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Supplementary Information

Nickel/Brønsted acid dual-catalyzed regioselective C-H bond allylation of phenols with 1,3-dienes

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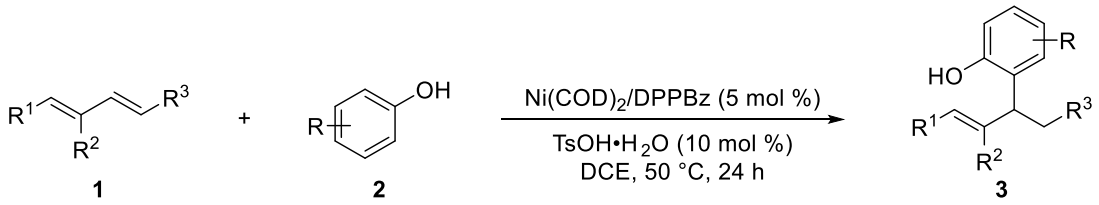
1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers (Energy Chemical, Adamas-beta®, *J*&K, laajoo and so on) and used without further purification. All reactions were assembled on a Schlenk vacuum line or in a glovebox using oven-dried glass tube and were stirred with Teflon-coated magnetic stirring bars unless otherwise specified. Reactions were monitored using thin-layer chromatography (TLC), visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Purification and isolation of products were performed *via* silica gel (200-300 mesh) chromatography. ^{1}H, ^{2}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 600 MHz spectrometer. ^{1}H NMR spectra were internally referenced to TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, m = multiplet), coupling constants (Hz) and integration. GC analysis were performed on a Shimadzu GC-2010 Pro gas chromatograph with an FID detector. All new products were further characterized by high resolution mass spectra (HRMS). HRMS were measured with a Thermo Orbitrap Elite instrument (ESI or APCI).

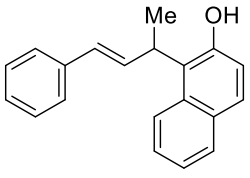
2. General procedure for nickel/brønsted acid dual-catalyzed regioselective C-H bond allylation

Scheme S1:



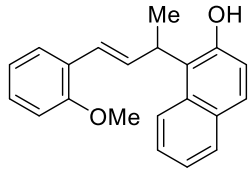
A reaction tube was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.05 equiv *vs* phenols **2**), DPPBz (4.5 mg, 0.01 mmol, 0.05 equiv *vs* phenols **2**), $TsOH{\cdot}H_2O$ (3.8 mg, 0.02 mmol, 0.10 equiv *vs* phenols **2**), phenols **2** (0.2 mmol, 1.0 equiv) and 1.0 mL DCE in an argon-filled glovebox, then 1,3-dienes **1** (0.24 mmol, 1.2 equiv *vs* phenols **2**) was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 50 ℃ for 24 h. After complete conversion, the resulting mixture was cooled to rt, then the residue was purified by SiO_2 column chromatography to give the desired product **3**.

(*E*)-1-(4-phenylbut-3-en-2-yl)naphthalen-2-ol (3aa)[1]: yellow oil 52.7 mg, 96% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.6, 6.8, 1.4 Hz, 1H), 7.41-7.38 (m, 2H), 7.36-7.29 (m, 3H), 7.26-7.22 (m, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.80-6.71 (m, 2H), 5.88 (s, 1H), 4.67-4.61 (m, 1H), 1.63 (d, *J* = 7.1 Hz, 3H)



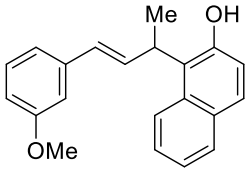
ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 136.6, 133.5, 132.5, 130.5, 129.6, 128.9, 128.8, 128.7, 127.7, 126.5, 126.4, 123.1, 122.4, 121.2, 119.2, 33.5, 17.2 ppm.

(*E*)-1-(4-(2-methoxyphenyl)but-3-en-2-yl)naphthalen-2-ol (3ba): yellow oil 51.0 mg, 84% isolated



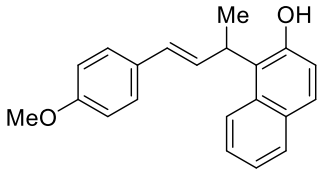
yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.78 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.48 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.33 (ddd, *J* = 8.0, 6.7, 1.0 Hz, 1H), 7.22 (ddd, *J* = 8.8, 6.5, 1.7 Hz, 1H), 7.13 (dd, *J* = 16.6, 2.5 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.90 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.75 (dd, *J* = 16.6, 4.0 Hz, 1H), 6.16 (s, 1H), 4.66-4.59 (m, 1H), 3.83 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 152.5, 134.3, 132.5, 129.6, 128.9, 128.8, 128.7, 126.9, 126.5, 125.7, 123.0, 122.3, 121.3, 120.7, 119.4, 110.8, 55.4, 33.8, 17.0 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{21}H_{21}O_2$ = 305.1536**,** found: 305.1530.

(*E*)-1-(4-(3-methoxyphenyl)but-3-en-2-yl)naphthalen-2-ol (3ca): yellow oil 53.3 mg, 88% isolated



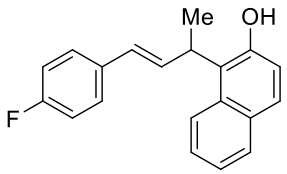
yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.80 (dt, *J* = 8.1, 0.7 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.35 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 2.0 Hz, 1H), 6.81-6.74 (m, 2H), 6.70 (dd, *J* = 16.4, 1.6 Hz, 1H), 5.83 (s, 1H), 4.67-4.61 (m, 1H), 3.80 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 152.2, 138.1, 133.9, 132.5, 130.3, 129.6, 128.9, 128.8, 126.5, 123.1, 122.4, 121.2, 119.2, 119.0, 113.5, 111.5, 55.2, 33.5, 17.2 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{21}H_{21}O_2$ = 305.1536**,** found: 305.1531.

(*E*)-1-(4-(4-methoxyphenyl)but-3-en-2-yl)naphthalen-2-ol (3da): yellow oil 25.4 mg, 42% isolated



yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.36-7.32 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.87-6.83 (m, 2H), 6.71 (dd, *J* = 16.5, 2.2 Hz, 1H), 6.61 (dd, *J* = 16.4, 3.7 Hz, 1H), 6.02 (s, 1H), 4.65-4.58 (m, 1H), 3.80 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 152.4, 132.5, 131.0, 130.1, 129.6, 129.3, 128.9, 128.7, 127.6, 126.5, 123.0, 122.3, 121.3, 119.3, 114.1, 55.3, 33.3, 17.2 ppm. **HRMS (ESI)** calculated $[M-H]^-$ for $C_{21}H_{19}O_2$ = 303.1391**,** found: 303.1392.

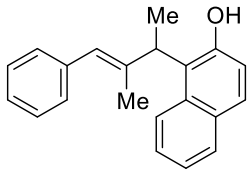
(*E*)-1-(4-(4-fluorophenyl)but-3-en-2-yl)naphthalen-2-ol (3ea): yellow oil 58.5 mg, > 99% isolated



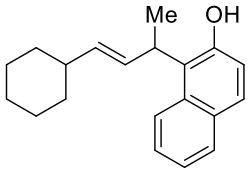
yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.38-7.33 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.03-6.97 (m, 2H), 6.73-6.64 (m, 2H), 5.77 (s, 1H), 4.66-4.61 (m, 1H), 1.63 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.0 Hz), 152.1, 133.4, 132.8 (d, *J* = 3.0

Hz), 132.5, 129.6, 129.2, 128.9, 128.8, 127.8 (d, *J* = 8.1 Hz), 126.6, 123.1, 122.4, 121.2, 119.2, 115.5 (d, *J* = 21.6 Hz), 33.5, 17.3 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.19 ppm. **HRMS (ESI)** calculated $[M-H]^-$ for $C_{20}H_{16}FO$ = 291.1191**,** found: 291.1196.

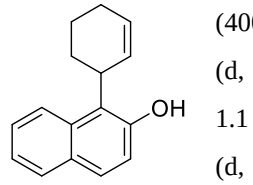
(*E*)-1-(3-methyl-4-phenylbut-3-en-2-yl)naphthalen-2-ol (3fa): yellow oil 49.1 mg, 85% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.80 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.51 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.40-7.32 (m, 5H), 7.28-7.24 (m, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.89 (s, 1H), 6.53 (s, 1H), 4.45 (q, *J* = 6.7 Hz, 1H), 1.84 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 143.5, 137.2, 133.1, 129.5, 128.9, 128.7, 128.3, 126.8, 126.6, 125.7, 123.0, 122.0, 120.3, 119.2, 39.7, 18.6, 16.8 ppm. **HRMS (ESI)** calculated $[M-H]^-$ for $C_{21}H_{19}O$ = 287.1441**,** found: 287.1433.



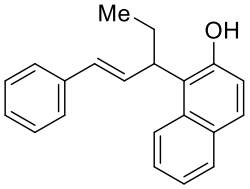
(*E*)-1-(4-cyclohexylbut-3-en-2-yl)naphthalen-2-ol (3ga): yellow oil 42.1 mg, 75% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.76 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.45 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.31 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.36 (s, 1H), 5.97 (ddd, *J* = 16.1, 3.4, 1.0 Hz, 1H), 5.86 (ddd, *J* = 16.1, 6.7, 2.2 Hz, 1H), 4.43-4.36 (m, 1H), 2.12-2.04 (m, 1H), 1.79-1.71 (m, 4H), 1.69-1.62 (m, 1H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.34-1.23 (m, 2H), 1.21-1.07 (m, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.8, 138.3, 132.4, 131.2, 129.4, 128.8, 128.6, 126.4, 122.9, 122.1, 121.0, 119.4, 40.8, 33.0, 32.93, 32.88, 26.0, 25.94, 25.91, 16.7 ppm. **HRMS (ESI)** calculated $[M-H]^-$ for $C_{20}H_{23}O$ = 279.1754**,** found: 279.1748.



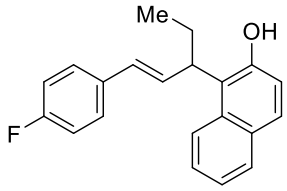
1-(cyclohex-2-en-1-yl)naphthalen-2-ol (3ha)[2]: colorless oil 37.8 mg, 84% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 1H), 7.77 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.47 (ddd, *J* = 8.5, 6.7, 1.4 Hz, 1H), 7.32 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 6.59 (s, 1H), 6.28 (d, *J* = 8.6 Hz, 1H), 6.08 (d, *J* = 9.9 Hz, 1H), 4.33-4.28 (m, 1H), 2.29-2.21 (m, 2H), 2.15-2.09 (m, 1H), 1.98-1.92 (m, 1H), 1.86-1.77 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 133.4, 132.6, 130.3, 129.3, 128.8, 128.5, 126.4, 122.9, 121.9, 120.6, 119.4, 34.4, 28.7, 25.1, 22.0 ppm.



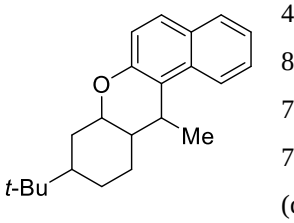
(*E*)-1-(1-phenylpent-1-en-3-yl)naphthalen-2-ol (3ia): yellow oil 25.1 mg, 44% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.47 (ddd, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.37-7.26 (m, 5H), 7.23-7.18 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.74 (dd, *J* = 16.3, 4.7 Hz, 1H), 6.60 (dd, *J* = 16.3, 2.1 Hz, 1H), 5.52 (s, 1H), 4.47-4.41 (m, 1H), 2.24-2.14 (m, 1H), 2.12-2.01 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 137.0, 133.5, 132.3, 130.5, 129.7, 128.9, 128.7, 128.6, 127.5, 126.33, 126.25, 123.0, 120.5, 119.1, 40.9, 25.7, 12.6 ppm. **HRMS (ESI)** calculated $[M-H]^-$ for $C_{21}H_{19}O$ = 287.1441**,** found: 287.1439.



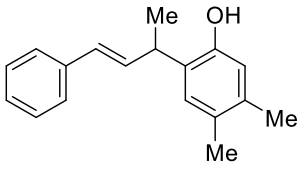
(*E*)-1-(1-(4-fluorophenyl)pent-1-en-3-yl)naphthalen-2-ol (3ja): yellow oil 27.7 mg, 45% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.7 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.47 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.36-7.29 (m, 3H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.99-6.94 (m, 2H), 6.66 (dd, *J* = 16.3, 4.8 Hz, 1H), 6.54 (dd, *J* = 16.3, 2.0 Hz, 1H), 5.45 (s, 1H), 4.45-4.40 (m, 1H), 2.23-2.12 (m, 1H), 2.12-2.01 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.6 Hz), 151.8, 133.4, 133.2 (d, *J* = 3.0 Hz), 132.2, 129.7, 129.2, 128.9, 128.7, 127.7 (d, *J* = 8.0 Hz), 126.4, 123.1, 120.5, 119.0, 115.4 (d, *J* = 21.5 Hz), 41.0, 25.8, 12.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.66 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{21}H_{20}FO$ = 307.1493**,** found: 307.1494.



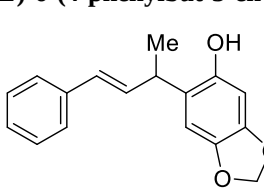
9-(tert-butyl)-12-methyl-7a,8,10,11,11a,12-hexahydro-9H-benzo[a]xanthene (3ka): colorless oil 49.8 mg, 81% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.68 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.42 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.25 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 3.31 (q, *J* = 7.1 Hz, 1H), 2.22-2.12 (m, 1H), 2.05 (dq, *J* = 13.7, 3.2 Hz, 1H), 1.85-1.76 (m, 1H), 1.62-1.47 (m, 4H), 1.32-1.24 (m, 4H), 1.13-1.05 (m, 1H), 0.91 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 131.0, 129.3, 129.0, 128.8, 126.3, 124.4, 122.23, 122.20, 112.9, 89.6, 47.7, 44.9, 37.5, 32.5, 31.9, 27.6, 23.5, 23.2, 15.2 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{22}H_{29}O$ = 309.2213**,** found: 309.2211.



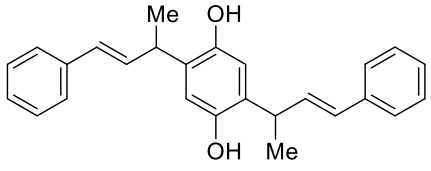
(*E*)-4,5-dimethyl-2-(4-phenylbut-3-en-2-yl)phenol (3ab): yellow oil 42.7 mg, 85% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 1H), 6.93 (s, 1H), 6.59 (s, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 6.41 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.89 (s, 1H), 3.86-3.79 (m, 1H), 2.18 (s, 6H), 1.46 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 137.2, 135.7, 134.3, 129.0, 128.7, 128.5, 127.8, 127.2, 126.2, 117.4, 36.4, 19.6, 19.3, 18.9 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{18}H_{21}O$ = 253.1587**,** found: 253.1581.



(*E*)-6-(4-phenylbut-3-en-2-yl)benzo[d][1,3]dioxol-5-ol (3ac)[1]: yellow oil 50.6 mg, 94% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.3-7.33 (m, 2H), 7.30-7.25 (m, 2H), 7.22-7.17 (m, 1H), 6.68 (s, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.40 (s, 1H), 6.34 (dd, *J* = 16.0, 6.2 Hz, 1H), 5.86 (s, 2H), 4.97 (s, 1H), 3.83-3.76 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 146.3, 141.7, 137.0, 133.9, 129.2, 128.5, 127.3, 126.2, 122.8, 107.2, 101.0, 98.8, 36.3, 19.6 ppm.

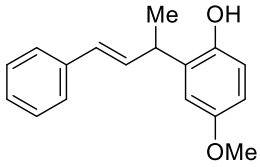


2,5-bis((*E*)-4-phenylbut-3-en-2-yl)benzene-1,4-diol (3ad): yellow oil 52.7 mg, 71% isolated yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.22-7.19 (m, 2H), 6.67 (s, 2H), 6.50 (d, *J* = 16.1 Hz, 2H), 6.39 (dd, *J* = 16.0, 6.5 Hz, 2H), 4.68 (s,

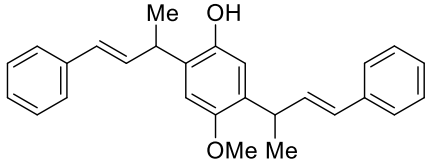


2H), 3.85-3.80 (m, 2H), 1.45 (d, *J* = 7.0 Hz, 6H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.4, 137.0, 133.7, 129.84, 129.83, 129.3, 128.5, 127.3, 126.2, 115.4, 36.40, 36.39, 19.44, 19.43 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{26}H_{27}O_2$ = 371.2006**,** found: 371.2004.

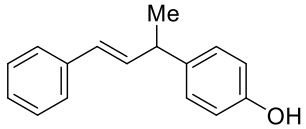
(*E*)-4-methoxy-2-(4-phenylbut-3-en-2-yl)phenol (3ae)[1]: yellow oil 17.0 mg, 33% isolated yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.66 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 6.40 (dd, *J* = 16.0, 6.3 Hz, 1H), 4.86 (s, 1H), 3.89-3.85 (m, 1H), 3.76 (s, 3H), 1.47 (d, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.8, 147.4, 137.0, 133.7, 132.1, 129.3, 128.5, 127.3, 126.2, 116.6, 113.9, 111.8, 55.7, 36.8, 19.4 ppm.



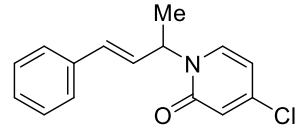
4-methoxy-2,6-bis((*E*)-4-phenylbut-3-en-2-yl)phenol (3ae'): yellow oil 23.1 mg, 30% isolated yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 1.8 Hz, 2H), 6.50 (d, *J* = 16.1 Hz, 2H), 6.40 (ddd, *J* = 16.0, 7.8, 6.4 Hz, 2H), 4.95 (d, *J* = 5.8 Hz, 1H), 3.92-3.88 (m, 2H), 3.78 (d, *J* = 2.4 Hz, 3H), 1.47 (d, *J* = 7.0 Hz, 6H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.66, 153.65, 145.41, 145.36, 137.0, 133.9, 133.8, 132.6, 132.5, 129.38, 129.36, 128.5, 127.3, 126.2, 111.2, 111.1, 55.7, 36.99, 36.97, 19.53, 19.51 ppm. **HRMS (ESI)** calculated $[M-H]^-$ for $C_{27}H_{27}O_2$ = 383.2017**,** found: 383.2017.



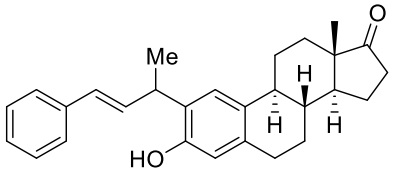
(*E*)-4-(4-phenylbut-3-en-2-yl)phenol (3af)[3]: yellow oil 26.5 mg, 59% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.17 (m, 1H), 7.15-7.11 (m, 2H), 6.80-6.76 (m, 2H), 6.41-6.31 (m, 2H), 4.81 (s, 1H), 3.61-3.55 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 137.8, 137.6, 135.5, 128.5, 128.4, 128.2, 127.0, 126.1, 115.2, 41.7, 21.3 ppm.



(*E*)-4-chloro-1-(4-phenylbut-3-en-2-yl)pyridin-2(1H)-one (3ag): yellow oil 28.1 mg, 54% isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.37-7.32 (m, 3H), 7.31-7.28 (m, 1H), 7.27-7.24 (m, 1H), 6.65 (dd, *J* = 16.2, 1.8 Hz, 1H), 6.57 (dd, *J* = 9.7, 0.6 Hz, 1H), 6.26 (dd, *J* = 16.1, 5.2 Hz, 1H), 5.92-5.85 (m, 1H), 1.55 (d, *J* = 6.9 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 139.9, 135.7, 133.1, 131.7, 128.7, 128.3, 127.9, 126.6, 121.7, 112.6, 51.8, 18.9 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{15}ClNO$ = 260.0837**,** found: 260.0833.

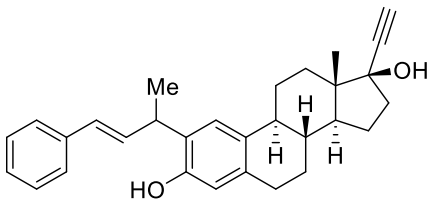


(*8R,9S,13S,14S*)-3-hydroxy-13-methyl-2-((*E*)-4-phenylbut-3-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3ah): white solid 65.7 mg (a mixture of diastereomers), 82% isolated yield; **^{1}H NMR** (600 MHz, $CDCl_3$, reported as a mixture of



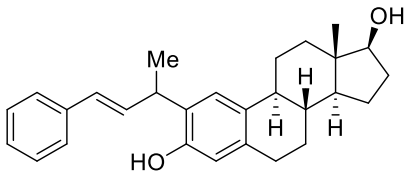
diastereomers) δ 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.23-7.20 (m, 1H), 7.11 (s, 1H), 6.57 (s, 1H), 6.52 (ddd, *J* = 16.0, 6.9, 1.4 Hz, 1H), 6.43 (dd, *J* = 16.0, 6.2 Hz, 1H), 4.98 (s, 1H), 3.87-3.81 (m, 1H), 2.90-2.80 (m, 2H), 2.51 (dd, *J* = 19.2, 8.4 Hz, 1H), 2.43-2.39 (m, 1H), 2.28-2.24 (m, 1H), 2.15 (dt, *J* = 19.1, 9.0 Hz, 1H), 2.07-2.03 (m, 1H), 2.01-1.97 (m, 1H), 1.97-1.94 (m, 1H), 1.66-1.59 (m, 2H), 1.54-1.40 (m, 7H), 0.91 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 151.6, 151.5, 137.2, 135.8, 135.7, 134.22, 134.20, 131.91, 131.89, 129.0, 128.9, 128.5, 128.40, 128.37, 127.2, 126.2, 124.8, 116.03, 115.99, 50.29, 50.27, 48.0, 44.04, 44.01, 38.31, 38.30, 36.9, 36.7, 35.9, 31.5, 29.0, 26.48, 26.46, 25.94, 25.92, 21.5, 19.63, 19.61, 13.8 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{28}H_{33}O_2$ = 401.2475**,** found: 401.2467.

(*8R,9S,13S,14S,17R*)-17-ethynyl-13-methyl-2-((*E*)-4-phenylbut-3-en-2-yl)-



7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (3ai)[1]: white solid 47.3 mg (a mixture of diastereomers), 55% isolated yield; **^{1}H NMR** (600 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 7.36 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.23-7.19 (m, 1H), 7.11 (s, 1H), 6.54 (s, 1H), 6.51 (dd, J = 16.1, 6.2 Hz, 1H), 6.44 (dd, J = 16.0, 6.1 Hz, 1H), 5.05 (s, 1H), 3.88-3.82 (m, 1H), 2.84-2.75 (m, 2H), 2.60 (d, J = 2.5 Hz, 1H), 2.39-2.31 (m, 2H), 2.25-2.20 (m, 1H), 2.05-2.00 (m, 2H), 1.93-1.84 (m, 2H), 1.81-1.72 (m, 3H), 1.50-1.33 (m, 7H), 0.88 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 151.4, 151.3, 137.1, 136.10, 136.08, 134.25, 134.23, 132.59, 132.58, 129.1, 129.0, 128.5, 128.1, 128.0, 127.2, 126.2, 124.94, 124.93, 116.09, 116.05, 87.41, 87.39, 79.9, 74.1, 49.38, 49.37, 47.1, 43.62, 43.60, 39.38, 39.37, 38.9, 37.1, 36.8, 32.7, 29.2, 27.17, 27.16, 26.44, 26.43, 22.8, 19.61, 19.57, 12.7 ppm.

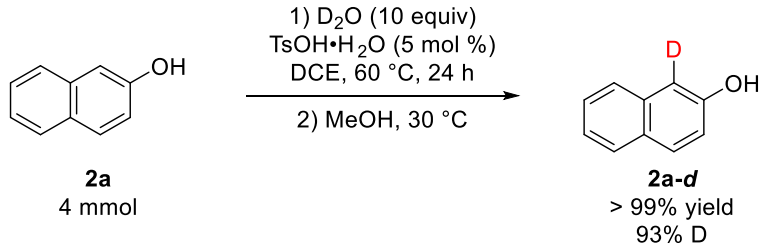
(*8R,9S,13S,14S,17S*)-13-methyl-2-((*E*)-4-phenylbut-3-en-2-yl)-7,8,9,11,12,13,14,15,16,17-



decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (3aj): white solid 62.7 mg (a mixture of diastereomers), 78% isolated yield; **^{1}H NMR** (600 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23-7.20 (m, 1H), 7.11 (s, 1H), 6.54 (s, 1H), 6.52 (dd, *J* = 16.1, 5.8 Hz, 1H), 6.44 (dd, *J* = 16.0, 6.1 Hz, 1H), 4.96 (s, 1H), 3.87-3.81 (m, 1H), 3.74 (t, *J* = 8.6 Hz, 1H), 2.85-2.76 (m, 2H), 2.35-2.30 (m, 1H), 2.22-2.16 (m, 1H), 2.15-2.09 (m, 1H), 1.96-1.93 (m, 1H), 1.88-1.85 (m, 1H), 1.72-1.67 (m, 1H), 1.49-1.47 (m, 4H), 1.44-1.25 (m, 6H), 1.22-1.17 (m, 1H), 0.78 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 151.4, 151.3, 137.1, 136.19, 136.16, 134.22, 134.21, 132.74, 132.72, 129.14, 129.07, 128.5, 128.01, 127.97, 127.2, 126.2, 124.94, 124.93, 116.12, 116.08, 81.9, 49.96, 49.95, 44.1, 44.0, 43.22, 43.21, 38.83, 38.82, 37.2, 36.9, 36.7, 30.6, 29.2, 27.19, 27.18, 26.38, 26.37, 23.1, 19.58, 19.57, 11.1 ppm. **HRMS (APCI)** calculated $[M+H]^+$ for $C_{28}H_{35}O_2$ = 403.2632**,** found: 403.2628.

3. Deuterium-labeled experiments

Scheme S2. Synthesis of **2a-*d***.[4]



2a
4 mmol

2a-*d*
> 99% yield
93% D

Under nitrogen atmosphere, 2-naphthol **2a** (576.7 mg, 4 mmol) was treated with 10 equiv of 99.8% D_2O (800 μL, 40 mmol) in the presence of 5 mol % *p*-toluenesulfonic acid catalyst (38.0 mg, 0.2 mmol) at 60 ℃ for 24 h in 3 mL dry 1,2-dichloroethane solvent. Then the resulting mixture was cooled to room temperature, the layers were separated and the aqueous phase extracted with ethyl acetate (3×10 mL). The combined organic phases dried over Na_2SO_4 and concentrated in vacuo. Subsequently, 2 mL MeOH was added and the mixture was concentrated using rotatory evaporator (400 mbar) for 6 minutes (this process was repeated three times). Selective deuterium incorporation was observed exclusively at the C1-position of **2a** to produce **2a-*d*** with quantitative (>99%) yield. ^{1}H NMR spectrum showed 93% D incorporation. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 0.07H), 7.10 (d, *J* = 8.9 Hz, 1H), 4.98 (s, 1H) ppm.

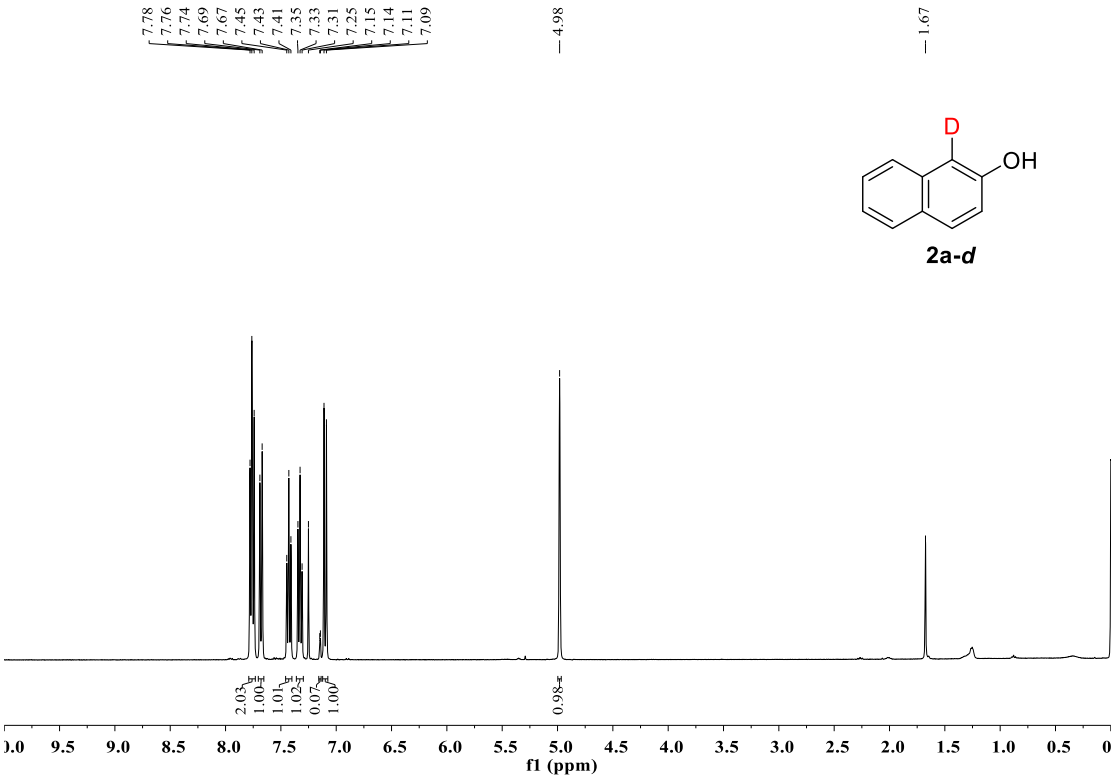
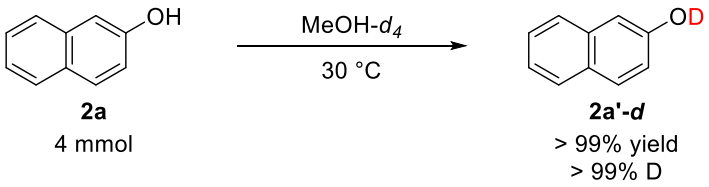


Figure S1. ^{1}H NMR spectra of **2a-*d***.

Scheme S3. Synthesis of **2a'-*d***.



An oven dried flask (20 mL) was rinsed with MeOH-d_4 twice, and then charged with 2-naphthol **2a** (576.7 mg, 4 mmol). MeOH-d_4 (99.8 % D, 2 mL) was added and the mixture was concentrated using rotatory evaporator (400 mbar) for 6 minutes (this process was repeated six times); The residual solvent was evaporated with high vacuum and resulted in quantitative (>99%) yield of the title compound **2a'-*d***. ^{1}H NMR spectrum showed > 99% D incorporation. **^{1}H NMR** (400 MHz, MeOH-d_4) δ 7.70 (t, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.23 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.10 (s, 1H), 7.06 (dd, *J* = 8.8, 2.4 Hz, 1H) ppm.

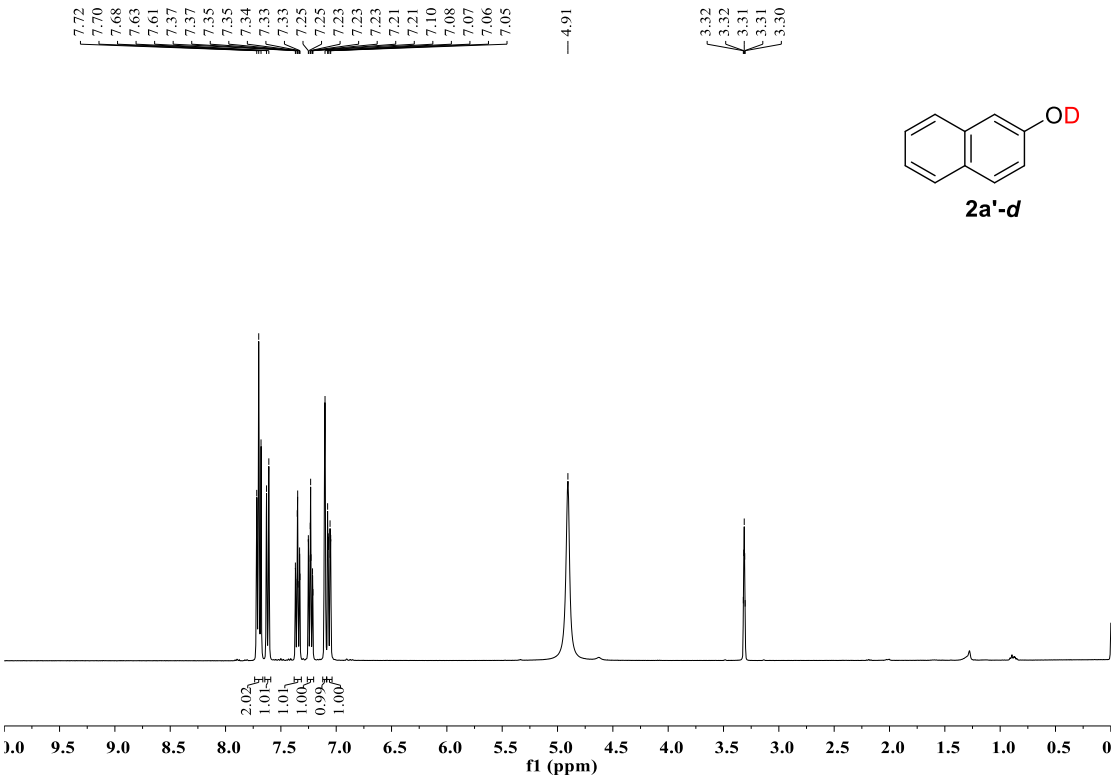
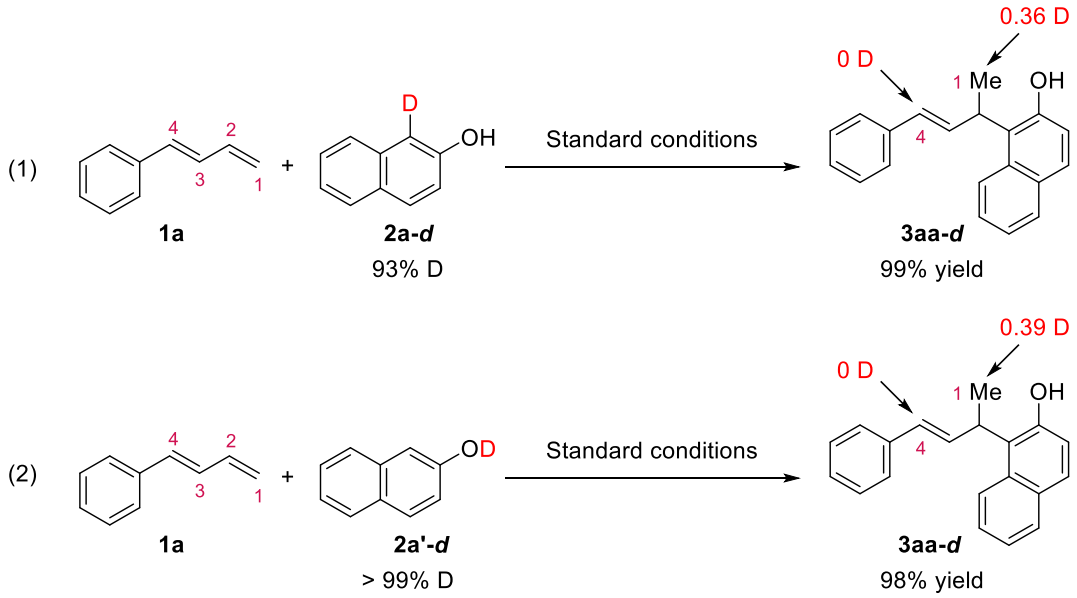


Figure S2. ^{1}H NMR spectra of **2a'-*d***.

Scheme S4. Synthesis of **3aa-*d***.



The deuterium-labeled experiments were carried out with 1,3-dienes **1a** and deuterium-labeled 2-naphthol **2a-*d*** or **2a'-*d*** under the standard conditions, the desired C-H allylated products **3aa-*d*** were obtained with 99% or 98% yield, respectively. The **3aa-*d*** were determined by ^{1}H NMR and ^{2}H NMR analysis. Deuterium incorporation was determined by ^{1}H NMR.

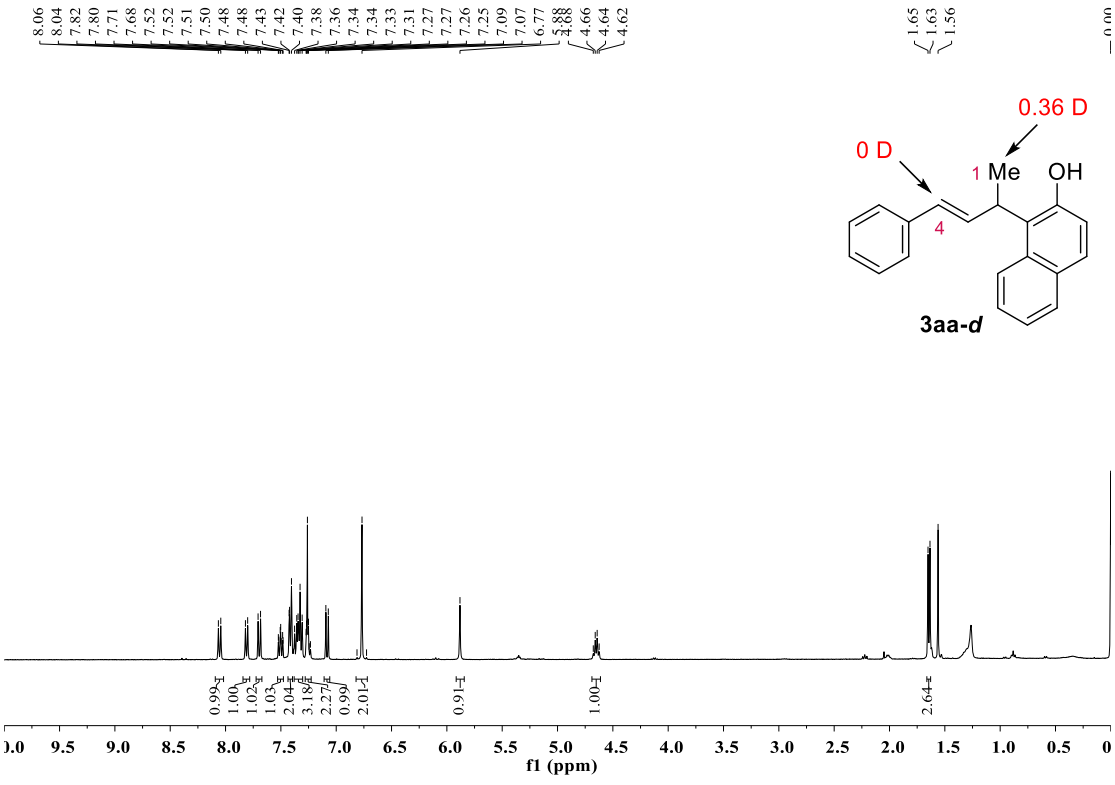


Figure S3. ^{1}H NMR spectra of **3aa-*d*** (from **2a-*d***).

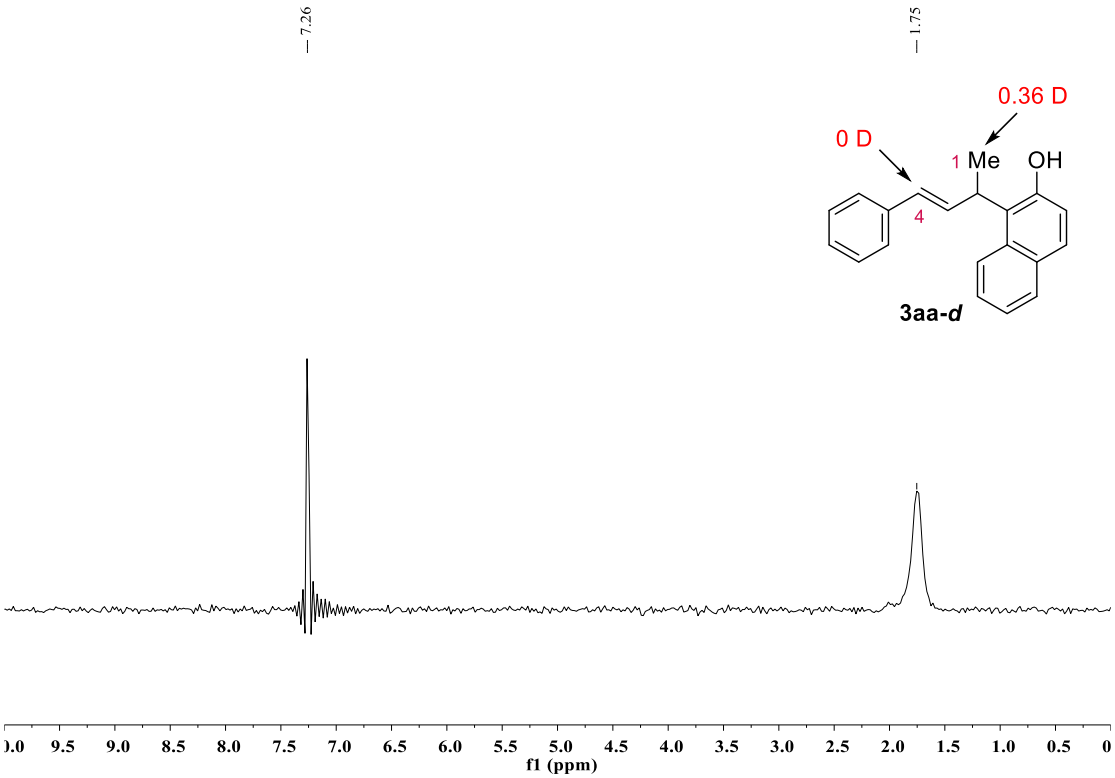


Figure S4. ^{2}H NMR spectra of **3aa-*d*** (from **2a-*d***).

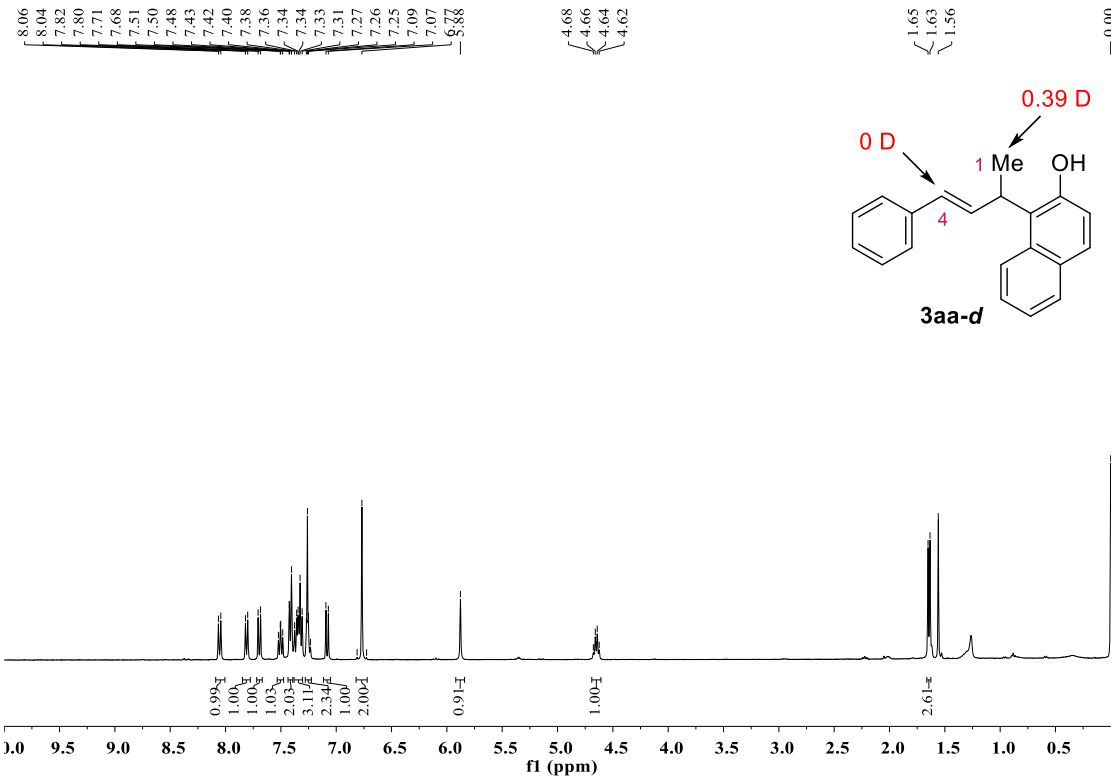


Figure S5. ^{1}H NMR spectra of **3aa-*d*** (from **2a'-*d***).

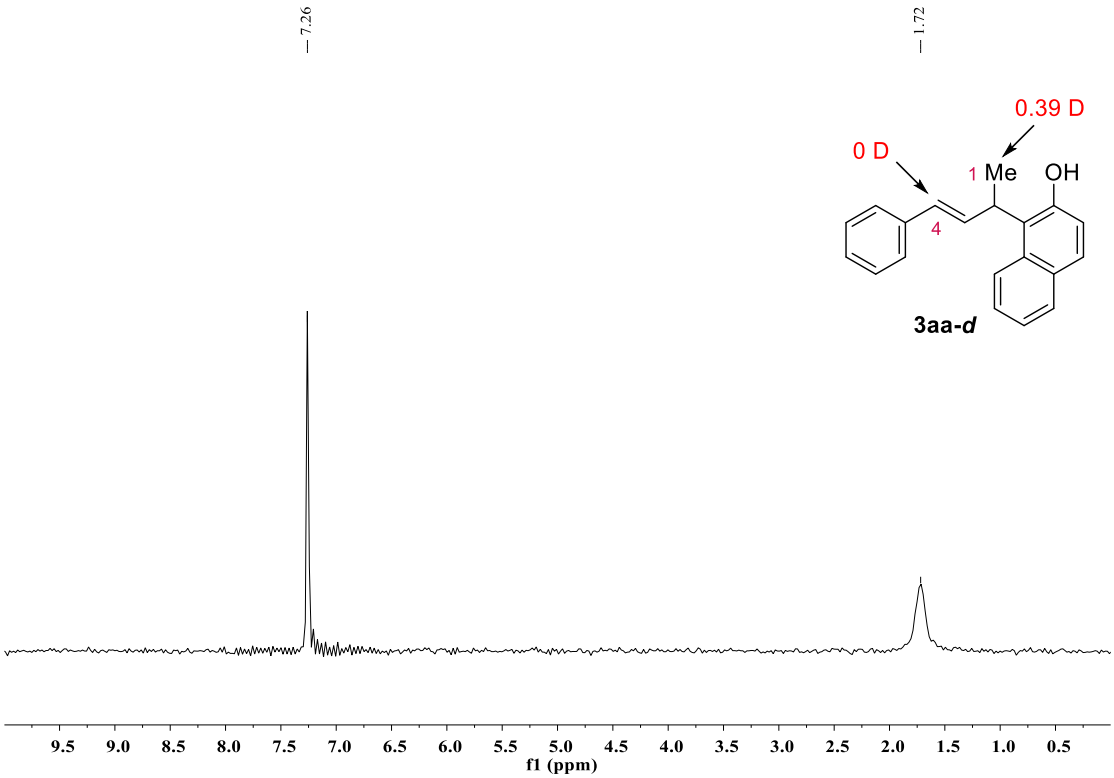


Figure S6. ^{2}H NMR spectra of **3aa-*d*** (from **2a'-*d***).

4. References

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4. A. K. Mishra and S. Biswas, Bronsted acid catalyzed functionalization of aromatic alcohols through nucleophilic substitution of hydroxyl group, *J. Org. Chem.*, 2016, **81**, 2355-2363.

5. NMR spectra

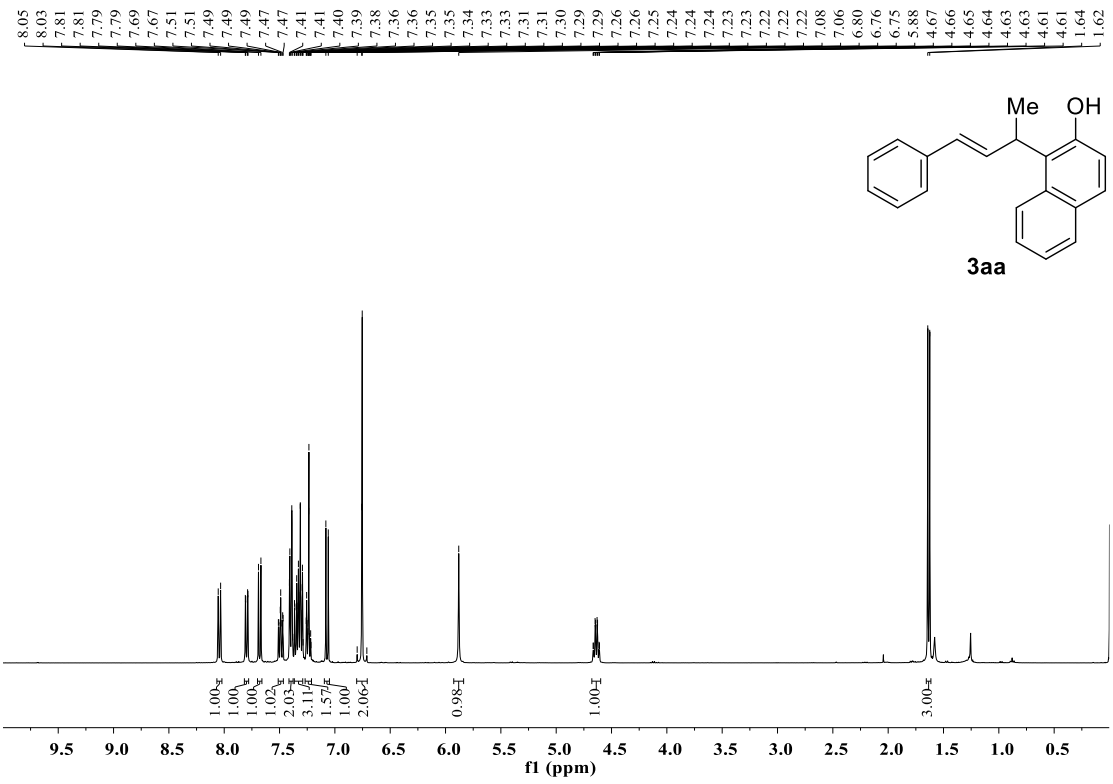

Figure S7. ^{1}H NMR spectra of **3aa**.

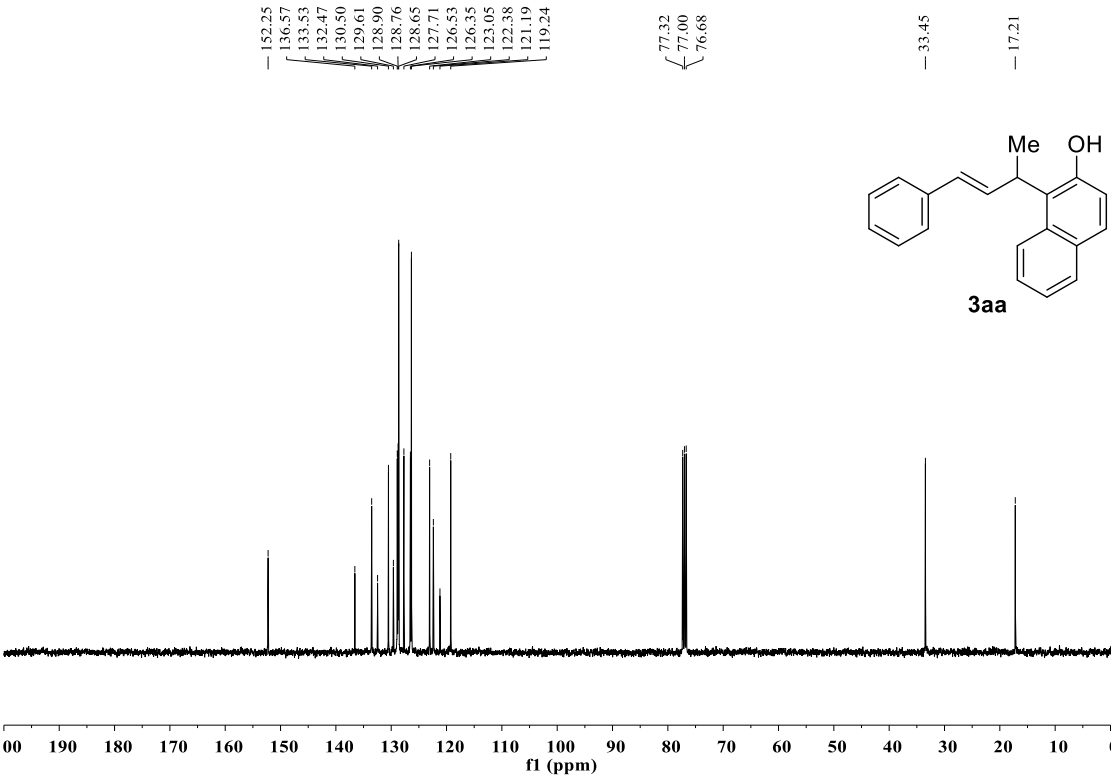

Figure S8. ^{13}C NMR spectra of **3aa**.

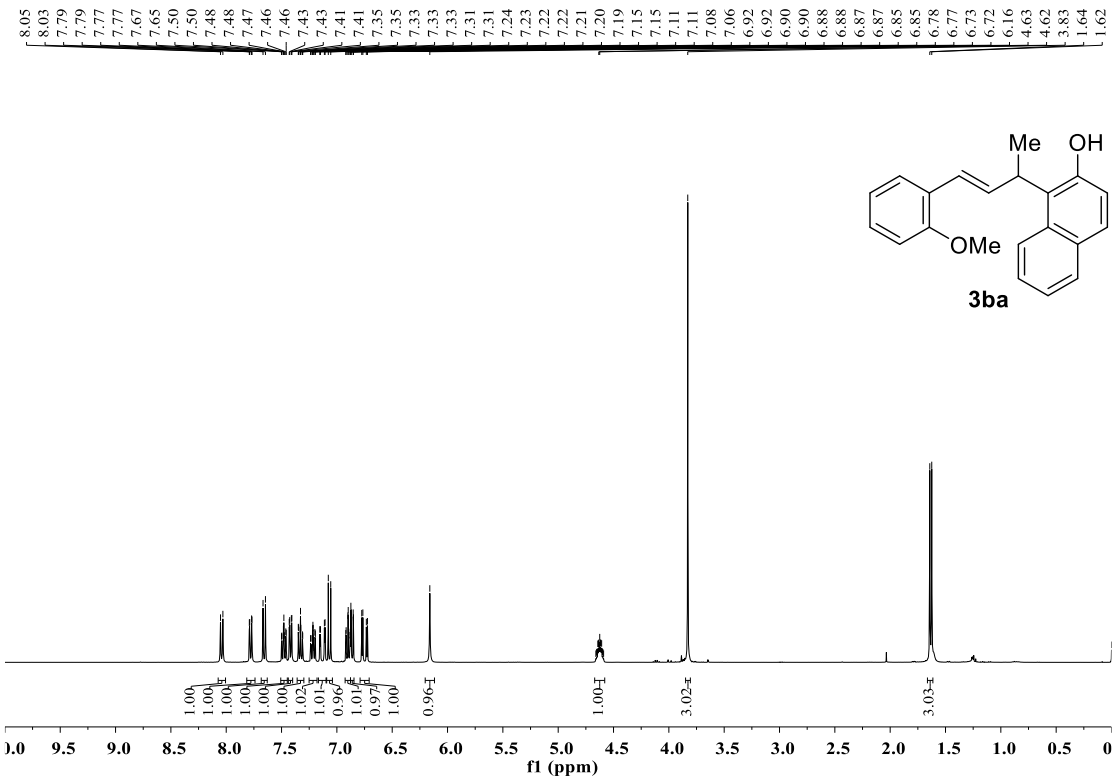

Figure S9. [1]H NMR spectra of **3ba**.

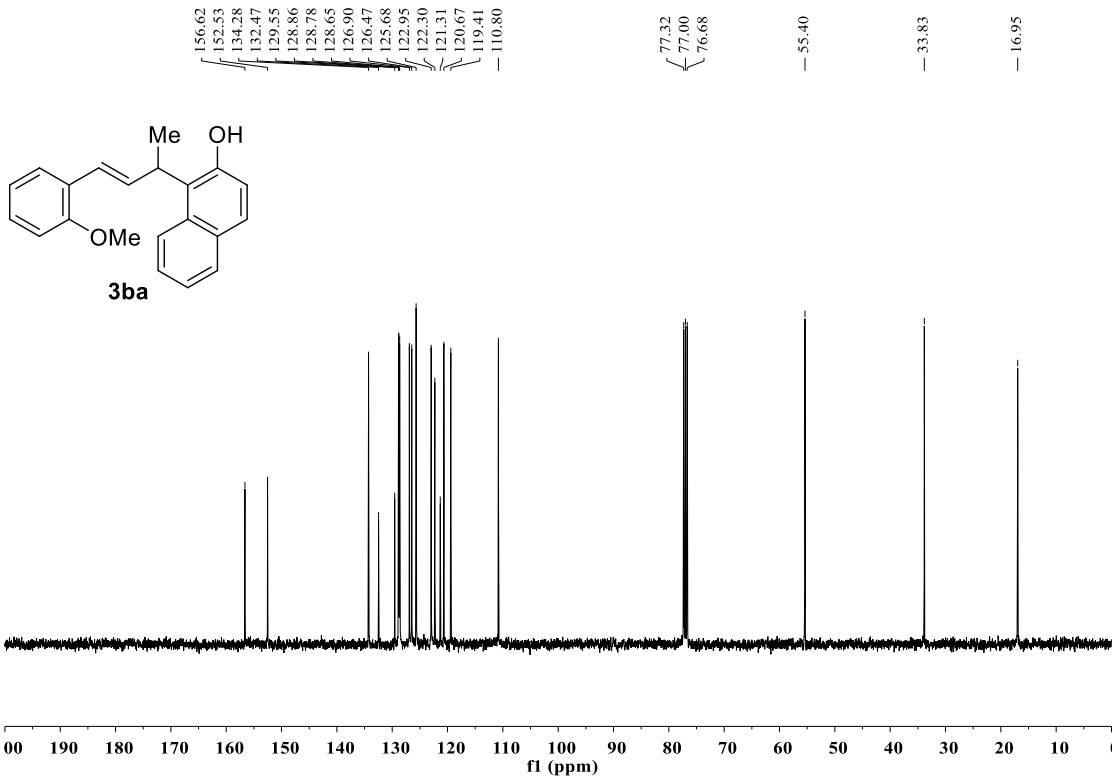

Figure S10. [13]C NMR spectra of **3ba**.

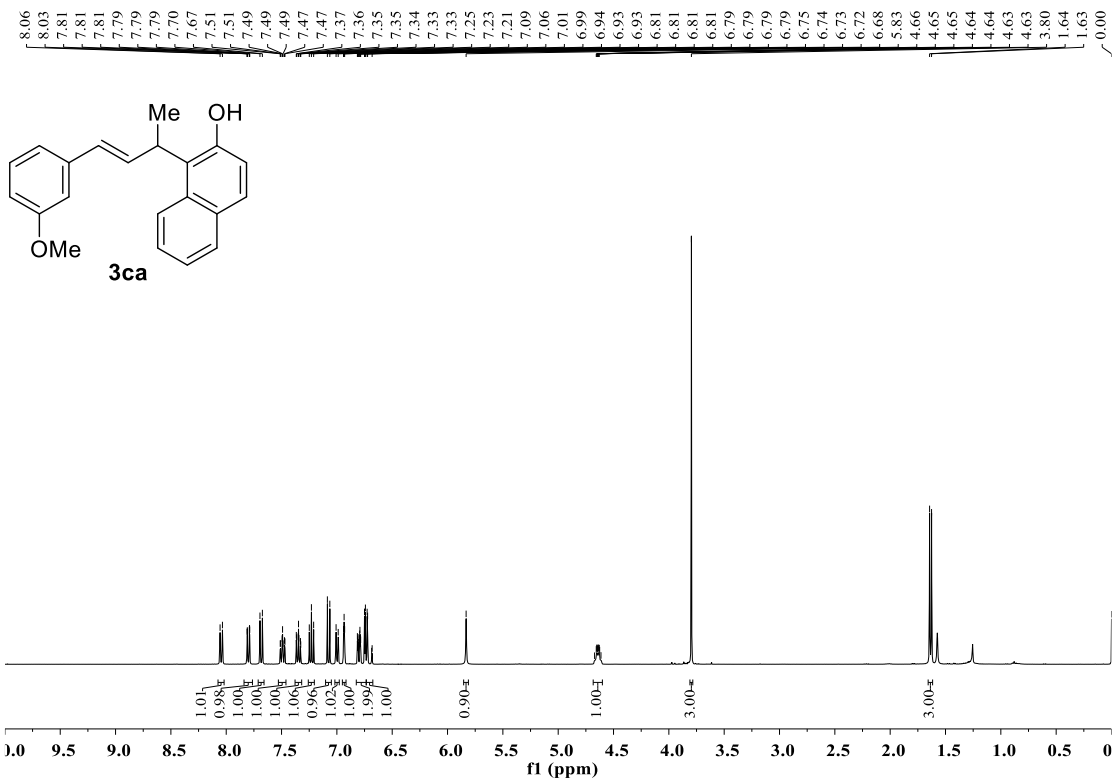

Figure S11. ^{1}H NMR spectra of **3ca**.

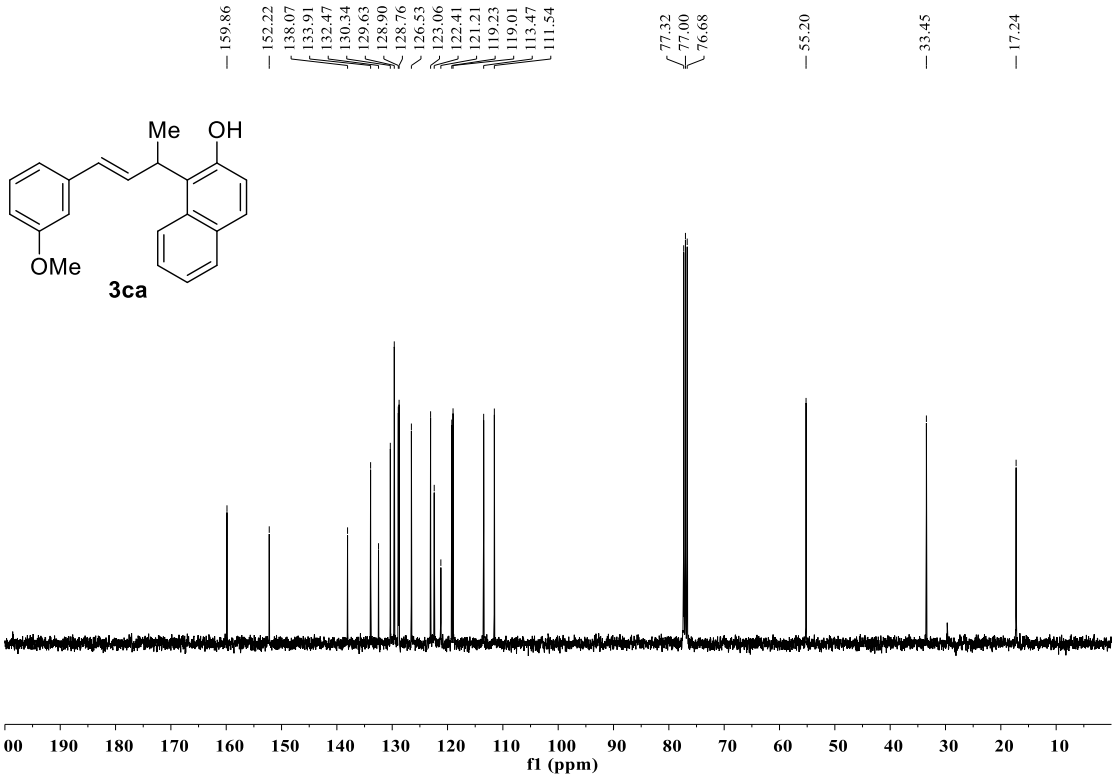

Figure S12. ^{13}C NMR spectra of **3ca**.

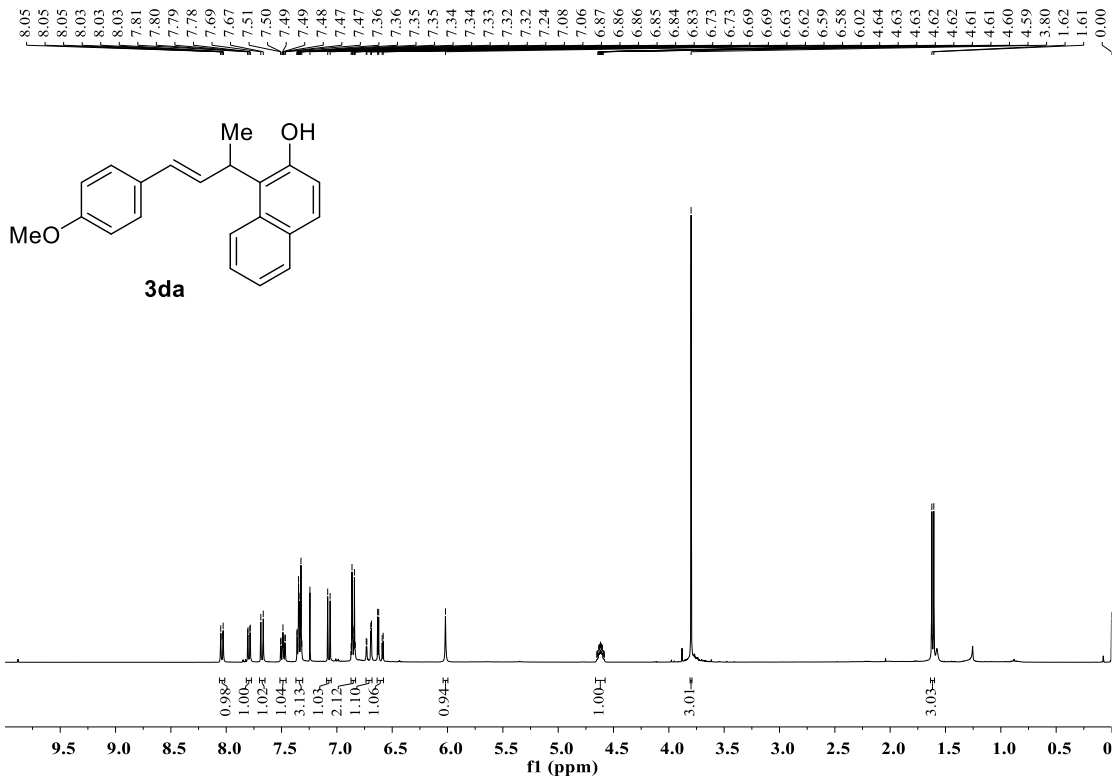

Figure S13. ^{1}H NMR spectra of **3da**.

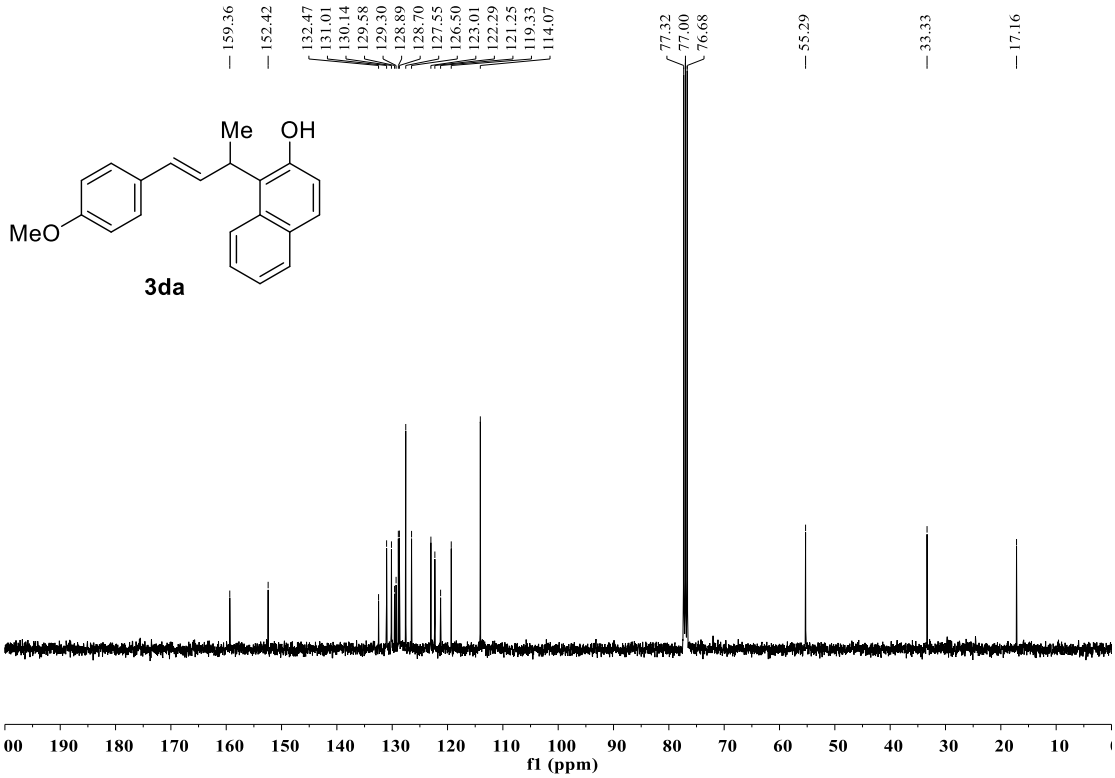

Figure S14. ^{13}C NMR spectra of **3da**.

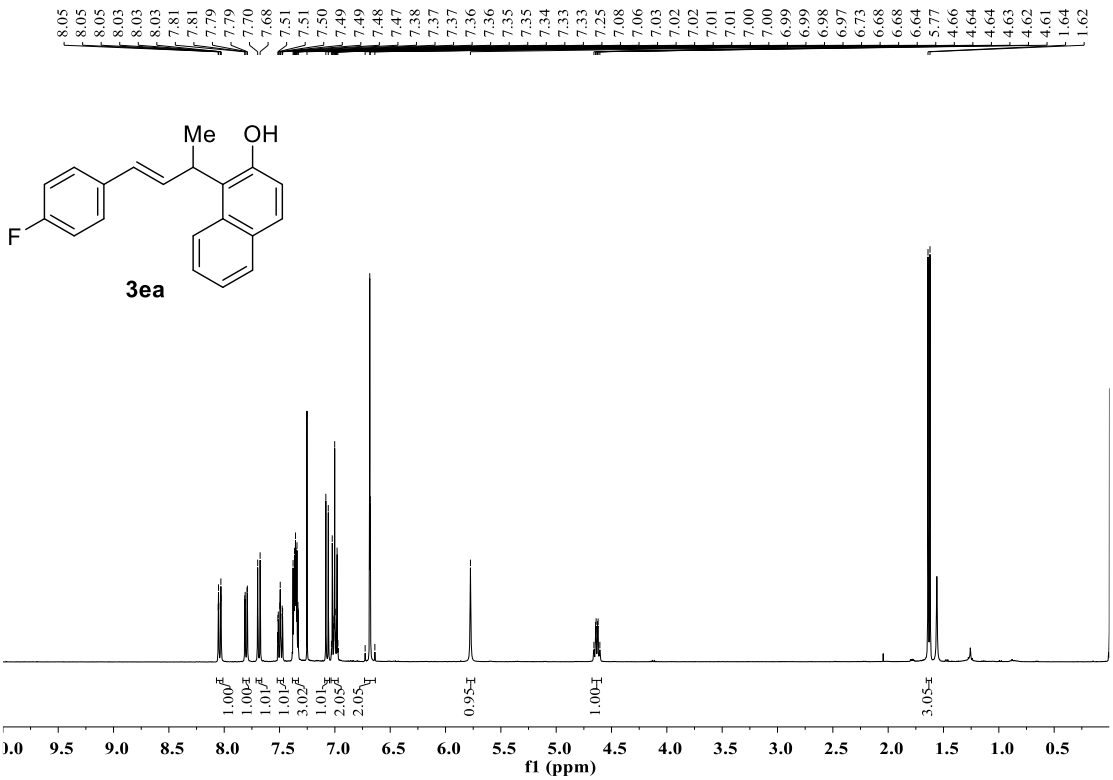

Figure S15. ^{1}H NMR spectra of **3ea**.

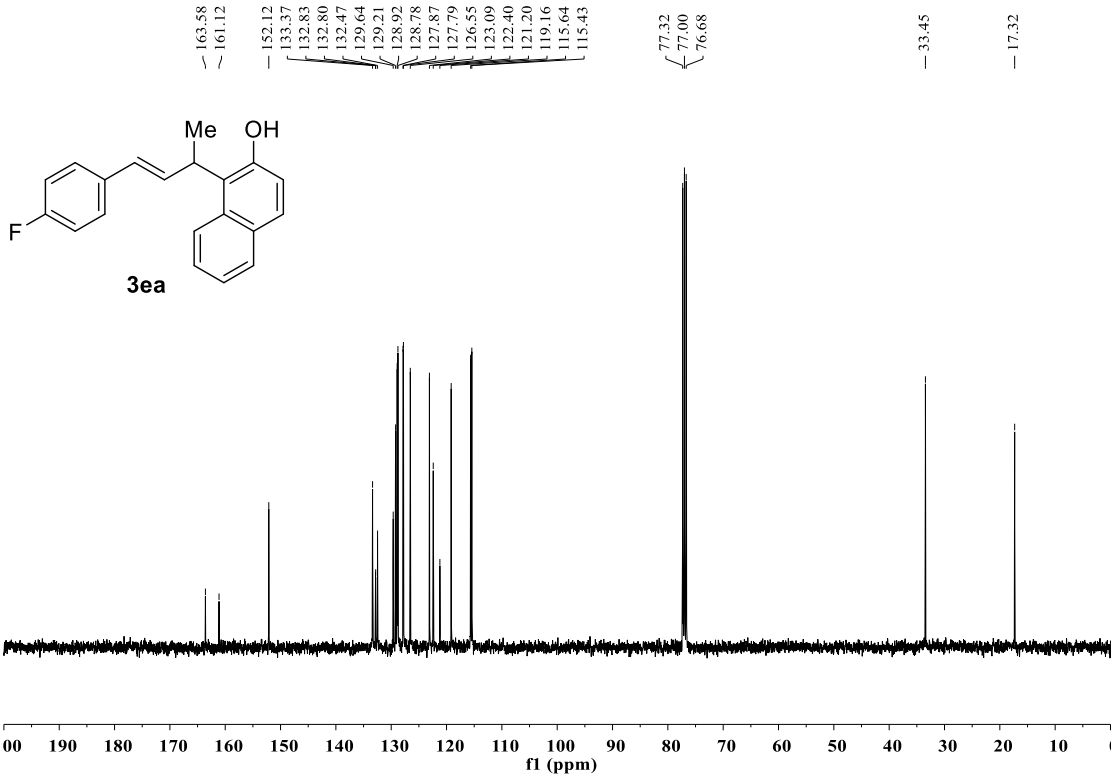

Figure S16. ^{13}C NMR spectra of **3ea**.

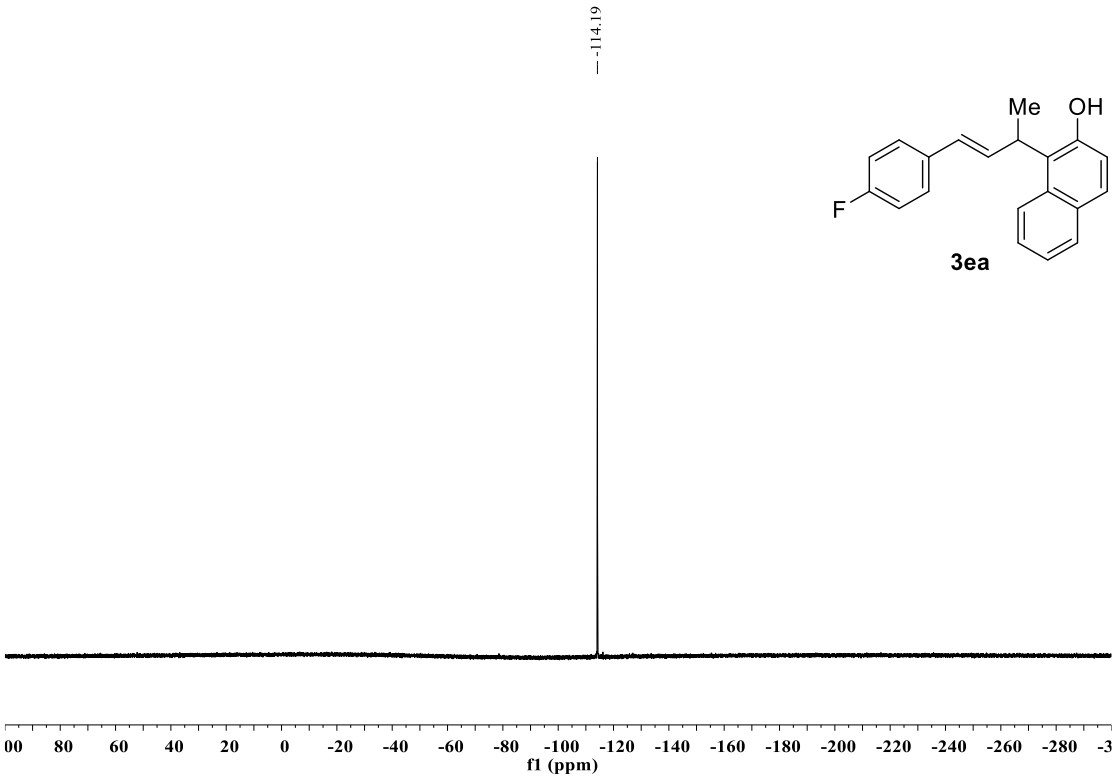

Figure S17. ^{19}F NMR spectra of **3ea**.

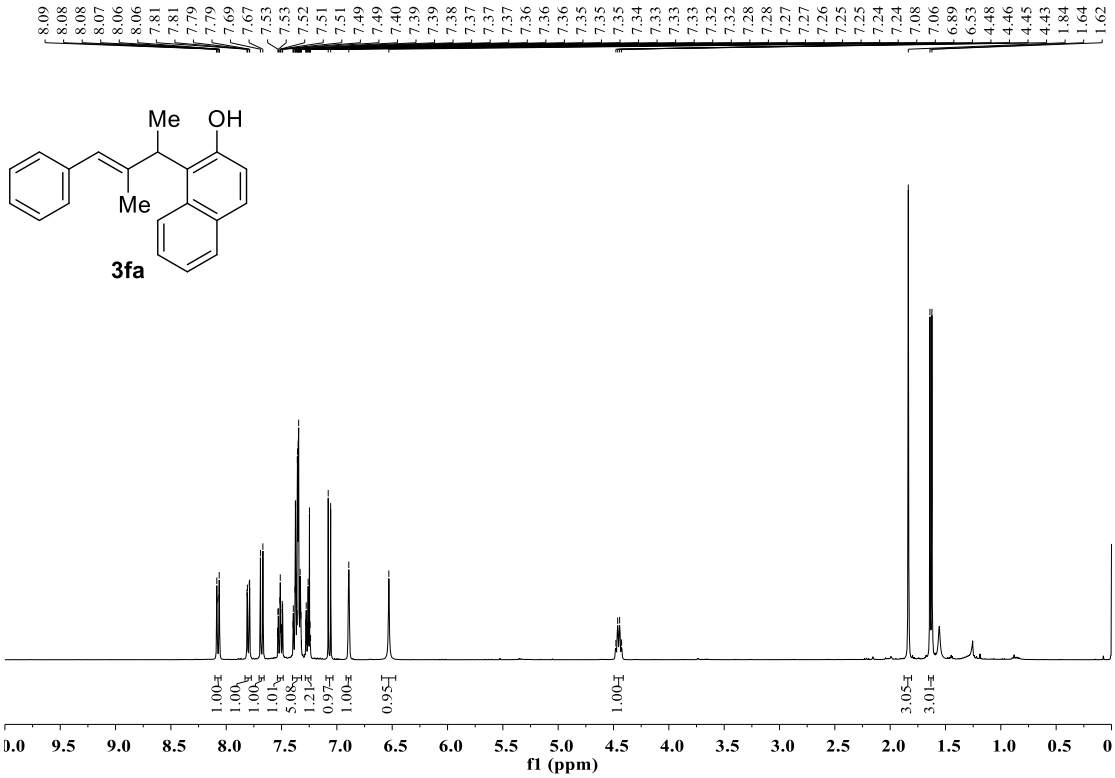

Figure S18. ^{1}H NMR spectra of **3fa**.

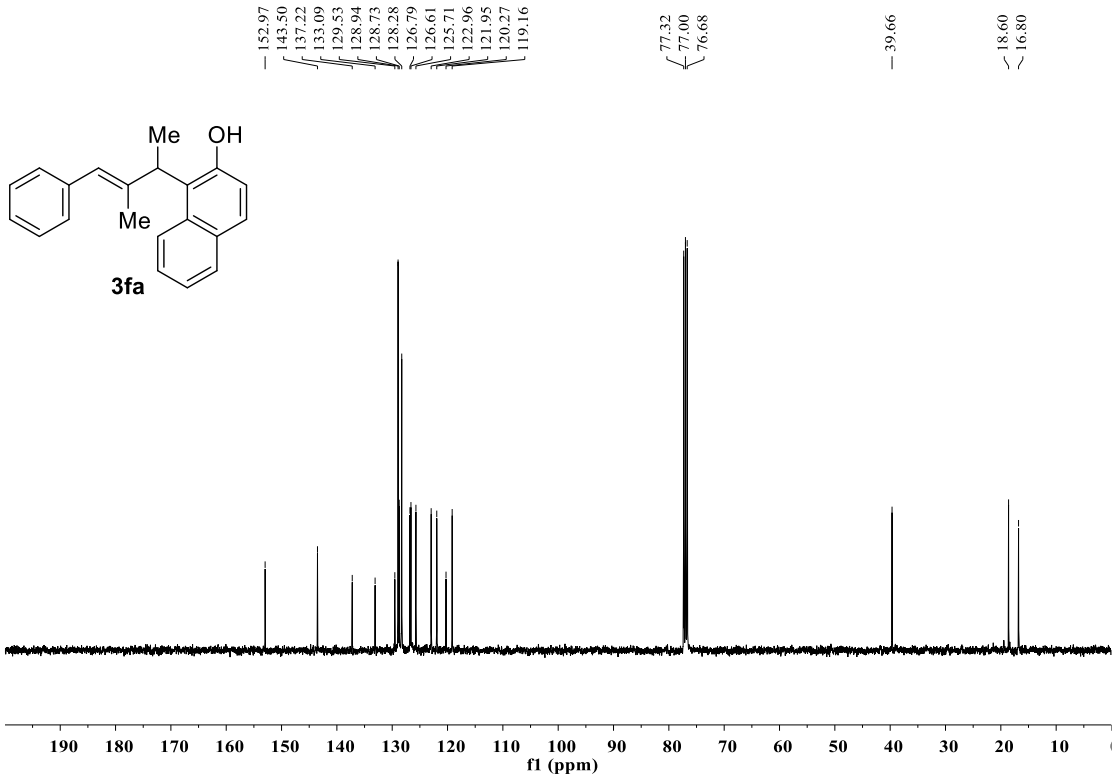

Figure S19. ^{13}C NMR spectra of **3fa**.

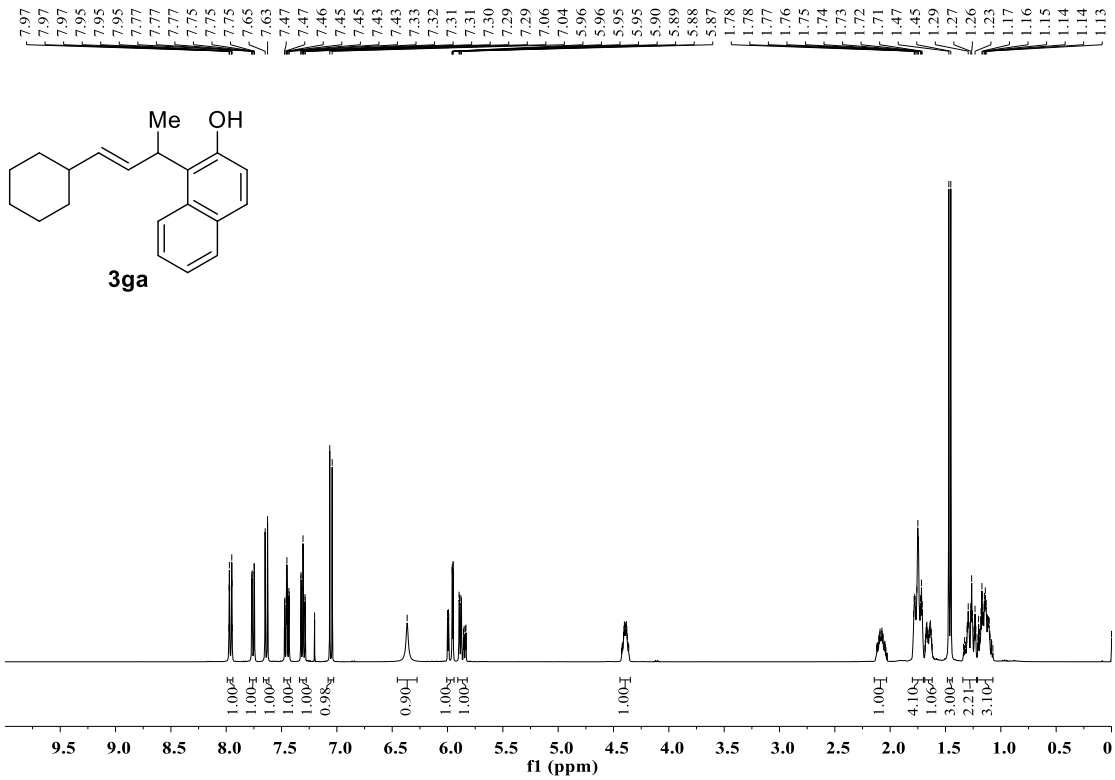

Figure S20. ^{1}H NMR spectra of **3ga**.

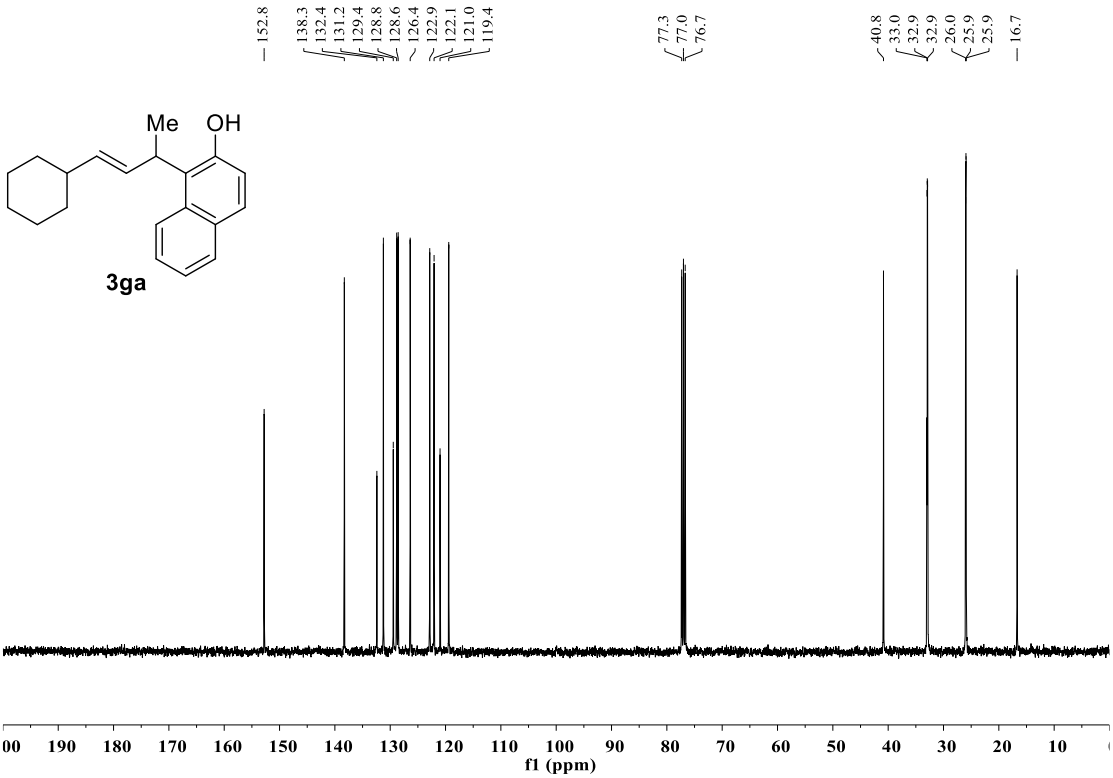

Figure S21. ^{13}C NMR spectra of **3ga**.

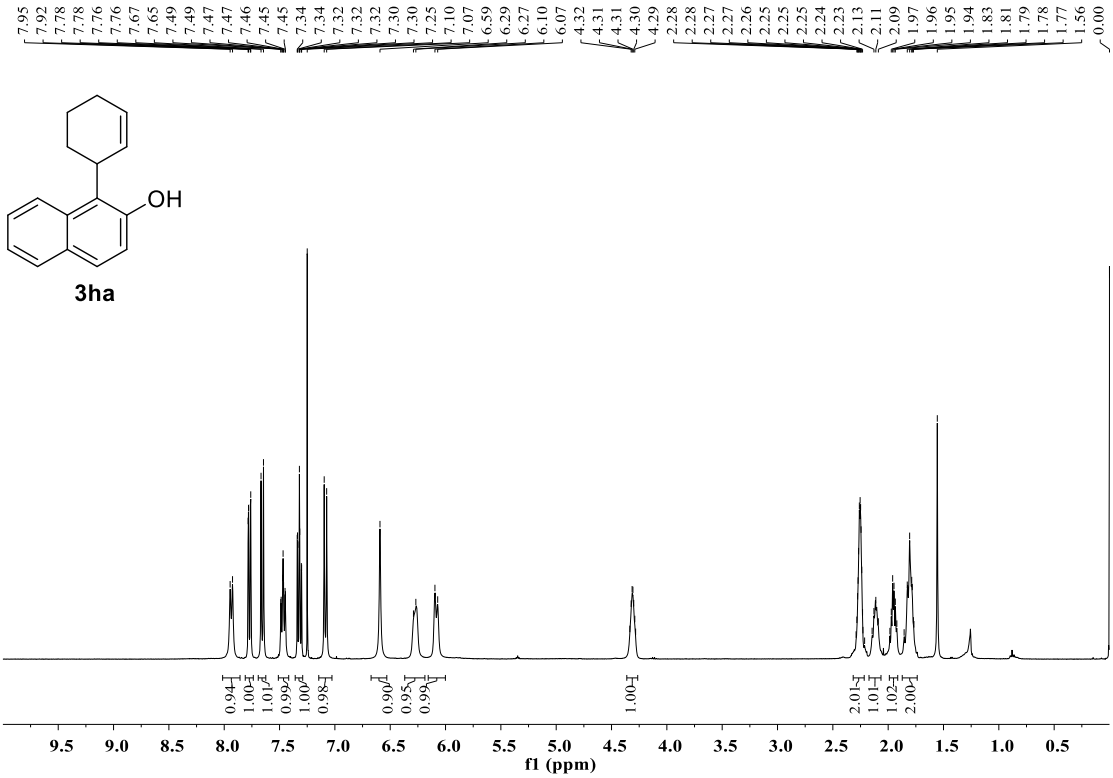

Figure S22. ^{1}H NMR spectra of **3ha**.

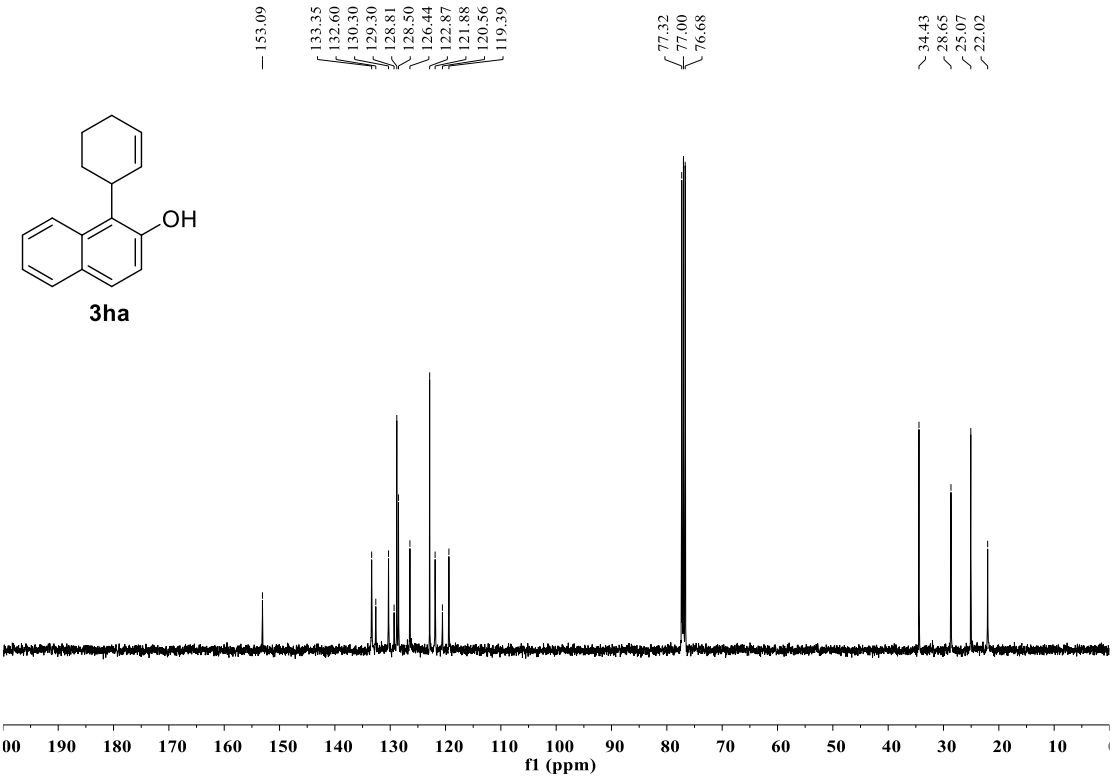

Figure S23. ^{13}C NMR spectra of **3ha**.

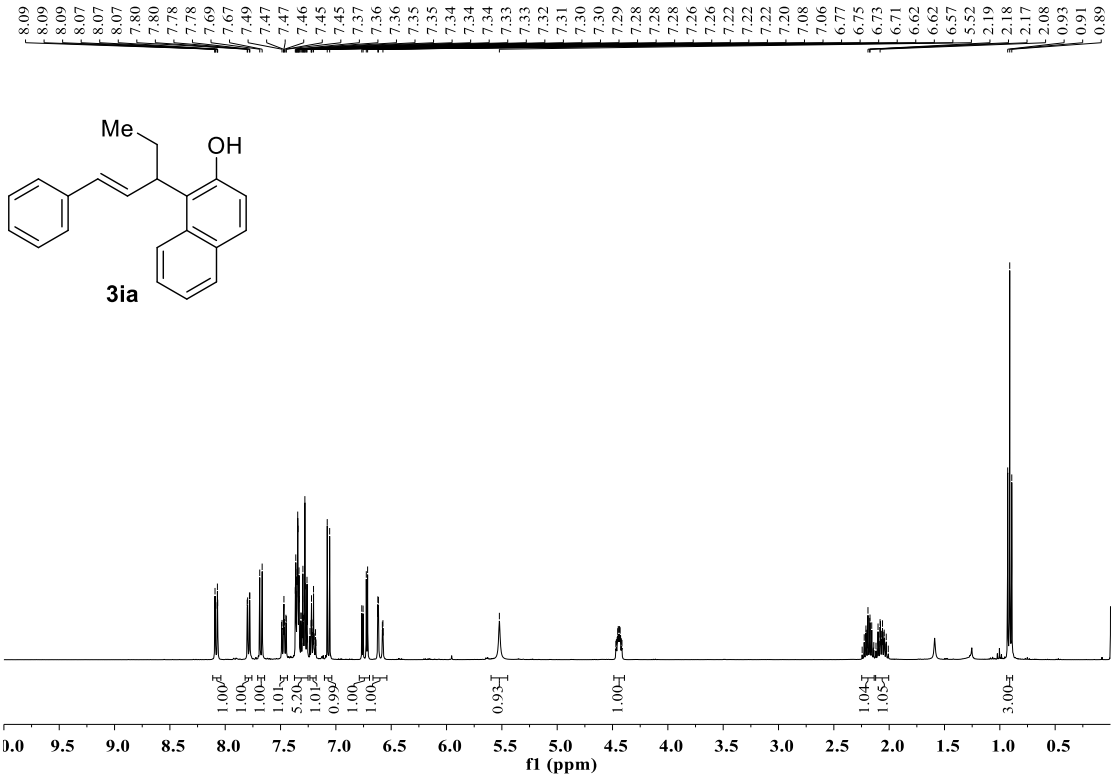

Figure S24. ^{1}H NMR spectra of **3ia**.

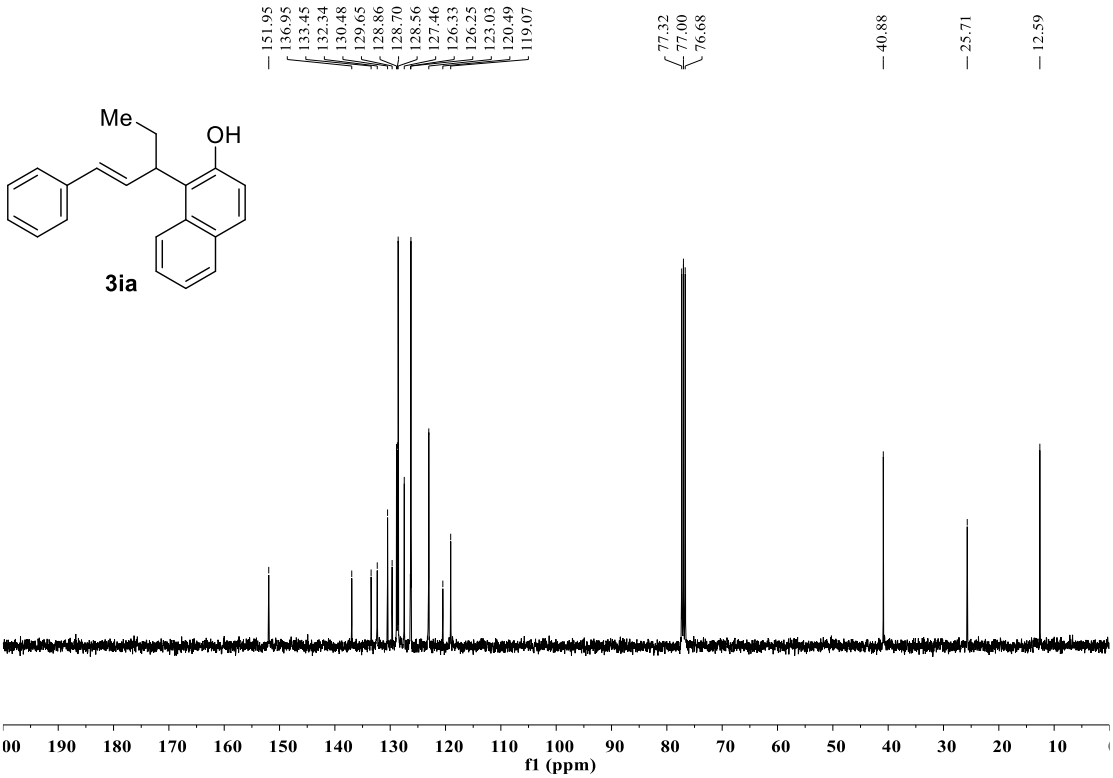

Figure S25. ^{13}C NMR spectra of **3ia**.

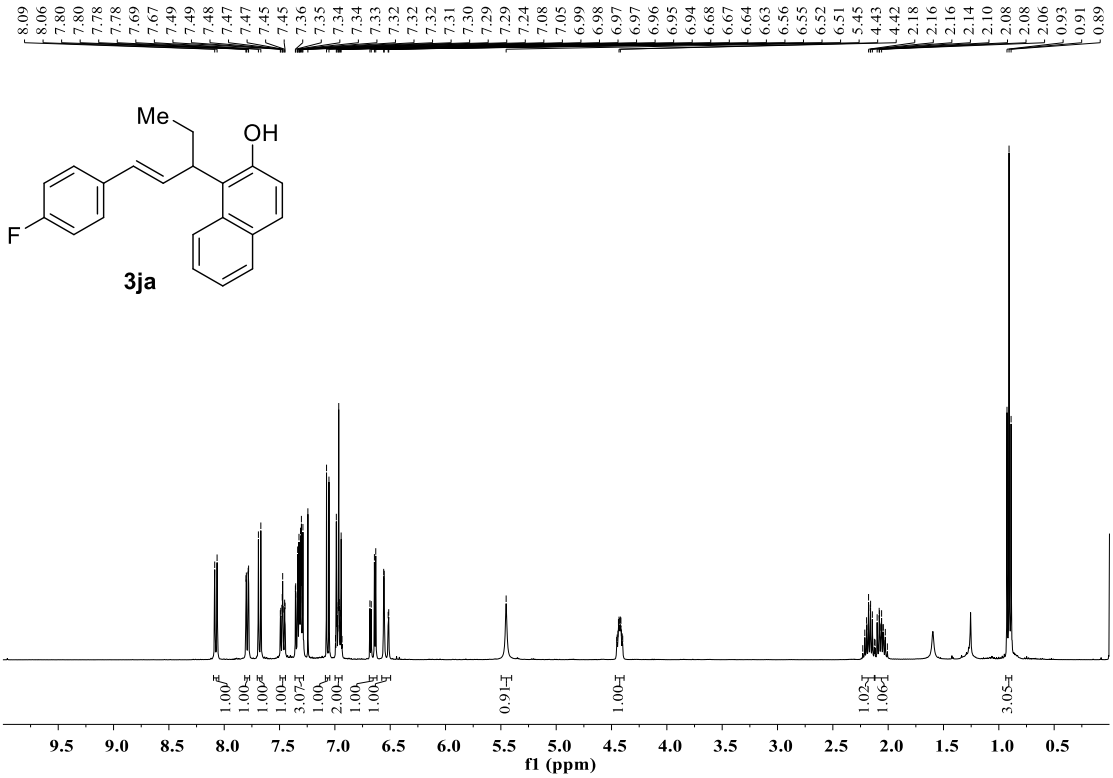

Figure S26. ^{1}H NMR spectra of **3ja**.

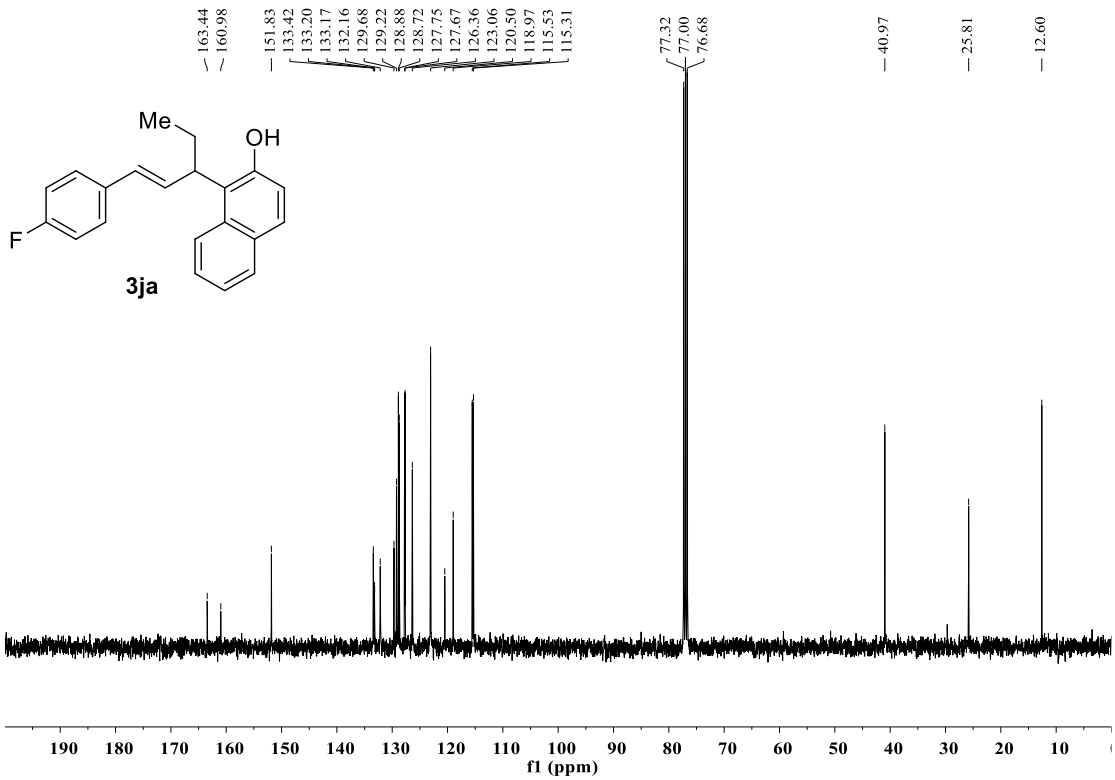

Figure S27. ^{13}C NMR spectra of **3ja**.

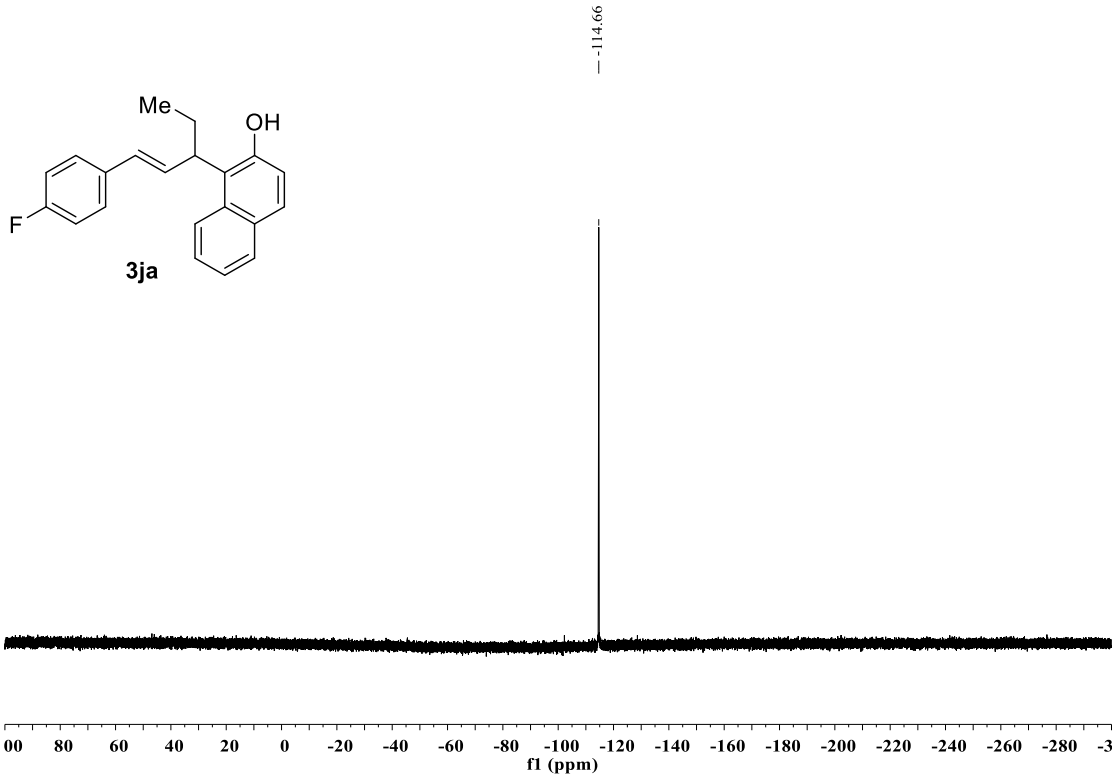

Figure S28. ^{19}F NMR spectra of **3ja**.

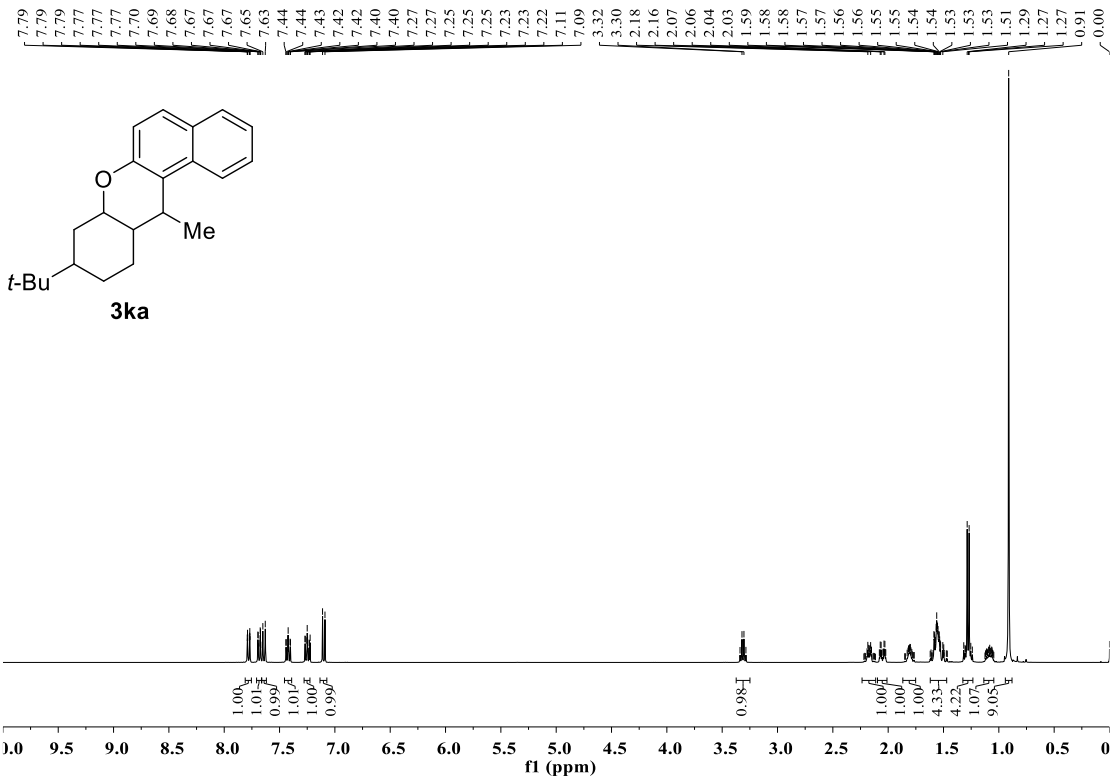

Figure S29. ^{1}H NMR spectra of **3ka**.

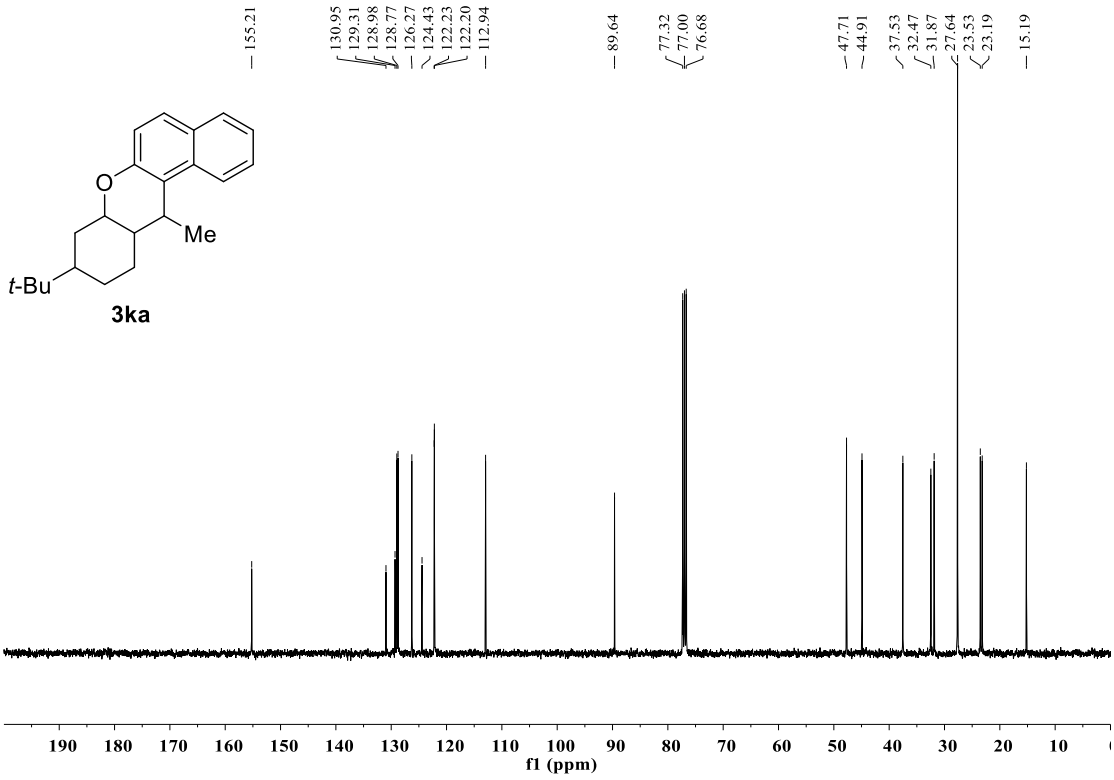

Figure S30. ^{13}C NMR spectra of **3ka**.

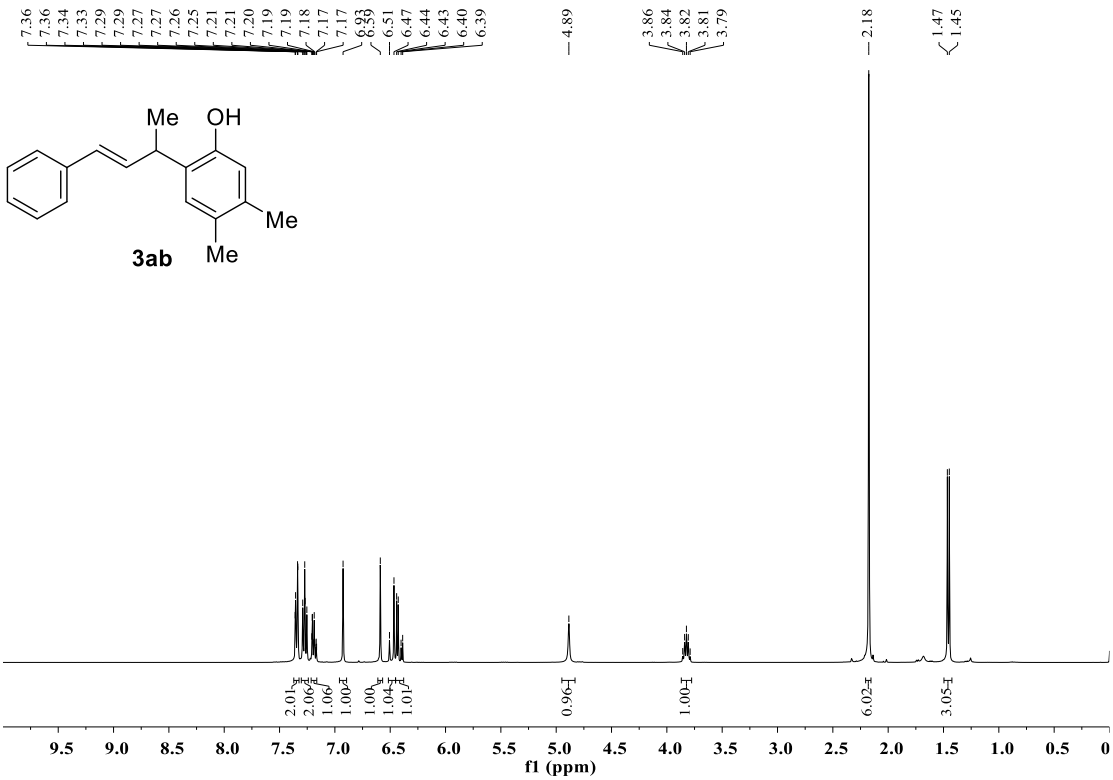

Figure S31. ^{1}H NMR spectra of **3ab**.

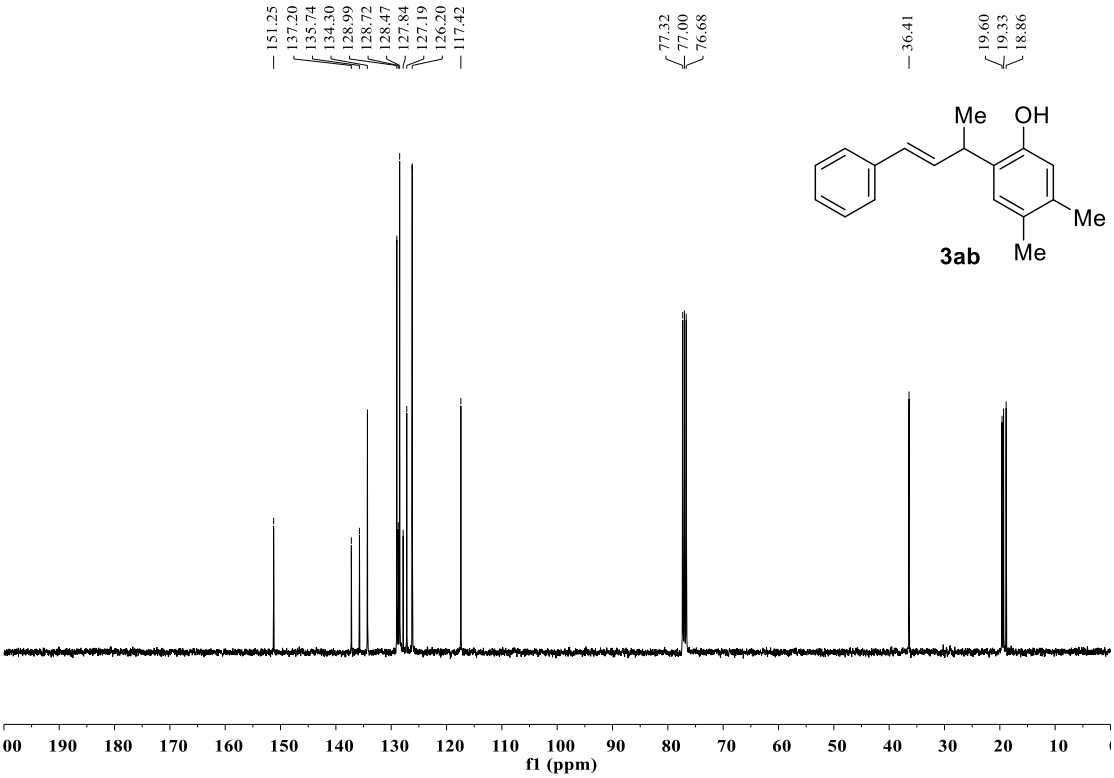

Figure S32. ^{13}C NMR spectra of **3ab**.

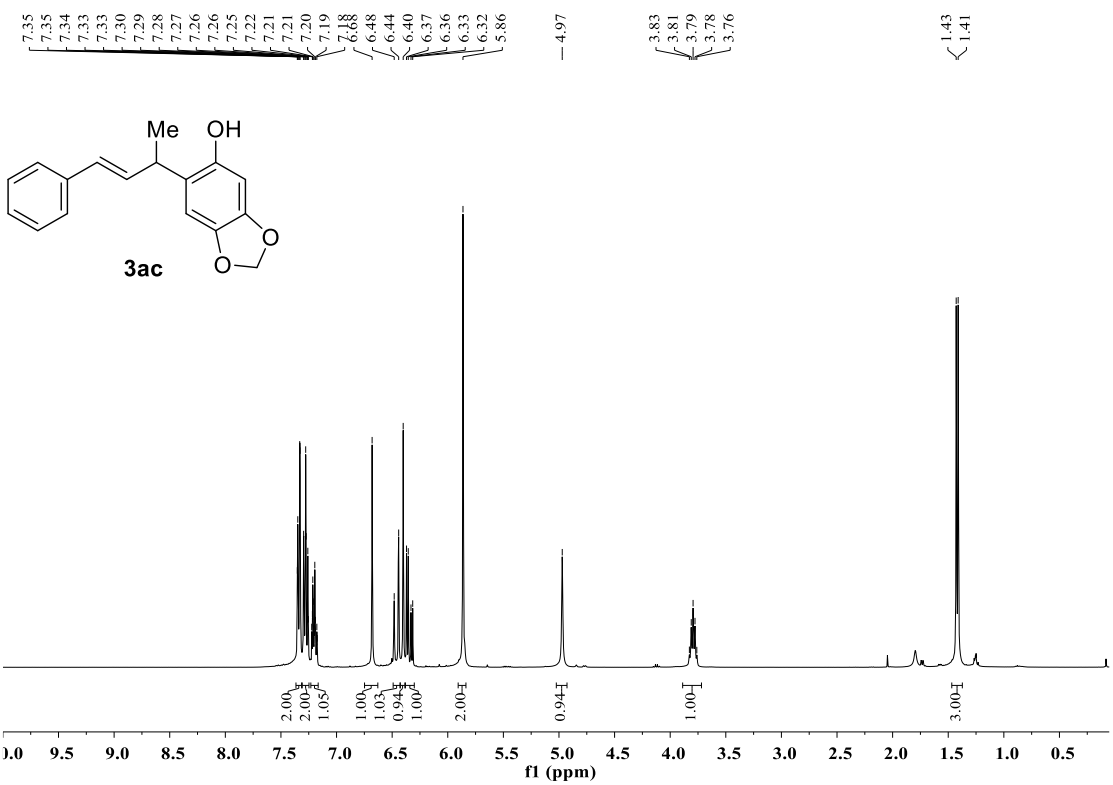

Figure S33. ^{1}H NMR spectra of **3ac**.

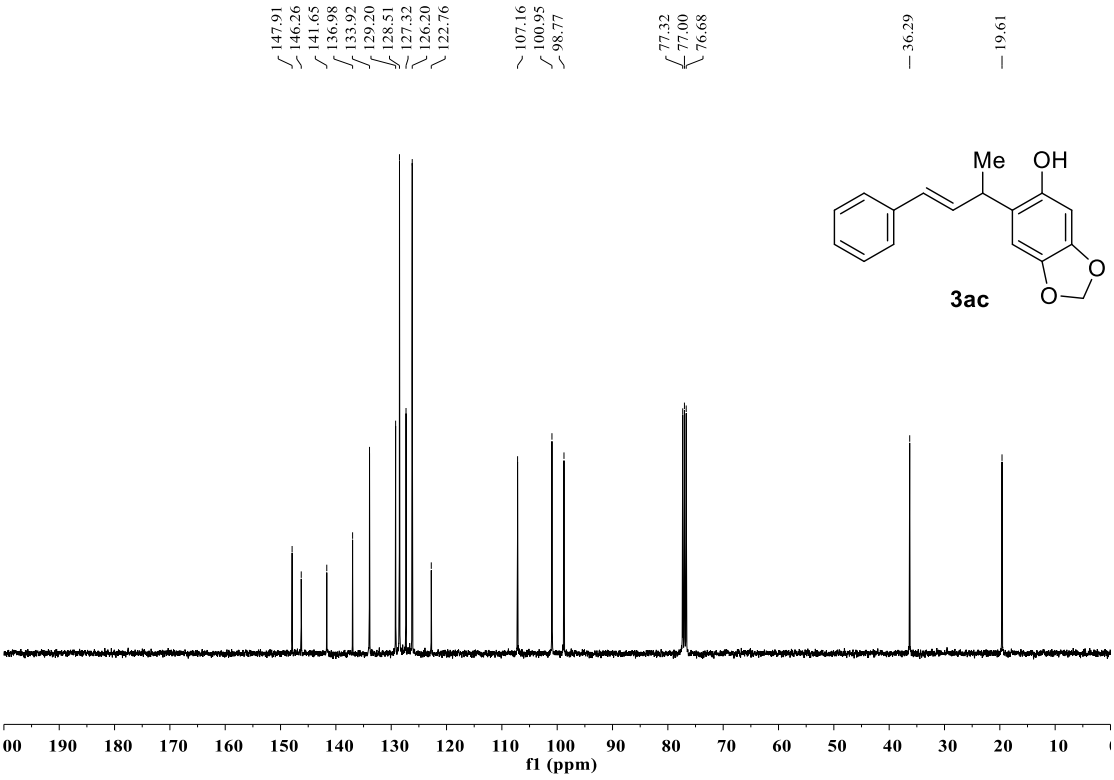

Figure S34. ^{13}C NMR spectra of **3ac**.

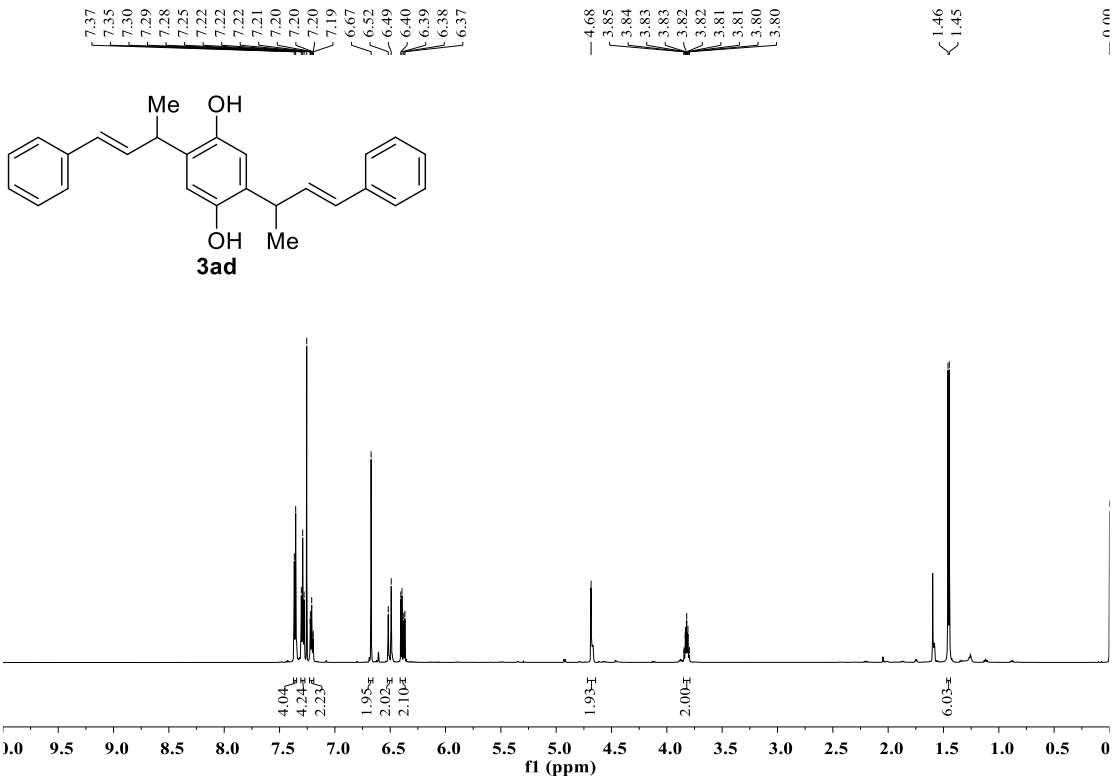

Figure S35. ^{1}H NMR spectra of **3ad**.

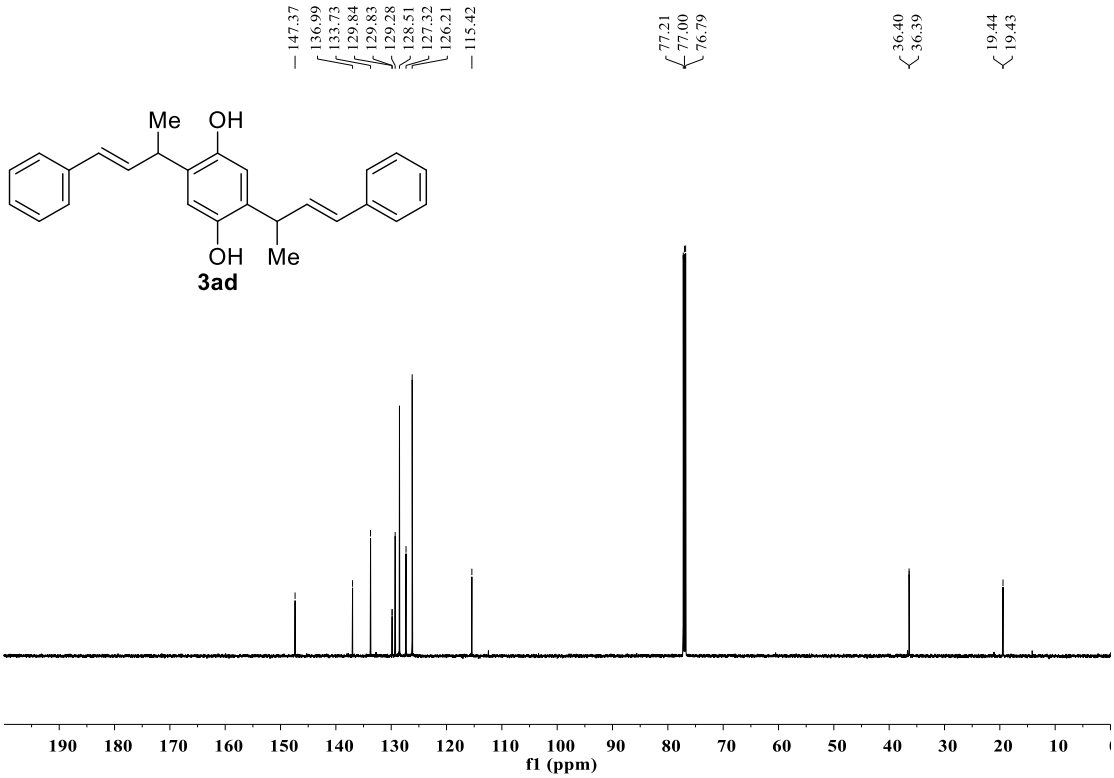

Figure S36. ^{13}C NMR spectra of **3ad**.

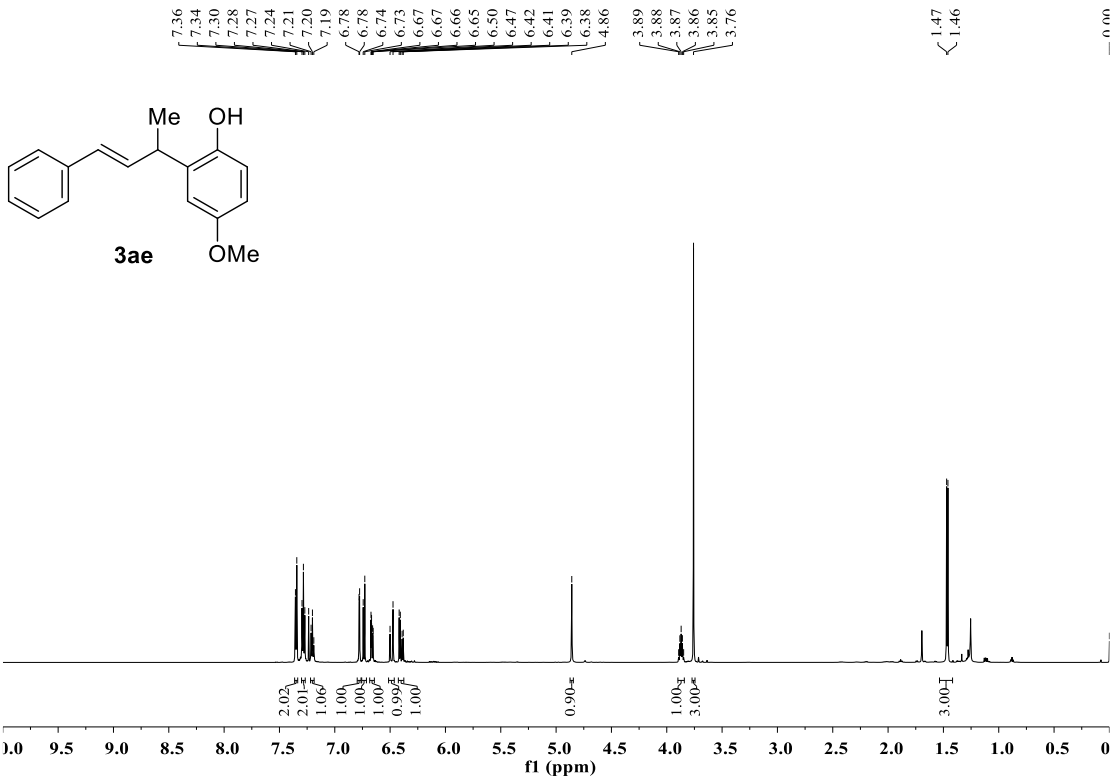

Figure S37. ^{1}H NMR spectra of **3ae**.

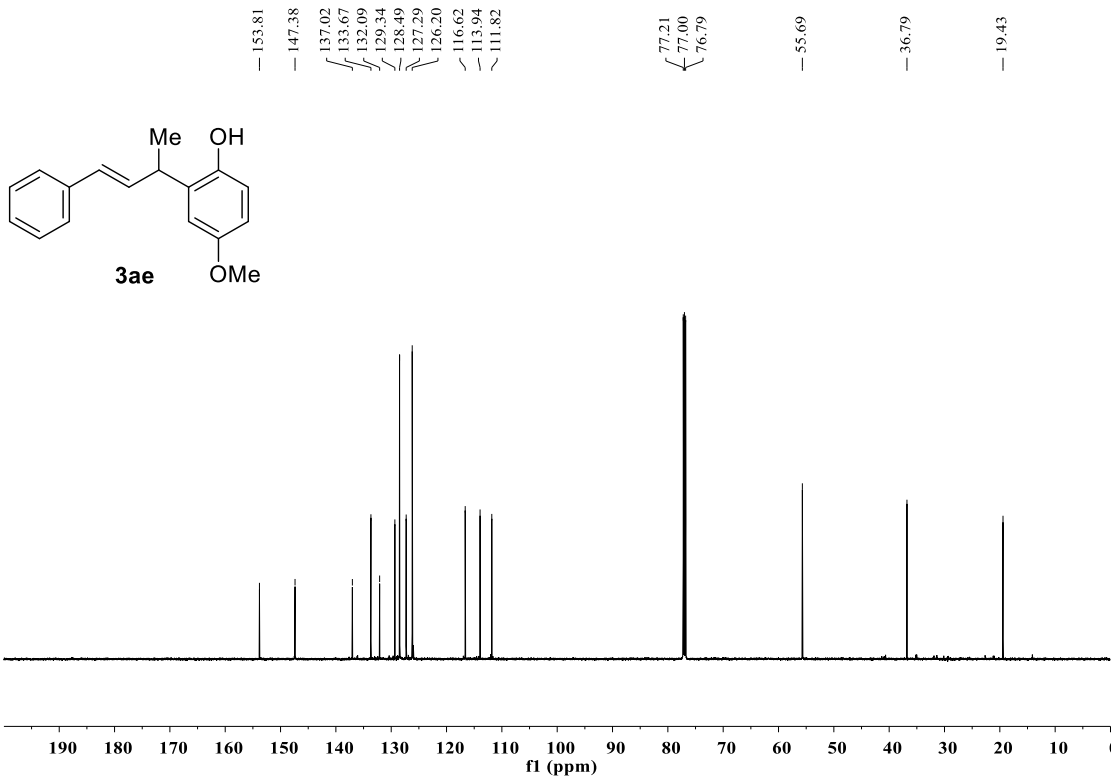

Figure S38. ^{13}C NMR spectra of **3ae**.

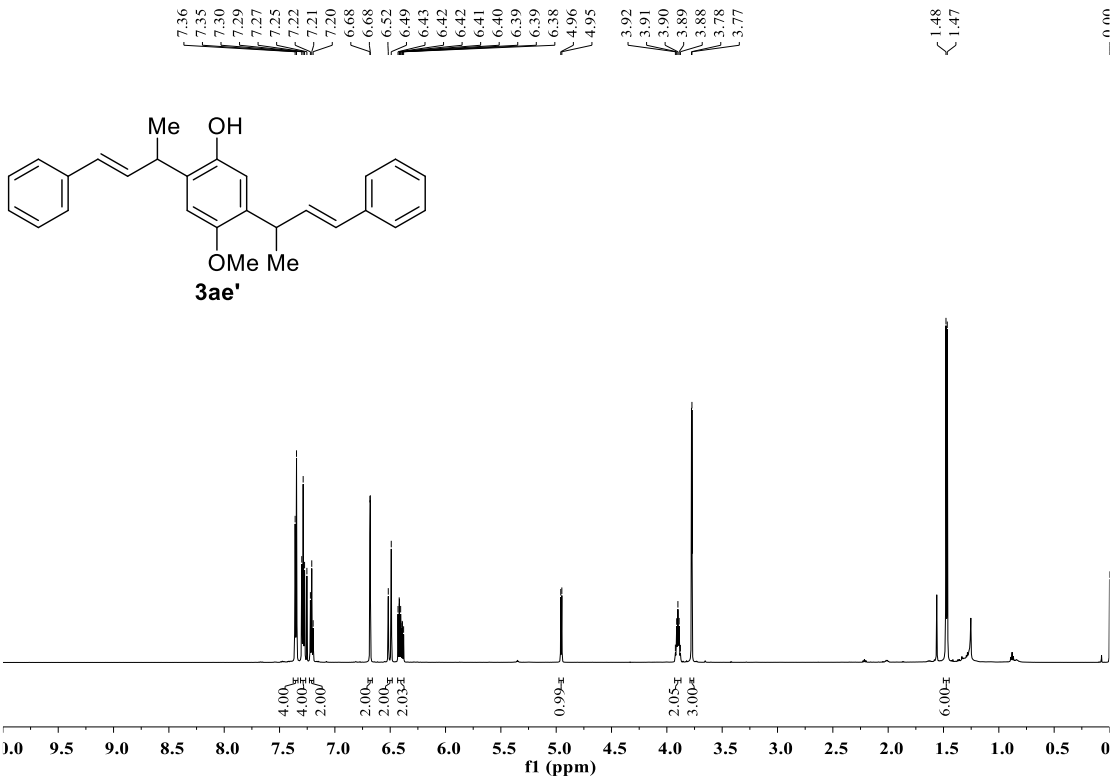

Figure S39. ^{1}H NMR spectra of **3ae'**.

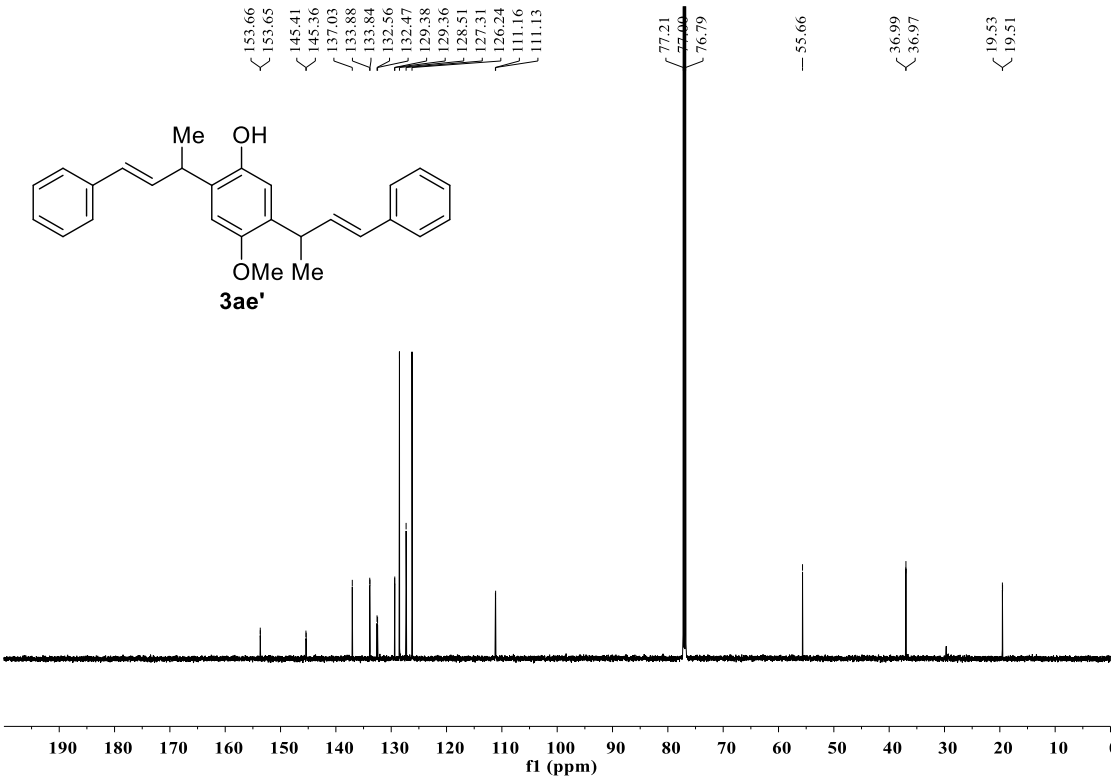

Figure S40. ^{13}C NMR spectra of **3ae'**.

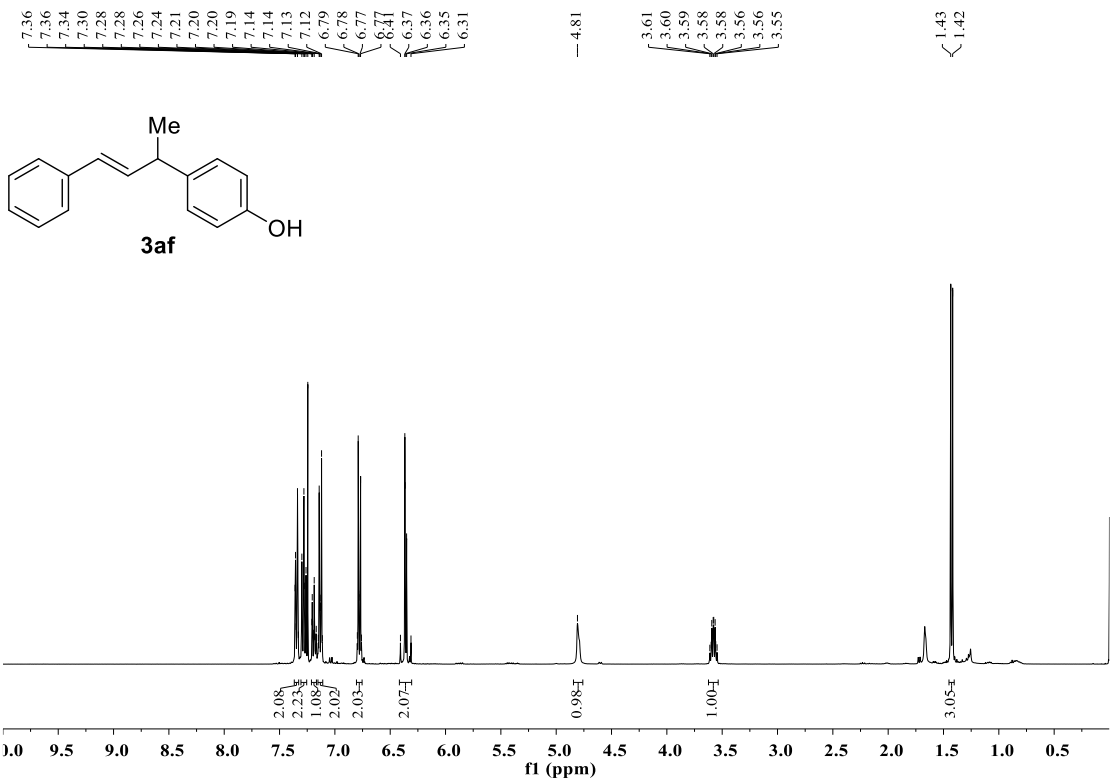

Figure S41. ^{1}H NMR spectra of **3af**.

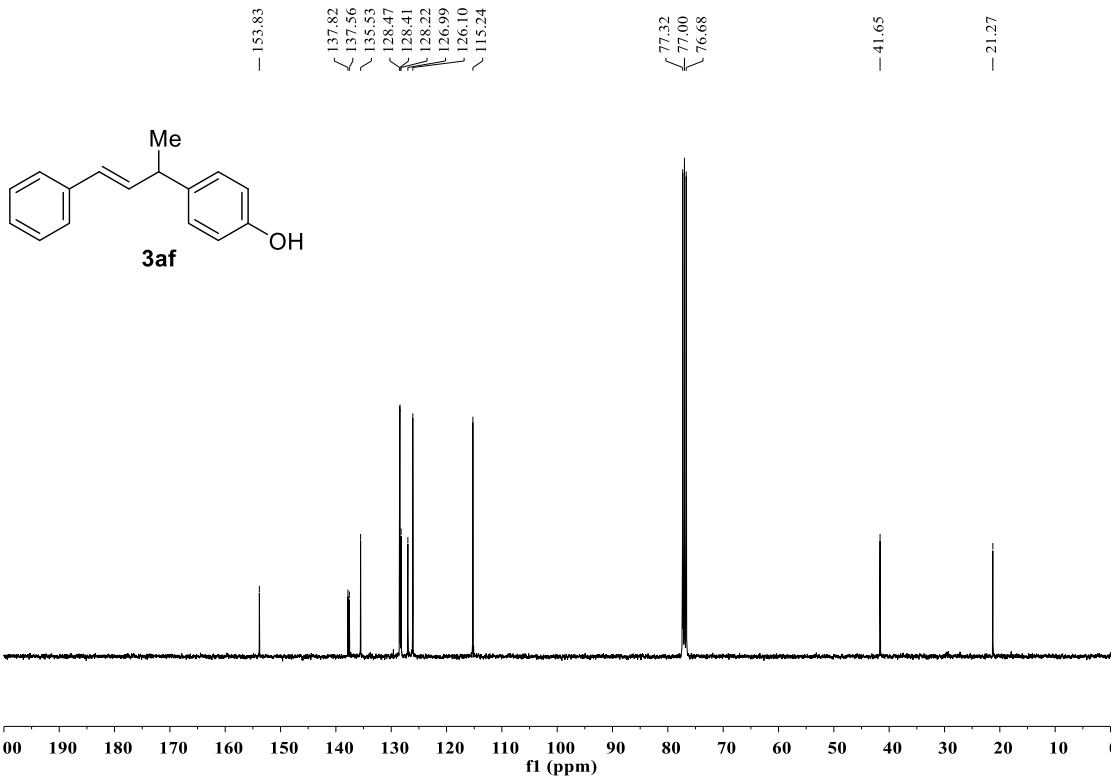

Figure S42. ^{13}C NMR spectra of **3af**.

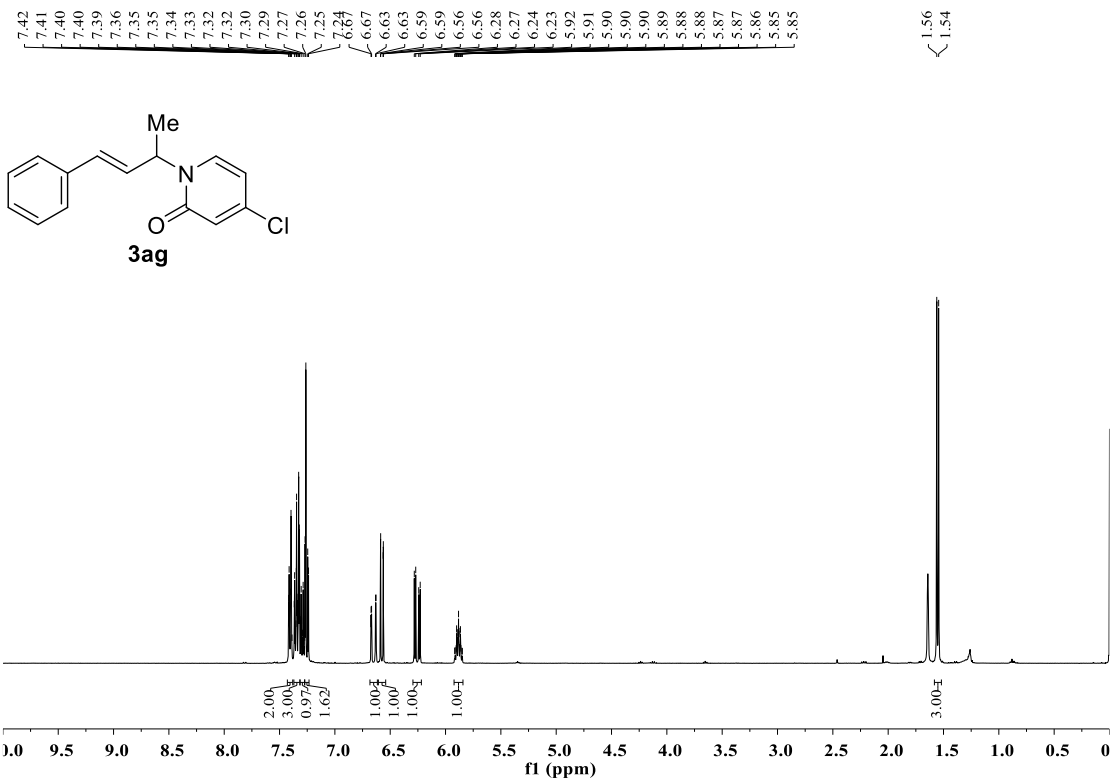

Figure S43. ^{1}H NMR spectra of **3ag**.

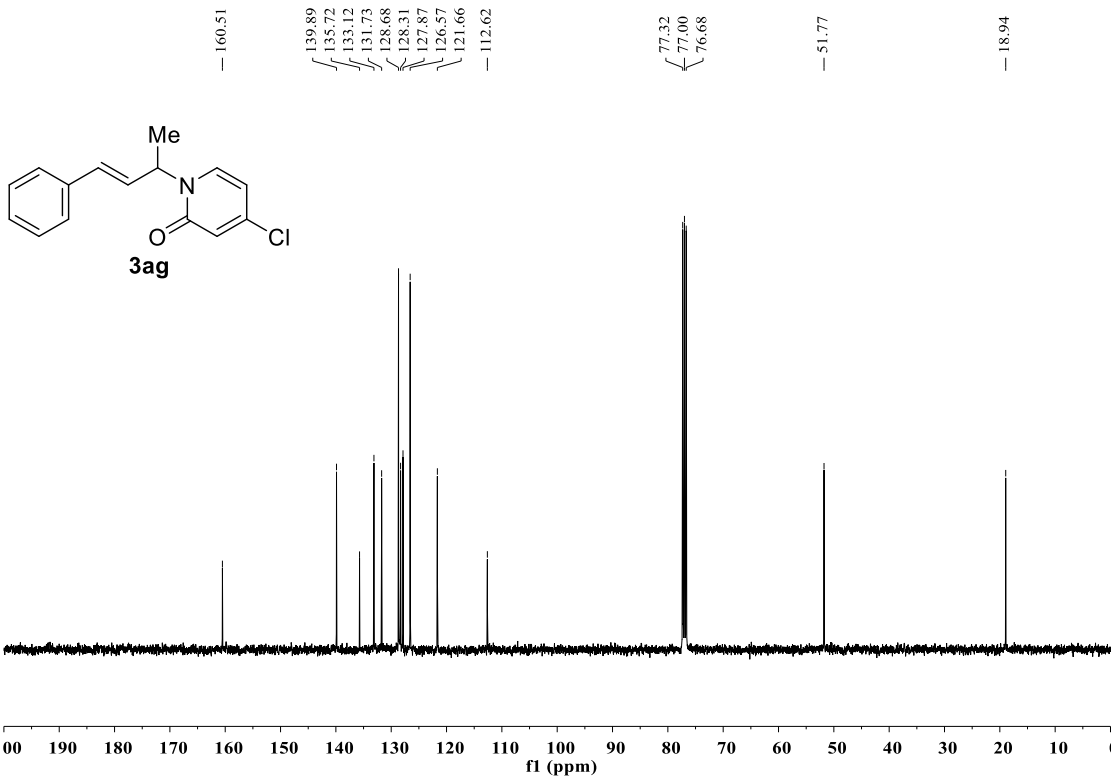

Figure S44. ^{13}C NMR spectra of **3ag**.

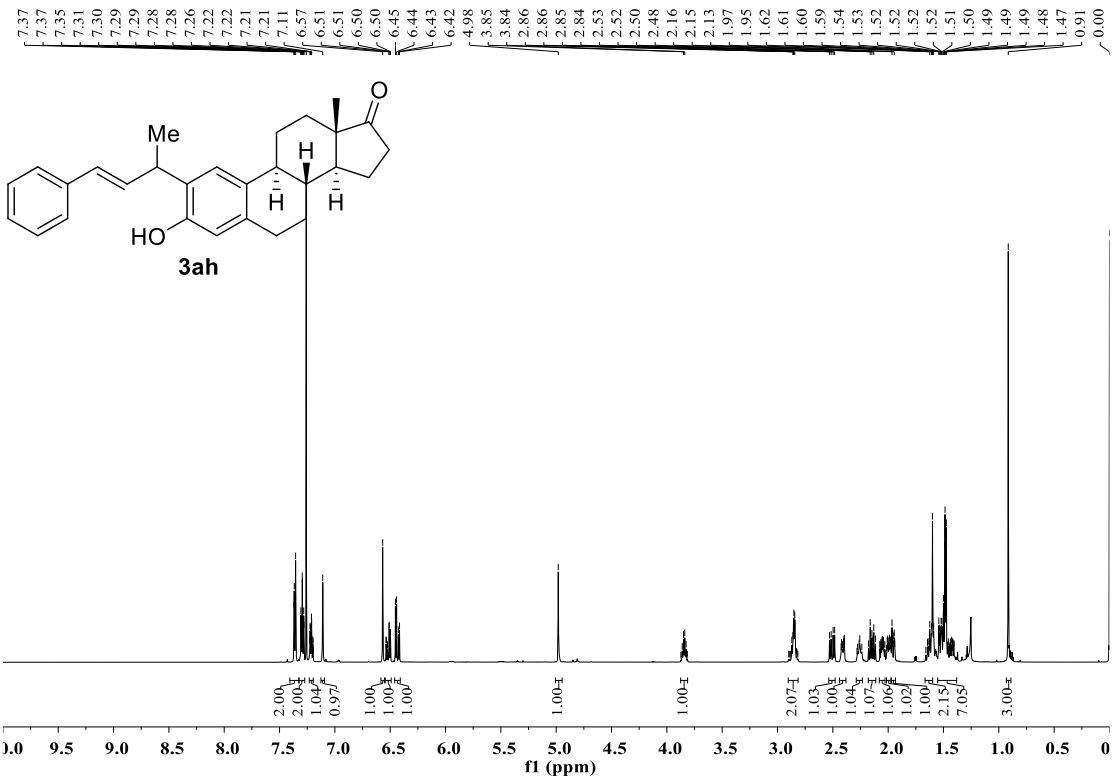

Figure S45. ^{1}H NMR spectra of **3ah**.

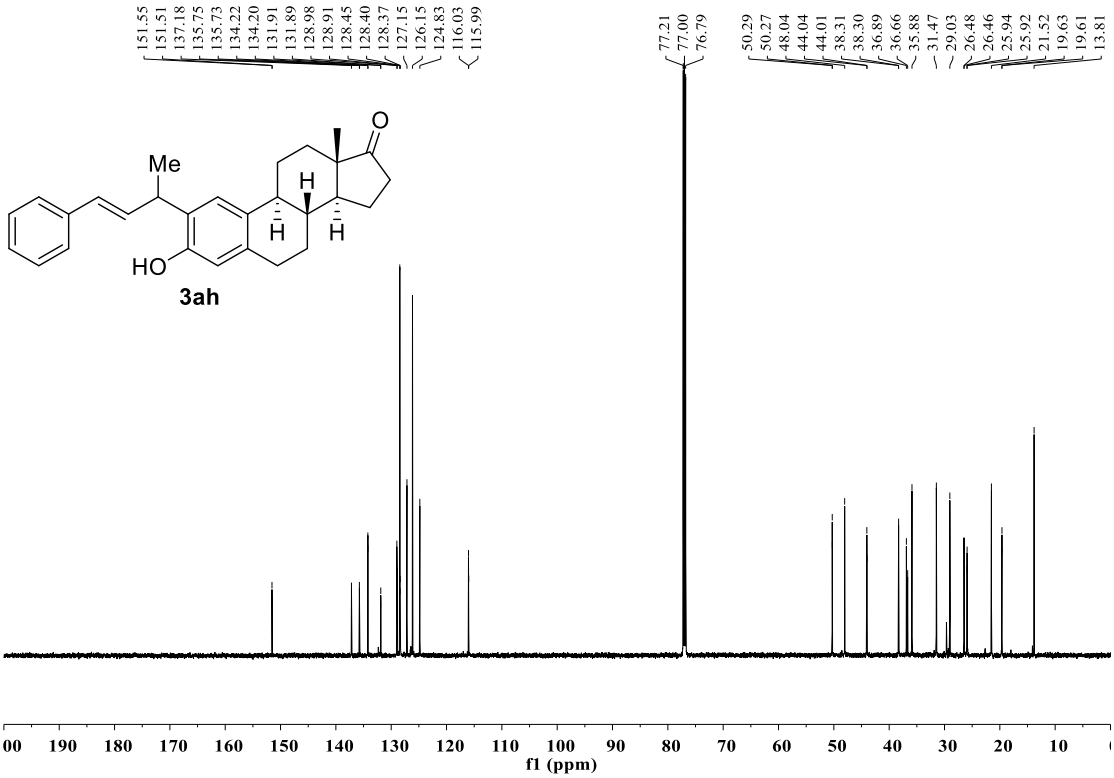

Figure S46. ^{13}C NMR spectra of **3ah**.

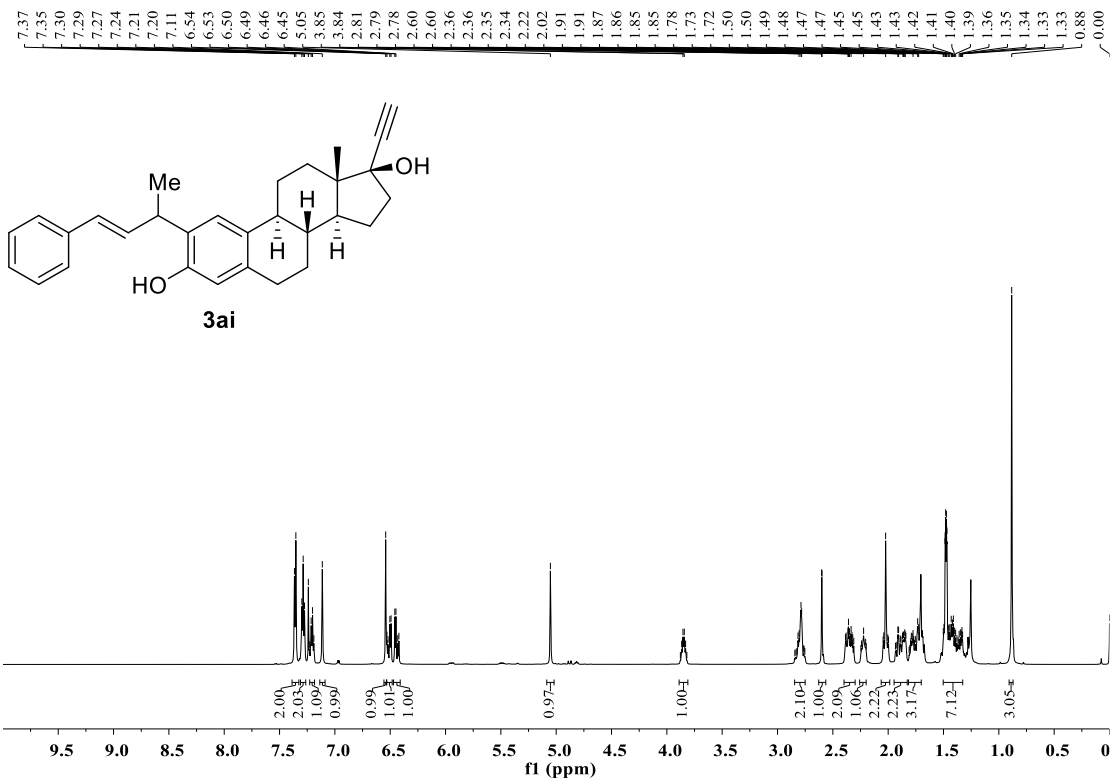

Figure S47. ^{1}H NMR spectra of **3ai**.

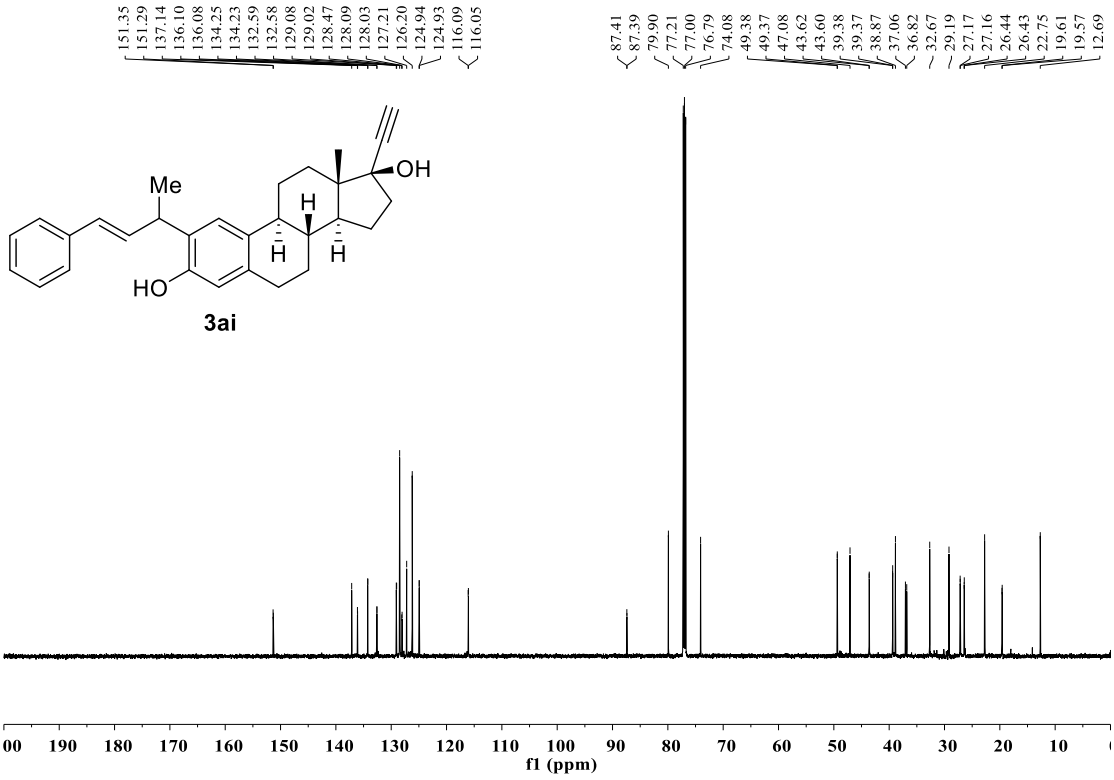

Figure S48. ^{13}C NMR spectra of **3ai**.

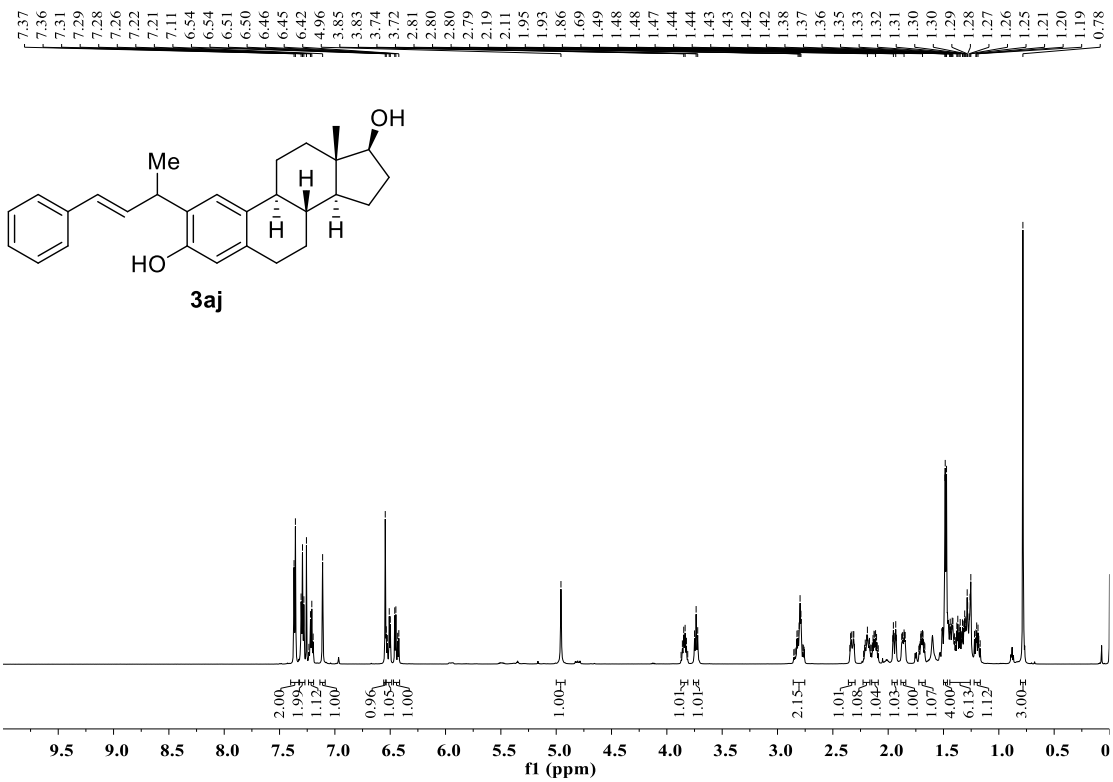

Figure S49. ^{1}H NMR spectra of **3aj**.

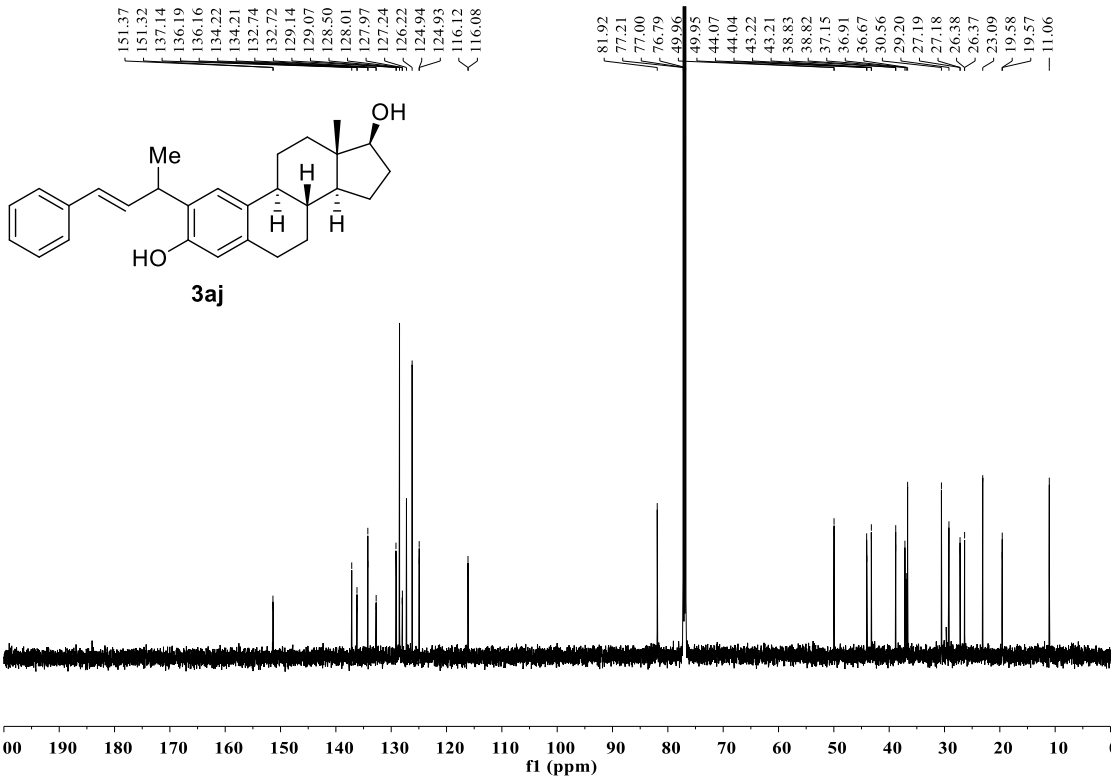

Figure S50. ^{13}C NMR spectra of **3aj**.