Palladium/norbornene-catalyzed trifunctionalization of aryl-thianthreniums

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Electronic Supplementary Information

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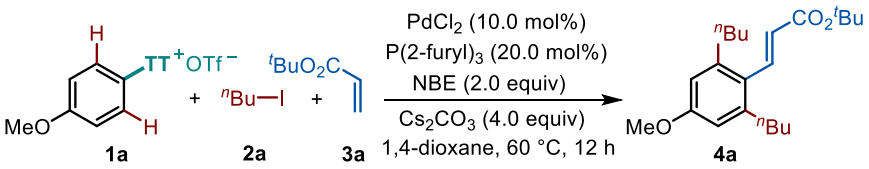
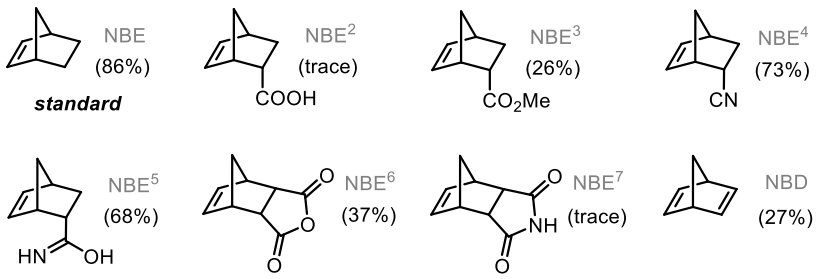
A. General information

All reagents were used from commercial received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$. High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer.

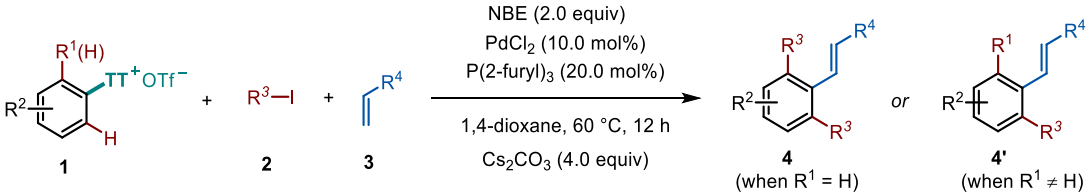
B. Optimization of Reaction Conditions



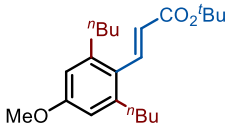
Entry	Variations from standard conditions	Yield[b] of **4a**
1	None	86%
2	$Pd(OAc)_2$ instead of $PdCl_2$	80%
3	$Pd(TFA)_2$ instead of $PdCl_2$	25%
4	$Pd_2(dba)_3$ instead of $PdCl_2$	trace
5	P(*p*-MeO-C_6H_4)$_3$ instead of P(2-furyl)$_3$	55%
6	PCy_3 instead of P(2-furyl)$_3$	43%
7	X-Phos instead of P(2-furyl)$_3$	59%
8	K_2CO_3 instead of Cs_2CO_3	57%
9	Na_2CO_3 instead of Cs_2CO_3	21%
10	K_2PO_4 instead of Cs_2CO_3	73%
11	toluene instead of 1,4-dioxane	68%
12	MeCN instead of 1,4-dioxane	65%
13	THF instead of 1,4-dioxane	79%
14	Other NBEs and anologues	seeing below
15	1.0 equiv NBE instead of 2.0 equiv NBE	44%
16	0.5 equiv NBE instead of 2.0 equiv NBE	34%



C. Substrate Scope

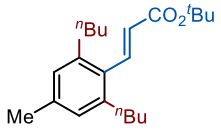


A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$, (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1** (0.2 mmol), **2** (0.6 mmol), **3** (0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **4** or **4'**.



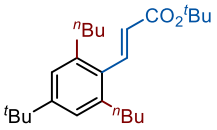
***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-methoxyphenyl) acrylate (4aa)**

White solid (61.6 mg, 89% yield). PE:EA = 40:1, R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.3 Hz, 1H), 6.61 (s, 2H), 5.89 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 2.62 (t, *J* = 8.0 Hz, 4H), 1.54 (s, 9H), 1.54 – 1.50 (m, 4H), 1.41 – 1.33 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.0, 143.2, 142.1, 126.2, 124.7, 112.4, 80.3, 55.0, 33.8, 33.3, 28.2, 22.6, 13.9. IR (KBr): 2961, 2542, 2313, 1708, 1464, 1287, 1146, 758 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{35}O_3$ $[M+H]^+$ 347.2581, found 347.2576.



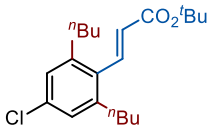
***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-methylphenyl) acrylate (4ab)**

White solid (51.5 mg, 78% yield). PE:EA = 40:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.3 Hz, 1H), 6.89 (s, 2H), 5.92 (d, *J* = 16.3 Hz, 1H), 2.60 (t, *J* = 7.2 Hz,4H), 2.31 (s, 3H), 1.55 (s, 9H), 1.55 – 1.48 (m, 4H), 1.41 – 1.33 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 142.5, 141.2, 137.6, 130.8, 127.8, 125.3, 80.3, 33.4, 28.2, 22.6, 21.2, 13.9. IR (KBr): 2919, 2541, 2313, 1982, 1714, 1517, 1270, 1103 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{35}O_2$ $[M+H]^+$ 331.2632, found 331.2624.



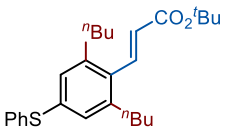
***tert*-Butyl (*E*)-3-(4-(tert-butyl)-2,6-dibutylphenyl) acrylate (4ac)**

White oil (63.3 mg, 85% yield). PE:EA = 40:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.3 Hz, 1H), 7.07 (s, 2H), 5.93 (d, *J* = 16.3 Hz, 1H), 2.62 (t, *J* = 7.2 Hz, 4H), 1.55 (s, 9H), 1.54 – 1.47 (m, 4H), 1.41 – 1.35 (m, 4H), 1.32 (s, 9H), 0.93 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 150.7, 142.5, 140.8, 130.8, 125.3, 124.1, 80.3, 34.4, 33.8, 33.5, 31.2, 28.2, 22.7, 13.9. IR (KBr): 2985, 2718, 2362, 1984, 1624, 1527, 1370, 1002 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{25}H_{41}O_2$ $[M+H]^+$ 373.3101, found 373.3092.



***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-chlorophenyl) acrylate (4ad)**

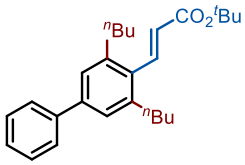
White solid (61.0 mg, 88% yield). PE:EA = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.3 Hz, 1H), 7.04 (s, 2H), 5.90 (d, *J* = 16.3 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 4H), 1.54 (s, 9H), 1.63 – 1.46 (m, 4H), 1.38 – 1.31 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 143.0, 141.4, 133.5, 132.4, 126.7, 126.5, 33.3, 33.0, 28.2, 22.5, 13.8. IR (KBr): 2971, 2569, 2313, 1983, 1706, 1640, 1293, 1147 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{21}H_{32}ClO_2$ $[M+H]^+$ 351.2085, found 351.2092.



***tert*-Butyl (*E*)-3-(3,5-dibutyl-[1,1'-biphenyl]-4-yl) acrylate (4ae)**

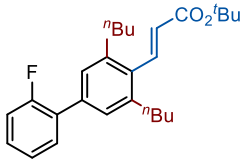
White oil (67.5 mg, 86% yield). PE:EA = 30:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72

(d, J = 16.3 Hz, 1H), 7.34 (t, J = 5.9 Hz, 3H), 7.31 (d, J = 16.3 Hz, 1H), 7.26 (d, J = 2.6 Hz, 1H), 7.03 (s, 2H), 5.93 (d, J = 16.3 Hz, 1H), 2.56 (d, J = 7.1 Hz, 4H), 1.54 (s, 9H), 1.52 – 1.44 (m, 4H), 1.35 – 1.29 (m, 4H), 0.89 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 142.2, 141.7, 135.6, 135.0, 132.8, 130.9, 129.1, 129.1, 127.0, 126.0, 80.5, 33.3, 33.0, 28.2, 22.4, 13.8. IR (KBr): 2961, 2516, 2313, 1710, 1639, 1464, 1304, 746 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{37}O_2S$ $[M+H]^+$ 425.2509, found 425.2504.



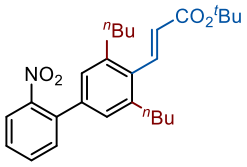
***tert*-Butyl (*E*)-3-(3,5-dibutyl-[1,1'-biphenyl]-4-yl) acrylate (4af)**

White solid (67.3 mg, 86% yield). PE:EA = 40:1, R_f = 0.45, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 16.3 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.9 Hz, 2H), 7.35 (t, J = 8.1 Hz, 1H), 7.31 (s, 2H), 6.00 (d, J = 16.4 Hz, 1H), 2.71 (t, J = 8.0 Hz, 4H), 1.65 – 1.58 (m, 4H), 1.57 (s, 9H), 1.44 – 1.36 (m, 4H), 0.95 (t, J = 8.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 142.2, 141.7, 140.9, 140.6, 132.9, 128.7, 127.3, 127.1, 125.8, 125.8, 80.5, 33.6, 33.4, 28.2, 22.6, 13.9. IR (KBr): 2963, 2745, 2313, 2103, 1709, 1640, 1587, 1307, 757 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{37}O_2$ $[M+H]^+$ 393.2788, found 393.2792.



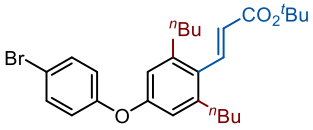
***tert*-Butyl (*E*)-3-(3,5-dibutyl-2'-fluoro-[1,1'-biphenyl]-4-yl) acrylate (4ag)**

White solid (69.7 mg, 85% yield). PE:EA = 40:1, R_f = 0.35, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 16.3 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.26 (s, 2H), 7.22 (d, J = 7.5 Hz, 1H), 7.16 (d, J = 9.5 Hz, 1H), 5.99 (d, J = 16.3 Hz, 1H), 2.68 (t, J = 7.9 Hz, 4H), 1.65 – 1.57 (m, 4H), 1.56 (s, 9H), 1.43 – 1.35 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 161.0, 158.5, 142.1, 141.3, 135.2, 133.3, 130.6 (d, J = 3.6 Hz), 128.9, 128.9, 127.5 (d, J = 2.8 Hz), 126.0, 124.3 (d, J = 3.6 Hz), 116.2, 115.9, 33.5, 33.3, 28.2, 22.6, 13.9. IR (KBr): 2964, 2593, 2313, 1709, 1640, 1512, 1151, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{36}FO_2$ $[M+H]^+$ 411.2694, found 411.2700.



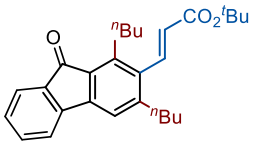
***tert*-Butyl (*E*)-3-(3,5-dibutyl-2'-nitro-[1,1'-biphenyl]-4-yl) acrylate (4ah)**

White solid (45.5 mg, 52% yield). PE:EA = 20:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 16.3 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.01 (s, 2H), 5.98 (d, *J* = 16.3 Hz, 1H), 2.68 – 2.60 (t, *J* = 8.0 Hz, 4H), 1.55 (s, 9H), 1.55 – 1.49 (m, 4H), 1.40 – 1.33 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 149.3, 141.8, 141.5, 136.7, 136.1, 134.0, 132.1, 131.8, 128.0, 126.3, 124.0, 80.6, 33.4, 33.1, 28.2, 22.5, 13.9. IR (KBr): 2959, 2556, 2313, 1902, 1709, 1526, 1152, 753 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{36}NO_4$ $[M+H]^+$ 438.2639, found 438.2635.



***tert*-Butyl (*E*)-3-(4-(4-bromophenoxy)-2,6-dibutylphenyl) acrylate (4ai)**

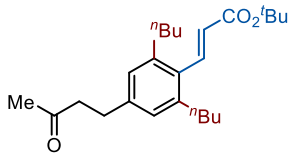
White solid (76.8 mg, 79% yield). PE:EA = 40:1, R_f = 0.45, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7. 72 (d, *J* = 16.3 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.69 (s, 2H), 5.92 (d, *J* = 16.3 Hz, 1H), 2.59 (t, *J* = 8.6 Hz, 4H), 1.54 (s, 9H), 1.53 – 1.46 (m, 4H), 1.38 – 1.31 (m, 4H), 0. 90 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 156.3, 156.1, 143.5, 141.7, 132.6, 12 9.3, 125.8, 120.4, 117.1, 115.6, 80.5, 33.5, 33.1, 28.2, 22.5, 13.8. IR (KBr): 2922, 2563, 2313, 170 9, 1474 1282, 1152, 754cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{36}BrO_3$ $[M+H]^+$ 487.1842, found 48 7.1832.



***tert*-Butyl (*E*)-3-(1,3-dibutyl-9-oxo-9H-fluoren-2-yl) acrylate (4aj)**

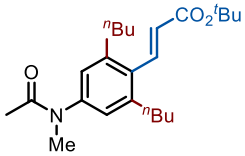
White solid (49.4 mg, 59% yield). PE:EA = 30:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.3 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.24 (s, 1H), 5.94 (d, *J* = 16.3 Hz, 1H), 3.05 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.55 (s, 9H), 1.53 – 1.45 (m, 4H), 1.45 – 1.34 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 194.3, 165.4, 148.2, 144.6, 143.5, 143.3, 141.3, 136.0, 134.9, 134.2, 129.0, 128.6, 126.9, 123.8, 119.9, 119.1, 80.8, 34.3, 32.9, 32.6, 28.2, 27.9, 22.9, 22.6, 13.9, 13.8. IR (KBr): 2953, 2638, 2380, 2313, 1706, 1639, 1517, 1161, 805 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{28}H_{35}O_3$ $[M+H]^+$ 419.2581, found 419.2574.



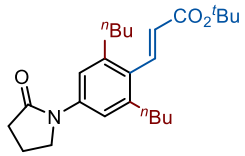
***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-(3-oxobutyl)phenyl) acrylate(4ak)**

Yellow solid (43.3 mg, 56% yield). PE:EA = 30:1, R_f = 0.35, ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 16.3 Hz, 1H), 6.94 (s, 2H), 5.95 (d, *J* = 16.3 Hz, 1H), 4.30 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 8.2 Hz, 4H), 2.09 (s, 3H), 1.58 (s, 9H), 1.57 – 1.50 (m, 4H), 1.43 – 1.3 6 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 165.9, 142.3, 141.3, 137. 3, 132.2, 127.5, 125.7, 80.4, 64.9, 34.8, 33.4, 33.3, 28.2, 22.6, 21.0, 13.9. IR (KBr): 2981, 2546, 23 13, 1742, 1634, 1518, 1021, 786 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{25}H_{39}O_3$ $[M+H]^+$ 387.2894, fo und 387.2892.



***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-(*N*-methylacetamido)phenyl) acrylate(4al)**

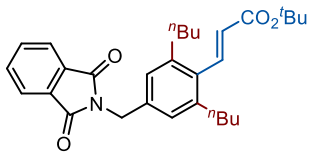
White solid (51.9 mg, 67% yield). PE:EA = 20:1, R_f = 0.3, ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.3 Hz, 1H), 6.85 (s, 2H), 5.92 (d, *J* = 16.3 Hz, 1H), 3.23 (s, 3H), 2.59 (t, *J* = 7.9 Hz,4H), 1.87 (s, 3H), 1.52 (s, 9H), 1.51 – 1.46 (m, 4H), 1.37 – 1.30 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 165.5, 143.9, 142.8, 141.3, 133.4, 126.6, 125.0, 37.0, 33.3, 33.0, 28.1, 22.4, 13.8. IR (KBr): 2896, 2745, 2553, 2013, 1752, 1638, 1329, 1052, 784 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{24}H_{38}NO_3$ $[M+H]^+$ 388.2846, found 388.2853.



***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-(2-oxopyrrolidin-1-yl)phenyl) acrylate(4am)**

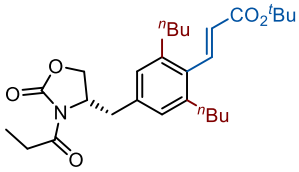
Yellow solid (66.3 mg, 83% yield). PE:EA = 20:1, R_f = 0.3, ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.3 Hz, 1H), 7.31 (s, 2H), 5.90 (d, *J* = 16.3 Hz, 1H), 3.85 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 7.1 Hz 4H),

2.59 (t, J = 8.2 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.53 (s, 9H), 1.53 – 1.47 (m, 4H), 1.39 – 1.32 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 166.0, 142.2, 142.0, 139.0, 130.1, 125.7, 118.5, 80.5, 48.8, 33.8, 33.4, 32.9, 28.3, 22.6, 18.1, 13.9. IR (KBr): 2857, 2579, 2312, 1963, 1704, 1467 1151, 752 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{25}H_{38}NO_3$ $[M+H]^+$ 400.2846, found 400.2843.



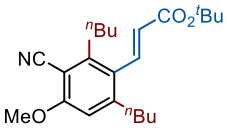
***tert*-Butyl (*E*)-3-(2,6-dibutyl-4-((1,3-dioxoisoindolin-2-yl)methyl) phenyl)acrylate (4an)**

White solid (78.0 mg, 82% yield). PE:EA = 30:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 3.1 Hz, 1H), 7.85 (d, J = 3.1 Hz, 1H), 7.72 (t, J = 2.9 Hz, 2H), 7.69 (d, J = 4.6 Hz, 1H), 7.12 (s, 2H), 5.88 (d, J = 16.3 Hz, 1H), 4.78 (s, 2H), 2.57 (t, J = 3.2 Hz, 4H), 1.53 (s, 9H), 1.52 – 1.45 (m, 4H), 1.37 – 1.30 (m, 4H), 0.90 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.02, 165.75, 142.13, 141.61, 135.83, 133.93, 133.52, 132.16, 127.19, 126.01, 123.32, 80.47, 41.43, 33.41, 33.20, 28.18, 22.56, 13.80. IR (KBr): 2982, 2675, 2432, 2313, 1705, 1640, 1517, 756 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{30}H_{38}NO_4$ $[M+H]^+$ 476.2795, found 476.2799.



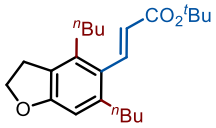
***tert*-Butyl (S, E)-3-(2,6-dibutyl-4-((2-oxo-3-propionyloxazolidin-4-yl)methyl)phenyl)acrylate (4ao)**

White solid (66.9 mg, 70% yield). PE:EA = 20:1, R_f = 0.2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 16.3 Hz, 1H), 6.89 (s, 2H), 5.90 (d, J = 16.4 Hz, 1H), 4.65 (t, J = 8.5 Hz, 1H), 4.24 – 4.14 (m, 2H), 3.24 (d, J = 10.1 Hz, 1H), 2.96 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 8.0 Hz,1H), 2.58 (t, J = 7.2 Hz, 4H), 1.52 – 1.44 (m, 4H), 1.37 – 1.31 (m, 4H), 1.21 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 165.7, 153.5, 141.9, 141.9, 134.8, 133.0, 128.0, 126.1, 80.6, 66.3, 55.2, 37.6, 33.4, 33.3, 29.2, 28.2, 22.6, 13.9, 8.3. IR (KBr): 2947, 2312, 2138, 1785, 1633, 1426, 1025, 751 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{28}H_{41}NO_5Na$ $[M+Na]^+$ 494.3057, found 494.3046.



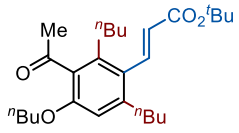
***tert*-Butyl (*E*)-3-(2,6-dibutyl-3-cyano-4-methoxyphenyl) acrylate (4ap)**

White solid (62.4 mg, 84% yield). PE:EA = 20:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 16.3 Hz, 1H), 6.65 (s, 1H), 5.88 (d, *J* = 16.3 Hz, 1H), 3.90 (s, 3H), 2.82 – 2.75 (m, 2H), 2.65 – 2.59 (m, 2H), 1.52 (s, 9H), 1.49 (dd, *J* = 8.8, 6.6 Hz, 4H), 1.43 – 1.33 (m, 4H), 0.92 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 160.9, 148.2, 146.9, 140.3, 127.2, 126.9, 115.8, 109.5, 100.3, 80.8, 55.9, 34.3, 32.9, 32.5, 32.2, 28.1, 22.6, 22.5, 13.8, 13.6. IR (KBr): 2988, 2865, 2313, 1956, 1706, 1517, 1203, 756 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{23}H_{34}NO_3$ $[M+H]^+$ 372.2533, found 372.2530.



***tert*-Butyl (*E*)-3-(5,7-dibutyl-2,3-dihydrobenzofuran-6-yl) acrylate (4aq)**

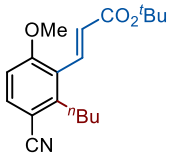
White oil (33.7 mg, 47% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.3 Hz, 1H), 6.54 (s, 1H), 5.88 (d, *J* = 16.3 Hz, 1H), 4.57 (t, *J* = 8.6 Hz, 2H), 3.14 (t, *J* = 8.6 Hz, 2H), 2.62 – 2.53 (m, 4H), 1.53 (s, 9H), 1.52 – 1.43 (m, 4H), 1.40 – 1.32 (m, 4H), 0.92 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 159.7, 142.5, 142.5, 138.4, 125.8, 124.4, 123.8, 108.0, 80.2, 71.2, 33.9, 33.4, 31.8, 31.1, 28.7, 28.2, 22.8, 22.5, 13.9, 13.8. IR (KBr): 2964, 2743, 2313, 1962, 1740, 1516, 1149, 795 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{23}H_{35}O_3$ $[M+H]^+$ 359.2581, found 359.2574.



***tert*-Butyl (*E*)-3-(3-acetyl-4-butoxy-2,6-dibutylphenyl) acrylate (4ar)**

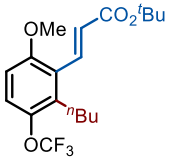
White solid (55.9 mg, 65% yield). PE:EA = 20:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.2 Hz, 1H), 6.60 (s, 1H), 5.87 (d, *J* = 16.3 Hz, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* =6.2 Hz, 2H), 2.49 (s, 3H), 2.45 (t, *J* = 8.3 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.52 (s, 9H), 1.50 – 1.42 (m, 4H), 1.36 – 1.29 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 165.8, 155.0, 143.4, 141.9, 138.7, 129.7, 127.0, 125.9, 110.2,

80.4, 67.9, 33.9, 33.3, 33.3, 32.6, 31.2, 30.3, 28.2, 22.8, 22.5, 19.3, 13.8, 13.8, 13.6. IR (KBr): 2955, 2789, 2313, 2108, 1706, 1518, 1147, 751 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{27}H_{43}O_4$ $[M+H]^+$ 431.3156, found 431.3150.



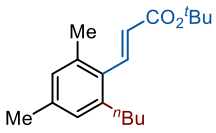
***tert*-Butyl (*E*)-3-(2-butyl-3-cyano-6-methoxyphenyl) acrylate (4aa')**

White solid (50.4 mg, 80% yield). PE:EA = 20:1, R_f = 0.2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 16.1 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 3.91 (s, 3H), 2.94 (t, *J* = 8.6 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.53 (s, 9H), 1.50 – 1.41 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 161.7, 148.1, 135.4, 134.6, 126.6, 123.4, 118.5, 109.2, 105.6, 80.6, 55.9, 32.9, 32.0, 28.2, 22.6, 13.7. IR (KBr): 2954, 2744, 2452, 2313, 1762, 1640, 1516, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{26}NO_3$ $[M+H]^+$ 316.1907, found 316.1913.



***tert*-Butyl (*E*)-3-(2-butyl-6-methoxy-3-(trifluoromethoxy)phenyl) acrylate (4ab')**

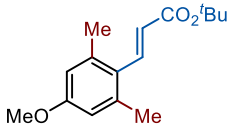
White solid (41.1 mg, 55% yield). PE:EA = 30:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.1 Hz, 1H), 7.17 (d, *J* = 10.9 Hz, 1H), 6.76 (d, *J* = 9.1 Hz, 1H), 6.60 (d, *J* = 16.1 Hz, 1H), 3.86 (s, 3H), 2.77 (t, *J* = 10.9 Hz, 2H), 1.54 (s, 9H), 1.52 – 1.47 (m, 2H), 1.45 – 1.39 (m, 2H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 157.1, 141.4, 137.1, 136.4, 125.9, 123.5, 124.5 (q, *J* = 5.1 Hz), 121.7, 108.8, 80.3, 55.7, 32.3, 28.2, 26.5, 22.7, 13.7. IR (KBr): 2981, 2765, 2382, 2213, 1780, 1672, 1406, 765 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{26}F_3O_4$ $[M+H]^+$ 375.1778, found 375.1772.



***tert*-Butyl (*E*)-3-(2-butyl-4,6-dimethylphenyl) acrylate (4ac')**

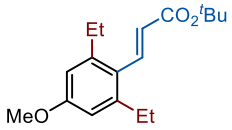
White solid (38.6 mg, 67% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.3 Hz, 1H), 6.88 (s, 2H), 5.95 (d, *J* = 16.5 Hz, 1H), 2.61 (t, *J* = 8.3 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 1.54 (s, 9H), 1.53 – 1.48 (m, 2H), 1.40 – 1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 166.3, 142.2, 141.7, 137.8, 136.4, 130.8, 129.1, 127.9, 125.1, 80.4, 33.5, 33.4, 28.2, 22.6, 21.3, 21.1, 13.9. IR (KBr): 2924, 2738, 2430, 2313, 1709, 1517, 1306, 1151 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{29}O_2$ $[M+H]^+$ 289.2162, found 289.2157.



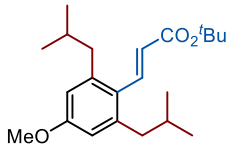
***tert*-Butyl (*E*)-3-(4-methoxy-2,6-dimethylphenyl) acrylate (4ba)**

White solid (28.9 mg, 55% yield). PE:EA = 40:1, R_f = 0.5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.3 Hz, 1H), 6.61 (s, 2H), 5.96 (d, *J* = 16.3 Hz, 1H), 3.79 (s, 3H), 2.36 (s, 6H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.1, 141.5, 139.0, 126.4, 123.8, 113.7, 80.3, 55.1, 28.2, 21.7. IR (KBr): 2974, 2769, 2313, 1706, 1517, 1285, 1146, 735 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{23}O_3$ $[M+H]^+$ 263.1642, found 263.1639.



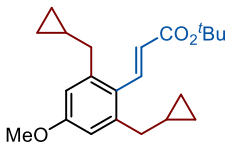
***tert*-Butyl (*E*)-3-(2,6-diethyl-4-methoxyphenyl) acrylate (4bb)**

White solid (37.8 mg, 65% yield). PE:EA = 40:1, R_f = 0.45, ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.2 Hz, 1H), 6.65 (s, 2H), 5.92 (d, *J* = 16.3 Hz, 1H), 3.81 (s, 3H), 2.67 (q, *J* = 7.5 Hz, 4H), 1.54 (s, 9H), 1.20 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 159.7, 144.8, 142.1, 126.1, 124.9, 112.0, 80.6, 55.3, 28.5, 27.4, 15.5. IR (KBr): 2894, 2543, 2213, 1721, 1506, 1205, 1046, 765 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{27}O_3$ $[M+H]^+$ 291.1955, found 291.1947.



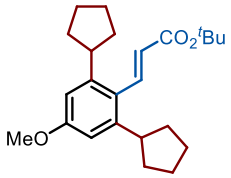
***tert*-Butyl (*E*)-3-(2,6-diisobutyl-4-methoxyphenyl) acrylate (4bc)**

White solid (49.8 mg, 72% yield). PE:EA = 40:1, R_f = 0.5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.3 Hz, 1H), 6.58 (s, 2H), 5.86 (d, *J* = 16.3 Hz, 1H), 3.79 (s, 3H), 2.50 (d, *J* = 7.1 Hz, 4H), 1.81 (dq, *J* = 13.5, 6.7 Hz, 2H), 1.54 (s, 9H), 0.89 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 158.5, 142.8, 141.9, 127.1, 124.9, 113.4, 80.2, 55.0, 43.2, 29.7, 28.2, 22.4. IR (KBr): 2962, 2741, 2448, 2313, 1705, 1516, 1146, 792 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{35}O_3$ $[M+H]^+$ 347.2581, found 347.2575.



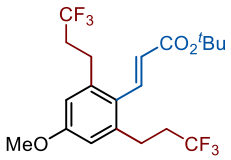
***tert*-Butyl (*E*)-3-(2,6-bis(cyclopropylmethyl)-4-methoxyphenyl) acrylate (4bd)**

White oil (42.5 mg, 62% yield). PE:EA = 40:1, R_f = 0.55, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.2 Hz, 1H), 6.88 (s, 2H), 5.91 (d, *J* = 16.3 Hz, 1H), 3.83 (s, 3H), 2.58 (d, *J* = 6.6 Hz, 4H), 1.54 (s, 9H), 1.00 – 0.92 (m, 2H), 0.55 (q, *J* = 4.8 Hz, 4H), 0.21 (q, *J* = 4.9 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 159.2, 142.4, 142.2, 126.3, 125.0, 112.3, 80.4, 55.1, 38.3, 28.2, 11.1, 4.9. IR (KBr):. 2936, 2456, 2313, 1986, 1721, 1639, 1517, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{31}O_3$ $[M+H]^+$ 343.2268, found 343.2260.



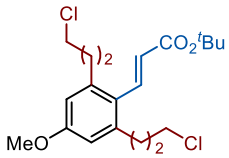
tert-Butyl (*E*)-3-(2,6-dicyclopentyl-4-methoxyphenyl) acrylate(4be)

White solid (42.5 mg, 62% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.1 Hz, 1H), 6.71 (s, 2H), 5.81 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H), 3.15 (p, *J* = 8.0 Hz, 2H), 1.99 (q, *J* = 8.8 Hz, 4H), 1.80 (q, *J* = 5.7 Hz, 4H), 1.69 – 1.62 (m, 4H), 1.61 – 1.55 (m, 4H), 1.55 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.5, 146.3, 143.5, 127.3, 125.7, 108.9, 80.5, 55.0, 42.4, 35.0, 28.3, 25.8. IR (KBr): 2978, 2737, 2313, 1713, 1517, 1325, 756 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{24}H_{35}O_3$ $[M+H]^+$ 371.2581, found 371.2578.



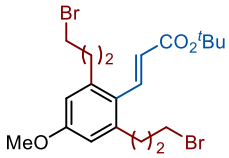
***tert*-Butyl (*E*)-3-(4-methoxy-2,6-bis(3,3,3-trifluoropropyl) phenyl) acrylate (4bf)**

White solid (34.9 mg, 41% yield). PE:EA = 40:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.3 Hz, 1H), 6.66 (s, 2H), 5.92 (d, *J* = 16.3 Hz, 1H), 3.81 (s, 3H), 2.88 (t, *J* = 8.2 Hz, 4H), 2.37 – 2.23 (m, 4H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 159.6, 140.0, 139.4, 126.9, 126.5, 126.5 (q, *J* = 276.9 Hz), 113.4, 81.0, 55.2, 34.8 (q, *J* = 28.5 Hz), 28.1, 26.4 (q, *J* = 3.3 Hz). IR (KBr): 2983, 2313, 1705, 1637, 1248, 1141, 754 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{25}F_6O_3$ $[M+H]^+$ 427.1702, found 427.1711.



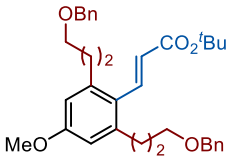
***tert*-Butyl (*E*)-3-(2,6-bis(2-chloroethyl)-4-methoxyphenyl) acrylate (4bg)**

White oil (50.3 mg, 74% yield). PE:EA = 40:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.2 Hz, 1H), 6.66 (s, 2H), 5.91 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 3.53 (t, *J* = 6.4 Hz, 4H), 2.79 (t, *J* = 7.6 Hz, 4H), 2.05 – 1.97 (m, 4H), 1.53 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 1 59.2, 141.2, 126.6, 125.8, 113.2, 80.6, 55.2, 44.3, 33.4, 31.1, 28.2. IR (KBr): 2971, 2742, 2434, 23 13, 1706, 1640, 1293, 1147 cm^{-1}.HRMS (ESI) m/z Calcd for $C_{18}H_{25}Cl_2O_3$ $[M+H]^+$ 359.1175, foun d 359.1179.



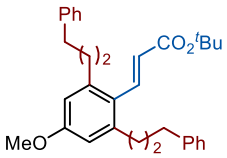
***tert*-Butyl (*E*)-3-(2,6-bis(2-bromoethyl)-4-methoxyphenyl) acrylate (4bh)**

White oil (61.5 mg, 69% yield). PE:EA = 40:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.2 Hz, 1H), 6.66 (s, 2H), 5.91 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 3.39 (t, *J* = 6.5 Hz, 4H), 2.79 (t, *J* = 6.3 Hz, 4H), 2.13 – 2.04 (m, 4H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 159.2, 141.2, 141.0, 126.6, 125.9, 113.2, 80.6, 55.2, 33.5, 33.1, 32.3, 28.2. IR (KBr): 2875, 2740, 2384, 2248, 1721, 1641, 1395, 1047, 762 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{25}Br_2O_3$ $[M+H]^+$ 447.0165, found 447.0168.



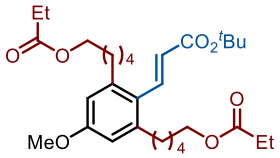
***tert*-Butyl (*E*)-3-(2,6-bis(2-(benzyloxy) ethyl)-4-methoxyphenyl) acrylate (4bi)**

White solid (52.2 mg, 52% yield). PE:EA = 40:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 18.3 Hz, 1H), 7.34 (s, 8H), 7.29 (t, *J* = 4.1 Hz, 2H), 6.65 (s, 2H), 5.94 (d, *J* = 16.3 Hz, 1H), 4.51 (s, 4H), 3.77 (s, 3H), 3.50 (t, *J* = 6.4 Hz, 4H), 2.75 (t, *J* = 10.0 Hz, 4H), 1.93 – 1.84 (m, 4H), 1.52 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.1, 142.4, 141.7, 138.5, 128.4, 127.6, 127.5, 126.4, 125.0, 112.8, 80.4, 72.8, 69.6, 55.1, 30.8, 30.6, 28.2. IR (KBr): 2935, 2760, 2448, 2254, 1760, 1541, 1325, 1027, 763 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{32}H_{39}O_5$ $[M+H]^+$ 503.2792, found 503.2785.



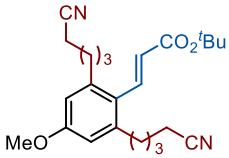
***tert*-Butyl (*E*)-3-(4-methoxy-2,6-diphenethylphenyl) acrylate (4bj)**

White solid (57.5 mg, 65% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.2 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 6H), 6.61 (s, 2H), 5.88 (d, *J* = 16.6 Hz, 1H), 3.78 (s, 3H), 2.67 (t, *J* = 10.2 Hz, 8H), 1.94 – 1.83 (m, 4H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 159.1, 142.7, 142.1, 141.9, 128.3, 128.3, 126.3, 125.7, 124.9, 112.6, 80.4, 55.1, 35.7, 32.6, 28.3. IR (KBr): 2920, 2735, 2308, 2154, 1754, 1305, 1127, 795 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{30}H_{35}O_3$ $[M+H]^+$ 443.2581, found 443.2588.



(*E*)-(2-(3-(tert-Butoxy)-3-oxoprop-1-en-1-yl)-5-methoxy-1,3-phenylene) bis(ethane-2,1-diyl) dipropionate (4bk)

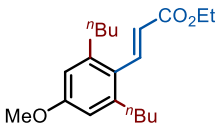
White solid (48.6 mg, 56% yield). PE:EA = 20:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.2 Hz, 1H), 6.59 (s, 2H), 5.86 (d, *J* = 16.3 Hz, 1H), 4.11 (q, *J* = 16.1 Hz, 4H), 3.78 (s, 3H), 2.60 (t, *J* = 7.9 Hz, 4H), 2.28 (t, *J* = 7.5 Hz, 4H), 1.68 – 1.61 (m, 4H), 1.61 – 1.54 (m, 4H), 1.53 (s, 9H), 1.41 – 1.32 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 166.1, 159.1, 142.8, 141.9, 126.1, 124.8, 112.5, 80.3, 60.1, 55.0, 34.2, 33.9, 30.6, 28.9, 28.2, 24.7, 14.2. IR (KBr): 2855, 2792, 2328, 2144, 1771, 1705, 1541, 1325, 1154, 1027 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{24}H_{35}O_7$ $[M+H]^+$ 435.2377, found 435.2373.



***tert*-Butyl (*E*)-3-(2,6-bis(2-cyanoethyl)-4-methoxyphenyl) acrylate (4bl)**

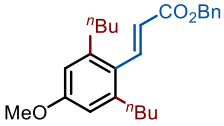
White solid (45.6 mg, 67% yield). PE:EA = 20:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.2 Hz, 1H), 6.61 (s, 2H), 5.87 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 3H), 2.66 (t, *J* = 7.0 Hz, 4H), 2.35 (t, *J* = 8.1 Hz,4H), 1.69 (t, *J* = 8.0 Hz, 8H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.2, 141.6, 141.4, 126.1, 125.5, 119.4, 112.7, 80.7, 55.1, 33.0, 29.7, 28.2, 25.0, 17.0. IR (KBr):

2722, 2658, 2554, 2102, 1698, 1586, 1225, 1147, 780 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{25}N_2O_3$ $[M+H]^+$ 341.1860, found 341.1856.



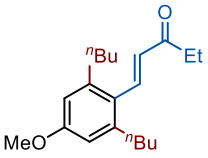
Ethyl (*E*)-3-(2,6-dibutyl-4-methoxyphenyl) acrylate (4ca)

White solid (47.7 mg, 75% yield). PE:EA = 40:1, R_f = 0.5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.3 Hz, 1H), 6.62 (s, 2H), 5.97 (d, *J* = 16.3 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.62 (t, *J* = 7.8 Hz, 4H), 1.58 – 1.50 (m, 4H), 1.41 – 1.35 (m, 4H), 1.34 (t, *J* = 8.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 159.3, 143.3, 126.1, 122.9, 112.5, 60.4, 55.1, 33.8, 33.3, 22.6, 14.3, 13.9. IR (KBr): 2940, 2866, 2674, 2313, 1716, 1518, 1145, 753cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{31}O_3$ $[M+H]^+$ 319.2268, found 319.2273.



Benzyl (*E*)-3-(2,6-dibutyl-4-methoxyphenyl) acrylate (4cb)

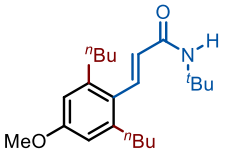
White solid (50.9 mg, 67% yield). PE:EA = 40:1, R_f = 0.5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 16.3 Hz, 1H), 7.46 – 7.31 (m, 5H), 6.62 (s, 2H), 6.04 (d, *J* = 16.1 Hz, 1H), 5.27 (s, 2H), 3.80 (s, 3H), 2.62 (t, *J* = 8.2 Hz, 4H), 1.58 – 1.51 (m, 4H), 1.39 – 1.32 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 159.3, 144.0, 143.4, 136.2, 128.5, 128.1, 128.1, 125.9, 122.4, 112.6, 66.2, 55.1, 33.9, 33.3, 22.6, 13.9. IR (KBr): 2987, 2845, 2613, 2305, 1706, 1565, 1045, 721 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{32}H_{39}O_5$ $[M+H]^+$ 503.2719, found 503.2712.



(*E*)-1-(2,6-Dibutyl-4-methoxyphenyl) pent-1-en-3-one (4cc)

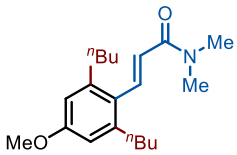
White solid (36.8 mg, 61% yield). PE:EA = 40:1, R_f = 0.5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.4 Hz, 1H), 6.62 (s, 2H), 6.28 (d, *J* = 16.5 Hz, 1H), 3.80 (s, 3H), 2.68 (q, *J* = 7.3 Hz, 2H), 2.64 – 2.58 (m, 4H), 1.57 – 1.49 (m, 4H), 1.39 – 1.33 (m, 4H), 1.18 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 159.3, 143.3, 141.0, 131.0, 126.2, 112.6, 55.1,

34.0, 33.9, 33.3, 22.6, 13.9, 8.3. IR (KBr): 2744, 2562, 2313,1802, 1601, 1462 1145, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{31}O_3$ $[M+H]^+$ 319.2268, found 319.22655.



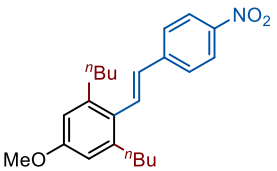
(*E*)-N-(tert-Butyl)-3-(2,6-dibutyl-4-methoxyphenyl) acrylamide (4cd)

White solid (37.9 mg, 55% yield). PE:EA = 20:1, R_f = 0.2, ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.8 Hz, 1H), 6.60 (s, 2H), 5.80 (d, *J* = 15.8 Hz, 1H), 5.32 (s, 1H), 3.79 (s, 3H), 2.60 (t, *J* = 15.2 Hz,4H), 1.56 – 1.48 (m, 4H), 1.44 (s, 9H), 1.38 – 1.32 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 158.8, 142.9, 138.8, 126.8, 112.2, 55.1, 51.4, 33.7, 33.2, 28.9, 22.6, 14.0. IR (KBr): 2960, 2740, 2434, 2313, 1644, 1516, 1102, 785 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{36}NO_2$ $[M+H]^+$ 346.2741, found 346.2750.



(*E*)-3-(2,6-Dibutyl-4-methoxyphenyl)-N,N-dimethylacrylamide (4ce)

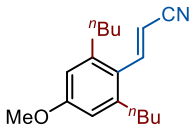
White solid (47.6 mg, 75% yield). PE:EA = 30:1, R_f = 0.3, ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.7 Hz, 1H), 6.62 (s, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 3.80 (s, 3H), 3.10 (s, 3H), 3.08 (s, 3H), 2.61 (t, *J* = 7.9 Hz, 4H), 1.58 – 1.50 (m, 4H), 1.39 – 1.32 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 158.8, 142.9, 140.9, 127.3, 122.4, 112.3, 55.1, 37.2, 35.8, 33.9, 33.4, 22.6, 14.0. IR (KBr): 2740, 2313, 1982, 1650, 1517, 1389, 1135, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{32}NO_2$ $[M+H]^+$ 318.2428, found 318.2436.



(*E*)-1,3-Dibutyl-5-methoxy-2-(4-nitrostyryl) benzene (4cf)

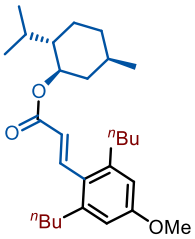
Yellow solid (50.7 mg, 69% yield). PE:EA = 20:1, R_f = 0.3, ^1H NMR (400 MHz, $CDCl_3$) δ 8. 23 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 16.5 Hz, 1H), 6.65 (s, 2H), 6.59 (d, *J* = 16.5 Hz, 1H), 3.82 (s, 3H), 2.65 (t, *J* = 14.8 Hz, 4H), 1.60 – 1.54 (m, 4H), 1.40 – 1.31 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 146.7, 144.2, 142.8, 131.7, 131.3, 1

27.9, 126.5, 124.2, 112.4, 55.1, 33.9, 33.3, 22.6, 14.0. IR (KBr): 2923, 2657, 2312, 1707, 1598, 13 63, 1145, 738 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{23}H_{30}NO_3$ $[M+H]^+$ 368.2220, found 368.2225.



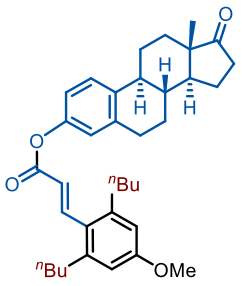
(*E*)-3-(2,6-Dibutyl-4-methoxyphenyl) acrylonitrile (4cg)

White solid (30.4 mg, 61% yield). PE:EA = 30:1, R_f = 0.4, ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 16.9 Hz, 1H), 7.38 (d, *J* = 11.3 Hz, 1H), 6.64 (s, 1H), 6.62 (s, 2H), 5.71 (d, *J* = 11.3 Hz, 1H), 5.46 (d, *J* = 17.0 Hz, 1H), 3.80 (s, 4H), 2.63 – 2.52 (m, 6H), 1.52 (p, *J* = 8.0, 7.4 Hz, 6H), 1.44 – 1.30 (m, 6H), 0.98 – 0.88 (m, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 159.9, 150.7, 149.8, 143.3, 142.0, 125.0, 118.2, 112.8, 112.2, 103.0, 101.0, 92.9, 55.3, 33.8, 33.6, 33.3, 32.9, 29.7, 22.6, 22.6, 13.9. IR (KBr): 2978, 2309, 1704, 1599, 1268, 1146, 754 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{26}NO$ $[M+H]^+$ 272.2009, found 272.2016.



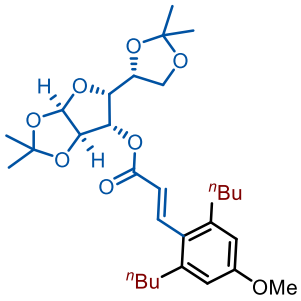
(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl (E)-3-(2,6-dibutyl-4-methoxyphenyl) acrylate(4ch)

White solid (61.2 mg, 72% yield). PE:EA = 40:1, R_f = 0.3, ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.3 Hz, 1H), 6.62 (s, 2H), 5.98 (d, *J* = 16.3 Hz, 1H), 4.83 (t, *J* = 8.7 Hz, 1H), 3.80 (s, 3H), 2.63 (t, *J* = 12.0 Hz, 4H), 2.11 (d, *J* = 12.3 Hz, 1H), 1.93 (t, *J* = 12.1 Hz, 1H), 1.71 (d, *J* = 13.2 Hz, 2H), 1.65 – 1.47 (m, 6H), 1.46 (d, *J* = 13.9 Hz, 1H), 1.42 – 1.34 (m, 4H), 1.23 – 0.99 (m, 3H), 0.93 (t, *J* = 8.0 Hz, 12H), 0.82 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 159.2, 143.2, 143.0, 126.1, 123.4, 112.5, 74.1, 55.0, 47.2, 41.0, 34.3, 33.9, 33.3, 31.4, 26.6, 23.8, 22.6, 22.0, 20.6, 16.6, 13.8. IR (KBr): 2998, 2739, 2546, 1705, 1554, 1269, 1046, 774 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{28}H_{45}O_3$ $[M+H]^+$ 429.3290, found 429.3276.



(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (E)-3-(2,6-dibutyl-4-methoxyphenyl) acrylate(4ci)

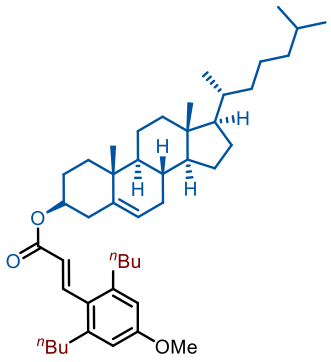
Yellow solid (67.3 mg, 62% yield). PE:EA = 20:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 16.3 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 1H), 6.65 (s, 2H), 6.18 (d, *J* = 16.2 Hz, 1H), 3.82 (s, 3H), 2.94 (t, *J* = 8.2 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 4H), 2.58 – 2.39 (m, 2H), 2.32 (t, *J* = 12.6 Hz, 1H), 2.21 – 1.97 (m, 4H), 1.65 – 1.59 (m, 4H), 1.58 – 1.47 (m, 6H), 1.43 – 1.37 (m, 4H), 0.95 (t, *J* = 8.4 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.77, 165.58, 159.53, 148.73, 145.21, 143.70, 137.95, 137.25, 126.36, 125.56, 121.65, 121.56, 118.84, 112.70, 55.10, 50.43, 47.94, 44.16, 38.01, 35.84, 33.93, 33.33, 31.54, 29.40, 26.35, 25.76, 22.59, 21.57, 13.92, 13.82.IR (KBr): 2898, 2762, 2446, 2108, 1705, 1657, 1534, 1169, 1004, 762 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{36}H_{47}O_4$ $[M+H]^+$ 543.3396, found 543.3382.



5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (E)-3-(2,6-dibutyl-4-methoxyphenyl)acrylate (4cj)

White solid (79.6 mg, 58% yield). PE:EA = 20:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 16.2 Hz, 1H), 6.62 (s, 2H), 5.98 (d, *J* = 16.3 Hz, 1H), 5.92 (d, *J* = 3.7 Hz, 1H), 5.41 (s, 1H), 4.60 (d, *J* = 3.7 Hz, 1H), 4.28 (t, *J* = 4.1 Hz, 2H), 4.07 (q, *J* = 4.9 Hz, 2H), 3.80 (s, 3H), 2.62 (t, 4H), 1.58 – 1.49 (m, 7H), 1.42 (s, 3H), 1.40 – 1.33 (m, 4H), 1.32 (s, 3H), 1.30 (s, 3H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 159.5, 144.7, 143.5, 125.4, 121.3, 112.7, 112.2, 109.2, 105.1, 83.4, 79.9, 76.0, 72.5, 67.0, 55.0, 33.9, 33.3, 26.7, 26.7, 26.2, 25.1, 22.5, 13.9. IR (KBr): 2978,

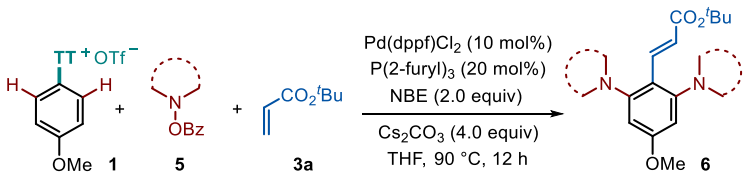
2662, 2346, 2025, 1725, 1637, 1524, 1069, 980, 736 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{30}H_{44}O_8$ $[M+H]^+$ 533.6740, found 533.6748.



(3R,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl (*E*)-3-(2,6-dibutyl-4-me thoxyphenyl) acrylate (4ck)

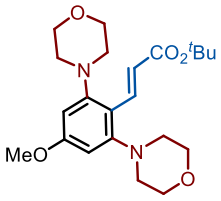
White solid (75.1 mg, 57% yield). PE:EA = 20:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.4 Hz, 1H), 6.62 (s, 2H), 5.96 (d, *J* = 16.2 Hz, 1H), 5.42 (s, 1H), 4.83 – 4.69 (m, 1H), 3.80 (s, 3H), 2.63 (t, *J* = 7.9 Hz, 4H), 2.41 (t, *J* = 7.8 Hz, 2H), 2.07 – 1.83 (m, 5H), 1.68 (t, *J* = 8.1 Hz, 2H), 1.59 – 1.49 (m, 8H), 1.41 – 1.32 (m, 7H), 1.26 – 1.08 (m, 8H), 1.06 (s, 3H), 1.04 – 0.96 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 9H), 0.87 (d, *J* = 4.8 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 159.2, 143.3, 143.1, 139.7, 126.0, 123.2, 122.6, 112.5, 74.0, 56.7, 56.1, 55.0, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 33.8, 33.3, 31.9, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 22.5, 21.0, 19.3, 18.7, 13.9, 11.8. IR (KBr): 2925, 2761, 2658, 1713, 1463, 1273, 1155, 775 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{45}H_{71}O_3$ $[M+H]^+$ 659.5398, found 659.5384.

D. Substrate Scope of Electrophilic Amination



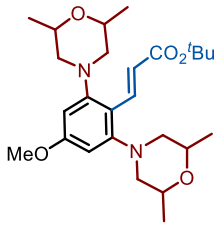
A 15.0 mL vial equipped with a stir bar was charged with $Pd(dppf)Cl_2$ (14.6 mg, 10.0 mol%), $P(2\text{-furyl})_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1** (0.2 mmol), **5** (0.6 mmol), **3a** (0.24 mmol) and THF (2.0 mL) was then added under argon atmos phere. The reaction mixture was stirred at 90 °C for 12 h in an oil bath. After cooling to room temp

erature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrate d under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **6**.



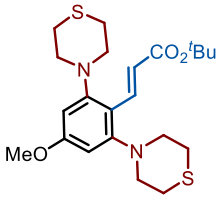
***tert*-Butyl (*E*)-3-(4-methoxy-2,6-dimorpholinophenyl)acrylate (6a)**

White oil (58.2 mg, 72% yield). PE:EA = 10:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.4 Hz, 1H), 6.94 (d, *J* = 16.4 Hz, 1H), 6.37 (s, 2H), 3.86 (t, *J* = 8.0 Hz, 8H), 3.82 (s, 3H), 2.93 (t, *J* = 8.1 Hz, 8H), 1.53 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 161.7, 155.7, 138.3, 119.7, 114.9, 100.4, 79.7, 67.0, 55.2, 52.9, 28.3. IR (KBr): 2927, 2428, 2313, 1707, 1600, 1461, 1145, 745 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{33}N_2O_5$ $[M+H]^+$ 405.2384, found 405.2380.



***tert*-Butyl (*E*)-3-(2,6-bis(2,6-dimethylmorpholino)-4-methoxyphenyl)acrylate (6b)**

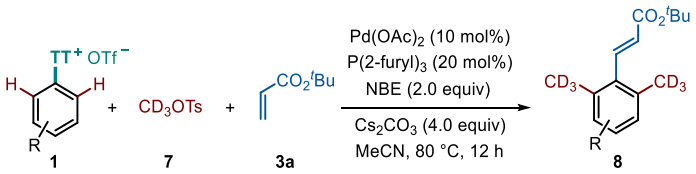
White solid (69.0 mg, 75% yield). PE:EA = 10:1, R_f = 0.35, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.4 Hz, 1H), 6.86 (d, *J* = 16.3 Hz, 1H), 6.32 (s, 2H), 3.90 (d, *J* = 16.4 Hz,4H), 3.81 (s, 3H), 2.99 (d, *J* = 11.4 Hz, 4H), 2.40 (t, *J* = 10.8 Hz, 4H), 1.52 (s, 9H), 1.19 (d, *J* = 6.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 161.7, 155.4, 138.5, 119.5, 100.3, 79.6, 71.8, 59.1, 55.7, 28.3, 19.6. IR (KBr): 2928, 2897, 2223, 1707, 1548, 1261 1045, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{26}H_{41}N_2O_5$ $[M+H]^+$ 461.3010, found 461.3005.



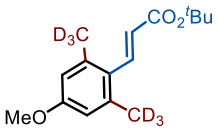
***tert*-Butyl (*E*)-3-(4-methoxy-2,6-dithiomorpholinophenyl)acrylate (6c)**

White solid (56.2 mg, 61% yield). PE:EA = 10:1, R_f = 0.3, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.4 Hz, 1H), 6.88 (d, *J* = 16.4 Hz, 1H), 6.38 (s, 2H), 3.81 (s, 3H), 3.15 (t, *J* = 16.4 Hz, 8H), 2.80 (t, *J* = 8.1 Hz, 8H), 1.55 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 161.4, 156.5, 138.3, 120.6, 116.1, 101.7, 79.8, 55.2, 55.1, 28.4, 28.1. IR (KBr): 2928, 2827, 2123, 1715, 1584, 1321, 1125, 768 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{33}N_2O_3S_2$ $[M+H]^+$ 437.1927, found 437.1924.

E. Substrate Scope of Electrophilic Deuterated-Methylation

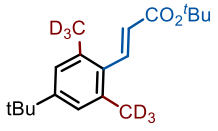


A 15.0 mL vial equipped with a stir bar was charged with $Pd(OAc)_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1** (0.2 mmol), **7** (0.6 mmol), **3a** (0.24 mmol) and MeCN (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 80 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **8**.



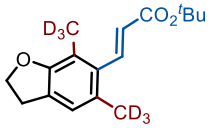
***tert*-Butyl (*E*)-3-(4-methoxy-2,6-bis(methyl-d3)phenyl)acrylate (8a)**

White solid (38.6 mg, 72% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.2 Hz, 1H), 6.61 (s, 2H), 5.96 (d, *J* = 16.3 Hz, 1H), 3.79 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.1, 141.5, 138.9, 123.8, 113.8, 80.3, 55.1, 28.2. IR (KBr): 2875, 2722, 2413, 1702, 1507, 1245, 1126, 765 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{16}D_6O_3$ $[M+H]^+$ 268.1940, found 268.1946.



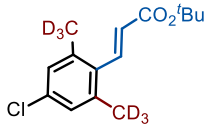
***tert*-Butyl (*E*)-3-(4-(tert-butyl)-2,6-bis(methyl-d3)phenyl)acrylate (8b)**

White solid (39.4 mg, 67% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 16.3 Hz, 1H), 7.08 (s, 2H), 5.99 (d, *J* = 16.4 Hz, 1H), 1.54 (s, 9H), 1.31 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 151.2, 142.0, 136.4, 125.3, 124.9, 80.4, 34.4, 31.2, 28.2. IR (KBr): 2864, 2645, 2503, 1745, 1467, 1245, 1095, 735 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{22}D_6O_2$ $[M+H]^+$ 294.2460, found 294.2454.



***tert*-Butyl (*E*)-3-(5,7-bis(methyl-d3)-2,3-dihydrobenzofuran-6-yl)acrylate (8c)**

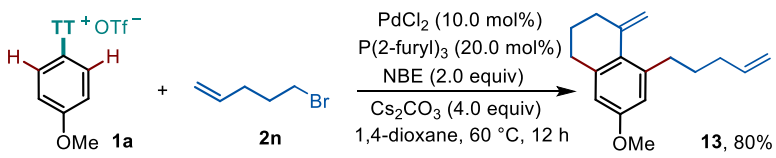
White solid (35.3 mg, 63% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.3 Hz, 1H), 6.53 (s, 1H), 5.92 (d, *J* = 16.3 Hz, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.12 (t, *J* = 8.7 Hz, 2H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.6, 141.9, 138.0, 133.7, 126.2, 124.6, 123.5, 109.1, 80.2, 71.3, 29.0, 28.2. IR (KBr): 2785, 2765, 2543, 1705, 1325, 1198, 1022, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{17}D_6O_3$ $[M+H]^+$ 281.2018, found 282.2013.



***tert*-Butyl (*E*)-3-(4-chloro-2,6-bis(methyl-d3)phenyl)acrylate (8d)**

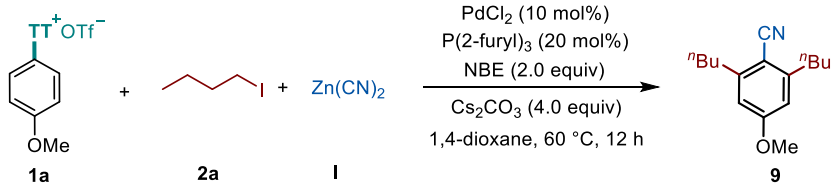
White solid (29.9 mg, 55% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.3 Hz, 1H), 7.05 (s, 2H), 5.96 (d, *J* = 16.4 Hz, 1H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 140.9, 138.4, 133.4, 132.6, 128.0, 126.1, 80.7, 28.2. IR (KBr): 2964, 2706, 2535, 1705, 1432, 1245, 735 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{13}D_6ClO_2$ $[M+H]^+$ 272.1445, found 272.1440.

F. Behavior of Two-Component Catellani Reaction

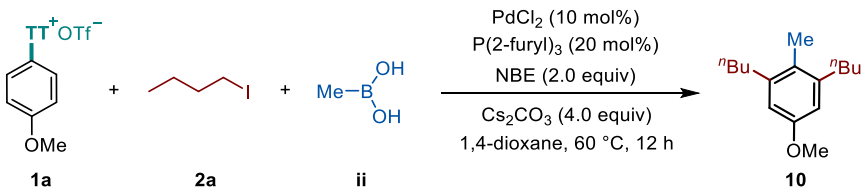


A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2n** (88.8 mg, 0.6 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **13**. White solid (38.7 mg, 80% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.53 (s, 1H), 5.91 – 5.81 (m, 1H), 5.15 (s, 1H), 5.06 – 4.95 (m, 3H), 3.79 (s, 3H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.44 (t, *J* = 8.0 Hz, 2H), 2.12 (t, *J* = 6.4 Hz, 2H), 1.84 (t, *J* = 12.0 Hz, 2H), 1.71 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 143.2, 141.3, 140.9, 138.7, 130.0, 114.7, 113.4, 112.2, 110.6, 55.2, 33.8, 33.6, 32.9, 31.0, 30.5, 23.3. IR (KBr): 2964, 2706, 2535, 1432, 1245, 1152, 956, 735 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{23}O$ $[M+H]^+$ 243.1671, found 243.1678.

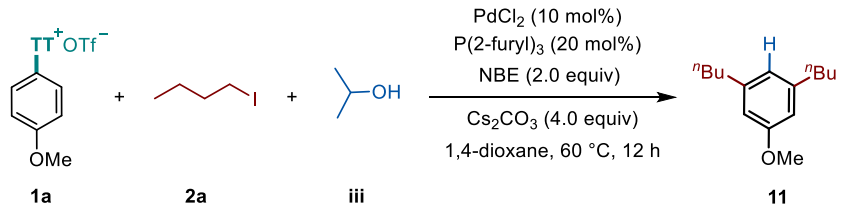
G. Substrate Scope of Terminating Reagents



A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2a** (110.0 mg, 0.6 mmol), $Zn(CN)_2$ (27.8 mg, 0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **9**. White oil (29.9 mg, 61% yield). PE:EA = 20:1, R_f = 0.6, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 2H), 3.83 (s, 3H), 2.78 (t, *J* = 7.9 Hz, 4H), 1.64 (p, *J* = 7.6 Hz, 4H), 1.40 (h, *J* = 7.5 Hz, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 149.3, 117.7, 112.3, 104.3, 55.3, 34.8, 32.9, 22.4, 13.8. IR (KBr): 2978, 2657, 2475, 1436, 1268, 754 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{24}NO$ $[M+H]^+$ 246.1852, found 246.1847.

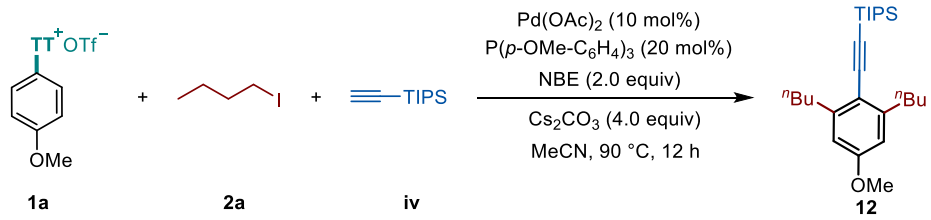


A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2a** (110.0 mg, 0.6 mmol), $MeB(OH)_2$ (14.4 mg, 0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **10**. White solid (30.0 mg, 64% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 2H), 3.81 (s, 3H), 2.62 (t, J = 7.3 Hz, 4H), 2.20 (s, 3H), 1.64 – 1.55 (m, 4H), 1.49 – 1.41 (m, 4H), 0.99 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 142.5, 125.7, 112.2, 55.0, 34.2, 32.7, 22.8, 14.0, 13.7. IR (KBr): 2950, 2602, 2398, 1426, 1211, 745 cm^{-1}.HRMS (ESI) m/z Calcd for $C_{16}H_{27}O$ $[M+H]^+$ 235.2056, found 235.2061.



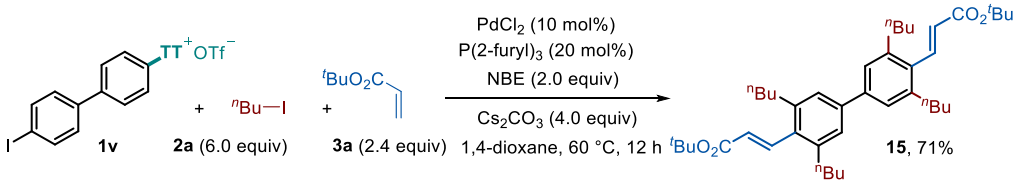
A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2a** (110.0 mg, 0.6 mmol), ^{i}PrOH (14.4 mg, 0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **11**. White solid (29.5 mg, 67% yield). PE:EA = 40:1, R_f = 0.5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 2H), 5.30 (s, 1H), 3.83 (s, 3H), 2.79 (t, J = 7.4 Hz, 4H), 1.68 – 1.60 (m, 4H), 1.43 – 1.37 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 162.3, 149.3, 117.7, 112.3, 104.3, 55.3, 34.8, 32.9, 22.4, 13.9. IR (KBr): 2895, 2655, 2435, 1428, 1255, 776 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{25}O$ $[M+H]^+$ 221.1900, found 221.1907.



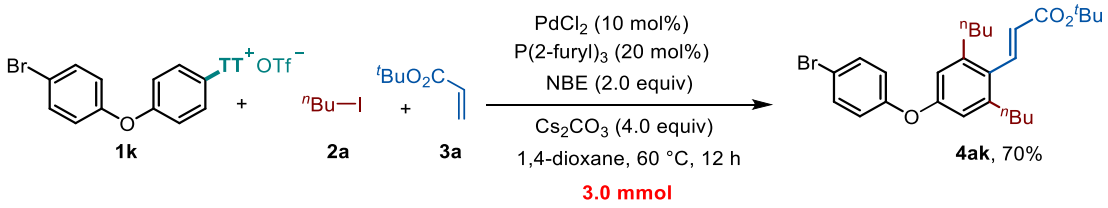
A 15.0 mL vial equipped with a stir bar was charged with $Pd(OAc)_2$ (3.6 mg, 10.0 mol%), P(p-OMe-$C_6H_4)_3$ (7.1 mg, 20.0 mol%), norbornene (72.0 mg, 4.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2a** (220.0 mg, 1.2 mmol), **iv** (43.6 mg, 0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **12**. White solid (44.0 mg, 55% yield). PE:EA = 40:1, R_f = 0.5, ^1H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 3.79 (s, 3H), 2.79 (t, J = 7.4 Hz, 4H), 1.67 – 1.58 (m, 4H), 1.44 – 1.36 (m, 4H), 1.14 (s, 21H), 0.92 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.6, 114.8, 111.6, 104.2, 96.0, 55.1, 35.4, 33.0, 29.7, 22.8, 18.7, 14.0, 11.4. IR (KBr): 2951, 2527, 2355, 1386, 1258, 1120, 765 cm^{-1}.HRMS (ESI) m/z Calcd for $C_{26}H_{45}OSi$ $[M+H]^+$ 401.3234, found 401.3230.

H. Reactivity of Aryl-TTs and Recovery Study

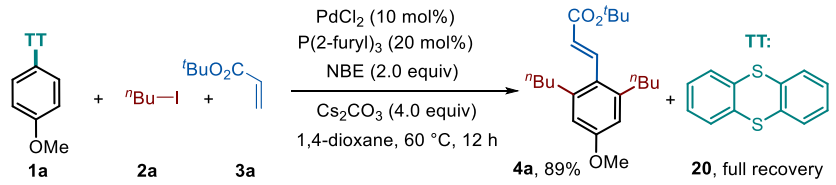


A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (72.0 mg, 4.0 equiv), Cs_2CO_3 (260.0 mg, 8.0 equiv), **1v** (86.8 mg, 0.2 mmol), **2a** (220.0 mg, 1.2 mmol), **3a** (61.6 mg, 0.48 mmol) and 1,4-dioxane (2.0 mL was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed

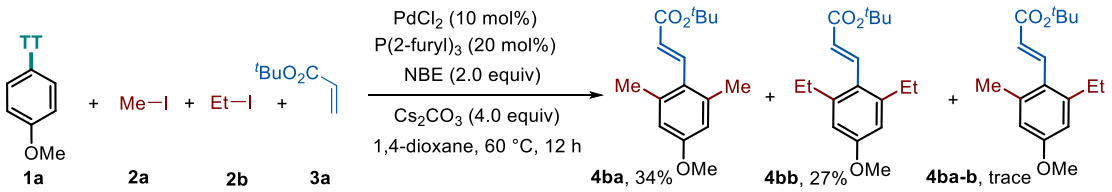
on silica gel to afford the desired product **15**. White solid (89.5 mg, 71% yield). PE:EA = 40:1, R_f = 0.4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.3 Hz, 2H), 5.97 (d, *J* = 16.3 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 8H), 1.62 – 1.56 (m, 8H), 1.55 (s, 18H), 1.42 – 1.36 (m, 8H), 0.93 (t, *J* = 7.4 Hz, 12H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 142.2, 141.7, 140.4, 133.0, 125.8, 125.7, 80.5, 33.7, 33.4, 28.2, 22.6, 13.9. IR (KBr): 2933, 2645, 1986, 1706, 1524, 1121, 734 cm^{-1}.HRMS (ESI) m/z Calcd for $C_{34}H_{47}O_4$ $[M+H]^+$ 518.3396, found 518.3389.



A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (53.1 mg, 10.0 mol%), P(2-furyl)$_3$ (139.2 mg, 20.0 mol%), norbornene (564.0 mg, 2.0 equiv), Cs_2CO_3 (3.9 g, 4.0 equiv), **1k** (1.2 g, 3.0 mmol), **2a** (1.6 g, 9.0 mmol), **3a** (460.8 mg, 3.6 mmol) and 1,4-dioxane (10.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **4ak** (1.02 g, 70%).



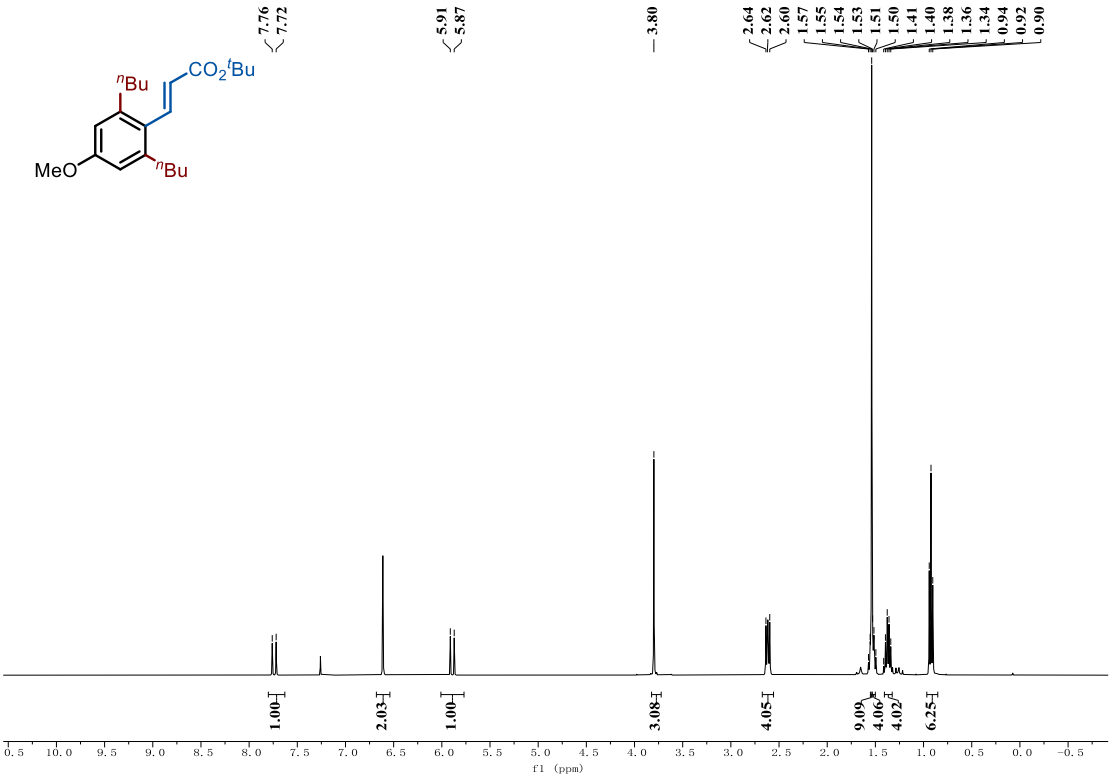
A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2** (110.0 mg, 0.6 mmol), **3a** (30.8 mg, 0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **4a** (61.63 mg, 89%) and compound **20** (41.5 mg, 96%).



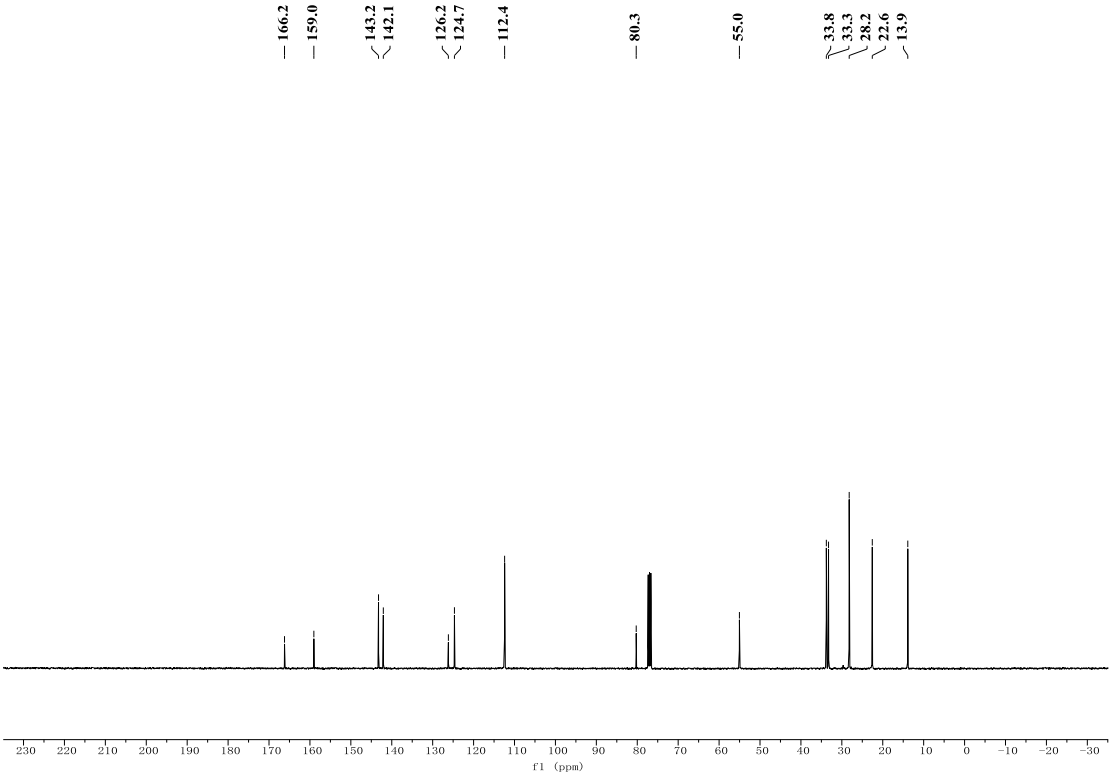
A 15.0 mL vial equipped with a stir bar was charged with $PdCl_2$ (3.6 mg, 10.0 mol%), P(2-furyl)$_3$ (9.3 mg, 20.0 mol%), norbornene (36.0 mg, 2.0 equiv), Cs_2CO_3 (260.0 mg, 4.0 equiv), **1a** (95.0 mg, 0.2 mmol), **2a** (34.5 mg, 0.3 mmol), **2b** (46.8 mg, 0.3 mmol), **3a** (30.8 mg, 0.24 mmol) and 1,4-dioxane (2.0 mL) was then added under argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h in an oil bath. After cooling to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **4ba** (17.9 mg, 34%), **4bb** (15.7 mg, 27%), **4ba-b** (trace).

I. NMR spectra

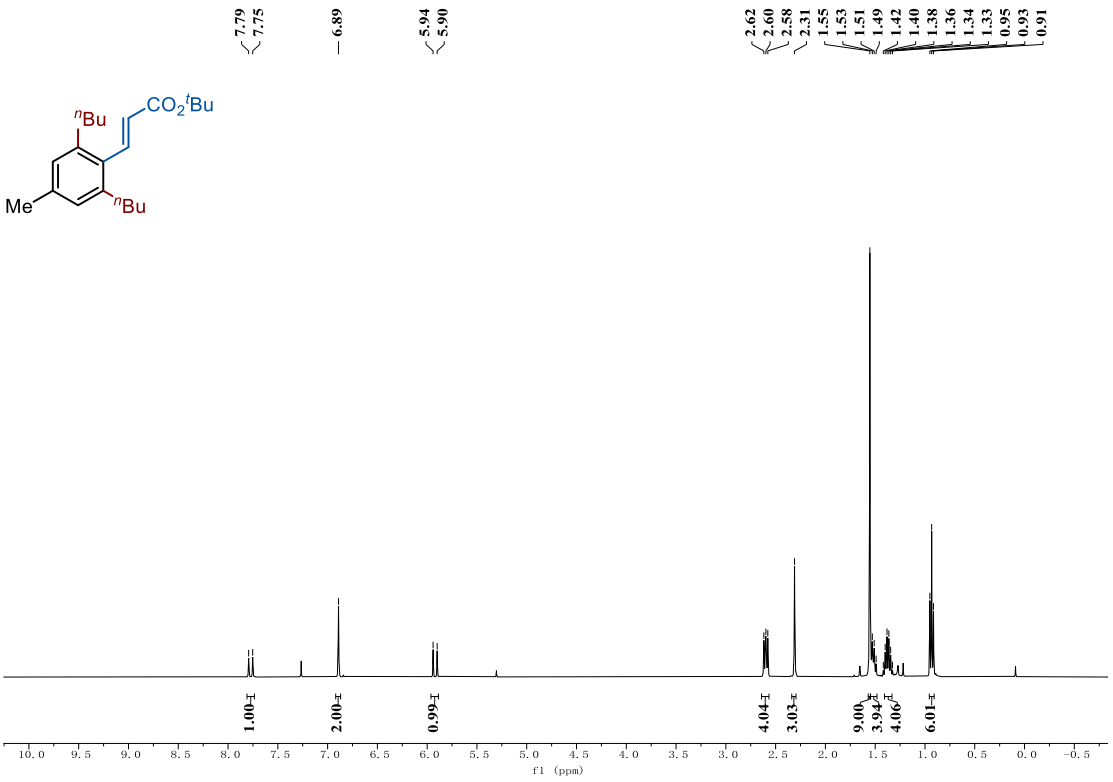
^{1}H NMR of **4aa** (400 MHz, $CDCl_3$)



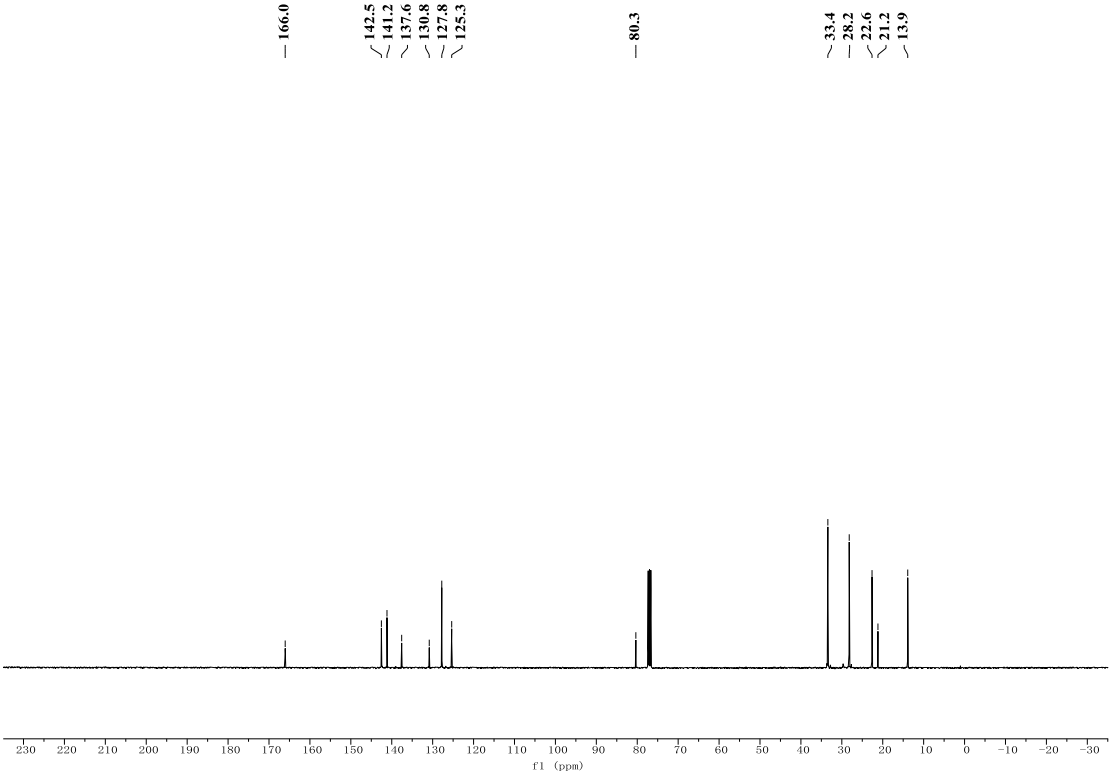
^{13}C NMR of **4aa** (100 MHz, $CDCl_3$)



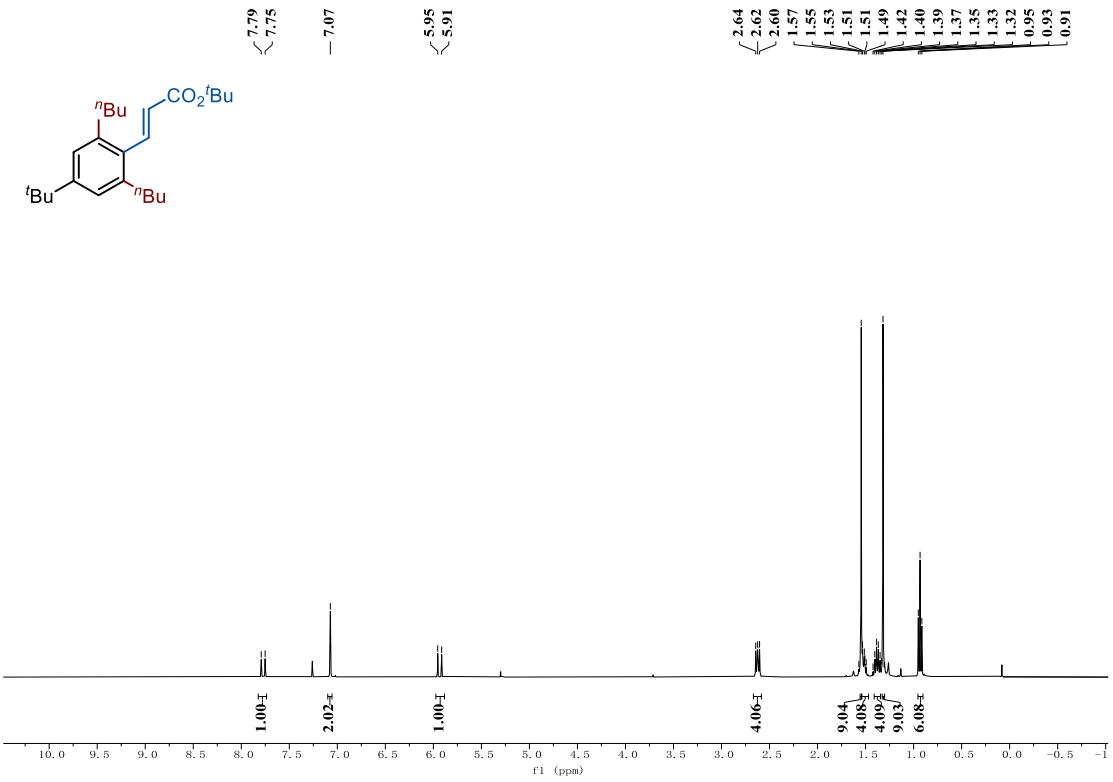
^{1}H NMR of **4ab** (400 MHz, $CDCl_3$)



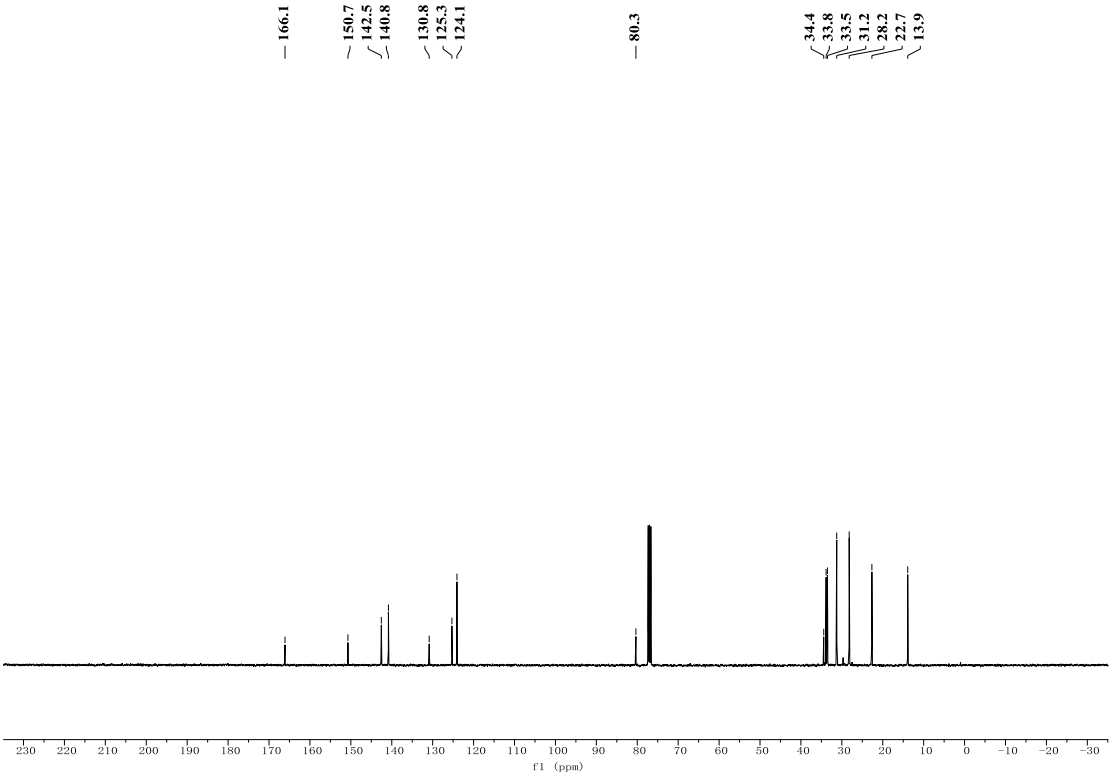
^{13}C NMR of **4ab** (100 MHz, $CDCl_3$)



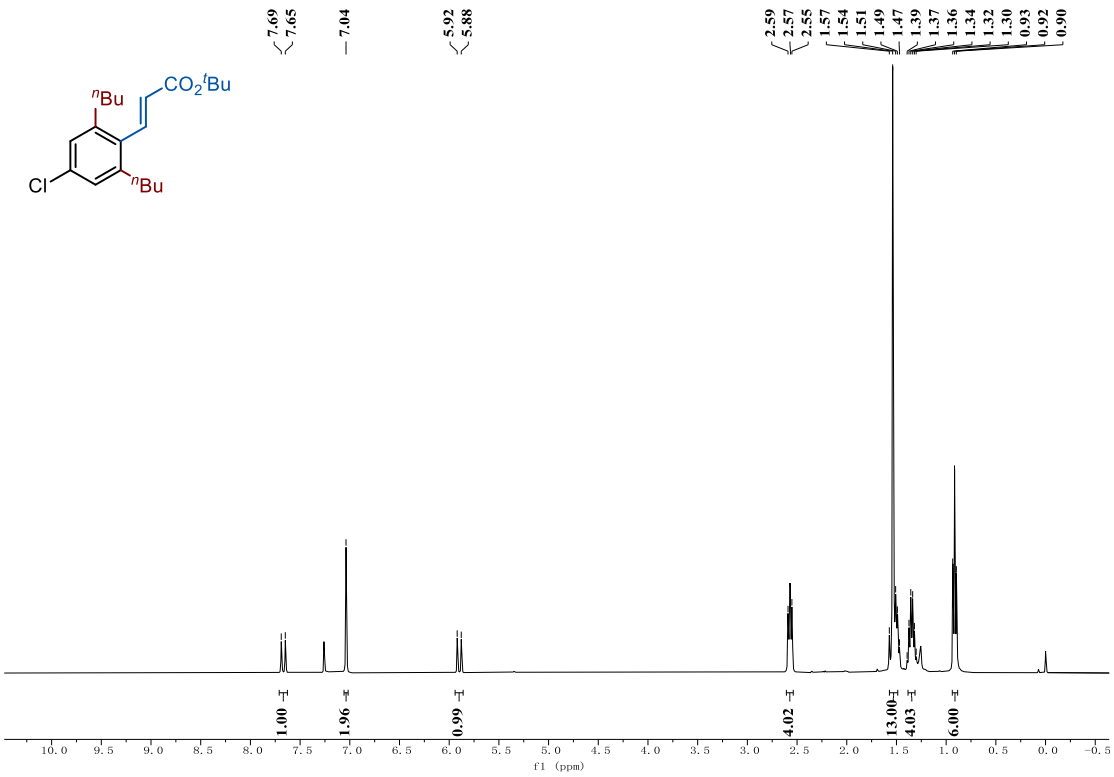
^{1}H NMR of **4ac** (400 MHz, $CDCl_3$)



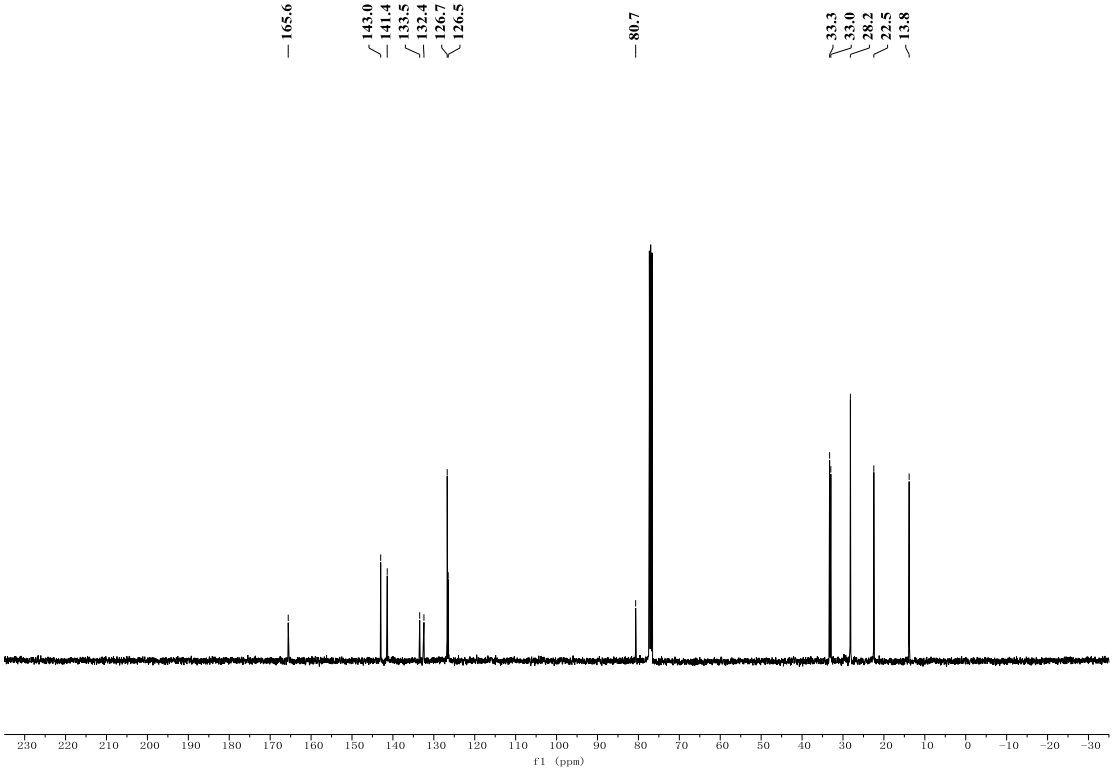
^{13}C NMR of **4ac** (100 MHz, $CDCl_3$)



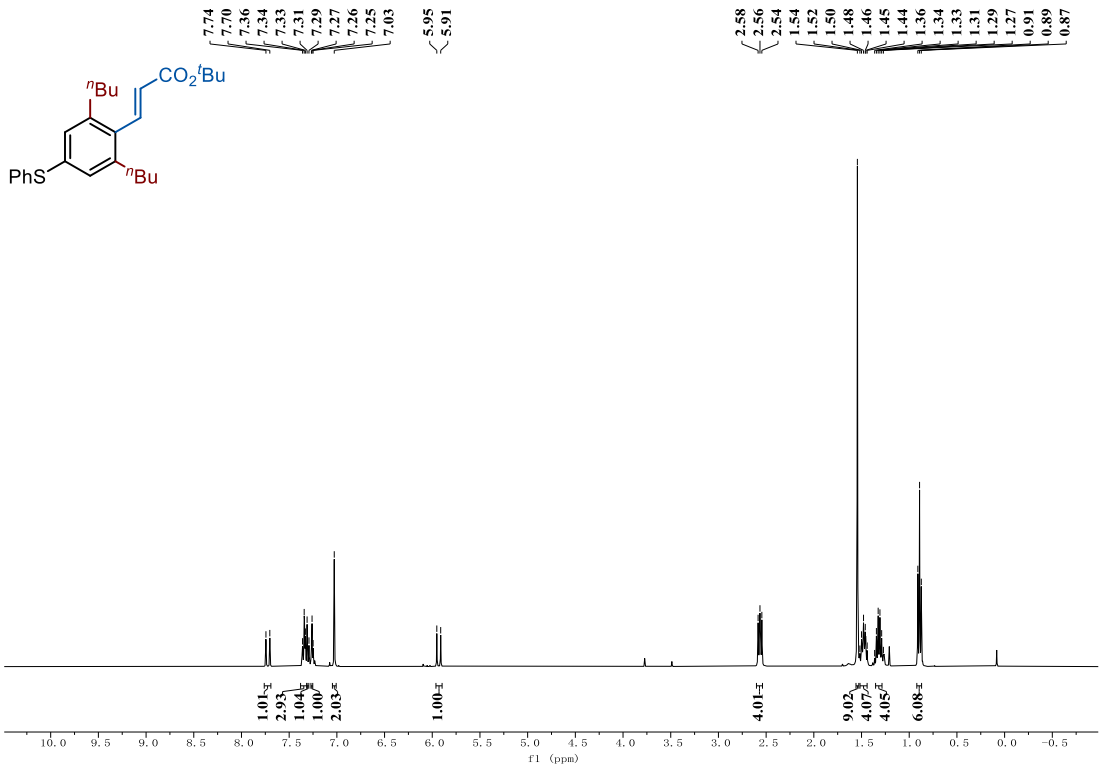
^{1}H NMR of **4ad** (400 MHz, $CDCl_3$)



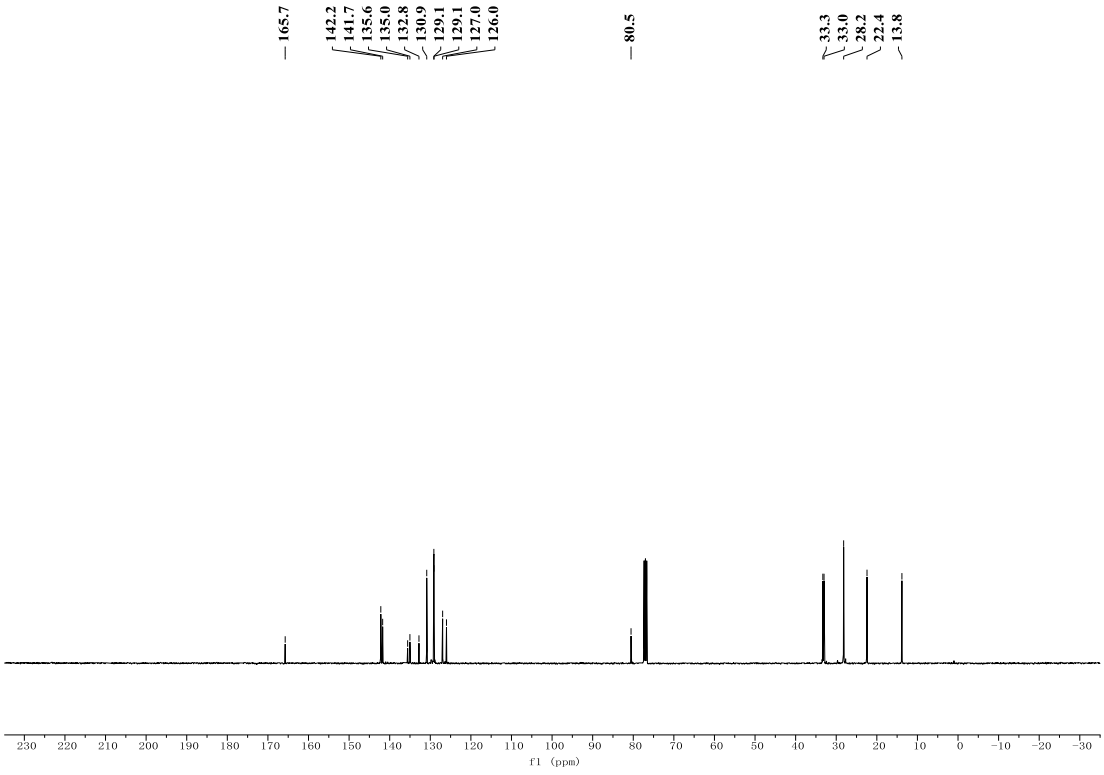
^{13}C NMR of **4ad** (100 MHz, $CDCl_3$)



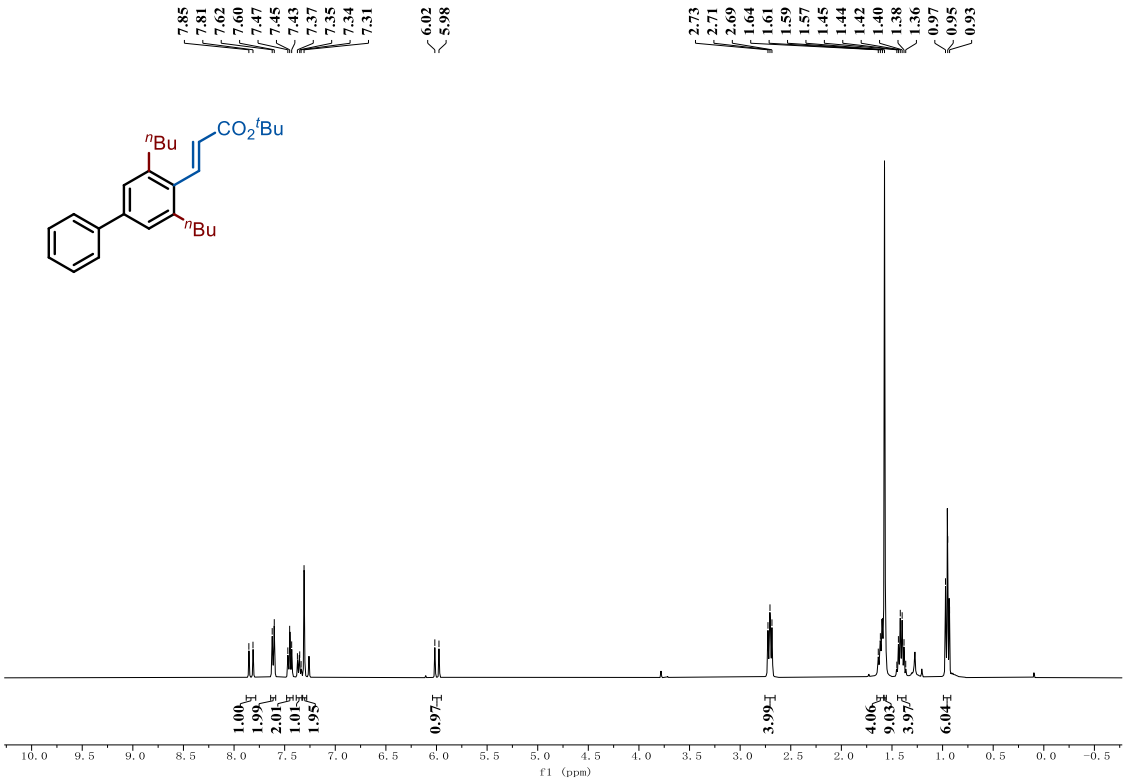
^{1}H NMR of **4ae** (400 MHz, $CDCl_3$)



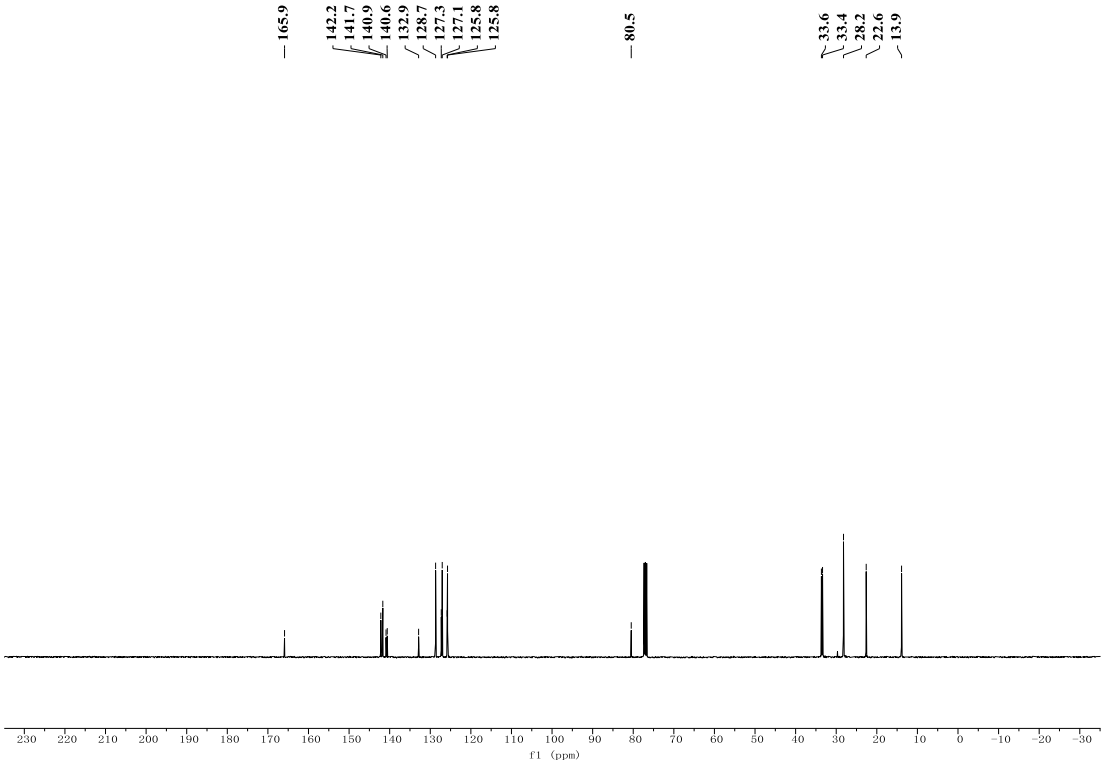
^{13}C NMR of **4ae** (100 MHz, $CDCl_3$)



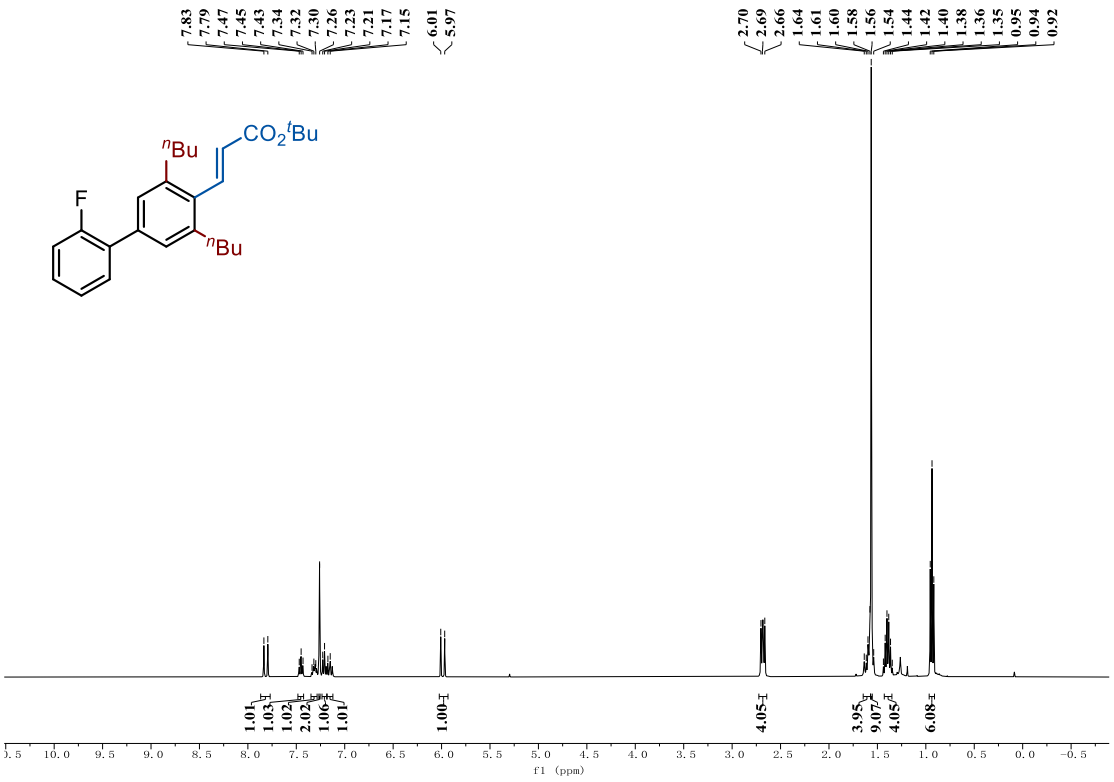
^{1}H NMR of **4af** (400 MHz, $CDCl_3$)



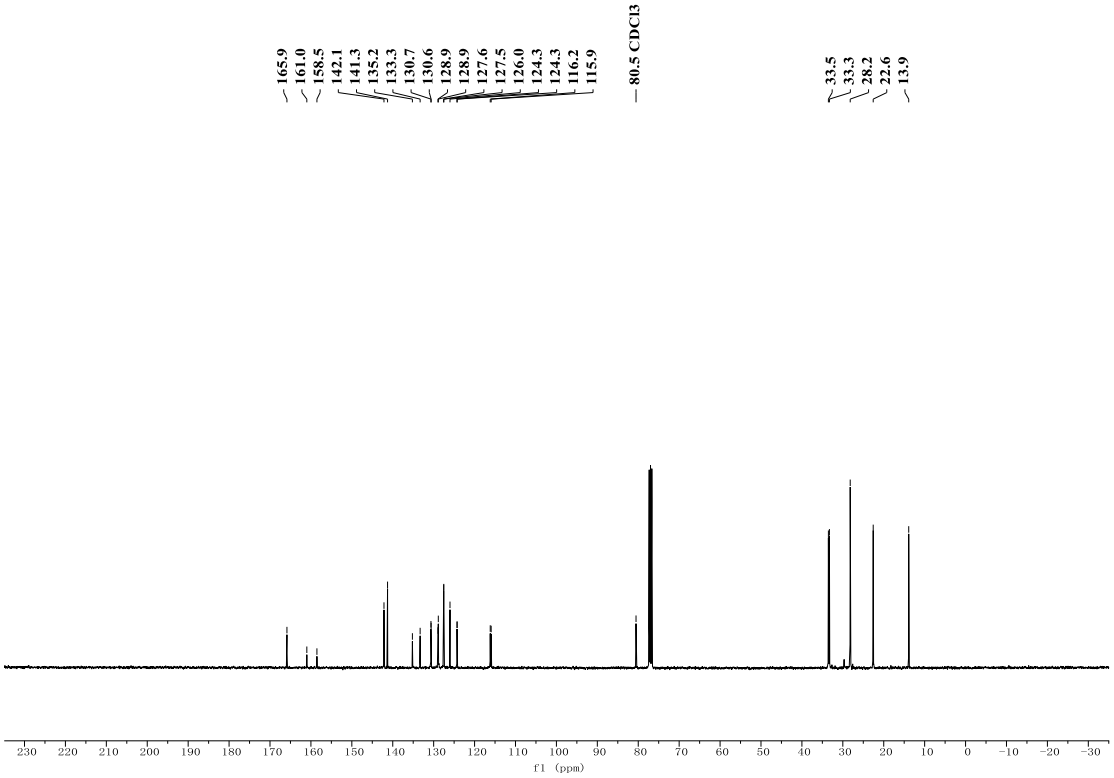
^{13}C NMR of **4af** (100 MHz, $CDCl_3$)



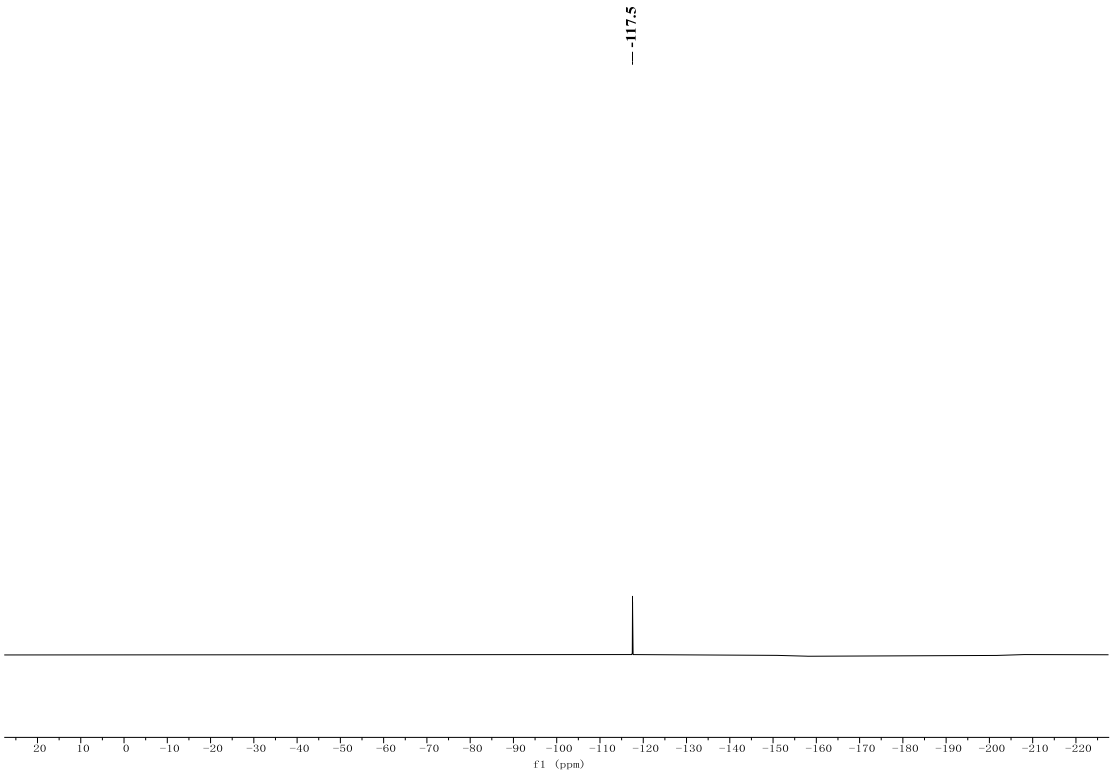
^{1}H NMR of **4ag** (400 MHz, $CDCl_3$)



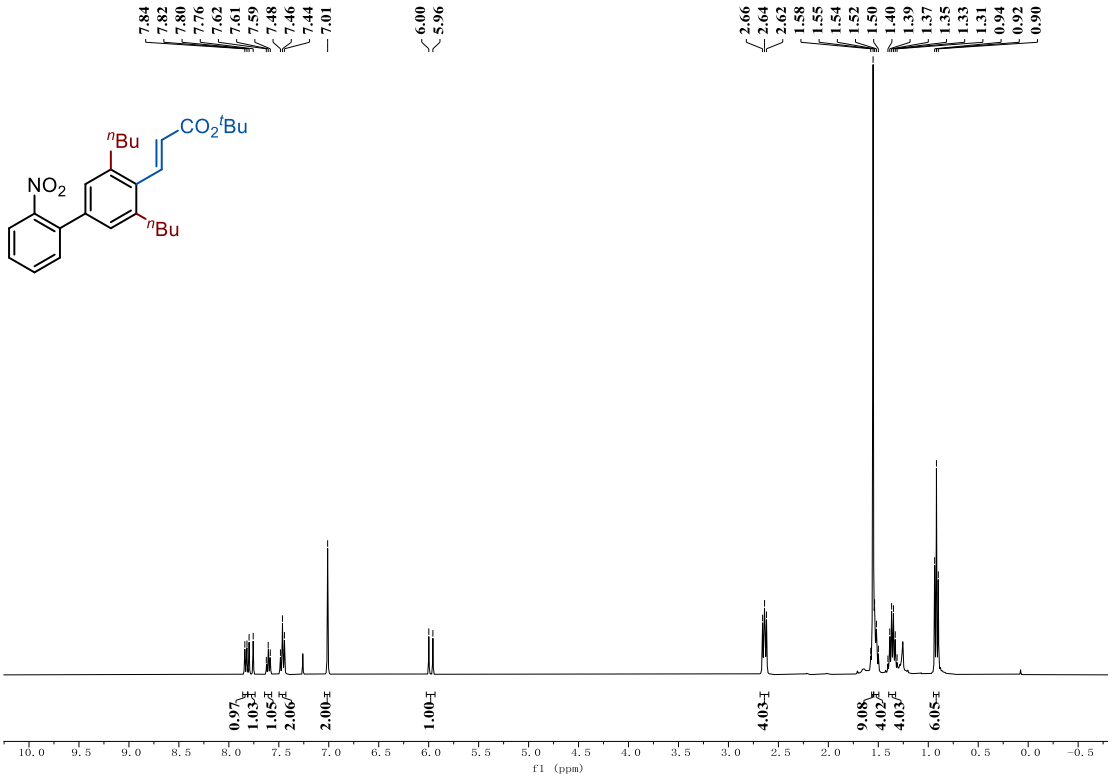
^{13}C NMR of **4ag** (100 MHz, $CDCl_3$)



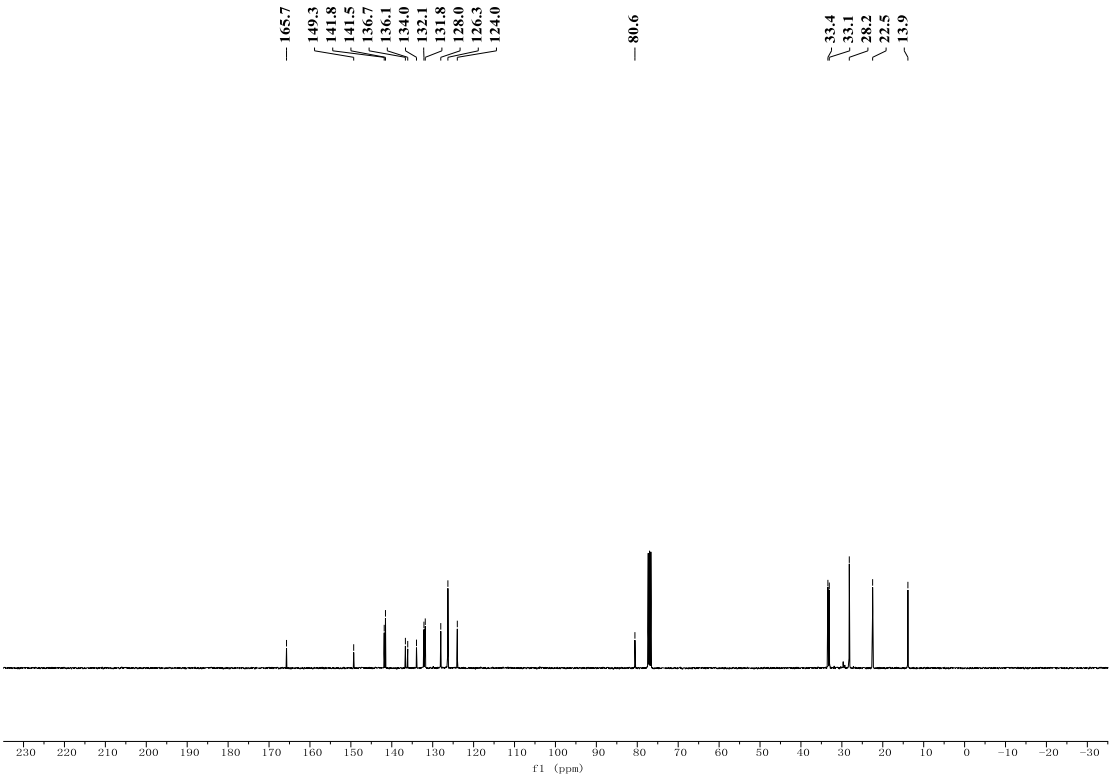
^{19}F NMR of **4ag** (400 MHz, $CDCl_3$)



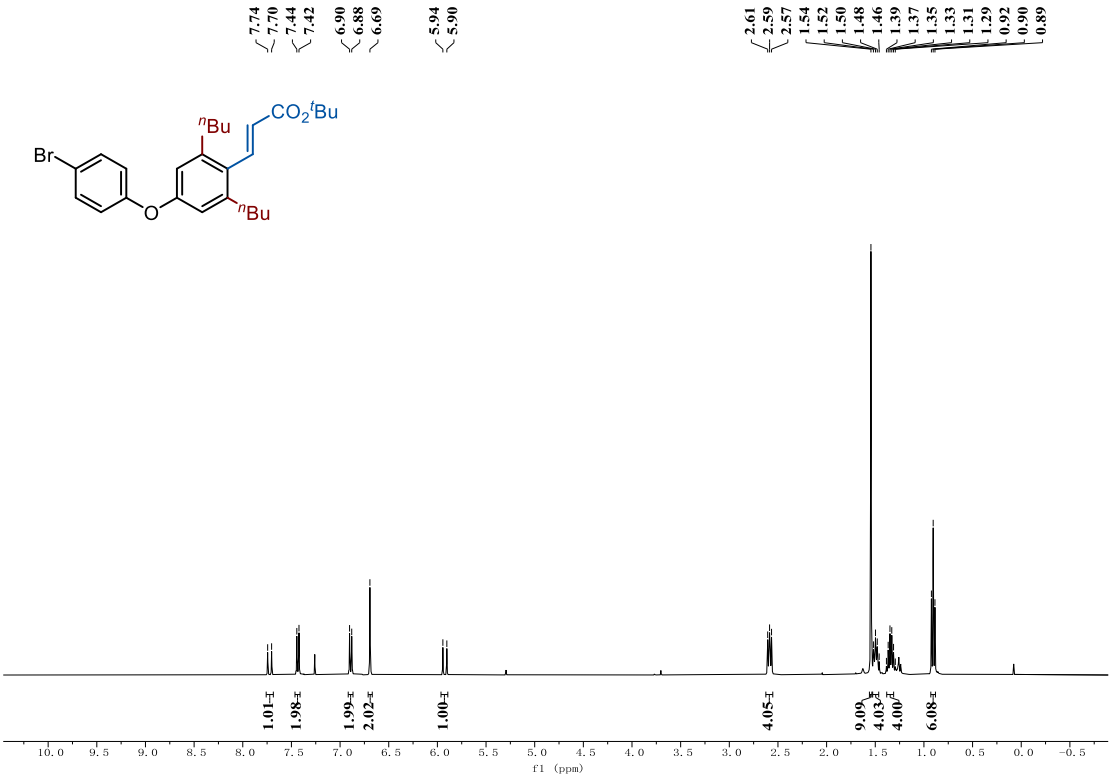
^{1}H NMR of **4ah** (400 MHz, $CDCl_3$)



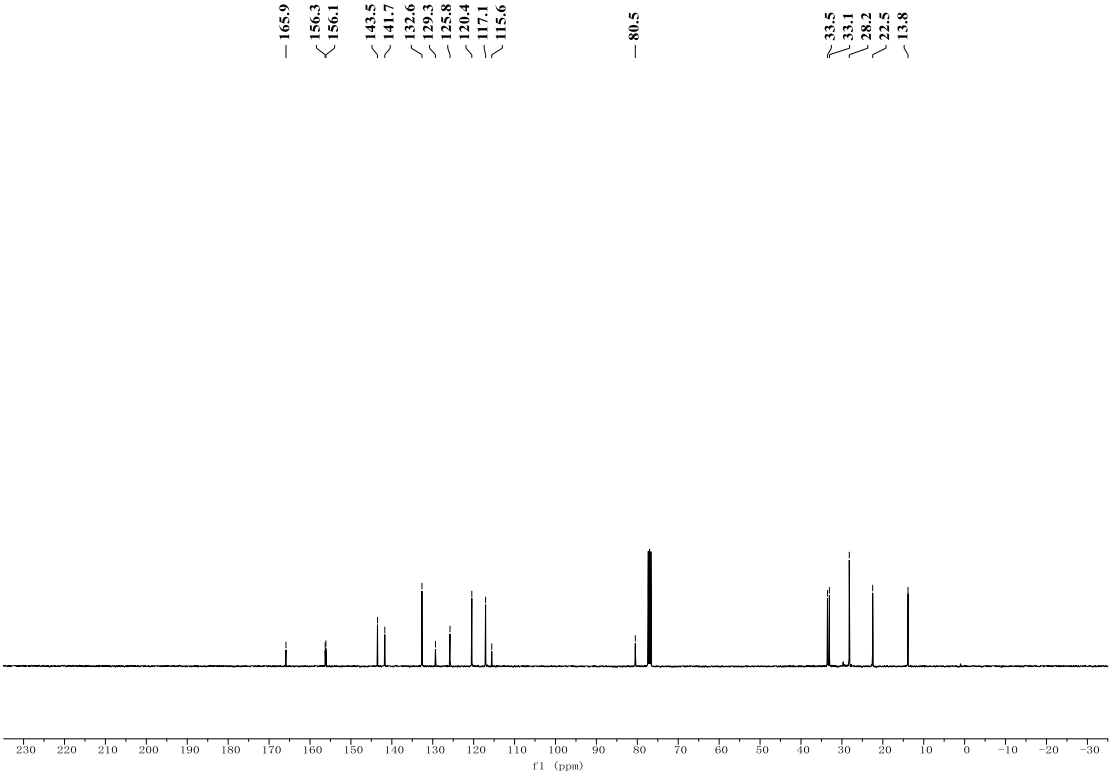
^{13}C NMR of **4ah** (100 MHz, $CDCl_3$)



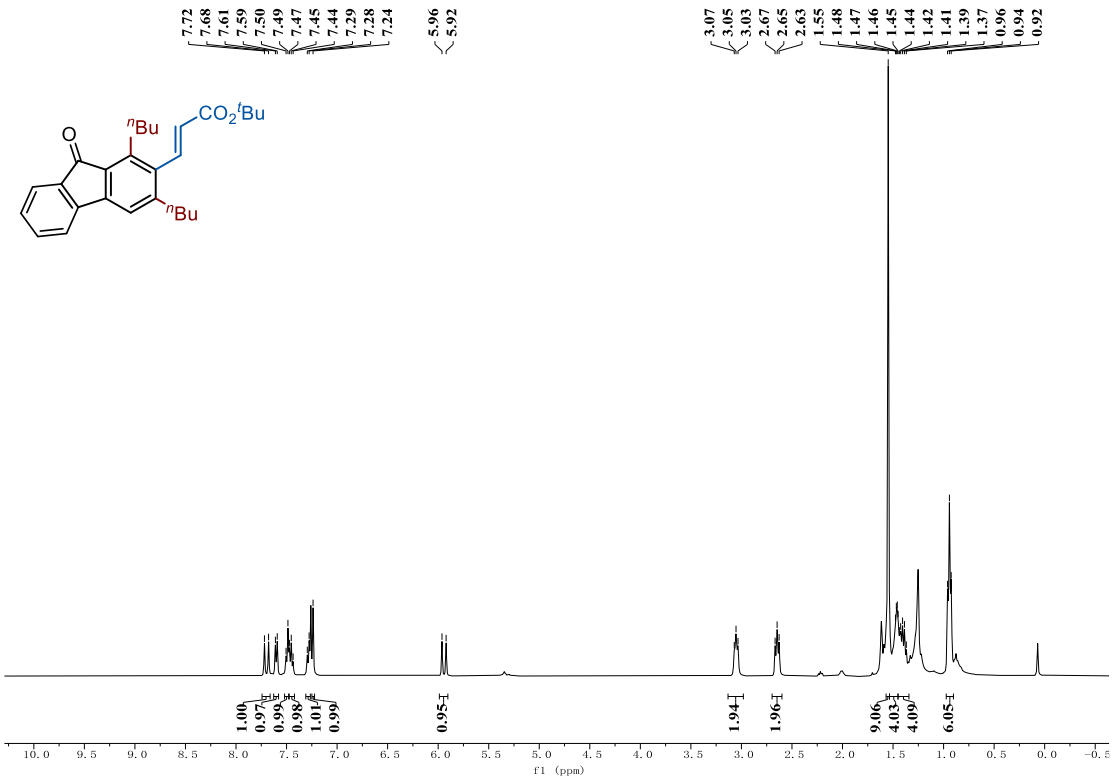
^{1}H NMR of **4ai** (400 MHz, $CDCl_3$)



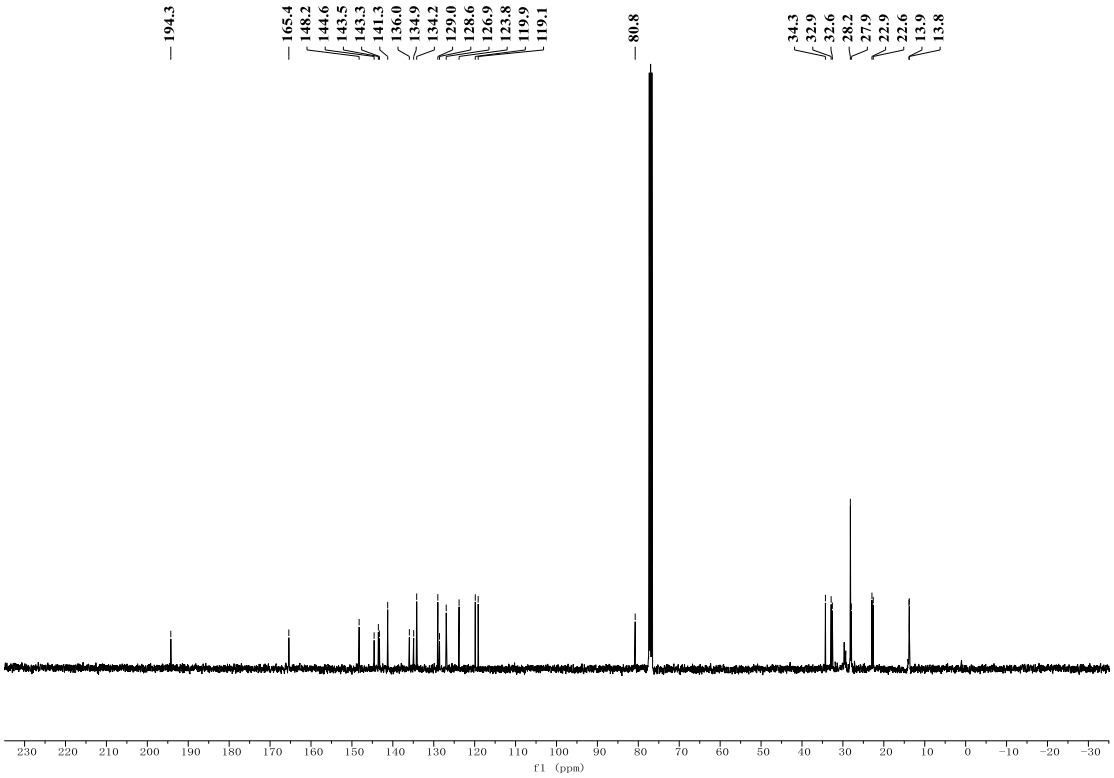
^{13}C NMR of **4ai** (100 MHz, $CDCl_3$)



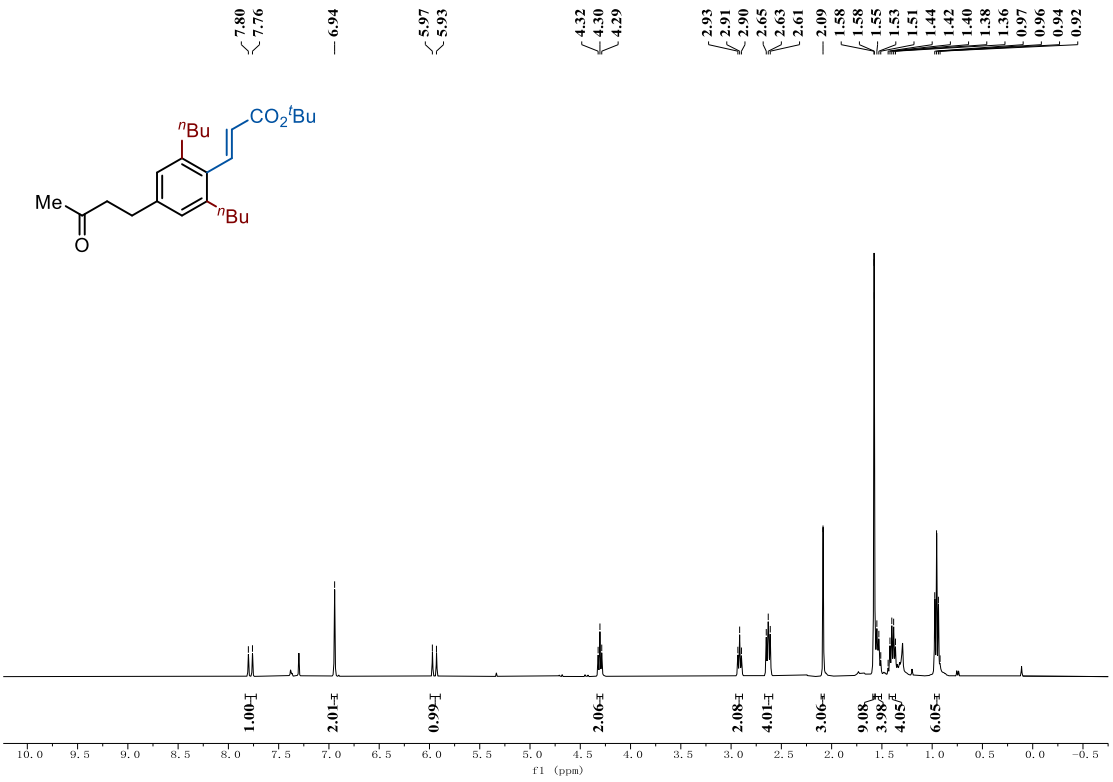
^{1}H NMR of **4aj** (400 MHz, $CDCl_3$)



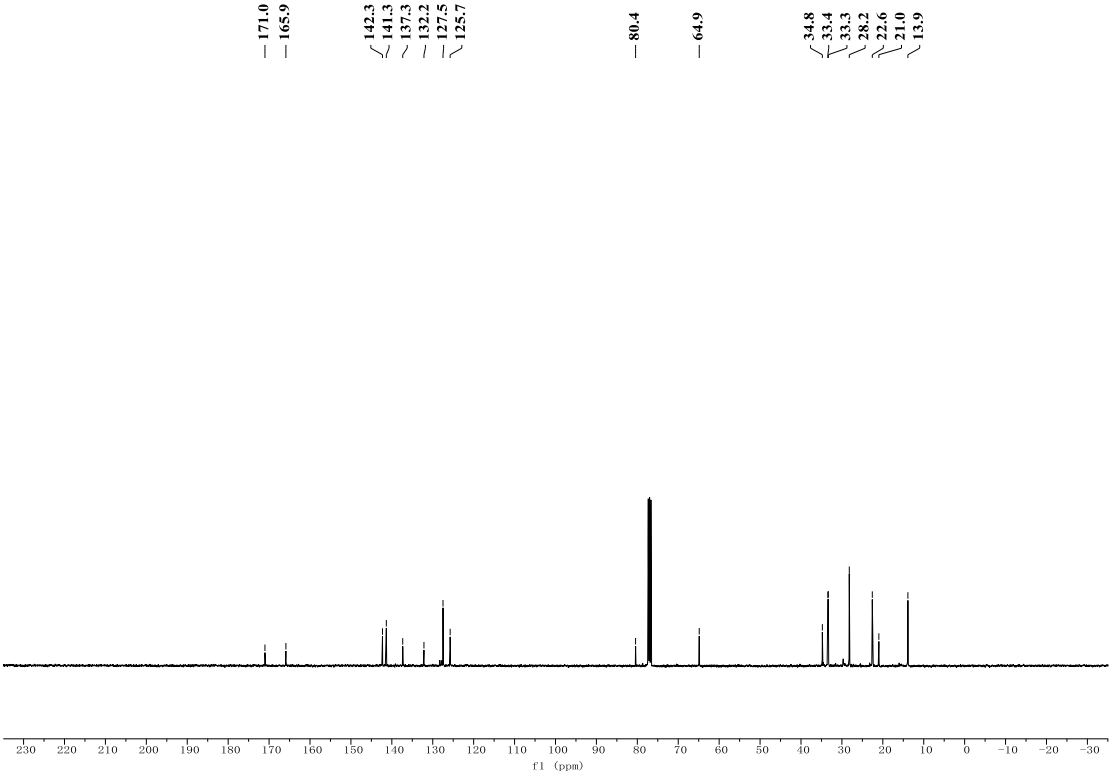
^{13}C NMR of **4aj** (100 MHz, $CDCl_3$)



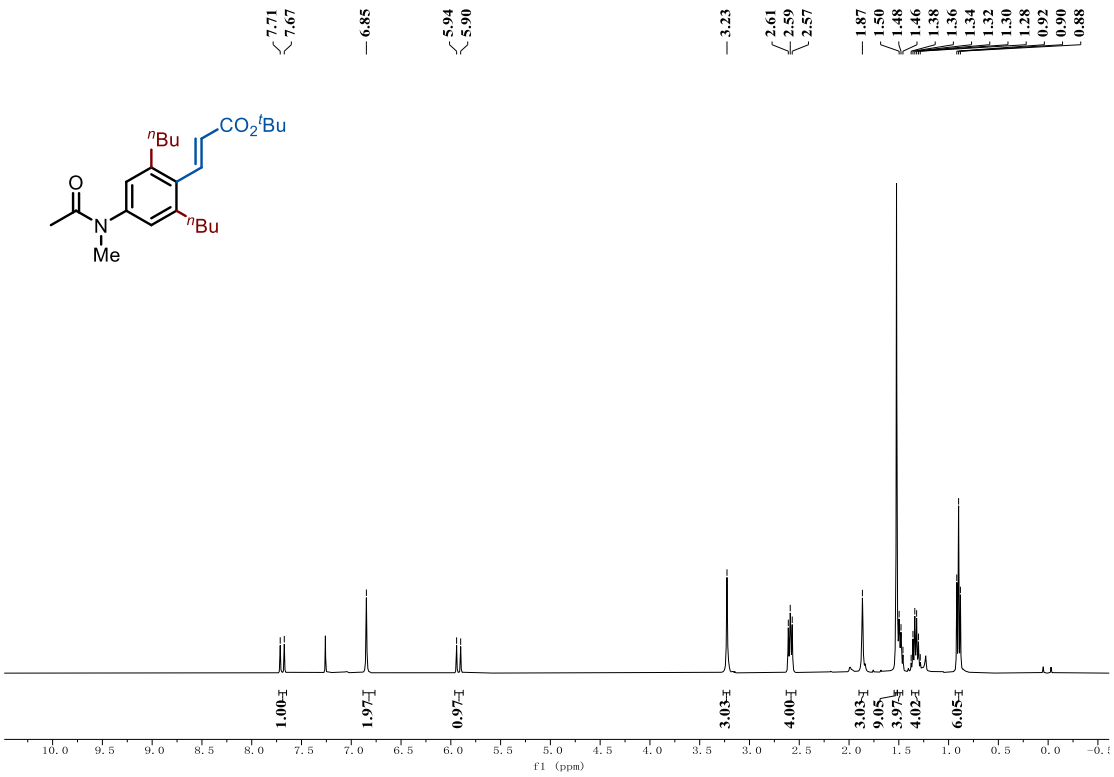
^{1}H NMR of **4ak** (400 MHz, $CDCl_3$)



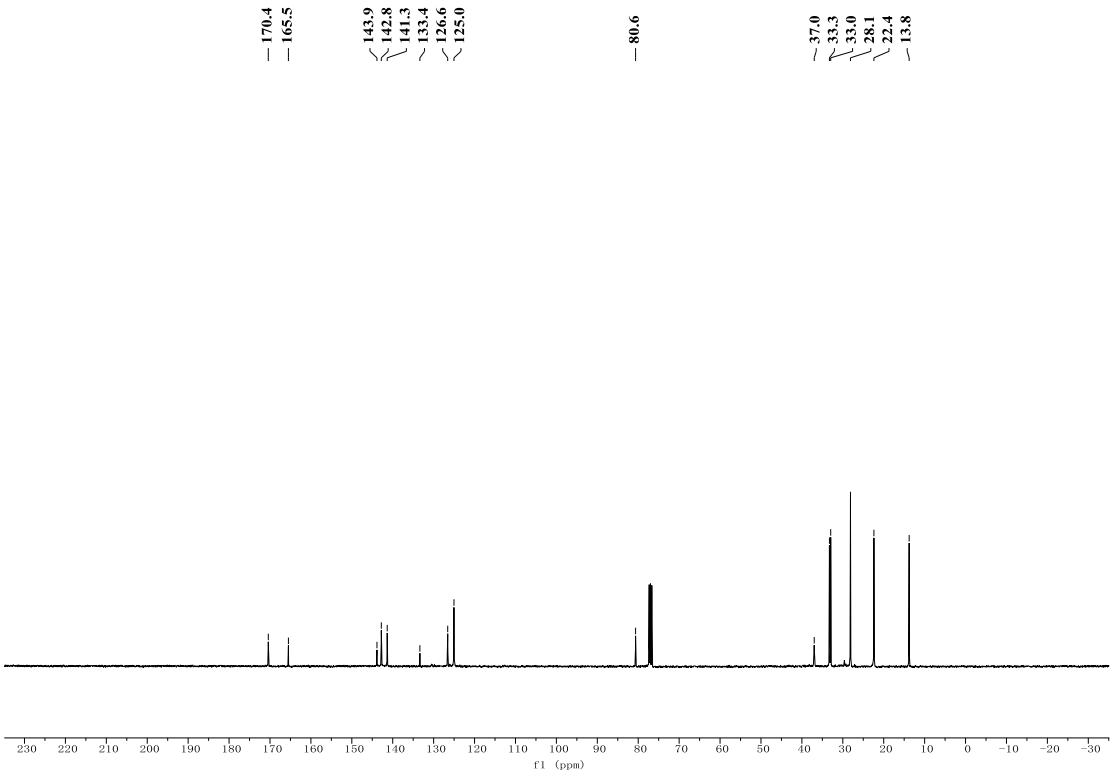
^{13}C NMR of **4ak** (100 MHz, $CDCl_3$)



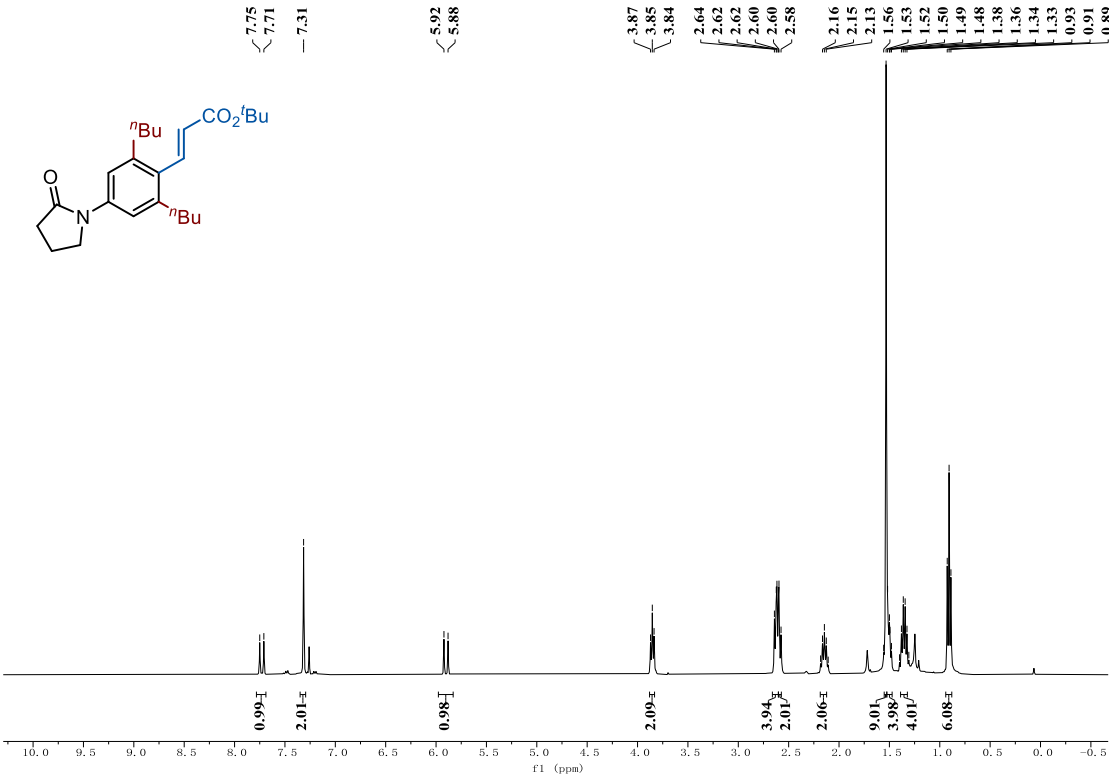
^{1}H NMR of **4al** (400 MHz, $CDCl_3$)



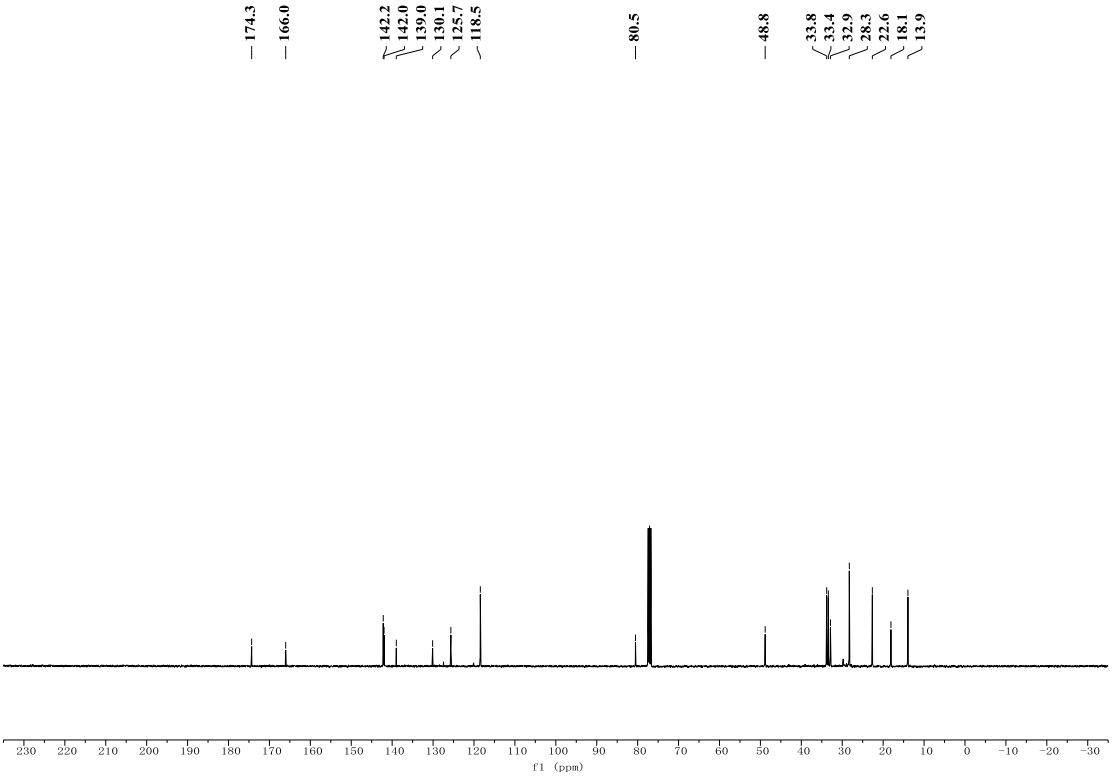
^{13}C NMR of **4al** (000 MHz, $CDCl_3$)



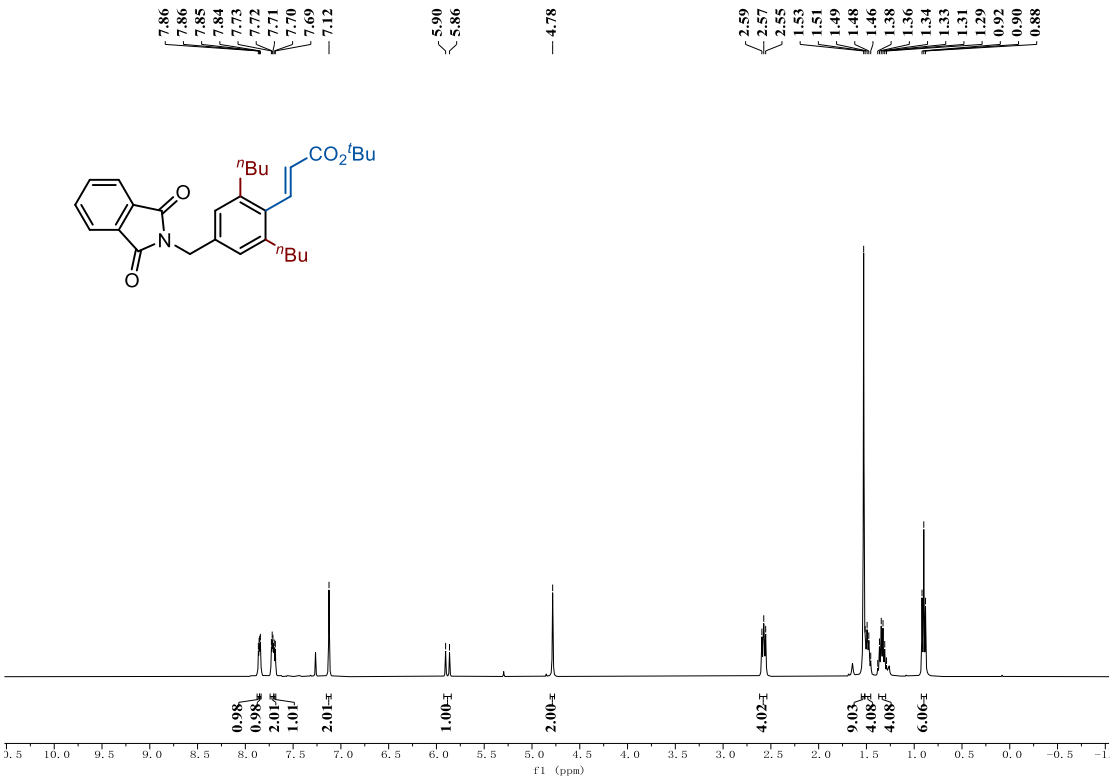
^{1}H NMR of **4am** (400 MHz, $CDCl_3$)



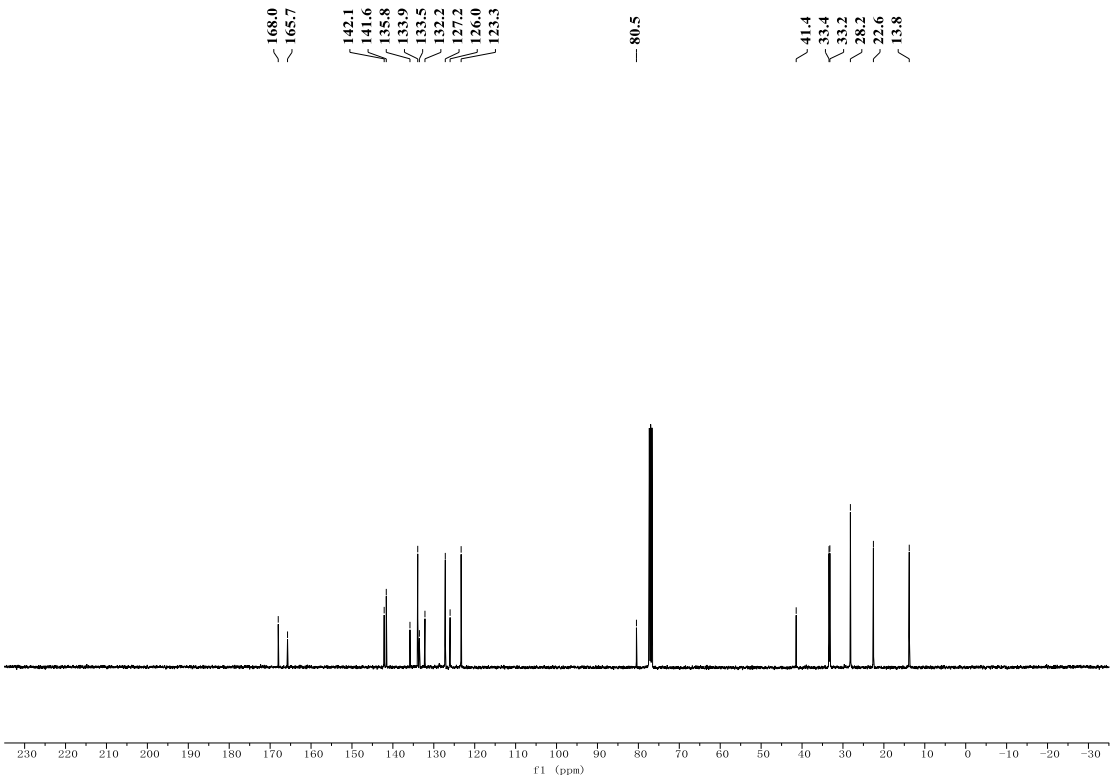
^{13}C NMR of **4am** (100 MHz, $CDCl_3$)



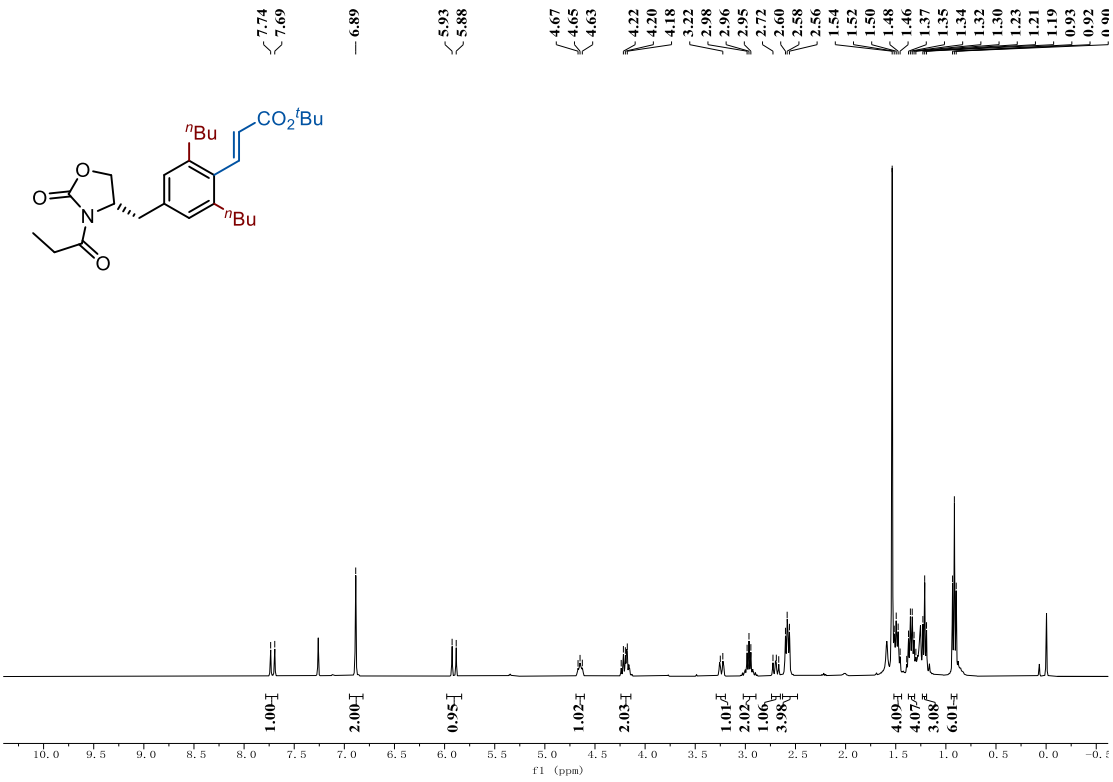
^{1}H NMR of **4an** (400 MHz, $CDCl_3$)



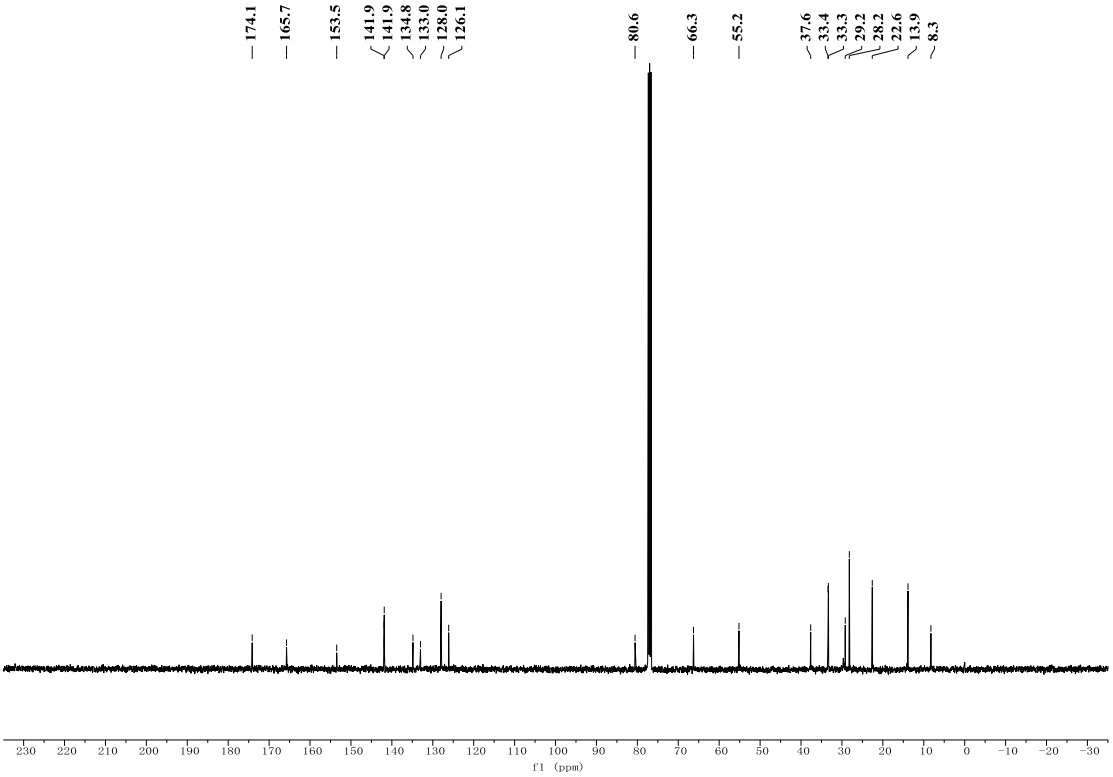
^{13}C NMR of **4an** (100 MHz, $CDCl_3$)



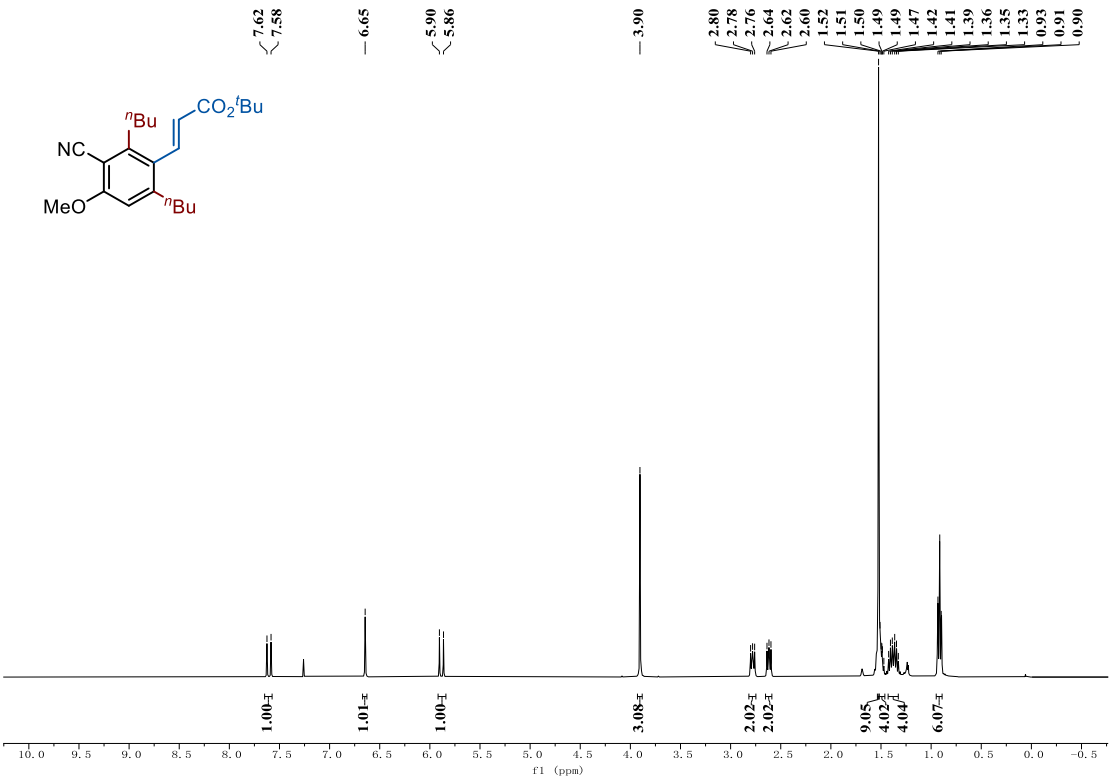
^{1}H NMR of **4ao** (400 MHz, $CDCl_3$)



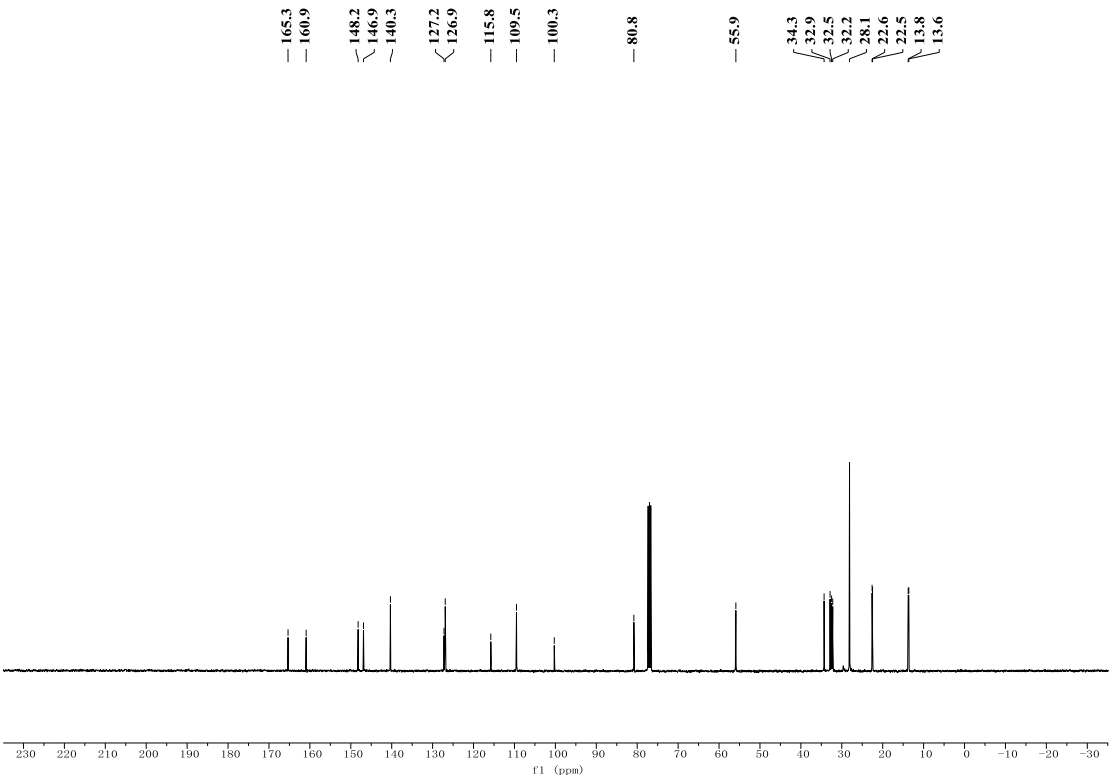
^{13}C NMR of **4ao** (100 MHz, $CDCl_3$)



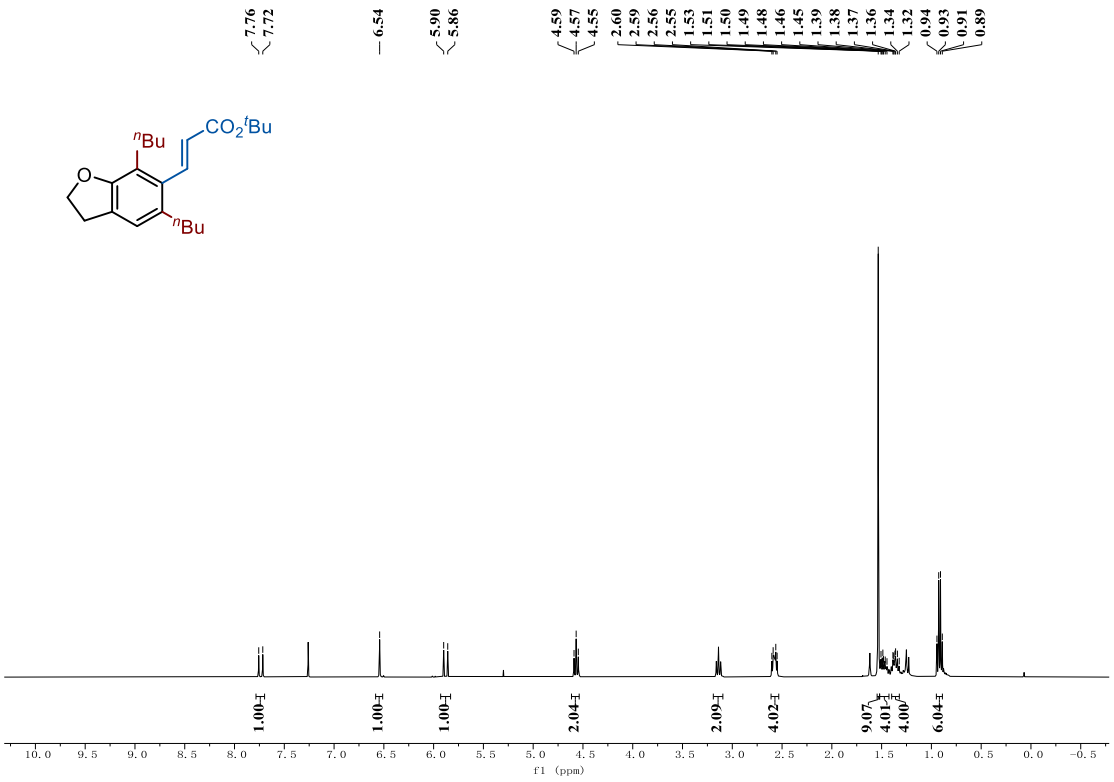
^{1}H NMR of **4ap** (400 MHz, $CDCl_3$)



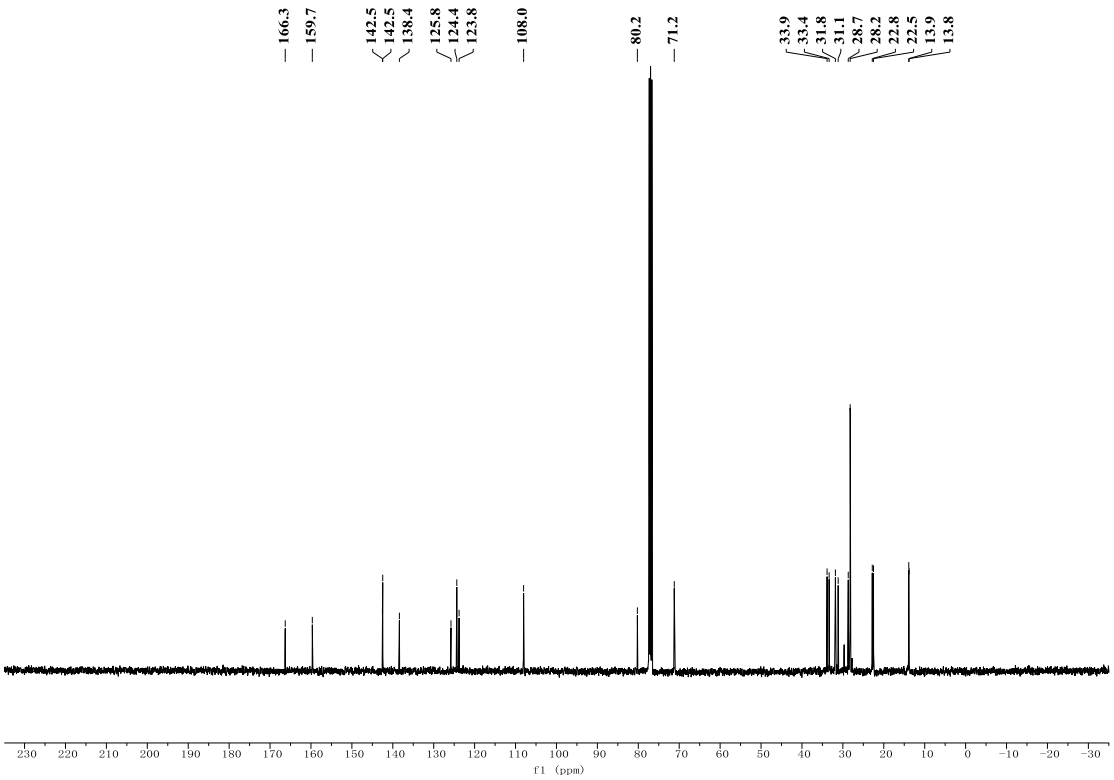
^{13}C NMR of **4ap** (100 MHz, $CDCl_3$)



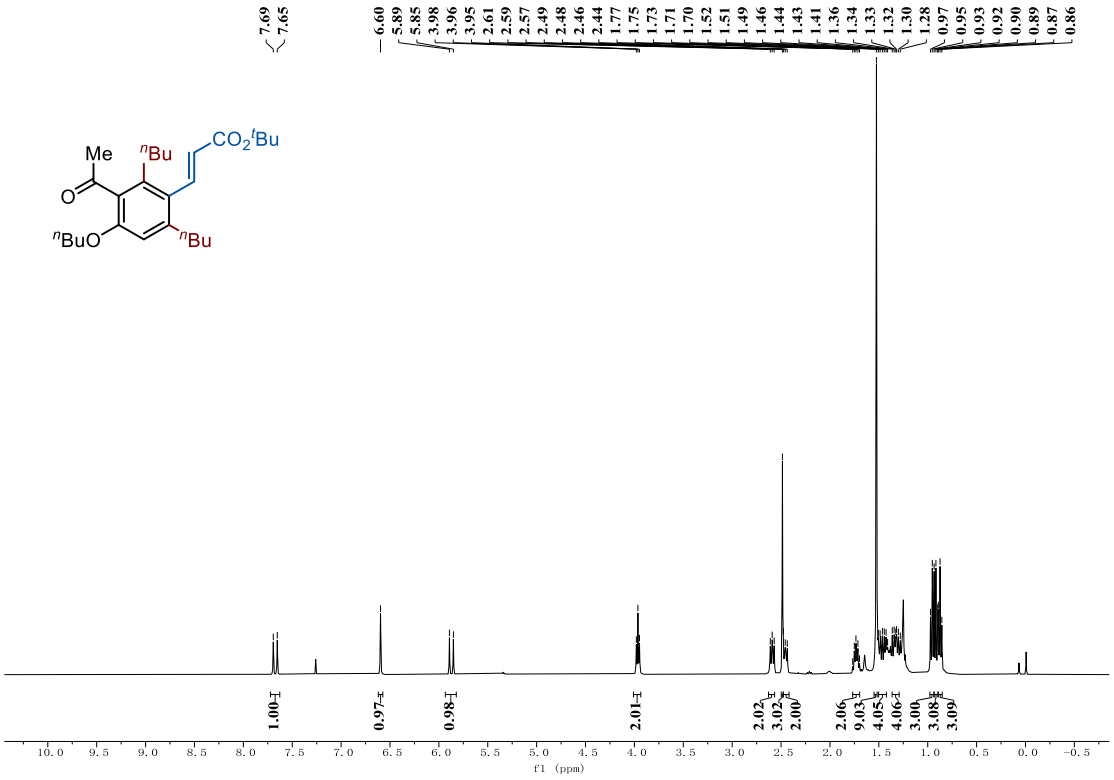
^{1}H NMR of **4aq** (400 MHz, $CDCl_3$)



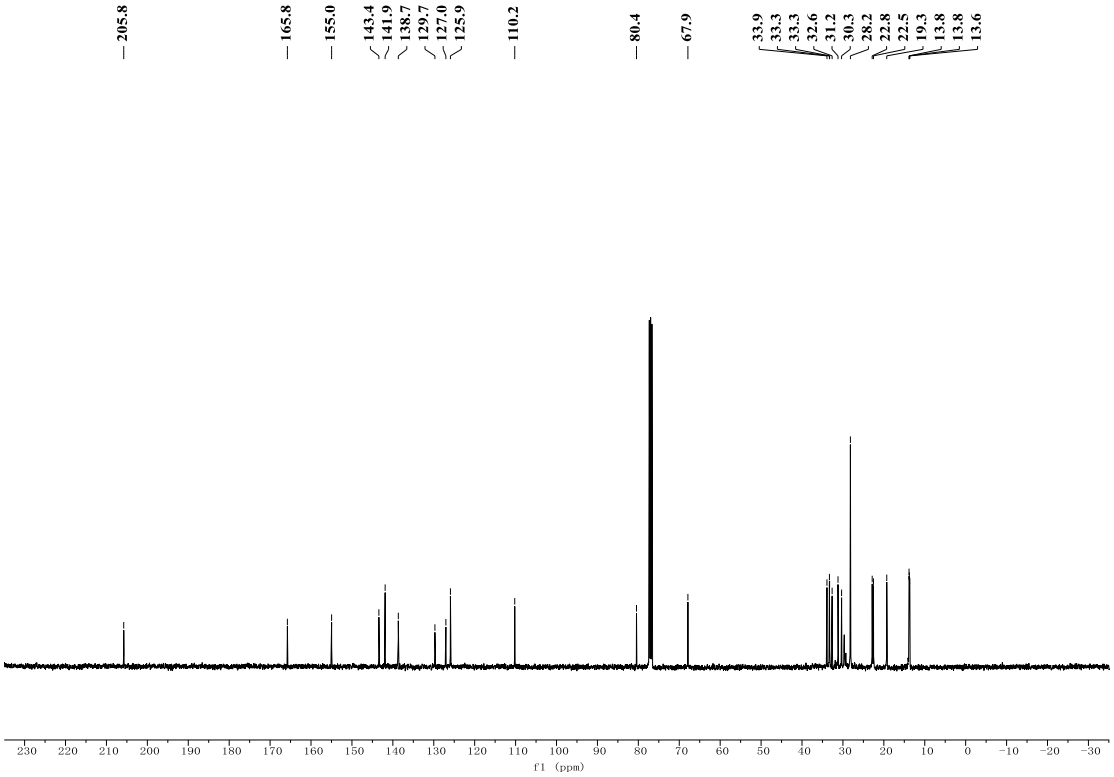
^{13}C NMR of **4aq** (100 MHz, $CDCl_3$)



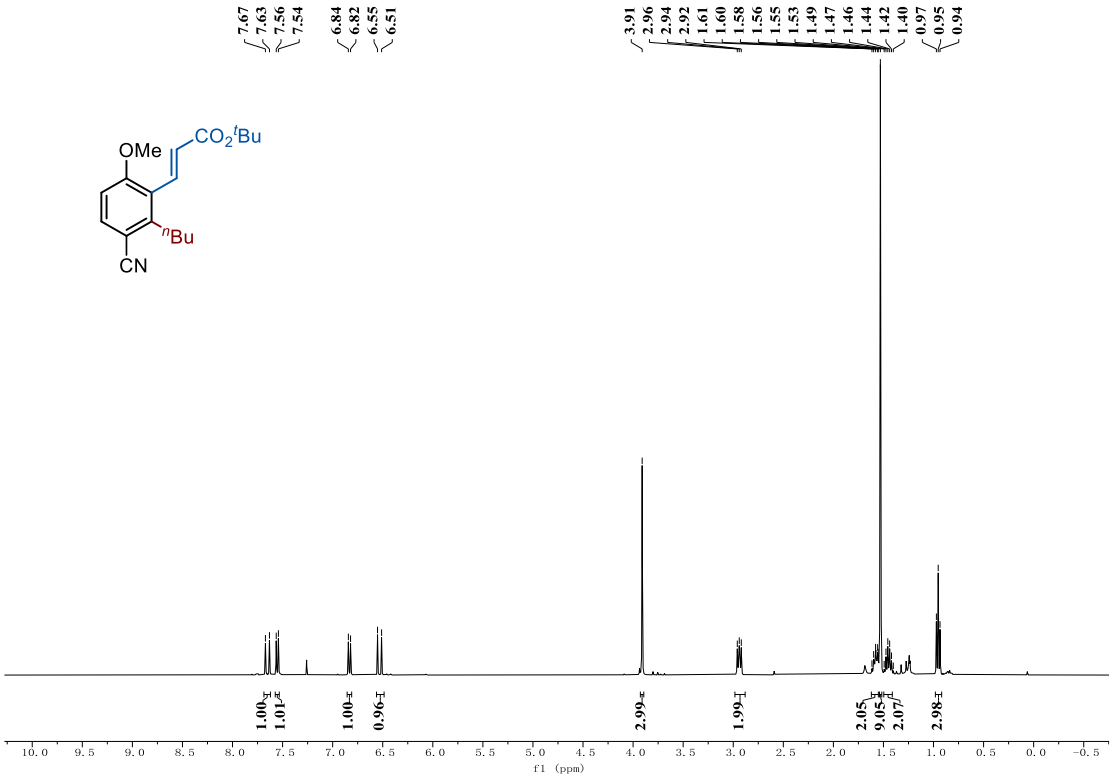
^{1}H NMR of **4ar**(400 MHz, $CDCl_3$)



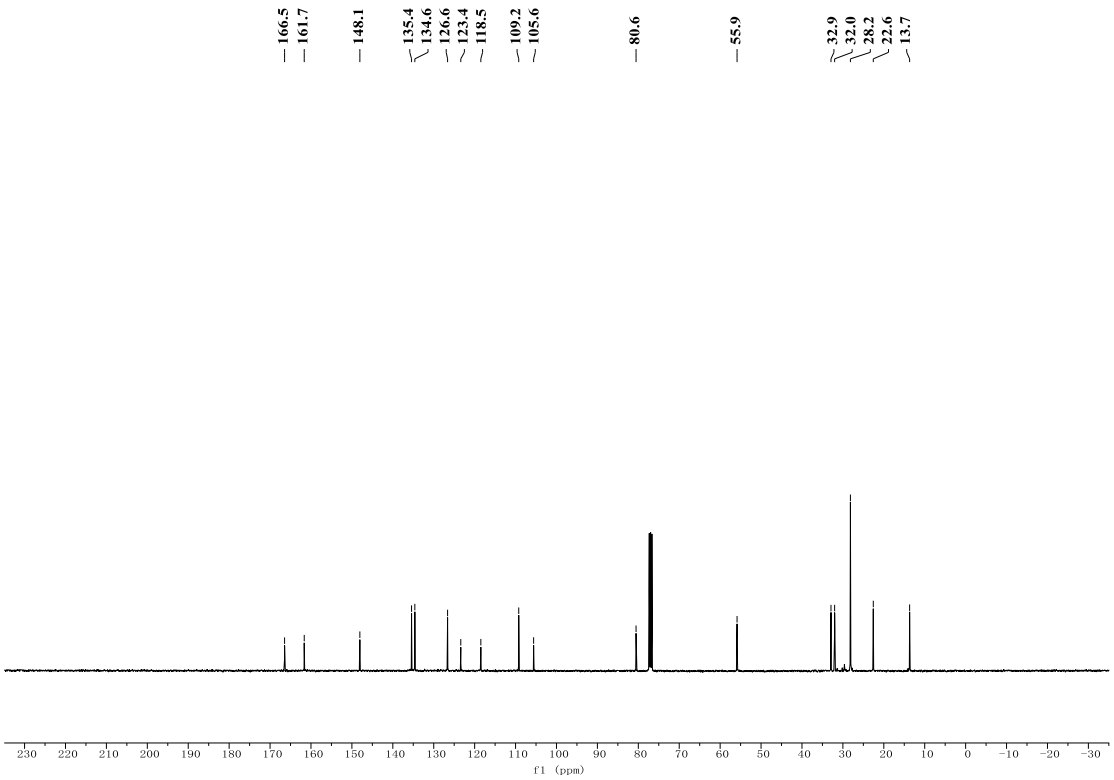
^{13}C NMR of **4ar** (100 MHz, $CDCl_3$)



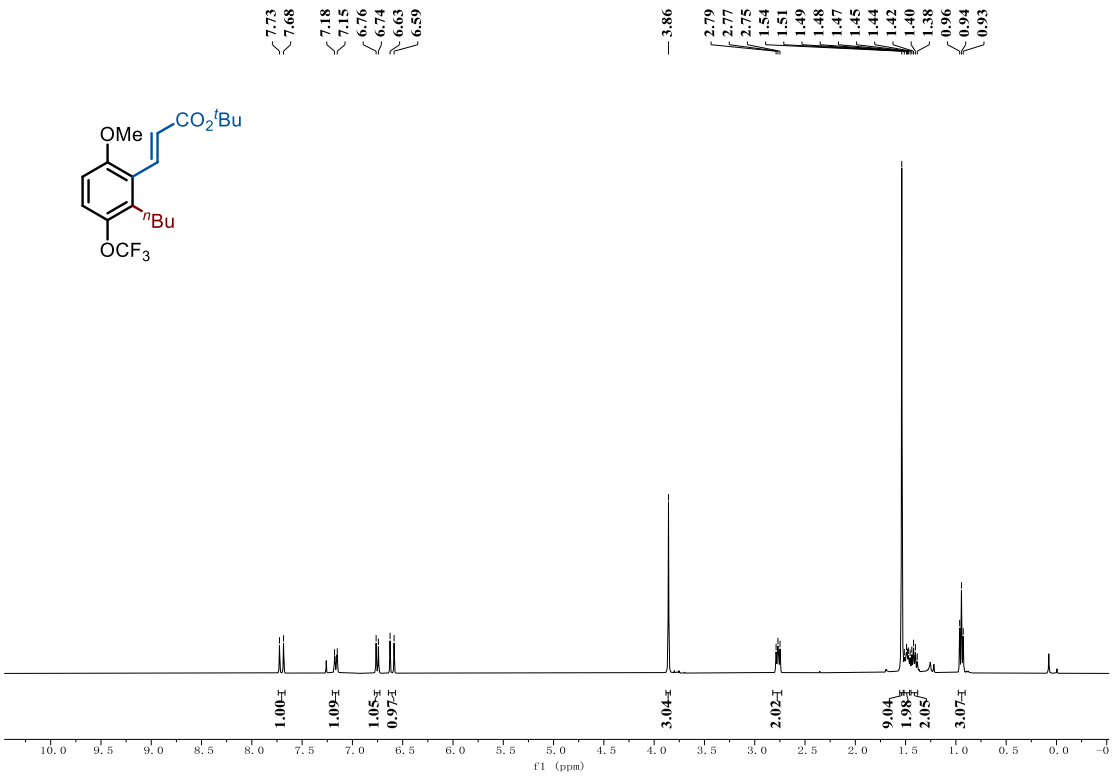
^{1}H NMR of **4aa'** (400 MHz, $CDCl_3$)



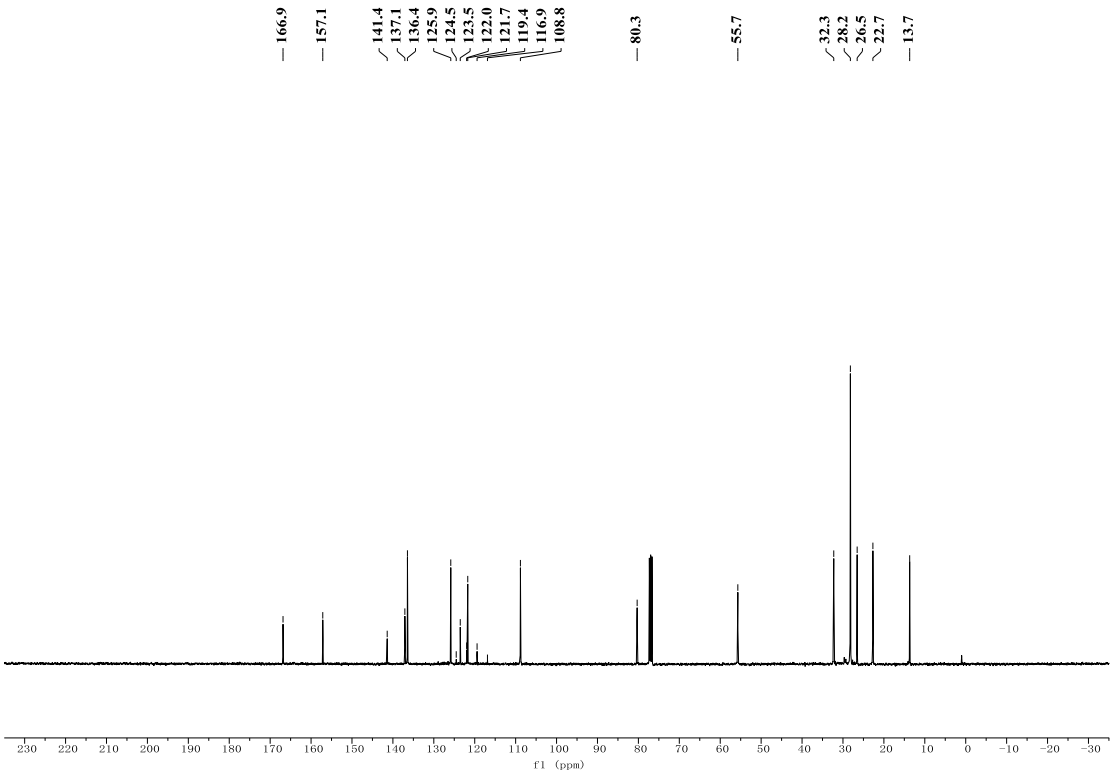
^{13}C NMR of **4aa'** (100 MHz, $CDCl_3$)



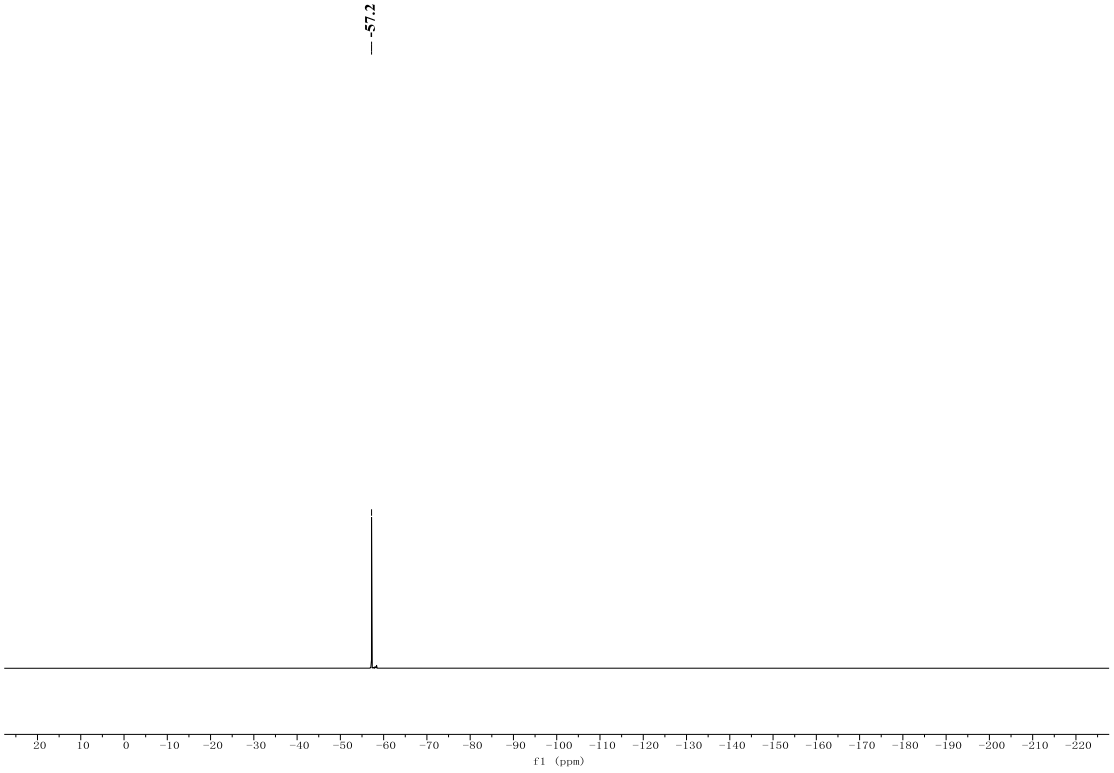
^{1}H NMR of **4ab'** (400 MHz, $CDCl_3$)



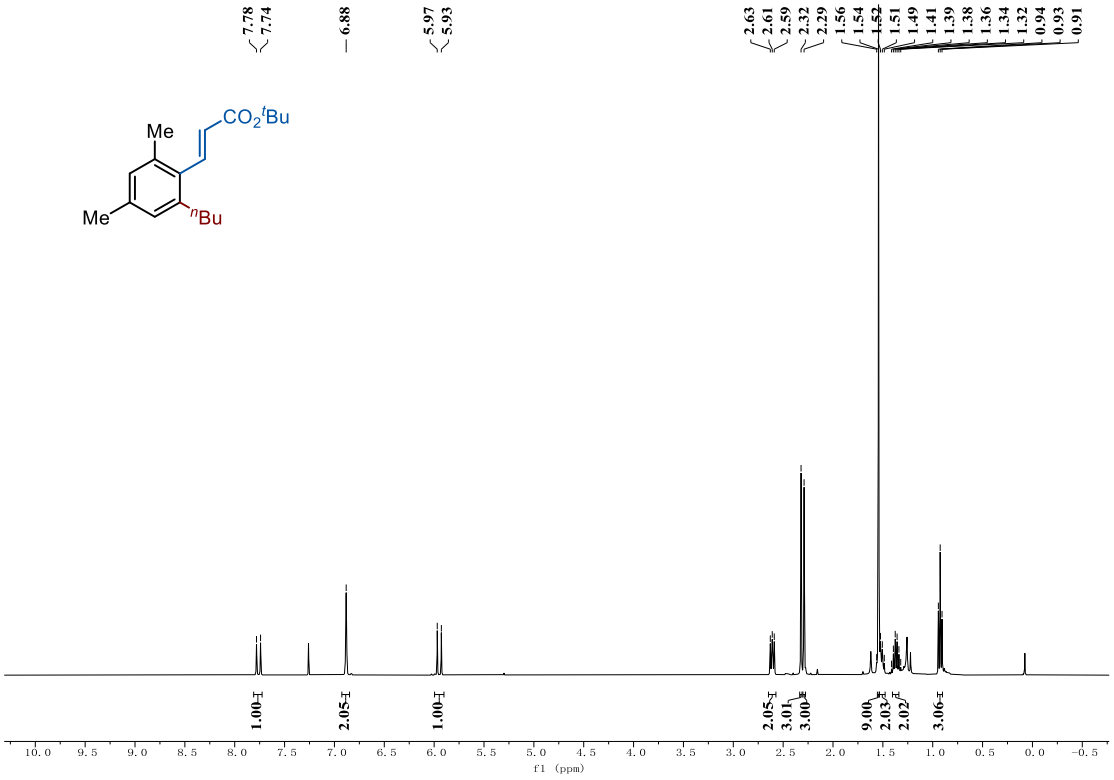
^{13}C NMR of **4ab'** (100 MHz, $CDCl_3$)



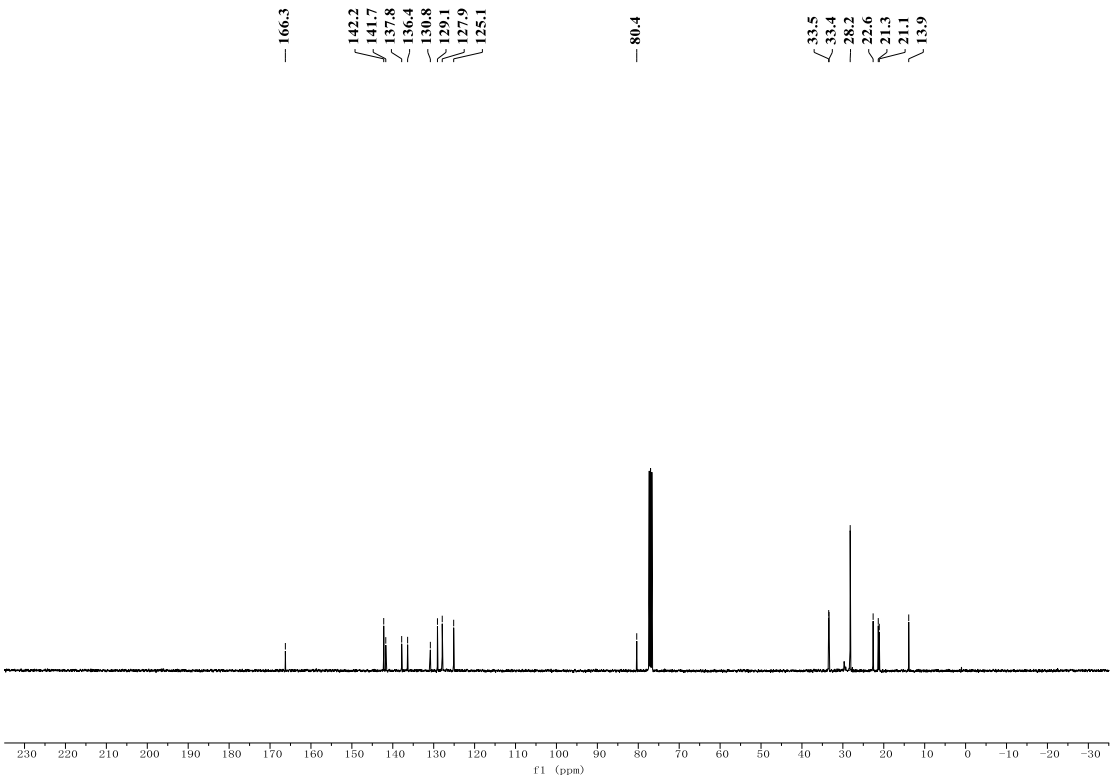
^{19}F NMR of **4ab'** (400 MHz, $CDCl_3$)



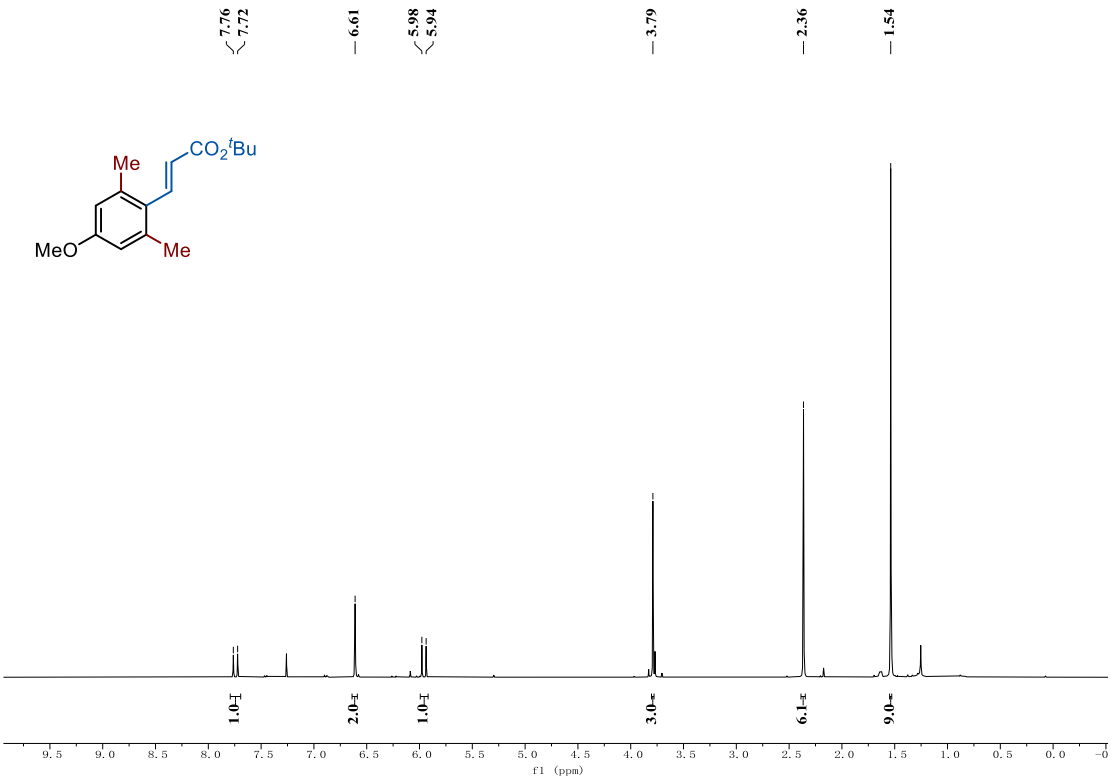
^{1}H NMR of **4ac'** (400 MHz, $CDCl_3$)



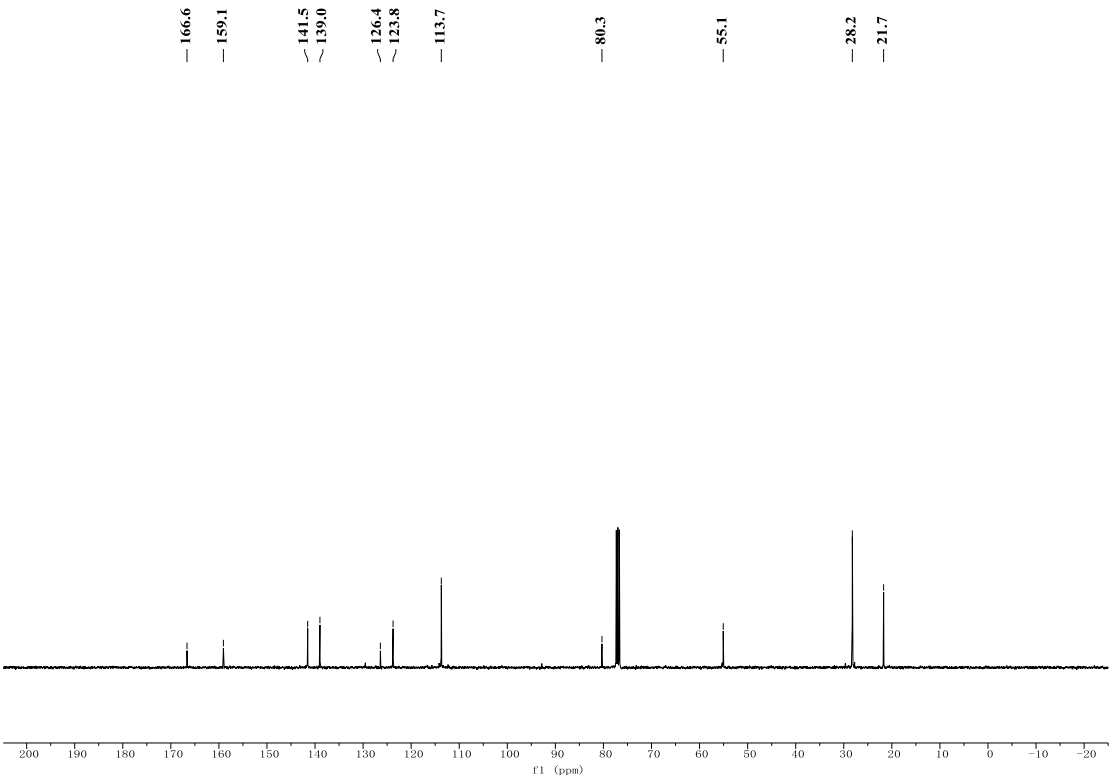
^{13}C NMR of **4ac'** (100 MHz, $CDCl_3$)



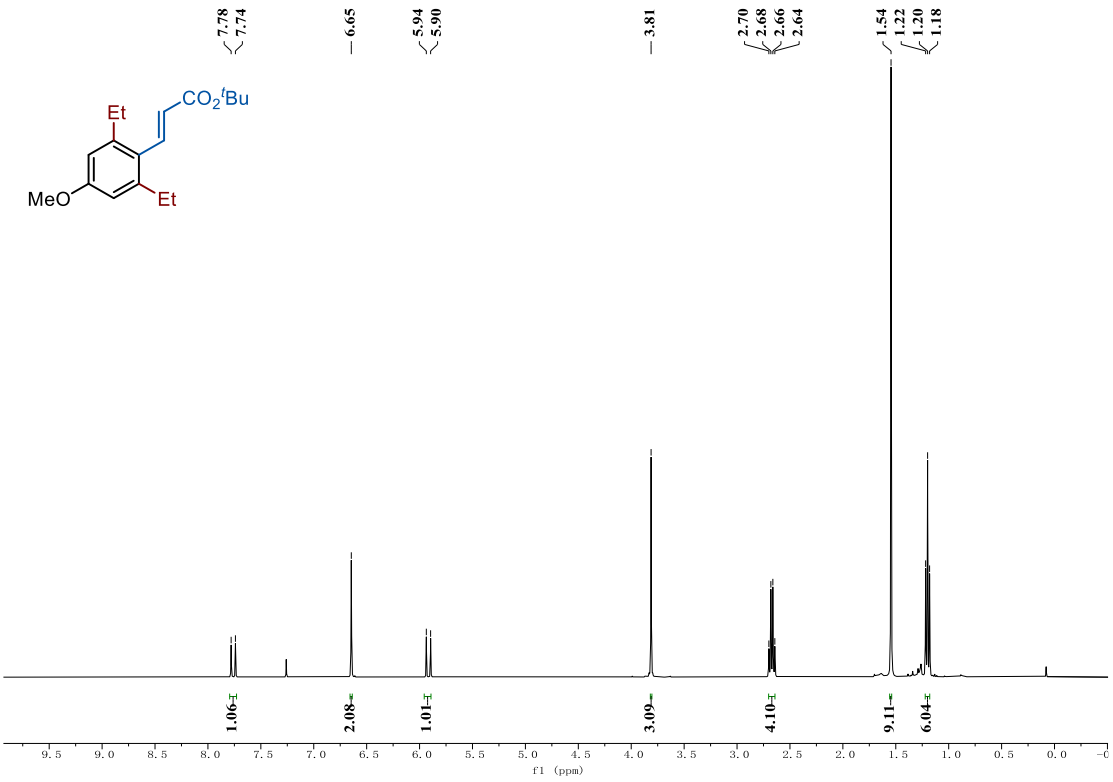
^{1}H NMR of **4ba** (400 MHz, $CDCl_3$)



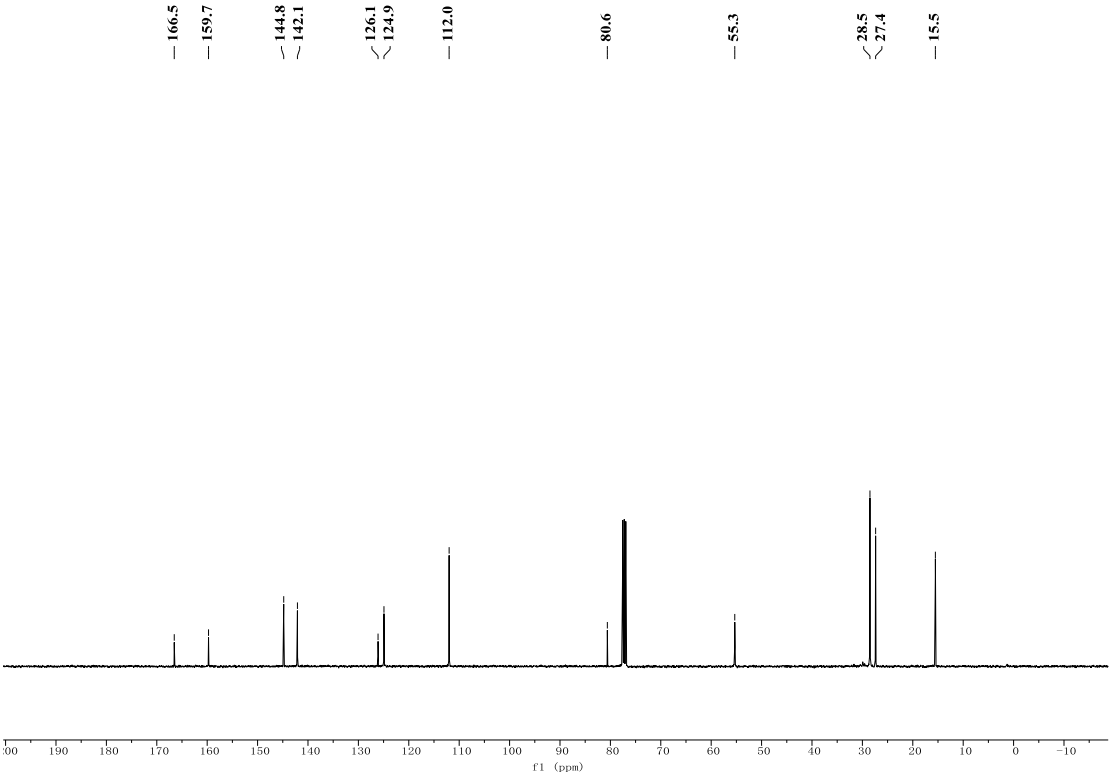
^{13}C NMR of **4ba** (100 MHz, $CDCl_3$)



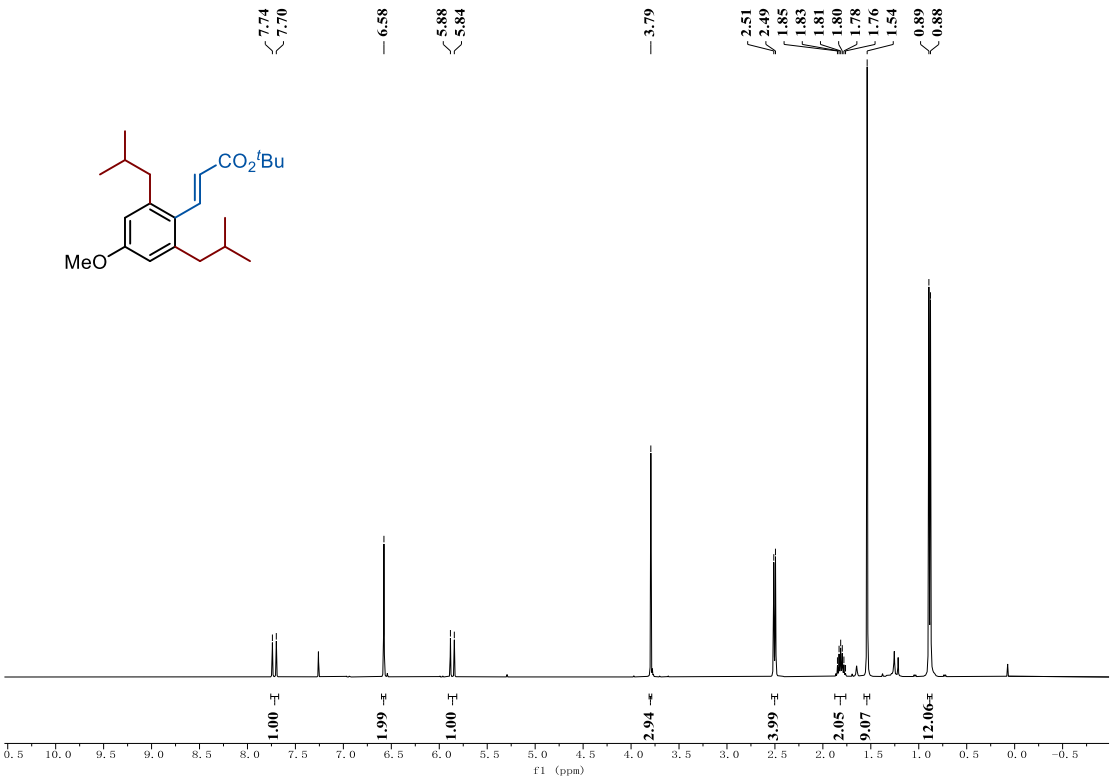
^{1}H NMR of **4bb** (400 MHz, $CDCl_3$)



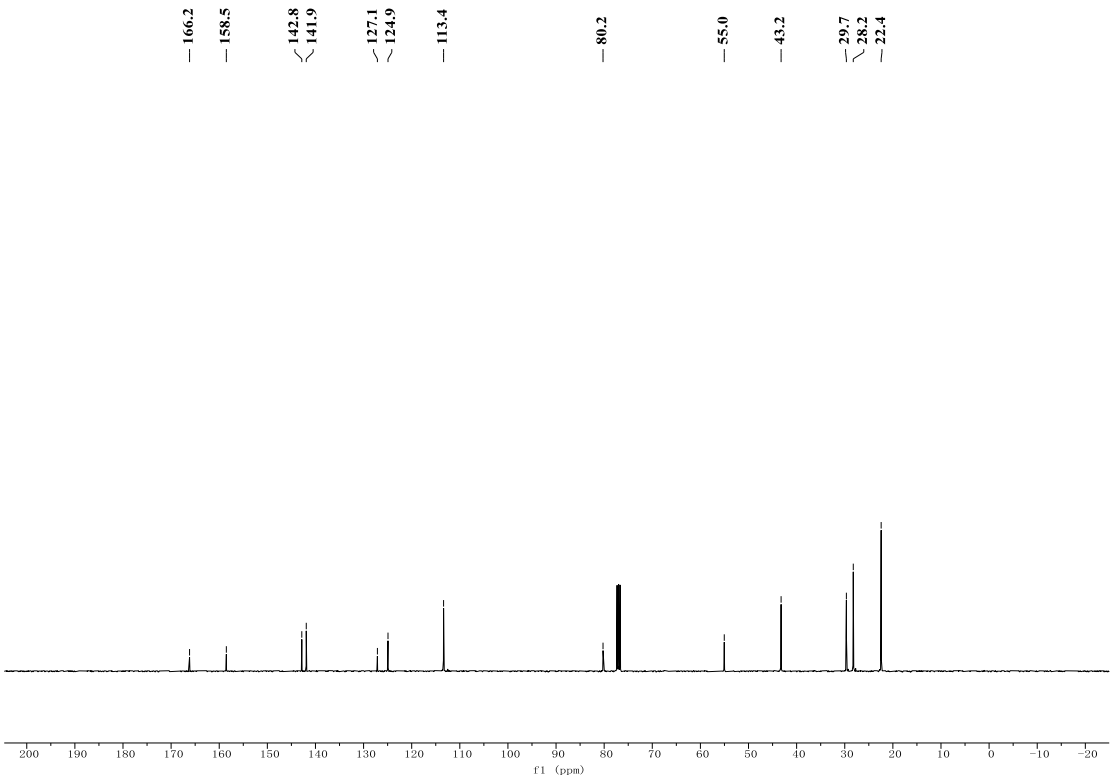
^{13}C NMR of **4bb** (100 MHz, $CDCl_3$)



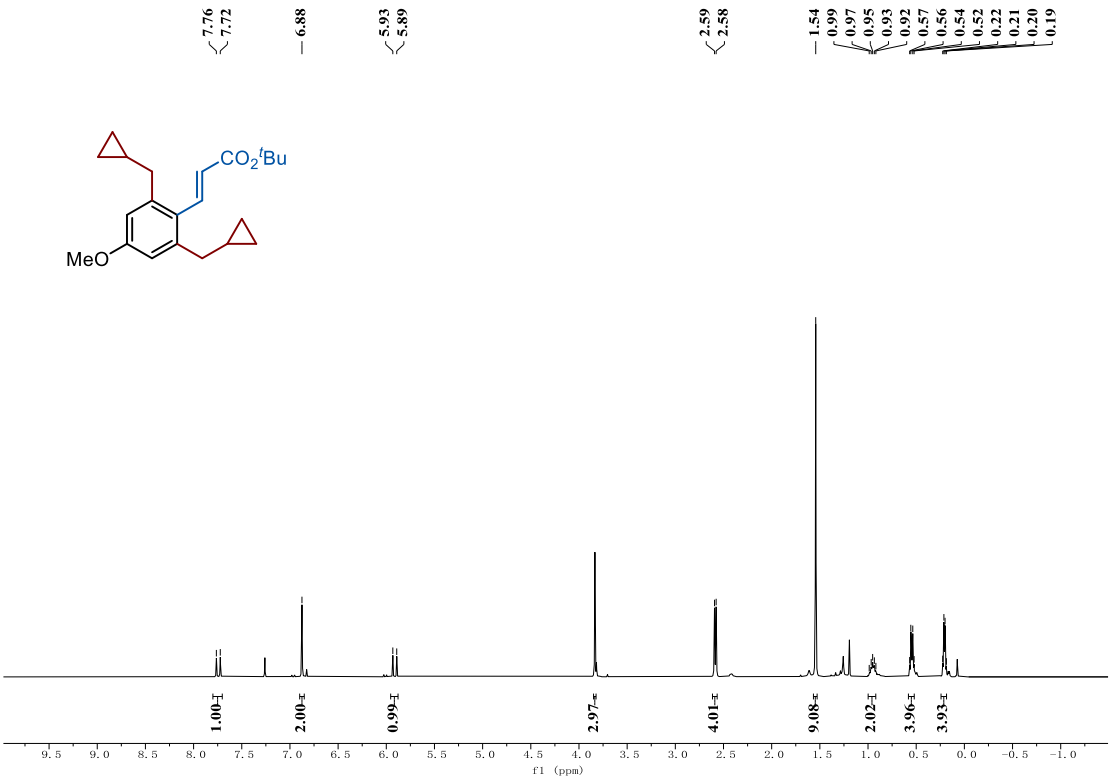
^{1}H NMR of **4bc** (400 MHz, $CDCl_3$)



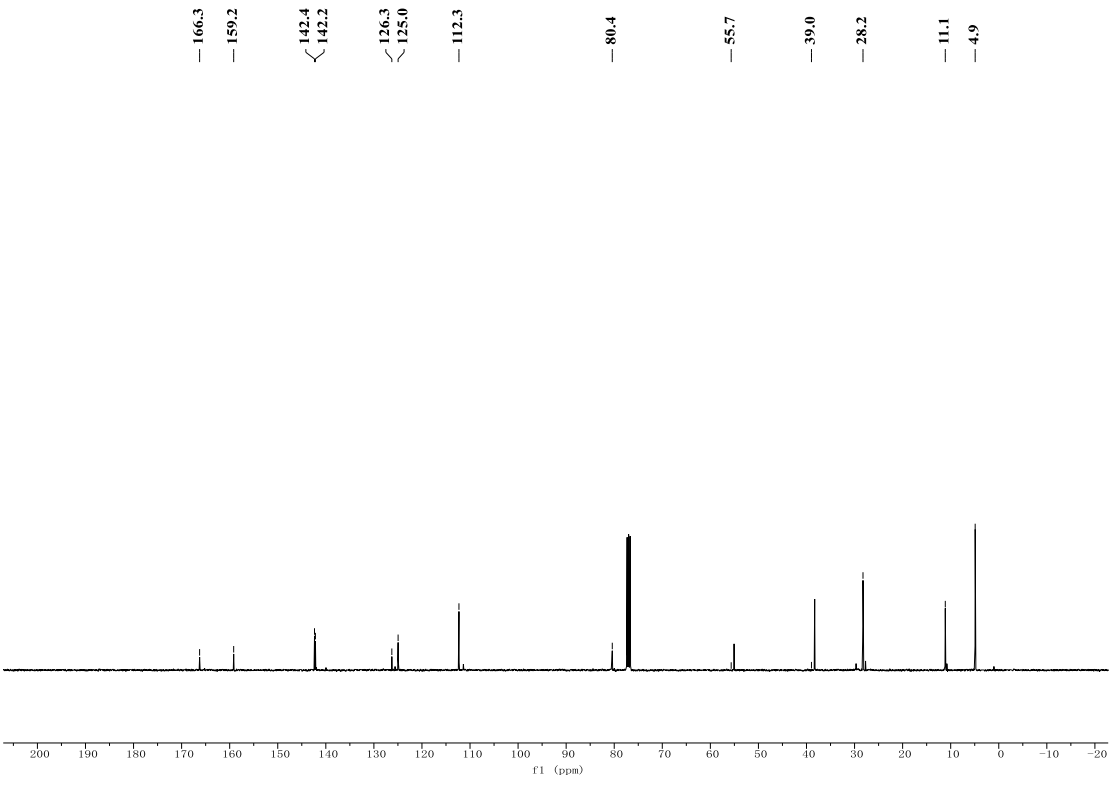
^{13}C NMR of **4bc** (100 MHz, $CDCl_3$)



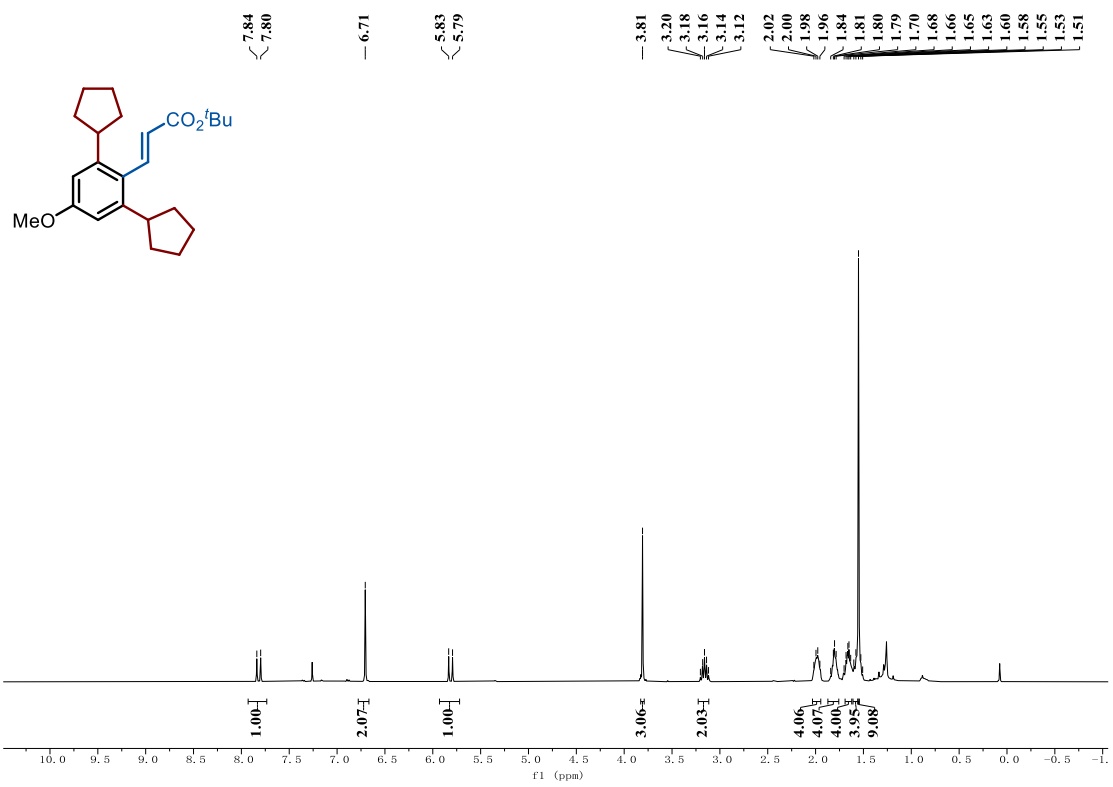
^{1}H NMR of **4bd** (400 MHz, $CDCl_3$)



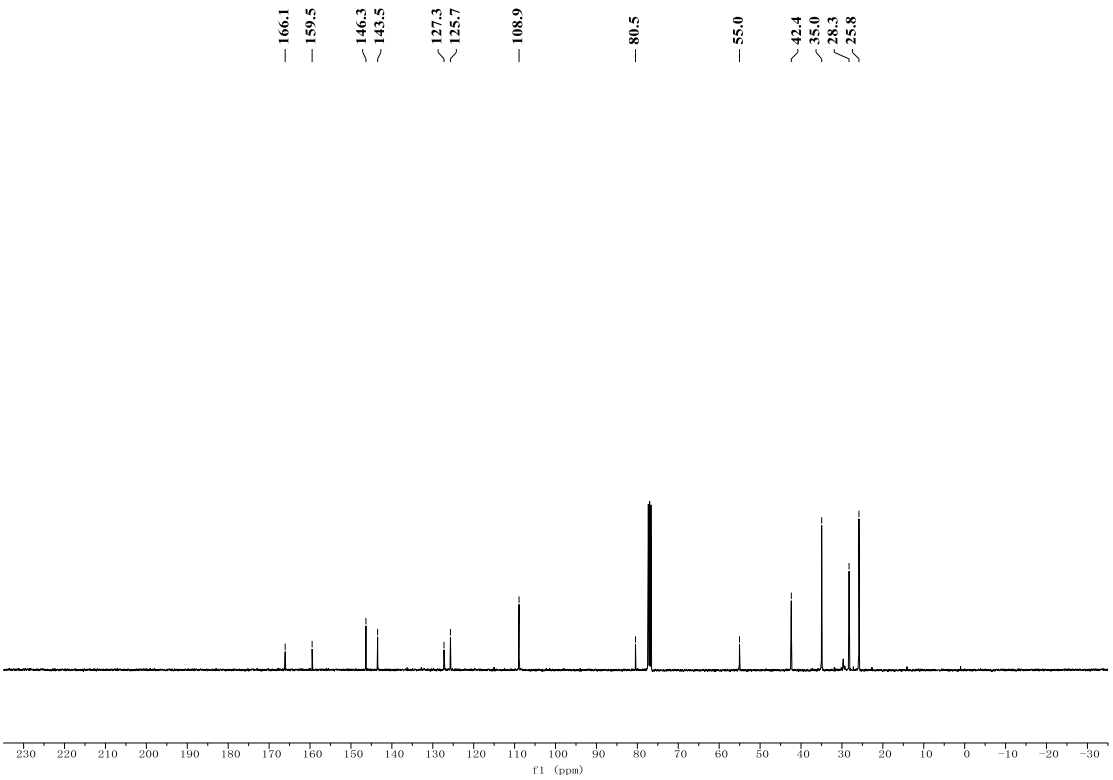
^{13}C NMR of **4bd** (100 MHz, $CDCl_3$)



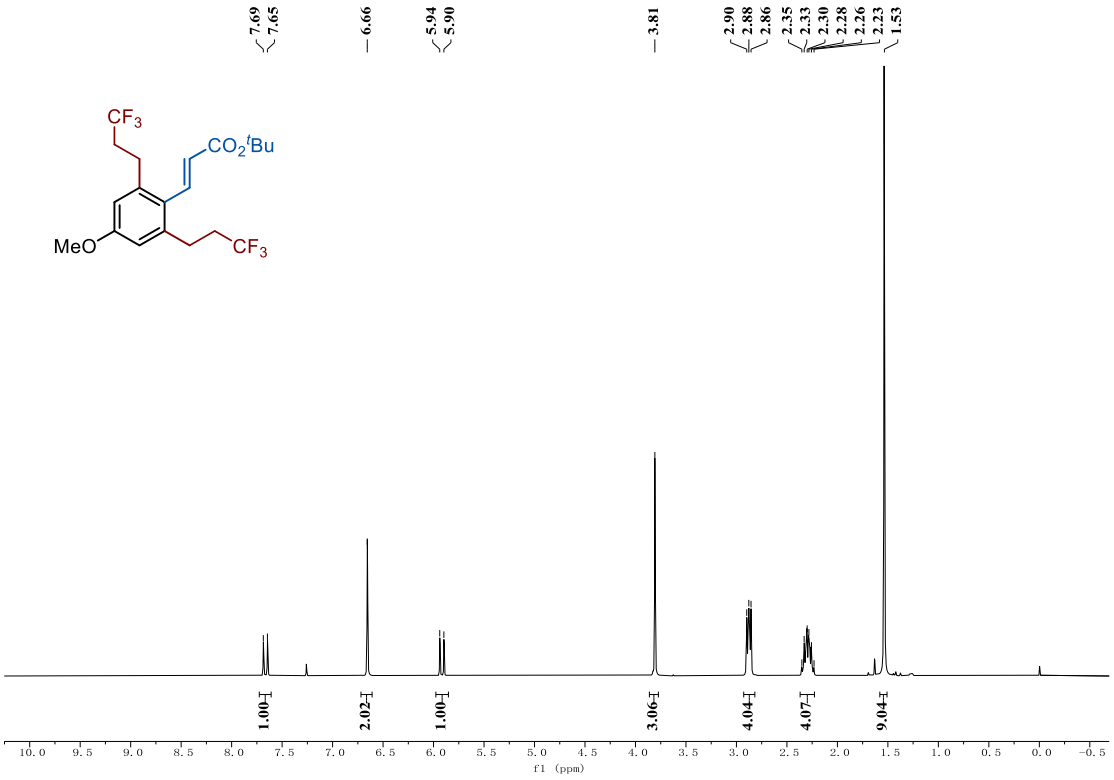
^{1}H NMR of **4be** (400 MHz, $CDCl_3$)



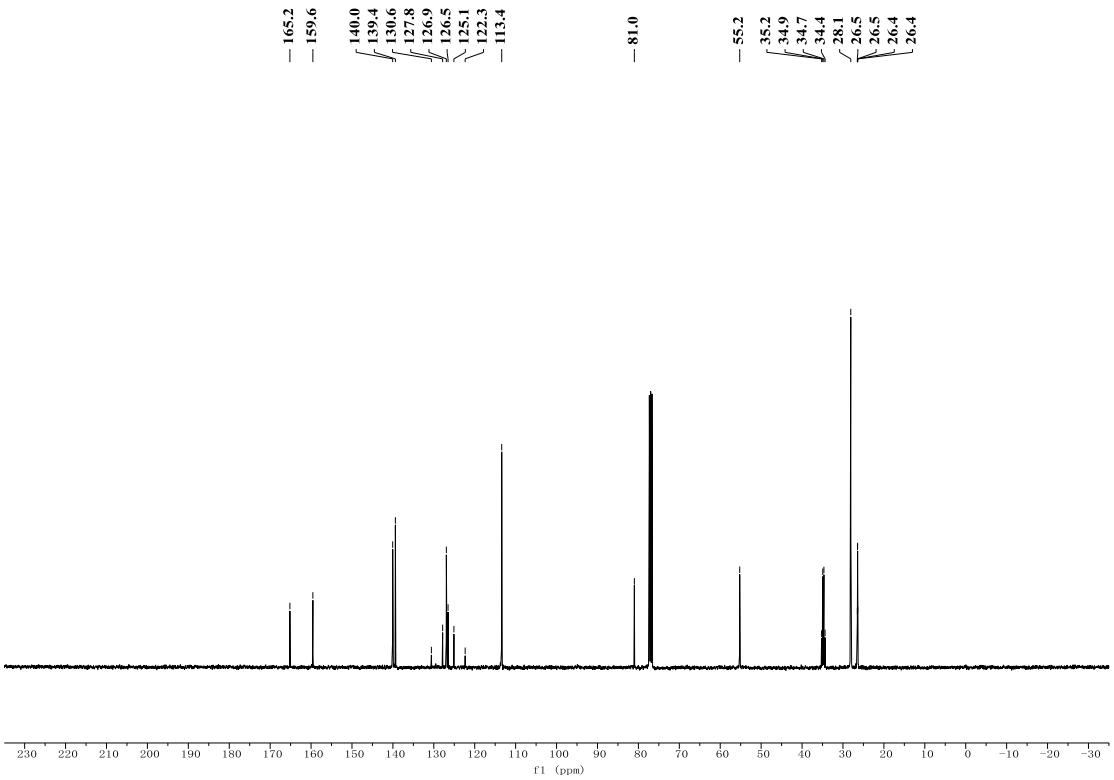
^{13}C NMR of **4be** (100 MHz, $CDCl_3$)



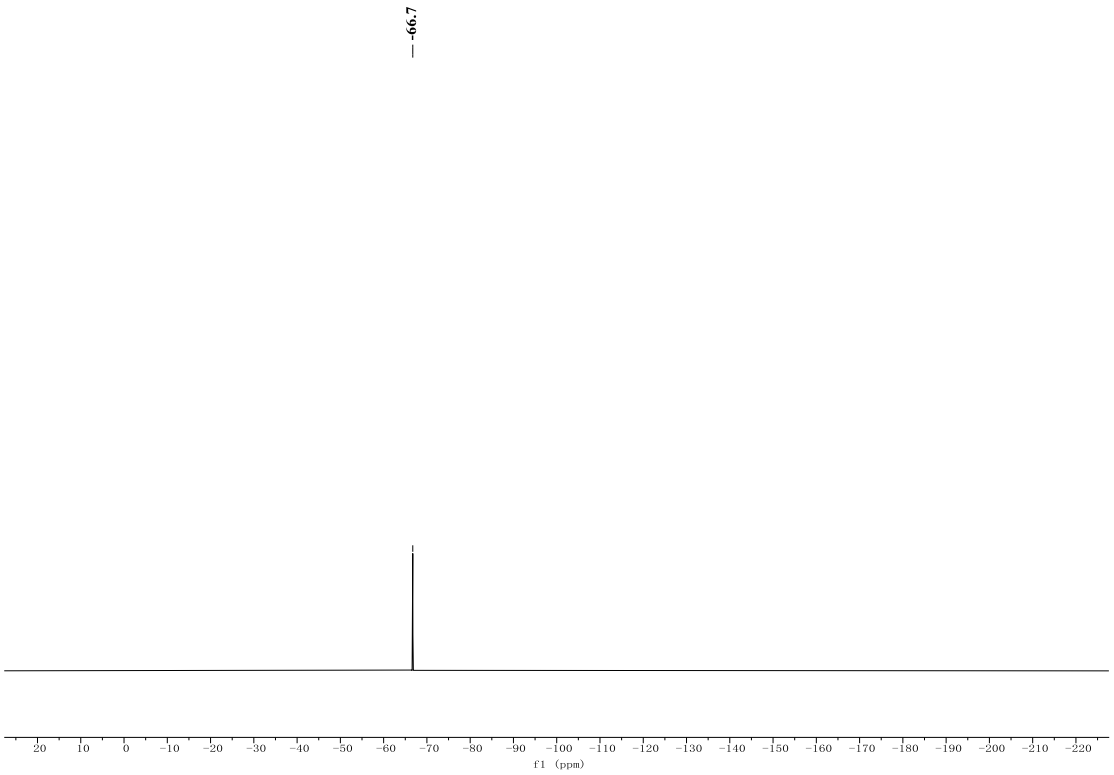
^{1}H NMR of **4bf** (400 MHz, $CDCl_3$)



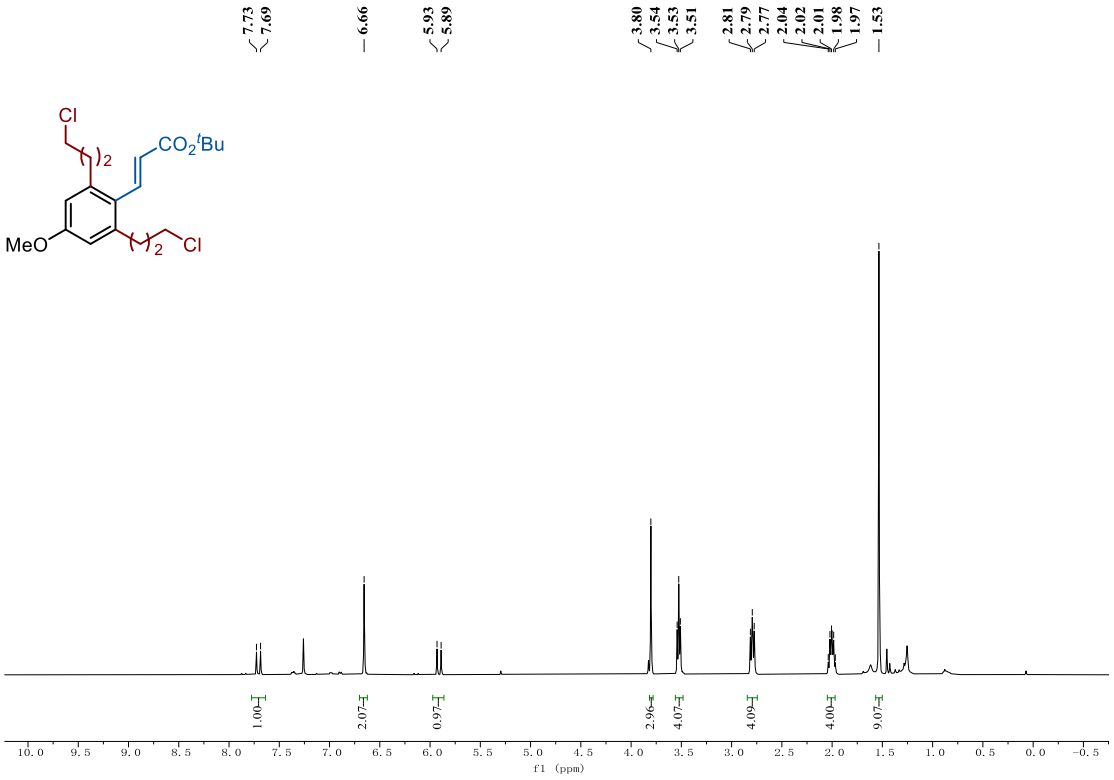
^{13}C NMR of **4bf** (100 MHz, $CDCl_3$)



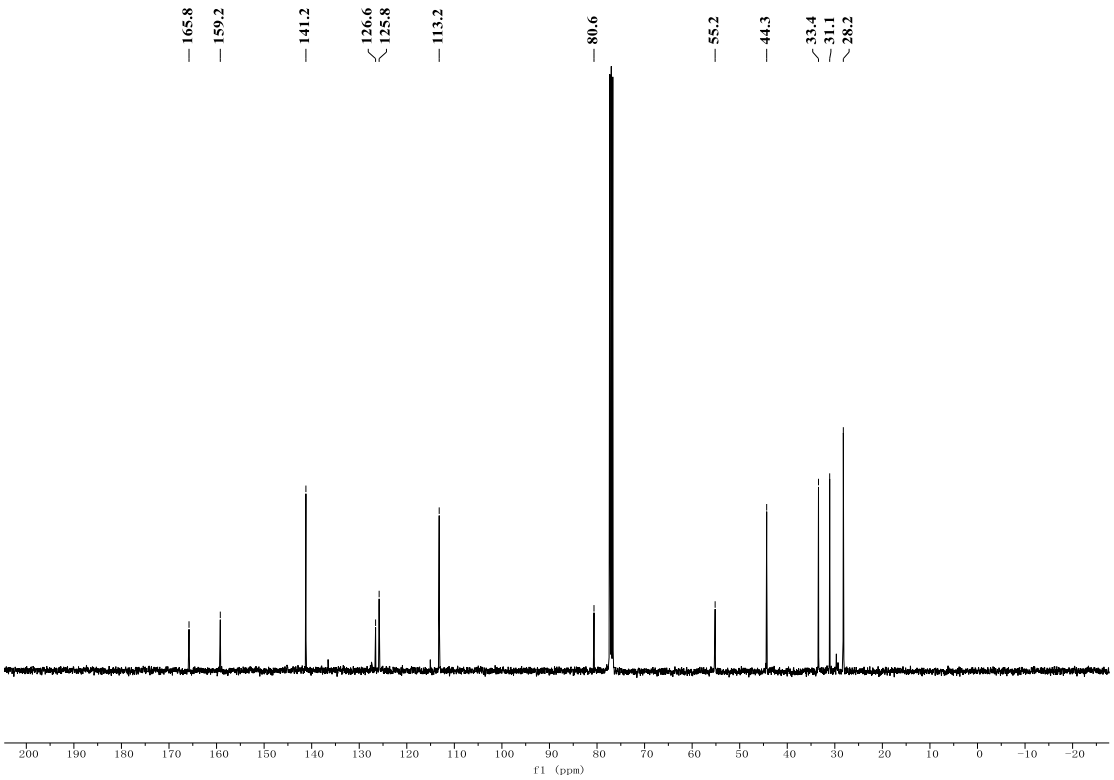
^{9}F NMR of **4bf** (400 MHz, $CDCl_3$)



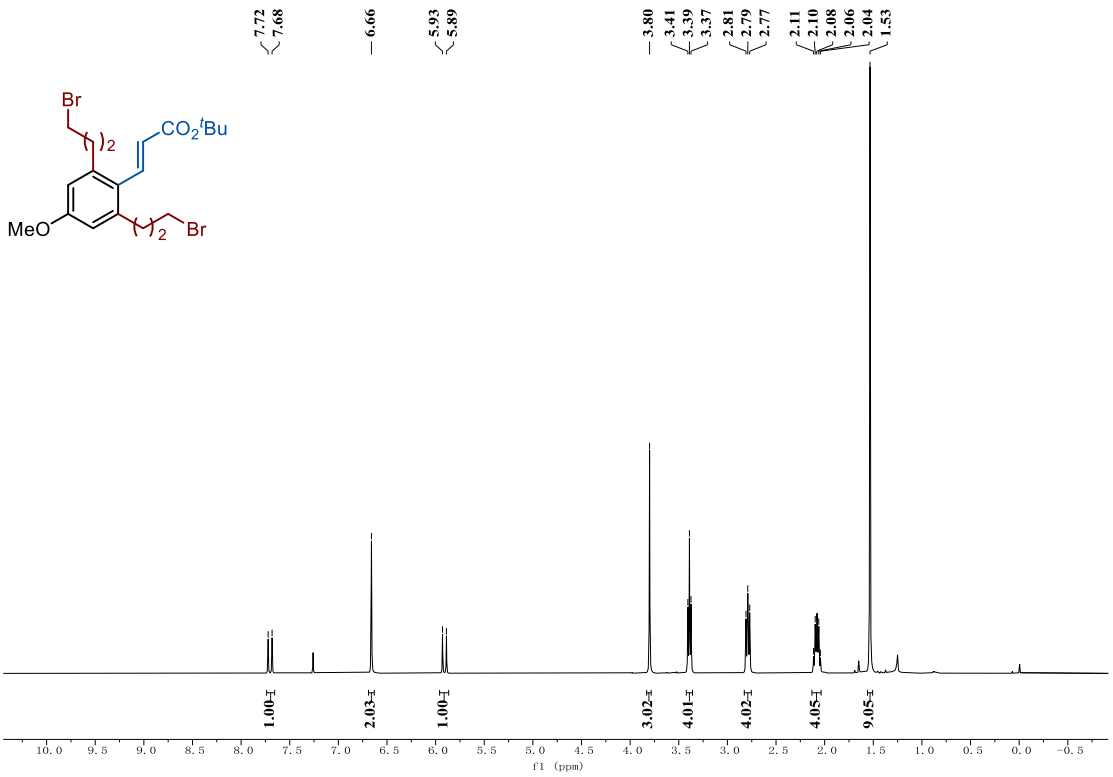
^{1}H NMR of **4bg** (400 MHz, $CDCl_3$)



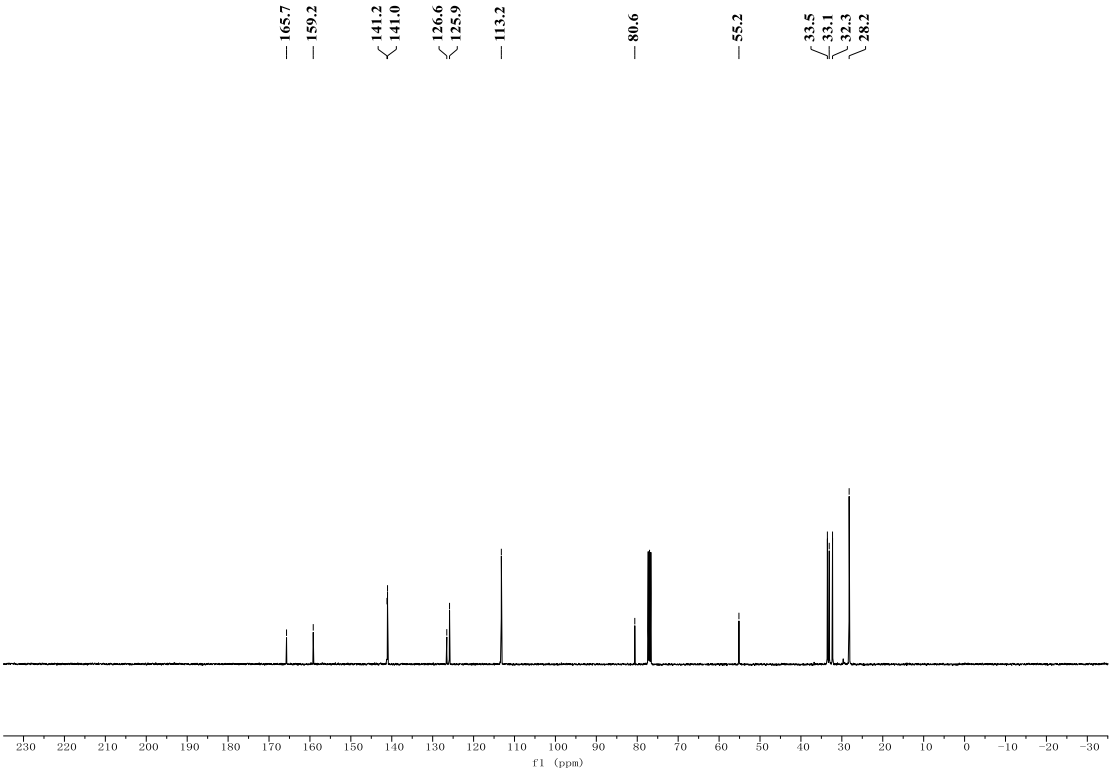
^{13}C NMR of **4bg** (100 MHz, $CDCl_3$)



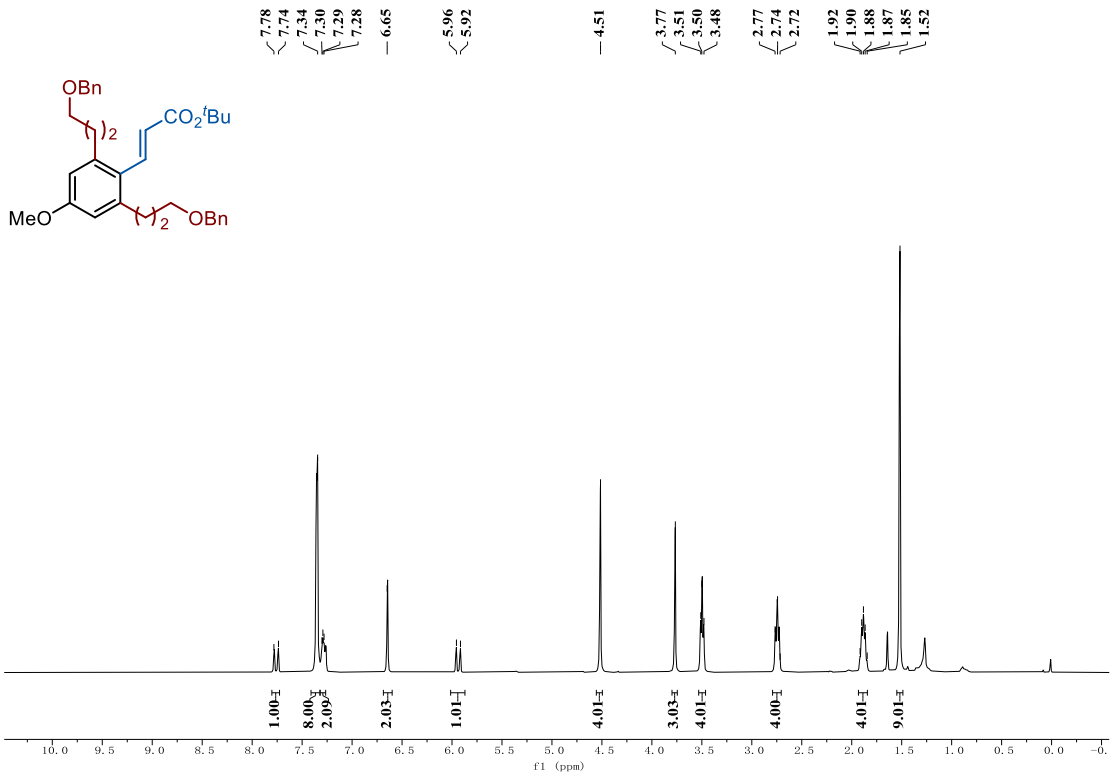
^{1}H NMR of **4bh** (400 MHz, $CDCl_3$)



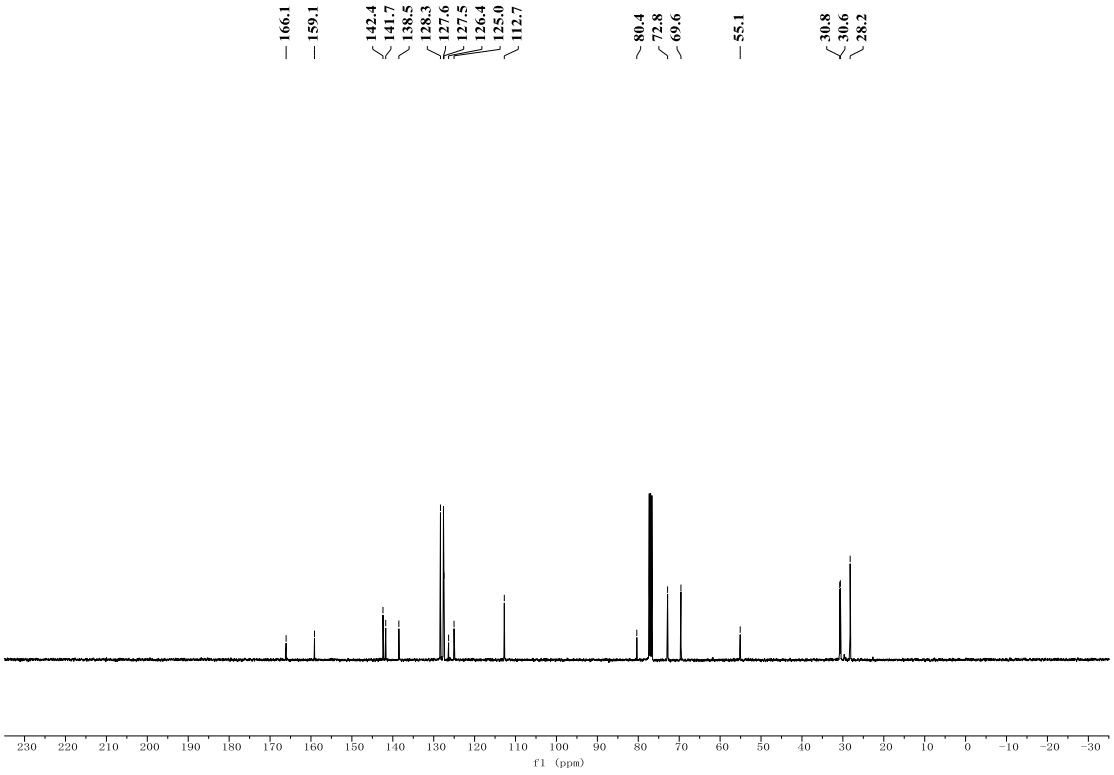
^{13}C NMR of **4bh** (100 MHz, $CDCl_3$)



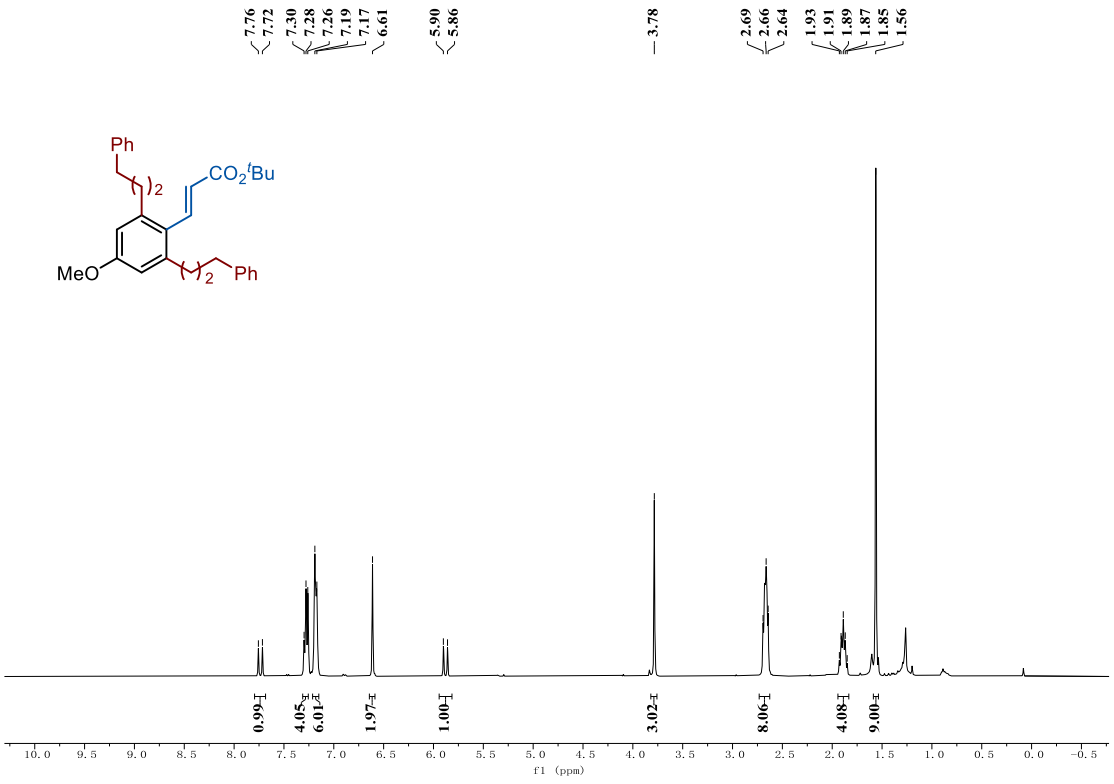
^{1}H NMR of **4bi** (400 MHz, $CDCl_3$)



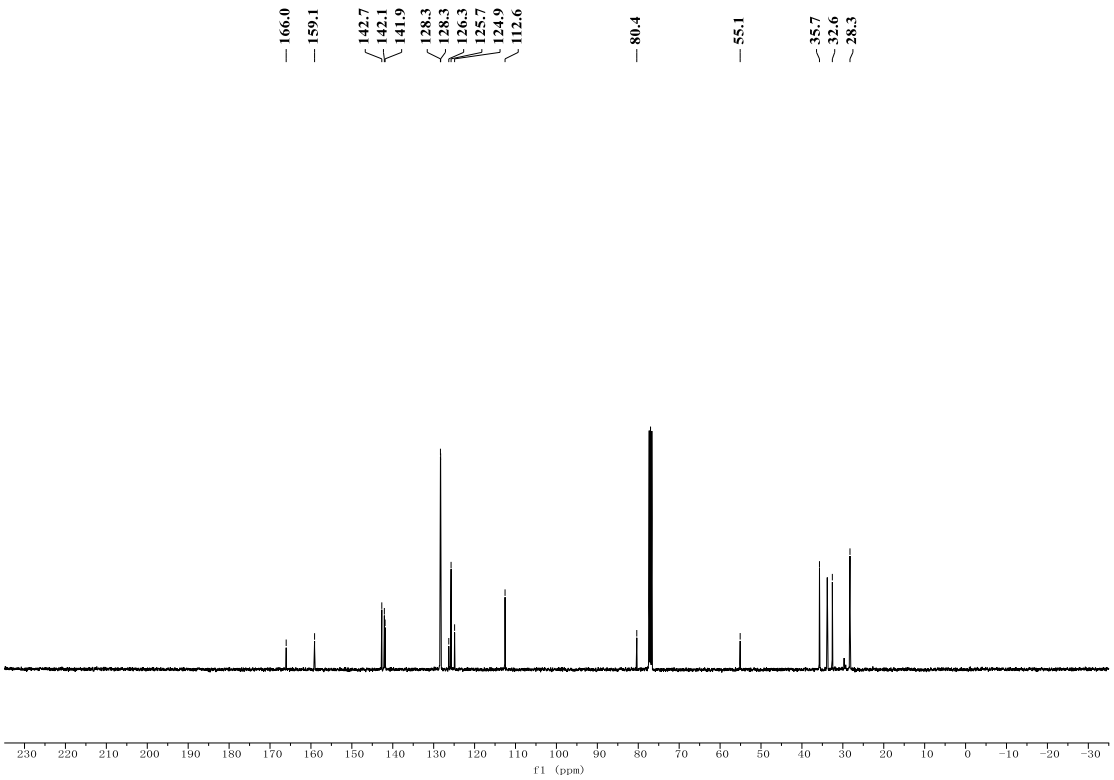
^{13}C NMR of **4bi** (100 MHz, $CDCl_3$)



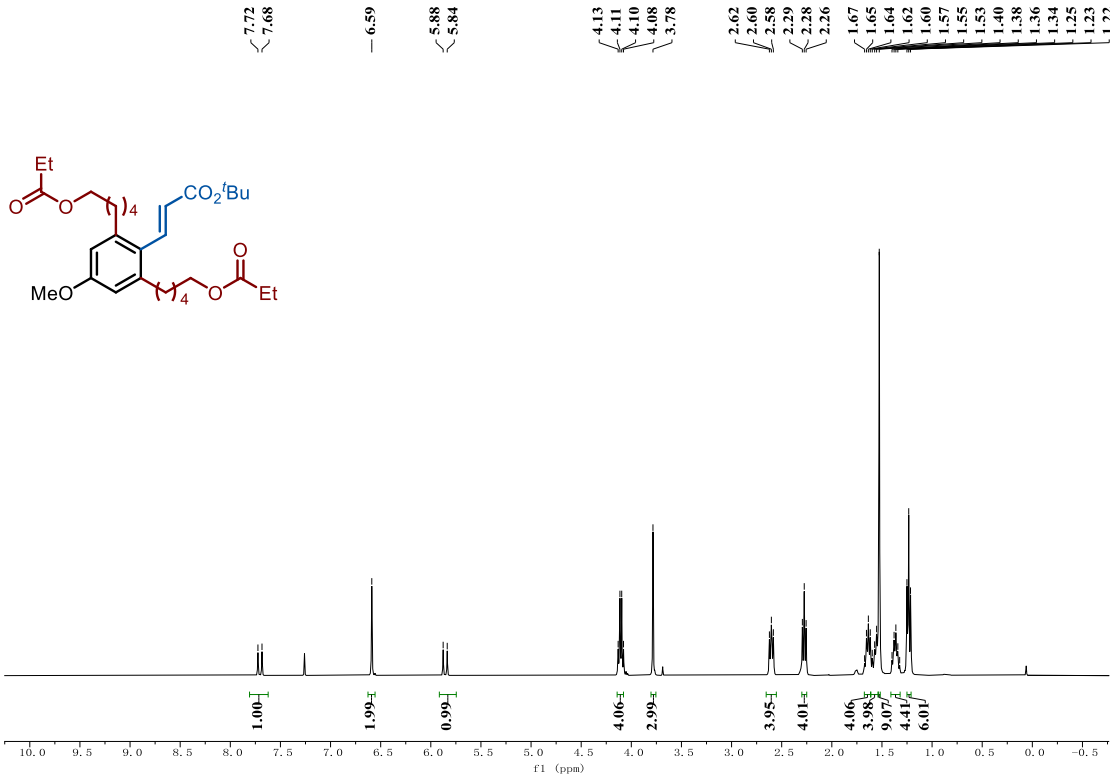
^{1}H NMR of **4bj** (400 MHz, $CDCl_3$)



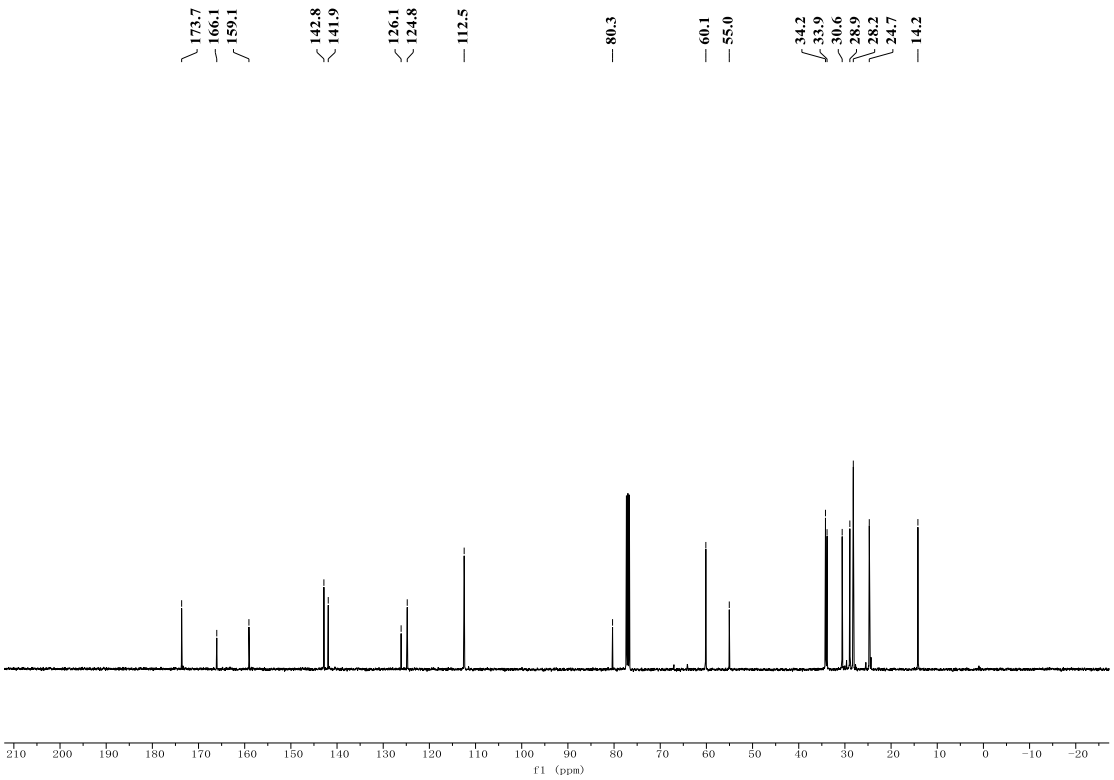
^{13}C NMR of **4bj** (100 MHz, $CDCl_3$)



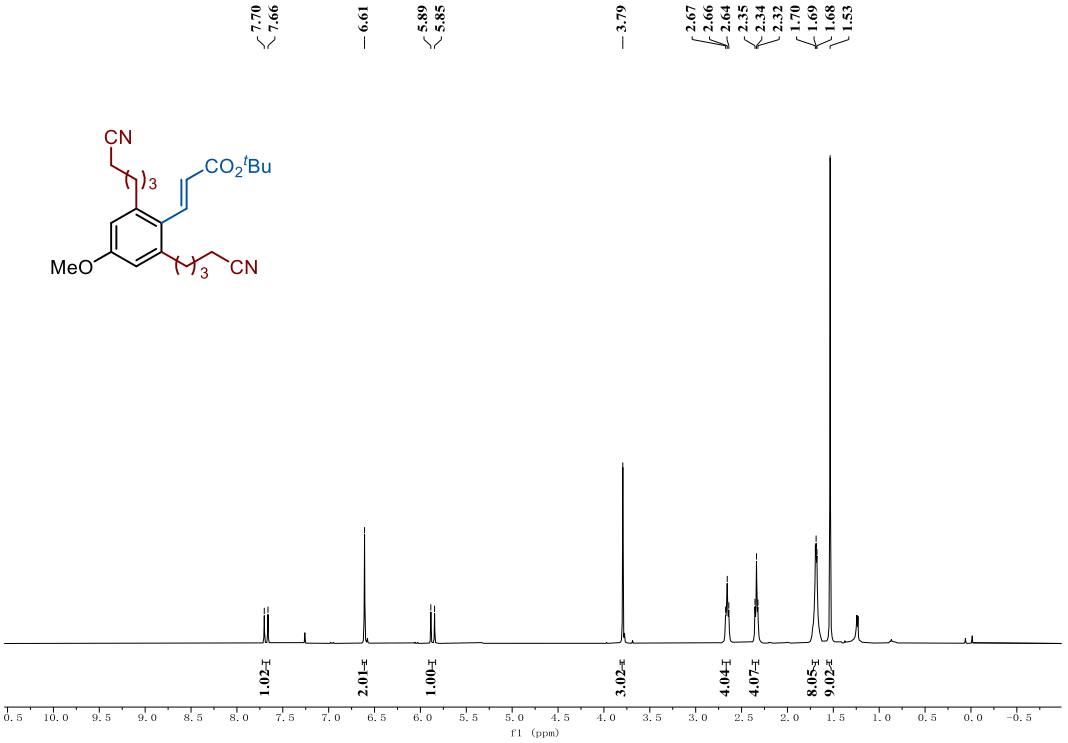
^{1}H NMR of **4bk** (400 MHz, $CDCl_3$)



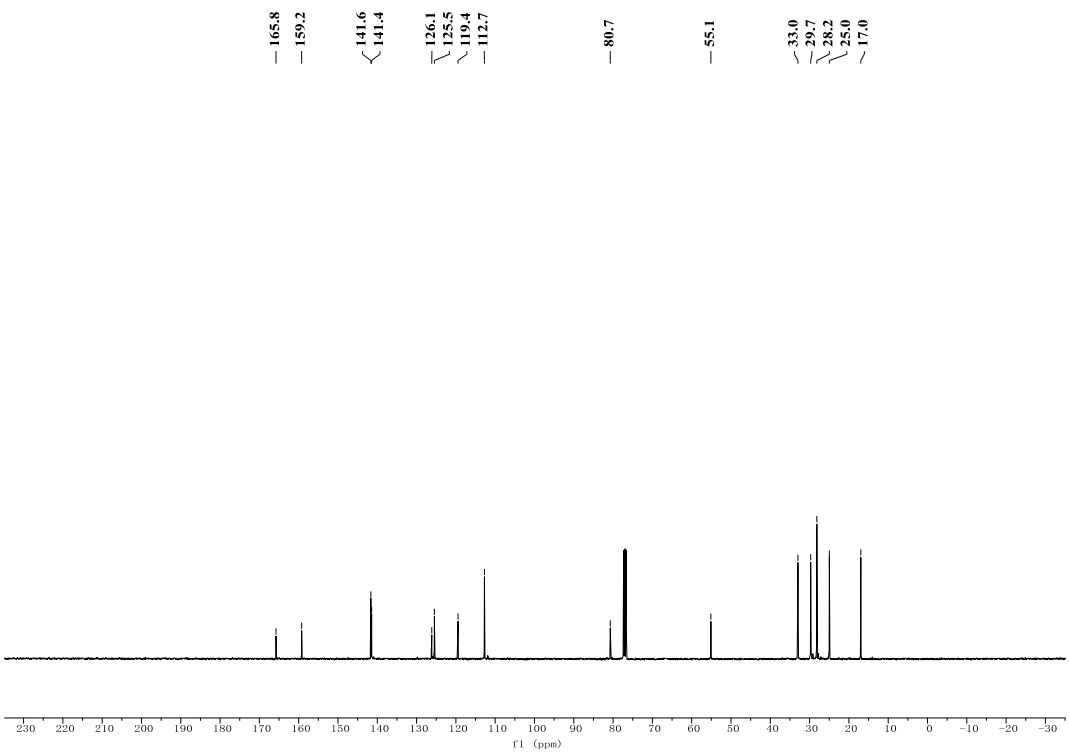
^{13}C NMR of **4bk** (100 MHz, $CDCl_3$)



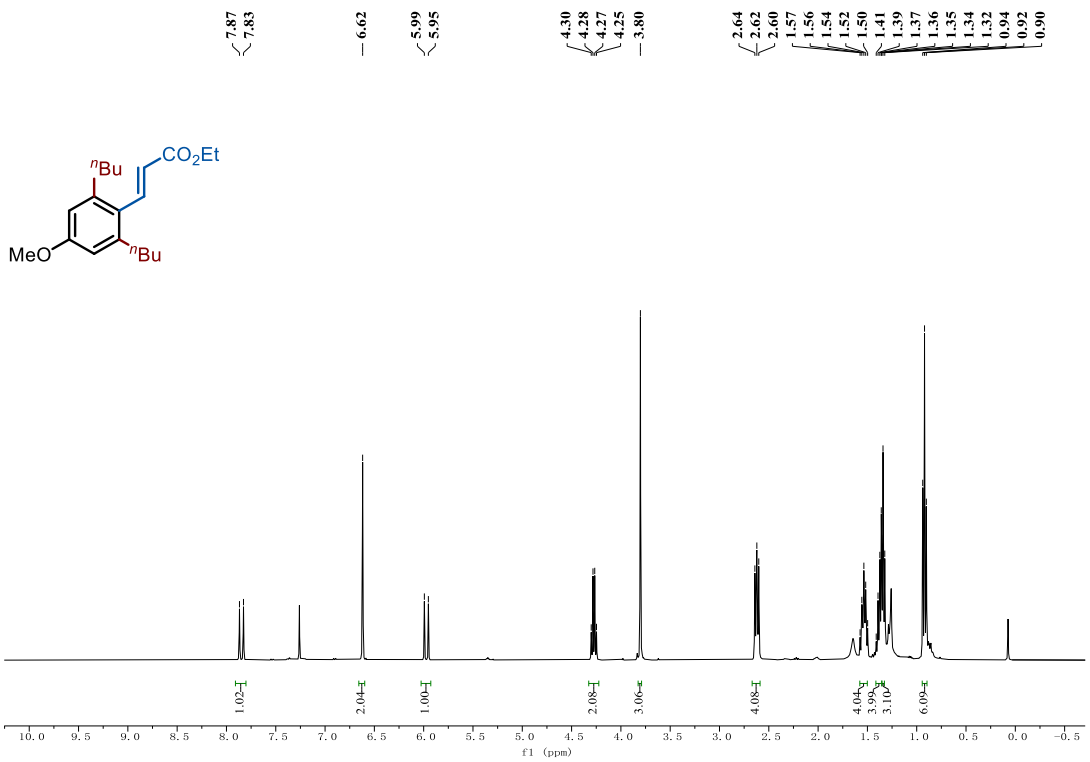
^{1}H NMR of **4bl** (400 MHz, $CDCl_3$)



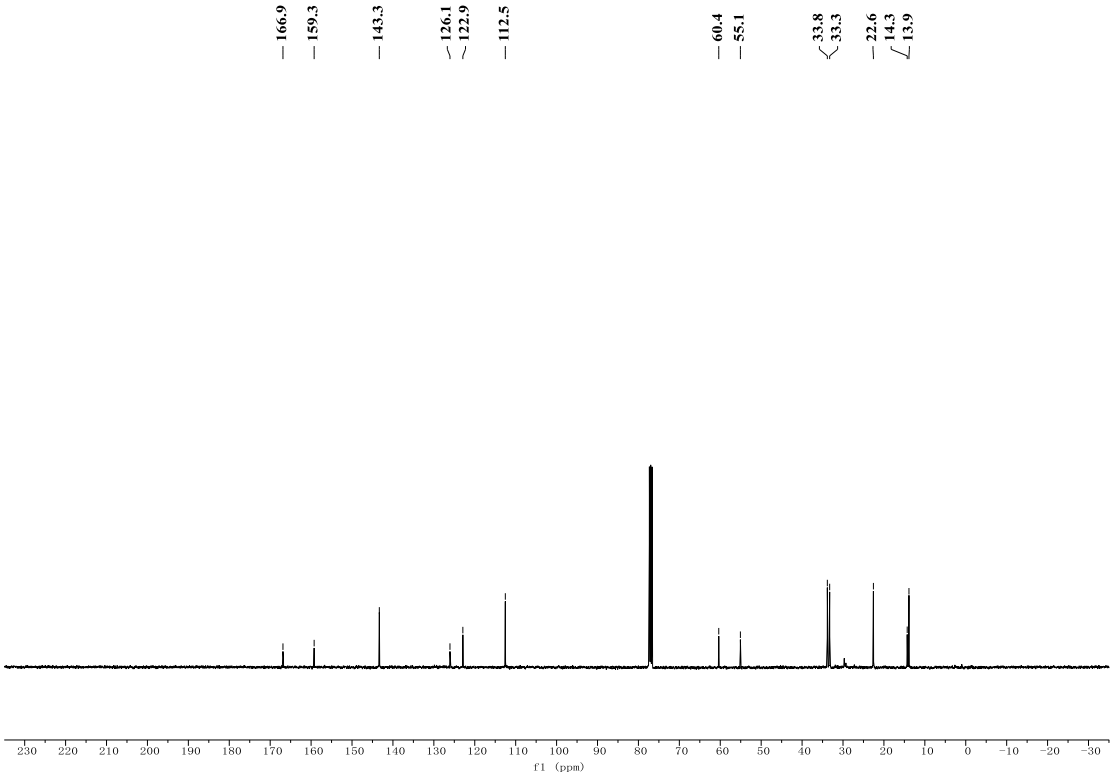
^{13}C NMR of **4bl** (100 MHz, $CDCl_3$)



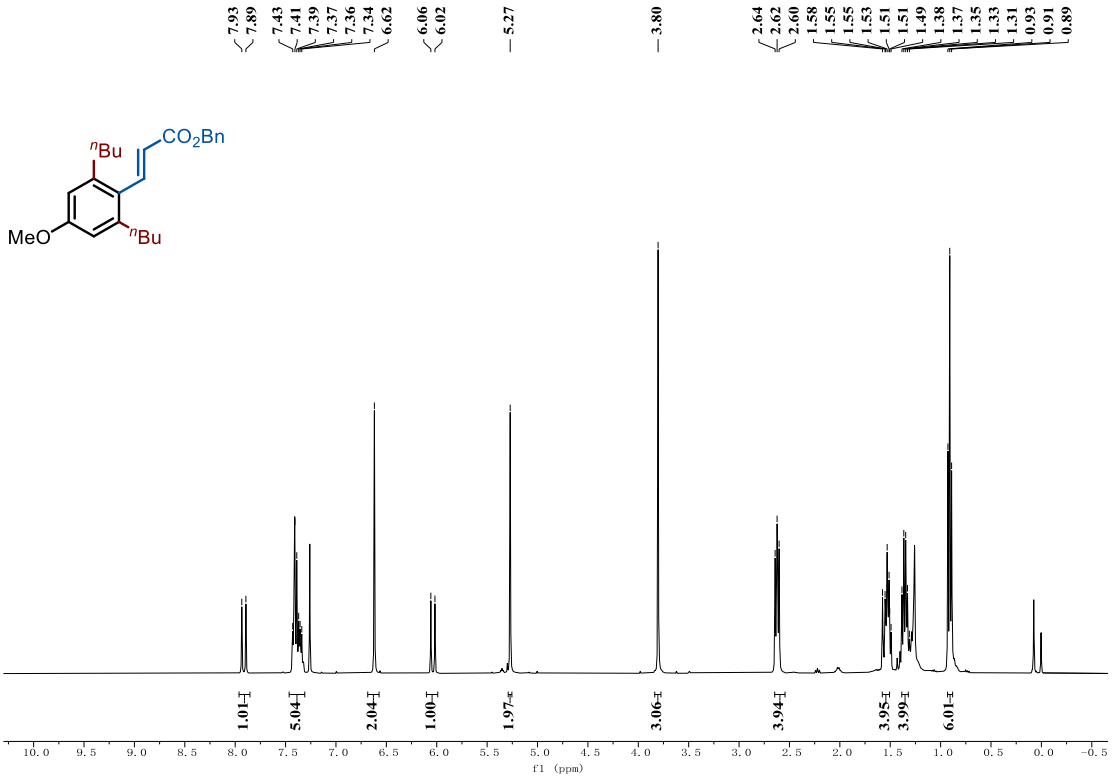
^{1}H NMR of **4ca** (400 MHz, $CDCl_3$)



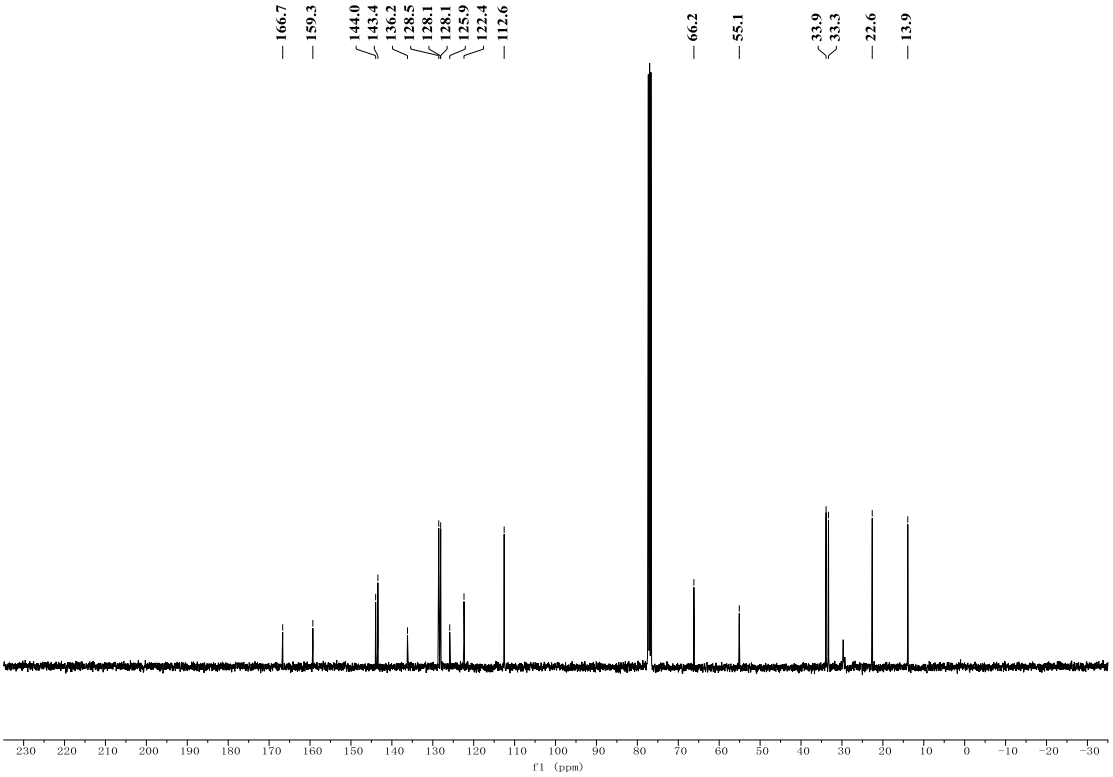
^{13}C NMR of **4ca** (100 MHz, $CDCl_3$)



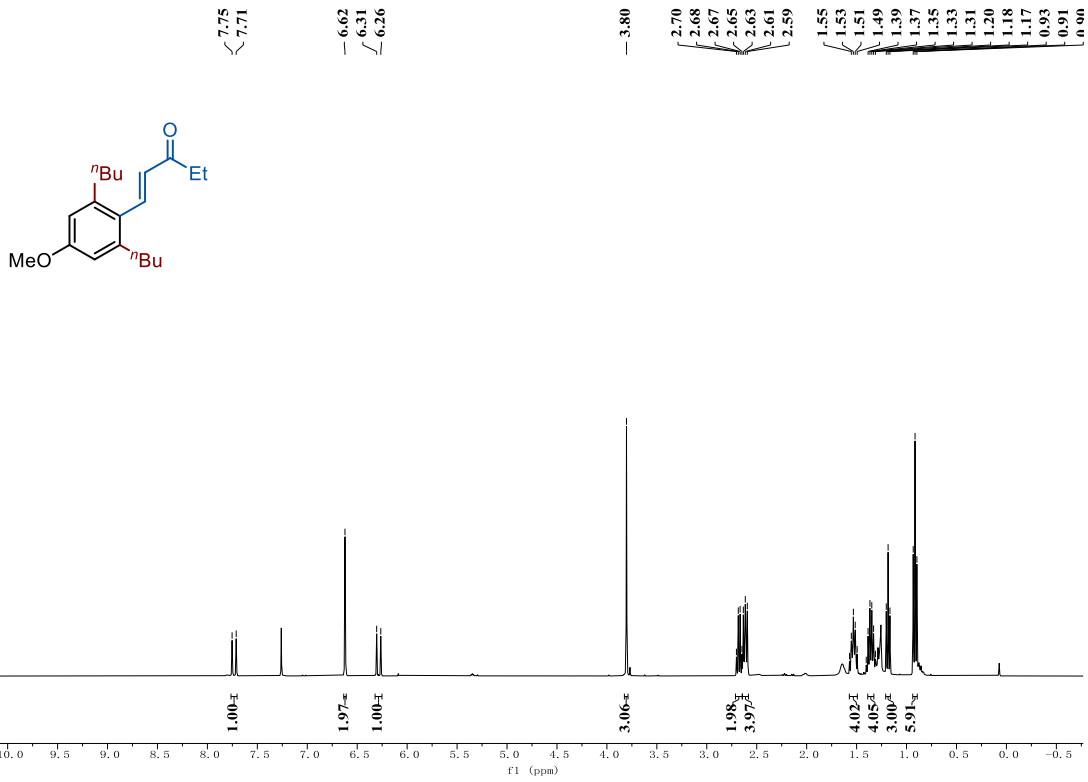
^{1}H NMR of **4cb** (400 MHz, $CDCl_3$)



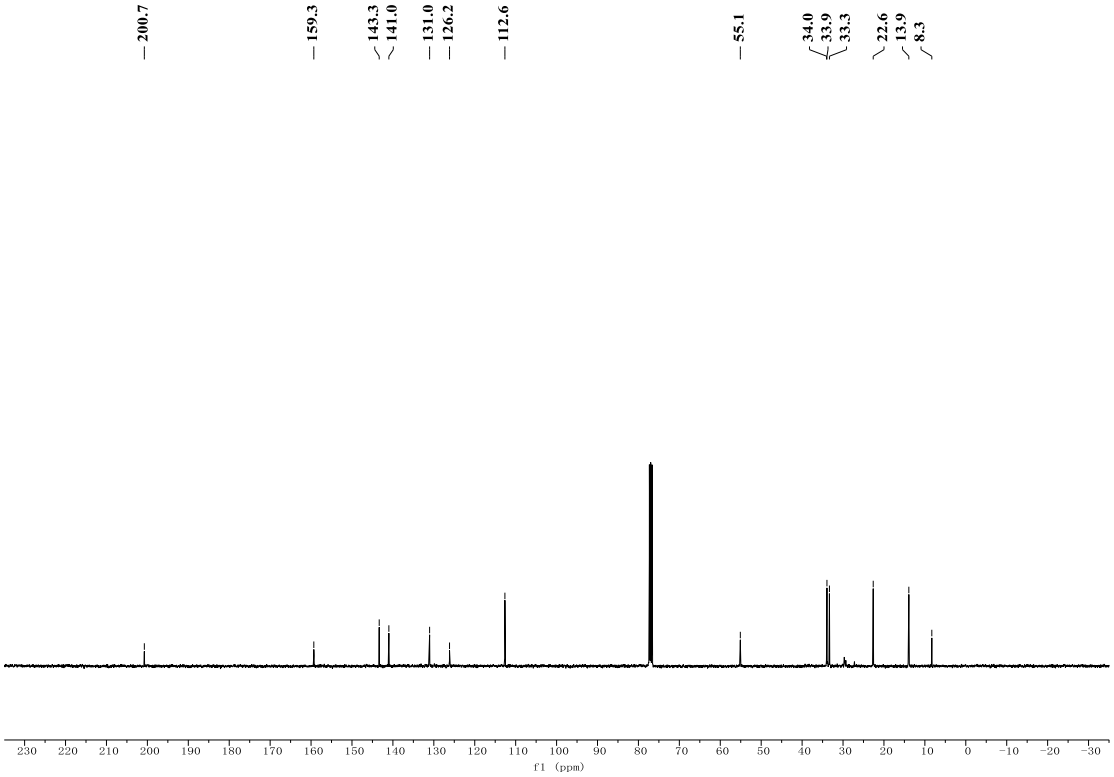
^{13}C NMR of **4cb** (100 MHz, $CDCl_3$)



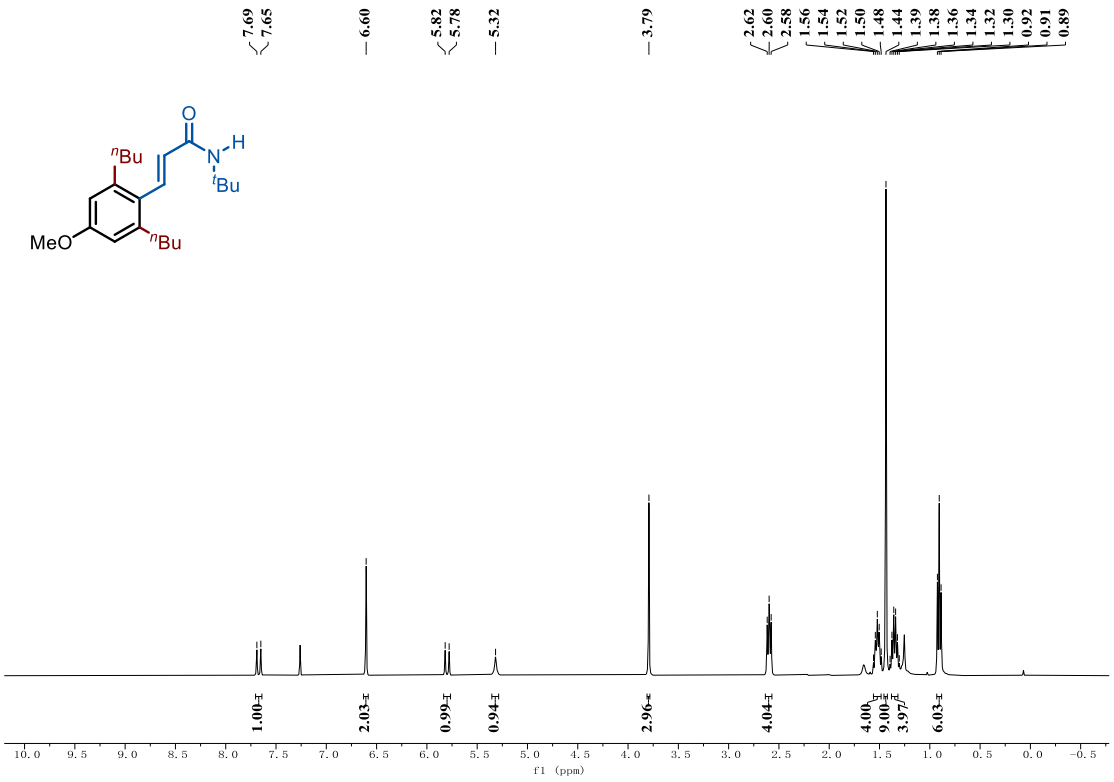
^{1}H NMR of **4cc** (400 MHz, $CDCl_3$)



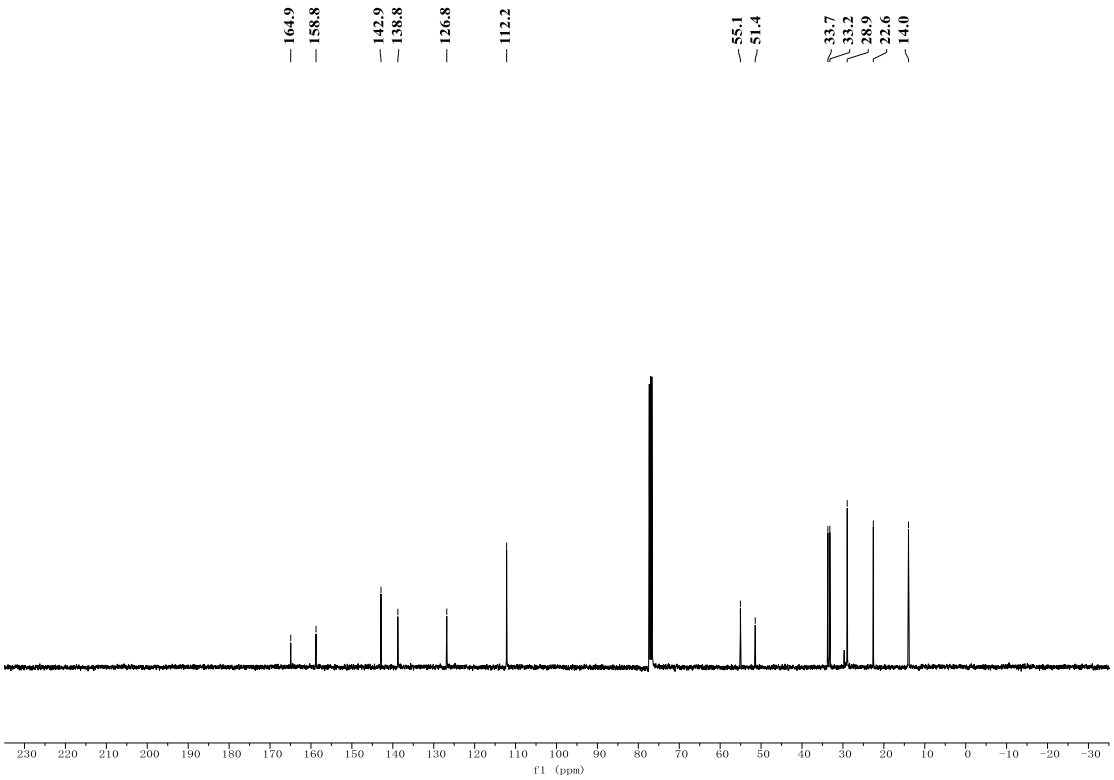
^{13}C NMR of **4cc** (100 MHz, $CDCl_3$)



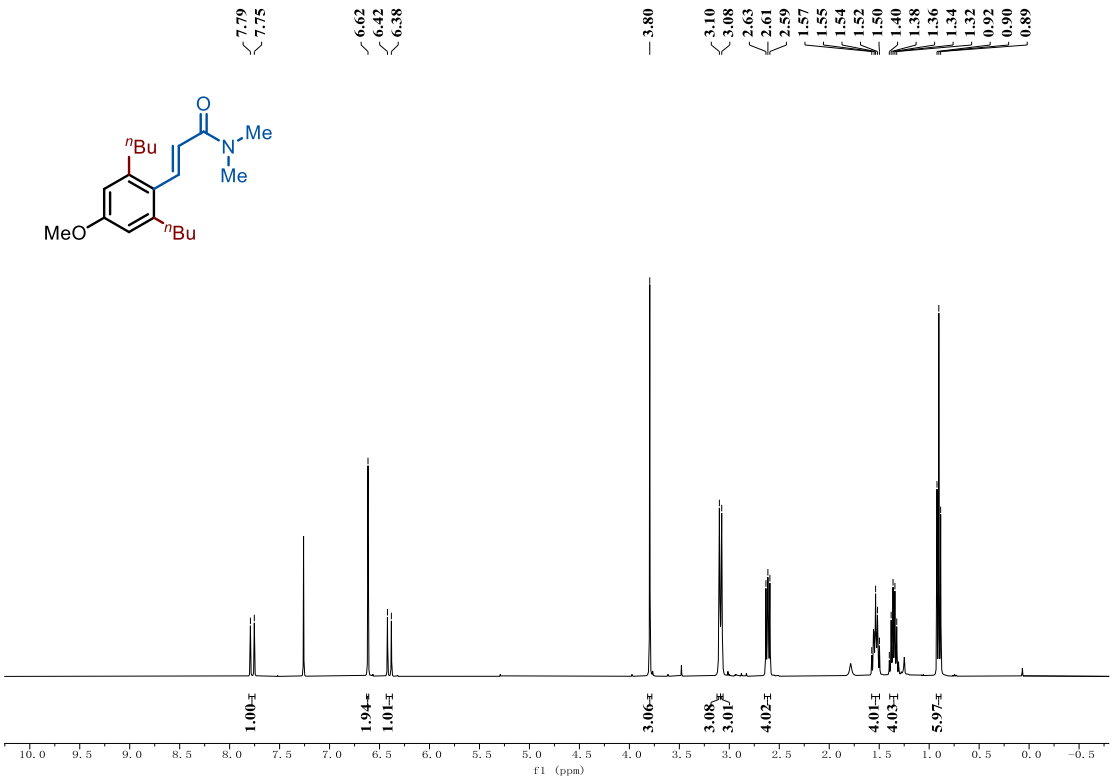
^{1}H NMR of **4cd** (400 MHz, $CDCl_3$)



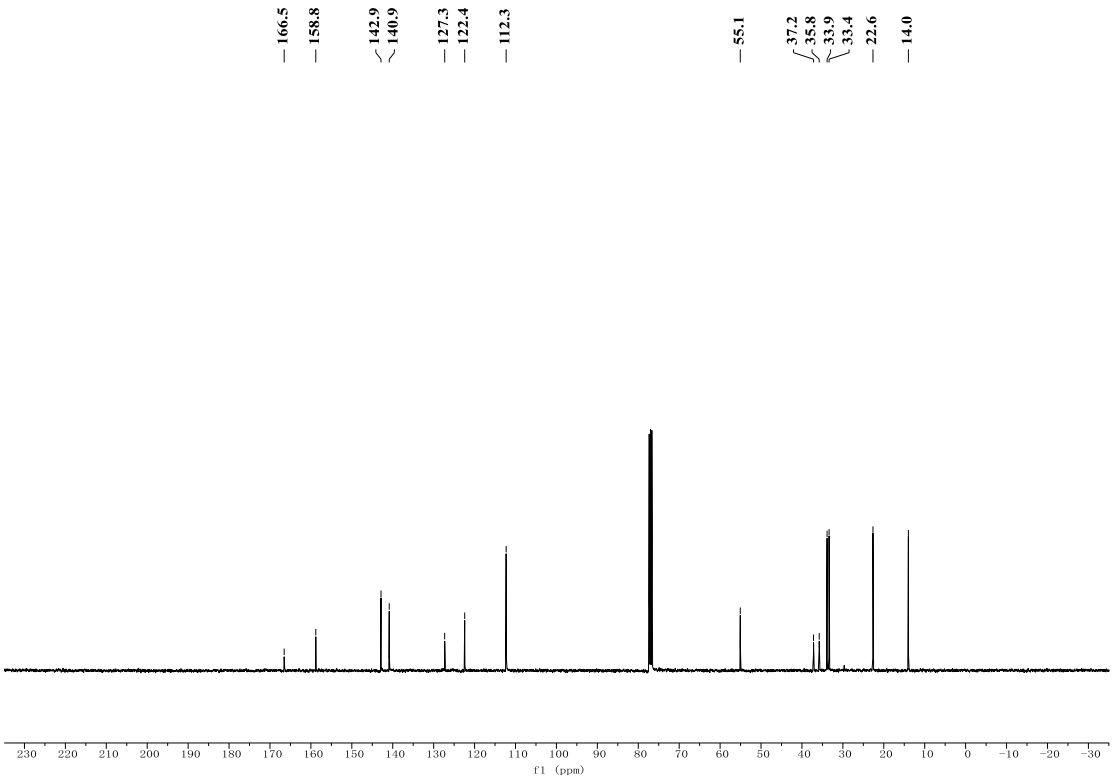
^{13}C NMR of **4cd** (100 MHz, $CDCl_3$)



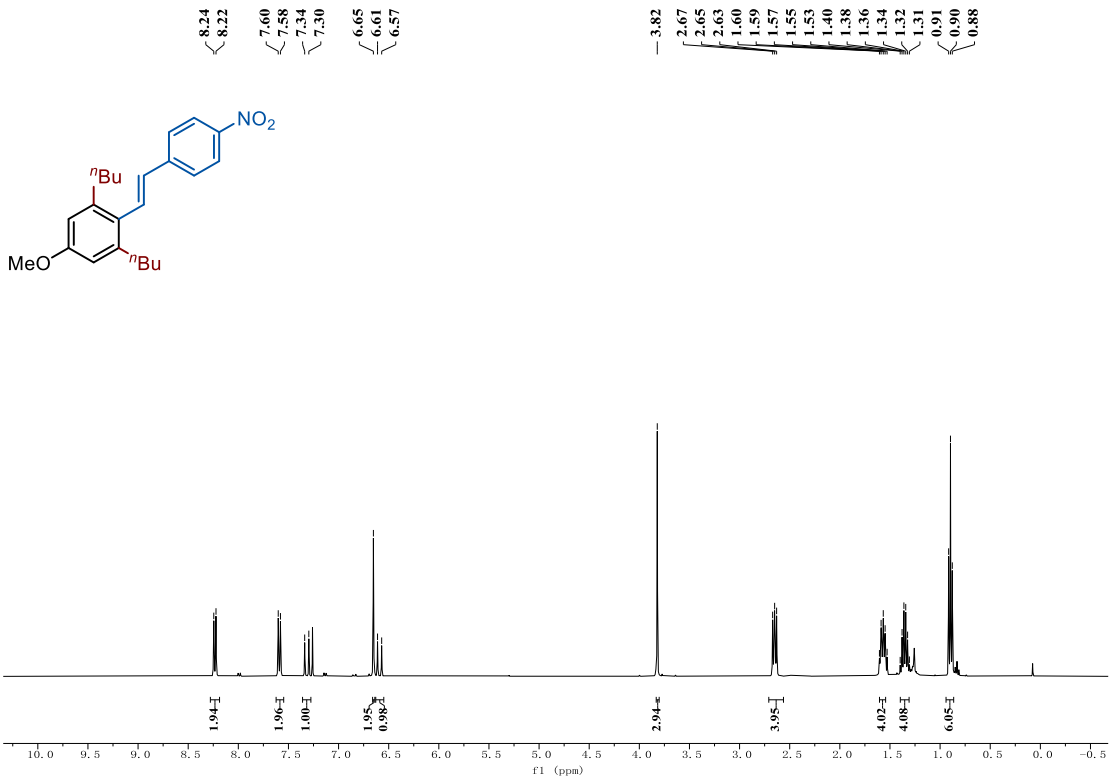
^{1}H NMR of **4ce**(400 MHz, $CDCl_3$)



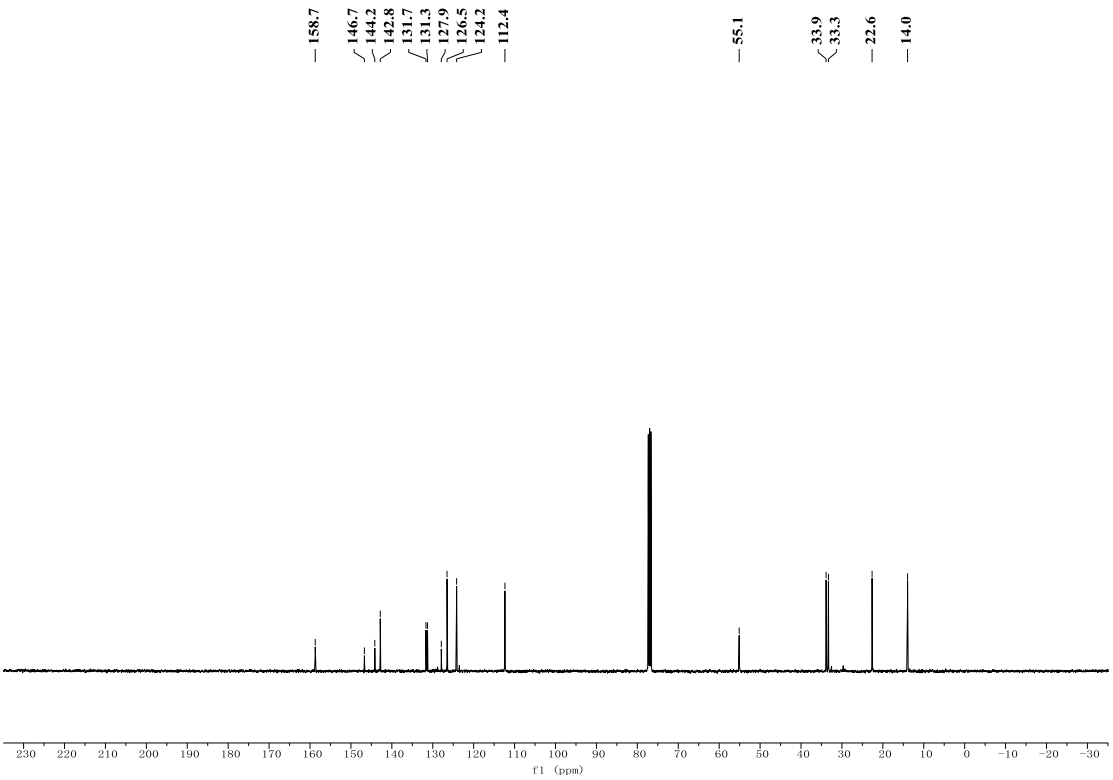
^{13}C NMR of **4ce** (100 MHz, $CDCl_3$)



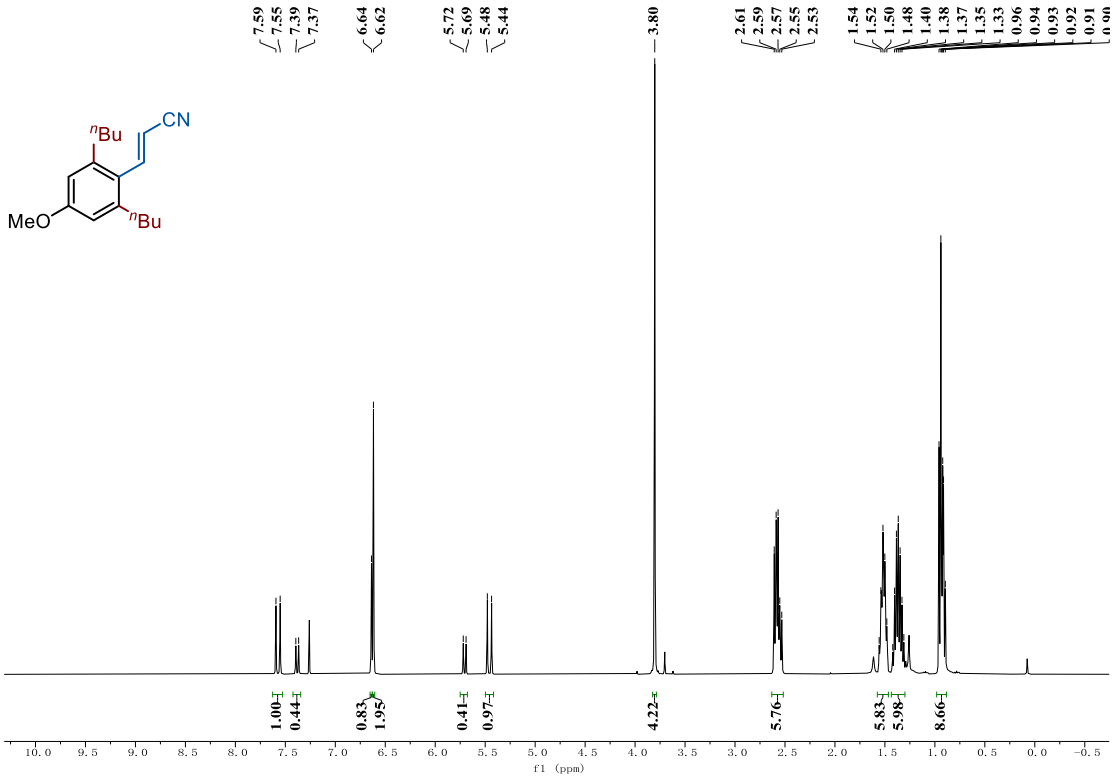
^{1}H NMR of **4cf** (400 MHz, $CDCl_3$)



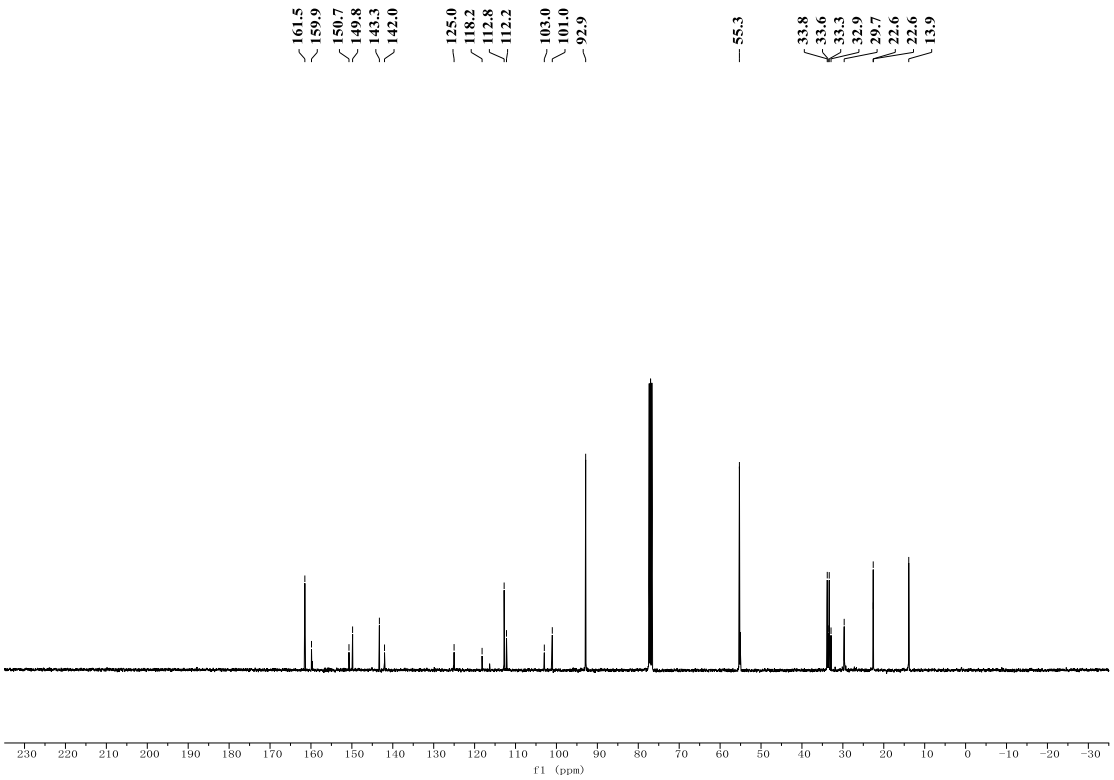
^{13}C NMR of **4cf** (100 MHz, $CDCl_3$)



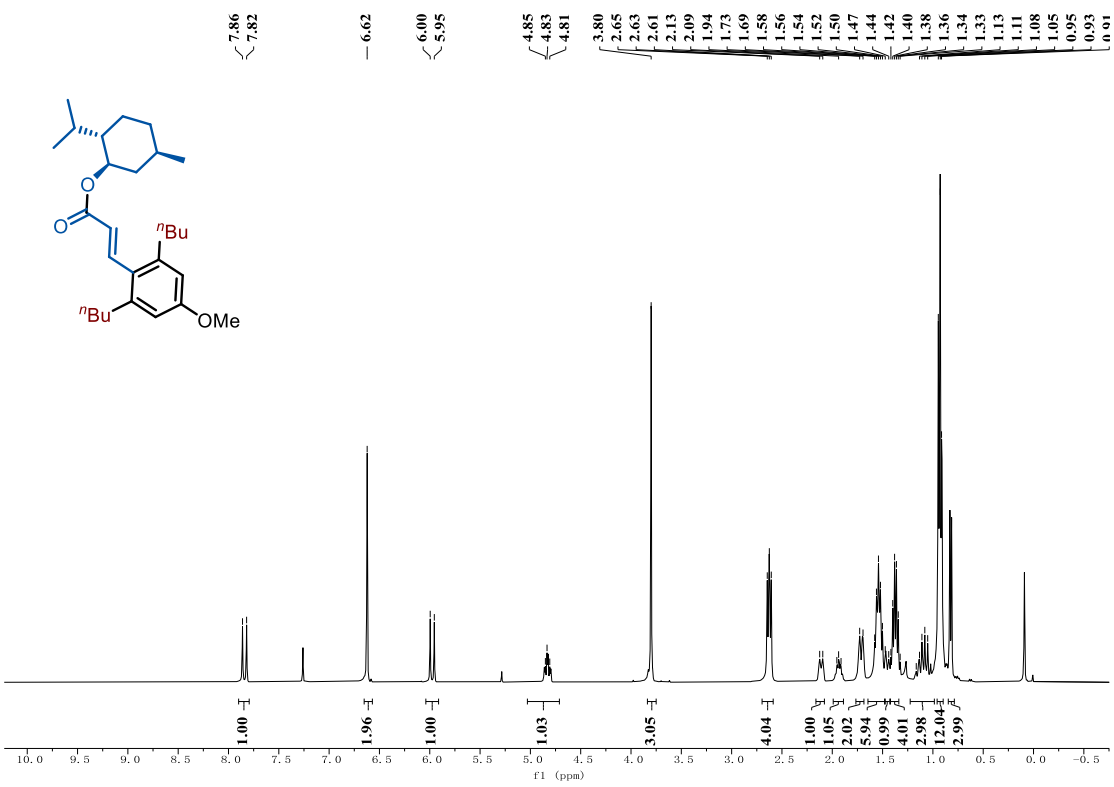
^{1}H NMR of **4cg** (400 MHz, $CDCl_3$)



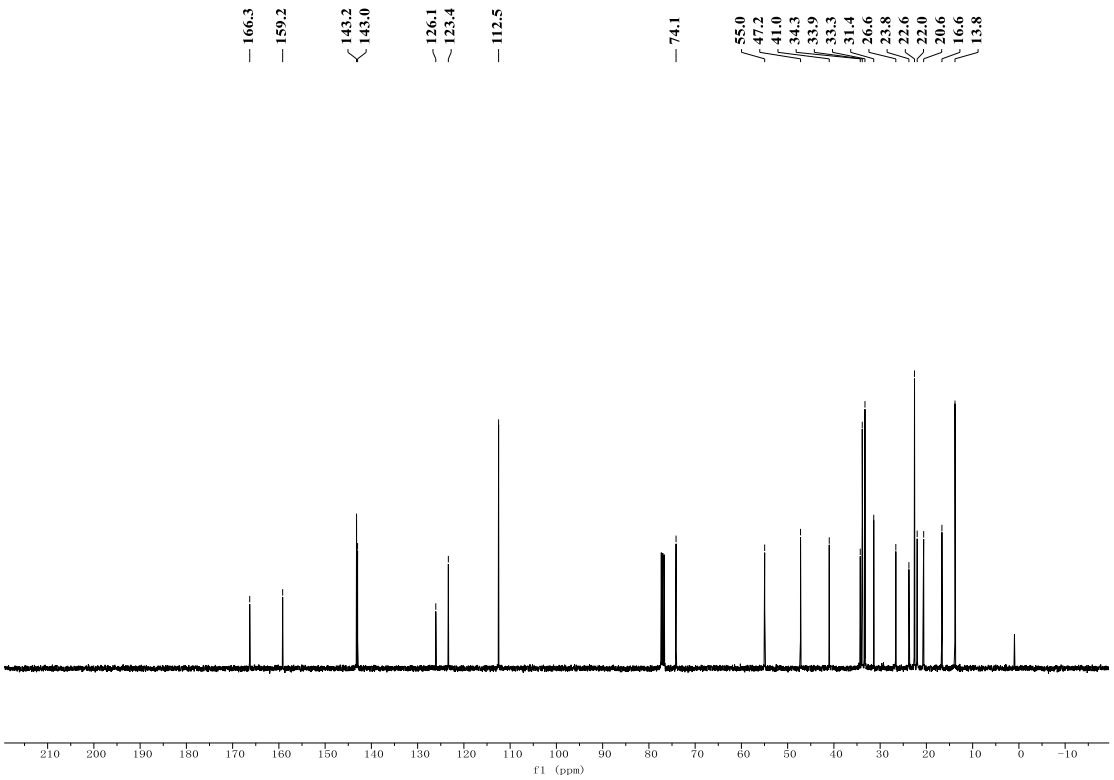
^{13}C NMR of **4cg** (100 MHz, $CDCl_3$)



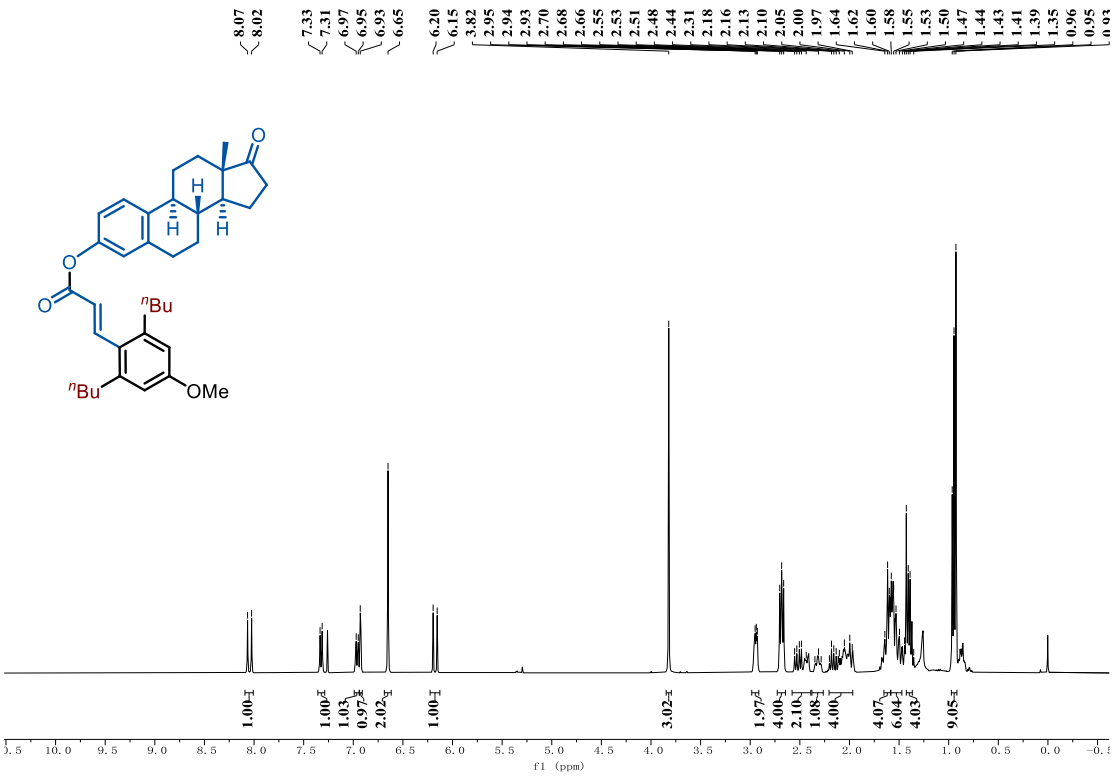
^{1}H NMR of **4ch** (400 MHz, $CDCl_3$)



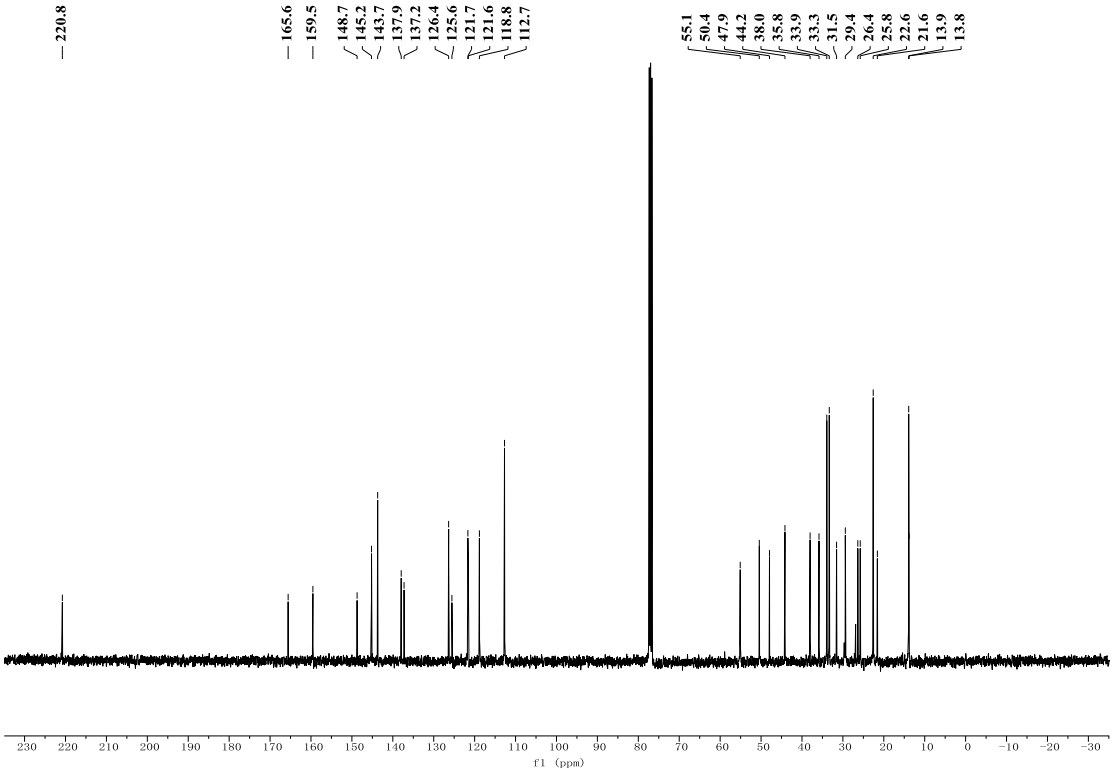
^{13}C NMR of **4ch** (100 MHz, $CDCl_3$)



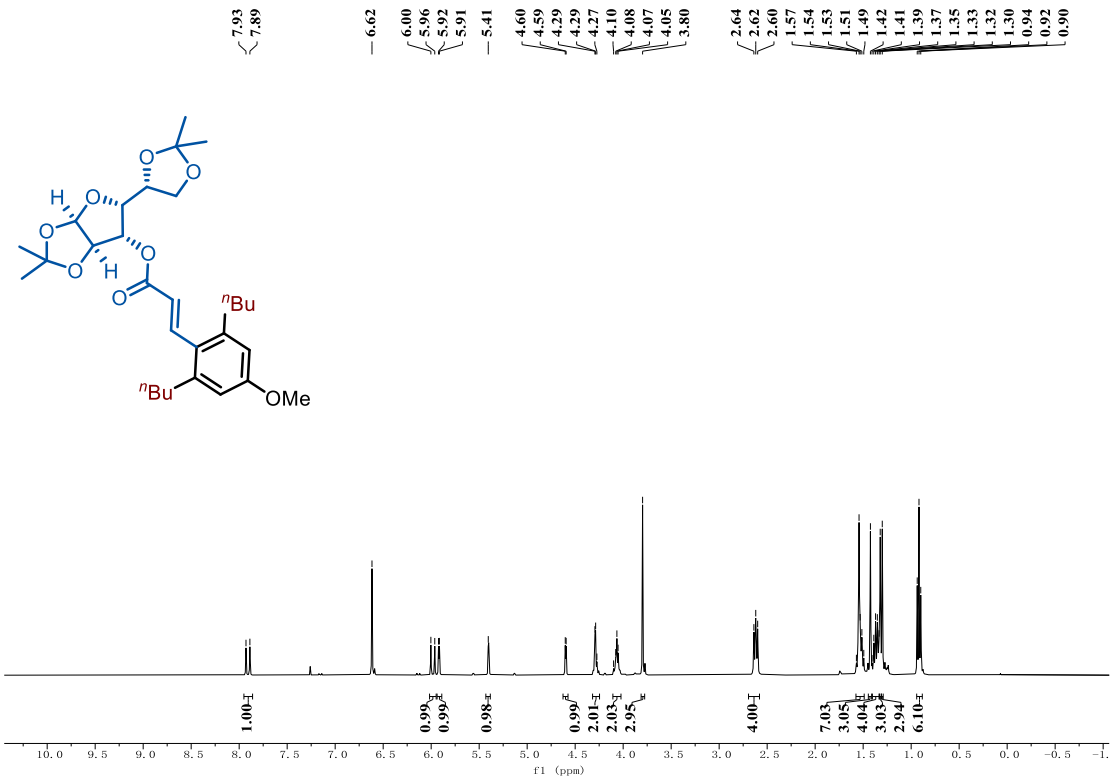
^{1}H NMR of **4ci** (400 MHz, $CDCl_3$)



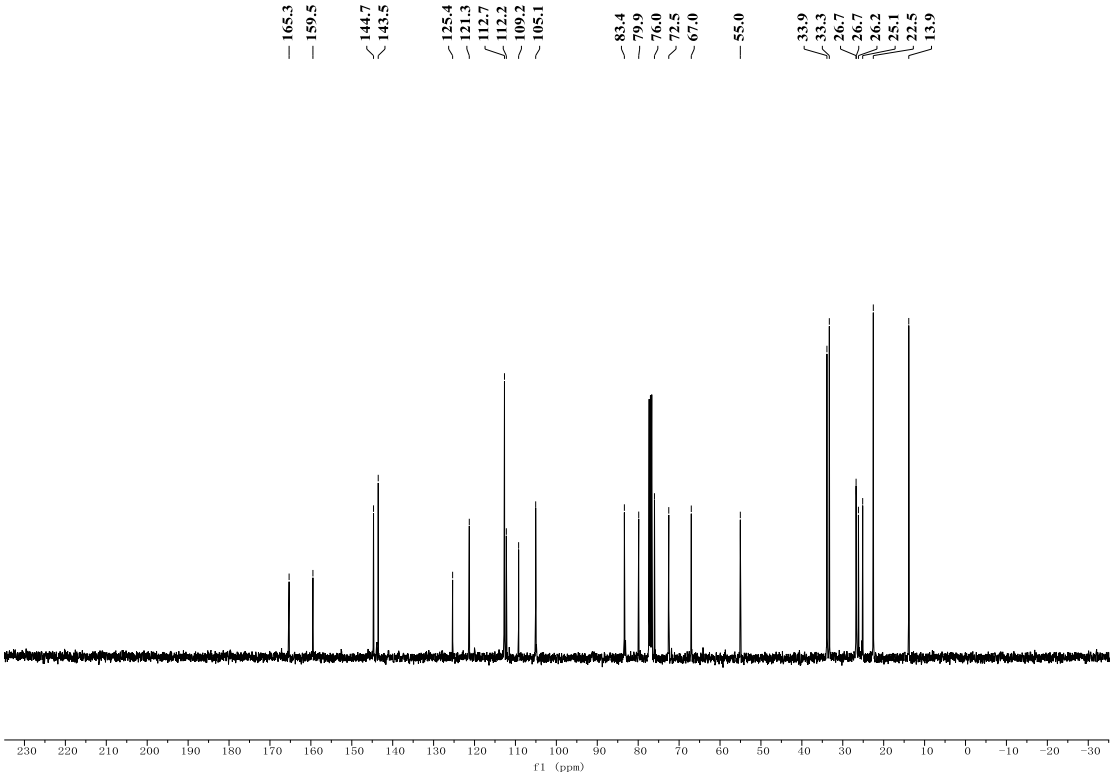
^{13}C NMR of **4ci** (100 MHz, $CDCl_3$)



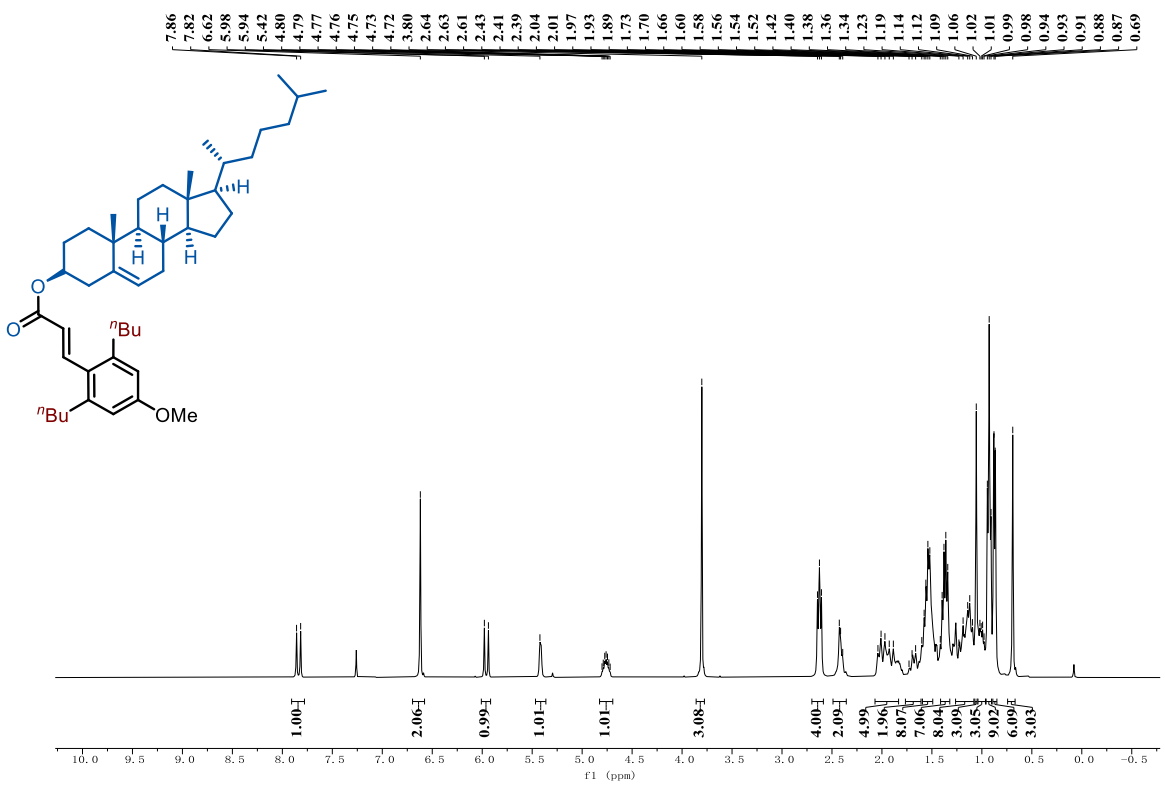
^{1}H NMR of **4cj** (400 MHz, $CDCl_3$)



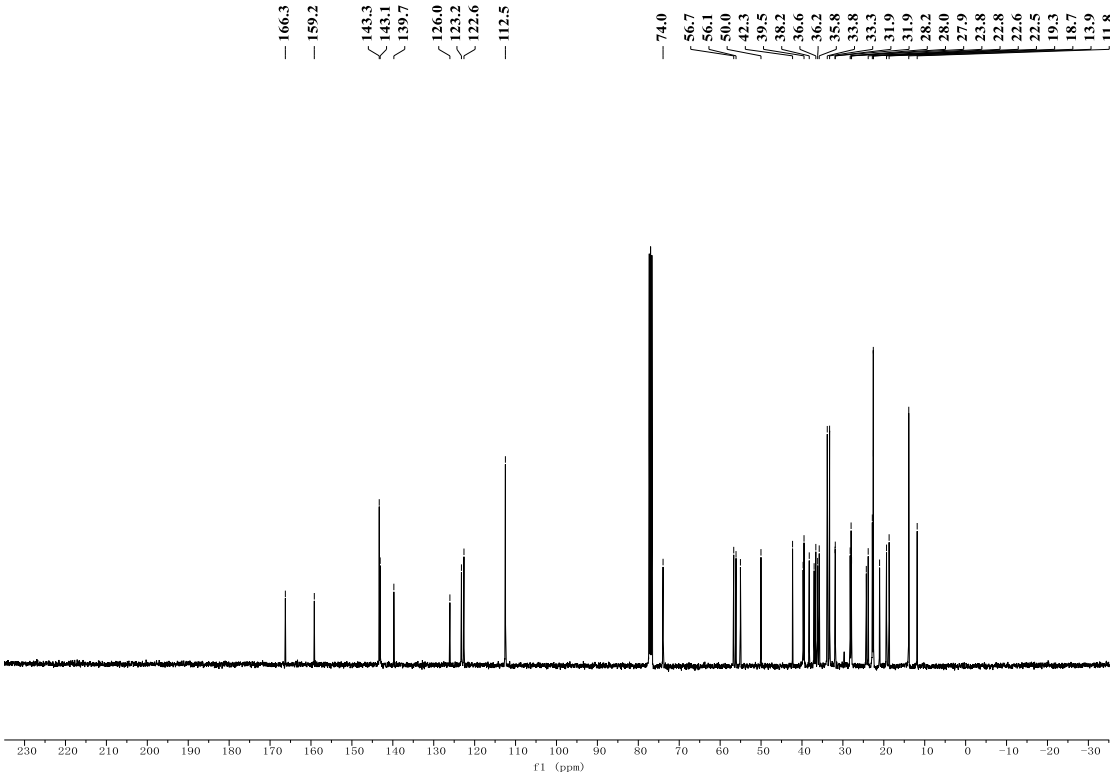
^{13}C NMR of **4cj** (100 MHz, $CDCl_3$)



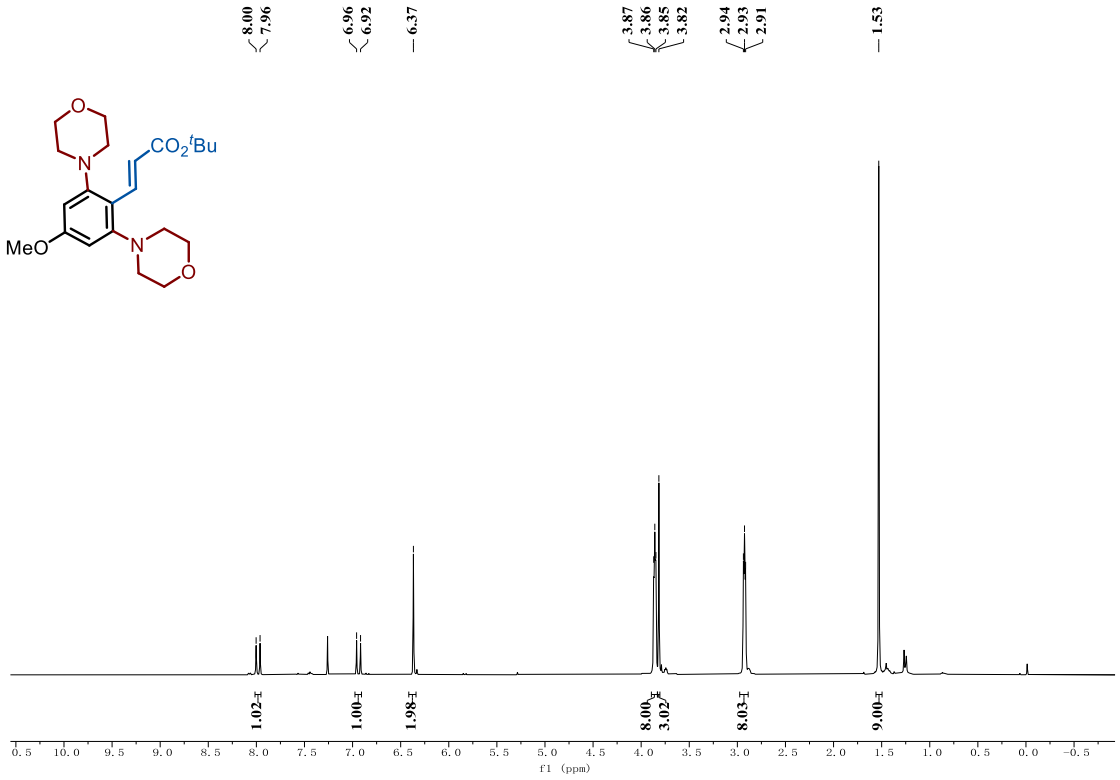
^{1}H NMR of **4ck** (400 MHz, $CDCl_3$)



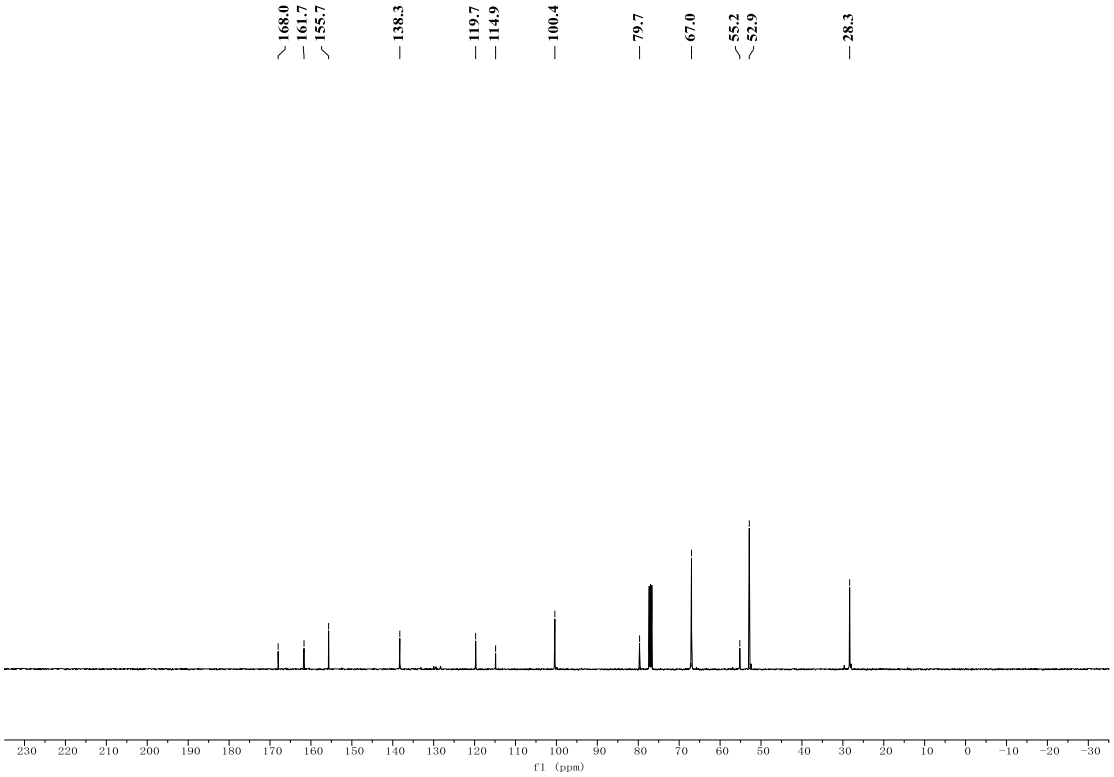
^{13}C NMR of **4ck** (100 MHz, $CDCl_3$)



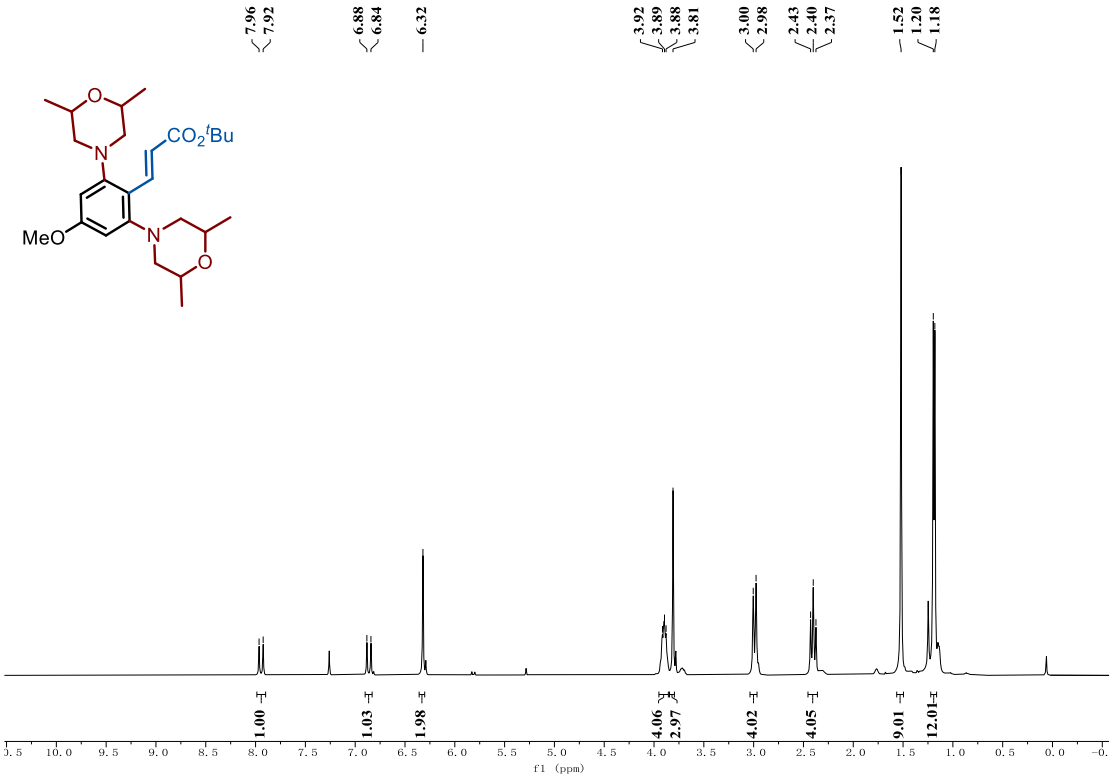
^{1}H NMR of **6a** (400 MHz, $CDCl_3$)



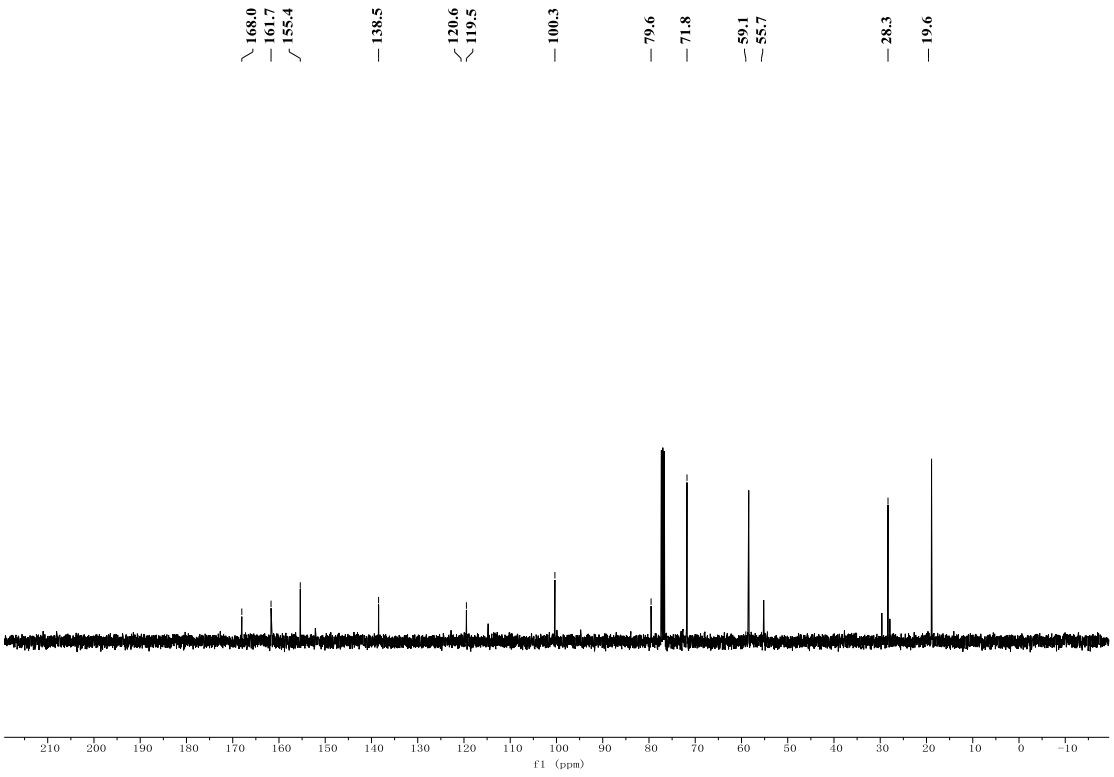
^{13}C NMR of **6a** (100 MHz, $CDCl_3$)



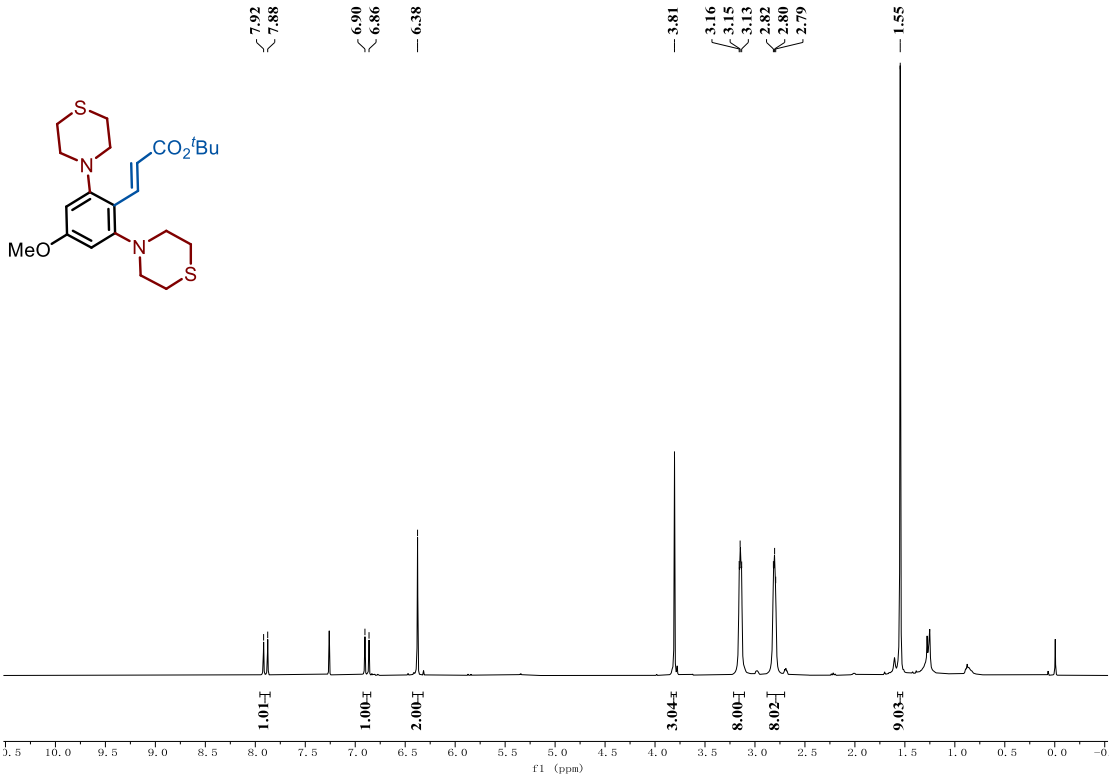
^{1}H NMR of **6b** (400 MHz, $CDCl_3$)



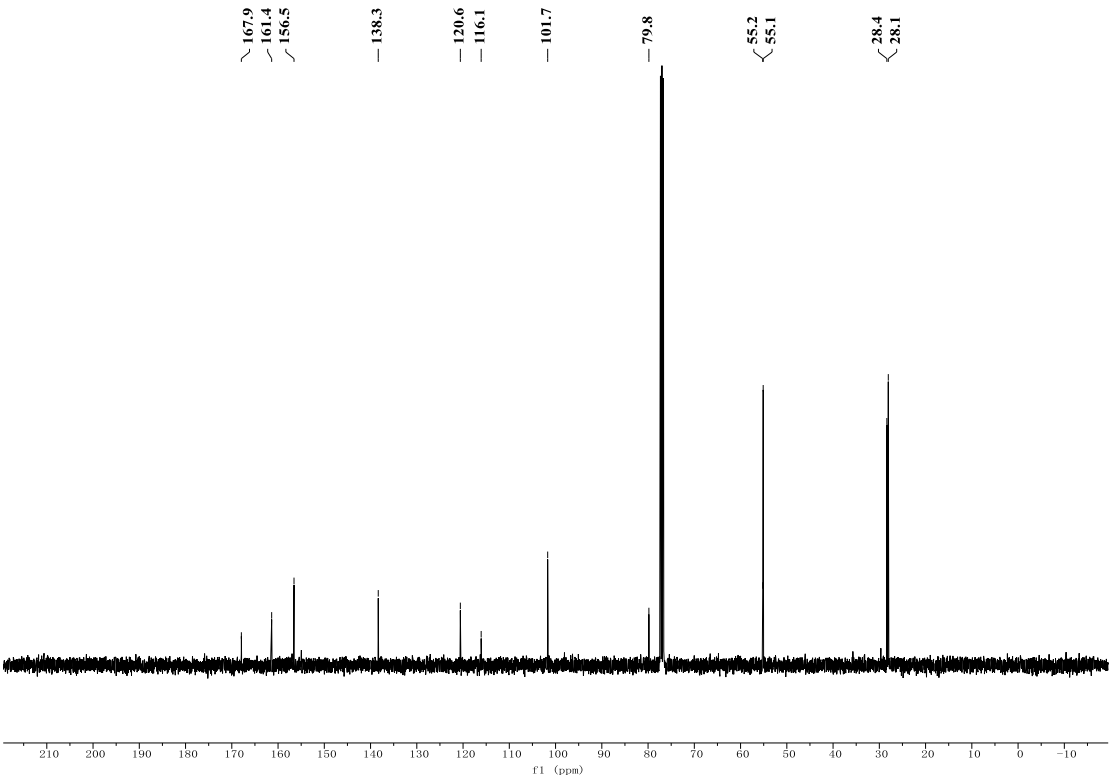
^{13}C NMR of **6b** (100 MHz, $CDCl_3$)



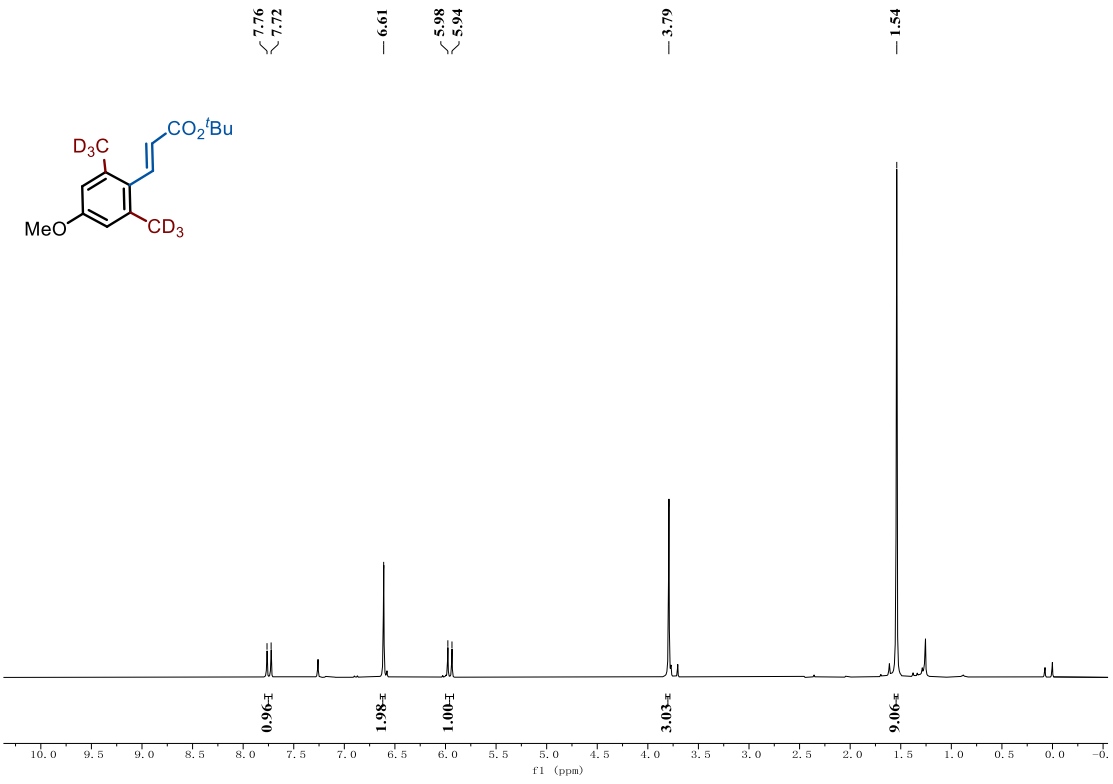
^{1}H NMR of **6c** (400 MHz, $CDCl_3$)



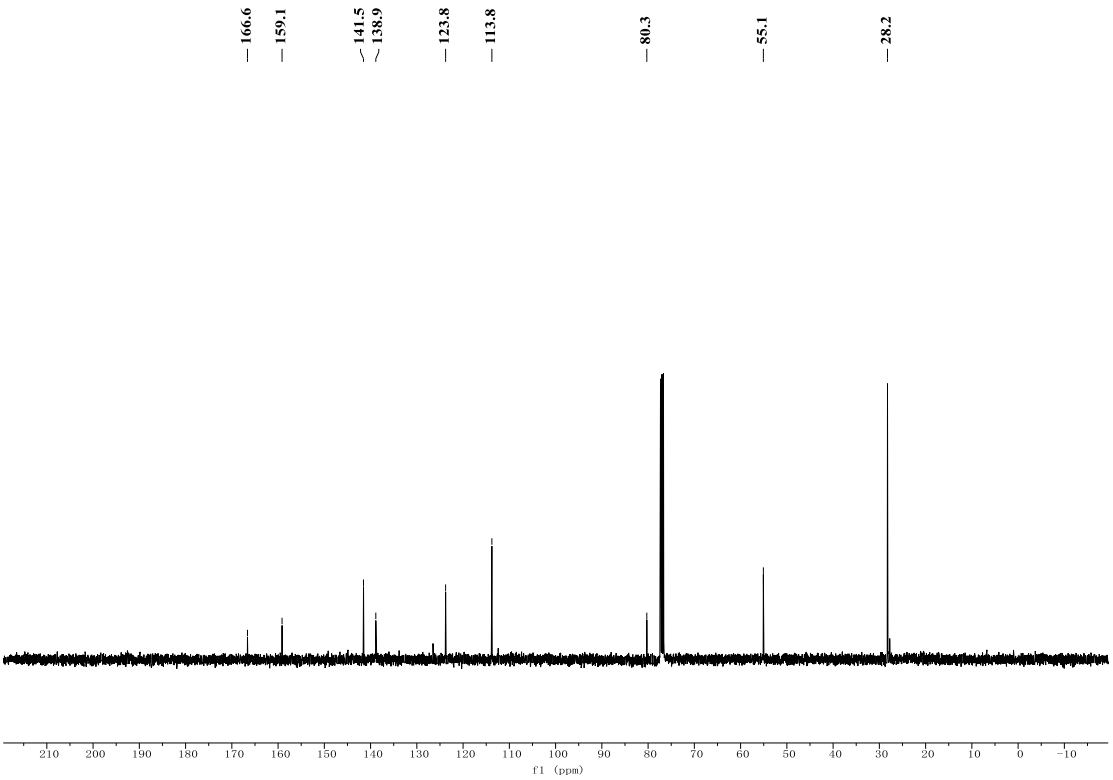
^{13}C NMR of **6c** (100 MHz, $CDCl_3$)



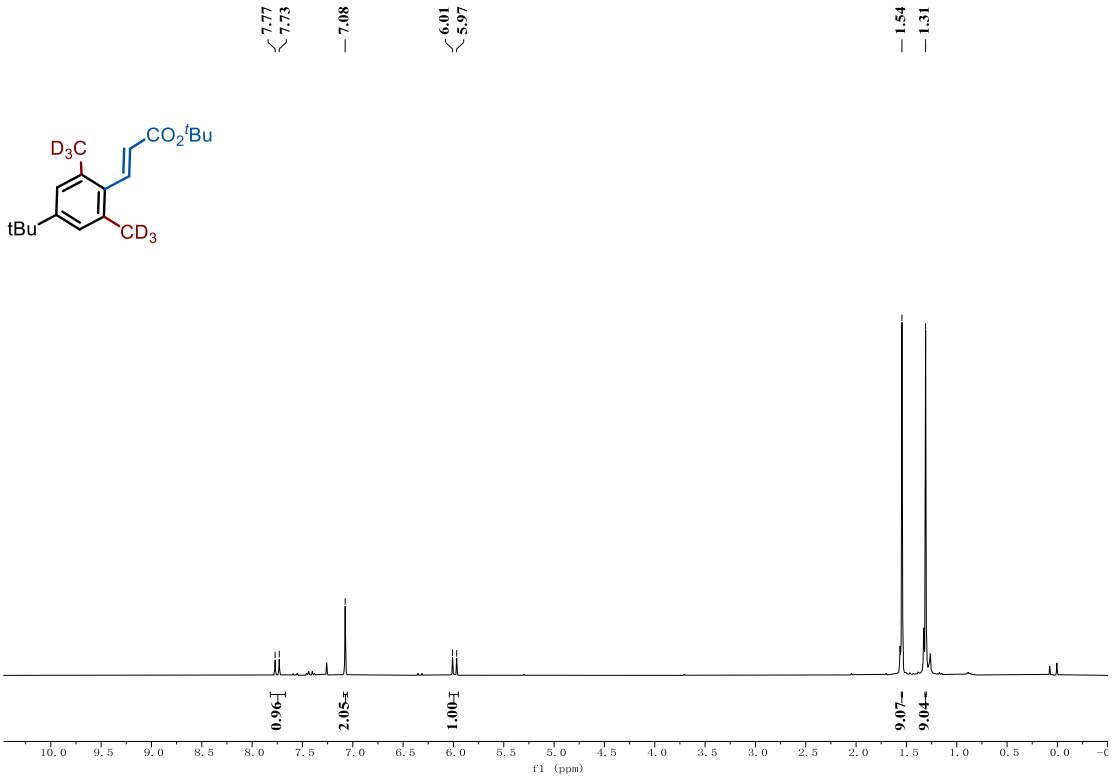
^{1}H NMR of **8a** (400 MHz, $CDCl_3$)



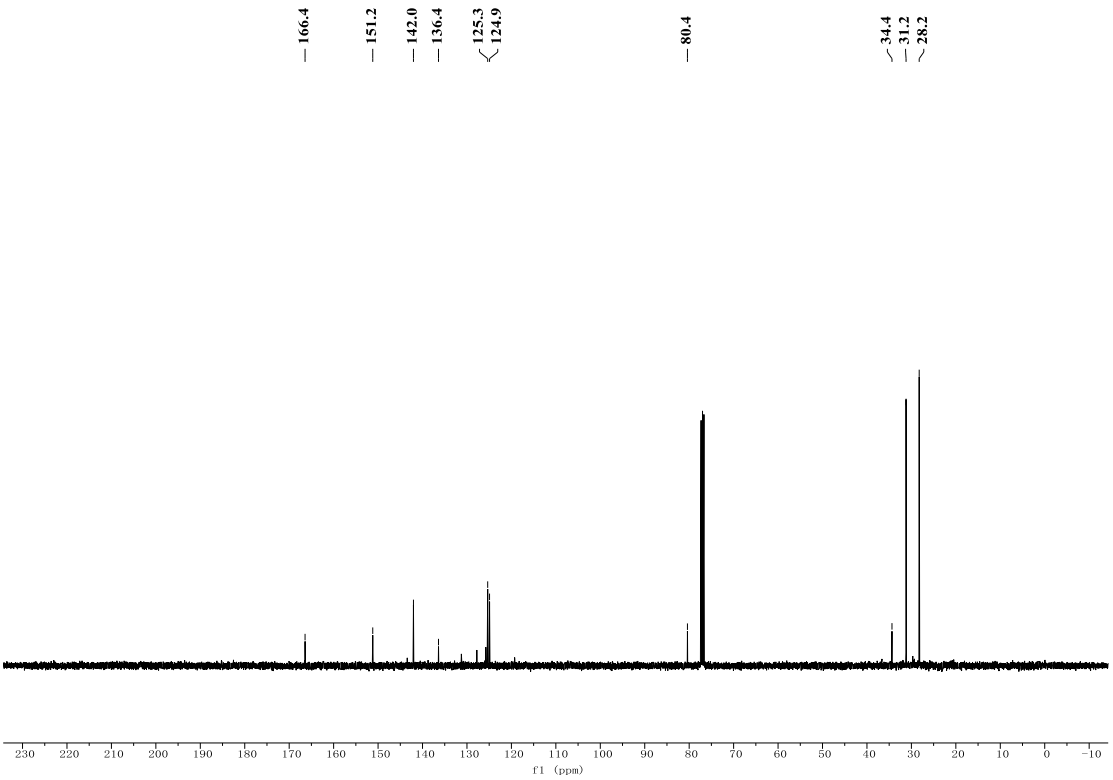
^{13}C NMR of **8a** (100 MHz, $CDCl_3$)



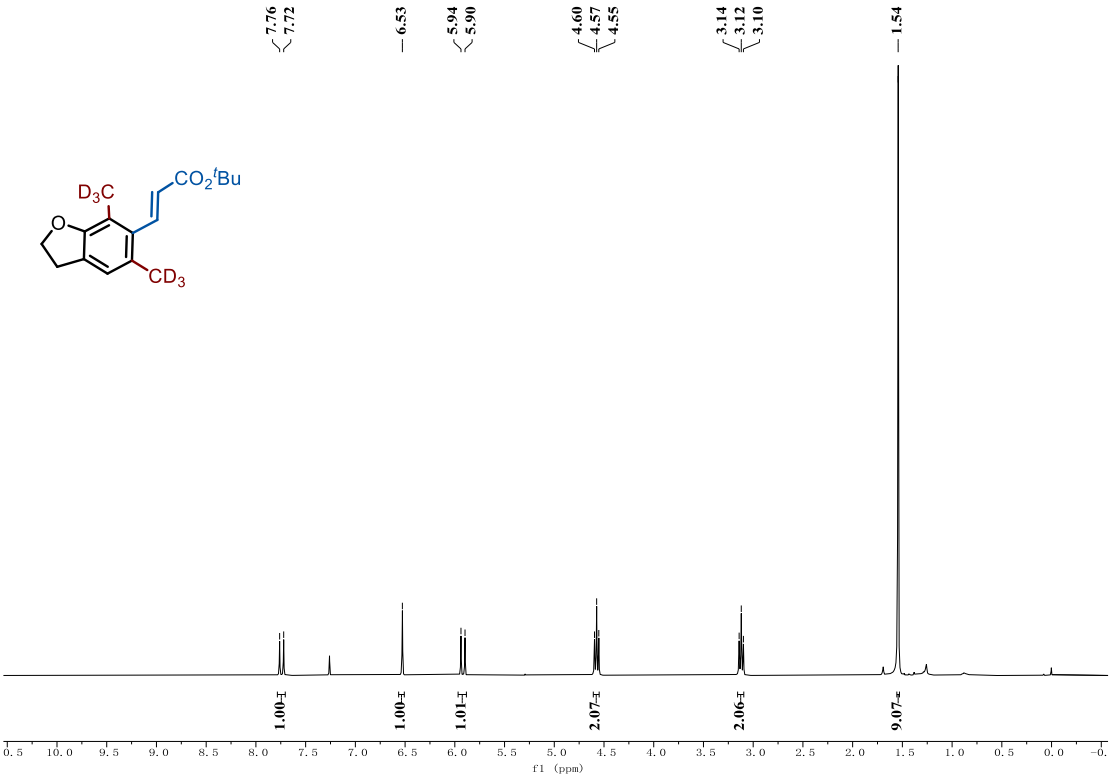
^{1}H NMR of **8b** (400 MHz, $CDCl_3$)



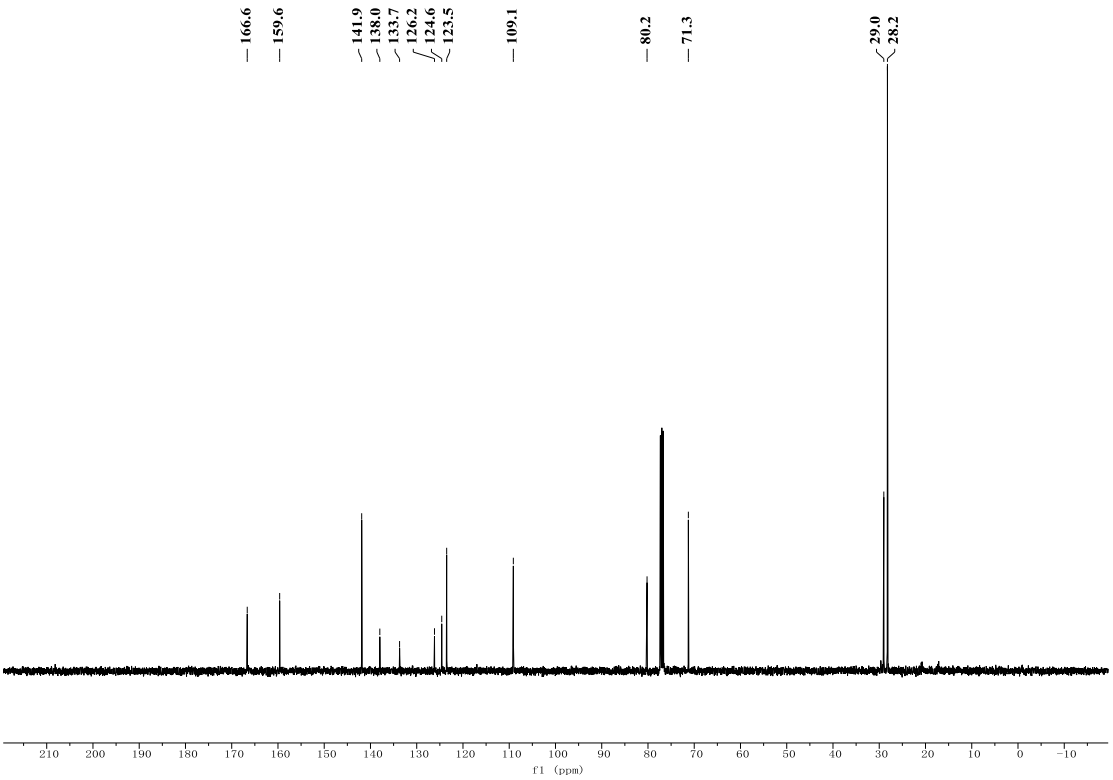
^{13}C NMR of **8b** (100 MHz, $CDCl_3$)



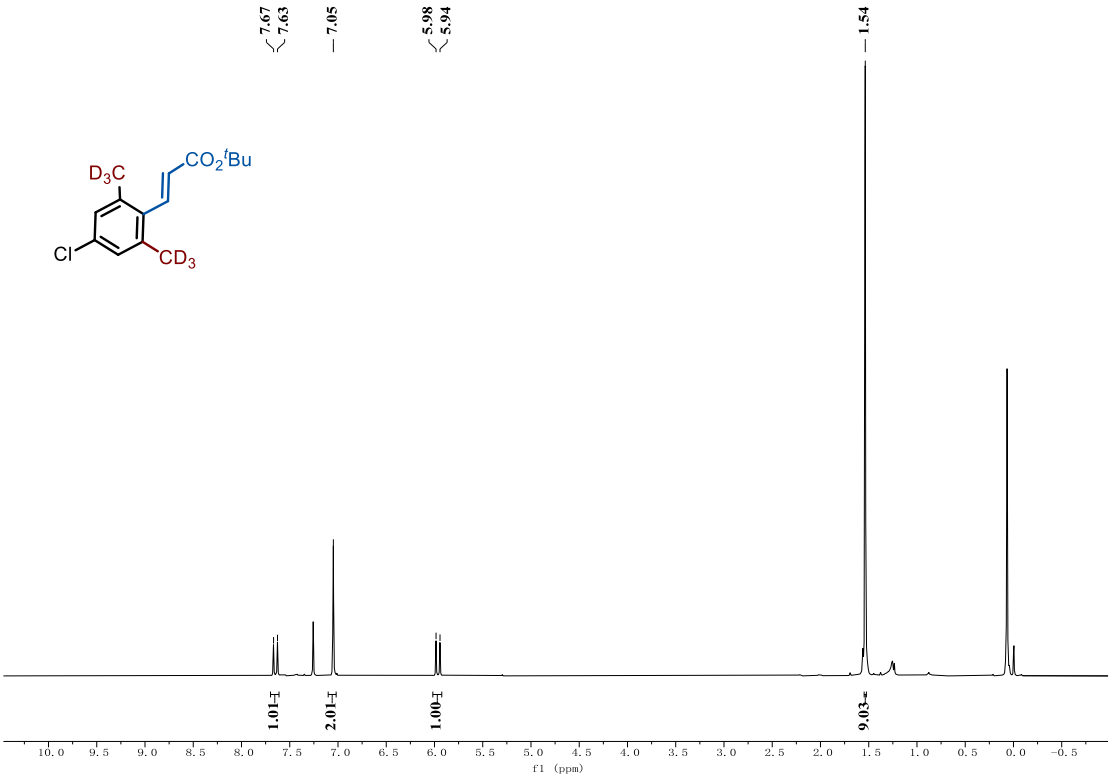
^{1}H NMR of **8c** (400 MHz, $CDCl_3$)



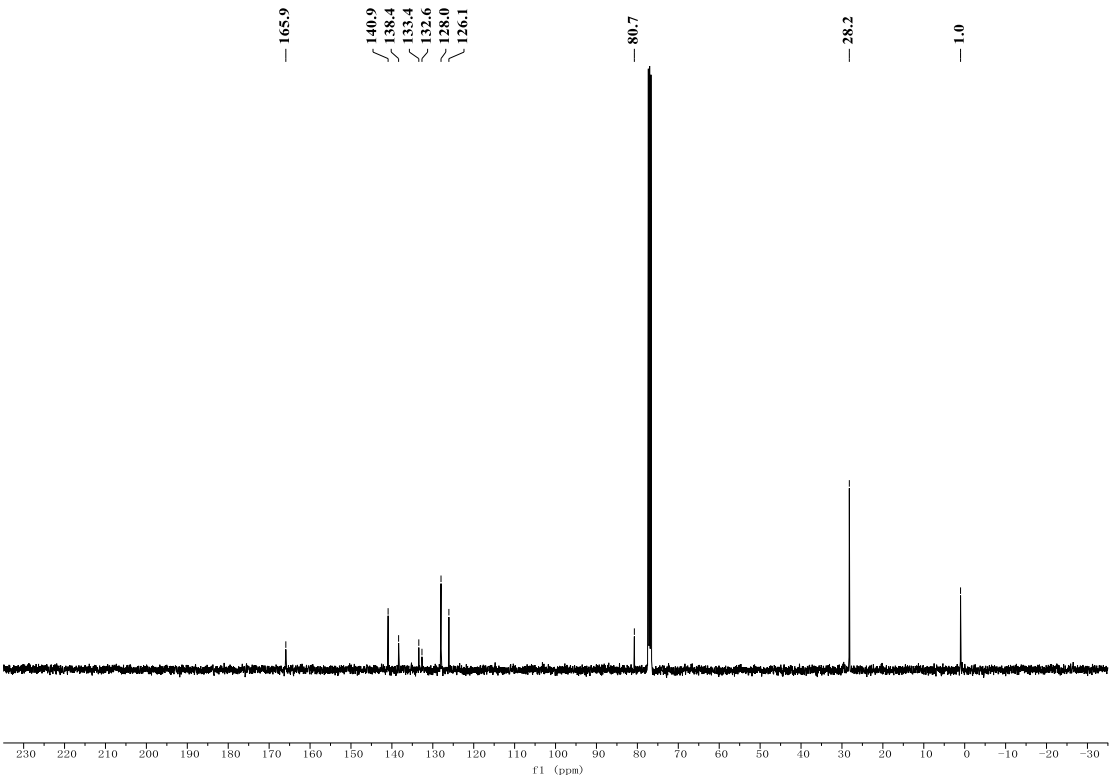
^{13}C NMR of **8c** (100 MHz, $CDCl_3$)



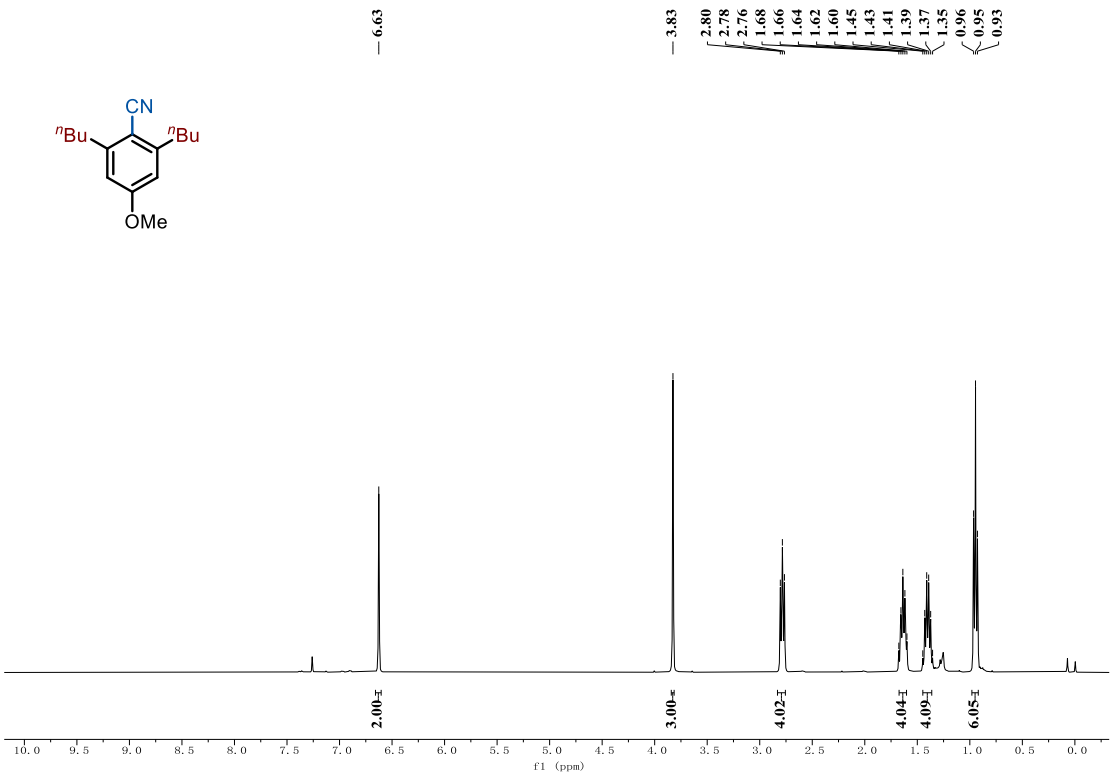
^{1}H NMR of **8d** (400 MHz, $CDCl_3$)



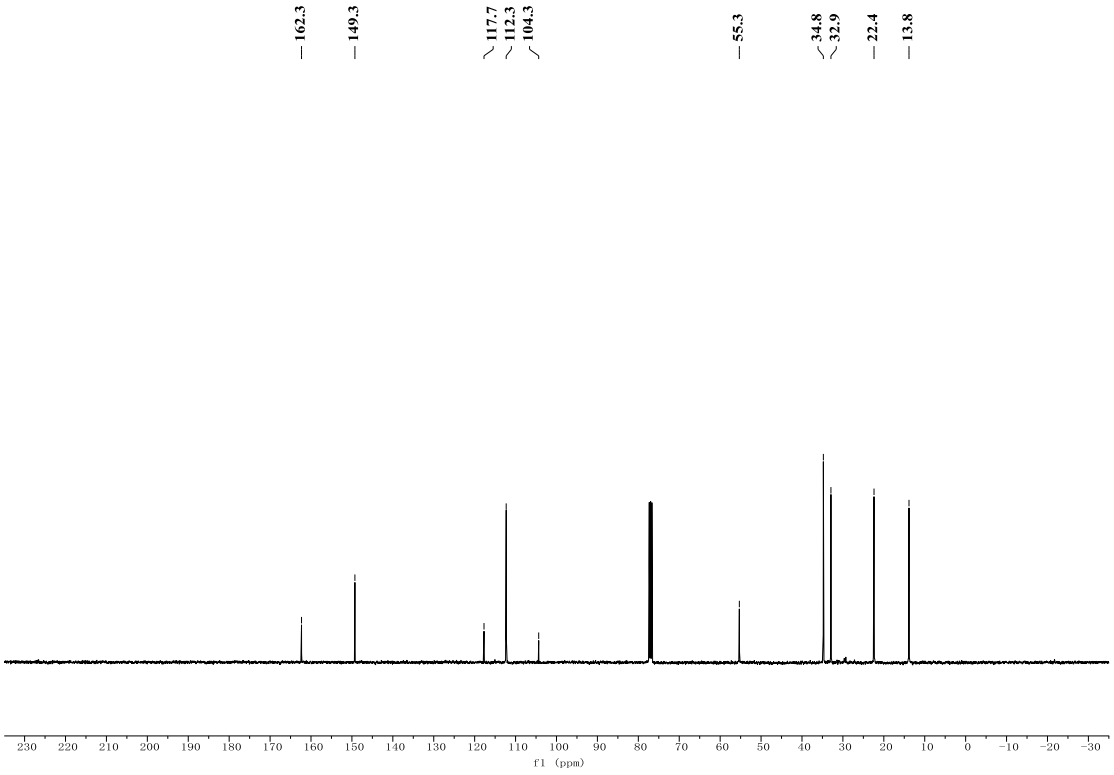
^{13}C NMR of **8d** (100 MHz, $CDCl_3$)



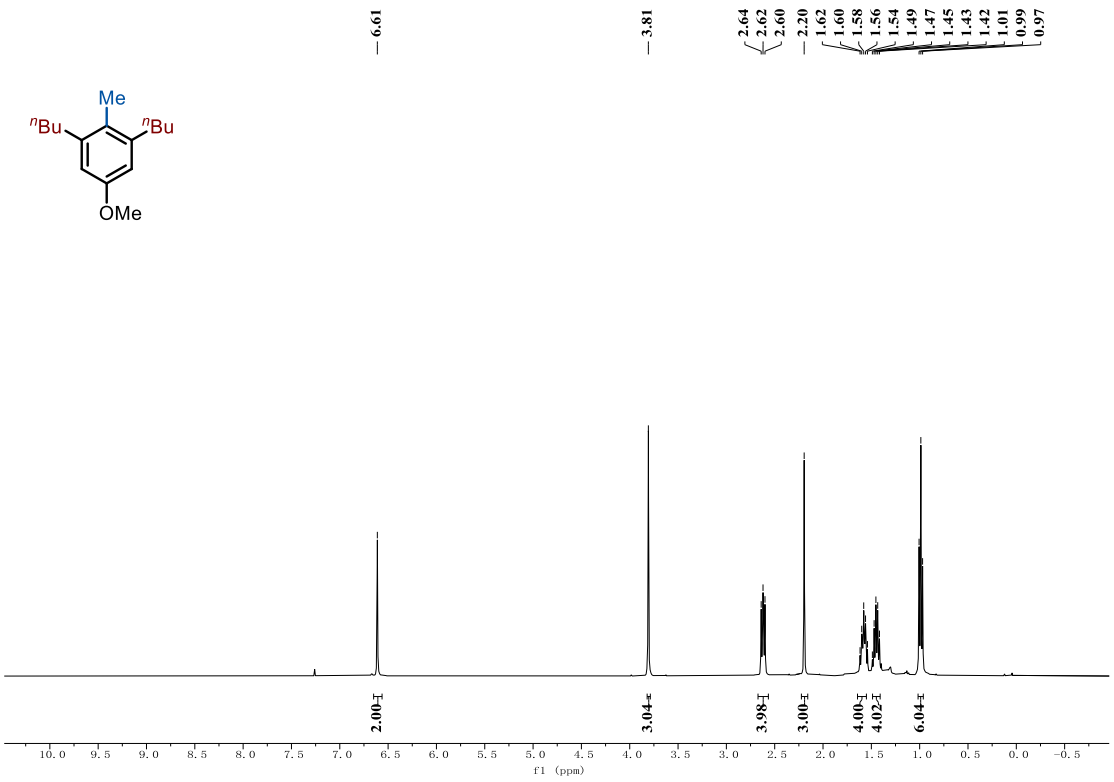
^{1}H NMR of **9** (400 MHz, $CDCl_3$)



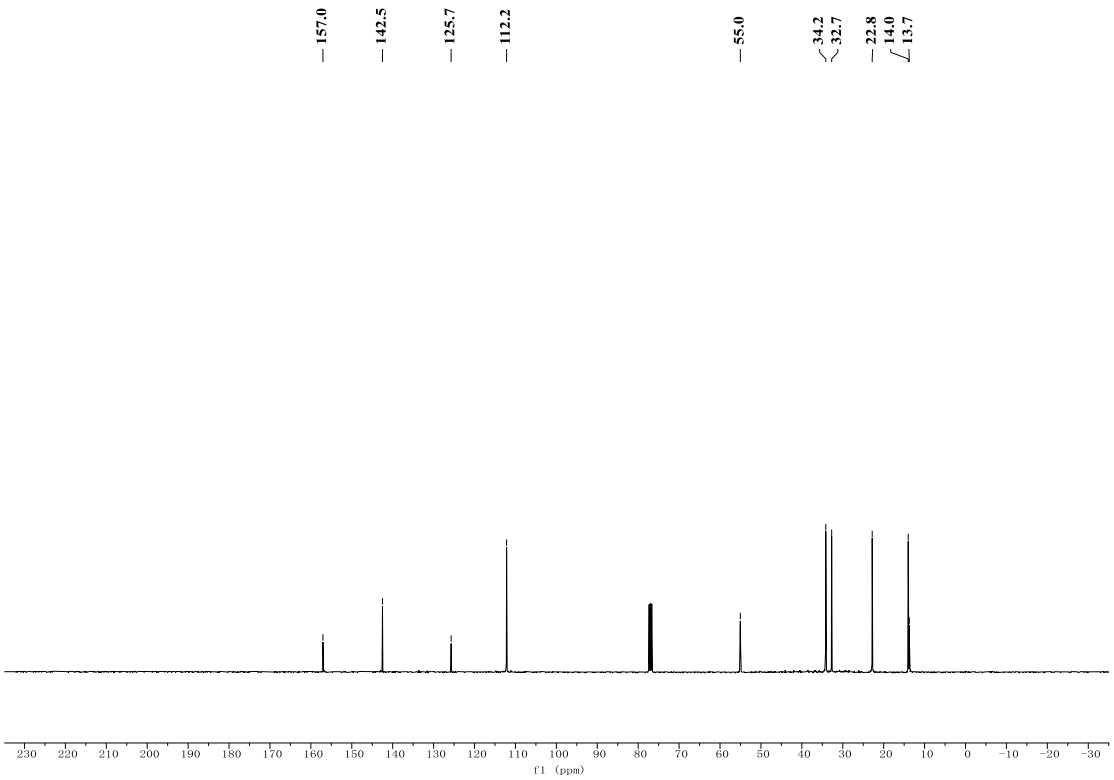
^{13}C NMR of **9** (100 MHz, $CDCl_3$)



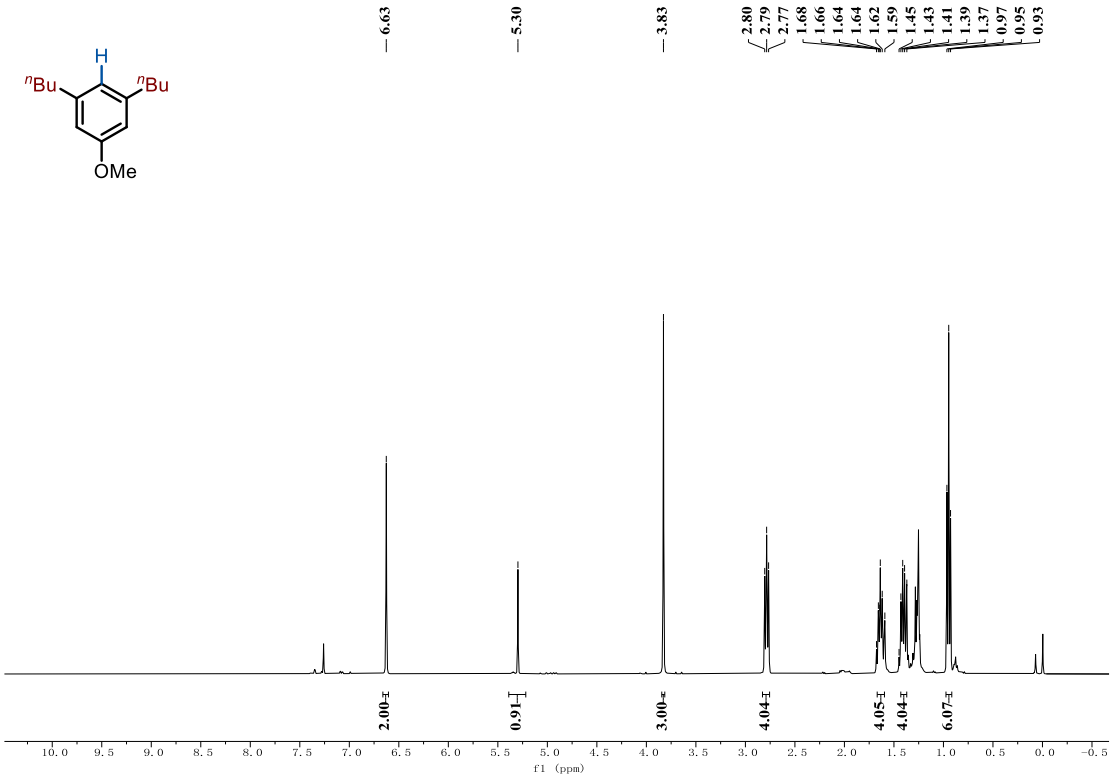
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



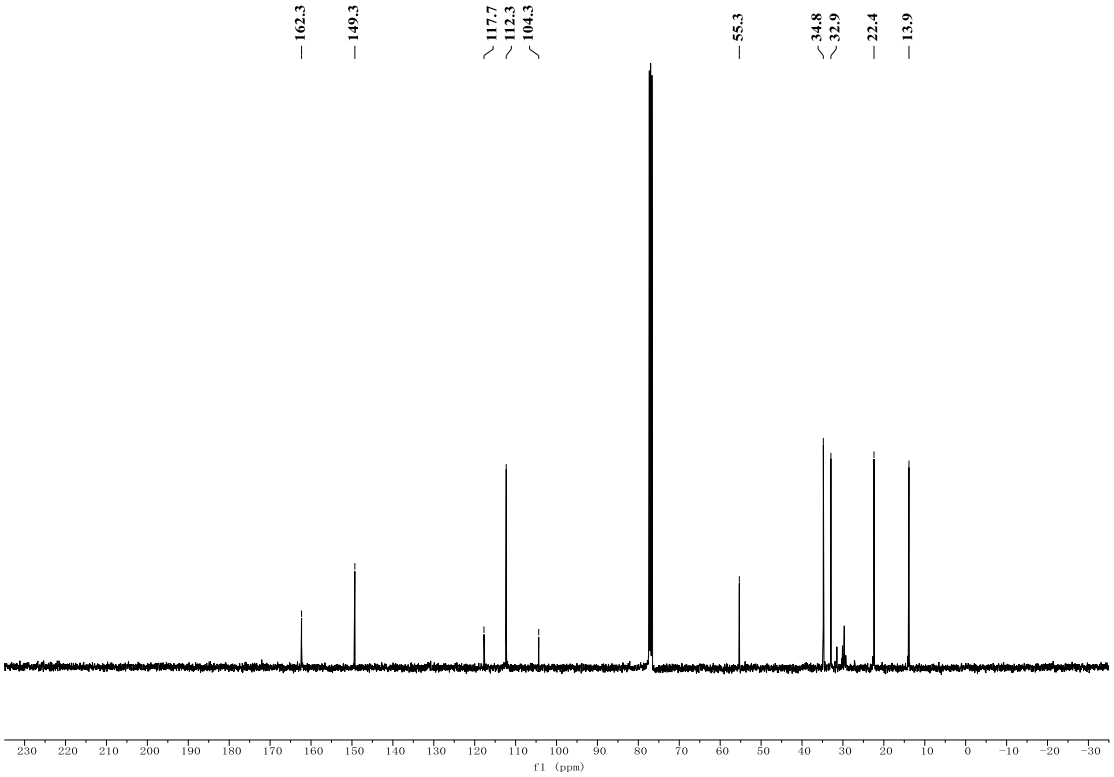
^{13}C NMR of **10** (100 MHz, $CDCl_3$)



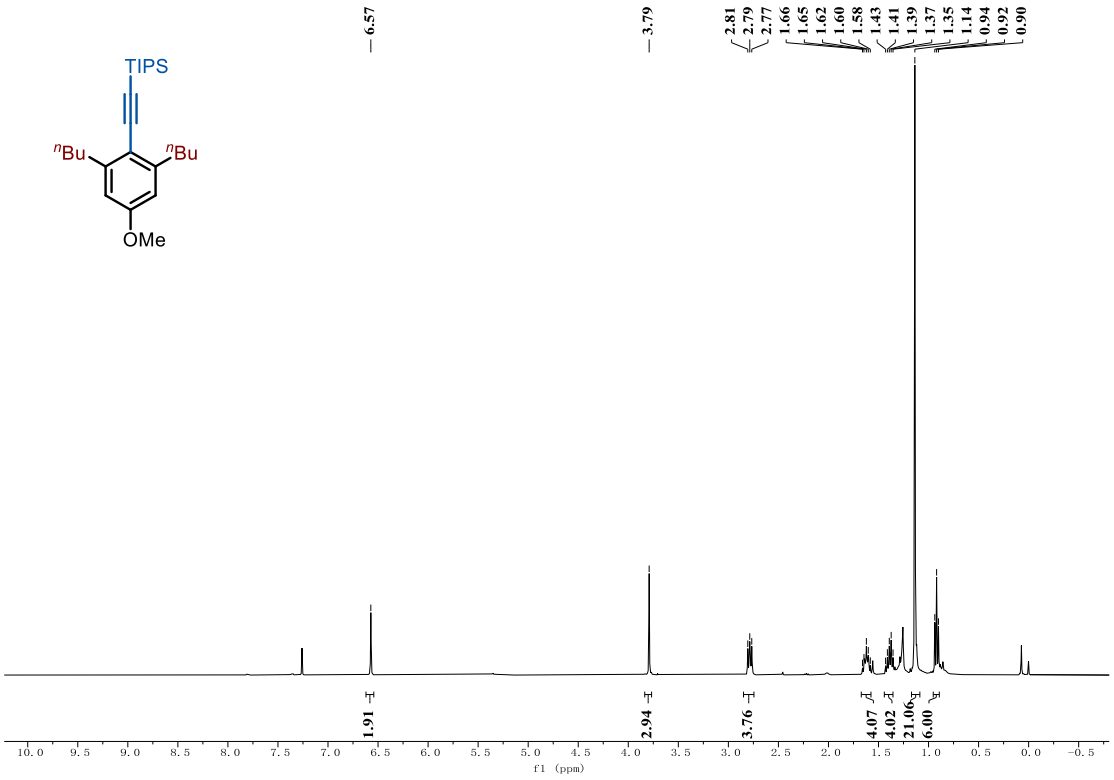
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



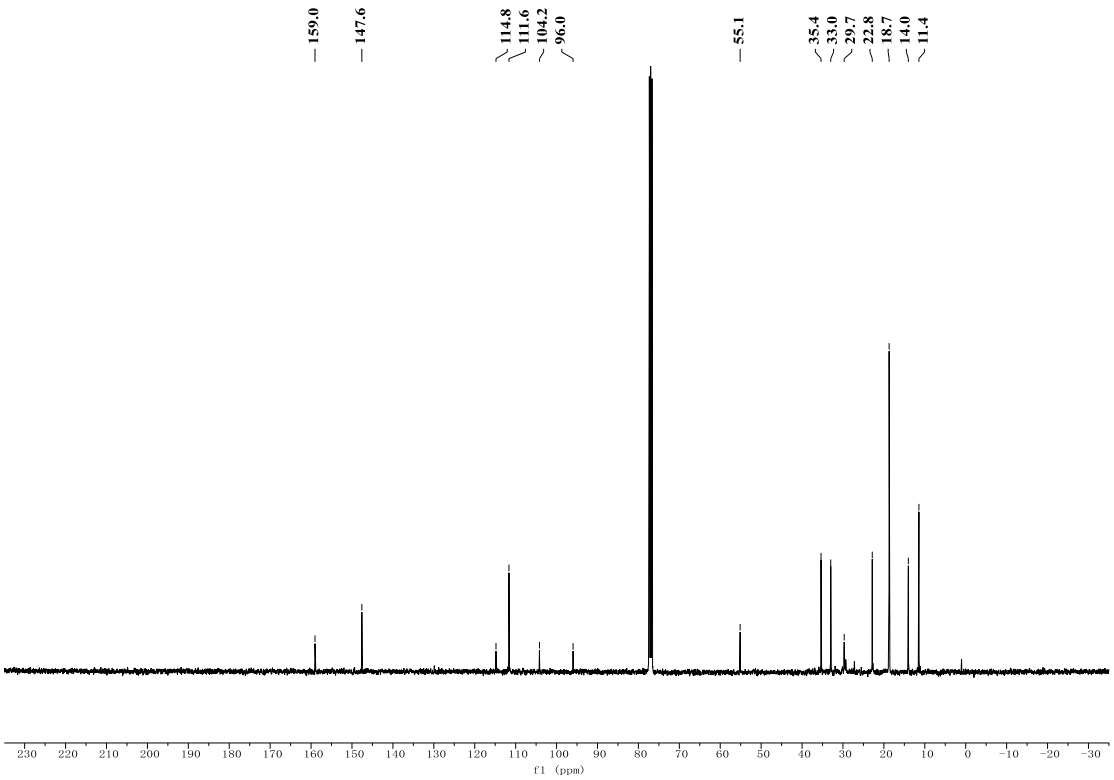
^{13}C NMR of **11** (100 MHz, $CDCl_3$)



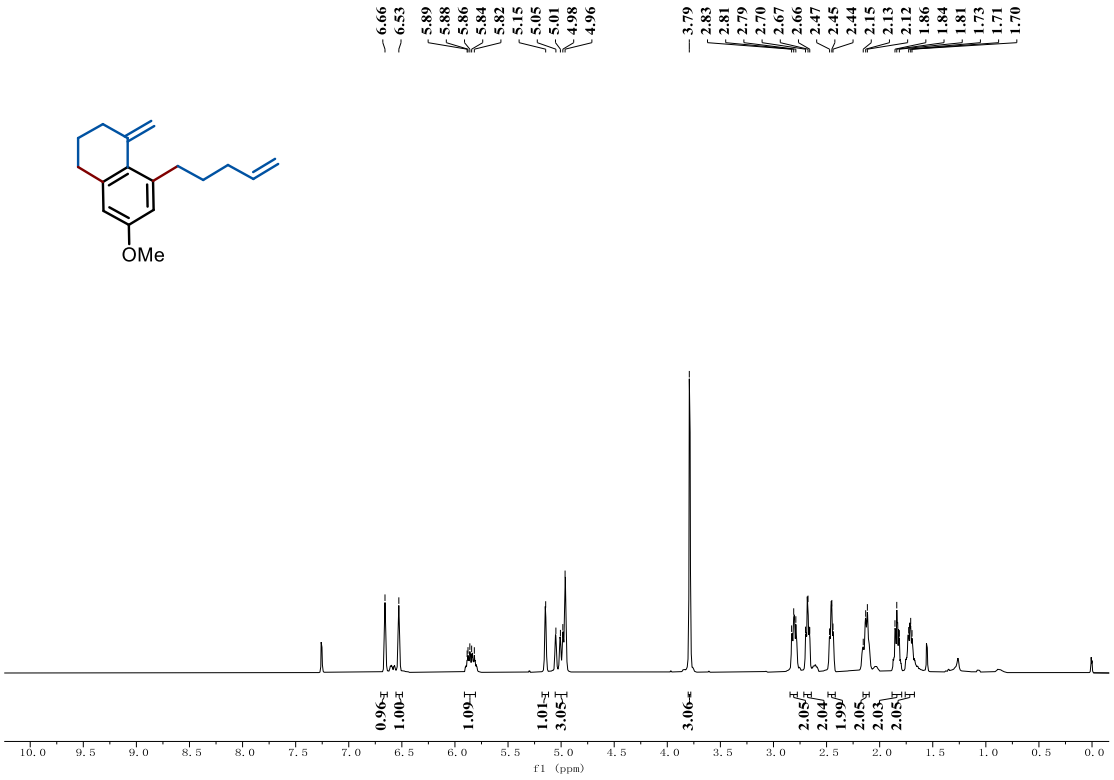
^{1}H NMR of **12** (400 MHz, $CDCl_3$)



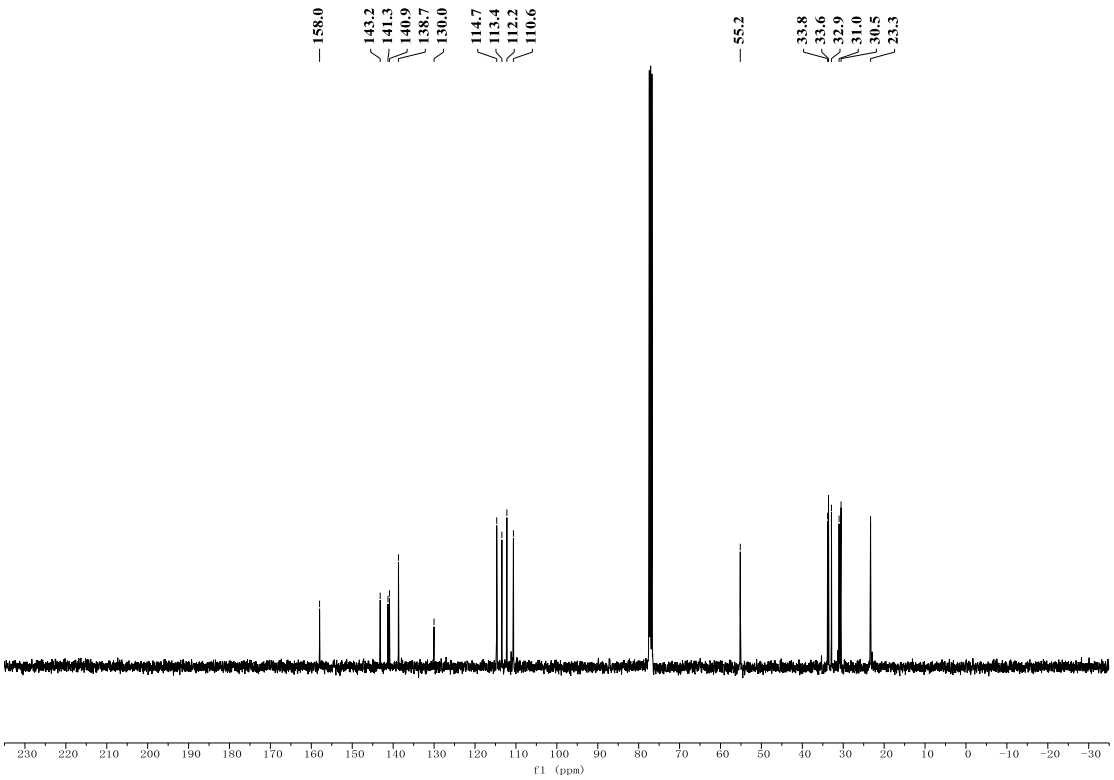
^{13}C NMR of **12** (100 MHz, $CDCl_3$)



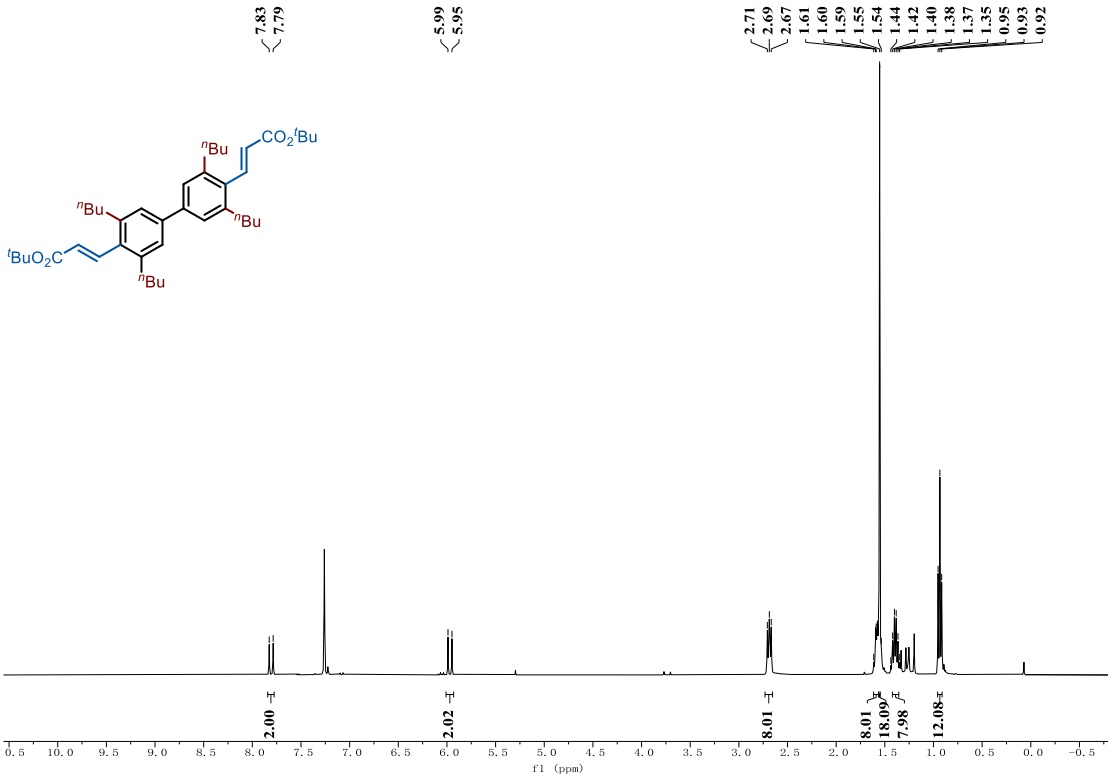
^{1}H NMR of **13** (400 MHz, $CDCl_3$)



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



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



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