Supporting Information For:

Cobalt-Catalyzed Hydroxymethylarylation of Terpenes with Formaldehyde and Arenes

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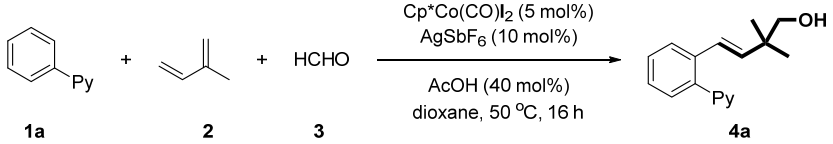
1. General experimental details.

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. Unless otherwise stated, all reactions were conducted under inert atmosphere using standard Schlenk techniques or in an argon-filled glove-box. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ or DMSO-d_6 on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF). The 2-phenylpyridine derivatives and terpenes were synthesized by the known methods.[1, 2]

2. Typical procedure for Co-catalyzed hydroxymethylarylation reaction of terpenes.

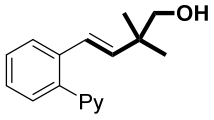


1a **2** **3** **4a**

To a sealed tube (4 mL) was sequentially added 2-phenylpyridine **1a** (0.20 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (10.0 mol%), AcOH (40 mol%), paraformaldehyde **3** (3.0 equiv), dioxane (0.50 mL), and isoprene **2** (2.0 equiv). The resulting mixture was then stirred at 50 ^oC for 16 h. The system was diluted with DCM and washed with water. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4:1) to afford **4a** (43.3 mg, 86%) as a colorless oil.

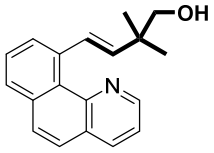
We also evaluated other directing groups. For example, the amide[phenyl(pyrrolidin-1-yl)methanone] and 2-phenyl-4,5-dihydrooxazole could not facilitate the coupling, while 1-phenyl-1H-pyrazole and acetophenone oxime led to the desired products in low yields.

Unfortunately, the employment of N-(2-Pyridinyl)pyrrole as substrate only gave a trace amount of coupling product.



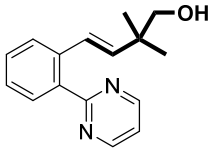
4a

(*E*)-2,2-dimethyl-4-(2-(pyridin-2-yl)phenyl)but-3-en-1-ol (4a): colorless oil, 43.3 mg, 86% yield, R_f = 0.15 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.2 Hz, 1H), 7.75 (td, *J* = 7.7, 1.7 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.50–7.44 (m, 2H), 7.34 (pd, *J* = 7.3, 1.4 Hz, 2H), 7.29–7.21 (m, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 5.95 (d, *J* = 16.2 Hz, 1H), 3.35 (s, 2H), 2.70 (brs, 1H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.1, 138.8, 138.4, 136.7, 136.3, 129.8, 128.8, 128.7, 127.2, 126.9, 124.5, 121.9, 71.5, 39.1, 24.0. **HRMS** calculated for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1534.



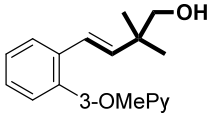
4b

(*E*)-4-(benzo[*h*]quinolin-10-yl)-2,2-dimethylbut-3-en-1-ol (4b): yellow solid, m.p. 90–91 ^oC, 55.4 mg, >99% yield, R_f = 0.60 (petroleum ether/EtOAc 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.81 (m, 3H), 7.67–7.58 (m, 3H), 7.47 (dd, *J* = 8.0, 4.4 Hz, 1H), 5.76 (d, *J* = 16.3 Hz, 1H), 4.47 (brs, 1H), 3.55 (s, 2H), 1.26 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 147.4, 139.1, 136.2, 136.1, 135.2, 134.7, 128.6, 128.4, 128.0, 127.9, 127.8, 127.7, 125.7, 121.0, 71.6, 38.8, 24.9. **HRMS** calculated for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1539, found 278.1538.



4c

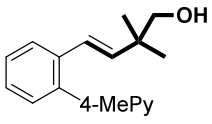
(*E*)-2,2-dimethyl-4-(2-(pyrimidin-2-yl)phenyl)but-3-en-1-ol (4c): yellow oil, 20.4 mg, 40% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.9 Hz, 2H), 7.99 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.47–7.35 (m, 2H), 7.22 (t, *J* = 4.9 Hz, 1H), 6.81 (d, *J* = 16.3 Hz, 1H), 5.88 (d, *J* = 16.2 Hz, 1H), 3.40 (s, 2H), 3.15 (brs, 1H), 1.12 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 157.0, 138.5, 138.2, 135.8, 130.8, 130.7, 130.1, 127.7, 127.3, 118.7, 71.4, 39.2, 24.1. **HRMS** calculated for $C_{16}H_{19}N_2O$ $[M+H]^+$ 255.1492, found 255.1495.



4d

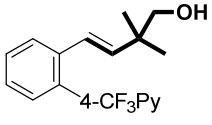
(*E*)-4-(2-(3-methoxypyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4d): colorless oil, 39.0 mg, 69% yield, R_f = 0.15 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34–8.22 (m, 1H), 7.55 (d, *J* = 7.1 Hz, 1H),

7.42–7.33 (m, 2H), 7.31 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.29–7.23 (m, 2H), 6.20 (d, *J* = 16.2 Hz, 1H), 5.91 (d, *J* = 16.2 Hz, 1H), 3.76 (s, 3H), 3.26 (s, 2H), 2.13 (brs, 1H), 0.96 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 149.2, 141.2, 137.9, 136.6, 136.0, 130.1, 128.4, 128.0, 126.8, 125.7, 123.3, 118.4, 71.3, 55.6, 39.0, 23.8. **HRMS** calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1647.



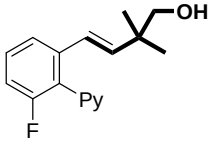
4e

(*E*)-2,2-dimethyl-4-(2-(4-methylpyridin-2-yl)phenyl)but-3-en-1-ol (4e): yellow oil, 35.3 mg, 66% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.0 Hz, 1H), 7.50 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.40–7.27 (m, 3H), 7.10–7.04 (m, 1H), 6.48 (d, *J* = 16.3 Hz, 1H), 5.94 (d, *J* = 16.2 Hz, 1H), 3.36 (s, 2H), 2.65 (brs, 1H), 2.40 (s, 3H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 148.8, 147.4, 138.5, 138.4, 136.8, 129.7, 129.2, 128.5, 127.2, 126.9, 125.4, 122.9, 71.6, 39.1, 24.0, 21.1. **HRMS** calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1700.



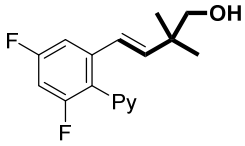
4f

(*E*)-2,2-dimethyl-4-(2-(4-(trifluoromethyl)pyridin-2-yl)phenyl)but-3-en-1-ol (4f): yellow oil, 30.2 mg, 47% yield, R_f = 0.50 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 5.1 Hz, 1H), 7.73 (s, 1H), 7.57–7.52 (m, 2H), 7.49–7.46 (m, 1H), 7.44–7.34 (m, 2H), 6.46 (d, *J* = 16.2 Hz, 1H), 6.03 (d, *J* = 16.2 Hz, 1H), 3.39 (s, 2H), 2.19 (brs, 1H), 1.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 150.2, 139.7, 138.7 (q, *J* = 33.9 Hz), 137.0, 136.8, 129.9, 129.4, 128.2, 127.5, 127.3, 124.2 (q, *J* = 273.4 Hz), 120.3 (q, *J* = 3.6 Hz), 117.3 (q, *J* = 3.5 Hz), 71.5, 39.1, 23.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.77. **HRMS** calculated for $C_{18}H_{19}F_3NO$ $[M+H]^+$ 322.1413, found 322.1412.



4g

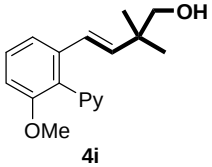
(*E*)-4-(3-fluoro-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4g): colorless oil, 46.9 mg, 86% yield, R_f = 0.30 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.3 Hz, 1H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30 (m, 3H), 7.03 (dq, *J* = 9.4, 1.8 Hz, 1H), 6.16 (d, *J* = 16.2 Hz, 1H), 5.96 (d, *J* = 16.2 Hz, 1H), 3.27 (s, 2H), 2.84 (s, 1H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 246.1 Hz), 158.8, 153.3, 149.3, 140.2, 139.5 (d, *J* = 2.8 Hz), 136.2, 129.7 (d, *J* = 9.2 Hz), 126.9 (d, *J* = 3.2 Hz), 126.3 (d, *J* = 2.7 Hz), 122.5, 122.0 (d, *J* = 3.1 Hz), 114.2 (d, *J* = 22.9 Hz), 71.4, 39.1, 23.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.20. **HRMS** calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1448.



4h

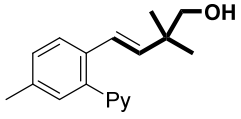
(*E*)-4-(3,5-difluoro-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4h): yellow oil, 54.2 mg, 94% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72–8.64 (m, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48–7.37 (m, 1H), 7.34–7.23 (m, 1H), 7.16–6.99 (m, 1H), 6.79 (ddd, *J* = 9.8, 8.6, 2.5 Hz, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 5.99 (d, *J* = 16.2 Hz, 1H), 3.29 (s, 2H), 2.68 (brs, 1H), 0.96 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8 (dd, *J* = 248.6 Hz), 161.7 (dd, *J* = 248.4 Hz), 152.5, 149.4, 141.2, 140.9 (d, *J* = 4.4 Hz), 140.8 (d, *J* = 4.4 Hz), 136.3, 126.4 (d, *J* = 2.7 Hz), 126.3 (t, *J* = 2.9 Hz), 122.6, 108.9 (d, *J* = 3.4 Hz), 108.8 (d, *J* = 3.4 Hz) 102.6 (d, *J* = 25.8 Hz), 102.3 (d, *J* = 25.8 Hz), 71.3, 39.1, 23.6. **^{19}F NMR** (376

MHz, $CDCl_3$) δ -109.96 (d, *J* = 8.1 Hz), -112.85 (d, *J* = 8.1 Hz). **HRMS** calculated for $C_{17}H_{18}F_2NO$ $[M+H]^+$ 290.1351, found 290.1349.



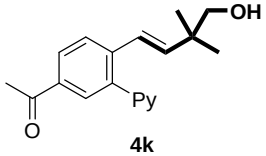
4i

(*E*)-4-(3-methoxy-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4i): colorless oil, 29.6 mg, 52% yield, R_f = 0.25 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75–8.59 (m, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.35–7.26 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.97 (d, *J* = 16.2 Hz, 1H), 5.89 (d, *J* = 16.2 Hz, 1H), 3.72 (s, 3H), 3.24 (s, 2H), 2.99 (brs, 1H), 0.91 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 155.6, 148.6, 139.4, 138.5, 136.4, 129.5, 127.5, 127.3, 126.8, 122.2, 118.7, 109.7, 71.4, 55.8, 39.0, 23.7. **HRMS** calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1643.



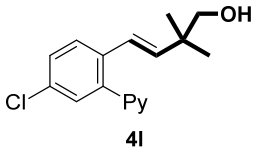
4j

(*E*)-2,2-dimethyl-4-(4-methyl-2-(pyridin-2-yl)phenyl)but-3-en-1-ol (4j): colorless oil, 40.2 mg, 75% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.2 Hz, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.26–7.21 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 5.92 (d, *J* = 16.2 Hz, 1H), 3.34 (s, 2H), 2.63 (brs, 1H), 2.38 (s, 3H), 1.03 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 149.1, 138.3, 137.9, 137.0, 136.2, 133.8, 130.4, 129.4, 128.6, 126.7, 124.5, 121.8, 71.6, 39.0, 24.0, 21.1. **HRMS** calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1695.



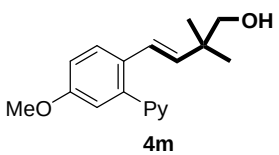
4k

(*E*)-1-(4-(4-hydroxy-3,3imethylbut-1-en-1-yl)-3-(pyridin-2-yl)phenyl) ethan-1-one (4k): yellow oil, 48.3 mg, 82% yield, R_f = 0.20 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 1.7 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.80 (td, *J* = 7.7, 1.7 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 7.1, 5.3 Hz, 1H), 6.50 (d, *J* = 16.3 Hz, 1H), 6.13 (d, *J* = 16.2 Hz, 1H), 3.38 (s, 2H), 2.78 (brs, 1H), 2.62 (s, 3H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 158.1, 149.2, 141.38, 141.36, 138.5, 136.6, 135.7, 130.2, 128.3, 127.6, 127.0, 124.7, 122.4, 71.4, 39.3, 26.6, 23.8. **HRMS** calculated for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1645, found 296.1645.



4l

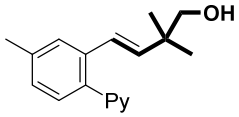
(*E*)-4-(4-chloro-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4l): colorless oil, 35.6 mg, 62% yield, R_f = 0.30 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 4.9 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 5.96 (d, *J* = 16.2 Hz, 1H), 3.35 (s, 2H), 2.75 (brs, 1H), 1.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 149.3, 139.7, 139.5, 136.5, 135.2, 132.8, 129.7, 128.6, 128.2, 127.5, 124.5, 122.4, 71.5, 39.1, 23.9. **HRMS** calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1152.



4m

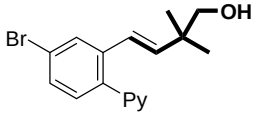
(*E*)-4-(4-methoxy-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4m): colorless oil, 31.7 mg, 56% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.0 Hz,

1H), 7.74 (qd, *J* = 8.8, 8.3, 1.8 Hz, 1H), 7.51–7.42 (m, 2H), 7.29–7.19 (m, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 5.86 (d, *J* = 16.2 Hz, 1H), 3.84 (d, *J* = 2.1 Hz, 3H), 3.34 (s, 2H), 2.48 (brs, 1H), 1.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.85, 158.77, 149.1, 139.5, 137.0, 136.3, 129.3, 128.1, 128.0, 124.6, 122.0, 114.9, 114.6, 71.6, 55.4, 39.0, 24.0. **HRMS** calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1636.



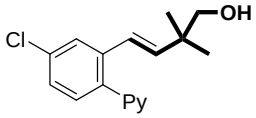
4n

(*E*)-2,2-dimethyl-4-(5-methyl-2-(pyridin-2-yl)phenyl)but-3-en-1-ol (4n): white solid, m.p. 105–106 °C, 18.8 mg, 35% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71–8.59 (m, 1H), 7.73 (t, *J* = 7.1 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.40–7.31 (m, 2H), 7.25–7.18 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 5.94 (d, *J* = 16.2 Hz, 1H), 3.37 (s, 2H), 2.68 (brs, 1H), 2.40 (s, 3H), 1.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.1, 138.5, 138.4, 136.5, 136.3, 135.7, 129.8, 129.2, 128.1, 127.5, 124.4, 121.6, 71.6, 39.1, 24.0, 21.3. **HRMS** calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1695.



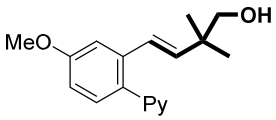
4o

(*E*)-4-(5-bromo-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4o): colorless oil, 48.5 mg, 73% yield, R_f = 0.40 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.3 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.27 (t, *J* = 6.0 Hz, 1H), 6.42 (d, *J* = 16.2 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 3.36 (s, 2H), 2.63 (brs, 1H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 149.2, 140.1, 138.7, 137.1, 136.5, 131.4, 130.1, 129.7, 127.6, 124.4, 122.9, 122.2, 71.5, 39.2, 23.9. **HRMS** calculated for $C_{17}H_{19}BrNO$ $[M+H]^+$ 332.0645, found 332.0647.



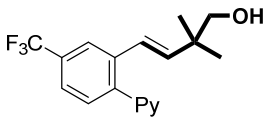
4p

(*E*)-4-(5-chloro-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4p): yellow oil, 29.4 mg, 51% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.4 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34–7.23 (m, 2H), 6.43 (d, *J* = 16.2 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 3.37 (s, 2H), 2.62 (brs, 1H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 149.2, 140.0, 138.4, 136.7, 136.5, 134.6, 131.2, 127.7, 127.2, 126.7, 124.4, 122.1, 71.5, 39.2, 23.9. **HRMS** calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1154.



4q

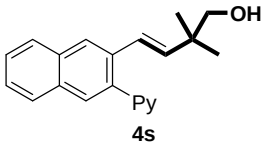
(*E*)-4-(5-methoxy-2-(pyridin-2-yl)phenyl)-2,2-dimethylbut-3-en-1-ol (4q): yellow oil, 35.4 mg, 62% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.2 Hz, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (dd, *J* = 10.7, 8.2 Hz, 2H), 7.20 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 5.96 (d, *J* = 16.2 Hz, 1H), 3.87 (s, 3H), 3.37 (s, 2H), 2.75 (brs, 1H), 1.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 158.8, 149.0, 138.8, 138.2, 136.3, 131.3, 131.2, 129.2, 124.3, 121.4, 113.0, 112.0, 71.6, 55.4, 39.1, 24.0. **HRMS** calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1648.



4r

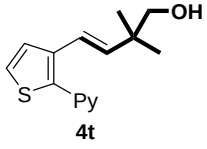
(*E*)-2,2-dimethyl-4-(2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl)but-3

-en-1-ol (4r): colorless oil, 40.0 mg, 62% yield, R_f = 0.35 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 7.82–7.73 (m, 2H), 7.57 (s, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.34–7.28 (m, 1H), 6.48 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.2 Hz, 1H), 3.38 (s, 2H), 2.63 (brs, 1H), 1.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 149.4, 141.4, 140.5, 137.5, 136.6, 130.9 (q, *J* = 32.4 Hz), 130.5, 130.3, 127.6, 124.5, 124.1 (q, *J* = 272.3 Hz). 123.7 (q, *J* = 3.8 Hz), 122.6, 71.5, 39.2, 23.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.59. **HRMS** calculated for $C_{18}H_{19}F_3NO$ $[M+H]^+$ 322.1413, found 322.1414.



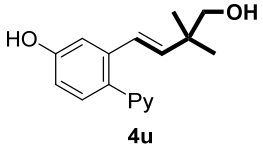
4s

(*E*)-2,2-dimethyl-4-(3-(pyridin-2-yl)naphthalen-2-yl)but-3-en-1-ol (4s): yellow oil, 60.6 mg, >99% yield, R_f = 0.35 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79–8.60 (m, 1H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.86–7.79 (m, 2H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.51–7.40 (m, 2H), 7.25 (ddd, *J* = 7.5, 4.4, 1.0 Hz, 1H), 6.55 (d, *J* = 16.1 Hz, 1H), 6.04 (d, *J* = 16.1 Hz, 1H), 3.38 (s, 2H), 2.91 (brs, 1H), 1.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.1, 139.0, 137.1, 136.5, 135.1, 133.4, 132.5, 129.33, 129.28, 128.0, 127.6, 126.7, 126.0, 125.7, 124.6, 122.0, 71.6, 39.2, 24.0. **HRMS** calculated for $C_{21}H_{22}NO$ $[M+H]^+$ 304.1696, found 304.1695.



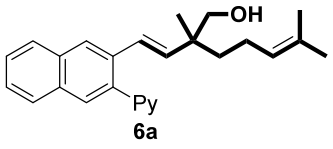
4t

(*E*)-2,2-dimethyl-4-(2-(pyridin-2-yl)thiophen-3-yl)but-3-en-1-ol (4t): colorless oil, 12.8 mg, 25% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.2 Hz, 1H), 7.71 (td, *J* = 7.8, 1.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 5.3 Hz, 1H), 7.23 (d, *J* = 5.3 Hz, 1H), 7.20–7.15 (m, 1H), 6.87 (d, *J* = 16.3 Hz, 1H), 6.09 (d, *J* = 16.3 Hz, 1H), 3.43 (s, 2H), 1.90 (brs, 1H), 1.13 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 149.7, 139.0, 138.0, 137.1, 136.5, 127.2, 126.1, 123.1, 122.7, 121.7, 71.6, 39.1, 24.0. **HRMS** calculated for $C_{15}H_{18}NOS$ $[M+H]^+$ 260.1104, found 260.1103.



4u

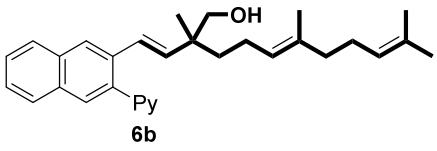
(*E*)-3-(4-hydroxy-3,3imethylbut-1-en-1-yl)-4-(pyridin-2-yl)phenol (4u): white solid, m.p. 190–191 °C, 34.2 mg, 64% yield, R_f = 0.25 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 8.66–8.60 (m, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.36–7.28 (m, 2H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 16.2 Hz, 1H), 6.12 (d, *J* = 16.2 Hz, 1H), 4.64 (s, 1H), 3.21 (s, 2H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 158.5, 158.0, 149.4, 139.8, 137.6, 136.6, 131.9, 130.4, 125.8, 125.0, 121.9, 114.8, 112.5, 70.7, 39.0, 24.3. **HRMS** calculated for $C_{17}H_{20}NO_2$ $[M+H]^+$ 270.1489, found 270.1485.



6a

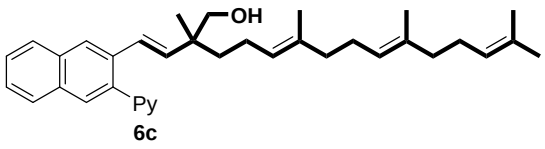
(*E*)-2,6-dimethyl-2-(2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)hept-5-en-1-ol (6a): colorless oil, 56.5 mg, 76% yield, R_f = 0.30 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.3 Hz, 1H), 7.92 (s, 2H), 7.83 (dd, *J* = 7.7, 3.1 Hz, 2H), 7.75 (td, *J* = 7.7, 1.7 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51–7.40 (m, 2H), 7.29–7.24 (m, 1H), 6.54 (d, *J* = 16.2 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 5.11 (td, *J* = 7.1, 6.4, 3.5 Hz, 1H), 3.45 (d, *J* = 10.7 Hz, 1H), 3.37 (d, *J* = 10.7 Hz, 1H), 2.90 (s, 1H), 2.00 (m, 2H), 1.69 (s, 3H), 1.59 (s, 3H),

1.50–1.32 (m, 2H), 1.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 149.1, 138.2, 137.0, 136.5, 135.3, 133.4, 132.5, 131.3, 130.2, 129.3, 128.0, 127.6, 126.7, 126.0, 125.8, 124.9, 124.6, 122.0, 70.7, 42.5, 37.9, 25.8, 22.9, 20.4, 17.7. **HRMS** calculated for $C_{26}H_{30}NO$ $[M+H]^+$ 372.2322, found 372.2323.



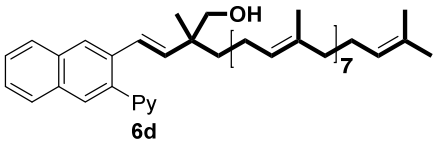
6b

(*E*)-2,6,10-trimethyl-2-((*E*)-2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)undeca-5,9-dien-1-ol (6b): colorless oil, 54.9 mg, 63% yield, R_f = 0.40 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, 1H), 7.93 (d, *J* = 3.8 Hz, 2H), 7.87–7.81 (m, 2H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.52–7.42 (m, 2H), 7.31–7.22 (m, 1H), 6.56 (d, *J* = 16.2 Hz, 1H), 6.01 (d, *J* = 16.2 Hz, 1H), 5.19–5.04 (m, 2H), 3.47 (d, *J* = 10.7 Hz, 1H), 3.38 (d, *J* = 10.7 Hz, 1H), 2.70 (brs, 1H), 2.02 (dq, *J* = 7.3 Hz, 6H), 1.67 (s, 3H), 1.59 (s, 6H), 1.53–1.43 (m, 1H), 1.38 (m, 1H), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.1, 138.1, 137.0, 136.5, 135.3, 135.0, 133.4, 132.6, 131.4, 130.4, 129.3, 128.0, 127.6, 126.7, 126.0, 125.8, 124.7, 124.6, 124.3, 122.0, 70.7, 42.5, 39.7, 37.9, 26.8, 25.7, 22.7, 20.4, 17.7, 16.0. **HRMS** calculated for $C_{31}H_{38}NO$ $[M+H]^+$ 440.2948, found 440.2947.



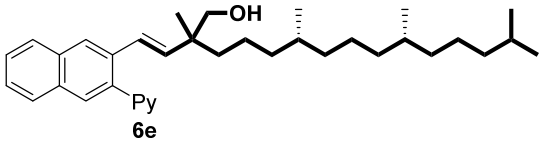
6c

(5*E*,9*E*)-2,6,10,14-tetramethyl-2-((*E*)-2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)pentadeca-5,9,13-trien-1-ol (6c): colorless oil, 77.5 mg, 76% yield, R_f = 0.40 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, 1H), 7.93 (d, *J* = 1.8 Hz, 2H), 7.87–7.81 (m, 2H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.53–7.41 (m, 2H), 7.30–7.22 (m, 1H), 6.56 (d, *J* = 16.2 Hz, 1H), 6.01 (d, *J* = 16.2 Hz, 1H), 5.12 (dt, *J* = 13.8, 7.0 Hz, 3H), 3.47 (d, *J* = 10.7 Hz, 1H), 3.38 (d, *J* = 10.7 Hz, 1H), 2.87 (brs, 1H), 2.03 (m, 10H), 1.67 (s, 3H), 1.59 (s, 9H), 1.53–1.33 (m, 2H), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.1, 138.1, 137.0, 136.5, 135.3, 135.04, 134.99, 133.4, 132.6, 131.3, 130.5, 129.3, 128.0, 127.6, 126.7, 126.0, 125.8, 124.7, 124.6, 124.4, 124.2, 122.0, 70.7, 42.5, 39.7, 37.9, 26.8, 26.7, 25.7, 22.8, 20.4, 17.7, 16.1. **HRMS** calculated for $C_{36}H_{46}NO$ $[M+H]^+$ 508.3574, found 508.3583.



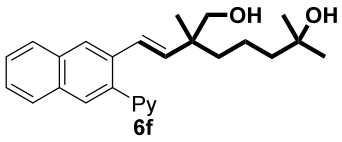
6d

(5*E*,9*E*,13*E*,17*E*,21*E*,25*E*,29*E*)-2,6,10,14,18,22,26,30,34-nonamethyl-2-((*E*)-2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)pentatriaconta-5,9,13,17,21,25,29,33-octaen-1-ol (6d): colorless oil, 25.6 mg, 30% yield, R_f = 0.30 (petroleum ether/EtOAc 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.2 Hz, 1H), 7.94 (s, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.83–7.78 (m, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (p, *J* = 6.9 Hz, 2H), 7.34–7.27 (m, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 6.02 (d, *J* = 16.2 Hz, 1H), 5.11 (t, *J* = 6.6 Hz, 8H), 3.49 (d, *J* = 10.7 Hz, 1H), 3.40 (d, *J* = 10.7 Hz, 1H). 2.07 (m, 16H), 1.98 (m, 16H), 1.60 (s, 30H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 149.0, 138.1, 136.9, 136.7, 135.3, 135.1, 135.05, 134.96, 134.94, 134.93, 134.91, 134.88, 133.5, 132.6, 131.2, 130.5, 129.3, 128.0, 127.6, 126.7, 126.0, 125.8, 124.6, 124.4, 124.27, 124.26, 124.24, 124.16, 122.0, 70.7, 42.6, 39.8, 39.7, 37.9, 26.8, 26.72, 26.69, 25.7, 22.7, 20.4, 17.7, 16.1, 16.04, 16.02. **HRMS** calculated for $C_{61}H_{86}NO$ $[M+H]^+$ 848.6704, found 848.6703.



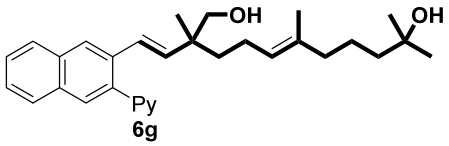
6e

(*E*)-2,6,10,14-tetramethyl-2-(2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)pentadecan-1-ol (6e): colorless oil, 60.5 mg, 59% yield, R_f = 0.40 (petroleum ether/EtOAc 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.4 Hz, 1H), 7.92 (s, 2H), 7.83 (t, *J* = 6.9 Hz, 2H), 7.76 (td, *J* = 7.7, 1.5 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.46 (dt, *J* = 15.4, 6.7 Hz, 2H), 7.26 (dd, *J* = 7.5, 5.4 Hz, 1H), 6.54 (d, *J* = 16.2 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 3.45 (d, *J* = 10.7 Hz, 1H), 3.36 (d, *J* = 10.7 Hz, 1H). 2.80 (brs, 1H), 1.52 (m, 1H), 1.45–1.10 (m, 17H), 1.06 (d, *J* = 8.5 Hz, 6H), 0.94–0.75 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.1, 138.5, 137.0, 136.5, 135.3, 133.5, 132.6, 130.2, 129.3, 128.0, 127.6, 126.7, 126.0, 125.8, 124.6, 122.0, 70.8, 42.5, 39.4, 38.14, 38.13, 37.95, 37.93, 37.55, 37.53, 37.50, 37.3, 32.83, 32.78, 32.76, 28.0, 24.8, 24.5, 22.8, 22.7, 21.5, 20.5, 19.79, 19.77. **HRMS** calculated for $C_{36}H_{52}NO$ $[M+H]^+$ 514.4043, found 514.4049.



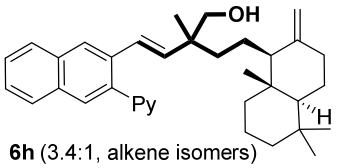
6f

(*E*)-2,6-dimethyl-2-(2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)heptane-1,6-diol (6f): colorless oil, 63.5 mg, 79% yield, R_f = 0.15 (petroleum ether/EtOAc 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71–8.65 (m, 1H), 7.91 (d, *J* = 7.0 Hz, 2H), 7.83 (t, *J* = 7.3 Hz, 2H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51–7.42 (m, 2H), 7.28 (ddd, *J* = 7.5, 5.0, 0.9 Hz, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 3.47–3.31 (m, 2H), 2.66 (s, 2H), 1.33 (ddd, *J* = 13.9, 9.1 Hz, 6H), 1.16 (s, 6H), 1.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 148.9, 138.5, 136.84, 136.81, 135.2, 133.4, 132.5, 129.8, 129.3, 128.0, 127.6, 126.7, 126.0, 125.7, 124.7, 122.1, 70.9, 70.6, 44.6, 42.5, 38.1, 29.35, 29.29, 20.5, 18.8. **HRMS** calculated for $C_{26}H_{32}NO_2$ $[M+H]^+$ 390.2428, found 390.2427.



6g

2,6,10-trimethyl-2-((*E*)-2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)undecane-1,10-diol (6g): colorless oil, 74.0 mg, 81% yield, R_f = 0.15 (petroleum ether/EtOAc 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.2 Hz, 1H), 7.92 (d, *J* = 6.4 Hz, 2H), 7.84 (t, *J* = 6.5 Hz, 2H), 7.77 (td, *J* = 7.7, 1.7 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52–7.41 (m, 2H), 7.27 (dd, *J* = 6.5, 4.9 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 6.01 (d, *J* = 16.2 Hz, 1H), 5.12 (t, *J* = 6.6 Hz, 1H), 3.51–3.33 (m, 2H), 2.46 (s, 2H), 1.98 (m, 4H), 1.57 (s, 3H), 1.51–1.33 (m, 6H), 1.17 (s, 6H), 1.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 149.0, 138.2, 137.0, 136.6, 135.3, 134.9, 133.4, 132.5, 130.1, 129.3, 128.0, 127.6, 126.7, 126.0, 125.7, 124.8, 124.6, 122.0, 70.9, 70.7, 43.5, 42.5, 40.0, 37.9, 29.2, 22.73, 22.66, 20.4, 15.9. **HRMS** calculated for $C_{31}H_{40}NO_2$ $[M+H]^+$ 458.3054, found 458.3056.

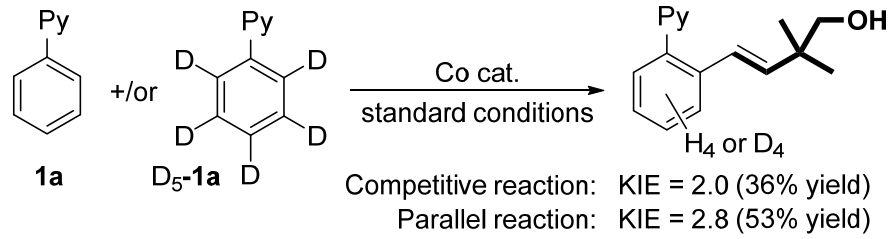


6h (3.4:1, alkene isomers)

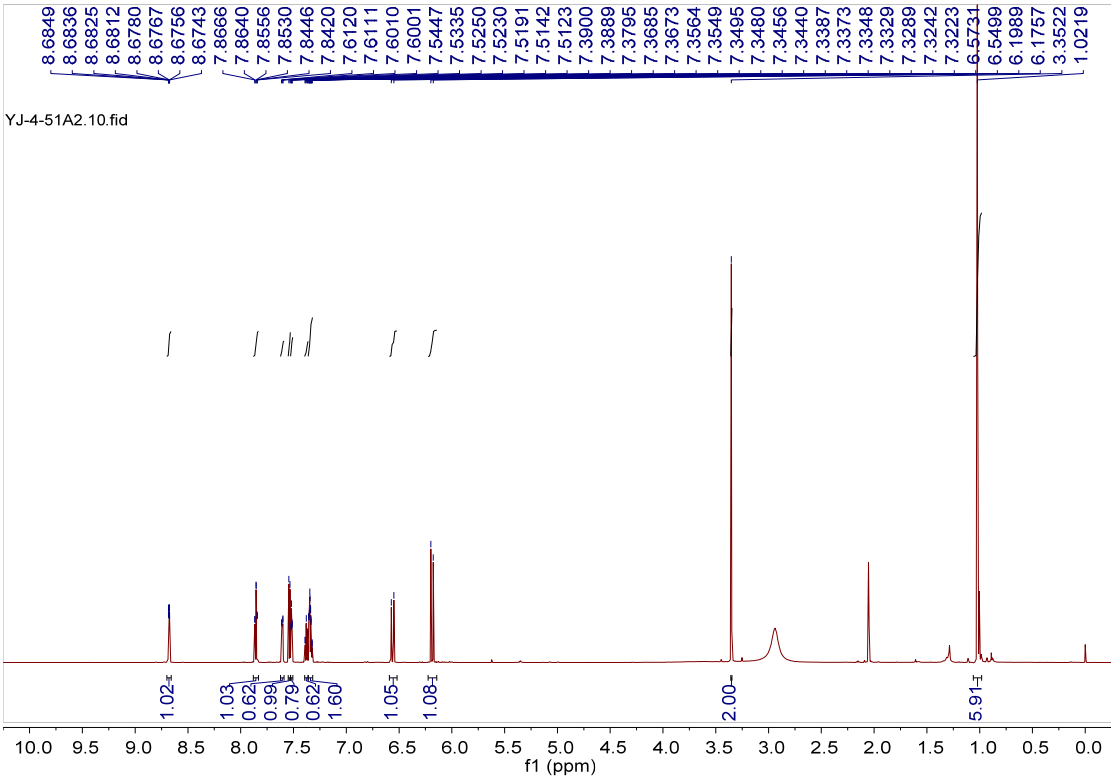
(*E*)-2-methyl-4-(3-(pyridin-2-yl)naphthalen-2-yl)-2-(2-((1S,4aS,8aS)-5,5,8a-trimethyl-2-methylenedecahydronaphthalen-1-yl)ethyl)but-3-en-1-ol (6h): colorless oil, 67.3 mg, 64% yield, R_f = 0.30 (petroleum ether/EtOAc 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, 1H), 7.93 (d, *J* = 1.8 Hz, 2H), 7.87–7.81 (m, 2H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.53–7.41 (m, 2H), 7.30–7.22 (m, 1H), 6.56 (d, *J* = 16.2 Hz, 1H), 6.01 (d, *J* = 16.2 Hz, 1H), 5.12 (dt, *J* = 13.8, 7.0 Hz, 2H),

3.51–3.34 (m, 2H), 2.87 (s, 1H), 2.43–2.34 (m, 1H), 2.03 (m, 2H), 1.79–1.12 (m, 13H), 1.08 (s, 3H), 0.90–0.64 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 149.2, 148.9, 148.8, 138.4, 138.3, 136.5, 135.4, 133.4, 132.6, 130.44, 130.36, 129.3, 128.0, 127.6, 126.7, 126.0, 125.83, 125.75, 124.6, 122.0, 106.4, 70.8, 57.9, 57.8, 55.6, 50.2, 43.0, 42.4, 42.2, 39.9, 39.1, 38.4, 37.2, 33.60, 24.5, 21.7, 20.3, 19.5, 17.9, 17.8, 14.6, 14.5, 13.7. **HRMS** calculated for $C_{36}H_{46}NO$ $[M+H]^+$ 508.3574, found 508.3575.

3. Mechanistic experiments[3, 4]

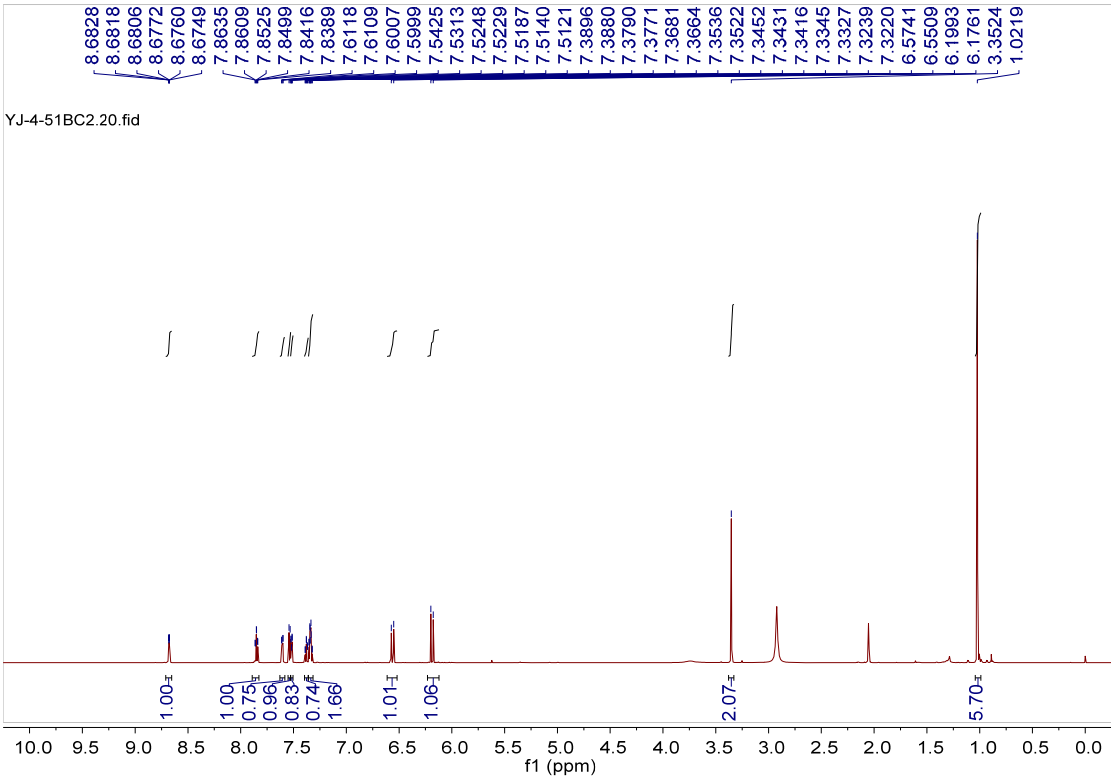


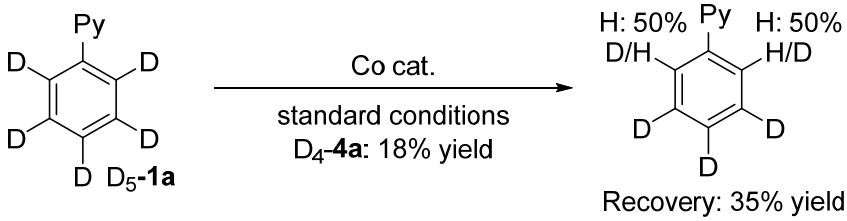
To a sealed tube (4 mL) was sequentially added 2-phenylpyridine **1a** (0.10 mmol), $[D_5]$-2-phenylpyridine $[D_5]$-**1a** (0.10 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (10.0 mol%), AcOH (40 mol%), paraformaldehyde **3** (3.0 equiv), dioxane (0.50 mL), and isoprene **2** (2.0 equiv). The resulting mixture was then stirred at 50 °C for 8 h. The system was diluted with DCM and washed with water. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4:1) to obtain **4a** and $[D_4]$-**4a** (18.2 mg, 36%) as a colorless oil.



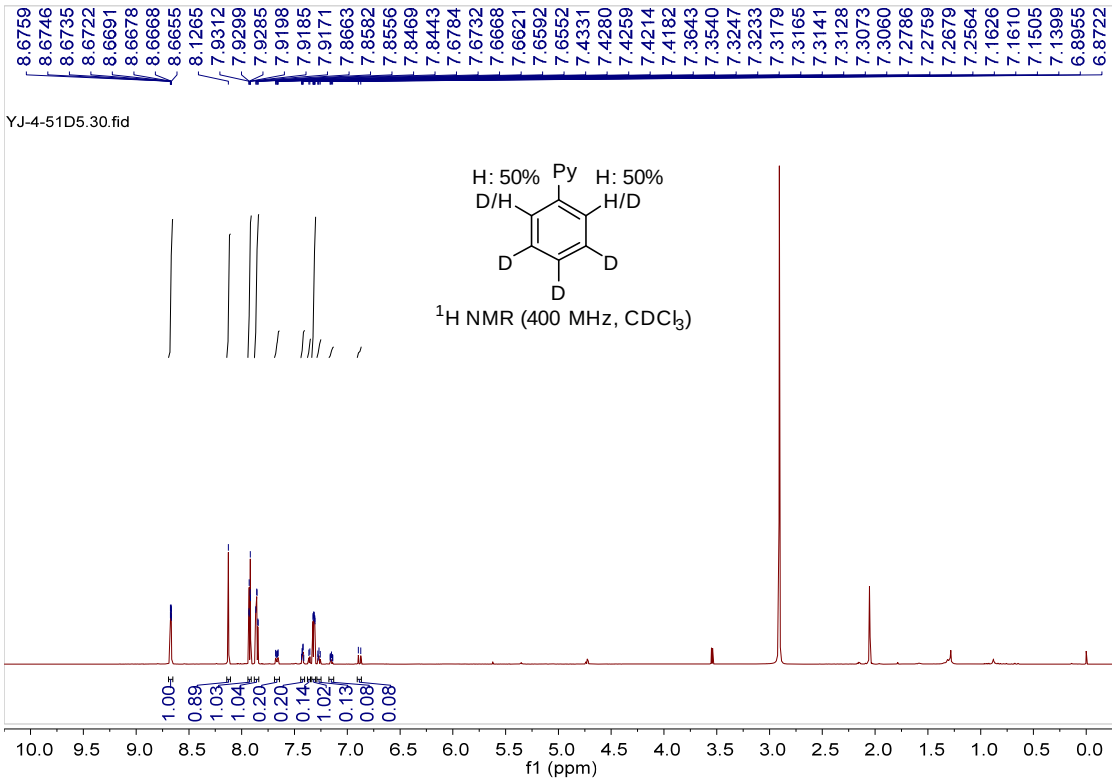
To two sealed tubes (4 mL) was sequentially added 2-phenylpyridine **1a** (0.20 mmol) or $[D_5]$-2-phenylpyridine **1a** (0.20 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (10.0 mol%), AcOH (40 mol%), paraformaldehyde **3a** (3.0 equiv), dioxane (0.50 mL), and isoprene **2** (2.0 equiv). The two

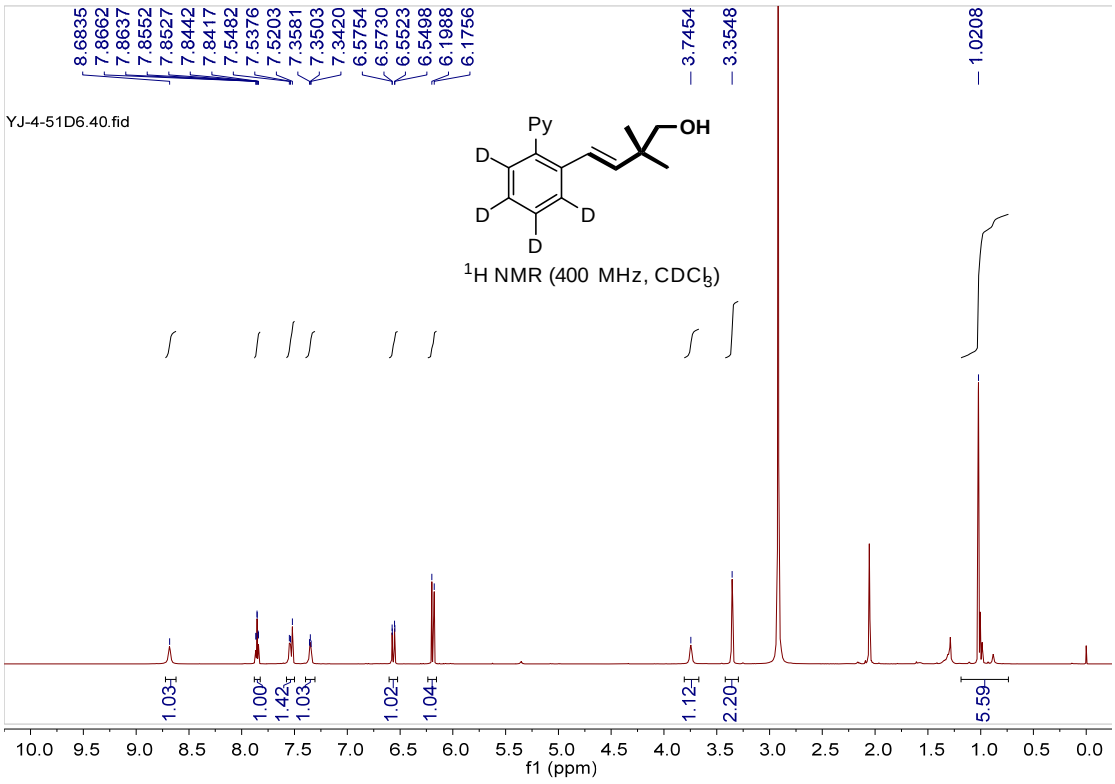
resulting mixture was then stirred at 50 °C for 8 h. The system was diluted with DCM and washed with water. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. And the residues of the two reactions were combined and purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4:1) to deliver **4a** and [D_4]-**4a** (27.0 mg, 53%) as a colorless oil.

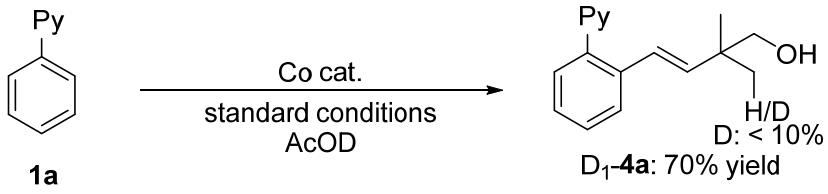




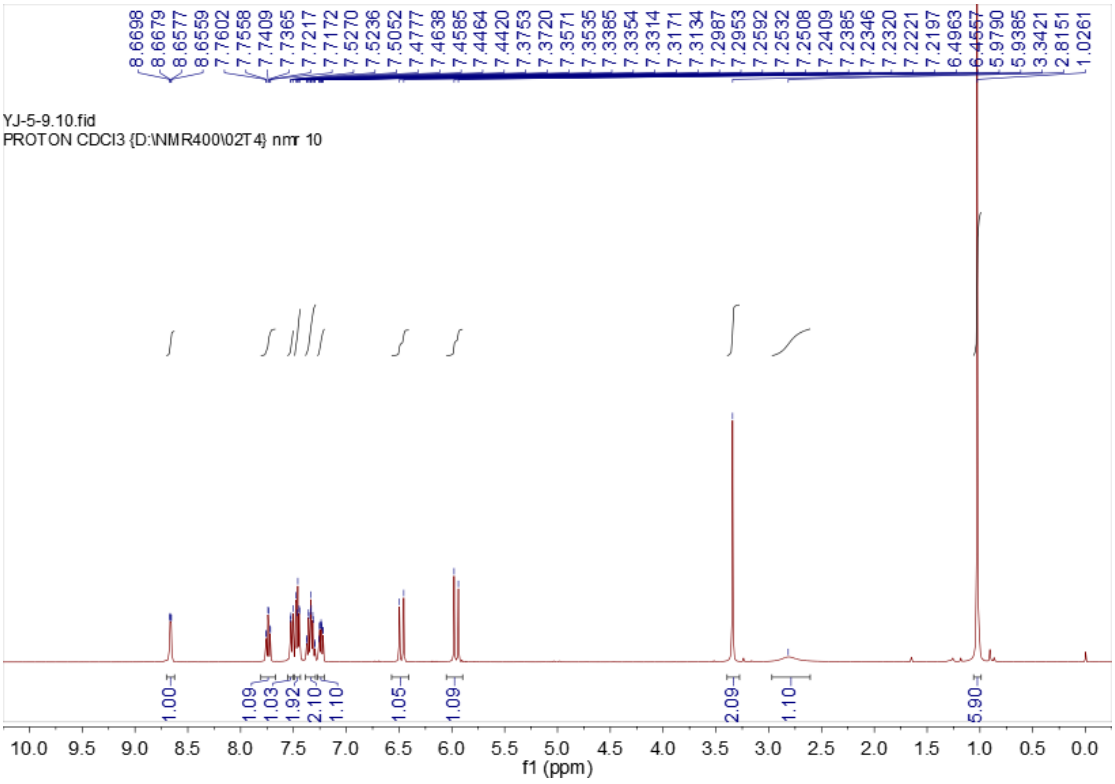
To a sealed tube (4 mL) was sequentially added [D_5]-2-phenylpyridine [D_5]-**1a** (0.20 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (10.0 mol%), AcOH (40 mol%), paraformaldehyde **3** (3.0 equiv), dioxane (0.50 mL), and isoprene **2** (2.0 equiv). The resulting mixture was then stirred at 50 °C for 8 h. The system was diluted with DCM and washed with water. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4:1) to give [D_4]-**4a** (9.0 mg, 18%) as a colorless oil.

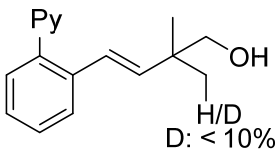

YJ-4-51D5.30.fid
H: 50%
D/H
Py
H: 50%
H/D
D
D
D
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


YJ-4-51D6.40.fid
Py
OH
D
D
D
D
D
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

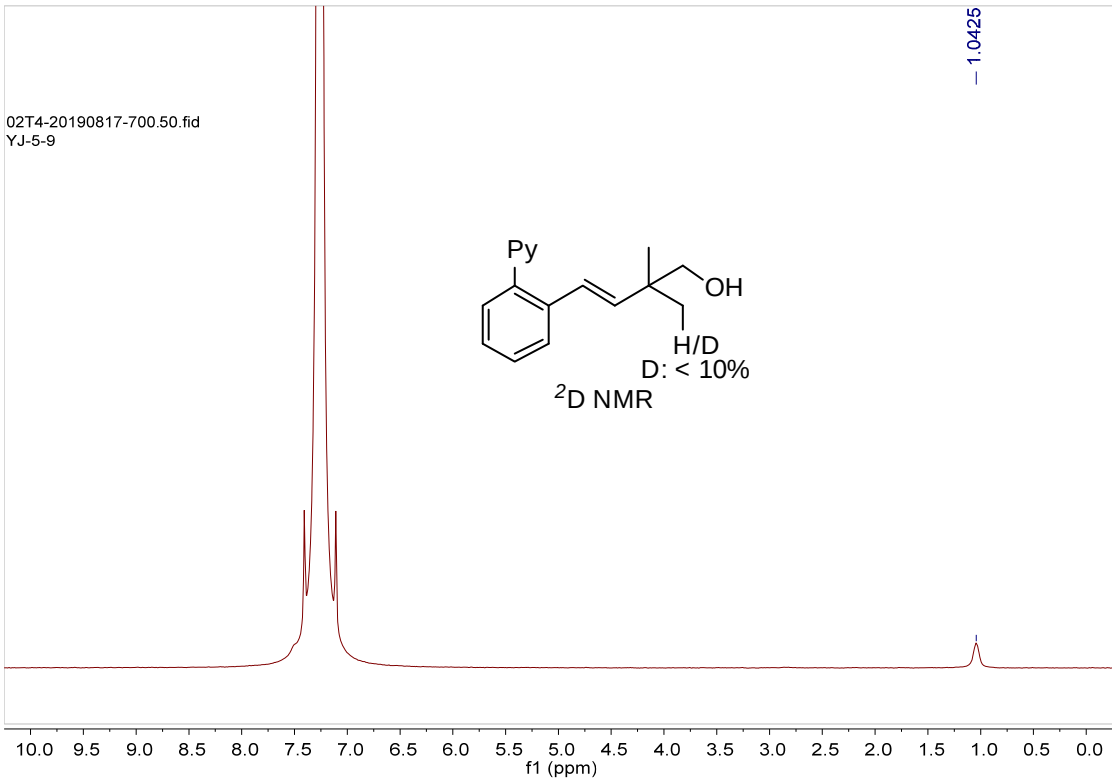


To a sealed tube (4 mL) was sequentially added 2-phenylpyridine **1a** (0.20 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (10.0 mol%), AcOD (40 mol%), paraformaldehyde **3** (3.0 equiv), dioxane (0.50 mL), and isoprene **2** (2.0 equiv). The resulting mixture was then stirred at 50 ^{o}C for 16 h. The system was diluted with DCM and washed with water. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4:1) to give [D_1]-**4a** (35.0 mg, 70%) as a colorless oil.

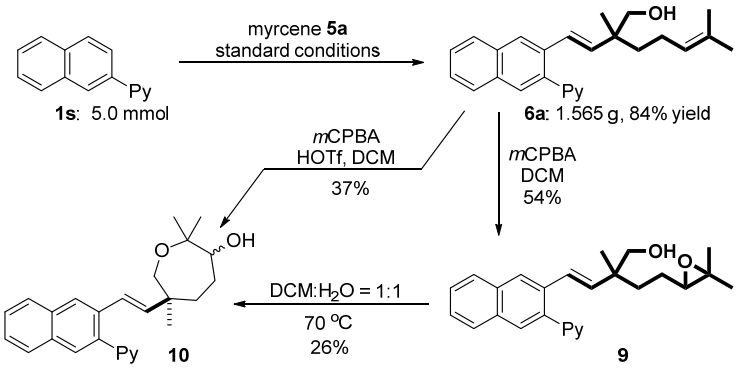




^{1}H NMR (400 MHz, $CDCl_3$)



4. Synthetic transformations.

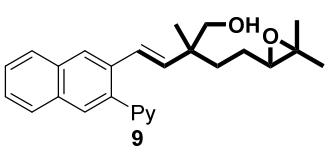


To a sealed tube (100 mL) was sequentially added 2-phenylpyridine **1a** (5.0 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (10.0 mol%), AcOH (40 mol%), paraformaldehyde **3** (3.0 equiv), dioxane (12.50 mL), and myrcene **5a** (2.0 equiv). The resulting mixture was then stirred at 50 °C for 16 h. The system was diluted with DCM and washed with water. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4:1) to afford **6a** (1.565g, 84%) as a colorless oil.

In a Schlenk tube (4 mL), **6a** (37.2 mg, 0.10 mmol) was dissolved in DCM (1.0 mL). *m*CPBA (1.5 equiv) was added, and the mixture was stirred at room temperature for 4 h. The reaction was quenched by water and extracted with DCM. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, petroleum ether/EtOAc = 5:1) yielded the desired product.

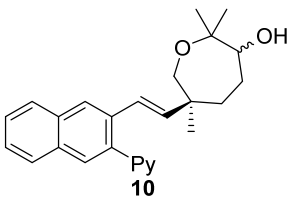
In a Schlenk tube (4 mL), **6a** (37.2 mg, 0.10 mmol) was dissolved in DCM (1.0 mL). *m*CPBA (1.5 equiv), HOTf (0.3 equiv) was added, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by water and extracted with DCM. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, petroleum ether/EtOAc = 5:1) yielded the desired product.

In a Schlenk tube (4 mL), **9** (38.8 mg, 0.10 mmol) was dissolved in DCM and water (1:1, 1.0 mL). And the mixture was stirred at 70 ^{o}C for 48 h. The reaction was quenched by water and extracted with DCM. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, petroleum ether/EtOAc = 5:1) yielded the desired product.



9

(*E*)-2-(2-(3,3imethyloxiran-2-yl)ethyl)-2-methyl-4-(3-(pyridin-2-yl)naphthalen-2-yl)but-3-en-1-ol (9): colorless oil, 20.9 mg, 54% yield, R_f = 0.30 (petroleum ether/EtOAc 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.2 Hz, 1H), 7.92 (s, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.53–7.40 (m, 2H), 7.27 (dd, *J* = 6.7, 4.7 Hz, 1H), 6.56 (dd, *J* = 16.2, 1.7 Hz, 1H), 5.99 (dd, *J* = 16.2, 3.1 Hz, 1H), 3.51–3.33 (m, 2H), 3.12 (s, 1H), 2.70 (t, *J* = 5.9 Hz, 1H), 1.72–1.37 (m, 4H), 1.30 (d, *J* = 2.3 Hz, 3H), 1.25 (d, *J* = 5.7 Hz, 3H), 1.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 149.1, 137.5, 137.0, 136.6, 135.1, 133.4, 132.6, 130.7, 129.3, 128.0, 127.6, 126.7, 126.1, 125.7, 124. 6, 122.0, 70.7, 64.7, 58.4, 42.2, 34.0, 24.9, 23.9, 20.4, 18.7. **HRMS** calculated for $C_{26}H_{30}NO_2$ $[M+H]^+$ 388.2271, found 388.2269.



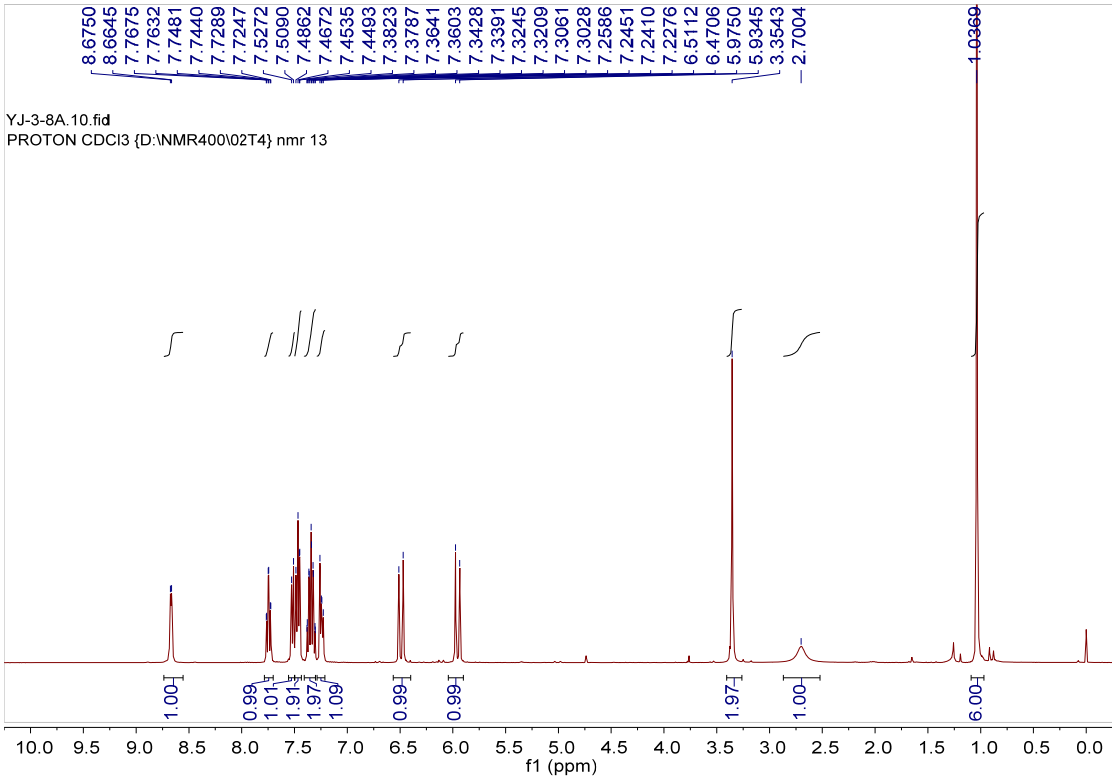
10

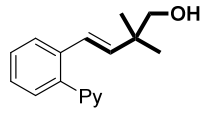
2,2,6-trimethyl-6-((*E*)-2-(3-(pyridin-2-yl)naphthalen-2-yl)vinyl)oxepan-3-ol (10): colorless oil, 14.4 mg, 37% yield, R_f = 0.30 (petroleum ether/EtOAc 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80–8.69 (m, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.84 (t, *J* = 6.7 Hz, 2H), 7.75 (tt, *J* = 7.7, 2.1 Hz, 1H), 7.58–7.39 (m, 3H), 7.31–7.24 (m, 1H), 6.71 (d, *J* = 16.3 Hz, 1H), 6.31 (d, *J* = 16.2 Hz, 1H), 3.90 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.28 (d, *J* = 11.3 Hz, 1H), 3.07 (dd, *J* = 11.2, 2.1 Hz, 1H), 2.59 (d, *J* = 10.7 Hz, 1H), 1.88–1.80 (m, 1H), 1.69–1.39 (m, 3H), 1.21–0.94 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 149.4, 138.0, 137.7, 135.9, 134.7, 133.4, 132.5, 129.4, 128.0, 127.8, 127.6, 126.5, 125.9, 125.3, 125.1, 121.8, 84.3, 76.9, 71.8, 36.2, 36.1, 26.2, 25.2, 24.0, 22.5. **HRMS** calculated for $C_{26}H_{30}NO_2$ $[M+H]^+$ 388.2271, found 388.2273.

5. References

1. C. Liu, W. B. Yang, *Chem. Commun.,* **2009**, 6267.
2. E. Arkoudis, M. Stratakis, *J. Org. Chem.* **2008**, *73*, 4484.
3. H. Zhang, K. Wang, B. Wang, H. Yi, F. Hu, C. Li, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 13234.
4. P. Gandeepan, P. Rajamalli, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2016**, *55*, 4308.

6. Copies of NMR spectra

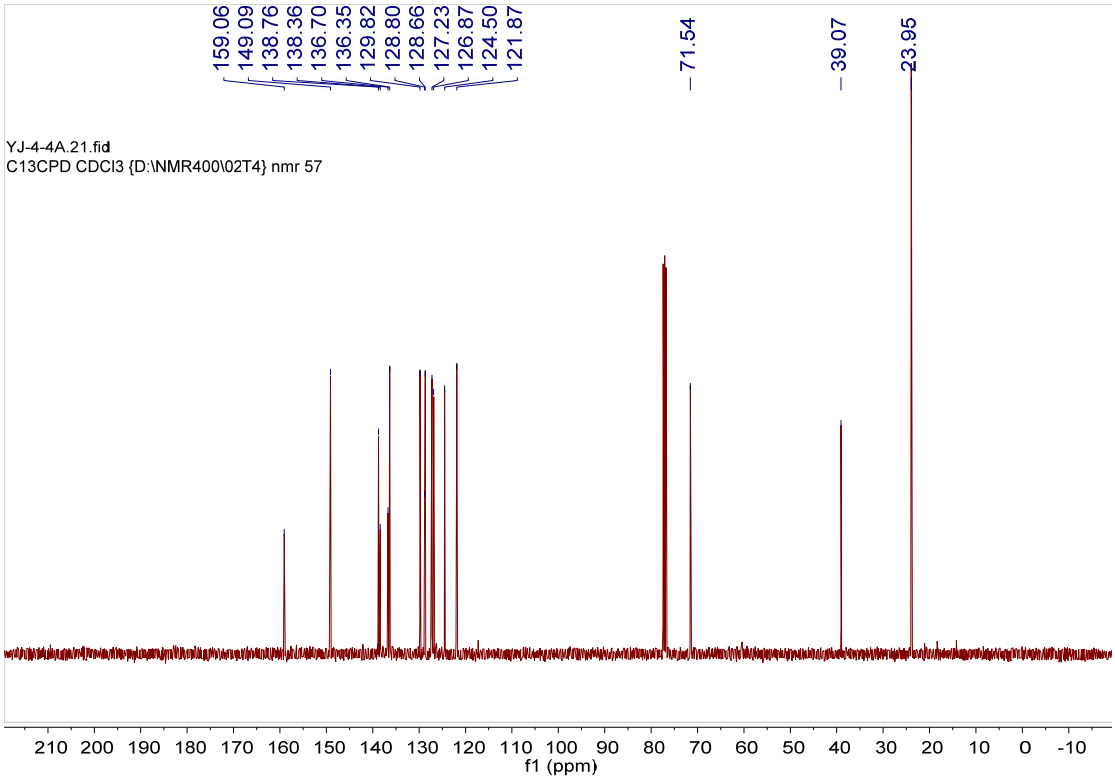


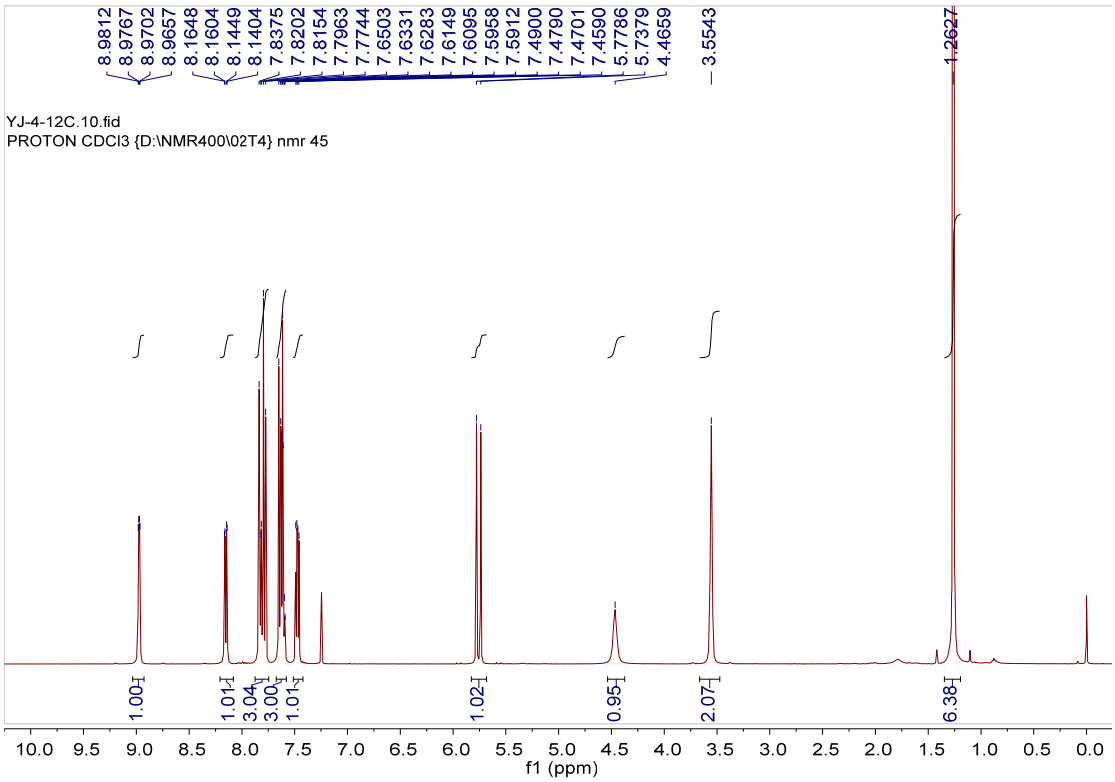


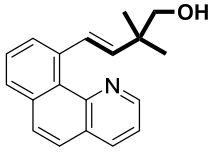
4a

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

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



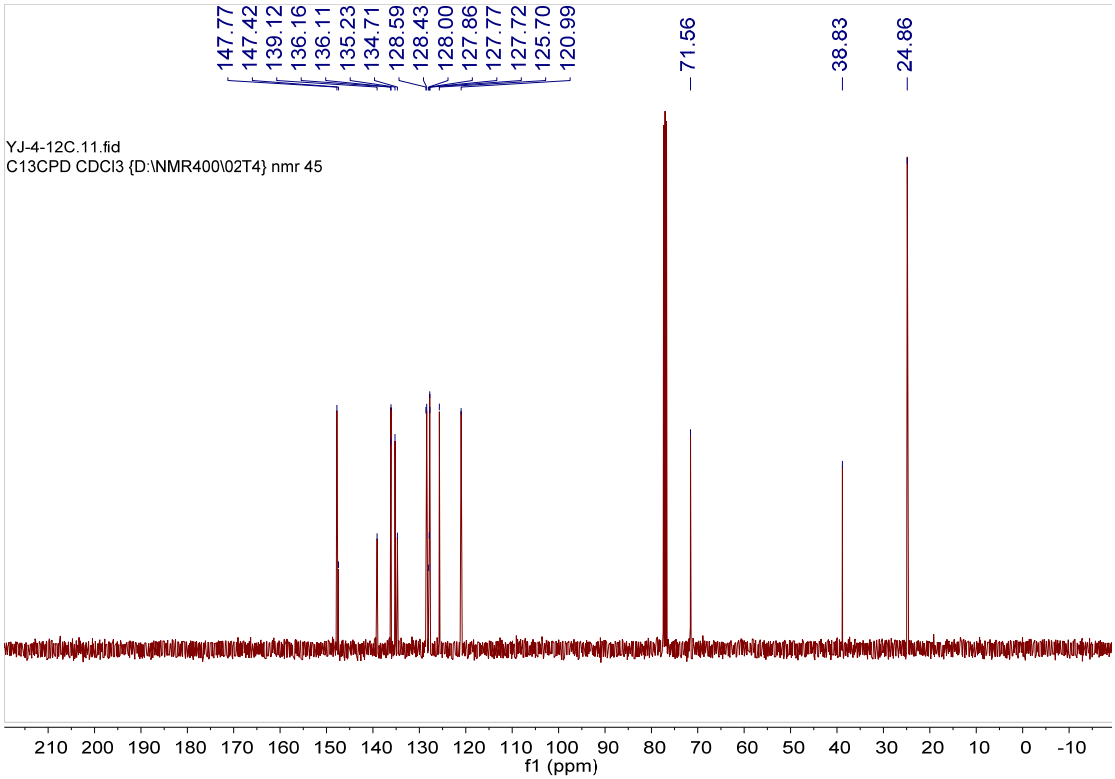


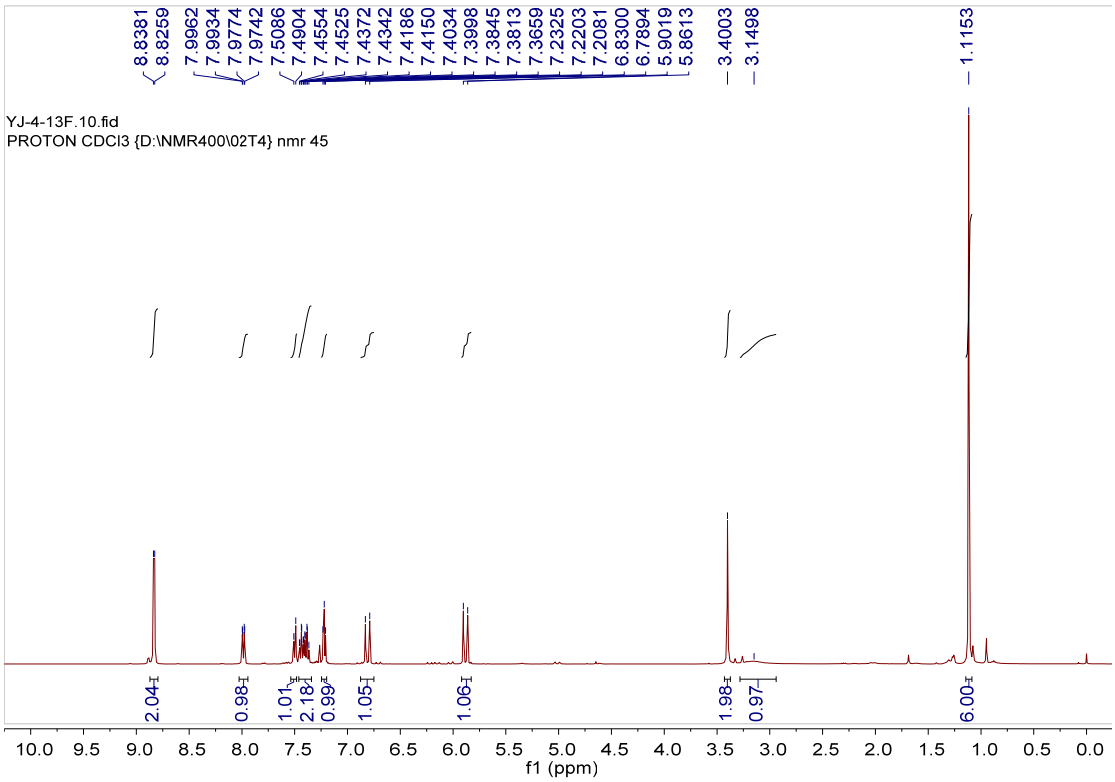


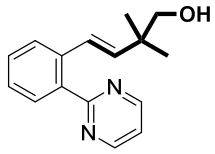
4b

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

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



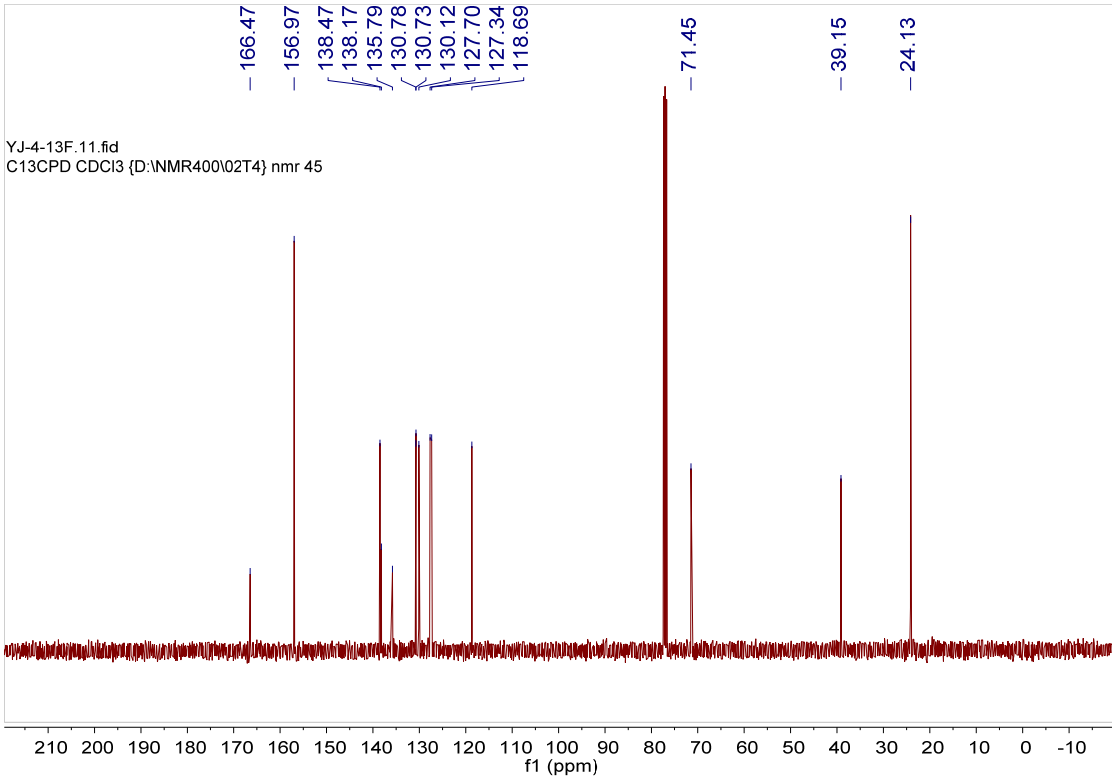


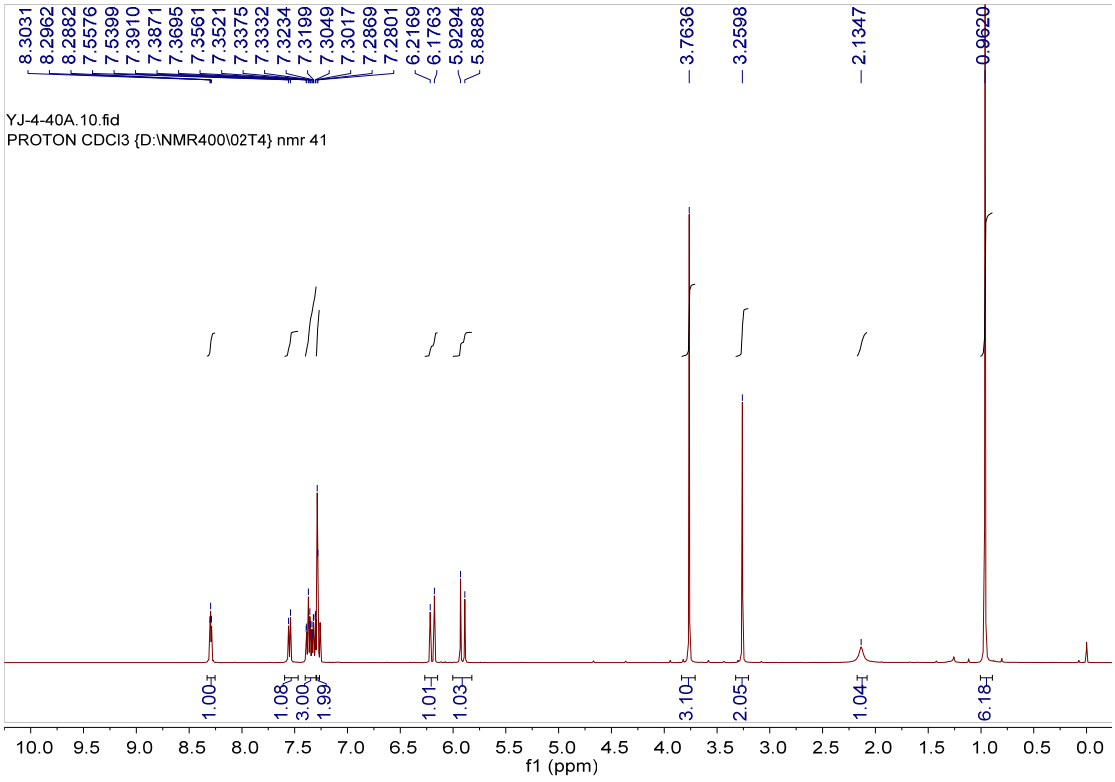


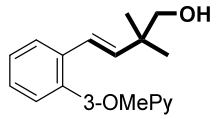
4c

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

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



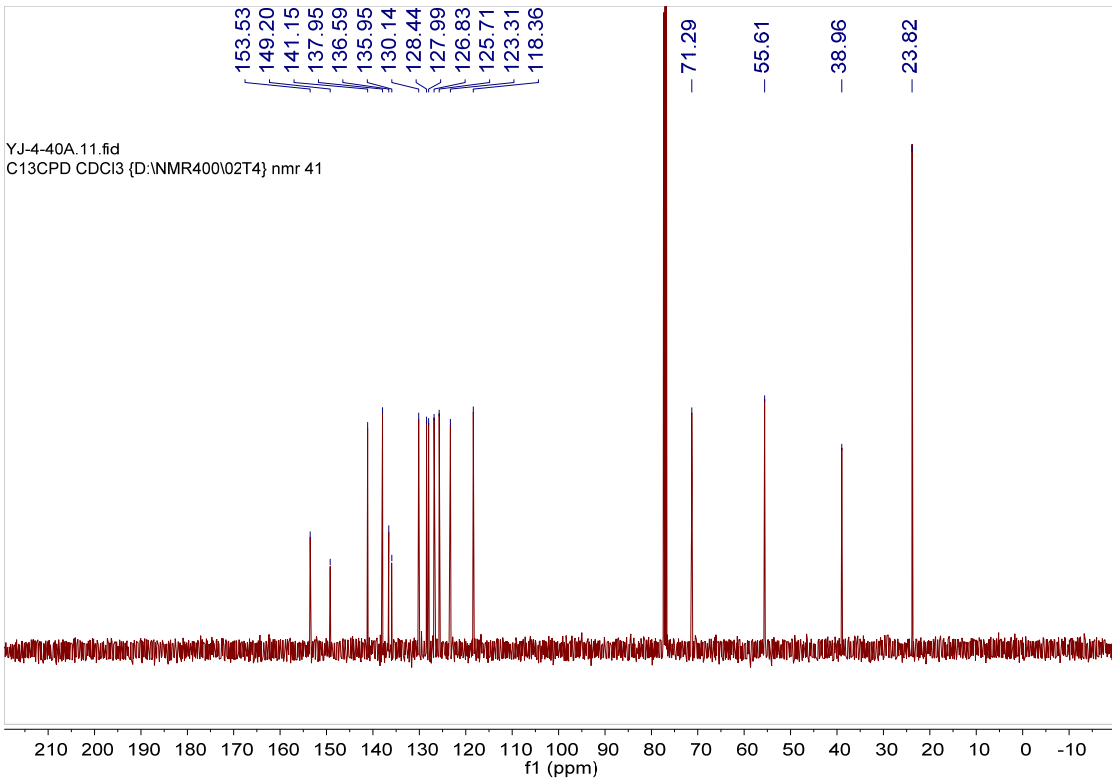


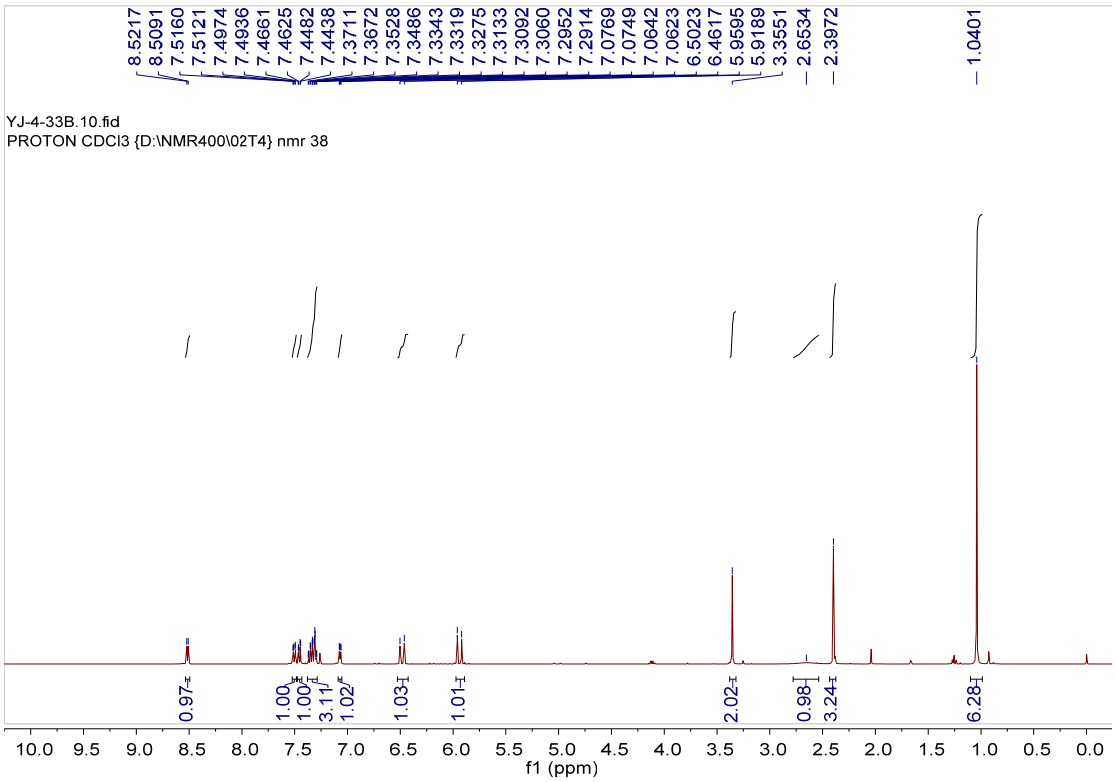


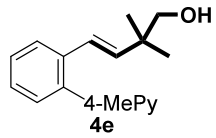
4d

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

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



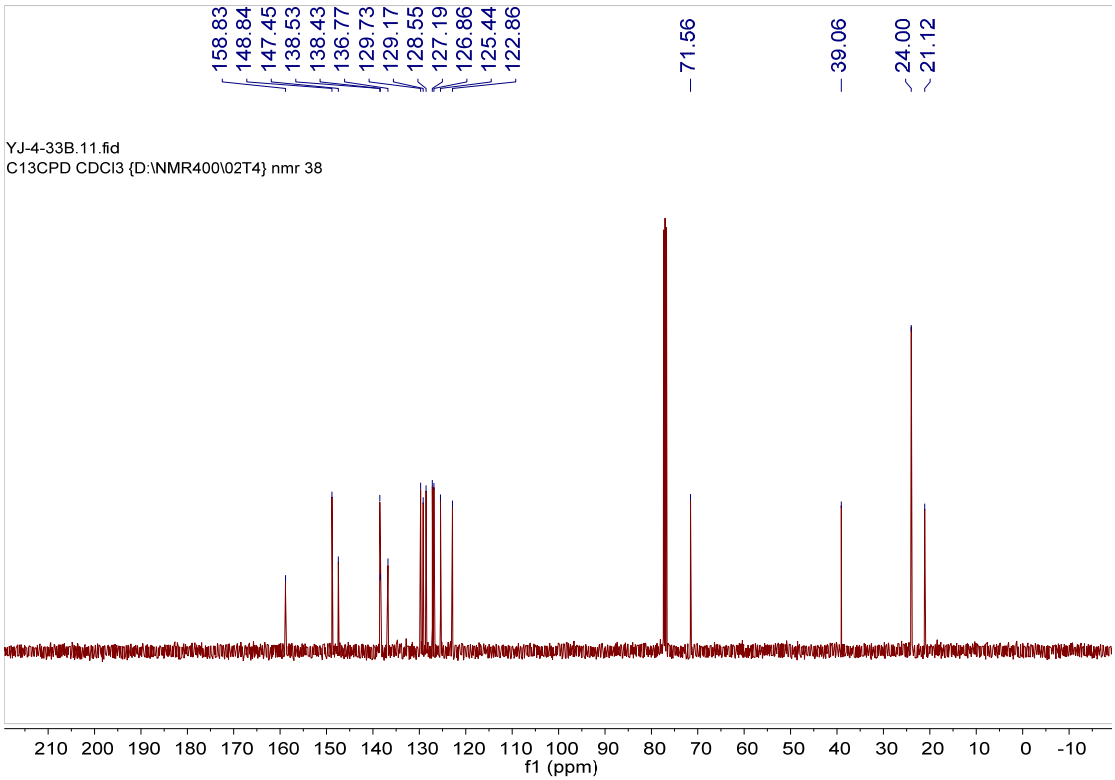


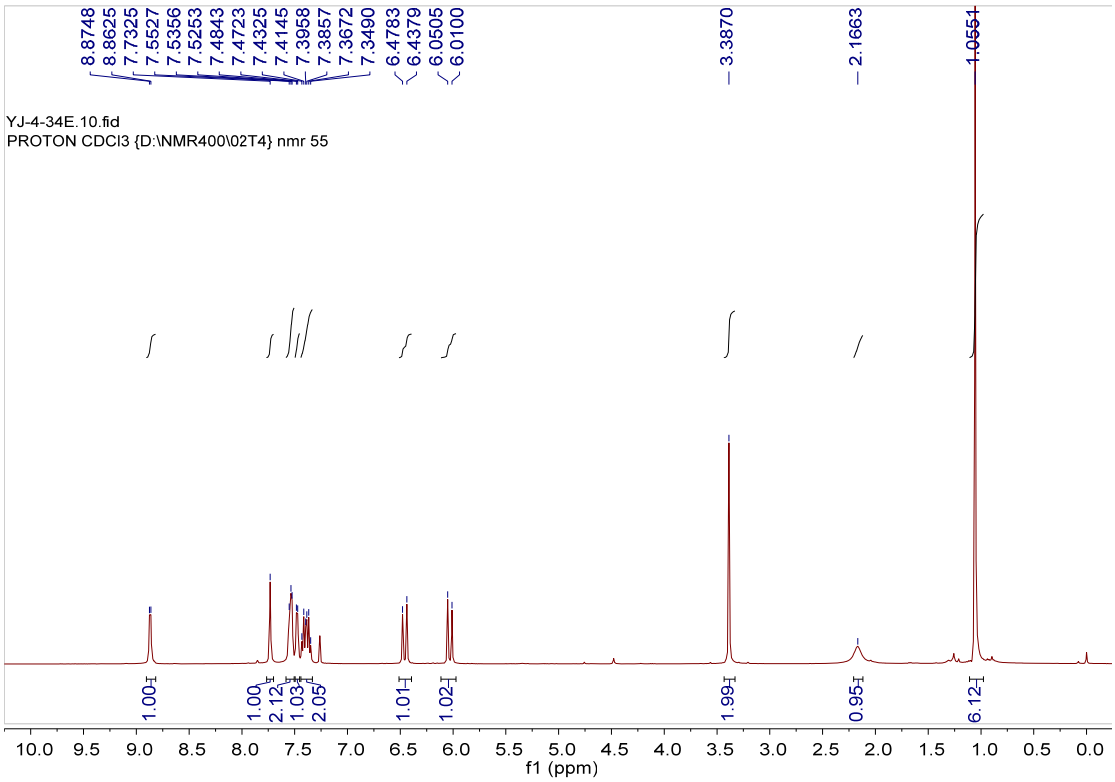


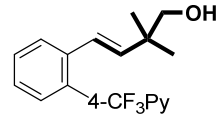
4e

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

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



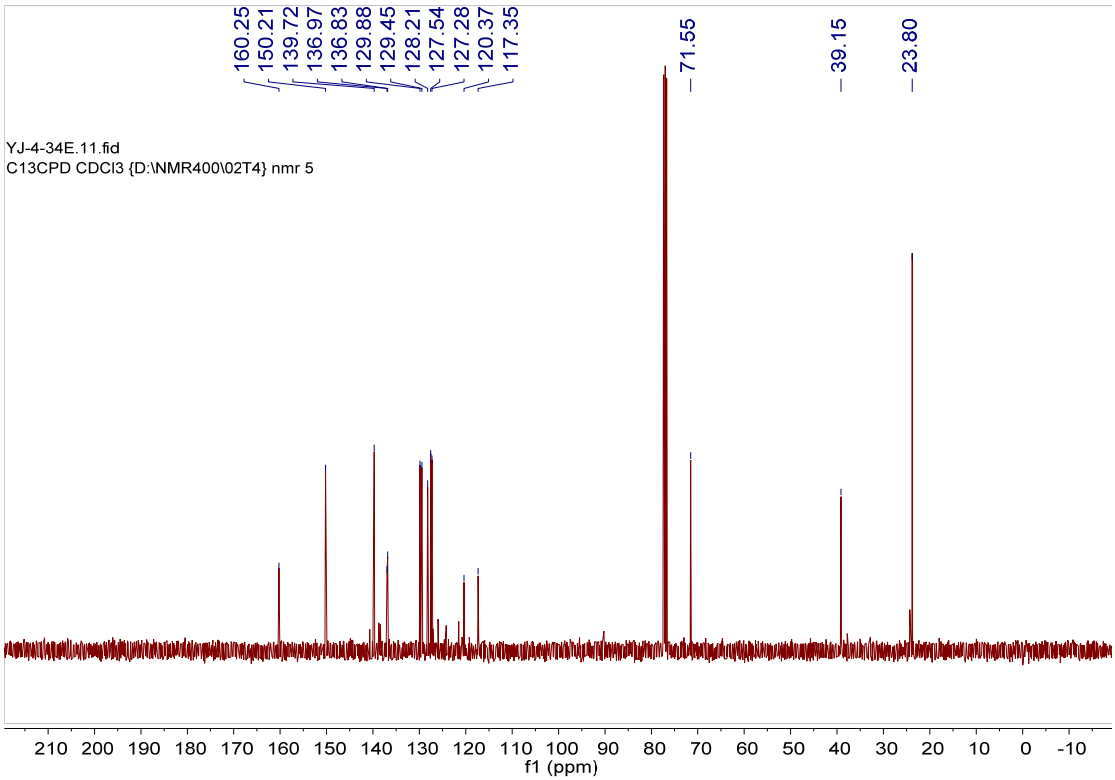


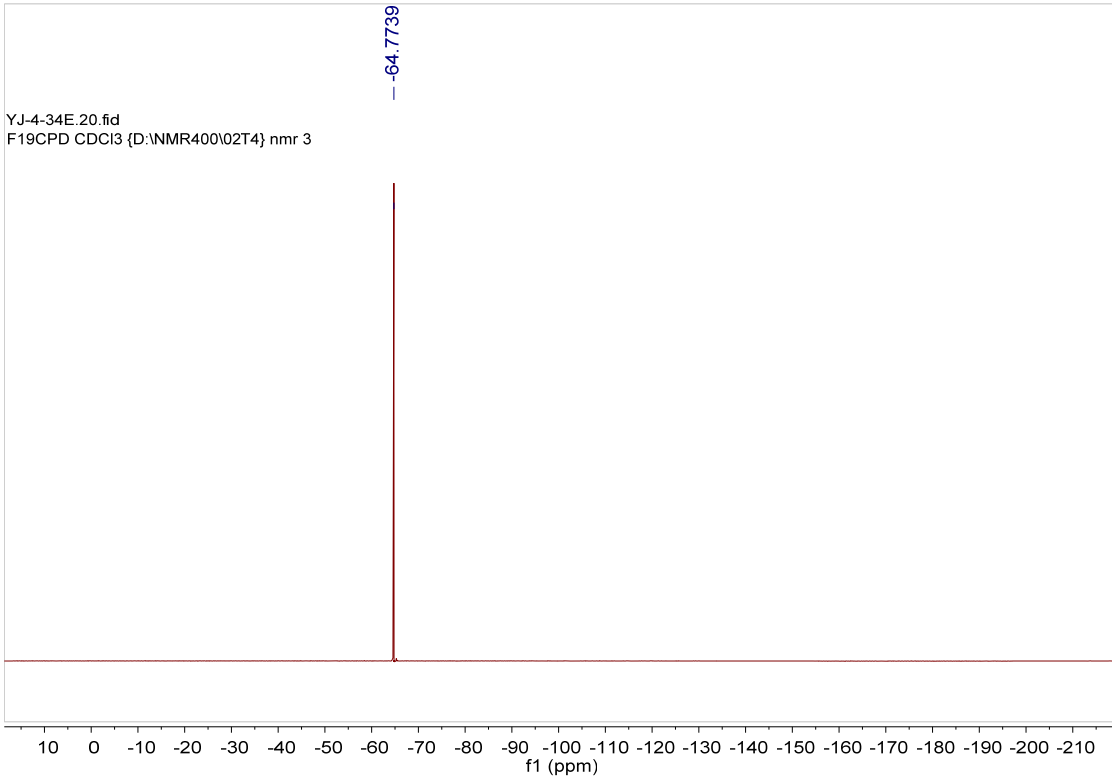


4f

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

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

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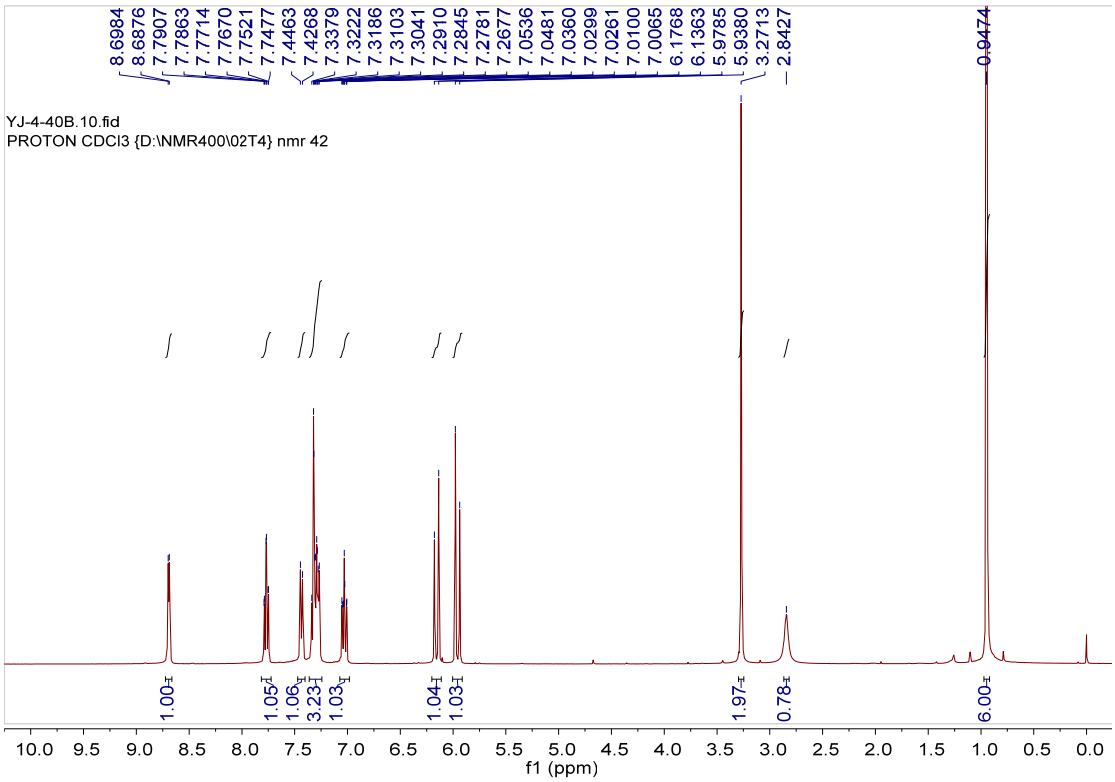
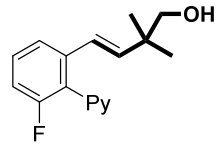
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

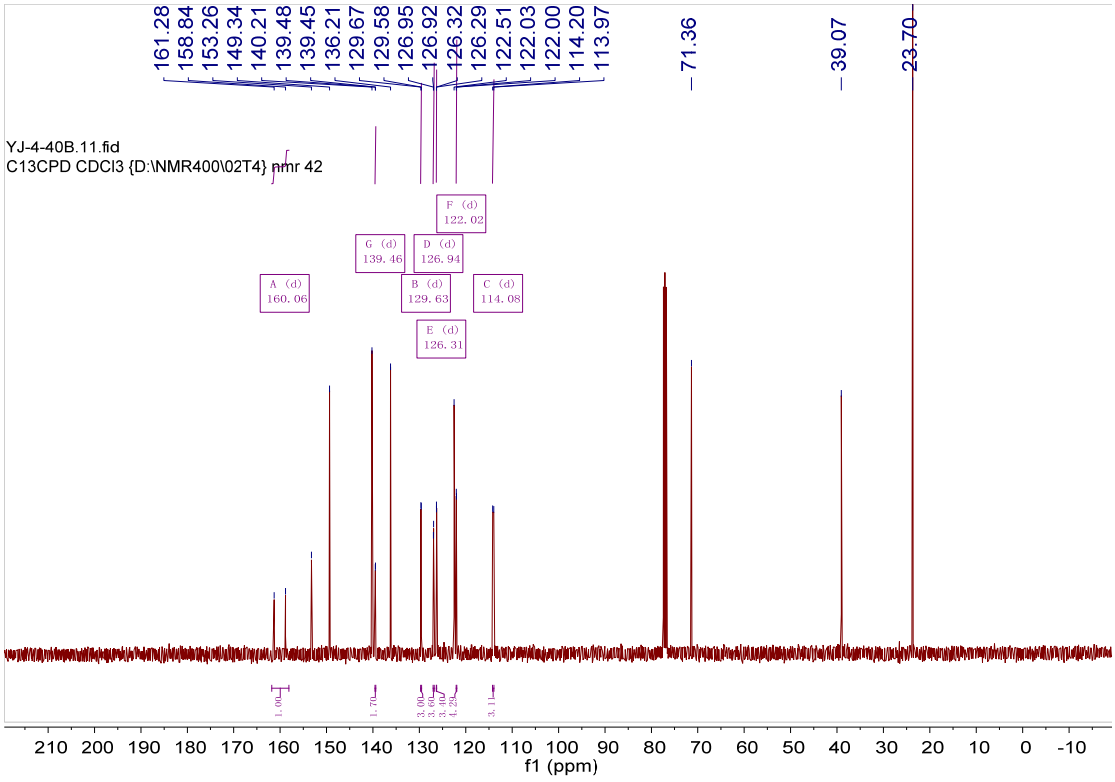


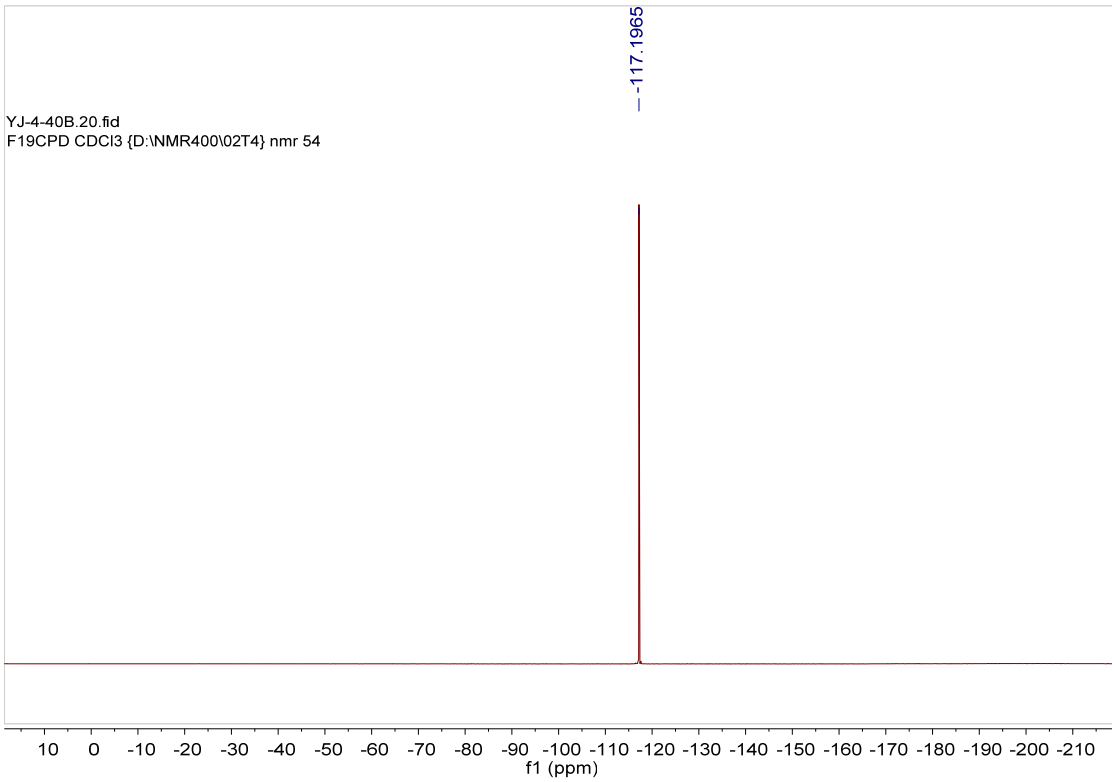


4g

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

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

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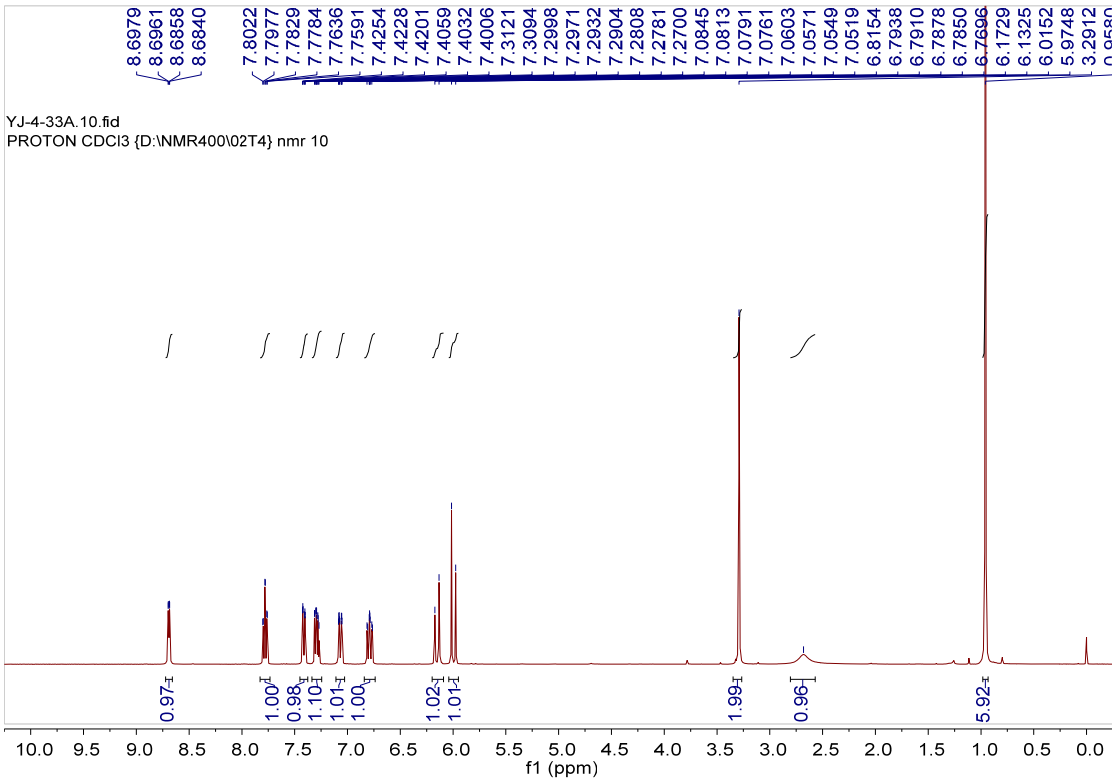
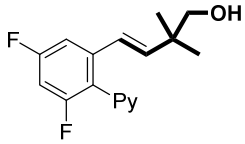
f1 (ppm)

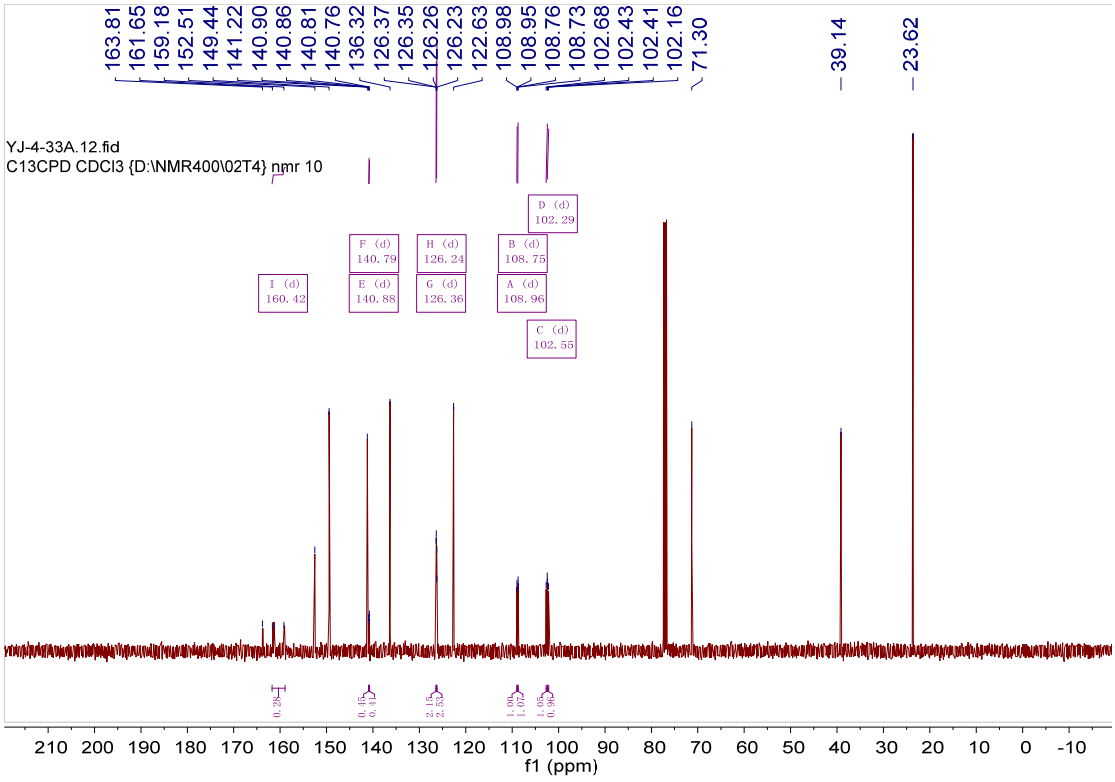


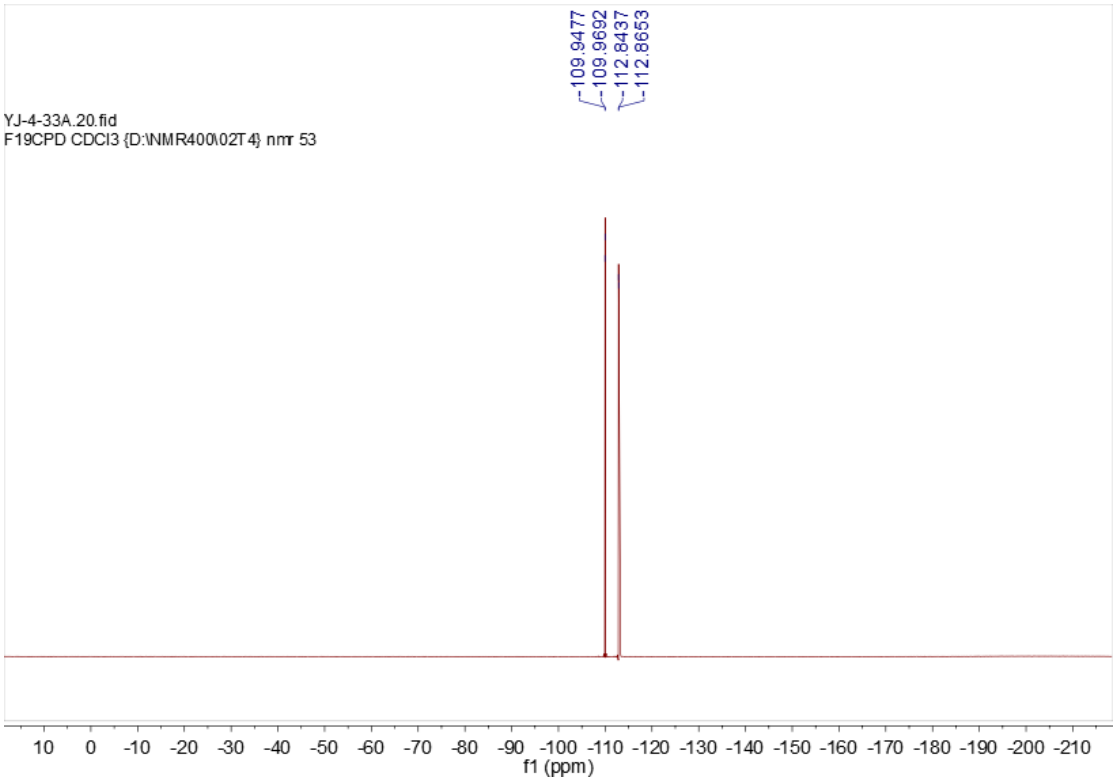


4h

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

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

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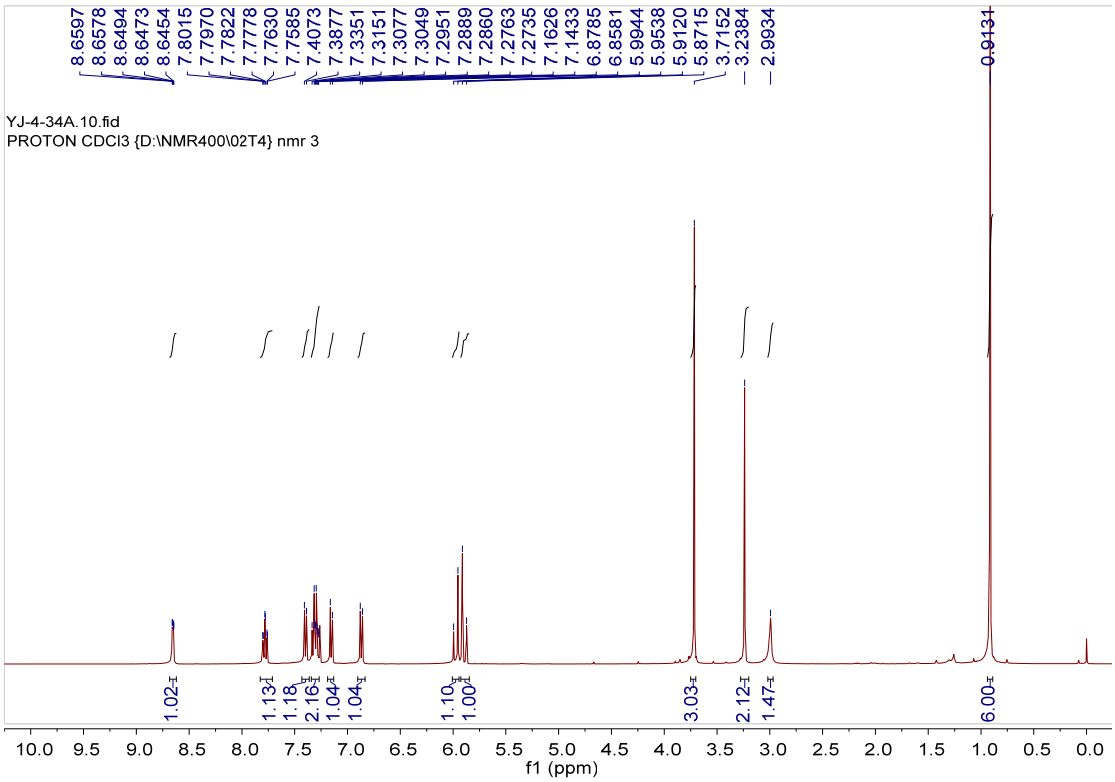
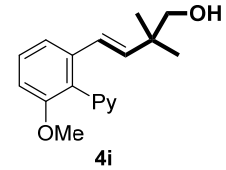
f1 (ppm)

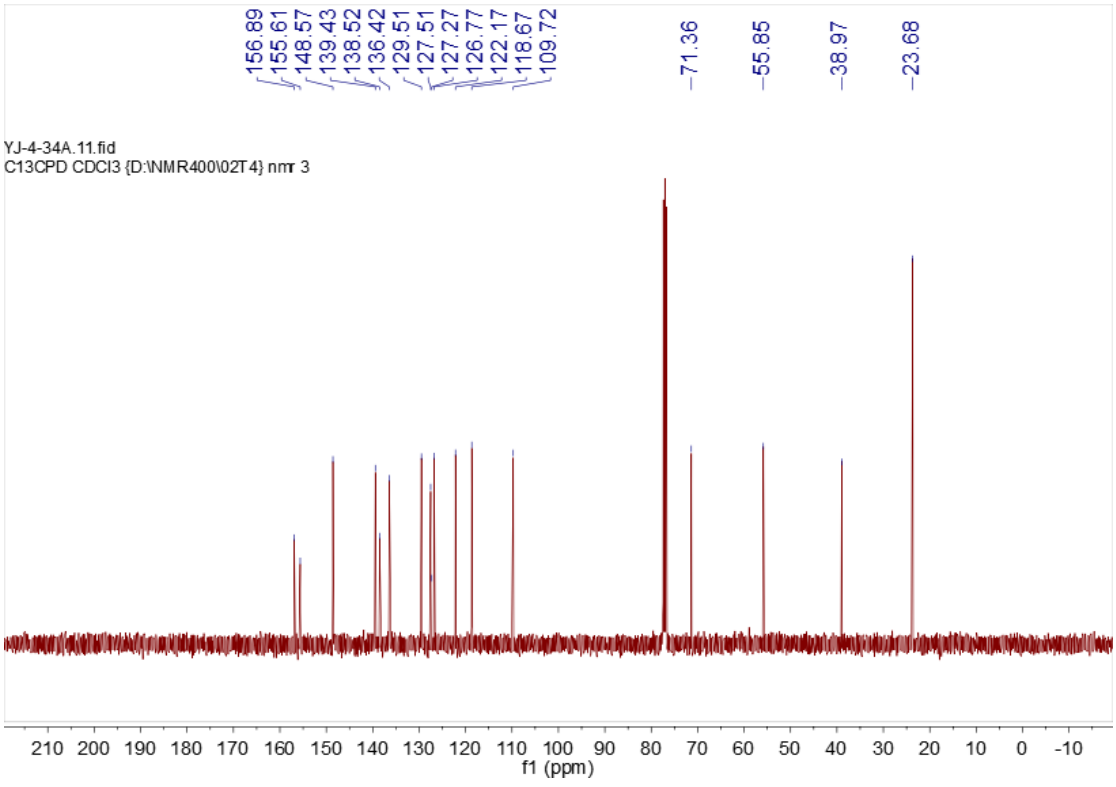


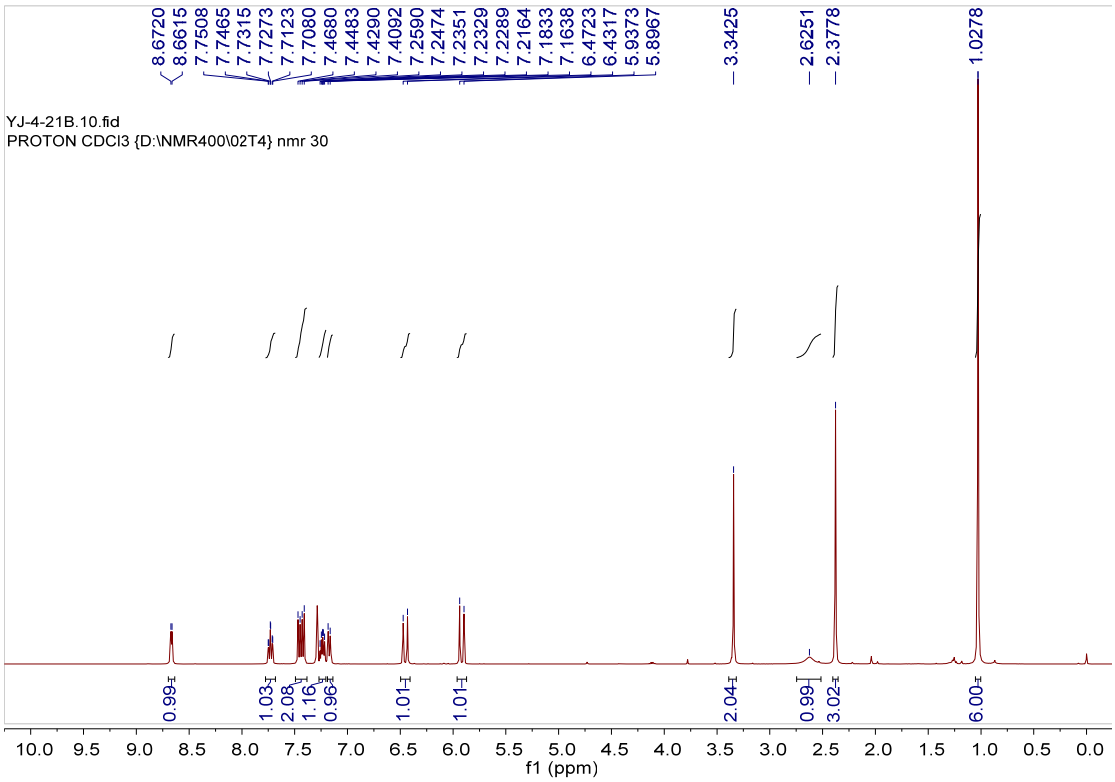


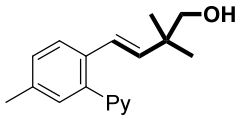
4i

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

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



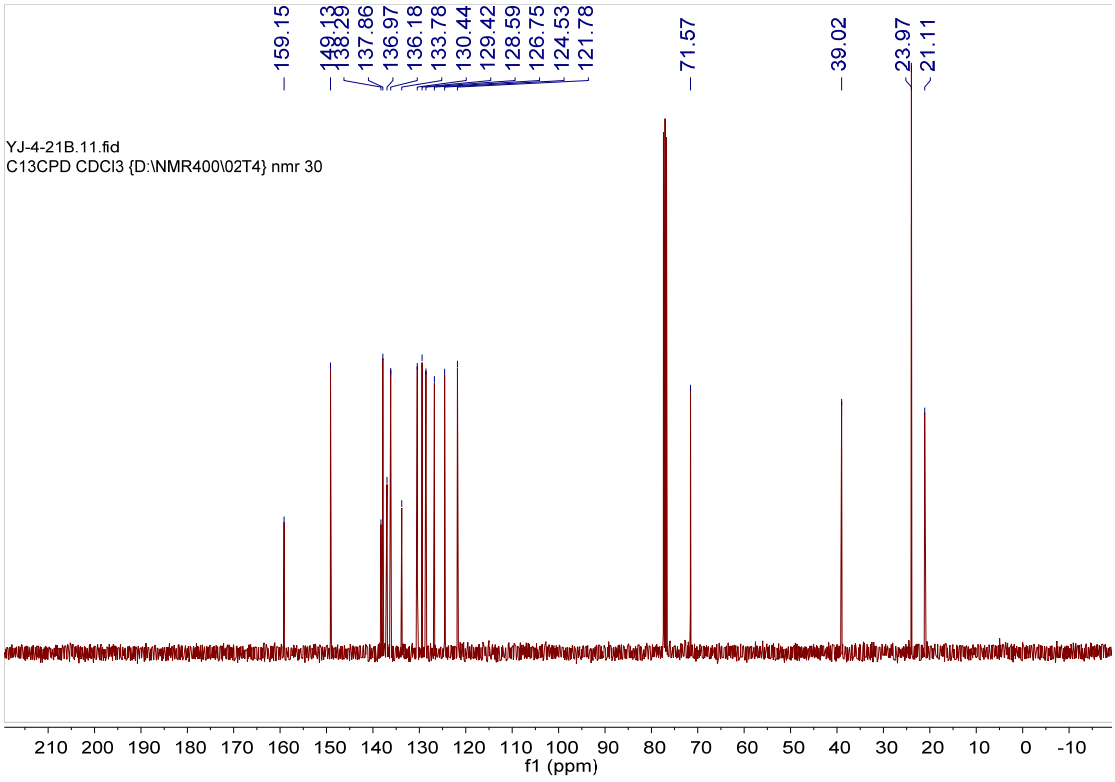


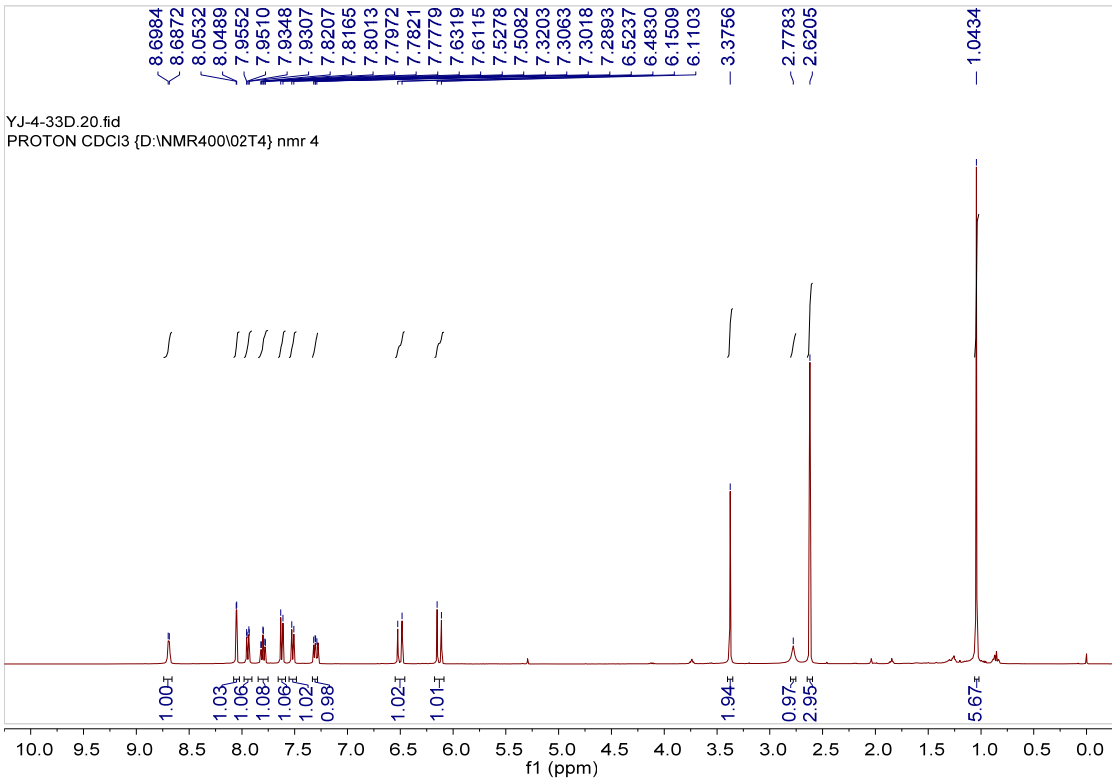


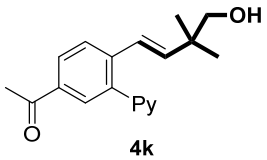
4j

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

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



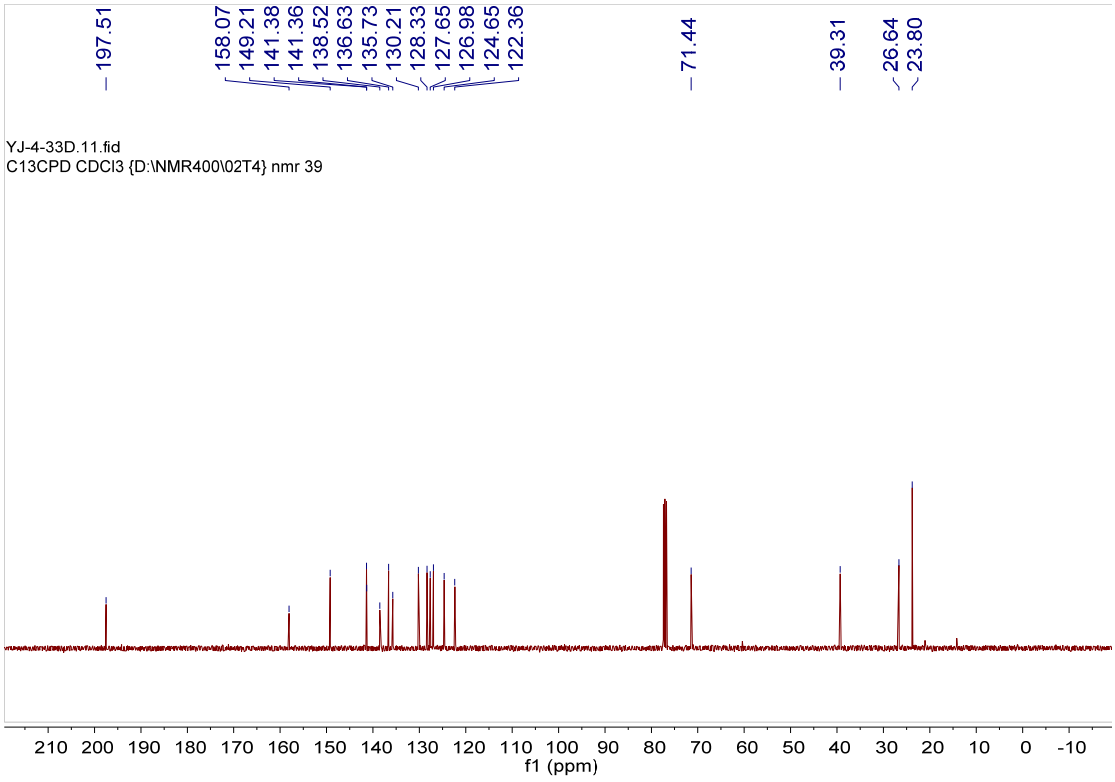


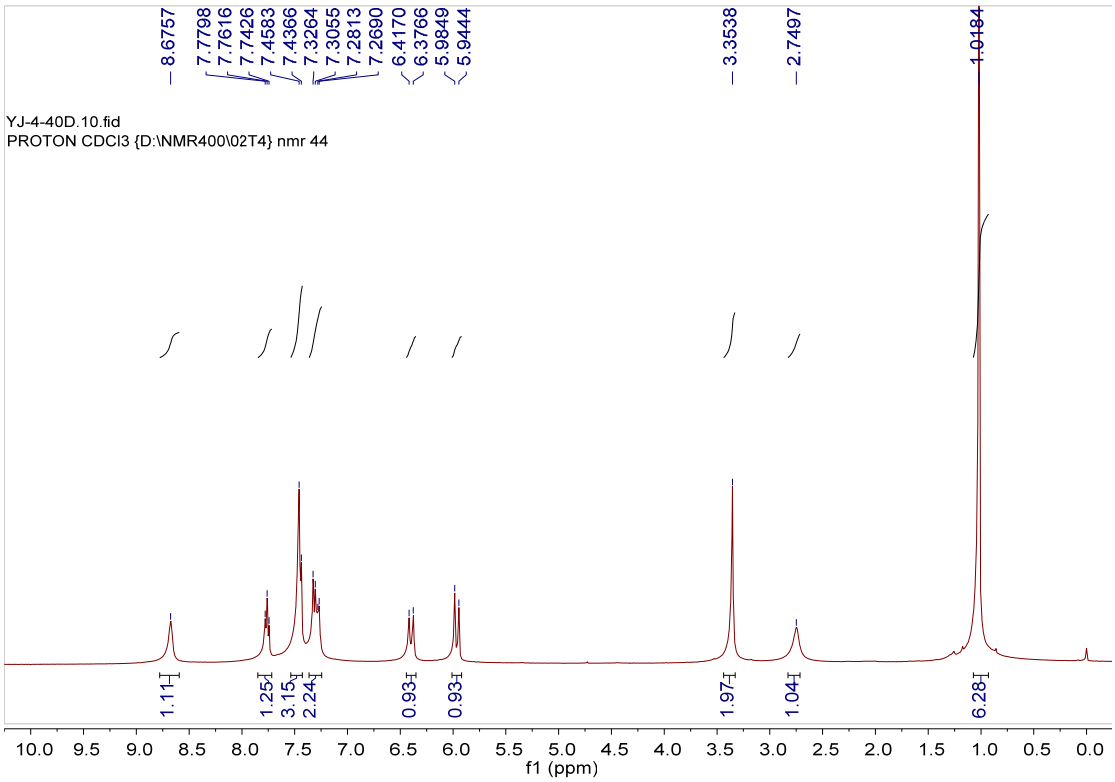


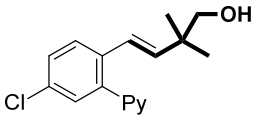
4k

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

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



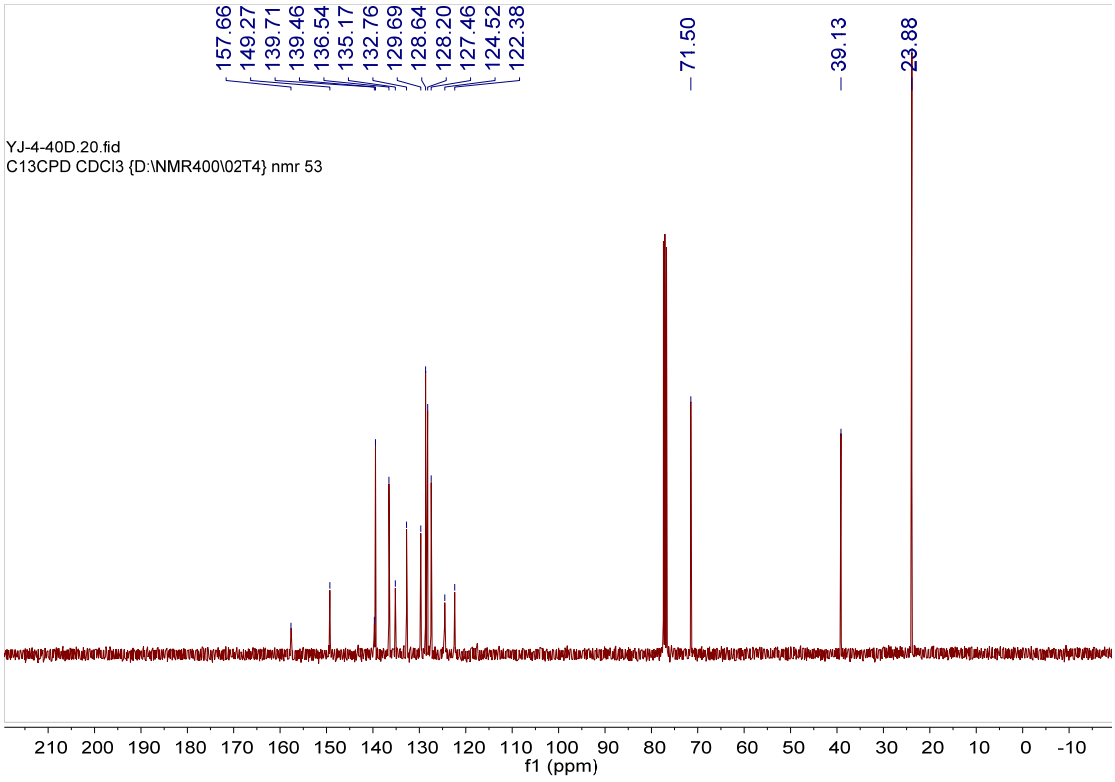


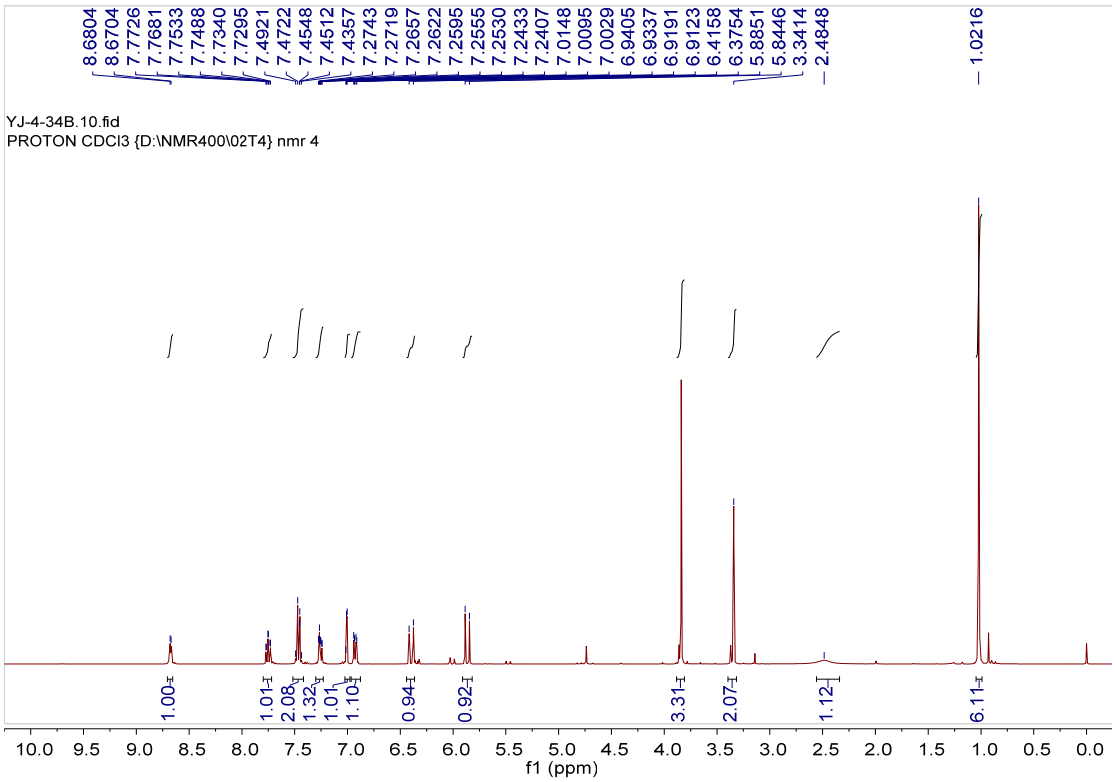


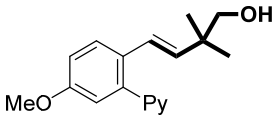
4l

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

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



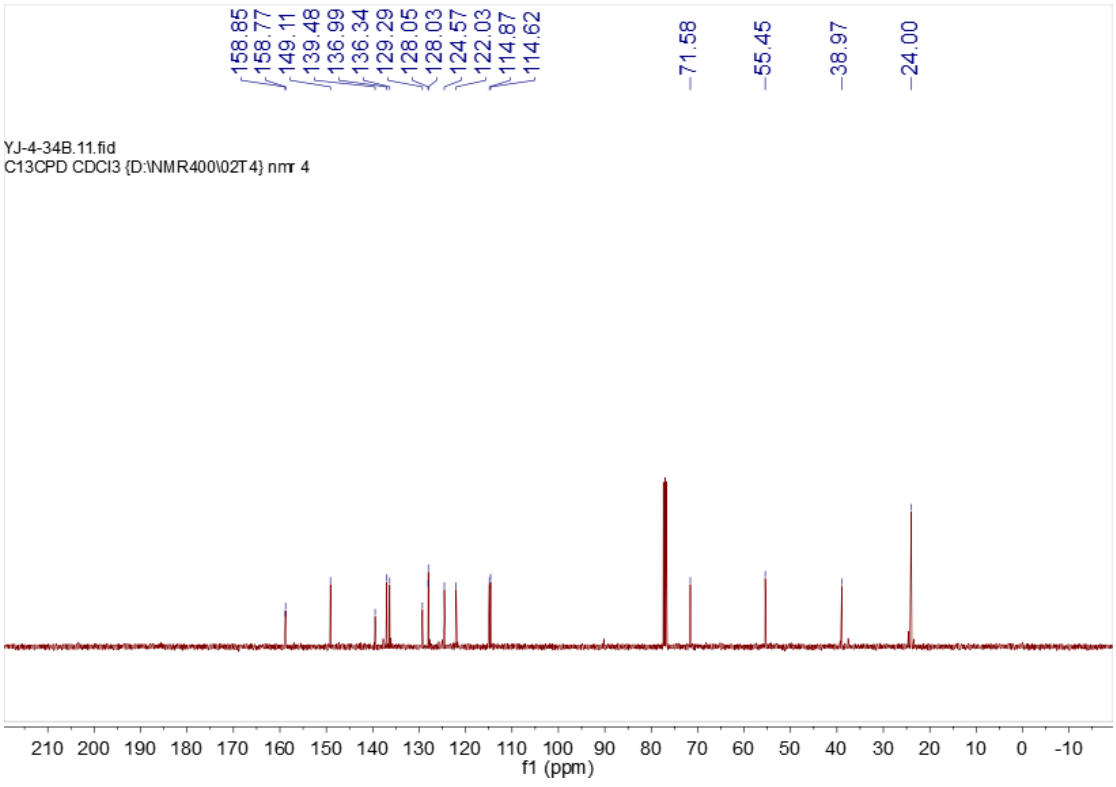


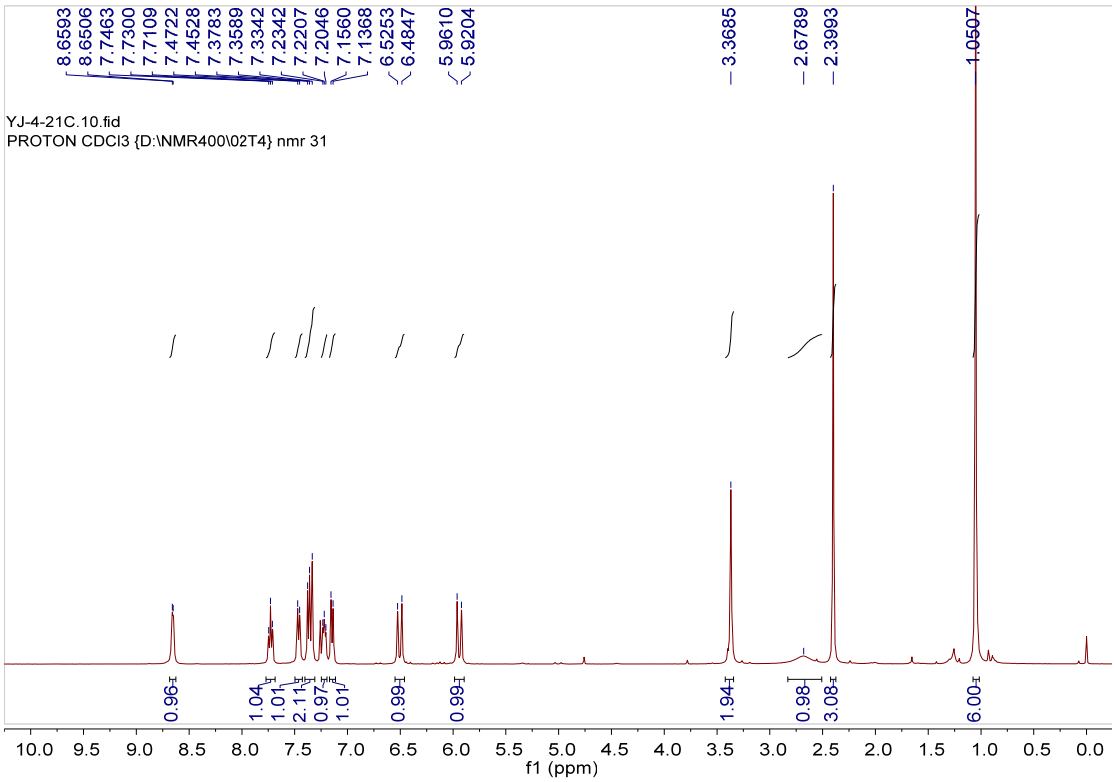


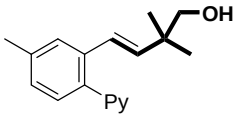
4m

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

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



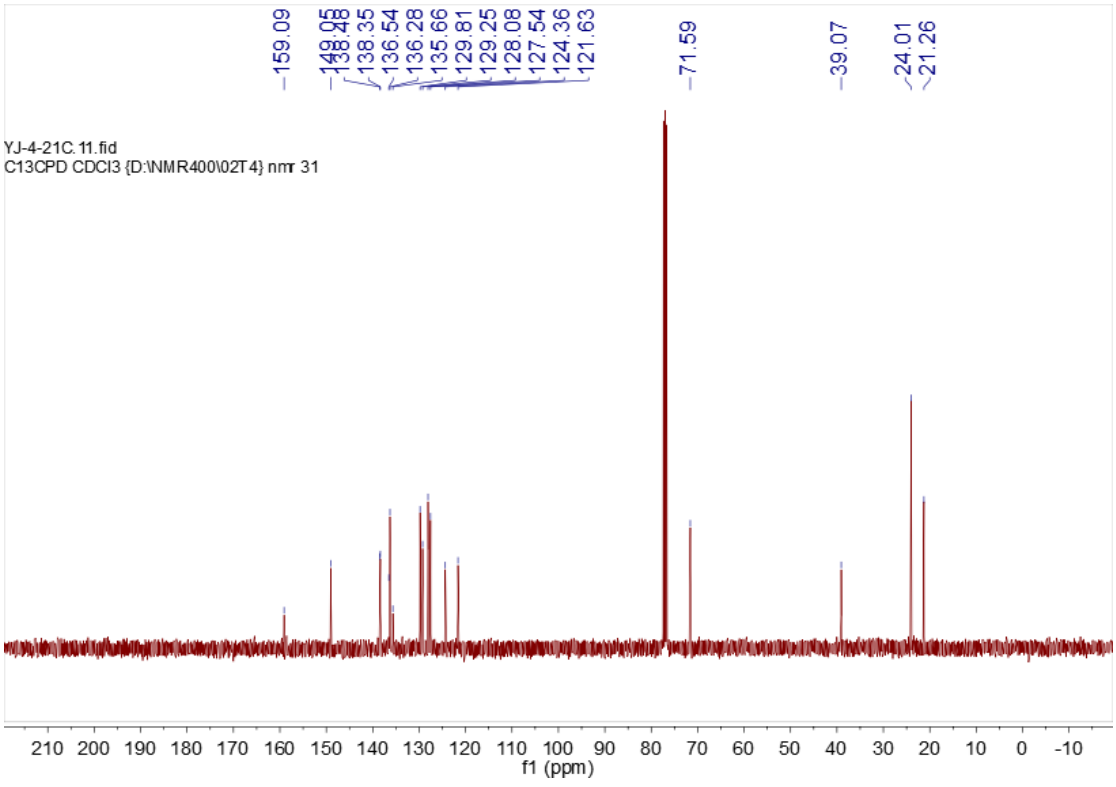


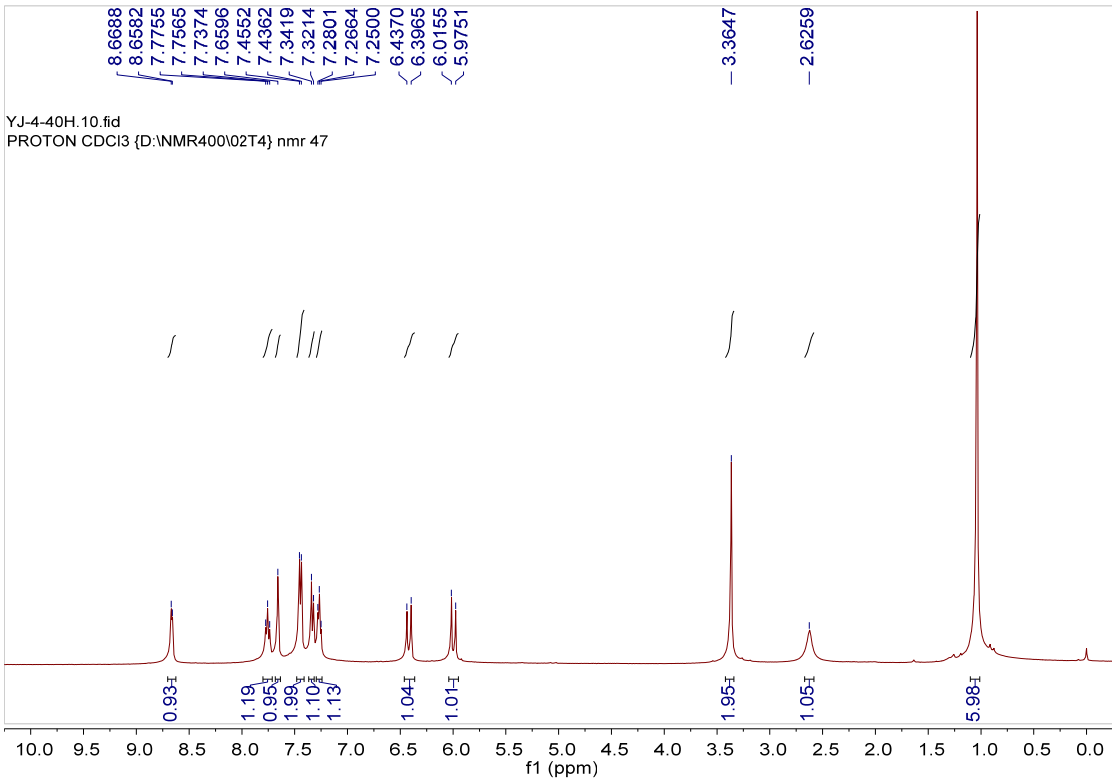


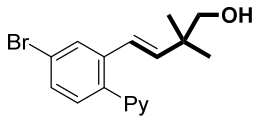
4n

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

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



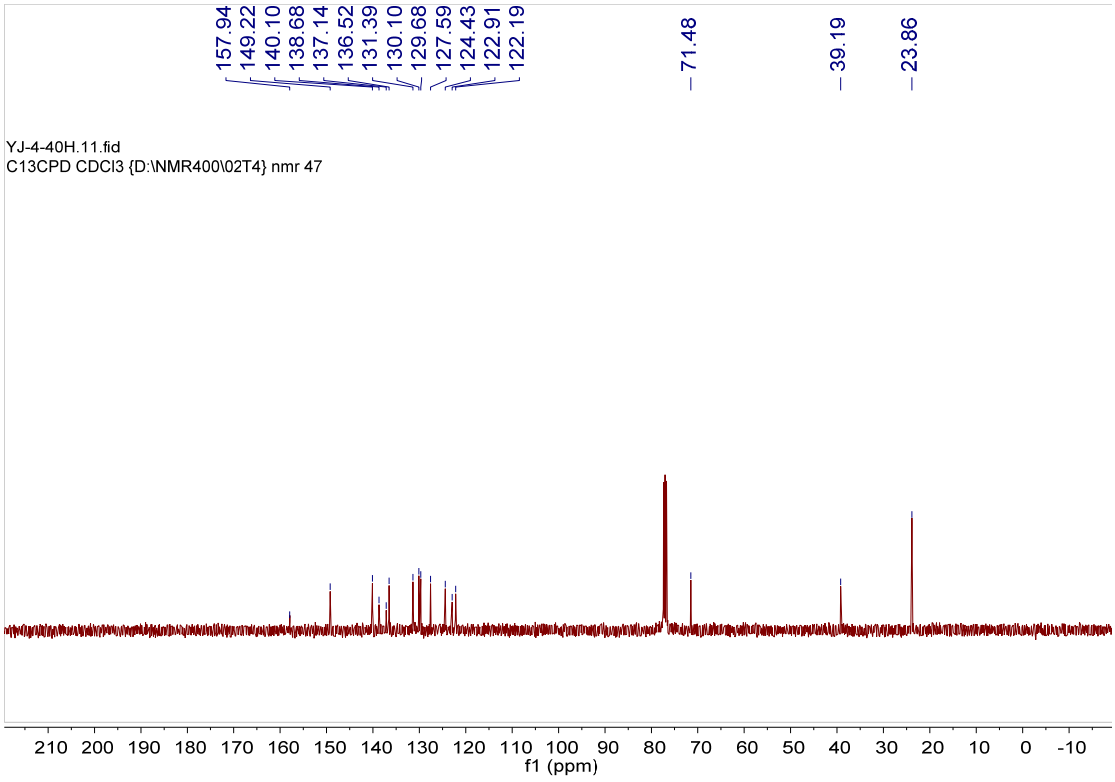


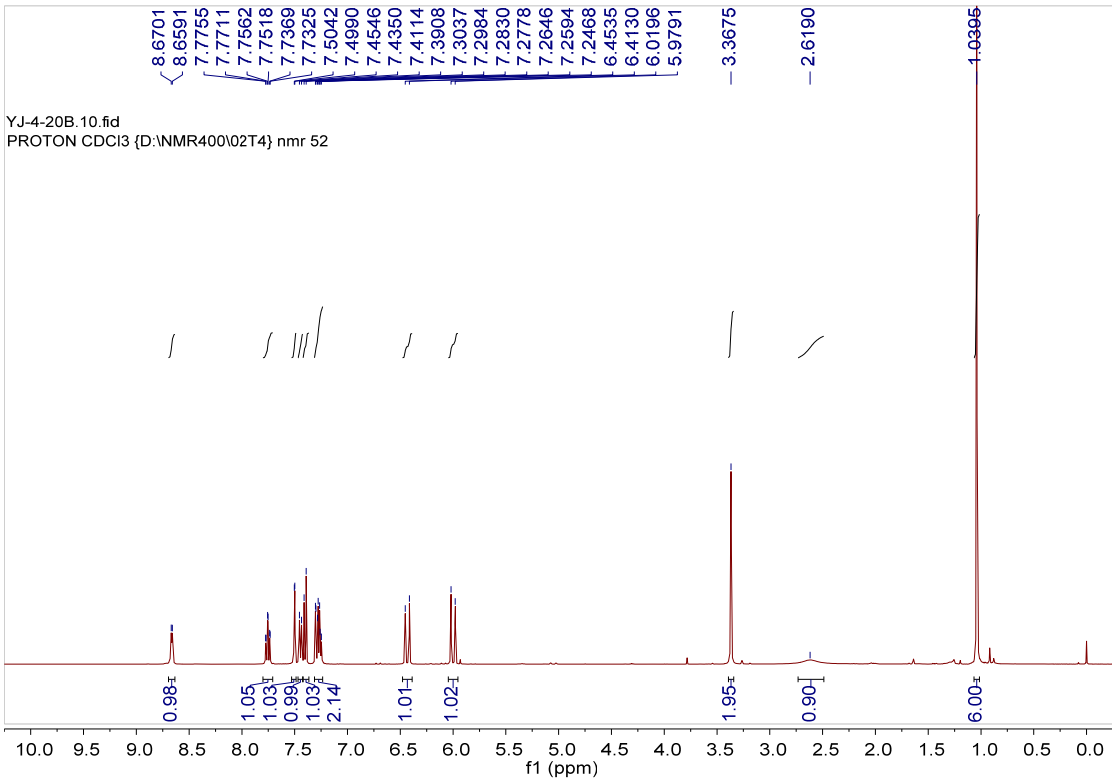


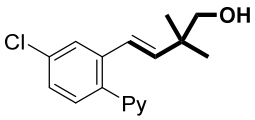
4o

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

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



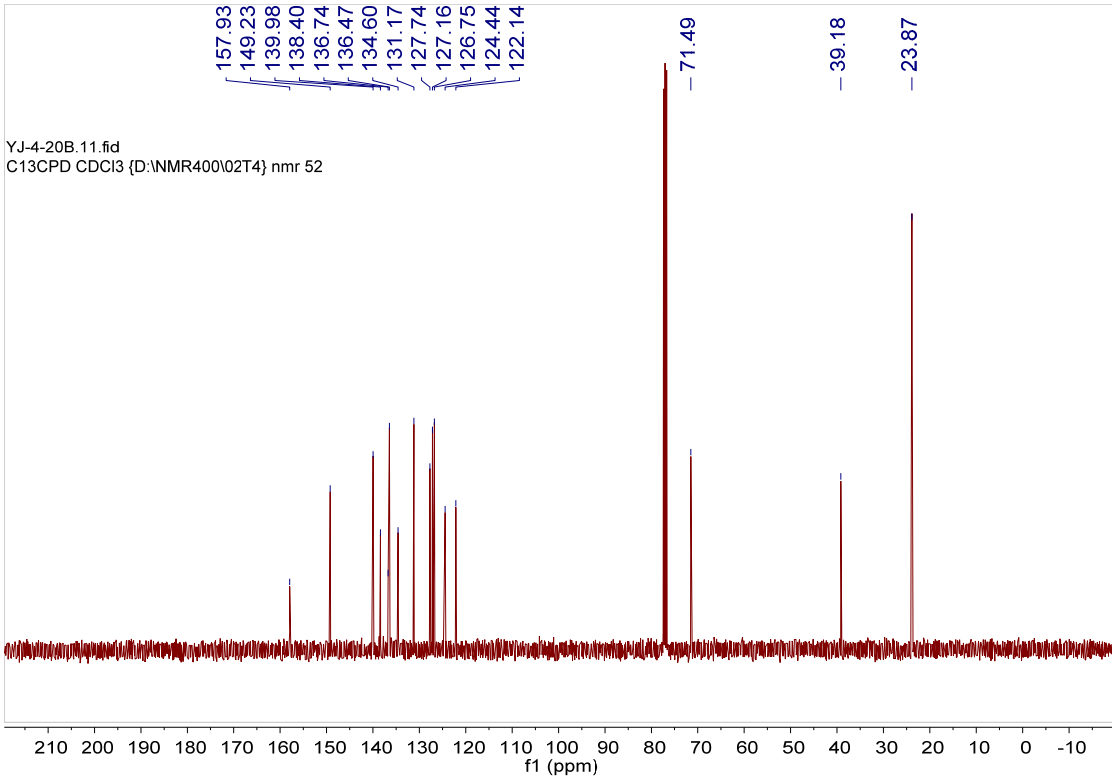


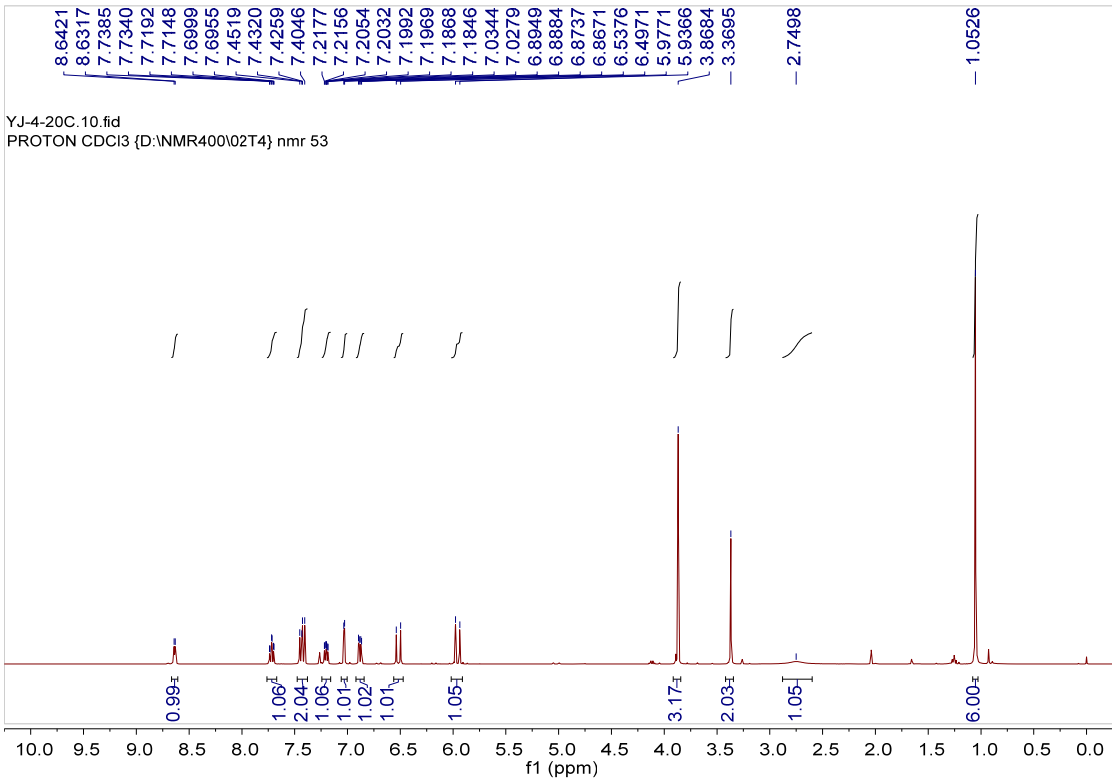


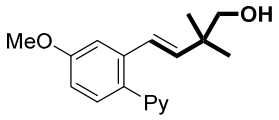
4p

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

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



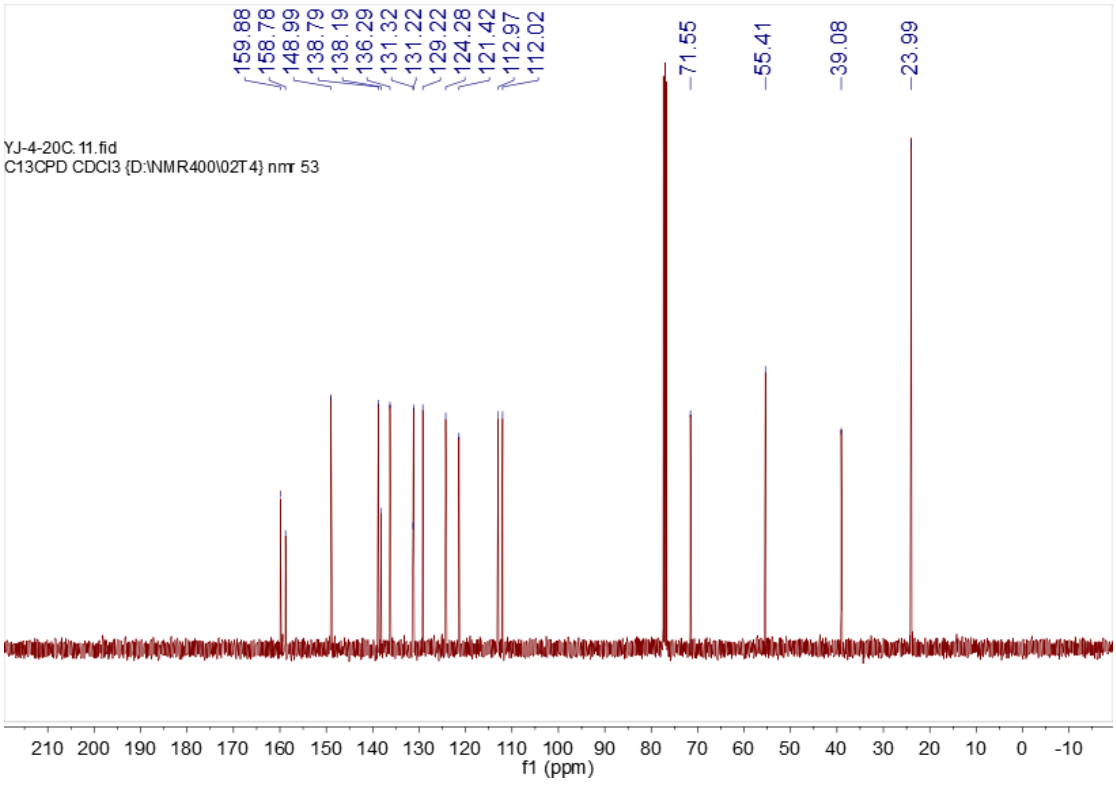


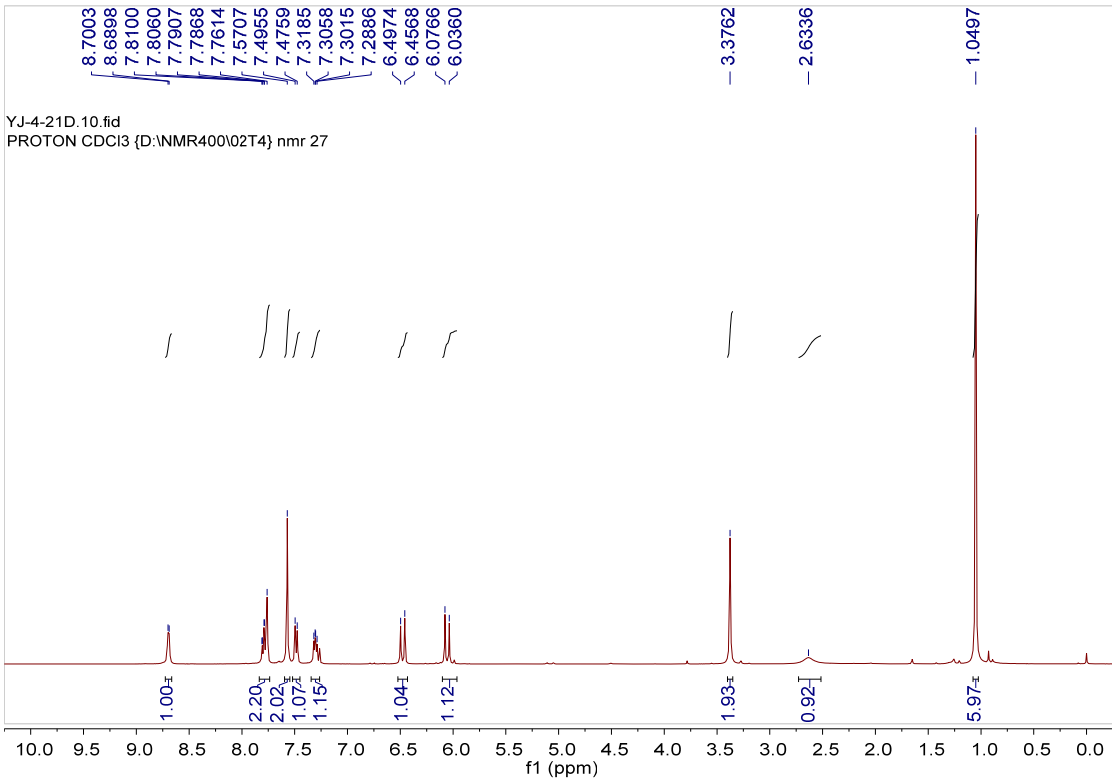


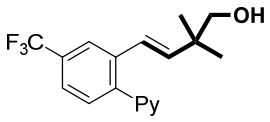
4q

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

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



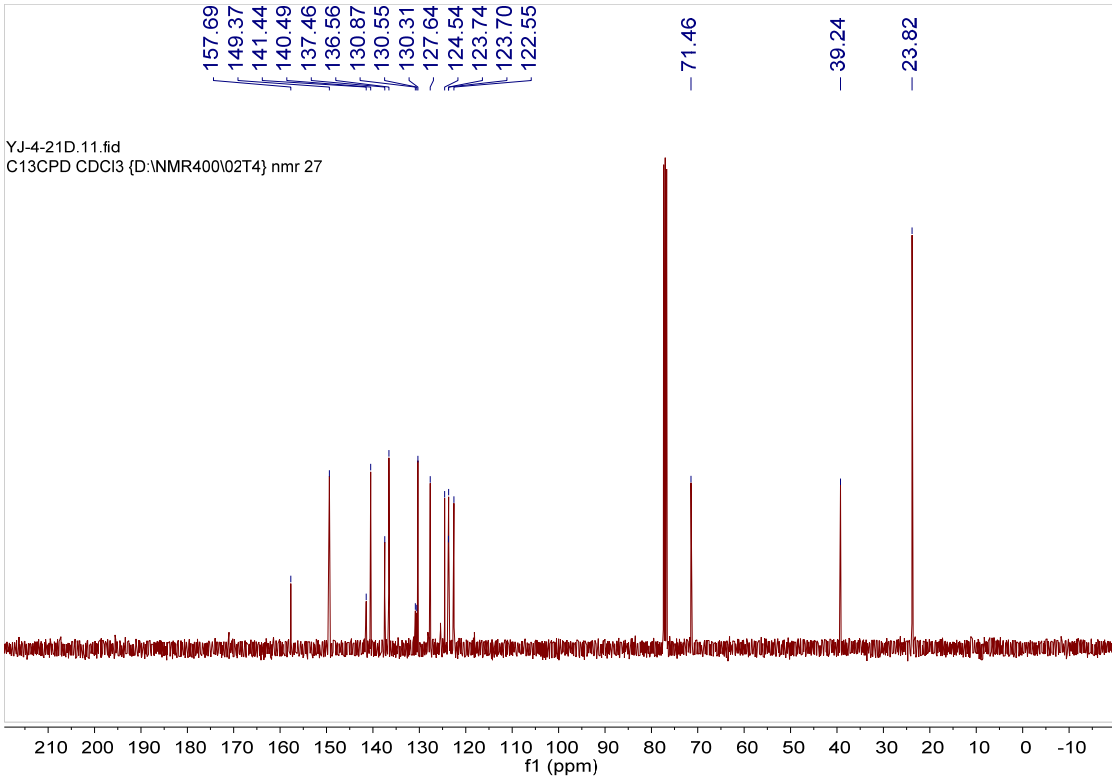


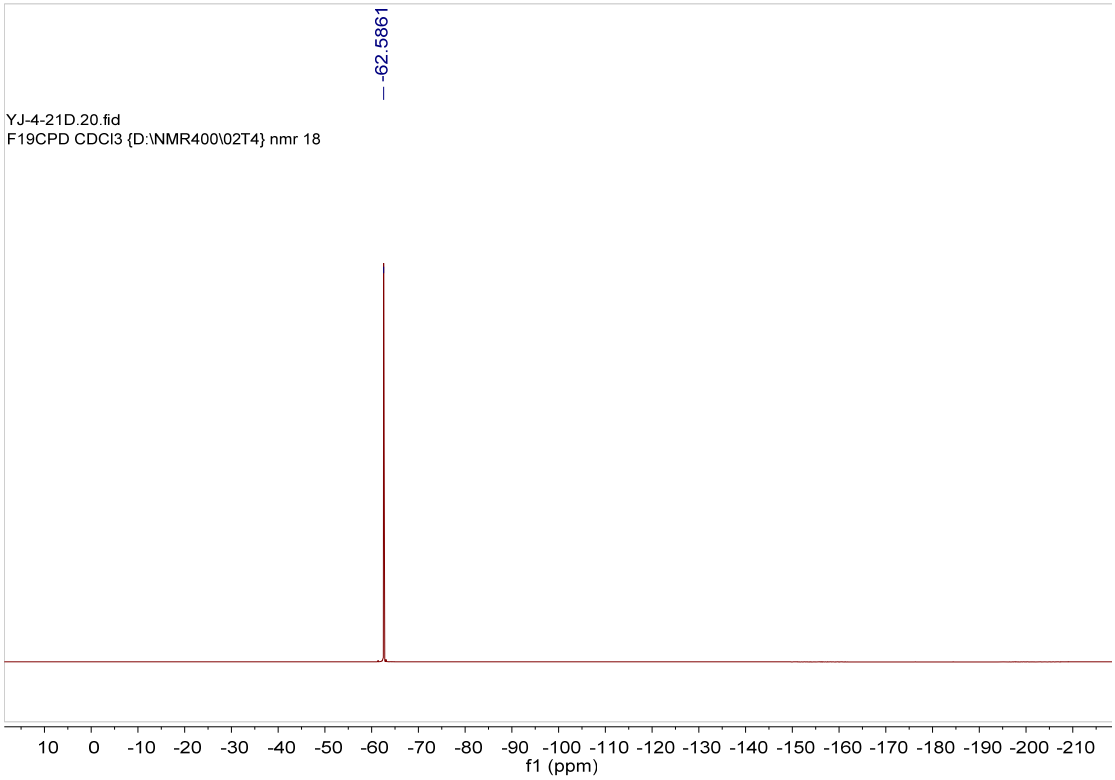


4r

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

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

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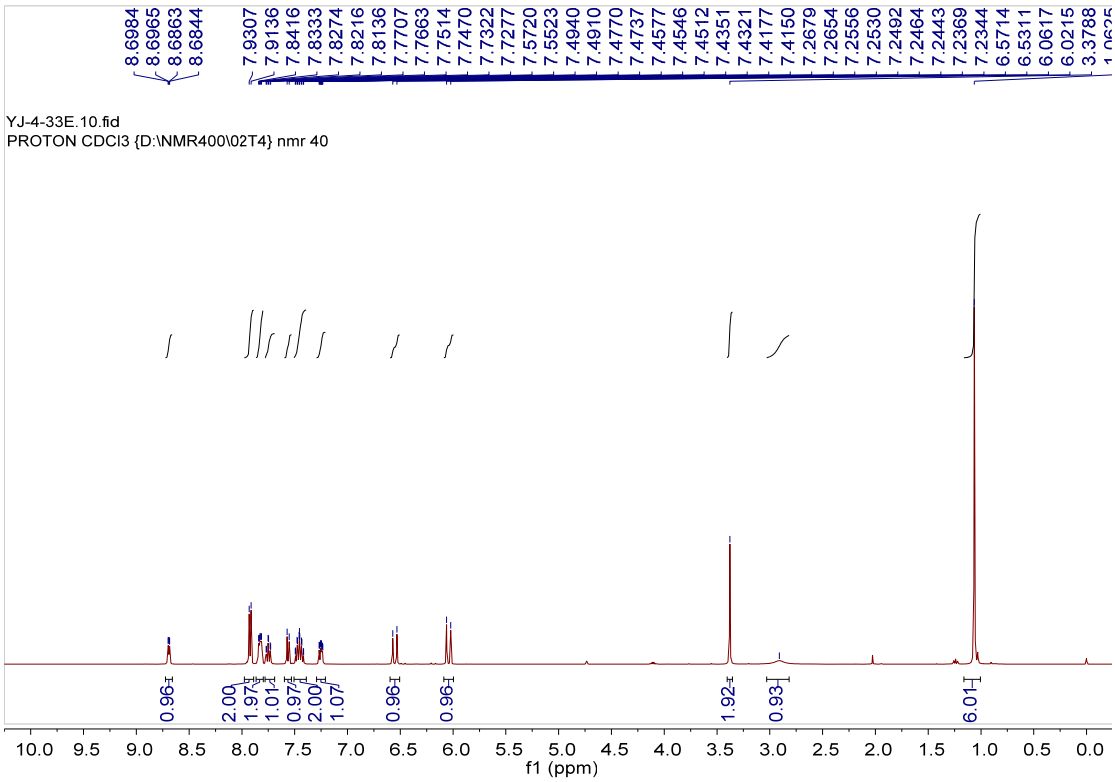
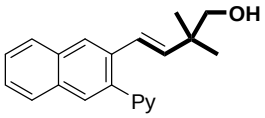
f1 (ppm)

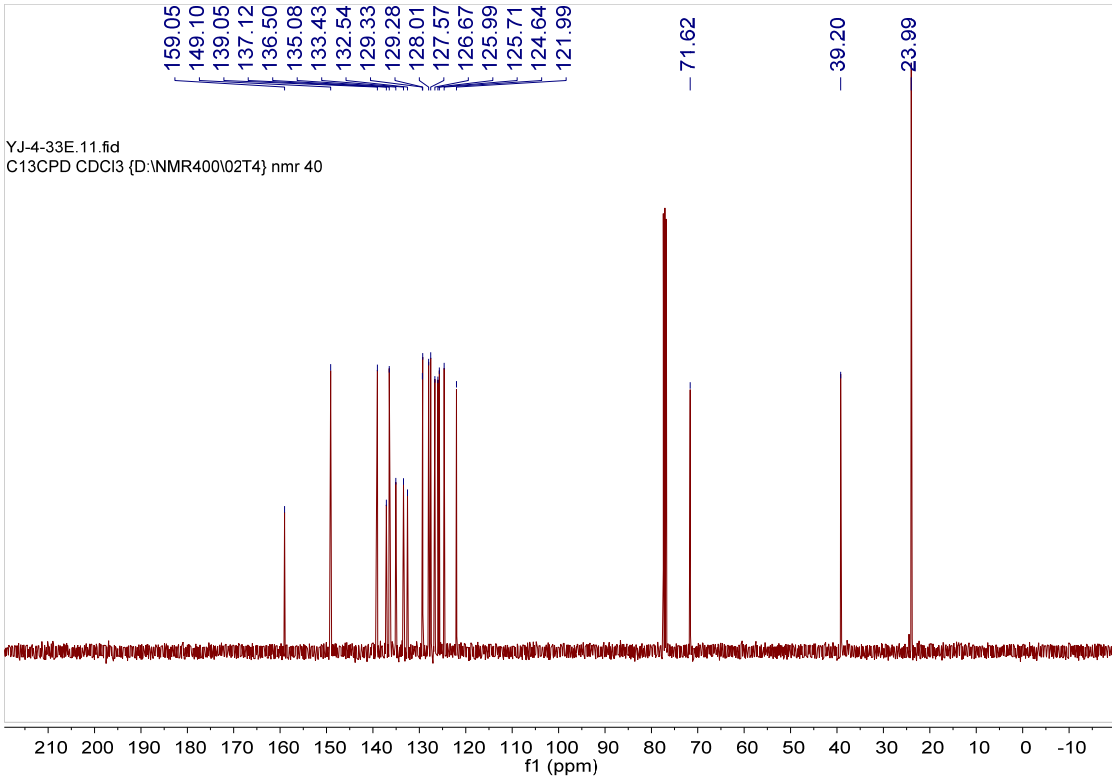


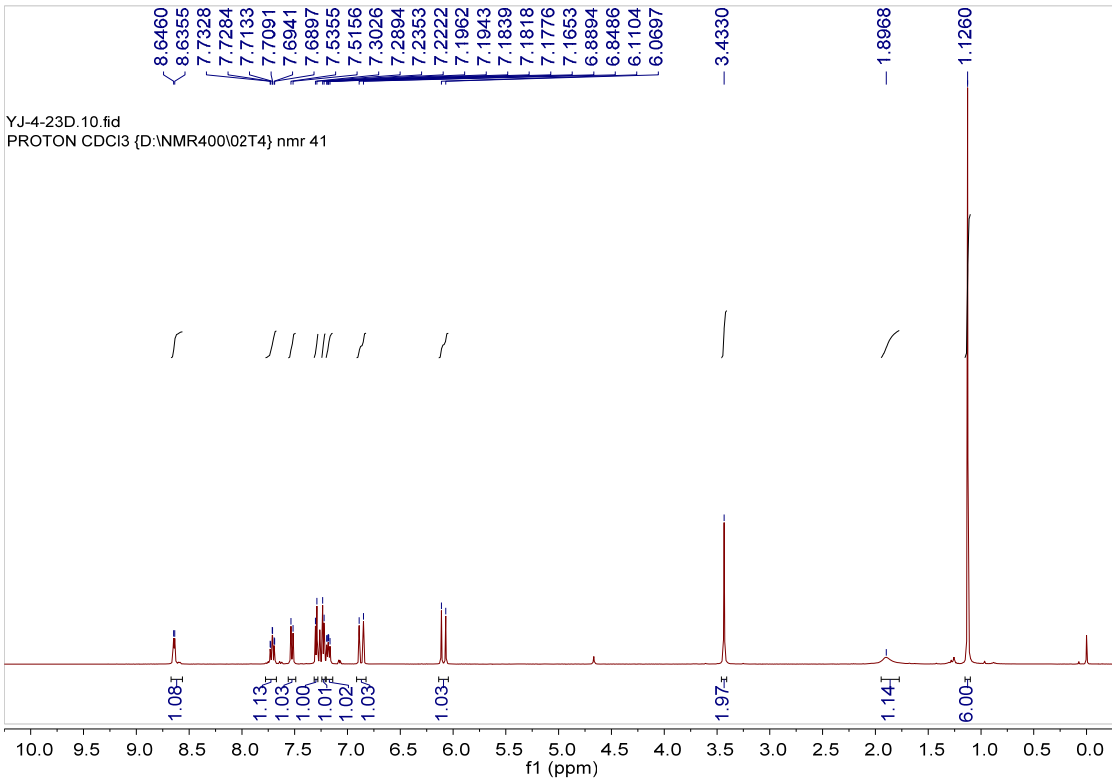


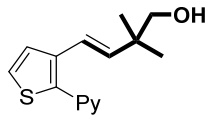
4s

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

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



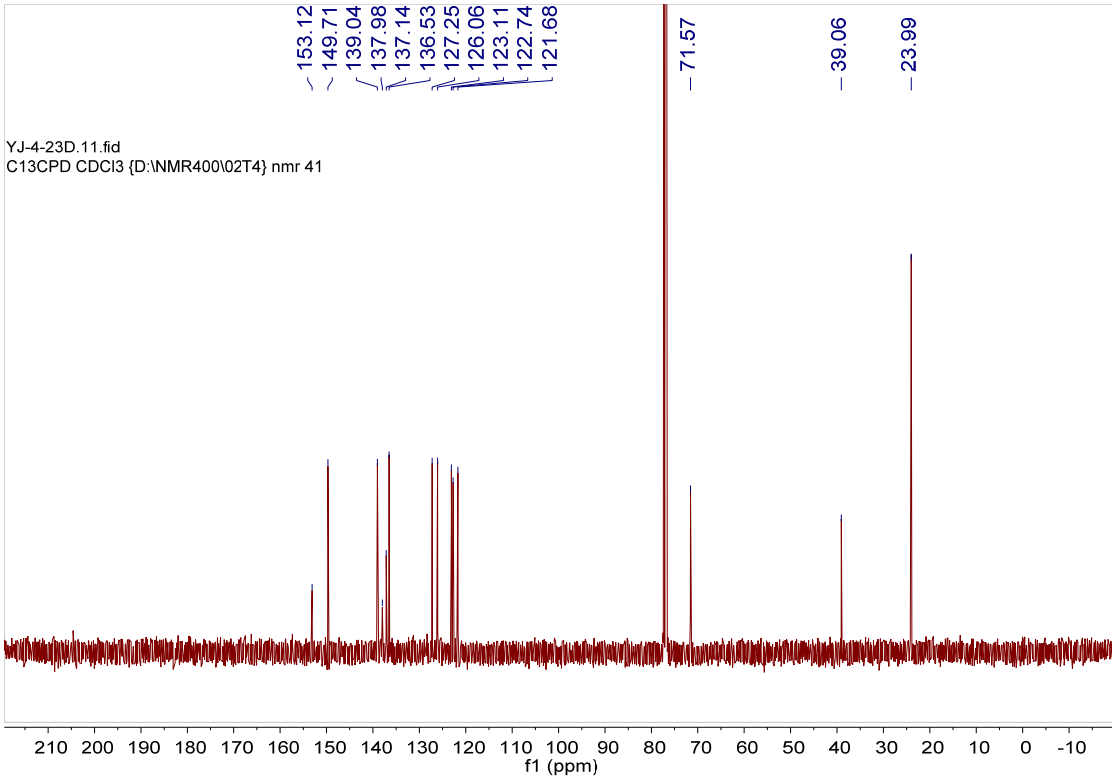


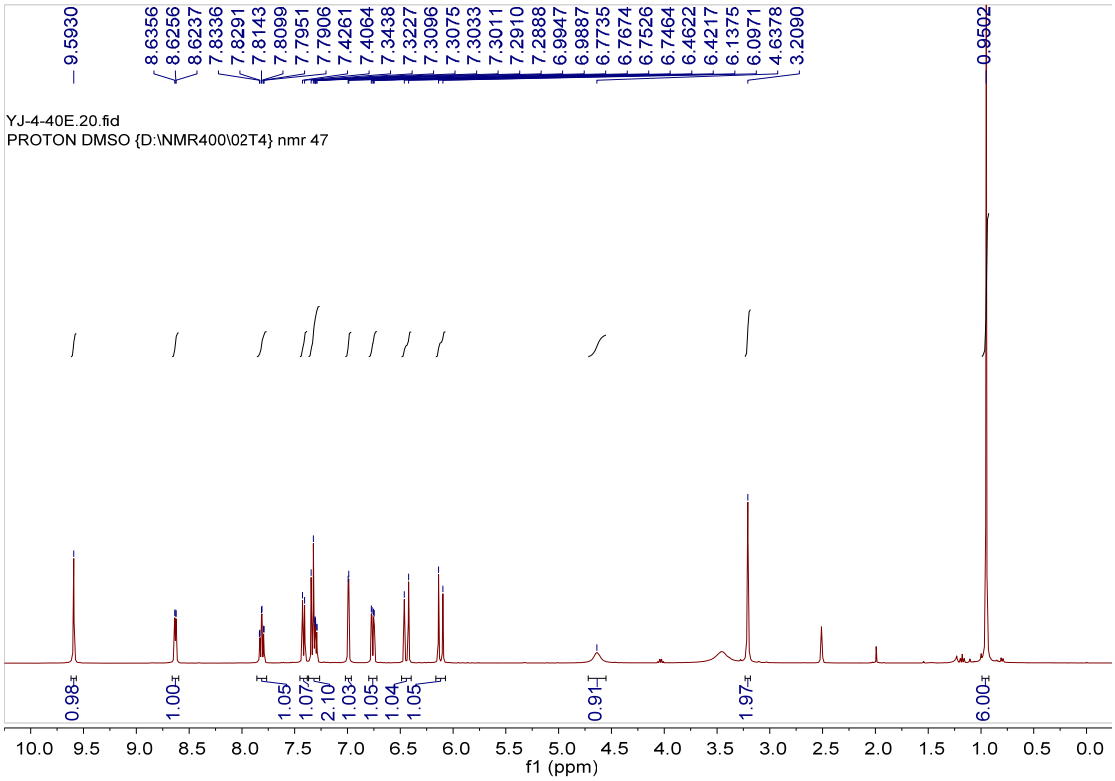


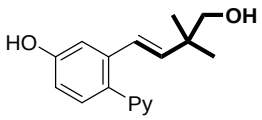
4t

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

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



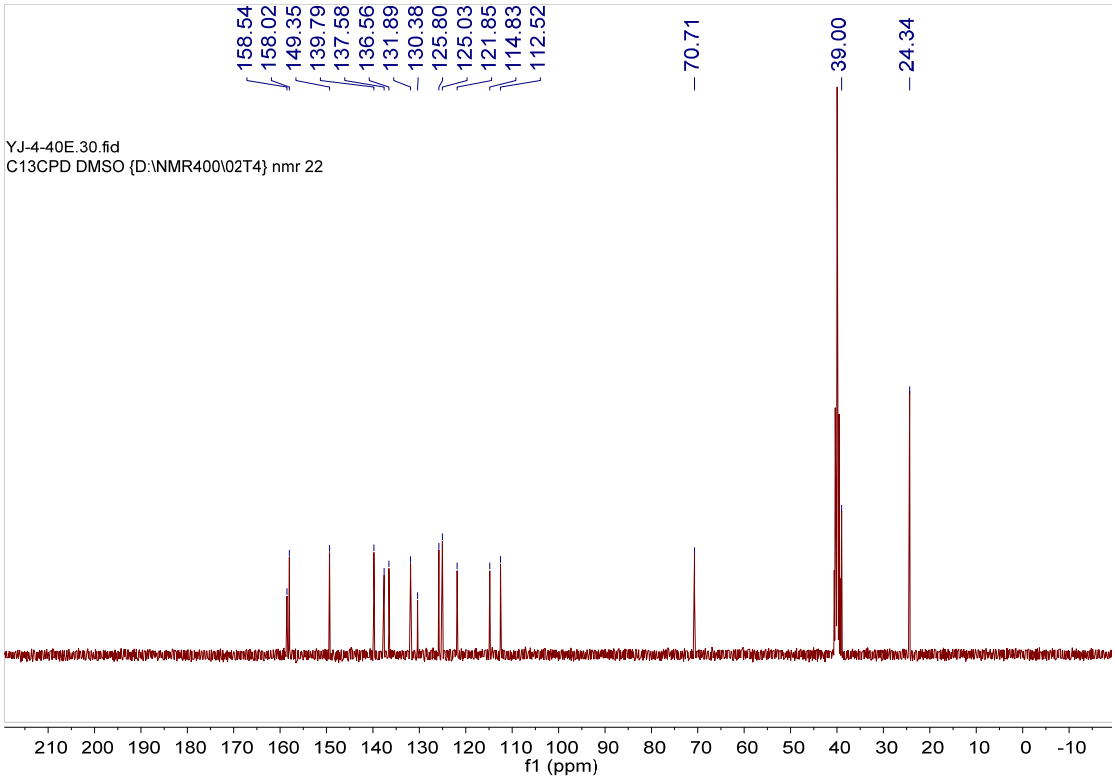


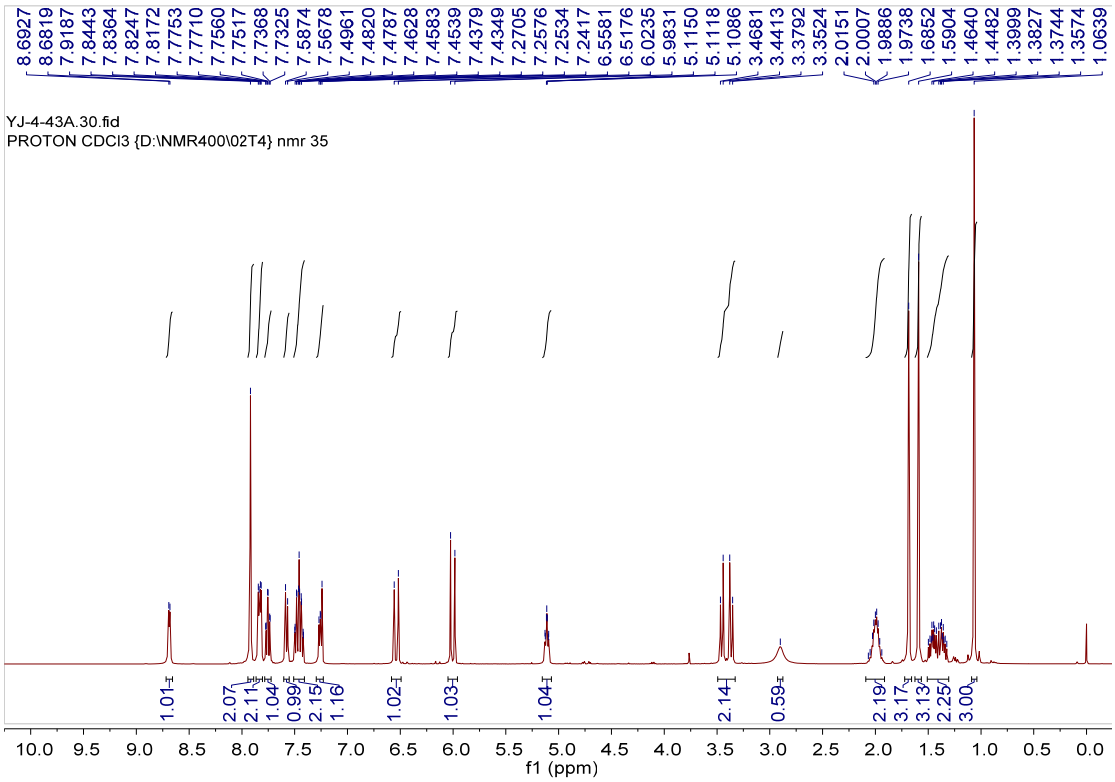


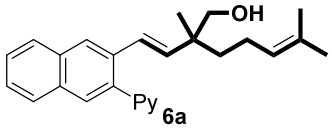
4u

^{1}H NMR (400 MHz, DMSO-d_6)

^{13}C NMR (100 MHz, DMSO-d_6)



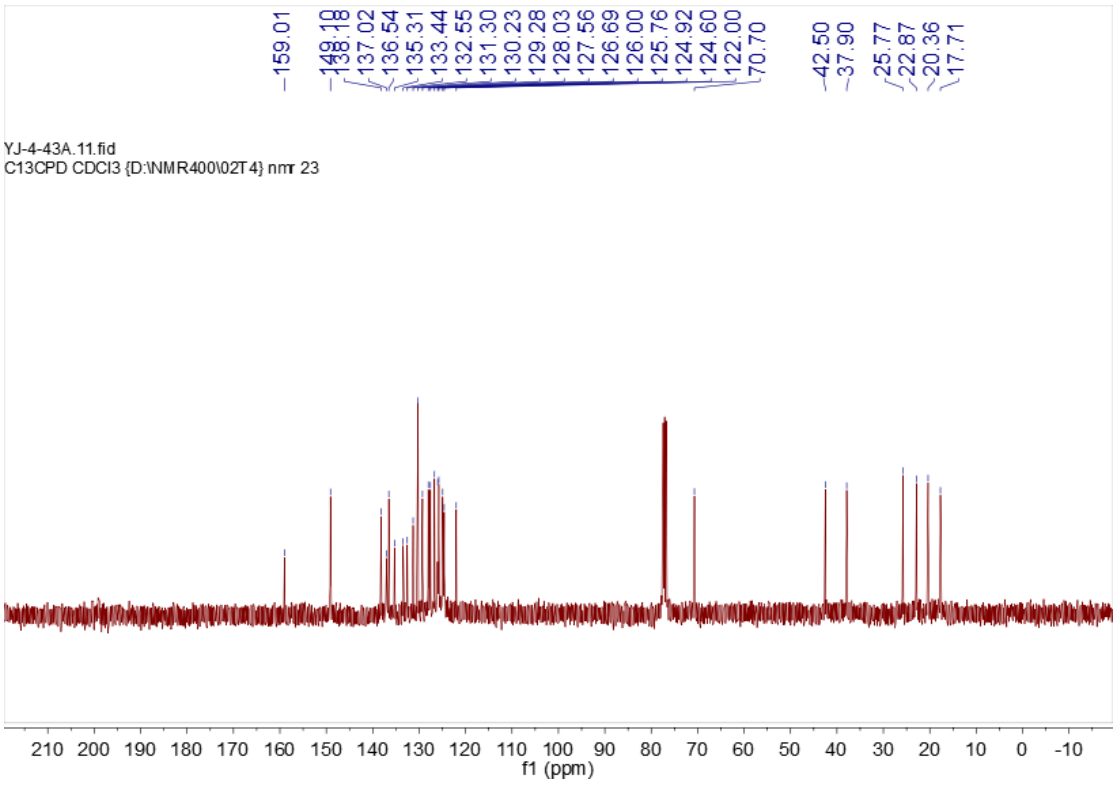


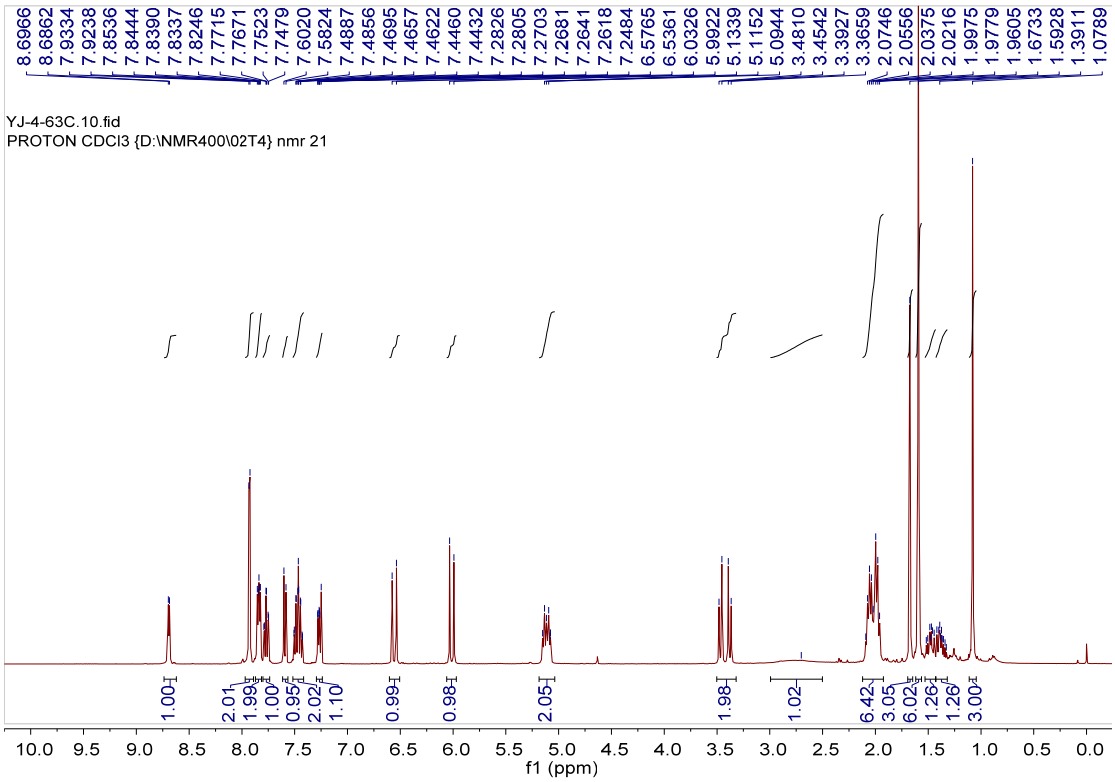


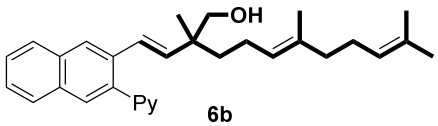
6a

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

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



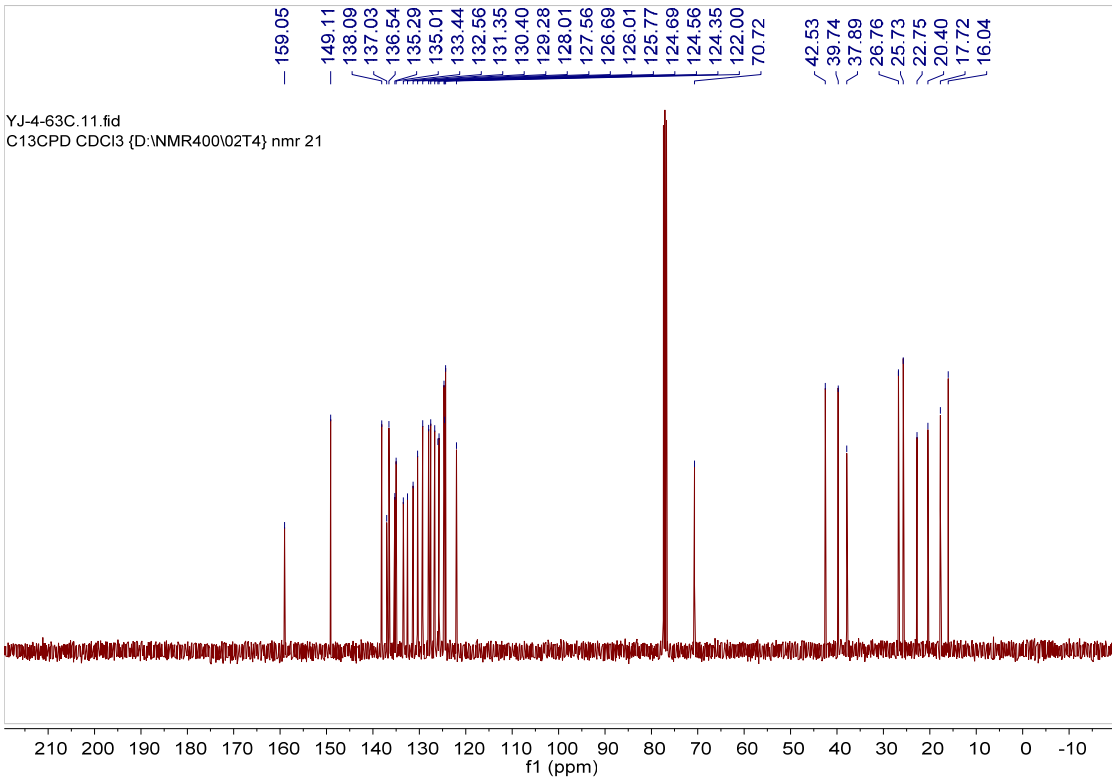


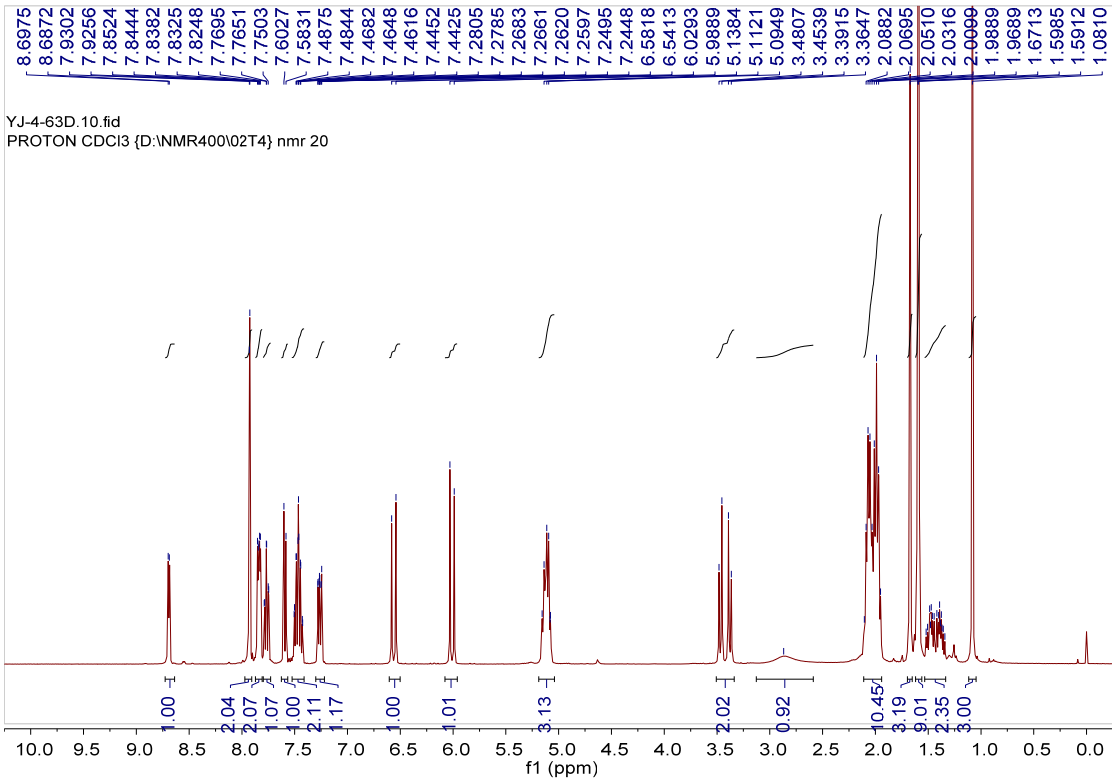


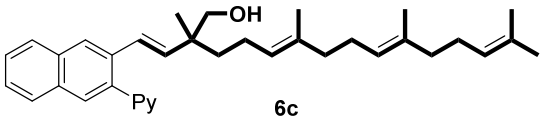
6b

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

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



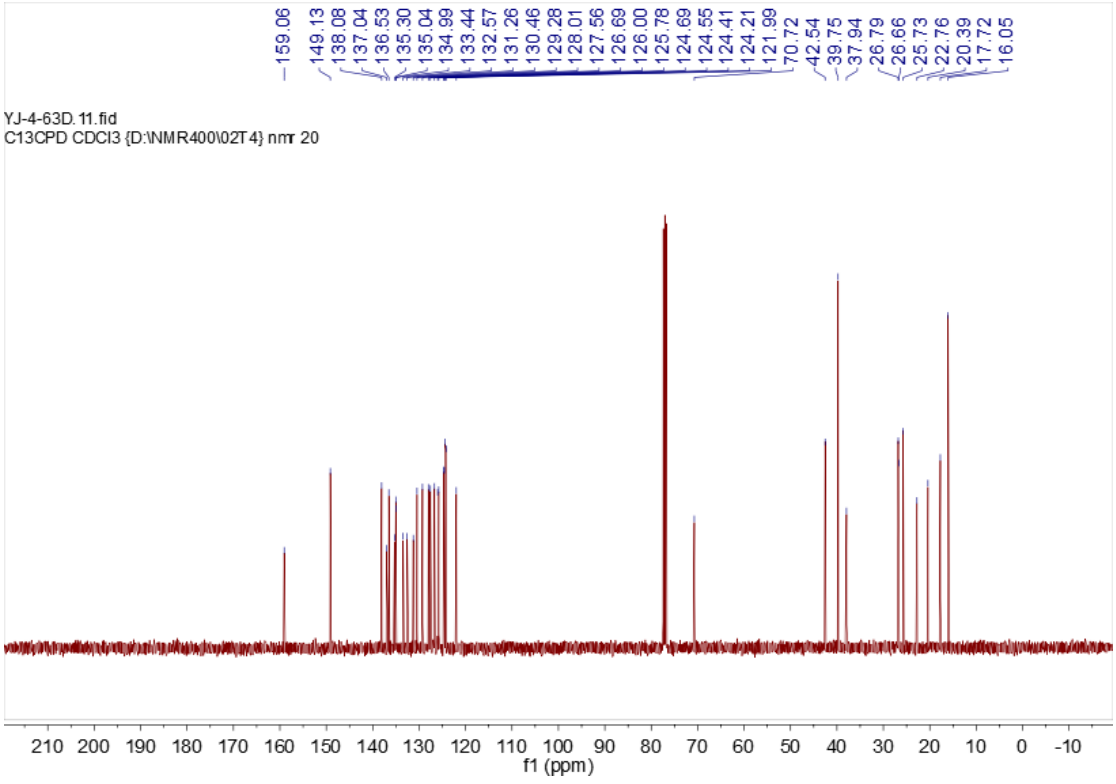


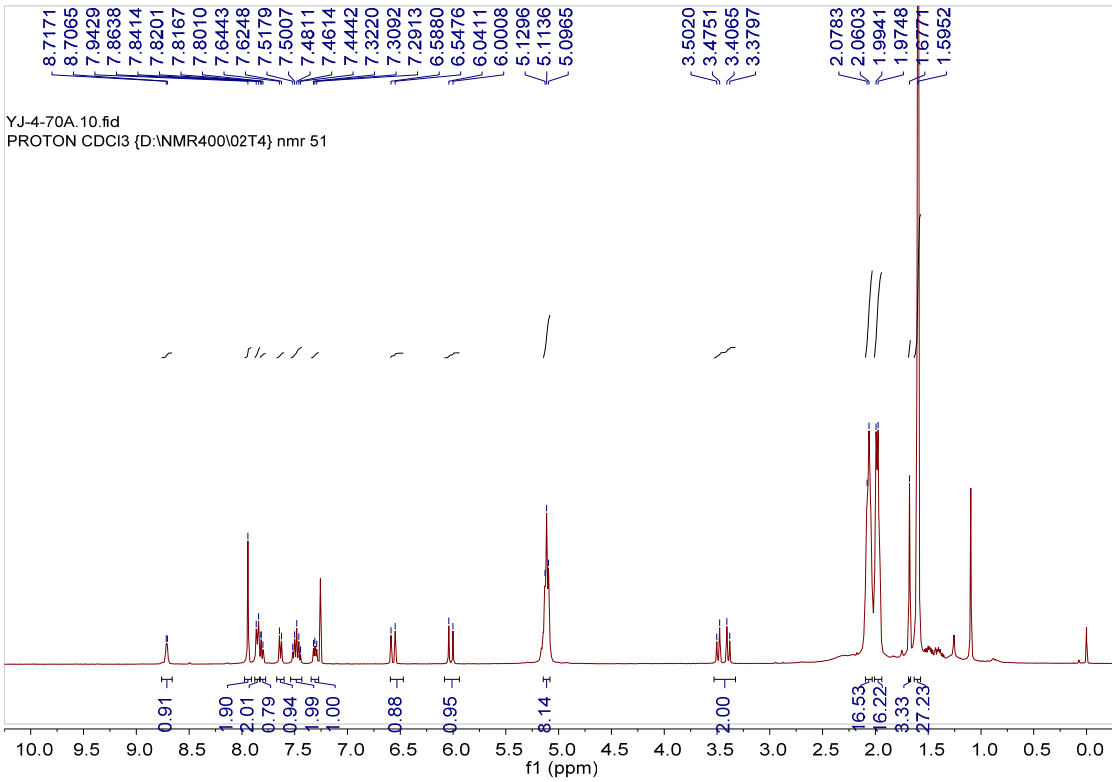


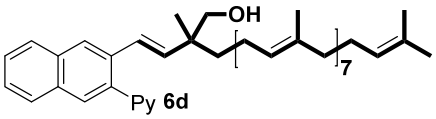
6c

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

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



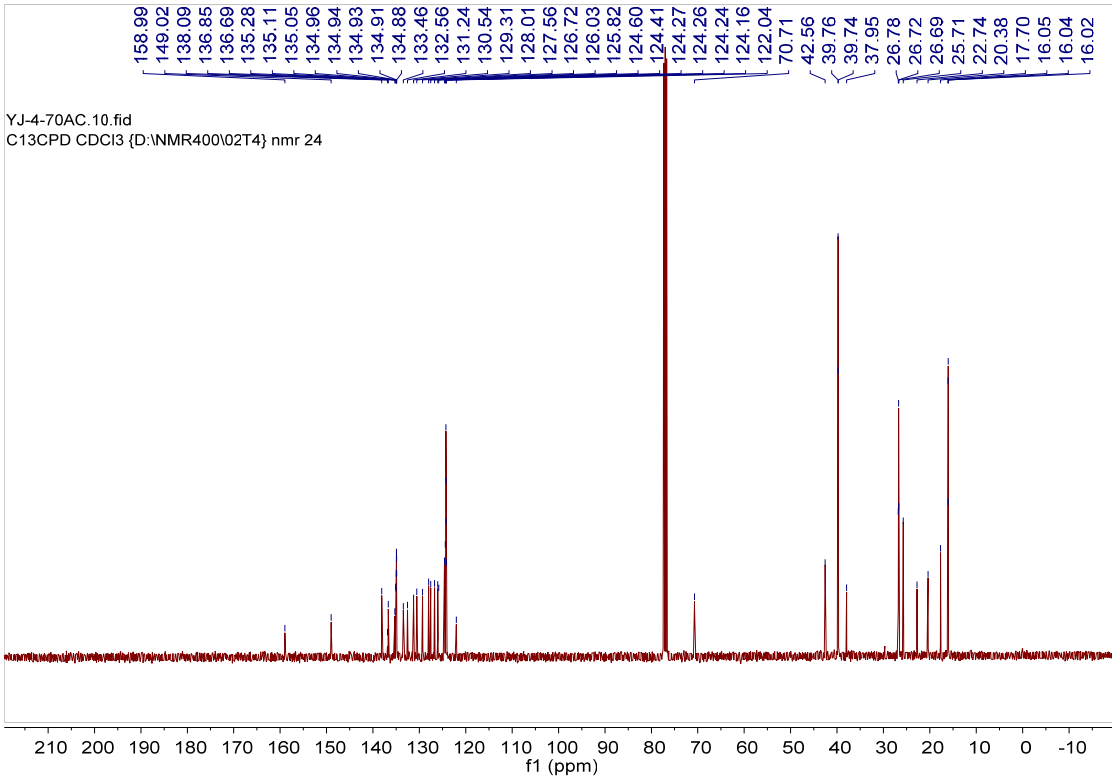


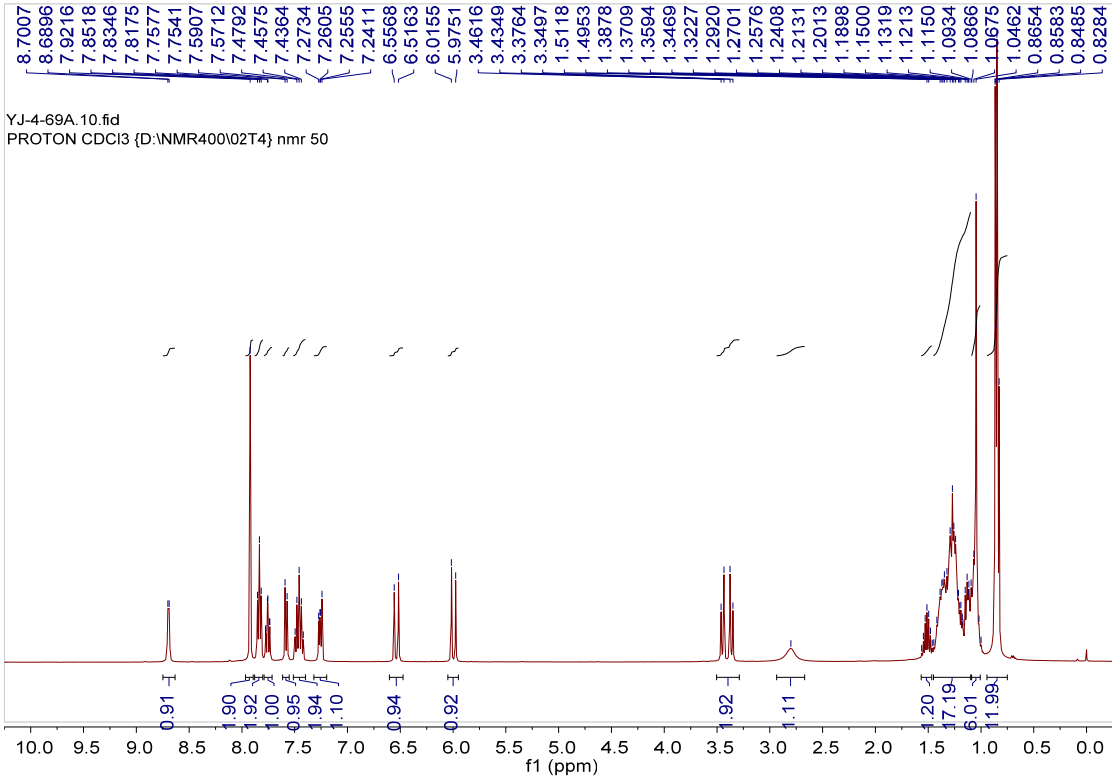


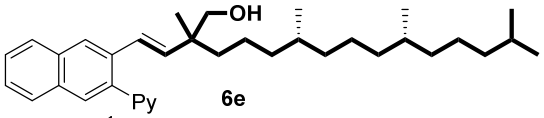
Py **6d**

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

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



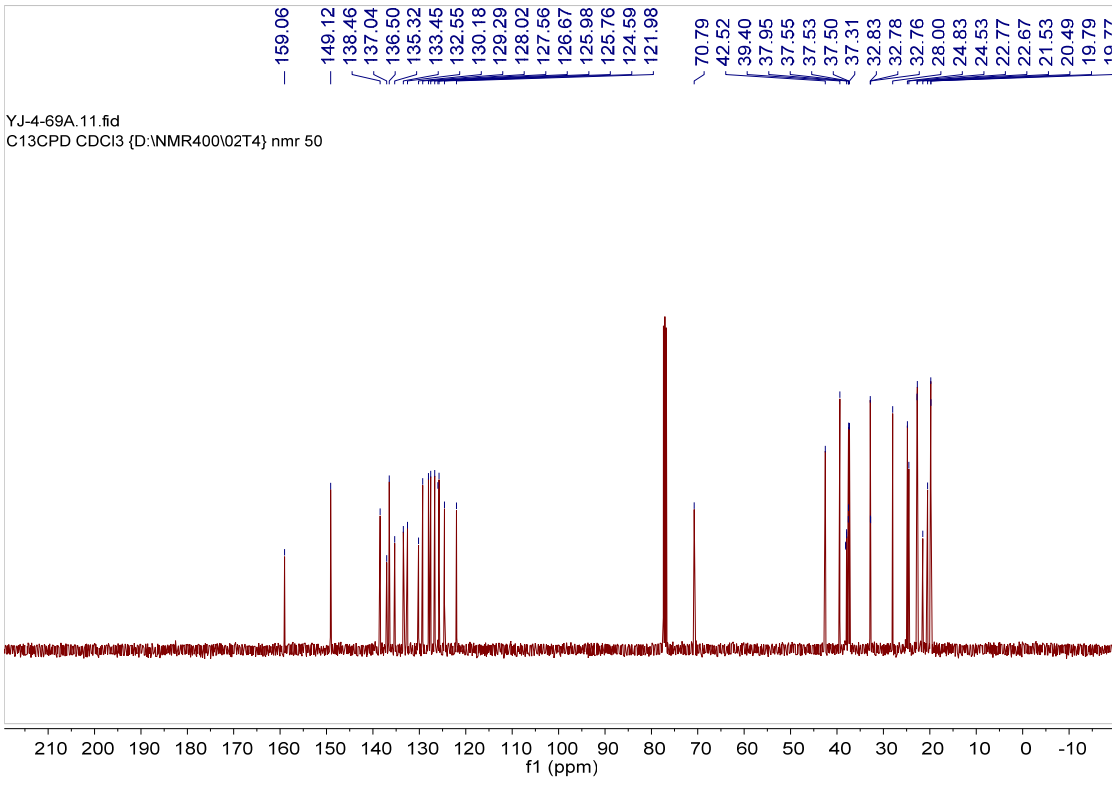


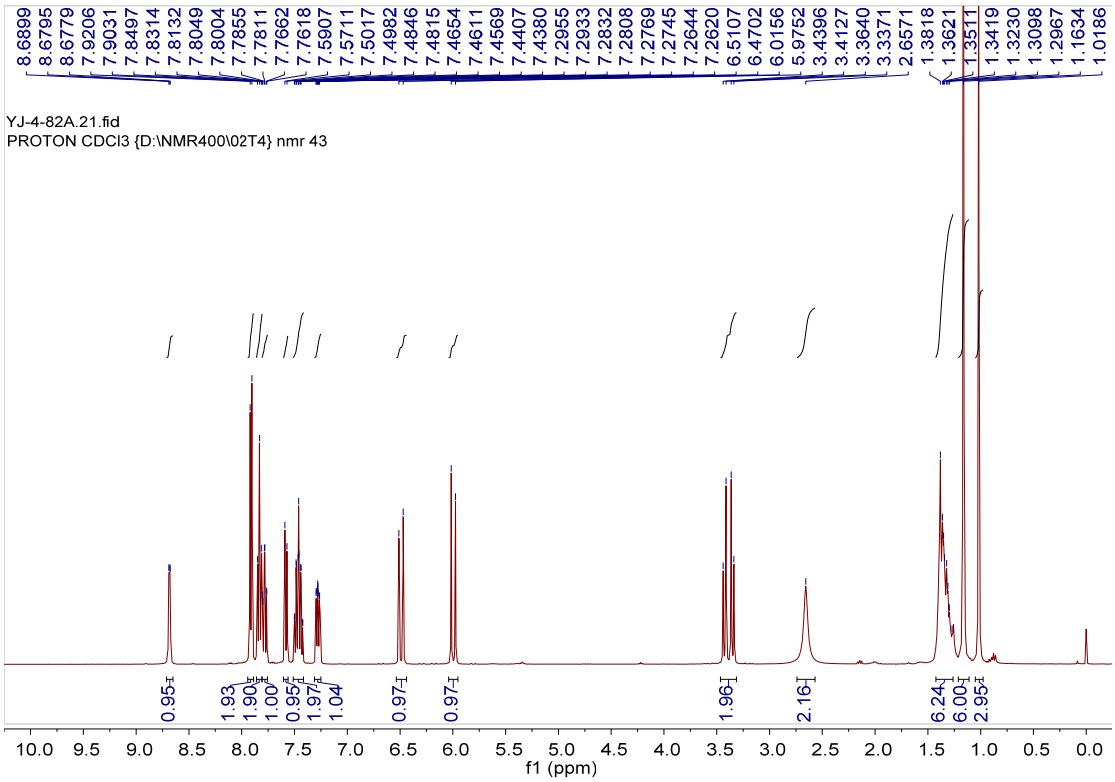


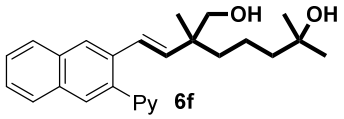
6e

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

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



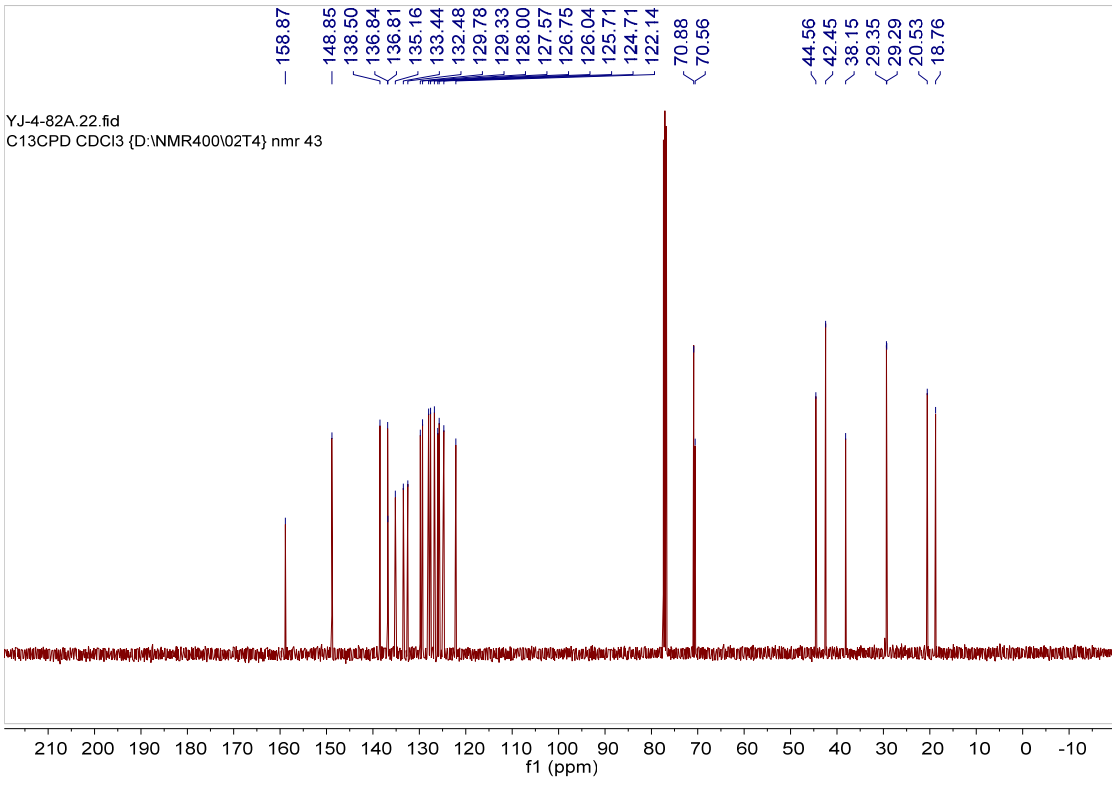


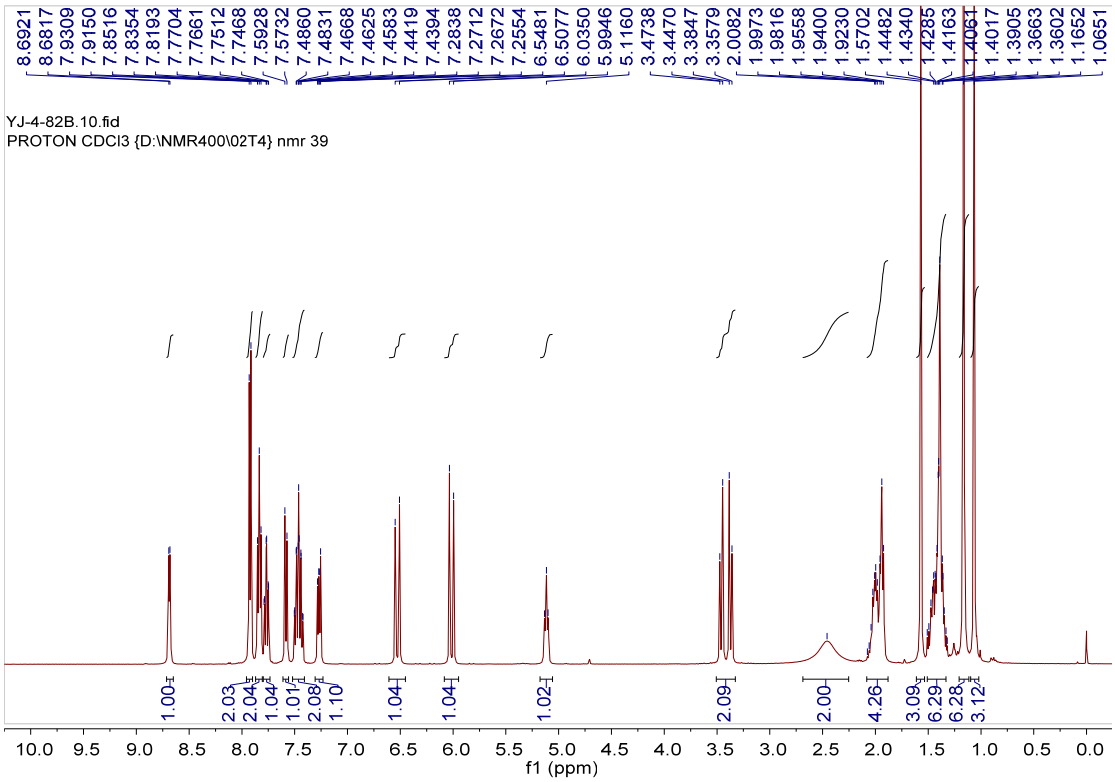


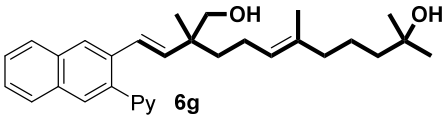
6f

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

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



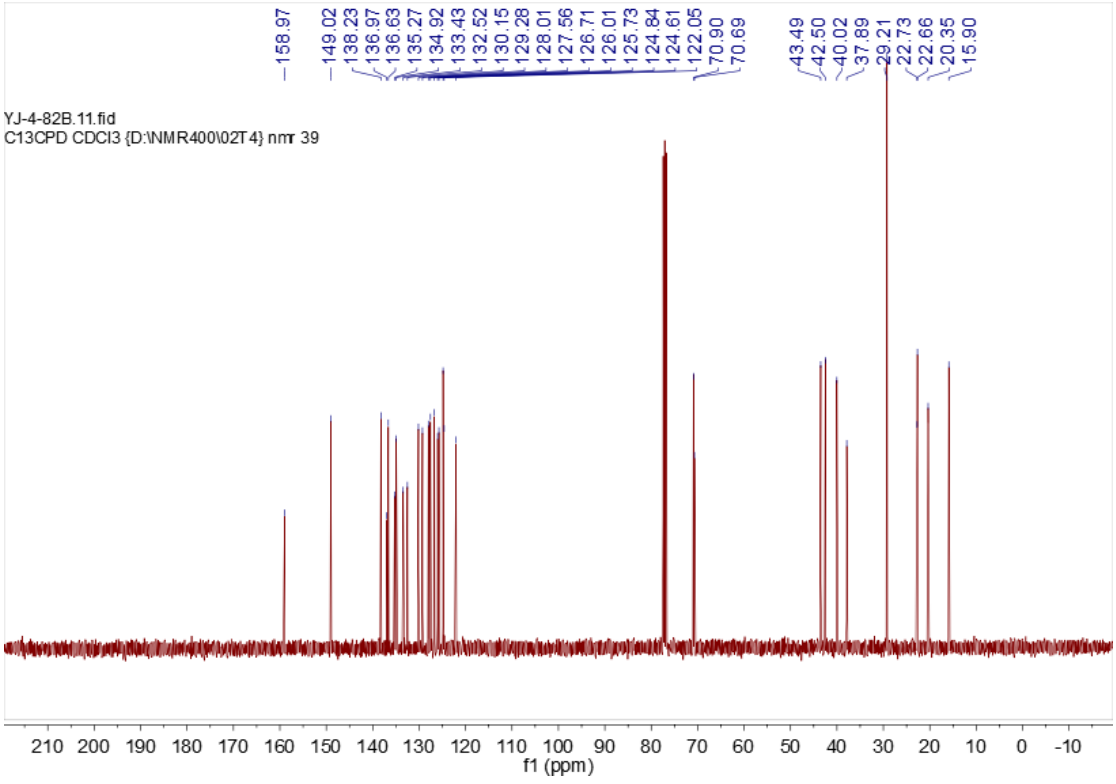


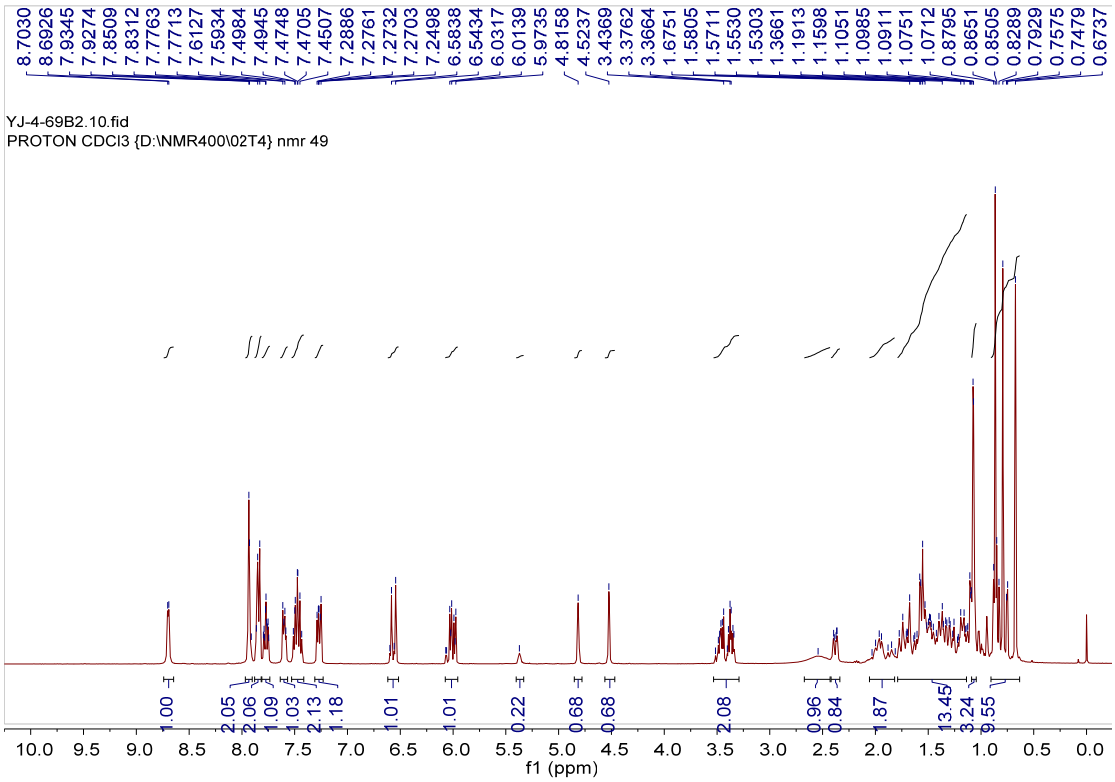


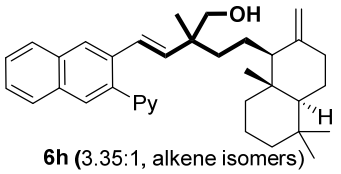
6g

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

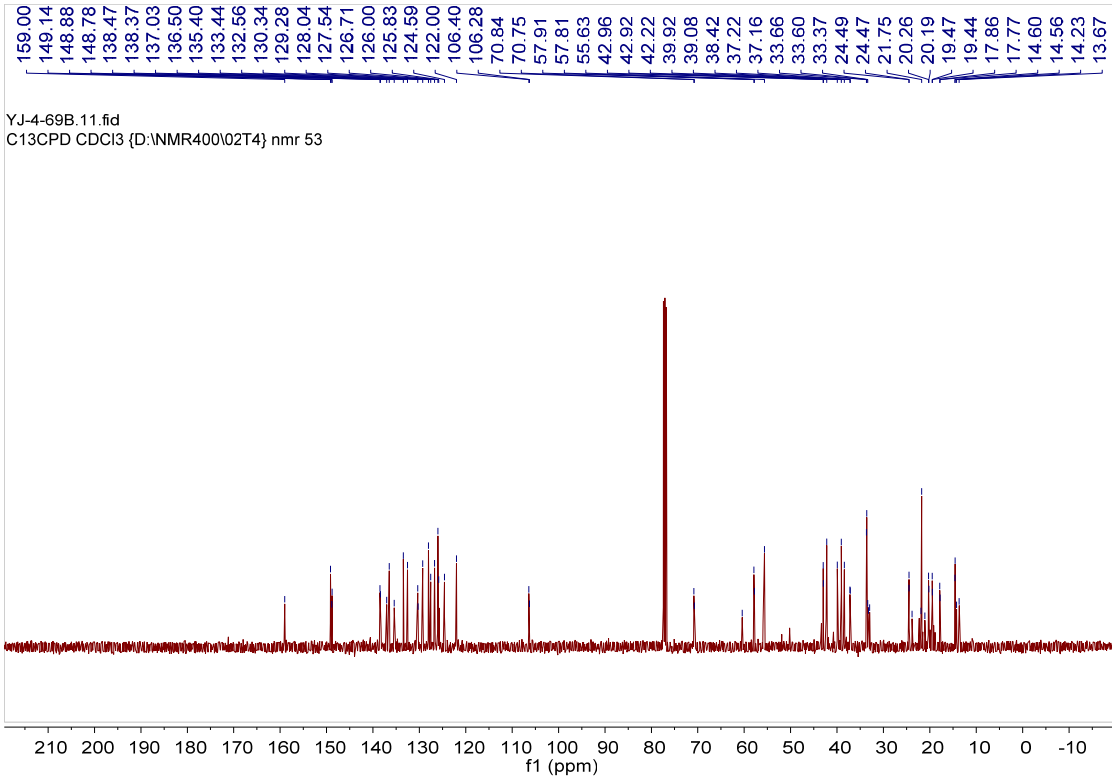
^{13}C NMR (100 MHz, $CDCl_3$)

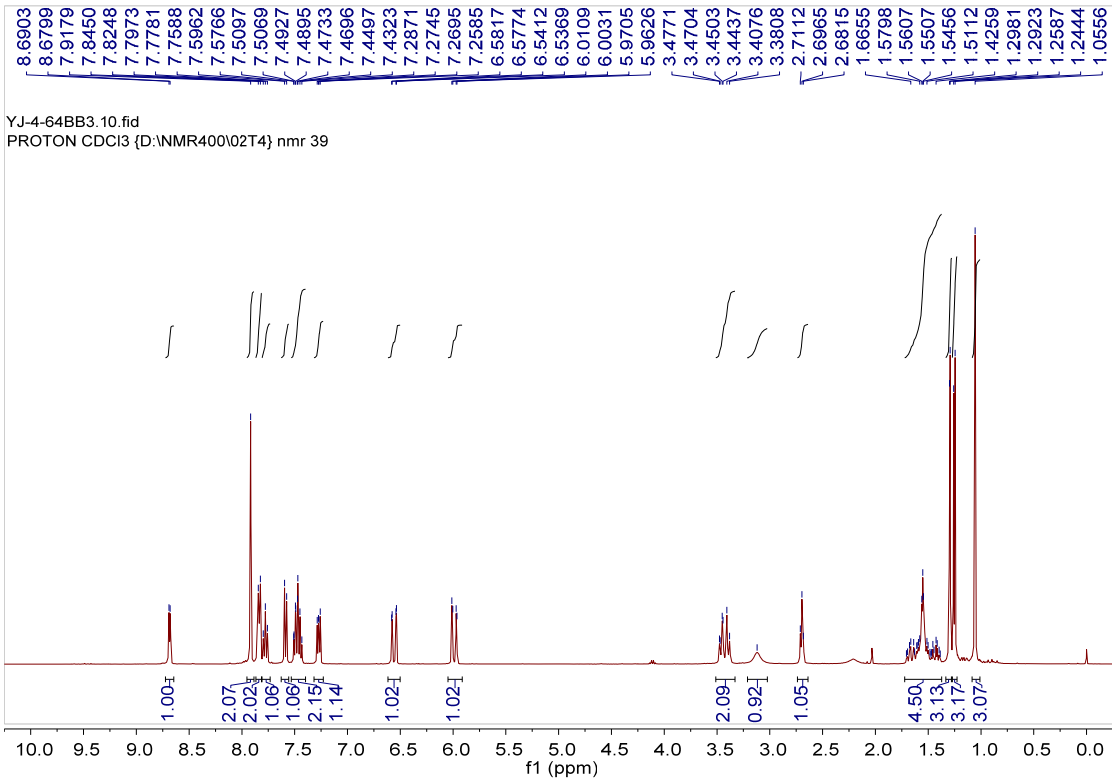


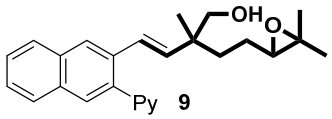




6h (3.35:1, alkene isomers)
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



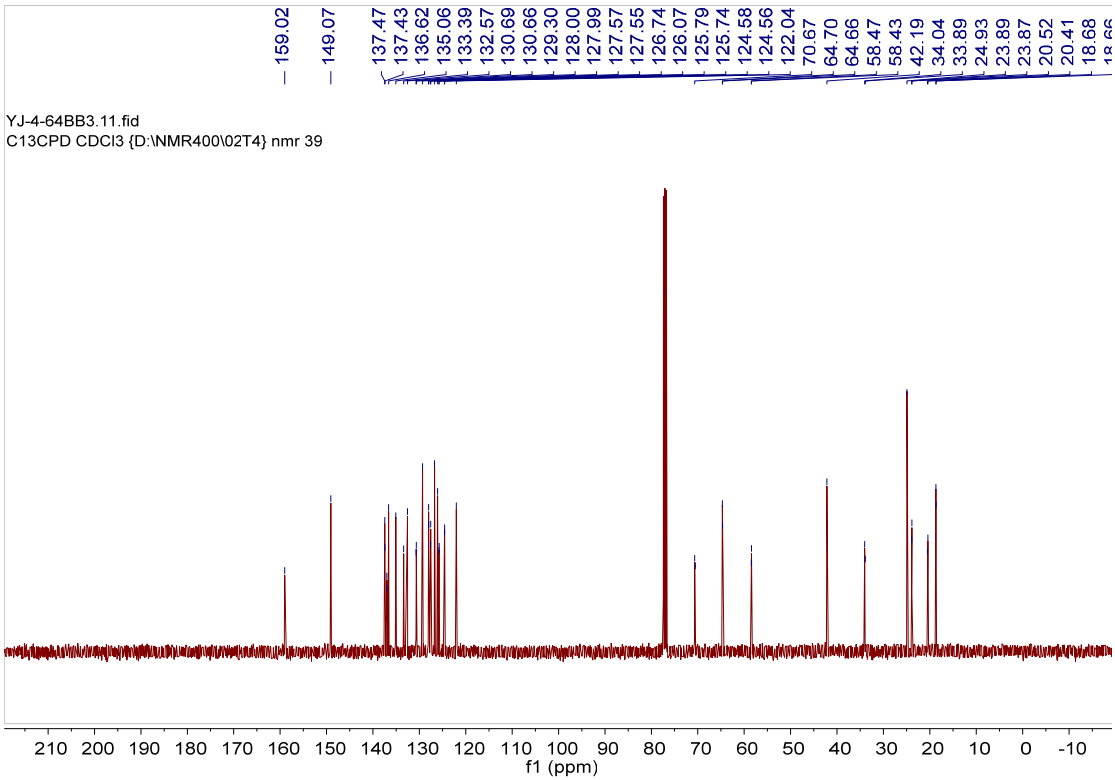


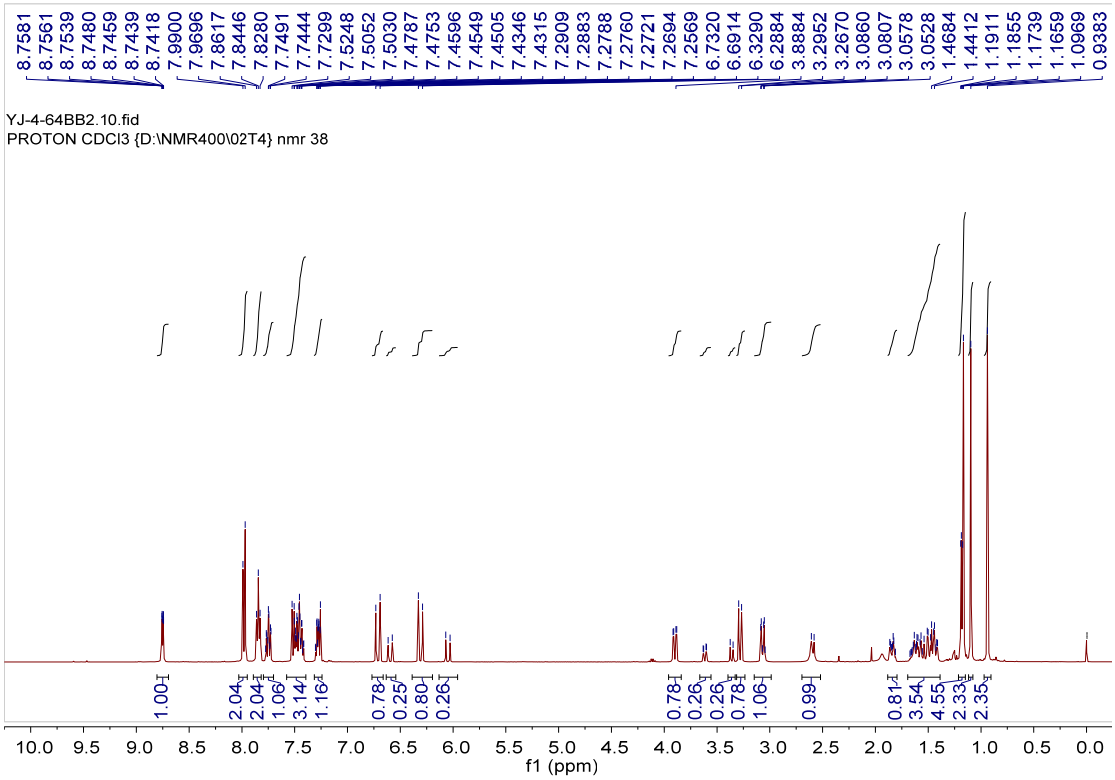


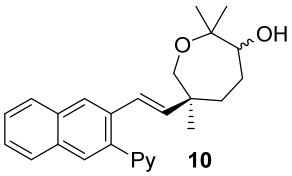
9

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

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







10

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

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