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# 1. General Considerations

Air and moisture sensitive reactions were carried out in glovebox or in oven-dried glassware sealed with rubber septa using standard schlenk techniques. Solvents used in moisture and oxygen sensitive reactions were firstly degassed by three freeze-pump-thaw cycles and then distilled under Ar protection after dehydration (ether solvents were dried over sodium metal). Regular chemicals were purchased from commercial sources with purity over 95% and used without further purification. NMR spectra were collected using a Bruker 400 MHz spectrometer and JEOL JNM-ECZL500G. Chemical shifts are reported in ppm relative to the deuterated solvents. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. GC analysis was carried out on an SHIMADAZU GC 2010 PLUS system. GC/MS analysis was carried out on a Thermo Trace ISQ system equipped with a Thermo SCIENTIFIC TG-5MS (30 m x 250 μm x 25 μm). High resolution exact mass measurements (HRMS) were performed on Thermo SCIENTIFIC Q EXACTIVE. Cyclic voltammetry was recorded using a CHI760E potentiostation.

# 2. Synthesis and Characterization Data of Substrates

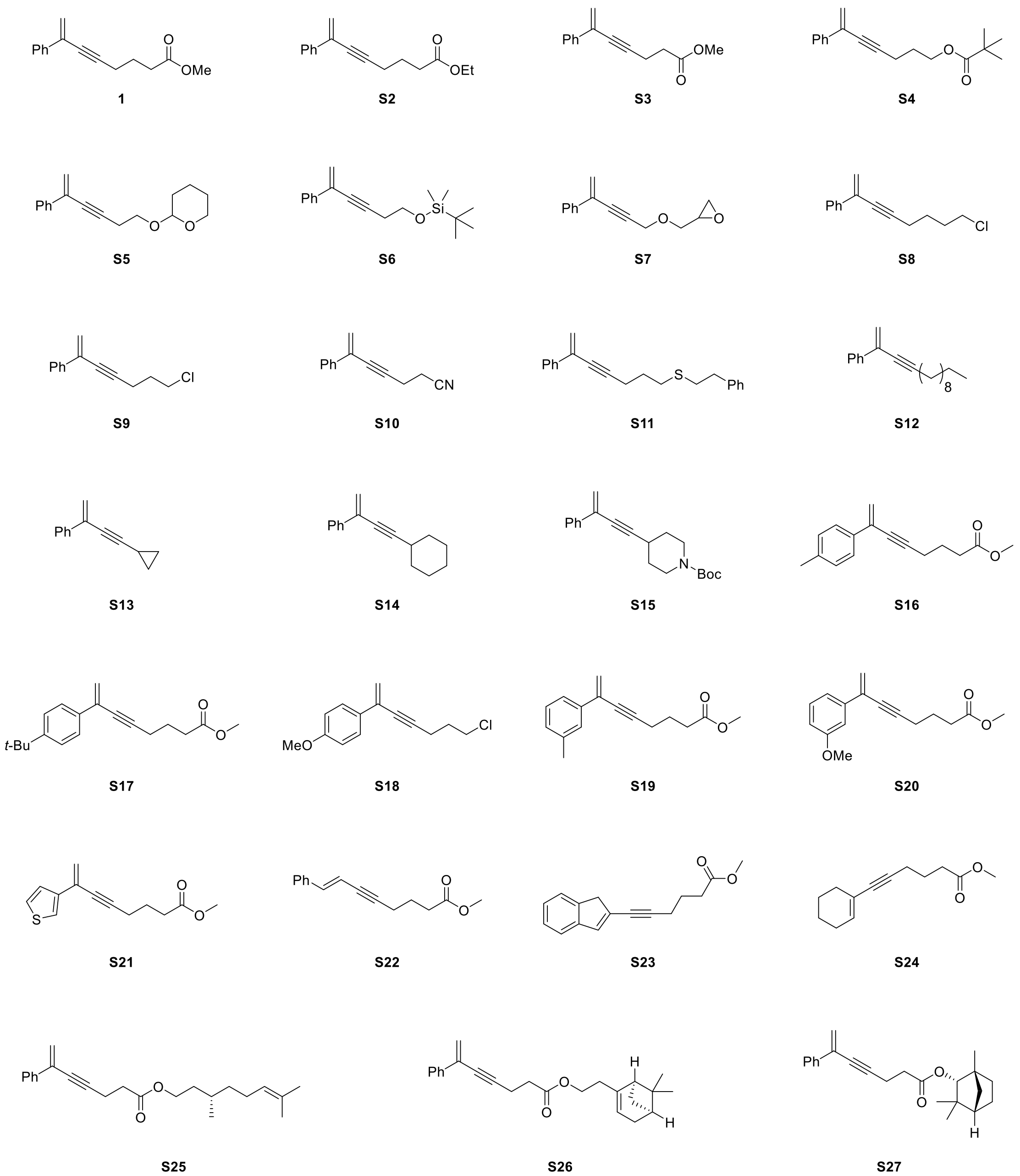
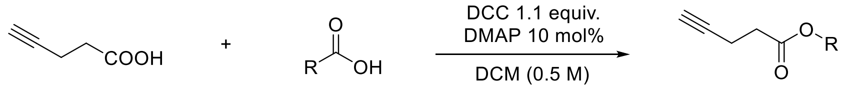


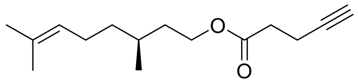

**Fig. S1** Investigated enynes.

**General procedure for synthesis of alkynes**




To a solution of pent-4-ynoic acid (1.96 g, 20 mmol) and ROH (1.0 equiv., 20 mmol) in DCM (40 mL) were added N, N'-Dicyclohexylcarbodiimide (4.54 g, 22 mmol), 4-dimethylaminopyridine (244 mg, 2.0 mmol). After stirring at room temperature for 12 h, the solution was extracted with DCM (2 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated in vacuo[1].

**(*S*)-3,7-dimethyloct-6-en-1-yl pent-4-ynoate**



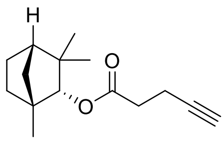
Compound **S28** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (4.06 g, 86% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.17-4.98 (m, 1H), 4.19-4.08 (m, 2H), 2.58-2.43 (m, 4H), 2.05-1.87 (m, 3H), 1.70-1.63 (m, 4H), 1.59 (s, 3H), 1.57-1.50 (m, 1H), 1.48-1.40 (m, 1H), 1.36-1.29 (m, 1H), 1.22-1.12 (m, 1H), 0.90 (d, $J$ = 6.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.86, 131.41, 124.62, 82.59, 69.02, 63.35, 37.03, 35.50, 33.51, 29.52, 25.76, 25.45, 19.46, 17.71, 14.47.

**HRMS** (APCI) calcd. for $C_{15}H_{25}O_2^+$ $[M+H]^+$: 237.1850; found: 237.1848.

**(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl pent-4-ynoate**



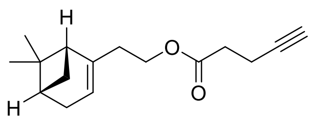
Compound **S29** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (3.5 g, 75% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.38 (d, J = 2.0 Hz, 1H), 2.64-2.56 (m, 2H), 2.55-2.46 (m, 2H), 1.96 (t, J = 2.5 Hz, 1H), 1.77-1.65 (m, 3H), 1.60-1.54 (m, 1H), 1.49-1.39 (m, 1H), 1.18 (dd, J = 10.3, 1.7 Hz, 1H), 1.09 (s, 3H), 1.04 (s, 3H), 0.77 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.07, 86.59, 82.65, 69.01, 48.33, 48.27, 41.36, 39.41, 33.58, 29.67, 26.62, 25.79, 20.13, 19.34, 14.57.

**HRMS** (APCI) calcd. for $C_{15}H_{23}O_2^+$ $[M+H]^+$: 235.1693; found: 235.1687.

**2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl pent-4-ynoate**

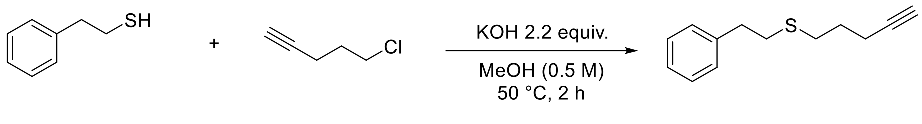


Compound **S30** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (4.51 g, 92% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.33-5.24 (m, 1H), 4.15-4.05 (m, 2H), 2.55-2.45 (m, 4H), 2.35 (dt, $J$ = 8.5, 5.6 Hz, 1H), 2.30-2.25 (m, 2H), 2.24-2.09 (m, 2H), 2.09-1.99 (m, 2H), 1.96 (t, $J$ = 2.4 Hz, 1H), 1.26 (s, 3H), 1.13 (d, $J$ = 8.6 Hz, 1H), 0.81 (s, 3H).

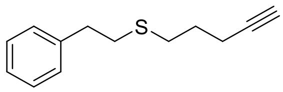
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.81, 131.35, 124.55, 82.52, 68.96, 63.28, 36.95, 35.42, 33.43, 29.44, 25.70, 25.37, 19.38, 17.64, 14.40.

**HRMS** (APCI) calcd. for $C_{16}H_{23}O_2^+$ $[M+H]^+$: 247.1693; found: 247.1689.




KOH (2.47 g, 44 mmol) was dissolved in MeOH (40 mL) in a 100 mL round bottom flask with a magnetic stir bar. 2-phenylethane-1-thiol (2.7 mL, 20 mmol) was added to the solution, and the resulting mixture was stirring at room temperature for 10 min. The 5-chloropent-1-yne (2.3 mL, 22 mmol) was then added to the solution. After stirring at 50 °C for 2 h, the reaction was concentrated in vacuo. Water (20 mL) was added to the reaction mixture, followed by neutralization with HCl aq. (3M). The solution was extracted with DCM (2 × 30 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the products[2].

**pent-4-yn-1-yl(phenethyl)sulfane**

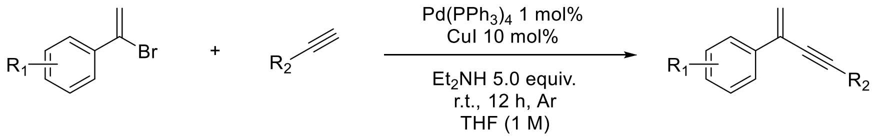



Compound **S31** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (3.15 g, 77% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.25-7.17 (m, 3H), 2.90 (dd, *J* = 9.7, 6.4 Hz, 2H), 2.78 (dd, *J* = 9.0, 5.9 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.32 (td, *J* = 6.9, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.86-1.76 (m, 2H).

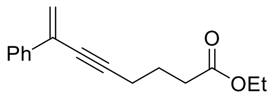
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.57, 128.49, 126.37, 83.53, 68.94, 36.36, 33.61, 30.99, 28.32, 17.51.

**HRMS** (APCI) calcd. for $C_{13}H_{17}S^+$ $[M+H]^+$: 205.1046; found: 205.1041.




An oven-dried 100 mL Schlenk tube, which was equipped with a magnetic stir bar and charged with Pd $(PPh_3)_4$ (116 mg, 1 mol%) and CuI (190 mg, 10 mol%). Then aryl bromide (1.1 equiv., 11 mmol), substituted alkyne (1.0 equiv., 10 mmol), and $Et_2NH$ (5.2 mL ,50 mmol) were added under Ar. After stirring at room temperature for 12 h, the reaction mixture was quenched by sat. aq. $NH_4Cl$ (40 mL). Then the solution was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the products[3,4].

**ethyl 7-phenyloct-7-en-5-ynoate**



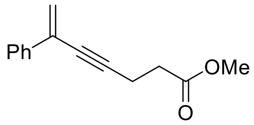

Compound **S2** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.98 g, 82% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.56 (m, 2H), 7.41-7.33 (m, 2H), 7.33-7.26 (m, 1H), 5.87 (s, 1H), 5.61 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.50 (dd, *J* = 8.4, 6.8 Hz, 4H), 1.98-1.90 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.14, 137.63, 130.80, 128.32, 128.20, 126.04, 119.79, 90.52, 80.61, 60.40, 33.21, 23.98, 18.89, 14.26.

**HRMS** (APCI) calcd. for $C_{16}H_{19}O_2^+$ $[M+H]^+$: 243.1380; found: 243.1378.

**methyl 6-phenylhept-6-en-4-ynoate**



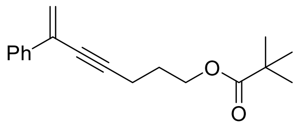

Compound **S3** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.59 g, 74% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, $J$ = 7.0 Hz, 2H), 7.35 (t, $J$ = 7.1 Hz, 2H), 7.30 (d, $J$ = 6.7 Hz, 1H), 5.87 (s, 1H), 5.60 (s, 1H), 3.72 (s, 3H), 2.75 (t, $J$ = 7.6 Hz, 2H), 2.65 (t, $J$ = 7.0 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.38, 137.46, 130.58, 128.31, 128.22, 126.03, 120.00, 89.54, 80.46, 51.85, 33.44, 15.42.

**HRMS** (APCI) calcd. for $C_{14}H_{15}O_2^+$ $[M+H]^+$: 215.1067; found: 215.1065.

**6-phenylhept-6-en-4-yn-1-yl pivalate**



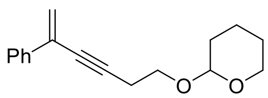

Compound **S4** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.45 g, 66% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.56 (m, 2H), 7.40-7.28 (m, 3H), 5.86 (s, 1H), 5.60 (s, 1H), 4.22 (t, $J$ = 6.3 Hz, 2H), 2.53 (t, $J$ = 7.1 Hz, 2H), 2.00-1.91 (m, 2H), 1.22 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 178.47, 137.63, 130.78, 128.32, 128.18, 126.04, 119.84, 90.20, 80.46, 63.07, 38.81, 27.92, 27.22, 16.21.

**HRMS** (APCI) calcd. for $C_{18}H_{23}O_2^+$ $[M+H]^+$: 271.1693; found: 271.1690.

**2-((5-phenylhex-5-en-3-yn-1-yl)oxy)tetrahydro-2H-pyran**



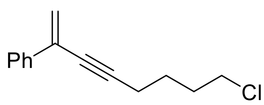

Compound **S5** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.23 g, 48% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75-7.54 (m, 2H), 7.37-7.28 (m, 3H), 5.86 (s, 1H), 5.60 (s, 1H), 4.70 (t, $J$ = 3.6 Hz, 1H), 3.95-3.88 (m, 2H), 3.65 (dt, $J$ = 9.6, 7.0 Hz, 1H), 3.55-3.49 (m, 1H), 2.73 (t, $J$ = 7.0 Hz, 2H), 1.91-1.82 (m, 1H), 1.77-1.70 (m, 1H), 1.68-1.62 (m, 1H), 1.59-1.48 (m, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.56, 130.76, 128.26, 128.16, 126.06, 119.71, 98.76, 88.66, 80.67, 65.72, 62.13, 30.60, 25.46, 20.96, 19.35.

**HRMS** (APCI) calcd. for $C_{17}H_{21}O_2^+$ $[M+H]^+$: 257.1536; found: 219.1506.

**(8-chlorooct-1-en-3-yn-2-yl)benzene**



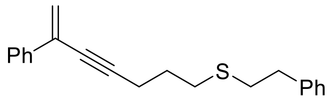

Compound **S8** was isolated via column chromatography (PE/EA=80:1~40:1) as pale yellow oil (700 mg, 32% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, $J$ = 7.3 Hz, 2H), 7.37 (t, $J$ = 7.2 Hz, 2H), 7.32 (d, $J$ = 7.0 Hz, 1H), 5.87 (s, 1H), 5.61 (s, 1H), 3.61 (t, $J$ = 6.5 Hz, 2H), 2.49 (t, $J$ = 6.9 Hz, 2H), 2.00-1.94 (m, 2H), 1.82-1.76 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.68, 130.83, 128.33, 128.20, 126.05, 119.73, 90.87, 80.44, 44.56, 31.69, 25.92, 18.76.

**HRMS** (APCI) calcd. for $C_{14}H_{16}Cl^+$ $[M+H]^+$: 219.0936; found: 219.0933.

**phenethyl(6-phenylhept-6-en-4-yn-1-yl)sulfane**



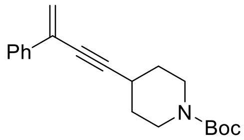

Compound **S11** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (2.39 g, 78% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.58 (m, 2H), 7.39-7.30 (m, 5H), 7.26-7.22 (m, 3H), 5.89 (s, 1H), 5.63 (s, 1H), 2.94 (t, $J$ = 7.7 Hz, 2H), 2.86-2.81 (m, 2H), 2.76-2.72 (m, 2H), 2.59 (td, $J$ = 7.0, 2.0 Hz, 2H), 1.97-1.89 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.60, 137.71, 130.86, 128.53, 128.37, 128.24, 126.41, 126.09, 119.81, 90.77, 80.58, 36.41, 33.73, 31.30, 28.68, 18.60.

**HRMS** (APCI) calcd. for $C_{21}H_{23}S^+$ $[M+H]^+$: 307.1515; found: 307.1509.

**tert-butyl 4-(3-phenylbut-3-en-1-yn-1-yl)piperidine-1-carboxylate**



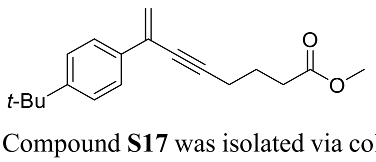

Compound **S15** was isolated via column chromatography (PE/EA=20:1~10:1) as pale yellow oil (2.03 g, 65% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, $J$ = 7.2 Hz, 2H), 7.36-7.32 (m, 2H), 7.29 (d, $J$ = 6.9 Hz, 1H), 5.86 (s, 1H), 5.59 (s, 1H), 3.73 (dt, $J$ = 10.6, 3.0 Hz, 2H), 3.29-3.21 (m, 2H), 2.80 (tt, $J$ = 7.9, 4.0 Hz, 1H), 1.89-1.81 (m, 2H), 1.73-1.64 (m, 2H), 1.46 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.77, 137.58, 130.65, 128.33, 128.21, 125.99, 119.88, 93.38, 81.16, 79.48, 42.27, 31.44, 28.47, 27.64.

**HRMS** (APCI) calcd. for $C_{20}H_{26}ON_2^+$ $[M+H]^+$: 312.1958; found: 312.1931.

**methyl 7-(4-(tert-butyl)phenyl)oct-7-en-5-ynoate**



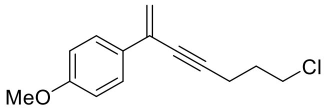

Compound **S17** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (2.35 g, 50% yield).

**$^1$H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.63-7.54 (m, 2H), 7.40-7.35 (m, 2H), 5.83 (s, 1H), 5.56 (s, 1H), 3.69 (s, 3H), 2.51 (dt, $J$ = 9.8, 7.2 Hz, 4H), 1.98-1.91 (m, 2H), 1.34 (s, 9H).

**$^{13}$C NMR** (126 MHz, CHLOROFORM-*D*) δ 173.69, 151.36, 134.93, 130.58, 125.83, 125.32, 119.15, 90.21, 80.87, 51.68, 34.66, 33.03, 31.37, 24.03, 18.97.

**HRMS** (APCI) calcd. for $C_{19}H_{25}O_2^+$ $[M+H]^+$: 285.1850; found: 285.1842.

**1-(7-chlorohept-1-en-3-yn-2-yl)-4-methoxybenzene**



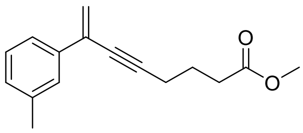

Compound **S18** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.51 g, 64% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.78 (s, 1H), 5.52 (s, 1H), 3.85 (s, 3H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.13-2.04 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.72, 130.22, 129.99, 127.25, 118.05, 113.67, 89.33, 80.97, 55.33, 43.77, 31.45, 16.87.

**HRMS** (APCI) calcd. for $C_{14}H_{16}ClO^+$ $[M+H]^+$: 235.0885; found: 235.0882.

**methyl 7-(m-tolyl)oct-7-en-5-ynoate**



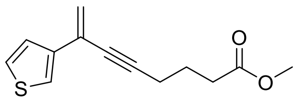

Compound **S19** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.84 g, 76% yield).

**$^{1}$H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 5.84 (s, 1H), 5.58 (s, 1H), 3.69 (s, 3H), 2.51 (dt, *J* = 8.8, 7.2 Hz, 4H), 2.38 (s, 3H), 1.97-1.91 (m, 2H).

**$^{13}$C NMR** (126 MHz, CHLOROFORM-*D*) δ 173.70, 137.96, 137.66, 130.89, 129.03, 128.29, 126.83, 123.24, 119.81, 90.33, 80.84, 51.69, 33.00, 24.00, 21.55, 18.97.

**HRMS** (APCI) calcd. for $C_{16}H_{19}O_2^+$ $[M+H]^+$: 243.1380; found: 243.1376.

**methyl 7-(thiophen-3-yl)oct-7-en-5-ynoate**



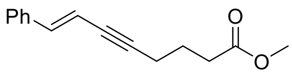

Compound **S21** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.06 g, 43% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 2.1 Hz, 1H), 7.26-7.23 (m, 2H), 5.72 (s, 1H), 5.48 (s, 1H), 3.66 (s, 3H), 2.50-2.44 (m, 4H), 1.94-1.88 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.50, 140.19, 126.03, 125.63, 124.80, 123.14, 118.53, 89.29, 80.57, 51.58, 32.90, 23.92, 18.79.

**HRMS** (APCI) calcd. for $C_{13}H_{15}O_2S^+$ $[M+H]^+$: 235.0788; found: 235.0784.

**methyl (*E*)-8-phenyloct-7-en-5-ynoate**

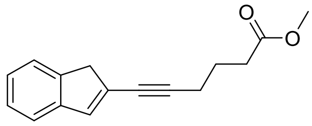



Compound **S22** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.89 g, 83% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31-7.26 (m, 1H), 6.90

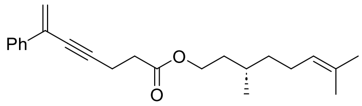
(d, $J$ = 16.2 Hz, 1H), 6.17 (dt, $J$ = 16.3, 2.3 Hz, 1H), 3.71 (s, 3H), 2.54-2.45 (m, 4H), 1.96-1.88 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.61, 140.41, 136.47, 128.68, 128.34, 126.10, 108.59, 91.35, 80.66, 51.60, 32.91, 23.96, 19.13.
**HRMS** (APCI) calcd. for $C_{15}H_{17}O_2^+$ $[M+H]^+$: 229.1224; found: 229.1218.

**methyl 6-(1H-inden-2-yl)hex-5-ynoate**



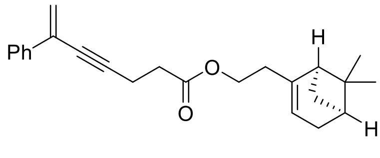
Compound **S23** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (1.78 g, 74% yield).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, $J$ = 7.3 Hz, 1H), 7.33 (d, $J$ = 7.4 Hz, 1H), 7.25 (t, $J$ = 7.4 Hz, 1H), 7.19 (td, $J$ = 7.3, 1.2 Hz, 1H), 6.96 (s, 1H), 3.68 (s, 3H), 3.47 (s, 2H), 2.50 (t, $J$ = 6.9 Hz, 4H), 1.91 (q, $J$ = 7.2 Hz, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.60, 144.26, 142.66, 136.13, 127.91, 126.67, 125.40, 123.47, 121.12, 93.85, 78.62, 51.61, 42.87, 32.94, 23.93, 19.29.
**HRMS** (APCI) calcd. for $C_{16}H_{17}O_2^+$ $[M+H]^+$: 241.1224; found: 241.1219.

**(*S*)-3,7-dimethyloct-6-en-1-yl 6-phenylhept-6-en-4-ynoate**



Compound **S25** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (2.49 g, 72% yield).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, $J$ = 7.0 Hz, 2H), 7.38-7.32 (m, 2H), 7.31-7.27 (m, 1H), 5.86 (s, 1H), 5.59 (s, 1H), 5.11-5.04 (m, 1H), 4.20-4.12 (m, 2H), 2.74 (t, $J$ = 7.2 Hz, 2H), 2.63 (t, $J$ = 7.2 Hz, 2H), 2.03-1.90 (m, 2H), 1.72-1.66 (m, 4H), 1.60 (s, 3H), 1.58-1.52 (m, 1H), 1.49-1.42 (m, 1H), 1.37-1.29 (m, 1H), 1.22-1.14 (m, 1H), 0.90 (d, $J$ = 6.5 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.97, 137.49, 131.36, 130.63, 128.28, 128.18, 126.03, 124.57, 119.93, 89.61, 80.43, 63.32, 36.97, 35.44, 33.74, 29.49, 25.72, 25.38, 19.40, 17.66, 15.45.
**HRMS** (APCI) calcd. for $C_{23}H_{31}O_2^+$ $[M+H]^+$: 339.2319; found: 339.2315.

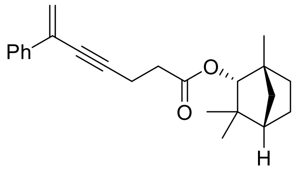
**2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 6-phenylhept-6-en-4-ynoate**



Compound **S26** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (2.03 g, 65% yield).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, $J$ = 6.8 Hz, 2H), 7.44-7.32 (m, 2H), 7.32-7.27 (m, 1H), 5.86 (s, 1H), 5.59 (s, 1H), 5.32-5.28 (m, 1H), 4.13 (td, $J$ = 7.0, 4.4 Hz, 2H), 2.73 (t, $J$ = 7.3 Hz, 2H), 2.64-2.59 (m, 2H), 2.39-2.33 (m, 1H), 2.29 (t, $J$ = 7.0 Hz, 2H), 2.25-2.16 (m, 2H), 2.10-2.02 (m, 2H), 1.27 (s, 3H), 1.14 (d, $J$ = 8.5 Hz, 1H), 0.82 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.86, 144.02, 137.50, 130.63, 128.29, 128.19, 126.04, 119.95, 118.87, 89.63, 80.42, 62.99, 45.67, 40.73, 38.00, 35.93, 33.70, 31.66, 31.36, 26.28, 21.12, 15.41.
**HRMS** (APCI) calcd. for $C_{24}H_{29}O_2^+$ $[M+H]^+$: 349.2163; found: 349.2133.

**(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 6-phenylhept-6-en-4-ynoate**




Compound **S27** was isolated via column chromatography (PE/EA=50:1~20:1) as pale yellow oil (2.68 g, 80% yield).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.37-7.32 (m, 2H), 7.30 (d, *J* = 6.9 Hz, 1H), 5.85 (s, 1H), 5.58 (s, 1H), 4.42 (d, *J* = 2.0 Hz, 1H), 2.82-2.73 (m, 2H), 2.71-2.64 (m, 2H), 1.78-1.67 (m, 3H), 1.61-1.56 (m, 1H), 1.49-1.40 (m, 1H), 1.19 (dd, *J* = 10.3, 1.6 Hz, 1H), 1.11 (s, 4H), 1.04 (s, 3H), 0.79 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.22, 137.52, 130.68, 128.28, 128.16, 126.06, 119.96, 89.75, 86.60, 80.43, 48.34, 48.30, 41.37, 39.44, 33.84, 29.70, 26.64, 25.83, 20.17, 19.37, 15.58.
**HRMS** (APCI) calcd. for $C_{23}H_{29}O_2^+$ $[M+H]^+$: 337.2163; found: 337.2159.

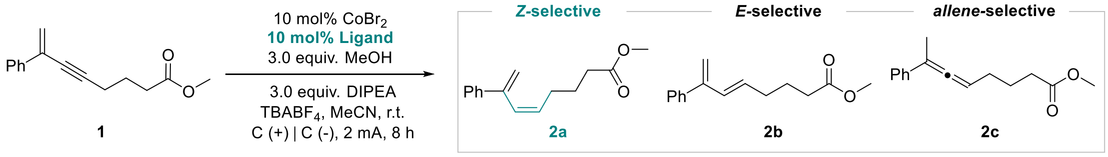
# 3. Optimization of Reaction Conditions for Hydrogenation

## General procedure

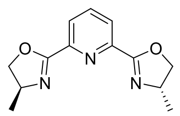
In the glovebox, a 15 mL tube equipped with a magnetic stirrer was charged with electrolyte, ligand, cobalt salt, then solvent was added. The resulting solution was stirred for 10 min at room temperature. substrate **1**, proton source and other reagent were added sequentially to the tube. The electrochemical cell was then sealed, brought out from the glove box. The resulting solution was electrolyzed under a constant current. Yields, *Z*/*E* and r.r. value were determined by GC using diphenyl as the internal standard.

## Optimization of reaction condition for *Z*-selective hydrogenation

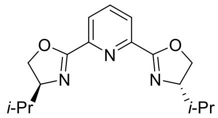
**Table S1** Screening of ligands



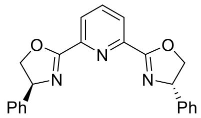

| Entry | Ligand | Yield(%) | *Z*/*E*(2a:2b) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | **L1** | 37 | 12:1 | 9:1 |
| 2 | **L2** | 35 | 15:1 | 18:1 |
| 3 | **L3** | 39 | 17:1 | >20:1 |
| **4** | **L4** | **36** | **>20:1** | **18:1** |
| 5 | **L8** | 24 | 10:1 | 1:1 |
| 6 | **L9** | 22 | 8:1 | 15:1 |
| 7 | **L10** | 36 | 4:1 | 18:1 |
| 8 | **L11** | n.p. | - | - |
| 9 | **L12** | n.p. | - | - |
| 10 | **L13** | trace | - | - |
| 11 | **L14** | trace | - | - |
| 12 | **L15** | trace | - | - |



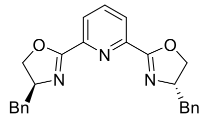

**L1**



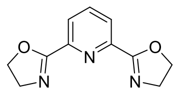

**L2**



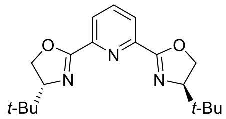

**L3**



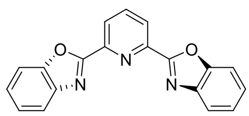

**L4**



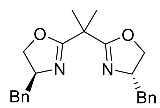
**L8**



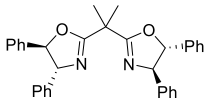

**L9**



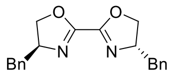
**L10**



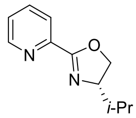

**L11**



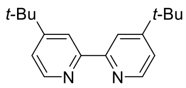
**L12**



**L13**



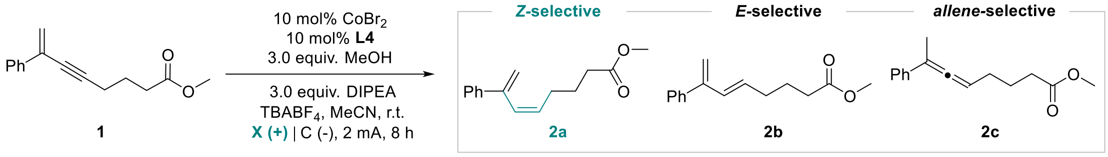
**L14**



**L15**

Reaction Conditions: substrate **1** (0.2 mmol), $CoBr_2$ (10 mol%), Ligand (10 mol%), MeOH (3.0 equiv.), DIPEA (3.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, C felt (+) | C felt (-), in MeCN (5 mL) at r.t. for 8 h. Yields were determined by GC using diphenyl as the internal standard, *Z/E* and r.r. value were determined by GC analysis.

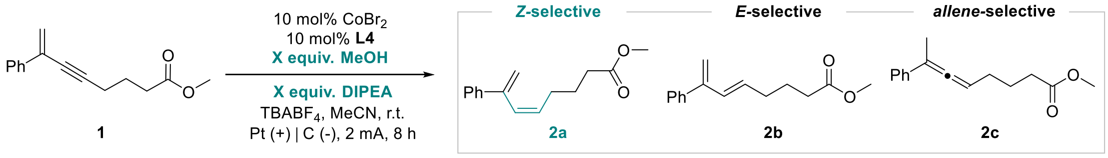
**Table S2** Screening of electrode




| Entry | Anode | Yield(%) | *Z/E*(2a:2b) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | C felt | 36 | >20:1 | 18:1 |
| **2** | **Pt** | **65** | **>20:1** | **>20:1** |
| 3 | RVC | 19 | >20:1 | 2:1 |
| 4 | SS | 60 | - | 1:17 |
| 5 | Ni foam | trace | - | - |
| 6 | Zn, no DIPEA | messy | - | - |

Reaction Conditions: substrate **1** (0.2 mmol), $CoBr_2$ (10 mol%), L4 (10 mol%), MeOH (3.0 equiv.), DIPEA (3.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, Anode (+) | C felt (-), in MeCN (5 mL) at r.t. for 8 h. Yields were determined by GC using diphenyl as the internal standard, *Z/E* and r.r. value were determined by GC analysis.

**Table S3** Screening of the amount of DIPEA and MeOH

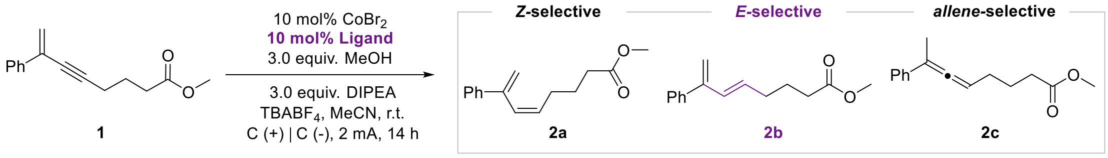



| Entry | X equiv. | Yield(%) | *Z/E*(2a:2b) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | 3.0 | 65 | >20:1 | >20:1 |
| **2** | **4.5** | **77** | **>20:1** | **>20:1** |
| 3 | 6.0 | 73 | >20:1 | >20:1 |
| 4 | 10.0 | 69 | >20:1 | >20:1 |

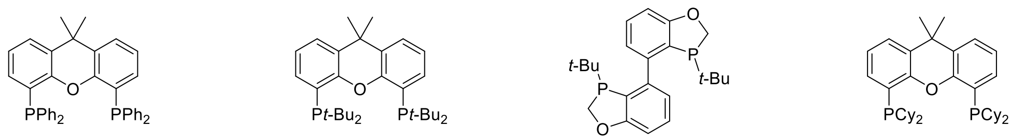
Reaction Conditions: substrate **1** (0.2 mmol), $CoBr_2$ (10 mol%), L4 (10 mol%), MeOH (X equiv.), DIPEA (X equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, Pt (+) | C felt (-), in MeCN (5 mL) at r.t. for 8 h. Yields were determined by GC using diphenyl as the internal standard, *Z/E* and r.r. value were determined by GC analysis.

# Optimization of reaction condition for *E*-selective hydrogenation

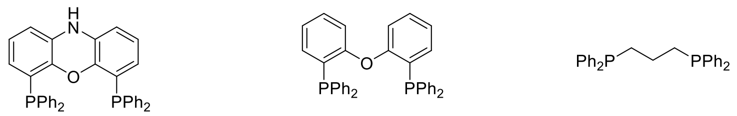
**Table S4** Screening of ligands




| Entry | Ligand | Yield(%) | *E/Z*(2b:2a) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | **L5** | 13 | 5:1 | 12:1 |
| 2 | **L6** | 6 | 2:1 | 5:1 |
| 3 | **L7** | 25 | 1.5:1 | 12:1 |
| 4 | **L16** | trace | - | - |
| 5 | **L17** | 11 | 2:1 | 4:1 |
| 6 | **L18** | trace | - | - |
| 7 | **L19** | trace | - | - |
| 8[a] | **L5** | 27 | - | <1:20 |
| **9[a]** | **L7** | **40** | **14:1** | **16:1** |



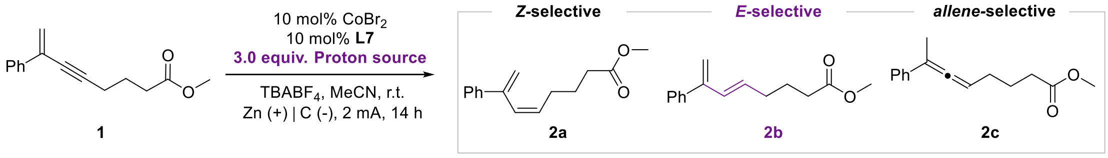

**L5** **L6** **L7** **L16**




**L17** **L18** **L19**

Reaction Conditions: substrate **1** (0.2 mmol), $CoBr_2$ (10 mol%), Ligand (10 mol%), MeOH (3.0 equiv.), DIPEA (3.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, C felt (+) | C felt (-), in MeCN (5 mL) at r.t. for 8 h. Yields were determined by GC using diphenyl as the internal standard, *E/Z* and r.r. value were determined by GC analysis. [a]Zn (+) instead of C felt (+), no DIPEA.

**Table S5** Screening of proton sources

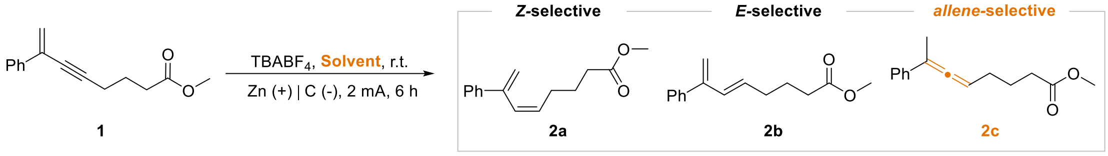


| Entry | Proton source | Yield(%) | *E/Z*(2b:2a) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | MeOH | 40 | 14:1 | 16:1 |
| 2 | 4-tert-Butylphenol | 54 | 18:1 | 8:1 |
| 3 | 4-Trifluoromethylphenol | 27 | 7:1 | 4:1 |
| 4 | HOAc | 61 | 2:1 | 5:1 |
| 5 | HFIP | 28 | >20:1 | 5:1 |
| **6** | **$CF_3CH_2OH$** | **71** | **20:1** | **13:1** |

Reaction Conditions: substrate **1** (0.2 mmol), $CoBr_2$ (10 mol%), L7 (10 mol%), Proton source (3.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, Zn (+) | C felt (-), in MeCN (5 mL) at r.t. for 14 h. Yields were determined by GC using diphenyl as the internal standard, *E/Z* and r.r. value were determined by GC analysis.

## Optimization of reaction condition for *allene*-selective hydrogenation

**Table S6** Screening of solvents



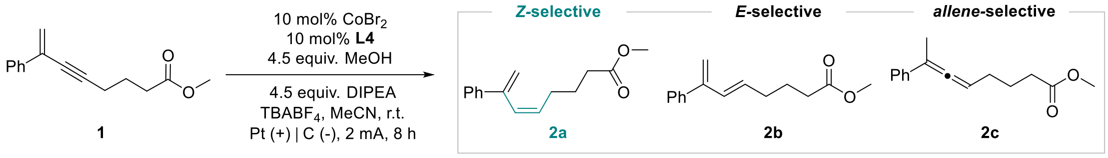

| Entry | Solvent | Yield(%) | r.r.(2c:2a+2b) |
|---|---|---|---|
| 1 | Acetone | 50 | >20:1 |
| 2 | MeCN | 85 | 17:1 |
| 3 | DMA | 43 | 19:1 |
| 4 | NMP | 44 | >20:1 |
| 5 | THF | 52 | 17:1 |
| **6[a]** | **MeCN** | **95** | **>20:1** |

Reaction Conditions: substrate **1** (0.2 mmol), MeOH (2.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, Zn (+) | C felt (-), in MeCN (5 mL) at r.t. for 6 h. Yields were determined by GC using diphenyl as the internal standard, r.r. value was determined by GC analysis.

[a]stainless steel felt (-) instead of C (-)

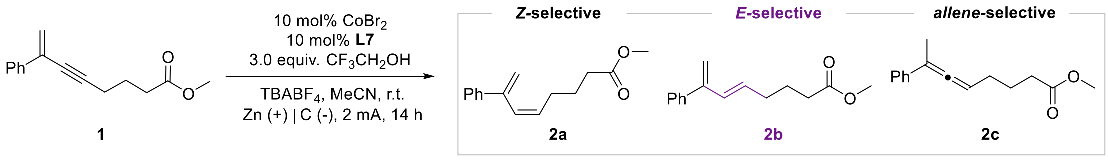
## Reaction procedures of hydrogenation

### *Z* condition:



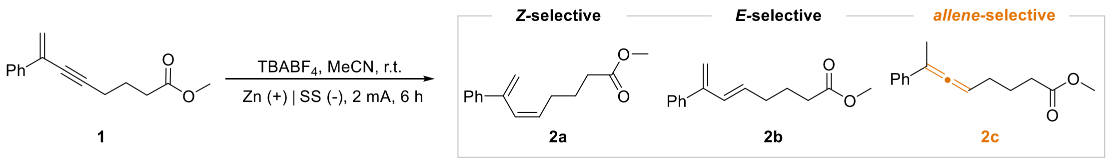

Carbon felt electrodes were polished with 600 grit silicon carbide sandpaper before use. In the glovebox, a 15 mL dried tube equipped with a magnetic stirrer was charged with $TBABF_4$ (165mg, 0.5 mmol), **L4** (7.9 mg, 0.02 mmol), $CoBr_2$ (4.3 mg, 0.02 mmol), then 5 mL MeCN was added, the resulting solution was stirred for 10 min at room temperature. Substrate **1** (41 µL, 0.2 mmol), MeOH (37 µL, 0.9 mmol) and DIPEA (157 µL, 0.9 mmol) were added sequentially to the tube. The tube was sealed with the pre-assembled electrochemical cap, equipped with anode (Pt felt, 25×10×1 mm) and cathode (carbon felt, 25×10×1 mm), and then the assembly was brought out of the glove box. The resulting solution was electrolyzed under a constant current of 2 mA for 8 h at room temperature. Once reaction was completed, the reaction solvent was concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give the products.

### *E* condition:




Carbon felt electrodes were polished with 600 grit silicon carbide sandpaper before use. In the glovebox, a 15 mL dried tube equipped with a magnetic stirrer was charged with $TBABF_4$ (165mg, 0.5 mmol), **L7** (7.7 mg, 0.02 mmol), $CoBr_2$ (4.3 mg, 0.02 mmol), then 5 mL MeCN was added, the resulting solution was stirred for 10 min at room temperature. Substrate **1** (41 µL, 0.2 mmol) and $CF_3CH_2OH$ (43 µL, 0.6 mmol) were added sequentially to the tube. The tube was sealed with the pre-assembled electrochemical cap, equipped with anode (Zn felt, 25×10×1 mm) and cathode (carbon felt, 25×10×1 mm), and then the assembly was brought out of the glove box. The resulting solution was electrolyzed under a constant current of 2 mA for 14 h at room temperature. Once reaction was completed, the reaction solvent was concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give the products.

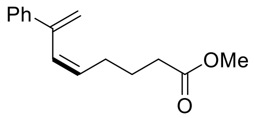
### *Allene* condition:




Carbon felt electrodes were polished with 600 grit silicon carbide sandpaper before use. In the glovebox, a 15 mL dried tube equipped with a magnetic stirrer was charged with $TBABF_4$ (165mg, 0.5 mmol), then 5 mL MeCN was added, the resulting solution was stirred for 10 min at room temperature. Substrate **1** (41 µL, 0.2 mmol) and MeOH (16 µL, 0.4 mmol) were added sequentially to the tube. The tube was sealed with the pre-assembled electrochemical cap, equipped with anode (Zn felt, 25×10×1 mm) and cathode (stainless steel felt, 25×10×1 mm), and then the assembly was brought out of the glove box. The resulting solution was electrolyzed under a constant current of 2 mA for 6 h at room temperature. Once reaction was completed, the reaction solvent was concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give the products.

# 4. Characterization Data of Products

**methyl *(Z)*-7-phenylocta-5,7-dienoate**



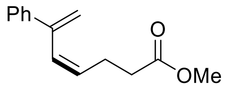

Compound **2a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (34.5 mg, 75% yield, *Z:E* >20:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 6.19 (d, *J* = 11.5 Hz, 1H), 5.68 (dt, *J* = 11.5, 7.3 Hz, 1H), 5.54 (s, 1H), 5.13 (s, 1H), 3.63 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.75-1.68 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.97, 144.33, 140.67, 133.03, 129.90, 128.26, 127.58, 126.53, 114.90, 51.46, 33.58, 27.98, 25.05.

**HRMS** (APCI) calcd. for $C_{15}H_{19}O_2^+$ $[M+H]^+$: 231.1380; found: 231.1372.

**methyl *(Z)*-6-phenylhepta-4,6-dienoate**



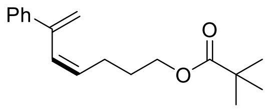

Compound **3a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (32.4 mg, 72% yield, *Z:E* = 17:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 1H), 6.20 (d, *J* = 11.4 Hz, 1H), 5.69 (dt, *J* = 11.4, 7.2 Hz, 1H), 5.58 (s, 1H), 5.16 (s, 1H), 3.65 (s, 3H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 173.46, 144.19, 140.53, 131.81, 130.40, 128.36, 127.71, 126.57, 115.12, 51.60, 34.24, 24.17.

**HRMS** (APCI) calcd. for $C_{14}H_{17}O_2^+$ $[M+H]^+$: 217.1224; found: 217.1217.

***(Z)*-6-phenylhepta-4,6-dien-1-yl pivalate**



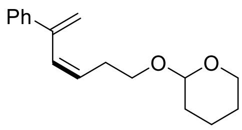

Compound **4a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (41.4 mg, 76% yield, *Z:E* >20:1, r.r. = 9:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 2H), 7.35-7.28 (m, 3H), 6.19 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.71 (dt, *J* = 11.4, 7.3 Hz, 1H), 5.54 (d, *J* = 1.7 Hz, 1H), 5.14 (s, 1H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.21 (qd, *J* = 7.5, 1.8 Hz, 2H), 1.74-1.68 (m, 2H), 1.15 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 178.55, 144.33, 140.64, 132.92, 129.86, 128.28, 127.60, 126.52, 114.83, 63.80, 38.70, 28.83, 27.22, 27.16, 25.12.

**HRMS** (APCI) calcd. for $C_{18}H_{25}O_2^+$ $[M+H]^+$: 273.1850; found: 273.1838.

**(Z)-2-((5-phenylhexa-3,5-dien-1-yl)oxy)tetrahydro-2H-pyran**



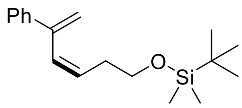

Compound **5a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (39.3 mg, 76% yield, *Z:E* >20:1, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.36-7.28 (m, 3H), 6.23 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.79 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.55 (d, *J* = 1.7 Hz, 1H), 5.20 (s, 1H), 4.58 (t, *J* = 3.5 Hz, 1H), 3.85 (td, *J* = 8.1, 4.0 Hz, 1H), 3.79-3.74 (m, 1H), 3.51-3.46 (m, 1H), 3.46-3.41 (m, 1H), 2.46 (qd, *J* = 7.0, 1.8 Hz, 2H), 1.86-1.79 (m, 1H), 1.72-1.67 (m, 1H), 1.61-1.58 (m, 1H), 1.55-1.51 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.28, 140.65, 130.58, 130.46, 128.24, 127.56, 126.57, 114.96, 98.62, 66.98, 62.18, 30.67, 29.27, 25.49, 19.50.

**HRMS** (APCI) calcd. for $C_{17}H_{23}O_2^+$ $[M+H]^+$: 259.1693; found: 259.1685.

**(Z)-tert-butyldimethyl((5-phenylhexa-3,5-dien-1-yl)oxy)silane**



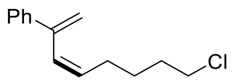

Compound **6a** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (35.2 mg, 61% yield, *Z:E* = 14:1, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.7 Hz, 2H), 7.35-7.29 (m, 3H), 6.23 (d, *J* = 11.5 Hz, 1H), 5.77 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.55 (s, 1H), 5.19 (s, 1H), 3.65 (t, *J* = 6.6 Hz, 2H), 2.37 (qd, *J* = 6.8, 1.8 Hz, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.41, 140.73, 130.59, 130.46, 128.24, 127.54, 126.58, 114.83, 62.99, 32.37, 25.97, 18.37, -5.26.

**HRMS** (APCI) calcd. for $C_{18}H_{29}OSi^+$ $[M+H]^+$: 289.1983; found: 289.1984.

**(Z)-(8-chloroocta-1,3-dien-2-yl)benzene**



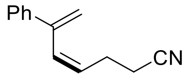

Compound **7a** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (21.2 mg, 48% yield, *Z:E* = 17:1, r.r. = 8:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.18 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.69 (dt, *J* = 11.6, 7.4 Hz, 1H), 5.54 (d, *J* = 1.7 Hz, 1H), 5.14 (s, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.14 (qd, *J* = 7.5, 1.8 Hz, 2H), 1.77-1.71 (m, 2H), 1.54-1.50 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.47, 140.77, 133.53, 129.56, 128.28, 127.58, 126.55, 114.91, 44.84, 32.13, 27.76, 26.96.

**HRMS** (APCI) calcd. for $C_{14}H_{18}Cl^+$ $[M+H]^+$: 221.1092; found: 221.1088.

**(Z)-6-phenylhepta-4,6-dienenitrile**



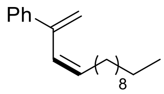
Compound **8a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (22.7 mg, 62% yield, *Z:E* >20:1, r.r. = 5:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 6.8 Hz, 1H), 6.35 (d, *J* = 11.4 Hz, 1H), 5.71 (dt, *J* = 11.5, 7.1 Hz, 1H), 5.59 (s, 1H), 5.17 (s, 1H), 2.47-2.43 (m, 2H), 2.38-2.34 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.92, 140.00, 132.41, 129.05, 128.45, 127.93, 126.53, 119.21, 115.69, 24.42, 17.51.

**HRMS** (APCI) calcd. for $C_{13}H_{14}N^+$ $[M+H]^+$: 184.1121; found: 184.1116.

**(Z)-tetradeca-1,3-dien-2-ylbenzene**



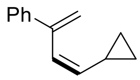
Compound **9a** was isolated via column chromatography (PE) as pale yellow oil (36.2 mg, 67% yield, *Z:E* = 14:1, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.35-7.29 (m, 3H), 6.12 (d, *J* = 11.5 Hz, 1H), 5.71 (dt, *J* = 11.5, 7.4 Hz, 1H), 5.53 (s, 1H), 5.14 (s, 1H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.28-1.22 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.58, 140.97, 134.71, 128.71, 128.20, 127.47, 126.58, 114.64, 31.92, 29.85, 29.62, 29.47, 29.35, 29.31, 28.64, 22.70, 14.12.

**HRMS** (APCI) calcd. for $C_{20}H_{31}^+$ $[M+H]^+$: 271.2421; found: 271.2412.

**(Z)-(4-cyclopropylbuta-1,3-dien-2-yl)benzene**



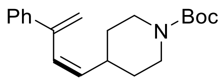
Compound **10a** was isolated via column chromatography (PE) as pale yellow oil (14.6 mg, 43% yield, *Z:E* >20:1, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.39-7.31 (m, 3H), 6.09 (d, *J* = 11.4 Hz, 1H), 5.56 (s, 1H), 5.37 (s, 1H), 5.07 (t, *J* = 10.7 Hz, 1H), 1.67-1.57 (m, 1H), 0.73-0.69 (m, 2H), 0.43-0.40 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.05, 141.09, 138.53, 128.20, 127.49, 126.95, 126.84, 114.96, 11.51, 7.76.

**HRMS** (APCI) calcd. for $C_{13}H_{15}^+$ $[M+H]^+$: 171.1169; found: 171.1161.

**tert-butyl (Z)-4-(3-phenylbuta-1,3-dien-1-yl)piperidine-1-carboxylate**

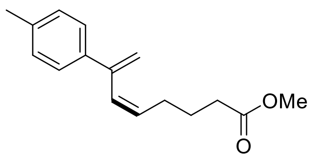


Compound **11a** was isolated via column chromatography (PE/EA=20:1~10:1) as pale yellow oil (45.0 mg, 72% yield, *Z:E* >20:1, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.35-7.29 (m, 3H), 6.11 (d, *J* = 11.4 Hz, 1H), 5.53-5.46 (m, 2H), 5.14 (s, 1H), 4.03 (s, 2H), 2.58 (t, *J* = 12.8 Hz, 2H), 2.48 (dt, *J* = 10.2, 3.8 Hz, 1H),

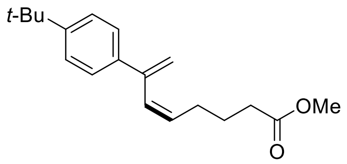
1.54 (d, $J$ = 10.6 Hz, 2H), 1.45 (s, 9H), 1.36-1.28 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.86, 144.74, 140.51, 137.85, 128.57, 128.28, 127.70, 126.55, 114.45, 79.30, 43.50, 35.26, 32.09, 28.47.
**HRMS** (ESI) calcd. for $C_{20}H_{28}NO_2^+$ $[M+H]^+$: 314.2115; found: 314.2112.

**methyl *(Z)*-7-(p-tolyl)octa-5,7-dienoate**



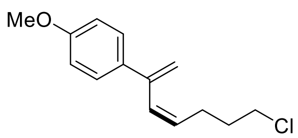

Compound **12a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (32.5 mg, 67% yield, *Z:E* >20:1, r.r. = 8:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, $J$ = 7.9 Hz, 2H), 7.13 (d, $J$ = 7.9 Hz, 2H), 6.17 (d, $J$ = 11.4 Hz, 1H), 5.67 (dt, $J$ = 11.3, 7.3 Hz, 1H), 5.51 (s, 1H), 5.08 (s, 1H), 3.64 (s, 3H), 2.35 (s, 3H), 2.28 (t, $J$ = 7.6 Hz, 2H), 2.17 (q, $J$ = 7.5 Hz, 2H), 1.74-1.69 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 174.02, 144.05, 137.74, 137.38, 132.87, 130.06, 128.97, 126.39, 114.06, 51.47, 33.60, 27.97, 25.08, 21.14.
**HRMS** (APCI) calcd. for $C_{16}H_{21}O_2^+$ $[M+H]^+$: 245.1537; found: 245.1528.

**methyl *(Z)*-7-(4-(tert-butyl)phenyl)octa-5,7-dienoate**




Compound **13a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (36.7 mg, 64% yield, *Z:E* >20:1, r.r. >20:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (s, 4H), 6.18 (d, $J$ = 11.5 Hz, 1H), 5.69 (dt, $J$ = 11.5, 7.3 Hz, 1H), 5.54 (s, 1H), 5.09 (s, 1H), 3.64 (s, 3H), 2.29 (t, $J$ = 7.6 Hz, 2H), 2.19 (q, $J$ = 7.8 Hz, 2H), 1.75-1.69 (m, 2H), 1.33 (s, 9H).
**$^{13}$C NMR** (101 MHz, CDCl3) δ 174.03, 150.67, 143.83, 137.60, 132.87, 130.03, 126.14, 125.19, 114.07, 51.48, 34.54, 33.62, 31.33, 27.95, 25.10.
**HRMS** (APCI) calcd. for $C_{19}H_{27}O_2^+$ $[M+H]^+$: 287.2006; found: 287.1996.

***(Z)*-1-(7-chlorohepta-1,3-dien-2-yl)-4-methoxybenzene**

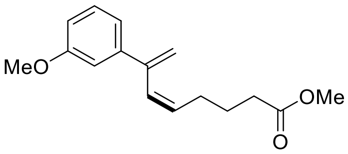



Compound **14a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (27.9 mg, 59% yield, *Z:E* = 14:1, r.r. >20:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, $J$ = 8.8 Hz, 2H), 6.87 (d, $J$ = 8.7 Hz, 2H), 6.20 (dd, $J$ = 11.4, 1.7 Hz, 1H), 5.67 (dt, $J$ = 11.5, 7.3 Hz, 1H), 5.48 (d, $J$ = 1.6 Hz, 1H), 5.05 (s, 1H), 3.82 (s, 3H), 3.50 (t, $J$ = 6.8 Hz, 2H), 2.29 (qd, $J$ = 7.5, 1.7 Hz, 2H), 1.88-1.81 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.32, 143.54, 133.09, 132.01, 130.54, 127.65, 113.67, 113.32, 55.31,

44.48, 32.79, 26.01.

**HRMS** (APCI) calcd. for $C_{14}H_{18}ClO^+$ $[M+H]^+$: 237.1041; found: 237.1032.

**methyl *(Z)*-7-(3-methoxyphenyl)octa-5,7-dienoate**



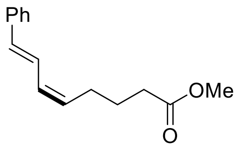
Compound **15a** was isolated via column chromatography (PE/EA=30:1~15:1) as pale yellow oil (32.3 mg, 62% yield, *Z:E* = 10:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.17 (d, *J* = 11.5 Hz, 1H), 5.67 (dt, *J* = 11.4, 7.3 Hz, 1H), 5.54 (s, 1H), 5.13 (s, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.74-1.68 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.98, 159.56, 144.19, 142.19, 133.10, 129.80, 129.24, 119.09, 115.11, 113.01, 112.30, 55.24, 51.48, 33.58, 27.97, 25.04.

**HRMS** (APCI) calcd. for $C_{16}H_{21}O_3^+$ $[M+H]^+$: 261.1486; found: 261.1481.

**methyl (5*Z*,7*E*)-8-phenylocta-5,7-dienoate**



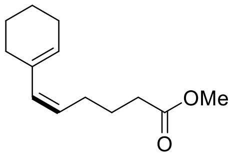
Compound **16a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (30.0 mg, 66% yield, *Z:E* >20:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.03 (ddd, *J* = 15.5, 11.0, 1.1 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.21 (t, *J* = 10.9 Hz, 1H), 5.49 (dt, *J* = 10.8, 7.7 Hz, 1H), 3.67 (s, 3H), 2.40-2.32 (m, 4H), 1.83-1.75 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.97, 137.54, 132.61, 131.44, 129.84, 128.60, 127.47, 126.38, 124.13, 51.50, 33.32, 27.22, 24.83.

**HRMS** (APCI) calcd. for $C_{15}H_{19}O_2^+$ $[M+H]^+$: 231.1380; found: 230.1374.

**methyl *(Z)*-6-(cyclohex-1-en-1-yl)hex-5-enoate**



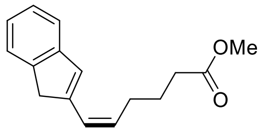
Compound **17a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (24.6 mg, 59% yield, *Z:E* >20:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.77 (d, *J* = 11.8 Hz, 1H), 5.60 (s, 1H), 5.22 (dt, *J* = 11.7, 7.4 Hz, 1H), 3.66 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.31-2.25 (m, 2H), 2.13-2.07 (m, 4H), 1.74-1.68 (m, 2H), 1.65-1.61 (m, 2H), 1.60-1.54 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 174.14, 135.26, 132.69, 128.03, 127.47, 51.49, 33.60, 28.99, 28.21, 25.60, 25.49, 22.89, 22.11.

**HRMS** (APCI) calcd. for $C_{13}H_{21}O_2^+$ $[M+H]^+$: 209.1537; found: 209.1535.

**methyl *(Z)*-6-(1H-inden-2-yl)hex-5-enoate**



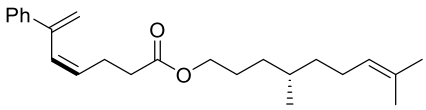

Compound **18a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (35.4 mg, 73% yield, *Z:E* = 12:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.16 (td, *J* = 7.4, 1.2 Hz, 1H), 6.76 (s, 1H), 6.36 (d, *J* = 11.5 Hz, 1H), 5.51 (dt, *J* = 11.6, 7.4 Hz, 1H), 3.68 (s, 3H), 3.60 (s, 2H), 2.49-2.43 (m, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.87-1.79 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.97, 144.91, 144.62, 143.42, 131.71, 131.14, 126.54, 125.71, 124.67, 123.52, 120.83, 51.58, 41.13, 33.56, 28.64, 25.07.

**HRMS** (APCI) calcd. for $C_{16}H_{19}O_2^+$ $[M+H]^+$: 243.1380; found: 243.1374.

**(*S*)-4,8-dimethylnon-7-en-1-yl *(Z)*-6-phenylhepta-4,6-dienoate**



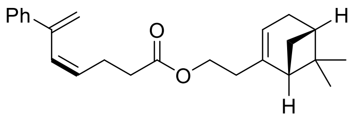

Compound **19a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (51.0 mg, 75% yield, *Z:E* >20:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.20 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.70 (dt, *J* = 11.5, 7.2 Hz, 1H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.16 (s, 1H), 5.11-5.07 (m, 1H), 4.12-4.06 (m, 2H), 2.48-2.43 (m, 2H), 2.38-2.33 (m, 2H), 2.02-1.93 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.56-1.50 (m, 1H), 1.47-1.28 (m, 3H), 1.21-1.14 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.07, 144.13, 140.50, 131.87, 131.33, 130.24, 128.29, 127.63, 126.51, 124.59, 115.08, 62.99, 36.99, 35.45, 34.47, 29.51, 25.72, 25.40, 24.17, 19.42, 17.66.

**HRMS** (APCI) calcd. for $C_{23}H_{33}O_2^+$ $[M+H]^+$: 341.2476; found: 341.2467.

**2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl *(Z)*-6-phenylhepta-4,6-dienoate**



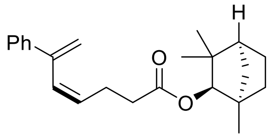

Compound **20a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (40.0 mg, 57% yield, *Z:E* = 12:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.19 (d, *J* = 11.4 Hz, 1H), 5.69 (dt, *J* = 11.4, 7.1 Hz, 1H), 5.56 (s, 1H), 5.27 (s, 1H), 5.15 (s, 1H), 4.06 (td, *J* = 6.8, 4.6 Hz, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 2.37-2.32 (m, 3H), 2.28-2.19 (m, 4H), 2.09-2.06 (m, 1H), 2.04-2.01 (m, 1H), 1.26 (s, 3H), 1.13 (d, *J* = 8.5 Hz, 1H), 0.81 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.99, 144.11, 144.09, 140.48, 131.89, 130.20, 128.29, 127.65, 126.50, 118.77, 115.06, 62.69, 45.66, 40.72, 38.00, 35.93, 34.46, 31.65, 31.36, 26.28, 24.14, 21.12.

**HRMS** (APCI) calcd. for $C_{24}H_{31}O_2^+$ $[M+H]^+$: 351.2319; found: 351.2311.

**(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl *(Z)*-6-phenylhepta-4,6-dienoate**



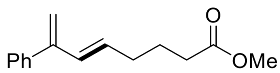

Compound **21a** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (39.0 mg, 58% yield, *Z:E* >20:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.21 (d, *J* = 11.5 Hz, 1H), 5.70 (dt, *J* = 11.8, 7.0 Hz, 1H), 5.55 (s, 1H), 5.17 (s, 1H), 4.35 (s, 1H), 2.48-2.42 (m, 2H), 2.41-2.36 (m, 2H), 1.73-1.66 (m, 3H), 1.62-1.52 (m, 2H), 1.49-1.41 (m, 1H), 1.19-1.15 (m, 1H), 1.09 (s, 3H), 1.01 (s, 3H), 0.73 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.38, 144.29, 140.65, 132.02, 130.15, 128.29, 127.63, 126.59, 115.31, 86.15, 48.34, 48.24, 41.36, 39.39, 34.57, 29.69, 26.64, 25.83, 24.44, 20.19, 19.39.

**HRMS** (APCI) calcd. for $C_{23}H_{31}O_2^+$ $[M+H]^+$: 339.2319; found: 339.2312.

**methyl *(E)*-7-phenylocta-5,7-dienoate**



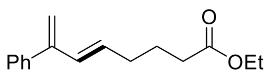

Compound **2b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (32.7 mg, 71% yield, *E:Z* >20:1, r.r. = 13:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 6.32 (d, *J* = 15.6 Hz, 1H), 5.61 (dt, *J* = 15.8, 7.1 Hz, 1H), 5.20 (s, 1H), 5.08 (s, 1H), 3.66 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.78-1.70 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.99, 147.91, 140.53, 132.86, 132.40, 128.22, 128.08, 127.35, 115.06, 51.50, 33.45, 32.16, 24.36.

**HRMS** (APCI) calcd. for $C_{15}H_{19}O_2^+$ $[M+H]^+$: 231.1380; found: 231.1371.

**ethyl *(E)*-7-phenylocta-5,7-dienoate**



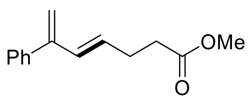

Compound **3b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (28.0 mg, 57% yield, *E:Z* >20:1, r.r. = 8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 6.32 (d, *J* = 15.6 Hz, 1H), 5.61 (dt, *J* = 14.9, 7.0 Hz, 1H), 5.19 (s, 1H), 5.08 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.17 (q, *J* = 7.3 Hz, 2H), 1.77-1.69 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.60, 147.92, 140.53, 132.96, 132.36, 128.26, 128.09, 127.37, 115.10, 60.29, 33.74, 32.20, 24.40, 14.27.

**HRMS** (APCI) calcd. for $C_{16}H_{20}O_2^+$ $[M+H]^+$: 245.1537; found: 245.1528.

**methyl *(E)*-6-phenylhepta-4,6-dienoate**



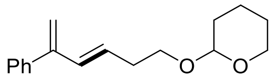
Compound **4b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (28.5 mg, 66% yield, *E:Z* >20:1, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 5H), 6.34 (d, *J* = 15.7 Hz, 1H), 5.63 (dt, *J* = 15.6, 6.3 Hz, 1H), 5.21 (s, 1H), 5.10 (s, 1H), 3.67 (s, 3H), 2.47-2.41 (m, 4H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.42, 147.70, 140.37, 132.50, 131.72, 128.22, 128.11, 127.42, 115.49, 51.62, 33.68, 28.10.

**HRMS** (APCI) calcd. for $C_{14}H_{17}O_2^+$ $[M+H]^+$: 217.1224; found: 217.1220.

***(E)*-2-((5-phenylhexa-3,5-dien-1-yl)oxy)tetrahydro-2H-pyran**



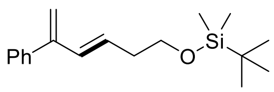
Compound **5b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (29.8 mg, 58% yield, *E:Z* = 11:1, r.r. = 10:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 5H), 6.38 (d, *J* = 15.7 Hz, 1H), 5.66 (dt, *J* = 14.9, 7.0 Hz, 1H), 5.20 (s, 1H), 5.09 (s, 1H), 4.60 (t, *J* = 3.5 Hz, 1H), 3.86-3.81 (m, 1H), 3.79-3.73 (m, 1H), 3.51-3.48 (m, 1H), 3.47-3.43 (m, 1H), 1.84-1.78 (m, 1H), 1.73-1.68 (m, 1H), 1.60-1.49 (m, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 147.98, 140.50, 133.17, 130.48, 128.25, 128.04, 127.34, 115.11, 98.67, 66.79, 62.17, 33.28, 30.66, 25.50, 19.48.

**HRMS** (APCI) calcd. for $C_{17}H_{23}O_2^+$ $[M+H]^+$: 259.1693; found: 259.1687.

***(E)*-tert-butyldimethyl((5-phenylhexa-3,5-dien-1-yl)oxy)silane**



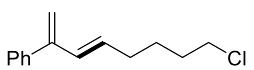
Compound **6b** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (35.3 mg, 62% yield, *E:Z* >20:1, r.r. = 8:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 5H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.64 (dt, *J* = 15.5, 7.4 Hz, 1H), 5.20 (s, 1H), 5.08 (s, 1H), 3.65 (t, *J* = 6.8 Hz, 2H), 2.35 (q, *J* = 6.9 Hz, 2H), 0.88 (s, 9H), 0.03 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 148.09, 140.55, 133.23, 130.65, 128.27, 128.23, 128.02, 127.29, 114.96, 62.80, 36.43, 25.92, 18.33, -5.29.

**HRMS** (APCI) calcd. for $C_{18}H_{29}OSi^+$ $[M+H]^+$: 289.1983; found: 289.1976.

***(E)*-(8-chloroocta-1,3-dien-2-yl)benzene**



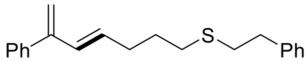
Compound **7b** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (18.1 mg, 41% yield, *E:Z* >20:1, r.r. = 5:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 6.32 (d, *J* = 15.5 Hz, 1H), 5.63 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.19 (s, 1H), 5.08 (d, *J* = 1.9 Hz, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.16 (q, *J* = 7.9 Hz, 2H), 1.82-1.75 (m, 2H), 1.63-1.55 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 147.98, 140.59, 133.43, 132.05, 128.24, 128.08, 127.34, 114.94, 44.90, 32.10, 32.03, 26.41.

**HRMS** (APCI) calcd. for $C_{14}H_{18}Cl^+$ $[M+H]^+$: 221.1092; found: 221.1085.

**(E)-phenethyl(6-phenylhepta-4,6-dien-1-yl)sulfane**



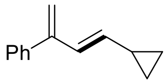

Compound **8b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (33.9 mg, 55% yield, *E:Z* = 12:1, r.r. = 12:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 7.22 (t, *J* = 7.6 Hz, 5H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.62 (dt, *J* = 14.8, 6.8 Hz, 1H), 5.20 (s, 1H), 5.09 (s, 1H), 2.89 (s, 2H), 2.78 (d, *J* = 8.1 Hz, 2H), 2.54 (t, *J* = 7.9 Hz, 2H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.70 (p, *J* = 7.4 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 147.96, 140.65, 140.57, 133.08, 132.28, 128.49, 128.27, 128.10, 127.37, 126.35, 115.05, 36.39, 33.63, 31.90, 31.71, 29.08.

**HRMS** (APCI) calcd. for $C_{21}H_{25}S^+$ $[M+H]^+$: 309.1672; found:309.1662.

**(E)-(4-cyclopropylbuta-1,3-dien-2-yl)benzene**



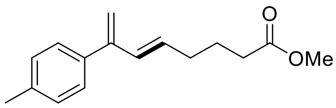

Compound **9b** was isolated via column chromatography (PE) as pale yellow oil (22.5 mg, 66% yield, *E:Z* = 7:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 6.41 (d, *J* = 15.6 Hz, 1H), 5.19-5.11 (m, 2H), 5.00 (s, 1H), 1.52-1.44 (m, 1H), 0.79-0.72 (m, 2H), 0.40-0.35 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 147.92, 140.73, 138.17, 129.10, 128.30, 128.04, 127.26, 113.91, 14.37, 7.25.

**HRMS** (APCI) calcd. for $C_{13}H_{15}^+$ $[M+H]^+$: 171.1169; found: 171.1163.

**methyl (E)-7-(p-tolyl)octa-5,7-dienoate**



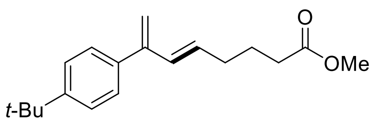

Compound **10b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (30.3 mg, 62% yield, *E:Z* >20:1, r.r. = 7:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 5.62 (dt, *J* = 15.0, 7.0 Hz, 1H), 5.16 (s, 1H), 5.06 (s, 1H), 3.66 (s, 3H), 2.36 (s, 3H), 2.32-2.28 (m, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.76-1.69 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 174.04, 147.73, 137.57, 137.08, 132.72, 132.49, 128.79, 128.11, 114.69, 51.53, 33.45, 32.16, 24.37, 21.17.

**HRMS** (APCI) calcd. for $C_{16}H_{21}O_2^+$ $[M+H]^+$: 245.1537; found: 245.1529.

**methyl (E)-7-(4-(tert-butyl)phenyl)octa-5,7-dienoate**



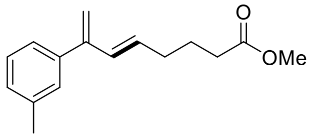

Compound **11b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (26.9 mg, 47% yield, *E:Z* >20:1, r.r. = 5:1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 1.9 Hz, 2H), 6.32 (dd, *J* = 15.6, 1.9 Hz, 1H), 5.68 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.10 (d, *J* = 1.9 Hz, 1H), 3.68 (s, 3H), 2.34 (t, $J$ = 7.5 Hz, 2H), 2.20-2.16 (m, 2H), 1.78-1.73 (m, 2H), 1.36 (s, 9H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 174.11, 150.37, 147.69, 137.55, 132.73, 132.48, 127.89, 125.06, 114.74, 51.59, 34.61, 33.54, 32.27, 31.44, 31.40, 24.47, 24.45.

**HRMS** (APCI) calcd. for $C_{19}H_{27}O_2^+$ $[M+H]^+$: 287.2006; found: 287.1996.

**methyl *(E)*-7-(m-tolyl)octa-5,7-dienoate**



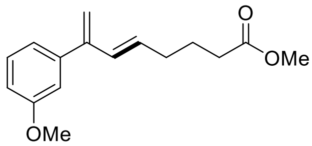

Compound **12b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (24.9 mg, 51% yield, *E:Z* >20:1, r.r. = 6:1).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.22-7.18 (m, 1H), 7.14-7.00 (m, 3H), 6.30 (d, $J$ = 15.6 Hz, 1H), 5.61 (dt, $J$ = 15.0, 7.0 Hz, 1H), 5.17 (s, 1H), 5.06 (s, 1H), 3.66 (s, 3H), 2.36 (s, 3H), 2.31 (t, $J$ = 7.6 Hz, 2H), 2.16 (q, $J$ = 6.9 Hz, 2H), 1.77-1.68 (m, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 174.09, 148.06, 140.54, 137.75, 132.86, 132.51, 129.00, 128.17, 128.01, 125.39, 114.97, 51.60, 33.52, 32.23, 24.44, 21.53.

**HRMS** (APCI) calcd. for $C_{16}H_{21}O_2^+$ $[M+H]^+$: 245.1537; found: 245.1531.

**methyl *(E)*-7-(3-methoxyphenyl)octa-5,7-dienoate**



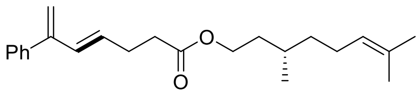

Compound **13b** was isolated via column chromatography (PE/EA=30:1~15:1) as pale yellow oil (27.1 mg, 52% yield, *E:Z* = 12:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 1H), 6.89 (dd, $J$ = 7.7, 1.3 Hz, 1H), 6.87-6.83 (m, 2H), 6.29 (d, $J$ = 15.6 Hz, 1H), 5.63 (dt, $J$ = 15.0, 7.0 Hz, 1H), 5.18 (s, 1H), 5.09 (s, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 2.32 (t, $J$ = 7.5 Hz, 2H), 2.16 (q, $J$ = 7.2 Hz, 2H), 1.76-1.69 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 174.01, 159.35, 147.76, 141.98, 132.95, 132.22, 129.06, 120.76, 115.09, 113.94, 112.79, 55.23, 51.53, 33.45, 32.16, 24.34.

**HRMS** (APCI) calcd. for $C_{16}H_{21}O_3^+$ $[M+H]^+$: 261.1486; found: 261.1484.

**(*S*)-3,7-dimethyloct-6-en-1-yl *(E)*-6-phenylhepta-4,6-dienoate**



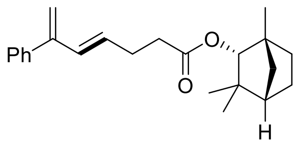

Compound **14b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (37.4 mg, 55% yield, *E:Z* = 14:1, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 6.34 (d, $J$ = 15.6 Hz, 1H), 5.64 (dt, $J$ = 14.4, 6.4 Hz, 1H), 5.20 (s, 1H), 5.09 (s, 2H), 4.14-4.08 (m, 2H), 2.49-2.39 (m, 4H), 2.01-1.93 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.53 (t, $J$ = 6.8 Hz, 1H), 1.46-1.41 (m, 1H), 1.39-1.28 (m, 3H), 1.23-1.17 (m, 1H), 0.90 (d, $J$ = 6.5 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.05, 147.74, 132.47, 131.82, 131.36, 128.22, 128.09, 127.40, 124.59,

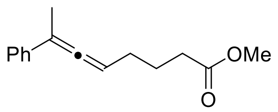
115.42, 63.00, 36.99, 35.46, 33.98, 29.50, 28.17, 25.73, 25.39, 19.41, 17.67.
**HRMS** (APCI) calcd. for $C_{23}H_{33}O_2^+$ [M+H]$^+$: 341.2476; found: 341.2467.

**(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl *(E)*-6-phenylhepta-4,6-dienoate**



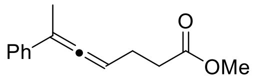

Compound **15b** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (46.1 mg, 68% yield, *E:Z* >20:1, r.r. >20:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 6.36 (d, *J* = 15.6 Hz, 1H), 5.64 (dt, *J* = 16.5, 6.2 Hz, 1H), 5.19 (s, 1H), 5.08 (s, 1H), 4.36 (d, *J* = 1.9 Hz, 1H), 2.49-2.42 (m, 4H), 1.73-1.66 (m, 3H), 1.60-1.54 (m, 2H), 1.47-1.41 (m, 1H), 1.20-1.15 (m, 1H), 1.09 (s, 3H), 1.01 (s, 3H), 0.74 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.31, 147.82, 140.42, 132.51, 131.96, 128.25, 128.08, 127.35, 115.44, 86.22, 48.34, 48.26, 41.36, 39.39, 34.03, 29.70, 28.22, 26.64, 25.82, 20.19, 19.37.
**HRMS** (APCI) calcd. for $C_{23}H_{31}O_2^+$ [M+H]$^+$: 339.2319; found: 339.2309.

**methyl 7-phenylocta-5,6-dienoate**



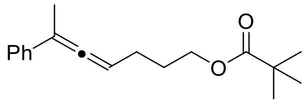

Compound **2c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (42.8 mg, 93% yield, r.r. >20:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.44 (tq, *J* = 6.1, 2.9 Hz, 1H), 3.67 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.16 (q, *J* = 6.8 Hz, 2H), 2.10 (d, *J* = 2.9 Hz, 3H), 1.87-1.79 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.31, 173.98, 137.47, 128.28, 126.45, 125.63, 100.91, 92.07, 51.49, 33.45, 28.40, 24.38, 17.17.
**HRMS** (APCI) calcd. for $C_{15}H_{19}O_2^+$ [M+H]$^+$: 231.1380; found: 231.1376.

**methyl 6-phenylhepta-4,5-dienoate**




Compound **3c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (35.9 mg, 88% yield, r.r. >20:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.56-5.50 (m, 1H), 3.59 (s, 3H), 2.50-2.42 (m, 4H), 2.08 (d, *J* = 2.9 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.90, 173.48, 137.18, 128.27, 126.59, 125.65, 102.18, 91.79, 51.54, 33.02, 24.03, 17.12.
**HRMS** (APCI) calcd. for $C_{14}H_{17}O_2^+$ [M+H]$^+$: 217.1224; found: 217.1221.

**6-phenylhepta-4,5-dien-1-yl pivalate**



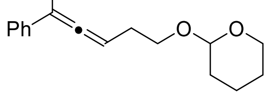
Compound **4c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (47.9 mg, 92% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, $J$ = 8.4 Hz, 2H), 7.32 (t, $J$ = 7.7 Hz, 2H), 7.20 (t, $J$ = 7.3 Hz, 1H), 5.47 (tq, $J$ = 6.0, 2.9 Hz, 1H), 4.13 (t, $J$ = 6.4 Hz, 2H), 2.20 (q, $J$ = 7.1 Hz, 2H), 2.10 (d, $J$ = 2.9 Hz, 3H), 1.86-1.78 (m, 2H), 1.20 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.25, 178.58, 137.46, 128.30, 126.49, 125.62, 101.03, 92.00, 63.66, 38.77, 28.11, 27.22, 25.43, 17.17.

**HRMS** (APCI) calcd. for $C_{18}H_{25}O_2^+$ $[M+H]^+$: 273.1850; found: 273.1842.

**2-((5-phenylhexa-3,4-dien-1-yl)oxy)tetrahydro-2H-pyran**



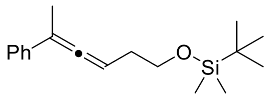
Compound **5c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (37.9 mg, 77% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 7.7 Hz, 2H), 7.32 (t, $J$ = 7.6 Hz, 2H), 7.19 (t, $J$ = 7.3 Hz, 1H), 5.53-5.46 (m, 1H), 4.62 (dt, $J$ = 13.6, 3.7 Hz, 1H), 3.92-3.85 (m, 2H), 3.57-3.48 (m, 2H), 2.42 (q, $J$ = 6.7 Hz, 2H), 2.10 (d, $J$ = 2.9 Hz, 3H), 1.88-1.80 (m, 1H), 1.74-1.69 (m, 1H), 1.61-1.48 (m, 4H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.74, 204.71, 137.48, 128.23, 126.42, 125.71, 100.68, 100.62, 98.85, 98.81, 89.91, 66.87, 66.82, 62.20, 62.11, 30.71, 30.67, 29.67, 29.61, 25.51, 19.51, 19.46, 17.09.

**HRMS** (APCI) calcd. for $C_{17}H_{23}O_2^+$ $[M+H]^+$: 259.1693; found: 259.1685.

**tert-butyldimethyl((5-phenylhexa-3,4-dien-1-yl)oxy)silane**



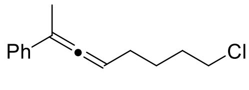
Compound **6c** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (43.1 mg, 78% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, $J$ = 7.3 Hz, 2H), 7.32 (t, $J$ = 7.6 Hz, 2H), 7.20 (t, $J$ = 7.3 Hz, 1H), 5.47 (tq, $J$ = 6.2, 2.9 Hz, 1H), 3.76 (t, $J$ = 6.6 Hz, 2H), 2.35 (q, $J$ = 6.7 Hz, 2H), 2.10 (d, $J$ = 2.9 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.74, 137.55, 128.24, 126.37, 125.69, 100.25, 89.79, 63.02, 32.77, 25.98, 18.39, 17.13, -5.23.

**HRMS** (APCI) calcd. for $C_{18}H_{29}OSi^+$ $[M+H]^+$: 289.1983; found: 289.1980.

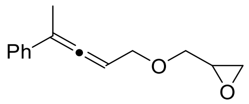
**(8-chloroocta-2,3-dien-2-yl)benzene**



Compound **7c** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (25.1 mg, 60% yield, r.r. >20:1).

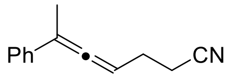
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.45 (tq, *J* = 6.1, 2.9 Hz, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.16 (q, *J* = 7.1 Hz, 2H), 2.10 (d, *J* = 2.9 Hz, 3H), 1.90-1.82 (m, 2H), 1.64 (qd, *J* = 7.3, 2.2 Hz, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.23, 137.53, 128.29, 126.45, 125.61, 100.78, 92.40, 44.86, 32.08, 28.21, 26.35, 17.20.
**HRMS** (APCI) calcd. for $C_{14}H_{18}Cl^+$ $[M+H]^+$: 221.1092; found: 221.1086.

**2-(((4-phenylpenta-2,3-dien-1-yl)oxy)methyl)oxirane**



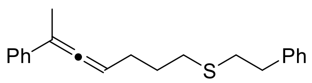

Compound **8c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (30.2 mg, 73% yield, r.r. >20:1).
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 5.59-5.52 (m, 1H), 4.21-4.13 (m, 2H), 3.79-3.74 (m, 1H), 3.47 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.20-3.15 (m, 1H), 2.80 (t, *J* = 4.1 Hz, 1H), 2.65-2.60 (m, 1H), 2.13 (d, *J* = 2.9 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 205.19, 136.60, 128.37, 126.87, 125.80, 101.66, 90.33, 90.30, 70.50, 69.45, 50.73, 44.44, 17.00.
**HRMS** (APCI) calcd. for $C_{14}H_{17}O_2^+$ $[M+H]^+$: 217.1224; found: 184.1217.

**6-phenylhepta-4,5-dienenitrile**



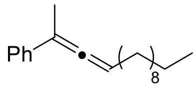

Compound **9c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (27.4 mg, 80% yield, r.r. >20:1).
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.58-5.51 (m, *J* = 2.9 Hz, 1H), 2.49-2.44 (m, 4H), 2.15 (d, *J* = 2.9 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.20, 136.54, 128.41, 127.00, 125.76, 119.35, 103.48, 90.08, 24.99, 17.14, 16.66.
**HRMS** (APCI) calcd. for $C_{13}H_{14}N^+$ $[M+H]^+$: 184.1121; found: 184.1116.

**phenethyl(6-phenylhepta-4,5-dien-1-yl)sulfane**




Compound **10c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (30.8 mg, 52% yield, r.r. >20:1).
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.37-7.30 (m, 4H), 7.22 (t, *J* = 8.5 Hz, 4H), 5.52-5.45 (m, 1H), 2.92-2.87 (m, 2H), 2.81-2.74 (m, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.25 (q, *J* = 7.0 Hz, 2H), 2.13 (d, *J* = 2.9 Hz, 3H), 1.85-1.76 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.30, 140.68, 137.50, 128.50, 128.33, 126.50, 126.35, 125.65, 100.96, 92.21, 36.43, 33.73, 31.79, 29.01, 28.07, 17.26.
**HRMS** (APCI) calcd. for $C_{21}H_{24}SNa^+$ $[M+Na]^+$: 331.1491; found:331.1490.

**tetradeca-2,3-dien-2-ylbenzene**



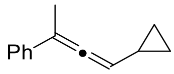

Compound **11c** was isolated via column chromatography (PE) as pale yellow oil (46.1 mg, 89% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 5.44 (tq, *J* = 6.2, 2.9 Hz, 1H), 2.09 (d, *J* = 3.0 Hz, 3H), 1.36-1.22 (m, 18H), 0.89 (t, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.14, 137.84, 128.21, 126.25, 125.59, 100.22, 93.11, 31.92, 29.68, 29.62, 29.48, 29.35, 29.25, 29.22, 28.99, 22.69, 17.20, 14.12.

**HRMS** (APCI) calcd. for $C_{20}H_{31}^+$ $[M+H]^+$: 271.2421; found: 271.2415.

**(4-cyclopropylbuta-2,3-dien-2-yl)benzene**



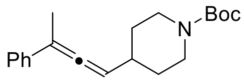

Compound **12c** was isolated via column chromatography (PE) as pale yellow oil (30.0 mg, 95% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.37-5.29 (m, 1H), 2.11 (d, *J* = 2.8 Hz, 3H), 1.37-1.31 (m, 1H), 0.77-0.71 (m, 2H), 0.46-0.41 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.64, 137.61, 128.26, 126.47, 125.66, 102.04, 97.45, 17.34, 9.72, 6.97, 6.87.

**HRMS** (APCI) calcd. for $C_{13}H_{15}^+$ $[M+H]^+$: 171.1169; found: 171.1165.

**tert-butyl 4-(3-phenylbuta-1,2-dien-1-yl)piperidine-1-carboxylate**



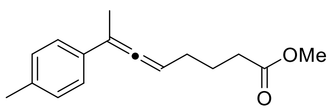

Compound **13c** was isolated via column chromatography (PE/EA=20:1~10:1) as pale yellow oil (57.0 mg, 91% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.49-5.43 (m, 1H), 4.03 (s, 2H), 2.82 (d, *J* = 11.1 Hz, 2H), 2.31-2.22 (m, 1H), 2.10 (d, *J* = 2.9 Hz, 3H), 1.78 (d, *J* = 13.6 Hz, 2H), 1.46 (s, 9H), 1.41-1.32 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.27, 154.87, 137.27, 128.32, 126.54, 125.50, 102.01, 97.41, 79.33, 43.60, 35.91, 31.92, 28.47, 17.24.

**HRMS** (ESI) calcd. for $C_{20}H_{28}NO_2^+$ $[M+H]^+$: 314.2115; found: 314.2018.

**methyl 7-(p-tolyl)octa-5,6-dienoate**

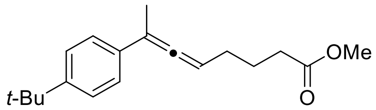



Compound **14c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (38.6 mg, 83% yield, r.r. >20:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.45-5.38 (m, 1H), 3.67 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 2.15 (q, *J* = 7.1 Hz, 2H), 2.08 (d, *J* = 3.0 Hz, 3H), 1.85-1.77 (m, 2H).

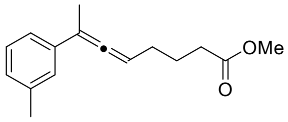
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.02, 174.04, 136.15, 134.51, 129.01, 125.53, 100.75, 91.93, 51.51, 33.47, 28.47, 24.38, 21.06, 17.25.
**HRMS** (APCI) calcd. for $C_{16}H_{21}O_2^+$ [M+H]$^+$: 245.1537; found: 245.1536.

**methyl 7-(4-(tert-butyl)phenyl)octa-5,6-dienoate**



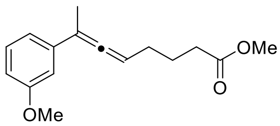

Compound **15c** was isolated via column chromatography (PE/EA=30:1~15:1) as pale yellow oil (44.4 mg, 81% yield, r.r. >20:1).
**$^1$H NMR** (500 MHz, CDCL$_3$) δ 7.35 (s, 4H), 5.46-5.39 (m, 1H), 3.67 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.15 (q, *J* = 6.9 Hz, 2H), 2.09 (s, 3H), 1.85-1.78 (m, 2H), 1.32 (s, 9H).
**$^{13}$C NMR** (126 MHz, CDCL$_3$) δ 204.23, 174.11, 149.53, 134.60, 125.40, 125.30, 100.70, 92.00, 51.59, 34.53, 33.57, 31.41, 28.57, 24.48, 17.26.
**HRMS** (APCI) calcd. for $C_{19}H_{27}O_2^+$ [M+H]$^+$: 287.2006; found: 287.1998.

**methyl 7-(m-tolyl)octa-5,6-dienoate**



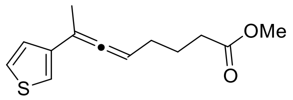

Compound **16c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (40.5 mg, 87% yield, r.r. >20:1).
**$^1$H NMR** (500 MHz, CDCL$_3$) δ 7.24-7.20 (m, 3H), 7.04-7.00 (m, 1H), 5.42 (tq, *J* = 6.0, 2.9 Hz, 1H), 3.67 (s, 3H), 2.42-2.38 (m, 2H), 2.36 (s, 3H), 2.19-2.13 (m, 2H), 2.09 (d, *J* = 2.9 Hz, 3H), 1.86-1.76 (m, 2H).
**$^{13}$C NMR** (126 MHz, CDCL$_3$) δ 204.36, 174.11, 137.86, 137.46, 128.26, 127.35, 126.43, 122.82, 100.95, 91.99, 51.60, 33.53, 28.50, 24.43, 21.61, 17.35.
**HRMS** (APCI) calcd. for $C_{16}H_{21}O_2^+$ [M+H]$^+$: 245.1537; found: 245.1531.

**methyl 7-(3-methoxyphenyl)octa-5,6-dienoate**




Compound **17c** was isolated via column chromatography (PE/EA=30:1~15:1) as pale yellow oil (45.7 mg, 92% yield, r.r. >20:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.43 (tq, *J* = 6.1, 2.9 Hz, 1H), 3.81 (s, 3H), 3.66 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.15 (q, *J* = 7.1 Hz, 2H), 2.08 (d, *J* = 2.9 Hz, 3H), 1.85-1.77 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.38, 173.98, 159.66, 139.09, 129.18, 118.22, 111.80, 111.53, 100.84, 92.12, 55.20, 51.52, 33.45, 28.37, 24.37, 17.23.
**HRMS** (APCI) calcd. for $C_{16}H_{21}O_3^+$ [M+H]$^+$: 261.1486; found: 261.1479.

**methyl 7-(thiophen-3-yl)octa-5,6-dienoate**



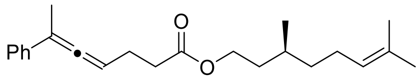

Compound **18c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (33.6 mg, 75% yield, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.09 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.04-7.01 (m, 1H), 5.38 (tq, *J* = 6.2, 2.9 Hz, 1H), 3.66 (s, 3H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.13 (q, *J* = 7.3 Hz, 2H), 2.06 (d, *J* = 2.8 Hz, 3H), 1.84-1.76 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 204.32, 173.98, 139.80, 126.65, 125.33, 118.69, 97.42, 91.62, 51.52, 33.44, 28.49, 24.35, 17.72.

**HRMS** (APCI) calcd. for $C_{13}H_{17}O_2S^+$ $[M+H]^+$: 237.0944; found: 237.0936.

**(*S*)-3,7-dimethyloct-6-en-1-yl 6-phenylhepta-4,5-dienoate**



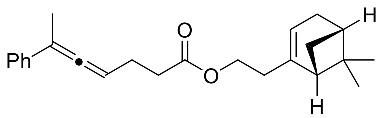

Compound **19c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (53.9 mg, 82% yield, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.55-5.49 (m, 1H), 5.08 (t, *J* = 7.3 Hz, 1H), 4.09-3.97 (m, 2H), 2.49-2.40 (m, 4H), 2.08 (d, *J* = 2.9 Hz, 3H), 2.02-1.90 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.54-1.46 (m, 1H), 1.44-1.31 (m, 2H), 1.30-1.25 (m, 1H), 1.20-1.11 (m, 1H), 0.88 (d, *J* = 6.5 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.92, 173.10, 137.20, 131.33, 128.26, 126.57, 125.64, 124.59, 102.04, 91.84, 63.01, 36.97, 35.42, 33.39, 29.47, 25.72, 25.38, 24.08, 19.40, 17.66, 17.13.

**HRMS** (APCI) calcd. for $C_{23}H_{33}O_2^+$ $[M+H]^+$: 341.2476; found: 341.2464.

**2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 6-phenylhepta-4,5-dienoate**



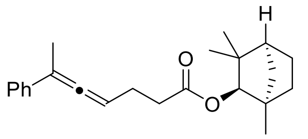

Compound **20c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (24.4 mg, 36% yield, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.55-5.48 (m, 1H), 5.25 (s, 1H), 4.05-3.95 (m, 2H), 2.48-2.40 (m, 4H), 2.37-2.32 (m, 1H), 2.29-2.09 (m, 5H), 2.08 (d, *J* = 3.0 Hz, 3H), 2.00 (t, *J* = 5.7 Hz, 1H), 1.26 (s, 3H), 1.12 (d, *J* = 8.5 Hz, 1H), 0.80 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.92, 172.99, 144.11, 137.21, 128.26, 126.57, 125.64, 118.71, 102.02, 91.84, 62.74, 45.68, 40.71, 37.99, 35.90, 33.40, 31.64, 31.35, 26.27, 24.09, 21.11, 17.14.

**HRMS** (APCI) calcd. for $C_{24}H_{31}O_2^+$ $[M+H]^+$: 351.2319; found: 351.2309.

**(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 6-phenylhepta-4,5-dienoate**



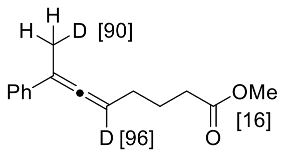
Compound **21c** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (54.2 mg, 83% yield, r.r. >20:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.57-5.51 (m, 1H), 4.37 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.54-2.49 (m, 2H), 2.48-2.43 (m, 2H), 2.10 (d, *J* = 2.9 Hz, 3H), 1.81-1.60 (m, 4H), 1.60-1.54 (m, 1H), 1.48-1.41 (m, 1H), 1.20-1.16 (m, 1H), 1.10 (d, *J* = 10.2 Hz, 3H), 1.02 (d, *J* = 16.7 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.98, 173.36, 137.28, 137.25, 128.29, 126.57, 125.68, 101.83, 91.87, 86.19, 86.17, 48.36, 48.26, 48.24, 41.38, 39.43, 33.70, 33.67, 29.70, 29.67, 26.66, 25.85, 24.37, 24.33, 20.19, 20.16, 19.44, 19.37, 17.19, 17.16.

**HRMS** (APCI) calcd. for $C_{23}H_{31}O_2^+$ $[M+H]^+$: 339.2319; found: 339.2316.

**methyl 7-phenylocta-5,6-dienoate-5,8-d$_2$**



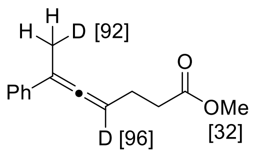
Compound **2d** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (34.8 mg, 75% yield, r.r. >20:1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24-7.16 (m, 1H), 3.67 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.15 (t, *J* = 7.3 Hz, 2H), 2.09 (d, *J* = 7.3 Hz, 2H), 1.87-1.75 (m, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 204.37, 174.09, 137.52, 128.35, 126.53, 125.68, 100.97, 91.91, 51.60, 33.54, 28.38, 24.41, 17.15, 17.00, 16.84.

**HRMS** (APCI) calcd. for $C_{15}H_{17}D_2O_2^+$ $[M+H]^+$: 233.1506; found: 233.1497.

**methyl 6-phenylhepta-4,5-dienoate-4,7-d$_2$**



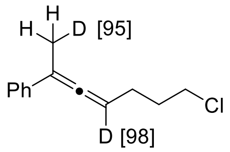
Compound **3d** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (35.8 mg, 82% yield, r.r. >20:1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 3.59 (s, 2H), 2.53-2.36 (m, 4H), 2.08 (d, *J* = 7.7 Hz, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 203.99, 173.54, 137.24, 128.34, 126.66, 125.72, 102.27, 91.86, 91.64, 91.44, 51.61, 33.07, 24.01, 17.20, 17.09, 16.94, 16.78.

**HRMS** (APCI) calcd. for $C_{14}H_{15}D_2O_2^+$ $[M+H]^+$: 219.13490; found: 219.1347.

**(7-chlorohepta-2,3-dien-2-yl-1,4-d₂)benzene**



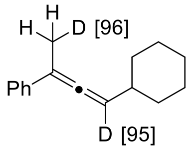

Compound **4d** was isolated via column chromatography (PE/EA=100:1~70:1) as pale yellow oil (37.0 mg, 89% yield, r.r. >20:1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, $J$ = 7.7 Hz, 2H), 7.33 (t, $J$ = 7.6 Hz, 2H), 7.21 (t, $J$ = 7.3 Hz, 1H), 3.61 (t, $J$ = 6.6 Hz, 2H), 2.27 (t, $J$ = 7.3 Hz, 2H), 2.12-2.07 (m, 2H), 2.00-1.91 (m, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 204.37, 137.39, 128.41, 126.64, 125.69, 101.37, 91.60, 91.40, 91.20, 44.53, 31.85, 26.07, 17.16, 17.01, 16.85.

**HRMS** (APCI) calcd. for $C_{13}H_{14}D_2Cl^+$ [M+H]$^+$: 209.1061; found: 209.1055.

**(4-cyclohexylbuta-2,3-dien-2-yl-1,4-d₂)benzene**



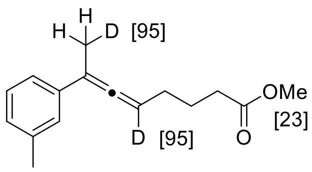

Compound **5d** was isolated via column chromatography (PE) as pale yellow oil (36.4 mg, 85% yield, r.r. >20:1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 7.8 Hz, 2H), 7.32 (t, $J$ = 7.5 Hz, 2H), 7.19 (t, $J$ = 7.3 Hz, 1H), 2.18-2.04 (m, 3H), 1.84 (dd, $J$ = 12.8, 3.9 Hz, 2H), 1.77-1.71 (m, 2H), 1.67-1.62 (m, 1H), 1.33-1.27 (m, 2H), 1.23-1.14 (m, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 203.14, 137.87, 128.32, 126.32, 125.53, 101.17, 99.17, 98.98, 98.78, 37.89, 33.33, 33.27, 26.26, 26.16, 17.39, 17.28, 17.13, 16.97.

**HRMS** (APCI) calcd. for $C_{16}H_{19}D_2^+$ [M+H]$^+$: 215.1764; found: 215.1757.

**methyl 7-(m-tolyl)octa-5,6-dienoate-5,8-d₂**




Compound **6d** was isolated via column chromatography (PE/EA=40:1~20:1) as pale yellow oil (37.4 mg, 76% yield, r.r. = 16:1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.23-7.17 (m, 3H), 7.06-6.97 (m, 1H), 3.67 (s, 3H), 2.39 (t, $J$ = 7.5 Hz, 2H), 2.35 (s, 3H), 2.15 (t, $J$ = 7.2 Hz, 2H), 2.11-2.04 (m, 2H), 1.86-1.77 (m, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 204.37, 174.10, 137.86, 137.45, 128.25, 127.34, 126.42, 122.81, 100.97, 91.98, 91.74, 91.55, 51.59, 33.53, 28.40, 24.40, 21.60, 17.23, 17.08, 16.92.

**HRMS** (APCI) calcd. for $C_{16}H_{19}D_2O_2^+$ [M+H]$^+$: 247.1662; found: 247.1653.

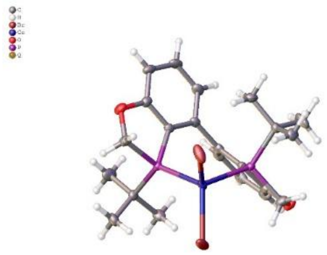


**Fig. S2** Crystal structure of **$CoBr_2$·L7**

Crystal data and structure refinement for **$CoBr_2$·L7**

| Compound | **$CoBr_2$·L7** |
|---|---|
| CCDC | 2536099 |
| Identification code | 12.17_auto |
| Empirical formula | $C_{22}H_{28}Br_2CoO_2P_2$ |
| Formula weight | 605.13 |
| Temperature/K | 100.00(10) |
| Crystal system | trigonal |
| Space group | $P3_221$ |
| a/Å | 10.13310(10) |
| b/Å | 10.13310(10) |
| c/Å | 20.9219(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 120 |
| Volume/Å$^3$ | 1860.44(5) |
| Z | 3 |
| $\rho_{calc}$g/cm$^3$ | 1.620 |
| μ/mm$^{-1}$ | 10.540 |
| F(000) | 909.0 |
| Crystal size/mm$^3$ | 0.2 × 0.2 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 10.08 to 152.654 |
| Index ranges | $-12 \le h \le 12$, $-12 \le k \le 12$, $-25 \le l \le 26$ |
| Reflections collected | 11981 |
| Independent reflections | 2522 [$R_{int}$ = 0.0350, $R_{sigma}$ = 0.0245] |
| Data/restraints/parameters | 2522/0/136 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0222, $wR_2$ = 0.0519 |
| Final R indexes [all data] | $R_1$ = 0.0231, $wR_2$ = 0.0522 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.47/-0.51 |

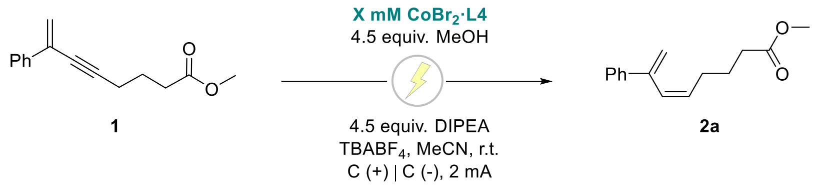
# 5. Mechanistic Studies

## Reaction Progress Kinetic Analysis (RPKA)

### *Z*-selective hydrogenation kinetic analysis

General method for kinetic studies: according to the general procedure of *Z*-hydrogenation reactions, using substrate **1**, $CoBr_2$/**L4**, MeOH and DIPEA in several different equivalents, and diphenyl was used as an internal standard. The stopwatch was immediately started when the current was turned on. A small amount of the reaction mixture was taken out by syringe. The obtained mixture was immediately diluted by EA (0.5 mL), which was further sampled for GC analysis.

**The rate on the concentration of $CoBr_2$/L4**



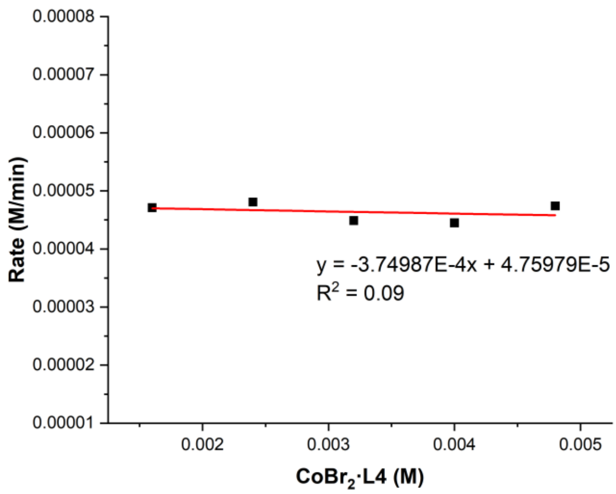




**Fig. S3** Rate on the concentration of **$CoBr_2$·L4** from the reaction of substrate **1** (0.04 M), MeOH (0.18 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.0016 M, 0.0024 M, 0.0032 M, 0.004 M, 0.0048 M of **$CoBr_2$·L4**.

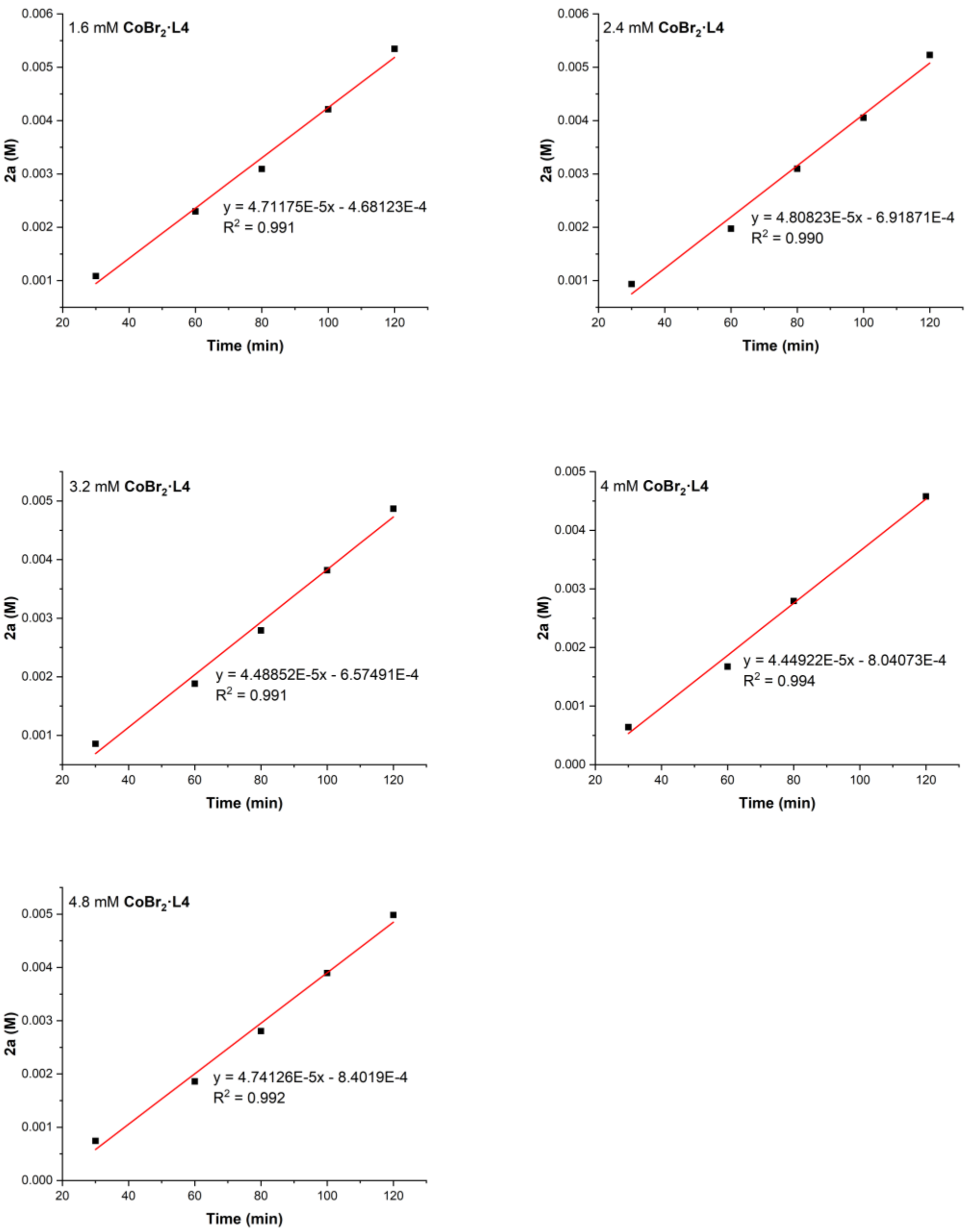
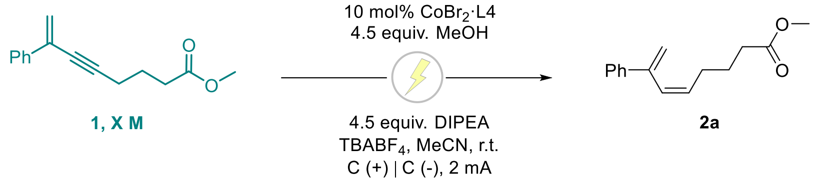



**Fig. S4** Plot of the rise of product from the reaction of substrate **1** (0.04 M), MeOH (0.18 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.0016 M, 0.0024 M, 0.0032 M, 0.004 M, 0.0048 M of **$CoBr_2$·L4**.

**The rate on the concentration of substrate 1**



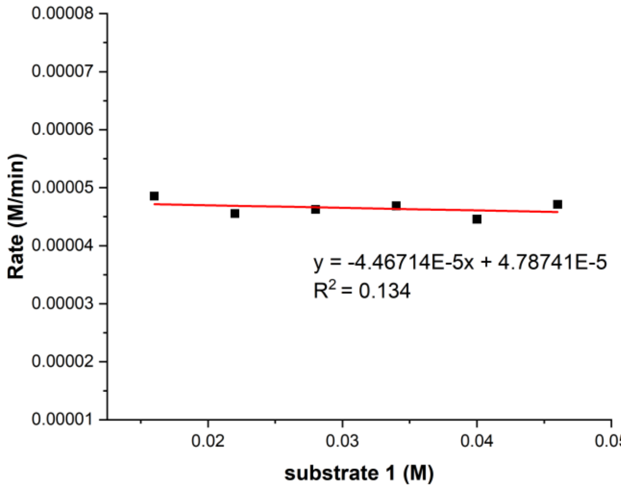
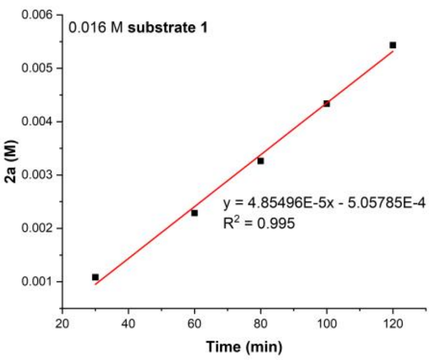
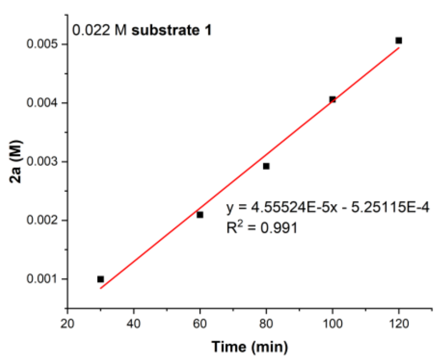
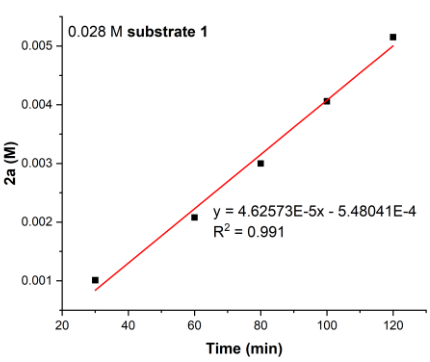
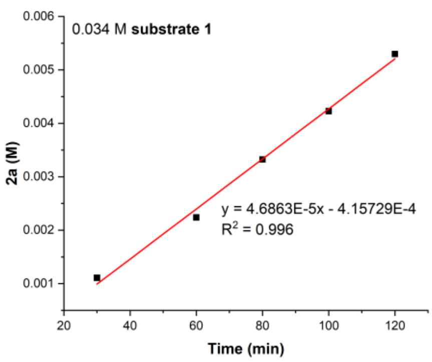




**Fig. S5** Rate on the concentration of **substrate 1** from the reaction of $CoBr_2$·L4 (0.004 M), MeOH (0.18 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.016 M, 0.022 M, 0.028 M, 0.034 M, 0.04 M, 0.046 M of **substrate 1**.



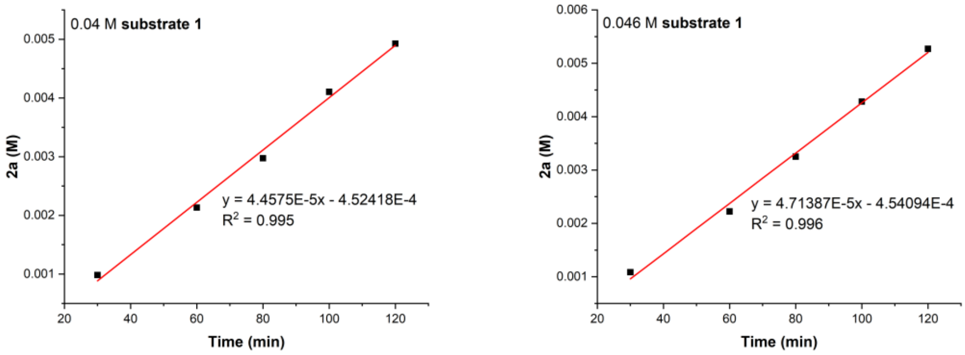
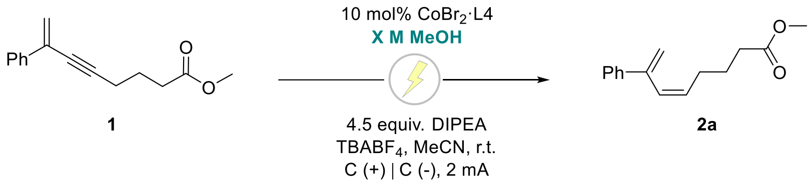



**Fig. S6** Plot of the rise of product from the reaction of $CoBr_2 \cdot L4$ (0.004 M), MeOH (0.18 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.016 M, 0.022 M, 0.028 M, 0.034 M, 0.04 M, 0.046 M of **substrate 1**.

**The rate on the concentration of MeOH**



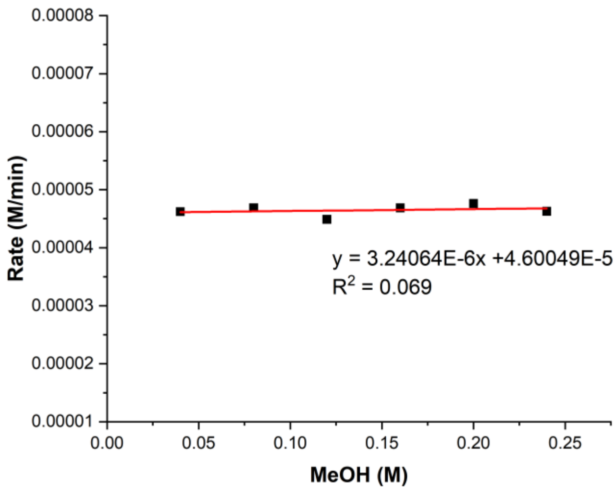




**Fig. S7** Rate on the concentration of **MeOH** from the reaction of $CoBr_2 \cdot L4$ (0.004 M), substrate **1** (0.04 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.04 M, 0.08 M, 0.12 M, 0.16 M, 0.2 M, 0.24 M of **MeOH**.

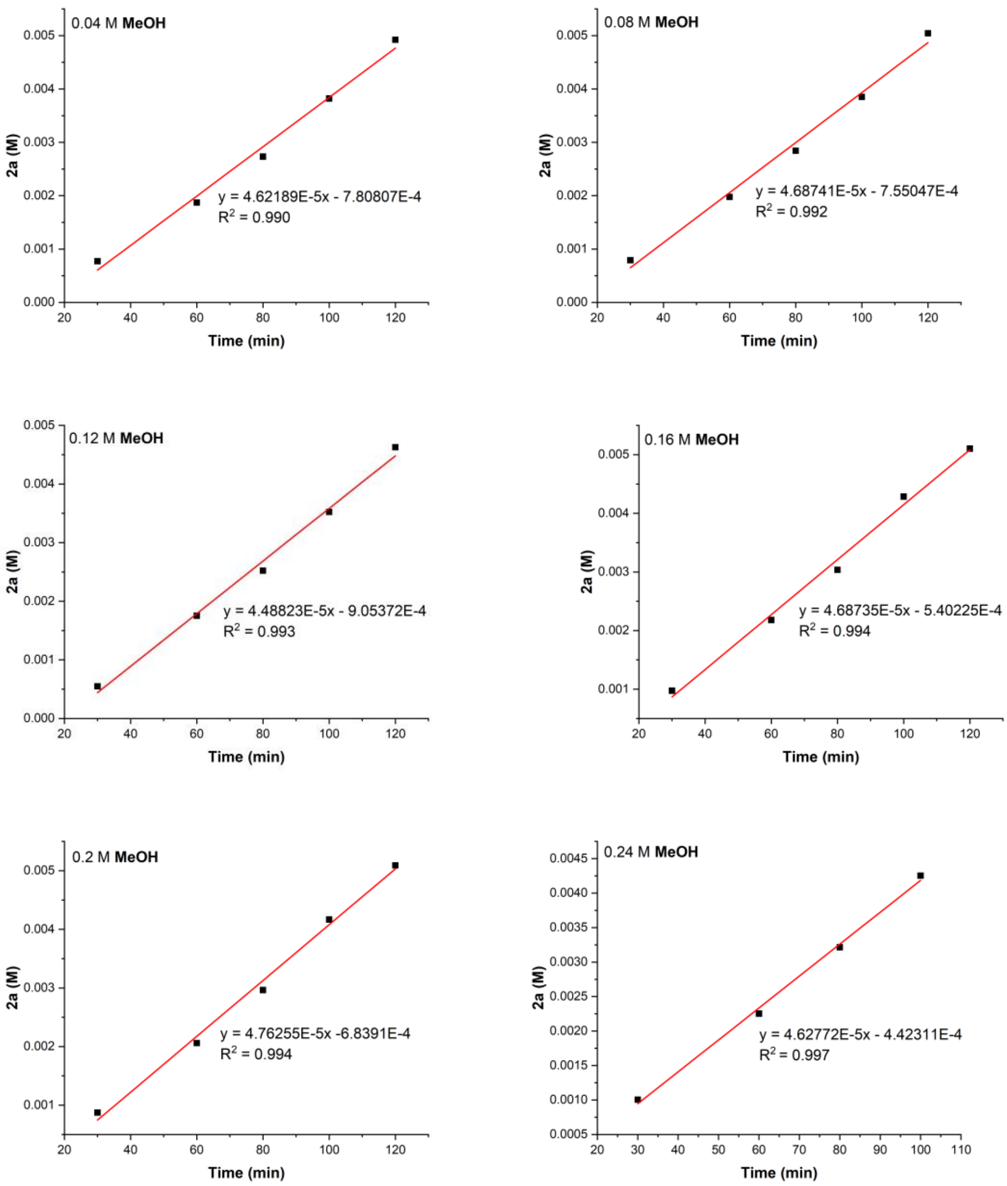
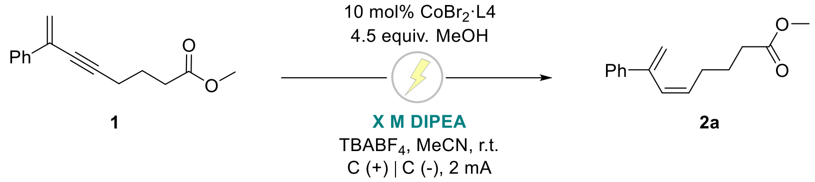



**Fig. S8** Plot of the rise of product from the reaction of $CoBr_2 \cdot L4$ (0.004 M), substrate **1** (0.04 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.04 M, 0.08 M, 0.12 M, 0.16 M, 0.2 M, 0.24 M of **MeOH**.

## The rate on the concentration of DIPEA



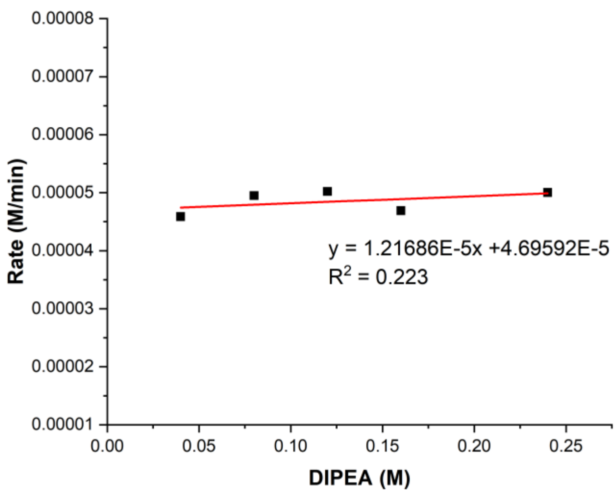
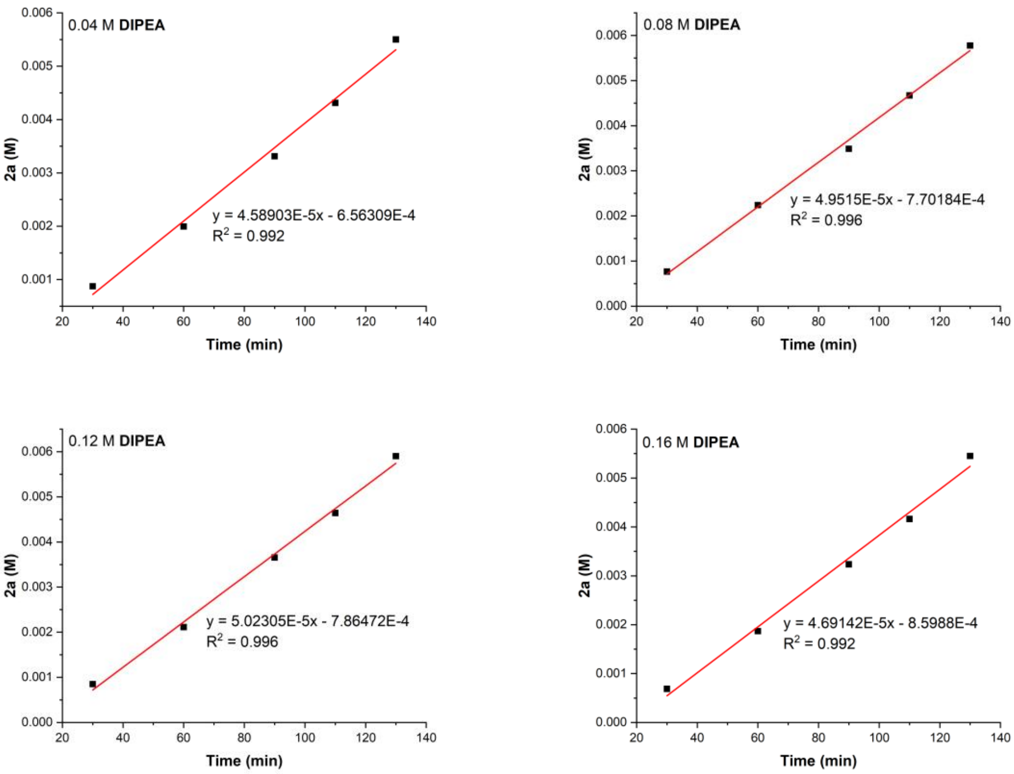




**Fig. S9** Rate on the concentration of **DIPEA** from the reaction of CoBr$_2$·L4 (0.004 M), substrate **1** (0.04 M), MeOH (0.18 M), TBABF$_4$ (0.1 M), Current = 2 mA with 0.04 M, 0.08 M, 0.12 M, 0.16 M, 0.24 M of **DIPEA**.



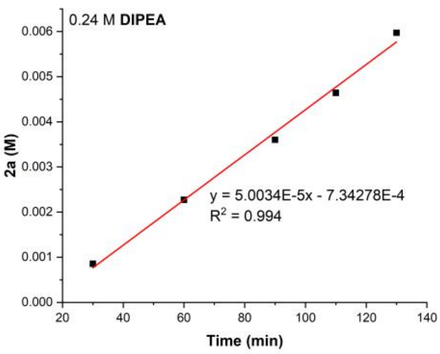
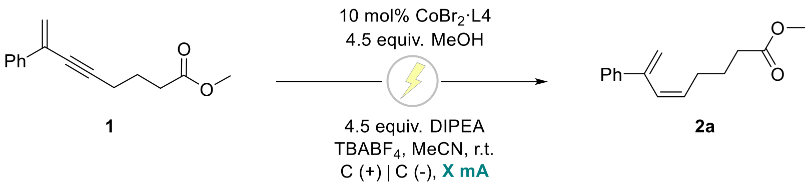



**Fig. S10** Plot of the rise of product from the reaction of $CoBr_2$·L4 (0.004 M), substrate **1** (0.04 M), MeOH (0.18 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.04 M, 0.08 M, 0.12 M, 0.16 M, 0.24 M of **DIPEA**.

**The rate on the value of current**



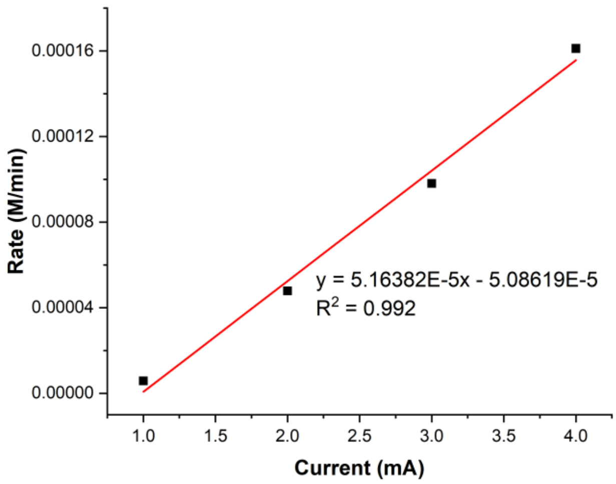




**Fig. S11** Rate on the concentration of **Current** from the reaction of $CoBr_2$·L4 (0.004 M), substrate **1** (0.04 M), MeOH (0.18 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M) with 1 mA, 2 mA M, 3 mA, 4 mA of **Current**.

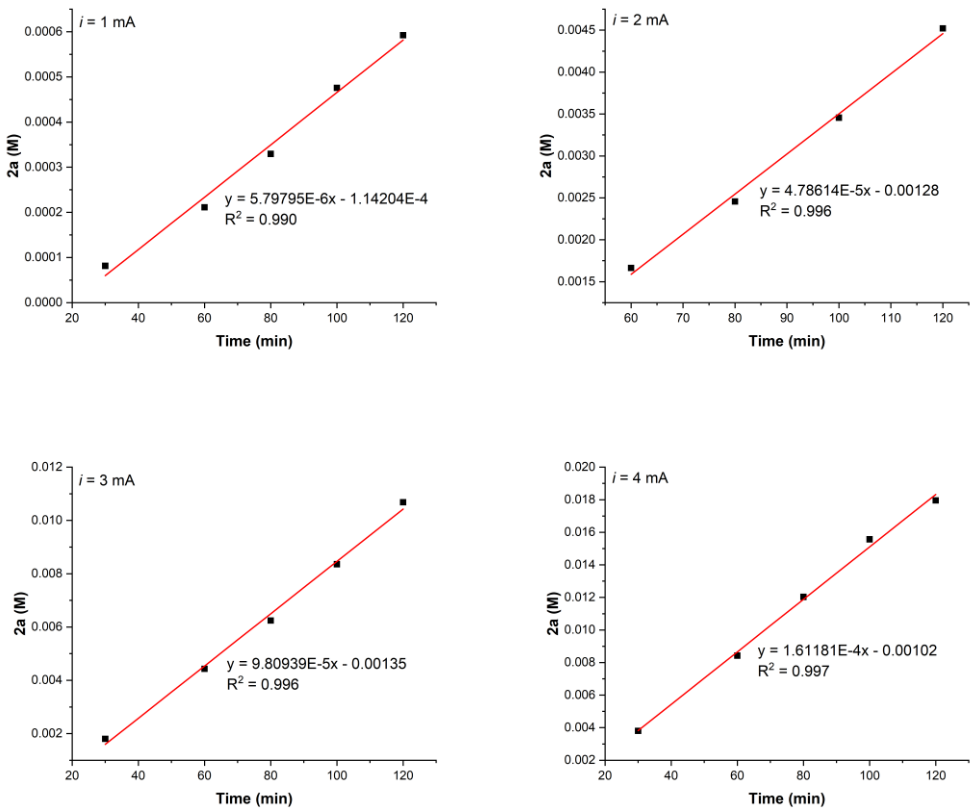
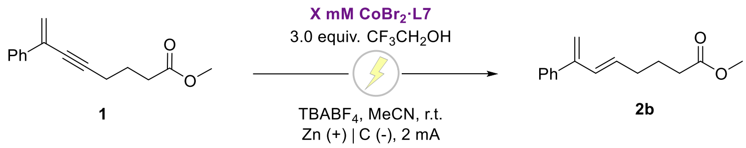



**Fig. S12** Plot of the rise of product from the reaction of $CoBr_2 \cdot L4$ (0.004 M), substrate **1** (0.04 M), MeOH (0.18 M), DIPEA (0.18 M), $TBABF_4$ (0.1 M) with 1 mA, 2 mA M, 3 mA, 4 mA of **Current**.

## *E*-selective hydrogenation kinetic analysis

General method for kinetic studies: according to the general procedure of *E*-hydrogenation reactions, using substrate **1**, $CoBr_2$/**L7** and $CF_3CH_2OH$ in several different equivalents, and diphenyl was used as an internal standard. The stopwatch was immediately started when the current was turned on. A small amount of the reaction mixture was taken out by syringe. The obtained mixture was immediately diluted by EA (0.5 mL), which was further sampled for GC analysis.

**The rate on the concentration of $CoBr_2$/L7**



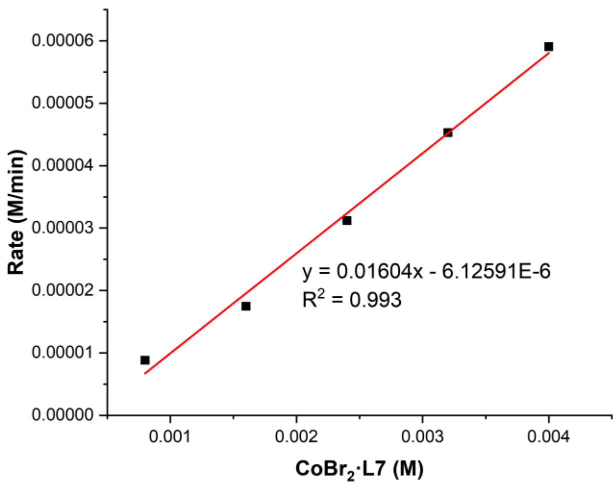
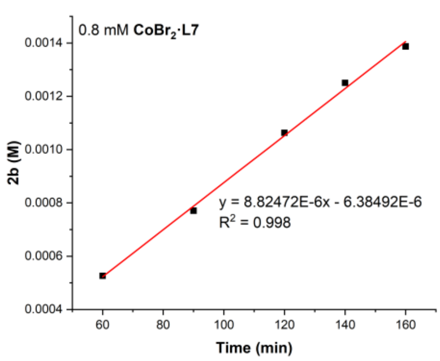
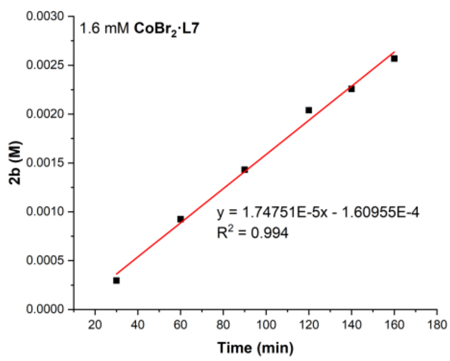




**Fig. S13** Rate on the concentration of **$CoBr_2$·L7** from the reaction of substrate **1** (0.04 M), $CF_3CH_2OH$ (0.12 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.8 mM, 1.6 mM, 2.4 mM, 3.2 mM, 4 mM of **$CoBr_2$·L7**.



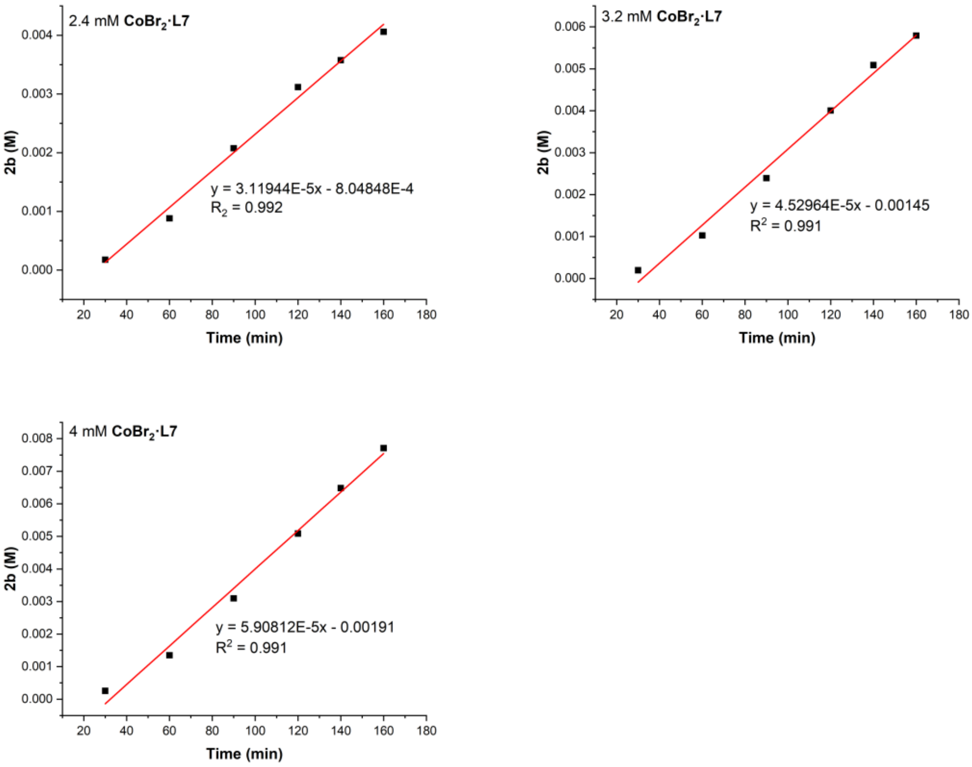
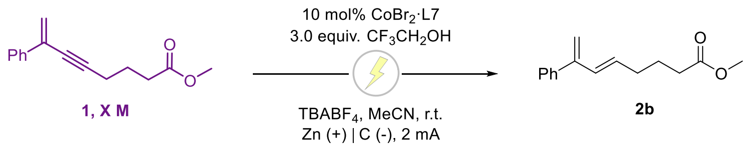



**Fig. S14** Plot of the rise of product from the reaction of substrate **1** (0.04 M), $CF_3CH_2OH$ (0.12 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.8 mM, 1.6 mM, 2.4 mM, 3.2 mM, 4 mM of **$CoBr_2$·L7**.

**The rate on the concentration of substrate 1**



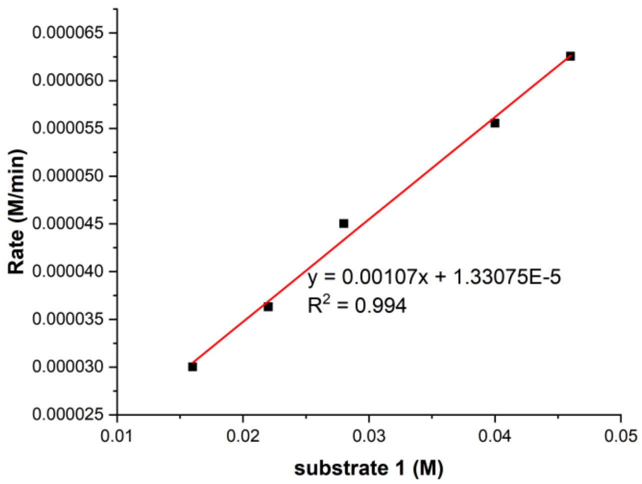




**Fig. S15** Rate on the concentration of **substrate 1** from the reaction of $CoBr_2$·L7 (0.004 M), $CF_3CH_2OH$ (0.12 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.016 M, 0.022 M, 0.028 M, 0.04 M, 0.046 M of

**substrate 1**.

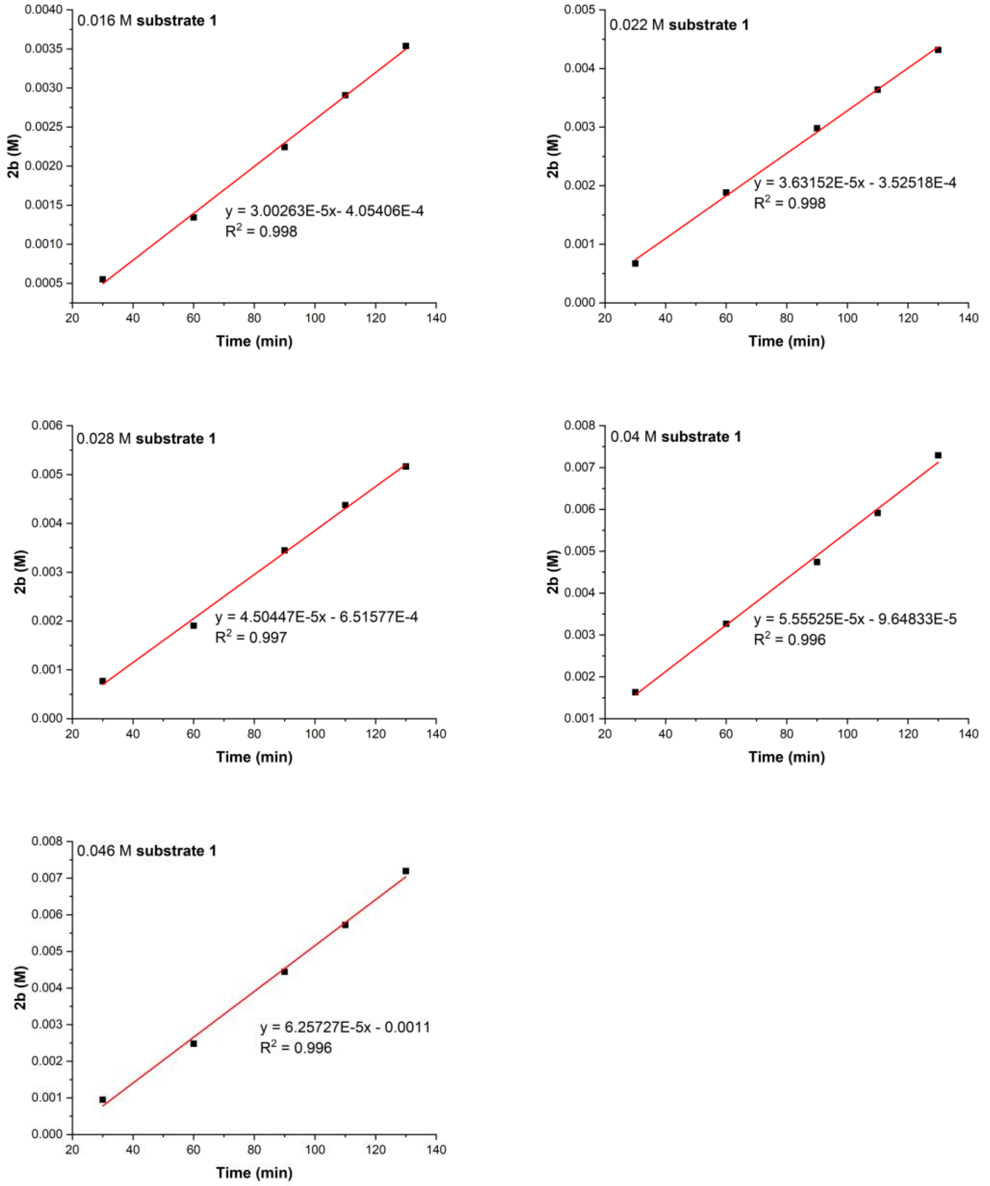
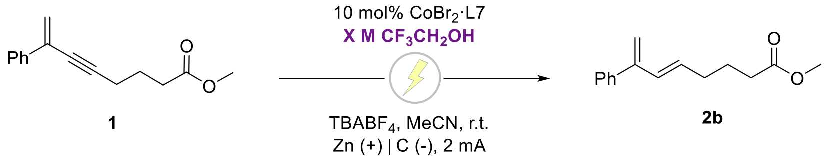



**Fig. S16** Plot of the rise of product from the reaction of $CoBr_2$·L7 (0.004 M), $CF_3CH_2OH$ (0.12 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.016 M, 0.022 M, 0.028 M, 0.04 M, 0.046 M of **substrate 1**.

**The rate on the concentration of $CF_3CH_2OH$**



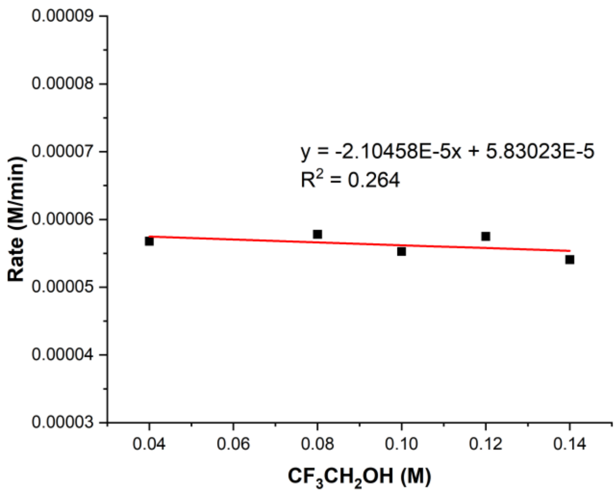
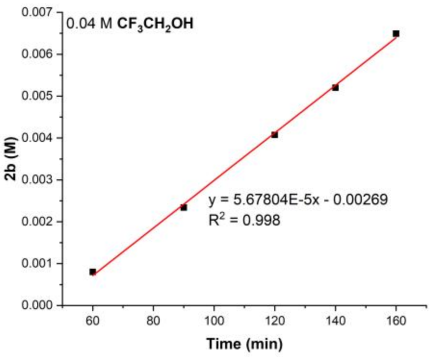
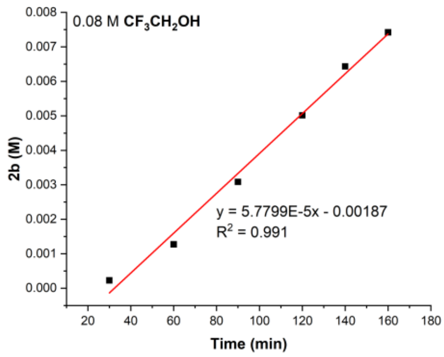
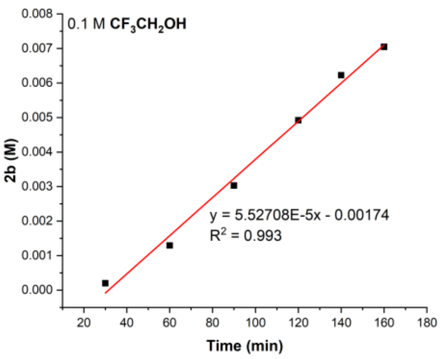
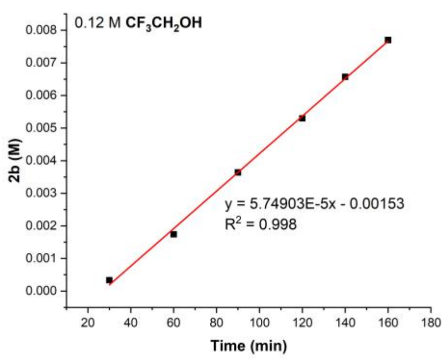




**Fig. S17** Rate on the concentration of **$CF_3CH_2OH$** from the reaction of $CoBr_2$·L7 (0.004 M), substrate **1** (0.04 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.04 M, 0.08 M, 0.1 M, 0.12 M, 0.14 M of **$CF_3CH_2OH$**.



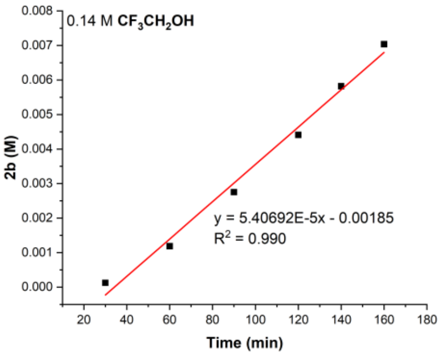
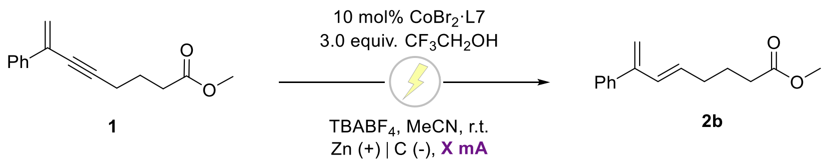



**Fig. S18** Plot of the rise of product from the reaction of $CoBr_2$·L7 (0.004 M), substrate **1** (0.04 M), $TBABF_4$ (0.1 M), Current = 2 mA with 0.04 M, 0.08 M, 0.1 M, 0.12 M, 0.14 M of $\mathbf{CF_3CH_2OH}$.

**The rate on the value of current**



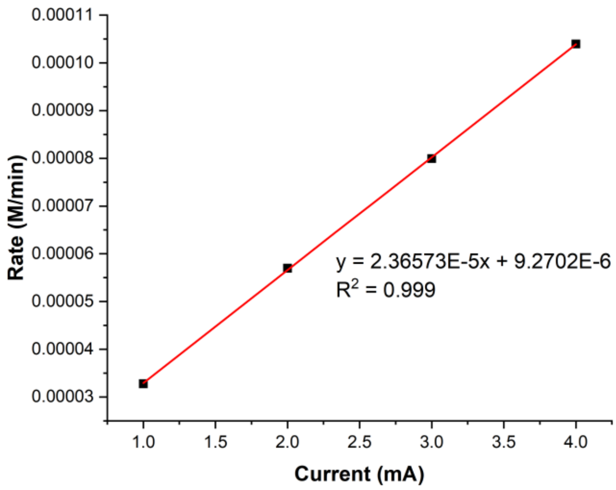




**Fig. S19** Rate on the concentration of **Current** from the reaction of $CoBr_2$·L7 (0.004 M), substrate **1** (0.04 M), $CF_3CH_2OH$ (0.12 M), $TBABF_4$ (0.1 M) with 1 mA, 2 mA M, 3 mA, 4 mA of **Current**.

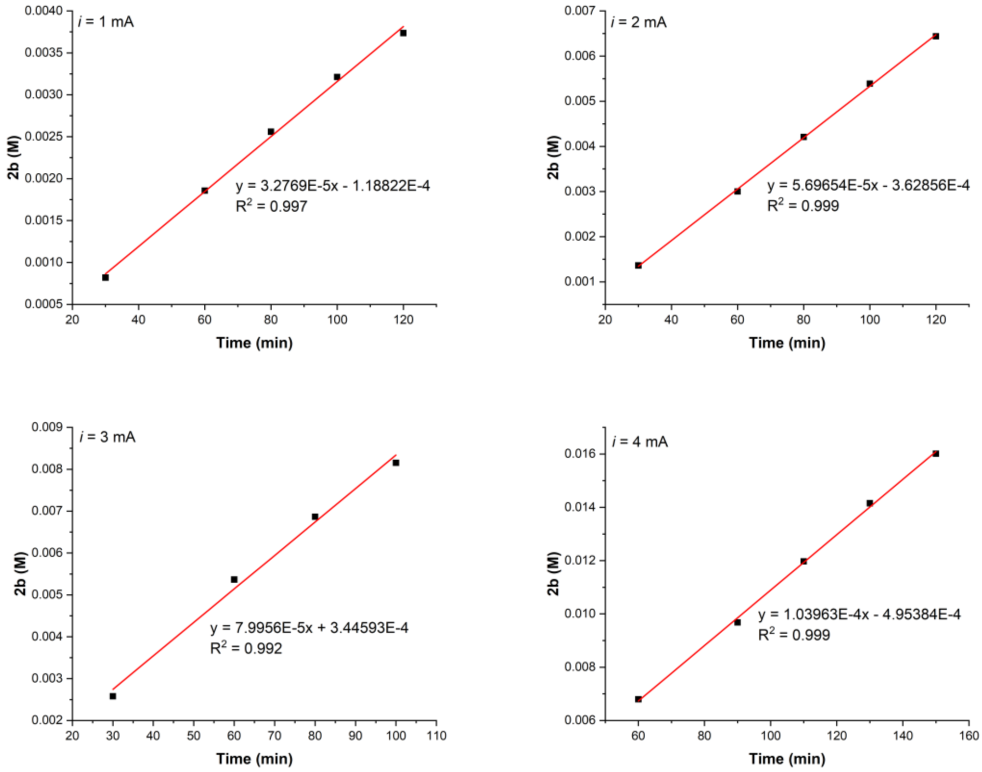



**Fig. S20** Plot of the rise of product from the reaction of $CoBr_2$·L7 (0.004 M), substrate **1** (0.04 M), $CF_3CH_2OH$ (0.12 M), $TBABF_4$ (0.1 M) with 1 mA, 2 mA M, 3 mA, 4 mA of **Current**.

# Cyclic Voltammetry (CV) Experiments

Cyclic voltammetry was recorded using a CHI760E potentiostat at room temperature. A glassy carbon electrode (3 mm diameter), Pt wire (0.5 mm diameter), and Ag/$AgNO_3$ (0.1 M in 0.1 M $TBAPF_6$ in $CH_3CN$) were used as the working, counter, and reference electrodes, respectively. All potentials were referenced to an internal $Fc/Fc^+$ standard added in the last step of each experiment. Prior to the experiment, glassy carbon electrode was polished using 0.5 µm α-$Al_2O_3$ polishing powder. Before beginning electrochemical testing, the solution was purged with Ar gas for 10 minutes to remove oxygen from the solution. In all electrochemical studies, MeCN was used as the solvent in the presence of 0.1 M $TBAPF_6$ as supporting electrolyte. Unless otherwise noted, scan rate = 100 mV/s.

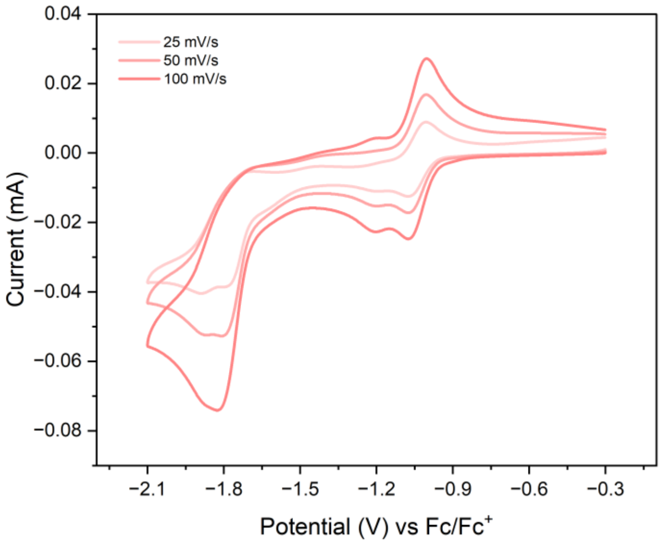



**Fig. S21** Cyclic voltametric profiles of 3.0 mM $CoBr_2$·L4 in 0.1 M $TBAPF_6$ in MeCN (8 mL) at varied sweep rates. Two reduction peaks at -1.07 V and -1.82 V vs. $Fc^+/Fc$ corresponds to the Co(II/I) and Co(I/0) reduction processes.

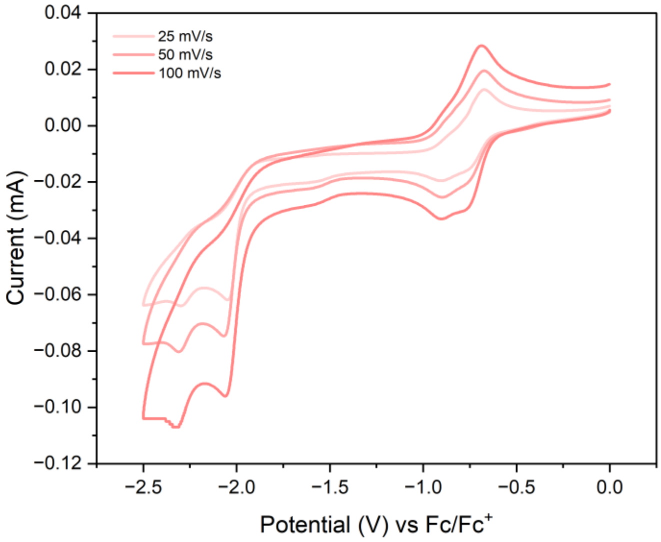



**Fig. S22** Cyclic voltametric profiles of 3.0 mM $CoBr_2$·L7 in 0.1 M $TBAPF_6$ in MeCN (8 mL) at varied sweep rates. Two reduction peaks at -0.83 V and -2.05 V vs. $Fc^+/Fc$ corresponds to the Co(II/I) and Co(I/0) reduction processes.

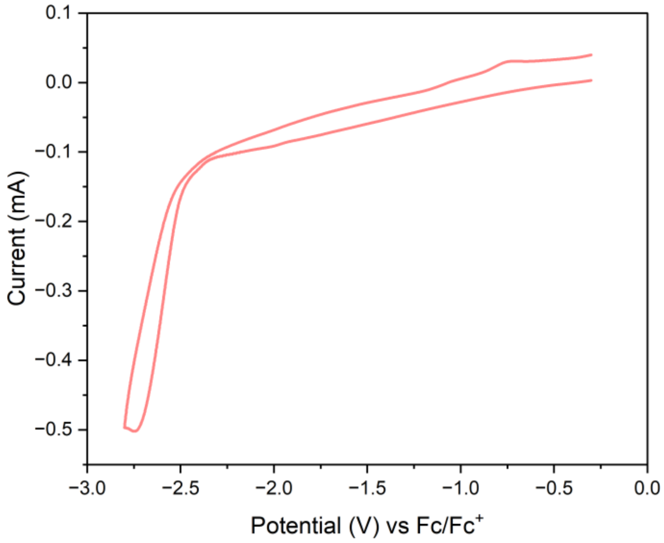



**Fig. S23** Cyclic voltametric profiles of 15.0 mM substrate **1** in 0.1 M $TBAPF_6$ in MeCN (8 mL). A reduction peak at -2.74 V vs. $Fc^+/Fc$ corresponds to the substrate **1** reduction processes.

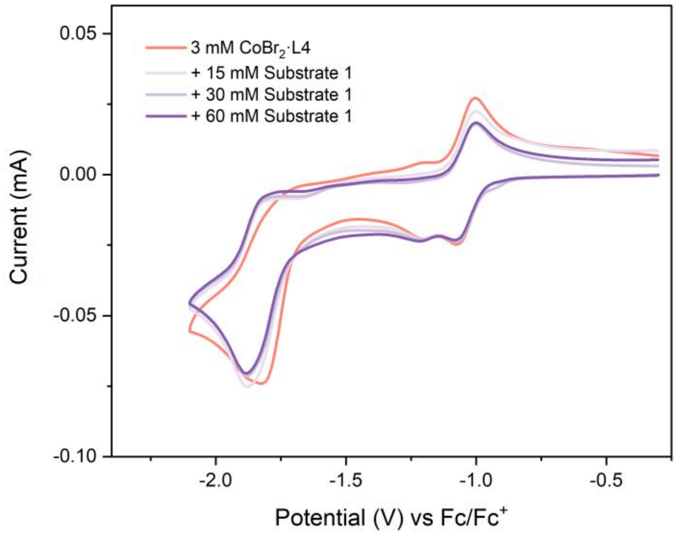



**Fig. S24** Cyclic voltammetry of 3.0 mM CoBr$_2$·L4 in 0.1 M TBAPF$_6$ in MeCN (8 mL) in the presence of varying concentrations of substrate **1**. The cathodic shift may correspond to the coordination of substrate **1** with Co(0).

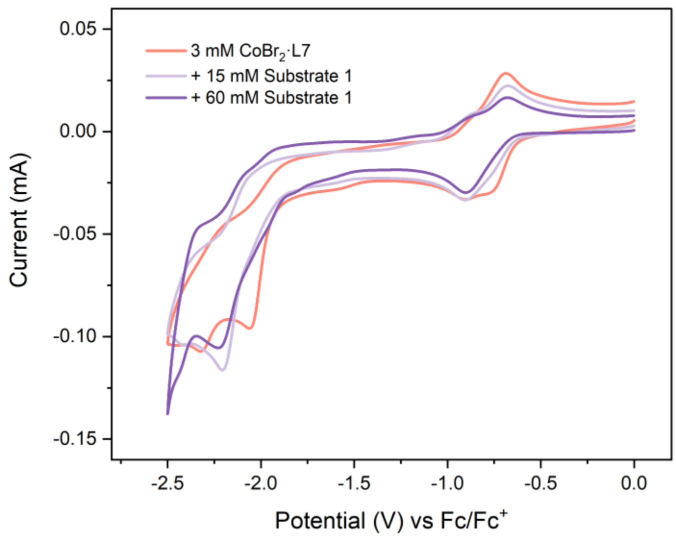



**Fig. S25** Cyclic voltammetry of 3.0 mM CoBr$_2$·L7 in 0.1 M TBAPF$_6$ in MeCN (8 mL) in the presence of varying concentrations of substrate **1**. The cathodic shift may correspond to the coordination of substrate **1** with Co(0).

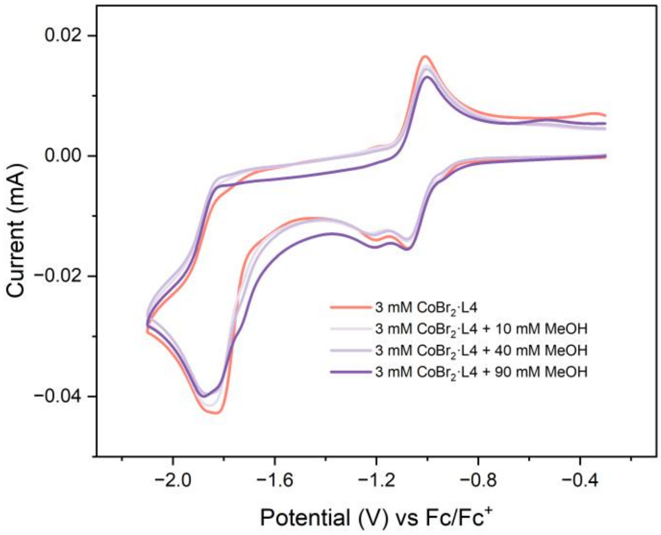



**Fig. S26** Cyclic voltammetry of 3.0 mM $CoBr_2$·L4 in 0.1 M $TBAPF_6$ in MeCN (8 mL) in the presence of varying concentrations of MeOH.

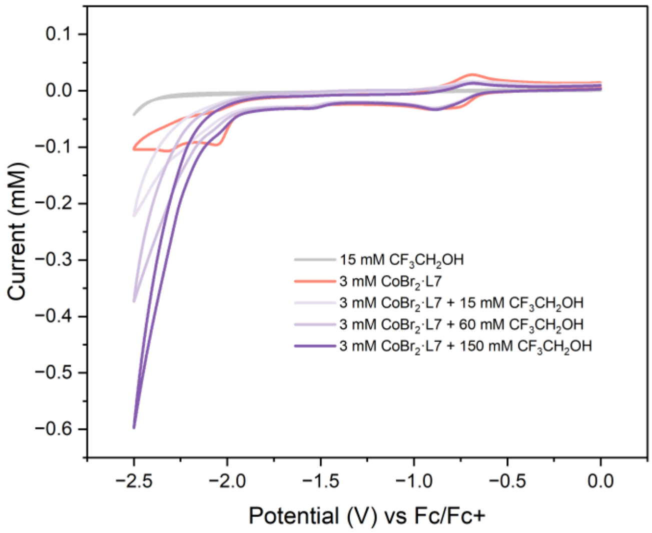



**Fig. S27** Cyclic voltammetry of 3.0 mM $CoBr_2$·L7 in 0.1 M $TBAPF_6$ in MeCN (8 mL) in the presence of varying concentrations of $CF_3CH_2OH$. By increasing the concentration of $CF_3CH_2OH$, the catalytic current increases, the process corresponding to the production of Co(II)-H and the release of $H_2$.

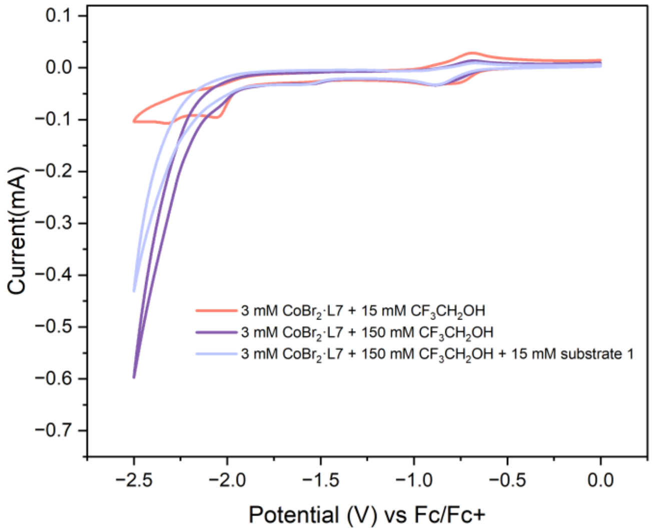


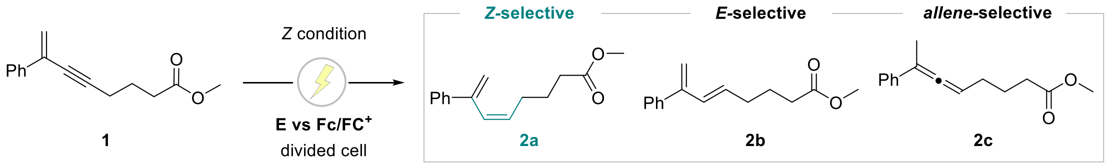

**Fig. S28** Cyclic voltammetry of 3.0 mM $CoBr_2$·L7 and 150 mM $CF_3CH_2OH$ in 0.1 M $TBAPF_6$ in MeCN (8 mL) in the presence of substrate **1**. By adding the substrate **1**, the catalytic current decreases, the process corresponding to the reaction of substrate **1** with Co(II)-H.

# Controlled Potential Electrolysis

Controlled potential electrolysis was proceeded using a CHI760E potentiostat. Electrolyses were conducted in a two-chamber system using a glass frit to separate the two compartments. The two-chamber system was equipped with magnetic stir bars, and in each of the chambers $TBAPF_6$ (0.1 M) was dissolved in MeCN in the glove box. Either according to the general procedure of *Z*-selective, *E*-selective or *allene*-selective hydrogenation reactions, using substrate **1**, cobalt complex, proton source and additives, then equipped with the electrodes. The second chamber was equipped with $Ag/AgNO_3$ (0.1 M in 0.1 M $TBAPF_6$ in $CH_3CN$) reference electrode. Then the mixture was respectively electrolyzed under a constant voltage (vs $Fc/Fc^+$). After reaction was completed, a small amount of the reaction mixture was taken out and was sampled for GC analysis.

## *Z*-selective hydrogenation

**Table S7** Controlled potential electrolysis of *Z*-selective hydrogenation

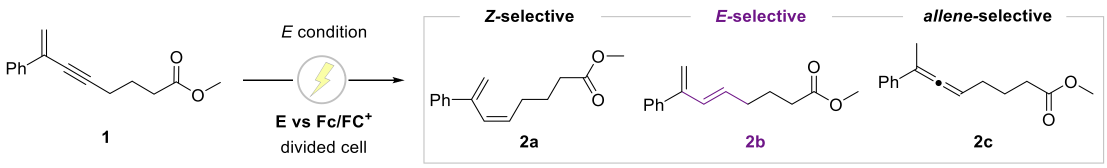



| Entry | E vs. $Fc/FC^+$ | Yield(%) | *Z/E*(2a:2b) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | -1.1 V | n.p. | - | - |
| 2 | -1.3 V | trace | - | - |
| 3 | -1.7 V | 54 | >20:1 | 15:1 |
| 4 | -1.9 V | 59 | >20:1 | 7:1 |

Reaction Conditions: substrate **1** (0.32 mmol), $CoBr_2 \cdot L4$ (10 mol%), MeOH (4.5 equiv.), DIPEA (4.5 equiv.), $TBAPF_6$ (0.1 M), Ar, Pt (+) | C felt (-), MeCN (8 mL) at r.t. for 13 h. Yields and selectivity were determined by GC using diphenyl as the internal standard.

## *E*-selective hydrogenation

**Table S8** Controlled potential electrolysis of *E*-selective hydrogenation

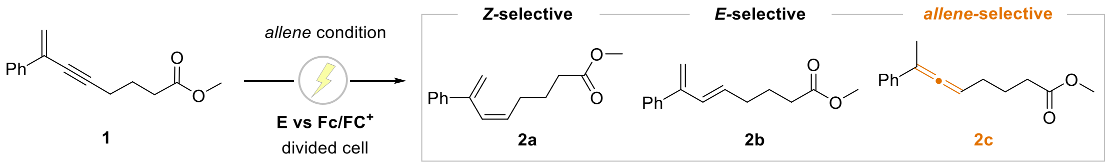



| Entry | E vs. $Fc/FC^+$ | Yield(%) | *E/Z*(2b:2a) | r.r.(2a+2b:2c) |
|---|---|---|---|---|
| 1 | -0.8 V | n.p. | - | - |
| 2 | -1.5 V | 51 | 20:1 | 12:1 |
| 3 | -1.6 V | 71 | >20:1 | >20:1 |
| 4 | -1.7 V | 68 | 19:1 | 18:1 |
| 5 | -1.8 V | 60 | 6:1 | 15:1 |

Reaction Conditions: substrate **1** (0.32 mmol), $CoBr_2 \cdot L7$ (10 mol%), $CF_3CH_2OH$ (3.0 equiv.), $TBAPF_6$ (0.1 M), Ar, Zn (+) | C felt (-), MeCN (8 mL) at r.t. for 22 h. Yields and selectivity were determined by GC using diphenyl as the internal standard.

## *allene*-selective hydrogenation

**Table S9** Controlled potential electrolysis of *allene*-selective hydrogenation




| Entry | E vs. Fc/FC$^+$ | Yield(%) | r.r.(2c:2a+2b) |
|---|---|---|---|
| 1 | -1.5 V | - | - |
| 2 | -2.0 V | - | - |
| 3 | -2.5 V | 48 | >20:1 |

Reaction Conditions: substrate **1** (0.32 mmol), MeOH (2.0 equiv.), $TBAPF_6$ (0.1 M), Ar, Zn (+) | SS felt (-), MeCN (8 mL) at r.t. for 10 h. Yields and selectivity were determined by GC using diphenyl as the internal standard.

## Controlled Current Electrolysis

Controlled current electrolysis was proceeded using a CHI760E potentiostat. Electrolyses were conducted in a two-chamber system using a glass frit to separate the two compartments. The two-chamber system was equipped with magnetic stir bars, and in each of the chambers $TBAPF_6$ (0.1 M) was dissolved in MeCN (8 mL) in the glove box. Either according to the general procedure of *Z*-selective, *E*-selective or *allene*-selective hydrogenation reactions, using substrate **1**, cobalt complex, proton source and additives, then equipped with the electrodes. The second chamber was equipped with Ag/$AgNO_3$ (0.1 M in 0.1 M $TBAPF_6$ in $CH_3CN$) reference electrode. Then the mixture was electrolyzed under 2 mA.

### *Z*-selective hydrogenation

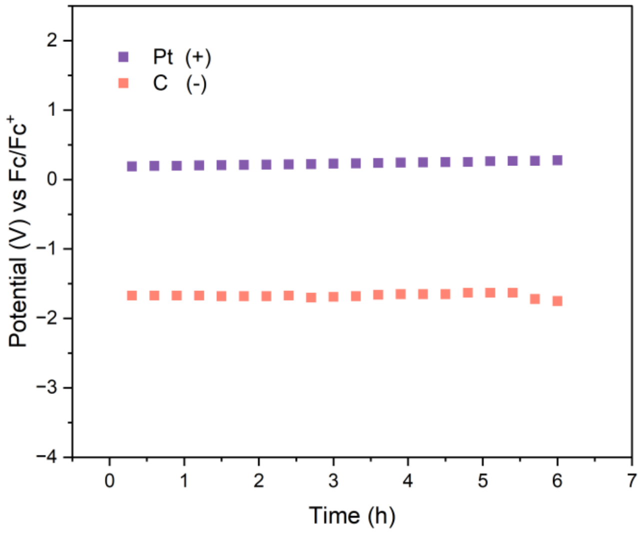



**Fig. S29** Potential profiles of Pt felt cathode and carbon felt anode during the electrolysis under the *Z*-selective hydrogenation condition. The average cathode potential is about -1.7 V vs $Fc/Fc^+$.

### *E*-selective hydrogenation

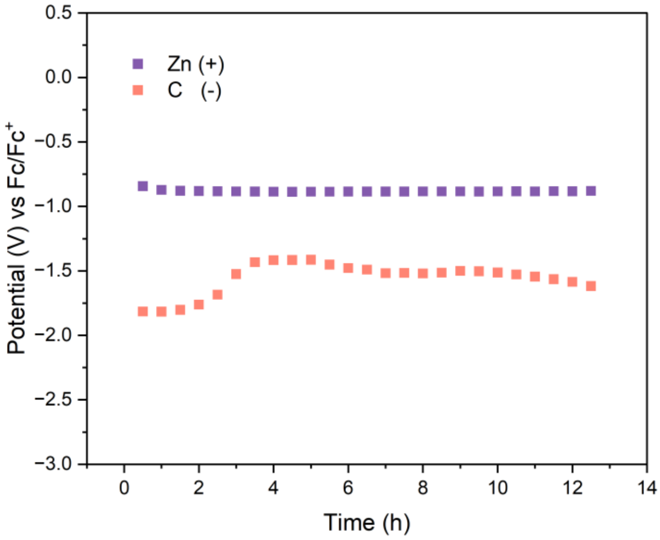



**Fig. S30** Potential profiles of carbon felt cathode and Zn felt anode during the electrolysis under the *E*-selective hydrogenation condition. The average cathode potential is about -1.6 V vs $Fc/Fc^{+}$.

### *allene*-selective hydrogenation

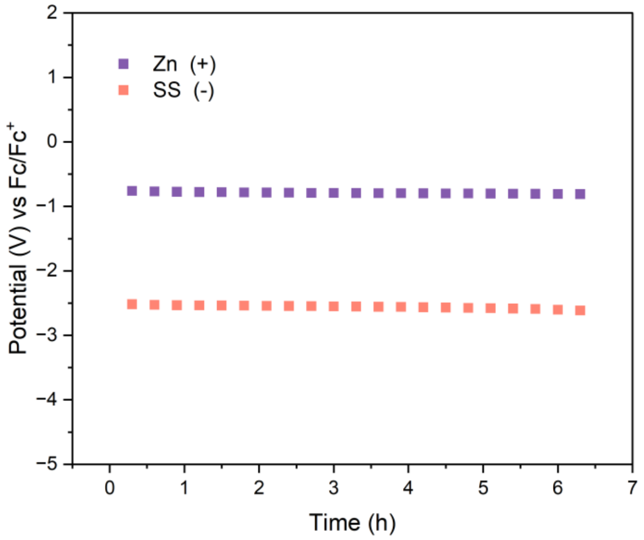



**Fig. S31** Potential profiles of stainless steel felt cathode and Zn felt anode during the electrolysis under the *allene*-selective hydrogenation condition. The average cathode potential is about -2.5 V vs $Fc/Fc^{+}$.

# Hydrogenation Product Interconversion Experiments

General method for interconversion experiments: according to the general procedure of hydrogenation reactions, diphenyl was used as an internal standard. A small amount of the reaction mixture was taken out by syringe. The obtained mixture was immediately diluted by EA (0.5 mL), which was further sampled for GC analysis.

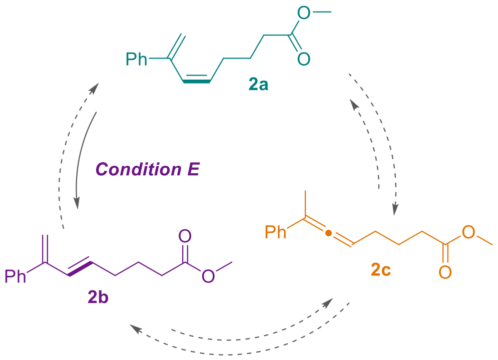
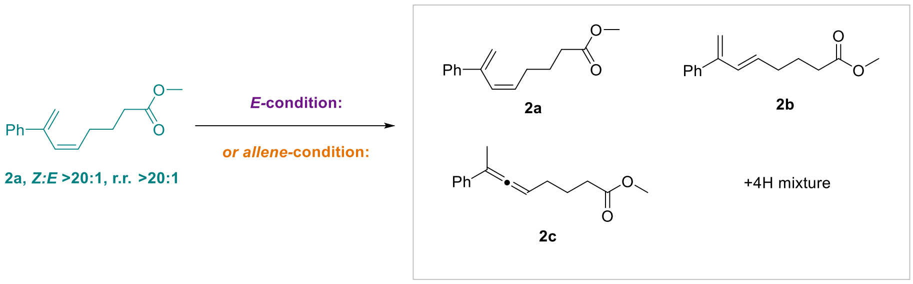



**Fig. S32** Inter-isomerization of hydrogenated products

## *Z*- product isomerization

**Table S10** *Z*- product isomerization experiment



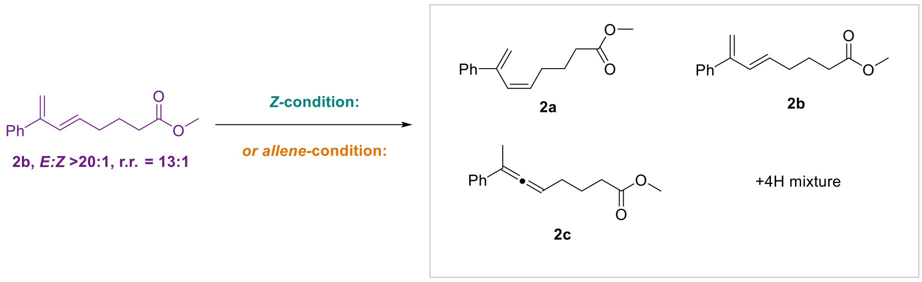

| Entry | Condition | 2a:2b:2c:+4H mixture |
|---|---|---|
| 1 | *E*-condition | 6:**66**:4:14 |
| 2 | *allene*-condition | 50:3:3:44 |

Reaction Conditions: **2a** (*Z*:*E* >20:1, r.r. >20:1, 0.2 mmol). Yields and selectivity were determined by GC using diphenyl as the internal standard.

According to the results of entry 1, the *Z*- product can be converted into the *E*- product under standard *E*- conditions, but it cannot be concluded that the *E*- product is formed by isomerization of the *Z*- product under standard *E*- selective conditions. This requires further experimental verification or ruling out.

## *E*- product isomerization

**Table S11** *E*- product isomerization experiment



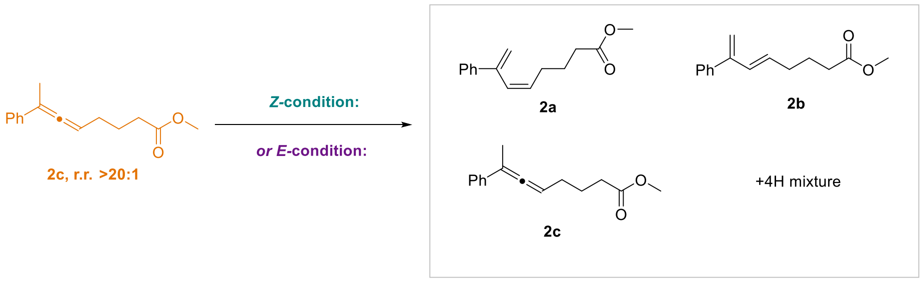

| Entry | Condition | 2a:2b:2c:+4H mixture |
|---|---|---|
| 1 | *Z*-condition | 1:40:0:59 |
| 2 | *allene*-condition | 1:37:4:58 |

Reaction Conditions: **2b** (*E:Z* >20:1, r.r. = 13:1, 0.2 mmol). Yields and selectivity were determined by GC using diphenyl as the internal standard.

According to the results of entry 1, the *E*- product can't be converted to the *Z*- product under standard *Z*-selective conditions.

## *allene*- product isomerization

**Table S12** *allene*- product isomerization experiment




| Entry | Condition | 2a:2b:2c:+4H mixture |
|---|---|---|
| 1 | *Z*-condition | 0:0:55:45 |
| 2 | *E*-condition | 4:6:77:13 |

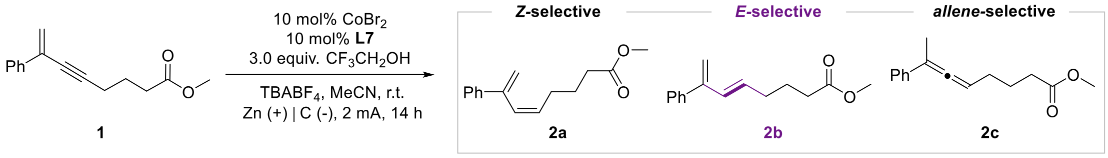
Reaction Conditions: **2c** (r.r. >20:1, 0.2 mmol). Yields and selectivity were determined by GC using diphenyl as the internal standard.

Based on the results of entry 1, the *allene*- product cannot be converted to the *Z*- product under standard *Z*-selective conditions.

Based on the results of entry 2, the *allene*- product can be converted into the *E*- product in small amounts under standard *E*-selective conditions, but the *Z/E* selectivity is poor. It can be inferred that under standard *E*-selective conditions, the *E*- product is not formed through the isomerization of the allene.

# Monitor the Reaction Process

General method: according to the general procedure of *E*-hydrogenation reactions, using substrate **1**, $CoBr_2$/**L7** and $CF_3CH_2OH$, and diphenyl was used as an internal standard. The stopwatch was immediately started when the current was turned on. A small amount of the reaction mixture was taken out by syringe. The obtained mixture was immediately diluted by EA (0.5 mL), which was further sampled for GC analysis.



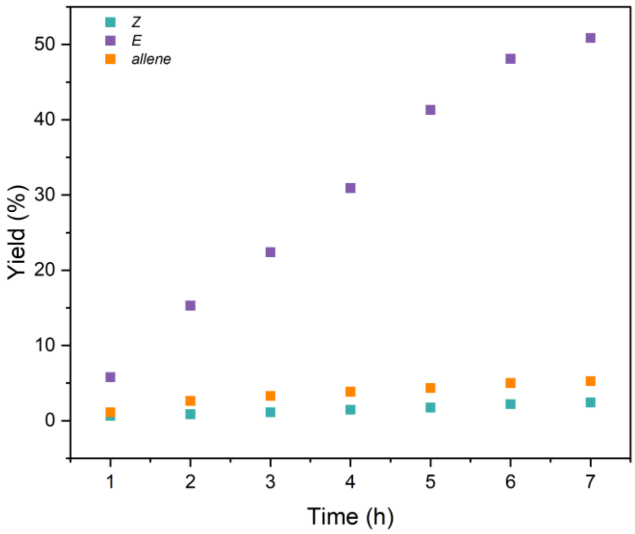




**Fig. S33** Reaction process profiles under standard E-selective condition

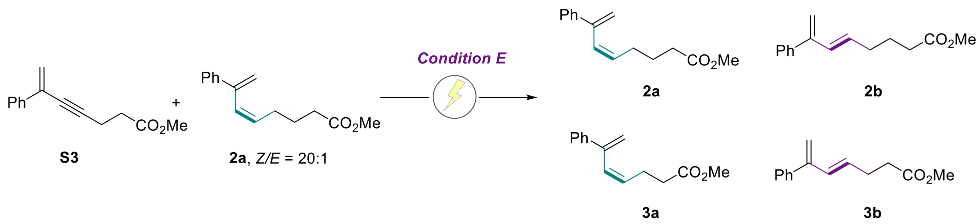
Reaction Conditions: substrate **1** (0.2 mmol), $CoBr_2$ (10 mol%), L7 (10 mol%), $CF_3CH_2OH$ (3.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, Zn (+) | C felt (-), in MeCN (5 mL) at r.t. Yields and selectivity were determined by GC using diphenyl as the internal standard.

Based on the results of monitoring the reaction, under standard *E*-selective conditions, we did not detect the formation or consumption of *Z*- products. This may indicate that under *E*- conditions, the formation of *E*- products may occur directly through hydrogenation, rather than through isomerization of *Z*-products.

# Crossover Experiments

General method: according to the general procedure of *E*-hydrogenation reactions, using substrate **S3**, **2a**, $CoBr_2$/**L7** and $CF_3CH_2OH$, and diphenyl was used as an internal standard. The resulting solution was electrolyzed under a constant current of 2 mA for 14 h at room temperature. A small amount of the reaction mixture was taken out by syringe. The obtained mixture was immediately diluted by EA (0.5 mL), which was further sampled for GC analysis. Additionally, crude NMR spectra were used to assist in analyzing the selectivity.

**Table S13** Crossover experiments




| Entry | 2a:2b | 3a:3b |
|---|---|---|
| 1 | 17:1 | 16:1 |
| | isomerization:20:1 → 17:1 | from hydrogenation |
| | 95% | 62% |

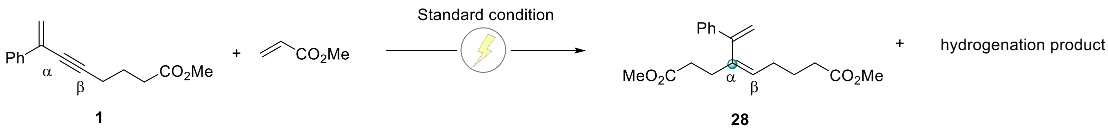
Reaction Conditions: substrate **S3** (0.2 mmol), **2a** (*Z*:*E* = 20:1, 0.2 mmol), $CoBr_2$ (10 mol%), L7 (10 mol%), $CF_3CH_2OH$ (3.0 equiv.), $TBABF_4$ (0.1 M), Ar, 2 mA, undivided cell, Zn (+) | C felt (-), in MeCN (5 mL) at r.t. for 14 h. Selectivity were determined by GC and $^1$H NMR.

Based on the aforementioned crossover experiments, it is evident that hydrogenation proceeds much faster than isomerization. Combined with the experimental observation that no accumulation or consumption of the *Z*-isomer product was detected during the monitoring of the reaction progress, it can be concluded that under standard *E*-selective conditions, the *E*-isomer is obtained directly through hydrogenation rather than through isomerization from the *Z*-isomer.

# C-Co Bond Trapping Experiments

General method: according to the general procedure of *E*- or Z- hydrogenation reactions.

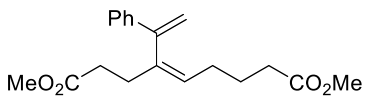
**Table S14** C-Co bond trapping experiments



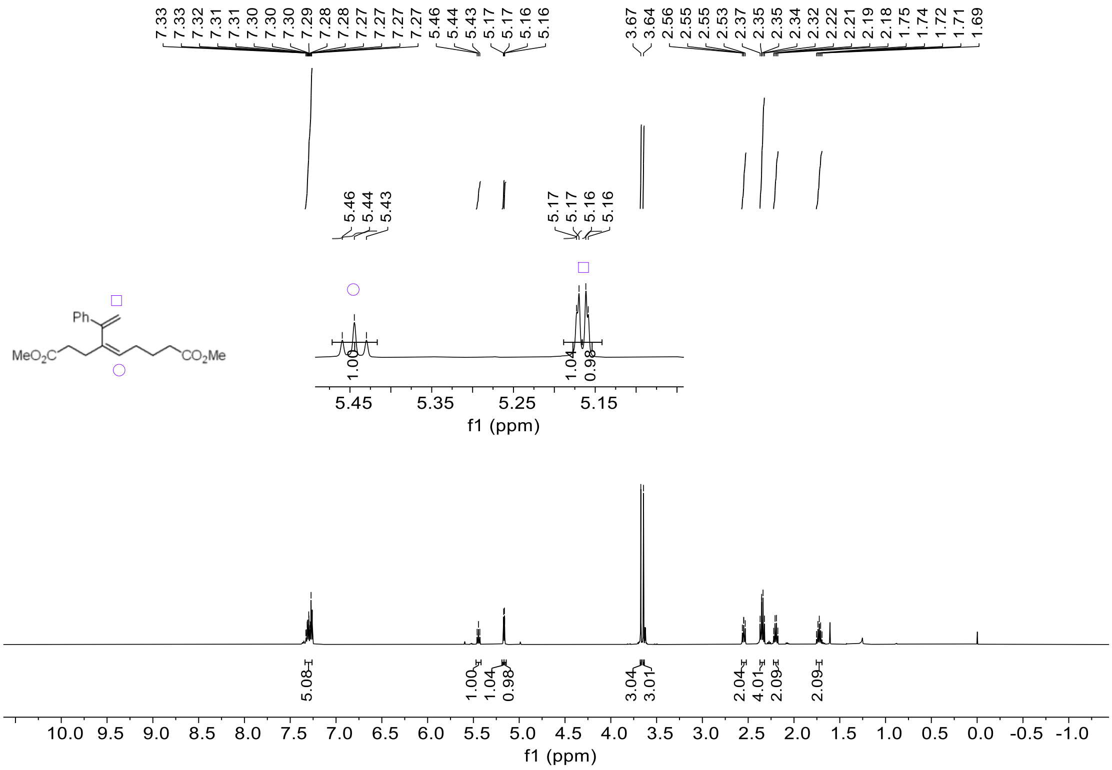

| Entry | Condition | Yield of 28 |
|---|---|---|
| 1 | *Z*-condition | 4% |
| 2 | *E*-condition | 10% |

Reaction Conditions: substrate **1** (0.2 mmol), methyl acrylate (0.2 mmol). Yields were determined by GC using diphenyl as the internal standard.

### dimethyl (Z)-4-(1-phenylvinyl)non-4-enedioate



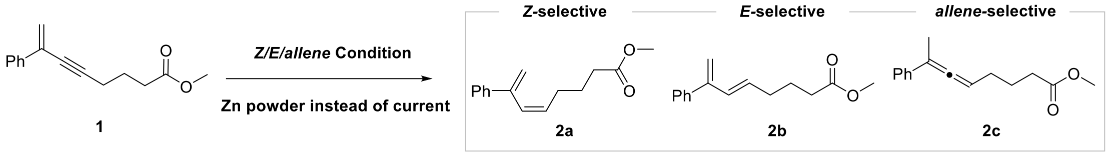
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 5.44 (t, *J* = 7.4 Hz, 1H), 5.17 (d, *J* = 1.5 Hz, 1H), 5.16 (d, *J* = 1.5 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 2.57-2.52 (m, 2H), 2.37-2.32 (m, 4H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.76-1.69 (m, 2H).



# Control Experiments

General method: according to the general procedure of *E*- or Z- hydrogenation reactions.

**Table S15** Control experiments

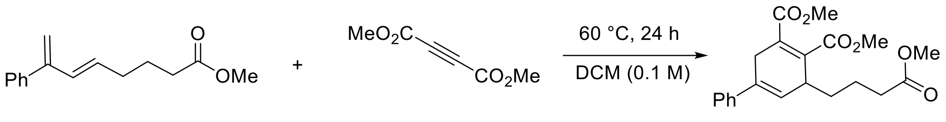



| Entry | Condition | Yield |
|---|---|---|
| 1 | Condition *allene*, r.t. | - |
| 2 | Condition *allene*, 60 °C | - |
| 3 | Condition *allene*, 90 °C | - |
| 4 | Condition *Z*, r.t. | - |
| 5 | Condition *Z*, 60 °C | - |
| 6 | Condition *Z*, 90 °C | - |
| 7 | Condition *E*, r.t. | 13% yield, *E/Z* = 12:1, r.r. = 8:1 |
| 8 | Condition *E*, 60 °C | 13% yield, *E/Z* = 7:1, r.r. > 20:1 |
| 9 | Condition *E*, 90 °C | 12% yield, *E/Z* = 3:1, r.r. > 20:1 |

Reaction Conditions: substrate **1** (0.2 mmol), Zn powder (2.0 equiv.) instead of current. Yields and selectivity were determined by GC using diphenyl as the internal standard.

# 6. Synthetic Applications

**dimethyl 5-(4-methoxy-4-oxobutyl)-2,5-dihydro-[1,1'-biphenyl]-3,4-dicarboxylate**




**2b** **22**

To a solution of **2b** (46 mg, 0.2 mmol) in DCM (2 mL) was added dimethyl acetyl dicarboxylate (30 μL, 0.24 mmol). After stirring at 60 °C for 24 hours, the solution was cooled to room temperature and concentrated in vacuo. The concentrated residue was purified by column chromatography on silica gel with a gradient eluent of PE/EA to give the desired products[5].

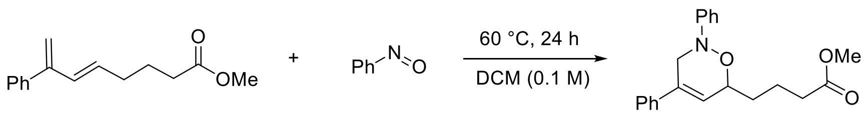
Compound **22** was isolated via column chromatography (PE/EA=10:1~3:1) as colorless oil (32.0 mg, 43% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 6.06 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.64 (s, 3H), 3.55-3.38 (m, 2H), 3.37-3.22 (m, 1H), 2.30 (t, *J* = 5.5 Hz, 2H), 1.73-1.58 (m, 4H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.73, 169.02, 167.41, 139.70, 138.51, 133.37, 130.86, 128.50, 127.68, 125.21, 123.52, 52.32, 51.54, 38.84, 34.07, 33.42, 29.43, 20.83.

**HRMS** (APCI) calcd. for $C_{21}H_{25}O_6^+$ $[M+H]^+$: 373.1646; found: 373.1642.

**methyl 4-(2,4-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-6-yl)butanoate**




**2b** **23**

To a solution of **2b** (46 mg, 0.2 mmol) in DCM (2 mL) was added nitrosobenzene (32.2 mg, 0.3 mmol). After stirring at 60 °C for 24 hours, the solution was cooled to room temperature and concentrated in vacuo. The concentrated residue was purified by column chromatography on silica gel with a gradient eluent of PE/EA to give the desired products[5].

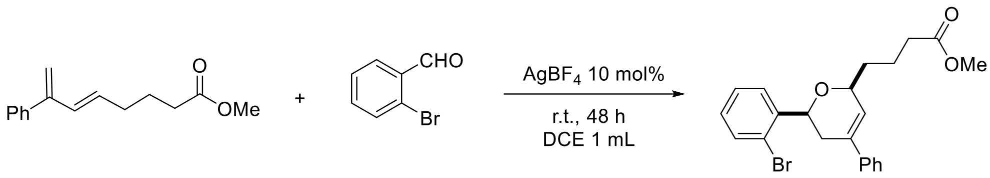
Compound **23** was isolated via column chromatography (PE/EA=20:1~10:1) as colorless oil (44.5 mg, 66% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.30 (m, 7H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.19 (s, 1H), 4.71 (s, 1H), 4.23 (d, *J* = 15.3 Hz, 1H), 4.09 (d, *J* = 15.3 Hz, 1H), 3.67 (s, 3H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.99-1.74 (m, 4H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.92, 150.50, 138.14, 134.08, 128.93, 128.68, 127.89, 125.72, 125.04, 122.35, 115.91, 77.10, 53.59, 51.58, 33.97, 33.07, 21.20.

**HRMS** (APCI) calcd. for $C_{21}H_{24}NO_3^+$ $[M+H]^+$: 338.1751; found: 338.1745.

**methyl 4-((2*S*,6*S*)-6-(2-bromophenyl)-4-phenyl-5,6-dihydro-2*H*-pyran-2-yl)butanoate**




**2b** **24**

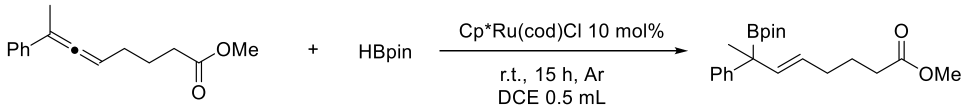
In a glove box, an oven dried 10 mL vial was charged with **2b** (92 mg, 0.4 mmol), $AgBF_4$ (2 mg, 10 mol%), 2-bromobenzaldehyde (12 μL, 0.2 mmol) and DCE (1 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 48 h, and then concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give the desired product[6]. Compound **24** was isolated via column chromatography (PE/EA=20:1~10:1) as colorless oil (48.0 mg, 55% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, $J$ = 7.7 Hz, 1H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.40 (t, $J$ = 7.8 Hz, 3H), 7.33 (t, $J$ = 7.6 Hz, 2H), 7.25 (d, $J$ = 4.5 Hz, 1H), 7.15 (t, $J$ = 7.7 Hz, 1H), 6.10 (d, $J$ = 2.5 Hz, 1H), 5.01 (dd, $J$ = 10.7, 3.0 Hz, 1H), 4.58-4.48 (m, 1H), 3.67 (d, $J$ = 1.3 Hz, 3H), 2.86 (dd, $J$ = 16.5, 3.2 Hz, 1H), 2.46-2.37 (m, 3H), 1.93-1.72 (m, 4H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 174.11, 142.05, 139.91, 135.11, 132.48, 128.82, 128.48, 127.92, 127.55, 127.49, 125.67, 124.92, 121.63, 75.26, 75.07, 51.54, 35.00, 34.09, 33.51, 20.65.

**HRMS** (ESI) calcd. for $C_{22}H_{23}BrO_3Na^+$ $[M+H]^+$: 437.0723; found: 437.0724.

**methyl (*E*)-7-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-5-enoate**




**2c** **25**

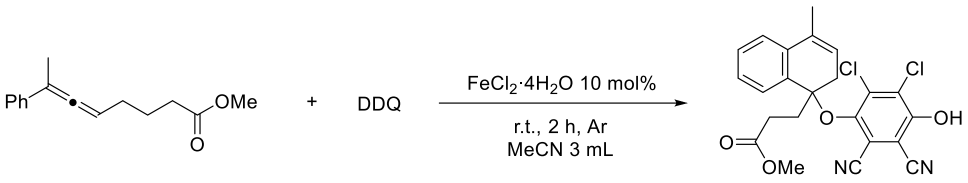
In a glove box, an oven-dried 10 mL vial was charged with **2b** (46 mg, 0.2 mmol), Cp*Ru(cod)Cl (7.6 mg, 10 mol%), pinacolborane (43 μL, 0.3 mmol) and DCE (0.5 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 12 h, and then concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give the desired product[7]. Compound **25** was isolated via column chromatography (PE/EA=20:1~10:1) as colorless oil (53.7 mg, 75% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 3H), 7.16-7.12 (m, 1H), 5.84 (dt, $J$ = 15.6, 1.4 Hz, 1H), 5.40 (dt, $J$ = 15.7, 6.8 Hz, 1H), 3.66 (s, 3H), 2.34 (t, $J$ = 7.7 Hz, 2H), 2.17-2.10 (m, 2H), 1.78-1.70 (m, 2H), 1.39 (s, 3H), 1.22 (d, $J$ = 7.9 Hz, 12H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 174.36, 147.50, 136.98, 128.26, 127.42, 127.34, 125.46, 83.59, 51.56, 33.45, 32.40, 25.00, 24.60, 24.59, 23.46.

**HRMS** (APCI) calcd. for $C_{21}H_{32}BO_4^+$ $[M+H]^+$: 359.2389; found: 359.2382.

**methyl 3-(1-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-4-methyl-1,2-dihydronaphthalen-1-yl)propanoate**




2c 25

In a glove box, an oven dried 10 mL vial was charged with **2b** (46 mg, 0.2 mmol), $FeCl_2·4H_2O$ (2.9 mg, 10 mol%), DDQ (45.4 mg, 0.2 mmol) and MeCN (3 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 48 h, and then concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give the desired product[8].

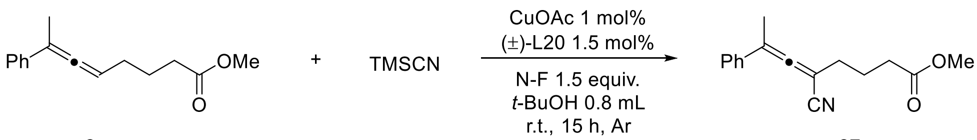
Compound **26** was isolated via column chromatography (PE/EA=20:1~10:1) as pale yellow oil (53.7 mg, 63% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.45-7.42 (m, 2H), 6.18 (t, $J$ = 7.8 Hz, 1H), 3.60 (s, 3H), 2.26 (q, $J$ = 7.3 Hz, 2H), 2.07 (q, $J$ = 7.7 Hz, 2H), 1.77-1.68 (m, 2H), 1.65 (s, 3H).

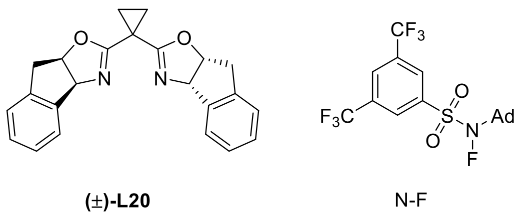
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.92, 175.20, 173.27, 146.18, 145.52, 138.07, 136.61, 131.98, 129.76, 129.70, 126.42, 113.00, 112.72, 63.35, 51.91, 33.15, 28.49, 24.89, 23.58.

**HRMS** (APCI) calcd. for $C_{23}H_{19}Cl_2N_2O_4^+$ $[M+H]^+$: 457.0717; found: 457.0710.

**methyl 5-cyano-7-phenylocta-5,6-dienoate**




2c 27




(±)-L20 N-F

In a dried sealed 10 mL Schlenk tube, (±)-**L20** (10.8 mg, 0.03 mmol), CuOAc (2.5 mg, 0.02 mmol) were dissolved in 2.0 mL of DCE. The resulting mixture was stirred for 1 hour. Then a catalyst solution (0.2 mL, 0.002 mol %) was added to a 10 mL sealed tube under an argon atmosphere, and the solvent was removed under vacuum. The residue was redissolved in 0.8 mL of ultra-dry *t*-BuOH. After that, N-F (134 mg, 0.3 mmol), **2c** (46mg, 0.2 mmol), and TMSCN (50 μL, 0.4 mmol) were added sequentially. After stirring at room temperature for 15 h, the reaction mixture was concentrated in vacuo. The concentrated residue was purified by column chromatography on silica gel with a gradient eluent of PE/EA to give the desired products[9].

Compound **27** was isolated via column chromatography (PE/EA=20:1~10:1) as pale yellow oil (38.0 mg, 75% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.29 (m, 5H), 3.66 (s, 3H), 2.38 (dt, $J$ = 14.0, 7.5 Hz, 4H), 2.19 (s, 3H), 1.94-1.86 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.53, 173.16, 133.59, 128.81, 128.54, 126.40, 115.27, 107.54, 83.00,

51.70, 32.77, 31.07, 22.84, 16.59.

**HRMS** (APCI) calcd. for $C_{16}H_{18}NO_2^+$ $[M+H]^+$: 256.1333; found: 256.1325.

# 7. References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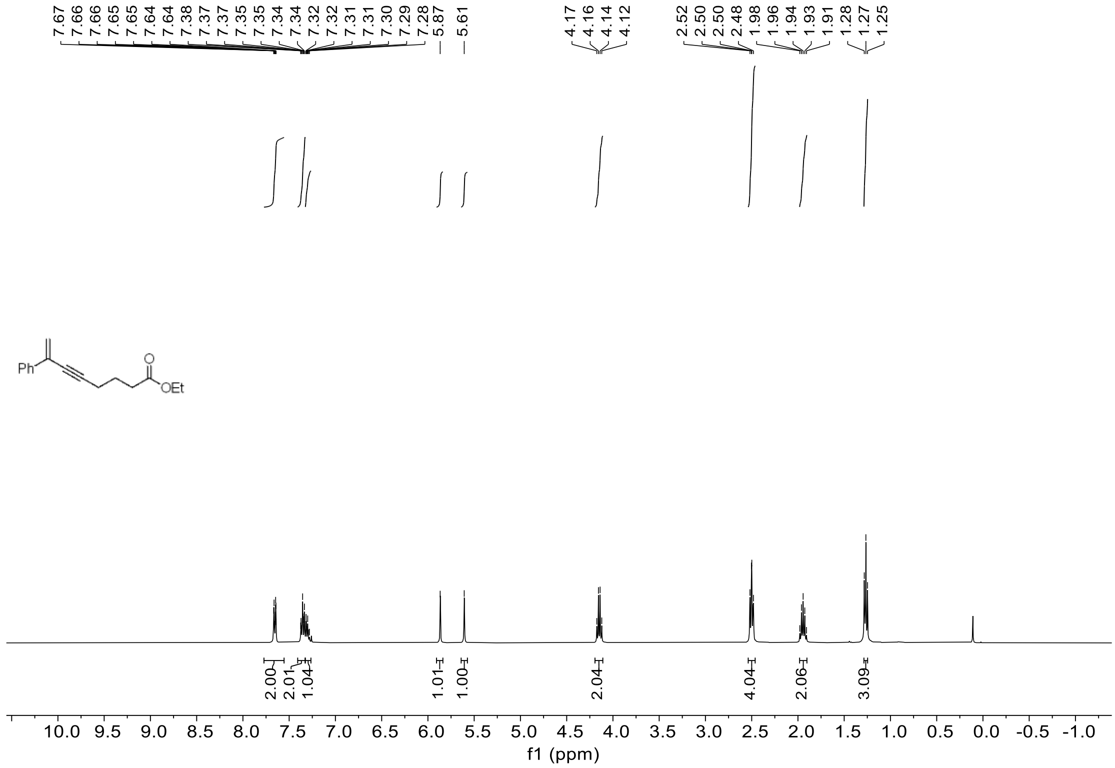
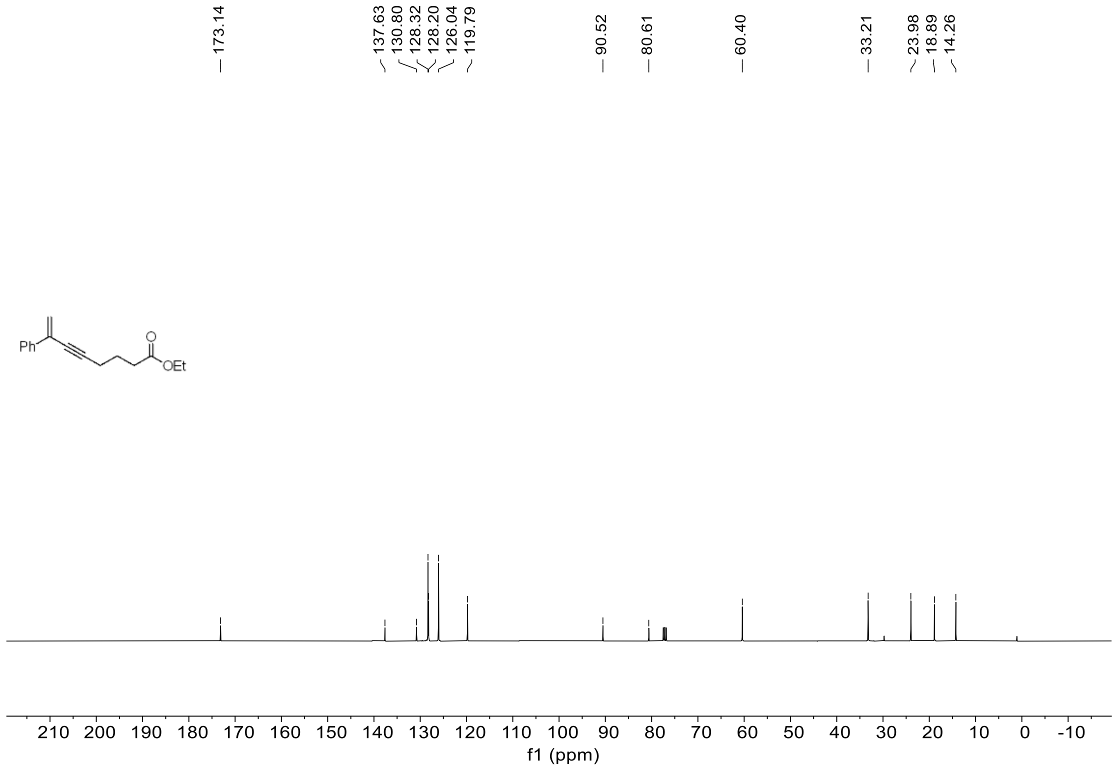
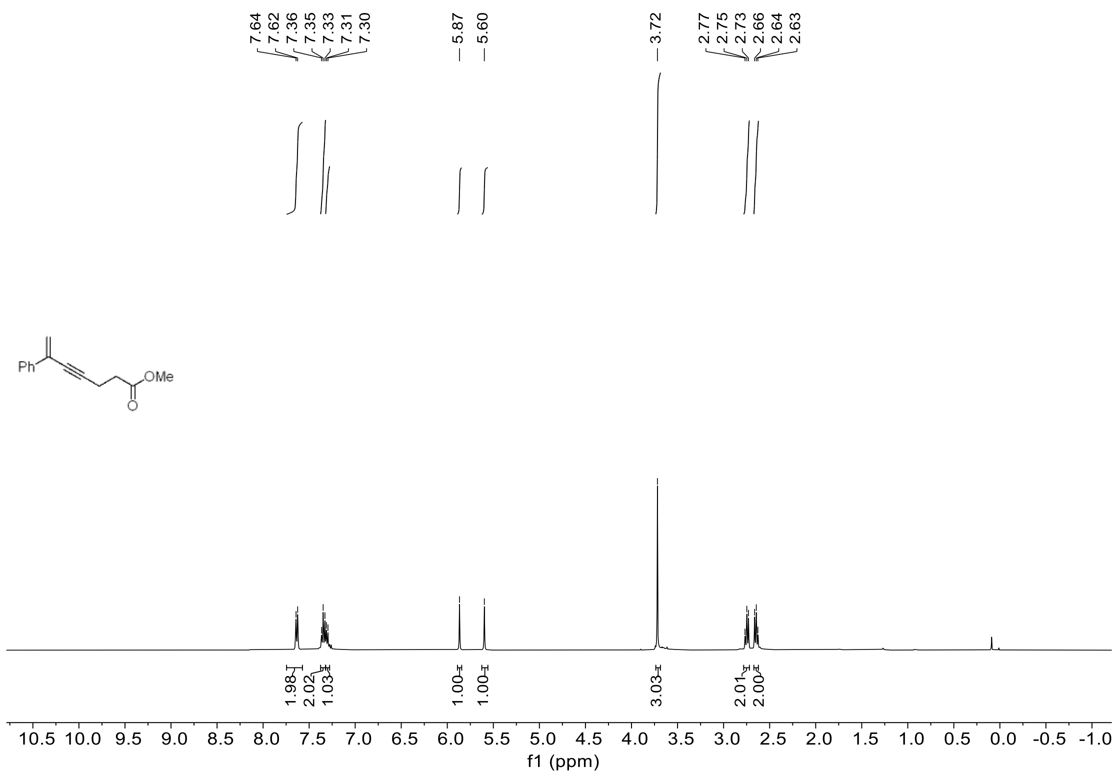
# 8. NMR Spectra



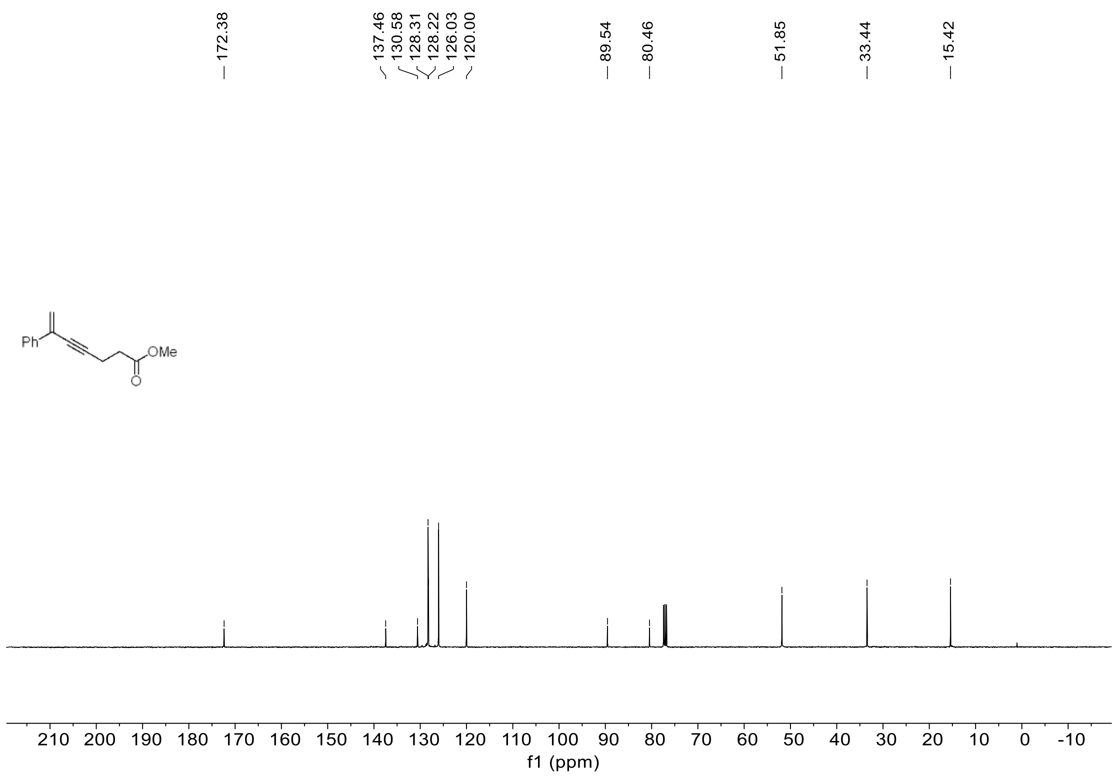

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **S2**



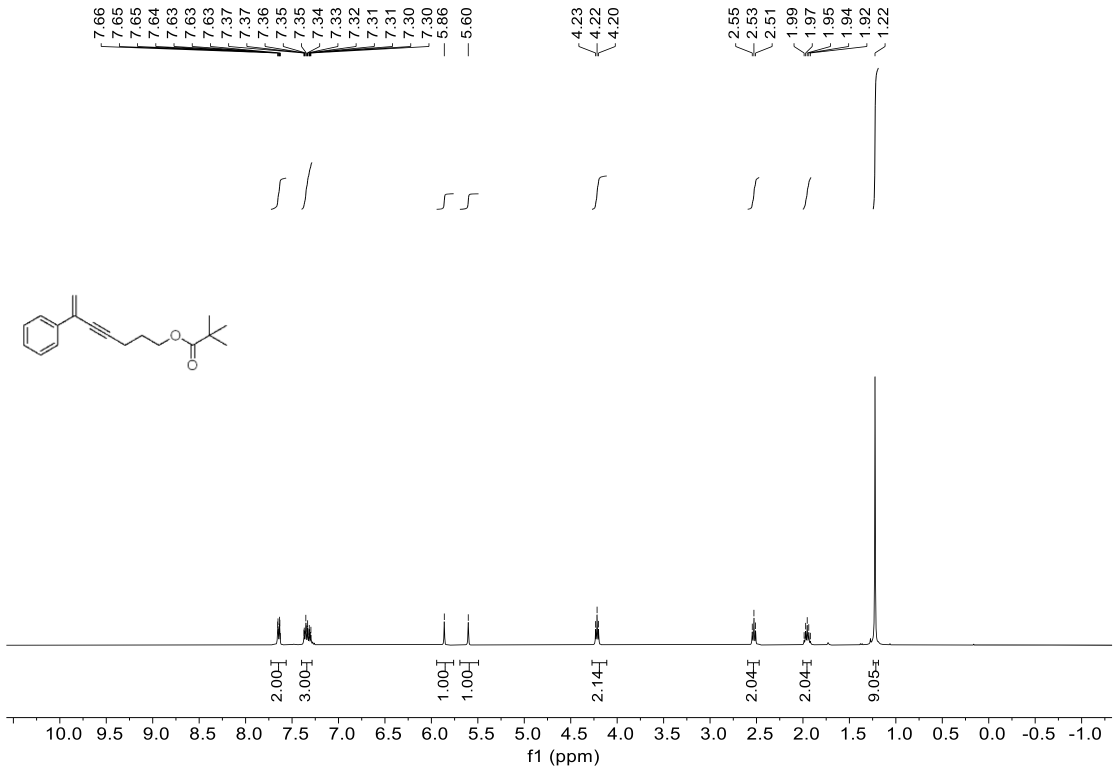

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **S2**



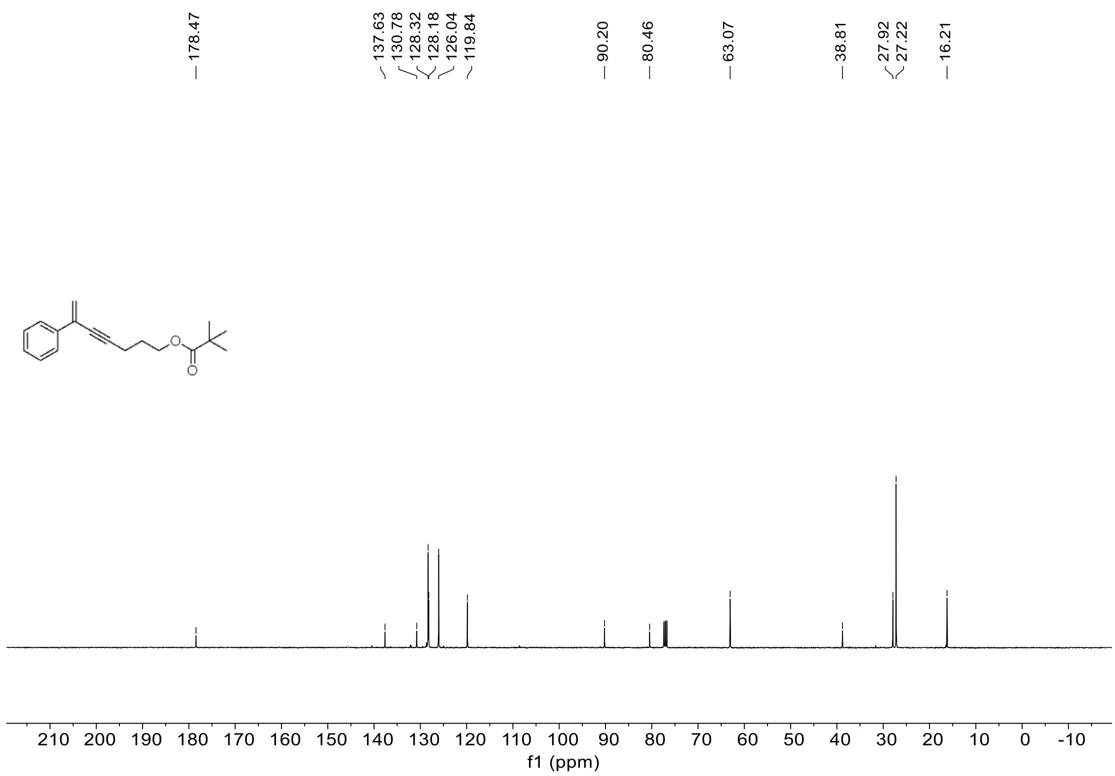

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S3**



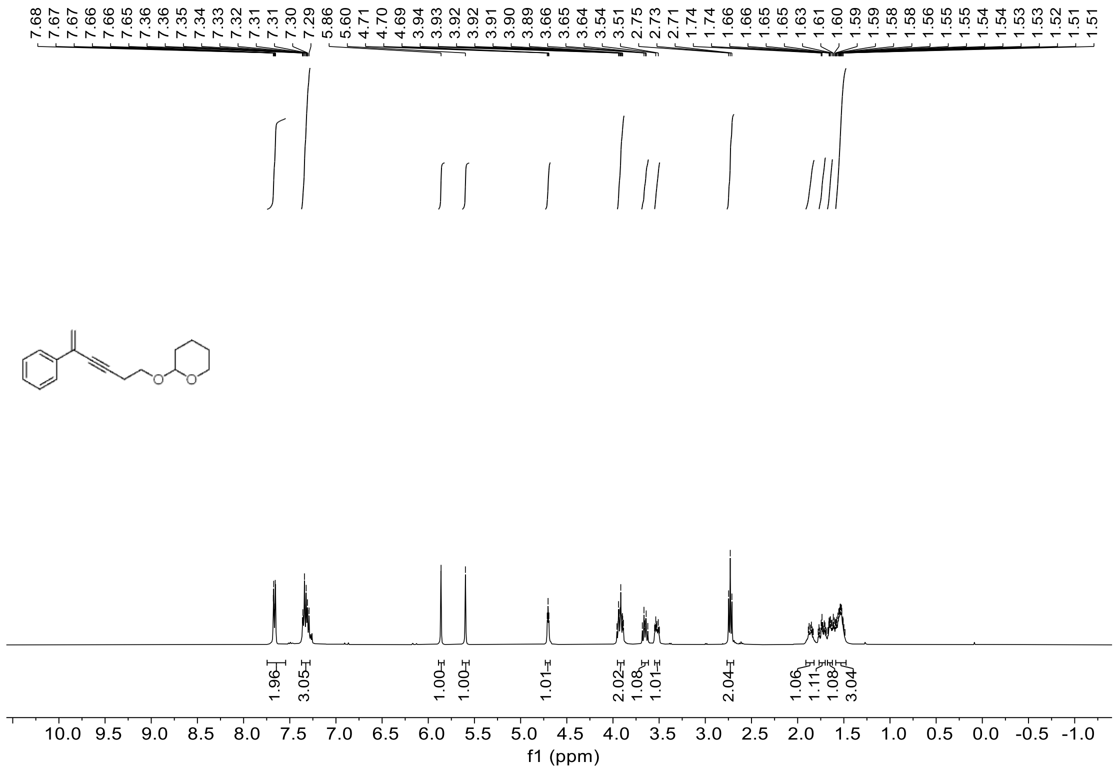

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S3**



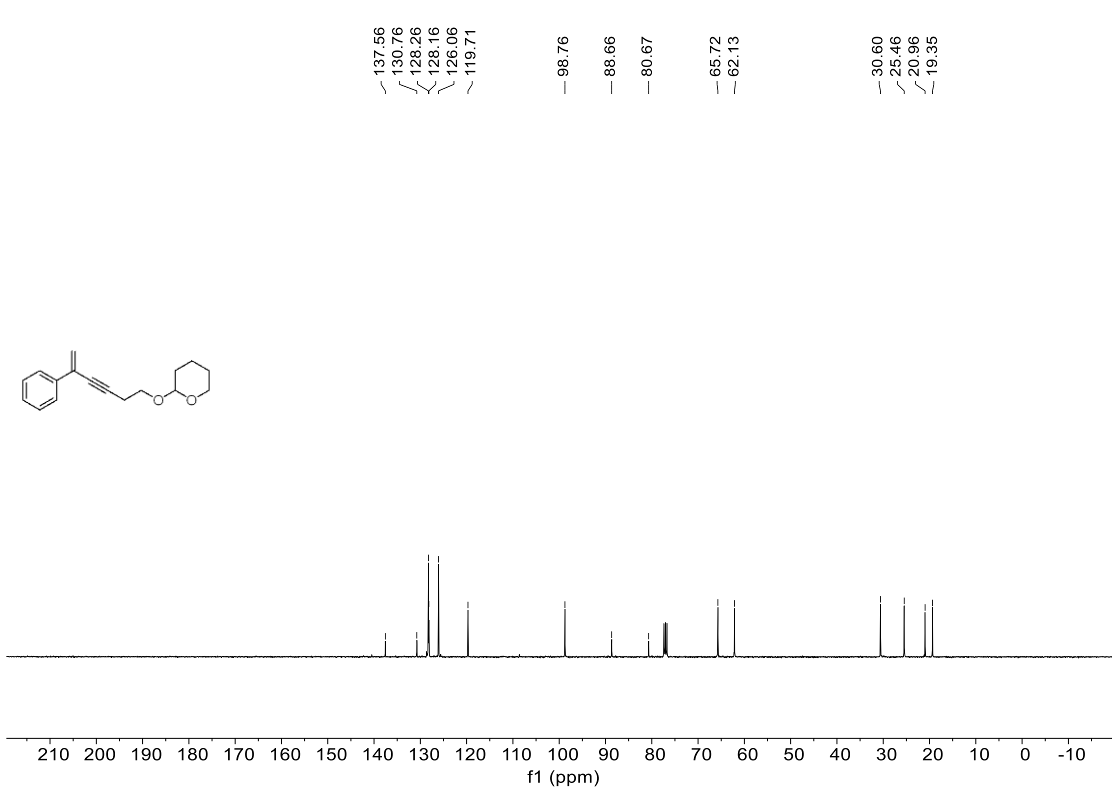

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **S4**



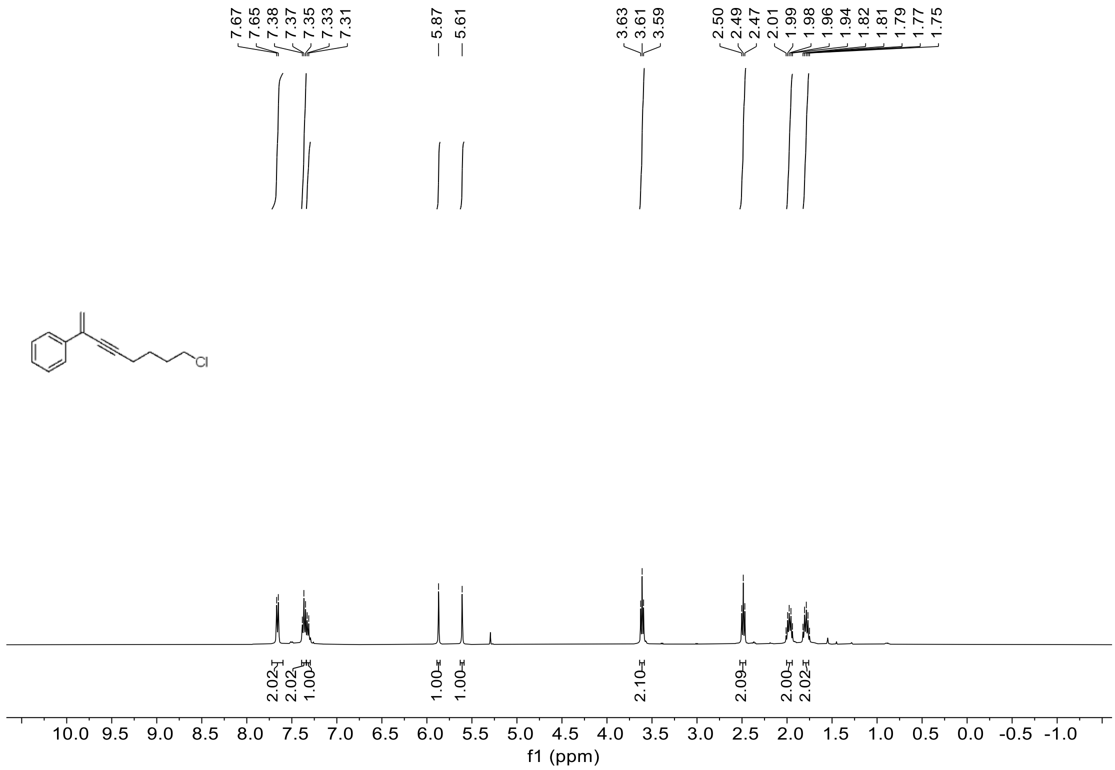

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **S4**



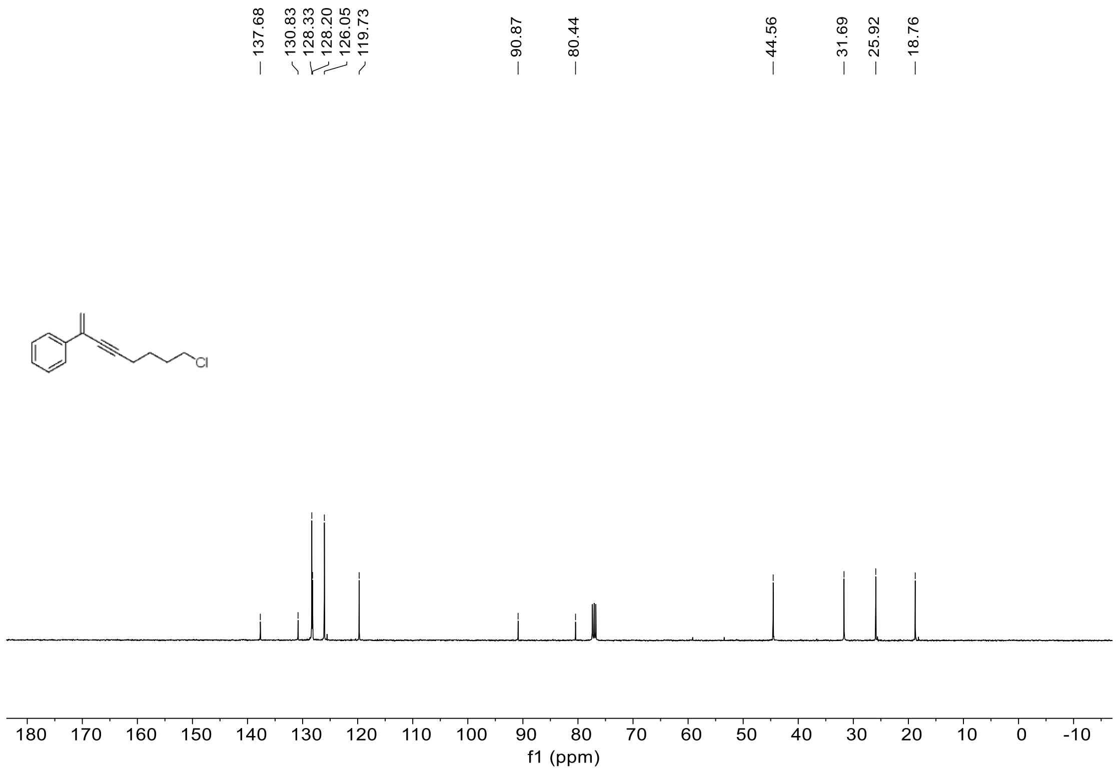

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **S5**



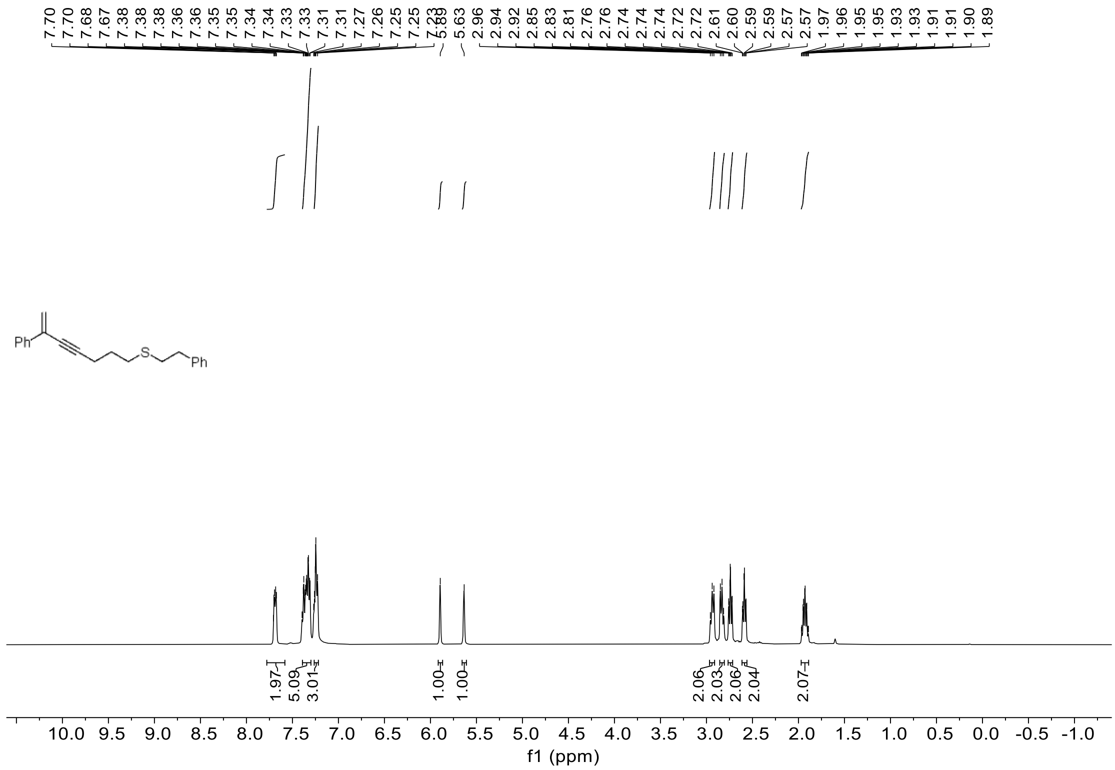

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **S5**



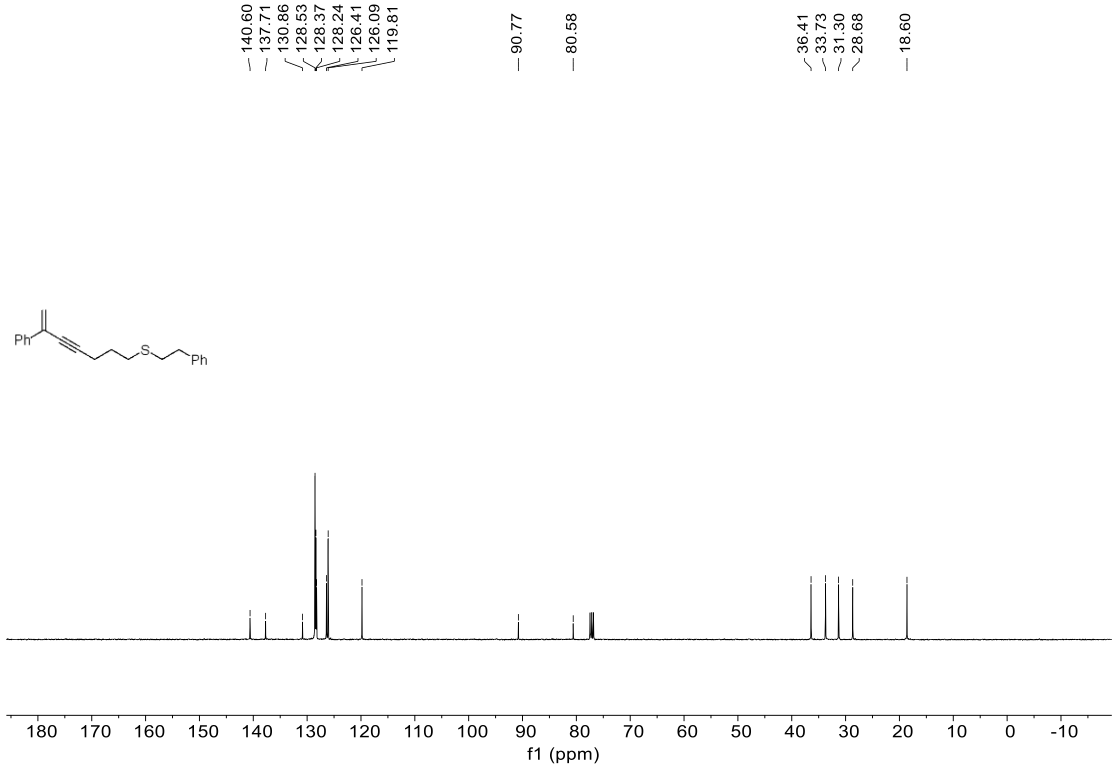

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S8**



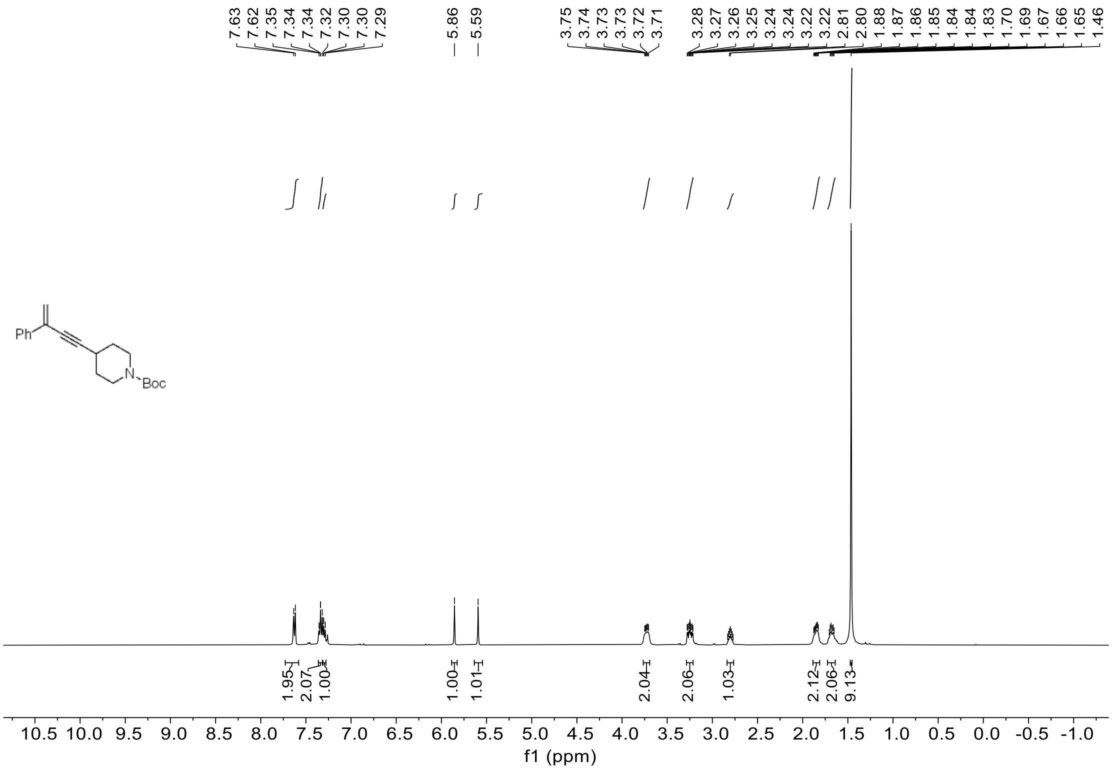

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S8**



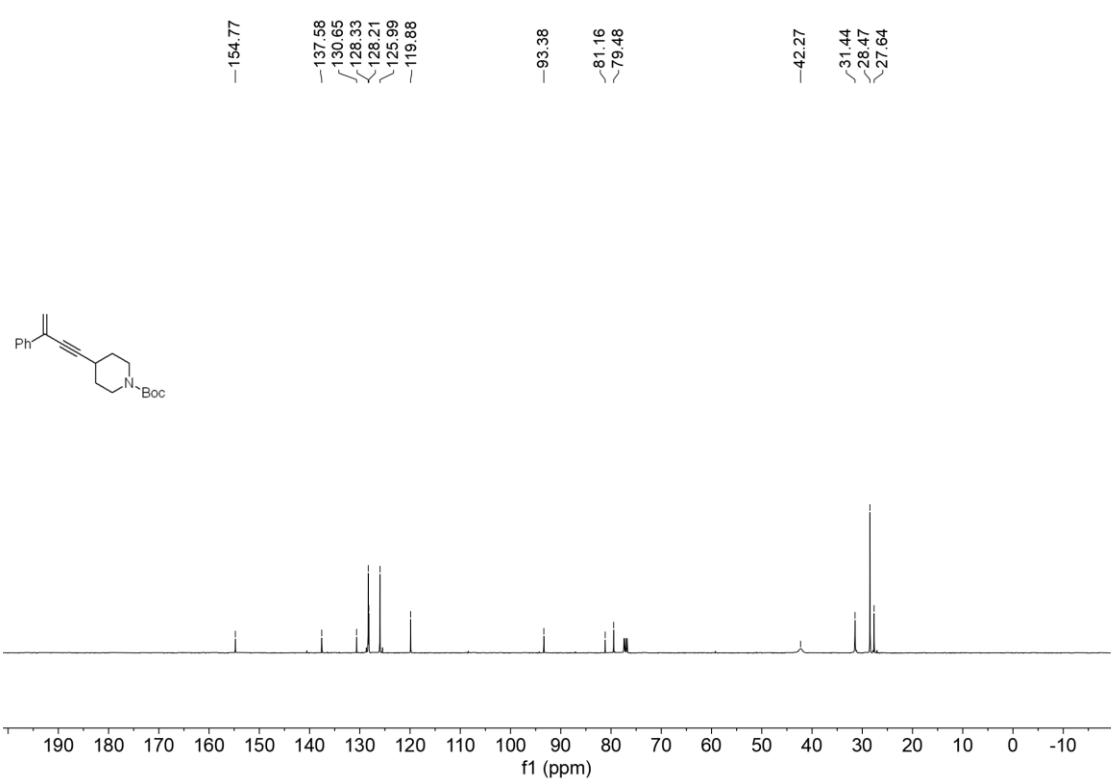
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S11**



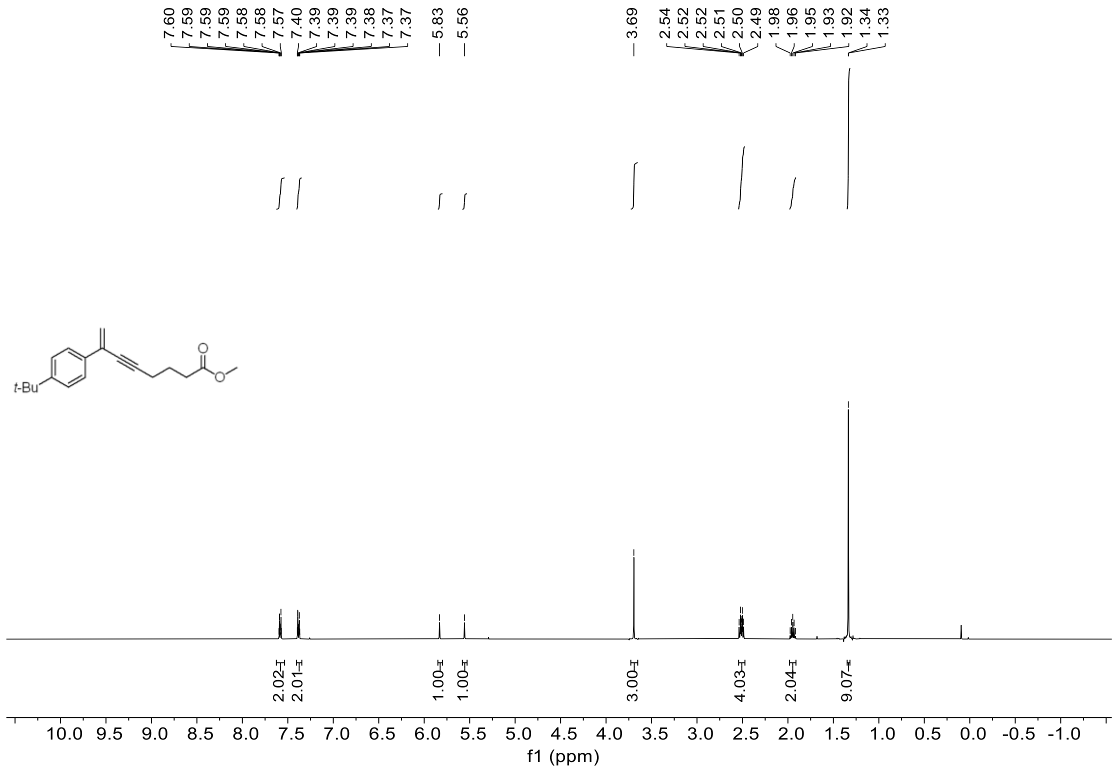
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S11**



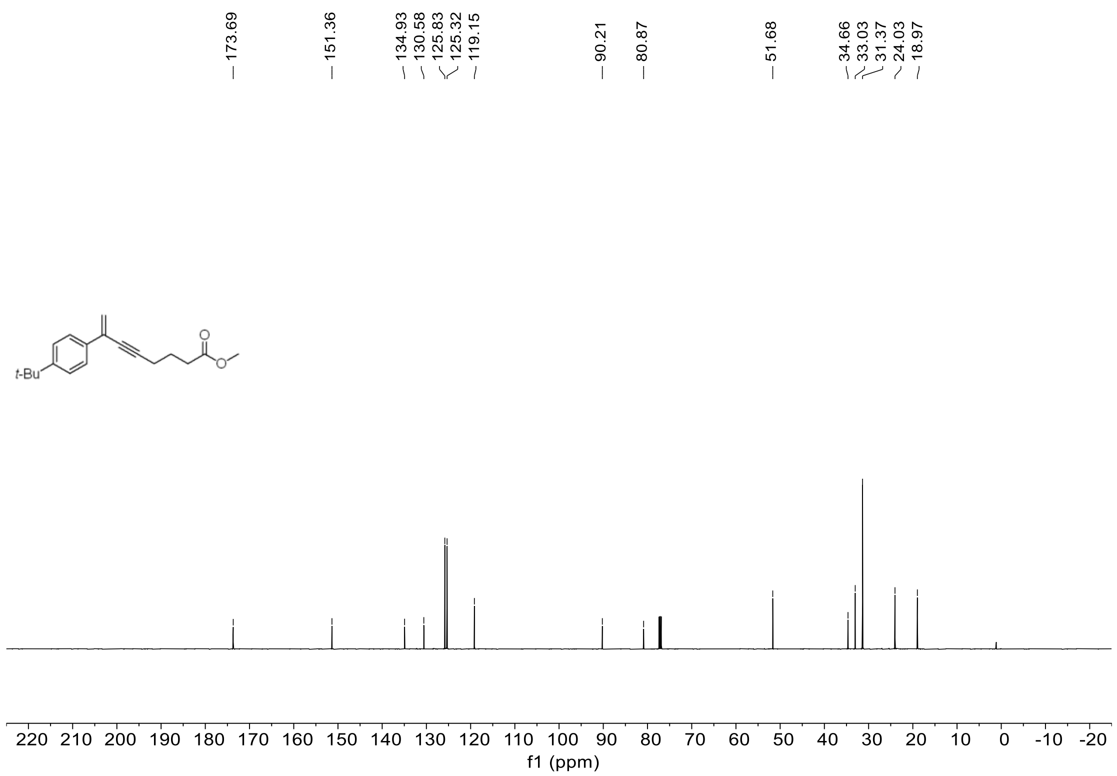
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S15**



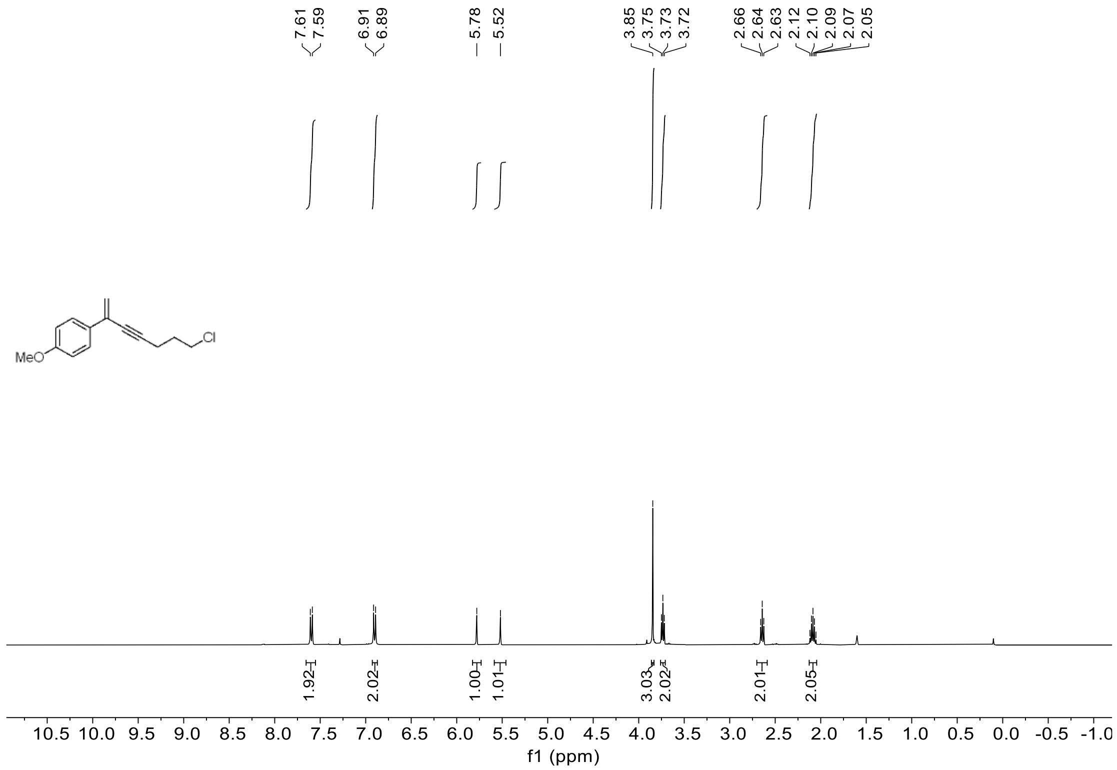
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S15**



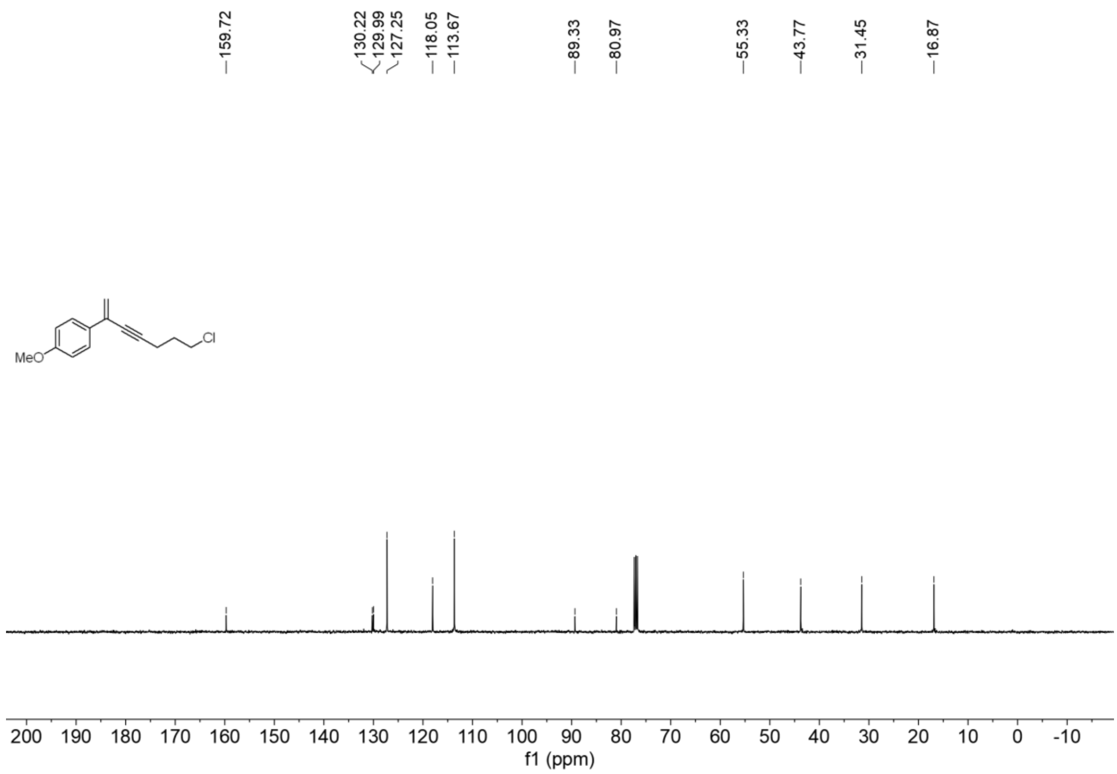
**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **S17**



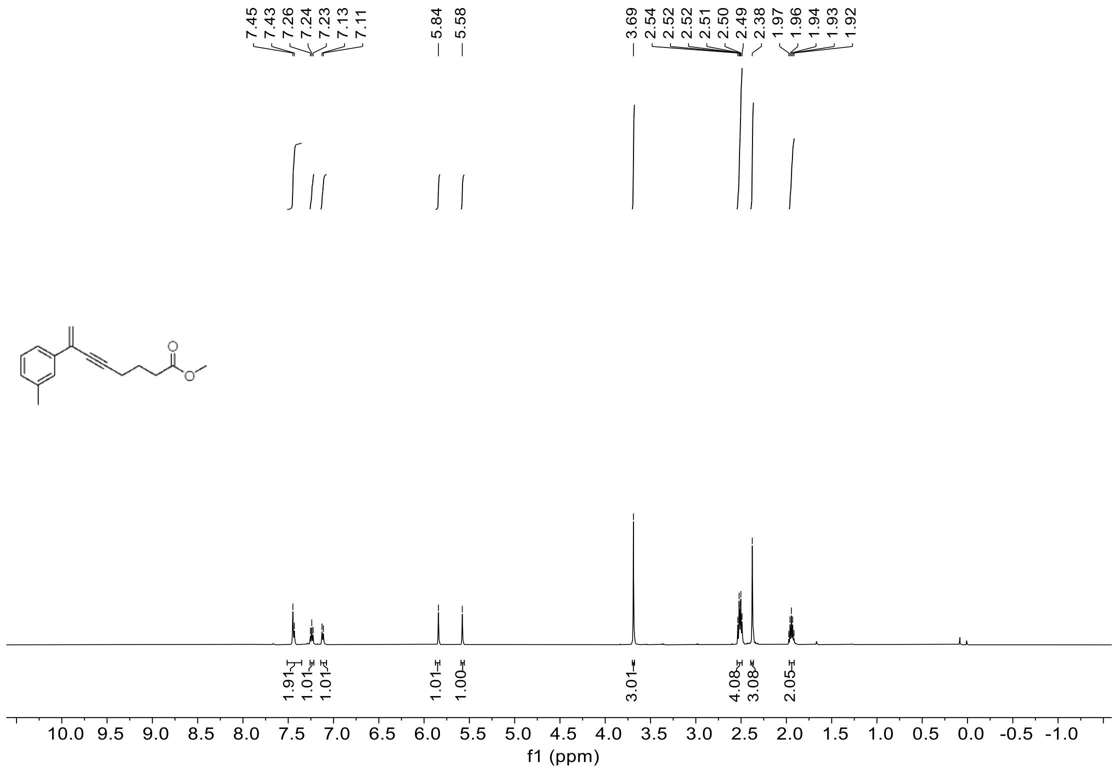
**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **S17**



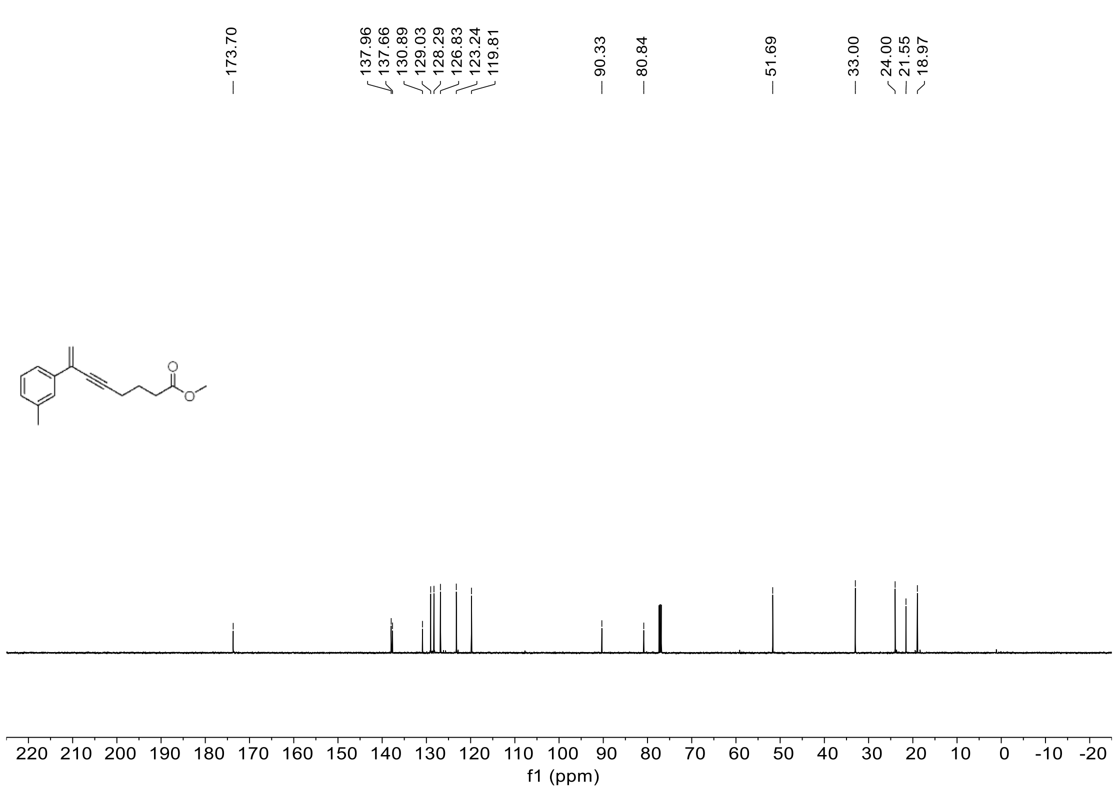

**¹H NMR** (400 MHz, $CDCl_3$) spectra of **S18**



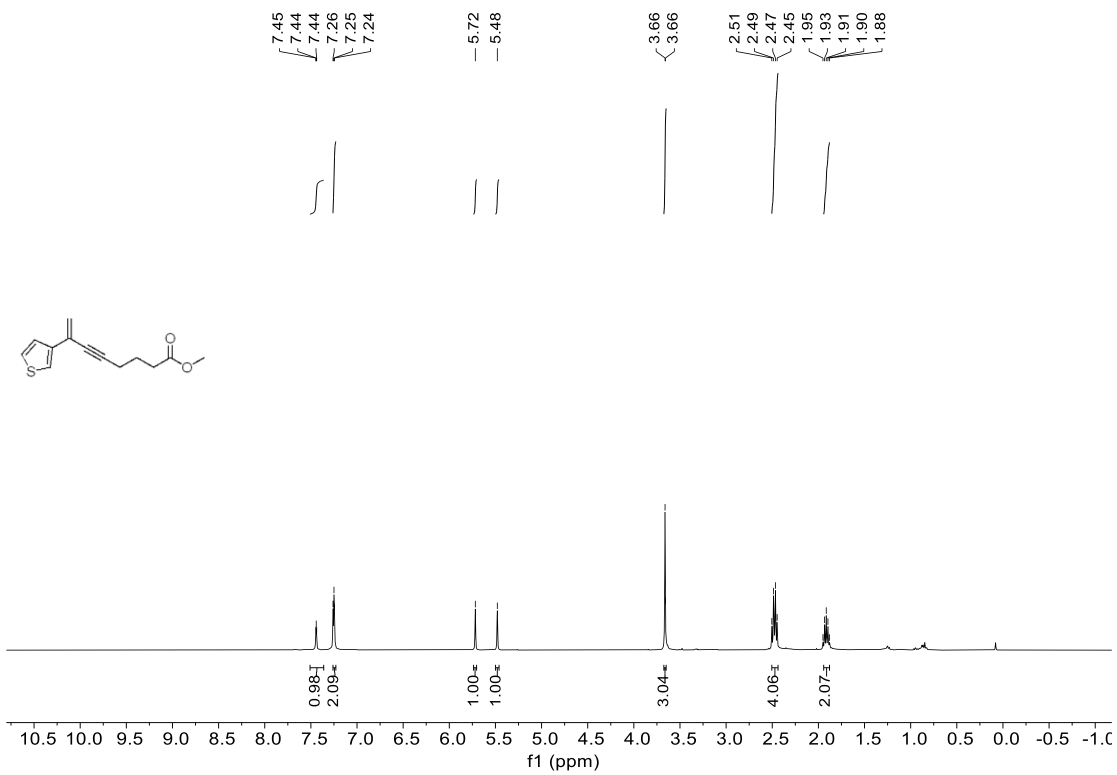

**¹³C NMR** (101 MHz, $CDCl_3$) spectra of **S18**



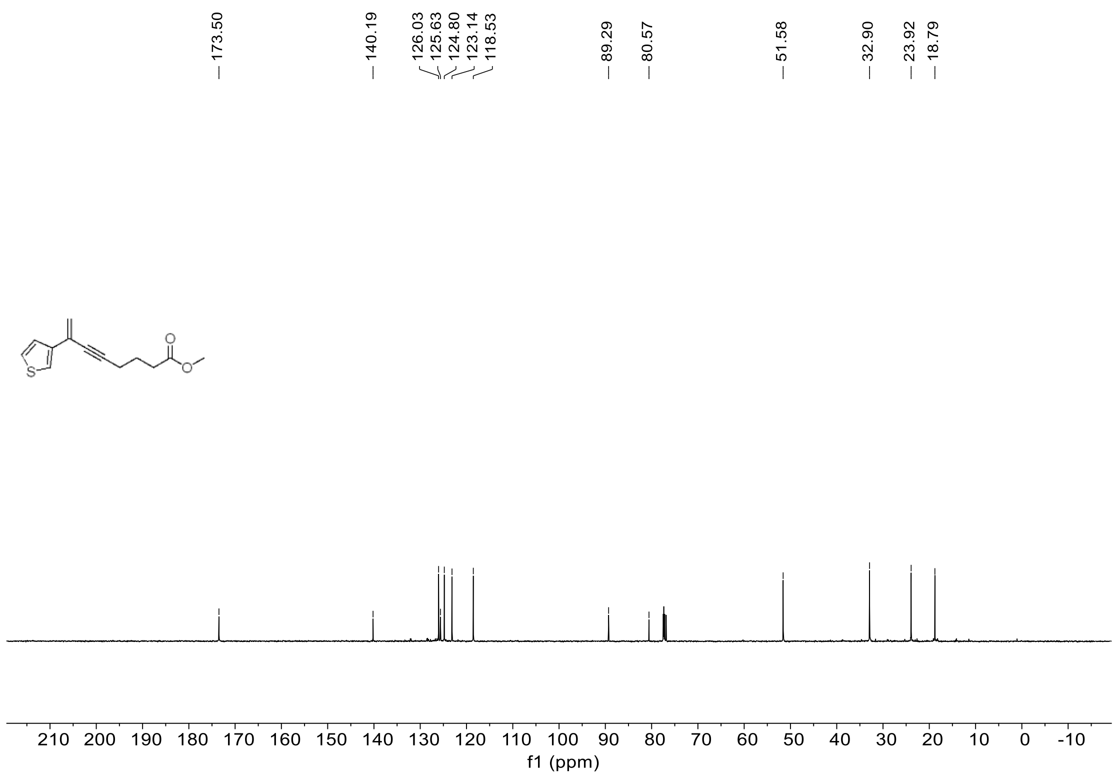

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **S19**



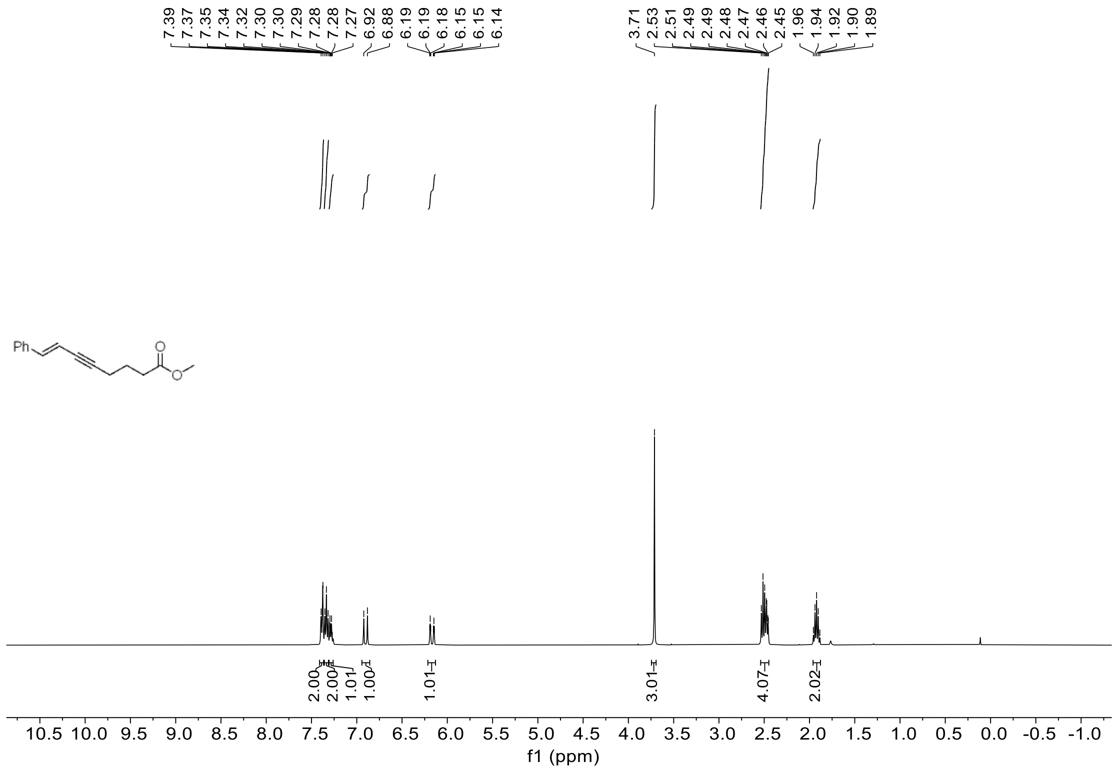

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **S19**



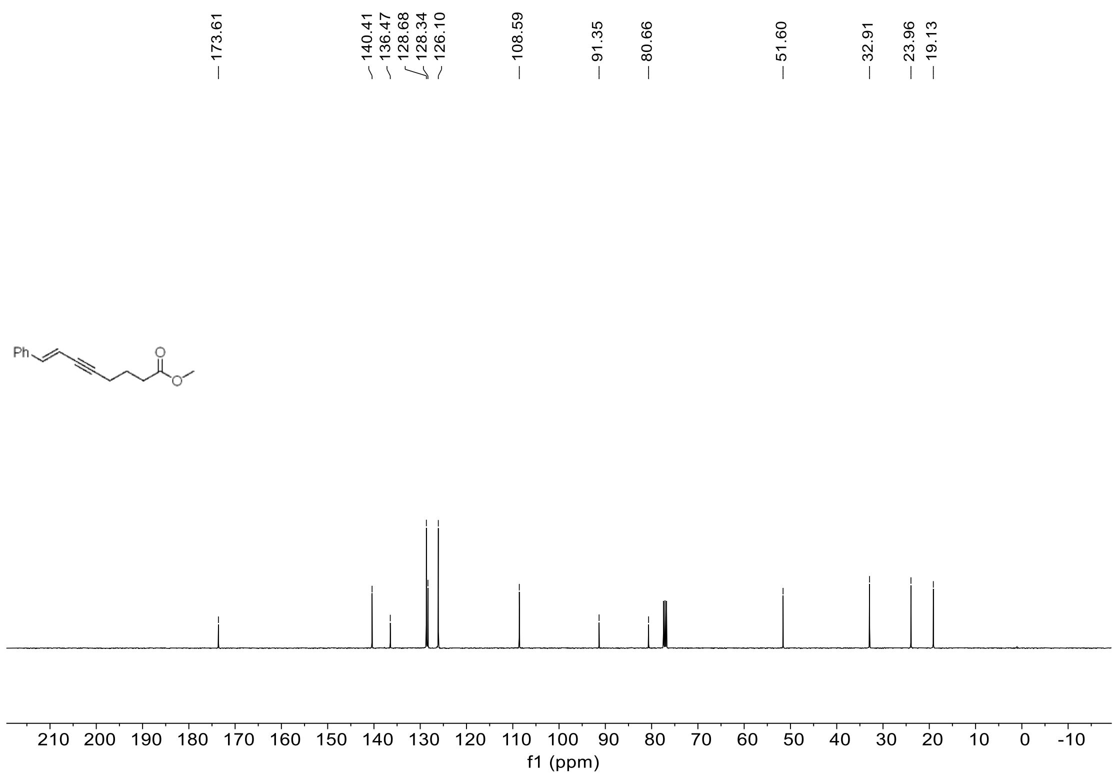
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S21**



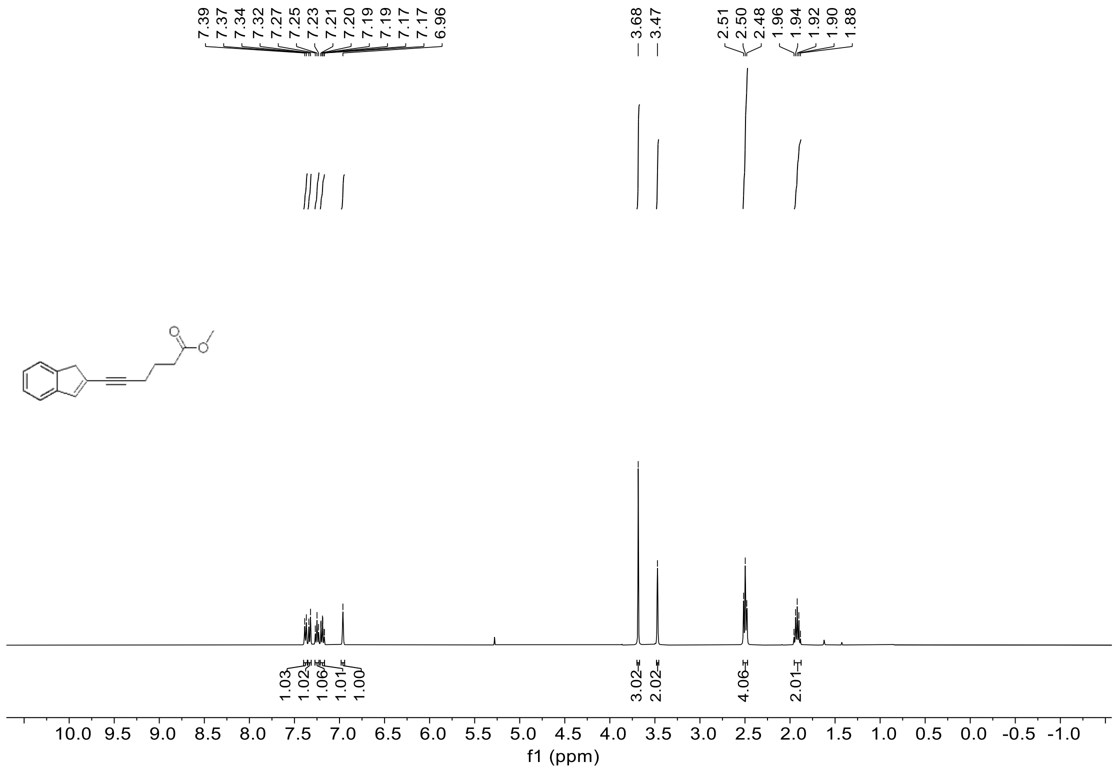
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S21**



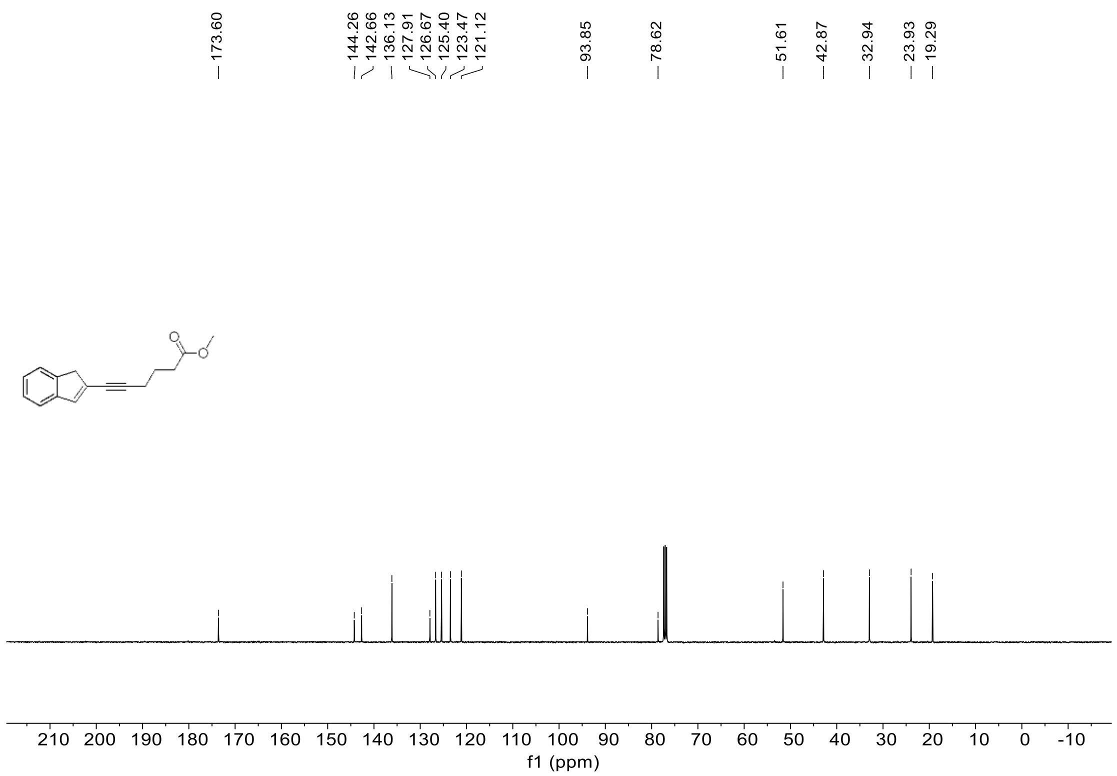

**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **S22**



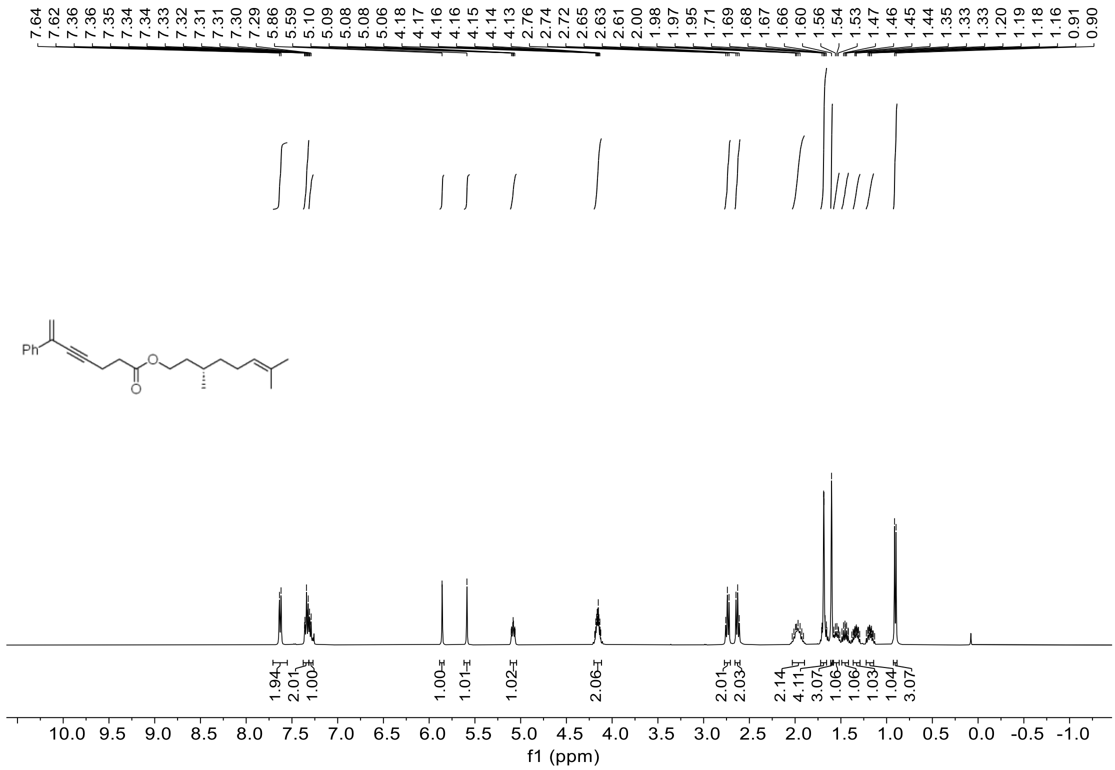

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S22**



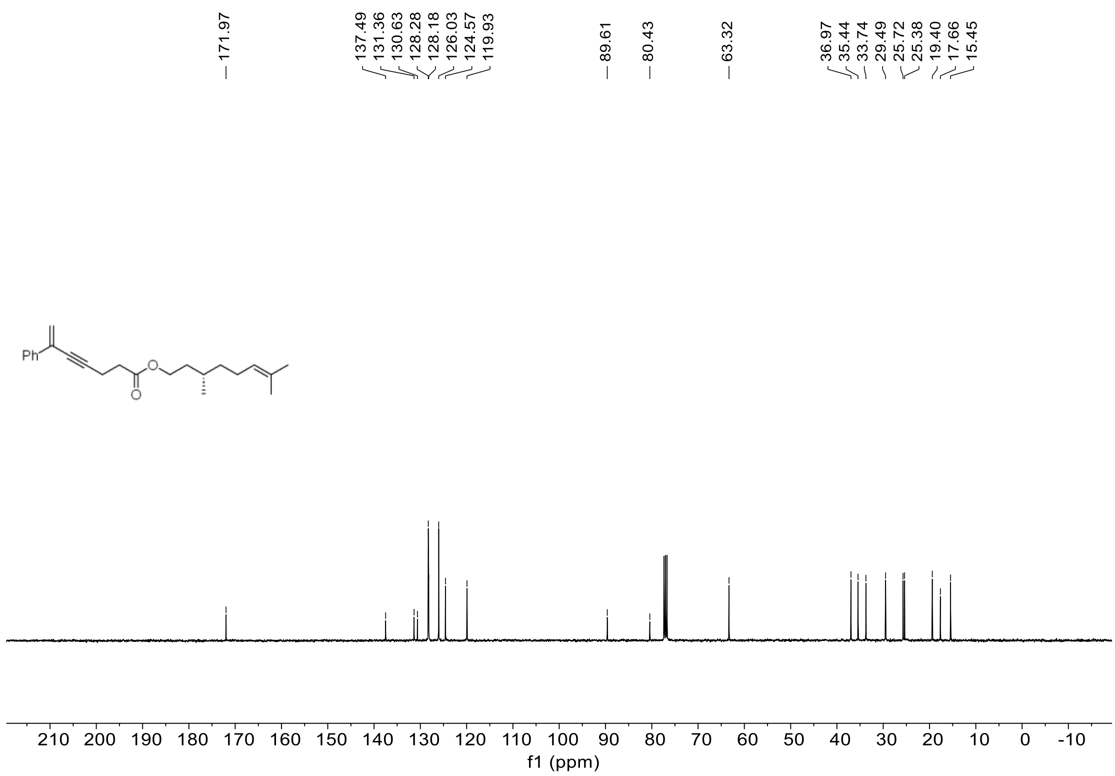
**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **S23**



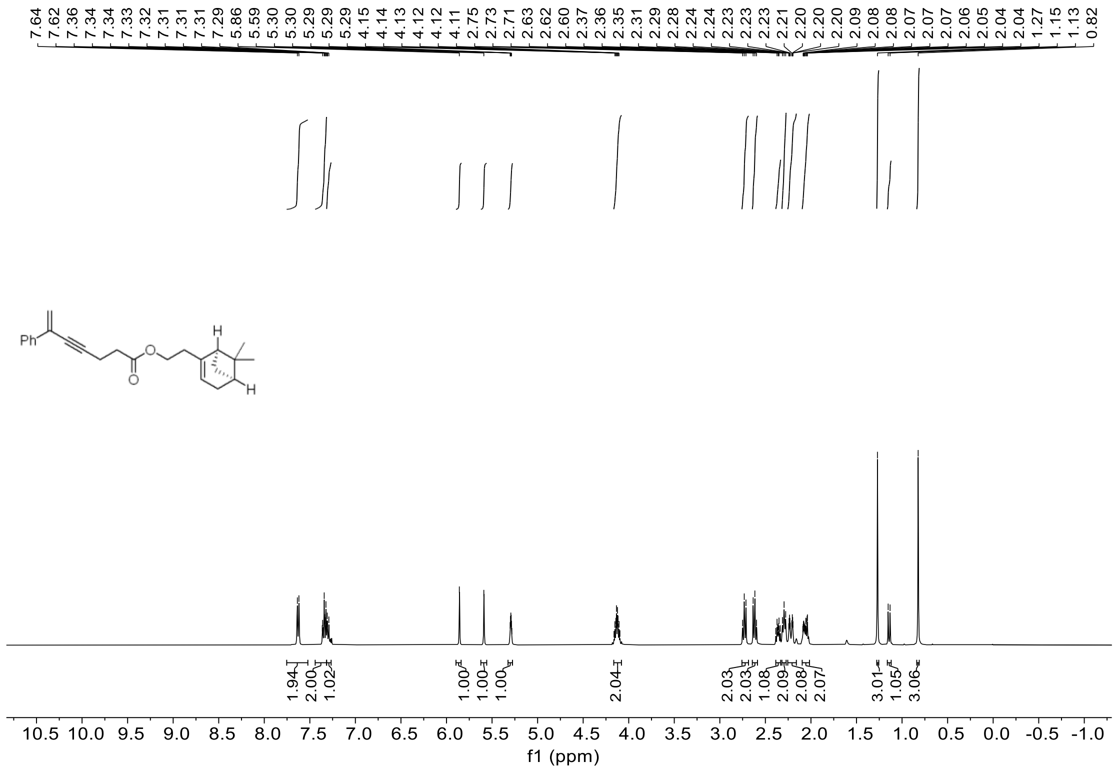
**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **S23**



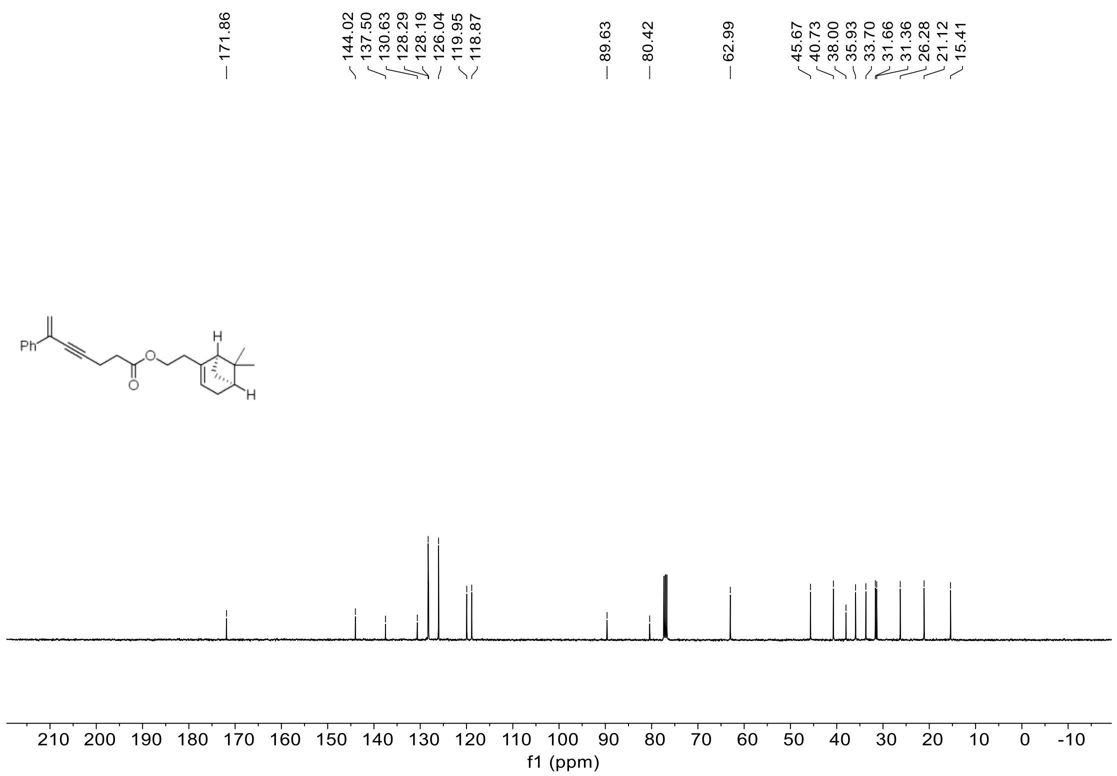
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S25**



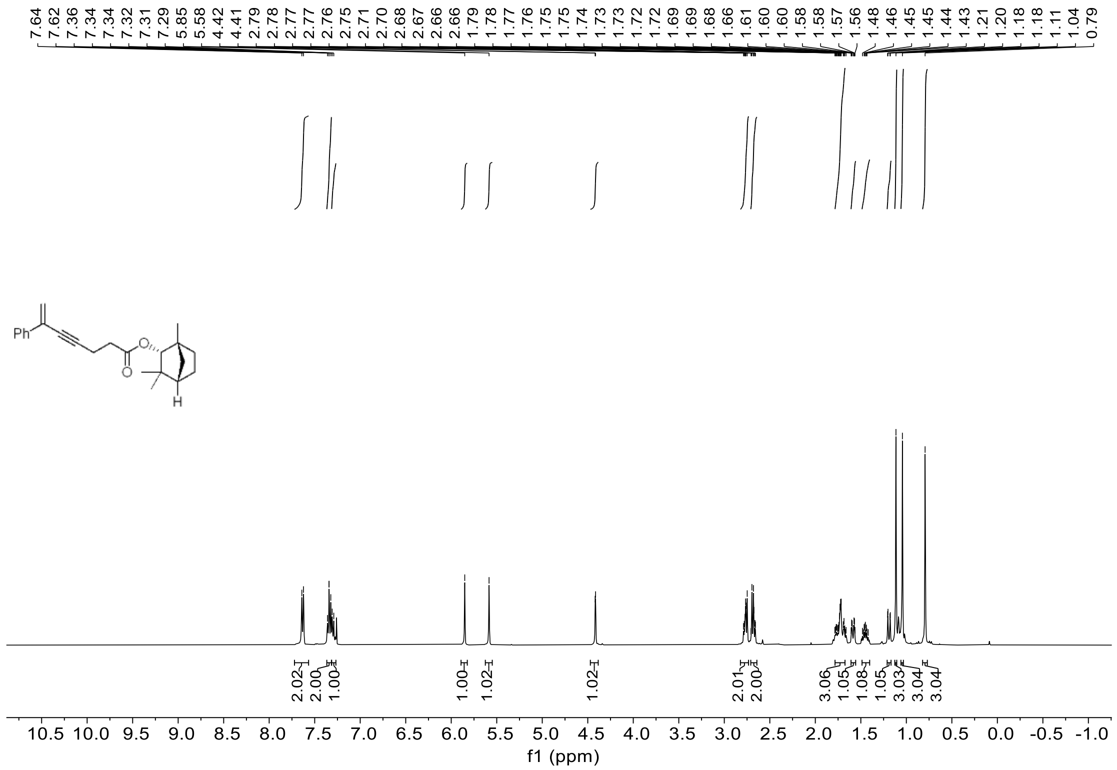
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S25**



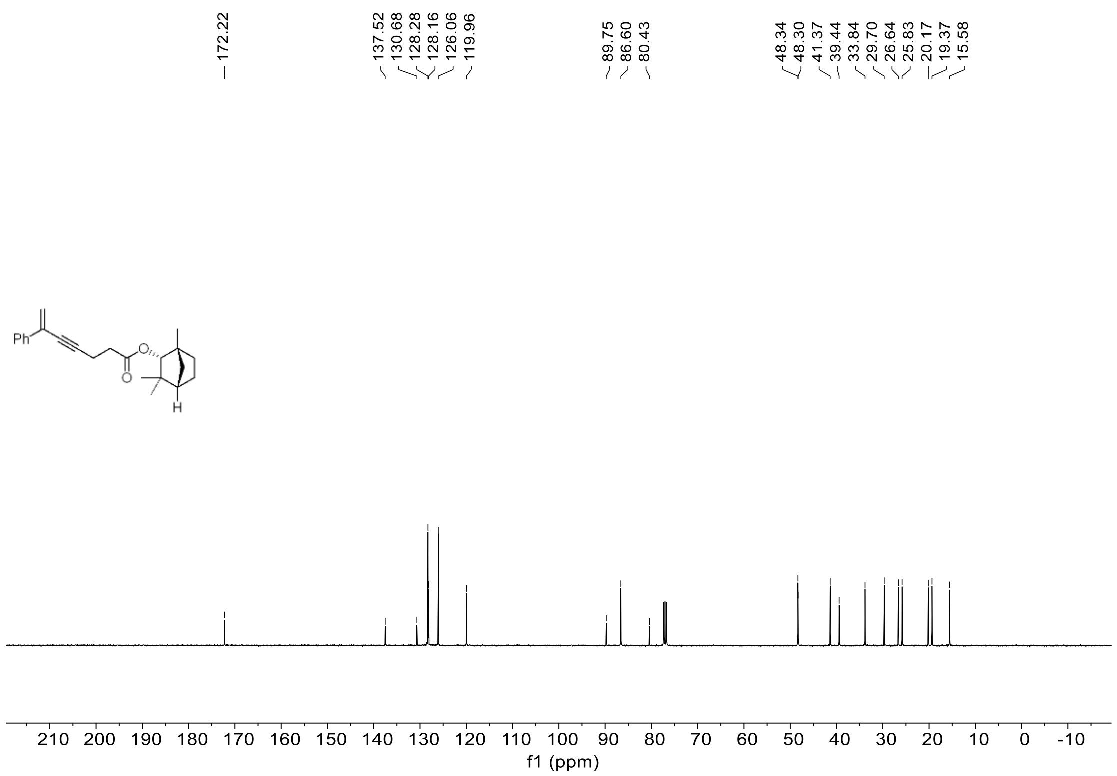

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **S26**



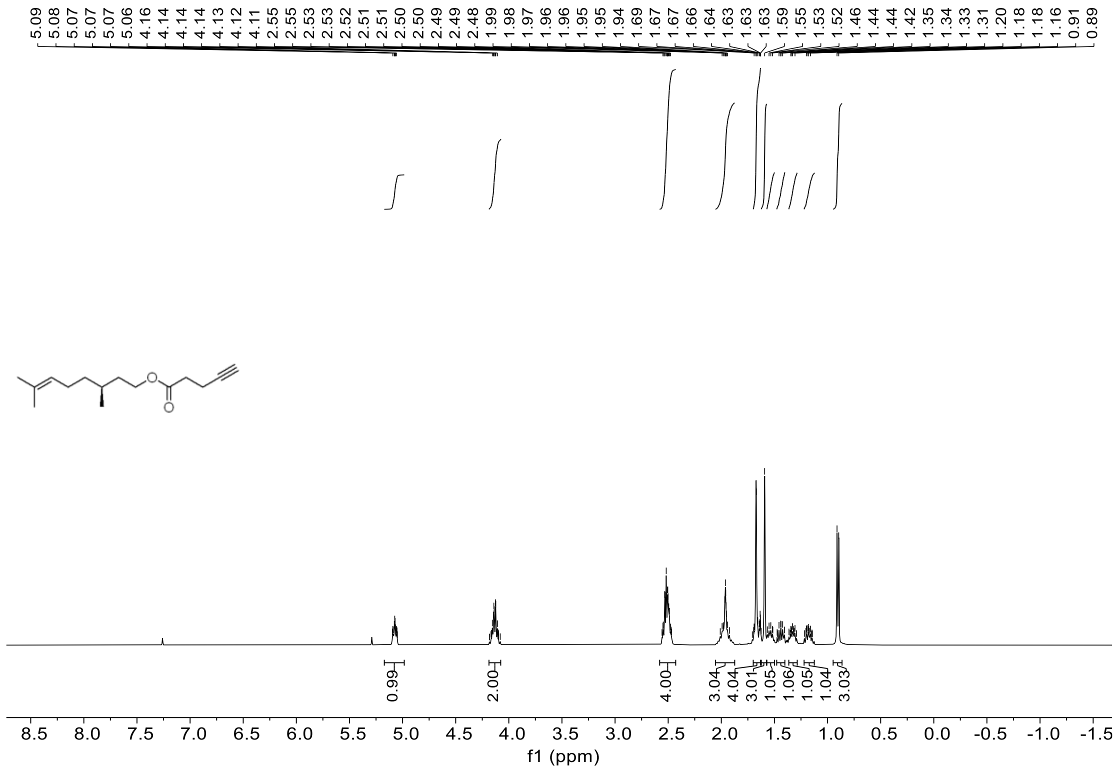

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **S26**



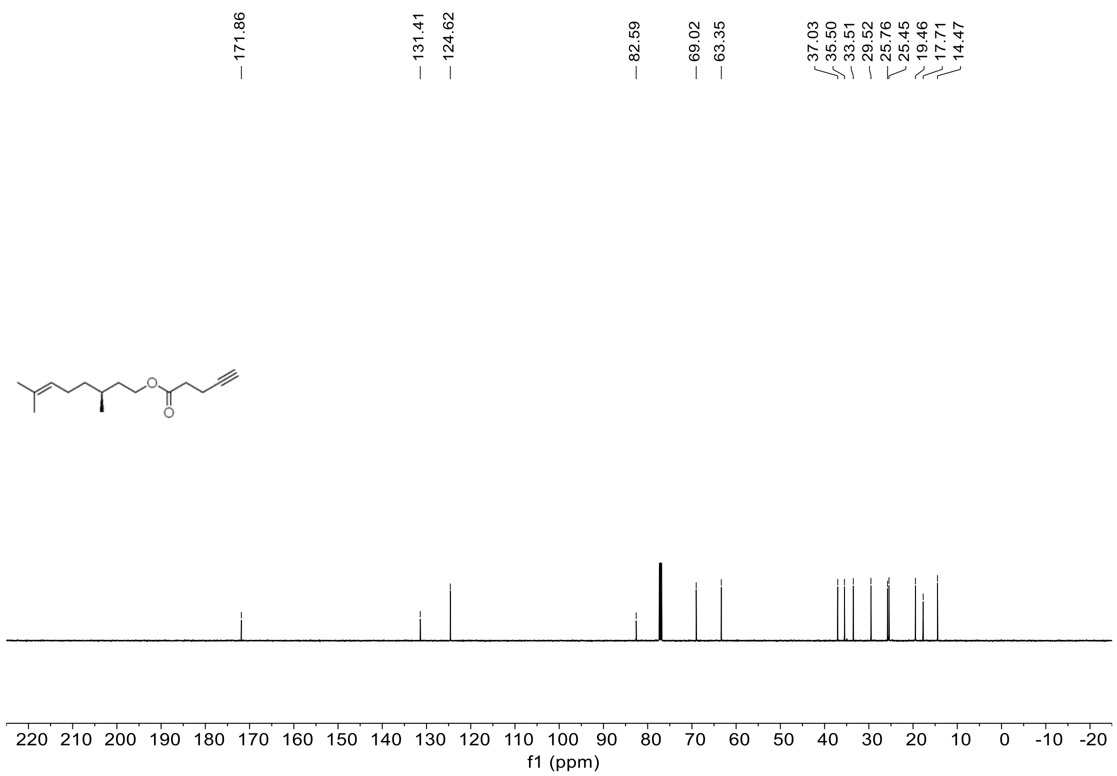

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S27**



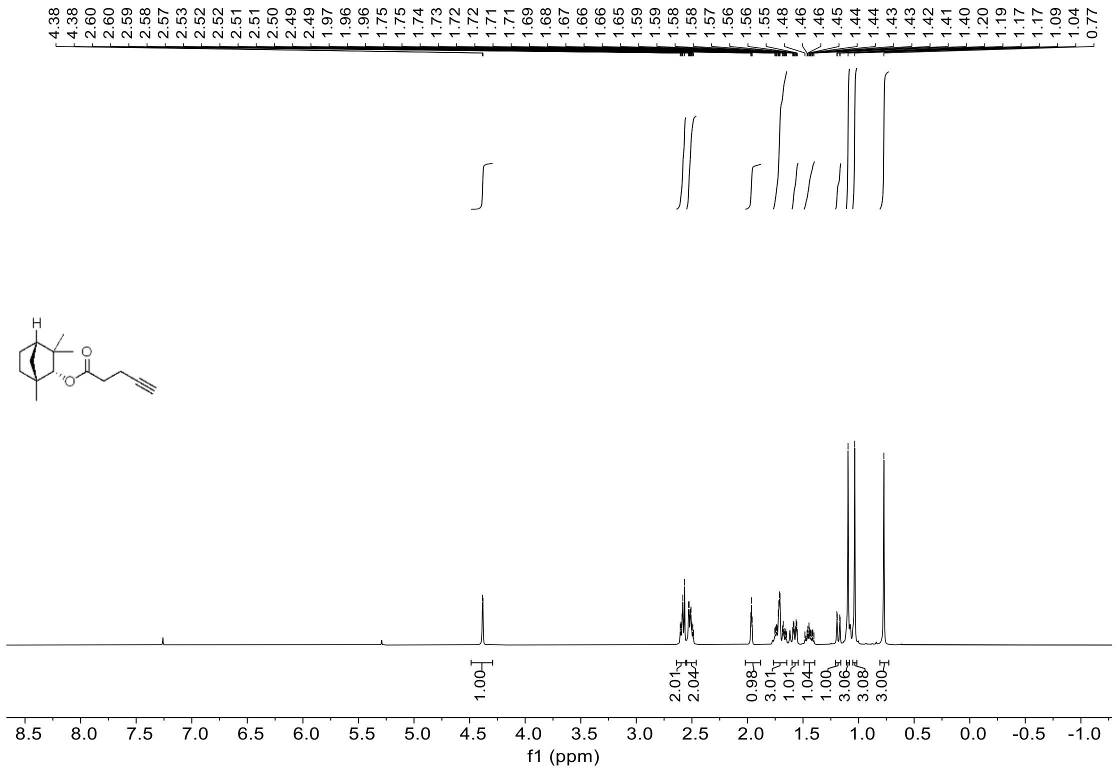

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S27**



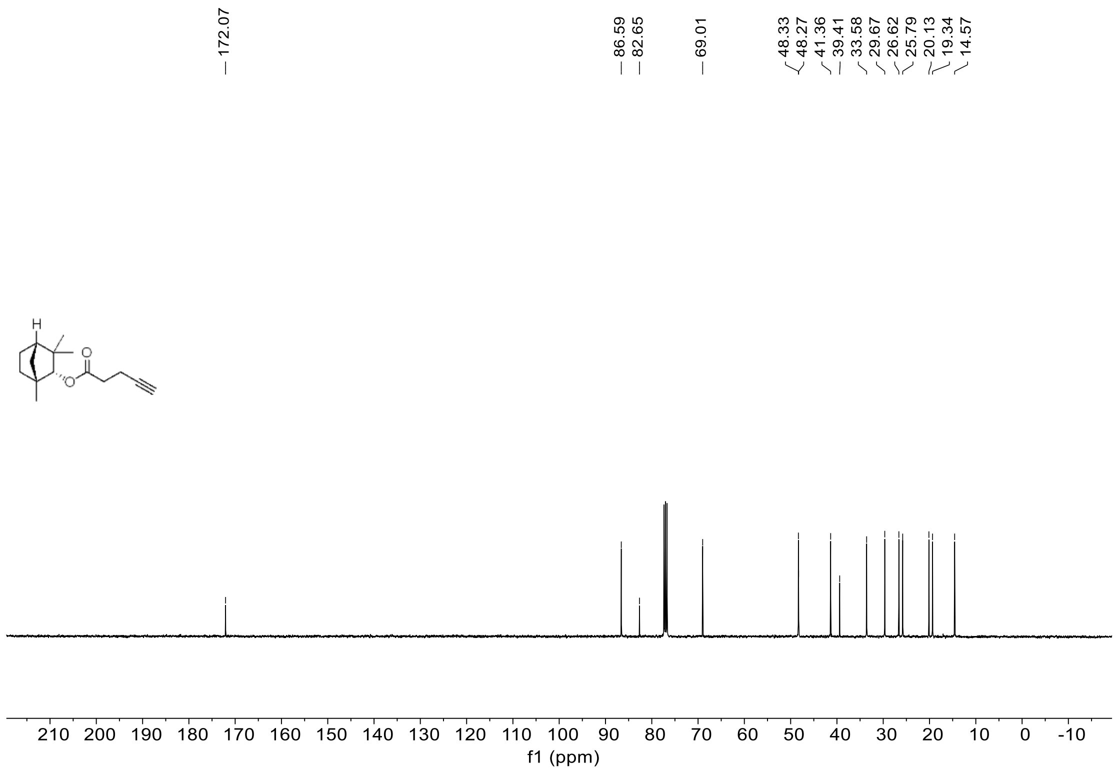

**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **S28**



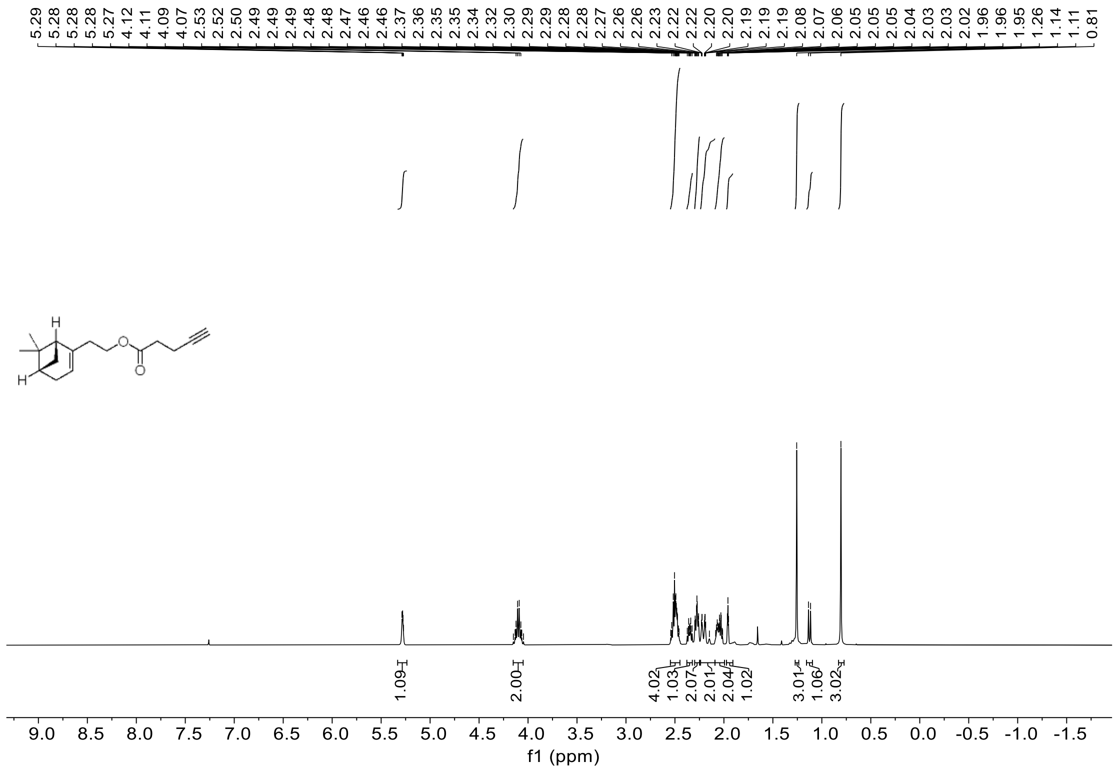

**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **S28**



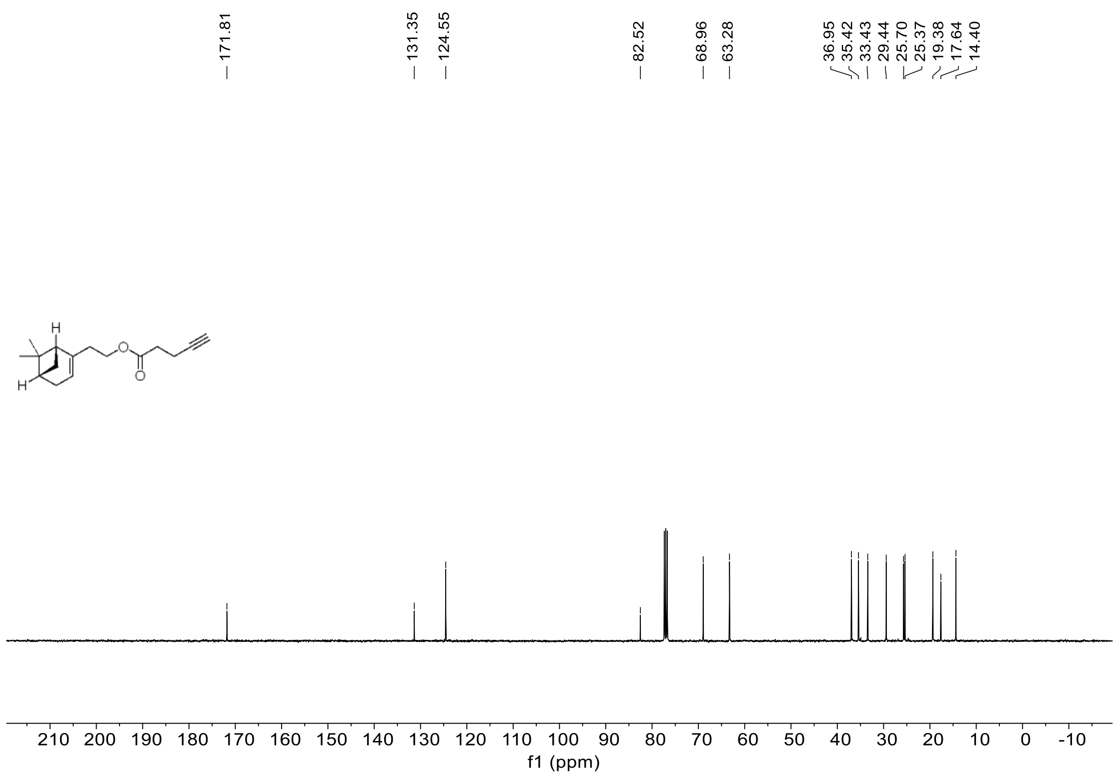

**¹H NMR** (400 MHz, CDCl$_3$) spectra of **S29**



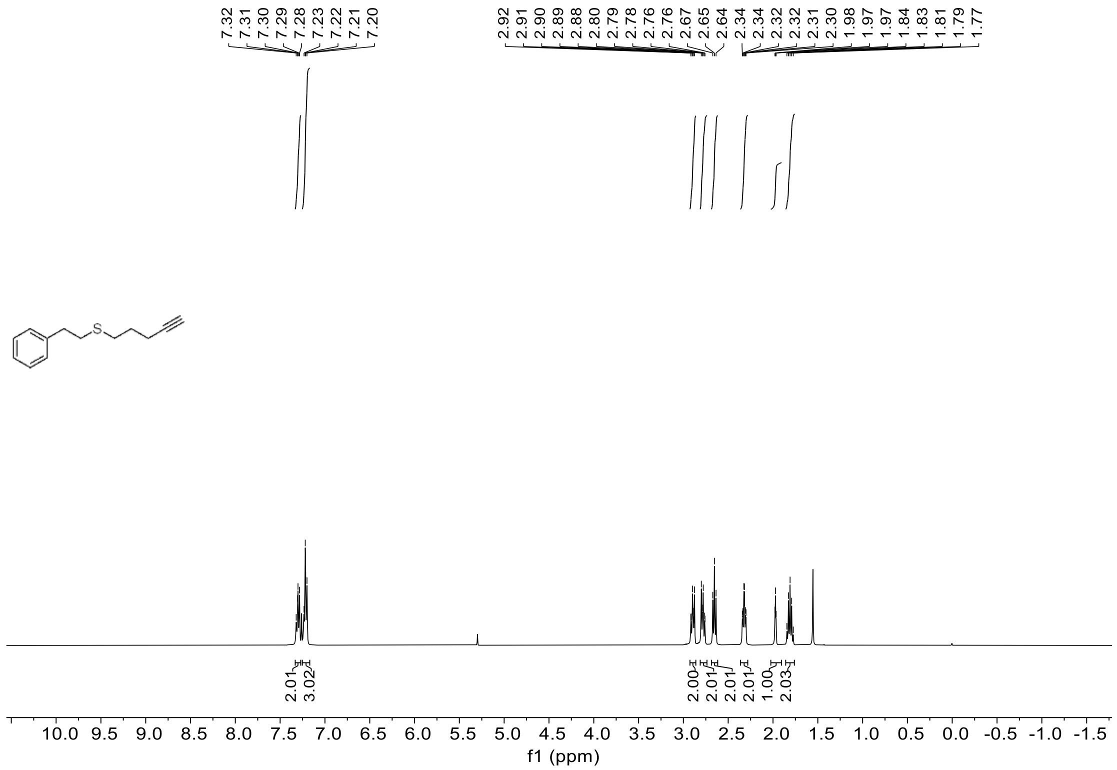

**¹³C NMR** (101 MHz, CDCl$_3$) spectra of **S29**



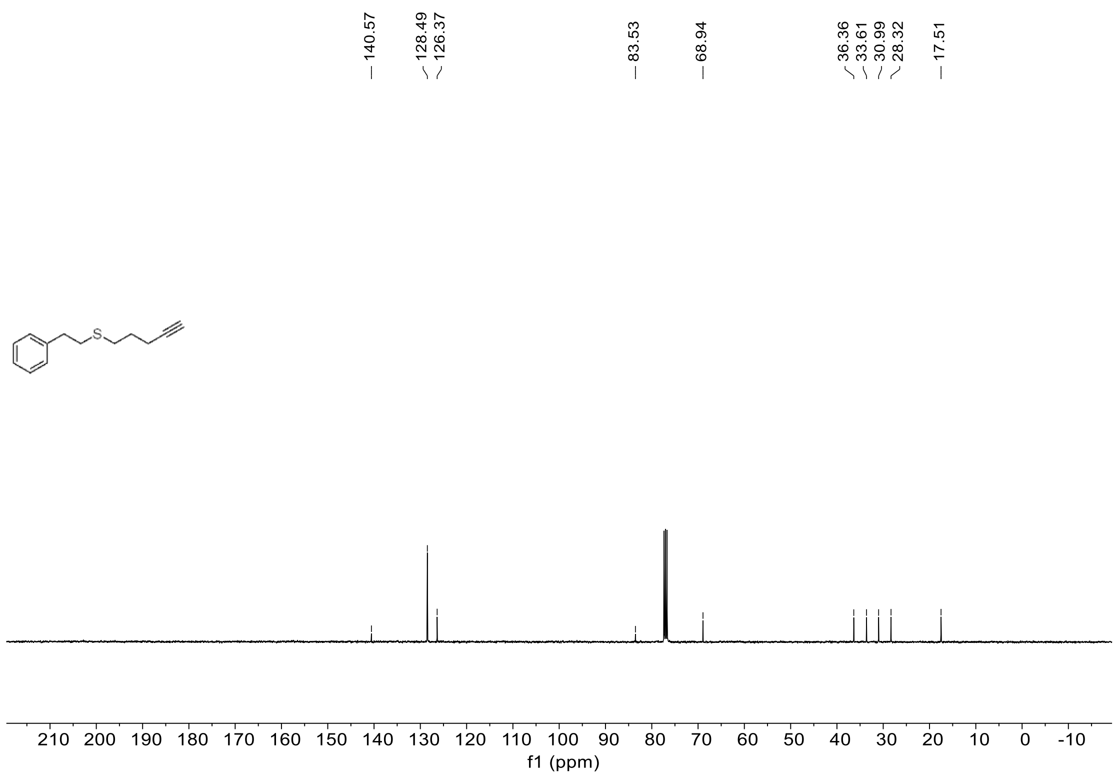

**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **S30**



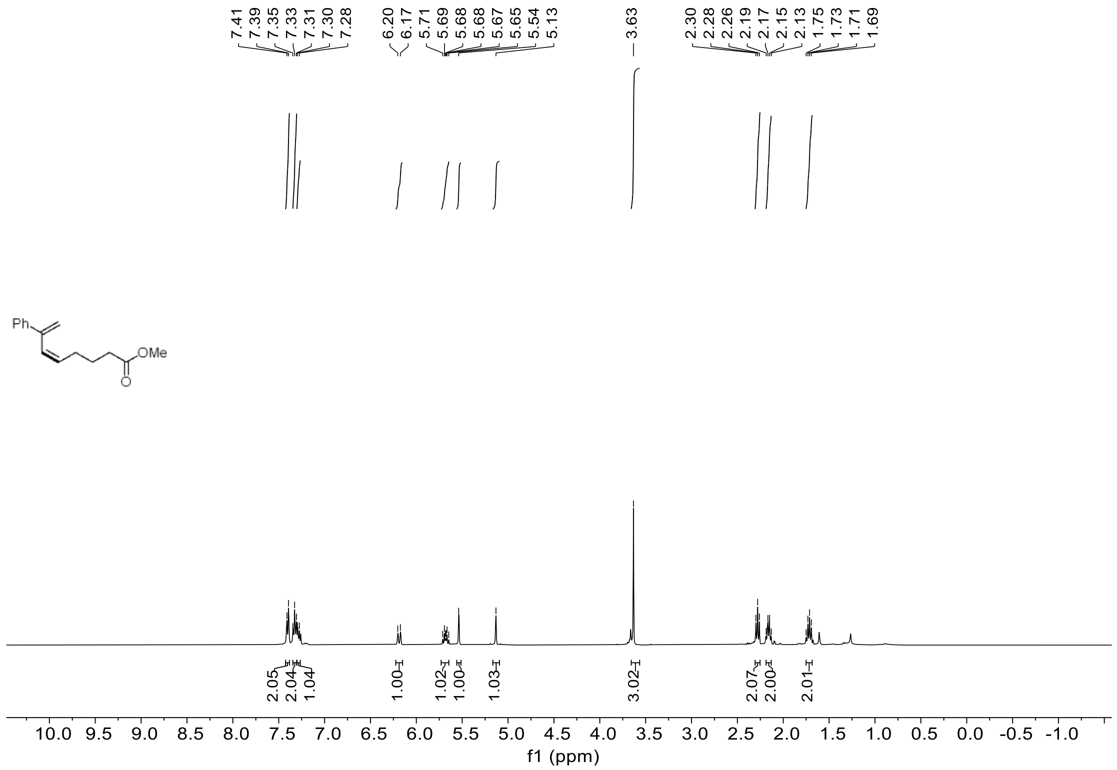

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S30**



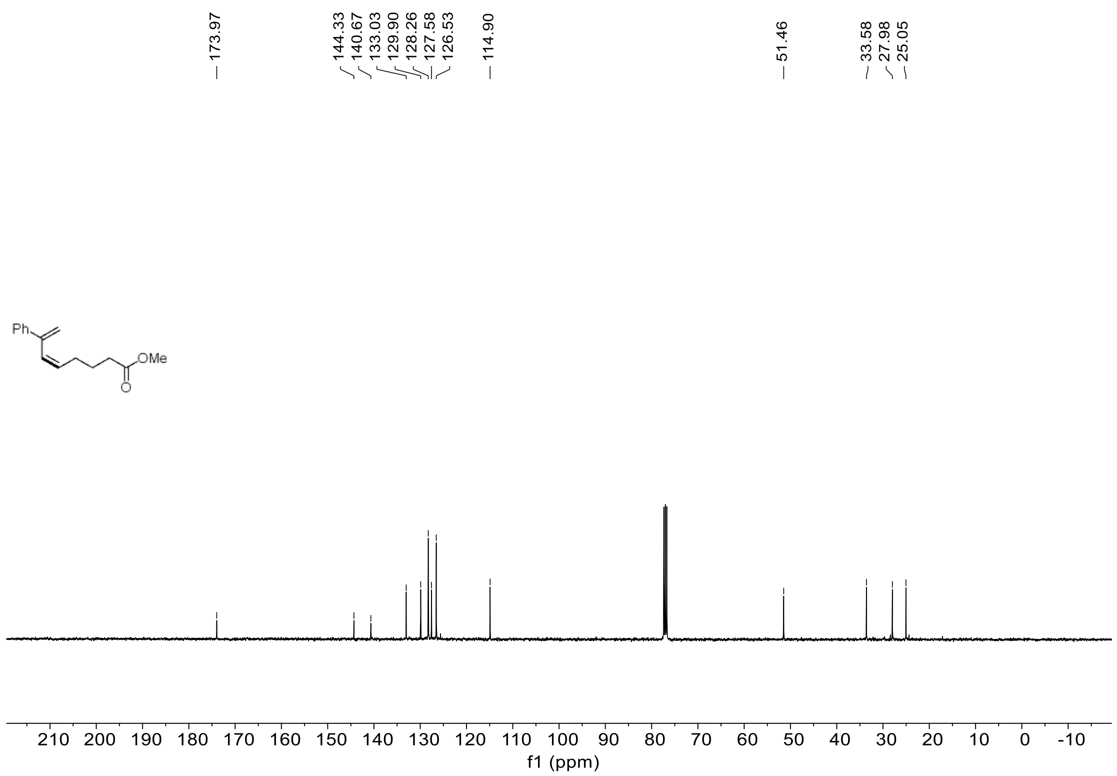
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **S31**



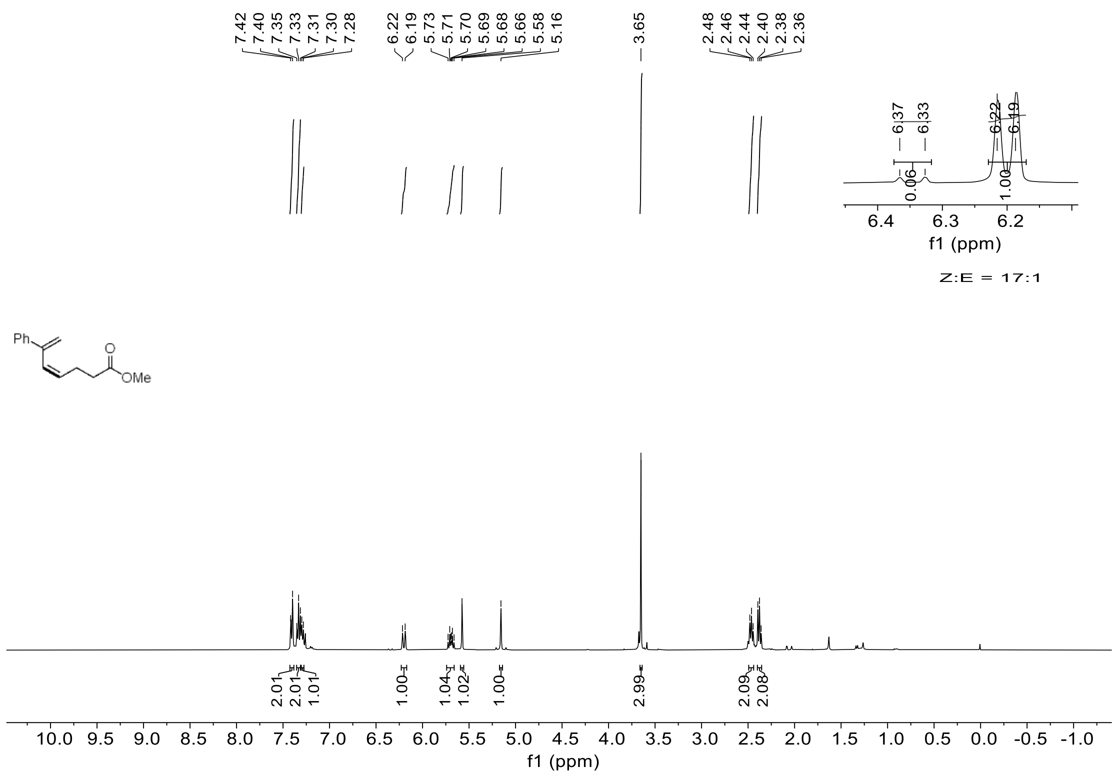
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **S31**



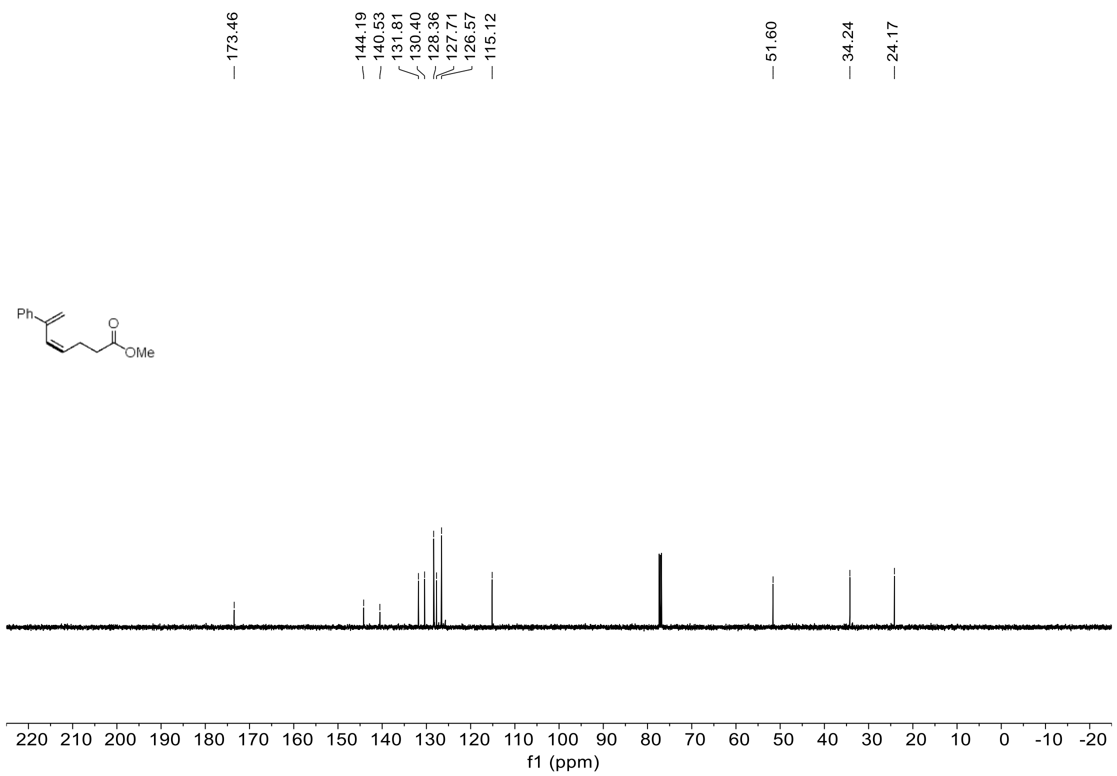

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **2a**



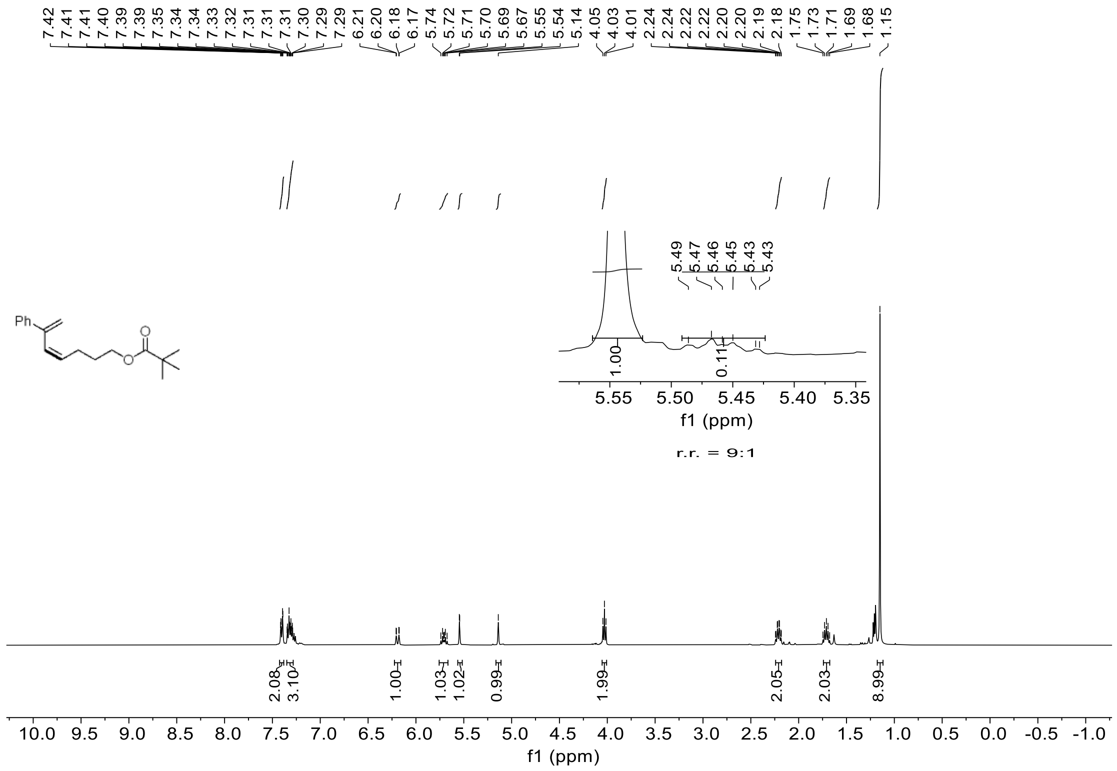

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **2a**



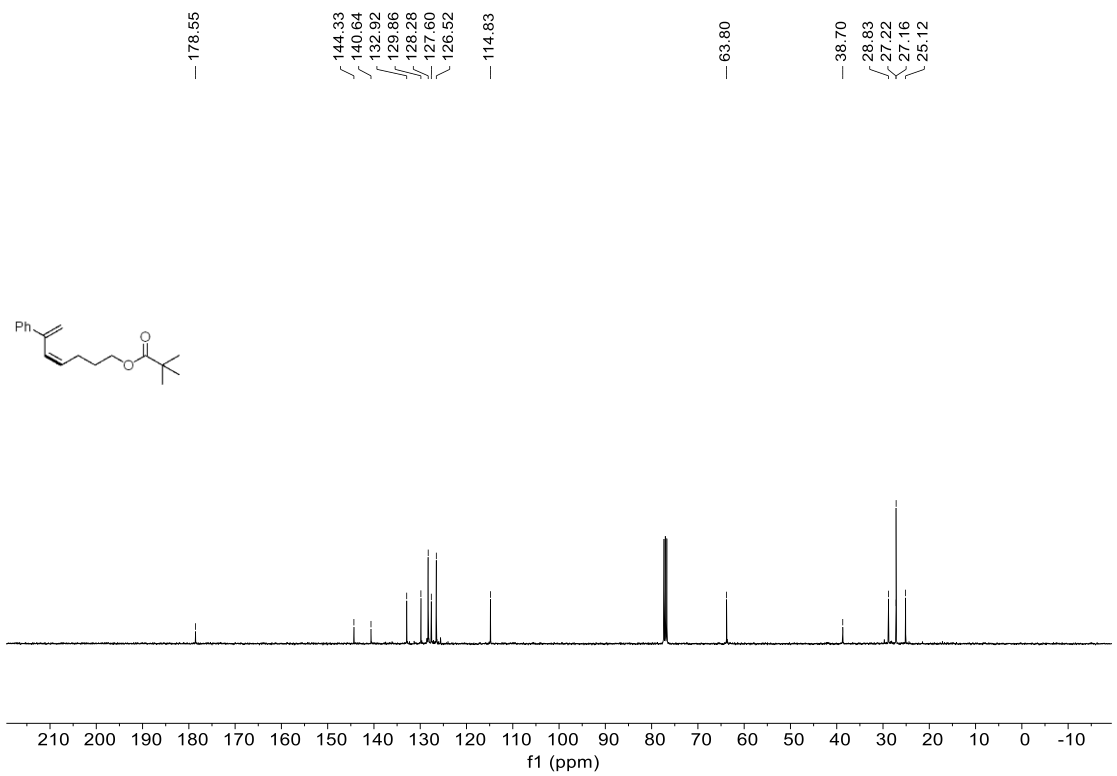

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **3a**



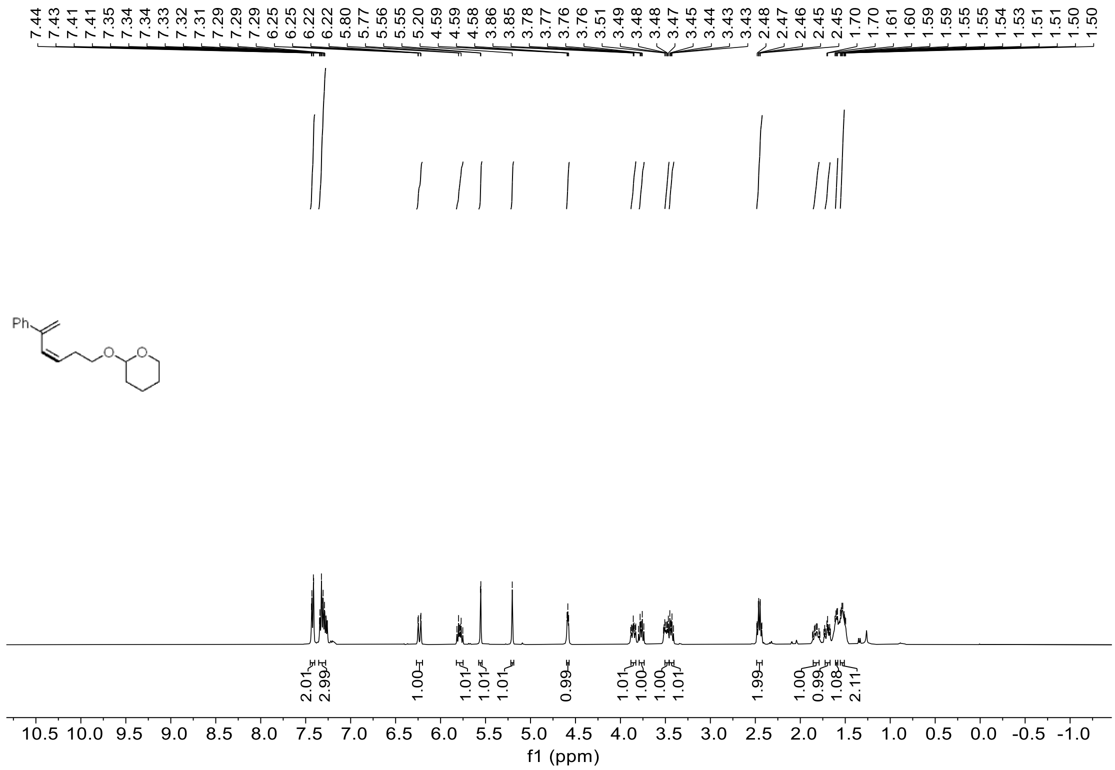

**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **3a**



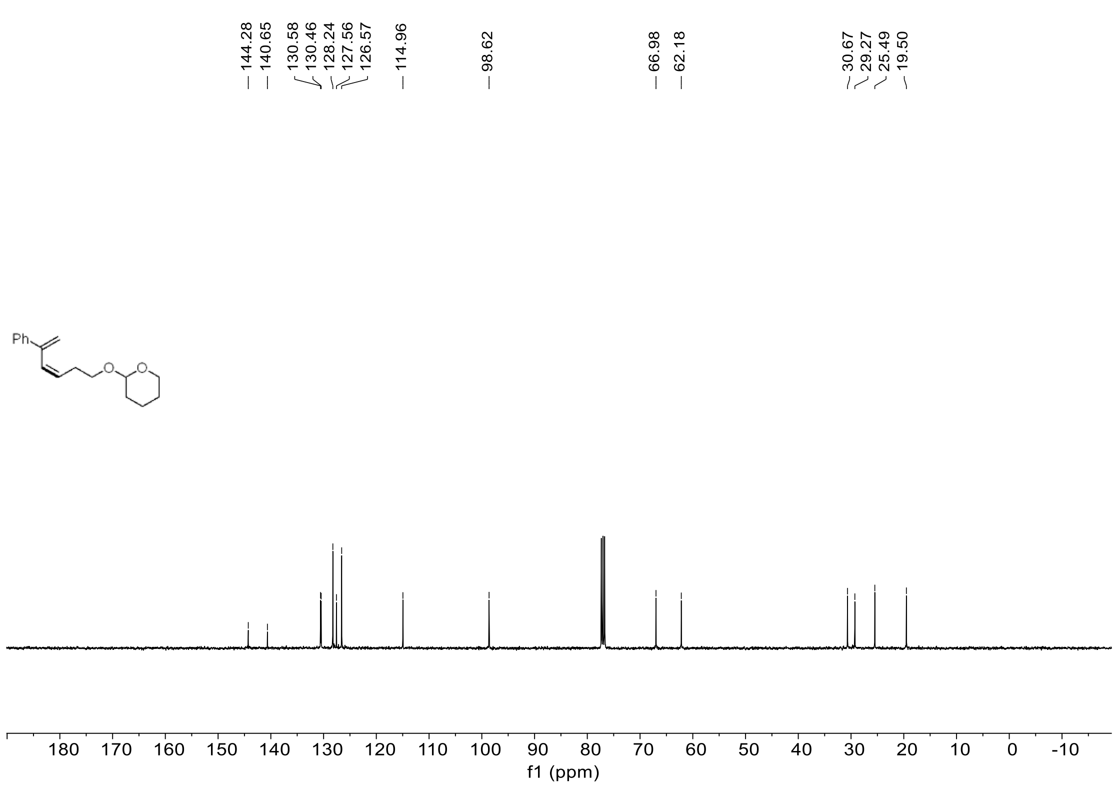
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **4a**



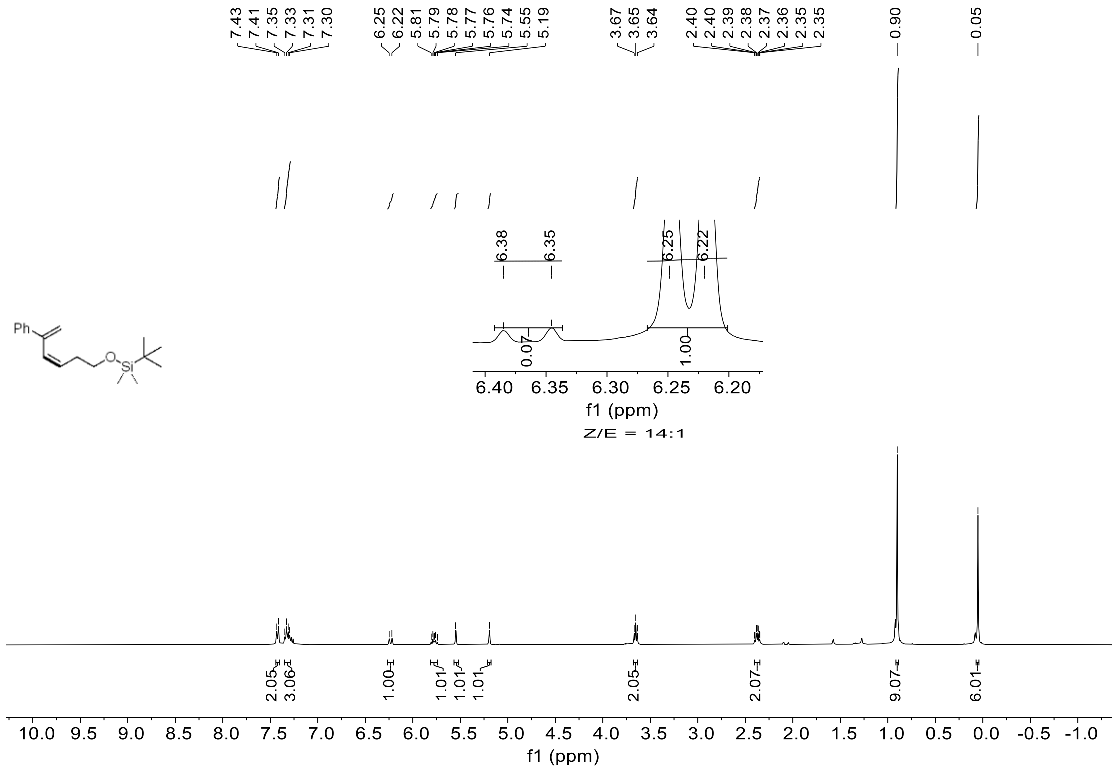
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **4a**



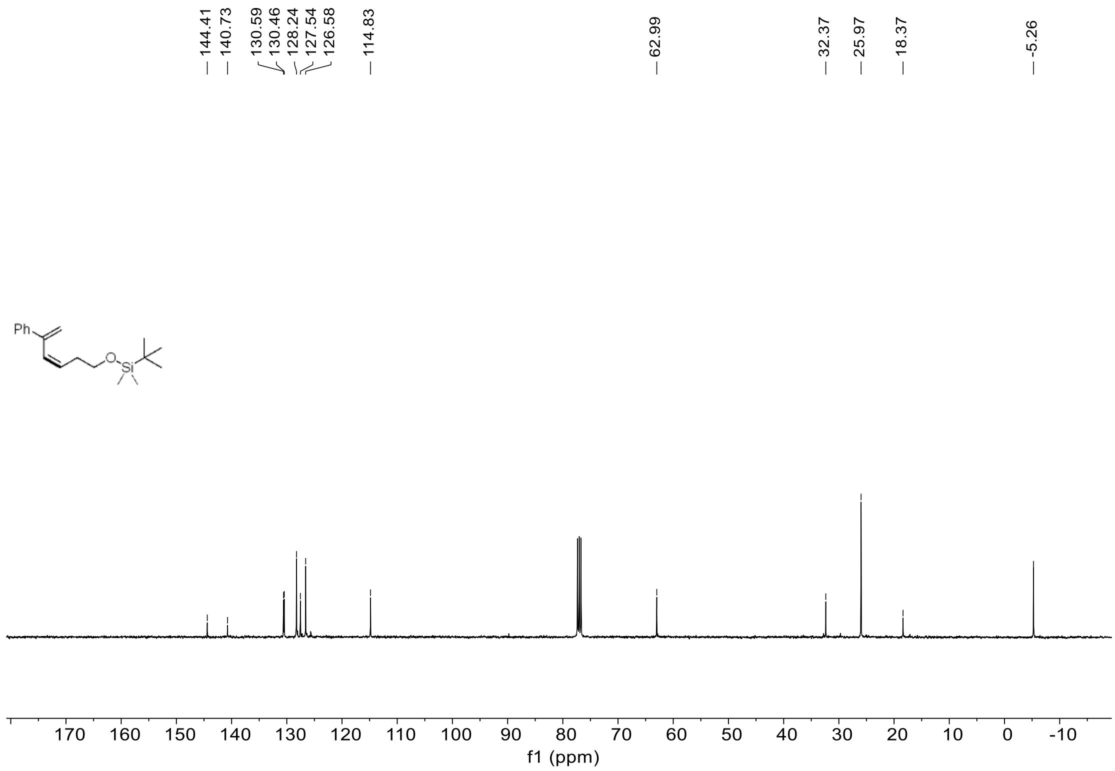

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **5a**



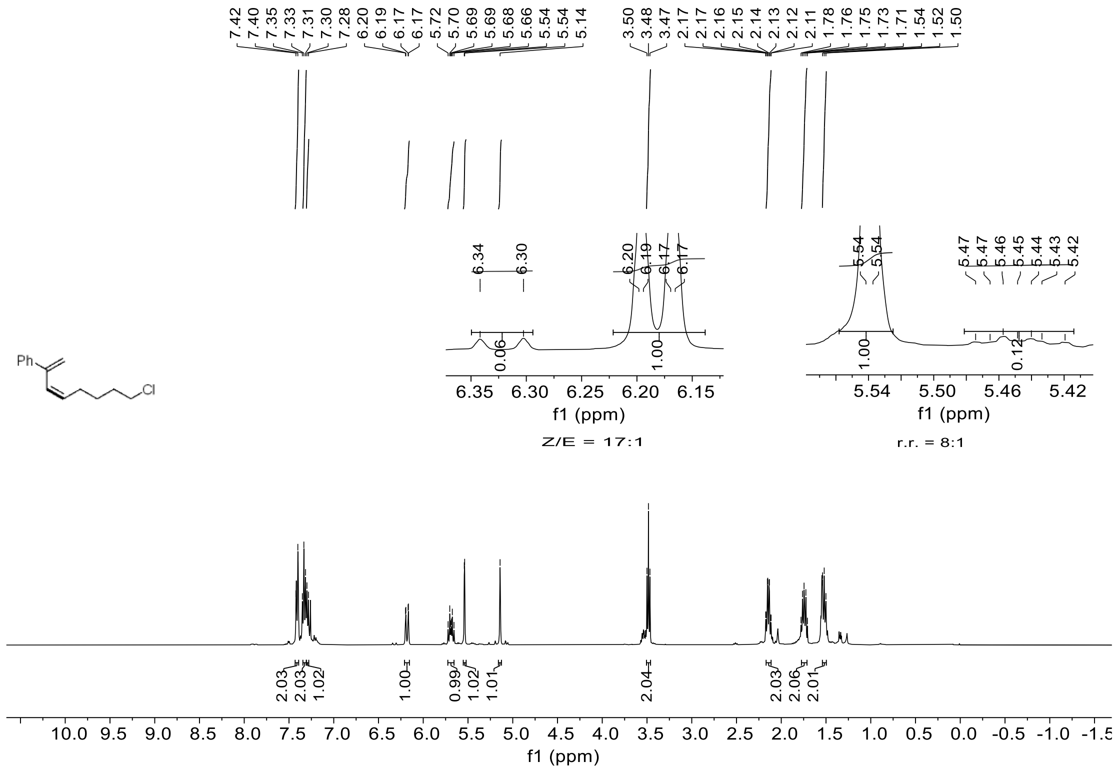

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **5a**



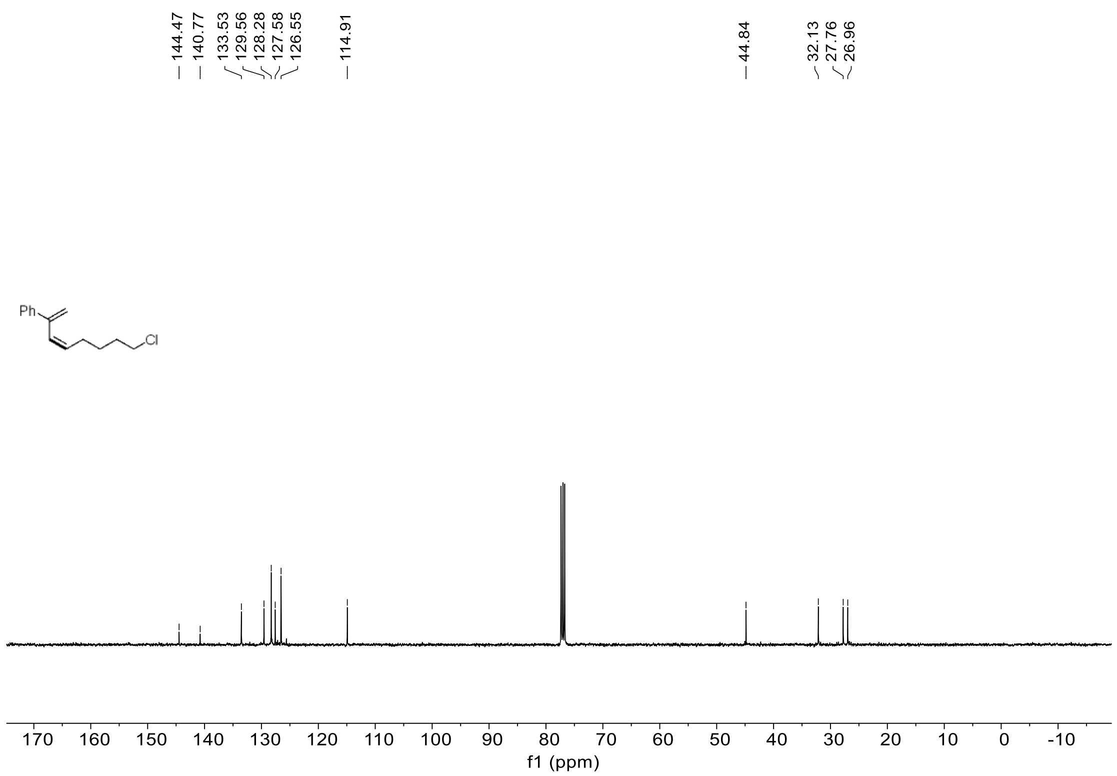

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **6a**



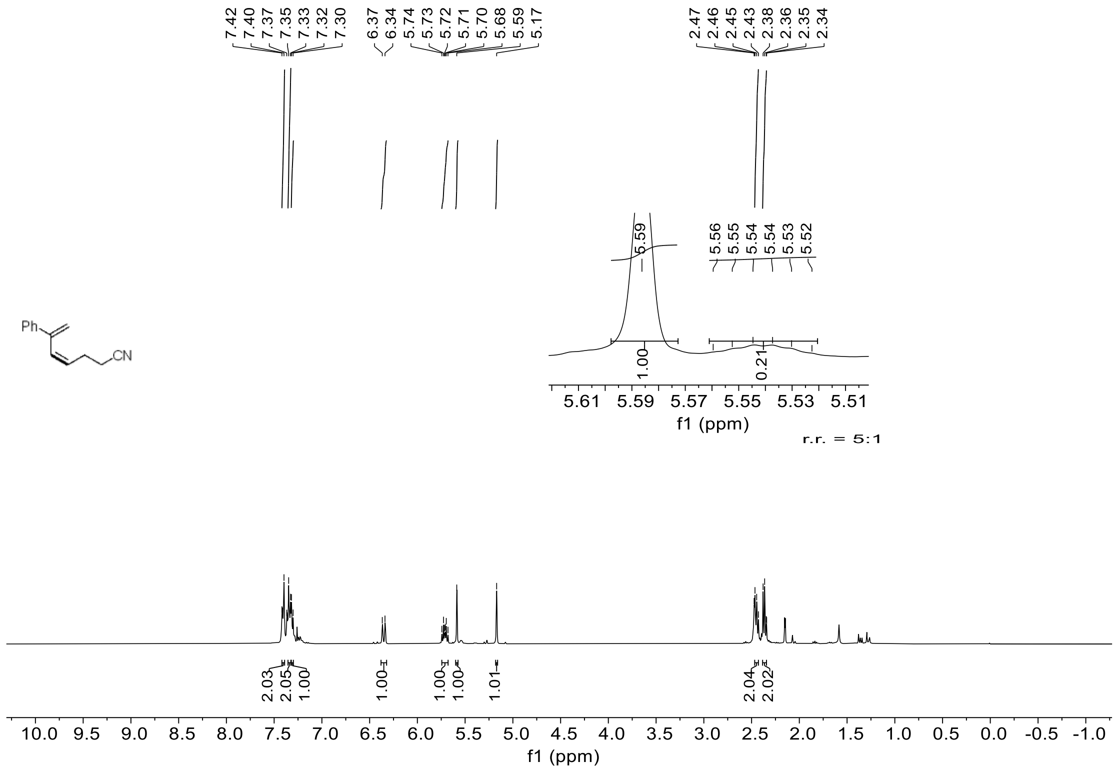

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **6a**



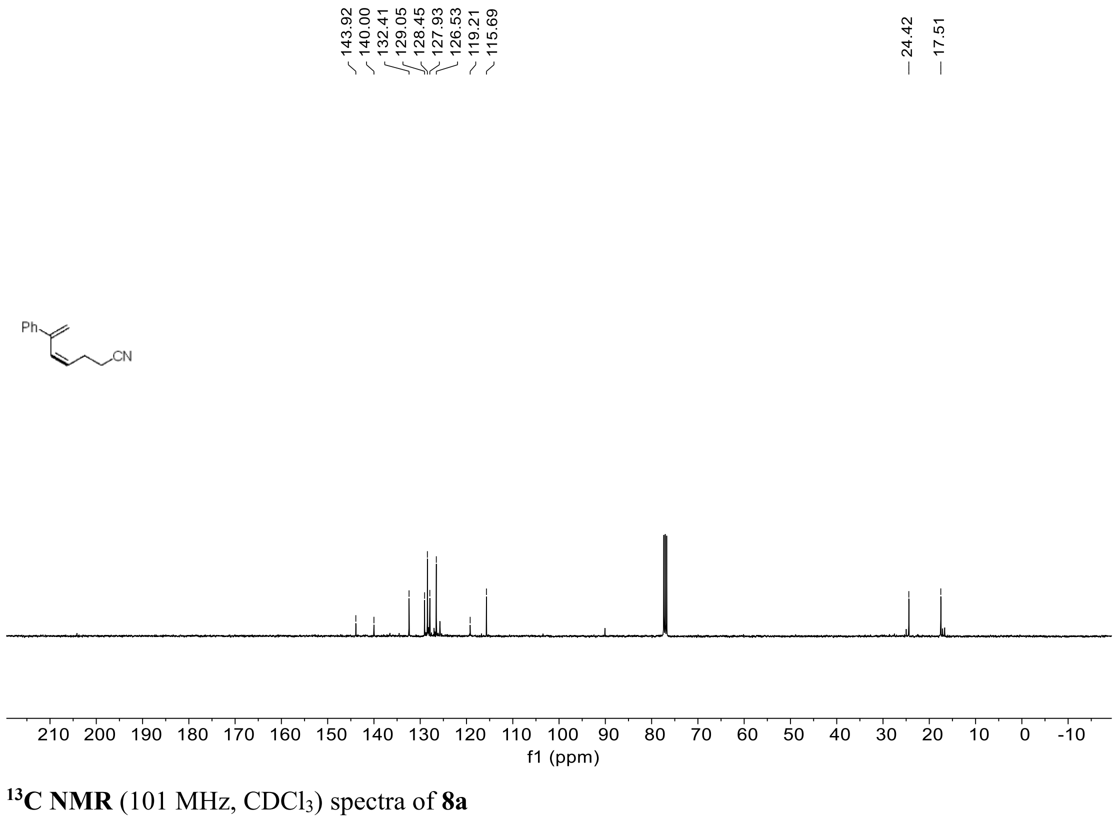
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **7a**



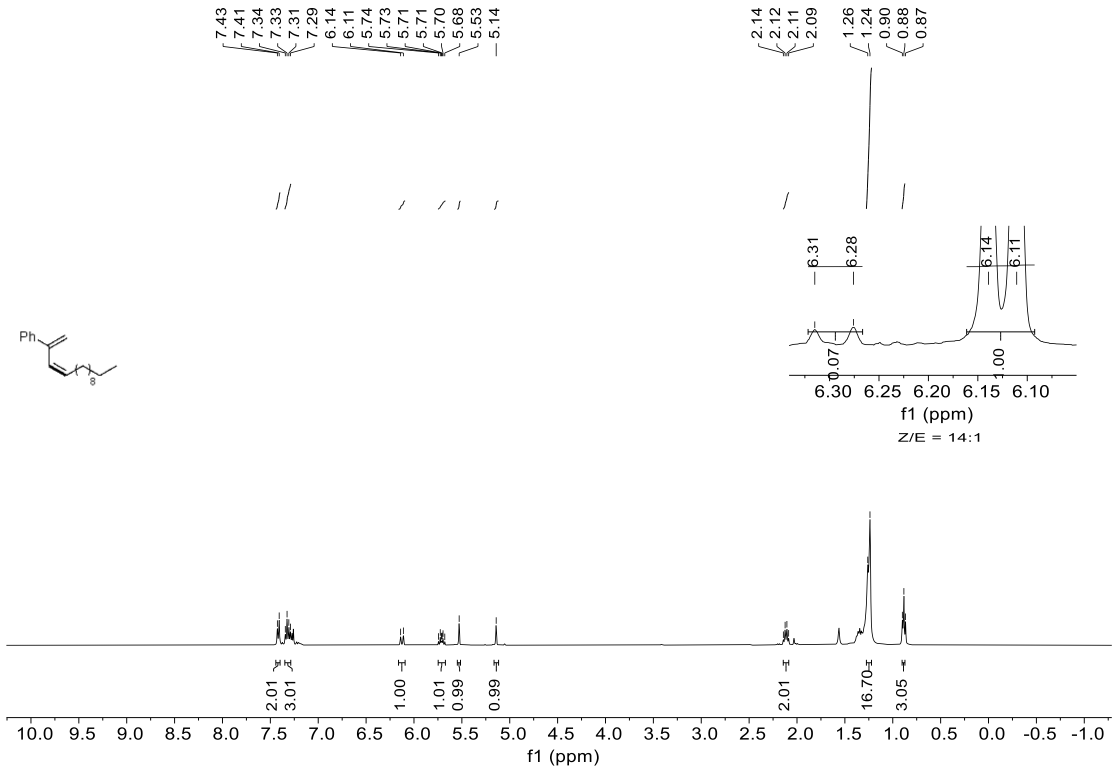
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **7a**



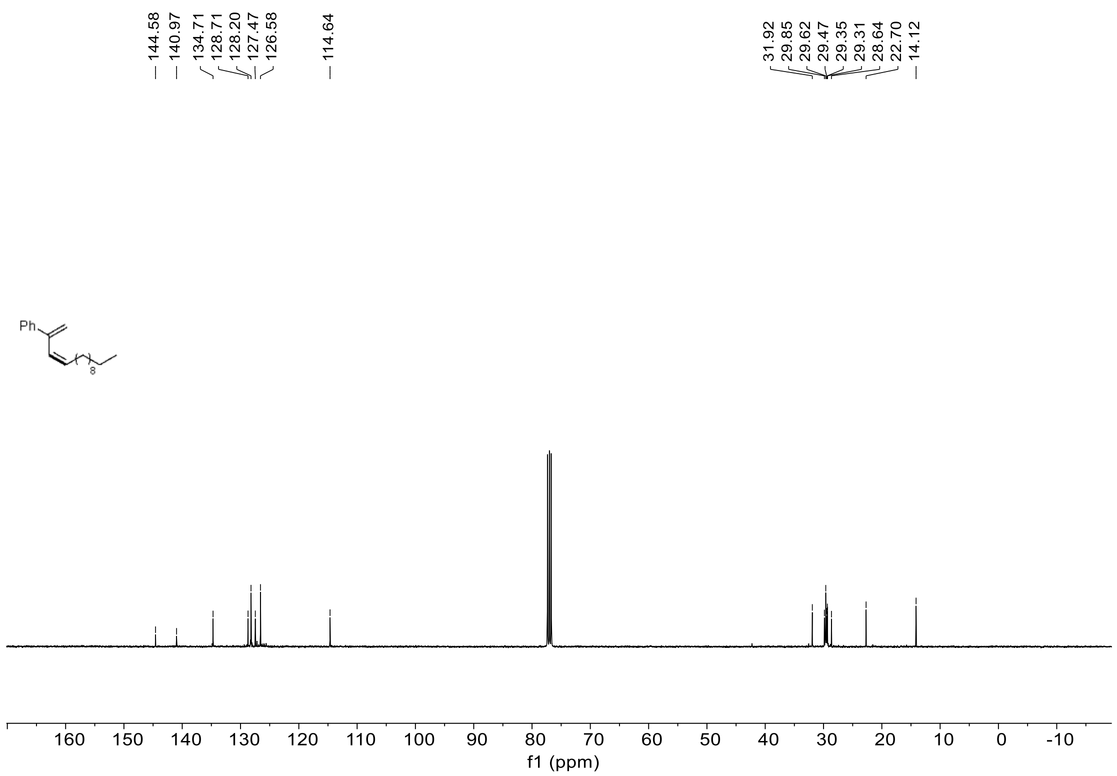

**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **8a**



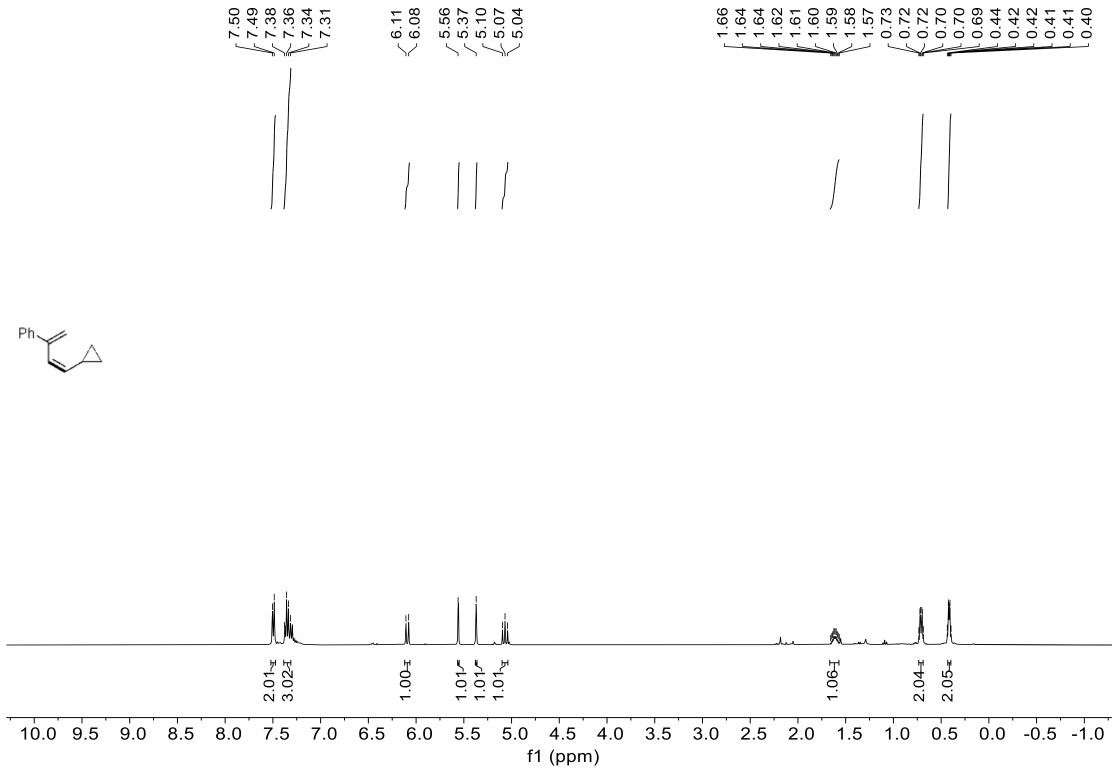

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **8a**



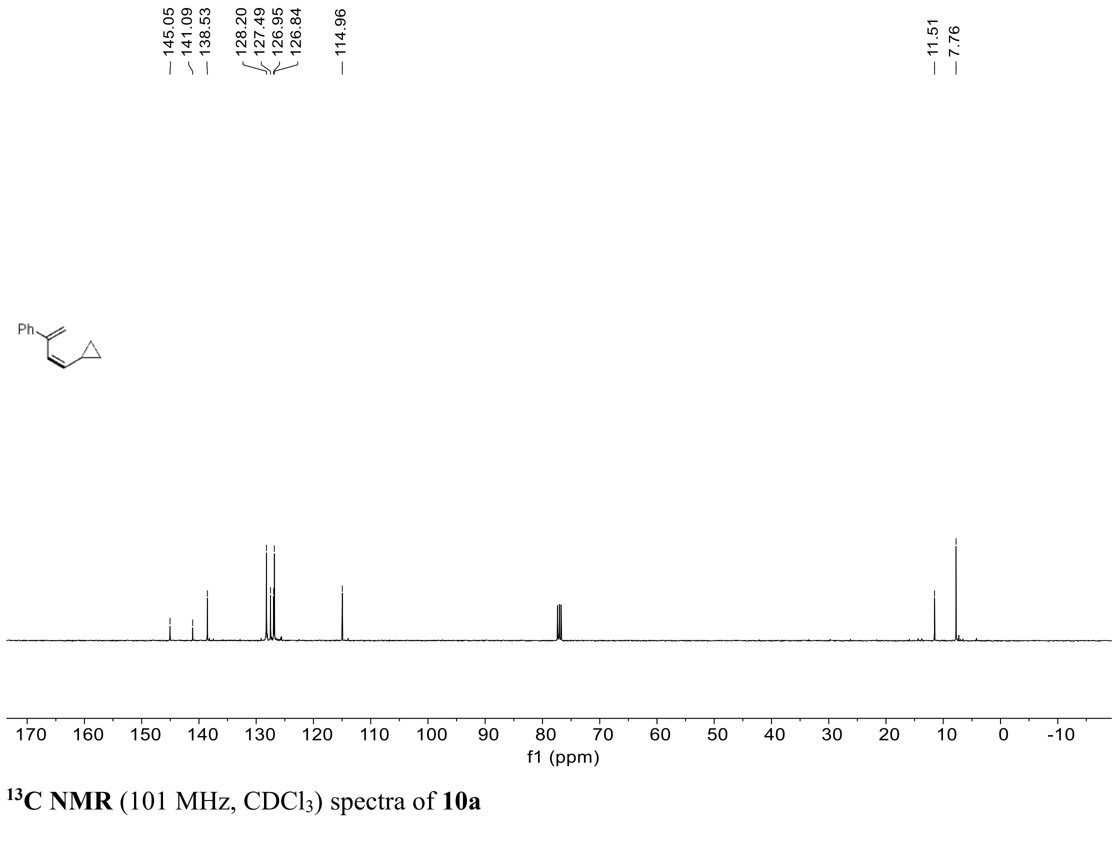

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **9a**



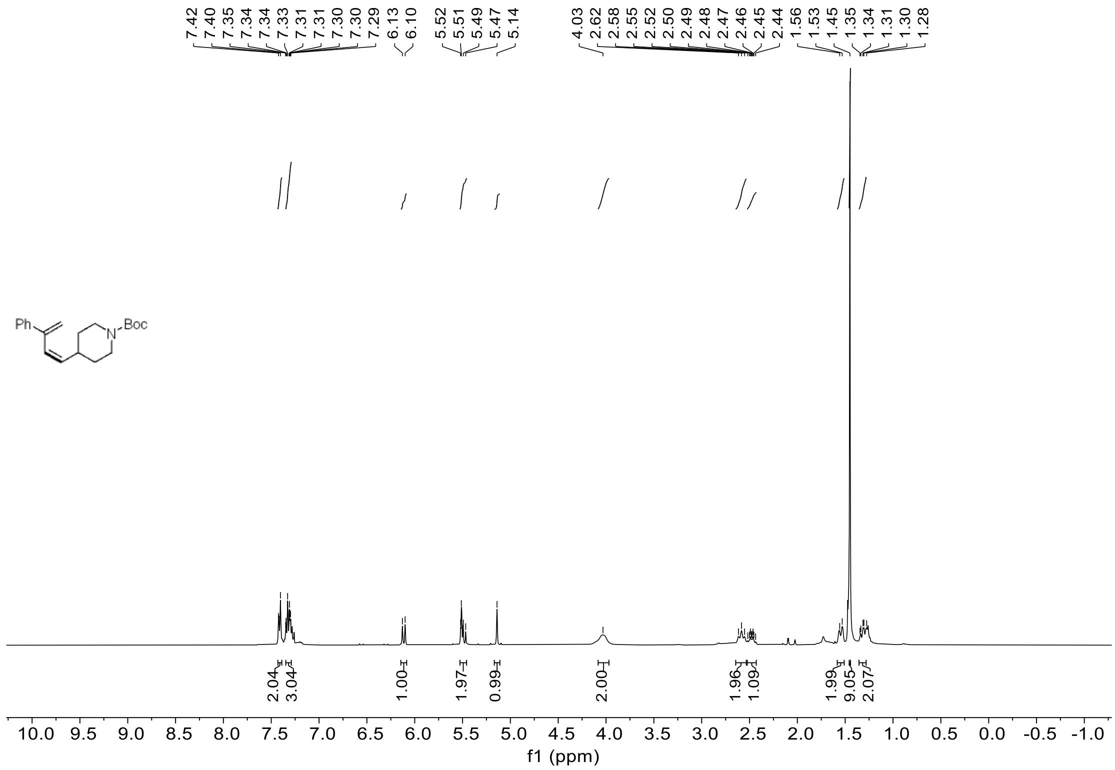

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **9a**



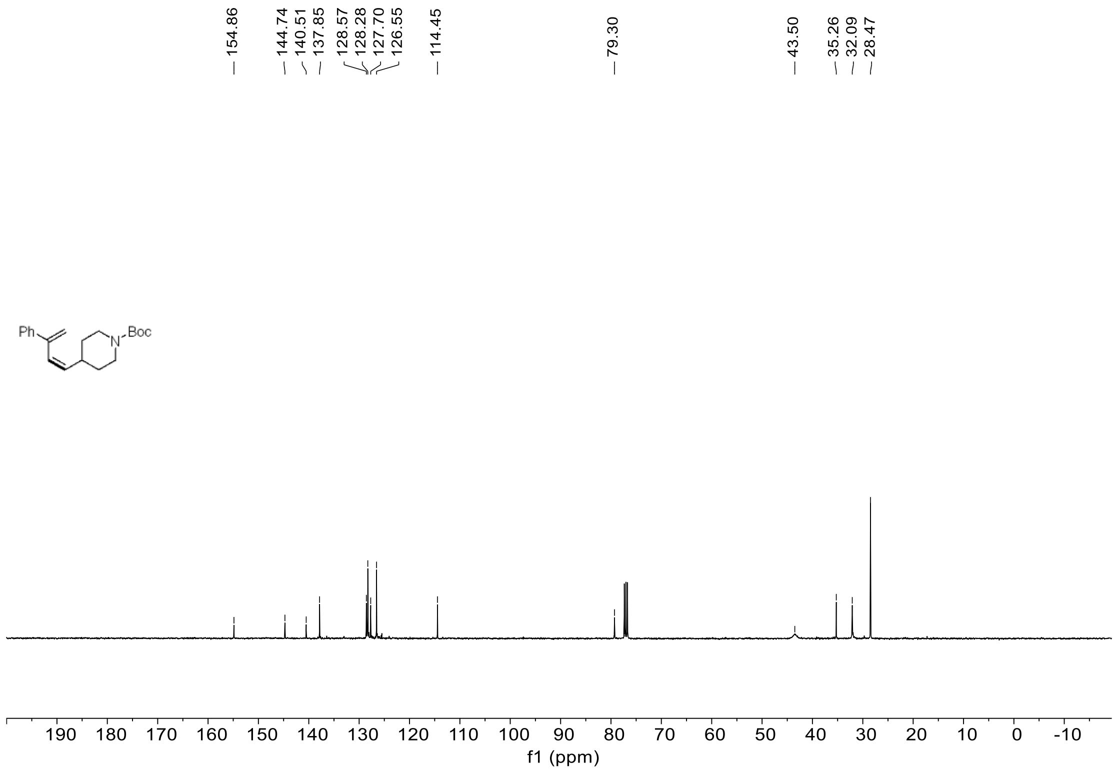

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **10a**



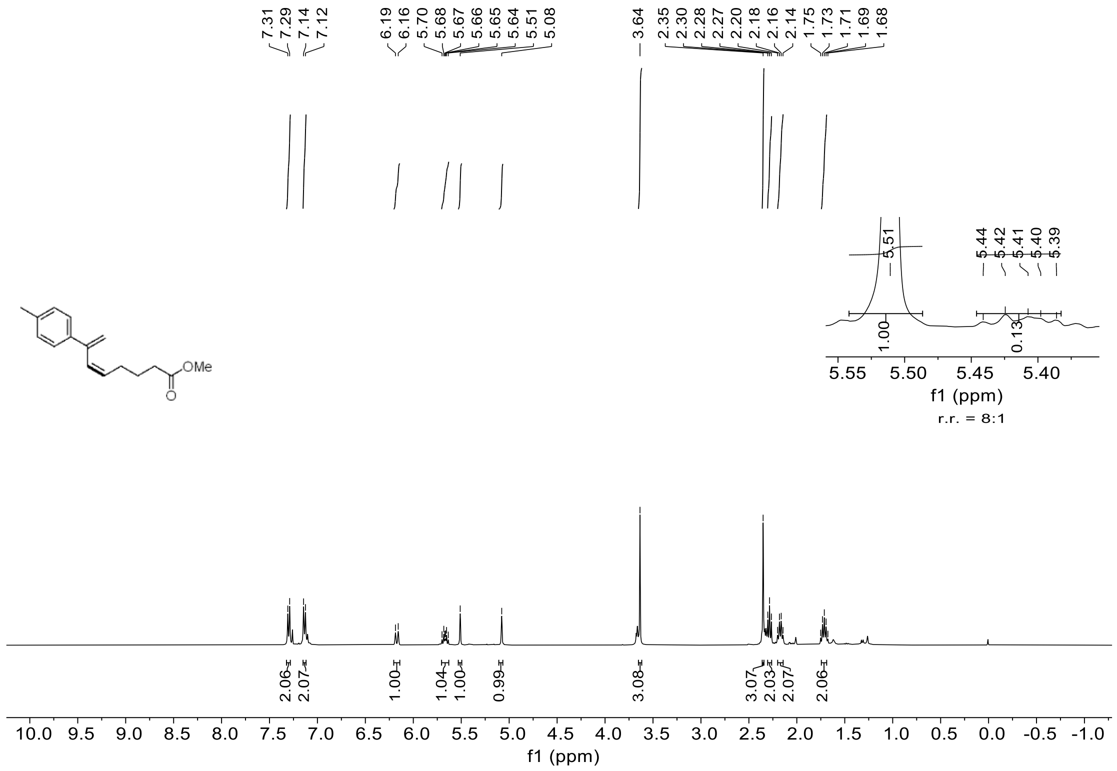

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **10a**



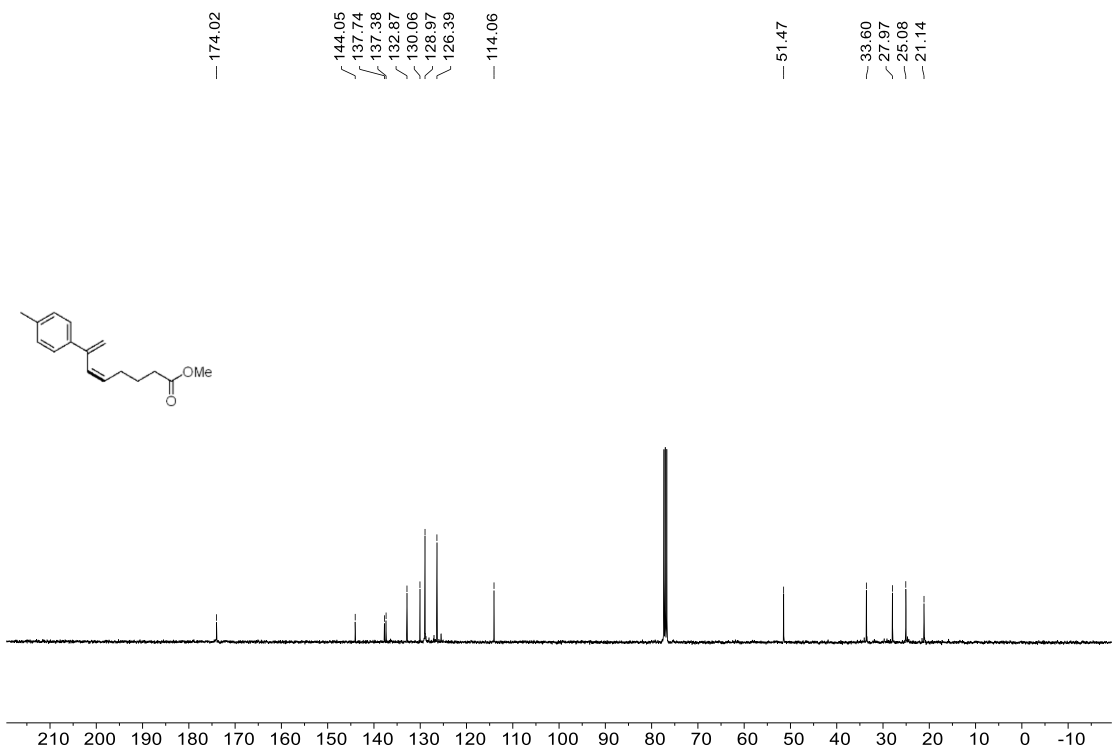

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **11a**



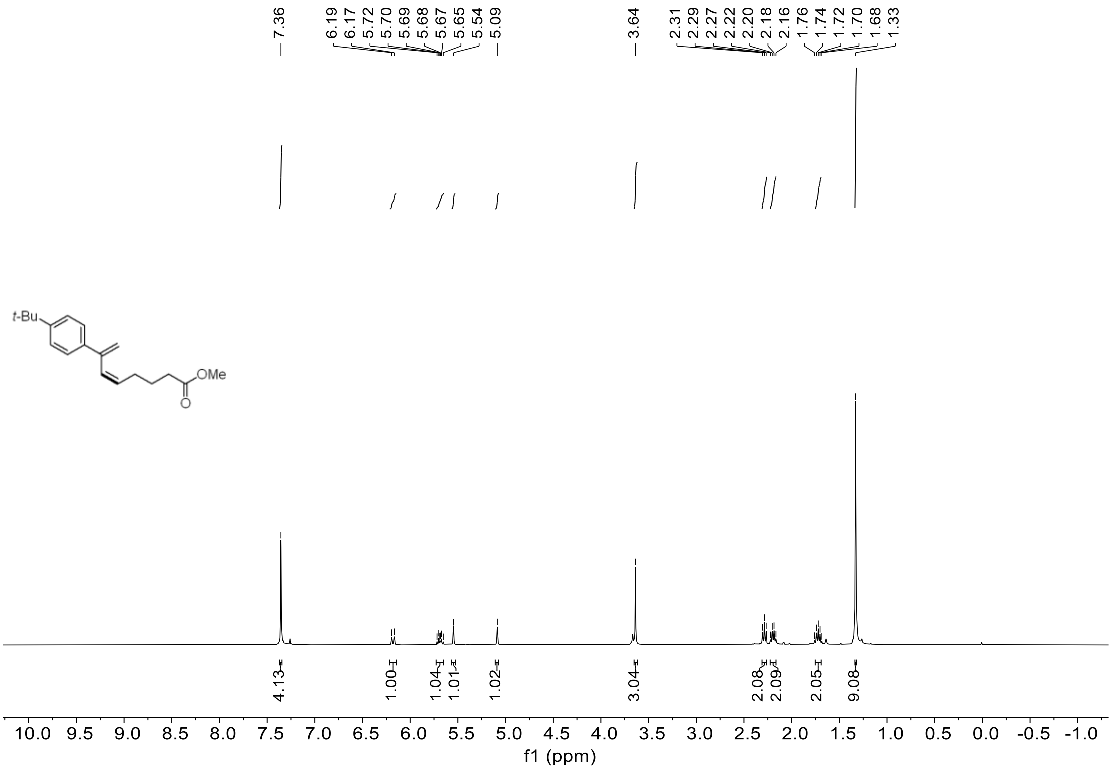

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **11a**



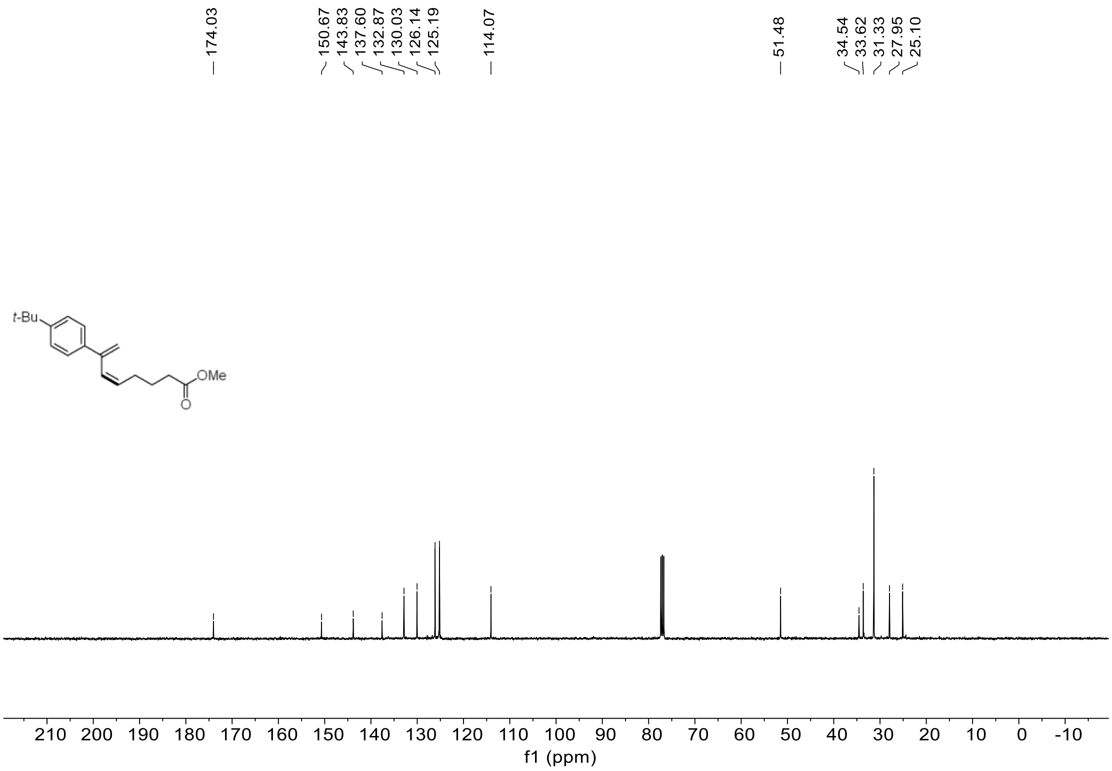
$^{1}$**H NMR** (400 MHz, $CDCl_3$) spectra of **12a**



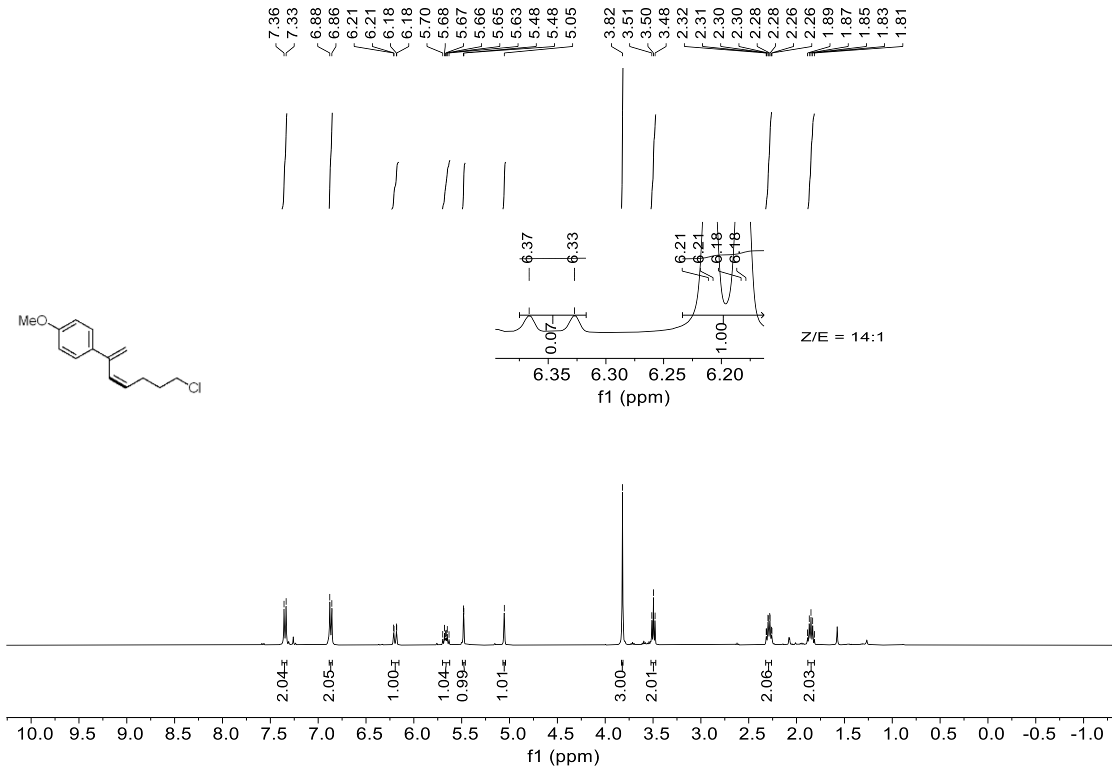
$^{13}$**C NMR** (101 MHz, $CDCl_3$) spectra of **12a**



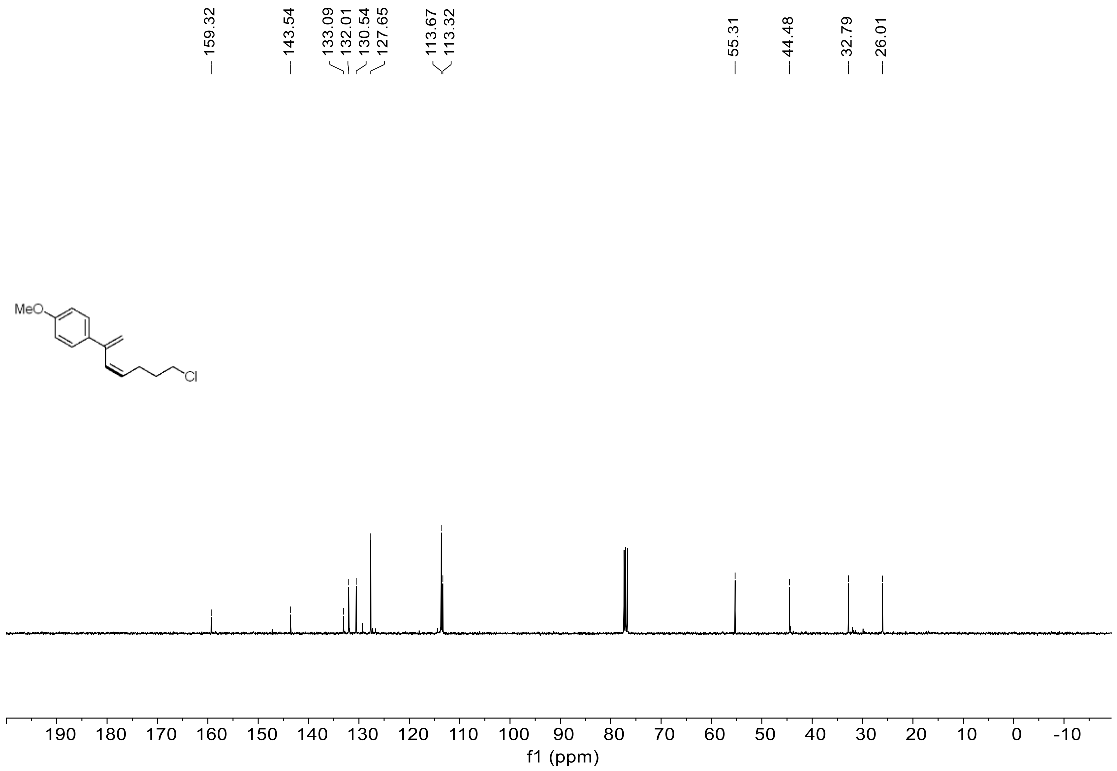

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **13a**



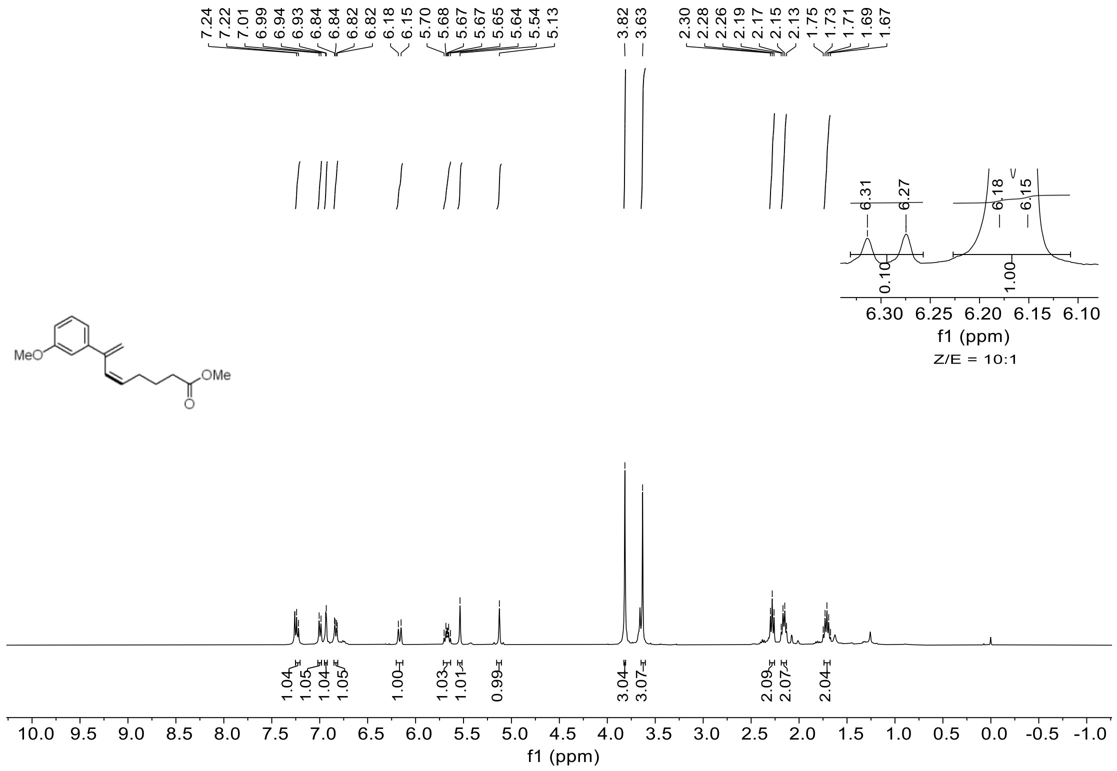

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **13a**



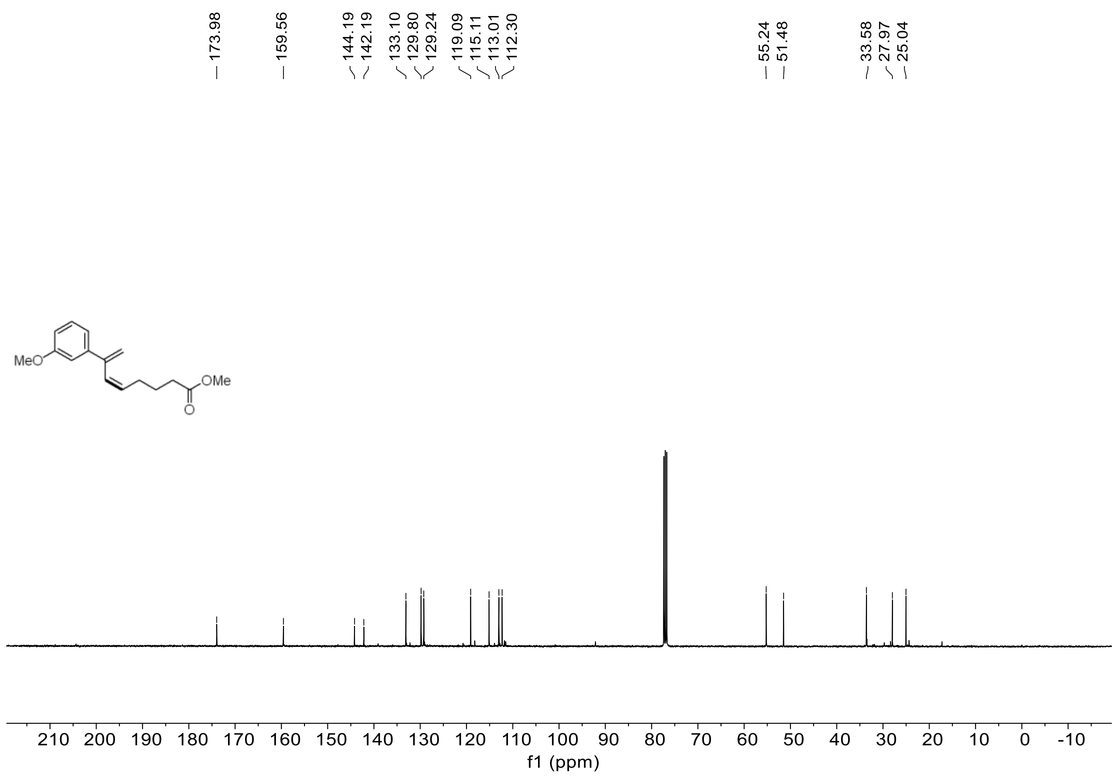
**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **14a**



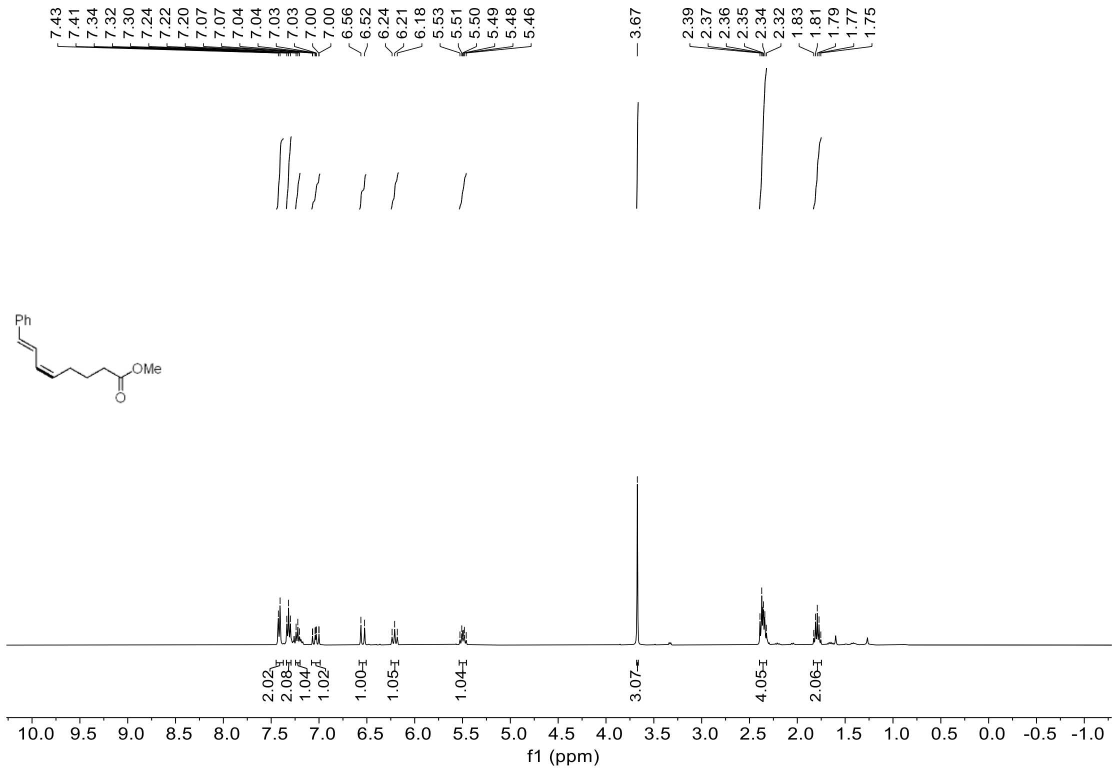
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **14a**



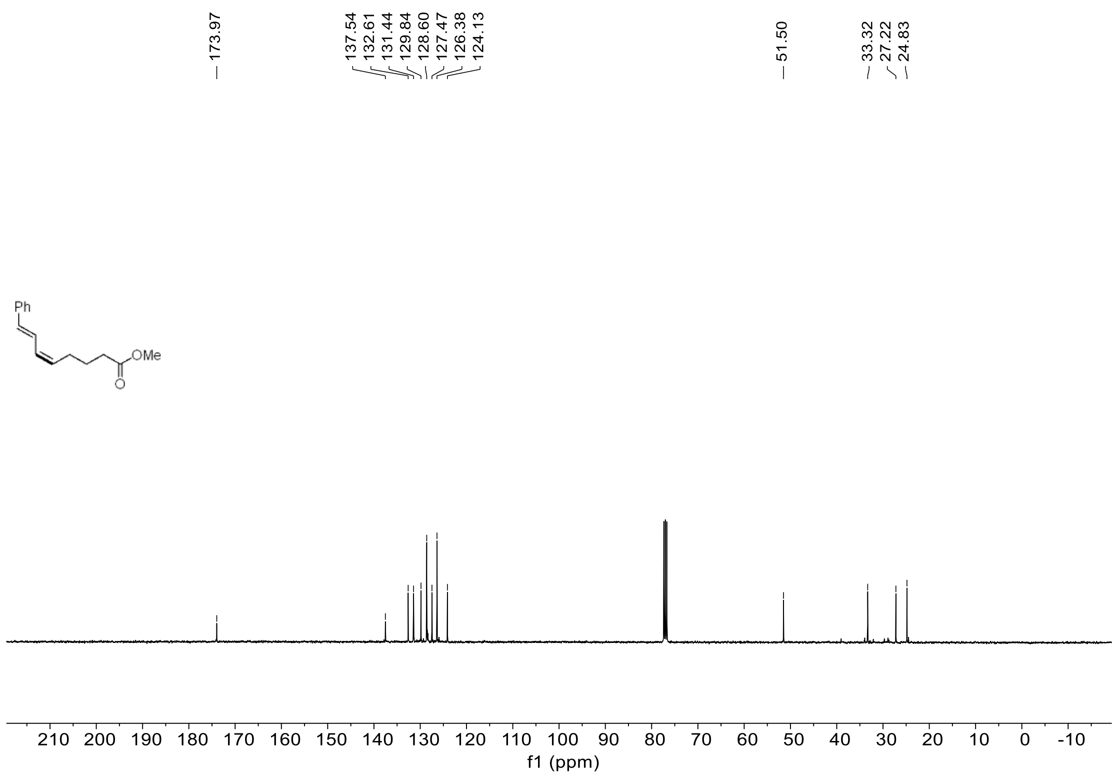

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **15a**



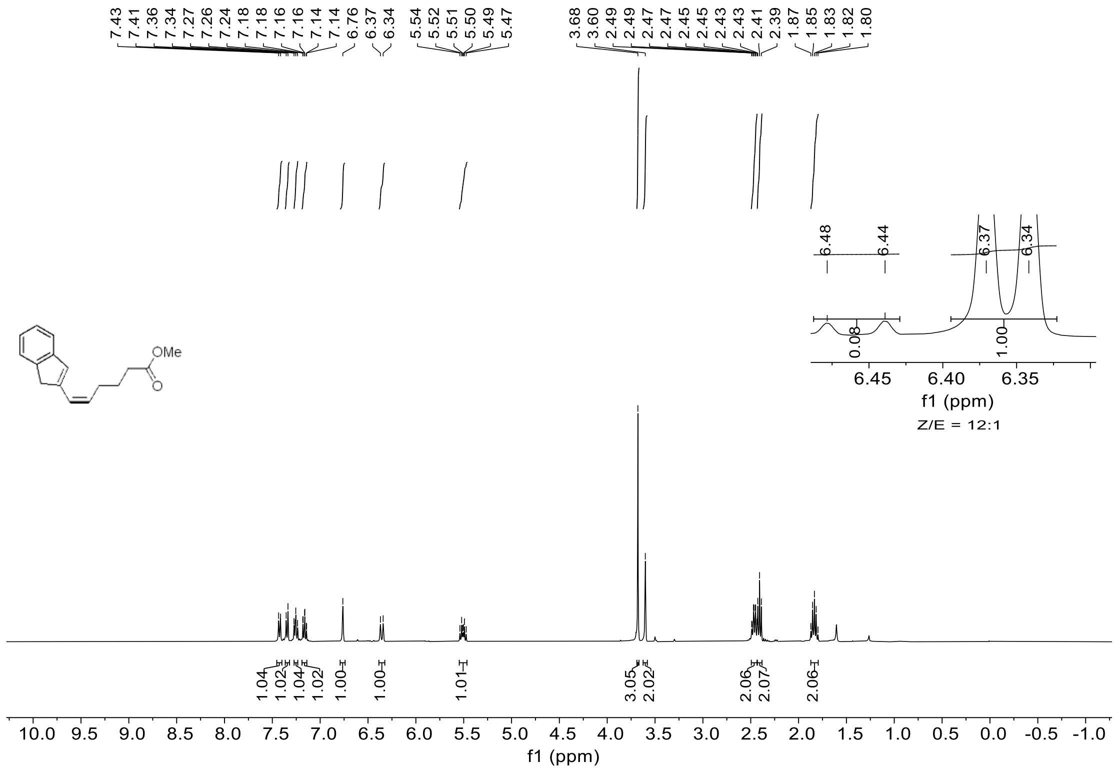

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **15a**



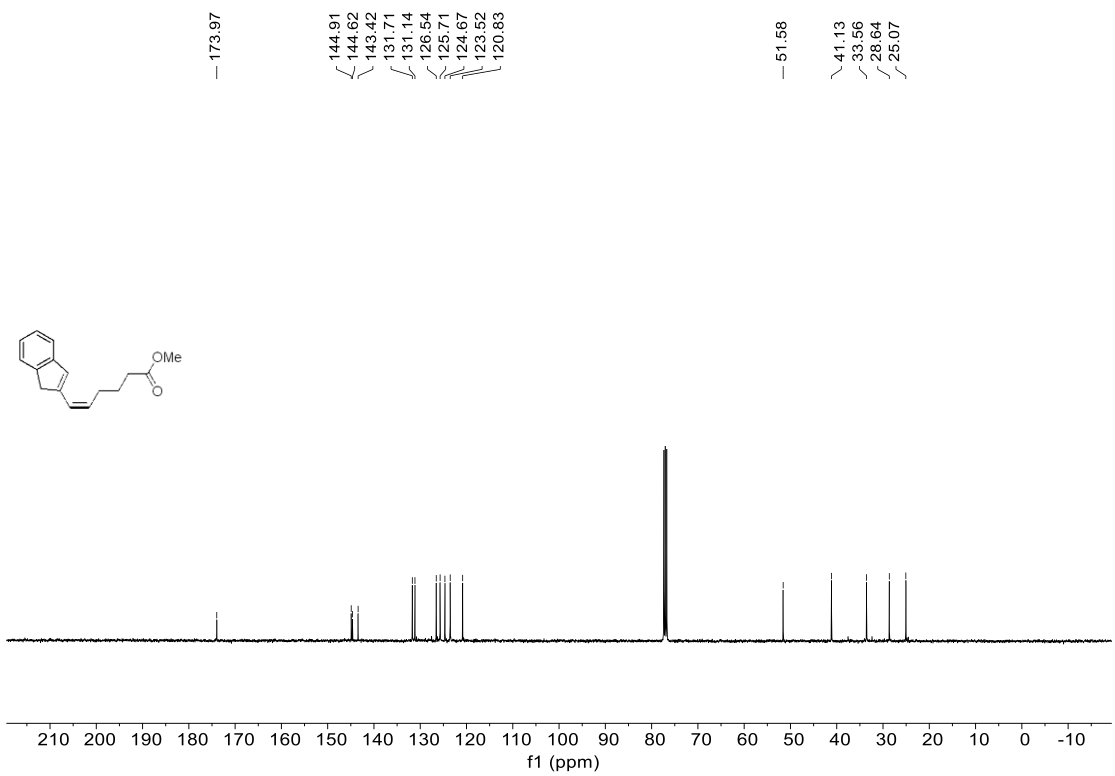
$^{1}$**H NMR** (400 MHz, CDCl$_3$) spectra of **16a**



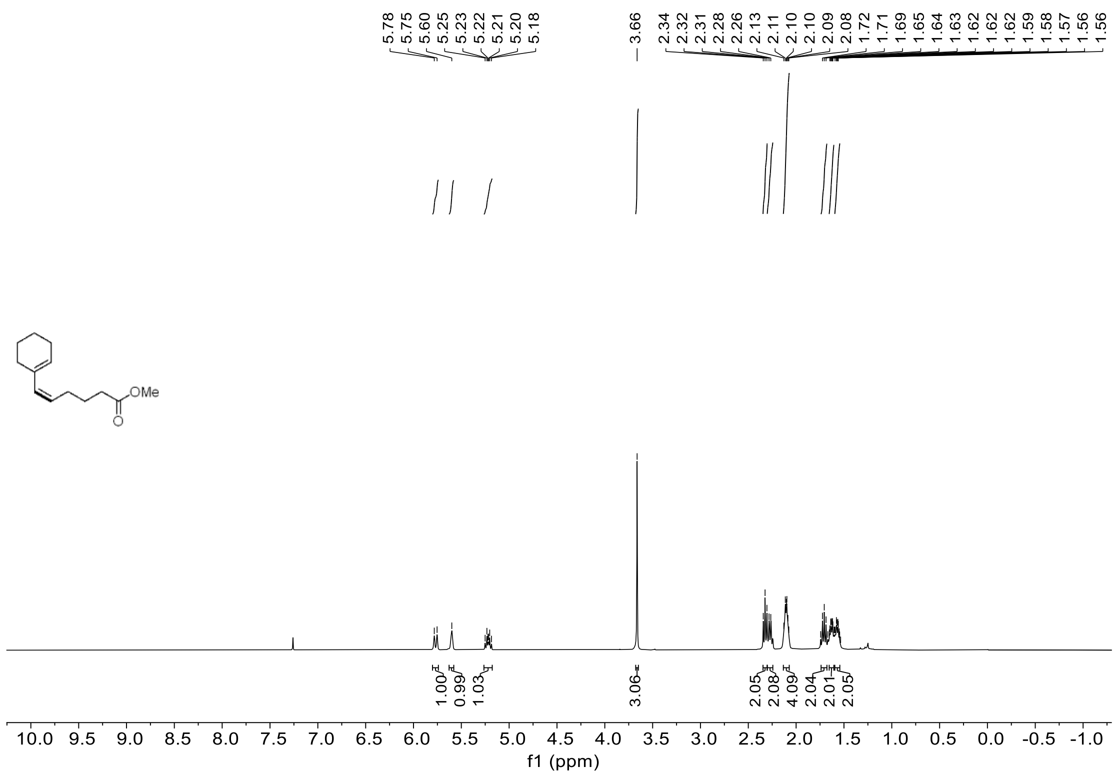
$^{13}$**C NMR** (101 MHz, CDCl$_3$) spectra of **16a**



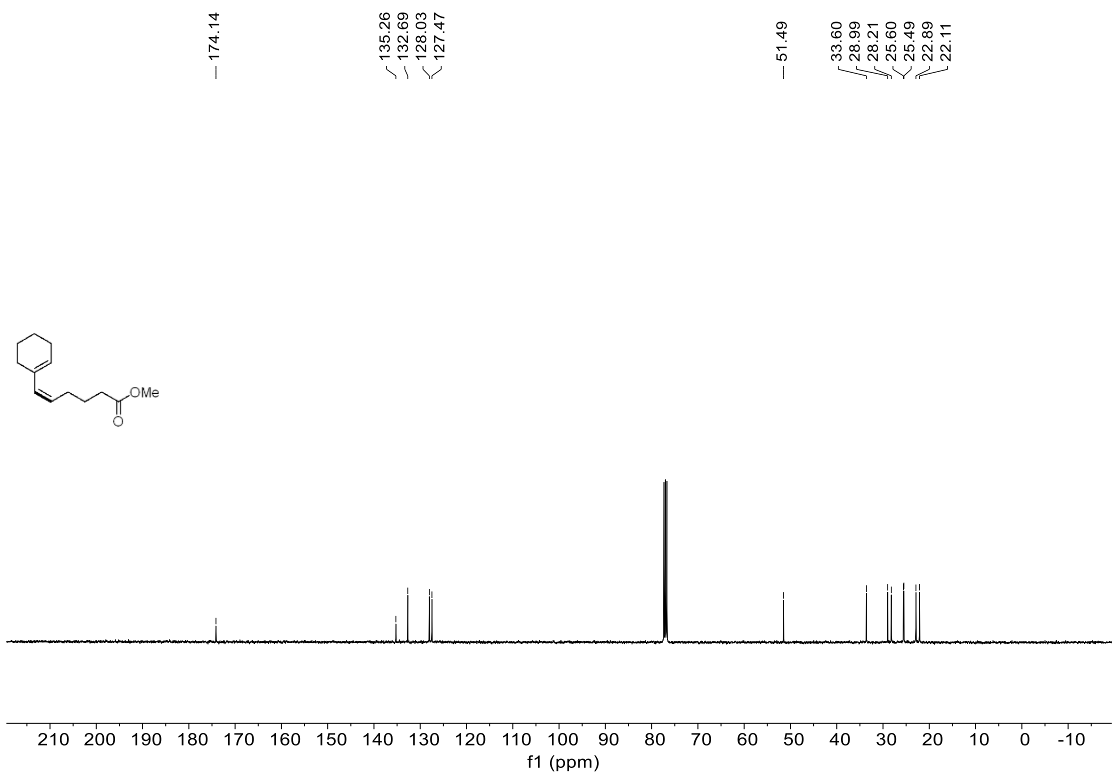

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **17a**



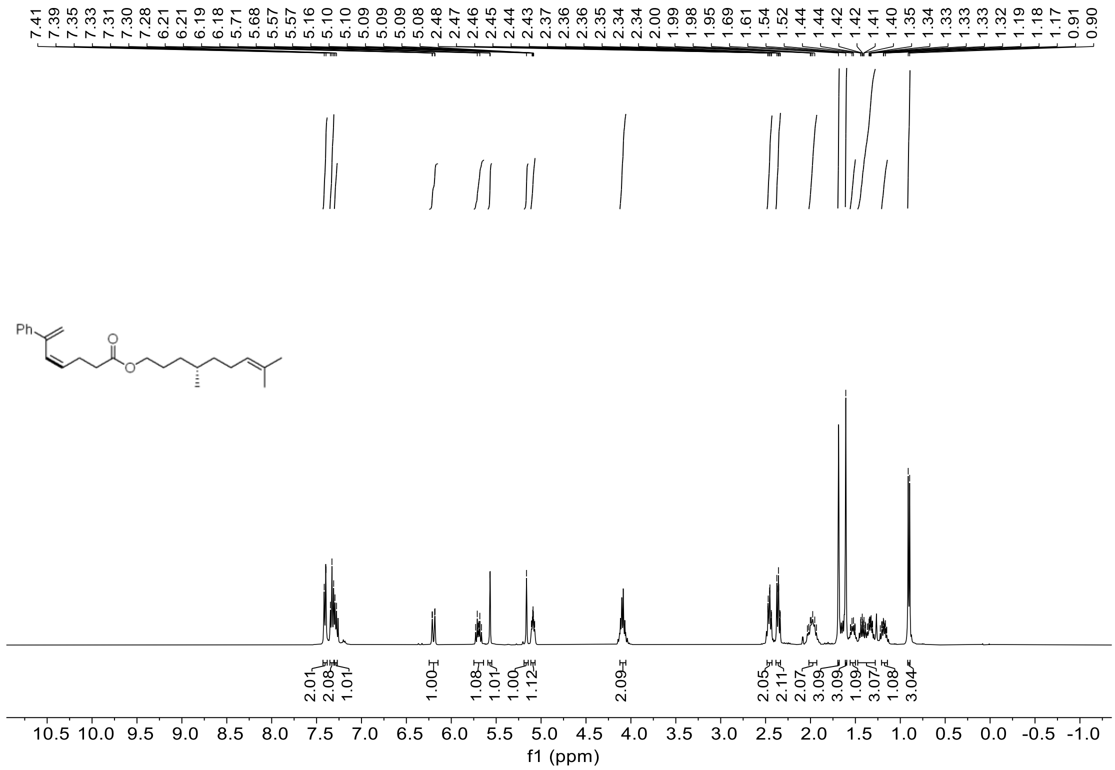

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **17a**



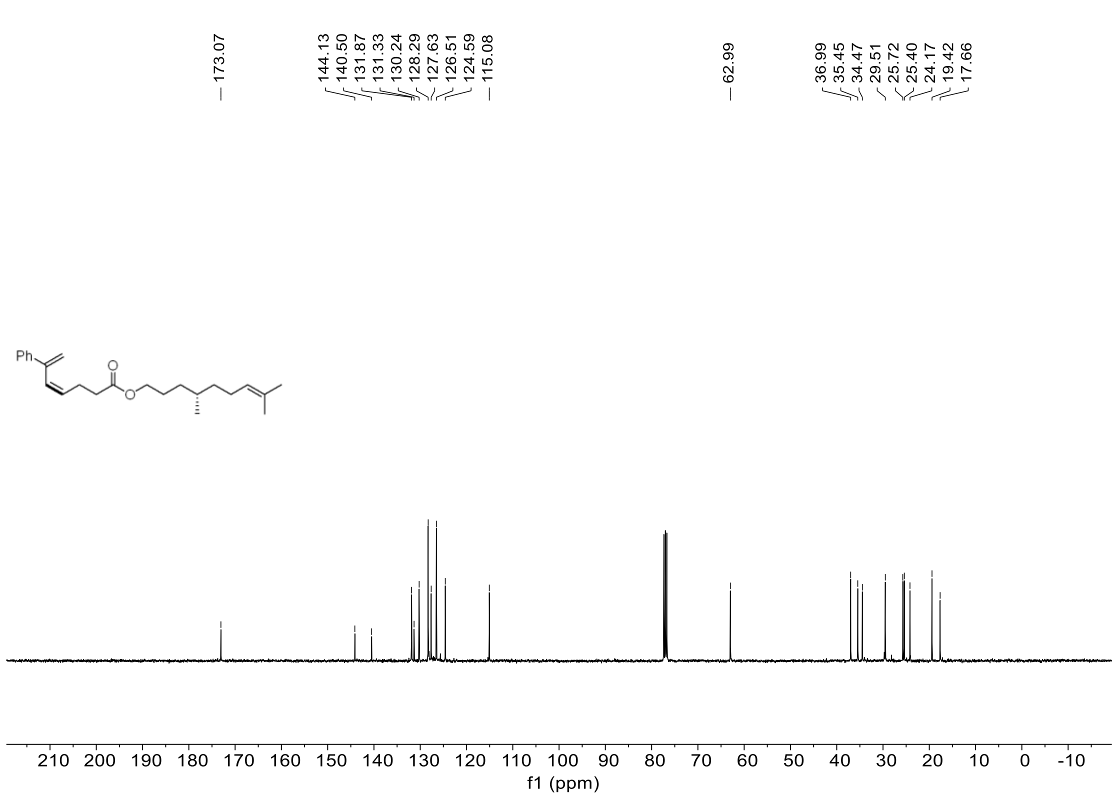

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **18a**



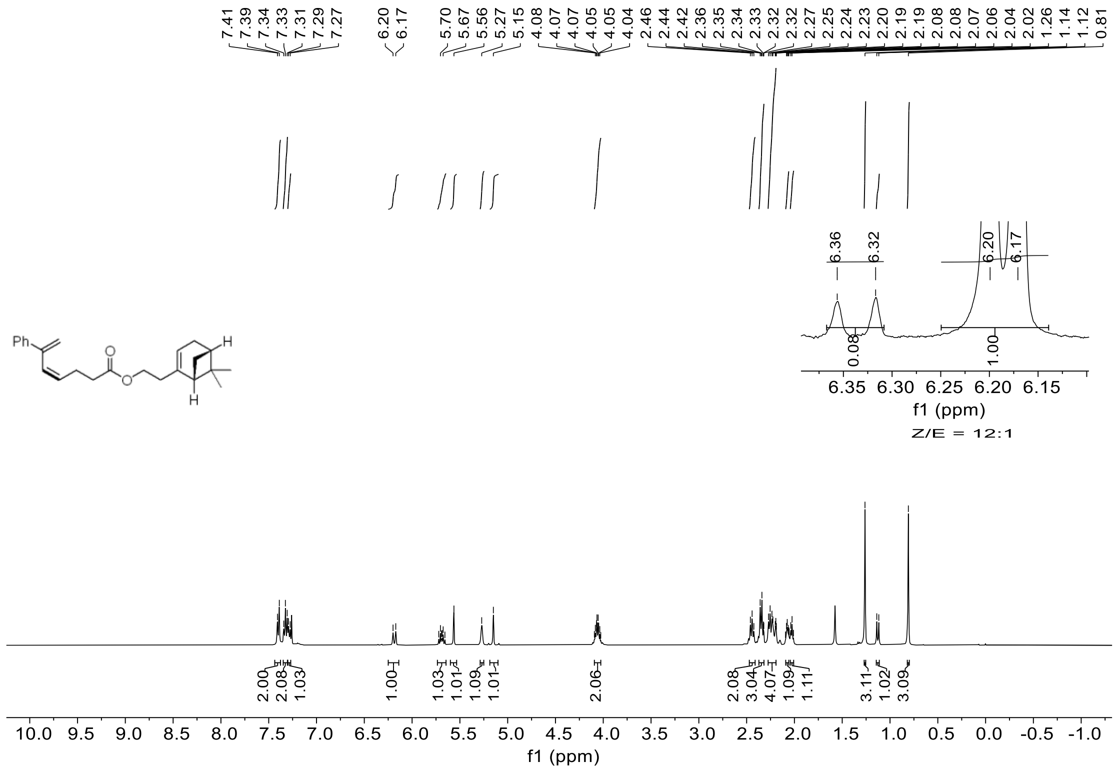

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **18a**



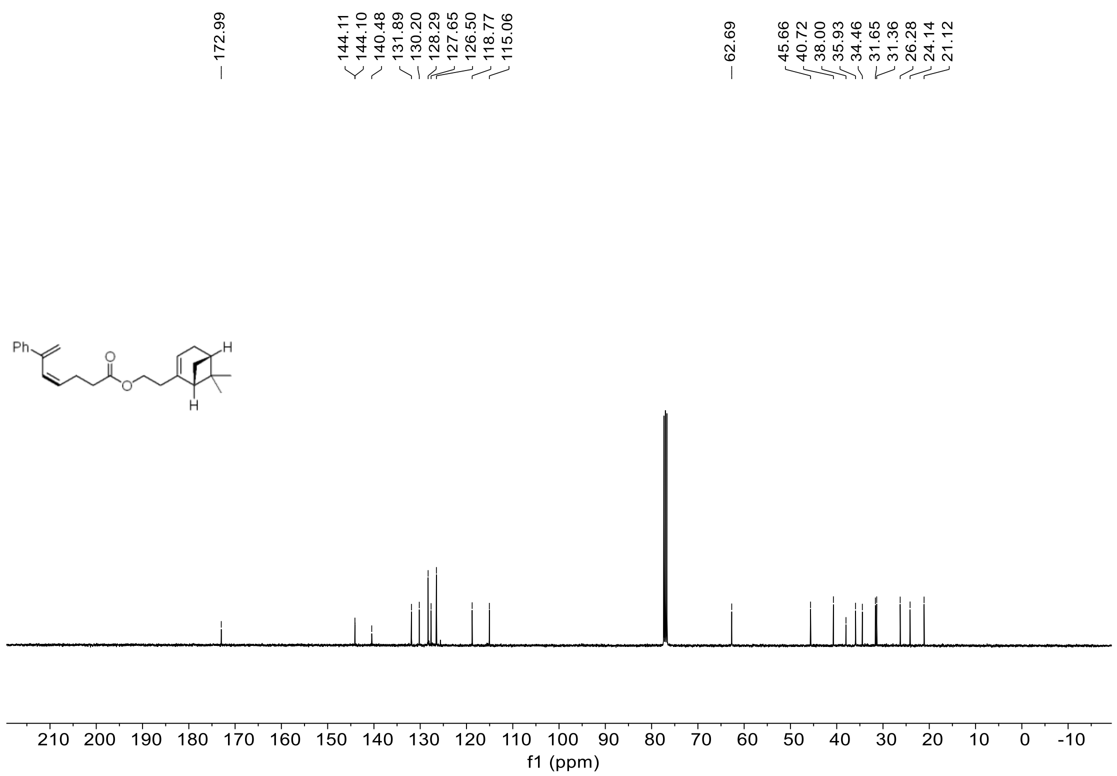

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **19a**



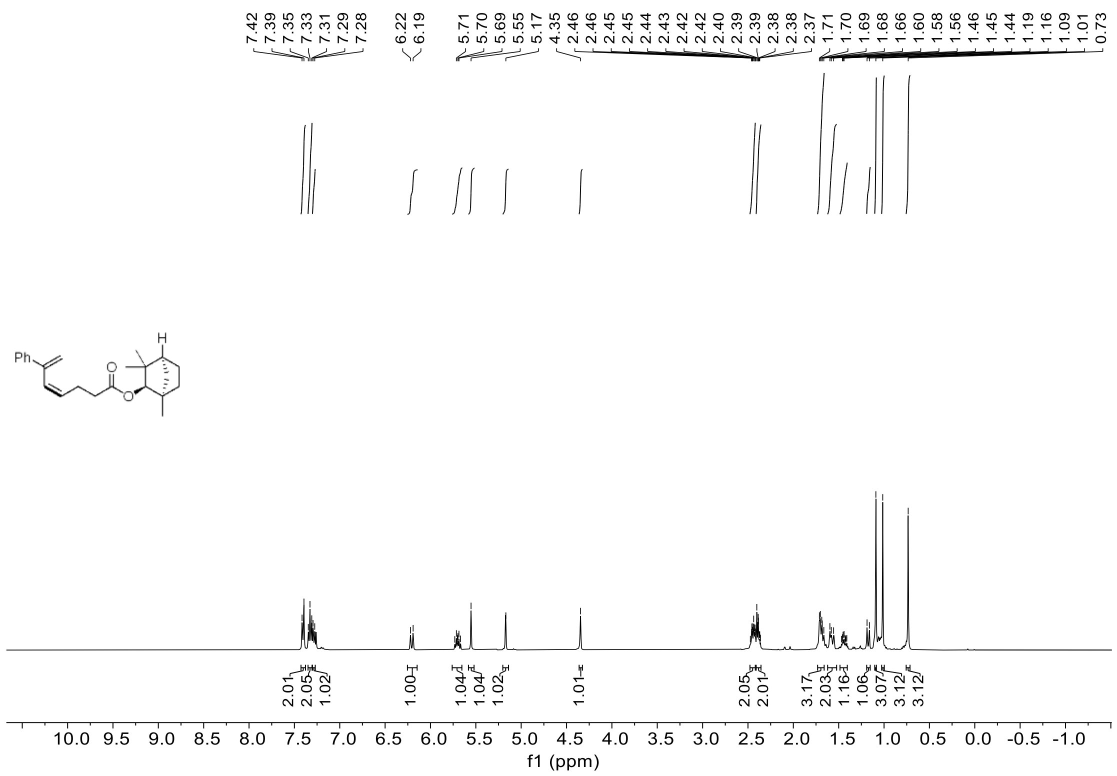

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **19a**



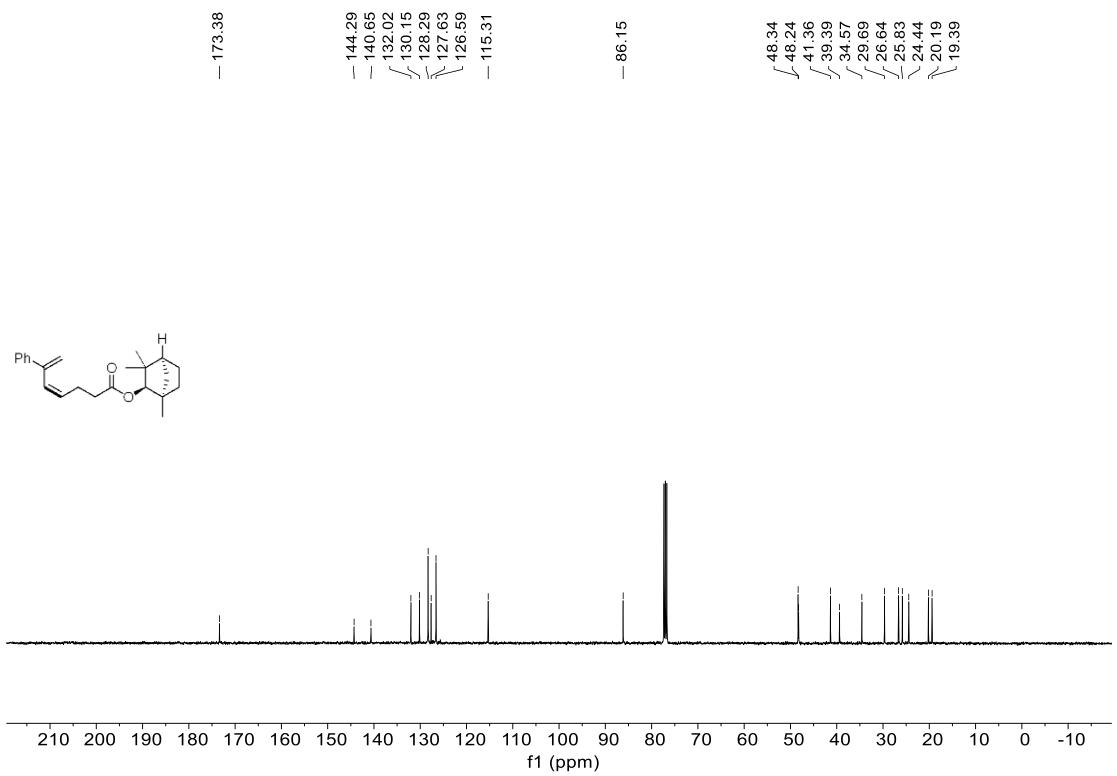

**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **20a**



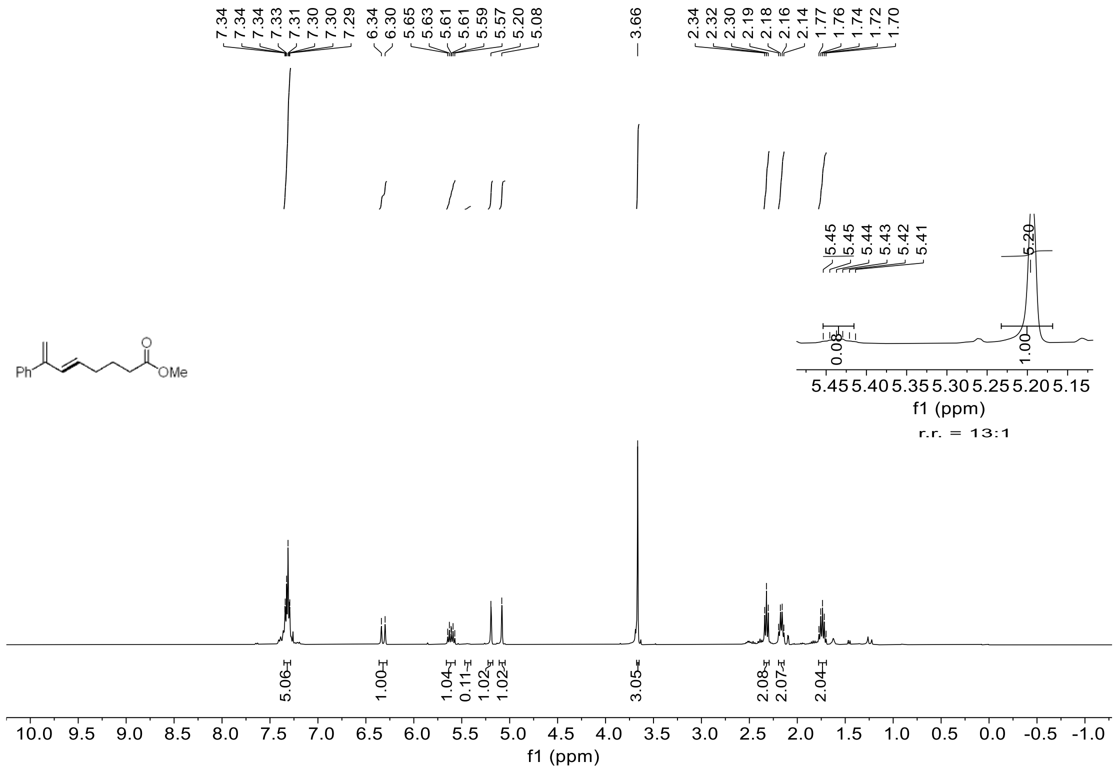

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **20a**



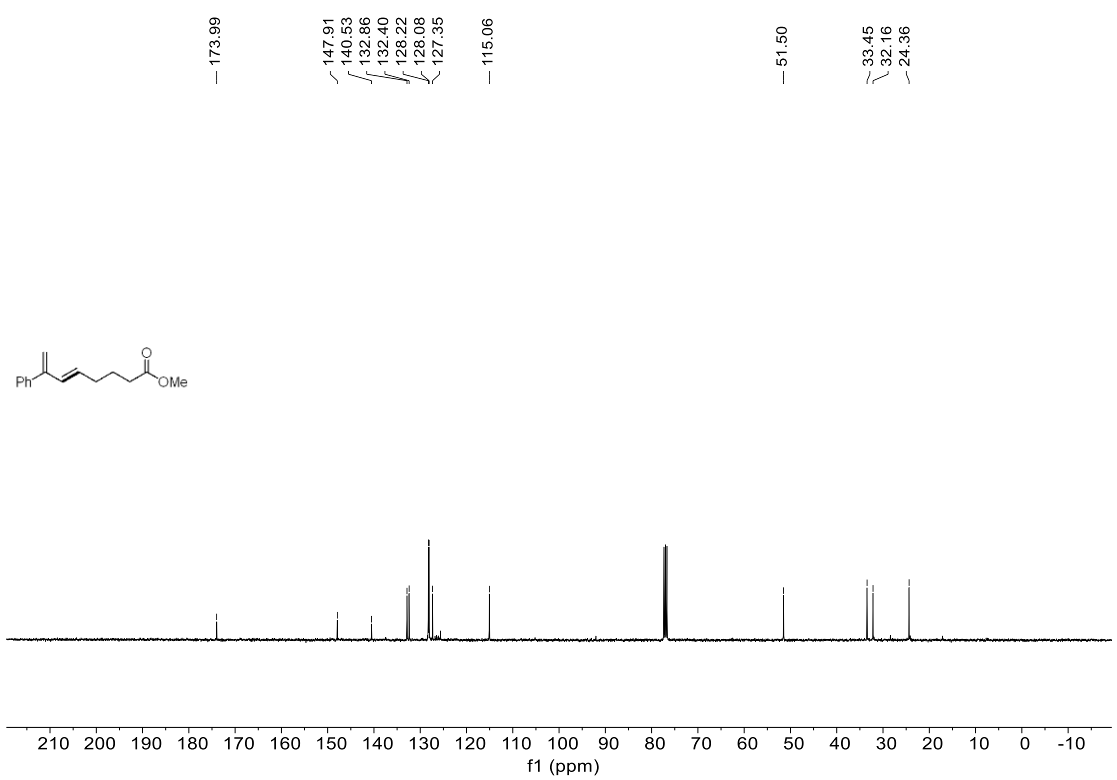

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **21a**



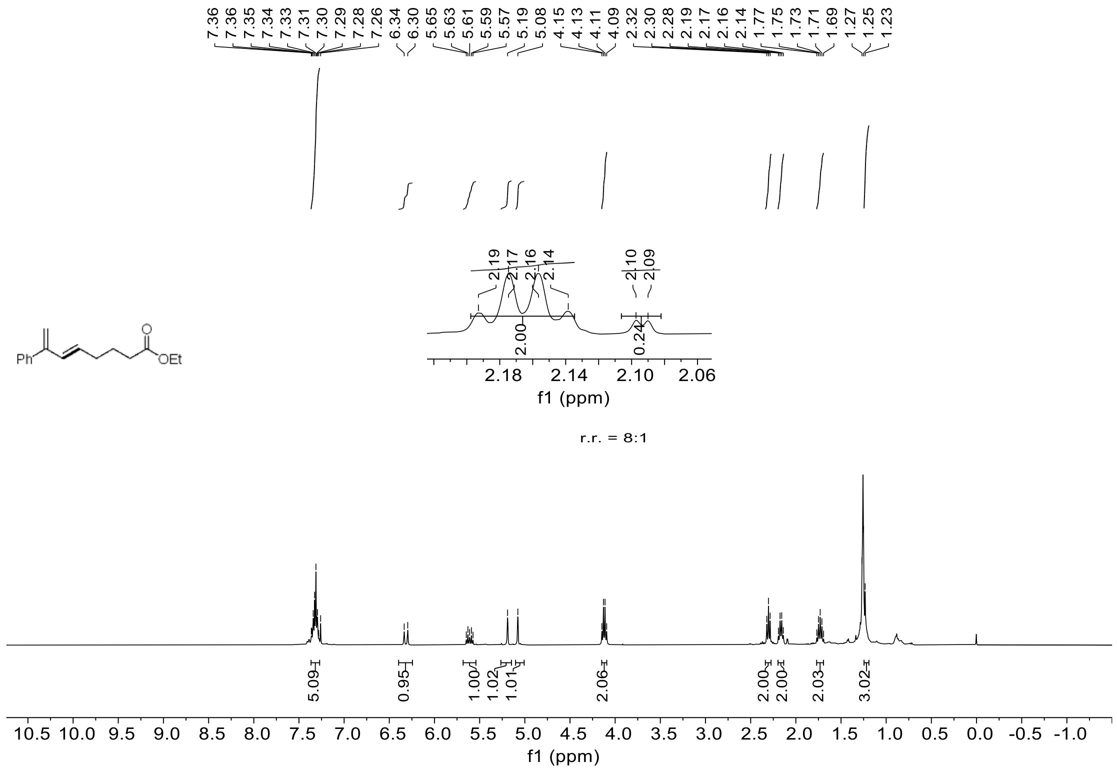

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **22a**



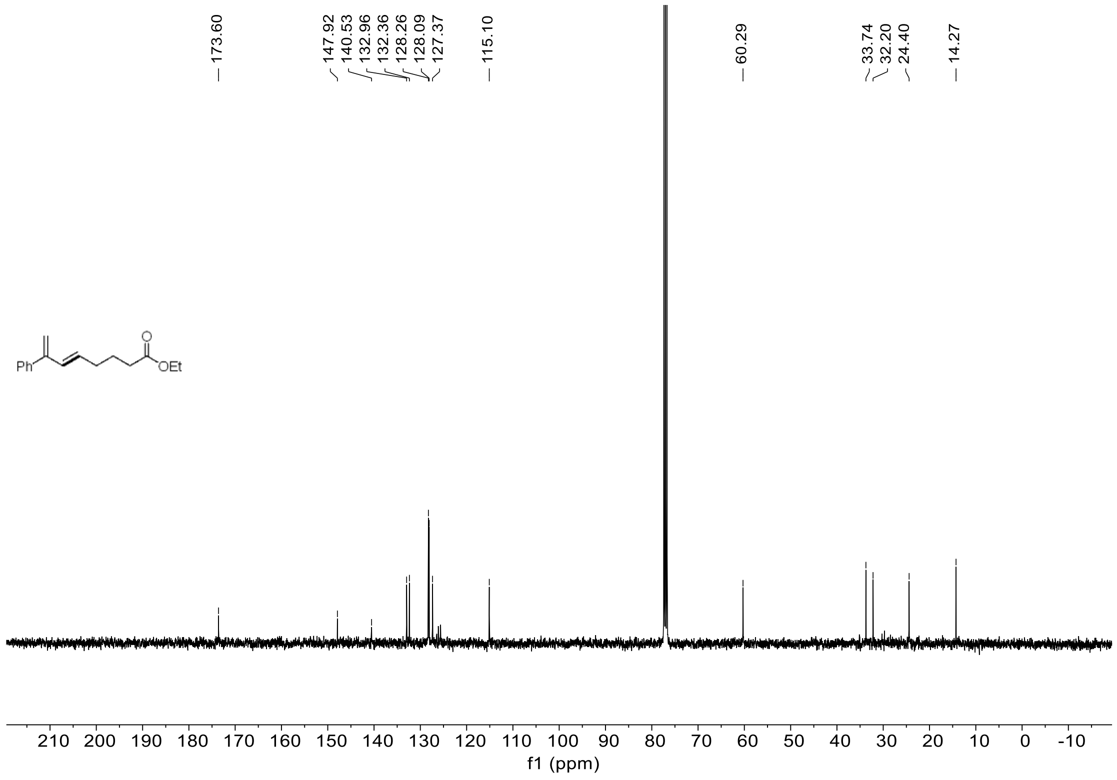
$^{1}$**H NMR** (400 MHz, $CDCl_3$) spectra of **2b**



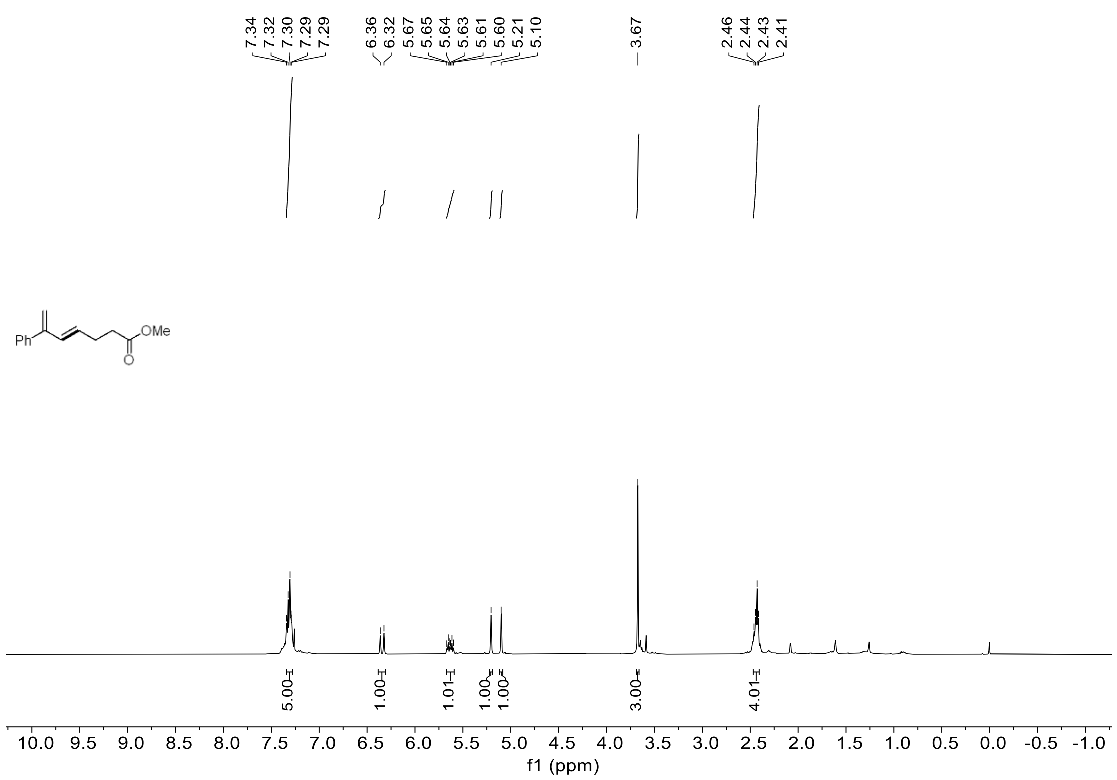
$^{13}$**C NMR** (101 MHz, $CDCl_3$) spectra of **2b**



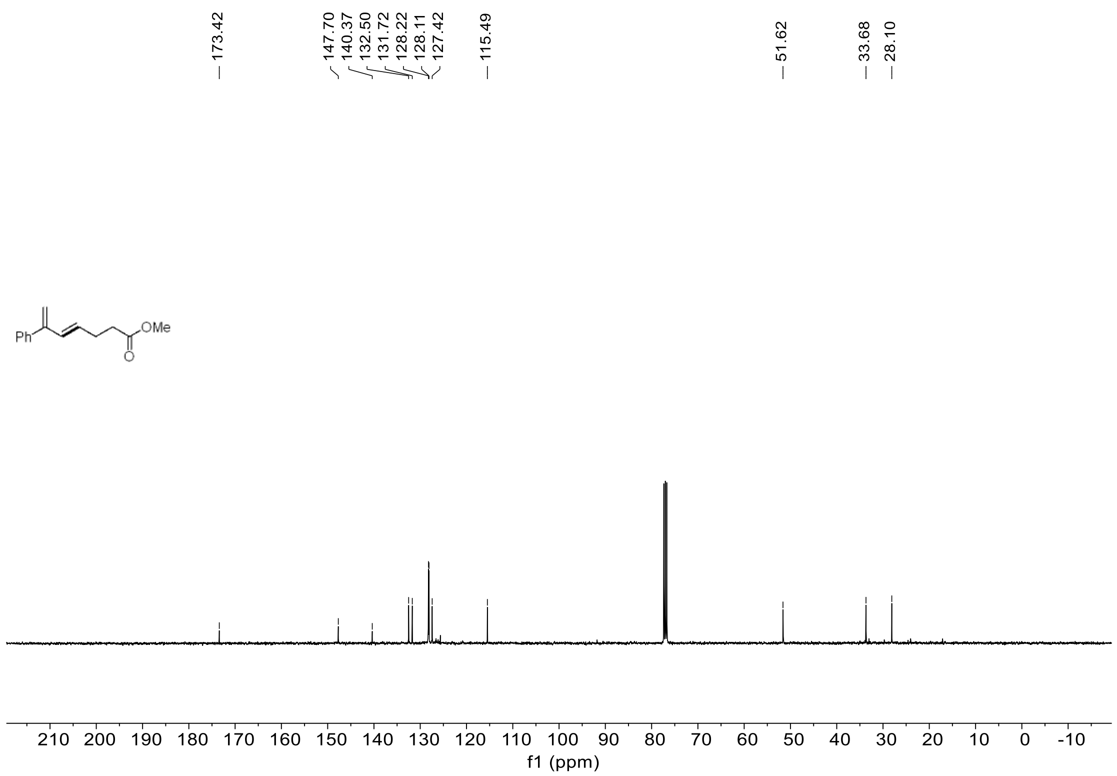

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **3b**



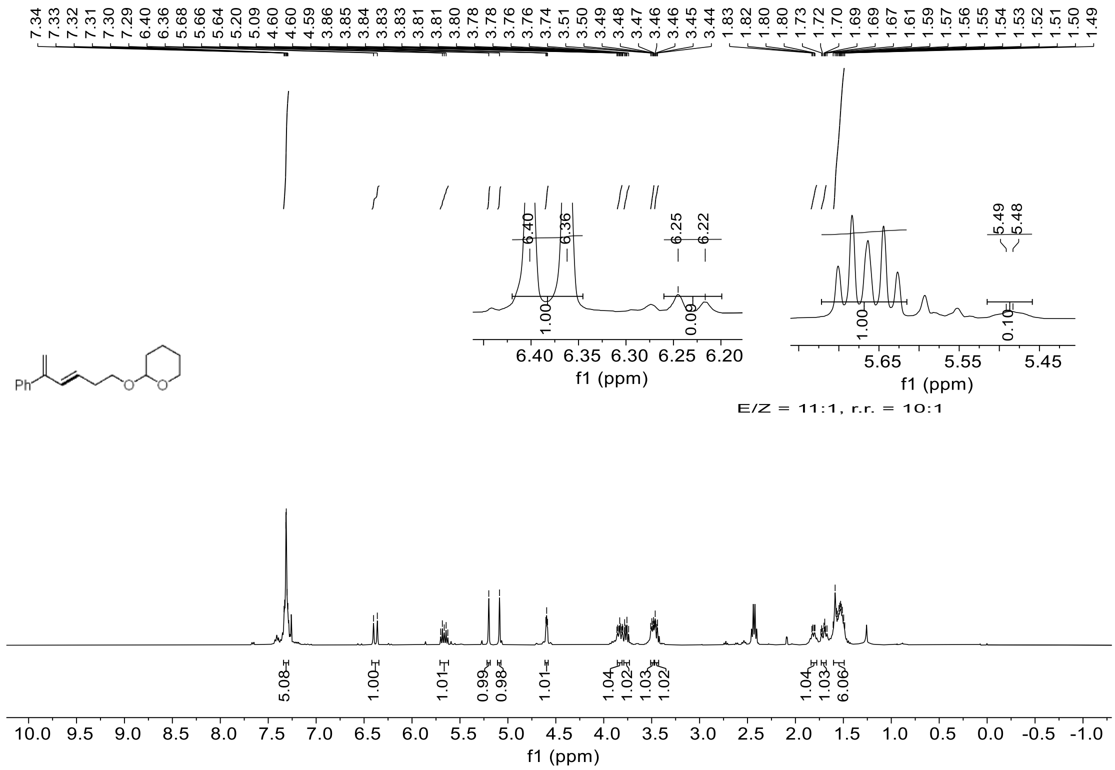

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **3b**



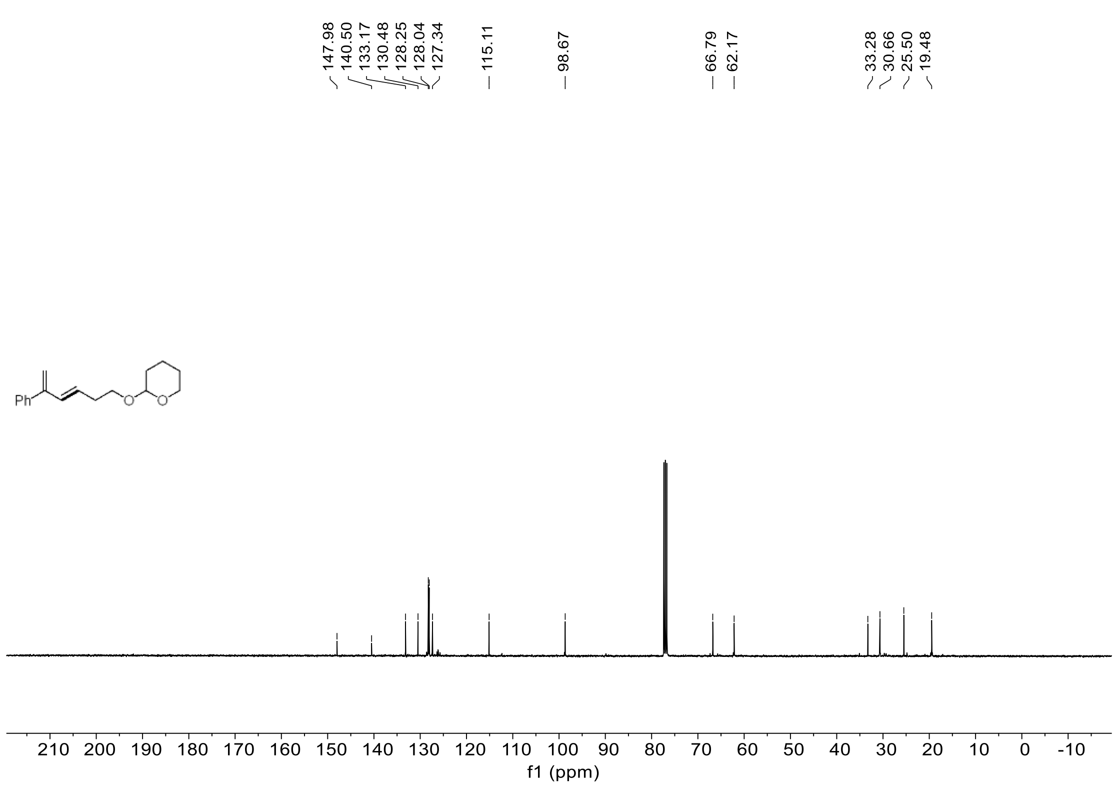
$^{1}$**H NMR** (400 MHz, CDCl$_3$) spectra of **4b**



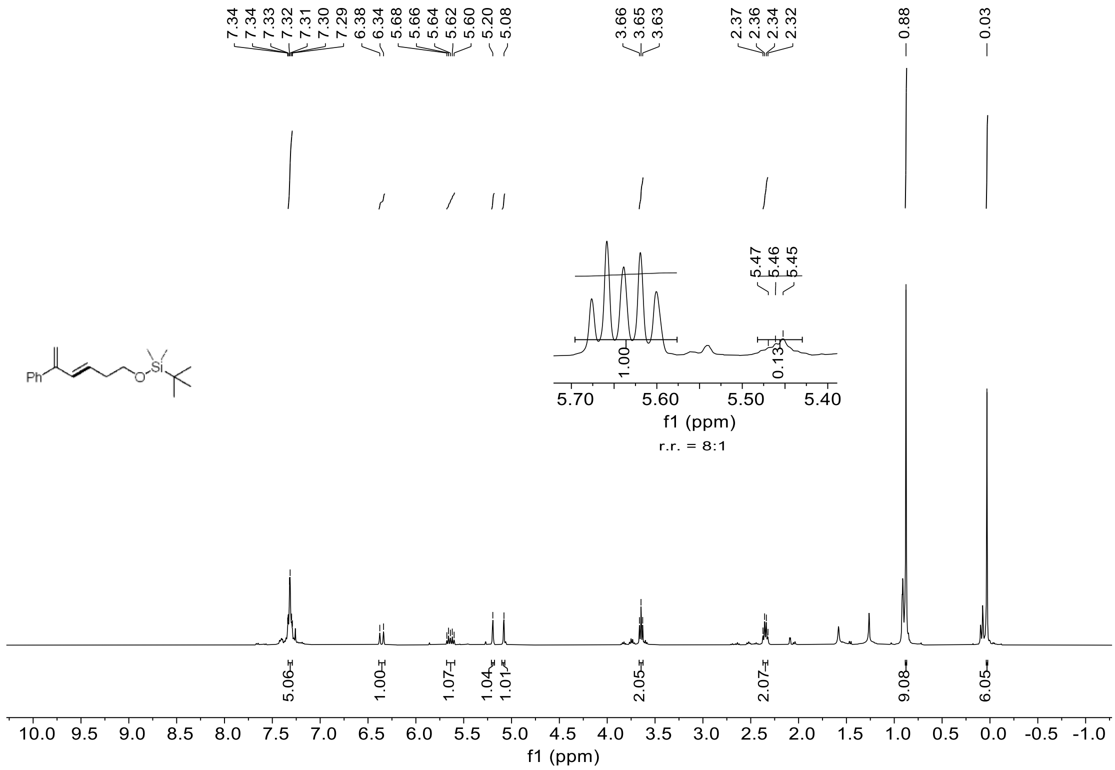
$^{13}$**C NMR** (101 MHz, CDCl$_3$) spectra of **4b**



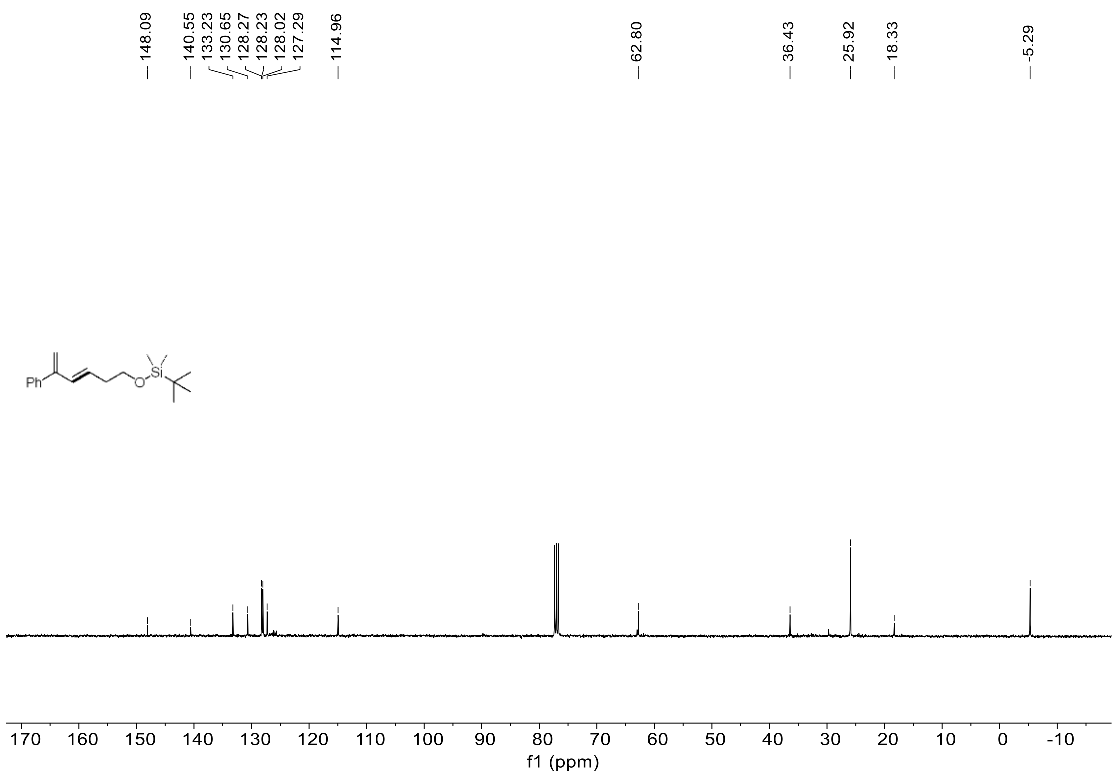
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **5b**



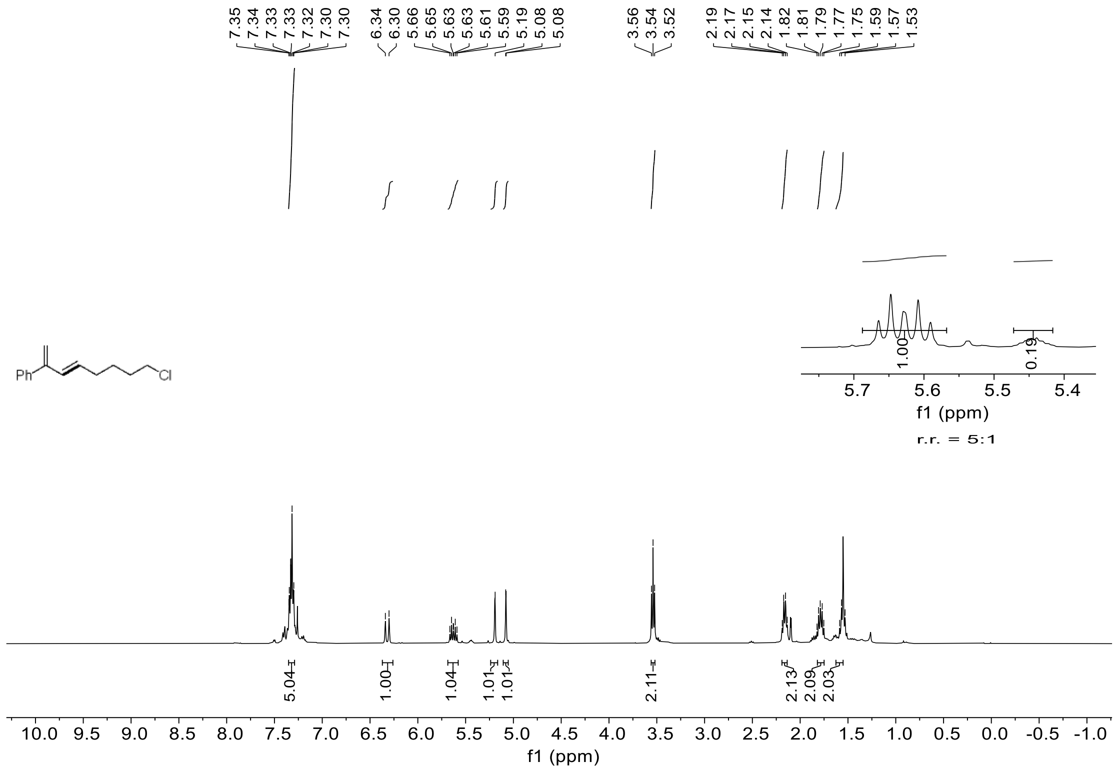
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **5b**



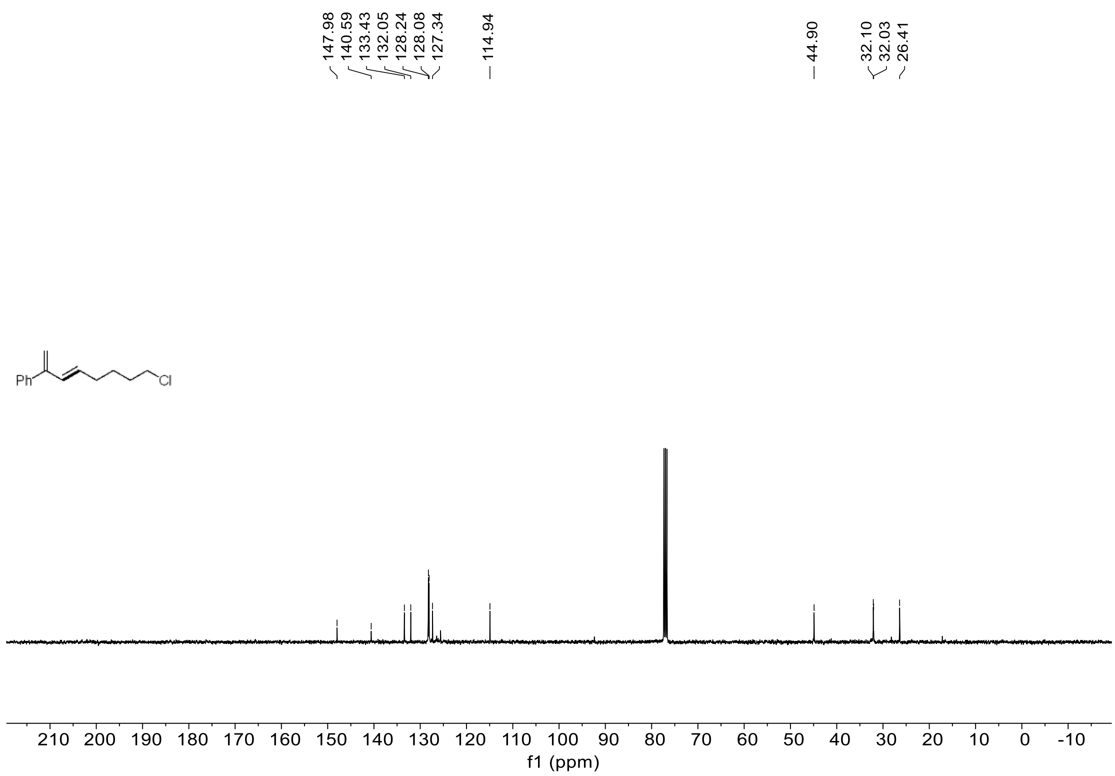
**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **6b**



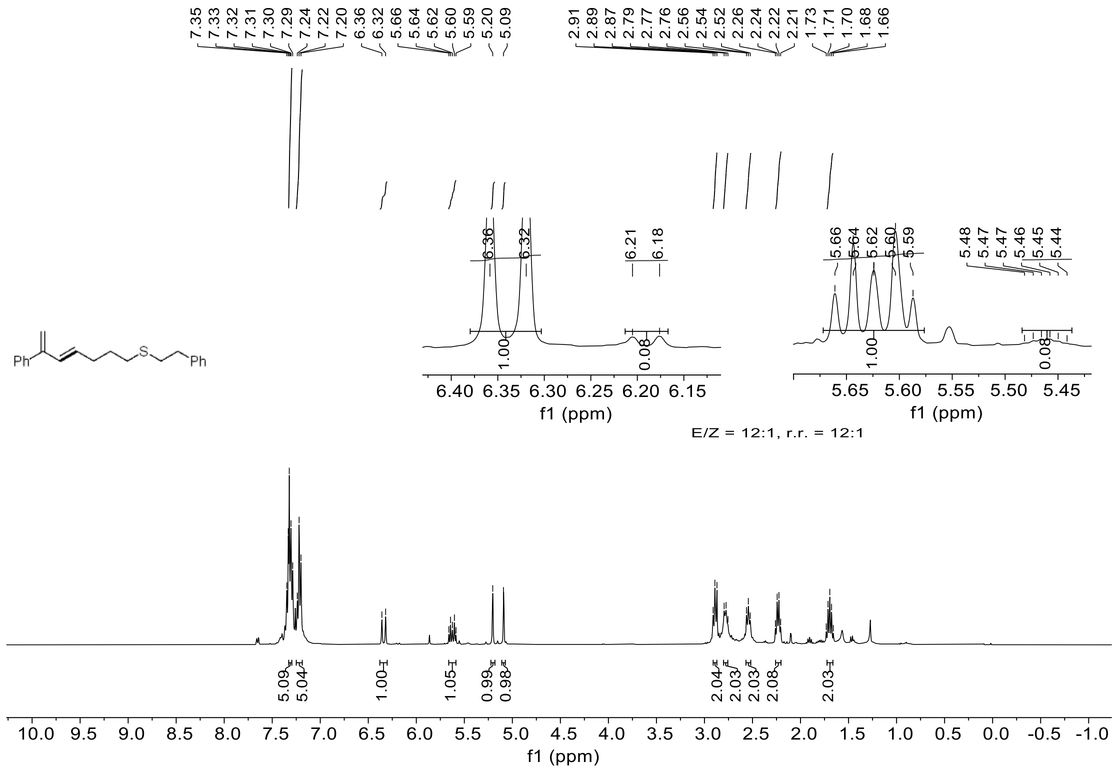
**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **6b**



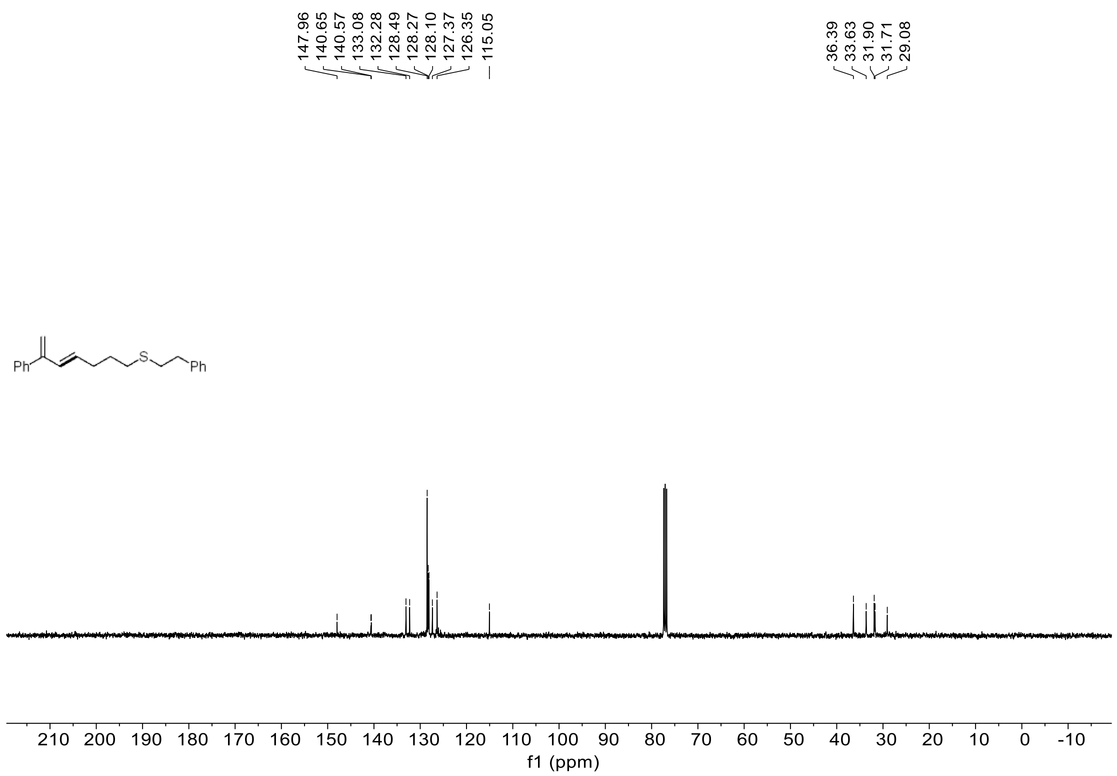
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **7b**



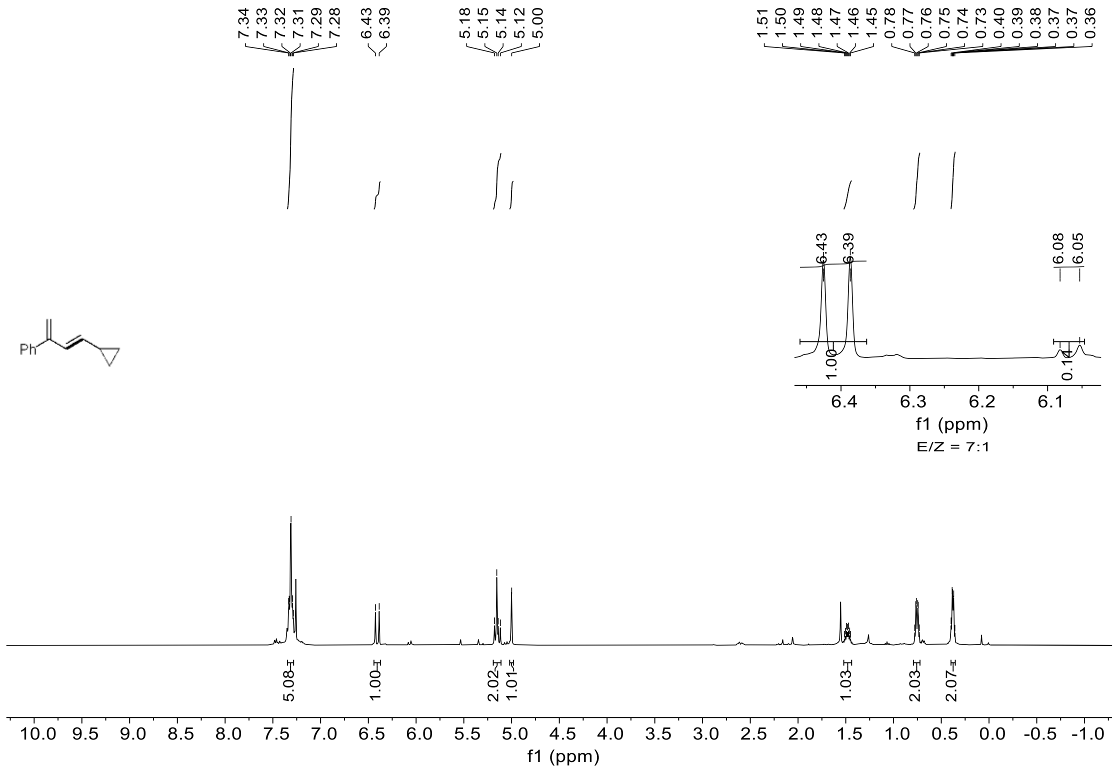
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **7b**



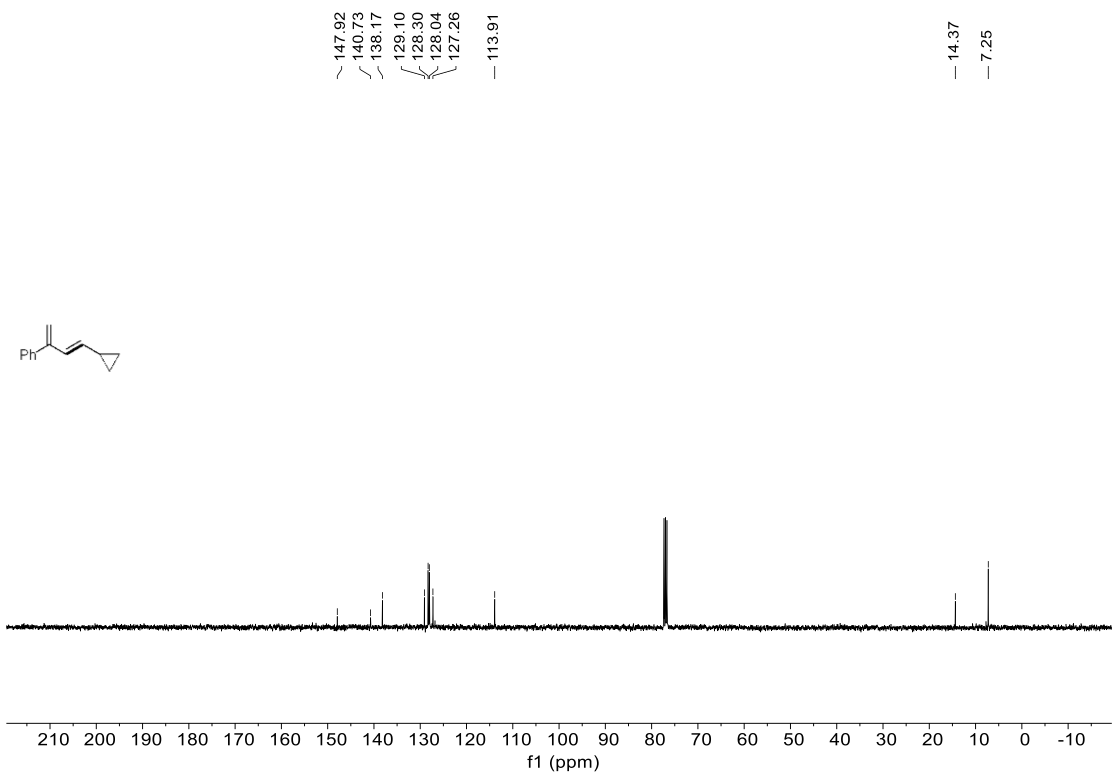
**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **8b**



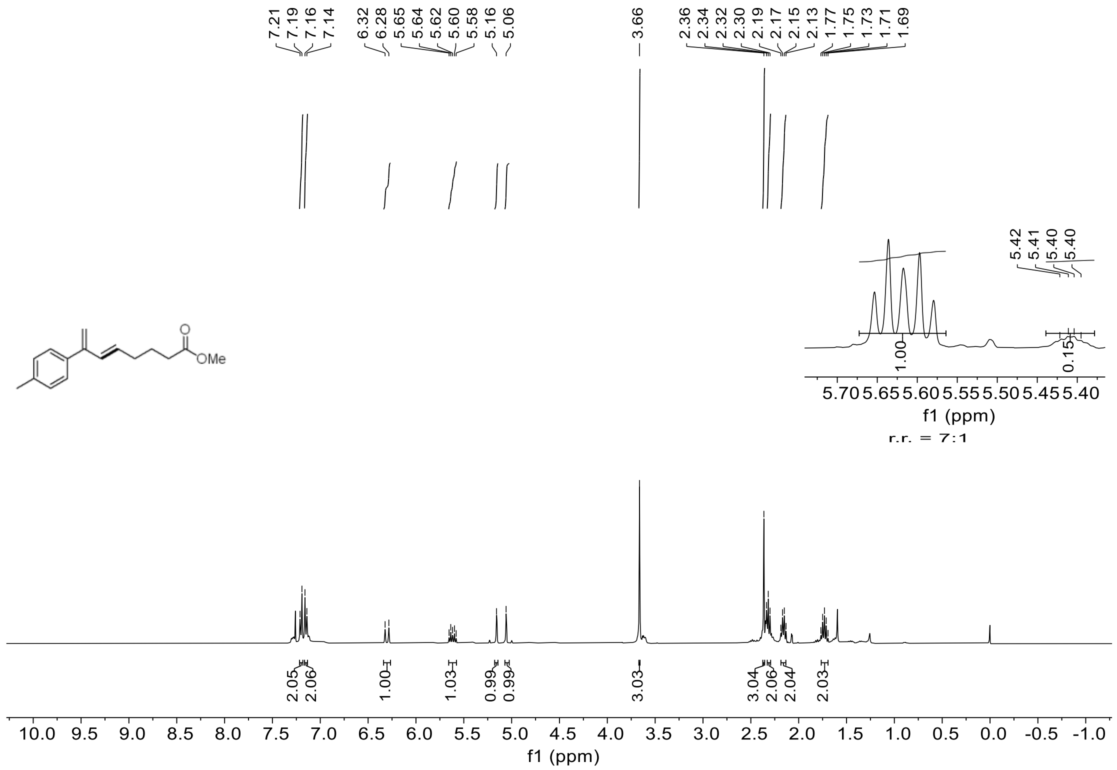
**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **8b**



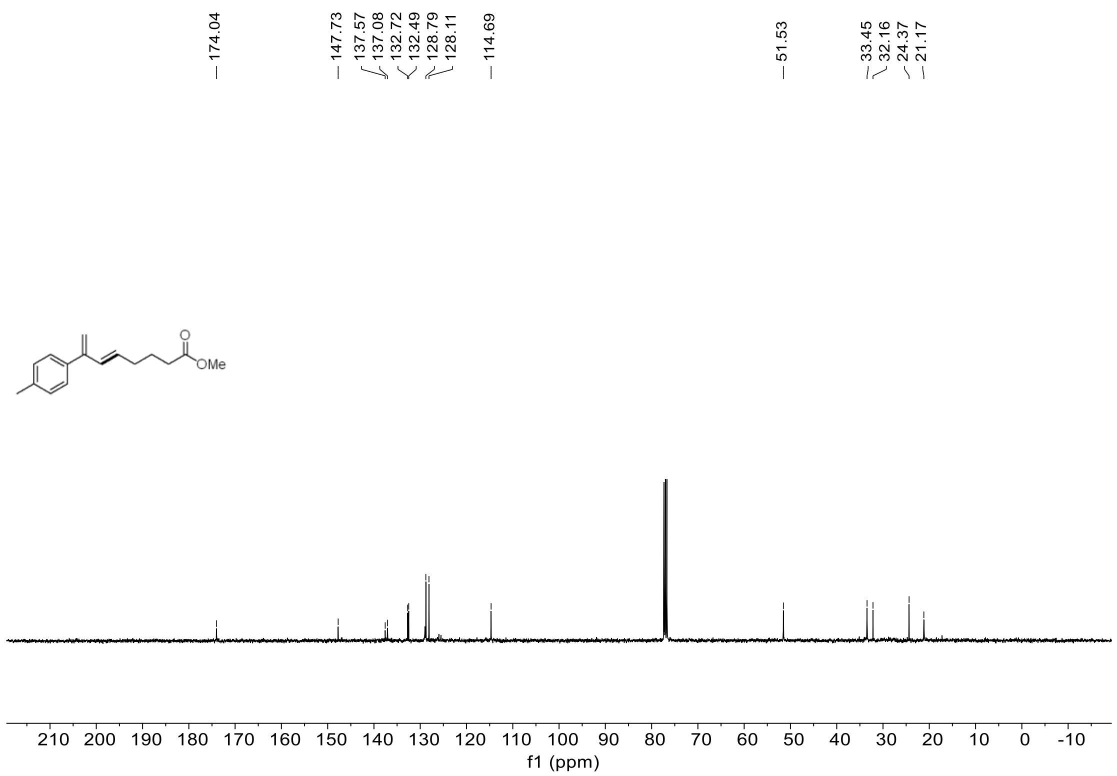

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **9b**



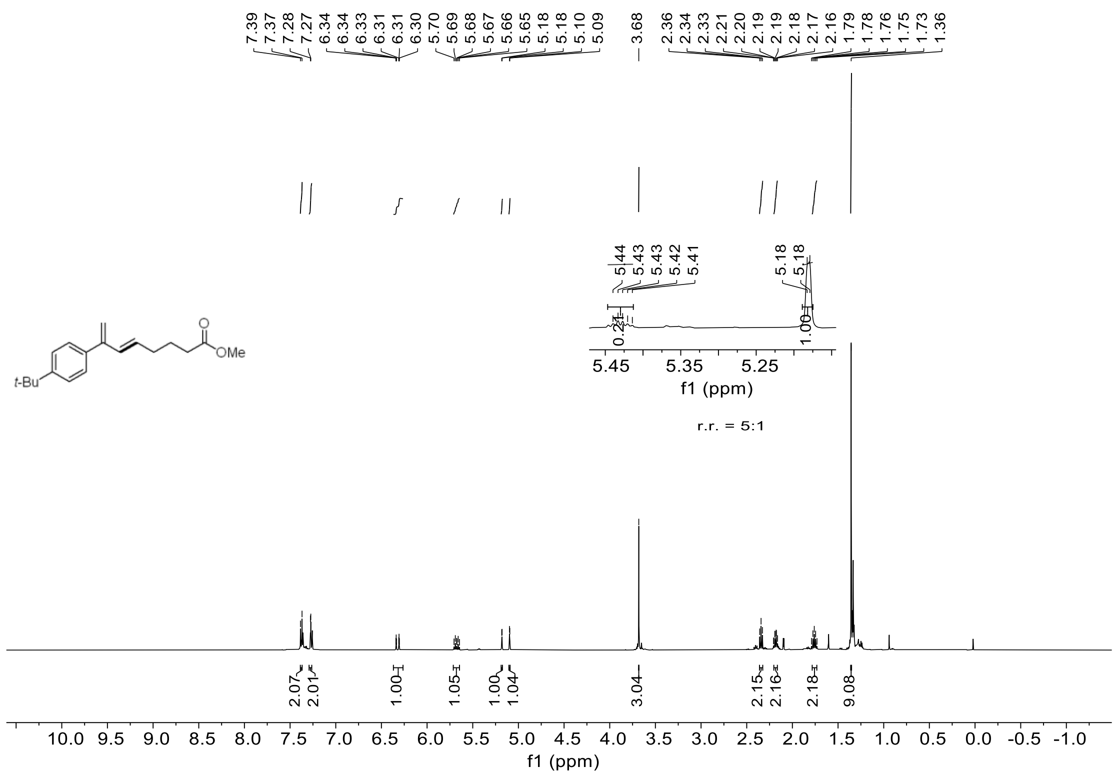

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **9b**



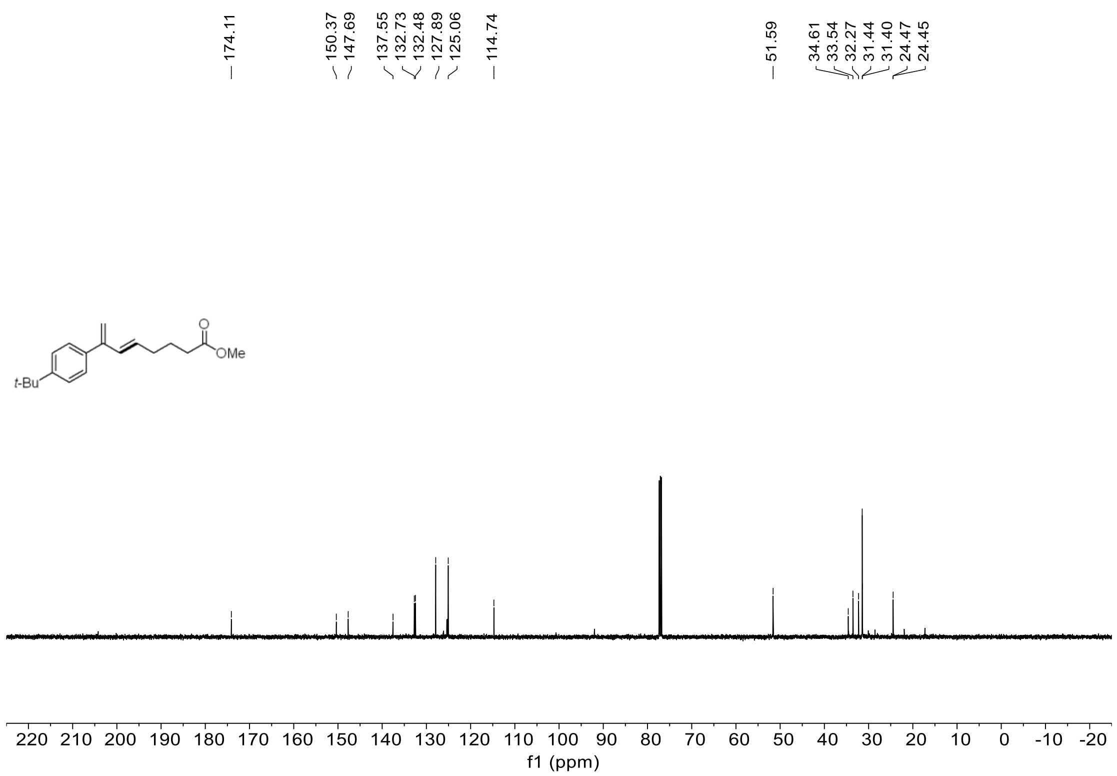

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **10b**



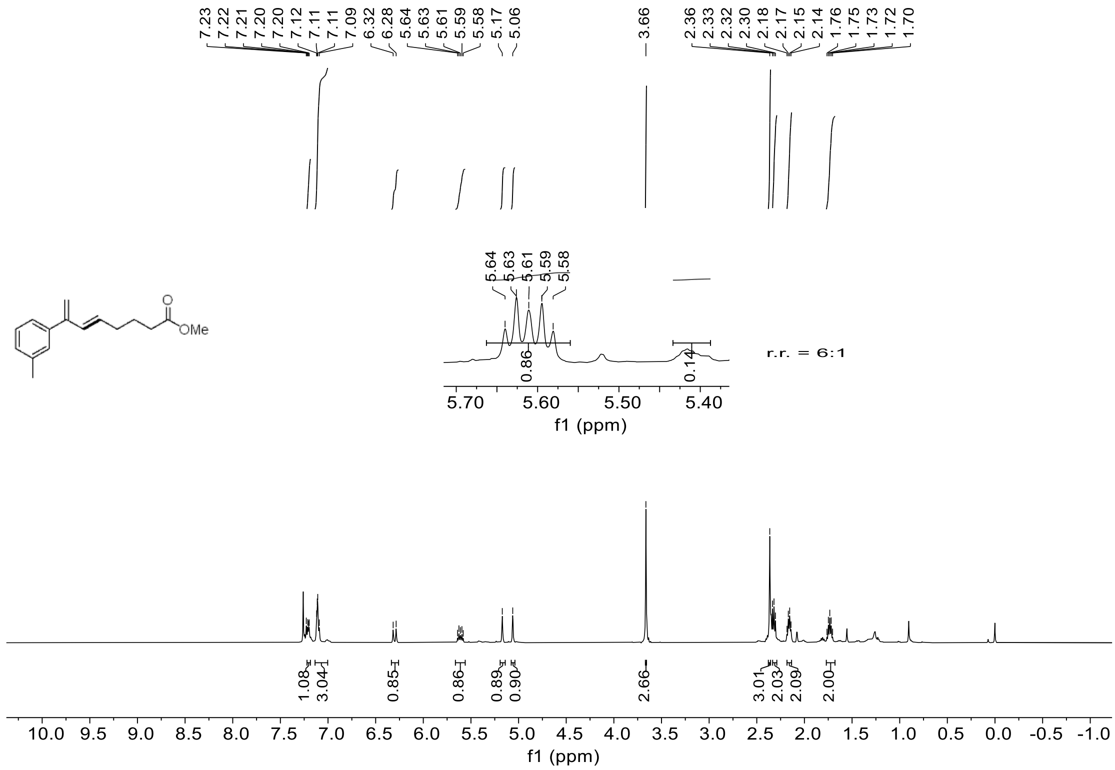

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **10b**



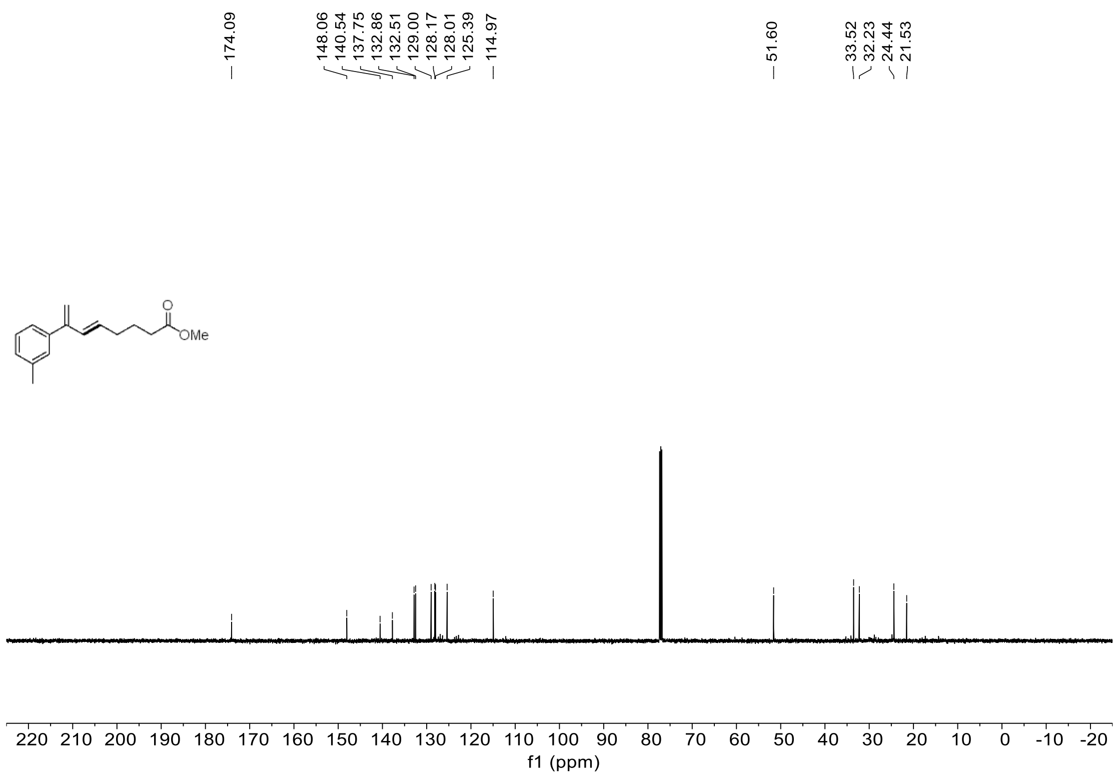

**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **11b**



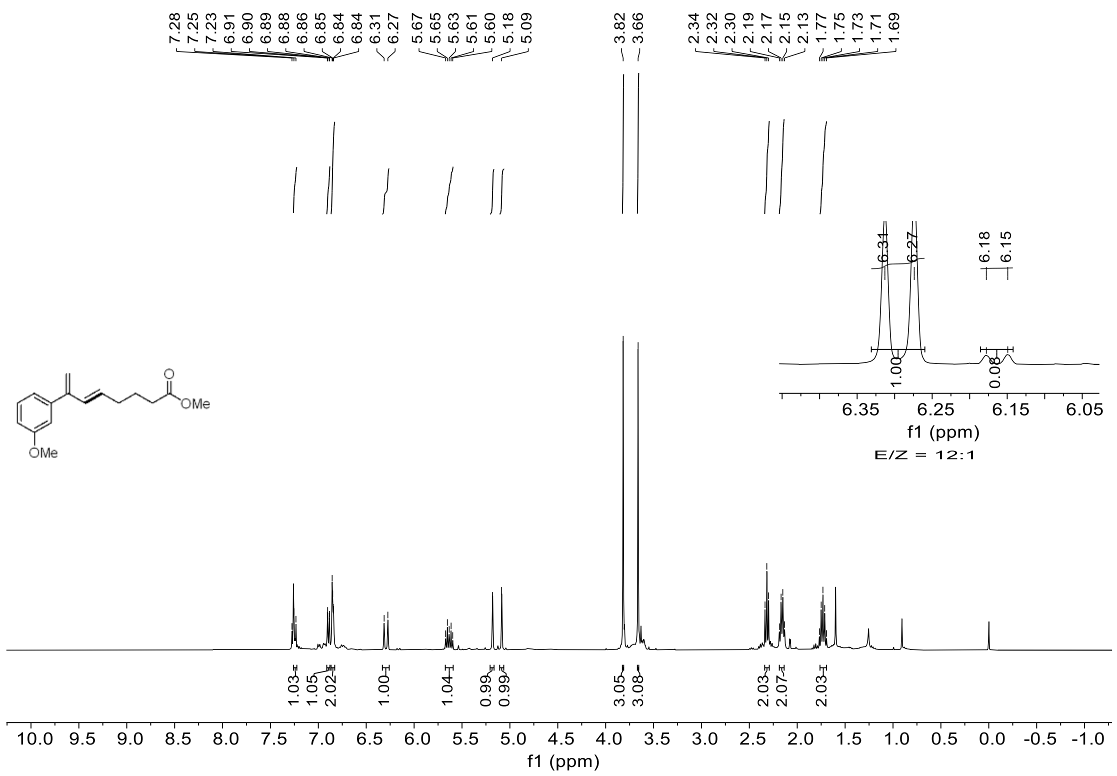

**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **11b**



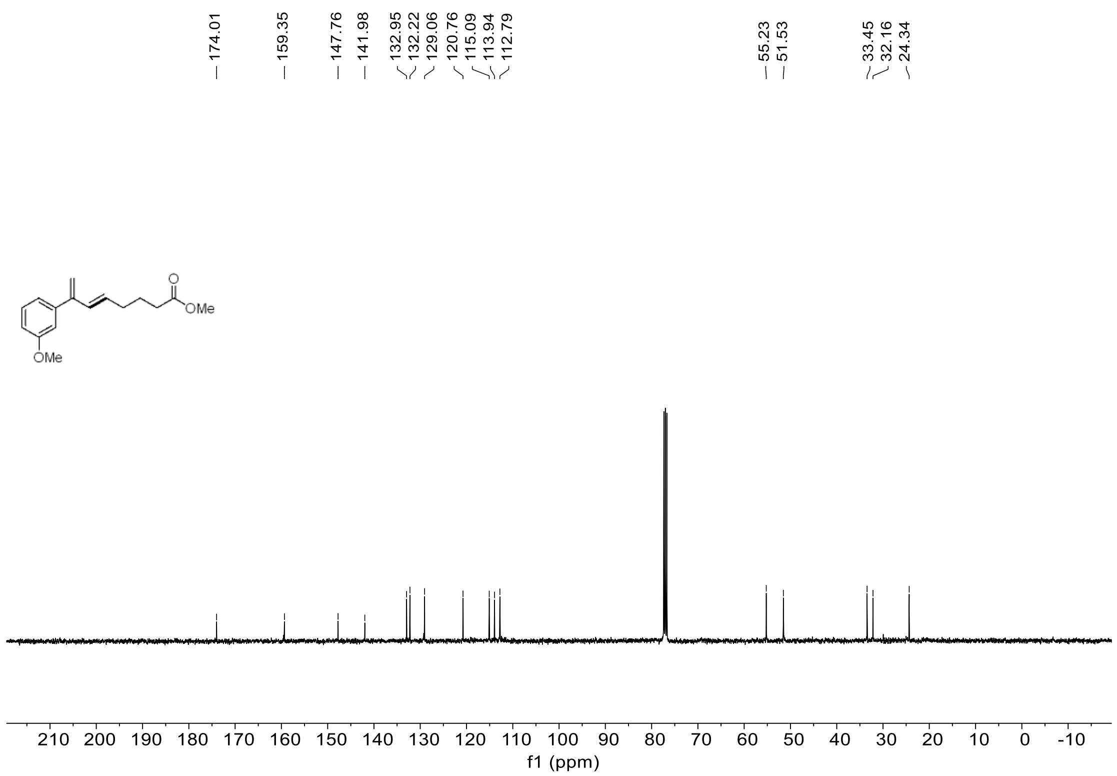
$^{1}$**H NMR** (500 MHz, $CDCl_3$) spectra of **12b**



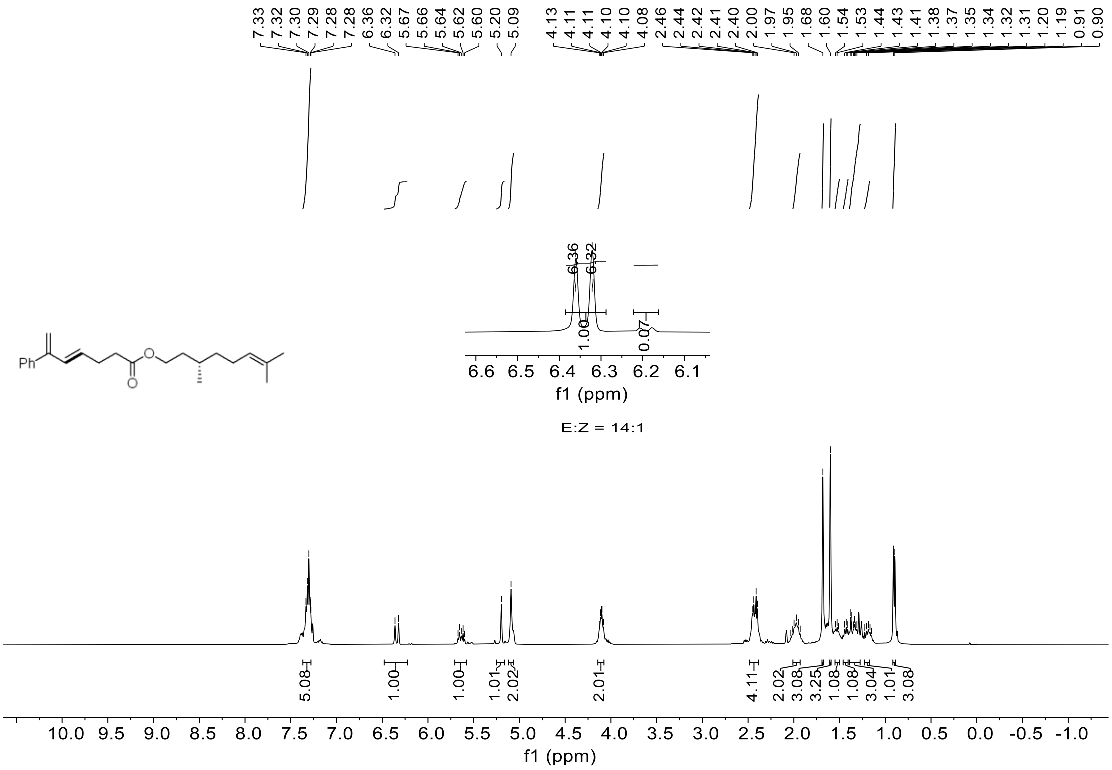
$^{13}$**C NMR** (126 MHz, $CDCl_3$) spectra of **12b**



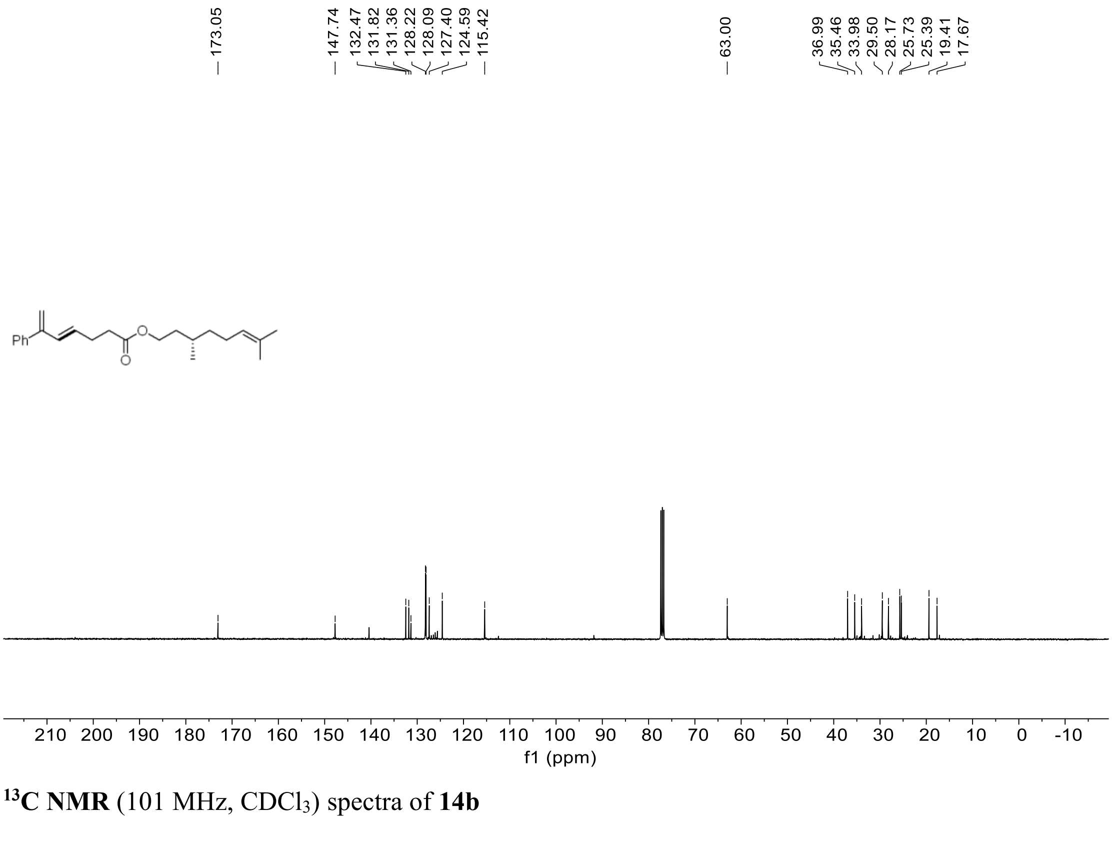
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **13b**



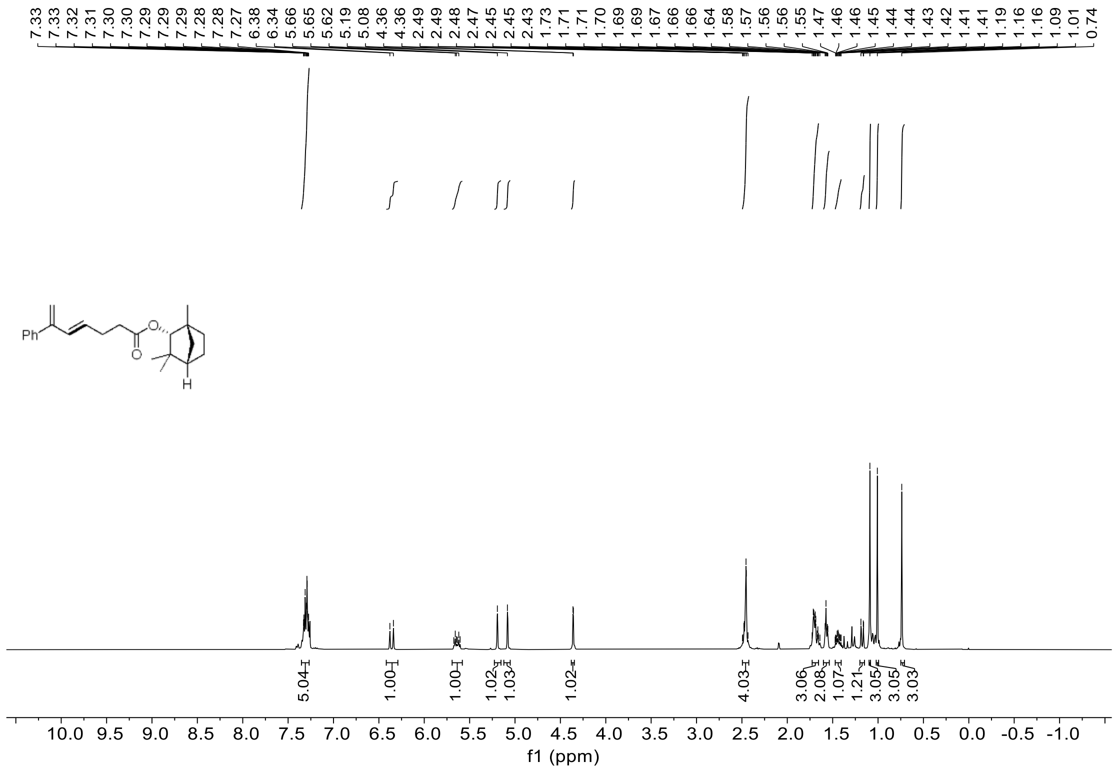
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **13b**



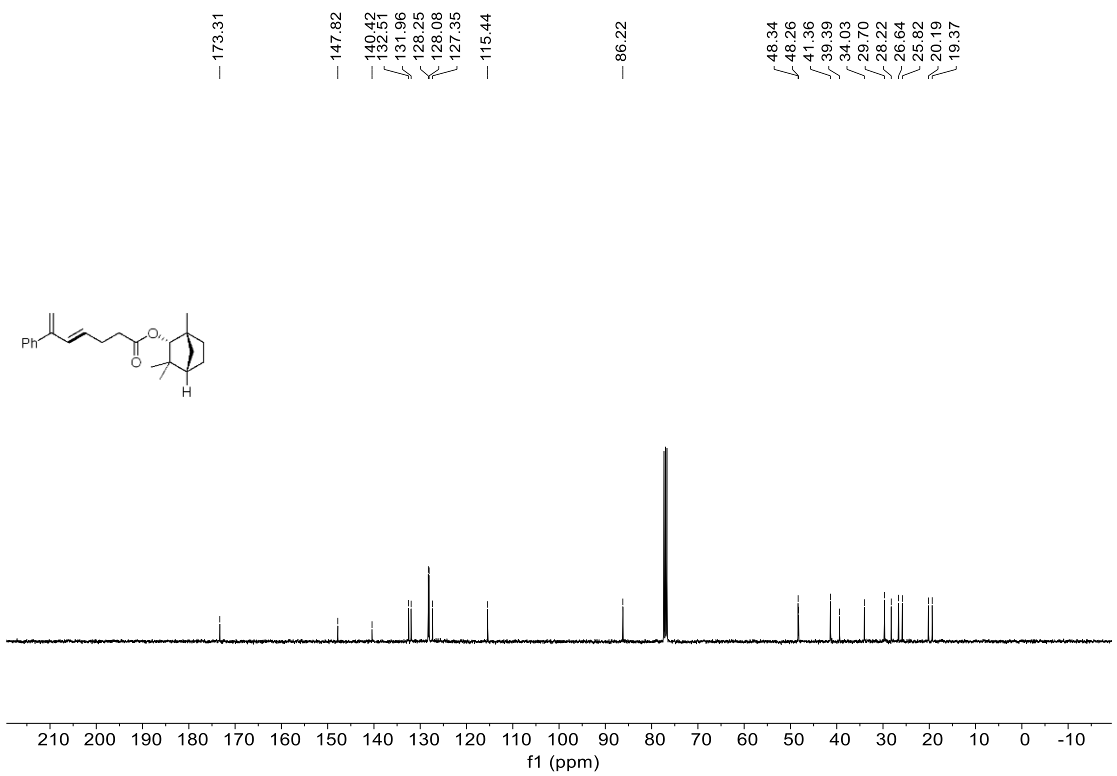

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **14b**



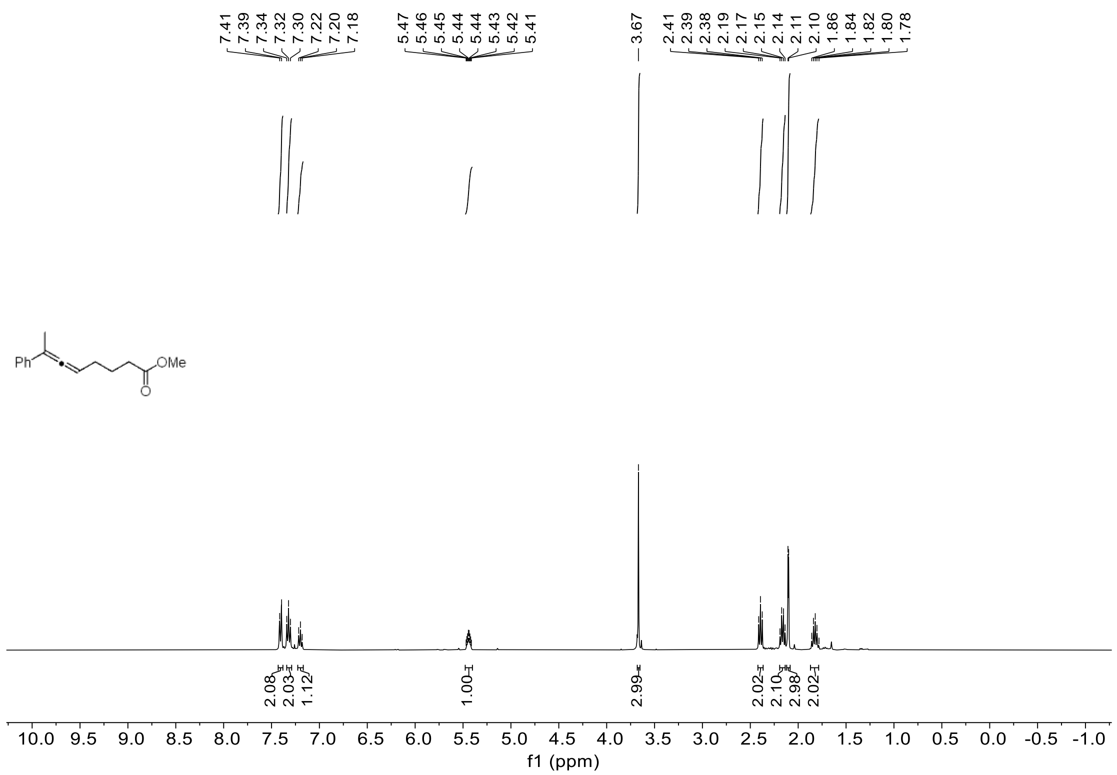

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **14b**



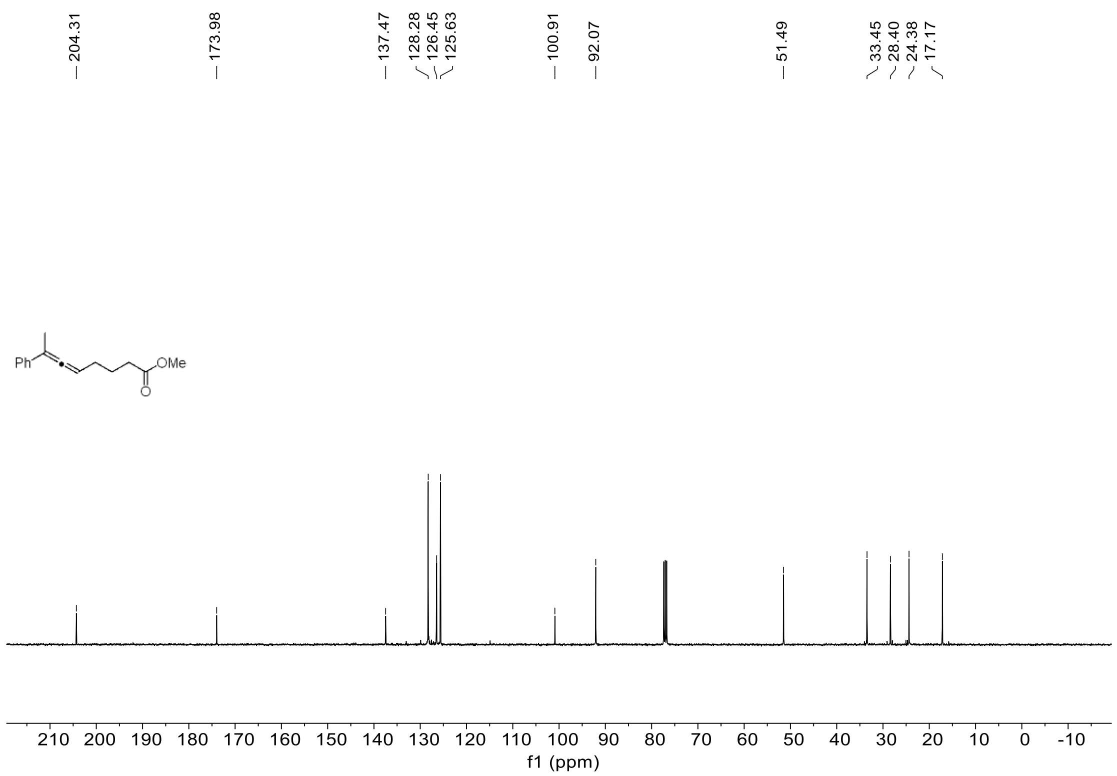
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **15b**



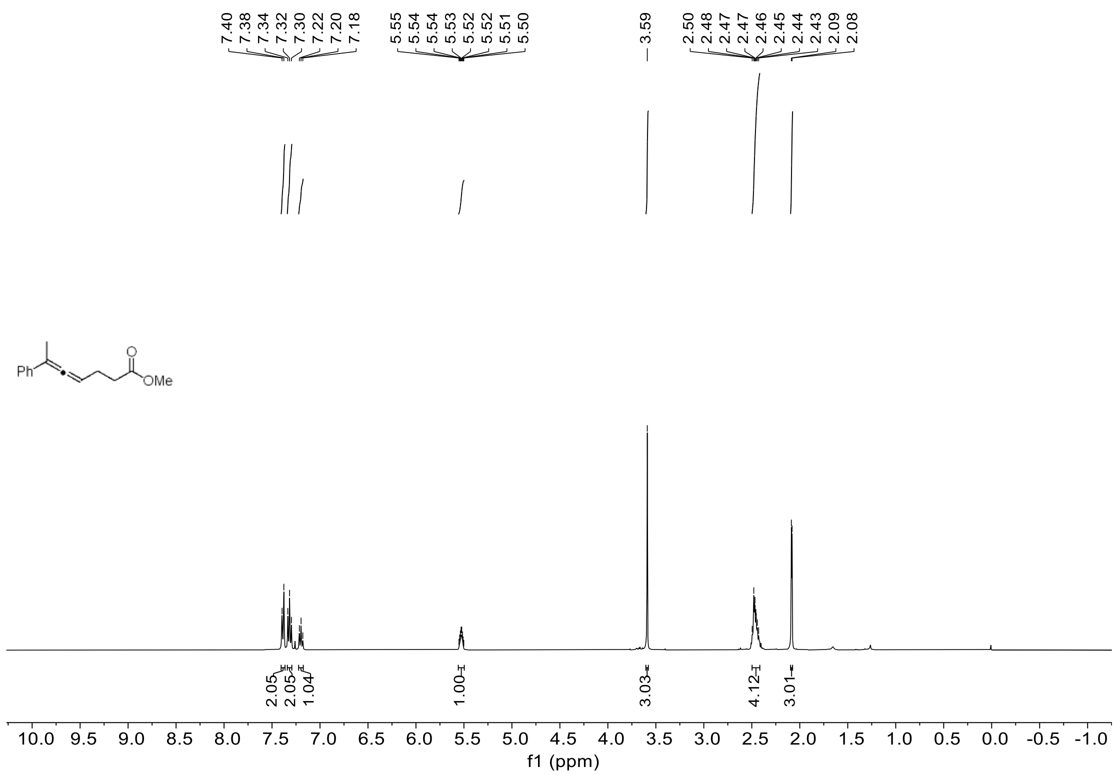
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **15b**



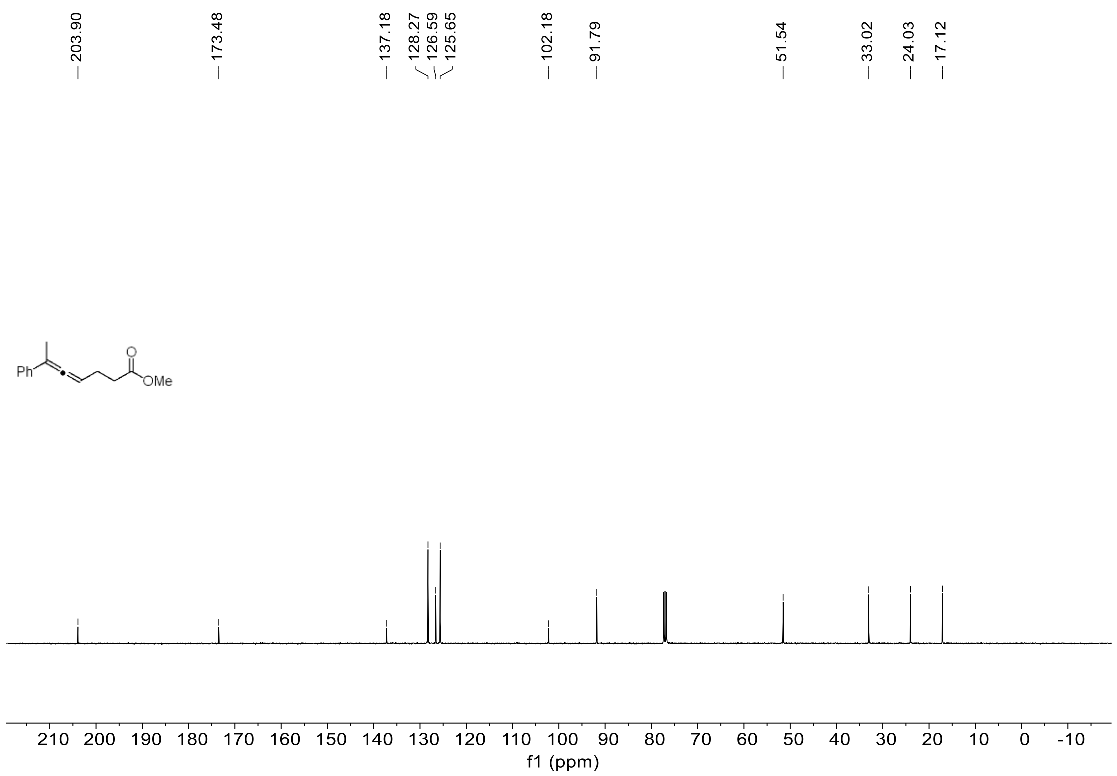
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **2c**



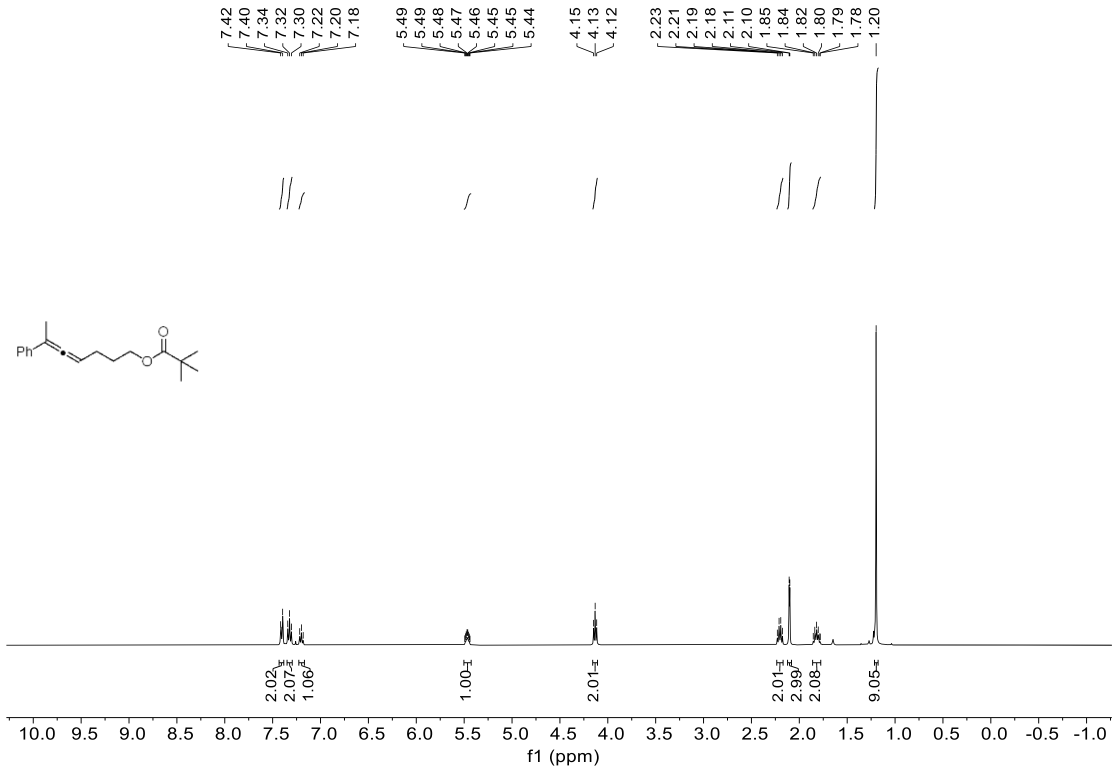
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **2c**



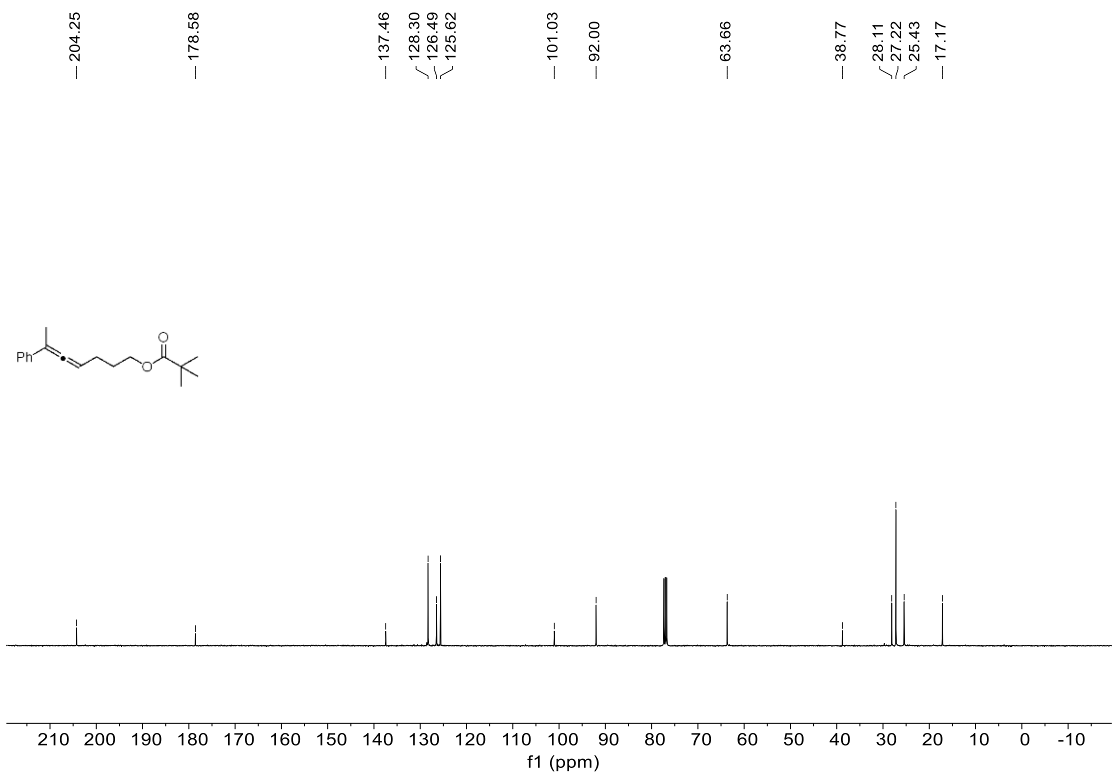

**¹H NMR** (400 MHz, $CDCl_3$) spectra of **3c**



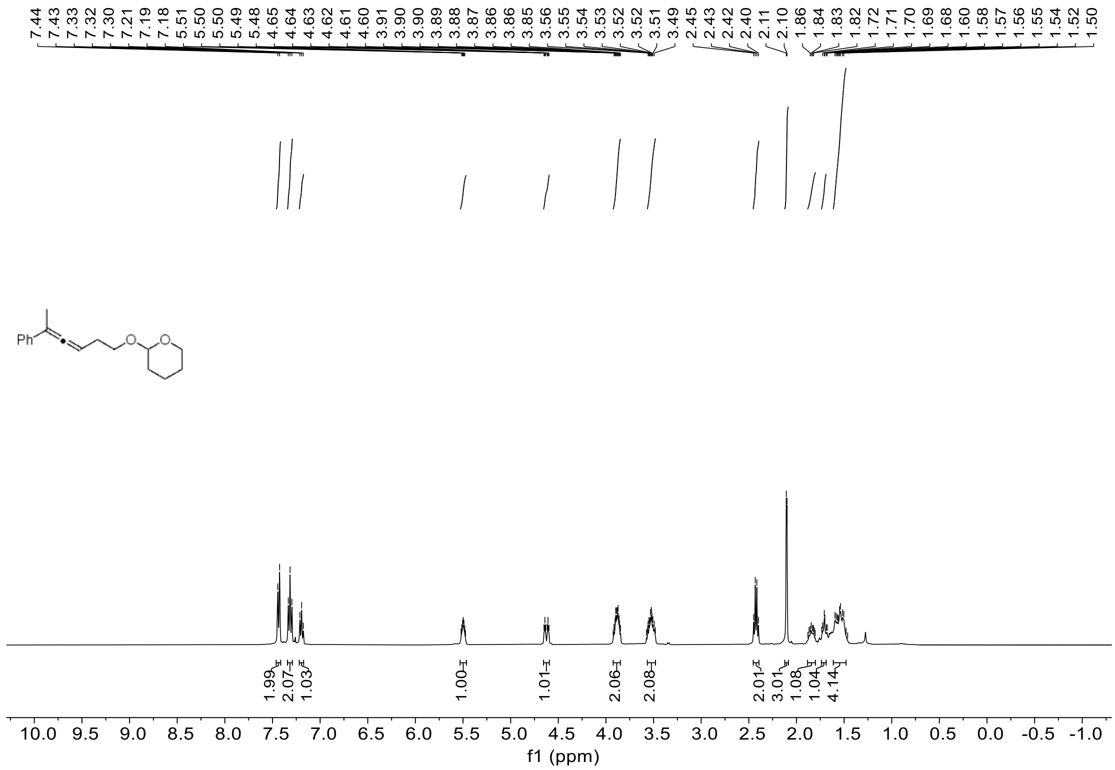

**¹³C NMR** (101 MHz, $CDCl_3$) spectra of **3c**



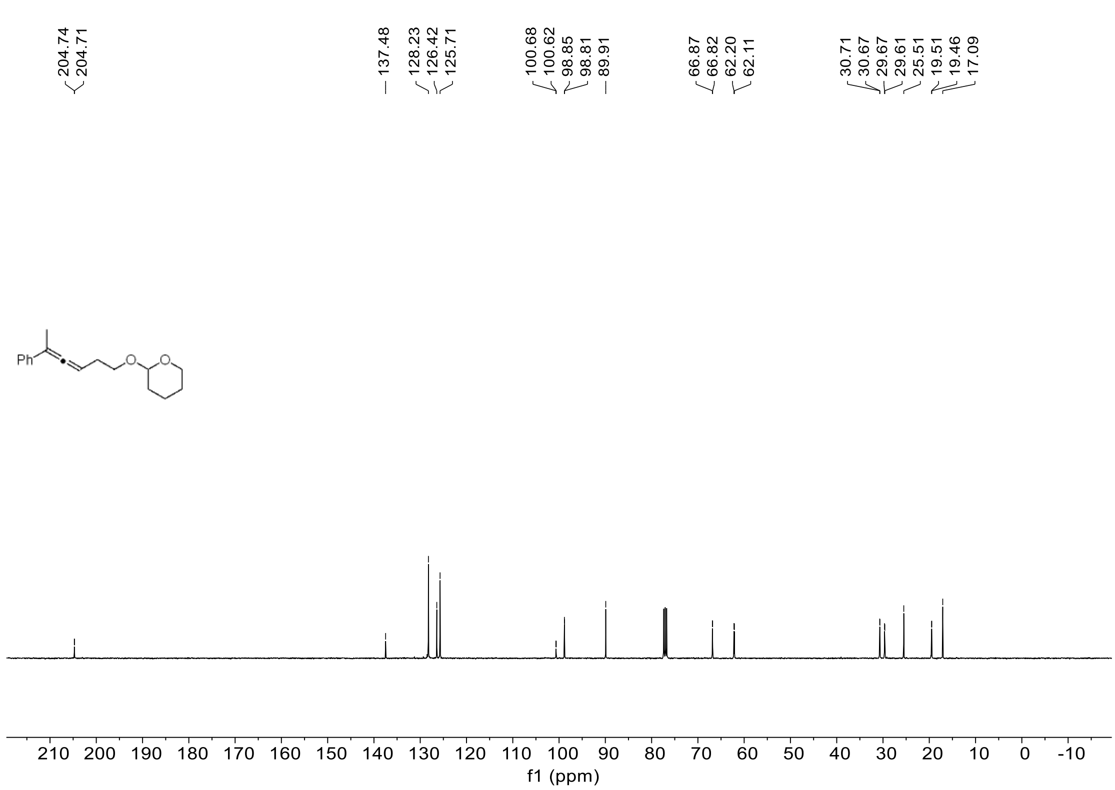
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **4c**



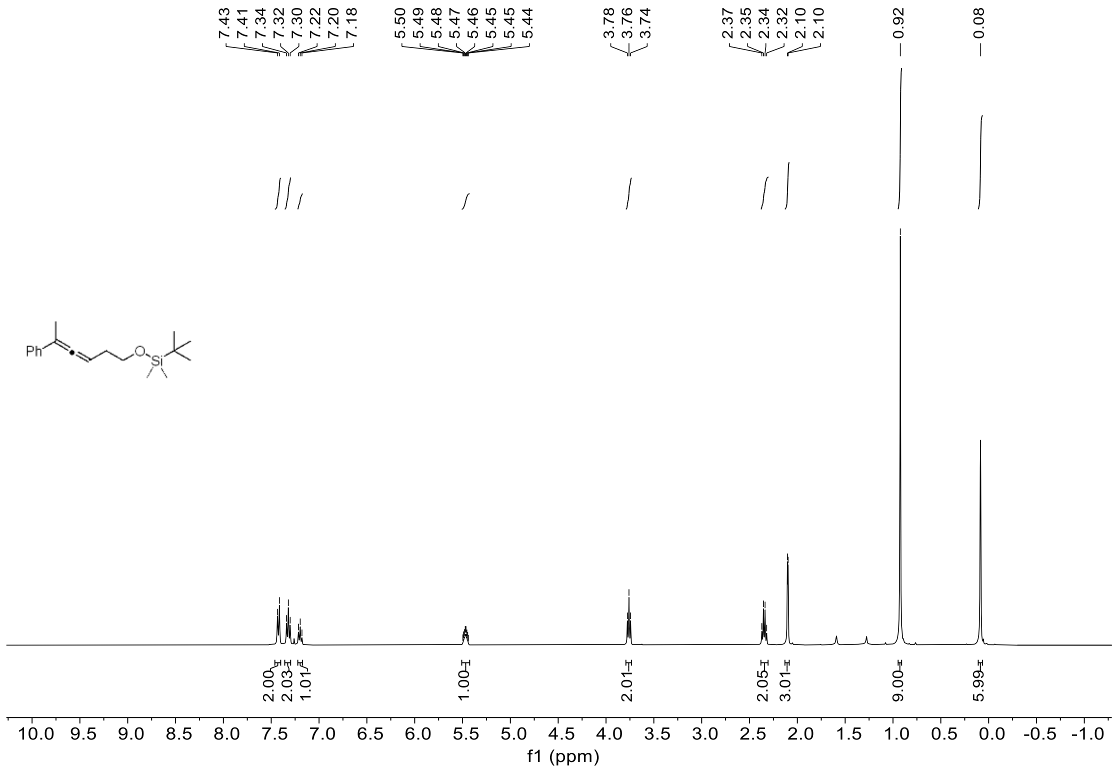
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **4c**



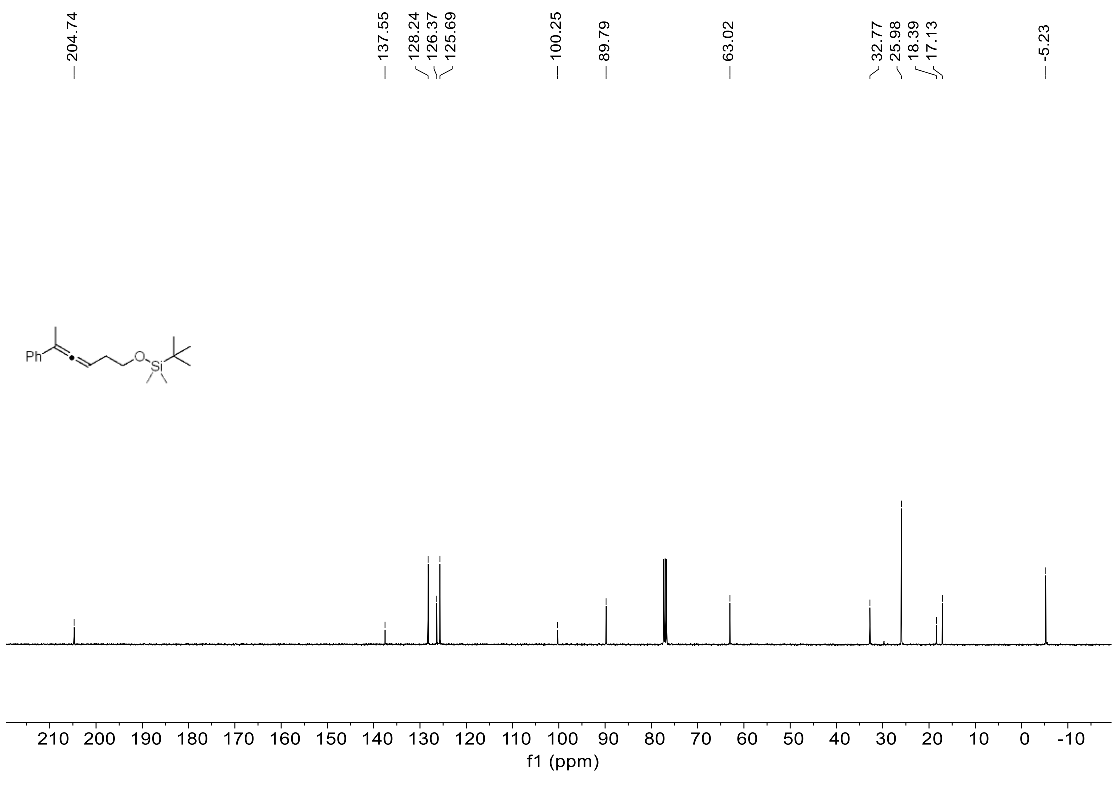
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **5c**



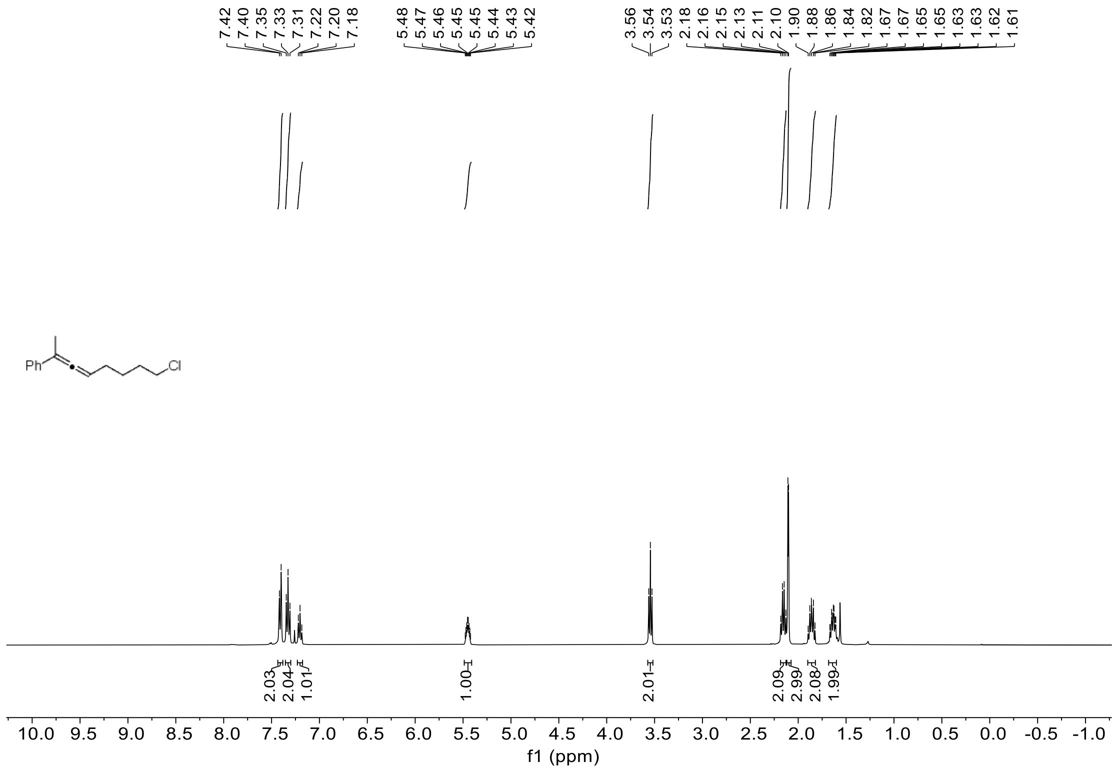
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **5c**



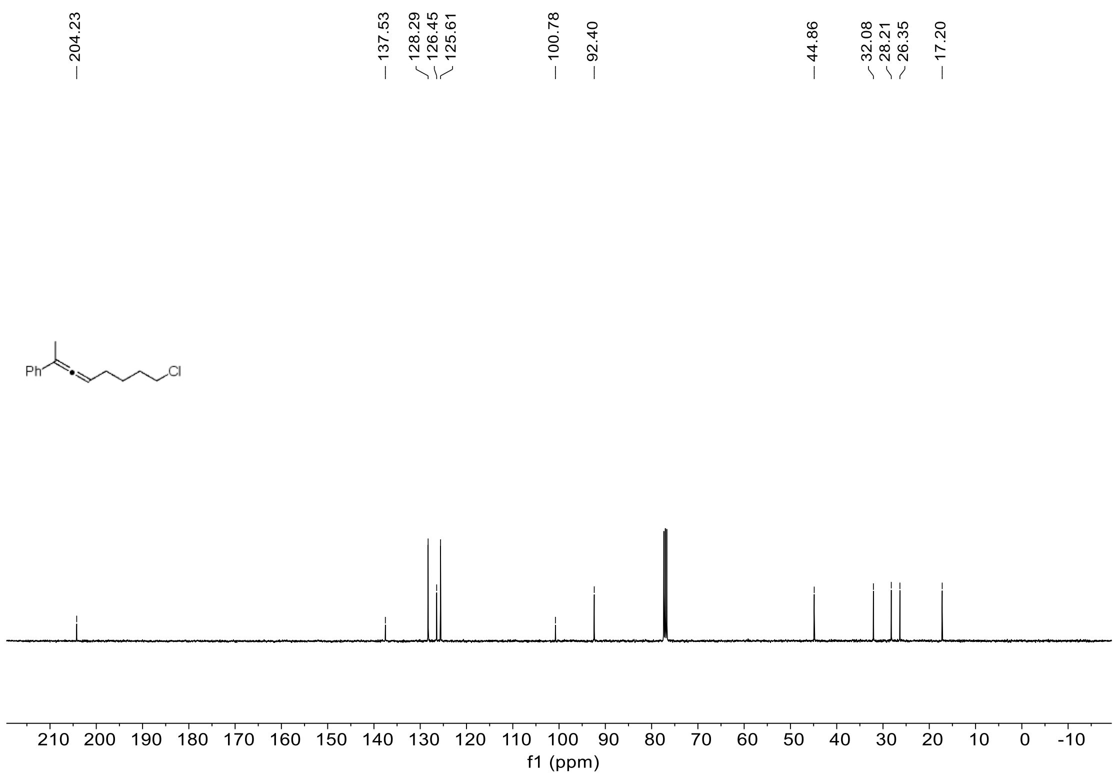
**¹H NMR** (400 MHz, $CDCl_3$) spectra of **6c**



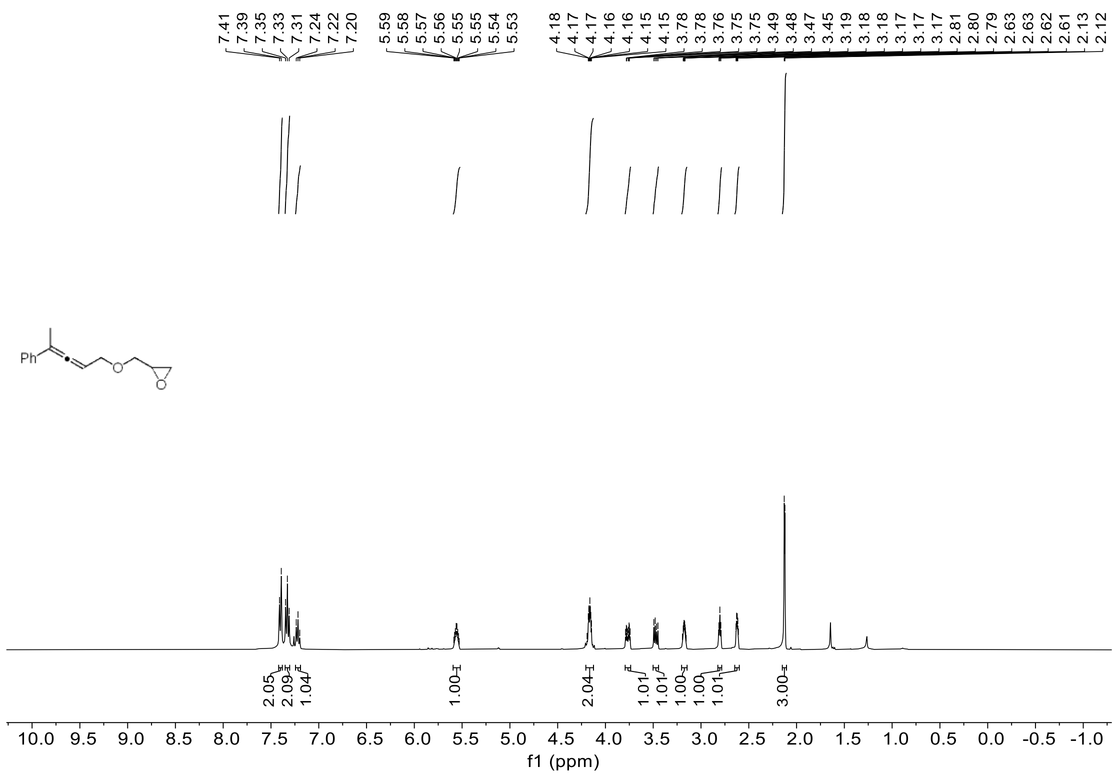
**¹³C NMR** (101 MHz, $CDCl_3$) spectra of **6c**



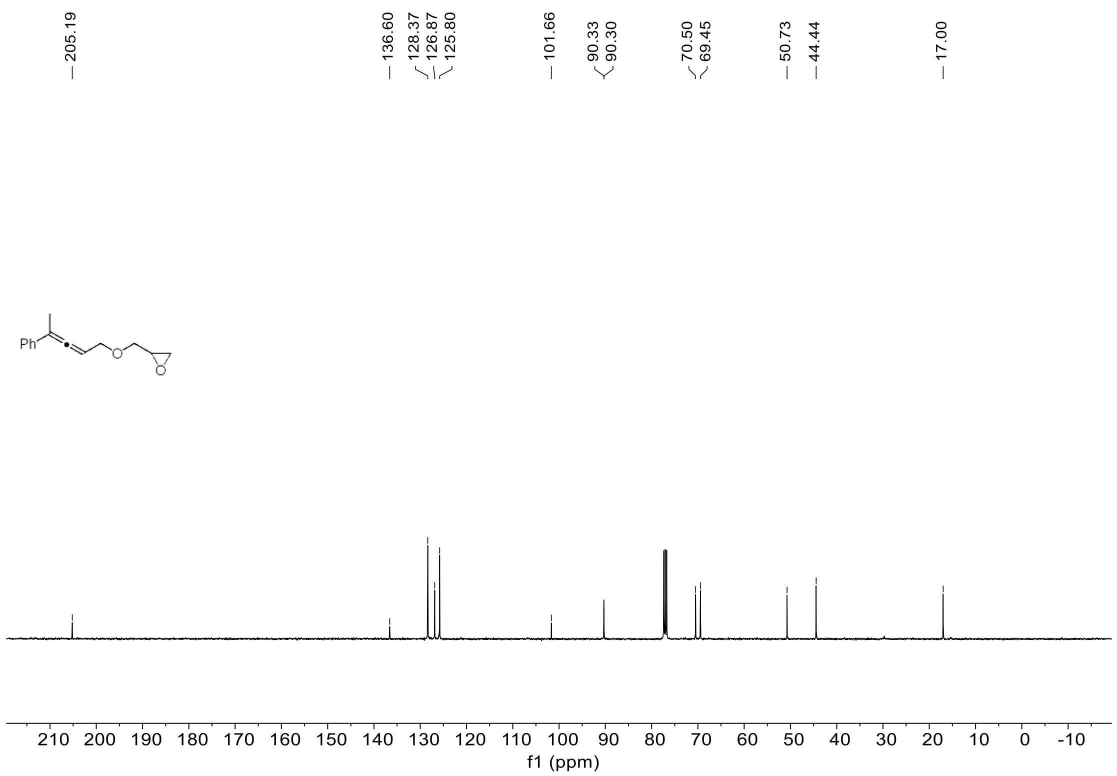

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **7c**



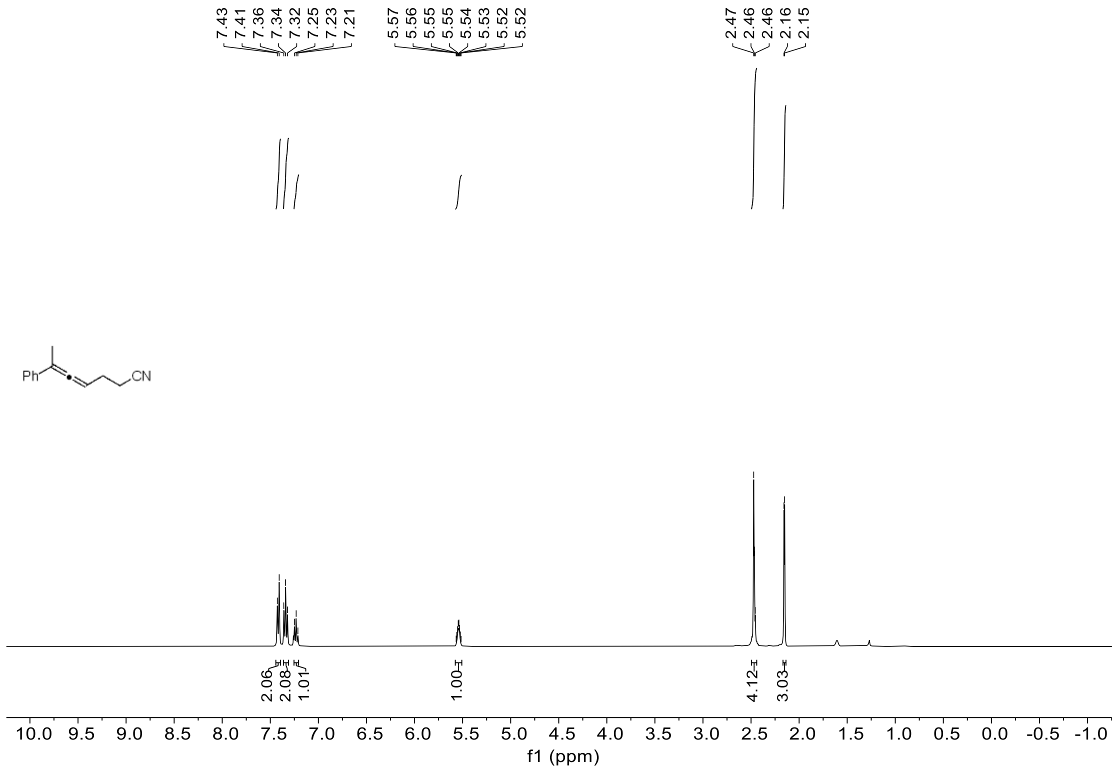

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **7c**



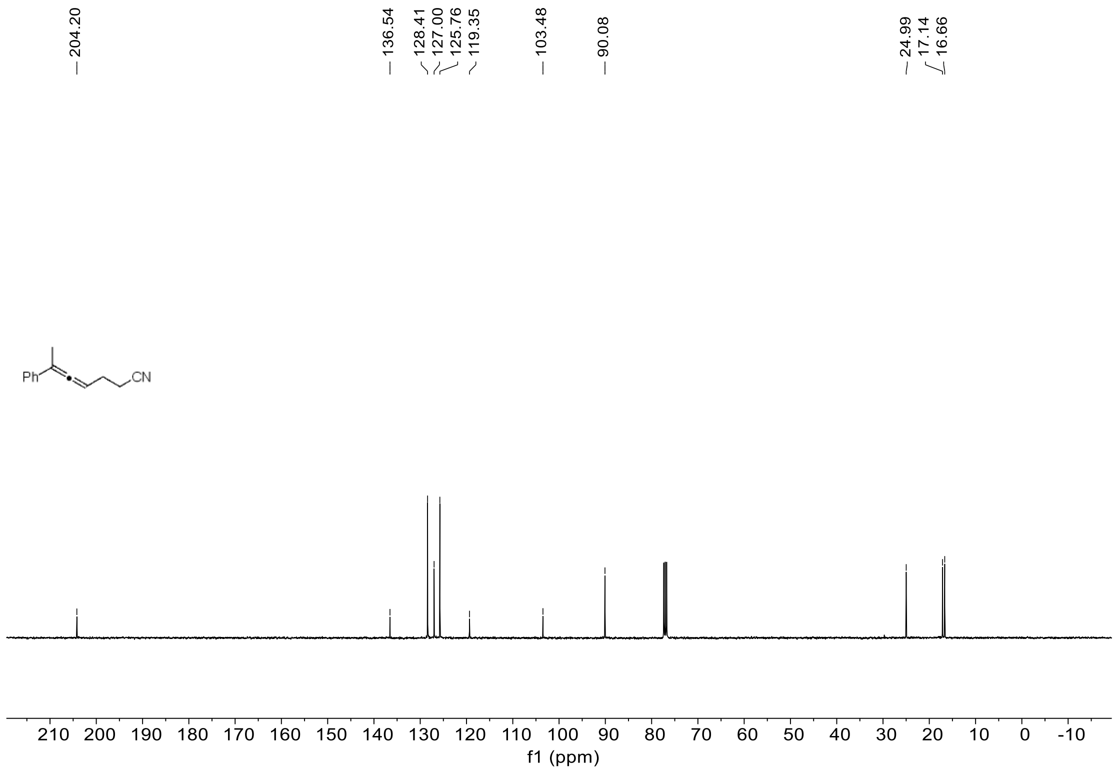
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **8c**



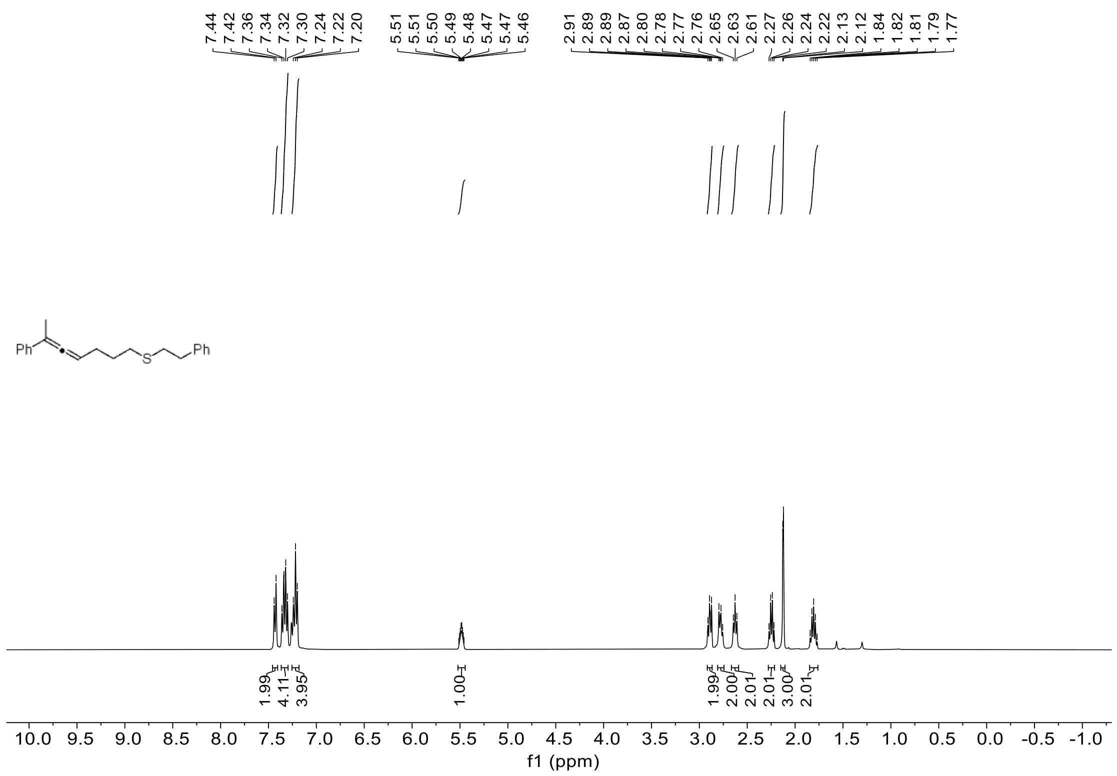
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **8c**



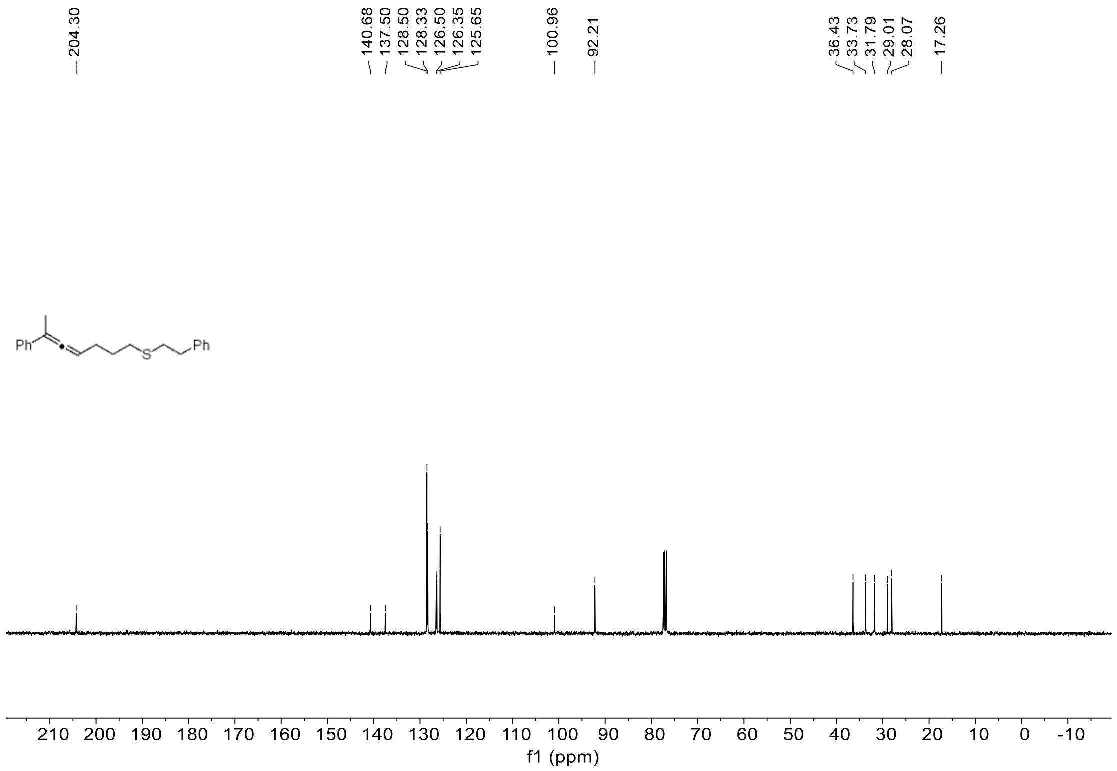
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **9c**



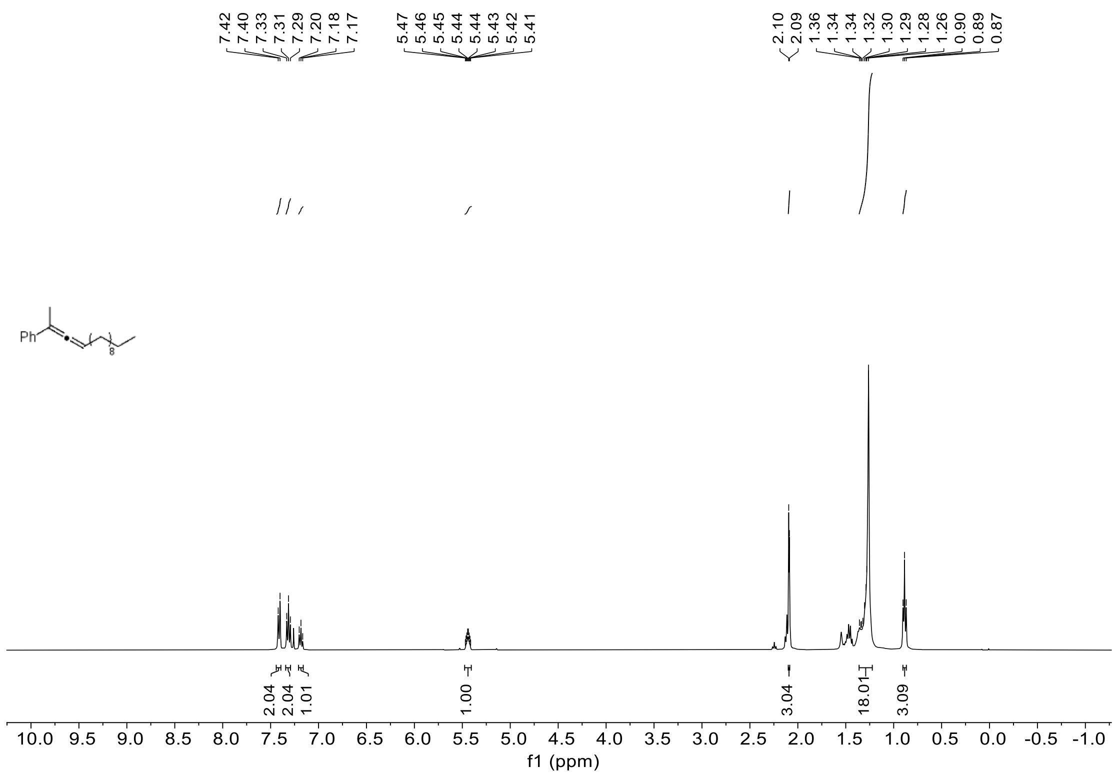
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **9c**



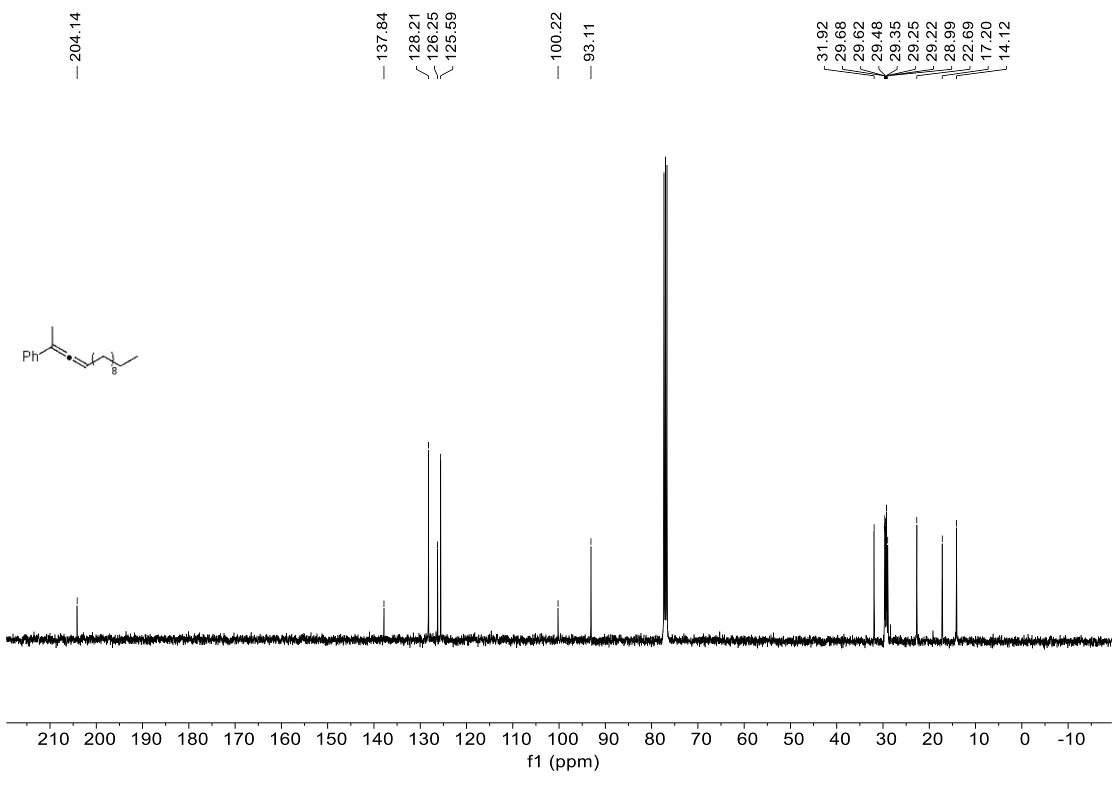
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **10c**



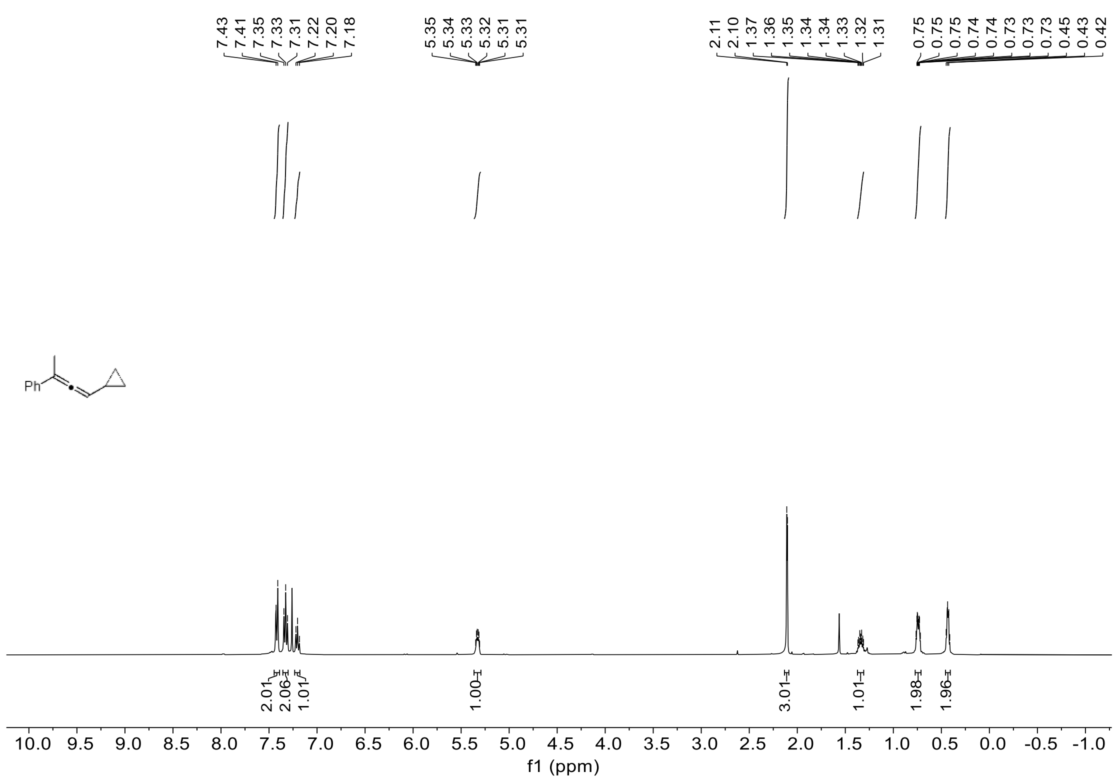
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **10c**



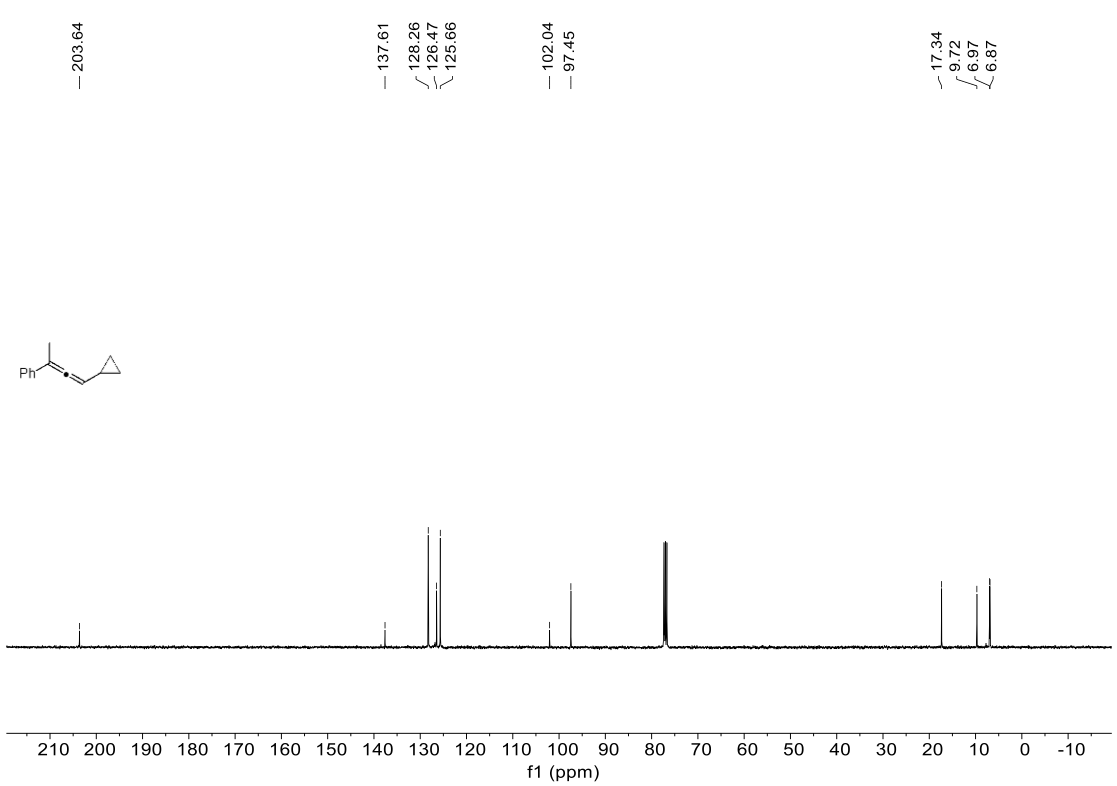
**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **11c**



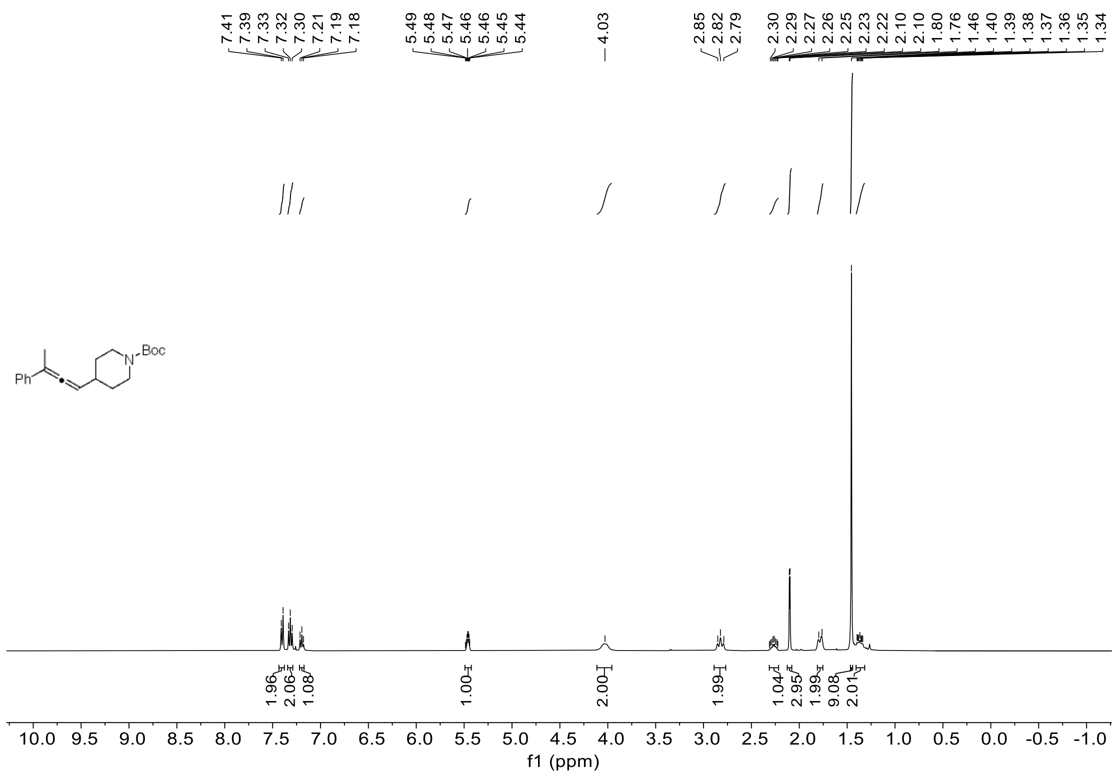
**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **11c**



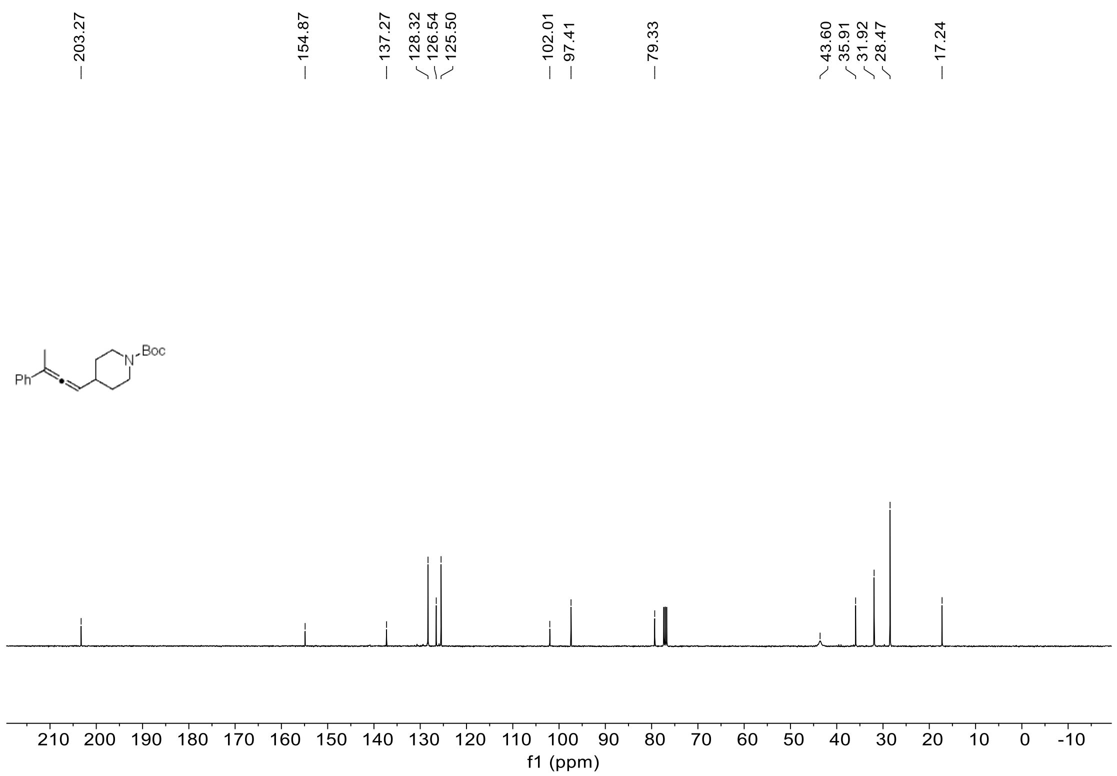

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **12c**



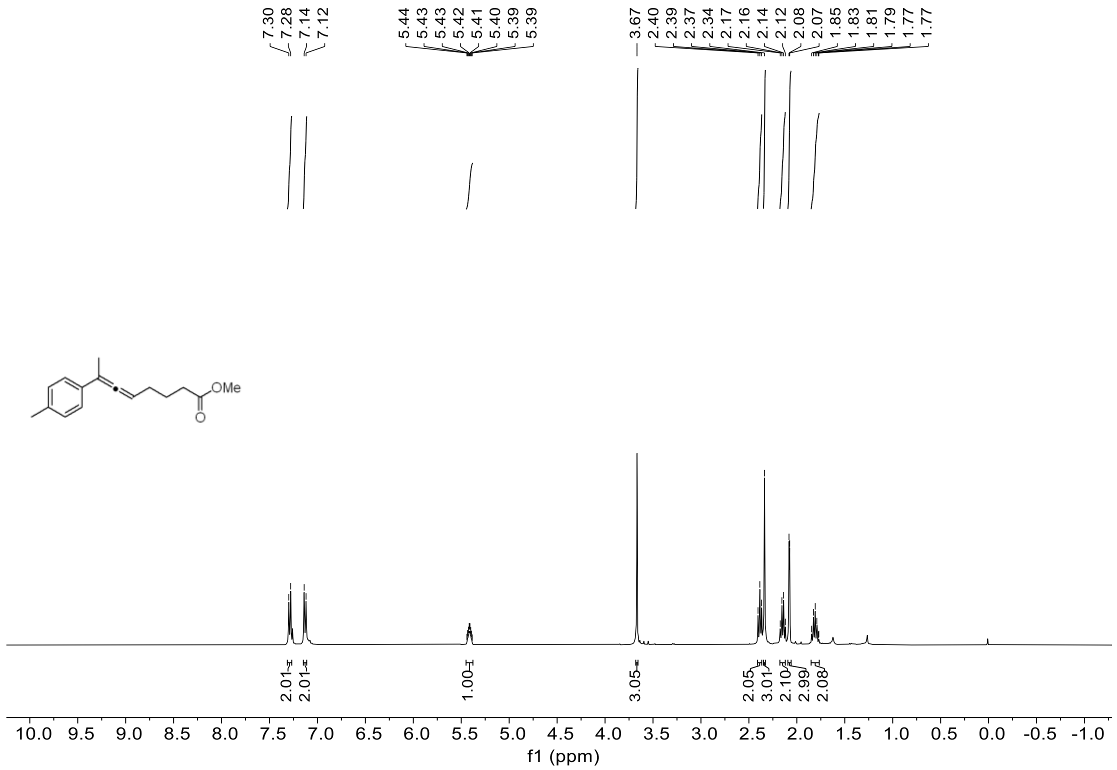

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **12c**



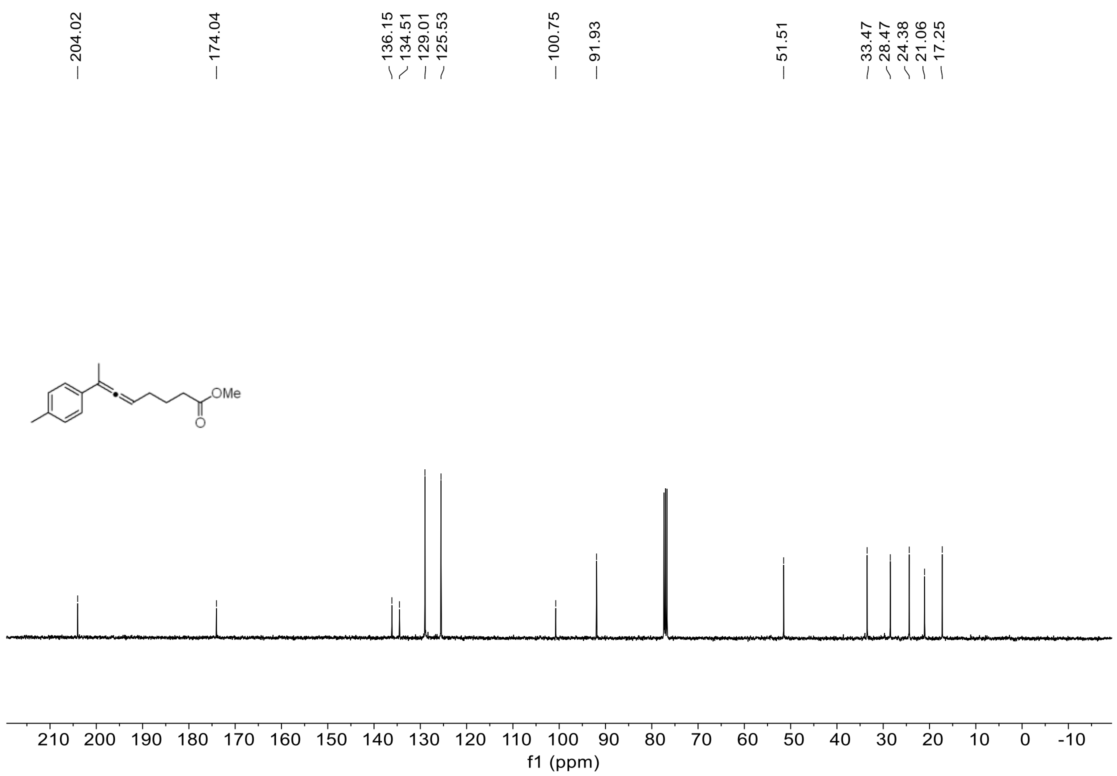
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **13c**



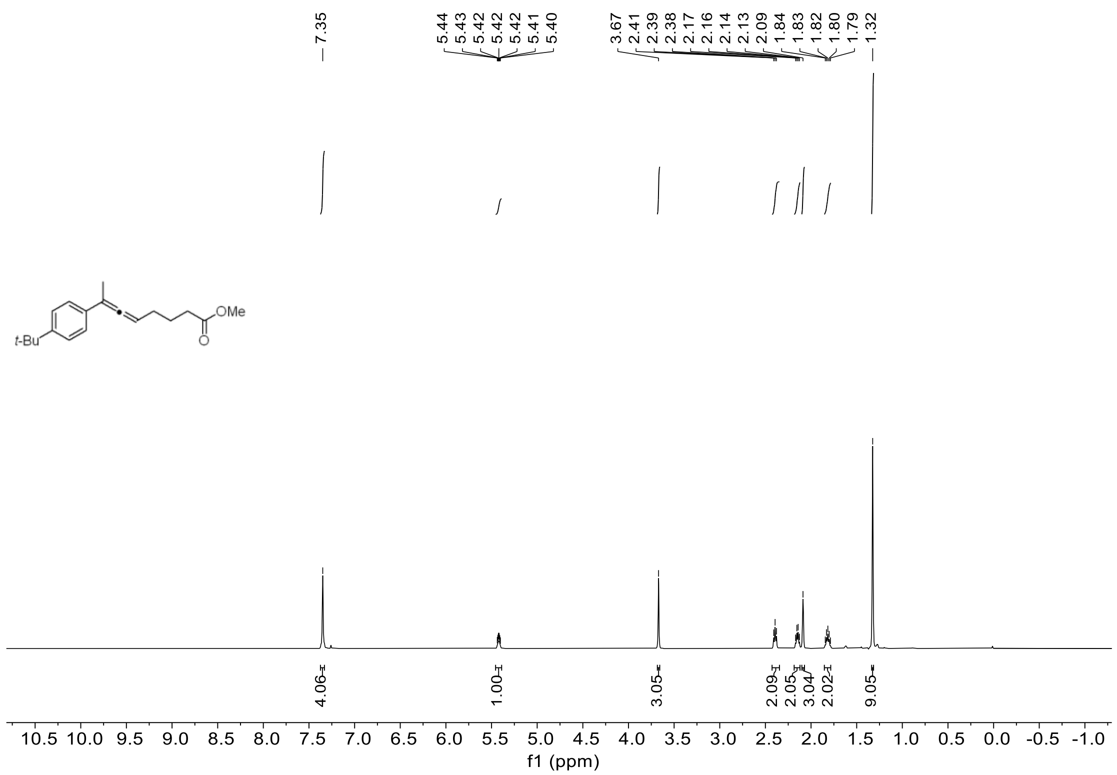
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **13c**



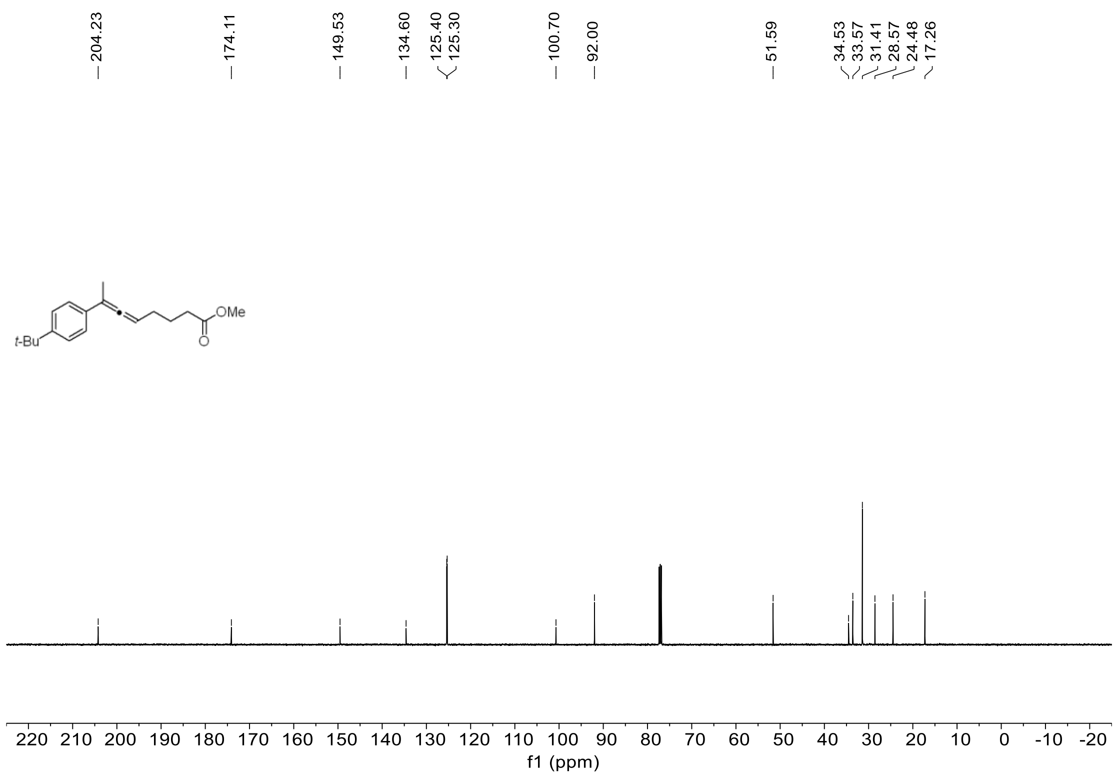

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **14c**



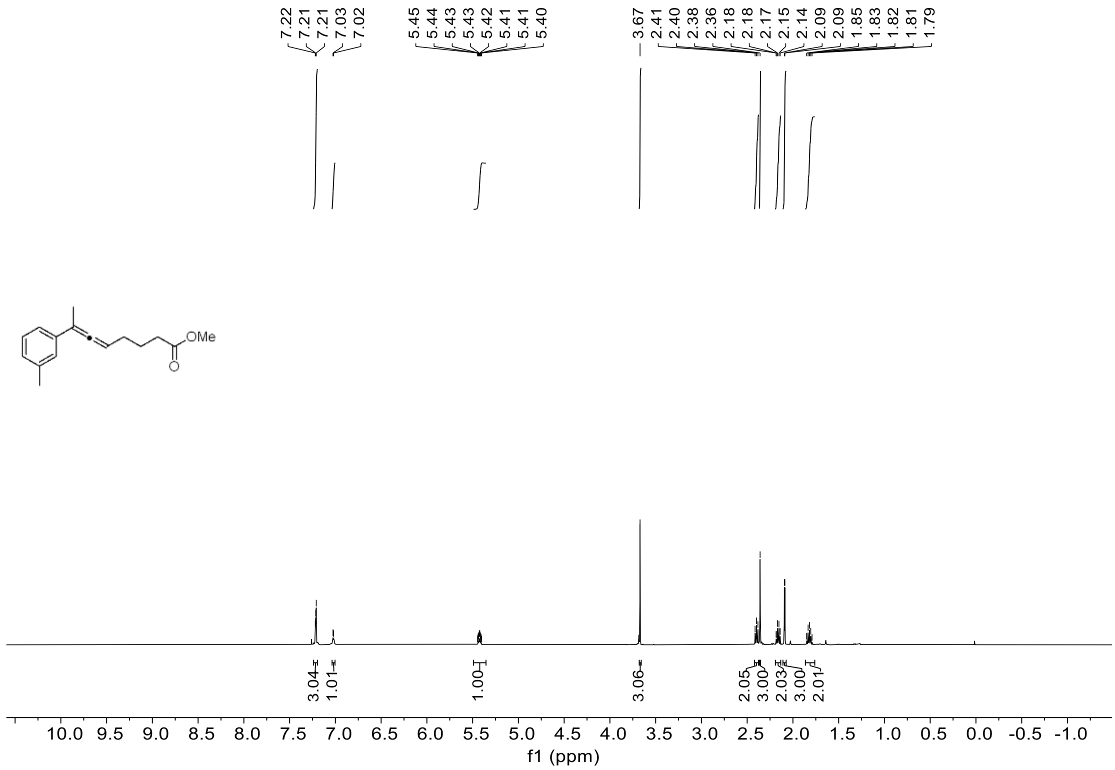

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **14c**



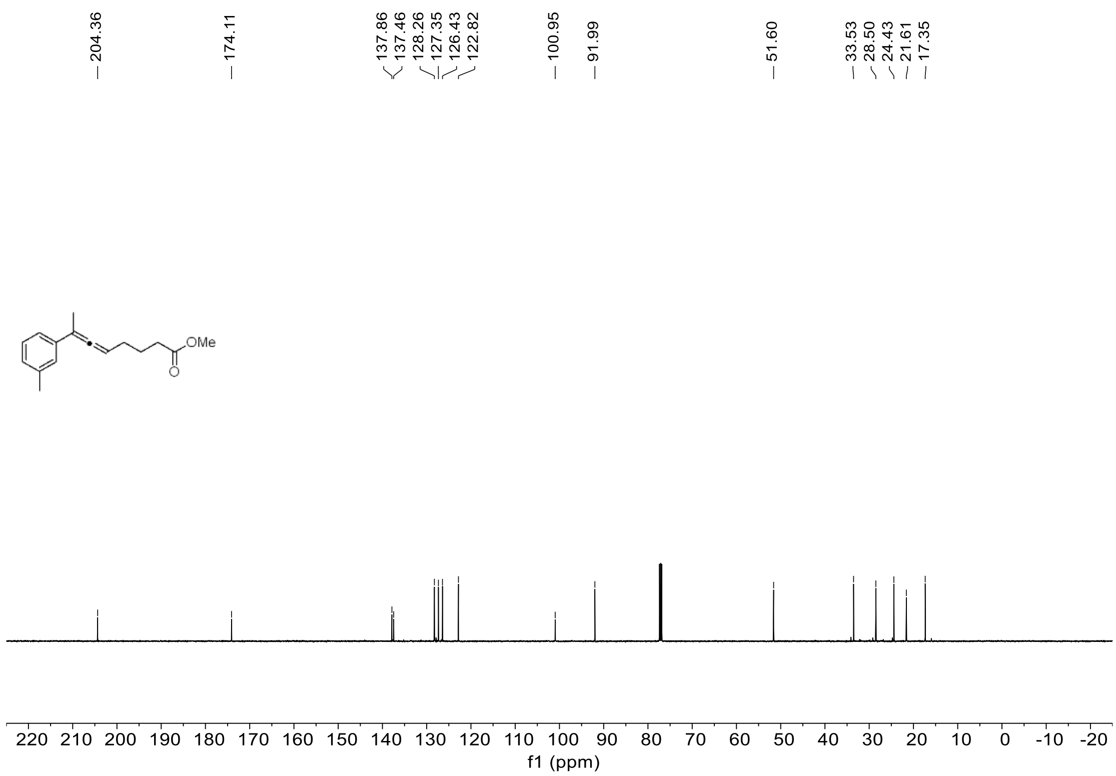
**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **15c**



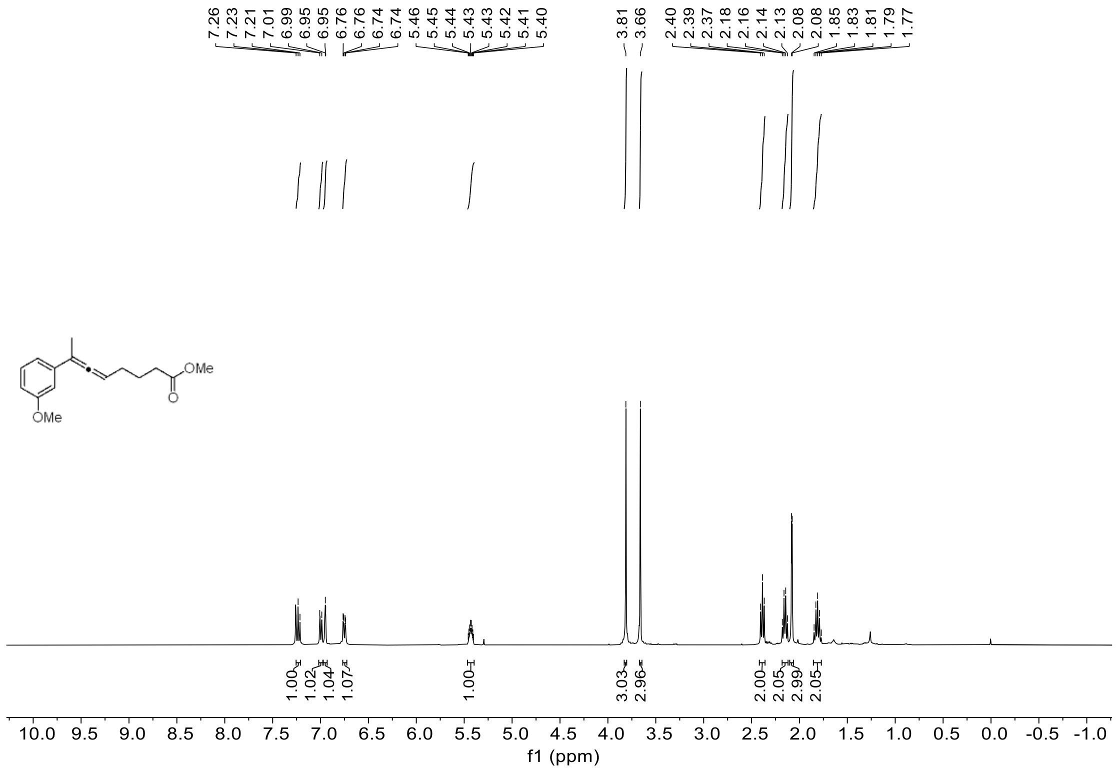
**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **15c**



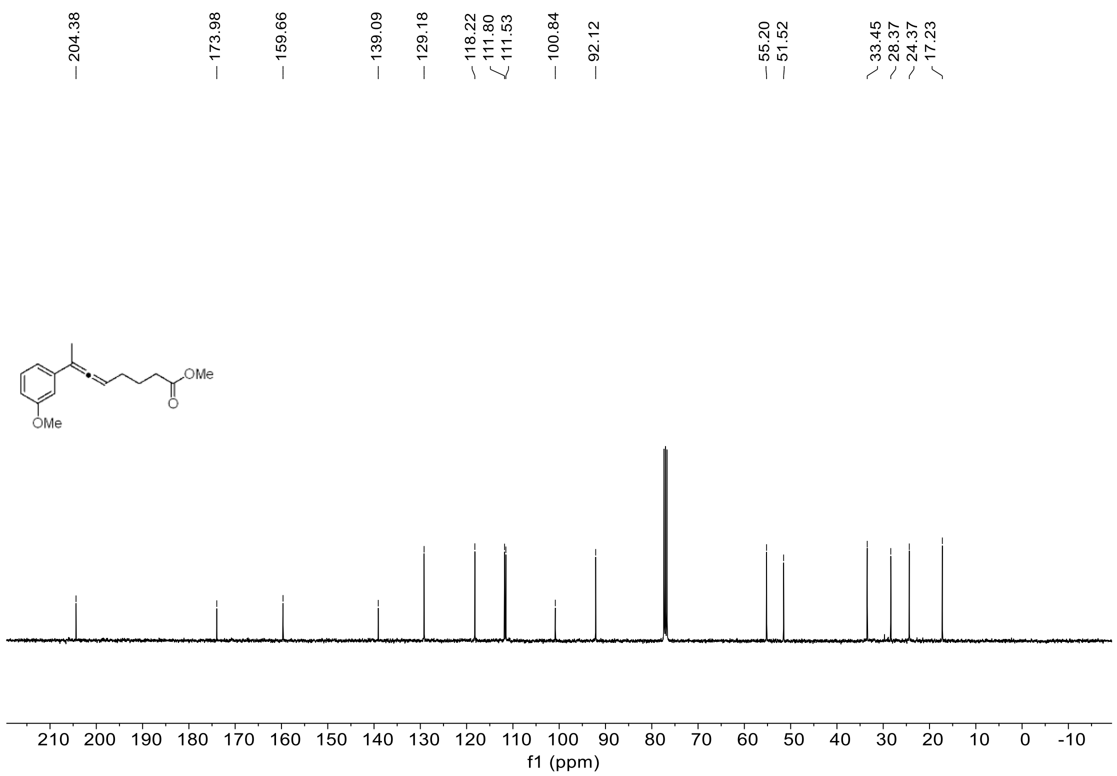
**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **16c**



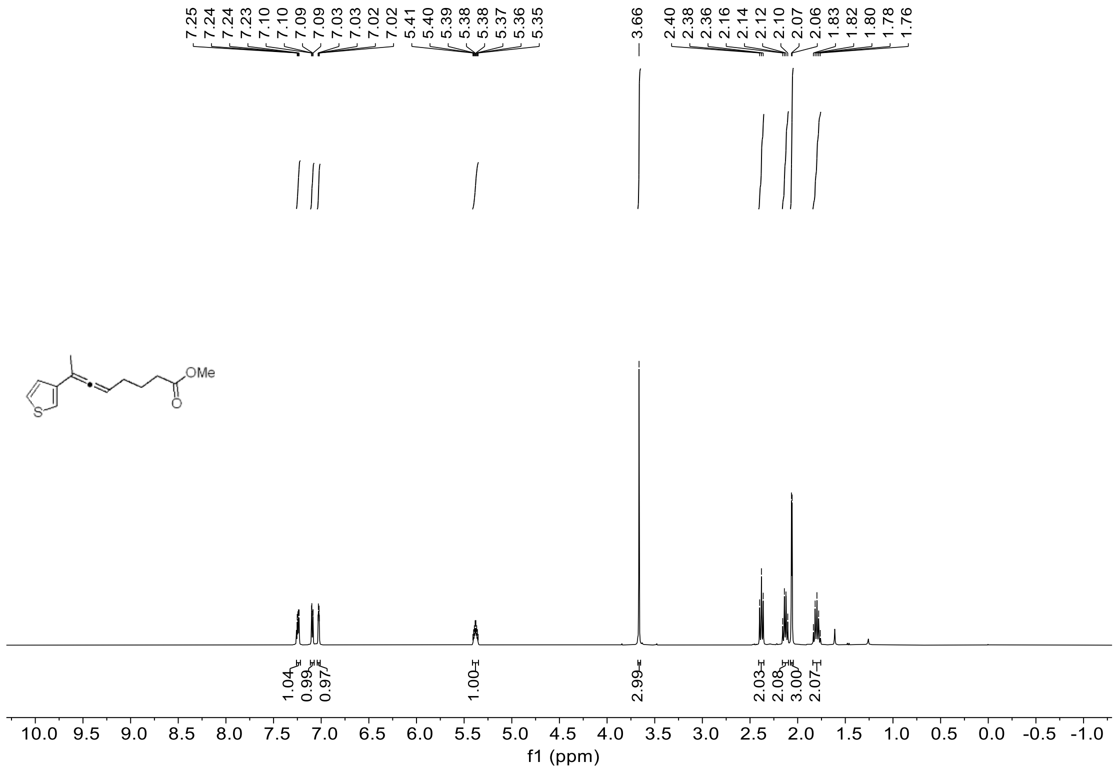
**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **16c**



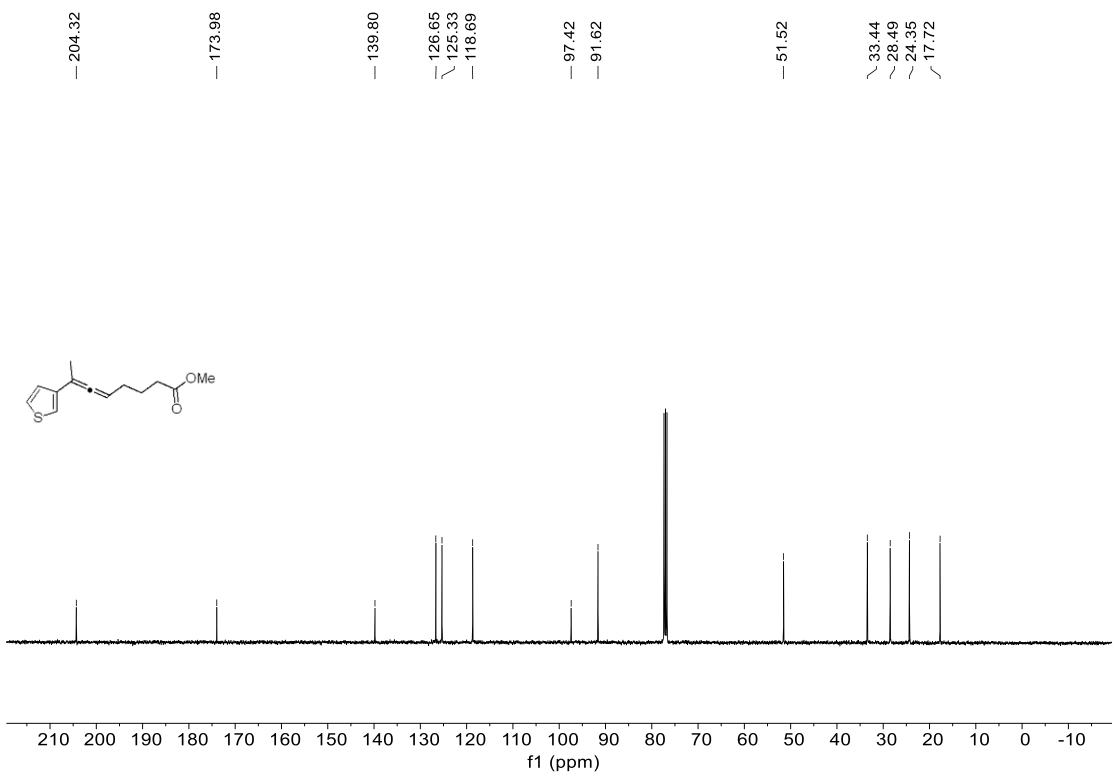
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **17c**



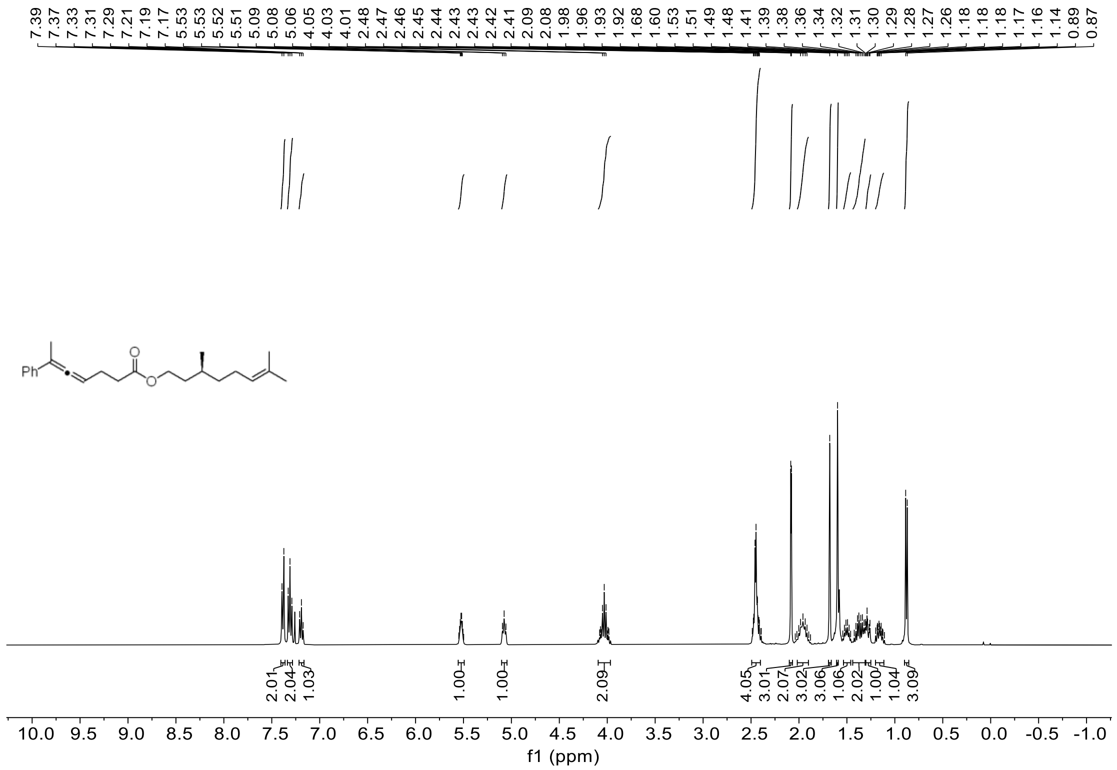
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **17c**



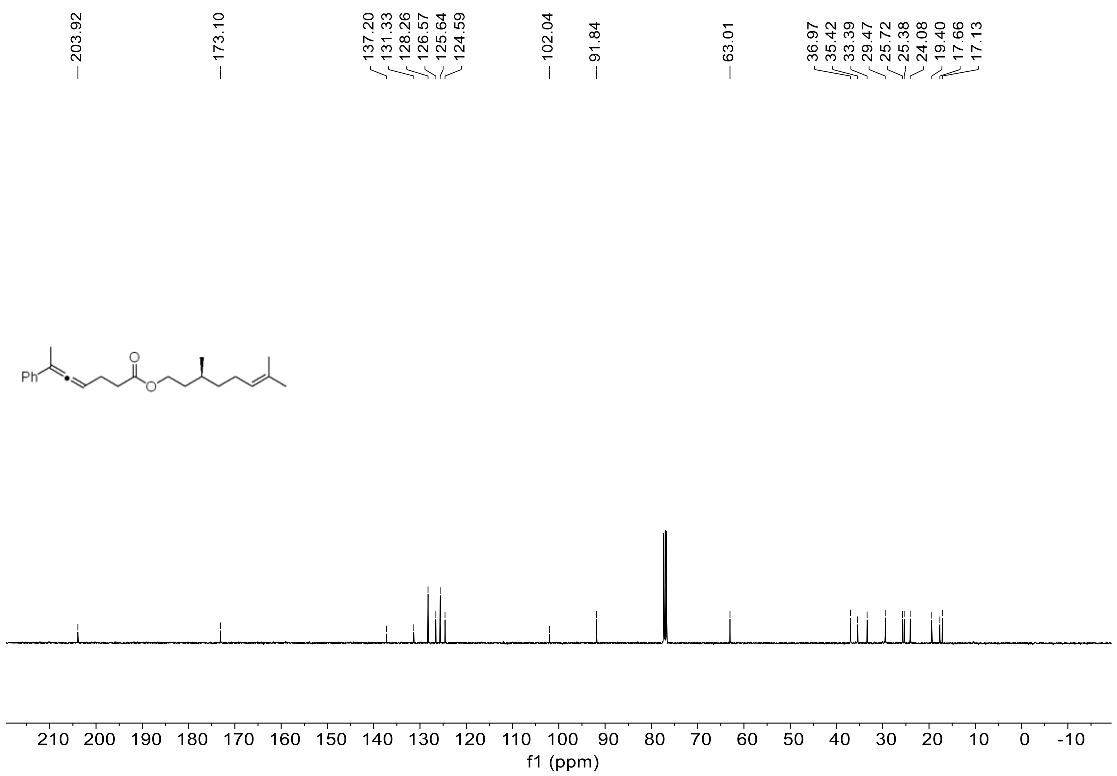

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **18c**



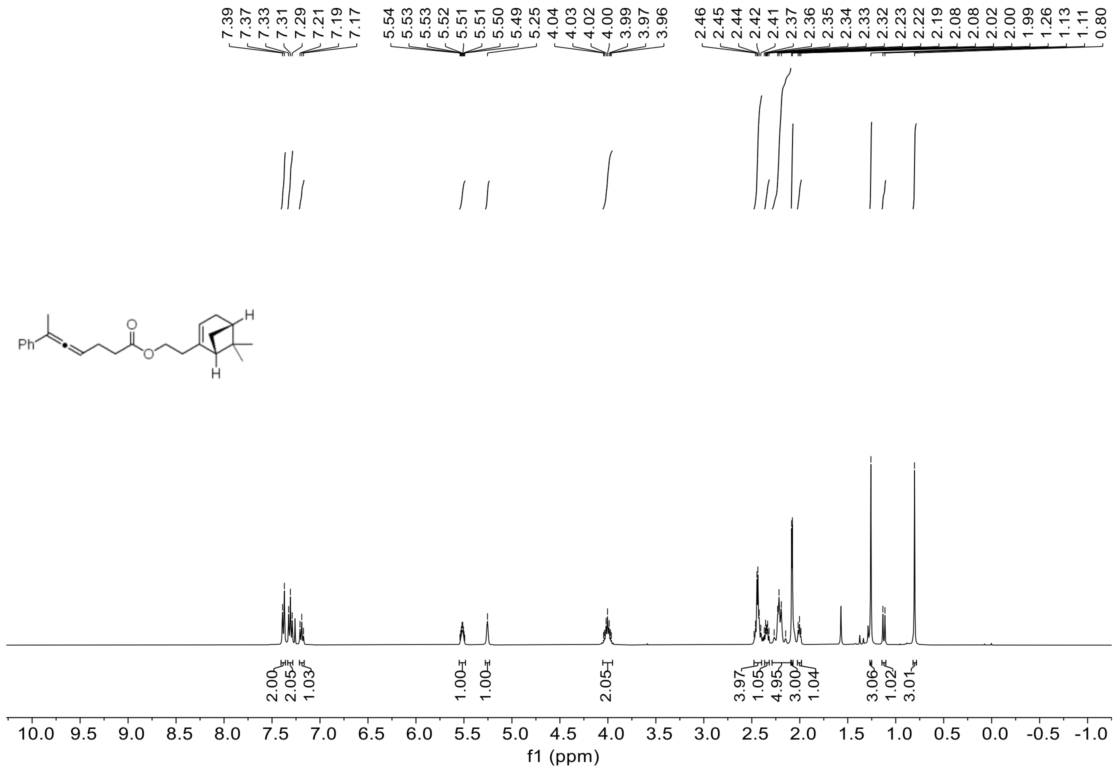

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **18c**



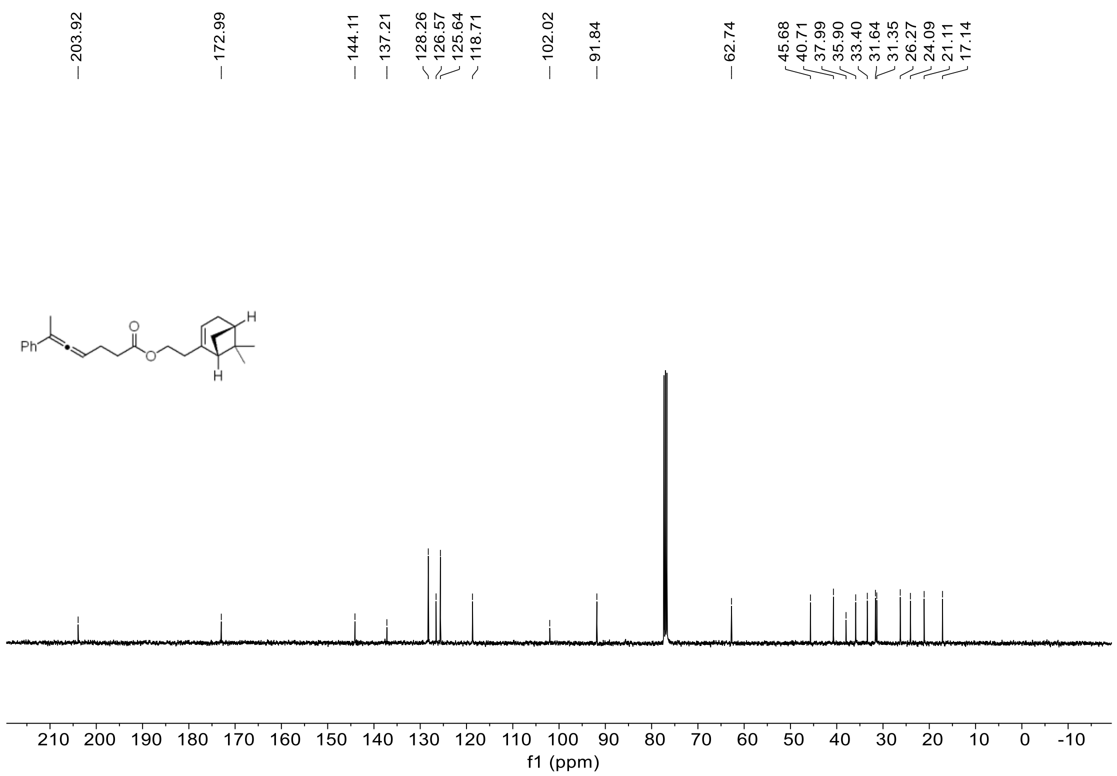
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **19c**



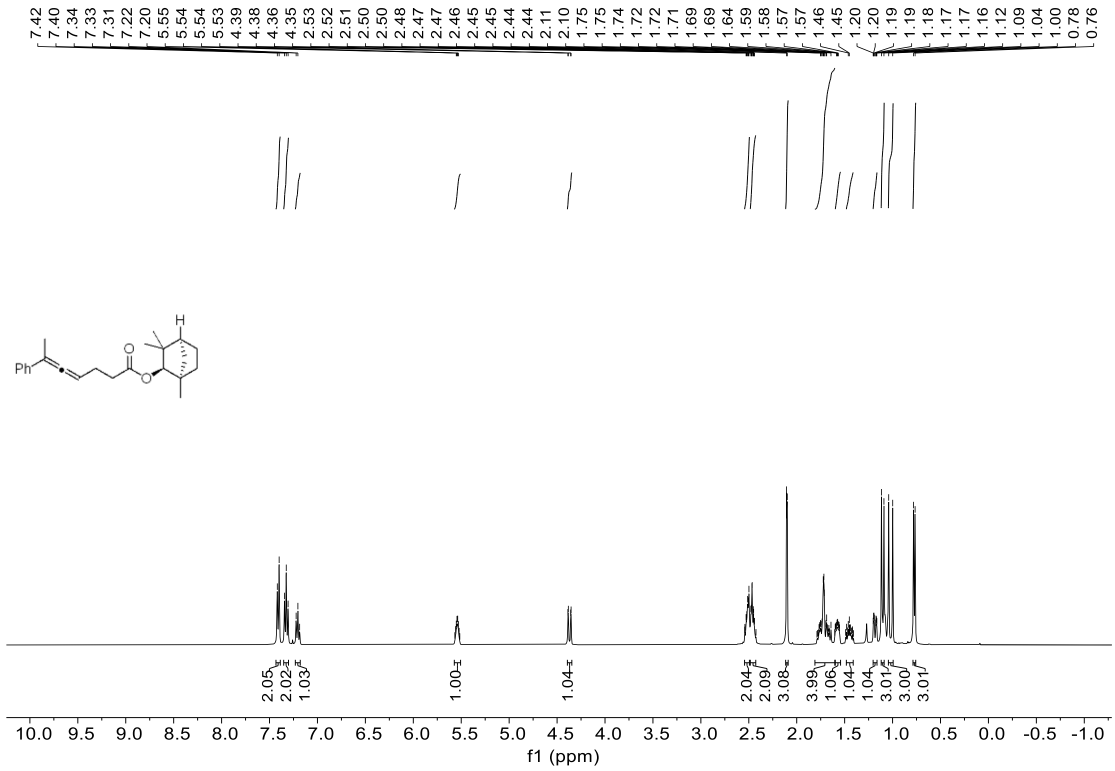
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **19c**



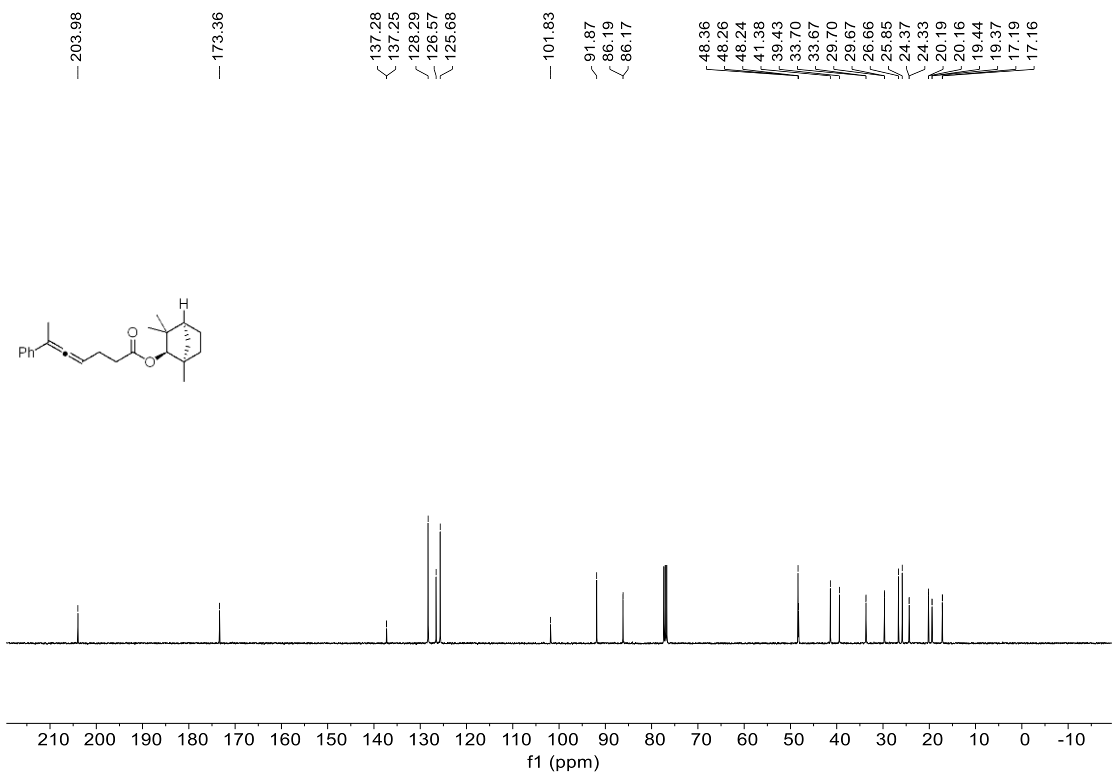

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **20c**



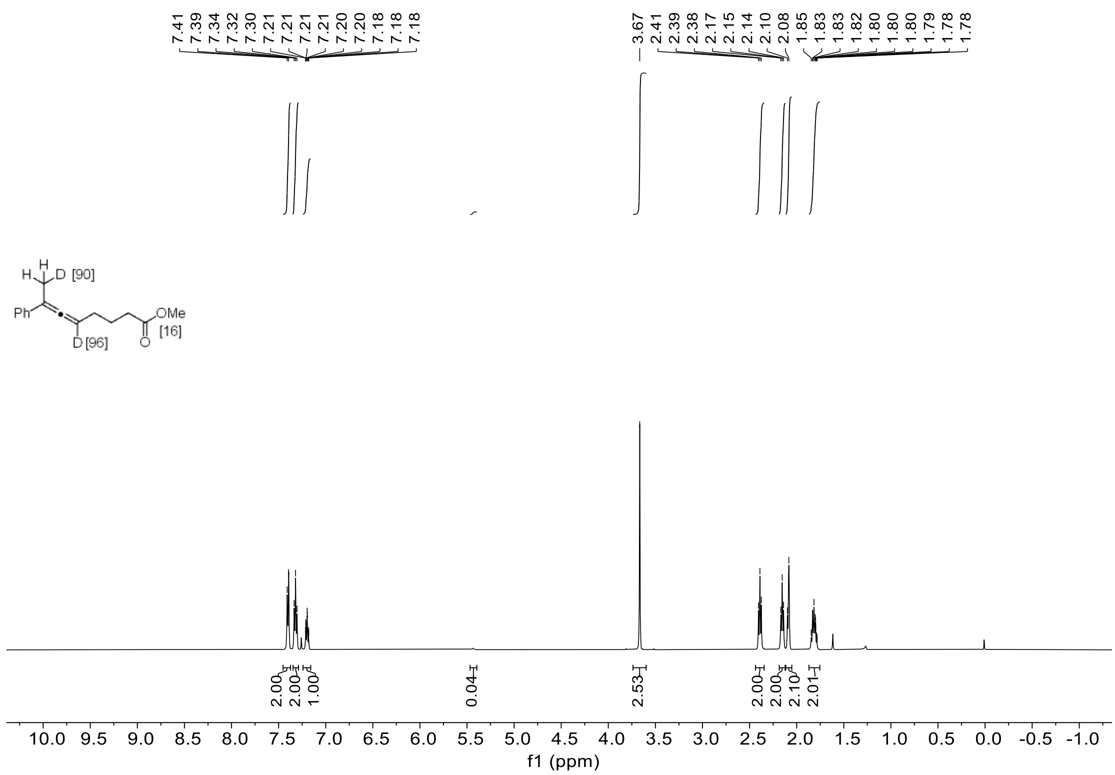

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **20c**



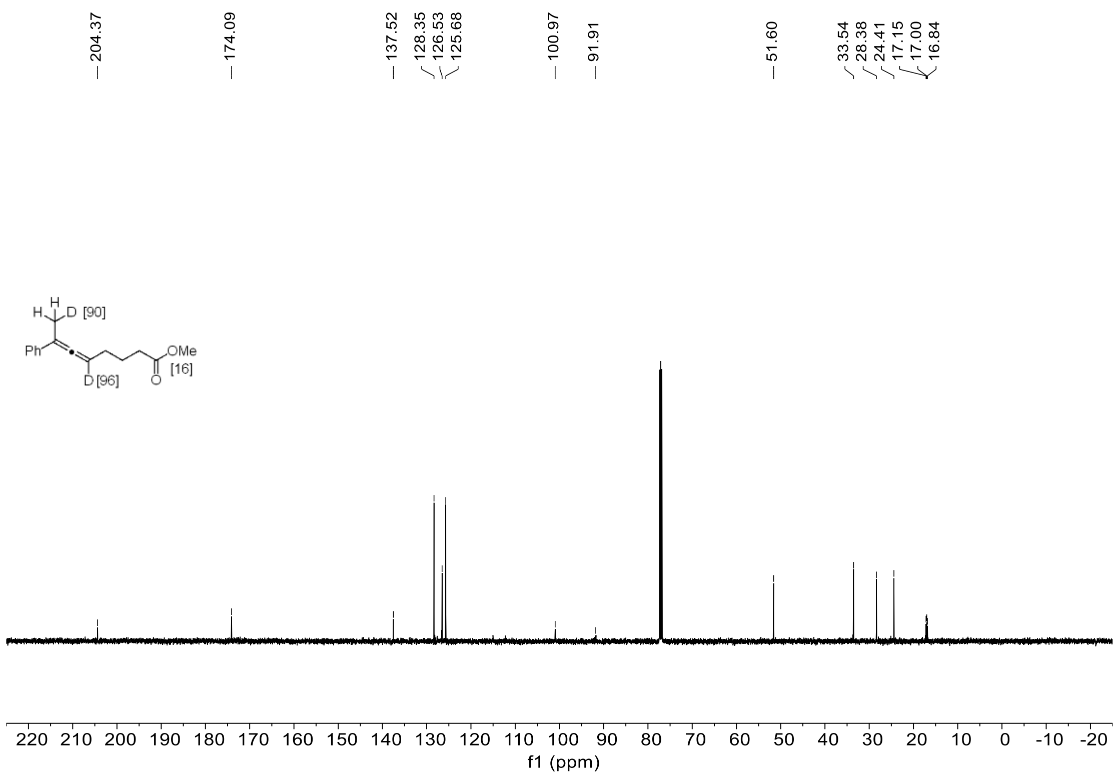
$^{1}$**H NMR** (400 MHz, CDCl$_3$) spectra of **21c**



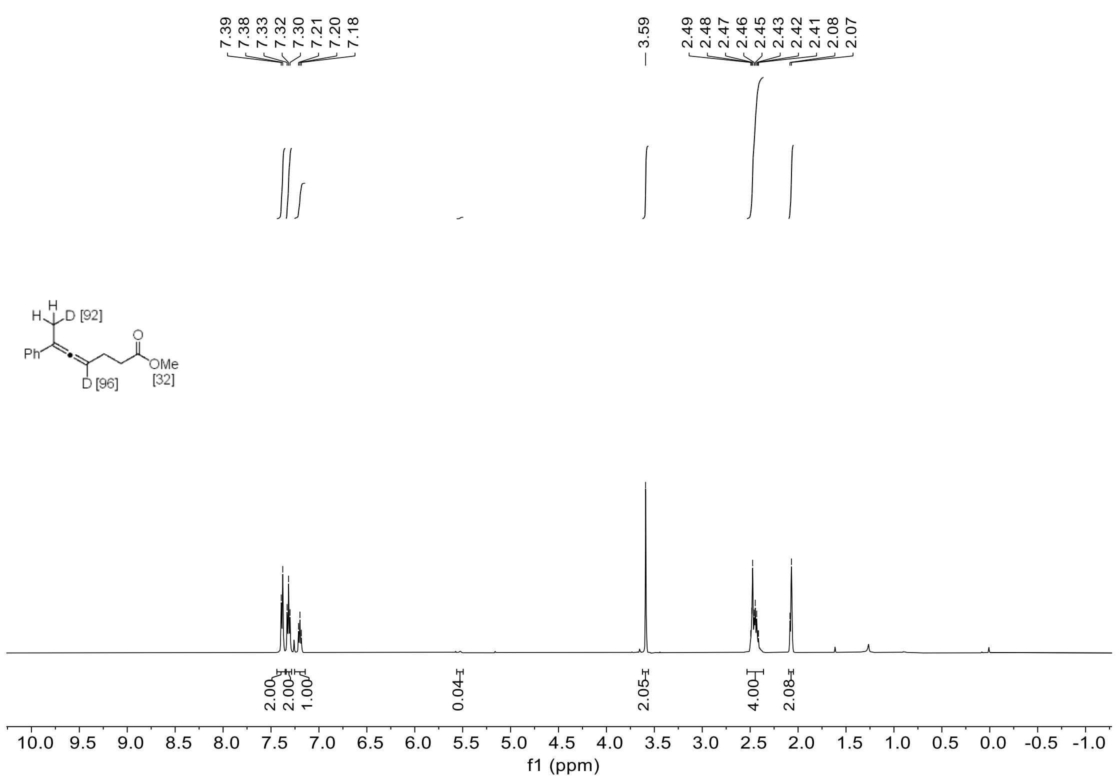
$^{13}$**C NMR** (101 MHz, CDCl$_3$) spectra of **21c**



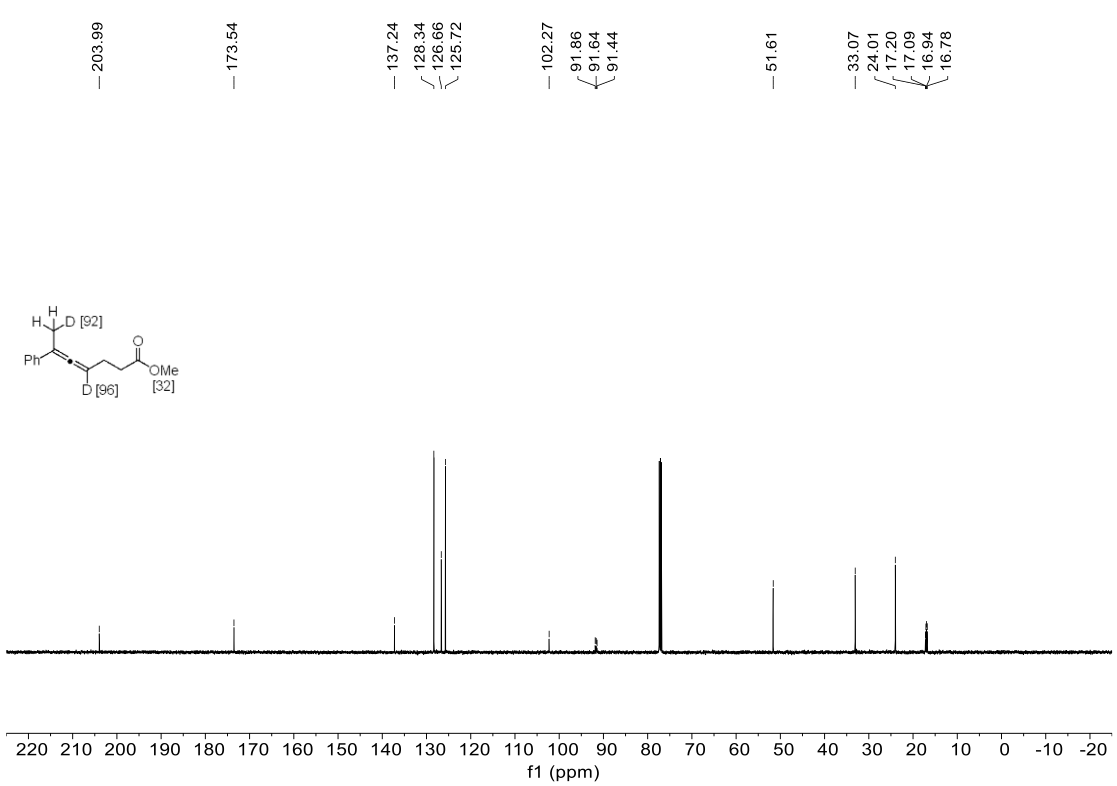

**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **2d**



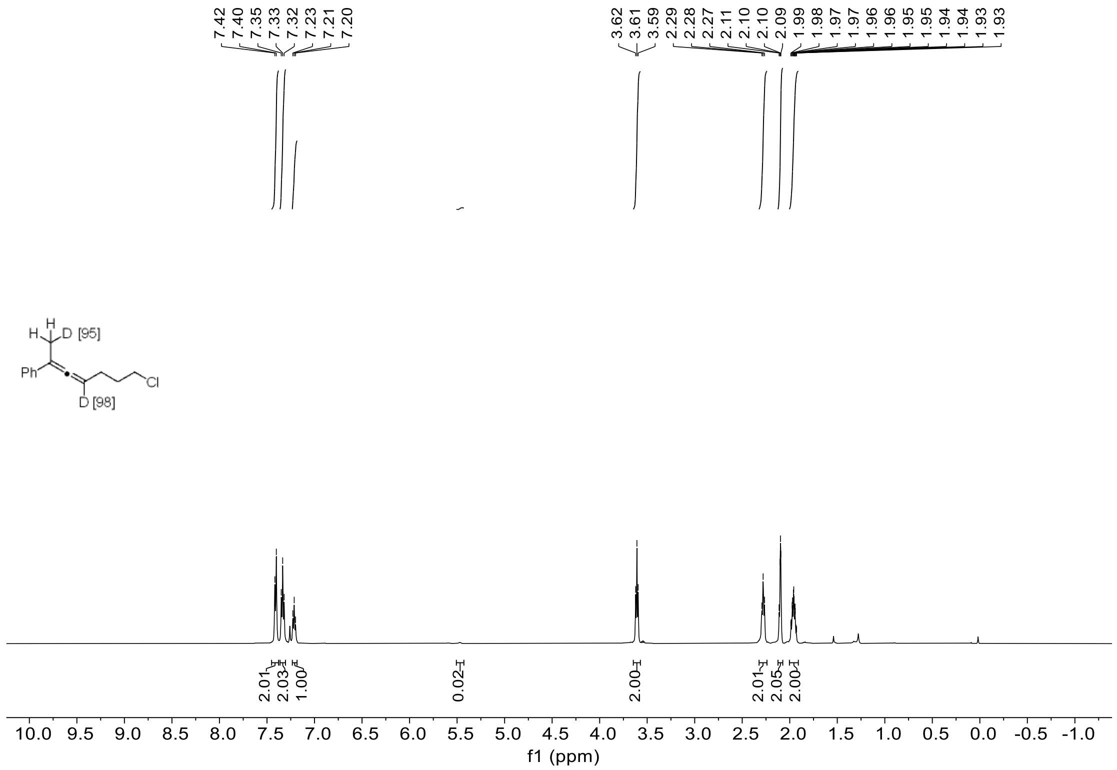

**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **2d**



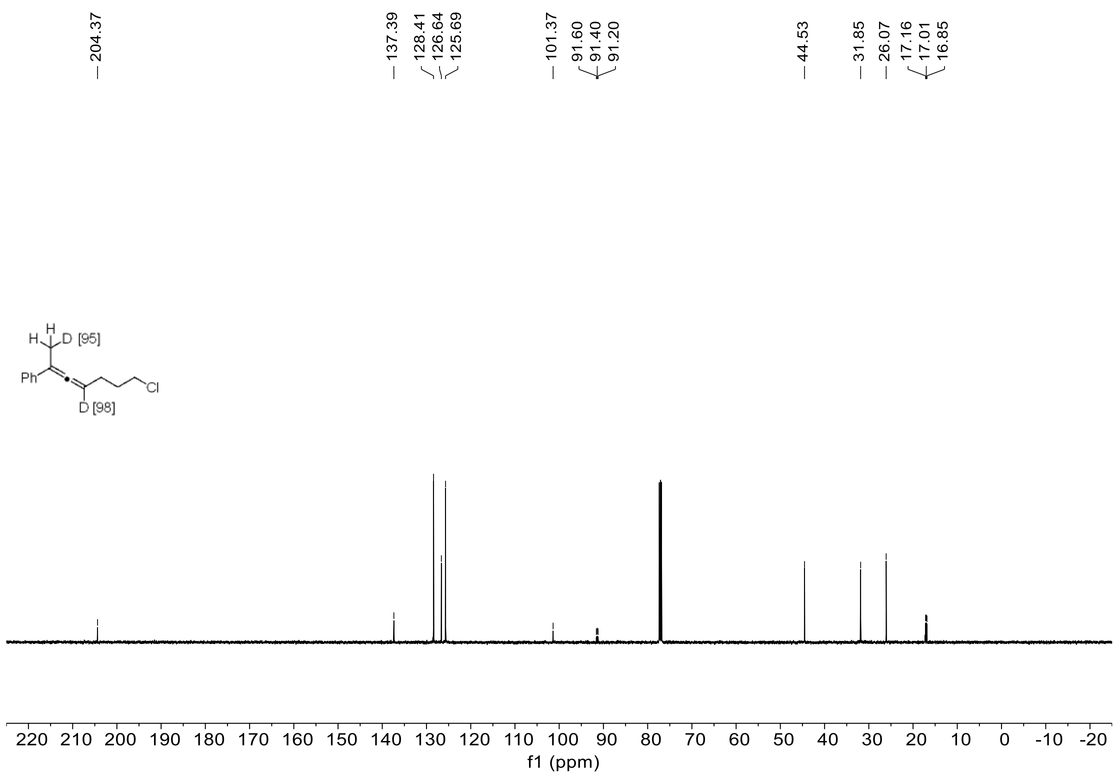
**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **3d**



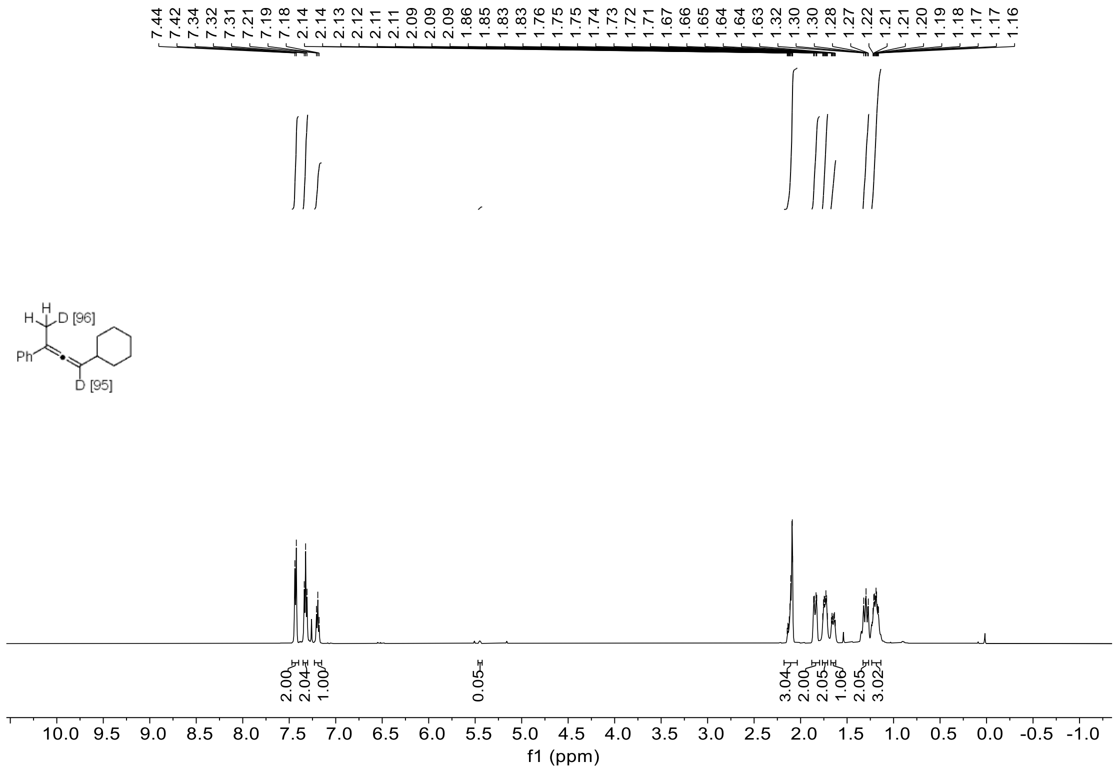
**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **3d**



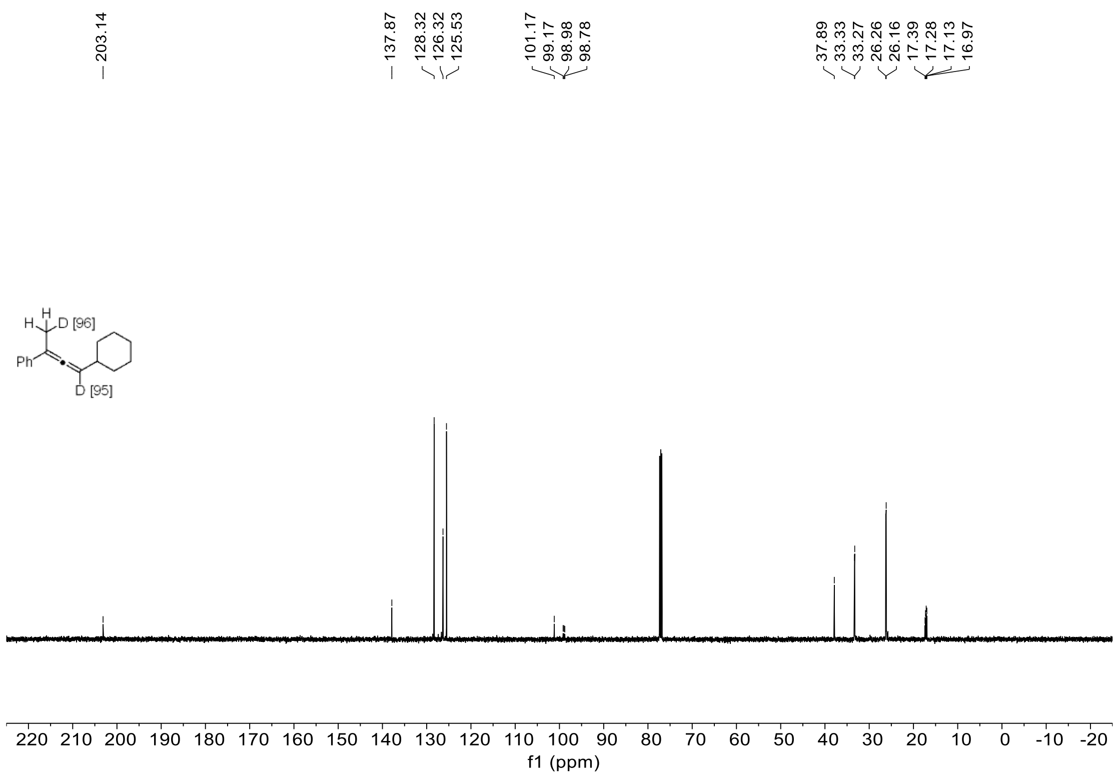
**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectra of **4d**



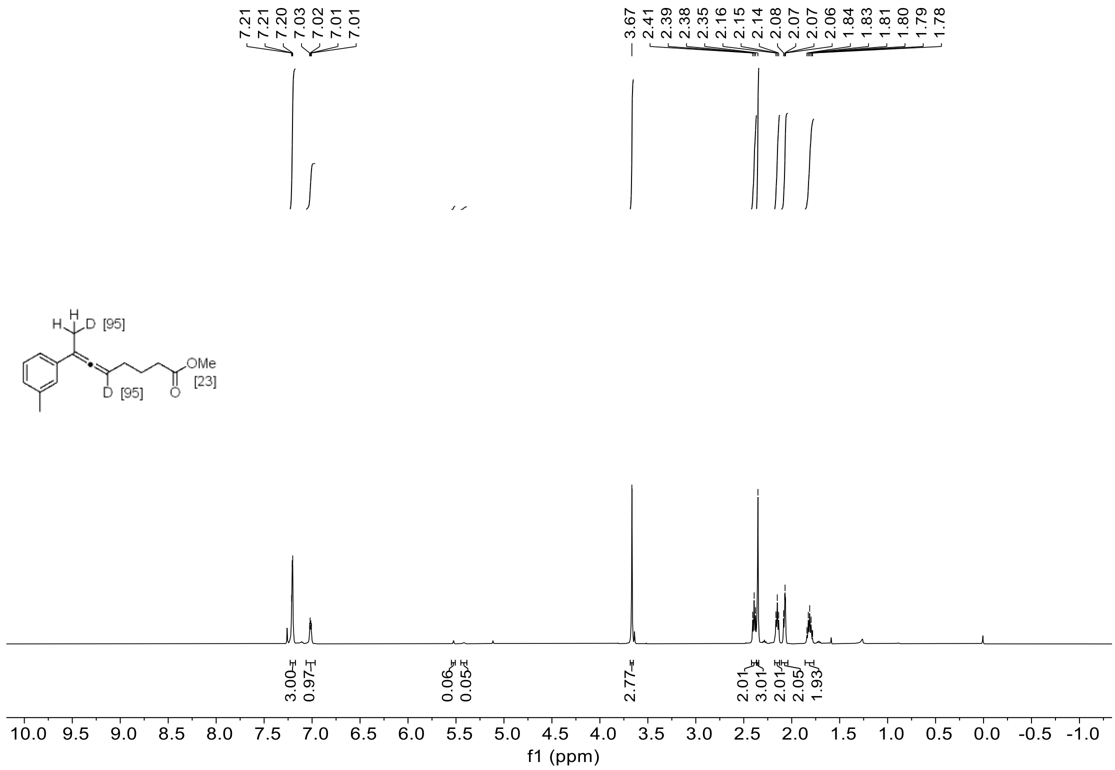
**$^{13}$C NMR** (126 MHz, $CDCl_3$) spectra of **4d**



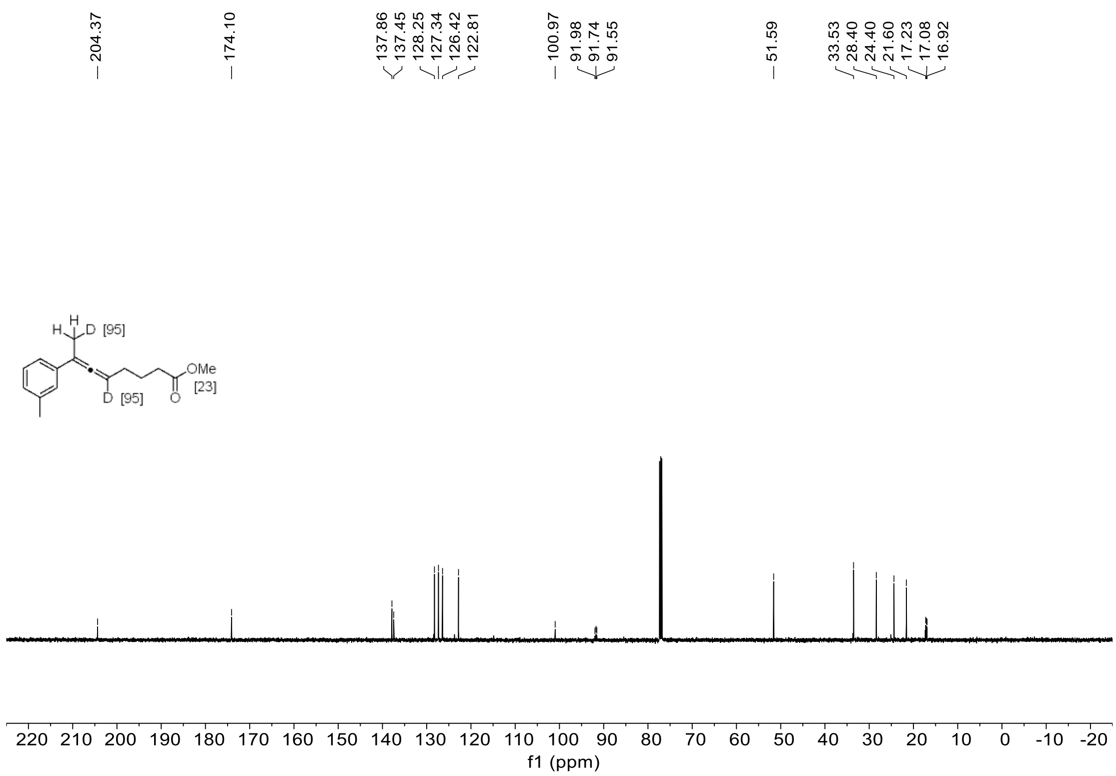

**¹H NMR** (500 MHz, $CDCl_3$) spectra of **5d**



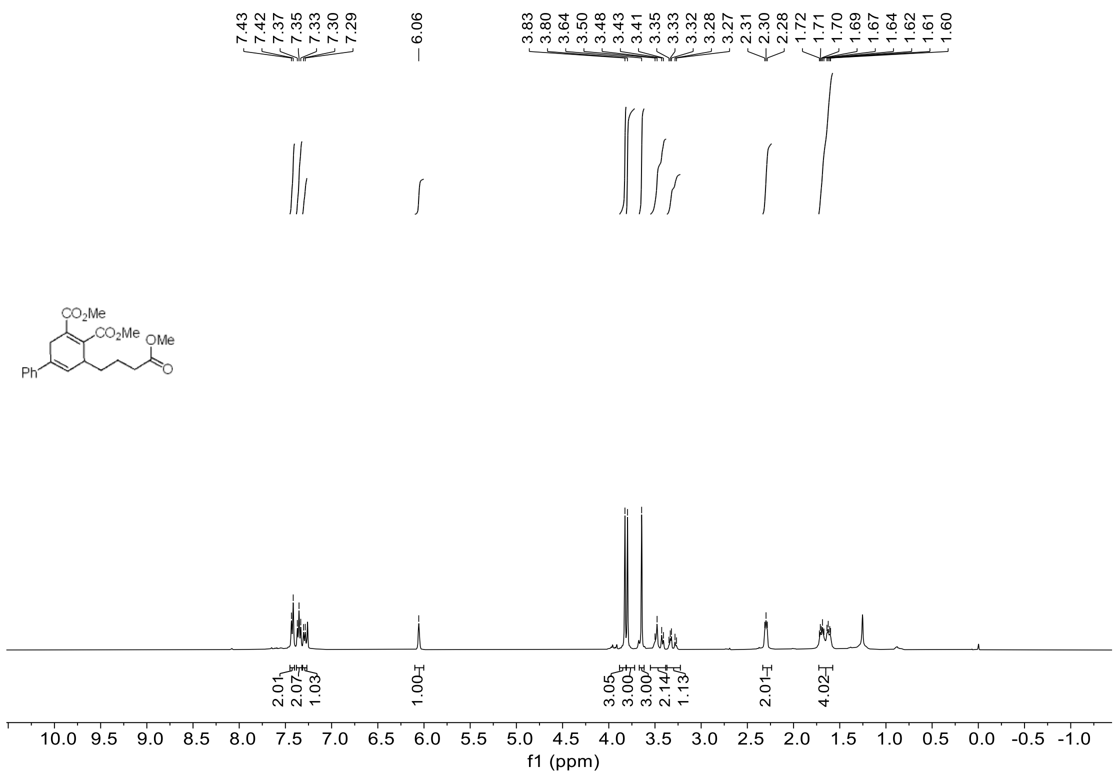

**¹³C NMR** (126 MHz, $CDCl_3$) spectra of **5d**



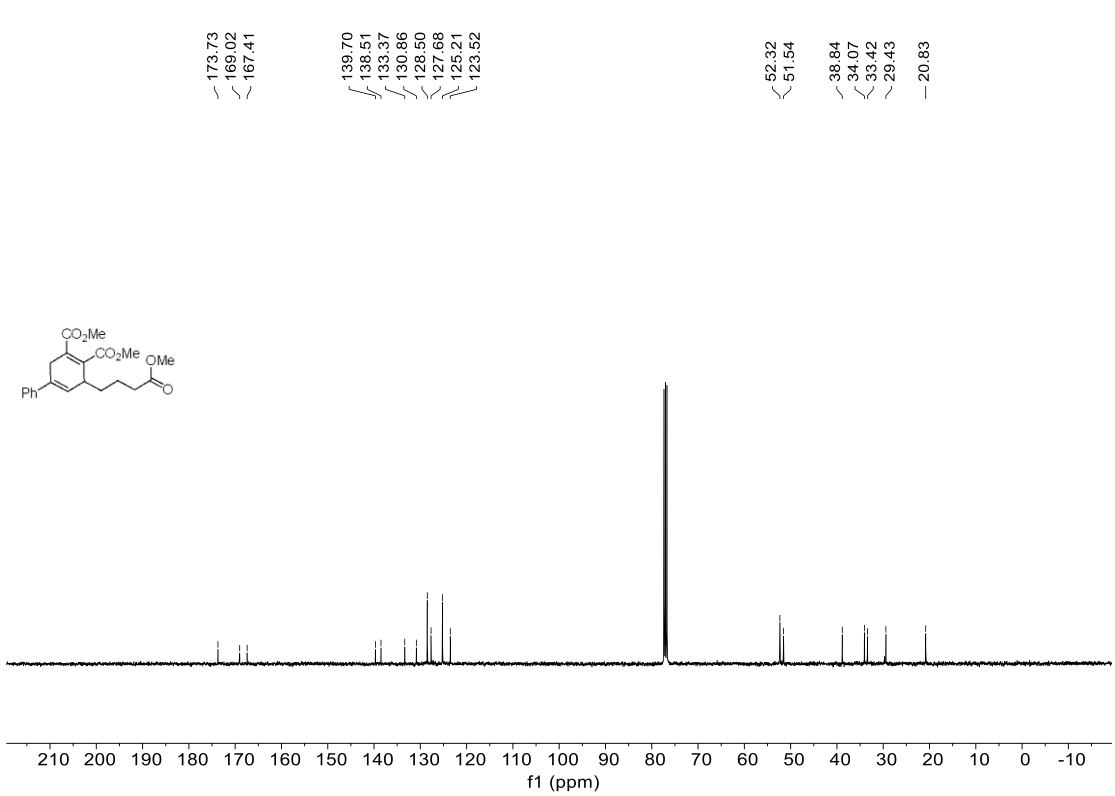
$^{1}$**H NMR** (500 MHz, $CDCl_3$) spectra of **6d**



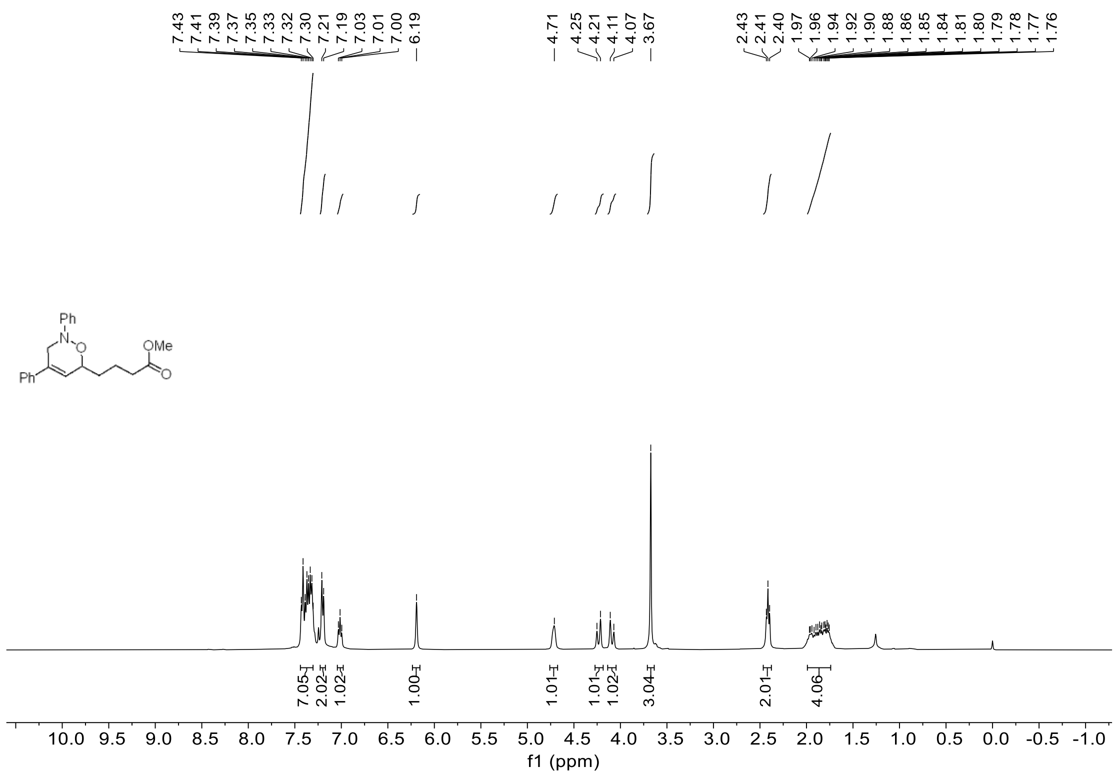
$^{13}$**C NMR** (126 MHz, $CDCl_3$) spectra of **6d**



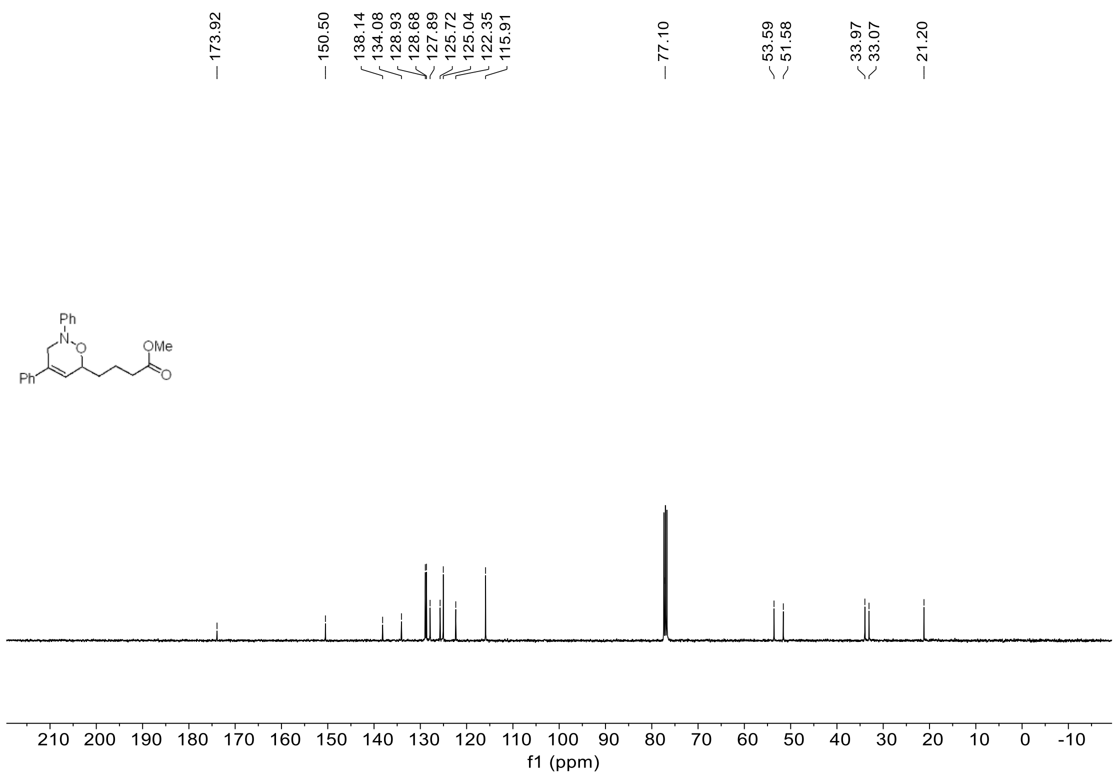

**$^1$H NMR** (400 MHz, $CDCl_3$) spectra of **22**



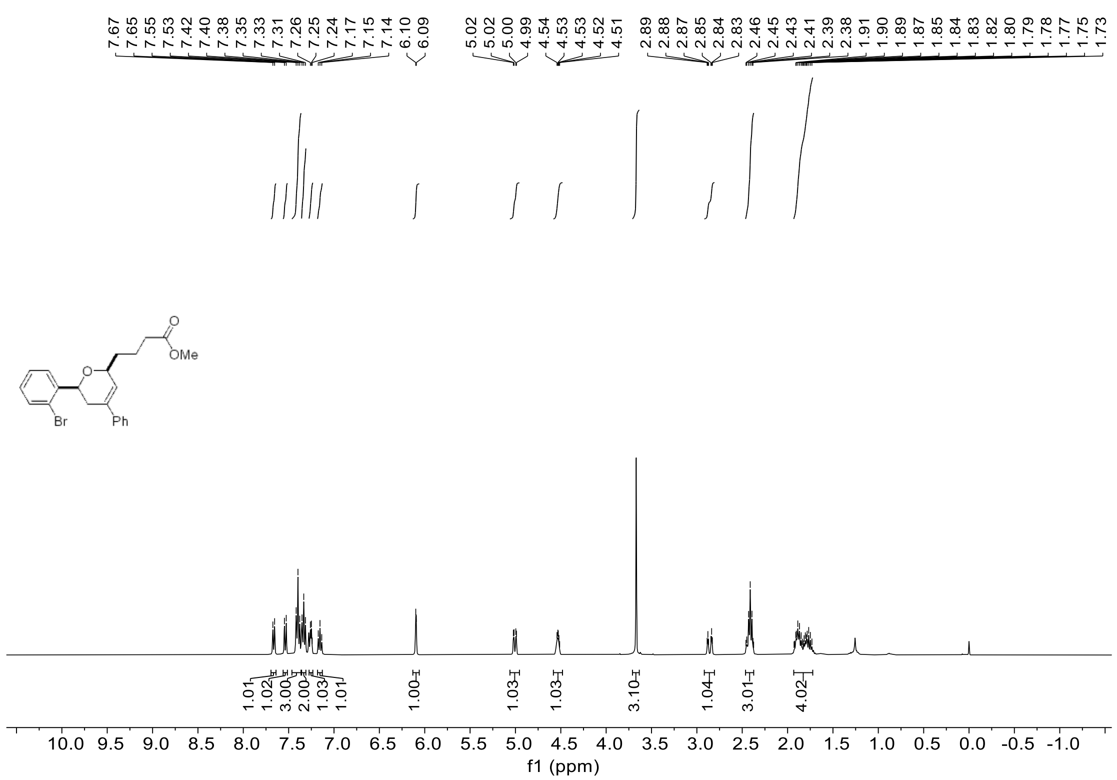

**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **22**



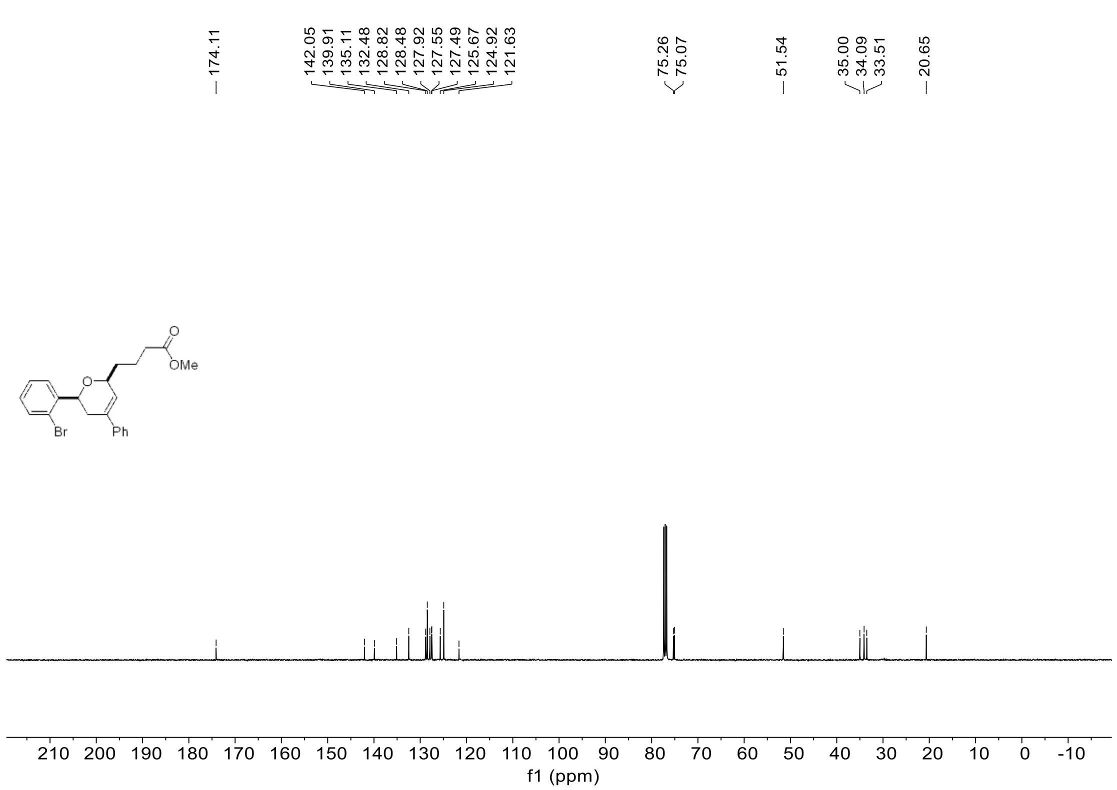
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **23**



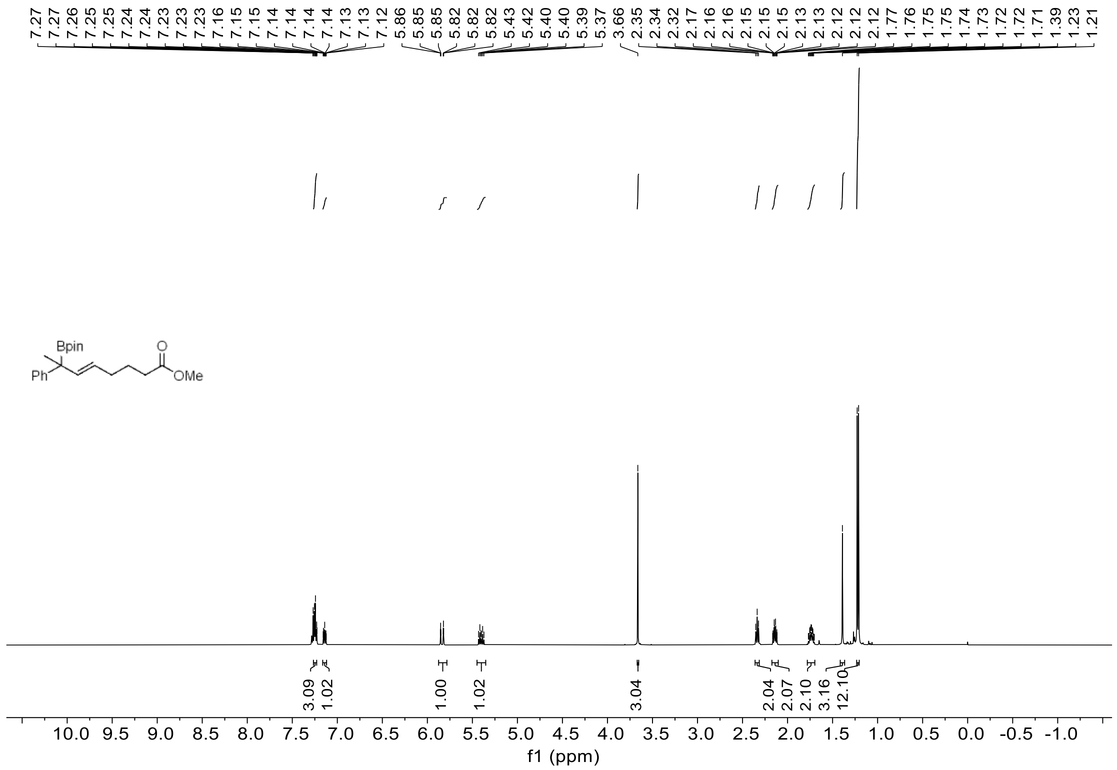
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **23**



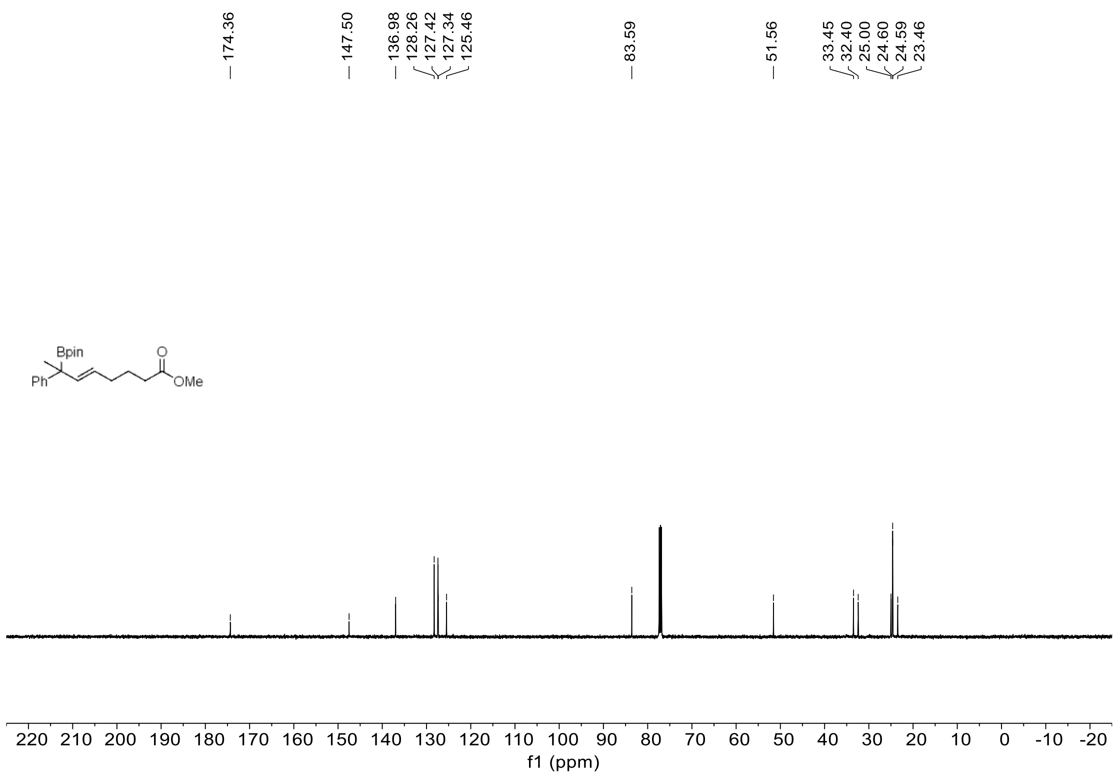
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **24**



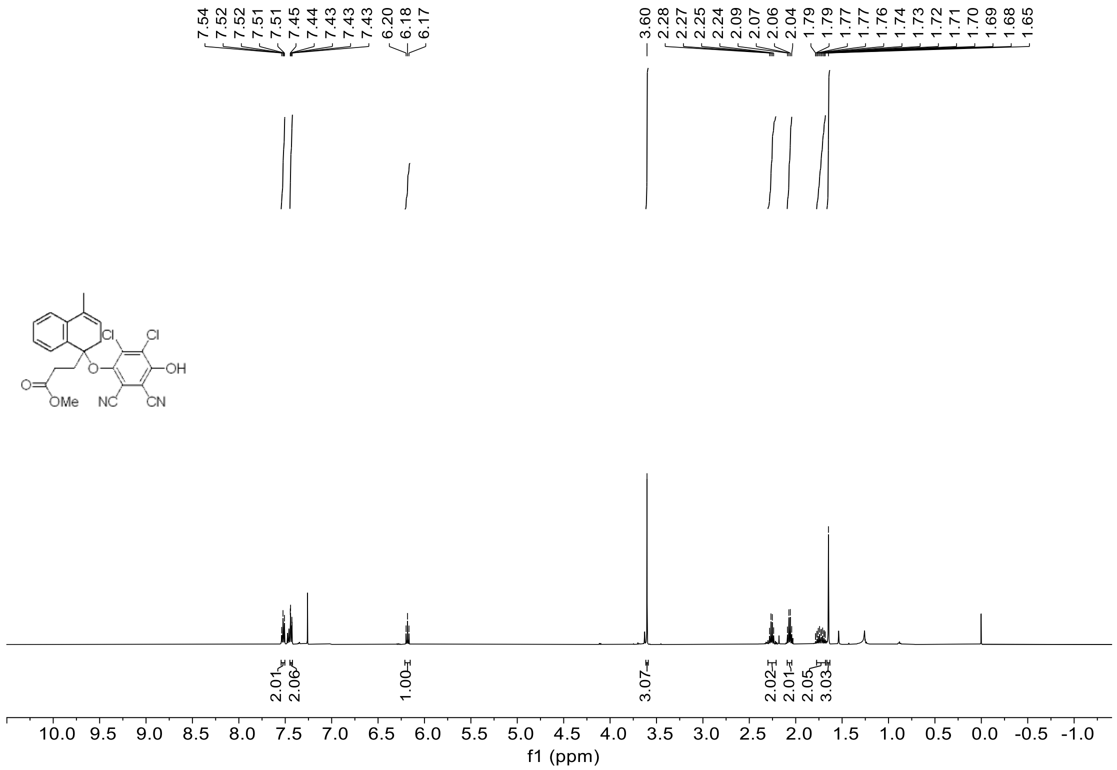
**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **24**



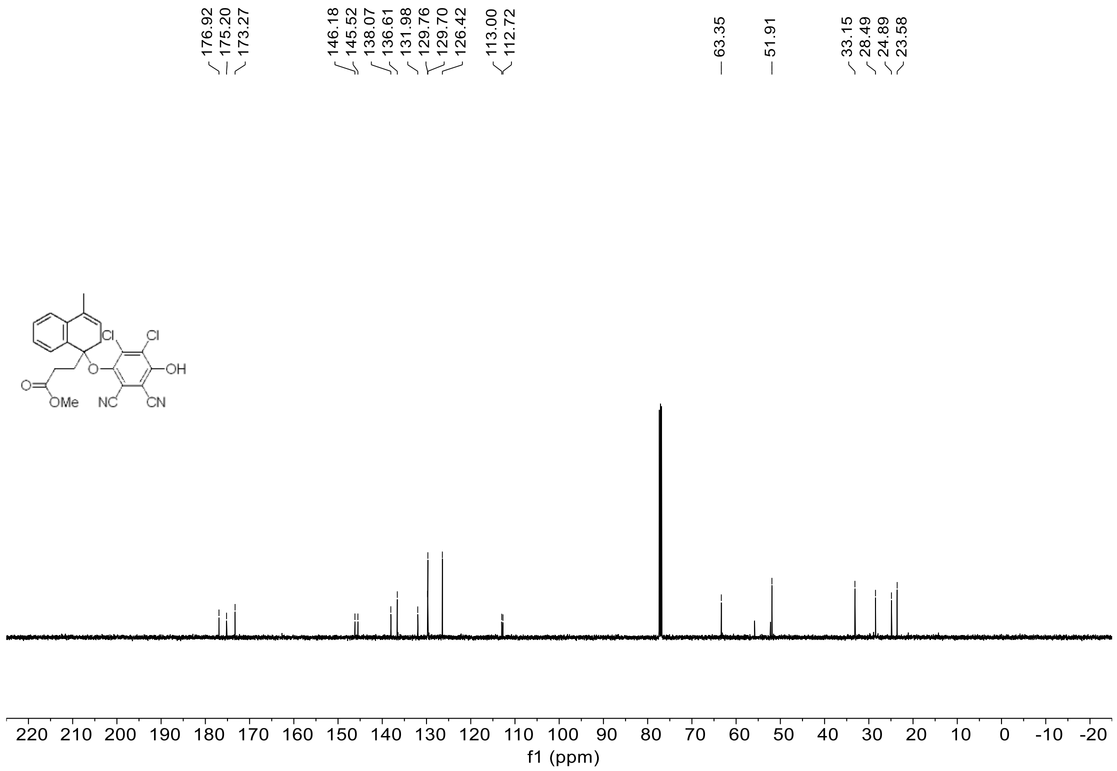

**[1]H NMR** (400 MHz, $CDCl_3$) spectra of **25**



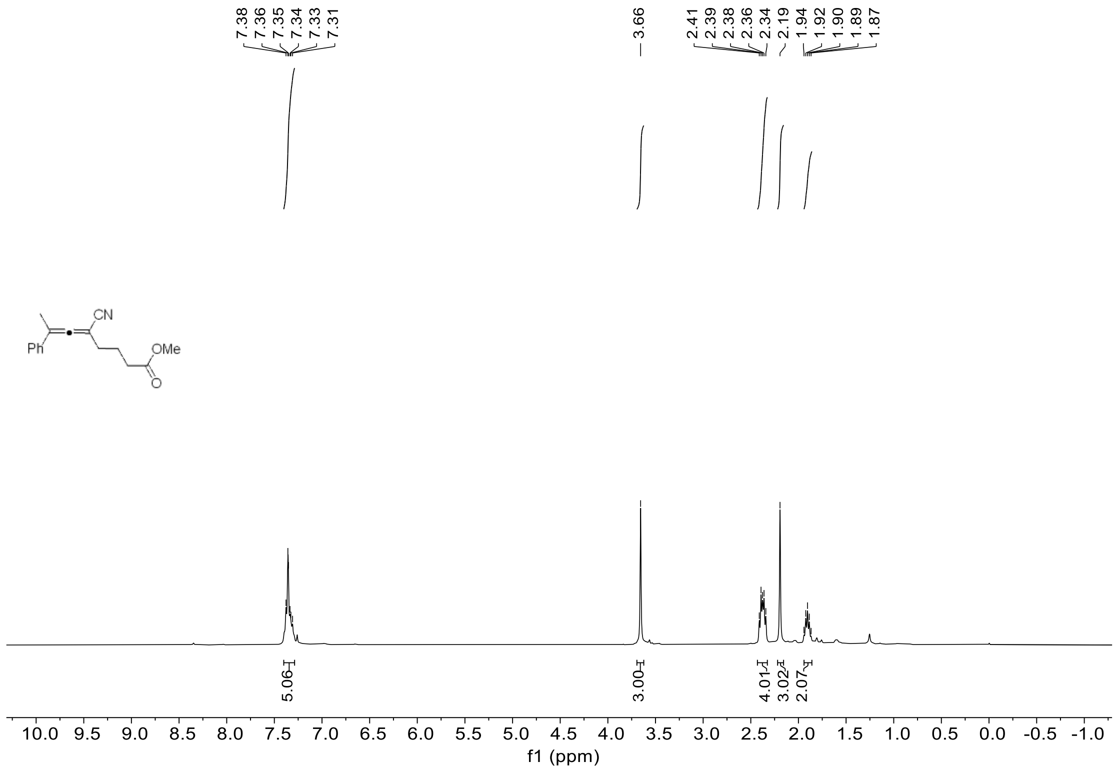

**[13]C NMR** (101 MHz, $CDCl_3$) spectra of **25**



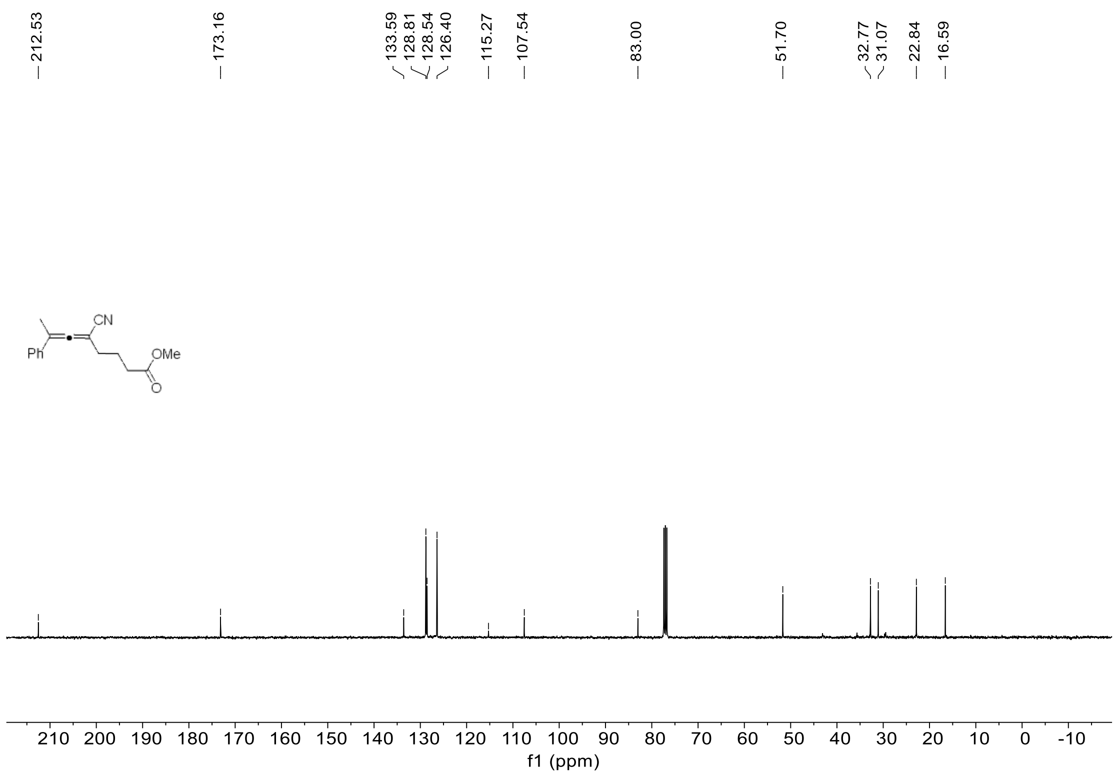
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectra of **26**



**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectra of **26**




**¹H NMR** (400 MHz, $CDCl_3$) spectra of **27**




**¹³C NMR** (101 MHz, $CDCl_3$) spectra of **27**