Supplementary Information

Dicarbonylative Benzannulation of 3-Acetoxy-1,4-enynes with CO and Silylboranes by Pd and Cu Cooperative Catalysis: One-Step Access to 3-Hydroxyarylacylsilanes

Li-Jun Wu,[ab‡] Liang-Feng Yang,[ab‡] Jin-Heng Li*[abc] and Qiu-An Wang*[a]

[a] *State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China*

[b] *Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China*

[c] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*

E-mail: jhli@hnu.edu.cn, wangqa@hnu.edu.cn

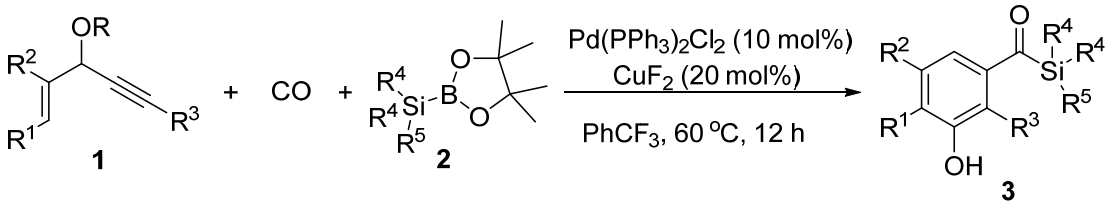
[‡] *These authors contributed equally to this work.*

List of Contents

(A) General Information

^{1}H NMR,^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz advance spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. Low-resolution mass spectra (LRMS) data weremeasured on GCMS-QP2010 Ultra. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting Point were recorded on Hanon MP100 Apparatus. All products were identified by ^{1}H and ^{13}C NMR, LRMS, HRMS. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques. 3-Acetoxy-1,4-enynes were prepared according to the literature,[1] and the other starting materials and solvents were commercially available and were used without further purification. Columnchromatography was performed on silica gel (300-400 mesh) using petroleum ether/ethyl acetate.

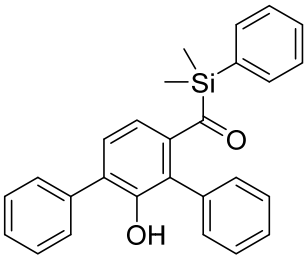
(a) Typical Experimental Procedure for the Synthesis of 3-Hydroxyarylacylsilane (3):



To a Schlenk tube were added 3-acetoxy-1,4-enyne **1** (0.2 mmol), silylborane **2** (0.4 mmol), $Pd(PPh_3)_2Cl_2$ (10 mol%; 0.02 mmol), CuF_2 (20 mol%; 0.04 mmol) and $PhCF_3$ (2 mL). Then the tube was charged with CO (1 atm), and was stirred at 60 °C for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/hexanes = 1:9) to afford the desired products **3**.

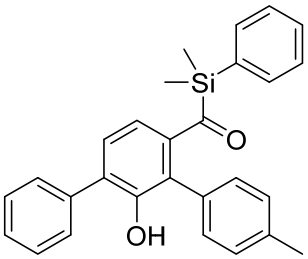
(B) Analytical data of Products 3 and 4

(Dimethyl(phenyl)silyl)(2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3aa):



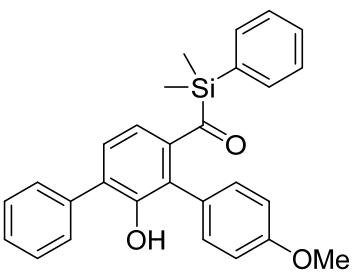
59.6 mg, 73%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.38-7.29 (m, 10H), 7.16-7.14 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.34 (s, 1H), 0.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.9, 149.5, 145.4, 137.1, 134.9, 134.0, 133.9, 131.0, 130.4, 129.9, 129.6, 129.2, 128.8, 128.6, 128.2, 127.8, 127.8, 124.9, 118.7, -3.8; LRMS (EI, 70 eV) m/z (%): 408 (M^+, 51), 330 (100), 257 (26), 135 (96); HRMS m/z (ESI) calcd for $C_{27}H_{25}O_2Si$ ($[M+H]^+$) 409.1618, found 409.1631.

(Dimethyl(phenyl)silyl)(2'-hydroxy-4''-methyl-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ba):



55.7 mg, 66%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.2 Hz, 2H), 7.35-7.25 (m, 13H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.34 (s, 1H), 2.40 (s, 3H), 0.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.9, 149.5, 145.2, 137.7, 135.0, 134.1, 134.1, 134.0, 131.0, 130.4, 129.8, 129.6, 129.4, 129.1, 128.8, 128.2, 127.8, 124.8, 118.7, 21.2, -3.7; LRMS (EI, 70 eV) m/z (%): 422 (M^+, 37), 344 (41), 255 (14), 135 (100); HRMS m/z (ESI) calcd for $C_{28}H_{27}O_2Si$ ($[M+H]^+$) 423.1775, found 423.1783.

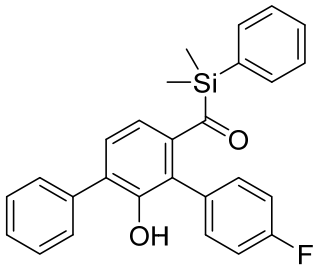
(Dimethyl(phenyl)silyl)(2'-hydroxy-4''-methoxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ca):



63.9 mg, 73%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 6.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.39-7.26 (m, 7H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.87-6.82 (m, 3H), 5.36 (s, 1H), 3.81 (s, 3H), 0.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 242.5, 159.5, 149.6, 145.7, 137.2, 134.8, 133.9, 132.4, 130.2, 129.7, 129.5, 129.2, 128.6, 127.8, 125.5, 124.6, 118.2, 114.3, 55.2, -3.7; LRMS (EI, 70 eV) m/z (%): 438 (M^+, 78), 345 (100), 207

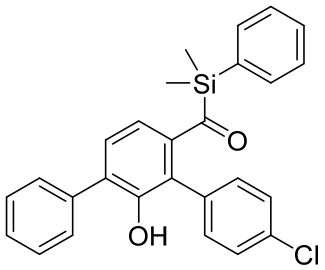
(20), 135 (62); HRMS m/z (ESI) calcd for $C_{28}H_{27}O_3Si$ ($[M+H]^+$) 439.1724, found 439.1737.

(Dimethyl(phenyl)silyl)(4''-fluoro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3da):



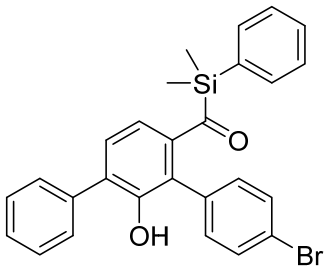
58.8 mg, 69%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.29 (m, 7H), 7.11-7.07 (m, 2H), 6.98 (t, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.25 (s, 1H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.9, 162.4 (d, *J* = 246.6 Hz), 149.6, 145.5, 136.8, 134.6, 133.9, 132.8 (d, *J* = 8.1 Hz), 130.4, 129.9, 129.8 (d, *J* = 3.5 Hz), 129.7, 129.2, 128.9, 128.0, 127.9, 123.9, 118.8, 115.6 (d, *J* =21.4 Hz), -3.7; LRMS (EI, 70 eV) m/z (%): 426 (M^+, 53), 348 (98), 275 (26), 135 (100); HRMS m/z (ESI) calcd for $C_{27}H_{24}FO_2Si$ ($[M+H]^+$) 427.1524, found 427.1537.

(4''-Chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)-methanone (3ea):



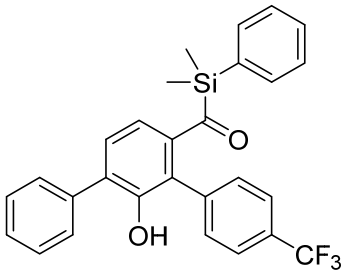
62.8 mg, 71%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.45 (m, 4H), 7.41-7.37 (m, 2H), 7.33-7.29 (m, 4H), 7.25-7.23 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.25 (s, 1H), 0.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.7, 149.5, 145.3, 136.7, 134.5, 134.1, 133.9, 132.5, 132.3, 130.5, 123.0, 129.7, 129.2, 128.9, 128.7, 128.1, 127.9, 123.8, 118.9, -3.7; LRMS (EI, 70 eV) m/z (%): 444 (M^+ + 2, 21), 442 (M^+, 45), 349 (100), 135 (62); HRMS m/z (ESI) calcd for $C_{27}H_{24}{}^{35}ClO_2Si$ ($[M+H]^+$) 443.1229, found 443.1244.

(4''-Bromo-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)-methanone (3fa) :



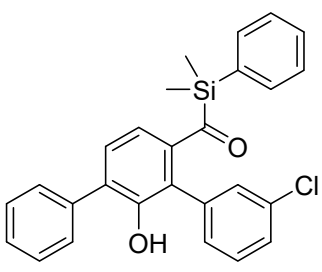
68.0 mg, 70%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.44 (m, 4H), 7.39-7.38 (m, 4H), 7.32-7.24 (m, 5H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.27 (s, 1H), 0.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.7, 149.4, 145.2, 136.6, 134.4, 133.9, 133.0, 132.6, 131.7, 130.5, 130.0, 129.7, 129.1, 128.9, 128.1, 127.9, 123.8, 122.4, 118.9, -3.7; LRMS (EI, 70 eV) m/z (%): 488 (M^+ + 2, 8), 486 (M^+, 8), 329 (41), 135 (100); HRMS m/z (ESI) calcd for $C_{27}H_{24}{}^{79}BrO_2Si$ ($[M+H]^+$) 487.0723, found 487.0731.

(Dimethyl(phenyl)silyl)(2'-hydroxy-4''-(trifluoromethyl)-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ga):



60.0 mg, 63%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.46 (m, 6H), 7.43-7.36 (m, 2H), 7.32-7.28 (m, 5H), 7.24-7.20 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.4, 149.5, 145.3, 138.5, 136.4, 134.4, 133.9, 131.2, 130.7, 130.2, 129.8, 129.7 (d, *J* = 32.2 Hz), 129.1, 129.1, 128.3, 128.0, 125.2 (d, *J* = 3.7Hz), 124.0 (d, *J* = 270.4 Hz), 123.8, 119.3, -3.7; LRMS (EI, 70 eV) m/z (%): 476 (M^+, 79), 461 (100), 355 (42), 135 (67); HRMS m/z (ESI) calcd for $C_{28}H_{24}F_3O_2Si$ ($[M+H]^+$) 477.1492, found 477.1507.

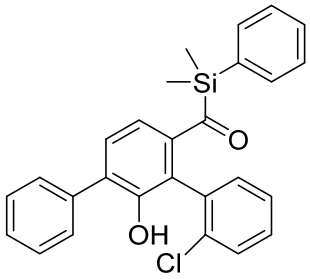
(3''-Chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)-methanone (3ha):



55.7 mg, 63%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.41-7.37 (m, 2H), 7.34-7.29 (m, 6H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.27 (s, 1H), 0.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 241.6, 149.4, 145.4, 136.6, 136.2, 134.6, 134.4, 133.9, 130.8, 130.6, 130.1, 129.7, 129.7, 129.3, 129.2, 129.0, 128.2, 128.1, 127.9, 123.7, 119.0, -3.7; LRMS (EI,

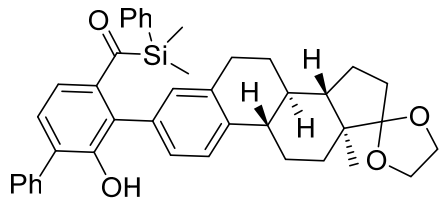
70 eV) m/z (%): 444 (M^+ + 2, 20), 442 (M^+, 51), 349 (100), 135 (64); HRMS m/z (ESI) calcd for $C_{27}H_{24}ClO_2Si$ ($[M+H]^+$) 443.1229, found 443.1237.

(2''-Chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)-methanone (3ia):



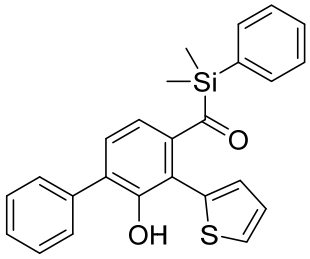
39.8 mg, 45%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.2 Hz, 4H), 7.49-7.42 (m, 3H), 7.38-7.30 (m, 7H), 7.23-7.18 (m, 2H), 5.12 (s, 1H), 0.56 (s, 3H), 0.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 236.6, 150.2, 142.3, 136.8, 135.4, 134.0, 133.9, 133.8, 131.9, 131.5, 130.0, 129.8, 129.7, 129.5, 129.2, 128.7, 128.1, 128.0, 127.1, 122.2, 121.9, -3.0, -3.2; HRMS m/z (ESI) calcd for $C_{27}H_{24}ClO_2Si$ ($[M+H]^+$) 443.1229, found 443.1233.

(Dimethyl(phenyl)silyl)(2-hydroxy-3-(13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-[1,1'-biphenyl]-4-yl)methanone (3ja):



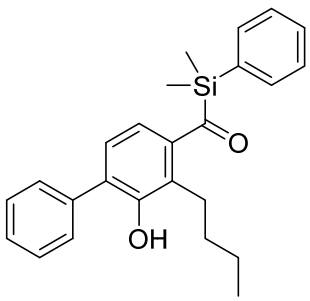
85.4 mg, 68%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61-7.54 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.39-7.34 (m, 2H), 7.30-7.24 (m, 6H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.77 (s, 1H), 5.48 (s, 1H), 3.99-3.87 (m, 4H), 2.70-2.68 (m, 2H), 2.35-2.24 (m, 2H), 2.08-2.02 (m, 1H), 1.90-1.76 (m, 4H), 1.66-1.31 (m, 6H), 0.92 (s, 3H), 0.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 242.5, 149.5, 145.7, 140.7, 137.6, 137.4, 135.0, 133.9, 133.0, 131.5, 130.6, 130.2, 129.8, 129.4, 129.3, 128.5, 128.1, 127.7, 126.0, 125.0, 119.4, 118.1, 65.3, 64.6, 49.5, 46.1, 44.0, 38.6, 34.2, 30.7, 29.3, 26.8, 25.8, 22.4, 14.4, -3.6; HRMS m/z (ESI) calcd for $C_{41}H_{45}O_4Si$ ($[M+H]^+$) 629.3081, found 629.3090.

(Dimethyl(phenyl)silyl)(2-hydroxy-3-(thiophen-2-yl)-[1,1'-biphenyl]-4-yl)methanone (3ka):



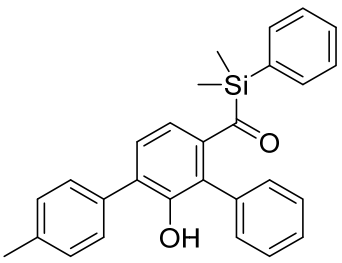
38.1 mg, 46%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.52 (m, 2H), 7.49-7.42 (m, 2H), 7.99-7.35 (m, 5H), 7.32-7.28 (m, 3H), 7.03-7.01 (m, 1H), 6.88-6.87 (m, 1H), 6.80 (d, *J* =8.0 Hz, 1H), 5.74 (s, 1H), 0.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.7, 149.7, 146.2, 136.7, 134.9, 134.7, 133.9, 130.4, 130.3, 130.2, 129.6, 129.2, 128.8, 128.2, 128.0, 127.8, 127.4, 118.3, 117.6, -3.9; LRMS (EI, 70 eV) m/z (%): 414 (M^+, 48), 336 (57), 207 (27), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{23}O_2SSi$ ($[M+H]^+$) 415.1183, found 415.1175.

(3-Butyl-2-hydroxy-[1,1'-biphenyl]-4-yl)(dimethyl(phenyl)silyl)methanone (3la):



39.6 mg, 51%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 6.4 Hz, 2H), 7.50-7.46 (m, 2H), 7.43-7.35 (m, 6H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.32 (s, 1H), 2.71-2.67 (m, 2H), 1.49-1.43 (m, 2H), 1.35-1.28 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 240.7, 151.0, 143.9, 136.7, 135.3, 134.0, 129.9, 129.8, 129.4, 129.0, 128.3, 128.1, 126.9, 126.7, 120.9, 32.7, 26.2, 23.0, 14.0, -3.2; LRMS (EI, 70 eV) m/z (%): 388 (M^+, 6), 304 (100), 215 (19), 135 (12); HRMS m/z (ESI) calcd for $C_{25}H_{29}O_2Si$ ($[M+H]^+$) 389.1931, found 389.1939.

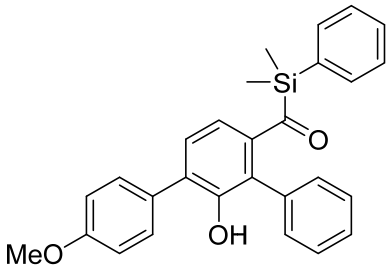
(Dimethyl(phenyl)silyl)(2'-hydroxy-4-methyl-[1,1':3',1''-terphenyl]-4'-yl)methanone (3na):



55.7 mg, 66%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.2 Hz, 2H), 7.37-7.25 (m, 11H), 7.17-7.14 (m, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.34 (s, 1H), 2.40 (s, 3H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.9, 149.5, 145.2, 137.7, 135.8, 135.0, 134.1, 134.0,

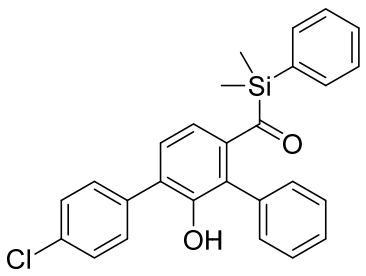
131.0, 130.4, 129.8, 129.6, 129.4, 129.1, 128.8, 128.2, 127.8, 124.8, 118.7, 21.2, -3.8; LRMS (EI, 70 eV) m/z (%): 422 (M^+, 60), 407 (63), 329 (100), 135 (43); HRMS m/z (ESI) calcd for $C_{28}H_{27}O_2Si$ ($[M+H]^+$) 423.1775, found 423.1789.

(Dimethyl(phenyl)silyl)(2'-hydroxy-4-methoxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3oa):



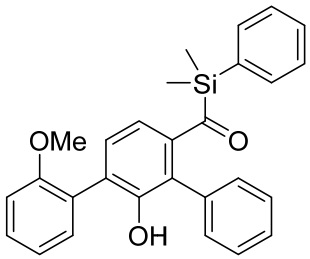
62.2 mg, 71%; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 7.6 Hz, 2H), 7.34-7.24 (m, 9H), 7.16-7.13 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 3.84 (s, 3H), 0.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 241.7, 159.3, 149.5, 144.9, 135.0, 134.1, 134.0, 131.0, 130.4, 130.1, 129.7, 129.6, 129.3, 128.8, 128.2, 127.8, 124.8, 118.6, 114.1, 55.3, -3.8; LRMS (EI, 70 eV) m/z (%): 438 (M^+, 100), 345 (86), 135 (50); HRMS m/z (ESI) calcd for $C_{28}H_{27}O_3Si$ ($[M+H]^+$) 439.1724, found 439.1735.

(4-Chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)-methanone (3pa):



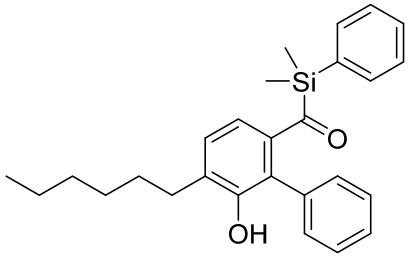
60.1 mg, 68%; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 6.8 Hz, 2H), 7.68-7.52 (m, 11H), 7.41-7.39 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 5.58 (s, 1H), 0.55 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 241.5, 149.6, 145.3, 135.8, 134.8, 134.0, 133.7, 133.5, 130.9, 130.7, 129.8, 129.7, 129.2, 128.6, 128.5, 127.9, 124.9, 119.0, -3.8; LRMS (EI, 70 eV) m/z (%): 444 (M^+ + 2, 23), 442 (M^+, 60), 349 (100), 135 (63); HRMS m/z (ESI) calcd for $C_{27}H_{24}ClO_2Si$ ($[M+H]^+$) 443.1229, found 443.1241.

(Dimethyl(phenyl)silyl)(2'-hydroxy-2-methoxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3qa):



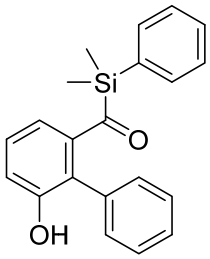
55.2 mg, 63%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.19 (m, 13H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.17 (s, 1H), 3.83 (s, 3H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 243.4, 155.7, 150.4, 146.6, 135.0, 134.9, 134.0, 132.3, 131.6, 130.8, 129.6, 129.4, 128.3, 128.0, 127.7, 127.7, 126.5, 126.3, 121.8, 118.0, 111.4, 56.0, -3.9; LRMS (EI, 70 eV) m/z (%): 438 (M^+, 29), 423 (100), 255 (39), 135 (51); HRMS m/z (ESI) calcd for $C_{28}H_{27}O_3Si$ ($[M+H]^+$) 439.1724, found 439.1728.

(Dimethyl(phenyl)silyl)(5-hexyl-6-hydroxy-[1,1'-biphenyl]-2-yl)methanone (3ra):



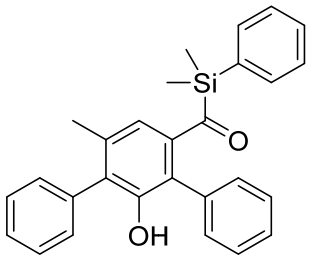
47.4 mg, 57%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 7.5 Hz, 2H), 7.49-7.46 (m, 2H), 7.43-7.35 (m, 6H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.33 (s, 1H), 2.71-2.68 (m, 2H), 1.50-1.46 (m, 2H), 1.31-1.24 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 240.7, 151.0, 143.8, 136.7, 135.3, 134.0, 129.9, 129.7, 129.4, 129.0, 128.2, 128.1, 126.9, 126.7, 120.9, 31.7, 30.5, 29.7, 26.4, 22.6, 14.1, -3.2; LRMS (EI, 70 eV) m/z (%): 416 (M^+, 52), 338 (34), 269 (68), 135 (100); HRMS m/z (ESI) calcd for $C_{27}H_{33}O_2Si$ ($[M+H]^+$) 417.2244, found 417.2253.

(Dimethyl(phenyl)silyl)(6-hydroxy-[1,1'-biphenyl]-2-yl)methanone (3sa):



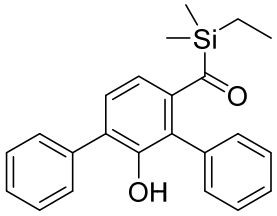
27.9 mg, 42%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-7.33 (m, 4H), 7.30-7.27 (m, 4H), 7.26-7.25 (m, 1H), 7.07-7.05 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 5.22 (s, 1H), 0.23 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 242.5, 152.6, 146.2, 134.7, 134.0, 133.4, 130.7, 129.6, 129.2, 129.1, 128.4, 127.8, 123.9, 118.5, 117.4, -3.9; LRMS (EI, 70 eV) m/z (%): 332 (M^+, 35), 254 (100), 181 (32), 135 (63); HRMS m/z (ESI) calcd for $C_{21}H_{21}O_2Si$ ($[M+H]^+$) 333.1305, found 333.1318.

(Dimethyl(phenyl)silyl)(2'-hydroxy-6'-methyl-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ta):



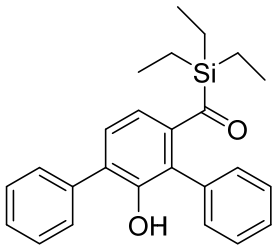
38.8 mg, 46%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.47 (m, 2H), 7.43-7.38 (m, 1H), 7.36-7.28 (m, 10H), 7.17-7.15 (m, 2H), 6.69 (s, 1H), 4.98 (s, 1H), 2.07 (s, 3H), 0.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 243.3, 149.6, 145.8, 137.1, 135.5, 135.1, 134.4, 134.0, 131.3, 130.3, 129.9, 129.5, 129.1, 128.5, 128.1, 127.8, 127.7, 122.1, 119.4, 20.4, -3.8; LRMS (EI, 70 eV) m/z (%): 422 (M^+, 41), 329 (41), 271 (16), 135 (100); HRMS m/z (ESI) calcd for $C_{28}H_{27}O_2Si$ ($[M+H]^+$) 423.1775, found 423.1779.

(Ethyldimethylsilyl)(2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ab):



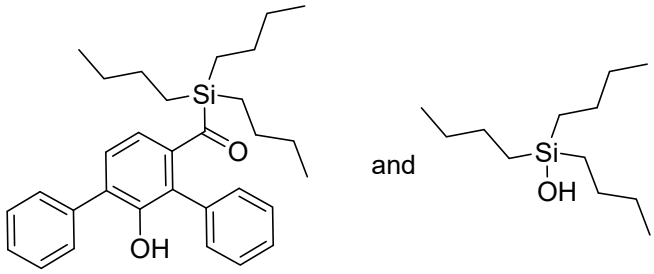
47.5 mg, 66%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.5 Hz, 2H), 7.49-7.44 (m, 4H), 7.42-7.39 (m, 2H), 7.37-7.34 (m, 3H), 6.91 (d, *J* = 7.5 Hz, 1H), 5.40 (s, 1H), 0.81 (t, *J* = 8.0 Hz, 3H), 0.46 (q, *J* = 8.0 Hz, 2H), -0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 244.7, 149.5, 146.4, 137.1, 134.1, 131.3, 130.1, 130.0, 129.3, 129.0, 128.7, 128.4, 127.9, 124.6, 117.9, 76.8, 7.1, 6.0, -4.6; LRMS (EI, 70 eV) m/z (%): 360 (M^+, 100), 331 (81), 257 (96), 87 (44); HRMS m/z (ESI) calcd for $C_{23}H_{25}O_2Si$ ($[M+H]^+$) 361.1618, found 361.1632.

(2'-Hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(triethylsilyl)methanone (3ac):



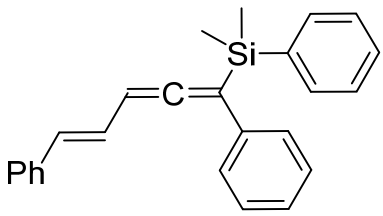
55.1 mg, 71%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.5 Hz, 2H), 7.47-7.44 (m, 4H), 7.41-7.37 (m, 5H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 1H), 0.83 (t, *J* = 8.0 Hz, 9H), 0.51 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 243.9, 149.6, 146.8, 137.2, 134.1, 131.1, 130.0, 129.9, 129.3, 128.9, 128.6, 128.3, 127.8, 124.4, 117.9, 7.2, 2.7; LRMS (EI, 70 eV) m/z (%): 388 (M^+, 38), 359 (100), 257 (67), 115 (8); HRMS m/z (ESI) calcd for $C_{25}H_{29}O_2Si$ ($[M+H]^+$) 389.1931, found 389.1943.

(2'-Hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(tributylsilyl)methanone (3ad) and tributylsilanol (3ad')：



48 mg in total, (3ad, 33mg, 35%; 3ad', 15 mg) ; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59-7.57 (m, 2H), 7.48-7.43 (m, 4H), 7.41-7.33 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 1H), 1.56 (s, 1H), 1.35-1.32 (m, 12H), 1.26-1.21 (m, 6H), 1.23-1.10 (m, 6H), 0.90 (t, *J* = 7.5 Hz, 9H), 0.83(t, *J* = 7.5 Hz, 9H), 0.61-0.58 (m, 6H), 0.51-0.47 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 244.3, 149.6, 146.8, 137.3, 134.1, 131.2, 130.0, 129.9, 129.3, 128.9, 128.7, 128.3, 127.8, 124.4, 117.9, 26.5 (d), 25.7, 25.3, 14.7, 13.8, 13.7, 11.2; LRMS (EI, 70 eV) m/z (%): 472 (M^+, 42), 415 (100), 285 (79), 142 (9); LRMS (EI, 70 eV) m/z (%): 216 (M^+, 0.3), 159 (89), 103 (100), 61 (42); HRMS m/z (ESI) calcd for $C_{31}H_{41}O_2Si$ ($[M+H]^+$) 473.2870, found 473.2877; HRMS m/z (ESI) calcd for $C_{12}H_{29}OSi$ ($[M+H]^+$) 217.1982, found 217.1991.

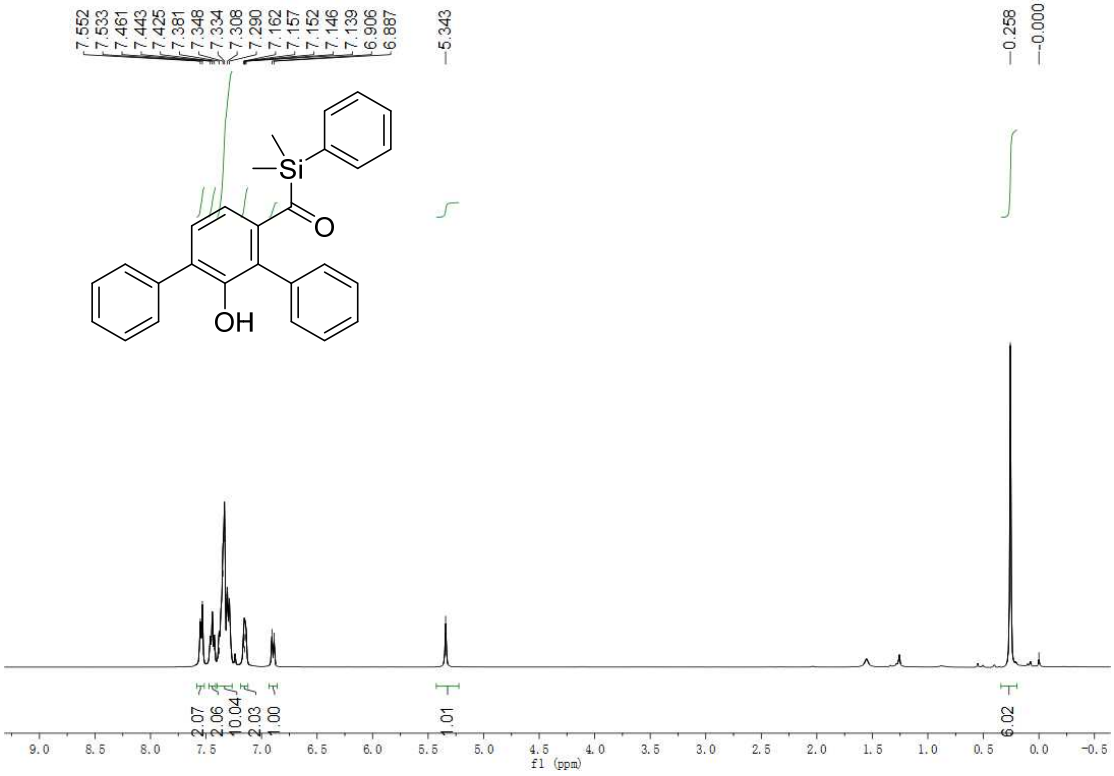
(*E*)-(1,5-Diphenylpenta-1,2,4-trien-1-yl)dimethyl(phenyl)silane (4aa):

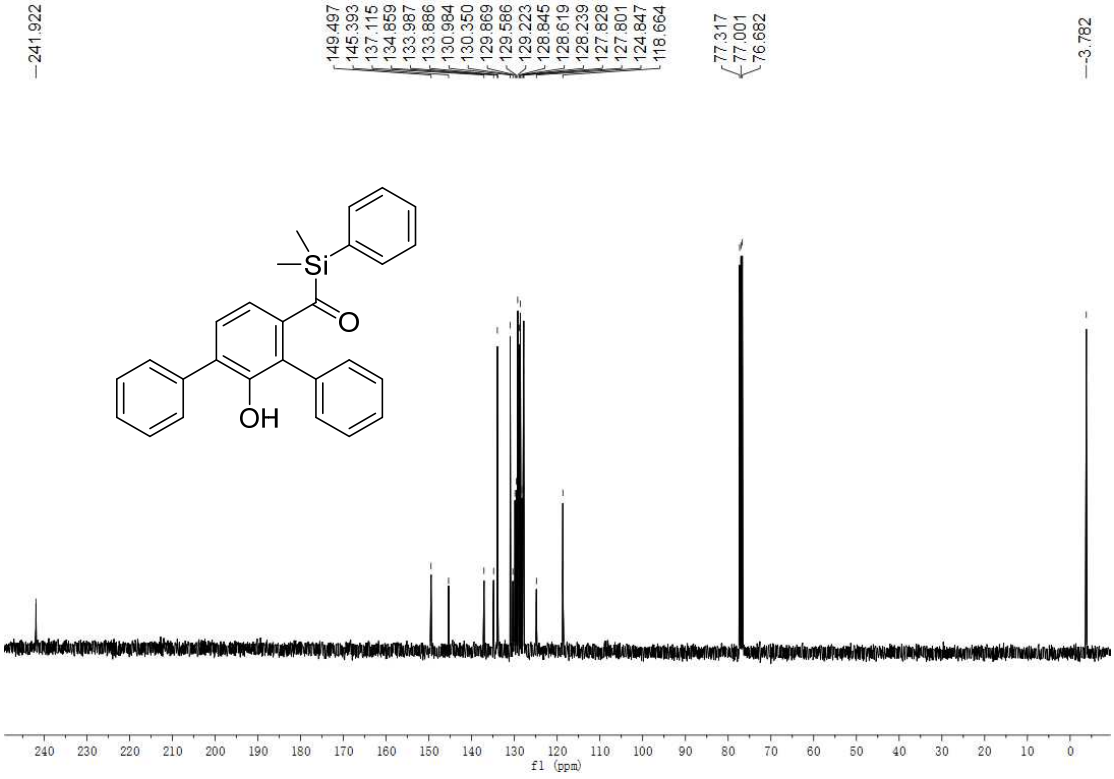


32.4 mg, 46%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62-7.60 (m, 2H), 7.39-7.36 (m, 5H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.24-7.19 (m, 5H), 7.15-7.12 (m, 1H), 6.70-6.65 (m, 1H), 6.52 (d, *J* = 15.5 Hz, 1H), 6.15 (d, *J* = 10.5 Hz, 1H), 0.49 (s, 3H), 0.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 213.6, 138.0, 137.4, 136.2, 133.9, 129.5, 129.3, 128.6, 128.4, 128.0, 127.9, 127.2, 126.5, 126.1, 124.2, 100.8, 92.0, -1.7, -1.8; LRMS (EI, 70 eV) m/z (%): 352 (M^+, 5), 215 (4), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{25}Si$ ($[M+H]^+$) 353.1720, found 353.1733.

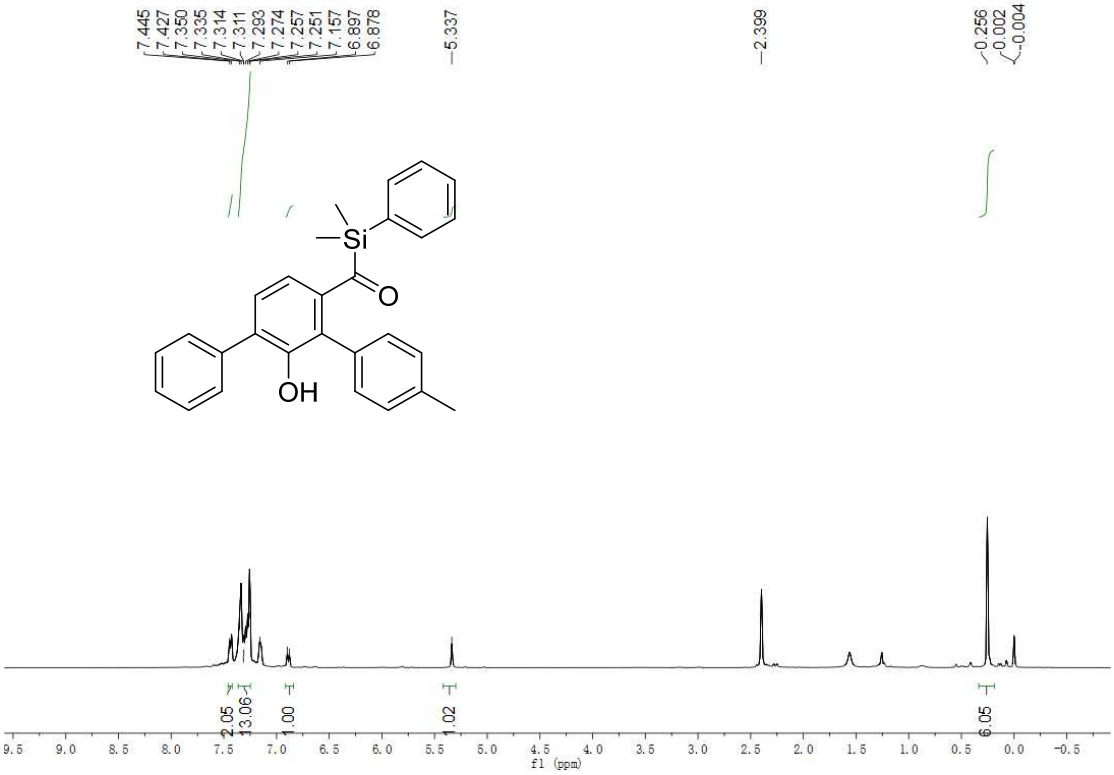
(C) Spectra of Products 3 and 4

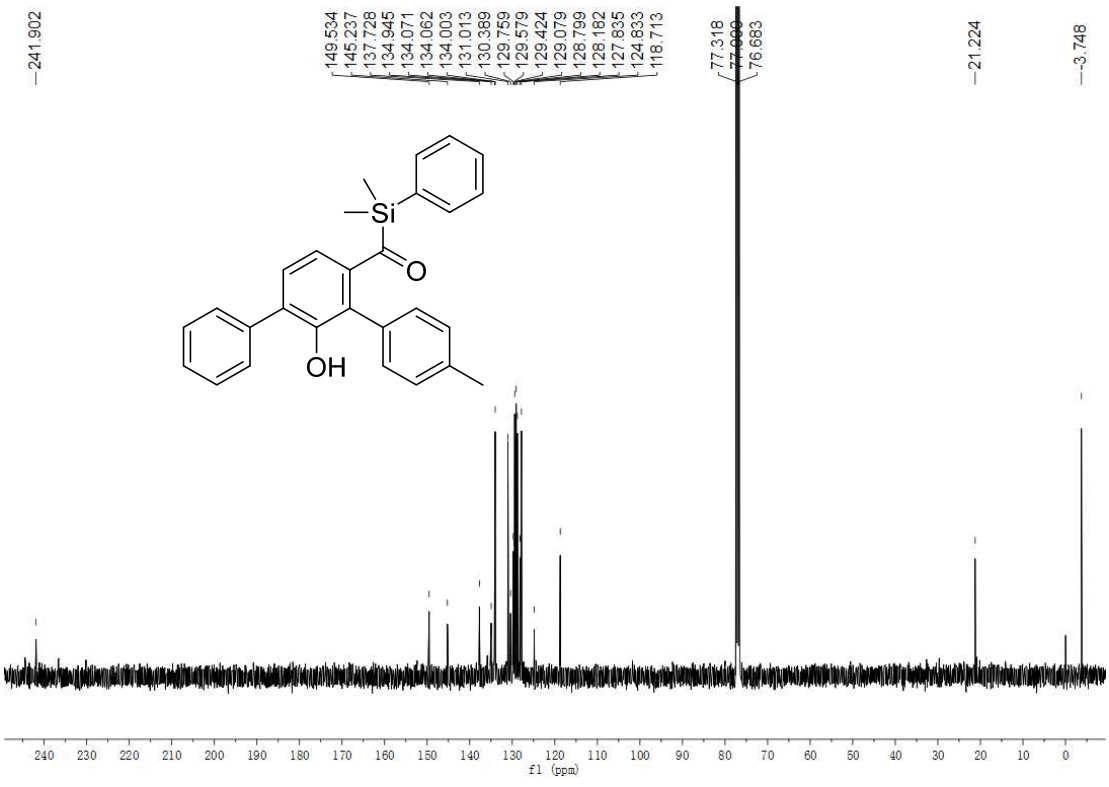
(dimethyl(phenyl)silyl)(2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3aa)





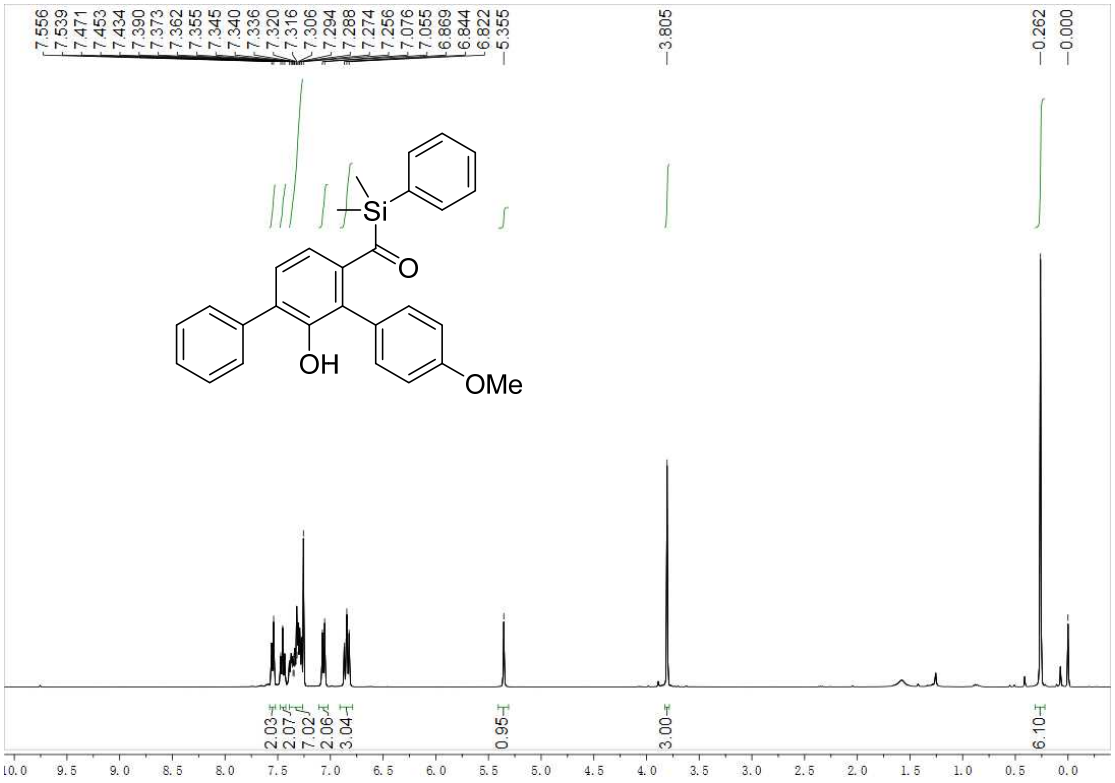
(dimethyl(phenyl)silyl)(2'-hydroxy-4''-methyl-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ba)

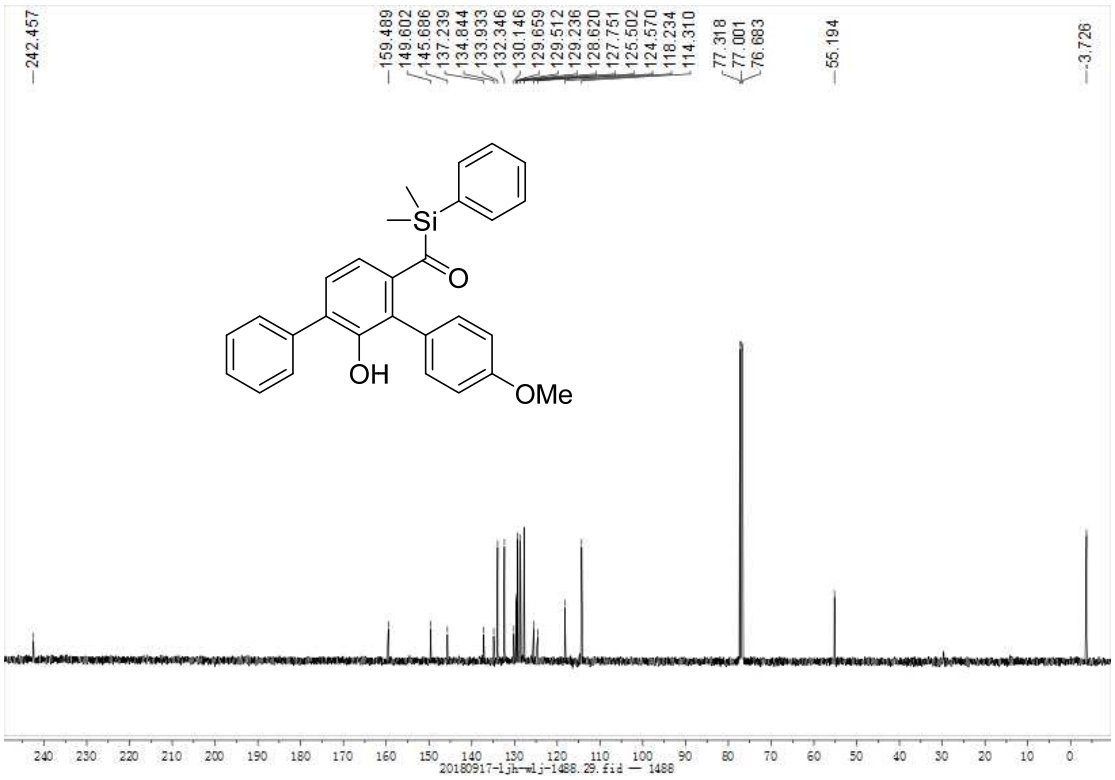




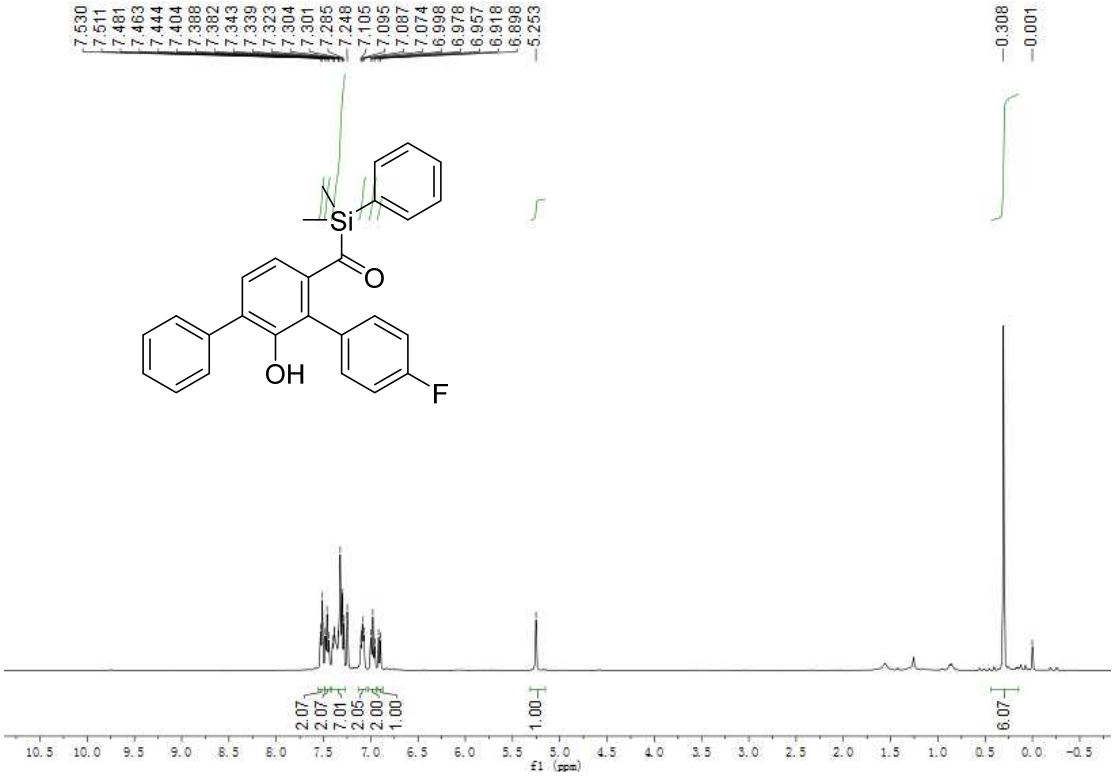
(dimethyl(phenyl)silyl)(2'-hydroxy-4''-methoxy-[1,1':3',1''-terphenyl]-4'-yl)methanone

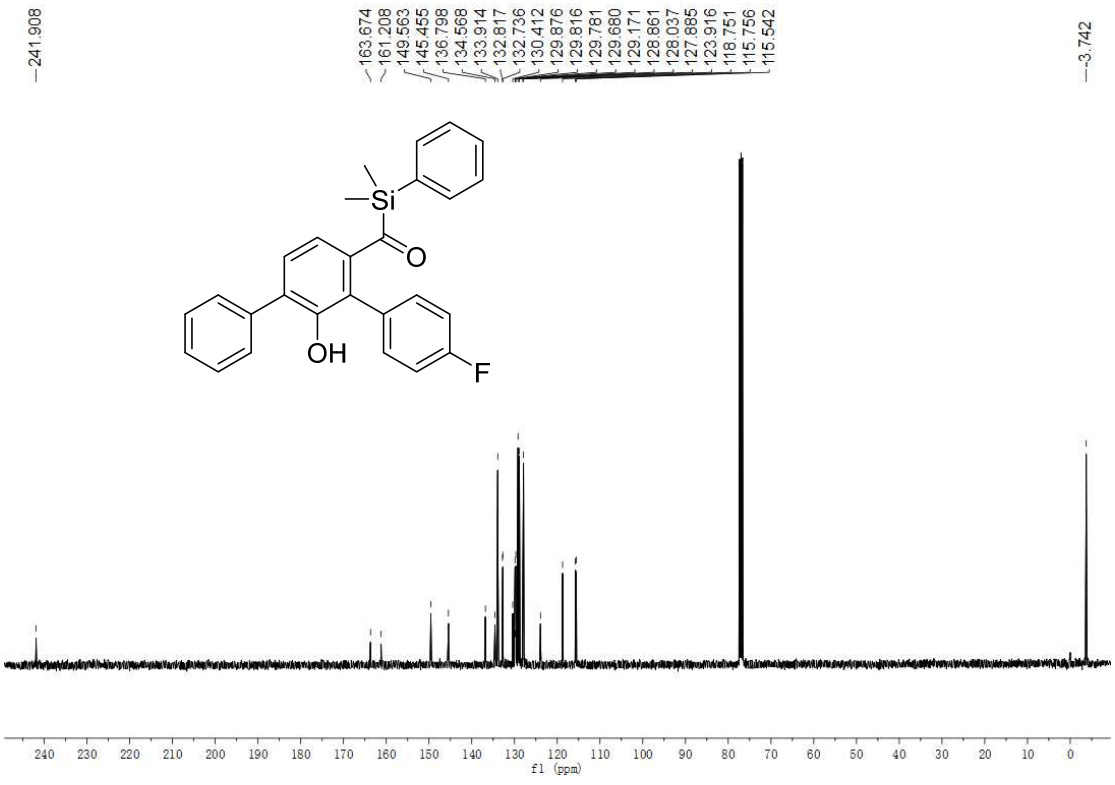
(3ca)



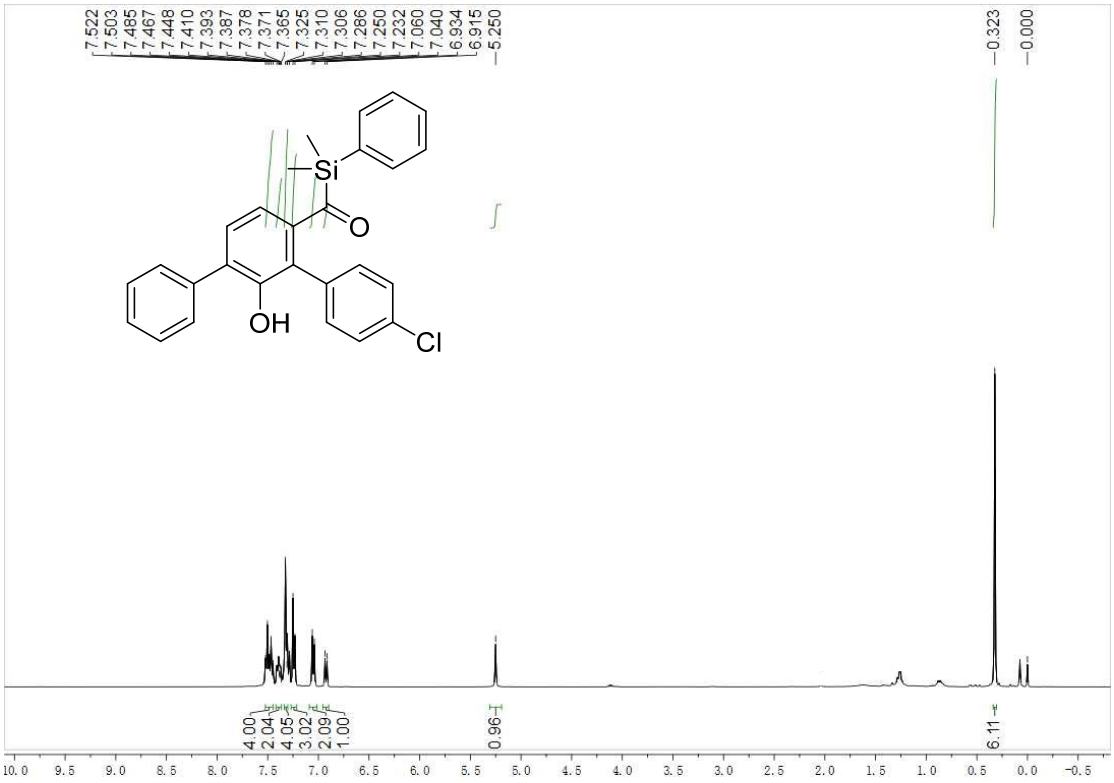


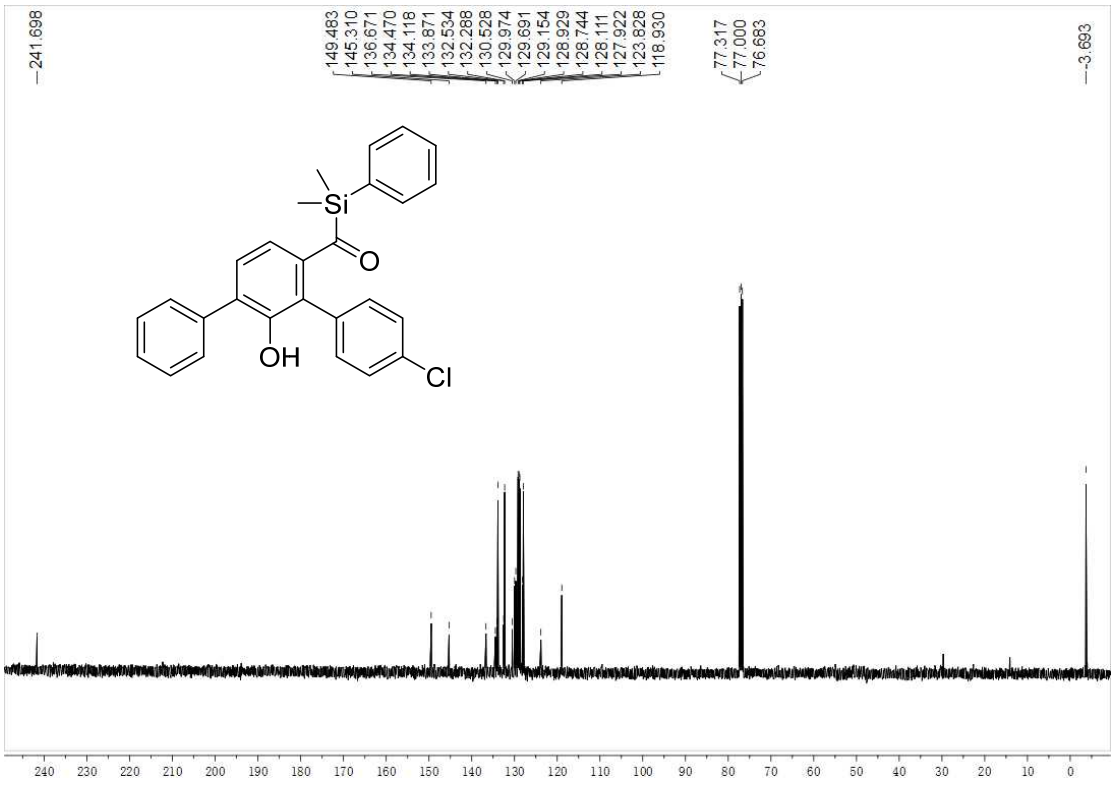
(dimethyl(phenyl)silyl)(4''-fluoro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3da)



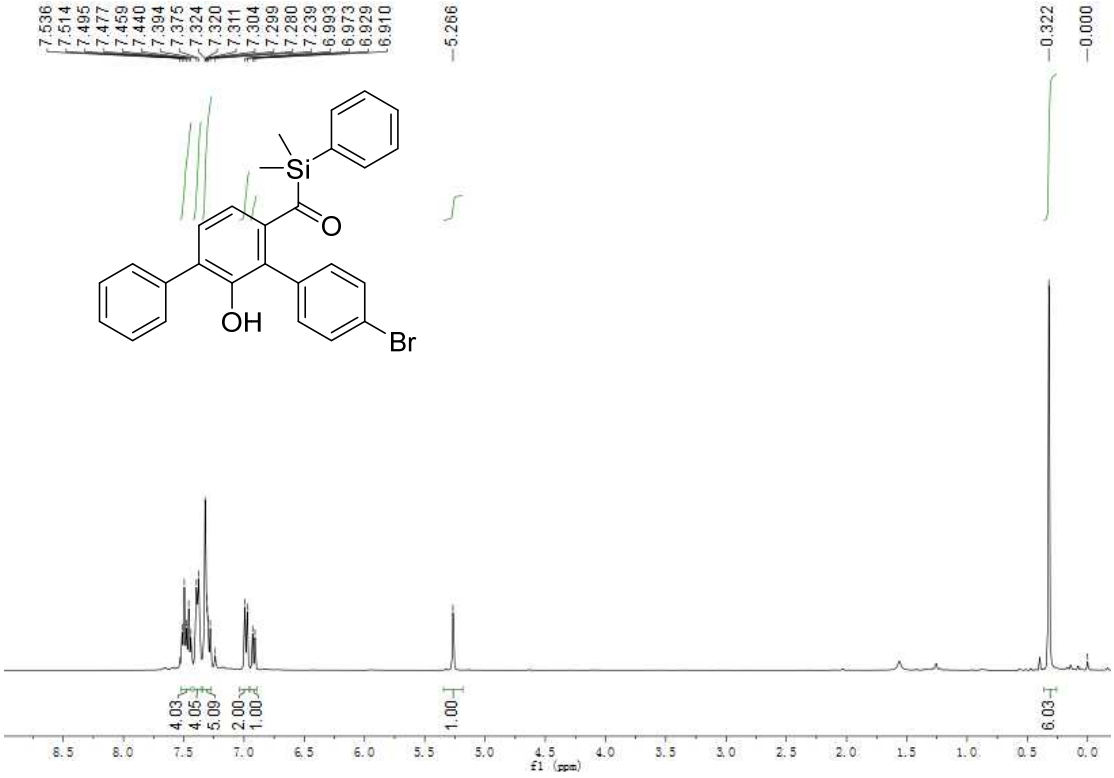


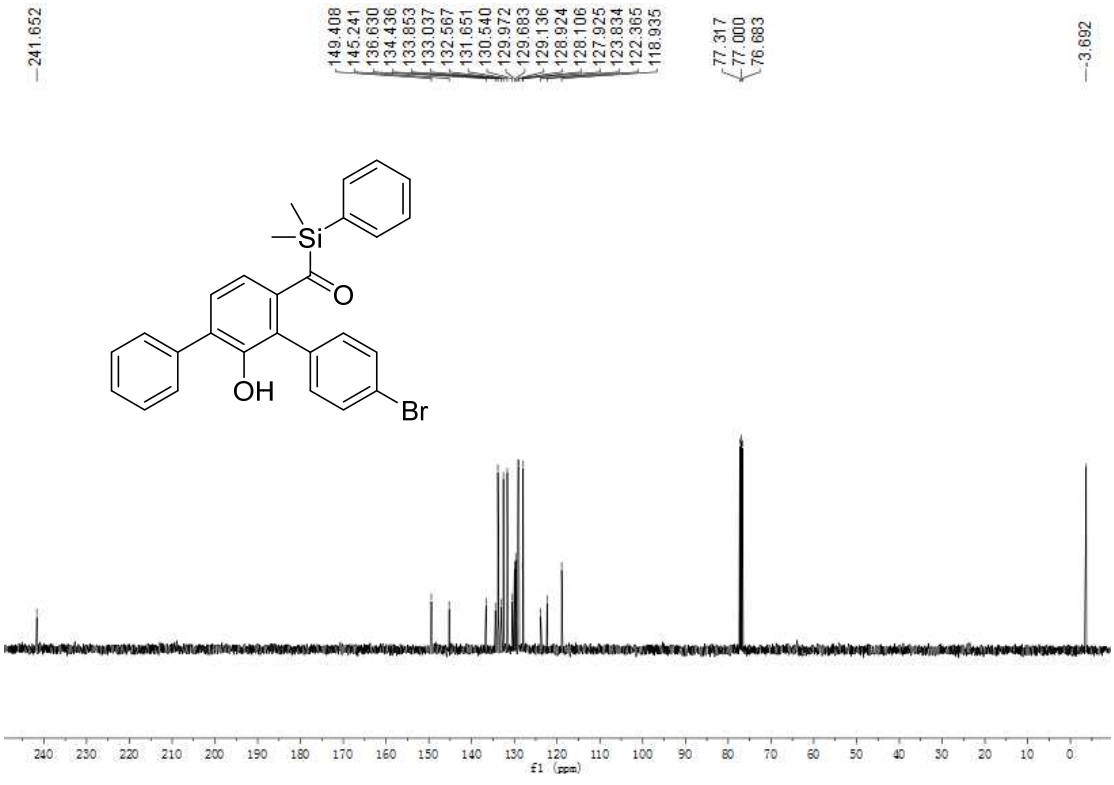
(4''-chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)methanone (3ea)



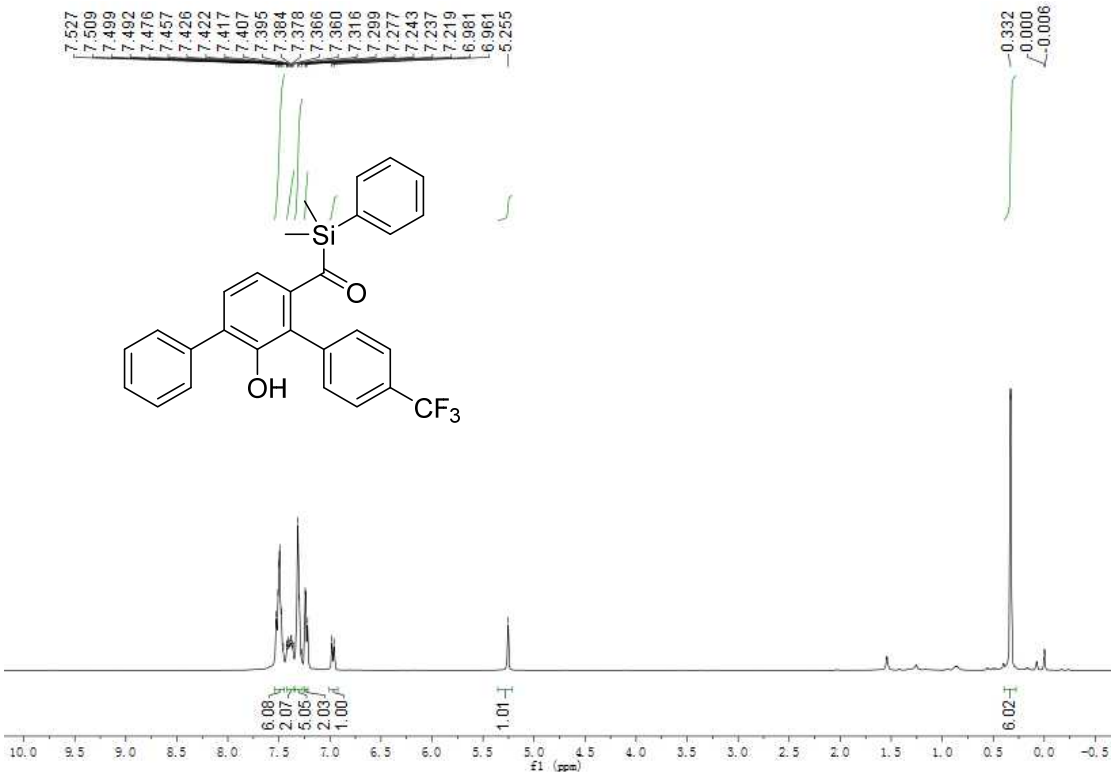


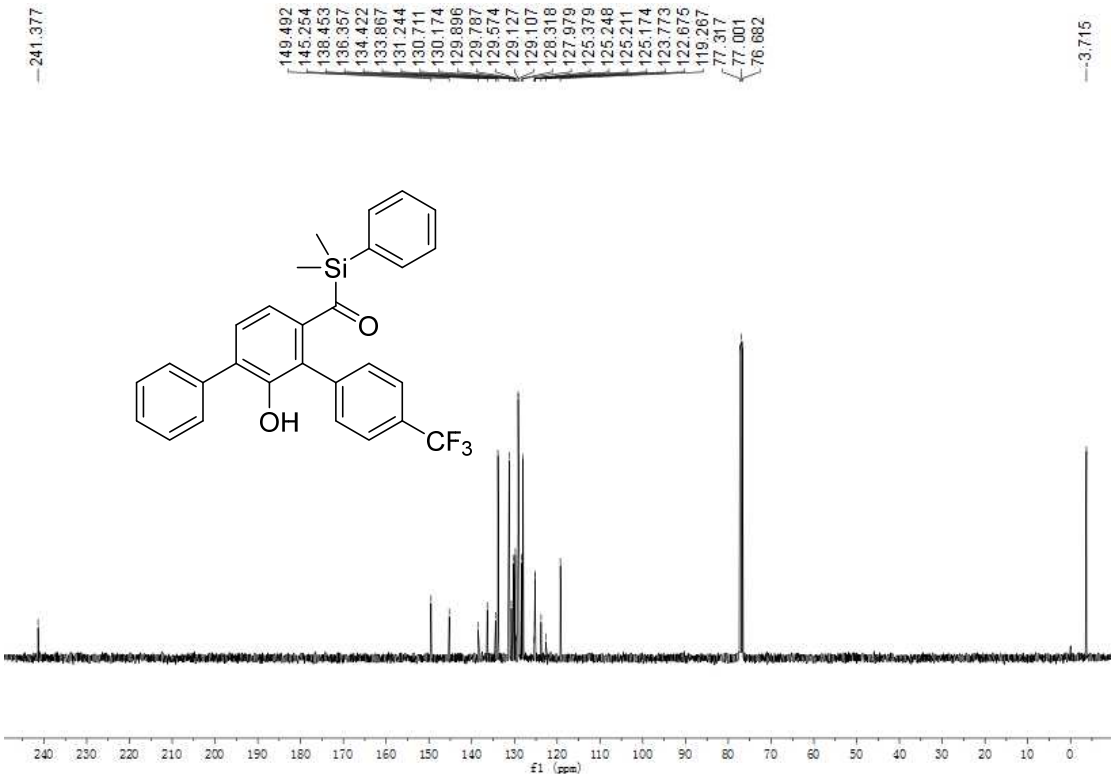
(4''-bromo-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)methanone (3fa)



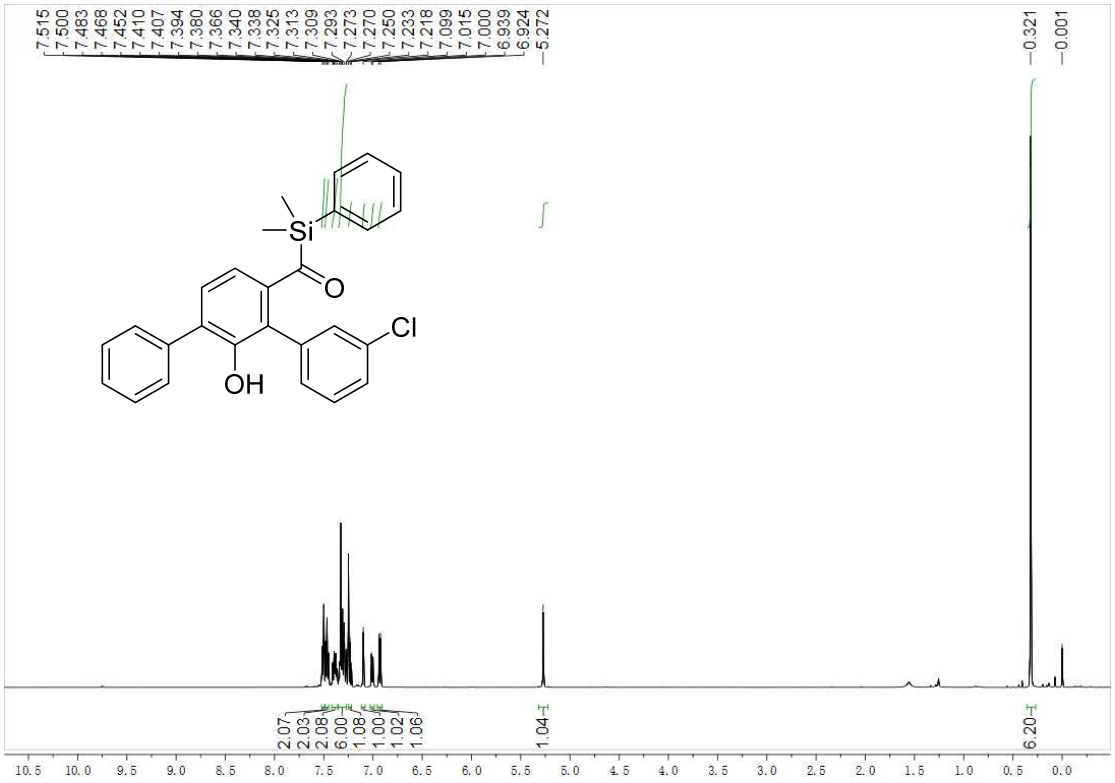


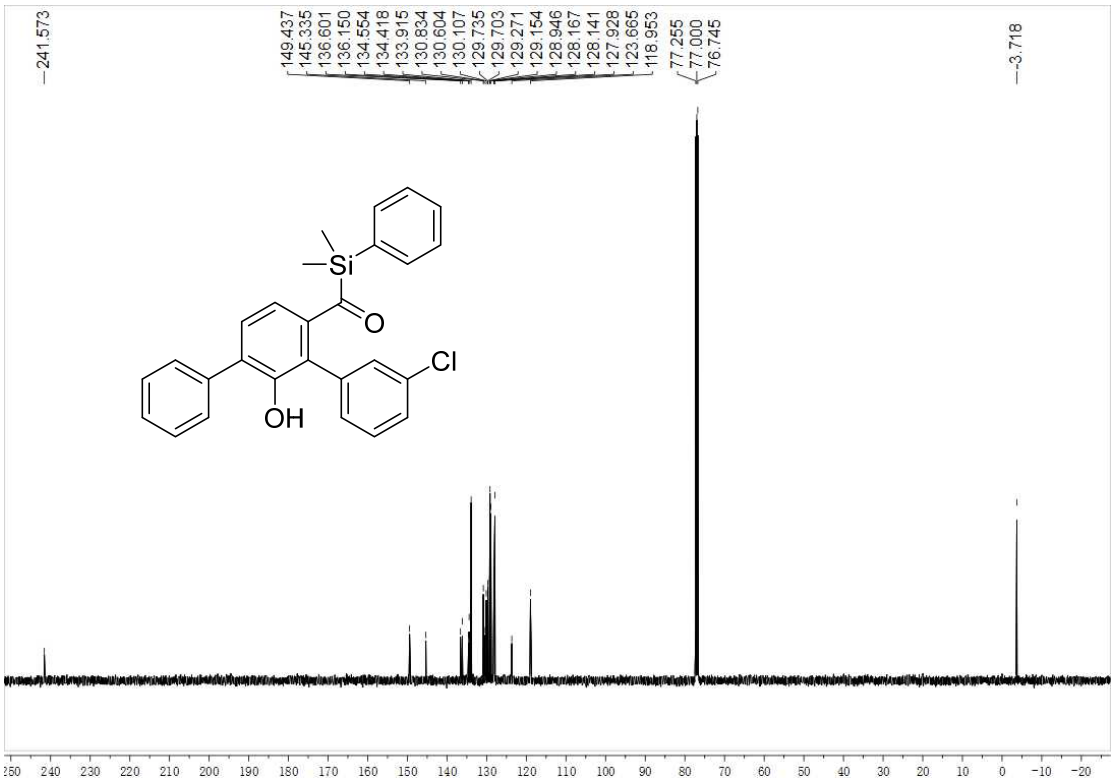
(dimethyl(phenyl)silyl)(2'-hydroxy-4''-(trifluoromethyl)-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ga)



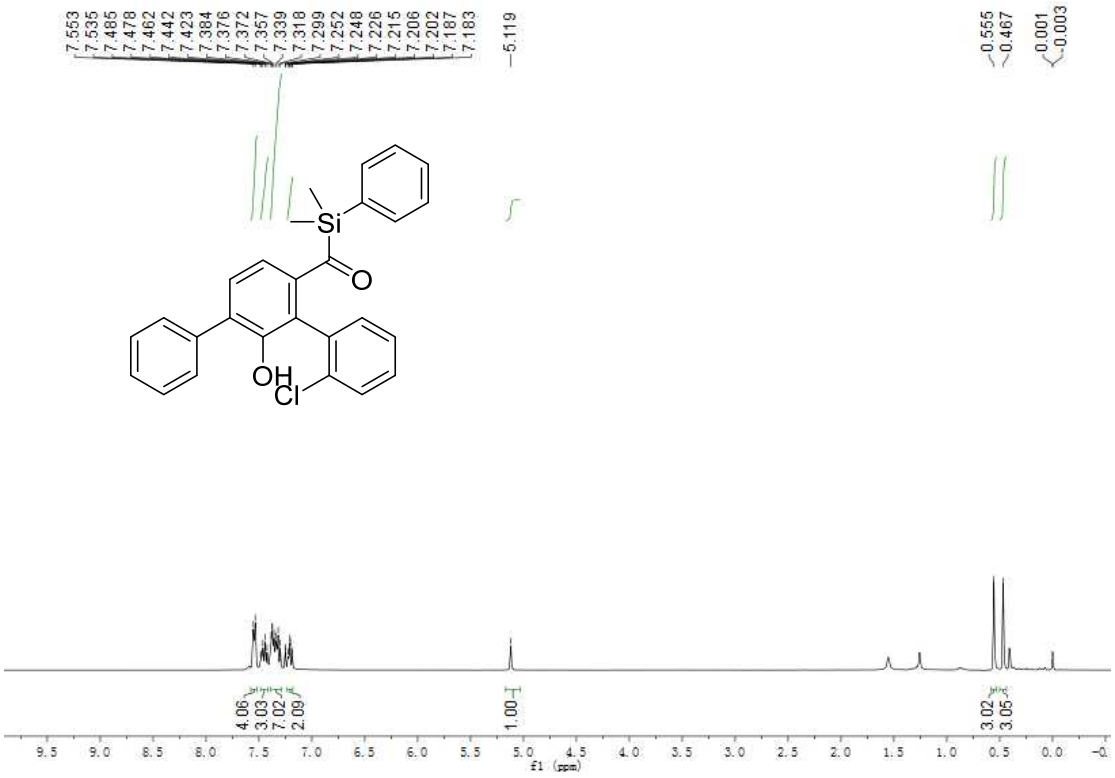


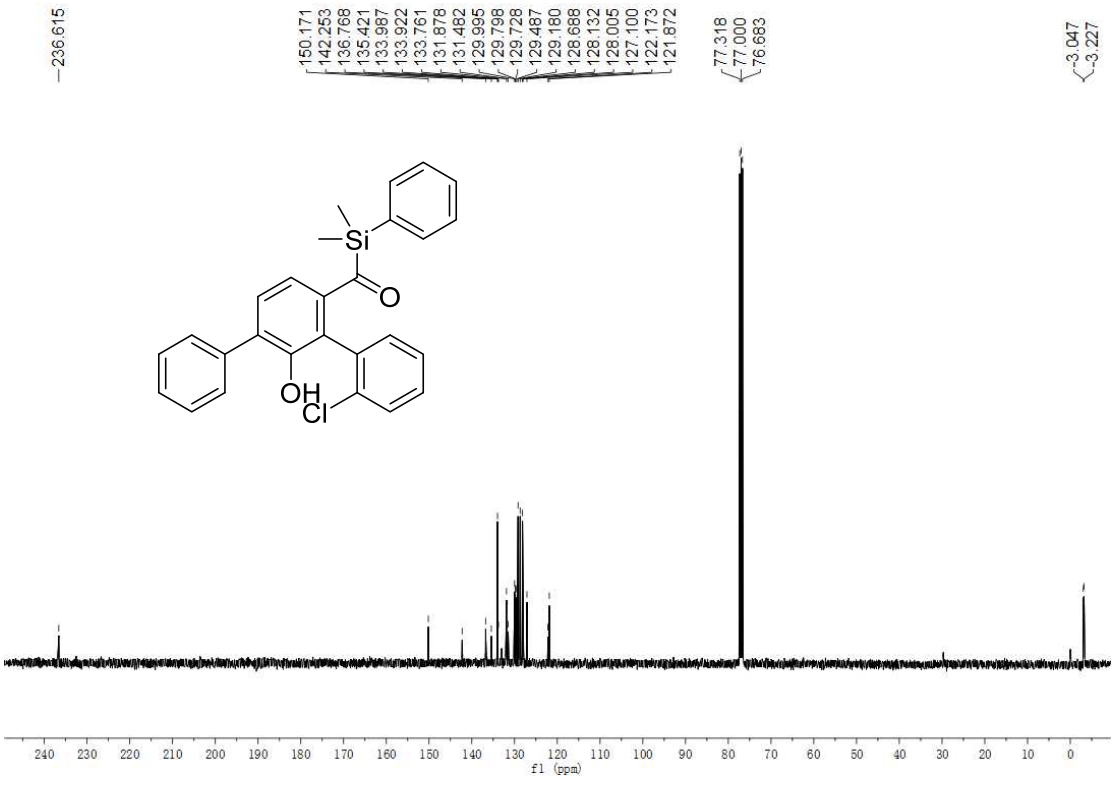
(3''-chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)methanone (3ha)



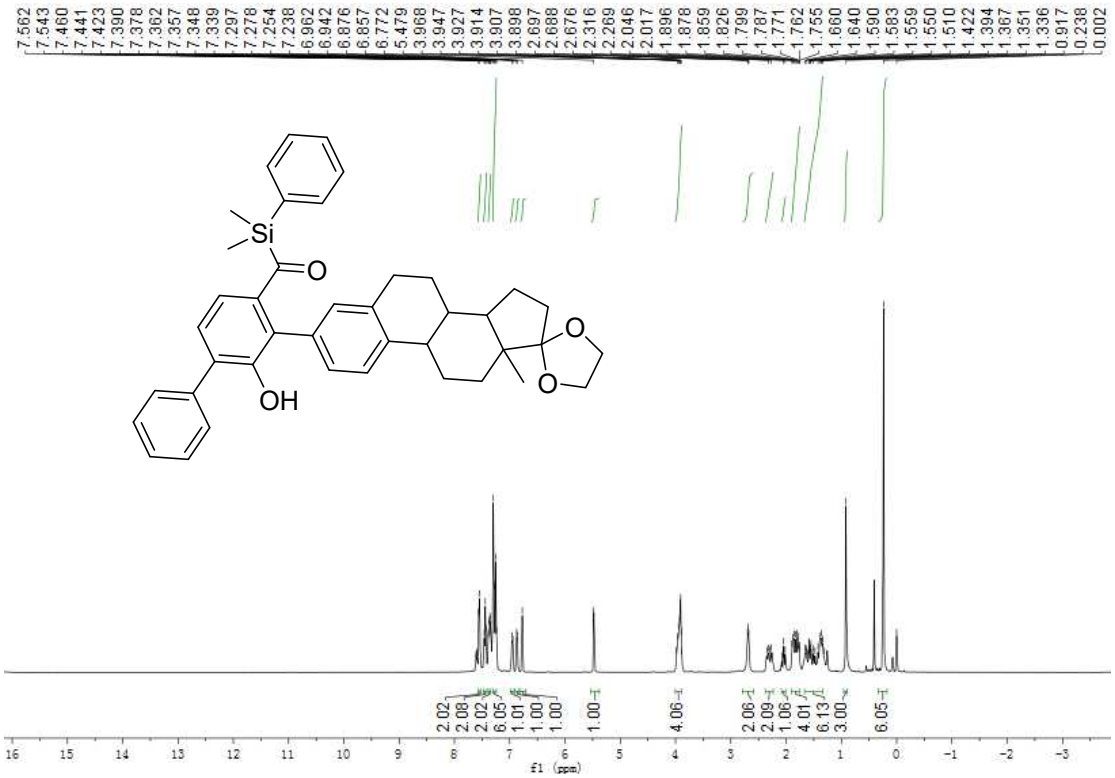


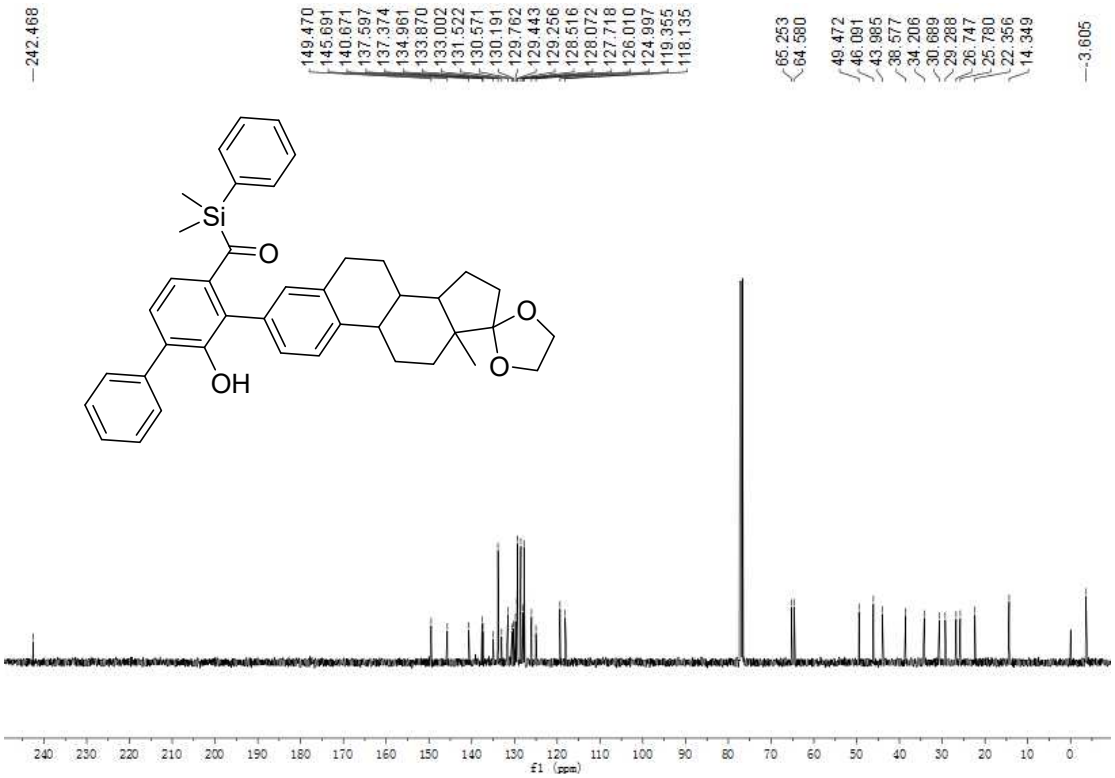
(2''-chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)methanone (3ia)



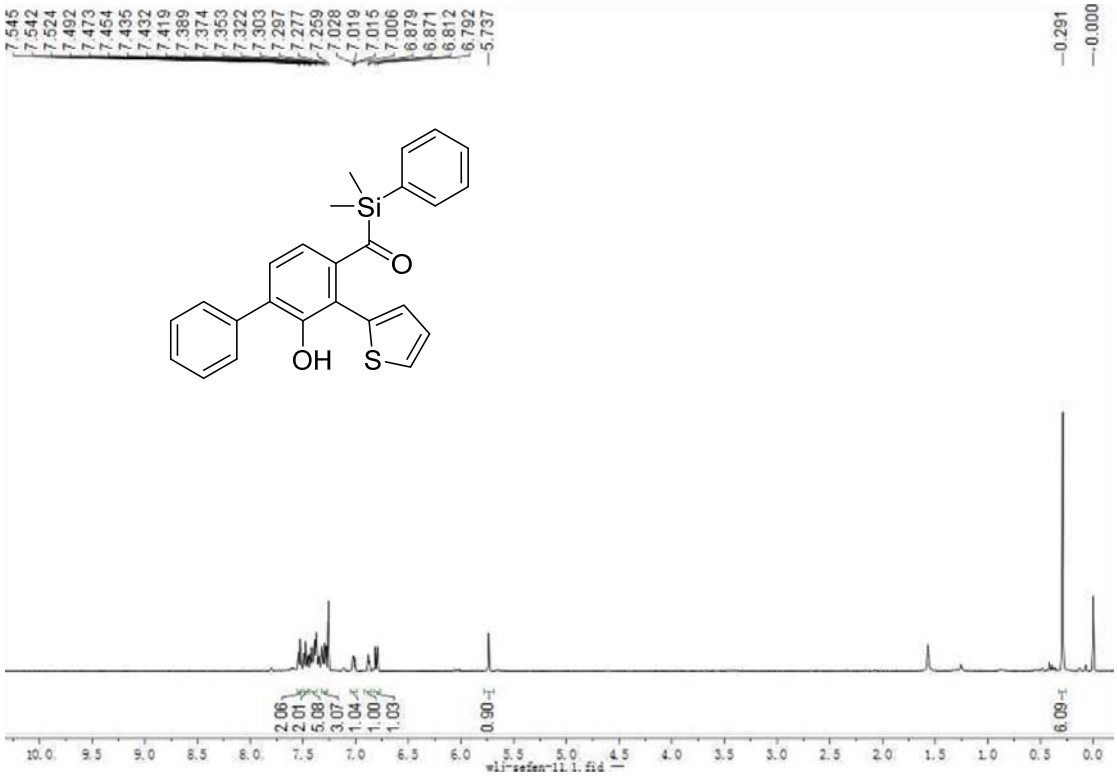


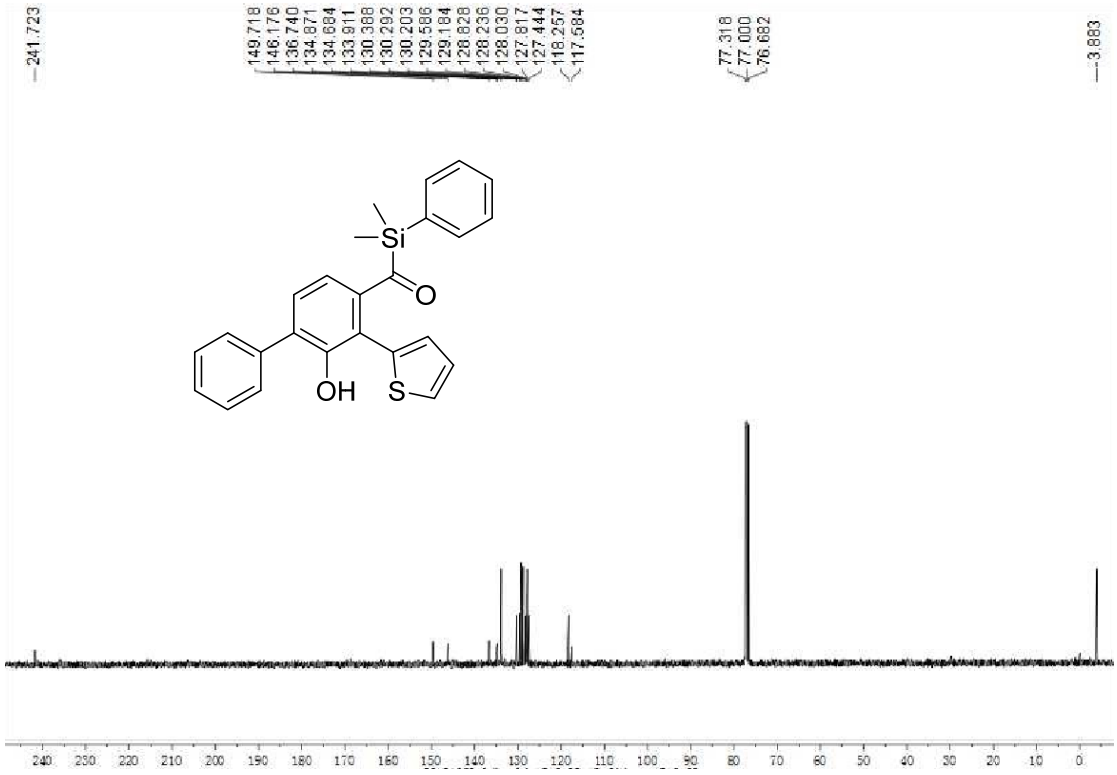
(dimethyl(phenyl)silyl)(2-hydroxy-3-(13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-[1,1'-biphenyl]-4-yl)methanone (3ja)



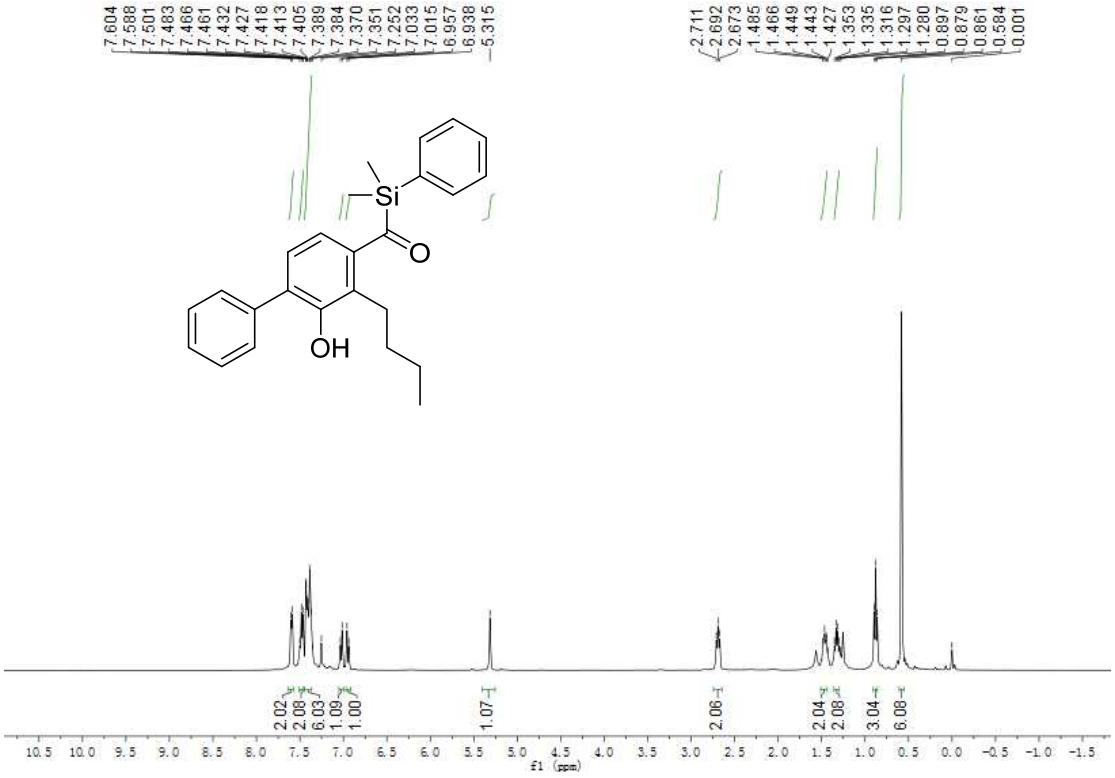


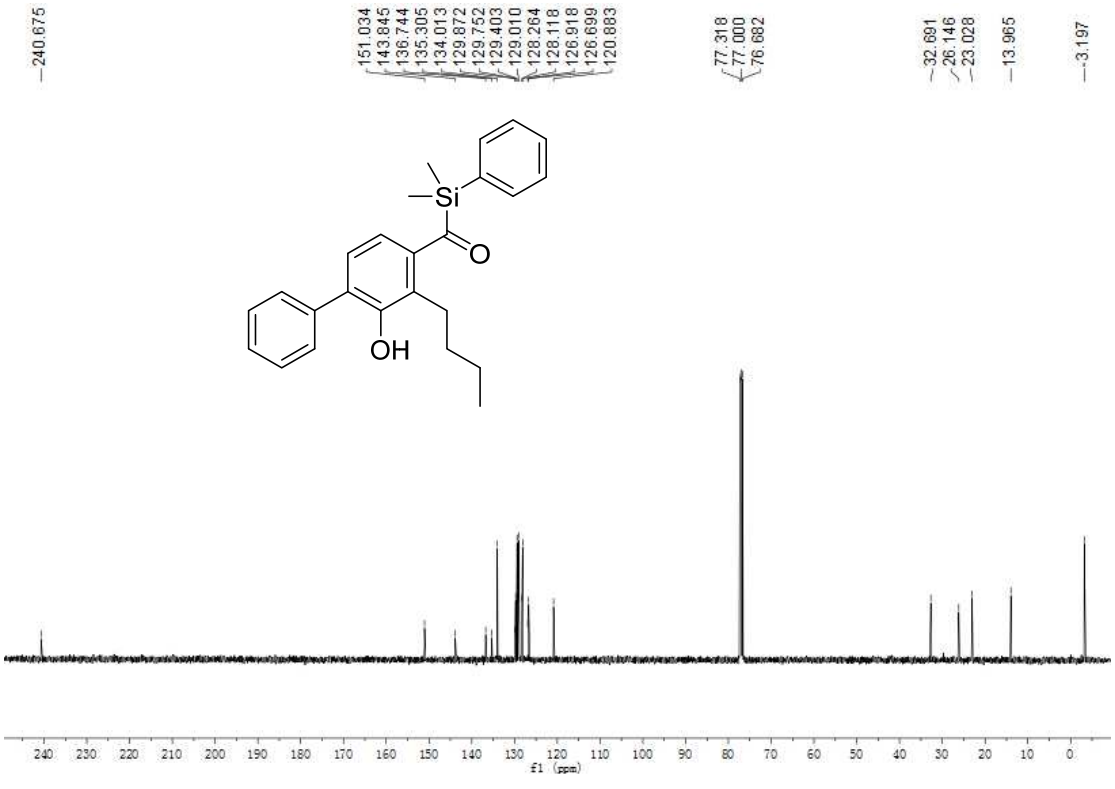
(dimethyl(phenyl)silyl)(2-hydroxy-3-(thiophen-2-yl)-[1,1'-biphenyl]-4-yl)methanone (3ka)



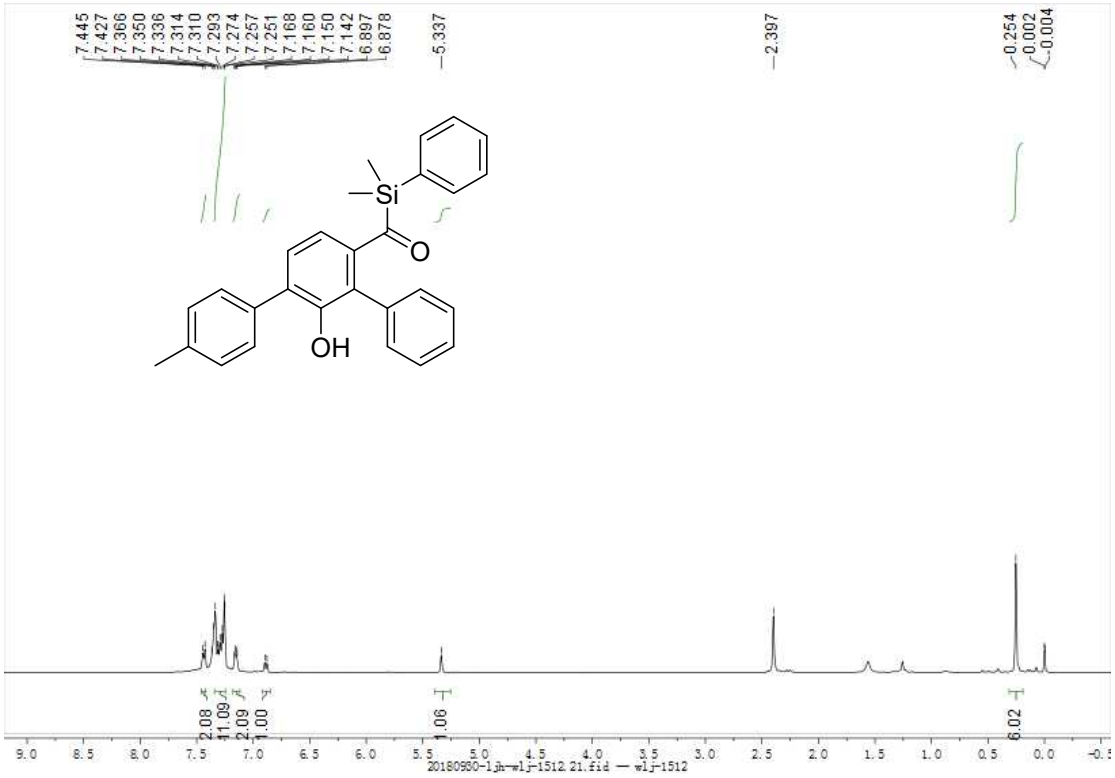


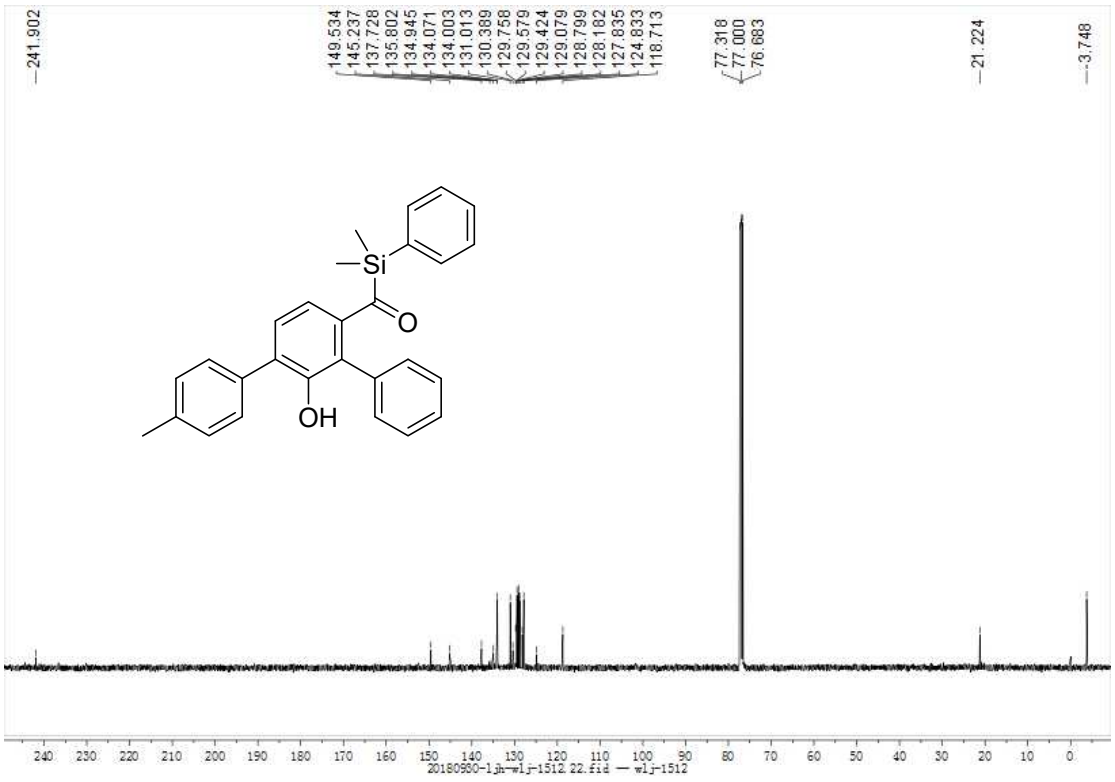
(3-butyl-2-hydroxy-[1,1'-biphenyl]-4-yl)(dimethyl(phenyl)silyl)methanone (3la)



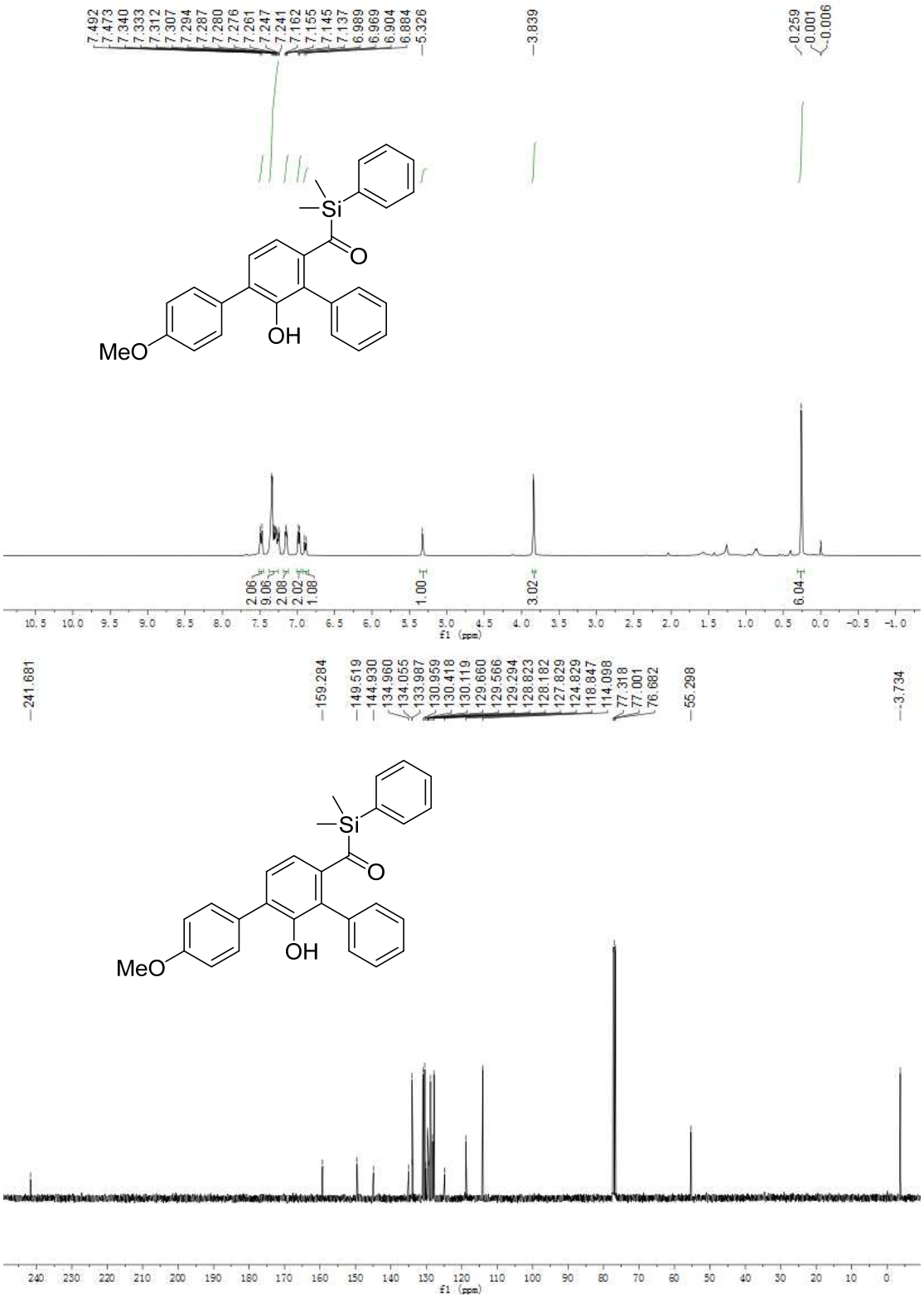


(dimethyl(phenyl)silyl)(2'-hydroxy-4-methyl-[1,1':3',1''-terphenyl]-4'-yl)methanone (3na)

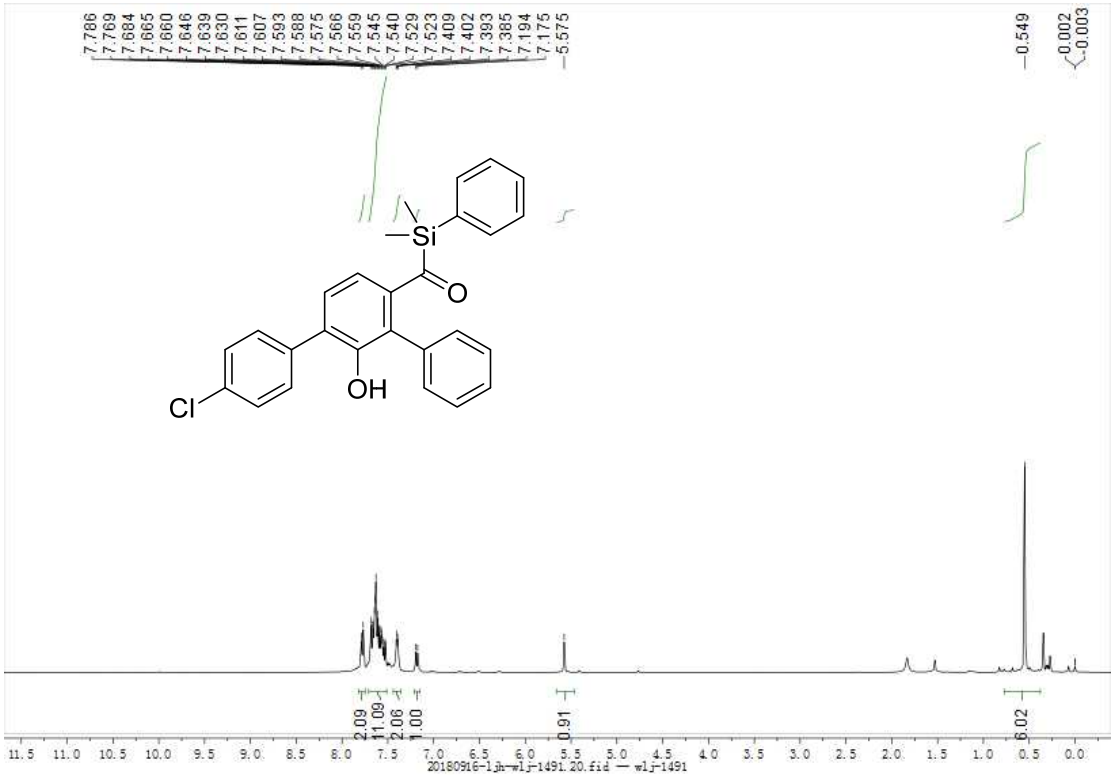


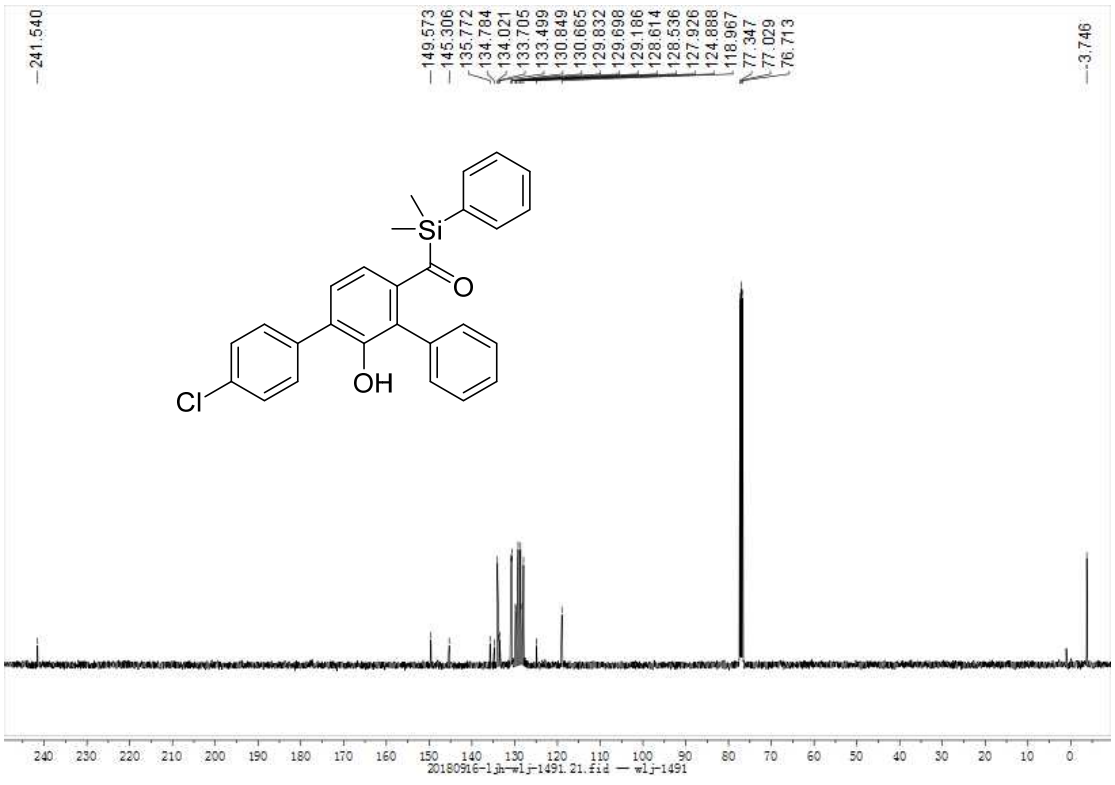


(dimethyl(phenyl)silyl)(2'-hydroxy-4-methoxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3oa)

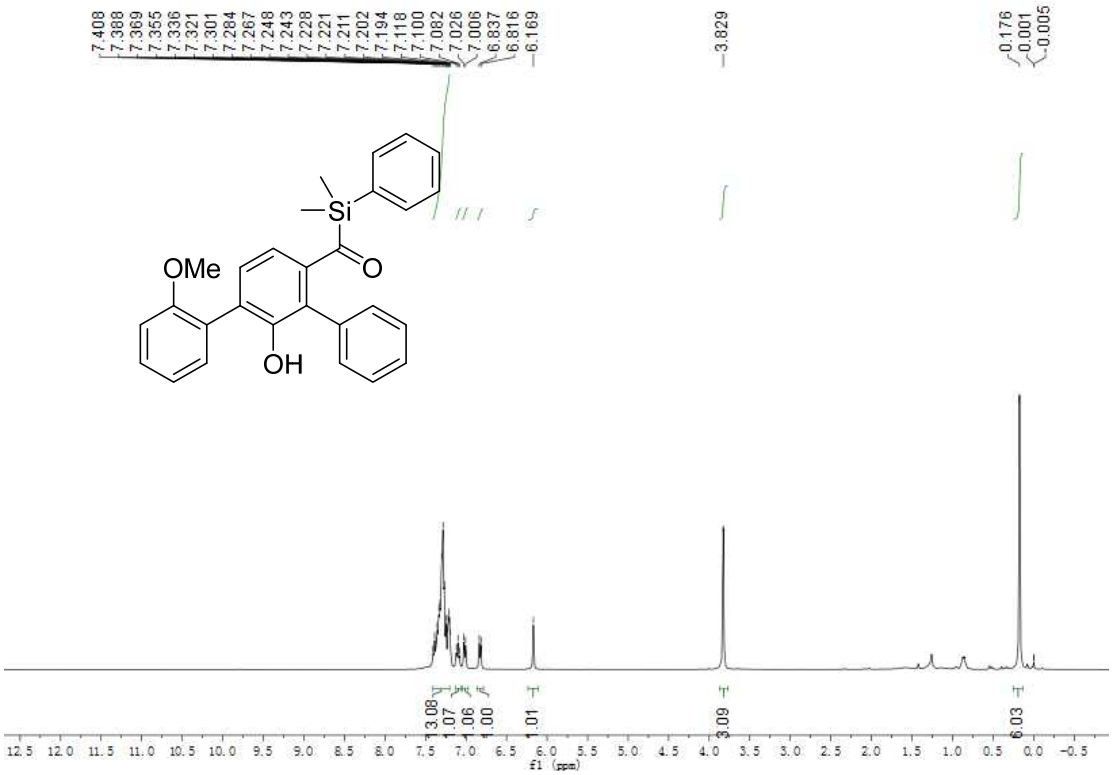


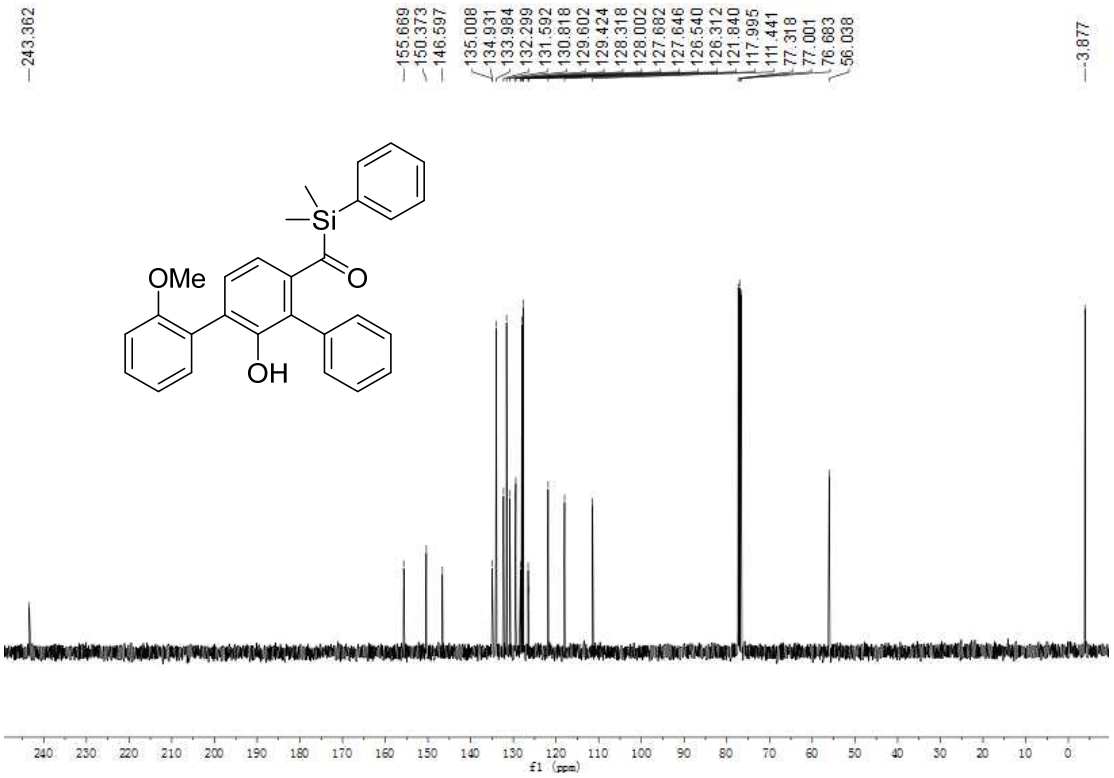
(4-chloro-2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(dimethyl(phenyl)silyl)methanone (3pa)



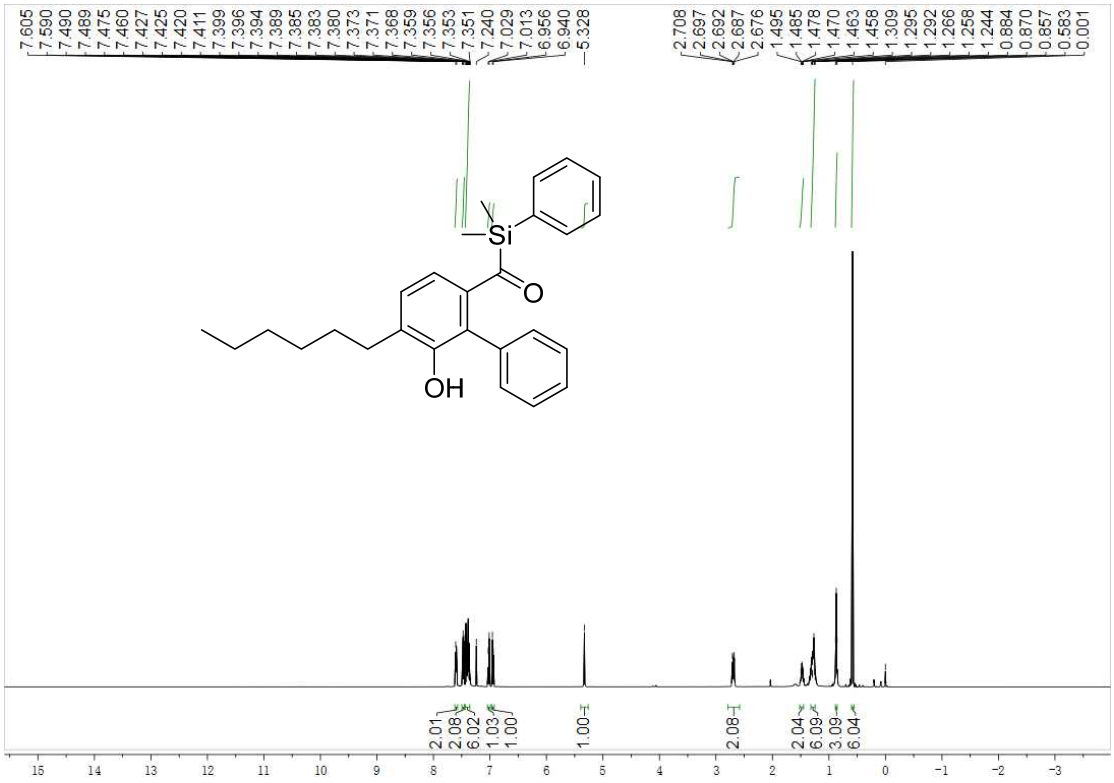


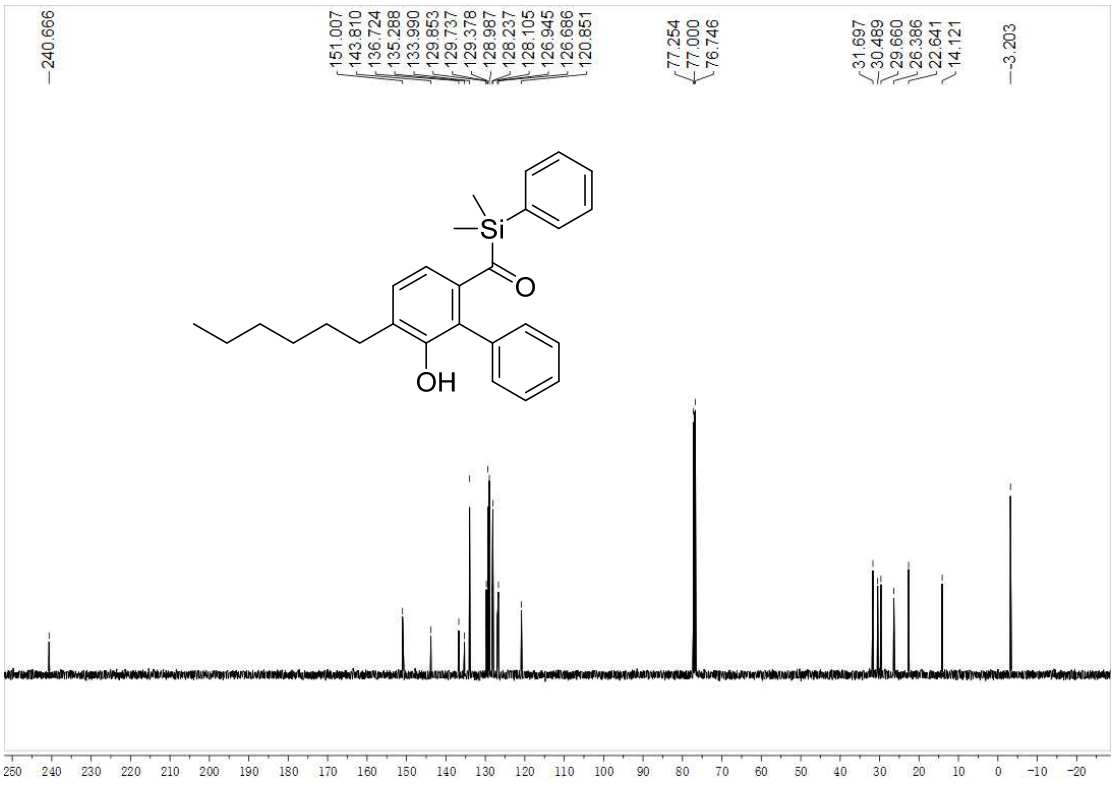
(dimethyl(phenyl)silyl)(2'-hydroxy-2-methoxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3qa):



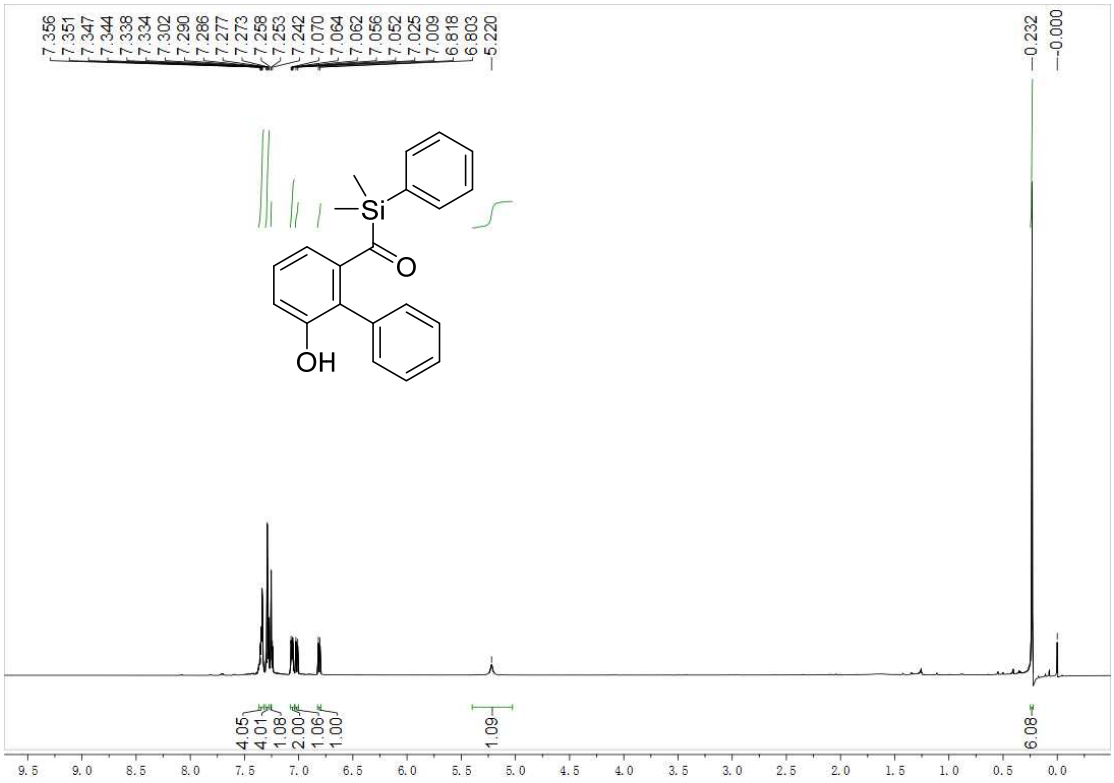


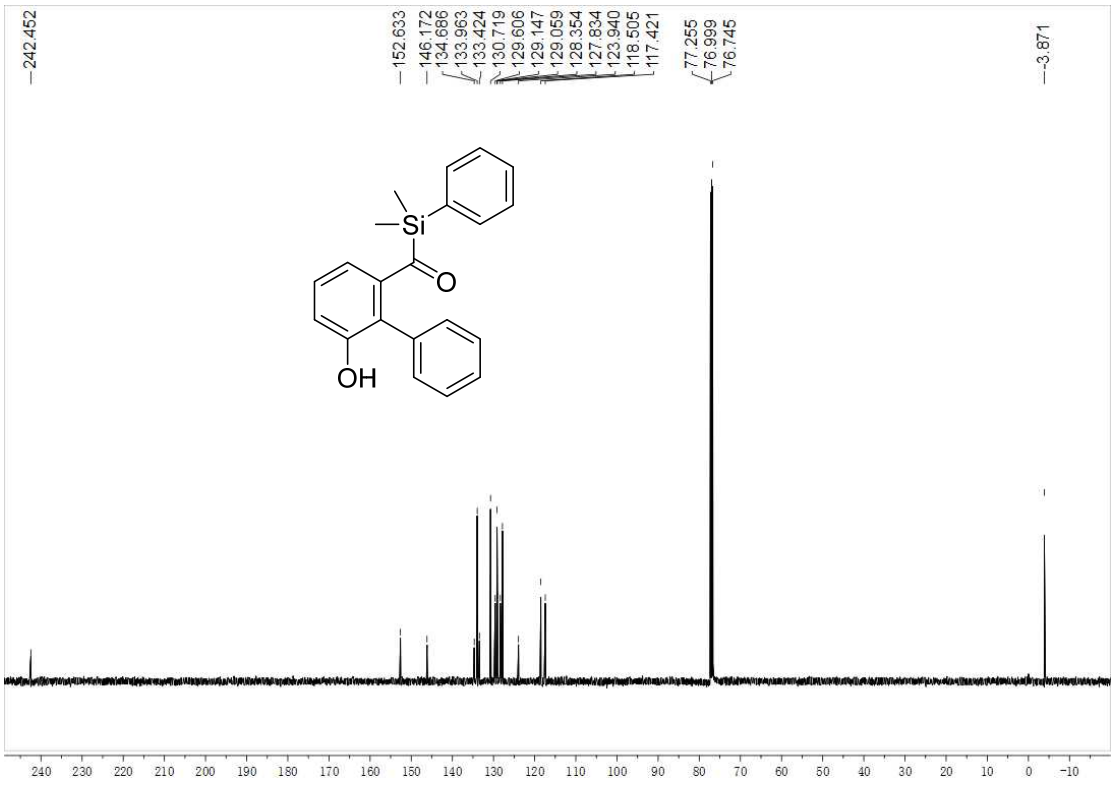
(dimethyl(phenyl)silyl)(5-hexyl-6-hydroxy-[1,1'-biphenyl]-2-yl)methanone (3ra)



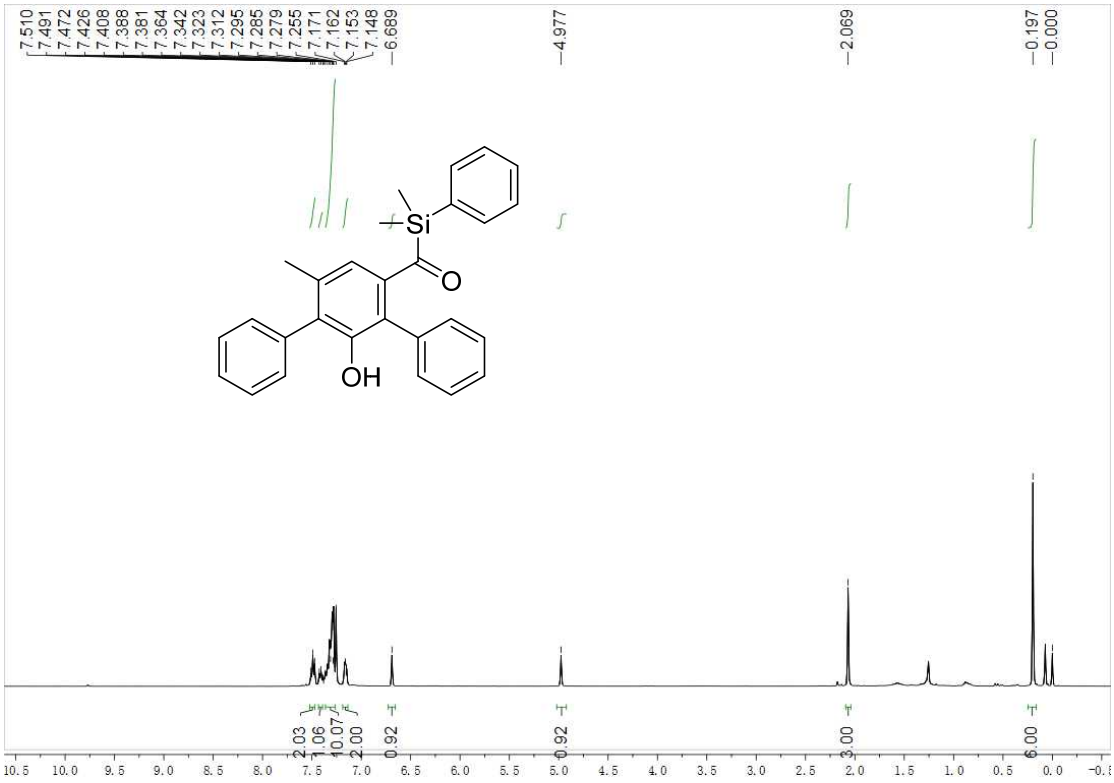


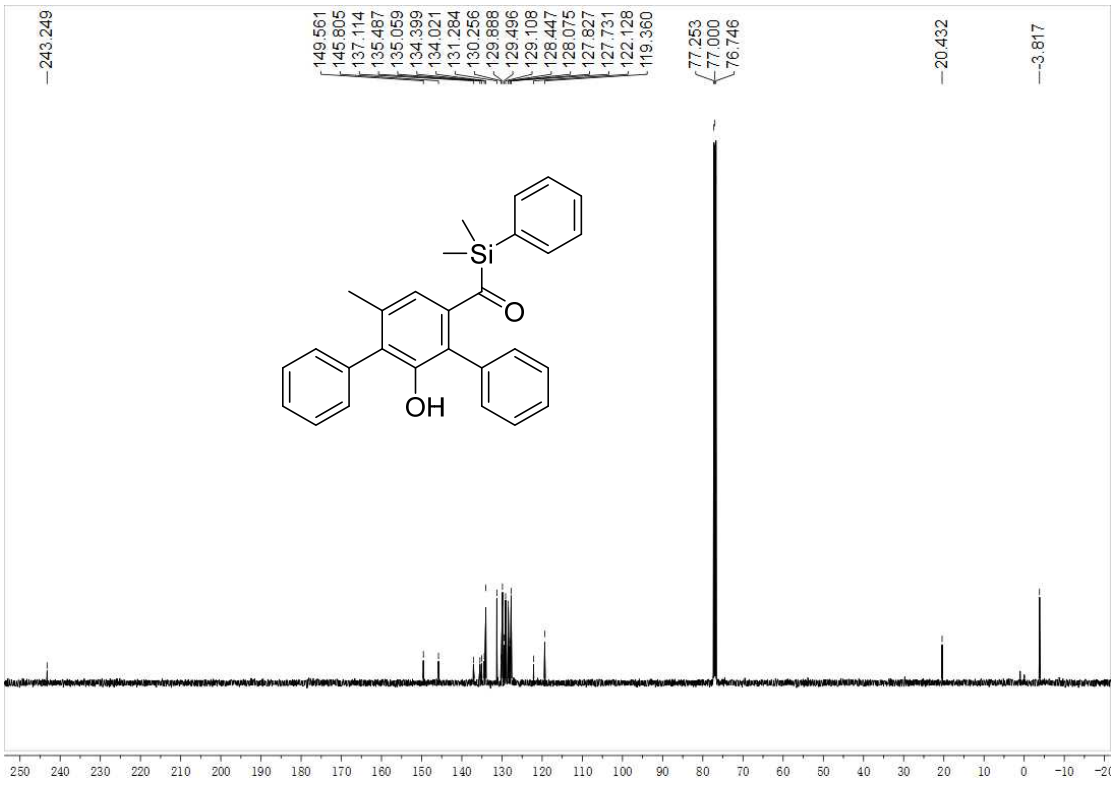
(dimethyl(phenyl)silyl)(6-hydroxy-[1,1'-biphenyl]-2-yl)methanone (3sa)



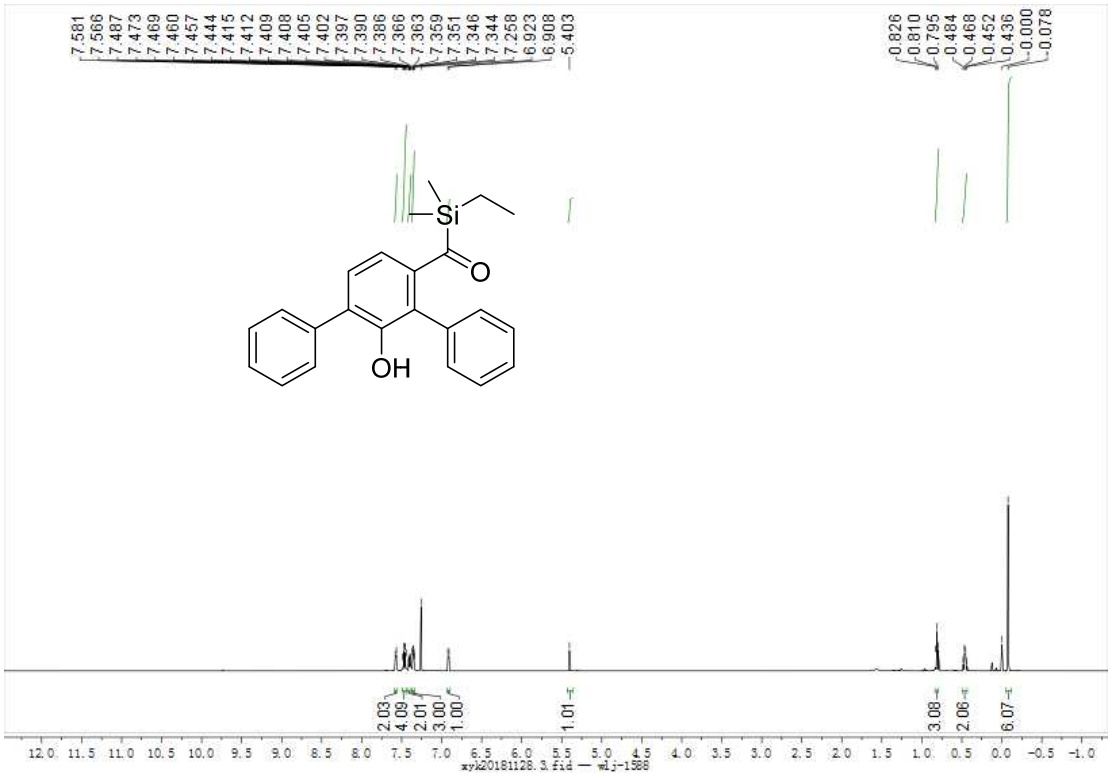


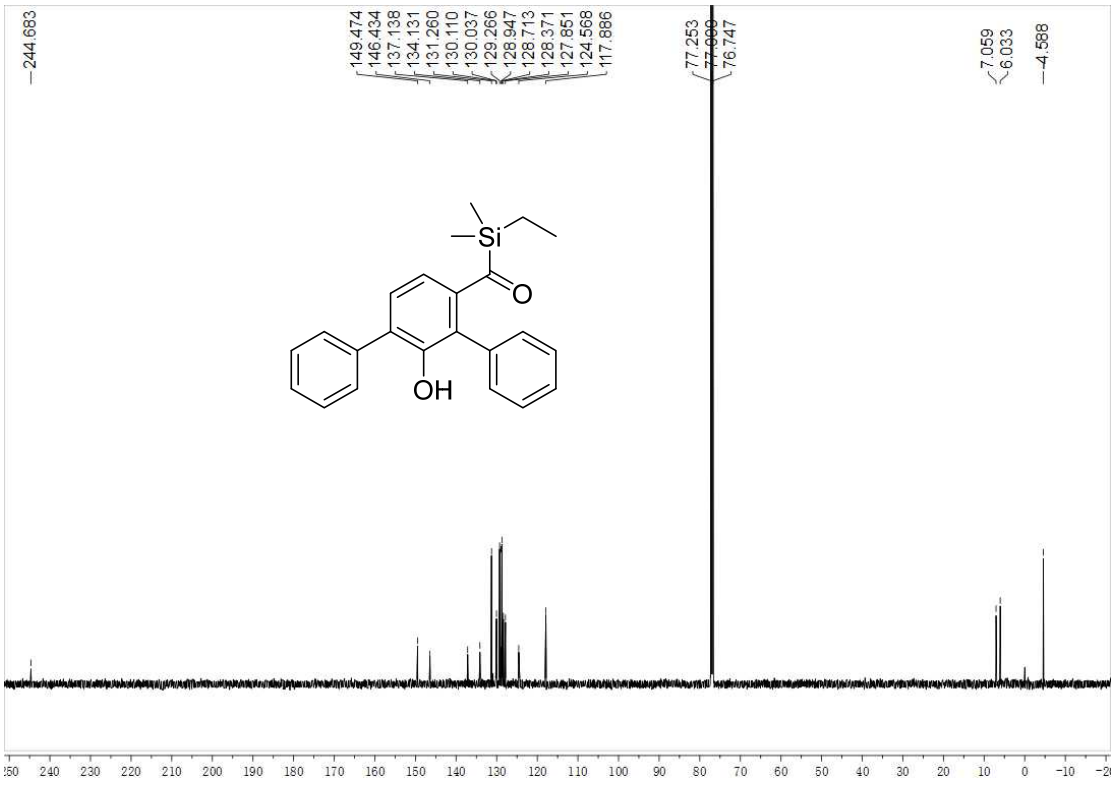
(dimethyl(phenyl)silyl)(2'-hydroxy-6'-methyl-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ta)



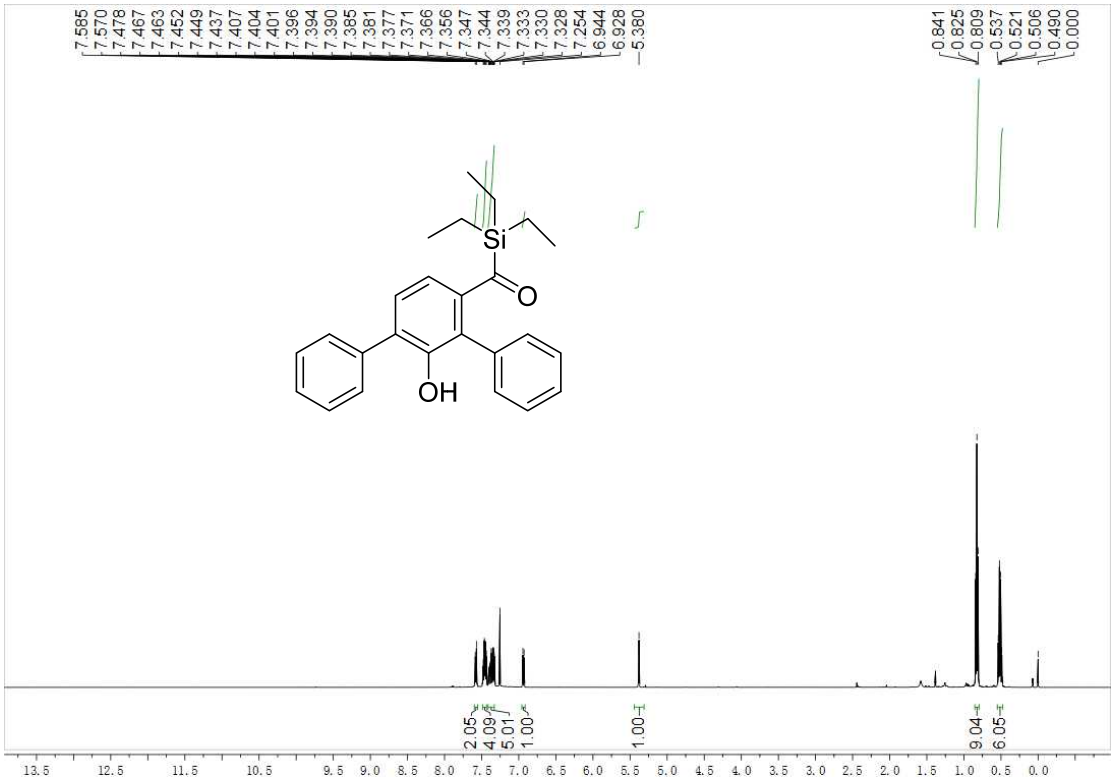


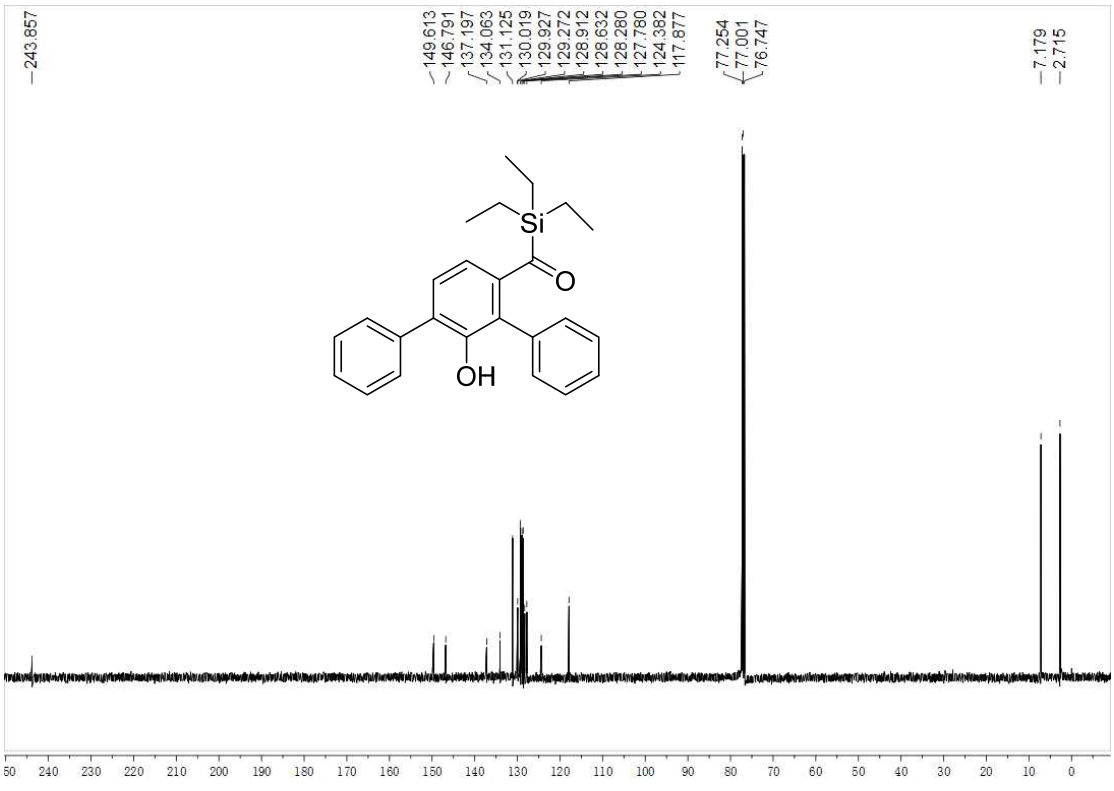
(ethyldimethylsilyl)(2'-hydroxy-[1,1':3',1''-terphenyl]-4'-yl)methanone (3ab)



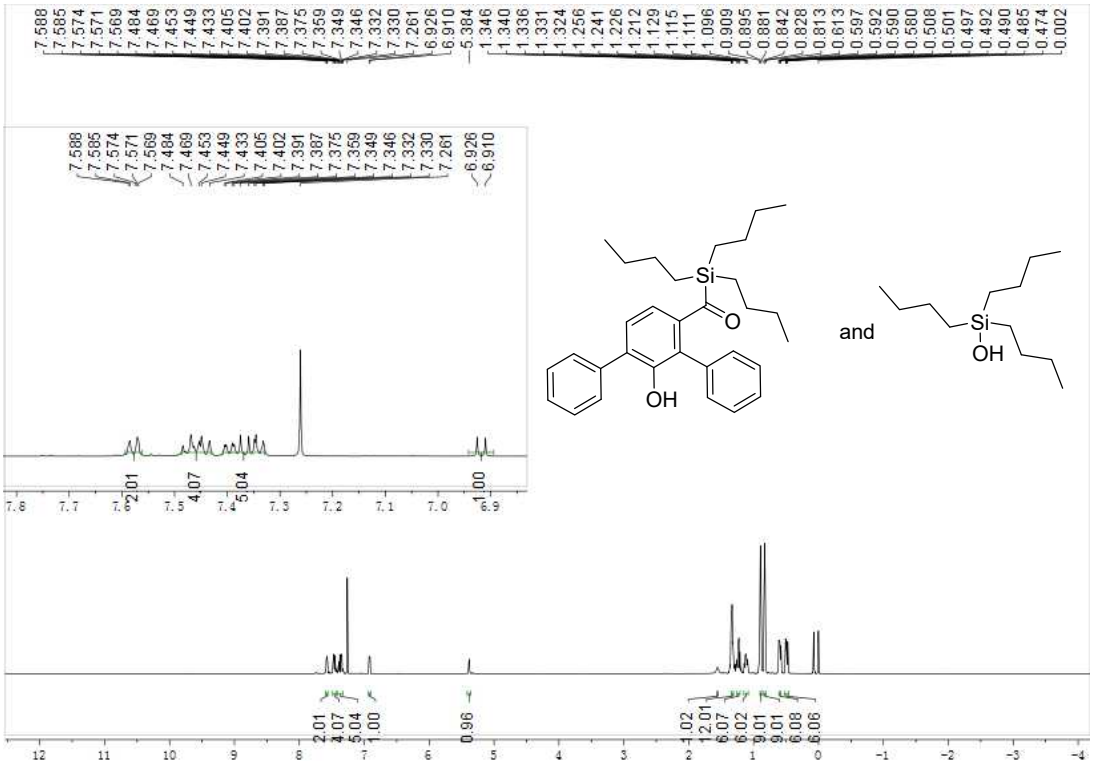


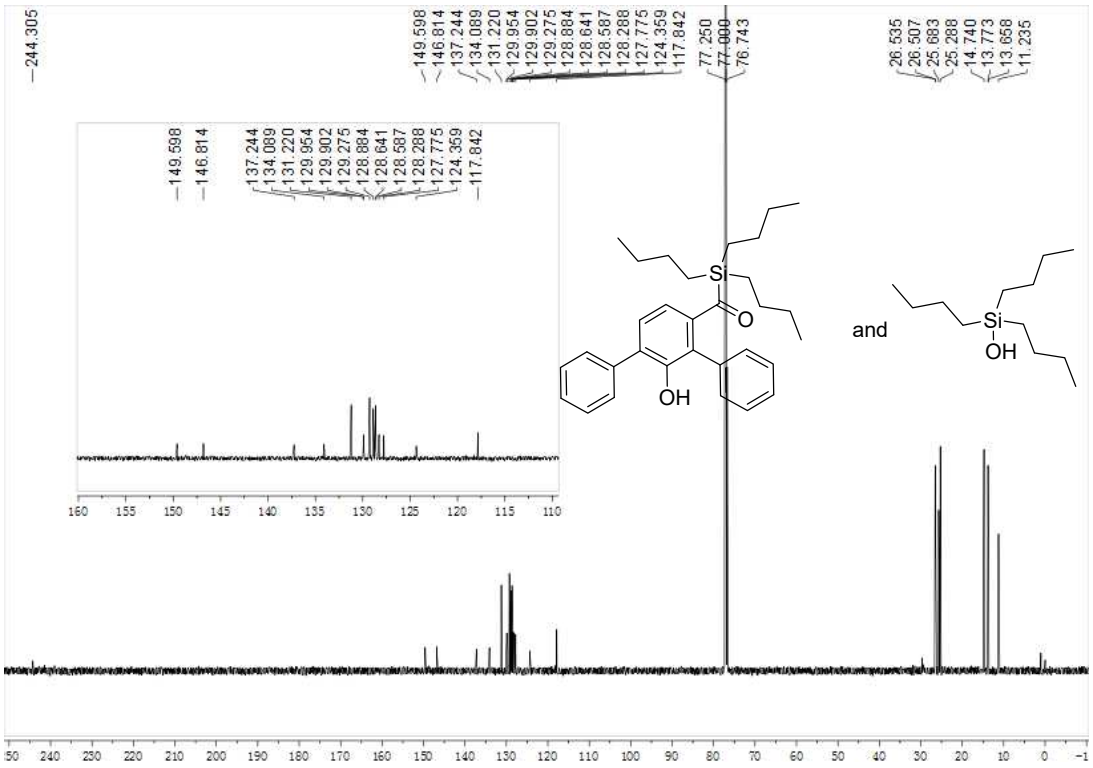
(2’-hydroxy-[1,1’:3’,1”-terphenyl]-4’-yl)(triethylsilyl)methanone (3ac)



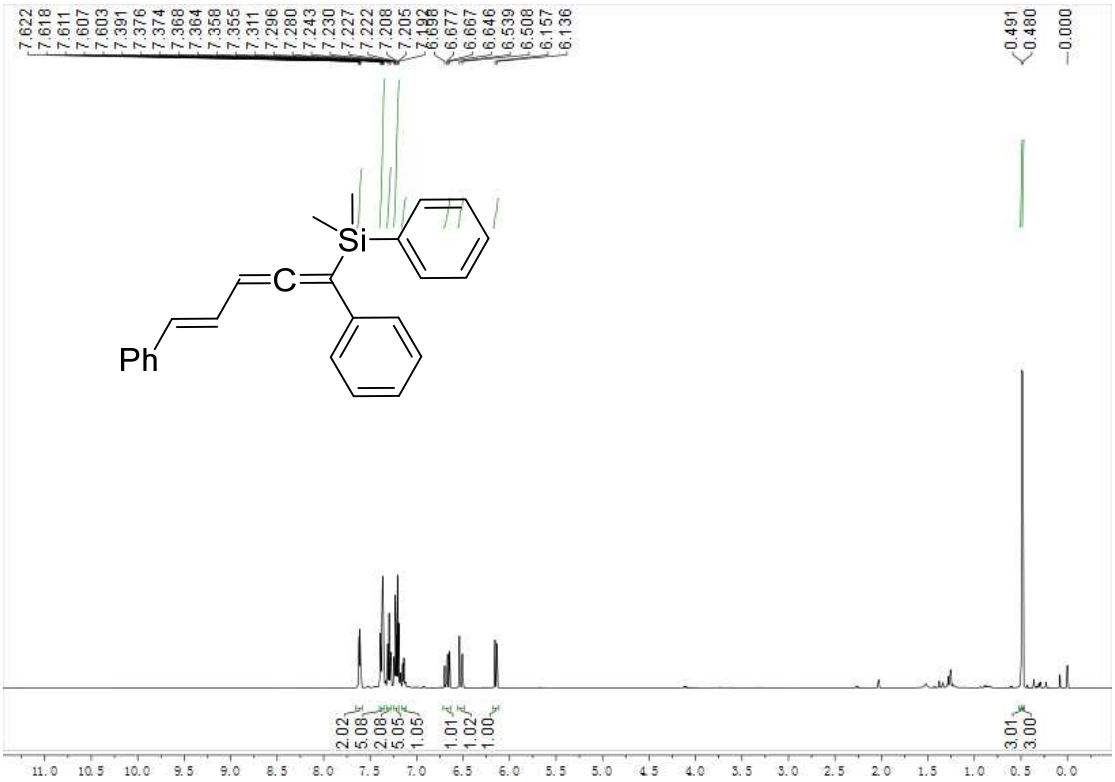


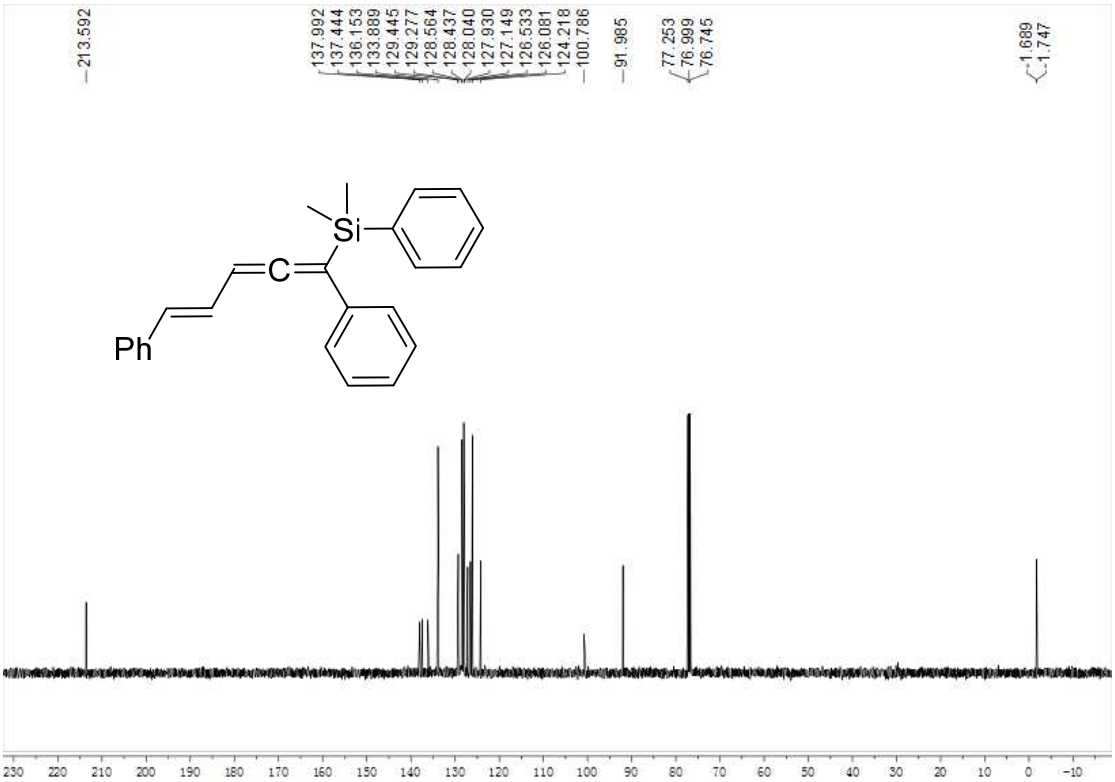
(2'-Hydroxy-[1,1':3',1''-terphenyl]-4'-yl)(tributylsilyl)methanone (3ad) and tributylsilanol (3ad')





(*E*)-(1,5-diphenylpenta-1,2,4-trien-1-yl)dimethyl(phenyl)silane (4aa)





(D) Reference

(1) X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.-N. Guo, C.-Z. Qi and Y.-M. Liang, *Adv. Synth. Catal.*, 2007, **349**, 2493.