Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Enantioselective Pd(II)/Pd(IV) Catalysis Utilizing SPRIX Ligand: Efficient Construction of Chiral 3-Oxy-Tetrahydrofurans

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Contents

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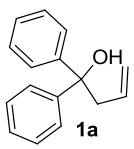
General information

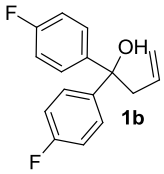
NMR spectra were recorded at 25 °C on JEOL ECS400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or BRUKER Avance III 700 (700 MHz for ^{1}H). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ (δ 77.0). ESI and APCI mass spectra were recorded on a Thermo Fisher, LTQ ORBITRAP XL. IR spectra were obtained using a JASCO FT/IR-4100 instrument. Optical rotations were measured with a JASCO P-1030 polarimeter. HPLC analyses were performed on JASCO HPLC system (JASCO PU 2080 pump and MD-2010 UV/Vis detector). Anhydrous diethyl ether, acetic acid, and dimethoxyethane were purchased from Kanto Chemicals and were used without further purification. Other solvents were purified prior to use by standard techniques.[1] *i*-Pr-SPRIX was prepared according to the method reported by our laboratory.[2] Complex **3b** was prepared from **3a** and MeOTf.[3] All other chemicals were purchased from commercial suppliers and used as received. All reactions were performed with standard Schlenk technique under a nitrogen atmosphere. Column chromatography was conducted on Kishida Silica Gel (spherical, 63–200 μm).

Typical procedure for the preparation of homoallyl alcohol substrates 1

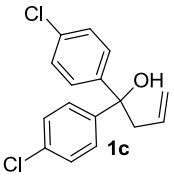
To an oven-dried two-necked flask equipped with a condenser was added preheated magnesium turnings (6 equiv) followed by dry diethyl ether (5 mL) and one crystal of iodine at room temperature. To this mixture was added allyl bromide (1 equiv) dropwise at 0 °C, which was refluxed for 1 h. The reaction mixture was then cooled to 0 °C, to which a solution of ketone (0.623 equiv) in diethyl ether was added dropwise at that temperature (for **1b**, **1c**, and **1d**: a solution of the Grignard reagent was added to a solution of ketone to avoid formation of diaryl methanol byproduct). The reaction mixture was refluxed for 12 h. To the mixture was added sat. aq. NH_4Cl to quench the reaction, which was extracted three times with diethyl ether. The organic layer was dried over Na_2SO_4 and evaporated under vacuum to dryness. The crude material was then chromatographed on silica gel using hexane-ethyl acetate solvent.



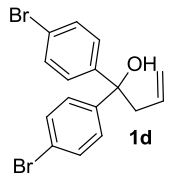
1,1-Diphenyl-3-buten-1-ol (1a): Colorless oil; yield: 2.00 g (86%). IR (KBr): 3553, 3058, 2345, 1492, 1447, 1344, 1166, 991, 726, 699, 620 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 1H), 3.08 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 5.16–5.27 (m, 2H), 5.61–5.71 (m, 1H), 7.20–7.24 (m, 2H), 7.29–7.33 (m, 4H), 7.43–7.46 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.6, 76.9, 120.5, 125.9, 126.8, 128.1, 133.3, 146.4. HRMS (APCI): m/z [M–OH]$^+$ calcd for $C_{16}H_{15}$: 207.1173; found: 207.1163.



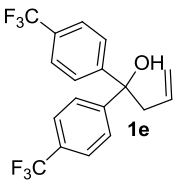
1,1-Bis(4-fluorophenyl)but-3-en-1-ol (1b): Colorless oil; yield: 2.46 g (93%). IR (KBr): 3548, 3077, 2980, 1896, 1602, 1508, 1344, 1227, 1160, 1013, 927, 835, 565 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.56 (s, 1H), 3.02 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 5.19–5.27 (m, 2H), 5.57–5.67 (m, 1H), 6.96–7.02 (m, 4H), 7.36–7.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.8, 77.2, 115.0 (d, $J_{C\text{-}F}$ = 21.0 Hz), 121.0, 127.6 (d, $J_{C\text{-}F}$ = 8.6 Hz), 132.8, 142.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 161.7 (d, $J_{C\text{-}F}$ = 244 Hz). HRMS (APCI): m/z [M–OH]$^+$ calcd for $C_{16}H_{13}F_2$: 243.0985; found: 243.0976.



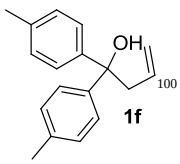
1,1-Bis(4-chlorophenyl)but-3-en-1-ol (1c): Colorless oil; yield: 2.84 g (95%). IR (KBr): 3631, 3548, 3076, 2925, 1903, 1638, 1489, 1401, 1093, 1012, 820, 755, 526 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 1H), 3.01 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 5.19–5.27 (m, 2H), 5.56–5.66 (m, 1H), 7.59–7.29 (m, 4H), 7.33–7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.4, 76.2, 121.2, 127.3, 128.4, 132.5, 132.9, 144.6. HRMS (APCI): m/z [M–OH]$^+$ calcd for $C_{16}H_{13}Cl_2$: 275.0394; found: 257.0384.



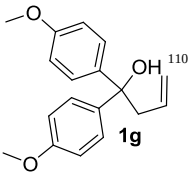
1,1-Bis(4-bromophenyl)but-3-en-1-ol (1d): Colorless oil; yield: 2.72 g (70%). IR (KBr): 3547, 3076, 2924, 2372, 1904, 1485, 1397, 1163, 1074, 1008, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 1H), 3.00 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 5.20–5.28 (m, 2H), 5.56–5.66 (m, 1H), 7.27–7.31 (m, 4H), 7.42–7.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.3, 76.2, 121.1, 121.3, 127.7, 131.3, 132.4, 145.0. HRMS (APCI): m/z [M–OH]$^+$ calcd for $C_{16}H_{13}Br_2$: 362.9383; found: 362.9374.



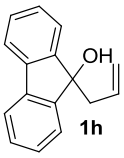
1,1-Bis(4-(trifluoromethyl)phenyl)but-3-en-1-ol (1e): Colorless oil; yield: 2.20 g (60%). IR (KBr): 3553, 3081, 2934, 1617, 1413, 1326, 1125, 1016, 833, 509 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (s, 1H), 3.10 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 5.24–5.32 (m, 2H), 5.56–5.67 (m, 1H), 7.56–7.61 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.6, 76.6, 122.2, 122.9, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.5, 129.8 (q, $J_{C\text{-}F}$ = 97.0 Hz), 132.3, 149.8. HRMS (APCI): No corresponding peaks were observed.



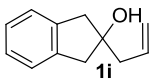
1,1-Bis(4-methylphenyl)but-3-en-1-ol (1f): Colorless oil; yield: 1.93 g (75%). IR (KBr): 3554, 3024, 2921, 2345, 1638, 1510, 1439, 1163, 992, 815, 566 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 1H), 2.31 (s, 6H), 3.04 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 5.15–5.26 (m, 2H), 5.62–5.72 (m, 1H), 7.10–7.13 (m, 4H), 7.31–7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 46.7, 77.2, 120.2, 125.8, 128.8, 133.6, 136.3. 143.7. HRMS (APCI): m/z [M–OH]$^+$ calcd for $C_{18}H_{19}$: 235.1486; found: 235.1477.



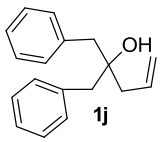
1,1-Bis(4-methoxyphenyl)but-3-en-1-ol (1g): Colorless oil; yield: 2.54 g (85%). IR (KBr): 3503, 3073, 3002, 2934, 2835, 2050, 1509, 1440, 1345, 1247, 1177, 1034, 830, 577 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 1H), 3.00 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 3.70 (s, 6H), 5.12–5.23 (m, 2H), 5.60–5.71 (m, 1H), 6.80–6.83 (m, 4H), 7.30–7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.9, 55.3, 76.4, 113.3, 120.0, 127.1, 133.6, 139.0, 158.2. HRMS (APCI): m/z [M–OH]$^+$ calcd for $C_{18}H_{19}O_2$: 267.1385; found: 267.1373.



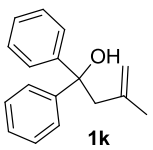
9-Allyl-9H-fluoren-9-ol (1h): Colorless crystals; yield: 2.20 g (97%). IR (KBr): 3307, 3075, 2831, 1913, 1839, 1448, 1065, 997, 916, 768, 578 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 1H), 2.84 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 4.94–4.99 (m, 2H), 5.55–5.65 (m, 1H), 7.28–7.39 (m, 4H), 7.53–7.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.0, 81.5, 118.7, 119.9, 123.8, 127.8, 128.9, 132.6, 134.3, 148.2. HRMS (APCI): m/z $[M–OH]^+$ calcd for $C_{16}H_{13}$: 205.1017; found: 205.1006.



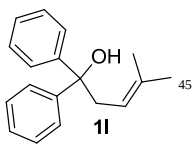
2-Allyl-2,3-dihydro-1H-inden-2-ol (1i): Brown oil.Yield: 800 mg (45%). IR (KBr): 3401, 3072, 2902, 1639, 1481, 1275, 916, 740, 599 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 1H), 2.52 (br d, J = 7.4 Hz, 2H), 2.95 (d, J = 16.0 Hz, 2H,) 3.09 (d, J = 16.0 Hz, 2H), 5.19–5.24 (br m, 2H), 5.92–6.03 (m, 1H), 7.15–7.22 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.9, 46.4, 81.4, 119.0, 124.9, 126.5, 133.9, 141.1. HRMS (APCI): m/z $[M–OH]^+$ calcd for $C_{12}H_{13}$: 157.1017; found: 157.1007.



2-Benzyl-1-phenylpent-4-en-2-ol (1j): Colorless oil; yield; 1.98 g (77%). IR (KBr): 3568, 3475, 3062, 2977, 1638, 1494, 1364, 1058, 916, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 1H), 2.00 (dt, J = 7.3 Hz, J = 1.4 Hz, 2H), 2.70 (s, 4H,) 5.00–5.05 (m, 1H), 5.10–5.13 (m, 1H), 5.82–5.92 (m, 1H), 7.15–7.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.0, 45.5, 73.7, 118.9, 126.4, 128.1, 130.7, 134.0, 137.2. HRMS (APCI): m/z $[M–OH]^+$ calcd for $C_{18}H_{19}$: 235.1486; found: 235.1476.



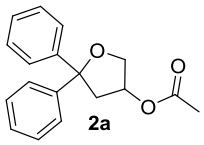
3-Methyl-1,1-diphenylbut-3-en-1-ol (1k): White solid; yield: 616 mg (45%). IR (KBr): 3058, 2345, 1638, 1491, 1447, 1056, 901, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H), 2.89 (s, 1H), 3.11 (s, 2H), 4.80–4.81 (m, 1H), 4.94–4.96 (m, 1H), 7.18–7.22 (m, 2H), 7.27–7.32 (m, 4H). 7.45–7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 49.8, 75.8, 116.7, 125.8, 126.7, 128.0, 142.2, 146.9. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{18}NaO_3$: 261.1255; found: 261.1248.



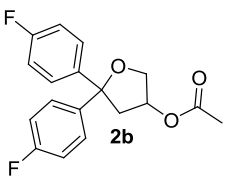
4-Methyl-1,1-diphenylpent-3-en-1-ol (1l): Pale green oil; yield: 1.35 g (98%). IR (KBr): 3537, 2914, 1662, 1492, 1376, 1266, 1168, 1054, 753, 643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.69 (s, 6H), 2.56 (s, 1H), 3.02 (d, J = 7.32 Hz, 2H), 5.02–5.07 (m, 1H), 7.20–7.24 (m, 2H), 7.29–7.33 (m, 4H), 7.44–7.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 26.1, 40.7, 77.6, 118.3, 125.9, 126.6, 128.0, 137.9, 146.9. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{20}NaO$: 275.1411; found: 275.1402.

Typical procedure for the enantioselective cyclative acetoxylation of homoallyl alcohols

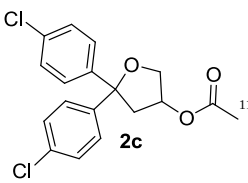
A solution of $PdCl_2(MeCN)_2$ (4.6 μmol, 10 mol%) and (*P*,*R*,*R*)-*i*-Pr-SPRIX (6.6 μmol, 15 mol%) in dry CH_2Cl_2 (0.5 mL) was stirred at 25 °C for 2 h. The volatiles were then removed by evaporation to afford Pd–*i*-Pr-SPRIX complex as a yellow powder. Into the vessel containing the complex was added a solution of TfOH (8.2 μmol, 18 mol%) in DME (0.15 mL) [prepared by mixing 1.5 mL of DME and 7.2 μL of TfOH] and the resulting mixture was stirred for 5 min at 25 °C. To this suspension was added $PhI(OAc)_2$ (0.137 mmol, 3 equiv) followed by alkenyl alcohol substrates **1** (0.046 mmol) dissolved in AcOH (0.15 mL), which was stirred at 25 °C for 4 h unless otherwise mentioned. After completion of the reaction, the solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel by using hexane/ethyl acetate = 99.3/0.7 to afford 3-acetoxy-tetrahydrofurans **2**.



5,5-Diphenyltetrahydrofuran-3-yl acetate (2a): Colorless wax; yield: 11.5 mg (92%); 90% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 99.5/0.5, flow rate = 1 mL/min, λ = 220 nm): 10.8 min (minor), 13.7 min (major)]; $[\alpha]_D^{22}$ +16.92 (*c* 0.26, $CHCl_3$). IR (KBr): 3058, 2963, 2372, 2345, 1737, 1448, 1365, 1238, 1082, 1049, 1020, 701, 535 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3H), 2.73 (dd, J = 13.8 Hz, J = 3.2 Hz, 1H), 3.04 (dd, J = 13.8 Hz, J = 7.3 Hz, 1H), 4.01 (dd, J = 10.5 Hz, J = 2.8 Hz, 1H), 4.17 (dd, J = 10.5 Hz, J = 5.9 Hz, 1H), 5.26–5.30 (m, 1H), 7.17–7.24 (m, 2H), 7.27–7.33 (m, 4H), 7.41–7.43 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 44.9, 71.7, 75.2, 87.8, 125.6, 127.7, 126.8, 127.0, 128.1, 128.3, 145.0, 145.6, 170.8. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_3$: 305.1153; found: 305.1174.

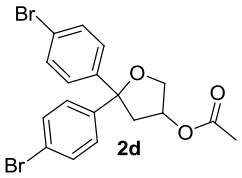


5,5-Bis(4-fluorophenyl)tetrahydrofuran-3-yl acetate (2b): Colorless wax; yield: 12.2 mg (86%); 88% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 99.5/0.5, flow rate = 1 mL/min, λ = 220 nm): 15.3 min (minor), 19.9 min (major)]; $[\alpha]_D^{25}$ +20.22 (*c* 0.267, $CHCl_3$). IR (KBr): 2964, 2878, 2372, 2345, 1738, 1602, 1508, 1408, 1366, 1234, 1159, 1076, 1014, 835, 561, 540 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 3H), 2.70 (dd, J = 13.7 Hz, J = 3.2 Hz, 1H), 2.9 (dd, J = 13.7 Hz, J = 6.8 Hz, 1H), 4.0 (dd, J = 10.5 Hz, J = 2.7 Hz, 1H), 4.15 (dd, J = 10.5 Hz, J = 5.9 Hz, 1H), 5.26–5.30 (m, 1H), 6.95–7.02 (m, 4H), 7.33–7.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 45.1, 71.8, 75.1, 87.1, 114.9 (d, $J_{C\text{-}F}$ = 31.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 30.5 Hz), 127.4 (d, $J_{C\text{-}F}$ = 3.8 Hz), 127.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 140.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 141.2 (d, $J_{C\text{-}F}$ = 2.8 Hz), 160.6 (d, $J_{C\text{-}F}$ = 15.2 Hz), 163.0 (d, $J_{C\text{-}F}$ = 15.2 Hz), 170.7. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{16}F_2NaO_3$: 341.0965; found: 341.0955.

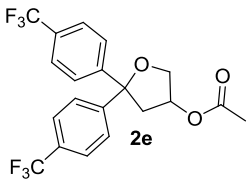


5,5-Bis(4-chlorophenyl)tetrahydrofuran-3-yl acetate (2c): Colorless wax; yield: 13.0 mg (83%); 79% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 99.5/0.5, flow rate = 1 mL/min, λ = 227 nm): 20.0 min (minor), 26.1 min (major)]; $[\alpha]_D^{24}$ +9.68 (*c* 0.95, $CHCl_3$). IR (KBr): 2928, 2372, 2345, 1738, 1490, 1237, 1092, 1012, 831, 537 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3H), 2.70 (dd, J = 13.7 Hz, J = 3.2 Hz, 1H), 2.9 (dd, J = 13.7 Hz, J = 6.8 Hz, 1H), 4.0 (dd, J = 10.5 Hz, J = 2.7 Hz, 1H), 4.15 (dd, J = 10.5 Hz, J = 5.5 Hz, 1H), 5.25–5.30 (m, 1H), 7.25–7.28 (m, 4H), 7.30–7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 44.8, 71.9, 75.0, 87.0, 127.0, 127.0, 128.3, 128.6, 132.9,

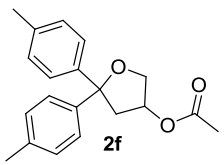
133.2, 143.3, 143.8, 170.7. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}Cl_2NaO_3$: 373.0374; found: 373.0364.



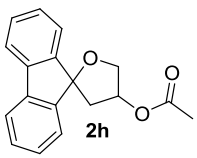
5,5-Bis(4-bromophenyl)tetrahydrofuran-3-yl acetate (2d): Colorless wax; yield: 15.4 mg (79%); 78% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 99.5/0.5, flow rate = 1 mL/min, λ = 221 nm): 24.2 min (minor), 34.8 min (major)]; $[\alpha]_D^{23}$ +10.25 (*c* 1.12, $CHCl_3$). IR (KBr): 2973, 2877, 2372, 2345, 1737, 1486, 1365, 1238, 1077, 1008, 821, 738, 534 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3H), 2.68 (dd, *J* = 13.7 Hz, *J* = 3.2 Hz, 1H), 2.92 (dd, *J* = 13.7 Hz, *J* = 6.8 Hz, 1H), 4.0 (dd, *J* = 10.5 Hz, *J* = 2.8 Hz, 1H), 4.14 (dd, *J* = 10.5 Hz, *J* = 5.9 Hz, 1H), 5.25–5.30 (m, 1H), 7.24–7.28 (m, 4H), 7.40–7.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 44.7, 71.9, 74.9, 87.1, 121.0, 121.3, 127.4, 127.4, 131.3, 131.5, 143.8, 144.2, 170.7. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}Br_2NaO_3$: 460.9363; found: 460.9358.



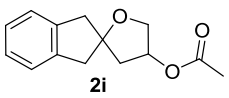
5,5-Bis(4-(trifluoromethyl)phenyl)-tetrahydrofuran-3-yl acetate (2e): Colorless wax; yield: 13 mg (70%); 44% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 99.5/0.5, flow rate = 1 mL/min, λ = 221 nm): 11.6 min (minor), 16.2 min (major)]; $[\alpha]_D^{24}$ +2.14 (*c* 0.28, $CHCl_3$). IR (KBr): 2936, 2372, 2345, 1741, 1617, 1412, 1367, 1325, 1238, 1165, 1122, 1069, 1016, 847, 606, 522 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 3H), 2.82 (dd, *J* = 13.7 Hz, *J* = 2.7 Hz, 1H), 2.98 (dd, *J* = 13.7 Hz, *J* = 6.8 Hz, 1H), 4.04 (dd, *J* = 10.5 Hz, *J* = 2.7 Hz, 1H), 4.19 (dd, *J* = 10.5 Hz, *J* = 5.5 Hz, 1H), 5.28–5.32 (m, 1H), 7.53–7.59 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 44.8, 72.2, 74.8, 87.2, 122.5, 122.6, 125.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.95, 125.98, 129.4 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.7 (q, $J_{C\text{-}F}$ = 32.4 Hz), 148.5, 148.9, 179.6. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{16}F_6NaO_3$: 441.0901; found: 441.0894.



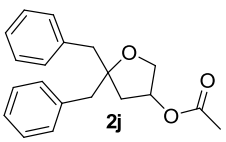
5,5-Bis(4-methylphenyl)tetrahydrofuran-3-yl acetate (2f): Colorless wax; yield: 4.1 mg (30%); 90% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 99.7/0.3, flow rate = 1 mL/min, λ = 219 nm): 20.3 min (minor), 23.9 min (major)]; $[\alpha]_D^{23}$ +11 (*c* 0.218, $CHCl_3$). IR (KBr): 2923, 2372, 2345, 1737, 1509, 1439, 1325, 1238, 1075, 1019, 813, 564, cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 2.65 (dd, *J* = 13.7 Hz, *J* = 3.7 Hz, 1H), 3.02 (dd, *J* = 13.7 Hz, *J* = 6.9 Hz, 1H), 4.0 (dd, *J* = 10.5 Hz, *J* = 2.8 Hz, 1H), 4.1 (dd, *J* = 10.5 Hz, *J* = 6.0 Hz, 1H), 5.23–5.28 (m, 1H), 7.07–7.11 (m, 4H), 7.26–7.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.92, 20.94, 20.94, 44.9, 71.5, 75.4, 87.7, 125.6, 125.7, 128.7, 129.0, 136.3, 136.6, 142.2, 142.9, 170.9. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1466; found: 333.1463.



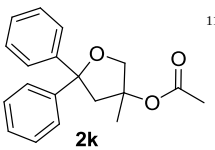
4',5'-Dihydro-3'H-spiro[fluorene-9,2'-furan]-4'-yl acetate (2h): The reaction was performed at –10 °C for 96 h. Pale yellow solid; yield: 10.6 mg (85%); 50% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 98/2, flow rate = 1 mL/min, λ = 298 nm): 17.3 min (minor), 24.5 min (major)]; $[\alpha]_D^{24}$ –10.68 (*c* 0.5, $CHCl_3$). IR (KBr): 3061, 2930, 2858, 2345, 1737, 1449, 1375, 1236, 1152, 1070, 1048, 759, 505 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.54 (dd, *J* = 14.6 Hz, *J* = 3.6 Hz, 1H), 2.85 (dd, *J* = 14.6 Hz, *J* = 3.2 Hz, 1H), 4.35 (dd, *J* = 10.5 Hz, *J* = 3.2 Hz, 1H), 4.50 (dd, *J* = 10.5 Hz, *J* = 3.6 Hz, 1H), 5.70–5.74 (m, 1H), 7.26–7.43 (m, 5H), 7.59–7.60 (m, 2H), 7.07–7.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3 42.6, 74.3, 75.9, 77.2, 89.8, 119.8, 119.9, 123.2, 124.4, 128.1, 128.2, 129.0, 129.1, 139.6, 147.8, 148.7, 170.7. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}NaO_3$: 303.0997; found: 333.0991.



1',3',4,5-Tetrahydro-3H-spiro[furan-2,2'-inden]-4-yl acetate (2i): The reaction was performed at –10 °C for 50 h. Colorless wax; yield: 7.7 mg (75%); 37% ee [HPLC (Chiralpak AD-H, hexane/EtOH = 98/2, flow rate = 1 mL/min, λ = 216 nm): 12.5 min (major), 17.1 min (minor)]; $[\alpha]_D^{24}$ –56 (*c* 0.05, $CHCl_3$). IR (KBr): 3022, 2940, 2372, 2345, 1737, 1480, 1432, 1365, 1240, 1150, 1098, 1057, 1022, 742, 506 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 3H), 2.18 (dd, *J* = 14.2 Hz, *J* = 2.3 Hz, 1H), 2.35 (dd, *J* = 14.2 Hz, *J* = 6.8 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 3.10 (d, *J* = 16.4 Hz, 1H), 3.16 (d, *J* = 16.0 Hz, 1H), 3.23 (d, *J* = 16.4 Hz, 1H), 3.89 (dd, *J* = 10.5 Hz, *J* = 2.3 Hz, 1H), 4.14 (dd, *J* = 10.5 Hz, *J* = 5.0 Hz, 1H), 5.33–5.38 (m, 1H), 7.12–7.20 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 42.4, 45.0, 45.2, 72.3, 75.4, 90.9, 124.5, 124.6, 126.57, 126.61, 140.9, 141.3, 170.9. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_{16}NaO_3$: 255.0997; found: 255.0990.



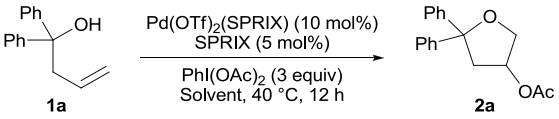
5,5-Dibenzyltetrahydrofuran-3-yl acetate (2j): The reaction was performed at –10 °C for 12 h. Colorless wax; yield: 7.6 mg (55%); 54% ee [HPLC (Chiralpak IC, hexane/EtOH = 99.7/0.3, flow rate = 0.5 mL/min, λ = 219 nm): 21.0 min (major), 25.8 min (minor)]; $[\alpha]_D^{24}$ –13.45 (*c* 0.055, $CHCl_3$). IR (KBr): 3027, 2922, 2863, 2372, 2345, 1737, 1453, 1244, 1108, 1082, 1052, 1021, 701, 517 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 3H), 1.94 (dd, *J* = 14.2 Hz, *J* = 2.7 Hz, 1H), 2.10 (dd, *J* = 14.2 Hz, *J* = 3.2 Hz, 1H), 2.71 (d, *J* = 13.8 Hz, 1H), 2.88 (d, *J* = 13.8 Hz, 1H), 2.94 (d, *J* = 13.8 Hz, 1H), 2.98 (d, *J* = 13.8 Hz, 1H), 3.73 (d, *J* = 3.7 Hz, 2H), 4.84–4.89 (m, 1H), 7.20–7.32 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 38.5, 44.8, 46.1, 72.2, 75.4, 85.8, 126.3, 126.4, 127.99, 128.03, 130.75, 130.84, 137.3, 137.7, 170.7. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1466; found: 333.1459.



3-Methyl-5,5-diphenyltetrahydrofuran-3-yl acetate (2k): Colorless wax; yield: 6.1 mg (56%); racemic [HPLC (Chiralpak As-H, hexane, flow rate = 1 mL/min, λ = 221 nm): 18.3 min, 22.86 min]. IR (KBr): 3058, 2345, 1735, 1490, 1448, 1368, 1242, 1058, 738, 701, 494 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 3H), 1.68 (s, 3H), 2.73 (d, *J* = 13.8 Hz, 1H), 3.39 (d, *J* = 13.8 Hz, 1H), 3.95 (d, *J* = 10.1 Hz, 1H), 4.26 (d, *J* = 10.1 Hz, 1H), 7.14–7.21 (m, 2H), 7.27–7.31 (m, 4H), 7.41–7.46 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 22.4, 50.7, 77.3, 87.2, 87.9, 125.4, 125.4, 126.5, 126.8, 128.1, 128.3, 146.0, 146.1, 170.6. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{20}NaO_3$: 319.1310; found: 319.1301.

Optimization of reaction conditions

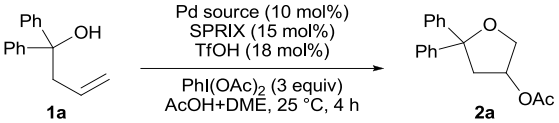
Table S1 Solvent Screening[a]



Entry	Solvent	Yield (%)[b]	Ee (%)[c]
1[d]	AcOH	66	28
2	AcOH+DME	68	40
3	AcOH+CPME	58	29
4	AcOH+THF	60	14
5	AcOH+Et_2O	72	34
6	AcOH+dioxane	66	26
7	AcOH+acetone	66	21
8	AcOH+CH_2Cl_2	63	34
9	AcOH+toluene	75	16

[a] Reaction conditions: **1a**/Pd(OTf)$_2${(*P*,*R*,*R*)-*i*-Pr-SPRIX}/(*P*,*R*,*R*)-*i*-Pr-SPRIX/PhI(OAc)$_2$ = 1:0.1:0.05:3, **1a** = 0.14 mmol/mL in solvent (1:1), 40 °C, 12 h. [b] Isolated yield. [c] Determined by HPLC analysis. [d] 18 h.

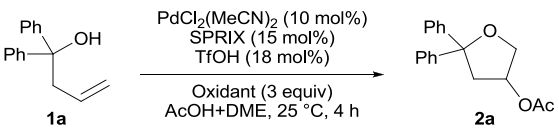
Table S2 Effect of Pd Source[a]



Entry	Pd source	Yield (%)[b]	Ee (%)[c]
1	$PdCl_2(MeCN)_2$	92	90
2	$PdCl_2(PhCN)_2$	82	74
3	[PdCl(π-allyl)]$_2$	80	72
4	$PdCl_2$(cod)	66	57
5	$Pd(OAc)_2$	73	35
6	$Pd(OCOCF_3)_2$	43	7
7	$Pd(acac)_2$	48	24
8	Pd(hfacac)$_2$	56	32
9	$Pd(NO_3)_2$	68	41
10	$PdCl_2$	26	4
11	$PdBr_2$	31	14
12	$Pd_2(dba)_3{\cdot}CHCl_3$	64	14

[a] Reaction conditions: **1a**/Pd/(*P*,*R*,*R*)-*i*-Pr-SPRIX/TfOH/PhI(OAc)$_2$ = 1:0.1:0.15:0.18:3, **1a** = 0.14 mmol/mL in AcOH+DME (1:1), 25 °C, 4 h. [b] Isolated yield. [c] Determined by HPLC analysis.

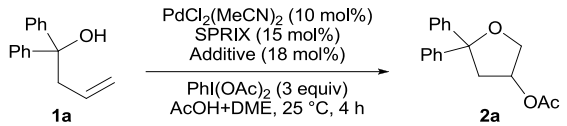
Table S3 Effect of Oxidant[a]



Entry	Oxidant	yield (%)[b]	Ee (%)[c]
1	$PhI(OAc)_2$	92	90
2	$PhI(OCOCF_3)_2$	52	55
3	PhI(OH)(OTs)	32	55
4	PhIO	54	72
5	*p*-benzoquinone	no reaction	—
6	$PhI(OAc)_2$ (1 equiv)	72	69
7	$PhI(OAc)_2$ (2 equiv)	90	86
8	$PhI(OAc)_2$ (4 equiv)	85	73

[a] Reaction conditions: **1a**/$PdCl_2(MeCN)_2$/(*P*,*R*,*R*)-*i*-Pr-SPRIX/TfOH/oxidant = 1:0.1:0.15:0.18:3, **1a** = 0.14 mmol/mL in AcOH+DME (1:1), 25 °C, 4 h. [b] Isolated yield. [c] Determined by HPLC analysis.

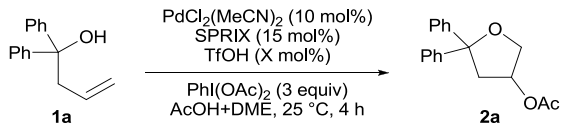
Table S4 Effect of Additive[a]



Entry	Additive	Yield (%)[b]	Ee (%)[c]
1	None	33	27
2	TfOH	92	90
3	AgOTf	57	48
4	$AgBF_4$	74	50
5	$AgPF_6$	73	11
6	AgOTs	48	20
7	MeOTf	67	54
8	TMSOTf	65	70
9	Tf_2NH	72	70
10	H_3PO_4	69	20
11	MS4A	93	26

[a] Reaction conditions: **1a**/$PdCl_2(MeCN)_2$/(*P*,*R*,*R*)-*i*-Pr-SPRIX/additive/PhI(OAc)$_2$ = 1:0.1:0.15:0.18:3, **1a** = 0.14 mmol/mL in AcOH+DME (1:1), 25 °C, 4 h. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S5 Effect of Amount of TfOH[a]



Entry	TfOH (equiv)	Yield (%)[b]	Ee (%)[c]
1	1	48	20
2	5	56	15
3	10	88	36
4	15	93	80
5	18	92	90
6	20	92	85
7	50	40	54
8	100	20	56

[a] Reaction conditions: **1a**/ $PdCl_2(MeCN)_2$/(*P*,*R*,*R*)-*i*-Pr-SPRIX/TfOH/PhI(OAc)$_2$ = 1:0.1:0.15:X:3, **1a** = 0.14 mmol/mL in AcOH+DME (1:1), 25 °C, 4 h. [b] Isolated yield. [c] Determined by HPLC analysis.

Hammett plot

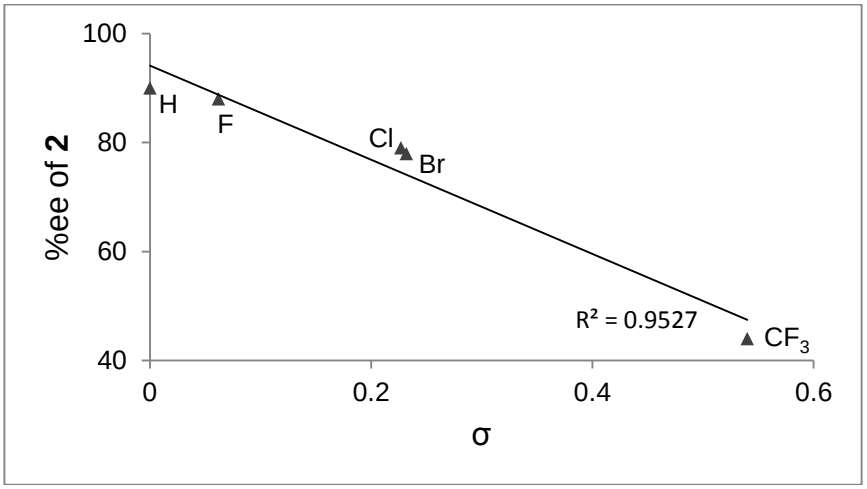


Figure S1. Substituent effects on the enantioselectivity in the cyclative acetoxylation of **1**.

^{1}H NMR analysis for the additive effect of TfOH

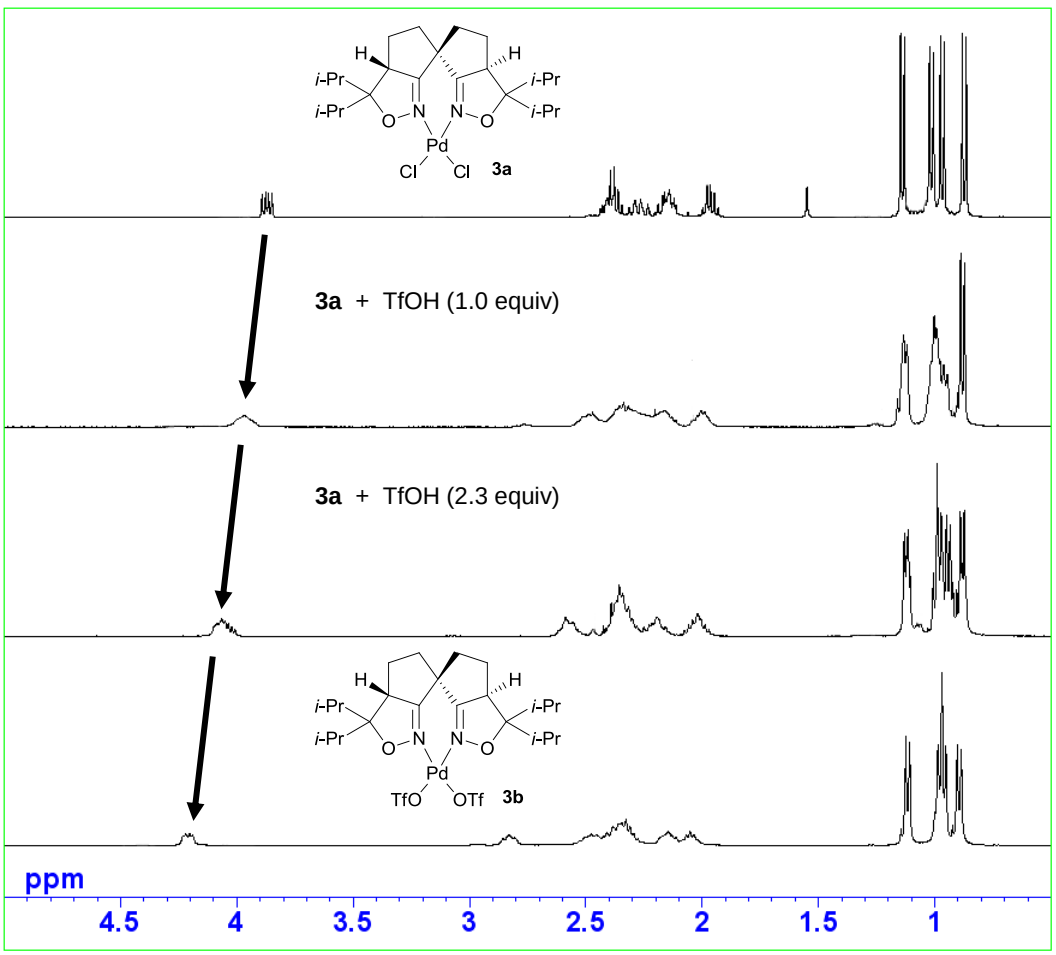
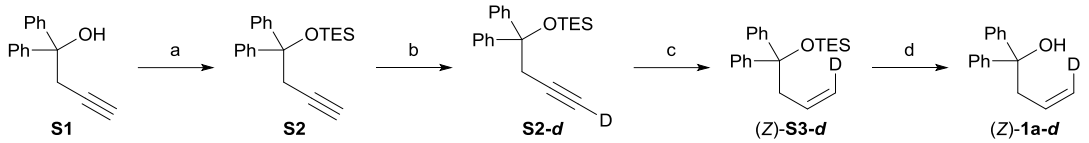


Figure S2. ^{1}H NMR analysis for the additive effect of TfOH.

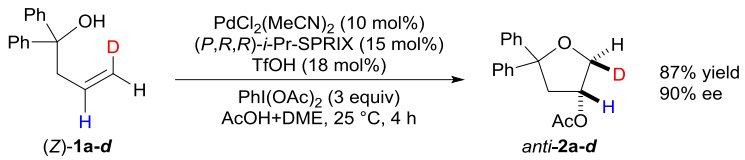
Deuterium labeling experiment



Scheme S1 Preparation of substrate (*Z*)-**1a-*d***. (a) TESOTf (3 equiv), 2,6-lutidine (7 equiv), CH_2Cl_2, 0 °C, 3 h, 75%; (b) *n*-BuLi (1.2 equiv), THF, –78 °C to –30 °C, 1 h, then D_2O, quant (97%D); (c) Pd/$CaCO_3$ (Pd: 1.7 mol %), quinoline (2.6 equiv), H_2 (1 atm), toluene, rt, 1.5 h, 92%; (d) TBAF (2.3 equiv), THF, 0 °C to rt, 1 h, 93% (ratio: (*Z*)-**1a-*d***:(*E*)-**1a-*d***:**1a** = 81:13:6).

Substrate (*Z*)-**1a-*d*** was prepared from homopropargyl alcohol **S1**[4] over 4 steps as shown in Scheme S1: First, the alcohol unit of **S1** was protected with a triethylsilyl (TES) group.[5] A deuterium atom was then introduced at the alkyne terminal of silyl ether **S2**.[6] Subsequent Lindlar reduction of **S2-*d*** furnished *Z*-olefin (*Z*)-**S3-*d***.[7] Finally, the desired substrate (*Z*)-**1a-*d*** was obtained as an inseparable mixture with its isomer (*E*)-**1a-*d*** and non-deuterated **1a** (ratio: (*Z*)-**1a-*d***:(*E*)-**1a-*d***:**1a** = 81:13:6) by the removal of the TES group.

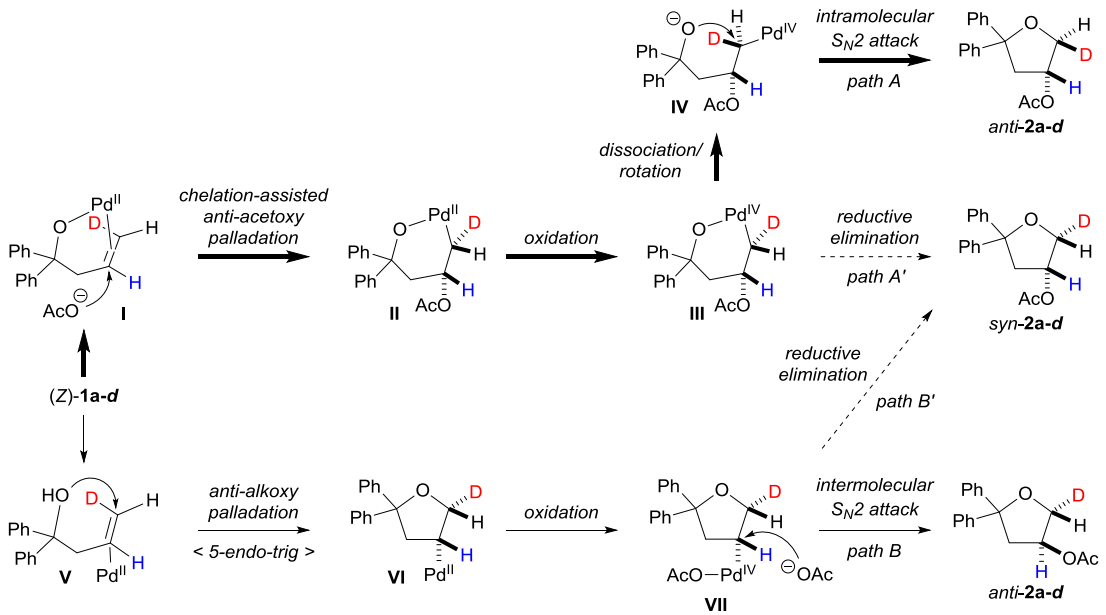
(*Z*)-**1a-*d***: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 1H), 3.10–3.12 (br dd, J = 6.9 Hz, J = 0.9 Hz, 2H), 5.16 (d, J = 10.1 Hz, 1H), 5.61–5.70 (m, 1H), 7.20–7.46 (m, 10H).



Scheme S2 Enantioselective cyclative acetoxylation of (*Z*)-**1a-*d*** promoted by Pd/SPRIX/TfOH catalyst.

According to the typical procedure, product consisting of *anti*-**2a-*d*** (80%), *syn*-**2a-*d*** (14%), and **2a** (6%) was obtained in 87% yield with 90% ee (Scheme S2). Relative configuration of the major product, *anti*-**2a-*d***, was determined by the comparison of chemical shifts[8] and coupling constant[9] in the ^{1}H NMR spectrum with reported values and was eventually established by NOE.

anti-**2a-*d***: ^{1}H NMR (700 MHz, $CDCl_3$): δ 1.91 (s, 3H), 2.73 (dd, J = 3.0 Hz, J = 13.5 Hz, 1 H), 3.04 (dd, J = 6.9 Hz, J = 13.5 Hz, 1 H), 3.99 (d, J = 2.2 Hz, 1 H). 5.26–5.29 (m, 1 H), 7.18–7.43 (m, 10 H).



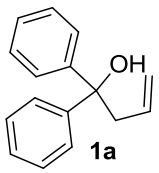
Scheme S3 Stereochemical pathway of enantioselective cyclative acetoxylation of (*Z*)-**1a-*d***.

Since the isomeric ratio was not changed throughout the process, i.e. from the substrate ((*Z*)-**1a-*d***:(*E*)-**1a-*d*** = 81:13) to the product (*anti*-**2a-*d***:*syn*-**2a-*d*** = 80:14), this Pd(II)/Pd(IV) catalysis is thought to proceed in a stereospecific manner. Thus, treatment of

substrate (*Z*)-**1a-*d*** with the catalytic system afforded only *anti*-**2a-*d***. There are two possibilities for the formation of *anti*-**2a-*d*** from (*Z*)-**1a-*d*** (Scheme S3). One is initiated by *anti*-acetoxypalladation through the coordination of the alkoxy moiety, which is followed by the oxidation of alkyl–Pd(II) species **II** to Pd(IV) intermediate **III**. Then, dissociation of the alkoxy ligand and rotation of the C–C bond take place to result in intermediate **IV**. Finally, intramolecular S_N2 attack of the alkoxy (or alcohol) nucleophile furnishes *anti*-**2a-*d*** (path A).[10] The other pathway involves cyclization via *anti*-alkoxypalladation, oxidation, and S_N2 attack of an external acetoxy anion (path B). From Pd(IV) intermediates **III** or **VII**, no direct reductive elimination leading to *syn*-**2a-*d*** occurs (paths A' and B'). Although path B cannot be ruled out at the present time, path A is preferable for the following reasons:

1. The relationship between the electronic property of the aromatic substituent and the enantioselectivity is better explained.
2. Path B contains 5-endo-trig-type cyclization, which is classified as an unfavorable process according to the Baldwin's rule.
3. The use of TfOH drastically accelerates the reaction: In addition to the generation of the catalyticall active species, TfOH may also facilitate the dissociation step.

NMR spectra



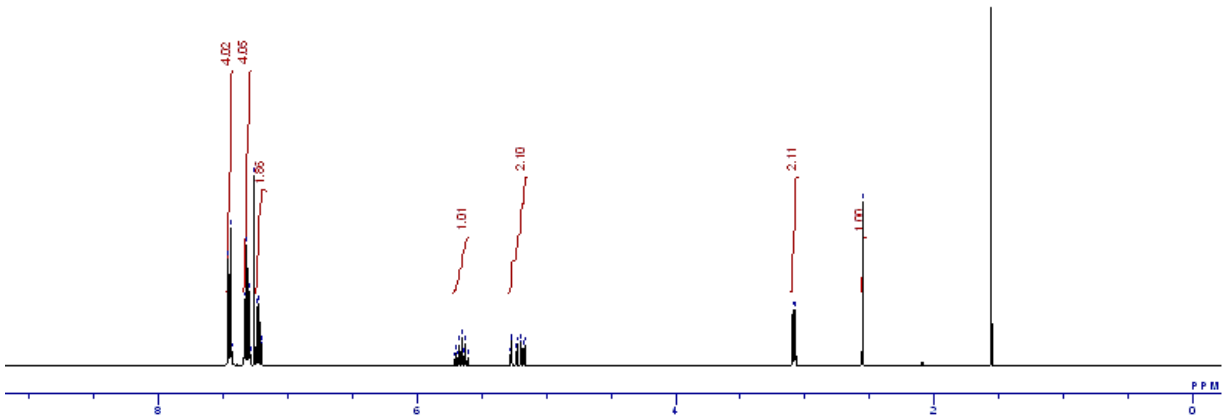
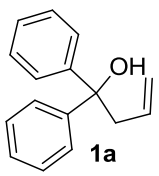


Figure S3-1. ^{1}H NMR spectrum of compound **1a** (400 MHz, $CDCl_3$).



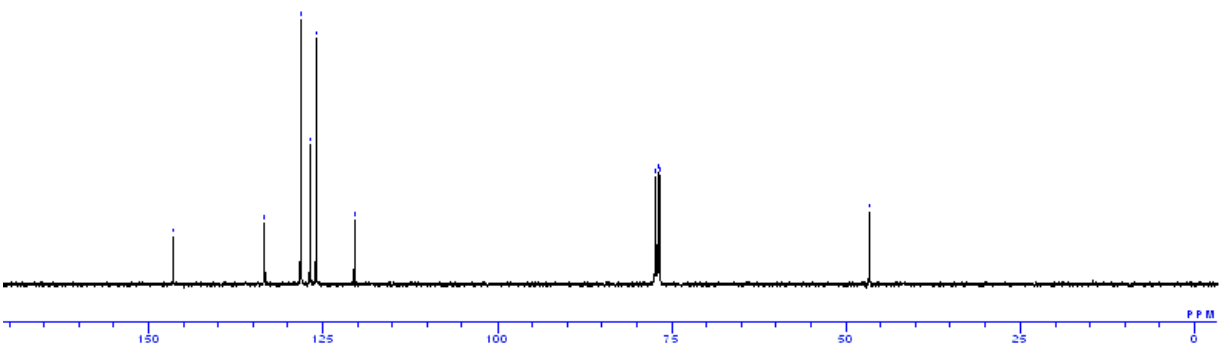


Figure S3-2. ^{13}C NMR spectrum of compound **1a** (100 MHz, $CDCl_3$).

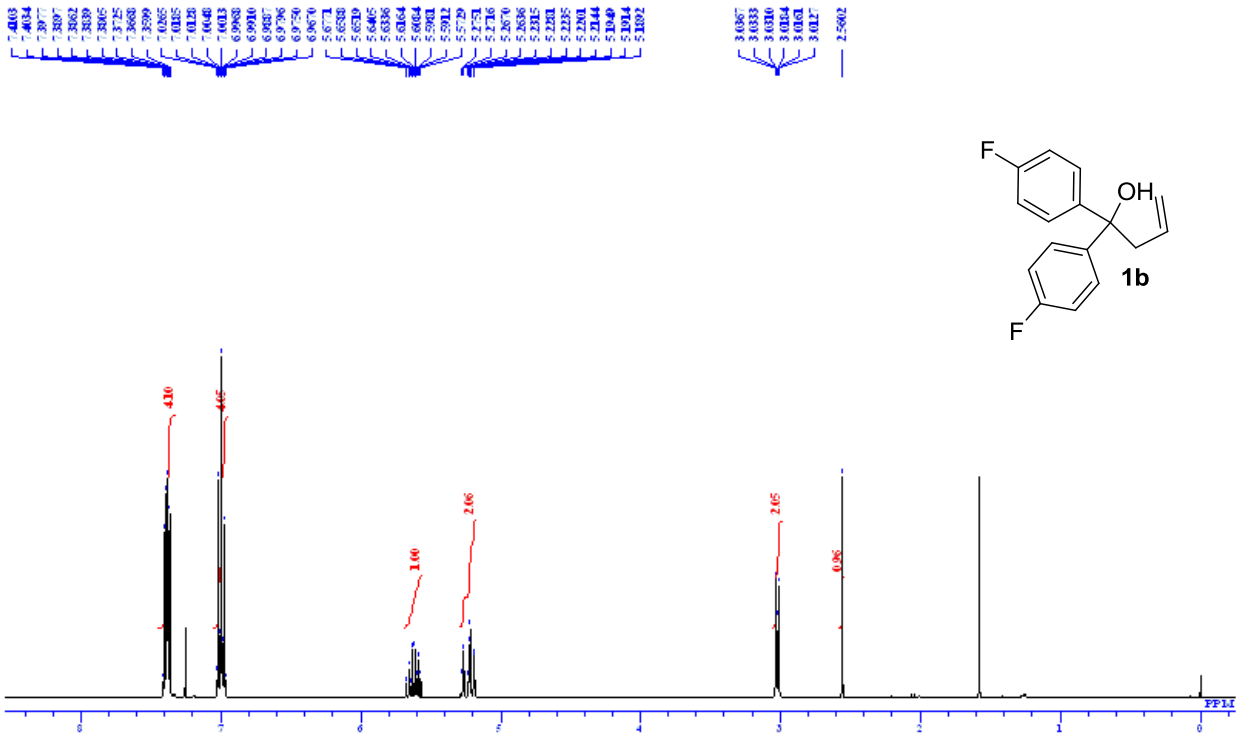


Figure S4-1. ^{1}H NMR spectrum of compound **1b** (400 MHz, $CDCl_3$).

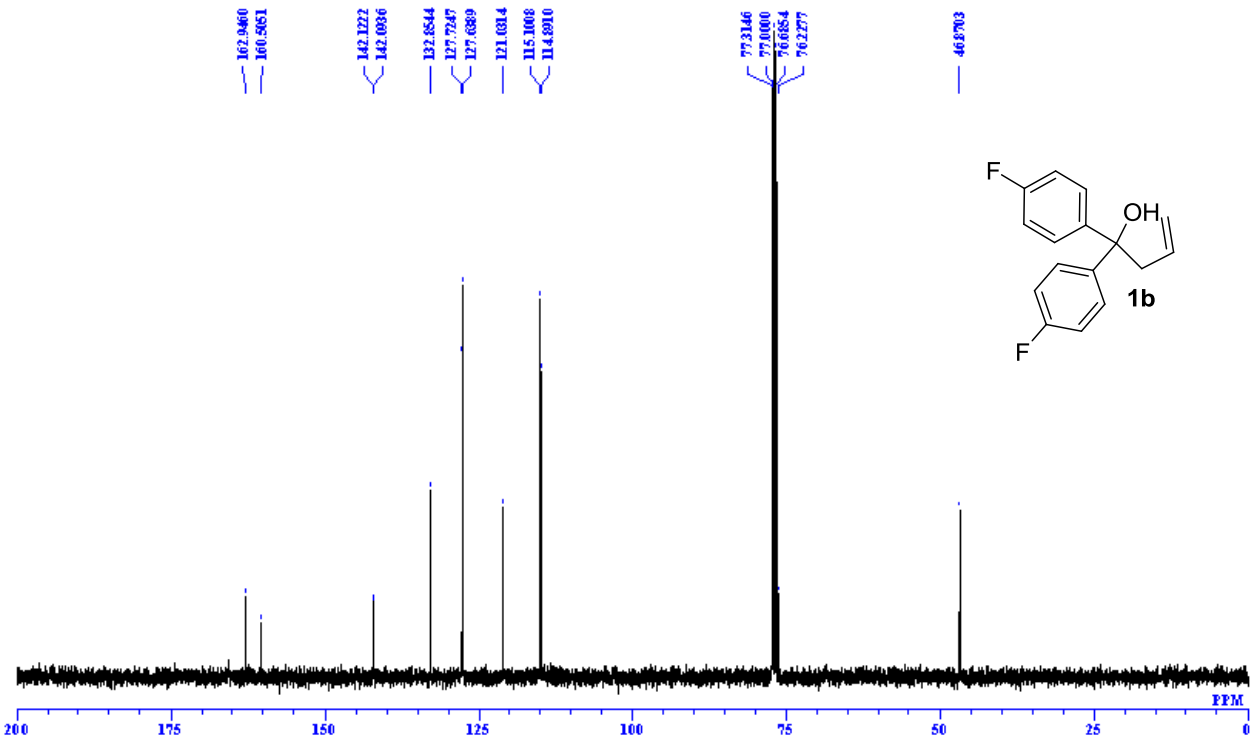


Figure S4-2. ^{13}C NMR spectrum of compound **1b** (100 MHz, $CDCl_3$).

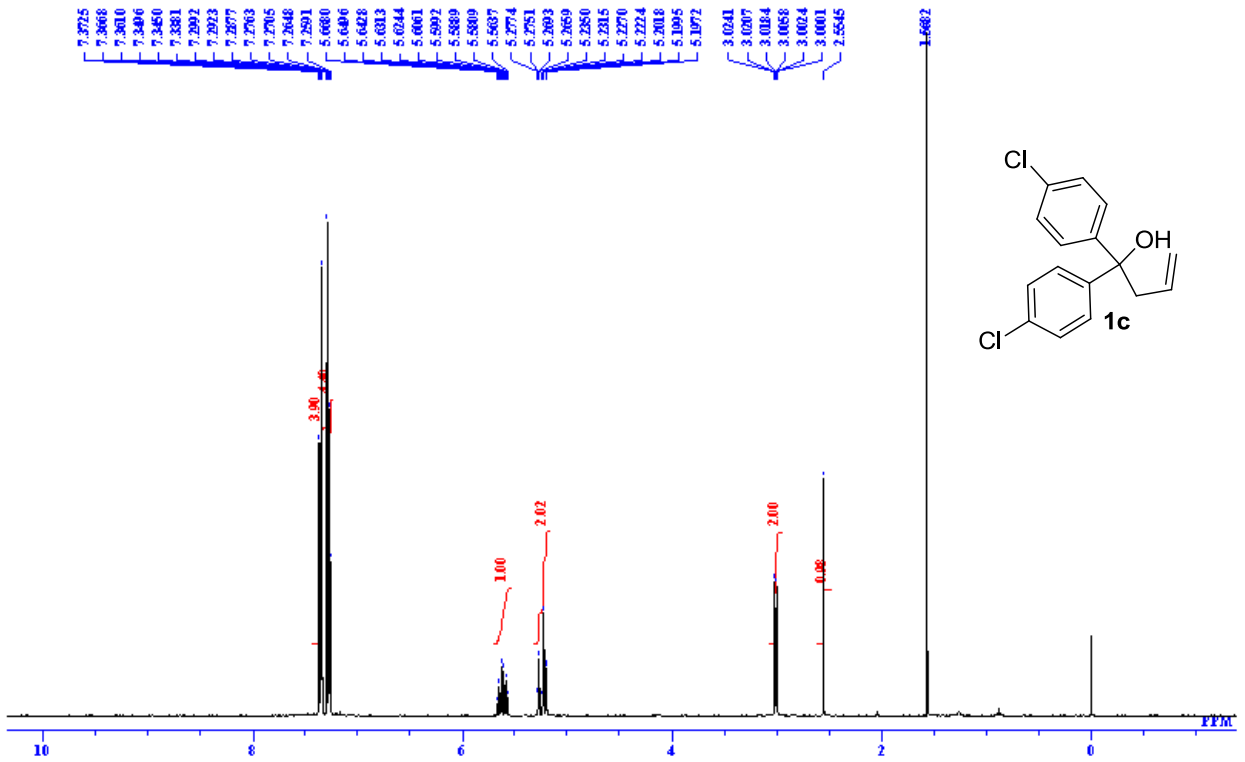


Figure S5-1. ^{1}H NMR spectrum of compound **1c** (400 MHz, $CDCl_3$).

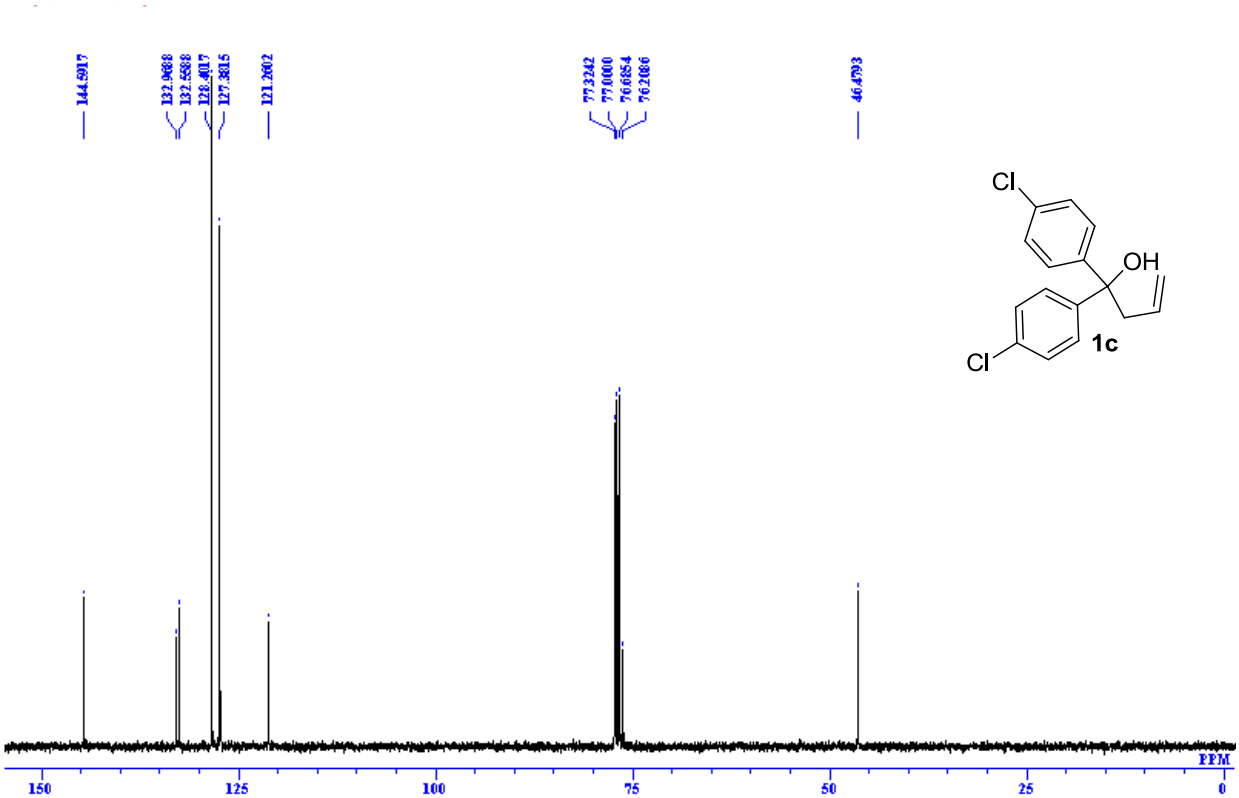


Figure S5-2. ^{13}C NMR spectrum of compound **1c** (100 MHz, $CDCl_3$).

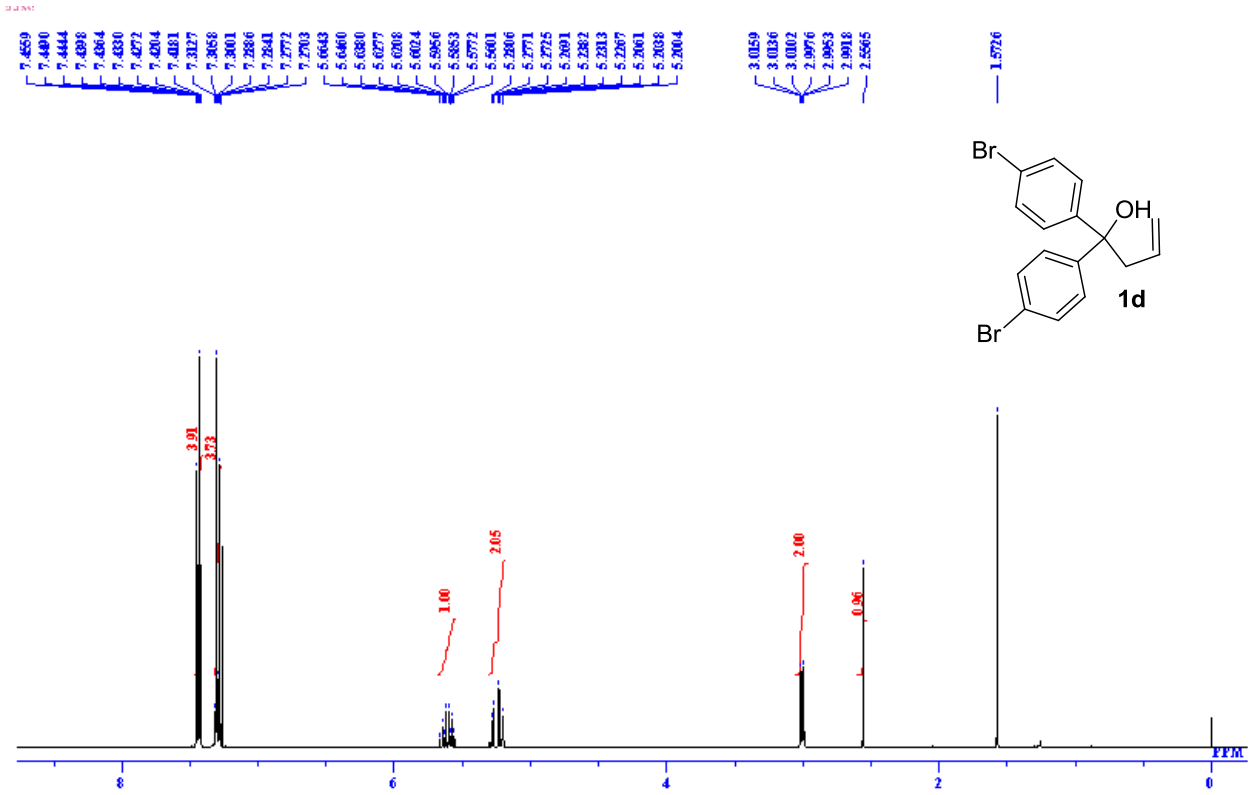


Figure S6-1. ^{1}H NMR spectrum of compound **1d** (400 MHz, $CDCl_3$).

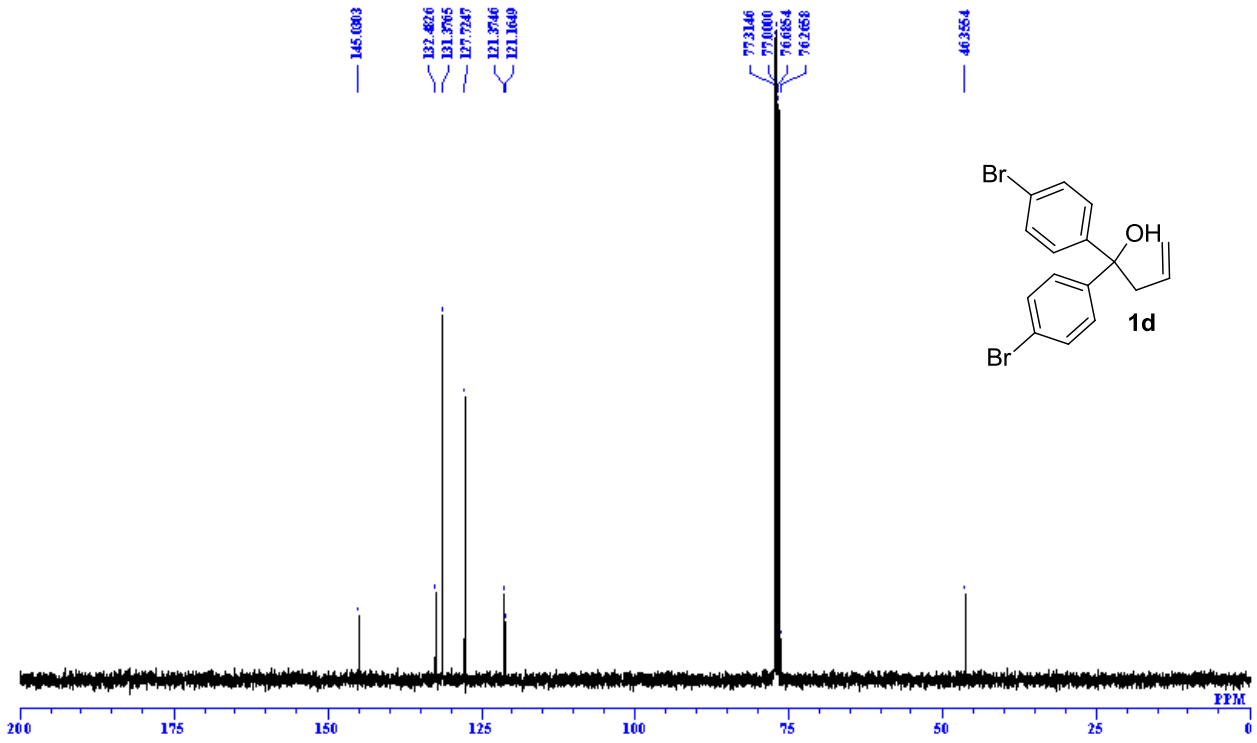


Figure S6-2. ^{13}C NMR spectrum of compound **1d** (100 MHz, $CDCl_3$).

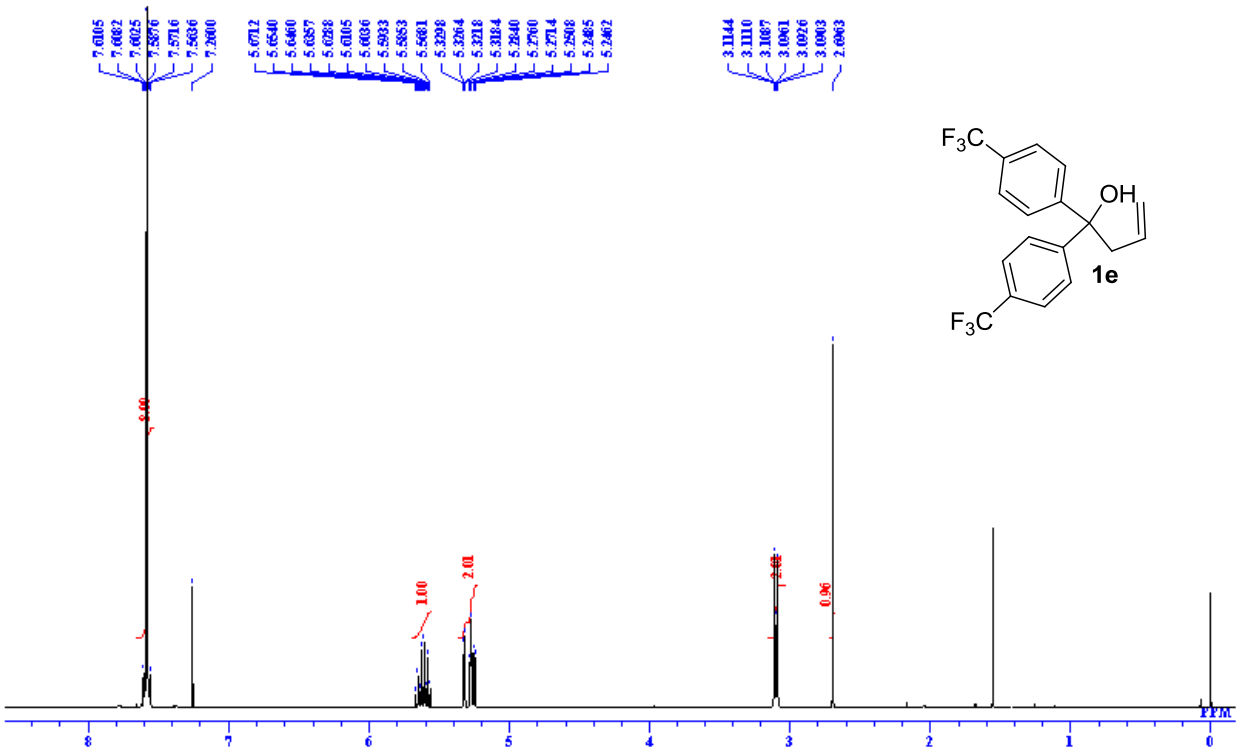


Figure S7-1. ^{1}H NMR spectrum of compound **1e** (400 MHz, $CDCl_3$).

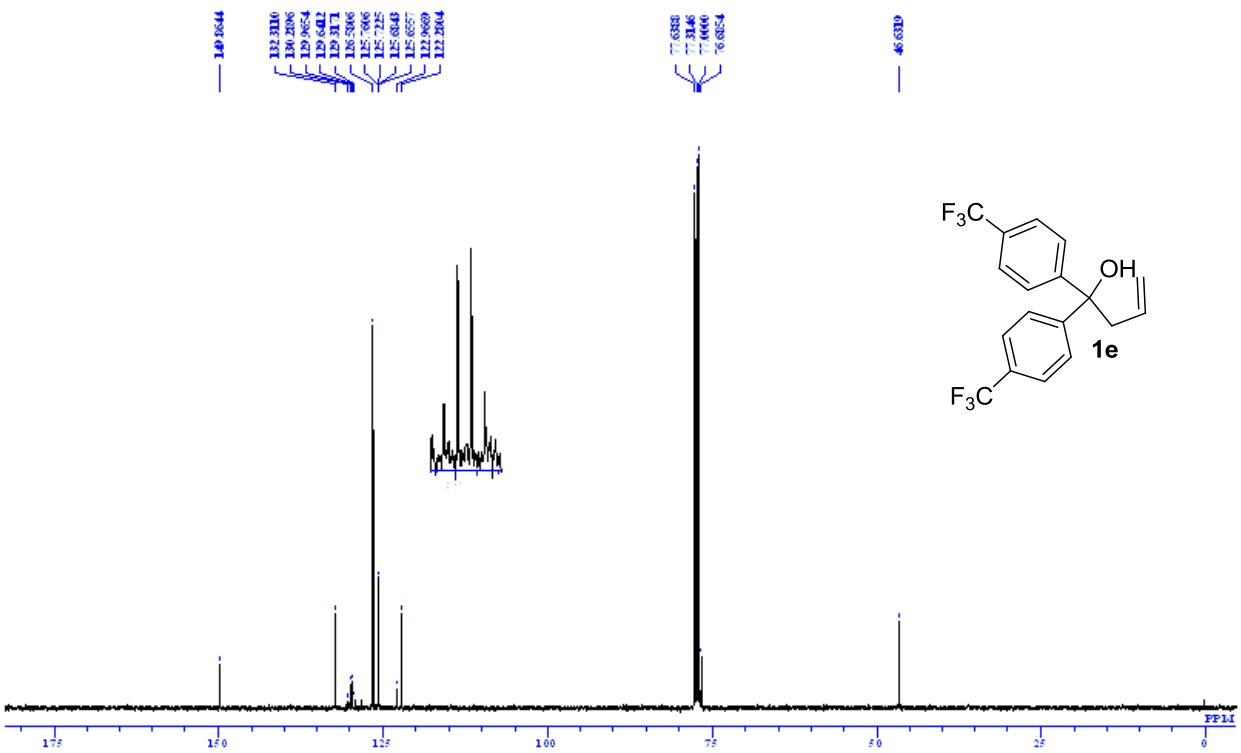


Figure S7-2. ^{13}C NMR spectrum of compound **1e** (100 MHz, $CDCl_3$).

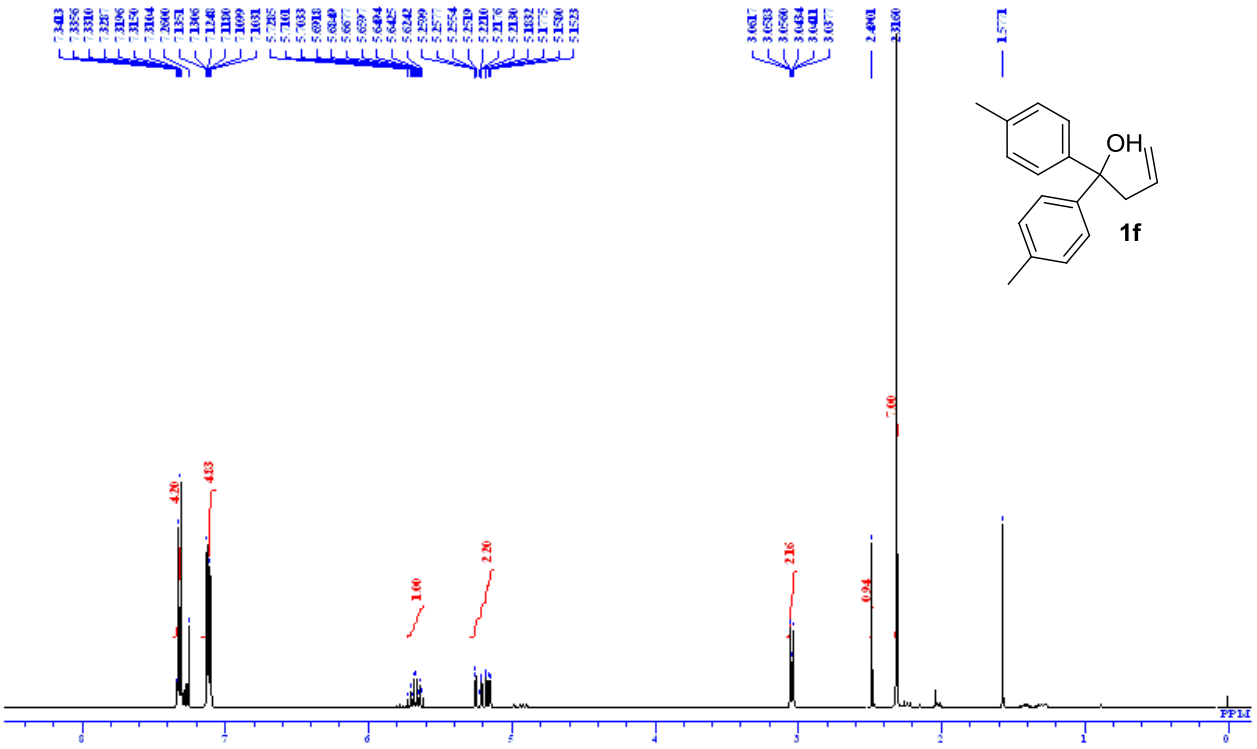


Figure S8-1. ^{1}H NMR spectrum of compound **1f** (400 MHz, $CDCl_3$).

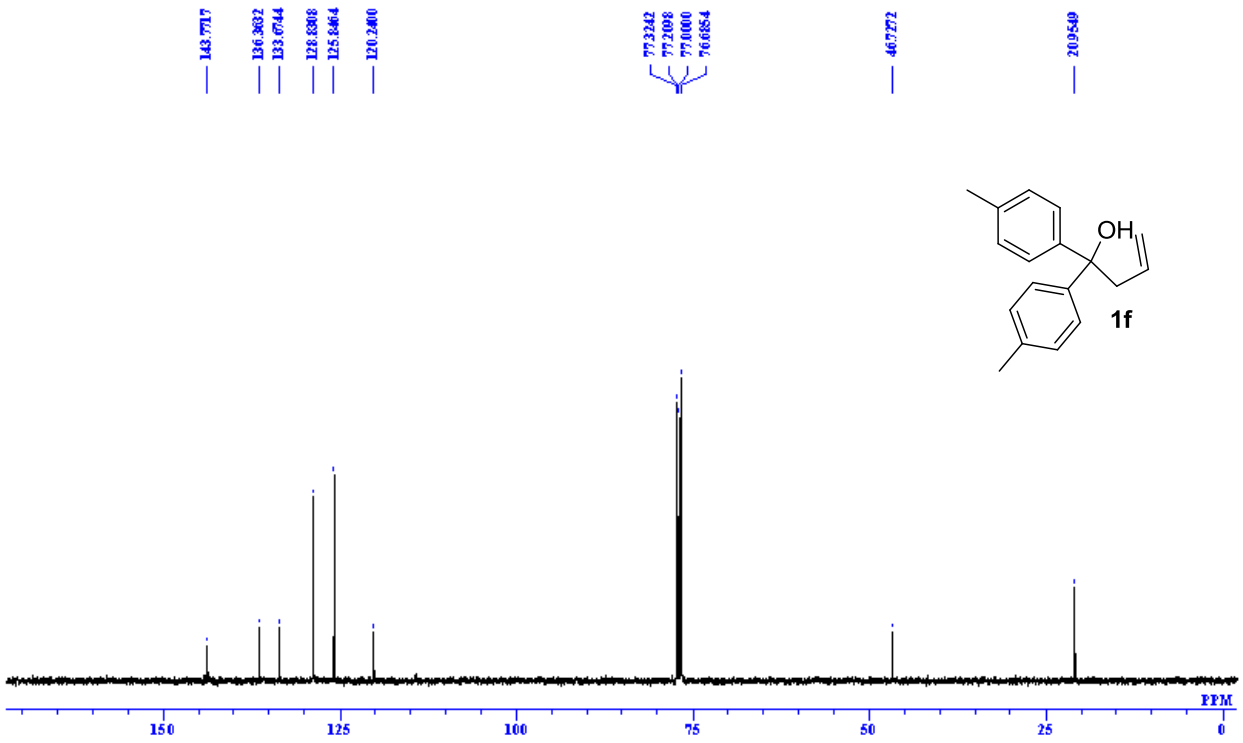


Figure S8-2. ^{13}C NMR spectrum of compound **1f** (100 MHz, $CDCl_3$).

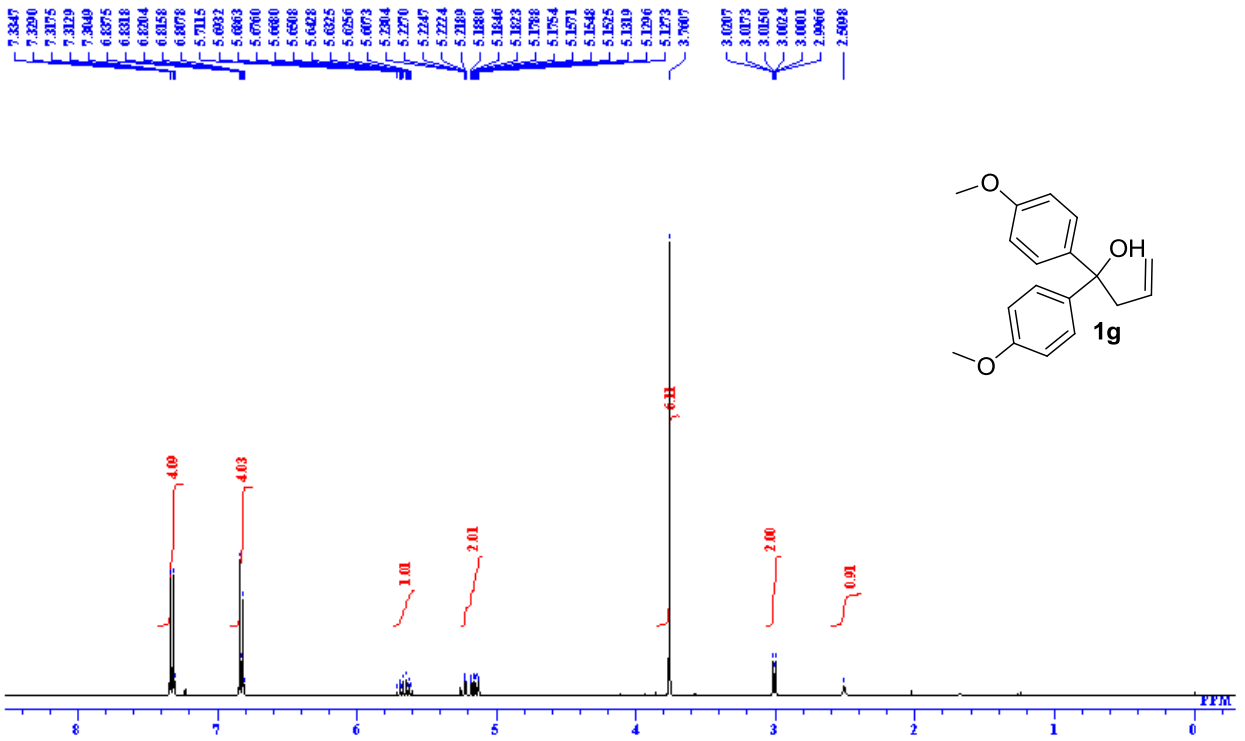


Figure S9-1. ^{1}H NMR spectrum of compound **1g** (400 MHz, $CDCl_3$).

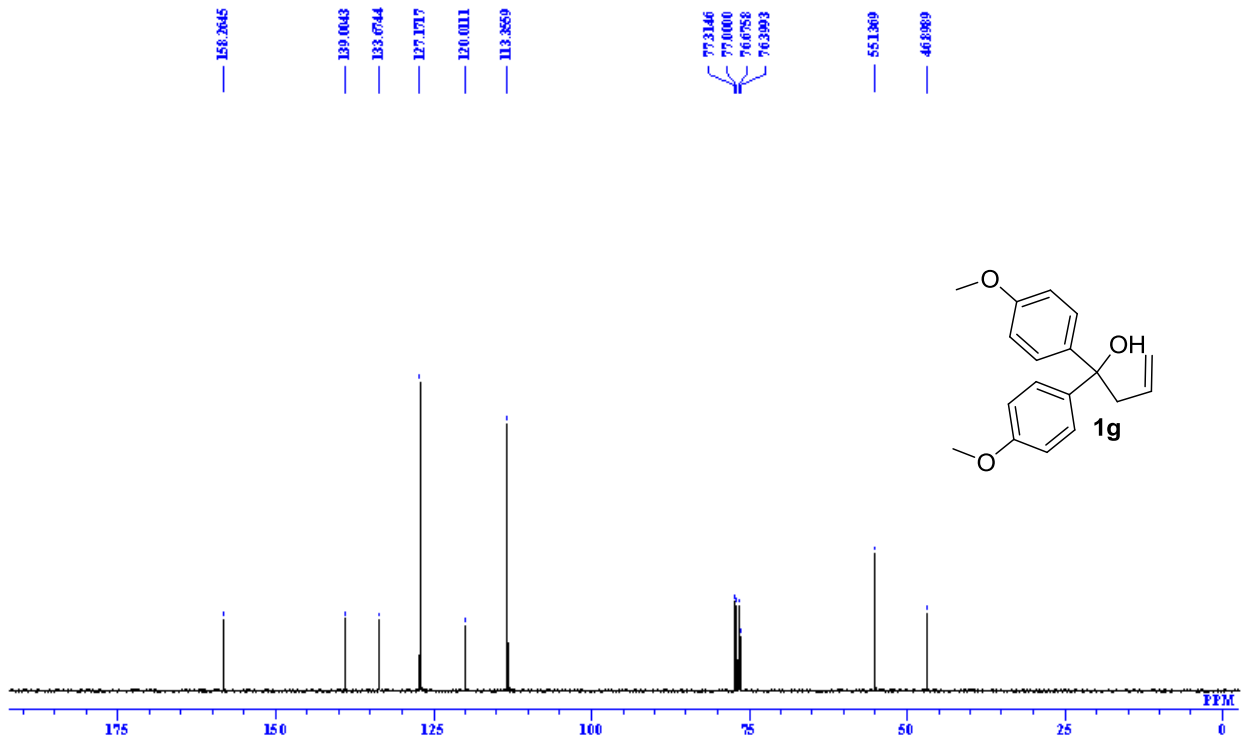


Figure S9-2. ^{13}C NMR spectrum of compound **1g** (100 MHz, $CDCl_3$).

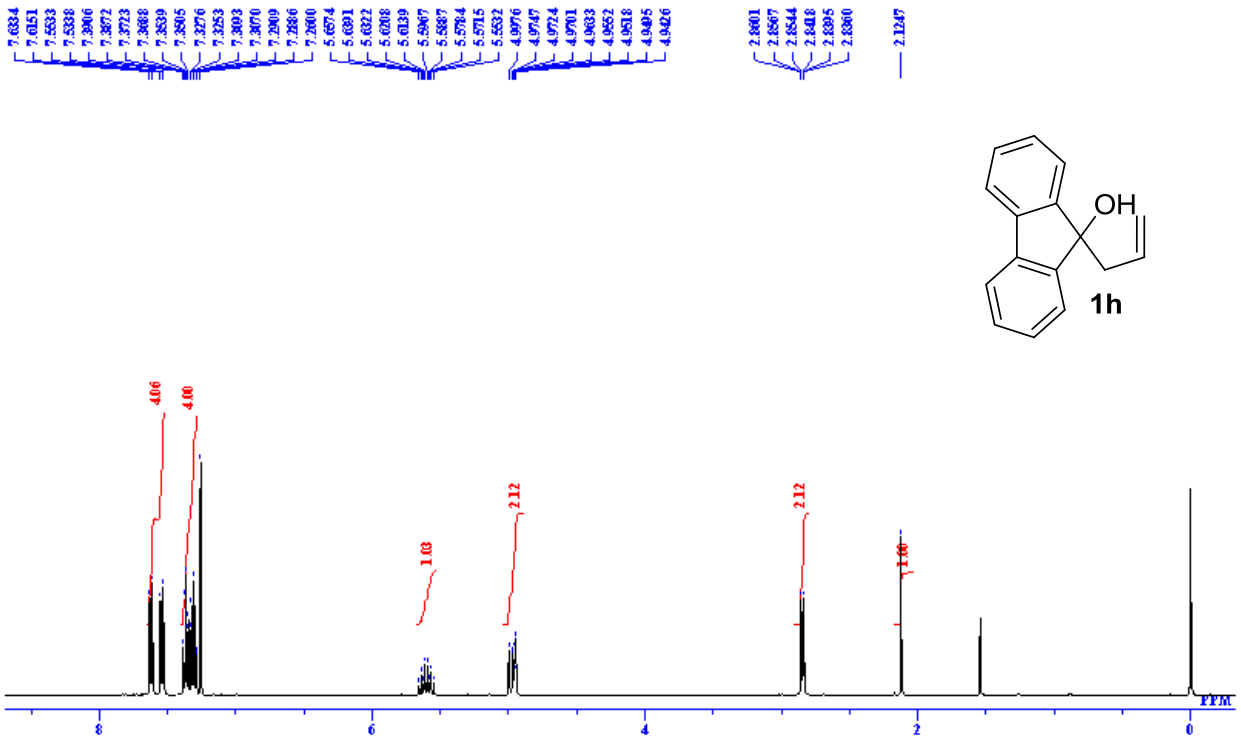


Figure S10-1. ^{1}H NMR spectrum of compound **1h** (400 MHz, $CDCl_3$).

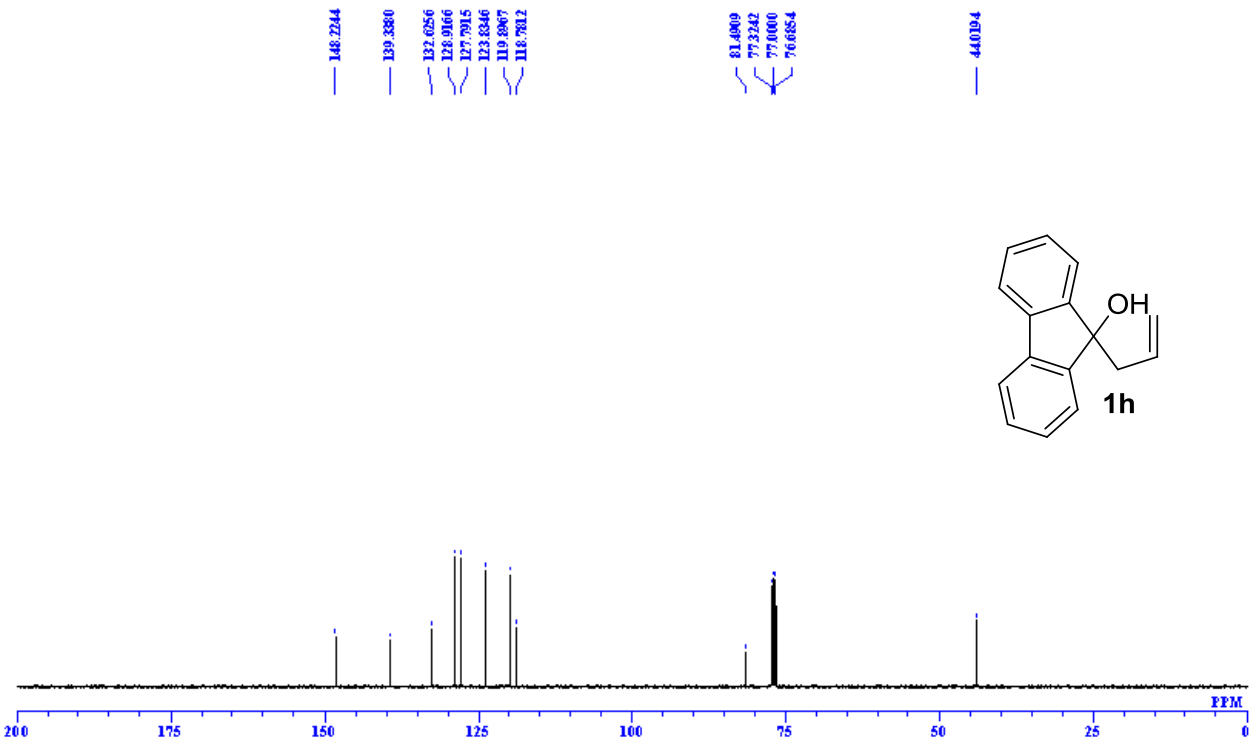


Figure S10-2. ^{13}C NMR spectrum of compound **1h** (100 MHz, $CDCl_3$).

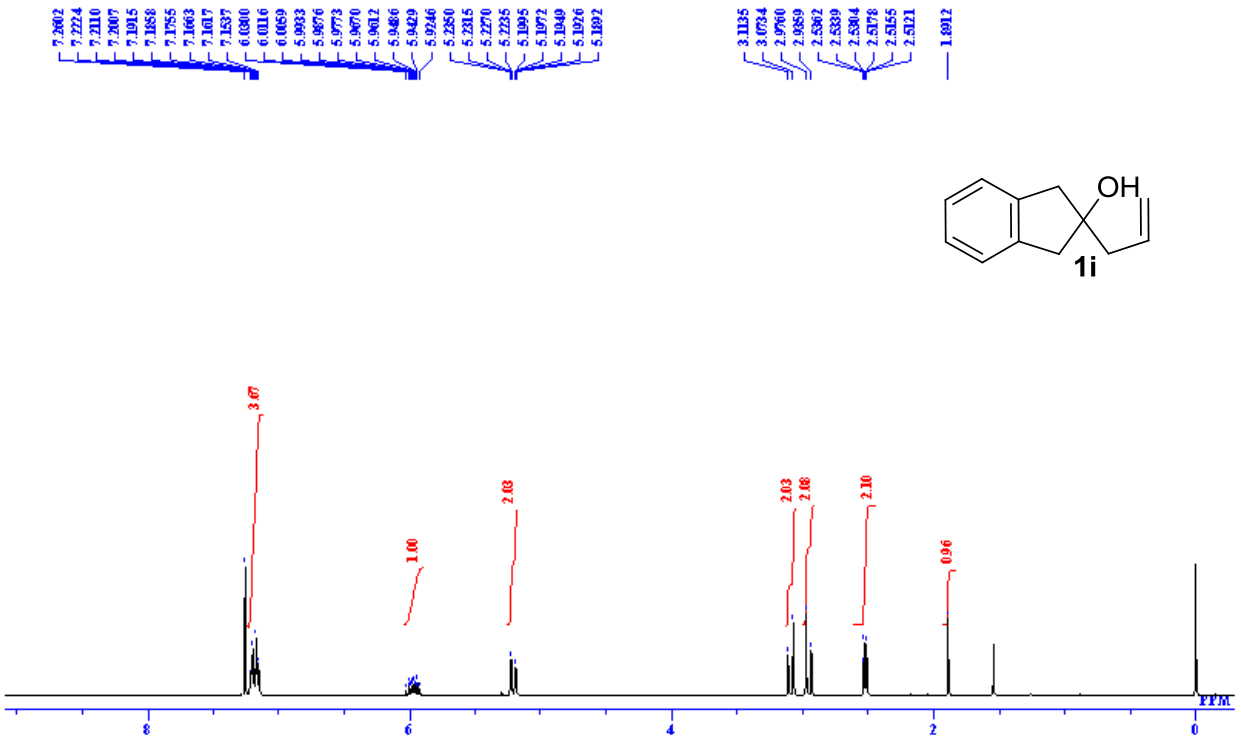


Figure S11-1. ^{1}H NMR spectrum of compound **1i** (400 MHz, $CDCl_3$).

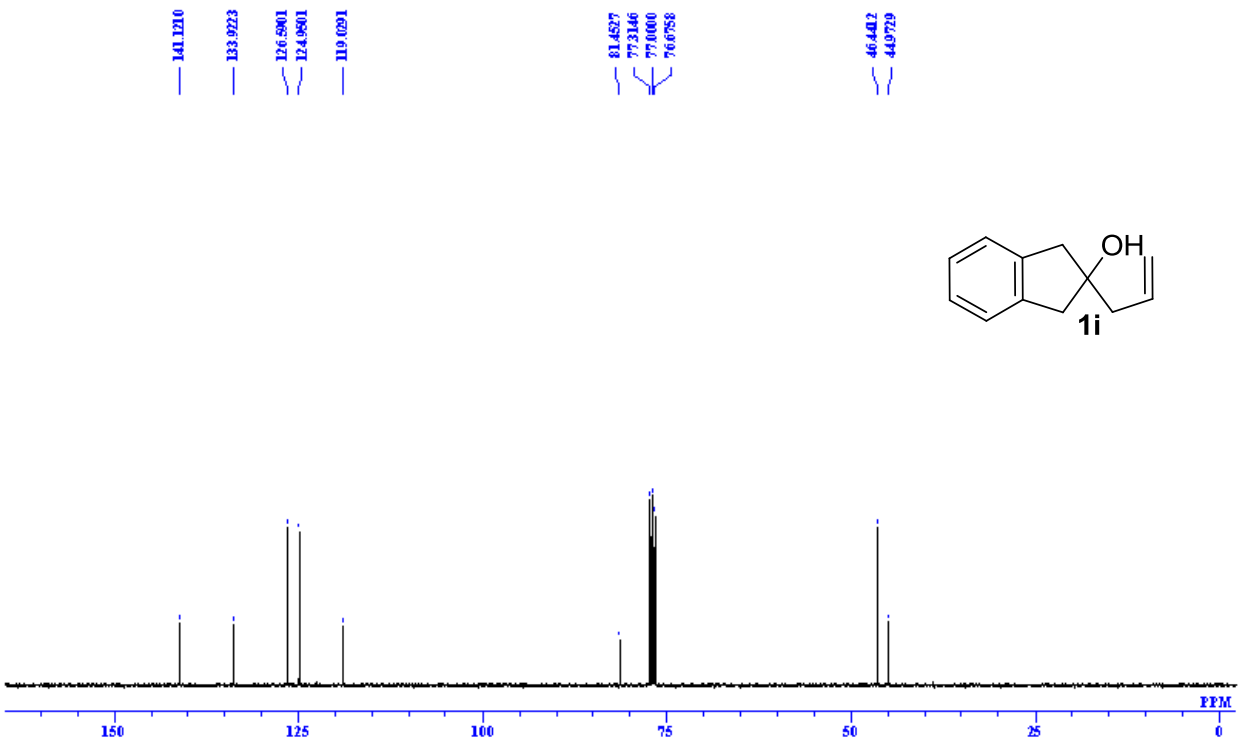


Figure S11-2. ^{13}C NMR spectrum of compound **1i** (100 MHz, $CDCl_3$).

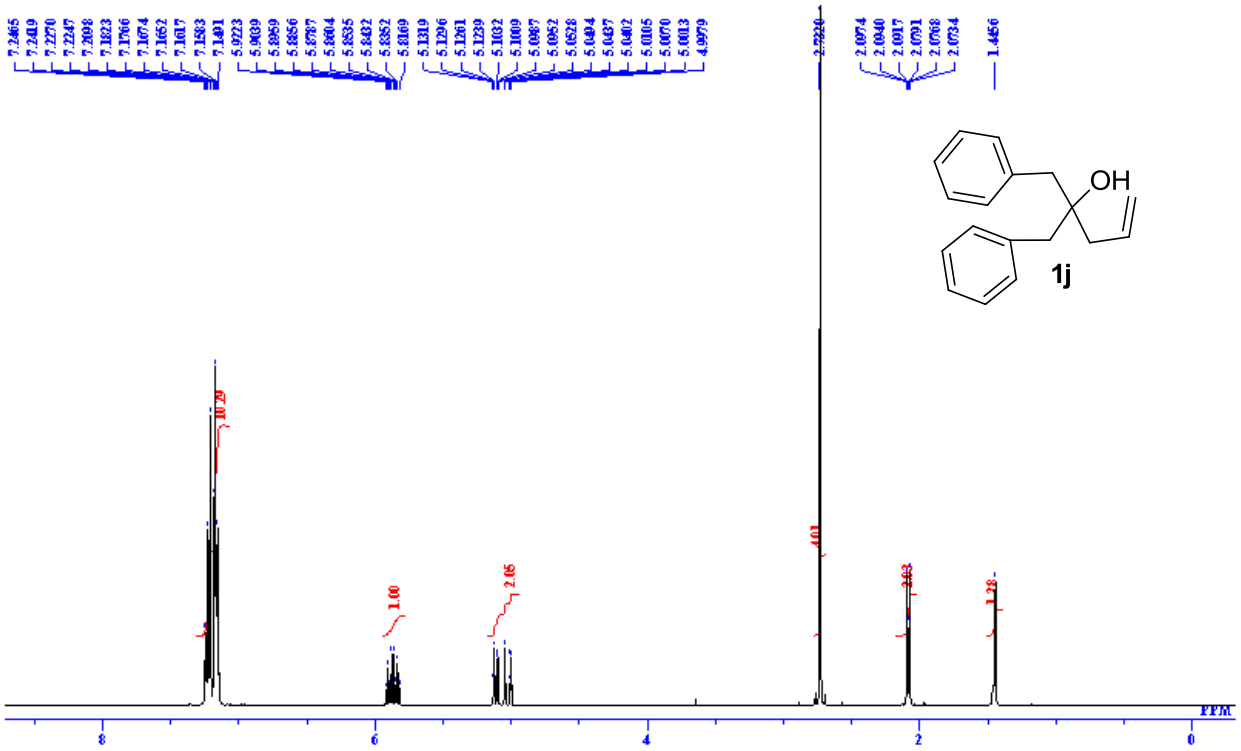


Figure S12-1. ^{1}H NMR spectrum of compound **1j** (400 MHz, $CDCl_3$).

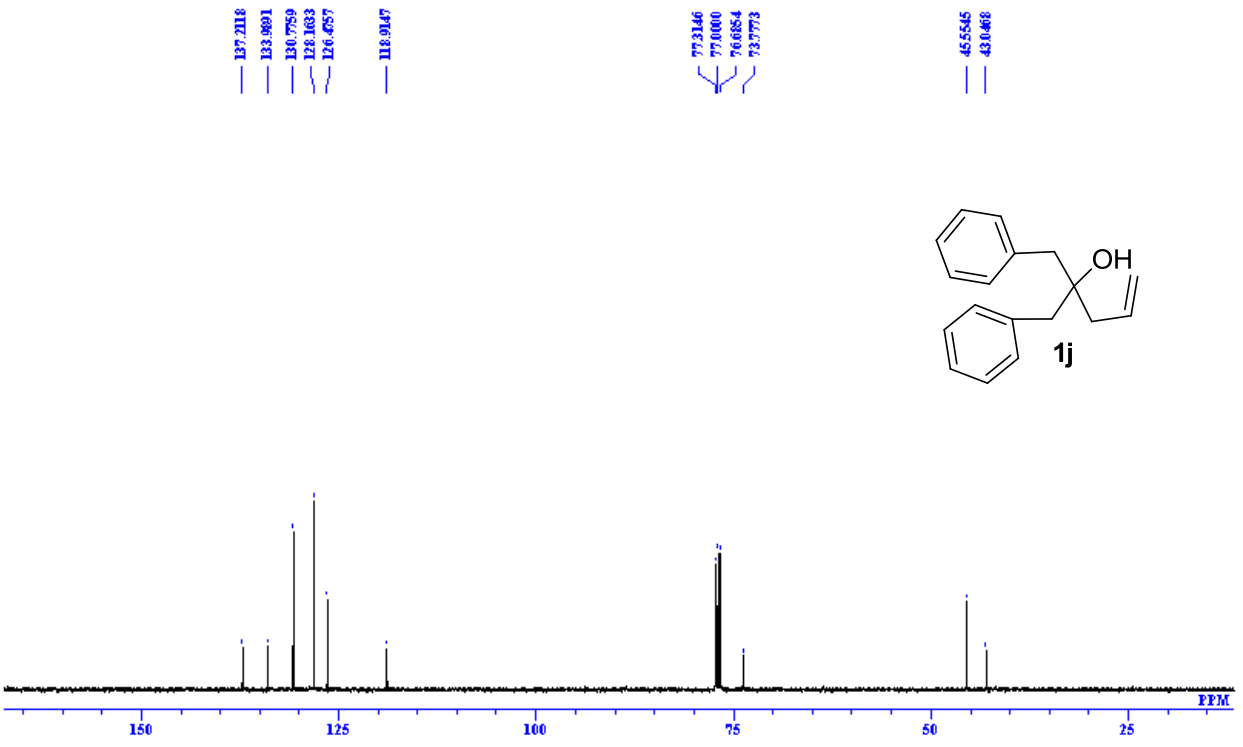


Figure S12-2. ^{13}C NMR spectrum of compound **1j** (100 MHz, $CDCl_3$).

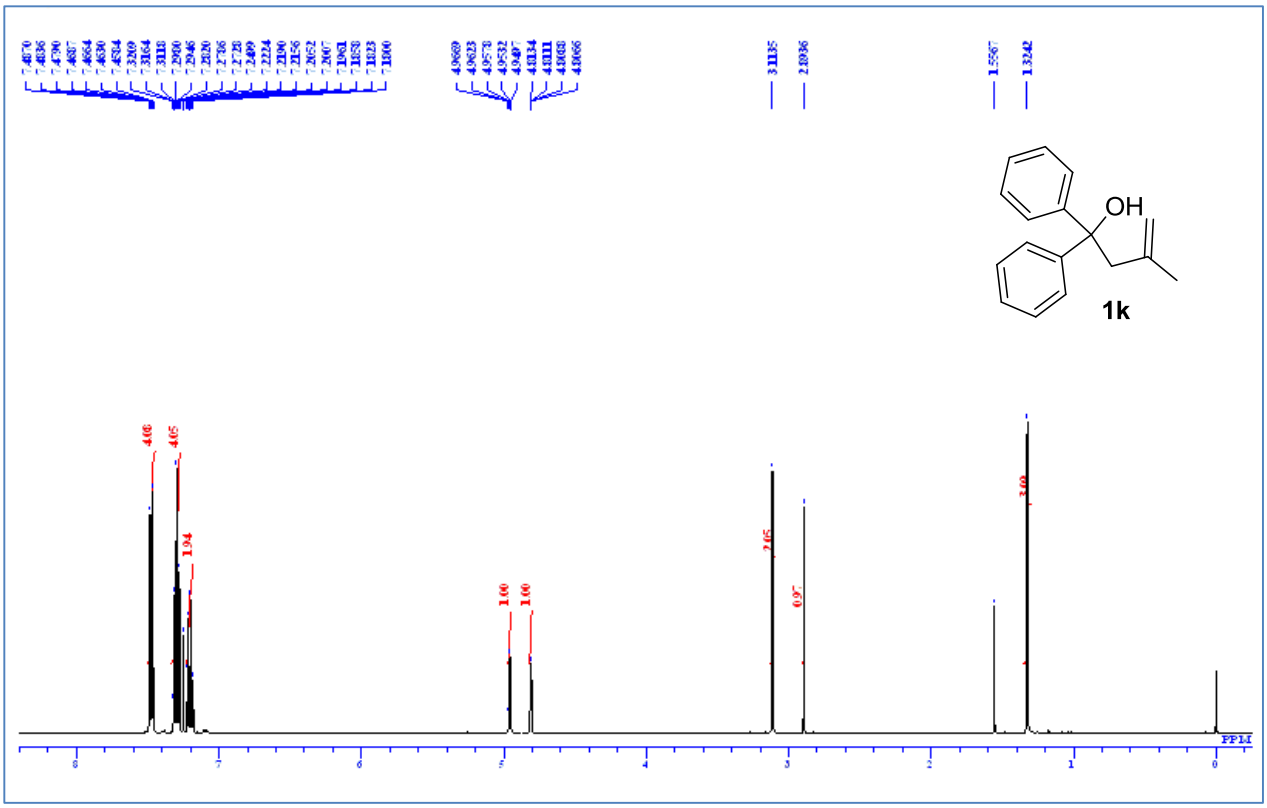


Figure S13-1. ^{1}H NMR spectrum of compound **1k** (400 MHz, $CDCl_3$).

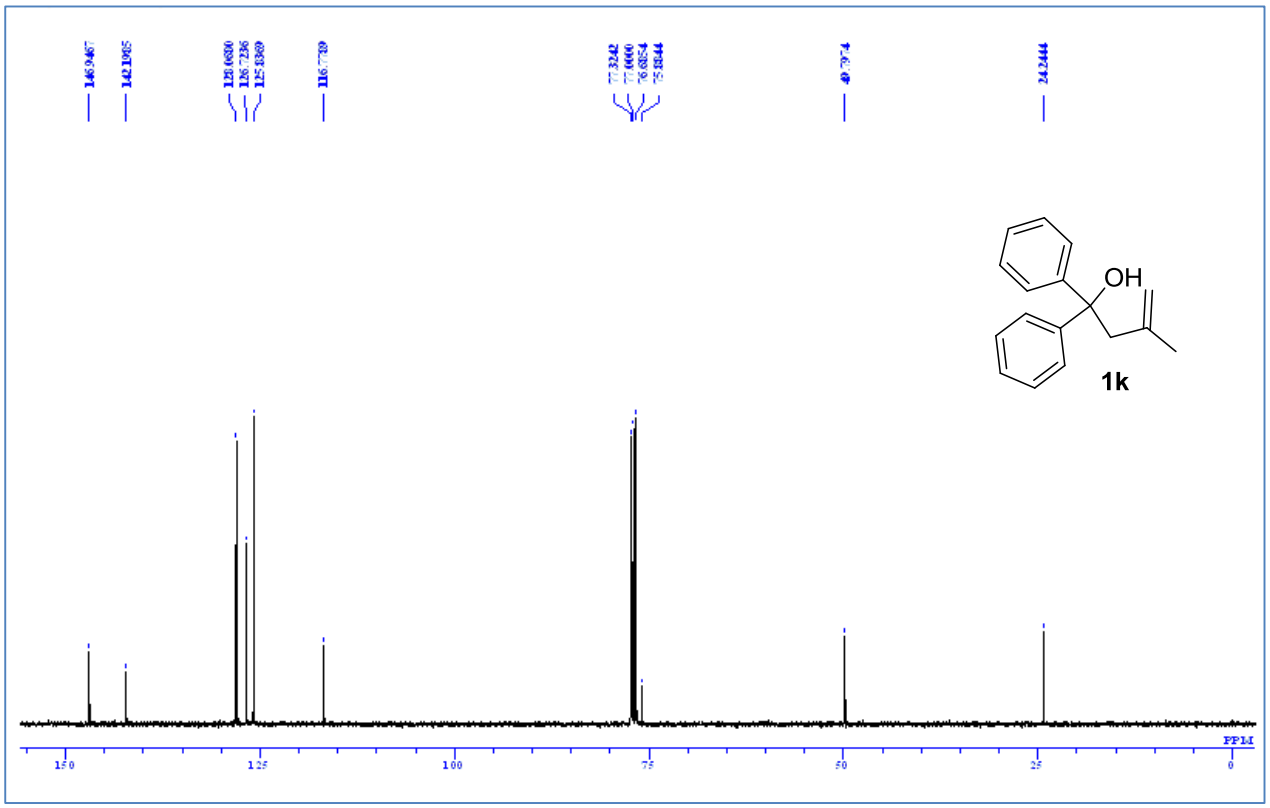


Figure S13-2. ^{13}C NMR spectrum of compound **1k** (100 MHz, $CDCl_3$).

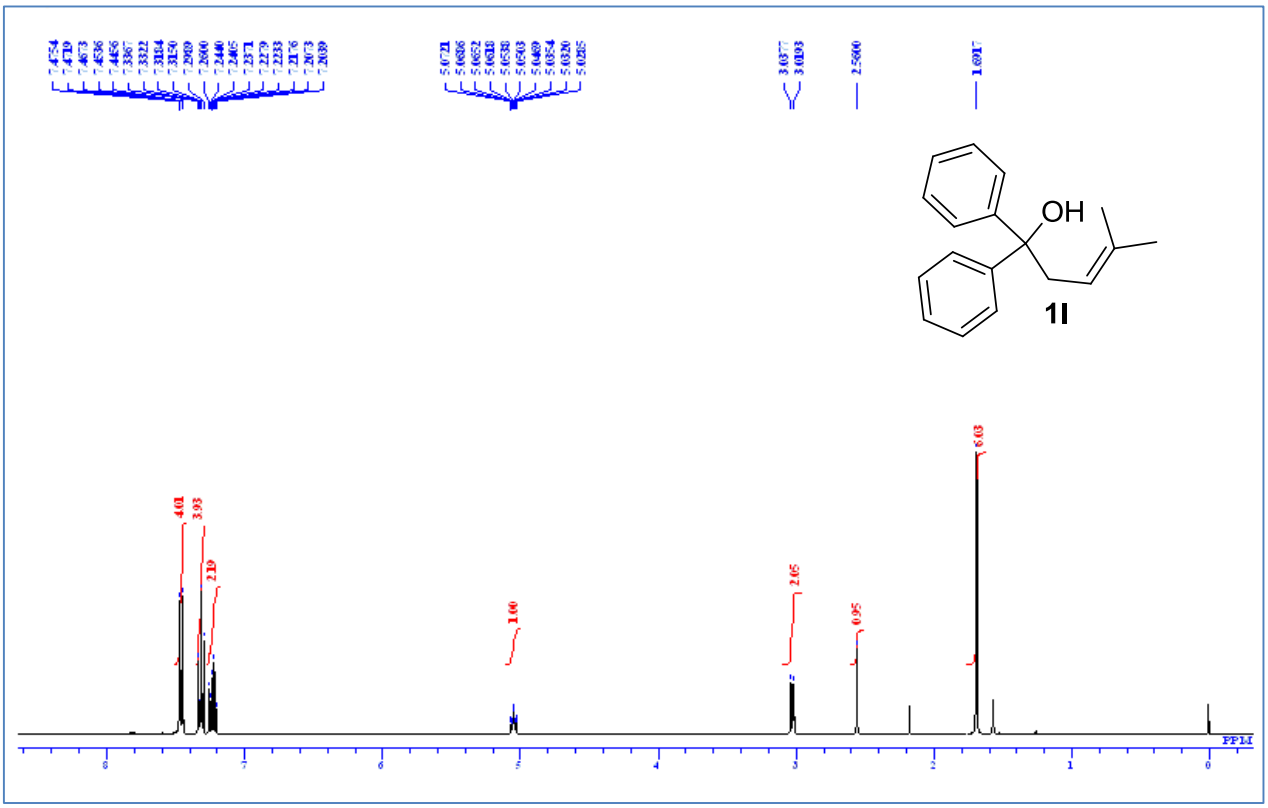


Figure S14-1. ^{1}H NMR spectrum of compound **1l** (400 MHz, $CDCl_3$).

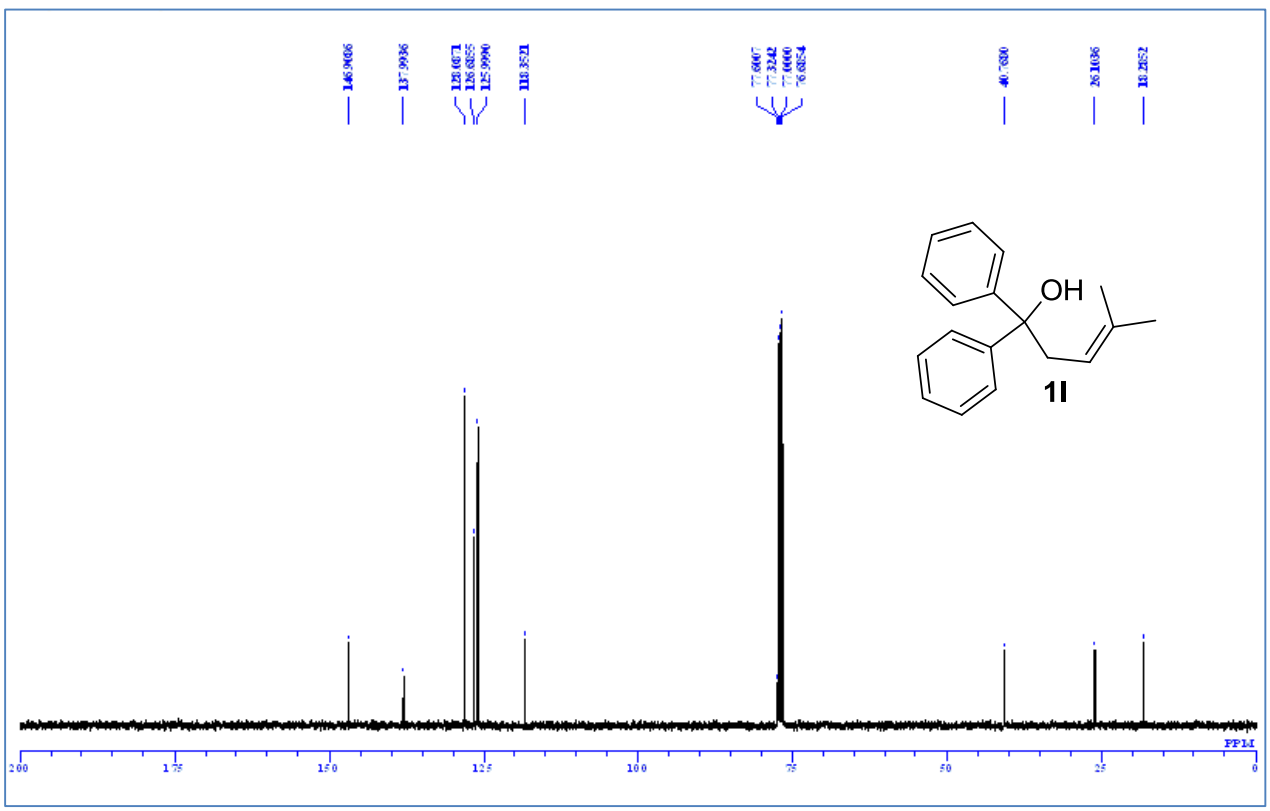


Figure S14-2. ^{13}C NMR spectrum of compound **1l** (100 MHz, $CDCl_3$).

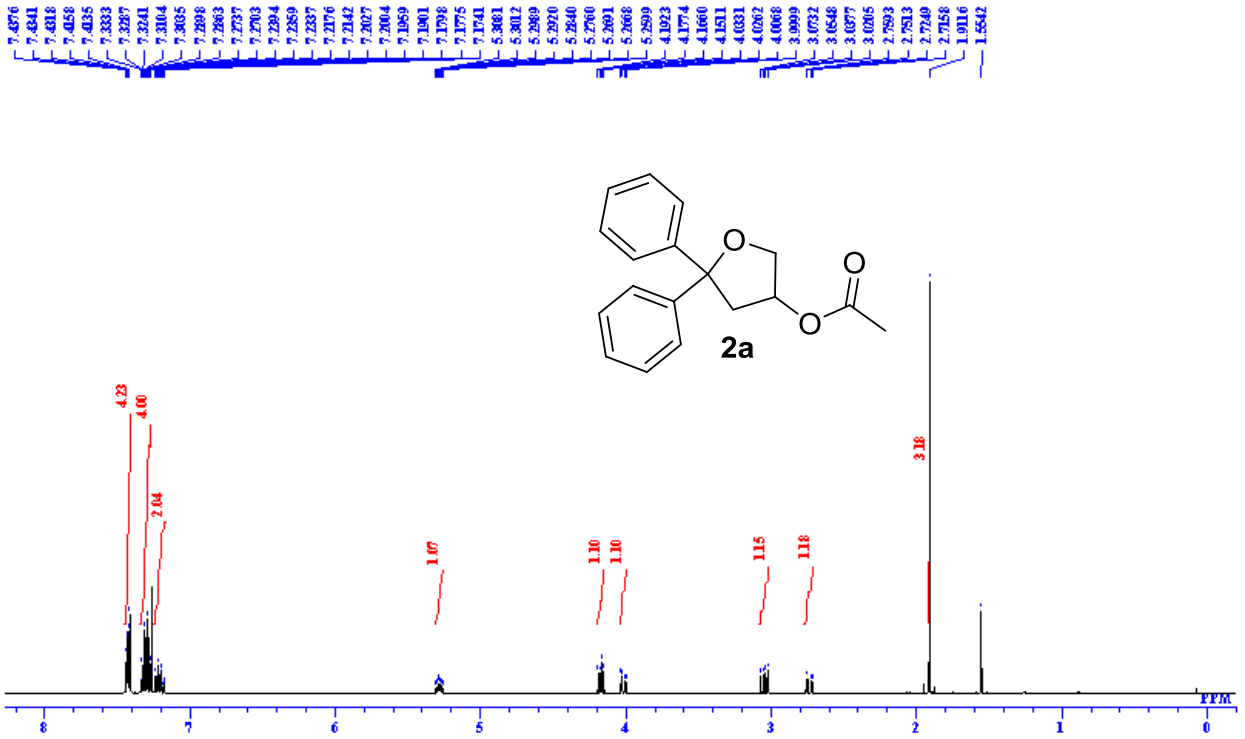


Figure S15-1. ^{1}H NMR spectrum of compound **2a** (400 MHz, $CDCl_3$).

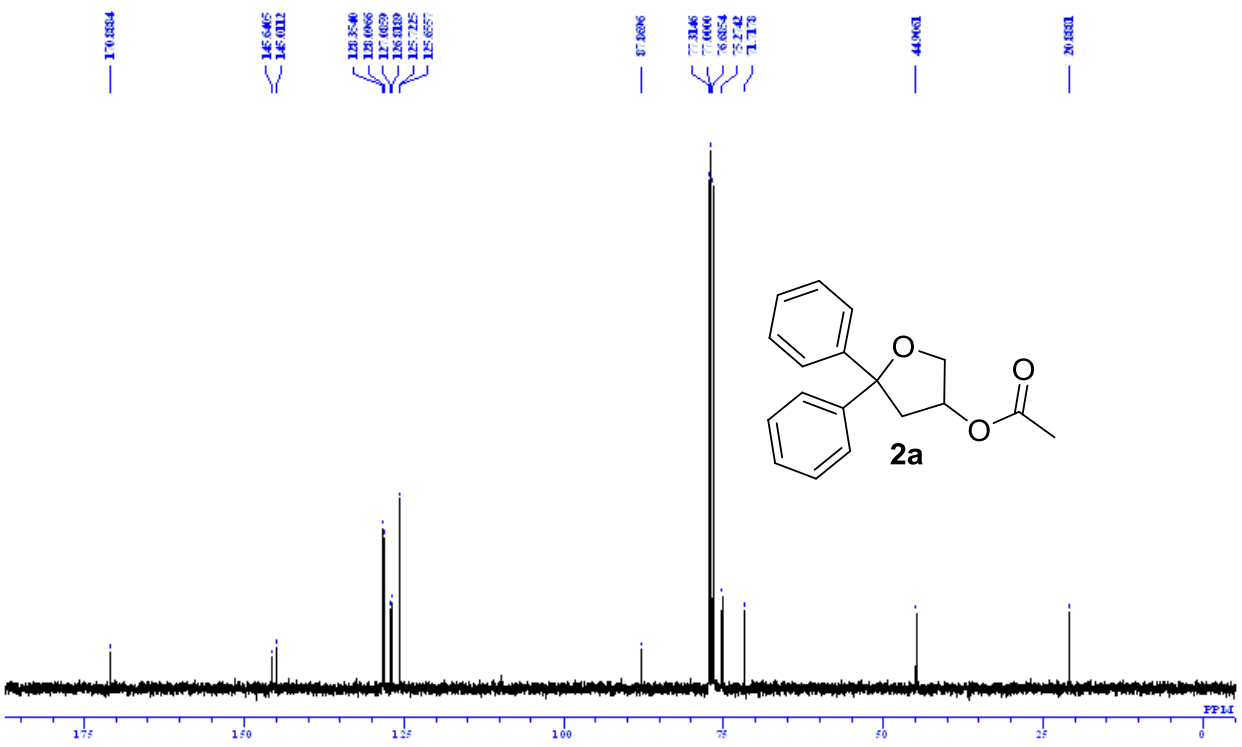


Figure S15-2. ^{13}C NMR spectrum of compound **2a** (100 MHz, $CDCl_3$).

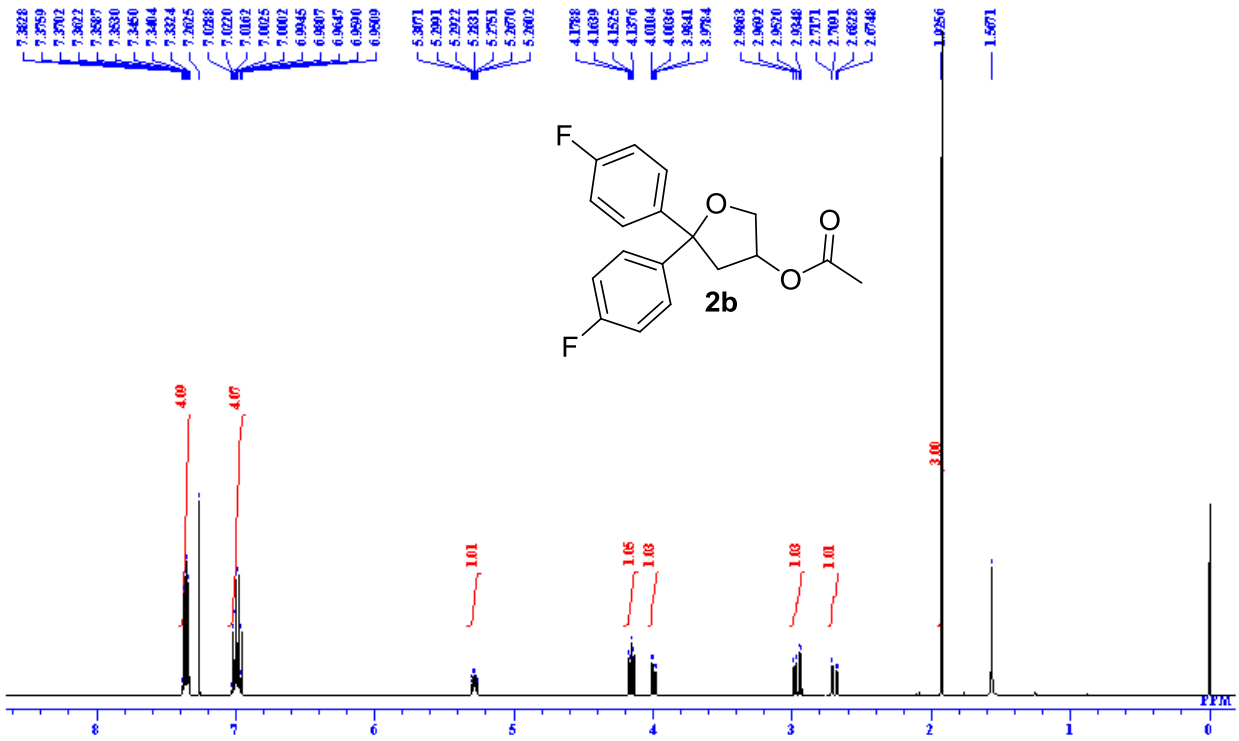


Figure S16-1. ^{1}H NMR spectrum of compound **2b** (400 MHz, $CDCl_3$).

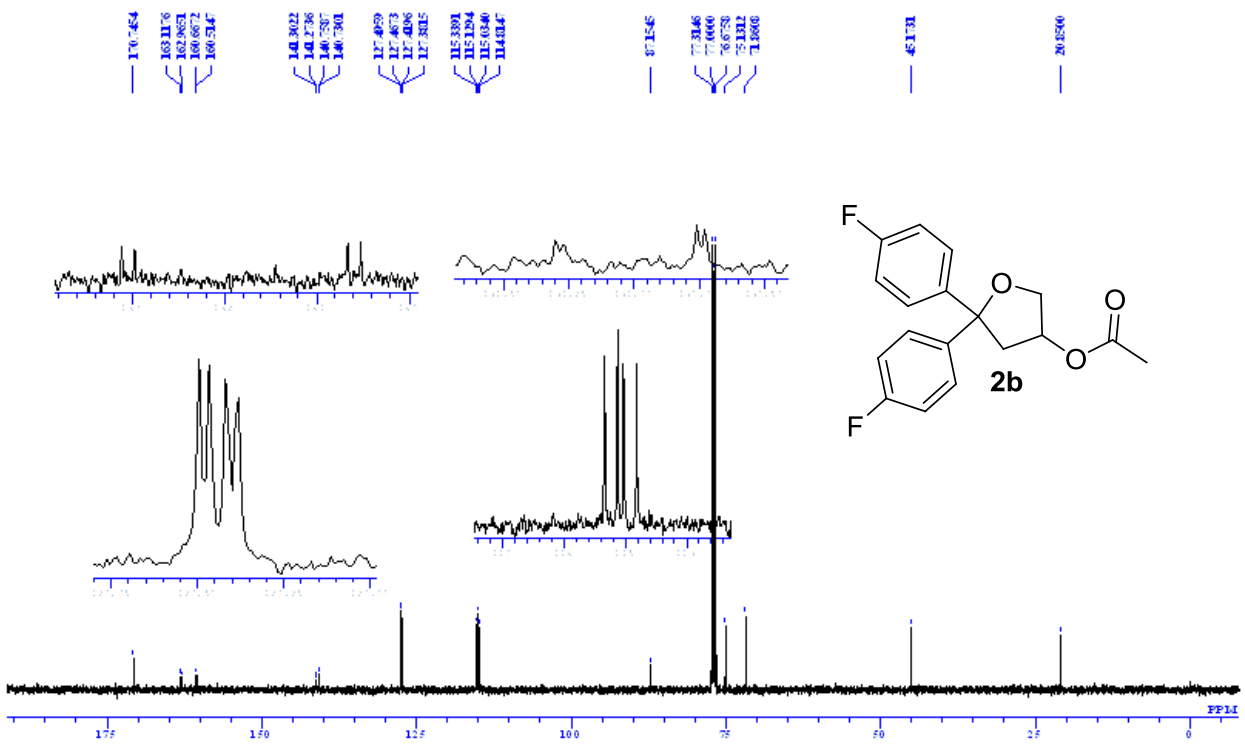


Figure S16-2. ^{13}C NMR spectrum of compound **2b** (100 MHz, $CDCl_3$).

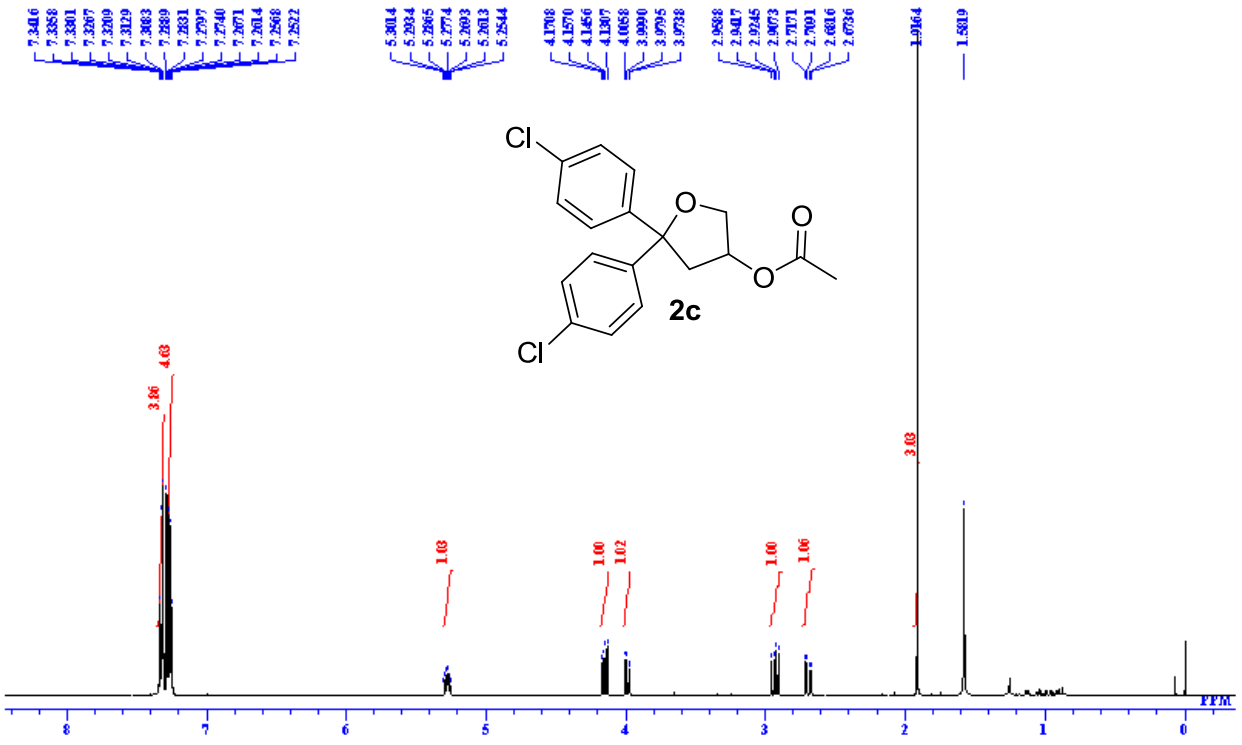


Figure S17-1. ^{1}H NMR spectrum of compound **2c** (400 MHz, $CDCl_3$).

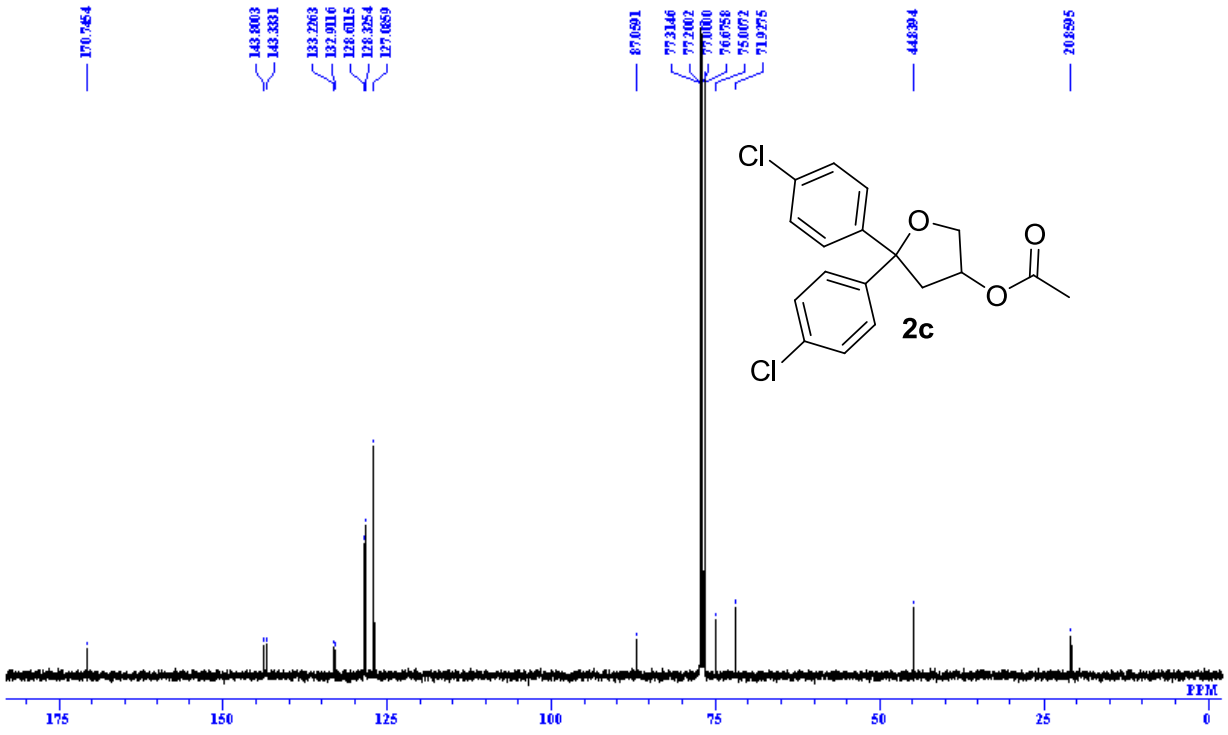


Figure S17-2.^{13}C NMR spectrum of compound **2c** (100 MHz, $CDCl_3$).

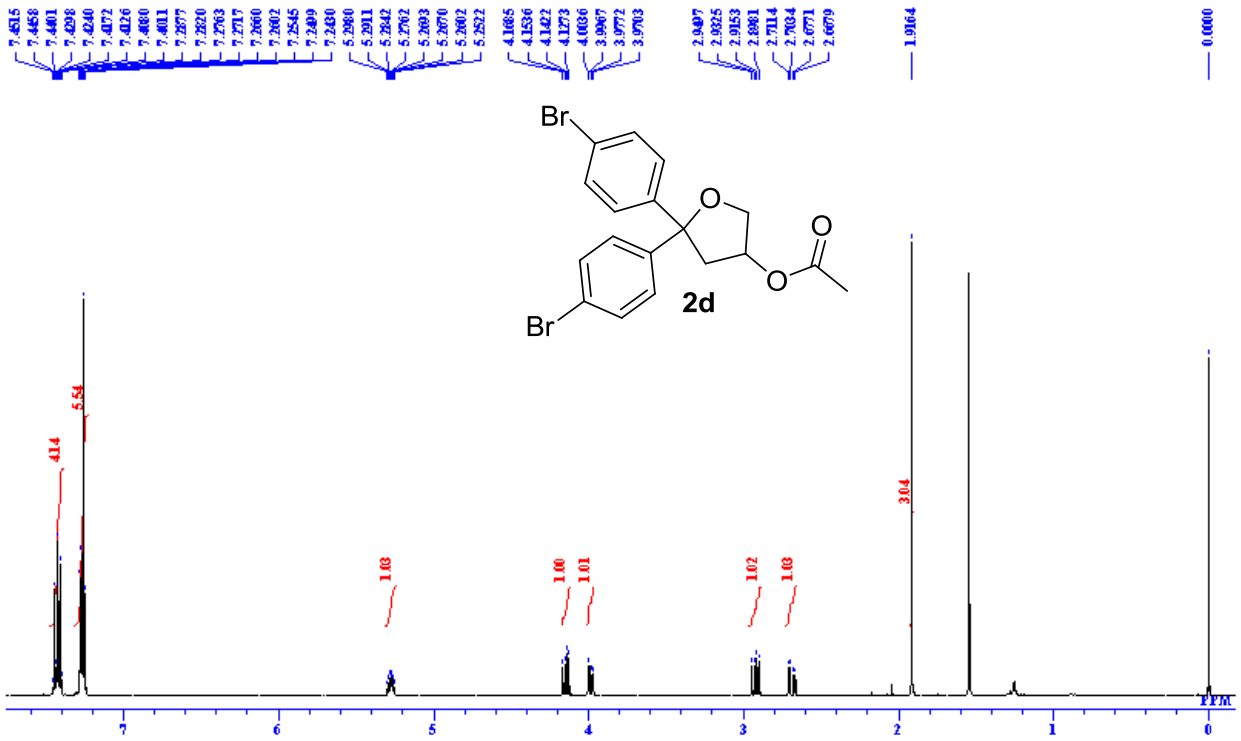


Figure S18-1. ^{1}H NMR spectrum of compound **2d** (400 MHz, $CDCl_3$).

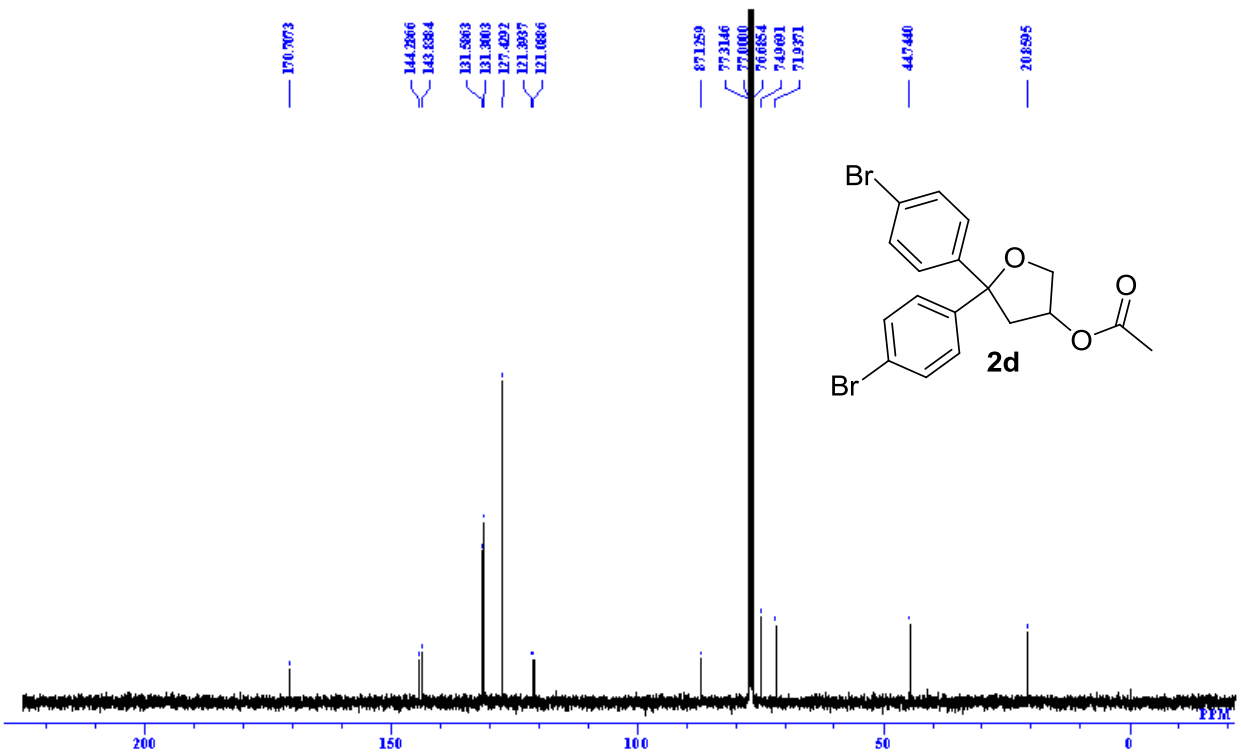


Figure S18-2. ^{13}C NMR spectrum of compound **2d** (100 MHz, $CDCl_3$).

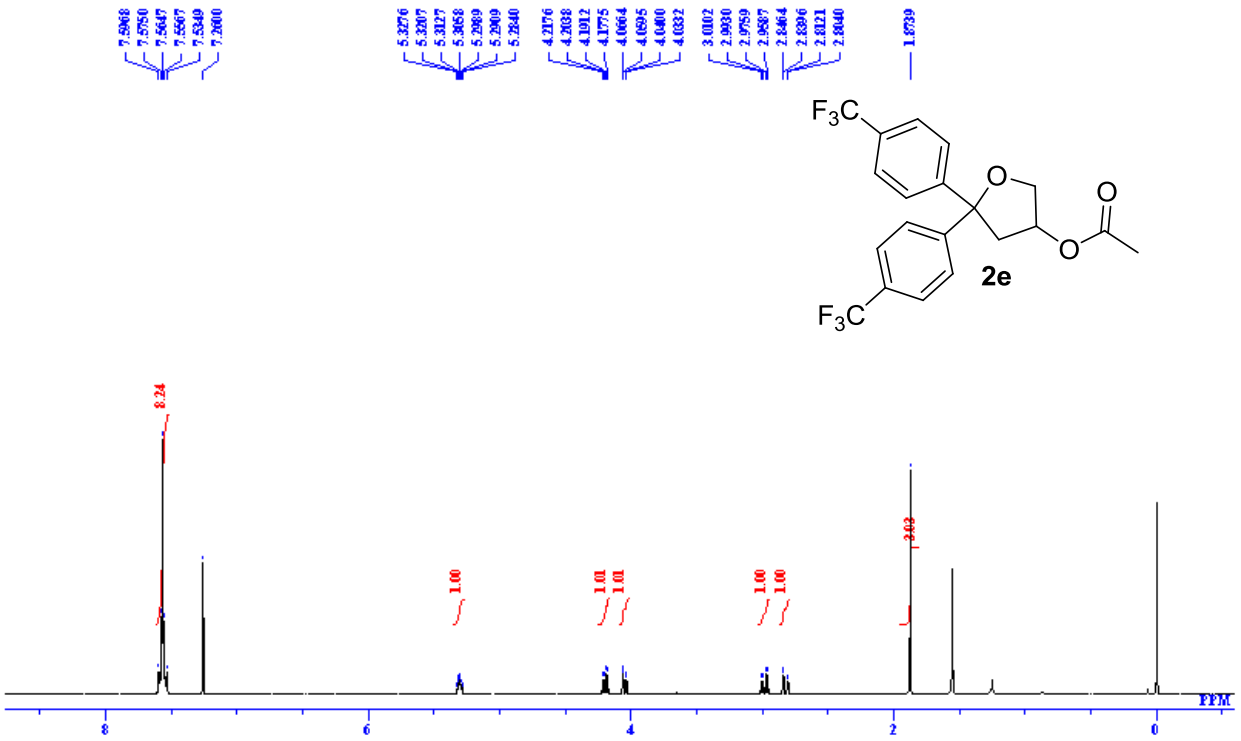


Figure S19-1. ^{1}H NMR spectrum of compound **2e** (400 MHz, $CDCl_3$).

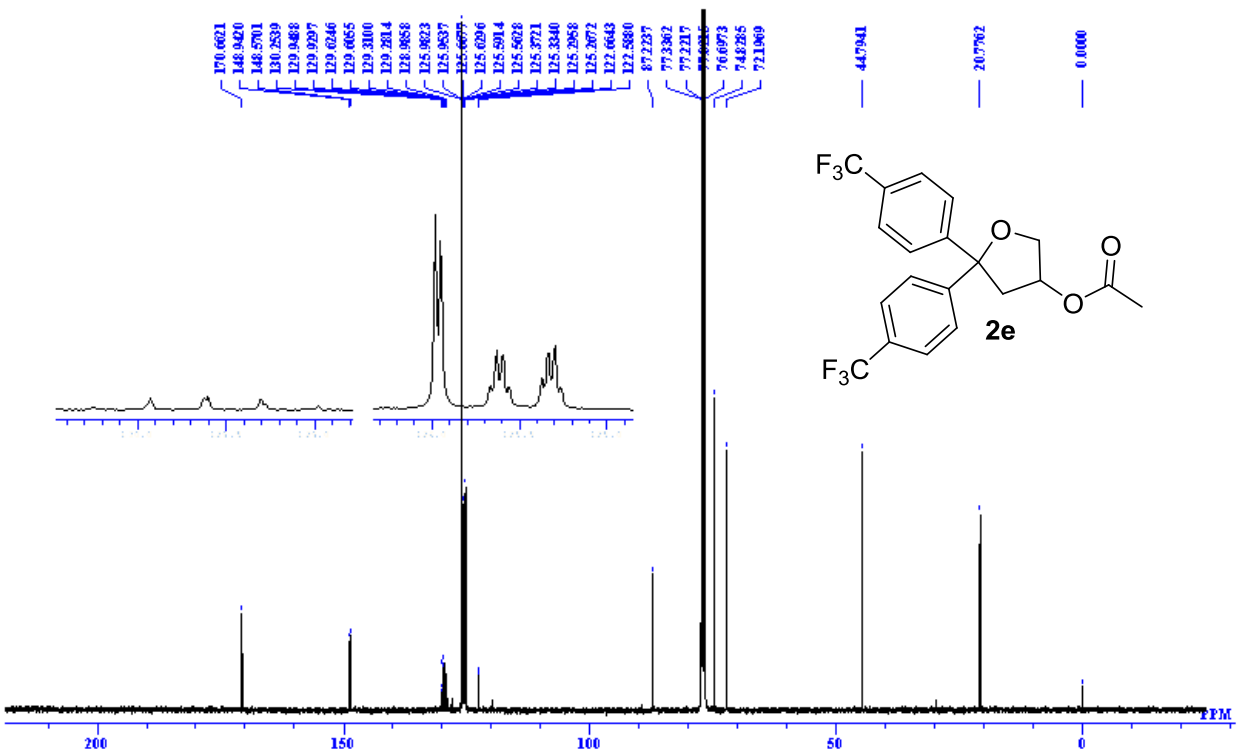


Figure S19-2. ^{13}C NMR spectrum of compound **2e** (100 MHz, $CDCl_3$).

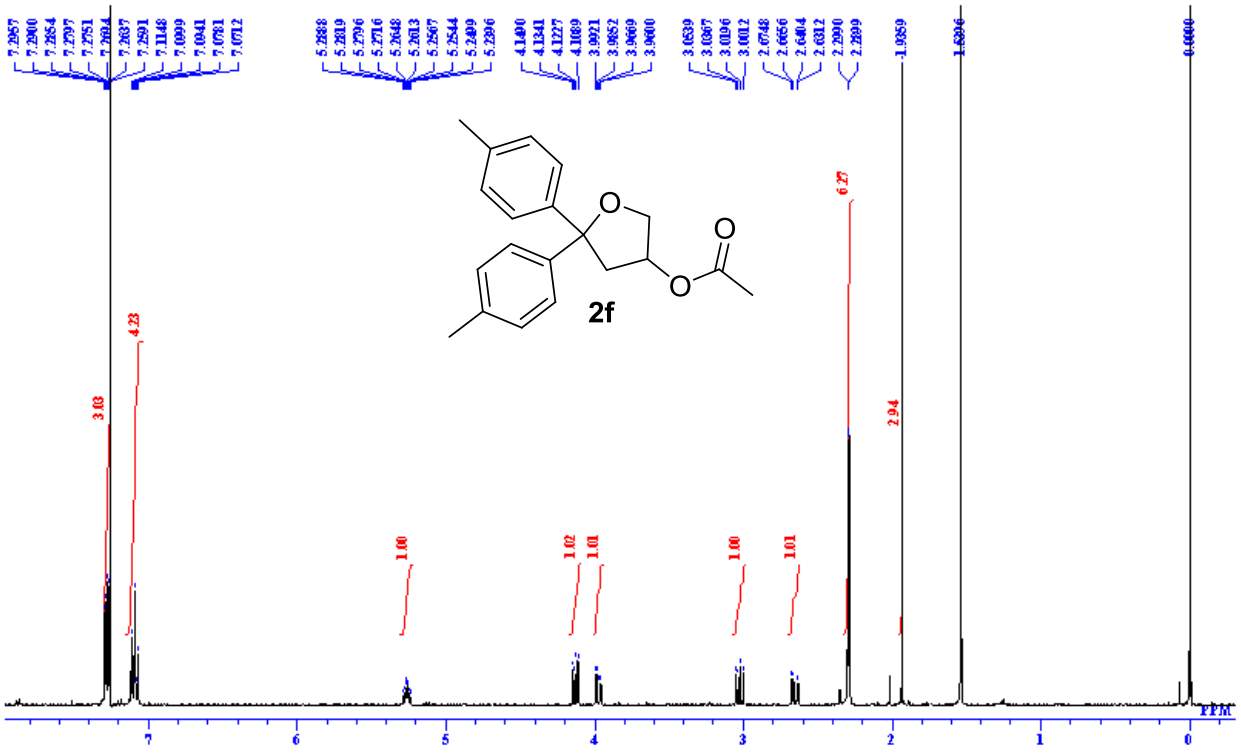


Figure S20-1. ^{1}H NMR spectrum of compound **2f** (400 MHz, $CDCl_3$).

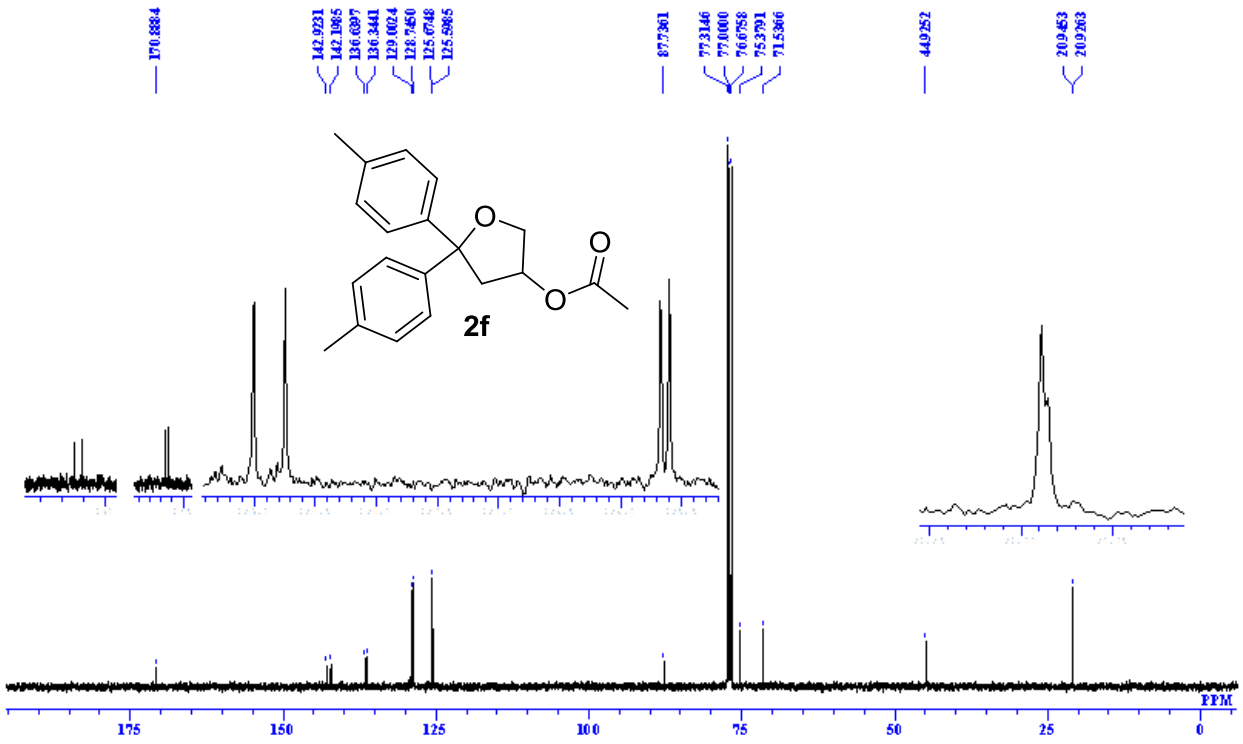


Figure S20-2. ^{13}C NMR spectrum of compound **2f** (100 MHz, $CDCl_3$).

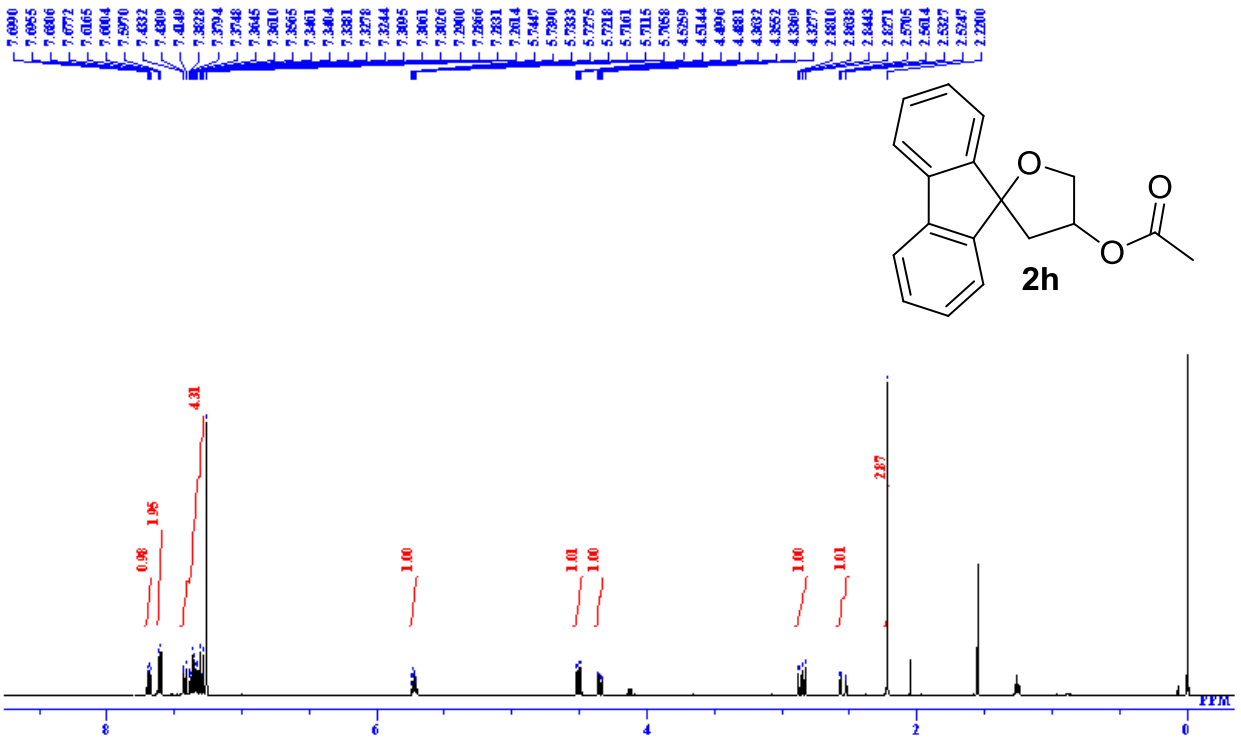


Figure S21-1. ^{1}H NMR spectrum of compound **2h** (400 MHz, $CDCl_3$).

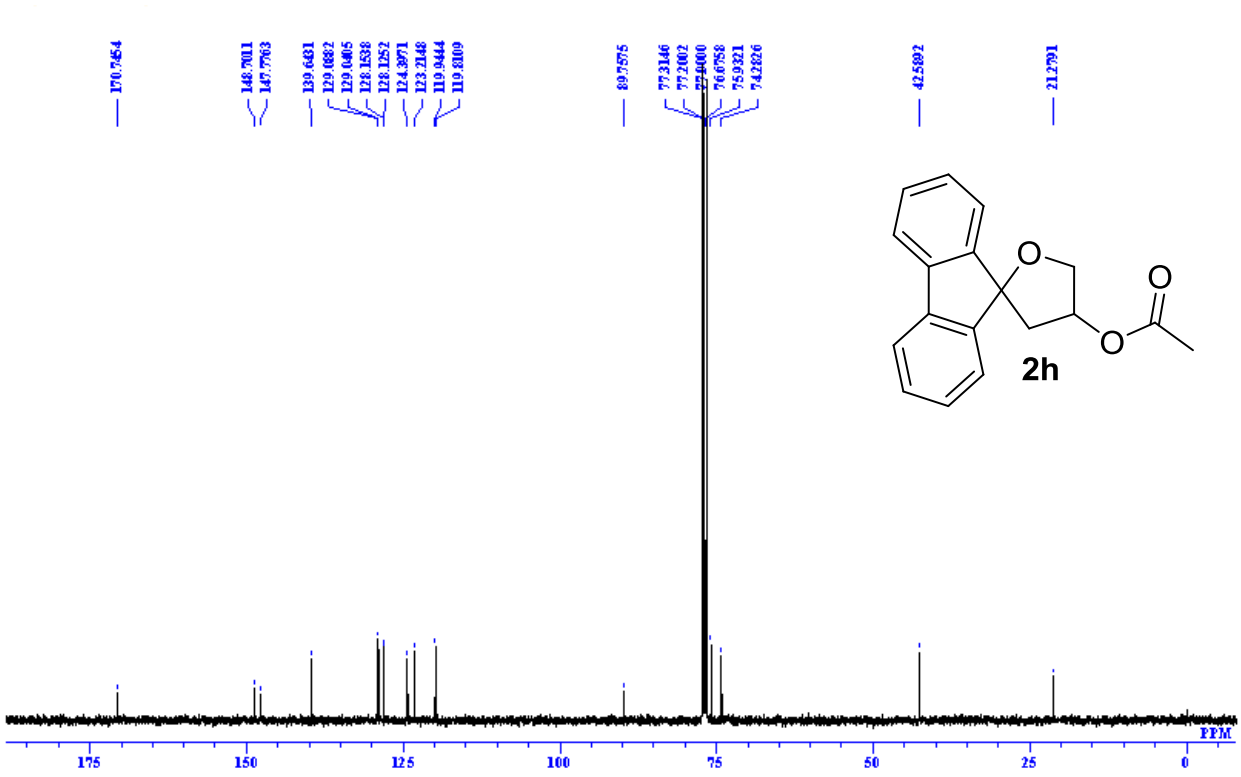


Figure S21-2. ^{13}C NMR spectrum of compound **2h** (100 MHz, $CDCl_3$).

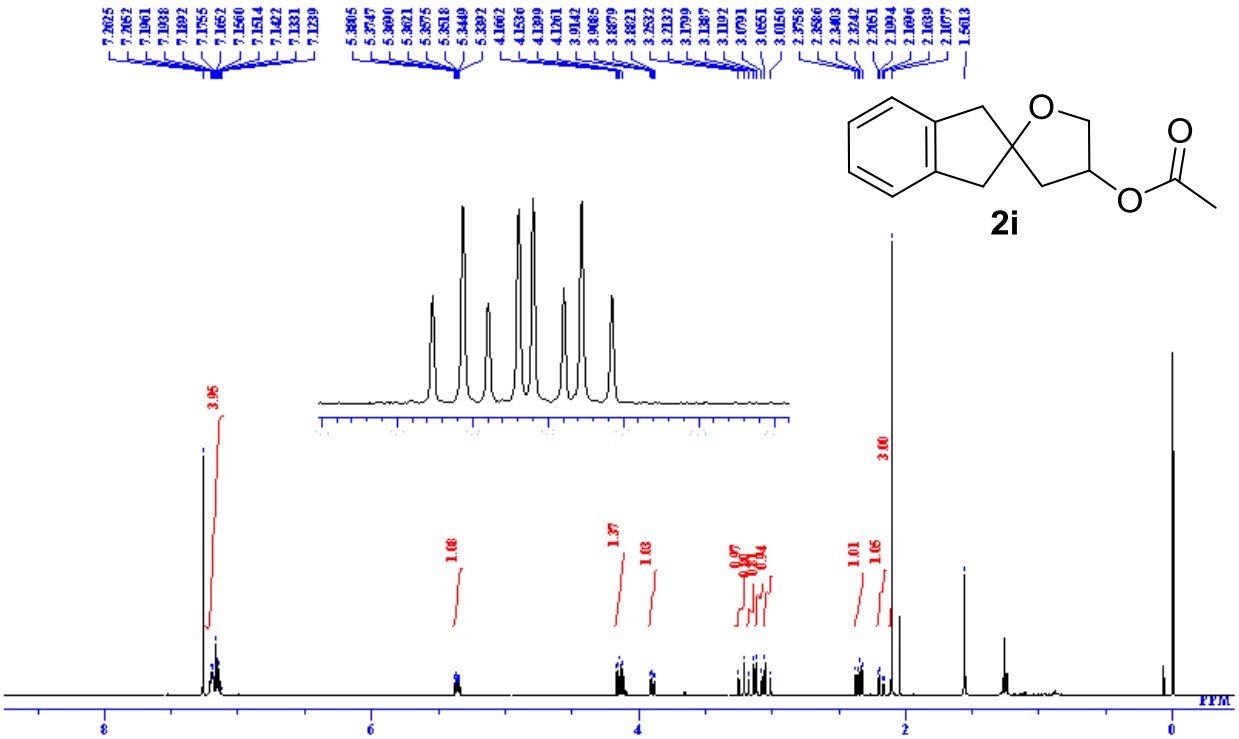


Figure S22-1. ^{1}H NMR spectrum of compound **2i** (400 MHz, $CDCl_3$).

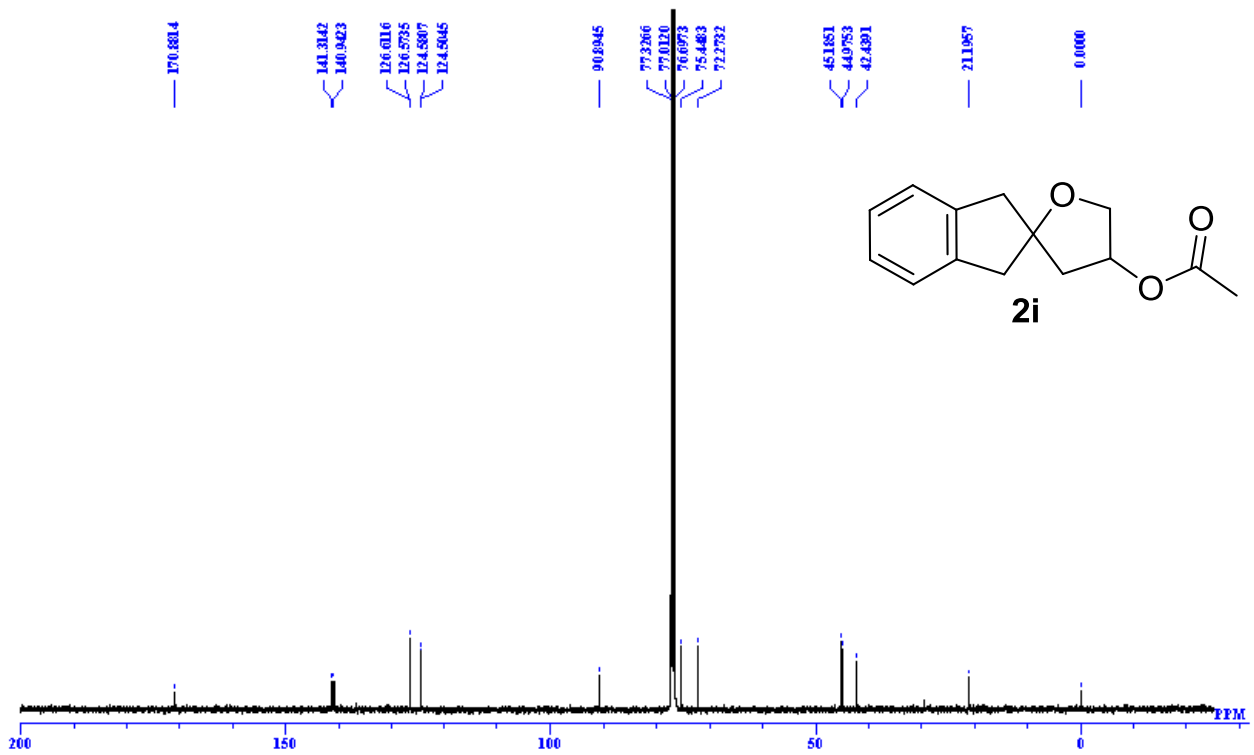


Figure S22-2. ^{13}C NMR spectrum of compound **2i** (100 MHz, $CDCl_3$).

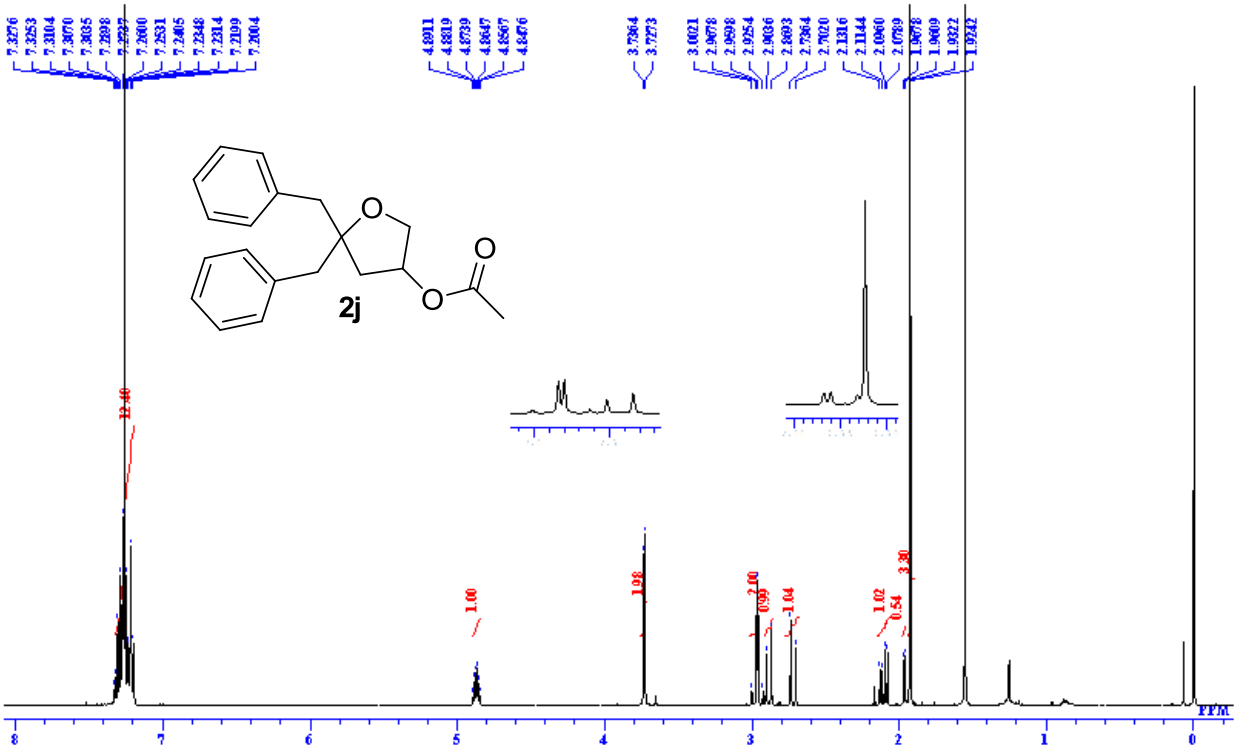


Figure S23-1. ^{1}H NMR spectrum of compound **2j** (400 MHz, $CDCl_3$).

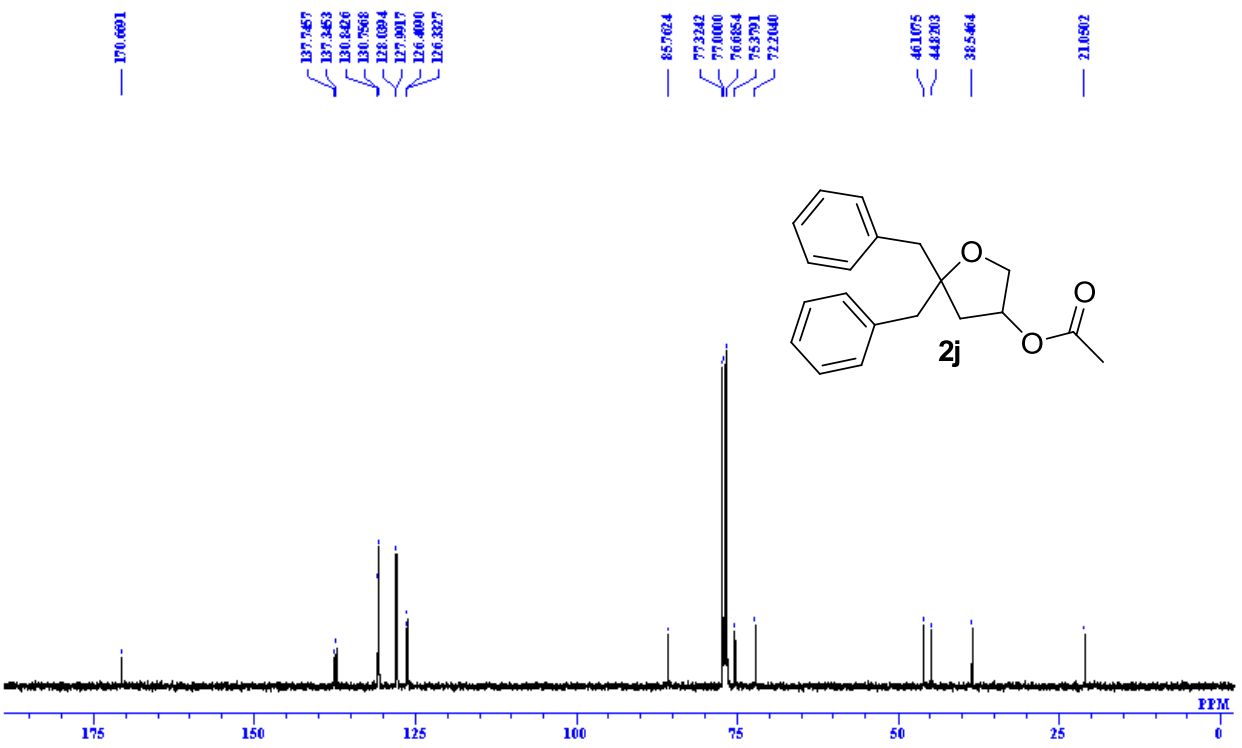


Figure S23-2. ^{13}C NMR spectrum of compound **2j** (100 MHz, $CDCl_3$).

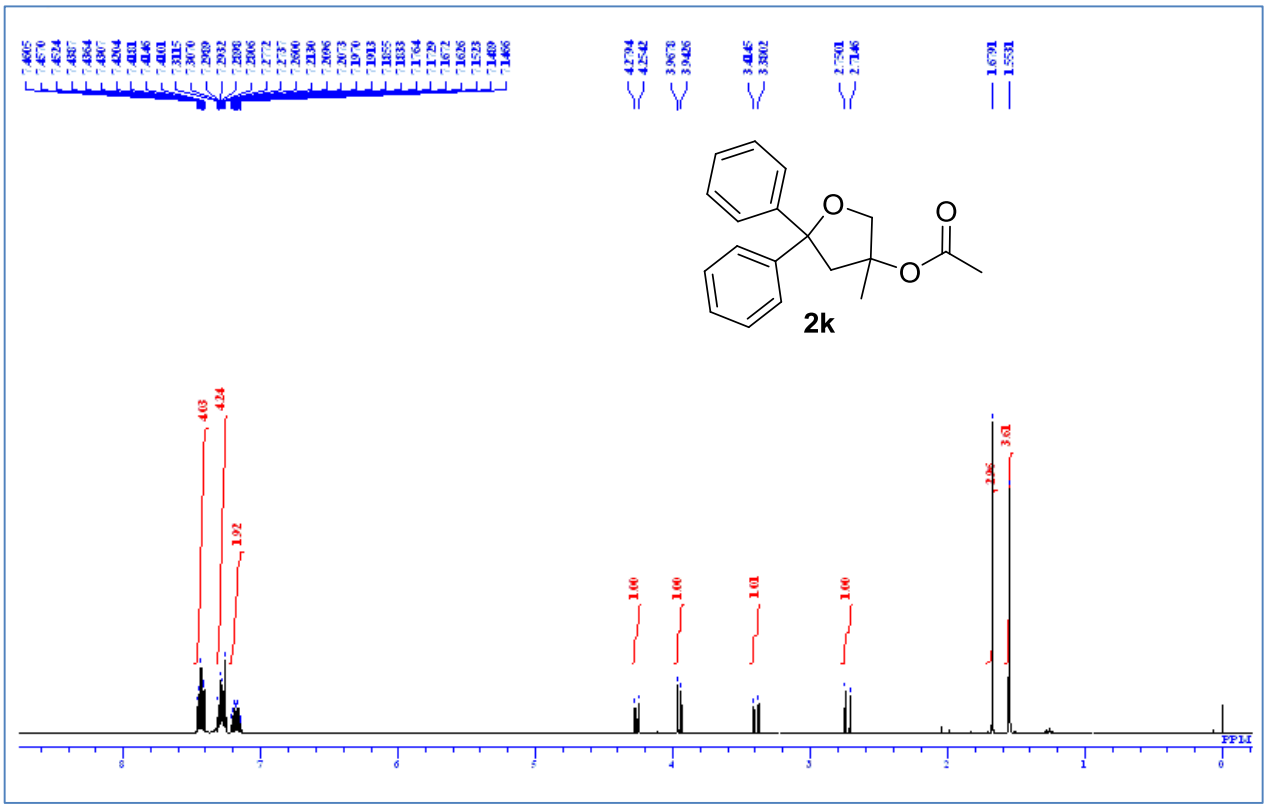


Figure S24-1. ^{1}H NMR spectrum of compound **2k** (400 MHz, $CDCl_3$).

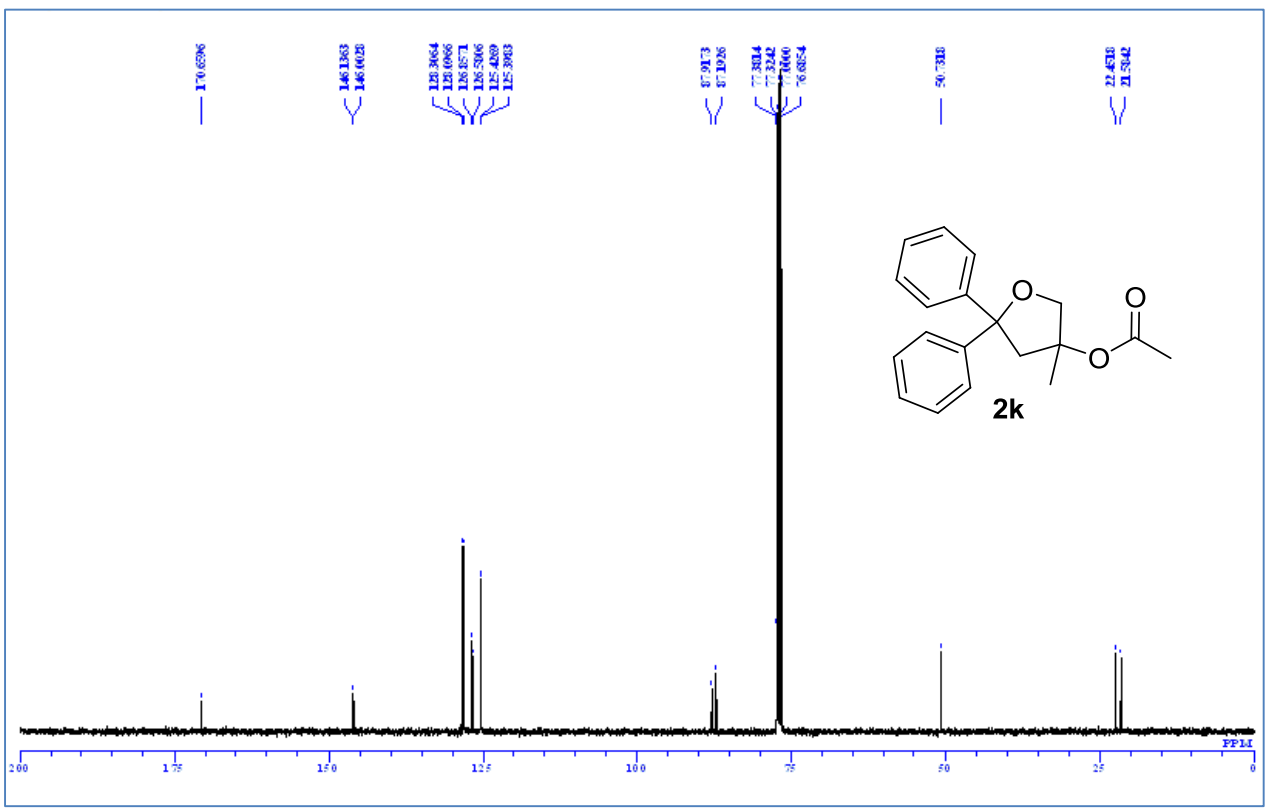


Figure S24-2. ^{13}C NMR spectrum of compound **2k** (100 MHz, $CDCl_3$).

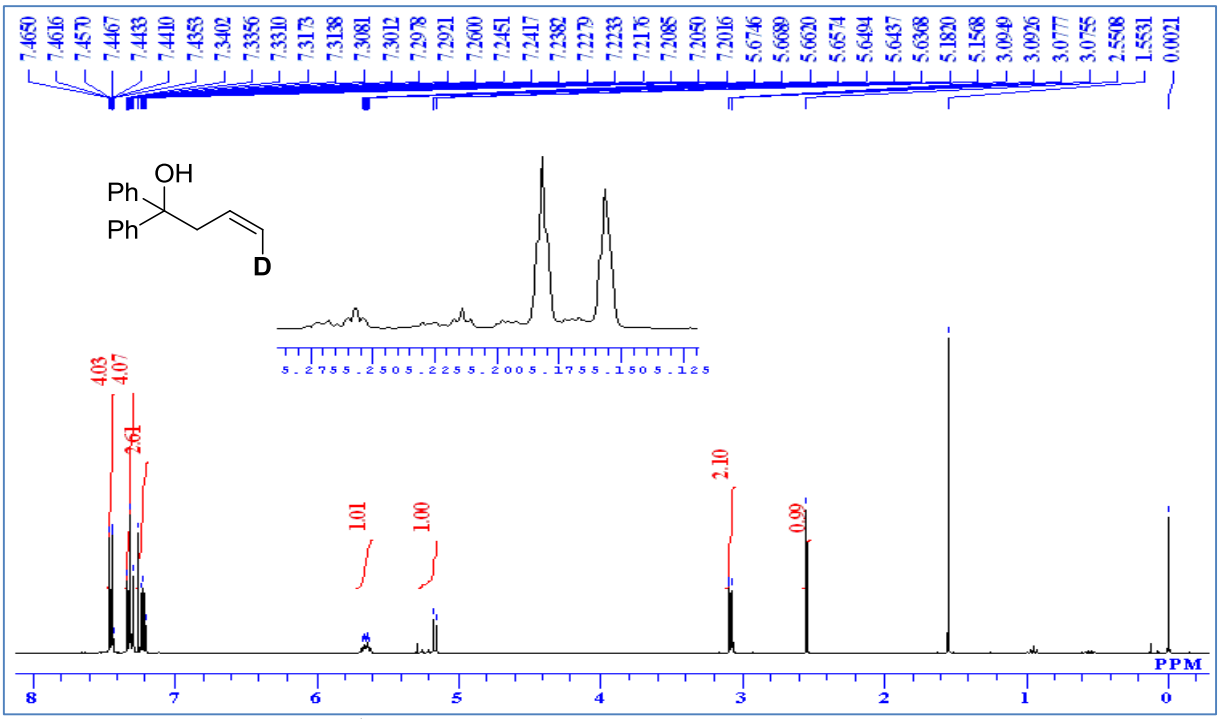


Figure S25. ^{1}H NMR spectrum of compound **1a-*d*** (400 MHz, $CDCl_3$).

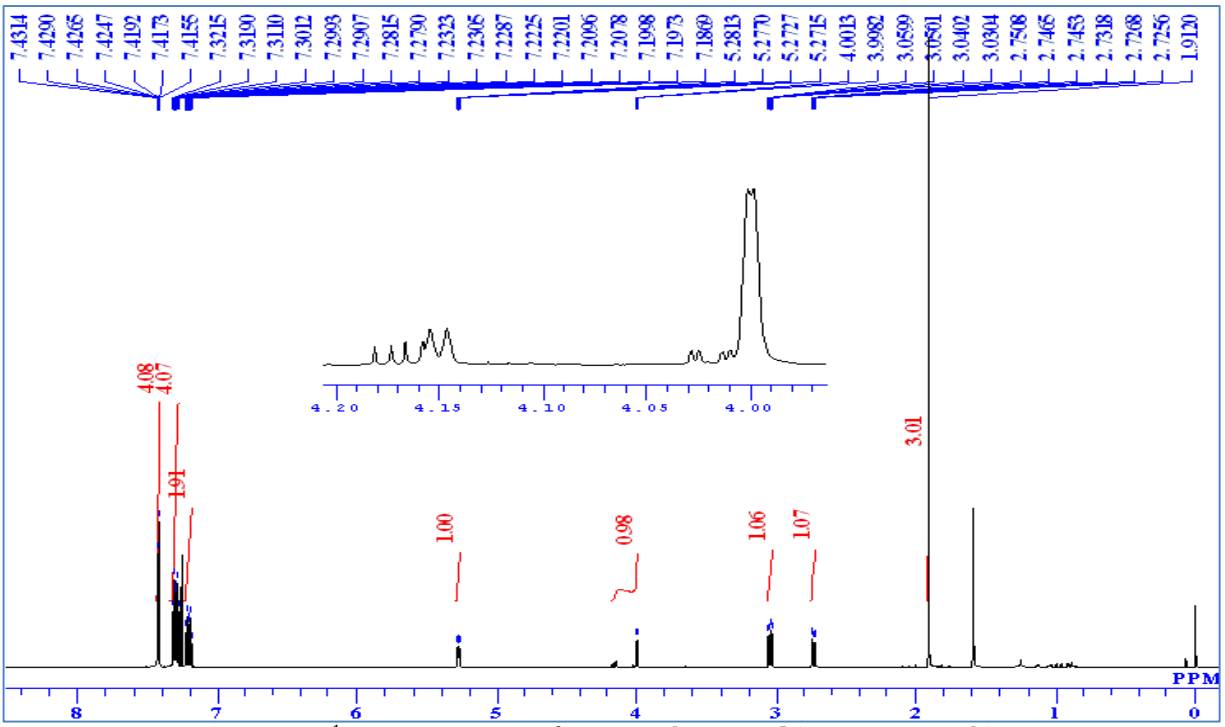
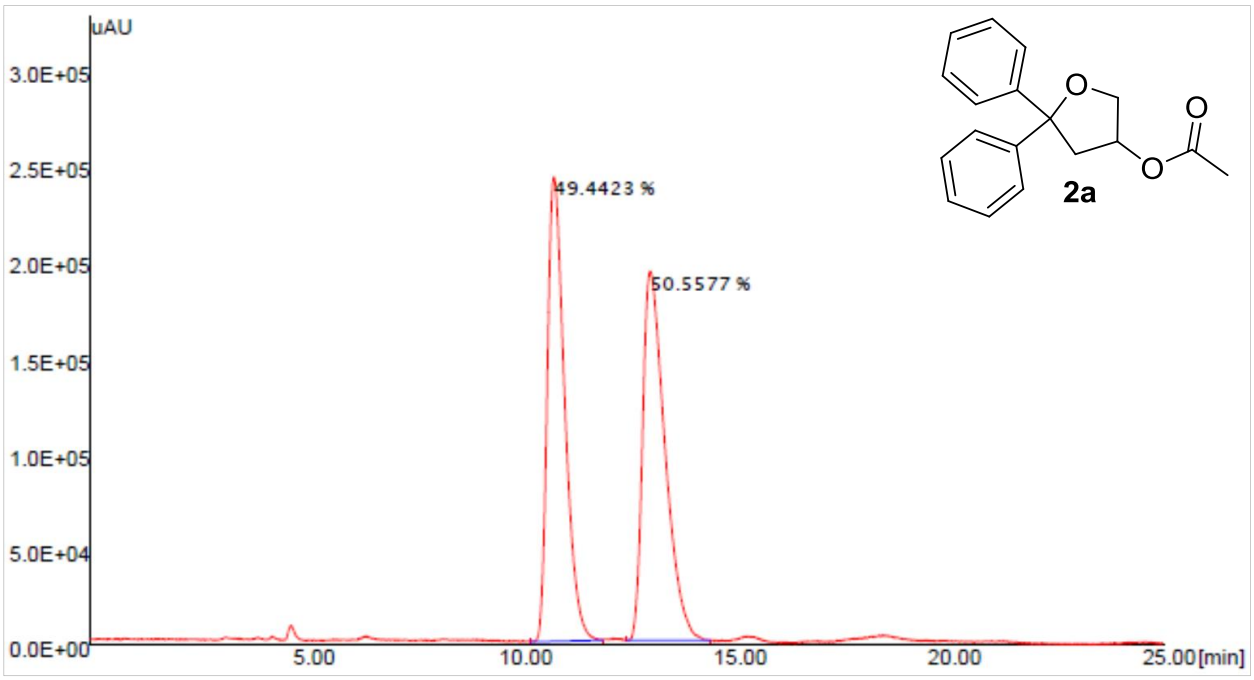


Figure S26. ^{1}H NMR spectrum of compound *anti*-**2a-*d*** (700 MHz, $CDCl_3$).



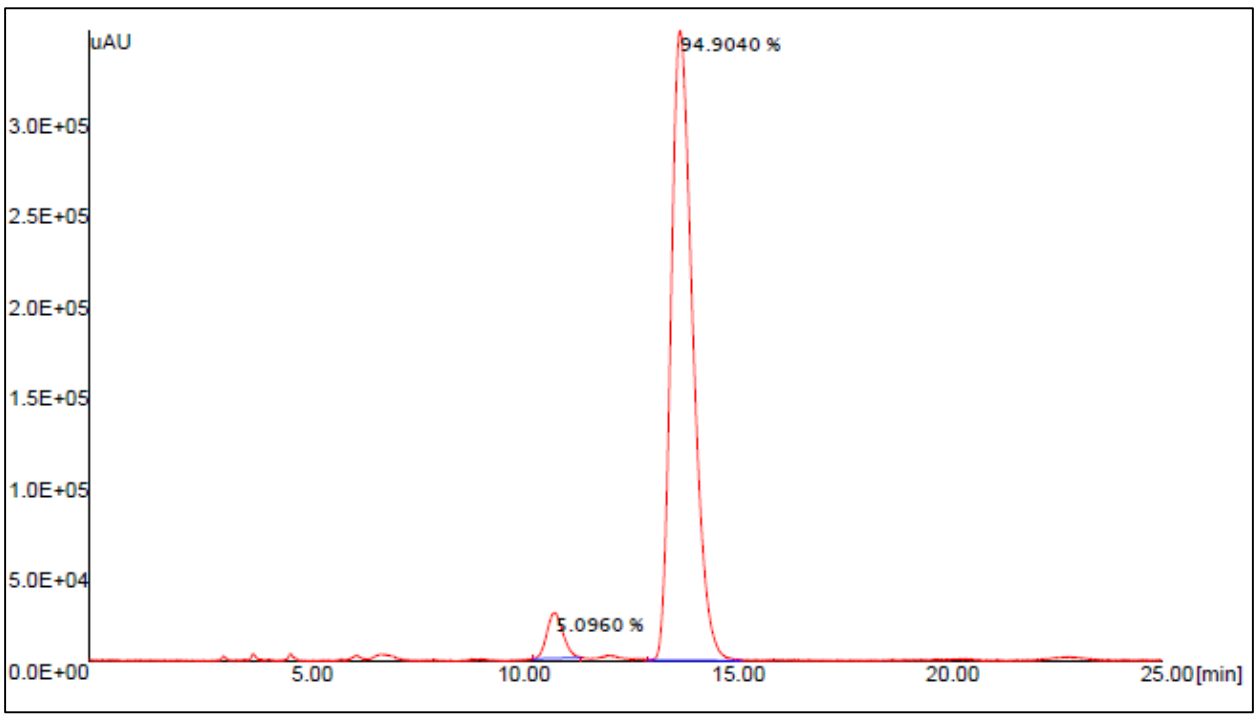


Figure S27. HPLC chart of compound **2a**.

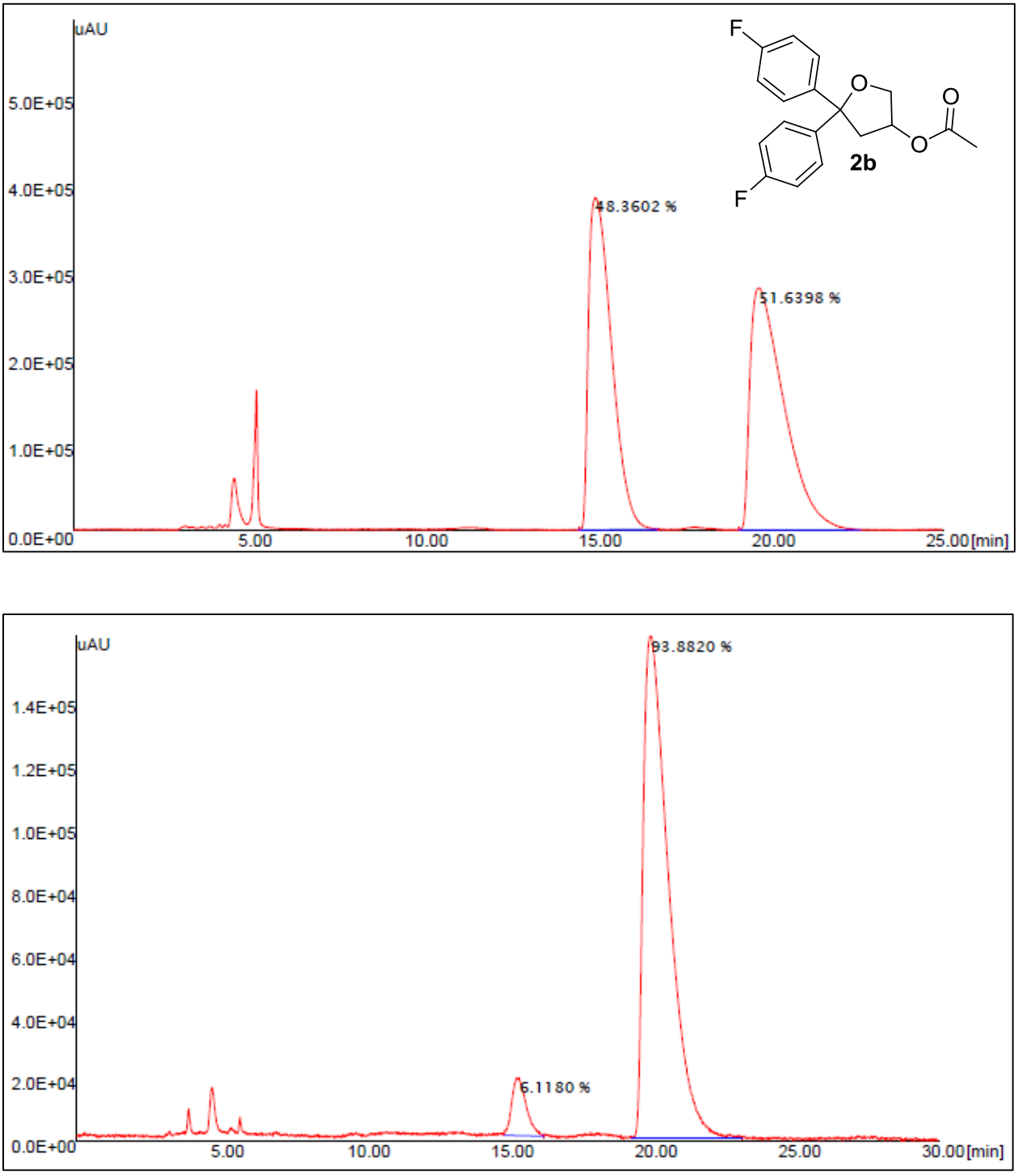


Figure S28. HPLC chart of compound **2b**.

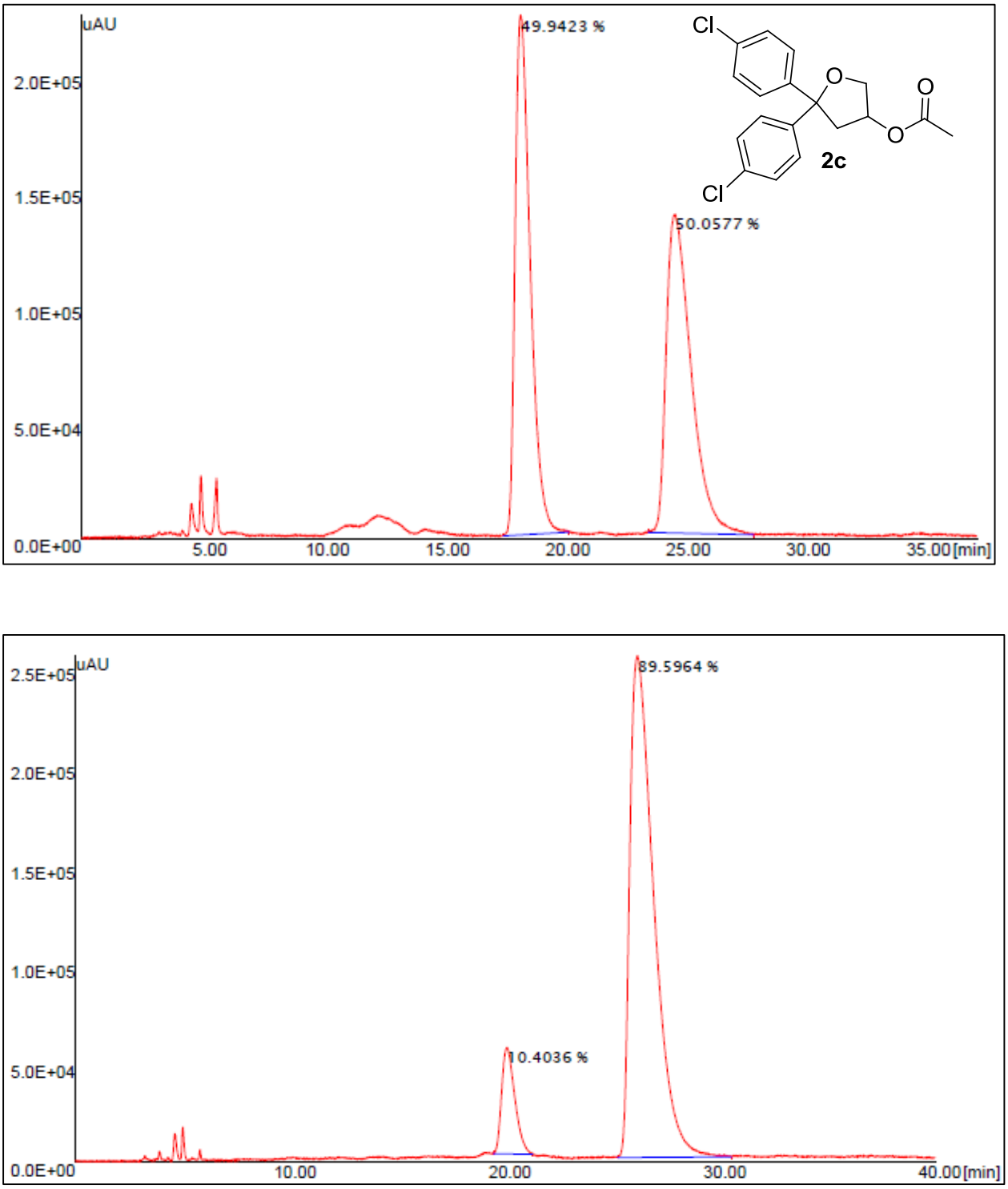
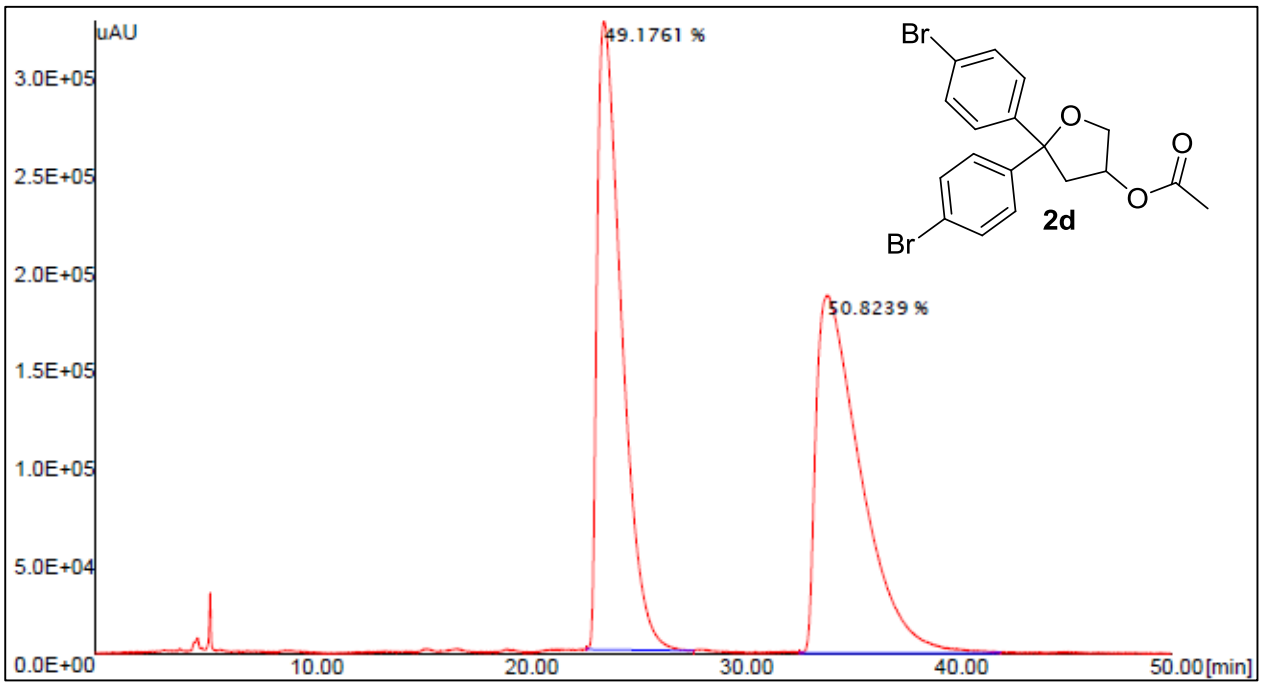


Figure S29. HPLC chart of compound **2c**.



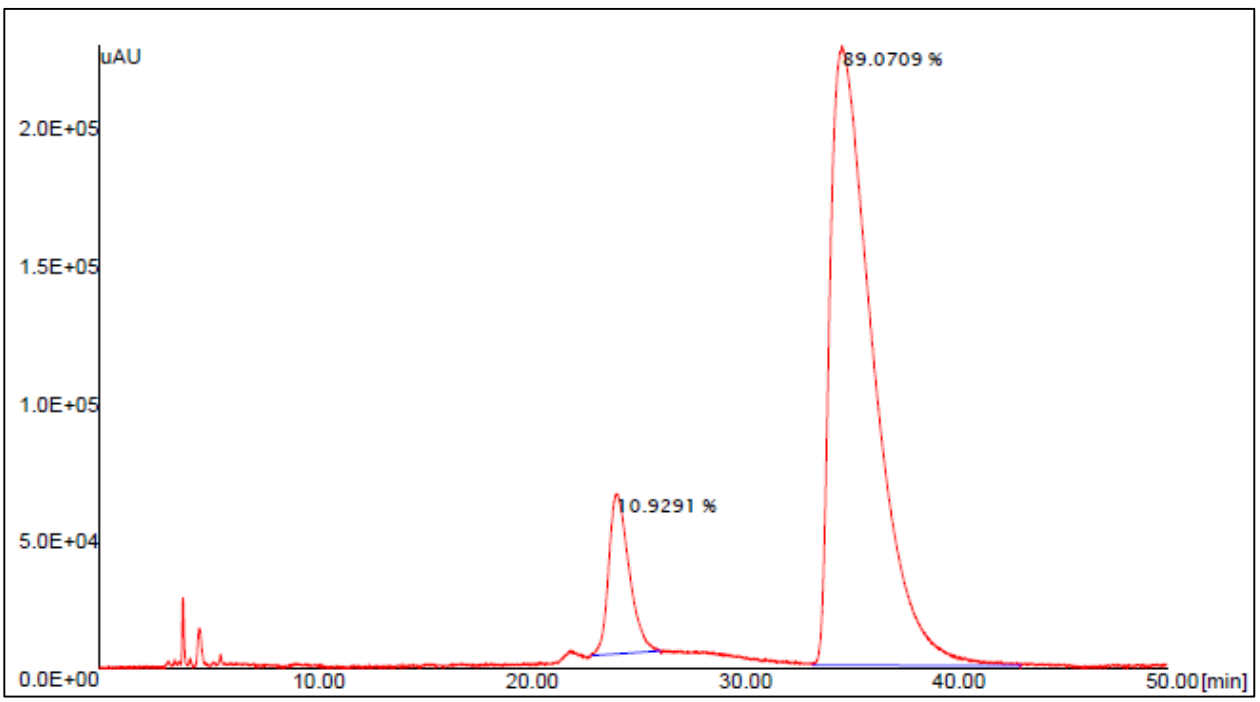


Figure S30. HPLC chart of compound **2d**.

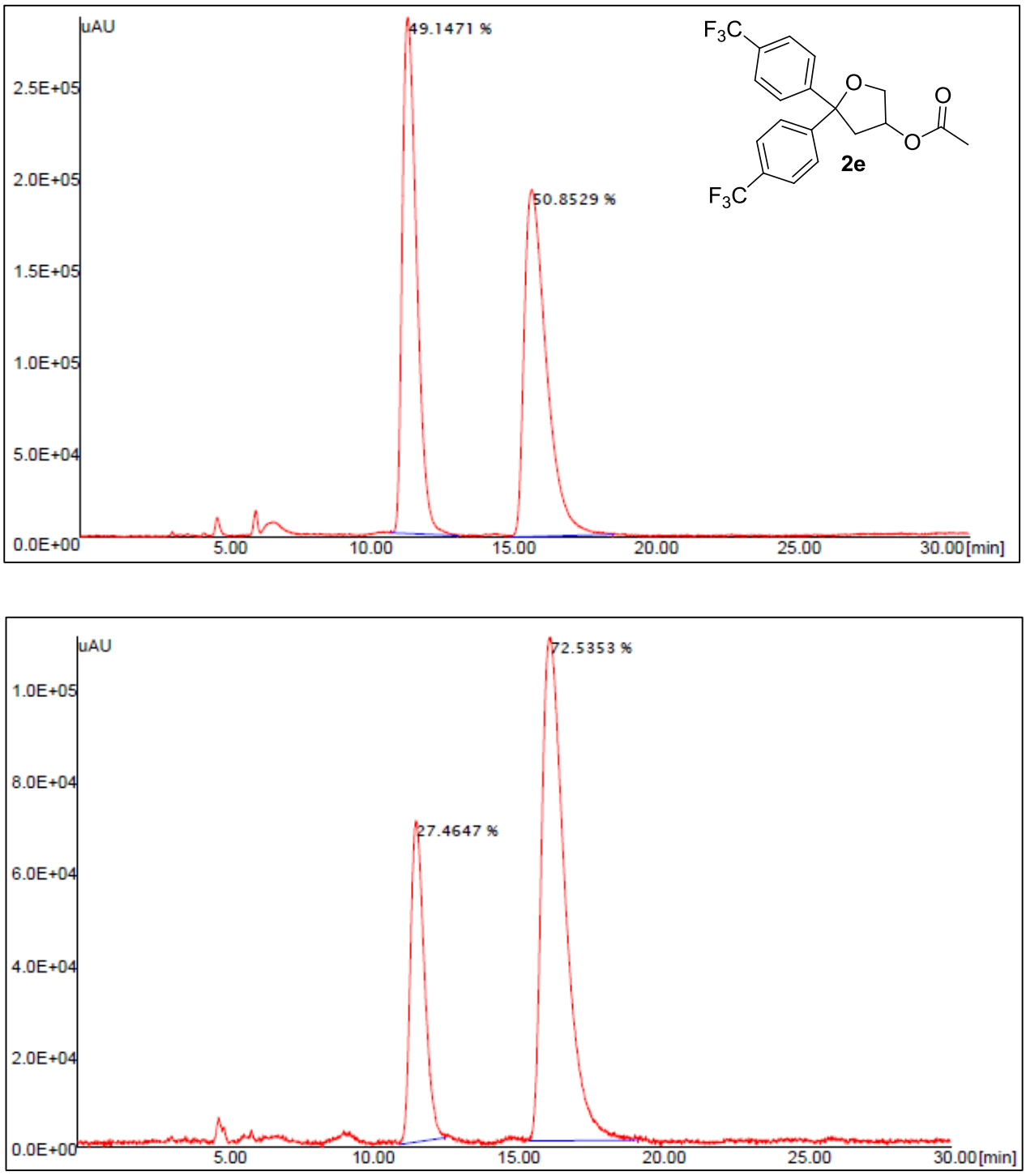


Figure S31. HPLC chart of compound **2e**.

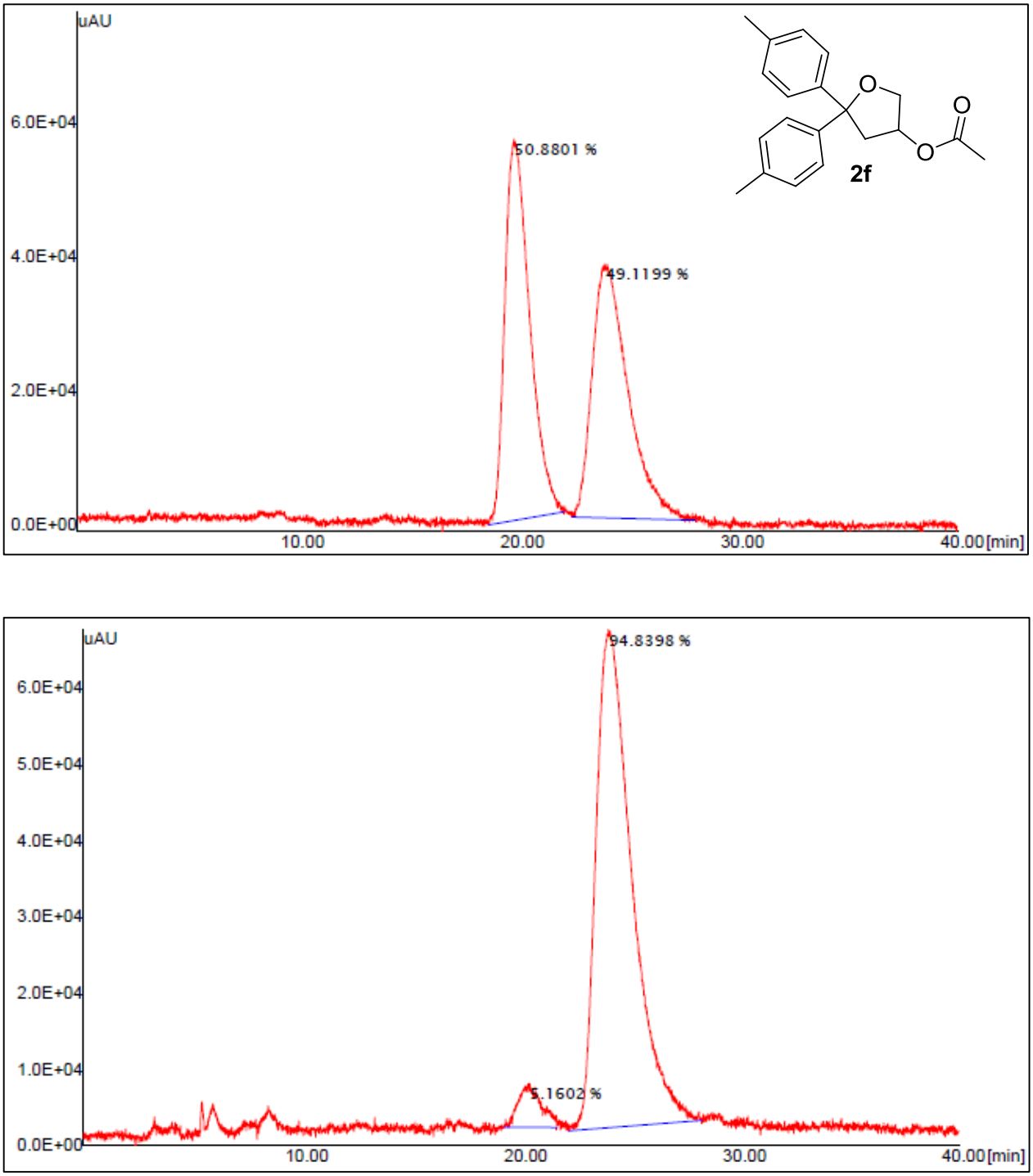
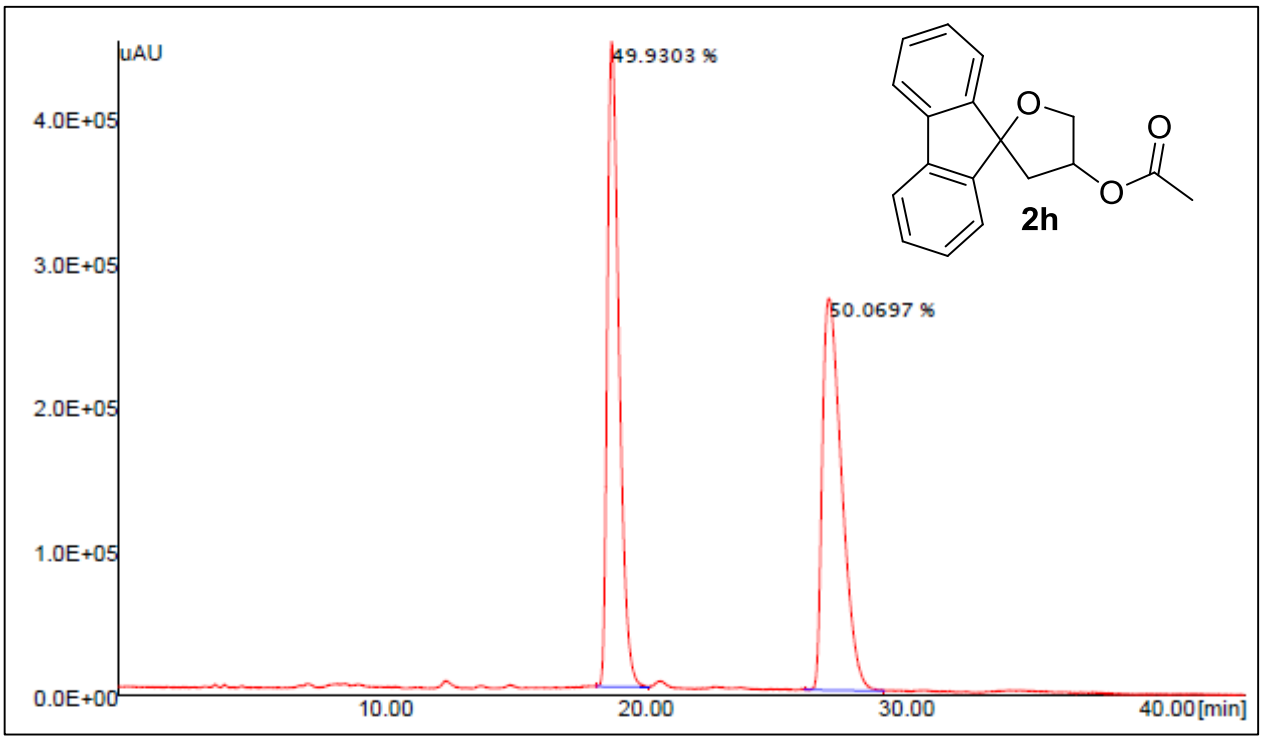


Figure S32. HPLC chart of compound **2f**.



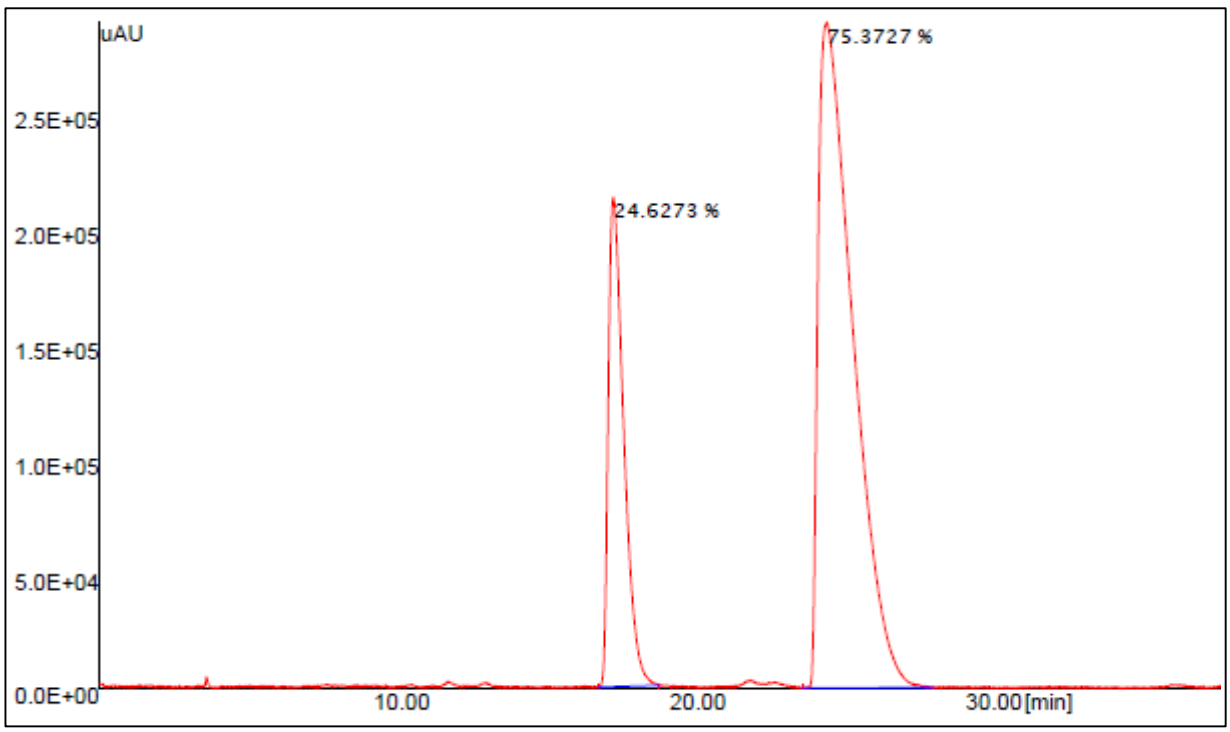
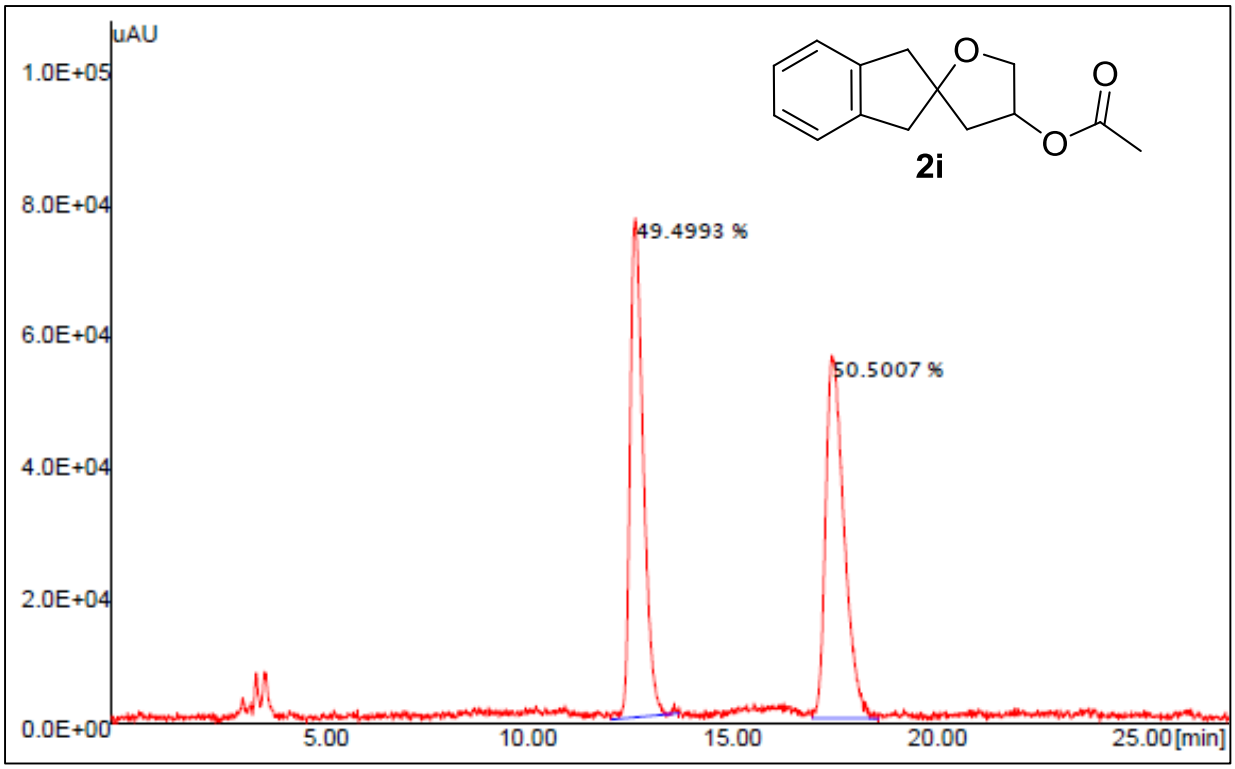


Figure S33. HPLC chart of compound **2h**.



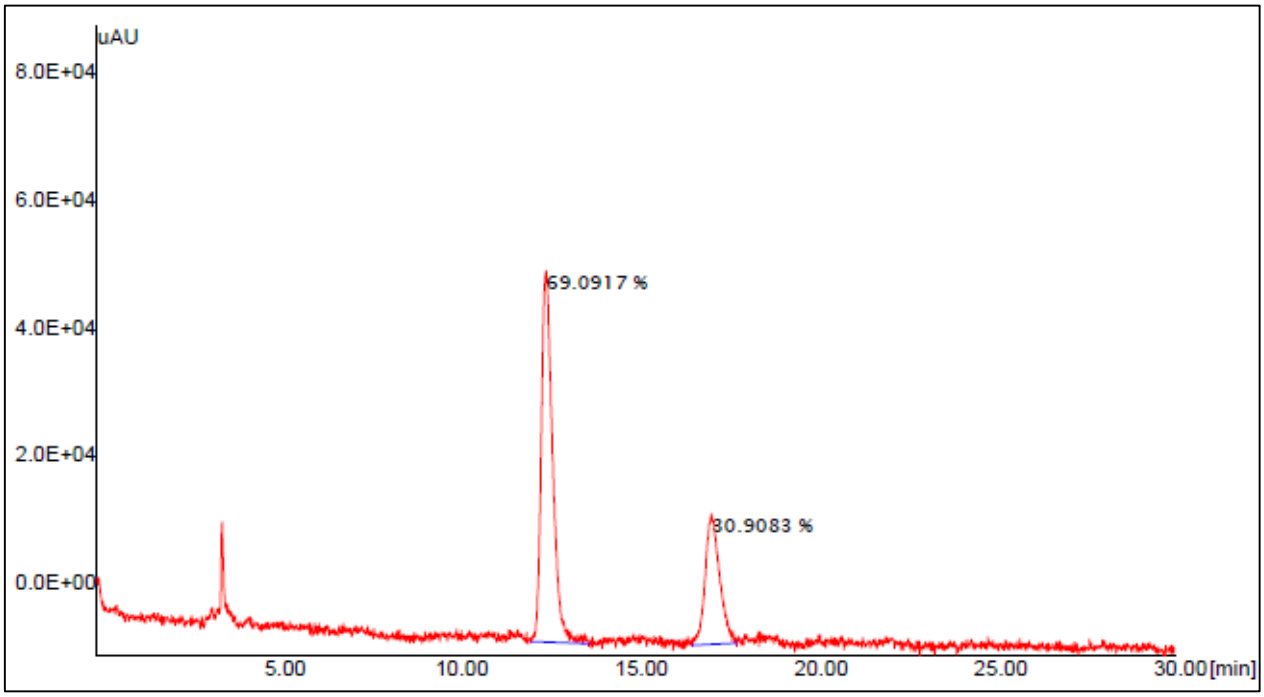


Figure S34. HPLC chart of compound **2i**.

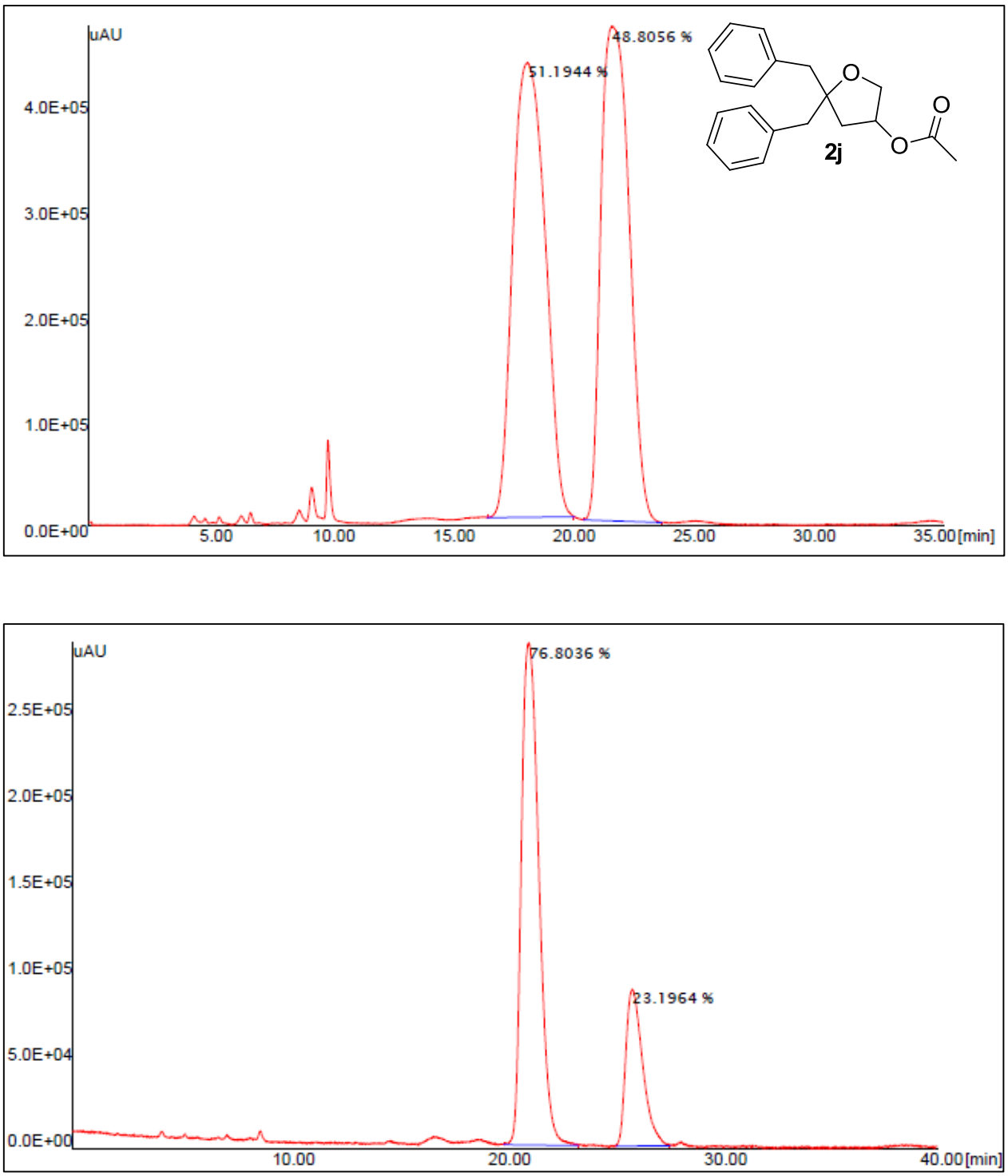


Figure S35. HPLC chart of compound **2j**.

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