Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information for

Catalytic desulfitative homocoupling of sodium arylsulfinates in water using $PdCl_2$ as the recyclable catalyst and O_2 as the terminal oxidant

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1. General procedure for the preparation of sodium arylsulfinates[1]

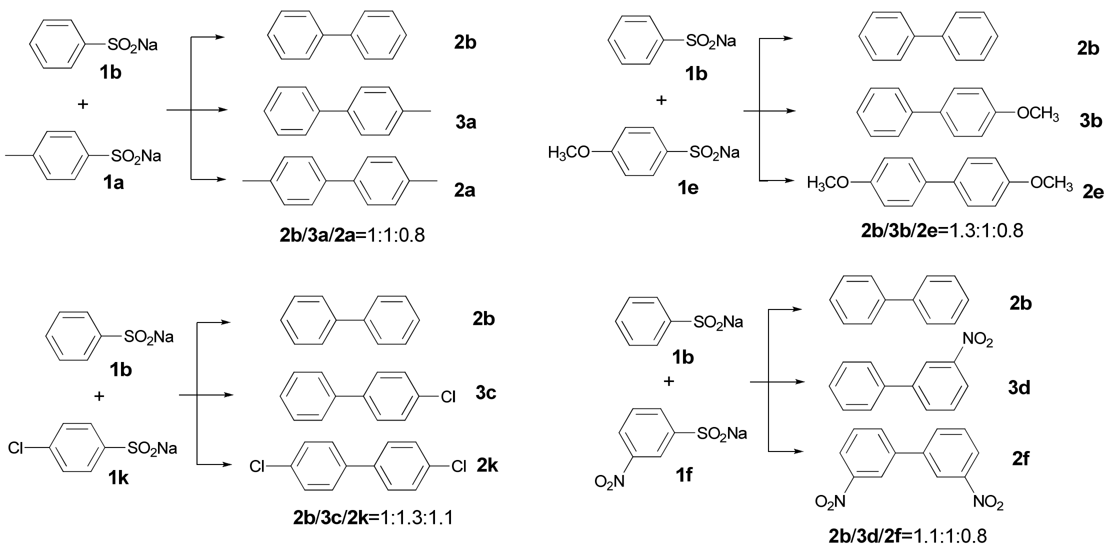
4-*tert*-Butylbenzenesulfonyl chloride (1.16 g, 5 mmol) was added to the mixture of sodium sulfite (1.26 g, 10 mmol) and sodium bicarbonate (0.84 g 10 mmol) in water (5mL) at 80 °C for 4 h. After cooling to room temperature, the water was removed in vacuum and the residue was refluxed in anhydrous EtOH for 1 h. Then the resultant suspension was filtered through Celite and the filtrate was evaporated under vacuum. The recrystal product can be attained in ethanol up to 70% yield (0.77 g). Other sodium arylsulfinates were prepared similarly from the corresponding sulfonyl chloride except **1a** and **1b**.

2. Determination of $NaHSO_4$ released from the reaction system[2]

Sodium arylsulfinates (0.75 mmol) and Cu_2O (21 mg, 20 mol%) were added in H_2O (2 mL). The pH of the mixture was about 8 by pH paper. After addition of $PdCl_2$ (3.4 mg, 2.5 mol%), the pH of the mixture turned to be 5. The mixture was allowed to react in a sealed tube at 100 ^{o}C under the atmosphere of 1 atm O_2 for 24 h. After cooling to room temperature and extracted with ether (3 × 10 mL), the pH of the resulting aqueous solution was reduced to 1, indicating production of H^+. Saturated aqueous $BaSO_4$ was then added to the aqueous solution (0.5 mL), and there formed white precipitate which was not dissolved in aqueous HCl (1M), indicating formation of $BaSO_4$.

3. The coupling reaction between different sodium arylsulfinates

The coupling between two different sodium arylsulfinates was tested under the optimum reaction conditions. As shown in Scheme 1, the cross-experiments were performed by combining two sodium arylsulfinates with the different and similar electron density. In addition to the homocoupling products of the individual sodium arylsulfinate components, GC-MS analysis showed that the unsymmetrical biaryls from the cross-coupling of two different sodium arylsulfinates were also formed. No significant selectivity was observed.



Scheme 1 Desulfinative coupling of different sodium arylsulfinates

4. The spectra data of products

(1) 4,4′-Dimethylbiphenyl (**2a**)[3]
Colorless solid (mp 123–124 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.0 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 136.7, 129.4, 126.8, 21.1.

(2) Biphenyl (**2b**)[3]
Colorless solid (mp 67–68 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.2 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 2H).

(3) 4, 4′-Di-tert-butylbiphenyl (**2c**)[3]
Colorless solid (mp 128–129 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.4 Hz, 4H), 7.46 (d, *J* = 8.4 Hz, 4H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 138.2, 126.7, 125.7, 34.5, 31.4.

(4) 2,2′-Binaphthyl (**2d**)[4]
Colorless solid (mp 183–185 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 2H), 7.98–7.88 (m, 8H), 7.55–7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 133.8, 132.7, 128.5, 128.3, 127.7, 126.4, 126.1, 126.0, 125.8.

(5) 4,4′-Dimethoxybiphenyl (**2e**)[4]
Colorless solid (mp 175–177 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.8 Hz, 4H), 6.97 (d, *J* = 8.4 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 133.5, 127.8, 114.2, 55.4.

(6) 3,3′-Dinitrobiphenyl (**2f**)[4]
Light yellow solid (mp 201–202 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 2 H), 8.32 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 140.4, 133.1, 130.3, 123.3, 122.1.

(7) 3,3′-Di(methoxycarbonyl)biphenyl (**2g**)[5]
Colorless solid (mp 102–103 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 3.96 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 140.4, 131.5, 130.9, 129.0, 128.8, 128.3, 52.2.

(8) 2,2′-dimethylbiphenyl (**2h**)[4]
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.20 (m, 6H), 7.11–7.09 (m, 2H), 2.06 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 135.8, 129.8, 129.3, 127.2, 125.5, 19.8.

(9) 4,4′-Di(trifluoromethyl)biphenyl (**2i**)[6]
Colorless solid (mp 82–83 °C); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75–7.69 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3, 130.3 (d, *J* = 33 Hz), 127.7, 126.0, 125.2 (d, *J* = 270 Hz)

(10) 4,4′-Difluorobiphenyl (**2j**)[7]

Colorless solid (mp 89–90 °C); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50–7.47 (m, 4H), 7.14–7.09 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.4 (d, *J* = 245), 136.4 (d, *J* = 3), 128.6 (d, *J* = 9), 115.7 (d, *J* = 21).

(11) 4,4′-Dichlorobiphenyl (**2k**)[4]
Colorless solid (mp mp 146–150 ˚C) ; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.4 Hz, 4H), 7.41 (d, *J* = 7.4 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 138.4, 133.7, 129.0, 128.2.

(12) 4,4′-Dibromobiphenyl (**2l**)[4]
Colorless solid (mp 164–166 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 132.0, 128.5, 121.9.

(13) 2,2'-Bithiophene (**2m**)[8]
Colorless solid (mp 31–33 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 2H), 7.18 (dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 2H), 7.03–7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 127.8, 124.4, 123.8.

(14) 1,4'''-Dimethoxy-4,1':4',1'':4'',1'''-quaterphenylene (MOP4)[9]
Colorless amorphous solid (mp > 300 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71(d, *J* = 8.0 Hz, 4H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 4H), 3.87 (s, 6H).

5. References

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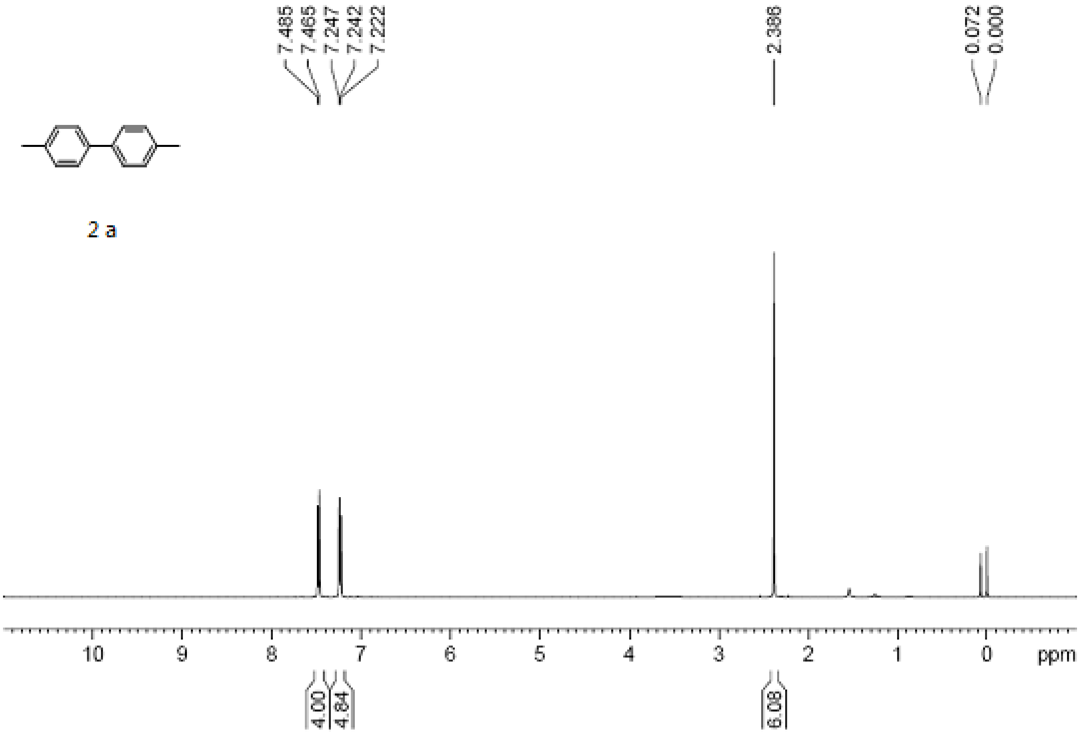
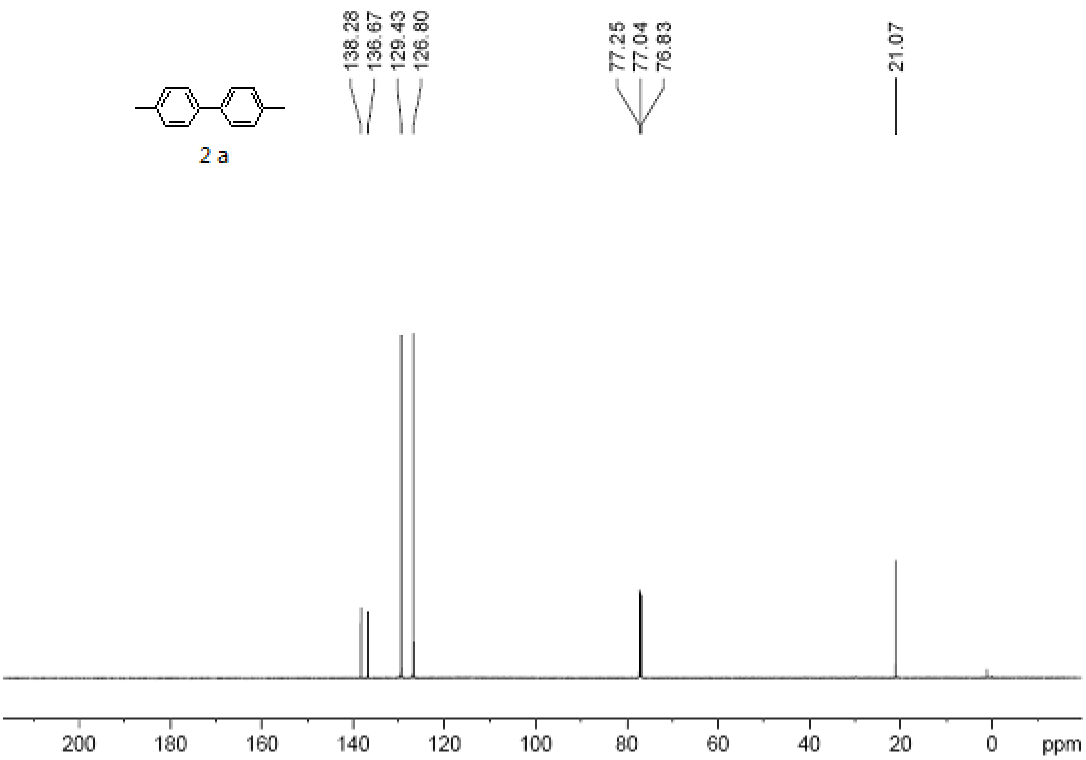
6. ^{1}H and ^{13}C NMR Spectra

(1) 4,4′-Dimethylbiphenyl (**2a**)





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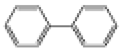
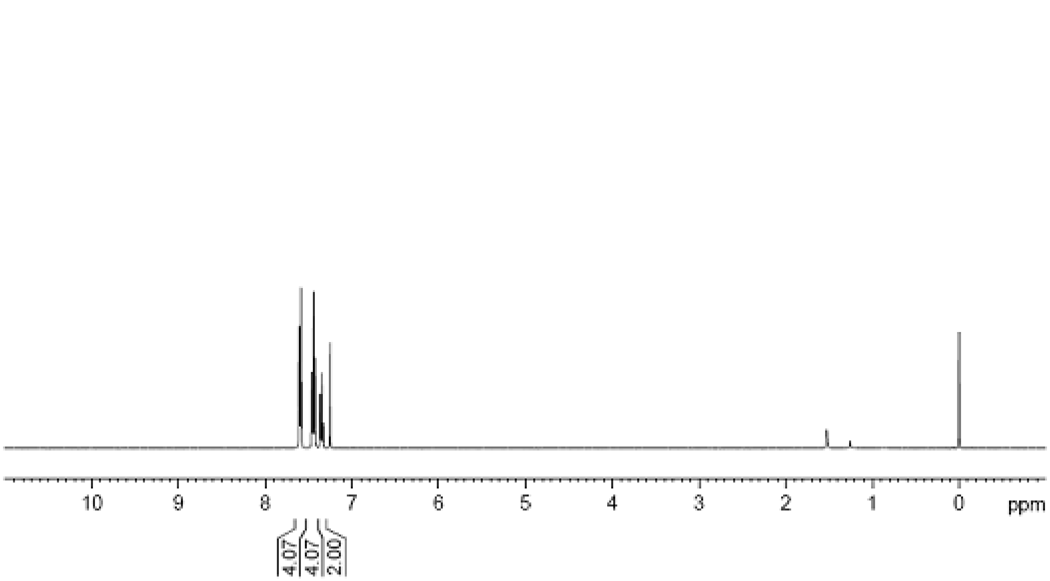
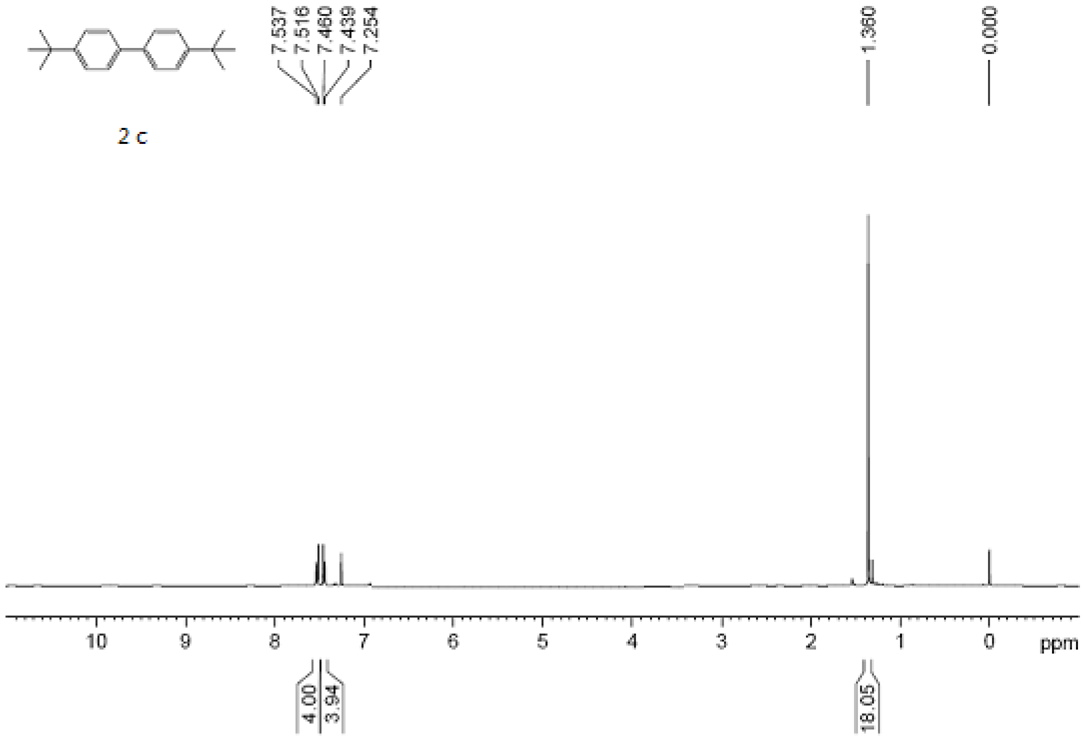
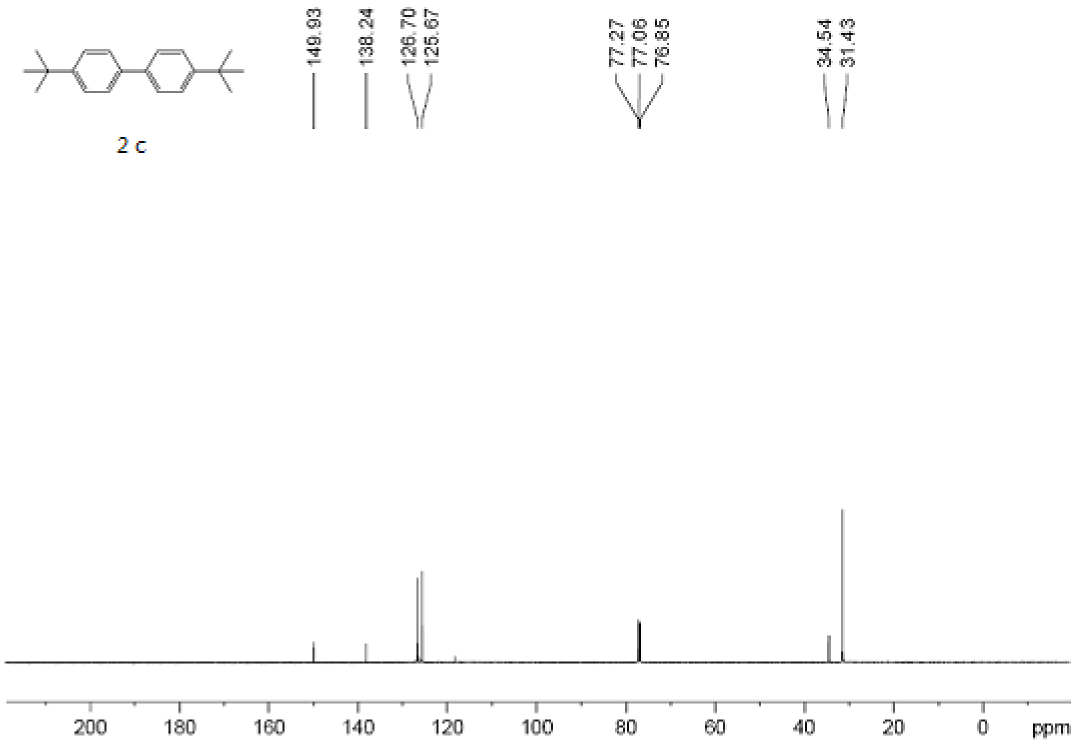


2 b

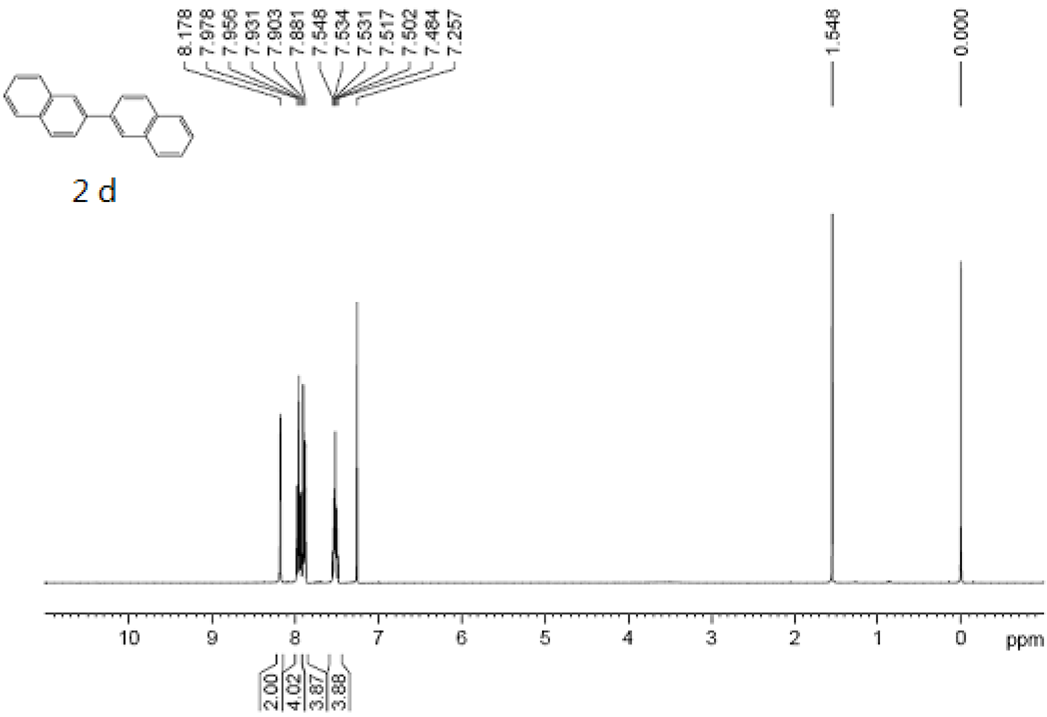


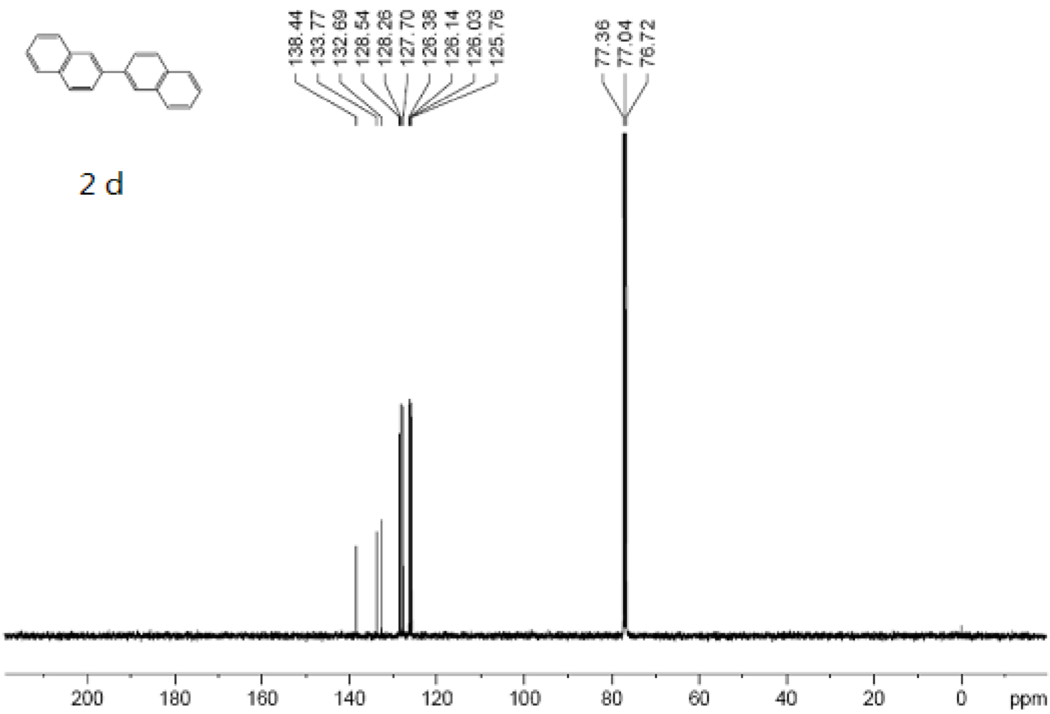
(3) 4, 4′-Di-tert-butylbiphenyl (**2c**)



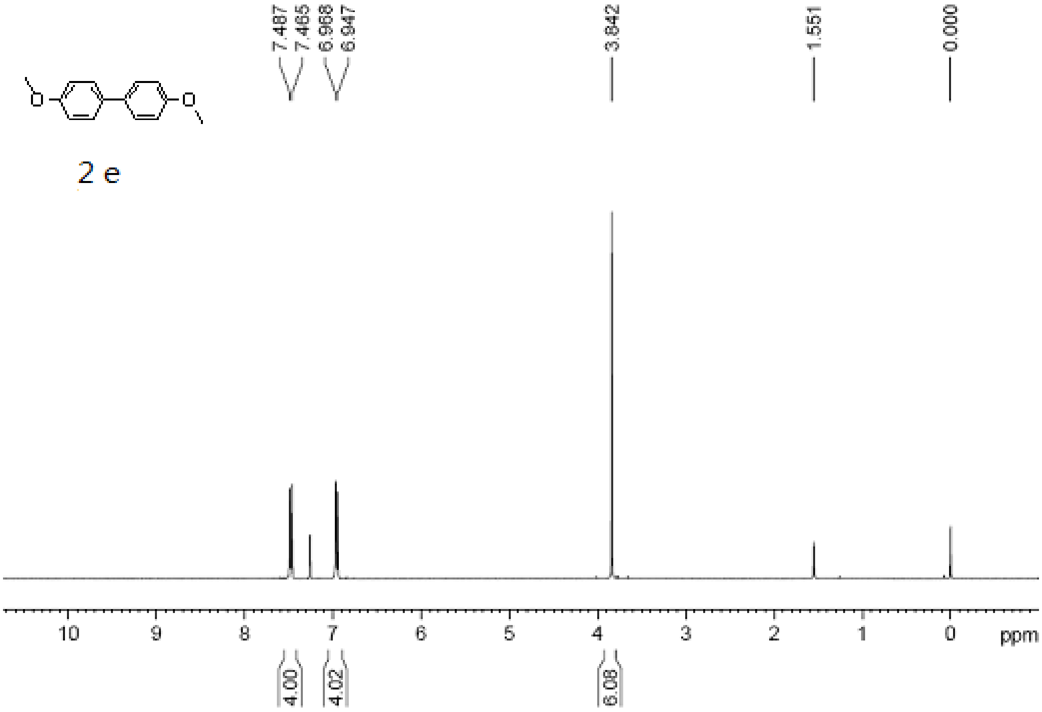


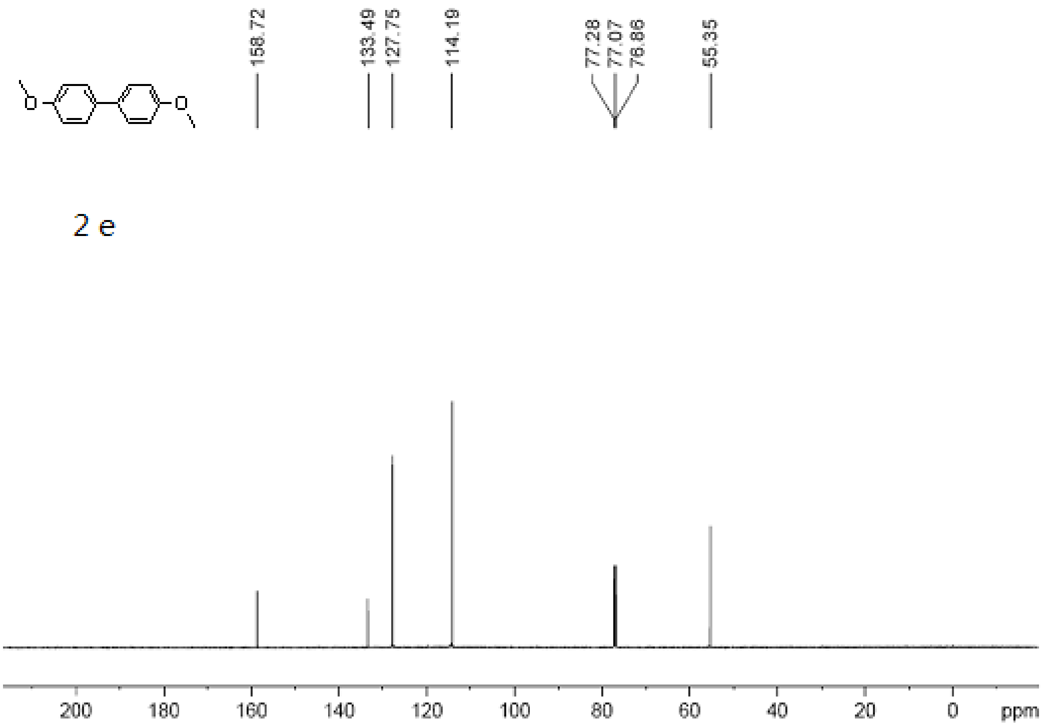
(4) 1,1′-Binaphthyl (**2d**)



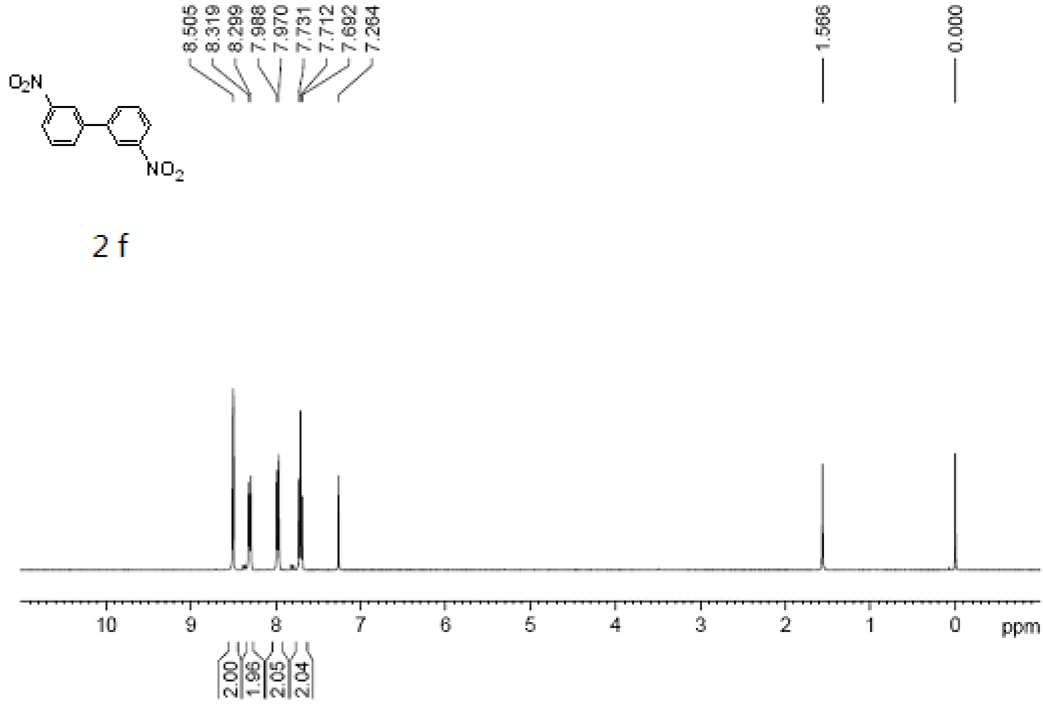


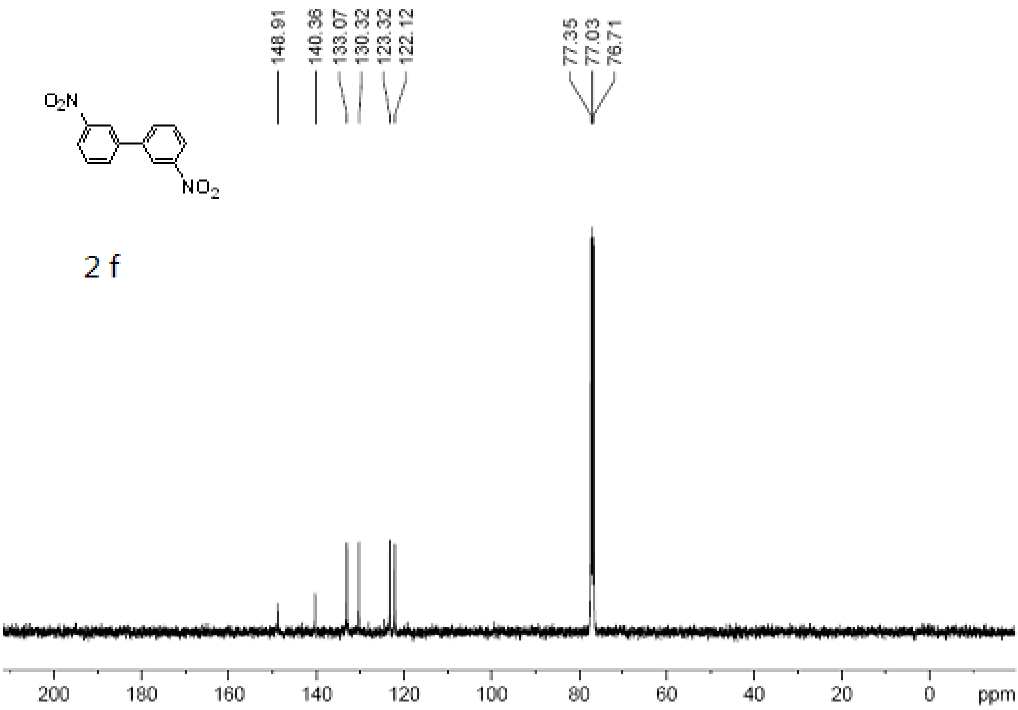
(5) 4,4′-Dimethoxy biphenyl (**2e**)



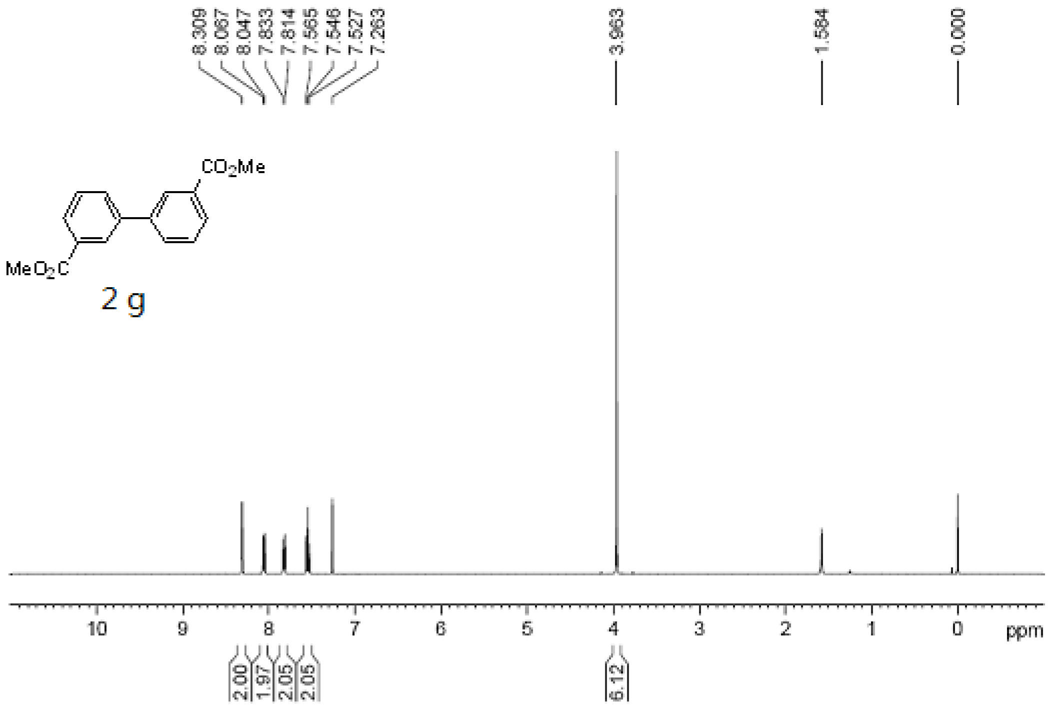


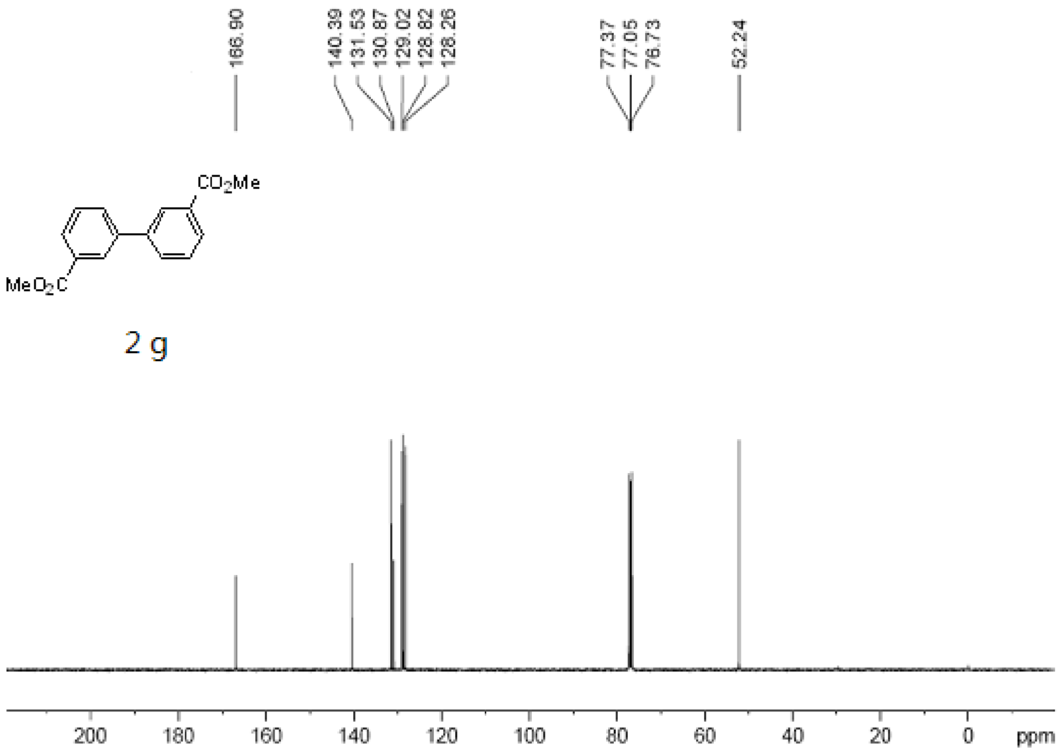
(6) 3,3′-Dinitrobiphenyl (**2f**)





(7) 3,3′-Di(methoxycarbonyl)biphenyl (**2g**)





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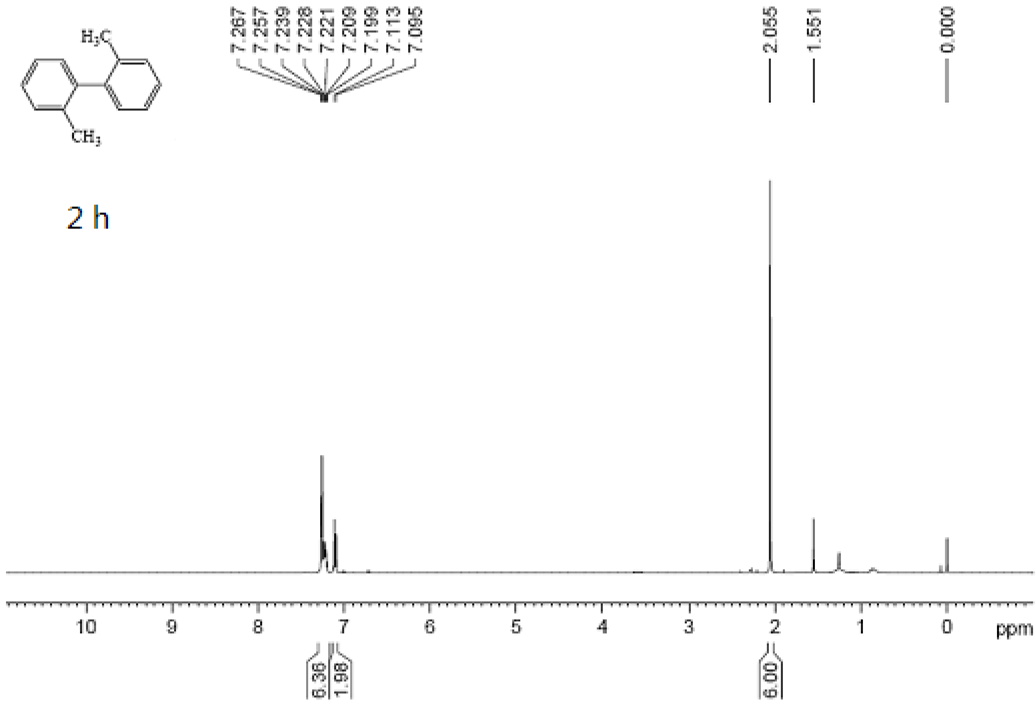
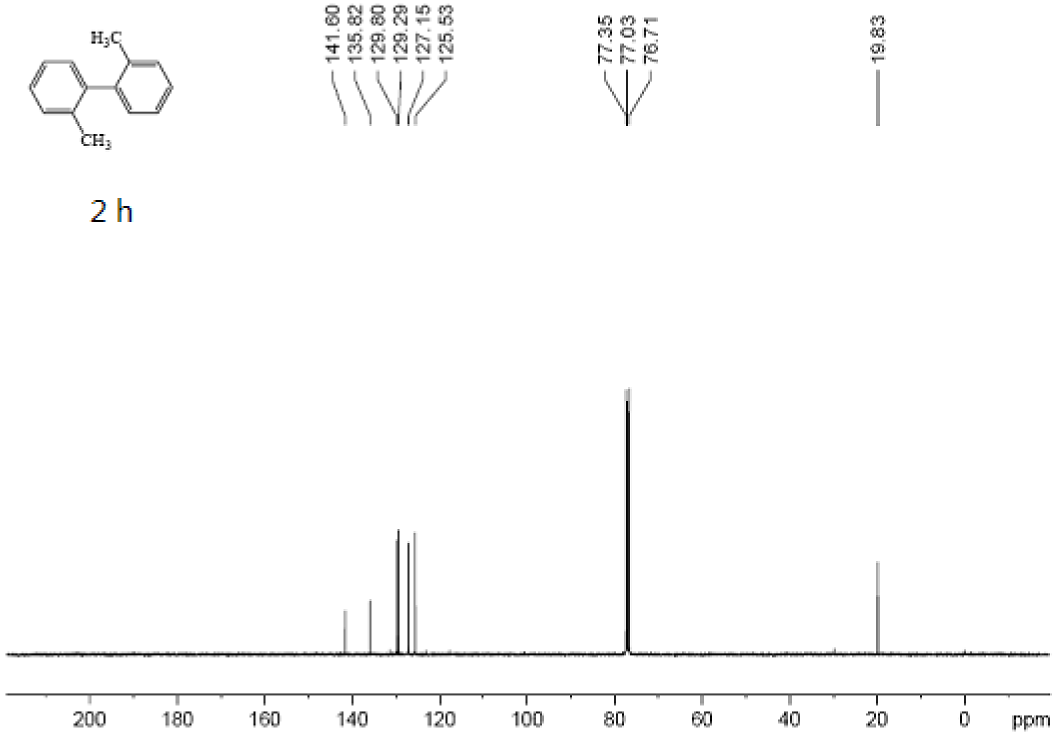
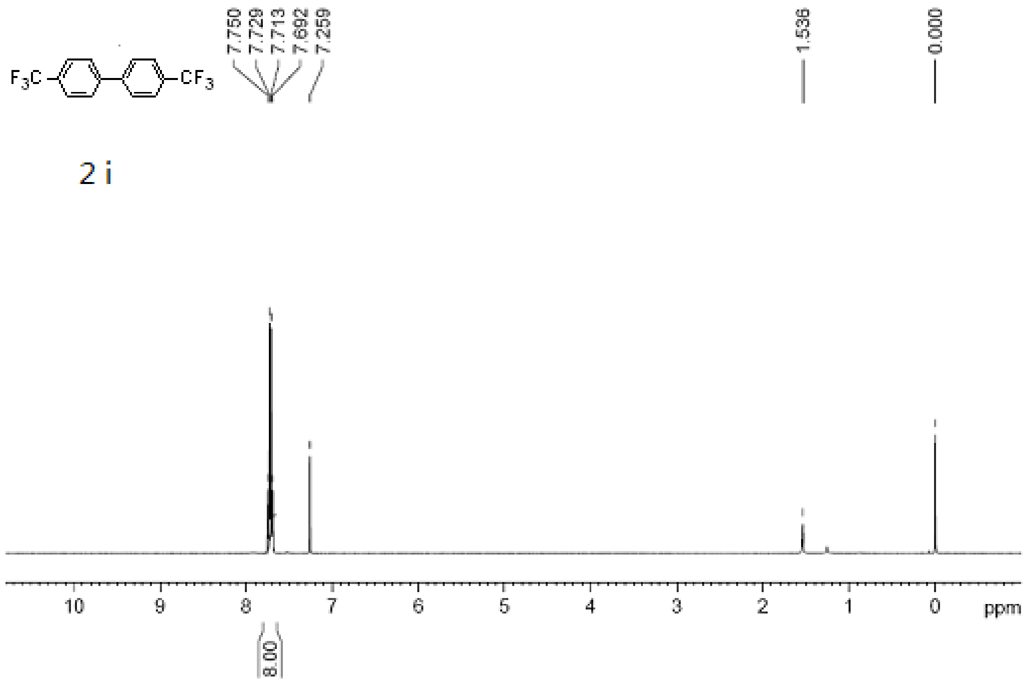
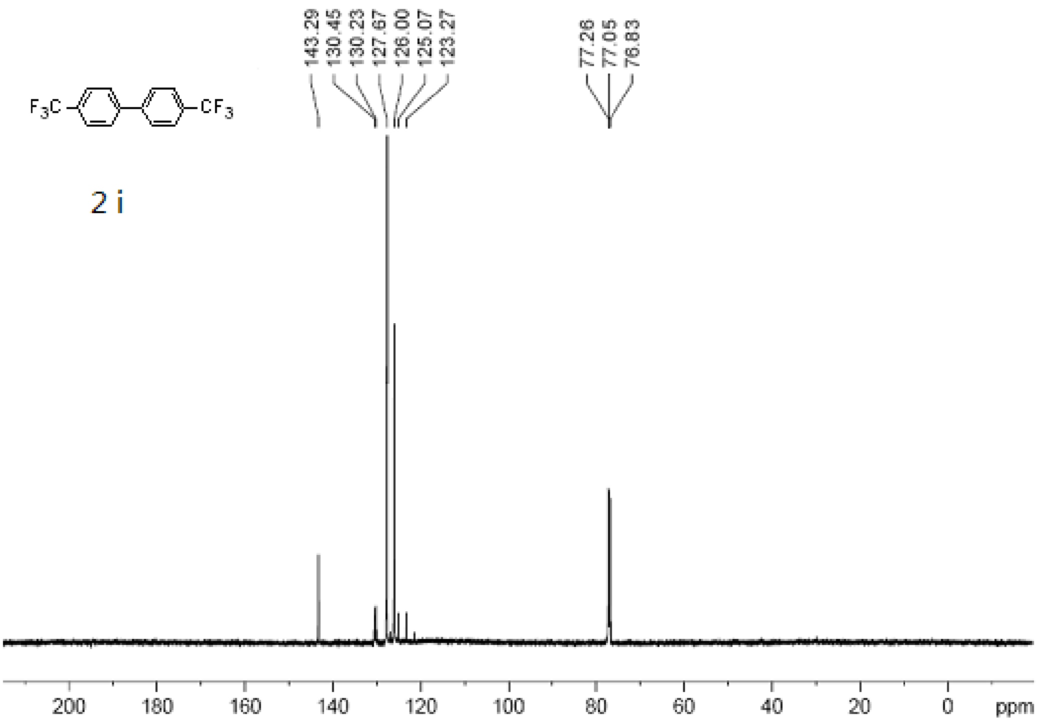
(8) 2,2′-dimethylbiphenyl (**2h**)



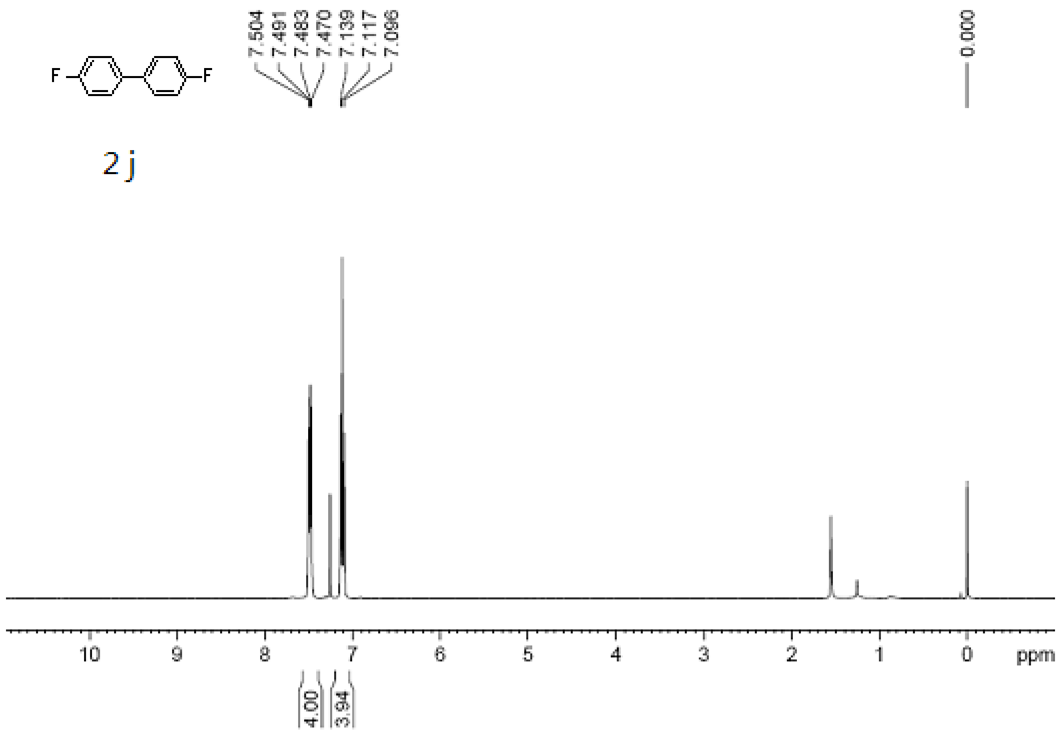


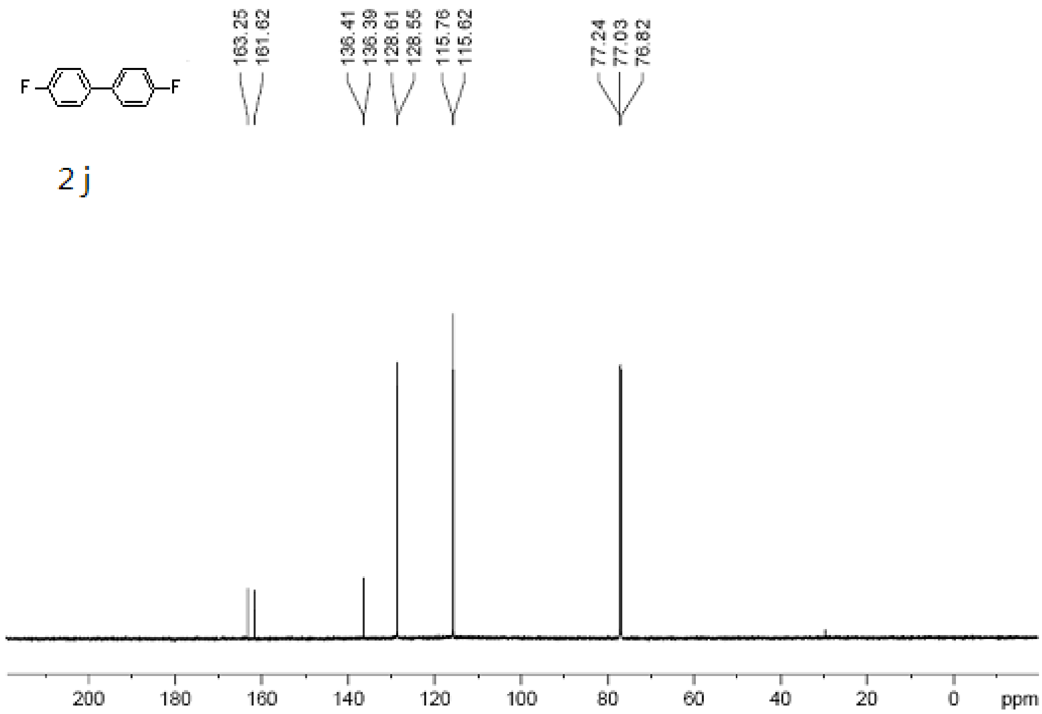
(9) 4,4′-Di(trifluoromethyl)methoxy biphenyl (**2i**)



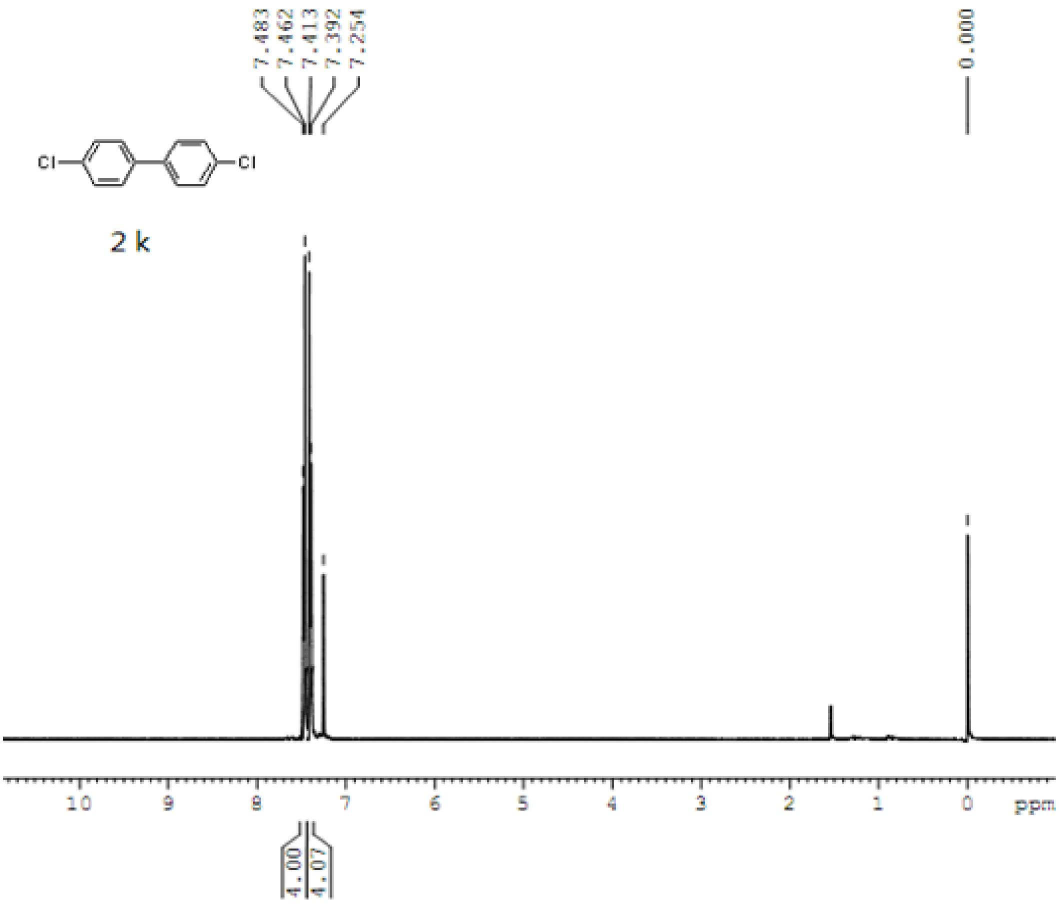


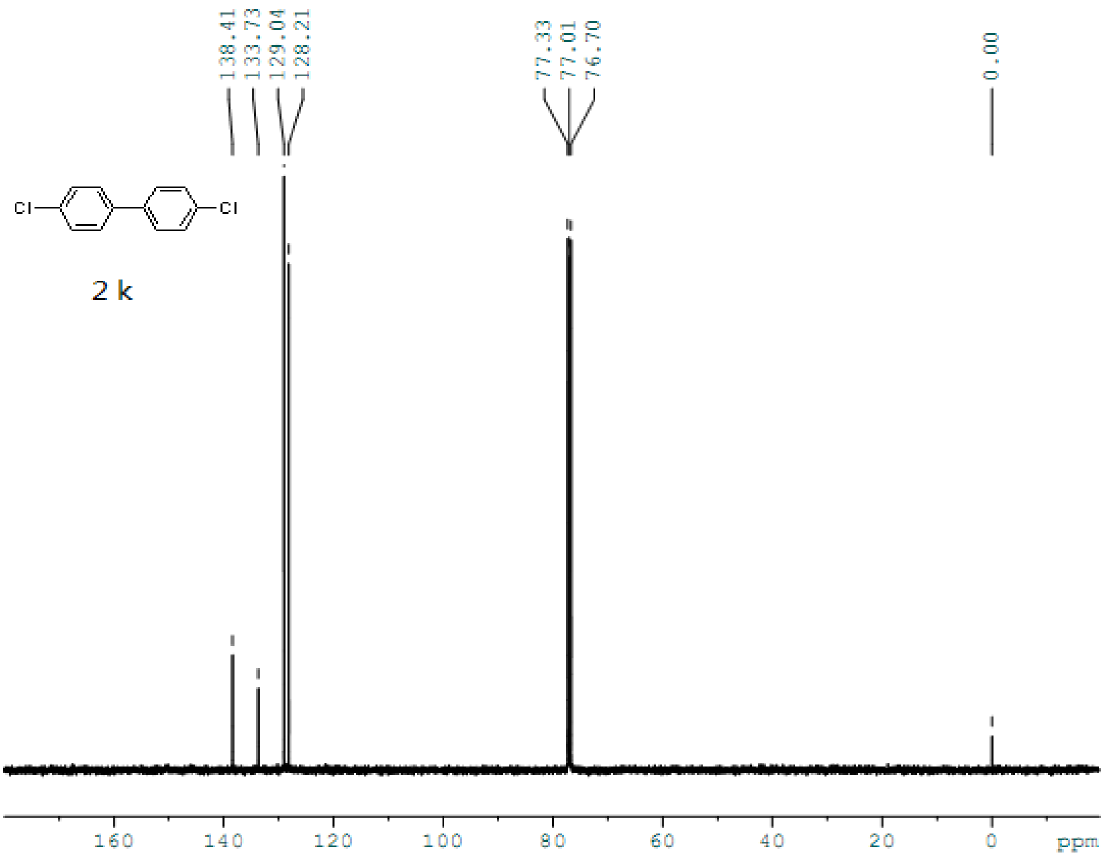
(10) 4,4′-Difluorobiphenyl (**2 j**)



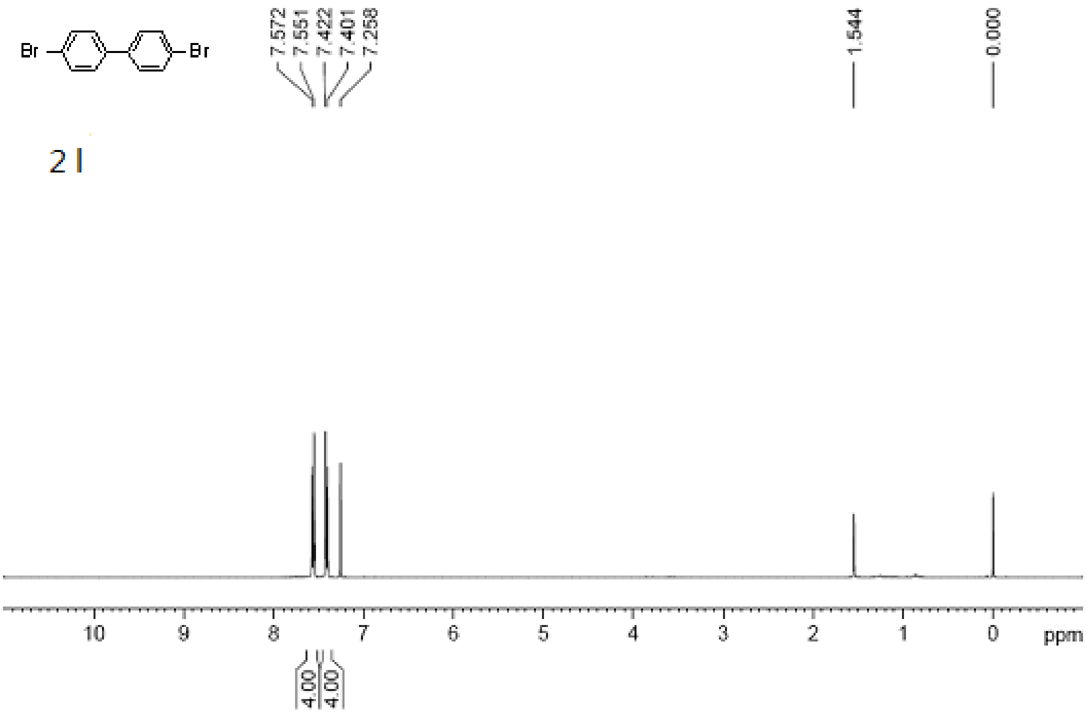


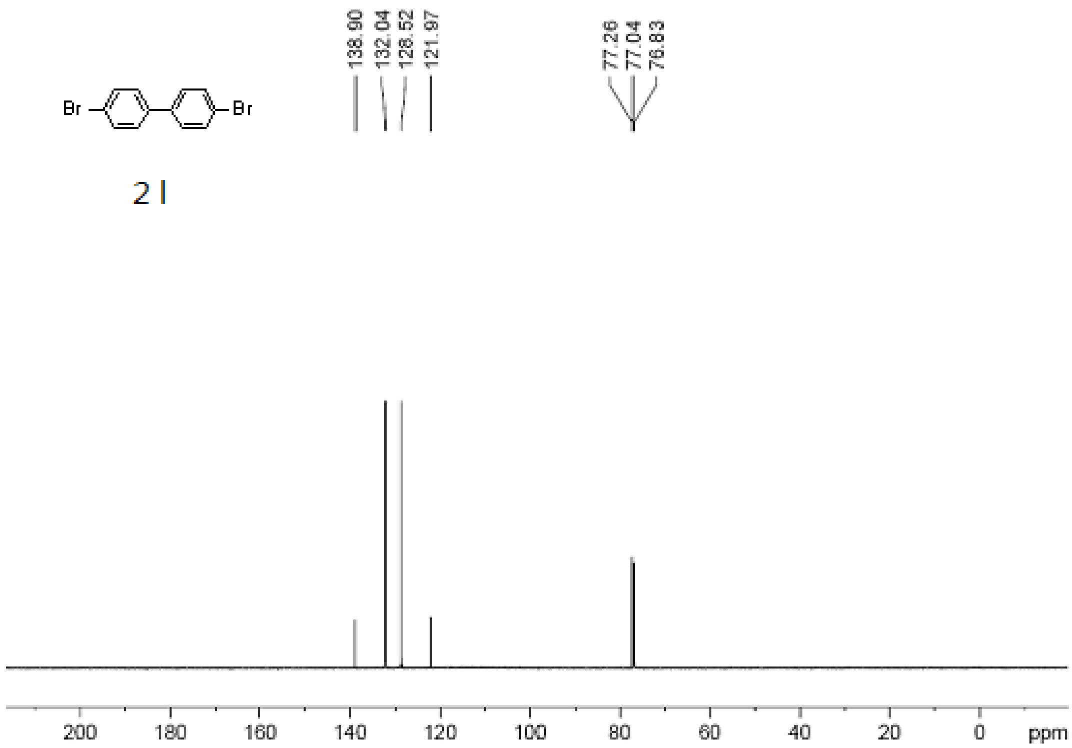
(11) 4,4′-Dichlorobiphenyl (**2k**)



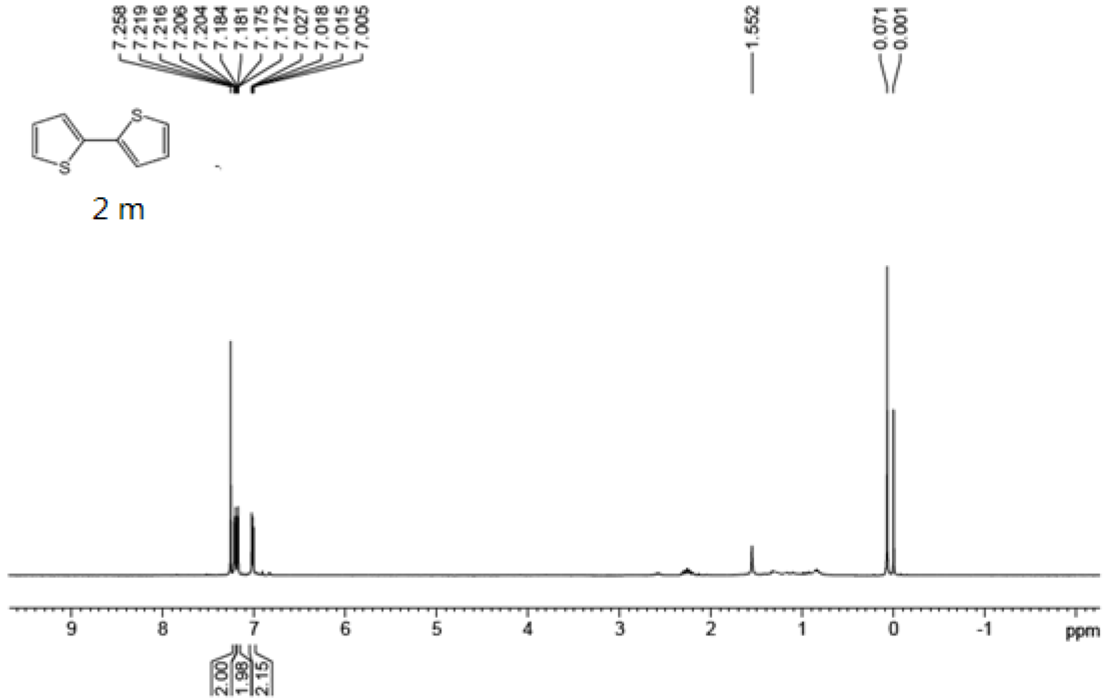


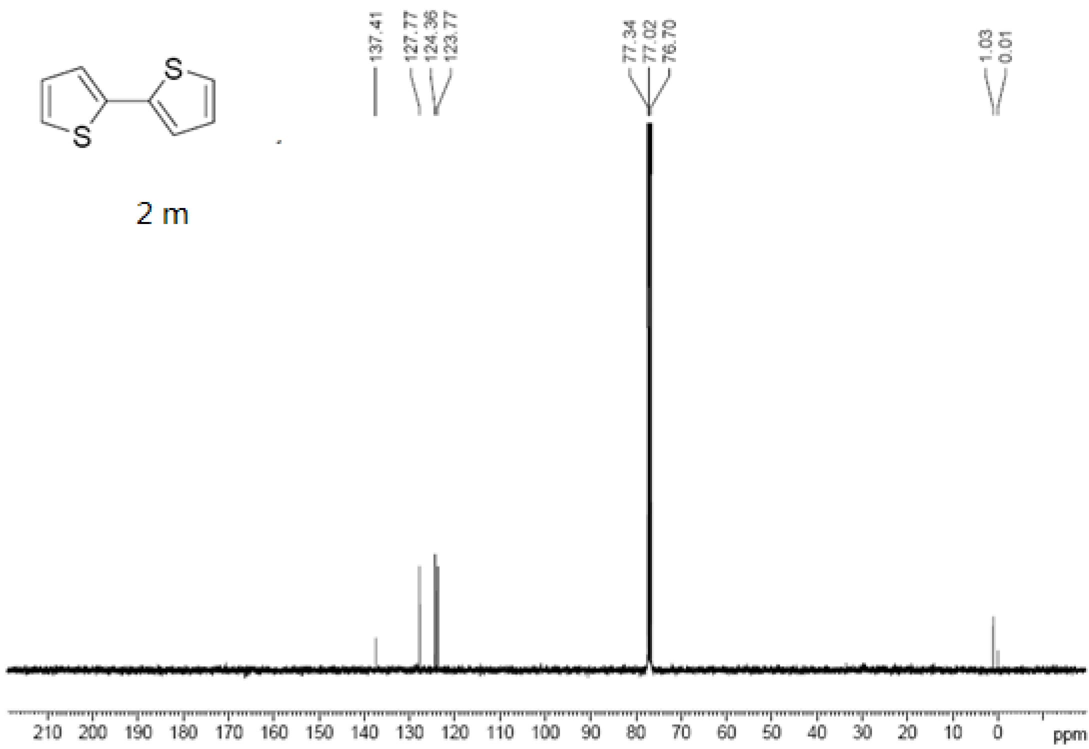
(12) 4,4′-dibromobiphenyl (**2l**)





(13) 2,2'-Bithiophene (**2m**)





MOP4 (low solubility in organic solvent)