Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Reductive Hydrobenzylation of Terminal Alkynes via Photoredox and Nickel Dual Catalysis

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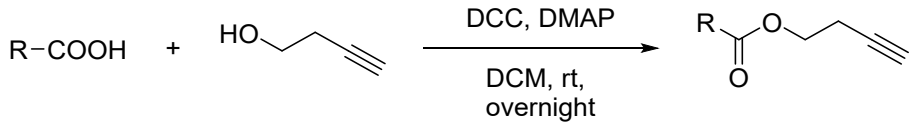
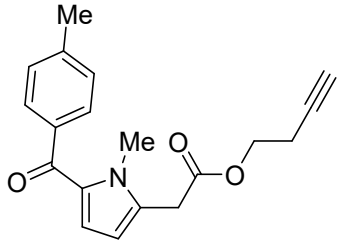
1. General Information.

Commercial reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in screw cap reaction tube under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates.^{1}H, ^{19}F NMR, and ^{13}C NMR spectra were recorded on Bruker 400 (400, 376, and 100 MHz) and Bruker 600 (600, 564, and 150 MHz), and are internally referenced to residual solvent signals (for $CDCl_3$, δ 7.26 and 77.0 ppm). Data for ^{1}H NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. All alkenes were used from commercial suppliers or prepared according to literature procedures or the preparation procedures described in this Supporting Information.

2. Preparation of Substrates



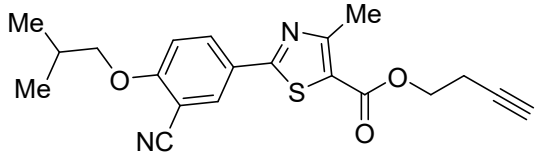
General procedure for the preparation of alkynes substrates: A solution of but-3-yn-1-ol (2.0 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was slowly added via cannula to a solution of dicyclohexylcarbodiimide (DCC) (2.4 mmol, 1.2 equiv.), 4-dimethylaminopyridine (DMAP) (0.2 mmol, 0.1 equiv.) and carboxylic acid (2.1 mmol, 1.05 equiv.) in CH_2Cl_2 (25 mL) at 22 °C. After overnight at the same temperature, the reaction mixture was filtrated, and the filtrate was concentrated. The residue was subsequently purified by silica gel flash chromatography to provide compounds.



5-(2-(but-3-yn-1-yloxy)-2-oxoethyl)-1-Methyl-1H-pyrrol-2-yl 4-methylbenzoate (S1): According to the general procedure, but-3-yn-1-ol (0.15 mL, 2.0 mmol, 1 equiv.), 2-(1-methyl-5-((4-methylbenzoyl)oxy)-1H-pyrrol-2-yl)acetic acid (540.3 mg, 2.1 mmol, 1.05 equiv.), dicyclohexylcarbodiimide (DCC) (495.2 mg, 2.4 mmol, 1.2 equiv.), 4-dimethylaminopyridine (DMAP) (24.4 mg, 0.2 mmol, 0.1 equiv.) and CH_2Cl_2 (27 mL) were used. After overnight, the product was isolated by flash chromatography (PE: EA= 5:1) as a white solid (556.8 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 4.0 Hz, 1H), 6.12 (d, *J* = 4.0 Hz, 1H), 4.26 (td, *J* = 6.7, 0.8 Hz, 2H), 3.95 (d, *J* = 0.8 Hz, 3H), 3.75 (s, 2H), 2.68 – 2.45 (m, 2H), 2.42 (s, 3H), 2.01 (td, *J* = 2.7, 0.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 169.1, 141.9, 137.3, 134.2, 131.5, 129.4, 128.7, 122.2, 109.5, 79.7, 70.2, 63.0, 33.3, 32.8, 21.6, 19.0.

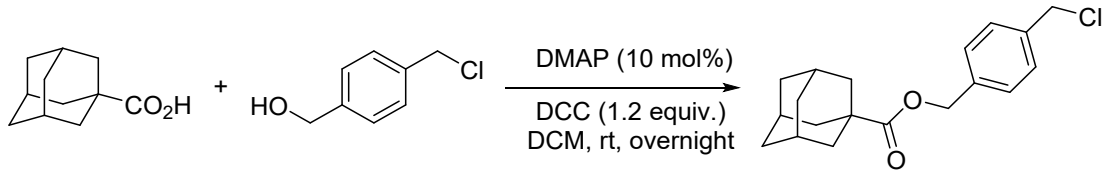


But-3-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (S2): According

to the general procedure, but-3-yn-1-ol (0.15 mL, 2.0 mmol, 1 equiv.), 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylic acid (664.4 mg, 2.1 mmol, 1.05 equiv.), dicyclohexylcarbodiimide (DCC) (495.2 mg, 2.4 mmol, 1.2 equiv.), 4-dimethylaminopyridine (DMAP) (24.4 mg, 0.2 mmol, 0.1 equiv.) and CH_2Cl_2 (27 mL) were used. After overnight, the product was isolated by flash chromatography (PE: EA= 10:1) as a white solid (353.8 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.3 Hz, 1H), 8.09 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.40 (t, *J* = 6.7 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 3H), 2.66 (td, *J* = 6.7, 2.6 Hz, 2H), 2.20 (dt, *J* = 13.3, 6.7 Hz, 1H), 2.04 (t, *J* = 2.7 Hz, 1H), 1.09 (d, *J* = 6.7 Hz, 6H).

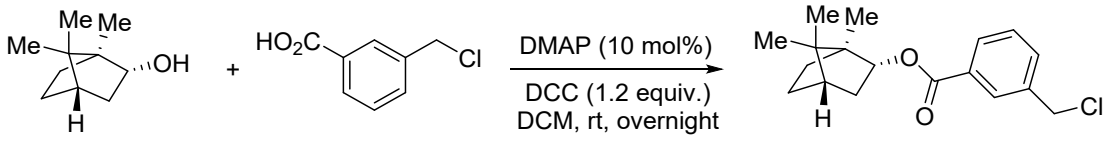
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 162.5, 161.7, 161.6, 132.6, 132.1, 126.0, 121.4, 115.3, 112.6, 103.0, 79.7, 75.7, 70.2, 62.9, 28.2, 19.1, 19.0, 17.6.



4-(chloromethyl)Benzyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (S3): A solution of (4-(chloromethyl)phenyl)methanol (313.2 mg, 2.0 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was slowly added via cannula to a solution of dicyclohexylcarbodiimide (DCC) (495.2 mg, 2.4 mmol, 1.2 equiv.), 4-dimethylaminopyridine (DMAP) (24.4 mg, 0.2 mmol, 0.1 equiv.) and (3r,5r,7r)-adamantane-1-carboxylic acid (378.5 mg, 2.1 mmol, 1.05 equiv.) in CH_2Cl_2 (25 mL) at 22 °C. After overnight at the same temperature, the reaction mixture was filtrated, and the filtrate was concentrated. The residue was subsequently purified by silica gel flash chromatography to provide compounds as a white solid (439.9 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.09 (s, 2H), 4.59 (s, 2H), 2.09 – 1.98 (m, 3H), 1.95 – 1.89 (m, 6H), 1.79 – 1.61 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 137.2, 136.9, 128.8, 128.0, 65.3, 45.9, 40.8, 38.8, 36.5, 27.9.



(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 3-(chloromethyl)benzoate (S4): A

solution of (1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (771.5 mg, 5.0 mmol) in CH_2Cl_2 (5 mL) was slowly added via cannula to a solution of dicyclohexylcarbodiimide (DCC) (1.2 g, 6.0 mmol, 1.2 equiv.), 4-dimethylaminopyridine (DMAP) (61.1 mg, 0.5 mmol, 0.1 equiv.) and 3-(chloromethyl)benzoic acid (895.7 mg, 5.3 mmol, 1.05 equiv) in CH_2Cl_2 (50 mL) at 22 °C. After overnight at the same temperature, the reaction mixture was filtrated, and the filtrate was concentrated. The residue was subsequently purified by silica gel flash chromatography to provide compounds as a white solid (900 mg, 59%).

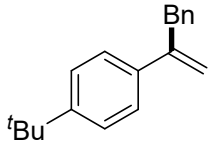
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (t, *J* = 1.9 Hz, 1H), 8.02 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 5.17 – 5.08 (m, 1H), 4.64 (s, 2H), 2.54 – 2.40 (m, 1H), 2.18 – 2.08 (m, 1H), 1.88 – 1.77 (m, 1H), 1.75 (t, *J* = 4.5 Hz, 1H), 1.49 – 1.38 (m, 1H), 1.35 – 1.28 (m, 1H), 1.12 (dd, *J* = 13.9, 3.5 Hz, 1H), 0.97 (s, 3H), 0.92 (d, *J* = 1.9 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 137.8, 132.9, 131.5, 129.5, 129.5, 128.9, 80.8, 49.1, 47.9, 45.6, 45.0, 36.9, 28.1, 27.4, 19.8, 18.9, 13.7.

3. General Procedure for the Catalytic Hydrobenzylation of Alkynes

To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with $Ir[dF(CF_3)(ppy)(Phen)](PF_6)$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%). After were added as a 0.025 M solution in DMAc (8 mL). The reaction mixture was degassed by nitrogen sparging for 15 min, followed by the addition of benzyl chloride (0.26 mol, 1.3 equiv.), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) and alkynes (0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with a 90 W blue LED for 24 h at 35 °C. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the products.

4. Characterization of Products

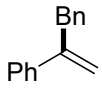


1-(Tert-butyl)-4-(3-phenylprop-1-en-2-yl)benzene (3): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.0 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: EA=50:1) as a colourless oil liquid (46.6 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.23 – 7.15 (m, 2H), 5.51 (d, *J* = 0.6 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 2H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 146.4, 139.8, 137.8, 129.0, 128.4, 126.1, 125.7, 125.2, 114.0, 41.6, 34.5, 31.3.

HRMS (ESI+): calcd for $C_{19}H_{23}^+$ (M+H) 251.1794, found 251.1795.



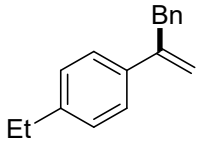
Prop-2-ene-1,2-diyldibenzene (4): According to the general procedure, ethynylbenzene (22.0 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: EA=50:1) as a colourless oil liquid (32.3 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.24 (m, 4H), 7.24 – 7.17 (m, 1H), 5.53 (s, 1H), 5.05 (s, 1H), 3.87 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 140.9, 139.6, 129.0, 128.4, 128.3, 127.5, 126.2, 126.1, 114.6,

41.7.

HRMS (ESI+): calcd for $C_{15}H_{15}^+$ (M+H) 195.1168, found 195.1165.

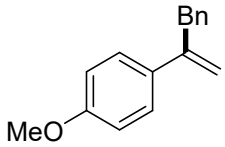


1-Ethyl-4-(3-phenylprop-1-en-2-yl)benzene (5): According to the general procedure, 1-ethyl-4-ethynylbenzene (28.0 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (40.0 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 1H), 5.03 (d, *J* = 0.6 Hz, 1H), 3.89 (s, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 146.7, 143.6, 139.7, 138.1, 129.0, 128.4, 127.8, 126.1, 126.1, 113.9, 41.6, 28.5, 15.5.

HRMS (ESI+): calcd for $C_{17}H_{19}^+$ (M+H) 223.1481, found 223.1485.

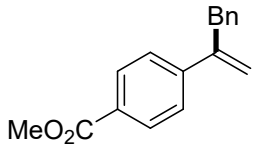


Methoxy-4-(3-phenylprop-1-en-2-yl)benzene (6): According to the general procedure, 1-ethynyl-4-methoxybenzene (25.9 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: EA=50:1) as a colourless oil liquid (44.4 mg, 99%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.19 – 7.14 (m, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.43 (s, 1H), 4.94 (s, 1H), 3.81 (s, 2H), 3.78 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 146.1, 139.7, 133.2, 128.9, 128.3, 127.3, 126.1, 113.6, 113.0, 55.3, 41.7.

HRMS (ESI+): calcd for $C_{16}H_{17}O^+$ (M+H) 225.1724, found 225.1722.

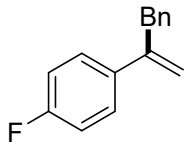


Methyl 4-(3-phenylprop-1-en-2-yl)benzoate (7): According to the general procedure, methyl 4-ethynylbenzoate (32.0 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: EA=20:1) as a colourless oil liquid (49.5 mg, 98%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.22 (m, 3H), 5.67 (s, 1H), 5.23 (d, *J* = 1.1 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 146.2, 145.3, 139.0, 129.6, 129.0, 128.9, 128.4, 126.3 126.1, 116.5, 52.1, 41.5.

HRMS (ESI+): calcd for $C_{17}H_{17}O_2^+$ (M+H) 253.1223, found 253.1229.



1-Fluoro-4-(3-phenylprop-1-en-2-yl)benzene (8): According to the general procedure, 1-ethynyl-4-fluorobenzene (22.9 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the

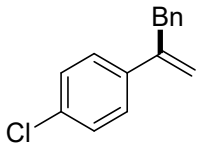
result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (31.0 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.17 (m, 3H), 7.00 – 6.94 (m, 2H), 5.44 (d, *J* = 0.6 Hz, 1H), 5.04 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 2H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -115.11 – -115.19 (m).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.4 Hz), 145.9, 139.2, 136.8 (d, *J* = 3.3 Hz), 128.9, 128.4, 127.8 (d, *J* = 7.9 Hz), 126.2, 115.1 (d, *J* = 21.3 Hz), 114.5 (d, *J* = 1.0 Hz), 41.8.

HRMS (ESI+): calcd for $C_{15}H_{14}F^+$ (M+H) 213.1074, found 213.1074.

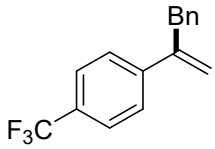


1-Chloro-4-(3-phenylprop-1-en-2-yl)benzene (9): According to the general procedure, 1-chloro-4-ethynylbenzene (22.0 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (30.2 mg, 66%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.29 – 7.22 (m, 5H), 7.21 – 7.14 (m, 2H), 5.47 (s, 1H), 5.05 (s, 1H), 3.80 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.8, 139.1, 133.2, 128.9, 128.5, 128.4, 127.5, 126.3, 115.2, 115.1, 41.6.

HRMS (ESI+): calcd for $C_{15}H_{14}Cl^+$ (M+H) 229.0779, found 229.0775.



1-(3-Phenylprop-1-en-2-yl)-4-(trifluoromethyl)benzene (10): According to the general procedure, 1-ethynyl-4-(trifluoromethyl)benzene (32.7 μL, 0.2 mmol, 1.0 equiv.),

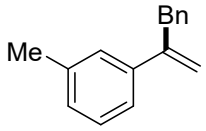
(chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (35.7 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 4H), 7.35 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 5.59 (s, 1H), 5.19 (s, 1H), 3.88 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49 (s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 144.3, 138.9, 129.4 (q, J = 32.5 Hz), 128.9, 128.5, 126.5, 126.4, 125.3 (q, J = 3.7 Hz), 124.7 (q, J = 271.9 Hz), 116.6, 41.6.

HRMS (ESI+): calcd for $C_{16}H_{14}F_3^+$ (M+H) 263.1042, found 263.1044.

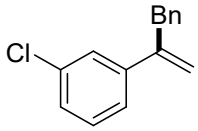


1-Methyl-3-(3-phenylprop-1-en-2-yl)benzene (11): According to the general procedure, 1-ethynyl-3-methylbenzene (25.8 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (38.3 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 6H), 7.13 – 7.08 (m, 2H), 6.98 (d, J = 7.3 Hz, 1H), 5.39 (s, 1H), 4.90 (d, J = 0.6 Hz, 1H), 3.75 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 141.0, 139.7, 137.8, 129.1, 128.4, 128.3, 128.2, 127.0, 126.2, 123.4, 114.5, 41.7, 21.6.

HRMS (ESI+): calcd for $C_{16}H_{17}^+$ (M+H) 209.1325, found 209.1325.

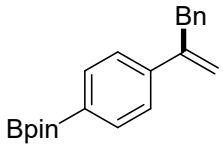


1-Chloro-3-(3-phenylprop-1-en-2-yl)benzene (12): According to the general procedure, 1-chloro-3-ethynylbenzene (24.6 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (32.9 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.34 – 7.26 (m, 3H), 7.26 – 7.18 (m, 5H), 5.51 (s, 1H), 5.09 (s, 1H), 3.83 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.9, 142.7, 139.0, 134.2, 129.5, 128.9, 128.5, 127.5, 126.4, 126.3, 124.4, 115.7, 41.5.

HRMS (ESI+): calcd for $C_{15}H_{14}Cl^+$ (M+H) 229.0779, found 229.0775.

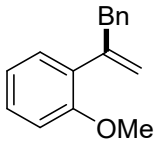


4,4,5,5-Tetramethyl-2-(4-(3-phenylprop-1-en-2-yl)phenyl)-1,3,2-dioxaborolane (13): According to the general procedure, 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45.6 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=20:1) as a white solide (32.2 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 5.51 (s, 1H), 5.04 (d, J = 1.2 Hz, 1H), 3.84 (s, 2H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 143.5, 139.4, 134.8, 129.0, 128.3, 126.1, 125.5, 115.2, 83.8, 41.5, 24.9.

HRMS (ESI+): calcd for $C_{21}H_{26}BO_2^+$ (M+H) 321.2020, found 321.2018.

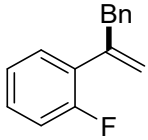


1-Methoxy-2-(3-phenylprop-1-en-2-yl)benzene (14): According to the general procedure, 1-ethynyl-2-methoxybenzene (25.9 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=50:1) as a colourless oil liquid (40.8 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 3H), 7.19 – 7.13 (m, 3H), 7.09 – 7.03 (m, 1H). 6.91 – 6.82 (m, 2H), 5.14 (s, 1H), 5.08 (s, 1H), 3.87 (s, 3H), 3.81 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 148.4, 134.0, 131.9, 130.3, 129.3, 128.5, 128.1, 125.9, 120.5, 115.9, 110.7, 55.5, 42.7.

HRMS (ESI+): calcd for $C_{16}H_{17}O^+$ (M+H) 225.1274, found 225.1277.



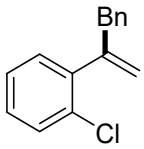
1-Fluoro-2-(3-phenylprop-1-en-2-yl)benzene (15): According to the general procedure, 1-ethynyl-2-fluorobenzene (22.7 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (34.4 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 7H), 7.07 – 6.99 (m, 2H), 5.32 (s, 1H), 5.20 (s, 1H), 3.82 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.70 – -114.79 (m).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.91 (d, J = 248.5 Hz), 144.12 (d, J = 1.1 Hz), 139.2, 130.17 (d, J = 4.3 Hz), 129.58 (d, J = 13.9 Hz), 129.1, 128.83 (d, J = 8.3 Hz), 128.3, 126.2, 123.91 (d, J = 3.5 Hz), 117.76 (d, J = 2.8 Hz), 115.72 (d, J = 22.7 Hz), 42.81 (d, J = 3.5 Hz).

HRMS (ESI+): calcd for $C_{15}H_{14}F^+$ (M+H) 213.1074, found 213.1074.

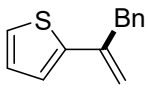


1-Chloro-2-(3-phenylprop-1-en-2-yl)benzene (16): According to the general procedure, 1-chloro-2-ethynylbenzene (24.3 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (28.4 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.7 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.14 (m, 4H), 7.14 – 7.10 (m, 1H), 7.03 – 6.98 (m, 1H), 5.13 (d, J = 0.8 Hz, 1H), 5.05 (s, 1H), 3.73 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 141.5, 138.8, 132.1, 130.6, 129.5, 129.4, 128.3, 128.3, 126.5, 126.2, 116.9, 43.1.

HRMS (ESI+): calcd for $C_{15}H_{14}Cl^+$ (M+H) 229.0779, found 229.0773.



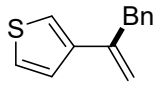
2-(3-Phenylprop-1-en-2-yl)thiophene (17): According to the general procedure, 2-ethynylthiophene (20.0 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0

equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=60:1) as a colourless oil liquid (24.2 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 5H), 7.12 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 3.5 Hz, 1H), 6.95 – 6.88 (m, 1H), 5.55 (s, 1H), 4.89 (s, 1H), 3.80 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.5, 139.0, 128.9, 128.4, 127.3, 126.3, 124.2, 124.0, 113.2, 41.8.

HRMS (ESI+): calcd for $C_{13}H_{13}S^+$ (M+H) 201.0732, found 201.0739.

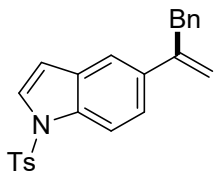


3-(3-Phenylprop-1-en-2-yl)thiophene (18): According to the general procedure, 3-ethynylthiophene (19.7 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=60:1) as a colourless oil liquid (29.2 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 6H), 7.16 – 7.14 (m, 1H), 5.53 (s, 1H), 4.97 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.5, 139.4, 128.9, 128.5, 126.3, 125.8, 125.4, 121.0, 113.5, 41.8.

HRMS (ESI+): calcd for $C_{13}H_{13}S^+$ (M+H) 201.0732, found 201.0737.



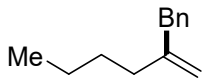
5-(3-phenylprop-1-en-2-yl)-1-Tosyl-1H-indole (19): According to the general procedure, 5-ethynyl-1-tosyl-1H-indole (59.1 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26

mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=10:1) as a white solide (55.0 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.54 (s, 1H), 7.52 – 7.49 (m, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.19 – 7.15 (m, 3H), 6.57 (s, 1H), 5.46 (s, 1H), 5.00 (s, 1H), 3.84 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 146.8, 145.0, 139.5, 136.3, 135.3, 134.2, 130.8, 129.9, 128.9, 128.3, 126.8, 126.7, 126.1, 123.2, 118.9, 114.5, 113.2, 109.3, 41.9, 21.6.

HRMS (ESI+): calcd for $C_{24}H_{22}NO_2S^+$ (M+H) 388.1366, found 388.1362.

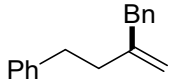


(2-Methylenehexyl)benzene (20)： According to the general procedure, hex-1-yne (23.0 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (21.8 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.15 (m, 3H), 4.82 (s, 1H), 4.73 (s, 1H), 3.34 (s, 2H), 2.02 – 1.93 (m, 2H), 1.48 – 1.38 (m, 2H), 1.35 – 1.27 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 134.0, 129.0, 128.3, 126.0, 110.9, 43.0, 35.2, 29.9, 22.4, 14.0.

HRMS (ESI+): calcd for $C_{13}H_{19}^+$ (M+H) 175.1481, found 175.1481.

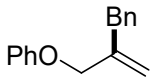


(2-methylenebutane-1,4-diyl)Dibenzene (21): According to the general procedure, but-3-yn-1-ylbenzene (28.1 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (43.1 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 4H), 7.14 – 7.03 (m, 6H), 4.79 (s, 1H), 4.72 (s, 1H), 3.29 (s, 2H), 2.67 (t, *J* = 8.0, Hz 2H), 2.20 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.1, 139.7, 129.1, 128.4, 128.4, 128.3, 126.2, 125.8, 111.6, 43.4, 37.2, 34.3.

HRMS (ESI+): calcd for $C_{17}H_{19}^+$ (M+H) 223.1481, found 223.1478.

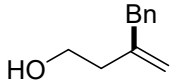


((2-Benzylallyl)oxy)benzene (22): According to the general procedure, (prop-2-yn-1-yloxy)benzene (25.7 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (37.2 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 6.99 (m, 7H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.81 – 6.76 (m, 2H), 5.14 (s, 1H), 4.94 (d, *J* = 1.0 Hz, 1H), 4.31 (s, 2H), 3.40 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 144.3, 138.8, 129.4, 129.1, 128.5, 126.4, 120.9, 114.9, 114.0, 70.0, 40.1.

HRMS (ESI+): calcd for $C_{16}H_{17}O^+$ (M+H) 225.1274, found 225.1270.

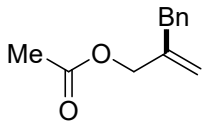


3-Benzylbut-3-en-1-ol (23): According to the general procedure, but-3-yn-1-ol (15.1 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=10:1) as a colourless oil liquid (25.0 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.15 (m, 3H), 4.94 (s, 1H), 4.92 (s, 1H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.38 (s, 2H), 2.27 (t, *J* = 6.3 Hz, 2H), 1.59 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 139.2, 129.0, 128.4, 126.3, 113.8, 60.4, 42.9, 38.5.

HRMS (ESI+): calcd for $C_{11}H_{15}O^+$ (M+H) 163.1117, found 163.1115.

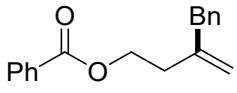


4-Benzylpent-4-en-2-one (24): According to the general procedure, pent-4-yn-2-one (18.4 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=20:1) as a colourless oil liquid (25.8 mg, 74%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 5.14 (s, 1H), 4.97 (s, 1H), 4.49 (s, 2H), 3.41 (s, 2H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 142.2, 137.5, 127.9, 127.4, 125.4, 113.3, 65.3, 39.2, 19.8.

HRMS (ESI+): calcd for $C_{12}H_{15}O^+$ (M+H) 175.1117, found 175.1122.

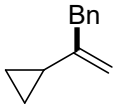


3-Benzylbut-3-en-1-yl benzoate (25): According to the general procedure, but-3-yn-1-yl benzoate (32.1 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=40:1) as a colourless oil liquid (49.9 mg, 94%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 3H), 5.00 (s, 1H), 4.93 (s, 1H), 4.44 (t, *J* = 6.8 Hz, 2H), 3.45 (s, 2H), 2.47 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 144.8, 139.2, 132.9, 130.4, 129.6, 129.0, 128.4, 128.4, 126.3, 113.7, 63.1, 43.2, 34.4.

HRMS (ESI+): calcd for $C_{18}H_{19}O_2^+$ (M+H) 267.1380, found 267.1385.

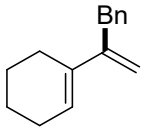


(2-cyclopropylallyl)Benzene (26): According to the general procedure, ethynylcyclopropane (16.9 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=40:1) as a colourless oil liquid (22.9 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 4.75 (s, 1H), 4.64 (d, *J* = 1.3 Hz, 1H), 3.40 (s, 2H), 1.32 – 1.25 (m, 1H), 0.63 – 0.58 (m, 2H), 0.47 – 0.43 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.3, 139.9, 129.0, 128.2, 126.0, 108.4, 42.9, 16.0, 6.3.

HRMS (ESI+): calcd for $C_{12}H_{15}^+$ (M+H) 159.1168, found 159.1163.

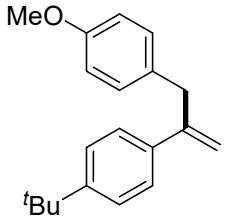


(2-(Cyclohex-1-en-1-yl)allyl)benzene (27): According to the general procedure, 1-Ethynylcyclohex-1-ene (23.5 μL, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (27.0 mg, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.17 (m, 3H), 5.94 (t, *J* = 4.0 Hz, 1H), 5.17 (s, 1H), 4.76 (s, 1H), 3.61 (s, 2H), 2.27 – 2.19 (m, 2H), 2.15 – 2.05 (m, 2H), 1.72 – 1.65 (m, 2H), 1.60 – 1.54 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 140.6, 135.6, 128.8, 128.2, 125.8, 125.5, 111.4, 40.1, 26.1, 25.9, 22.9, 22.2.

HRMS (ESI+): calcd for $C_{15}H_{19}^+$ (M+H) 199.1481, found 199.1488.

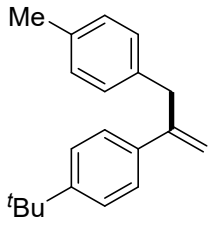


1-(*tert*-butyl)-4-(3-(4-methoxyphenyl)prop-1-en-2-yl)Benzene (28): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), 1-(chloromethyl)-4-methoxybenzene (35.3 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=80:1) as a colourless oil liquid (50.3 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.51 (s, 1H), 4.97 (d, *J* = 0.9 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 2H), 1.32 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 150.4, 146.8, 137.9, 131.8, 129.9, 125.7, 125.2, 113.8, 113.7, 55.2, 40.7, 34.5, 31.3.

HRMS (ESI+): calcd for $C_{20}H_{25}O^+$ (M+H) 281.1900, found 281.1905.

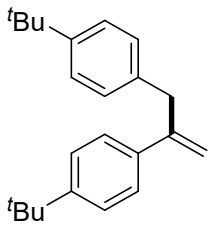


1-(Tert-butyl)-4-(3-(p-tolyl)prop-1-en-2-yl)benzene (29): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), 1-(chloromethyl)-4-methylbenzene (34.4 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (45.5 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.56 (s, 1H), 5.02 (d, *J* = 1.1 Hz, 1H), 3.85 (s, 2H), 2.37 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 146.6, 137.9, 136.7, 135.5, 129.1, 128.9, 125.8, 125.2, 113.8, 41.1, 34.5, 31.4, 21.1.

HRMS (ESI+): calcd for $C_{20}H_{25}^+$ (M+H) 265.1951, found 265.1953.

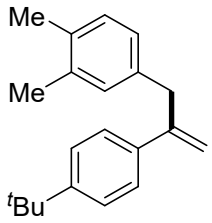


4,4'-(Prop-2-ene-1,2-diyl)bis(tert-butylbenzene) (30): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), 1-(tert-butyl)-4-(chloromethyl)benzene (50.3 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a colourless oil liquid (48.2 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.11 (d, *J* = 8.2 Hz, 2H), 5.44 (s, 1H), 4.89 (d, *J* = 1.1 Hz, 1H), 3.73 (s, 2H), 1.24 (s, 9H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.9, 146.5, 138.0, 136.7, 128.6, 125.7, 125.3, 125.2, 113.9, 40.9, 34.5, 34.4, 31.5, 31.3.

HRMS (ESI+): calcd for $C_{23}H_{31}^+$ (M+H) 307.2420, found 307.2416.

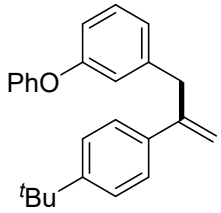


4-(2-(4-(Tert-butyl)phenyl)allyl)-1,2-dimethylbenzene (31): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), 4-(chloromethyl)-1,2-dimethylbenzene (38.1 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE) as a white solid (45.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.07 – 7.02 (m, 2H), 7.02 – 6.95 (m, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 4.97 (d, *J* = 1.3 Hz, 1H), 3.76 (s, 2H), 2.23 (s, 6H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 146.6, 138.0, 137.1, 136.4, 134.1, 130.2, 129.6, 126.3, 125.7, 125.2, 113.7, 41.1, 34.5, 31.3, 19.8, 19.4.

HRMS (ESI+): calcd for $C_{21}H_{27}^+$ (M+H) 279.2107, found 279.2105.

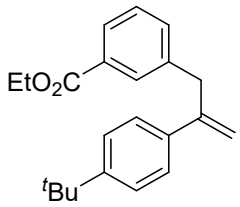


1-(2-(4-(Tert-butyl)phenyl)allyl)-3-phenoxybenzene (32): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), 1-(chloromethyl)-3-phenoxybenzene (47.8 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=80:1) as a white solid (49.9 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.30 (m, 4H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.98 – 6.94 (m, 2H), 6.85 (dd, *J* = 8.1, 2.1 Hz, 1H), 5.52 (s, 1H), 5.02 (s, 1H), 3.83 (s, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.1, 150.5, 146.1, 141.9, 137.6, 129.7, 129.6, 125.8, 125.2, 124.0, 123.0, 119.7, 118.7, 116.7, 114.2, 41.4, 34.5, 31.3.

HRMS (ESI+): calcd for $C_{25}H_{27}O^+$ (M+H) 343.2056, found 343.2056.

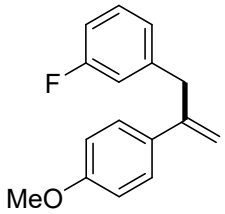


Ethyl 3-(2-(4-(tert-butyl)phenyl)allyl)benzoate (33): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), ethyl 3-(chloromethyl)benzoate (34.4 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=20:1) as a colourless oil liquid (44.9 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 5.53 (s, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 150.6, 146.0, 140.0, 137.5, 133.4, 130.6, 130.1, 128.4, 127.4, 125.7, 125.2, 114.4, 60.9, 41.3, 31.5, 31.3, 14.4.

HRMS (ESI+): calcd for $C_{22}H_{27}O^+$ (M+H) 323.2006, found 323.2008.



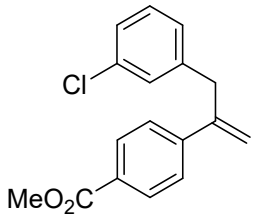
1-Fluoro-3-(2-(4-methoxyphenyl)allyl)benzene (34): According to the general procedure, 1-ethynyl-4-methoxybenzene (25.9 μL, 0.2 mmol, 1.0 equiv.), 1-(chloromethyl)-3-fluorobenzene (31.5 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=40:1) as a colorless oil liquid (28.1 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.25 – 7.16 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 10.0 Hz, 1H), 6.90 – 6.78 (m, 3H), 5.45 (d, *J* = 0.8 Hz, 1H), 4.98 (d, *J* = 1.1 Hz, 1H), 3.81 (s, 2H), 3.79 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.79 – -122.80 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 245.4 Hz), 159.2, 145.4, 142.4 (d, *J* = 7.2 Hz), 132.8, 129.7 (d, *J* = 8.2 Hz), 127.3, 124.5 (d, *J* = 2.6 Hz), 115.7 (d, *J* = 21.3 Hz), 113.7, 113.4, 113.0 (d, *J* = 21.1 Hz), 55.2, 41.5 (d, *J* = 1.4 Hz).

HRMS (ESI+): calcd for $C_{16}H_{16}FO^+$ (M+H) 243.1180, found 243.1181.

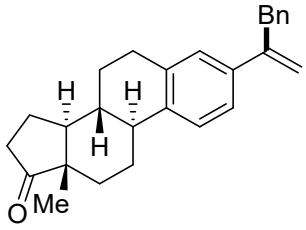


Methyl 4-(3-(3-chlorophenyl)prop-1-en-2-yl)benzoate (35): According to the general procedure, methyl 4-ethynylbenzoate (32.0 mg, 0.2 mmol, 1.0 equiv.), 1-chloro-3-(chloromethyl)benzene (33.0 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (26.4 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.23 – 7.15 (m, 3H), 7.11 – 7.06 (m, 1H), 5.60 (s, 1H), 5.16 (d, *J* = 1.1 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.5, 144.8, 141.1, 134.3, 129.7, 129.7, 129.2, 128.9, 127.1, 126.6, 126.1, 117.0, 52.1, 41.1.

HRMS (ESI+): calcd for $C_{17}H_{16}ClO_2^+$ (M+H) 287.0833, found 287.0836.

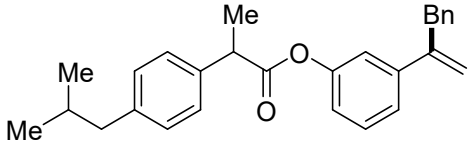


(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(3-phenylprop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (36): According to the general procedure, (8*R*,9*S*,13*S*,14*S*)-3-ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (27.8 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=40:1) as a white solid (55.6 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 6H), 7.12 – 7.09 (m, 2H), 5.40 (s, 1H), 4.87 (d, *J* = 1.1 Hz, 1H), 3.73 (s, 2H), 2.94 – 2.72 (m, 2H), 2.50 – 2.38 (m, 1H), 2.36 – 2.28 (m, 1H), 2.24 – 2.15 (m, 1H), 2.09 – 1.84 (m, 4H), 1.58 – 1.36 (m, 6H), 0.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 146.6, 139.7, 139.1, 138.4, 136.3, 129.0, 128.4, 126.7, 126.1, 125.3, 123.6, 114.1, 50.5, 48.0, 44.4, 41.5, 38.2, 35.9, 31.6, 29.5, 26.6, 25.7, 21.6, 13.9.

HRMS (ESI+): calcd for $C_{27}H_{31}O^+$ (M+H) 371.2369, found 371.2366.

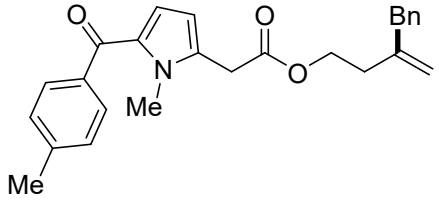


3-(3-phenylprop-1-en-2-yl)Phenyl 2-(3-isobutylphenyl)propanoate (37): According to the general procedure, 3-ethynylphenyl 2-(3-isobutylphenyl)propanoate (61.2 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=40:1) as a white solid (60.6 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 6H), 7.12 – 7.04 (m, 5H), 6.98 (s, 1H), 6.84 – 6.75 (m, 1H), 5.37 (s, 1H), 4.91 (s, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 2H), 2.39 (d, *J* = 7.2 Hz, 2H), 1.87 – 1.69 (m, 1H), 1.52 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 150.9, 146.2, 142.4, 140.8, 139.2, 137.3, 129.5, 129.1, 129.0, 128.4, 127.3, 126.2, 123.5, 120.4, 119.12, 115.3, 45.3, 45.1, 41.5, 30.2, 22.4, 18.6.

HRMS (ESI+): calcd for $C_{28}H_{31}O_2^+$ (M+H) 399.2319, found 399.2321.



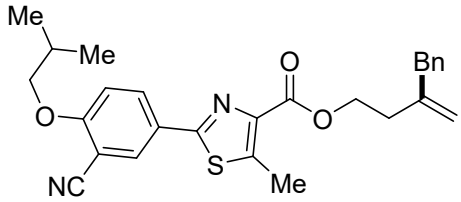
3-Benzylbut-3-en-1-yl 2-(1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl)acetate (38): According to the general procedure, 5-(2-(but-3-yn-1-yloxy)-2-oxoethyl)-1-methyl-1H-pyrrol-2-yl 4-methylbenzoate (65.1 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol,

1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=10:1) as a white solid (64.8 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.66 (d, *J* = 4.0 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 4.84 (s, 2H), 4.23 (t, *J* = 6.7 Hz, 2H), 3.92 (s, 3H), 3.67 (s, 2H), 3.34 (s, 2H), 2.41 (s, 3H), 2.30 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 169.3, 144.5, 141.9, 139.0, 137.4, 134.5, 131.4, 129.4, 129.0, 128.7, 128.4, 126.4, 122.3, 113.8, 109.5, 63.5, 43.0, 34.3, 33.2, 32.9, 21.5.

HRMS (ESI+): calcd for $C_{26}H_{28}NO_3^+$ (M+H) 402.2064, found 402.2073.

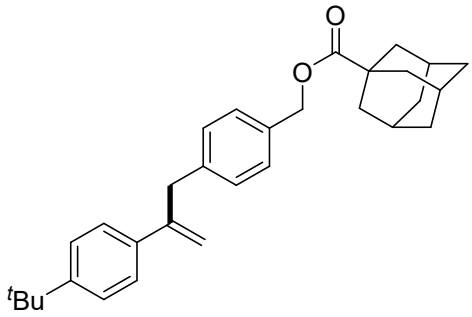


3-Benzylbut-3-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-5-methylthiazole-4-carboxylate (39): According to the general procedure, but-3-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-5-methylthiazole-4-carboxylate (73.7 mg, 0.2 mmol, 1.0 equiv.), (chloromethyl)benzene (29.9 μL, 0.26 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (2.1 mg, 0.002 mmol, 1 mol%), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=10:1) as a white solid (70.5 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.2 Hz, 1H), 8.12 – 8.04 (m, 1H), 7.35 – 7.27 (m, 2H), 7.22 (t, *J* = 6.5 Hz, 3H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.97 (s, 1H), 4.92 (s, 1H), 4.39 (t, *J* = 6.7 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.42 (s, 2H), 2.74 (s, 3H), 2.42 (t, *J* = 6.7 Hz, 2H), 2.28 – 2.16 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 162.5, 161.9, 161.2, 144.5, 139.1, 132.6, 132.1, 129.0, 128.4, 126.4, 126.0, 121.8, 115.4, 113.9, 112.7, 103.0, 75.7, 63.4, 43.1, 34.4, 28.2, 19.1, 17.5.

HRMS (ESI+): calcd for $C_{27}H_{29}N_2O_3S^+$ (M+H) 461.1893, found 461.1885.

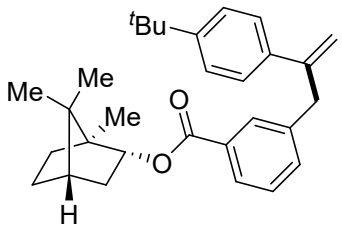


4-(2-(4-(tert-butyl)phenyl)allyl)Benzyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (40): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), 4-(chloromethyl)benzyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (82.9 mg, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=20:1) as a white solid (82.6 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 4H), 5.53 (s, 1H), 5.07 (s, 2H), 4.98 (s, 1H), 3.83 (s, 2H), 2.02 (s, 3H), 1.93 (d, *J* = 2.5 Hz, 6H), 1.72 (d, *J* = 1.8 Hz, 6H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 150.5, 146.2, 139.5, 137.7, 134.3, 129.0, 127.8, 125.7, 125.2, 114.0, 65.6, 41.2, 40.8, 38.9, 36.53 34.5, 31.3, 28.0.

HRMS (ESI+): calcd for $C_{31}H_{39}O_2^+$ (M+H) 443.2945, found 443.2951.



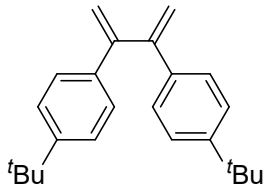
(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 3-(2-(4-(tert-butyl)phenyl)allyl)benzoate (41): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(chloromethyl)benzoate (79.8 mg, 0.26 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2

mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=40:1) as a white solid (49.9 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.38 – 7.30 (m, 3H), 5.54 (s, 1H), 5.15 – 5.06 (m, 1H), 5.00 (d, *J* = 0.8 Hz, 1H), 3.90 (s, 2H), 2.54 – 2.40 (m, 1H), 2.21 – 2.02 (m, 1H), 1.89 – 1.76 (m, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.47 – 1.33 (m, 2H), 1.31 (s, 9H), 1.12 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.98 (s, 3H), 0.92 (d, *J* = 5.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 150.6, 146.0, 140.1, 137.5, 133.4, 131.0, 130.1, 128.4, 127.4, 125.7, 125.3, 114.4, 80.5, 49.1, 47.9, 45.0, 41.2, 36.9, 34.5, 31.3, 28.1, 27.4, 19.8, 19.0, 13.7.

HRMS (ESI+): calcd for $C_{30}H_{39}O_2^+$ (M+H) 431.2945, found 431.2954.



4,4'-(buta-1,3-diene-2,3-diyl)Bis(tert-butylbenzene) (43): According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (36.1 μL, 0.2 mmol, 1.0 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (2.1 mg, 0.002 mmol, 1 mol%), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), dtbbpy (7.0 mg, 0.026 mmol, 13 mol%), 1-ethylpiperidine (82.4 μL, 0.6 mmol, 3.0 equiv.), CF_2HCOOH (25.2 μL, 0.4 mmol, 2.0 equiv.) in DMAc (8 ml) were used. After 24 h, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE:EA=100:1) as a white solid (14.9 mg, 47%).

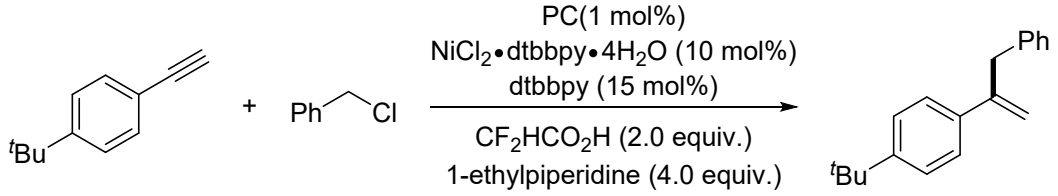
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.5 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 4H), 5.55 (d, *J* = 1.8 Hz, 2H), 5.23 (d, *J* = 1.8 Hz, 2H), 1.30 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 149.5, 137.3, 126.9, 125.1, 115.5, 34.5, 31.3.

HRMS (ESI+): calcd for $C_{24}H_{31}^+$ (M+H) 319.2420, found 319.2425.

5. Optimization of the Reaction Conditions

Table S1 Photocatalyst effect

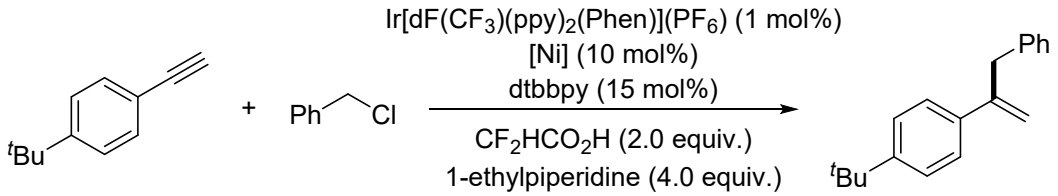


1, 0.1 mmol **2**, 1.0 equiv. **3**

entry	photocatalyst	GC yield of **3**
1	$Ir[dF(CF_3)(ppy)_2(Phen)](PF_6)$	78%
2	$Ir[dF(CF_3)(ppy)_2(dtbbpy)](PF_6)$	57%
3	$Ir[(ppy)_2(dtbbpy)](PF_6)$	55%
4	$Ir(ppy)_3$	17%
5	4-CzIPN	60%
6	Eosin Y	0%

Yields were determined by GC using dodecane as an internal standard.

Table S2 Nickel catalyst effect

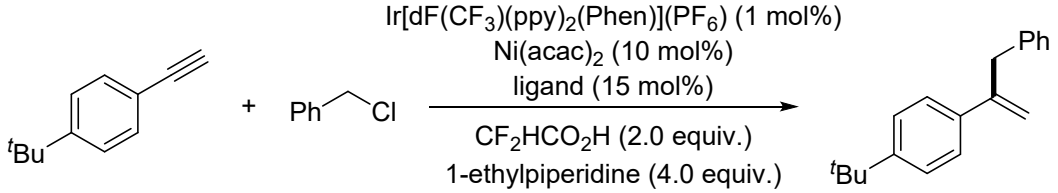


1, 0.1 mmol **2**, 1.0 equiv. **3**

entry	nickel catalyst	GC yield of **3**
1	$Ni(acac)_2$	82%
2	$NiCl_2$•DME	48%
3	$NiCl_2$	62%
4	$NiBr_2$•DME	58%
5	NiI_2	70%
6	$Ni(ClO_4)_2$•$6H_2O$	63%
7	$NiBr_2$	61%

Yields were determined by GC using dodecane as an internal standard.

Table S3 Ligand effect

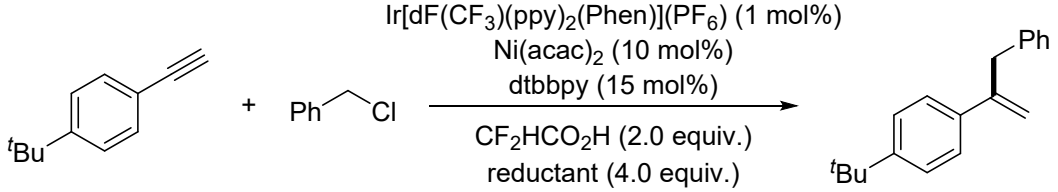


1, 0.1 mmol **2**, 1.0 equiv. **3**

entry	ligand	GC yield of **3**
1	dtbbpy	82%
2	4,4'-di(OMe)-bpy	80%
3	6,6-di(Me)-bpy	10%
4	Phen	67%
5	Py_3	2%
6	5,5'-Bn-BiOX	35%
7	TMEDA	6%
8	dppBz	4%
9	PPh_3	8%

Yields were determined by GC using dodecane as an internal standard.

Table S4 Reductant effect

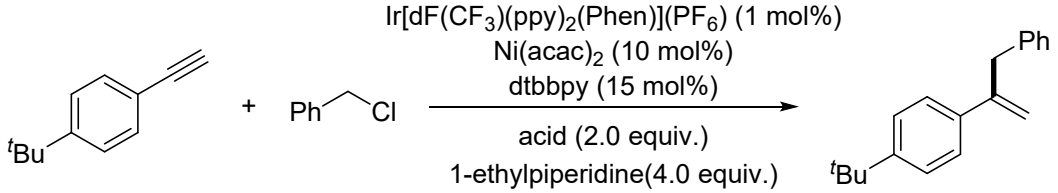


1, 0.1 mmol **2**, 1.0 equiv. **3**

entry	reductant	GC yield of **3**
1	1-ethylpiperidine	82%
2	NEt_3	69%
3	$^{i}Pr_2NEt$	79%
4	$^{i}Pr_2NH$	12%
5	DABCO	0%
6	Ph_3N	0%
7	DBU	0%
8	$BnNEt_2$	66%

Yields were determined by GC using dodecane as an internal standard.

Table S5 Additive effect

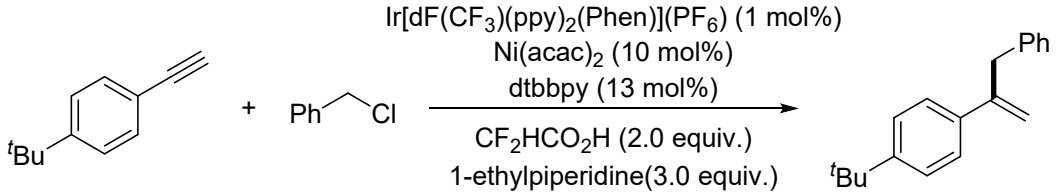


1, 0.1 mmol **2**, 1.0 equiv. **3**

entry	acid	GC yield of **3**
1	CF_3CO_2H	19%
2	$(CF_2HCO)_2O$	80%
3	HCO_2H	54%
4	AcOH	5%
5	$PhCO_2H$	20%
6[a]	CF_2HCO_2H	85%
7[a,b]	CF_2HCO_2H	99% (93%)

Yields were determined by GC using dodecane as an internal standard. [a] 1-ethylpiperidine (3.0 equiv.), [b] **2** (1.3 equiv.), dtbbpy (13 mol%).

Table S6 Control experiments



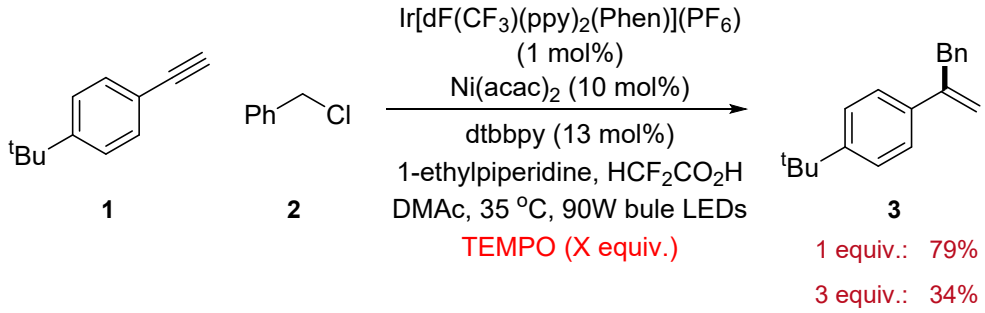
1, 0.1 mmol **2**, 1.3 equiv. **3**

entry	conditions	GC yield of **3**
1	none	99%
2	w/o $Ir[dF(CF_3)(ppy)_2(Phen)](PF_6)$	0%
3	w/o $Ni(acac)_2$	0%
4	w/o dtbbpy	16%
5	w/o 1-ethylpiperidine	trace
6	w/o CF_2HCO_2H	trace
7	w/o light	0%

Yields were determined by GC using dodecane as an internal standard.

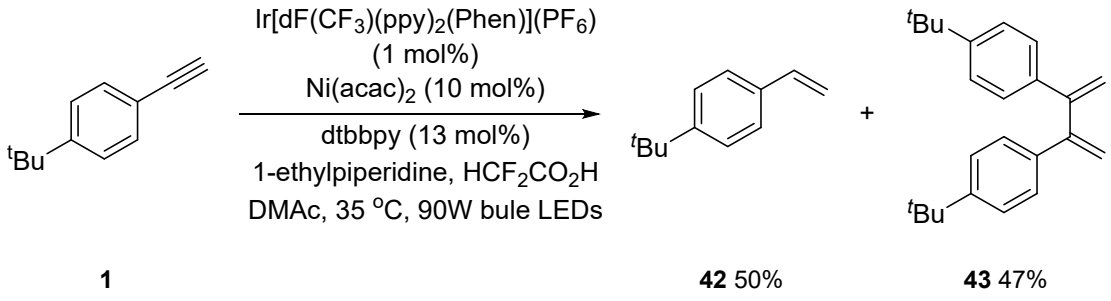
6. Mechanistic Studies

6.1 Radical inhibition reaction



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with Ir[dF(CF_3)(ppy)(Phen)](PF_6) (1.1 mg, 0.001 mmol, 1 mol%), Ni(acac)$_2$ (2.6 mg, 0.01 mmol, 10 mol%), dtbbpy (3.5 mg, 0.013 mmol, 13 mol%) and TEMPO (X equiv.). After DMAc were added as a solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 min, followed by the addition of benzyl chloride (15 µL, 0.13 mol, 1.3 equiv.), 1-ethylpiperidine (41.2 µL, 0.3 mmol, 3.0 equiv.), CF_2HCOOH (12.6 µL, 0.1 mmol, 2.0 equiv.) and 1-(tert-butyl)-4-ethynylbenzene (18 µL, 0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with a 90 W blue LEDs for 24 h at 35 °C. Dodecane (22.7 µL, 0.1 mmol, 1.0 equiv) was added and the mixture was analyzed by GC.

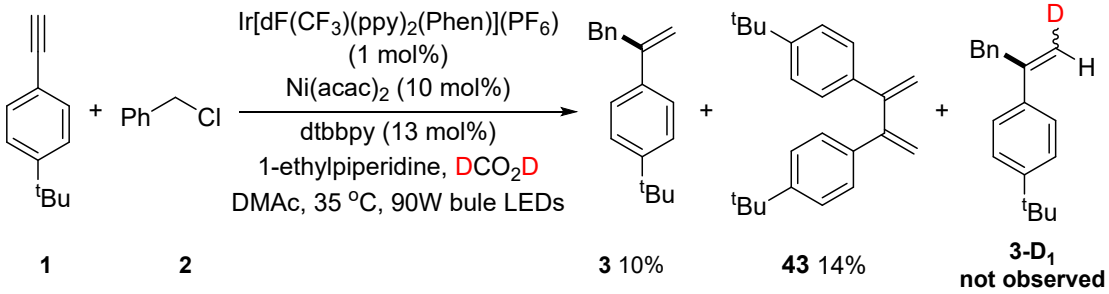
6.2 Control experiments



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with Ir[dF(CF_3)(ppy)(Phen)](PF_6) (1.1 mg, 0.001 mmol, 1 mol%), Ni(acac)$_2$ (2.6 mg, 0.01 mmol, 10 mol%), dtbbpy (3.5 mg, 0.013 mmol, 13 mol%) and TEMPO (X equiv.). After DMAc were added as a solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 min, followed by the addition of 1-ethylpiperidine (41.2 µL, 0.3 mmol, 3.0 equiv.), CF_2HCOOH (12.6 µL, 0.1

mmol, 2.0 equiv.) and 1-(tert-butyl)-4-ethynylbenzene (18 µL, 0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with a 90 W blue LEDs for 24 h at 35 °C. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the alkene **42** and 1,3-diene **43**.

6.3 Deuterium experiments



To a flame-dried 10 mL reaction vial equipped with a magnetic stir bar was charged with Ir[dF(CF_3)(ppy)(Phen)](PF_6) (1.1 mg, 0.001 mmol, 1 mol%), Ni(acac)$_2$ (2.6 mg, 0.01 mmol, 10 mol%), dtbbpy (3.5 mg, 0.013 mmol, 13 mol%). After DMAc were added as a solution (4 mL). The reaction mixture was degassed by nitrogen sparging for 15 min, followed by the addition of benzyl chloride (15 µL, 0.13 mol, 1.3 equiv.), 1-ethylpiperidine (41.2 µL, 0.3 mmol, 3.0 equiv.), DCO_2D (7.5 µL, 0.2 mmol, 2.0 equiv.) and 1-(tert-butyl)-4-ethynylbenzene (18 µL, 0.1 mmol, 1.0 equiv.). The reaction mixture was then irradiated with a 90 W blue LEDs for 24 h at 35 °C. The reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to afford the products **3** and **43**, but **3-D$_1$** not observed.

6.4 Determination of quantum yield

We utilized protocol reported by Shunsuke and co-workers to determine the photon flux of blue LED. All solutions were stored in the black vial and stored in the dark when not in use. Measurements were performed with the lights off to protect the samples from ambient light as much as possible.

a) Preparation of stock solutions

A 0.15 M solution of ferrioxalate was obtained by dissolving potassium ferrioxalate trihydrate($[K_3Fe^{III}(C_2O_4)_3]\bullet 3H_2O$; 1.11 g, 2.26 mmol) in 0.05 M H_2SO_4 (prepared by fresh deionized water) (15 mL total volume).

A buffered phenanthroline solution was obtained by dissolving 1,10-phenanthroline (10.0mg) and sodium acetate (2.25g) in 0.5M H_2SO_4 (prepared by fresh deionized water) (10 mL total volume).

b) Determination of background Fe^{2+} concentration

2 mL of the ferrioxalate solution was added to a 8 mL vial. Next, 0.35 mL of the phenanthroline solution was added and the mixture was stored in the dark for 1 hour. Then the solution was transferred to a cuvette and a UV–vis spectrum was measured using UV–vis absorption spectrometer (lambda 950). The absorbance value at 510 nm was recorded. This process was repeated twice. Average value: 0.635334.

c) Determination of photon flux

2 mL of the ferrioxalate solution was added to a 8 mL vial. The vial was immediately irradiated with blue LED (λ_{max}= 469 nm) for 10 seconds and removed from the blue LED. Then, 0.35 mL of the phenanthroline solution was added to the ferrioxalate solution, and the resulting mixture was stored in the dark for 1 hour. Then the solution was transferred to a cuvette and the UV–vis spectrum was measured. The absorbance value at 510 nm was recorded. This process was repeated twice. Average value: 2.12699.

d) Calculations

The amount of Fe^{2+}formed was calculated according to the following equation:

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

where V is the volume of the sample analyzed (2.35 mL), ΔA is the difference in average absorbances (between irradiated and unirradiated ferrioxalate solutions) at 510 nm, l is the path length, and ε is the molar absorptivity at 510 nm[11].

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{(0.00235\ L)(1.491656)}{(3\ cm)(11100\ {}^{L}/_{mol \cdot cm})} = 10.5267 \cdot 10^{-8}\ mol$$

The fraction of light absorbed by the ferrioxalate actinometer was calculated by the following

equation:

$$f = 1-10^{-A}$$

where A is the absorbance at 468 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline (**Figure S1**).

$$f = 1-10^{-A} = 1\text{-}10^{-0.89826} = 0.87360$$

The photon flux was calculated using the following equation:

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer at 468 nm, t is the time and f is the fraction of light absorbed by the ferrioxalate actinometer solution.

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{10.5267 \cdot 10^{-8} mol}{(0.92) \cdot (10s) \cdot (0.87360)} = 1.30976 \cdot 10^{-8} einsterin/s$$

e) Determination of fraction of light absorbed at 468 nm for the ferrioxalate solution

The absorbance at 468 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline was measured to be 0.89826.

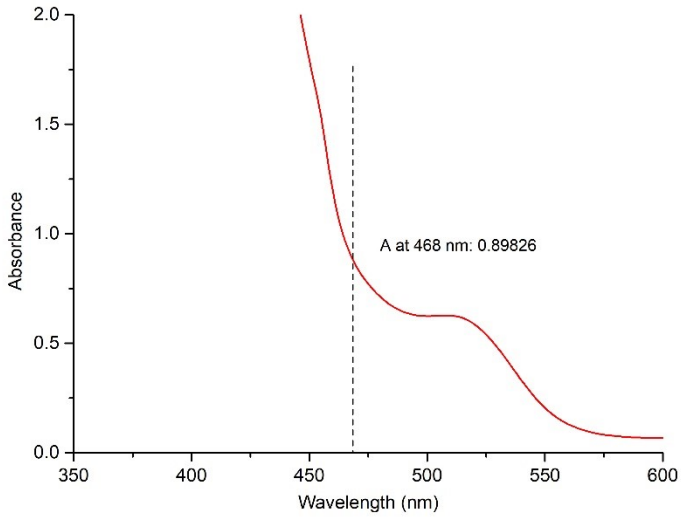


Figure S1 UV-vis absorbance spectra of ferrioxalate solution

f) Absorbance of photocatalyst Ir[dF(CF$_3$)(ppy)$_2$(Phen)](PF$_6$)

The absorbance of Ir[dF(CF$_3$)(ppy)$_2$(Phen)](PF$_6$) in DMAc was measured at the reaction concentration of 250 μM or a dilute concentration of 25 μM (**Figure S2**). The absorbance at 468 nm for a 250 μM is 0.4318.

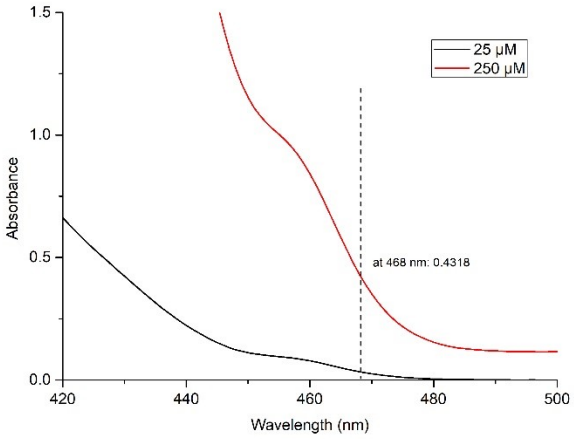
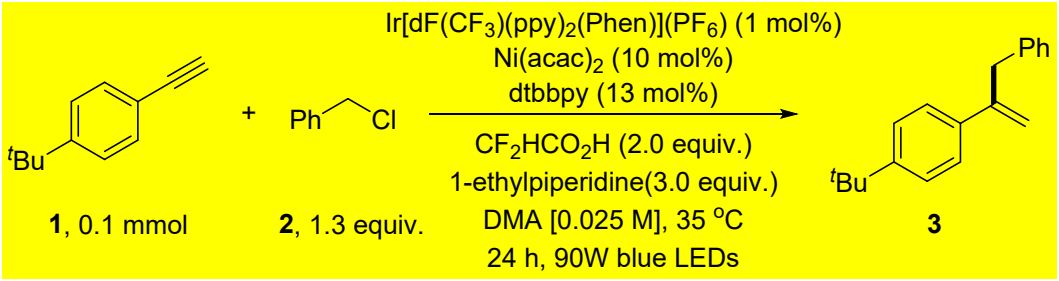


Figure S2 UV-vis absorbance spectra of Ir[dF(CF_3)(ppy)$_2$(Phen)](PF_6) black line: 25 μM in DMAc, red line: 250 μM in DMAc.

g) Determination of quantum yield



According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (18.0 μL, 0.1 mmol, 1.0 equiv.), (chloromethyl)benzene (15.0 μL, 0.13 mmol, 1.3 equiv.), Ir[dF(CF_3)(ppy)$_2$(Phen)]PF_6 (1.1 mg, 0.001 mmol, 1 mol%), Ni(acac)$_2$ (2.6 mg, 0.01 mmol, 10 mol%), dtbbpy (3.5 mg, 0.013 mmol, 13 mol%), 1-ethylpiperidine (41.2 μL, 0.3 mmol, 3.0 equiv.), CF_2HCOOH (12.6 μL, 0.2 mmol, 2.0 equiv.) in DMAc (4 ml) were used. The reaction mixture was then irradiated with one 90 W blue LED lamp (λ_{max}= 469 nm) for 600 seconds. After irradiation, the reaction mixtures were analyzed by GC with an internal standard. Provide the desired product (4.1 % GC yield).

The quantum yield (Φ) was calculated using the following equation:

$$\Phi = \frac{mol\ product}{photon\ flux \cdot t \cdot f}$$

Where t is the reaction time and f is the fraction of light absorbed by photocatalyst that was calculated using the following equation:

$$f = 1-10^{-A} = 1\text{-}10^{-0.4318} = 0.63$$

Where A is the absorbance at 468 nm of the photocatalyst solution (250 μM in DMAc) (**Figure S4**).

$$\Phi = \frac{mol\ product}{photon\ flux \cdot t \cdot f} = \frac{0.0000041\ mol}{\left(1.30976 \cdot 10^{-8} einsterin/_{s}\right) \cdot (600s) \cdot (0.63)} = 0.83$$

6.5 Stern-Volmer quenching experiments

Stern-Volmer quenching experiments were carried by Edinburgh Fluorescence Spectrometer FS5, using a 0.01 mM solution of photocatalyst Ir[dF(CF_3)(ppy)$_2$(Phen)](PF_6) and variable concentrations (0.5, 1.0, 1.5, 2.0, 2.5 mM) of CF_2HCO_2H , *N*-ethylpiperidine and benzyl chloride in solvent DMAc. The samples were prepared in 4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box. The intensity of the emission peak at 484 nm (λex= 376 nm) expressed as the ratio I_0/I, where I_0 is the emission intensity of photocatalyst at 484 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Stern-Volmer plots for each component are given in the Supplementary Figures below.

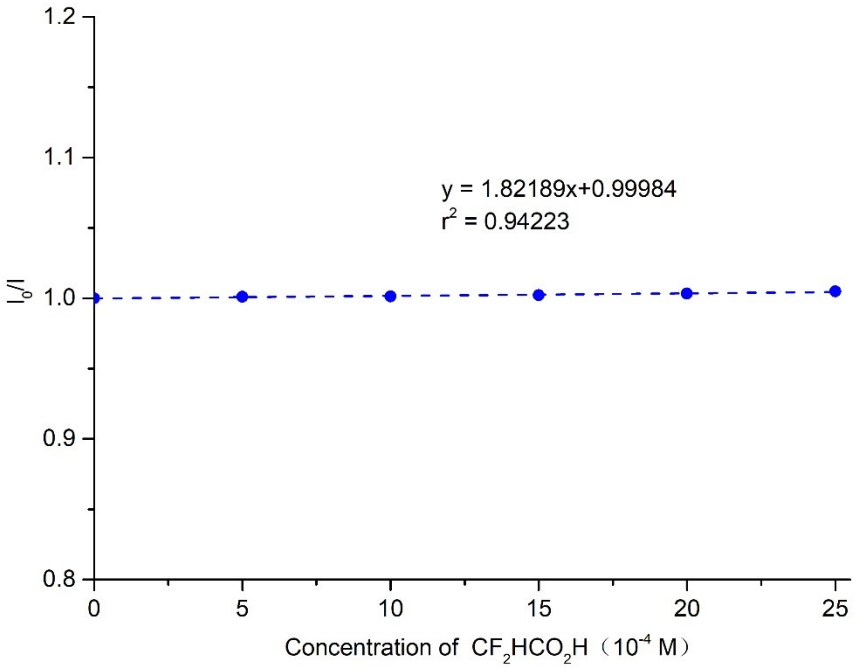


Figure S3 Stern-Volmer plot of photocatalyst (0.01 mM) at different concentrations of CF_2HCO_2H

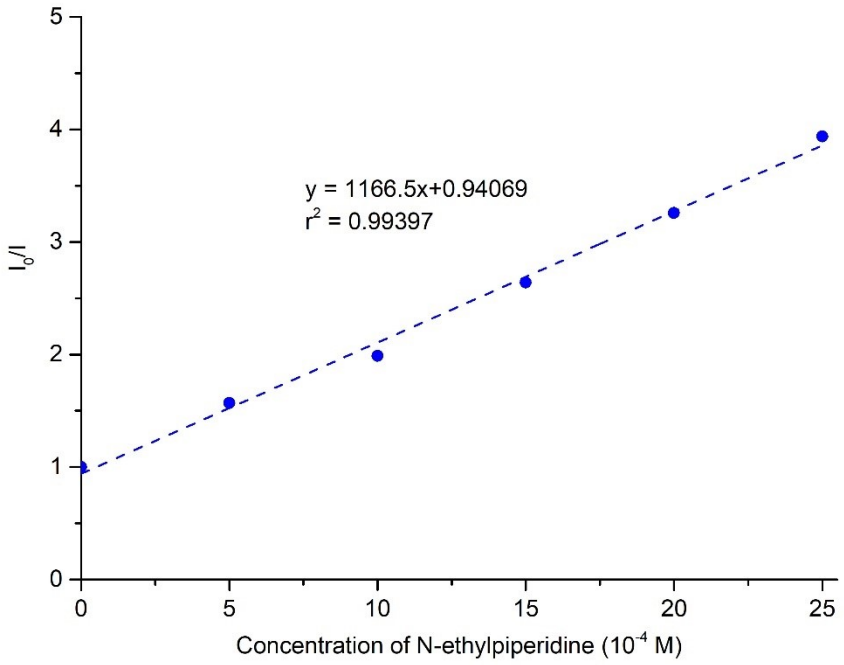


Figure S4 Stern-Volmer plot of photocatalyst (0.01 mM) at different concentrations of *N*-ethylpiperidine

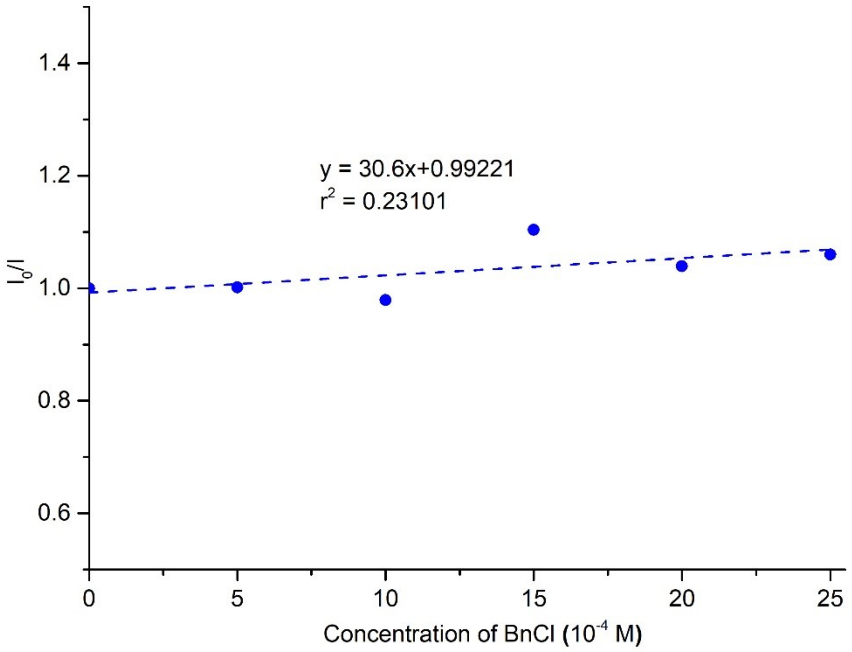
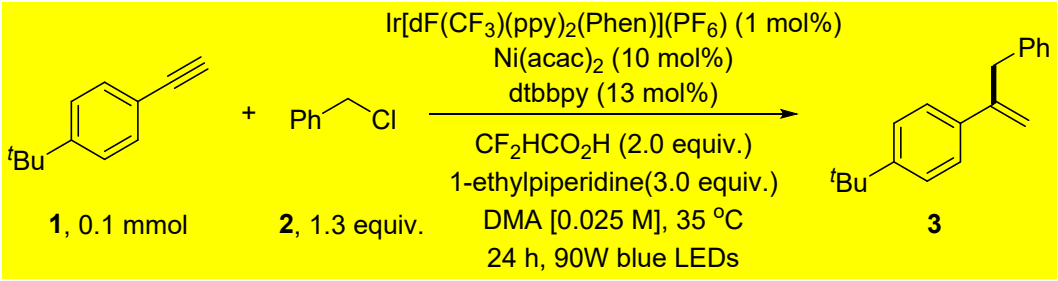


Figure S4 Stern-Volmer plot of photocatalyst (0.01 mM) at different concentrations of benzyl chloride

6.6 Light ON/OFF experiments over time



According to the general procedure, 1-(tert-butyl)-4-ethynylbenzene (18.0 μL, 0.1 mmol, 1.0 equiv.), (chloromethyl)benzene (15.0 μL, 0.13 mmol, 1.3 equiv.), $Ir[dF(CF_3)(ppy)_2(Phen)]PF_6$ (1.1 mg, 0.001 mmol, 1 mol%), $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%), dtbbpy (3.5 mg, 0.013 mmol, 13 mol%), 1-ethylpiperidine (41.2 μL, 0.3 mmol, 3.0 equiv.), CF_2HCOOH (12.6 μL, 0.2 mmol, 2.0 equiv.) and dodecane (22.7 μL, 0.1 mmol) in DMAc (4 ml) were used. The reaction mixture was then irradiated with one 90 W blue LED lamp. The reaction mixtures were analyzed by GC.

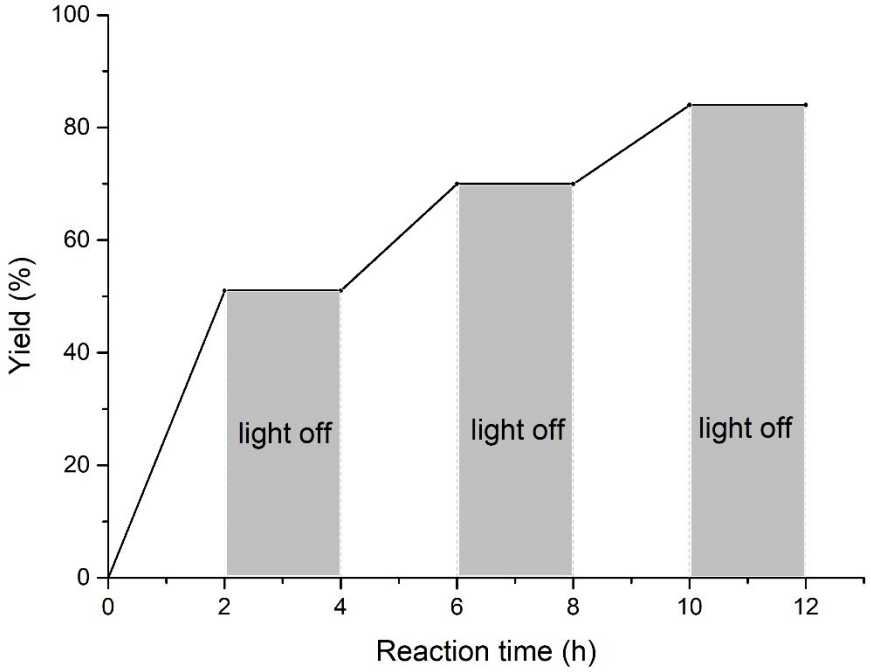
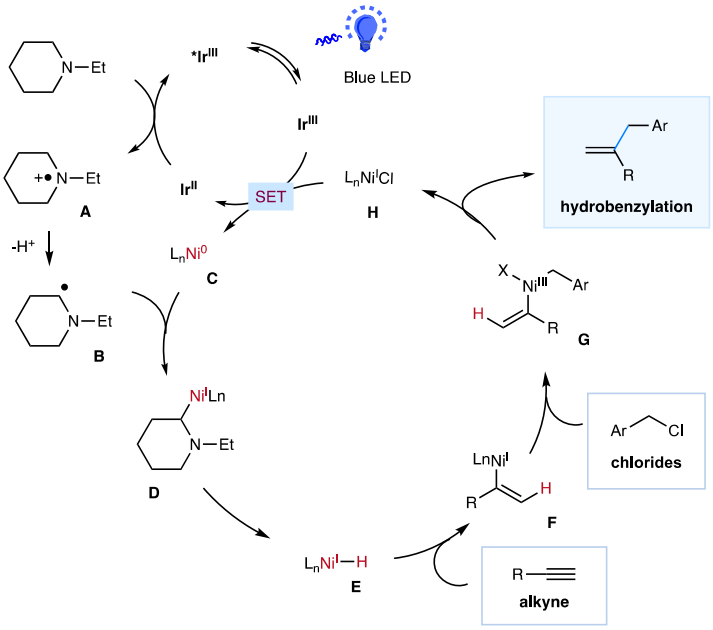


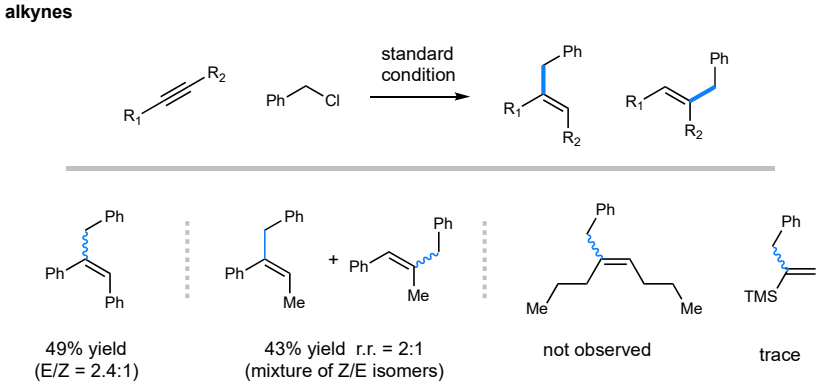
Figure S5 light on/off experiments

6.7 Proposed mechanism.



Scheme S1. Proposed catalytic cycle

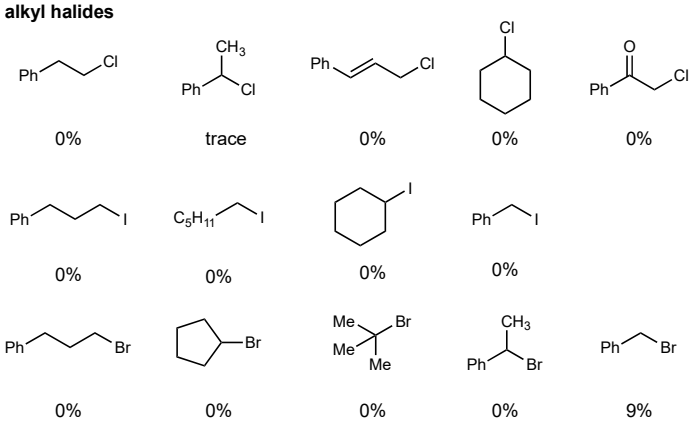
6.8 Unsuccessful substrates



Scheme S2. Examples of unsuccessful alkynes.

Unsuccessful substrates:

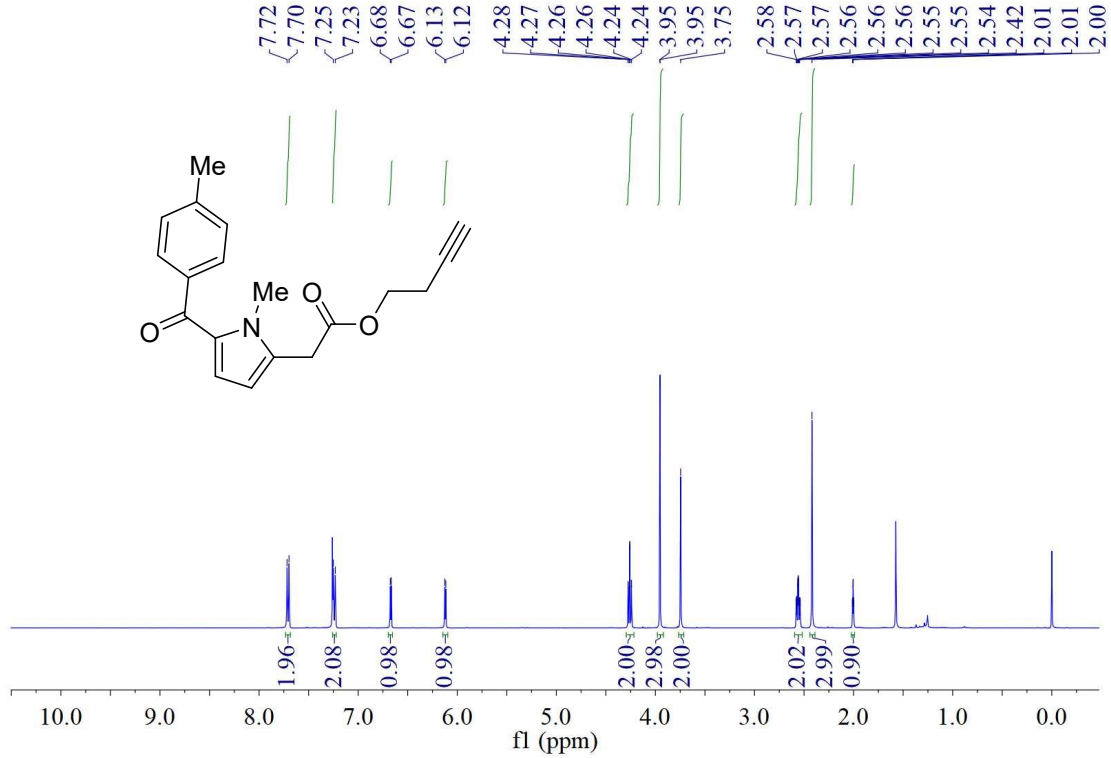
alkyl halides



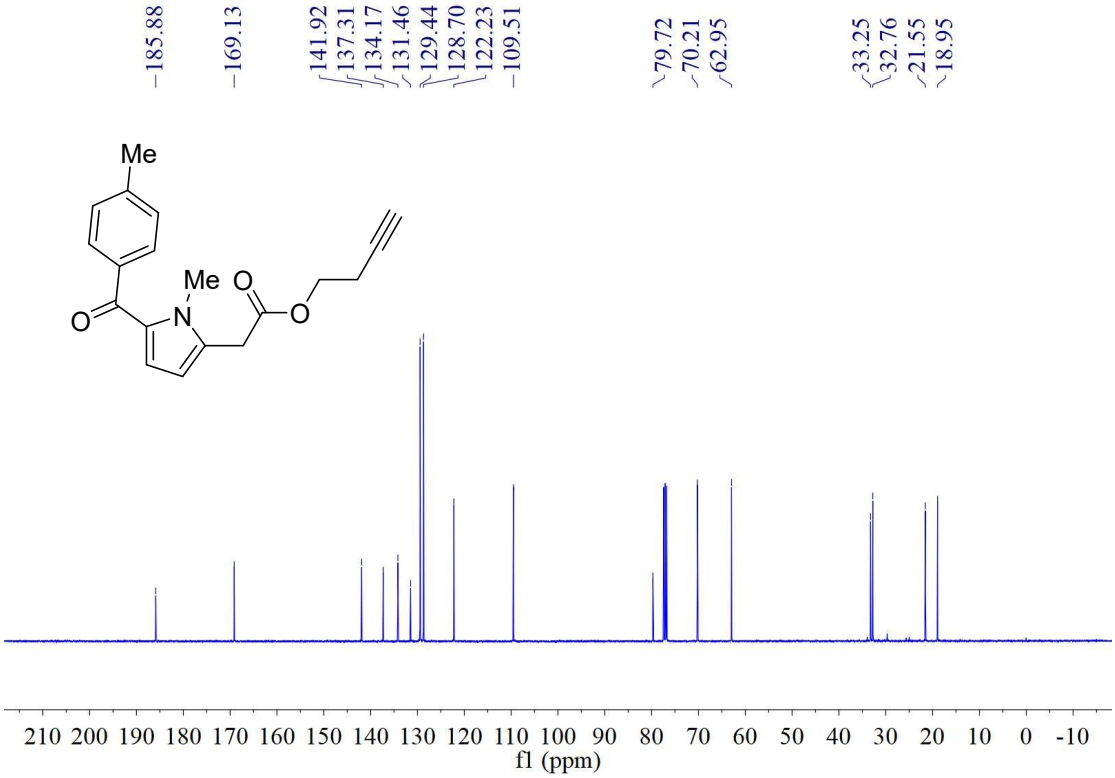
Scheme S3. Examples of unsuccessful halides.

7. NMR Spectra

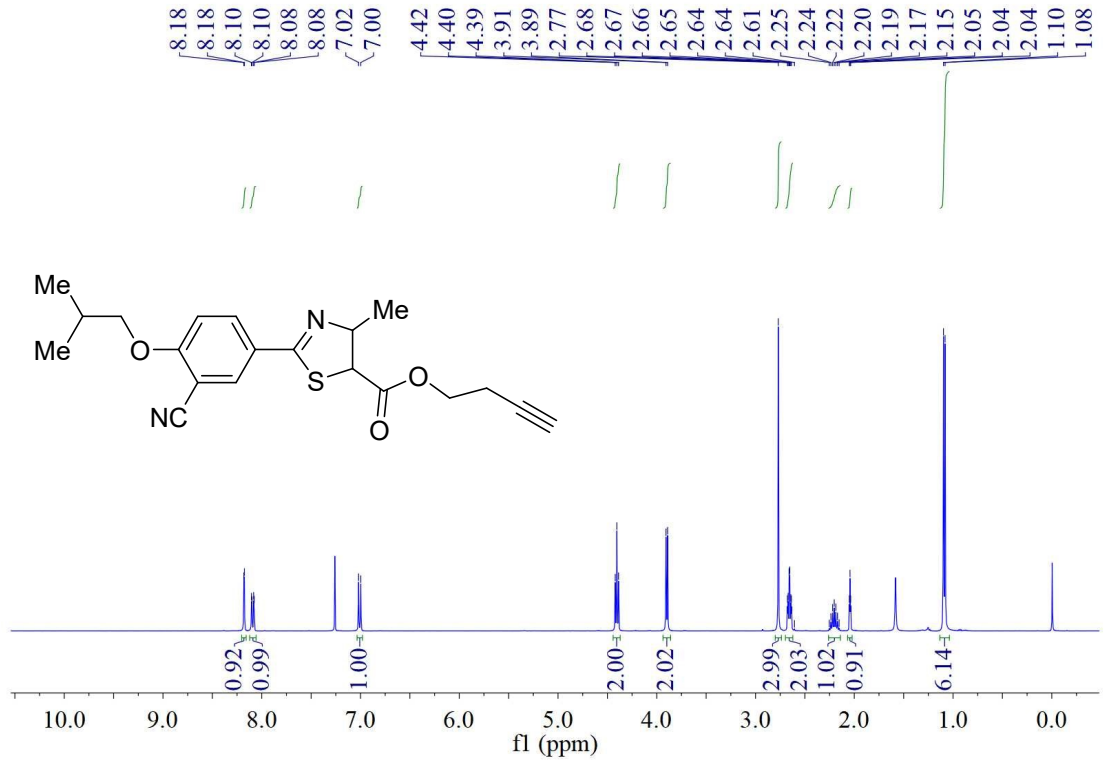
^{1}H NMR of **S1** (400 MHz, $CDCl_3$)



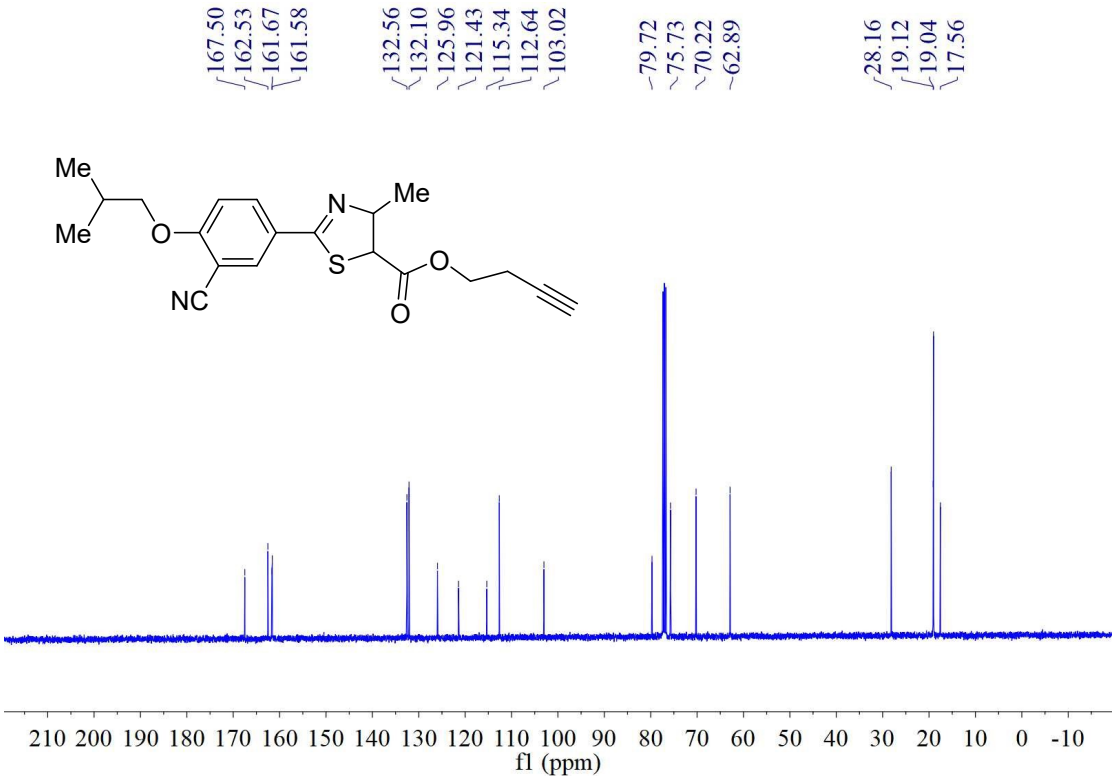
^{13}C NMR of **S1** (100 MHz, $CDCl_3$)



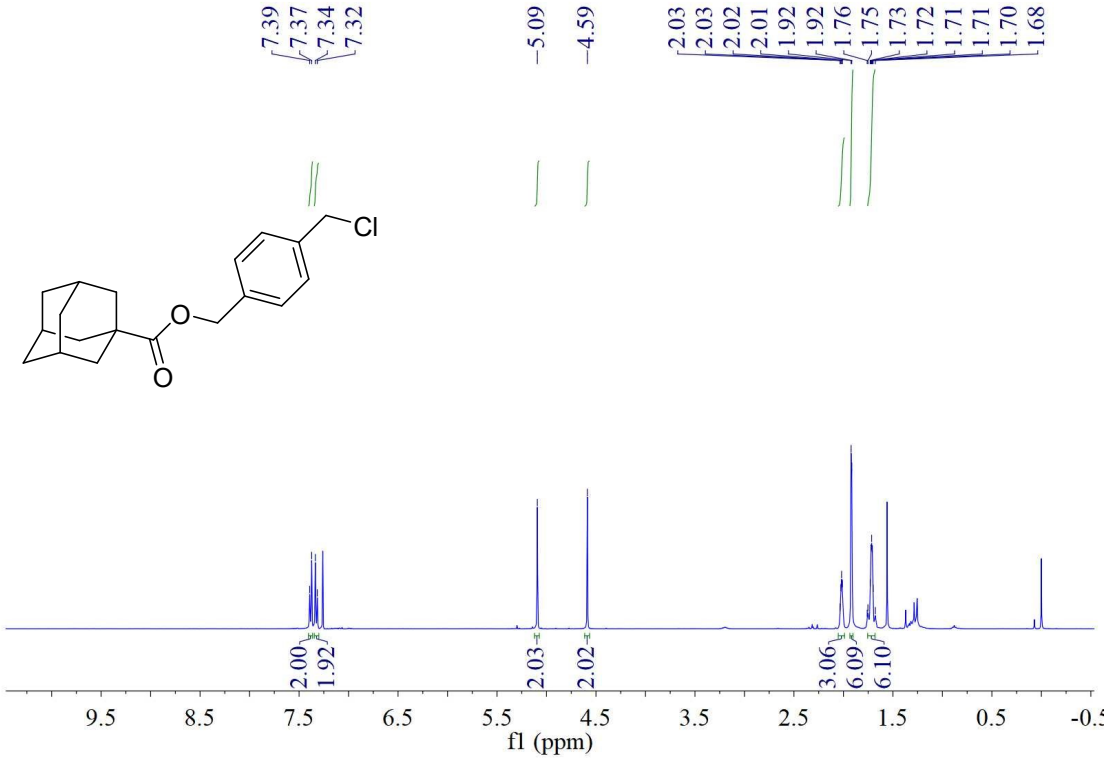
^{1}H NMR of **S2** (400 MHz, $CDCl_3$)



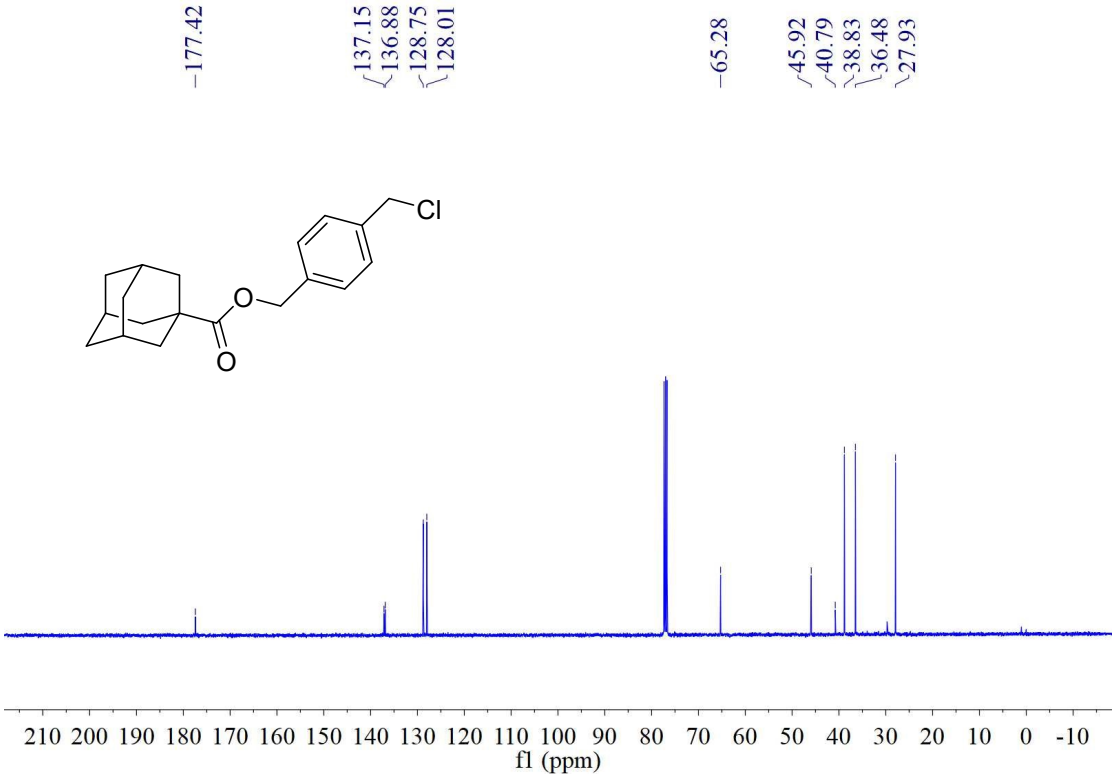
^{13}C NMR of **S2** (100 MHz, $CDCl_3$)



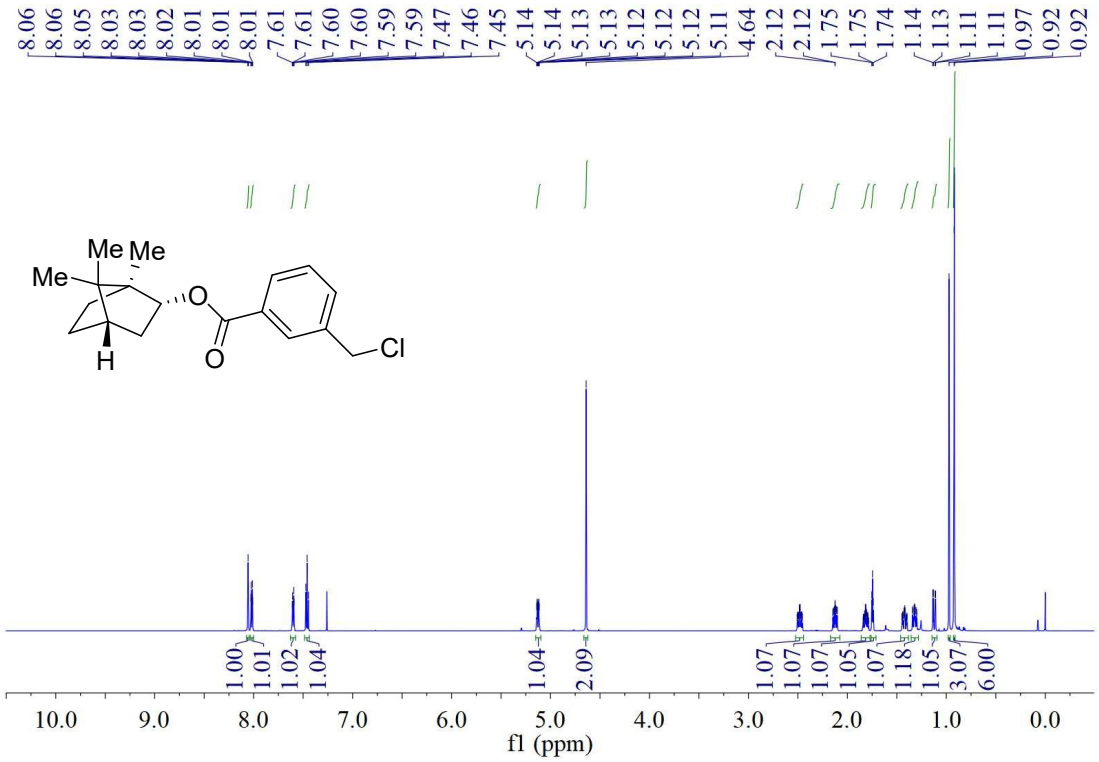
^{1}H NMR of **S3** (400 MHz, $CDCl_3$)



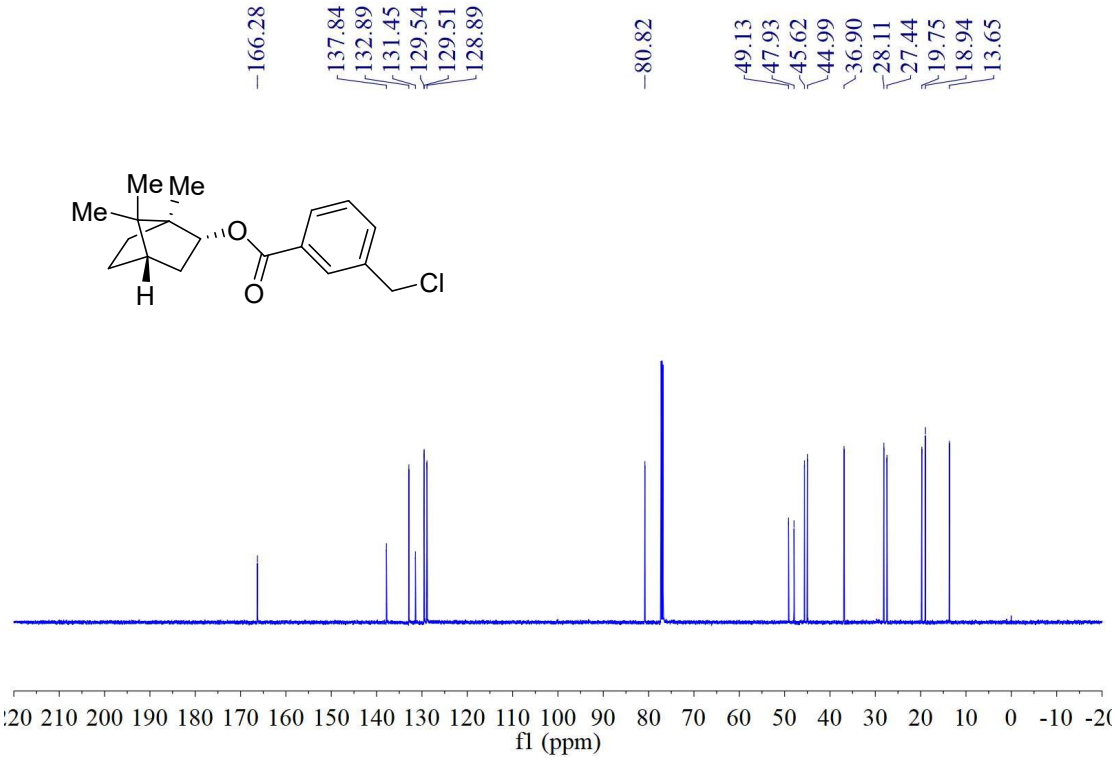
^{13}C NMR of **S3** (100 MHz, $CDCl_3$)



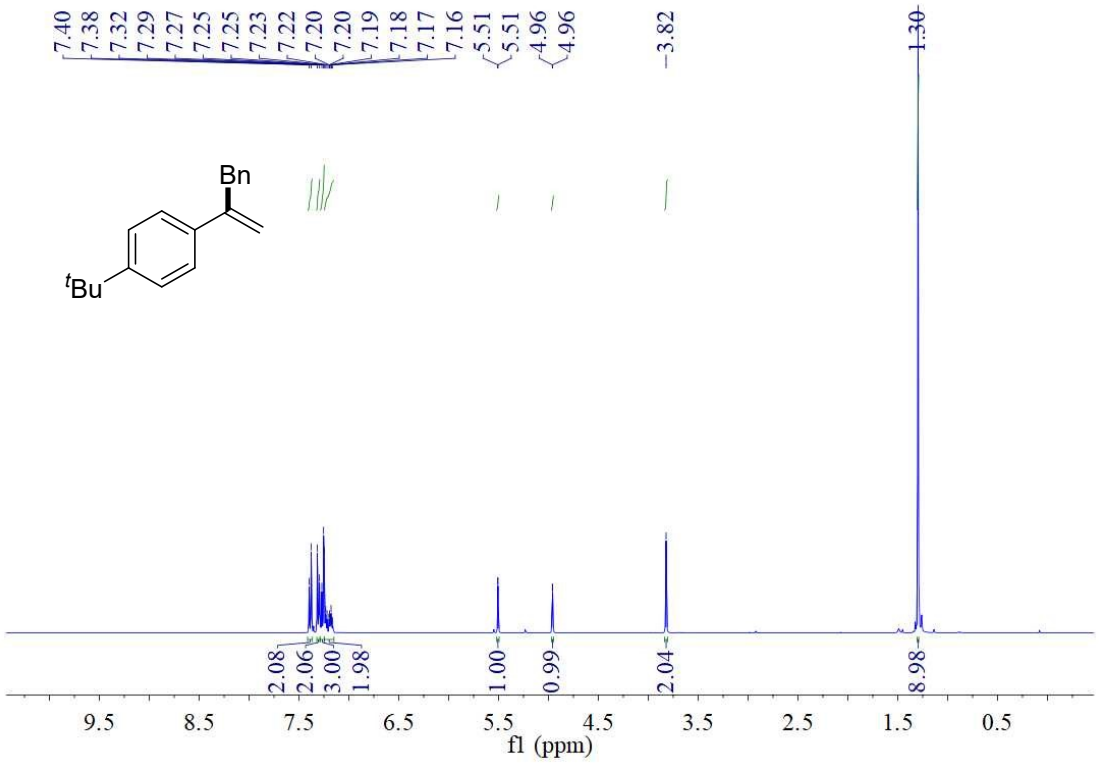
^{1}H NMR of **S4** (600 MHz, $CDCl_3$)



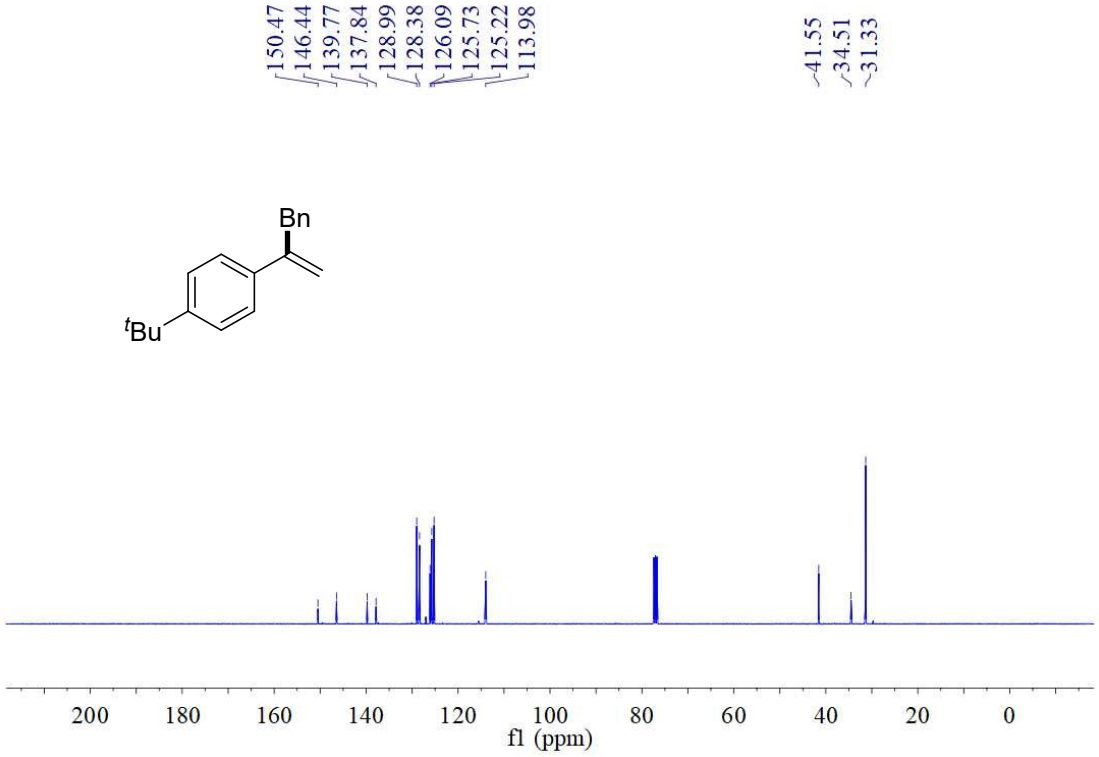
^{13}C NMR of **S4** (150 MHz, $CDCl_3$)



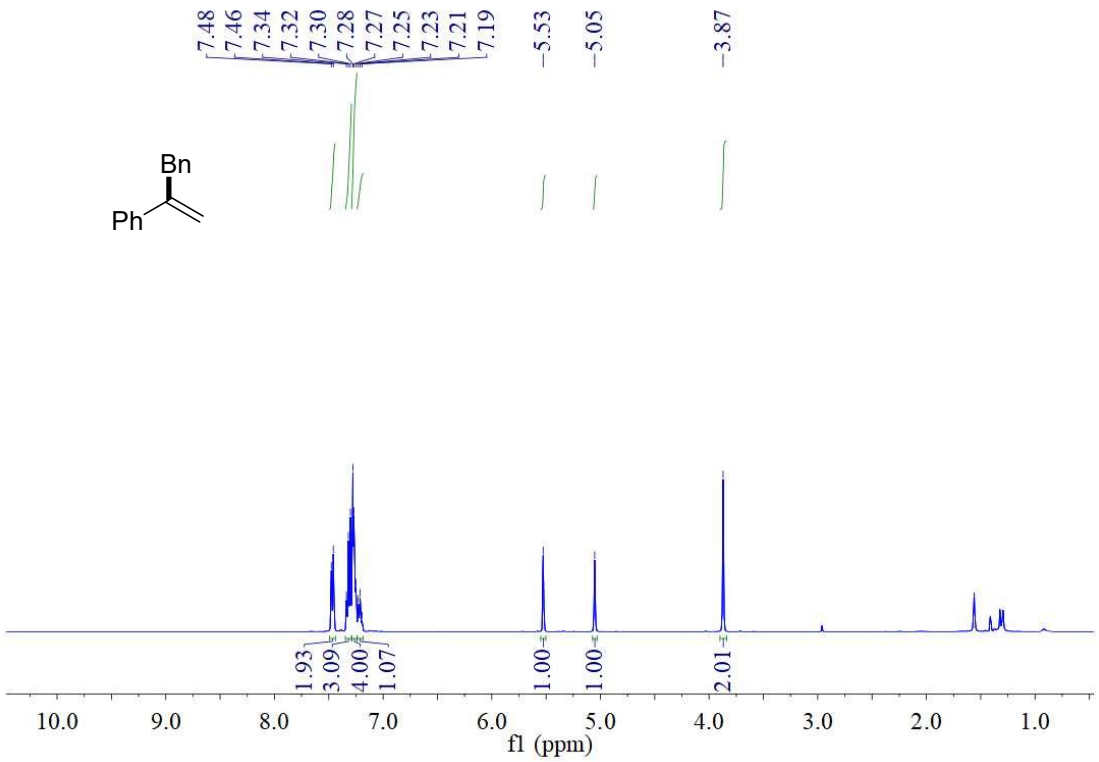
^{1}H NMR of **3** (400 MHz, $CDCl_3$)



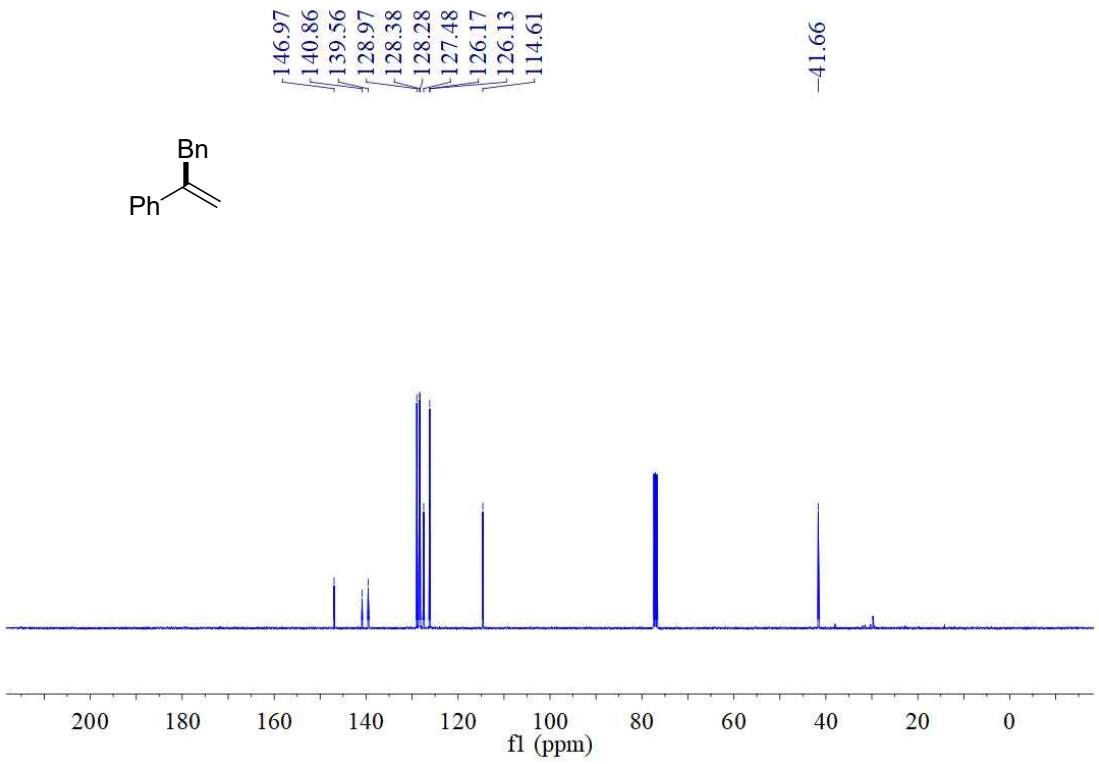
^{13}C NMR of **3** (100 MHz, $CDCl_3$)



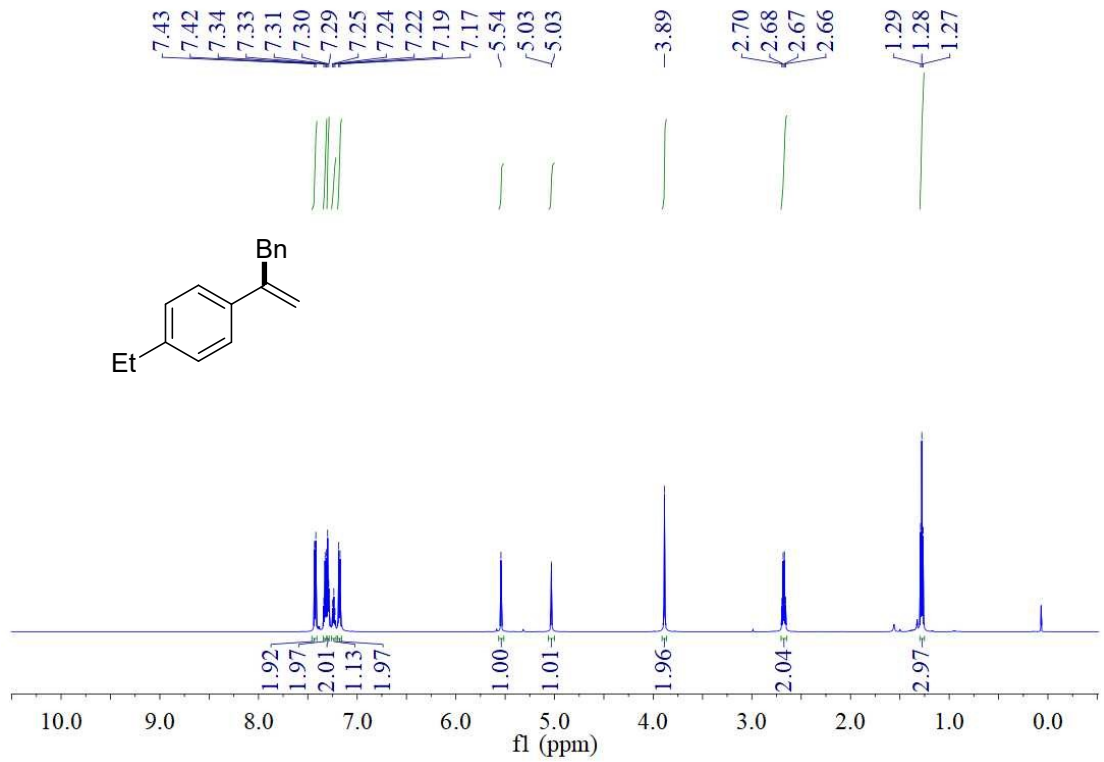
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



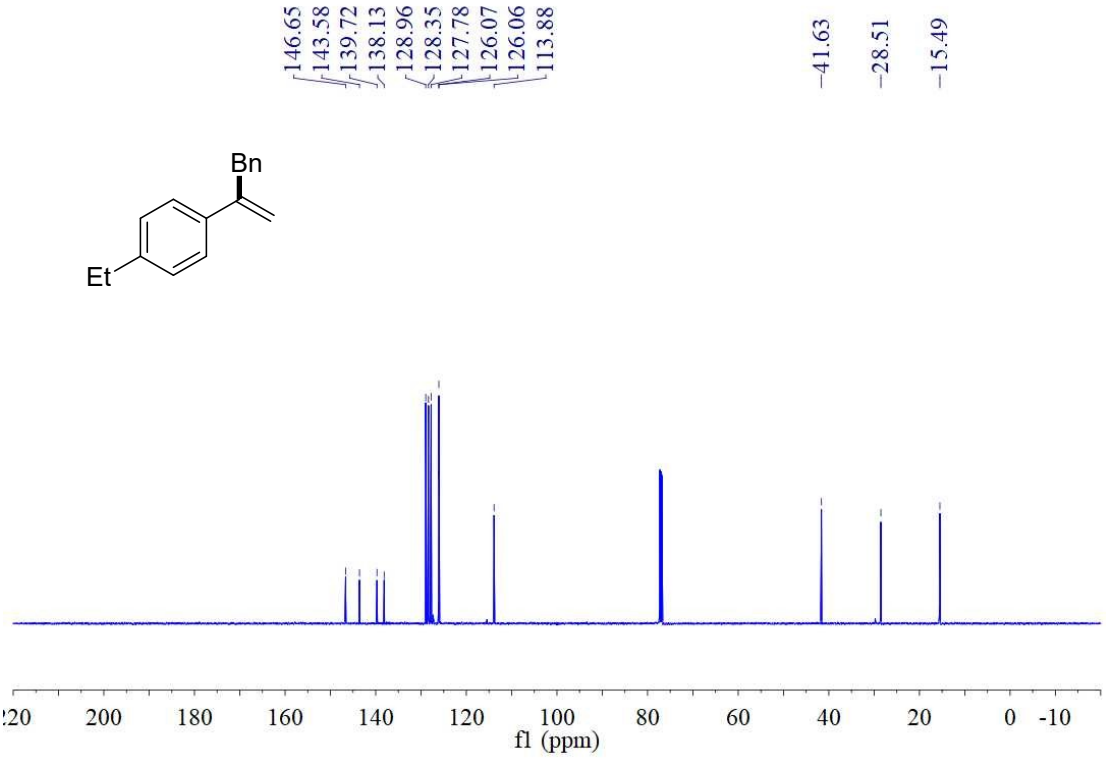
^{13}C NMR of **4** (100 MHz, $CDCl_3$)



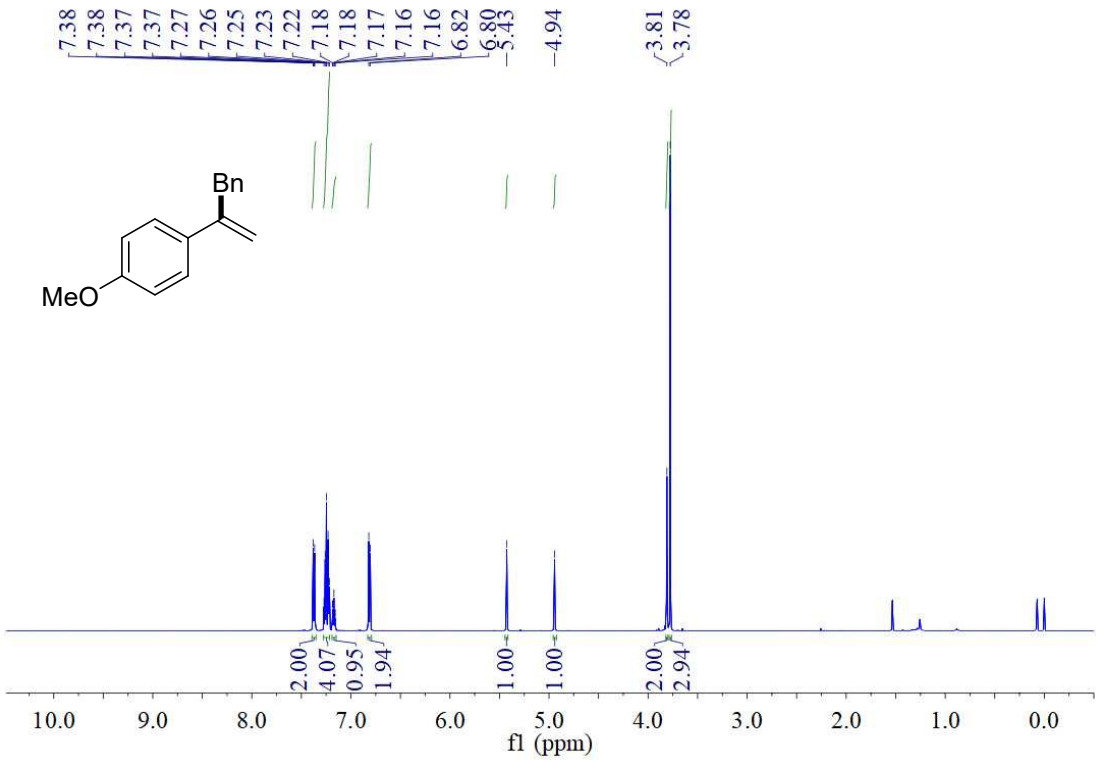
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



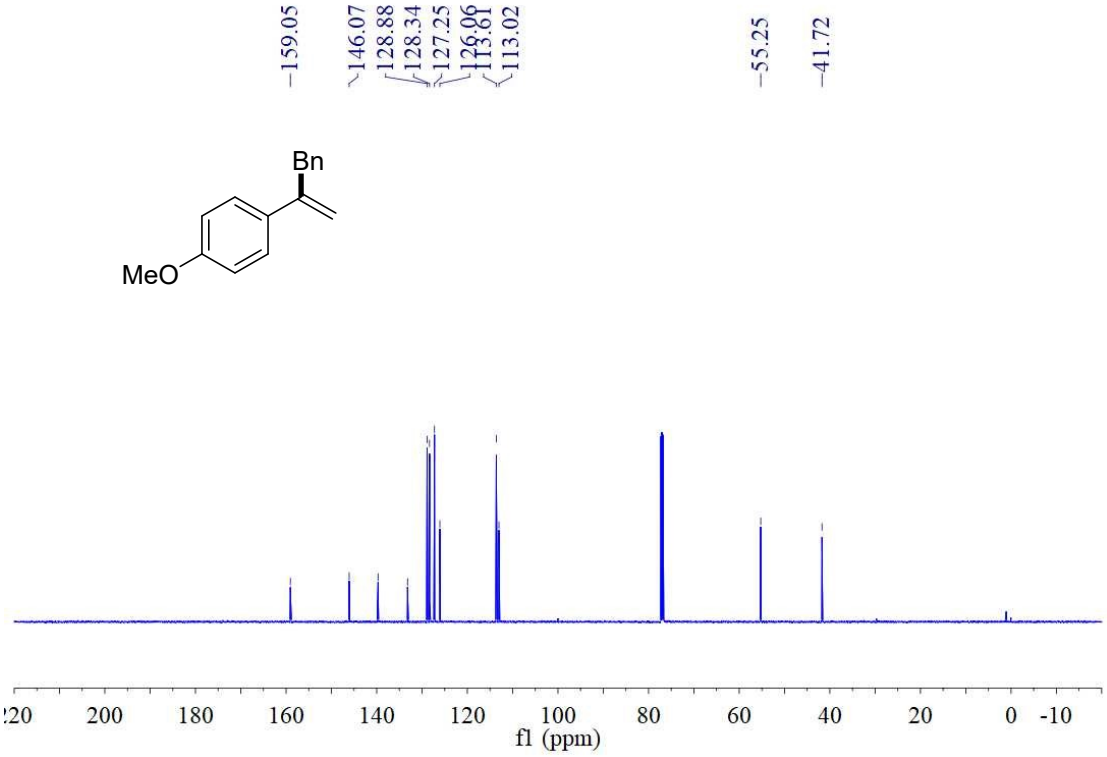
^{13}C NMR of **5** (100 MHz, $CDCl_3$)



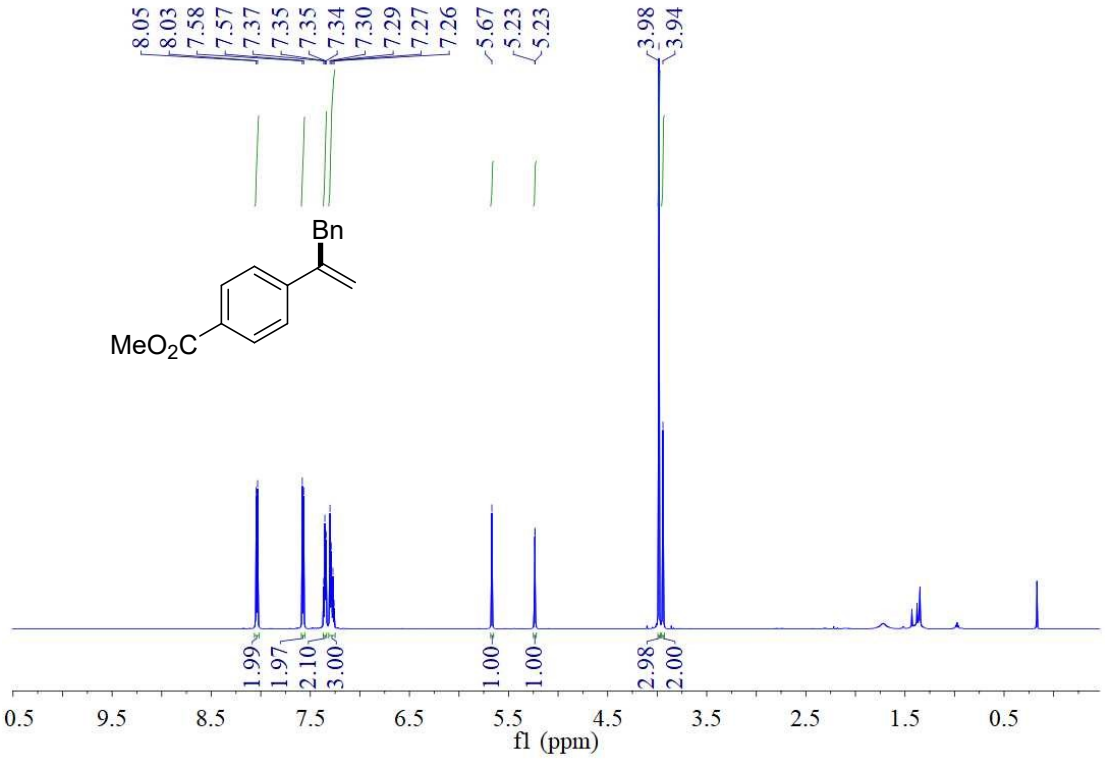
^{1}H NMR of **6** (400 MHz, $CDCl_3$)



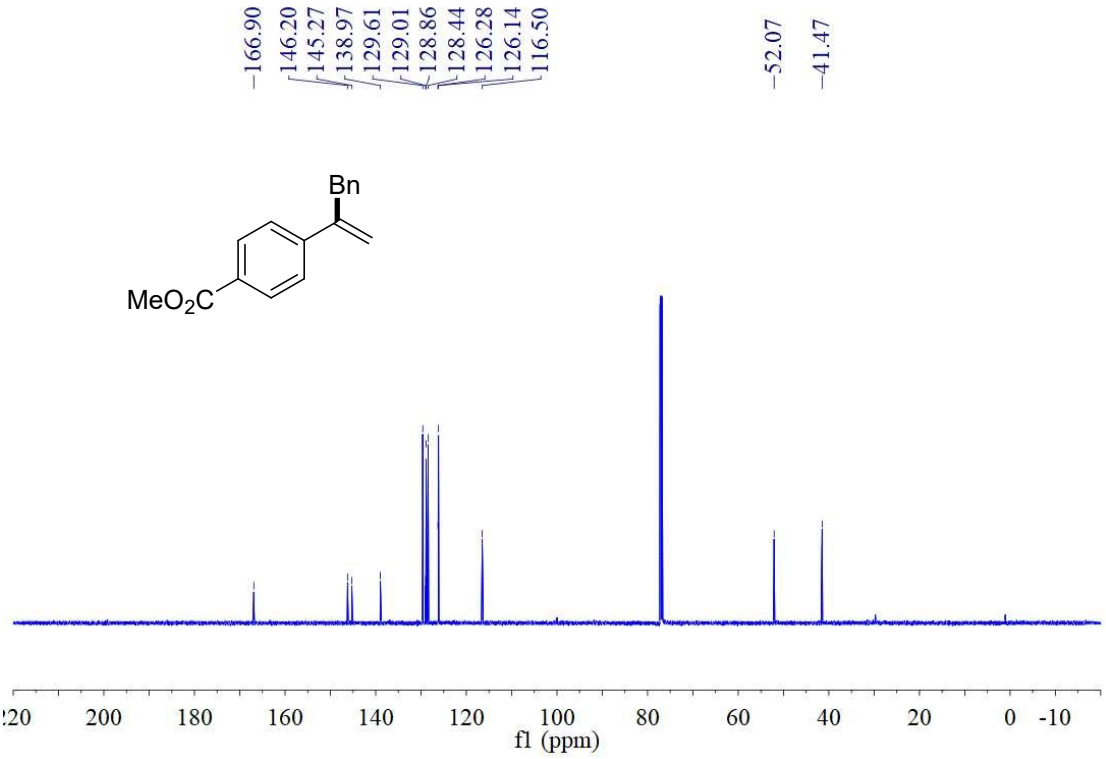
^{13}C NMR of **6** (100 MHz, $CDCl_3$)



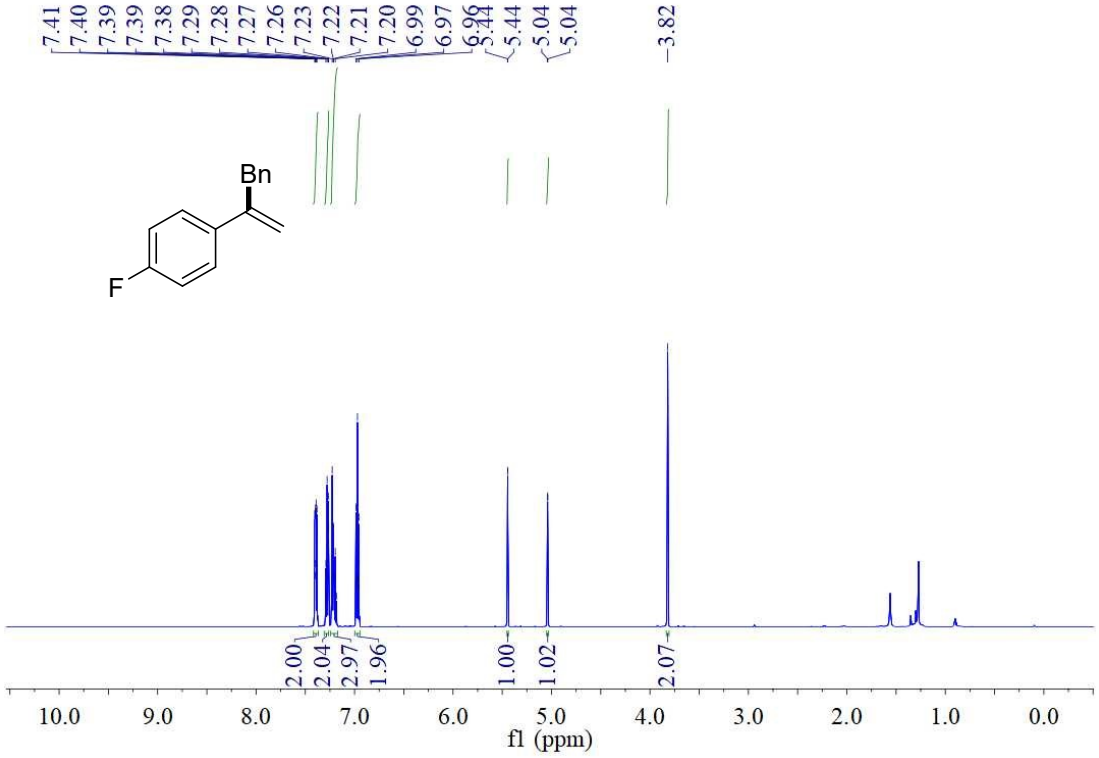
^{1}H NMR of **7** (600 MHz, $CDCl_3$)



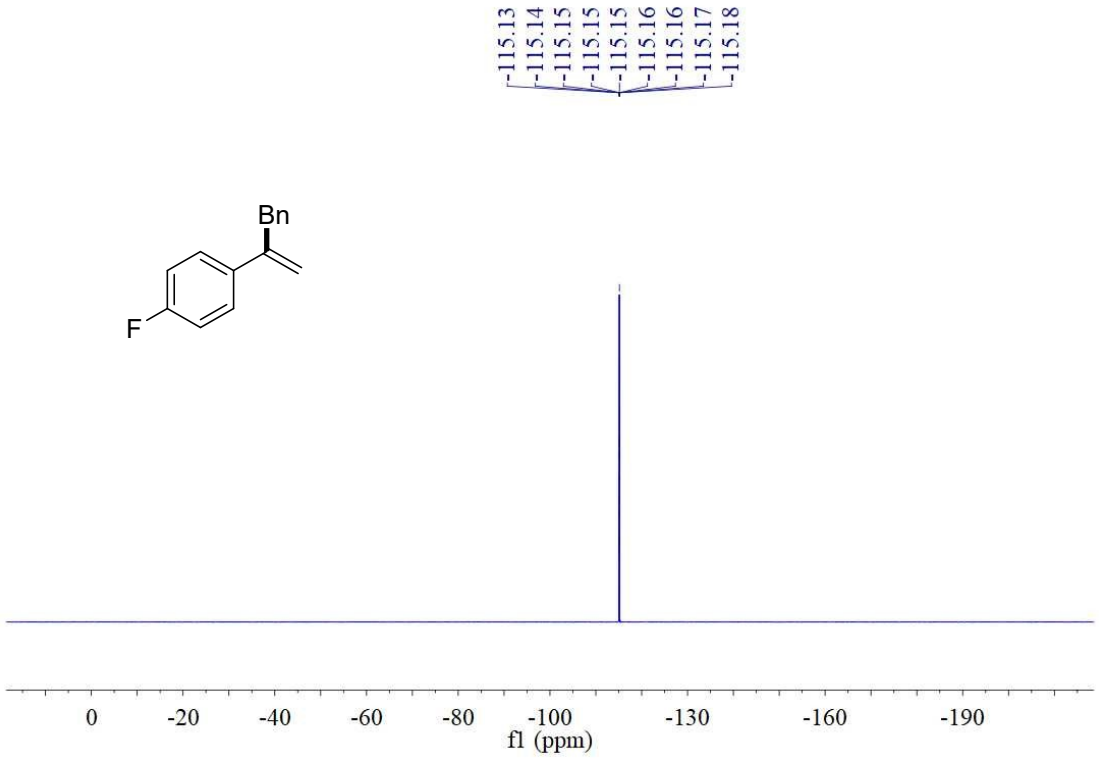
^{13}C NMR of **7** (150 MHz, $CDCl_3$)



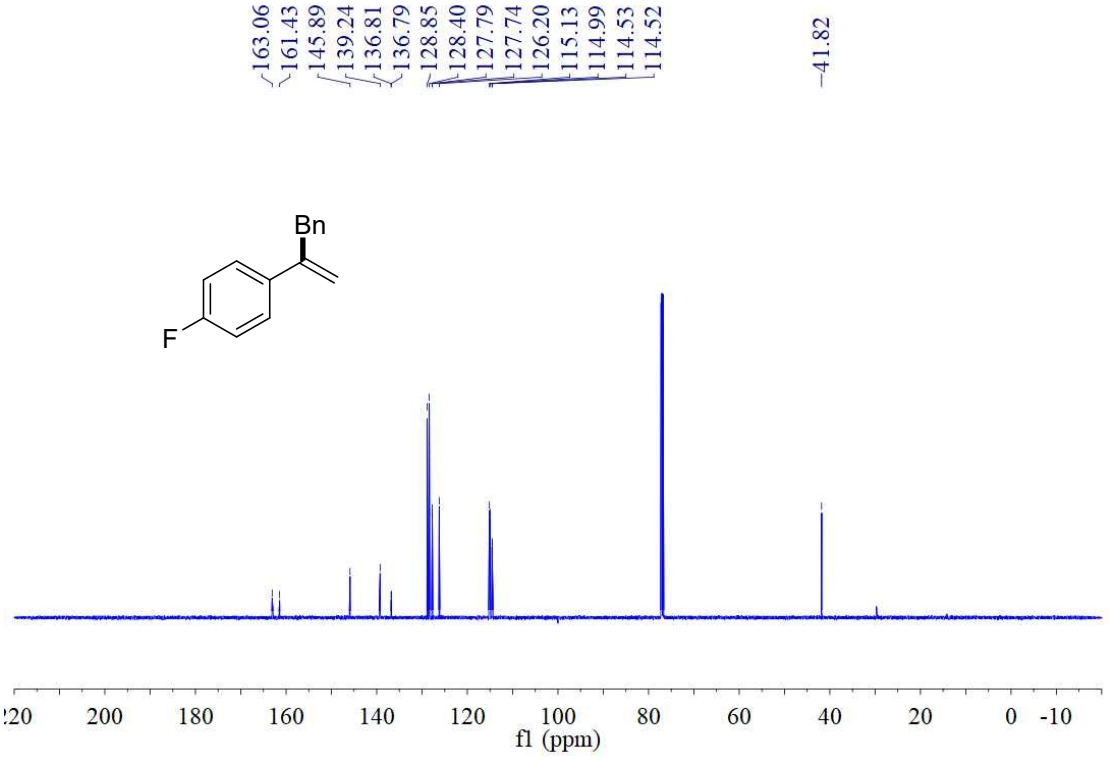
^{1}H NMR of **8** (600 MHz, $CDCl_3$)



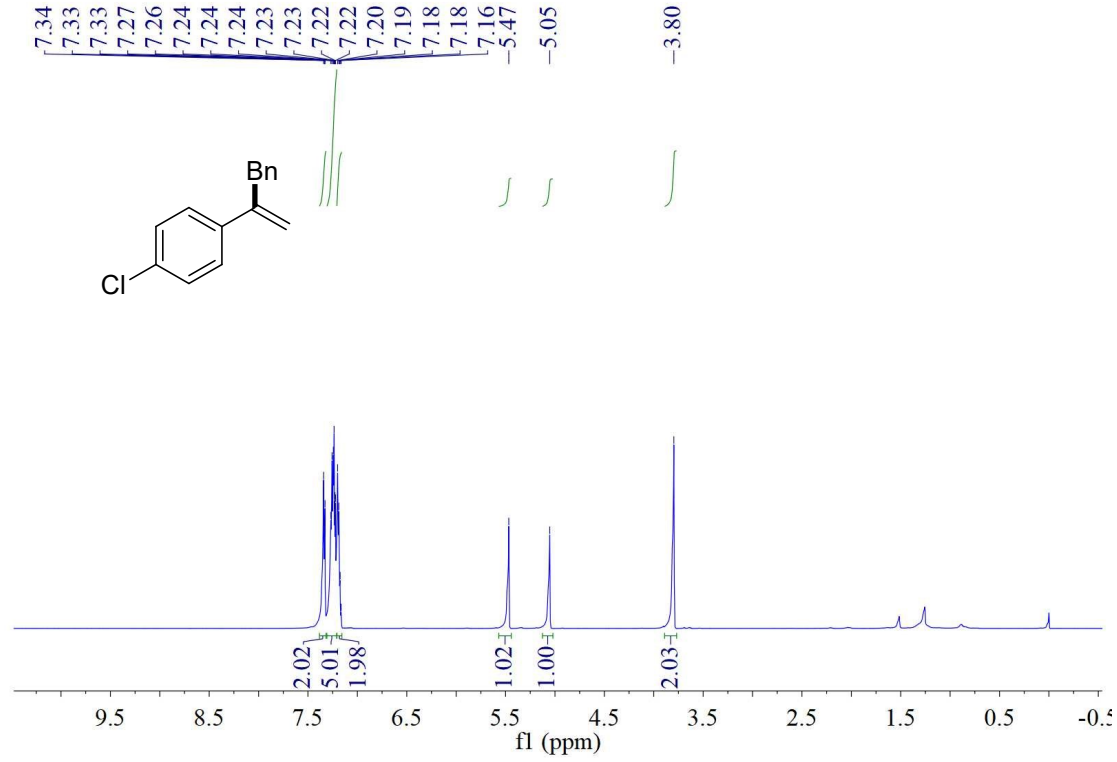
^{19}F NMR of **8** (564 MHz, $CDCl_3$)



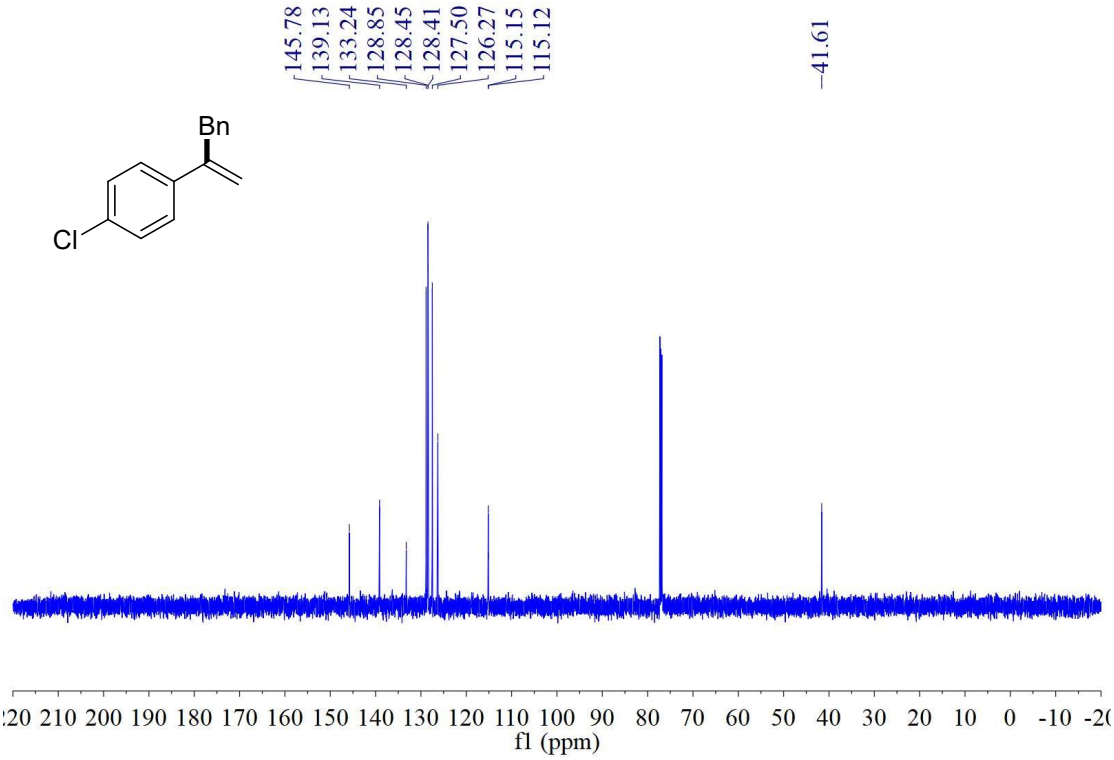
^{13}C NMR of **8** (150 MHz, $CDCl_3$)



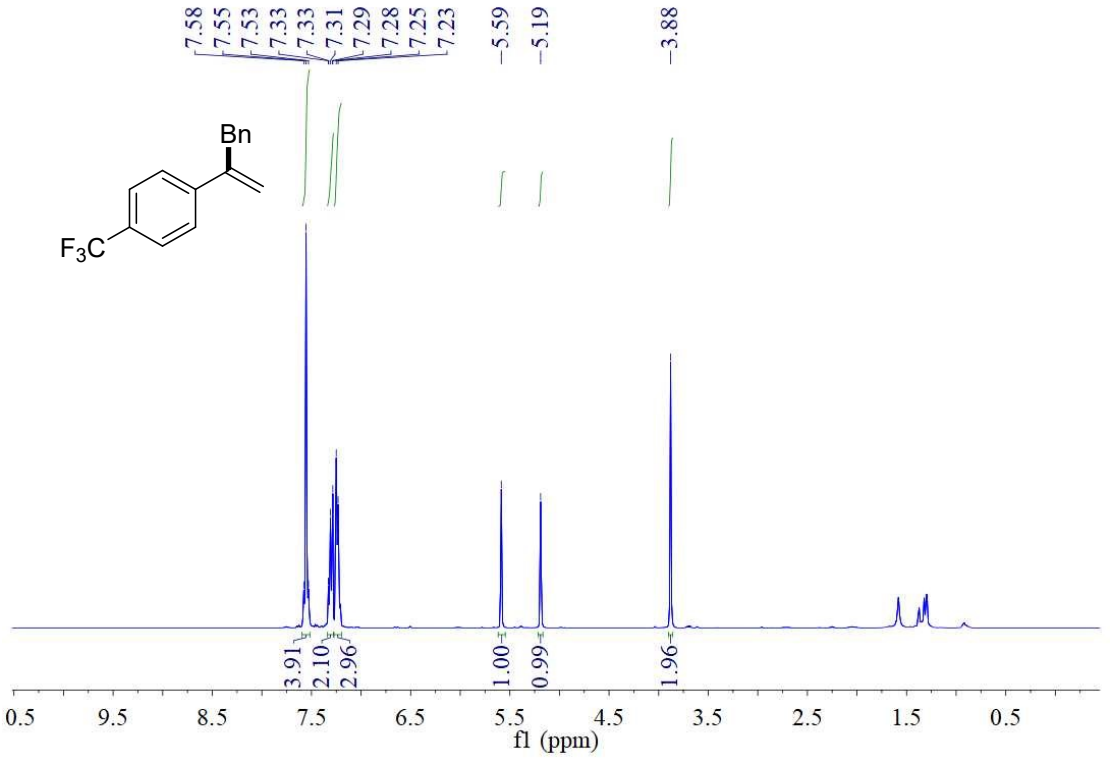
^{1}H NMR of **9** (600 MHz, $CDCl_3$)



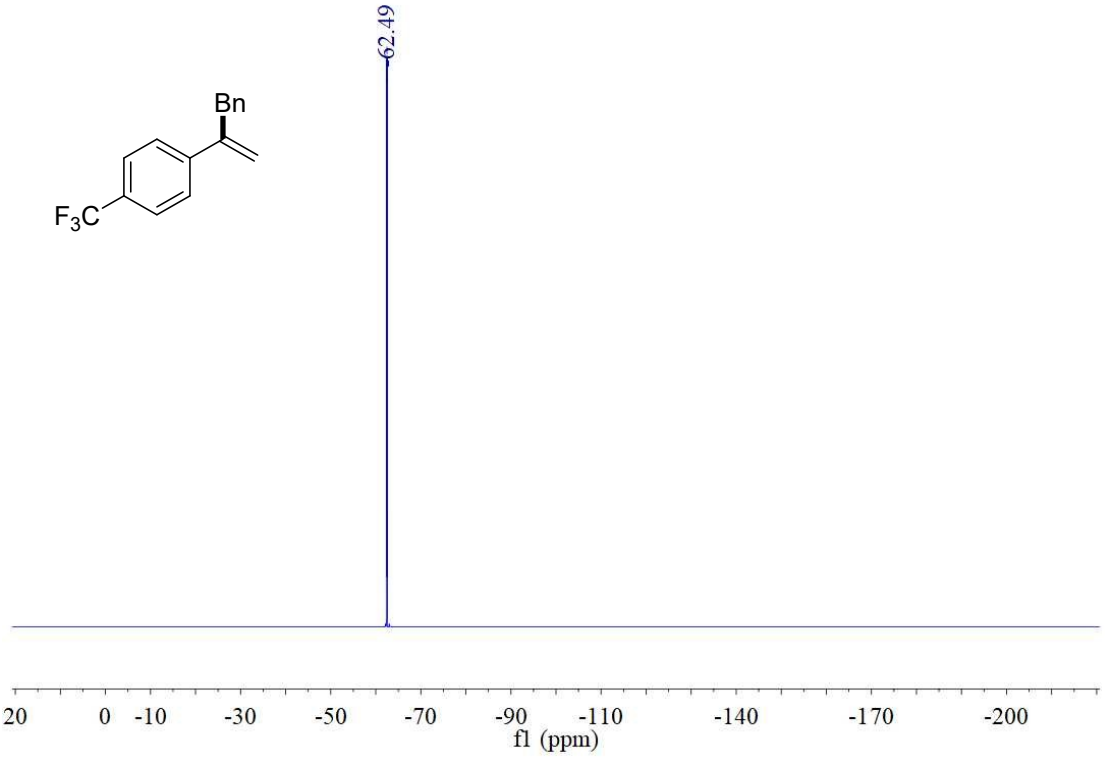
^{13}C NMR of **9** (150 MHz, $CDCl_3$)



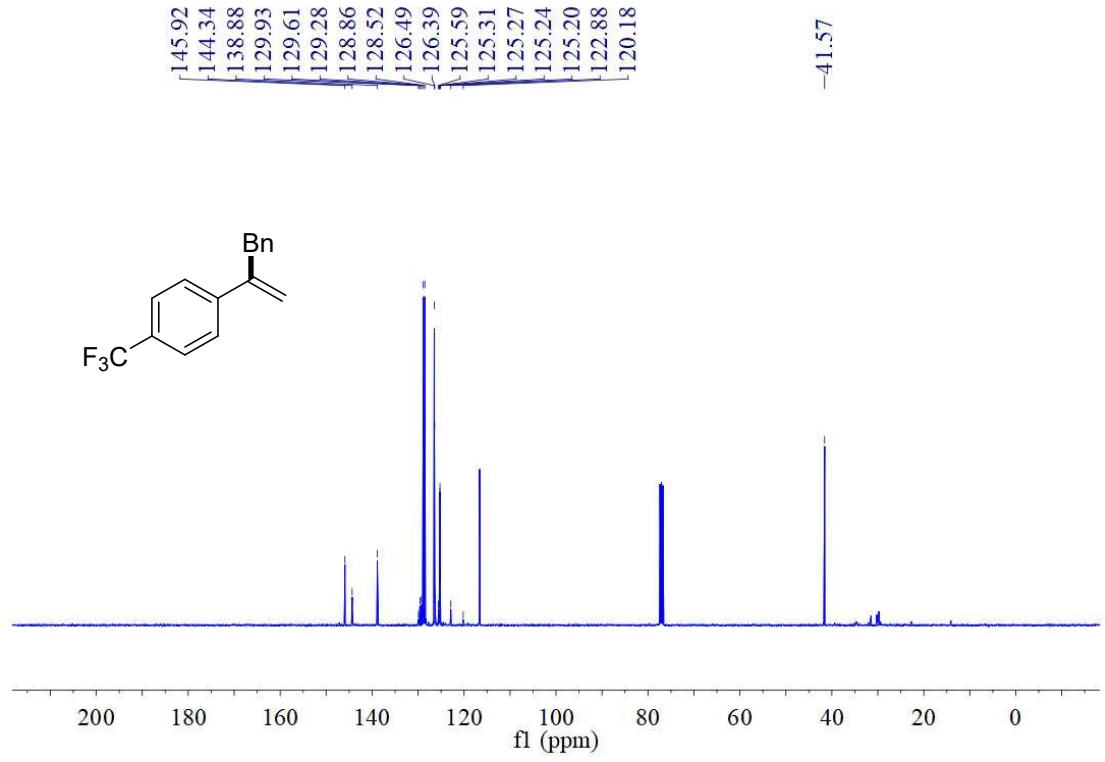
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



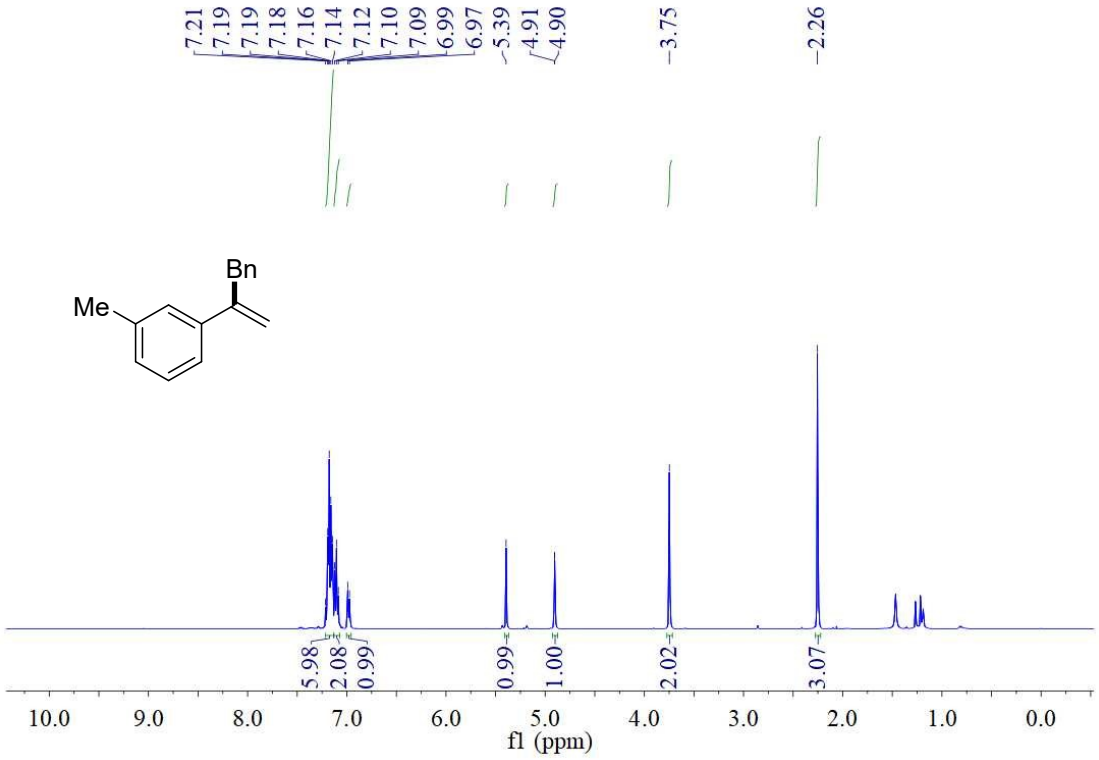
^{19}F NMR of **10** (376 MHz, $CDCl_3$)



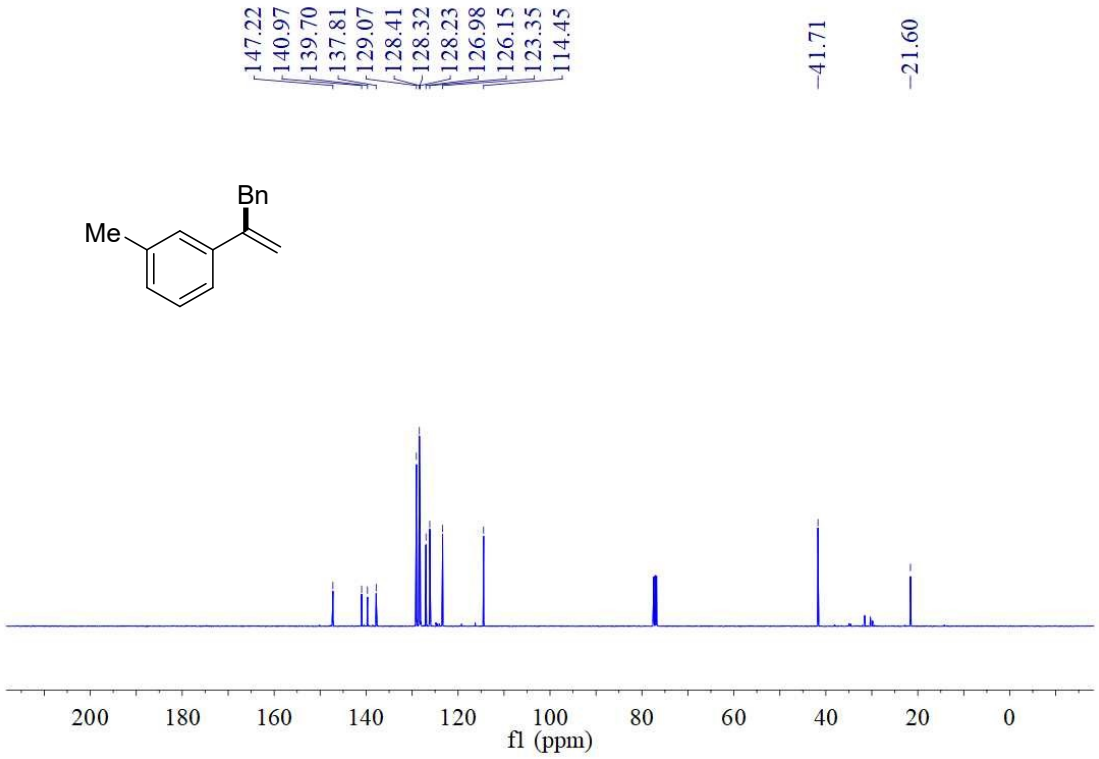
^{13}C NMR of **10** (100 MHz, $CDCl_3$)



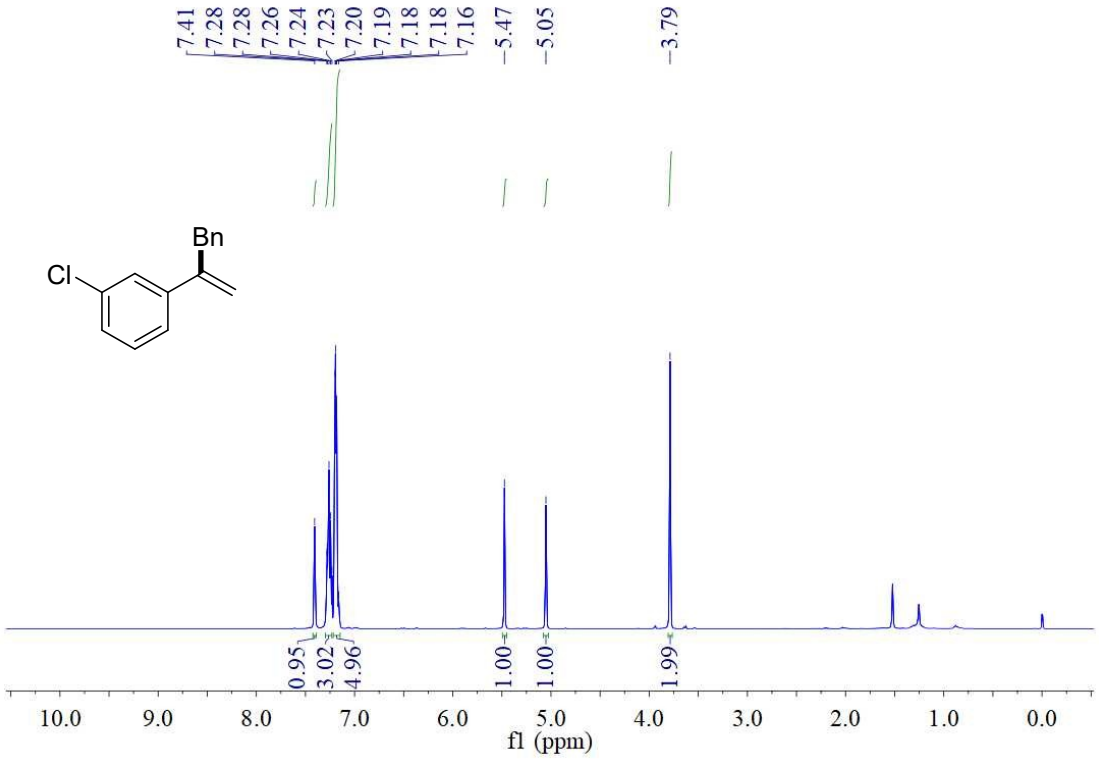
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



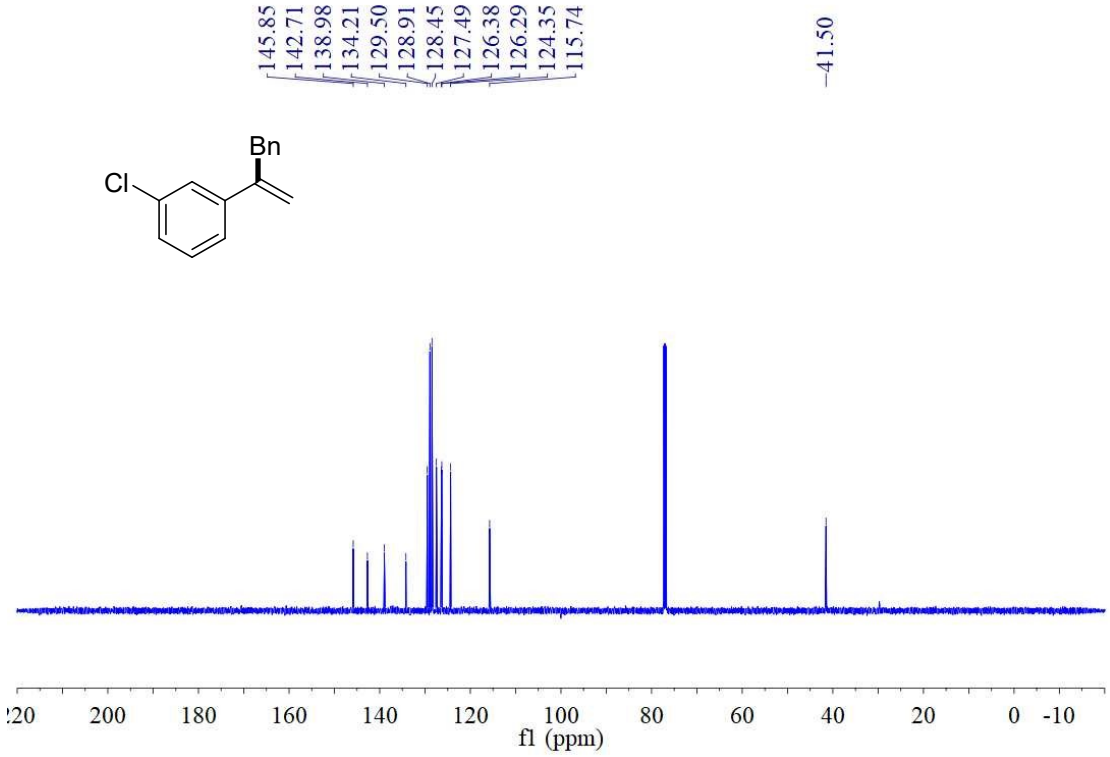
^{13}C NMR of **11** (100 MHz, $CDCl_3$)



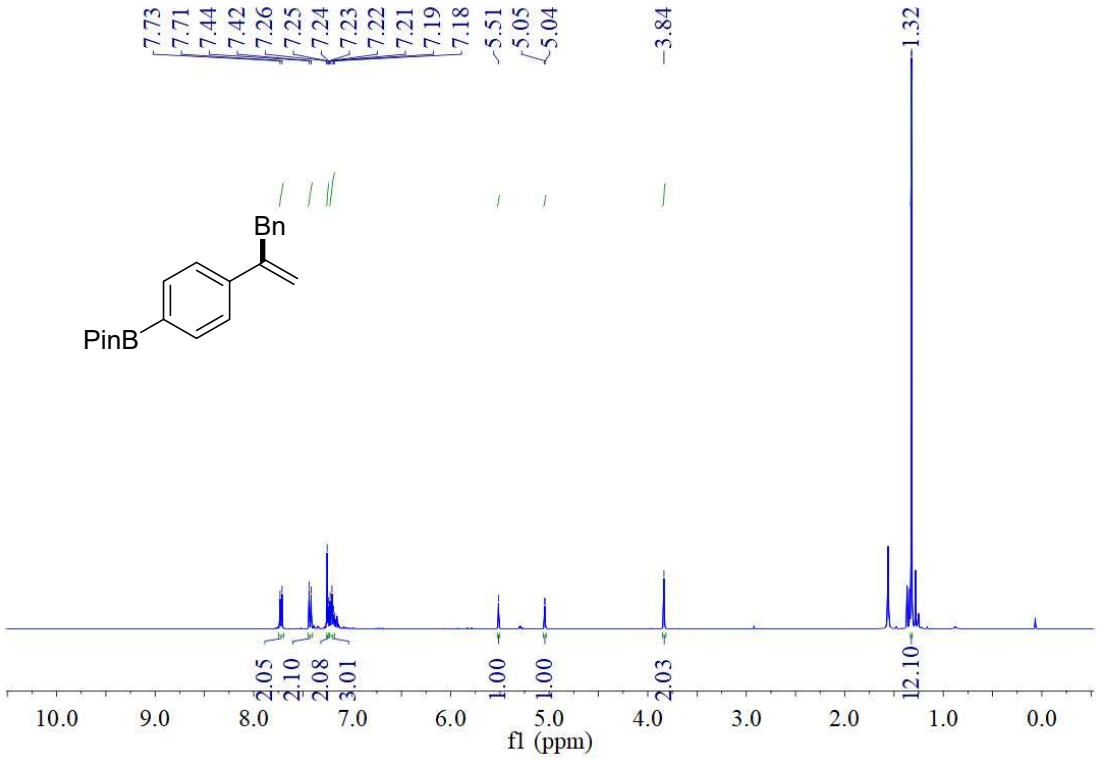
^{1}H NMR of **12** (400 MHz, $CDCl_3$)



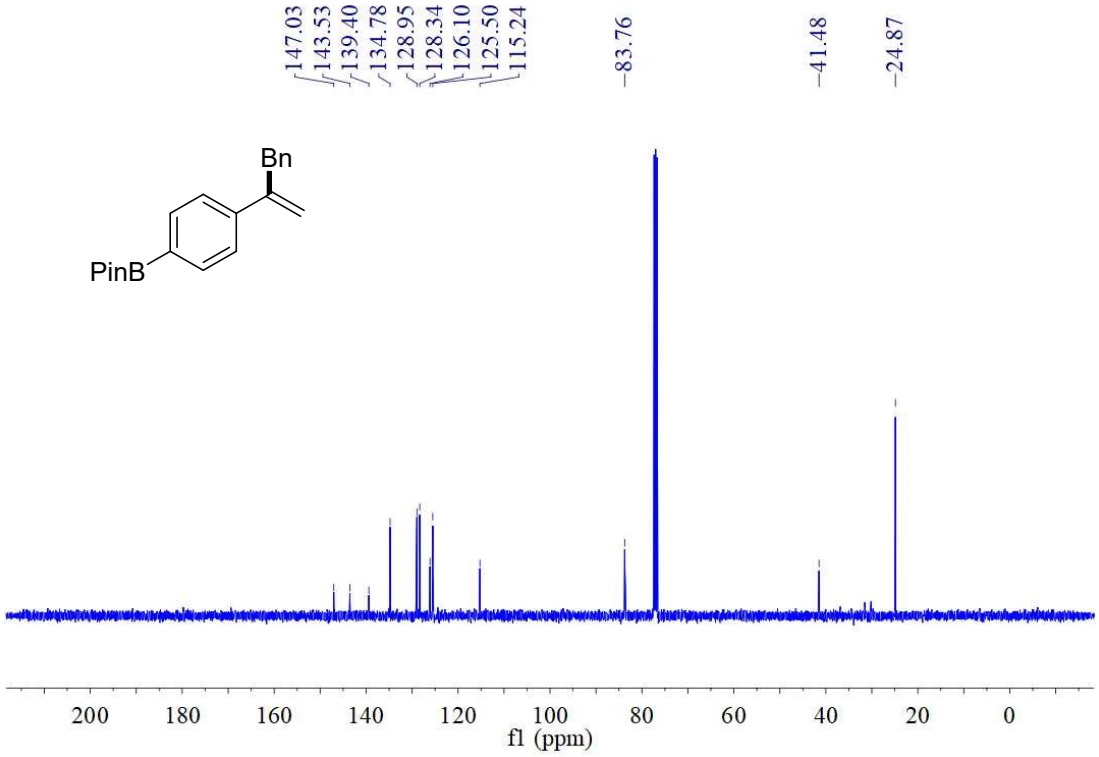
^{13}C NMR of **12** (150 MHz, $CDCl_3$)



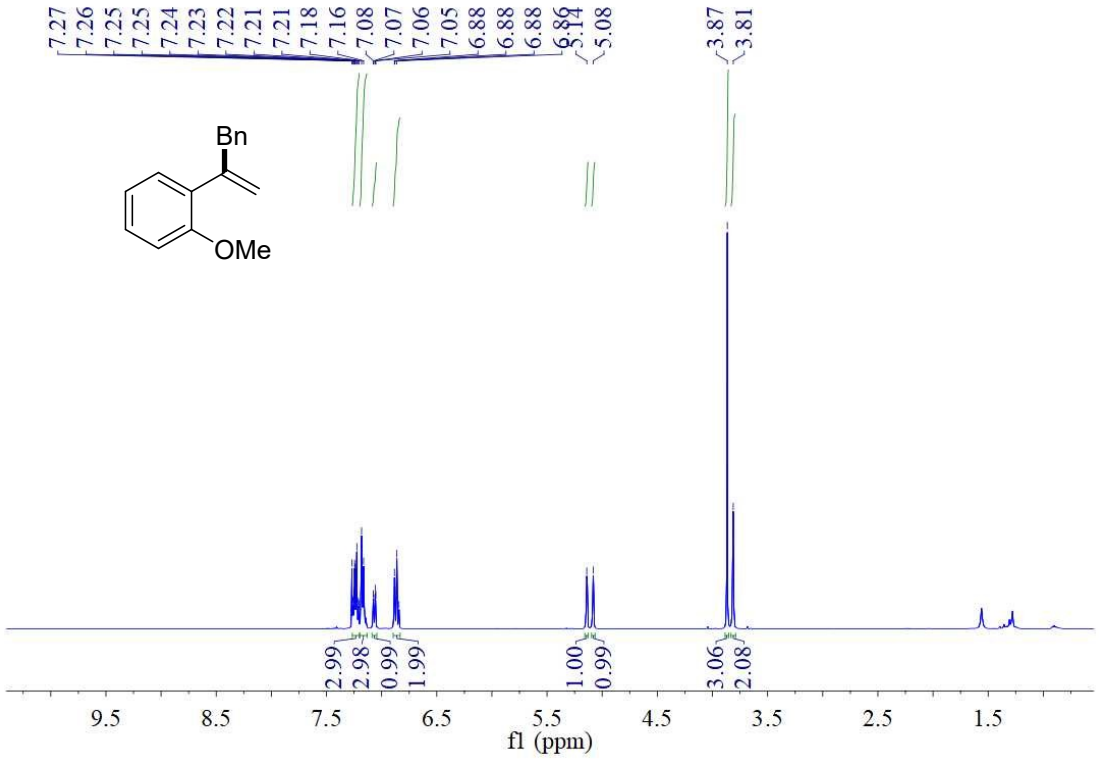
^{1}H NMR of **13** (400 MHz, $CDCl_3$)



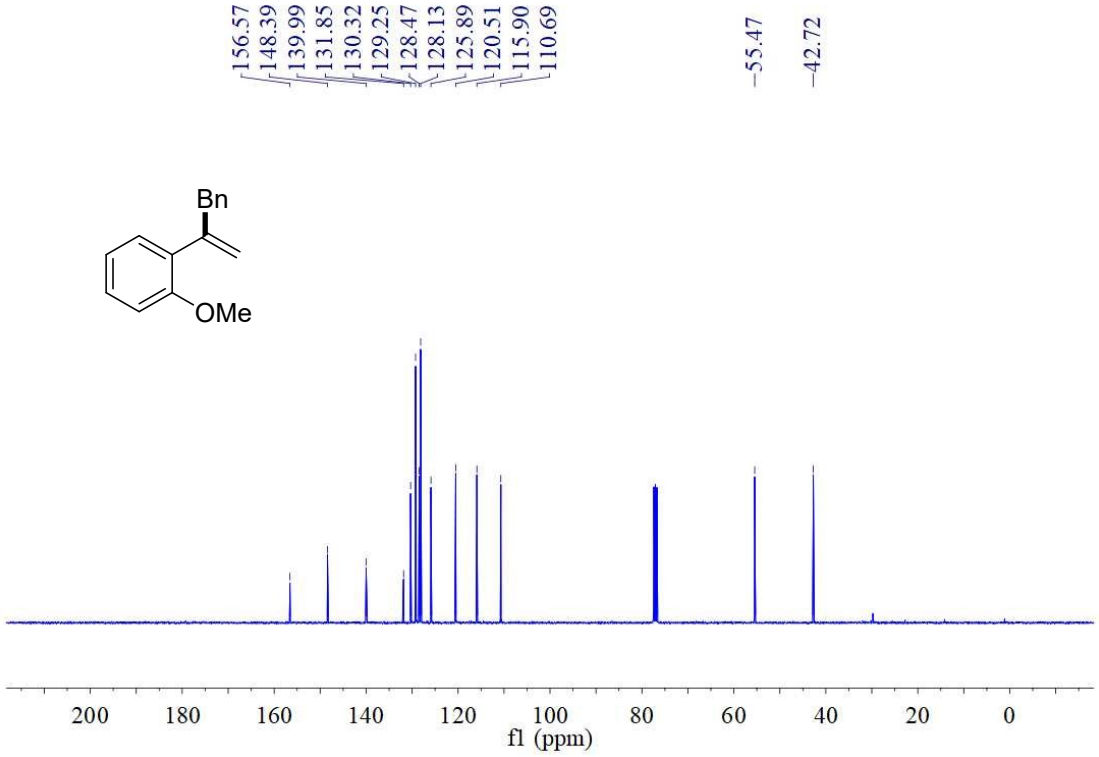
^{13}C NMR of **13** (100 MHz, $CDCl_3$)



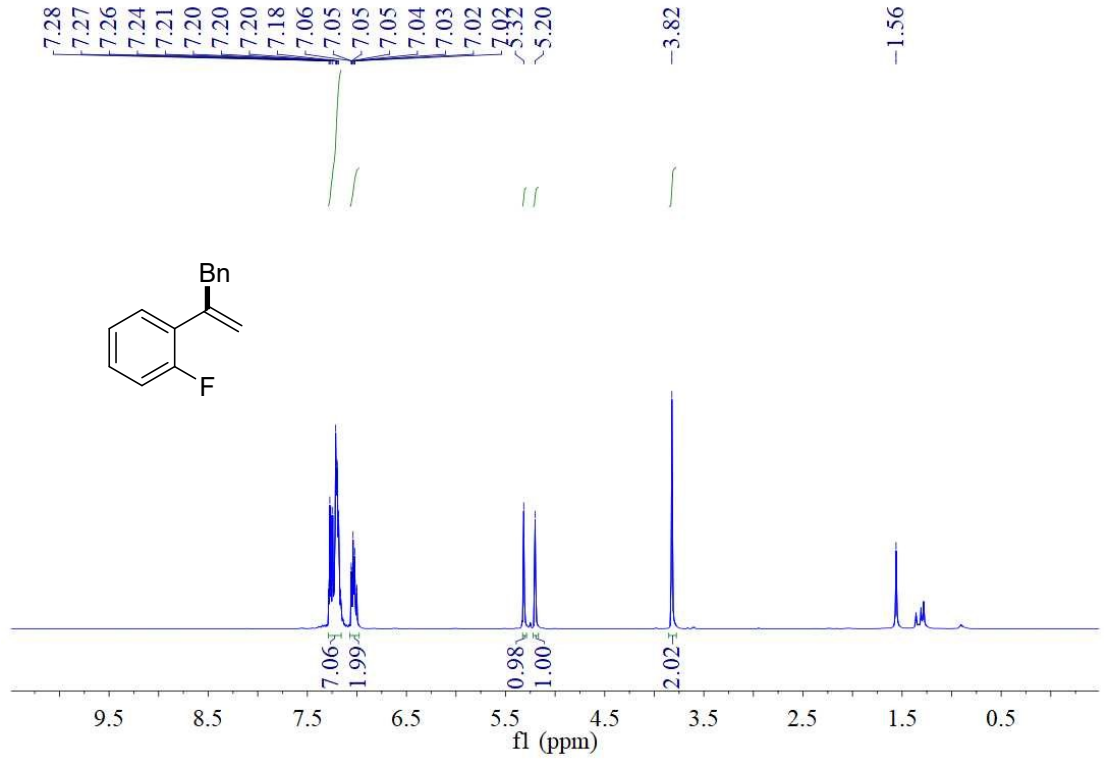
^{1}H NMR of **14** (400 MHz, $CDCl_3$)



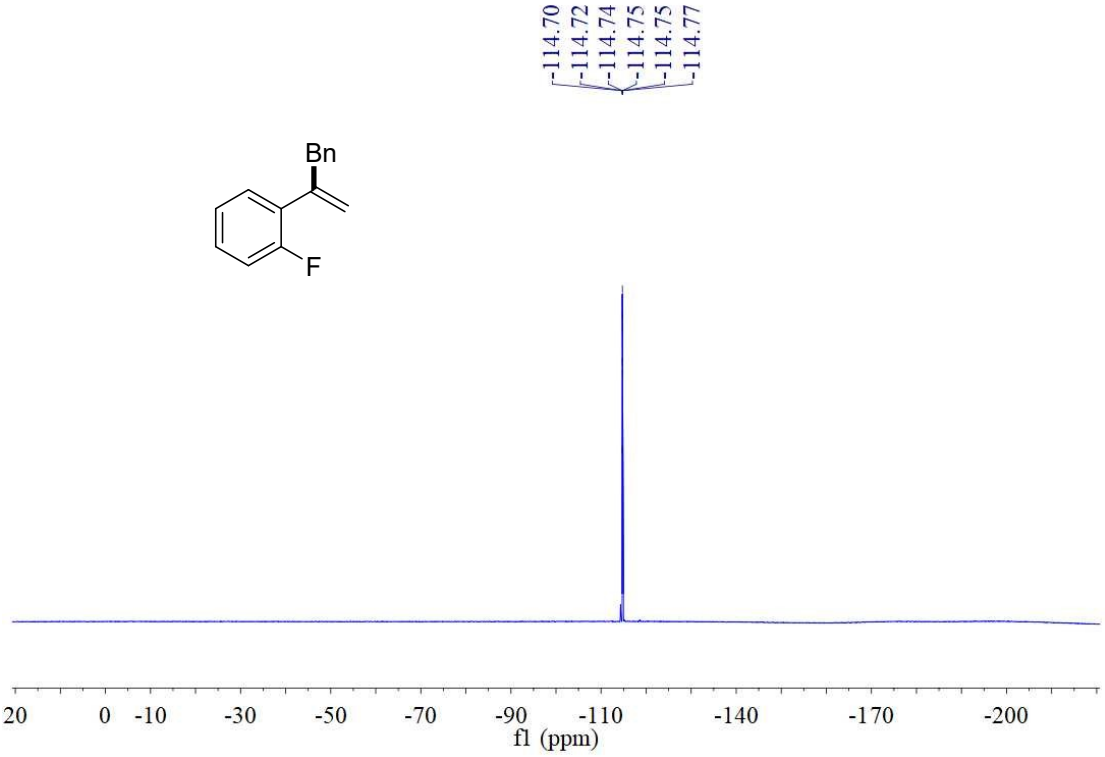
^{13}C NMR of **14** (100 MHz, $CDCl_3$)



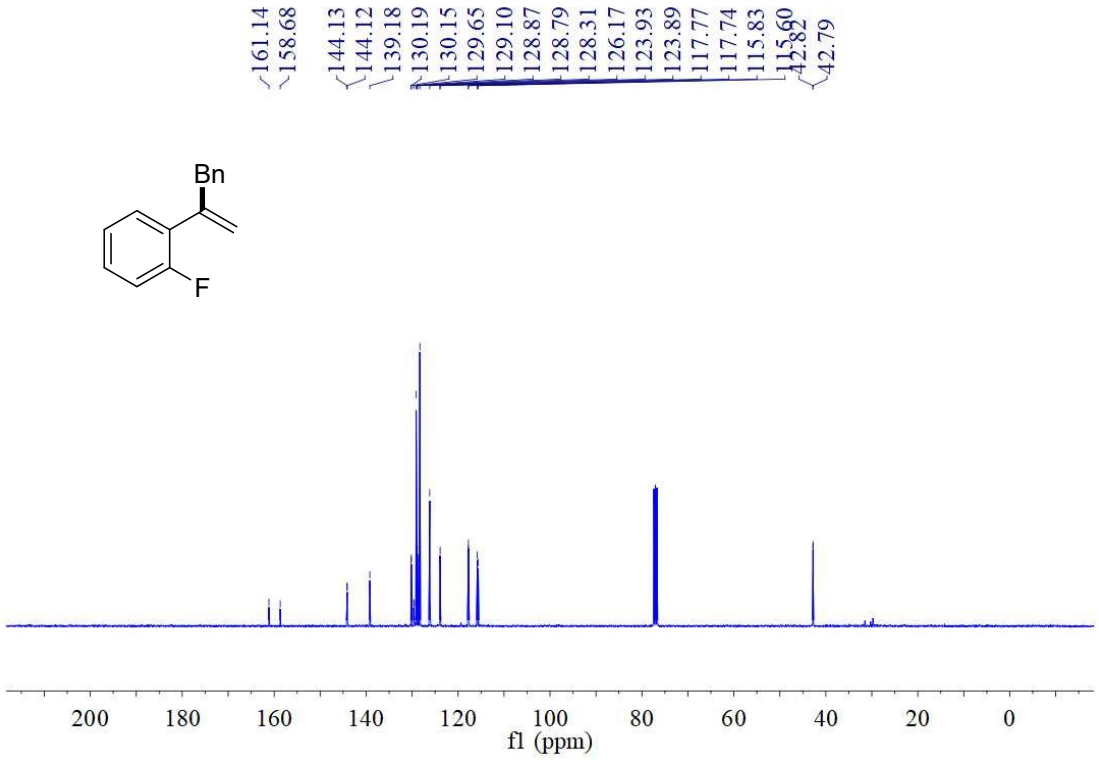
^{1}H NMR of **15** (400 MHz, $CDCl_3$)



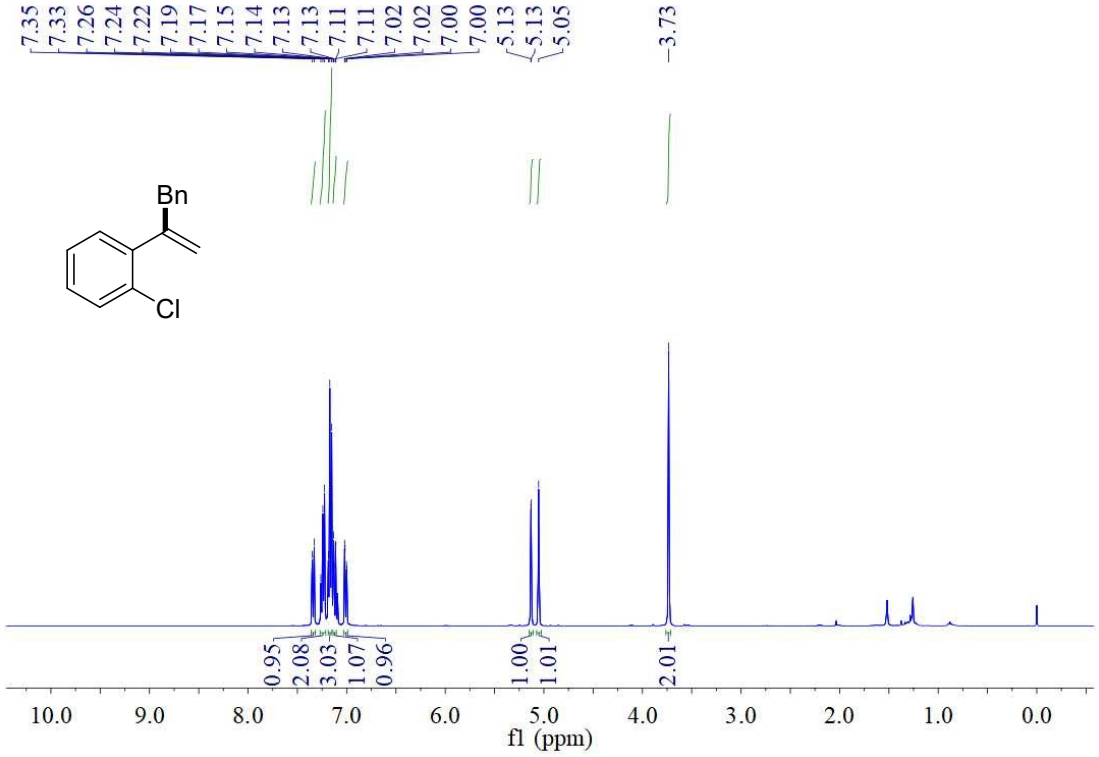
^{19}F NMR of **15** (376 MHz, $CDCl_3$)



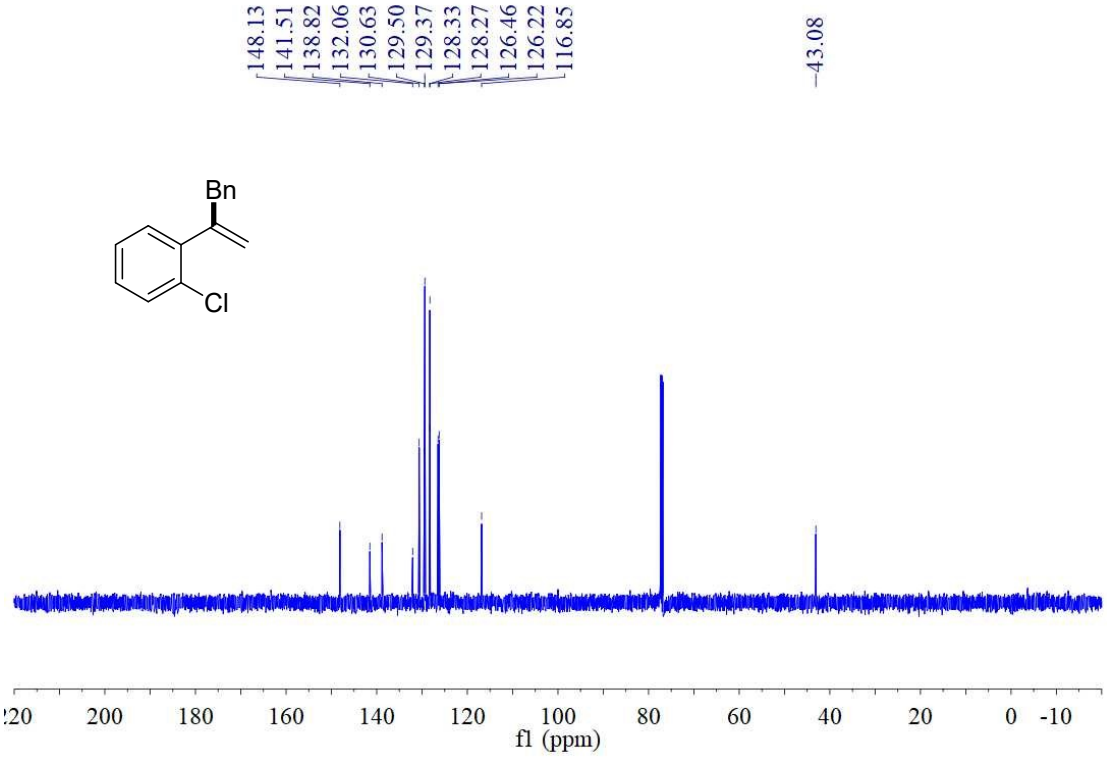
^{13}C NMR of **15** (100 MHz, $CDCl_3$)



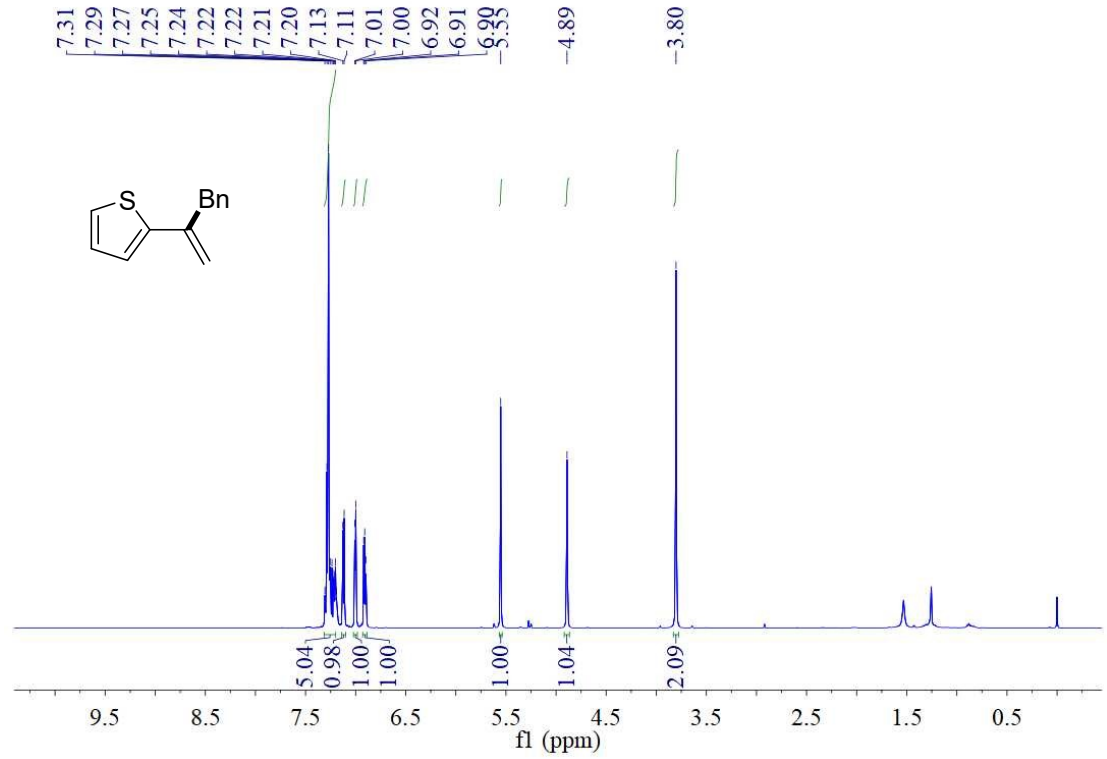
^{1}H NMR of **16** (400 MHz, $CDCl_3$)



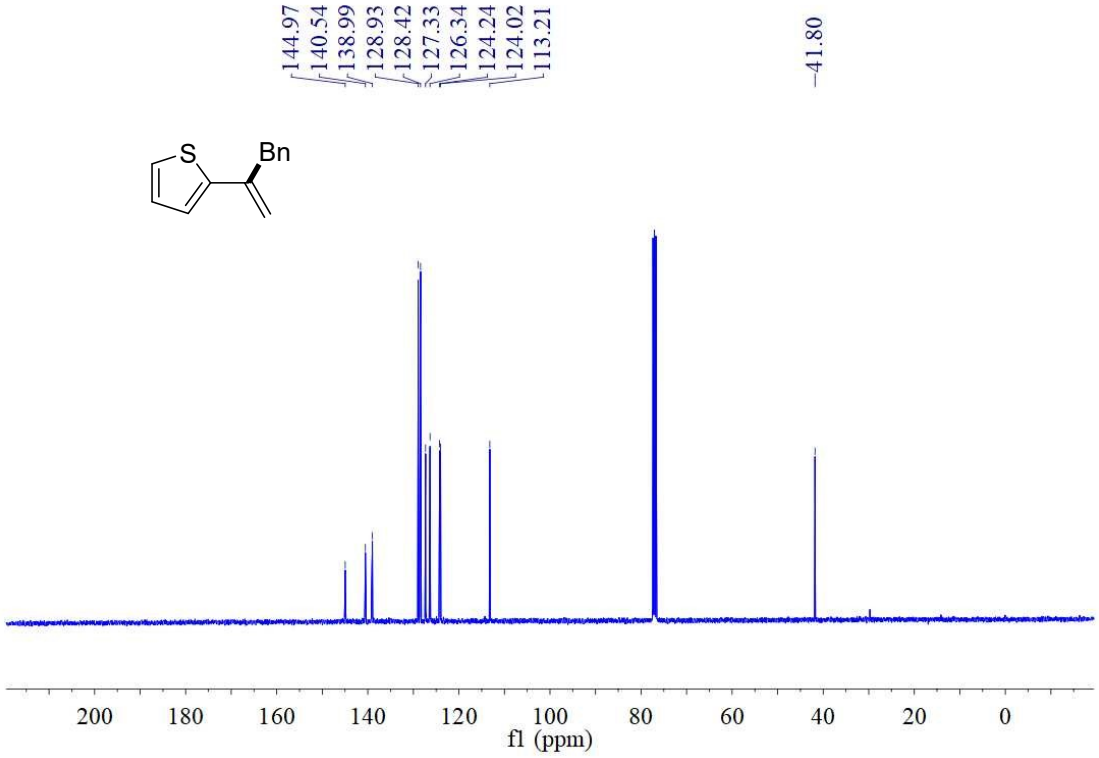
^{13}C NMR of **16** (150 MHz, $CDCl_3$)



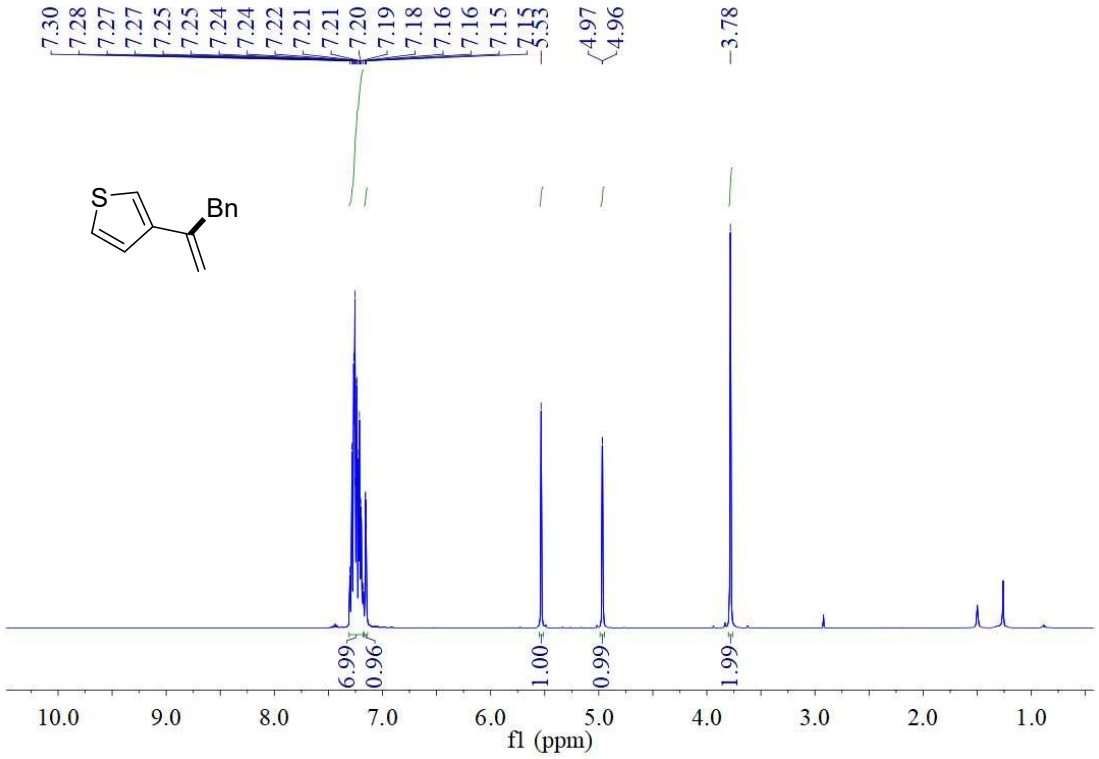
^{1}H NMR of **17** (400 MHz, $CDCl_3$)



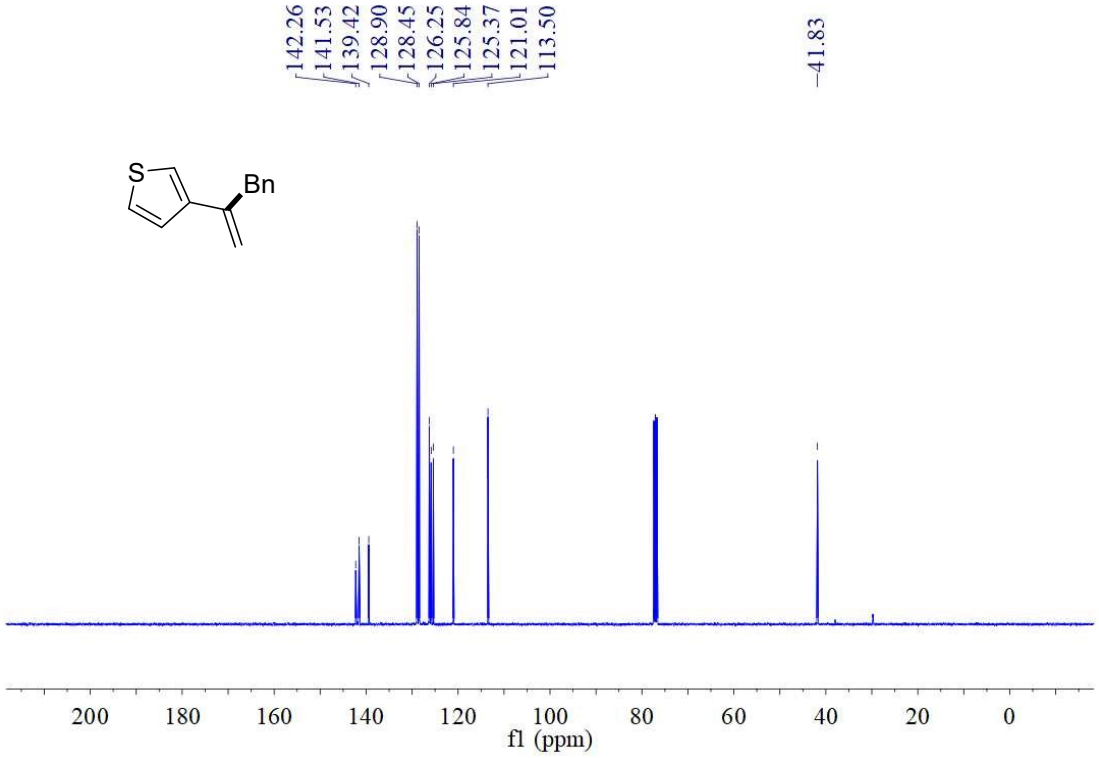
^{13}C NMR of **17** (100 MHz, $CDCl_3$)



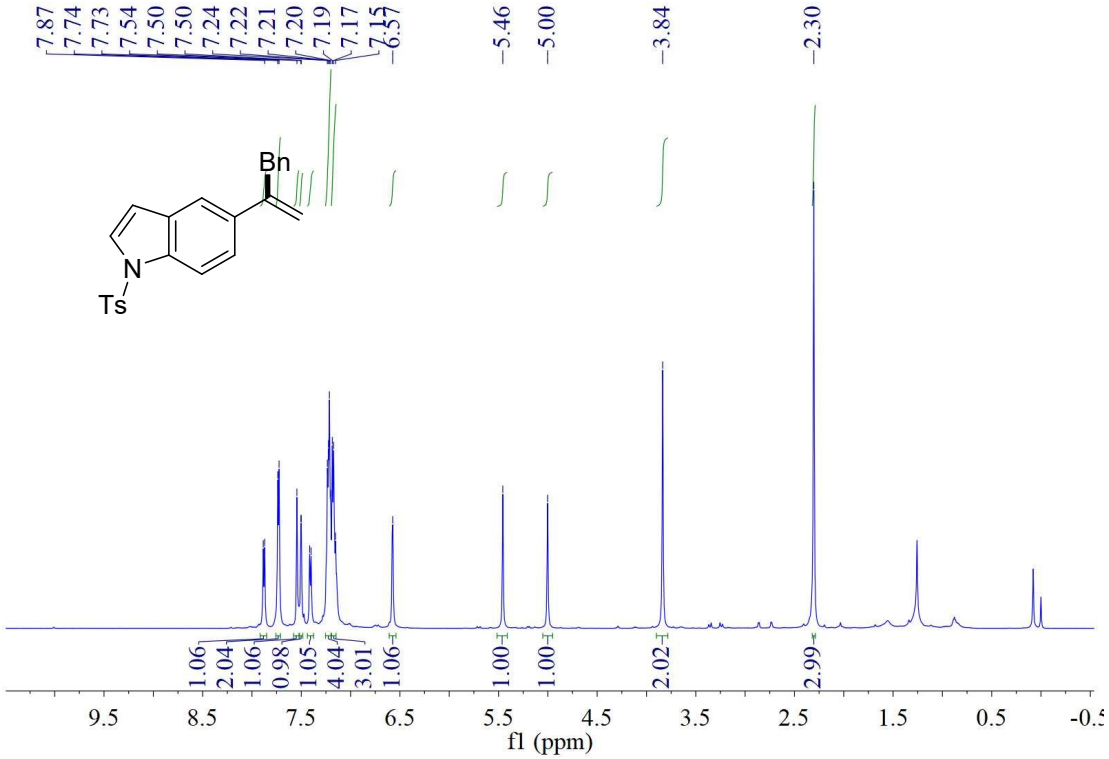
^{1}H NMR of **18** (400 MHz, $CDCl_3$)



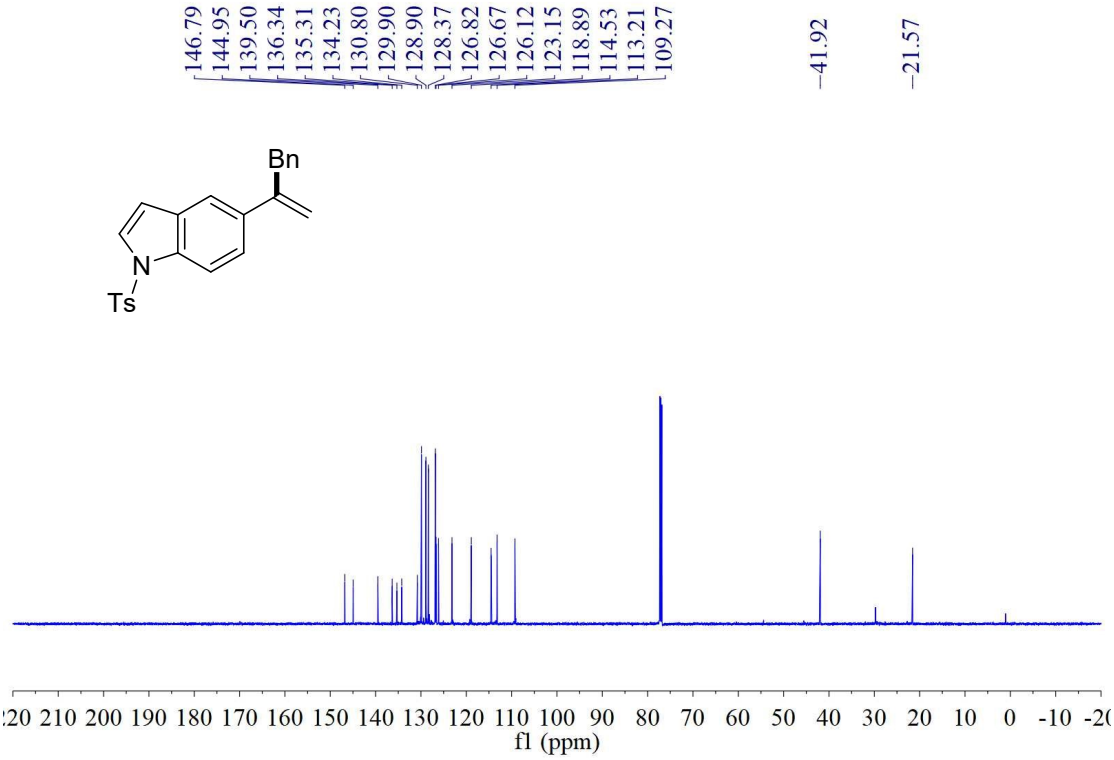
^{13}C NMR of **18** (100 MHz, $CDCl_3$)



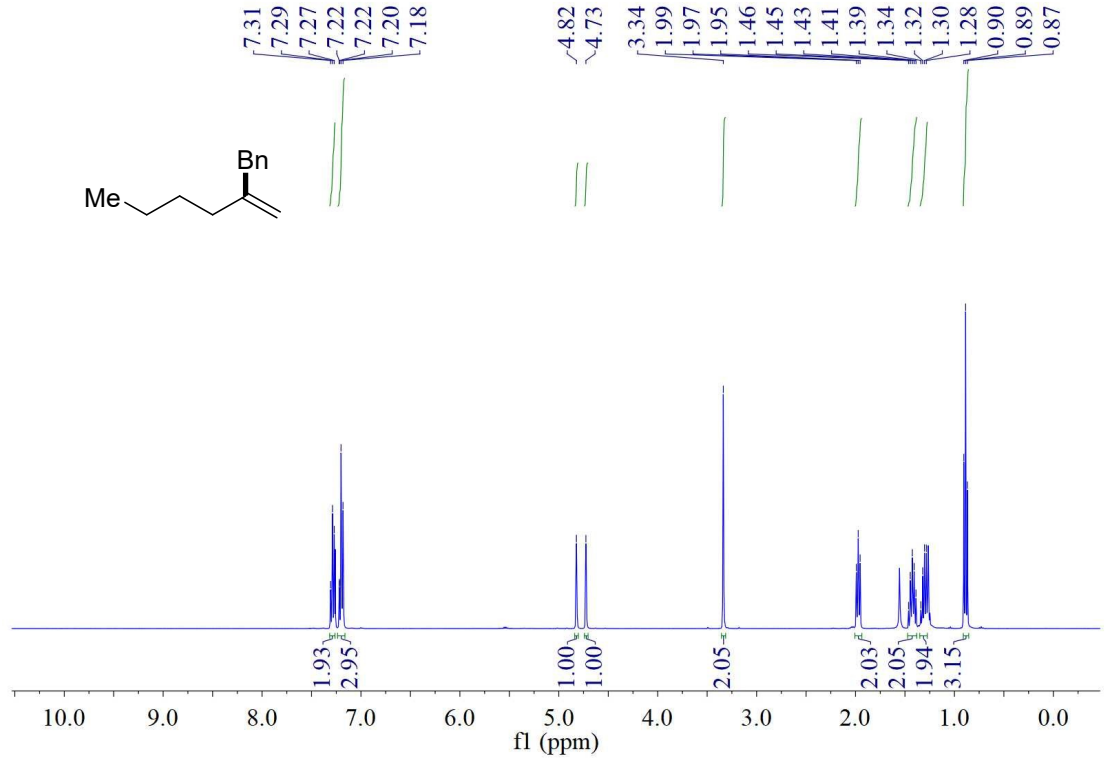
^{1}H NMR of **19** (600 MHz, $CDCl_3$)



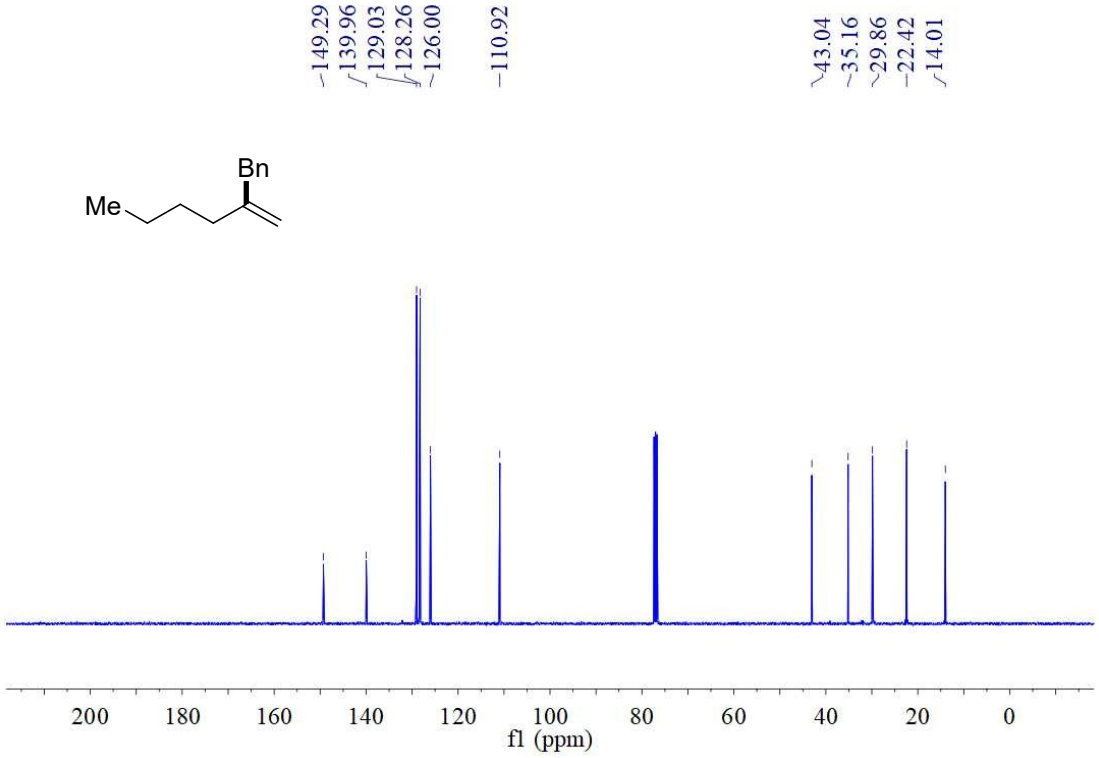
^{13}C NMR of **19** (150 MHz, $CDCl_3$)



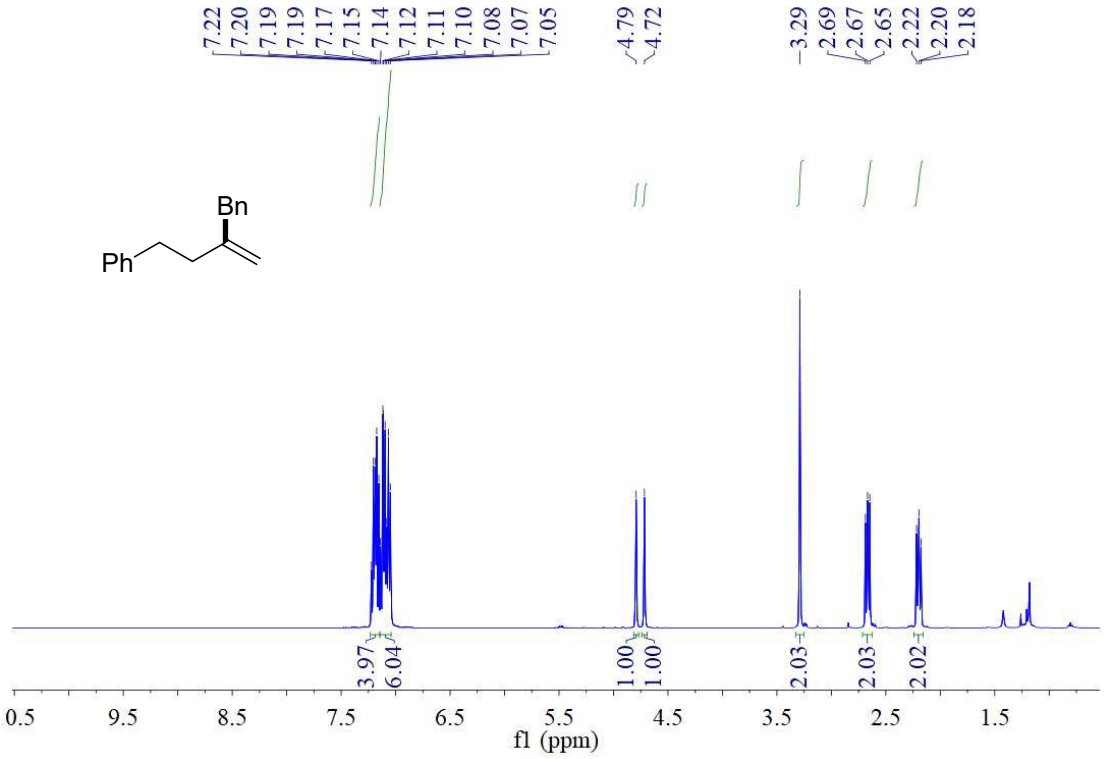
^{1}H NMR of **20** (400 MHz, $CDCl_3$)



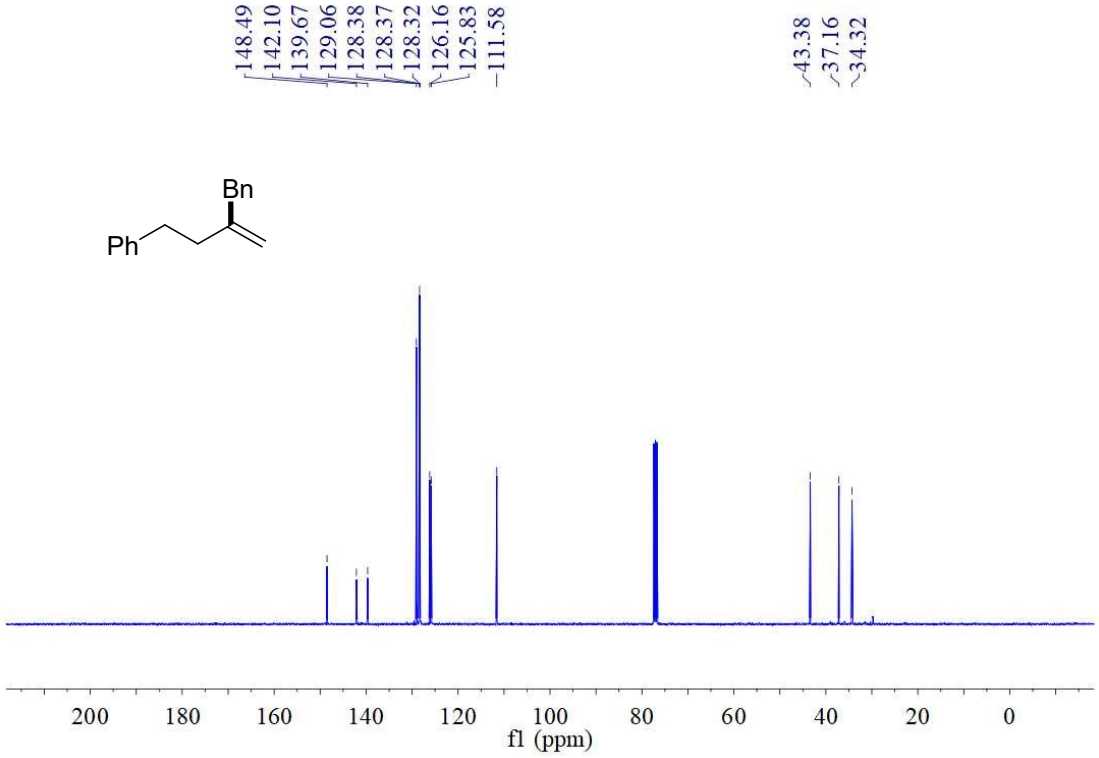
^{13}C NMR of **20** (100 MHz, $CDCl_3$)



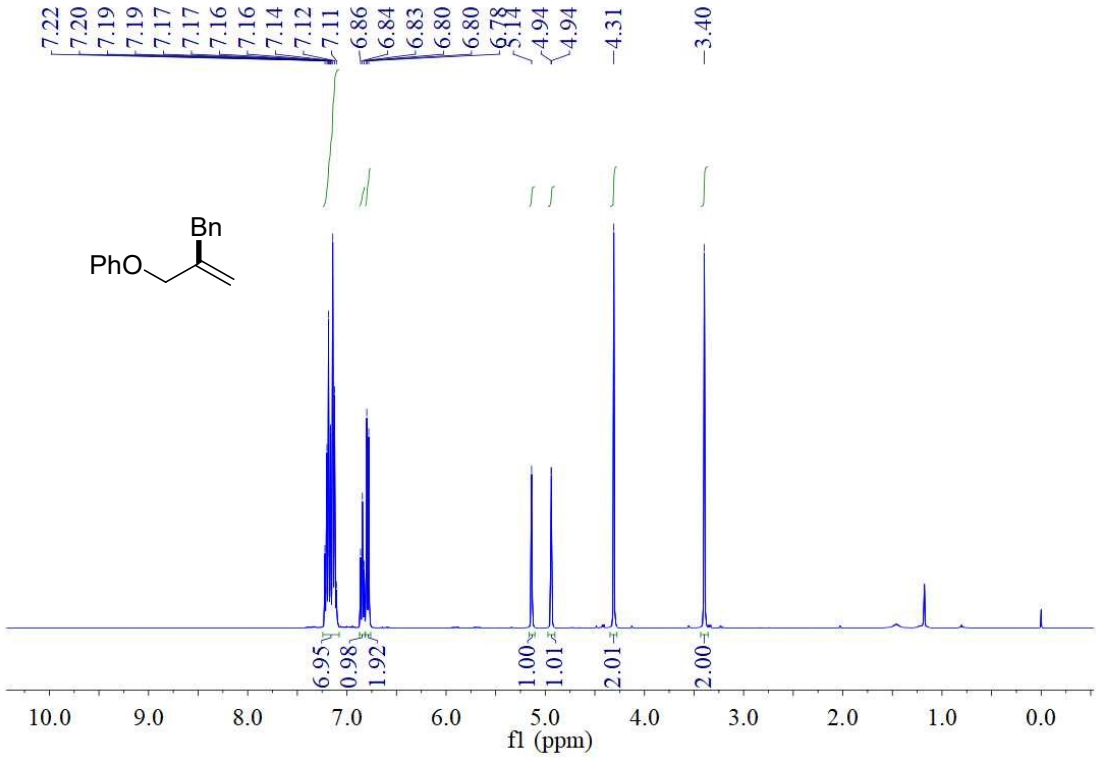
^{1}H NMR of **21** (400 MHz, $CDCl_3$)



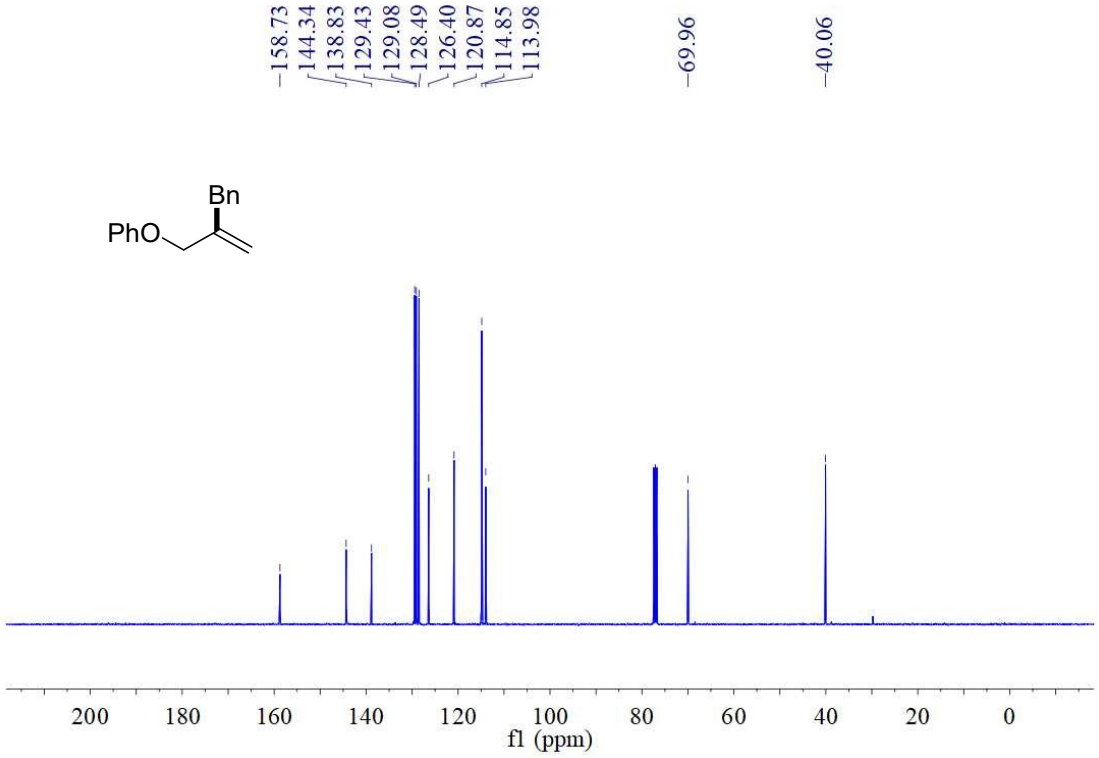
^{13}C NMR of **21** (100 MHz, $CDCl_3$)



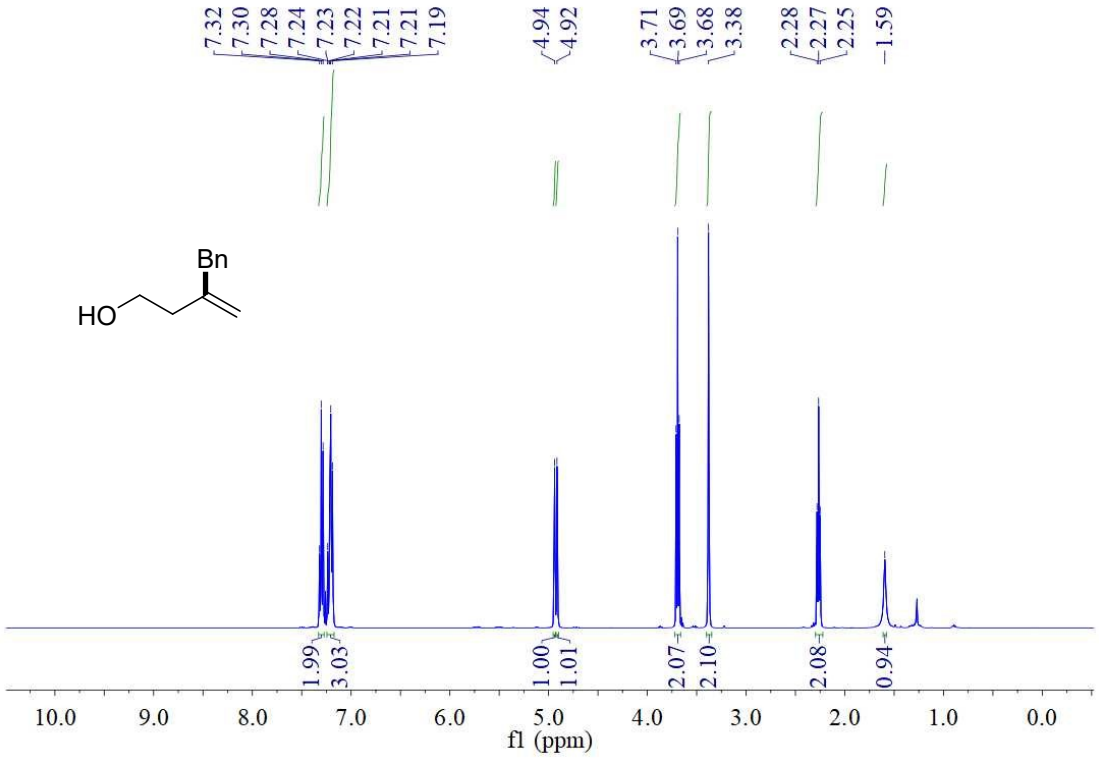
^{1}H NMR of **22** (400 MHz, $CDCl_3$)



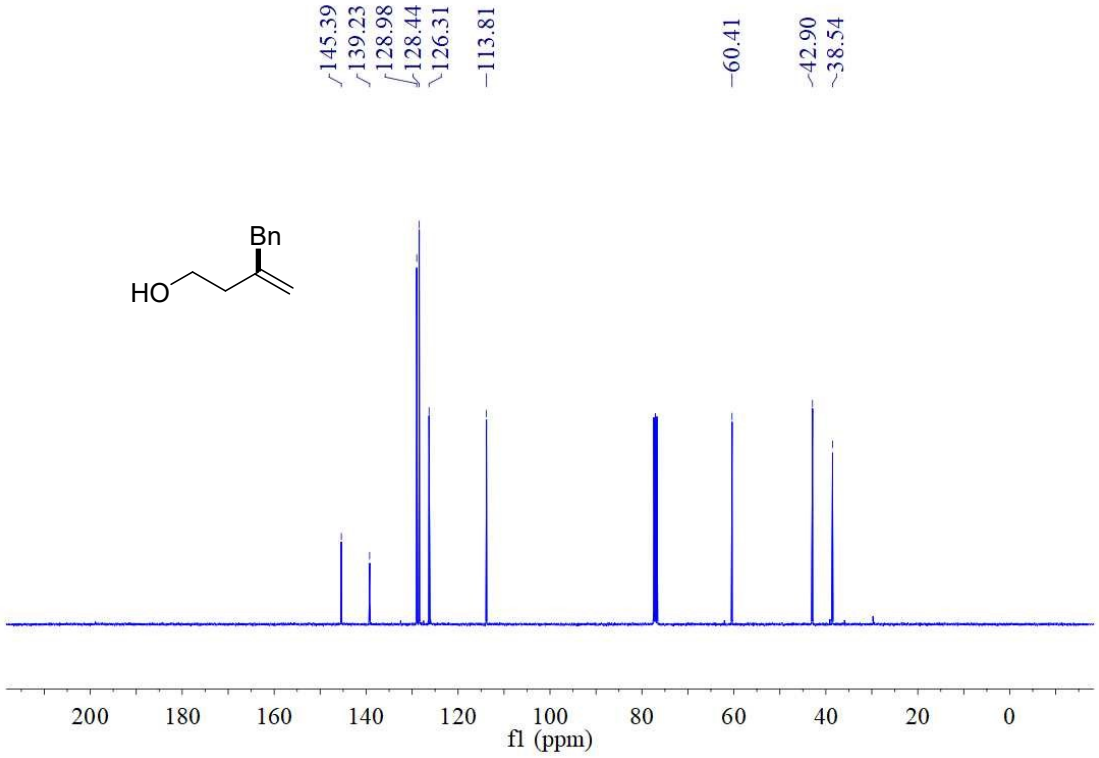
^{13}C NMR of **22** (100 MHz, $CDCl_3$)



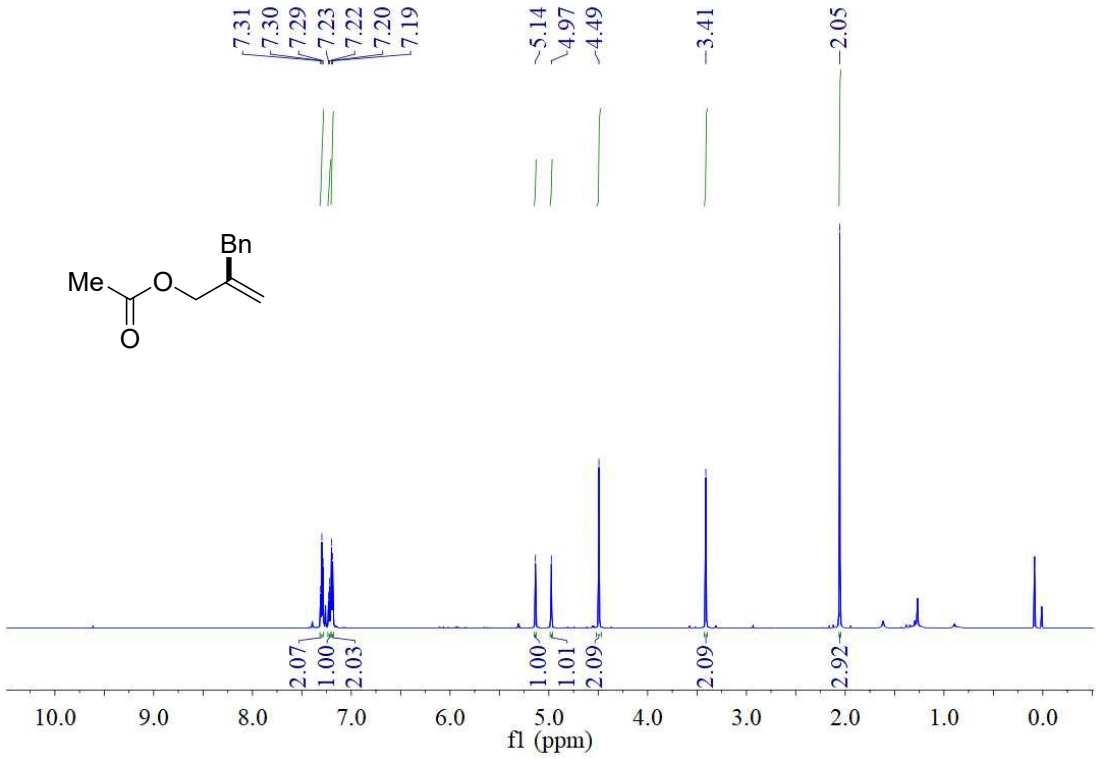
^{1}H NMR of **23** (400 MHz, $CDCl_3$)



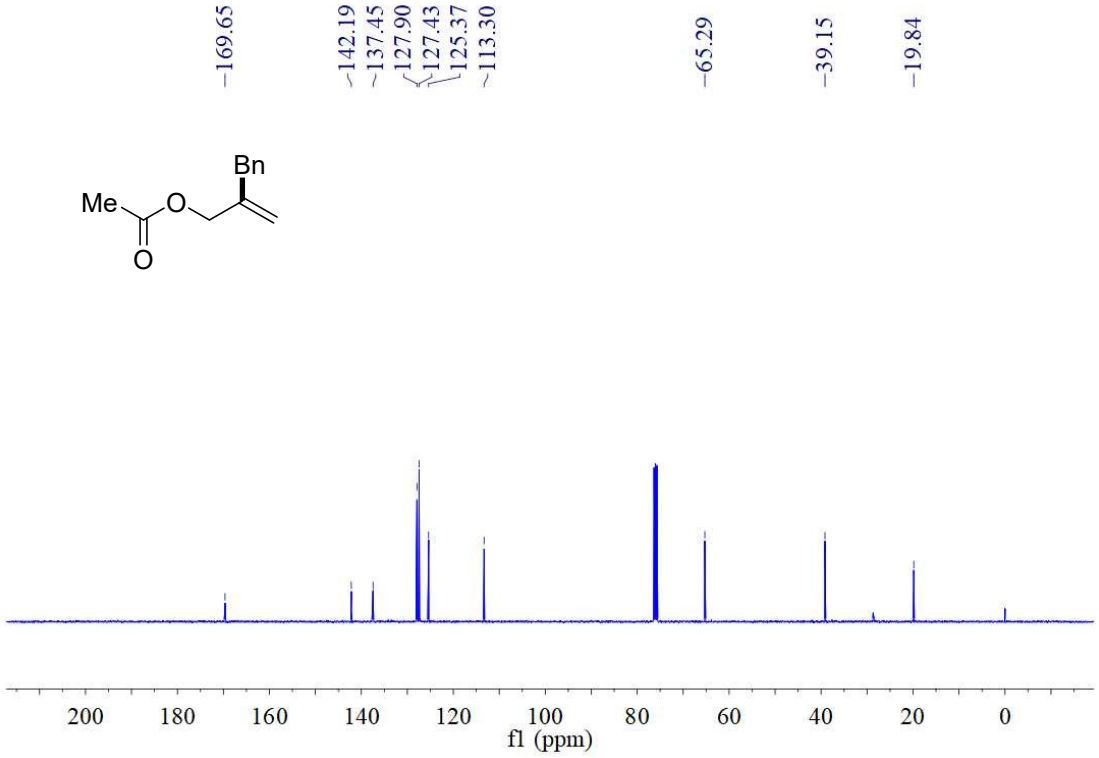
^{13}C NMR of **23** (100 MHz, $CDCl_3$)



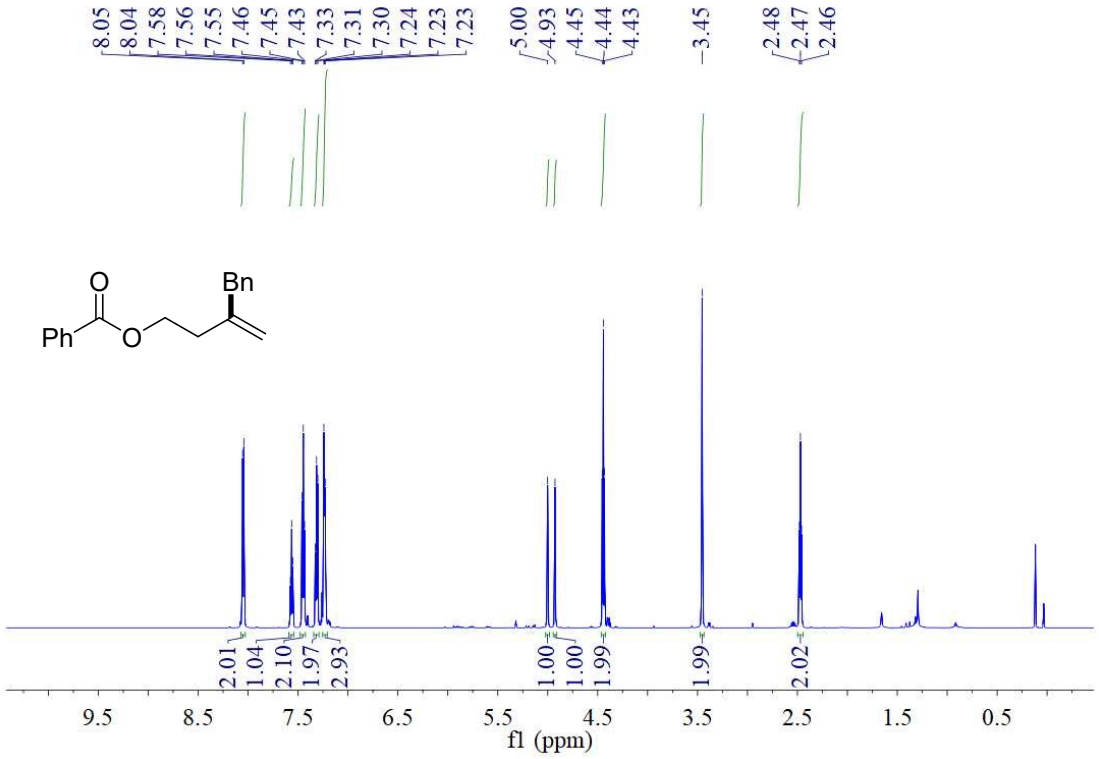
^{1}H NMR of **24** (600 MHz, $CDCl_3$)



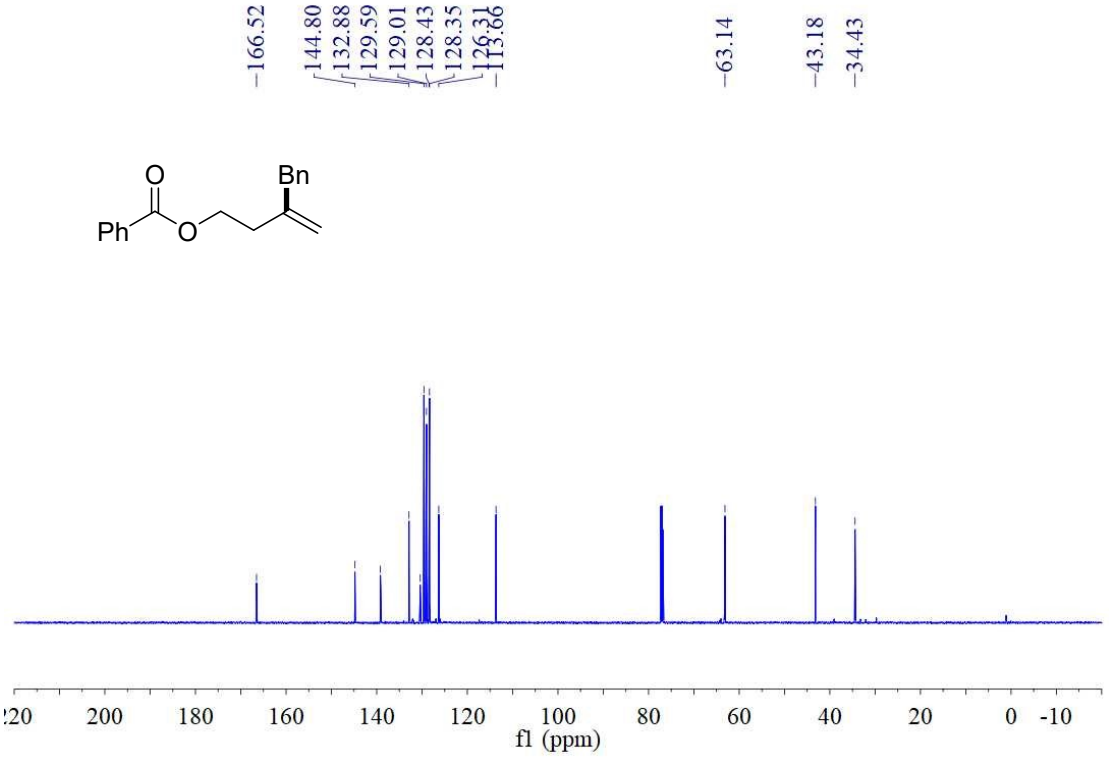
^{13}C NMR of **24** (100 MHz, $CDCl_3$)



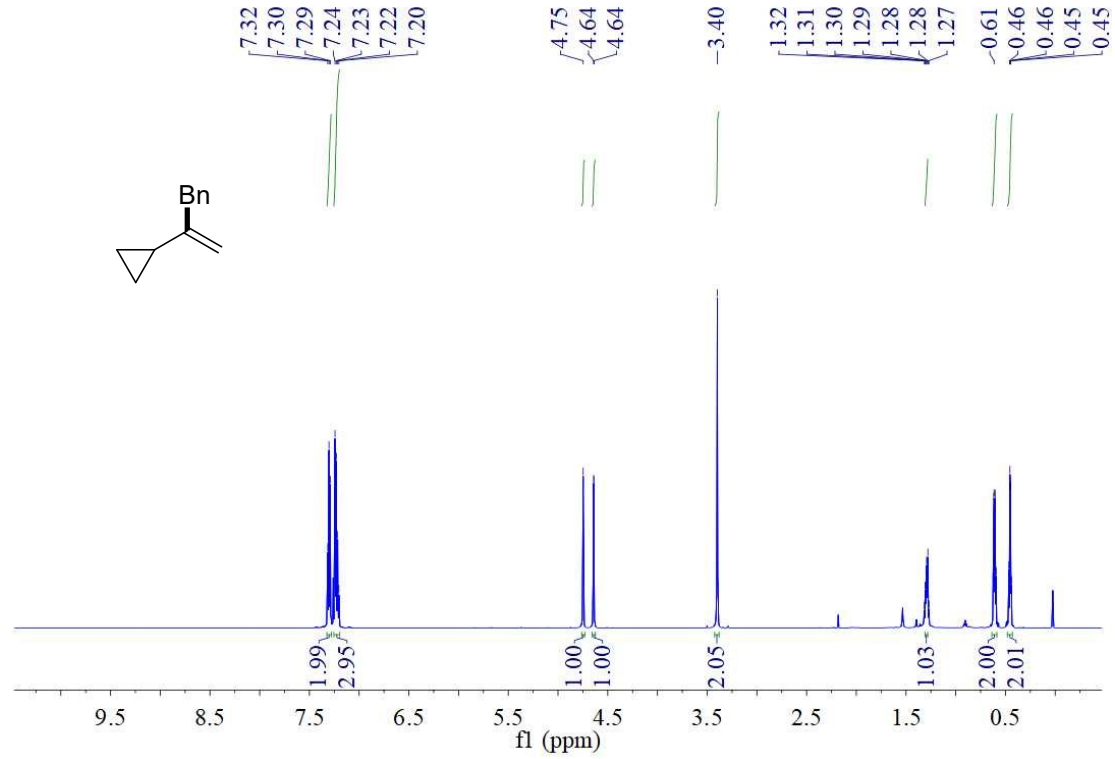
^{1}H NMR of **25** (600 MHz, $CDCl_3$)



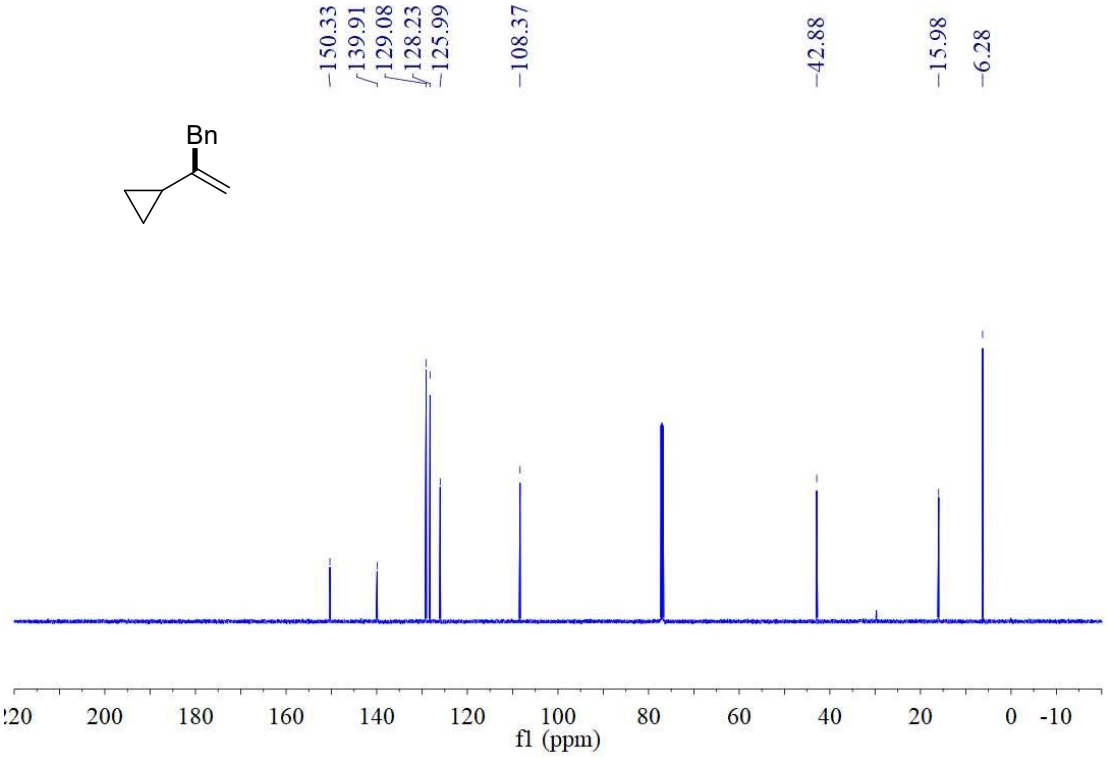
^{13}C NMR of **25** (150 MHz, $CDCl_3$)



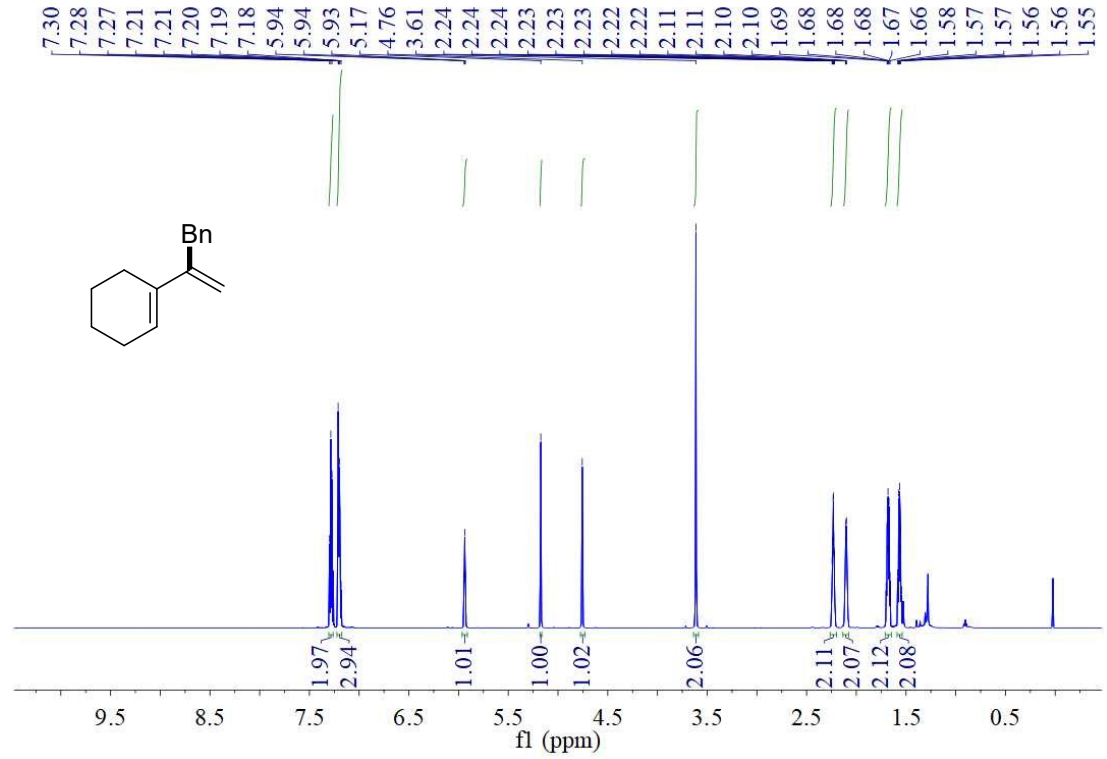
^{1}H NMR of **26** (600 MHz, $CDCl_3$)



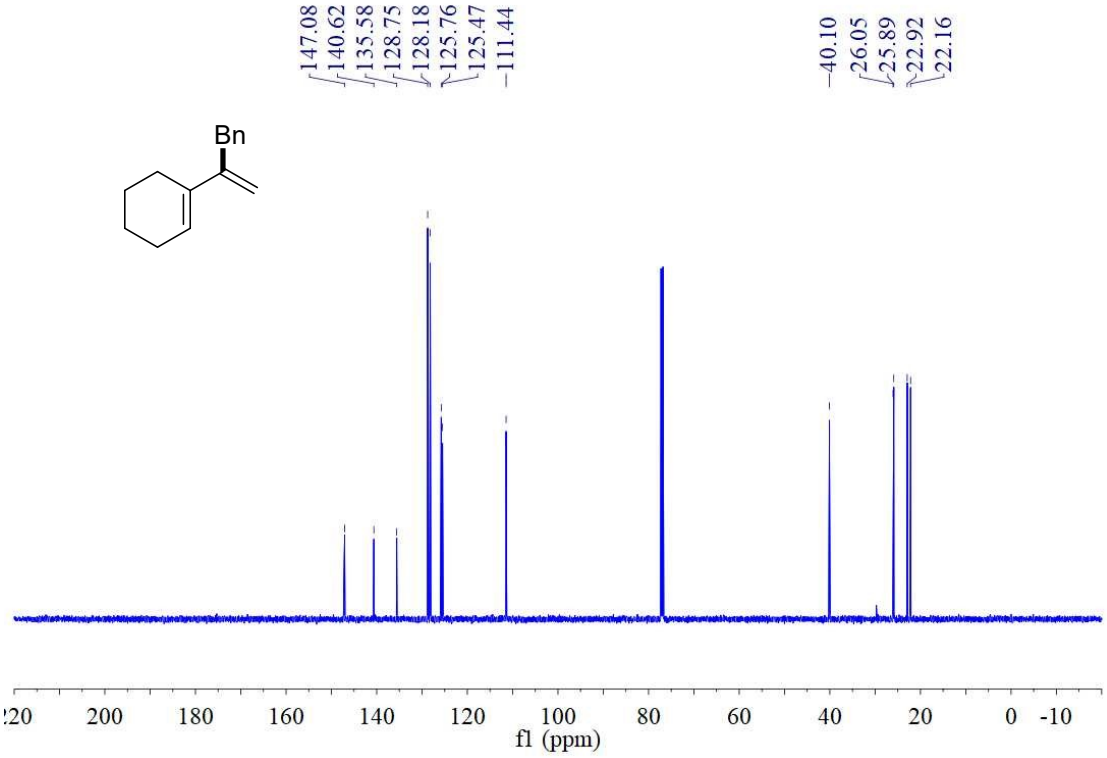
^{13}C NMR of **26** (150 MHz, $CDCl_3$)



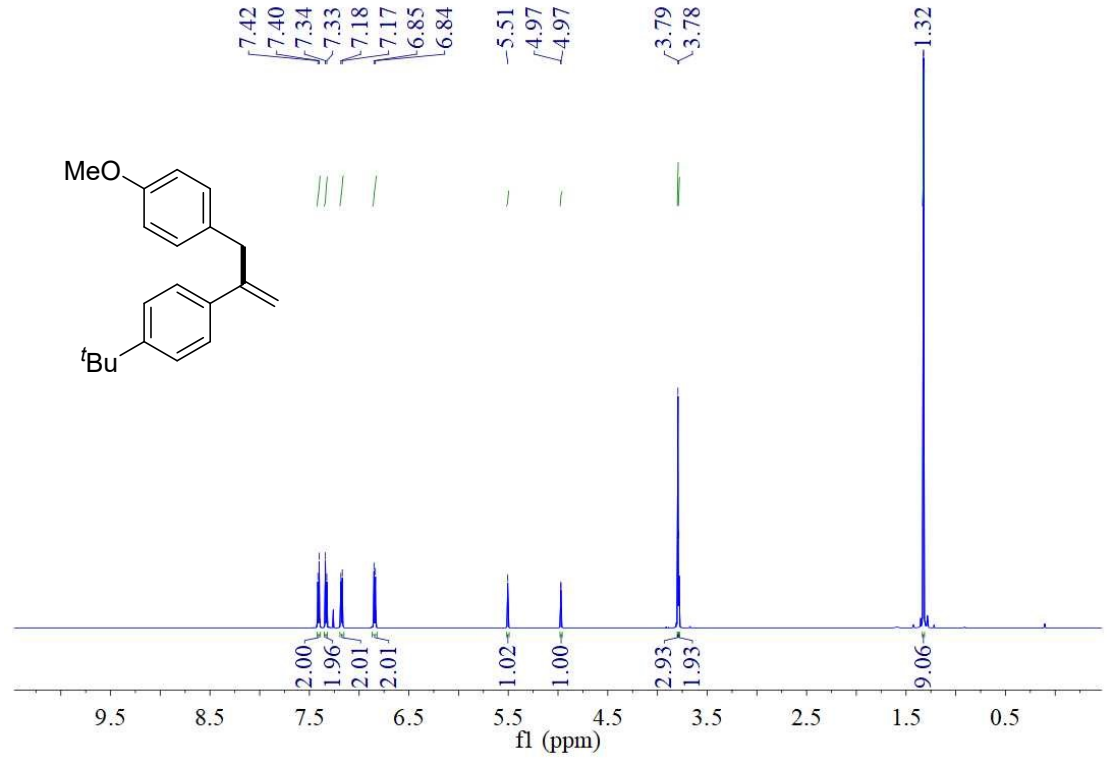
^{1}H NMR of **27** (600 MHz, $CDCl_3$)



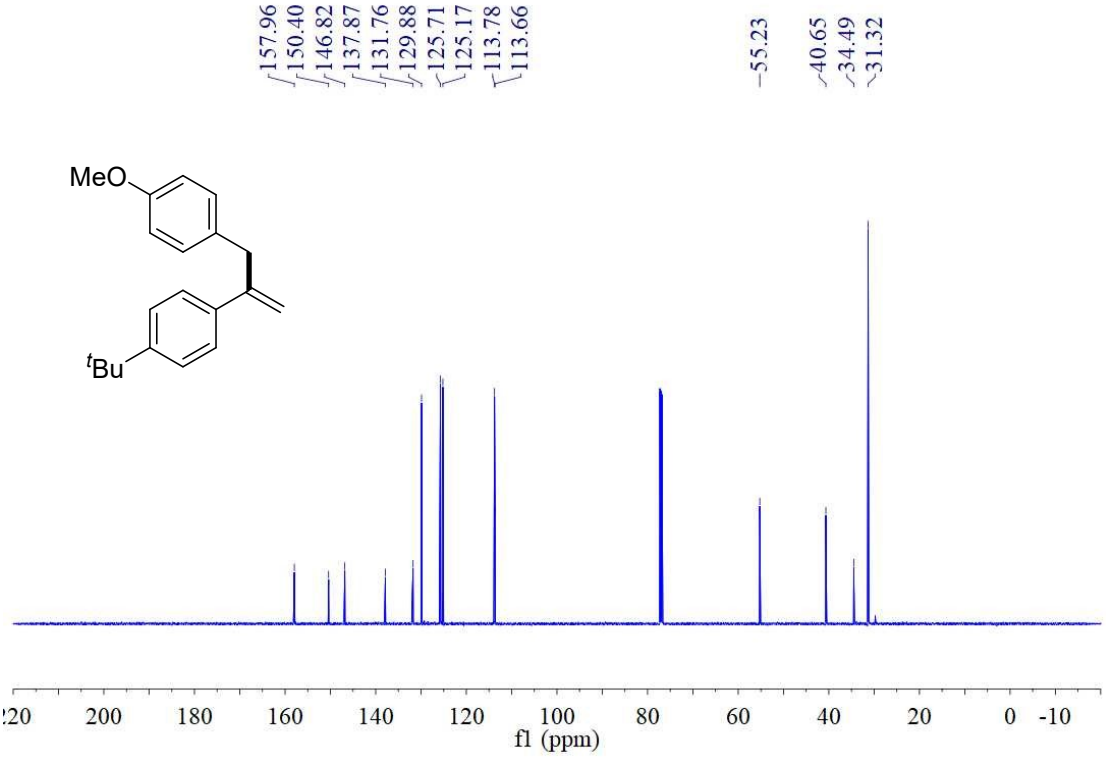
^{13}C NMR of **27** (150 MHz, $CDCl_3$)



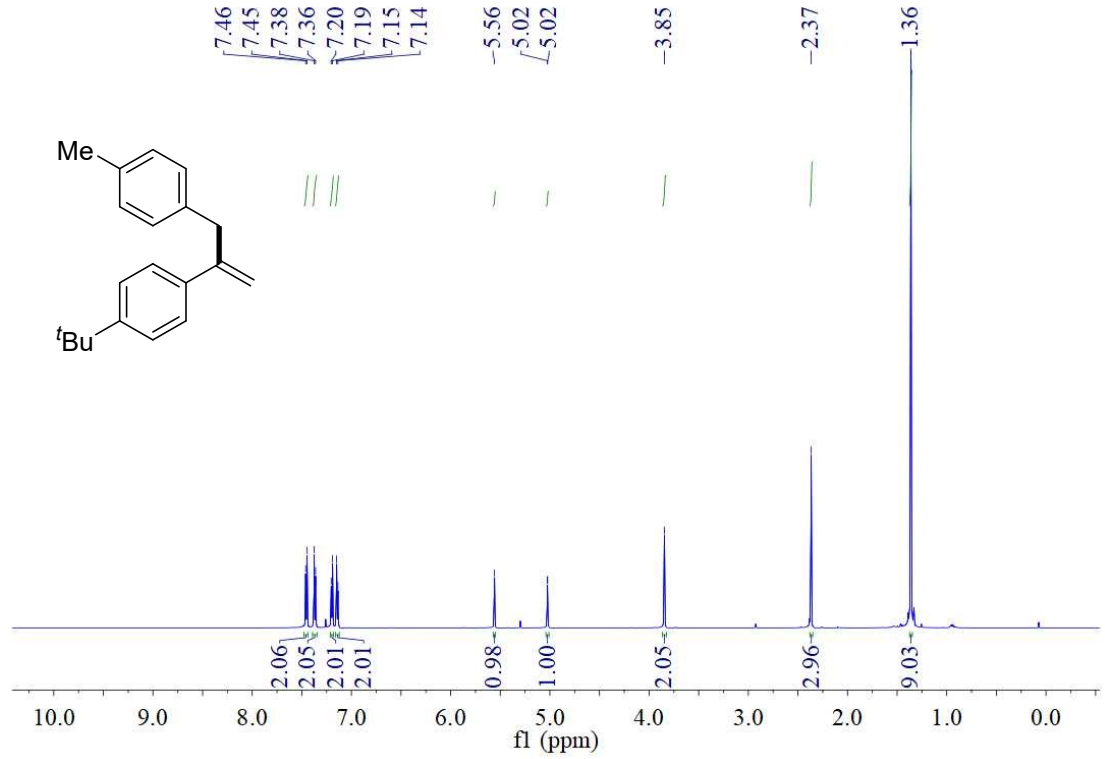
^{1}H NMR of **28** (600 MHz, $CDCl_3$)



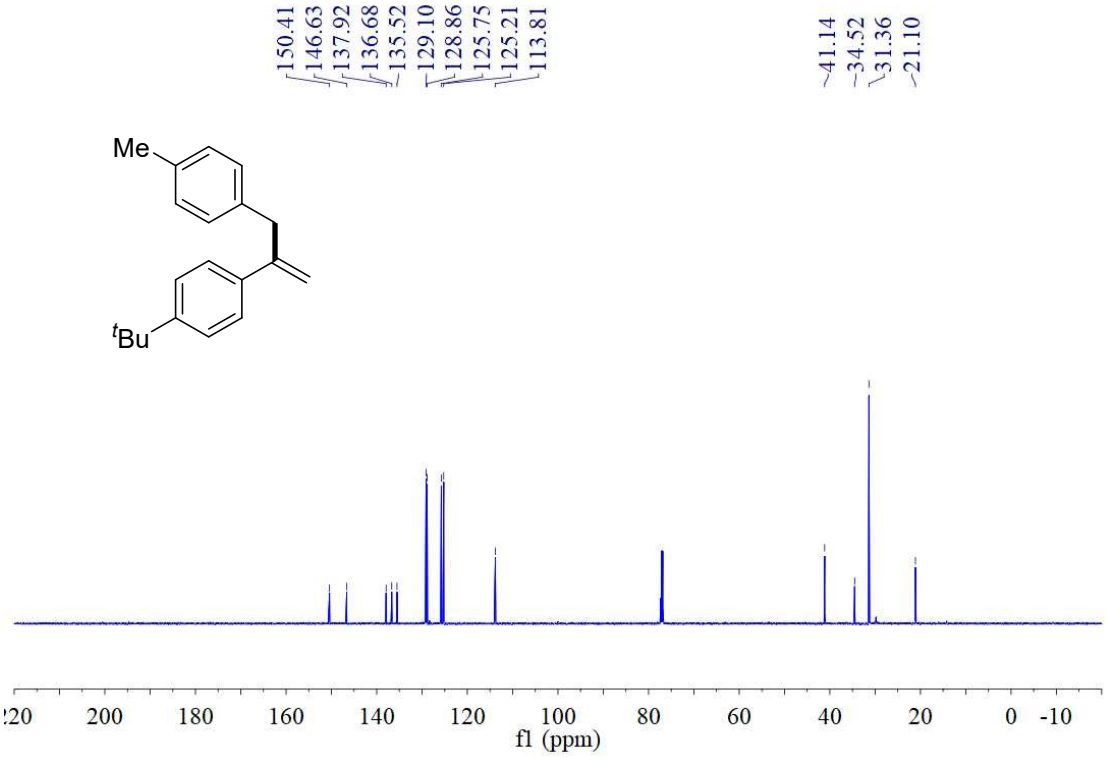
^{13}C NMR of **28** (150 MHz, $CDCl_3$)



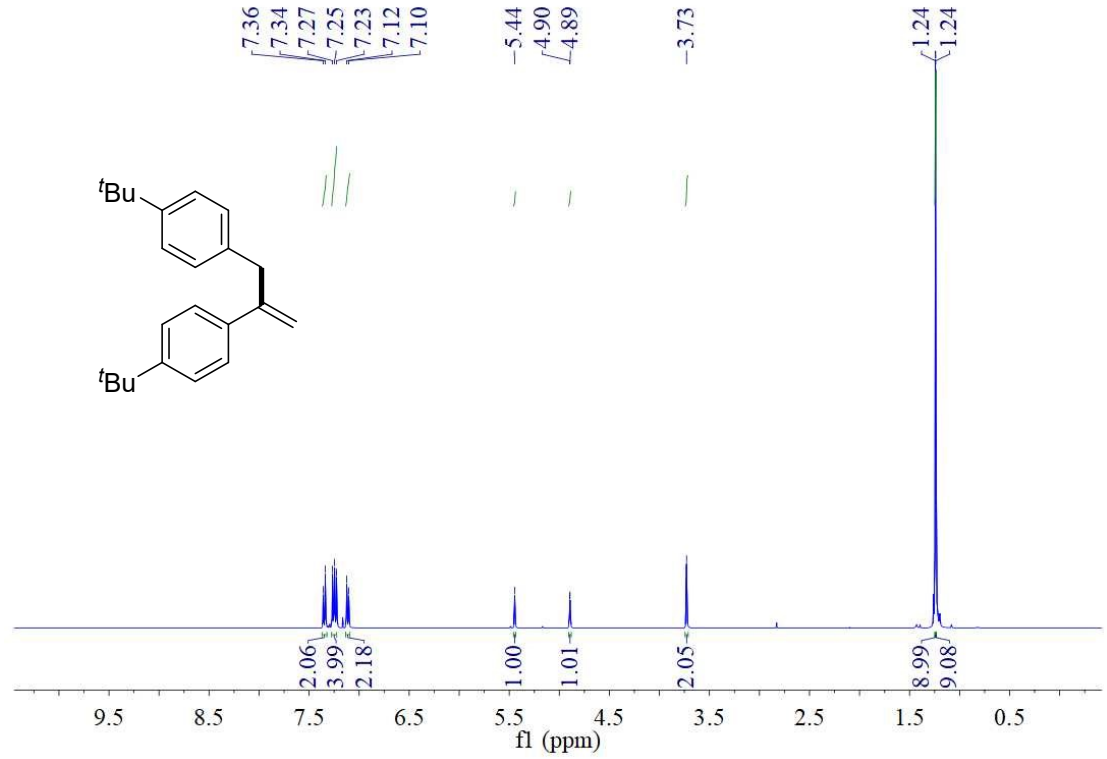
^{1}H NMR of **29** (600 MHz, $CDCl_3$)



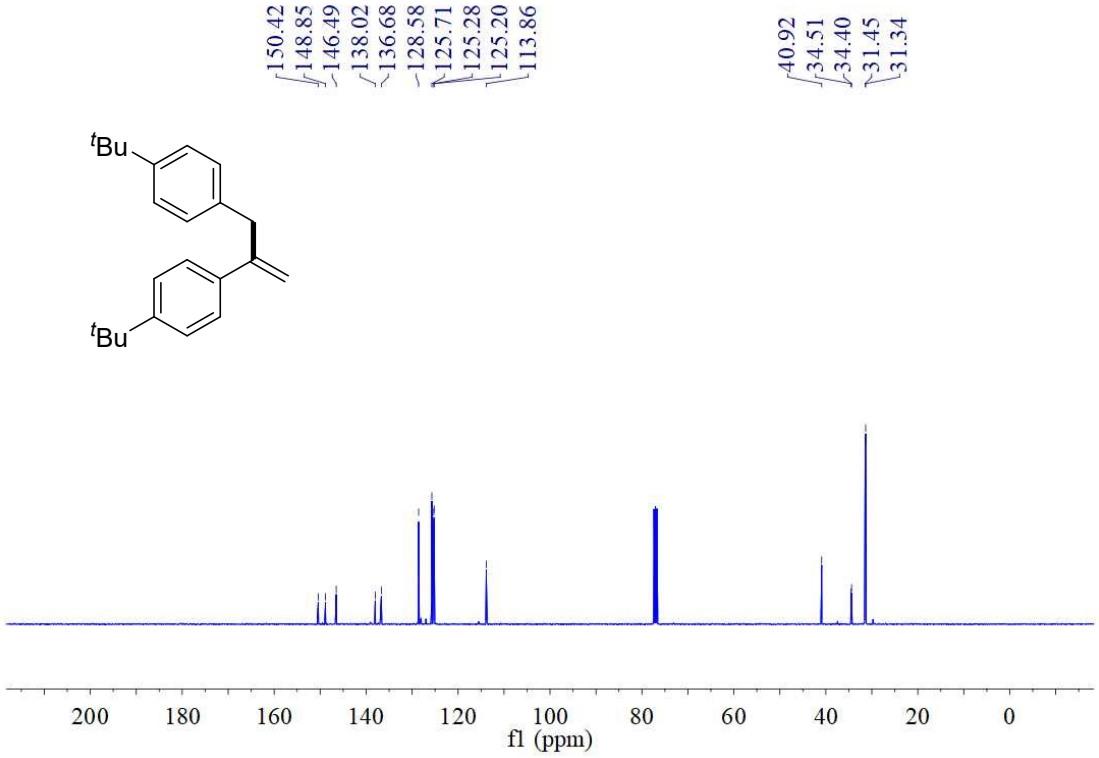
^{13}C NMR of **29** (150 MHz, $CDCl_3$)



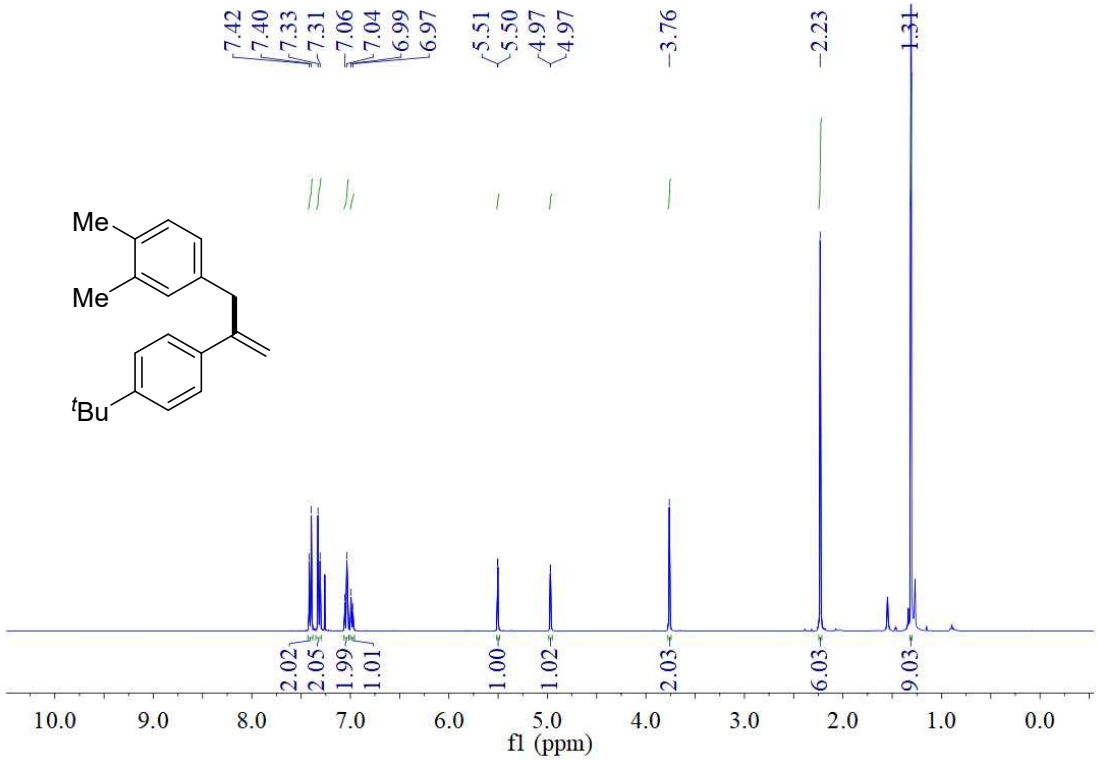
^{1}H NMR of **30** (400 MHz, $CDCl_3$)



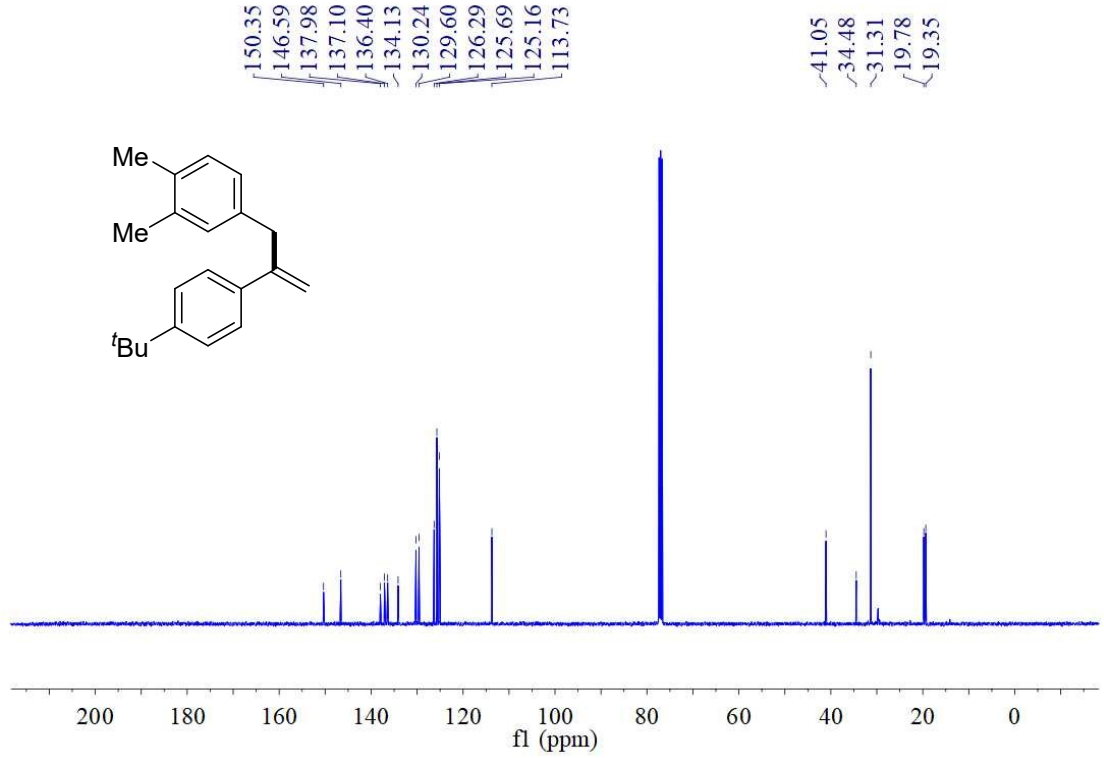
^{13}C NMR of **30** (100 MHz, $CDCl_3$)



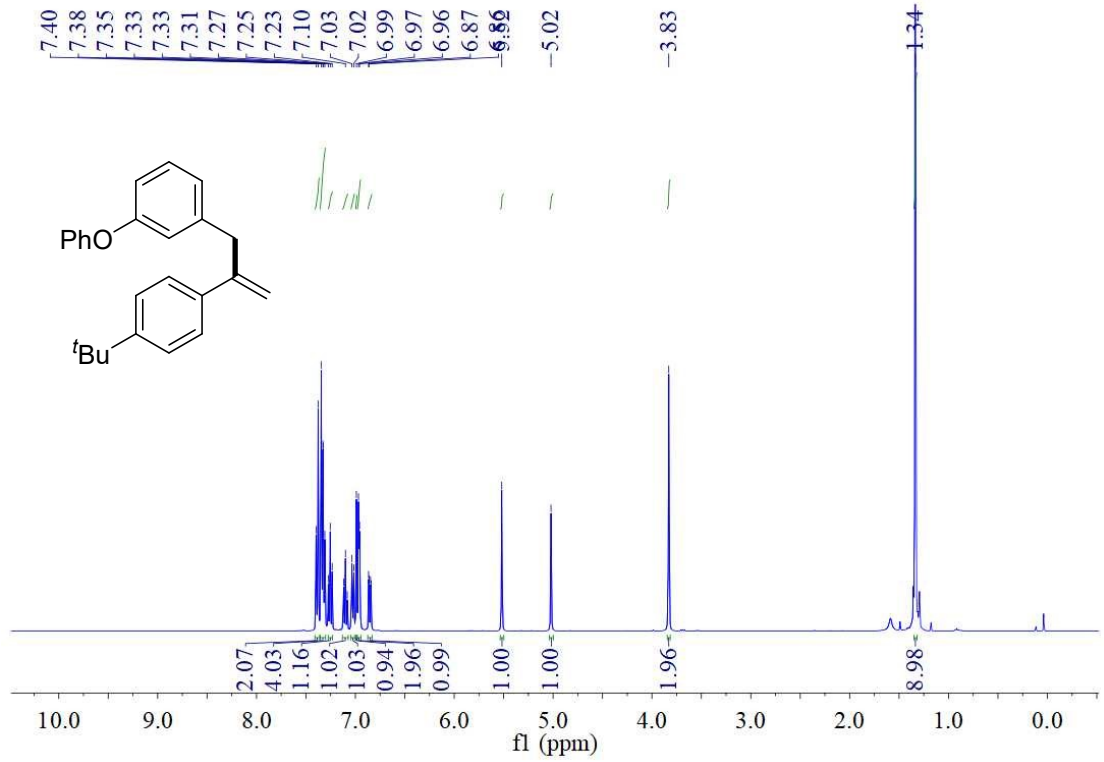
^{1}H NMR of **31** (400 MHz, $CDCl_3$)



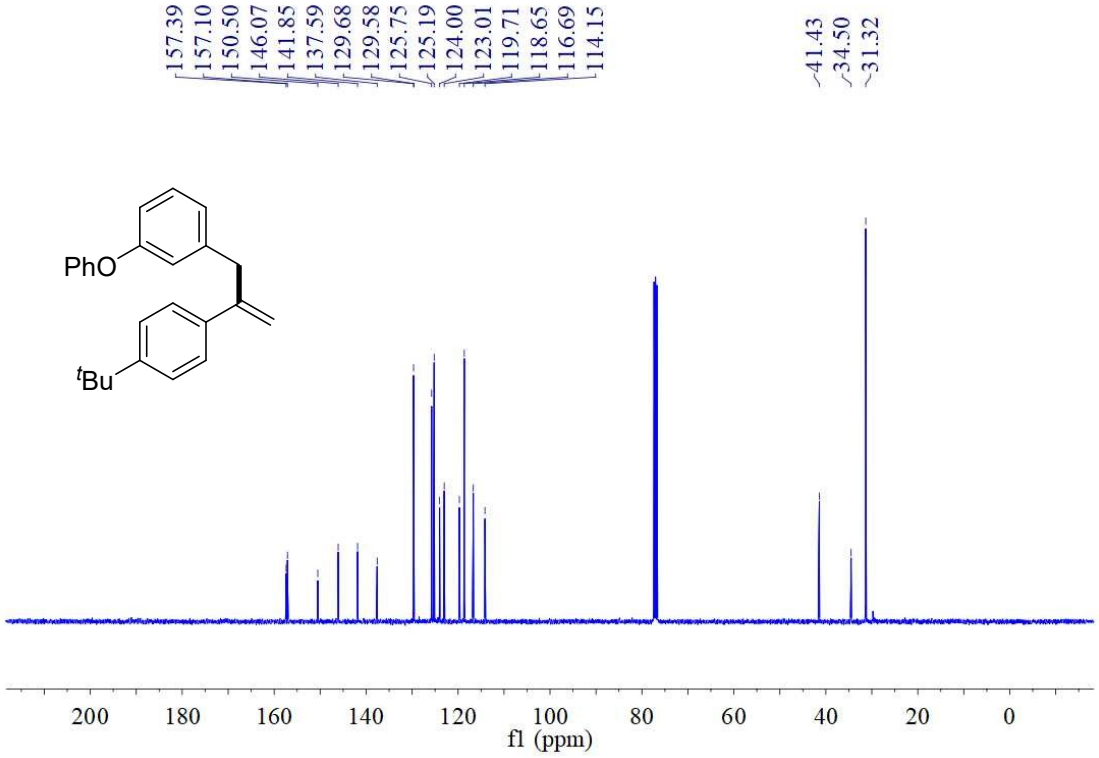
^{13}C NMR of **31** (100 MHz, $CDCl_3$)



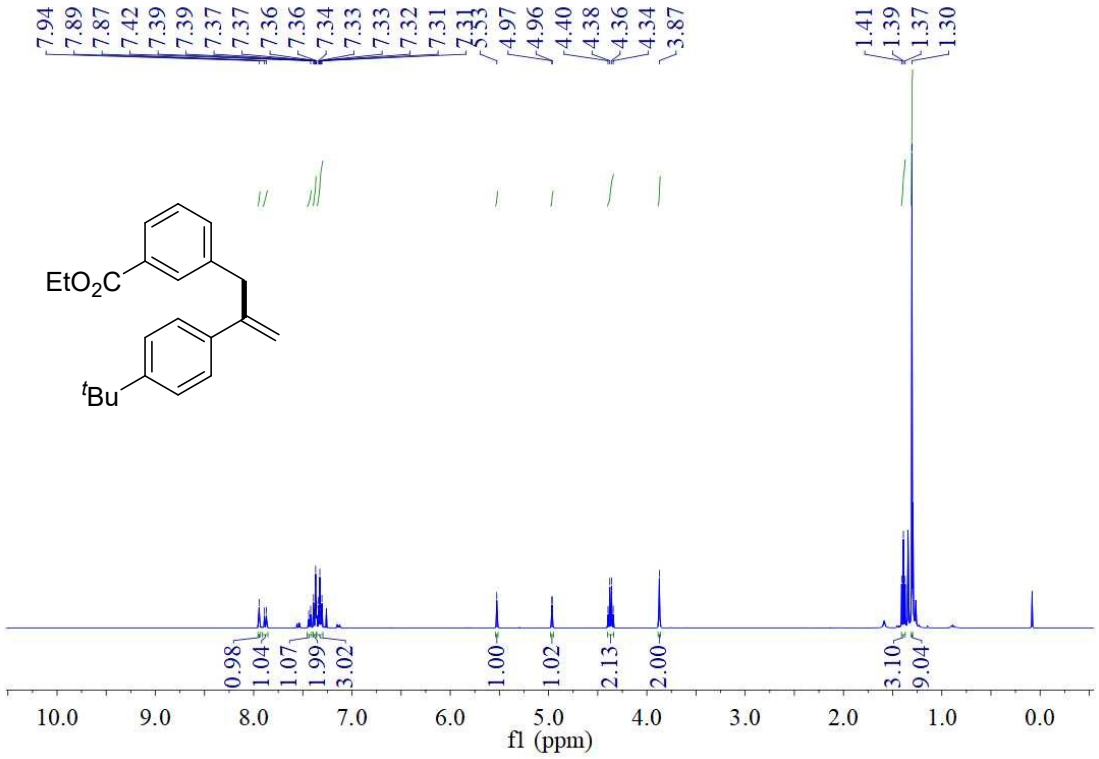
^{1}H NMR of **32** (400 MHz, $CDCl_3$)



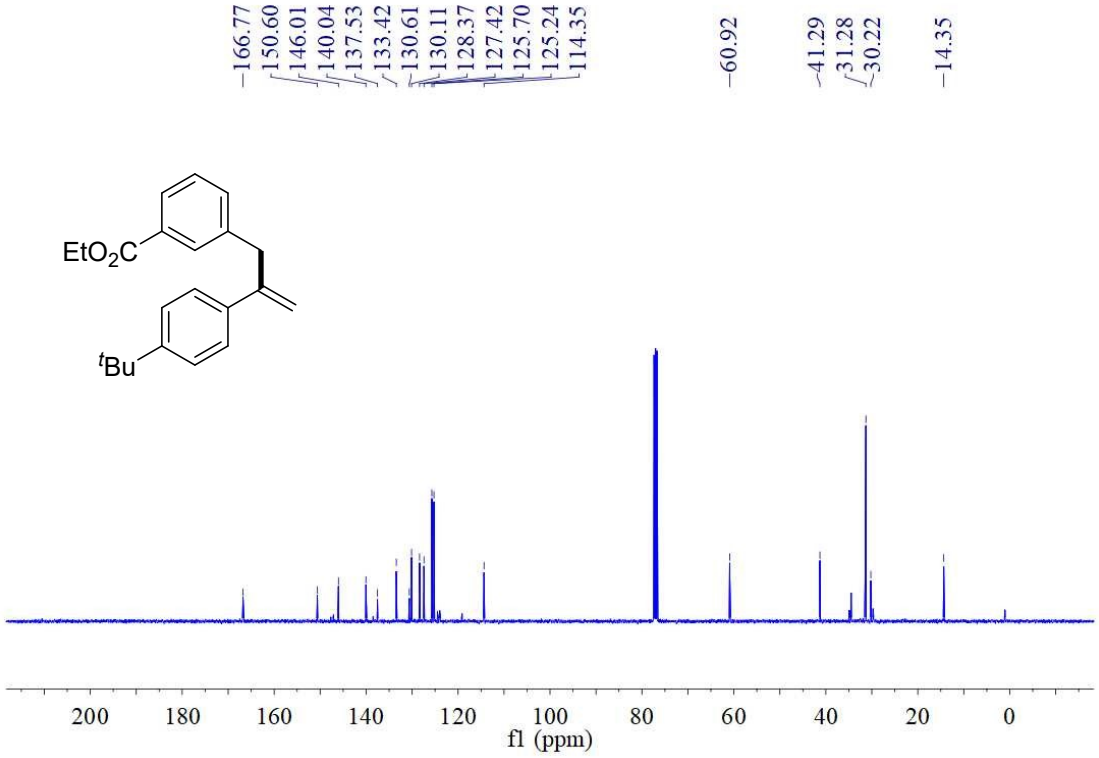
^{13}C NMR of **32** (100 MHz, $CDCl_3$)



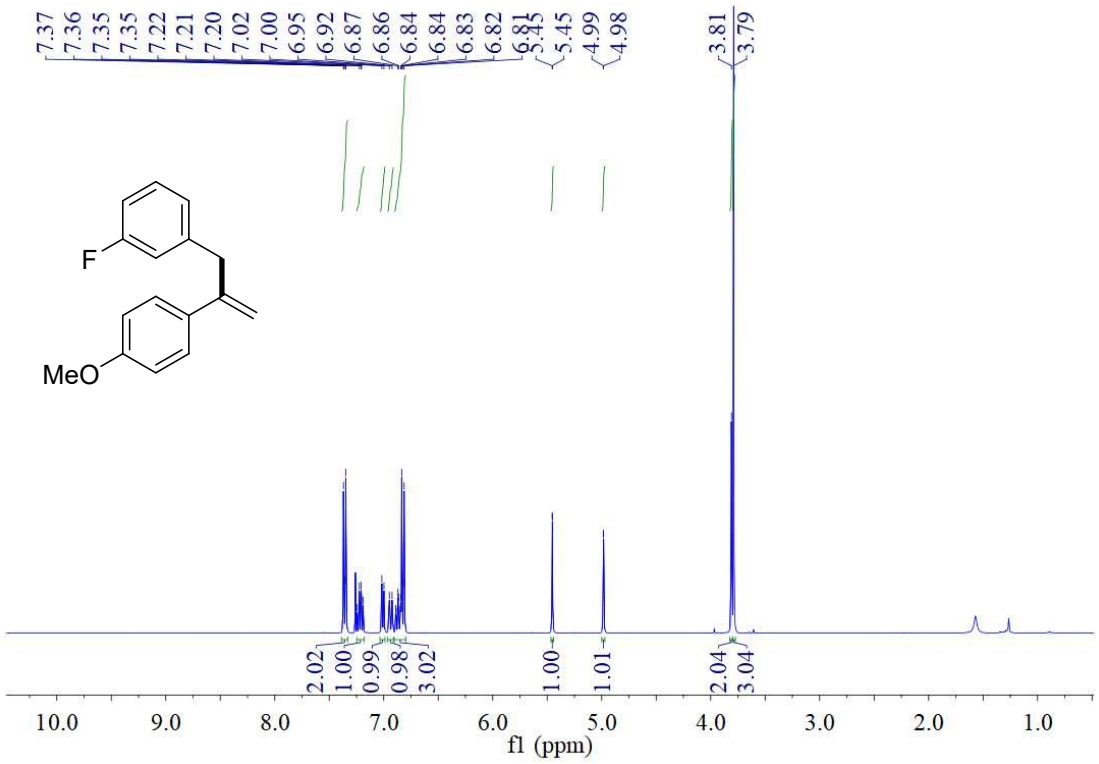
^{1}H NMR of **33** (400 MHz, $CDCl_3$)



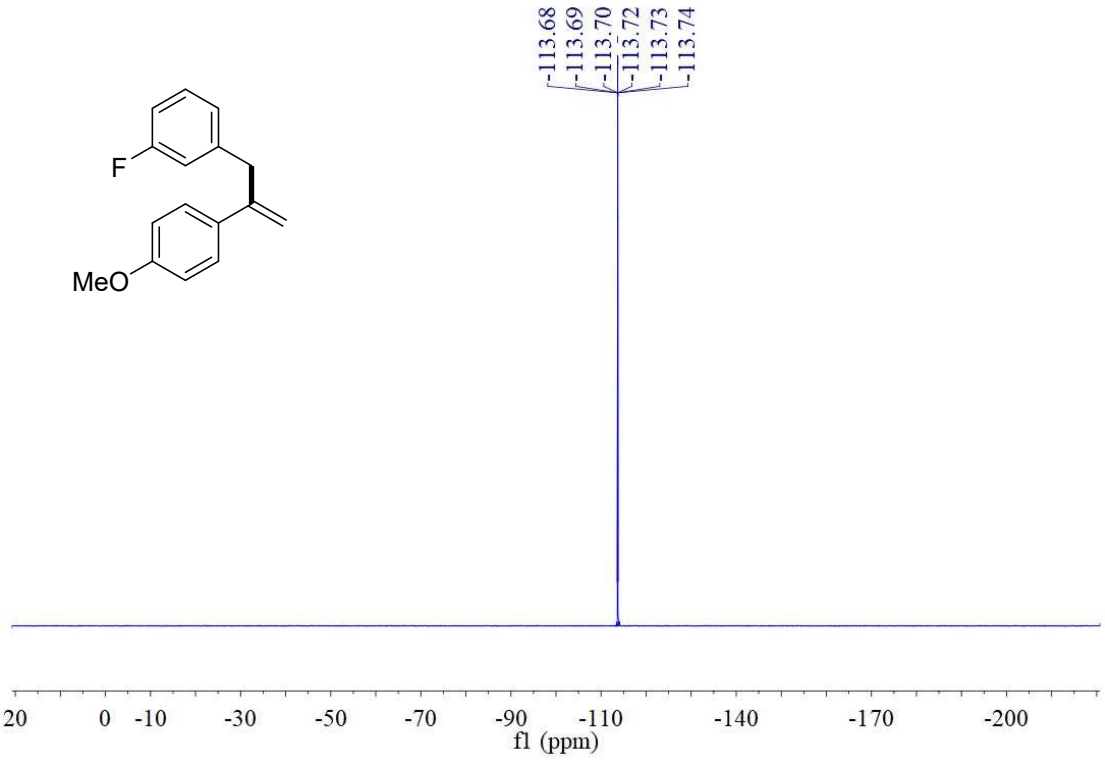
^{13}C NMR of **33** (100 MHz, $CDCl_3$)



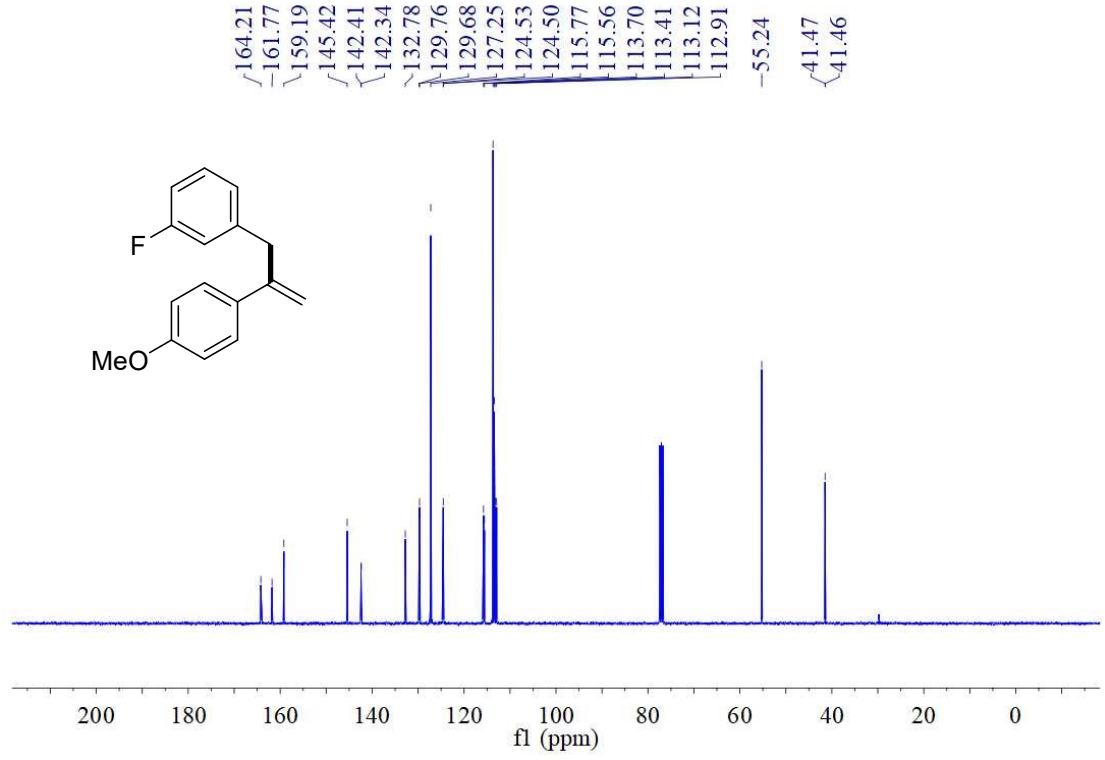
^{1}H NMR of **34** (400 MHz, $CDCl_3$)



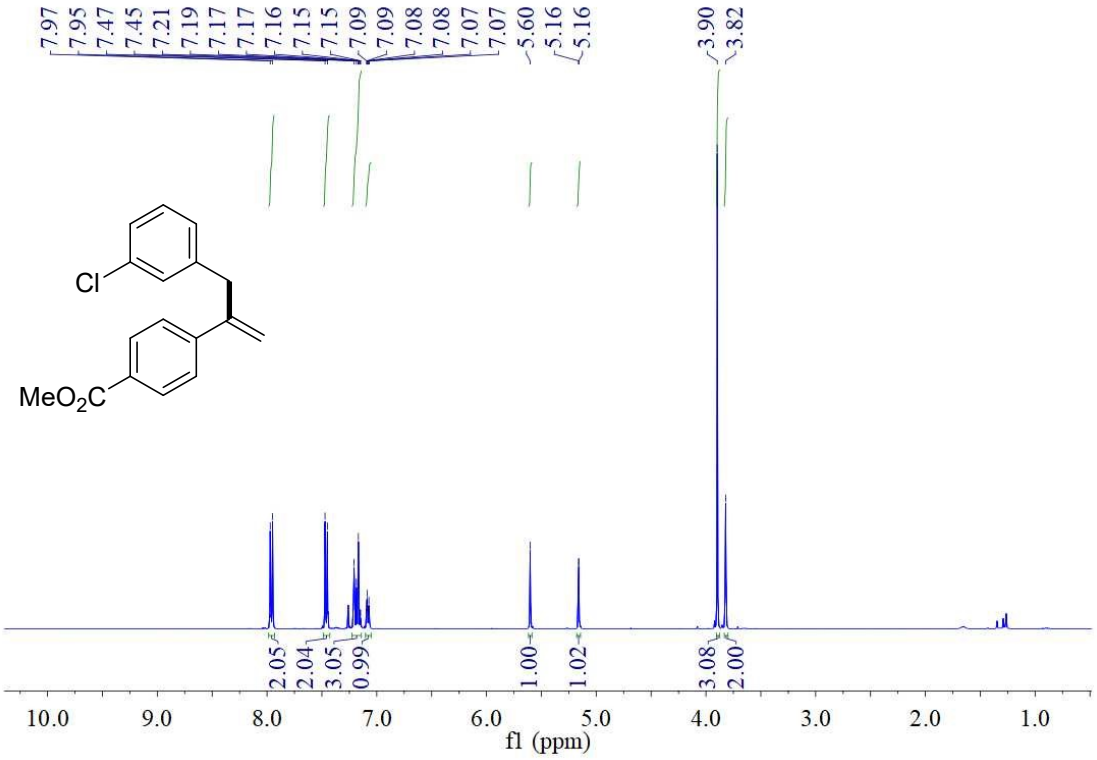
^{19}F NMR of **34** (376 MHz, $CDCl_3$)



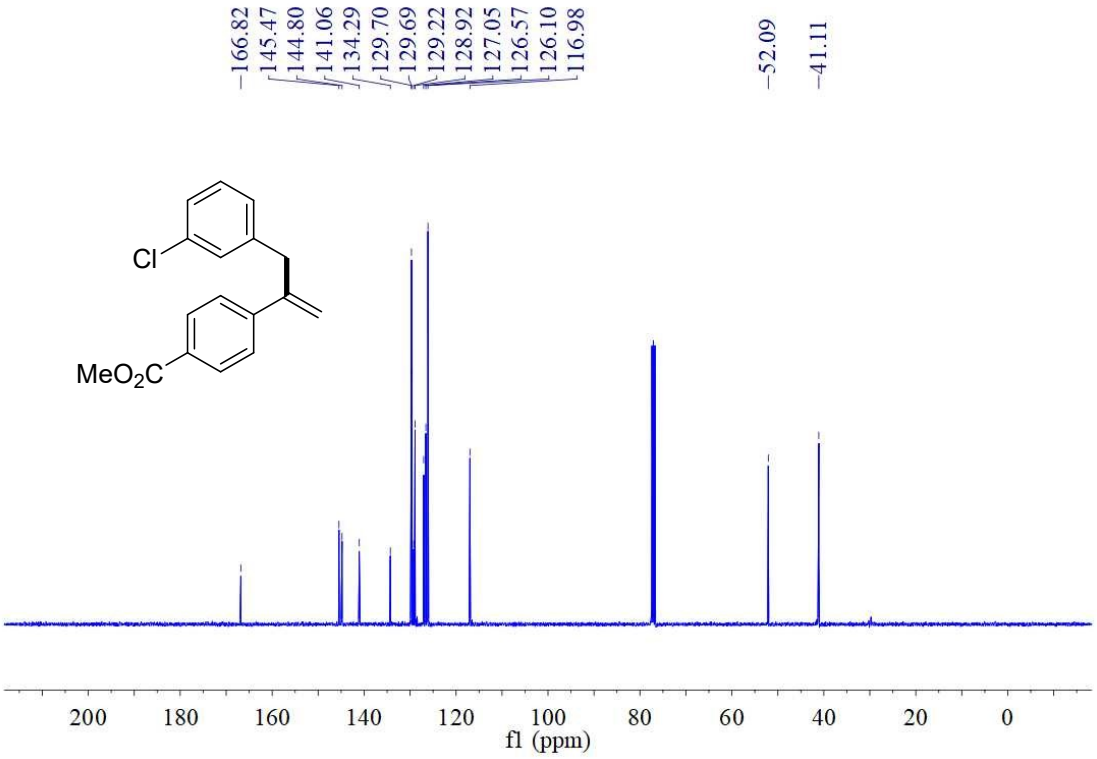
^{13}C NMR of **34** (100 MHz, $CDCl_3$)



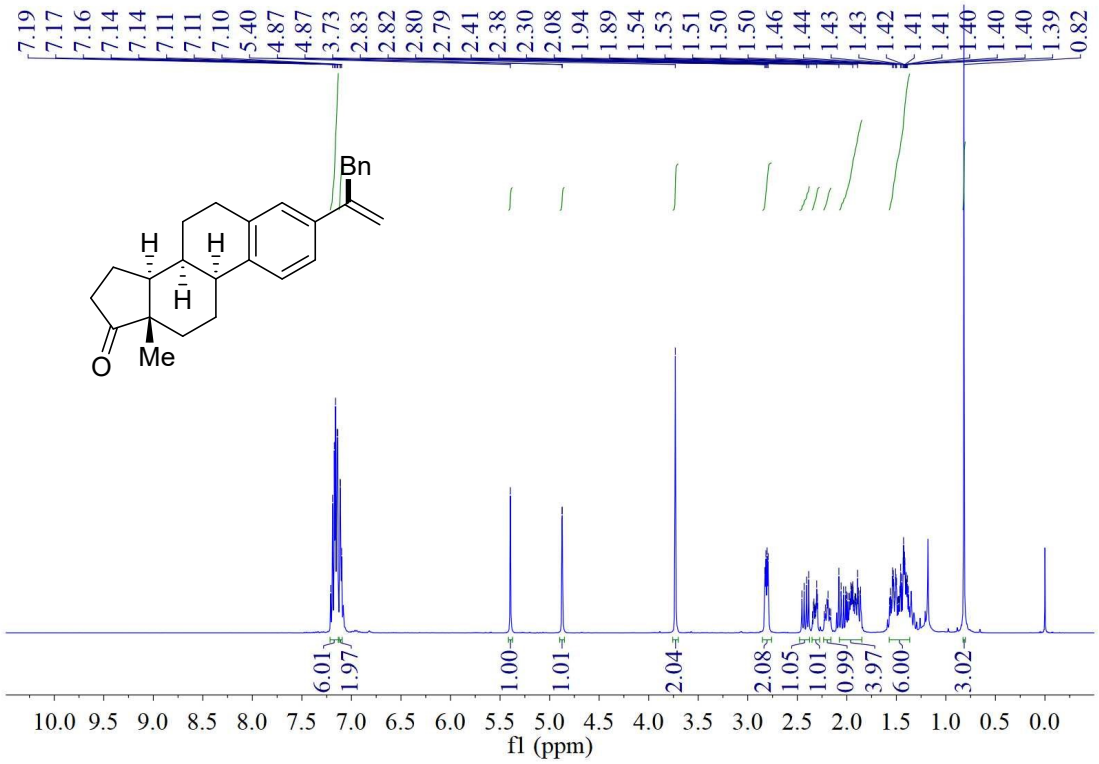
^{1}H NMR of **35** (400 MHz, $CDCl_3$)



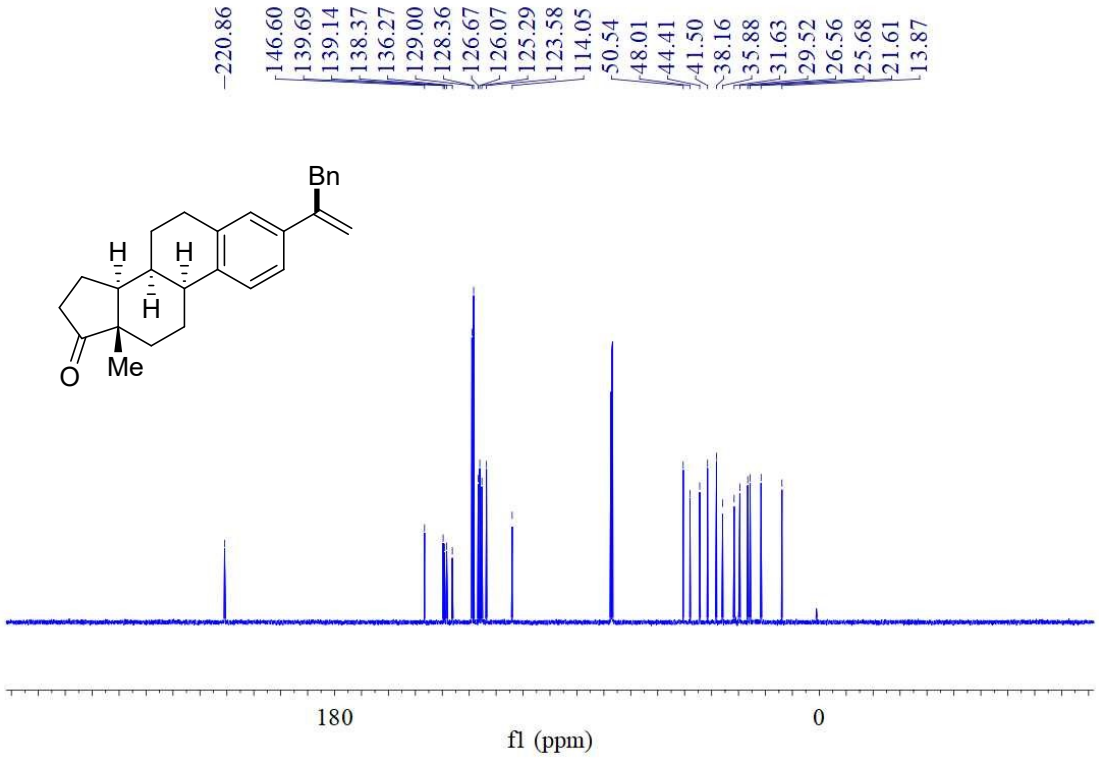
^{13}C NMR of **35** (100 MHz, $CDCl_3$)



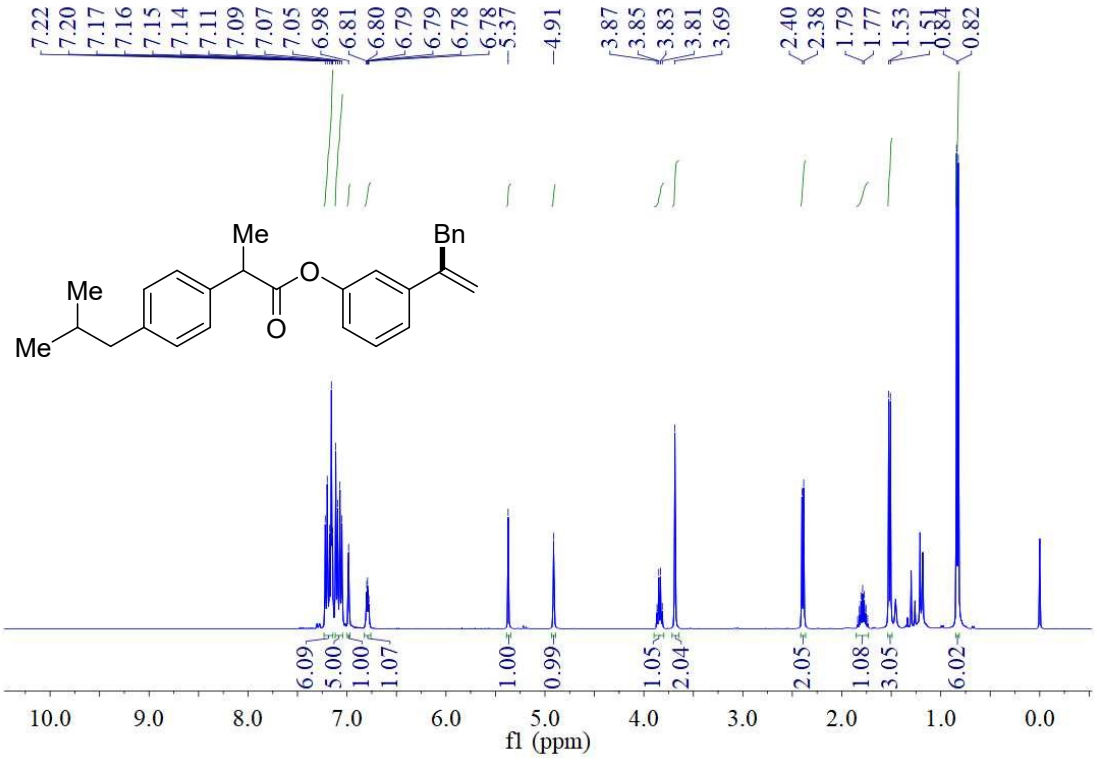
^{1}H NMR of **36** (400 MHz, $CDCl_3$)



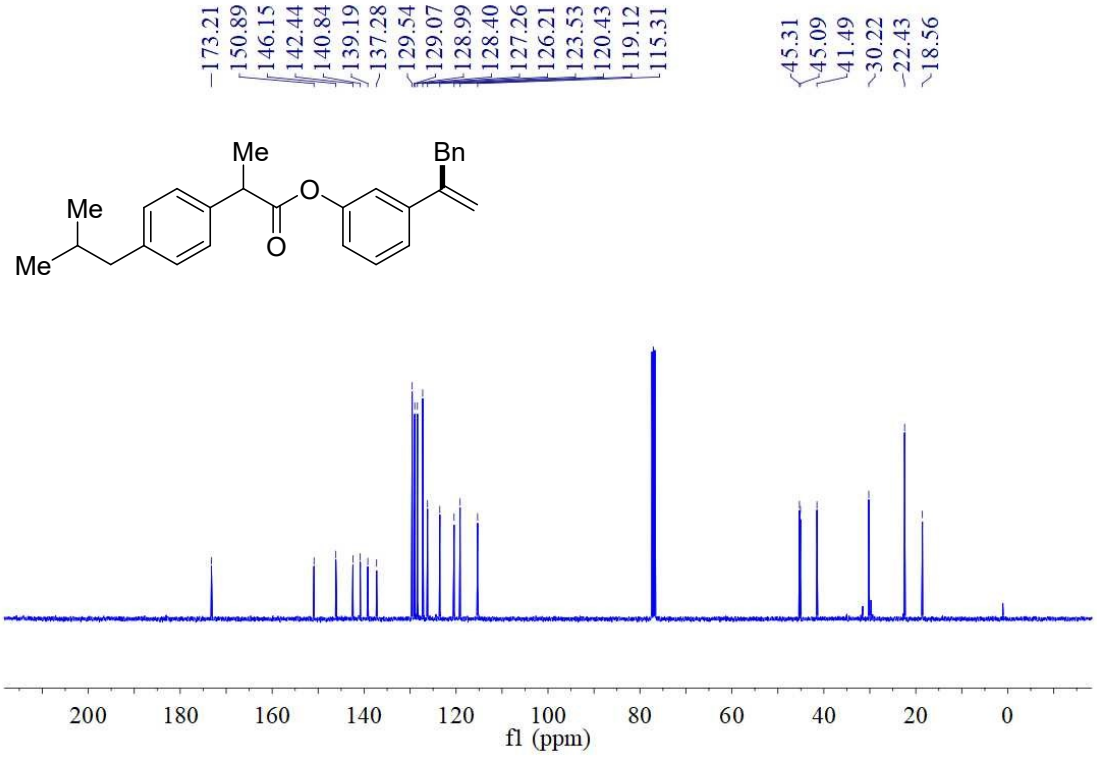
^{13}C NMR of **36** (100 MHz, $CDCl_3$)



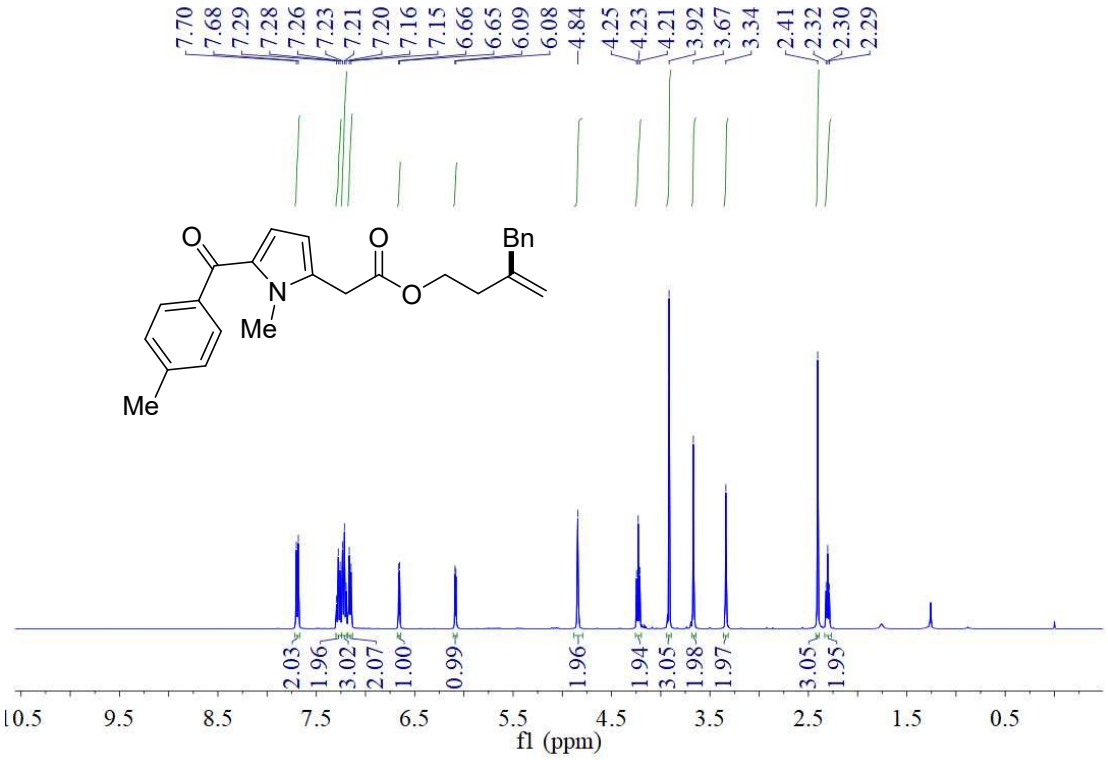
^{1}H NMR of **37** (400 MHz, $CDCl_3$)



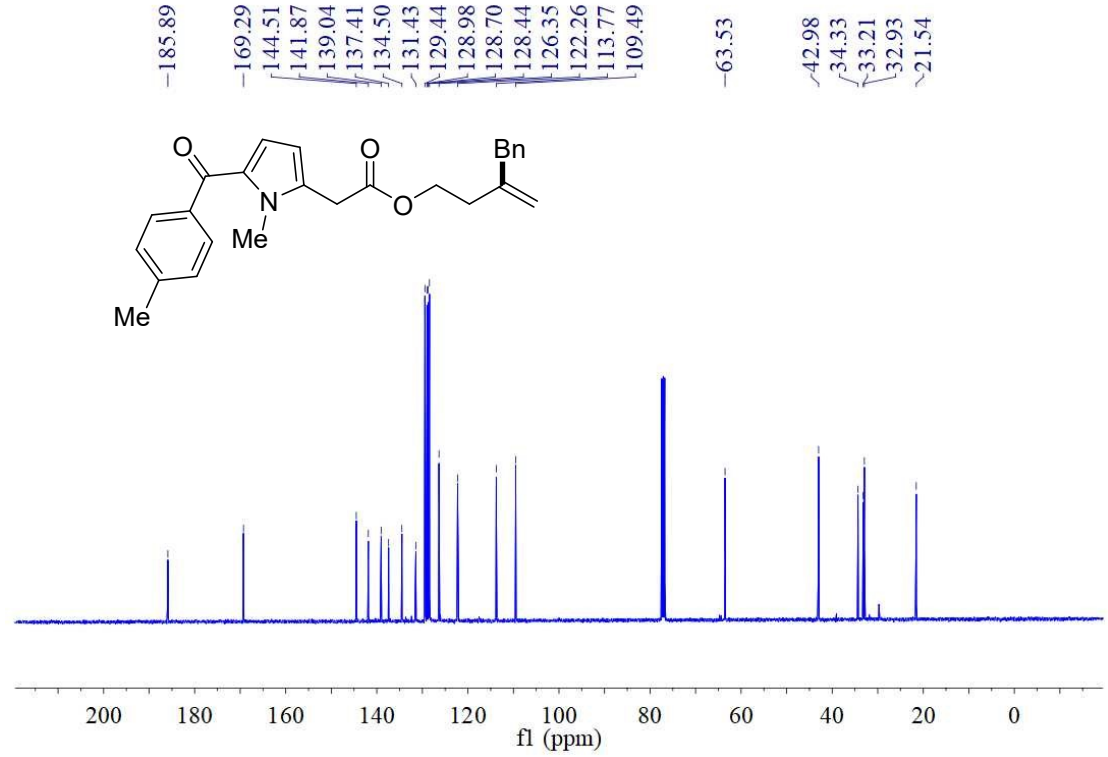
^{13}C NMR of **37** (100 MHz, $CDCl_3$)



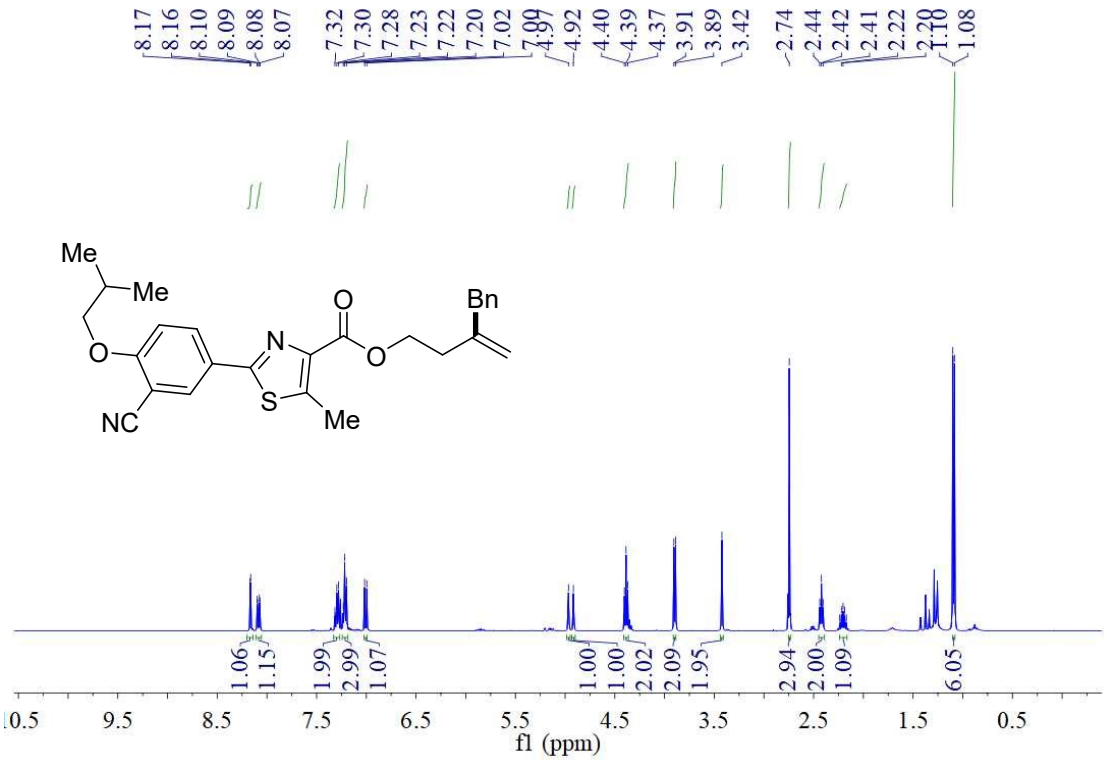
^{1}H NMR of **38** (400 MHz, $CDCl_3$)



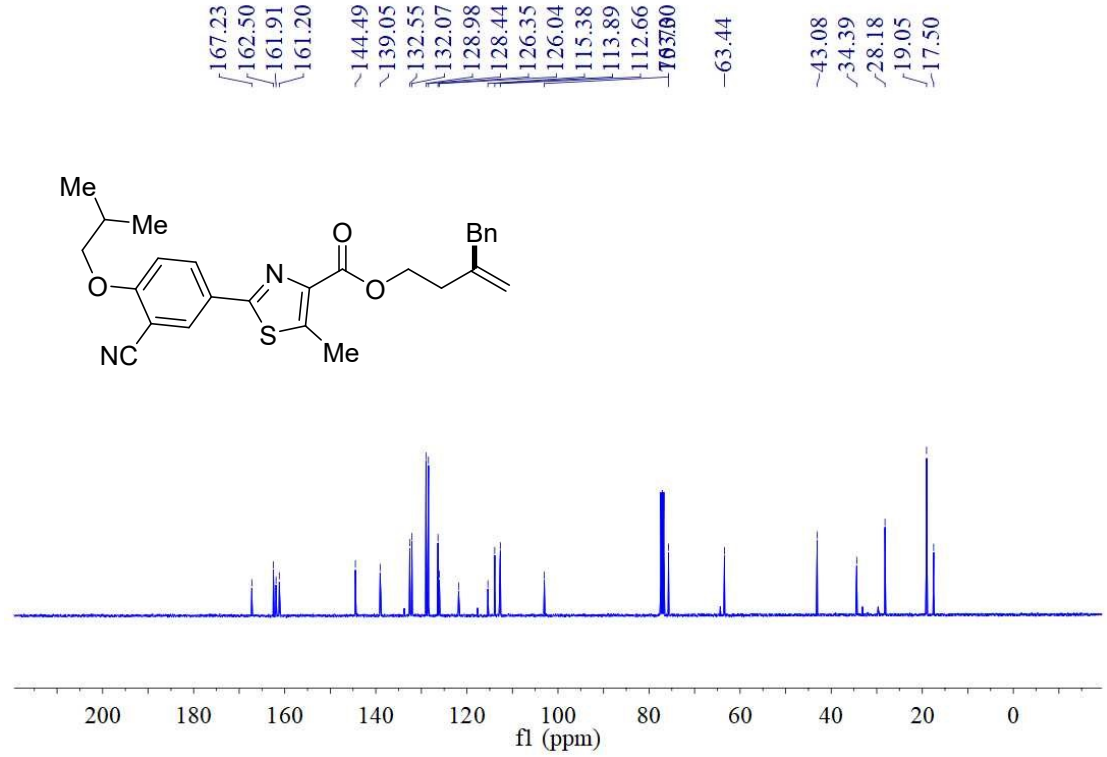
^{13}C NMR of **38** (100 MHz, $CDCl_3$)



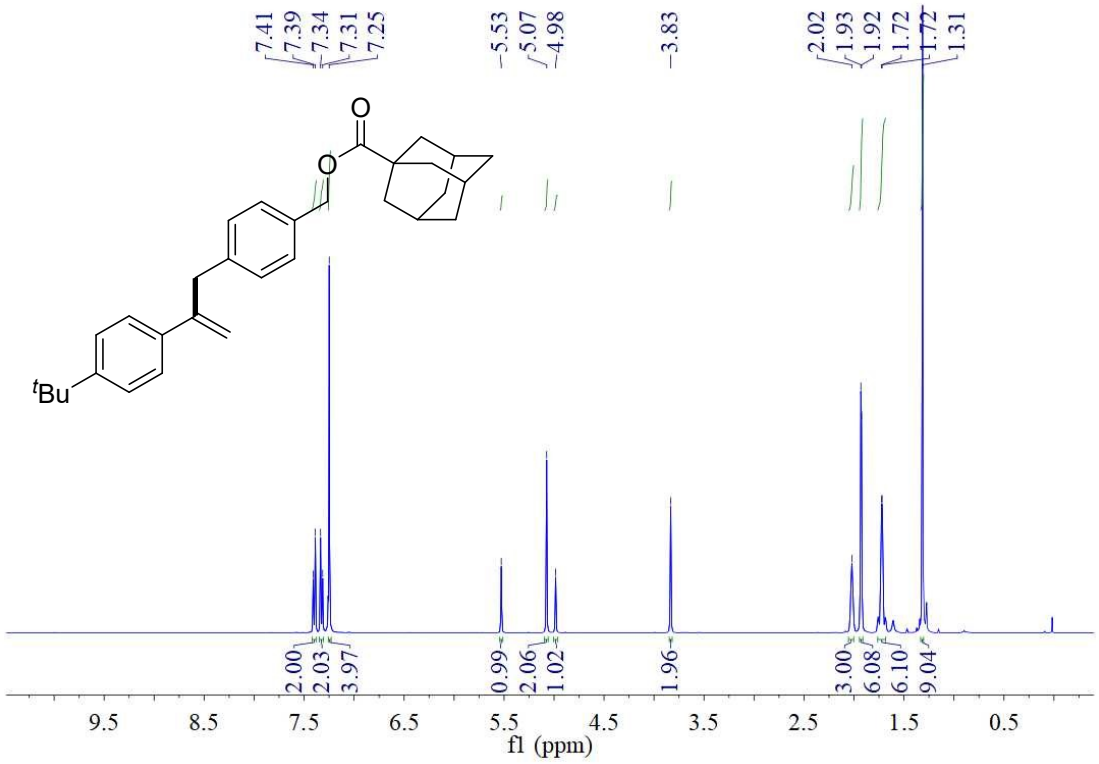
^{1}H NMR of **39** (400 MHz, $CDCl_3$)



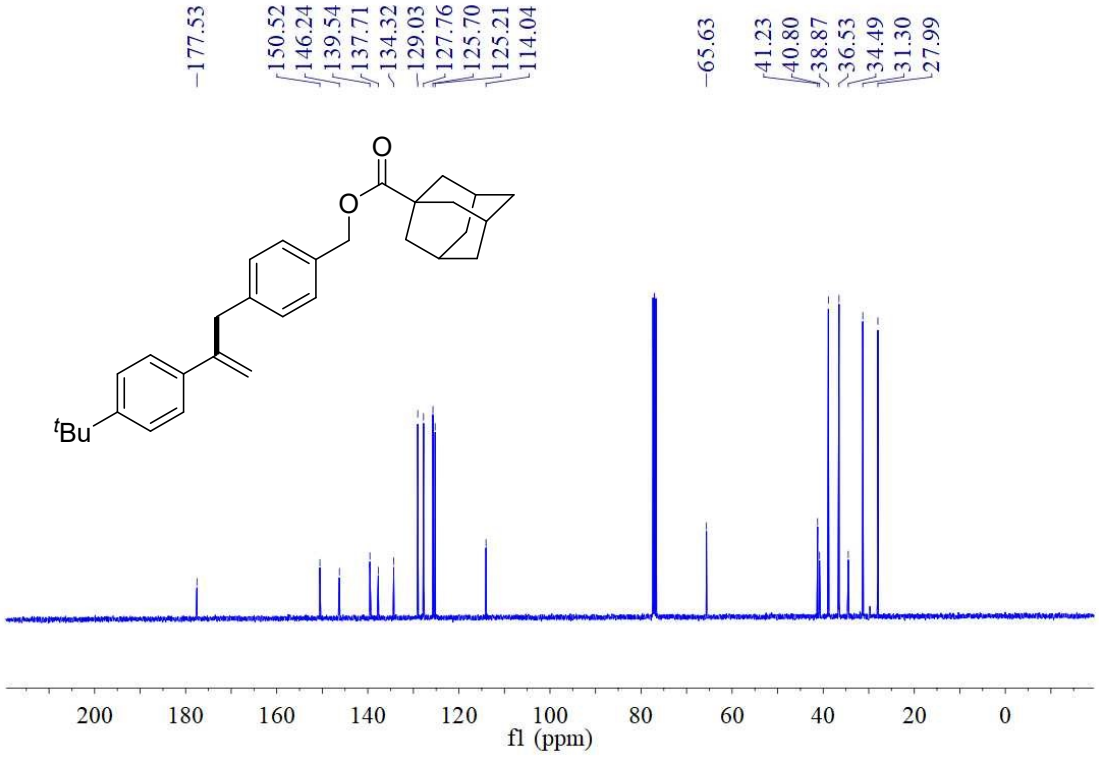
^{13}C NMR of **39** (100 MHz, $CDCl_3$)



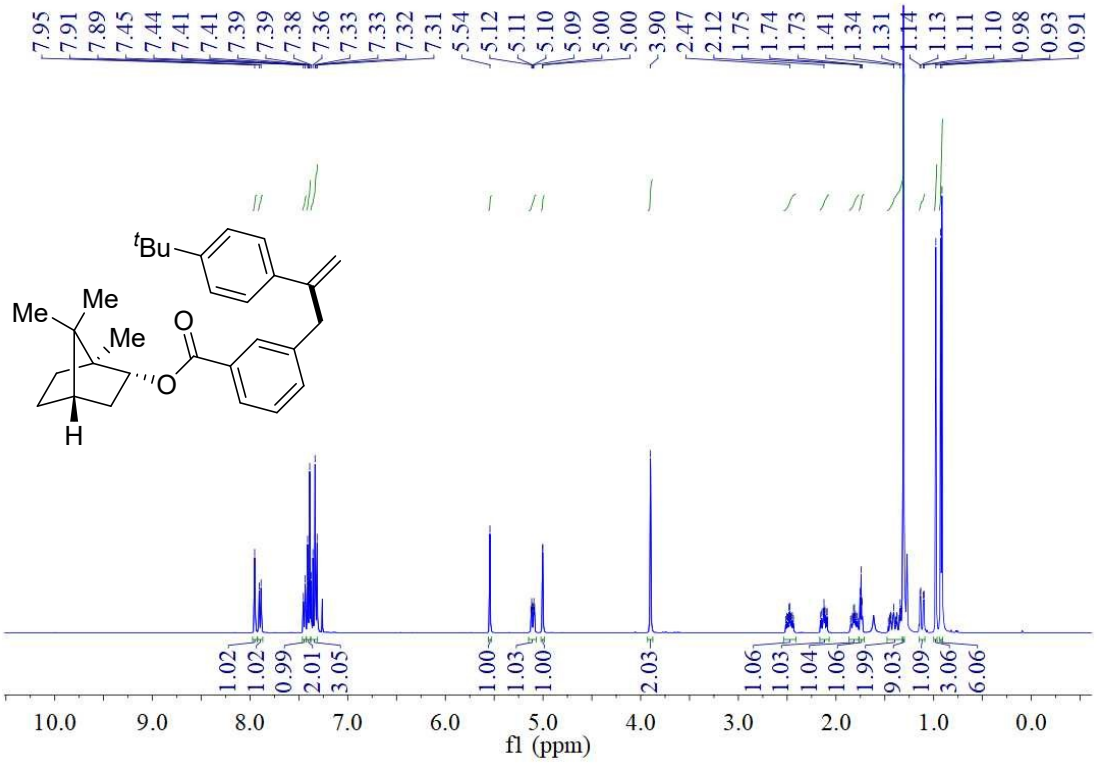
^{1}H NMR of **40** (400 MHz, $CDCl_3$)



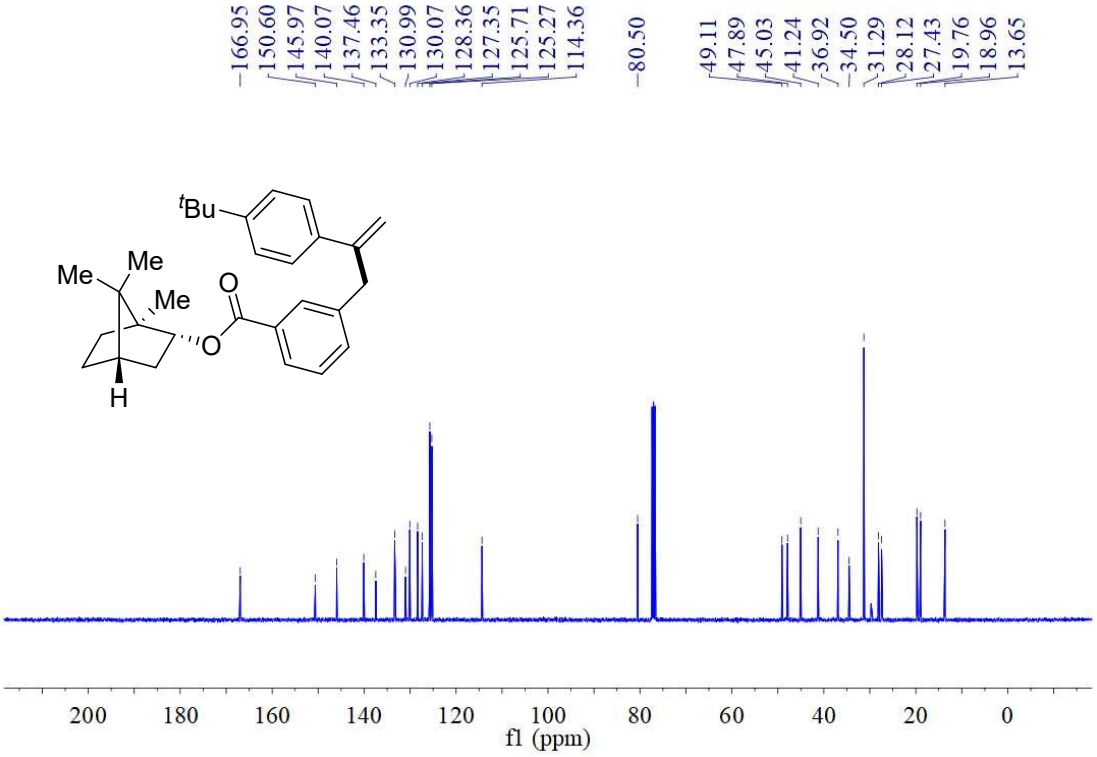
^{13}C NMR of **40** (100 MHz, $CDCl_3$)



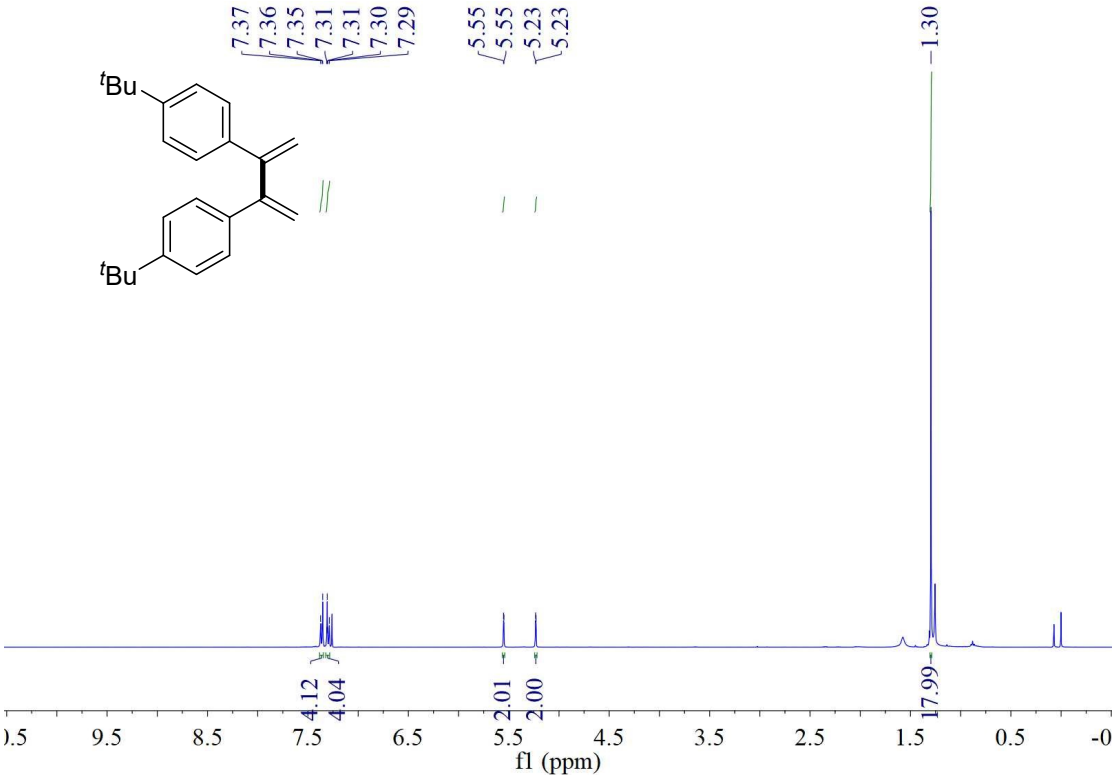
^{1}H NMR of **41** (400 MHz, $CDCl_3$)



^{13}C NMR of **41** (100 MHz, $CDCl_3$)



^{1}H NMR of **43** (400 MHz, $CDCl_3$)



^{13}C NMR of **43** (100 MHz, $CDCl_3$)