

# Supporting Information

## *Para*-Selective C-H Functionalization of Iodobenzenes

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## General Information

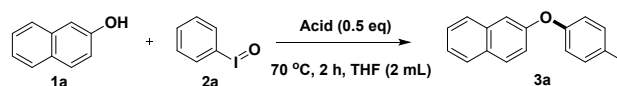
All glassware was oven dried at 120 °C for more than 1 hour and cooled down under vacuum. THF was dried and distilled from 4Å molecular sieves under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Substituted iodosobenzenes were all prepared following literature procedures.[1] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel with n-hexane. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. GC yields were recorded with a Varian GC 3900 gas chromatography instrument with a FID detector. All new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using Bruker-BioSpin spectrometers at 400 MHz ( $^1\text{H}$  NMR) and 100 MHz ( $^{13}\text{C}$  NMR). Chemical shift ( $\delta$ ) values are relative to DMSO- $d_6$  (2.50 ppm for  $^1\text{H}$  NMR spectra, 39.52 ppm for  $^{13}\text{C}$  NMR spectra). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion ( $[\text{M}]^+$  or  $[\text{M}+\text{H}]^+$ ). In-situ IR spectra were recorded on a Mettler Toledo React IRTM 10 spectrometer using a diamond comb.

## Experimental section

**1. One-pot two-step method for *para*-selective C-H functionalization of iodobenzene.** In an oven-dried Schlenk flask equipped with a stir-bar, iodosobenzene (1.0 mmol), mCPBA (0.5 mmol) and  $\text{CH}_2\text{Cl}_2$  (1 mL) were combined. Then, the reaction mixture was allowed to stir at 25 °C for 2 h. Subsequently, THF (2 mL), butyric acid (0.05 mmol) and 2-naphthol (0.25 mmol) were added under air. The Schlenk flask with the reaction mixture was further sealed and allowed to stir at 70 °C for 10 min. After the reaction was completed, the mixture was quenched by water and extracted with ethyl acetate ( $3 \times 10$  mL). The organic layers were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the crude mixture was concentrated under vacuum, the pure product was obtained by flash column chromatography on silica gel with n-hexane.

**2. General procedure for preparation of iodosobenzenes.** In an oven-dried Schlenk flask equipped with a stir-bar, 30% H<sub>2</sub>O<sub>2</sub> (50 mmol, 4.1 mL) and Ac<sub>2</sub>O (65 mmol, 6.2 mL) were combined. The mixture was allowed to stir at 40 °C for 4 hours. After that, substituted iodobenzene (5 mmol) was added under air, and the mixture was further stirred overnight at 40 °C. The reaction was quenched by adding water, and white solid was obtained after filtration and washing with water (10 mL × 3). The solid was suspended in a 3M NaOH solution (30 mL) for 40 min at room temperature. Finally, the pure substituted iodosobenzene was obtained as a light-yellow solid in 96% yield after washing with water (10 mL × 3), ethyl ether (10 mL × 3), and chloroform (10 mL × 3).

**Table S1.** Impact of reaction parameters on oxidative C-H/N-H coupling reaction



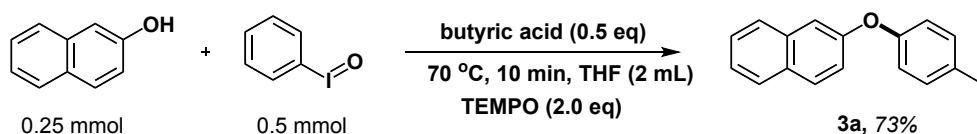
Entry	Acid	Solvent	Yield <sup>b</sup> (%)
1	none	THF	17
2	none	toluene	n.d.
3	none	CH <sub>3</sub> CN	n.d.
4	none	1,4-dioxane	trace
5	none	DCE	trace
6	HOAc	THF	36 (39)
7	TsOH	THF	n.d.
8	Propionic acid	THF	50
9	Pivalic acid	THF	51
10	n-valeric acid	THF	46
11	Heptanoic acid	THF	47
12	Butyric acid	THF	76 (70)
13 <sup>c</sup>	Butyric acid	THF	70
14	Butyric acid (1.0 eq)	THF	73
15 <sup>d</sup>	Butyric acid	THF	48
16 <sup>e</sup>	Butyric acid	THF	75

[a] **1a** (0.25 mmol), **2a** (2 eq, 0.5 mmol), Acid (0.125 mmol), THF (2 mL), 70 °C, 2 h, under air. [b] The GC yield with biphenyl as the internal standard. [c] Under N<sub>2</sub>. [d] **2a** (1.2 eq, 0.3 mmol). [e] Stirred for 10 mins.

**3. General procedure for the oxidative C-H/O-H cross-coupling reaction of iodosobenzene and 2-naphthol.** In an oven-dried Schlenk flask equipped with a stir-bar, iodosobenzene (0.5 mmol) and THF (2 mL) were combined. Butyric acid (11.5  $\mu$ L, 0.125 mmol) and 2-naphthol (0.25 mmol) were added subsequently under air. The Schlenk flask with the reaction mixture was sealed and allowed to stir at 70 °C for 10

min. After the reaction was completed, the mixture was quenched by water and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the crude mixture was concentrated under vacuum, the pure product was obtained by flash column chromatography on silica gel with n-hexane.

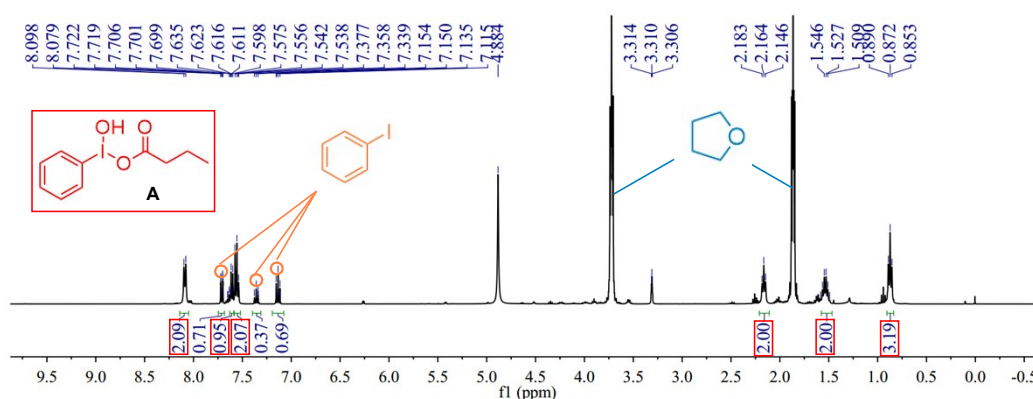
As shown in Table S1, various reaction parameters were examined for the coupling reaction between 2-naphthol **1a** and iodosobenzenes **2a**. THF was concluded to be the best choice after testing several solvents (entries 1-5). Acid might be beneficial for this transformation, since the addition of acetic acid could afford a better result (entry 6). In this respect, various acids were investigated, and butyric acid gave the best yield for this coupling reaction (entries 7-12). Further examination indicated that the reaction performed under air or nitrogen atmosphere could afford similar results (entry 13). Increasing the amount of butyric acid did not further improve the yield (entry 14). However, reducing **2a** from 2 equivalents to 1.2 equivalents decreased the product yield (entry 15). The examination revealed that the reaction could be finished in 10 min, thus complementing the click method for the rapid *para*-selective C-H functionalization. Finally, the optimized conditions involved the combination of **1a** and **2a** in a 1:2 ratio in the presence of 0.5 equivalent of butyric acid and 2 mL of THF at 70 °C for 10 min under air atmosphere. It is worth noting that this transformation occurs under metal-free conditions, which will avoid metal contamination in further applications.



**4. The Procedure for Radical Inhibition Experiment.** In an oven-dried Schlenk tube equipped with a stir-bar, iodosobenzene (110 mg, 0.5 mmol), TEMPO (78.2 mg, 0.5 mmol) and THF (2 mL) were combined. Butyric acid (11.5 uL, 0.125 mmol) and 2-naphthol (36 mg, 0.25 mmol) were added subsequently under air. The Schlenk flask with the reaction mixture was sealed and allowed to stir at 70 °C for 10 min. After the reaction was completed, the mixture was quenched by water and extracted with ethyl acetate (3 ×10 mL). The organic layers were combined and dried over anhydrous

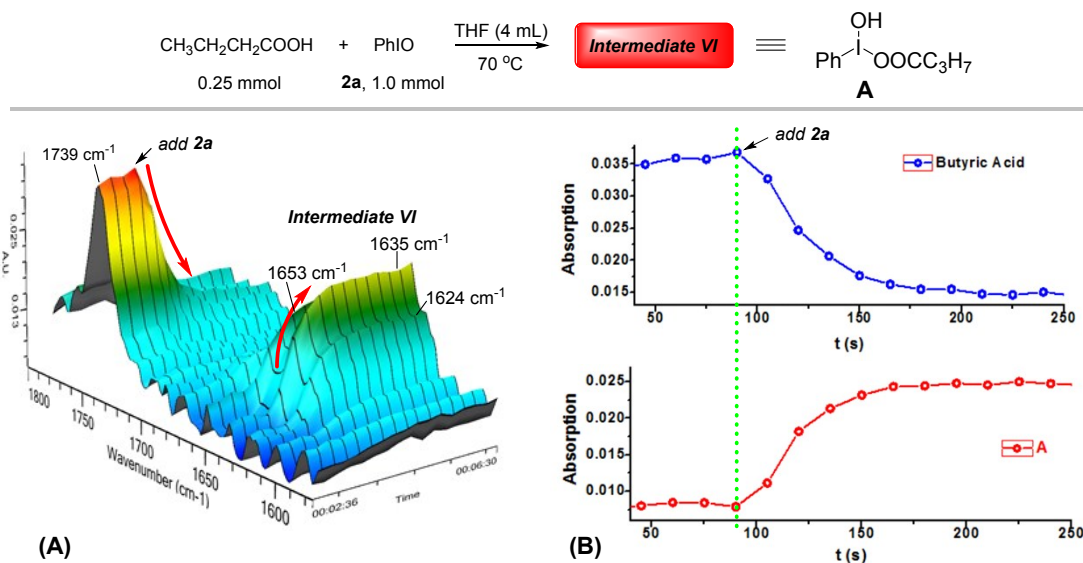
Na<sub>2</sub>SO<sub>4</sub>. After the crude mixture was concentrated under vacuum, the pure product was obtained in 73% yield by flash column chromatography on silica gel with n-hexane.

**5. <sup>1</sup>H NMR Experiment.** In an oven-dried Schlenk tube equipped with a stir-bar, iodosobenzene (110 mg, 0.5 mmol), and THF (2 mL) were combined. Butyric acid (11.5  $\mu$ L, 0.125 mmol) was added subsequently under air. The Schlenk flask with the reaction mixture was sealed and allowed to stir at 70 °C for 5 min. After the reaction was completed, the mixture was cooled down quickly and concentrated under vacuum. After the reaction solvent (THF) was almost removed, 1 mL of methanol-d<sub>4</sub> was added. 0.5 mL of the above solution was then transferred to a NMR tube to be analyzed.

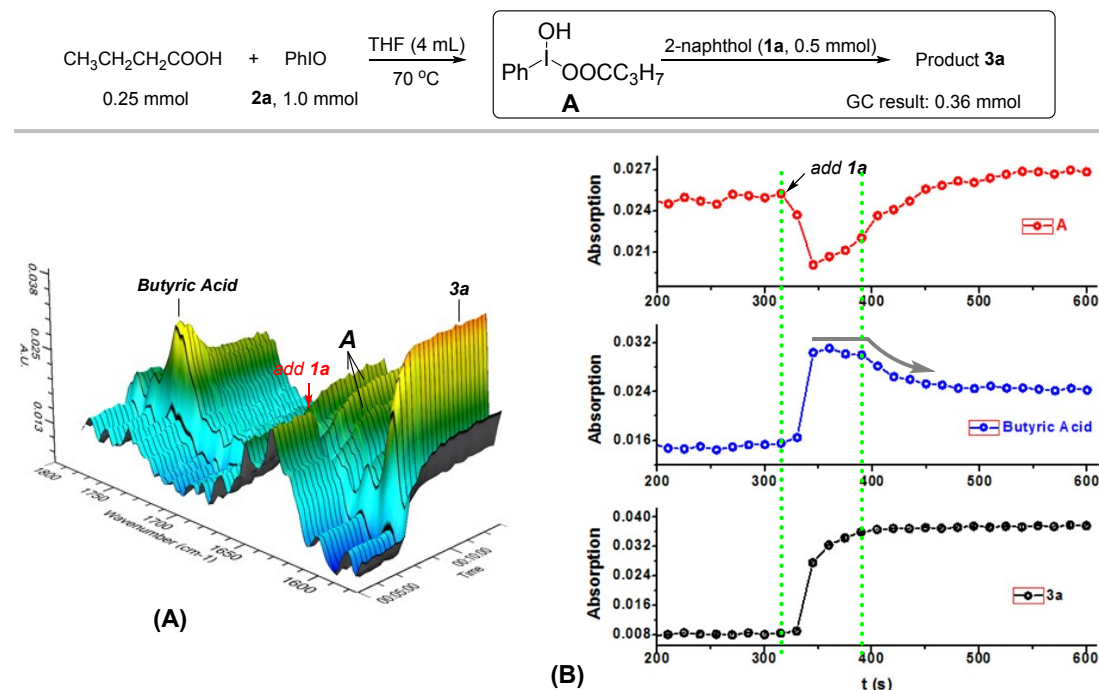


**6. The IR Experiment.** In an oven dried self-prepared three-necked micro reactor with a magnetic stirrer, THF (4 mL) and butyric acid (23  $\mu$ L, 0.5 mmol) was added via a syringe or micro-syringe, then PhIO **2a** (110 mg, 0.5 mmol) was added. The mixture was allowed to stir at 70 °C and recorded by React IR. The course of the reaction could be observed from the characteristic IR band of butyric acid (1739 cm<sup>-1</sup>). When the butyric acid did not decrease anymore and the increasing band of intermediate **VI** (1653 cm<sup>-1</sup>, 1635 cm<sup>-1</sup>, 1624 cm<sup>-1</sup>) was constant, 2-naphthol **1a** (36 mg, 0.5 mmol) was added. In the beginning, the absorption band of **VI** decreased quickly after the addition of **1a**. Meanwhile, the desired product **3a** and butyric acid appear proportionally. It is worth noting that the new formed band of butyric acid remains steady for a while accompanying the continuous accumulation of **3a**, then goes down gradually with the reformation of **A**. In addition, no absorption bands of **1a** was detected in the whole

reaction. These results suggested that one **VI** could consume two equivalent of **1a**, and this process is a quick step.

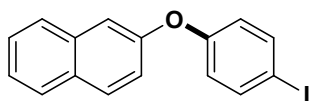


**Figure S1** (A) 3D-profile of the reaction between PhIO (1.0 mmol) and butyric acid (0.25 mmol) in THF (4 mL) at 70 °C through *in-situ* IR. (B) Detailed kinetic profile (blue line: butyric acid, band at 1739 cm<sup>-1</sup>; red line: A, band at 1653 cm<sup>-1</sup>, 1635 cm<sup>-1</sup>, 1624 cm<sup>-1</sup>).



**Figure S2** (A) 3D-profile of the reaction between 2-naphthol (**1a**, 0.5 mmol) and **A** in THF (4 mL) at 70 °C through *in-situ* IR. (B) Detailed kinetic profile (blue line: butyric acid; red line: **A**; black line: product **3a**).

### Analytical Data of Products.

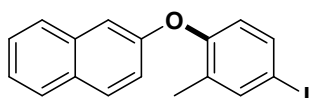


#### 2-(4-iodophenoxy)naphthalene (3a):

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.12 (d,  $J$  = 8.4 Hz, 1H), 7.92 – 8.06 (m, 2H), 7.63–7.74 (m, 1H), 7.59 – 7.53 (m, 1H), 7.41 – 7.34 (m, 2H), 7.21 (d,  $J$  = 8.8 Hz, 1H), 7.12 (t,  $J$  = 7.4 Hz, 1H), 6.90 – 6.99 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  156.89, 153.95, 135.08, 131.04, 131.02, 130.96, 130.10, 128.66, 128.62, 125.98, 123.20, 119.96, 117.34, 92.94.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{11}\text{IO}$   $[\text{M}]^+$ : 345.9855; found: 345.9849.

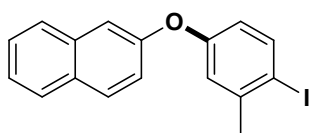


#### 2-(4-iodo-2-methylphenoxy)naphthalene (3b):

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.11 (d,  $J$  = 8.4 Hz, 1H), 8.05 - 7.90 (m, 2H), 7.68 (t,  $J$  = 7.6 Hz, 1H), 7.56 (t,  $J$  = 7.4 Hz, 1H), 7.29 – 7.15 (m, 2H), 6.94 (d,  $J$  = 7.2 Hz, 1H), 6.78 (s, 1H), 6.73 (d,  $J$  = 8.4 Hz, 1H), 2.26 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  156.93, 154.03, 139.89, 135.10, 131.06, 131.02, 130.96, 129.85, 128.70, 128.65, 125.98, 123.99, 120.00, 117.88, 114.44, 92.87, 21.00.

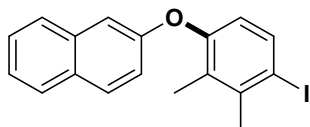
HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{13}\text{IO}$   $[\text{M}+\text{H}]^+$ : 361.0089; found: 361.0084



#### 2-(4-iodo-3-methylphenoxy)naphthalene (3c):

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.11 (d,  $J$  = 8.4 Hz, 1H), 8.00 - 7.88 (m, 2H), 7.69 - 7.62 (m, 1H), 7.56 – 7.49 (m, 1H), 7.33 (d,  $J$  = 7.6 Hz, 1H), 7.16 (td,  $J$  = 7.2, 1.2 Hz, 1H), 7.11 – 6.99 (m, 2H), 6.71 (dd,  $J$  = 8.0, 0.8 Hz, 1H), 2.26 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $\text{d}_6$ )  $\delta$  154.92, 154.85, 135.59, 132.04, 131.29, 131.11, 129.09, 129.07, 128.57, 127.90, 126.09, 124.28, 118.91, 117.97, 91.69, 16.54.  
HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{13}\text{IO}$   $[\text{M}+\text{H}]^+$ : 361.0089; found: 361.0079.

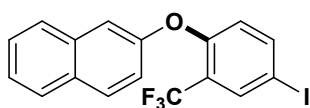


**2-(4-iodo-2,3-dimethylphenoxy)naphthalene (3d):**

$^1\text{H}$  NMR (400 MHz, DMSO- $\text{d}_6$ )  $\delta$  8.11 (d,  $J$  = 8.8 Hz, 1H), 7.95-7.87 (m, 2H), 7.68 – 7.62 (m, 1H), 7.55 – 7.48 (m, 1H), 7.10 - 6.94 (m, 3H), 6.60 (d,  $J$  = 8.0 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $\text{d}_6$ )  $\delta$  154.79, 154.11, 138.81, 135.12, 130.76, 130.73, 130.50, 128.60, 128.59, 126.99, 126.49, 125.47, 125.45, 118.00, 115.76, 90.60, 19.76, 12.07.

HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{IO}$   $[\text{M}+\text{H}]^+$ : 375.0246; found: 375.0240.

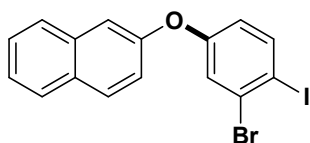


**2-(4-iodo-2-(trifluoromethyl)phenoxy)naphthalene (3e):**

$^1\text{H}$  NMR (400 MHz, DMSO- $\text{d}_6$ )  $\delta$  8.13 (d,  $J$  = 8.4 Hz, 1H), 8.04 (d,  $J$  = 8.8 Hz, 1H), 7.98 (d,  $J$  = 8.0 Hz, 1H), 7.71-7.65 (m, 1H), 7.60-7.55 (m, 2H), 7.46 (d,  $J$  = 8.0 Hz, 1H), 7.318 (d,  $J$  = 8.8 Hz, 1H), 7.282 (s, 1H), 7.17 (dd,  $J$  = 8.0, 2.0 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $\text{d}_6$ )  $\delta$  157.37, 153.03, 135.11, 131.44, 131.38, 131.35, 131.20, 130.83 (q,  $J$  = 64 Hz), 128.74, 126.36, 123.71 (q,  $J$  = 542 Hz), 120.71, 120.30, 119.56 (q,  $J$  = 7 Hz), 113.51 (q,  $J$  = 8 Hz), 93.88.

HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_3\text{IO}$   $[\text{M}]^+$ : 413.9728; found: 413.9719.

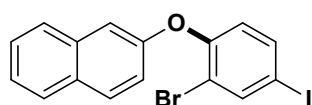


**2-(3-bromo-4-iodophenoxy)naphthalene (3f):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.13 (d,  $J$  = 8.4 Hz, 1H), 8.00 (d,  $J$  = 8.8, 1H), 7.96 (d,  $J$  = 8.0, 1H), 7.77 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.60-7.51 (m, 1H), 7.36 – 7.30 (m, 1H), 7.18-7.06 (m, 2H), 6.82 (dd,  $J$  = 8.0, 1.2 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  153.70, 153.05, 135.11, 133.85, 131.06, 131.01, 130.97, 129.41, 128.74, 128.69, 126.02, 125.32, 118.88, 118.80, 112.88, 92.12.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{10}\text{BrIO}$   $[\text{M}]^+$ : 423.8960; found: 423.8954.

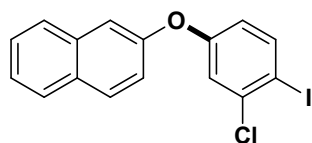


**2-(2-bromo-4-iodophenoxy)naphthalene (3g):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.12 (d,  $J$  = 8.4 Hz, 1H), 8.04 (d,  $J$  = 8.8 Hz, 1H), 7.99 (d,  $J$  = 7.6 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.61 – 7.56 (m, 1H), 7.34 – 7.27 (m, 3H), 7.17 – 7.10 (m, 1H), 6.95 – 6.89 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.92, 153.17, 135.07, 134.52, 131.86, 131.31, 131.26, 131.17, 128.74, 126.32, 125.93, 122.37, 120.34, 119.80, 116.06, 93.72.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{10}\text{BrIO}$   $[\text{M}]^+$ : 423.8960; found: 423.8954.

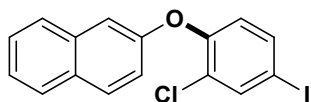


**2-(3-chloro-4-iodophenoxy)naphthalene (3h):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.13 (d,  $J$  = 8.4 Hz, 1H), 8.01 (d,  $J$  = 8.8 Hz, 1H), 7.97 (d,  $J$  = 8.0 Hz, 1H), 7.72-7.66 (m, 1H), 7.63 (dd,  $J$  = 7.8, 1.2 Hz, 1H), 7.60-7.53 (m, 1H), 7.34-7.26 (m, 1H), 7.19 (td,  $J$  = 7.6, 1.2 Hz, 1H), 7.14 (d,  $J$  = 8.8, 1H), 6.86 (dd,  $J$  = 8.2, 1.4 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  153.68, 152.01, 135.12, 131.12, 131.03, 130.86, 128.81, 128.79, 128.73, 126.08, 124.96, 123.38, 118.98, 118.80, 92.10.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{10}\text{ClIO}$   $[\text{M}]^+$ : 379.9465; found: 379.9459.

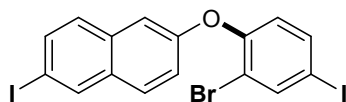


**2-(2-chloro-4-iodophenoxy)naphthalene (3i):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.12 (d,  $J$  = 8.4 Hz, 1H), 8.03 (d,  $J$  = 8.8 Hz, 1H), 7.97 (d,  $J$  = 8.0 Hz, 1H), 7.68 (t,  $J$  = 7.6 Hz, 1H), 7.57 (t,  $J$  = 7.6 Hz, 1H), 7.42-7.33 (m, 1H), 7.29 (d,  $J$  = 8.8 Hz, 1H), 7.17 (d,  $J$  = 8.0 Hz, 1H), 7.00 (s, 1H), 6.92 – 6.82 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.89, 153.17, 135.07, 134.13, 131.51, 131.31, 131.24, 131.17, 128.72, 126.30, 123.02, 120.31, 117.04, 115.66, 93.70.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{10}\text{ClIO}$   $[\text{M}]^+$ : 379.9465; found: 379.9459.

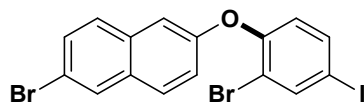


**2-(2-bromo-4-iodophenoxy)-6-iodonaphthalene (3j):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.44 (d,  $J$  = 1.6 Hz, 1H), 7.96 (d,  $J$  = 9.2 Hz, 1H), 7.93-7.83 (m, 2H), 7.33 – 7.26 (m, 3H), 7.16 – 7.11 (m, 1H), 6.94 – 6.89 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.67, 153.64, 136.84, 136.74, 134.15, 133.15, 132.70, 131.88, 130.27, 126.11, 122.41, 121.04, 119.96, 116.19, 93.56, 92.68.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_9\text{BrI}_2\text{O}$   $[\text{M}]^+$ : 549.7926; found: 549.7914.

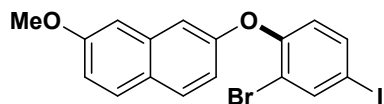


**2-bromo-6-(2-bromo-4-iodophenoxy)naphthalene (3k):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.30 (d,  $J$  = 2.0 Hz, 1H), 8.08-7.99 (m, 2H), 7.79 (dd,  $J$  = 9.2, 2.0 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.19 – 7.13 (m, 1H), 6.96 – 6.90 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.70, 153.71, 133.92, 133.51, 132.24, 131.91, 131.52, 130.47, 130.39, 126.15, 122.42, 121.35, 119.98, 119.59, 116.21, 93.53.

HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_9\text{Br}_2\text{IO}$   $[\text{M}]^+$ : 501.8065; found: 501.8061.

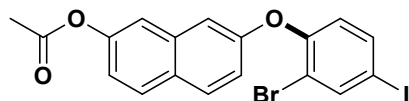


**2-(2-bromo-4-iodophenoxy)-7-methoxynaphthalene (3l):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.01 – 7.88 (m, 2H), 7.45 (d,  $J$  = 2.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.23 (dd,  $J$  = 9.2, 2.4 Hz, 1H), 7.16-7.10 (m, 2H), 6.95 – 6.89 (m, 1H), 3.94 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  159.53, 157.92, 153.73, 136.74, 131.84, 130.91, 130.65, 126.47, 125.87, 122.33, 119.77, 118.39, 117.70, 116.07, 110.32, 92.36, 55.33.

HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{12}\text{BrIO}_2$   $[\text{M}+\text{H}]^+$ : 454.9144; found: 454.9135.

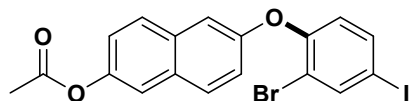


**7-(2-bromo-4-iodophenoxy)naphthalen-2-yl acetate (3m):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.07 (d,  $J$  = 8.8 Hz, 2H), 7.85 (d,  $J$  = 1.6 Hz, 1H), 7.39 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 7.36-7.25 (m, 3H), 7.17 (s, 1H), 6.97 – 6.91 (m, 1H), 2.36 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  169.48, 157.79, 154.03, 150.62, 136.09, 131.91, 131.19, 130.67, 129.21, 126.14, 122.54, 122.43, 122.02, 120.05, 116.26, 92.70, 21.05.

HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{12}\text{BrIO}_3$   $[\text{M}+\text{H}]^+$ : 482.9093; found: 482.9087.

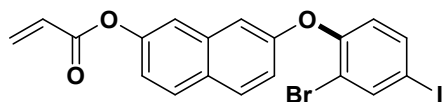


**6-(2-bromo-4-iodophenoxy)naphthalen-2-yl acetate (3n):**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.16 (d,  $J$  = 9.2 Hz, 1H), 8.03 (d,  $J$  = 8.8 Hz, 1H), 7.80 (d,  $J$  = 2.4 Hz, 1H), 7.50 (dd,  $J$  = 9.2, 2.4 Hz, 1H), 7.38-7.25 (m, 3H), 7.15 (s, 1H), 6.95 – 6.88 (m, 1H), 2.35 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $\text{d}^6$ )  $\delta$  169.41, 157.94, 153.14, 148.48, 133.12, 132.90, 131.87, 131.43, 130.84, 125.96, 124.24, 122.39, 121.07, 119.79, 119.45, 116.01, 93.57, 20.94.

HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{12}\text{BrIO}_3$   $[\text{M}+\text{H}]^+$ : 482.9093; found: 482.9087.



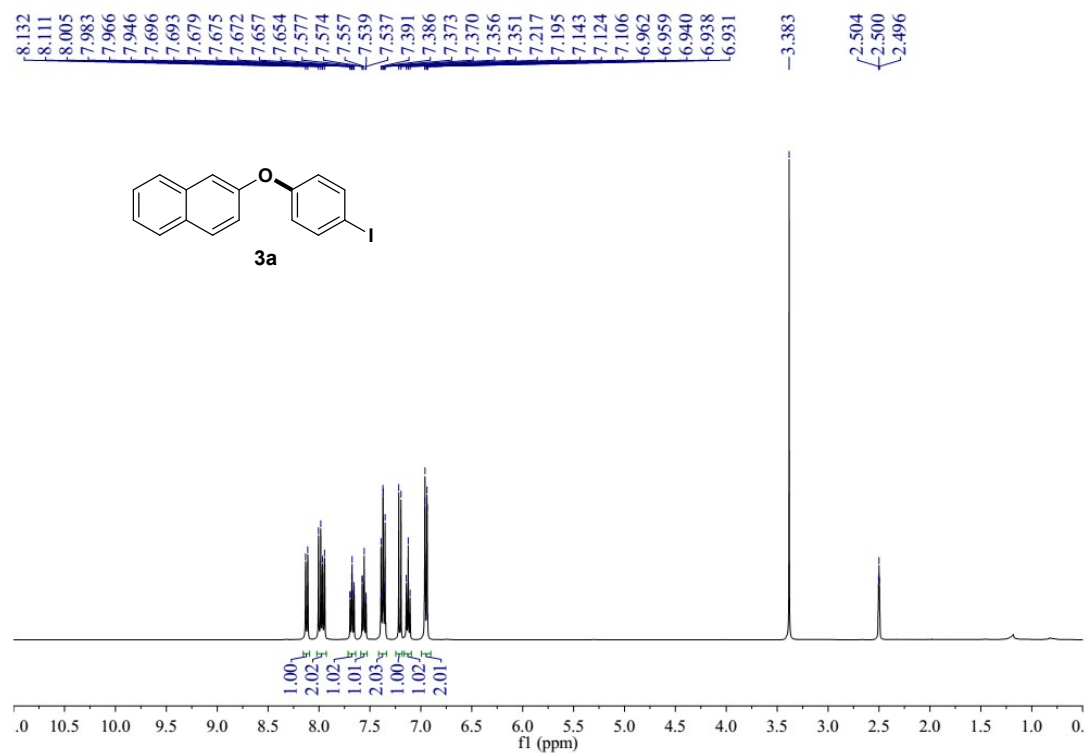
**7-(2-bromo-4-iodophenoxy)naphthalen-2-yl acrylate (3o):**

$^1\text{H}$  NMR (400 MHz, DMSO- $\text{d}^6$ )  $\delta$  8.16 - 8.04 (m, 2H), 7.89 (s, 1H), 7.44 (dd,  $J$  = 8.8, 1.6 Hz, 1H), 7.35-7.27 (m, 3H), 7.18 (s, 1H), 6.97 – 6.92 (m, 1H), 6.70-6.43 (m, 2H), 6.21 (d,  $J$  = 10.4 Hz, 1H).

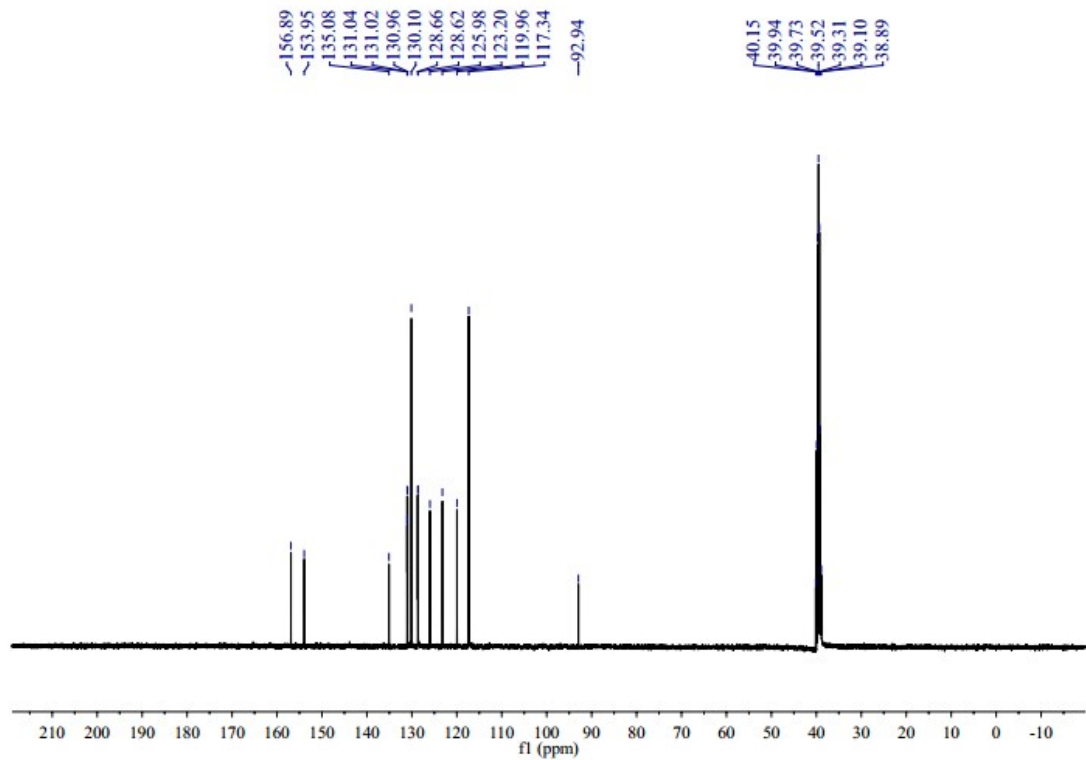
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $\text{d}^6$ )  $\delta$  164.30, 157.76, 154.10, 150.35, 136.07, 134.17, 131.91, 131.20, 130.79, 129.28, 127.55, 126.15, 122.43, 121.78, 120.11, 120.07, 116.28, 92.71.

HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{12}\text{BrIO}_3$   $[\text{M}+\text{H}]^+$ : 494.9093; found: 494.9087.

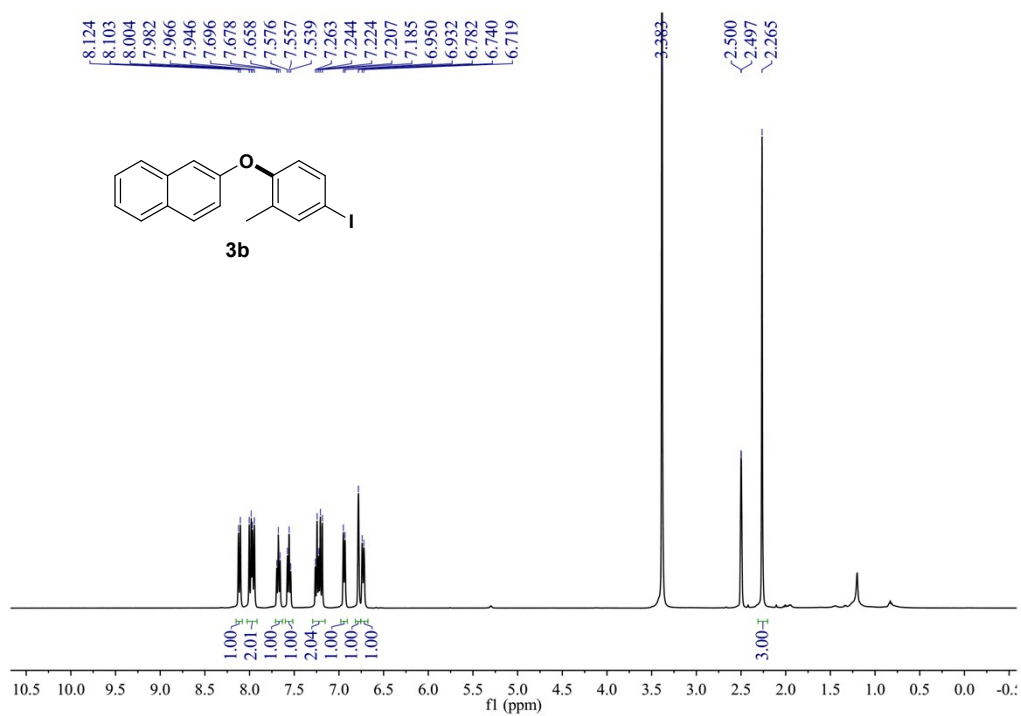
# <sup>1</sup>H NMR spectrum



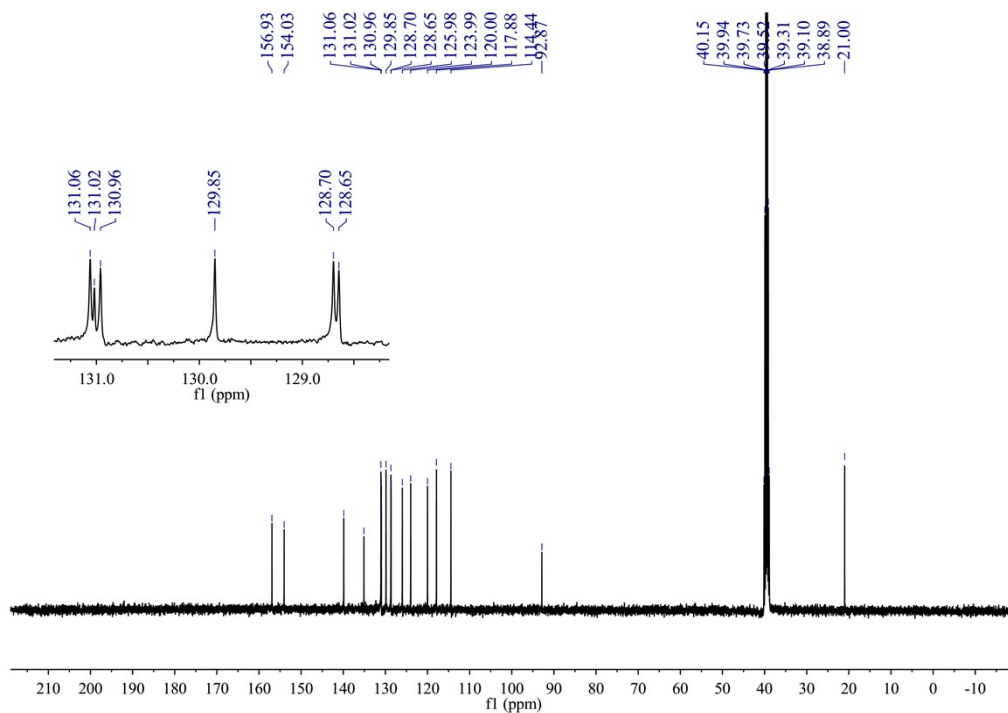
# <sup>13</sup>C NMR spectrum



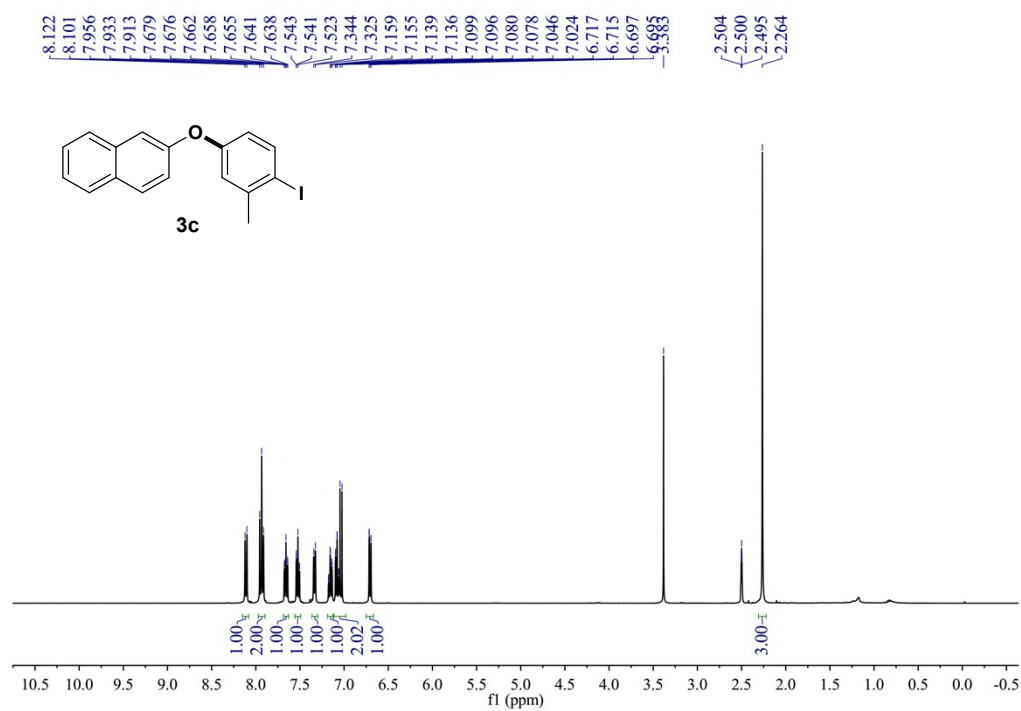
# <sup>1</sup>H NMR spectrum



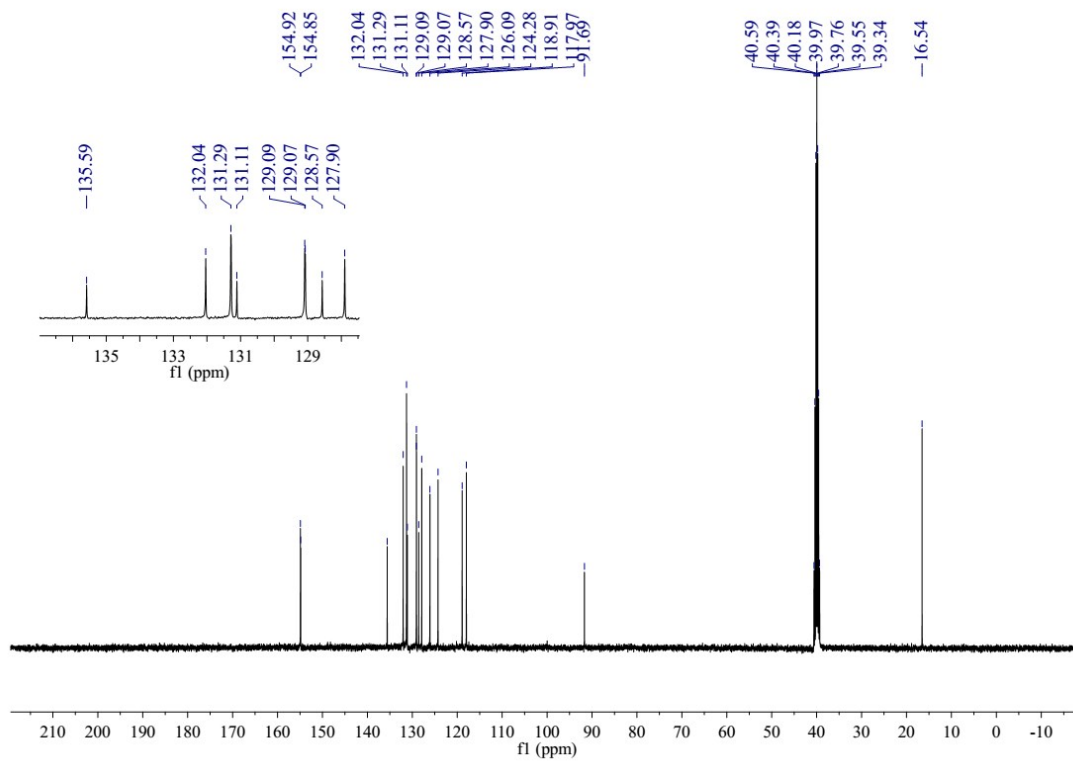
# <sup>13</sup>C NMR spectrum



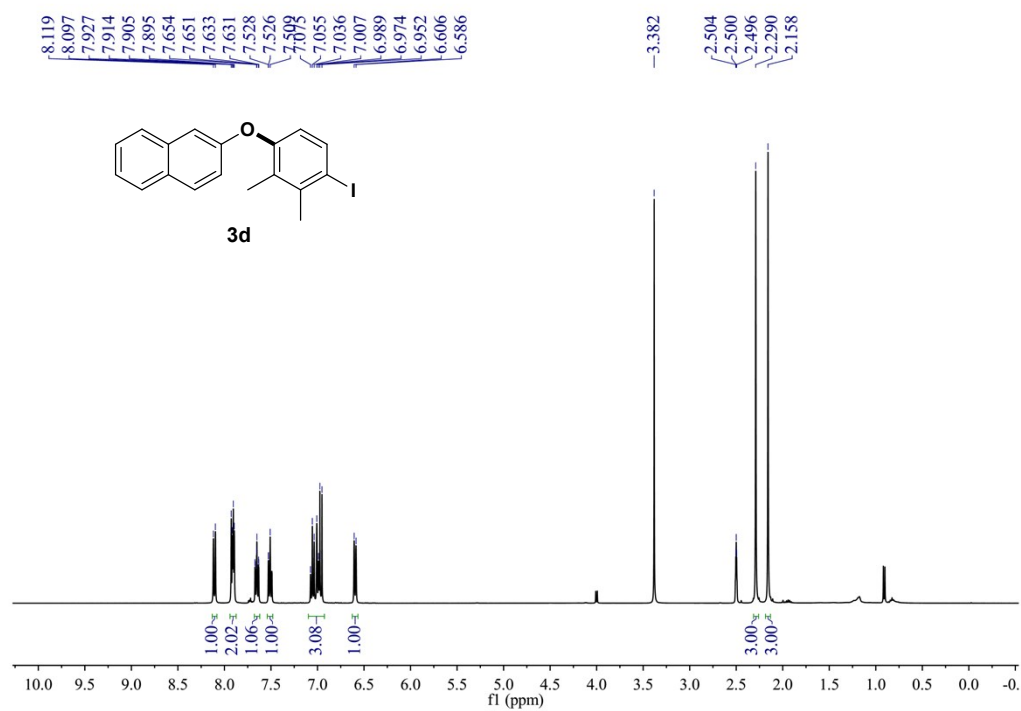
# <sup>1</sup>H NMR spectrum



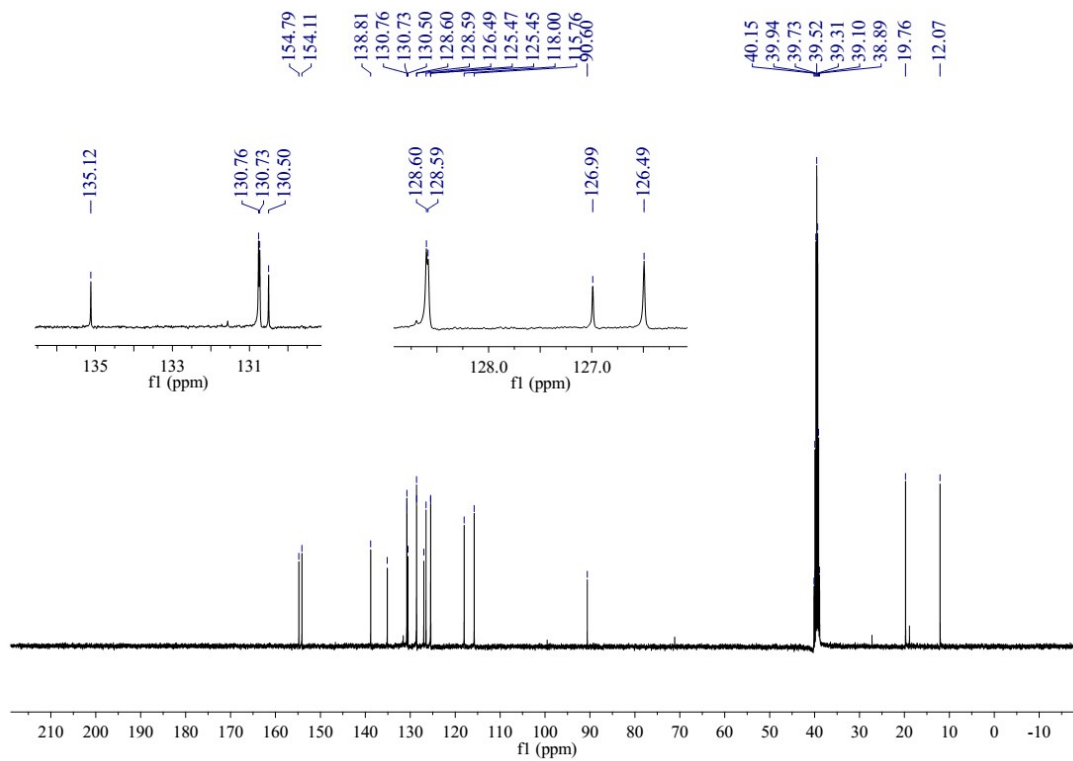
# <sup>13</sup>C NMR spectrum



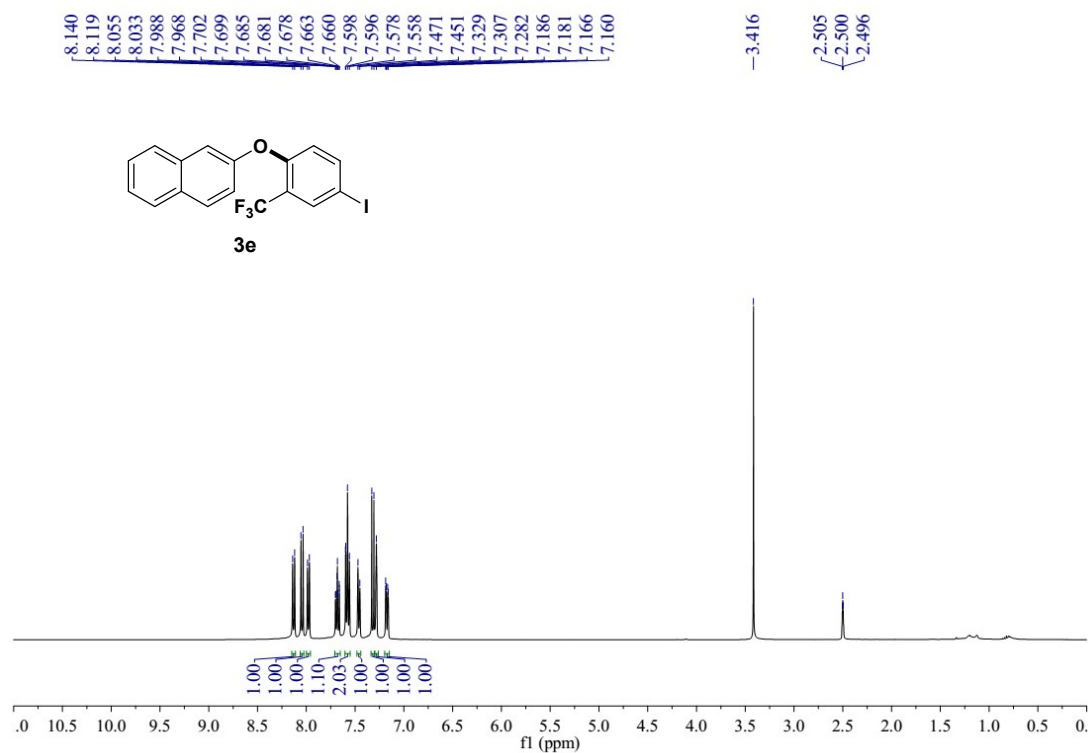
# <sup>1</sup>H NMR spectrum



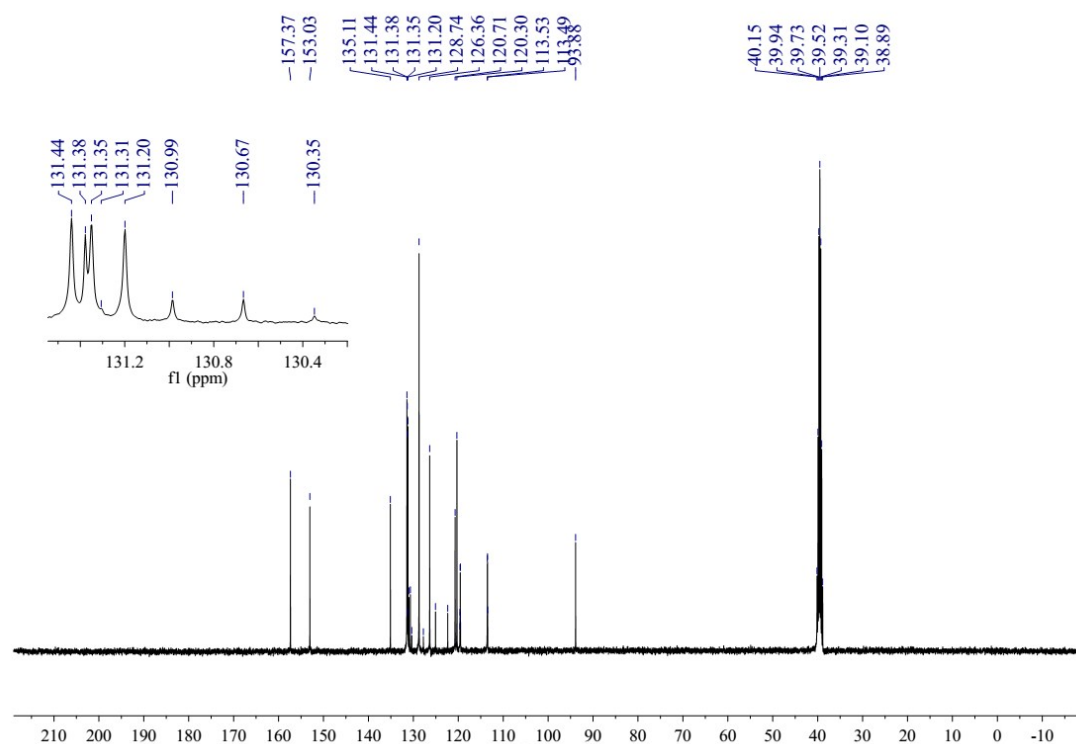
# <sup>13</sup>C NMR spectrum



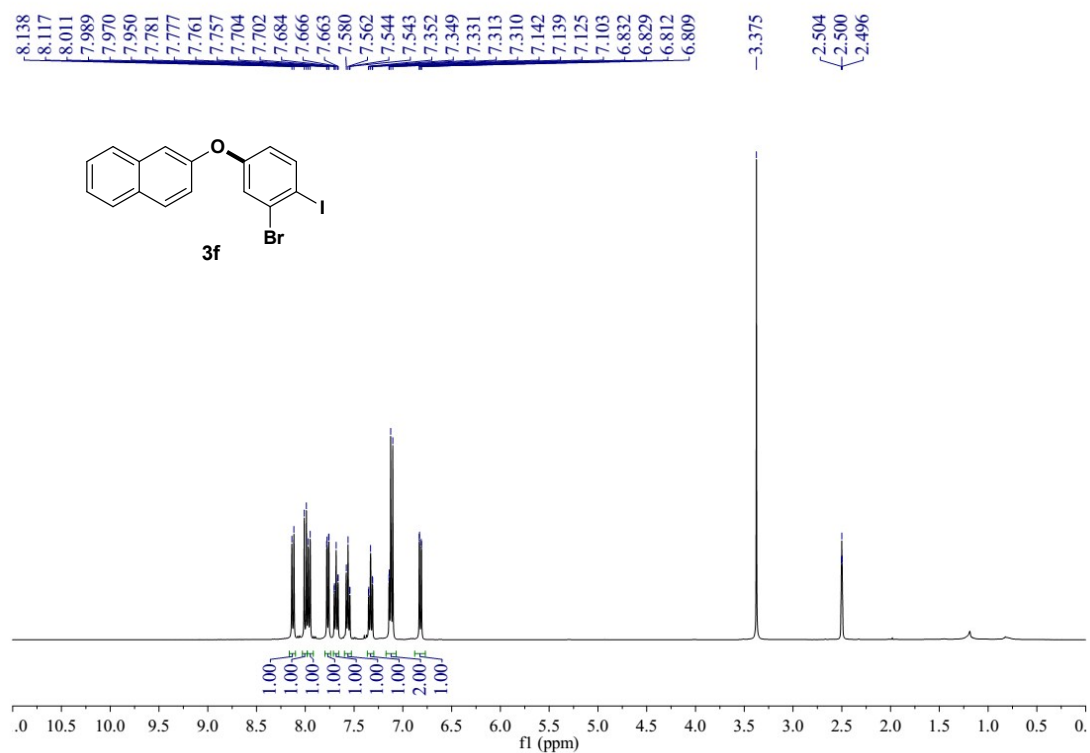
# <sup>1</sup>H NMR spectrum



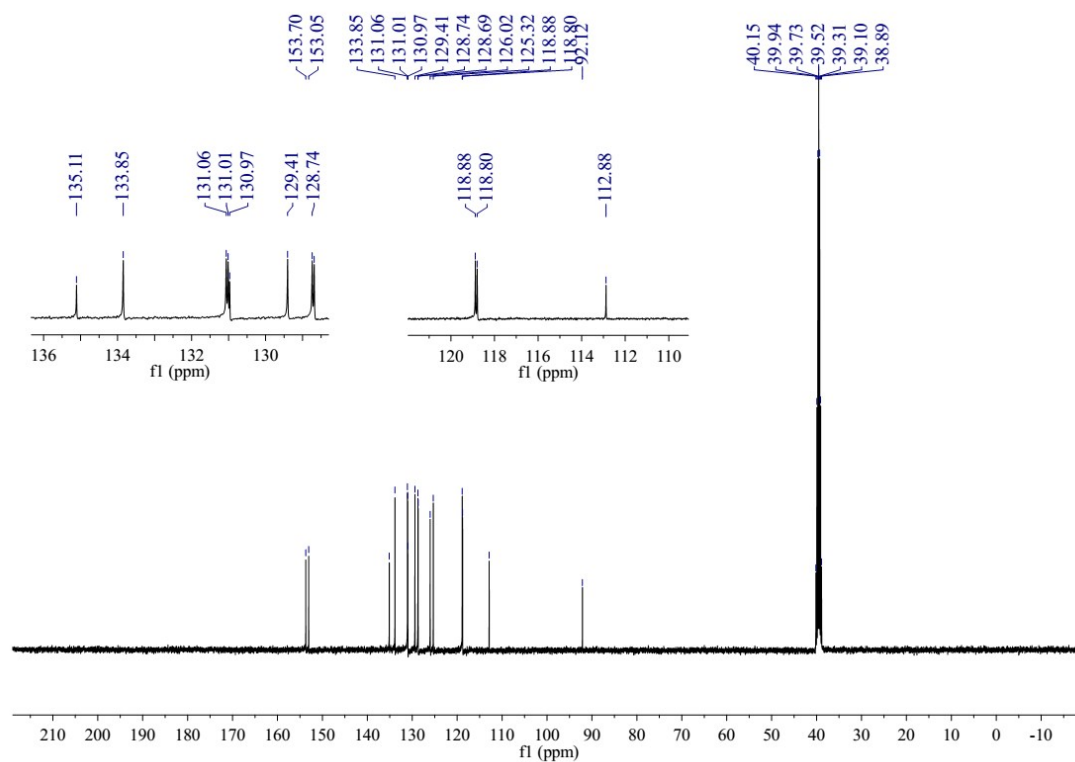
# <sup>13</sup>C NMR spectrum



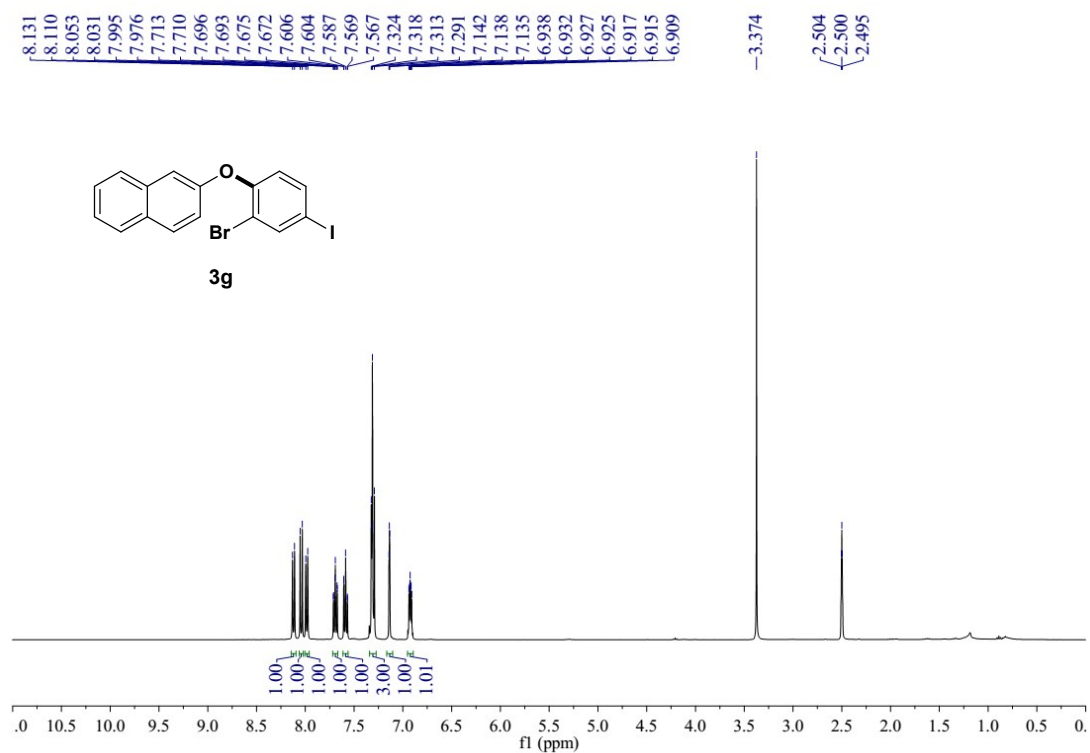
# <sup>1</sup>H NMR spectrum



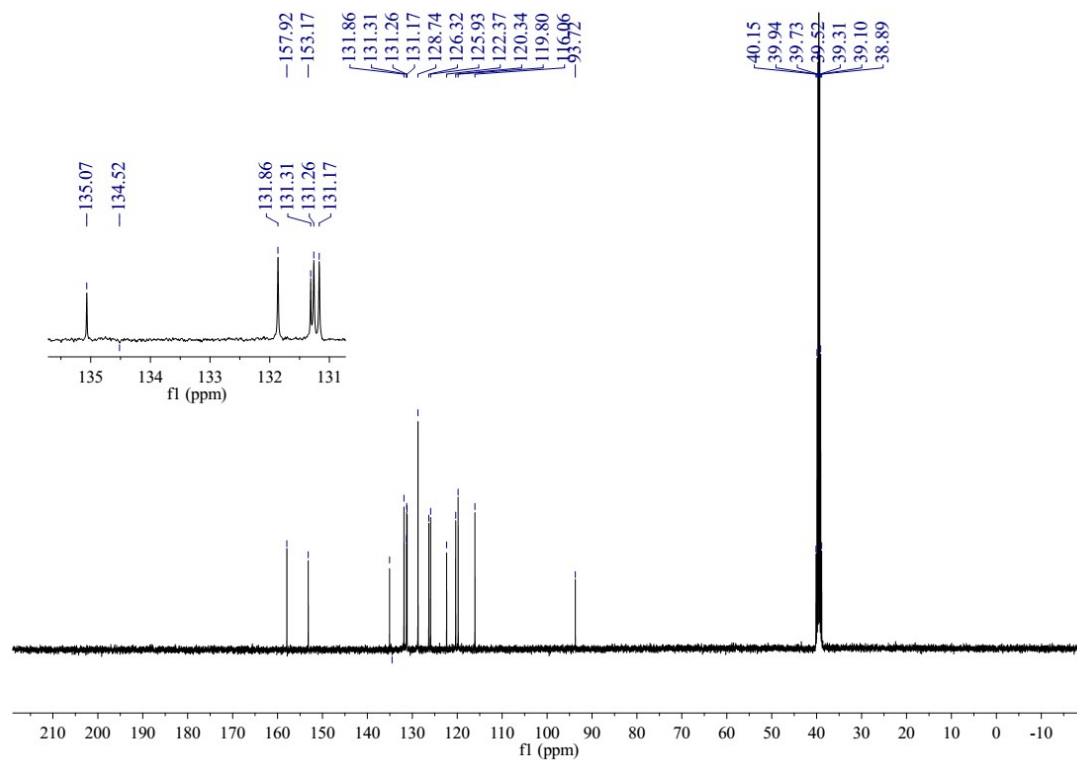
# <sup>13</sup>C NMR spectrum



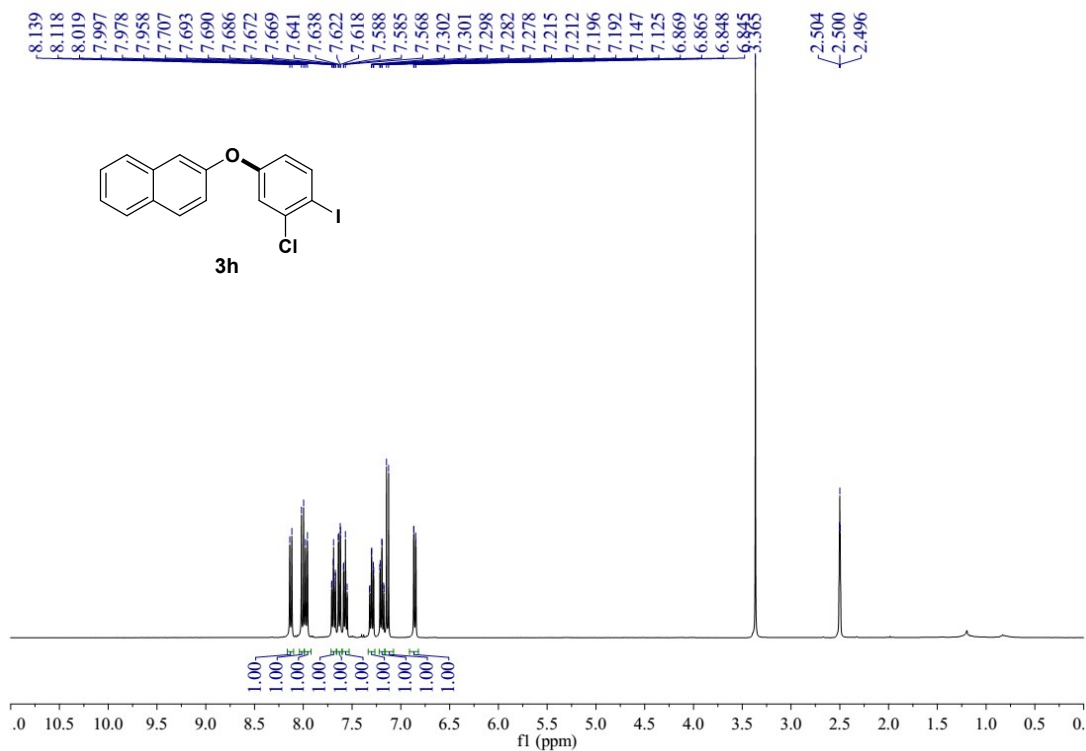
# <sup>1</sup>H NMR spectrum



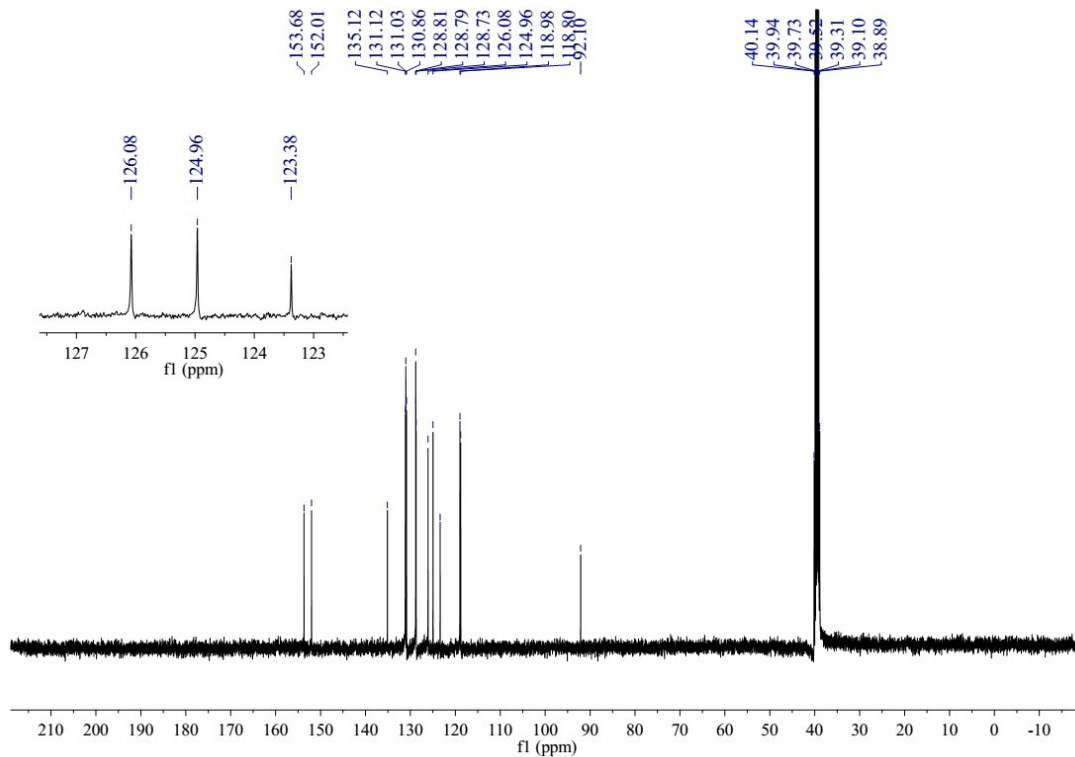
# <sup>13</sup>C NMR spectrum



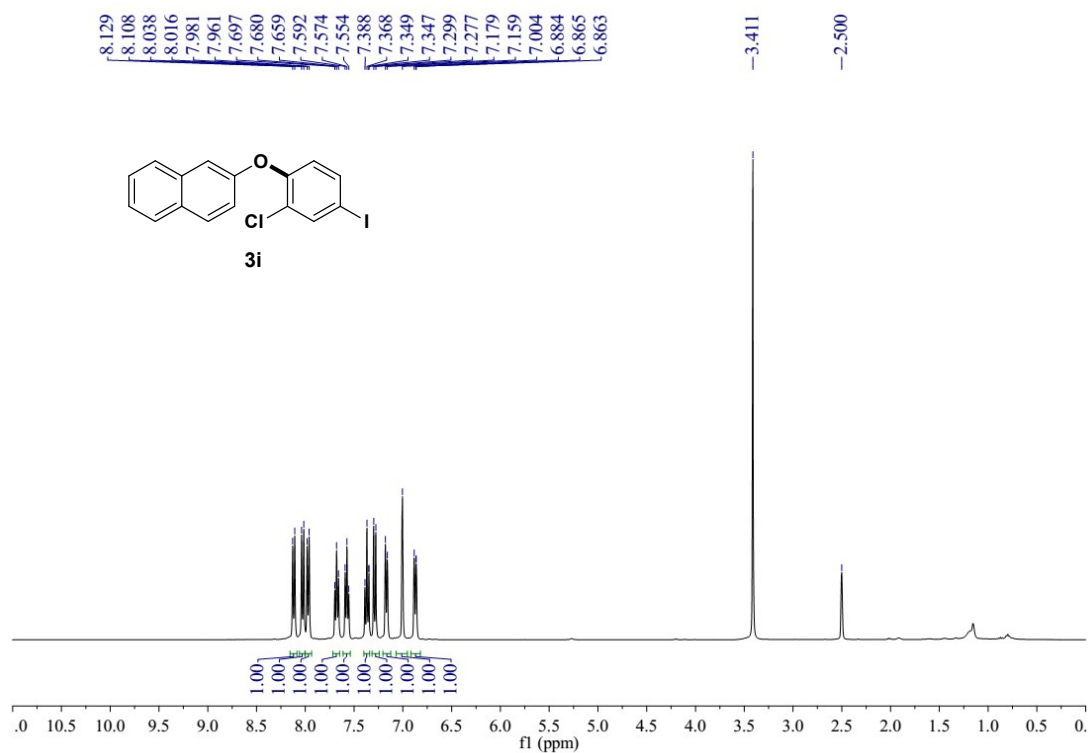
### <sup>1</sup>H NMR spectrum



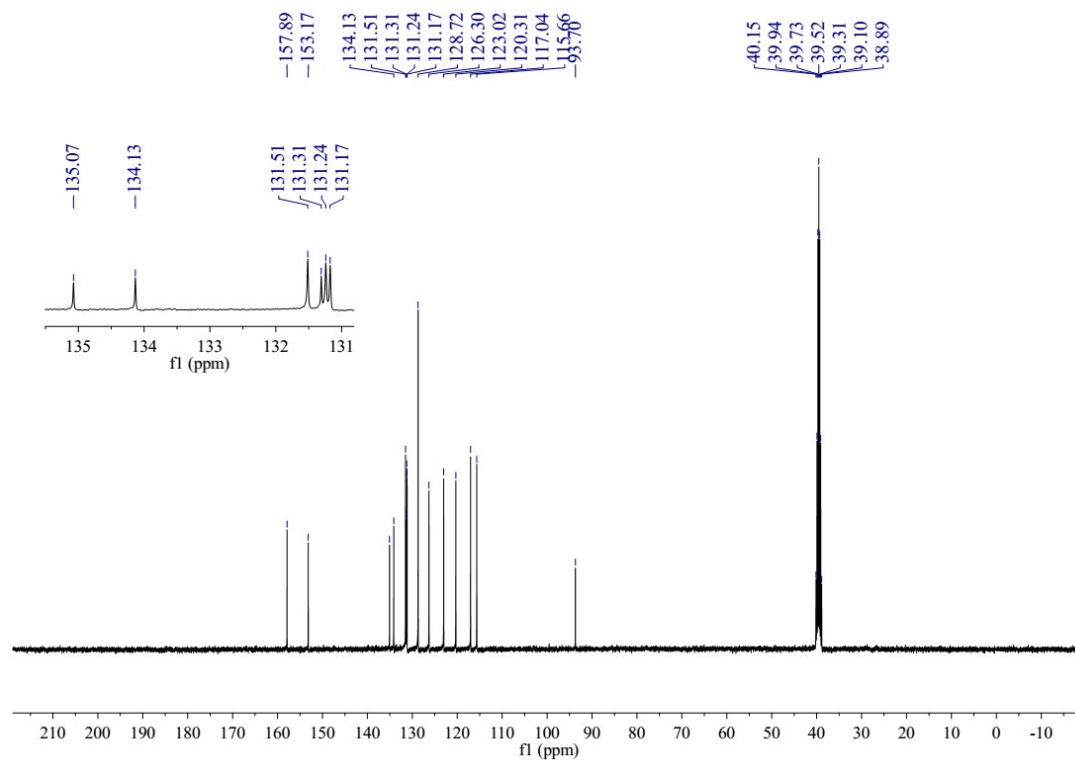
### <sup>13</sup>C NMR spectrum



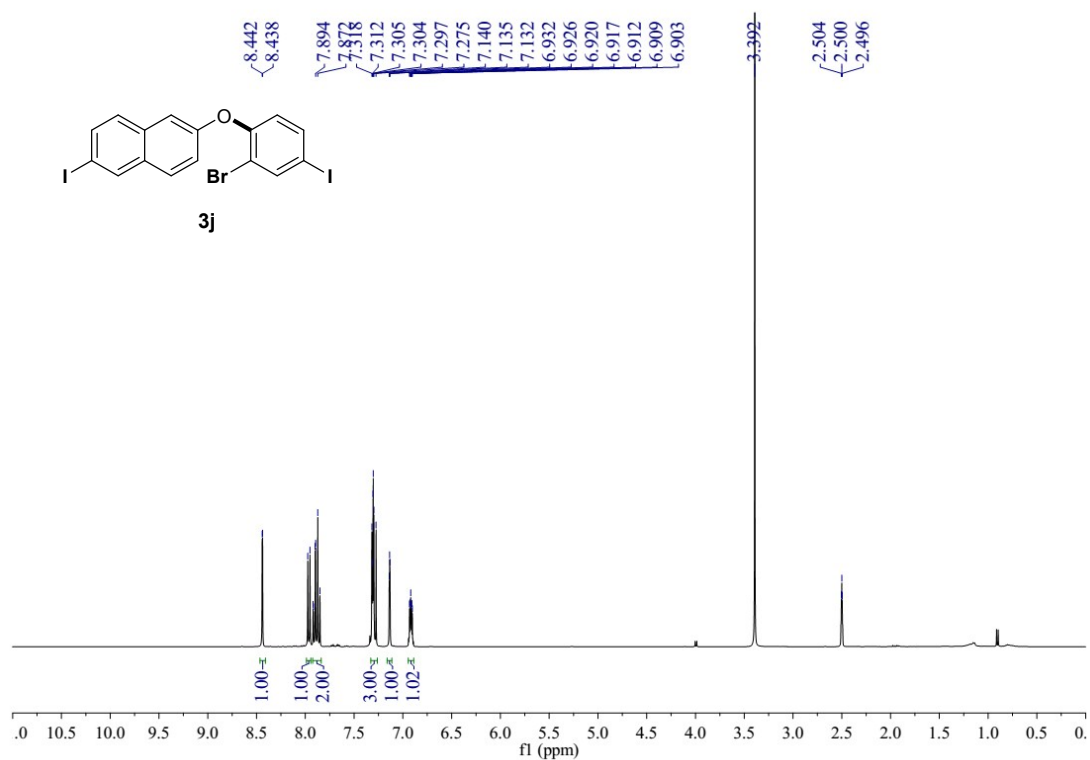
### <sup>1</sup>H NMR spectrum



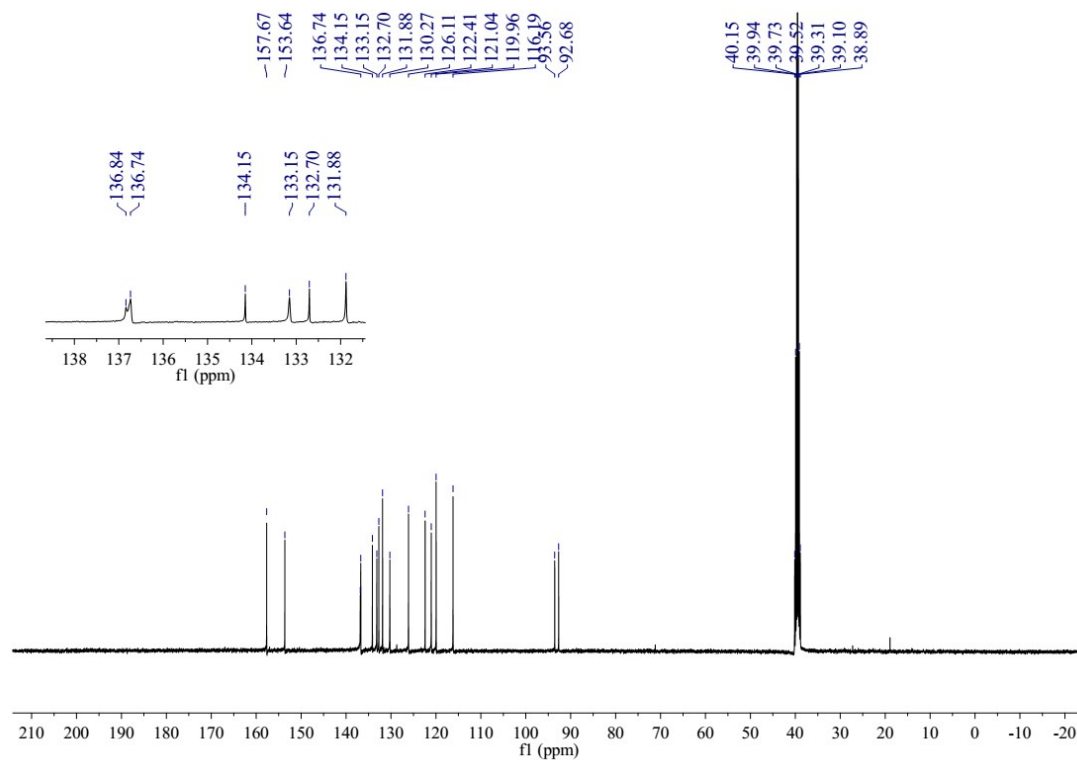
### <sup>13</sup>C NMR spectrum



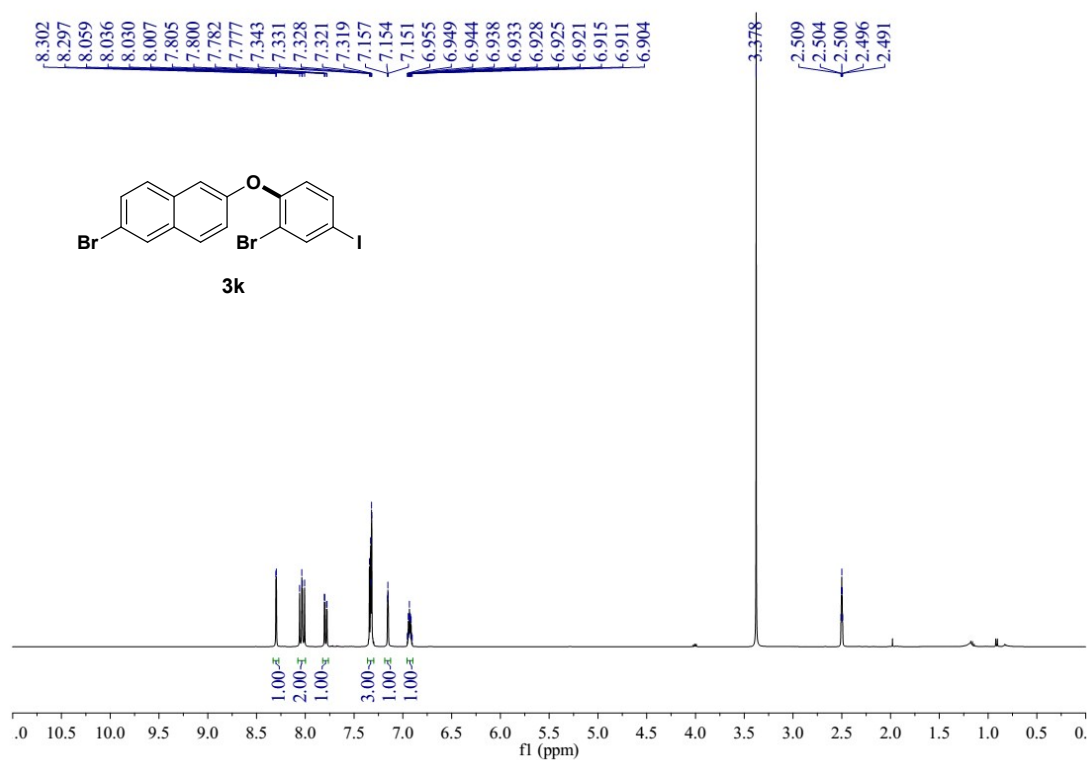
# <sup>1</sup>H NMR spectrum



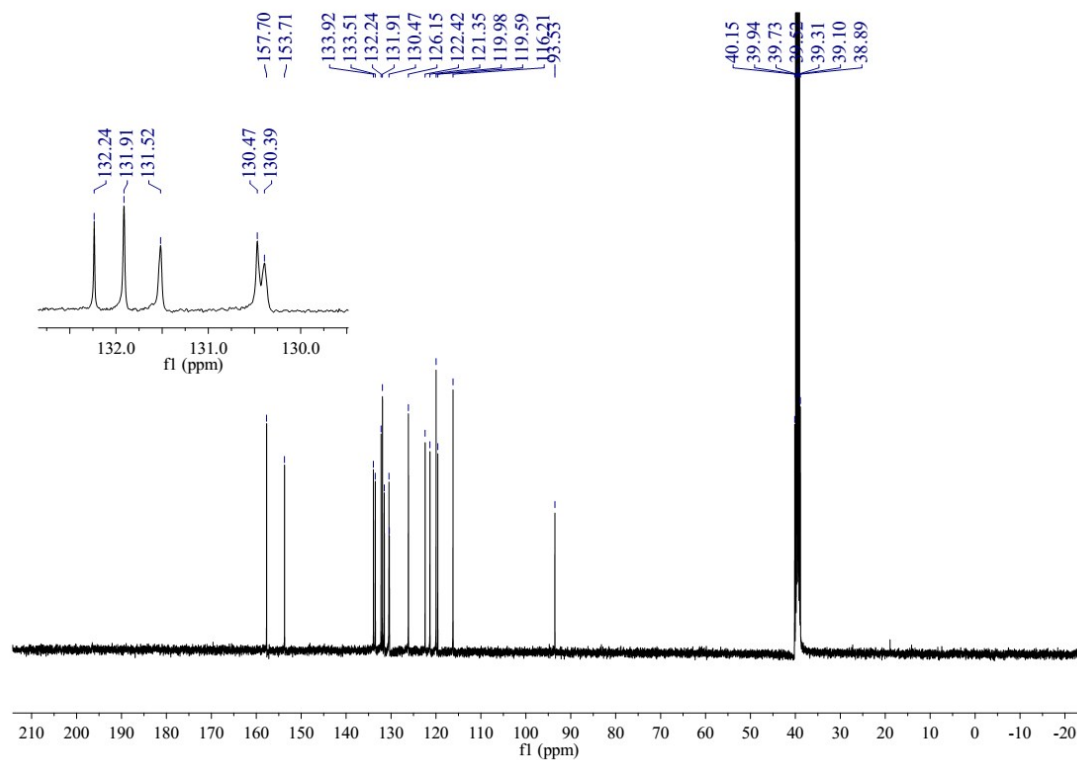
# <sup>13</sup>C NMR spectrum



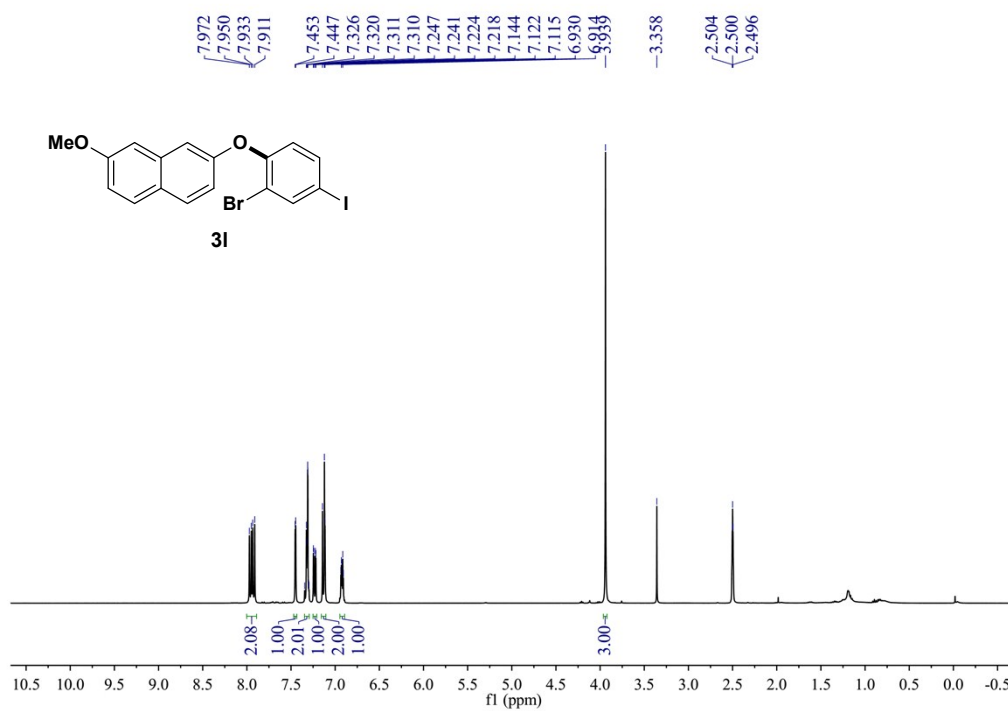
# <sup>1</sup>H NMR spectrum



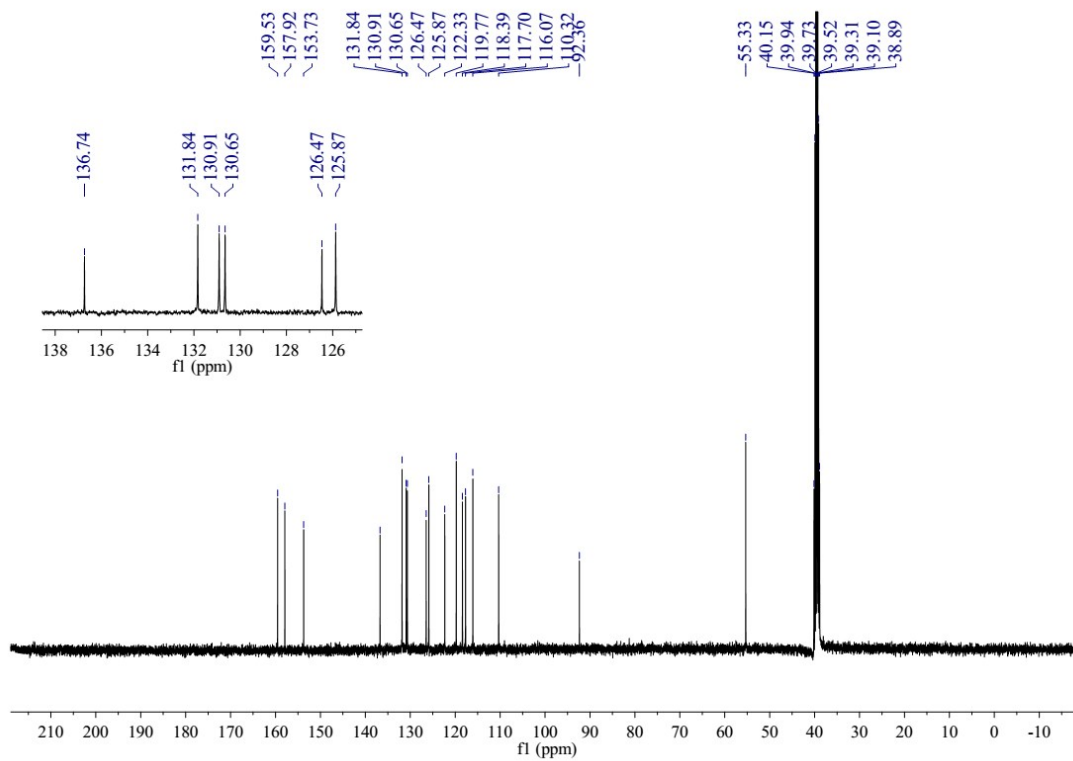
# <sup>13</sup>C NMR spectrum



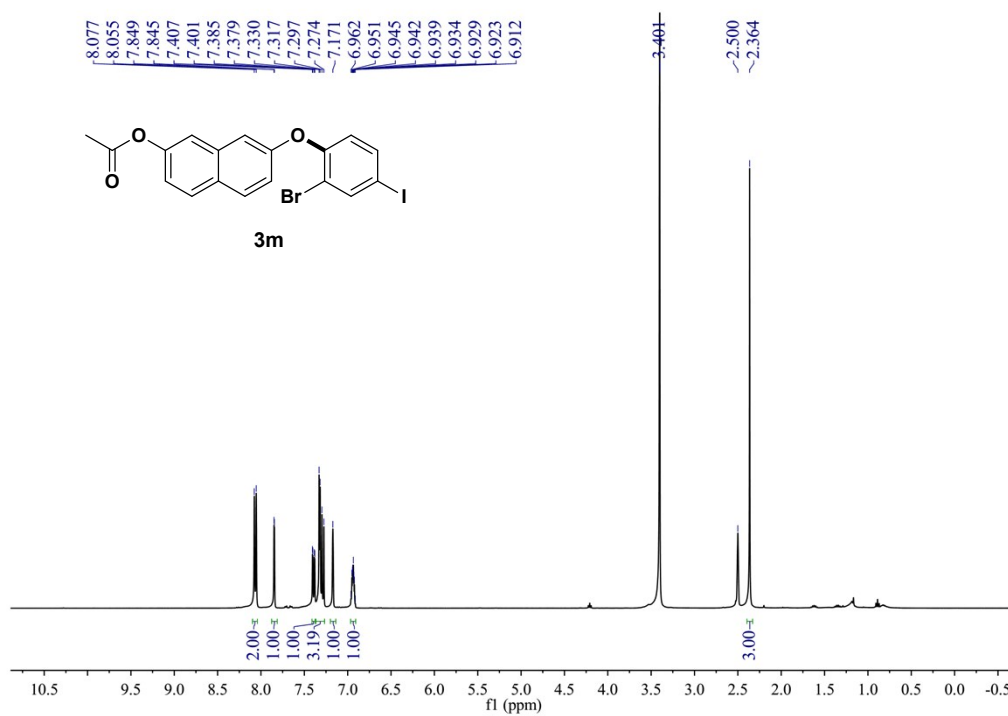
# <sup>1</sup>H NMR spectrum



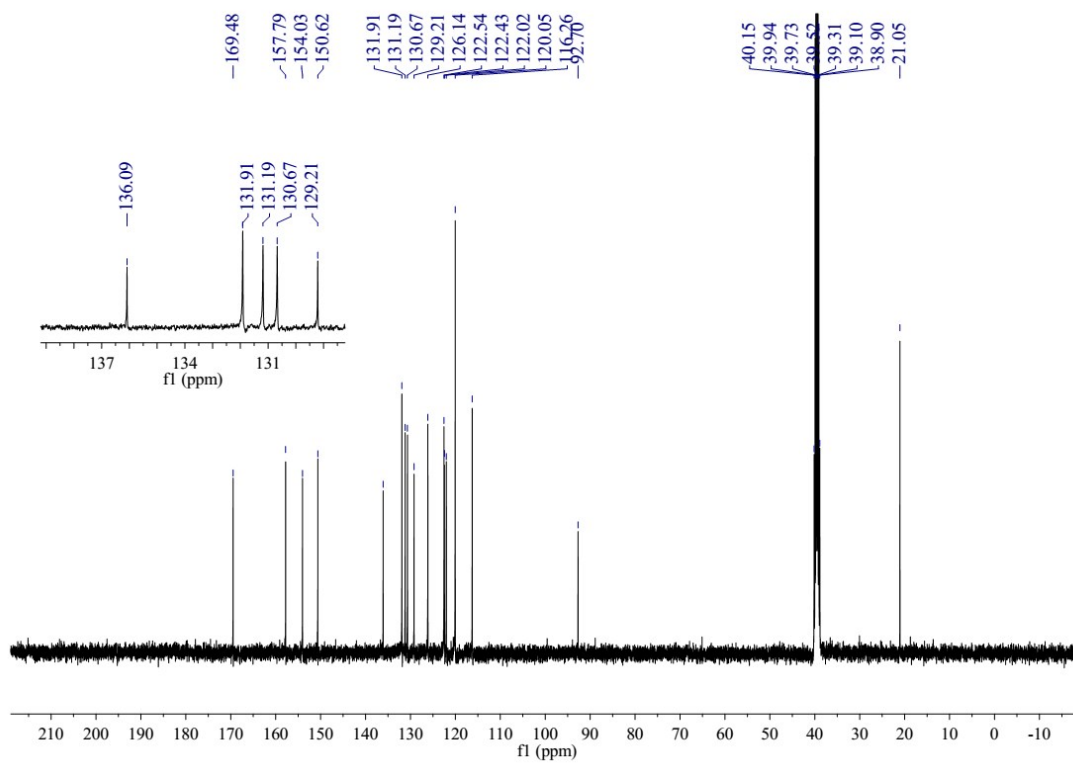
# <sup>13</sup>C NMR spectrum



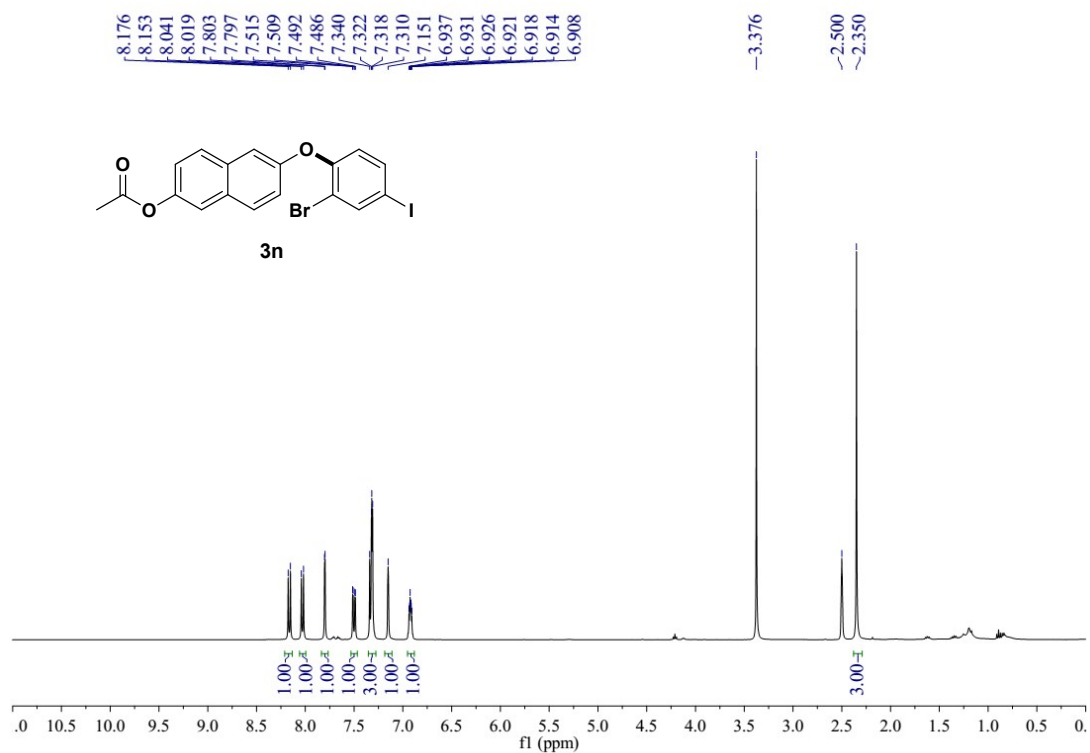
# <sup>1</sup>H NMR spectrum



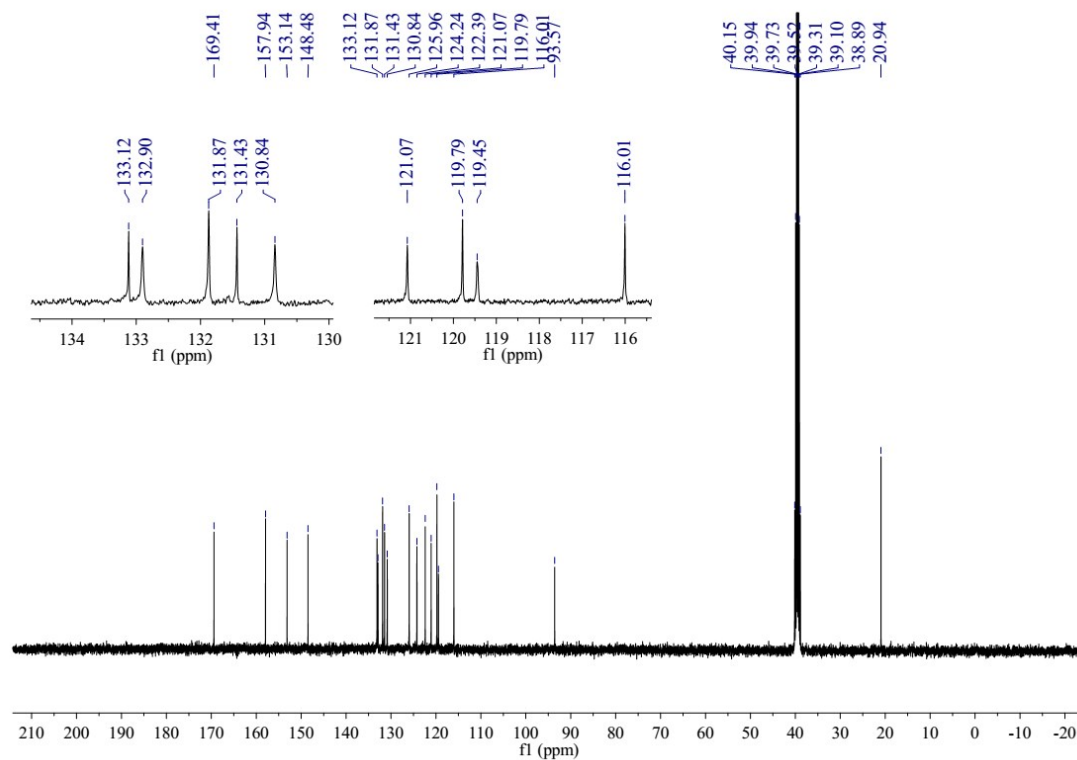
# <sup>13</sup>C NMR spectrum



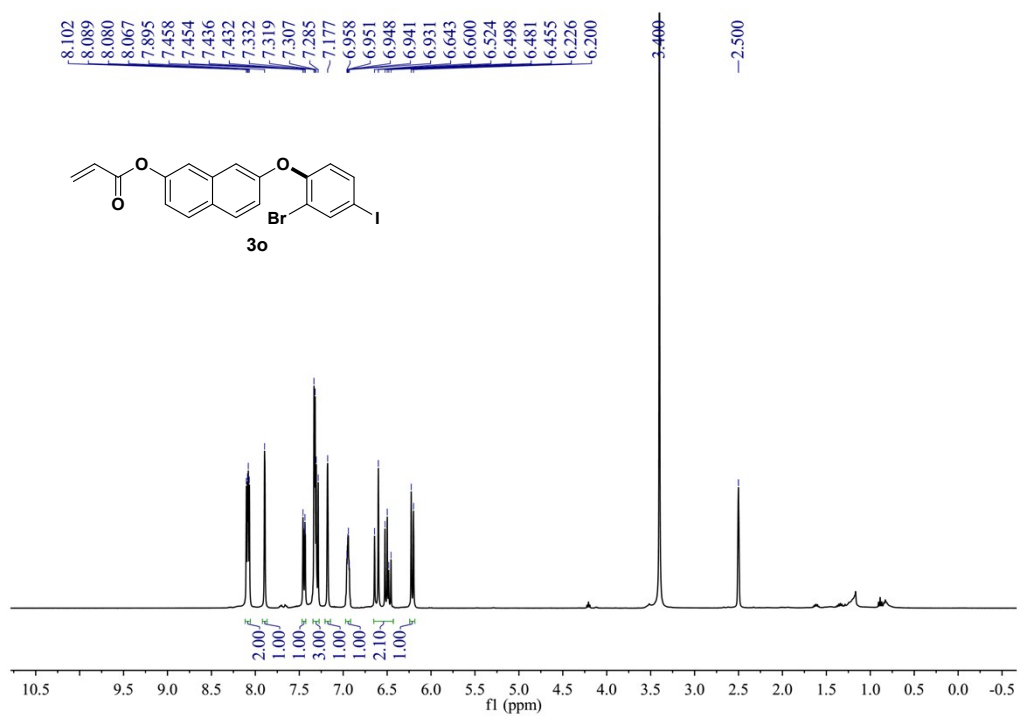
# <sup>1</sup>H NMR spectrum



# <sup>13</sup>C NMR spectrum



# <sup>1</sup>H NMR spectrum



# <sup>13</sup>C NMR spectrum

