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Trifunctionalization of Aryl Iodides by a Palladium/Norbornene-Catalyzed Intermolecular C–H Acylation/Intramolecular C–H Alkylation Approach

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Supporting Information

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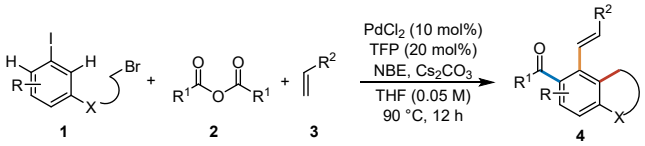
A. General information

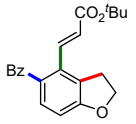
Unless noted otherwise, all reactions were carried out under an argon atmosphere using standard Schlenk-Lines or a glovebox (Innovative Technology). CH_3CN were dried over CaH_2. THF and 1,4-dioxane were dried over sodium. Chemicals were purchased from Sigma-Aldrich, TCI, Energy Chemical or Innochem and were used as received. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}). Flash chromatography was performed with silica gel (300-400 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; q, quartet; m, multiplet; br, broad. Coupling constants are quoted in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 101 MHz on Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d* and the center line of a septet at 44.0 ppm for DMSO-d_6. Fluorine nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 spectrometer, and the ^{19}F chemical shifts were not referenced. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Daltonics MicroTof-Q II mass spectrometer using electron spray ionization (ESI) or a GCT Premier GC-TOF mass spectrometer using electrospray ionization (EI). Single crystal structures were measured on a Bruker SMART APEX II CCD diffractometer with a graphite monochromated Mo Kα (λ = 0.71073 Å, at 296(2) K) or a Bruker D8 VENTURE PHOTON II diffractometer with a graphite monochromated Ga Kα (λ = 1.34138 Å, at 175(2) K) radiation. The structure was solved by direct methods and refined anisotropically based on F^2 by a full-matrix least-squares refinement with the SHELXL-2014 program. Anisotropic thermal parameters were applied to non-hydrogen atoms, and all hydrogen atoms of organic ligands were calculated and added at the theoretical positions.

B. General procedure of Pd/NBE catalyzed trifunctionalization reaction

Aryl iodides **1a-1o** were prepared by the literature methods.[1-2]



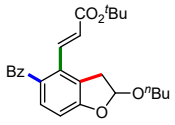
General procedure: Unless otherwise noted, in a glovebox, an oven-dried 10 mL vial was charged with $PdCl_2$ (3.5 mg, 0.02 mmol, 0.1 equiv.) and P(2-furyl)$_3$ (9.3 mg, 0.04 mmol, 0.2 equiv.). THF (4 mL) was added and the mixture was stirred for 10 min. Cs_2CO_3 (260.7 mg, 0.80 mmol, 4.0 equiv.), aryl iodide **1** (0.20 mmol, 1.0 equiv.), anhydrides **2** (0.30 mmol, 1.5 equiv.), olefin **3** (0.24 mmol, 1.2 equiv.) and NBE (18.8 mg, 0.2 mmol, 1.0 equiv.) were added to the vial. The vial was sealed with a Teflon screw cap, transferred out of glovebox and then stirred on a pie-block preheated to 90 °C for 12 h. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel to yield the desired product **4**.



Chemical Formula: $C_{22}H_{22}O_4$
Molecular Weight: 350.4140

***tert*-Butyl (E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)acrylate (4a)**

White solid, m.p. = 112.1–112.5 °C. 63.9 mg, 91% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 16.2 Hz, 1H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.42 (t, *J* = 6.9 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 5.7 Hz, 1H), 6.03 (d, *J* = 16.2 Hz, 1H), 4.66 (t, *J* = 7.4 Hz, 2H), 3.36 (t, *J* = 8.4 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.8, 165.5, 162.6, 140.6, 138.6, 132.7, 132.6, 131.9, 131.7, 130.1, 128.3, 127.1, 124.9, 109.0, 80.6, 71.9, 30.2, 28.1. **IR** (KBr): 3055.0, 2971.8, 2928.9, 1775.5, 1703.7, 1651.0, 1580.9, 1479.3, 1458.4, 1446.9, 1392.8, 1367.6, 1316.5, 1298.2, 1264.4, 1208.3, 1149.4, 1073.4, 1035.4, 1008.6, 979.4, 944.6, 850.2, 824.8, 799.9, 732.4, 701.1, 651.5, 615.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{23}O_4$ $[M+H]^+$ 351.1596, found 351.1601.

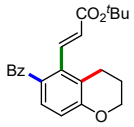


Chemical Formula: $C_{26}H_{30}O_5$
Molecular Weight: 422.5210

***tert*-Butyl (E)-3-(5-benzoyl-2-butoxy-2,3-dihydrobenzofuran-4-yl)acrylate (4b)**

Light yellow oil. 70.3 mg, 83% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 16.2 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 5.84 (dd, *J* = 6.5, 1.8 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.63 – 3.58 (m, 1H), 3.47 (dd, *J* = 17.0, 6.6 Hz, 1H), 3.22 (d, *J* = 17.0 Hz, 1H), 1.65 – 1.54

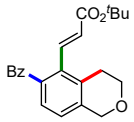
(m, 2H), 1.47 – 1.34 (m, 11H), 0.92 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.0, 165.6, 160.6, 140.6, 138.6, 132.9, 132.6, 132.5, 131.6, 130.3, 128.4, 125.7, 125.1, 109.6, 107.0, 80.7, 69.0, 37.4, 31.7, 28.2, 19.3, 13.9. **IR** (KBr): 3055.4, 2961.3, 2873.6, 1704.9, 1652.3, 1584.8, 1447.8, 1392.7, 1368.0, 1316.7, 1264.5, 1151.3, 1101.0, 1041.6, 1017.7, 970.3, 919.4, 860.0, 828.2, 799.4, 732.4, 702.2, 628.2 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{26}H_{30}NaO_5$ $[M+Na]^+$ 445.1991, found 445.1983.



Chemical Formula: $C_{23}H_{24}O_4$
Molecular Weight: 364.4410

***tert*-Butyl (E)-3-(6-benzoylchroman-5-yl)acrylate (4c)**

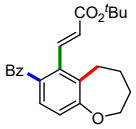
White solid, m.p. = 94.6–95.1 °C. 64.3 mg, 88% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.4 Hz, 2H), 7.56 – 7.46 (m, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 8.5 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 5.74 (d, J = 16.1 Hz, 1H), 4.26 – 4.19 (m, 2H), 2.76 (t, J = 6.5 Hz, 2H), 2.09 – 1.98 (m, 2H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9, 165.1, 157.0, 140.6, 138.8, 136.3, 132.6, 131.6, 129.7, 129.1, 128.4, 127.3, 121.3, 116.8, 80.6, 66.3, 28.1, 23.5, 22.0. **IR** (KBr): 3058.2, 2977.0, 2931.7, 2876.0, 1706.7, 1655.8, 1596.4, 1580.5, 1476.6, 1465.7, 1447.2, 1421.6, 1392.1, 1367.4, 1304.5, 1247.9, 1217.9, 1191.6, 1148.5, 1092.2, 1070.0, 1026.7, 983.2, 955.2, 916.9, 882.4, 850.4, 806.1, 733.6, 702.0, 665.4, 627.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{24}O_4Na$ $[M+Na]^+$ 387.1572, found 387.1571.



Chemical Formula: $C_{23}H_{24}O_4$
Molecular Weight: 364.4410

***tert*-Butyl (E)-3-(6-benzoylisochroman-5-yl)acrylate (4d)**

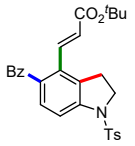
White solid, m.p. = 96.2–97.0 °C. 50.4 mg, 69% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.3 Hz, 2H), 7.52 (dd, J = 15.6, 8.7 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.9 Hz, 1H), 5.78 (d, J = 16.1 Hz, 1H), 4.84 (s, 2H), 4.00 (t, J = 5.7 Hz, 2H), 2.84 (t, J = 5.5 Hz, 2H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.3, 165.0, 139.7, 138.0, 137.7, 134.0, 133.2, 132.9, 129.9, 128.6, 127.8, 126.6, 124.7, 80.8, 68.2, 65.2, 28.2, 27.0. **IR** (KBr): 3057.8, 2976.3, 2931.3, 2851.7, 1706.7, 1663.3, 1595.6, 1448.0, 1418.4, 1392.0, 1367.4, 1334.1, 1285.2, 1264.9, 1224.6, 1148.7, 1110.6, 1074.1, 1043.3, 1026.4, 996.9, 978.4, 950.4, 922.3, 867.6, 848.8, 824.7, 808.5, 733.2, 702.4 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{24}O_4Na$ $[M+Na]^+$ 387.1572, found 387.1564.



Chemical Formula: $C_{24}H_{26}O_4$
Molecular Weight: 378.4680

***tert*-Butyl (E)-3-(7-benzoyl-2,3,4,5-tetrahydrobenzo[b]oxepin-6-yl)acrylate (4e)**

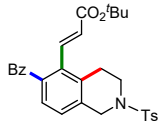
Yellow oil. 23.8 mg, 31% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.3 Hz, 2H), 7.57 (d, *J* = 16.1 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.67 (d, *J* = 16.1 Hz, 1H), 4.10 – 4.03 (m, 2H), 2.89 – 2.81 (m, 2H), 2.01 – 1.93 (m, 2H), 1.76 – 1.68 (m, 2H), 1.38 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 164.9, 162.7, 141.6, 138.4, 135.8, 135.0, 134.7, 132.9, 129.7, 128.5, 127.5, 121.1, 80.6, 73.8, 31.7, 29.1, 28.1, 25.2. **IR** (KBr): 3056.4, 2980.3, 2934.3, 1706.6, 1660.1, 1597.6, 1578.0, 1471.7, 1447.6, 1392.8, 1368.0, 1314.6, 1300.3, 1264.8, 1241.8, 1150.3, 1099.1, 1080.4, 1032.6, 979.1, 920.2, 896.0, 874.7, 849.5, 732.2, 702.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{24}H_{26}O_4Na$ $[M+Na]^+$ 401.1729, found 401.1721.



Chemical Formula: $C_{29}H_{29}NO_5S$
Molecular Weight: 503.6130

***tert*-Butyl (E)-3-(5-benzoyl-1-tosylindolin-4-yl)acrylate (4f)**

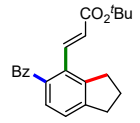
Light yellow solid, m.p. = 106.6–107.2 °C. 75.3 mg, 75% yield. R_f = 0.3 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.85 (d, *J* = 16.3 Hz, 1H), 4.00 (t, *J* = 8.4 Hz, 2H), 3.08 (t, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1, 165.3, 144.8, 144.7, 139.6, 138.0, 134.6, 133.9, 133.3, 132.3, 131.5, 130.6, 130.2, 130.1, 128.6, 127.4, 126.1, 113.8, 80.9, 50.2, 28.2, 21.7. **IR** (KBr): 3056.7, 2924.6, 1705.4, 1655.6, 1595.9, 1576.0, 1447.8, 1392.9, 1359.2, 1316.6, 1264.6, 1208.9, 1151.4, 1091.9, 1040.2, 1009.5, 977.3, 910.2, 844.6, 813.8, 733.3, 703.0, 675.6, 652.4, 592.0, 545.4 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{29}H_{29}NO_5SNa$ $[M+Na]^+$ 526.1664, found 526.1667.



Chemical Formula: $C_{30}H_{31}NO_5S$
Molecular Weight: 517.6400

***tert*-Butyl (E)-3-(6-benzoyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-5-yl)acrylate (4g)**

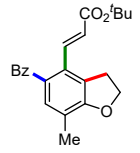
Light yellow solid, m.p. = 149.6–150.1 °C. 80.1 mg, 77% yield. R_f = 0.2 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.27 (m, 6H), 7.12 (d, *J* = 7.9 Hz, 1H), 5.71 (d, *J* = 16.1 Hz, 1H), 4.31 (s, 2H), 3.37 (t, *J* = 5.8 Hz, 2H), 2.89 (t, *J* = 5.7 Hz, 2H), 2.43 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 164.8, 144.1, 139.5, 138.3, 137.8, 134.6, 134.1, 133.3, 132.6, 129.9, 129.7, 128.6, 128.1, 127.9, 126.9, 126.6, 80.9, 48.0, 43.6, 28.1, 27.3, 21.6. **IR** (KBr): 3055.2, 2984.8, 1707.7, 1665.5, 1597.0, 1448.7, 1421.1, 1369.0, 1336.8, 1264.3, 1164.4, 1098.9, 1003.6, 967.2, 896.1, 815.5, 731.0, 702.4, 661.0, 601.0, 549.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{30}H_{31}NO_5SNa$ $[M+Na]^+$ 540.1821, found 540.1819.



Chemical Formula: $C_{23}H_{24}O_3$
Molecular Weight: 348.4420

***tert*-Butyl (E)-3-(5-benzoyl-2,3-dihydro-1H-inden-4-yl)acrylate (4h)**

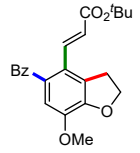
Light yellow solid, m.p. = 90.5–91.3 °C. 43.5 mg, 62% yield. R_f = 0.2 (hexane/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 16.2 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.21 (m, 2H), 5.99 (d, *J* = 16.2 Hz, 1H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.4, 165.8, 147.9, 144.3, 140.6, 138.1, 137.8, 133.1, 130.6, 130.2, 128.5, 127.8, 125.4, 124.4, 80.5, 33.4, 33.1, 28.2, 25.4. **IR** (KBr): 3058.1, 2974.6, 1704.4, 1660.0, 1636.2, 1596.1, 1448.1, 1420.6, 1392.0, 1367.0, 1317.0, 1265.0, 1206.7, 1148.6, 1072.1, 1004.3, 978.6, 962.6, 939.3, 888.4, 852.6, 824.0, 801.0, 733.9, 702.4, 629.5 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{24}O_3Na$ $[M+Na]^+$ 371.1623, found 371.1624.



Chemical Formula: $C_{23}H_{24}O_4$
Molecular Weight: 364.4410

***tert*-Butyl (E)-3-(5-benzoyl-7-methyl-2,3-dihydrobenzofuran-4-yl)acrylate (4i)**

White solid, m.p. = 143.5–143.9 °C. 65.1 mg, 89% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.50 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.12 (s, 1H), 5.98 (d, *J* = 16.2 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 2H), 3.38 (t, *J* = 8.7 Hz, 2H), 2.21 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.3, 165.9, 161.0, 140.8, 138.8, 132.8, 132.5, 132.3, 130.2, 130.0, 128.4, 126.3, 124.2, 120.1, 80.6, 71.7, 30.8, 28.2, 15.3. **IR** (KBr): 3056.9, 2978.0, 2927.3, 1703.2, 1649.8, 1597.0, 1573.8, 1447.5, 1412.9, 1392.2, 1367.2, 1315.8, 1294.2, 1264.6, 1201.1, 1149.0, 1103.9, 1074.6, 1038.6, 1012.6, 978.1, 945.2, 896.1, 853.6, 825.6, 805.3, 732.9, 701.8, 620.8 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{24}O_4Na$ $[M+Na]^+$ 387.1572, found 387.1562.

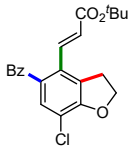


Chemical Formula: $C_{23}H_{24}O_5$
Molecular Weight: 380.4400

***tert*-Butyl (E)-3-(5-benzoyl-7-methoxy-2,3-dihydrobenzofuran-4-yl)acrylate (4j)**

White solid, m.p. = 112.7–113.1 °C. 70.2 mg, 92% yield. R_f = 0.3 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.59 – 7.47 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.88 (s, 1H), 5.93 (d, *J* = 16.2 Hz, 1H), 4.74 (t, *J* = 8.8 Hz, 2H), 3.82 (d, *J* = 15.0 Hz, 3H), 3.41 (t, *J* = 8.8 Hz, 2H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1, 165.9, 150.7, 144.6, 140.0, 138.4, 133.8, 133.1, 130.2,

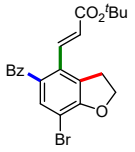
128.5, 128.0, 124.7, 123.3, 113.6, 80.5, 72.6, 56.3, 31.2, 28.2. **IR** (KBr): 3057.8, 2976.0, 2933.5, 1703.5, 1654.9, 1602.0, 1577.2, 1485.1, 1447.2, 1421.2, 1392.0, 1366.8, 1322.9, 1263.6, 1206.5, 1150.0, 1126.0, 1074.8, 1044.4, 1014.7, 976.8, 939.4, 853.9, 825.9, 809.6, 731.6, 697.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{24}O_5Na$ $[M+Na]^+$ 403.1521, found 403.1516.



Chemical Formula: $C_{22}H_{21}ClO_4$
Molecular Weight: 384.8560

***tert*-Butyl (E)-3-(5-benzoyl-7-chloro-2,3-dihydrobenzofuran-4-yl)acrylate (4k)**

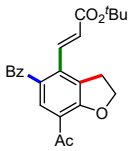
White solid, m.p. = 162.8–163.2 °C. 70.3 mg, 91% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.56 (dd, *J* = 12.0, 4.0 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.31 (s, 1H), 6.00 (d, *J* = 16.3 Hz, 1H), 4.79 (t, *J* = 8.6 Hz, 2H), 3.46 (t, *J* = 8.6 Hz, 2H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.8, 165.4, 158.3, 139.6, 138.0, 133.3, 131.2, 130.9, 130.2, 128.6, 125.5, 115.3, 80.9, 72.7, 31.2, 28.2. **IR** (KBr): 3060.0, 2980.9, 2932.5, 1708.1, 1649.5, 1631.1, 1596.0, 1573.5, 1493.7, 1476.3, 1453.8, 1444.2, 1420.7, 1391.0, 1366.4, 1316.1, 1265.2, 1235.8, 1206.5, 1175.6, 1148.9, 1063.9, 1042.5, 1013.5, 980.4, 942.2, 932.5, 903.3, 886.5, 858.1, 803.0, 760.2, 726.8, 700.5, 672.5, 659.7, 620.7, 594.1, 564.3, 532.8, 502.9 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{21}O_4ClNa$ $[M+Na]^+$ 407.1026, found 407.1028.



Chemical Formula: $C_{22}H_{21}BrO_4$
Molecular Weight: 429.3100

***tert*-Butyl (E)-3-(5-benzoyl-7-bromo-2,3-dihydrobenzofuran-4-yl)acrylate (4l)**

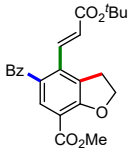
White solid, m.p. = 143.6–144.2 °C. 77.5 mg, 90% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 13.4 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 3H), 6.01 (d, *J* = 16.3 Hz, 1H), 4.79 (t, *J* = 8.7 Hz, 2H), 3.48 (t, *J* = 8.7 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.7, 165.5, 159.7, 139.6, 138.0, 133.9, 133.6, 133.3, 131.5, 130.3, 128.7, 128.2, 125.6, 102.8, 81.0, 72.4, 31.4, 28.2. **IR** (KBr): 3056.8, 2979.3, 2928.9, 1706.7, 1650.4, 1596.4, 1575.2, 1478.0, 1446.3, 1418.1, 1391.7, 1367.0, 1316.0, 1264.4, 1206.8, 1149.3, 1057.2, 1013.2, 979.0, 941.9, 894.4, 880.6, 855.2, 801.7, 732.0, 701.9, 671.6, 654.6, 616.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{21}O_4BrNa$ $[M+Na]^+$ 451.0521, found 451.0522.



Chemical Formula: $C_{24}H_{24}O_5$
Molecular Weight: 392.4510

***tert*-Butyl (E)-3-(7-acetyl-5-benzoyl-2,3-dihydrobenzofuran-4-yl)acrylate (4m)**

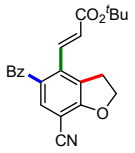
White solid, m.p. = 139.8–140.2 °C. 37.8 mg, 48% yield. R_f = 0.2 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 16.3 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 6.07 (d, *J* = 16.3 Hz, 1H), 4.82 (t, *J* = 8.7 Hz, 2H), 3.40 (t, *J* = 8.7 Hz, 2H), 2.61 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.3, 195.7, 165.3, 162.2, 139.7, 138.0, 136.4, 133.3, 132.0, 131.5, 130.3, 129.7, 128.6, 126.7, 119.5, 81.1, 73.0, 31.1, 29.8, 28.2. **IR** (KBr): 3059.6, 2977.0, 2925.2, 1706.9, 1676.1, 1654.9, 1596.5, 1569.0, 1476.7, 1442.5, 1422.7, 1392.6, 1366.8, 1306.7, 1284.1, 1227.9, 1207.7, 1177.2, 1146.7, 1061.8, 1015.4, 996.1, 973.1, 943.5, 906.7, 851.4, 814.9, 761.1, 723.5, 692.4, 654.7, 631.9 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{24}H_{24}O_5Na$ $[M+Na]^+$ xx, found xx.



Chemical Formula: $C_{24}H_{24}O_6$
Molecular Weight: 408.4500

Methyl (E)-5-benzoyl-4-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-2,3-dihydrobenzofuran-7-carboxylate (4n)

White solid, m.p. = 194.3–194.6 °C. 70.4 mg, 86% yield. R_f = 0.3 (hexane/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.76 (d, *J* = 7.3 Hz, 2H), 7.60 (dd, *J* = 21.7, 11.9 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.06 (d, *J* = 16.3 Hz, 1H), 4.84 (t, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 3.39 (t, *J* = 8.7 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.1, 165.3, 164.8, 162.6, 139.6, 138.1, 136.3, 133.3, 133.0, 131.8, 130.3, 129.8, 128.7, 126.8, 112.2, 81.1, 73.2, 52.4, 29.8, 28.2. **IR** (KBr): 3059.8, 2978.6, 1707.8, 1655.1, 1598.5, 1573.4, 1478.0, 1444.4, 1422.2, 1392.7, 1367.4, 1290.0, 1240.9, 1150.8, 1078.6, 1013.6, 979.8, 945.2, 853.3, 829.5, 809.9, 786.0, 734.1, 702.1, 619.2 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{24}H_{24}O_6Na$ $[M+Na]^+$ 431.1471, found 431.1464.

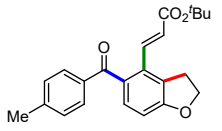


Chemical Formula: $C_{23}H_{21}NO_4$
Molecular Weight: 375.4240

***tert*-Butyl (E)-3-(5-benzoyl-7-cyano-2,3-dihydrobenzofuran-4-yl)acrylate (4o)**

White solid, m.p. = 87.6–88.4 °C. 35.4 mg, 47% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.60 (dd, *J* = 15.1, 8.5 Hz, 2H), 7.53 – 7.42 (m, 3H), 6.08 (d, *J* = 16.3 Hz, 1H), 4.87 (t, *J* = 8.6 Hz, 2H), 3.45 (t, *J* = 8.6 Hz, 2H), 1.44 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.1, 165.0, 164.3, 138.9, 137.5, 136.9, 133.7, 133.7, 132.6, 130.2, 128.9, 128.8, 127.5, 114.8, 93.6, 81.4, 73.7, 30.2, 28.2. **IR** (KBr): 3061.2, 2983.1, 2920.7, 2851.3, 2231.5, 1708.1, 1649.9, 1631.2, 1595.6, 1563.6, 1497.8, 1445.6, 1429.4, 1392.5, 1367.7, 1312.8, 1283.5, 1263.7, 1235.5, 1212.5, 1202.2, 1179.0, 1149.5, 1105.0, 1076.5, 1042.1, 1014.4, 981.7, 933.7, 905.4, 866.1, 851.0, 824.2, 804.3, 759.9, 730.0,

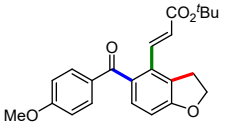
701.0, 677.6, 627.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{21}NO_4Na$ $[M+Na]^+$ 398.1368, found 398.1361.



Chemical Formula: $C_{23}H_{24}O_4$
Molecular Weight: 364.4410

***Tert*-butyl (E)-3-(5-(4-methylbenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4p)**

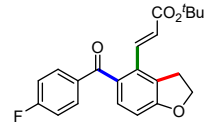
White solid, m.p. = 114.1–114.6 °C. 64.9 mg, 89% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 – 7.60 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 4.66 (t, *J* = 8.6 Hz, 2H), 3.36 (t, *J* = 8.6 Hz, 2H), 2.40 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.7, 165.7, 162.5, 143.7, 140.7, 136.0, 132.4, 131.5, 130.4, 129.1, 127.1, 125.0, 109.2, 80.7, 71.9, 30.4, 28.2, 21.7. **IR** (KBr): 2977.1, 2925.0, 1703.8, 1644.8, 1604.7, 1581.0, 1478.7, 1455.9, 1407.9, 1392.1, 1366.8, 1312.4, 1265.1, 1242.8, 1207.1, 1148.9, 1034.8, 1009.5, 980.0, 944.0, 838.8, 821.2, 791.3, 763.0, 734.0, 703.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{25}O_4$ $[M+H]^+$ 365.1753, found 365.1755.



Chemical Formula: $C_{23}H_{24}O_5$
Molecular Weight: 380.4400

***Tert*-butyl (E)-3-(5-(4-methoxybenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4q)**

White solid, m.p. = 113.8–114.5 °C. 70.2 mg, 92% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 16.3 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.03 (d, *J* = 16.3 Hz, 1H), 4.67 (t, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 3.37 (t, *J* = 8.6 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.8, 165.8, 163.6, 162.3, 140.6, 132.8, 132.7, 132.1, 131.4, 131.0, 127.0, 124.9, 113.7, 109.3, 80.7, 71.9, 55.6, 30.5, 28.2. **IR** (KBr): 2975.9, 2926.9, 2850.9, 1706.9, 1643.7, 1598.9, 1508.9, 1458.5, 1420.1, 1392.2, 1367.4, 1316.8, 1278.6, 1257.4, 1207.2, 1162.4, 1030.3, 984.9, 945.4, 847.7, 821.6, 775.4, 735.6, 698.5 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{25}O_5$ $[M+H]^+$ 381.1702, found 381.1705.

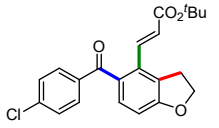


Chemical Formula: $C_{22}H_{21}FO_4$
Molecular Weight: 368.4044

***Tert*-butyl (E)-3-(5-(4-fluorobenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4r)**

White solid, m.p. = 108.5–109.1 °C. 67.2 mg, 91% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.63 (d, *J* = 16.2 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 4.69 (t, *J* = 8.7 Hz, 2H), 3.38 (t,

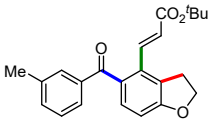
J = 8.6 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 195.5, 167.0, 165.7, 164.5, 162.8, 140.5, 135.0 (d, J = 2.9 Hz), 132.9 (d, J = 9.3 Hz), 132.6, 131.9, 131.6, 127.3, 125.3, 115.6 (d, J = 21.9 Hz), 109.3, 80.9, 72.0, 30.4, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.5. **IR** (KBr): 3078.6, 2976.7, 2931.0, 1704.7, 1647.1, 1596.4, 1578.0, 1502.0, 1479.2, 1457.0, 1403.1, 1390.6, 1365.9, 1316.8, 1295.7, 1271.2, 1243.7, 1219.7, 1193.7, 1179.3, 1148.0, 1093.4, 1041.0, 1009.4, 981.1, 937.9, 865.2, 848.2, 816.8, 772.9, 713.8 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{22}FO_4$ $[M+H]^+$ 369.1502, found 369.1505.



Chemical Formula: $C_{22}H_{21}ClO_4$
Molecular Weight: 384.8560

***Tert*-butyl (E)-3-(5-(4-chlorobenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4s)**

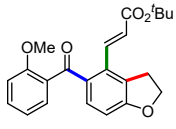
White solid, m.p. = 135.6–136.1 °C. 67.9 mg, 88% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.7 Hz, 2H), 7.63(d, J = 12.3 Hz, 1H) 7.41 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.01 (d, J = 16.3 Hz, 1H), 4.69 (t, J = 8.7 Hz, 2H), 3.38 (t, J = 8.6 Hz, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 195.7, 165.6, 162.9, 140.5, 139.4, 137.1, 132.8, 131.8, 131.6, 131.6, 128.8, 127.4, 125.4, 109.3, 80.9, 72.1, 30.3, 28.2. **IR** (KBr): 3057.9, 2977.1, 2928.0, 1703.7, 1650.8, 1582.2, 1480.7, 1456.5, 1395.1, 1367.0, 1316.1, 1299.6, 1264.4, 1243.4, 1207.1, 1191.9, 1148.9, 1089.0, 1035.8, 1008.7, 981.9, 944.4, 895.9, 847.6, 822.8, 767.3, 735.4, 703.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{22}ClO_4$ $[M+H]^+$ 385.1207, found 385.1211.



Chemical Formula: $C_{23}H_{24}O_4$
Molecular Weight: 364.4410

***Tert*-butyl (E)-3-(5-(3-methylbenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4t)**

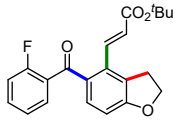
White solid, m.p. = 125.1–125.8 °C. 65.5 mg, 90% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, J = 16.3 Hz, 1H), 7.55 (s, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.34(d, J = 8.1 Hz 1H), 7.31 – 7.27 (m, 2H) 6.77 (d, J = 8.2 Hz, 1H), 6.02 (d, J = 16.3 Hz, 1H), 4.66 (t, J = 8.6 Hz, 2H), 3.36 (t, J = 8.6 Hz, 2H), 2.36 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1, 165.6, 162.6, 140.7, 138.6, 138.2, 133.6, 132.6, 132.2, 131.7, 130.5, 128.2, 127.5, 127.1, 124.9, 109.1, 80.6, 71.9, 30.3, 28.1, 21.3. **IR** (KBr): 2979.6, 1703.8, 1638.3, 1581.6, 1479.4, 1456.8, 1392.5, 1367.5, 1317.1, 1264.9, 1242.8, 1208.1, 1190.7, 1149.9, 1036.3, 977.6, 946.2, 893.3, 850.5, 832.8, 809.7, 731.7, 702.2, 651.9 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{24}O_4Na$ $[M+Na]^+$ 387.1572, found 387.1578.



Chemical Formula: $C_{23}H_{24}O_5$
Molecular Weight: 380.4400

***Tert*-butyl (E)-3-(5-(2-methoxybenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4u)**

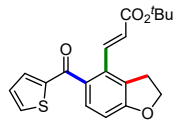
White solid, m.p. = 105.7–106.3 °C. 64.8 mg, 85% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.47 – 7.39 (m, 1H), 7.35 (dd, *J* = 9.3, 7.8 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.00 (d, *J* = 16.3 Hz, 1H), 4.66 (t, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 3.34 (t, *J* = 8.8 Hz, 2H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.1, 165.9, 163.3, 157.8, 142.1, 133.8, 133.5, 132.5, 132.4, 130.4, 130.2, 127.0, 124.6, 120.6, 111.7, 108.9, 80.8, 72.2, 55.8, 30.1, 28.3. **IR** (KBr): 3056.0, 2977.3, 2926.5, 1703.6, 1638.1, 1596.9, 1579.8, 1486.1, 1455.6, 1435.1, 1392.0, 1367.1, 1288.1, 1263.3, 1245.5, 1207.3, 1149.9, 1113.4, 1024.3, 1009.2, 975.9, 942.5, 896.0, 852.3, 827.1, 732.2, 702.1, 650.5, 618.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{25}O_5$ $[M+H]^+$ 381.1702, found 381.1708.



Chemical Formula: $C_{22}H_{21}FO_4$
Molecular Weight: 368.4044

***Tert*-butyl (E)-3-(5-(2-fluorobenzoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4v)**

White solid, m.p. = 120.1–120.8 °C. 64.0 mg, 87% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 16.2 Hz, 1H), 7.57-7.52 (m, 1H), 7.50 – 7.43 (m, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.02 (m, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.00 (d, *J* = 16.3 Hz, 1H), 4.65 (t, *J* = 8.7 Hz, 2H), 3.33 (t, *J* = 8.7 Hz, 2H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.0, 165.6, 163.6, 161.6, 159.1, 141.3, 133.6, 133.5, 133.2 (d, *J* = 1.3 Hz), 131.7, 131.1 (d, *J* = 2.2 Hz), 128.4, 128.2, 127.4, 125.1, 124.3 (d, *J* = 3.6 Hz), 116.44, 116.2, 109.1, 80.7, 72.2, 30.0, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ-111.0. **IR** (KBr): 3056.5, 2979.9, 1704.0, 1651.8, 1609.4, 1580.4, 1480.9, 1451.8, 1392.5, 1367.7, 1287.2, 1264.3, 1222.3, 1191.6, 1150.6, 1102.2, 1036.9, 1009.9, 975.9, 943.3, 896.1, 849.4, 829.4, 732.2, 702.3, 650.3, 615.2 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{22}FO_4$ $[M+H]^+$ 369.1502, found 369.1507.

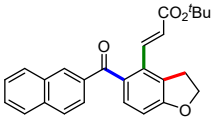


Chemical Formula: $C_{20}H_{20}O_4S$
Molecular Weight: 356.4360

***Tert*-butyl(E)-3-(5-(thiophene-2-carbonyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4w)**

White solid, m.p. = 137.3–137.9 °C. 59.4 mg, 83% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 – 7.67 (m, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.14 – 7.07 (m, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.08 (d, *J* = 16.3 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 2H), 3.39 (t, *J* = 8.6 Hz, 2H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.7, 165.8, 162.6, 145.3, 140.4, 135.2, 134.7, 132.3, 132.0, 130.9, 128.1, 127.4, 125.1, 109.2, 80.8, 72.0, 30.5, 28.3. **IR** (KBr): 3077.1, 2977.0, 2926.5, 1703.2, 1631.3, 1581.5, 1514.1, 1478.7, 1457.1, 1410.6, 1392.4, 1366.9, 1354.2, 1318.2, 1264.6, 1242.9, 1207.7, 1191.0, 1149.3, 1081.2,

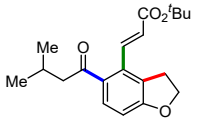
1051.2, 1037.8, 982.8, 936.2, 851.7, 833.4, 806.5, 730.6, 703.6, 653.8, 625.1 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{20}O_4SNa$ $[M+Na]^+$ 379.0980, found 379.0979.



Chemical Formula: $C_{26}H_{24}O_4$
Molecular Weight: 400.4740

***Tert*-butyl (E)-3-(5-(2-naphthoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4x)**

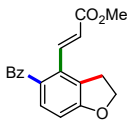
White solid, m.p. = 138.6–139.1 °C. 59.6 mg, 74% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.96 – 7.85 (m, 4H), 7.69 (d, *J* = 16.2 Hz, 1H), 7.62 – 7.50 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 1.9 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.05 (d, *J* = 16.3 Hz, 1H), 4.71 (t, *J* = 8.7 Hz, 2H), 3.41 (t, *J* = 8.6 Hz, 2H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.9, 165.6, 162.7, 140.6, 135.9, 135.5, 132.6, 132.3, 132.3, 132.2, 131.8, 129.5, 128.5, 128.3, 127.8, 127.2, 126.8, 125.5, 125.0, 109.2, 80.6, 71.9, 30.3, 28.0. **IR** (KBr): 3057.0, 2977.7, 2929.1, 1703.3, 1643.7, 1626.3, 1580.7, 1456.4, 1391.7, 1367.0, 1352.1, 1317.3, 1264.1, 1239.1, 1206.9, 1190.5, 1150.0, 1118.9, 1035.0, 1010.9, 977.5, 938.9, 866.4, 850.9, 822.0, 802.0, 779.9, 762.1, 732.4, 702.7 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{26}H_{24}O_4Na$ $[M+Na]^+$ 423.1572, found 423.1577.



Chemical Formula: $C_{20}H_{26}O_4$
Molecular Weight: 330.4240

***Tert*-butyl (E)-3-(5-(3-methylbutanoyl)-2,3-dihydrobenzofuran-4-yl)acrylate (4y)**

White solid, m.p. = 57.9–58.4 °C. 52.4 mg, 79% yield. R_f = 0.7 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 16.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.97 (d, *J* = 16.3 Hz, 1H), 4.62 (t, *J* = 8.6 Hz, 2H), 3.31 (t, *J* = 8.7 Hz, 2H), 2.71 (d, *J* = 6.9 Hz, 2H), 2.32 – 2.15 (m, 1H), 1.51 (s, 9H), 0.95 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.1, 166.0, 163.1, 142.6, 133.3, 132.2, 130.8, 127.5, 124.1, 109.1, 80.7, 72.1, 50.2, 30.1, 28.3, 25.7, 22.8. **IR** (KBr): 3056.1, 2959.9, 2871.4, 1704.0, 1668.7, 1635.8, 1581.5, 1456.8, 1392.2, 1367.2, 1317.4, 1288.4, 1264.4, 1244.8, 1227.4, 1209.0, 1190.2, 1149.3, 1057.3, 976.2, 944.9, 893.8, 866.2, 850.2, 813.1, 732.9, 702.4 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{26}O_4Na$ $[M+Na]^+$ 353.1729, found 353.1725.

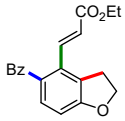


Chemical Formula: $C_{19}H_{16}O_4$
Molecular Weight: 308.3330

Methyl (E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)acrylate (4z)

White solid, m.p. = 113.7–114.3 °C. 54.9 mg, 89% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 (d, *J*=16.3, 1H), 7.75 (d, *J*=7.6, 2H), 7.55 (t, *J*=7.3, 1H), 7.43 (t, *J*=7.6, 2H), 7.30 (d, *J*=8.3, 1H), 6.79 (d, *J*=8.3, 1H), 6.12 (d, *J*=16.3, 1H), 4.68 (t, *J*=8.6, 2H), 3.72 (s, 3H), 3.37 (t,

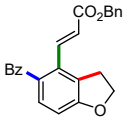
J=8.6, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.7, 166.8, 162.8, 142.2, 138.5, 132.9, 132.7, 132.1, 131.9, 130.3, 128.4, 127.5, 122.7, 109.2, 72.0, 51.8, 30.3. **IR** (KBr): 3058.1, 2950.4, 2901.0, 1713.9, 1642.0, 1580.3, 1479.1, 1458.8, 1446.6, 1434.7, 1366.1, 1315.2, 1265.3, 1242.2, 1194.9, 1170.8, 1074.4, 1038.1, 1021.1, 979.0, 944.5, 861.0, 824.7, 800.1, 729.8, 700.7, 653.1, 616.1 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1127, found 309.1135.



Chemical Formula: $C_{20}H_{18}O_4$
Molecular Weight: 322.3600

Ethyl (E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)acrylate (4aa)

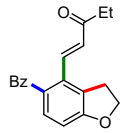
White solid, m.p. = 105.1–105.6 °C. 56.9 mg, 88% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 16.3 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.10 (d, *J* = 16.3 Hz, 1H), 4.66 (t, *J* = 8.7 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 8.6 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.7, 166.3, 162.7, 141.8, 138.5, 132.8, 132.7, 132.0, 131.8, 130.2, 128.4, 127.4, 123.1, 109.1, 71.9, 60.6, 30.2, 14.3. **IR** (KBr): 3056.2, 2983.7, 1709.4, 1649.4, 1581.8, 1447.2, 1392.2, 1367.6, 1314.0, 1264.3, 1243.2, 1176.4, 1095.7, 1038.6, 1006.1, 982.7, 944.5, 896.1, 869.0, 825.6, 800.1, 731.0, 701.5, 652.4, 616.2 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{19}O_4$ $[M+H]^+$ 323.1283, found 323.1289.



Chemical Formula: $C_{25}H_{20}O_4$
Molecular Weight: 384.4310

Benzyl (E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)acrylate (4ab)

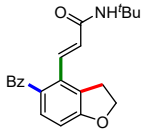
White solid, m.p. = 98.3–98.9 °C. 64.2 mg, 84% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 16.3 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 5H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.12 (d, *J* = 16.3 Hz, 1H), 5.13 (s, 2H), 4.63 (t, *J* = 8.7 Hz, 2H), 3.31 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.7, 166.2, 162.8, 142.5, 138.5, 136.0, 132.9, 132.6, 132.0, 132.0, 130.2, 128.6, 128.4, 128.3, 128.3, 127.4, 122.7, 109.3, 72.0, 66.4, 30.3. **IR** (KBr): 3061.1, 2899.3, 1711.5, 1640.2, 1580.1, 1497.5, 1478.9, 1447.1, 1375.9, 1314.5, 1264.5, 1242.3, 1193.3, 1163.3, 1075.6, 1037.4, 1015.9, 978.3, 944.6, 904.5, 858.1, 825.7, 800.3, 732.3, 700.3, 653.9, 620.1 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{25}H_{20}O_4Na$ $[M+Na]^+$ 407.1259, found 407.1263.



Chemical Formula: $C_{20}H_{18}O_3$
Molecular Weight: 306.3610

(E)-1-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)pent-1-en-3-one (4ac)

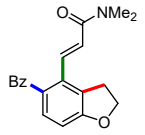
White solid, m.p. = 127.6–128.3 °C. 25.4 mg, 41% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 – 7.67 (m, 3H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.35 (d, *J* = 16.7 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 2H), 3.37 (t, *J* = 8.6 Hz, 2H), 2.57 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.3, 197.0, 163.0, 140.1, 138.7, 133.1, 132.9, 132.5, 131.6, 131.2, 130.2, 128.5, 127.4, 109.3, 72.1, 32.9, 30.3, 8.2. **IR** (KBr): 3058.0, 2975.8, 2937.4, 2901.4, 1694.1, 1650.3, 1614.0, 1595.5, 1579.0, 1479.1, 1457.9, 1446.7, 1355.6, 1315.9, 1264.0, 1242.0, 1192.1, 1171.0, 1119.9, 1072.5, 1051.2, 1035.6, 1025.5, 974.1, 943.2, 894.4, 824.9, 800.3, 731.5, 701.5, 643.1, 616.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1334, found 307.1339.



Chemical Formula: $C_{22}H_{23}NO_3$
Molecular Weight: 349.4300

(E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)-N-(tert-butyl)acrylamide (4ad)

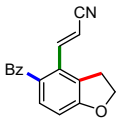
White solid, m.p. = 213.6–214.2 °C. 57.5 mg, 82% yield. R_f = 0.5 (hexane/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J*=7.3, 2H), 7.56 (t, *J*=7.4, 1H), 7.51 – 7.40 (m, 3H), 7.28 (s, 1H), 6.78 (d, *J*=8.2, 1H), 5.99 (d, *J*=15.9, 1H), 5.74 (s, 1H), 4.61 (t, *J*=8.7, 2H), 3.21 (t, *J*=8.7, 2H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.5, 164.8, 162.4, 138.4, 136.1, 133.2, 133.1, 131.6, 131.4, 130.2, 128.5, 128.3, 127.5, 108.6, 72.0, 51.5, 29.8, 28.9. **IR** (KBr): 3329.6, 3056.6, 2966.6, 2924.7, 1650.3, 1619.4, 1596.3, 1579.7, 1541.0, 1449.6, 1391.7, 1363.2, 1339.8, 1317.0, 1264.6, 1224.5, 1193.7, 1172.4, 1037.7, 1014.7, 988.5, 943.3, 895.9, 852.9, 825.4, 800.1, 730.1, 703.6, 651.7, 619.7 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{24}NO_3$ $[M+H]^+$ 350.1756, found 350.1762.



Chemical Formula: $C_{20}H_{19}NO_3$
Molecular Weight: 321.3760

(E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)-N,N-dimethylacrylamide (4ae)

White solid, m.p. = 177.8–178.3 °C. 50.9 mg, 79% yield. R_f = 0.2 (hexane/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.58 – 7.46 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 4.64 (t, *J* = 8.7 Hz, 2H), 3.32 (t, *J* = 8.7 Hz, 2H), 2.91 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4, 166.1, 162.1, 138.1, 138.0, 133.1, 133.0, 131.6, 130.9, 130.1, 128.4, 127.2, 123.8, 108.7, 71.8, 37.3, 35.7, 29.7. **IR** (KBr): 3054.9, 2923.5, 2895.3, 2854.2, 1720.8, 1649.6, 1597.7, 1478.0, 1445.6, 1432.1, 1407.9, 1390.6, 1313.0, 1262.9, 1240.4, 1189.8, 1170.6, 1141.0, 1075.0, 1055.9, 1037.0, 1007.0, 983.5, 970.9, 945.6, 863.9, 845.0, 828.2, 799.1, 732.8, 717.3, 698.3, 664.2, 618.3, 566.7, 554.6, 523.6 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{20}NO_3$ $[M+H]^+$ 322.1443, found 322.1447.

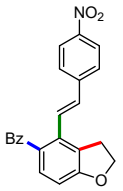


Chemical Formula: $C_{18}H_{13}NO_2$
Molecular Weight: 275.3070

(Containing ca. 42% of Z isomer)

(E)-3-(5-benzoyl-2,3-dihydrobenzofuran-4-yl)acrylonitrile (4af)

White solid, m.p. = 42.7–43.3 °C. 42.0 mg, 76% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). E/Z isomer = 1.4: 1. **^{1}H NMR (E+Z)** (400 MHz, $CDCl_3$): δ 7.77 – 7.52 (m, 4H), 7.49 – 7.31 (m, 3H), 6.86 – 6.77 (m, 1H), 5.60 (dd, *J* = 20.3, 14.3 Hz, 1H), 4.71 (td, *J* = 8.6, 4.0 Hz, 2H), 3.38 – 3.29 (m, 2H). **^{13}C NMR (E+Z)** (101 MHz, $CDCl_3$): δ 196.3, 196.0, 163.6, 163.1, 150.2, 148.4, 138.5, 138.2, 134.0, 133.4, 133.2, 132.5, 132.5, 131.8, 131.3, 130.2, 130.0, 129.4, 128.6, 128.4, 128.1, 127.3, 125.5, 117.6, 116.6, 109.9, 108.8, 101.3, 100.3, 72.4, 72.0, 30.1, 29.0. **IR** (KBr): 3058.3, 2963.8, 2921.3, 2853.1, 2639.0, 2218.6, 1906.3, 1644.8, 1618.4, 1579.5, 1478.7, 1446.4, 1365.0, 1316.0, 1274.1, 1243.2, 1172.0, 1136.8, 1074.9, 1035.4, 1021.1, 1003.0, 985.3, 942.3, 826.6, 801.3, 784.7, 731.3, 700.1, 638.8 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{13}NO_2Na$ $[M+Na]^+$ 298.0844, found 298.0840.

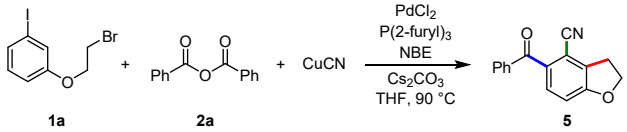


Chemical Formula: $C_{23}H_{17}NO_4$
Molecular Weight: 371.3920

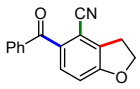
(E)-(4-(4-nitrostyryl)-2,3-dihydrobenzofuran-5-yl)(phenyl)methanone (4ag)

Yellow solid, m.p. = 124.6–125.0 °C. 32.1 mg, 43% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.40 (m, 5H), 7.36 (d, *J* = 8.3 Hz, 1H), 6.87 – 6.78 (m, 2H), 4.73 (t, *J* = 8.7 Hz, 2H), 3.47 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.6, 163.0, 147.2, 143.7, 139.0, 134.6, 132.9, 132.6, 131.2, 131.1, 130.2, 128.5, 127.2, 126.4, 124.2, 108.5, 72.0, 30.5. **IR** (KBr): 3059.5, 2923.9, 2853.4, 2446.8, 1711.4, 1648.0, 1594.5, 1578.4, 1514.2, 1479.8, 1446.8, 1338.7, 1317.0, 1266.2, 1243.6, 1171.5, 1132.5, 1109.4, 1074.3, 1035.9, 1003.1, 969.3, 944.7, 867.8, 823.5, 799.1, 735.1, 703.9, 646.4, 616.4 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{18}NO_4$ $[M+H]^+$ 372.1236, found 372.1240.

C. Terminating the trifunctionalization with CuCN



Unless otherwise noted, in a glovebox, an oven-dried 10 mL vial was charged with $PdCl_2$ (3.5 mg, 0.02 mmol, 0.1 equiv.) and P(2-furyl)$_3$ (9.3 mg, 0.04 mmol, 0.2 equiv.). THF (4 mL) was added and the mixture was stirred for 10 min. Cs_2CO_3 (260.7 mg, 0.80 mmol, 4.0 equiv.), aryl iodide **1a** (0.20 mmol, 1.0 equiv.), benzoic anhydride **2a** (0.30 mmol, 1.5 equiv.), CuCN (0.24 mmol, 1.2 equiv.) and NBE (18.8 mg, 0.2 mmol, 1.0 equiv.) were added to the vial. The vial was sealed with a Teflon screw cap, transferred out of glovebox and then stirred on a pie-block preheated to 90 °C for 12 h. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel to yield the desired product **5**.



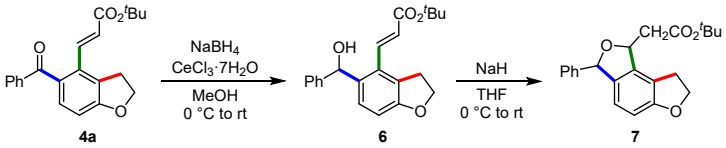
Chemical Formula: $C_{16}H_{11}NO_2$
Molecular Weight: 249.2690

5-Benzoyl-2,3-dihydrobenzofuran-4-carbonitrile (5)

White solid, m.p. = 113.3–113.8 °C. 41.5 mg, 83% yield. R_f = 0.4 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.1 Hz, 3H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.78 (t, *J* = 8.8 Hz, 2H), 3.48 (t, *J* = 8.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.8, 163.2, 136.9, 135.2, 133.1, 133.0, 132.4, 130.0, 128.4, 115.8, 111.7, 109.8, 72.5, 29.3. **IR** (KBr): 3060.6, 2973.3, 2922.8, 2852.1, 2651.4, 2229.9, 1718.0, 1650.5, 1587.0, 1478.7, 1467.2, 1445.7, 1367.7, 1317.2, 1274.5, 1247.1, 1206.5, 1175.0, 1140.3, 1075.1, 1034.5, 1016.3, 982.6, 929.1, 834.3, 798.4, 746.7, 701.0, 639.2, 617.3, 596.6, 536.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{11}NO_2Na$ $[M+Na]^+$ 272.0687, found 272.0688.

D. Preparation of polycyclic frameworks

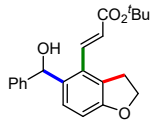
Procedure for the formation of 6 and 7:



A flask was charged with **4a** (175.1 mg, 0.5 mmol) and MeOH (4.0 mL). $CeCl_3 \cdot 7H_2O$ (190.2 mg, 0.5 mmol) was added to the solution at 0°C; after 10 min at this temperature $NaBH_4$ (38.0 mg, 1.0 mmol) was added and the mixture was warmed to room temperature stirred for 12 h. Solvent was removed under reduced pressure. Quenched with 1 M HCl (10.0 mL), followed by extraction with DCM (3×5 mL), The combined organic extracts were washed with brine and dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (n-Hex/EtOAc) to afford the **6**.

Under N_2 atmosphere, a two-necked round bottom flask was charged with **6** (105.7 mg, 0.3 mmol) in THF (2.0 mL) was added NaH (21.7 mg, 0.9 mmol) at 0°C, the mixture was warmed to room temperature stirred for 12 h. Quenched with H_2O, followed by extraction with EtOAc (3×5 mL), The combined organic

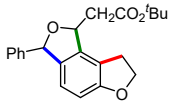
extracts were washed with brine and dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (n-Hex/EtOAc) to afford the **7**.



Chemical Formula: $C_{22}H_{24}O_4$
Molecular Weight: 352.4300

***tert*-Butyl (R,E)-3-(5-(hydroxy(phenyl)methyl)-2,3-dihydrobenzofuran-4-yl)acrylate (6)**

White solid, m.p. = 74.2–74.8 °C. 149.5 mg, 85% yield. R_f = 0.6 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 16.2 Hz, 1H), 7.31 (q, *J* = 8.0 Hz, 7H), 7.24 (dd, *J* = 10.1, 6.2 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.06 – 5.94 (m, 2H), 4.54 (t, *J* = 8.6 Hz, 2H), 3.23 (t, *J* = 8.6 Hz, 2H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.1, 159.9, 143.6, 140.3, 135.1, 130.5, 128.4, 127.9, 127.4, 126.8, 126.3, 124.6, 110.0, 80.8, 73.1, 71.4, 30.7, 28.3. **IR** (KBr): 3060.5, 2976.4, 2926.7, 1701.9, 1632.4, 1586.1, 1493.1, 1478.0, 1456.4, 1391.7, 1366.5, 1315.3, 1291.7, 1260.9, 1235.1, 1147.9, 1081.5, 1053.6, 1028.4, 983.0, 951.8, 938.9, 917.1, 868.5, 849.6, 815.2, 760.9, 733.7, 698.2 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{24}O_4Na$ $[M+Na]^+$ 375.1572, found 375.1553.

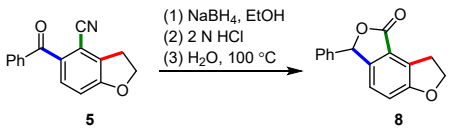


Chemical Formula: $C_{22}H_{24}O_4$
Molecular Weight: 352.4300

***tert*-Butyl 2-((1S,3R)-3-phenyl-1,3,7,8-tetrahydrobenzo[1,2-b:3,4-c']difuran-1-yl)acetate (7)**

Light red oil. 86.5 mg, 82% yield (1.2:1 dr). R_f = 0.6 (hexane/ethyl acetate = 5:1). Diastereoisomers of **7**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.22 (m, 5H), 6.81 – 6.62 (m, 2H), 6.11 (d, *J* = 51.8 Hz, 1H), 5.92 – 5.61 (m, 1H), 4.75 – 4.52 (m, 2H), 3.32 – 3.07 (m, 2H), 2.95 – 2.66 (m, 2H), 1.42 (d, *J* = 21.1 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.1, 160.9, 160.8, 142.8, 142.5, 137.9, 137.7, 135.1, 135.1, 128.6, 128.5, 128.0, 127.1, 126.9, 121.9, 121.8, 120.0, 119.7, 109.2, 109.2, 85.4, 81.2, 80.9, 79.9, 79.4, 77.5, 77.2, 76.8, 71.6, 71.6, 42.0, 41.6, 28.3, 28.1. **IR** (KBr): 2975.5, 2922.5, 2852.0, 1725.9, 1615.5, 1479.1, 1463.2, 1391.7, 1366.3, 1316.6, 1279.6, 1237.4, 1219.3, 1145.5, 1039.8, 1027.5, 1008.9, 968.6, 947.7, 917.9, 843.8, 819.1, 795.5, 737.2, 698.8, 657.4, 628.4 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{24}O_4Na$ $[M+Na]^+$ 375.1572, found 375.1578.

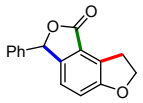
Procedure for the formation of 8:



5 **8**

A 10.0 mL, round bottom flask, equipped with a Teflon coated stir bar was charged with **5** (149.6 mg, 0.6 mmol). A suspension of $NaBH_4$ (32 mg, 0.6 mmol) in ethanol (3.0 mL) has stirred for 0.5 h was added to the reaction mixture, then the mixture was warmed to 50 °C stirred for 1 h, after that the reaction was left to stand for 24 h at 20°C. The reaction mixture was then neutralized slowly by adding 2 N aqueous HCl until

it was weakly acidic. Then poured the mixture into a 250.0 mL, round bottom flask, equipped with a Teflon coated stir bar and H_2O (90.0 mL), refluxed for 0.5 h at 100°C. Then purged with rotary evaporator to remove residual ethanol, extracted with EtOAc (3×30.0 mL), and the combined organic layers were washed with brine (30.0 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude reaction mixture was then purified by silica gel column chromatography eluting with a solvent mixture composed of hexane and ethyl acetate (10 : 1) to afford **8**.

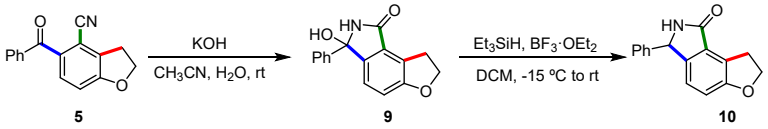


Chemical Formula: $C_{16}H_{12}O_3$
Molecular Weight: 252.2690

(R)-3-phenyl-7,8-dihydrobenzo[1,2-b:3,4-c']difuran-1(3H)-one (8)

Red solid, m.p. = 109.3–109.7 °C. 133.5 mg, 88% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 3H), 7.27 (dd, *J* = 6.6, 2.6 Hz, 2H), 7.07 – 6.98 (m, 2H), 6.35 (s, 1H), 4.73 (t, *J* = 8.9 Hz, 2H), 3.56 (t, *J* = 8.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.1, 162.2, 141.9, 137.2, 129.3, 129.0, 127.1, 125.7, 122.7, 122.5, 115.4, 83.2, 72.7, 28.1. **IR** (KBr): 3062.8, 3033.3, 2970.4, 2907.6, 2853.6, 1749.6, 1628.7, 1608.4, 1482.2, 1469.3, 1455.5, 1437.7, 1364.8, 1343.0, 1293.7, 1245.6, 1223.7, 1207.1, 1138.5, 1098.2, 1006.9, 948.4, 834.4, 812.8, 772.8, 723.6, 699.8, 656.7, 628.9 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{12}O_3Na$ $[M+Na]^+$ 275.0684, found 275.0682.

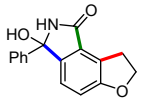
Procedure for the formation of 9 and 10:



5 **9** **10**

A flask was charged with **5** (0.6 mmol, 160.4 mg) in MeCN (6.0 mL). KOH (0.02 mmol, 12.0 mg) dissolved in H_2O (0.6 mL) was added to reaction mixture slowly, the solution was stirred at room temperature for 3 h, then extracted with DCM (3×5 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (n-Hex/EtOAc) to afford the **9**.

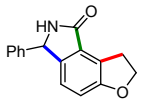
To a solution of **9** (0.3 mmol, 75.4 mg) in dry DCM (3.0 mL) was added dropwise triethylsilane (3.0 mmol, 0.5 mL) and trifluoroboron etherate (1.0 mmol, 0.2 mL) at -15°C under N_2. The solution was stirred at -15°C for 2 h then the mixture was allowed to stir at room temperature overnight. A saturated aqueous solution of $NaHCO_3$ (5 mL) was added, which was followed by DCM extraction (3×6 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuo. The crude was subjected to column chromatography purification on silica gel to afford **10**.



Chemical Formula: $C_{16}H_{13}NO_3$
Molecular Weight: 267.2840

(R)-3-hydroxy-3-phenyl-2,3,7,8-tetrahydro-1H-furo[3,2-e]isoindol-1-one (9)

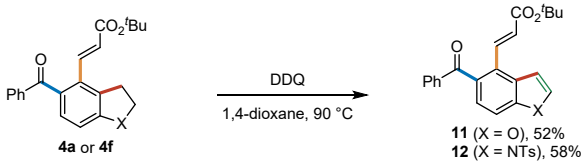
White solid, m.p. = 171.6–171.9 °C. 146.2 mg, 91% yield. R_f = 0.5 (hexane/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, DMSO): δ 9.15 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 4H), 7.29 – 7.24 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.73 (s, 1H), 4.69 – 4.55 (m, 2H), 3.48 – 3.33 (m, 2H). **^{13}C NMR** (101 MHz, DMSO): δ 168.7, 161.7, 143.6, 143.3, 128.6, 128.0, 127.8, 125.9, 123.8, 122.8, 112.6, 87.7, 72.6, 27.8. **IR** (KBr): 3056.9, 2968.7, 2907.8, 1698.0, 1662.6, 1626.1, 1483.3, 1470.2, 1453.4, 1433.5, 1400.2, 1369.6, 1347.8, 1241.5, 1201.9, 1172.1, 1133.3, 1102.3, 1065.8, 1044.8, 981.6, 966.3, 933.9, 923.4,874.0, 827.1, 776.3, 735.0, 716.3, 702.9, 669.3 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{13}NO_3Na$ $[M+Na]^+$ 290.0793, found 290.0789.



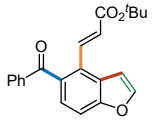
Chemical Formula: $C_{16}H_{13}NO_2$
Molecular Weight: 251.2850

(R)-3-phenyl-2,3,7,8-tetrahydro-1H-furo[3,2-e]isoindol-1-one (10)

White solid, m.p. = 186.9–187.5 °C. 65.3 mg, 87% yield. R_f = 0.6 (hexane/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 – 7.22 (m, 5H), 6.90 (dd, *J* = 20.5, 8.1 Hz, 2H), 6.63 (s, 1H), 5.55 (s, 1H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.56 (t, *J* = 8.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.9, 161.5, 140.3, 139.3, 129.1, 128.5, 127.6, 126.9, 124.3, 122.9, 113.2, 72.6, 60.8, 29.8, 28.1. **IR** (KBr): 3074.1, 2922.3, 2852.0, 1707.9, 1683.1, 1630.0, 1481.4, 1468.8, 1454.3, 1364.4, 1339.0, 1265.1, 1239.4, 1191.1, 1125.0, 1060.5, 1027.4, 984.2, 962.6, 932.1, 837.0, 807.7, 772.3, 733.6, 703.3, 630.9, 560.3, 516.9 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1025, found 252.1024.



A flask was charged with **4a** or **4f** (0.2 mmol) in dry 1,4-dioxane (4.0 mL). DDQ (0.8 mmol, 181.0 mg) was added to reaction mixture slowly, the solution was stirred at 90°C for 16h under nitrogen. Cool to room temperature, then pass the mixture through a short pad of silica gel and collect the filtrate. The combined organic layers were filtered and concentrated under vacuo. The crude was subjected to column chromatography purification on silica gel to afford **11** or **12**.

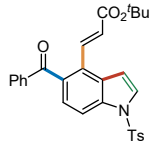


Chemical Formula: $C_{22}H_{20}O_4$
Molecular Weight: 348.3980

***tert*-Butyl (E)-3-(5-benzoylbenzofuran-4-yl)acrylate (11)**

White solid, m.p. = 92.4–92.7 °C. 36.3 mg, 52% yield. R_f = 0.5 (hexane/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 11.5, 7.0 Hz, 4H), 7.56 (dd, J = 15.1, 7.9 Hz, 2H), 7.49 – 7.37 (m, 3H),

7.12 (s, 1H), 6.32 (d, J = 16.1 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.8, 165.7, 156.1, 147.2, 140.0, 138.2, 134.6, 133.3, 130.4, 128.8, 128.6, 126.7, 125.9, 125.6, 111.9, 106.8, 80.8, 28.2. **IR** (KBr): 2975.9, 2926.0, 1703.9, 1658.4, 1633.8, 1351.7, 1314.0, 1273.5, 1201.7, 1139.2, 1021.1, 973.2, 729.3, 708.2, 673.1 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{20}O_4Na$ $[M+Na]^+$ 371.1529, found 371.1529.



Chemical Formula: $C_{29}H_{27}NO_5S$
Molecular Weight: 501.5970

***tert*-Butyl (E)-3-(5-benzoyl-1-tosyl-1H-indol-4-yl)acrylate (12)**

White oil. 58.4 mg, 58% yield. R_f = 0.5 (hexane/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.5 Hz, 1H), 7.82 – 7.68 (m, 6H), 7.56 (t, J = 7.4 Hz, 1H), 7.41 (dd, J = 15.8, 8.1 Hz, 3H), 7.27 (d, J = 6.5 Hz, 2H), 6.97 (d, J = 3.7 Hz, 1H), 6.19 (d, J = 16.1 Hz, 1H), 2.37 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.7, 165.3, 145.6, 139.5, 137.8, 135.9, 134.9, 134.4, 133.3, 130.2, 130.1, 129.4, 128.5, 128.3, 128.2, 126.9, 126.3, 125.6, 113.5, 108.3, 80.7, 28.1, 21.6. **IR** (KBr): 2924.1, 1704.6, 1660.0, 1369.8, 1313.7, 1283.9, 1264.9, 1173.4, 1143.1, 1089.0, 907.8, 731.2, 689.0, 666.8, 586.5, 543.0 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{29}H_{27}NO_5SNa$ $[M+Na]^+$ 524.1508, found 524.1508.

E. References

1. Pache, S.; Lautens, M. Palladium-Catalyzed Sequential Alkylation-Alkenylation Reactions: New Three-Component Coupling Leading to Oxacycles. *Org. Lett.* **2003**, *5*, 4827−4830.
2. Wang, J.; Wang, H.; Wang, Z.; Li, L.; Qin C.; Luan, X. Trifunctionalization of Aryl Iodides with Two Distinct Nitrogen and Carbon Electrophiles by Palladium/Norbornene Catalysis. *Chin. J. Chem*. **2021**, *39*, 2659– 2667.

F. NMR Spectra

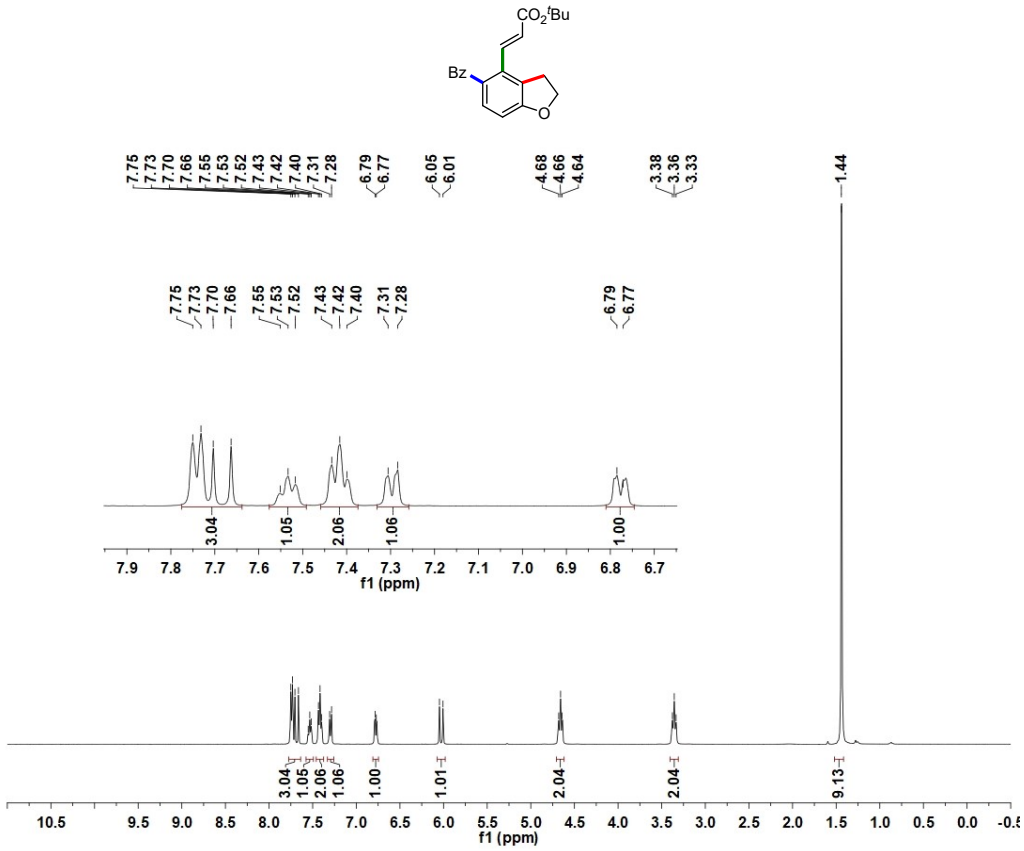


Figure S1. ^{1}H NMR spectrum of **4a**.

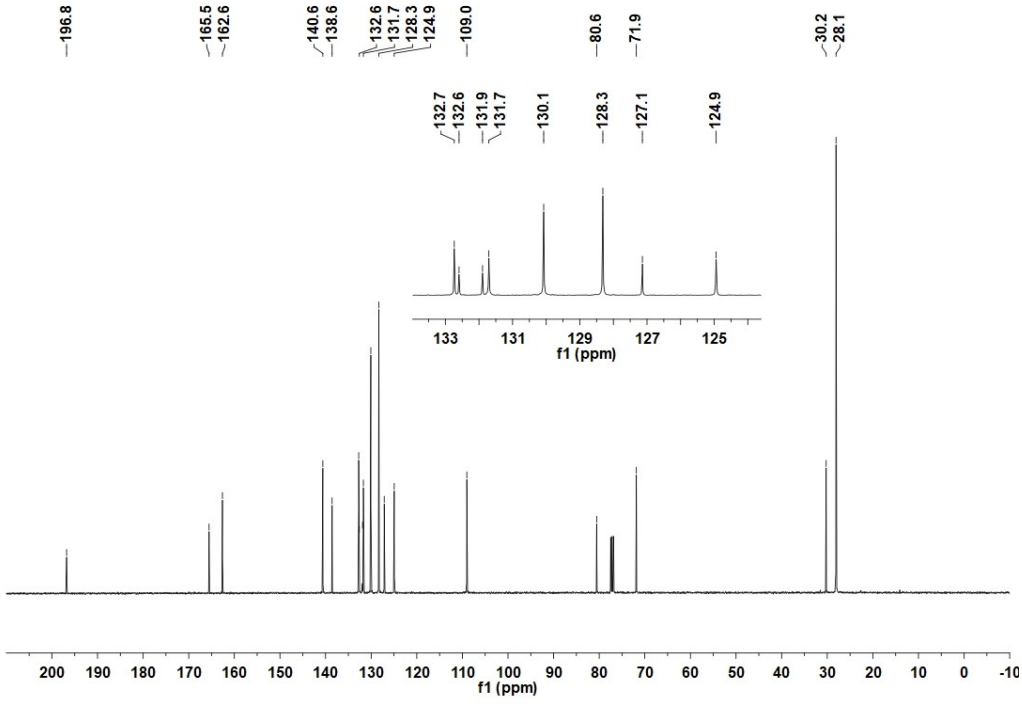


Figure S2. ^{13}C NMR spectrum of **4a**.

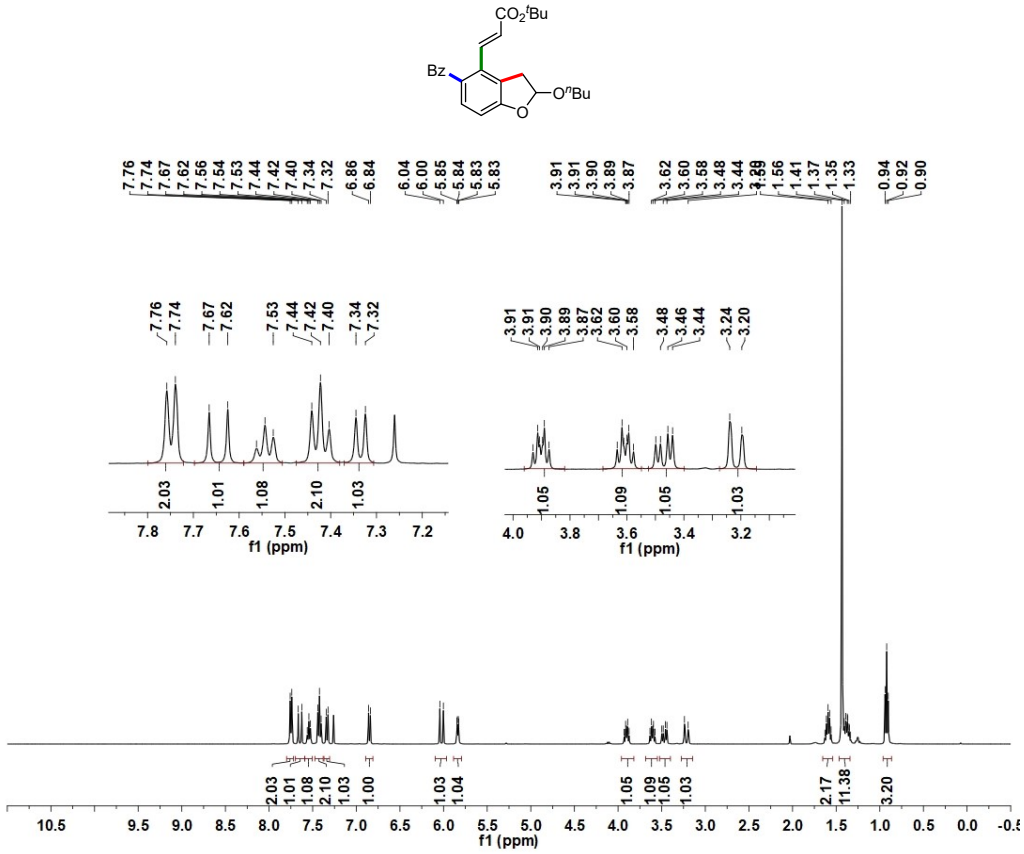


Figure S3. ^{1}H NMR spectrum of **4b**.

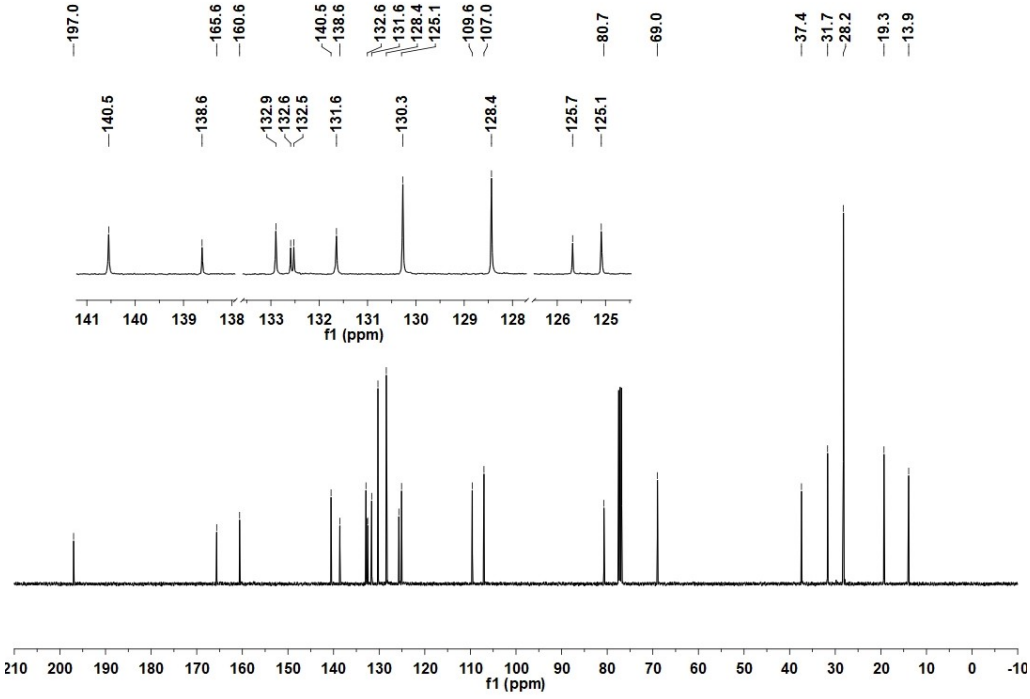


Figure S4. ^{13}C NMR spectrum of **4b**.

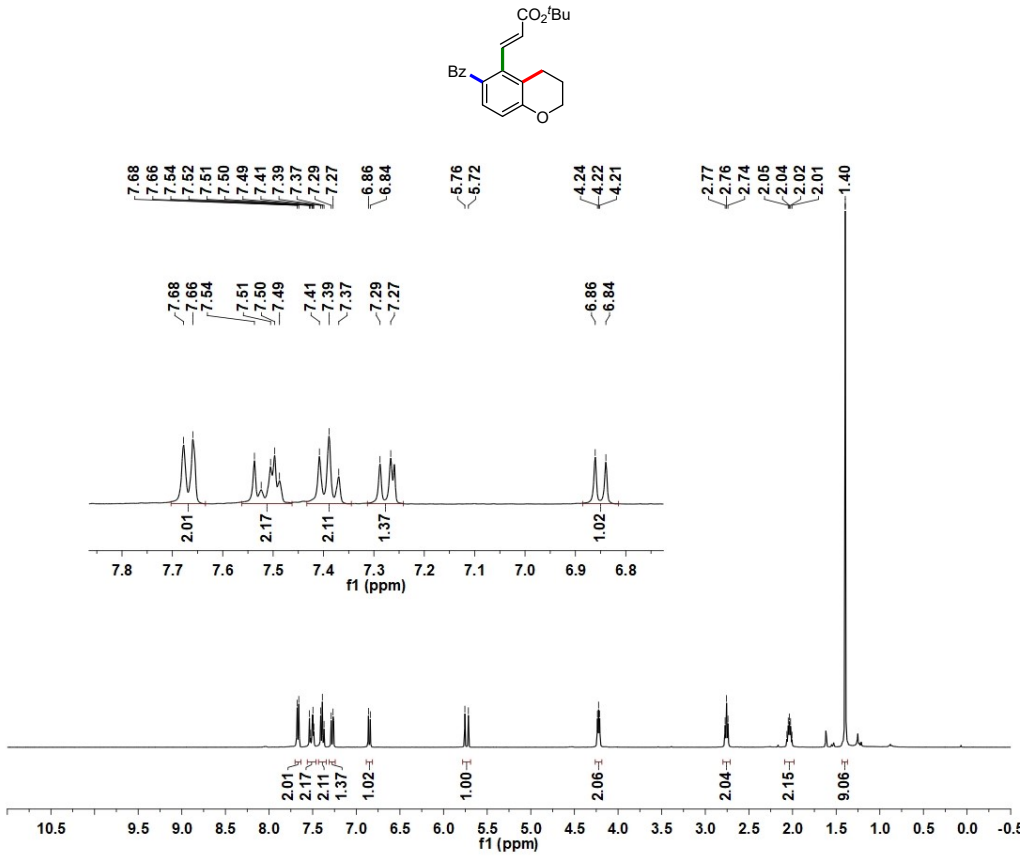


Figure S5. ^{1}H NMR spectrum of **4c**.

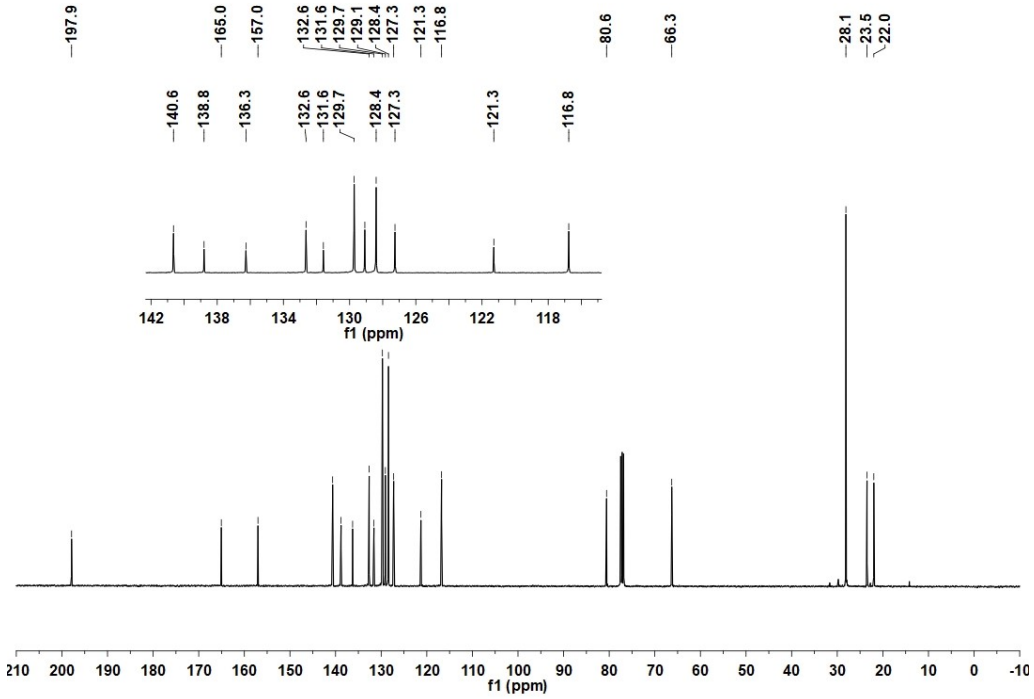


Figure S6. ^{13}C NMR spectrum of **4c**.

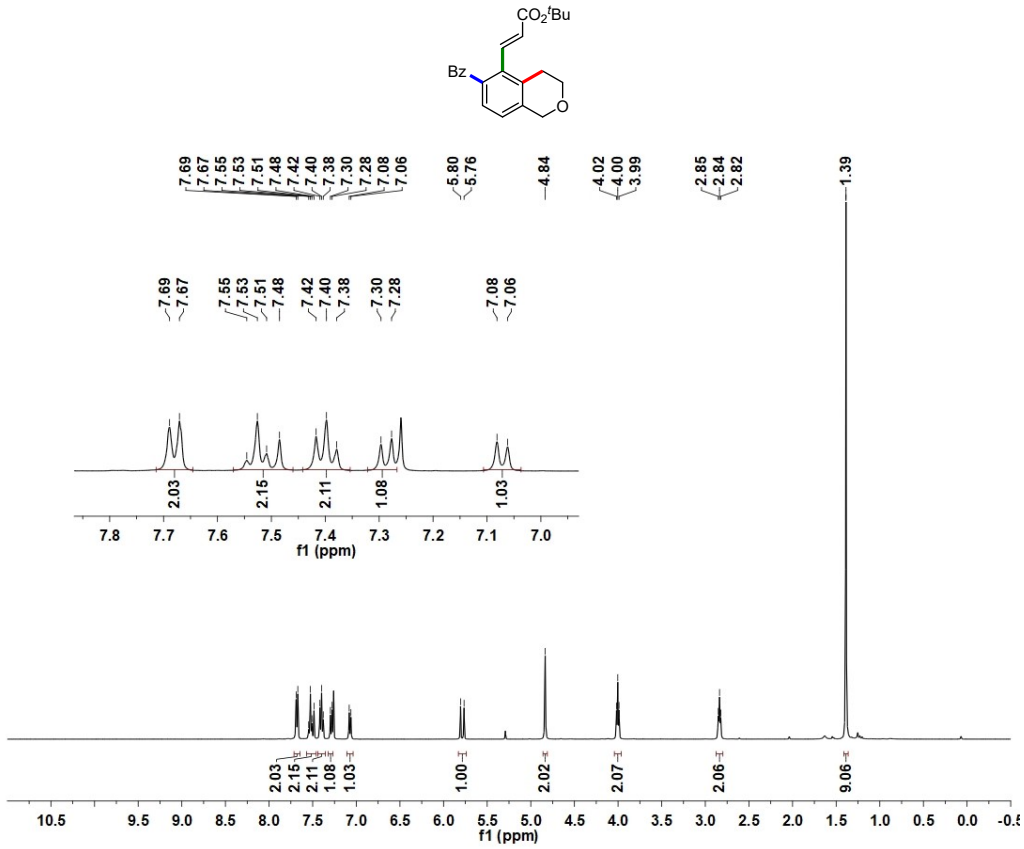


Figure S7. ^{1}H NMR spectrum of **4d**.

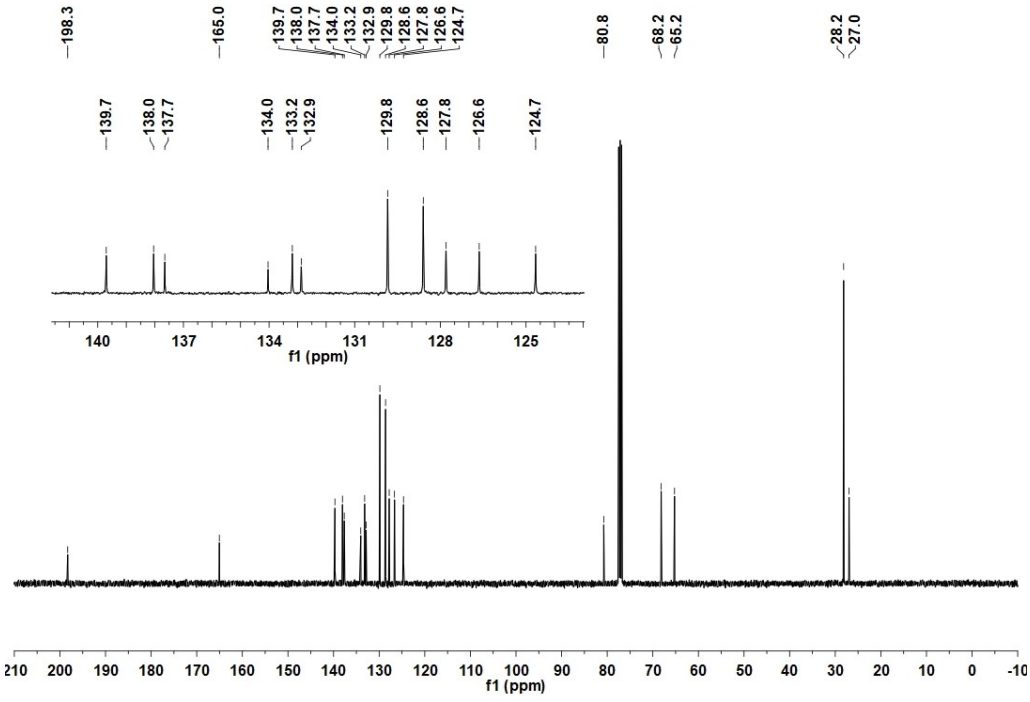


Figure S8. ^{13}C NMR spectrum of **4d**.

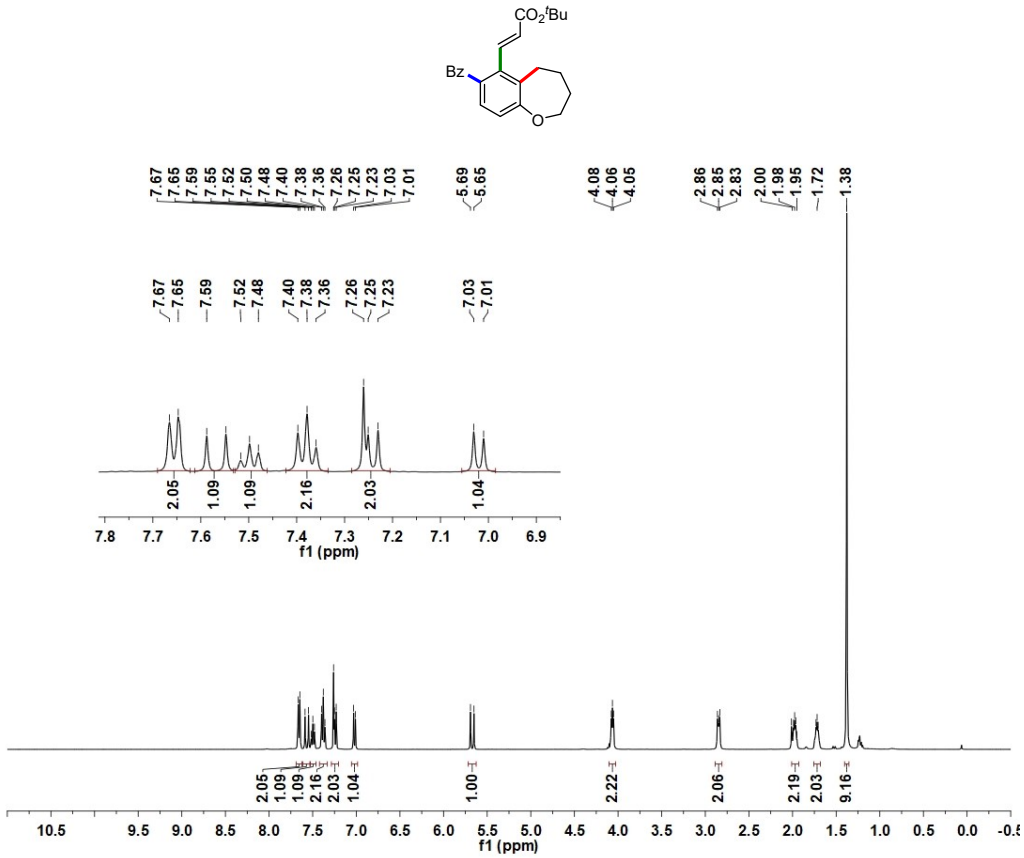


Figure S9. ^{1}H NMR spectrum of **4e**.

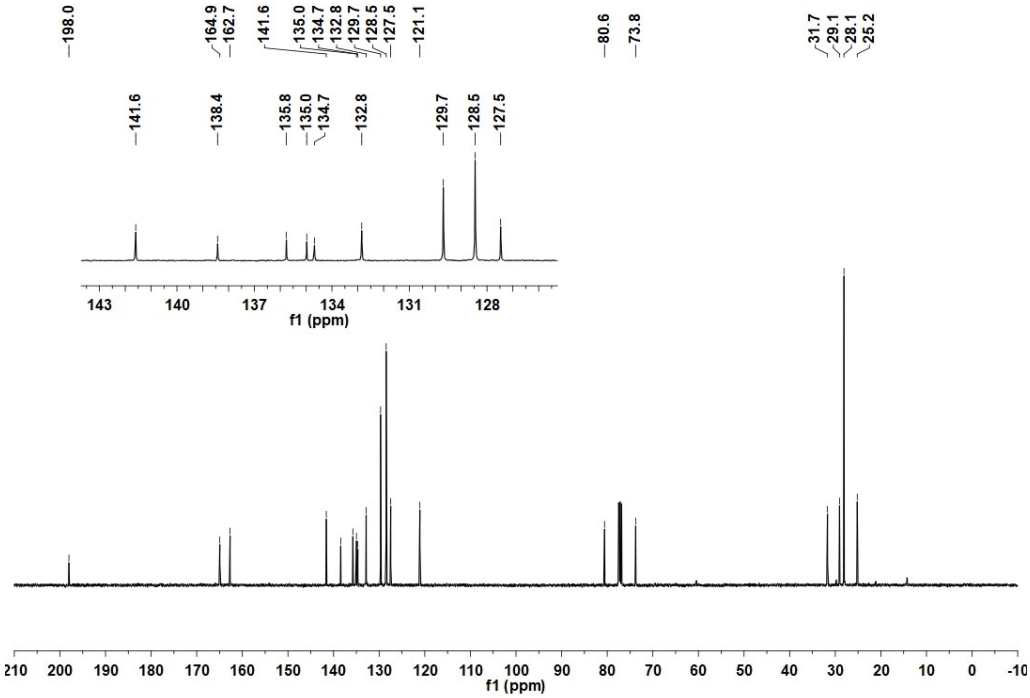


Figure S10. ^{13}C NMR spectrum of **4e**.

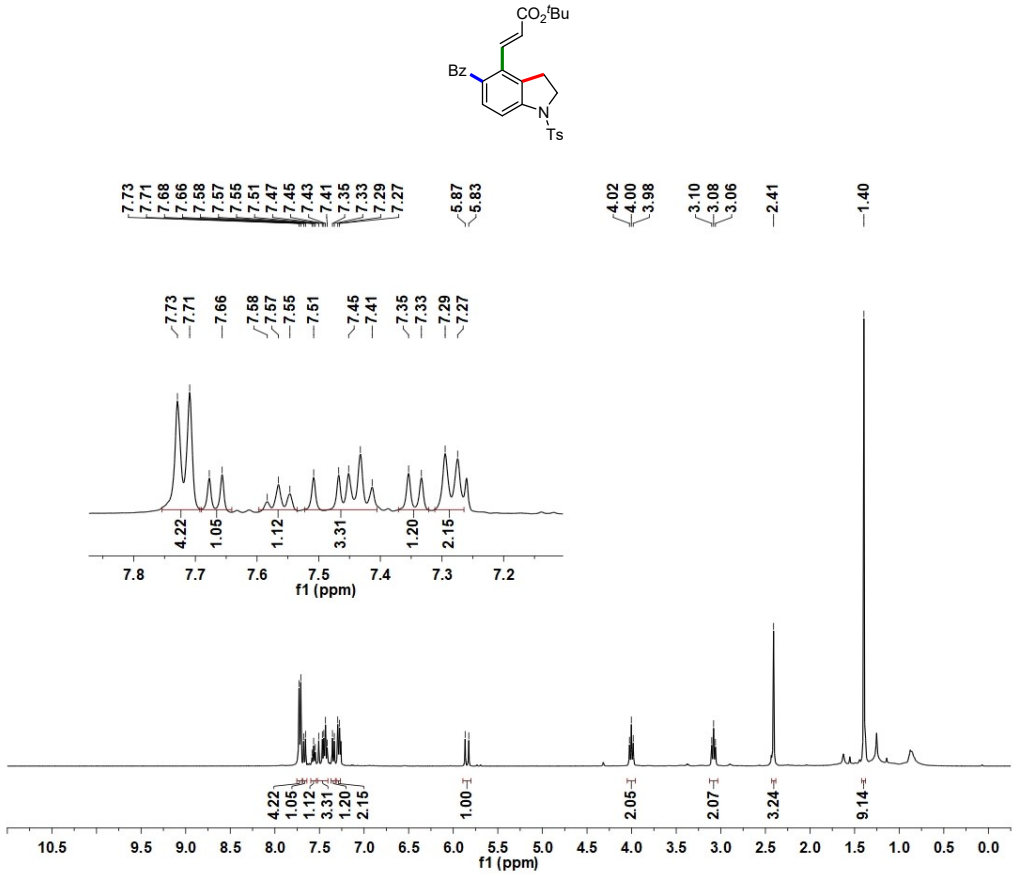


Figure S11. [1]H NMR spectrum of **4f**.

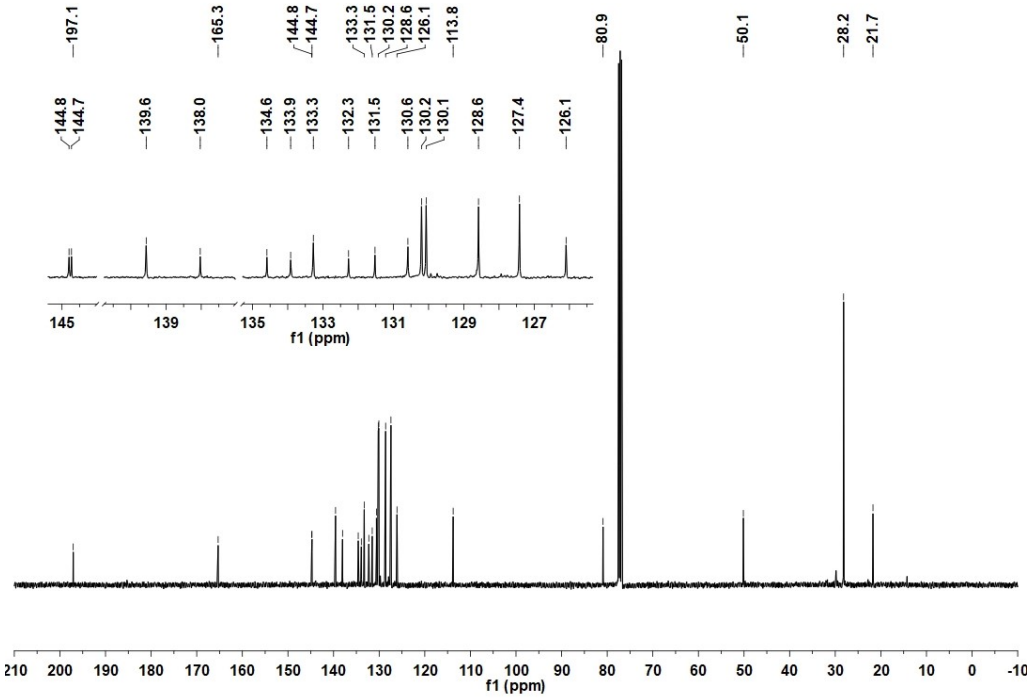


Figure S12. [13]C NMR spectrum of **4f**.

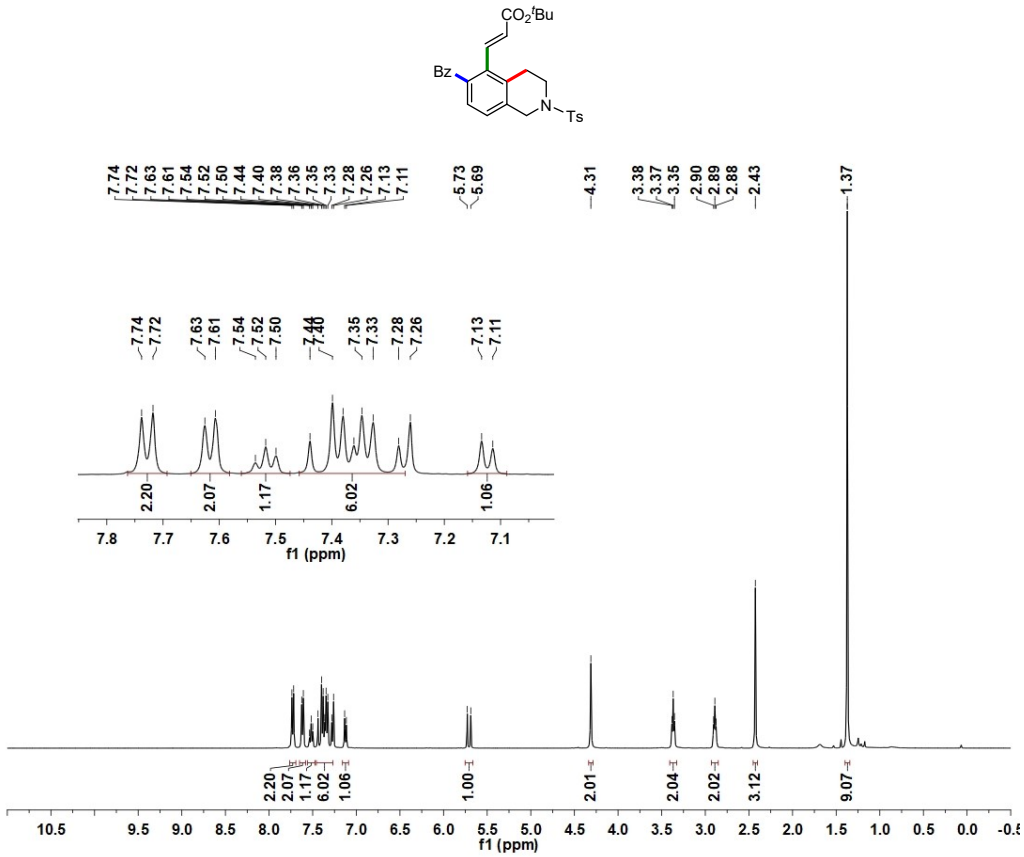


Figure S13. ^{1}H NMR spectrum of **4g**.

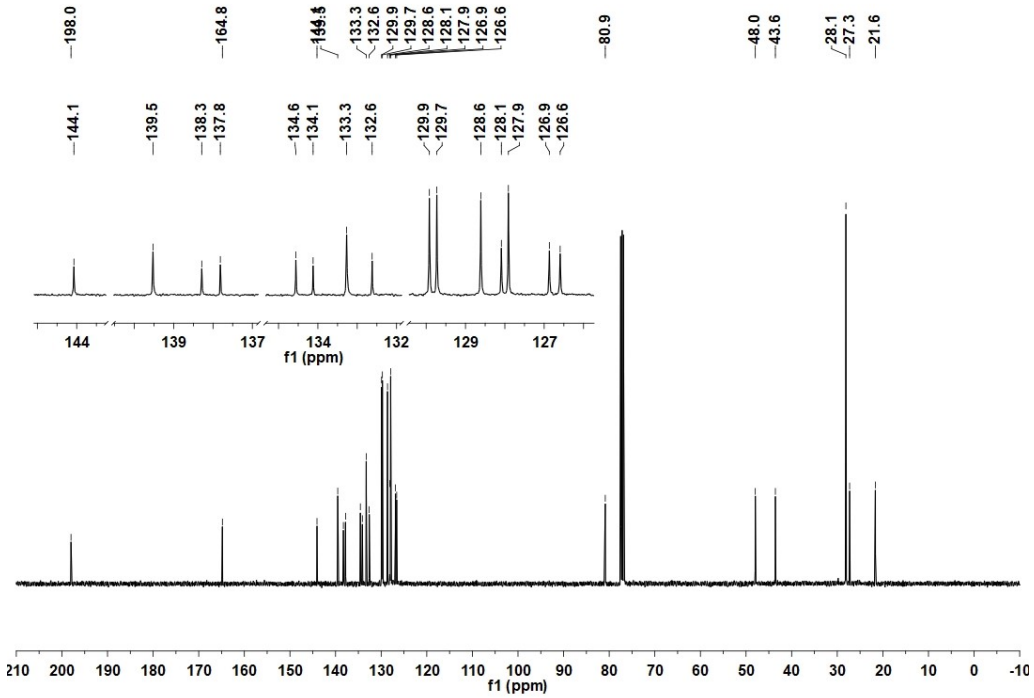


Figure S14. ^{13}C NMR spectrum of **4g**.

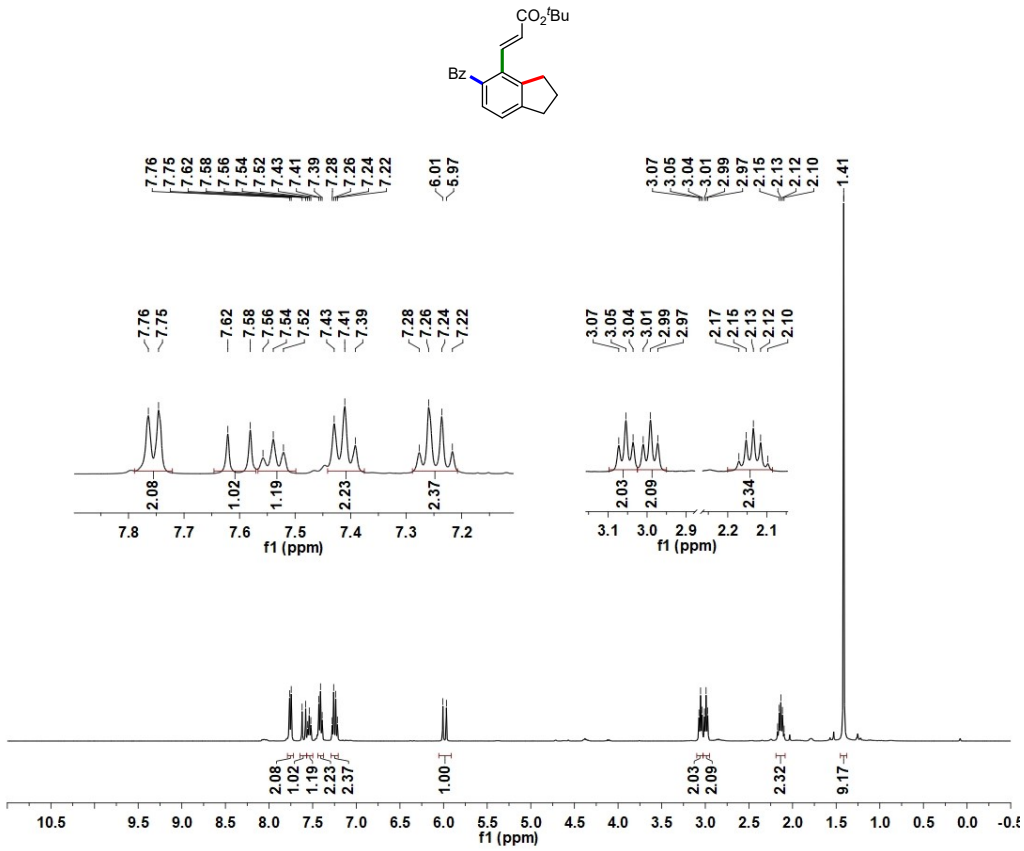


Figure S15. ^{1}H NMR spectrum of **4h**.

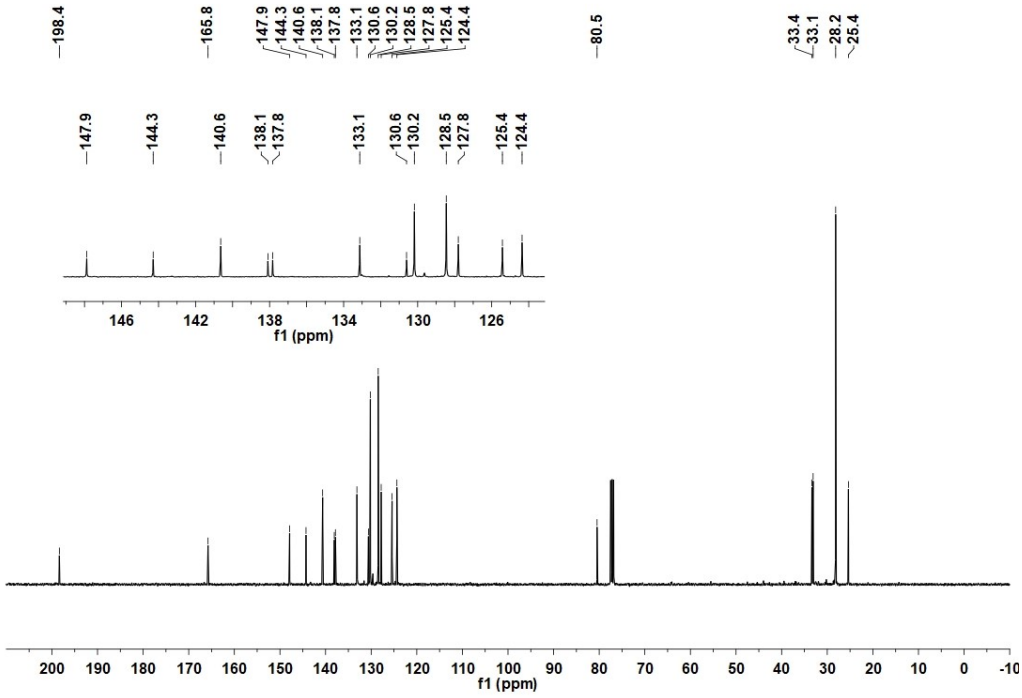


Figure S16. ^{13}C NMR spectrum of **4h**.

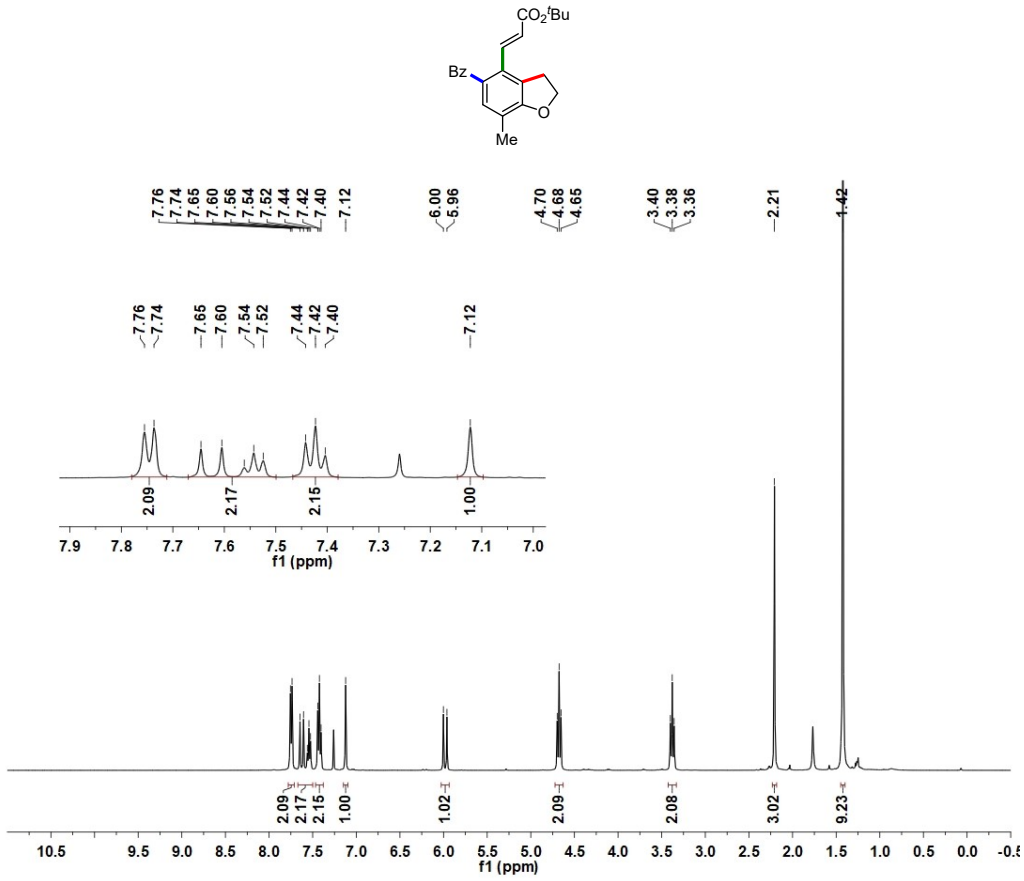


Figure S17. [1]H NMR spectrum of **4i**.

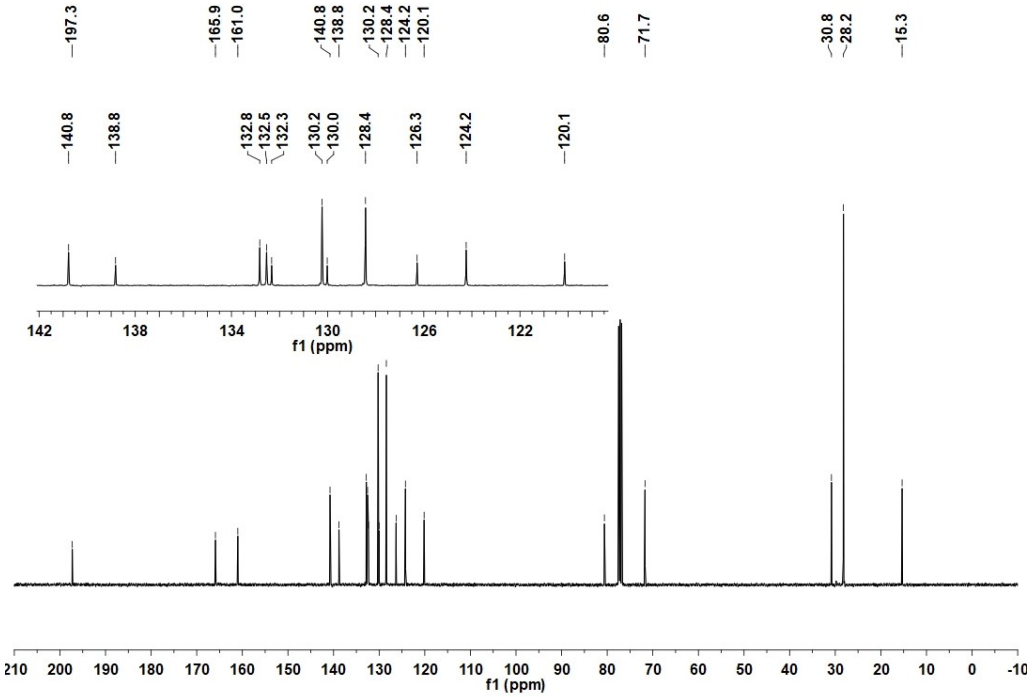


Figure S18. [13]C NMR spectrum of **4i**.

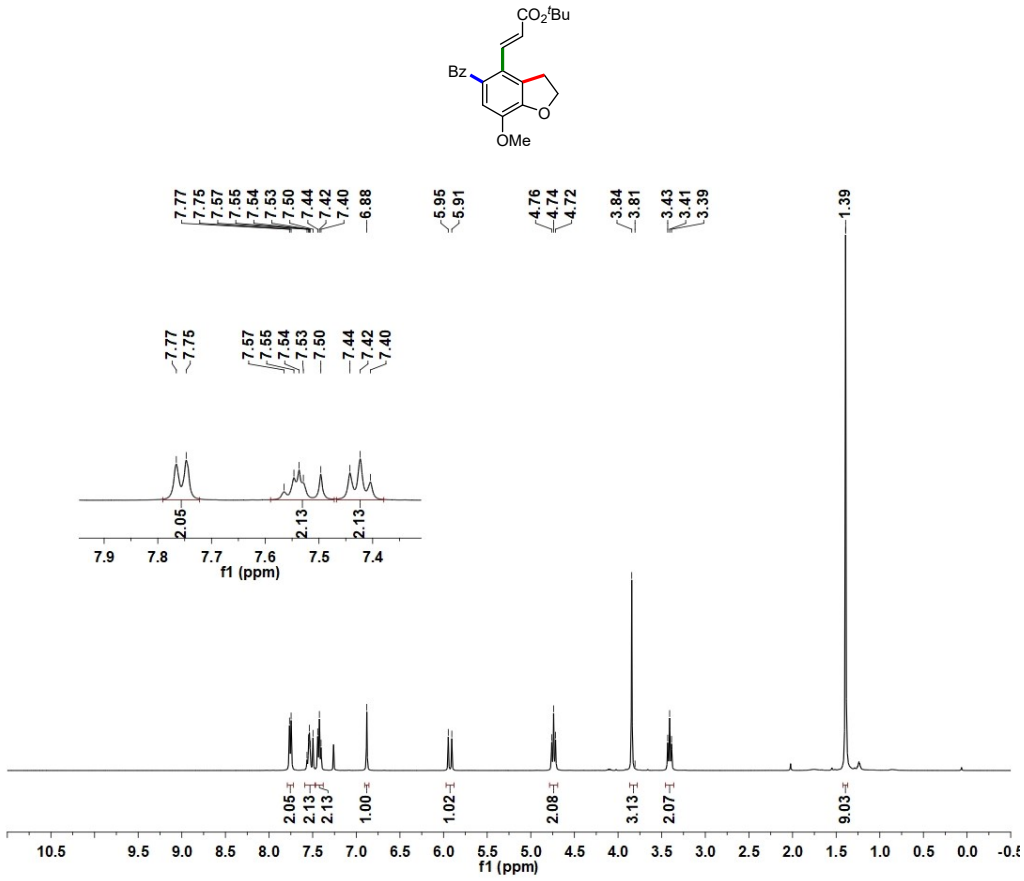


Figure S19. [1]H NMR spectrum of **4j**.

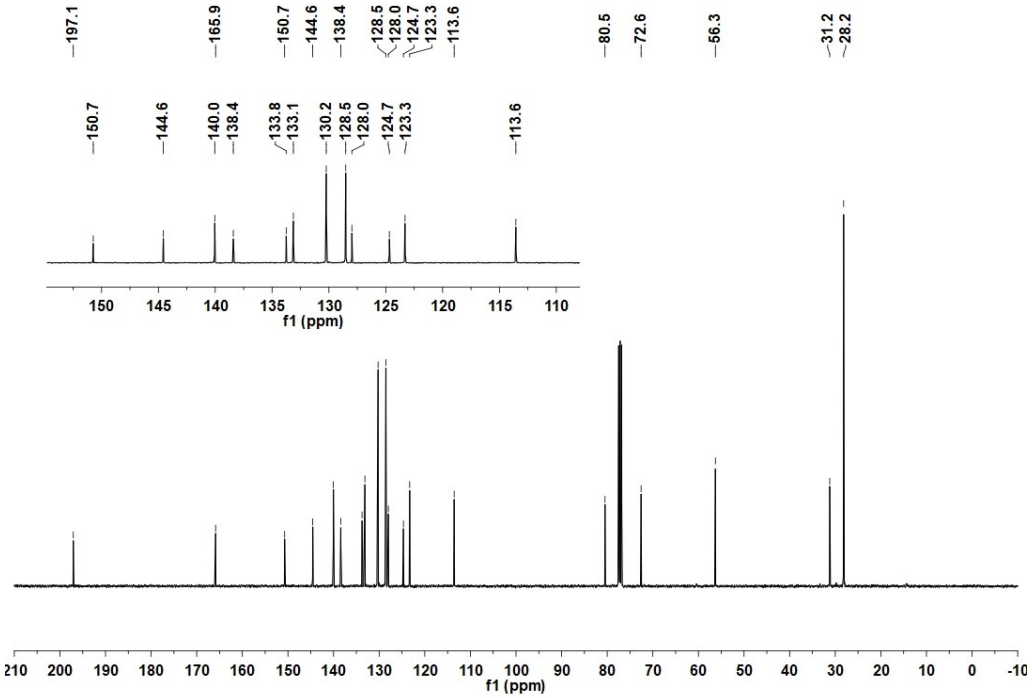


Figure S20. [13]C NMR spectrum of **4j**.

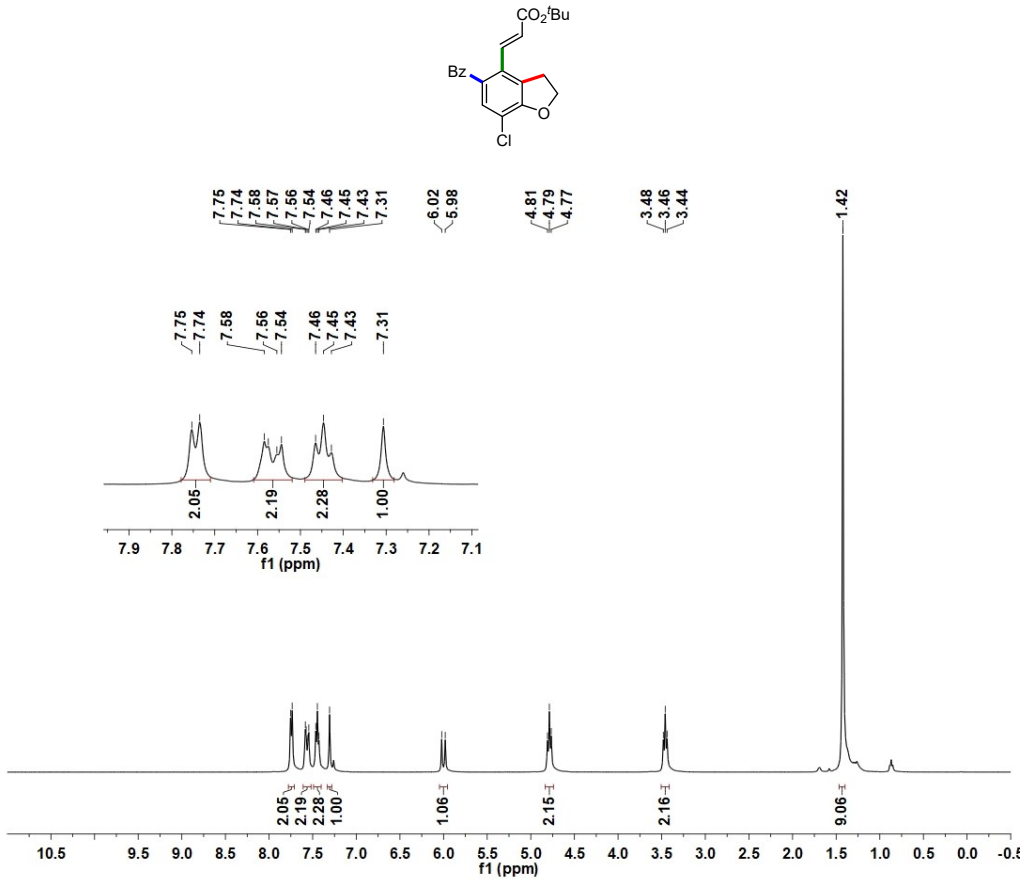


Figure S21. [1]H NMR spectrum of **4k**.

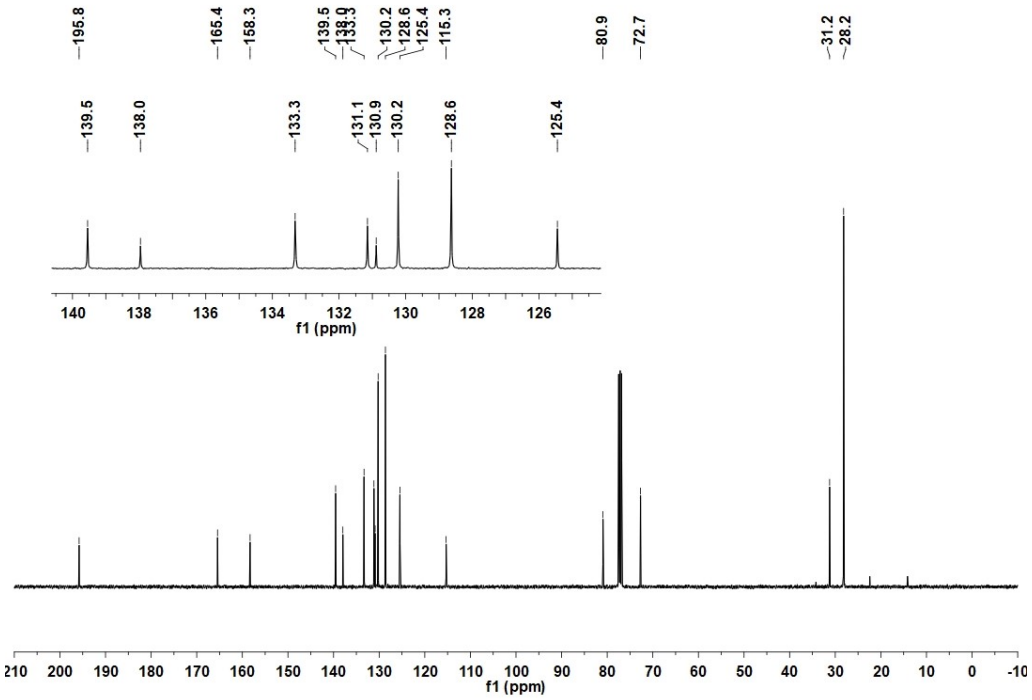


Figure S22. [13]C NMR spectrum of **4k**.

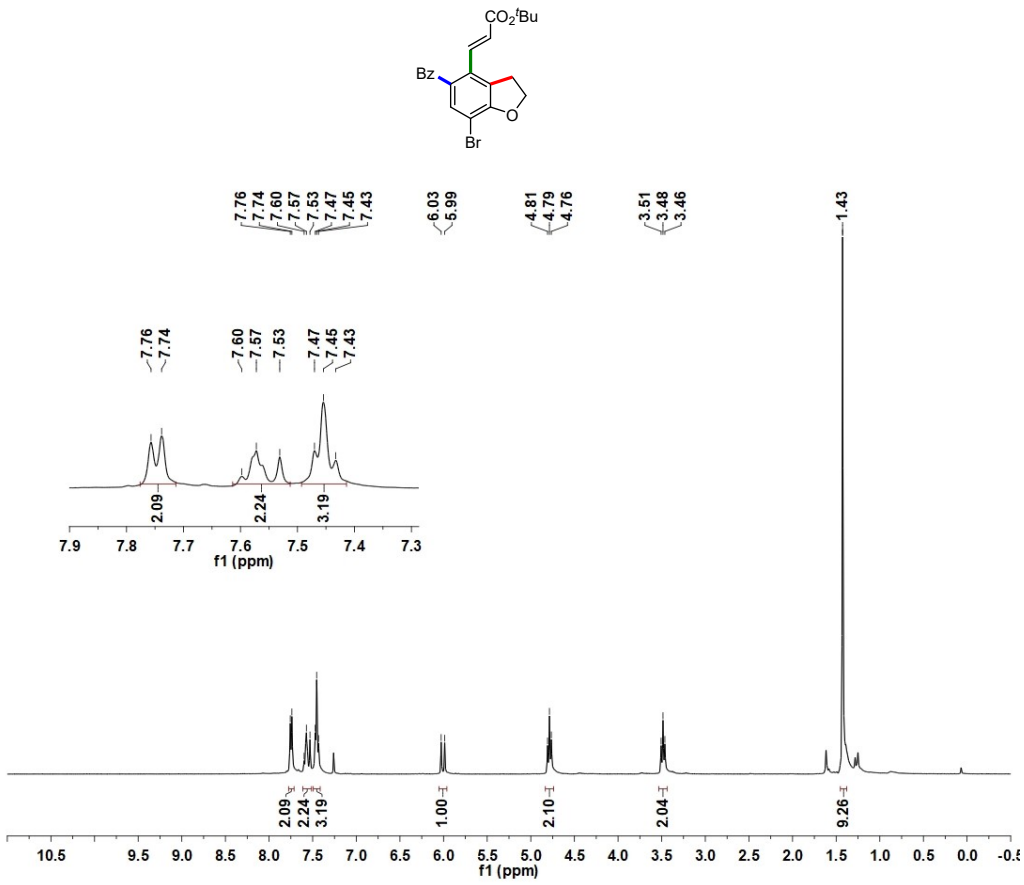


Figure S23. [1]H NMR spectrum of **4l**.

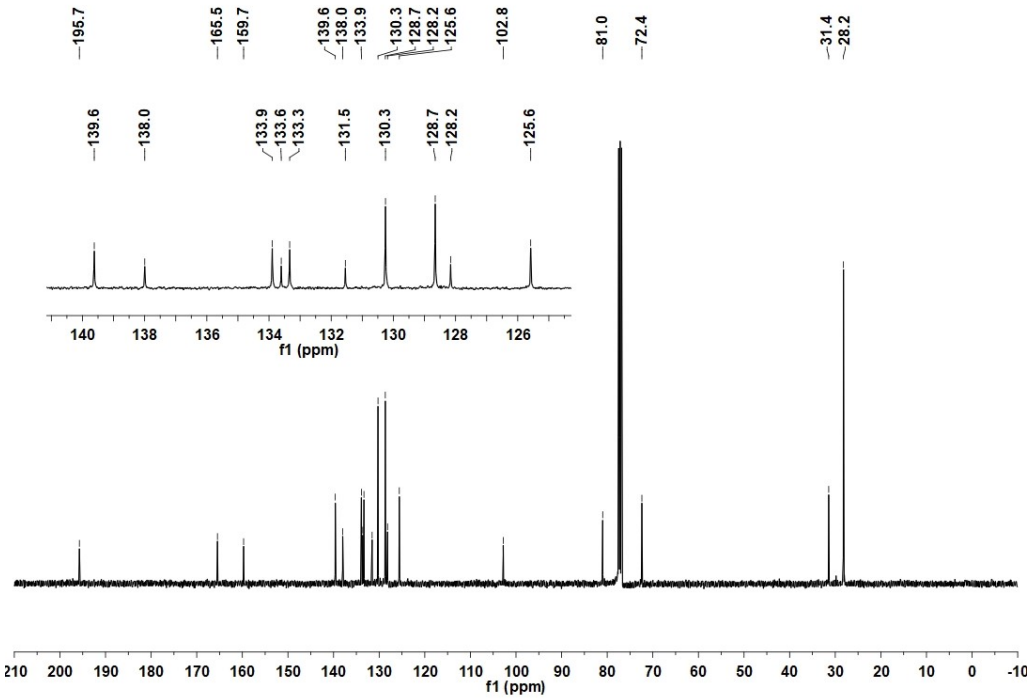


Figure S24. [13]C NMR spectrum of **4l**.

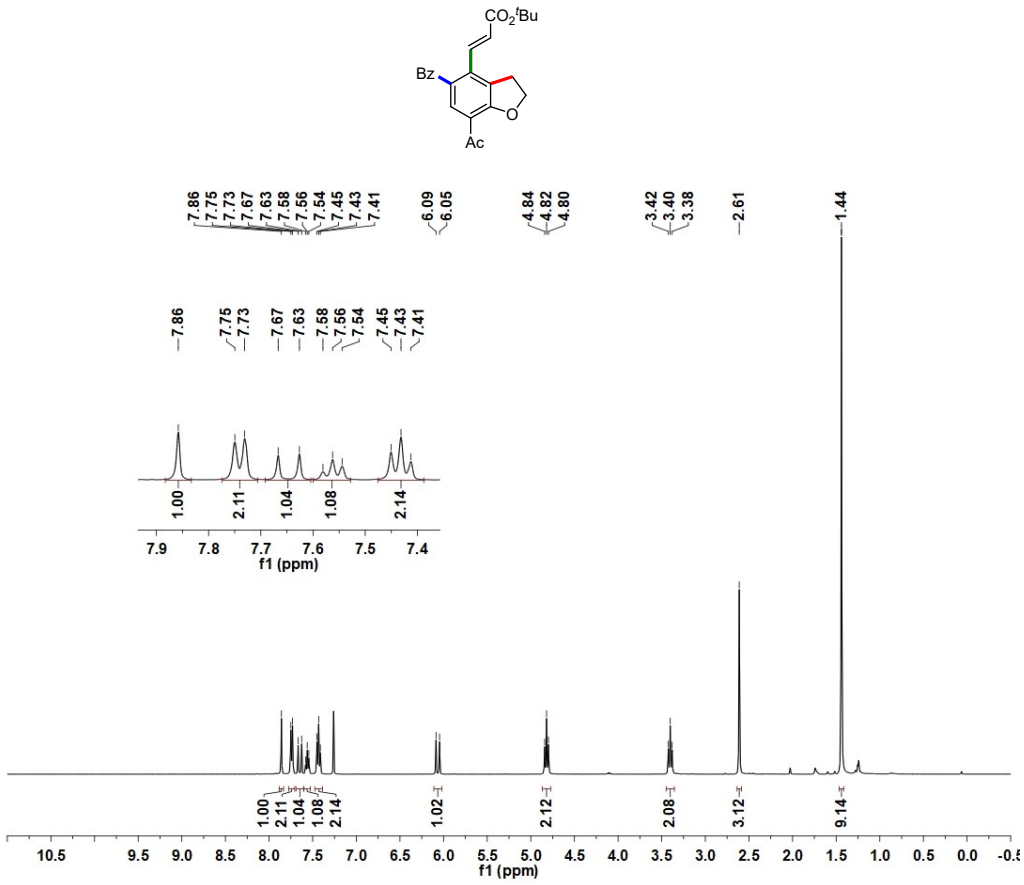


Figure S25. ^{1}H NMR spectrum of **4m**.

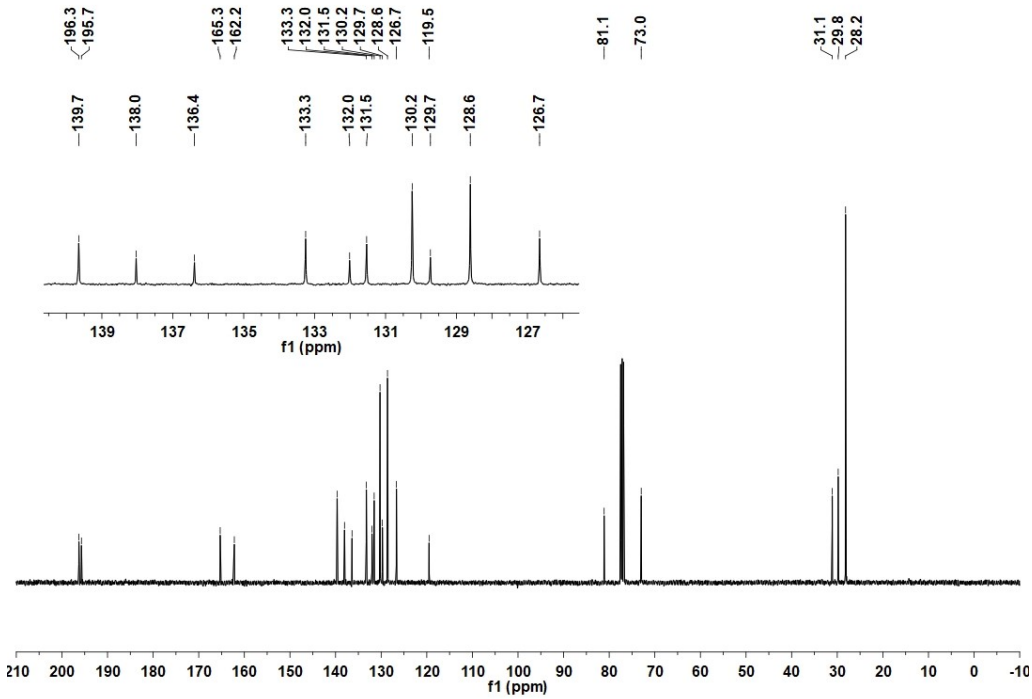


Figure S26. ^{13}C NMR spectrum of **4m**.

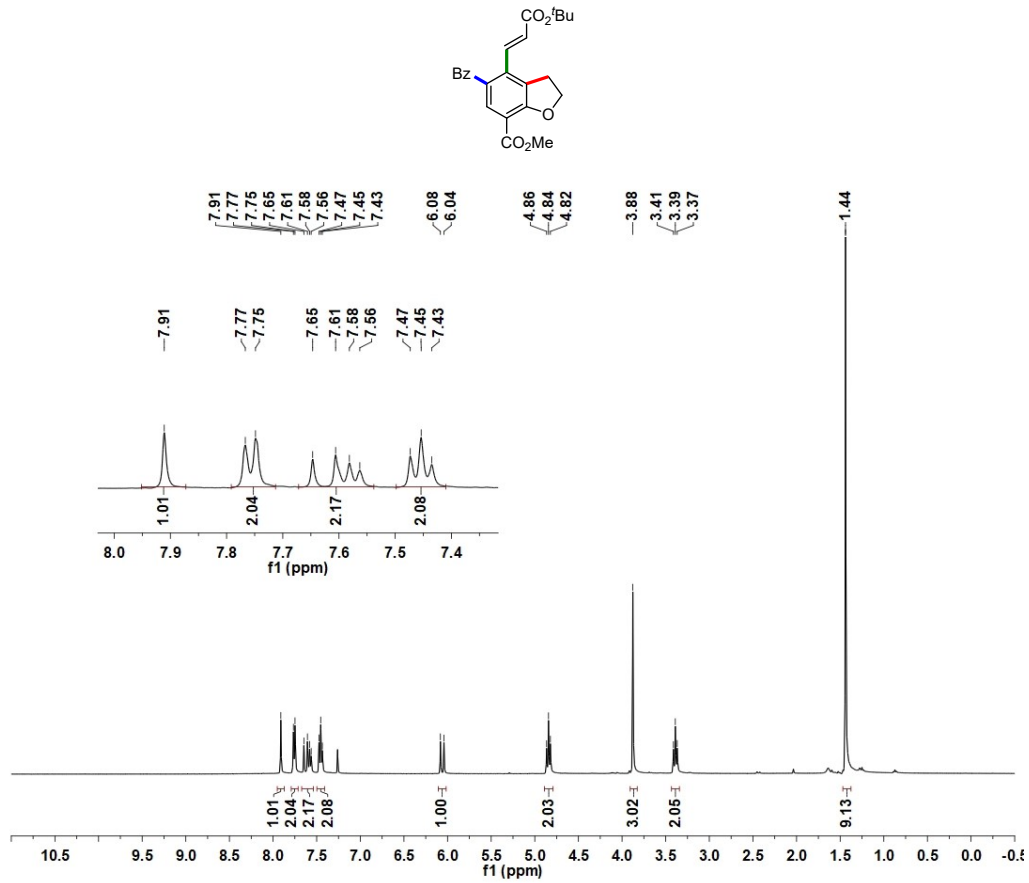


Figure S27. ^{1}H NMR spectrum of **4n**.

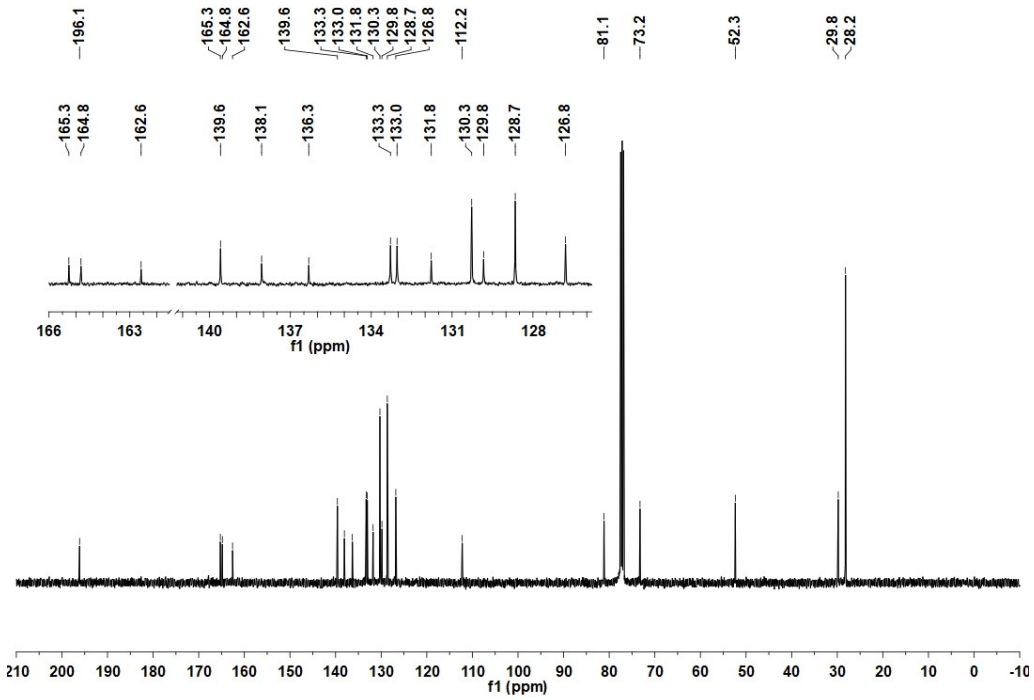


Figure S28. ^{13}C NMR spectrum of **4n**.

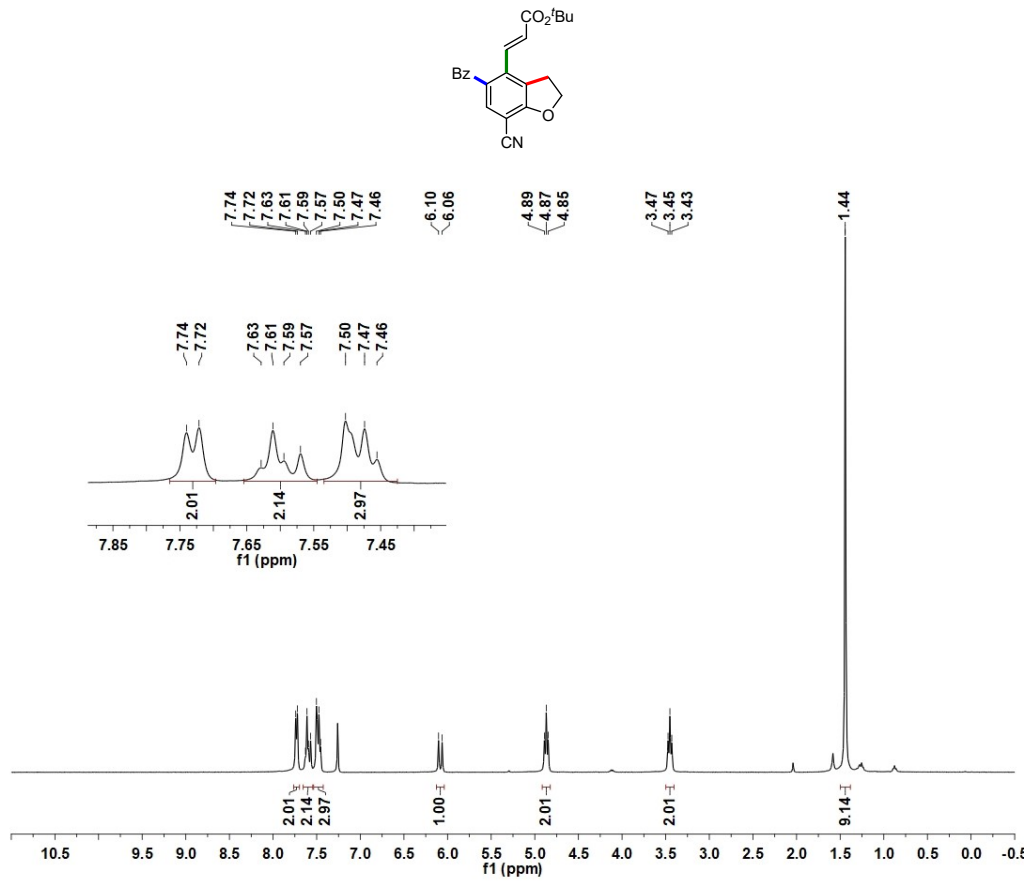


Figure S29. ^{1}H NMR spectrum of **4o**.

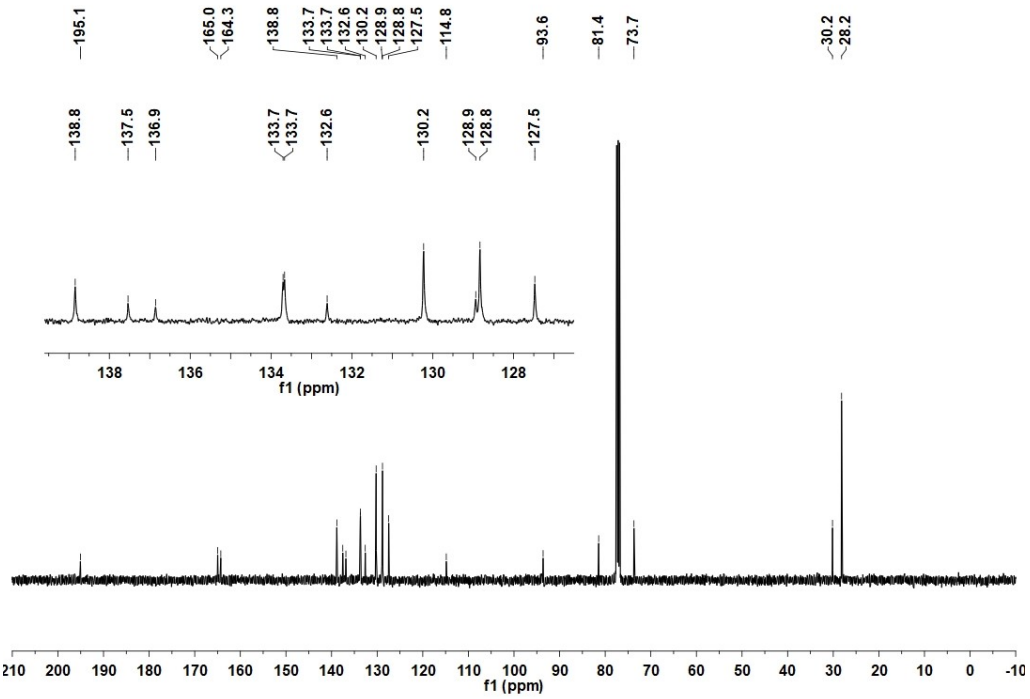


Figure S30. ^{13}C NMR spectrum of **4o**.

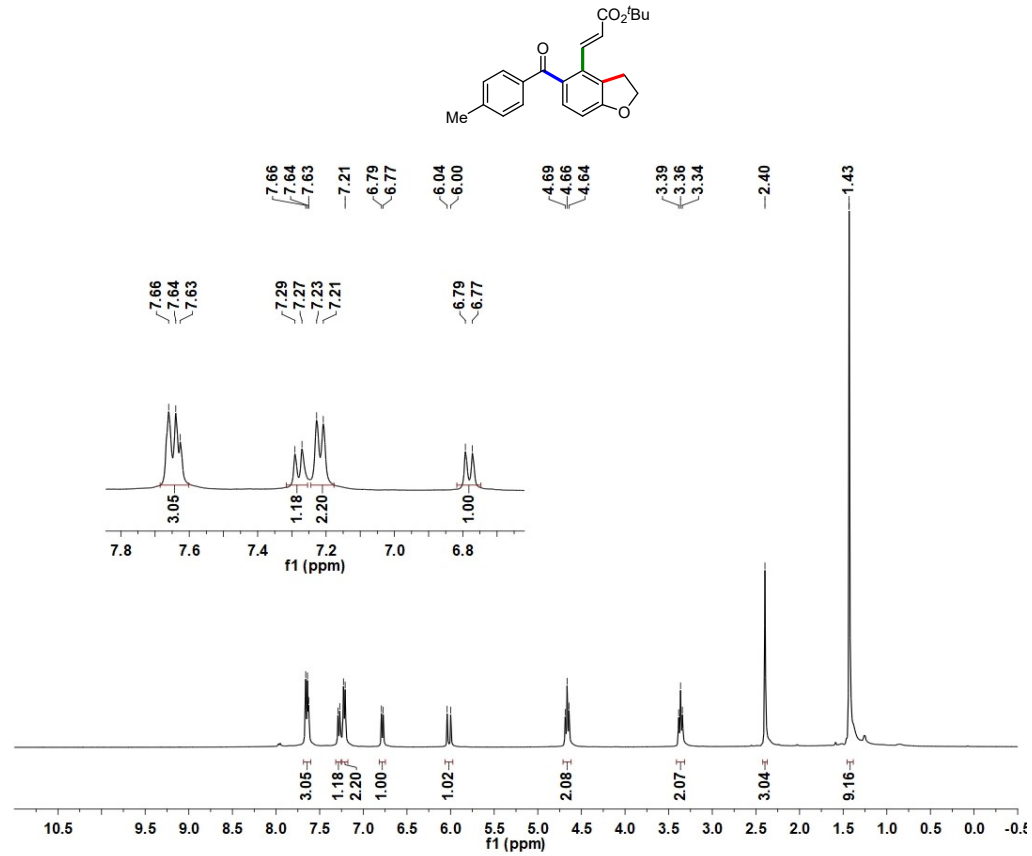


Figure S31. ^{1}H NMR spectrum of **4p**.

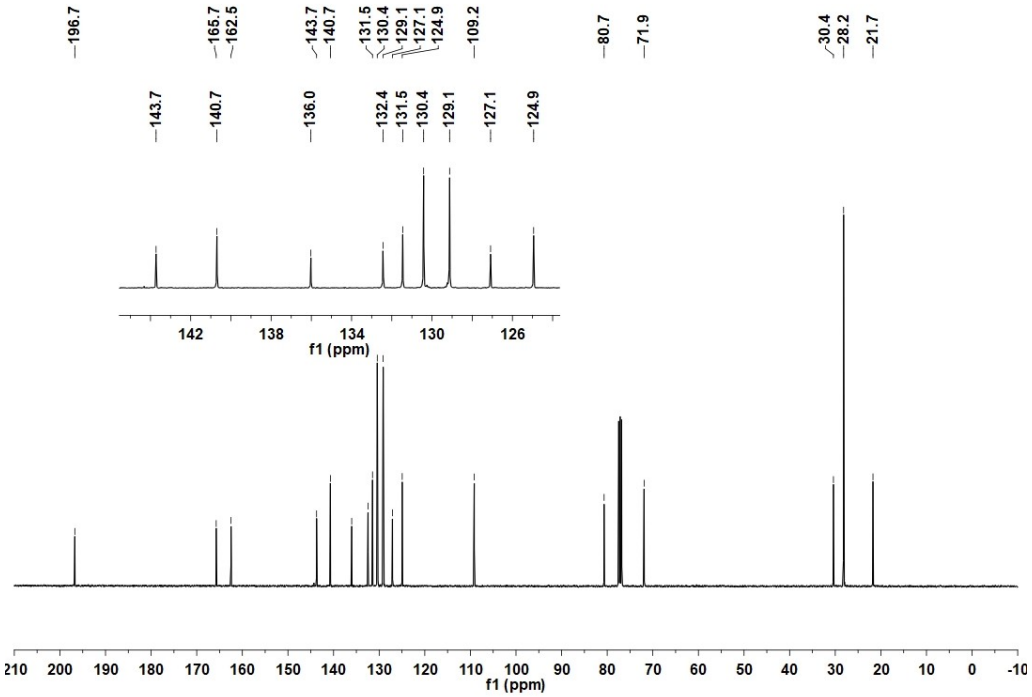


Figure S32. ^{13}C NMR spectrum of **4p**.

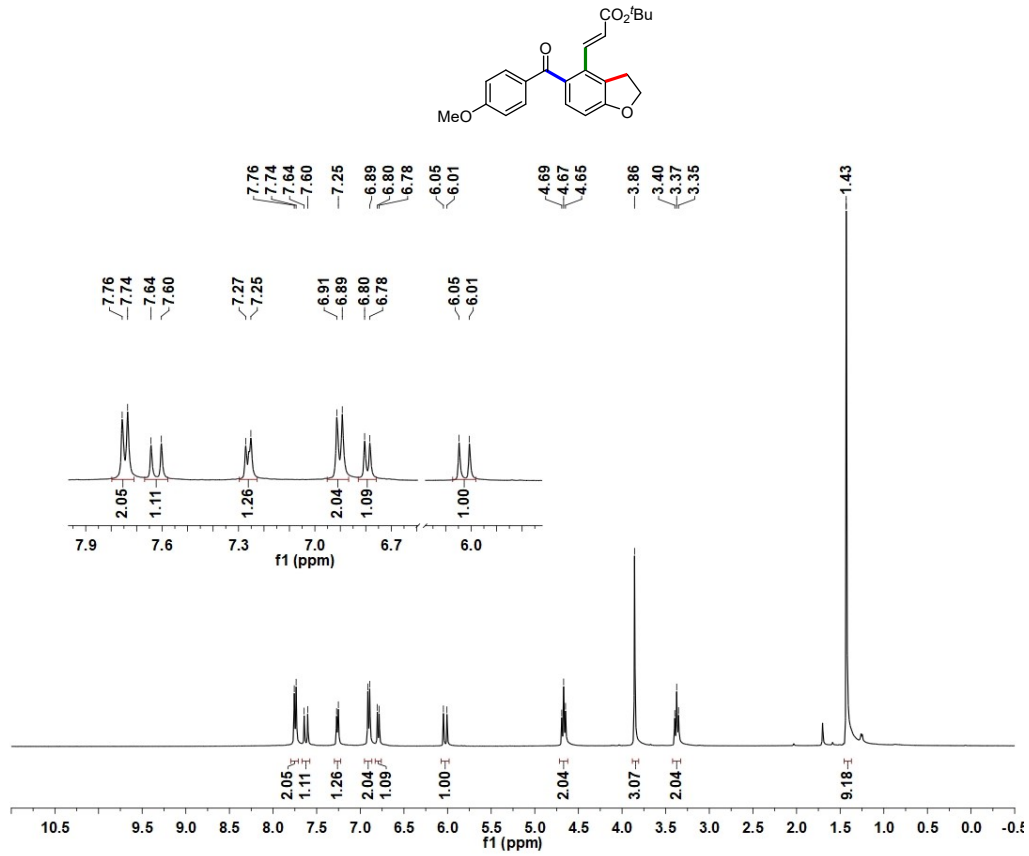


Figure S33. ^{1}H NMR spectrum of **4q**.

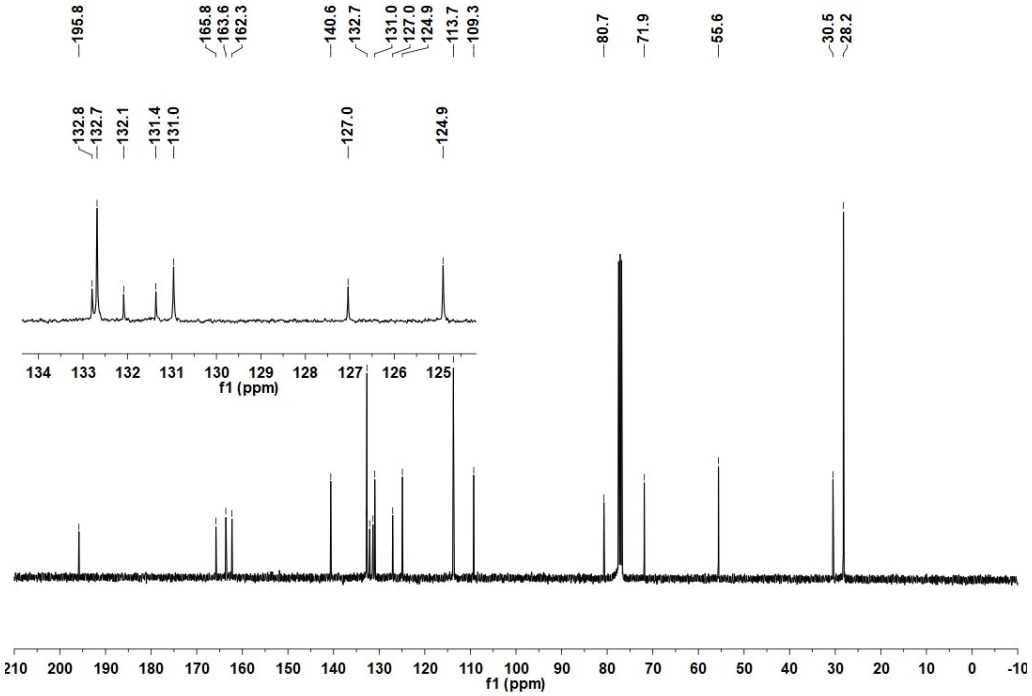


Figure S34. ^{13}C NMR spectrum of **4q**.

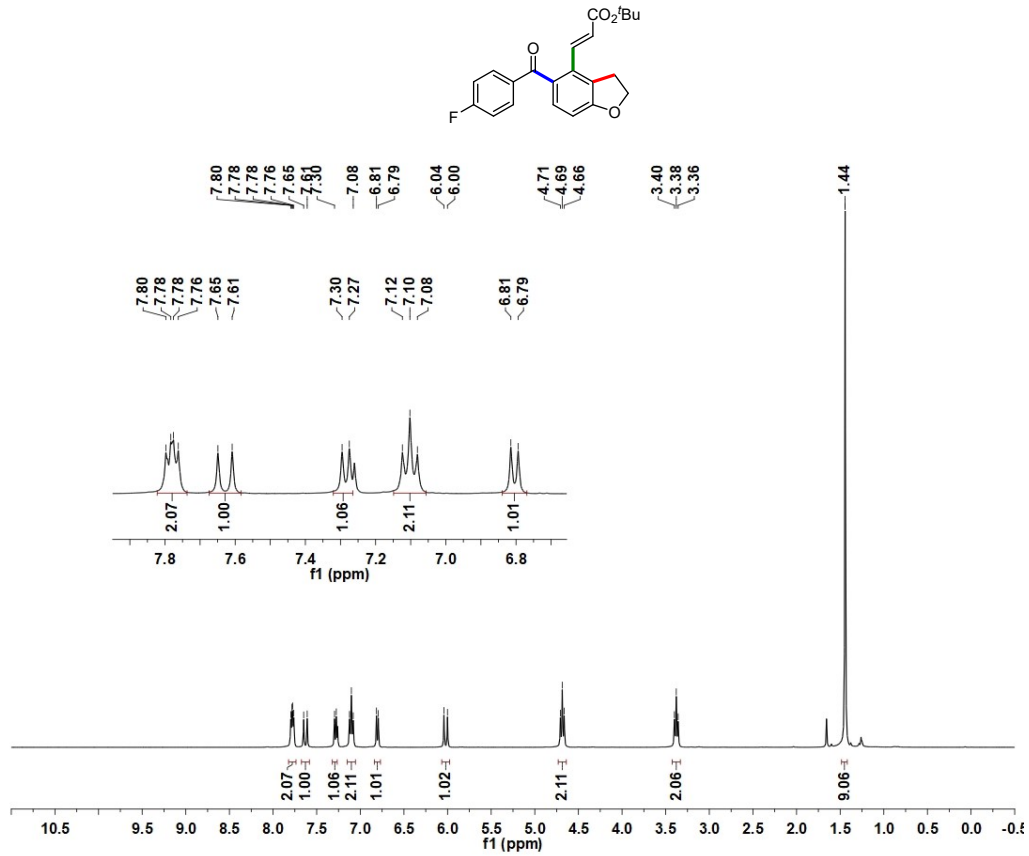


Figure S35. ^{1}H NMR spectrum of **4r**.

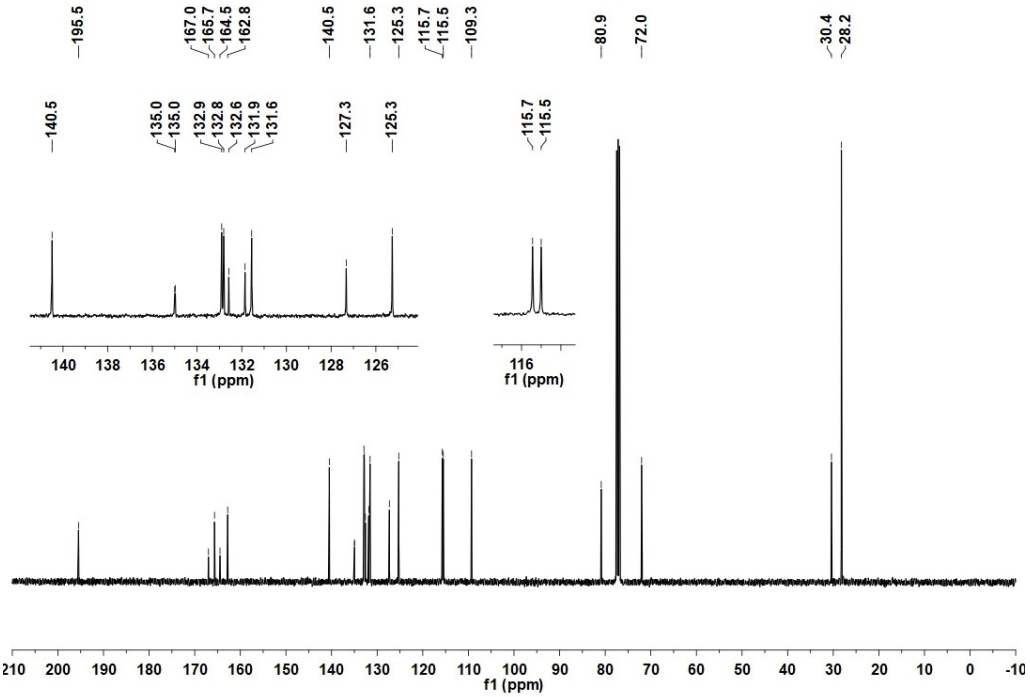


Figure S36. ^{13}C NMR spectrum of **4r**.

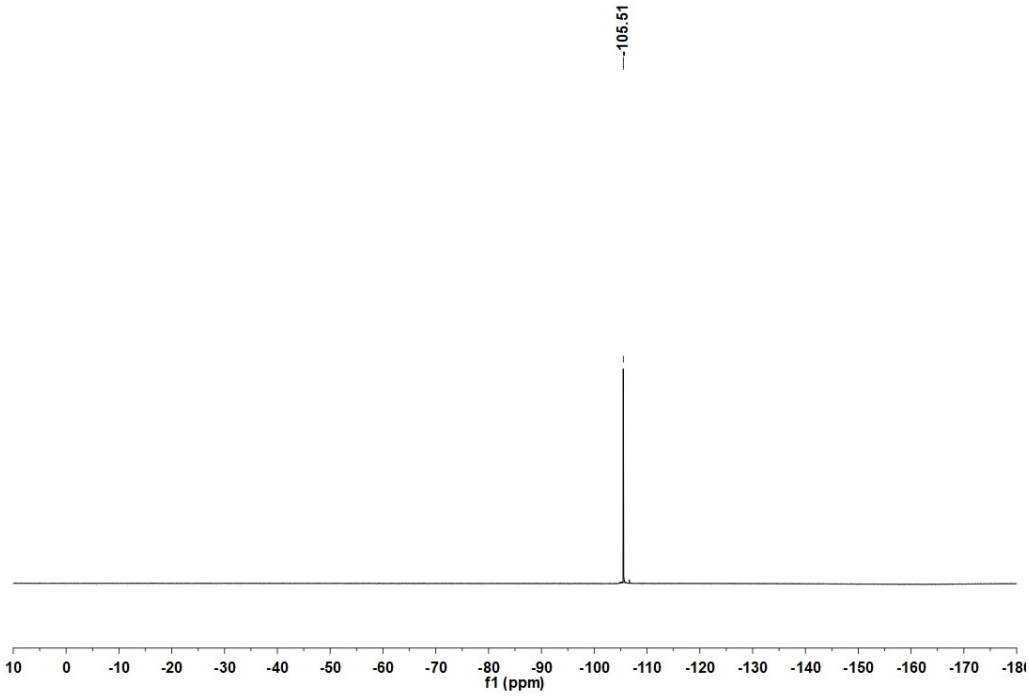


Figure S37. ^{19}F NMR spectrum of **4r**.

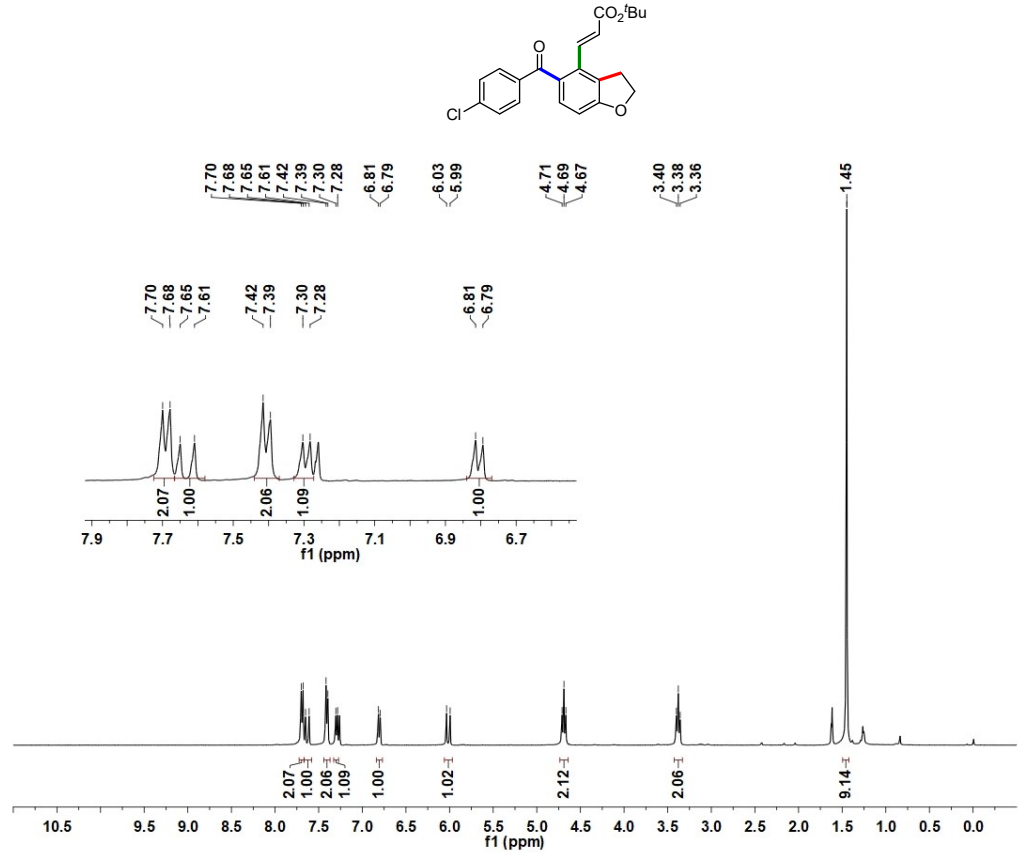


Figure S38. ^{1}H NMR spectrum of **4s**.

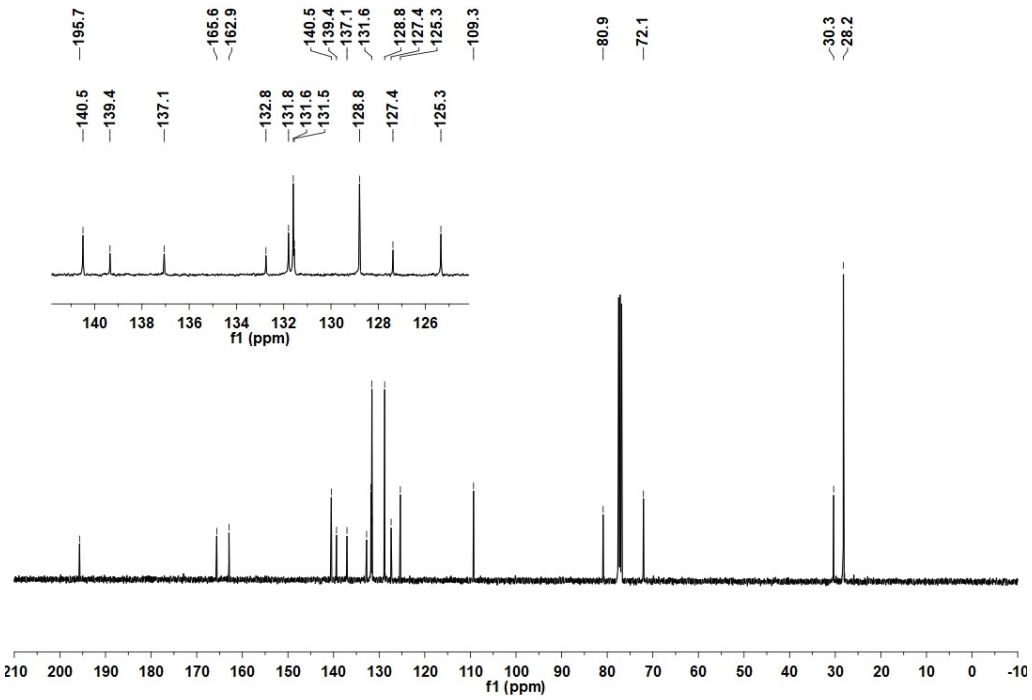


Figure S39. ^{13}C NMR spectrum of **4s**.

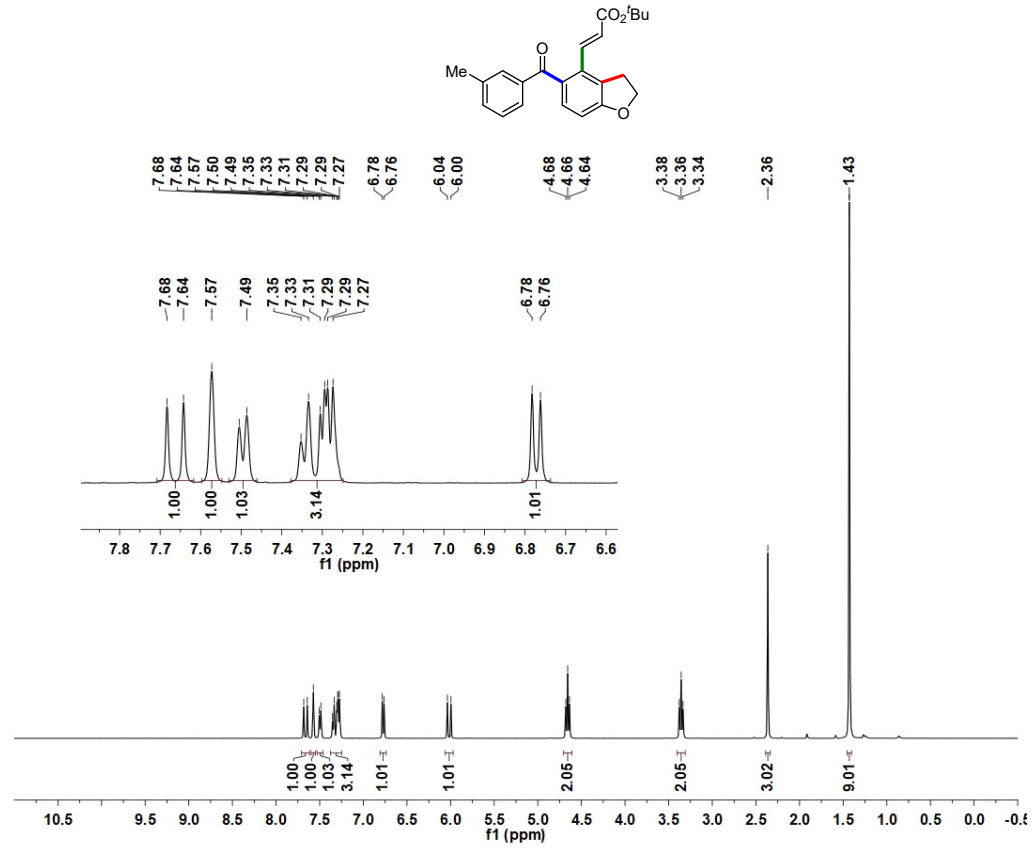


Figure S40. ^{1}H NMR spectrum of **4t**.

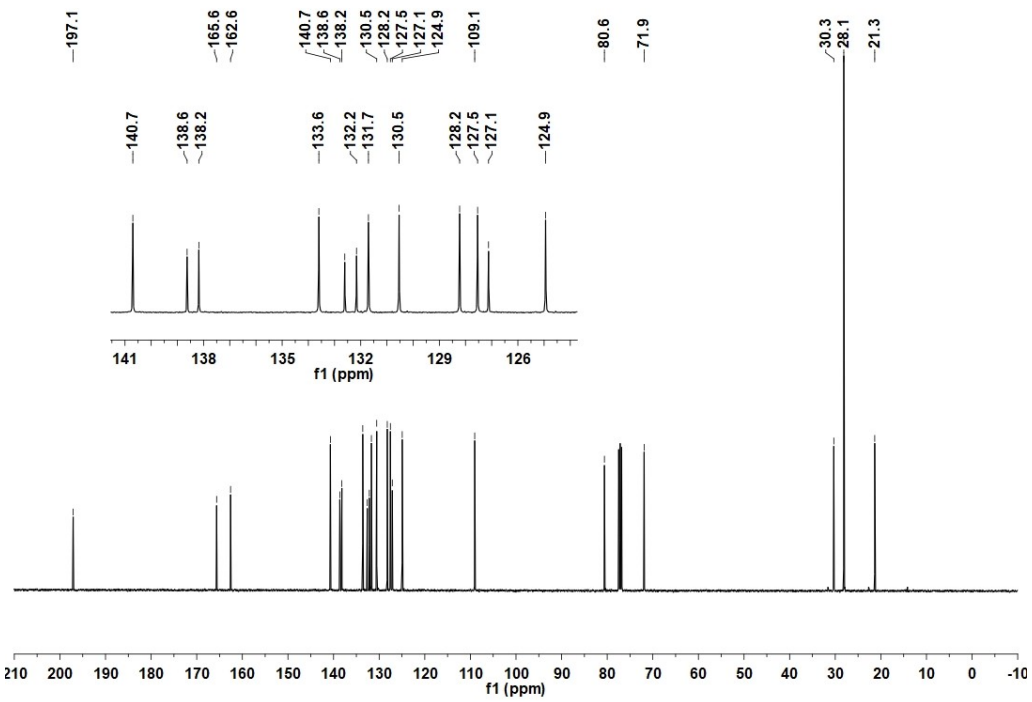


Figure S41. ^{13}C NMR spectrum of **4t**.

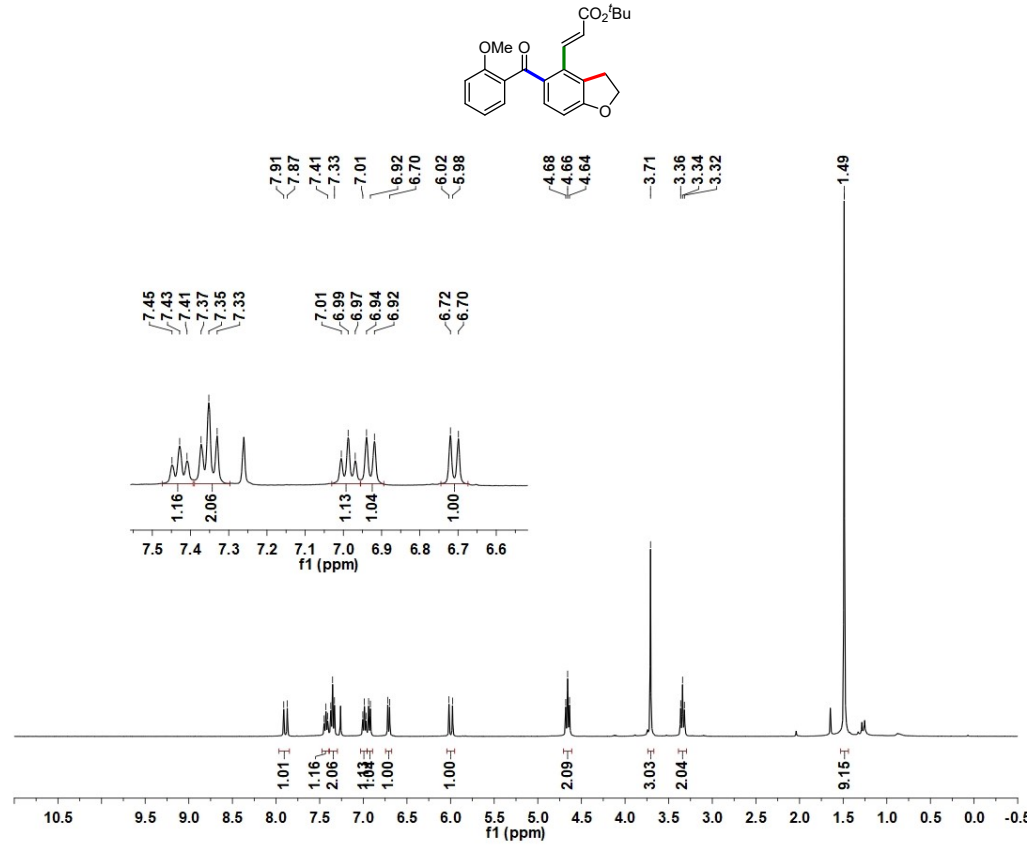


Figure S42. ^{1}H NMR spectrum of **4u**.

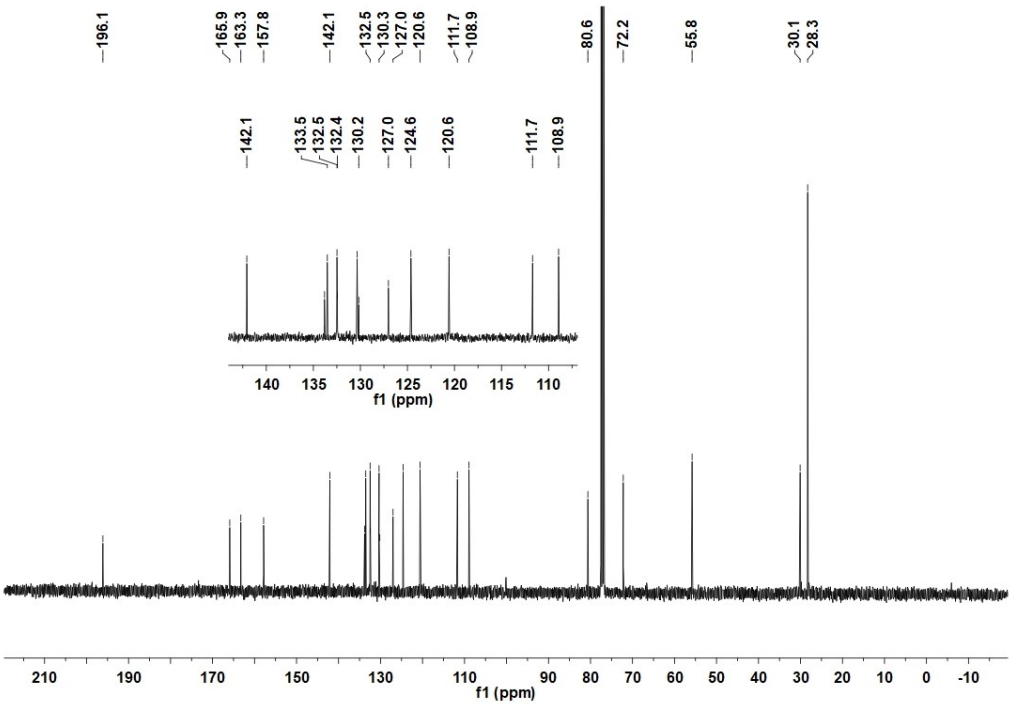


Figure S43. ^{13}C NMR spectrum of **4u**.

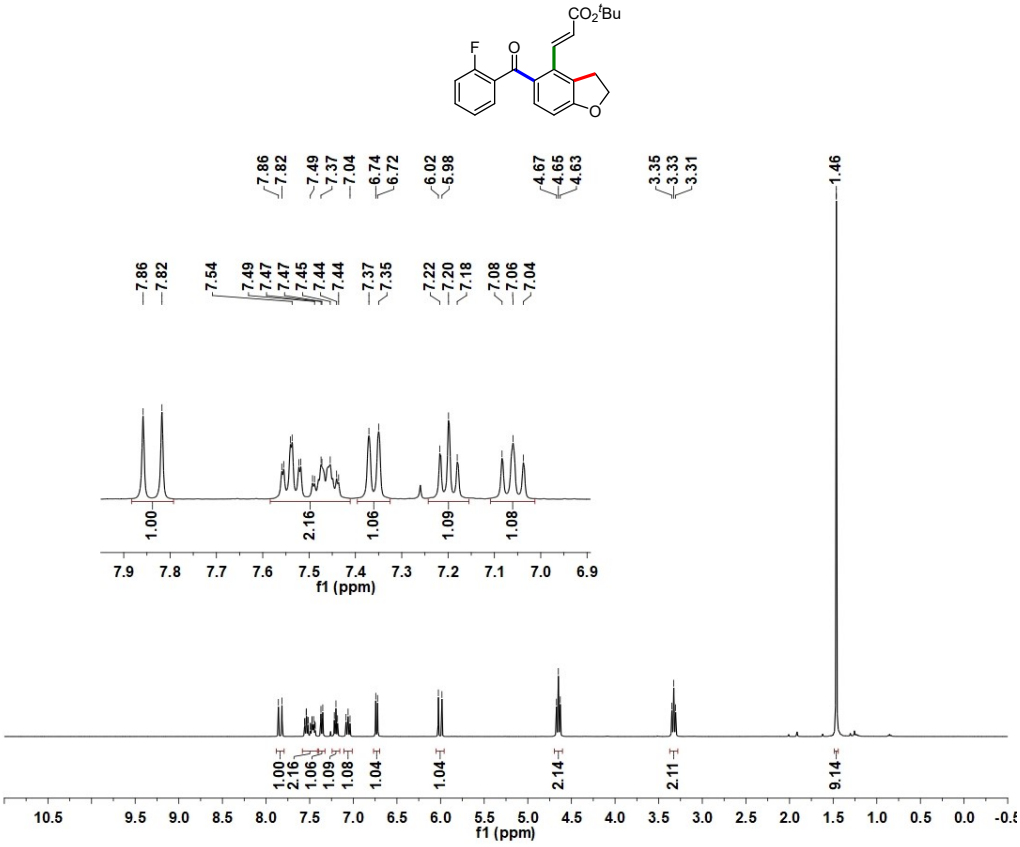


Figure S44. ^{1}H NMR spectrum of **4v**.

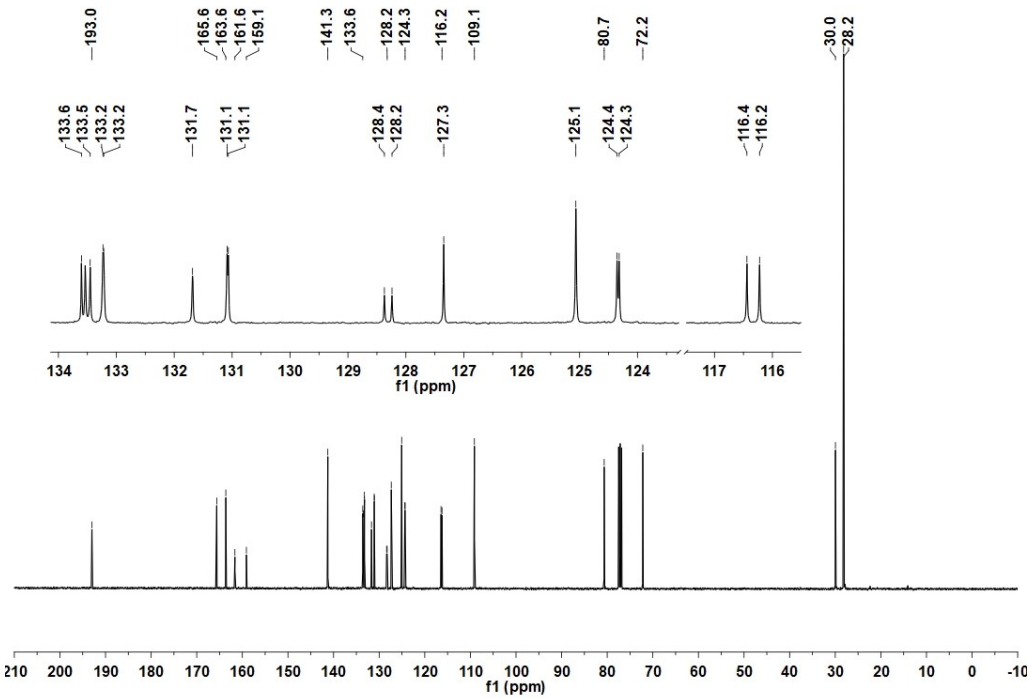


Figure S45. ^{13}C NMR spectrum of **4v**.

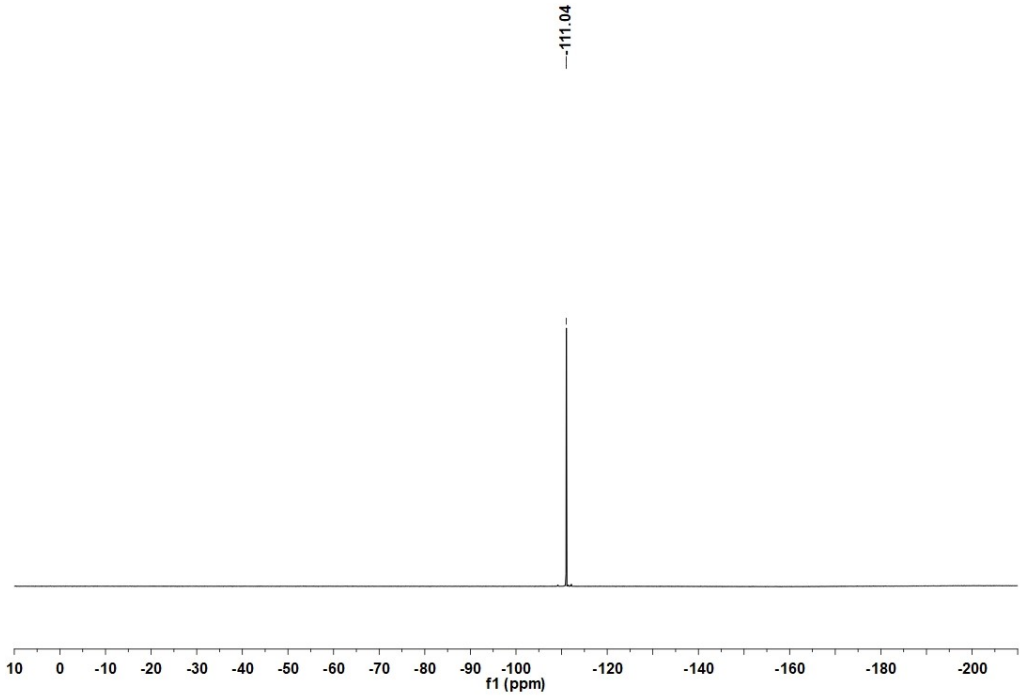


Figure S46. ^{19}F NMR spectrum of **4v**.

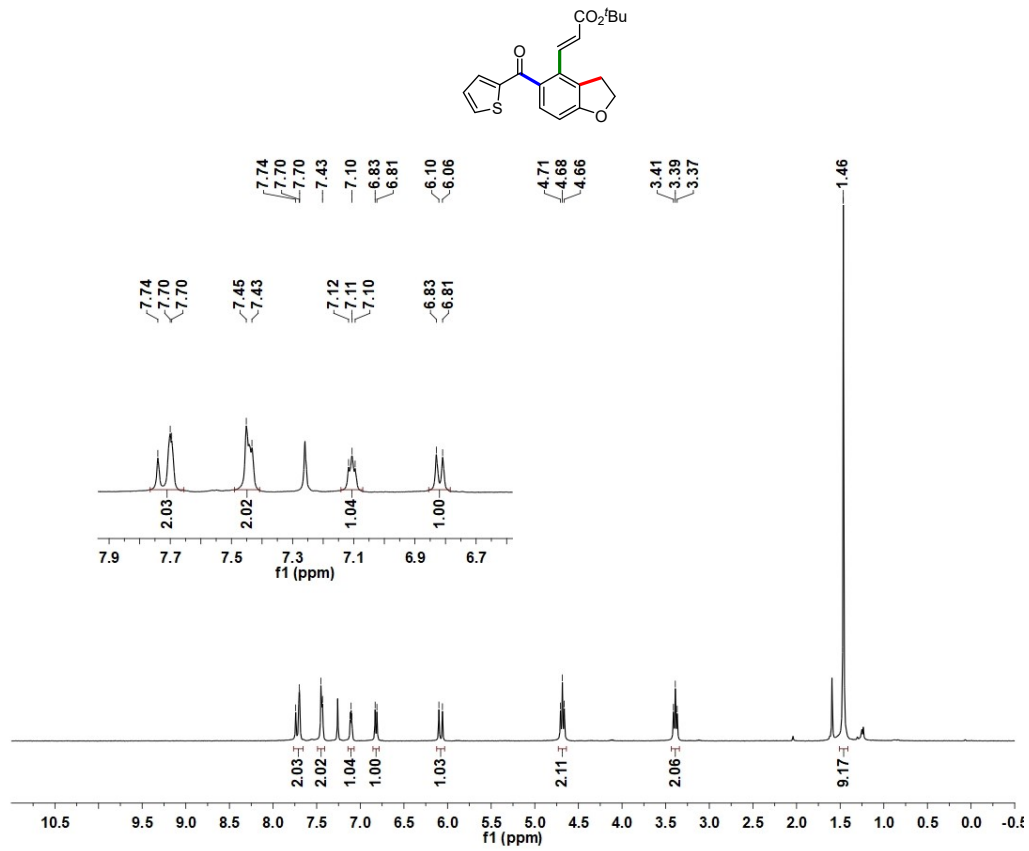


Figure S47. [1]H NMR spectrum of **4w**.

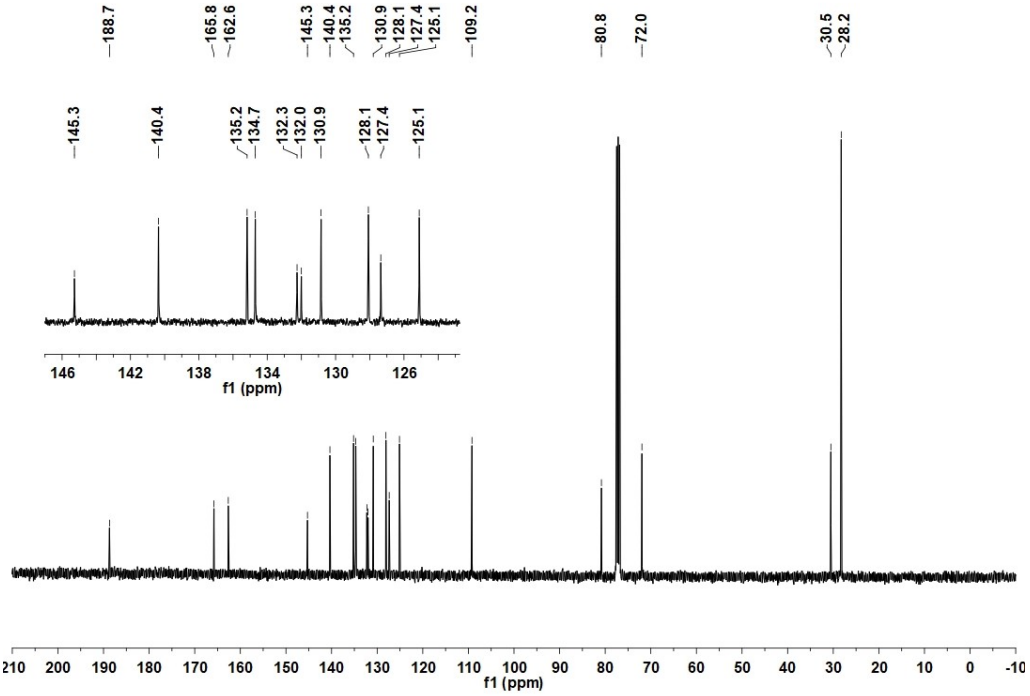


Figure S48. [13]C NMR spectrum of **4w**.

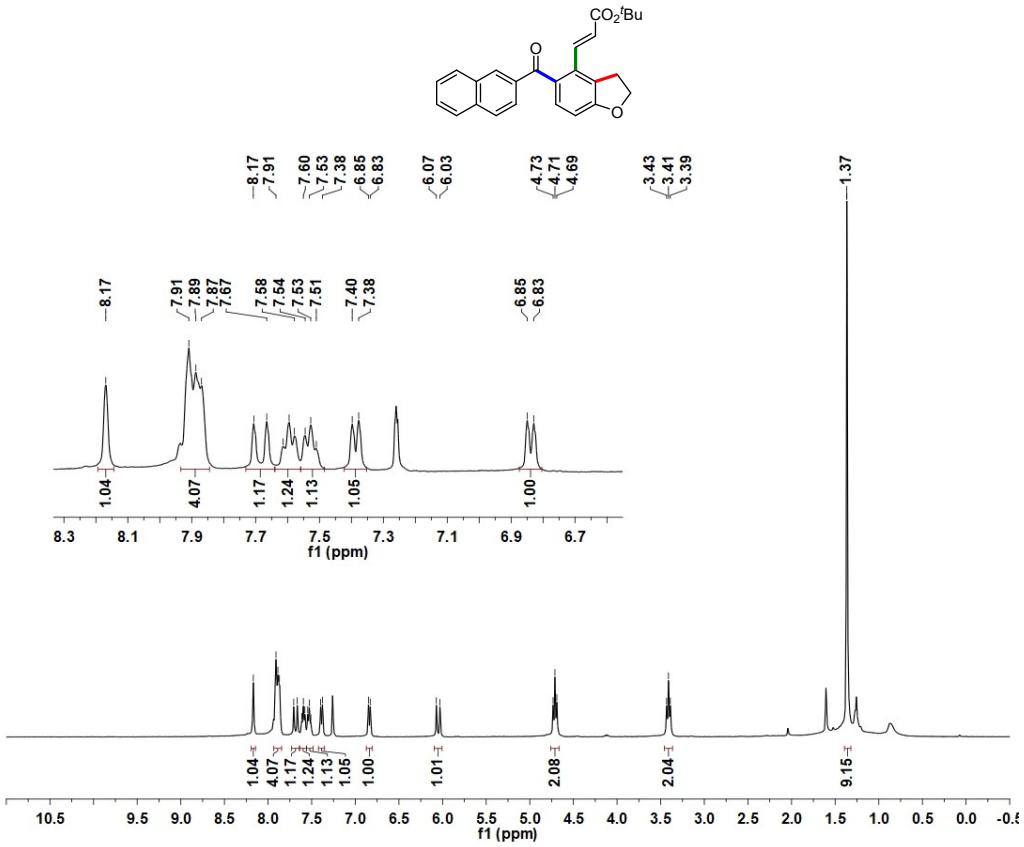


Figure S49. ^{1}H NMR spectrum of **4x**.

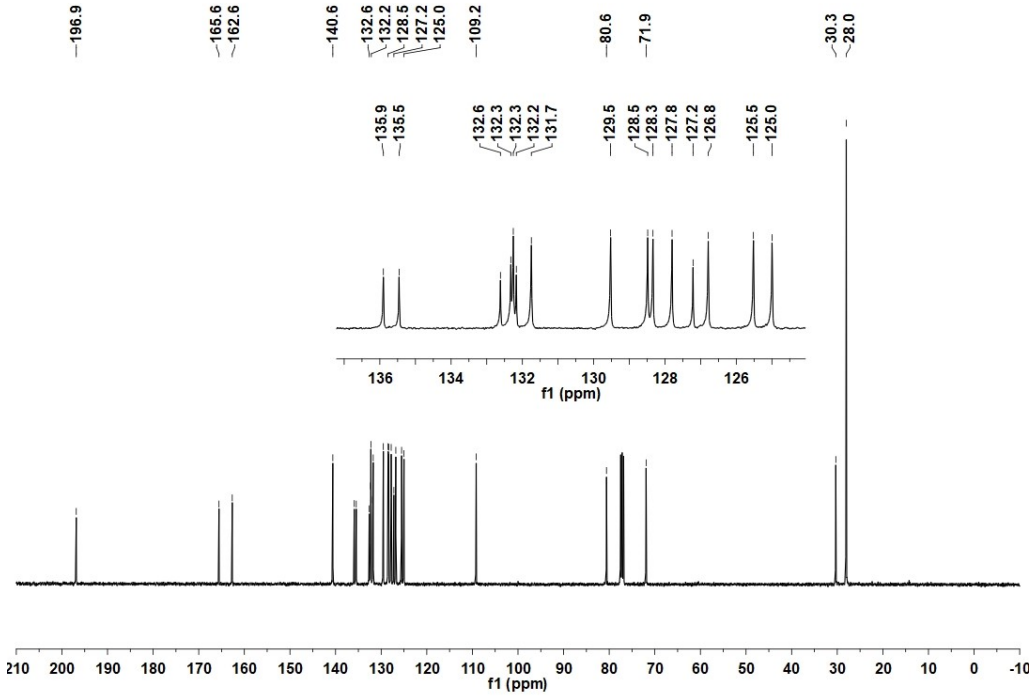


Figure S50. ^{13}C NMR spectrum of **4x**.

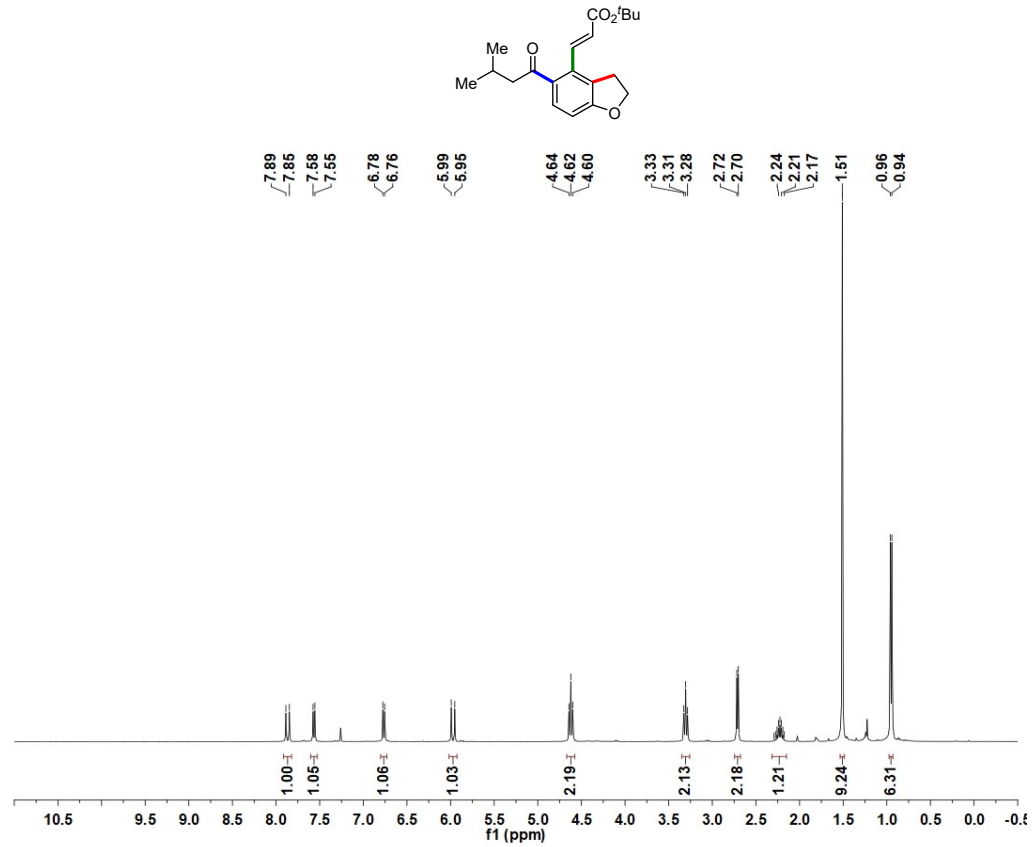


Figure S51. ^{1}H NMR spectrum of **4y**.

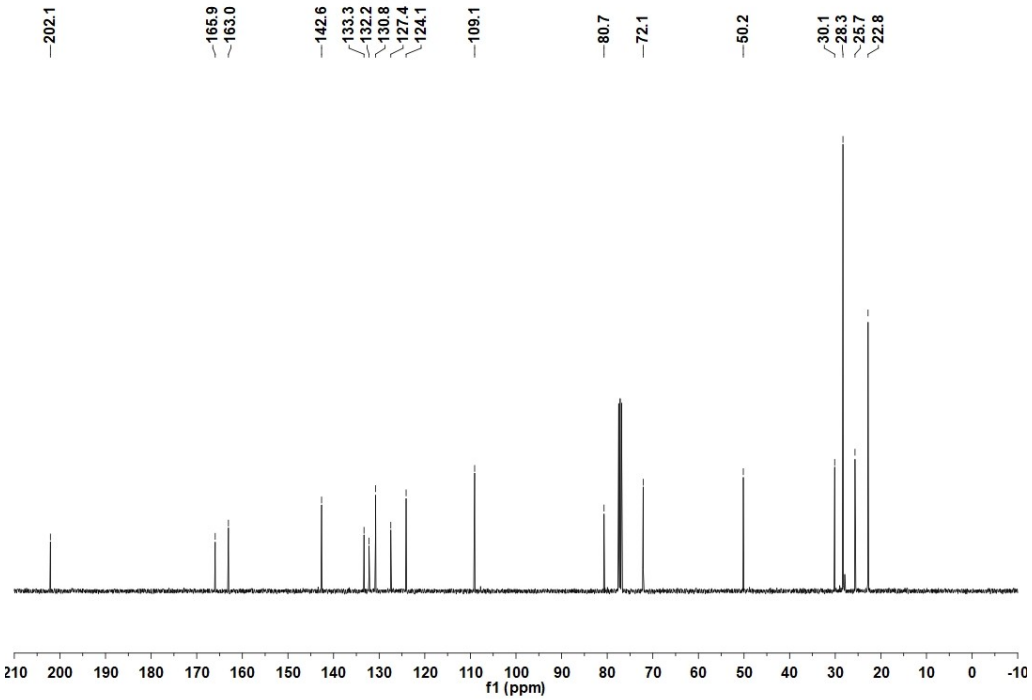


Figure S52. ^{13}C NMR spectrum of **4y**.

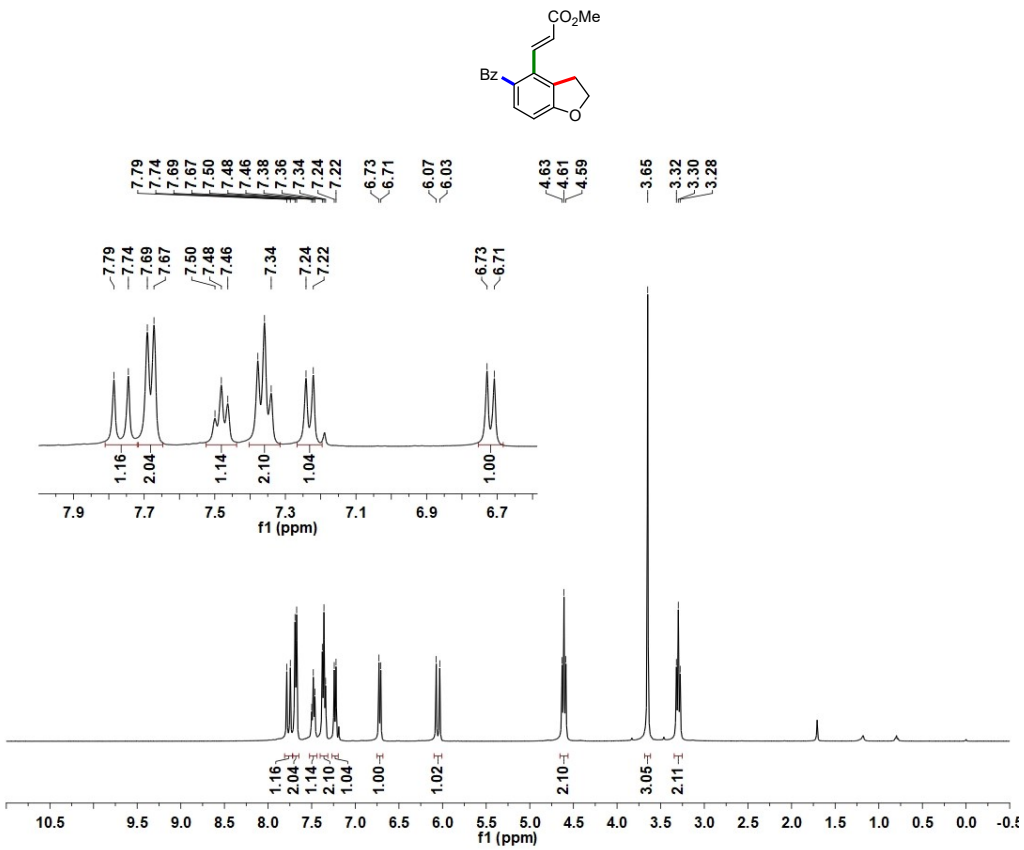


Figure S53. ^{1}H NMR spectrum of **4z**.

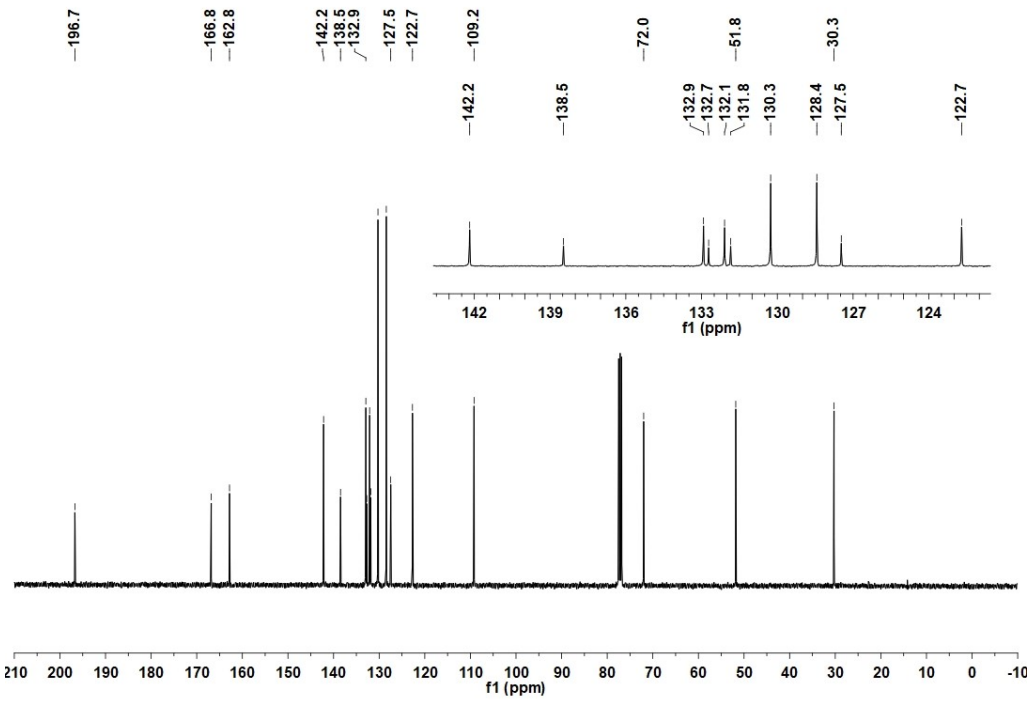


Figure S54. ^{13}C NMR spectrum of **4z**.

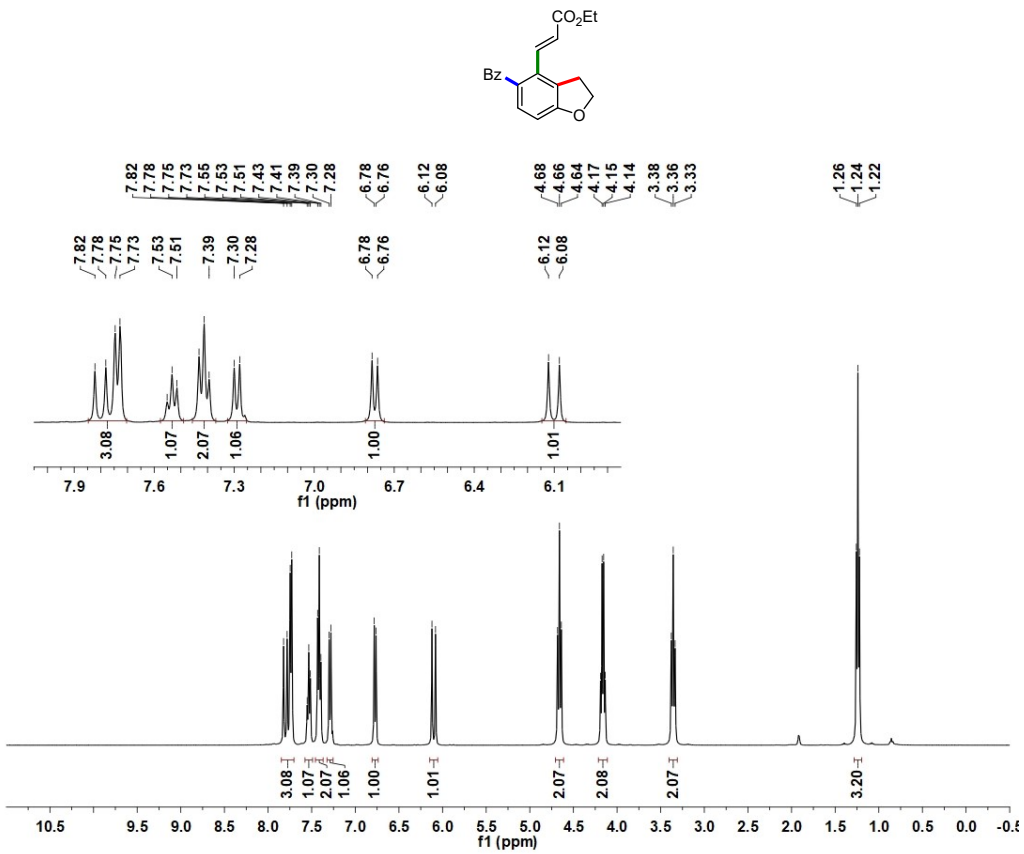


Figure S55. ^{1}H NMR spectrum of **4aa**.

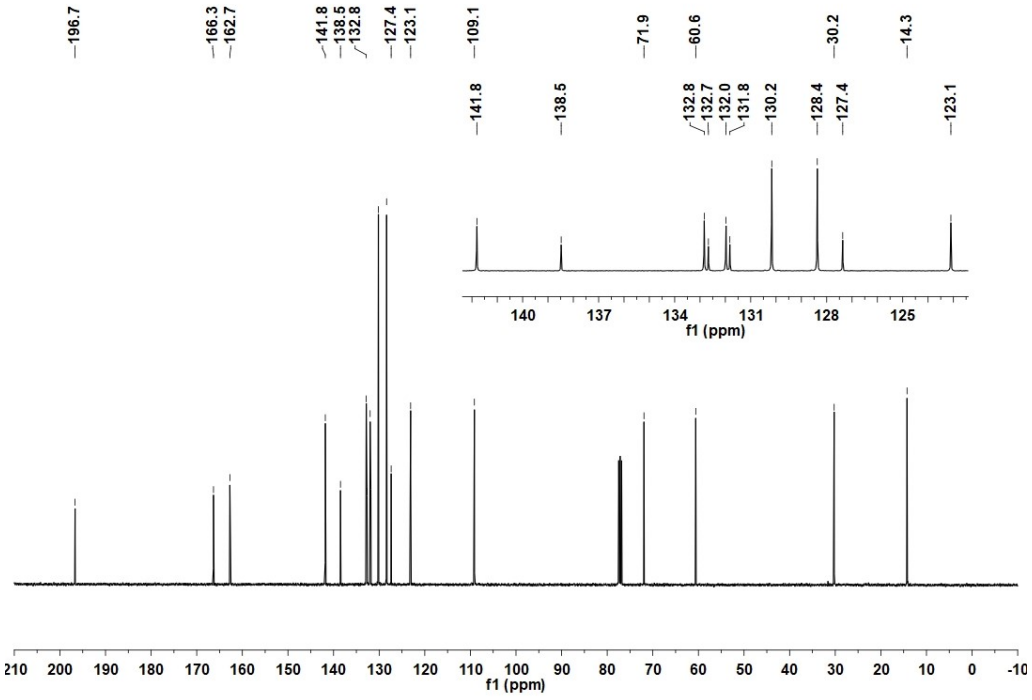


Figure S56. ^{13}C NMR spectrum of **4aa**.

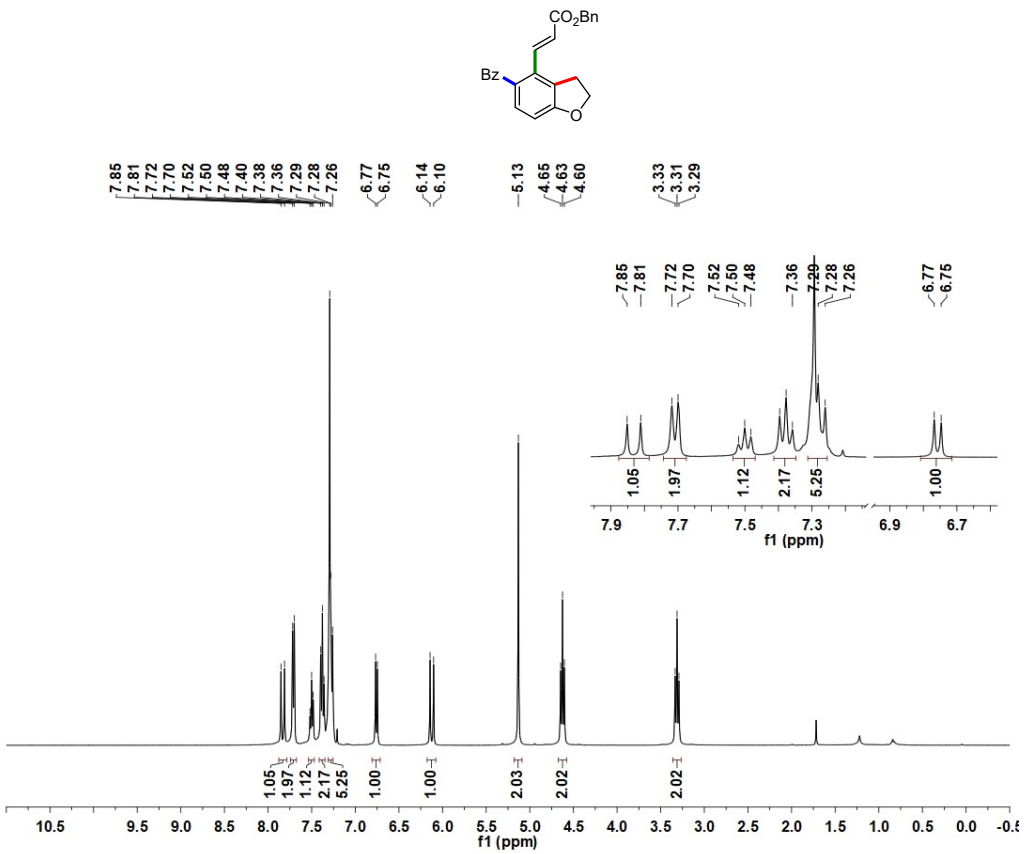


Figure S57. ^{1}H NMR spectrum of **4ab**.

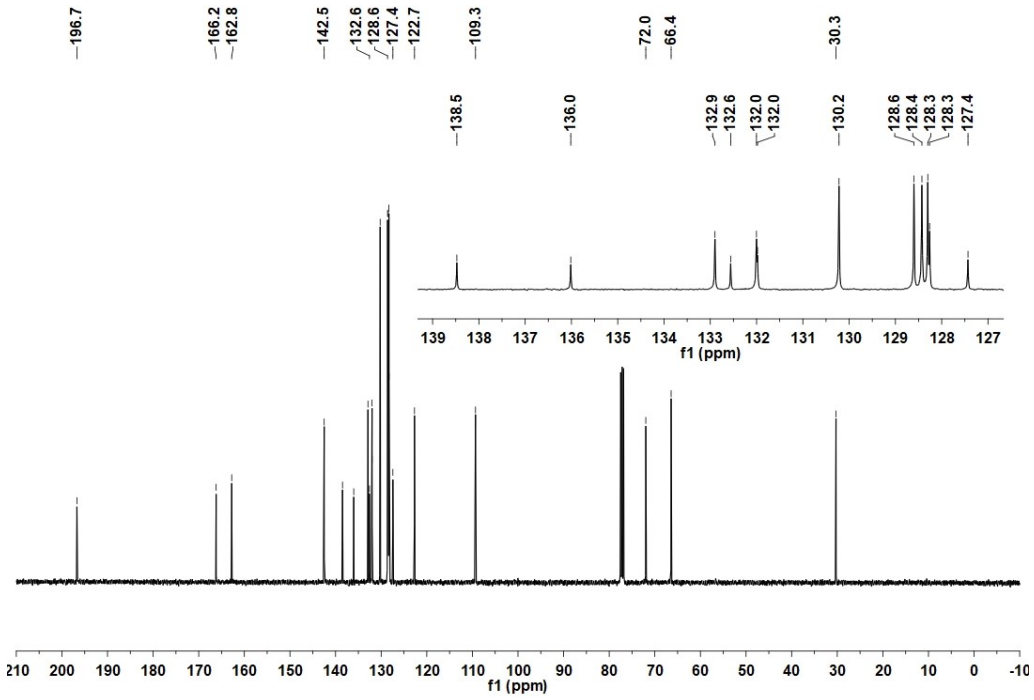


Figure S58. ^{13}C NMR spectrum of **4ab**.

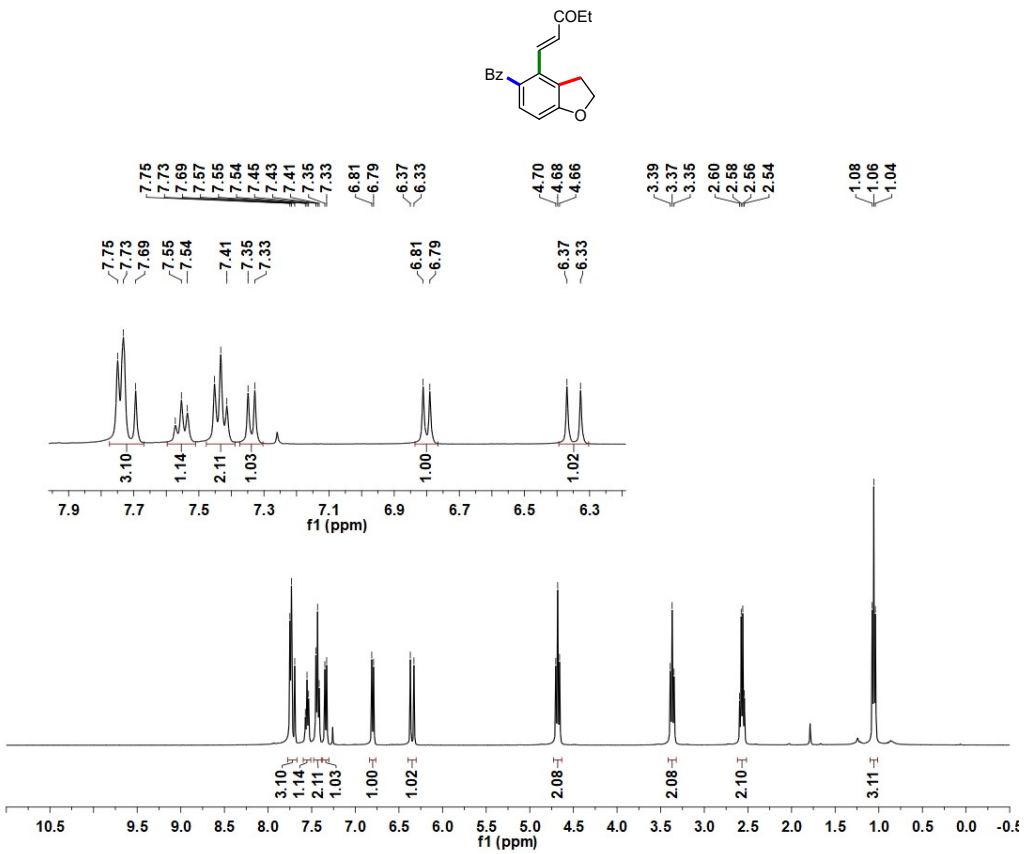


Figure S59. ^{1}H NMR spectrum of **4ac**.

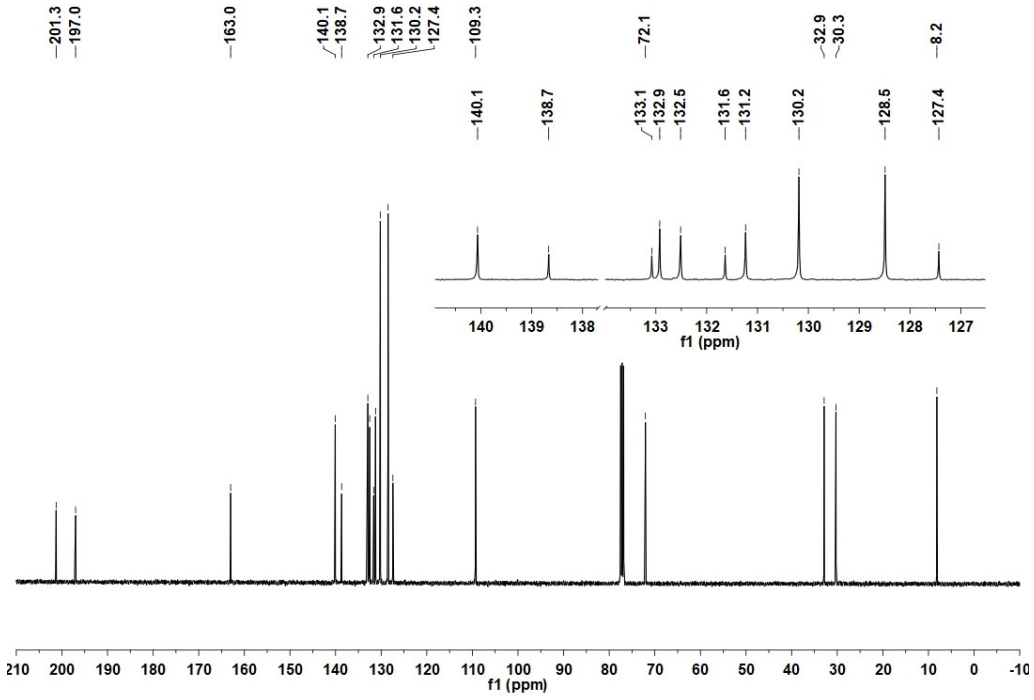


Figure S60. ^{13}C NMR spectrum of **4ac**.

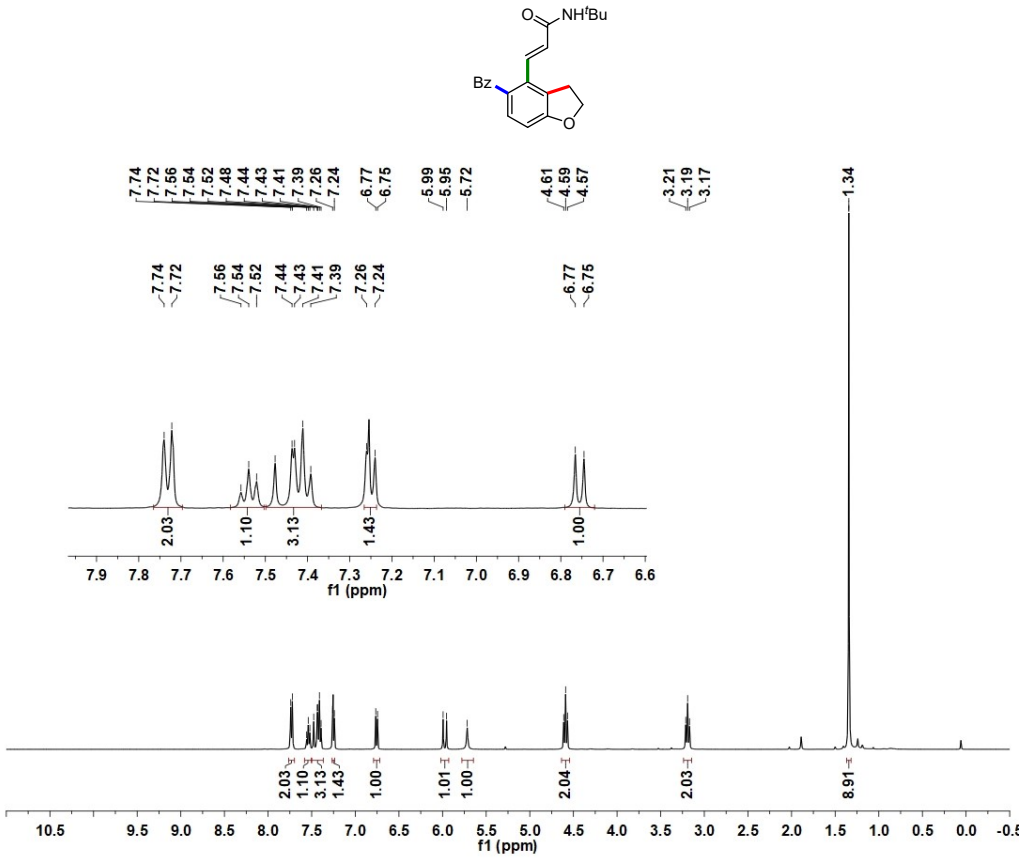


Figure S61. ^{1}H NMR spectrum of **4ad**.

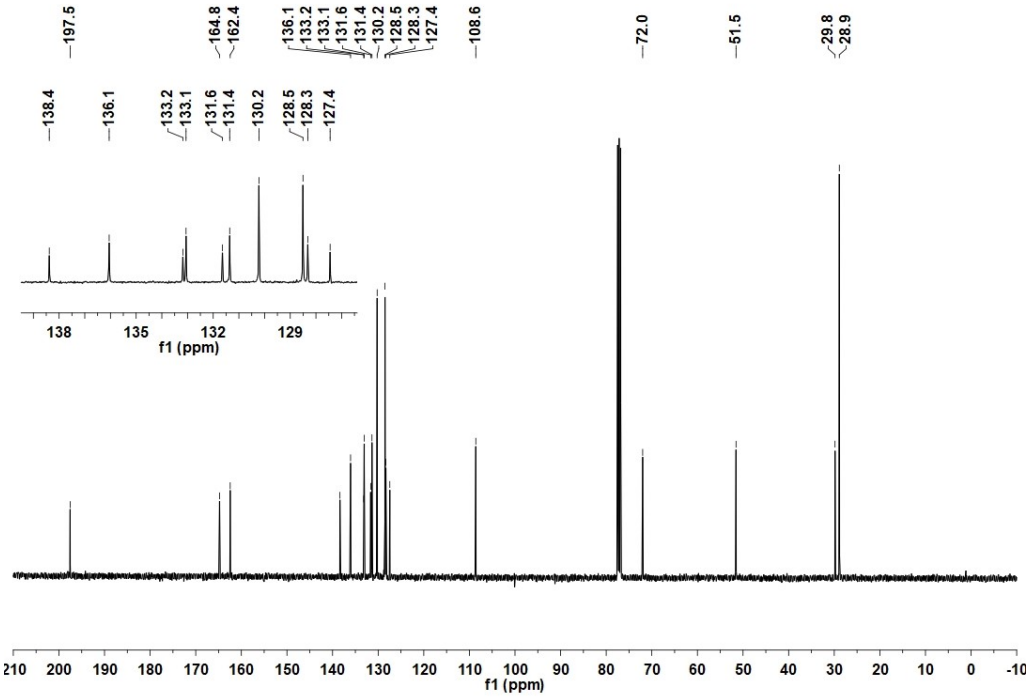


Figure S62. ^{13}C NMR spectrum of **4ad**.

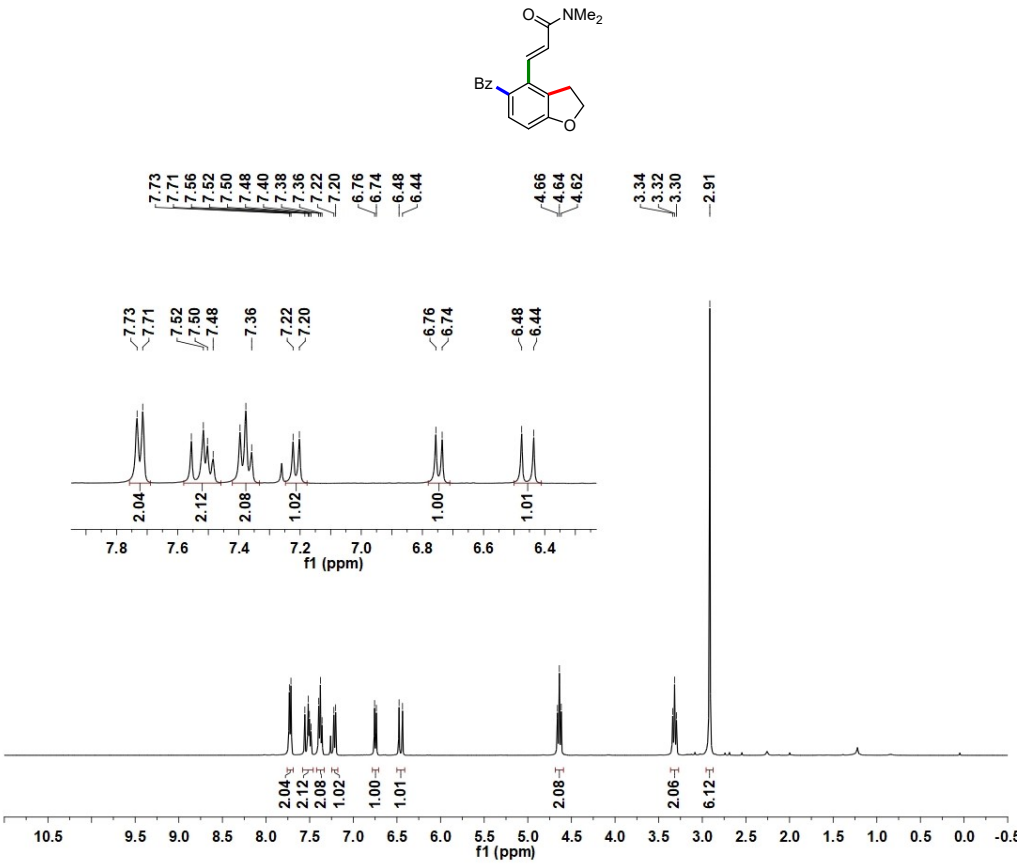


Figure S63. [1]H NMR spectrum of **4ae**.

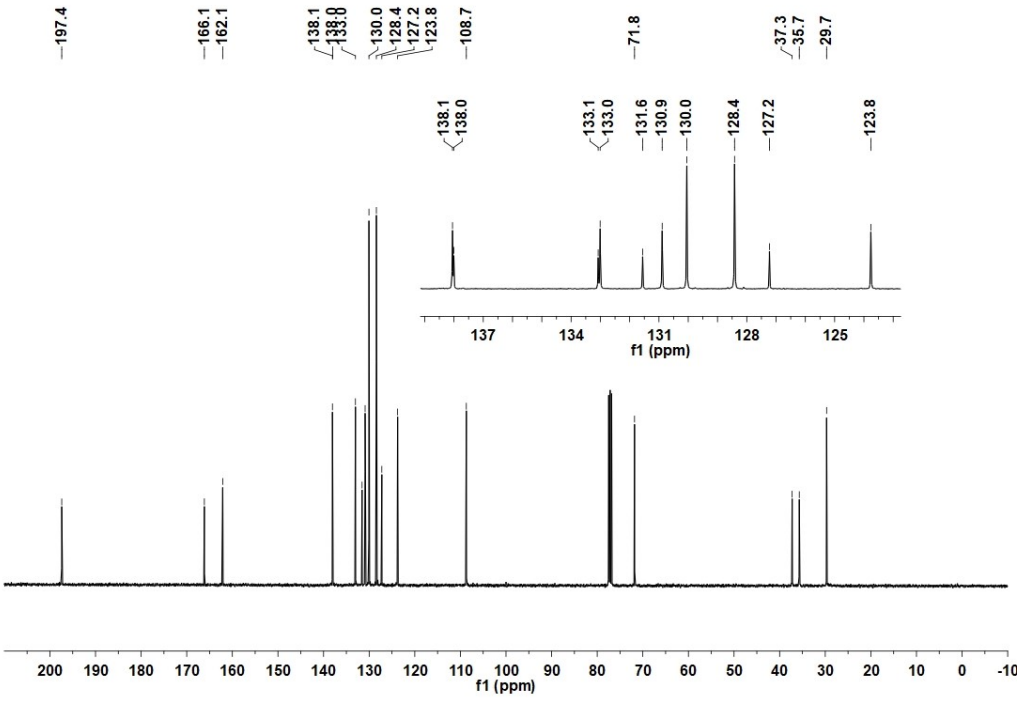


Figure S64. [13]C NMR spectrum of **4ae**.

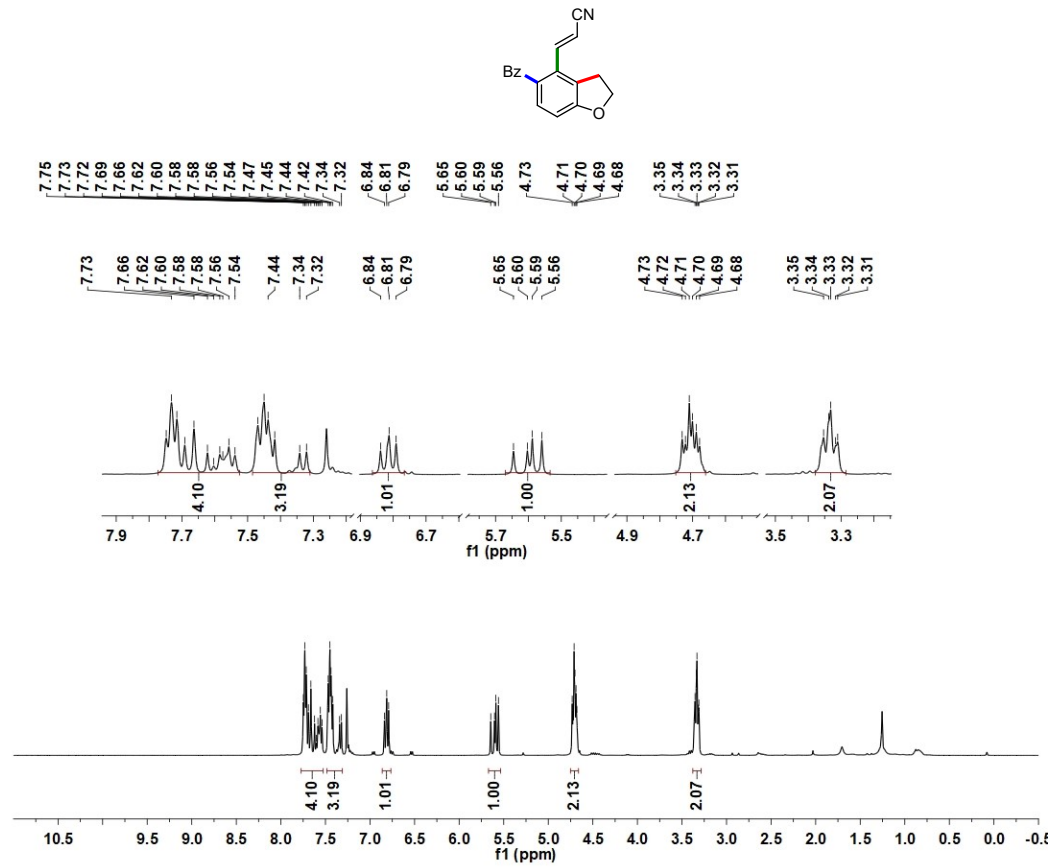


Figure S65. [1]H NMR spectrum of **4af**.

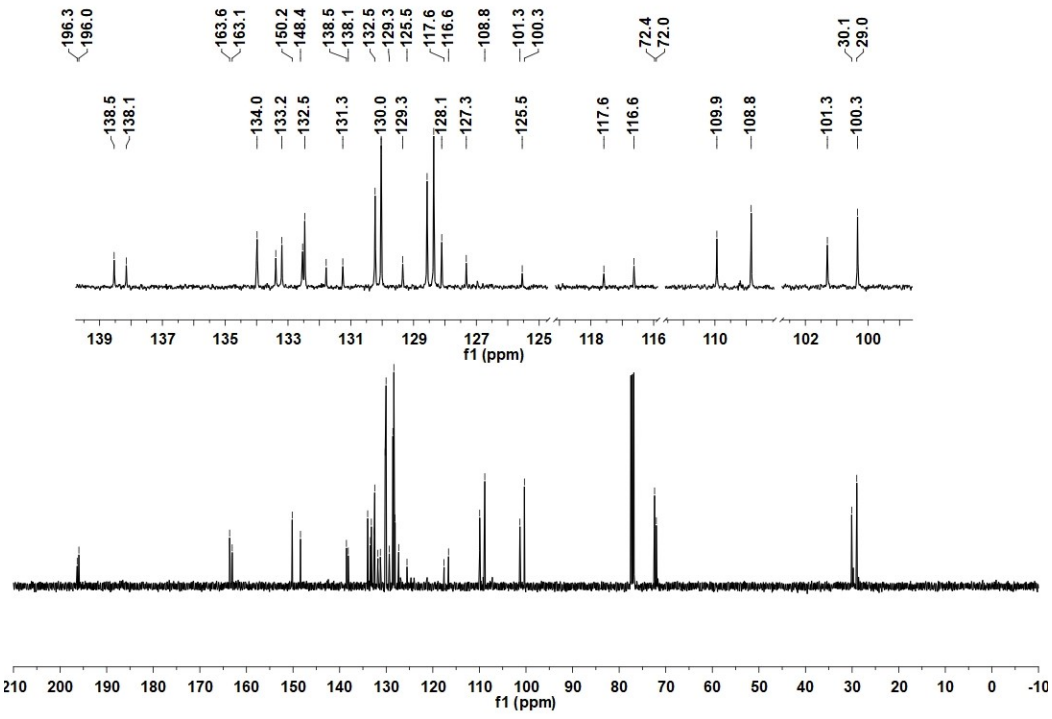


Figure S66. [13]C NMR spectrum of **4af**.

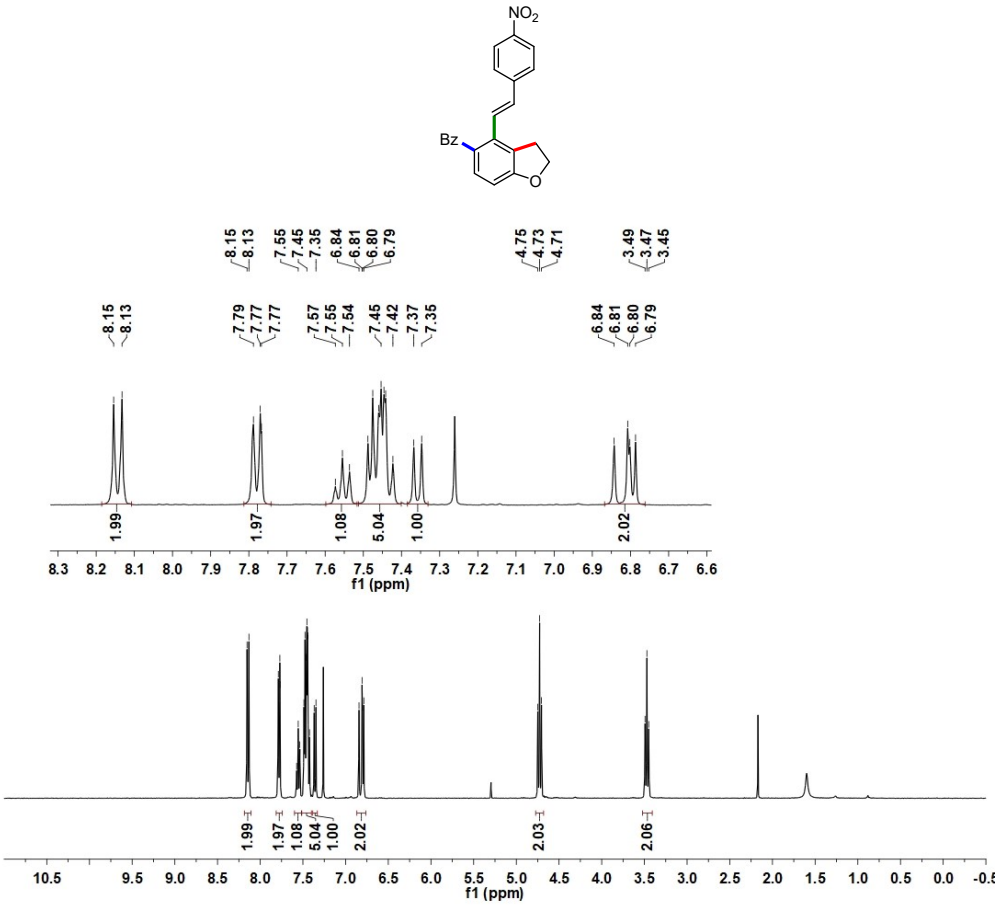


Figure S67. [1]H NMR spectrum of **4ag**.

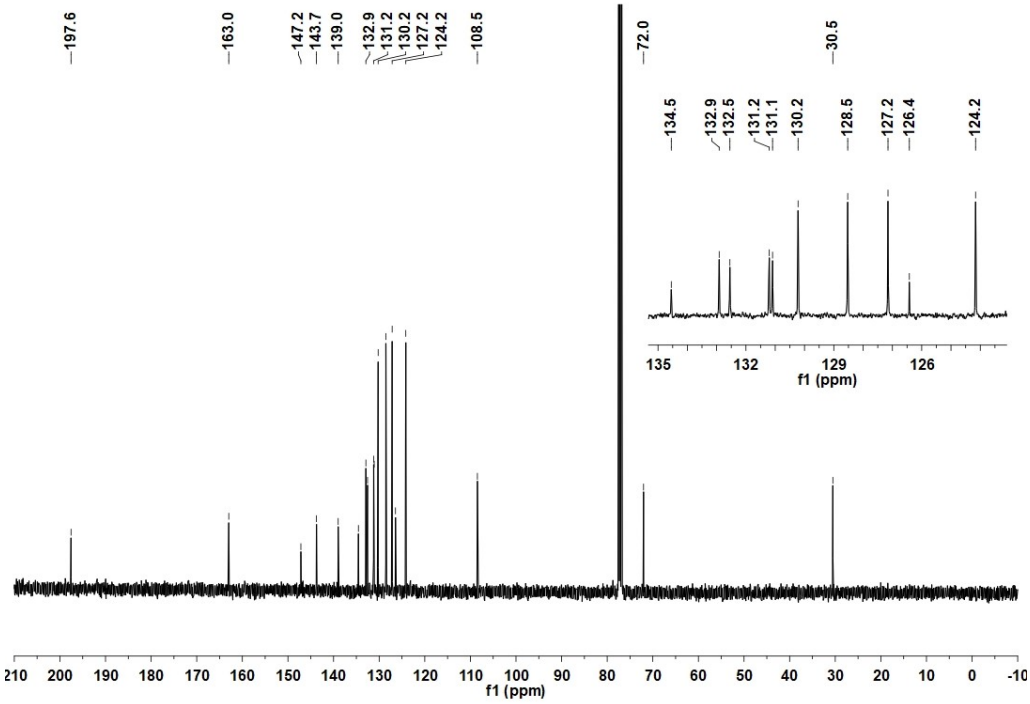


Figure S68. [13]C NMR spectrum of **4ag**.

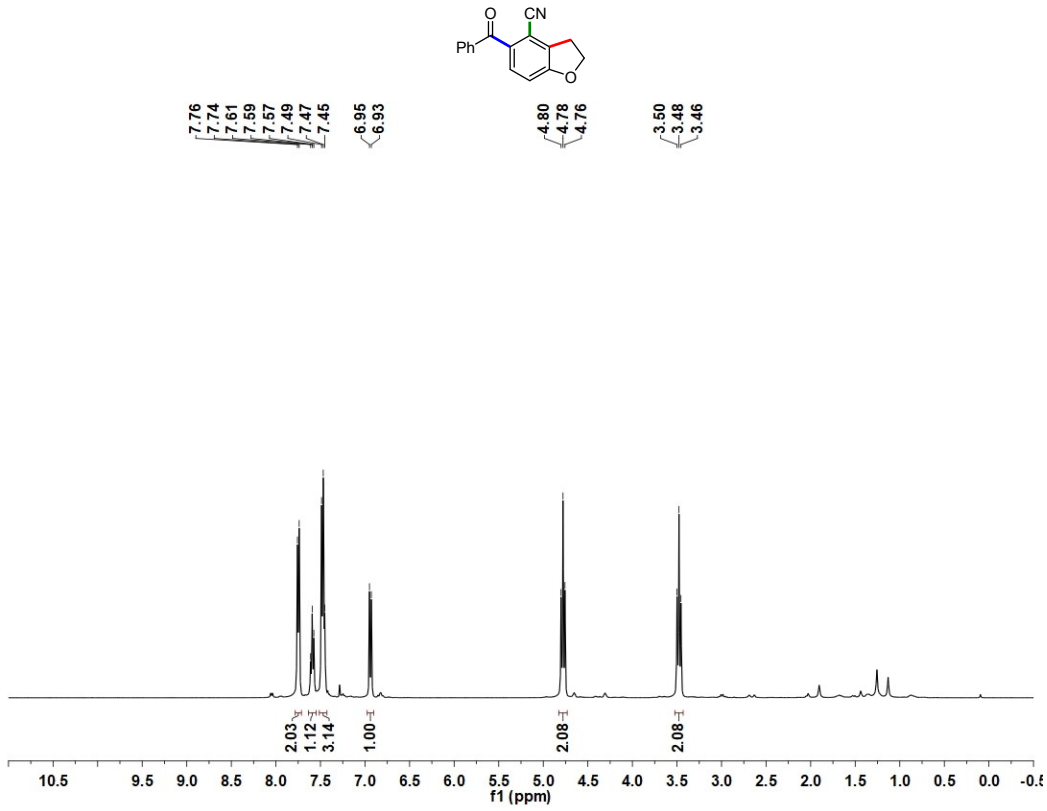


Figure S69. ^{1}H NMR spectrum of **5**.

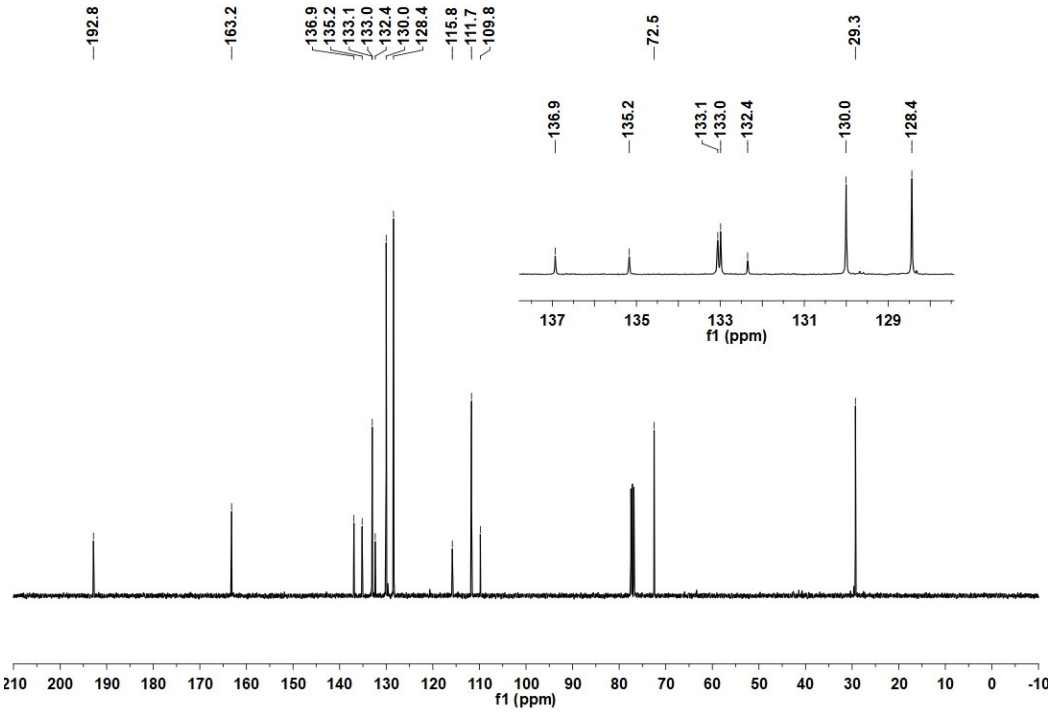


Figure S70. ^{13}C NMR spectrum of **5**.

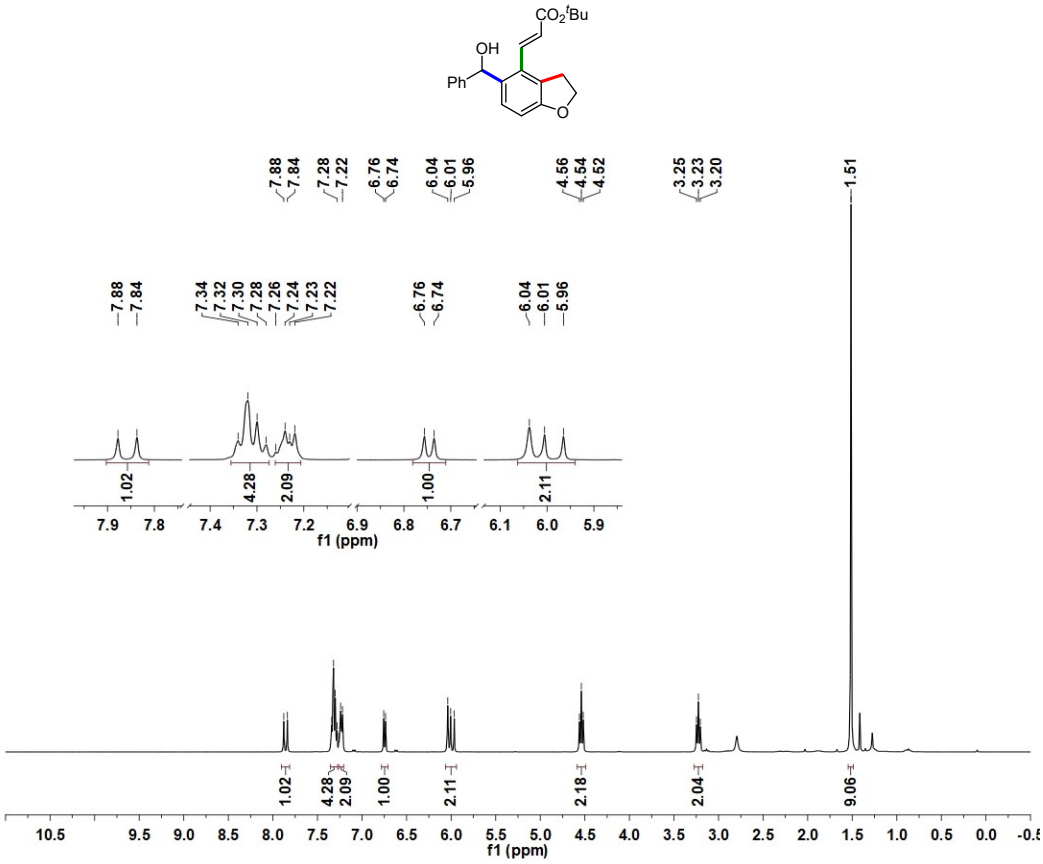


Figure S71. ^{1}H NMR spectrum of **6**.

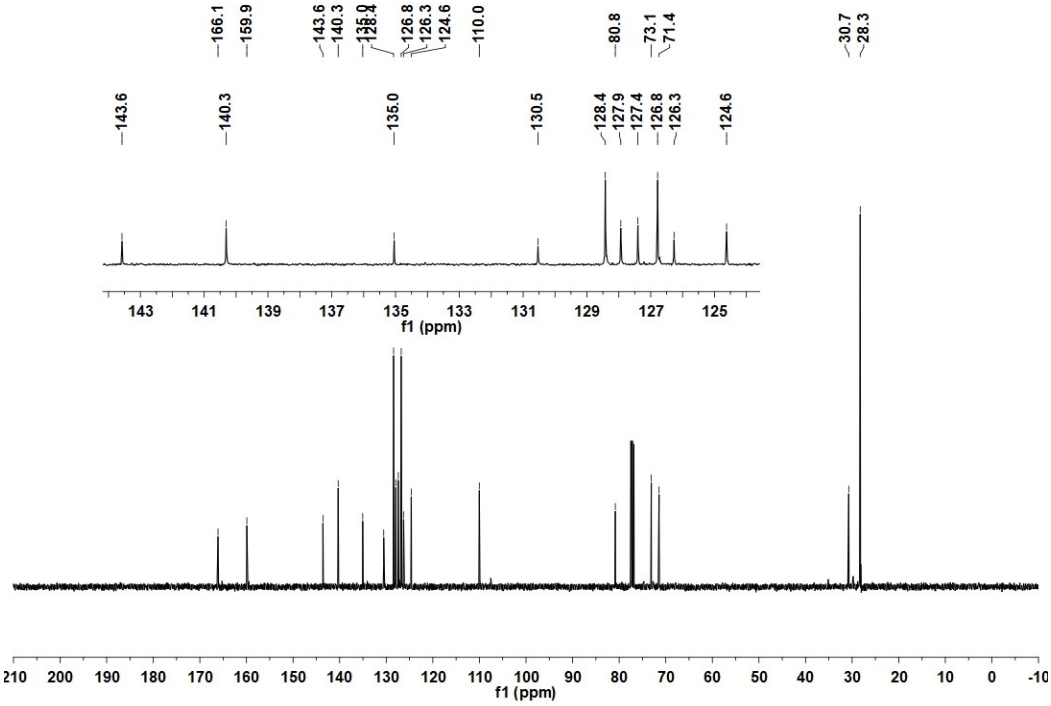


Figure S72. ^{13}C NMR spectrum of **6**.

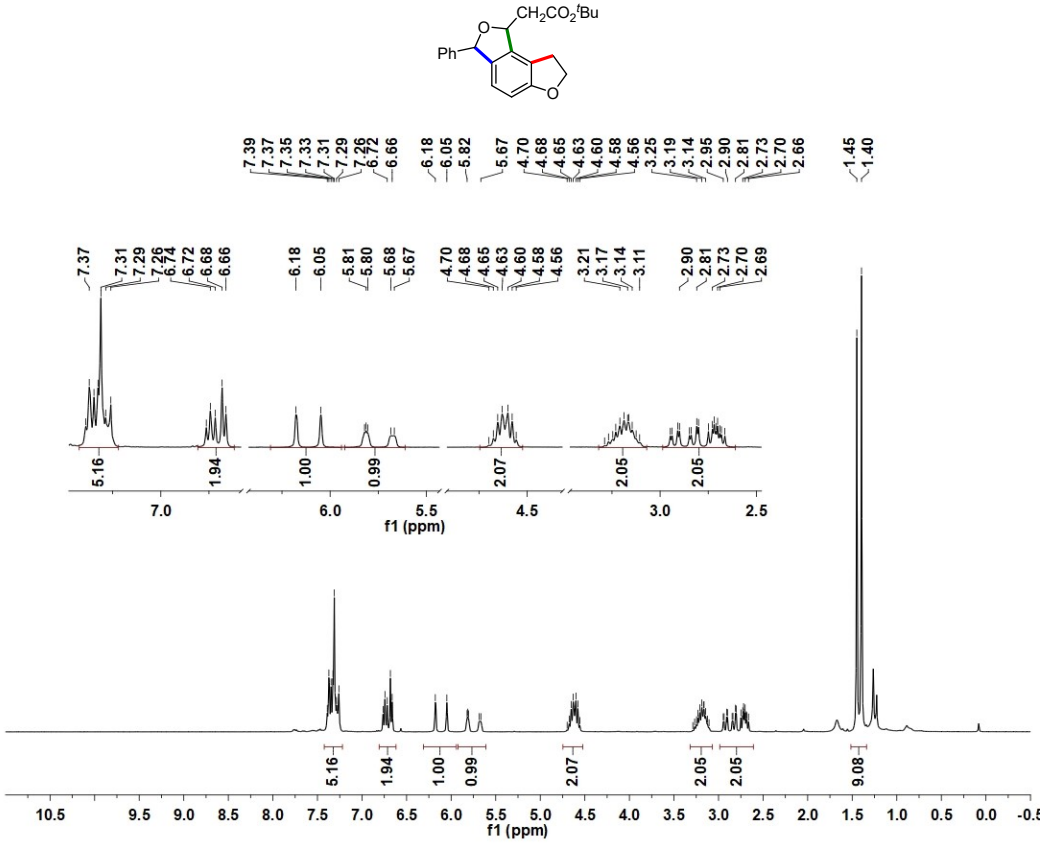


Figure S73. ^{1}H NMR spectrum of **7**.

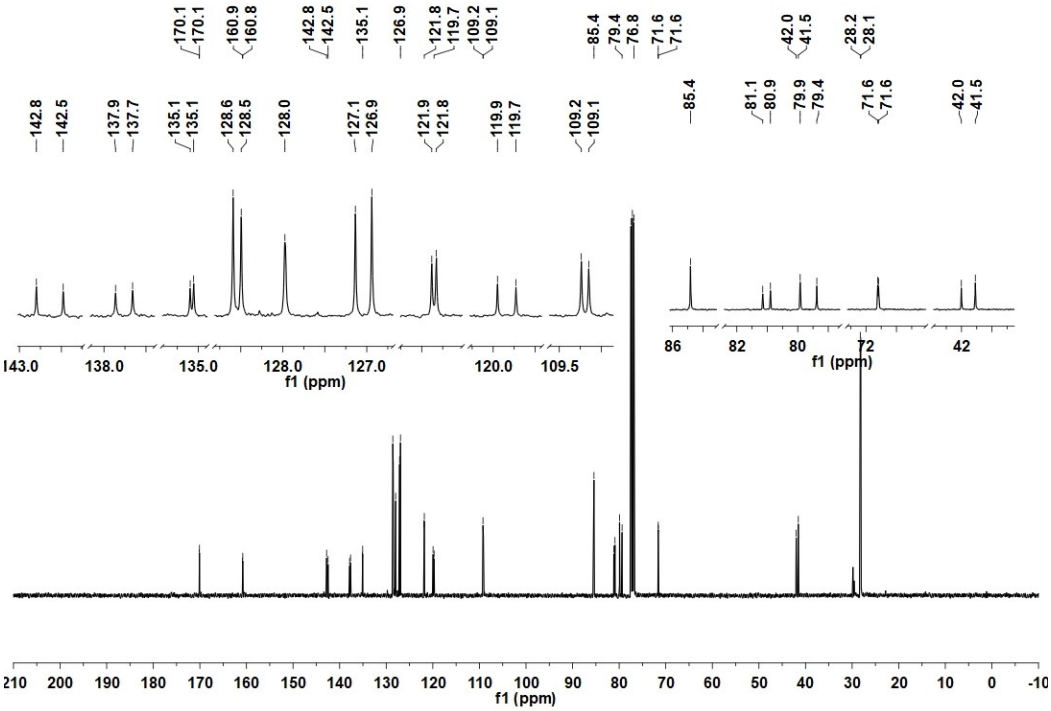


Figure S74. ^{13}C NMR spectrum of **7**.

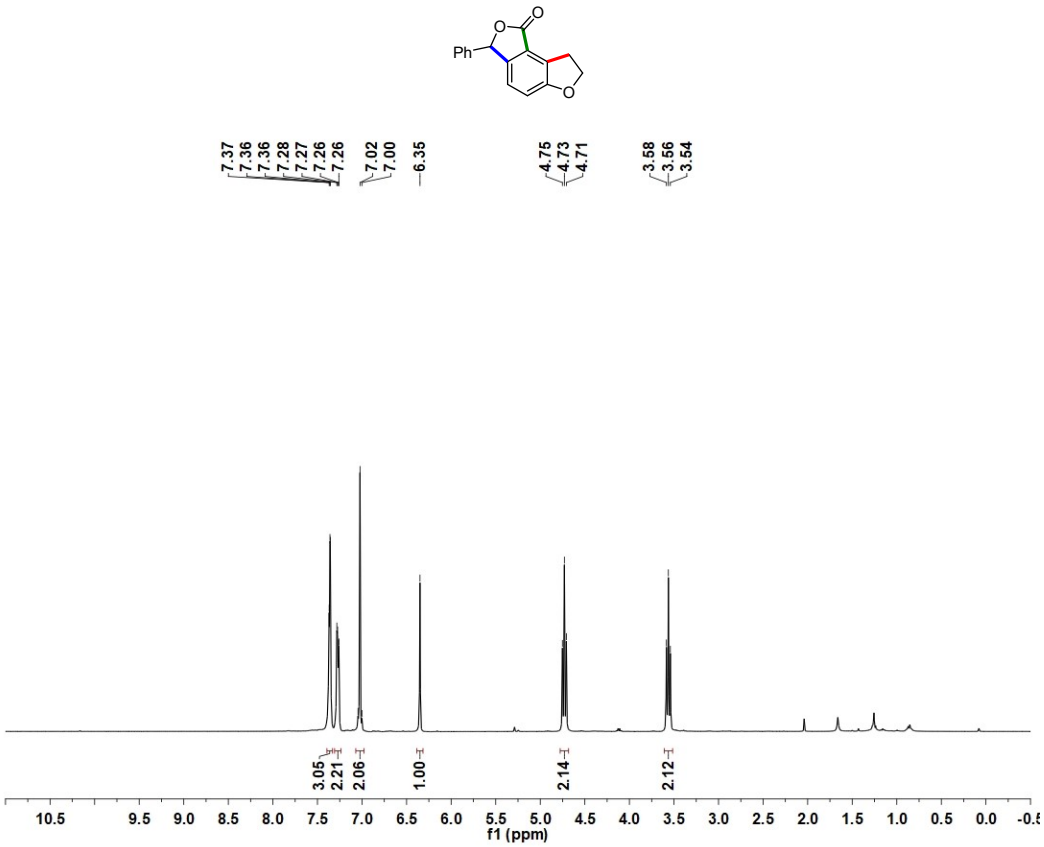


Figure S75. ^{1}H NMR spectrum of **8**.

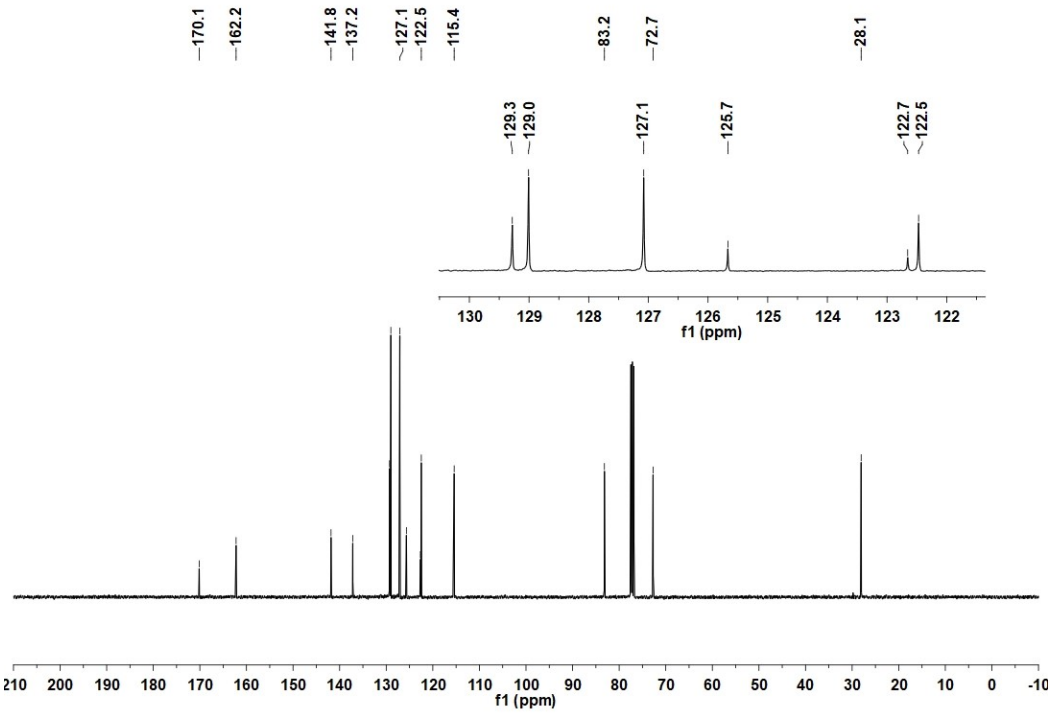


Figure S76. ^{13}C NMR spectrum of **8**.

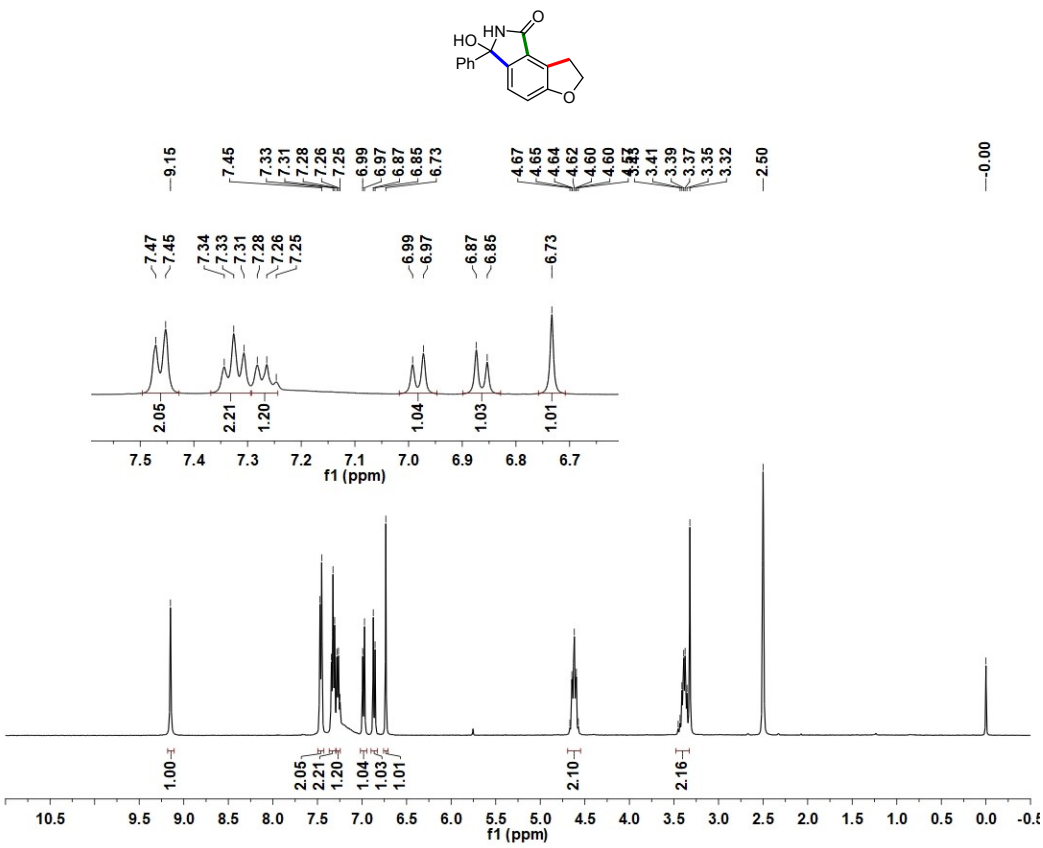


Figure S77. ^{1}H NMR spectrum of **9**.

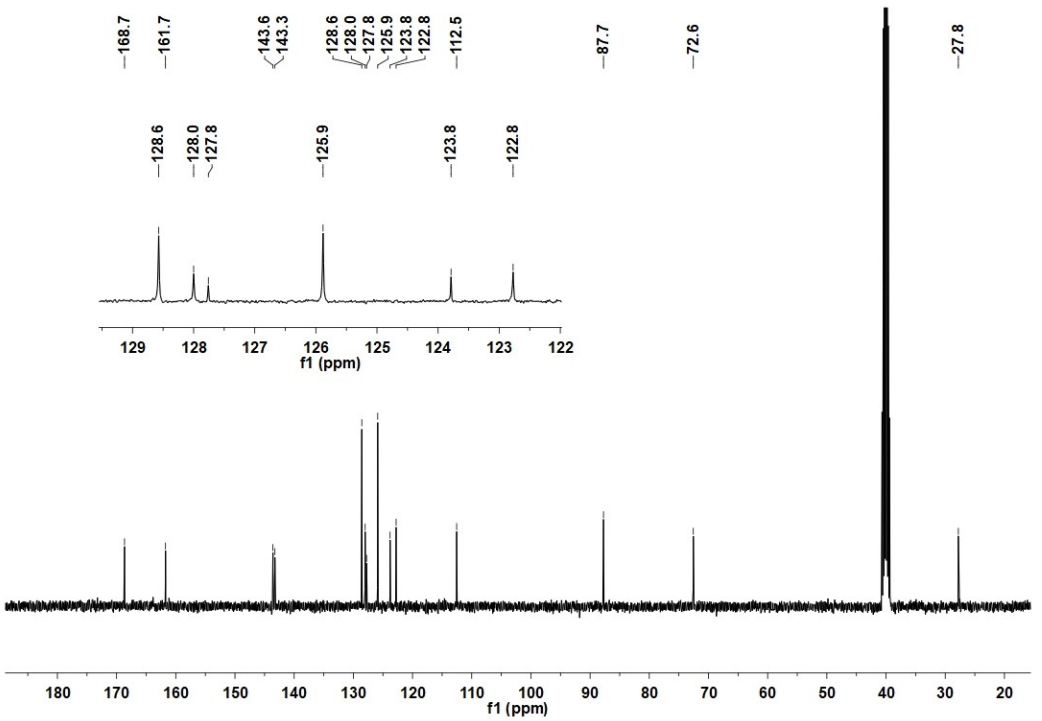


Figure S78. ^{13}C NMR spectrum of **9**.

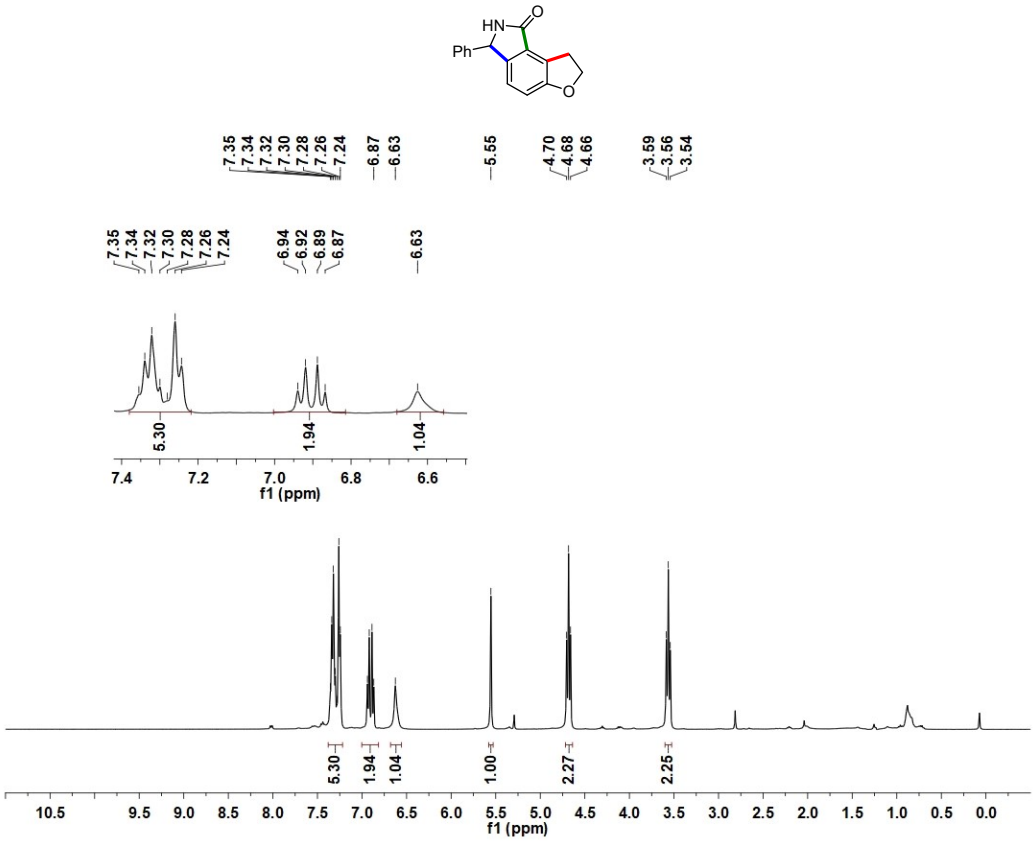


Figure S79. ^{1}H NMR spectrum of **10**.

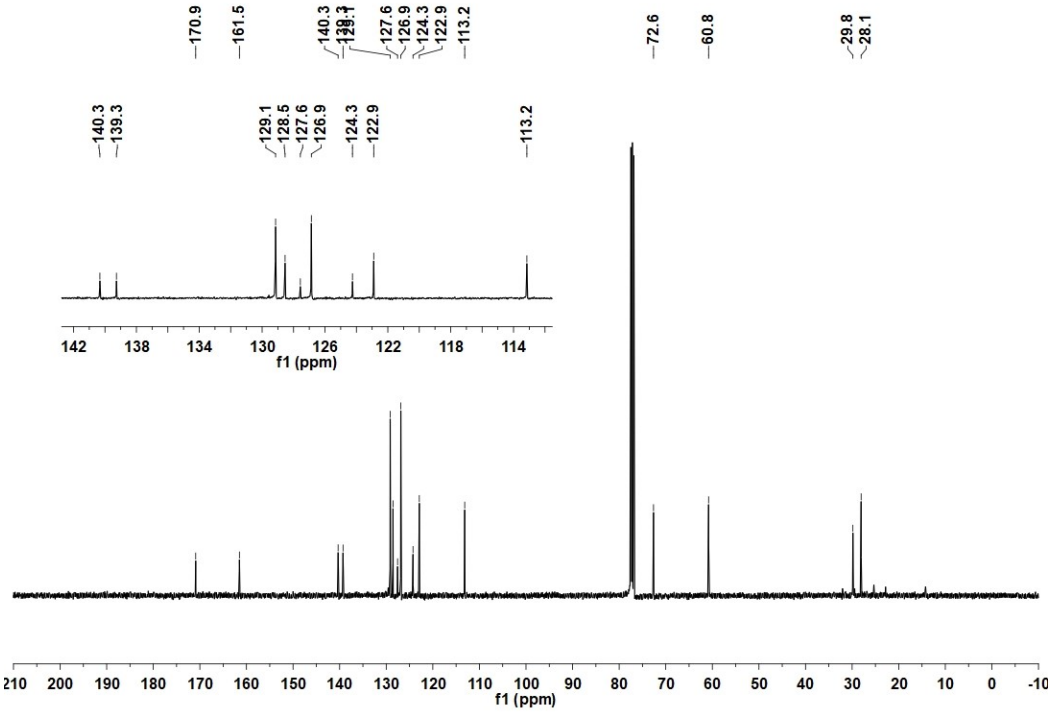


Figure S80. ^{13}C NMR spectrum of **10**.

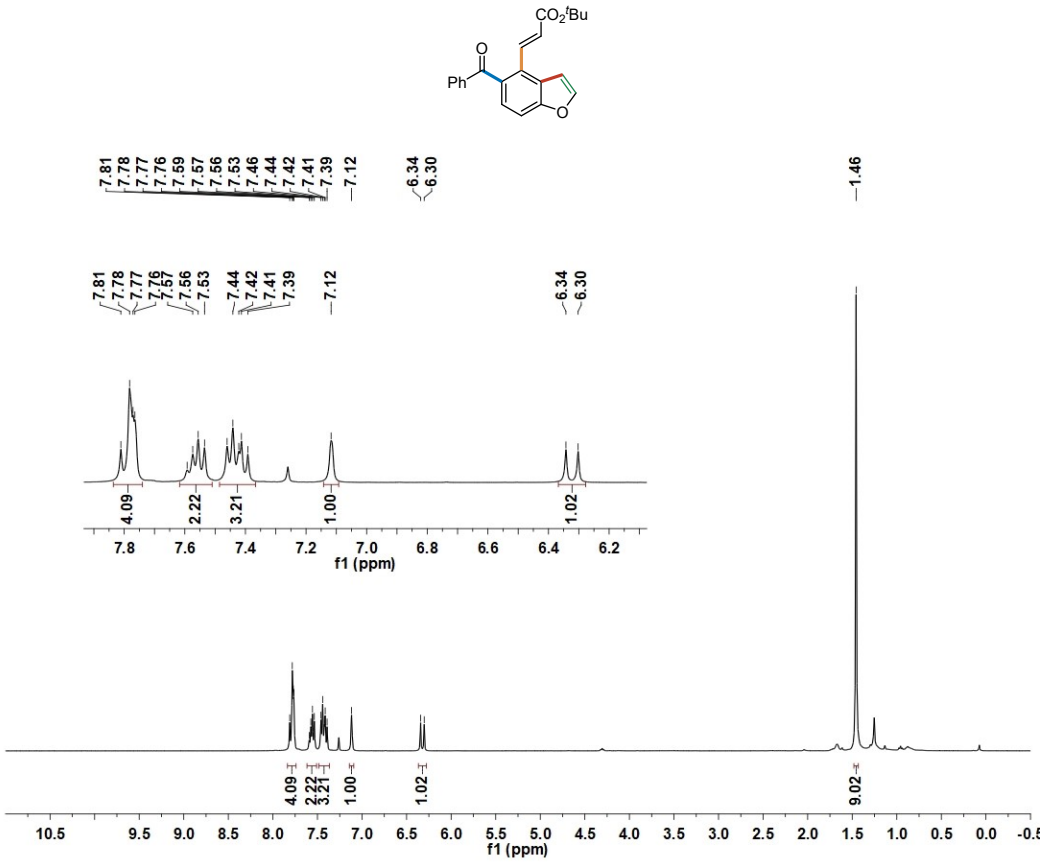


Figure S81. [1]H NMR spectrum of **11**.

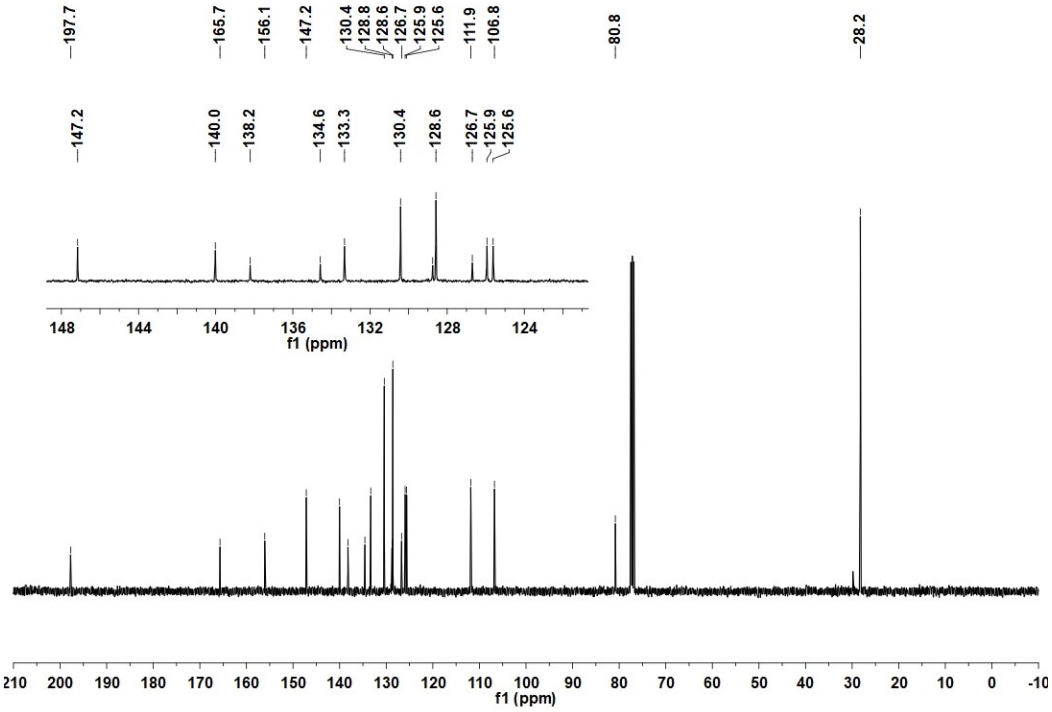


Figure S82. [13]C NMR spectrum of **11**.

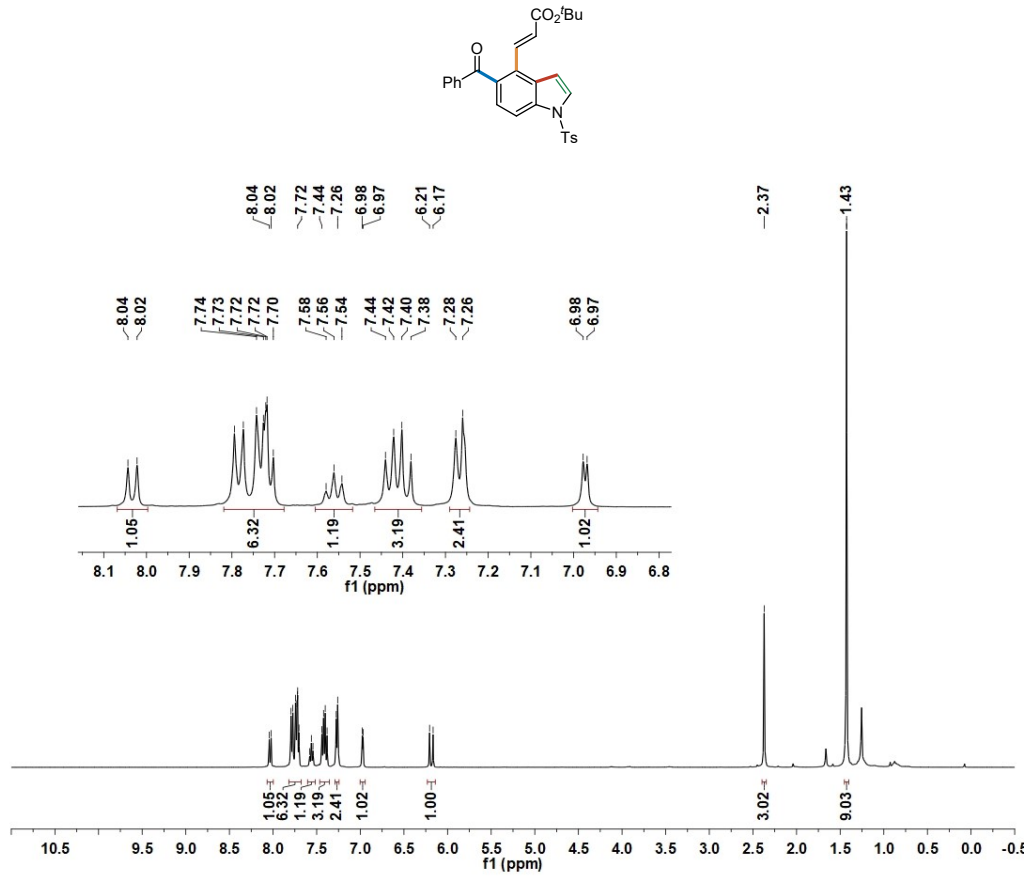


Figure S83. [1]H NMR spectrum of **12**.

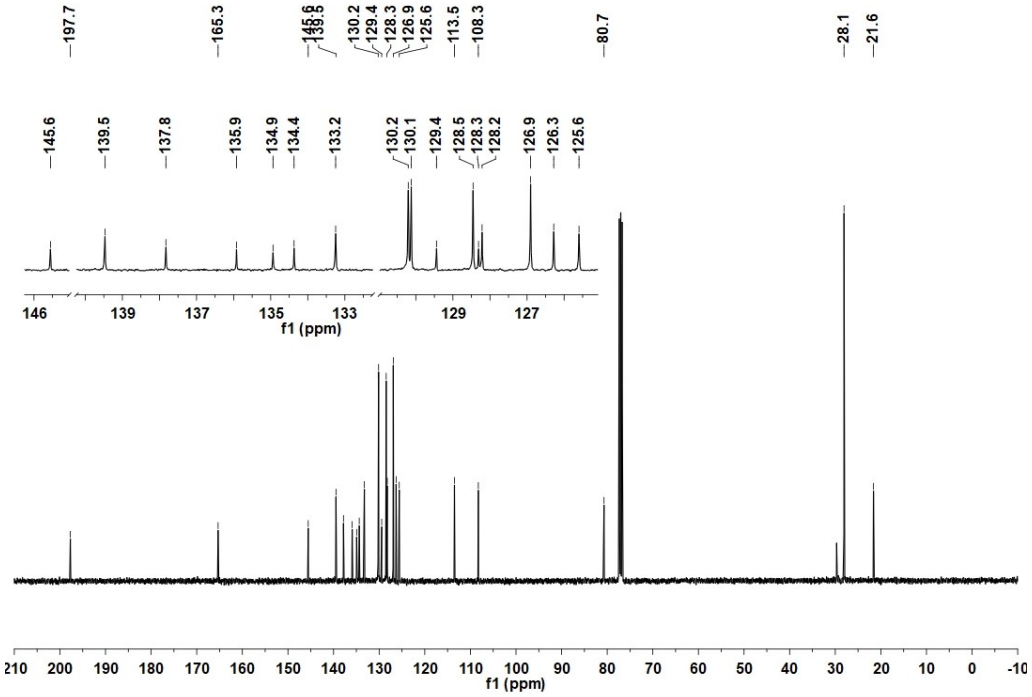


Figure S84. [13]C NMR spectrum of **12**.