Decatungstate-catalyzed α-C(sp^3)-H functionalizations of amides with *para*-quinone methides

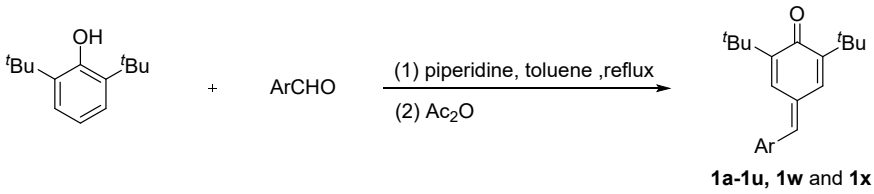
Lin He,*[a] Hongyu Chen,[a] Dan Yang,[b*] Liyuan Cheng,[a] Xile Jiang,[c] Mingsong Shi*[d]

(A) General Information

All reactions and manipulations which are sensitive to moisture or air were performed under inert atmosphere of argon. All chemicals were purchased from J&K, Acros and Aldrich, and were used as received. Anhydrous CH_2Cl_2, DMSO, DMF and MeCN were freshly distilled from calcium hydride. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 and chemical shifts are reported in δ (ppm) referenced to residual undeuterated solvent signal for ^1H NMR (7.26 ppm) and ^{13}C NMR (77.00 ppm). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD-MS-MS quadrupole mass spectrometer. The light source for the photocatalytic reaction is manufactured by GeAo chemistry with a power of 40 W, a broad band source (365–375 nm). A fan was used to maintain the reaction temperature at room temperature (about 25-30 ℃). The reactions were carried out in a borosilicate glass vessel and the distance from the light source to the irradiation vessel is about 1 cm.

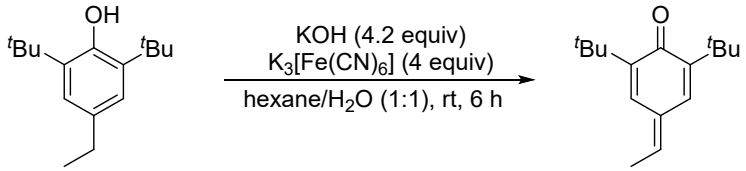
Figure S1. Photoreactor used in this research (40 W purple LEDs)

(B) General procedure for the synthesis of *p*-QMs 1.[1]



1a-1u, 1w and **1x**

In a Dean-Stark apparatus, to a mixture solution of 2,6-di-*tert*-butylphenol (5.0 mmol, 1.0 eq.) and the corresponding aromatic aldehyde (5.5 mmol, 1.1 eq.) in 30 mL toluene was heated with an oil bath to reflux. Then piperidine (10.0 mmol, 2.0 eq.) was added dropwise and the reaction mixture was continued to reflux for 24 h. after cooling the reaction mixture just below the boiling point of toluene, acetic anhydride (10.0 mmol, 2.0 eq.) was added and the reaction mixture was stirred for another 1 h at the same temperature. Then the reaction mixture was poured into ice water (100 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue were purified by flash column chromatography (petroleum ether/ethyl acetate) affording the desired products *p*-QMs **1a-1u, 1w** and **1x**.



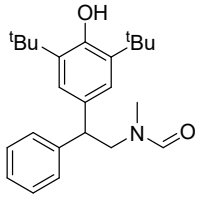
1v

To a solution of 2,6-di-*tert*-butyl-4-ethylphenol (2.34 g, 10 mmol) in hexane (20 mL) was added a solution of KOH (1.7 g, 42 mmol) and $K_3[Fe(CN)_6]$ (13.2 g, 40 mmol) in H_2O (20 mL) under an argon atmosphere. The reaction mixture was stirred vigorously at room temperature for 6 h. The aqueous layer was separated and extracted with hexane (20 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was recrystallization from CH_2Cl_2 and hexane, obtained **1v** (1.6 g, 69%) as a yellow solid.

(C) General Procedure for Synthesis of diarylmethyl-*N*-methylformamide

To an 8 mL vial equipped with a magnetic stir bar was added **1** (0.2 mmol), TBADT (5 mol%) and DMF (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W purple LED (365–375 nm) at room temperature for 24 h. Dilute with H_2O (2 mL), and extract with ethyl acetate (5 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue were purified by flash column chromatography (petroleum ether/ethyl acetate) affording the desired products **3**.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenylethyl)-*N*-methylformamide (3a)**



White solid, 66 mg, 90% yield, mp. 107-108 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1).

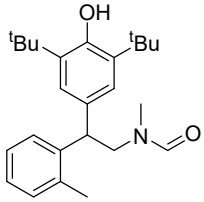
The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 0.4H), 7.73 (s, 0.6H), 7.34-7.21 (m, 5H), 7.08 (s, 0.7H), 7.01 (s, 1.3H), 5.17 (s, 0.6H), 5.13 (s, 0.4H), 4.30 (t, *J* = 8.4 Hz, 0.4H), 4.13 (t, *J* = 8.0 Hz, 0.6H), 4.04-4.00 (m, 0.4H), 3.86-3.77 (m, 1.6H), 2.85 (s, 2H), 2.70 (s, 1H), 1.42 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.6 (2), 152.6, 152.4, 141.9, 141.4, 136.0, 135.7, 131.9, 131.3, 128.6, 128.3, 127.9, 127.7, 126.8, 126.4, 124.3, 124.1, 55.1, 49.3, 49.1, 48.5, 34.9, 34.2, 30.2, 30.1, 29.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{34}NO_2$: 368.2584; Found: 368.2589.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(o-tolyl)ethyl)-*N*-methylformamide (3b)**



White solid, 60 mg, 79% yield, mp. 135-136 °C. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

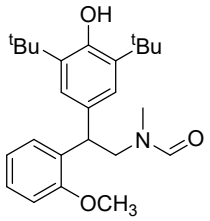
The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 0.4H), 7.71 (s, 0.6H), 7.23-7.11 (m, 4H), 7.03 (s, 0.8H), 6.94 (s, 1.2H), 5.11 (s, 0.6H), 5.08 (s, 0.4H), 4.52 (t, *J* = 8.4 Hz, 0.4H), 4.30 (t, *J* = 7.6 Hz, 0.6H), 4.07 (dd, *J* = 13.6, 8.8 Hz, 0.4H), 3.79 (d, *J* = 7.6 Hz, 1.3H), 3.71 (dd, *J* = 13.6, 7.6 Hz, 0.4H), 2.84 (s, 2H), 2.68 (s, 1H), 2.34 (s, 1H), 2.32 (s, 2H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 152.6, 152.4, 139.9, 139.7, 136.3, 136.2, 136.0, 135.7, 131.7, 131.1, 130.9, 130.6, 126.8, 126.6, 126.3, 126.2, 126.1, 126.0, 124.8, 124.5, 55.3, 49.2, 44.7, 43.8, 35.1, 34.3, 30.3, 30.2 19.9.(2).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{36}NO_2$: 382.2741; Found: 382.2748.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)ethyl)-*N*-methylformamide (3c)**



White solid, 38 mg, 48% yield, mp. 145-146 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

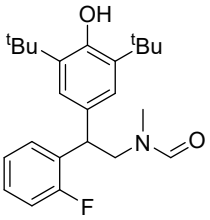
The presence of two rotamers (ratio 3:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 0.3H), 7.78 (s, 0.7H), 7.27-7.07 (m, 4H), 6.93-6.84 (m, 2H), 5.12 (s, 0.8H), 5.08 (s, 0.2H), 4.78 (t, *J* = 8.4 Hz, 0.4H), 4.60 (t, *J* = 8.0 Hz, 0.6H), 4.02 (dd, *J* = 13.6, 8.8 Hz, 0.3H), 3.90-3.82 (m, 4H), 3.74 (dd, *J* = 14.0, 8.0 Hz, 0.7H), 2.85 (s, 2.2H), 2.77(s, 0.8H), 1.42 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 156.9, 152.5, 152.3, 135.8, 135.5, 131.6, 131.0, 130.4, 129.9, 128.4 (2), 127.9, 127.4, 124.9, 124.8, 120.7, 120.6, 110.8, 110.5, 55.3 (2), 54.3, 47.2, 42.7, 40.7, 34.5, 34.3, 30.3 (2), 29.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{36}NO_3$: 398.2690; Found: 398.2687.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2-fluorophenyl)ethyl)-*N*-methylformamide (3d)**



White solid, 36 mg, 47% yield, mp. 128-129 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

The presence of two rotamers (ratio 1.4:1) were observed in the NMR spectra.

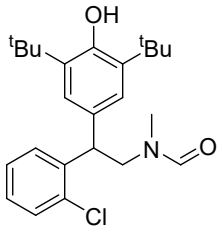
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 0.4H), 7.73 (s, 0.6H), 7.32-7.24 (m, 1H), 7.11-6.88 (m, 5H), 5.18 (s, 0.6H), 5.14 (s, 0.4H), 4.29 (t, *J* = 8.4 Hz, 0.4H), 4.12 (t, *J* = 8.0 Hz, 0.6H), 4.01 (dd, *J* = 13.6, 8.8 Hz, 0.4H), 3.84-3.73 (m, 1.6H), 2.85 (s, 1.7H), 2.70 (s, 1.2H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1 (d, *J* = 15.0 Hz), 162.8, 162.7, 161.7 (d, *J* = 14 Hz), 152.9, 152.7, 144.8 (d, *J* = 6.0 Hz), 144.2 (d, *J* = 6.0 Hz), 136.3, 136.0, 131.3, 130.7, 130.2 (d, *J* = 8.0 Hz), 129.9 (d, *J* = 8.0 Hz), 124.4, 124.2, 123.6 (d, *J* = 2.0 Hz), 1235 (d, *J* = 2.0 Hz), 115.2, 114.9, 114.7, 113.9 (d, *J* = 11.0 Hz), 113.5 (d, *J* = 11.0 Hz), 55.0, 49.2, 49.1 (2), 48.3, 35.1, 34.4, 30.2, 30.0 (2).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -112.3 (s, 1F), -113.0 (s, 1F).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{33}NFO_2$: 386.2490; Found: 386.2492.

***N*-(2-(2-chlorophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl)-*N*-methylformamide (3e)**



Yellow solid, 67.5 mg, 84% yield, mp. 132-133 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

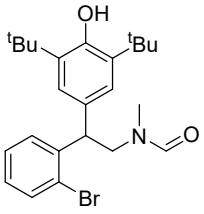
The presence of two rotamers (ratio 1.5:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (s, 0.4H), 7.82 (s, 0.6H), 7.43-7.32 (m, 3H), 7.24-7.13 (m, 2H), 7.05 (s, 1H), 5.19 (s, 0.6H), 5.16 (s, 0.4H), 4.89 (t, *J* = 8.4 Hz, 0.4H), 4.72 (t, *J* = 7.6 Hz, 0.6H), 4.18-4.11 (m, 0.5H), 3.86-3.76 (m, 1.6H), 2.88 (s, 1.8H), 2.82 (s, 1.2H), 1.42 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.7, 162.6, 139.2, 139.0, 136.1, 135.8, 134.2, 133.8, 130.4, 130.0, 128.9, 129.5, 128.9, 128.2, 128.0, 127.7, 127.1, 126.9, 124.7, 124.5, 54.1, 47.0, 44.7, 43.7, 34.3, 34.2, 30.2 (2), 29.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{33}NClO_2$: 402.2194; Found: 402.2195.

***N*-(2-(2-bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl)-*N*-methylformamide (3f)**



White solid, 73 mg, 81% yield, mp. 145-146°C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

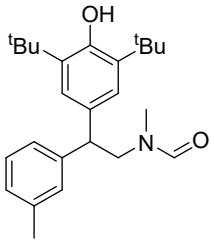
The presence of two rotamers (ratio 1.3:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (s, 0.4H), 7.83 (s, 0.6H), 7.56-7.50 (m, 1H), 7.42-7.24 (m, 2H), 7.14 (s, 1H), 7.09-7.01 (m, 2H), 5.17 (s, 0.6H), 5.14 (s, 0.4H), 4.86 (t, *J* = 8.0 Hz, 0.4H), 4.76 (t, *J* = 7.6 Hz, 0.6H), 4.17-4.11 (m, 0.5H), 3.85-3.73 (m, 1.7H), 2.88 (s, 1.7H), 2.83 (s, 1.2H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.7, 162.6, 152.8, 152.6, 140.9, 140.7, 136.1, 135.8, 133.4, 132.9, 130.4, 130.0, 129.1, 128.3 (2), 128.1, 127.8, 127.6, 125.2, 124.9, 124.7, 124.5, 54.2, 47.3, 47.1, 46.4, 34.3, 34.2, 30.2 (2), 30.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{33}NBrO_2$: 446.1689; Found: 446.1689.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(m-tolyl)ethyl)-*N*-methylformamide (3g)**



Yellow solid, 46 mg, 60% yield, mp. 118-119 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

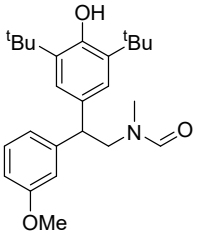
The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 0.4H), 7.74 (s, 0.6H), 7.24-7.02 (m, 5H), 5.16 (s, 0.6H), 5.12 (s, 0.4H), 4.25 (t, *J* = 8.4 Hz, 0.4H), 4.16-4.07 (m, 0.8H), 4.01-3.95 (m, 0.4H), 3.87-3.74 (m, 1.7H), 2.85 (s, 2H), 2.70 (s, 1H), 2.33 (s, 3H), 1.42 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.6, 152.4, 141.9, 141.4, 138.2, 137.9, 136.0, 135.7, 132.0, 131.2, 129.0, 128.8, 128.6, 128.3, 127.6, 127.3, 124.8, 124.6, 124.4, 124.2, 55.3, 49.4, 49.2, 48.6, 35.0, 34.3, 30.2 (2), 30.0, 21.5, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{36}NO_2$: 382.2741; Found: 382.2744.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-methoxyphenyl)ethyl)-*N*-methylformamide (3h)**



Yellow oil, 33.5 mg, 42% yield, mp. 118-119 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

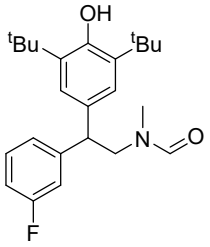
The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 0.4H), 7.74 (s, 0.6H), 7.24-7.19 (m, 1H), 7.08 (s, 0.8H), 7.01 (s, 1.2H), 6.93-6.74 (m, 3H), 5.15 (s, 0.6H), 5.11 (s, 0.4H), 4.25 (t, *J* = 8.4 Hz, 0.4H), 4.15-3.98 (m, 1.4H), 3.84-3.74 (m, 4.5H), 2.84 (s, 1.9H), 2.70 (s, 1.1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 159.7, 159.5, 152.7, 152.5, 143.7, 143.2, 136.1, 135.8, 131.9, 131.2, 129.7, 129.2, 124.4, 124.2, 120.4, 120.1, 114.2, 113.8, 111.9, 111.7, 55.2, 55.1, 49.5, 49.2, 48.7, 35.1, 34.3, 30.3, 30.2, 30.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{36}NO_3$: 398.2690; Found: 398.2696.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-fluorophenyl)ethyl)-*N*-methylformamide (3i)**



Yellow oil, 59mg, 77% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

The presence of two rotamers (ratio 1.4:1) were observed in the NMR spectra.

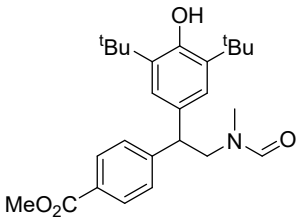
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 0.4H), 7.73 (s, 0.6H), 7.30-7.22 (m, 1H), 7.12-6.86 (s, 5H), 5.20 (s, 0.6H), 5.16 (s, 0.4H), 4.29 (t, *J* = 8.4 Hz, 0.4H), 4.12 (t, *J* = 8.0 Hz, 0.4H), 4.03-3.97 (m, 0.4H), 3.84-3.73 (m, 1.6H), 2.84 (s, 1.8H), 2.69 (s, 1.2H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1, 164.0, 162.7 (2), 161.7, 161.5, 152.8, 152.6, 144.8 (d, *J* = 7.0 Hz), 144.2 (d, *J* = 7.0 Hz), 136.3, 136.0, 131.3, 130.7, 130.2 (d, *J* = 9.0 Hz), 129.8 (d, *J* = 8.0 Hz), 124.4, 124.2, 123.6 (d, *J* = 3.0 Hz), 123.5 (d, *J* = 3.0 Hz), 115.1, 114.9, 114.7, 113.8 (d, *J* = 21.0 Hz), 113.4 (d, *J* = 21.0 Hz), 55.0, 49.1 (d, *J* = 2.0 Hz), 48.3 (d, *J* = 2.0 Hz), 35.0 ,34.3, 30.2 (2), 30.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ: -112.3 (s, 1F), -112.9 (s, 1F).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{33}NFO_2$: 386.2490; Found: 386.2492.

Methyl 4-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(*N*-methylformamido)ethyl)benzoate (3j)



White solid, 54.5 mg, 64% yield, mp. 133-134 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

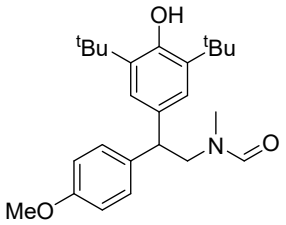
The presence of two rotamers (ratio 1.3:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (t, *J* = 8.4 Hz, 2H), 7.93 (s, 0.45H), 7.71 (s, 0.55H), 7.38 (d, *J* = 8.4 Hz, 0.9H), 7.31 (d, *J* = 8.0 Hz, 1.1H), 7.03 (s, 0.9H), 6.96 (s, 1.1H), 5.20 (s, 0.6H), 5.16 (s, 0.4H), 4.35 (t, *J* = 8.8 Hz, 0.4H), 4.19 (t, *J* = 7.6 Hz, 0.6H), 4.12-4.06 (m, 0.5H), 3.89 (s, 1.7H), 3.88 (s, 1.3H), 3.83-3.74 (m, 1.5H), 2.84 (s, 1.7H), 2.69 (s, 1.3H), 1.40 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.9, 166.7, 162.7, 126.6, 152.8, 152.7, 147.4, 146.8, 136.3, 136.0, 131.2, 130.6, 130.0, 129.8, 128.8, 128.4, 128.1, 127.9, 124.4, 124.2, 54.9, 52.0 (2), 49.3, 49.0, 48.5, 35.0, 34.3, 30.2 (2), 30.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{36}NO_4$: 426.2639; Found: 426.2643.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)ethyl)-*N*-methylformamide (3k)**



Colorless oil, 40 mg, 50% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

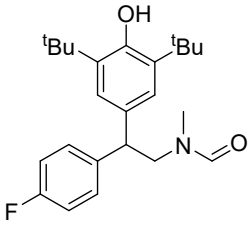
The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 0.4H), 7.71 (s, 0.6H), 7.23 (d, *J* = 8.8 Hz, 0.8H), 7.14 (d, *J* = 8.8 Hz, 1.2H), 7.06 (s, 0.7H), 6.99 (s, 1.3H), 6.87-6.83 (m, 2H), 5.15 (s, 0.6H), 5.11 (s, 0.4H), 4.24 (t, *J* = 8.4 Hz, 0.4H), 4.13-3.97 (m, 1.2H), 3.79-3.74 (m, 4.6H), 2.84 (s, 1.9H), 2.70 (s, 1.1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 158.3, 158.1, 152.6, 152.4, 136.0, 135.7, 134.1, 133.5, 132.4, 131.7, 129.8, 128.8, 124.3, 124.2, 114.1, 113.8, 55.4, 55.1 (2), 49.3, 48.5, 47.7, 35.0, 34.3, 30.2 (2), 30.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{36}NO_3$: 398.2690; Found: 398.2694.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)ethyl)-*N*-methylformamide (3l)**



White solid, 56 mg, 73% yield, mp. 126-127 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

The presence of two rotamers (ratio 1.3:1) were observed in the NMR spectra.

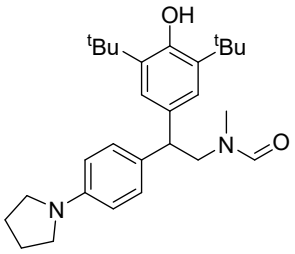
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 0.4H), 7.71 (s, 0.6H), 7.28-7.17 (m, 2H), 7.03-6.96 (m, 4H), 5.19 (s, 0.6H), 5.14 (s, 0.4H), 4.28 (t, *J* = 8.0 Hz, 0.4H), 4.14-4.02 (m, 1H), 3.78-3.69 (m, 1.5H), 2.95 (s, 0.5H), 2.88 (s, 0.5H), 2.84 (s, 1.7H), 2.70 (s, 1.2H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.7 (2), 160.4, 160.3, 152.7, 152.5, 137.7 (d, J = 3.0 Hz), 137.3 (d, J = 3.0 Hz), 136.2, 135.9, 131.8, 131.2, 129.5 (d, J = 8.0 Hz), 129.3 (d, J = 8.0 Hz), 124.3, 124.1, 115.5 (d, J = 21.0 Hz), 115.2 (d, J = 21.0 Hz), 55.2, 49.2, 48.5, 47.7, 34.9, 34.3, 30.2 (2), 30.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ: -115.7 (s, 1F), -116.4 (s, 1F).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{33}NFO_2$: 386.2490; Found: 386.2492.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(pyrrolidin-1-yl)phenyl)ethyl)-*N*-methylformamide (3m)**



White solid, 72 mg, 83% yield, mp. 171-172 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

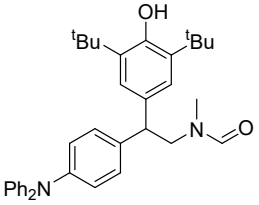
The presence of two rotamers (ratio 2:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 0.3H), 7.73 (s, 0.7H), 7.19-7.04 (m, 4H), 7.03-6.96 (s, 4H), 6.52 (d, *J* = 8.4 Hz, 2H), 5.14 (s, 0.7H), 5.10 (s, 0.3H), 4.21-4.11 (m, 0.6H), 4.04-3.39 (m, 1H), 3.86-3.80 (m, 0.4H), 3.76-3.74 (m, 1.2H), 3.26-3.24 (m, 4H), 2.86 (s, 2H), 2.71 (s, 1H), 2.01-1.97 (m, 4H), 1.43 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.6, 152.3, 152.1, 146.7, 146.5, 135.8, 135.5, 132.9, 132.3, 128.6, 128.4, 127.9, 124.3, 124.1, 111.7, 111.5, 55.6, 49.2, 48.5, 47.8, 47.5, 34.9, 34.2, 30.2 (2), 30.0, 25.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{41}N_2O_2$: 437.3163; Found: 438.3167.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(diphenylamino)phenyl)ethyl)-*N*-methylformamide (3n)**



White solid, 91 mg, 85% yield, mp. 185-186 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

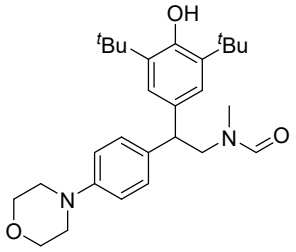
The presence of two rotamers (ratio 2:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 0.3H), 7.76 (s, 0.7H), 7.25-7.20 (m, 4H), 7.10-6.96 (s, 12H), 5.15-5.12 (m, 1H), 4.26-3.70 (m, 3H), 2.86 (s, 2H), 2.72 (s, 1H), 1.42 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.7, 152.5, 147.7, 147.6, 146.6, 146.2, 136.4, 136.0, 135.7, 135.4, 132.1, 131.6, 129.2, 129.1, 128.8, 128.6, 124.6, 124.3, 124.2, 124.0 (2), 123.9, 122.7, 122.5, 54.5, 49.6, 48.8, 48.0, 35.3, 34.4, 30.3, 30.2, 30.1.

HRMS (ESI) m/z: [$[M+H]^+$ calcd for $C_{36}H_{43}N_2O_2$: 535.3319; Found: 535.3322.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-morpholinophenyl)ethyl)-*N*-methylformamide (3o)**



White solid, 83 mg, 92% yield, mp. 155-156 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

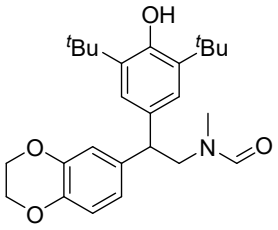
The presence of two rotamers (ratio 2:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (s, 0.35H), 7.71 (s, 0.65H), 7.22 (d, *J* = 8.4 Hz, 0.7H), 7.12 (d, *J* = 8.8 Hz, 1.3H), 7.06 (s, 0.7H), 6.99 (s, 1.3H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.13 (s, 0.7H), 5.09 (s, 0.3H), 4.23-3.97 (m, 2H), 3.86-3.83 (m, 4H), 3.79-3.73 (m, 1H), 3.14-3.11 (m, 4H), 2.83 (s, 2H), 2.69 (s, 1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.5, 152.4, 150.0, 136.0, 135.7, 133.5, 132.8, 132.4, 131.2, 128.7, 128.6, 124.3, 124.2, 115.8, 115.6, 66.9, 66.8, 55.4, 49.3, 49.2, 48.6, 47.8, 35.0, 34.3, 30.3, 30.2, 30.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{41}NO_3$: 453.3112; Found: 453.3114.

_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethyl)-_N_-methylformamide (3p)



White solid, 55 mg, 65% yield, mp. 139-140 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

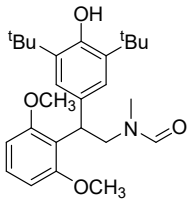
The presence of two rotamers (ratio 2:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 0.3H), 7.74 (s, 0.6H), 7.05 (s, 0.7H), 6.99 (s, 1.3H), 6.81-6.69 (m, 3H), 5.15 (s, 0.6H), 5.11 (s, 0.3H), 4.22-4.21 (m, 4H), 4.16-4.09 (m, 0.6H), 4.00 (t, *J* = 7.6 Hz, 0.7H), 3.93-3.68 (m, 2H), 2.84 (s, 2H), 2.70 (s, 1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.6, 152.4, 143.5, 143.2, 142.3, 142.1, 136.0, 135.7, 135.6, 134.9, 132.1, 131.6, 124.3, 124.1, 120.7, 120.6, 117.4, 117.0, 116.8, 116.5, 64.3, 64.2 (3), 55.2, 49.2, 48.7, 47.9, 35.1, 34.3, 30.2 (2), 29.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{36}NO_4$: 426.2639; Found: 426.2640.

_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2,6-dimethoxyphenyl)ethyl)-_N_-methylformamide (3q)



White solid, 26 mg, 30% yield, mp. 136-137 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

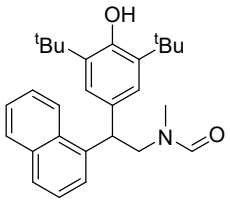
The presence of two rotamers (ratio 10:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 7.28 (s, 0.3H), 7.20 (s, 2H), 7.13 (t, *J* = 8.4 Hz, 1H), 6.54-6.51 (m, 2H), 5.05 (s, 1H), 4.94 (dd, *J* = 10, 6.4 Hz, 1H), 4.33 (dd, *J* = 13.6, 10 Hz, 1H), 3.81 (s, 6H), 3.74 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.82 (s, 3H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.9, 158.4, 152.1, 135.2, 132.0, 128.1, 124.9, 117.1, 104.3, 55.5, 52.6, 38.7, 34.3, 30.4, 30.3, 29.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{37}NNaO_4$: 450.2615; Found: 450.2614.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(naphthalen-1-yl)ethyl)-*N*-methylformamide (3r)**



Yellow soild, 46 mg, 55% yield, mp. 92-93 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

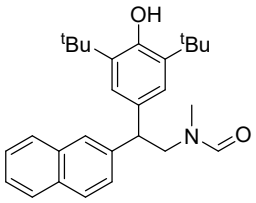
The presence of two rotamers (ratio 1.5:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.4 Hz, 0.4H), 8.12 (d, *J* = 8.4 Hz, 0.4H), 7.95 (s, 0.4H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.79-7.72 (m, 1.6H), 7.51-7.42 (m, 4H), 7.15 (s, 0.8H), 7.05 (s, 1.2H), 5.20 (t, *J* = 8.4 Hz, 0.4H), 5.11 (s, 1H), 4.93 (t, *J* = 7.6 Hz, 0.6H), 4.27 (dd, *J* = 13.6, 8.4 Hz, 0.5H), 3.94-3.92 (m, 1H), 3.80 (dd, *J* = 14, 8.4 Hz, 0.4H), 2.88 (s, 1.8H), 2.68 (s, 1.2H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.9 (2), 152.7, 152.5, 137.5, 137.3, 136.1, 135.8, 134.1, 134.0, 131.9, 131.7, 131.1, 129.0, 128.8, 127.6, 127.2, 126.3, 126.1, 125.6, 125.4, 125.2, 124.8 (2), 124.6, 124.1, 123.4, 123.1, 55.5, 49.5, 44.1, 43.1, 35.2, 34.3, 30.3, 30.2 (2).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{36}NO_2$: 418.2741; Found: 418.2745.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(naphthalen-2-yl)ethyl)-*N*-methylformamide (3s)**



Yellow solid, 26 mg, 31% yield, mp. 86-87 ºC. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

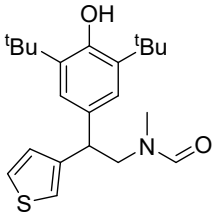
The presence of two rotamers (ratio 1.5:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 0.4H), 7.82-7.76 (m, 4H), 7.69 (s, 0.6H), 7.48-7.45 (m, 3H), 7.14 (s, 0.8H), 7.07 (s, 1.2H), 5.17 (s, 0.6H), 5.13 (s, 0.4H), 4.48 (t, *J* = 8.4 Hz, 0.4H), 4.31 (t, *J* = 7.6 Hz, 0.6H), 4.20-4.11 (m, 0.7H), 3.98-3.86 (m, 1.6H), 2.88 (s, 1.8H), 2.70 (s, 1.2H), 1.42 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8 (2), 152.7, 152.5, 139.5, 139.0, 136.1, 135.9, 133.4, 132.3 (2), 131.9, 131.4, 128.5, 128.1, 127.7 (2), 127.6, 127.5, 126.5 (2), 126.2, 126.0, 125.9, 125.8, 125.5, 124.5, 124.3, 55.1, 49.5, 49.1, 48.7, 35.1, 34.3, 30.3, 30.2, 30.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{35}NNaO_2$: 440.2560; Found: 440.2563.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(thiophen-3-yl)ethyl)-*N*-methylformamide (3t)**



Yellow oil, 37.5mg, 50% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

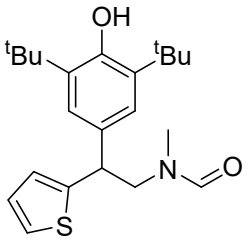
The presence of two rotamers (ratio 1.8:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 0.4H), 7.69 (s, 0.6H), 7.31-7.24 (m, 1H), 7.09-6.96 (m, 4H), 5.16 (s, 0.6H), 5.12 (s, 0.4H), 4.37 (t, *J* = 8.4 Hz, 0.4H), 4.20 (t, *J* = 7.6 Hz, 0.6H), 4.13-4.04 (m, 0.5H), 3.80-3.61 (m, 1.8H), 2.84 (s, 2H), 2.68 (s, 1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.8, 152.5, 142.7, 142.3, 136.1, 135.8, 131.9, 131.1, 127.7, 127.2, 126.1, 125.5, 124.4, 124.2, 121.2, 121.0, 55.6, 49.8, 45.2, 44.2, 35.1, 34.3, 30.3, 30.2, 30.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{32}NSO_2$: 374.2148; Found: 374.2153.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(thiophen-2-yl)ethyl)-*N*-methylformamide (3u)**



White solid, 27mg, 36% yield, mp. 98-99 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

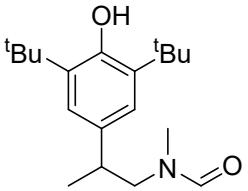
The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 0.4H), 7.69 (s, 0.6H), 7.31-7.24 (m, 1H), 7.09-6.96 (m, 4H), 5.15 (s, 0.6H), 5.12 (s, 0.4H), 4.37 (t, *J* = 8.4 Hz, 0.4H), 4.20 (t, *J* = 7.6 Hz, 0.6H), 4.09-4.04 (m, 0.4H), 3.80-3.61 (m, 1.7H), 2.84 (s, 1.9H), 2.68 (s, 1.1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.8, 152.5, 142.7, 142.3, 136.1, 135.8, 131.9, 131.1, 127.7, 127.2, 126.1, 125.5, 124.4, 124.3, 121.2, 121.0, 55.6, 49.8, 45.2, 44.2, 35.1, 34.3, 30.3, 30.2, 30.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{32}NSO_2$: 374.2148; Found: 374.2155.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl)-*N*-methylformamide (3v)**



White solid, 40mg, 65% yield, mp. 104-105 °C. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

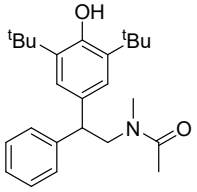
The presence of two rotamers (ratio 2.3:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 0.3H), 7.82 (s, 0.7H), 7.01 (s, 0.6H), 6.93 (s, 1.4H), 5.16 (s, 0.7H), 5.13 (s, 0.3H), 3.75 (dd, *J* = 13.6, 8.4 Hz, 0.3H), 3.30 (s, 0.8H), 3.28 (s, 0.8H), 3.17-2.92 (m, 1.7H), 2.84 (s, 2.1H), 2.72 (s, 0.9H), 1.44 (s, 18H), 1.23 (dd, *J* = 7.2, 3.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.8, 162.7, 152.5, 152.3, 136.1, 135.8, 134.3, 133.3, 123.5, 123.2, 57.4, 51.5, 37.8, 37.3, 35.2, 34.3, 30.3 (2), 30.2, 30.0, 19.3, 18.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{31}NNaO_2$: 328.2247; Found: 328.2254.

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenylethyl)-*N*-methylacetamide (3w)**



Yellow oil, 31mg, 41% yield, mp. 137-138°C. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

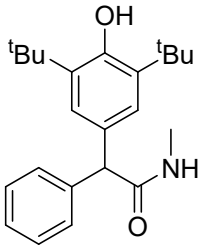
The presence of two rotamers (ratio 1.1:1) were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.13 (m, 5H), 7.01 (s, 1H), 6.94 (s, 1H), 5.11 (s, 0.4H), 5.05 (s, 0.5H), 4.26 (t, *J* = 8.4 Hz, 0.5H), 4.07 (t, *J* = 7.6 Hz, 0.6H), 3.97 (dd, *J* = 13.6, 8.8 Hz, 0.6H), 3.86-3.75 (m, 1.5H), 2.82 (s, 1.4H), 2.60 (s, 1.6H), 1.93 (s, 1.7H), 1.61 (s, 1.4H), 1.37 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.8, 170.6, 152.7, 152.3, 142.6, 142.1, 136.0, 135.7, 132.6, 132.0, 128.6, 128.3, 128.2, 128.1, 126.8,, 126.4, 124.6, 124.5, 56.8, 53.4, 49.6, 49.0, 37.0, 34.3, 33.9, 30.3, 30.2, 22.0, 20.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{36}NO_2$: 382.2741; Found: 382.2745.

2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-methyl-2-phenylacetamide (3x)



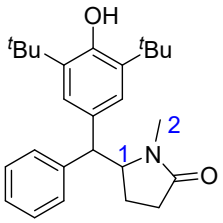
White solid, 25 mg, 35% yield, mp. 144-145 °C. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33-7.23 (m, 5H), 7.02 (s, 2H), 5.68 (s, 1H), 5.16 (s, 1H), 4.83 (s, 1H), 2.80 (d, *J* = 4.8 Hz, 3H), 1.38 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.3, 152.9, 140.0, 135.9, 129.9, 128.8, 128.5, 126.9, 125.5, 59.1, 34.3, 30.2, 26.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{31}NNaO_2$: 376.2247; Found: 376.2256.

(S)-5-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-1-methylpyrrolidin-2-one (3y)



White solid, 18 mg, 23% yield, mp. 164-165 °C. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1).

The presence of two rotamers (ratio 1.1:1) with 3:1 regioselectivities were observed in the NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.15 (m, 5H), 7.06 (s, 1H), 6.87 (s, 1H), 5.29 (s, 0.7H), 5.15 (s, 0.44 H), 5.11 (s, 0.55H), 4.30-4.25 (m, 1H), 4.12 (d, *J* = 6.0 Hz, 0.59H), 4.07 (d, *J* = 6.0 Hz, 0.44H), 3.00 (s, 0.41H), 2.71 (s, 0.58H), 2.67 (s, 1.6H), 2.61 (s, 1.4H), 2.23-1.99 (m, 2.6H), 1.91-1.86 (m, 1H), 1.75-1.67 (m, 1.4H), 1.58-1.52 (m, 1H), 1.43 (s, 9H), 1.37 (s, 9H).

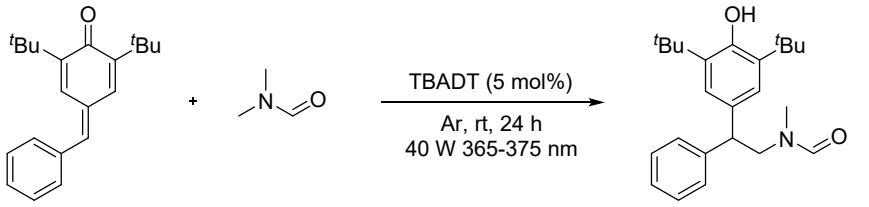
^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.3, 175.2, 152.3 (2), 141.7, 141.2, 135.8, 135.5, 131.5, 130.7,

128.3, 128.2, 128.1, 126.4, 124.8, 124.7, 63.8, 63.4, 53.4, 52.6, 34.1, 34.0, 30.0, 29.9, 29.4, 29.3, 29.1(2), 27.9, 22.9, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{36}NO_2$: 394.2741; Found: 394.2742.

(D) Scale-up reaction and synthetic transformation

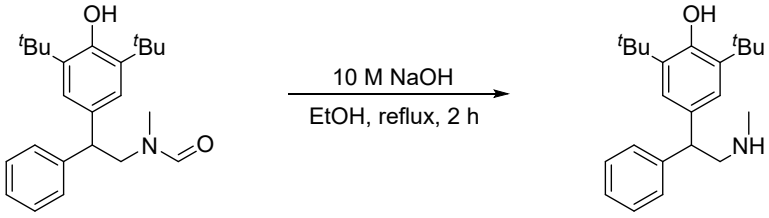
(a) Scale-up reaction



1a, 1 mmol 10 mL **3a**, 86% yield, 315 mg

To an 8 mL vial equipped with a magnetic stir bar was added **1a** (294 mg, 1 mmol), TBADT (130 mg, 5 mol%) and DMF (10 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W purple LED (365−375 nm) at room temperature for 24 h. Dilute with H_2O (20 mL), and extract with ethyl acetate (10 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue were purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1) affording the desired products **3a** (315 mg, 86%) as a white solid.

(b) Synthetic transformation



3a **4**

To a solution of **3a** (175 mg, 0.48 mmol) in ethanol (5 mL) was added 10 M NaOH (2 mL), then the reaction mixture was heated to reflux in an oil bath for 2 h. The reaction mixture was cooled to room temperature and quenched with 3M HCl (3 mL). Then solvent was evaporated, extracted with ethyl acetate (10 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue were purified by flash column chromatography (CH_2Cl_2/MeOH = 40:1) affording the desired products **4** (75 mg, 46%) as a brown oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.22-7.19 (m, 4H), 7.12-7.07 (m, 1H), 6.96 (s, 2H), 4.05 (t, *J* = 7.6 Hz, 1H), 3.13-3.04 (m, 2H), 2.34 (s, 3H), 1.32 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.3, 143.1, 135.8, 133.0, 128.5, 127.9, 126.3, 124.3, 56.9, 50.8, 36.0, 34.3, 30.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{34}NO$: 340.2635; Found: 340.2638.

(E) UV-vis absorption experiments

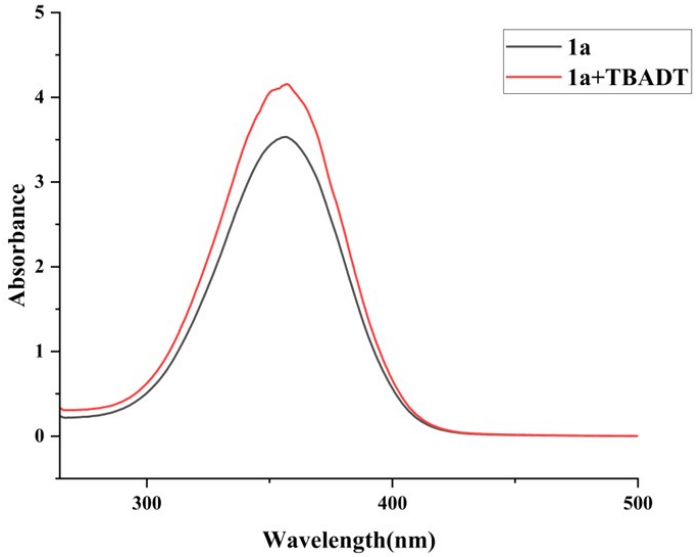
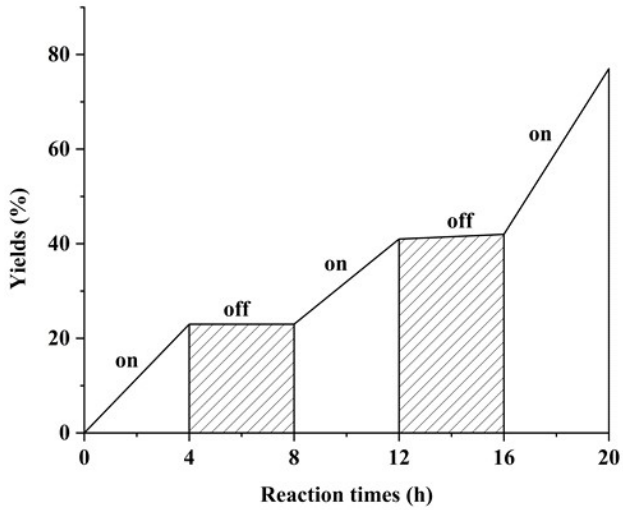


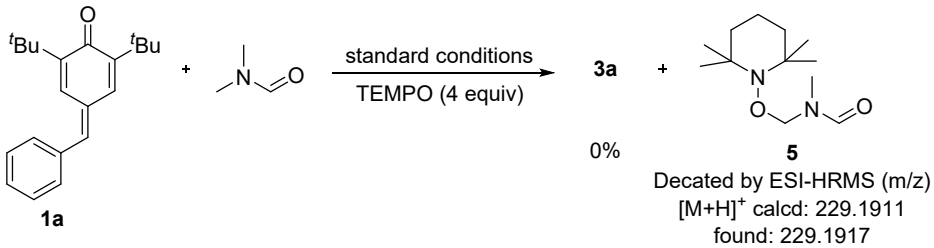
Figure S1 UV-vis absorption spectra of **1a** (0.1 mM); the mixture of **1a** (0.1 mM) and TBADT (0.005 mM) in DMF were performed on UV visible spectrophotometer, respectively.

(F) Light-on/off experiments

Five standard reaction mixtures in 8 mL vial equipped with a magnetic stir bar charged with **1a** (0.2 mmol), TBADT (5 mol%) and DMF (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was irradiated with 40 W 365–375 nm LED at room temperature. After 4 h, the 40 W 365–375 nm LED were turned off, and one vial was removed from the irradiation setup for analysis. The remaining four vials were stirred in the absence of light for additional 4 h, then one vial was removed for analysis. And the 40 W 365–375 nm LED were turned back on to irradiate the remaining three reaction mixtures. After an additional 4 h of irradiation, the 40 W 365–375 nm LED were turned off, one vial was removed for analysis. The remaining two vials were stirred in the absence of light for another 4 h. then, a vial was removed for analysis, and the 40 W 365–375 nm LED were turn back on to irradiate the remaining one for additional 4 h, then it was analyzed. The yield was isolated yield.

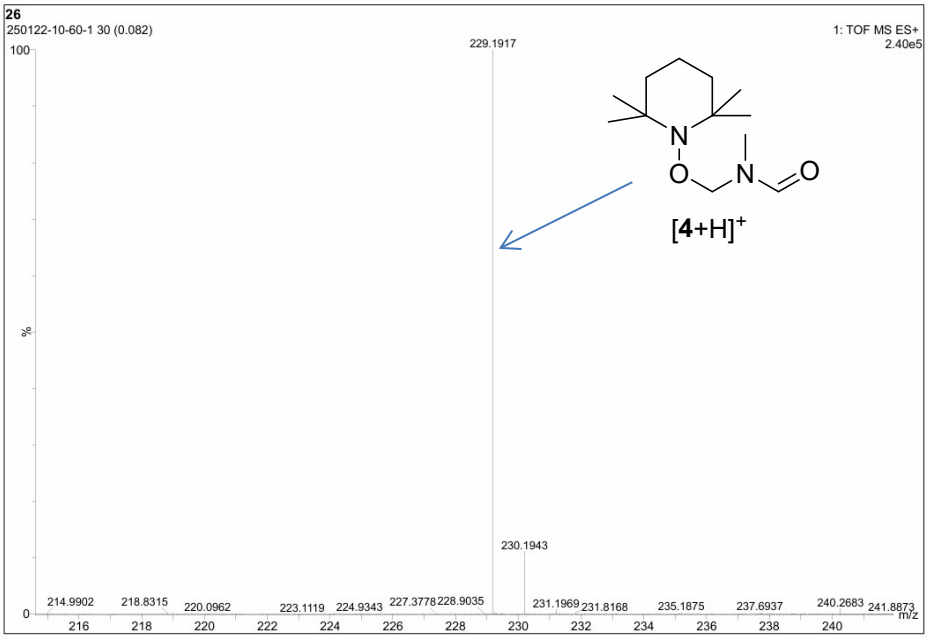


(G) Radical trapping experiment with TEMPO



Decated by ESI-HRMS (m/z)
$[M+H]^+$ calcd: 229.1911
found: 229.1917

To an 8 mL vial equipped with a magnetic stir bar was added **1a** (58.8 mg, 0.2 mmol), TBADT (26 mg, 5.0 mol%), TEMPO (62.4 mg, 0.4 mmol) and DMF (2 mL) under nitrogen atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W purple LED (365–375 nm) at room temperature for 24 h. HRMS (ESI) m/z: compound **5**, [**5**+H]$^+$ calcd for $C_{12}H_{25}O_2N_2$: 229.1911; found: 219.1917.

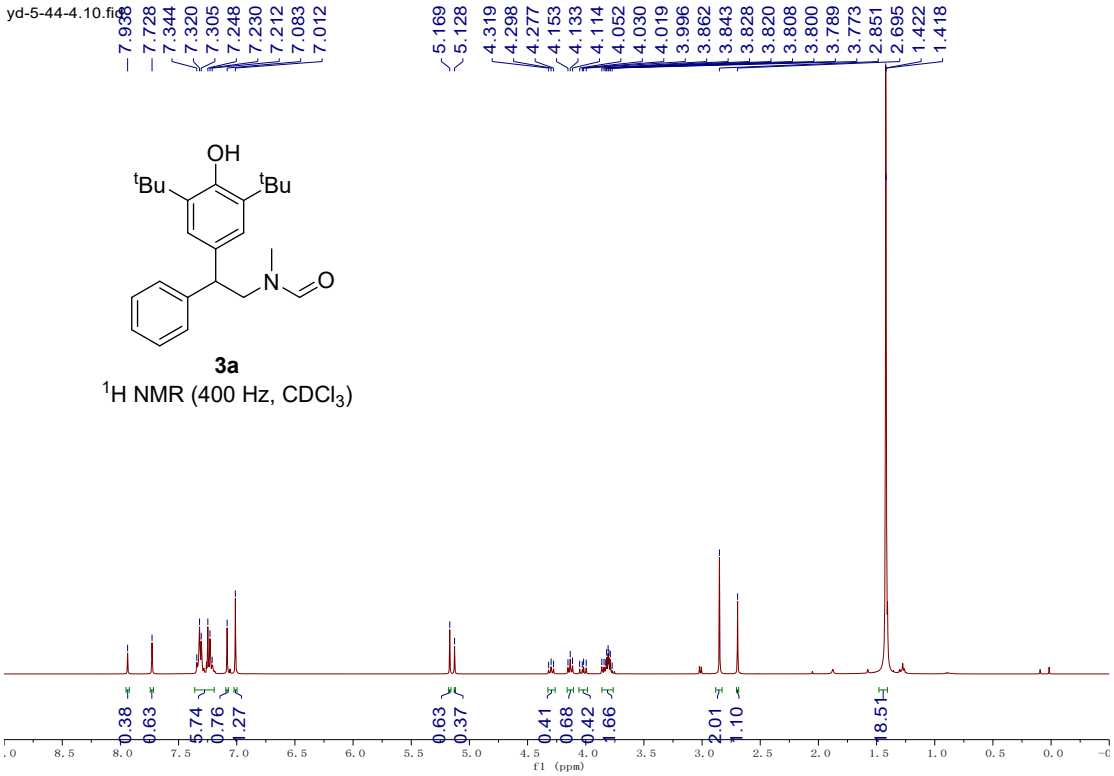


References:

[1] (a) Yan, Y.; Li, H.; Xie, F.; Lu, W.; Zhang, Z.; Jing, L.; Han, P. Electrochemical Reductive Carboxylation of *para*-Quinone Methides with CO_2. *Adv. Synth. Catal.* **2023**, *365*, 3830-3836. (b) Xiong, B.; Xu, S.; Liu, Y.; Tang, K.-W.; Wong, W.-Y. Metal-Free, Acid/Phosphine-Induced Regioselective Thiolation of *p*-Quinone Methides with Sodium Aryl/Alkyl Sulfinates. *J. Org. Chem.* **2021**, *86*, 1516-1527. (c) Dong, N.; Zhang, Z.-P.; Xue, X.-S.; Li, X.; Cheng, J.-P. Phosphoric Acid Catalyzed Aasymmetric 1,6-Conjugate Addition of Thioacetic Acid to *para*-Quinone Methides. *Angew. Chem. Int. Ed*. **2016**, *55*, 1460-1464.

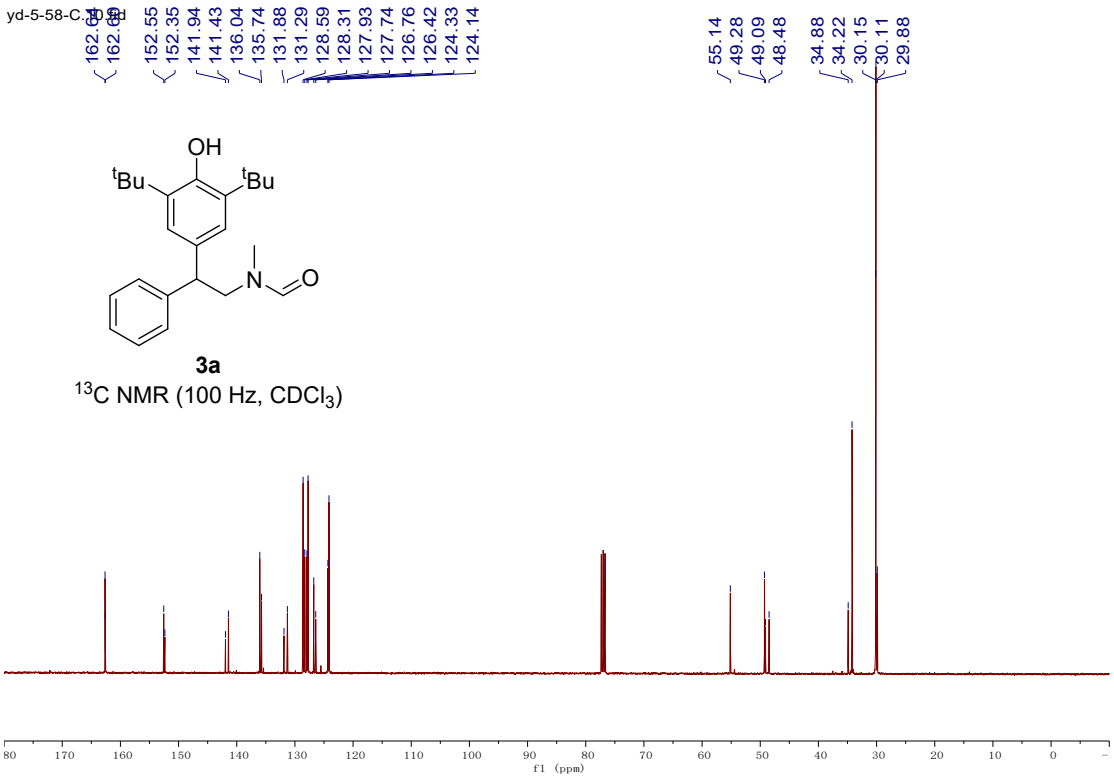
(H) NMR spectra of new compounds

N-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenylethyl)-*N*-methylformamide (3a)



3a

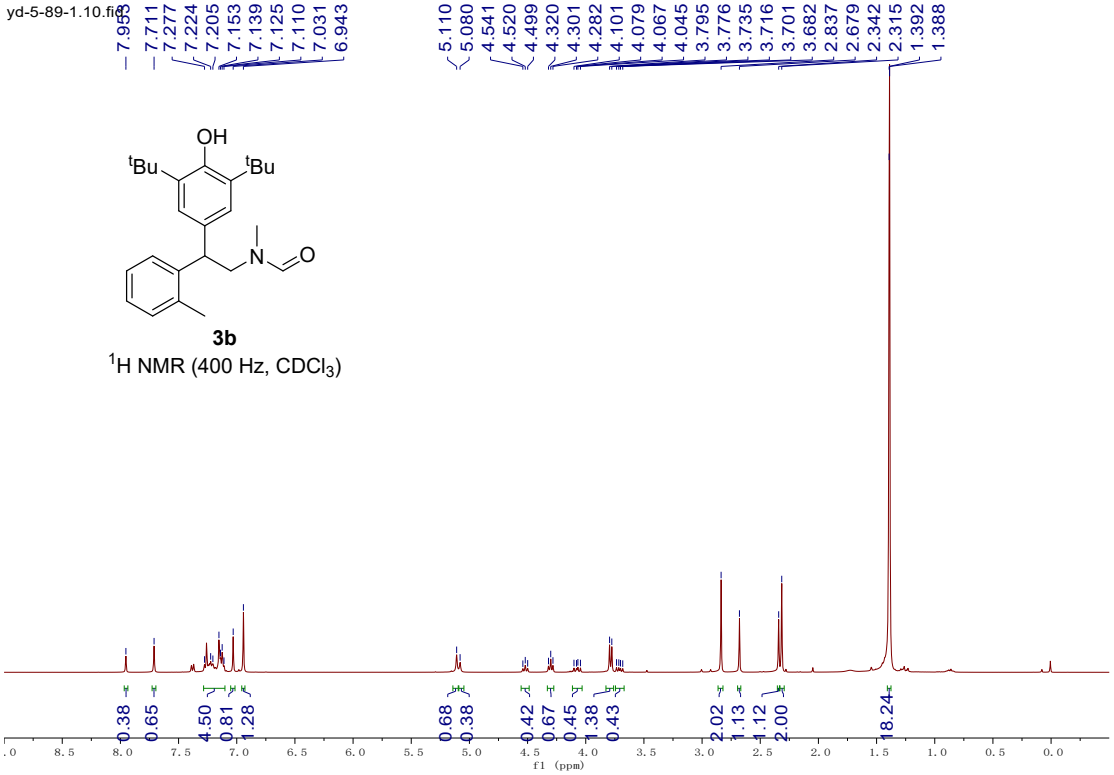
^{1}H NMR (400 Hz, $CDCl_3$)



3a

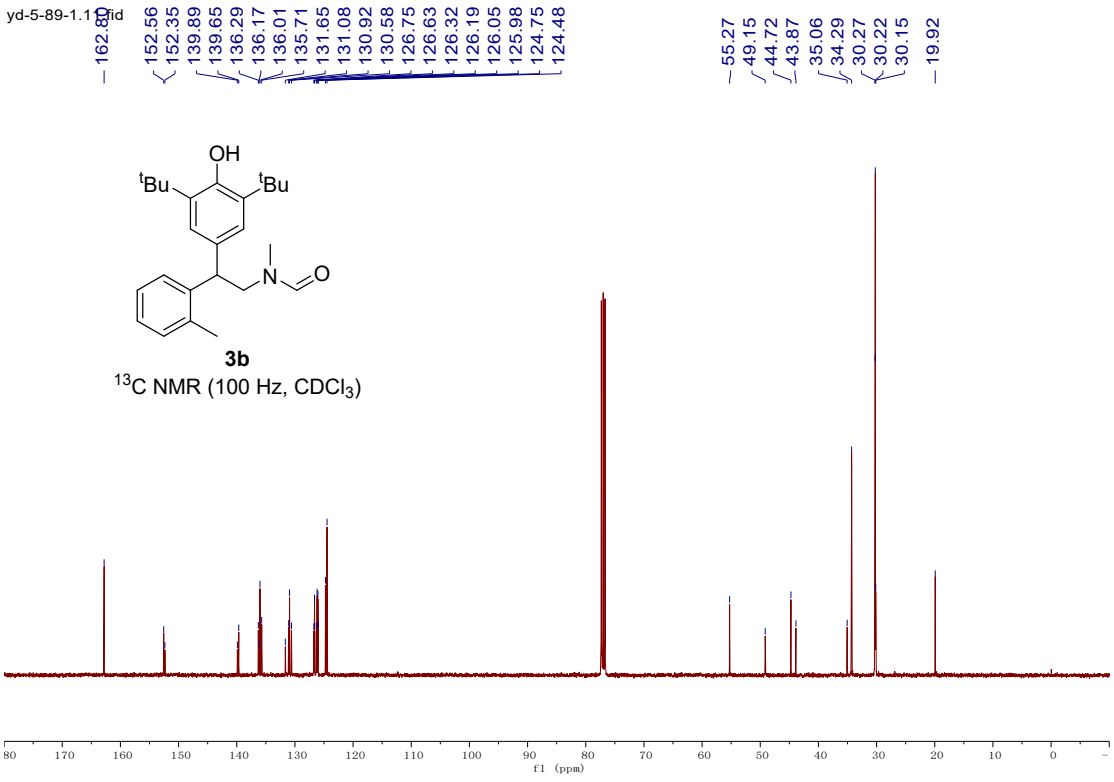
^{13}C NMR (100 Hz, $CDCl_3$)

N-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(o-tolyl)ethyl)-*N*-methylformamide (3b)



3b

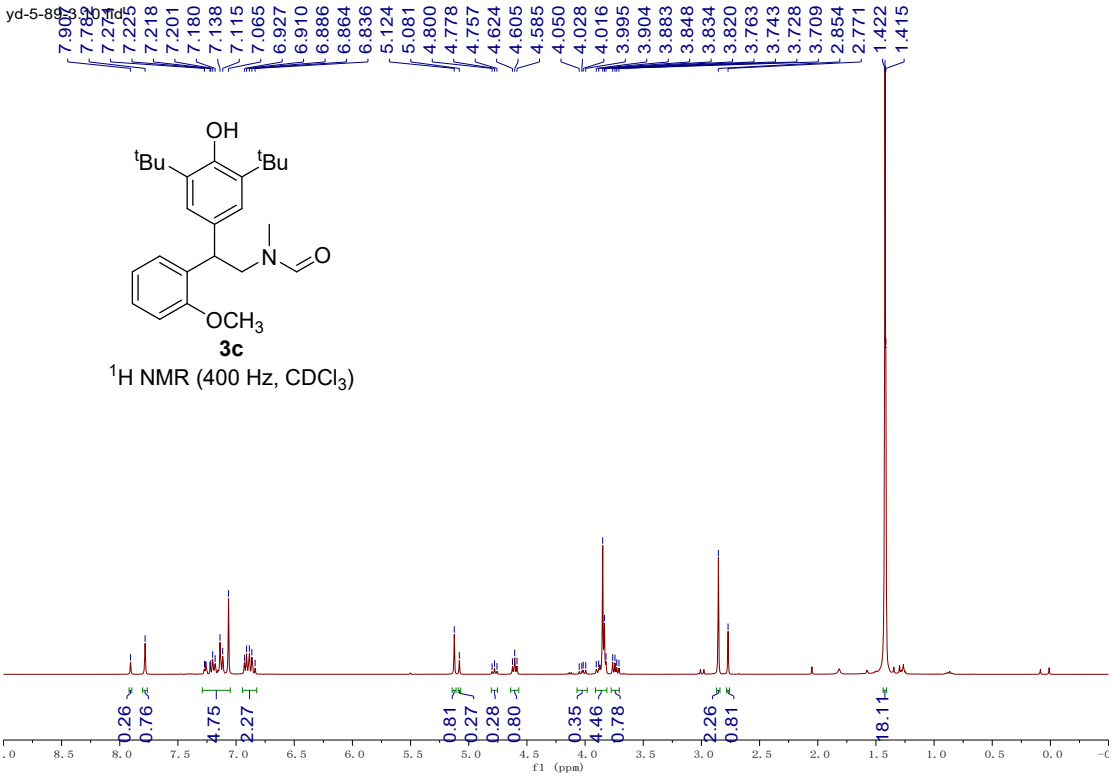
^{1}H NMR (400 Hz, $CDCl_3$)



3b

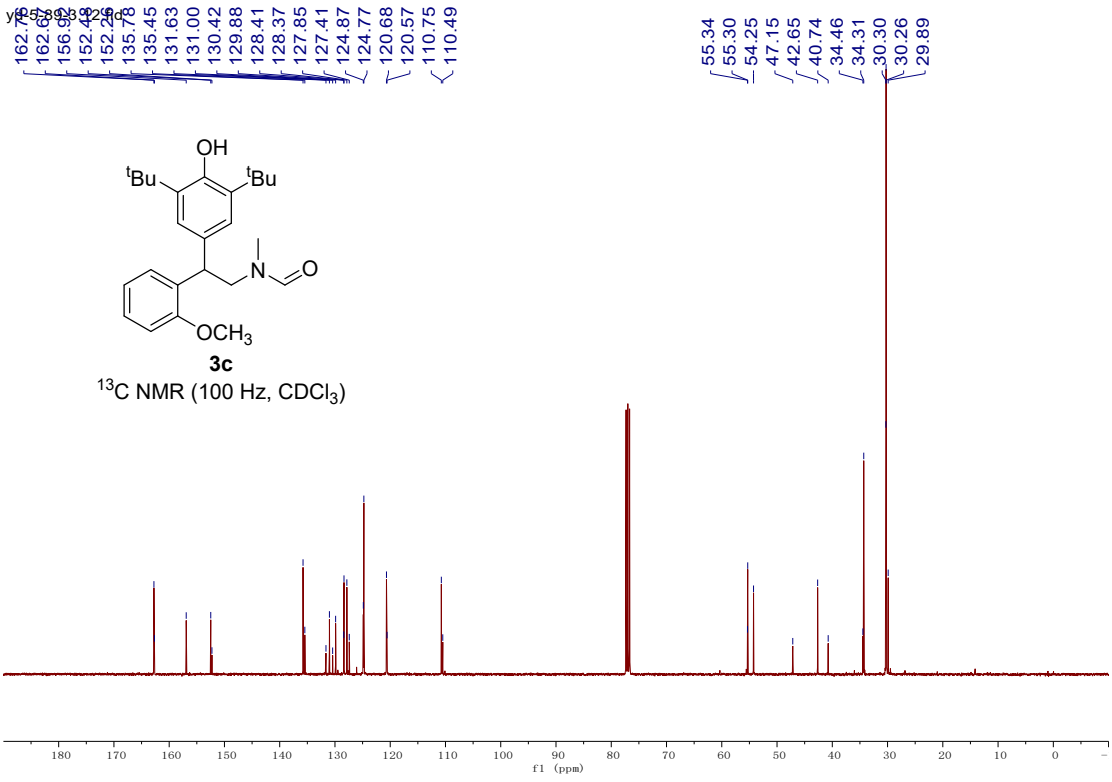
^{13}C NMR (100 Hz, $CDCl_3$)

_N_-(2-(3,5-di-_tert_-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)ethyl)-_N_-methylformamide (3c)



3c

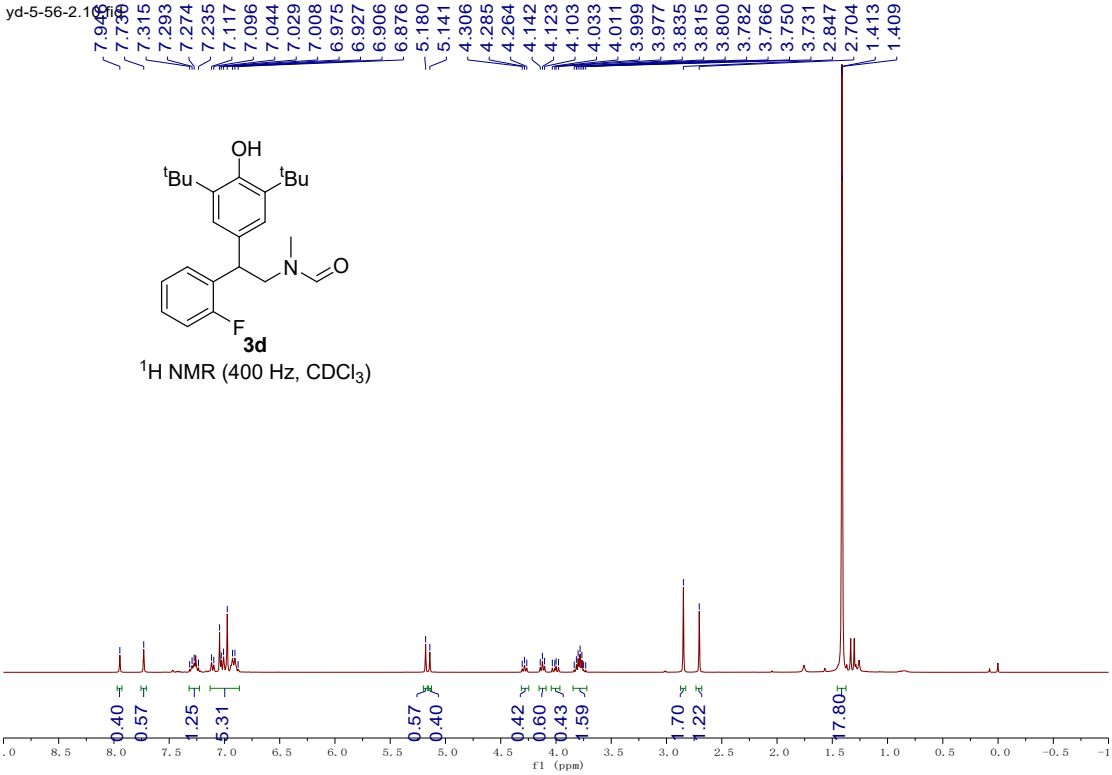
^{1}H NMR (400 Hz, $CDCl_3$)



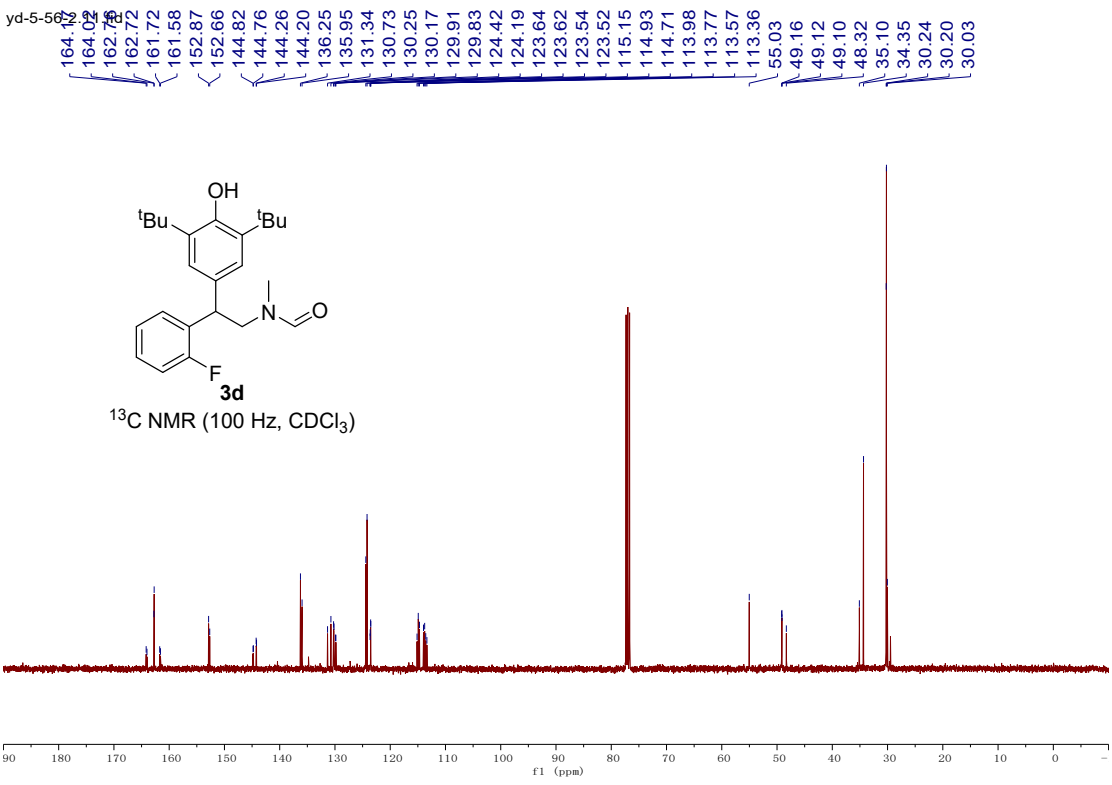
3c

^{13}C NMR (100 Hz, $CDCl_3$)

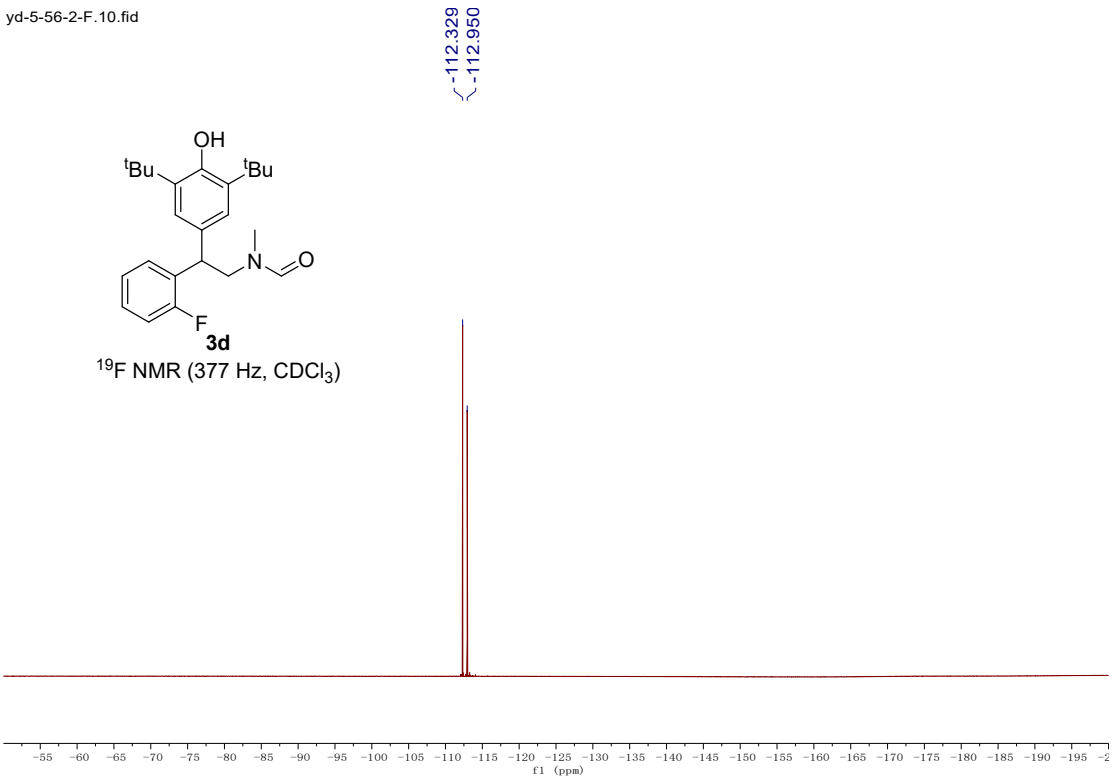
_N_-(2-(3,5-di-_tert_-butyl-4-hydroxyphenyl)-2-(2-fluorophenyl)ethyl)-_N_-methylformamide (3d)



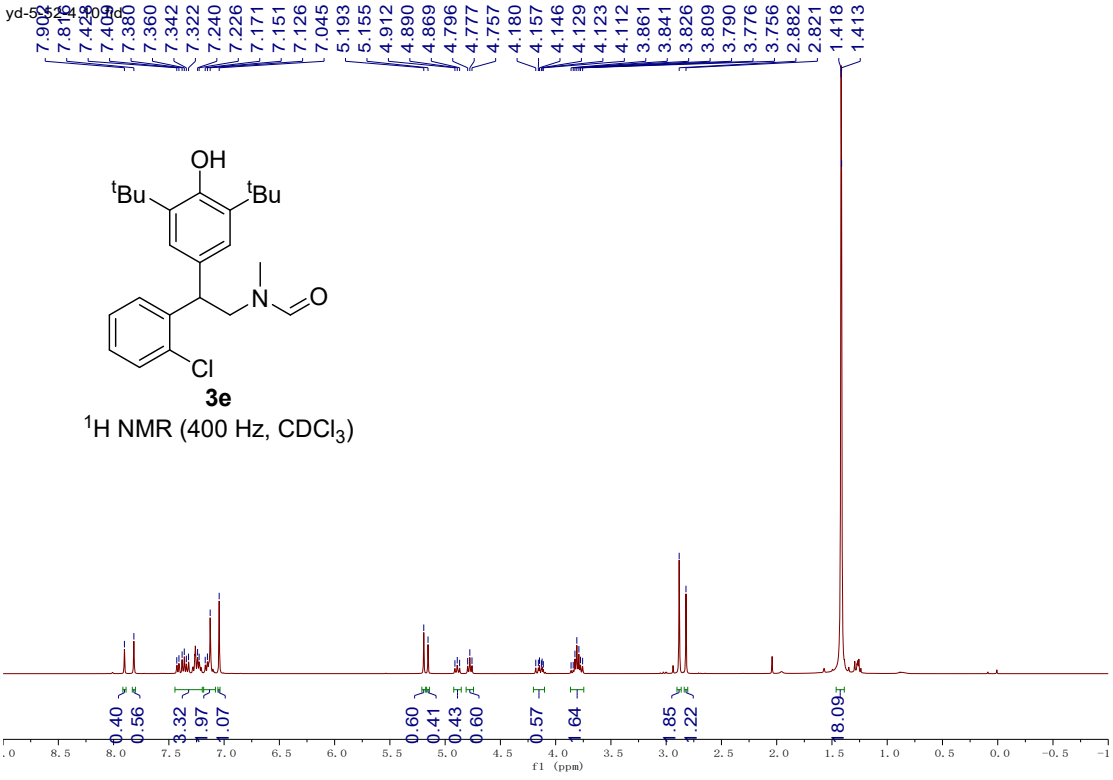
^{1}H NMR (400 Hz, $CDCl_3$)

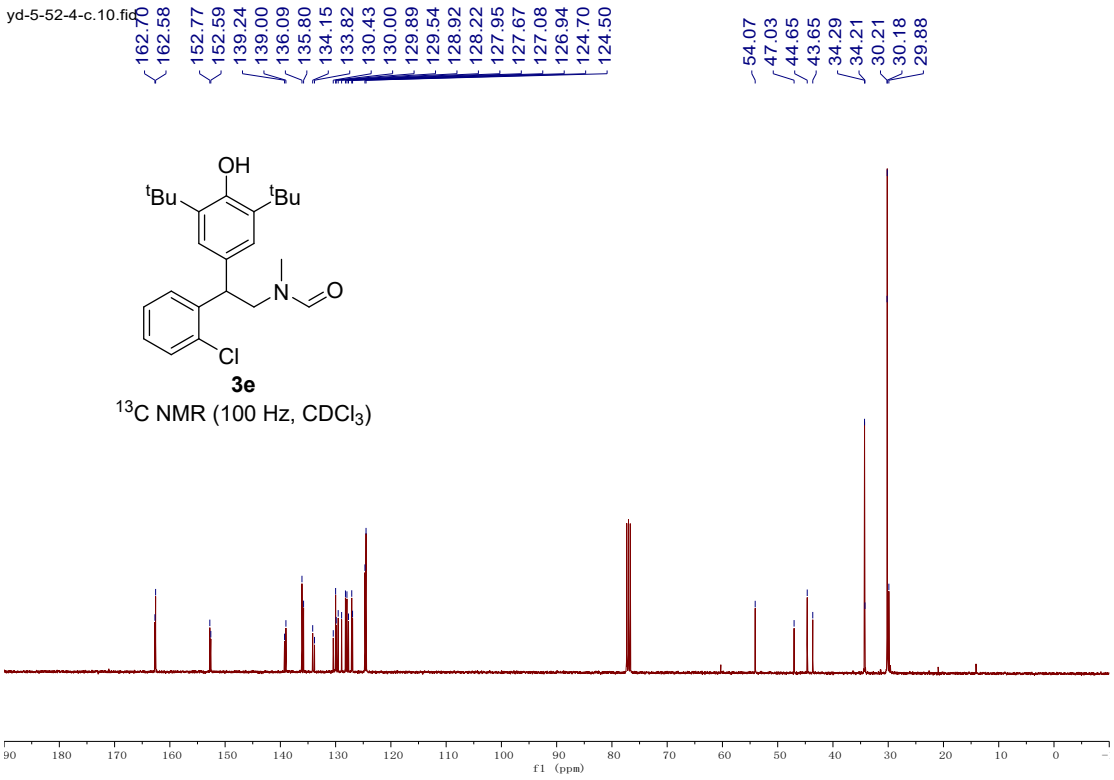


^{13}C NMR (100 Hz, $CDCl_3$)



***N*-(2-(2-chlorophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl)-*N*-methylformamide (3e)**

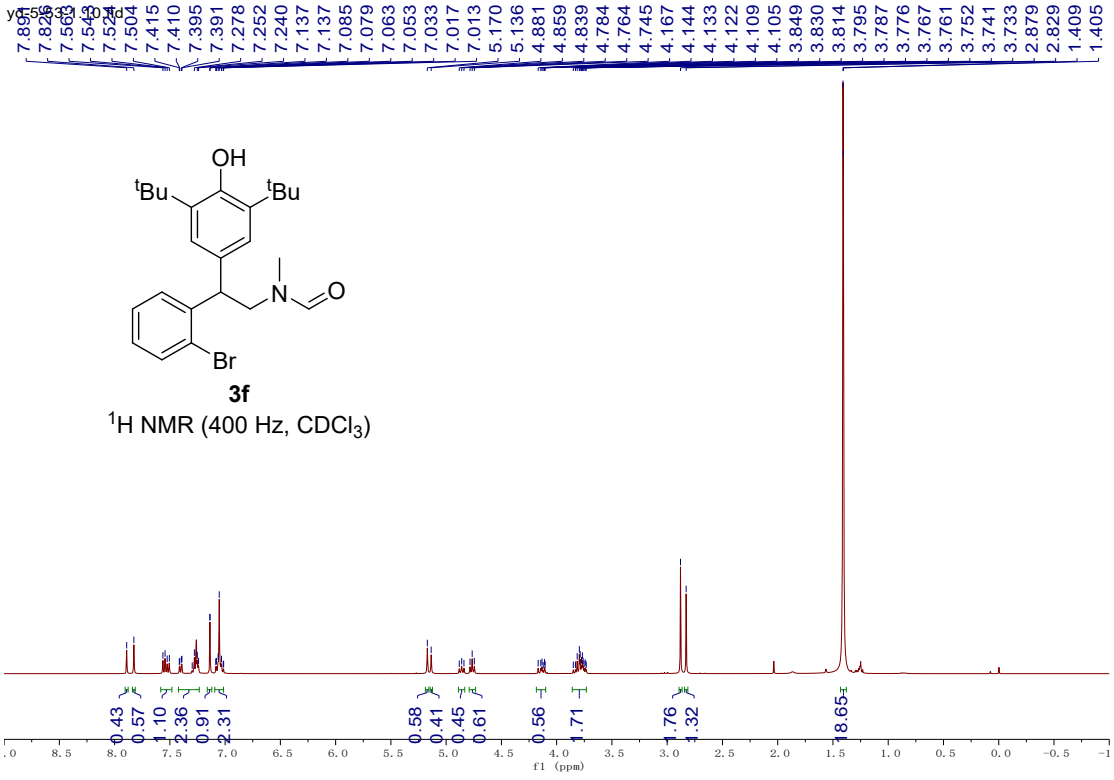




3e

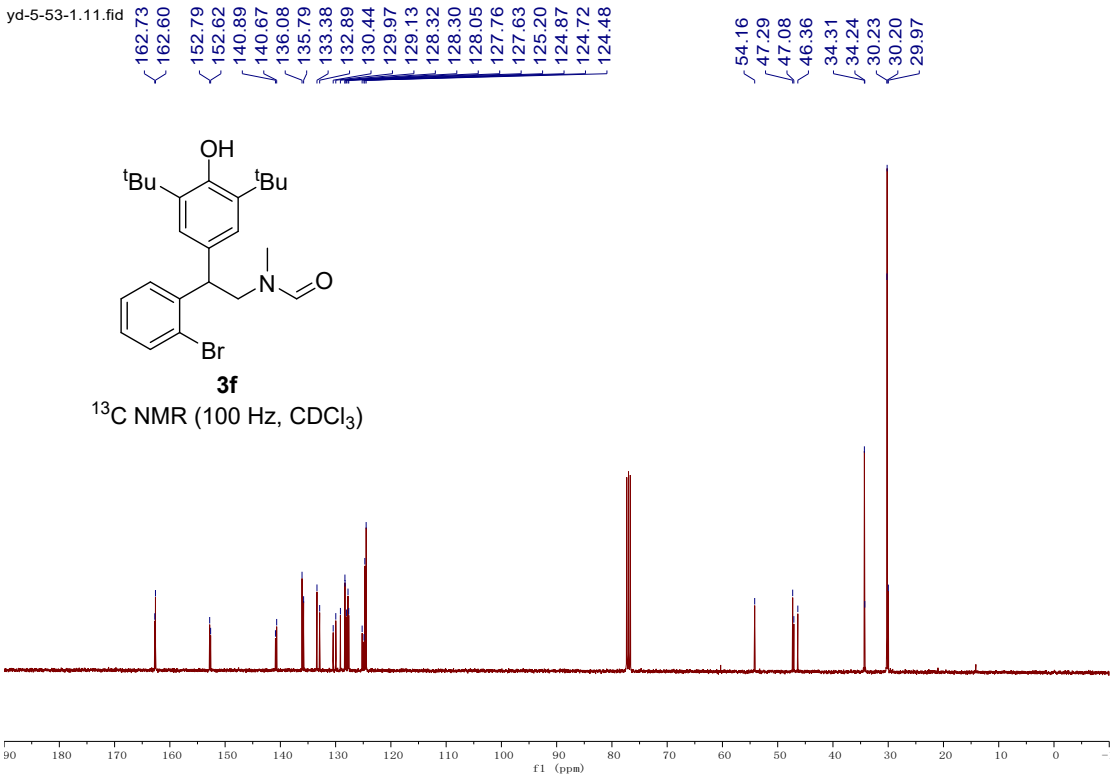
^{13}C NMR (100 Hz, $CDCl_3$)

_N_-(2-(2-bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl)-_N_-methylformamide (3f)



3f

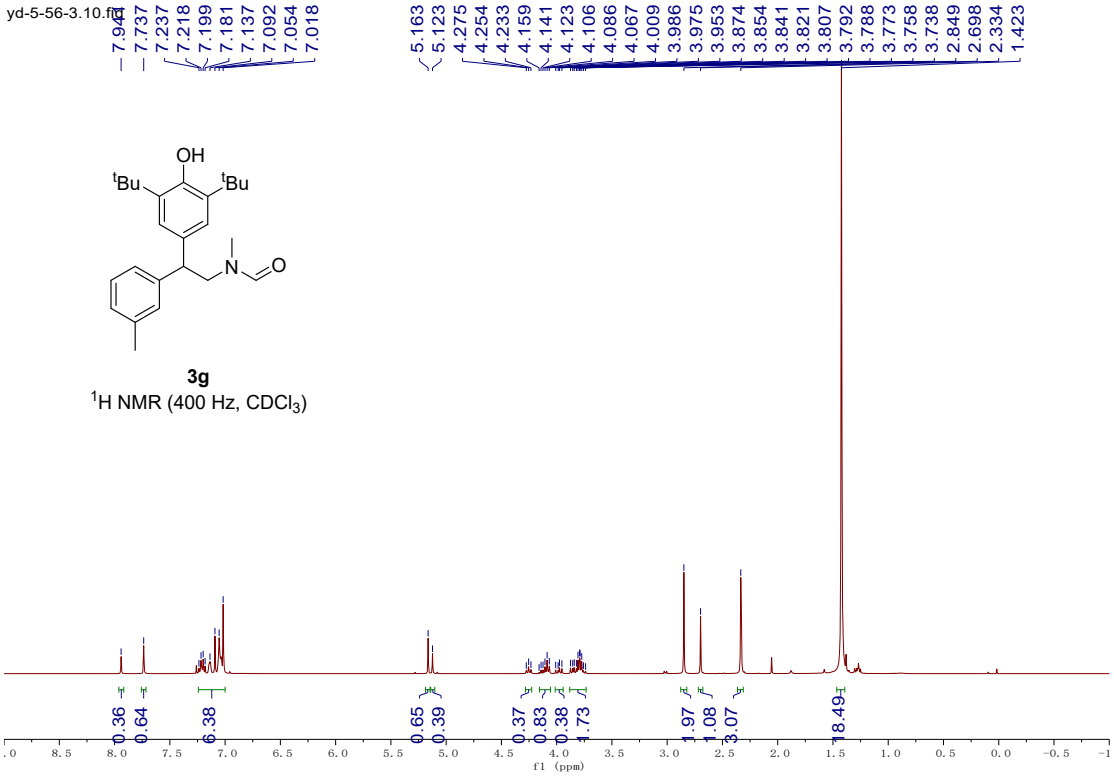
^{1}H NMR (400 Hz, $CDCl_3$)



3f

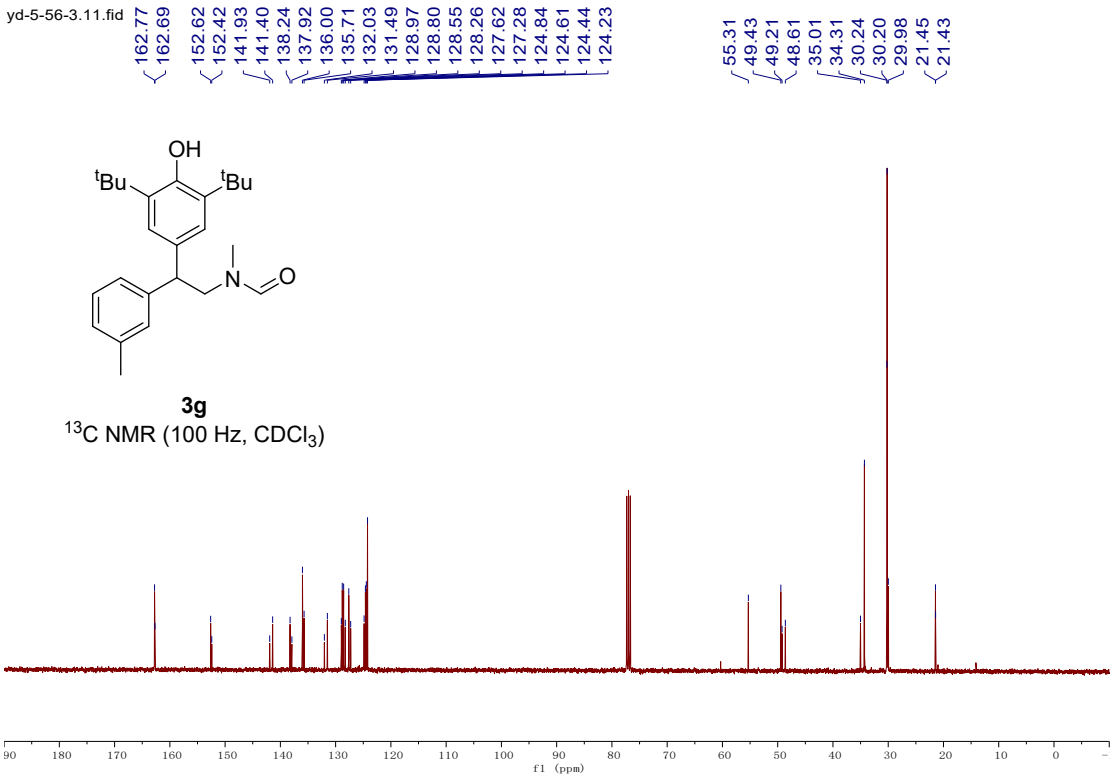
^{13}C NMR (100 Hz, $CDCl_3$)

N-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(m-tolyl)ethyl)-*N*-methylformamide (3g)



3g

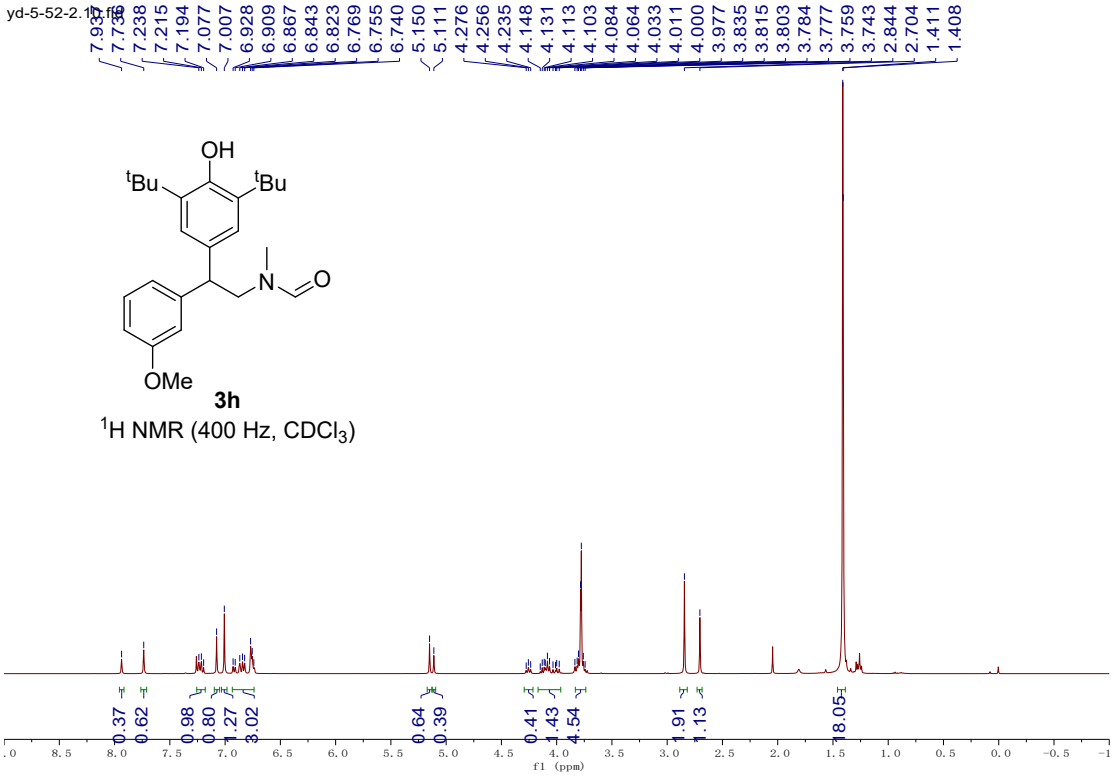
^{1}H NMR (400 Hz, $CDCl_3$)



3g

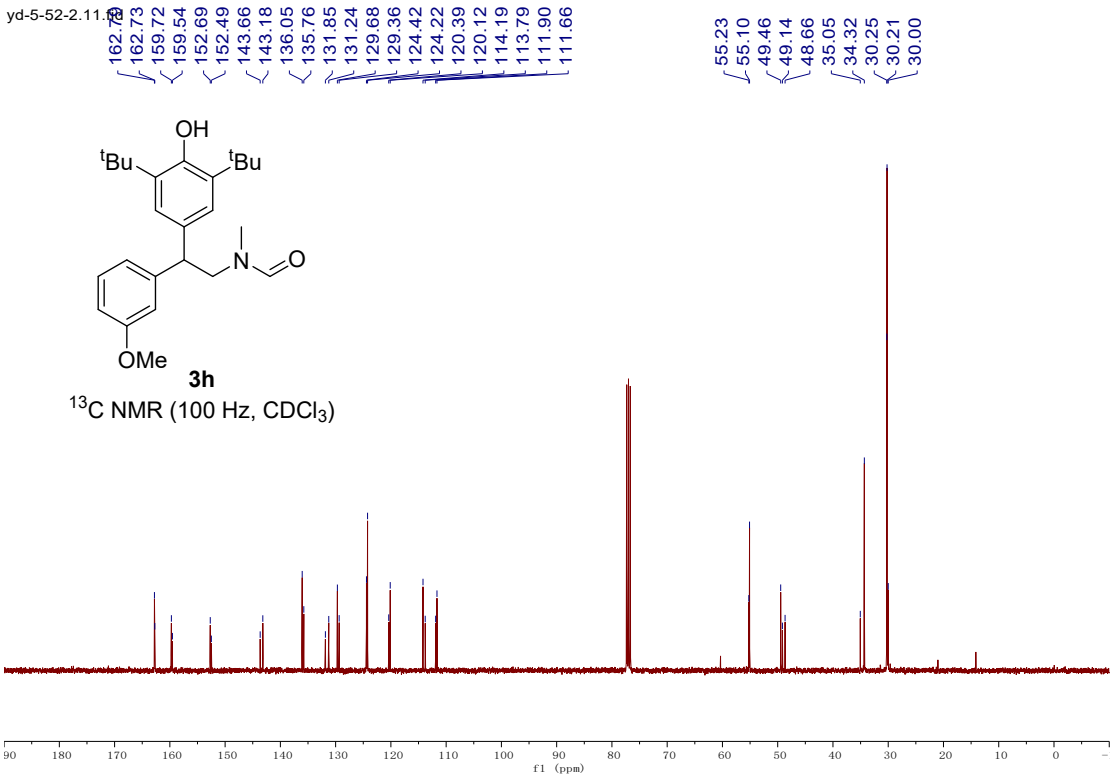
^{13}C NMR (100 Hz, $CDCl_3$)

_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-methoxyphenyl)ethyl)-_N_-methylformamide (3h)



3h

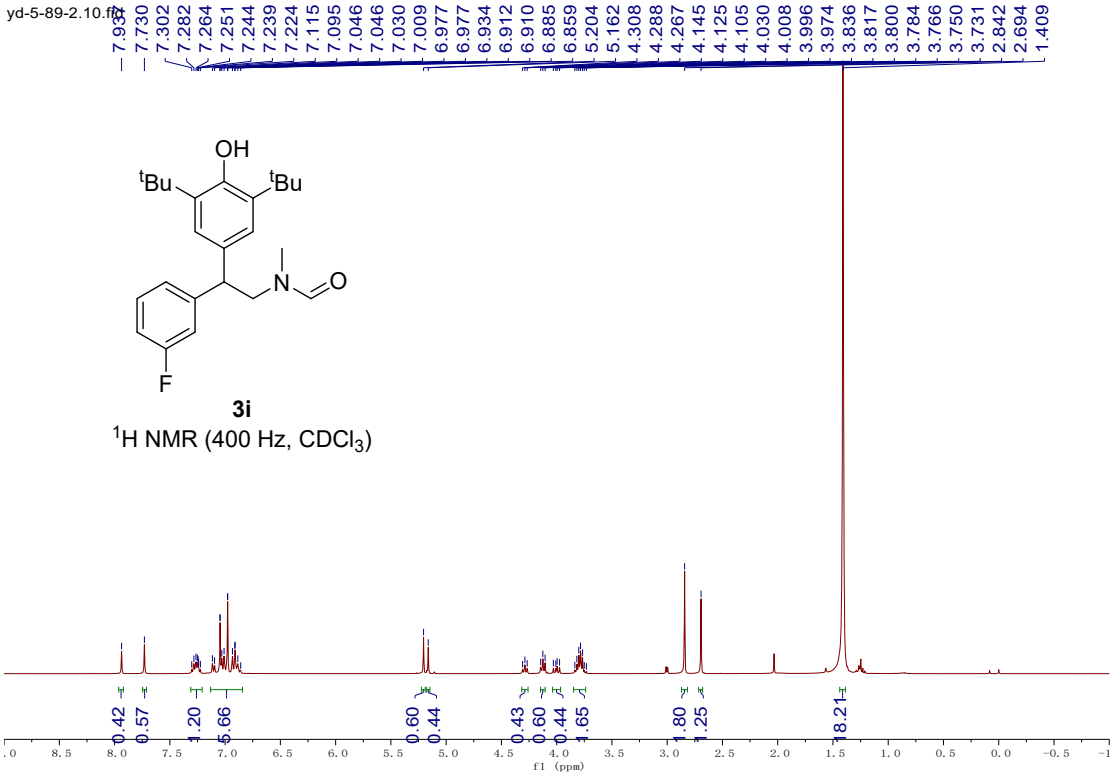
^{1}H NMR (400 Hz, $CDCl_3$)



3h

^{13}C NMR (100 Hz, $CDCl_3$)

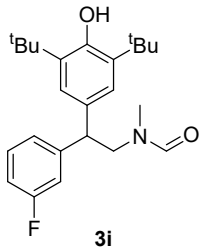
_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-fluorophenyl)ethyl)-_N_-methylformamide (3i)



3i

^{1}H NMR (400 Hz, $CDCl_3$)

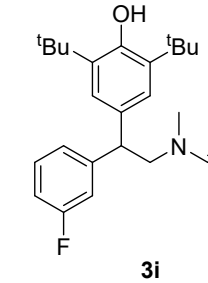
yd-5-89-2.13.fid



3i

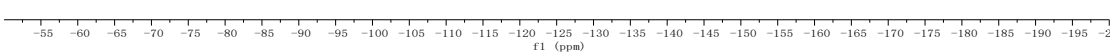
^{13}C NMR (100 Hz, $CDCl_3$)

yd-5-89-2.12.fid

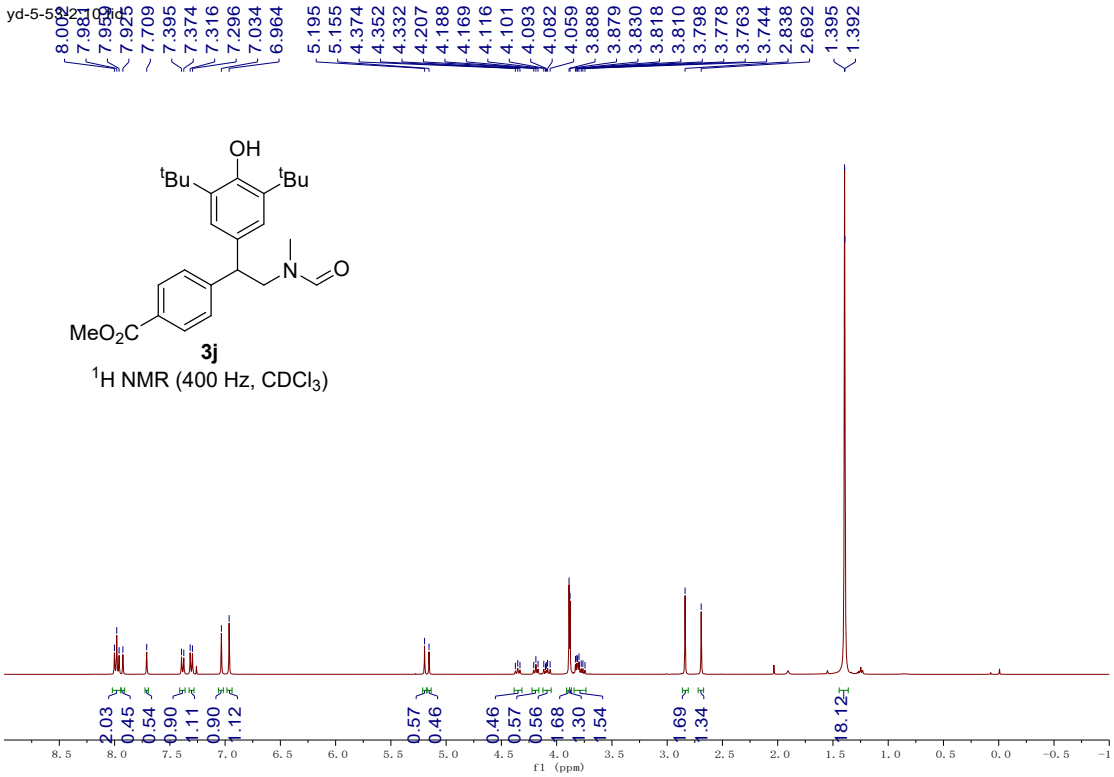


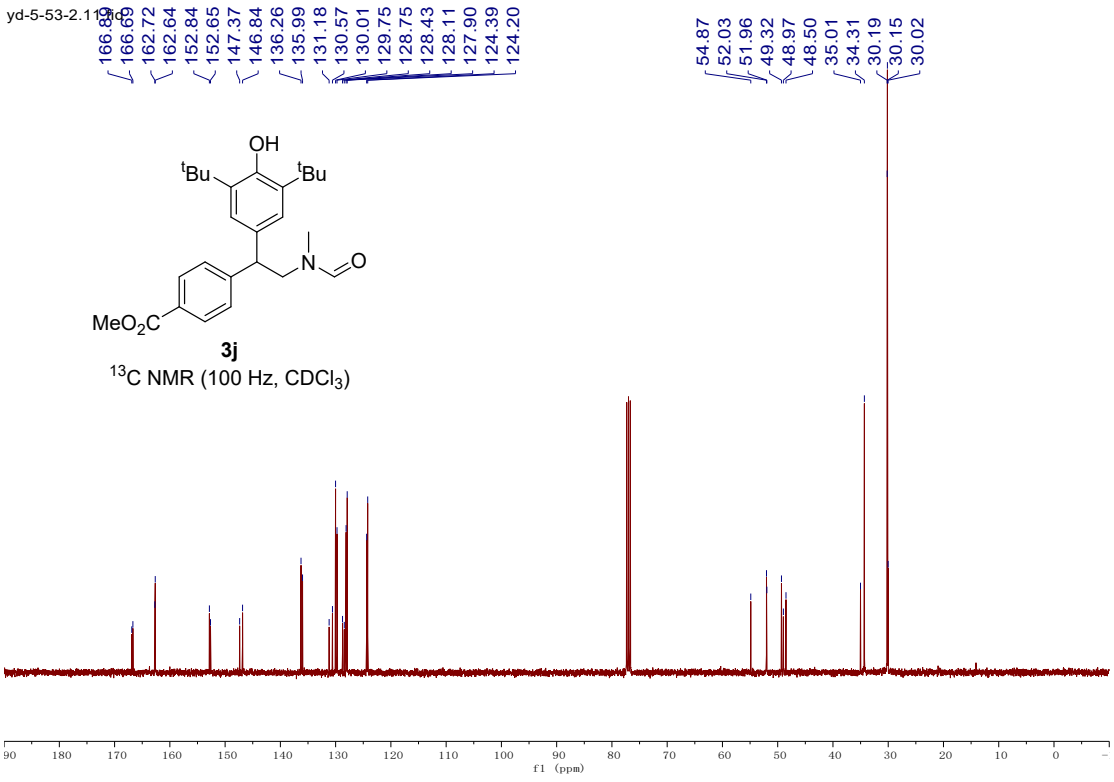
3i

^{19}F NMR (377 Hz, $CDCl_3$)

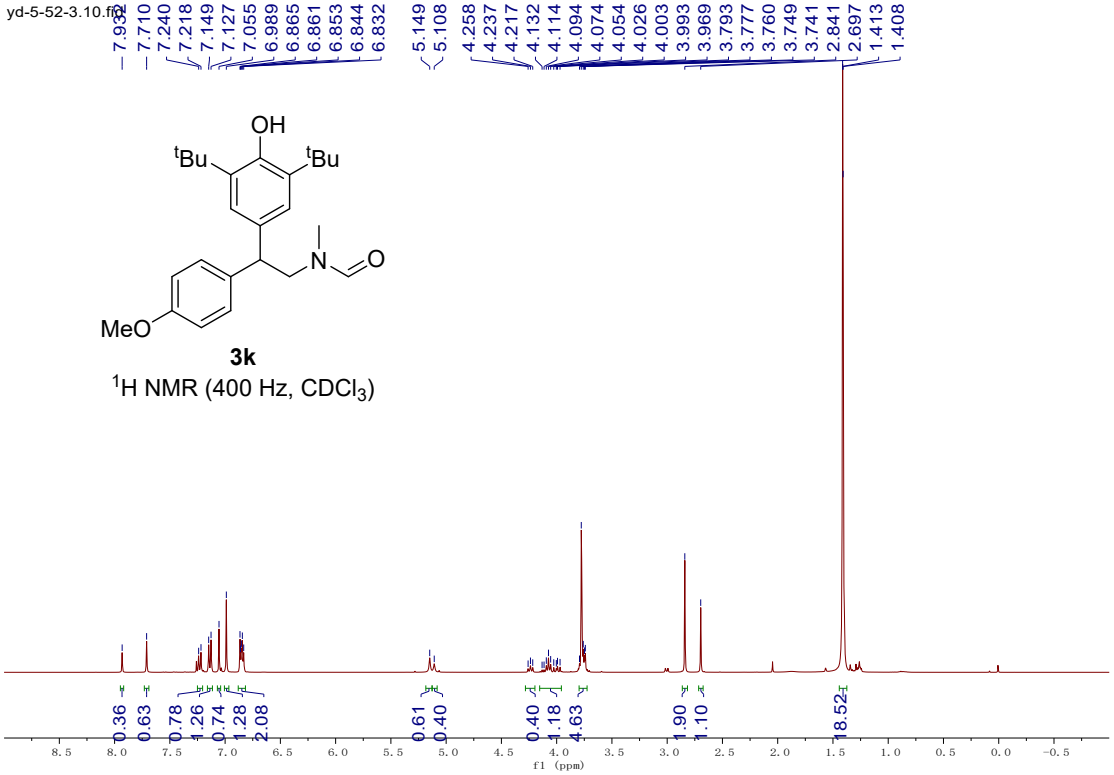


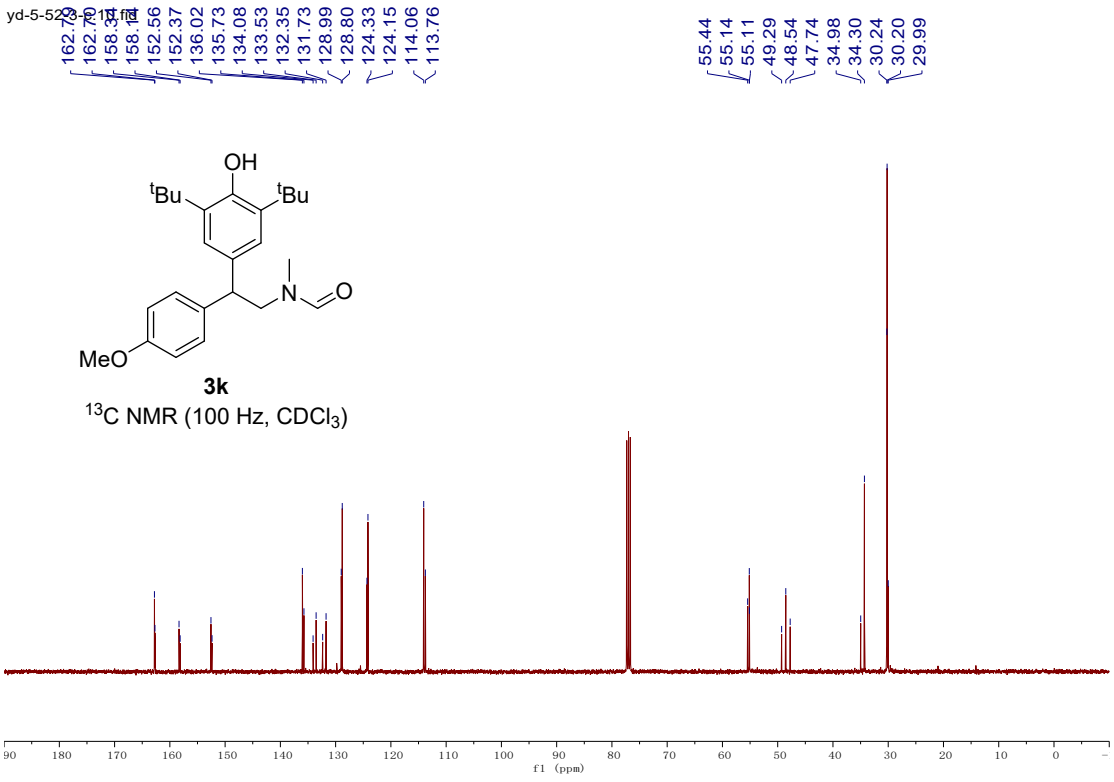
Methyl 4-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(*N*-methylformamido)ethyl)benzoate (3j)



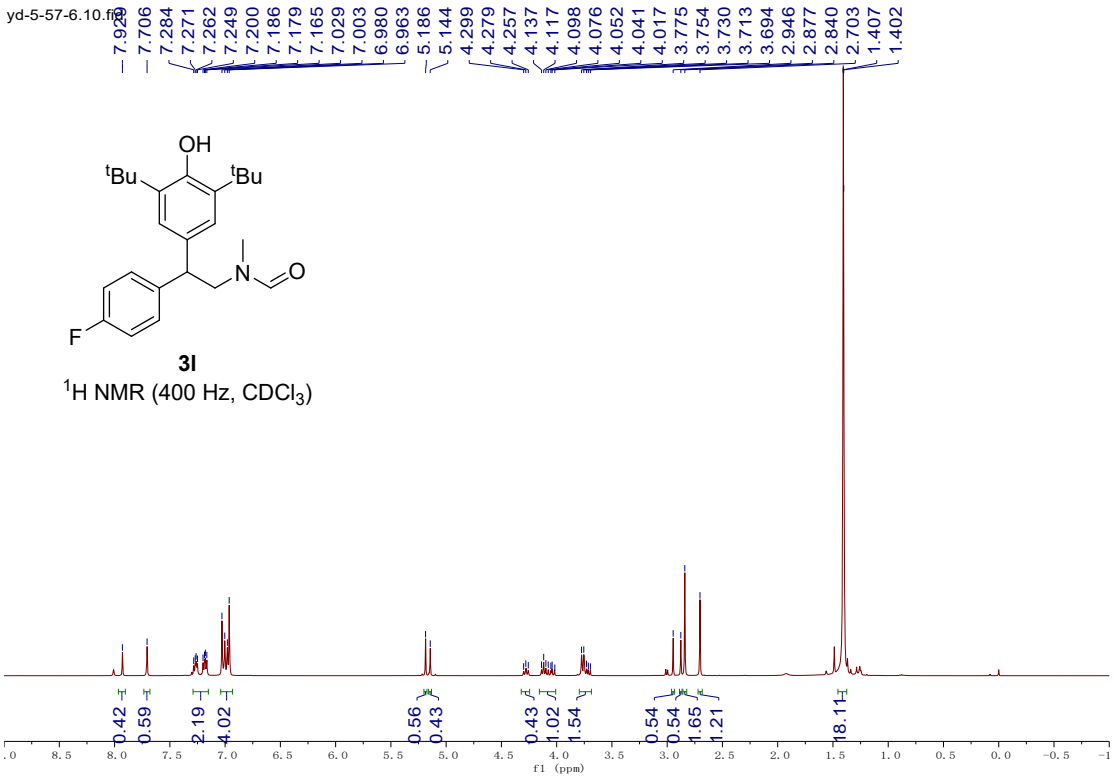


***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)ethyl)-*N*-methylformamide (3k)**



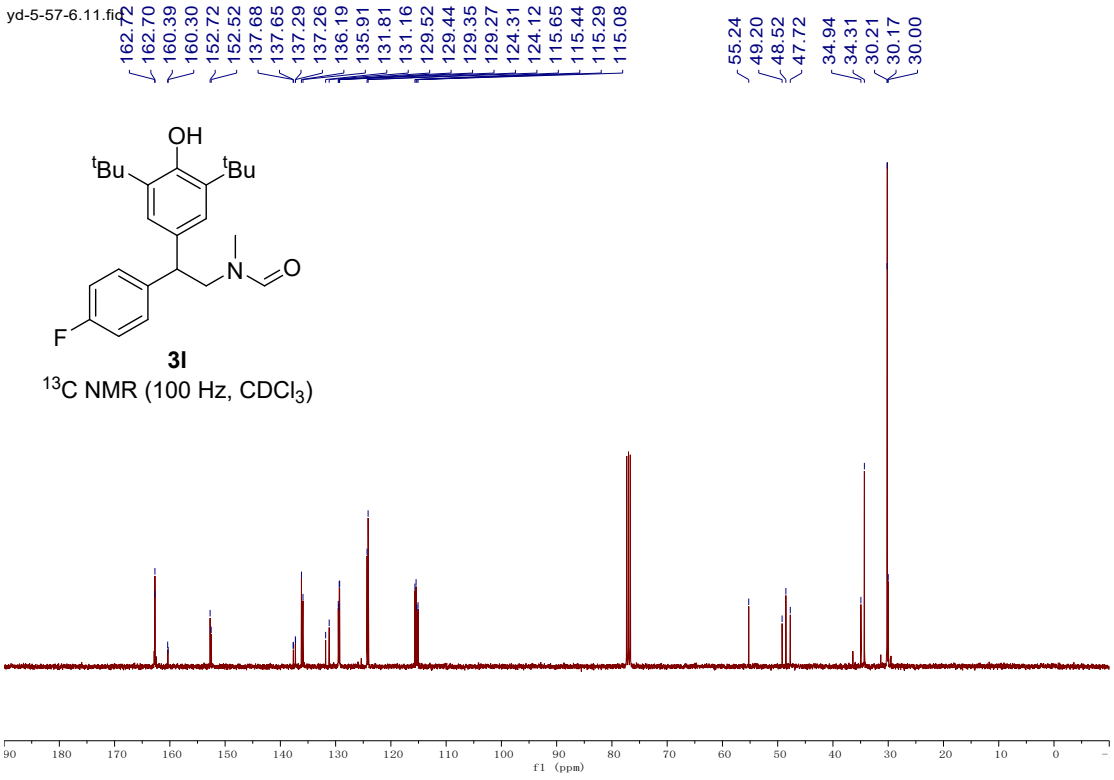


***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)ethyl)-*N*-methylformamide (3l)**



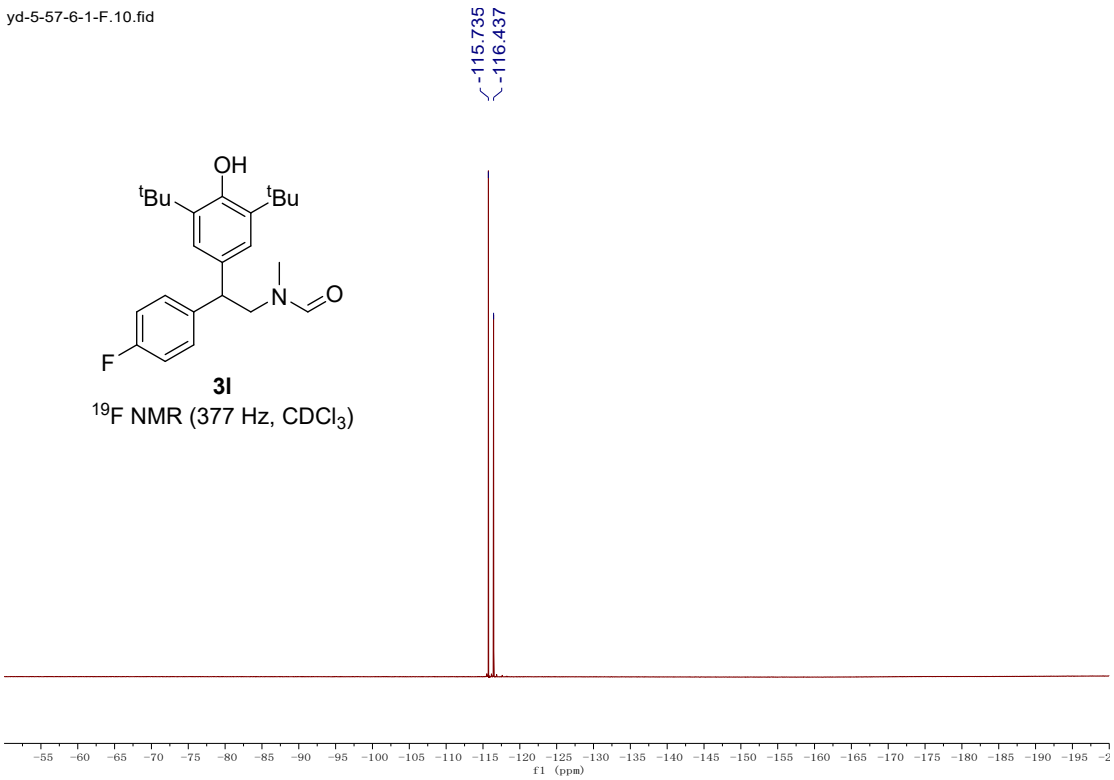
3l

^{1}H NMR (400 Hz, $CDCl_3$)



3l

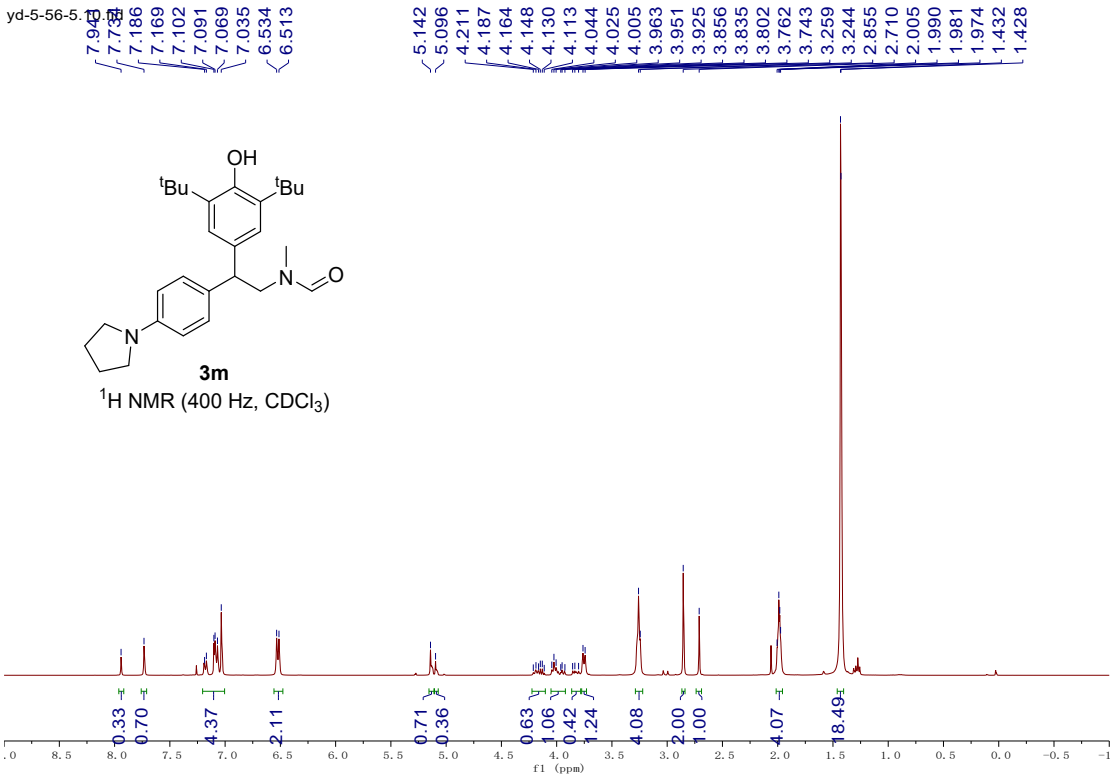
^{13}C NMR (100 Hz, $CDCl_3$)



3l

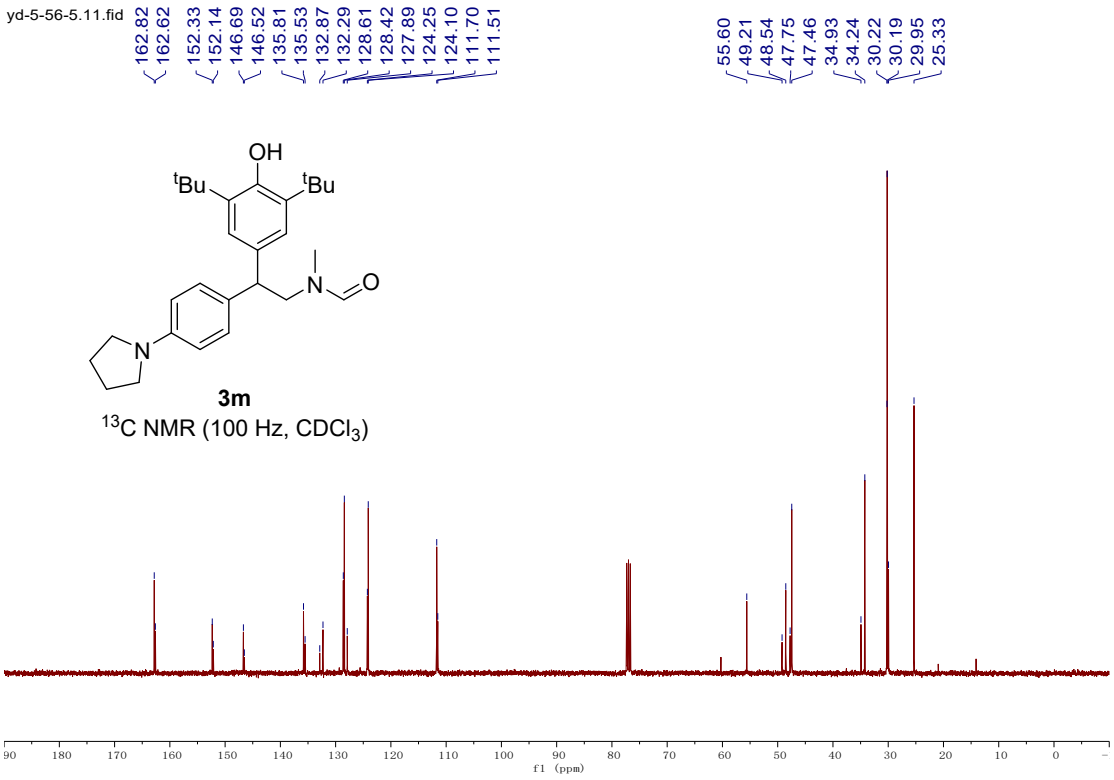
^{19}F NMR (377 Hz, $CDCl_3$)

***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(pyrrolidin-1-yl)phenyl)ethyl)-*N*-methylformamide (3m)**



3m

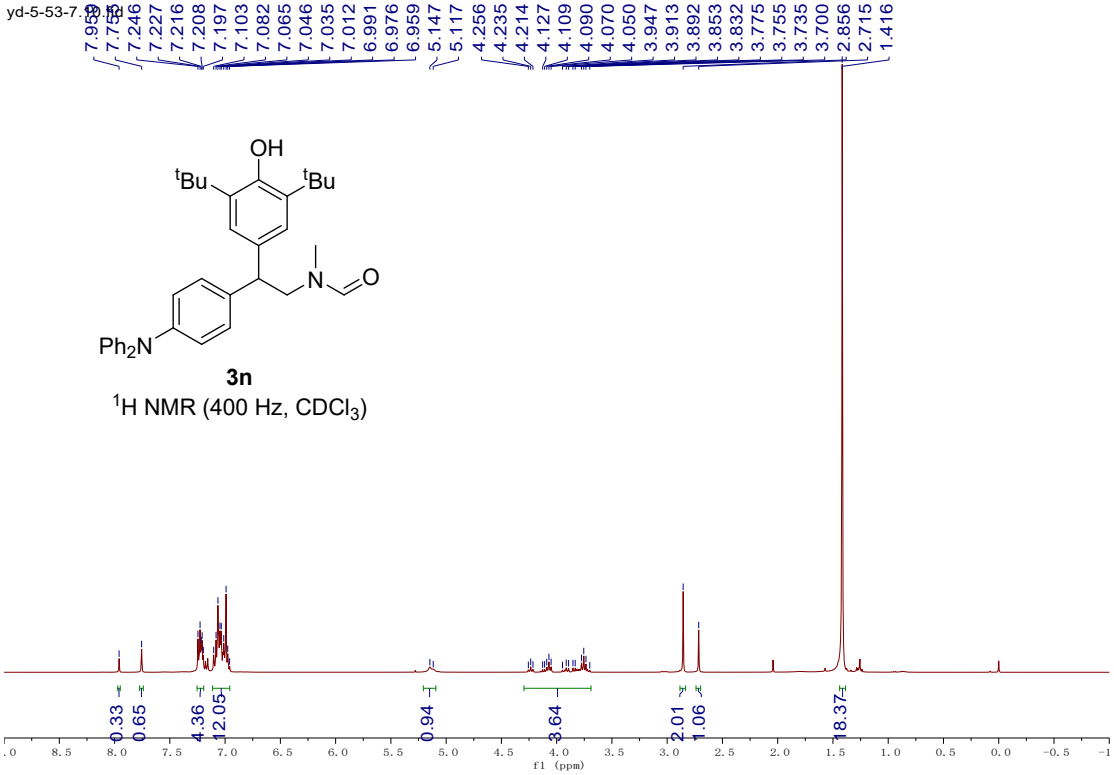
^{1}H NMR (400 Hz, $CDCl_3$)



3m

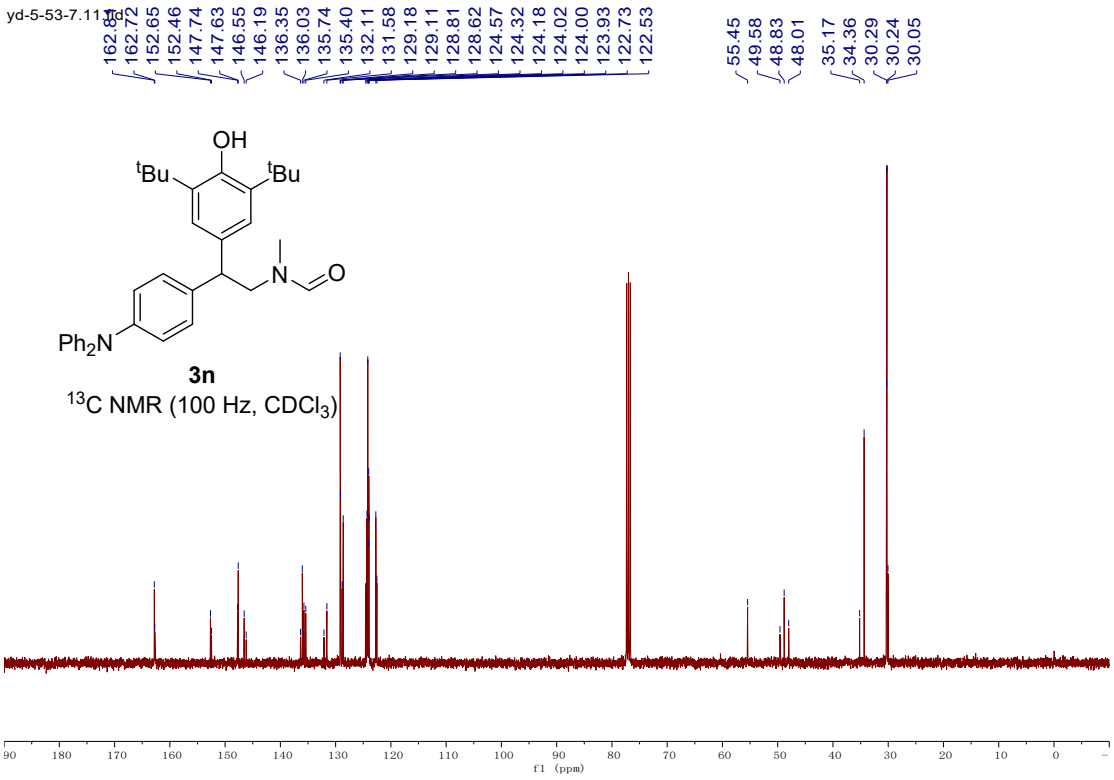
^{13}C NMR (100 Hz, $CDCl_3$)

_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(diphenylamino)phenyl)ethyl)-_N_-methylformamide (3n)

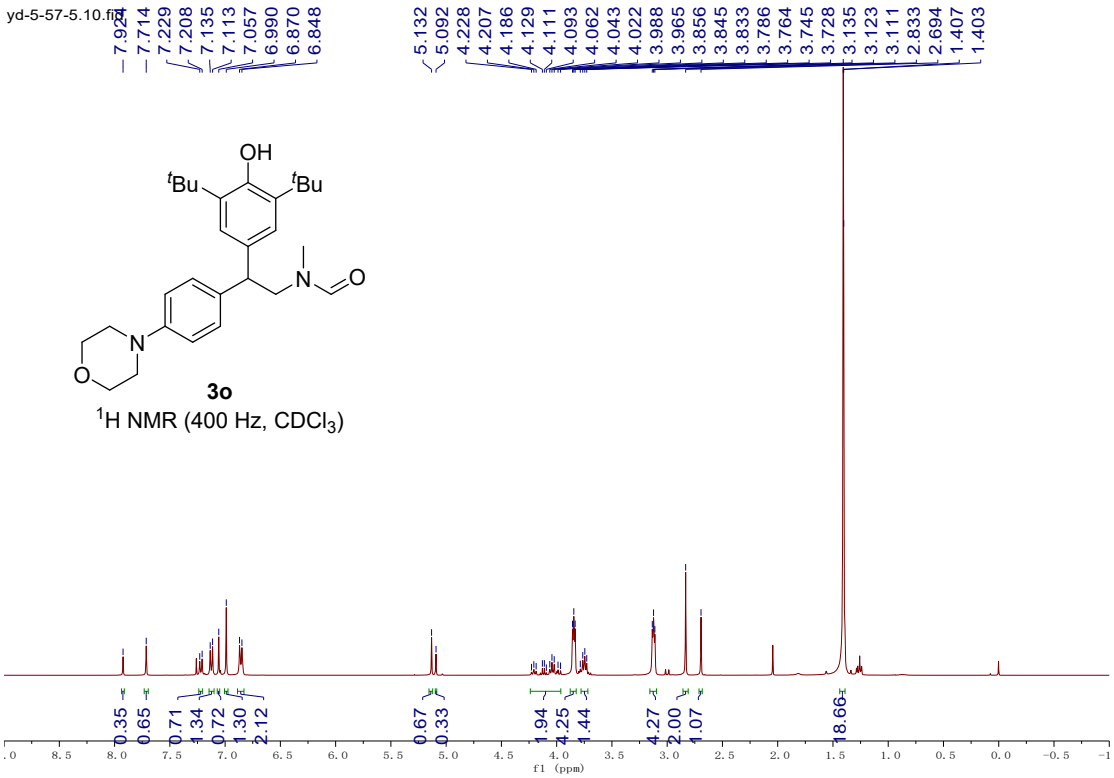


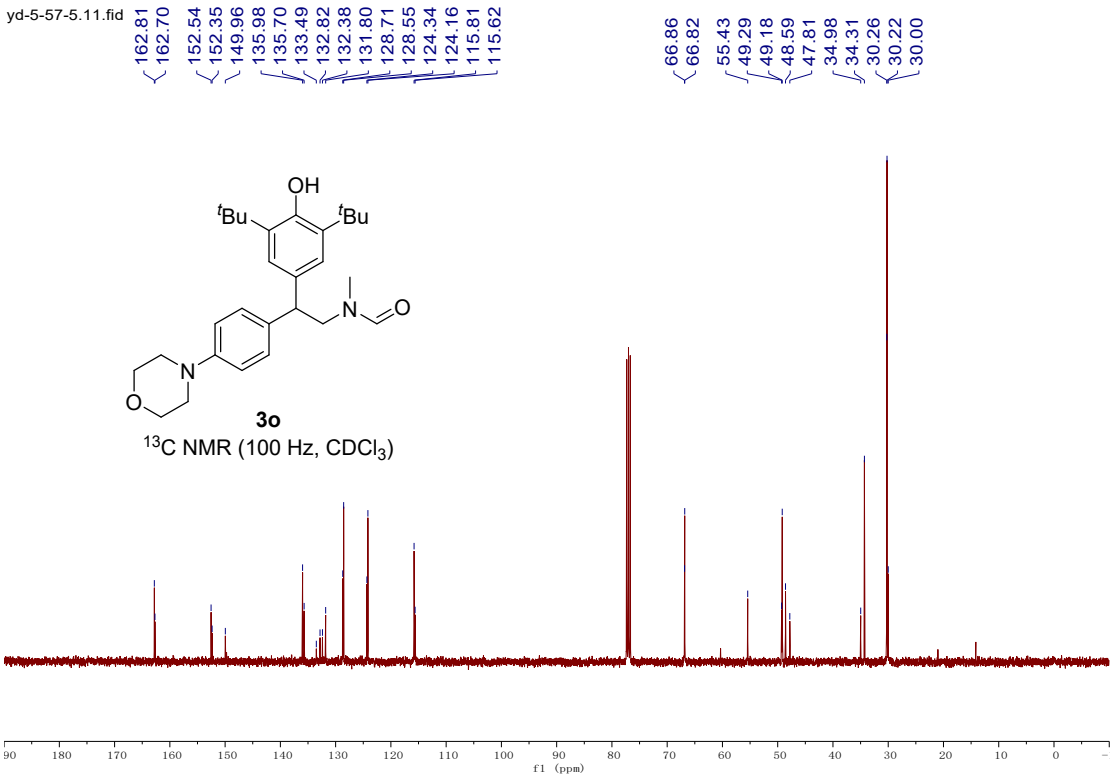
3n

^{1}H NMR (400 Hz, $CDCl_3$)

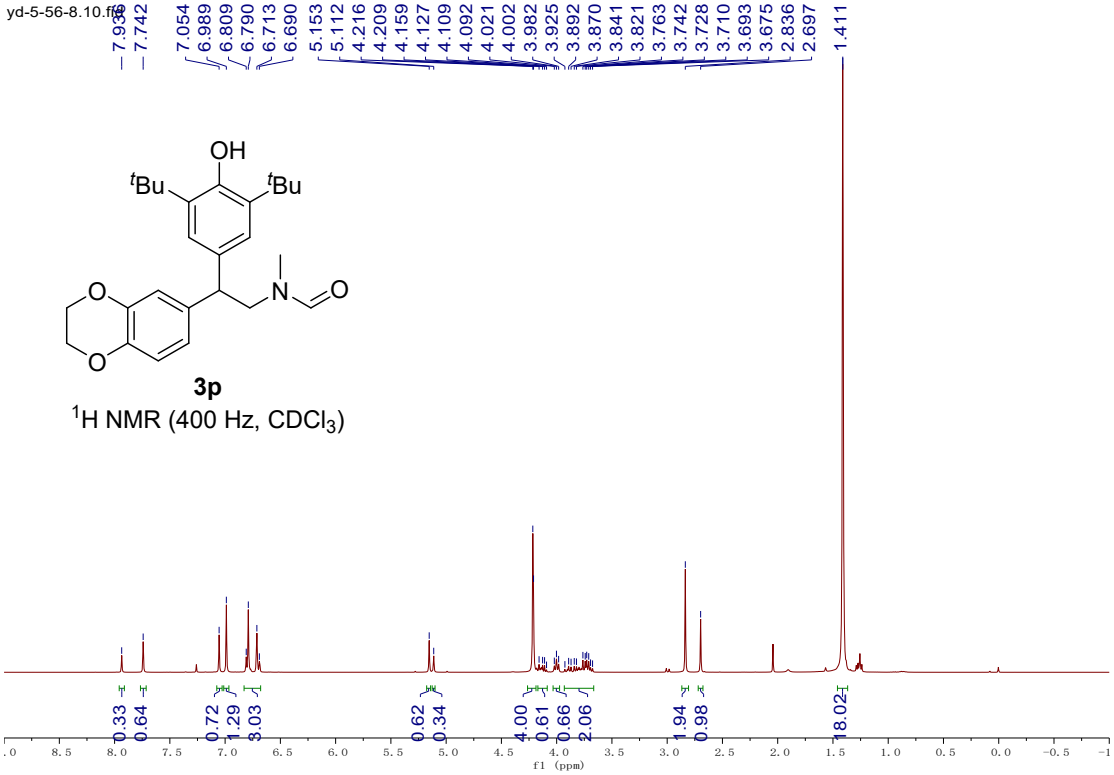


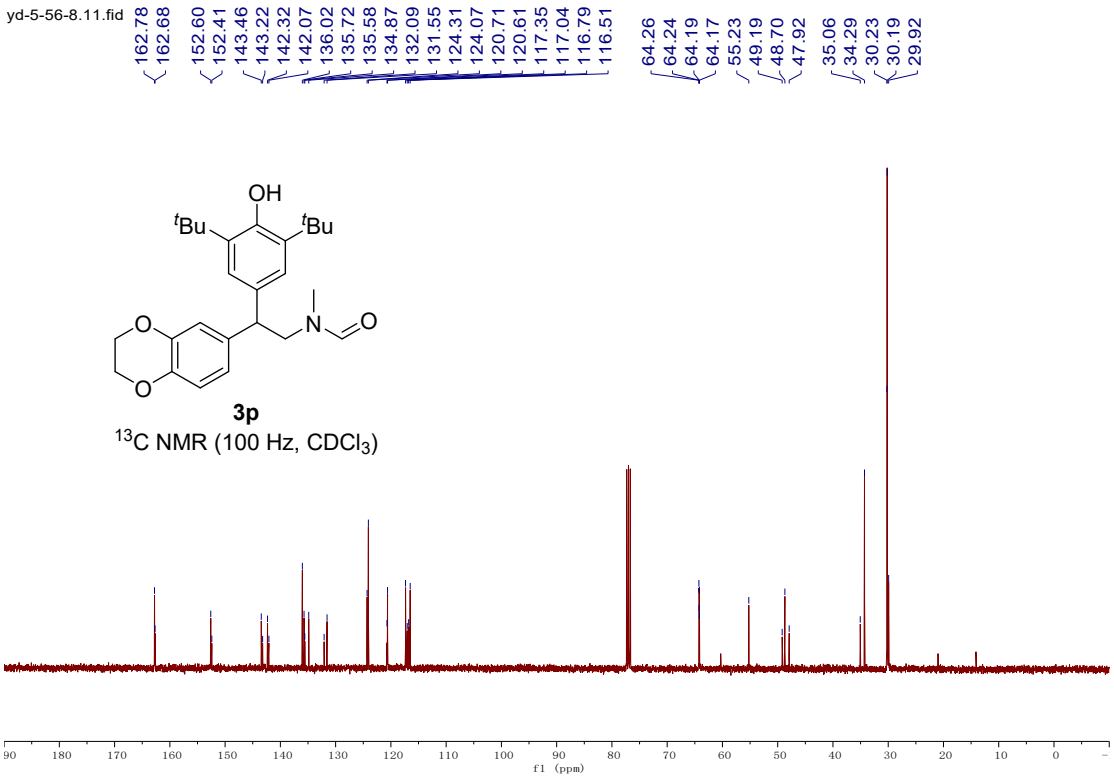
_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-morpholinophenyl)ethyl)-_N_-methylformamide (3o)



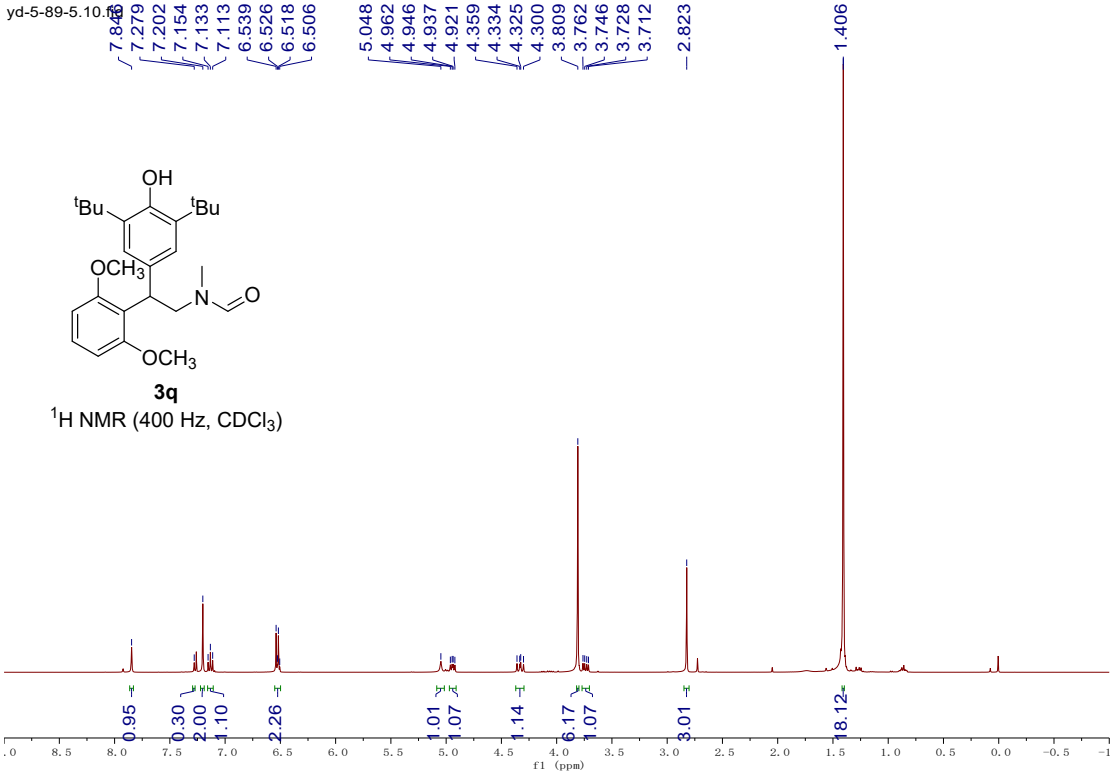


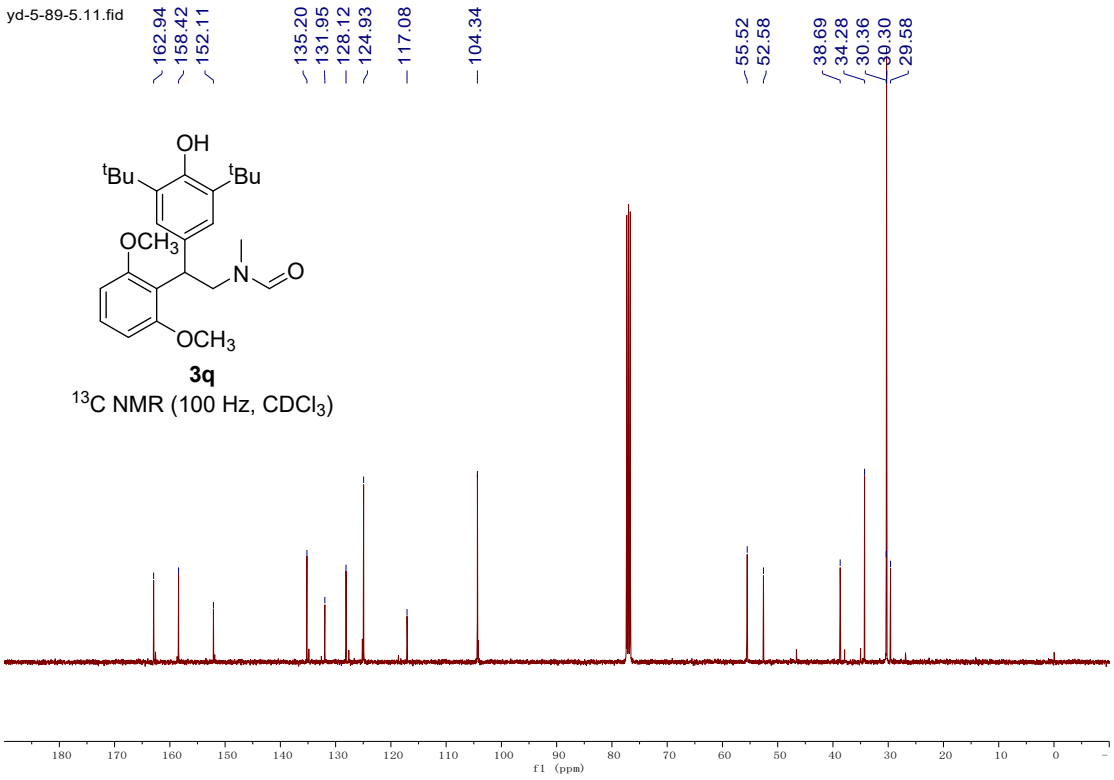
***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethyl)-*N*-methylformamide (3p)**





_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2,6-dimethoxyphenyl)ethyl)-_N_-methylformamide (3q)

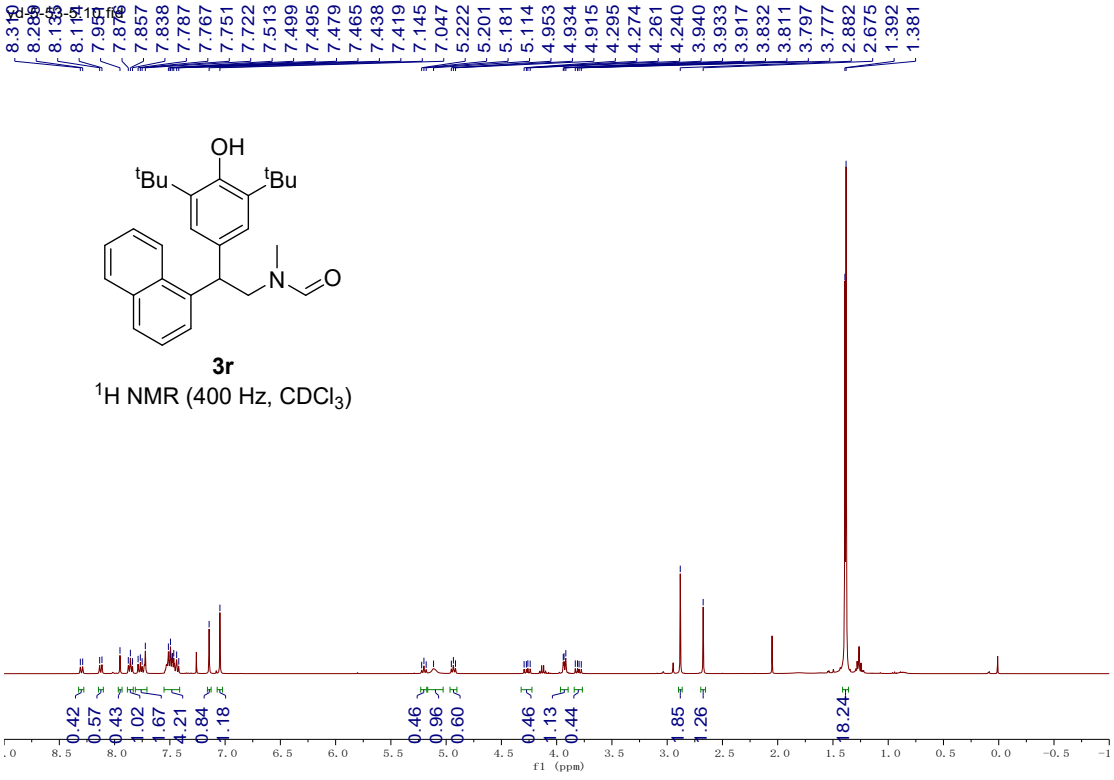




3q

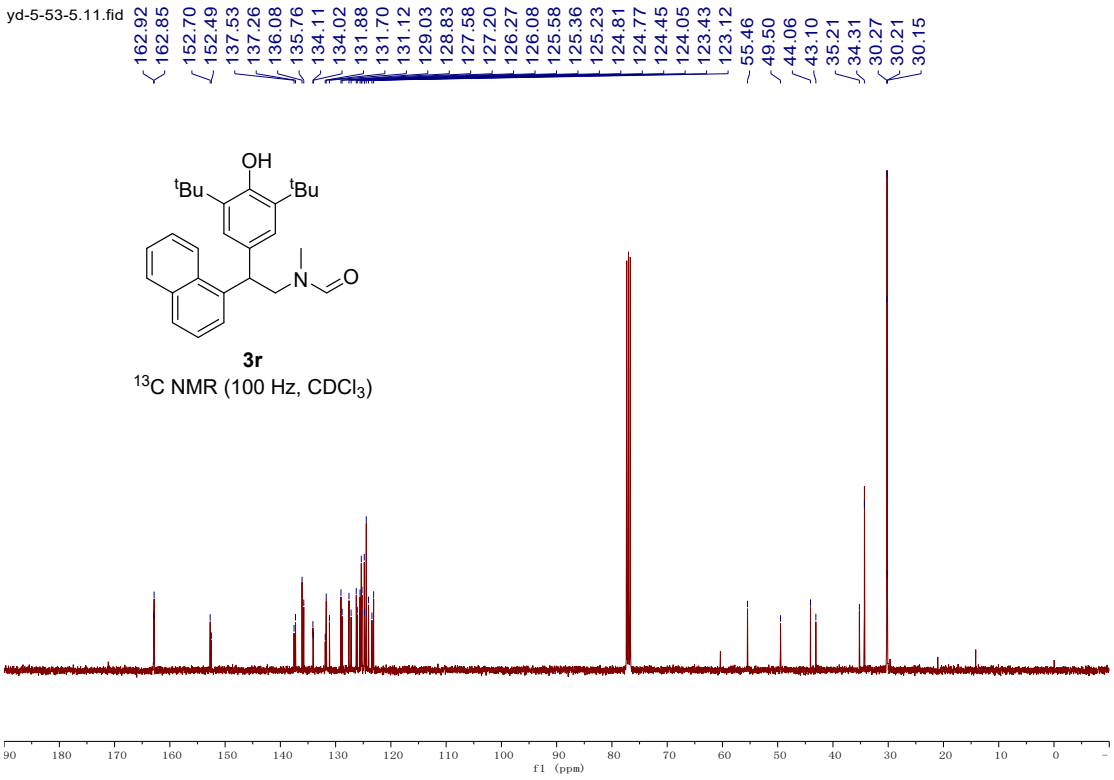
^{13}C NMR (100 Hz, $CDCl_3$)

_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(naphthalen-1-yl)ethyl)-_N_-methylformamide (3r)

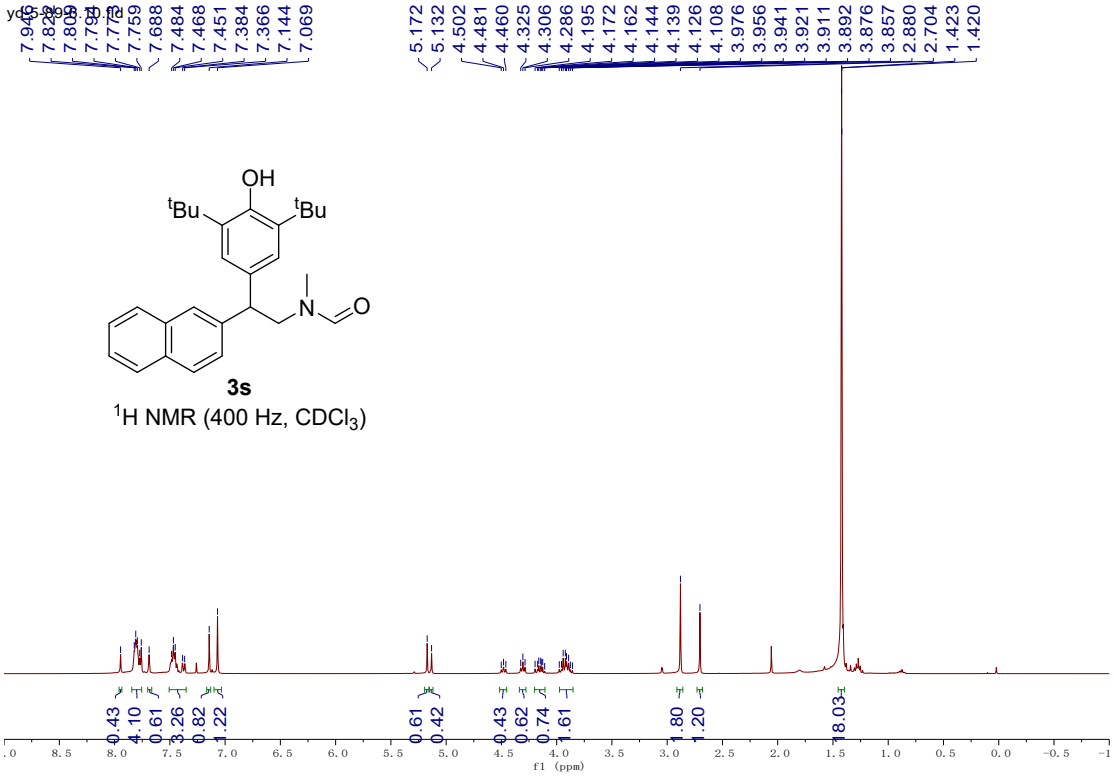


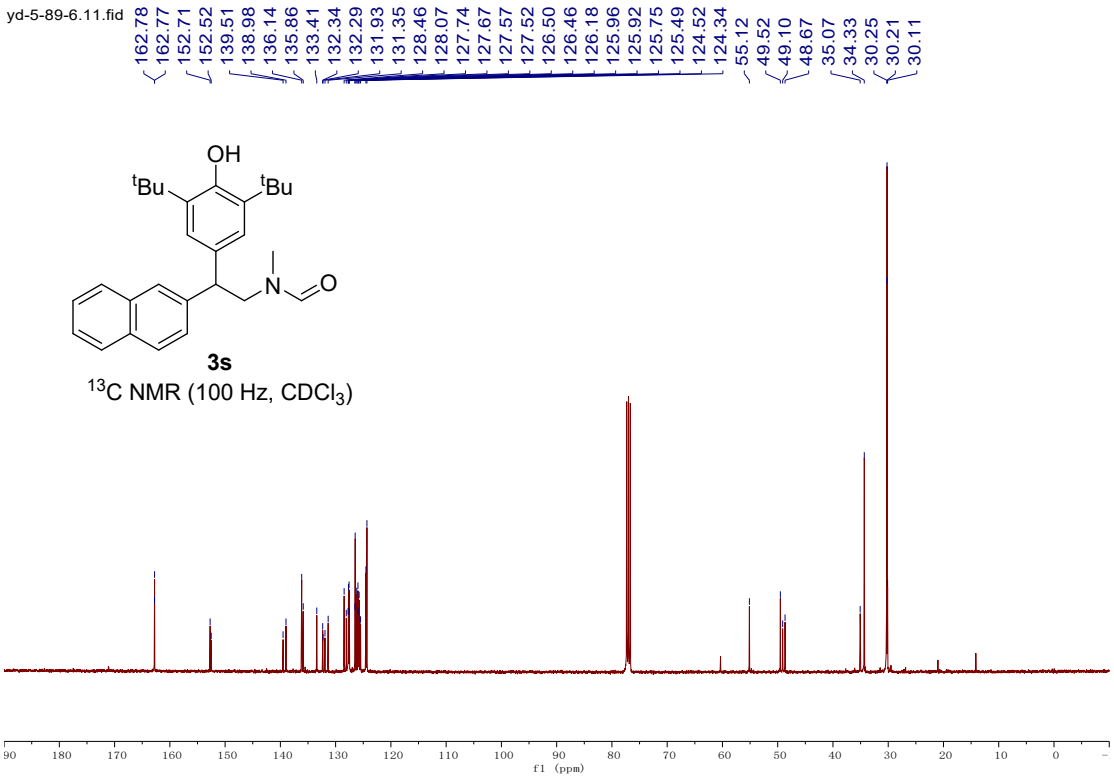
3r

^{1}H NMR (400 Hz, $CDCl_3$)

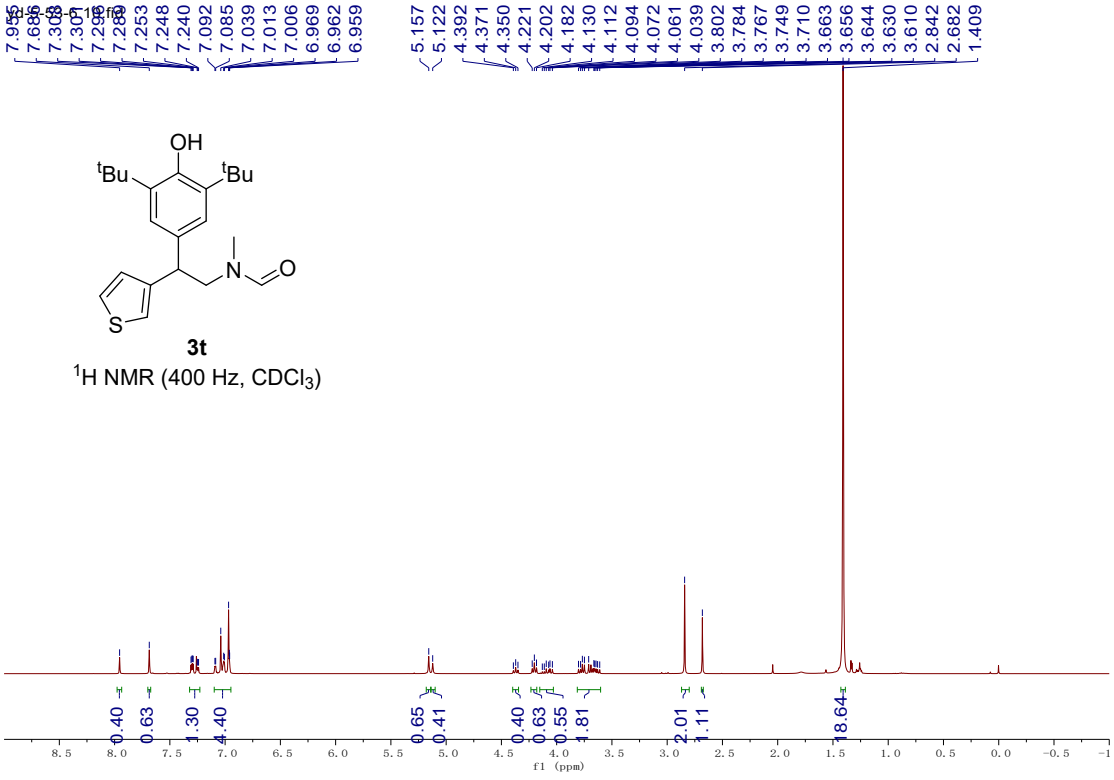


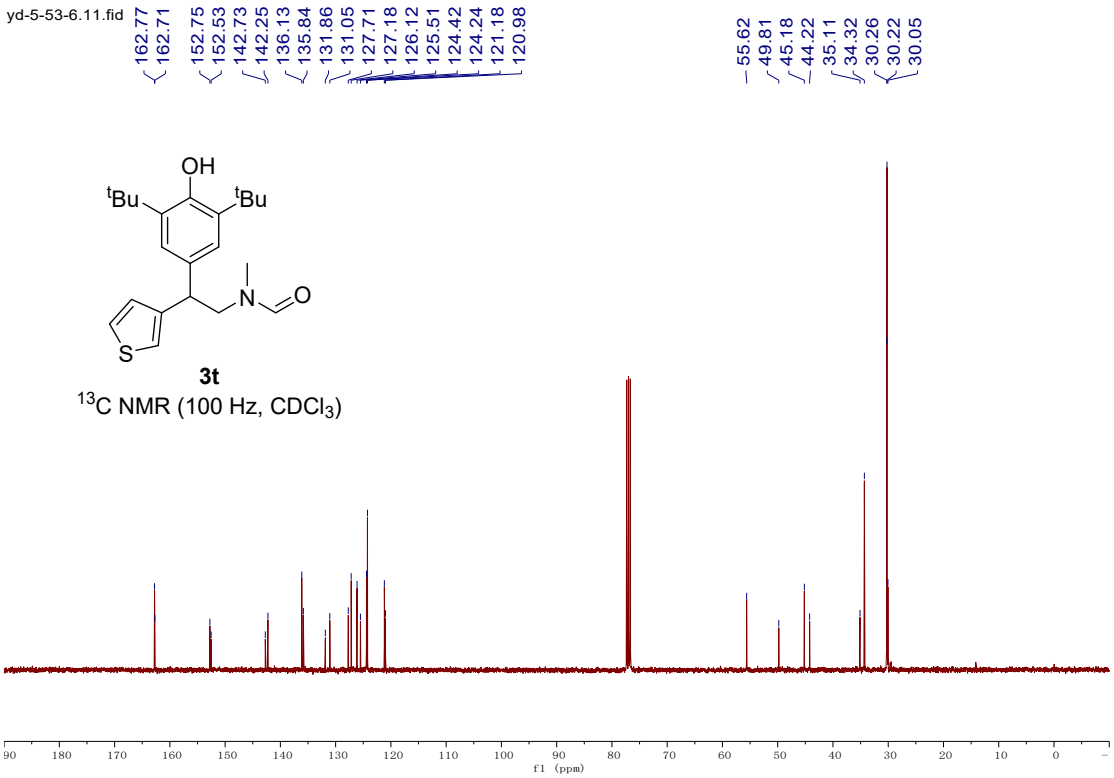
_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(naphthalen-2-yl)ethyl)-_N_-methylformamide (3s)





***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(thiophen-3-yl)ethyl)-*N*-methylformamide (3t)**

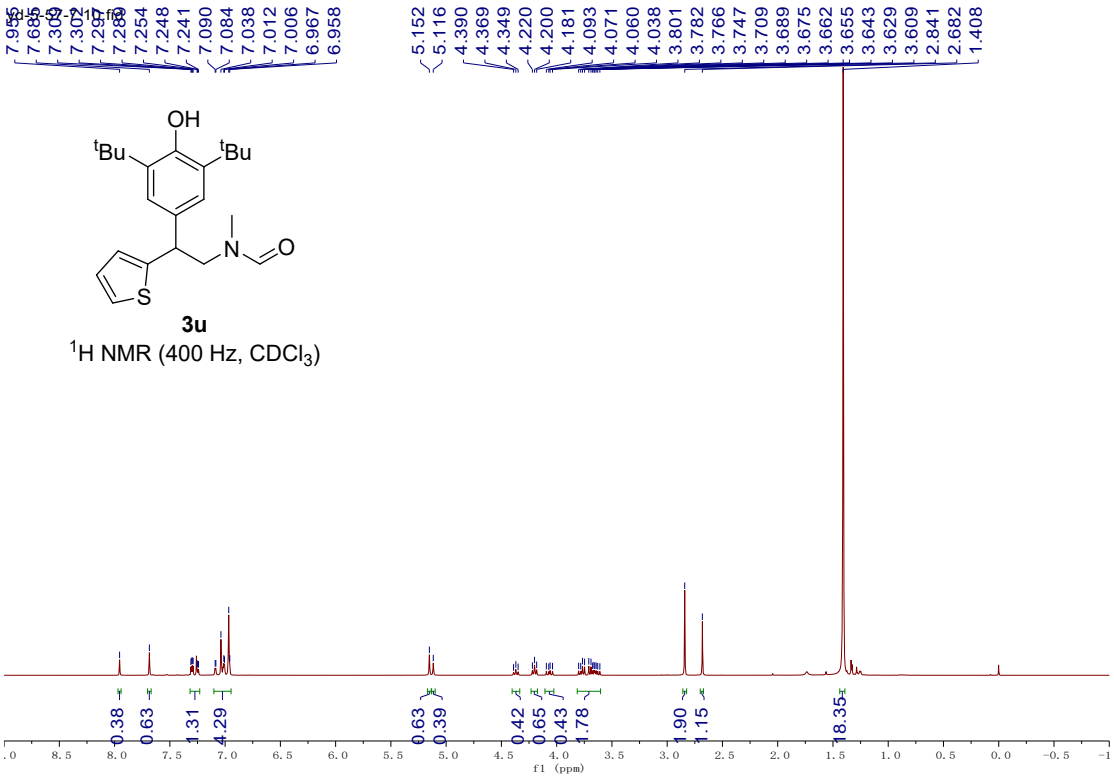




3t

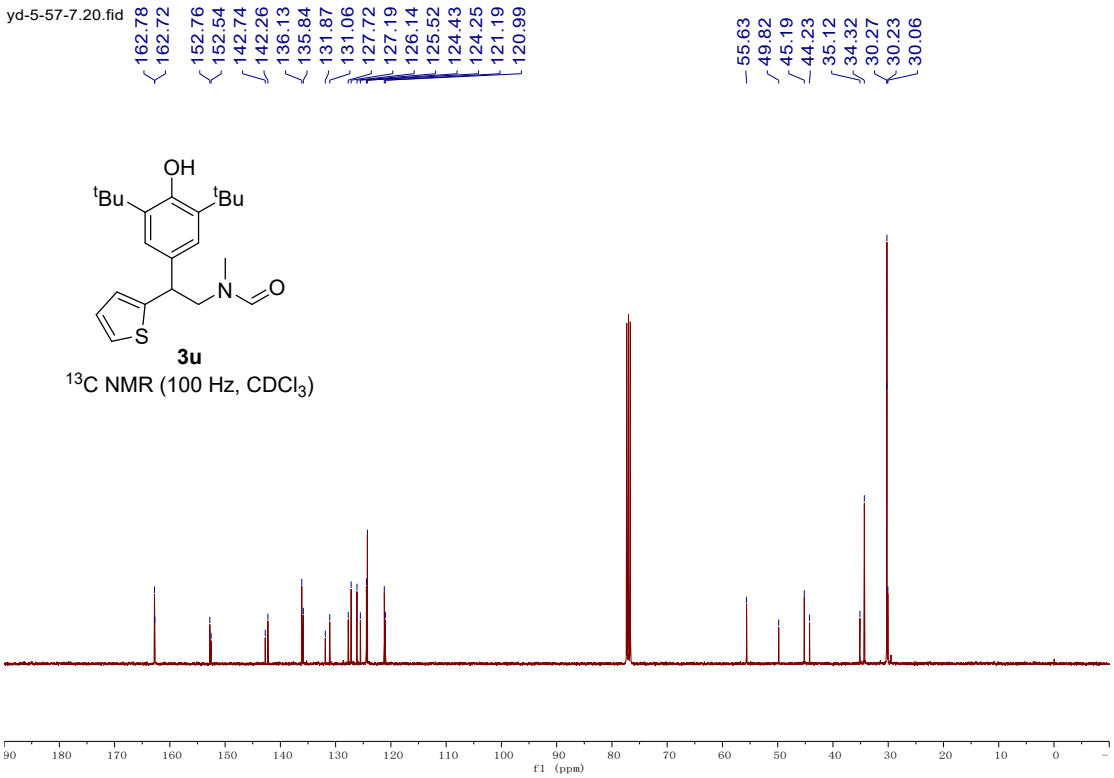
^{13}C NMR (100 Hz, $CDCl_3$)

_N_-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(thiophen-2-yl)ethyl)-_N_-methylformamide (3u)



3u

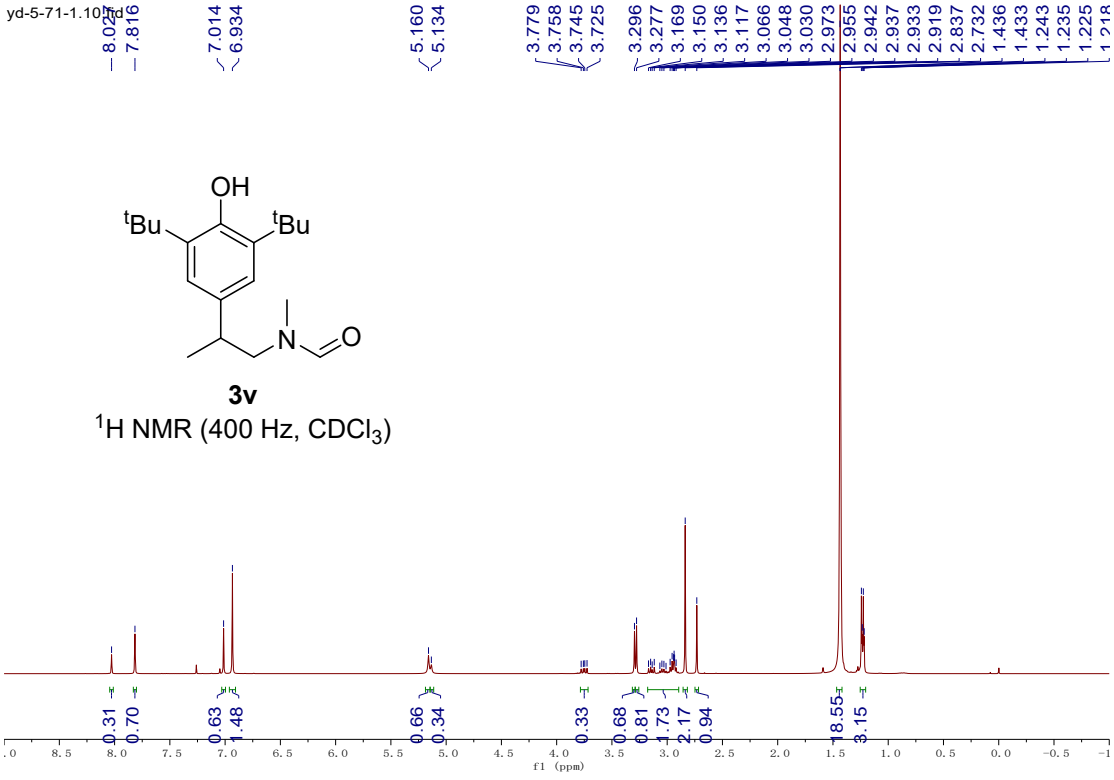
^{1}H NMR (400 Hz, $CDCl_3$)



3u

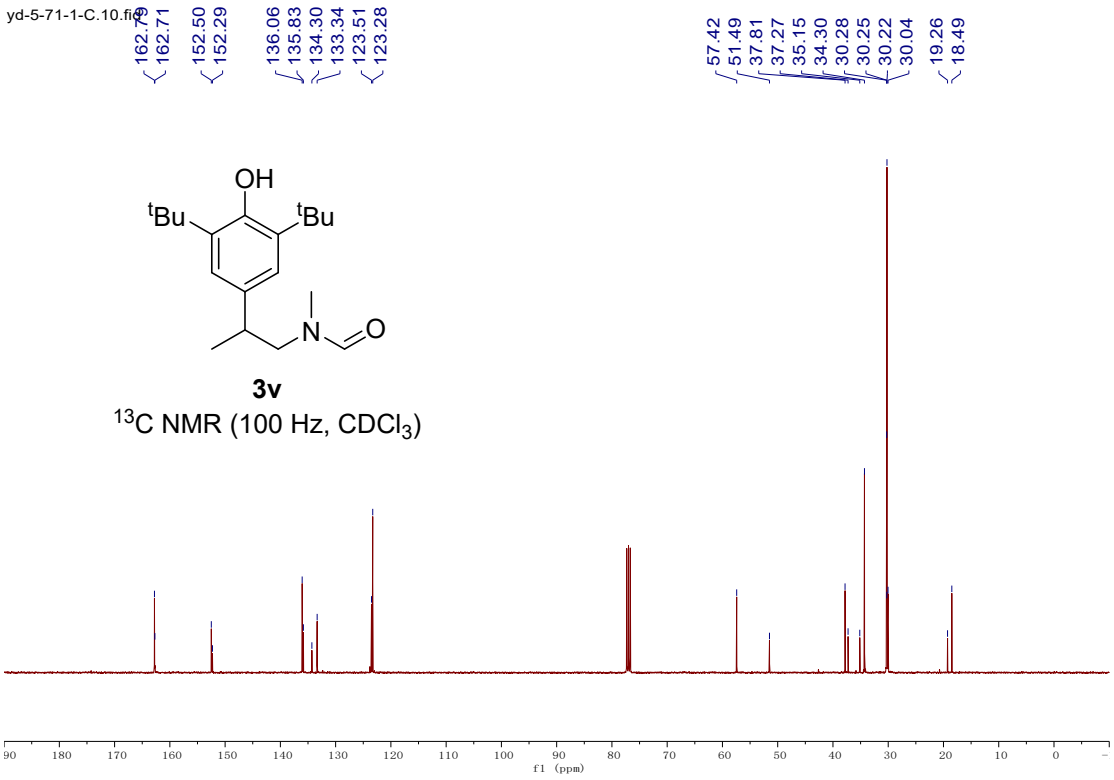
^{13}C NMR (100 Hz, $CDCl_3$)

N-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl)-*N*-methylformamide (3v)

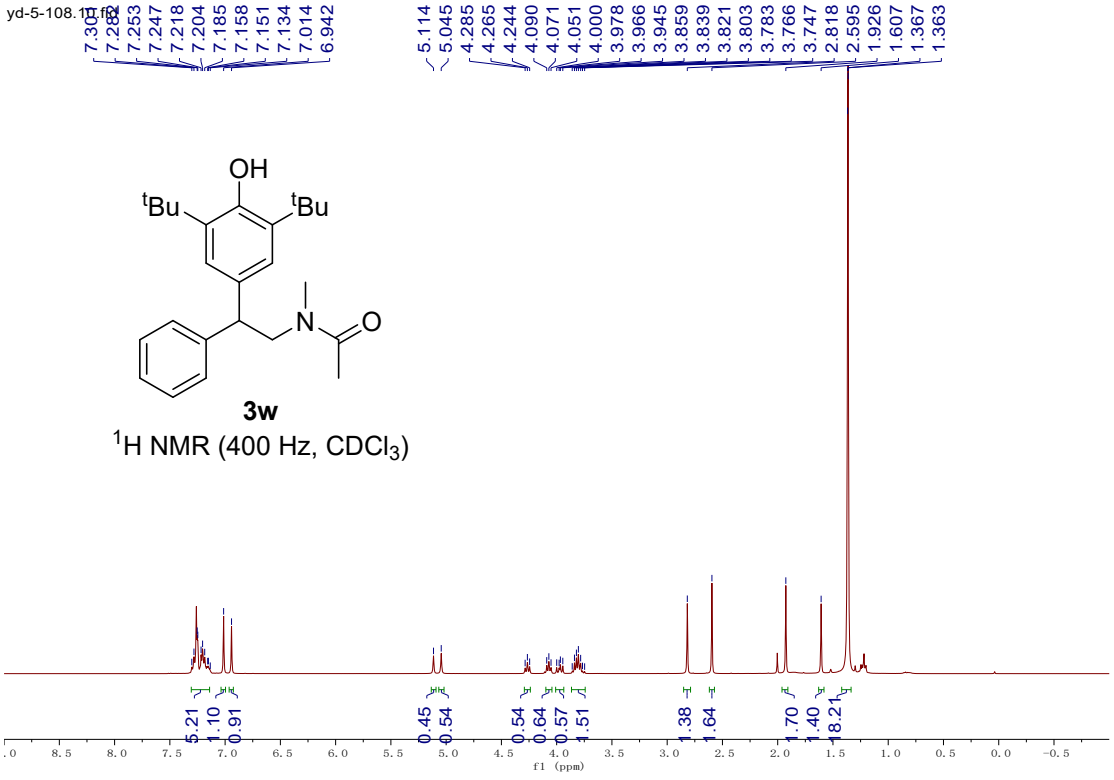


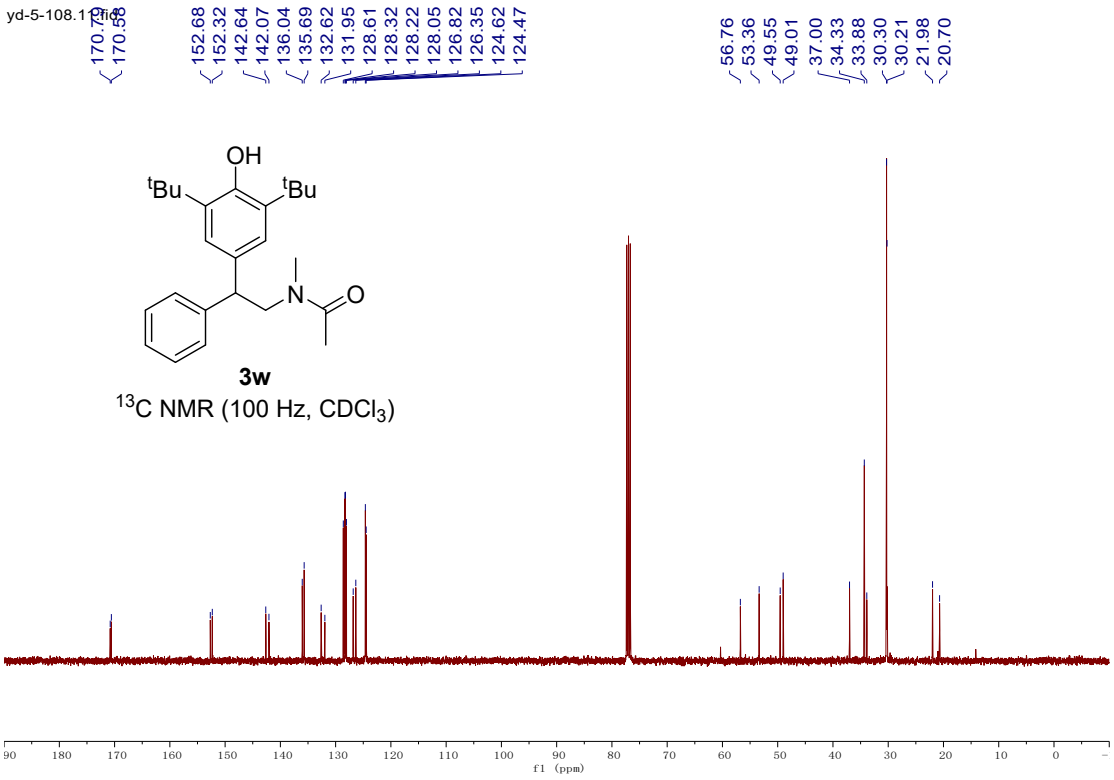
3v

^{1}H NMR (400 Hz, $CDCl_3$)



***N*-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenylethyl)-*N*-methylacetamide (3w)**

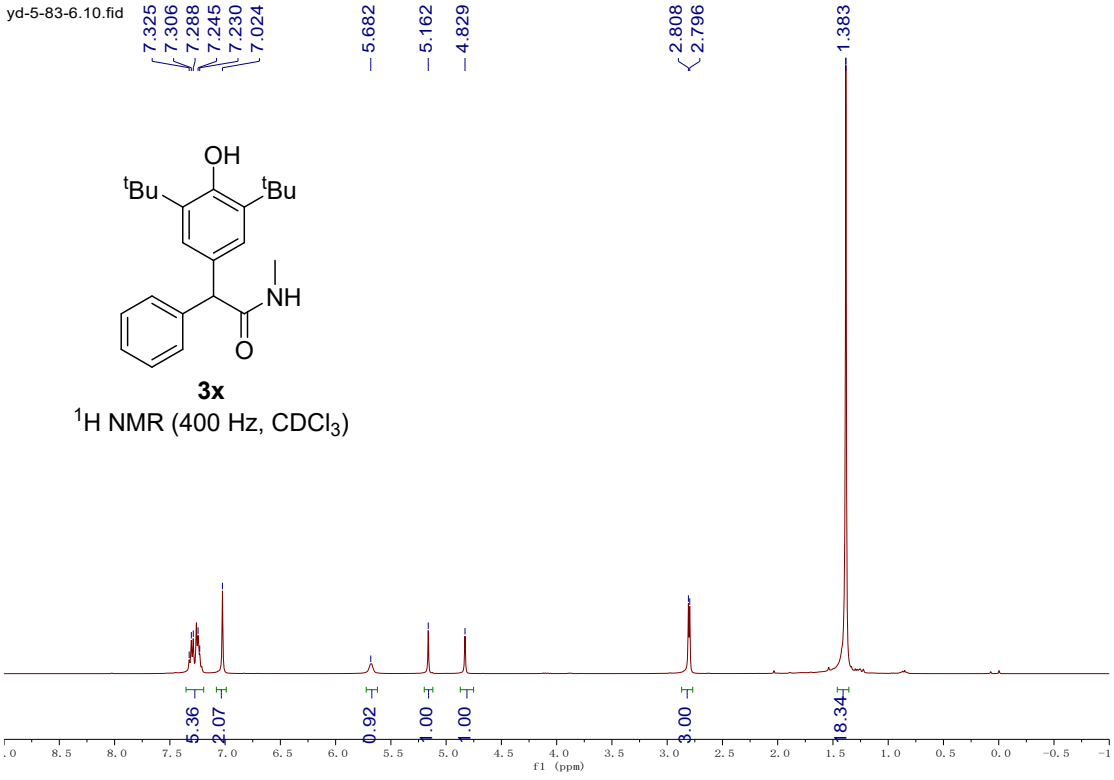




3w

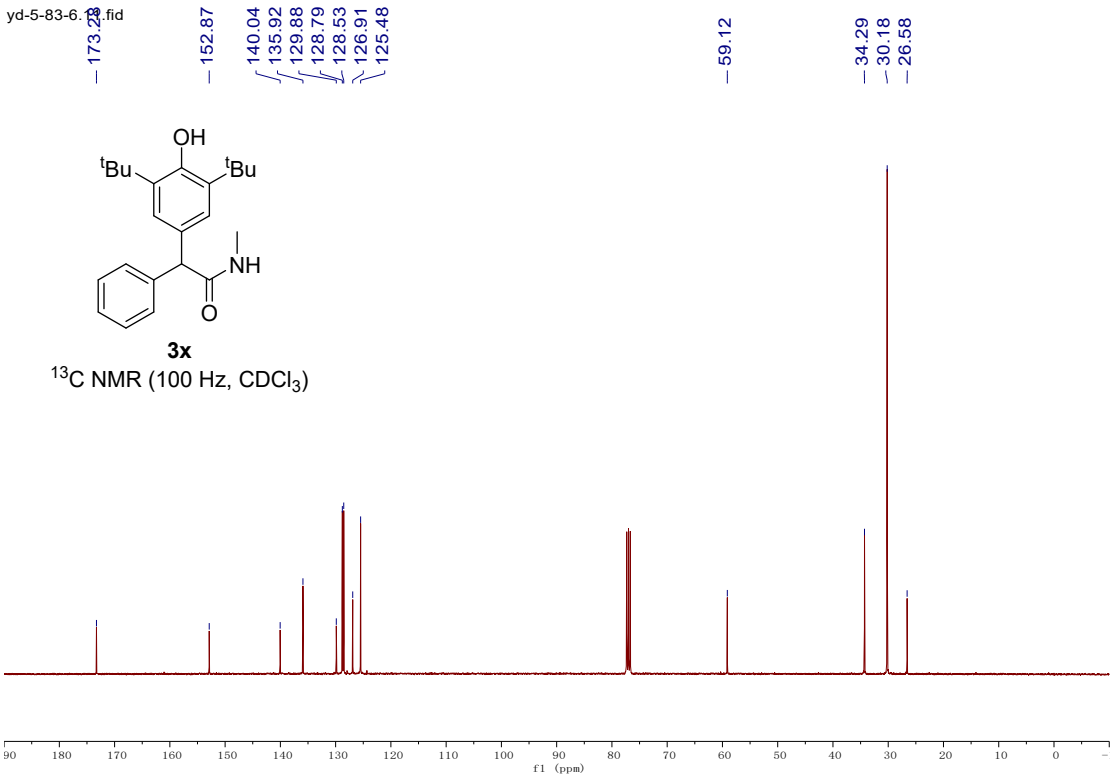
^{13}C NMR (100 Hz, $CDCl_3$)

2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-methyl-2-phenylacetamide (3x)



3x

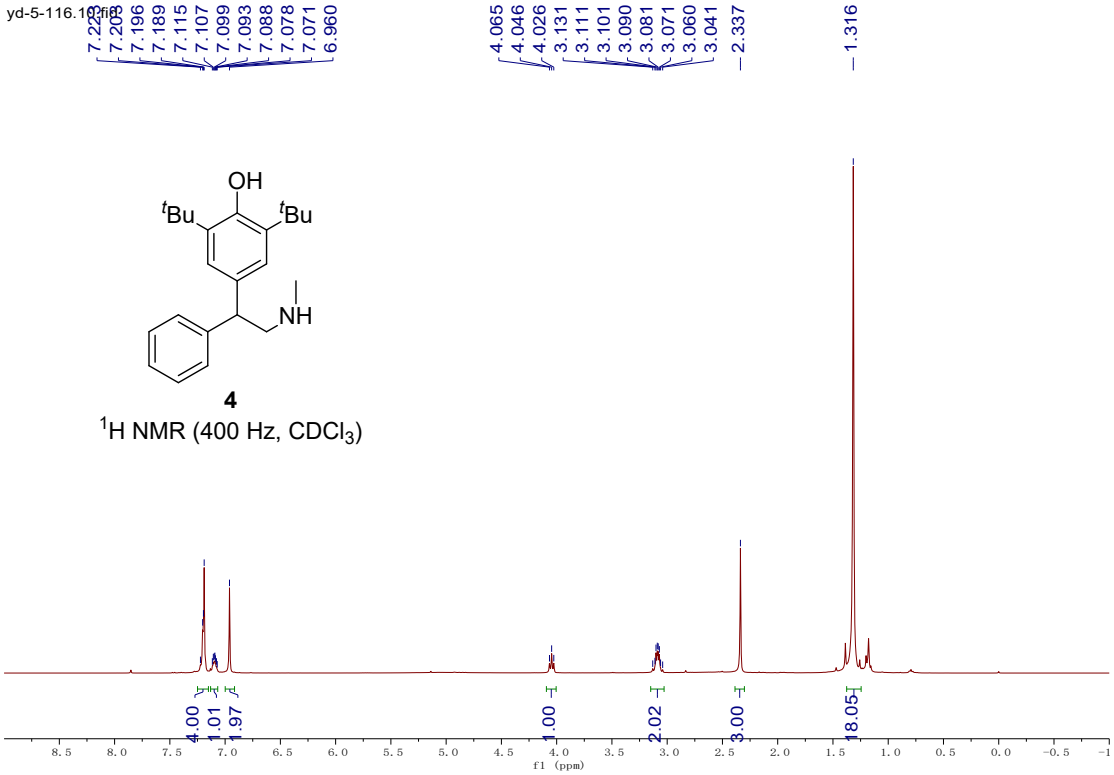
^{1}H NMR (400 Hz, $CDCl_3$)



3x

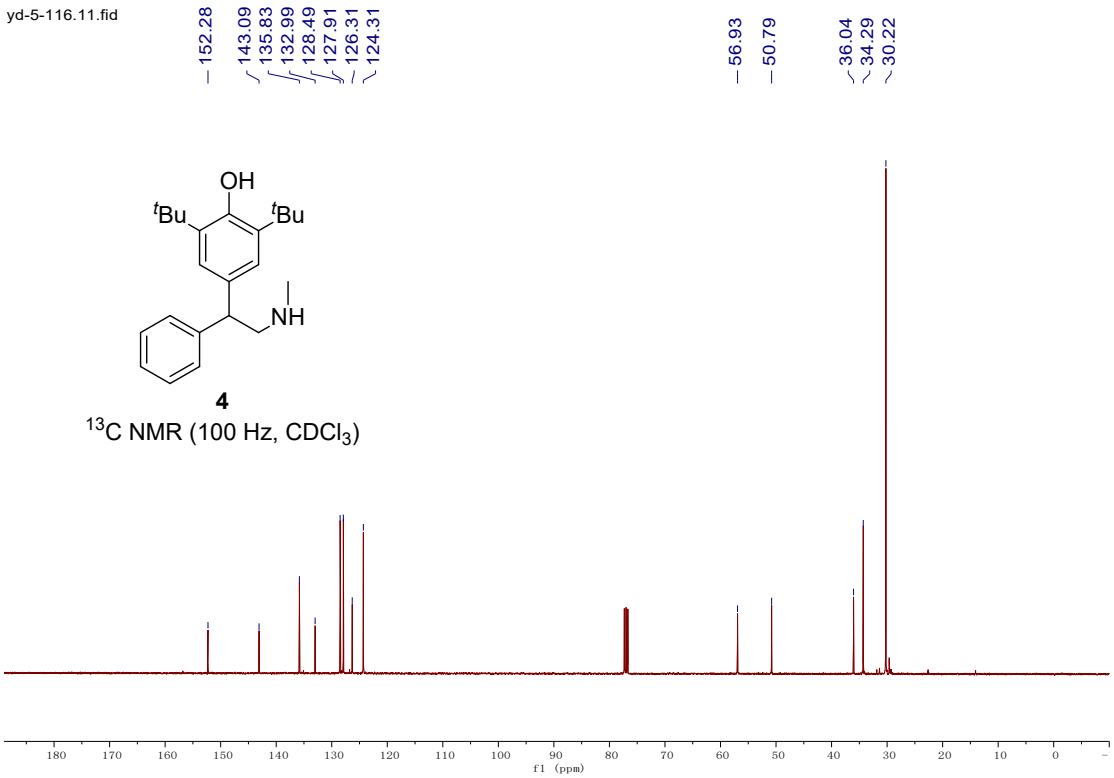
^{13}C NMR (100 Hz, $CDCl_3$)

Compound 4



4

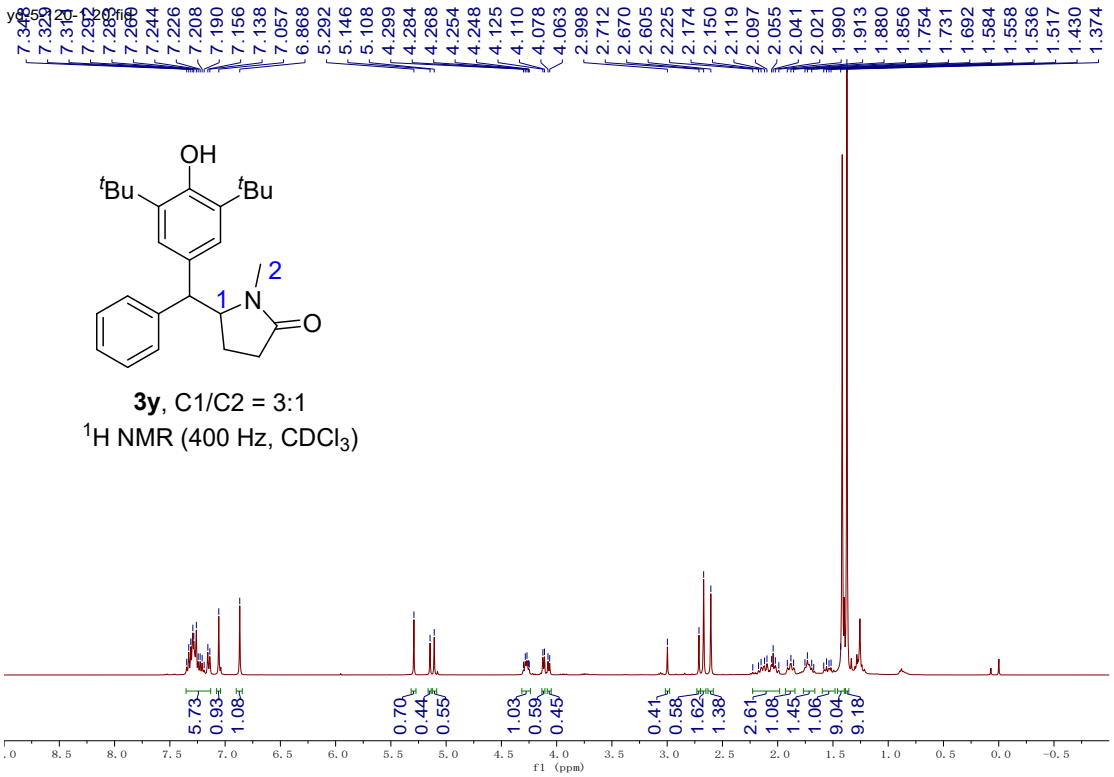
^{1}H NMR (400 Hz, $CDCl_3$)



4

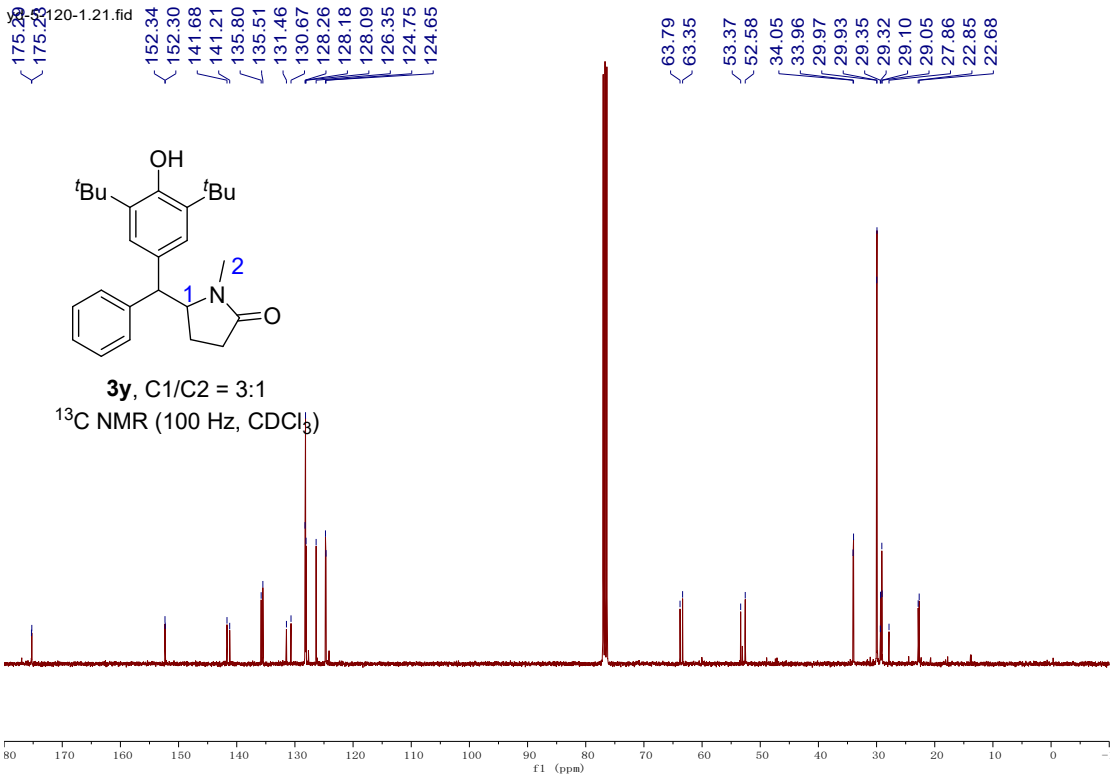
^{13}C NMR (100 Hz, $CDCl_3$)

5-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-1-methylpyrrolidin-2-one (3y)



3y, C1/C2 = 3:1

^{1}H NMR (400 Hz, $CDCl_3$)



3y, C1/C2 = 3:1

^{13}C NMR (100 Hz, $CDCl_3$)