Electronic Supplementary Material (ESI) for RSC Advances.

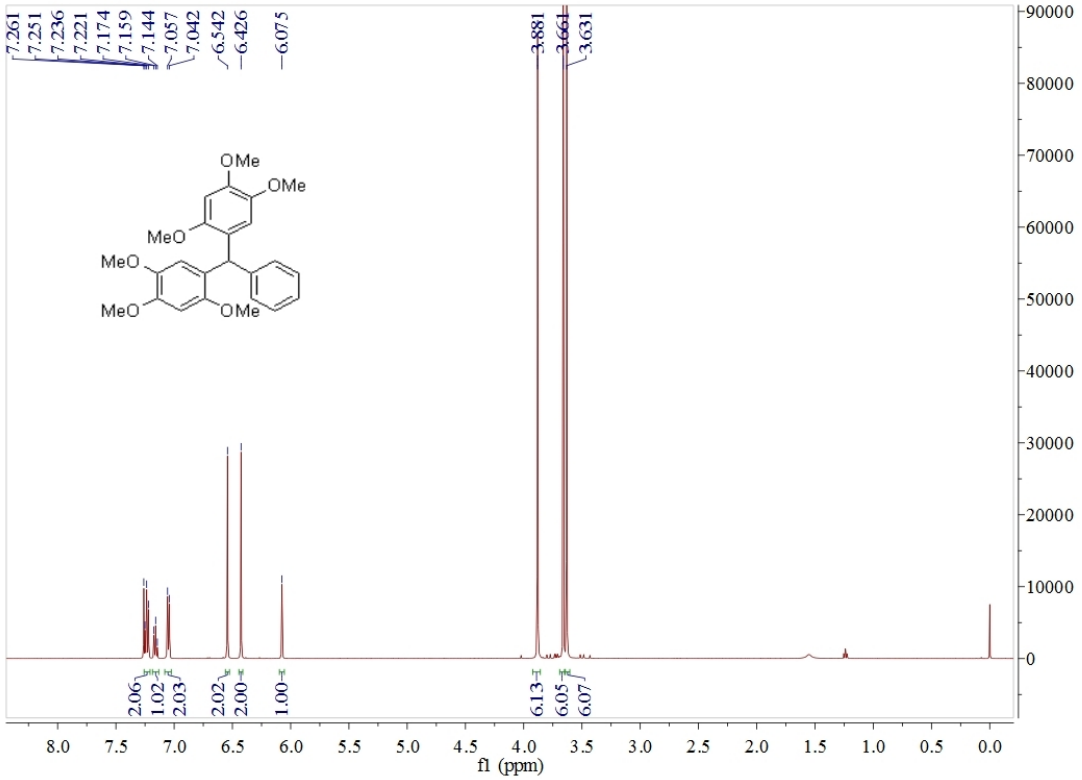
Supplementary Data

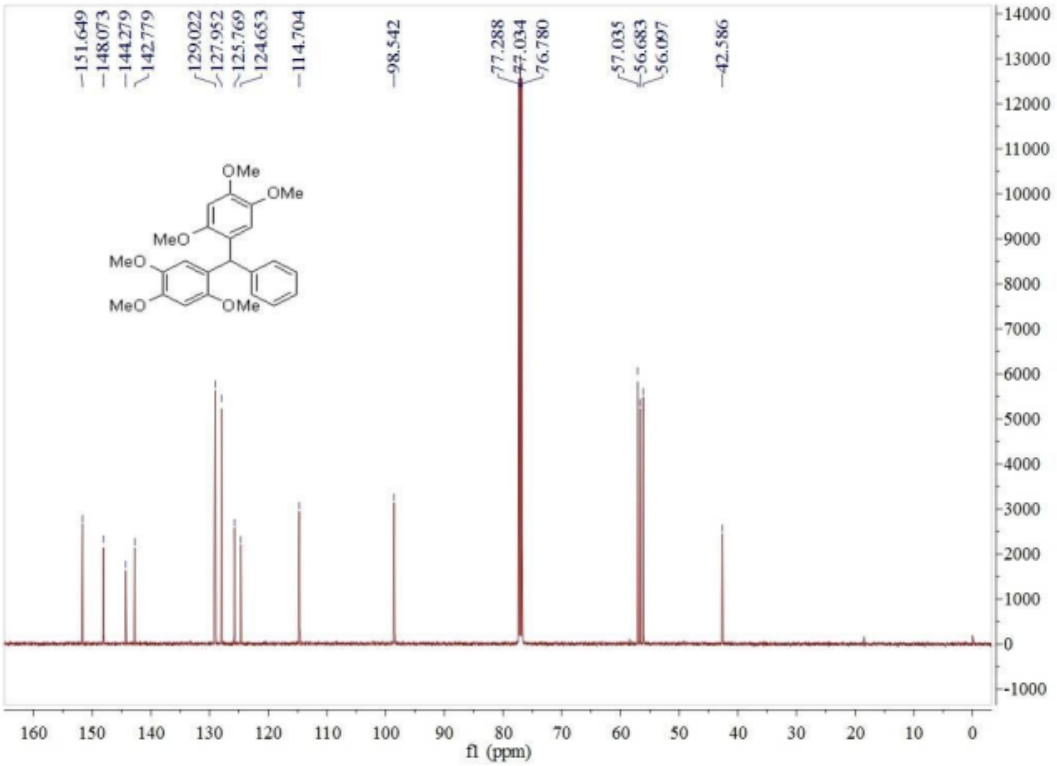
Deep eutectic solvent catalyzed Friedel–Crafts alkylation of electron-rich arenes with aldehydes

Ailing Wang[a*], Pengfei Xing[a], Xueliang Zheng[a, c], Hongyu Cao[b], Guang Yang[a] and Xuefang Zheng[b, c*]

*bis(2,4,5-trimethoxyphenyl)phenylmethane(**3a**)*

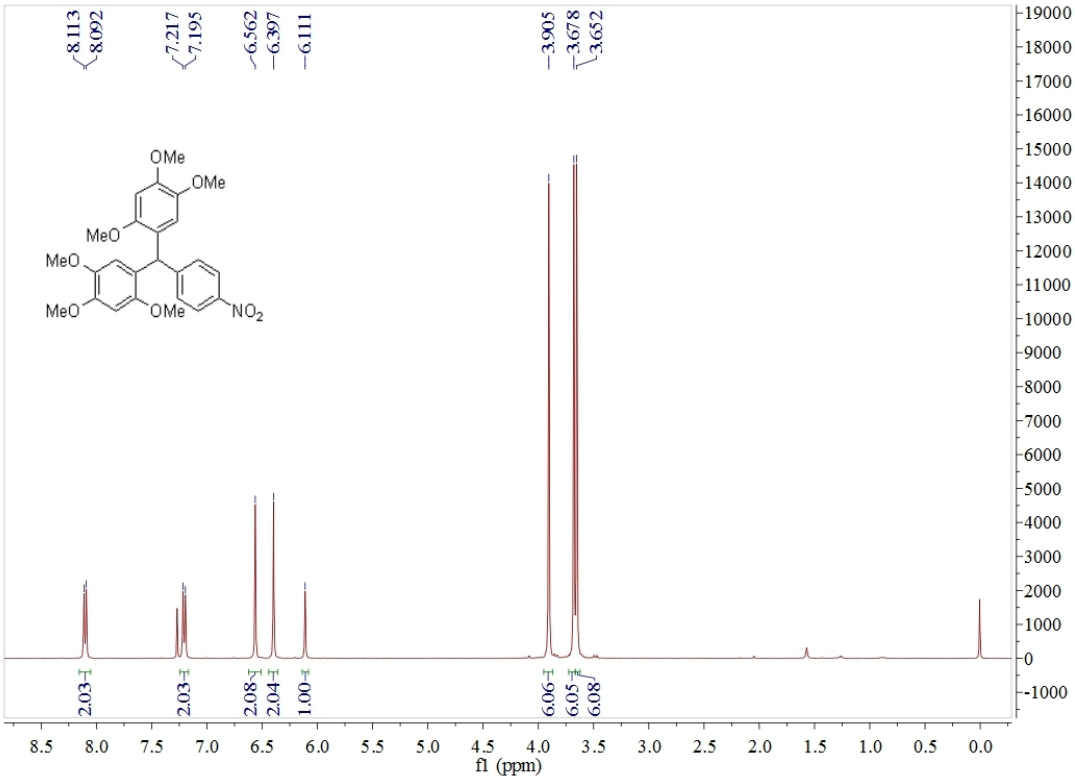
White solid m.p.: 127-128 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.63 (s, 6H), 3.66 (s, 6H), 3.88 (s, 6H), 6.08 (s, 1H), 6.43 (s, 2H), 6.54 (s, 2H), 7.05 (d, *J* = 6.0 Hz, 2H), 7.18 (m, 1H), 7.25 (m, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 42.6, 56.1, 56.7, 57.0, 98.5, 114.7, 124.7, 125.8, 128.0, 129.0, 142.8, 144.3, 148.1, 151.6.

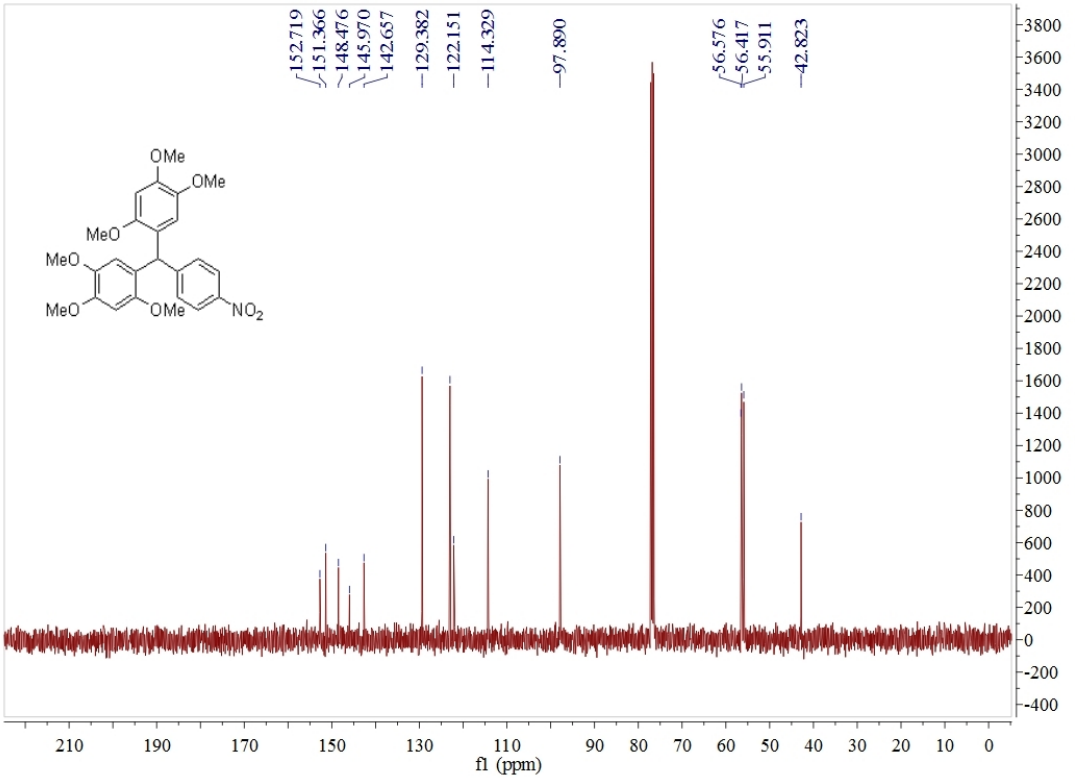




*5,5'-((4-nitrophenyl)methylene)bis(1,2,4-trimethoxybenzene) (**3b**)*

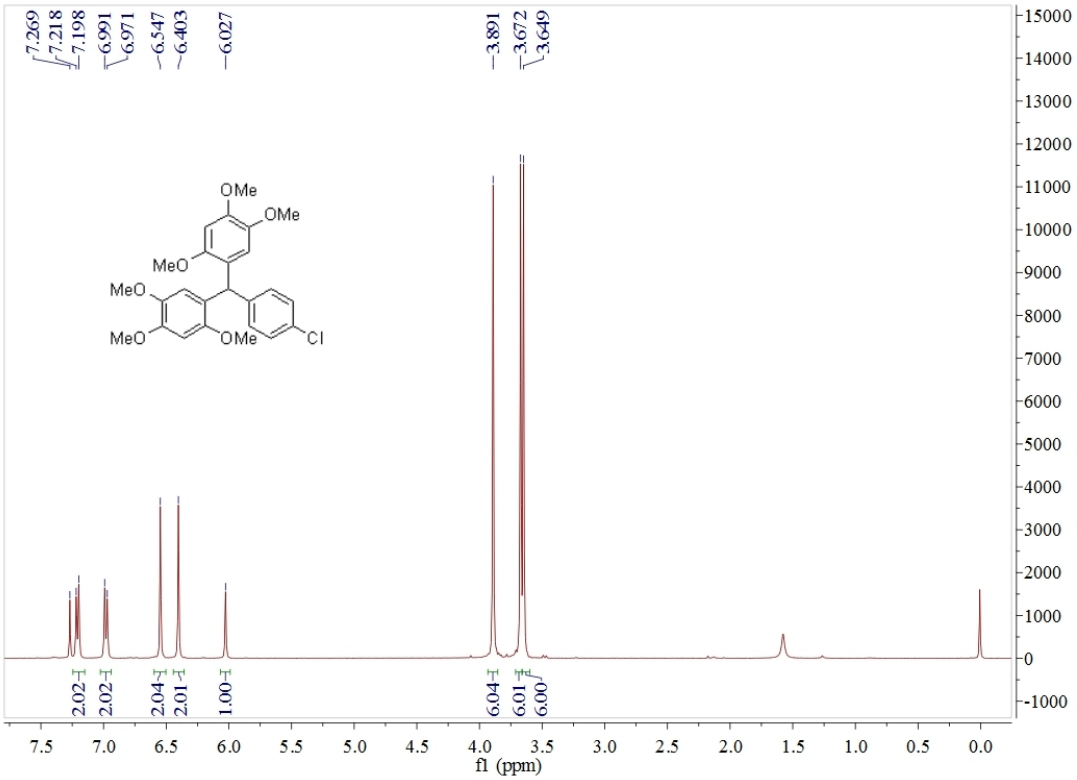
Yellow solid m.p.: 121-123 ˚C ; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.65 (s, 6H), 3.68 (s, 6H), 3.91 (s, 6H), 6.11 (s, 1H), 6.40 (s, 2H), 6.56 (s, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 42.8, 55.9, 56.4, 56.6, 97.9, 114.3, 122.2, 123.0, 129.4, 142.7, 146.0, 148.5, 151.4, 152.7.

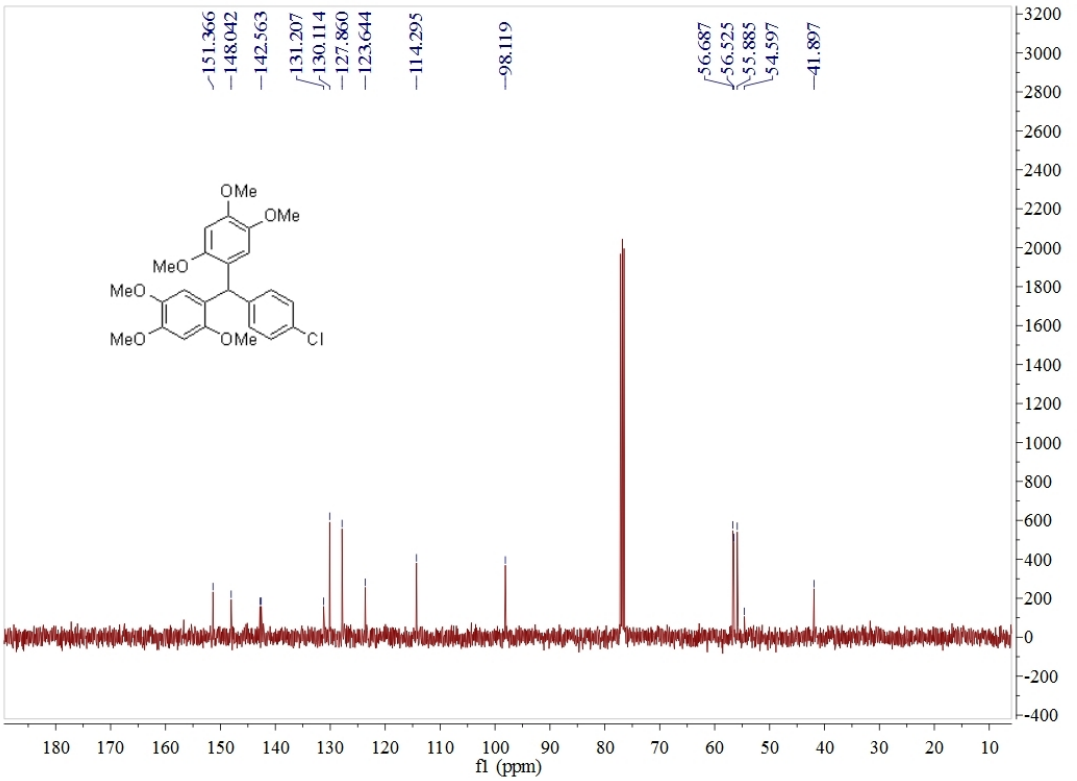




*1,1'-((4-chlorophenyl)methylene)bis(2,4,5-trimethoxybenzene) (**3c**)*

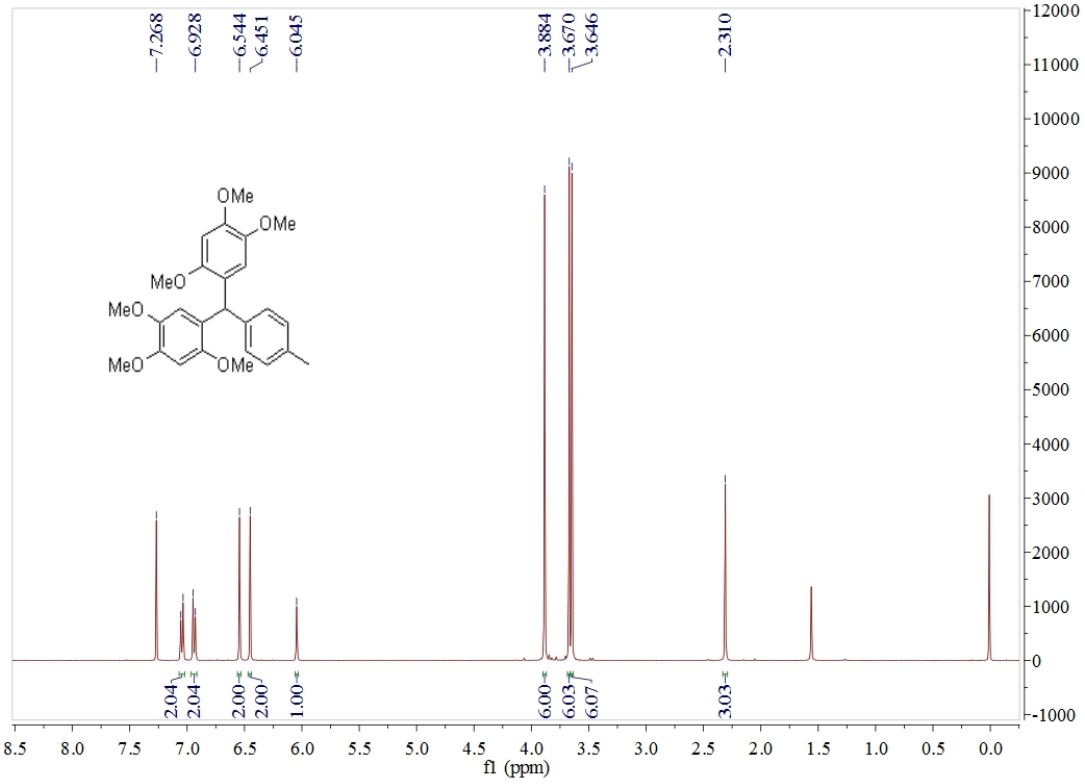
White solid m.p.: 167-169 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.65 (s, 6H), 3.67 (s, 6H), 3.90 (s, 6H), 6.03 (s, 1H), 6.40 (s, 2H), 6.55 (s, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 41.9, 55.9, 56.5, 56.7, 98.1, 114.3, 123.6, 127.9, 130.1, 131.2, 142.6, 142.8, 148.0, 151.4.

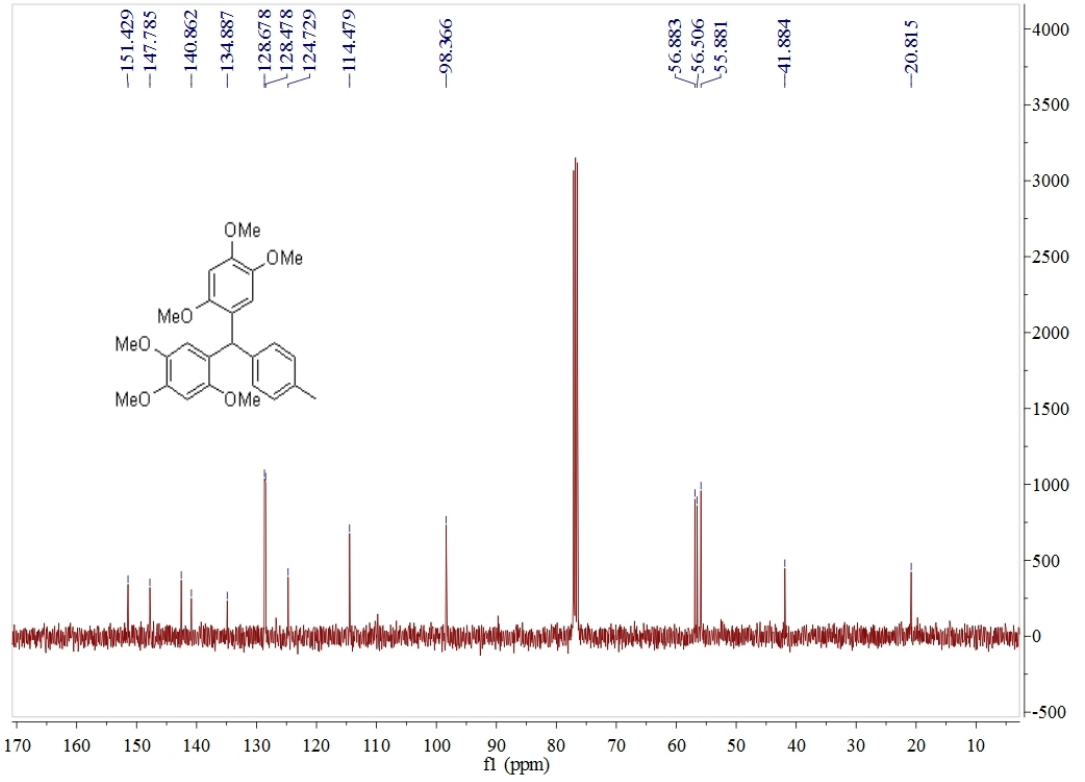




5,5'-(p-tolylmethylene)bis(1,2,4-trimethoxybenzene)(**3d**)

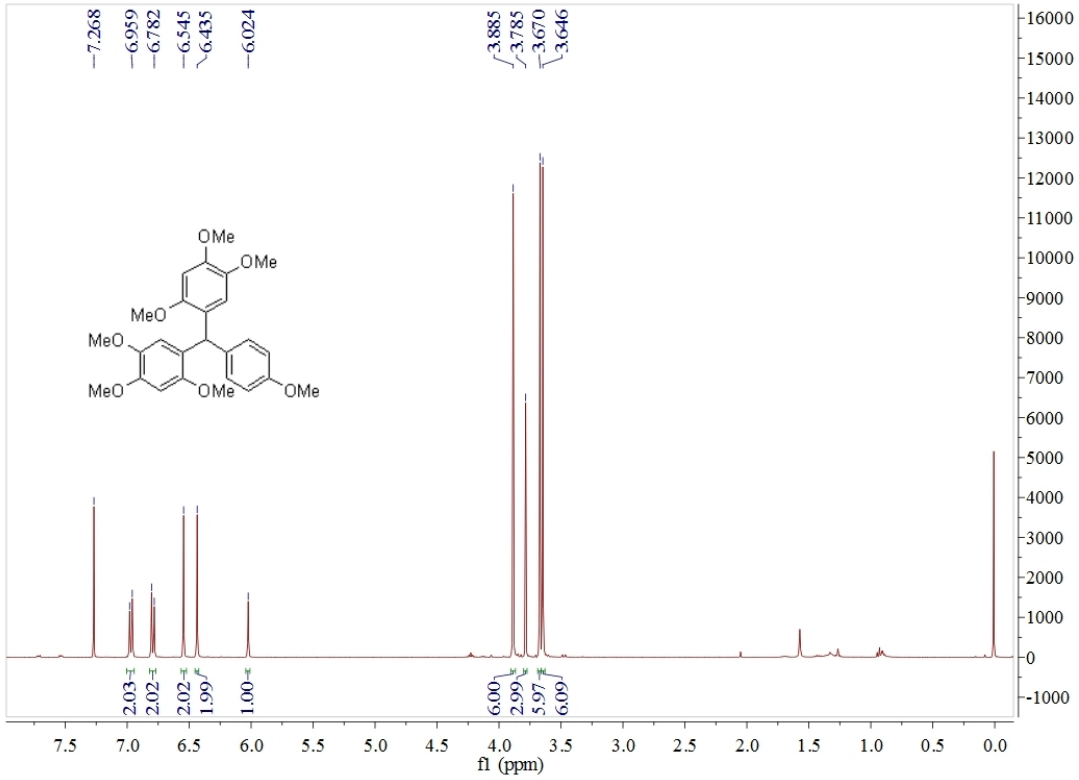
White solid m.p.:141-143 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 2.31 (s, 3H), 3.65 (s, 6H), 3.67 (s, 6H), 3.88 (s, 6H), 6.05 (s, 1H), 6.45 (s, 2H), 6.54 (s, 2H), 6.94(d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 20.8, 41.9, 55.9, 56.5, 56.9, 98.4, 114.5, 124.7, 128.5, 128.7, 134.9, 140.9, 142.6, 147.8, 151.4.

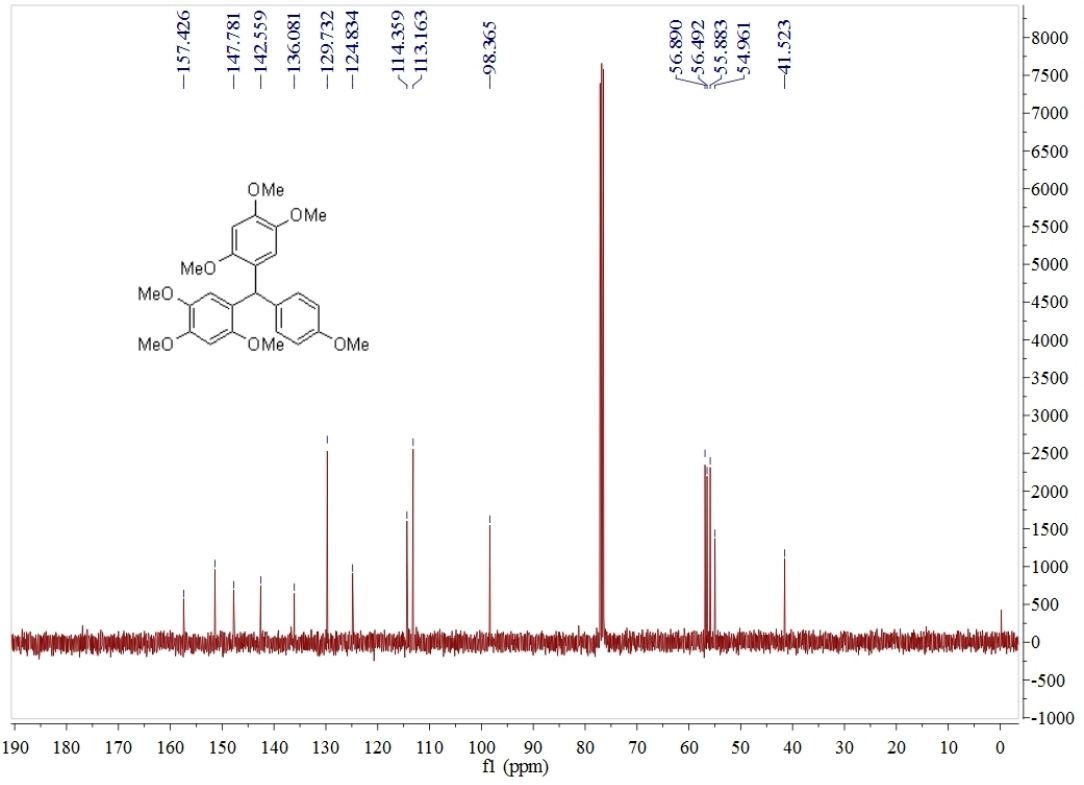




*bis(2,4,5-trimethoxyphenyl)(4-methoxyphenyl)methane(**3e**)*

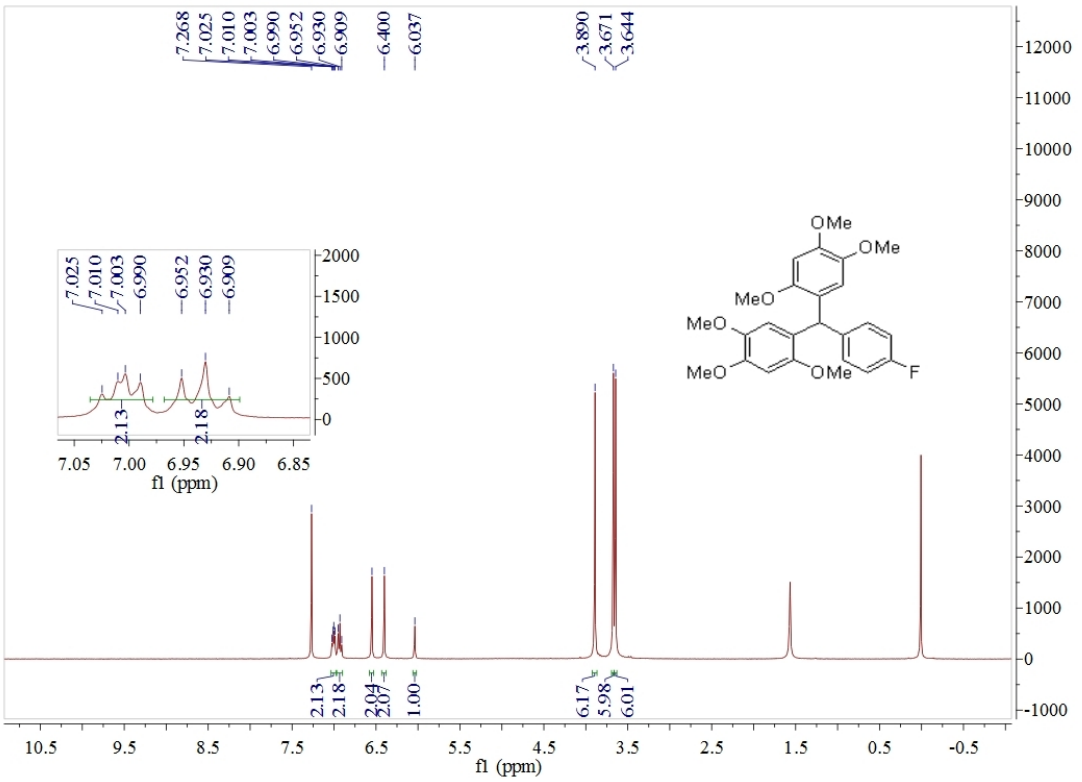
White solid m.p.: 130-132 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.65 (s, 6H), 3.67 (s, 6H), 3.79 (s, 3H), 3.89 (s, 6H), 6.02 (s, 1H), 6.44 (s, 2H), 6.55 (s, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 41.5, 55.0, 55.9, 56.5, 56.7, 98.4, 113.2, 114.4, 124.8, 129.7, 136.1, 142.6, 147.8, 151.5, 157.4.

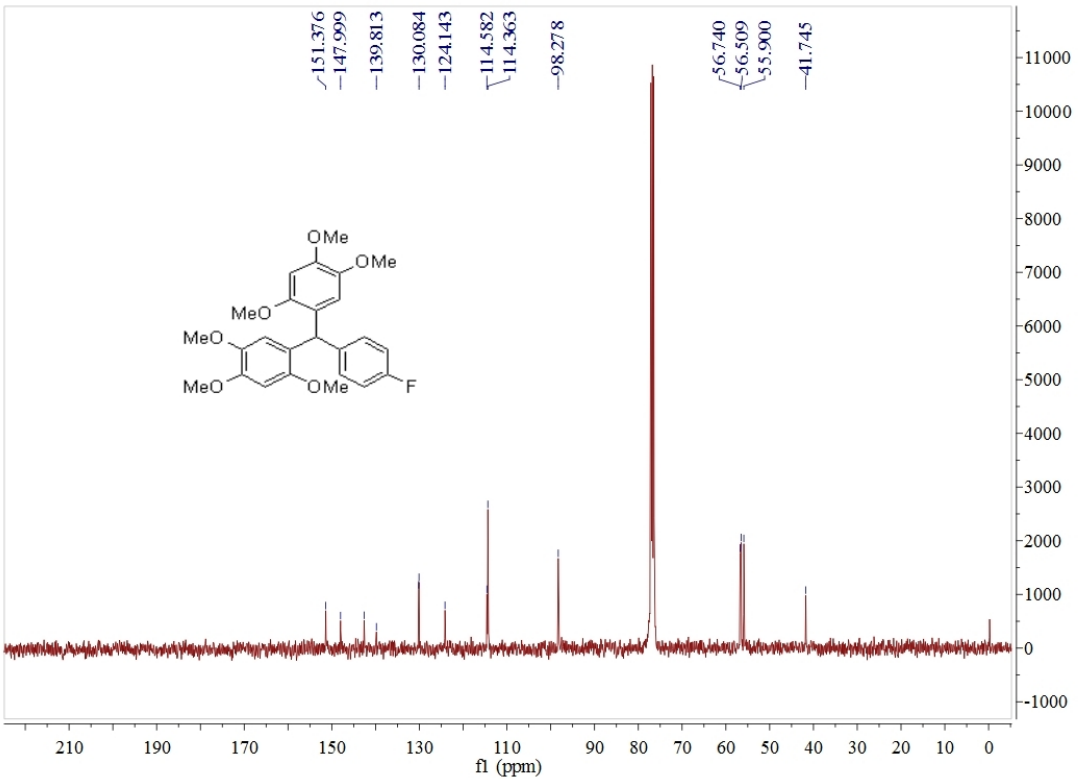




5,5'-((4-fluorophenyl)methylene)bis(1,2,4-trimethoxybenzene)(**3f**)

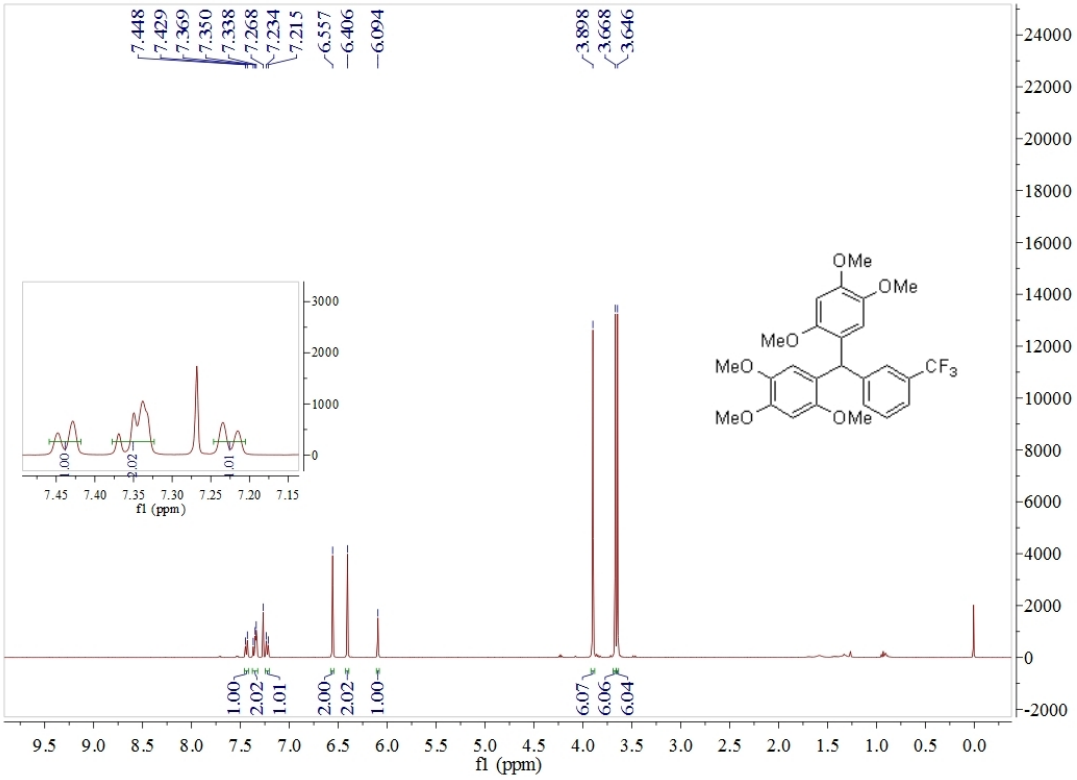
White solid m.p.: 127-128 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.64 (s, 6H), 3.67 (s, 6H), 3.89 (s, 6H), 6.04 (s, 1H), 6.40 (s, 2H), 6.55 (s, 2H), 6.91-6.95 (m, 2H), 6.70-7.03 (m, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 41.7, 55.9, 56.5, 56.7, 98.3, 114.4, 114.6, 124.1, 130.1, 130.2, 139.8, 148.0, 151.4. HRMS Calcd for $C_{25}H_{27}O_6F$: $[M+Na]^+$, 465.1684; Found: 465.1682.

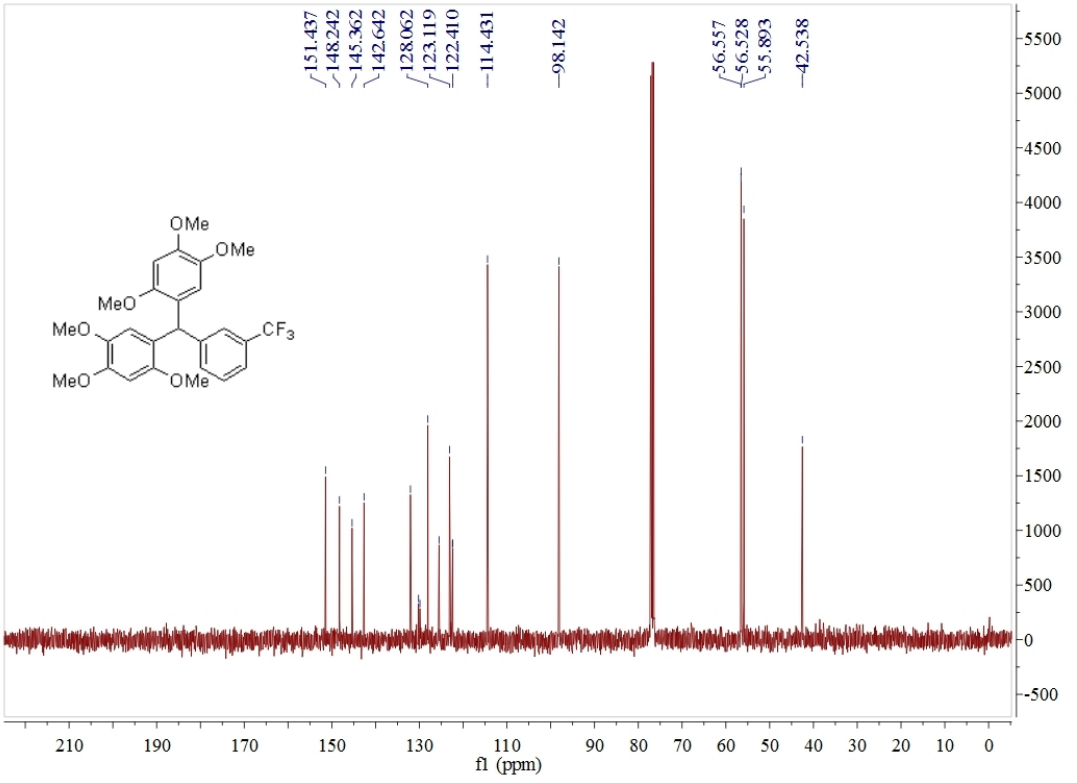




*5,5'-((3-(trifluoromethyl)phenyl)methylene)bis(1,2,4-trimethoxybenzene)(**3g**)*

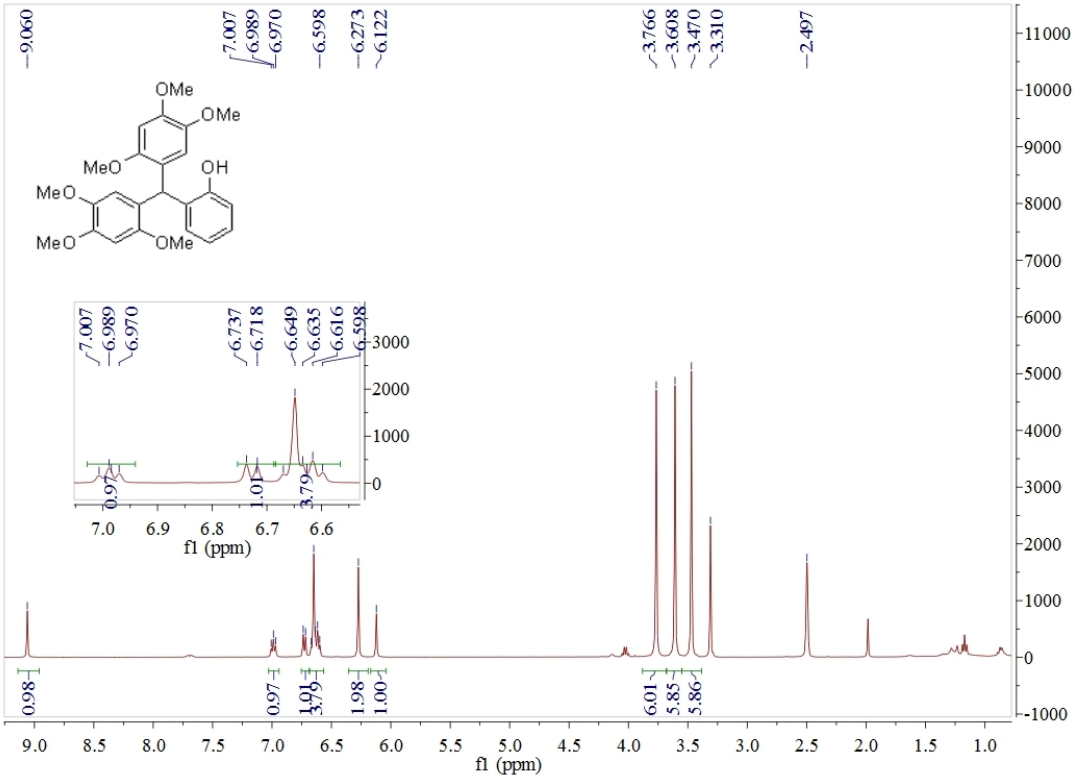
White solid m.p.: 135-136 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.65 (s, 6H), 3.67 (s, 6H), 3.90 (s, 6H), 6.09(s, 1H), 6.41 (s, 2H), 6.56 (s, 2H), 7.22 (d, J=7.6Hz, 1H), 7.34-7.37 (m, 2H), 7.44 (d, J=7.6Hz, 1H); ^{13}C NMR (100MHz; $CDCl_3$): δ 42.5, 55.9, 56.5, 56.6, 98.1, 114.4, 122.4, 123..1, 128.1, 142.6, 145.4, 148.2, 151.4. HRMS Calcd for $C_{26}H_{27}O_6F_3$: [M+Na]$^{+}$, 515.1652; Found: 515.1671.

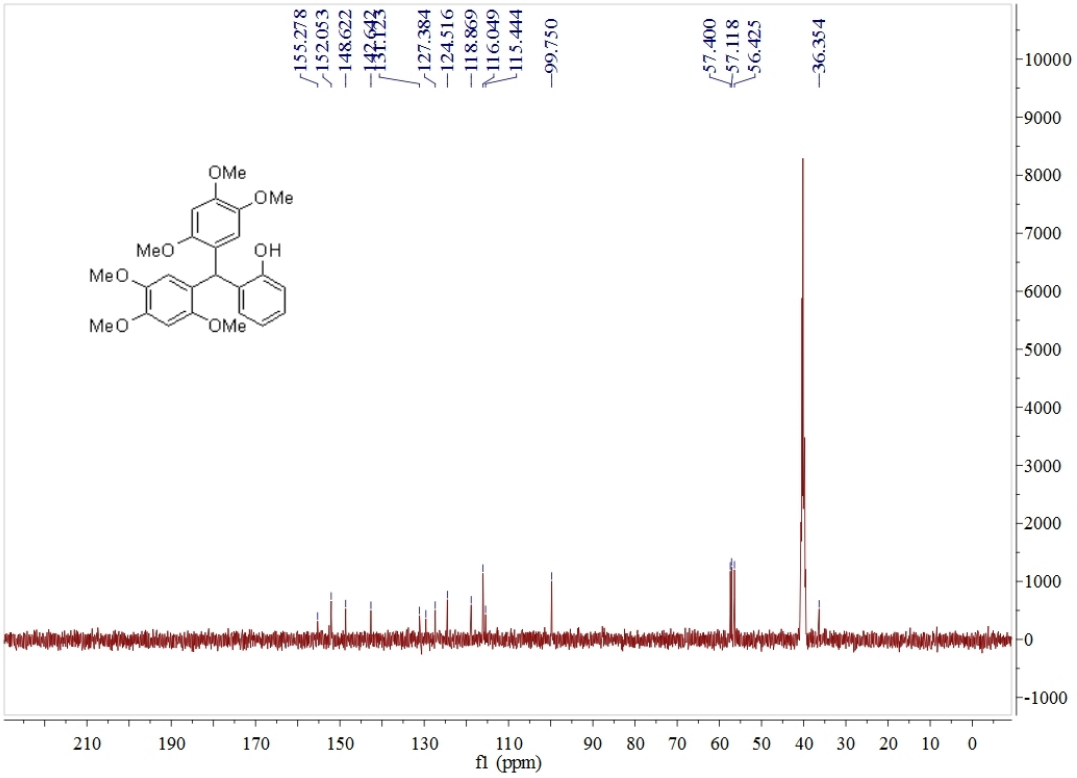




*2''-Oxy-2.4.5.2'.4'.5'-hexamethoxy-triphenylmethan (**3h**)*

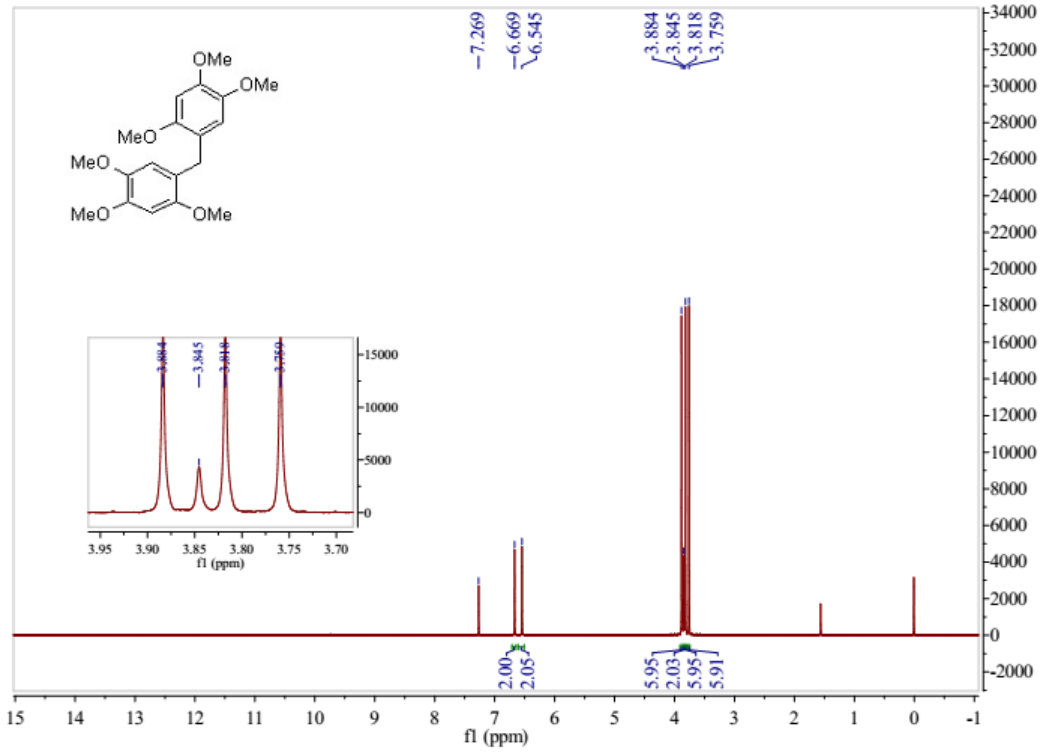
White solid m.p.: 169-170 °C; ^{1}H NMR (400MHz; DMSO-d_6): δ 3.47 (s, 6H), 3.61 (s, 6H), 3.77 (s, 6H), 6.12 (s, 1H), 6.27 (s, 2H), 6.60-6.67 (m, 4H), 6.73 (d, J = 8.0 Hz, 1H), 6.99 (t , J = 8.0 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR (100MHz; DMSO-d_6): δ 36.4, 56.4, 57.4, 99.7, 115.4, 116.0, 118.9, 124.5, 127.4, 129.6, 131.1, 142.0, 148.0, 152.1, 155.3.

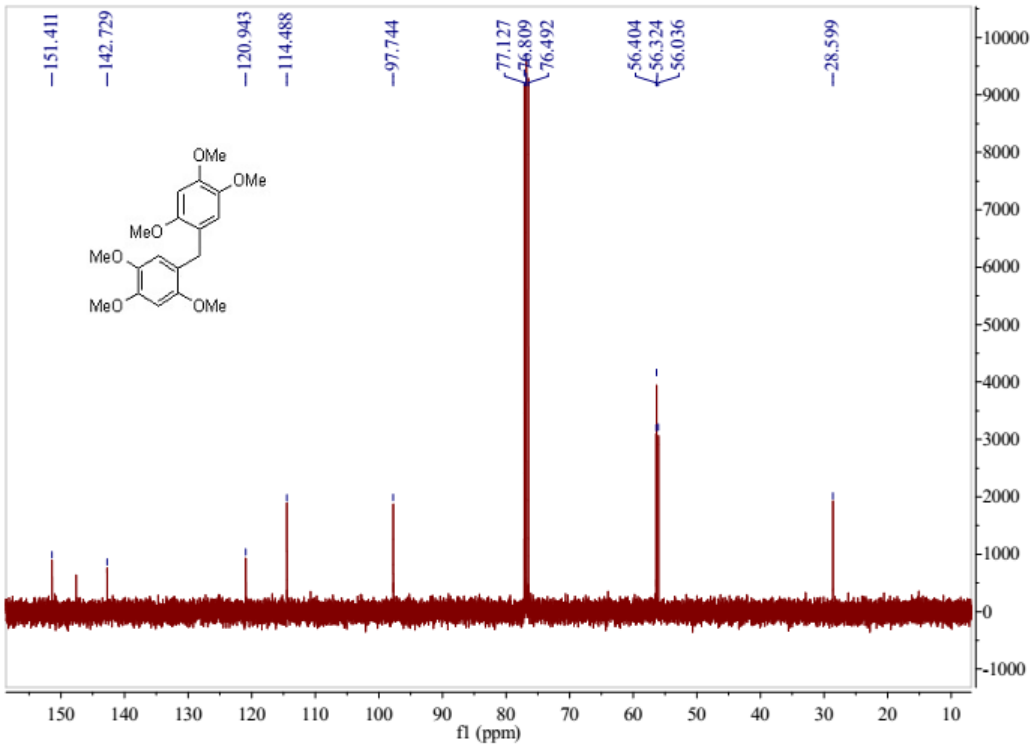




*bis(2,4,5-trimethoxyphenyl)methane (**3i**)*

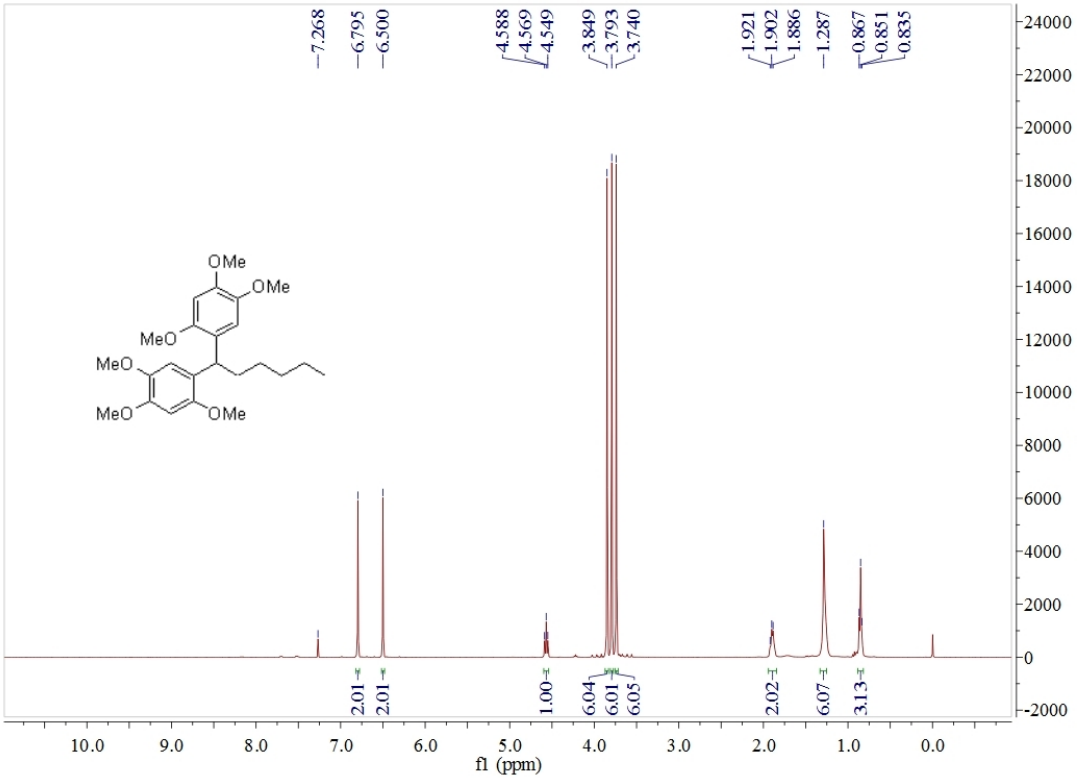
White solid m.p.: 100-101 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.76 (s, 6H), 3.82 (s, 6H), 3.85 (s, 2H), 3.88 (s, 6H), 6.55 (s, 2H), 6.67 (s, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 28.6, 56.0, 56.3, 56.4, 97.7, 114.5, 120.9, 142.7, 147.7, 151.4.

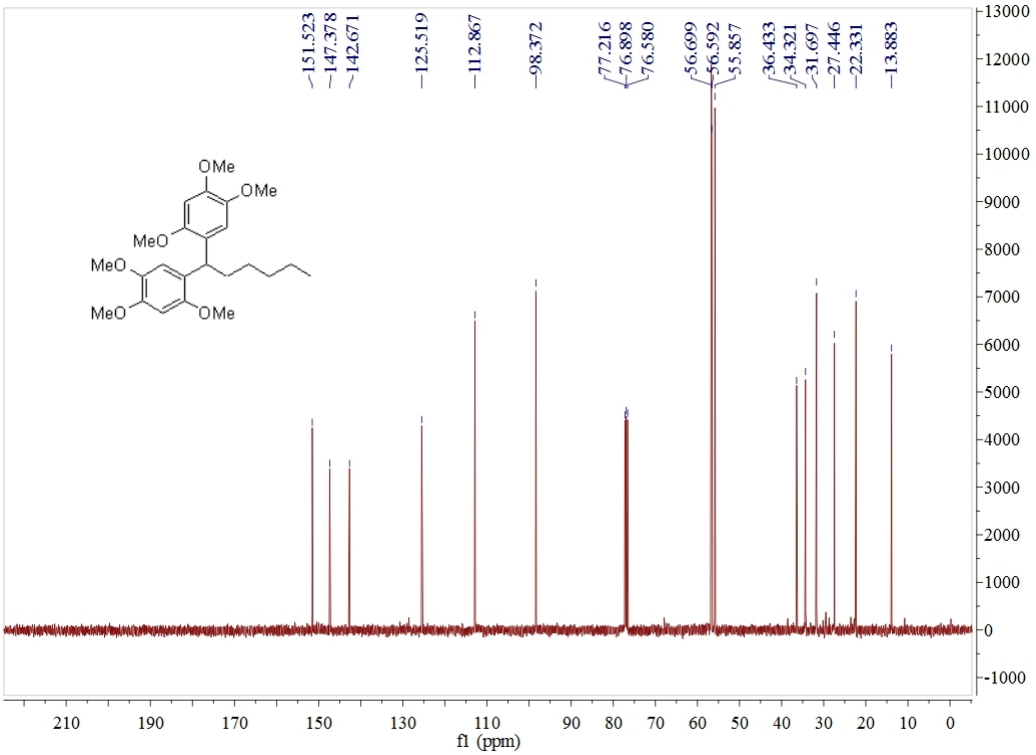




5,5'-(cyclopentylmethylene)bis(1,2,4-trimethoxybenzene)(**3j**)

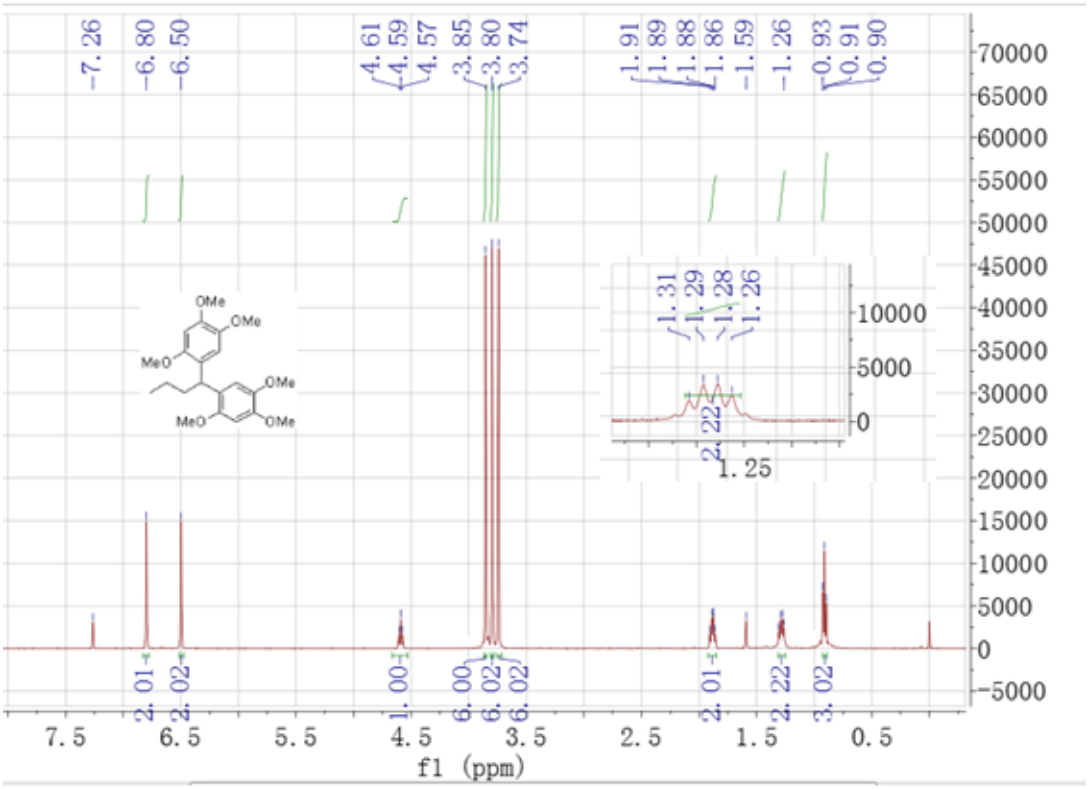
Colorless oil; ^{1}H NMR (400MHz; $CDCl_3$): δ 0.85 (t, *J* = 6.6 Hz, 3H), 1.29 (m, 6H), 1.89-1.92 (m, 2H), 3.74 (s, 6H), 3.85 (s, 6H), 4.57 (t, *J* = 7.8 Hz, 1H), 6.50 (s, 2H), 6.80 (s, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 13.9, 22.3, 27.5, 31.7, 34.3, 36.4, 98.4, 112.9, 125.5, 142.7, 147.4, 151.5.

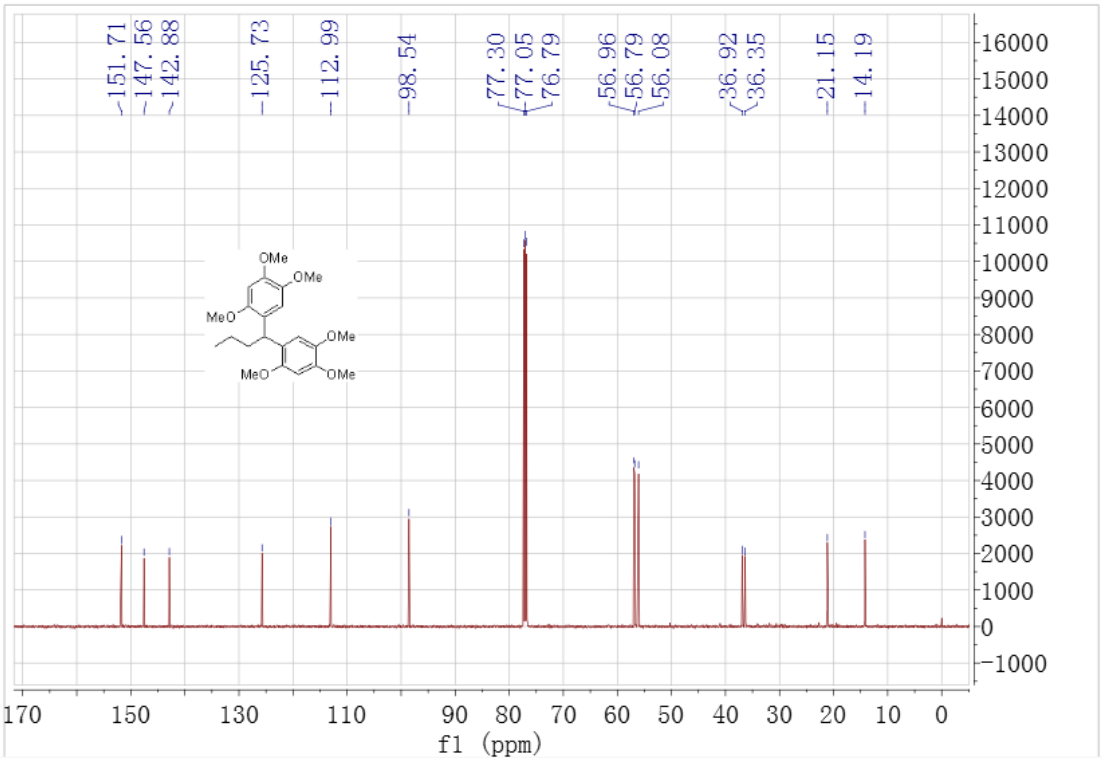




*5,5'-(butane-1,1-diyl)bis(1,2,4-trimethoxybenzene)(**3k**)*

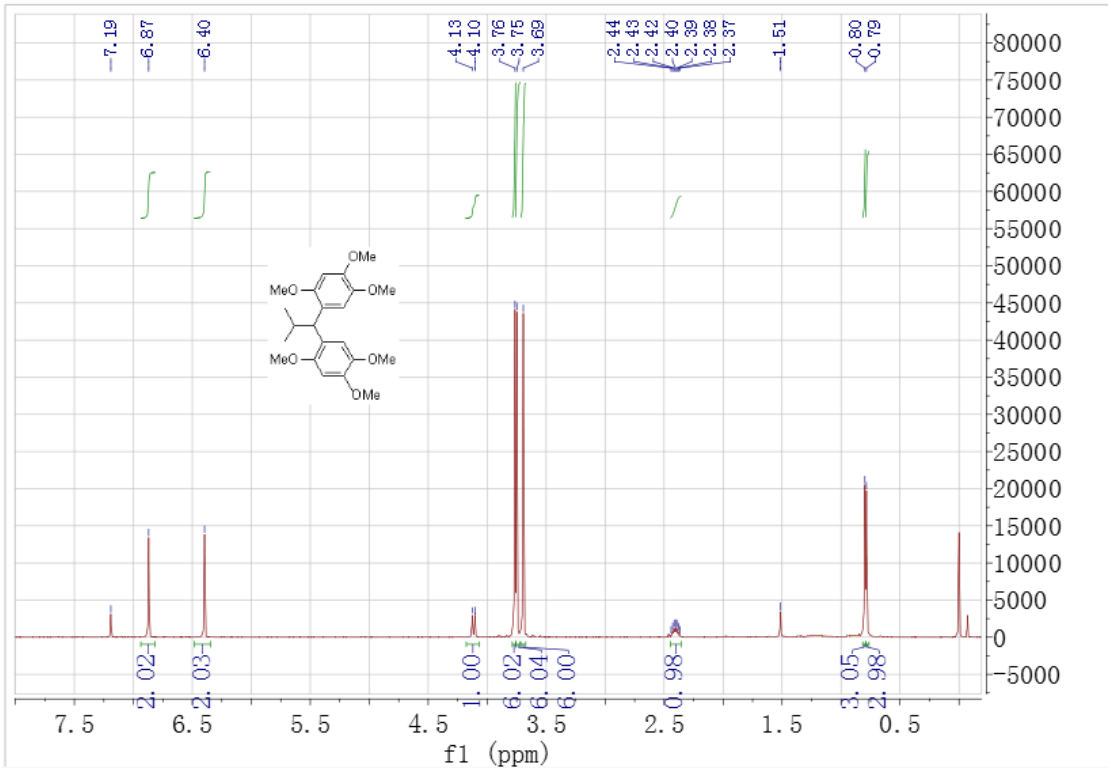
Colorless liquid; ^{1}H NMR (500MHz; $CDCl_3$): δ 0.91 (t, *J* = 6.6 Hz, 3H), 1.29 (m, 2H), 1.89 (dd, J_1=10Hz, J_2=15Hz, 2H), 3.74 (s, 6H), 3.80 (s, 6H), 3.85 (s, 6H), 4.59 (t, J=10Hz, 1H), 6.50 (s, 2H), 6.80 (s, 2H); ^{13}C NMR (125MHz; $CDCl_3$): δ 14.19, 21.15, 36.35, 36.92, 56.08, 56.79, 56.96, 98.54, 112.99, 125.73, 142.88, 147.56, 151.71.

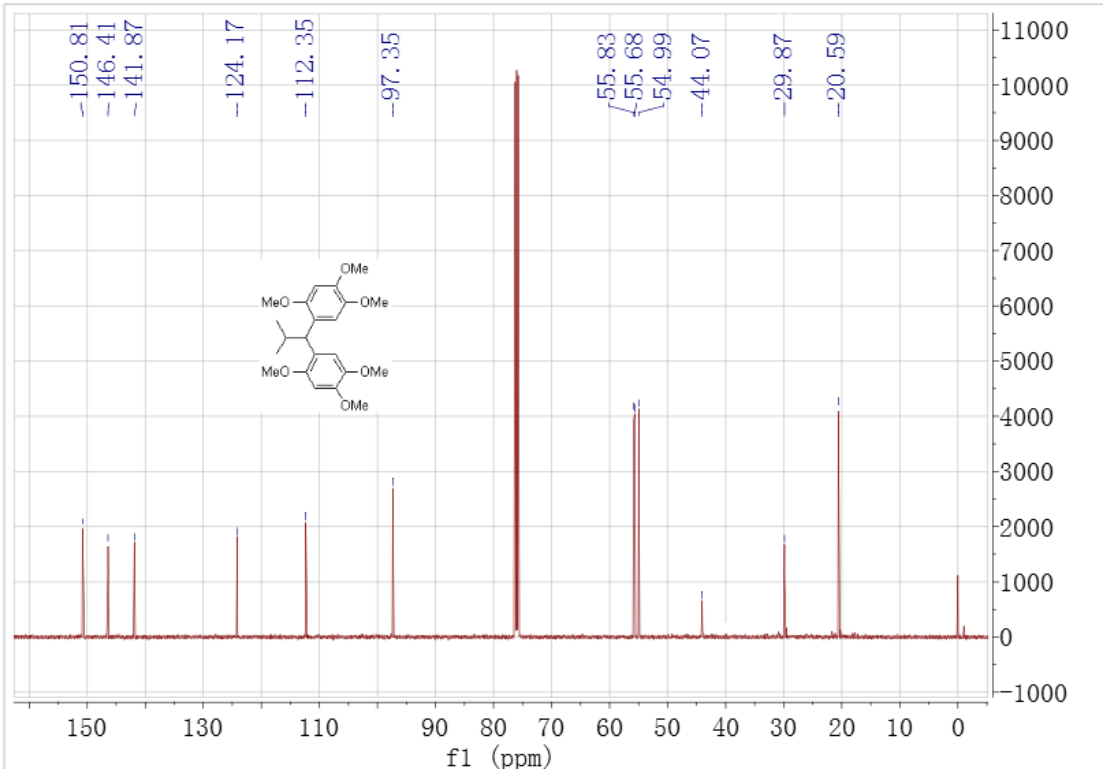




*5,5'-(2-methylpropane-1,1-diyl)bis(1,2,4-trimethoxybenzene)(**3l**)*

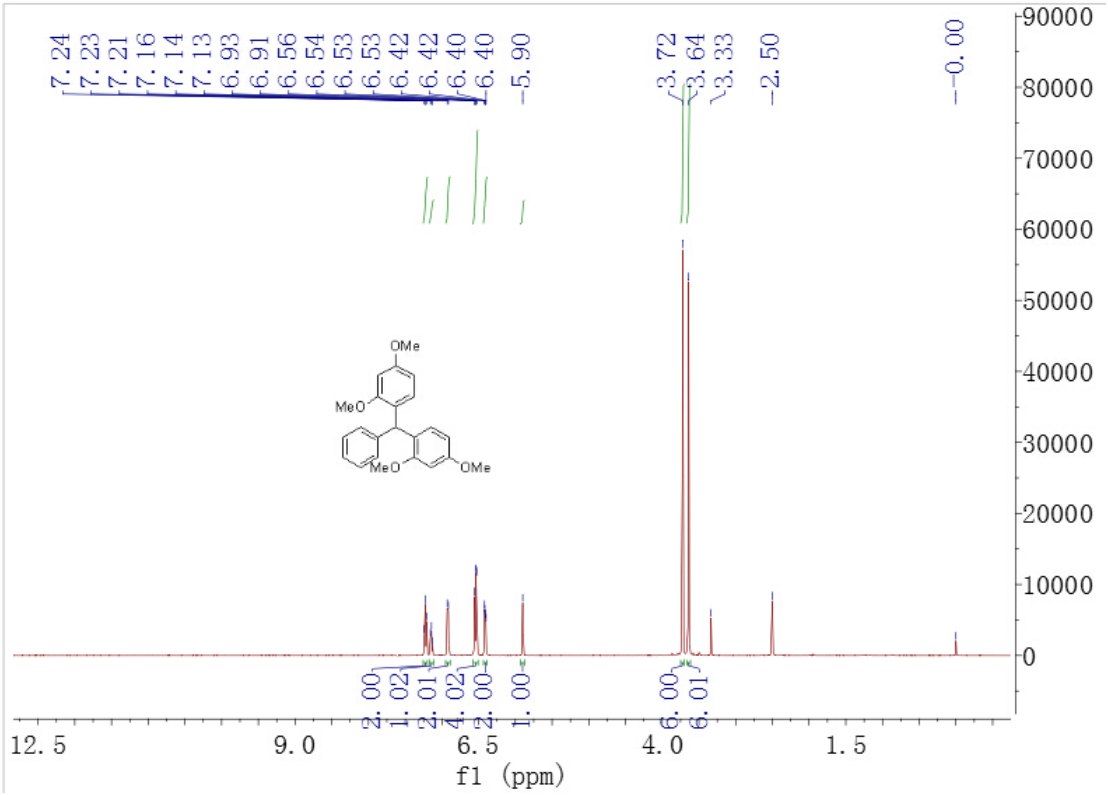
Colorless liquid; ^{1}H NMR (500MHz; $CDCl_3$): δ 0.79 (s, 3H), 0.80 (s, 3H), 2.40 (m, 1H), 3.69 (s, 6H), 3.75 (s, 1H), 3.76 (s, 6H), 4.12 (d, J=10Hz, 1H), 6.40 (s, 2H), 6.87 (s, 2H); ^{3}C NMR (125MHz; $CDCl_3$): δ 20.59, 29.87, 44.07, 54.99, 55.68, 55.83, 97.35, 112.35, 124.17, 141.87, 146.41, 150.81.

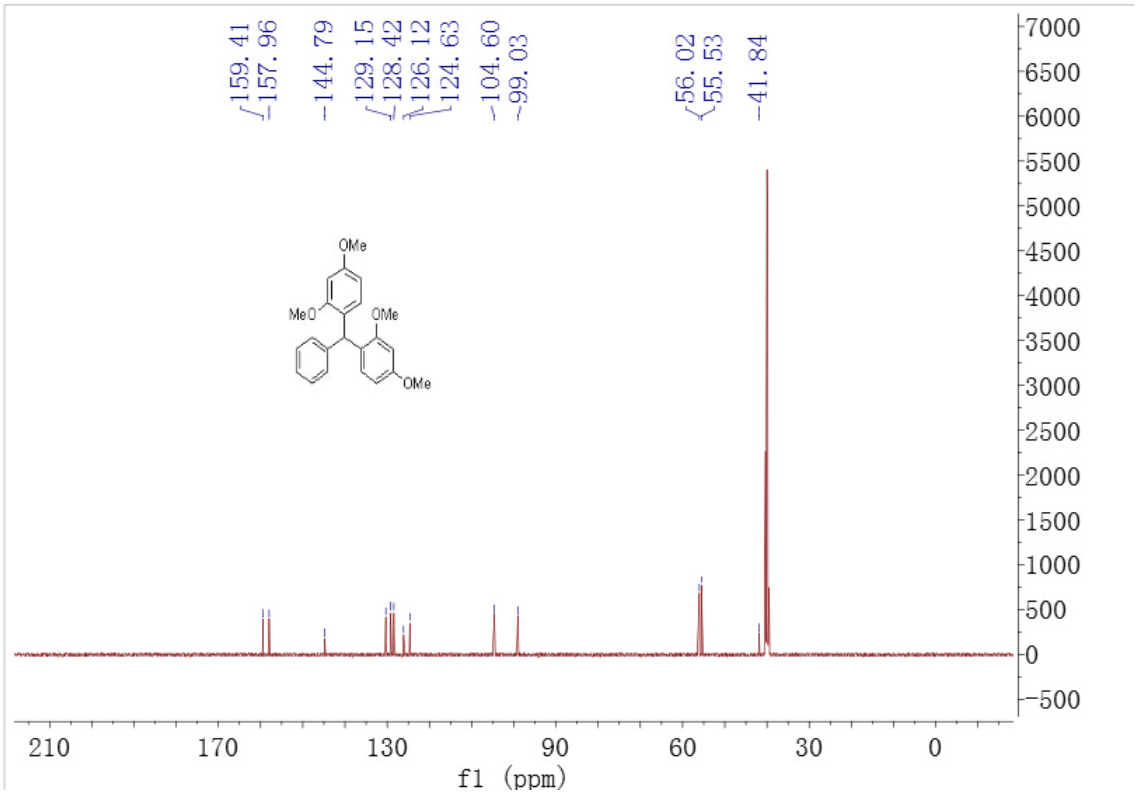




*4,4'-(phenylmethylene)bis(1,3-dimethoxybenzene)(**3m**)*

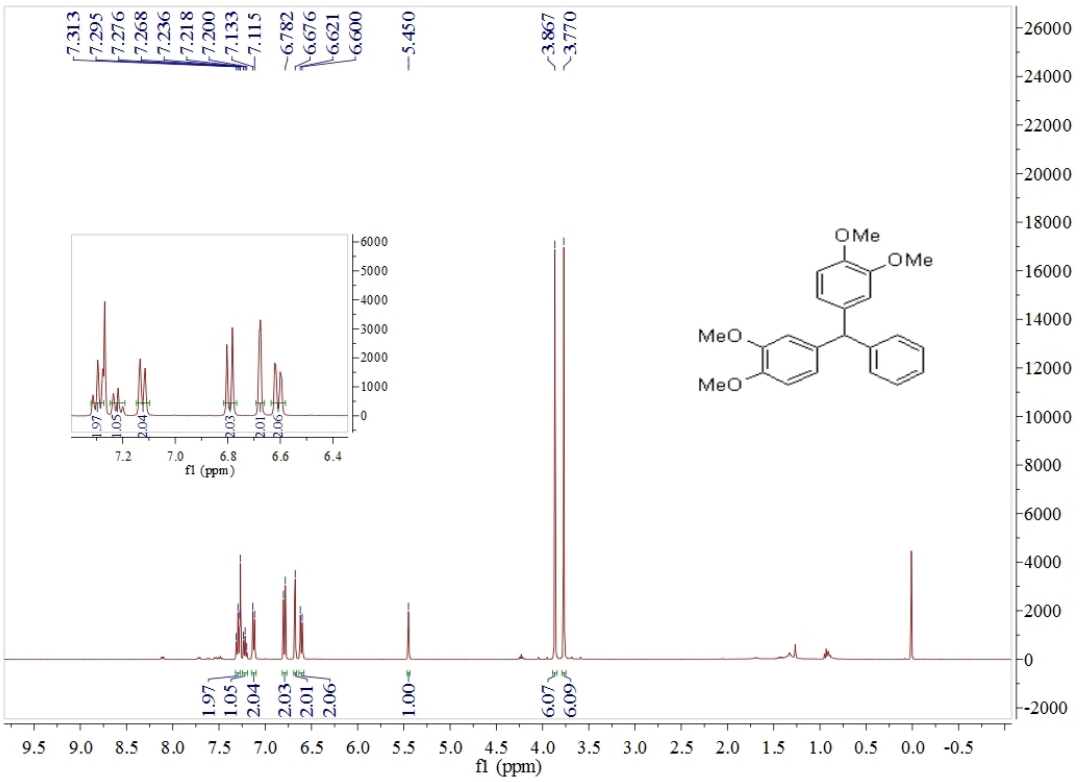
White solid m.p.:132-133 ˚C; ^{1}H NMR (500MHz; DMSO-d_6): δ 3.64 (s, 6H), 3.72 (s, 6H), 5.90 (s, 1H), 6.41 (dd, J=10 Hz,2H), 6.53-6.56 (m, 4H), 6.92 (d, J=10 Hz, 2H), 7.13-7.16 (m, 1H), 7.21-7.24 (m, 1H); ^{13}C NMR (125MHz; DMSO-d_6): δ 41.8, 55.5, 56.0, 99.0, 104.6, 124.6, 126.1, 128.4, 129.2, 144.8, 158.0, 159.4. HRMS Calcd for $C_{23}H_{24}O_4$: $[M+H]^+$, 365.1747; Found: 365.1746.

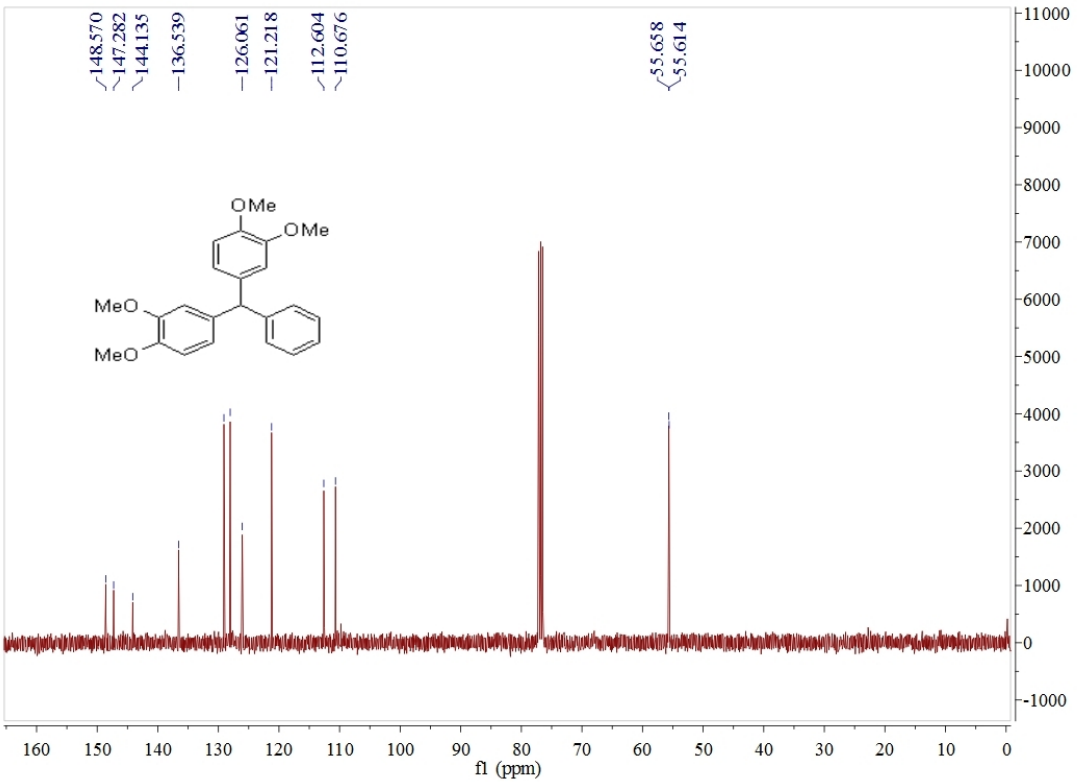




4,4'-(phenylmethylene)bis(1,2-dimethoxybenzene)(**3n**)

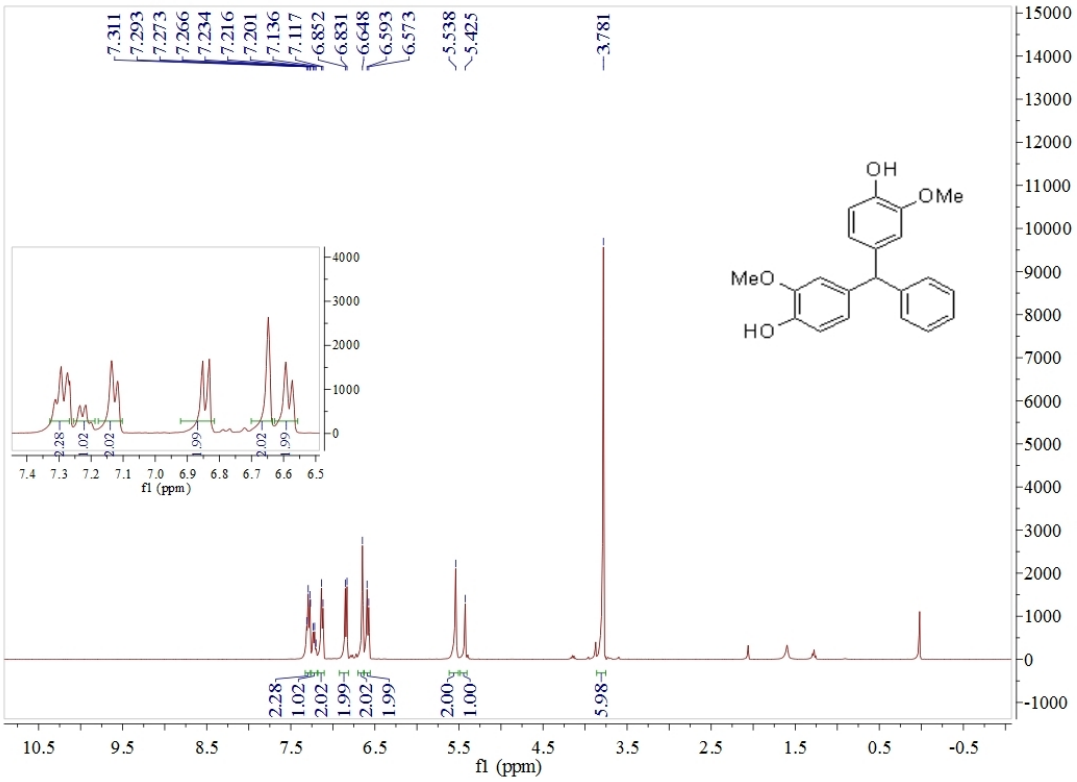
White solid m.p.: 123-124 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.77 (s, 6H), 3.87 (s, 6H), 5.45 (s, 1H), 6.61 (dd, J_1 = 1.3Hz, J_2 = 8.2 Hz, 2H), 6.68 (d, *J* = 1.5 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 55.6, 55.7, 110.7, 112.6, 121.2, 126.1, 128.1, 129.1, 136.5, 144.1, 147.3, 148.6.

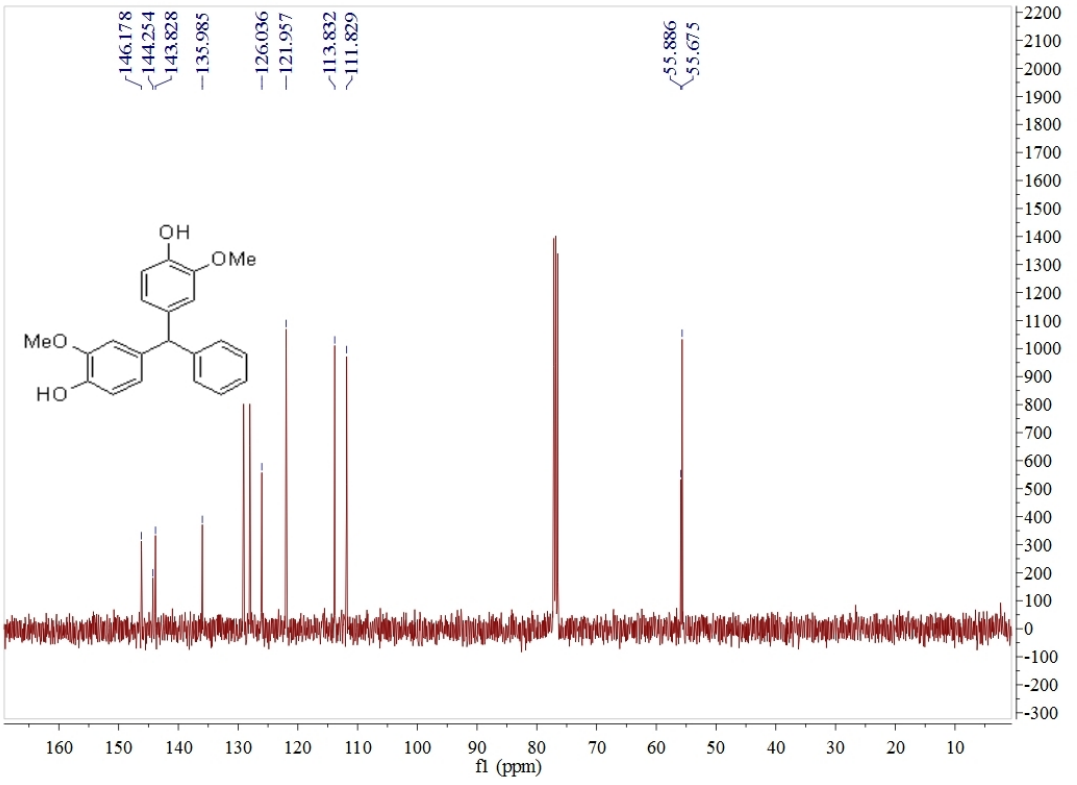




4,4'-(phenylmethylene)bis(2-methoxyphenol)(**3o**)

Yellow solid m.p.: 130-131 ˚C; ^{1}H NMR (400MHz; $CDCl_3$): δ 3.78 (s, 6H), 5.43 (s, 1H), 5.54 (s, 2H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.22 (m, 1H), 7.28 (m, 2H); ^{13}C NMR (100MHz; $CDCl_3$): δ 55.7, 55.9, 111.8, 113.8, 122.0, 126.0, 128.0, 129.1, 136.0, 143.8, 144.3, 146.2.





bis(4-hydroxyphenyl)-phenylmethane (**3p**)

Pink solid m.p.: 161-163 ˚C ; ^{1}H NMR (400MHz; $CDCl_3$): δ 4.62 (s, 2H), 5.43 (s, 1H), 6.70 (d, *J* = 8.6 Hz, 4H), 6.97 (d, *J* = 8.4 Hz, 4H), 7.09-7.11 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.1Hz, 2H): ^{13}C NMR (100MHz; $CDCl_3$); δ 55.0, 114.9, 126.0, 128.1, 129.1, 130.3, 136.4, 144.3, 153.6.