Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Mechanochemical Palladium-Catalyzed C(sp2)-H Homocoupling of N-Arylcarbamates: Synthesis of 2,2'-Biaryldiamines

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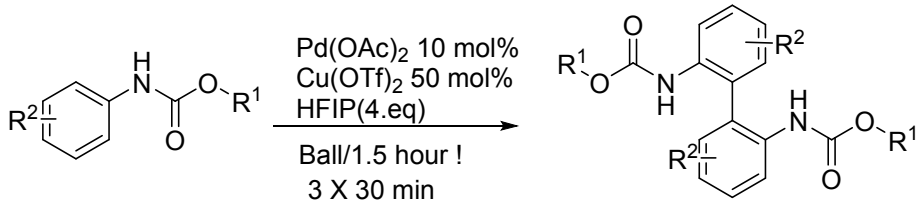
Contents

1. General information:

All the reagents were used as received, unless otherwise indicated. TLC analysis was performed using precoated glass plates. All of the cross-dehydrogenative coupling reactions were conducted in a Mixer Mill (MM 400 RetschGmbh, Hann, Germany) with 25 mL stainless-steel grinding vessels and stainless-steelballs (d = 12 mm). Melting points (m. p.) were obtained on a digital melting point apparatus and are uncorrected. NMR spectra were recorded with a 600 MHz spectrometer for ^{1}H and 151 MHz for ^{13}C, respectively, and TMS was used as an internal standard. The following abbreviations (or combinations there of) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J* were reported in Hertz unit (Hz). Mass spectra were measured with Thermo Finnigan LCQ-Advantage. High resolution mass spectral (HRMS) analyze were measured on a Bruker micr OTOF-Q II instrument using ESI or EI techniques. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR and MS data with those of literature.

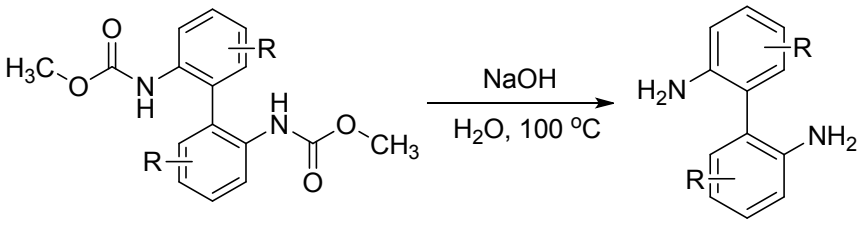
2. General experimental procedure for the synthesis of compounds 2



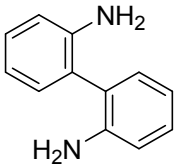
1 **2**

A mixture of the substrate methyl phenylcarbamate (0.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.05 mmol, 0.1 equiv), $Cu(OTf)_2$ (0.25 mmol, 0.5 equiv), HFIP (2 mmol, 4 equiv) and silica gel (0.6 g) was placed in a 25 mL screw-capped stainless-steel vessel, along with four stainless-steel balls two stainless-steel balls (12 mm, $\mathbf{\Phi_{MB}}$ = 0.057). Then, the vessel was placed in the mixer mill, and the contents were milled at 30 Hz for 90 min. At the end of the experiment, all of the reaction mixtures were scratched off from the vessel and dissolved in ethyl acetate followed by concentrating in vacuo to give a residue, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give the desired product **2**.

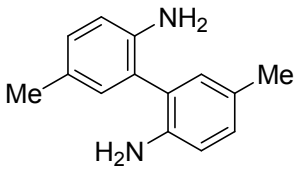
3. General experimental procedure for the synthesis of compounds 3



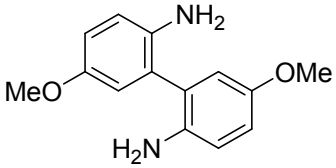
2 **3**



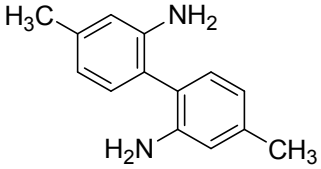
3a, 92%



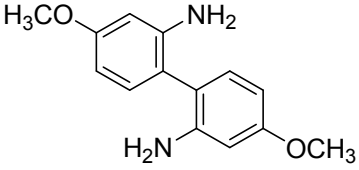
3d, 84%



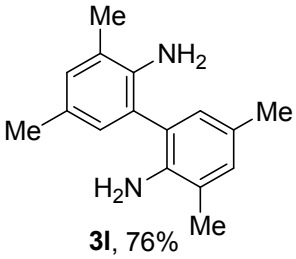
3e, 75%



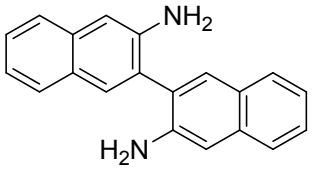
3i, 87%



3j, 89%



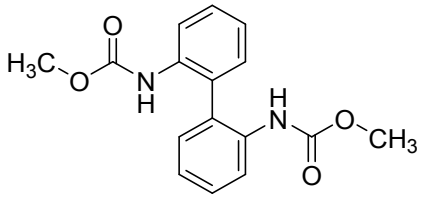
3l, 76%



3q, 87%

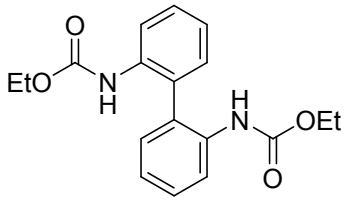
A mixture of **2** (0.5 mmol), sodium hydroxide (0.1mol), water (20 mL) as solvent in a 50 mL flask was heated at 100 °C for 4 - 24 hours. After being cooled to room temperature, the mixture was extracted with ethyl acetate, and the solvents were removed by rotary evaporation to provide raw product. Then the raw product was purified on silica gel (petroleum ether/ethyl acetate = 4:1) to give the desired product **3**.

^{1}H and ^{13}C NMR data



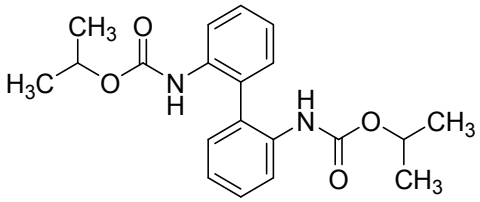
2 a

dimethyl N,N'-(biphenyl-2,2'-diyl)biscarbamate (2a)[1]: White solid, (56 mg, 75%), m. p. 142 - 143 °C, (lit.144.5 - 145.5 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.46 - 7.43 (m, 2H), 7.19 - 7.15 (m, 4H), 6.34 (s, 2H), 3.68 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 135.9, 130.4, 129.7, 126.3, 123.8, 120.0, 52.3. MS (ESI): *m/z* 323.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{16}N_2NaO_4$, m/z 323.1002, Found 323.1014.



2 b

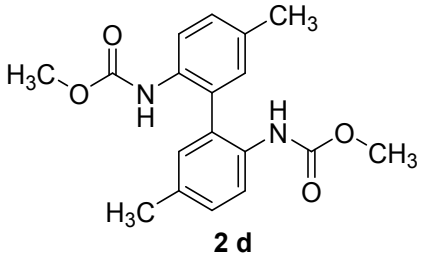
diethyl [1,1'-biphenyl]-2,2'-diyldicarbamate (2b): White solid, (62 mg, 76%), m. p. 125 - 126 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.5 Hz, 2H), 7.45 - 7.42 (m, 2H), 7.18 - 7.15 (m, 4H), 6.32 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 136.0, 130.4, 129.6, 126.3, 123.7, 120.0, 61.3, 14.4. MS (ESI): *m/z* = 351.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M+Na]^+$ $C_{18}H_{20}N_2NaO_4$, m/z 351.1315, Found 351.1315.



2 c

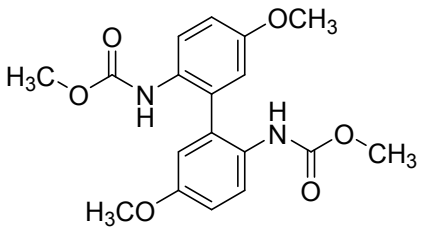
diisopropyl [1,1'-biphenyl]-2,2'-diyldicarbamate (2c): White solid, (69 mg, 77%), m. p. 94 - 95 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.45 - 7.42 (m, 2H), 7.18 - 7.15 (m, 4H), 6.28 (s, 2H), 4.94 (m, 2H), 1.22 - 1.21 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.1, 136.1, 130.5, 129.5, 126.2, 123.5, 119.9, 68.9, 21.9, 21.9.

MS (ESI): *m/z* = 379.2 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_4$, m/z 379.1628, Found 379.1610.



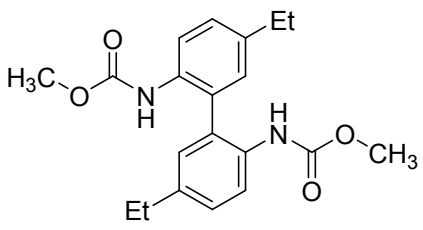
2 d

dimethyl (5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2d): White solid, (66 mg, 80%), m. p. 170 - 172 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.22 (dd , *J* = 1.7, 8.4 Hz, 2H), 6.95 (d, *J* = 1.6 Hz, 2H), 6.26 (s, 2H), 3.68 (s, 6H), 2.33 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 133.4, 133.2, 130.8, 130.1, 126.8, 120.1, 52.2, 20.7. MS (ESI): *m/z* = 351.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{18}H_{20}N_2NaO_4$, m/z 351.1315, Found 351.1311.



2 e

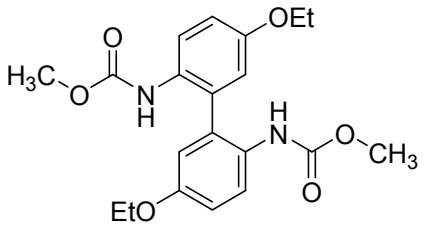
dimethyl (5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2e): White solid, (60 mg, 67%), m. p. 129 - 131 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 2H), 6.97 (dd, *J* = 2.8, 9.0 Hz, 2H), 6.70 (d, *J* = 2.8 Hz, 2H), 6.20 (s, 2H), 3.80 (s, 6H), 3.67 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 154.6, 128.7, 122.7, 117.6, 115.3, 114.8, 55.6, 52.3. MS (ESI): *m/z* = 383.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{18}H_{20}N_2NaO_6$, m/z 383.1214, Found 383.1196.



2 f

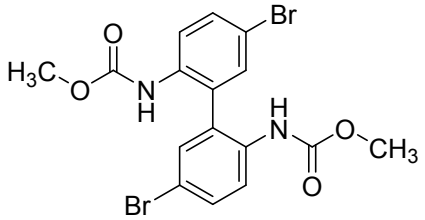
dimethyl (5,5'-diethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2f): White solid, (70 mg, 78%), m. p. 105 - 108 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.26 (dd, *J*

= 8.4, 2.6Hz, 2H), 6.99 (d, *J* = 1.9 Hz, 2H), 6.29 (s, 2H), 3.68 (s, 6H), 2.64 (q, *J* = 7.6 Hz, 4H), 1.24 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 139.9, 133.3, 129.6, 128.9, 127.0, 120.3, 52.2, 28.1, 15.5. MS (ESI): *m/z* = 379.2 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_4$, m/z 379.1628, Found 379.1612.



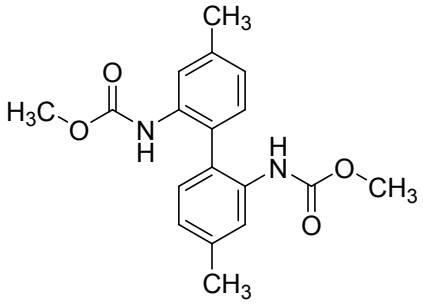
2 g

dimethyl (5,5'-diethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2g): White solid, (61 mg, 63%), m. p. 175 - 177 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 2H), 6.96 (dd, *J* = 9.0, 2.9 Hz, 2H), 6.69 (d, *J* = 2.9 Hz, 2H), 6.19 (s, 2H), 4.01 (q, *J* = 7.0 Hz, 4H), 3.66 (s, 6H), 1.40 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 154.5, 142.6, 128.6, 122.8, 115.9, 115.4, 63.8 , 52.2, 14.8. MS (ESI): *m/z* = 411.2 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_6$, m/z 411.1527, Found 411.1526.



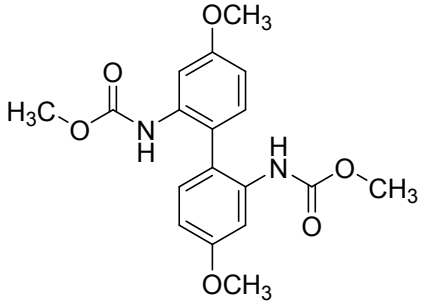
2 h

dimethyl (5,5'-dibromo-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2h): Yellow Oil, (40 mg, 35%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.57 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.29 (d, *J* = 2.3 Hz, 2H), 6.22 (s, 2H), 3.71 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 138.1, 134.1, 132.7, 131.2, 129.8, 119.2, 52.4. MS (ESI): *m/z* = 478.9 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{16}H_{14}N_2NaO_4$, *m/z* 478.9213, Found 478.9223.



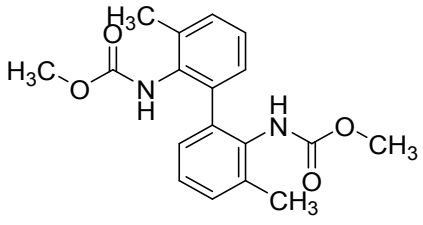
2 i

dimethyl (4,4'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2i): White solid, (71 mg, 87%), m. p. 153 - 154 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.33 (s, 2H), 3.68 (s, 6H), 2.41 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 139.6, 135.7, 130.3, 124.6, 123.4, 120.4, 52.2, 21.6. MS (ESI): *m/z* = 351.1 $[M + Na]^+$. HRMS (ESI) calcdfor $[M + Na]^+$ $C_{18}H_{20}N_2NaO_4$, *m/z* 351.1315, Found 351.1300.



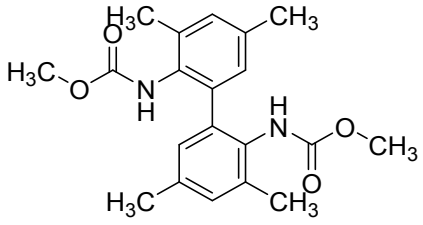
2 j

dimethyl (4,4'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2j): White solid, (79 mg, 88%), m. p. 177 - 179 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.69 (dd, *J* = 8.4, 2.6 Hz, 2H), 6.38 (s, 2H), 3.87 (s, 6H), 3.69 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 153.7, 137.4, 131.5, 117.5, 110.0, 104.5, 55.4, 52.3. MS (ESI): *m/z* = 383.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{18}H_{20}N_2NaO_6$, *m/z* 383.1214, Found 383.1201.



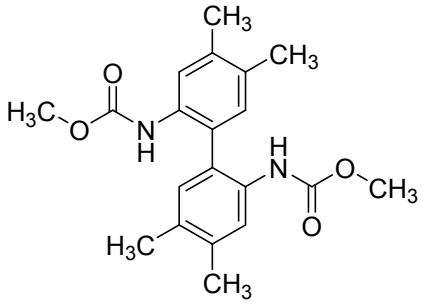
2 k

dimethyl (3,3'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2k): White solid, (57 mg, 70%), m. p. 165-167 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.3, Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.40 (s, 2H), 3.58 (s, 6H), 2.31 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 137.8, 136.4, 133.3, 130.3, 127.5, 126.8, 52.4, 18.3. MS (ESI): *m/z* = 351.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{18}H_{20}N_2NaO_4$, 351.1315, Found 351.1304.



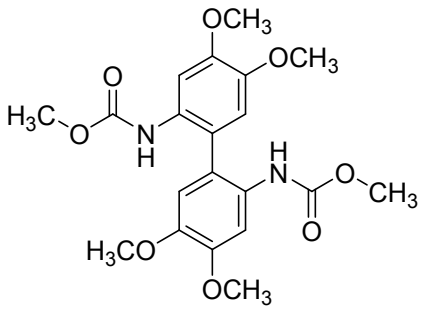
2 l

dimethyl (3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2l): White solid, (67 mg, 75%), m. p. 171 - 173 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.78 (s, 2H), 6.30 (s, 2H), 3.59 (s, 6H), 2.28 (d, *J* = 16.7 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 137.6, 136.4, 136.0, 130.9, 130.7, 128.0, 52.3, 20.9, 18.2. MS (ESI): *m/z* = 379.2 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_4$, 379.1628, Found 379.1609.



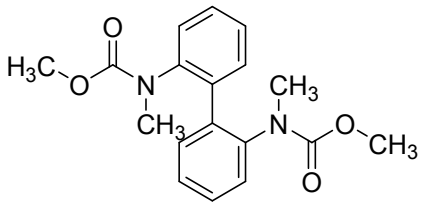
2 m

dimethyl (4,4',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2m): White solid, (67 mg, 75%), m. p. 188 - 190 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 2H), 6.88 (s, 2H), 6.26 (s, 2H), 3.68 (s, 6H), 2.32 (s, 6H), 2.23 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 137.9, 133.4, 132.2, 131.3, 121.2, 100.0, 52.2, 19.9, 19.1. MS (ESI): *m/z* = 379.2 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_4$, 379.1628, Found 379.1619.



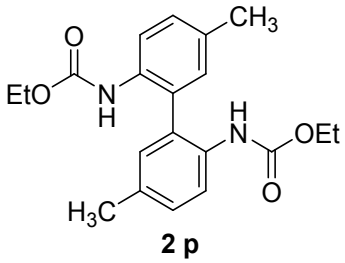
2 n

dimethyl (4,4',5,5'-tetramethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2n): White solid, (70 mg, 67%), m. p. 193 - 195 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 2H), 6.64 (s, 2H), 6.27 (s, 2H), 3.96 (s, 6H), 3.84 (s, 6H), 3.68 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 149.4, 145.3, 129.6, 117.7, 113.1, 104.3, 56.2, 60.0, 52.2. MS (ESI): *m/z* = 443.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_8$, 443.1425, Found 443.1413.



2 o

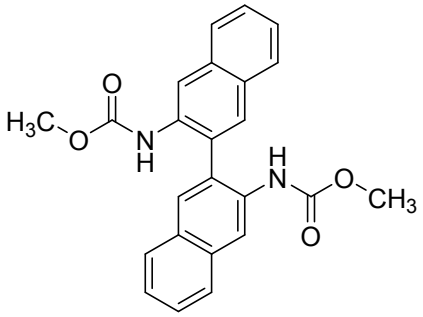
dimethyl [1,1'-biphenyl]-2,2'-diylbis(methylcarbamate) (2o): White solid, (69 mg, 84%), m. p. 130 - 133 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 - 7.30 (m, 5H), 7.26 - 7.22 (m, 3H), 3.69 - 3.50 (m, 6H), 2.88 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 140.6, 135.9, 130.9, 128.5, 127.1, 94.8, 52.8, 37.1. MS (ESI): *m/z* = 443.1 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{18}H_{20}N_2NaO_4$, 351.1315, Found 351.1330.



2 p

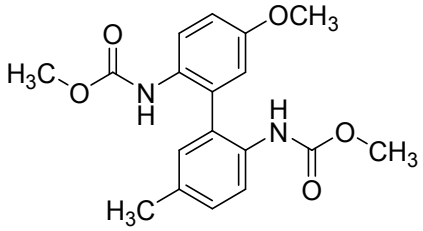
diethyl (5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2p): White solid, (77 mg, 87%), m. p. 138 - 140°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.22 (dd, *J* = 8.4, 1.3 Hz, 2H), 6.95 (d, *J* = 1.3 Hz, 2H), 6.24 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 2.33

(s, 6H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 133.3, 133.2, 130.8, 130.0, 126.7, 120.1, 61.1, 20.7, 14.4. MS (ESI): m/z = 379.2 $[M + Na]^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{20}H_{24}N_2NaO_4$, 379.1628, Found 379.1610.



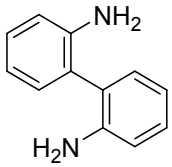
2 q

dimethyl [2,2'-binaphthalene]-3,3'-diyldicarbamate (2q): White solid, (67 mg, 67%), m. p. 209 - 211 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.76 (s, 2H), 7.55 (t, J = 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 2H), 6.47 (s, 2H), 3.69 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 134.2, 133.5, 130.2, 129.7, 127.7, 127.5, 127.2, 126.5, 125.4, 116.5, 52.3. MS (ESI): m/z = 423.1 [M + Na]$^+$. HRMS (ESI) calcd for $[M + Na]^+$ $C_{24}H_{20}N_2NaO_4$, 423.1315, Found 423.1310.



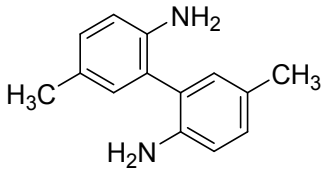
2 r

dimethyl (5-methoxy-5'-methyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate (2r): White solid, (63 mg, 73%), m. p. 119 - 121 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.23 (dd, J = 8.4, 1.7 Hz, 1H), 6.97 (dd, J = 9.2, 3.1 Hz, 2H), 6.69 (d, J = 3.0 Hz, 1H), 6.29 (s, 1H), 6.16 (s, 1H), 3.80 (s, 3H), 3.67 (d, J = 6.0 Hz, 6H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 154.1, 136.1, 133.5, 133.1, 130.6, 130.2, 128.8, 120.4, 115.4, 114.8, 107.9, 55.6, 52.2, 20.7, 20.7. MS (ESI): m/z = 367.1 $[M + Na]^+$. HRMS (ESI) calcd for $C_{18}H_{20}N_2NaO_5$, 367.1264, Found 367.1250.



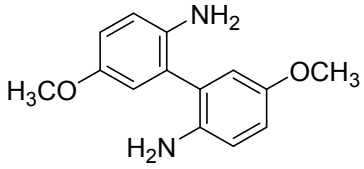
3 a

2,2′-diaminebiphenyl (3a)[2]: brown solid, (85 mg, 92%), m. p. 81.1 - 83.6 ºC, (lit. 79 - 80 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (t, *J* = 6.7 Hz, 2H), 7.14 (d, *J* = 6.7 Hz, 2H), 6.85 (t, *J* = 6.6 Hz, 2H), 6.79 (d, *J* = 7.5 Hz, 2H), 3.71 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 131.0, 128.7, 124.5, 118.7, 115.5. MS (ESI): *m/z* = 185.1 $[M + H]^+$.



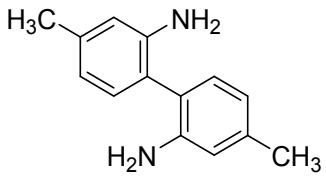
3d

2,2'-dibro-5,5'-dimethylbipheny (3d)[3]: Yellow solid, (92 mg, 87%), m. p. 145.1 - 148.7 ºC, (lit. 140 - 141 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 4H), 2.29 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 131.4, 129.2, 128.0, 125.0, 115.7, 20.4. MS (ESI): *m/z* = 213.1 $[M + H]^+$. HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{17}N_2$, 213.1386, Found 213.1394.



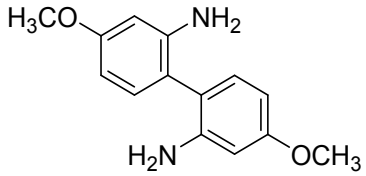
3e

5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diamine (3e): White solid, (92 mg, 75%), m. p. 102 - 105 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 (dd, *J* = 8.7, 2.9 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 2.9 Hz, 2H), 3.76 (s, 6H), 3.57 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 137.4, 125.9, 117.1, 115.8, 115.0, 55.7. MS (ESI): *m/z* = 225.1 $[M + H]^+$. HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{17}N_2O_2$, 245.1285, Found 245.1284.



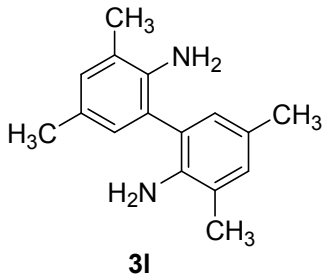
3i

4,4'-dimethyl-[1,1'-biphenyl]-2,2'-diamine (3i): Brown solid, (89 mg, 84%), m. p. 119 - 122 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.6 Hz, 2H), 6.67 (dd, *J* = 7.6, 0.4 Hz, 2H), 6.63 (s, 2H), 3.65 (s, 4H), 2.32 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 138.5, 131.0, 121.9, 119.8, 116.3, 21.2. MS (ESI): *m/z* = 213.1 $[M + H]^+$. HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{17}N_2$, 213.1386, Found 213.1385.



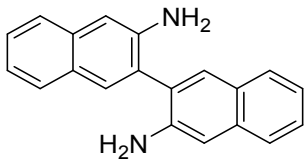
3j

2,2'-diamino-4,4'-dimethoxy-diphenyl (3j)[4]: White solid, (109 mg, 89%), m. p. 106.0 - 108.6 °C, (lit. 140 - 141 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.3 Hz, 2H), 6.40 (dd, *J* = 8.3, 2.5 Hz, 2H), 6.34 (d, *J* = 2.4 Hz, 2H), 3.80 (s, 6H), 3.68 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 145.5, 132.1, 117.1, 104.3, 100.9, 55.1. MS (ESI): *m/z* = 245.1 $[M + H]^+$. HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{17}N_2O_2$, 245.1285, Found 245.1278.



3l

3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-diamine (3l): White solid, (91 mg, 76%), m. p. 168 - 171 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.83 (s, 2H), 3.51 (s, 4H), 2.26 (s, 6H), 2.22 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.6, 130.5, 129.0, 127.5, 124.8, 122.7, 20.3, 17.8. MS (ESI): *m/z* = 241.2 $[M + H]^+$. HRMS (ESI) calcd for $[M + H]^+$ $C_{16}H_{21}N_2$, 241.1699, Found 241.1695.



3q

3,3'-diamino-2,2'-dinaphthyl (3q)[5]: brown solid, (124 mg, 87%), m. p. 217.2 - 219.4 °C, (lit. 215 - 220 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 - 7.69 (m, 4H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.14 (s, 2H), 3.82 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 134.8, 130.3, 128.0, 127.7, 127.5, 126.5, 125.5, 122.8, 109.3. MS (ESI): *m/z* = 285.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{20}H_{17}N_2$, 285.1386, Found 285.1392.

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1. A. L. J. Beckwith, *Aust. J. Chem.* 1990, **43**, 451.
2. A. E. Blood, C. R. Noller, *J. Org. Chem*. 1959, **22**, 711.
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5. R. F. Curtis, G. Viswanath, *J. Chem. Soc.* 1959, **331**, 1670.

Copies of ^{1}H and ^{13}C NMR Spectra

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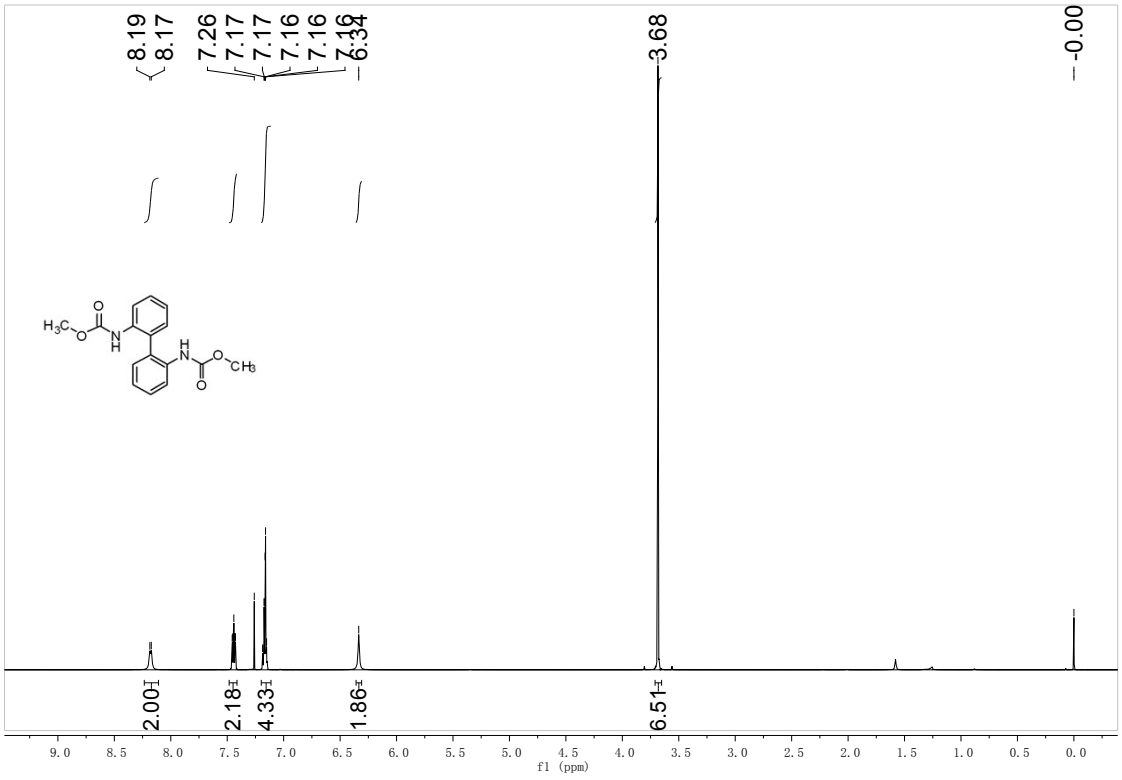
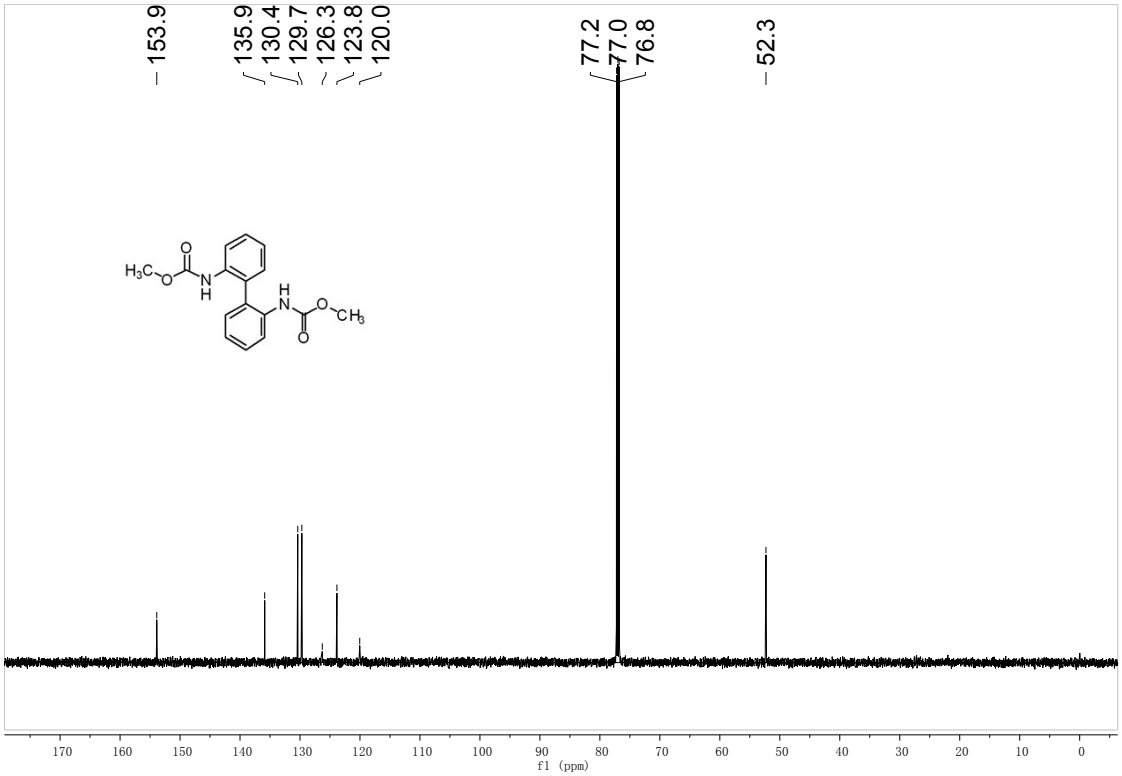
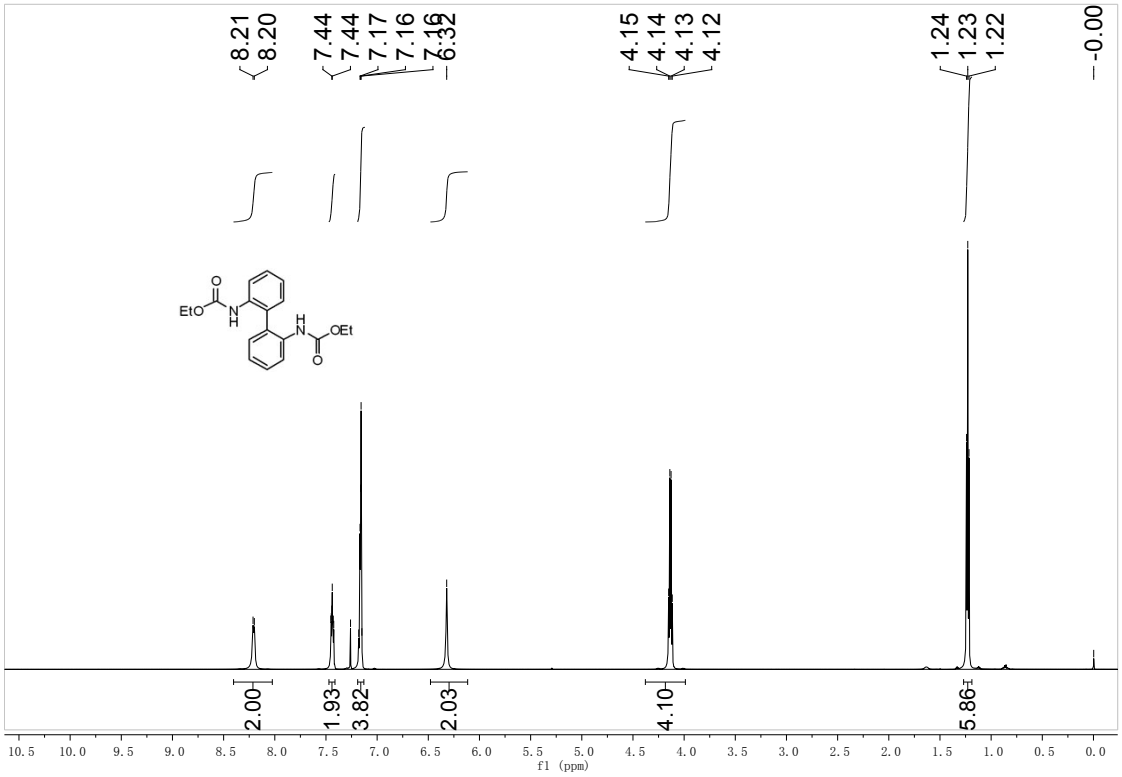
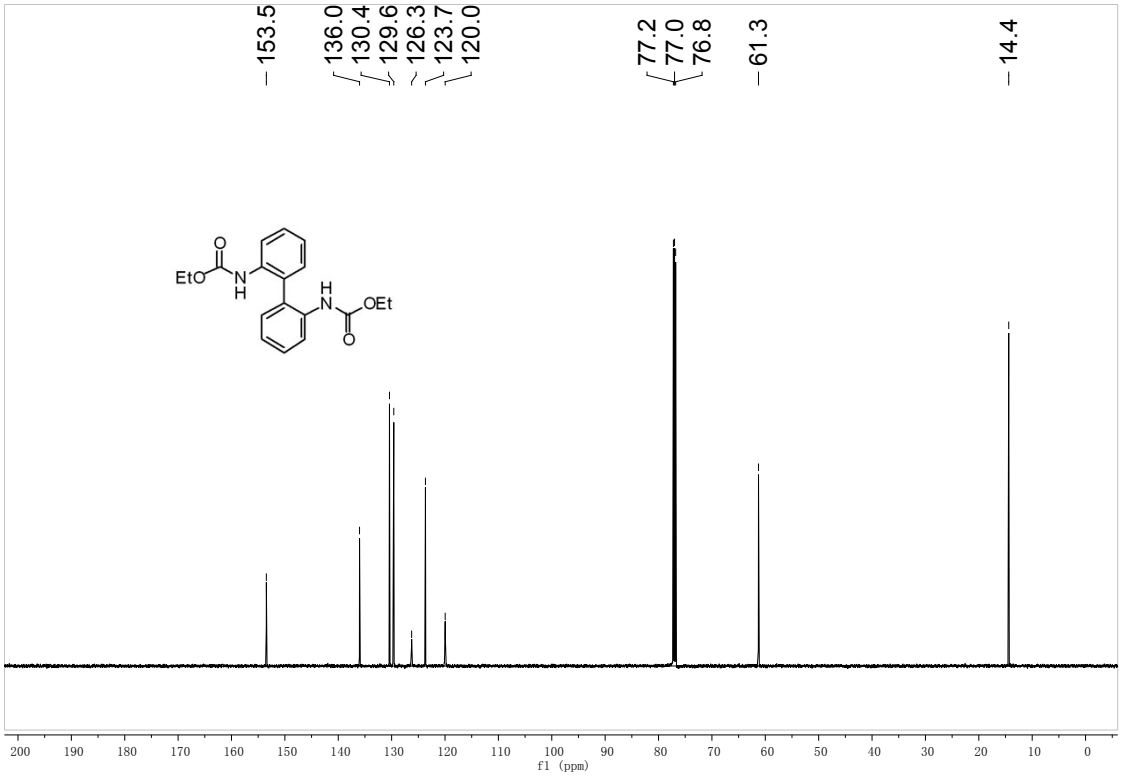


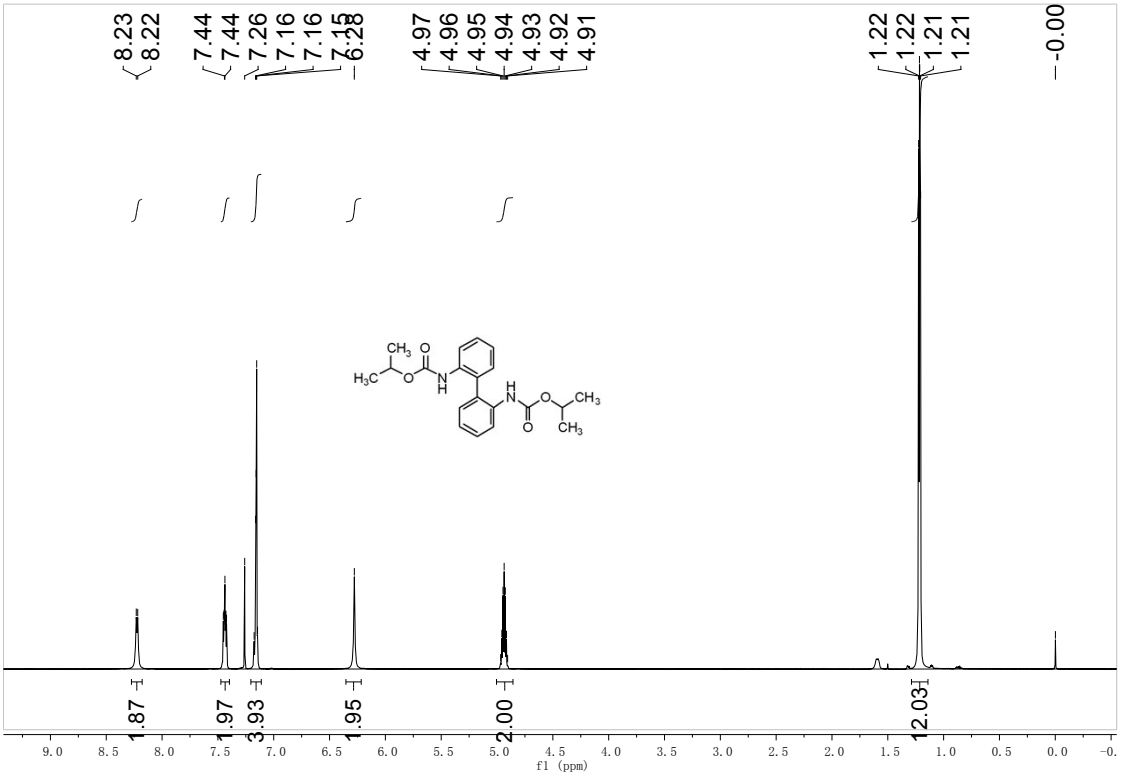


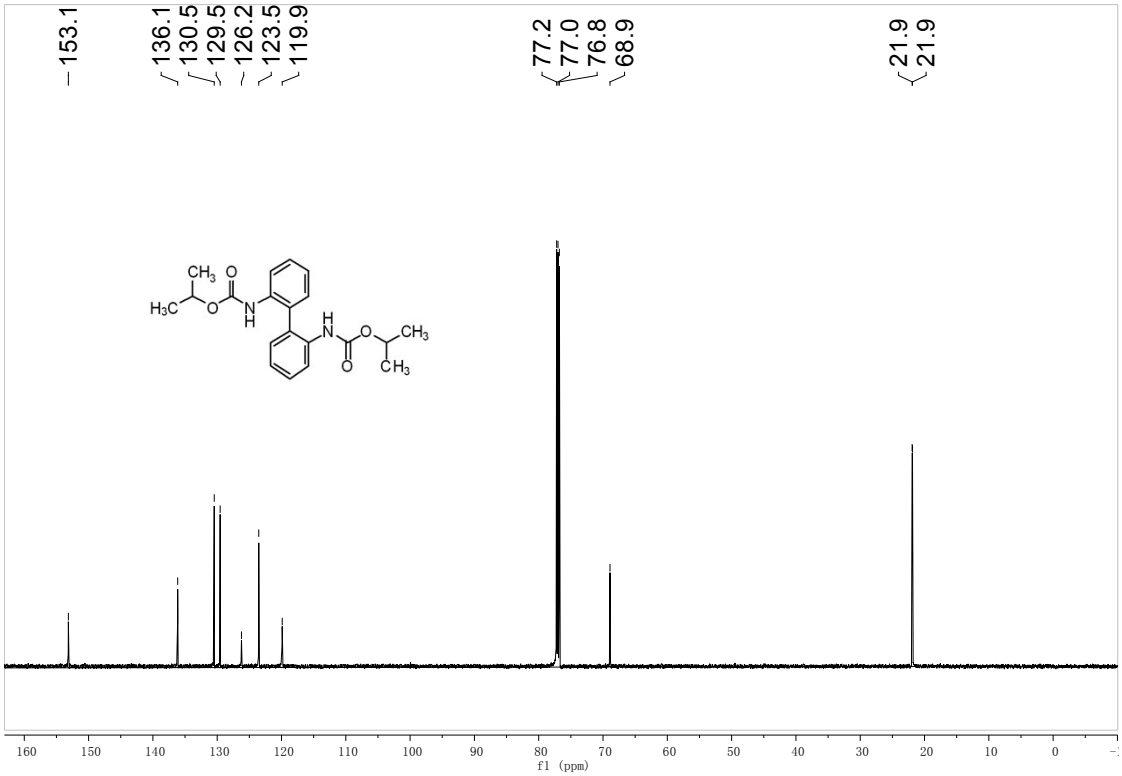
diethyl [1,1'-biphenyl]-2,2'-diyldicarbamate(2b)



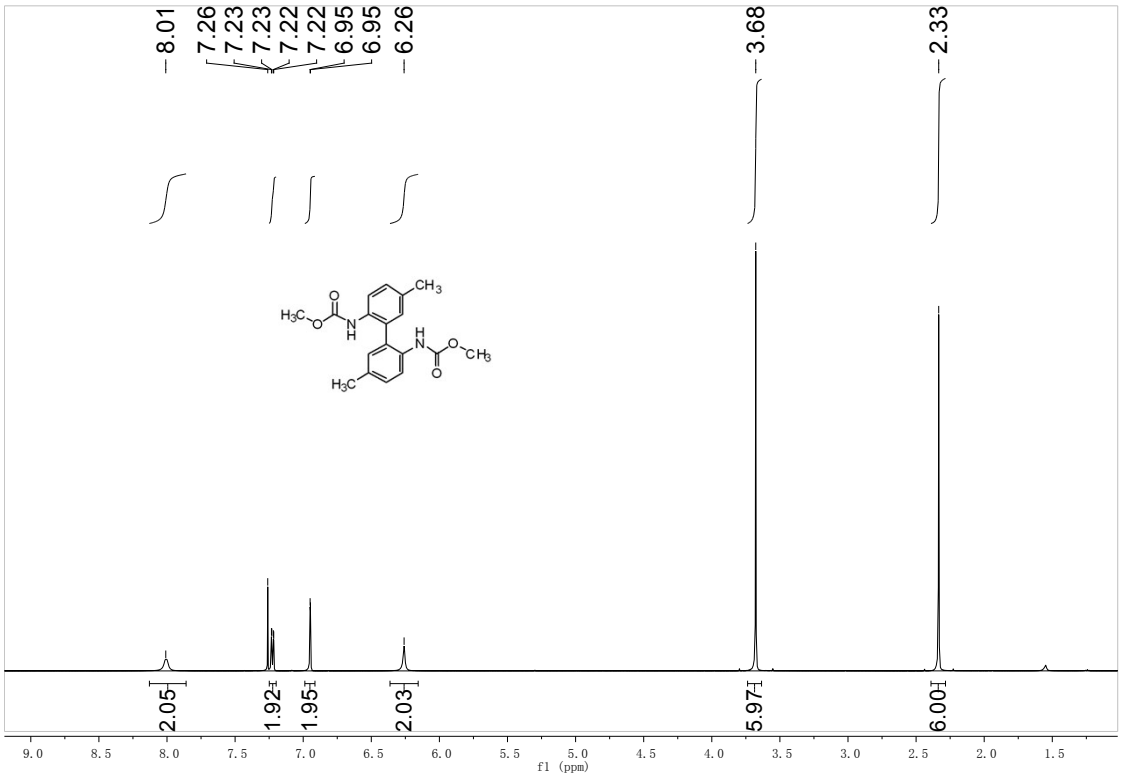


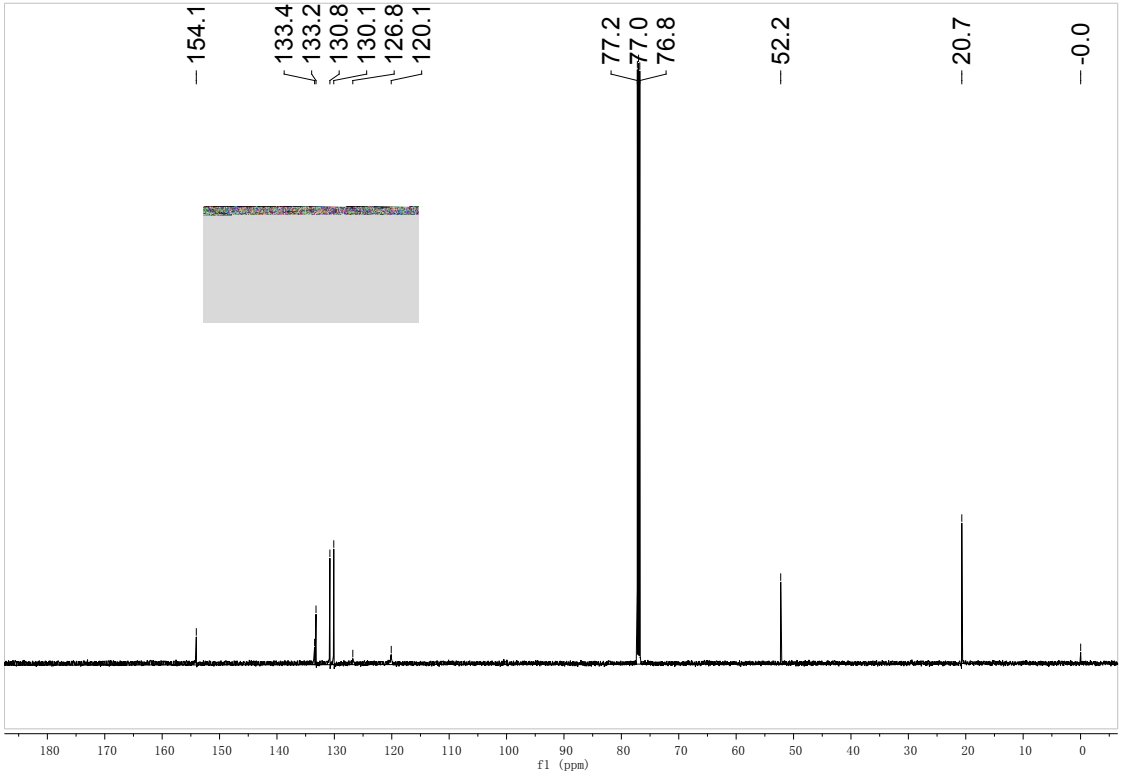
diisopropyl [1,1'-biphenyl]-2,2'-diyldicarbamate(2c)



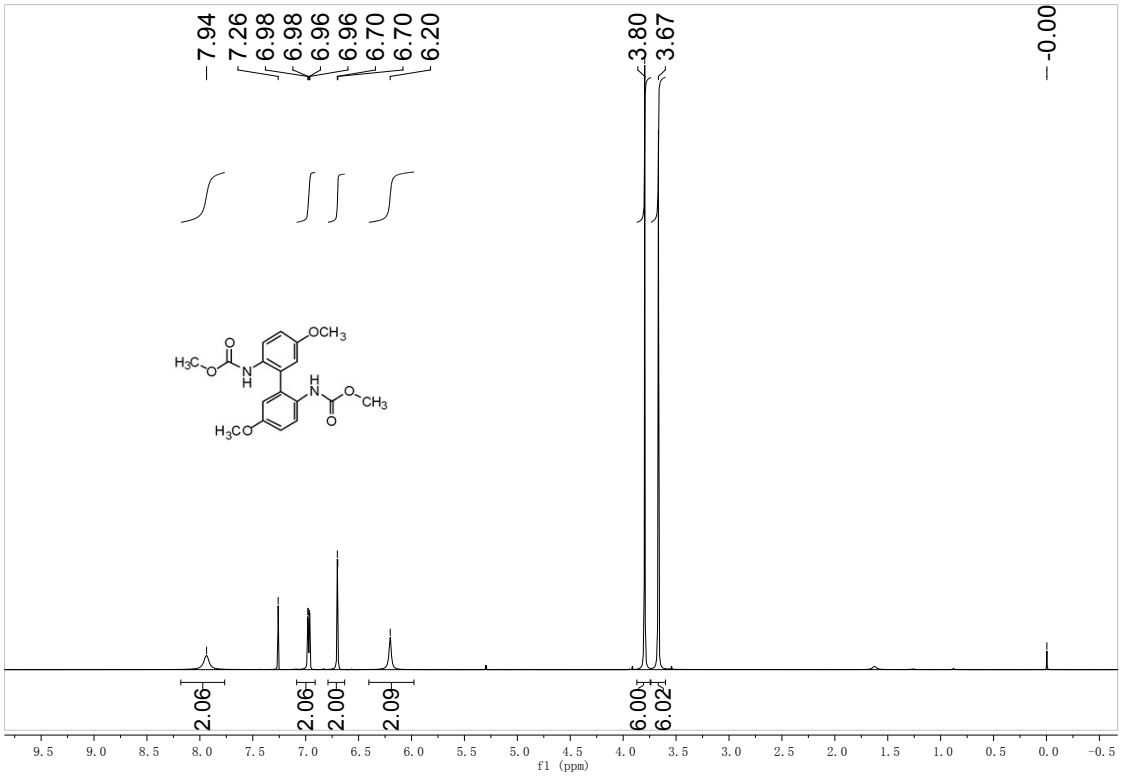


dimethyl (5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2d)





dimethyl (5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2e)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6.98
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6.96
6.70
6.70
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3.80
3.67
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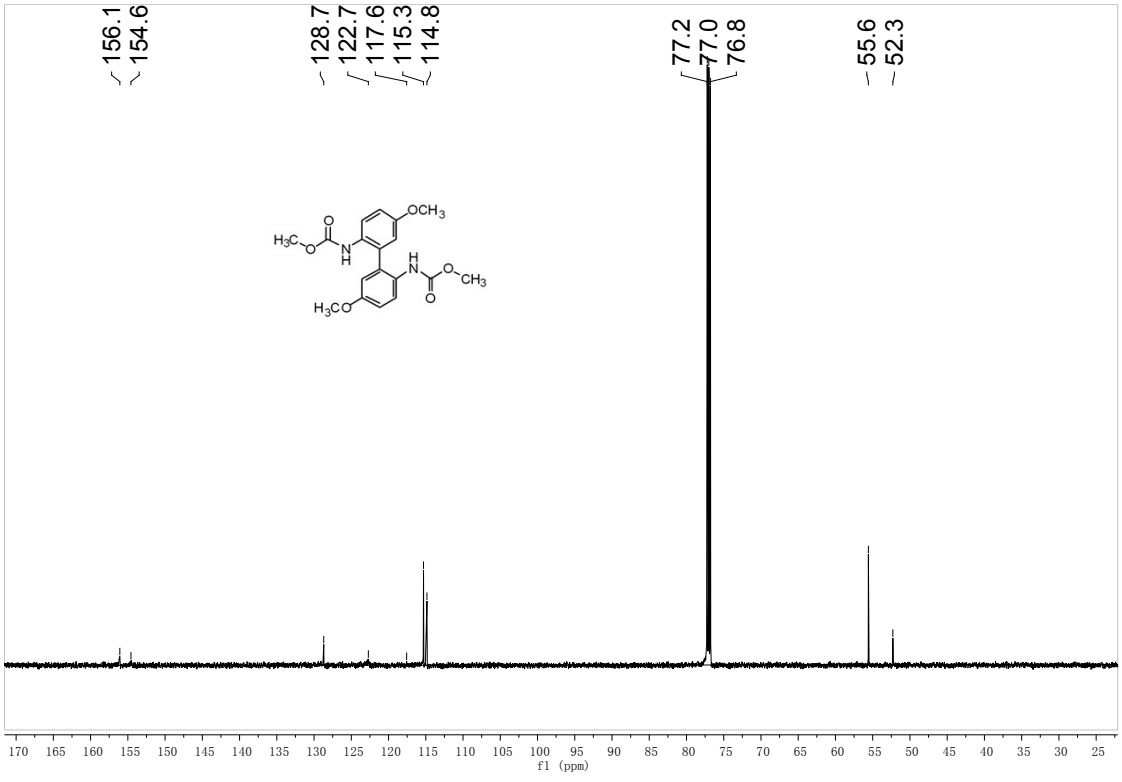
2.06
2.00
2.09
6.00
6.02
f1 (ppm)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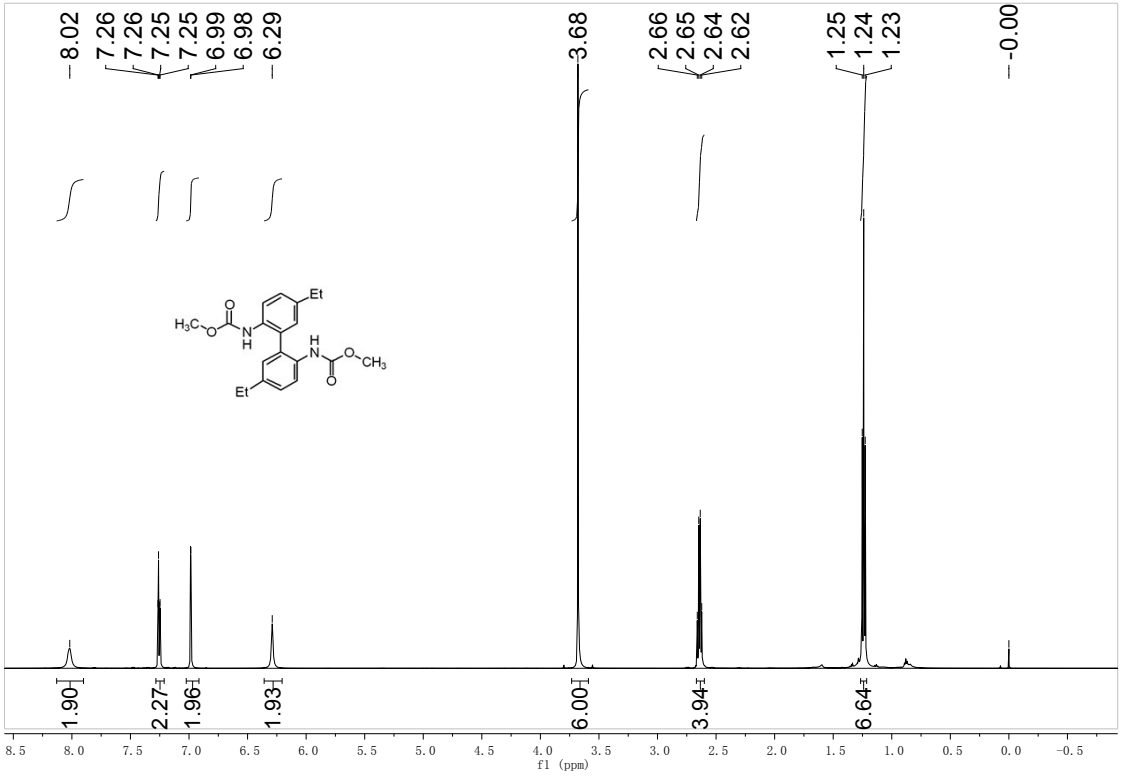
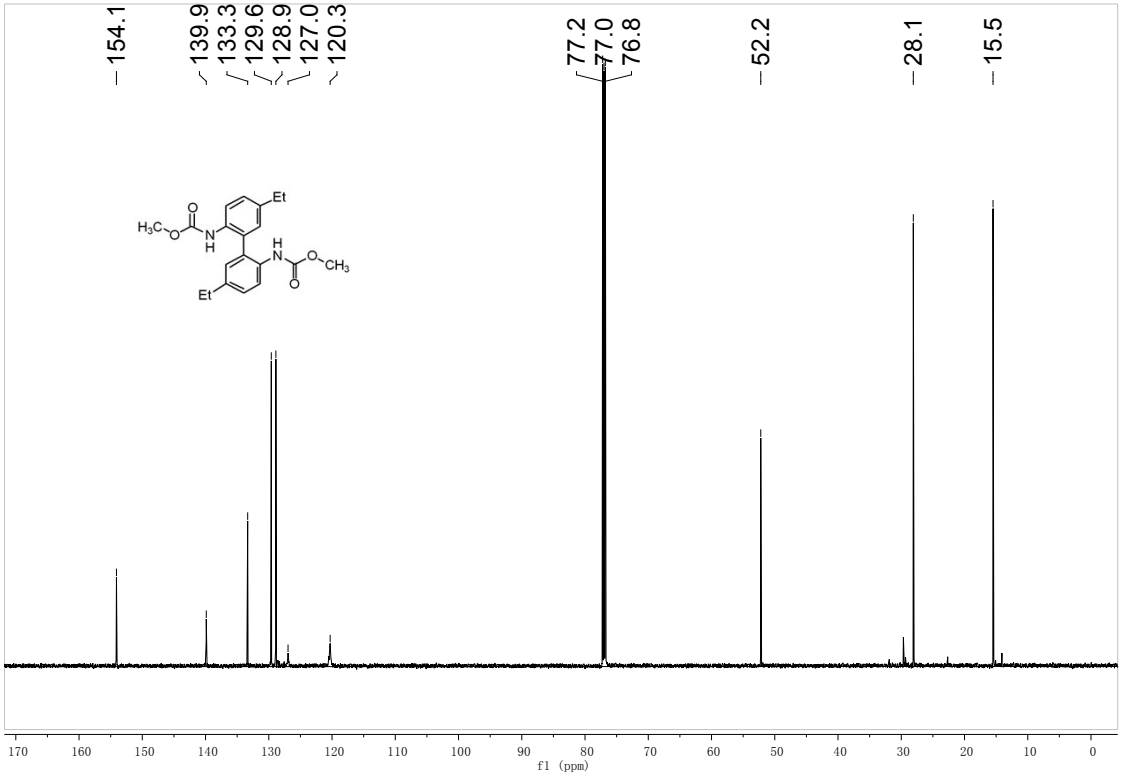
76.8
55.6
52.3
f1 (ppm)

dimethyl (5,5'-diethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2f)





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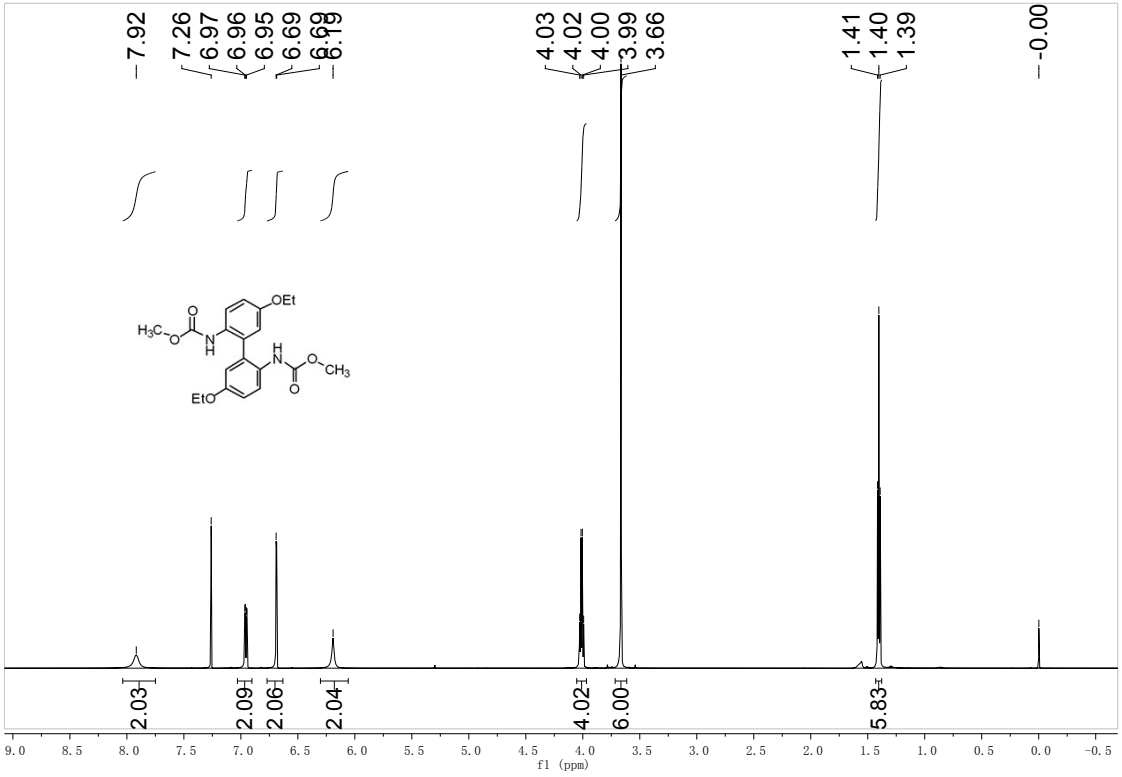
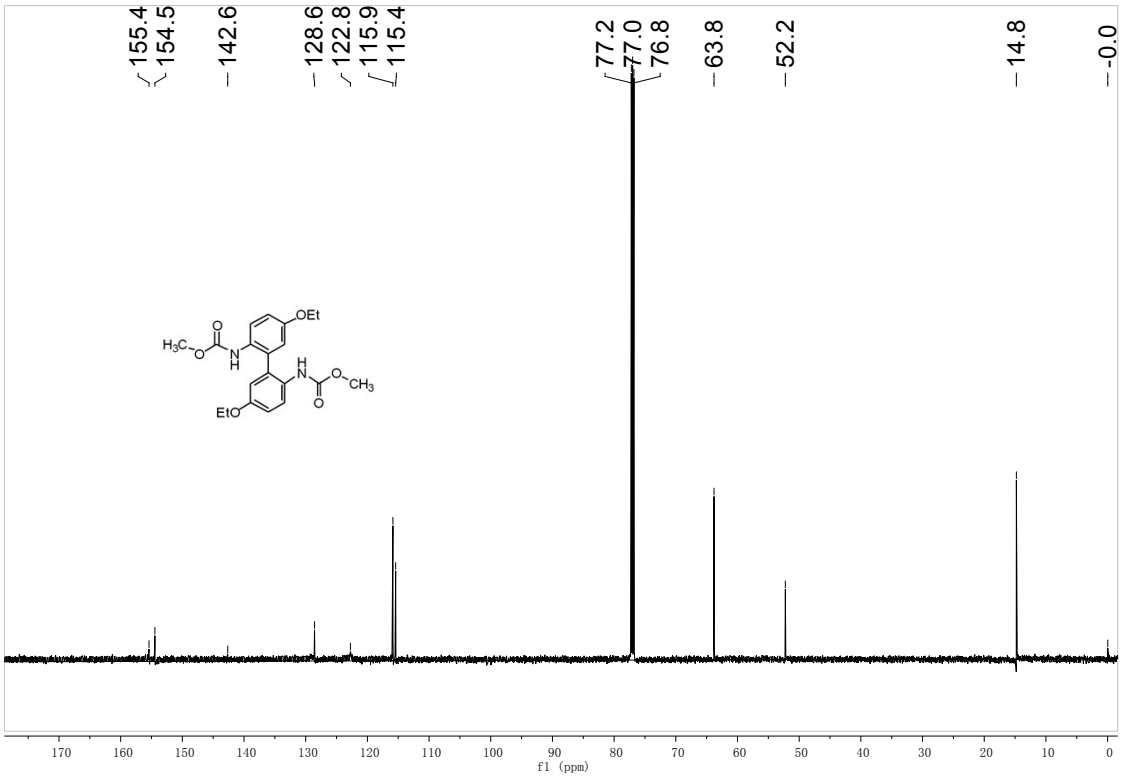
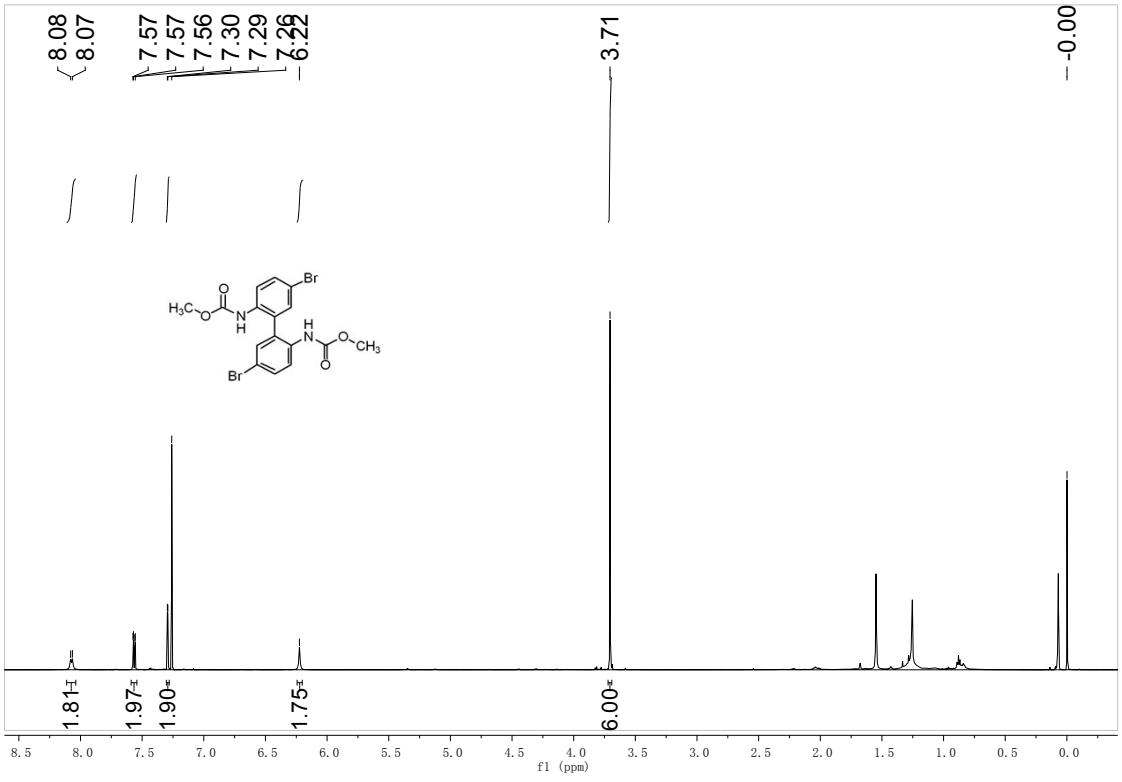
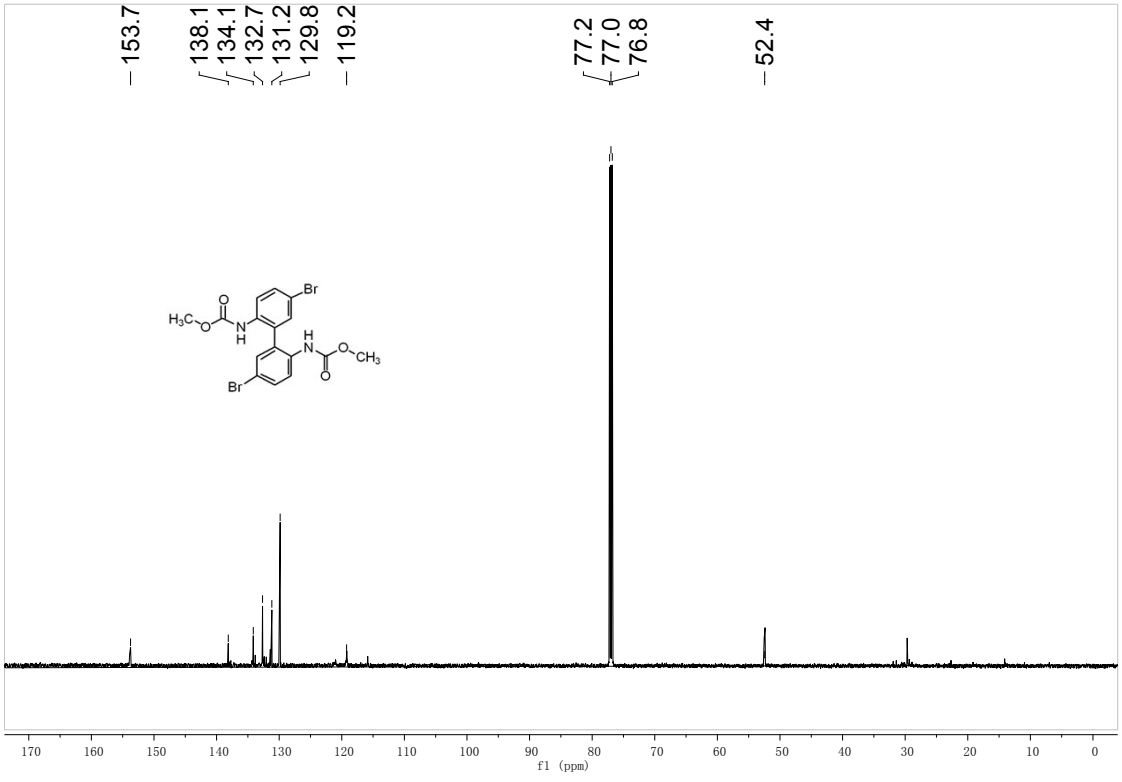


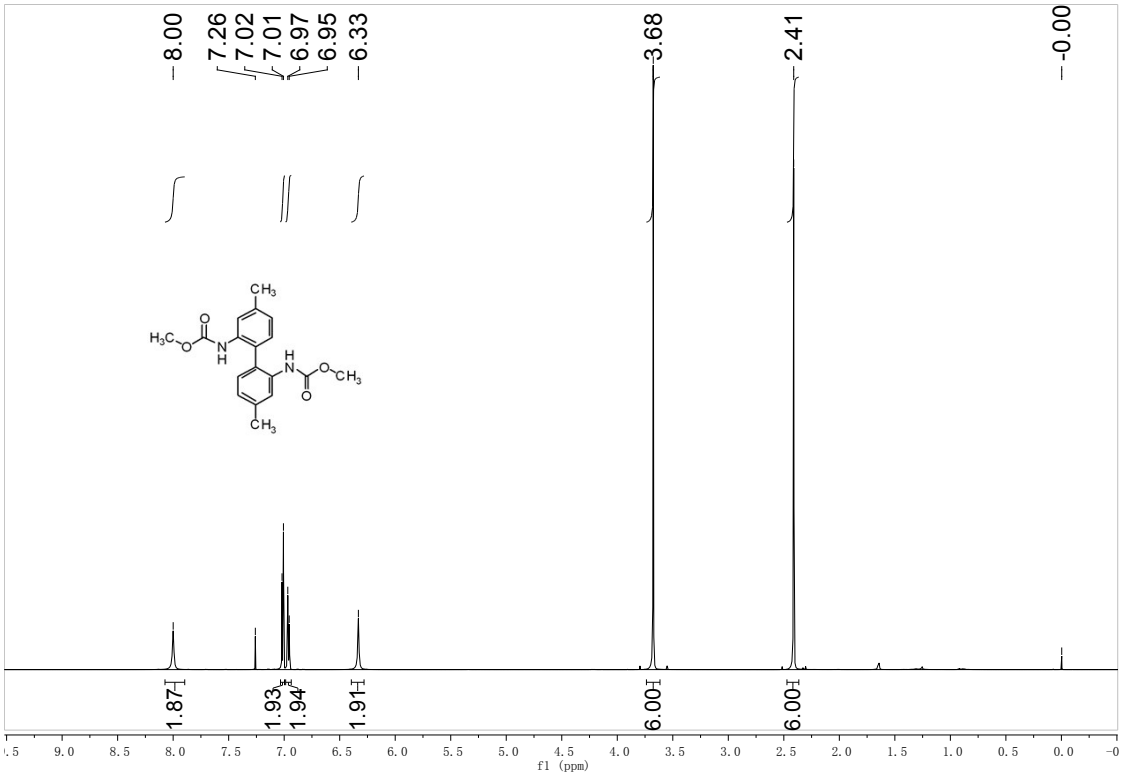


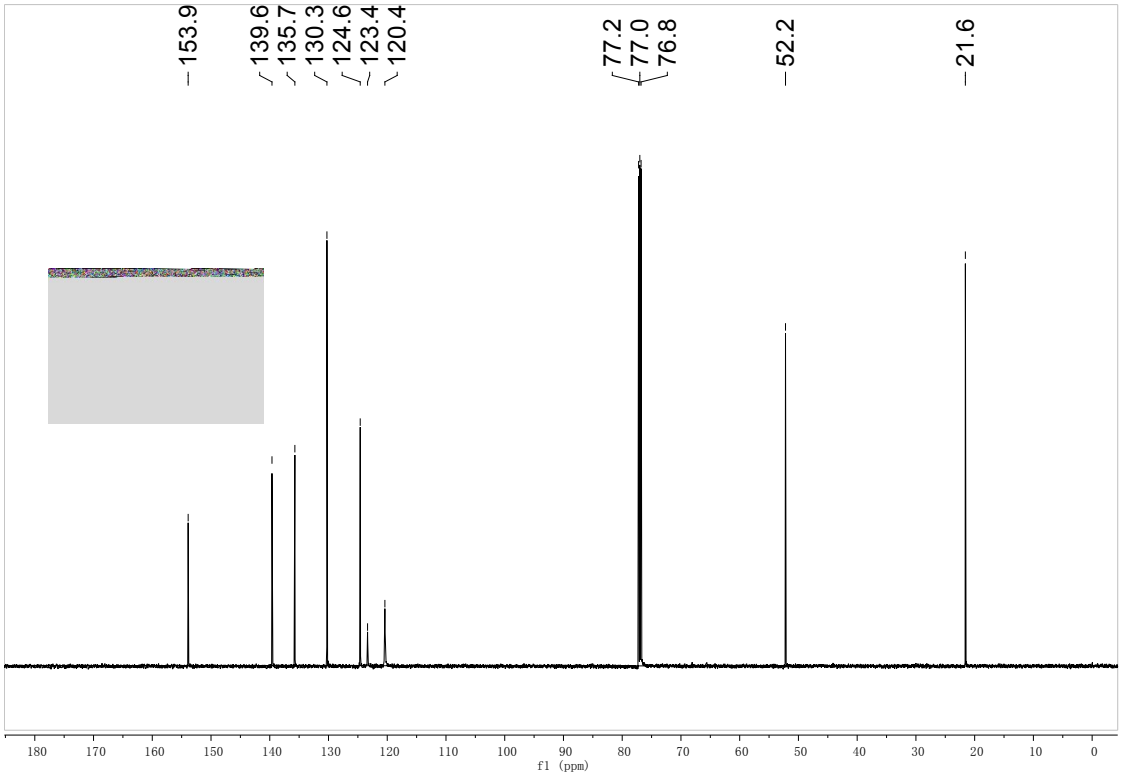
dimethyl (5,5'-dibromo-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2h)



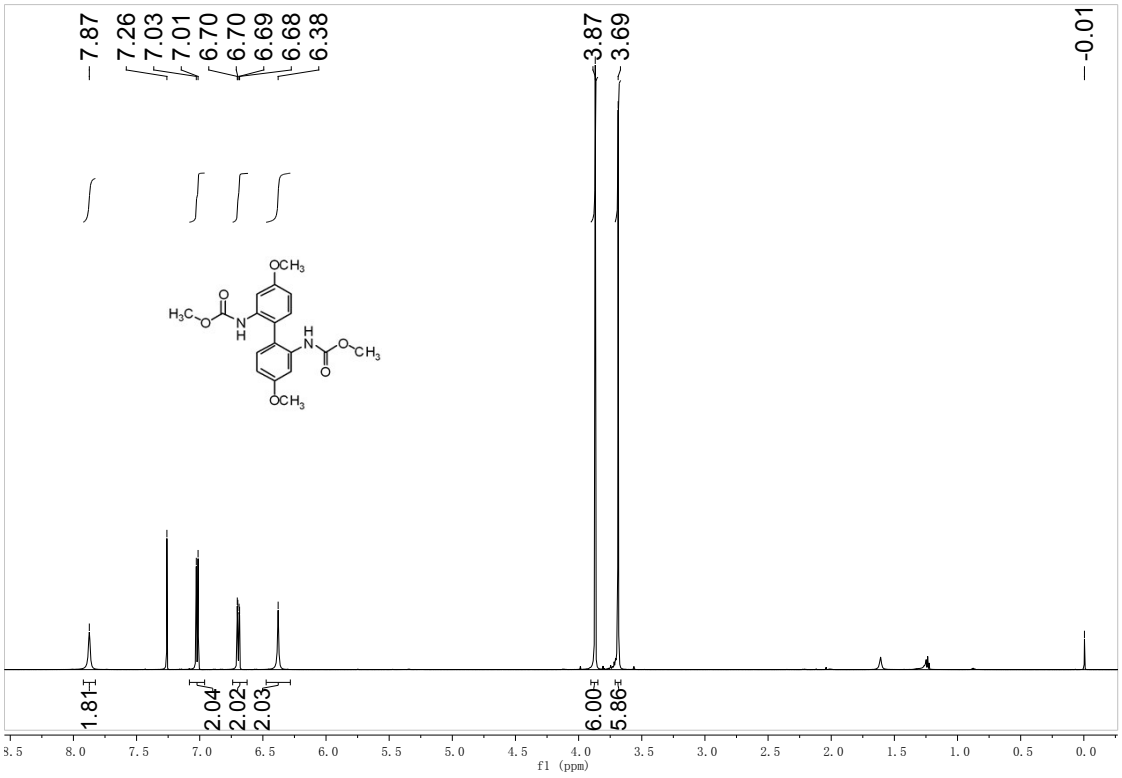


dimethyl (4,4'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2i)





dimethyl (4,4'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2j)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2.03
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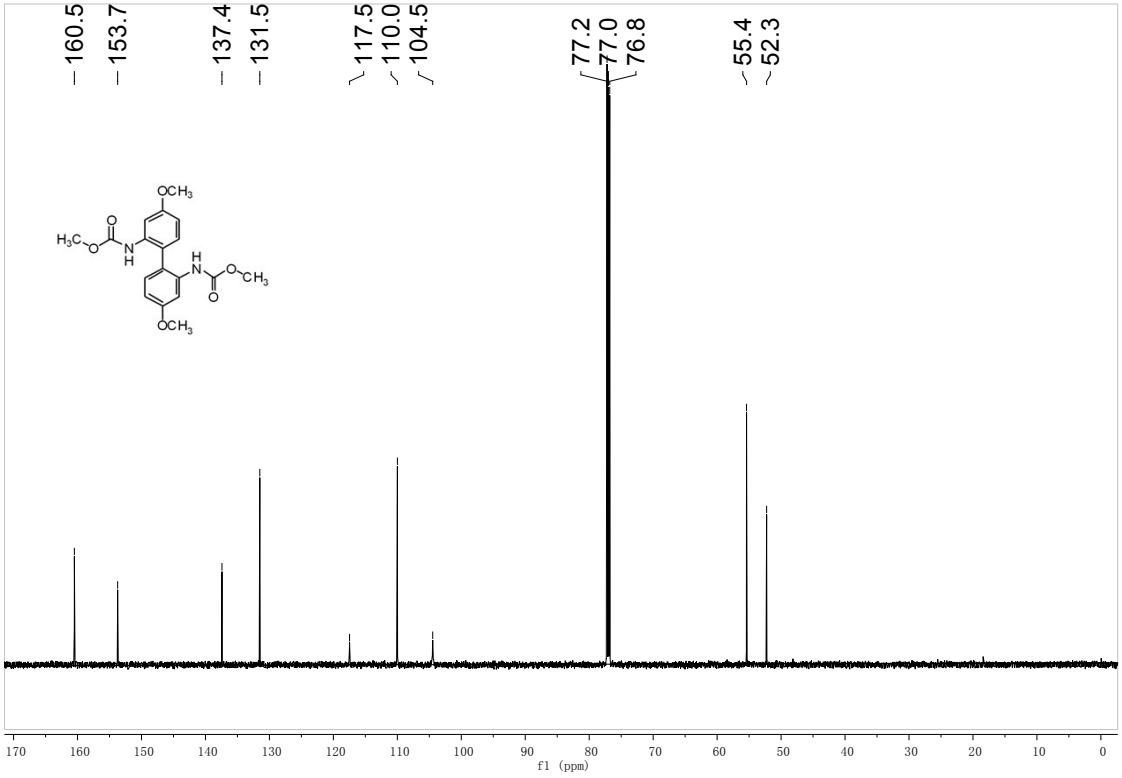
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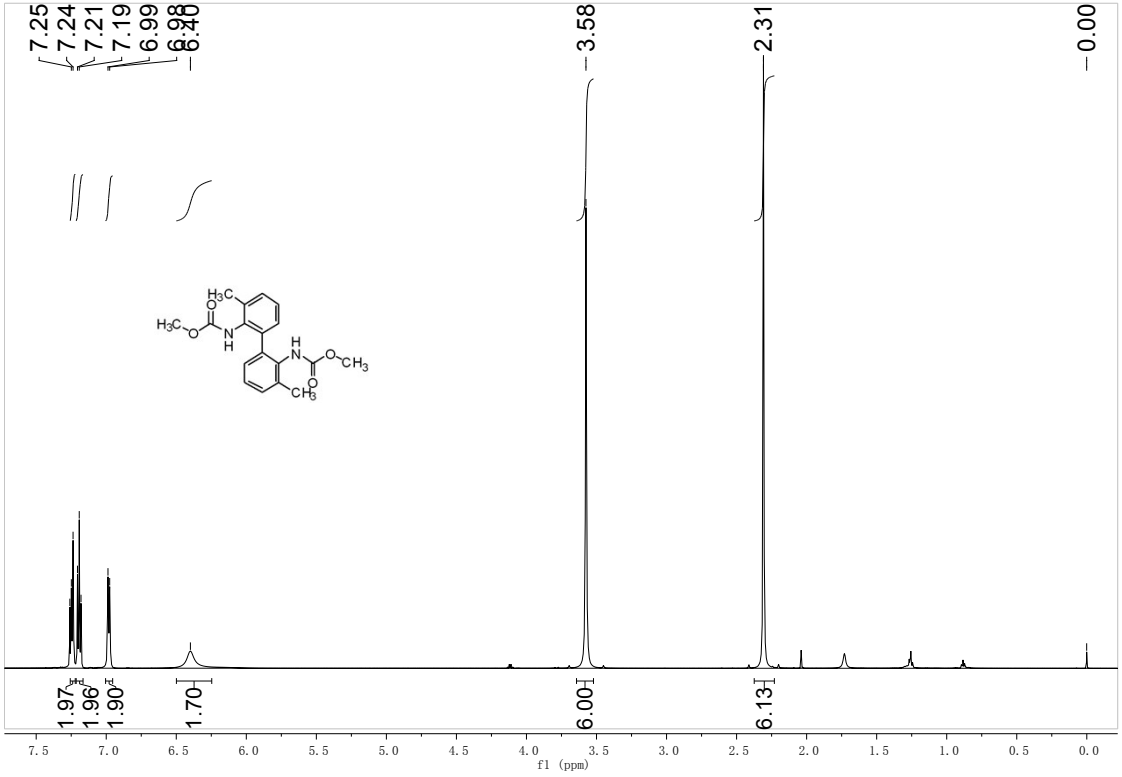
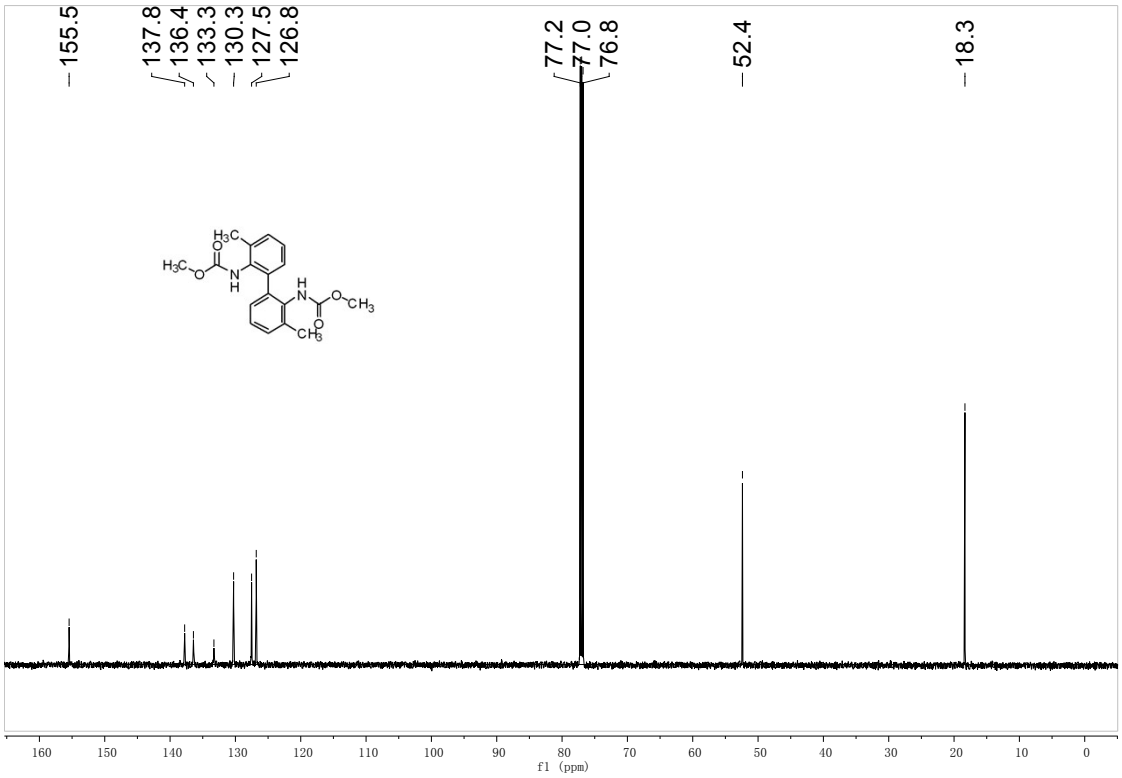
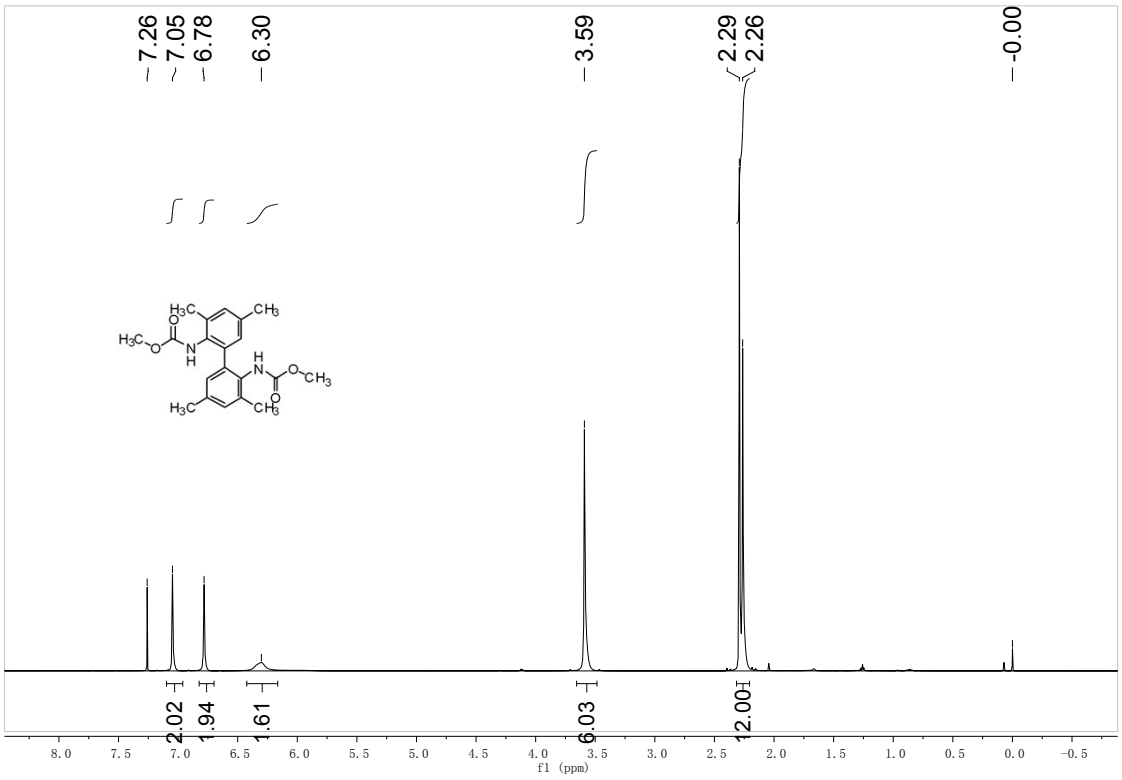
77.0
76.8
55.4
52.3
f1 (ppm)

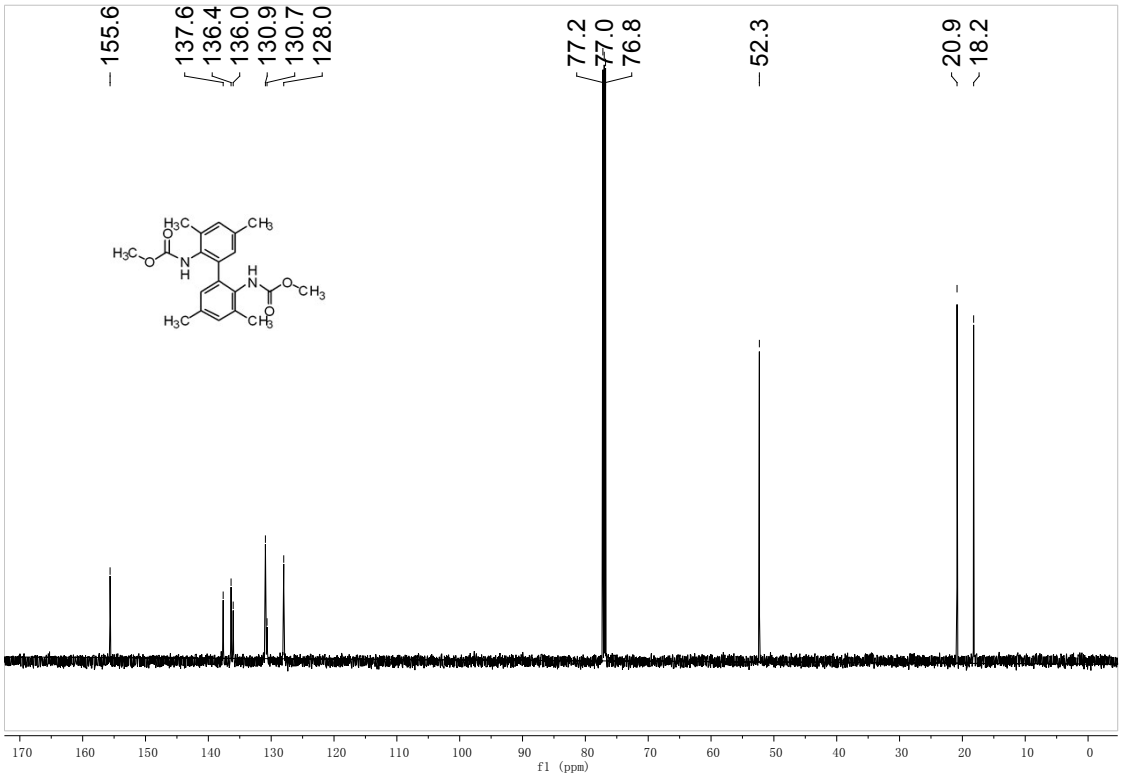
dimethyl (3,3'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2k)



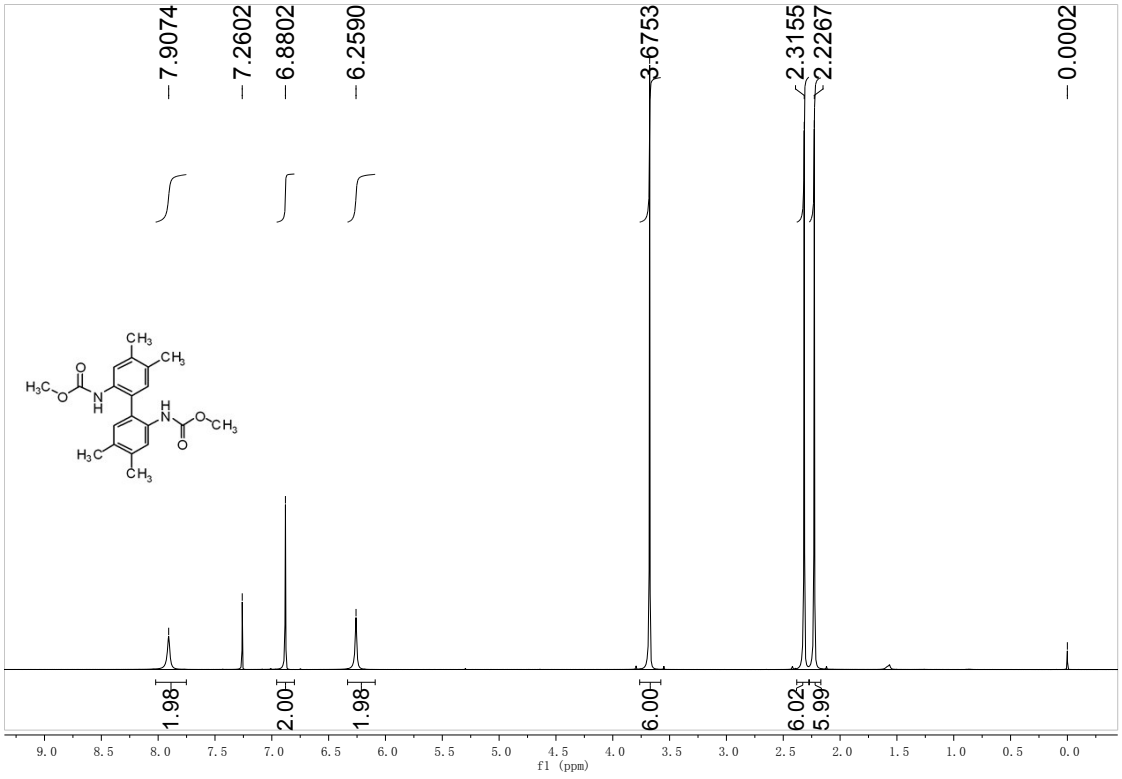


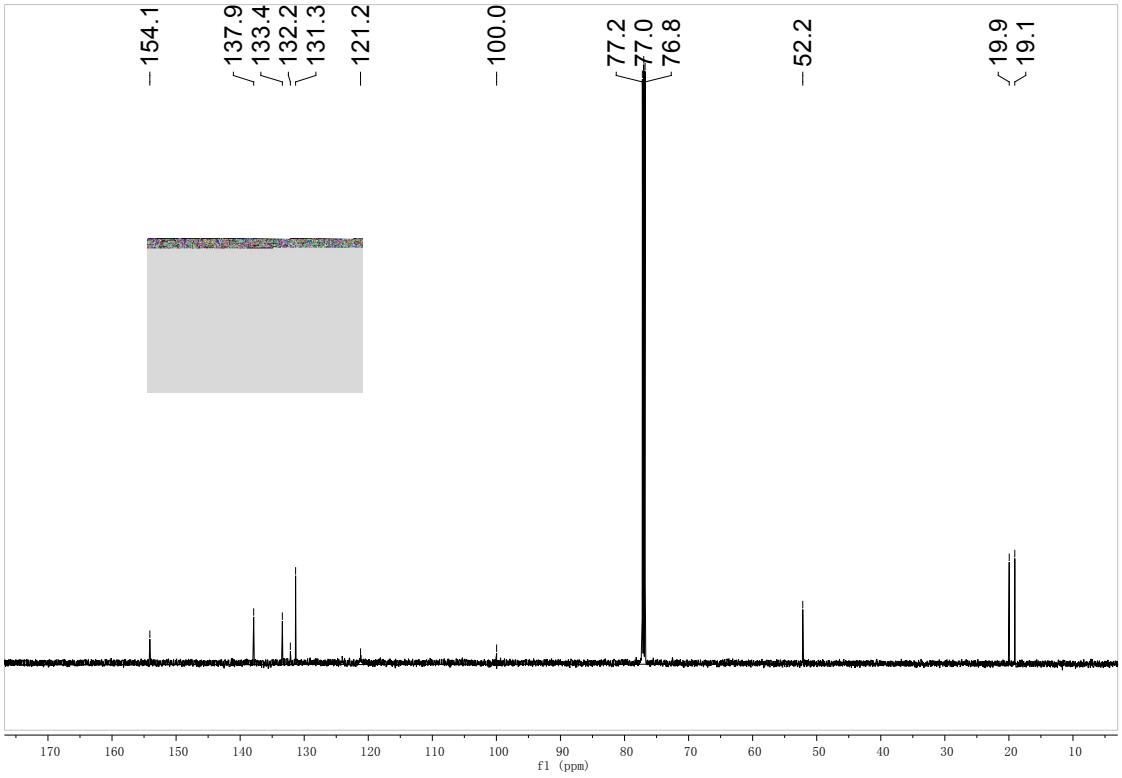
dimethyl (3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2l)



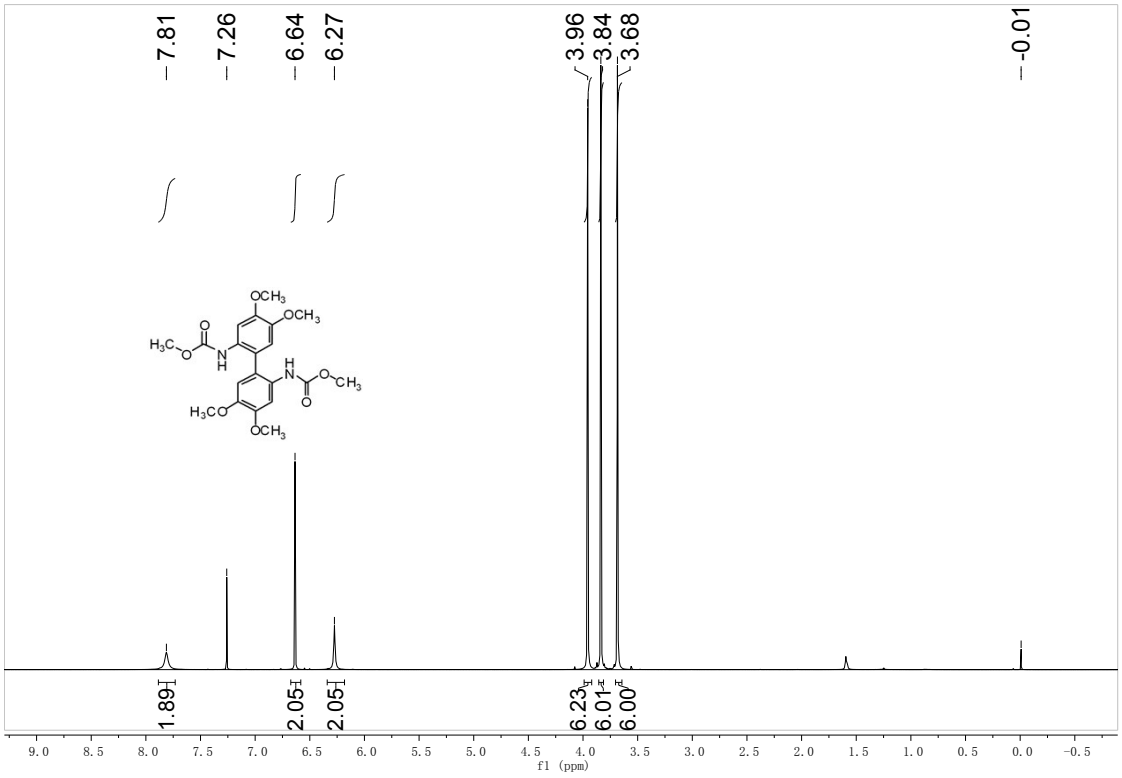


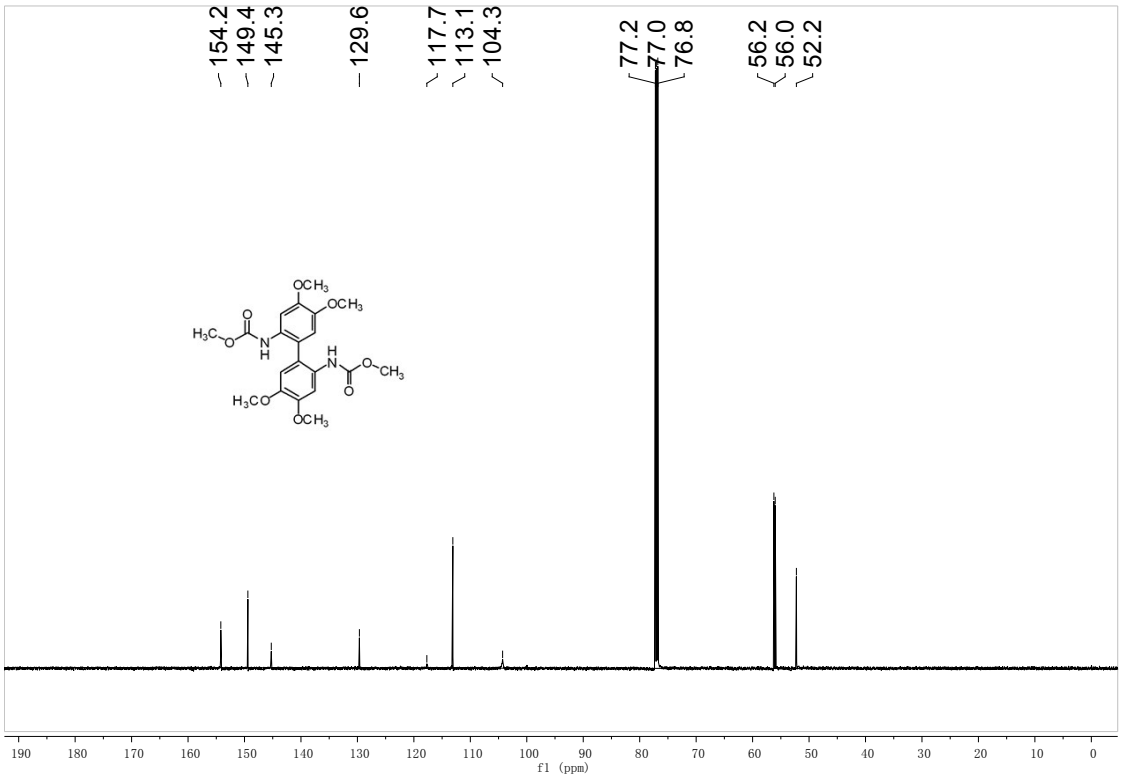
dimethyl (4,4',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2m)



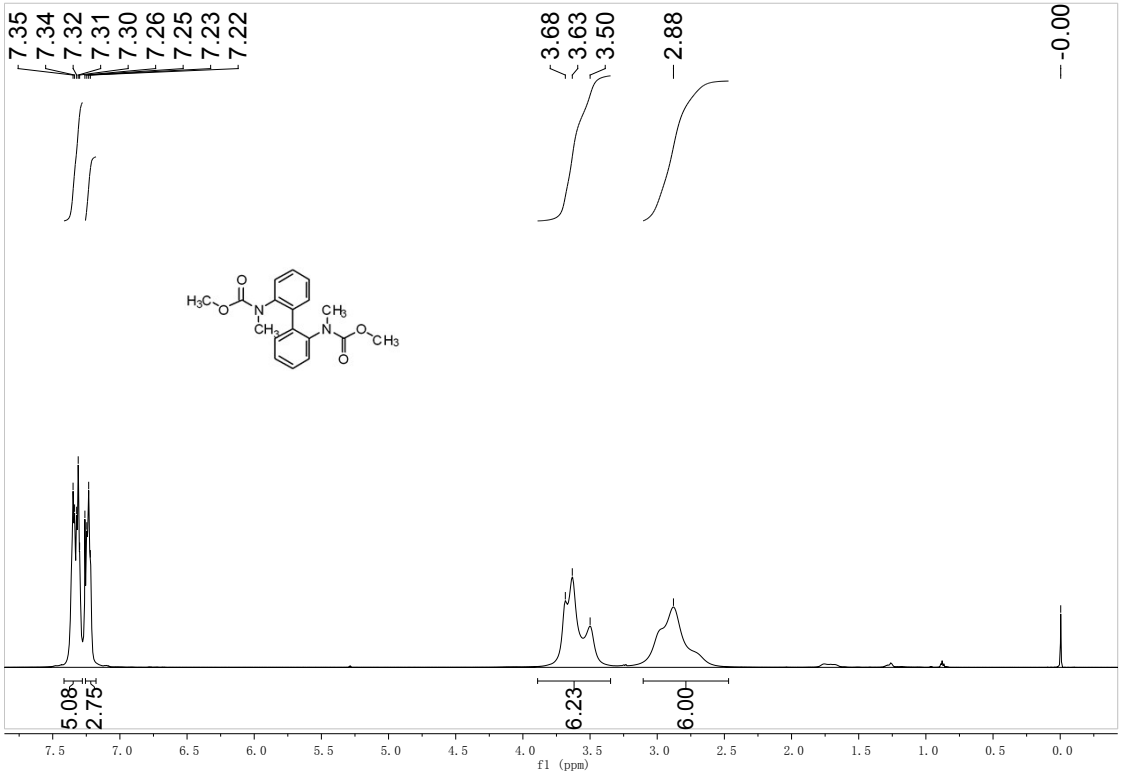


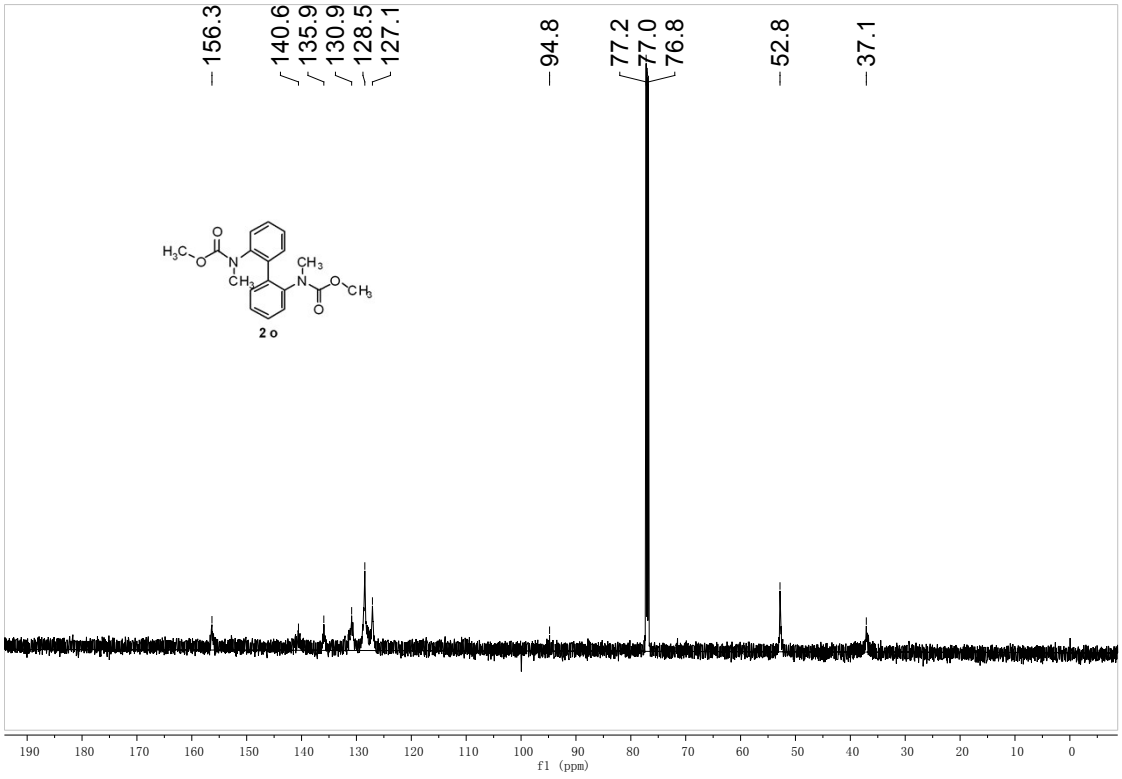
dimethyl (4,4',5,5'-tetramethoxy-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2n)


7.81
7.26
6.64
6.27
3.96
3.84
3.68
-0.01
1.89
2.05
2.05
6.23
6.01
6.00
f1 (ppm)

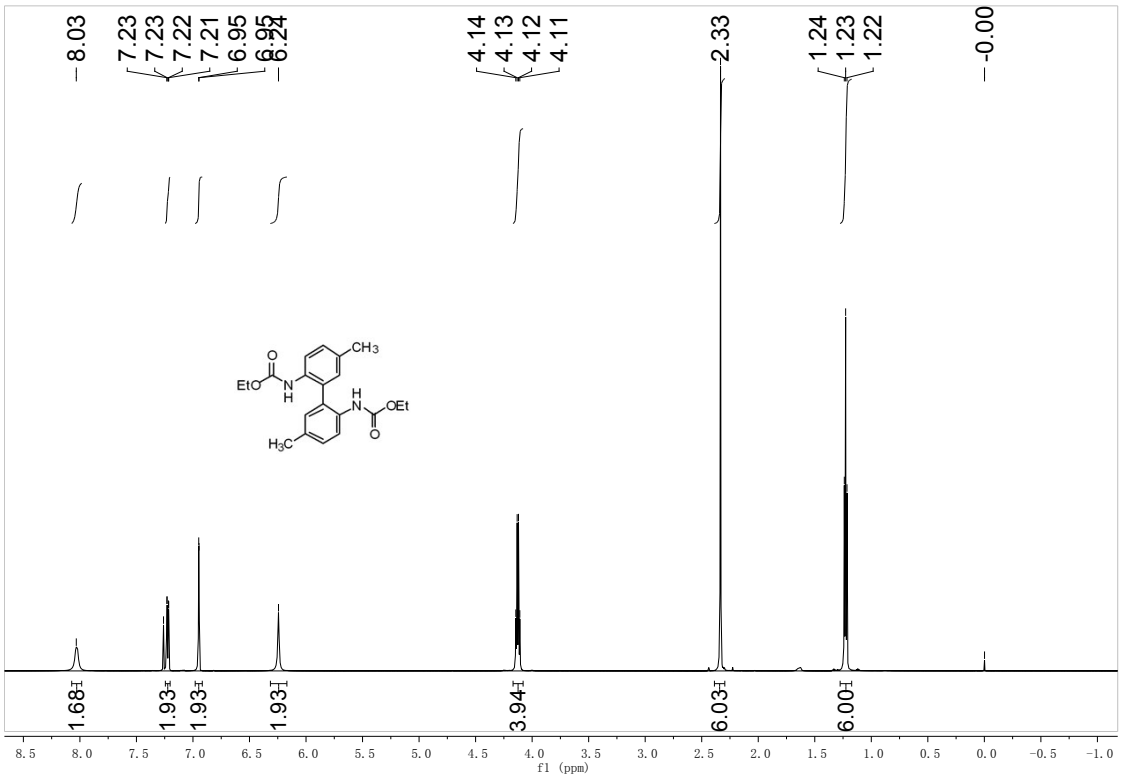

154.2
149.4
145.3
129.6
117.7
113.1
104.3
77.2
77.0
76.8
56.2
56.0
52.2
f1 (ppm)

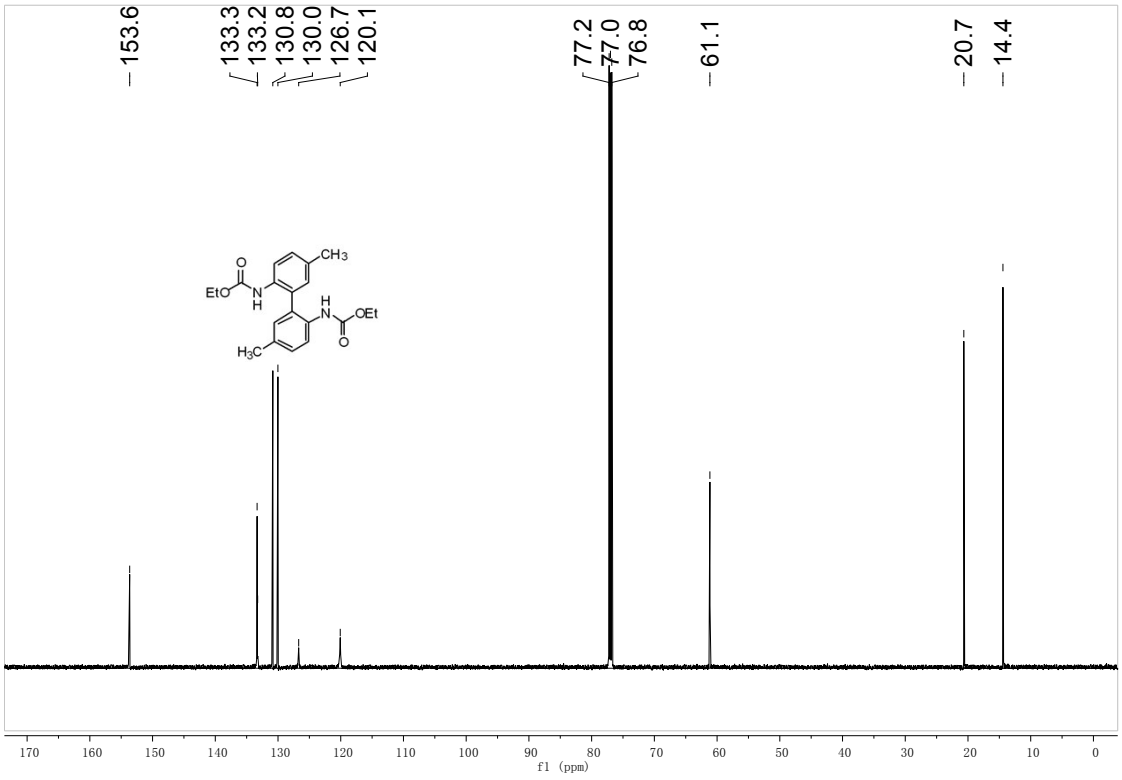
dimethyl [1,1'-biphenyl]-2,2'-diylbis(methylcarbamate) (2o)



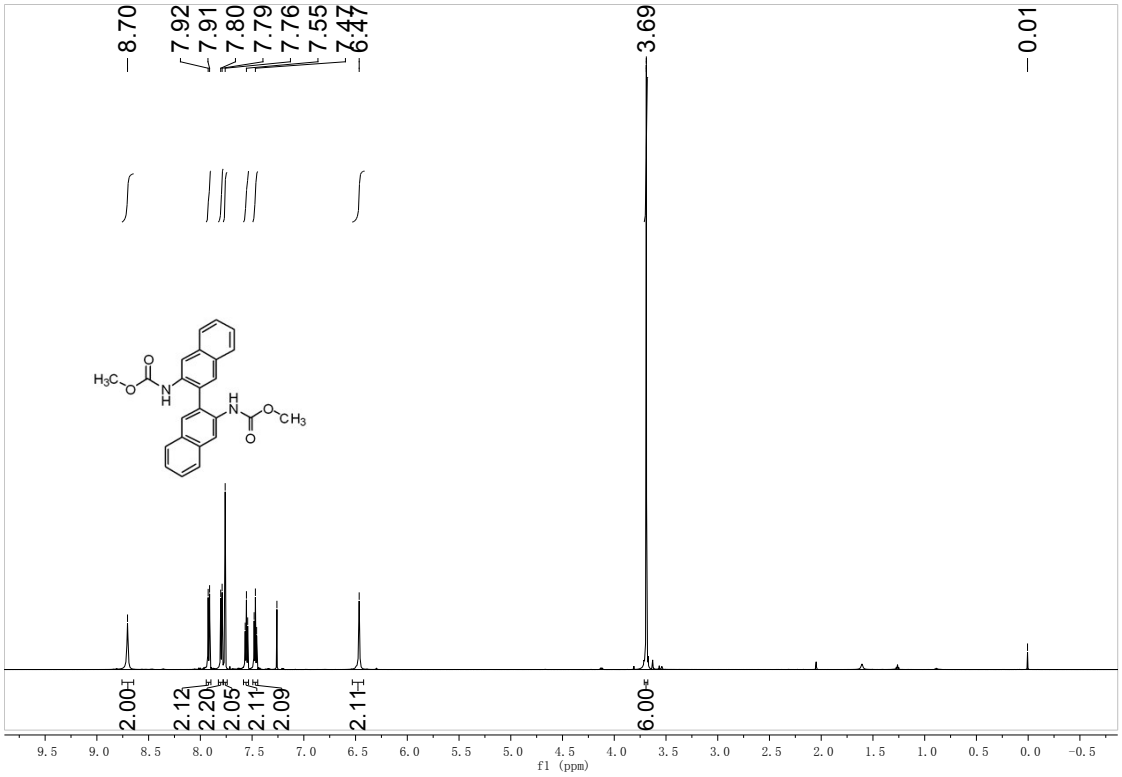


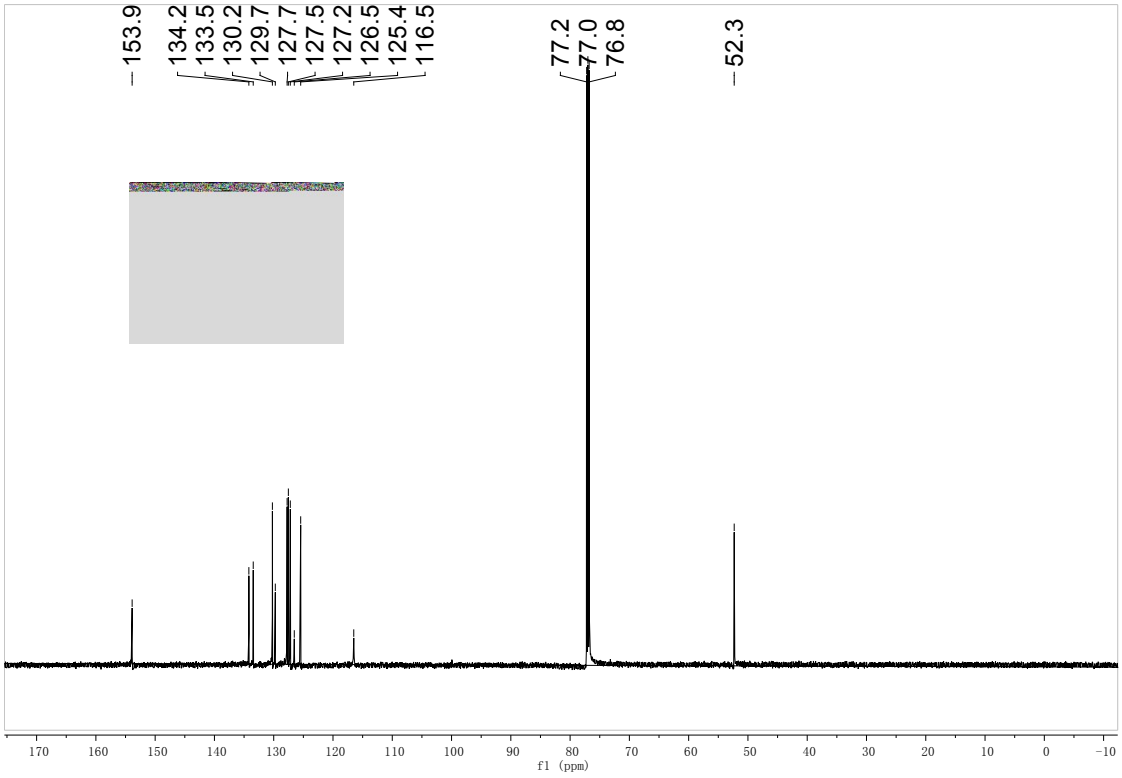
diethyl (5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2p)



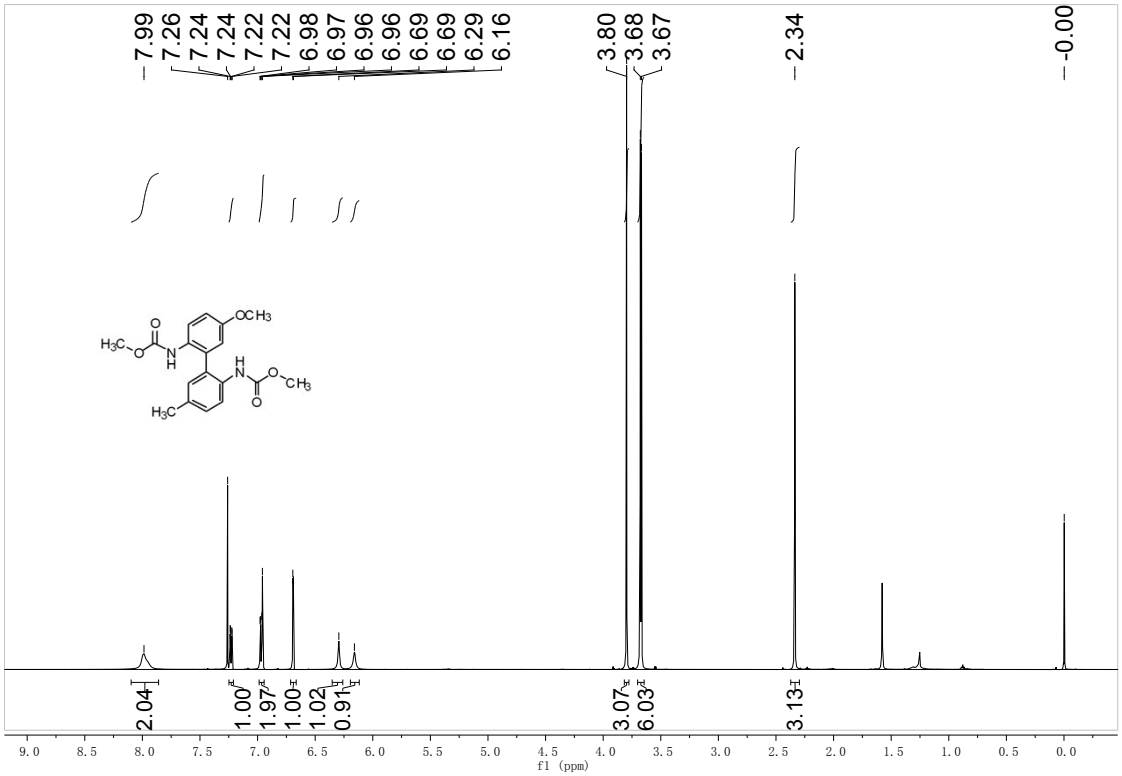


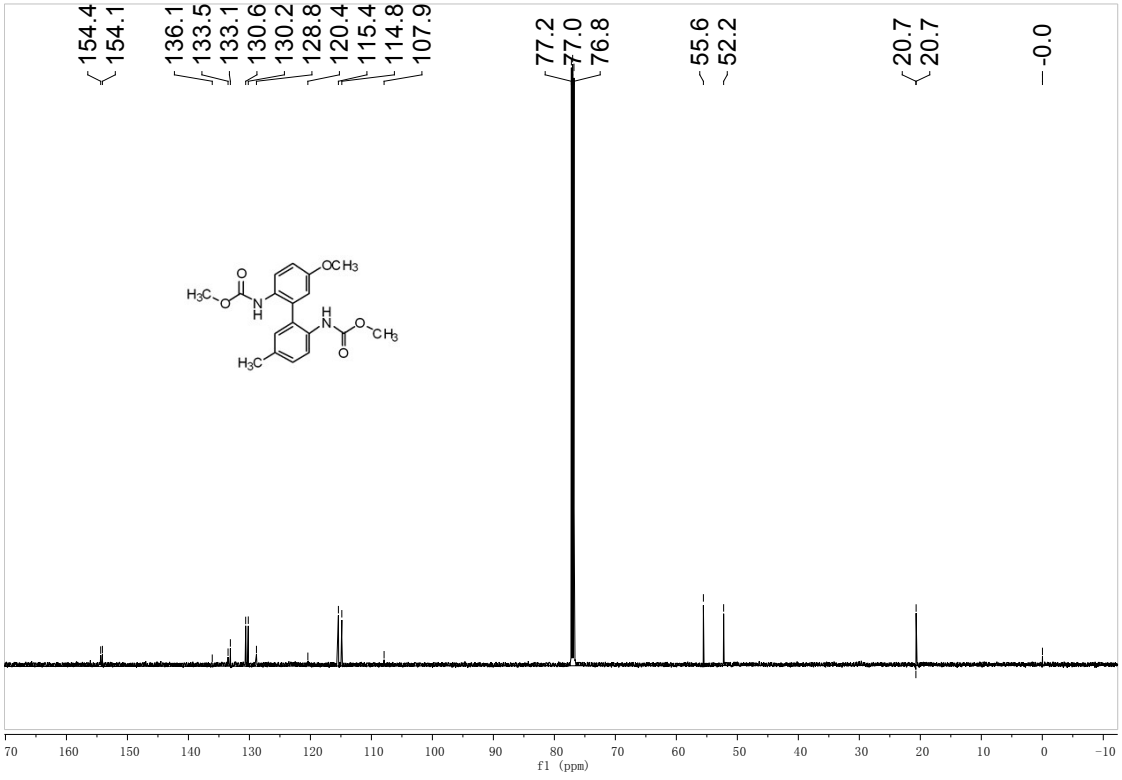
dimethyl [2,2'-binaphthalene]-3,3'-diyldicarbamate (2q)



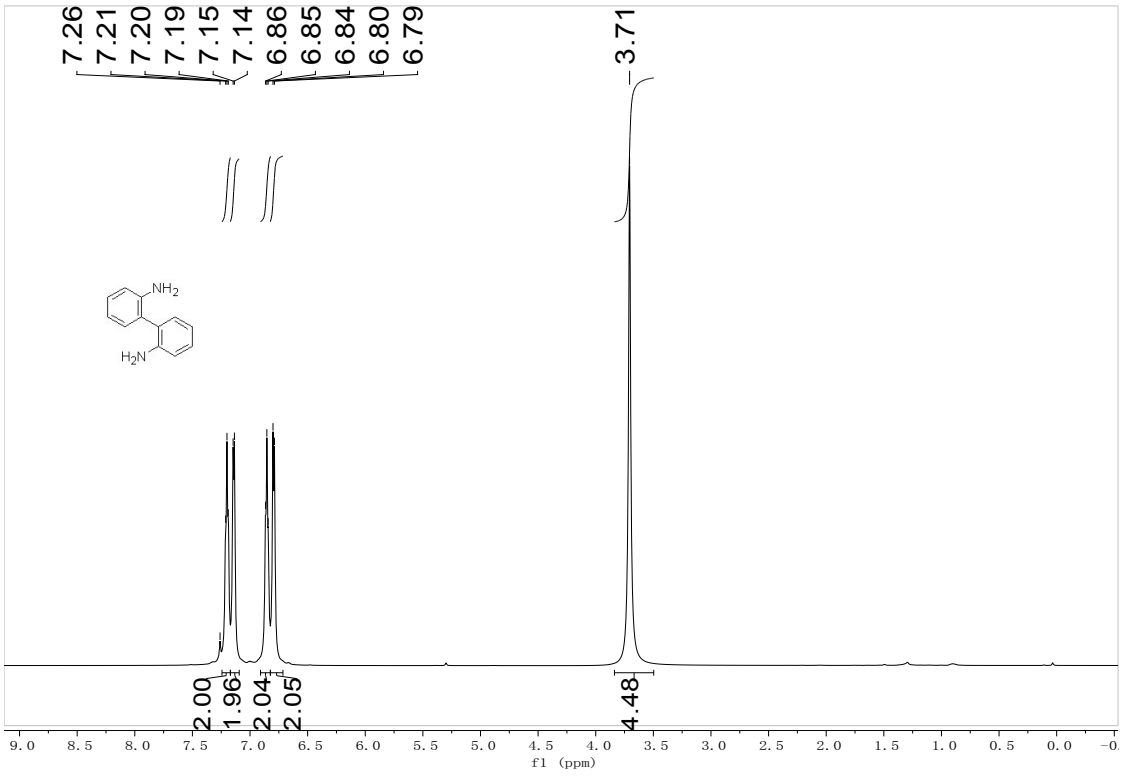


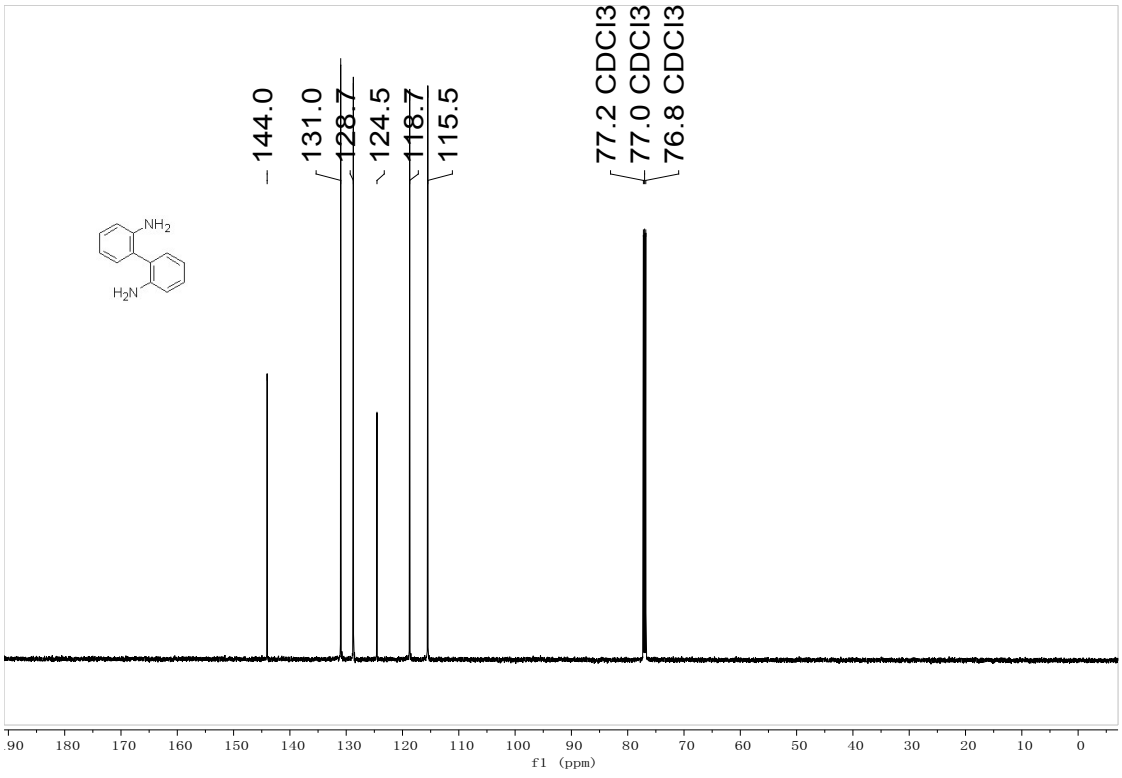
dimethyl (5-methoxy-5'-methyl-[1,1'-biphenyl]-2,2'-diyl)dicarbamate(2r)


7.99
7.26
7.24
7.24
7.22
7.22
6.98
6.97
6.96
6.96
6.69
6.69
6.29
6.16
3.80
3.68
3.67
2.34
-0.00
2.04
1.00
1.97
1.00
1.02
0.91
3.07
6.03
3.13
f1 (ppm)

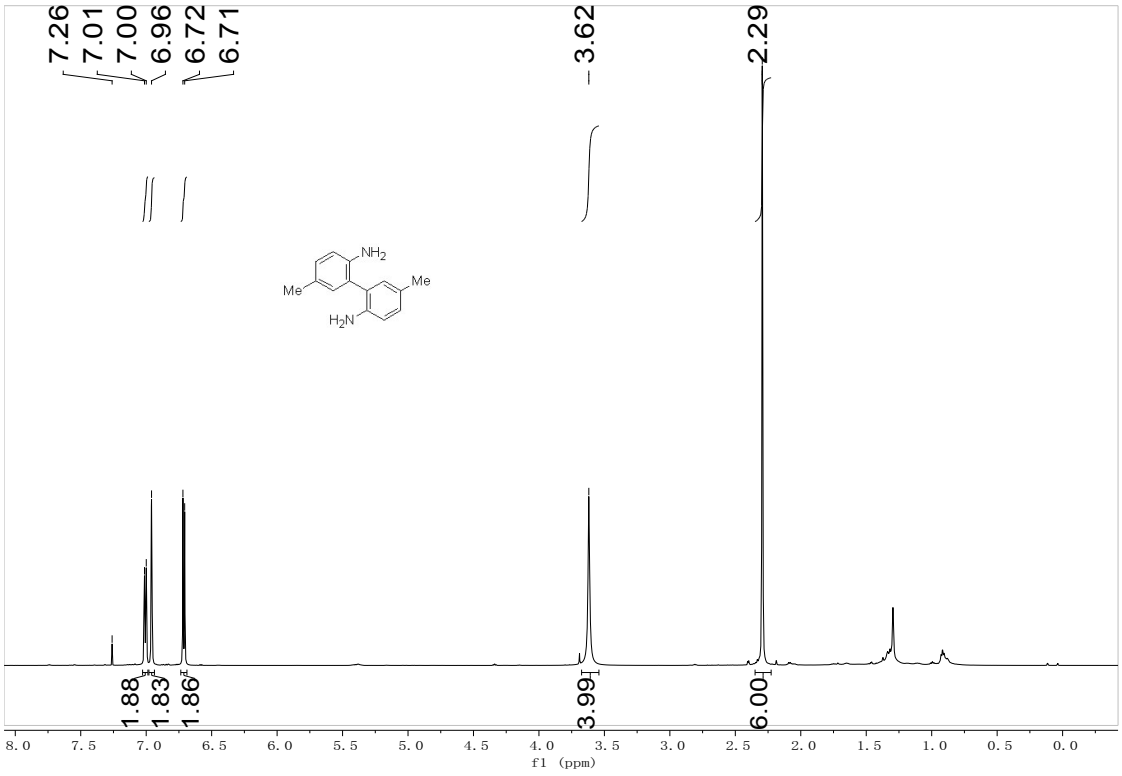

154.4
154.1
136.1
133.5
133.1
130.6
130.2
128.8
120.4
115.4
114.8
107.9
77.2
77.0
76.8
55.6
52.2
20.7
20.7
-0.0
f1 (ppm)

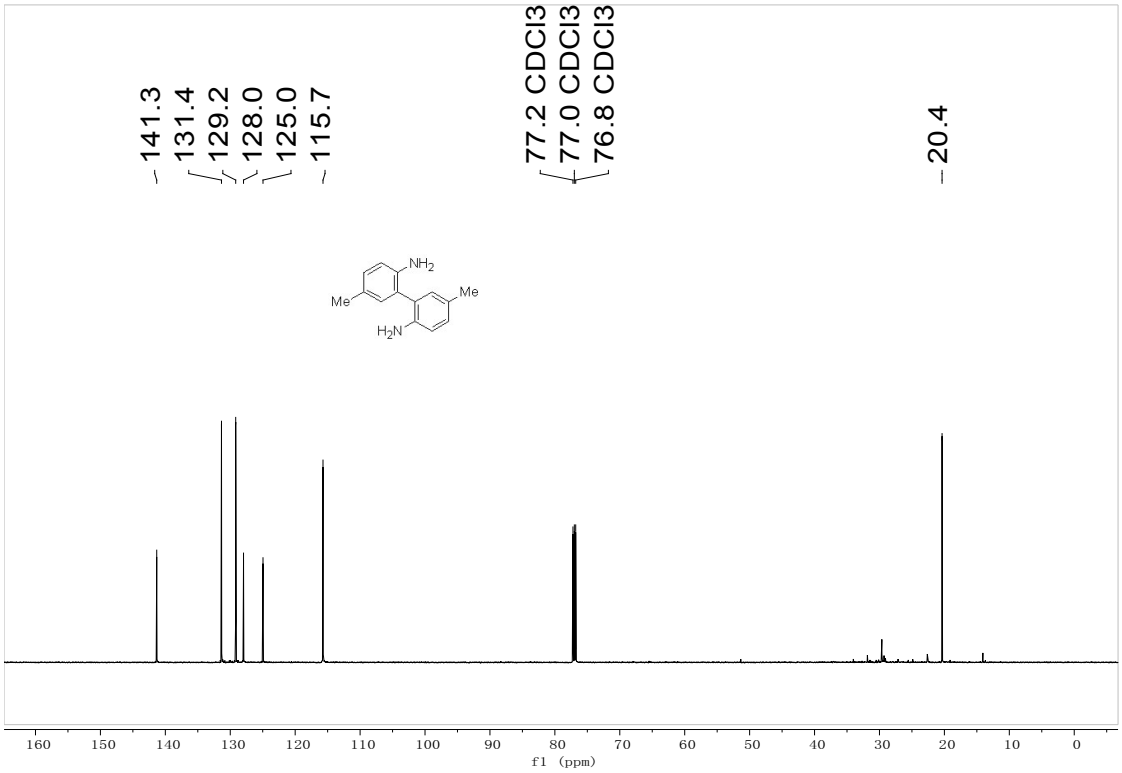
2,2′-diaminebiphenyl (3a)



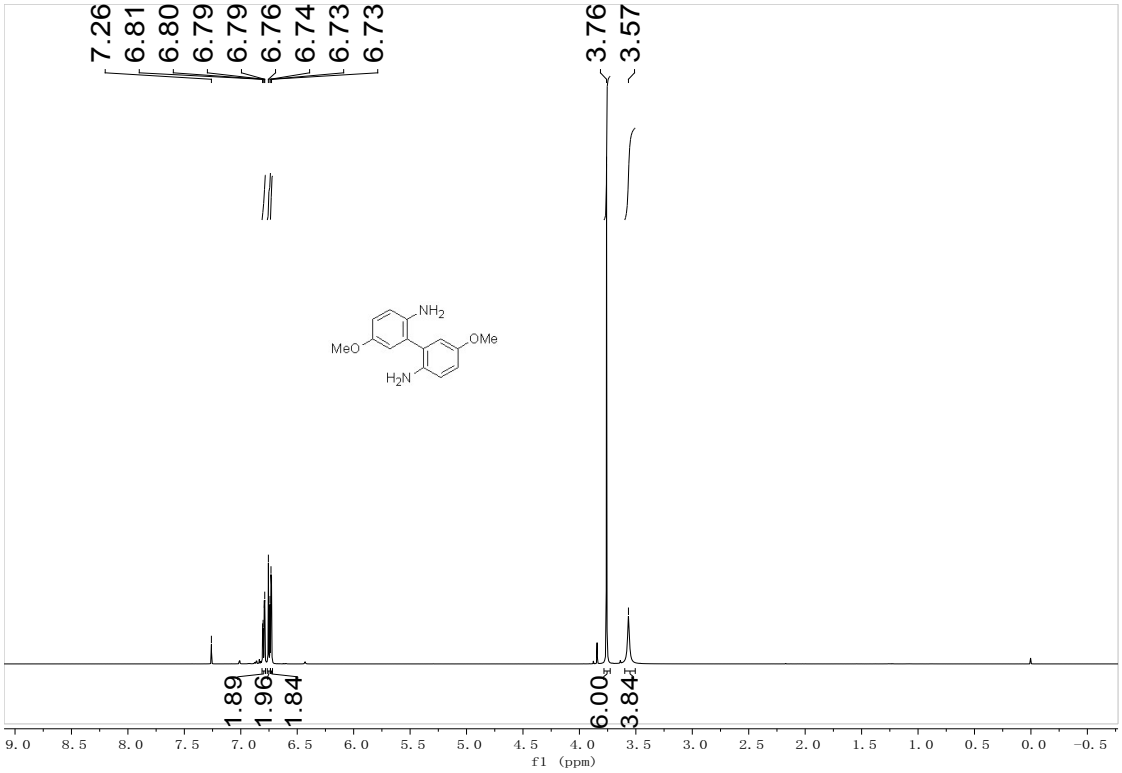


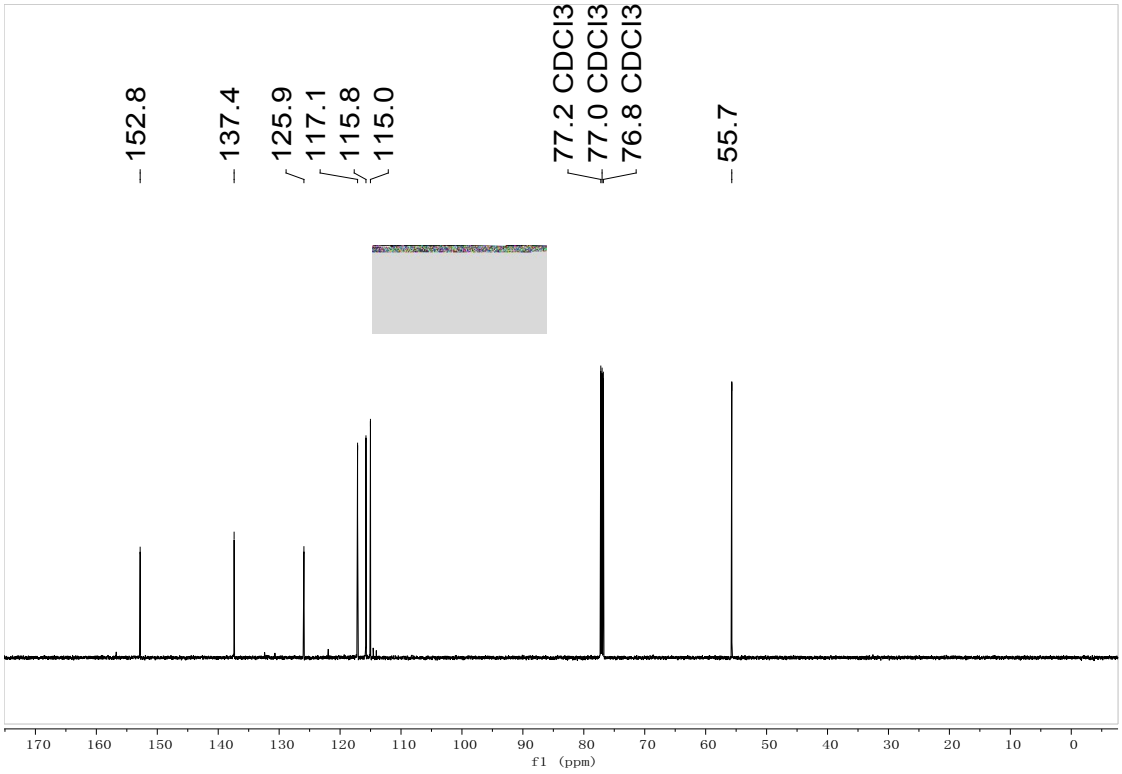
5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diamine(3d)



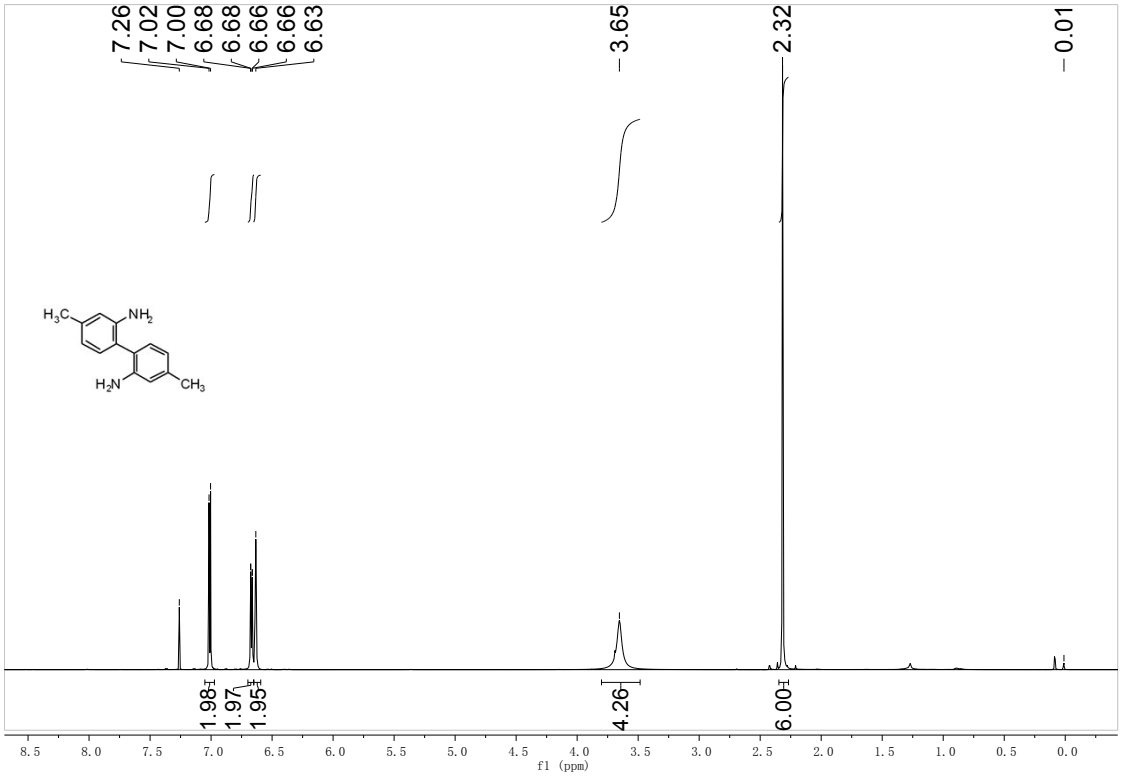


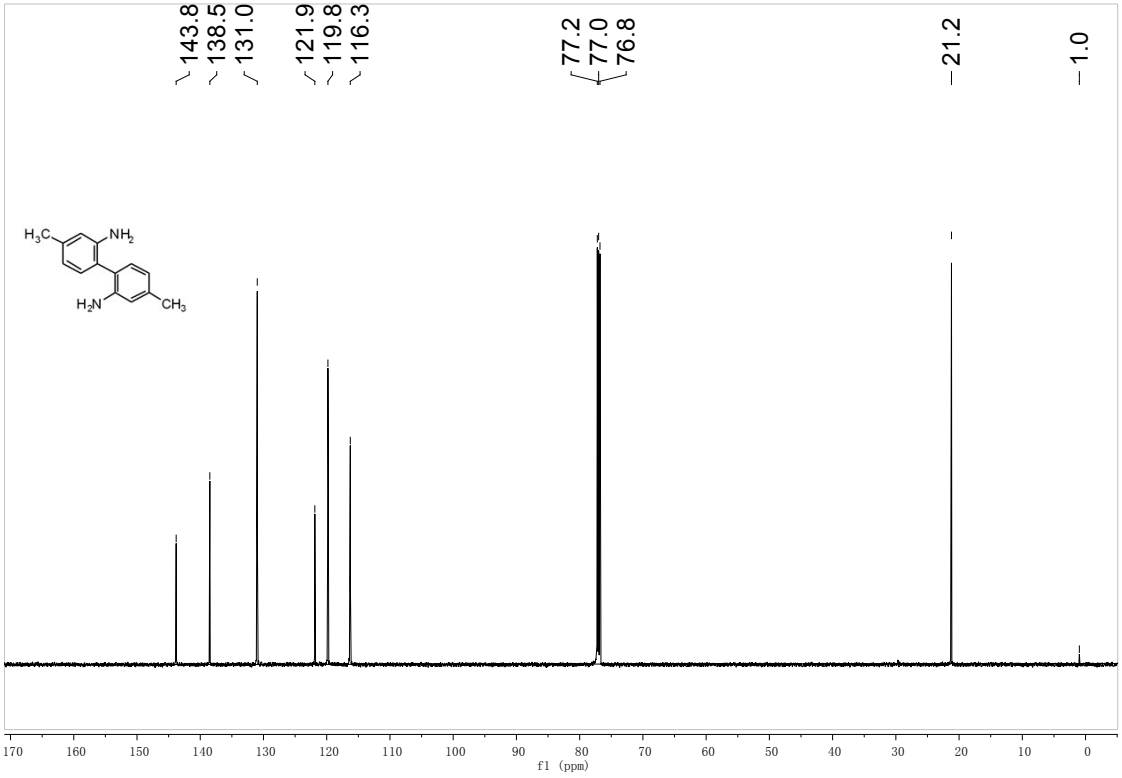
5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diamine(3e)



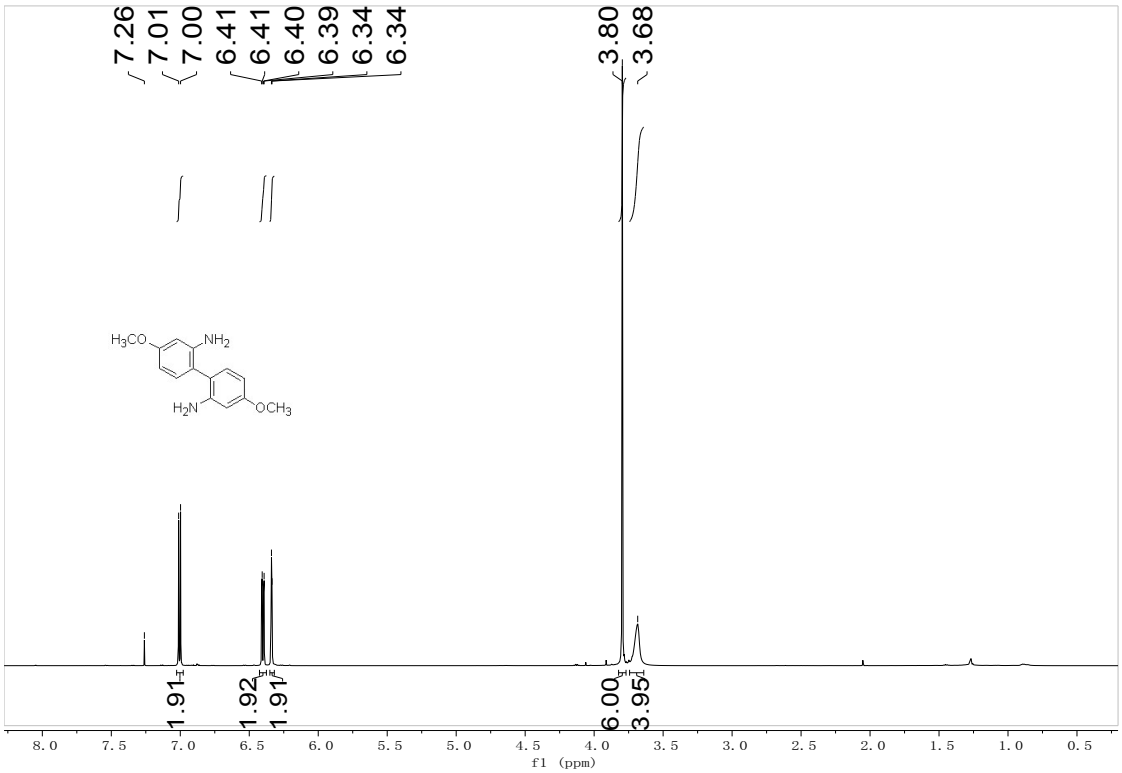


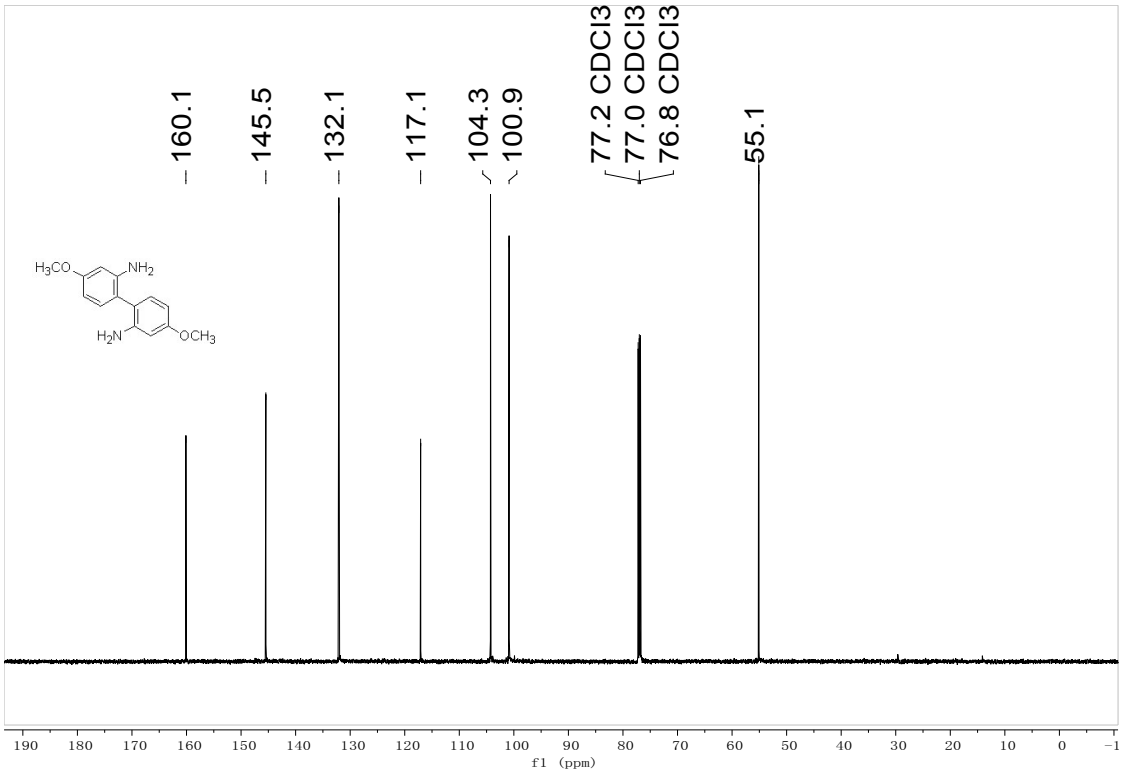
4,4'-dimethyl-[1,1'-biphenyl]-2,2'-diamine (3i)


7.26
7.02
7.00
6.68
6.68
6.66
6.66
6.63
3.65
2.32
0.01
1.98
1.97
1.95
4.26
6.00
f1 (ppm)

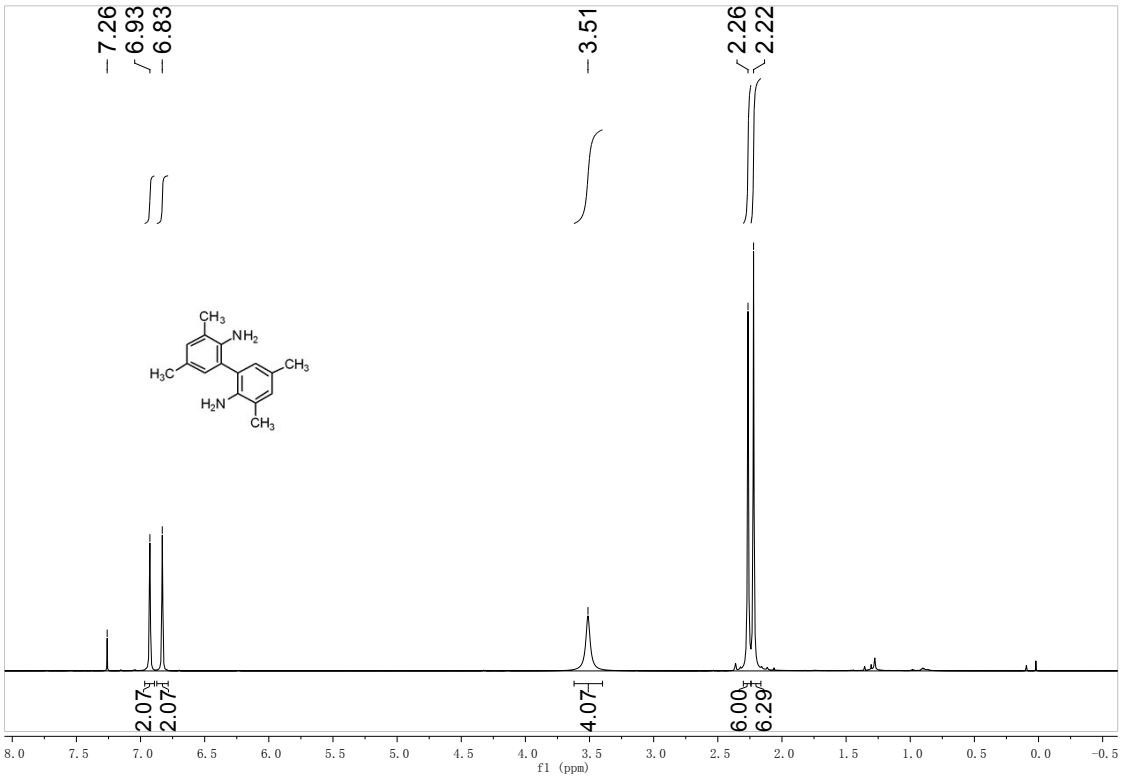

143.8
138.5
131.0
121.9
119.8
116.3
77.2
77.0
76.8
21.2
1.0
f1 (ppm)

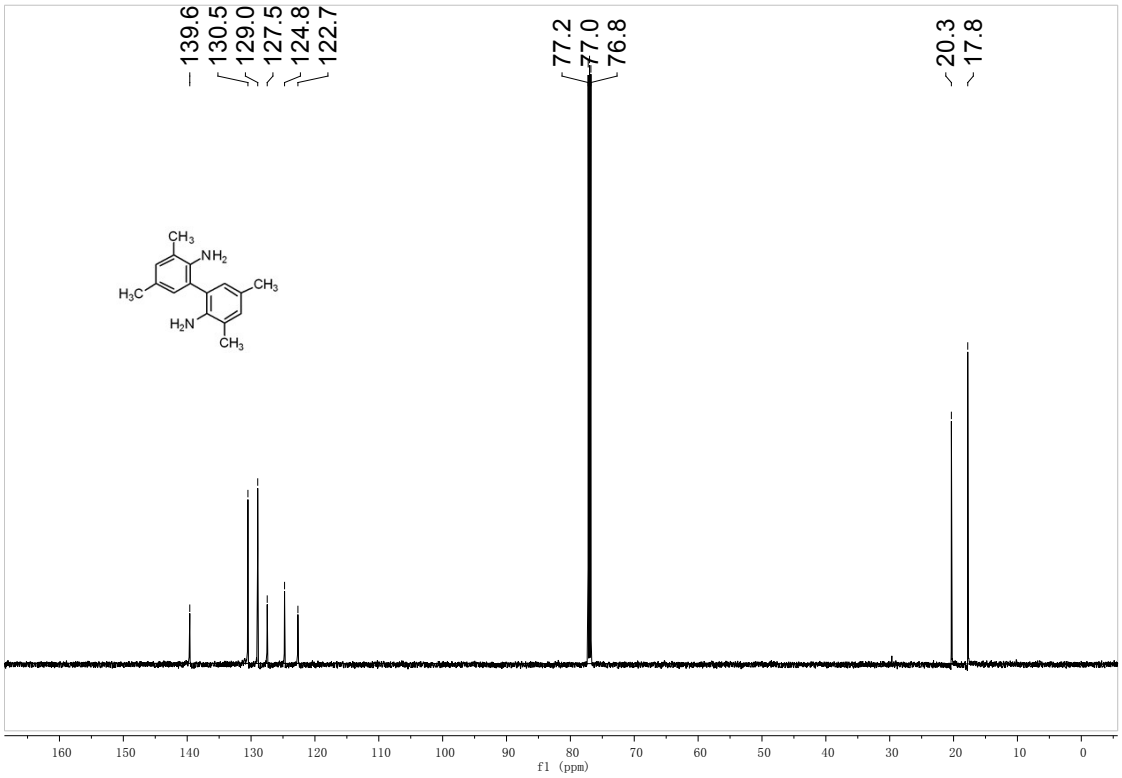
4,4'-dimethoxy-[1,1'-biphenyl]-2,2'-diamine(3j)



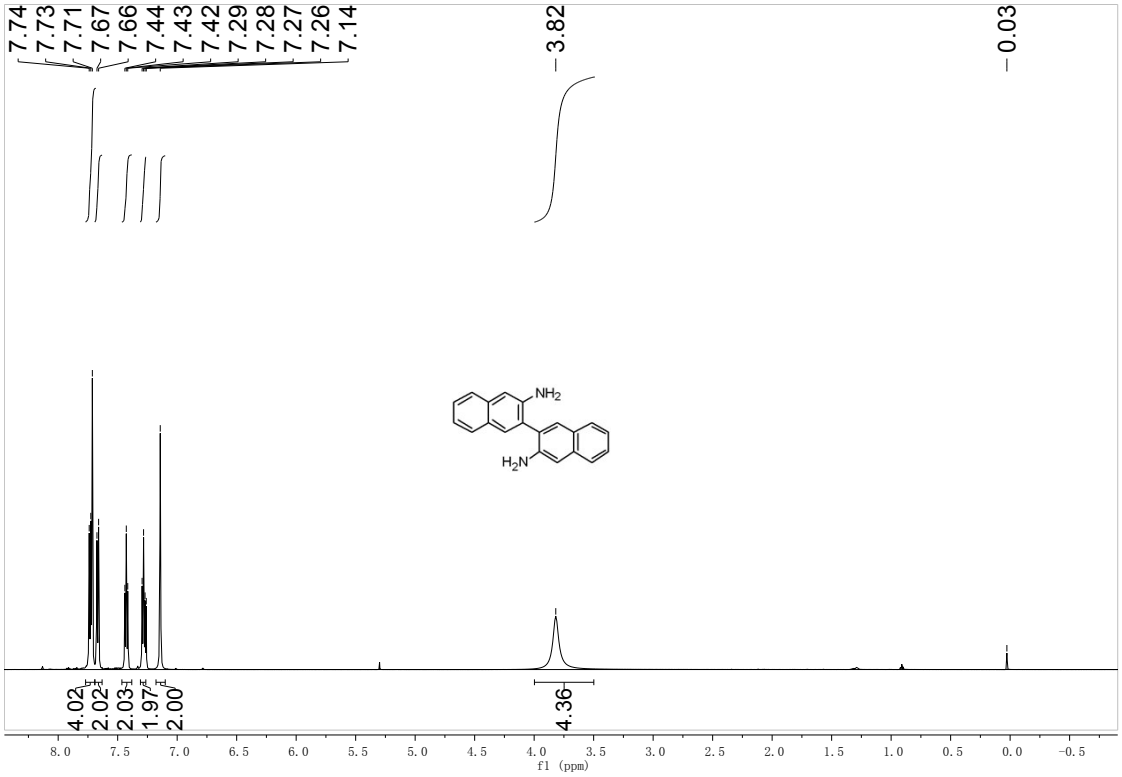


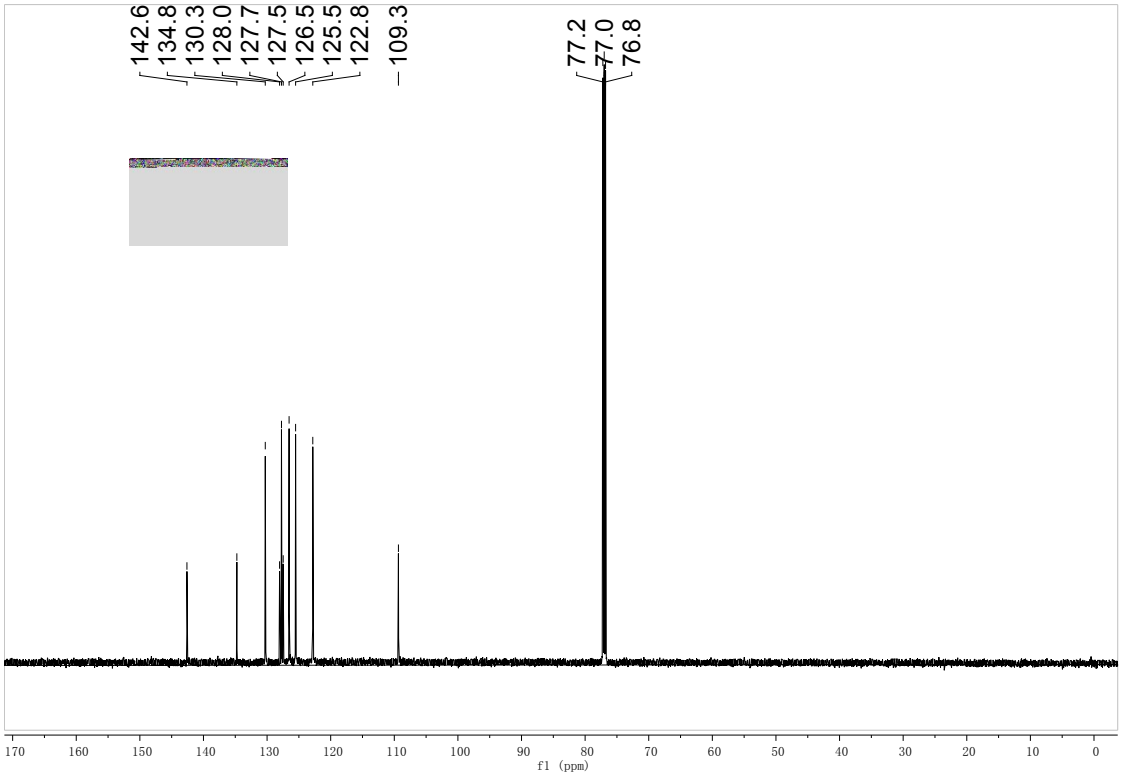
3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-diamine(3l)





[2,2'-binaphthalene]-3,3'-diamine(3q)




142.6
134.8
130.3
128.0
127.7
127.5
126.5
125.5
122.8
109.3
77.2
77.0
76.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)