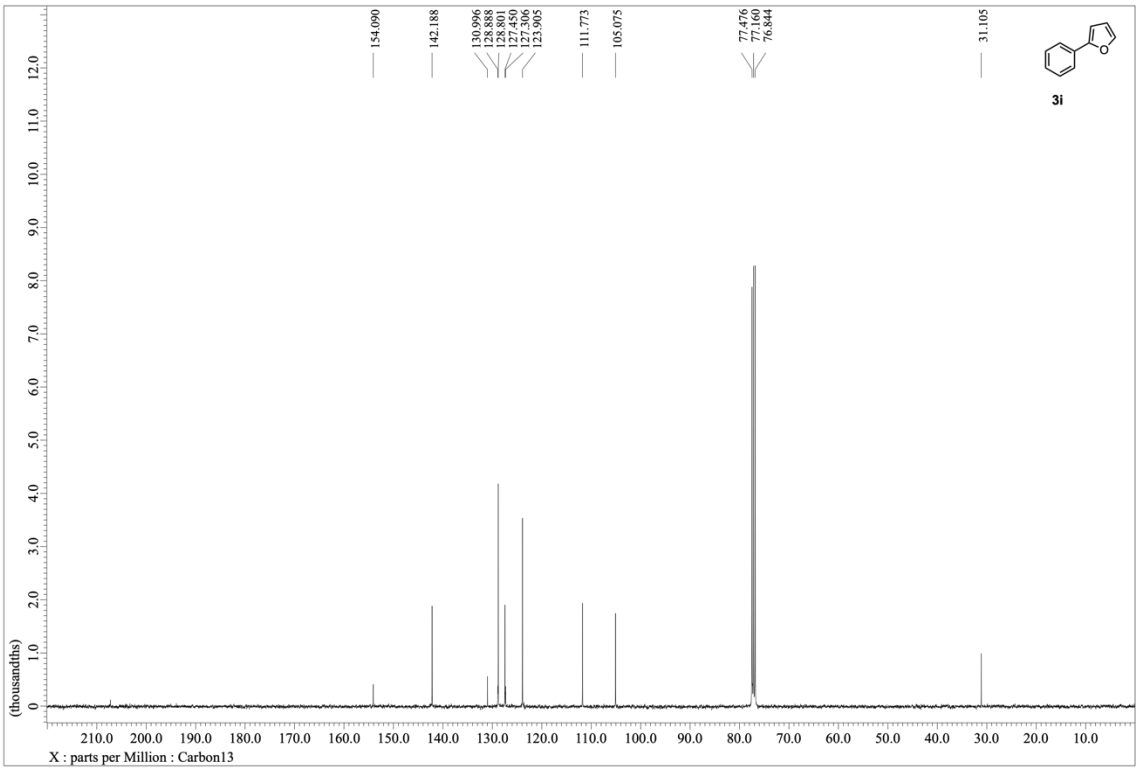
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3g** at 25°C in $CDCl_3$.



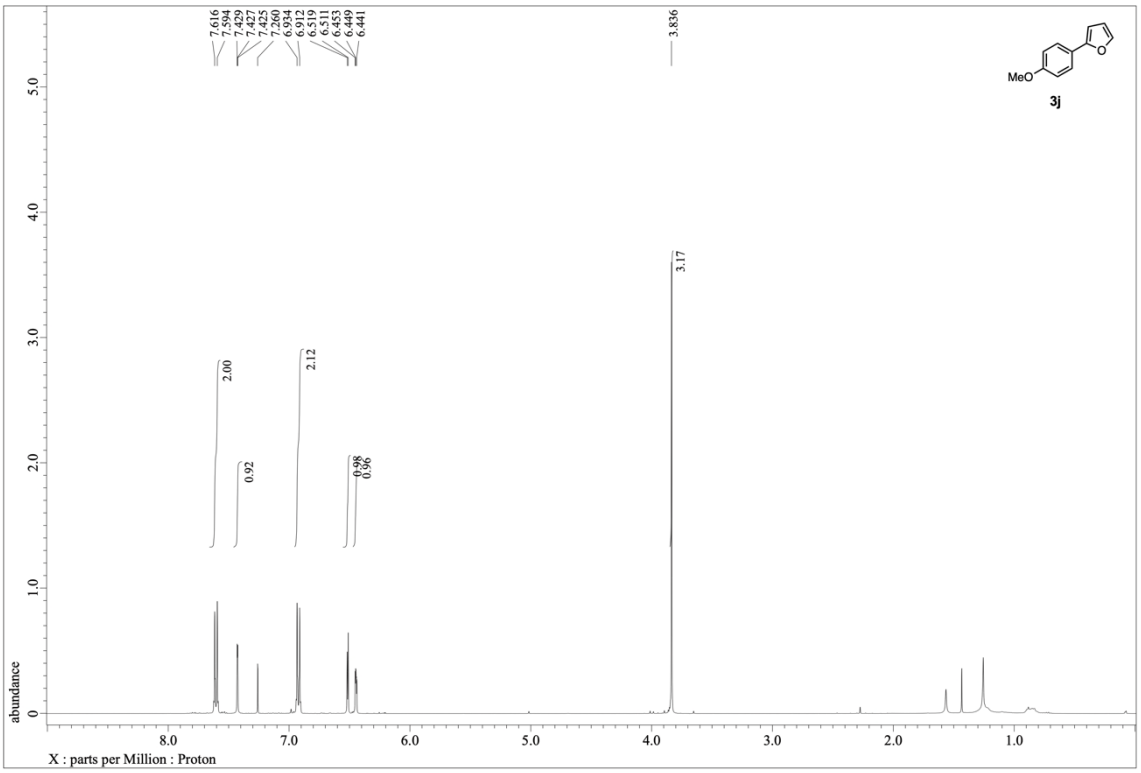


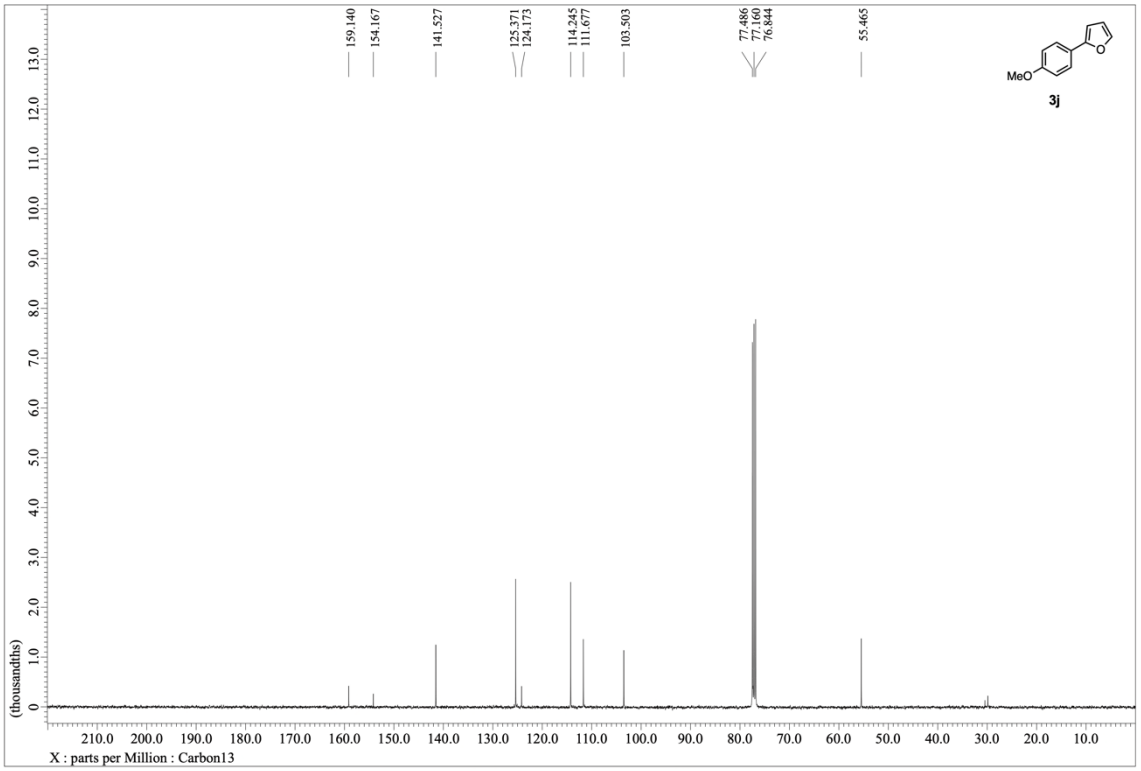
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3h** at 25°C in $CDCl_3$.



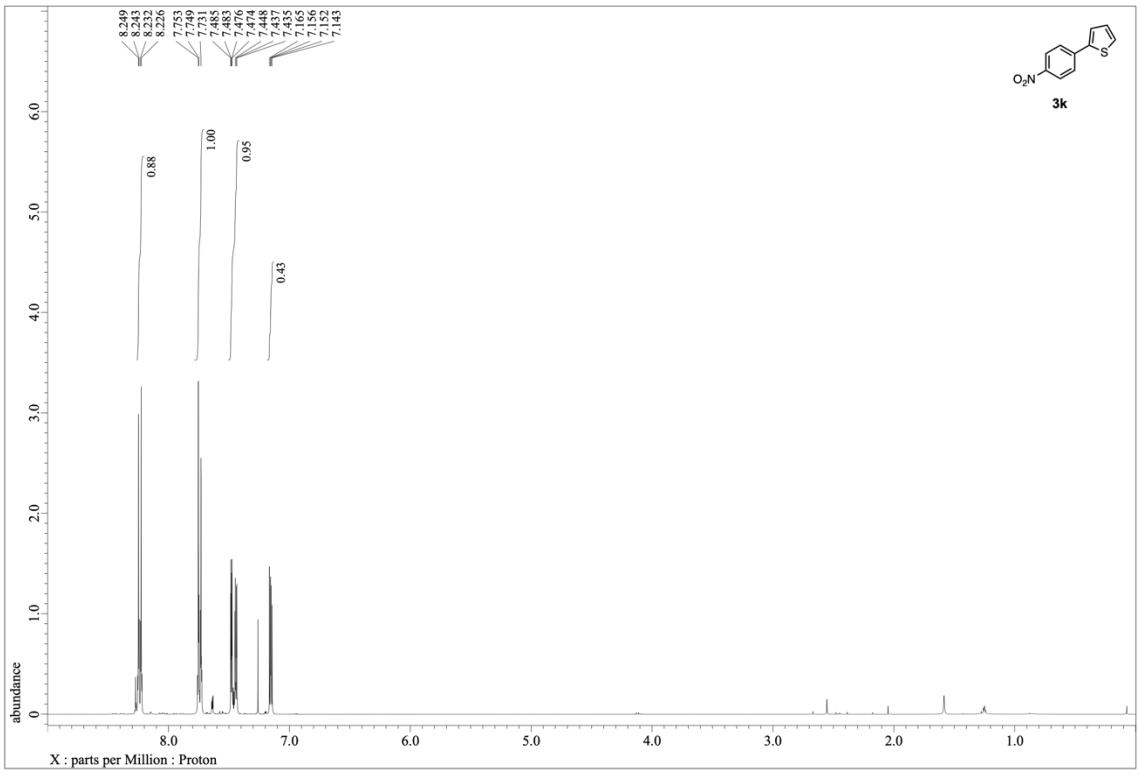


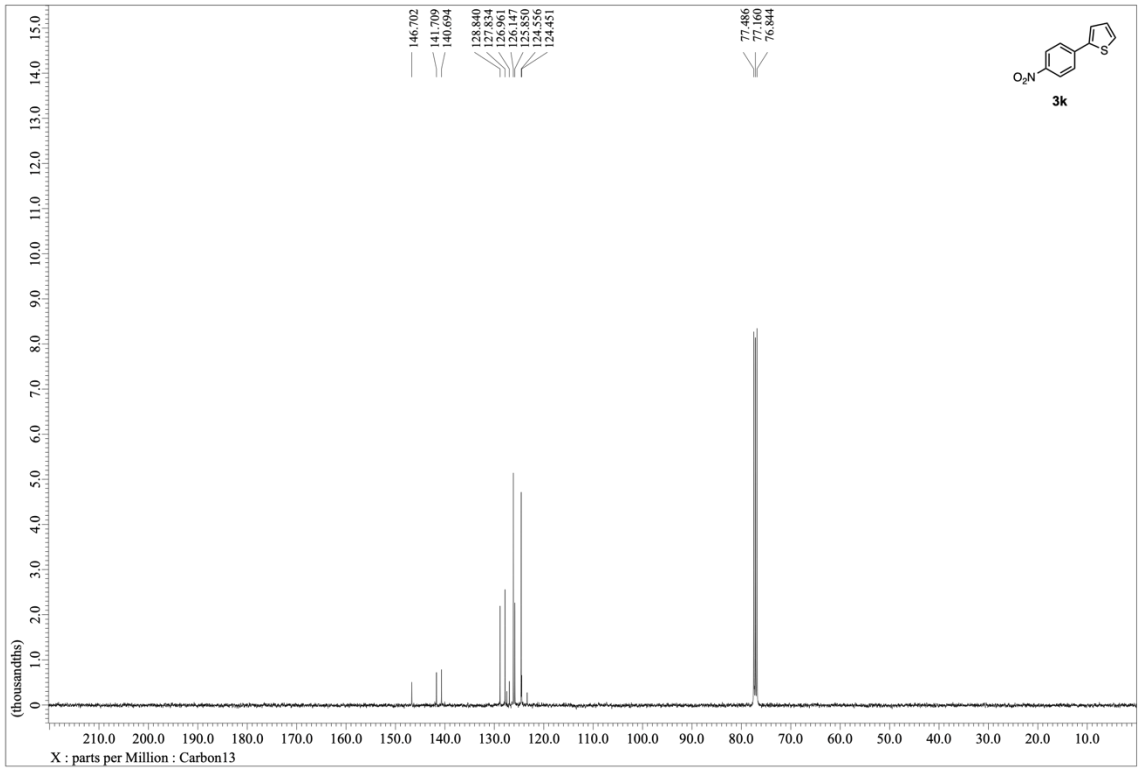
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3i** at 25°C in $CDCl_3$.



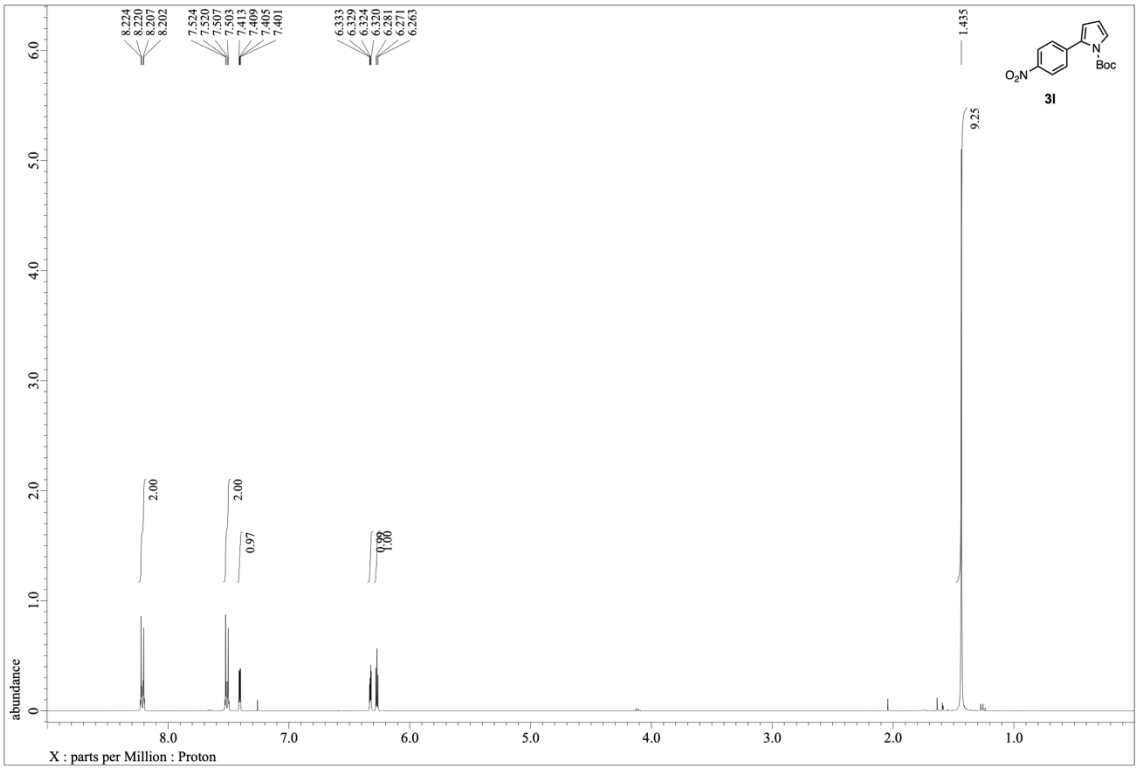


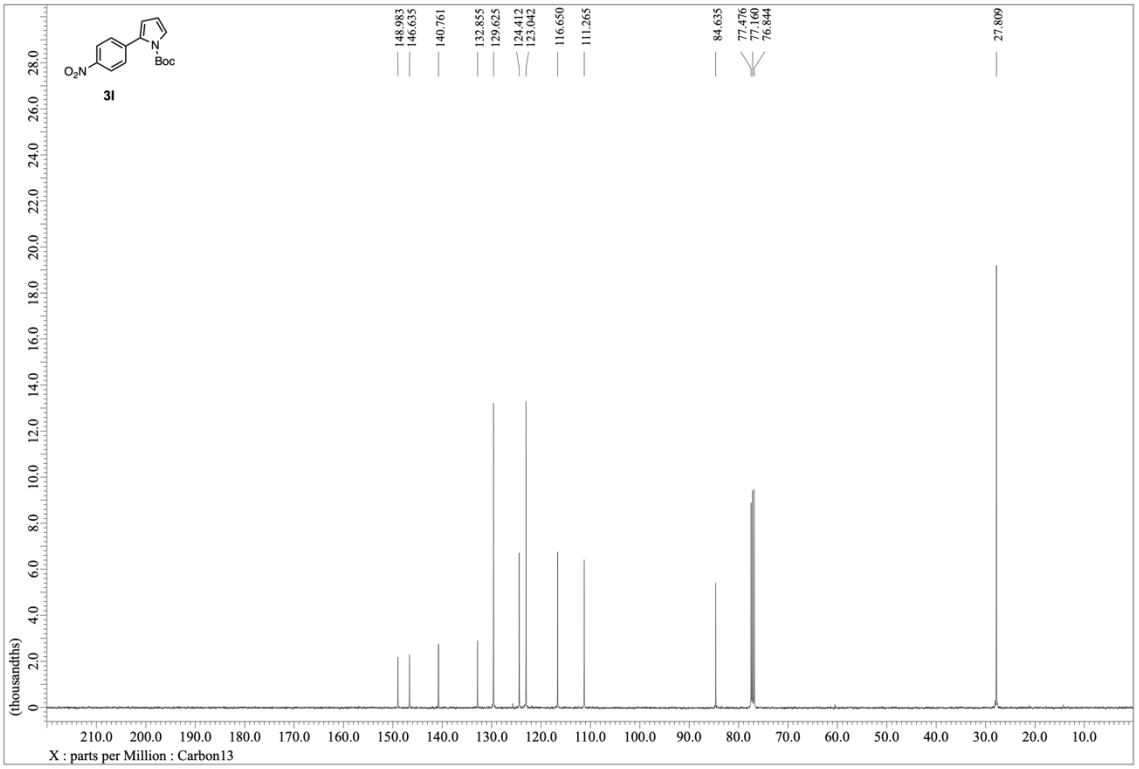
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3j** at 25°C in $CDCl_3$.



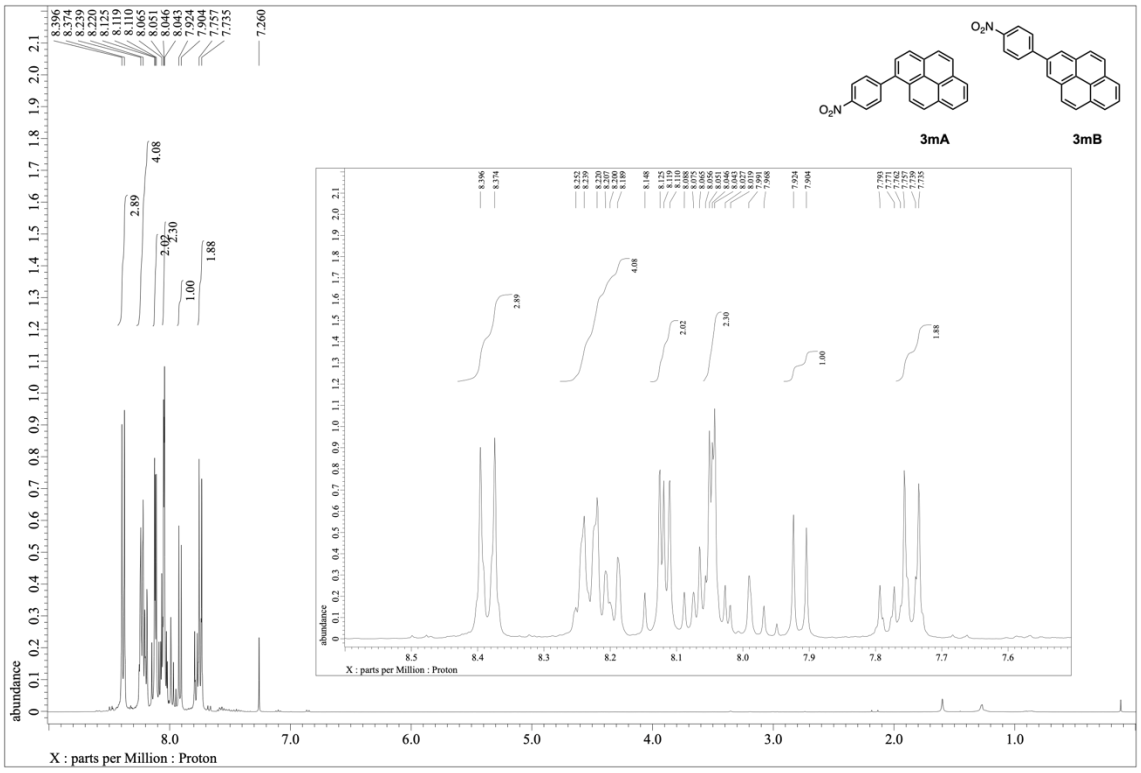


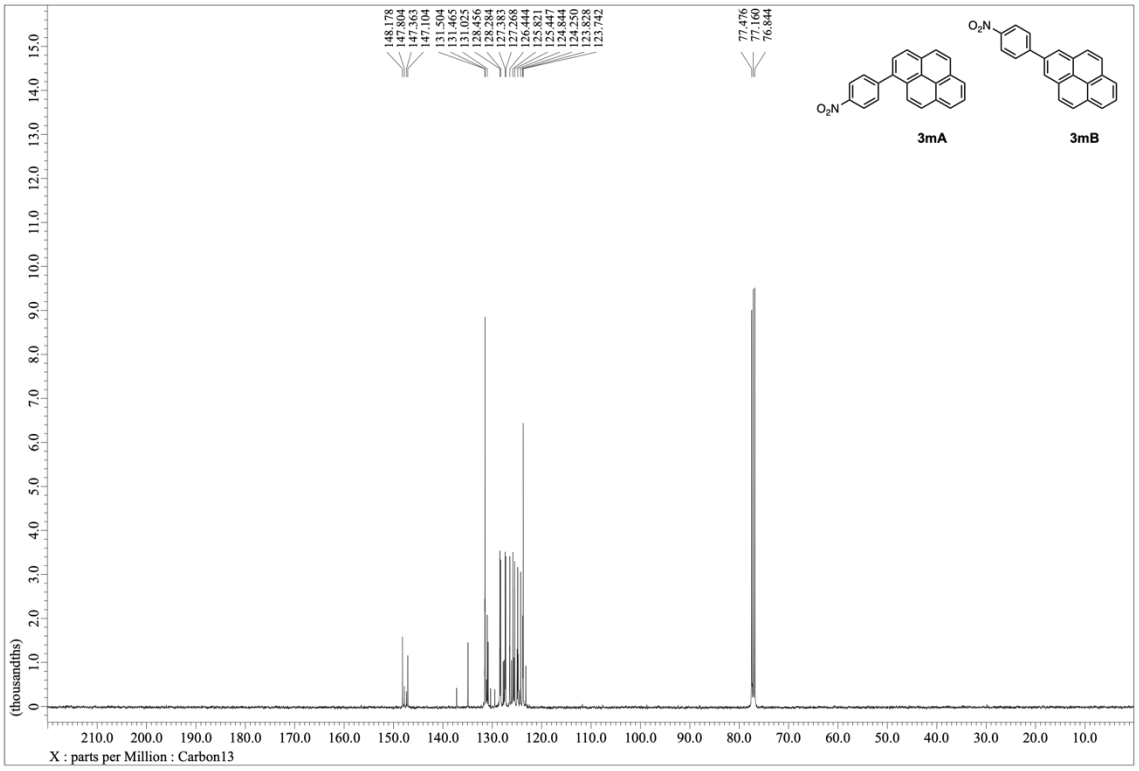
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3k** at 25°C in $CDCl_3$.



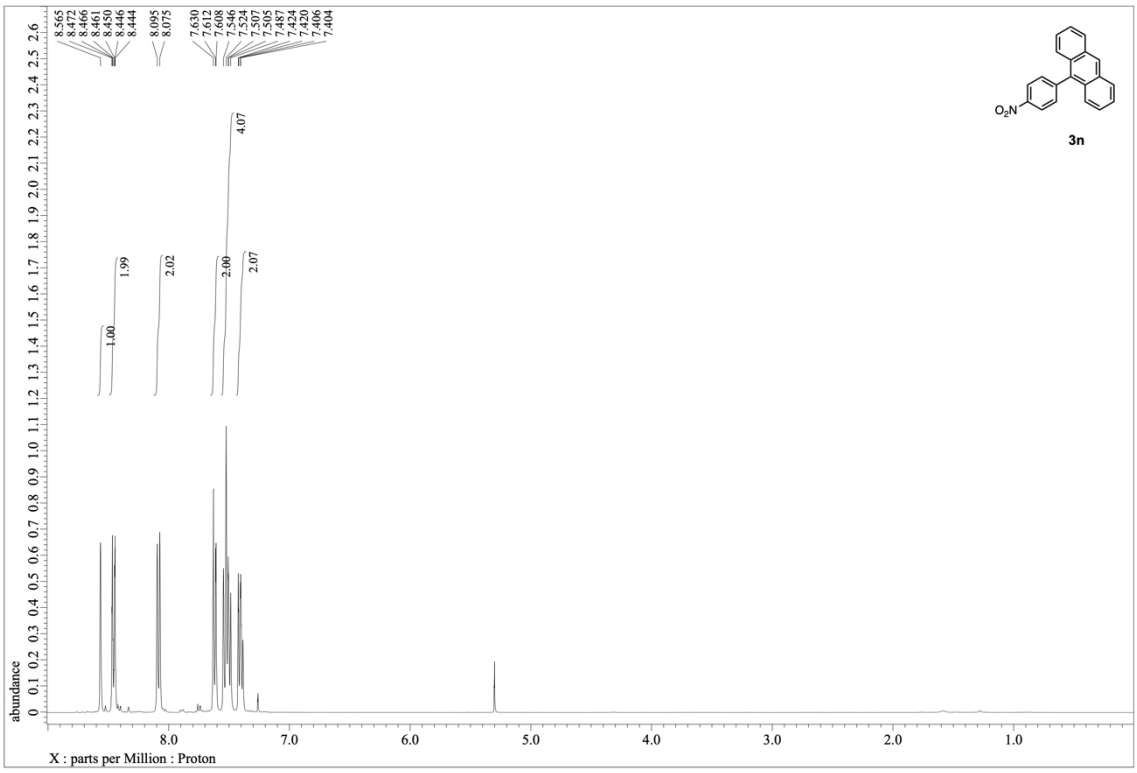


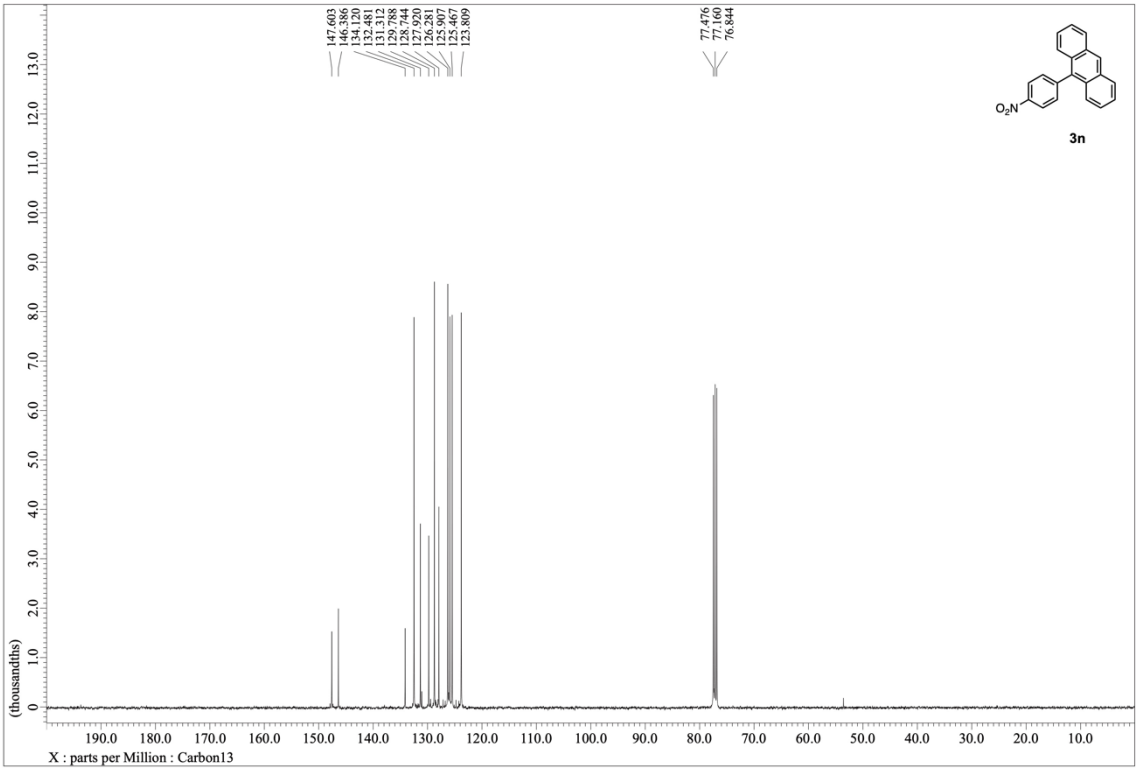
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3l** at 25°C in $CDCl_3$.



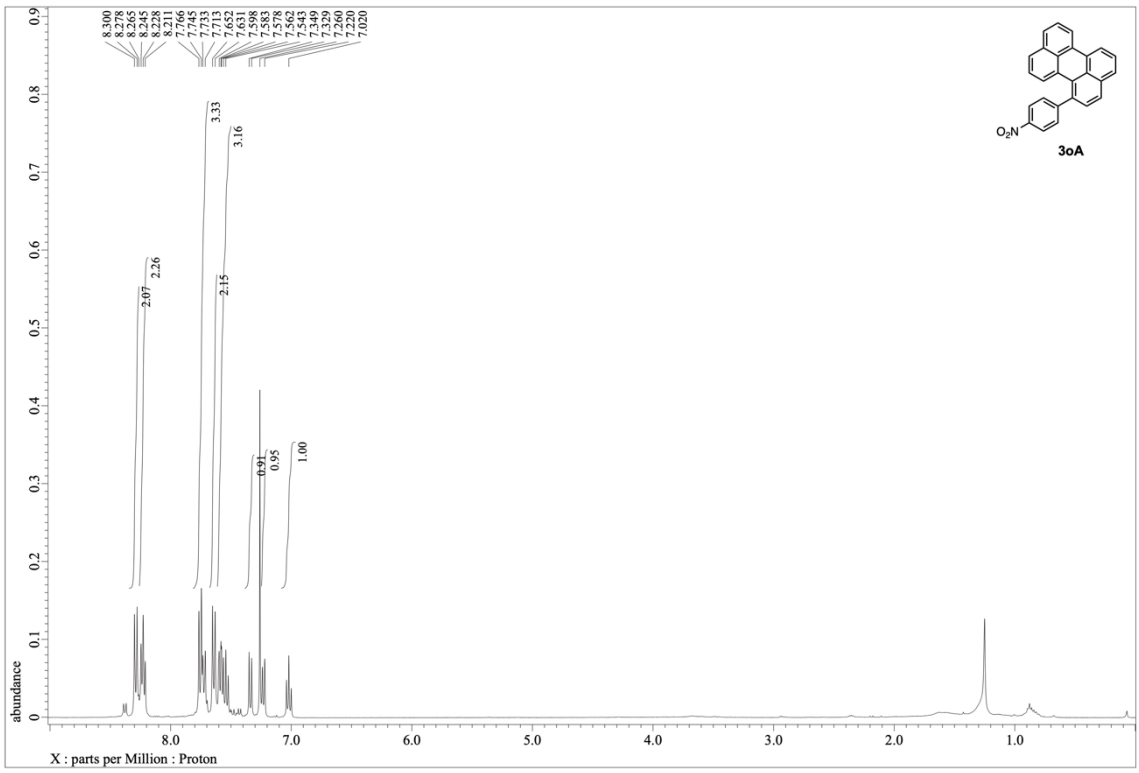


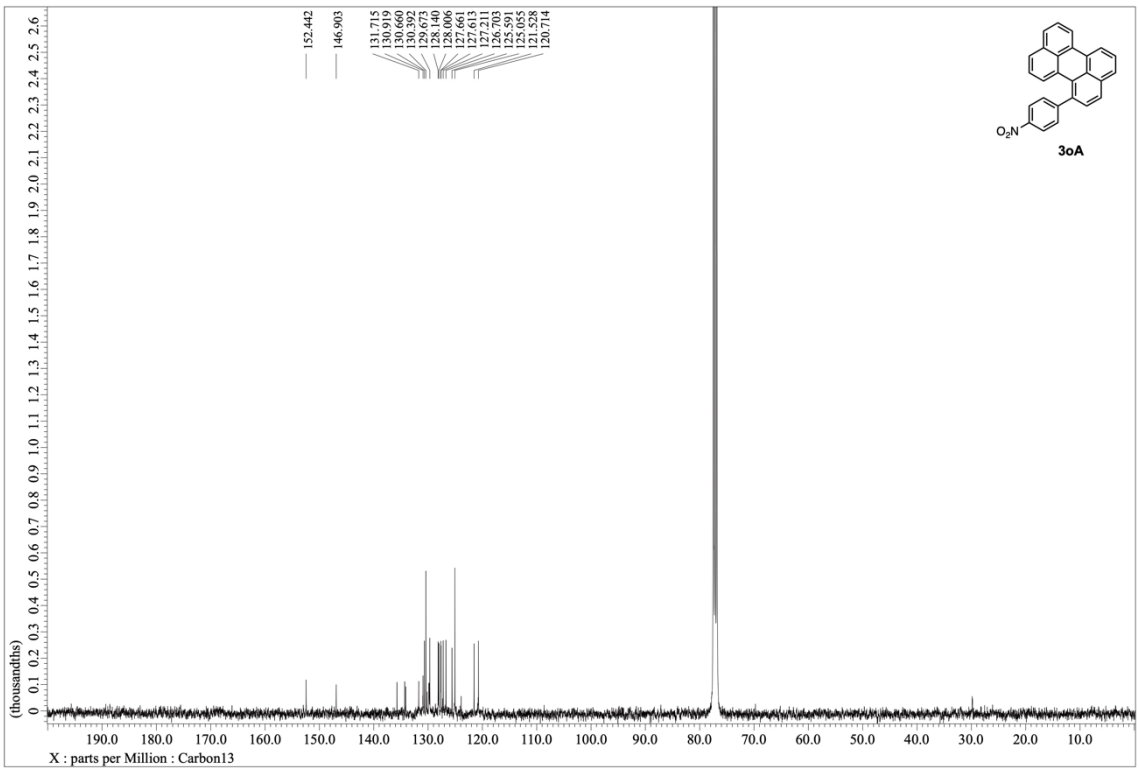
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3m** at 25°C in $CDCl_3$.



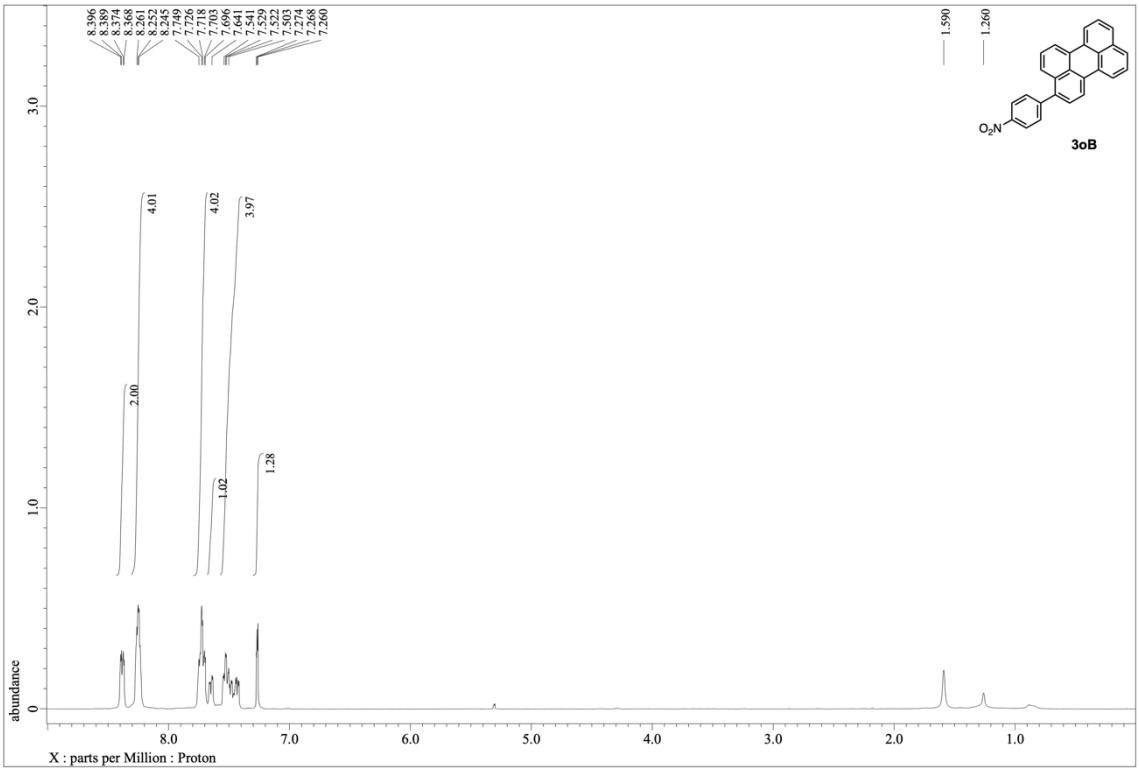


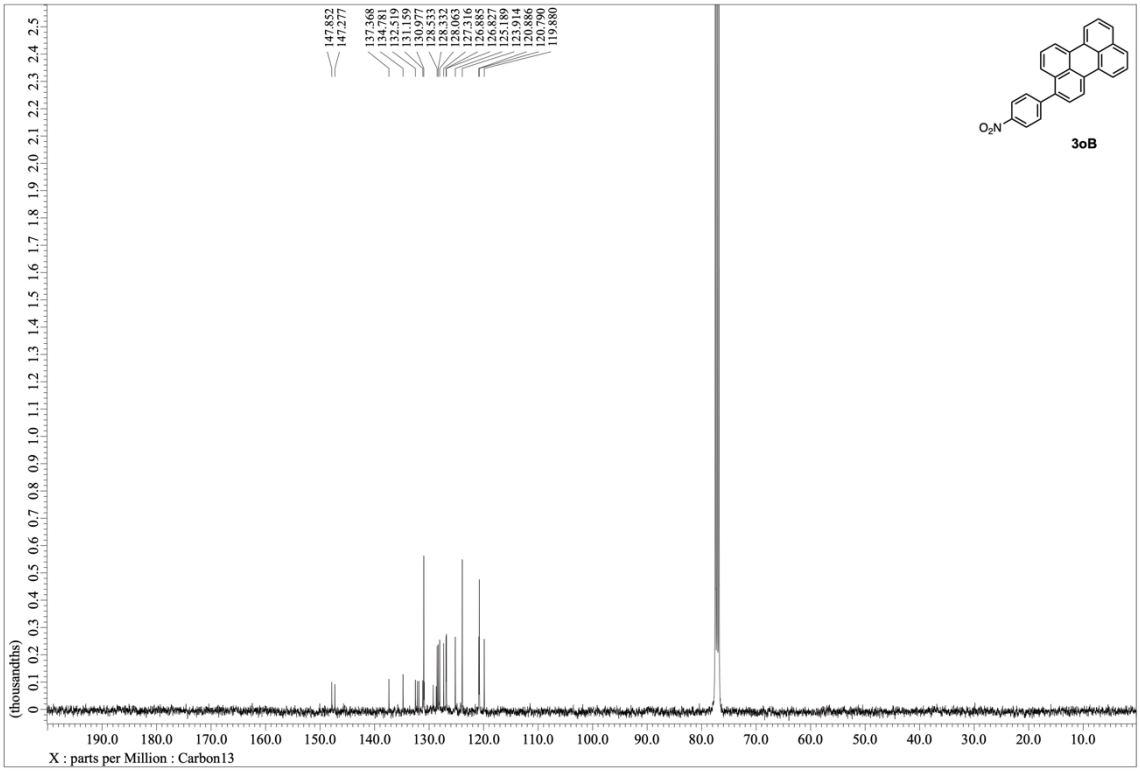
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3n** at 25°C in $CDCl_3$.



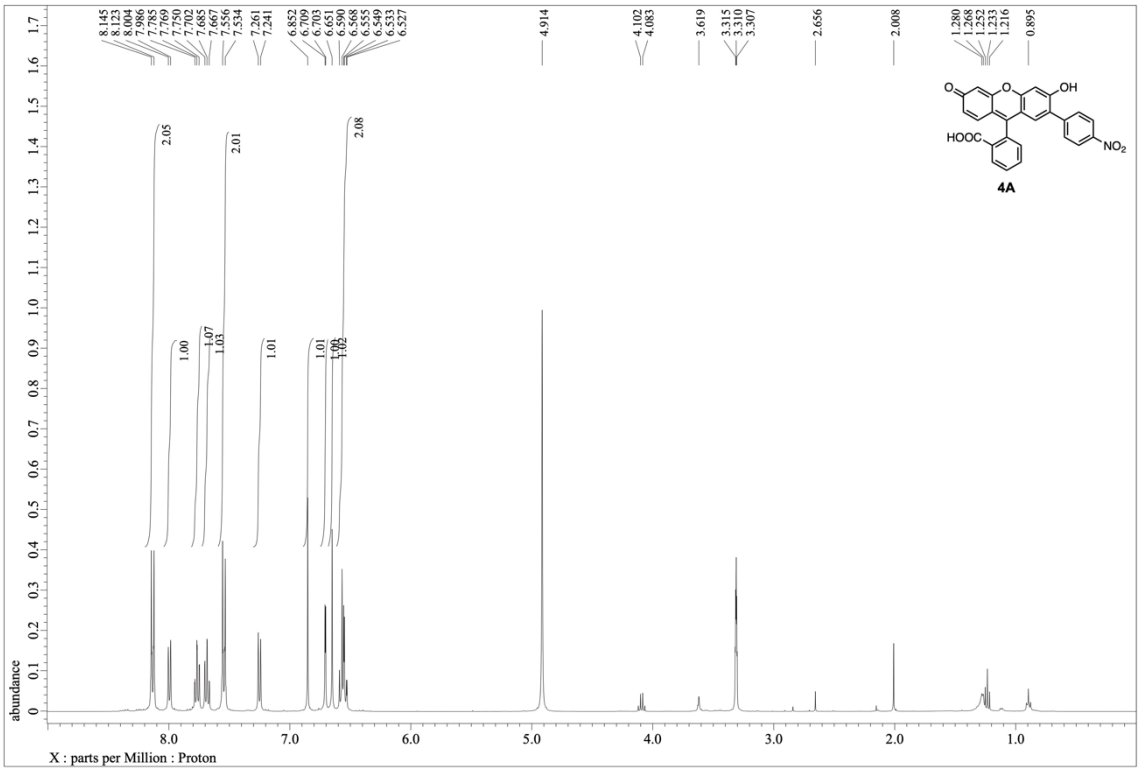


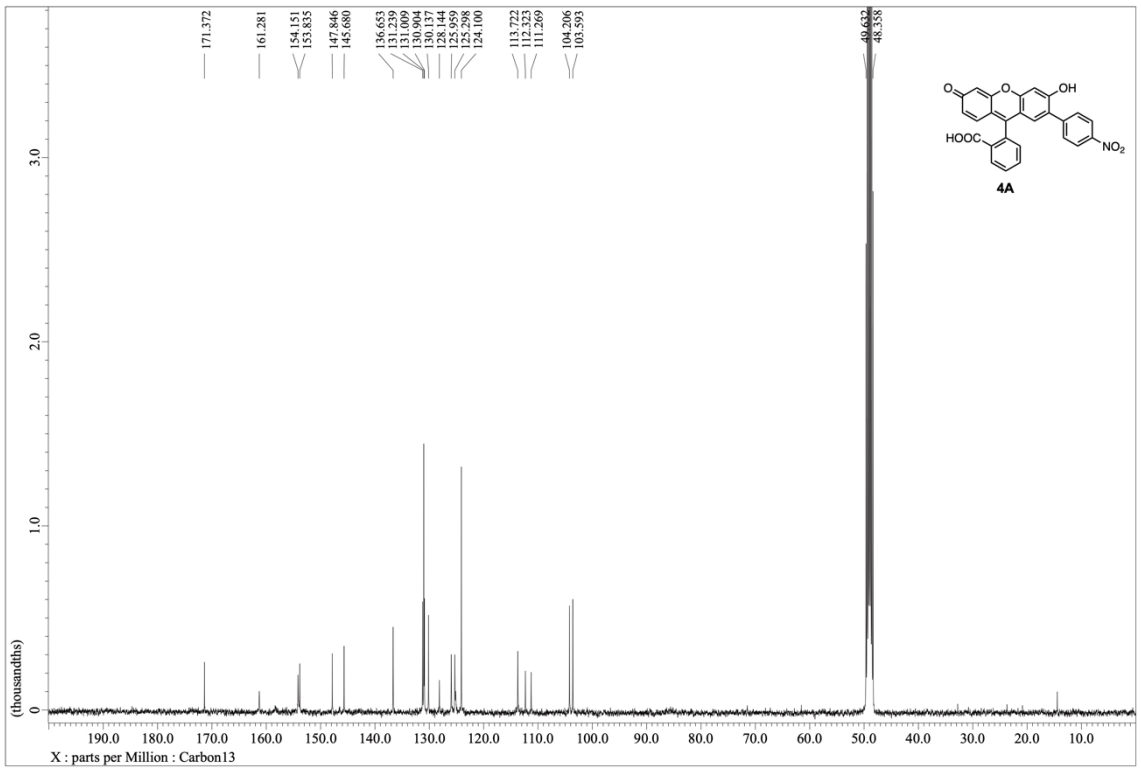
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3oA** at 25°C in $CDCl_3$.



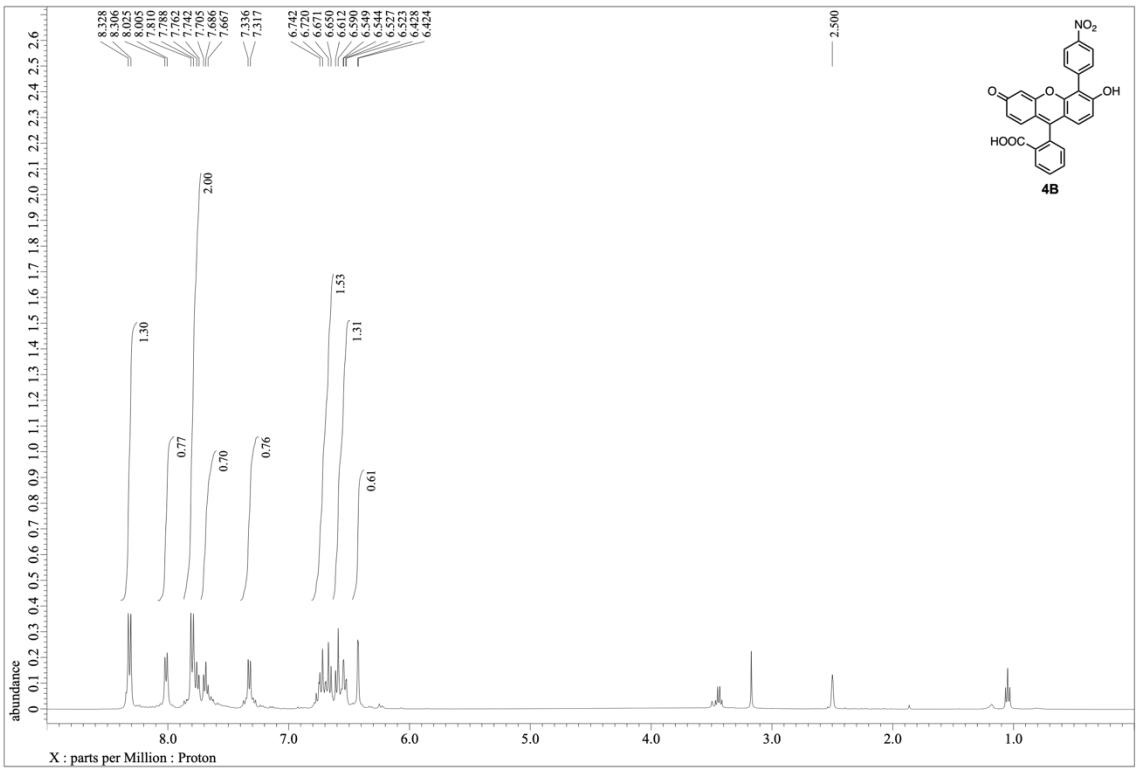


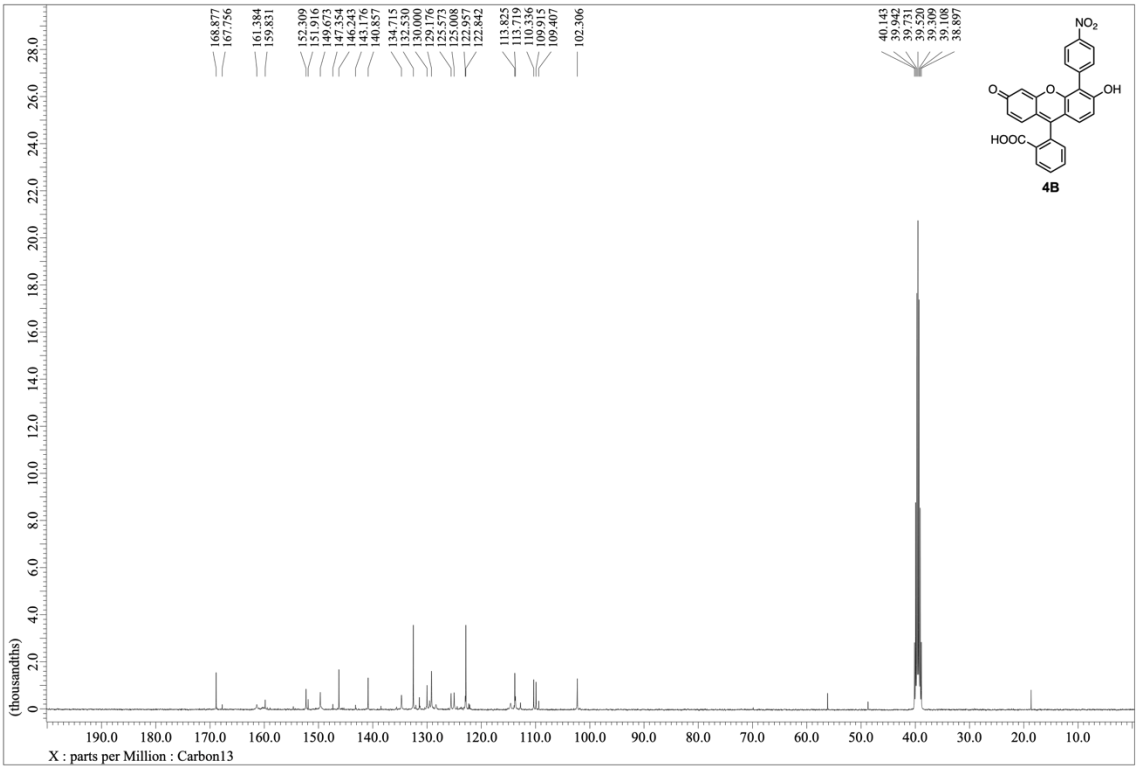
^{1}H (top) and ^{13}C (bottom) NMR spectra of **3oB** at 25°C in $CDCl_3$.



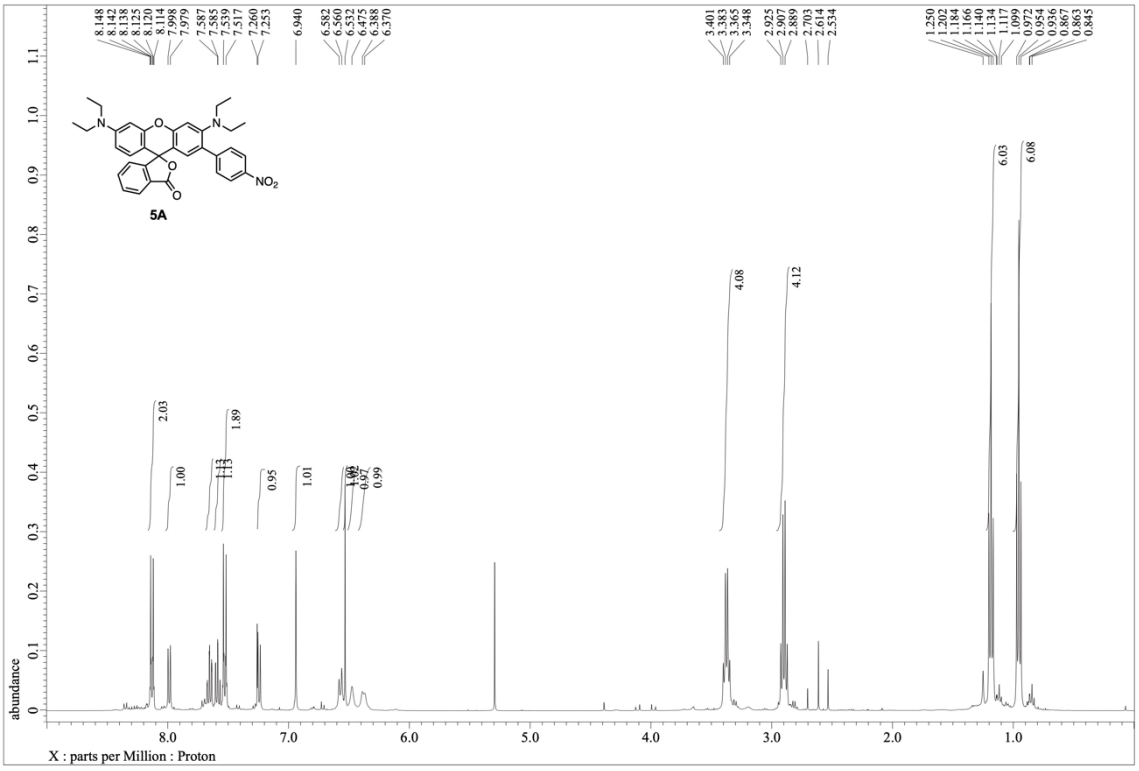


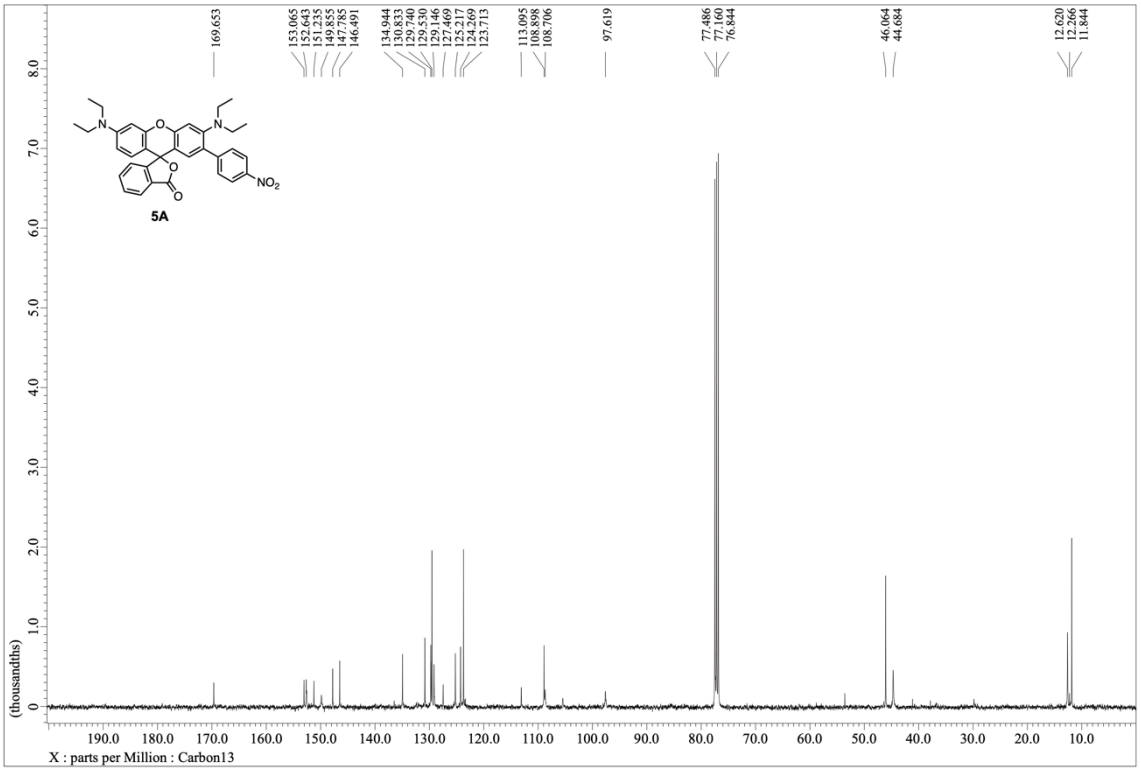
^{1}H (top) and ^{13}C (bottom) NMR spectra of **4A** at 25°C in CD_3OD.



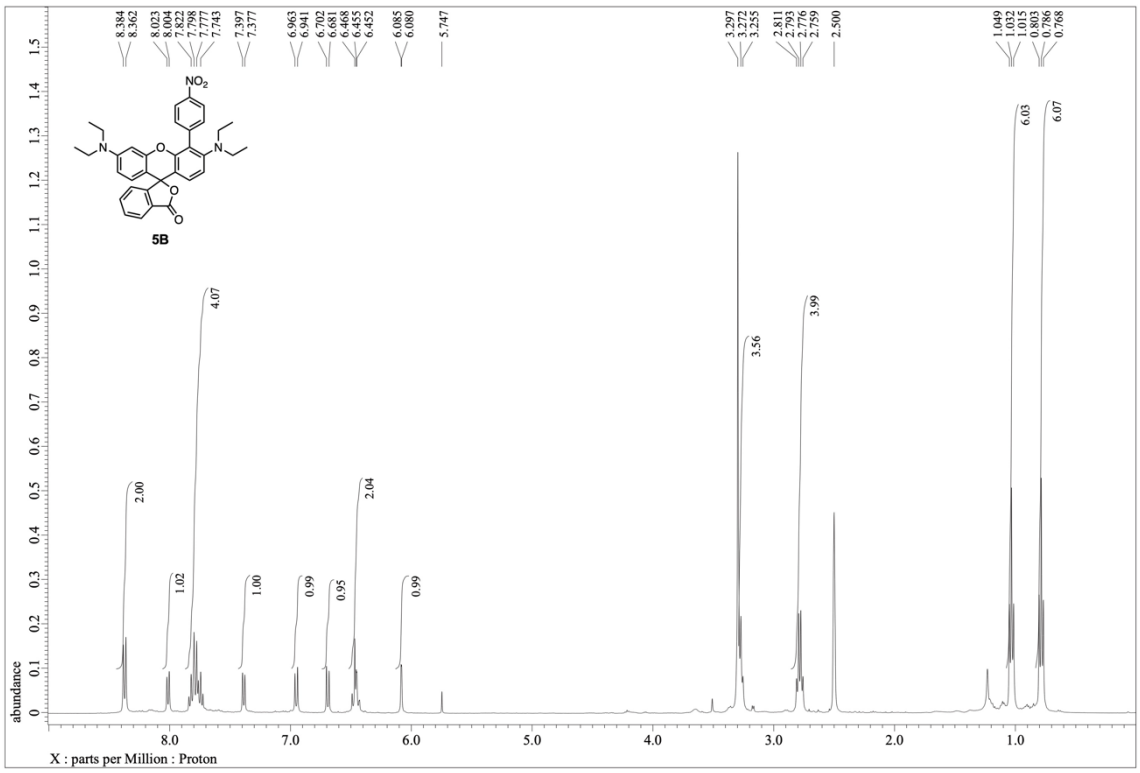


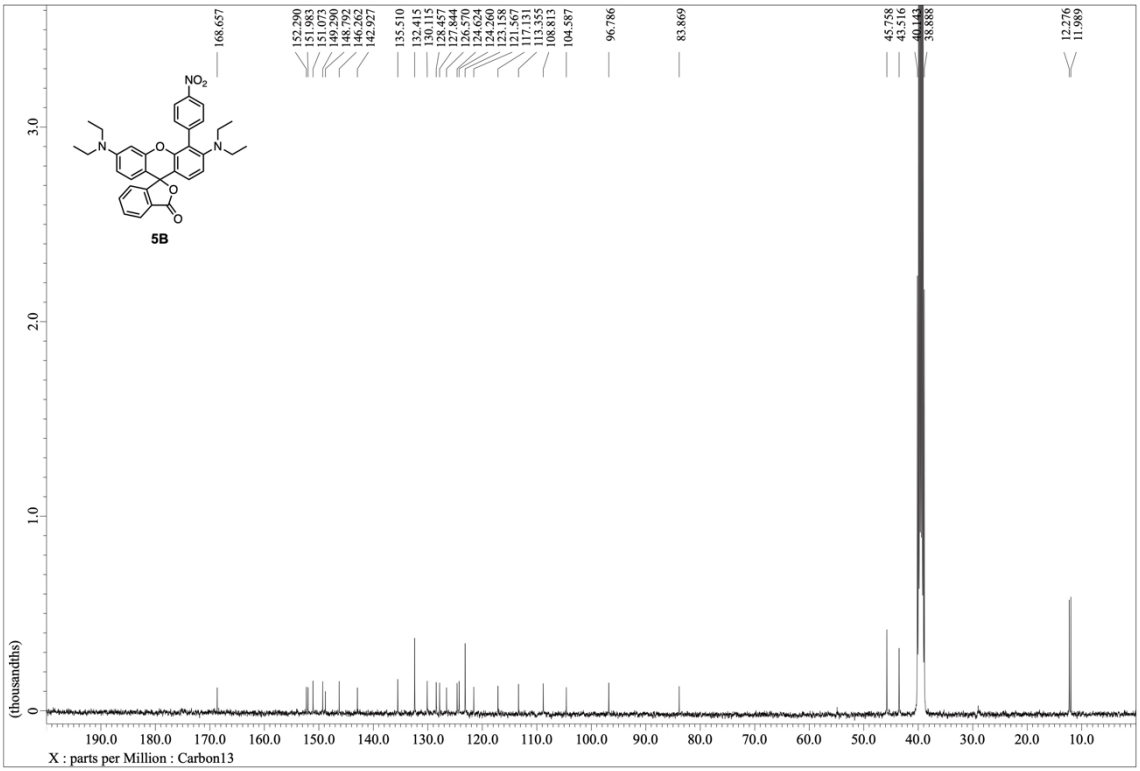
^{1}H (top) and ^{13}C (bottom) NMR spectra of **4B** at 25°C in DMSO-d6.





^{1}H (top) and ^{13}C (bottom) NMR spectra of **5A** at 25°C in $CDCl_3$.





^{1}H (top) and ^{13}C (bottom) NMR spectra of **5B** at 25°C in DMSO-d6.

10. Cartesian Coordinates (in Å) and Energies

2 (S_0)

B3LYP/6-31+G(d,p)

E = –8857.717334 A. U.

C	3.248341	-0.859686	-0.013659
C	2.000973	-1.47593	0.134845
C	0.837419	-0.701805	0.142412
C	0.860177	0.705271	0.044674
C	2.117587	1.295139	-0.186194
C	3.273632	0.53409	-0.194972
C	-0.419268	1.418294	0.116622
C	-1.584837	0.664334	-0.014003
C	-1.52996	-0.783726	0.034163
C	-2.634388	-1.591944	-0.051618
C	-3.971346	-1.052509	-0.251331
C	-4.068827	0.477137	-0.360046
C	-2.867791	1.275325	-0.186281
H	2.197165	2.349873	-0.399002
C	-0.554229	2.858799	0.30066
C	-1.81572	3.485541	0.056447
C	0.480887	3.689823	0.797762
C	-1.964116	4.884327	0.173147
C	0.311387	5.059036	0.934373
H	1.409862	3.252389	1.134287
C	-0.905566	5.671456	0.588716
H	-2.933173	5.319792	-0.041583
H	1.126028	5.657695	1.330902
H	-1.025318	6.745998	0.683064
C	-2.966592	2.669916	-0.230957
O	-4.987125	-1.725628	-0.33954
O	-0.332253	-1.391268	0.226936
Br	1.904478	-3.347635	0.303821
Br	-2.468669	-3.463163	0.082322
Br	4.961178	1.372218	-0.490391
O	-5.174927	0.995793	-0.585565
O	4.353334	-1.629566	0.000306
H	5.136775	-1.075329	-0.155265
O	-4.119734	3.277564	-0.468006
H	-4.806839	2.547414	-0.585337

2^{-} (S_0)

B3LYP/6-31+G(d,p)

E = –8857.213850 A. U.

C	3.299535	-1.069898	0.001886
C	1.946345	-1.590016	0.11054
C	0.828424	-0.782759	0.099975
C	0.907617	0.645498	0.020904
C	2.213997	1.178948	-0.187271
C	3.324138	0.383599	-0.187317
C	-0.303704	1.397039	0.098815
C	-1.528895	0.71025	-0.005488
C	-1.548887	-0.713288	0.034891
C	-2.724645	-1.441715	-0.029019
C	-4.018904	-0.823378	-0.199686
C	-3.97571	0.66018	-0.312516
C	-2.785315	1.38653	-0.182805
H	2.334776	2.230284	-0.401377
C	-0.365418	2.860402	0.290882
C	-1.573123	3.55844	0.019186
C	0.699407	3.61442	0.831853
C	-1.641262	4.954376	0.146322

C	0.614877	4.996455	0.973019
H	1.589315	3.112508	1.18412
C	-0.547478	5.681574	0.598719
H	-2.584142	5.436222	-0.089532
H	1.457801	5.538525	1.392786
H	-0.607108	6.761654	0.697165
C	-2.820484	2.826996	-0.286081
O	-0.389229	-1.401841	0.181793
Br	1.759601	-3.467457	0.261
Br	-2.676664	-3.327187	0.092427
Br	5.036645	1.172486	-0.469781
O	4.322699	-1.773245	0.035431
O	-3.882653	3.453574	-0.54761
O	-5.098132	-1.429908	-0.266458
O	-5.134101	1.258185	-0.543581
H	-4.927745	2.240296	-0.608221

2^{2-} (S_0)

B3LYP/6-31+G(d,p)

E = –8856.591447 A. U.

C	3.266124	-1.119944	-0.034445
C	1.905282	-1.60052	0.07321
C	0.792736	-0.767274	0.084528
C	0.887589	0.642654	0.019816
C	2.197587	1.149756	-0.173999
C	3.298109	0.32464	-0.18767
C	-0.333484	1.424107	0.083074
C	-1.579417	0.785363	-0.076023
C	-1.591083	-0.660902	0.003909
C	-2.757846	-1.391303	-0.010889
C	-4.053315	-0.780417	-0.171922
C	-4.07967	0.761428	-0.378527
C	-2.819906	1.485826	-0.290634
H	2.342921	2.204458	-0.357101
C	-0.354207	2.864992	0.31432
C	-1.531717	3.595295	0.003897
C	0.711719	3.575215	0.927466
C	-1.562256	4.989614	0.183565
C	0.652795	4.947874	1.126171
H	1.575363	3.033911	1.290742
C	-0.482748	5.673346	0.725896
H	-2.48091	5.495007	-0.098952
H	1.486648	5.453653	1.608613
H	-0.525929	6.75144	0.867655
C	-2.794007	2.927483	-0.448665
O	-5.113253	-1.414389	-0.165664
O	-0.439417	-1.360379	0.162074
Br	1.672117	-3.485415	0.195937
Br	-2.691859	-3.291452	0.184443
Br	5.033086	1.115893	-0.442712
O	-5.186828	1.265908	-0.588031
O	-3.732856	3.6412	-0.856978
O	4.284995	-1.853313	-0.022381

A (Table S8)

B3LYP/6-31+G(d,p)

E = –8857.190941 A. U.

C	3.1823062	-0.9892883	-0.0590447
C	1.9085687	-1.5507931	0.0678006
C	0.7740257	-0.7341997	0.0991351
C	0.846984	0.6741289	0.0432281
C	2.1343226	1.2160858	-0.1579243
C	3.2563415	0.4043186	-0.1877962
C	-0.3912309	1.4369618	0.1136556

C	-1.6159349	0.763152	-0.0687939
C	-1.5998219	-0.6954585	0.0160121
C	-2.7306201	-1.4583296	0.0002708
C	-4.0459955	-0.8642809	-0.1765333
C	-4.1011443	0.6787189	-0.3957927
C	-2.8526897	1.4279962	-0.3032439
H	2.2549142	2.2757236	-0.3248093
C	-0.435677	2.8749734	0.3352013
C	-1.6225158	3.5784288	0.0039558
C	0.6101195	3.613625	0.950142
C	-1.6905458	4.9712241	0.1757627
C	0.5149829	4.9852609	1.1391626
H	1.4817413	3.0995747	1.3353316
C	-0.6325443	5.6816314	0.7249698
H	-2.6152896	5.4566118	-0.1200632
H	1.3296322	5.5142093	1.6279378
H	-0.7017661	6.7577178	0.8613163
C	-2.8537465	2.8773273	-0.475277
O	-5.0816636	-1.5188578	-0.1705571
O	-0.4222338	-1.3642649	0.1837374
Br	1.7321705	-3.4275798	0.1854175
Br	-2.6282946	-3.345096	0.2052958
Br	4.9874373	1.1927082	-0.4344958
O	-5.2100957	1.1568932	-0.6127495
O	4.268573	-1.8065564	-0.0669919
H	5.0613601	-1.2619467	-0.2001564
O	-3.7967874	3.5462957	-0.9230031

A (Table S8)

M06-2X/6-31+G(d,p)

E = –8856.982844 A. U.

C	3.1802082	-0.965522	-0.0490203
C	1.9131222	-1.5306464	0.0756623
C	0.7796392	-0.7210899	0.1076678
C	0.843496	0.6802365	0.0447876
C	2.120712	1.227139	-0.1631519
C	3.247569	0.4235502	-0.1847992
C	-0.4037663	1.4306643	0.1096958
C	-1.6132733	0.7530133	-0.0661939
C	-1.5810546	-0.7107609	0.0175199
C	-2.6931935	-1.484178	-0.0050983
C	-4.020083	-0.9012294	-0.1825385
C	-4.0947648	0.6394771	-0.3846821
C	-2.8571062	1.3986165	-0.2859466
H	2.2366283	2.2867254	-0.3425093
C	-0.4581369	2.8686994	0.3164307
C	-1.6491816	3.5557503	-0.0009503
C	0.5858329	3.6160702	0.9149829
C	-1.7300272	4.9459791	0.1591593
C	0.4824709	4.9845178	1.0897945
H	1.4617154	3.1090816	1.3015783
C	-0.6722199	5.6679124	0.6821667
H	-2.6658868	5.4179043	-0.1244979
H	1.2968791	5.5234678	1.5663708
H	-0.7467612	6.7440118	0.8088948
C	-2.8881771	2.8432799	-0.4415728
O	-5.0363251	-1.5656227	-0.1847824
O	-0.4046867	-1.3612258	0.193493
Br	1.7369666	-3.3889745	0.1854039
Br	-2.5686892	-3.3465622	0.1929372
Br	4.9544446	1.2126755	-0.4287449
O	-5.2029394	1.0985417	-0.594141
O	4.2600201	-1.7794305	-0.0502673
H	5.0567027	-1.2463518	-0.1816371

O	-3.851937	3.499791	-0.8377458

A (Table S8)

wB97XD/6-31+G(d,p)

E = –8856.880502 A. U.

C	3.1734264	-0.972619	-0.0569953
C	1.9082643	-1.5385229	0.0782873
C	0.7757162	-0.7267575	0.1113057
C	0.842819	0.6717526	0.0466745
C	2.1166667	1.2181742	-0.1665368
C	3.2427319	0.4161488	-0.1950869
C	-0.4015056	1.427539	0.1165
C	-1.6092551	0.756195	-0.0679305
C	-1.5829892	-0.7062977	0.0170123
C	-2.6992575	-1.4736778	-0.0071153
C	-4.0198061	-0.8837641	-0.1907687
C	-4.087976	0.6578726	-0.398483
C	-2.8491254	1.4110031	-0.3015858
H	2.2295984	2.2783344	-0.3417429
C	-0.450036	2.8635332	0.3372287
C	-1.6311791	3.5579568	0.0054068
C	0.5890672	3.5981843	0.9576394
C	-1.7074628	4.9465491	0.1823308
C	0.4890914	4.9639694	1.1479998
H	1.4596959	3.0847711	1.3475554
C	-0.6568542	5.655878	0.7336278
H	-2.6339687	5.4291077	-0.1122401
H	1.2999383	5.4940109	1.6405359
H	-0.7316084	6.7301103	0.8752634
C	-2.85954	2.853472	-0.472639
O	-5.0412361	-1.5440107	-0.1940811
O	-0.4112376	-1.3598116	0.2021334
Br	1.7326915	-3.39847	0.2021026
Br	-2.5847014	-3.3394356	0.1966639
Br	4.9491329	1.2073525	-0.4508697
O	-5.1967643	1.1206983	-0.6097019
O	4.2550309	-1.7825487	-0.065725
H	5.0448678	-1.2443375	-0.2064255
O	-3.8013685	3.5179014	-0.9126956

B (Table S8)

B3LYP/6-31+G(d,p)

E = –8857.206145 A. U.

C	1.8634307	-1.6664071	0.0834773
C	0.7828156	-0.8094992	0.0738541
C	0.9201866	0.617595	0.0082919
C	2.2547523	1.1005643	-0.1873574
C	3.3236385	0.2572111	-0.1963674
C	-0.2400134	1.4209665	0.0949417
C	-1.5271666	0.8029269	-0.0412724
C	-1.574796	-0.6043036	0.0288099
C	-2.7954507	-1.3120974	-0.0075538
C	-3.958214	-0.6038635	-0.1728119
C	-3.9862505	0.8725081	-0.3338323
C	-2.7358284	1.5575135	-0.2517236
H	2.414171	2.1503825	-0.3843915
C	-0.2152034	2.872665	0.3246361
C	-1.3614297	3.6365879	-0.0009291
C	0.8684252	3.5388498	0.9431938
C	-1.3452095	5.0297053	0.1549755
C	0.860114	4.9179754	1.1191362
H	1.7039661	2.970126	1.3292892
C	-0.2392762	5.6759557	0.6947901
H	-2.2409589	5.5705542	-0.1324361

H	1.7053672	5.3996686	1.602971
H	-0.2418959	6.7554714	0.8198973
C	-2.6569395	3.0002497	-0.4209972
O	-0.4594825	-1.3554138	0.1625476
Br	1.5935406	-3.5333337	0.2305526
Br	-2.8182891	-3.2007125	0.1506912
Br	5.0701374	0.9638898	-0.4697659
O	-5.1459482	1.3362699	-0.5115965
O	4.2281698	-1.9433292	0.0050514
O	-3.5829665	3.7199043	-0.8137007
O	-5.1677856	-1.1535357	-0.2309537
H	-5.7330225	-0.3384816	-0.3791053

B (Table S8)

M06-2X/6-31+G(d,p)

E = –8856.992165 A. U.

C	3.2192611	-1.2107344	-0.0152004
C	1.8501992	-1.670236	0.0782794
C	0.779698	-0.8097339	0.0685999
C	0.9204674	0.61511	0.00411
C	2.2575564	1.0962259	-0.1901522
C	3.3170713	0.2525431	-0.1899044
C	-0.2306913	1.4113301	0.0886944
C	-1.5171262	0.7992567	-0.0369696
C	-1.5611342	-0.5978574	0.0311221
C	-2.7849965	-1.3037076	-0.0000663
C	-3.9421553	-0.5971813	-0.1567339
C	-3.9733639	0.8813769	-0.3174334
C	-2.7234939	1.5530918	-0.239705
H	2.4205491	2.1451871	-0.3963962
C	-0.200873	2.8665592	0.3076319
C	-1.3394421	3.6267473	-0.0200705
C	0.8812562	3.5238362	0.9253976
C	-1.3224629	5.0159885	0.1261521
C	0.8781248	4.9014774	1.0900293
H	1.7095838	2.9497742	1.3217098
C	-0.2140736	5.6588504	0.6579253
H	-2.2189863	5.5567329	-0.1601068
H	1.7224522	5.3836131	1.5732397
H	-0.2116155	6.7383854	0.7763143
C	-2.6463028	2.9908723	-0.4163585
O	-0.4531723	-1.3488531	0.1557758
Br	1.5565516	-3.5146321	0.209168
Br	-2.8084108	-3.1715883	0.1509258
Br	5.0536829	0.9346208	-0.4452877
O	-5.121647	1.3468997	-0.4910625
O	4.2052914	-1.9447555	0.0135682
O	-3.5684843	3.7088149	-0.7886738
O	-5.1427972	-1.1533061	-0.2086872
H	-5.7244504	-0.3609968	-0.3524245

B (Table S8)

wB97XD/6-31+G(d,p)

E = –8856.892474 A. U.

C	3.2137789	-1.2070063	-0.0180701
C	1.8469939	-1.6690479	0.0807362
C	0.7748915	-0.8094201	0.0680333
C	0.9162376	0.6128265	0.0013918
C	2.2513684	1.09445	-0.1959356
C	3.3115706	0.2534094	-0.1988337
C	-0.2337128	1.4100156	0.0907704
C	-1.5174135	0.7994542	-0.0385836
C	-1.5636997	-0.595631	0.0298243
C	-2.786414	-1.3039761	-0.0039396

C	-3.9407505	-0.5964419	-0.1667976
C	-3.9690058	0.8814106	-0.3303361
C	-2.7239099	1.5570782	-0.2488866
H	2.4111553	2.1437258	-0.4009718
C	-0.2032145	2.8625901	0.3225158
C	-1.3370963	3.6253176	-0.0100302
C	0.8748722	3.5119398	0.9531102
C	-1.3182169	5.0126334	0.1501755
C	0.8726742	4.8870136	1.1312846
H	1.7017641	2.9352079	1.3474523
C	-0.2155878	5.6483553	0.6998971
H	-2.2095358	5.5590564	-0.1405018
H	1.71563	5.3632289	1.6226892
H	-0.2142723	6.7265506	0.8298762
C	-2.6374622	2.9926012	-0.4305139
O	-0.4579615	-1.3453945	0.1581781
Br	1.5625152	-3.5171098	0.2265306
Br	-2.8043359	-3.1746357	0.1531775
Br	5.046861	0.9424356	-0.4678165
O	-5.1219343	1.3417274	-0.5079121
O	4.202205	-1.9420821	0.0127935
O	-3.5489309	3.7145251	-0.8280352
O	-5.1445203	-1.1406139	-0.2246451
H	-5.7074348	-0.3326508	-0.372654

C (Table S8)

B3LYP/6-31+G(d,p)

E = –8857.211425 A. U.

C	3.2567506	-1.1603027	-0.0221905
C	1.8903194	-1.6443382	0.0834985
C	0.7970569	-0.8049834	0.0803691
C	0.9167644	0.6215895	0.0157842
C	2.2405125	1.1233578	-0.1809668
C	3.3250072	0.2968649	-0.1927447
C	-0.2647226	1.4067835	0.092735
C	-1.522271	0.7680745	-0.0326251
C	-1.5739883	-0.6519026	0.0276496
C	-2.7699639	-1.3592225	-0.0062815
C	-4.0077677	-0.6826828	-0.1661819
C	-3.9396851	0.7881874	-0.3122121
C	-2.752516	1.4989072	-0.2353829
H	2.3873012	2.175477	-0.3755139
C	-0.2638411	2.8668462	0.3157461
C	-1.4201296	3.6178056	-0.0050262
C	0.8084167	3.5518237	0.9281216
C	-1.4291569	5.0104061	0.1494154
C	0.779144	4.9329624	1.1016307
H	1.6560369	2.998408	1.3087337
C	-0.3305135	5.6759307	0.6829243
H	-2.334038	5.5390269	-0.1319992
H	1.621309	5.4268495	1.5785228
H	-0.3485838	6.7552078	0.8062275
C	-2.7013999	2.957377	-0.411661
O	-0.4376003	-1.3792154	0.1685437
Br	1.650838	-3.5158805	0.2236233
Br	-2.7815195	-3.2433059	0.1452843
Br	5.0606526	1.0357668	-0.4612744
O	4.2593827	-1.8913126	0.0008833
O	-3.6508351	3.6371521	-0.8060956
O	-5.157088	-1.1951848	-0.2207826
O	-5.1419507	1.3299472	-0.5108183
H	-5.7343751	0.532721	-0.4825858

C (Table S8)

M06-2X/6-31+G(d,p)

E = –8856.998379 A. U.

C	3.2479211	-1.1541722	-0.0158416
C	1.8842217	-1.6377885	0.0785767
C	0.7982624	-0.7982462	0.0785946
C	0.9152874	0.6248118	0.0171943
C	2.2380728	1.1292364	-0.176206
C	3.3174235	0.3057415	-0.1818308
C	-0.265374	1.3973832	0.0867655
C	-1.5138387	0.7595288	-0.0287902
C	-1.5592905	-0.6566232	0.0304955
C	-2.7485863	-1.3654812	0.0048283
C	-3.9912096	-0.695798	-0.1439741
C	-3.9275736	0.7781644	-0.2931157
C	-2.7481673	1.4803045	-0.2250381
H	2.3861868	2.1817436	-0.3761522
C	-0.2676824	2.8618859	0.2985962
C	-1.4181468	3.6047658	-0.0281562
C	0.7975506	3.5435668	0.9131003
C	-1.4349306	4.9929189	0.116679
C	0.7655013	4.923317	1.0753877
H	1.6401319	2.9889259	1.3056121
C	-0.3389025	5.660647	0.6458028
H	-2.3422859	5.5167809	-0.1669497
H	1.6029044	5.4216008	1.5543364
H	-0.3576552	6.7398913	0.762405
C	-2.7039686	2.9379205	-0.4165687
O	-0.4260518	-1.3743669	0.1624013
Br	1.6276516	-3.4893719	0.1936238
Br	-2.7501594	-3.230735	0.148863
Br	5.0415134	1.0258573	-0.4333507
O	4.2443133	-1.8764447	0.0083966
O	-3.651058	3.6062598	-0.8010969
O	-5.1251005	-1.2131715	-0.1878813
O	-5.1222787	1.3256792	-0.488978
H	-5.7324891	0.5536431	-0.4607443

C (Table S8)

wB97XD/6-31+G(d,p)

E = –8856.89798 A. U.

C	1.8784166	-1.6407015	0.0802423
C	0.792008	-0.8000844	0.0745386
C	0.912118	0.620251	0.0094461
C	2.2338704	1.1230378	-0.1871709
C	3.3122234	0.3003269	-0.1934795
C	-0.2643514	1.3964989	0.0856785
C	-1.5131563	0.7630313	-0.0336154
C	-1.5623048	-0.6505162	0.0261847
C	-2.7541104	-1.3597611	-0.0017215
C	-3.9881377	-0.6859121	-0.1568969
C	-3.9222141	0.7879571	-0.3083008
C	-2.743747	1.4914272	-0.2359542
H	2.3802896	2.1753324	-0.3873441
C	-0.2631758	2.858067	0.3115625
C	-1.4087604	3.6060915	-0.0171078
C	0.8005443	3.5286298	0.9386288
C	-1.4200218	4.9924271	0.1438853
C	0.772638	4.9054366	1.1165868
H	1.6408737	2.9689965	1.3277684
C	-0.3272226	5.6495876	0.6902211
H	-2.3215188	5.5249819	-0.1407811
H	1.6102016	5.3953662	1.6037181
H	-0.3450022	6.7273005	0.8204462
C	-2.6904492	2.9456223	-0.4261007

O	-0.4336853	-1.3693533	0.1615332
Br	1.6277256	-3.4948394	0.2163947
Br	-2.7536053	-3.2282469	0.1499607
Br	5.0353072	1.0265413	-0.4566984
O	4.2385806	-1.8808385	0.0080014
O	-3.6293794	3.6203445	-0.827817
O	-5.1309099	-1.1912018	-0.2057014
O	-5.1187945	1.3222331	-0.5072647
H	-5.707835	0.5300174	-0.474384

D (Table S8)

M06-2X/6-31+G(d,p)

E = –8856.998858 A. U.

C	3.290191	-1.059172	0.004621
C	1.940741	-1.579407	0.10379
C	0.829165	-0.772282	0.098085
C	0.904023	0.651238	0.023018
C	2.208218	1.188427	-0.181911
C	3.314171	0.396604	-0.178157
C	-0.308997	1.388779	0.094583
C	-1.523379	0.704549	-0.000679
C	-1.53441	-0.718	0.039366
C	-2.699668	-1.452122	-0.014103
C	-3.996593	-0.840277	-0.171799
C	-3.963266	0.647647	-0.294216
C	-2.785751	1.370821	-0.175308
H	2.330001	2.240615	-0.399391
C	-0.374893	2.855857	0.277777
C	-1.57361	3.546459	-0.005913
C	0.681074	3.604611	0.827533
C	-1.650608	4.936833	0.113917
C	0.592968	4.984652	0.959818
H	1.564486	3.100586	1.195817
C	-0.562568	5.665125	0.570393
H	-2.594788	5.413415	-0.129411
H	1.429413	5.529655	1.38708
H	-0.623811	6.744808	0.664275
C	-2.826204	2.811235	-0.302663
O	-0.377999	-1.394161	0.176247
Br	1.741345	-3.438484	0.228897
Br	-2.63772	-3.318329	0.099277
Br	5.01637	1.165703	-0.442381
O	4.307421	-1.754149	0.036997
O	-3.874448	3.430345	-0.56865
O	-5.065938	-1.441484	-0.224801
O	-5.12844	1.218833	-0.524992
H	-4.953527	2.195222	-0.608443

D (Table S8)

wB97XD/6-31+G(d,p)

E = –8856.898956 A. U.

C	3.28274	-1.067179	0.002983
C	1.934532	-1.587084	0.107517
C	0.822878	-0.77814	0.096007
C	0.902095	0.642103	0.016254
C	2.204791	1.176531	-0.193465
C	3.309706	0.385306	-0.189692
C	-0.305819	1.386006	0.093017
C	-1.520731	0.708169	-0.006173
C	-1.538015	-0.712951	0.033611
C	-2.707413	-1.442693	-0.022613
C	-3.997207	-0.824755	-0.188693
C	-3.956537	0.663745	-0.313172
C	-2.777842	1.384056	-0.18651

H	2.325177	2.228134	-0.412566
C	-0.364539	2.851236	0.289674
C	-1.557612	3.549814	0.005376
C	0.692832	3.586725	0.85276
C	-1.624719	4.939367	0.141345
C	0.612705	4.964337	1.001184
H	1.572813	3.075443	1.218101
C	-0.536379	5.654815	0.614028
H	-2.562327	5.427852	-0.101403
H	1.450511	5.498723	1.438525
H	-0.594014	6.73323	0.722706
C	-2.80873	2.822326	-0.30733
O	-0.387121	-1.392115	0.176517
Br	1.73708	-3.447825	0.252091
Br	-2.650252	-3.312347	0.101293
Br	5.009282	1.163135	-0.468029
O	4.301623	-1.764326	0.03874
O	-3.854458	3.448239	-0.580695
O	-5.072308	-1.419585	-0.2462
O	-5.115818	1.24126	-0.550765
H	-4.931754	2.214728	-0.630222

E (Table S8)

B3LYP/6-31+G(d,p)

E = –8857.210809 A. U.

C	3.3176572	-1.023682	0.0157606
C	1.9686695	-1.5551961	0.1214364
C	0.8433695	-0.7565562	0.1065677
C	0.9038606	0.6672487	0.0185415
C	2.2021141	1.2107699	-0.1900833
C	3.3229607	0.4255354	-0.181103
C	-0.3260011	1.4045529	0.0924439
C	-1.5387542	0.6964553	-0.0102932
C	-1.5391592	-0.7329267	0.0280864
C	-2.6982461	-1.4926059	-0.0430973
C	-4.0062899	-0.9141624	-0.2117306
C	-4.0367147	0.6080087	-0.3210658
C	-2.8013502	1.3577937	-0.1733577
H	2.3163542	2.2609735	-0.413108
C	-0.4228992	2.8581044	0.2770881
C	-1.6625137	3.5265345	0.0373481
C	0.6371547	3.6518588	0.7770307
C	-1.760358	4.9293376	0.1513007
C	0.5203987	5.028847	0.9084537
H	1.5494881	3.1767463	1.1071619
C	-0.6732409	5.6823979	0.5616988
H	-2.7156304	5.3959596	-0.0613569
H	1.359274	5.597366	1.3000345
H	-0.7558202	6.7616835	0.6511266
C	-2.8497153	2.7501299	-0.2310066
O	-5.0648982	-1.5446751	-0.2795161
O	-0.3724639	-1.3945048	0.1791413
Br	1.7999511	-3.4353715	0.2740532
Br	-2.593358	-3.3790132	0.0718964
Br	5.0271876	1.2365792	-0.465094
O	-5.1271585	1.1883339	-0.5321416
O	4.3480643	-1.7188135	0.0552508
O	-3.98952	3.3983707	-0.4563515
H	-4.6938334	2.666101	-0.5489826

E (Table S8)

M06-2X/6-31+G(d,p)

E = –8856.996852 A. U.

C	3.3139044	-0.9927313	0.0222674

C	1.9715628	-1.5296751	0.1201021
C	0.8484588	-0.7356416	0.1086452
C	0.8967482	0.6807728	0.0215416
C	2.1883797	1.2326332	-0.1866605
C	3.3102504	0.4562086	-0.1721277
C	-0.3430365	1.3998862	0.0870281
C	-1.5390192	0.6878083	-0.0094724
C	-1.5209788	-0.7458413	0.0302031
C	-2.6591936	-1.5227632	-0.0340643
C	-3.9773626	-0.9624068	-0.1867729
C	-4.036214	0.5650685	-0.2999274
C	-2.8095192	1.3326787	-0.1657506
H	2.2994016	2.2832771	-0.4164991
C	-0.4562622	2.851728	0.2606193
C	-1.6949795	3.5016032	0.0187303
C	0.5952309	3.6524861	0.7580507
C	-1.8107197	4.9004961	0.1208532
C	0.4646844	5.0244414	0.8769926
H	1.5073917	3.1838319	1.100527
C	-0.7326961	5.6631259	0.5223136
H	-2.7726508	5.3532812	-0.0937455
H	1.2954822	5.6045038	1.267153
H	-0.8242891	6.7417002	0.6035745
C	-2.8782066	2.7130817	-0.2340115
O	-5.019876	-1.5958418	-0.2413266
O	-0.3548079	-1.3844782	0.1760703
Br	1.8020551	-3.3925317	0.2519105
Br	-2.5198076	-3.3873026	0.0661642
Br	4.9998352	1.2561072	-0.4401767
O	-5.1289559	1.1107962	-0.4989213
O	4.341784	-1.676145	0.0632401
O	-4.0184302	3.3562611	-0.4498915
H	-4.7221317	2.6413613	-0.5321659

E (Table S8)

wB97XD/6-31+G(d,p)

E = –8856.896724 A. U.

C	3.3052936	-1.007759	0.018557
C	1.9631375	-1.5422505	0.1252775
C	0.8415343	-0.7445859	0.1092411
C	0.8963466	0.6680312	0.0155372
C	2.1865281	1.2150819	-0.200187
C	3.3065597	0.4376346	-0.1869997
C	-0.3376039	1.3967475	0.0855437
C	-1.535498	0.694499	-0.0178233
C	-1.5253678	-0.7392445	0.0236162
C	-2.66897	-1.5080297	-0.0438185
C	-3.9782094	-0.9373148	-0.2147822
C	-4.0270558	0.5910793	-0.3328617
C	-2.8003229	1.350888	-0.1815488
H	2.2969358	2.2648671	-0.4325984
C	-0.4379363	2.8467234	0.2759012
C	-1.6687796	3.5088135	0.0359635
C	0.6187627	3.6301448	0.7892985
C	-1.7713597	4.9068564	0.1625447
C	0.4995071	4.9992372	0.9326629
H	1.5272809	3.1495505	1.1236192
C	-0.6909854	5.6524516	0.5854251
H	-2.7256385	5.3754603	-0.0493006
H	1.333549	5.5649641	1.336183
H	-0.7767986	6.7294592	0.6889775
C	-2.8537119	2.7323682	-0.2404085
O	-5.0263836	-1.5645409	-0.2790927
O	-0.3659845	-1.3832874	0.1816788

Br	1.7902727	-3.405998	0.2772405
Br	-2.5449247	-3.3759909	0.0784957
Br	4.9935112	1.2446346	-0.4735886
O	-5.1151052	1.143378	-0.5485504
O	4.3335983	-1.6950644	0.0614091
O	-3.9832536	3.3902781	-0.4679677
H	-4.68958	2.6887606	-0.5686983

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