

## Pyridine-boryl radicals-mediated reductive homocoupling of *para*-quinone methides

Yan-Zhao Cui,<sup>a</sup> He Li,<sup>a</sup> Huiyi Liu,<sup>b</sup> Hao-Qi Yuan,<sup>a</sup> Hao-Tian Zhou,<sup>a</sup> Xiao-Sai Wang<sup>a</sup> and Yan-Bo Wang<sup>\*a</sup>

<sup>a</sup> *College of Chemistry and Molecular Science, Henan University, Kaifeng, 475004, China.*

*E-mail: wangyanbokf@henu.edu.cn.*

<sup>b</sup> *College of Science, Qiongtai Normal University, Haikou 571100, Hainan, China*

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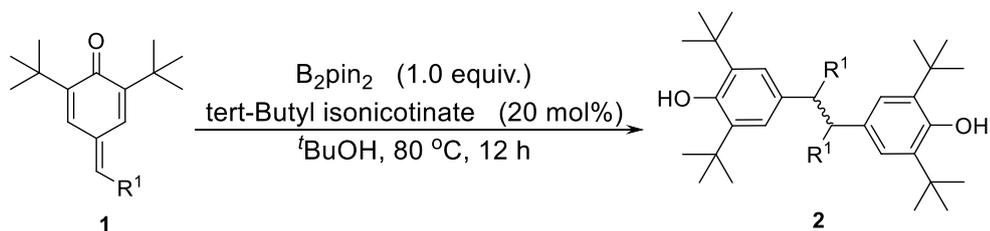
## 1. General information

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry nitrogen atmosphere. NMR spectra were recorded with tetramethylsilane as the internal standard. NMR spectra were recorded on a Bruker Avance II 400M type ( $^1\text{H}$  NMR, 400 MHz;  $^{13}\text{C}$  NMR, 100 MHz) spectrometer. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) was measured using a Nicolet NEXUS FT-IR spectrophotometer. The single crystal X-ray diffraction data were collected on a Bruker D8 Smart Apex II diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Fluorescence spectra were recorded on Hitachi F-7000. The reagents were all obtained from commercial sources and used without further purification. *p*-Benzoquinone methanes **1** were prepared by the previous reports <sup>1</sup>.

1. (a) Y. Lou, P. Cao, T. Jia, Y. Zhang, M. Wang, J. Liao, *Angew Chem Int Ed.*, 2015, **54**, 12134-12138; (b) W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F.-X. Wang, X.-Y. Ma, C.-A. Fan, *Angew. Chem. Int. Ed.*, 2013, **52**, 9229-9233; (c) D. Richter, N. Hampel, T. Singer, A. R. Ofial, H. Mayr, *Eur. J. Org. Chem.*, 2009, **2009**, 3203-3211.

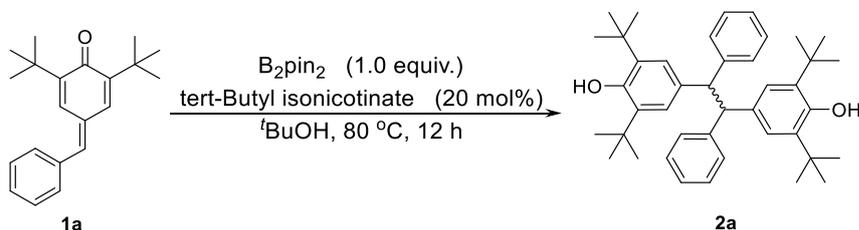
## 2. General procedure for the synthesis of products 2, 3, 4 and 5

### 2.1 General procedure for the synthesis of products 2



A 10 mL oven-dried Schlenk tube was successively charged with 0.20 mmol *p*-benzoquinone methanes **1**, 0.20 mmol B<sub>2</sub>pin<sub>2</sub>, 0.04 mmol tert-Butyl isonicotinate and 0.5 mL <sup>t</sup>BuOH. The tube was sealed, and the reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was quenched with 2M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (0.5 mL) for 0.5 h. Then, the reaction solution was acidified with 1.5 M HCl to pH = 2. The mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with brine (50 mL), afterward dried over Na<sub>2</sub>SO<sub>4</sub>, filtered. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give products **2**.

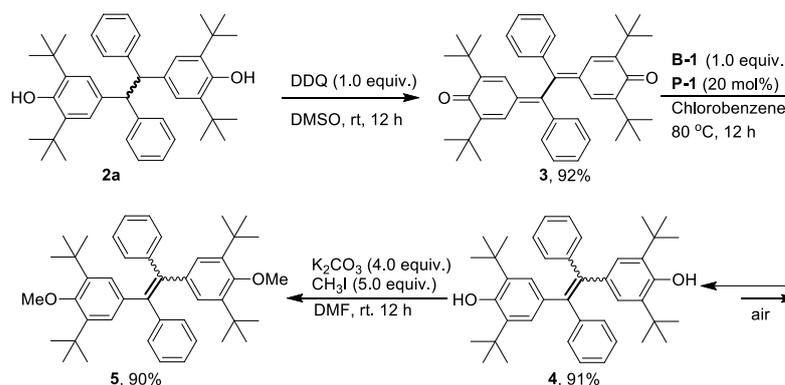
### Experimental procedure for gram scale synthesis of compound 2a



A 25 mL oven-dried Schlenk tube was successively charged with 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **1a** (1.1778 g, 4.0 mmol, 1.0 equiv.), B<sub>2</sub>pin<sub>2</sub> (1.0158 mg, 4.0 mmol, 1.0 equiv.), tert-butyl isonicotinate (0.1434 g, 0.8

mmol, 0.2 equiv.) and 10 mL *t*BuOH. The tube was sealed and the reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was quenched with 2M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL) for 0.5 h. Then, the reaction solution was acidified with 1.5 M HCl to pH = 2. The mixture was diluted with water (200 mL) and extracted with ethyl acetate (3 × 400 mL). The combined organic layers were washed with brine (500 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give product **2** (1.0625 mg, 90%).

## 2.2 General procedure for the synthesis of product **3**, **4** and **5**



A 10 mL oven-dried Schlenk tube was successively charged with 4,4'-(1,2-diphenylethane-1,2-diyl)bis(2,6-di-tert-butylphenol) **2a** (58.9 mg, 0.2 mmol, 1.0 equiv.), DDQ (45.4 mg, 0.2 mmol, 1.0 equiv.) and 3 mL DMSO. The tube was sealed, and the reaction mixture was stirred at 25 °C for 12 h. After completion of this reaction, the mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with brine (3 × 50 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude reaction mixture was purified by column

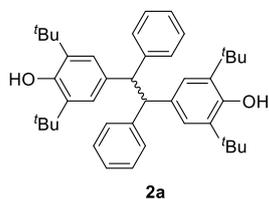
chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give product **3** (107.6 mg, 92%).

A 10 mL oven-dried Schlenck tube was successively charged with 2,6-di-tert-butyl-4-(2-(3,5-di-tert-butyl-4-hydroxycyclohexa-2,5-dien-1-ylidene)-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one **3** (117.4 mg, 0.2 mmol, 1.0 equiv.), B<sub>2</sub>pin<sub>2</sub> (50.8 mg, 0.2 mmol, 1.0 equiv.), tert-butyl isonicotinate (7.2 mg, 0.04 mmol, 0.2 equiv.) and 0.5 mL chlorobenzene. The tube was sealed, and the reaction mixture was stirred at 80 °C for 12 h. After completion of this reaction, the mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with brine (50 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give product **4** (107.2 mg, 91%).

A 10 mL oven-dried Schlenck tube was successively charged with 0.20 mmol 4,4'-(1,2-diphenylethene-1,2-diyl)bis(2,6-di-tert-butylphenol) **4** (117.8 mg, 0.2 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (110.6 mg, 0.8 mmol, 4.0 equiv.), CH<sub>3</sub>I (141.9 mg, 1.0 mmol, 5.0 equiv.) and 0.5 mL DMF. The tube was sealed, and the reaction mixture was stirred at 25 °C for 12 h. After completion of this reaction, the mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 × 70 mL). The combined organic layers were washed with brine (3 × 100 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give product **5** (111.3 mg, 90%).

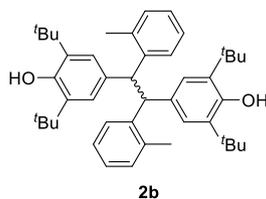
### 3. Characterization data of products 2, 3, 4 and 5

#### 4,4'-(1,2-diphenylethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2a):



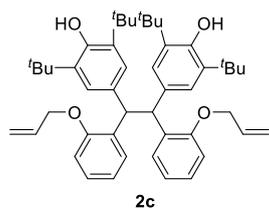
Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (55.0 mg, 93% yield, 1:1 d.r.); mp 19.4–196.4 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.24 – 7.18 (m, 2H), 7.17 – 7.08 (m, 6H), 7.03 (ddt,  $J = 9.1, 6.4, 2.2$  Hz, 2H), 6.87 (d,  $J = 9.2$  Hz, 4H), 4.89 (s, 1H), 4.86 (s, 1H), 4.56 (s, 1H), 4.49 (s, 1H), 1.31 (d,  $J = 4.6$  Hz, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.6, 151.5, 144.6, 144.4, 135.1, 135.0, 134.4, 133.9, 128.8, 128.6, 128.1, 127.9, 125.7, 125.6, 125.5, 125.4, 57.8, 57.7, 34.3, 34.3, 30.5, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3633, 3615, 3437, 2958, 1435, 1153; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{55}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 591.4197, found 591.4187.

#### 4,4'-(1,2-di-o-tolyloethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2b)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (55.3 mg, 89% yield, 2.4:1 d.r.); mp 184.4–186.1 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.29 (dd,  $J = 12.9, 7.7$  Hz, 5.7H), 7.04 (dq,  $J = 7.9, 3.7$  Hz, 4.7H), 7.01 – 6.95 (m, 3.0H), 6.94 – 6.89 (m, 9.9H), 6.72 (d,  $J = 3.0$  Hz, 11.5H), 4.83 (d,  $J = 2.9$  Hz, 5.8H), 4.76 (s, 4.1H), 4.69 (s, 1.7H), 2.30 (s, 5.0H), 2.10 (s, 12.0H), 1.25 (d,  $J = 13.1$  Hz, 104.2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.5, 151.4, 143.0, 142.3, 136.0, 135.9, 134.9, 134.7, 133.4, 133.3, 130.4, 130.0, 128.4, 126.5, 125.8, 125.8, 125.7, 125.5, 125.3, 53.0, 51.8, 34.3, 34.2, 30.6, 30.3, 20.4, 20.1; IR (KBr,  $\text{cm}^{-1}$ ): 3643, 2958, 2873, 1436, 1236, 1155; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{59}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 619.4510, found 619.4511.

#### 4,4'-(1,2-bis(2-(allyloxy)phenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2c)



Purified by column chromatography (petroleum ether/ethyl acetate

=50:1); White solid (69.1 mg, 98% yield, d.r. > 20:1); mp

165.4–167.4 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.38 (d,  $J =$

7.1 Hz, 1H), 7.02 – 6.91 (m, 3H), 6.80 (t,  $J = 7.5$  Hz, 1H), 6.63 (d,  $J = 8.2$  Hz, 1H), 6.05

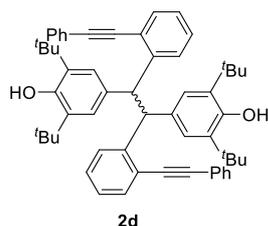
(ddt,  $J = 17.2, 10.1, 4.7$  Hz, 1H), 5.56 – 5.07 (m, 3H), 4.77 (s, 1H), 4.37 (td,  $J = 4.2, 2.0$  Hz,

2H), 1.27 (s, 18H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.3, 134.5, 134.1, 126.2, 125.5,

120.6, 116.5, 111.7, 68.7, 34.3, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3614, 2957, 2915, 1489, 1435, 1239,

1155, 750; HRMS (ESI-TOF) calcd for  $\text{C}_{48}\text{H}_{63}\text{O}_4^+$  ( $[\text{M}+\text{H}]^+$ ): 703.4721, found 703.4723.

#### 4,4'-(1,2-bis(2-(phenylethynyl)phenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2d)



Purified by column chromatography (petroleum ether/ethyl acetate

=50:1); White solid (65.3 mg, 83% yield, 1:2.5 d.r.); mp

193.4–195.4 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.84 – 7.78

(m, 0.9H), 7.78 – 7.72 (m, 2.0H), 7.66 (d,  $J = 8.0$  Hz, 1.0H), 7.53

(qd,  $J = 6.5, 3.5$  Hz, 4.9H), 7.48 – 7.42 (m, 1.8H), 7.38 – 7.28 (m, 2.3H), 7.18 (s, 1.0H),

7.10 (t,  $J = 7.5$  Hz, 1.5H), 5.75 (s, 1.0H), 5.65 (s, 0.4H), 4.94 (d,  $J = 2.2$  Hz, 1.4H), 1.35 (d,

$J = 1.5$  Hz, 25.2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.6, 151.5, 141.0, 139.6,

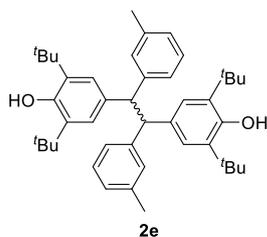
135.0, 134.7, 134.2, 133.7, 133.4, 132.5, 132.2, 129.0, 128.6, 126.4, 126.2, 125.8, 125.5,

125.45, 125.40, 125.1, 124.9, 124.0, 123.9, 123.5, 52.4, 51.1, 34.2, 34.1, 30.6, 30.2; IR

(KBr,  $\text{cm}^{-1}$ ): 3635, 2958, 1492, 1436, 1238, 1153, 754; HRMS (ESI-TOF) calcd for

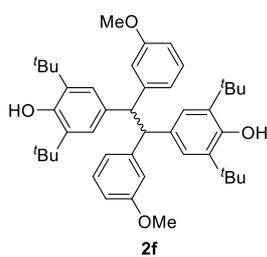
$\text{C}_{58}\text{H}_{63}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 791.4823, found 791.4817.

#### 4,4'-(1,2-di-m-tolyethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2e)



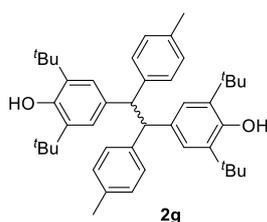
Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (61.2 mg, 99% yield, 1:1.3 d.r.); mp 166.5–168.0 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.02 (dd,  $J = 12.5$ , 6.6 Hz, 4.12H), 6.94 (d,  $J = 7.8$  Hz, 1.19H), 6.90 – 6.80 (m, 7.32H), 4.88 (s, 1.15H), 4.85 (s, 0.95H), 4.51 (s, 1.15H), 4.42 (s, 0.95H), 2.22 (d,  $J = 13.4$  Hz, 6.3H), 1.32 (s, 37.8H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.5, 151.4, 144.4, 144.3, 137.3, 137.0, 135.0, 134.9, 134.6, 134.1, 130.0, 129.7, 127.9, 127.8, 126.4, 126.1, 125.6, 125.5, 125.4, 125.4, 57.8, 57.8, 34.3, 34.3, 30.5, 30.4, 21.6, 21.5; IR (KBr,  $\text{cm}^{-1}$ ): 3618, 2958, 2915, 2362, 2336, 1436; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{59}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 619.4510, found 619.4495.

#### 4,4'-(1,2-bis(2-methoxyphenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2f)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (62.7 mg, 96% yield, 1.5:1 d.r.); mp 162.3–164.3 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.06 (q,  $J = 7.5$  Hz, 2.5H), 6.88 (d,  $J = 3.6$  Hz, 4.8H), 6.84 (d,  $J = 7.7$  Hz, 1.5H), 6.78 – 6.71 (m, 2.4H), 6.63 – 6.54 (m, 3.5H), 4.92 (s, 1.0H), 4.86 (s, 1.45H), 4.50 (s, 1.45H), 4.42 (s, 1.0H), 3.67 (d,  $J = 19.4$  Hz, 7.35H), 1.31 (d,  $J = 2.7$  Hz, 44.1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 159.3, 159.1, 151.7, 151.5, 146.1, 146.0, 135.1, 135.0, 134.2, 133.8, 129.0, 128.9, 125.5, 125.4, 121.4, 121.0, 114.5, 114.3, 111.6, 111.1, 57.8, 57.8, 55.2, 55.1, 34.3, 34.3, 30.5, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3614, 2958, 1605, 1587, 1485, 1435, 1265, 1235, 1150, 1050; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{58}\text{NaO}_4^+$  ( $[\text{M}+\text{Na}]^+$ ): 673.4227, found 673.4224.

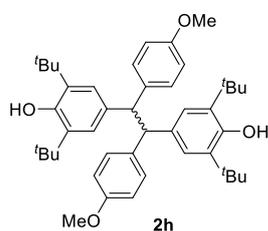
#### 4,4'-(1,2-di-p-tolyloethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2g):



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (61.5 mg, 99% yield, 1:1 d.r.); mp 170.5–172.3 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.12 (d,  $J =$

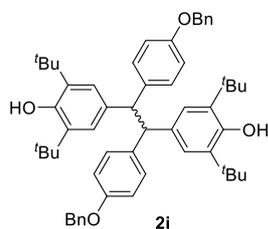
7.8 Hz, 2H), 6.99 – 6.93 (m, 4H), 6.91 (d,  $J = 7.8$  Hz, 2H), 6.85 (d,  $J = 6.1$  Hz, 4H), 4.86 (s, 1H), 4.82 (s, 1H), 4.52 (s, 1H), 4.41 (s, 1H), 2.22 (s, 6H), 1.30 (s, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.5, 151.3, 141.65, 141.56, 135.0, 134.9, 134.6, 134.2, 128.9, 128.63, 128.57, 128.3, 125.5, 125.3, 57.3, 57.3, 34.3, 34.3, 30.5, 30.4, 21.1, 21.0; IR (KBr,  $\text{cm}^{-1}$ ): 3617, 2956, 2917, 2871, 1435, 1235, 1155; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{59}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 619.4510, found 619.4499.

#### 4,4'-(1,2-bis(4-methoxyphenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2h)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (63.8 mg, 98% yield, 1.7:1 d.r.); mp 181.5–183.5 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.12 – 7.05 (m, 3.5H), 6.99 – 6.93 (m, 2.0H), 6.82 (d,  $J = 1.4$  Hz, 5.3H), 6.72 – 6.62 (m, 5.4H), 4.88 (s, 1.0H), 4.83 (s, 1.7H), 4.44 (s, 1.7H), 4.37 (s, 1.0H), 3.71 (d,  $J = 2.1$  Hz, 8.1H), 1.29 (d,  $J = 4.1$  Hz, 48.6H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 157.5, 157.4, 151.5, 151.3, 137.0, 136.9, 135.0, 135.0, 134.9, 134.3, 129.6, 129.4, 125.5, 125.3, 113.5, 113.3, 57.1, 56.9, 55.3, 55.2, 34.3, 34.3, 30.5, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3622, 2958, 2910, 1511, 1437, 1249, 1178; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{59}\text{O}_4^+$  ( $[\text{M}+\text{H}]^+$ ): 651.4408, found 651.4404.

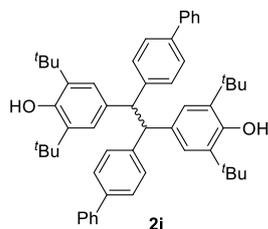
#### 4,4'-(1,2-bis(4-(benzyloxy)phenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2i)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (77 mg, 96% yield, 1:1 d.r.); mp 182.1–183.6 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.45 – 7.37 (m, 8H), 7.36 – 7.29 (m, 2H), 7.16 – 7.09 (m, 2H), 7.01 (d,  $J = 8.6$  Hz, 2H), 6.87 (d,  $J = 2.5$  Hz, 4H), 6.83 – 6.74 (m, 4H), 4.99 (s, 4H), 4.92 (s, 1H), 4.87 (s, 1H), 4.49 (s, 1H), 4.42 (s, 1H), 1.34 (d,  $J = 4.2$  Hz, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 156.8, 156.7, 151.5, 151.3, 137.4, 137.4, 137.3, 137.1, 135.0, 134.8, 134.3, 129.7, 129.5, 128.6, 128.0, 127.9, 127.6, 127.5, 125.5, 125.4, 114.5, 114.3, 70.1, 70.0, 57.1, 56.9, 34.3, 34.3, 30.5,

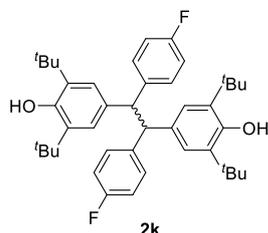
30.5; IR (KBr,  $\text{cm}^{-1}$ ): 3621, 2958, 1508, 1436, 1242, 1175; HRMS (ESI-TOF) calcd for  $\text{C}_{56}\text{H}_{67}\text{O}_4^+$  ( $[\text{M}+\text{H}]^+$ ): 803.5034, found 803.5037.

#### 4,4'-(1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2j)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (67.7 mg, 91% yield, 1:1 d.r.); mp 171.4–173.2 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.53 (dd,  $J = 7.7, 2.6$  Hz, 4H), 7.40 (dd,  $J = 11.9, 8.0$  Hz, 8H), 7.37 – 7.26 (m, 4H), 7.20 (d,  $J = 7.9$  Hz, 2H), 6.94 (d,  $J = 2.1$  Hz, 4H), 4.92 (s, 1H), 4.89 (s, 1H), 4.66 (s, 1H), 4.58 (s, 1H), 1.33 (d,  $J = 8.5$  Hz, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.7, 151.5, 143.8, 143.6, 141.4, 141.1, 138.4, 138.3, 135.18, 135.17, 134.4, 133.8, 129.2, 128.9, 128.8, 128.7, 127.1, 127.0, 126.98, 126.95, 126.9, 126.7, 125.6, 125.4, 57.43, 57.41, 34.4, 34.3, 30.5, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3638, 2958, 2913, 1485, 1436, 1236, 1154, 763; HRMS (ESI-TOF) calcd for  $\text{C}_{54}\text{H}_{63}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 743.4823, found 743.4820.

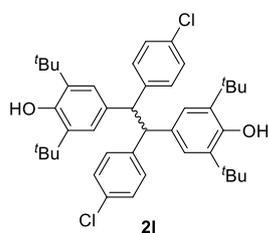
#### 4,4'-(1,2-bis(4-fluorophenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2k)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (58.8 mg, 94% yield, 1:1 d.r.); mp 173.9–175.6 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.16 – 7.08 (m, 2H), 7.06 – 6.98 (m, 2H), 6.82 (dd,  $J = 8.5, 4.9$  Hz, 8H), 4.94 (s, 1H), 4.89 (s, 1H), 4.48 (s, 1H), 4.42 (s, 1H), 1.31 (d,  $J = 3.5$  Hz, 36H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -117.6, -118.2;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 161.1 (d,  $J = 244.6$  Hz), 161.0 (d,  $J =$

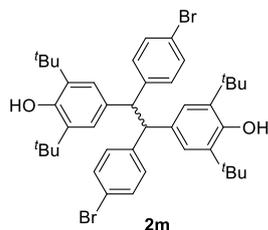
244.2 Hz), 151.8, 151.6, 140.2 (d,  $J = 3.2$  Hz), 140.0 (d,  $J = 3.2$  Hz), 135.33, 135.26, 134.0, 133.4, 130.0 (d,  $J = 7.7$  Hz), 129.9 (d,  $J = 7.8$  Hz), 125.4, 125.3, 115.0 (d,  $J = 21.0$  Hz), 114.7 (d,  $J = 21.1$  Hz), 57.1, 56.8, 34.4, 34.3, 30.5, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3637, 2960, 2913, 2872, 1508, 1436, 1226, 1154, 837; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{53}\text{F}_2\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 627.4008, found 627.3988.

#### 4,4'-(1,2-bis(4-chlorophenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2l)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (58 mg, 88% yield, 1:1 d.r.); mp 198.1–199.7 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm) 7.10 (d,  $J = 14.7$  Hz, 6H), 6.99 (d,  $J = 8.2$  Hz, 2H), 6.80 (d,  $J = 7.0$  Hz, 4H), 4.96 (s, 1H), 4.90 (s, 1H), 4.48 (s, 1H), 4.41 (s, 1H), 1.31 (d,  $J = 5.8$  Hz, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm) 151.9, 151.7, 142.9, 142.7, 135.4, 135.3, 133.6, 132.9, 131.5, 131.3, 130.0, 129.8, 128.4, 128.1, 125.4, 125.2, 57.0, 56.7, 34.4, 34.3, 30.44, 30.39; IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2959, 2914, 1488, 1435, 1236, 1156, 1093; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{53}\text{Cl}_2\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 659.3417, found 659.3422.

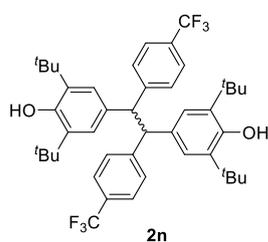
#### 4,4'-(1,2-bis(4-bromophenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2m)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (71.4 mg, 95% yield, 1:1.2 d.r.); mp 209.9–211.4 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.22 – 7.12 (m, 4.7H), 7.01 – 6.94 (m, 2.0H), 6.87 – 6.81 (m, 2.3H), 6.69 (dd,  $J = 6.9, 1.9$  Hz, 4.2H), 4.87 (d,  $J = 1.8$  Hz, 1.2H), 4.80 (d,  $J = 1.8$  Hz, 1.0H), 4.37 (d,  $J = 2.0$  Hz, 1.0H), 4.29 (d,  $J = 2.0$  Hz, 1.0H), 1.31 (d,  $J = 5.8$  Hz, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm) 151.9, 151.7, 142.9, 142.7, 135.4, 135.3, 133.6, 132.9, 131.5, 131.3, 130.0, 129.8, 128.4, 128.1, 125.4, 125.2, 57.0, 56.7, 34.4, 34.3, 30.44, 30.39; IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2959, 2914, 1488, 1435, 1236, 1156, 1093; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{53}\text{Br}_2\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 675.3417, found 675.3422.

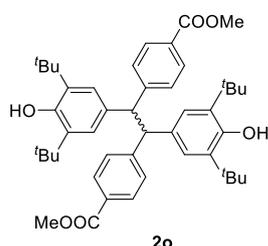
= 1.9 Hz, 1.2H), 1.21 (d,  $J = 7.5$  Hz, 39.6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.9, 151.7, 143.4, 143.1, 135.4, 135.3, 133.5, 132.8, 131.4, 131.0, 130.4, 130.2, 125.4, 125.2, 119.7, 119.4, 56.9, 56.7, 34.4, 34.3, 30.4, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2959, 2914, 1485, 1434, 1237, 1154; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{53}\text{Br}_2\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 747.2407, found 747.2409.

**4,4'-(1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2n)**



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (63.0 mg, 87% yield, 1:1 d.r.); mp 173.9–175.7 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.41 (t,  $J = 7.4$  Hz, 4H), 7.32 (d,  $J = 8.0$  Hz, 2H), 7.19 (d,  $J = 7.9$  Hz, 2H), 6.81 (dd,  $J = 18.4, 1.7$  Hz, 4H), 4.98 (d,  $J = 1.6$  Hz, 1H), 4.93 (d,  $J = 1.6$  Hz, 1H), 4.63 (s, 1H), 4.55 (s, 1H), 1.30 (dd,  $J = 6.1, 1.6$  Hz, 36H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -62.3;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.1, 151.9, 135.7, 135.5, 133.0, 132.2, 129.0, 128.7, 128.3 (d,  $J = 32.4$  Hz), 128.1 (d,  $J = 32.2$  Hz), 125.41, 125.37, 125.34, 125.28, 125.02 (d,  $J = 3.8$  Hz), 125.98 (d,  $J = 3.8$  Hz), 124.44 (d,  $J = 273.2$  Hz), 124.38 (d,  $J = 270.2$  Hz), 57.3, 57.2, 34.4, 34.3, 30.4, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3633, 2963, 1436, 1325, 1161, 1118, 1068; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{52}\text{F}_6\text{NaO}_2^+$  ( $[\text{M}+\text{Na}]^+$ ): 749.3764, found 749.3767.

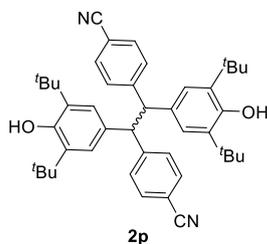
**Dimethyl 4,4'-(1,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,2-diyl)dibenzoate(2o)**



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (56.8 mg, 80% yield, 1:1 d.r.); mp 203.9–205.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.81 (d,  $J =$

8.0 Hz, 4H), 7.28 (d,  $J = 8.1$  Hz, 2H), 7.16 (d,  $J = 8.1$  Hz, 2H), 6.82 (d,  $J = 8.2$  Hz, 4H), 4.95 (s, 1H), 4.92 (s, 1H), 4.62 (s, 1H), 4.57 (s, 1H), 3.84 (d,  $J = 6.1$  Hz, 6H), 1.28 (d,  $J = 7.7$  Hz, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 167.2, 167.1, 152.0, 151.8, 149.8, 149.4, 135.5, 135.4, 133.1, 132.5, 129.7, 129.4, 128.7, 128.5, 127.8, 127.5, 125.4, 125.3, 57.4, 57.1, 52.0, 34.3, 34.3, 30.4, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3634, 2956, 1717, 1608, 1436, 1282, 1240, 1186, 1154, 1113; HRMS (ESI-TOF) calcd for  $\text{C}_{46}\text{H}_{59}\text{O}_6^+$  ( $[\text{M}+\text{H}]^+$ ): 707.4306, found 707.4307.

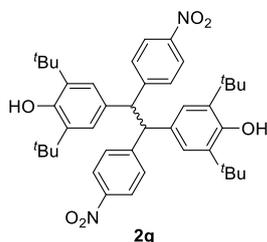
#### 4,4'-(1,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,2-diyl)dibenzonitrile(2p)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (53.6 mg, 84% yield, 1:1 d.r.); mp 212.8–214.5 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.36 (dd,  $J = 8.1, 6.5$  Hz, 4H), 7.19 (d,  $J = 8.3$  Hz, 2H), 7.09 (d,  $J = 8.1$  Hz, 2H),

6.69 (d,  $J = 14.4$  Hz, 4H), 4.95 (s, 1H), 4.89 (s, 1H), 4.50 (s, 1H), 4.44 (s, 1H), 1.21 (s, 36H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.3, 152.1, 149.6, 149.2, 135.9, 135.7, 132.3, 132.0, 131.9, 131.4, 129.4, 129.2, 125.2, 125.2, 119.1, 119.0, 110.0, 109.6, 57.3, 57.0, 34.4, 34.3, 30.4, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3638, 3592, 2959, 2873, 2230, 1606, 1437, 1238, 1155, 1118; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{53}\text{N}_2\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 641.4102, found 641.4097.

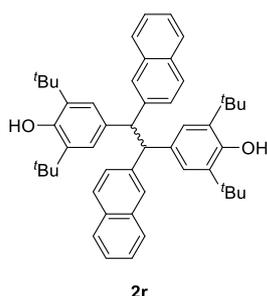
#### 4,4'-(1,2-bis(4-nitrophenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2q)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (60.7 mg, 89% yield, 1:1.5 d.r.); mp

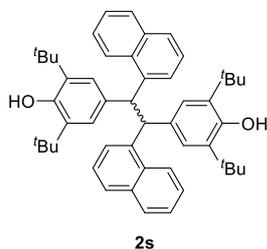
223.3–225.3 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.98 – 7.90 (m, 3.3H), 7.28 (d,  $J = 8.7$  Hz, 1.4H), 7.20 – 7.13 (m, 2.3H), 6.73 (d,  $J = 10.7$  Hz, 3.3H), 4.95 (s, 1.0H), 4.90 (s, 0.65H), 4.61 (s, 0.65H), 4.55 (s, 1.0H), 1.21 (d,  $J = 5.1$  Hz, 29.7H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.5, 152.2, 151.7, 151.3, 146.4, 146.2, 136.1, 135.9, 131.8, 131.2, 129.4, 129.2, 125.20, 125.17, 123.9, 123.4, 57.1, 56.8, 34.4, 34.3, 30.4, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3634, 2959, 1520, 1437, 1345; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{52}\text{N}_2\text{NaO}_6^+$  ( $[\text{M}+\text{Na}]^+$ ): 703.3718, found 703.3714.

#### 4,4'-(1,2-di(naphthalen-2-yl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2r)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (64.8 mg, 94% yield, 1:2.2 d.r.); mp 189.4–191.4 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.72 (d,  $J = 14.2$  Hz, 1.5H), 7.68 – 7.59 (m, 4.0H), 7.55 – 7.47 (m, 1.4H), 7.37 (dd,  $J = 7.8, 5.0$  Hz, 1.5H), 7.32 (ddd,  $J = 6.4, 3.4, 1.9$  Hz, 2.0H), 6.96 (d,  $J = 9.7$  Hz, 3.0H), 4.90 (s, 1.0H), 4.88 (s, 1.0H), 4.83 (s, 0.45H), 4.78 (s, 0.45H), 1.33 (s, 16H), 1.21 (s, 8.1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.7, 151.6, 142.0, 141.8, 135.2, 135.1, 134.4, 133.62, 133.58, 133.55, 132.02, 132.00, 127.82, 127.78, 127.7, 127.52, 127.51, 127.48, 127.46, 127.3, 127.2, 127.0, 125.6, 125.58, 125.5, 125.08, 125.06, 57.54, 57.47, 34.3, 34.2, 30.5, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3623, 2958, 2914, 2872, 1435, 1236, 1158; HRMS (ESI-TOF) calcd for  $\text{C}_{50}\text{H}_{58}\text{NaO}_2^+$  ( $[\text{M}+\text{Na}]^+$ ): 713.4329, found 713.4319.

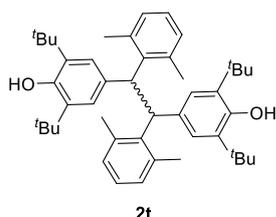
#### 4,4'-(1,2-di(naphthalen-1-yl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2s)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (63 mg, 91% yield, 1:1 d.r.); mp 195.3–197.3 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.40 (d,  $J = 8.6$  Hz, 1H), 8.16

– 8.12 (m, 1H), 7.77 (d,  $J = 7.9$  Hz, 2H), 7.65 (d,  $J = 8.1$  Hz, 2H), 7.52 (dd,  $J = 14.3, 8.0$  Hz, 3H), 7.43 (t,  $J = 7.4$  Hz, 2H), 7.38 (dd,  $J = 6.5, 3.2$  Hz, 2H), 7.16 (t,  $J = 7.7$  Hz, 1H), 6.92 (s, 2H), 6.83 (s, 2H), 5.62 (s, 1H), 5.56 (s, 1H), 4.89 (s, 1H), 4.73 (s, 1H), 1.33 (s, 18H), 1.12 (s, 18H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.7, 151.6, 142.0, 141.8, 135.2, 135.1, 134.4, 133.62, 133.58, 133.55, 132.02, 132.00, 127.82, 127.78, 127.7, 127.52, 127.51, 127.48, 127.46, 127.3, 127.2, 127.0, 125.6, 125.58, 125.5, 125.08, 125.06, 57.54, 57.47, 34.3, 34.2, 30.5, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3625, 2958, 1436, 1236, 1155, 777; HRMS (ESI-TOF) calcd for  $\text{C}_{50}\text{H}_{58}\text{NaO}_2^+$  ( $[\text{M}+\text{Na}]^+$ ): 713.4329, found 713.4320.

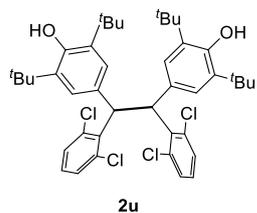
#### 4,4'-(1,2-bis(2,6-dimethylphenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2t)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (54.5 mg, 84% yield, 6.7:1 d.r.); mp 254.0–255.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.97 – 6.76

(m, 26.0H), 6.62 (s, 12.6H), 5.41 (s, 1.0H), 5.30 (s, 6.7H), 4.86 (d,  $J = 10.1$  Hz, 7.7H), 2.43 – 2.08 (m, 46.2H), 1.21 (d,  $J = 21.7$  Hz, 138.6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.3, 142.2, 137.4, 136.7, 134.2, 132.6, 130.7, 128.6, 126.2, 125.8, 48.9, 34.2, 30.3, 22.7, 22.1; IR (KBr,  $\text{cm}^{-1}$ ): 3644, 2958, 2912, 1467, 1436, 1238, 1156; HRMS (ESI-TOF) calcd for  $\text{C}_{46}\text{H}_{63}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 647.4823, found 647.4809.

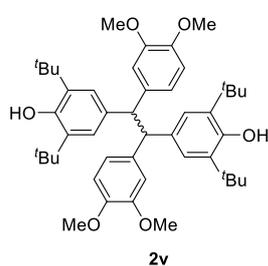
#### 4,4'-(1,2-bis(2,6-dichlorophenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2u)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (62.8 mg, 86% yield, d.r. > 20:1); mp 201.4–203.4 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm) 7.22 (s, 3H),

7.07 (dd,  $J = 8.1, 1.4$  Hz, 1H), 6.92 (t,  $J = 8.0$  Hz, 1H), 6.07 (s, 1H), 4.96 (s, 1H), 1.31 (s, 18H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm) 152.0, 139.1, 137.8, 135.0, 134.7, 131.9, 130.4, 128.9, 127.5, 127.0, 51.3, 34.3, 30.6; IR (KBr,  $\text{cm}^{-1}$ ): 3641, 2959, 1435, 1240, 1155, 771; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{50}\text{Cl}_4\text{NaO}_2^+$  ( $[\text{M}+\text{Na}]^+$ ): 749.2457, found 749.2448.

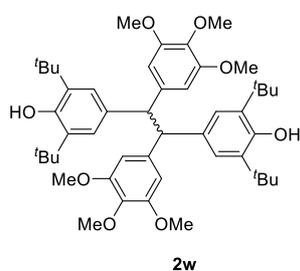
#### 4,4'-(1,2-bis(3,4-dimethoxyphenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2v)



Purified by column chromatography (petroleum ether/ethyl acetate =50:1); White solid (59.4 mg, 84% yield, 1:1 d.r.); mp 172.6–174.6 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.85 (d,  $J = 2.4$  Hz, 4H), 6.74 – 6.61 (m, 5H), 6.46 (s, 1H), 4.92 (s, 1H), 4.85 (s, 1H), 4.38 (s, 1H), 4.31 (s, 1H), 3.78 (s, 6H), 3.75 (s, 3H), 3.66 (s,

3H), 1.30 (d,  $J = 3.8$  Hz, 36H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 151.7, 151.4, 148.3, 148.1, 146.9, 146.8, 137.3, 137.2, 135.1, 135.0, 134.5, 134.1, 125.5, 125.3, 120.8, 120.7, 112.4, 112.0, 110.93, 110.91, 57.72, 57.65, 56.0, 55.9, 55.8, 55.6, 34.4, 34.3, 30.5, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3624, 3435, 2956, 2910, 1514, 1462, 1438, 1261, 1239, 1141, 1025; HRMS (ESI-TOF) calcd for  $\text{C}_{46}\text{H}_{62}\text{NaO}_6^+$  ( $[\text{M}+\text{Na}]^+$ ): 733.4439, found 733.4428.

#### 4,4'-(1,2-bis(3,4,5-trimethoxyphenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol)(2w)

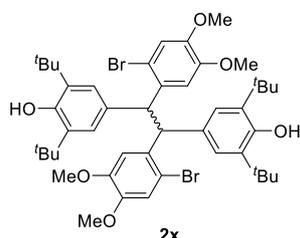


Purified by column chromatography (petroleum ether/ethyl acetate =5:1); White solid (76.2 mg, 99% yield, 1:1 d.r.); mp 178.4–180.4 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.89 (d,  $J = 10.5$  Hz, 4H), 6.38 (s, 2H), 6.25 (s, 2H), 4.97 (s, 1H), 4.89 (s,

1H), 4.32 (s, 1H), 4.26 (s, 1H), 3.78 – 3.71 (m, 12H), 3.68 (s, 6H), 1.32 (d,  $J = 7.4$  Hz, 36H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.7, 152.6, 151.9, 151.6, 140.1, 139.8,

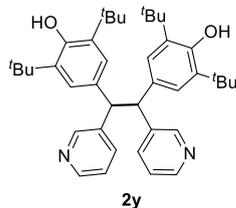
136.1, 135.8, 135.3, 135.2, 133.71, 133.68, 125.34, 125.33, 106.0, 105.9, 60.92, 60.90, 58.7, 58.6, 56.1, 55.9, 34.4, 34.3, 30.49, 30.47; IR (KBr,  $\text{cm}^{-1}$ ): 3435, 2955, 1592, 1506, 1460, 1432, 1327, 1234, 1194, 1126; HRMS (ESI-TOF) calcd for  $\text{C}_{48}\text{H}_{66}\text{NaO}_8^+$  ( $[\text{M}+\text{Na}]^+$ ): 793.4650, found 793.4633

**4,4'-(1,2-bis(2-bromo-4,5-dimethoxyphenyl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol) (2x)**



Purified by column chromatography (petroleum ether/ethyl acetate =5:1); White solid (86.1 mg, 99% yield, 1:10 d.r.); mp 194.7–196.7 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.04 (d,  $J = 5.6$  Hz, 3.3H), 6.81 (s, 1.1H), 5.13 (s, 1.0H), 5.05 (s, 0.1H), 4.91 (s, 1.1H), 3.91 (s, 0.3H), 3.84 (s, 3H), 3.75 (s, 3.3H), 1.33 (s, 19.8H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.0, 148.4, 147.5, 135.3, 135.1, 132.4, 125.0, 115.4, 115.1, 112.0, 112.0, 56.1, 56.0, 34.4, 30.4; IR (KBr,  $\text{cm}^{-1}$ ): 3626, 2958, 1503, 1461, 1437, 1272, 1237, 1193, 1153, 1026; HRMS (ESI-TOF) calcd for  $\text{C}_{46}\text{H}_{61}\text{Br}_2\text{O}_6^+$  ( $[\text{M}+\text{H}]^+$ ): 867.2829, found 867.2820.

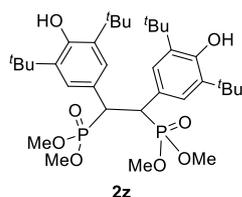
**4,4'-(1,2-di(pyridin-3-yl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol) (2y)**



Purified by column chromatography (petroleum ether/ethyl acetate =1:1); White solid (49.6 mg, 84% yield, d.r. > 20:1); mp 240.5–242.1 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.33 – 8.26 (m, 2H), 7.41 (dt,  $J = 7.9, 2.0$  Hz, 1H), 7.08 (ddd,  $J = 7.9, 4.8, 0.8$  Hz, 1H), 6.81 (s, 2H), 4.99 (s, 1H), 4.49 (s, 1H), 1.29 (s, 18H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.3, 150.1, 147.1, 139.5, 135.9, 131.9, 125.4, 123.1, 54.8, 34.4, 30.4; IR (KBr,  $\text{cm}^{-1}$ ):

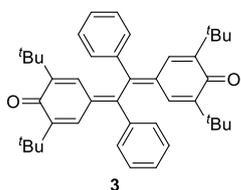
2958, 2913, 1432, 1232, 1199, 714; HRMS (ESI-TOF) calcd for  $C_{40}H_{53}N_2O_2^+$  ( $[M+H]^+$ ): 593.4102, found 593.4107.

**tetramethyl(1,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,2-diyl)bis(phosphonate)(2z)**



Purified by column chromatography (petroleum ether/ethyl acetate =1:1); White solid (59.2 mg, 90% yield, d.r. > 20:1); mp 180.5–182.5 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 6.80 (d,  $J = 1.6$  Hz, 2H), 4.95 (s, 1H), 3.85 (q,  $J = 7.2, 6.6$  Hz, 1H), 3.81 – 3.74 (m, 3H), 3.21 (d,  $J = 9.8$  Hz, 3H), 1.27 (s, 18H);  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  (ppm) 29.9;  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  (ppm) 152.6 (t,  $J = 1.2$  Hz), 135.1, 127.5 (t,  $J = 2.8$  Hz), 124.3 (t,  $J = 1.8$  Hz), 53.9 (t,  $J = 3.4$  Hz), 52.3 (t,  $J = 3.8$  Hz), 44.0 (d,  $J = 142.4$  Hz), 43.9 (d,  $J = 142.4$  Hz), 34.2, 30.4; IR (KBr,  $cm^{-1}$ ): 3424, 2955, 2913, 1437, 1231, 1185, 1112, 1046, 823, HRMS (ESI-TOF) calcd for  $C_{34}H_{56}NaO_8P_2^+$  ( $[M+Na]^+$ ): 677.3343, found 7677.3343.

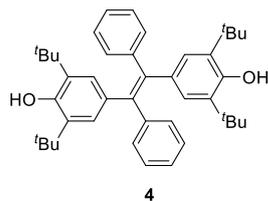
**4,4'-(1,2-diphenylethane-1,2-diylidene)bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one)(3)**



Purified by column chromatography (petroleum ether/ethyl acetate = 50:1); Red solid (107.6 mg, 92%); mp 230.4–232.4 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.34 – 7.25 (m, 4H), 7.22 (dd,  $J = 7.5, 2.1$  Hz, 2H), 7.00 (d,  $J = 2.6$  Hz, 1H), 1.24 (s, 9H), 1.16 (s, 9H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  (ppm) 186.4, 152.1, 149.4, 149.0, 138.3, 134.2, 131.3, 131.2, 130.3, 129.2, 128.4, 35.7,

35.4, 29.7, 29.6; IR (KBr,  $\text{cm}^{-1}$ ): 2956, 1608, 1359, 1336, 700; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{51}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 587.3884, found 587.3875.

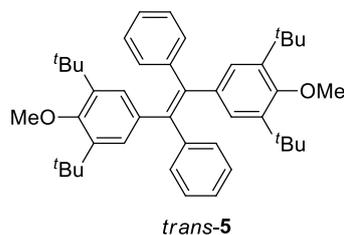
**(E)-4,4'-(1,2-diphenylethene-1,2-diyl)bis(2,6-di-tert-butylphenol)(4)**



Purified by column chromatography (petroleum ether/ethyl acetate = 50:1); Yellow solid (107.2 mg, 91%, Z:E=1.7:1); mp 187.6–188.7 °C;

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.06 – 6.92 (m, 8.3H), 6.67 (d,  $J = 1.6$  Hz, 3.1H), 4.94 (s, 0.6H), 4.93 (s, 1.0H), 1.16 (s, 18.0H), 1.12 (s, 10.8H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 152.2, 152.1, 145.0, 144.1, 141.3, 140.5, 136.1, 134.8, 134.7, 134.6, 131.7, 131.6, 128.8, 128.5, 127.52, 127.47, 126.1, 125.8, 34.20, 34.18, 30.5, 30.3; IR (KBr,  $\text{cm}^{-1}$ ): 3632, 2960, 2871, 1435, 1232, 1154, 1119, 888, 749, 699; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{53}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 589.4040, found 589.4027.

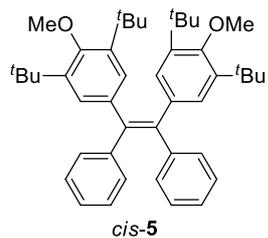
**(E)-1,2-bis(3,5-di-tert-butyl-4-methoxyphenyl)-1,2-diphenylethene(trans-5)**



Purified by column chromatography (petroleum ether/ethyl acetate = 50:1); White solid (37.6 mg, 34%); mp 158.4–160.4 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.07 (qd,  $J = 7.6, 6.7, 3.5$  Hz, 3H), 7.02 – 6.98 (m, 2H), 6.83 (s, 2H),

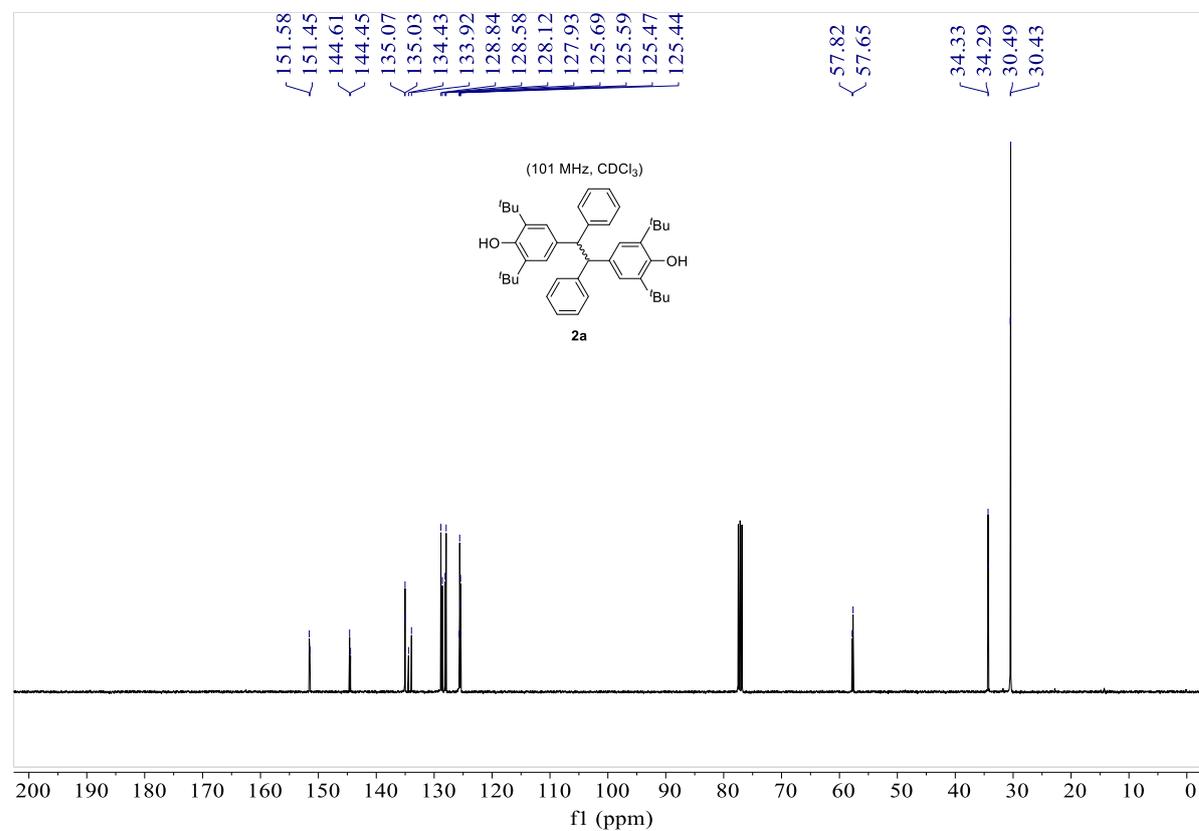
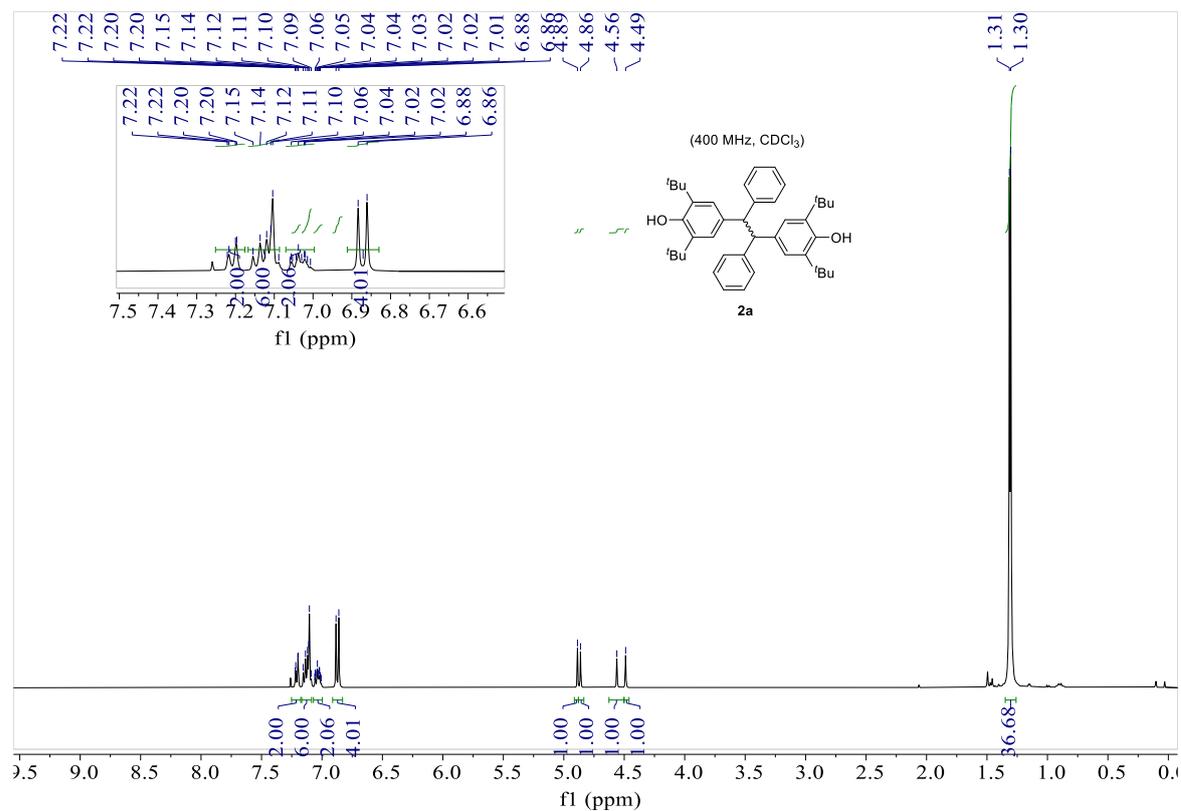
3.60 (s, 3H), 1.18 (s, 18H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 158.2, 144.5, 142.1, 140.8, 137.8, 131.5, 130.3, 127.5, 126.0, 64.3, 35.5, 32.1; IR (KBr,  $\text{cm}^{-1}$ ): 2960, 2864, 1260, 1220, 1113, 1012, 801, 700; HRMS (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{56}\text{KO}_2^+$  ( $[\text{M}+\text{K}]^+$ ): 655.3912, found 655.3912.

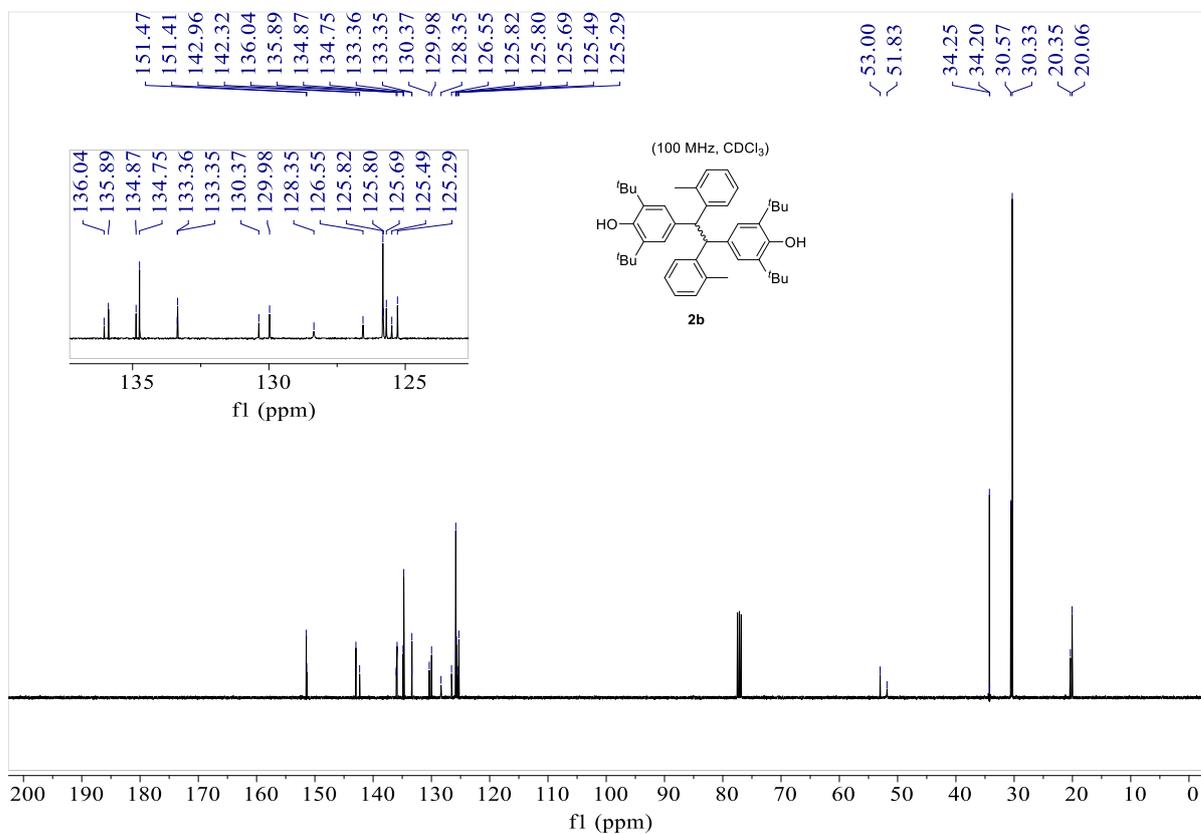
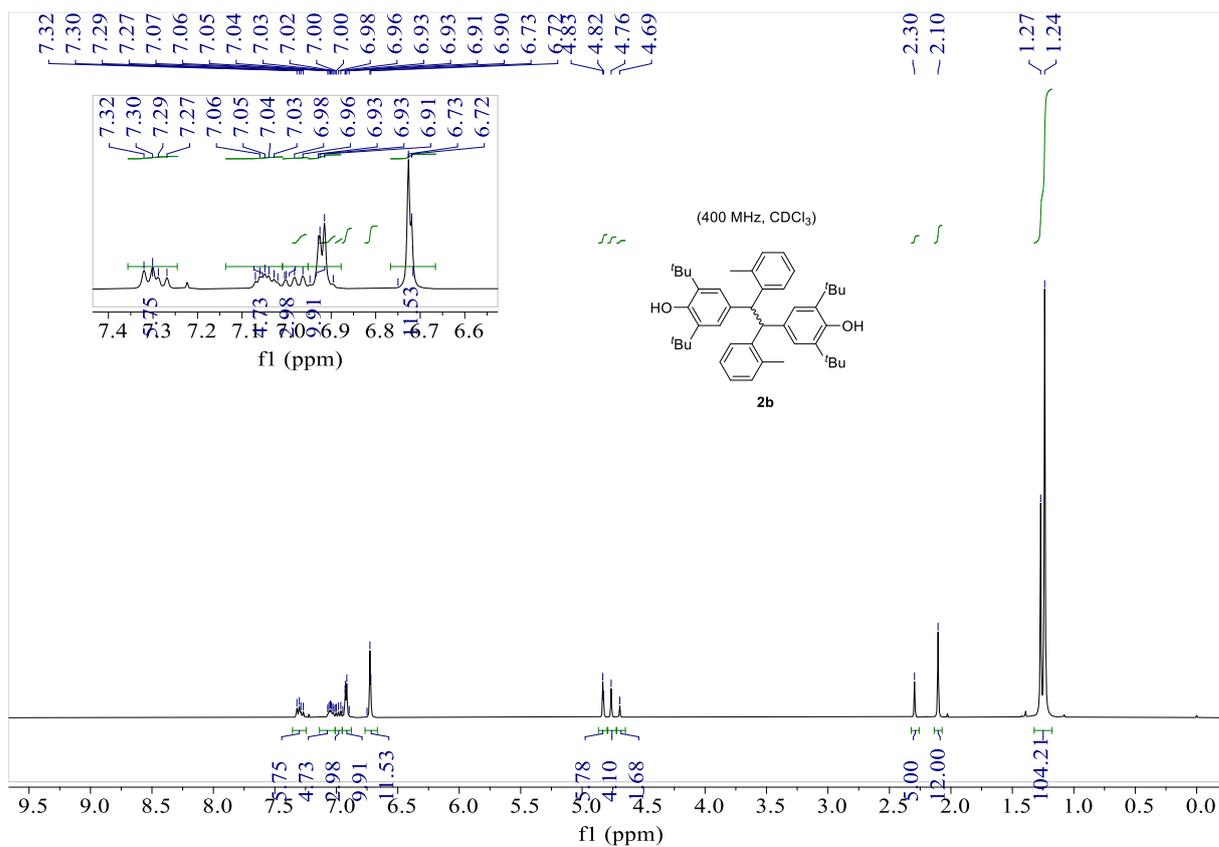
**(Z)-1,2-bis(3,5-di-tert-butyl-4-methoxyphenyl)-1,2-diphenylethene(cis-5)**

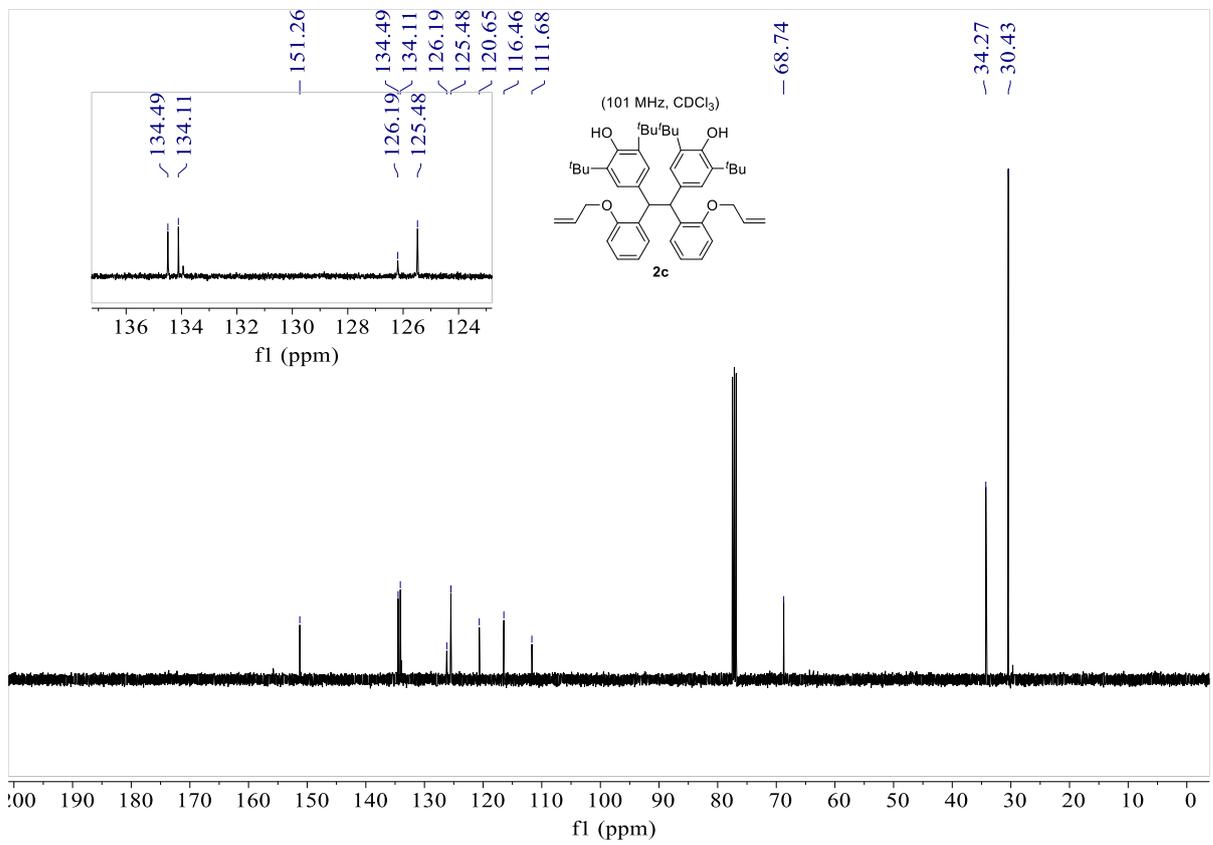
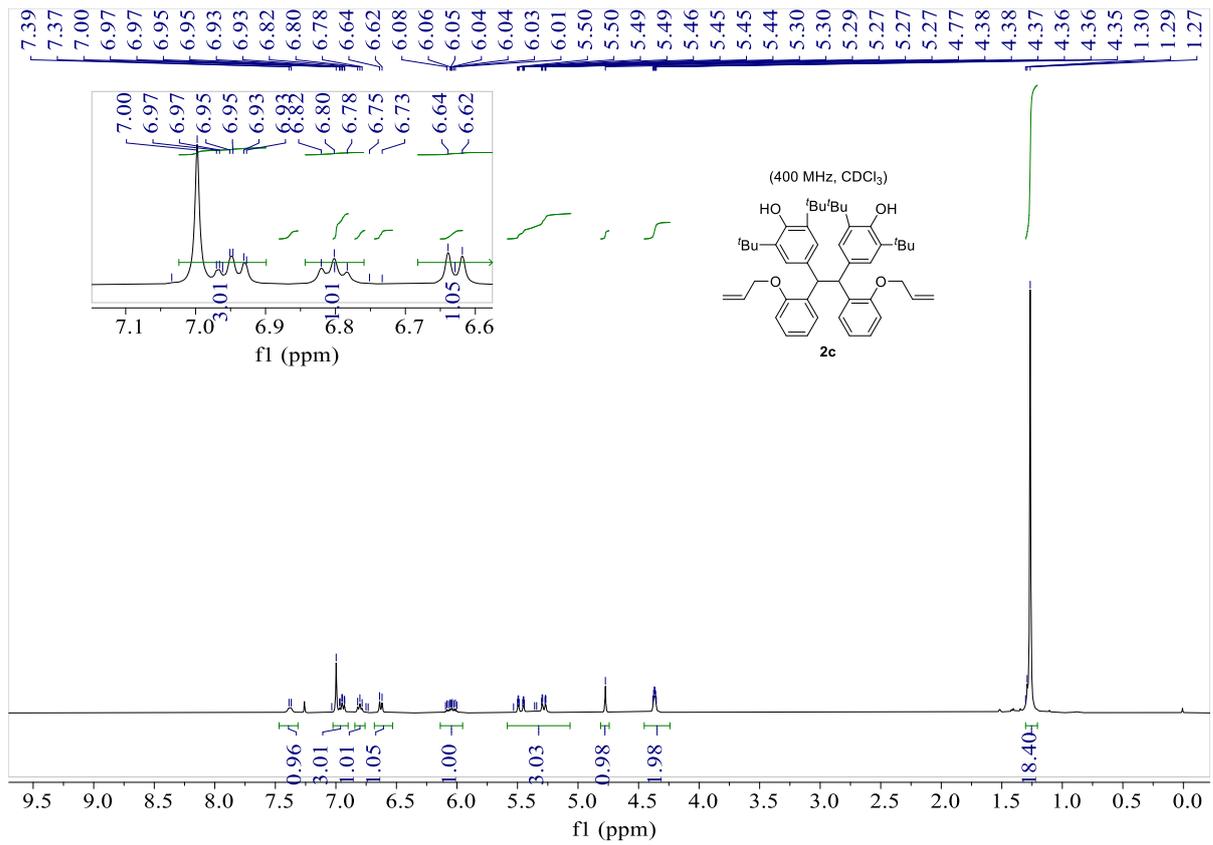


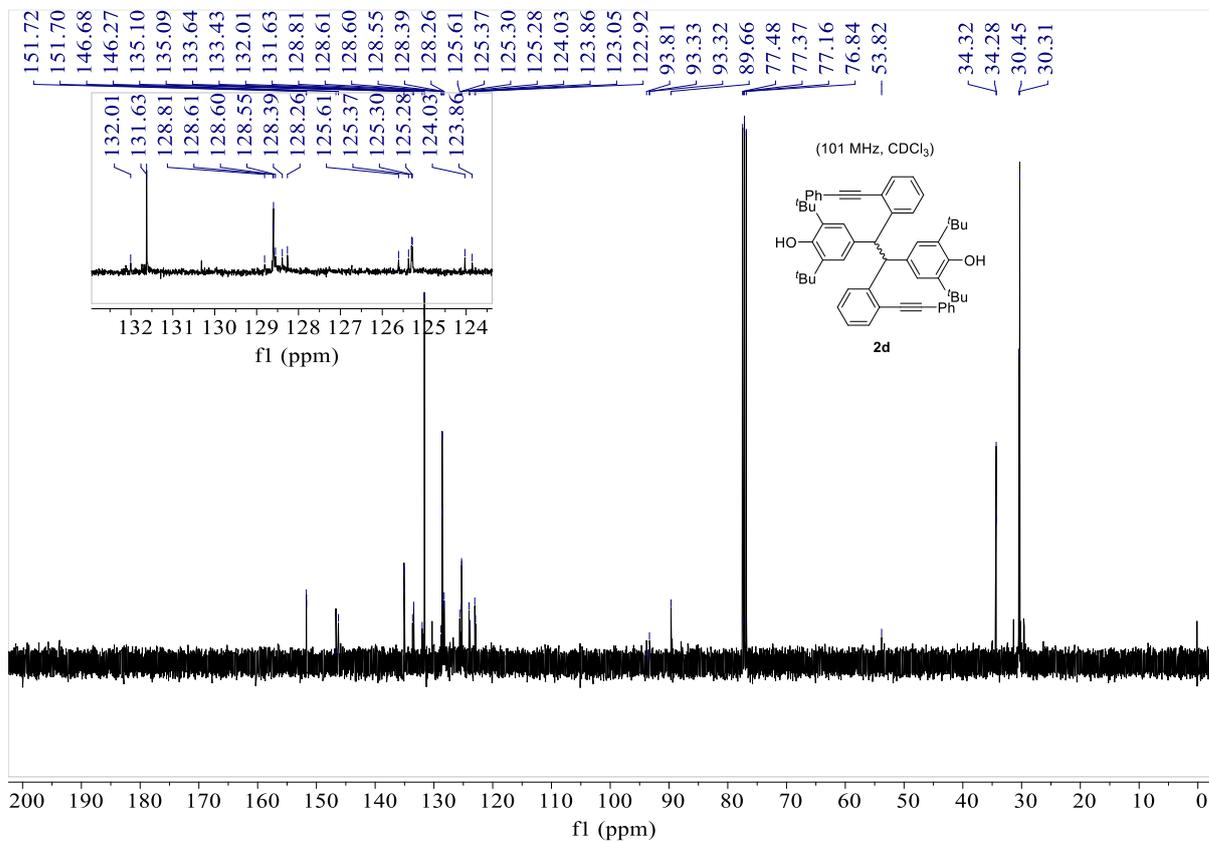
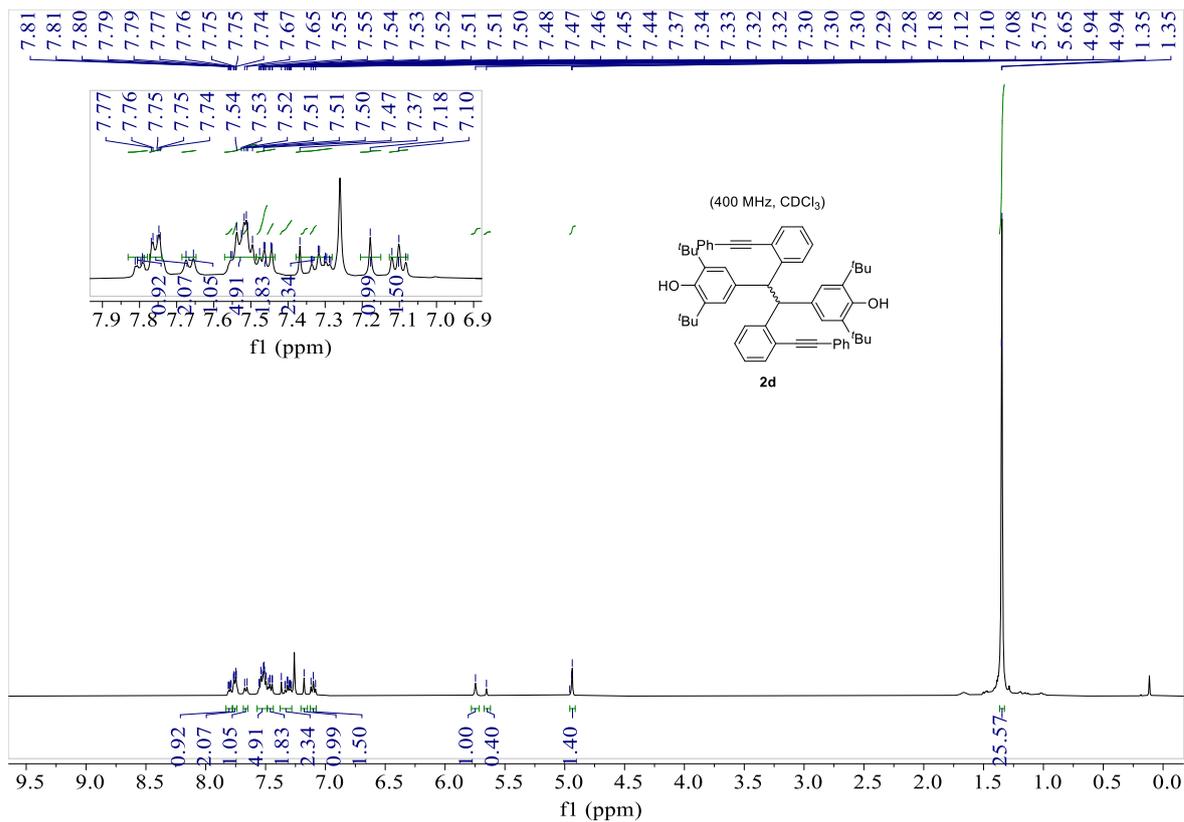
Purified by column chromatography (petroleum ether/ethyl acetate = 50:1); White solid (73.7 mg, 56%); mp 108.3–110.3 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm) 6.96 (qd, *J* = 7.8, 6.8, 3.3 Hz, 5H), 6.77 (s, 2H), 3.53 (s, 3H), 1.11 (s, 18H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ (ppm) 157.7, 144.2, 142.5, 141.0, 138.7, 131.7, 130.2, 127.5, 126.2, 64.1, 35.6, 32.2; IR (KBr, cm<sup>-1</sup>): 2960, 2866, 1260, 1218, 1110, 1011, 700; HRMS (ESI-TOF) calcd for C<sub>44</sub>H<sub>56</sub>KO<sub>2</sub><sup>+</sup> ([M+K]<sup>+</sup>): 655.3912, found 655.3900.

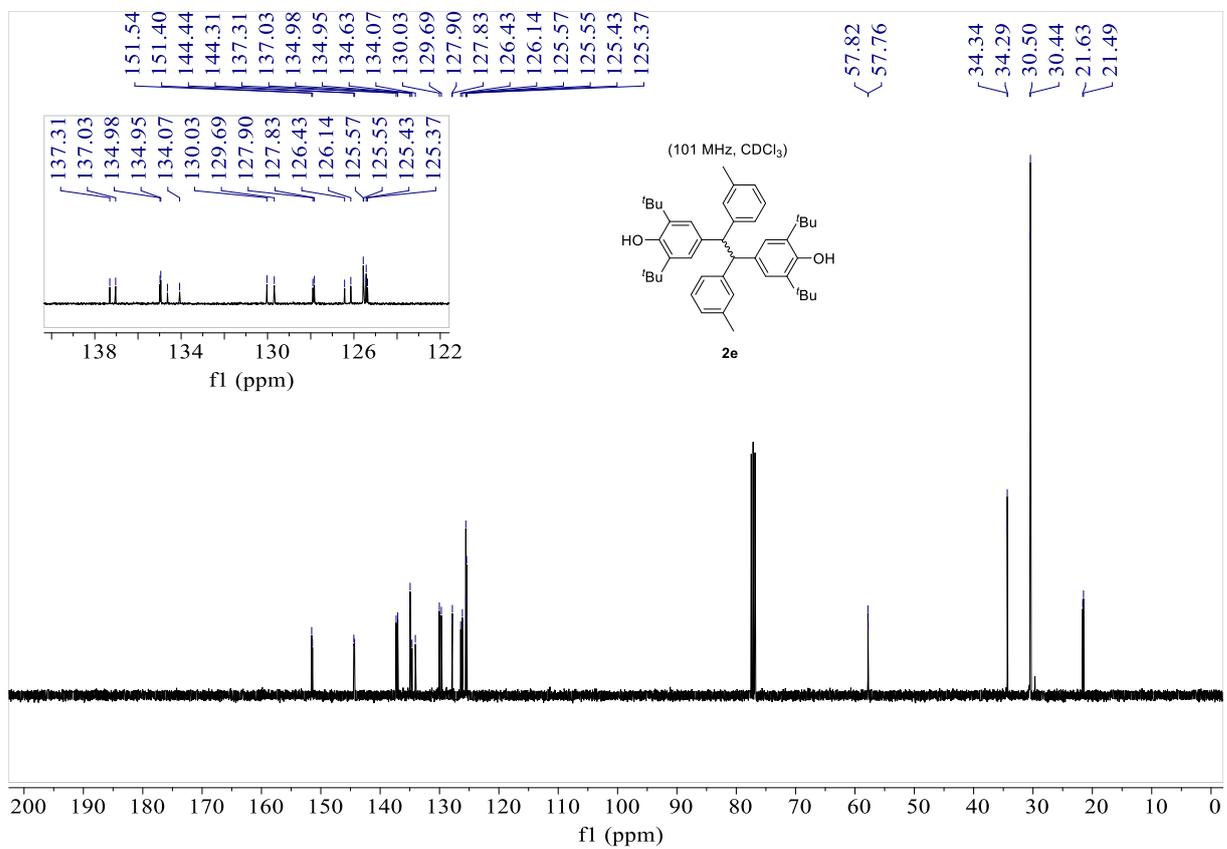
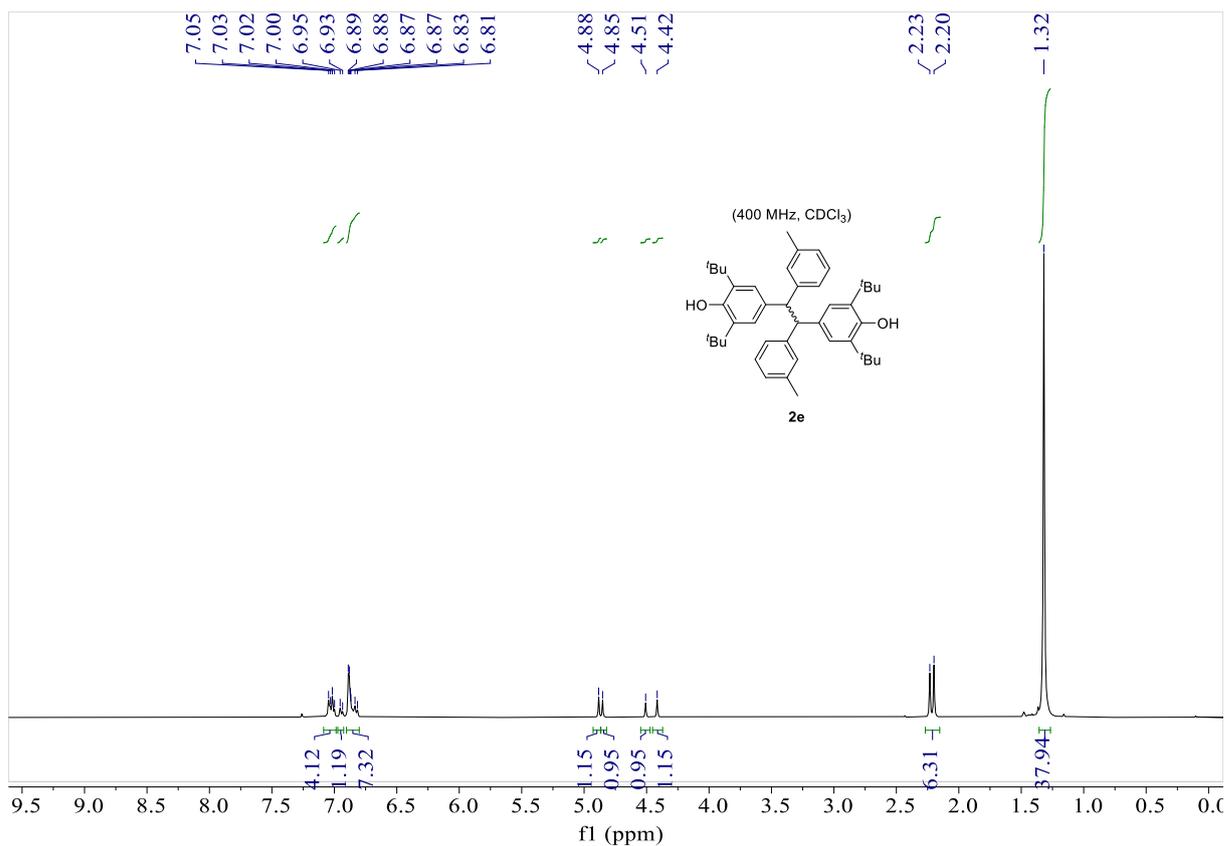
## 2. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Products 2, 3, 4 and 5

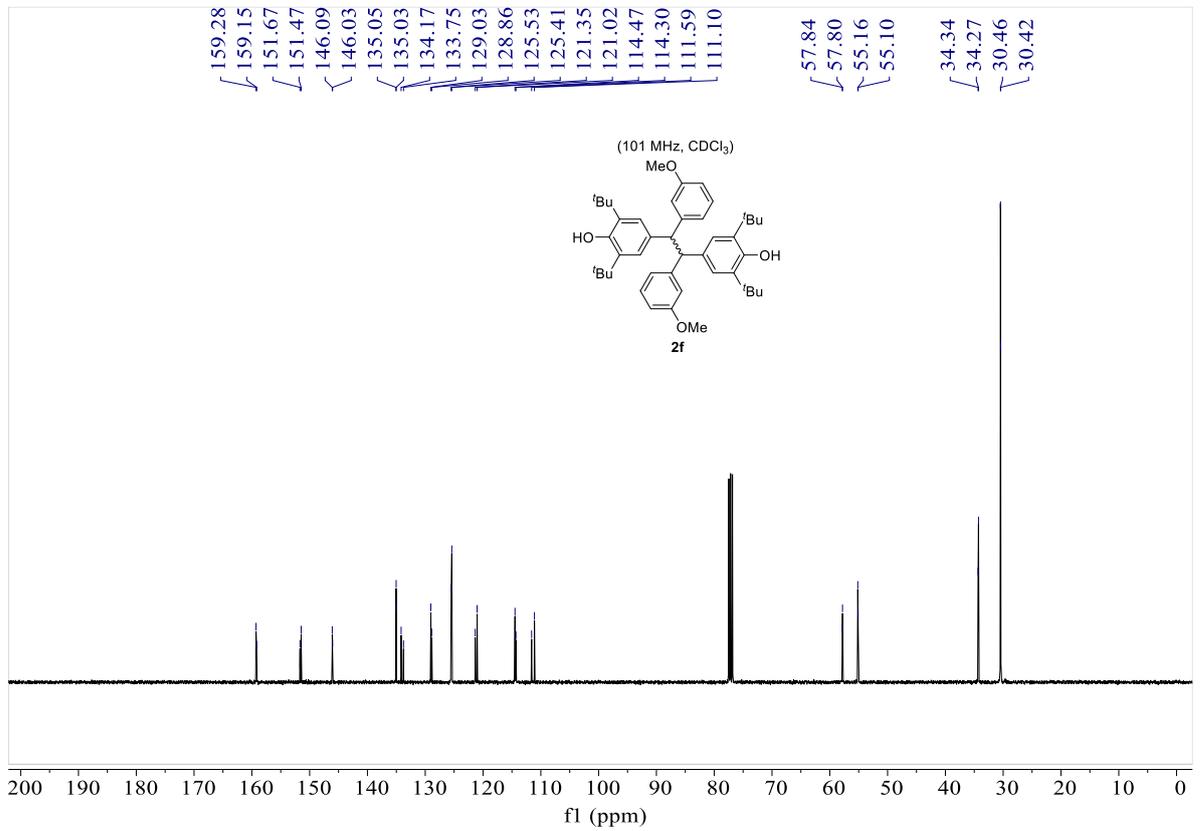
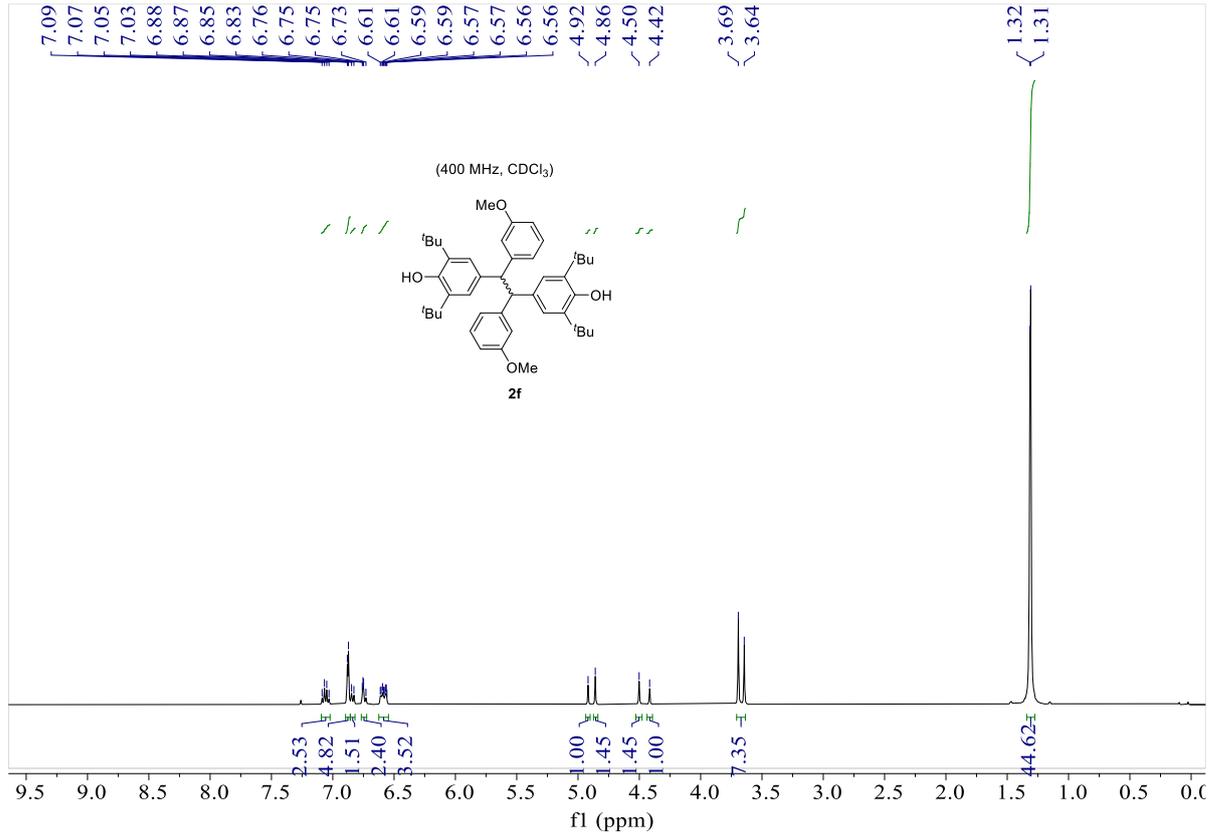


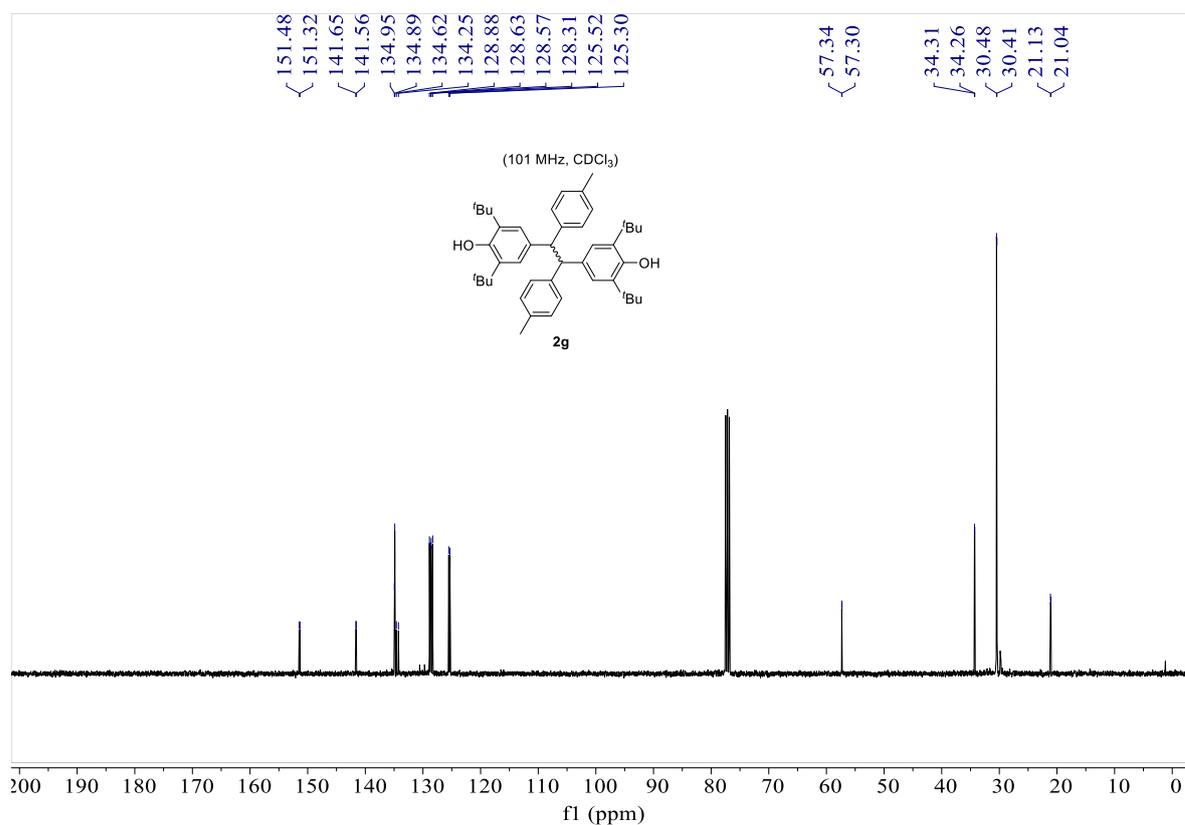
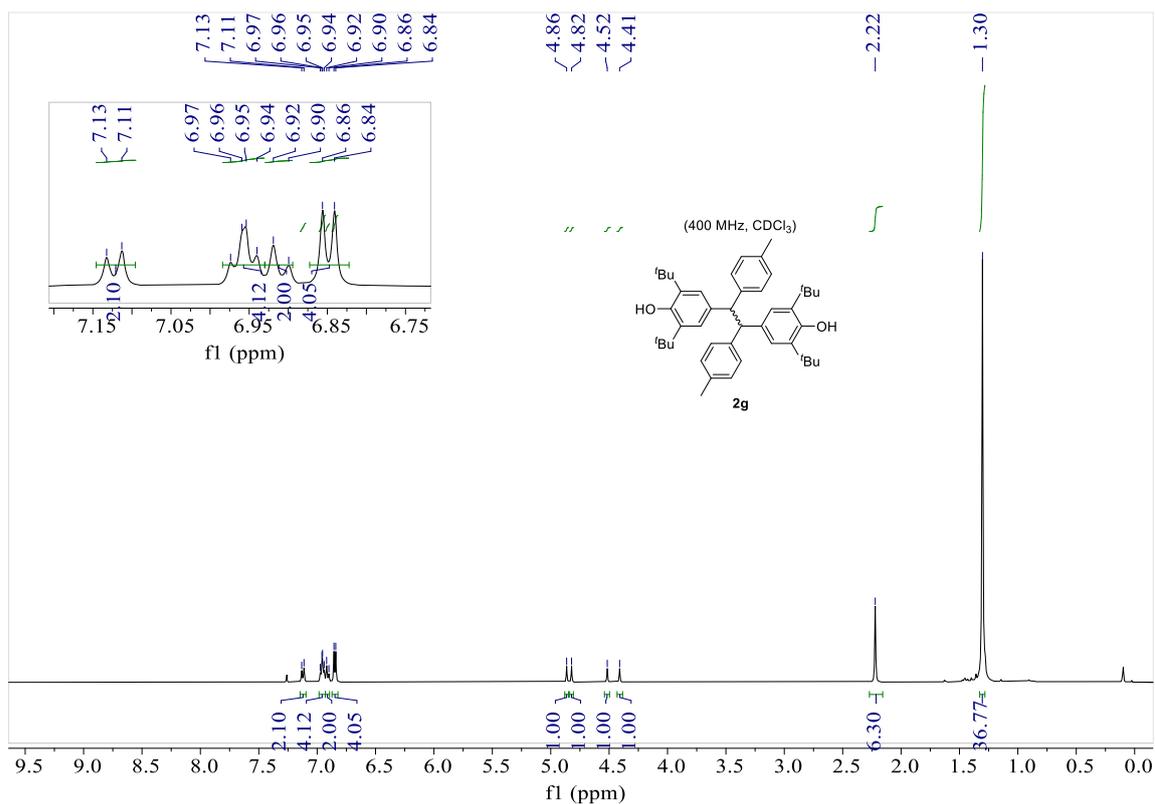


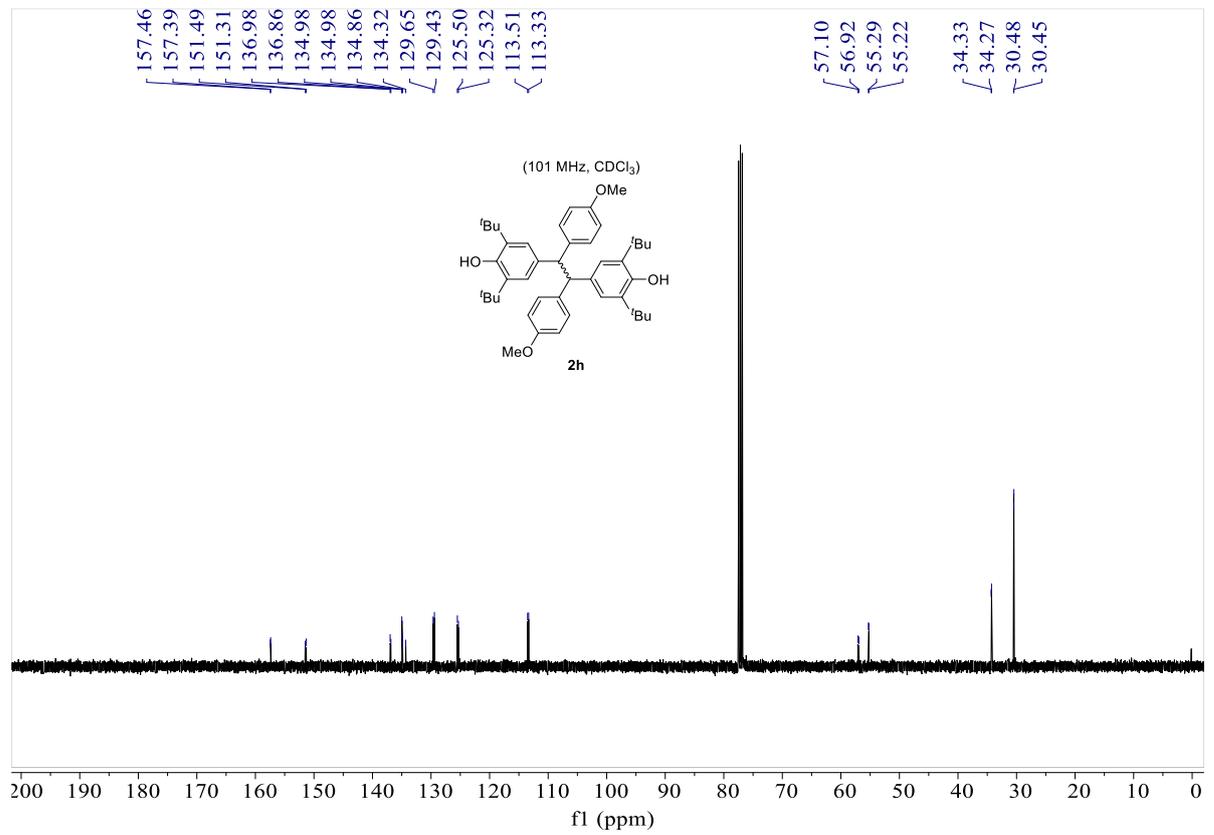
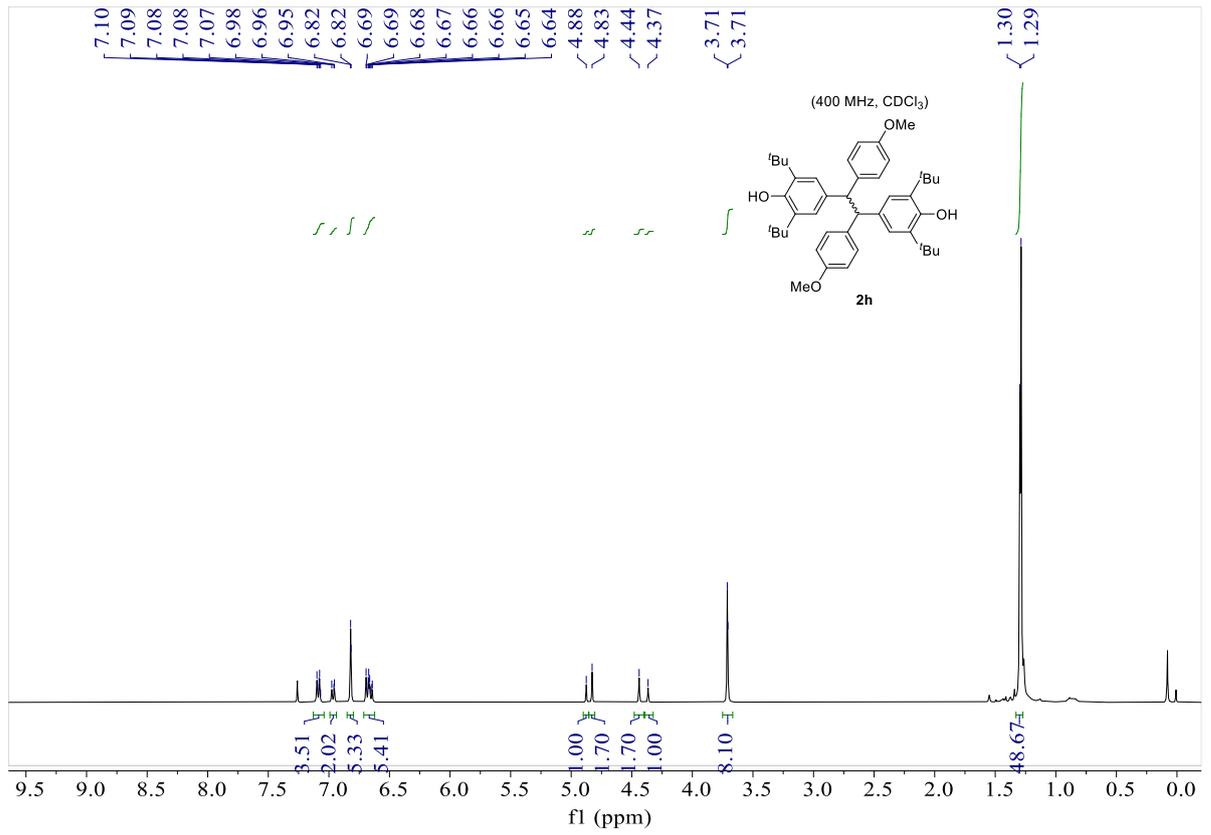


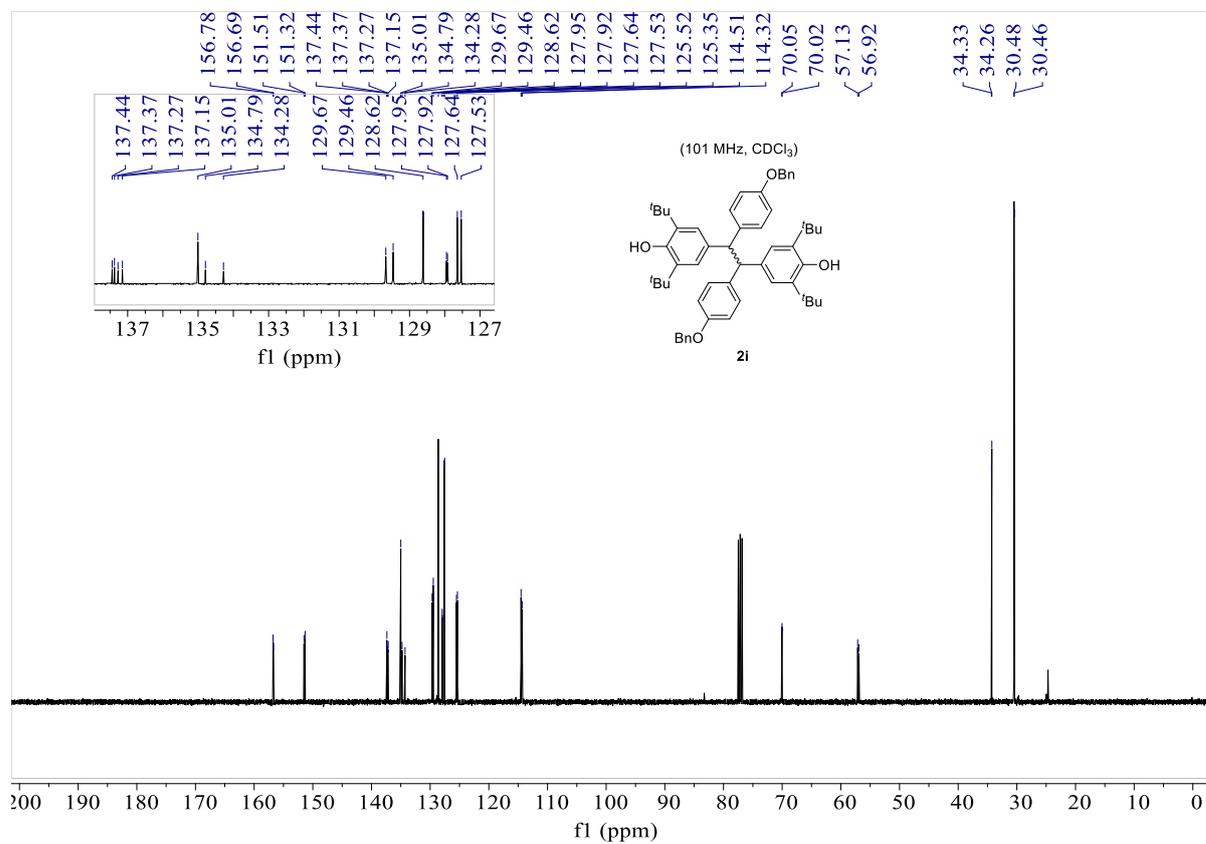
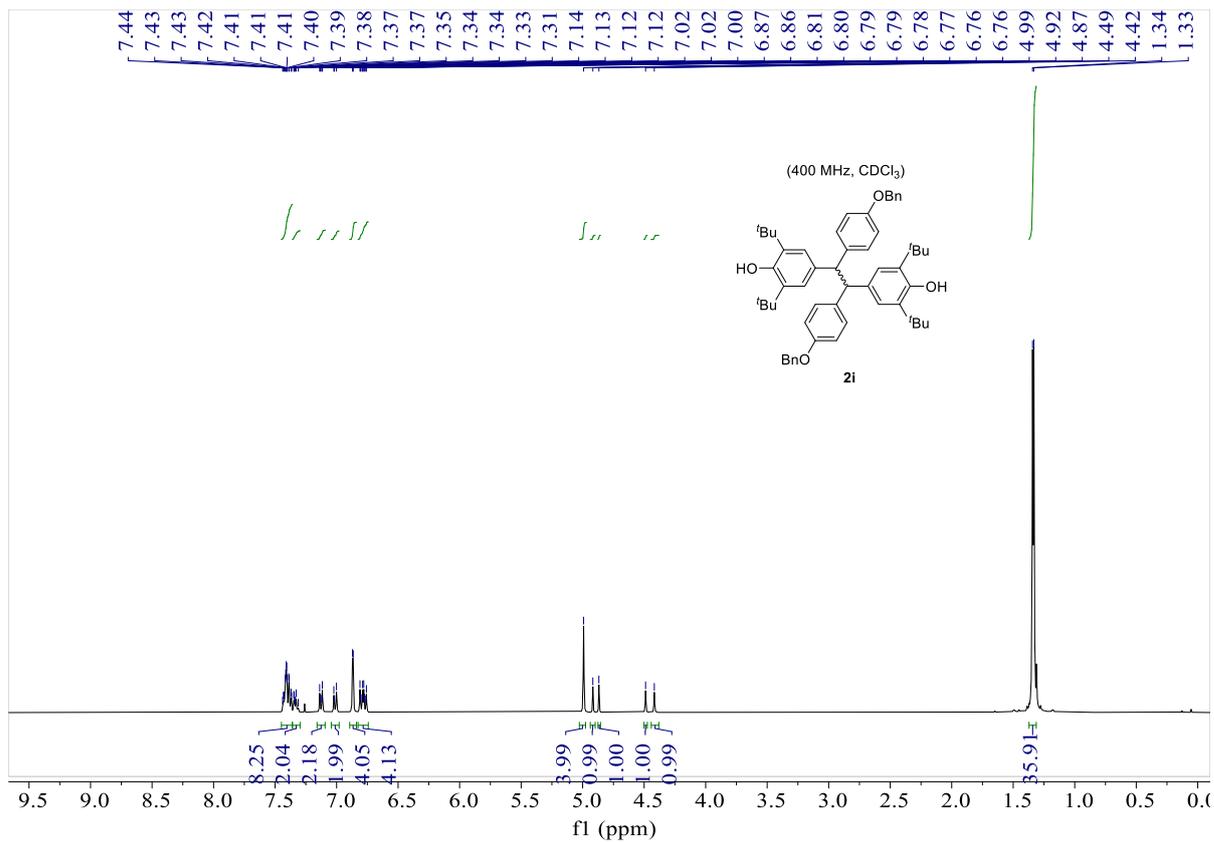


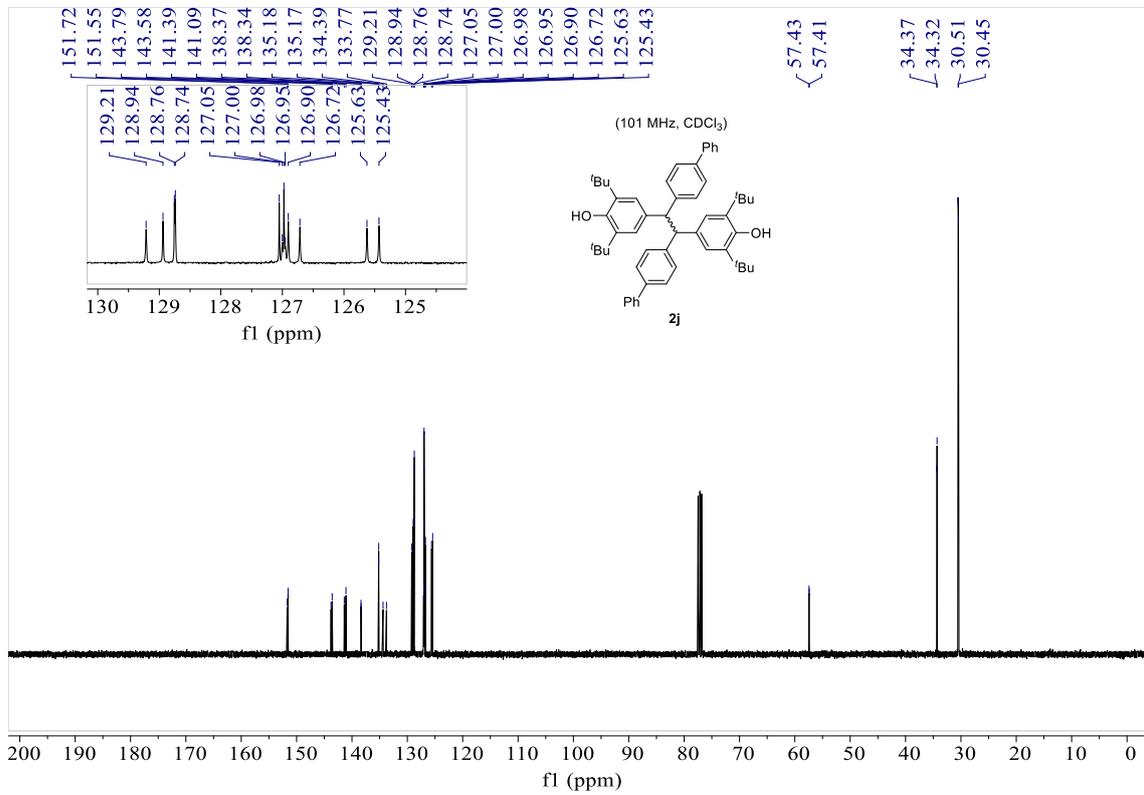
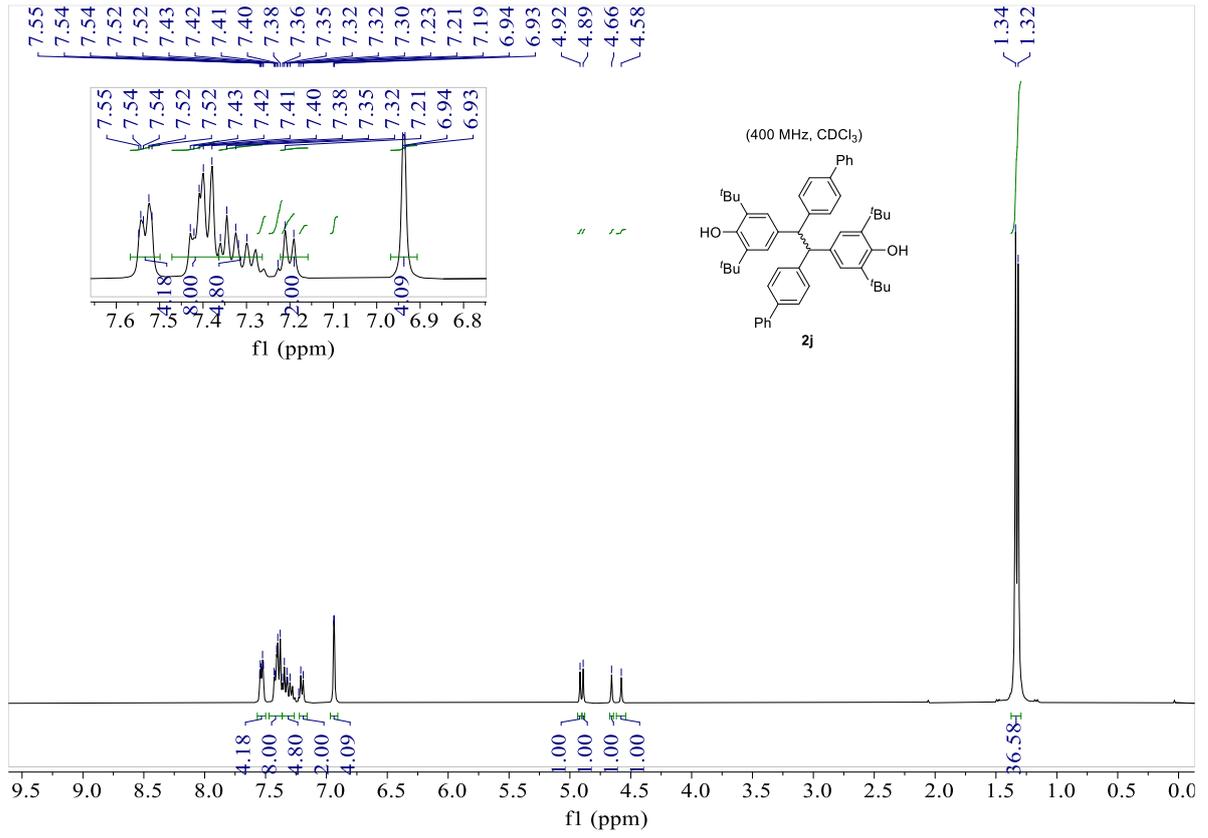


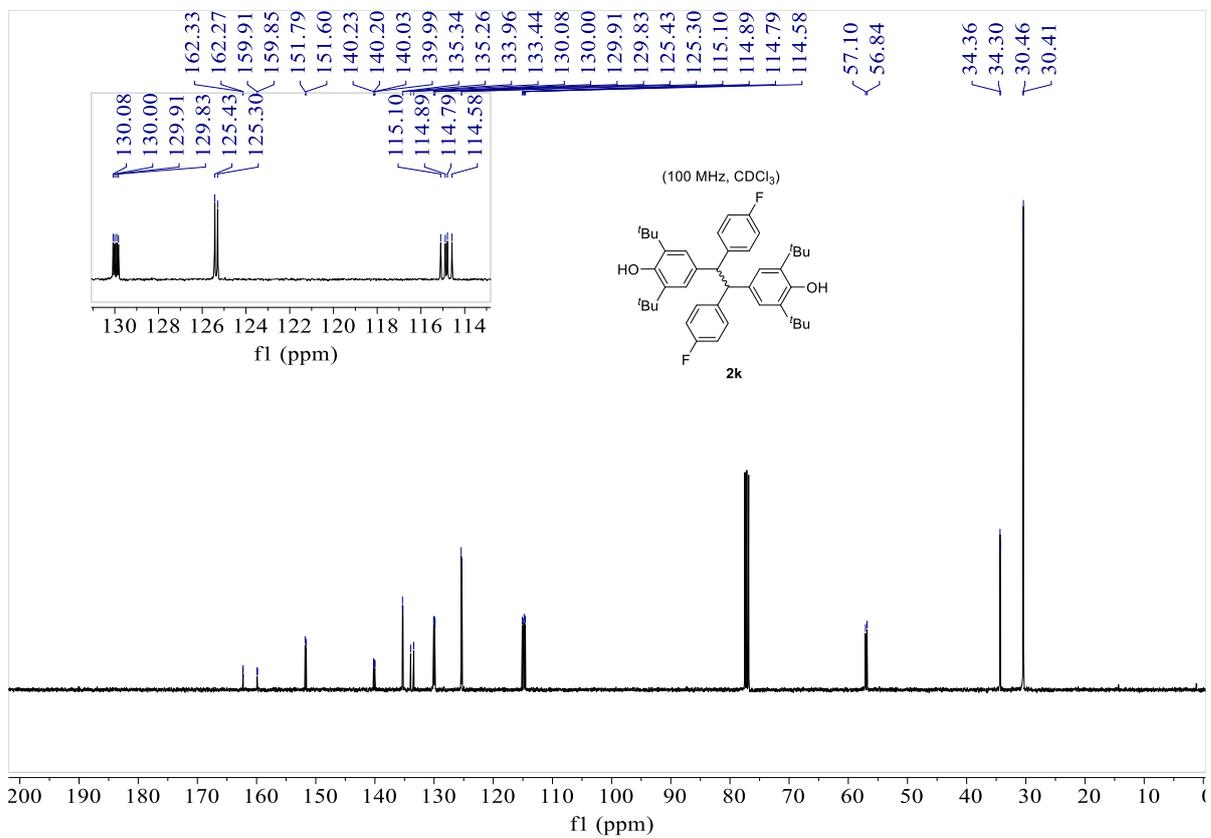
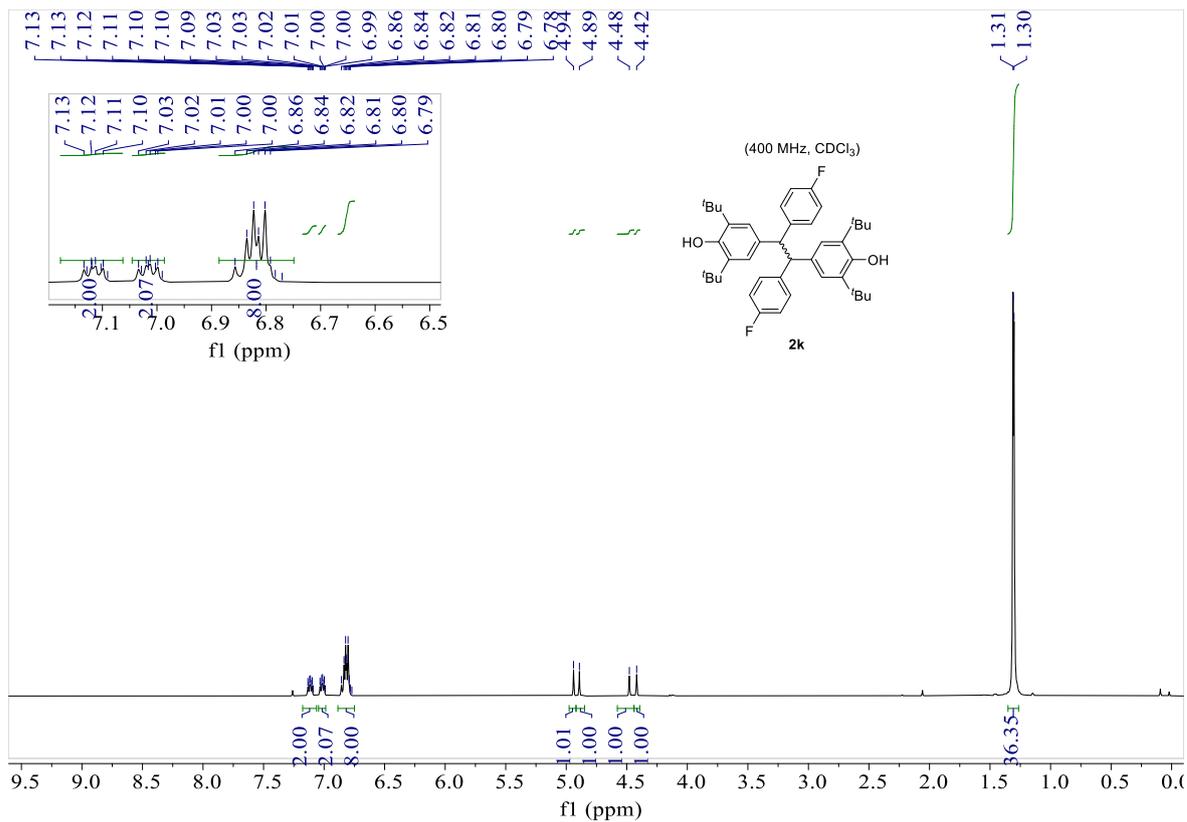


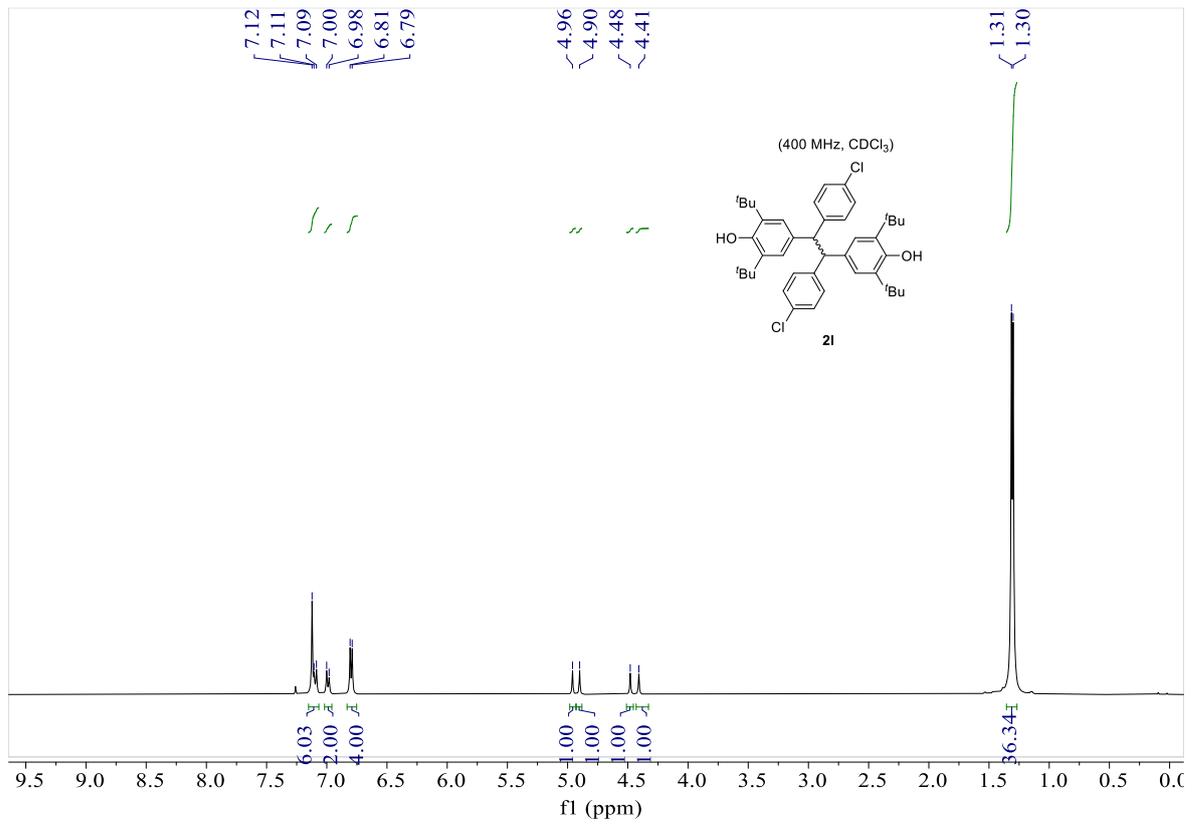
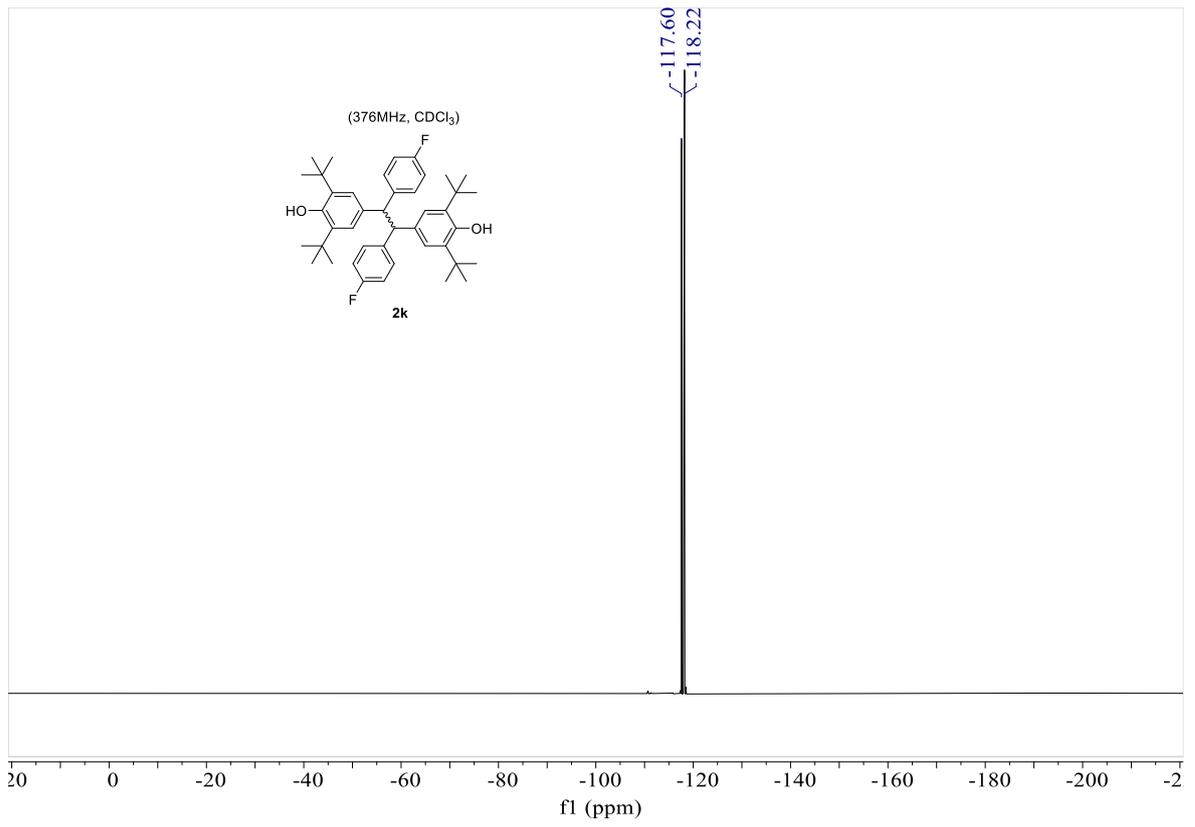


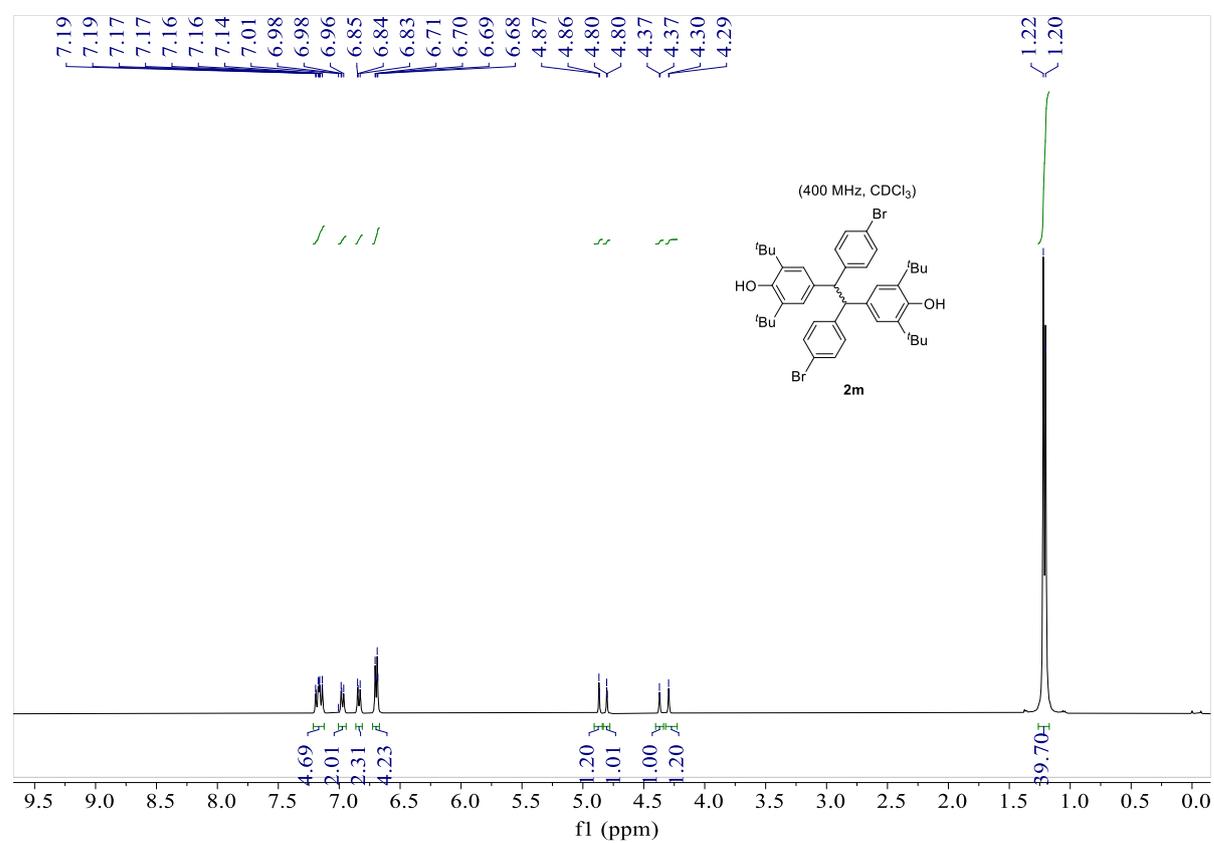
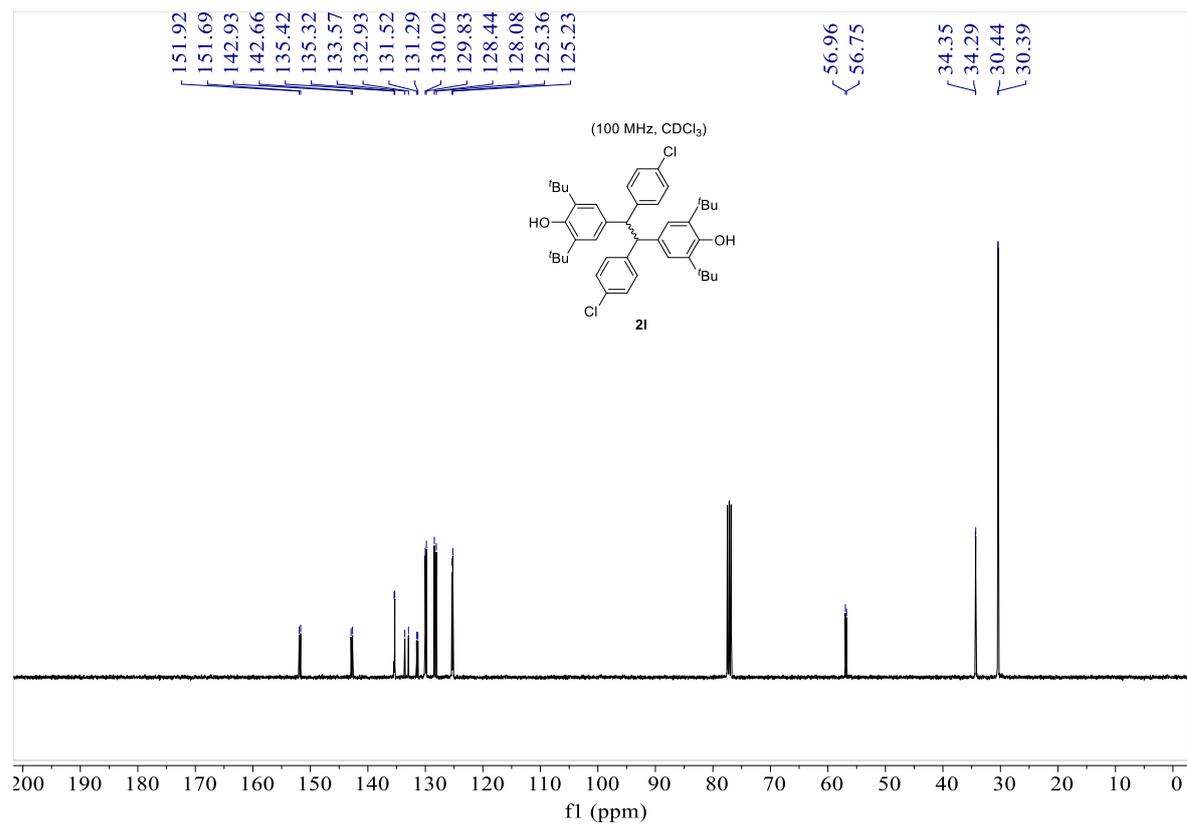


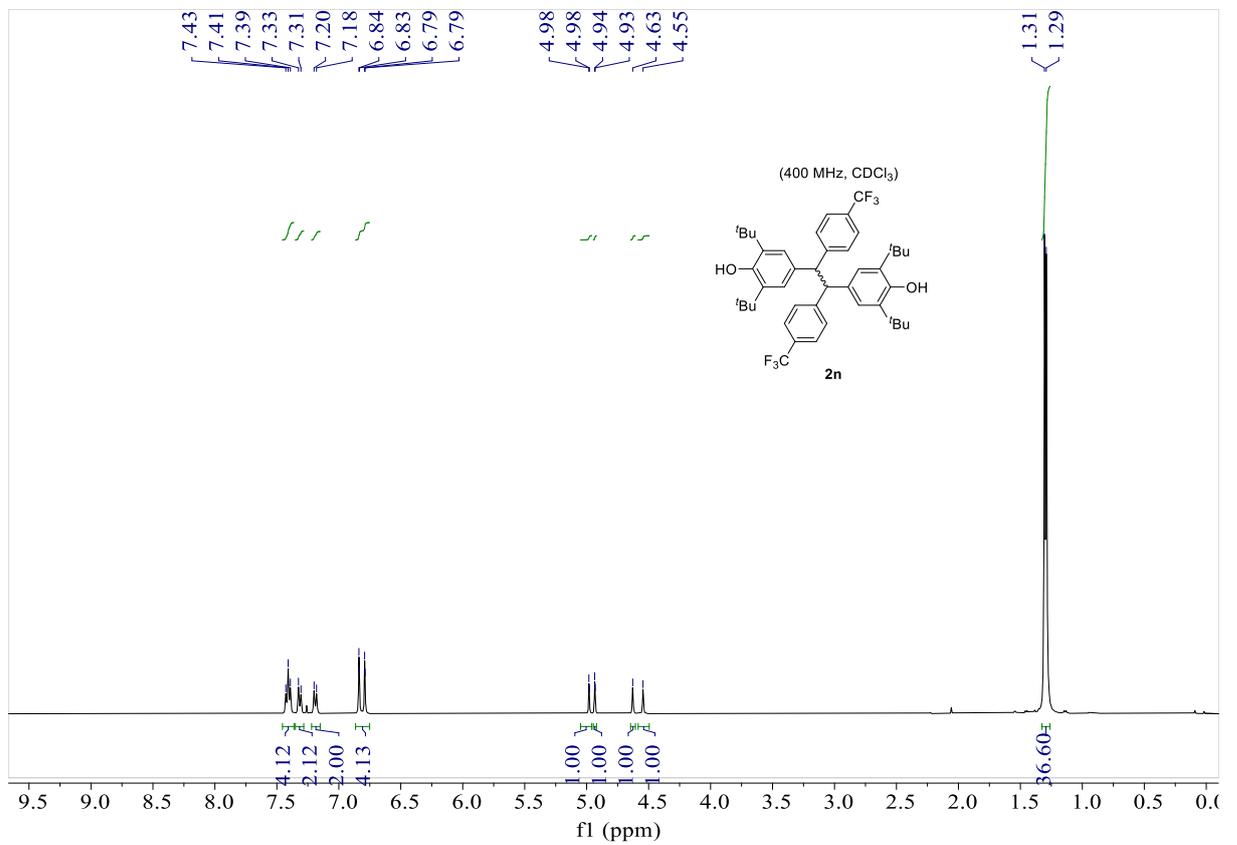
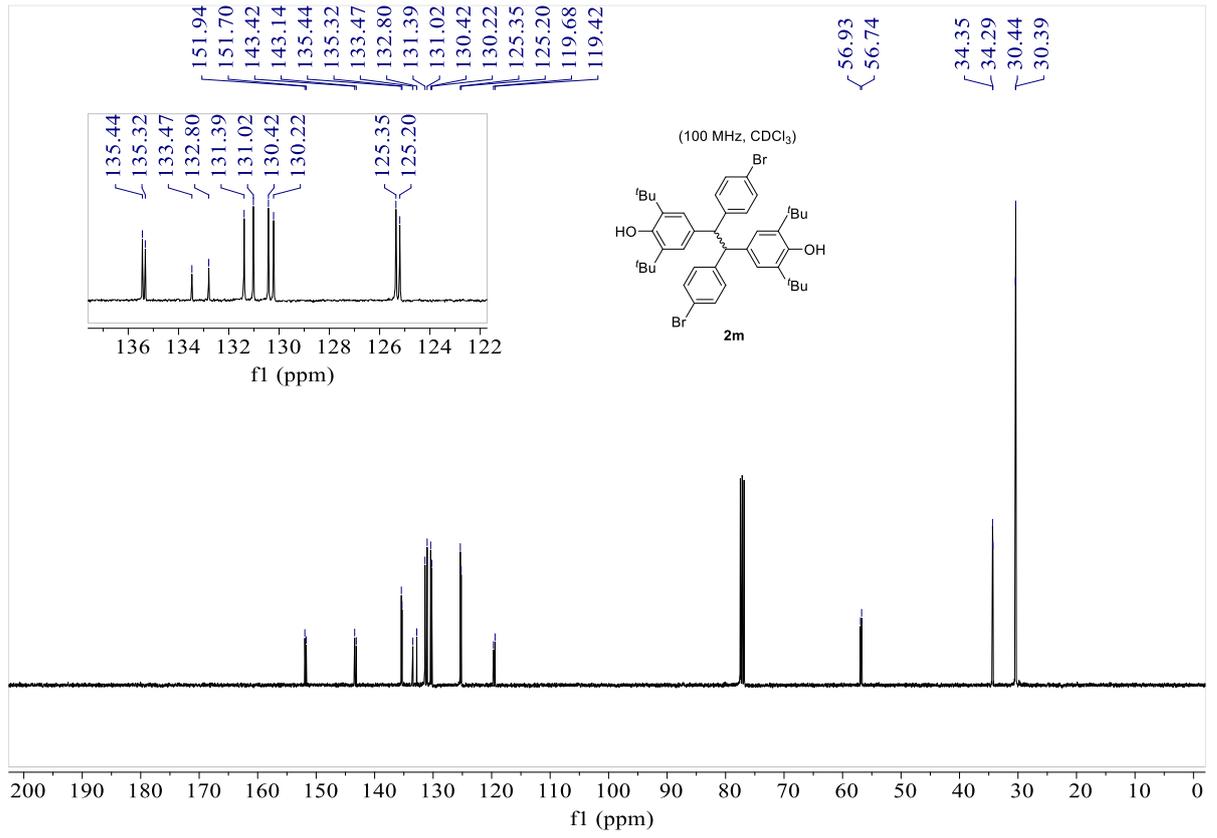


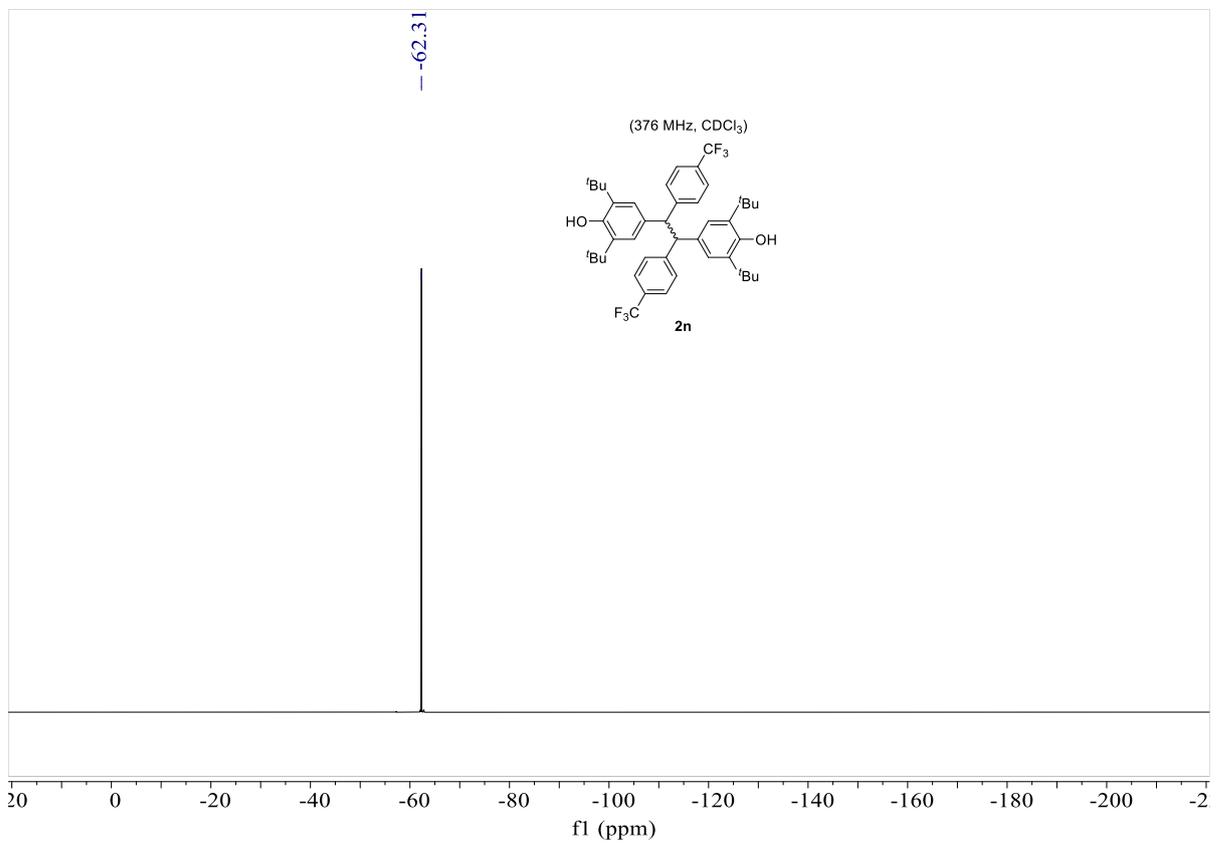
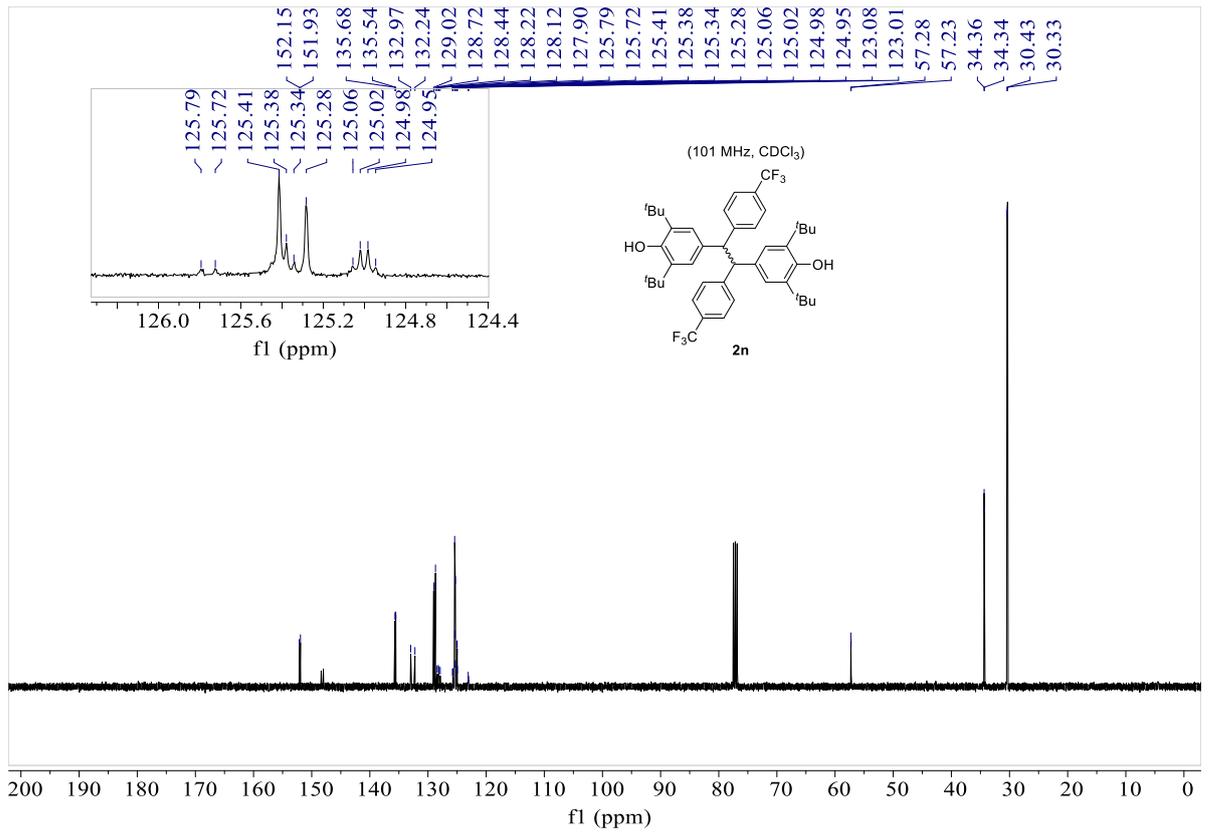


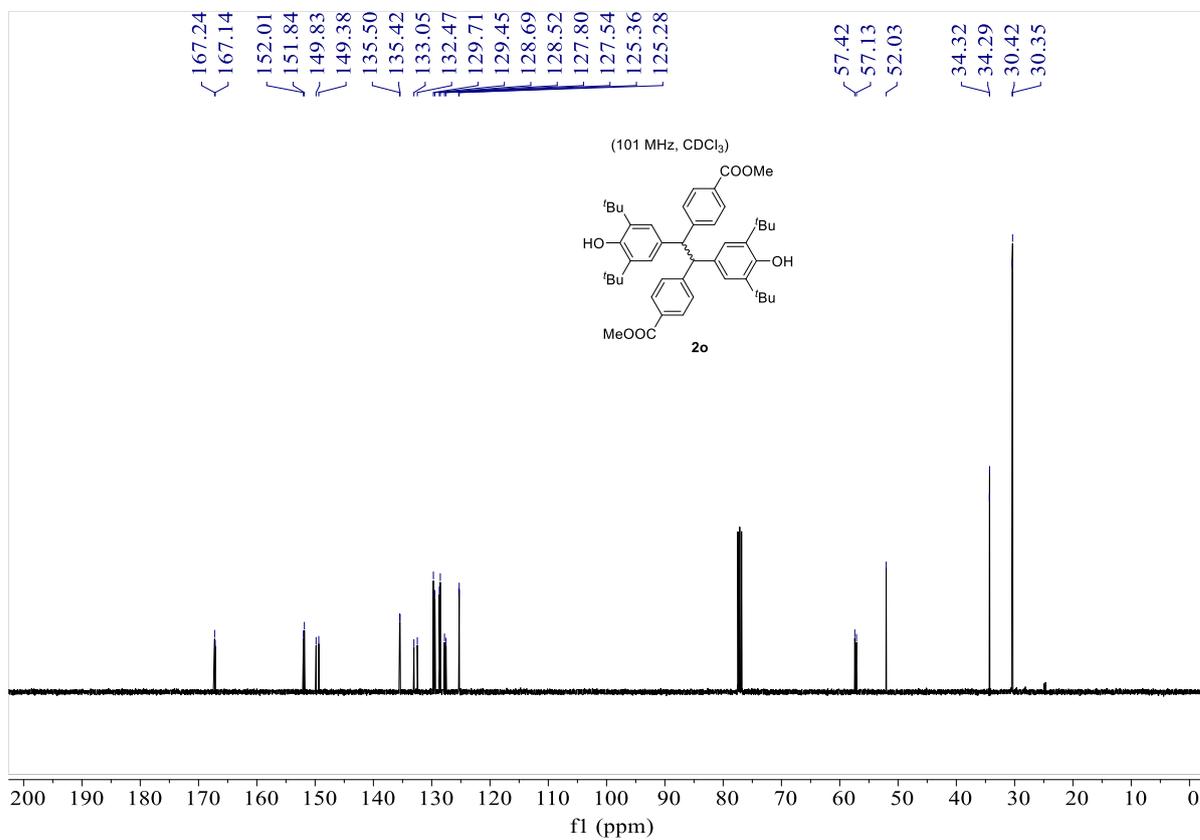
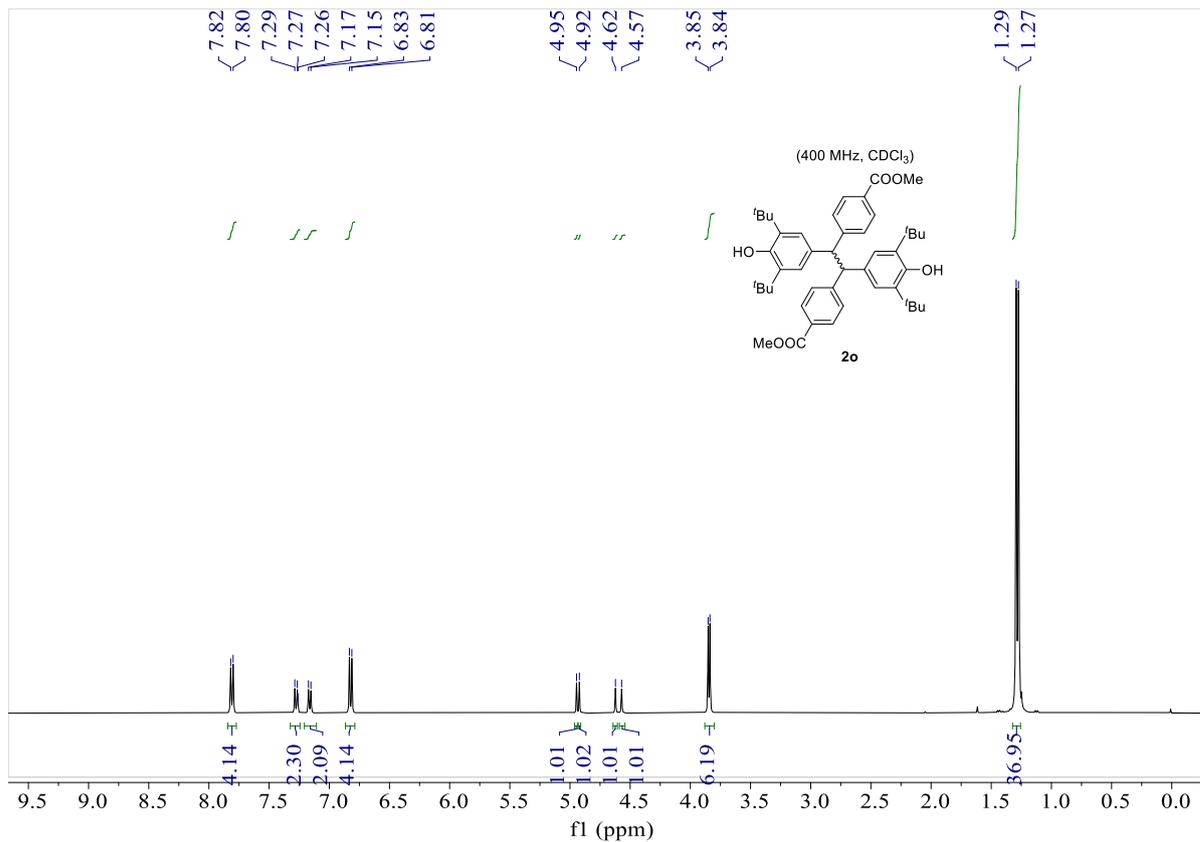


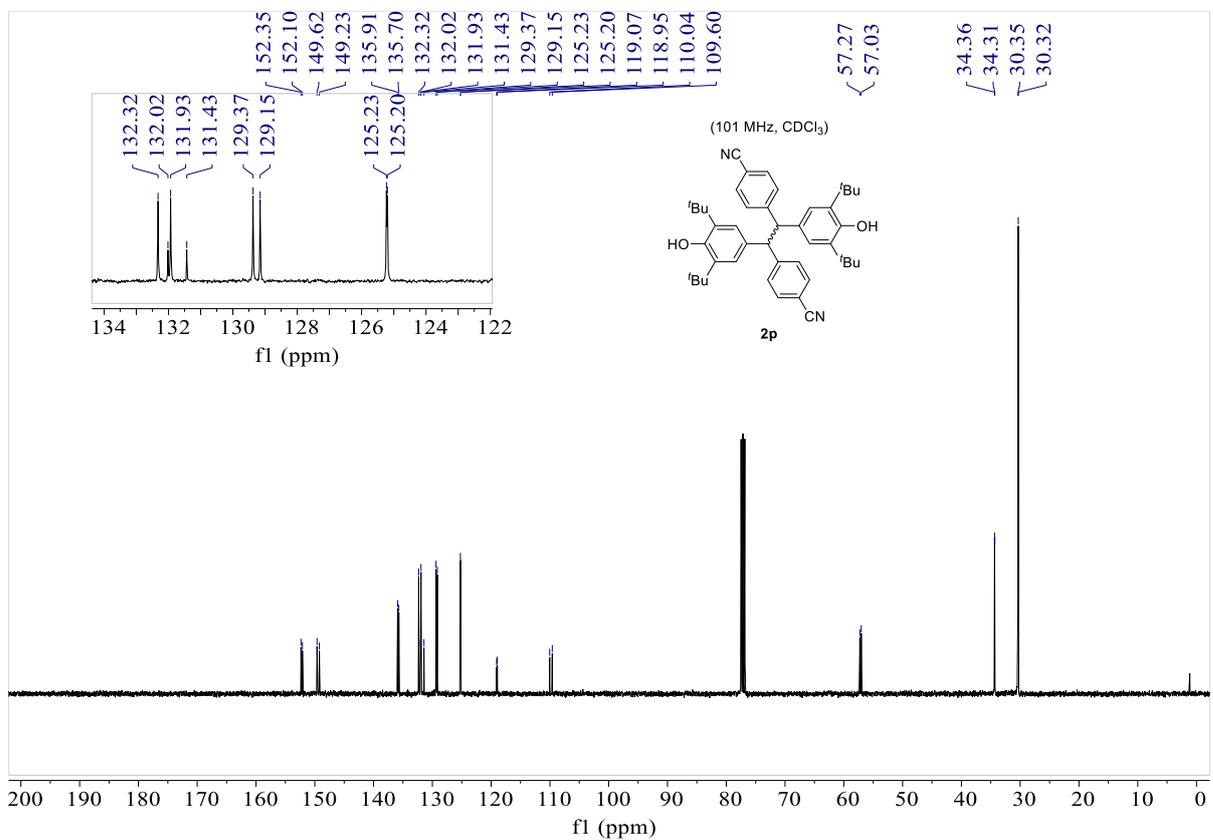
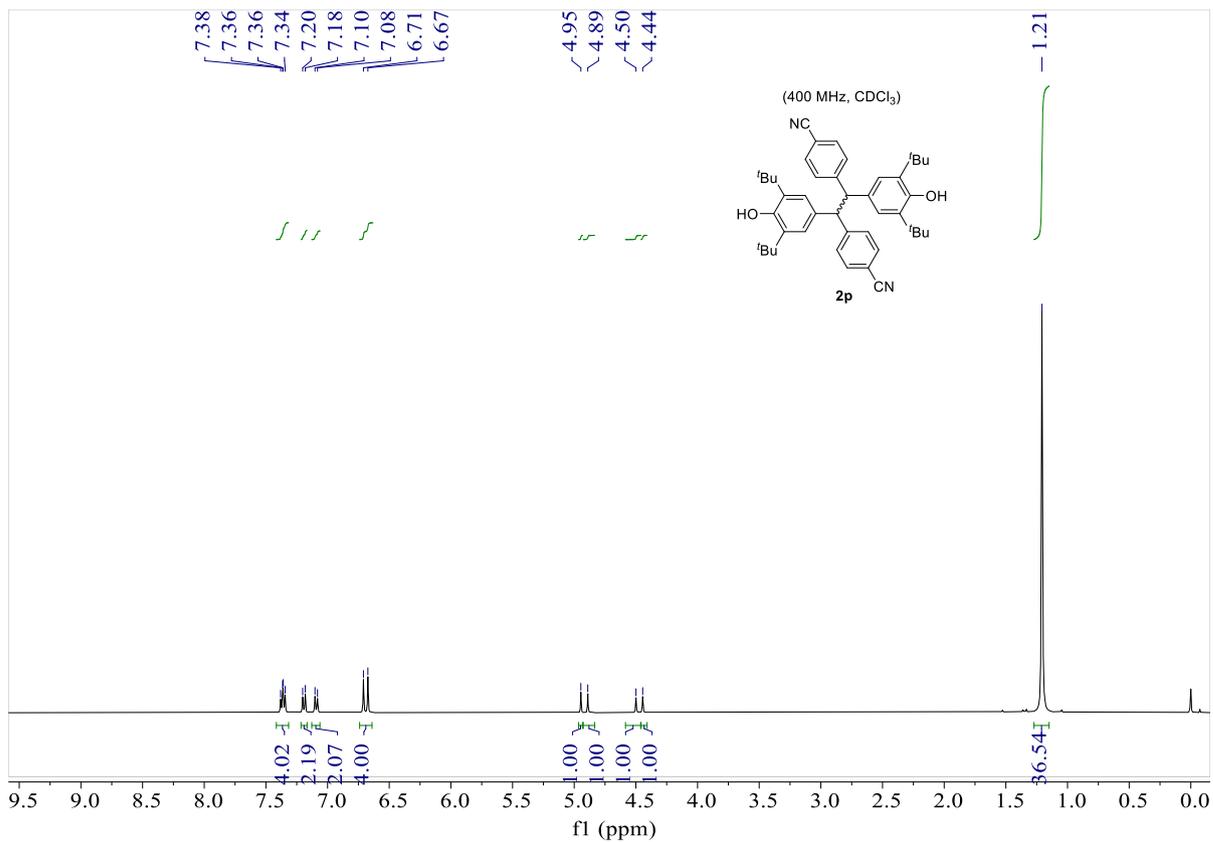


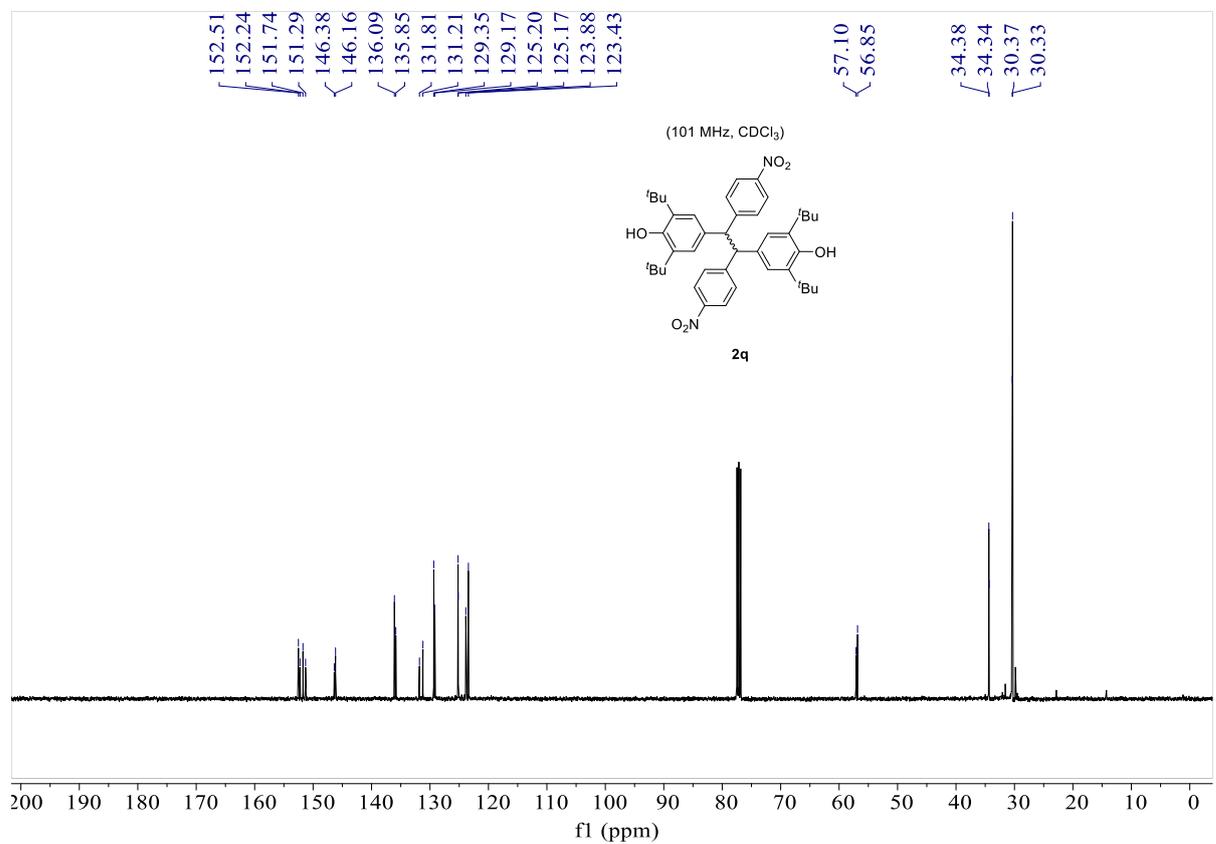
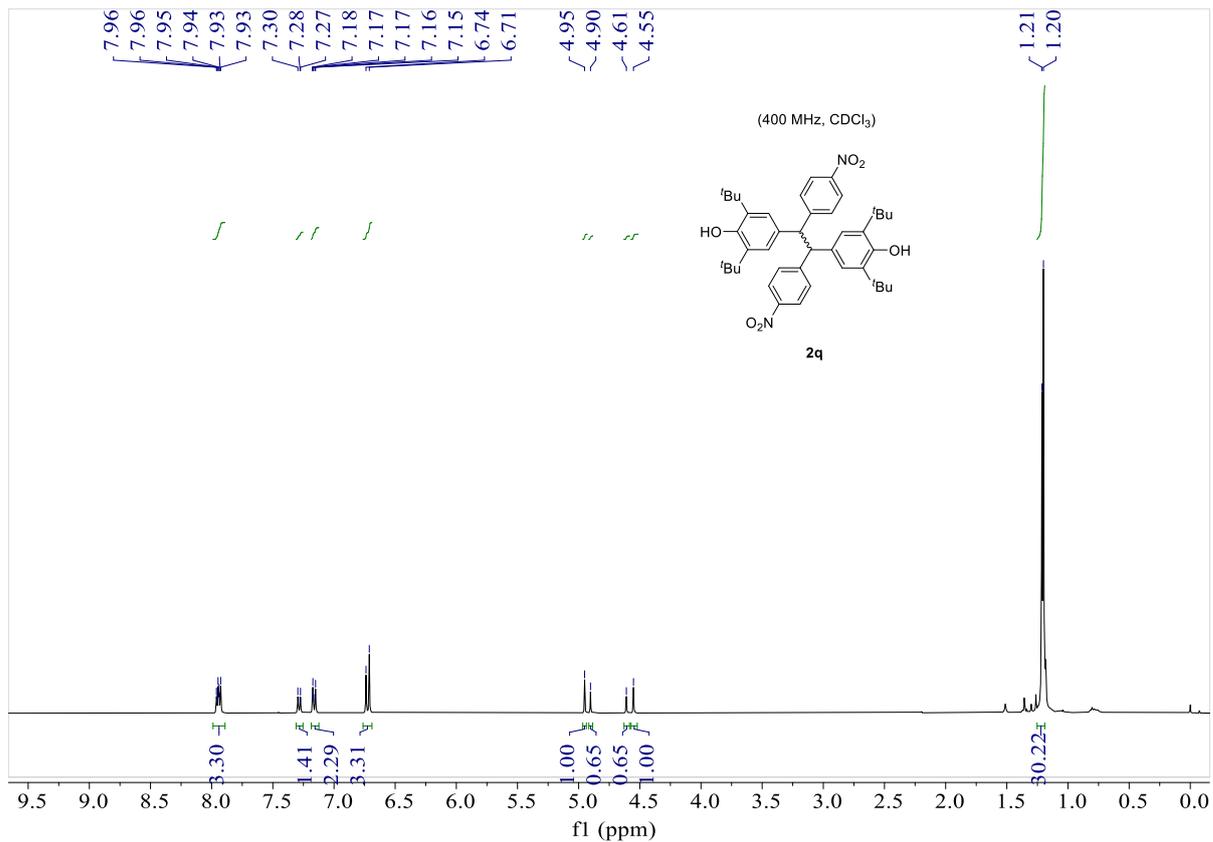


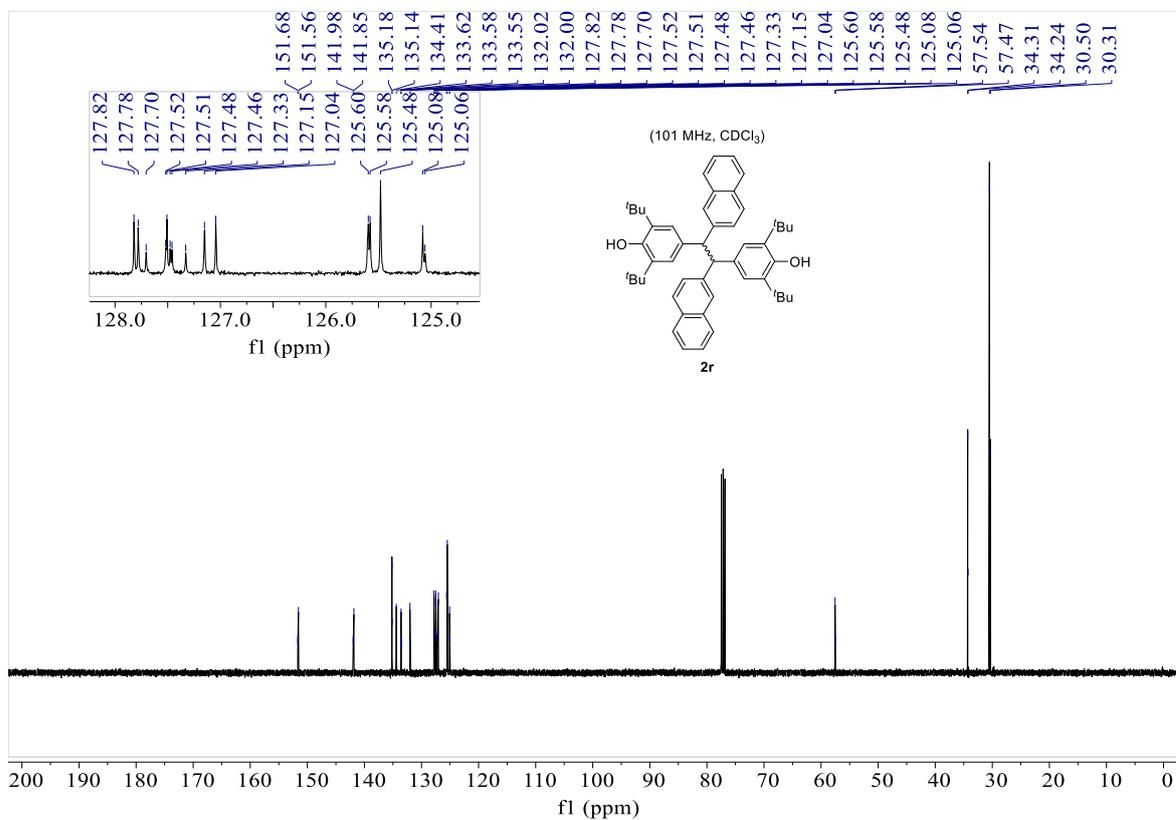
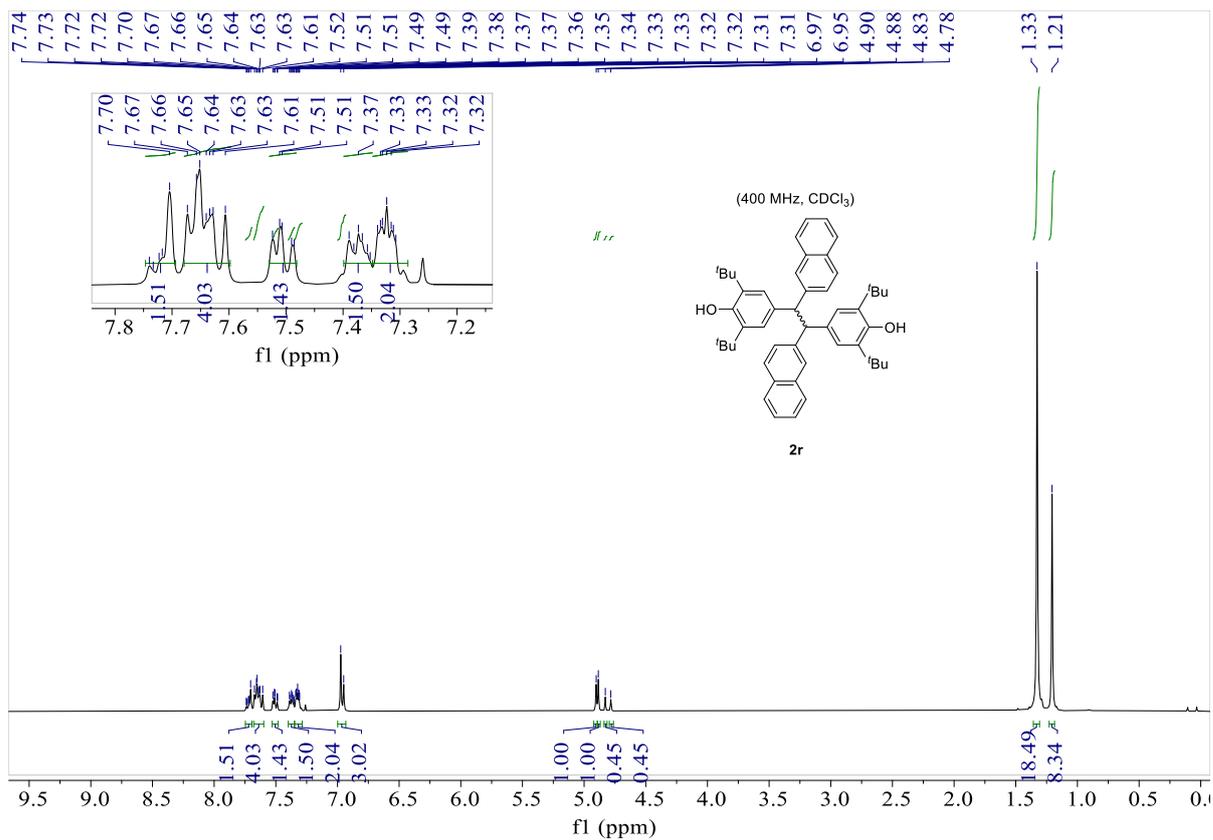


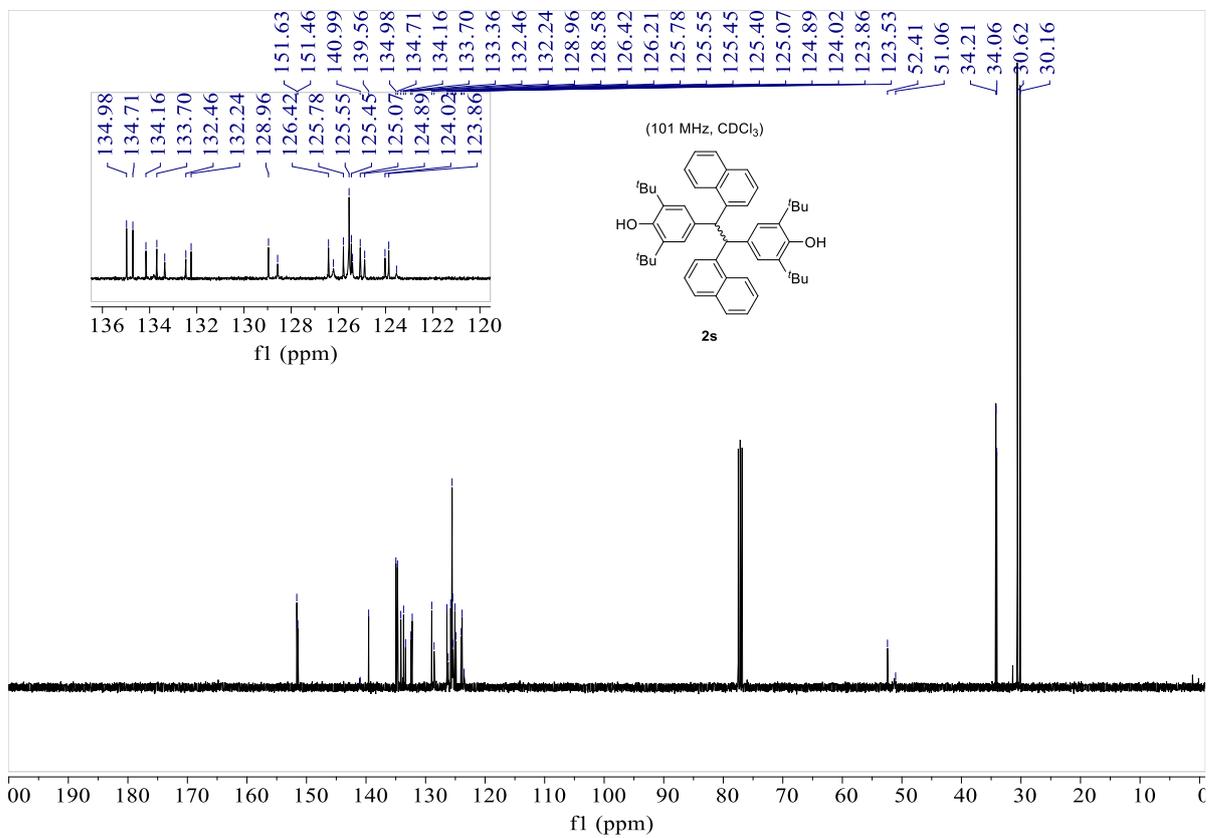
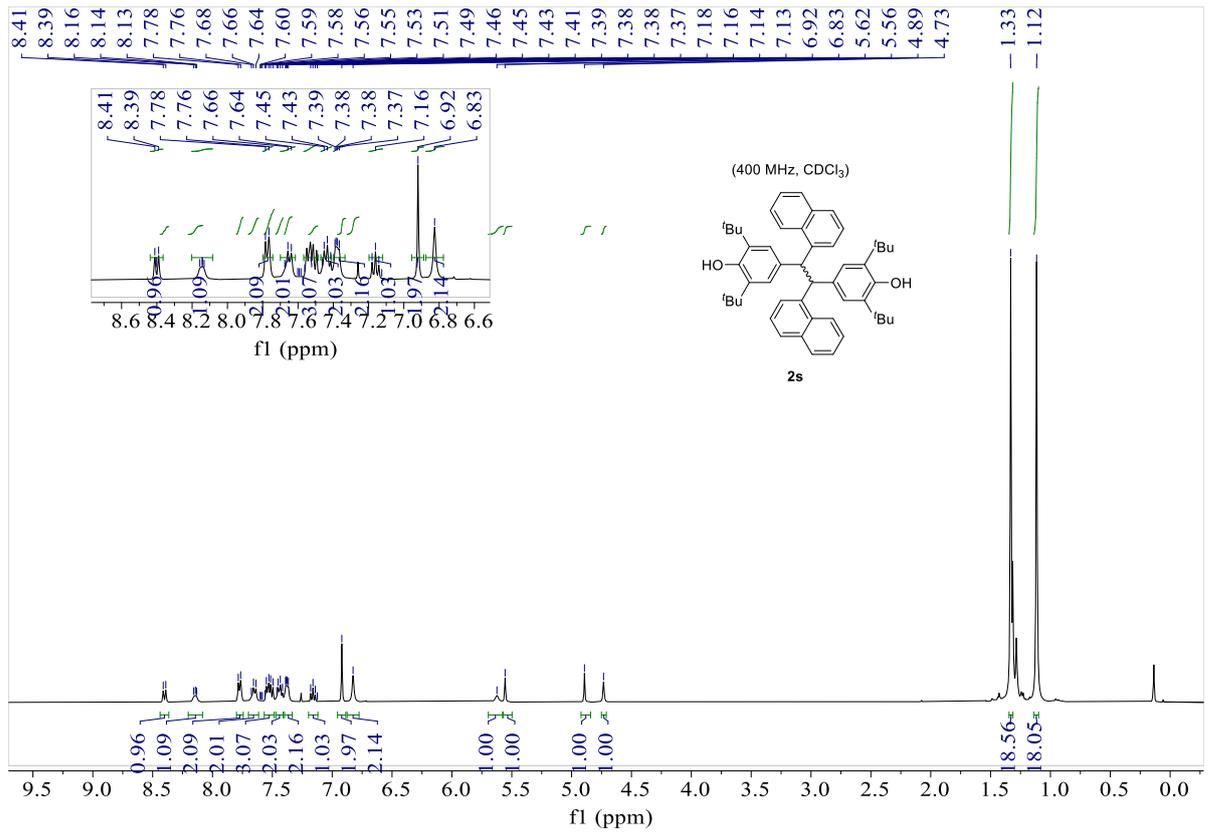


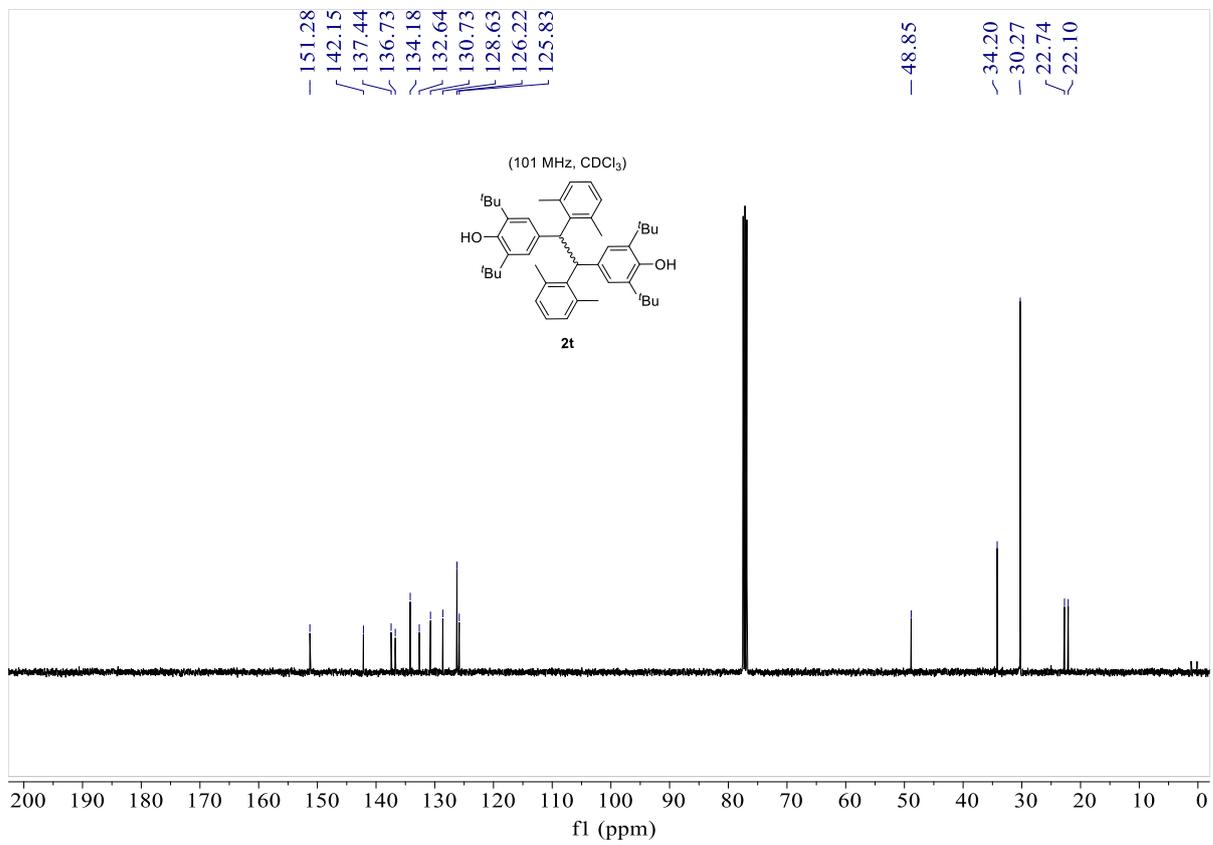
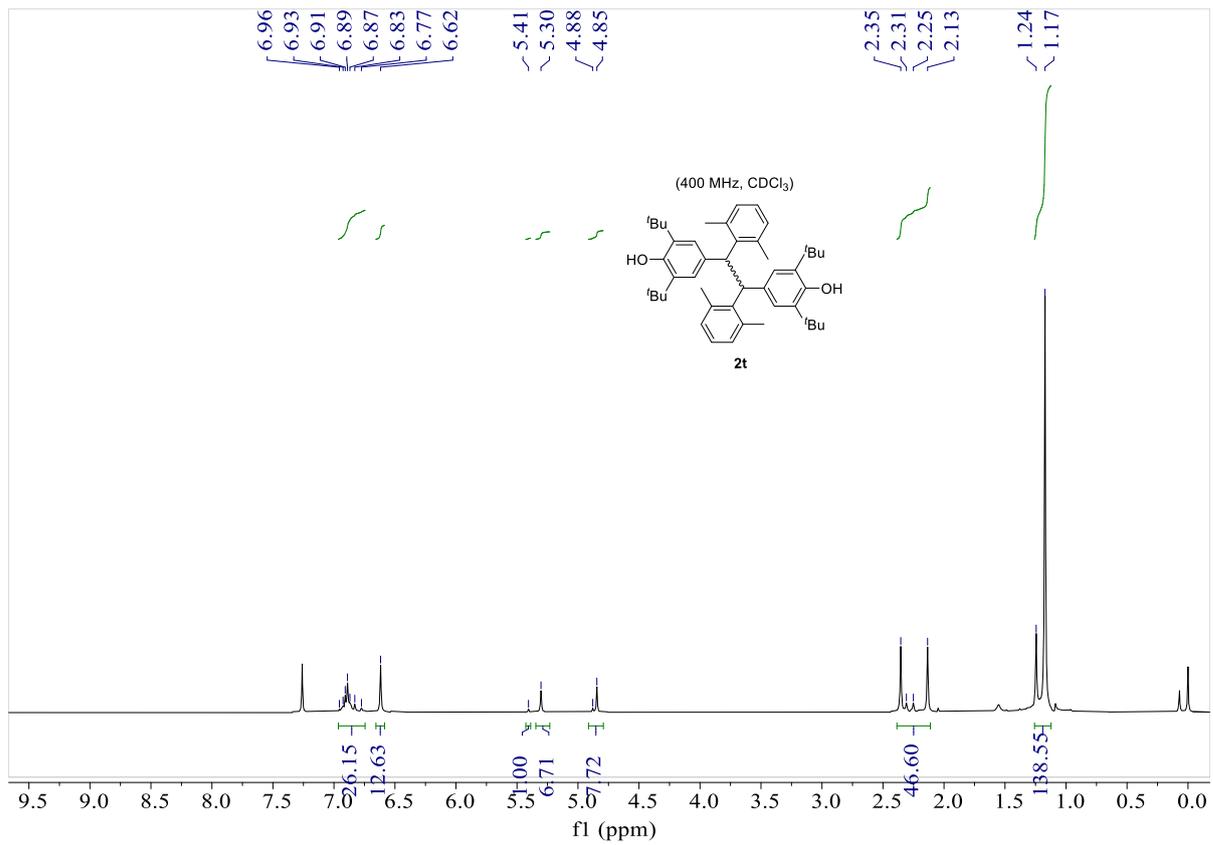


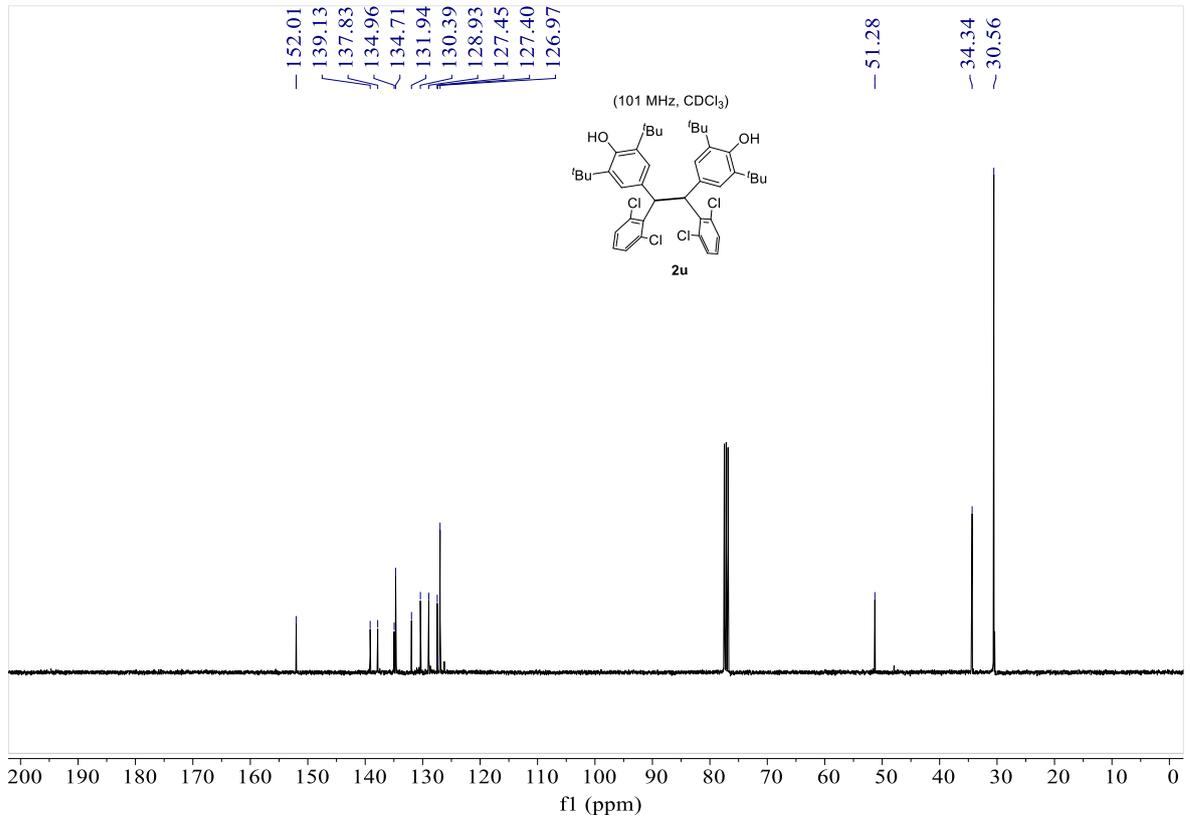
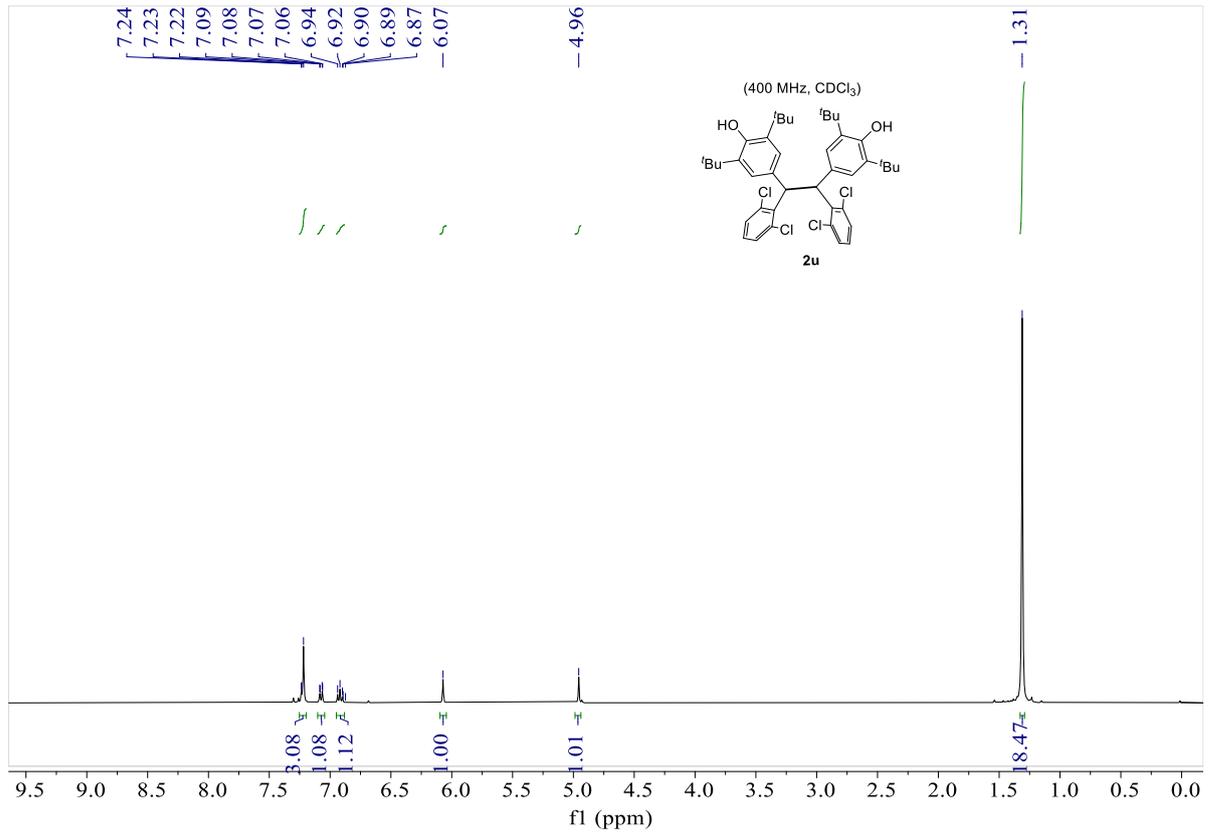


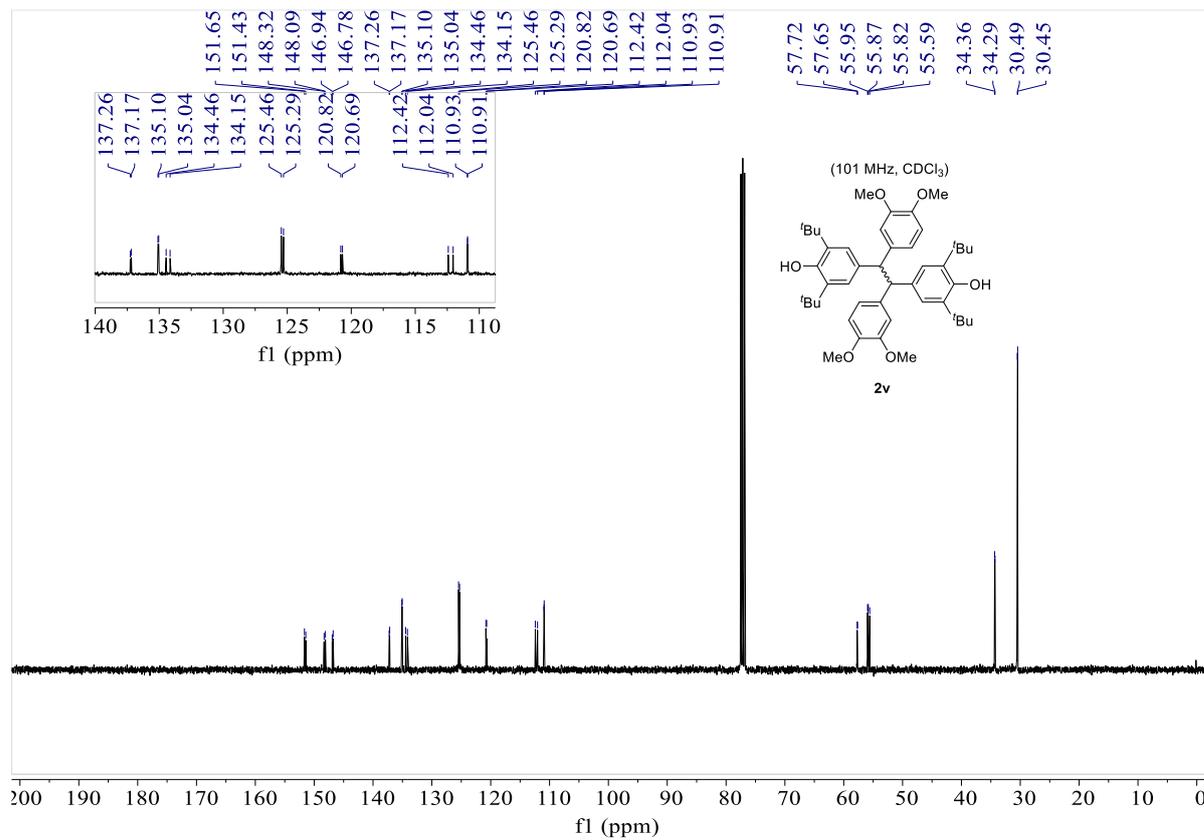
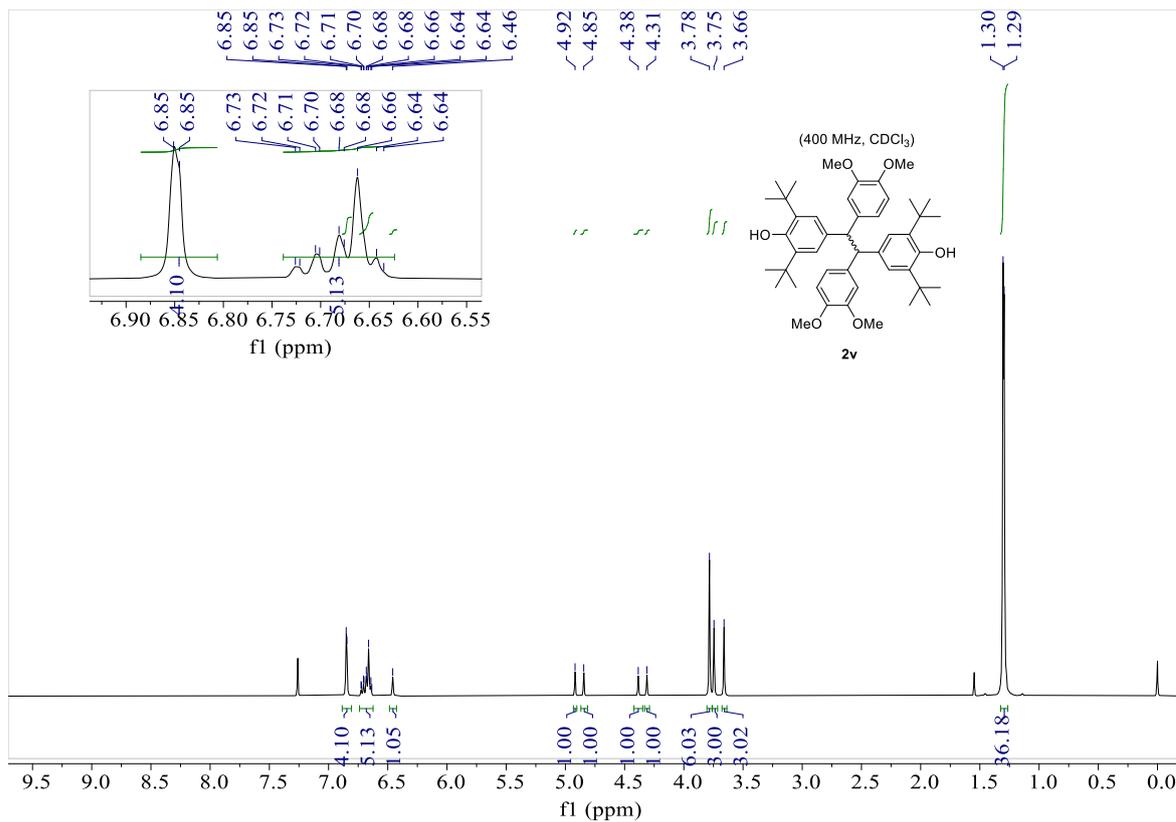


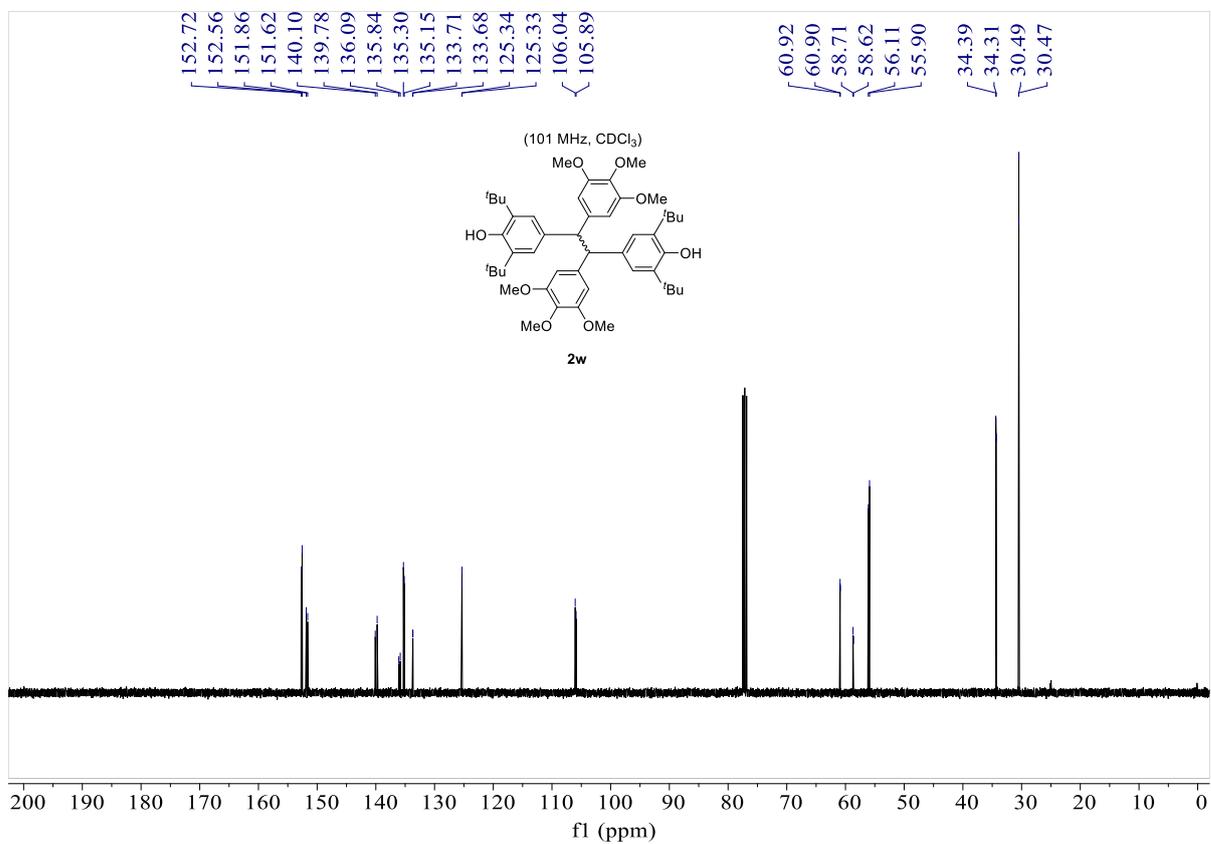
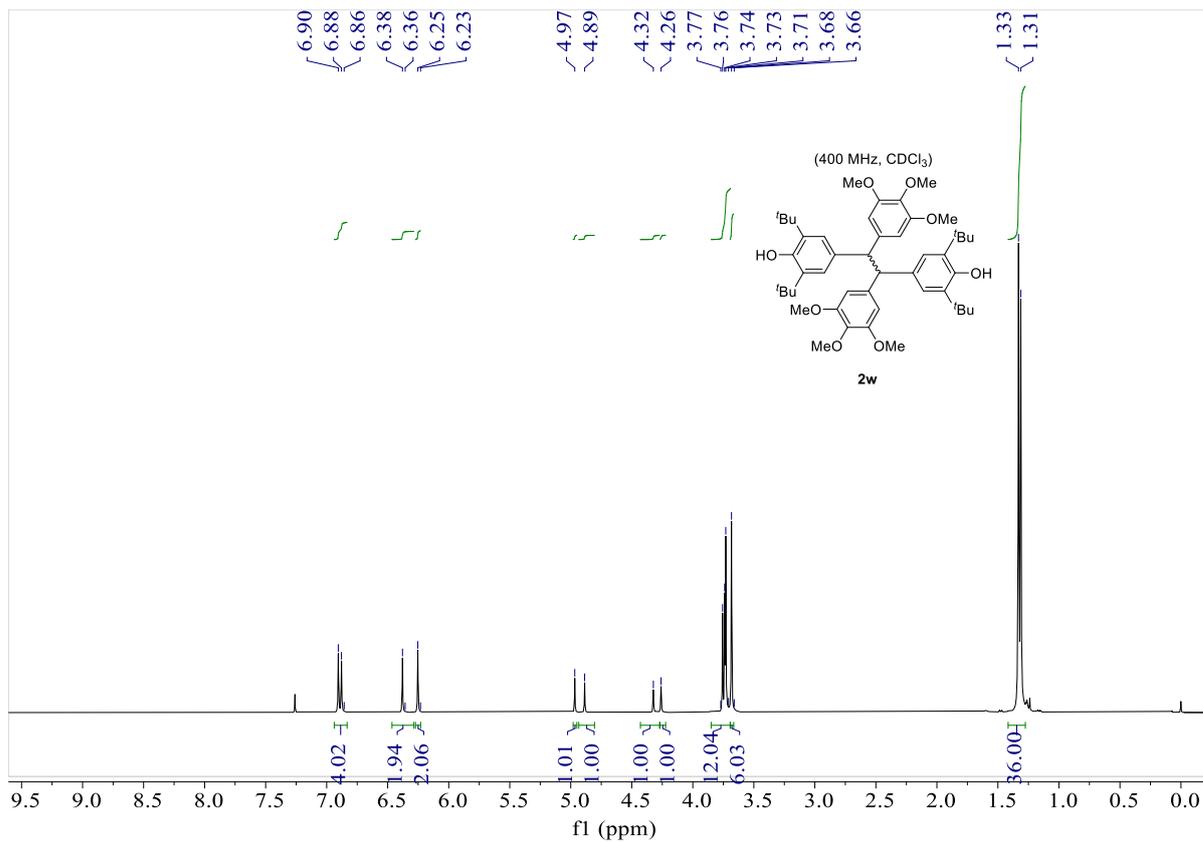


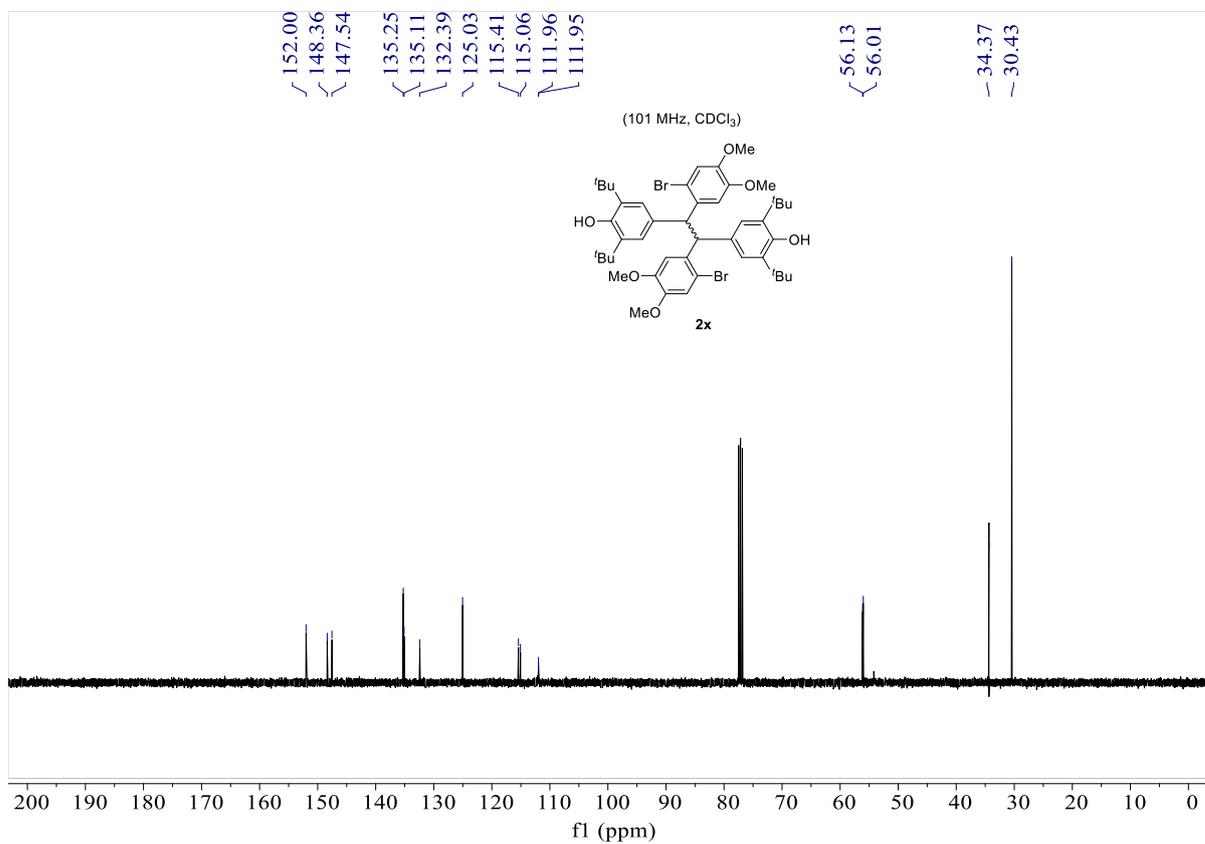
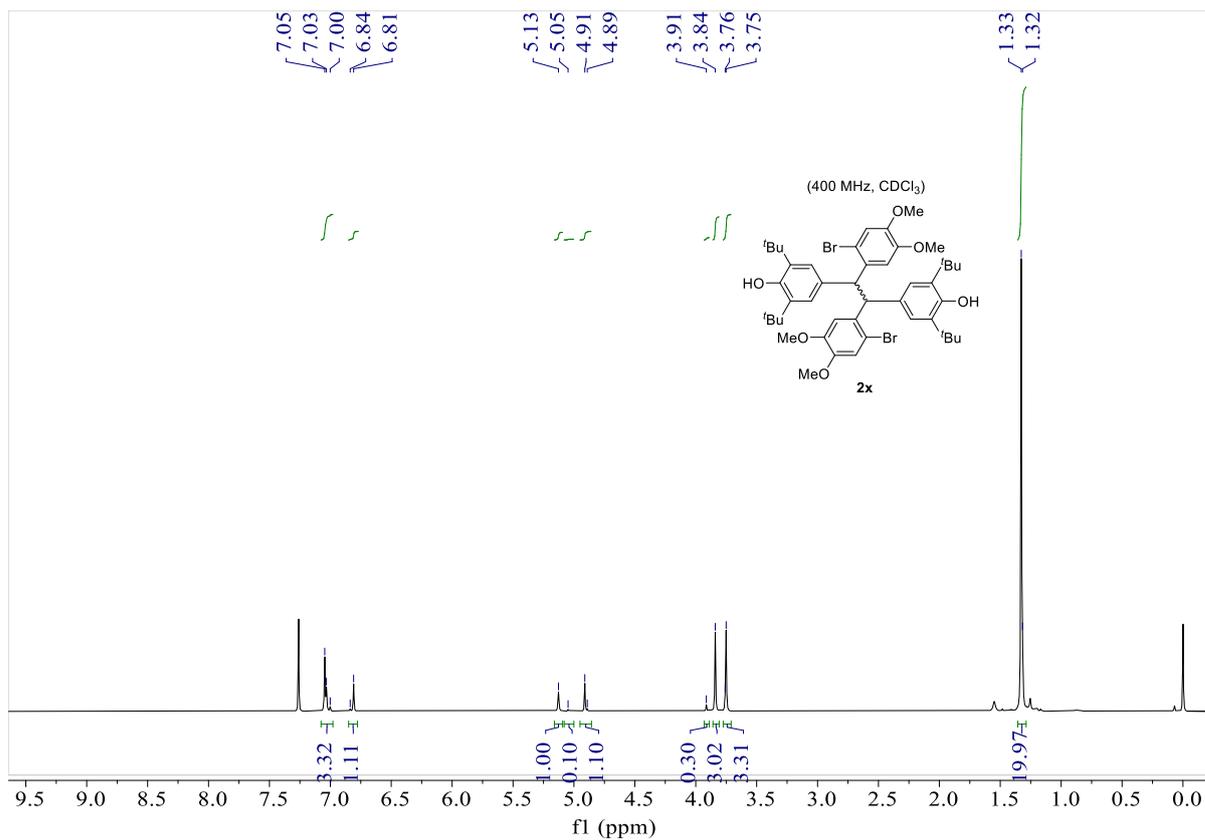


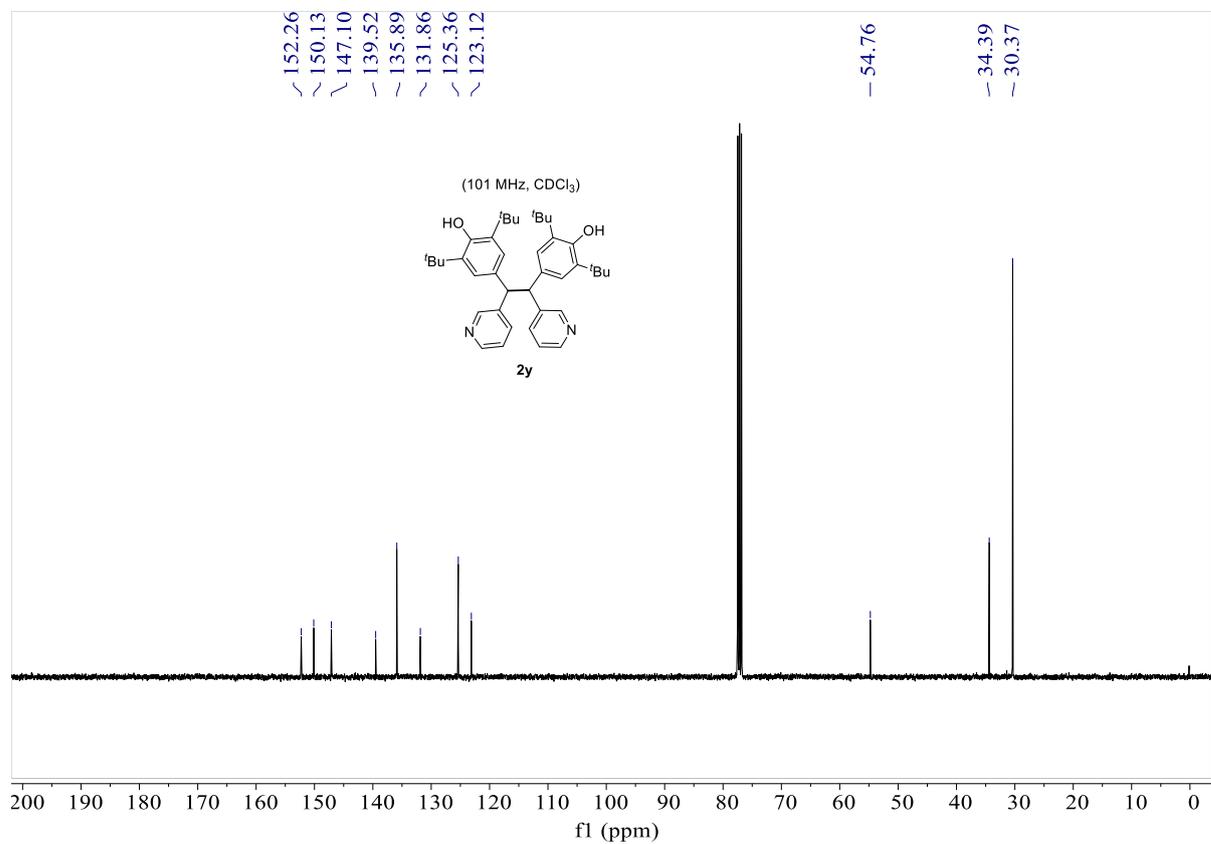
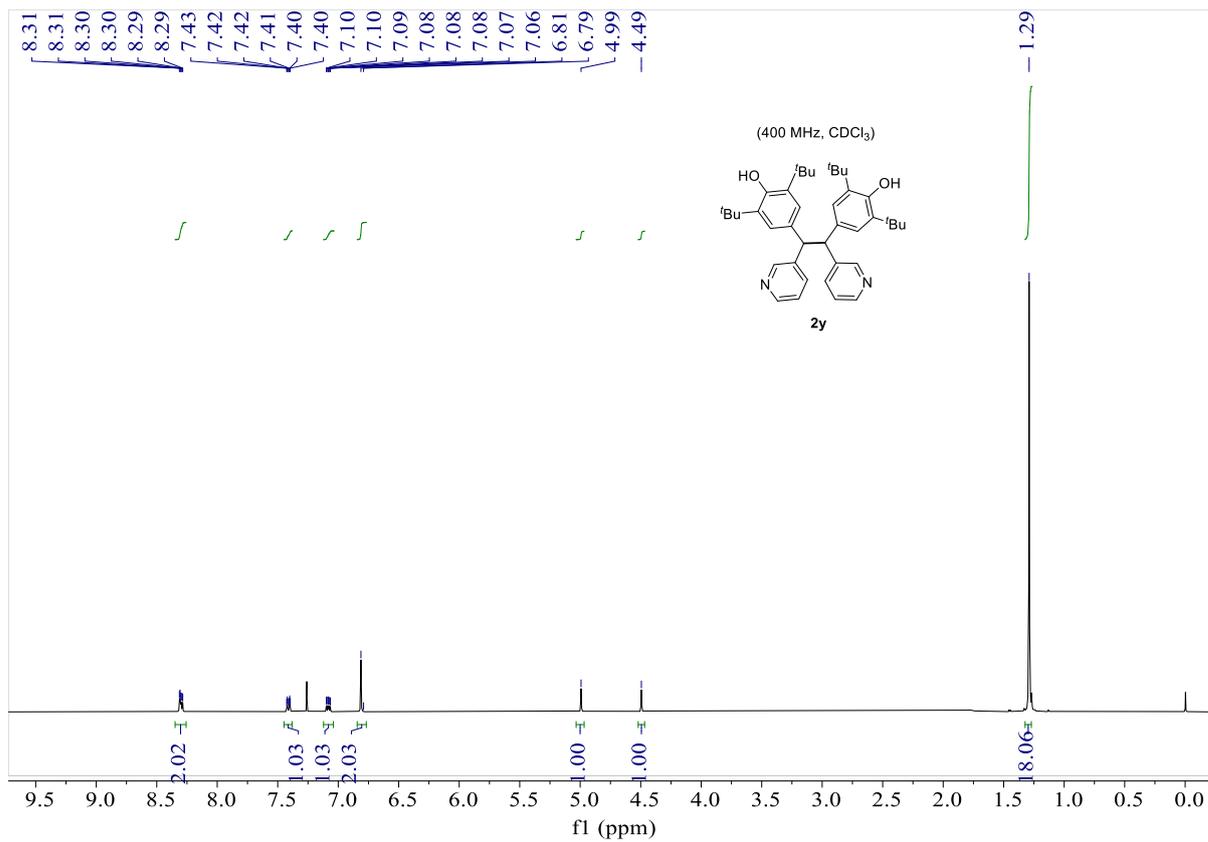


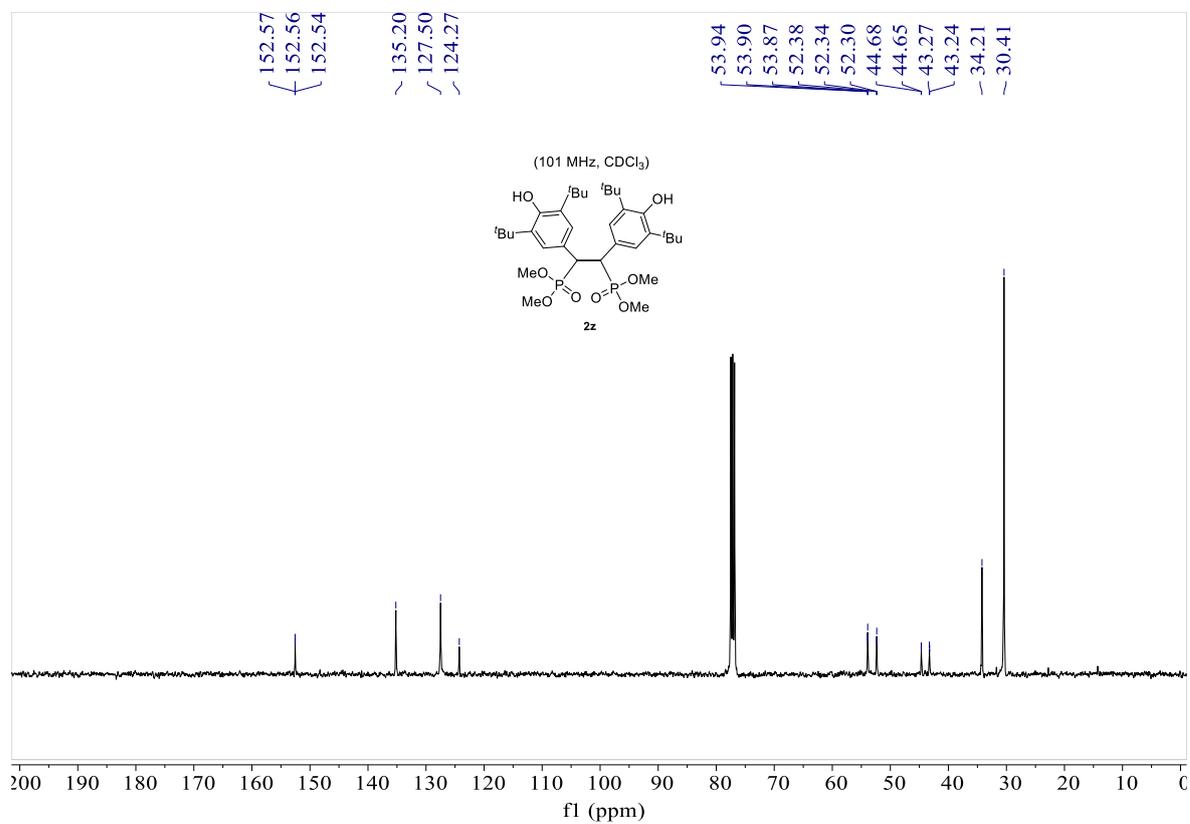
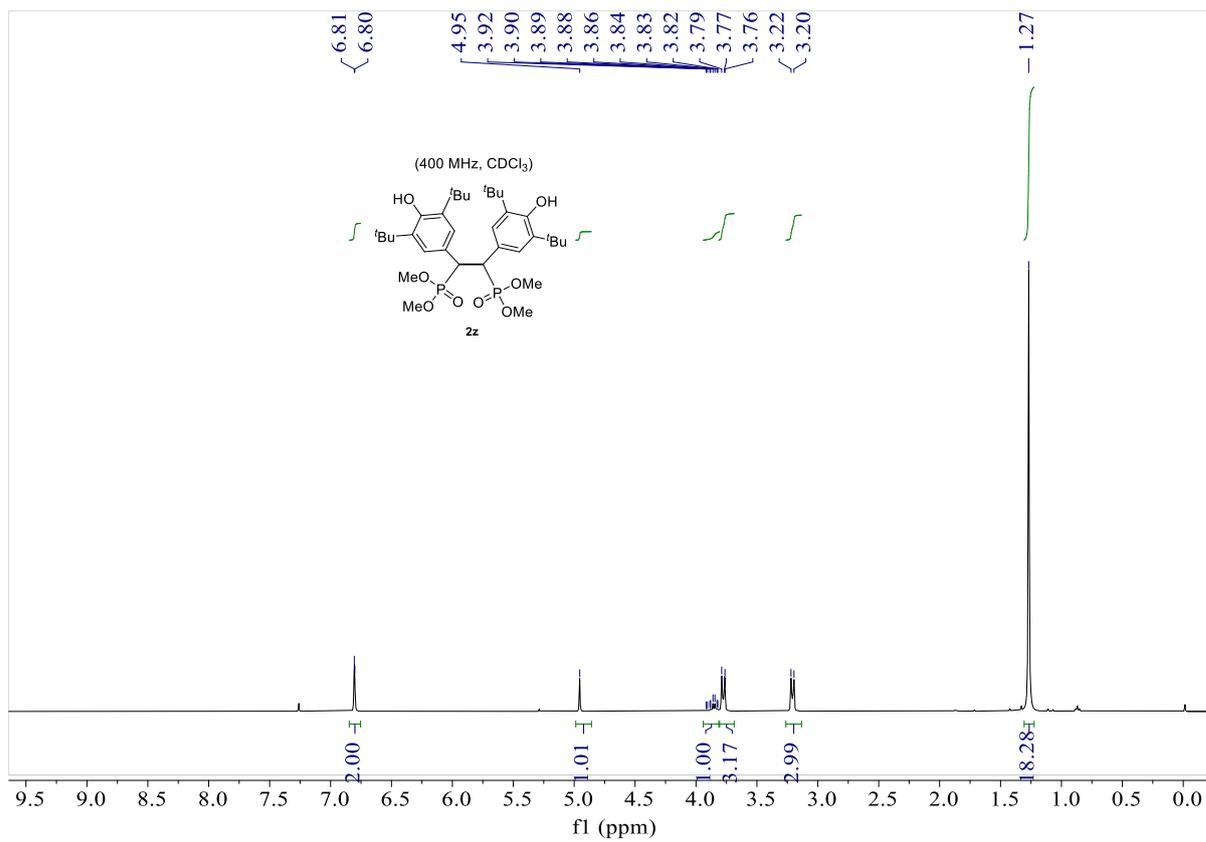


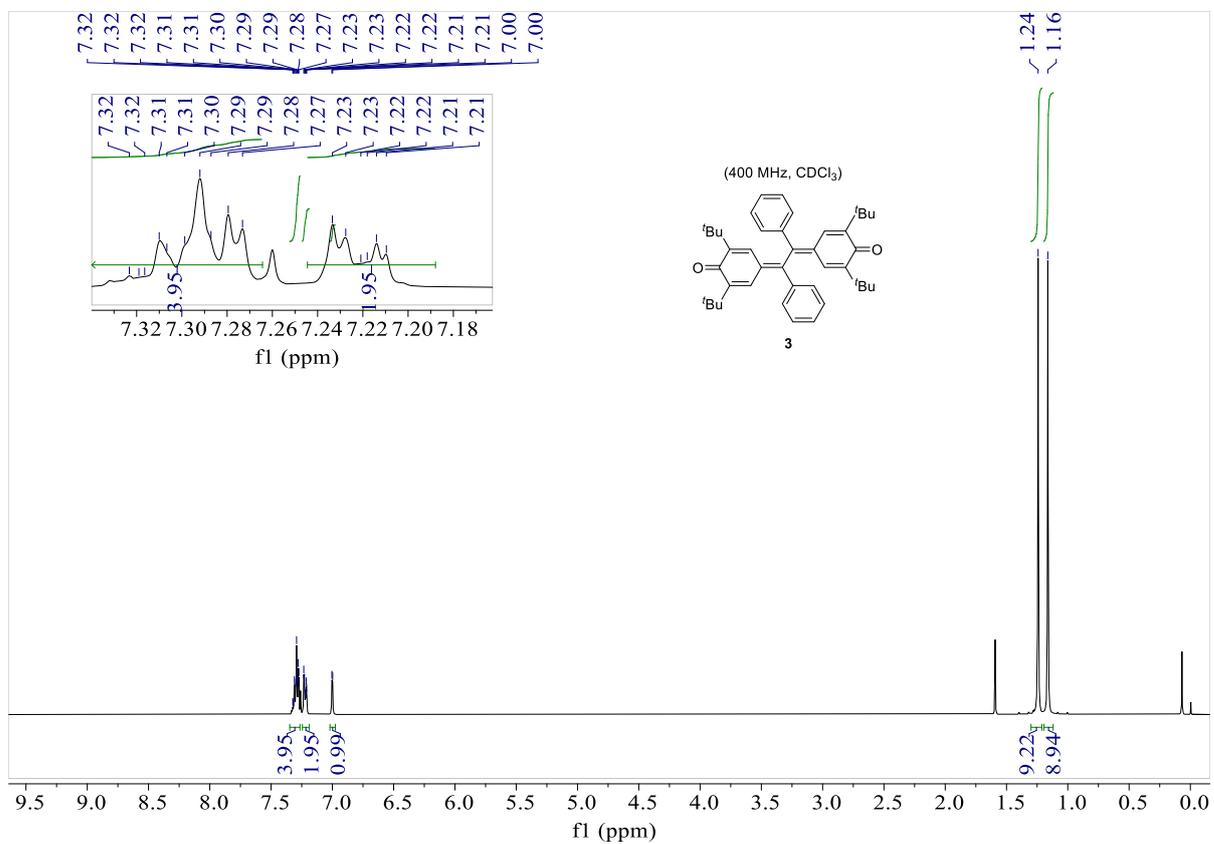
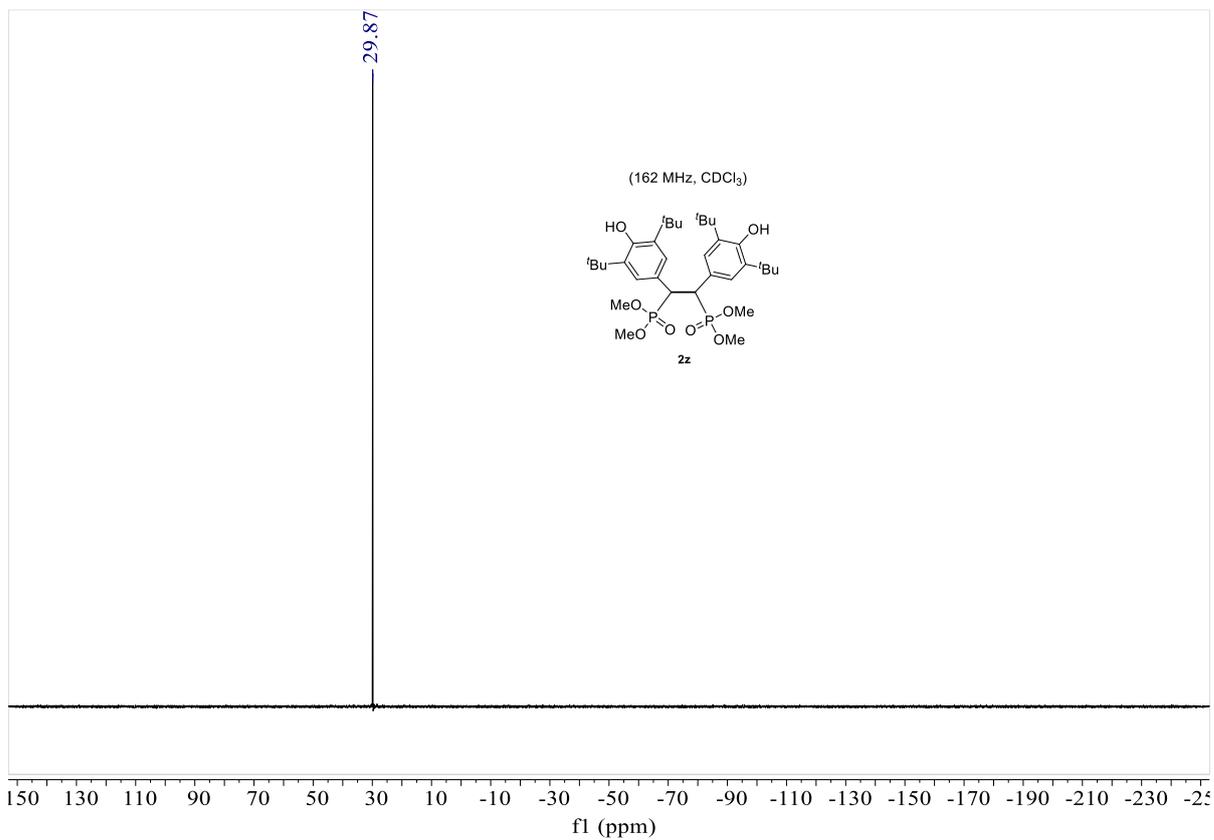


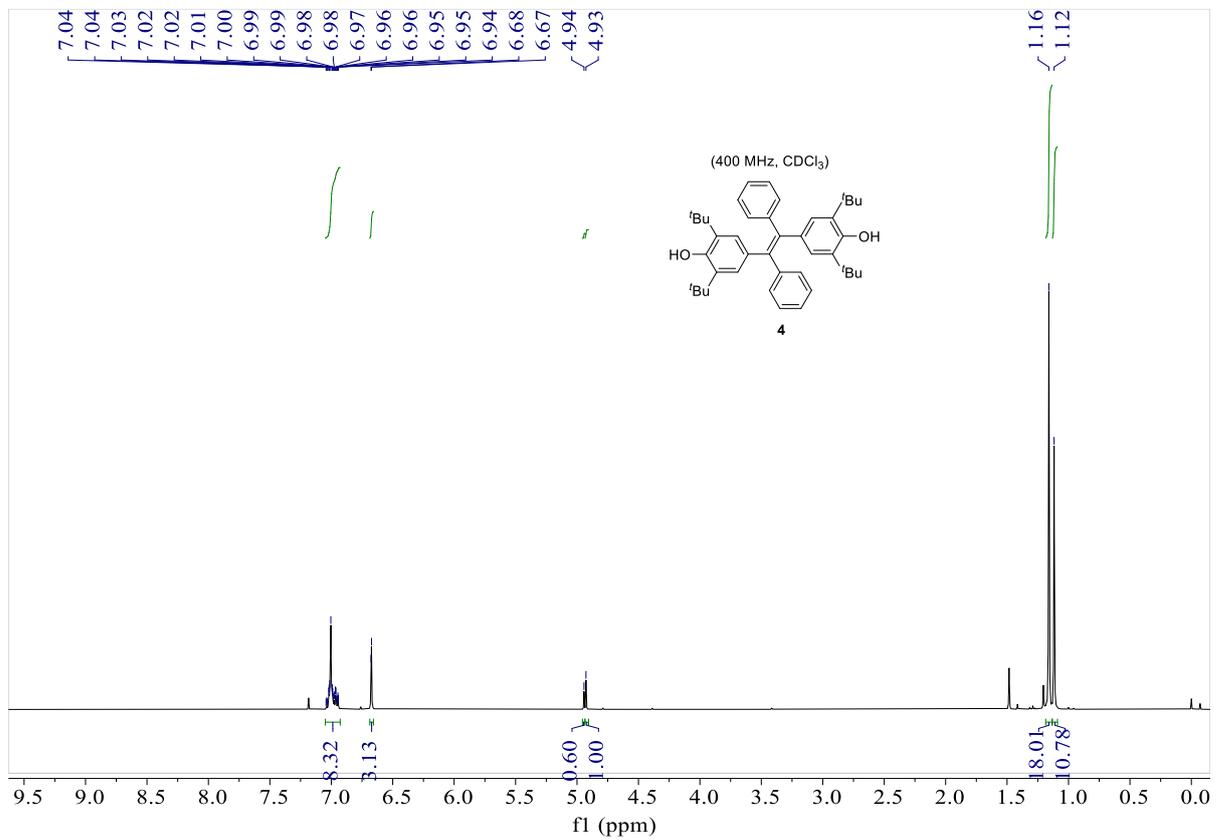
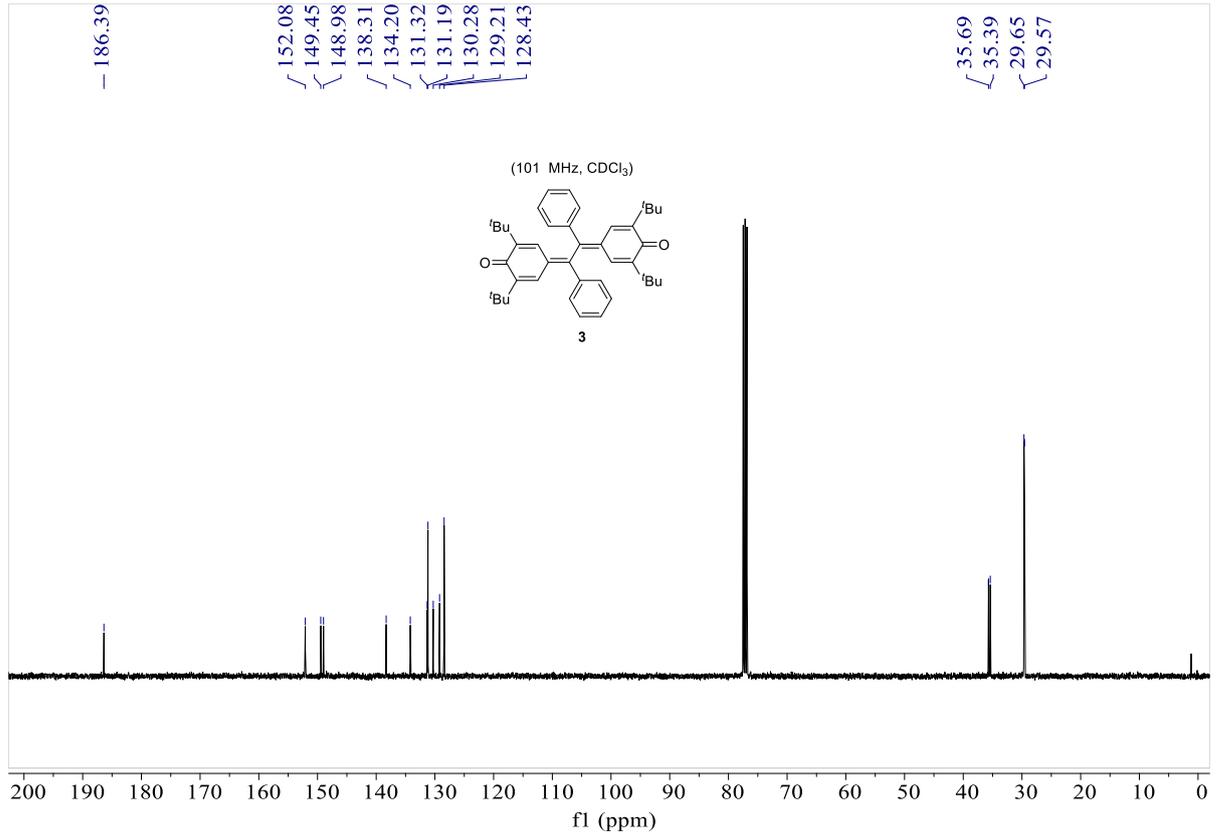


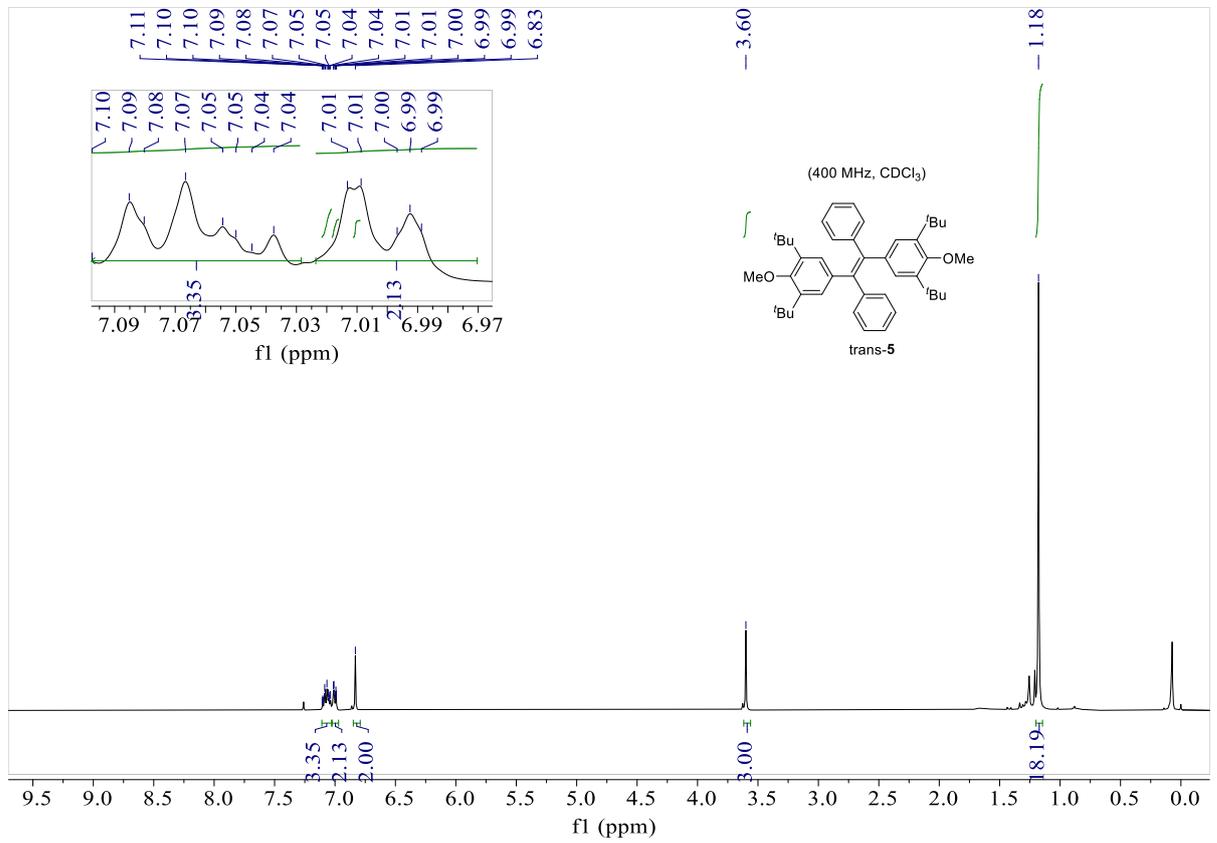
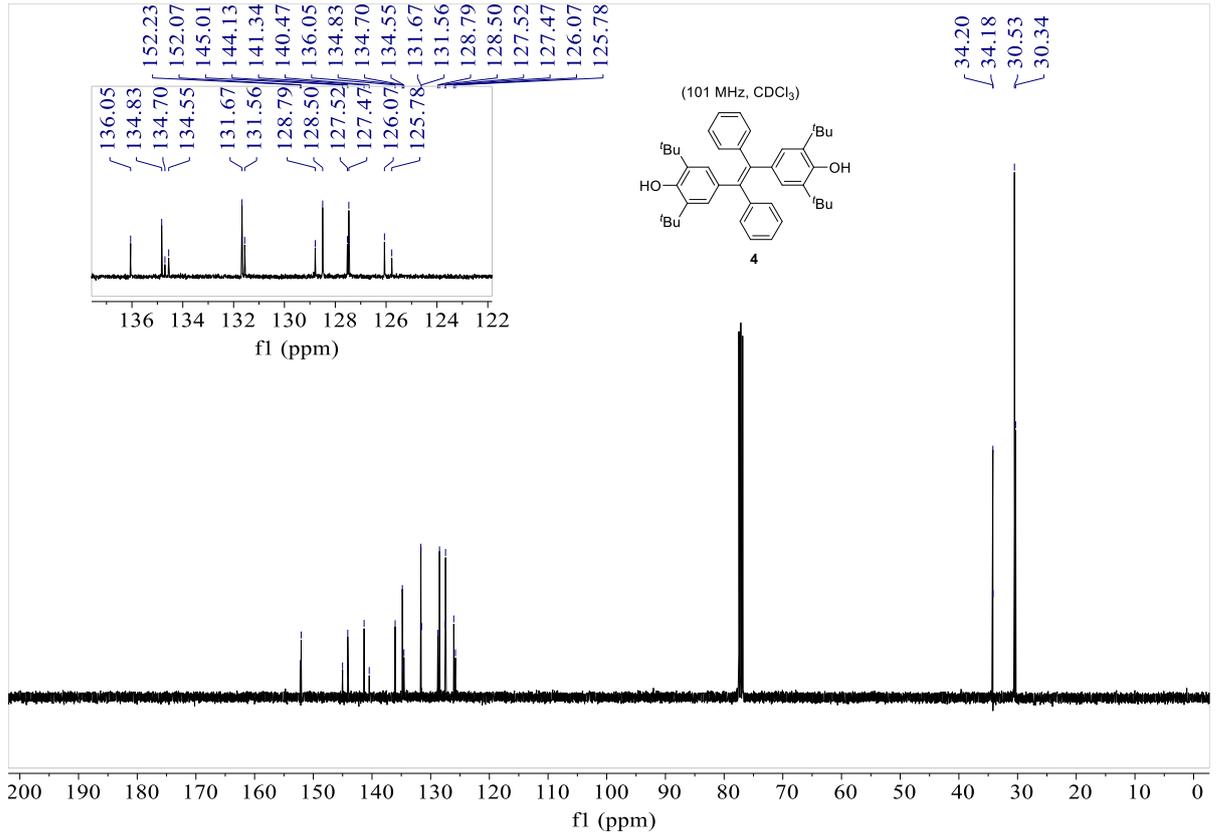


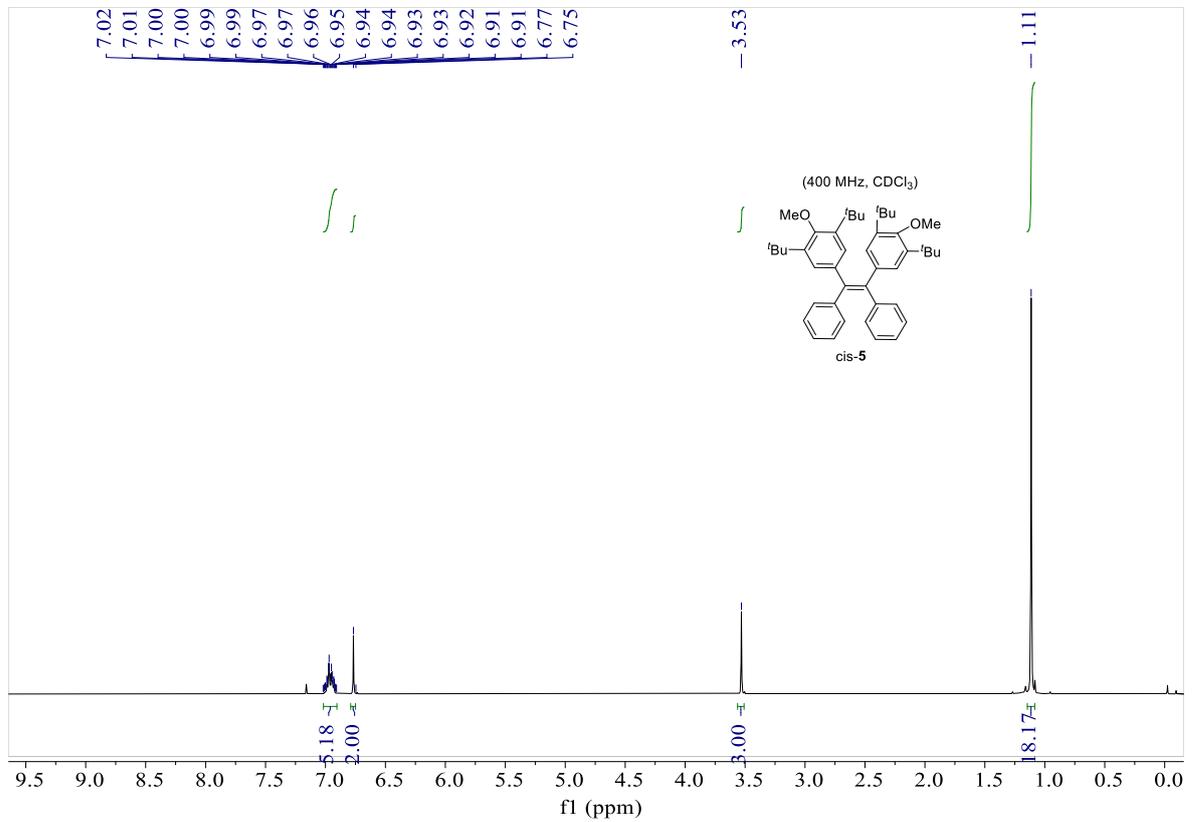
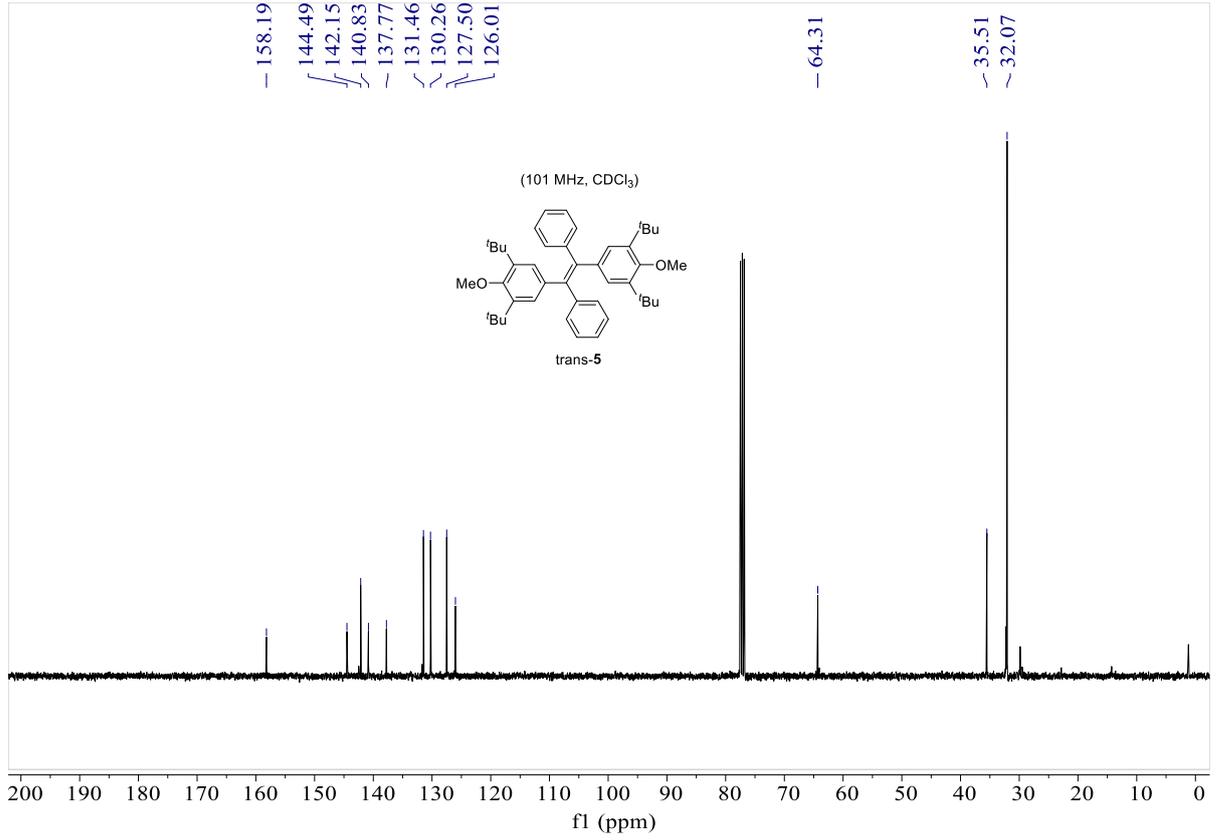


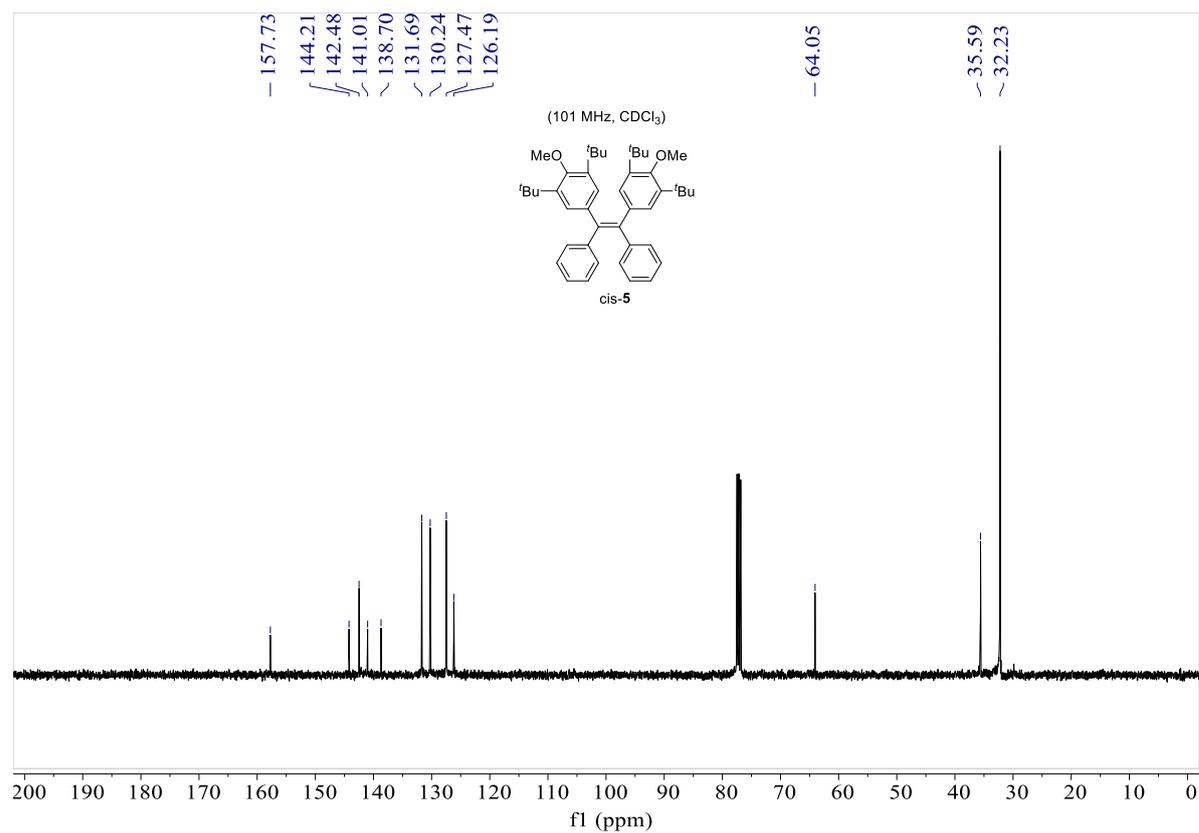






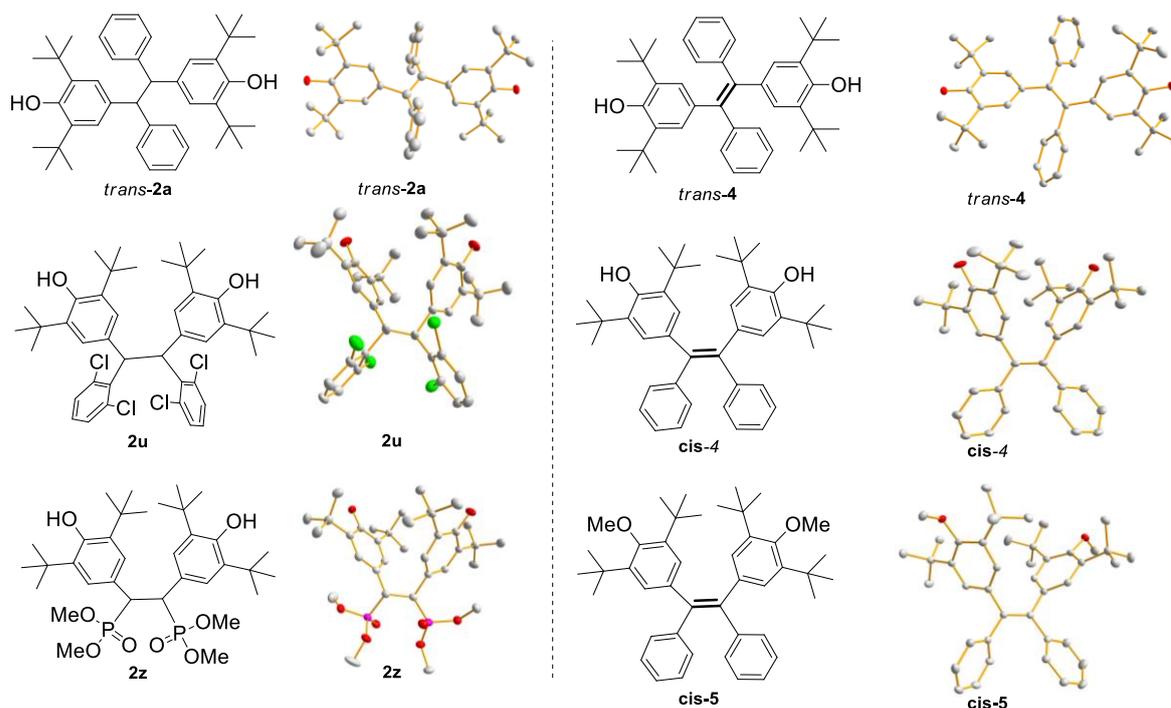






## 5. Crystallography

Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation. The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software packages. CCDC-2522467 (*trans-2a*), CCDC-2522469 (**2u**), CCDC-2522470 (**2z**), CCDC-2522471 (*trans-4*), CCDC-2522468 (*cis-4*) and CCDC-2522472 (*cis-5*) contain supplementary crystallographic data for this paper. Details of the crystal data, data collections, and structure refinements are summarized in Table S1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

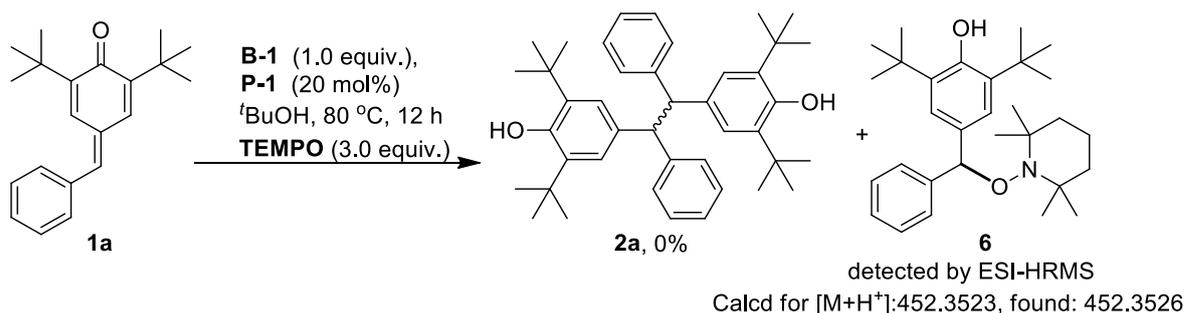


**Fig. S1** Molecular structures of *trans-2a*, **2u**, **2z**, *trans-4*, *cis-4* and *cis-5* with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

**Table S1** Crystal data and structural refinement details for the products *trans-2a*, **2u**, **2z**, *trans-4*, *cis-4* and *cis-5*

Complexes code	<i>trans-2a</i>	<b>2u</b>	<b>2z</b>	<i>trans-4</i>	<i>cis-4</i>	<i>cis-5</i>
empirical formula	C <sub>42</sub> H <sub>54</sub> O <sub>2</sub>	C <sub>42</sub> H <sub>50</sub> Cl <sub>4</sub> O <sub>2</sub>	C <sub>34</sub> H <sub>56</sub> O <sub>8</sub> P <sub>2</sub>	C <sub>42</sub> H <sub>52</sub> O <sub>2</sub>	C <sub>42</sub> H <sub>52</sub> O <sub>2</sub>	C <sub>44</sub> H <sub>56</sub> O <sub>2</sub>
formula weight	590.85	728.62	654.72	588.83	588.83	616.88
crystal system	triclinic	monoclinic	trigonal	orthorhombic	triclinic	triclinic
space group	P-1	C2/c	R -3	Pna2 <sub>1</sub>	P-1	P -1
<i>a</i> /Å	10.5638(10)	22.434(5)	25.8020(5)	29.342(2)	11.4985(16)	11.5516(11)
<i>b</i> /Å	12.2180(11)	15.147(3)	25.8020(5)	10.2930(8)	11.7455(17)	11.6796(12)
<i>c</i> /Å	13.9601(14)	18.526(5)	31.0745(17)	11.6592(10)	14.074(2)	15.6122(15)
<i>α</i> /deg	79.360(3)	90	90	90	79.778(5)	70.076(3)
<i>β</i> /deg	79.696(3)	132.633(6)	90	90	77.092(5)	89.930(3)
<i>γ</i> /deg	89.653(3)	90	120	90	77.618(5)	75.343(3)
<i>V</i> /Å <sup>3</sup>	1741.6(3)	4631.6(19)	17916.0(18)	3521.3(5)	1792.8(5)	1907.5(3)
<i>Z</i>	2	8	18	4	2	2
$\mu$ /mm <sup>-1</sup>	0.067	0.284	0.151	0.066	0.065	0.064
R <sub>int</sub>	0.0975	0.1081	0.0933	0.0891	0.1051	0.0959
R1 ( <i>I</i> > 2 $\sigma$ )	0.0811	0.0877	0.053	0.0686	0.0627	0.0486
wR2 ( <i>I</i> > 2 $\sigma$ )	0.1775	0.2672	0.1381	0.1395	0.1384	0.1277
GOF	1.030	1.097	1.060	1.012	1.016	1.035

## 6. Radical trapping experiment



Experimental procedure: TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv.) was added to a mixture of 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **1a** (58.9 mg, 0.2 mmol, 1.0 equiv.), B<sub>2</sub>pin<sub>2</sub> (50.8 mg, 0.2 mmol, 1.0 equiv.) and tert-butyl isonicotinate (7.2 mg, 0.04 mmol, 0.2 equiv.). Then, the mixture was mixed in 0.5 mL <sup>t</sup>BuOH in a Schlenk tube with N<sub>2</sub> protection. The mixture was stirred at 80 °C for 12h. After cooling to room temperature, the reaction mixture was not quenched with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution, the ESI-HRMS analysis of the crude reaction mixture was carried out. The mass for diarylmethyl radical trapping product **6** could be detected. The mass for **6** is C<sub>30</sub>H<sub>46</sub>NO<sub>2</sub><sup>+</sup>[M+H]<sup>+</sup> calcd. 452.3523, found 452.3526 (Fig. S2).

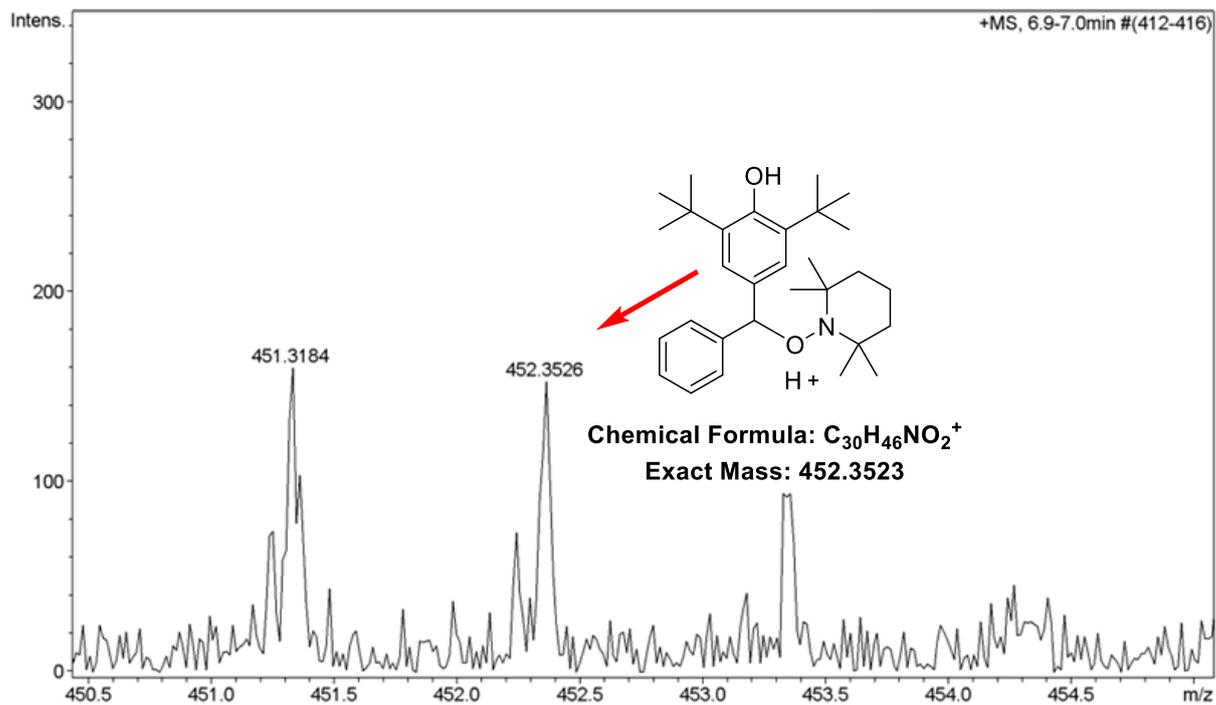


Fig. S2 HRMS analysis of the crude reaction mixture of **1a**, B<sub>2</sub>pin<sub>2</sub>, tert-butyl isonicotinate, TEMPO in <sup>t</sup>BuOH.