Supporting Information

# Ni-Catalyzed α-selective C–H borylations of naphthalene-based aromatic compounds

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**1. X-ray Crystallography**

Single crystal of **2b** were obtained slow evaporation method from $CHCl_3/CH_2Cl_2$ (20/1).

Details of the crystal data and a summary of the intensity data collection parameters for **2b** are listed in Table S1. A suitable crystal was mounted with mineral oil on a MiTeGen MicroMount and transferred to the goniometer of a Rigaku PILATUS diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) was used. The structures were solved by direct methods with (SIR-97)[S1] and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-2016/6)[S2] by using Yadokari-XG software package.[S3] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

**Table S1.** Crystallographic data and structure refinement details of **2b**

| | **2b**·$C_2H_4Cl_2$ |
|---|---|
| formula | $C_{42}H_{52}B_2Cl_2O_6$ |
| fw | 745.35 |
| $T$ (K) | 123(2) |
| $\lambda$ (Å) | 0.71073 |
| cryst syst | Monoclinic |
| space group | $C2/c$ |
| $a$ (Å) | 16.1154(5) |
| $b$ (Å) | 12.2973(3) |
| $c$ (Å) | 21.8677(6) |
| $\alpha$ (deg) | 90 |
| $\beta$ (deg) | 133.366(4) |
| $\gamma$ (deg) | 90 |
| $V$ (Å$^3$) | 3978.2(2) |
| $Z$ | 4 |
| $D_{calc}$ (g·cm$^{-3}$) | 1.244 |
| $\mu$ (mm$^{-1}$) | 0.209 |
| F(000) | 1584 |
| cryst size (mm) | 0.20 × 0.20 × 0.10 |
| $\theta$ range (deg) | 2.135–24.994 |
| reflns collected | 20892 |
| indep reflns/$R_{int}$ | 3486 / 0.0235 |
| params | 276 |
| GOF on $F^2$ | 1.056 |
| $R_1$, $wR_2$ [$I>2\sigma(I)$] | 0.0512, 0.1383 |
| $R_1$, $wR_2$ (all data) | 0.0570, 0.1431 |

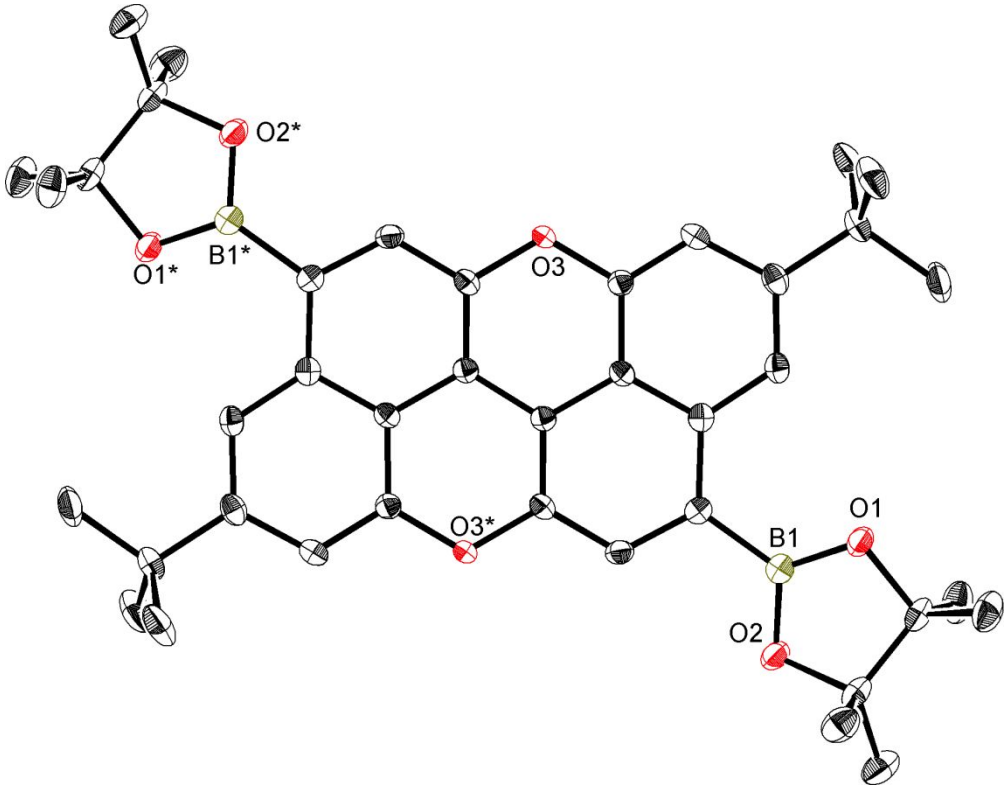
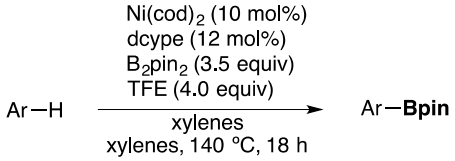
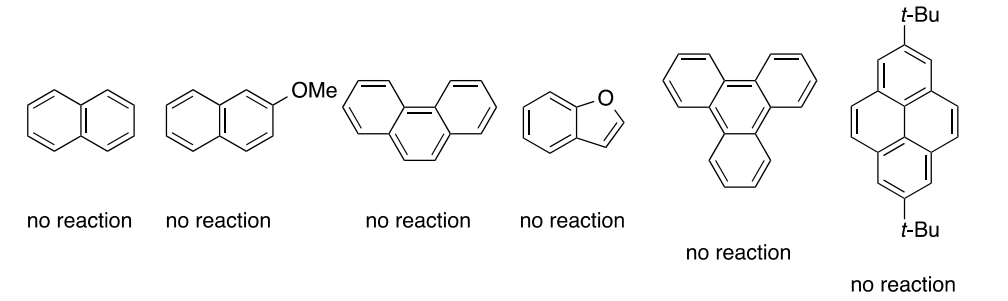


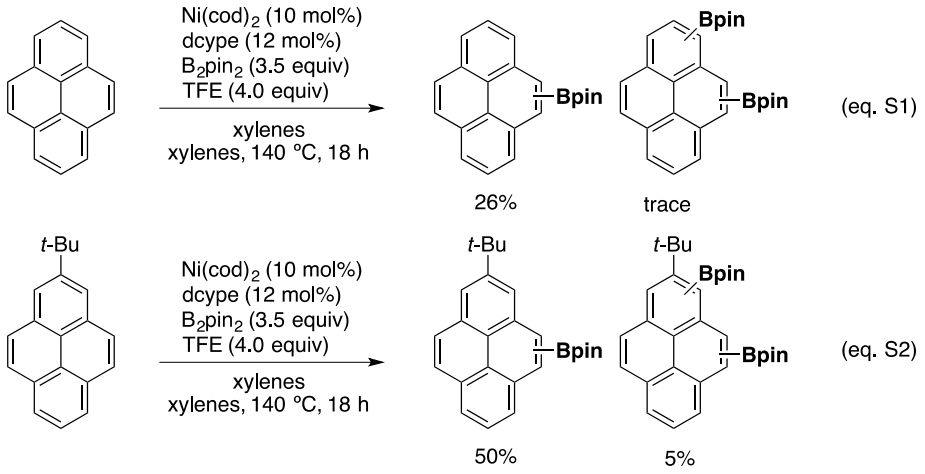

**Figure S1** ORTEP drawing of **2b** with 50% thermal ellipsoid (All hydrogen atoms and dichloromethane were omitted for clarity.)

## 2 Ni-Catalyzed C–H borylation of other aromatic compounds.

### Table S2 Ni-Catalyzed C–H borylation of other aromatic compounds



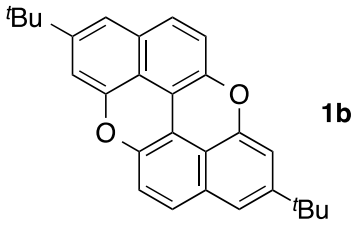




The borylation of other aromatic compounds were resulted in no reaction (phenanthrene, naphthalene,2-methoxynaphtharene, triphenylene, 2,7-di(*t*-butyl)pyrene).

The reaction of pyrene afforded the mixture of regioisomer of monoborylpyrenes, accompanied by diborylated pyrenes (eq. S1). The yields were determined by NMR using $Me_3SiOSiMe_3$ as internal standard.

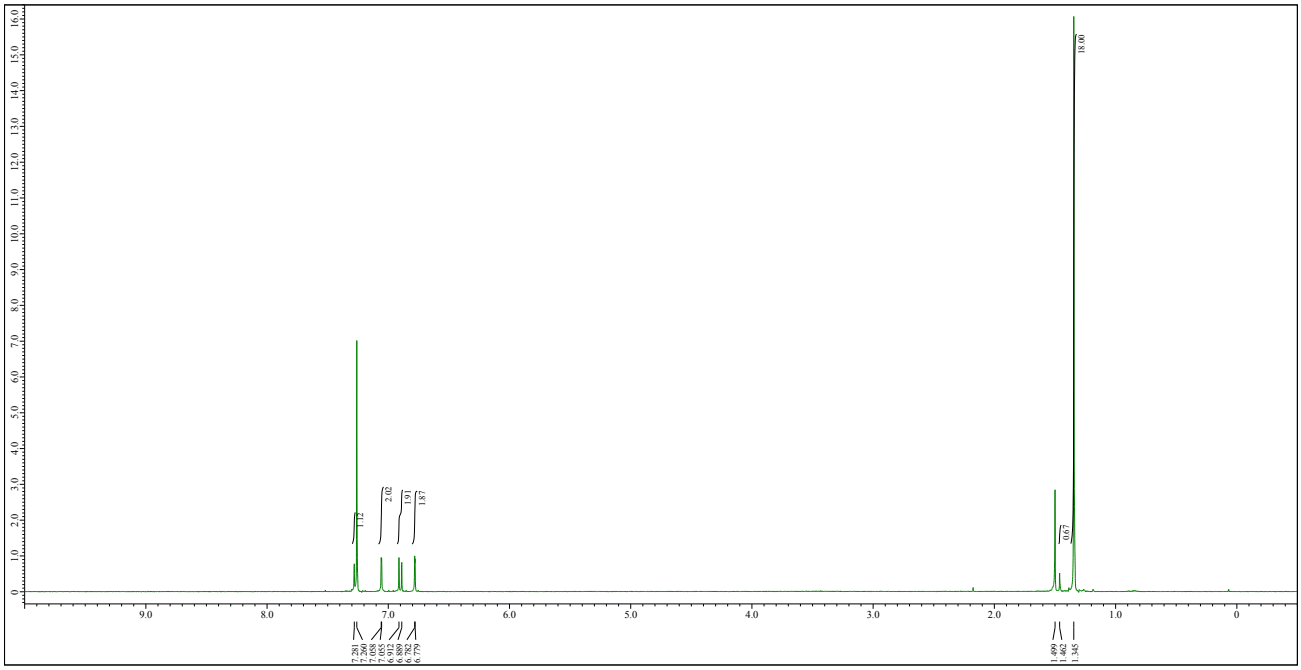
The C–H borylation of 2-*t*-butylpyrene pyrene also yielded the mixture of monoborylpyrenes in 50% yield and diborylated pyrenes in 5% yield, determined by NMR using $Me_3SiOSiMe_3$ as internal standard.

## 3. NMR spectra

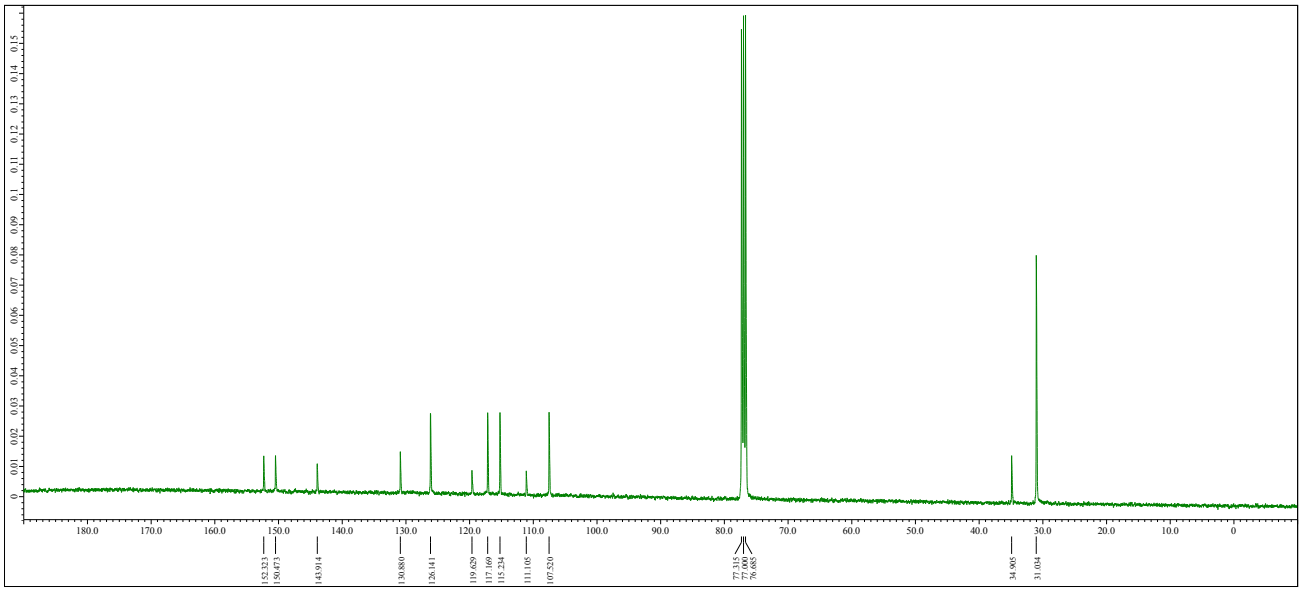


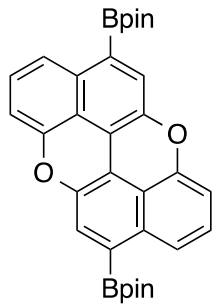

**1b**

$^{1}$H NMR



$^{13}$C NMR






**2a**

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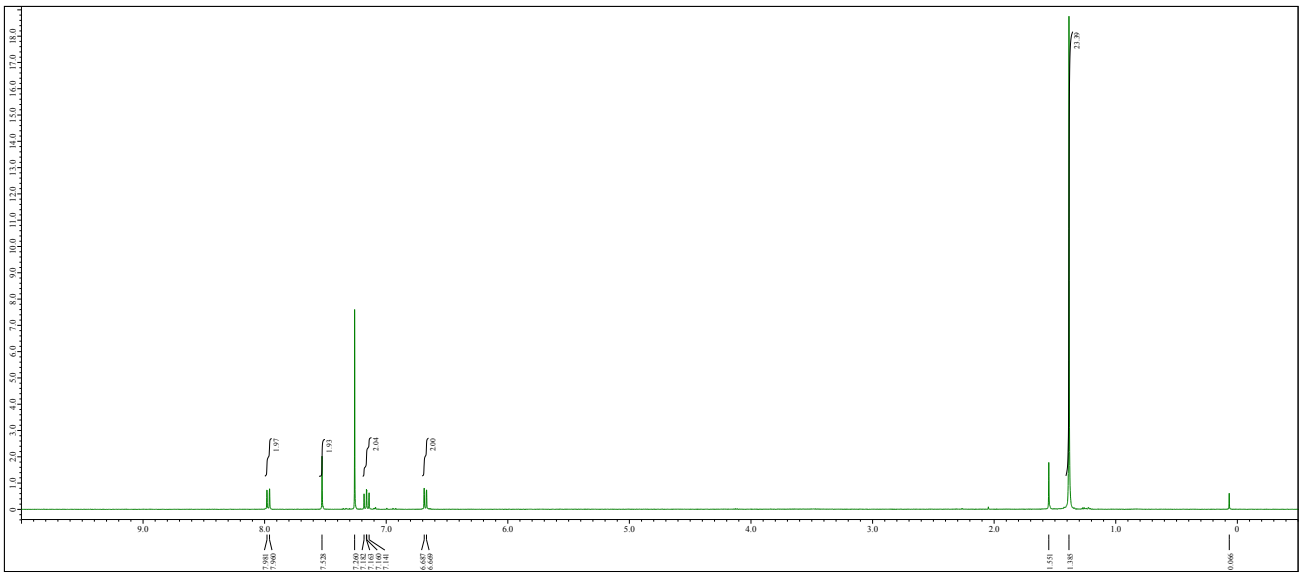

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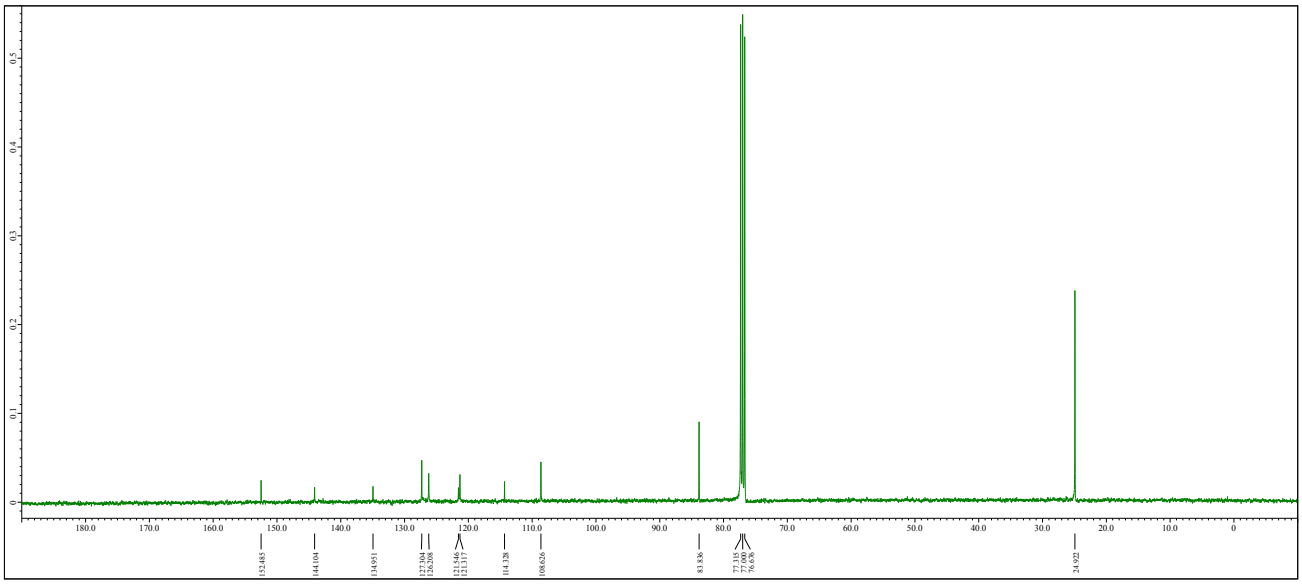
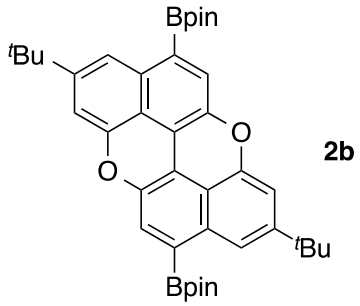
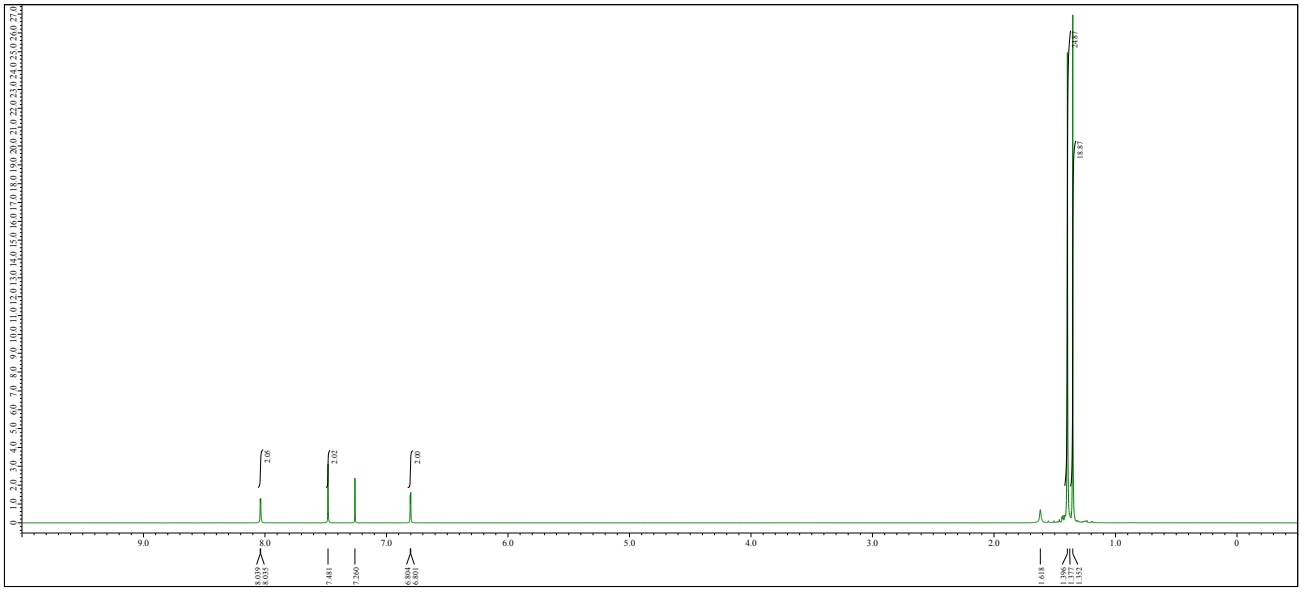





**2b**

$^{1}$H NMR



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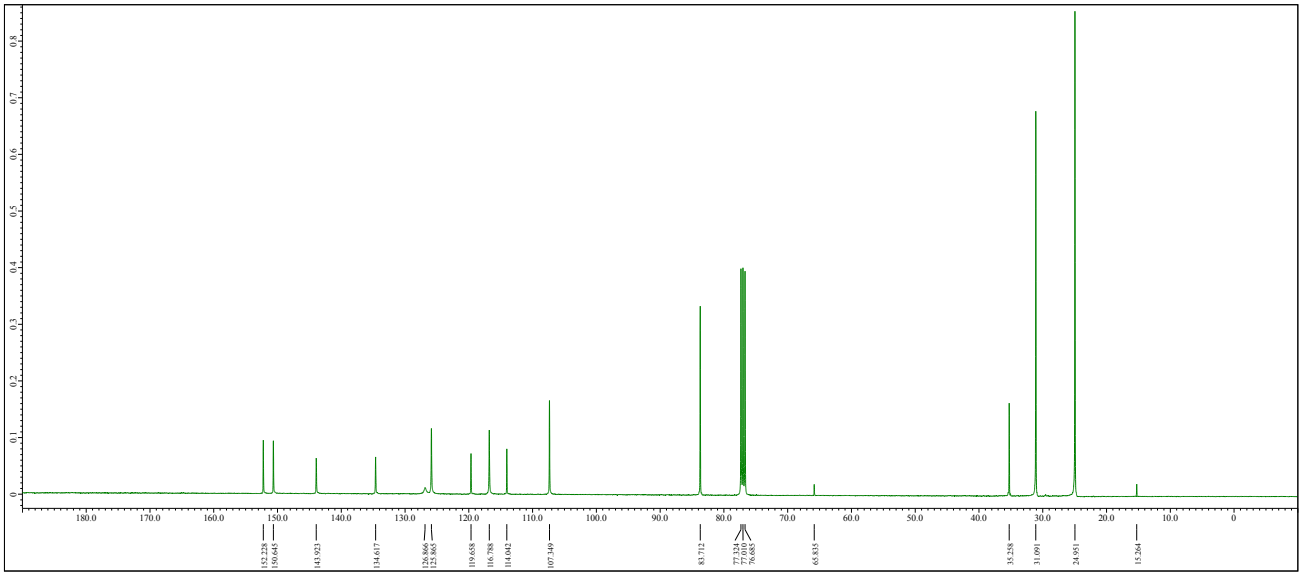

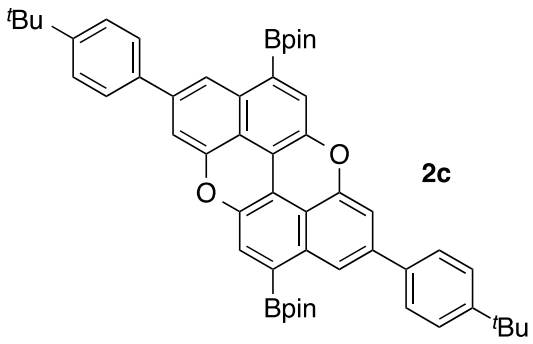


**2c**

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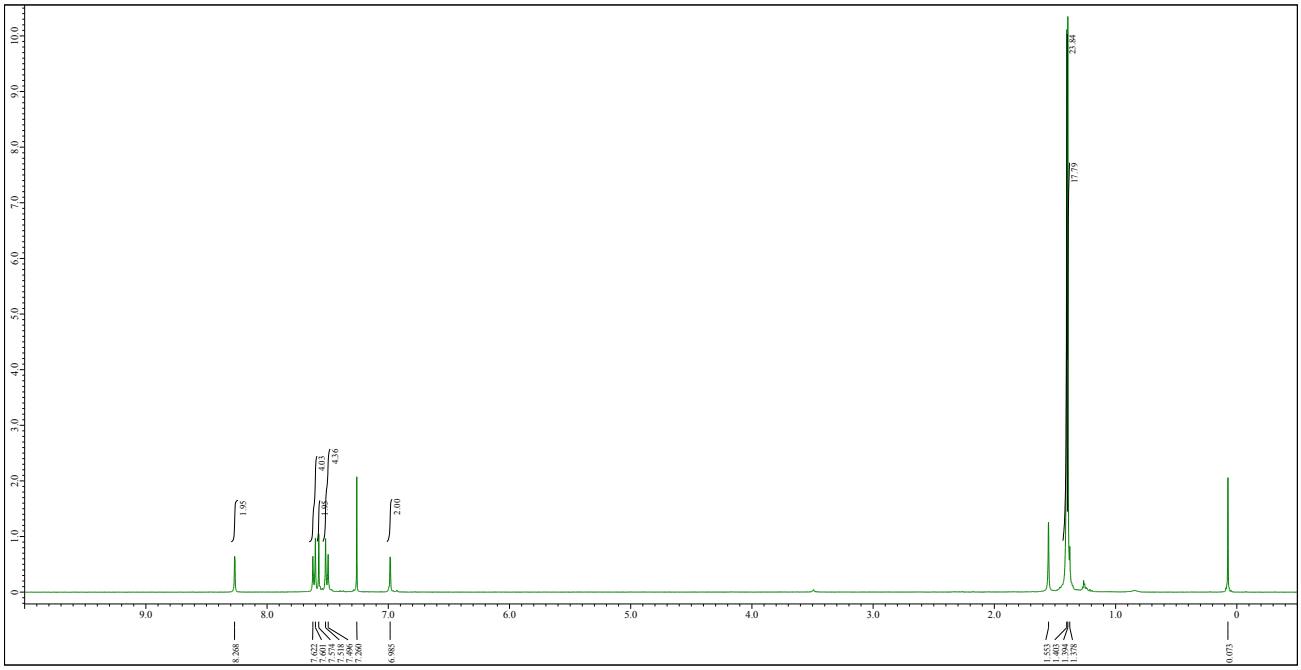

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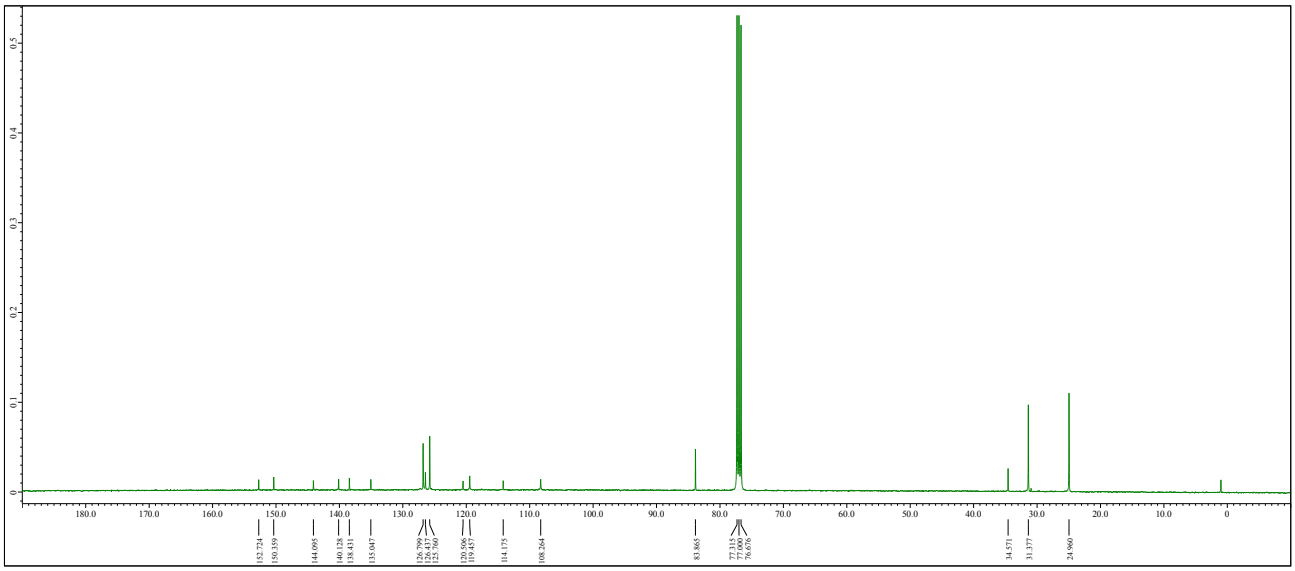
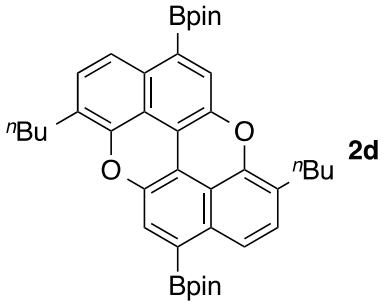
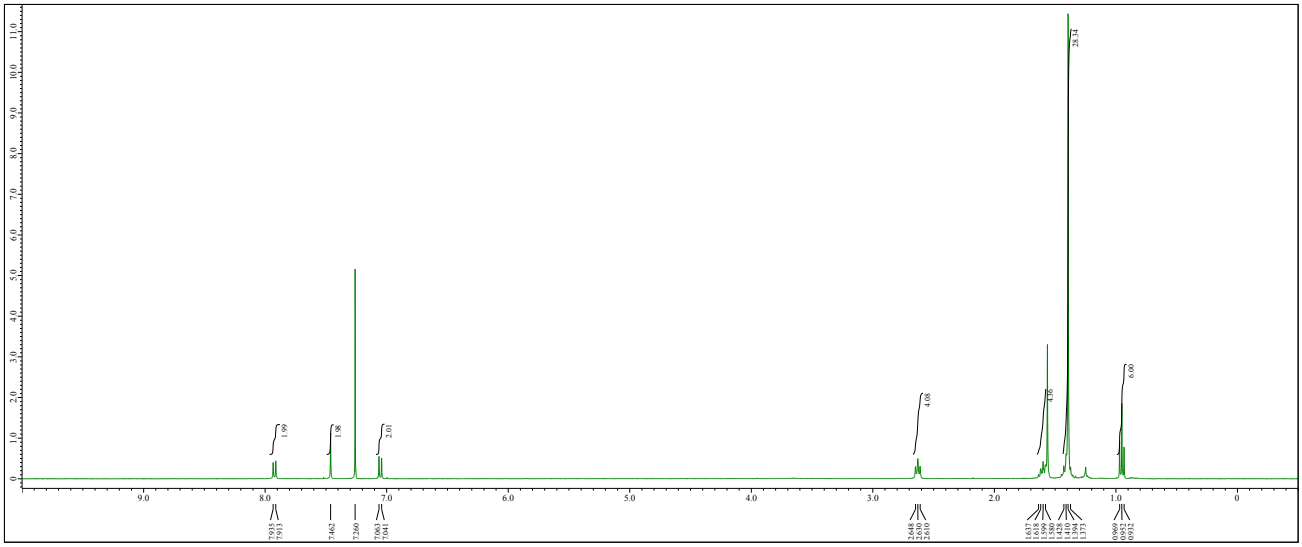





**2d**

$^{1}$H NMR



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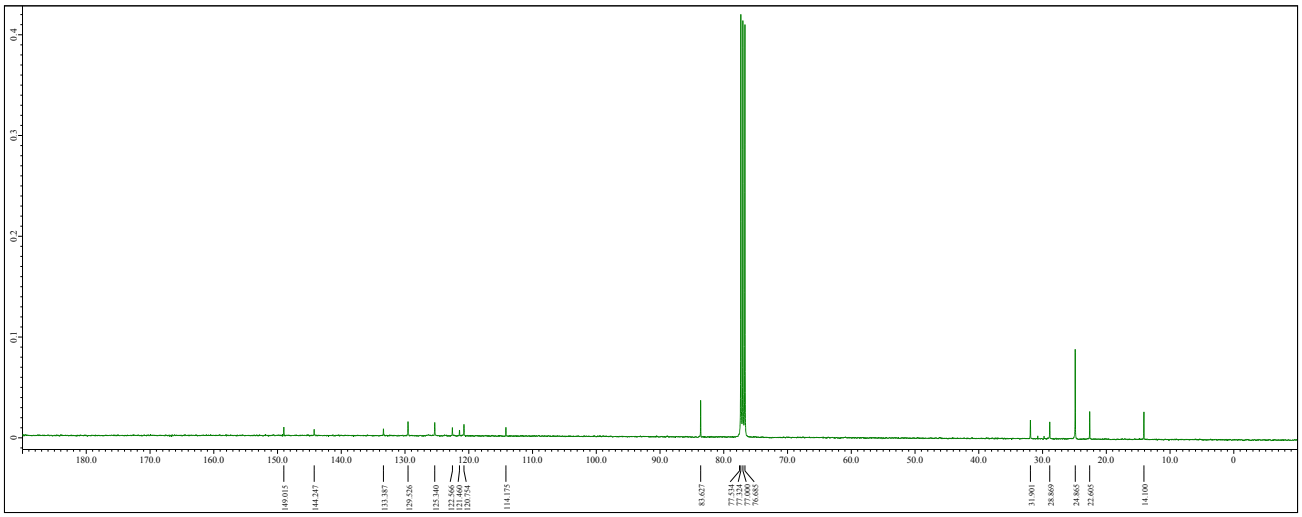
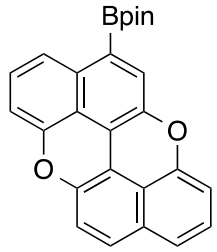
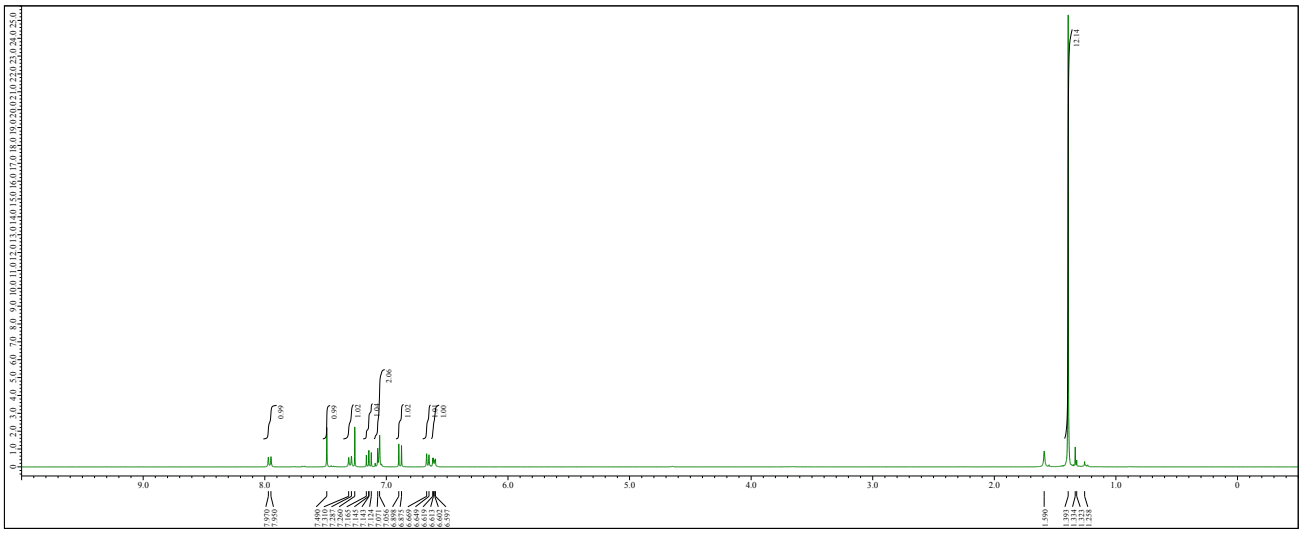





**3a**

$^{1}$H NMR



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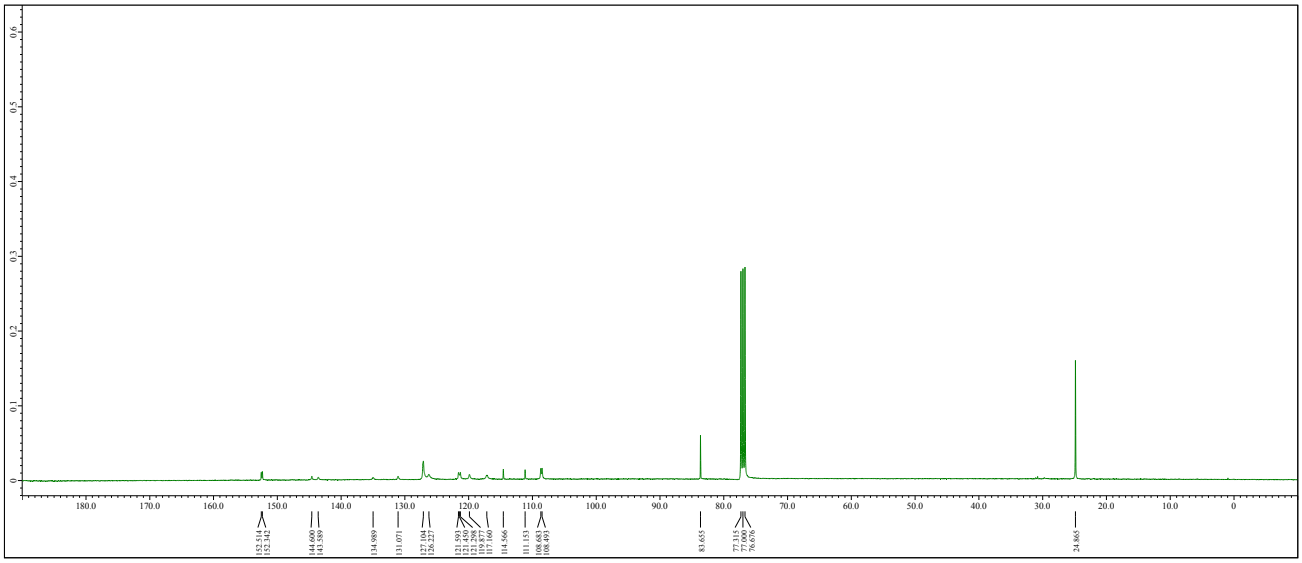
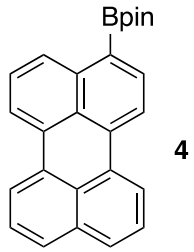
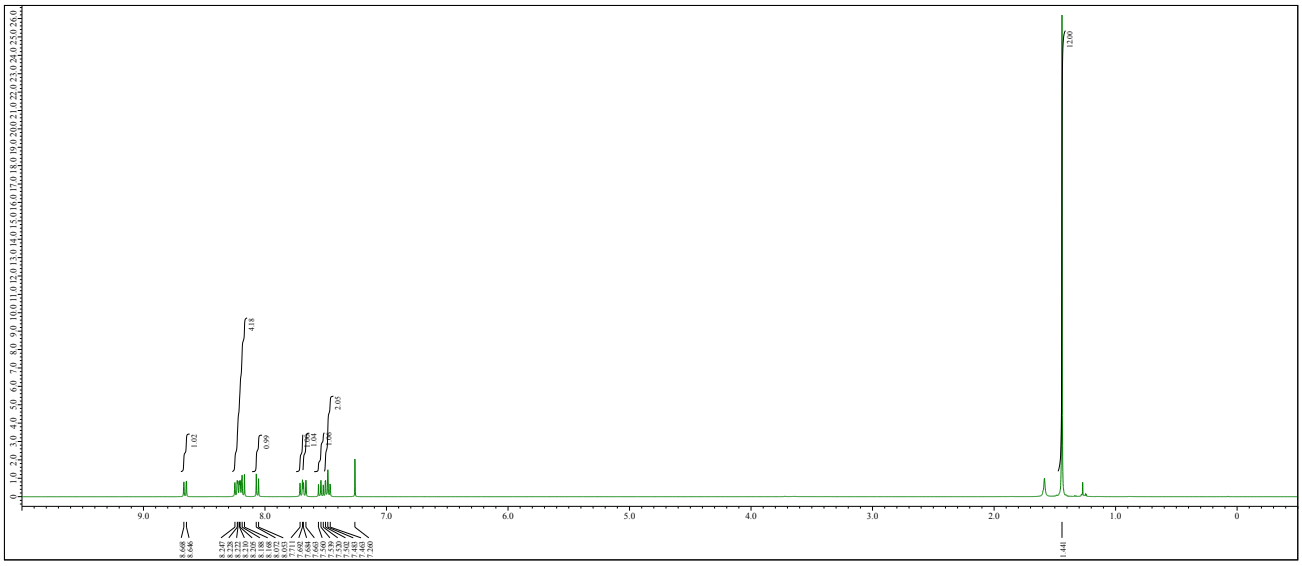





**4**

$^{1}$H NMR



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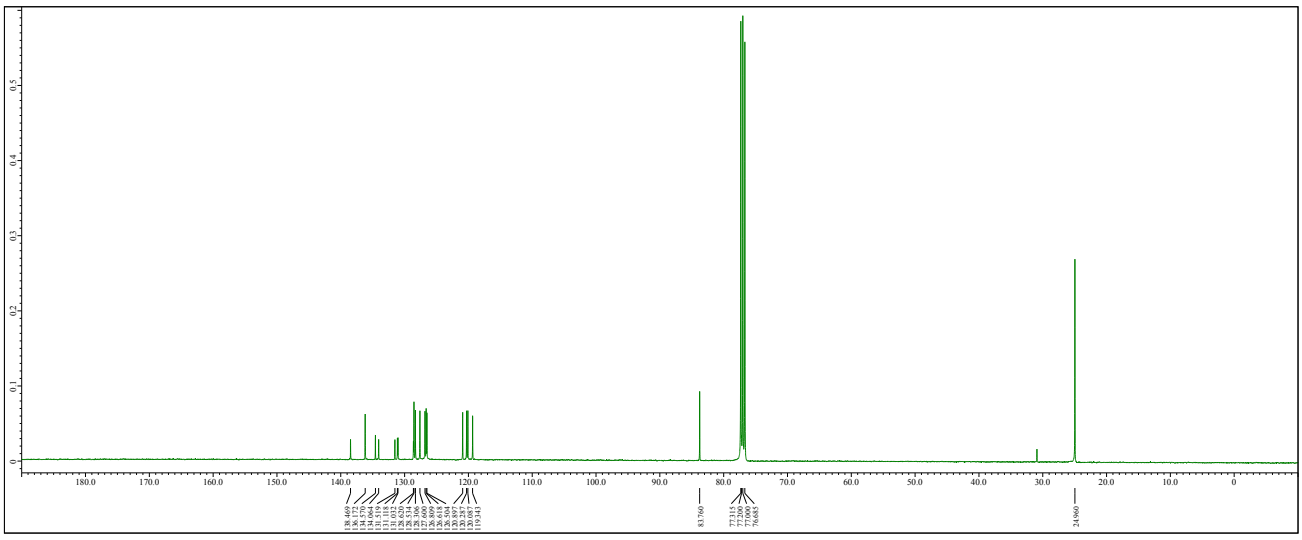

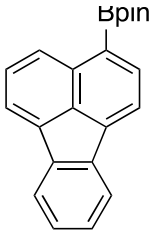


**5**

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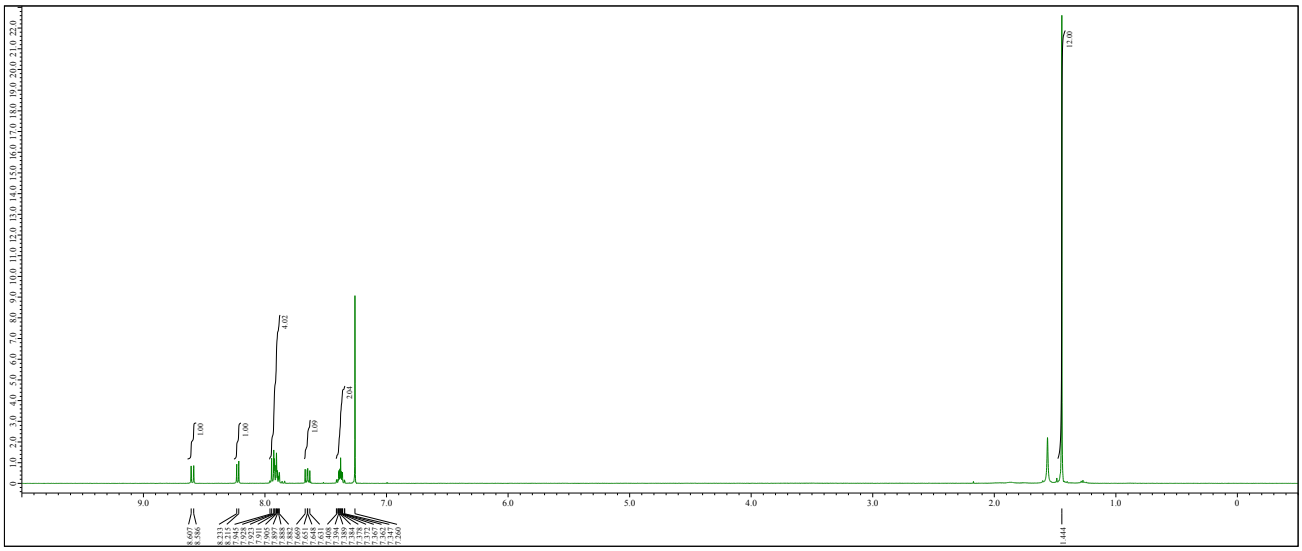

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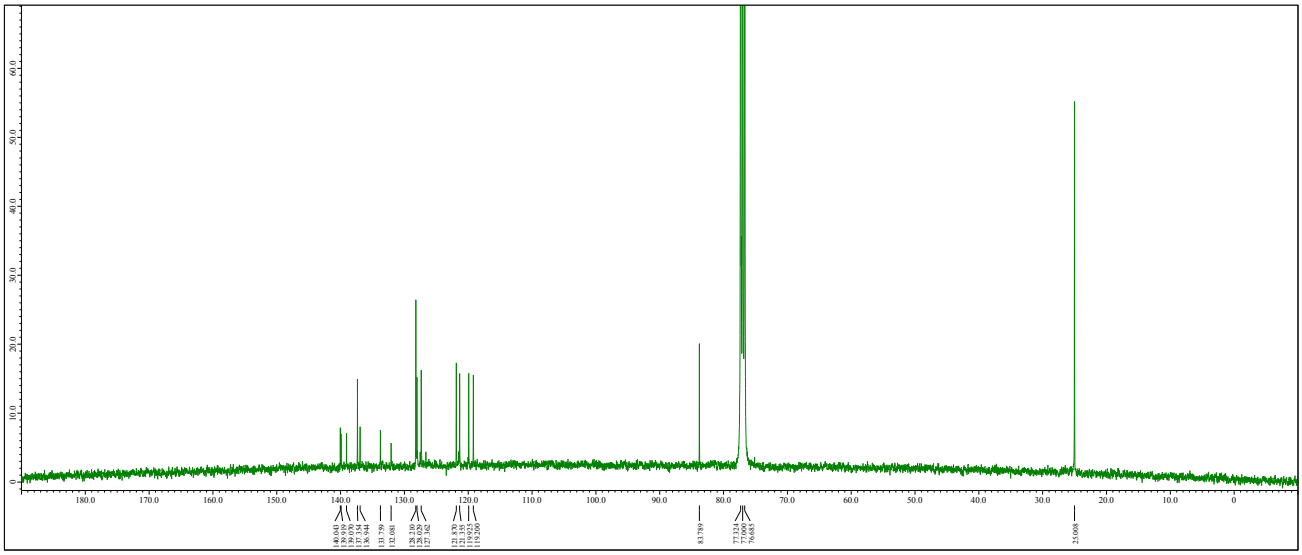

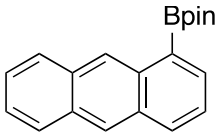


**6**

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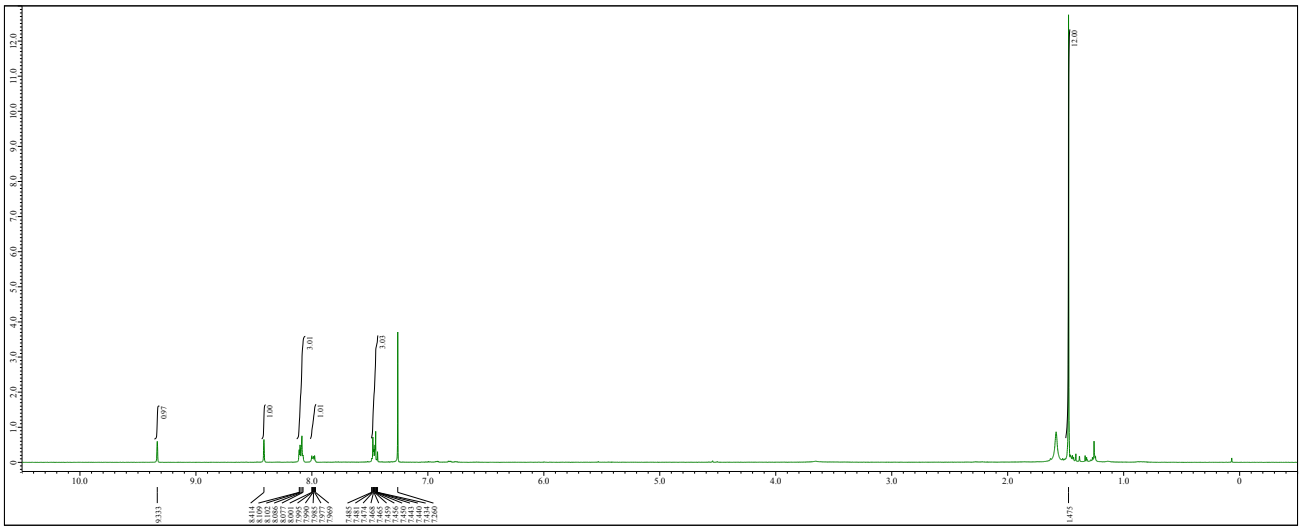

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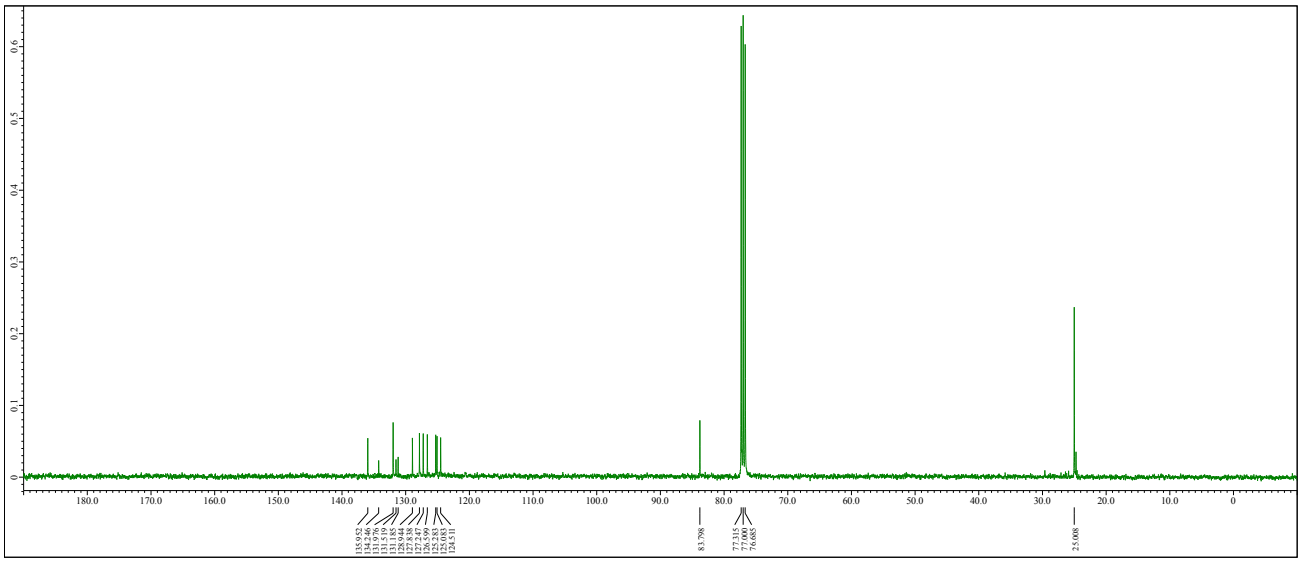

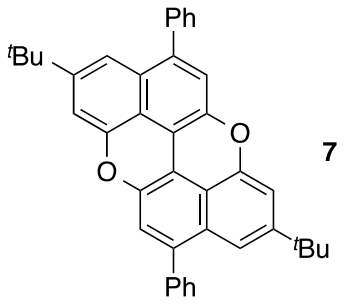


**7**

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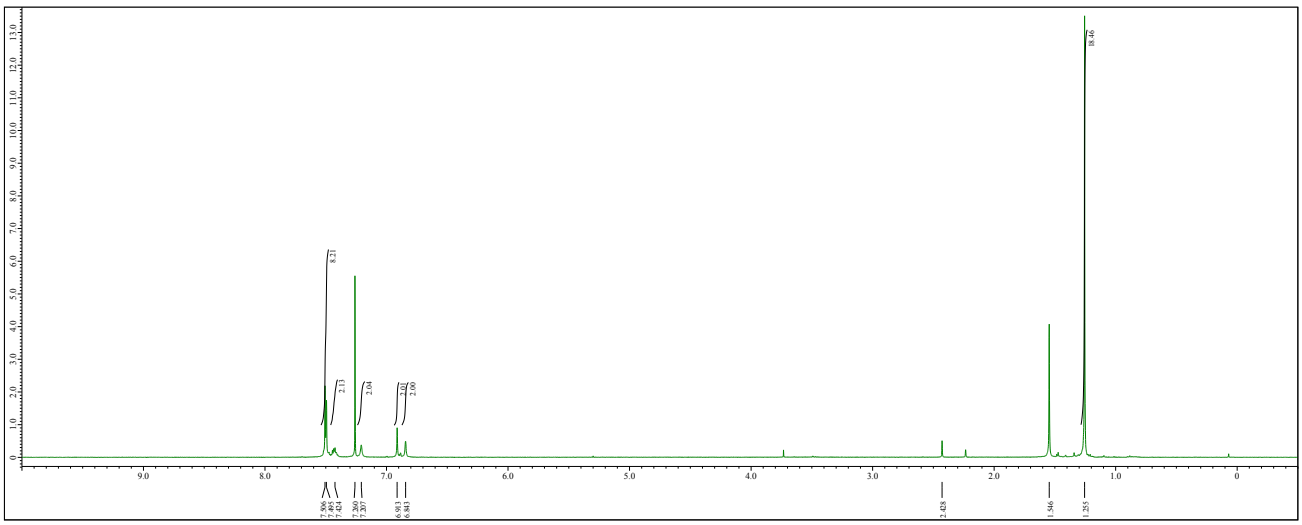

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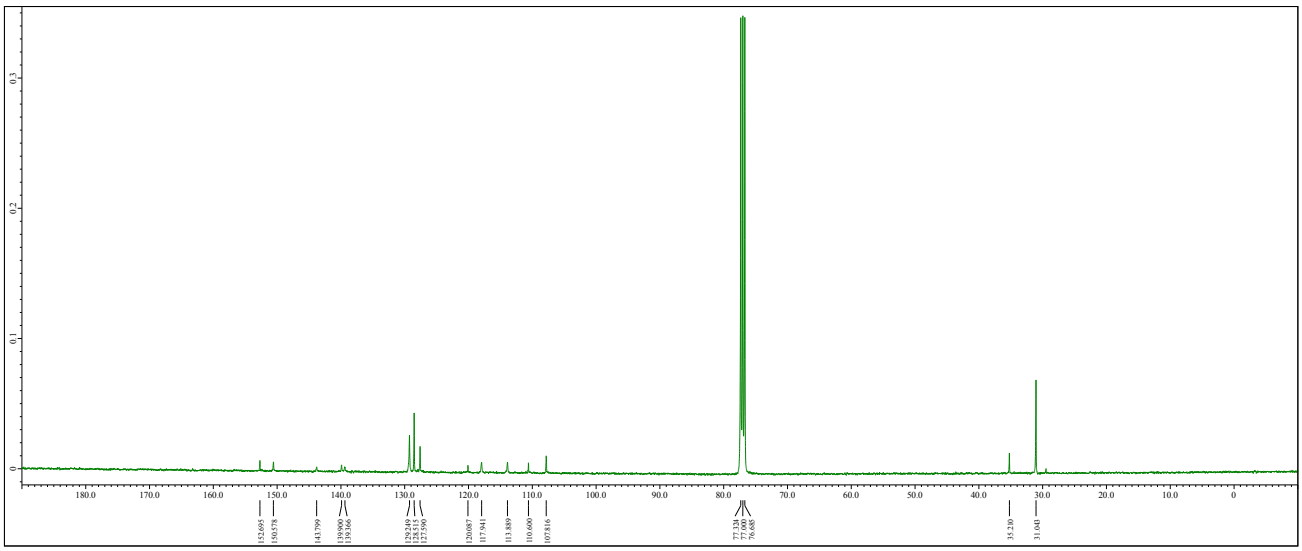

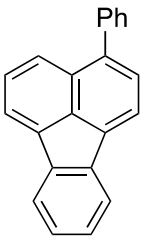


**8**

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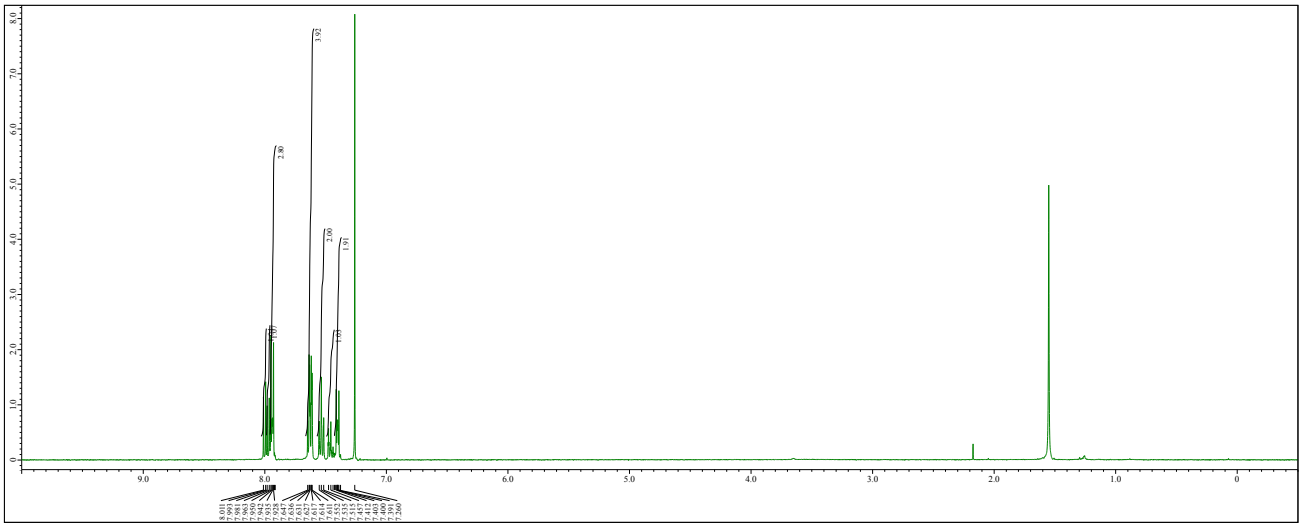

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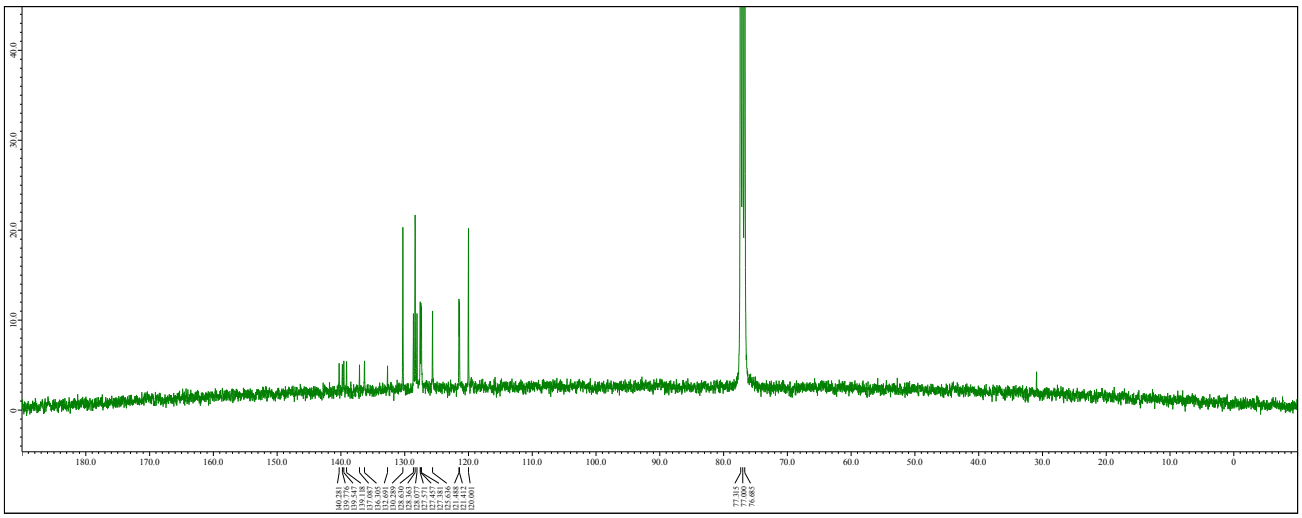

## 4. Reference

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S2) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112.

S3) (a) Wakita, K. Yadokari-XG, Software for crystal structure analyses, 2001. (b) Kabuto, C.; Akine, S.; Nemoto, T.; Kwon, E. *J. Cryst. Soc. Jpn.* **2009**, *51*, 218.