Supporting Information

Lewis acid catalyzed Markovnikov hydrobromination and hydroclhlorination of alkynes using TMSX (X = Br, Cl)

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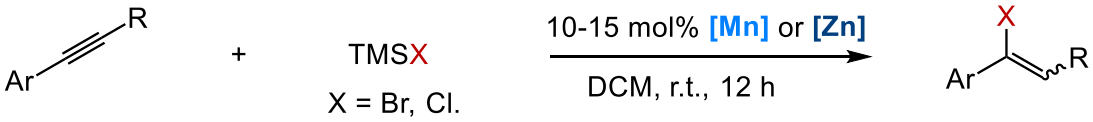
1 . General Information

All the chemicals were purchased from commercial suppliers and were directly used without further purification. Dry dichloromethane, acetonitrile, and hexane were purchased from Energy Chemical. Alkynes were purchased from Bidepharm, Energy. TMSBr and TMSCl were purchased from TCI Chemicals. Functionalization of **2c** was conducted based on the reported procedure.[1-4] Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co., or was carried out on 100-200 mesh of neutral aluminum oxide purchased from Tian Jin Ke Mi Ou Chemical Industry Co. All the ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz spectrometer operating at 400 MHz, 101 MHz, and 377 MHz, respectively. Proton chemical shifts δ were given in ppm using no tetramethylsilane as the internal standard. All NMR spectra were recorded in $CDCl_3$ at room temperature (20±3 °C). High-resolution mass spectra (HRMS) were obtained *via* electrospray ionization (ESI) mode using a UPLC G2-XS Qtof mass spectrometer, or *via* an electrospray ionization (ESI) mode using Thermo Scientific Q Exactive Combined Quadrupole Orbitrap Mass Spectrometer. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), q (quartet), and brs (broad singlet) with coupling constants (*J*) in hertz (Hz).

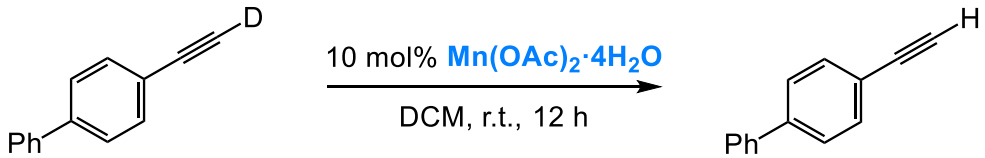
2. General experimental procedures



Alkyne (0.2 mmol) and Lewis acid (0.02-0.03 mmol, 10-15 mol%) were weighed into a 10 mL dry glass vial in an N_2-filled glovebox. 2.0 mL dichloromethane (DCM) and TMSX (X = Br, Cl) were then added to the vial successively. The vial was capped and removed from the box. The solution was allowed to stir for 12 h. The reaction mixture was then filtrated over celite, after which the residue was purified by column chromatography on silica gel.

3. Mechanistic studies

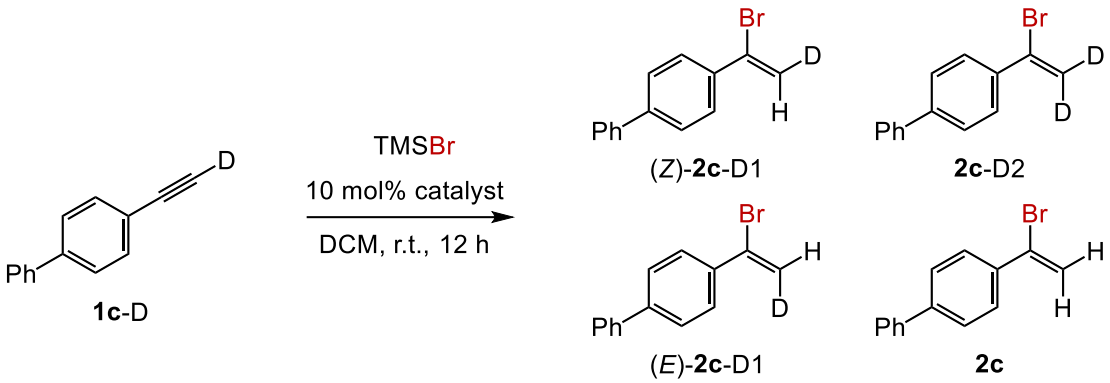
3.1 Control reaction with deuterium-labeled compound 1c-D



1c-D **1c**, <2% conv.

Alkyne (0.2 mmol) and manganese acetate tetrahydrate (0.02 mmol, 10 mol%) were weighed into a 10 mL dry glass vial in an N_2-filled glovebox. 2.0 mL DCM and TMSBr (40 μL, 0.03 mmol, 1.5 equiv.) were then added to the vial successively. The vial was capped and removed from the box. The solution was allowed to stir for 12 h. The reaction mixture was then filtrated over celite, after which the conversion was confirmed by ^{1}H NMR spectra of the crude mixture (<2 % conv.).

3.2 Reactions with deuterium-labeled compound 1c-D



1c-D (35.8 mg, 0.2 mmol) and Lewis acid (0.02 mmol, 10 mol%) were weighed into a 10 mL dry glass vial in an N_2-filled glovebox. 2.0 mL DCM and TMSBr (40 μL, 0.03 mmol, 1.5 equiv.) were then added to the vial successively. The vial was capped and removed from the box. The solution was allowed to stir for 12 h. The reaction mixture was then filtrated over celite, after which the residue was purified by column chromatography on silica gel. The results are summarized and shown below. The overall yields were based on the isolated amounts of products and the ratios were calculated from the NMR spectra of the mixture (see **Fig S87-89**).

entry	catalyst	ratio				overall yield/%
		(*Z*)-**2c**-D1	(*E*)-**2c**-D1	**2c**-D2	**2c**	
1	none	0.59	0.16	0.16	0.09	30
2	$Mn(OAc)_2$	0.39	0.20	0.25	0.16	37
3	$Mn(OAc)_2{\cdot}4H_2O$	0.26	0.21	0.25	0.28	88

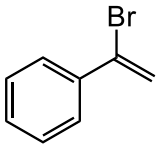
3.3 Reactions with TMS-substrated compound 1c-TMS

1c-TMS (50.0 mg, 0.2 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (4.9 mg, 0.02 mmol, 10 mol%) were weighed into a 10 mL dry glass vial in an N_2-filled glovebox. 2.0 mL DCM and TMSBr (40 μL, 0.03 mmol, 1.5 equiv.) were then added to the vial successively. The vial was capped and removed from the box. The solution was allowed to stir for 12 h. The reaction mixture was then filtrated over celite, after which the residue was purified by column chromatography on silica gel. **2c** and **1c** were isolated in 53% yield (27.4 mg, 0.106 mmol), and 15% yield (5.3 mg, calculated from the inseparable mixture of **1c** & **1c**-TMS), respectively.

3.4 Reactions in the presence of water

1c (50.0 mg, 0.2 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (4.9 mg, 0.02 mmol, 10 mol%) were weighed into a 10 mL dry glass vial in an N_2-filled glovebox. 2.0 mL DCM and TMSBr (40 μL, 0.03 mmol, 1.5 equiv.) were then added to the vial successively. The vial was capped and removed from the box, followed by the addition of H_2O (3.6 mg, 0.2 mmol%, 1.0 equiv.) into the vial. The solution was allowed to stir for 12 h. The reaction mixture was then filtrated over celite, after which the residue was purified by column chromatography on silica gel. 4-Acetylbiphenyl was isolated in 72% yield (28.2 mg, 0.144 mmol). The characterization data is the same with an authentic sample of 4-acetylbiphenyl.

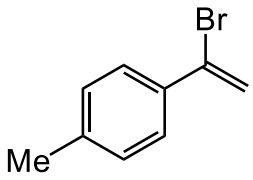
4. Character data for products



2a: yellow oil, 82%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.54 (m, 2H), 7.40–7.29 (m, 3H), 6.12 (d, *J* = 2.0 Hz, 1H), 5.79 (t, *J* = 3.1 Hz, 1H).

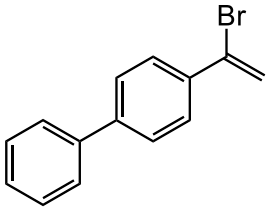
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 131.1, 129.2, 128.4, 127.5, 117.8.



2b: yellow oil, 81%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.37 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.44 (d, *J* = 1.7 Hz, 1H), 6.04 (d, *J* = 1.7 Hz, 1H), 2.36 (s, 3H).

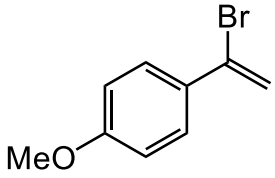
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 129.0, 128.1, 126.6, 107.8, 21.2.



2c: white solid, 88%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 13.2, 4.9 Hz, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 5.83 (d, *J* = 2.0 Hz, 1H).

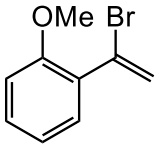
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 140.3, 137.5, 130.8, 129.0, 127.9, 127.8, 127.2, 127.1, 117.7.



2d: yellow oil, 73%.[6]

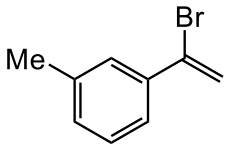
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.3, 3.6 Hz, 2H), 6.92–6.81 (m, 2H), 6.01 (d, *J* = 2.0 Hz, 1H), 5.67 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 131.3, 130.8, 128.8, 116.0, 113.7, 55.5.

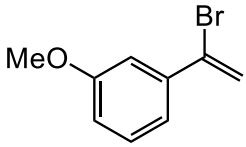


2e: yellow oil, 88%.[7]

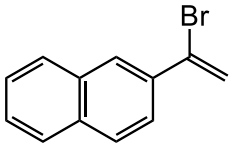
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.35–7.27 (m, 1H), 6.99–6.93 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.99 (d, *J* = 1.4 Hz, 1H), 5.92 (d, *J* = 1.4 Hz, 1H), 3.89 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 130.8, 130.4, 129.1, 126.3, 121.8, 120.5, 111.4, 55.8.



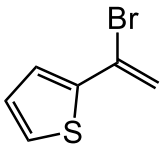
2f: yellow oil, 53%.[5]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.36 (m, 2H), 7.24 (dd, *J* = 11.2, 3.8 Hz, 1H), 7.18–7.12 (m, 1H), 6.10 (d, *J* = 2.0 Hz, 1H), 5.76 (d, *J* = 2.0 Hz, 1H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.1, 131.3, 130.0, 128.3, 128.1, 124.6, 117.6, 21.5.



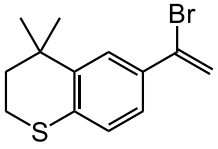
2g: yellow oil, 47%.[10]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.23 (t, 1H), 7.21–7.16 (m, 1H), 7.15–7.12 (m, 1H), 6.88 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 6.12 (d, *J* = 2.0 Hz, 1H), 5.78 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 140.1, 130.8, 129.4, 119.9, 118.0, 114.8, 113.3, 55.5.



2h: white solid, 68%.[7]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.6 Hz, 1H), 7.92–7.86 (m, 1H), 7.84 (dd, *J* = 5.3, 4.1 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.70 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.56–7.47 (m, 2H), 6.27 (d, *J* = 2.1 Hz, 1H), 5.89 (d, *J* = 2.1 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 133.6, 133.0, 131.2, 128.7, 128.1, 127.7, 127.0, 126.8, 124.3, 118.1.



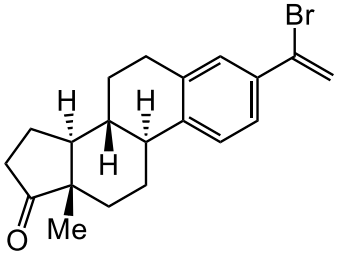
2i: yellow oil, 88%.[7]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 4.4 Hz, 2H), 7.01–6.98 (m, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 5.60 (d, *J* = 2.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 128.5, 127.4, 126.8, 122.1, 115.9.



2j: yellow oil, 80%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.0 Hz, 1H), 7.31–7.20 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.04 (d, J = 2.0 Hz, 1H), 5.70 (d, *J* = 2.0 Hz, 1H), 3.08–3.00 (m, 2H), 1.99–1.92 (m, 2H), 1.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 134.4, 133.8, 131.3, 126.4, 125.7, 124.8, 116.4, 37.5, 33.2, 30.2, 23.3.

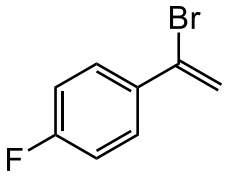


2k: yellow solid, 65%, melting point: 125 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.33 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 1.9 Hz, 1H), 5.73 (d, *J* = 1.9 Hz, 1H), 2.93 (dd, *J* = 9.6, 4.9 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.46–2.39 (m, 1H), 2.31 (td, *J* = 10.8, 4.4 Hz, 1H), 2.16 (dd, *J* = 18.4, 9.4 Hz, 1H), 2.11–2.01 (m, 2H), 2.00–1.93 (m, 1H), 1.66–1.59 (m, 2H), 1.57–1.43 (m, 4H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 141.1, 136.6, 136.3, 131.1, 128.1, 125.5, 124.8, 117.1, 50.6, 48.1, 44.5, 38.2, 36.0, 31.7, 29.5, 26.5, 25.8, 21.7, 14.0.

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{23}ONaBr$), requires m/z = 381.0830, found m/z = 381.0826.

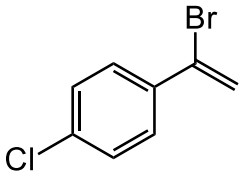


2l: yellow oil, 77%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.50 (m, 2H), 7.09–6.98 (m, 2H), 6.06 (t, *J* = 5.2 Hz, 1H), 5.76 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 249.5 Hz), 134.8 (d, *J* = 3.2 Hz), 129.7, 129.2 (d, *J* = 8.5 Hz), 117.7 (d, *J* = 1.1 Hz), 115.2 (d, *J* = 21.9 Hz).

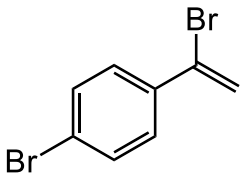
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.25 (s).



2m: yellow oil, 49%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.48 (m, 2H), 7.36–7.27 (m, 2H), 6.11 (d, *J* = 2.1 Hz, 1H), 5.79 (d, *J* = 2.1 Hz, 1H).

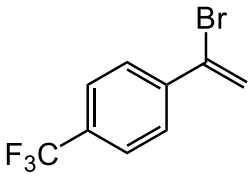
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 135.2, 129.8, 128.7, 128.6, 118.3.



2n: yellow oil, 77%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.41 (m, 4H), 6.11 (d, *J* = 2.2 Hz, 1H), 5.79 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 137.7, 131.6, 129.8, 129.0, 123.5, 118.4.

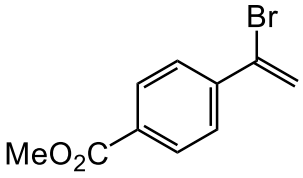


2o: yellow oil, 58%.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 6.20 (d, *J* = 2.2 Hz, 1H), 5.89 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 131.1 (q, *J* = 32.6 Hz), 129.4, 127.8, 125.5 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.3 Hz), 119.8.

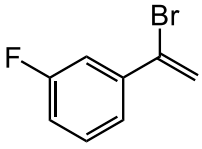
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.76 (s).



2p: yellow solid, 73%.[9]

^{1}H NMR (400 MHz, CDCl3) δ 8.03–7.98 (m, 2H), 7.68–7.62 (m, 2H), 6.22 (d, *J* = 2.2 Hz, 1H), 5.88 (d, *J* = 2.2 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 166.5, 142.7, 130.6, 129.9, 129.7, 127.4, 119.7, 52.4.

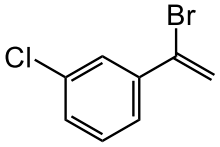


2q: yellow oil, 96%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 1H), 7.31 (ddd, *J* = 7.7, 6.6, 4.2 Hz, 2H), 7.03 (tdd, *J* = 8.3, 2.6, 1.1 Hz, 1H), 6.15 (d, *J* = 2.2 Hz, 1H), 5.82 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.2 Hz), 140.8 (d, *J* = 8.0 Hz), 129.9 (d, *J* = 8.5 Hz), 129.5 (d, *J* = 2.8 Hz), 123.1 (d, *J* = 2.9 Hz), 118.9, 116.1 (d, *J* = 21.2 Hz), 114.7 (d, *J* = 23.5 Hz).

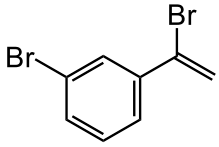
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.96 (s).



2r: yellow oil, 64%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 1.7 Hz, 1H), 7.47 (dt, *J* = 7.0, 1.8 Hz, 1H), 7.33–7.27 (m, 2H), 6.14 (d, *J* = 2.2 Hz, 1H), 5.82 (d, *J* = 2.2 Hz, 1H).

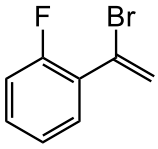
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 134.4, 129.7, 129.3, 129.2, 127.6, 125.6, 119.0.



2s: yellow oil, 55%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 1.8 Hz, 1H), 7.57-7.54 (m, 1H), 7.51-7.49 (m, 1H), 7.27 (dd, *J* = 15.5, 7.5 Hz, 1H), 6.17 (d, *J* = 2.2 Hz, 1H), 5.86 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 132.2, 130.4, 129.9, 129.2, 126.1, 122.5, 119.1.

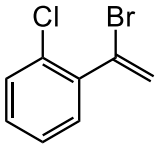


2t: yellow oil, 99%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.47 (m, 1H), 7.35–7.26 (m, 1H), 7.18–7.12 (m, 1H), 7.11–7.02 (m, 1H), 6.14 (dd, *J* = 1.8, 1.2 Hz, 1H), 6.03 (dd, *J* = 1.8, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (d, *J* = 251.8 Hz), 131.4 (d, *J* = 2.0 Hz), 130.7 (d, *J* = 8.6 Hz), 127.3 (d, *J* = 12.2 Hz), 124.1 (d, *J* = 3.8 Hz), 123.2 (d, *J* = 6.4 Hz), 122.9 (d, *J* = 1.7 Hz), 116.1 (d, *J* = 22.5 Hz).

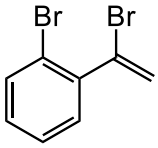
^{19}F NMR (377 MHz, $CDCl_3$) δ -113.31 (s).



2u: yellow oil, 65%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.34 (m, 2H), 7.30–7.22 (m, 2H), 5.96 (t, *J* = 2.8 Hz, 1H), 5.88 (d, *J* = 1.8 Hz, 1H).

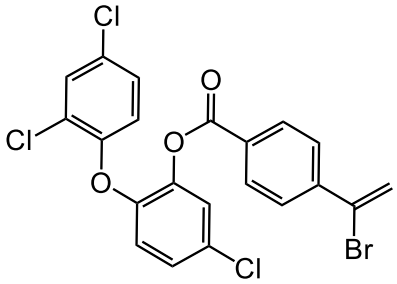
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 132.5, 130.8, 130.1, 130.1, 126.9, 126.0, 122.8.



2v: yellow oil, 67%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.40–7.35 (m, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.22–7.15 (m, 1H), 5.95 (d, *J* = 1.8 Hz, 1H), 5.86 (d, *J* = 1.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 133.3, 130.7, 130.3, 127.7, 127.5, 122.6, 122.2.

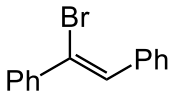


2w: yellow oil, 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.00 (m, 2H), 7.72–7.65 (m, 2H), 7.34 (dd, *J* = 3.7, 2.5 Hz, 2H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.91 (dd, *J* = 8.8, 4.0 Hz, 2H), 6.25 (d, *J* = 2.2 Hz, 1H), 5.92 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 151.2, 146.9, 143.7, 141.9, 130.5, 130.4, 129.7, 129.6, 129.5, 128.9, 128.2, 127.6, 127.3, 126.1, 124.7, 120.6, 120.5, 120.3.

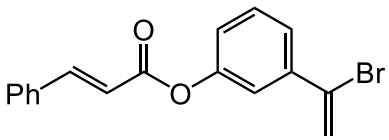
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{21}H_{12}O_3Cl_3NaBr$), requires m/z = 518.8933, found m/z = 518.8941.



2x: pale yellow oil, 98%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.36–7.31 (m, 3H), 7.20 (s, 1H), 7.18 – 7.13 (m, 3H), 7.00 (dt, *J* = 7.6, 3.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 136.1, 133.2, 129.4, 128.9, 128.8, 128.8, 128.4, 127.6, 123.5.

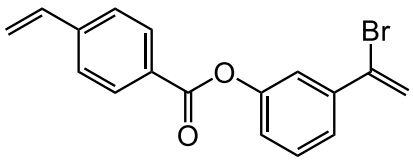


2y: pale yellow oil, 45%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 16.0, 3.7 Hz, 1H), 7.60 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.52–7.47 (m, 1H), 7.47–7.37 (m, 5H), 7.17 (ddd, *J* = 8.0, 2.1, 0.9 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 2.1 Hz, 1H), 5.82 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 150.8, 147.1, 140.2, 134.2, 130.9, 129.8, 129.4, 129.2, 128.5, 124.8, 122.5, 120.9, 118.7, 117.2.

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{17}H_{13}O_2NaBr$), requires m/z = 350.9997, found m/z = 350.9993.



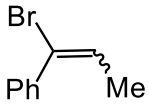
2z: colorless liquid, 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.13 (m, 2H), 7.57–7.49 (m, 3H), 7.46 (t, *J* = 2.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.21 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 1H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 1H),

6.18 (d, *J* = 2.1 Hz, 1H), 5.92 (d, *J* = 17.6 Hz, 1H), 5.83 (d, *J* = 2.1 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 150.9, 142.9, 140.2, 136.1, 130.7, 129.8, 129.4, 128.5, 126.5, 124.9, 122.6, 121.0, 118.7, 117.2.

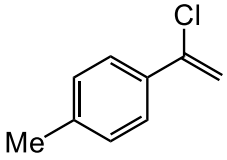
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{17}H_{13}O_2NaBr$), requires m/z = 350.9997, found m/z = 350.9985.



2aa: pale yellow oil, 70% (*E*:*Z* = 70:30).[11]

^{1}H NMR (400 MHz, C_6D_6) δ 7.31–7.25 (m, 1H), 7.12–7.07 (m, 2H), 7.01 (s, 1H), 6.93–6.84 (m, 3H), 6.84–6.78 (m, 1H), 5.92 (q, *J* = 7.2 Hz, 1H, *E*-**2aa**), 5.73 (q, *J* = 6.6 Hz, 1H, *Z*-**2aa**), 1.54 (d, *J* = 6.6 Hz, 1H, *Z*-**2aa**), 1.13 (d, *J* = 7.3 Hz, 3H, *E*-**2aa**).

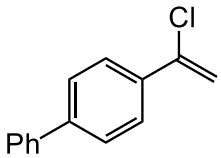
^{13}C NMR (101 MHz, C_6D_6) δ 140.53, 138.90, 129.45, 129.12, 128.47, 128.42, 128.18, 127.94, 127.20, 126.38, 121.17, 18.05, 16.25.



3a: pale yellow oil, 81%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.73 (d, *J* = 1.7 Hz, 1H), 5.47 (d, *J* = 1.7 Hz, 1H), 2.37 (s, 3H).

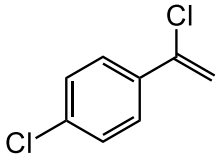
^{13}C NMR (101 MHz, CDCl3) δ 140.1, 139.3, 134.3, 129.1, 126.5, 111.9, 21.3.



3b: white solid, 59%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.70 (m, 2H), 7.64–7.60 (m, 4H), 7.50–7.44 (m, 2H), 7.43–7.35 (m, 1H), 5.84 (d, *J* = 1.8 Hz, 1H), 5.57 (d, *J* = 1.8 Hz, 1H).

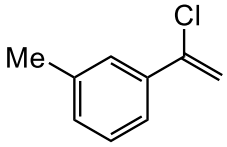
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.4, 139.8, 135.9, 129.0, 127.8, 127.2, 127.1, 127.0, 112.7.



3c: colorless liquid, 36%.[7]

^{1}H NMR (400 MHz, CDCl3) δ 7.60–7.53 (m, 2H), 7.37–7.30 (m, 2H), 5.76 (d, *J* = 1.9 Hz, 1H), 5.54 (d, J = 1.9 Hz, 1H).

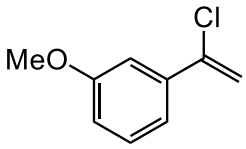
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 135.6, 135.3, 128.7, 127.9, 113.3.



3d: colorless liquid, 82%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 5.75 (d, *J* = 1.7 Hz, 1H), 5.51 (d, *J* = 1.6 Hz, 1H), 2.39 (s, 3H).

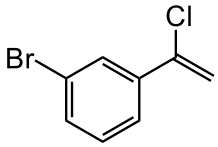
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 138.2, 137.1, 130.0, 128.4, 127.2, 123.7, 112.7, 21.5.



3e: colorless liquid, 47%.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 1H), 7.24–7.20 (m, 1H), 7.19–7.14 (m, 1H), 6.90 (ddd, *J* = 8.0, 2.5, 0.9 Hz, 1H), 5.77 (d, *J* = 1.7 Hz, 1H), 5.53 (d, *J* = 1.7 Hz, 1H), 3.84 (s, 3H).

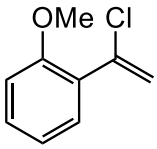
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 139.9, 138.5, 129.5, 119.0, 114.8, 113.1, 112.4, 55.5.



3f: colorless liquid, 47%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 1.8 Hz, 1H), 7.56 (ddd, *J* = 7.9, 1.6, 1.0 Hz, 1H), 7.48 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H), 7.27–7.21 (m, 1H), 5.78 (d, *J* = 2.0 Hz, 1H), 5.57 (d, *J* = 2.0 Hz, 1H).

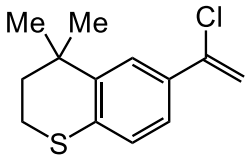
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.5, 132.2, 130.0, 129.6, 125.2, 122.6, 114.1.



3g: colorless liquid, 65%.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32 (td, *J* = 8.3, 1.7 Hz, 1H), 6.99–6.91 (m, 2H), 5.71 (s, 1H), 5.70 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 136.4, 130.4, 130.3, 127.2, 120.5, 117.4, 111.4, 55.8.

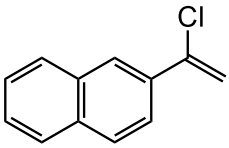


3h: pale yellow oil, 49%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.1 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 5.69 (d, *J* = 1.7 Hz, 1H), 5.44 (d, *J* = 1.7 Hz, 1H), 3.07 – 3.01 (m, 2H), 1.99 – 1.94 (m, 2H), 1.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.1, 133.8, 132.9, 126.5, 124.7, 124.0, 111.4, 37.5, 33.2, 30.2, 23.3.

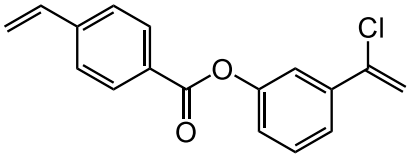
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{13}H_{15}SNaCl$), requires m/z = 261.0471, found m/z = 261.0471.



3i: white, solid, 49%.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.5 Hz, 1H), 7.90–7.87 (m, 1H), 7.86–7.80 (m, 2H), 7.72 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.54–7.49 (m, 2H), 5.92 (d, *J* = 1.8 Hz, 1H), 5.63 (d, *J* = 1.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 134.2, 133.6, 133.1, 128.8, 128.1, 127.7, 127.0, 126.8, 126.5, 123.6, 113.2.

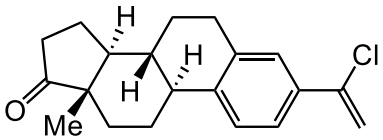


3j: pale yellow oil, 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.55 (ddd, *J* = 4.3, 3.4, 1.8 Hz, 3H), 7.50 (t, *J* = 1.9 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.25–7.19 (m, 1H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 5.82 (d, *J* = 1.9 Hz, 1H), 5.58 (d, *J* = 1.9 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 165.0, 151.1, 142.9, 139.0, 138.7, 136.0, 130.7, 129.5, 128.5, 126.5, 124.0, 122.6, 120.1, 117.2, 113.8.

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{17}H_{13}O_2NaCl$), requires m/z = 307.0502, found m/z = 307.0499.

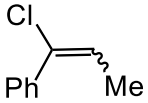


3k: pale yellow solid, 61%. melting point: 137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.37 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 5.73 (d, *J* = 1.7 Hz, 1H), 5.47 (d, *J* = 1.6 Hz, 1H), 2.97–2.91 (m, 2H), 2.51 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.47–2.40 (m, 1H), 2.31 (td, *J* = 10.7, 4.3 Hz, 1H), 2.16 (dd, *J* = 18.4, 9.4 Hz, 1H), 2.08–2.00 (m, 2H), 2.02–1.95 (m, 1H), 1.66–1.59 (m, 2H), 1.56–1.42 (m, 4H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 141.2, 140.0, 136.7, 134.7, 127.2, 125.5, 123.9, 112.1, 50.7, 48.1, 44.6, 38.2, 36.0, 31.7, 29.6, 26.6, 25.8, 21.7, 14.0.

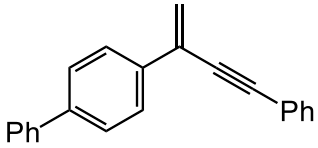
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{23}ONaCl$), requires m/z = 337.1322, found m/z = 337.1322.



3l: colorless liquid, 77% (*E*:*Z* = 75:25).[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.54 (m, 1H), 7.44–7.28 (m, 6H), 6.21 (q, *J* = 6.7 Hz, 1H, *Z*-**3l**), 6.05 (q, *J* = 7.3 Hz, 1H, *E*-**3l**), 1.96 (d, *J* = 6.7 Hz, 1H, *Z*-**3l**), 1.74 (d, *J* = 7.3 Hz, 3H, *E*-**3l**).

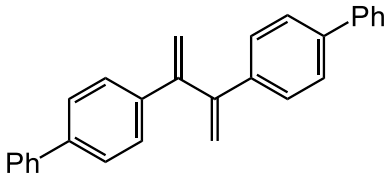
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.2, 133.9, 131.0, 129.0, 128.5, 128.4, 128.3, 126.4, 124.7, 122.5, 15.5, 15.3.



4a: yellow solid, 49%.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 2H), 7.56–7.51 (m, 4H), 7.49–7.44 (m, 2H), 7.39–7.33 (m, 2H), 7.27 (pt, *J* = 5.8, 2.8 Hz, 4H), 5.94 (d, *J* = 0.8 Hz, 1H), 5.70 (d, *J* = 0.7 Hz, 1H).

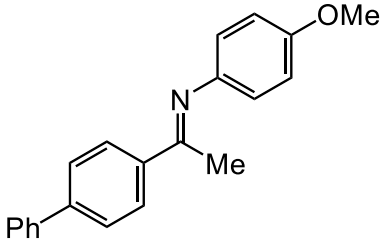
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 140.7, 136.4, 131.9, 130.3, 129.0, 128.6, 128.5, 127.6, 127.3, 127.2, 126.7, 123.2, 120.7, 91.0, 88.7.



4b: white solid, 43%.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.56 (m, 4H), 7.55–7.49 (m, 8H), 7.43 (dd, *J* = 10.4, 4.8 Hz, 4H), 7.33 (ddd, *J* = 7.3, 3.8, 1.1 Hz, 2H), 5.67 (d, *J* = 1.5 Hz, 2H), 5.40 (d, *J* = 1.5 Hz, 2H).

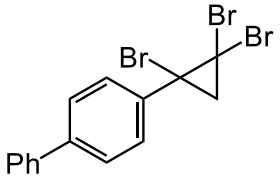
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 140.8, 140.5, 139.1, 128.9, 127.9, 127.4, 127.1, 116.4.



4c: brown-yellow solid, 43%.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.05 (m, 2H), 7.73–7.65 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (ddd, *J* = 7.3, 3.8, 1.2 Hz, 1H), 6.97–6.92 (m, 2H), 6.85–6.78 (m, 2H), 3.84 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 156.1, 144.9, 143.1, 140.5, 138.7, 129.0, 127.8, 127.7, 127.2, 127.1, 120.9, 114.4, 55.6, 17.4.



4c: white solid, 35%, melting point: 144 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48–7.42 (m, 2H), 7.37 (ddd, *J* = 7.3, 3.8, 1.2 Hz, 1H), 2.55 (d, *J* = 9.3 Hz, 1H), 2.29 (d, *J* = 9.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.3, 139.1, 129.7, 129.0, 127.9, 127.4, 127.3, 42.9, 37.3, 32.0.

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{15}H_{11}NaBr_3$), requires m/z = 450.8309, found m/z = 450.8296.

5. References

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6. Spectra of products

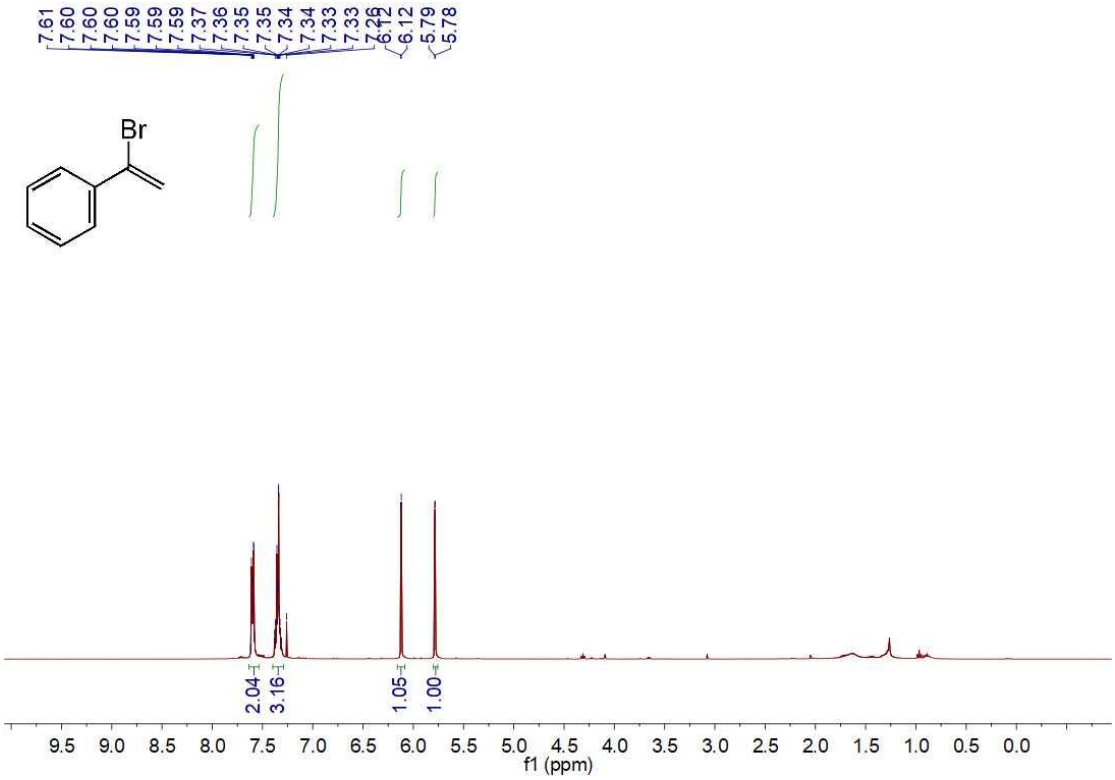

Figure S1 The ^{1}H NMR spectra of **2a** ($CDCl_3$, 400M)

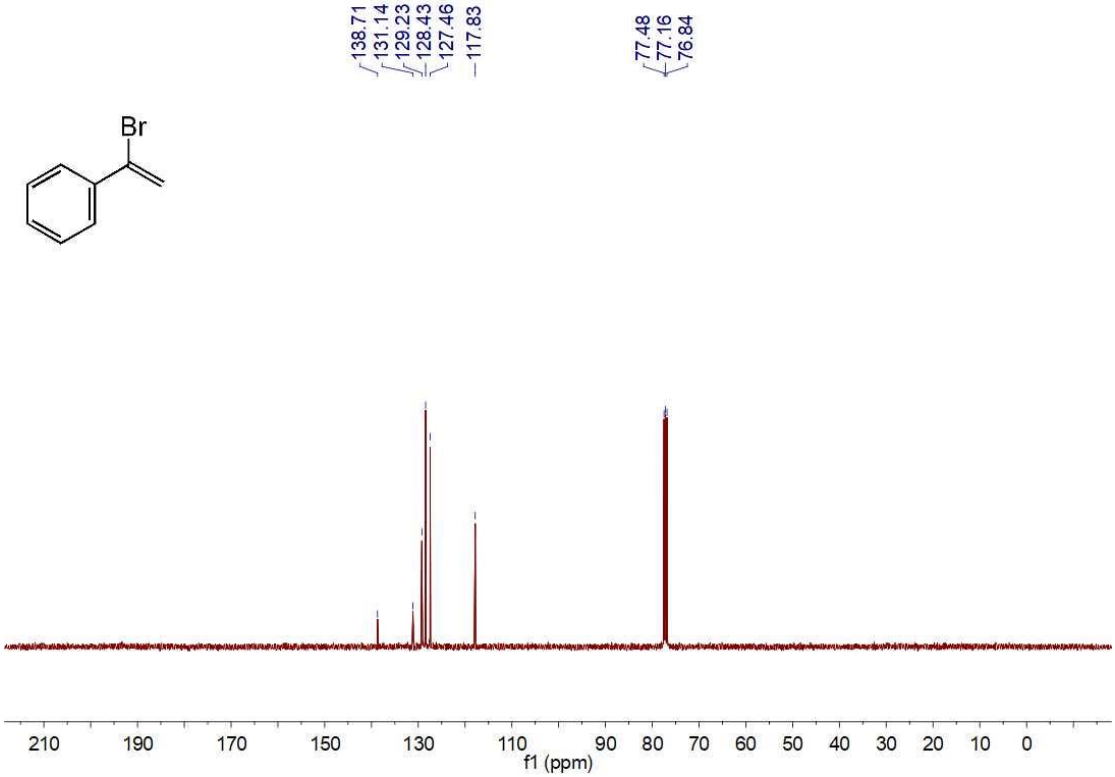

Figure S2 The ^{13}C NMR spectra of **2a** ($CDCl_3$, 101M)

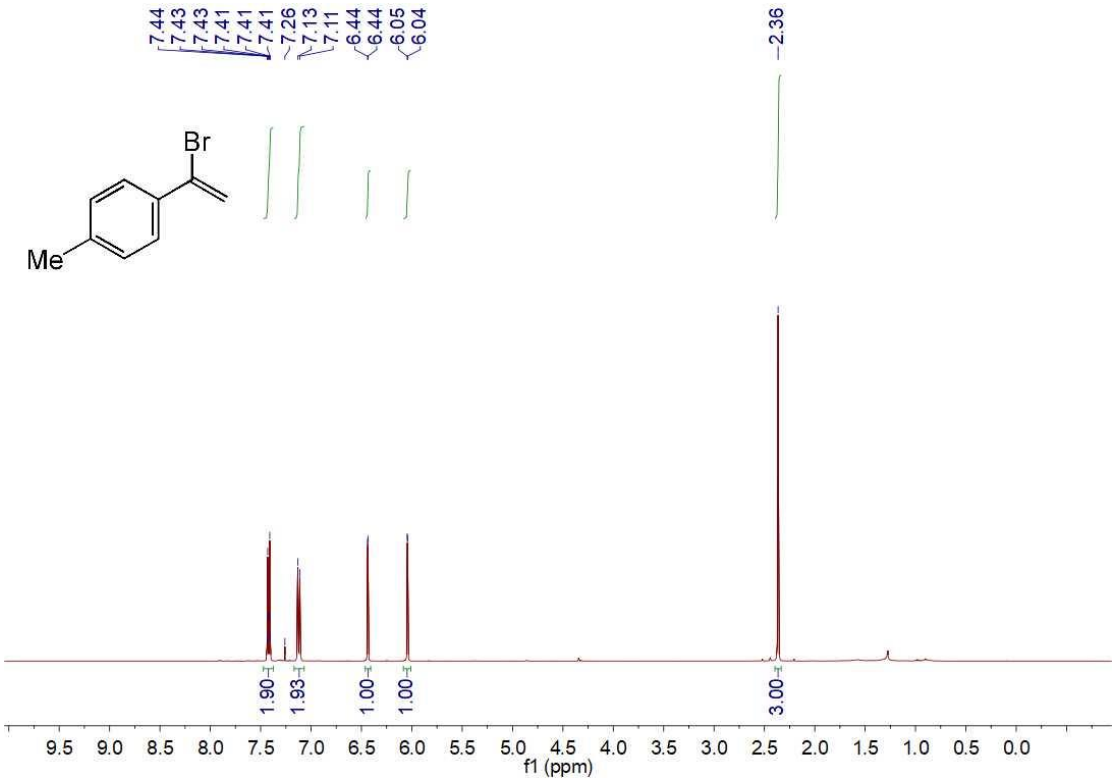

Figure S3 The ^{1}H NMR spectra of **2b** ($CDCl_3$, 400M)

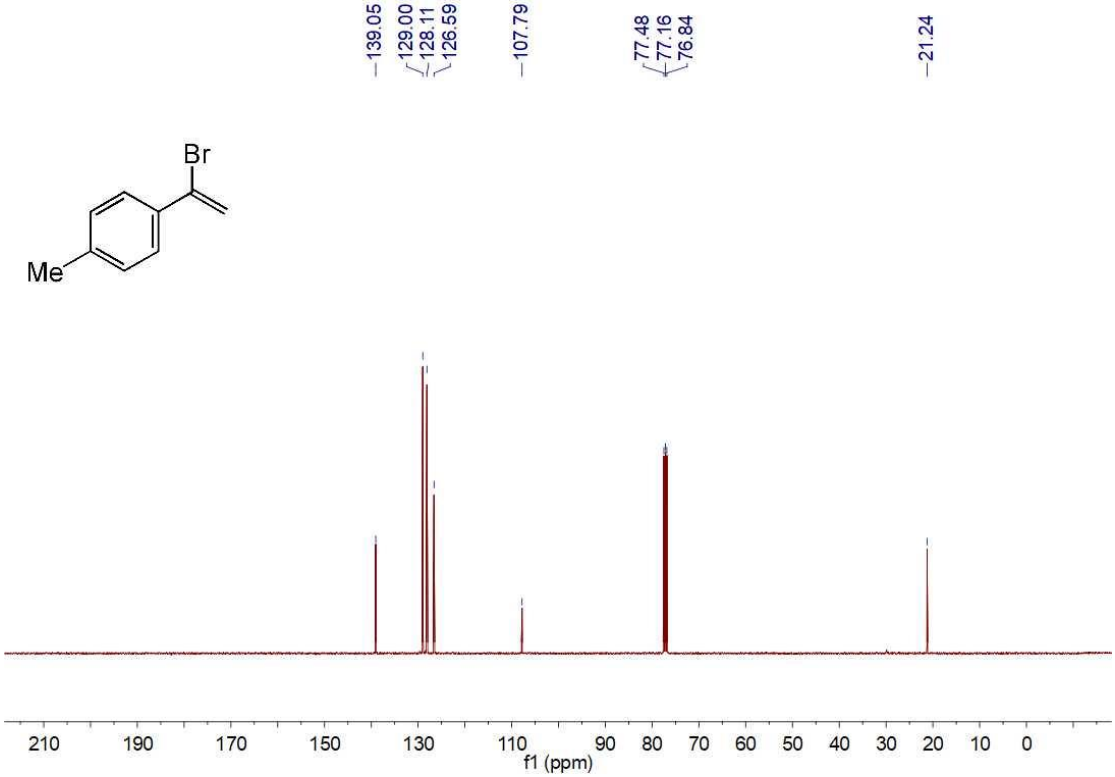

Figure S4 The ^{13}C NMR spectra of **2b** ($CDCl_3$, 101M)

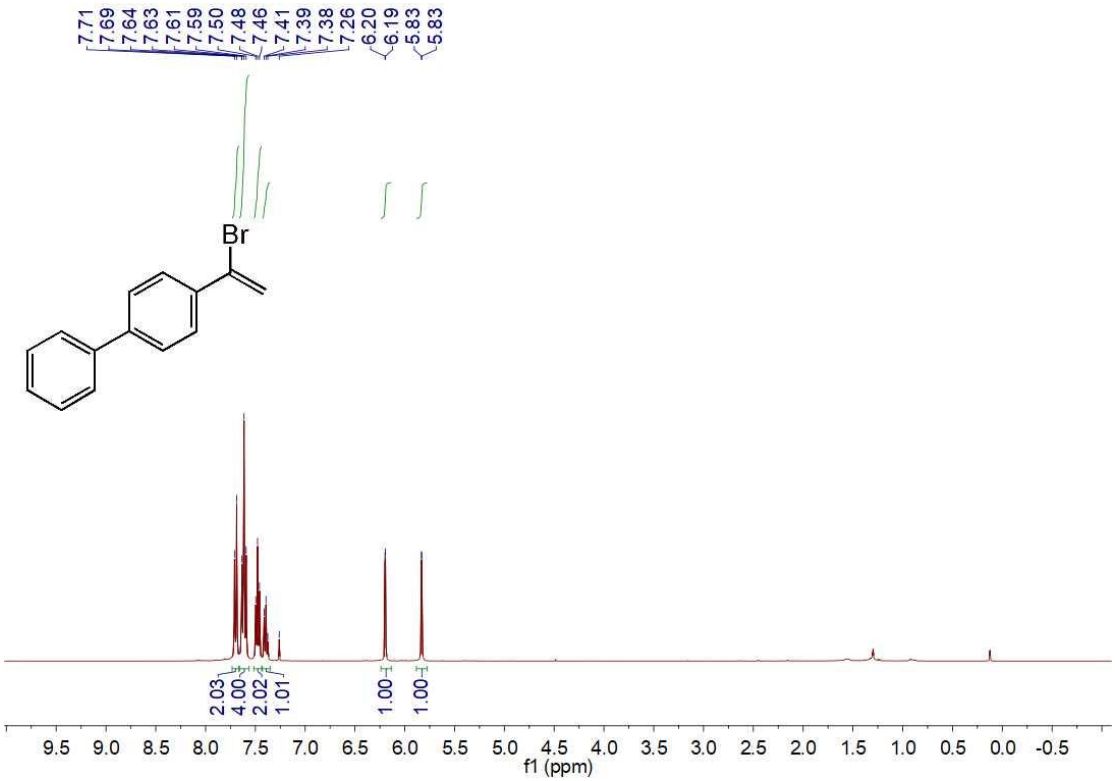

Figure S5 The ^{1}H NMR spectra of **2c** ($CDCl_3$, 400M)

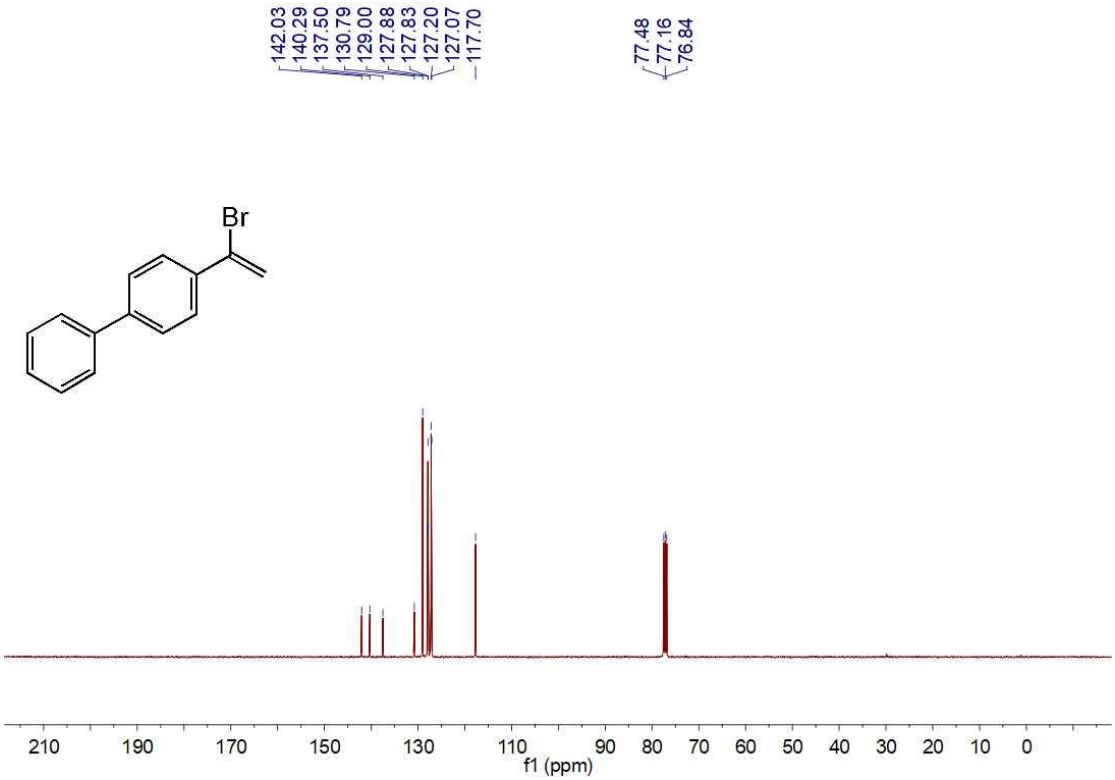

Figure S6 The ^{13}C NMR spectra of **2c** ($CDCl_3$, 101M)

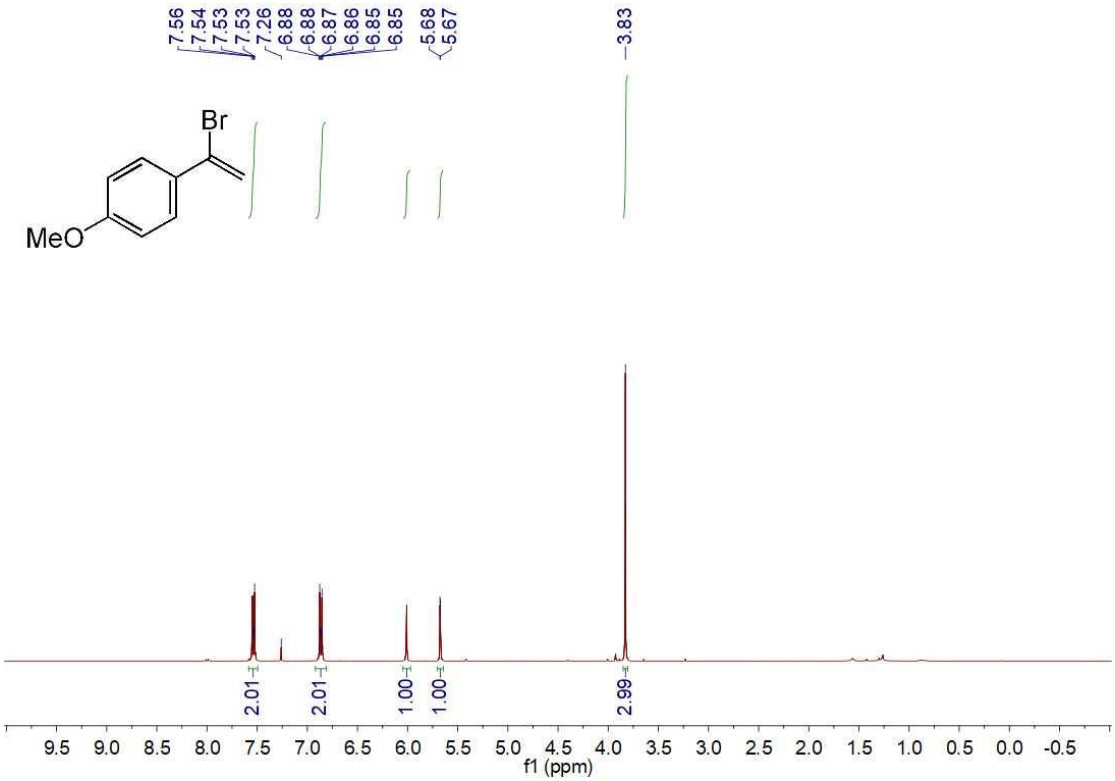

Figure S7 The ^{1}H NMR spectra of **2d** ($CDCl_3$, 400M)

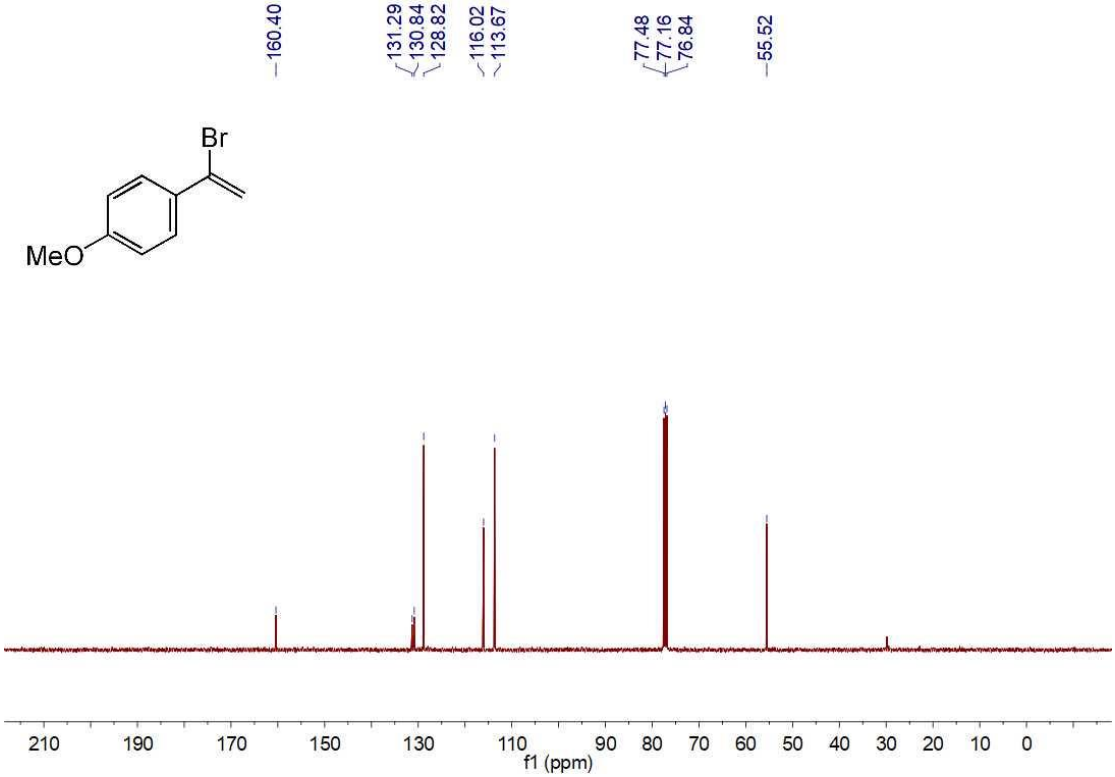

Figure S8 The ^{13}C NMR spectra of **2d** ($CDCl_3$, 101M)

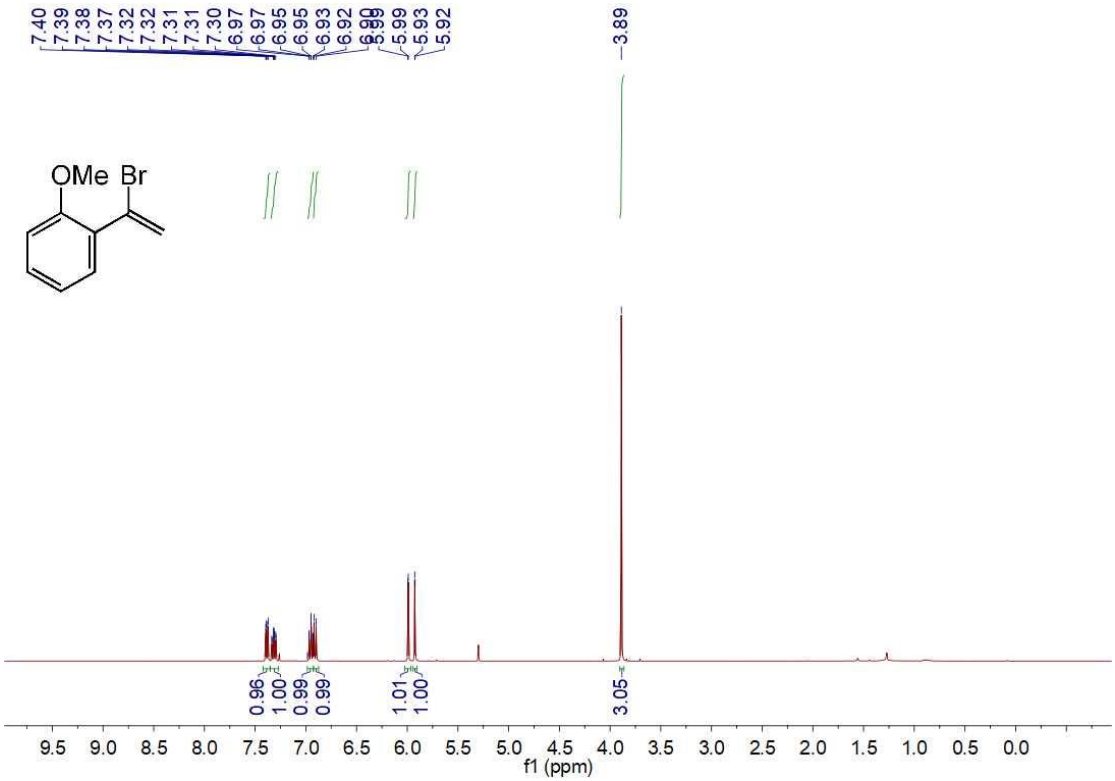

Figure S9 The ^{1}H NMR spectra of **2e** ($CDCl_3$, 400M)

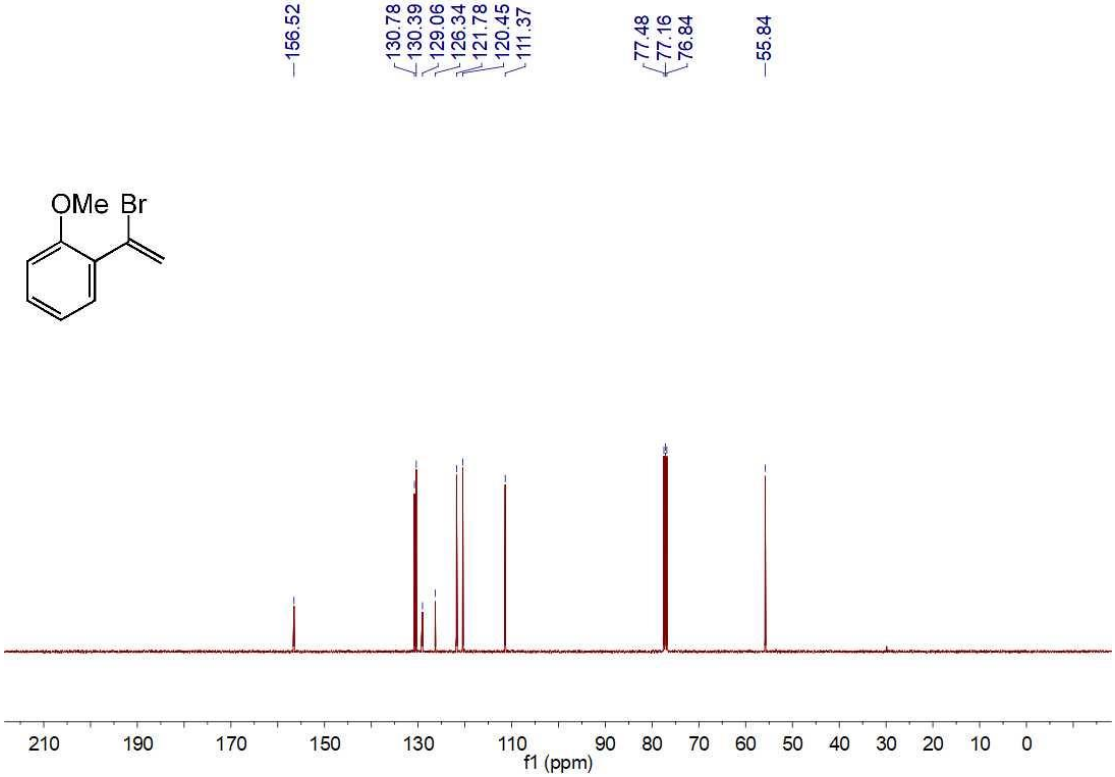

Figure S10 The ^{13}C NMR spectra of **2e** ($CDCl_3$, 101M)

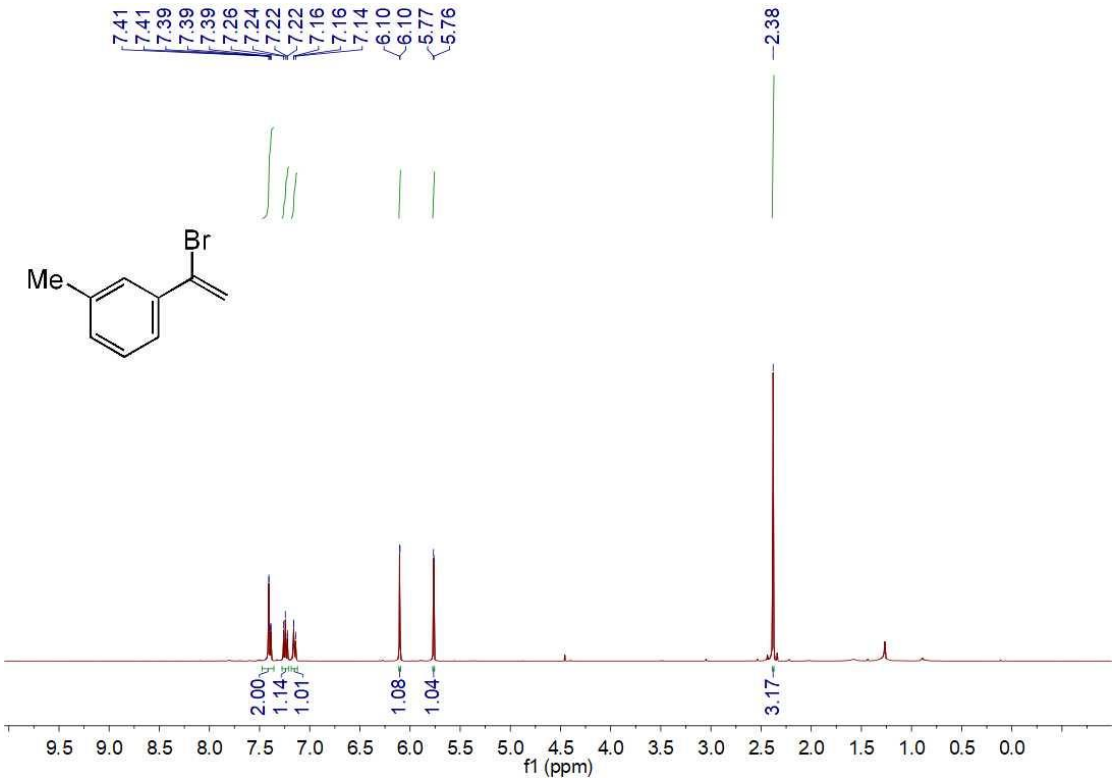

Figure S11 The ^{1}H NMR spectra of **2f** ($CDCl_3$, 400M)

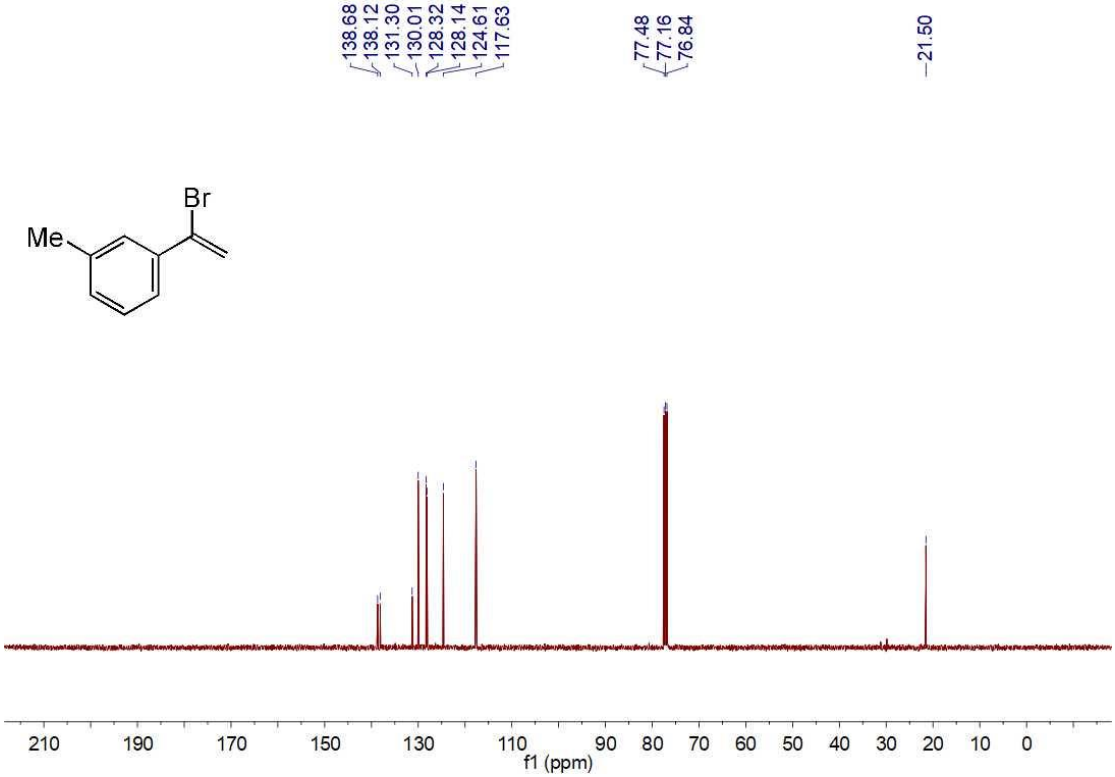

Figure S12 The ^{13}C NMR spectra of **2f** ($CDCl_3$, 101M)

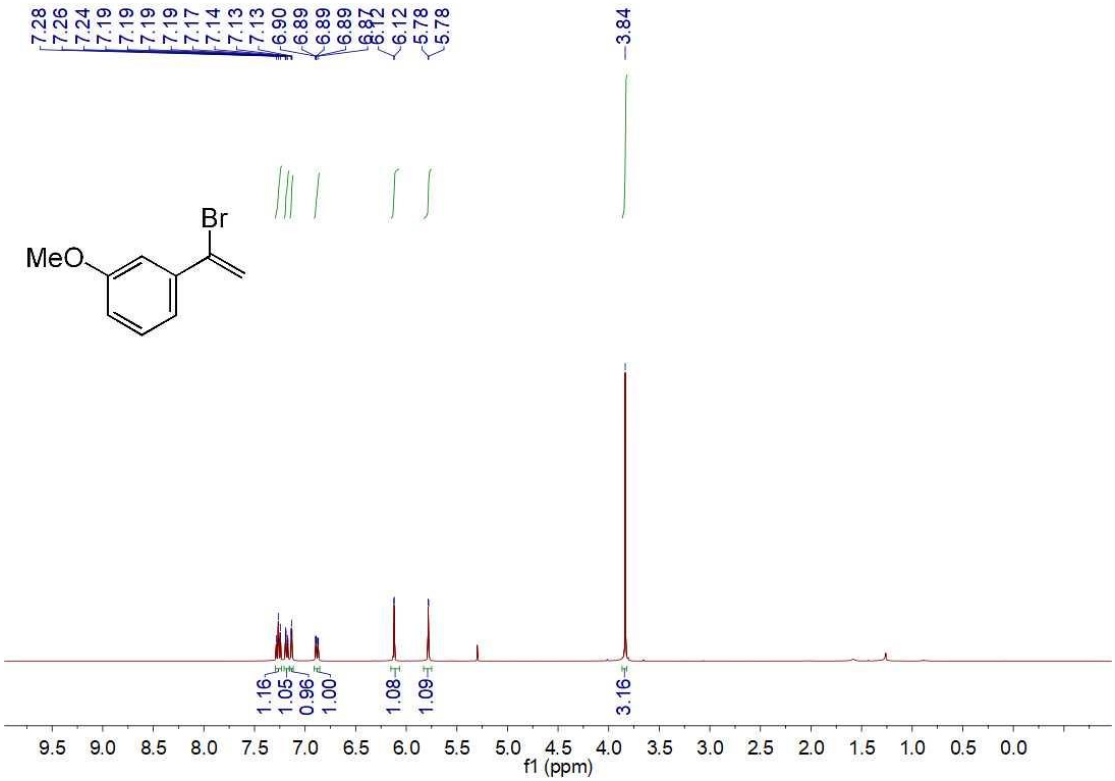

Figure S13 The ^{1}H NMR spectra of **2g** ($CDCl_3$, 400M)

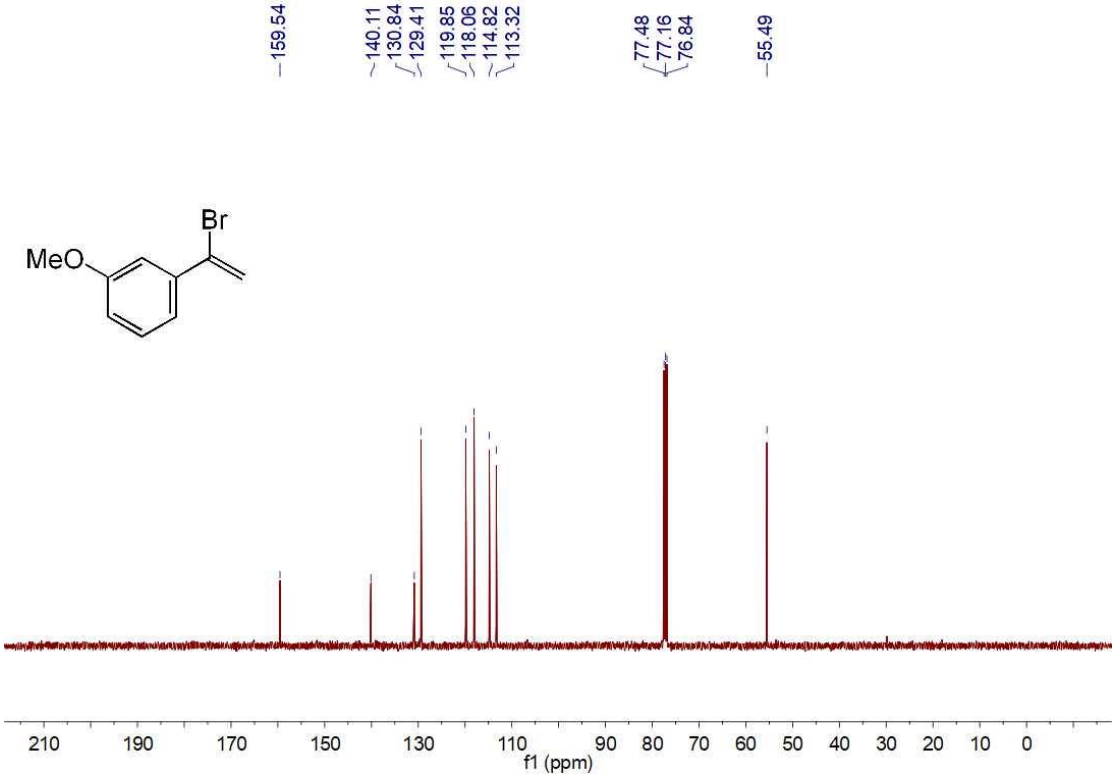

Figure S14 The ^{13}C NMR spectra of **2g** ($CDCl_3$, 101M)

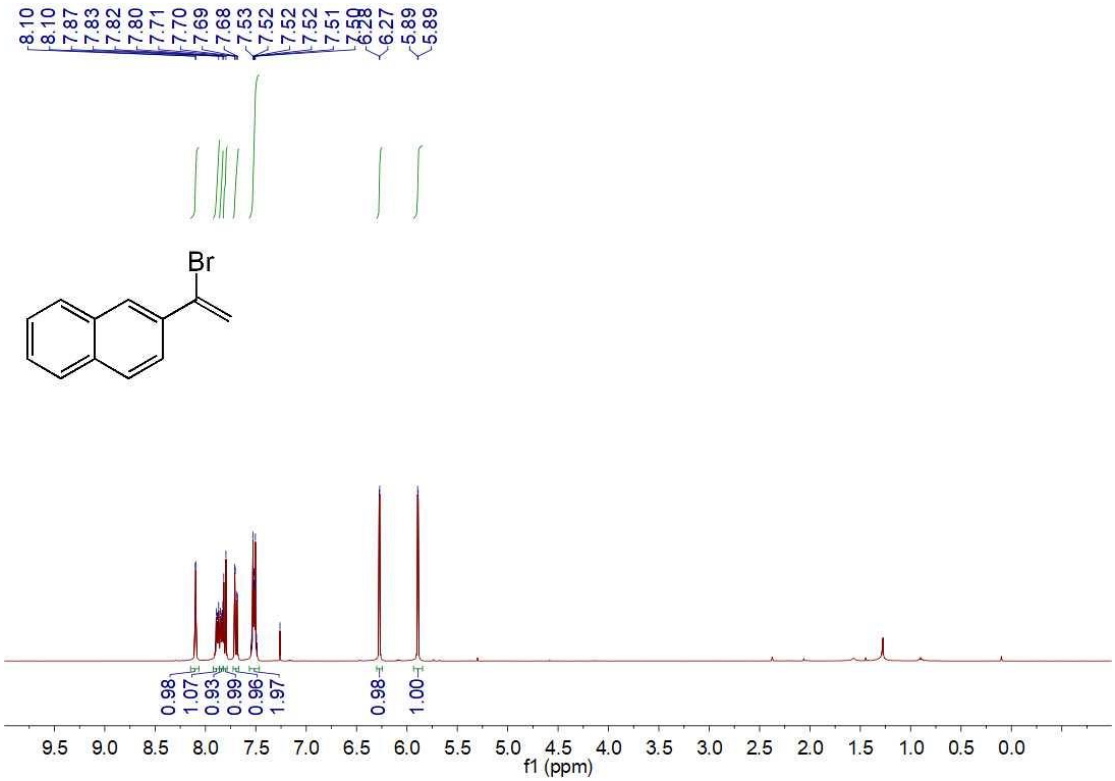

Figure S15 The ^{1}H NMR spectra of **2h** ($CDCl_3$, 400M)

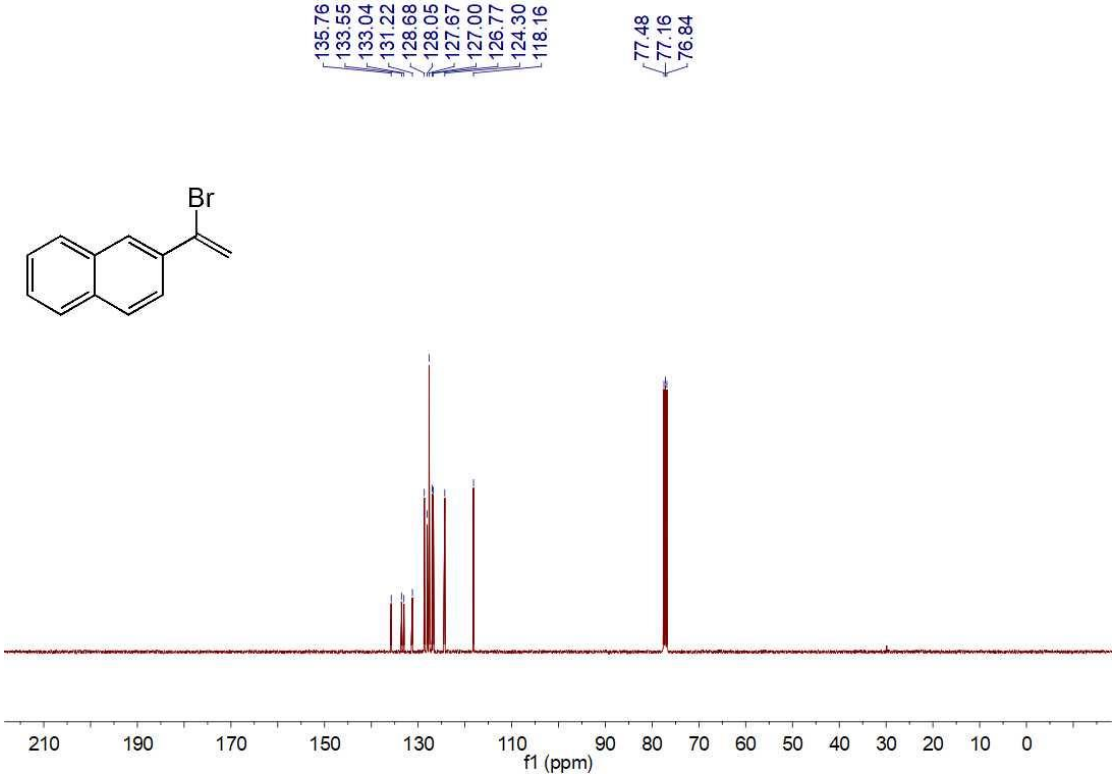

Figure S16 The ^{13}C NMR spectra of **2h** ($CDCl_3$, 101M)

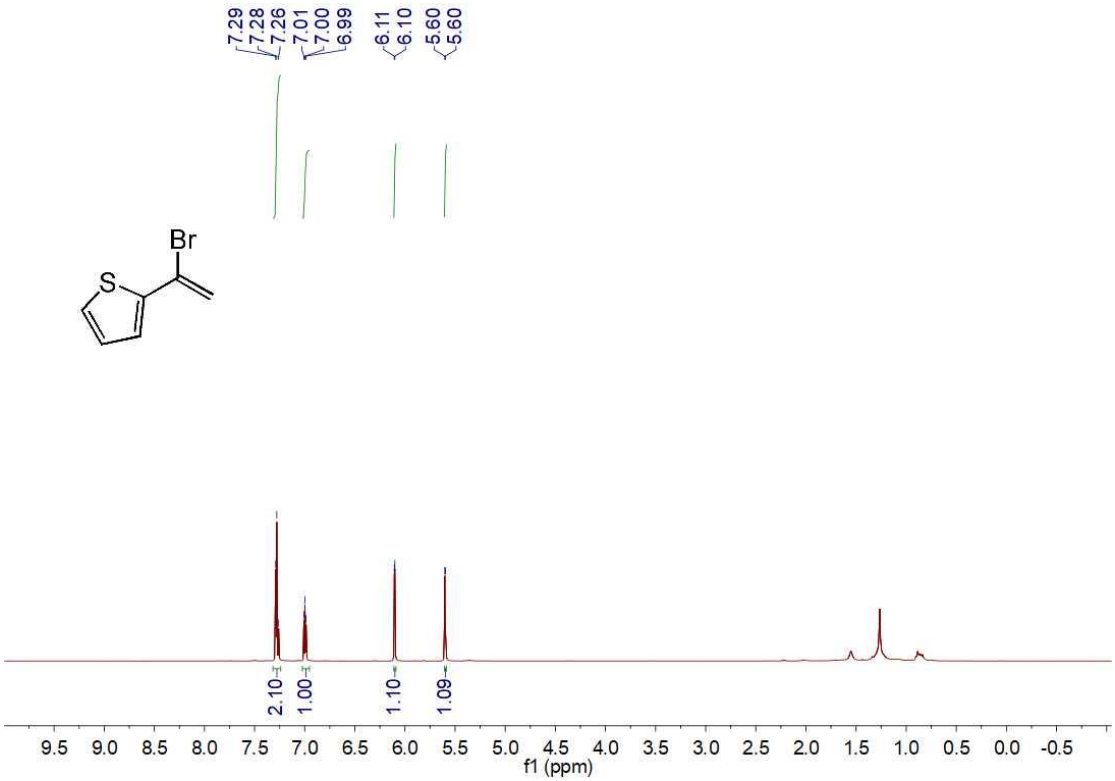

Figure S17 The ^{1}H NMR spectra of **2i** ($CDCl_3$, 400M)

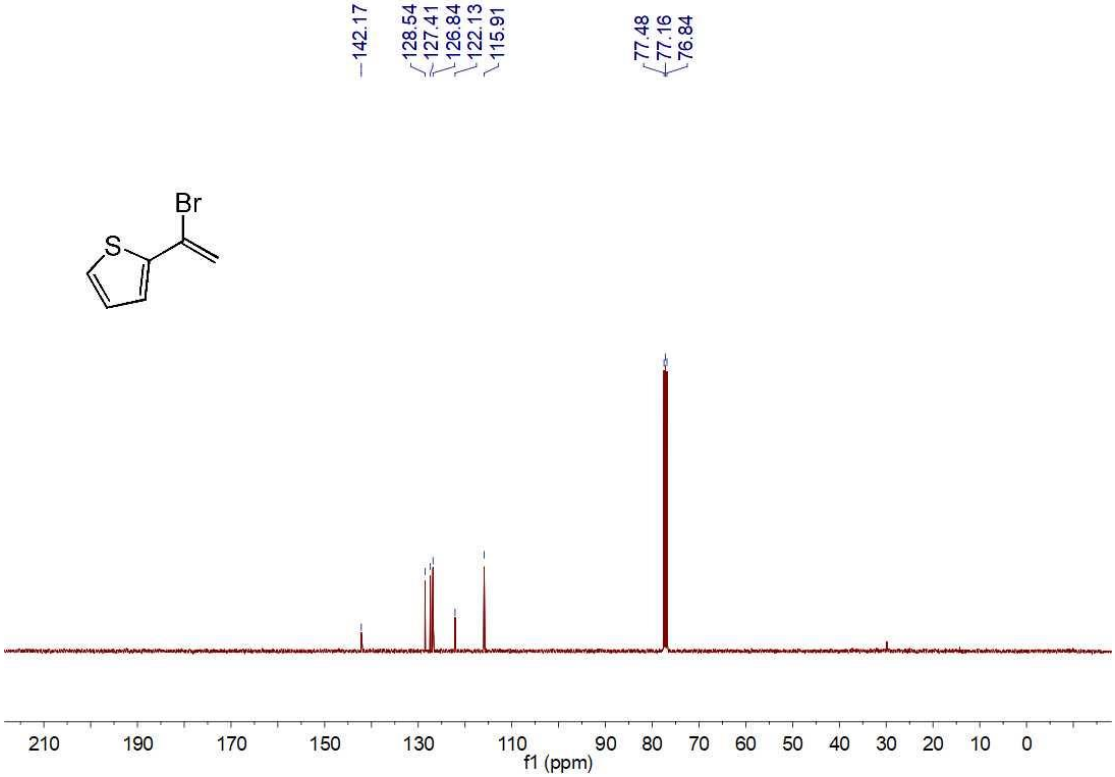

Figure S18 The ^{13}C NMR spectra of **2i** ($CDCl_3$, 101M)

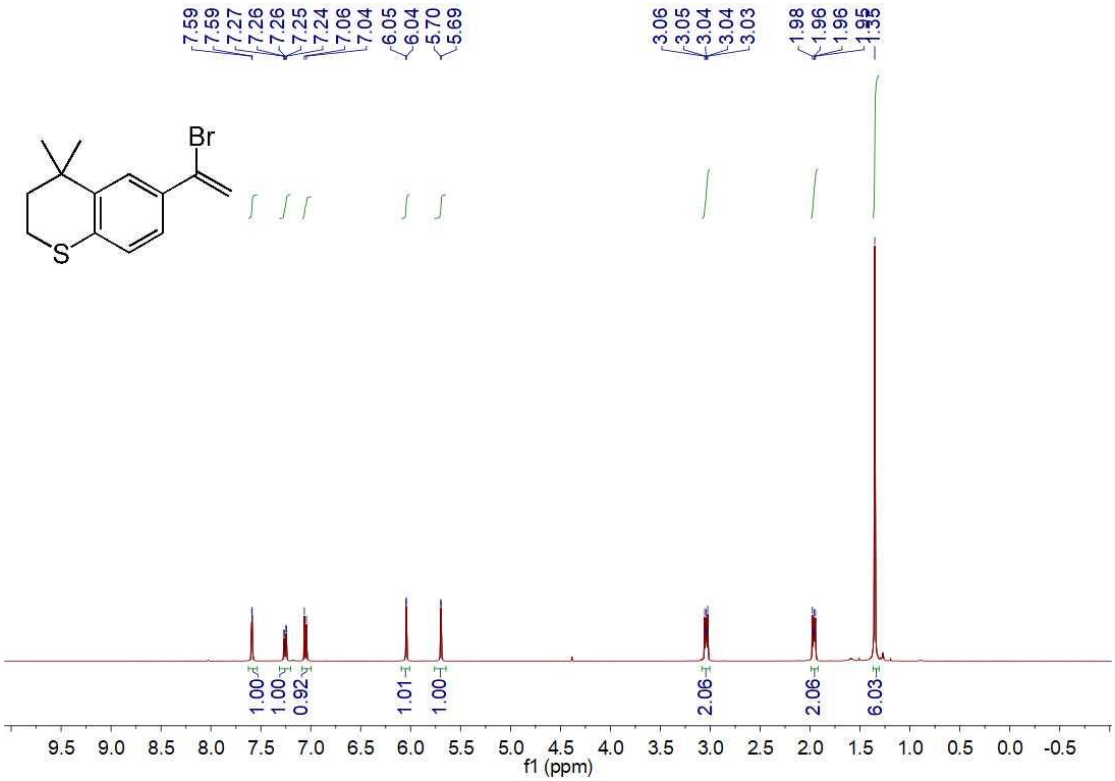

Figure S19 The ^{1}H NMR spectra of **2j** ($CDCl_3$, 400M)

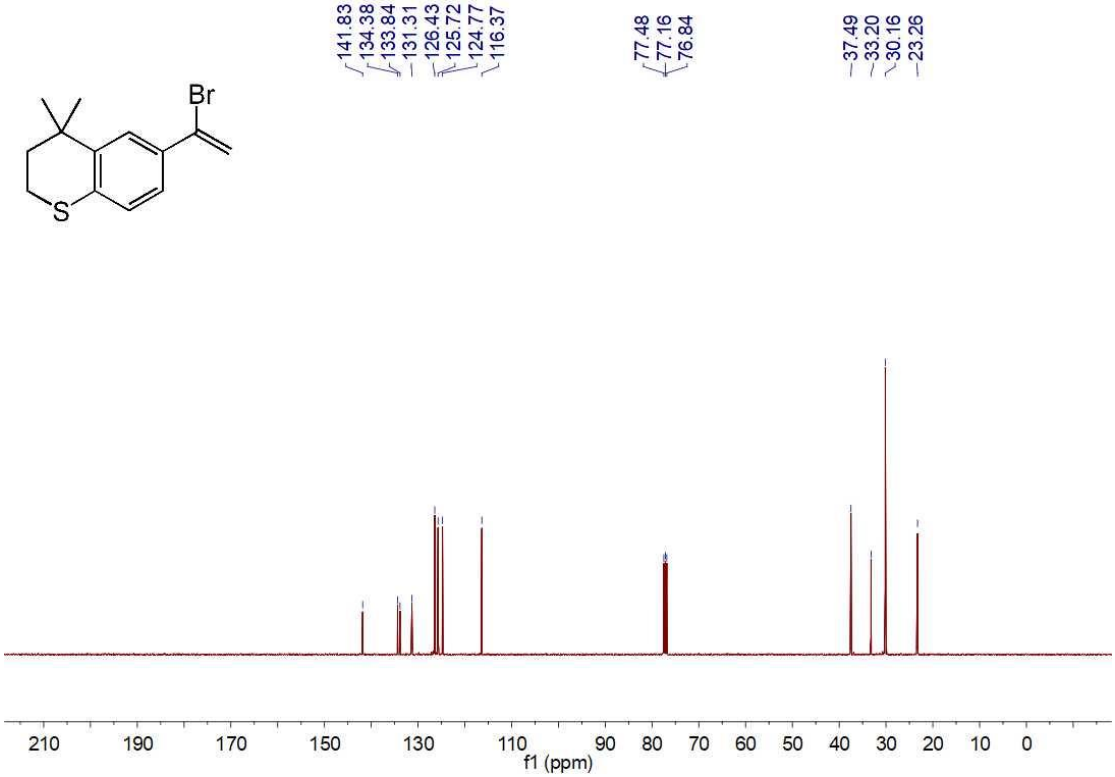

Figure S20 The ^{13}C NMR spectra of **2j** ($CDCl_3$, 101M)

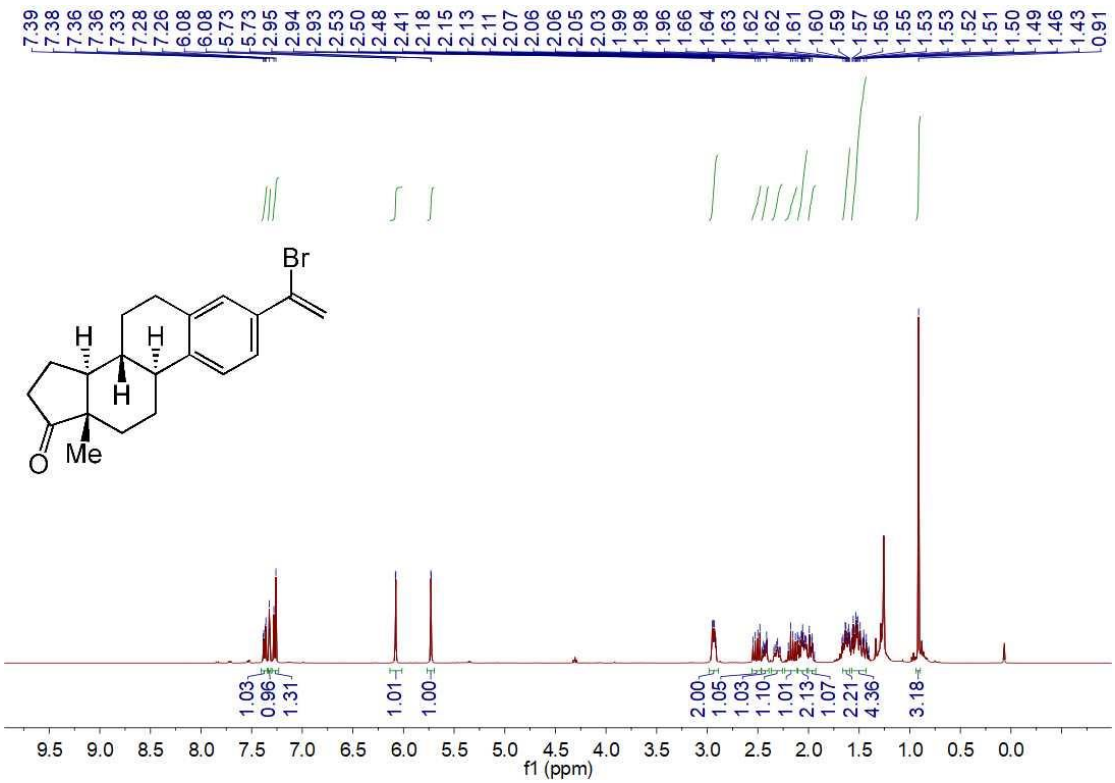

Figure S21 The ^{1}H NMR spectra of **2k** ($CDCl_3$, 400M)

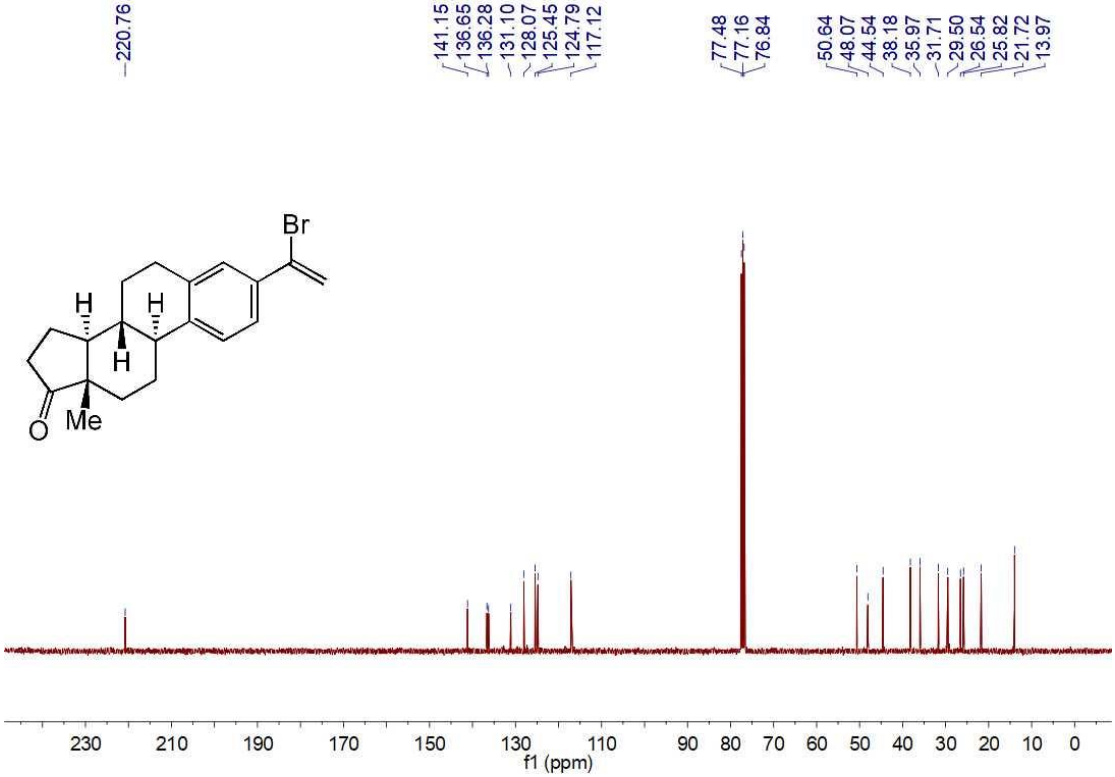

Figure S22 The ^{13}C NMR spectra of **2k** ($CDCl_3$, 101M)

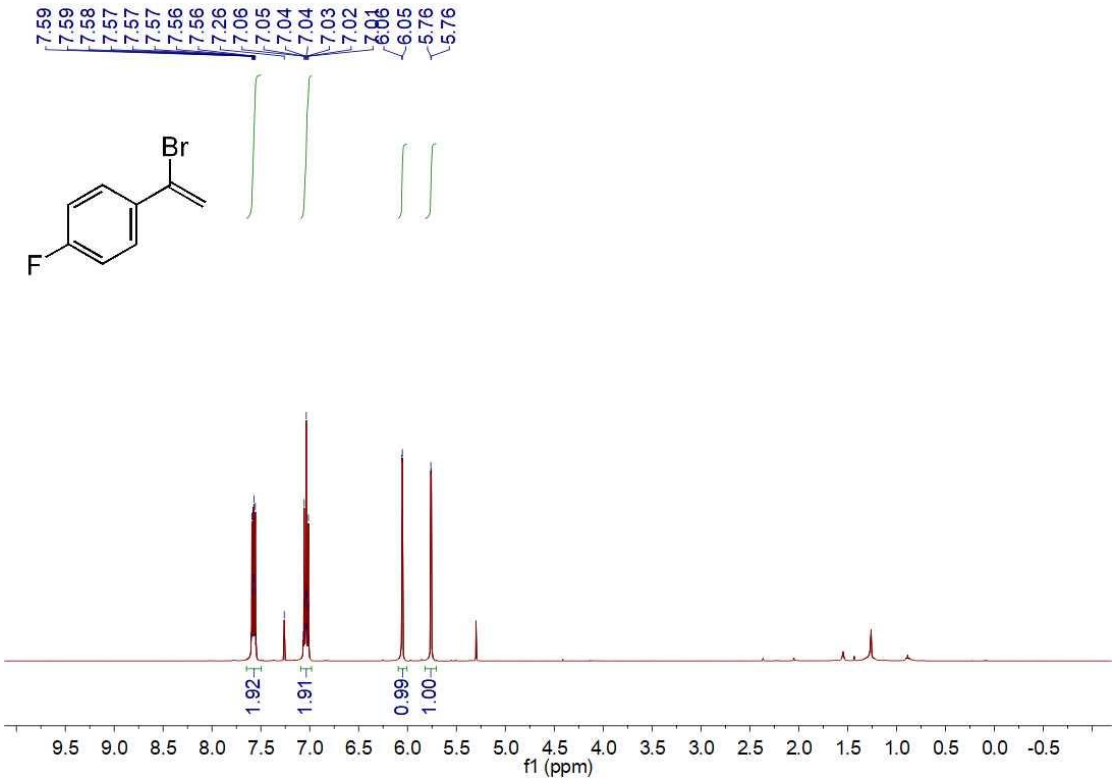

Figure S23 The ^{1}H NMR spectra of **2l** ($CDCl_3$, 400M)

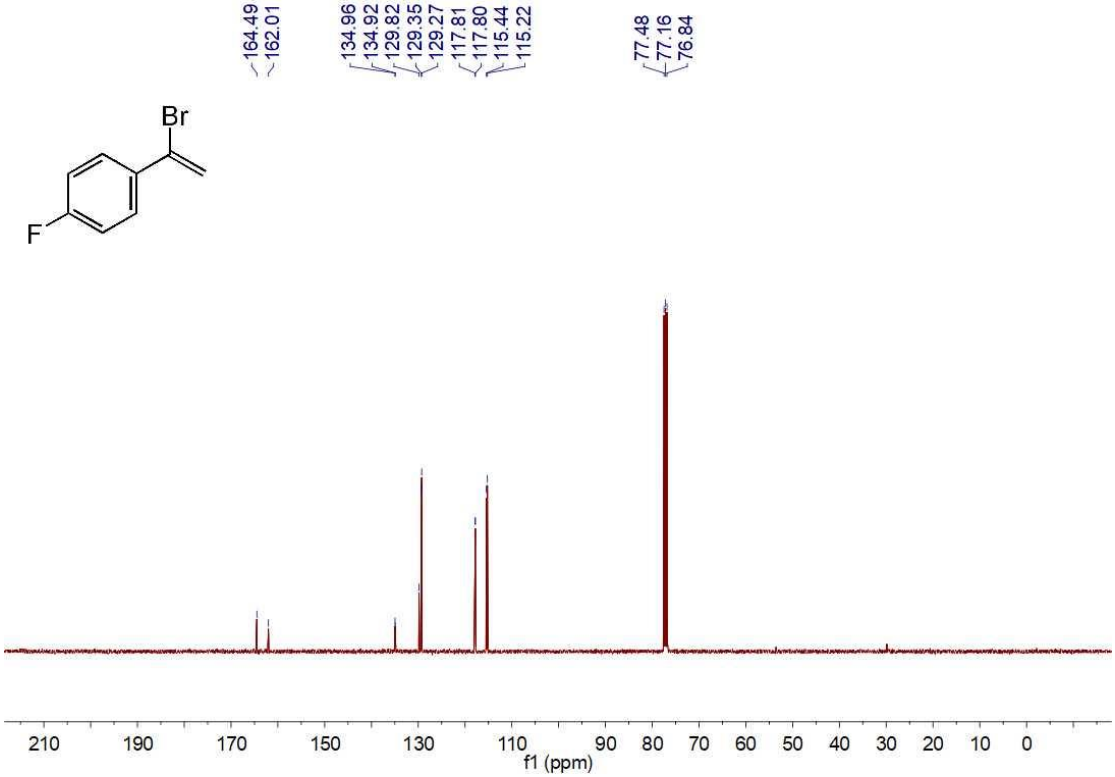

Figure S24 The ^{13}C NMR spectra of **2l** ($CDCl_3$, 101M)

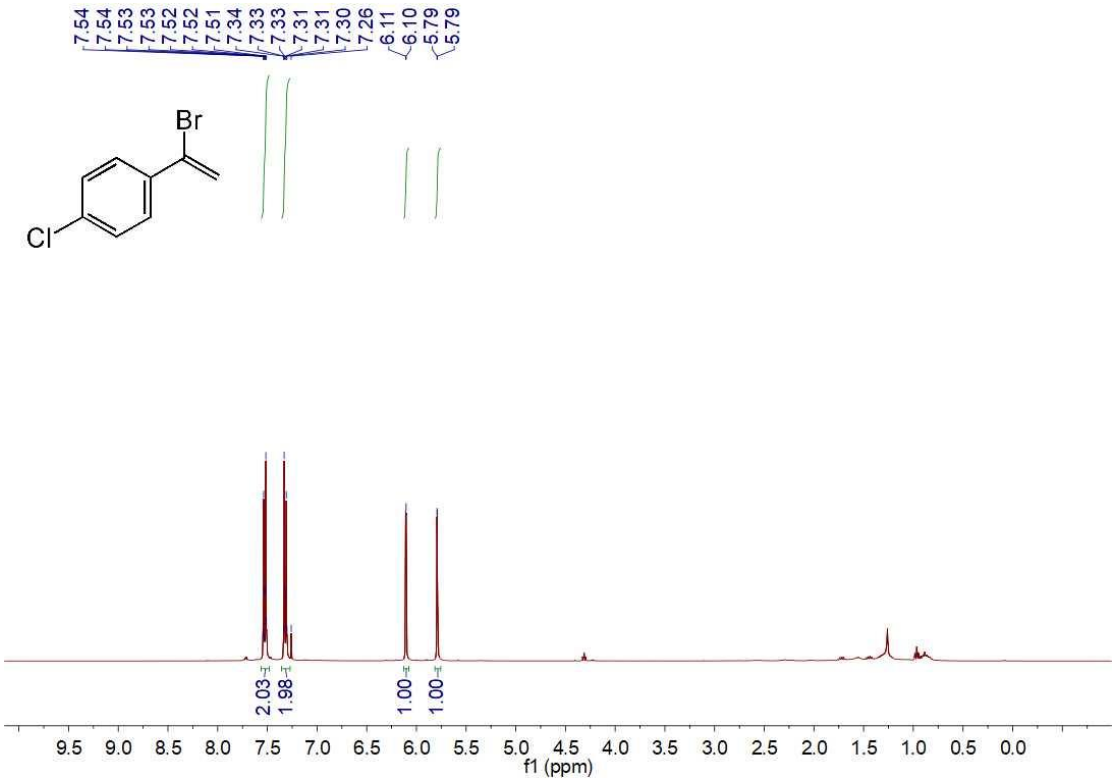

Figure S25 The ^{1}H NMR spectra of **2m** ($CDCl_3$, 400M)

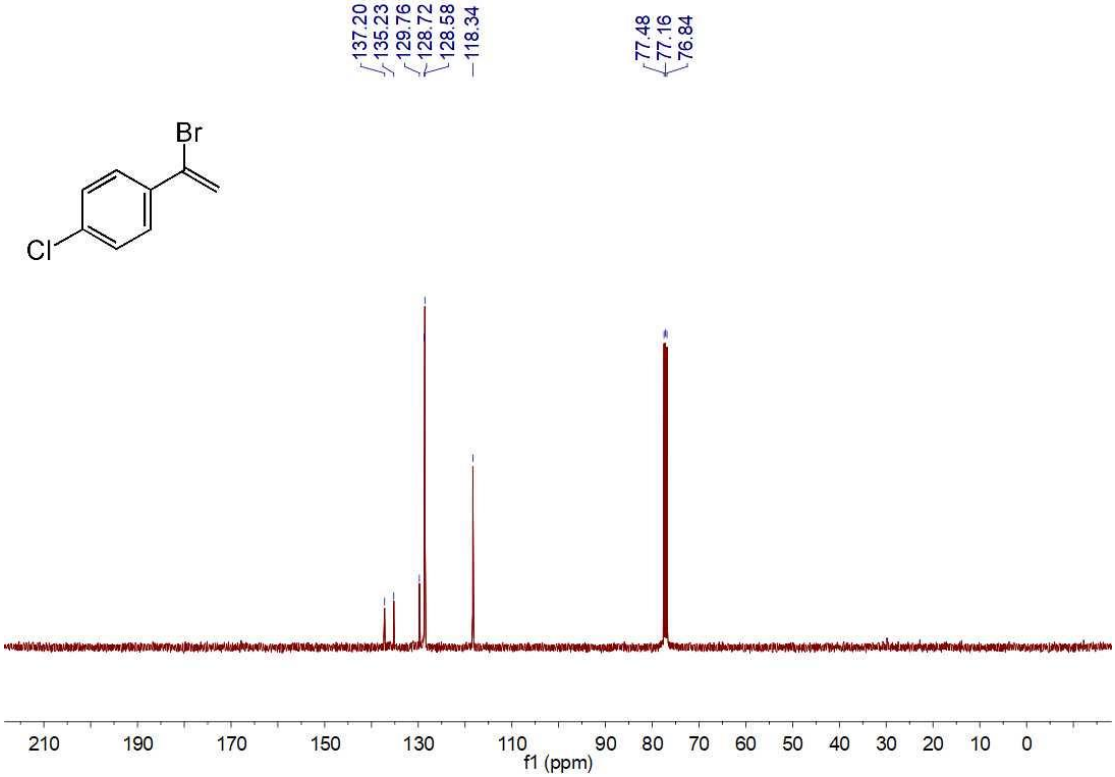

Figure S26 The ^{13}C NMR spectra of **2m** ($CDCl_3$, 101M)

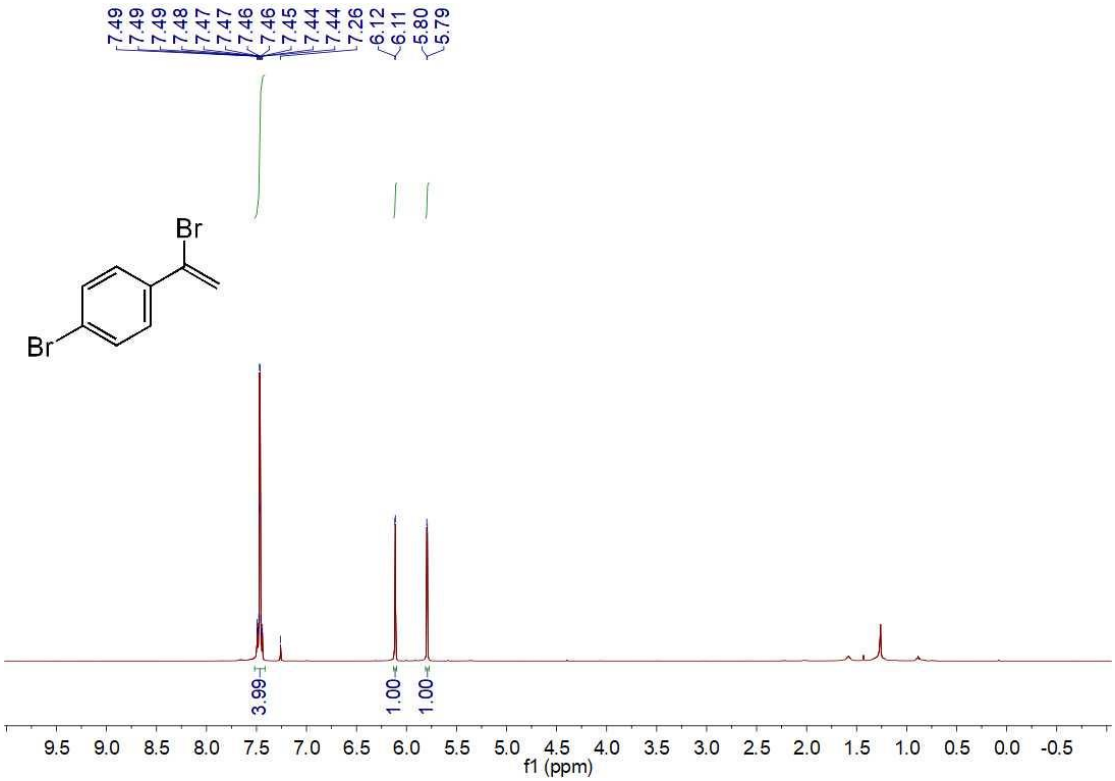

Figure S27 The ^{1}H NMR spectra of **2n** ($CDCl_3$, 400M)

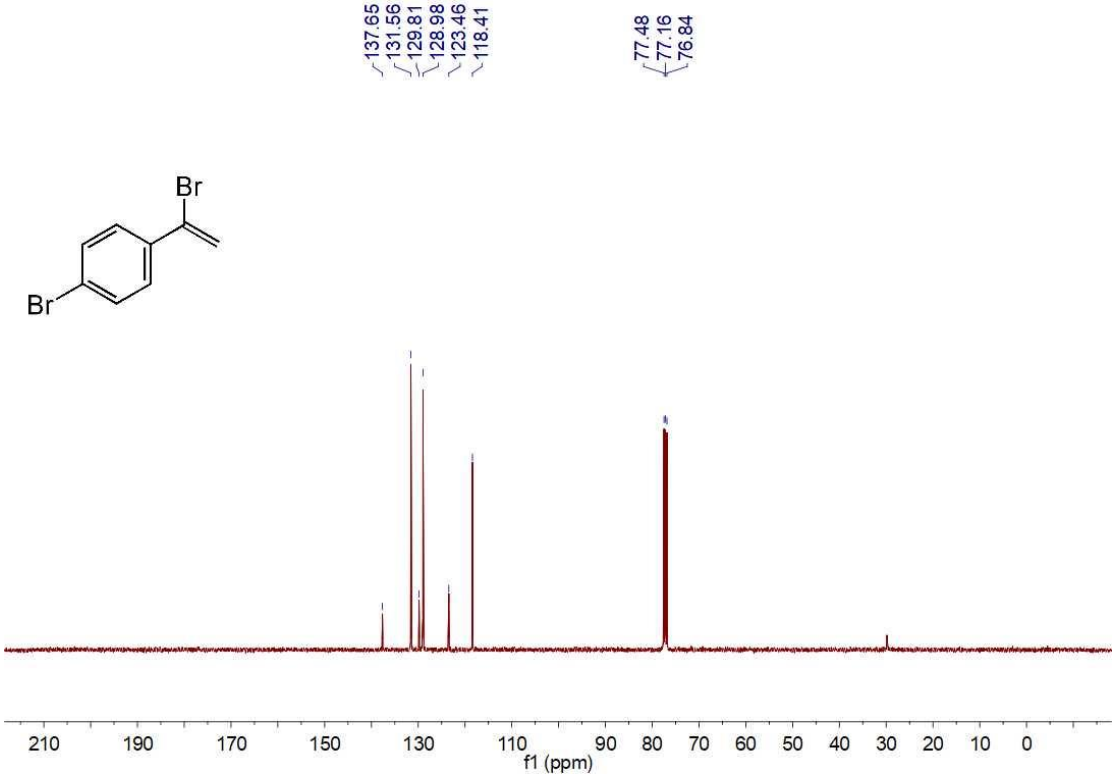

Figure S28 The ^{13}C NMR spectra of **2n** ($CDCl_3$, 101M)

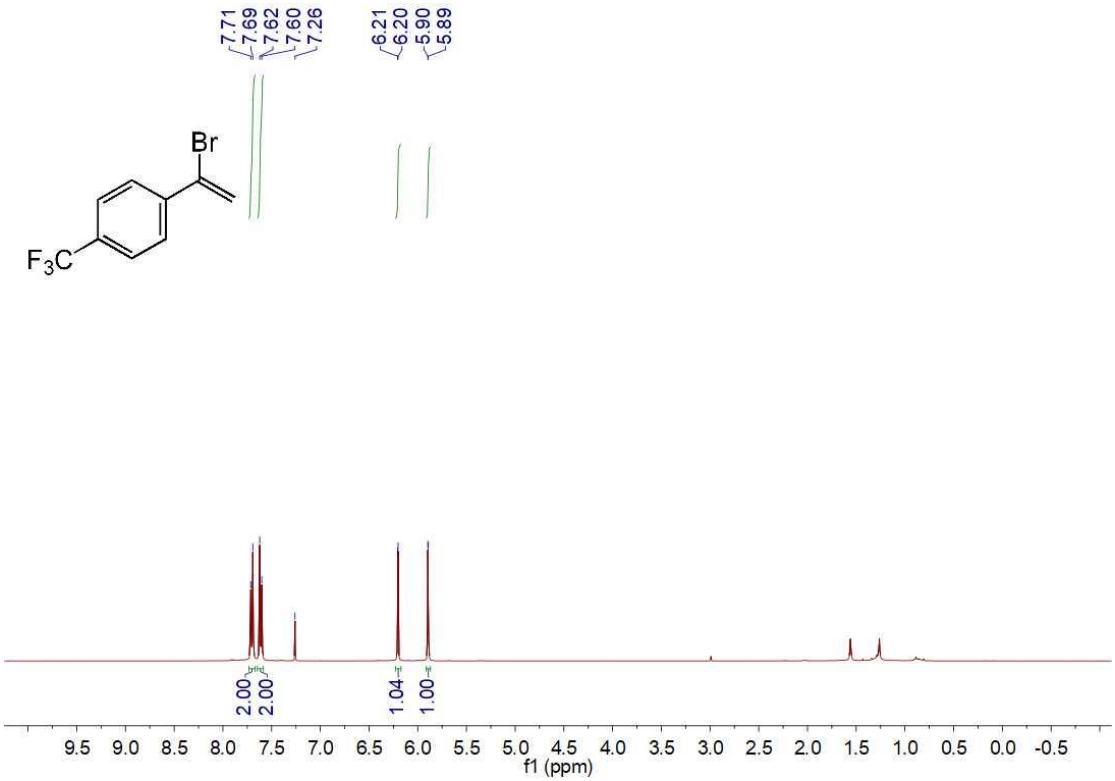

Figure S29 The ^{1}H NMR spectra of **2o** ($CDCl_3$, 400M)

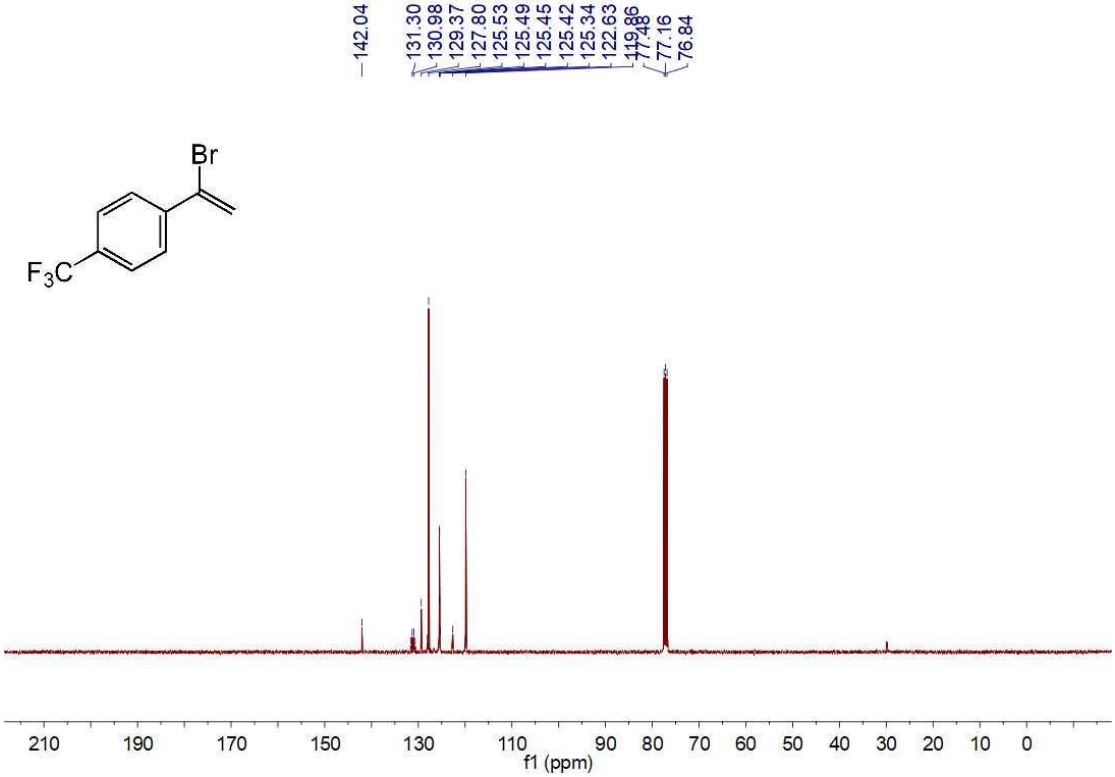

Figure S30 The ^{13}C NMR spectra of **2o** ($CDCl_3$, 101M)

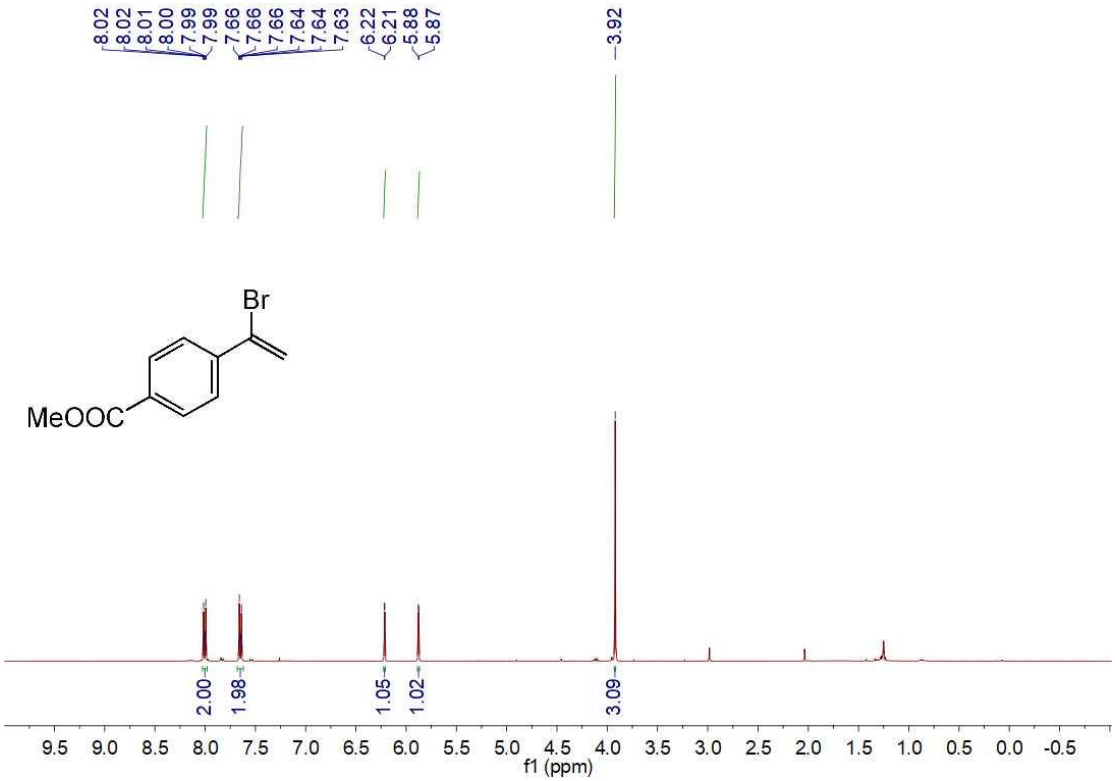

Figure S31 The ^{1}H NMR spectra of **2p** ($CDCl_3$, 400M)

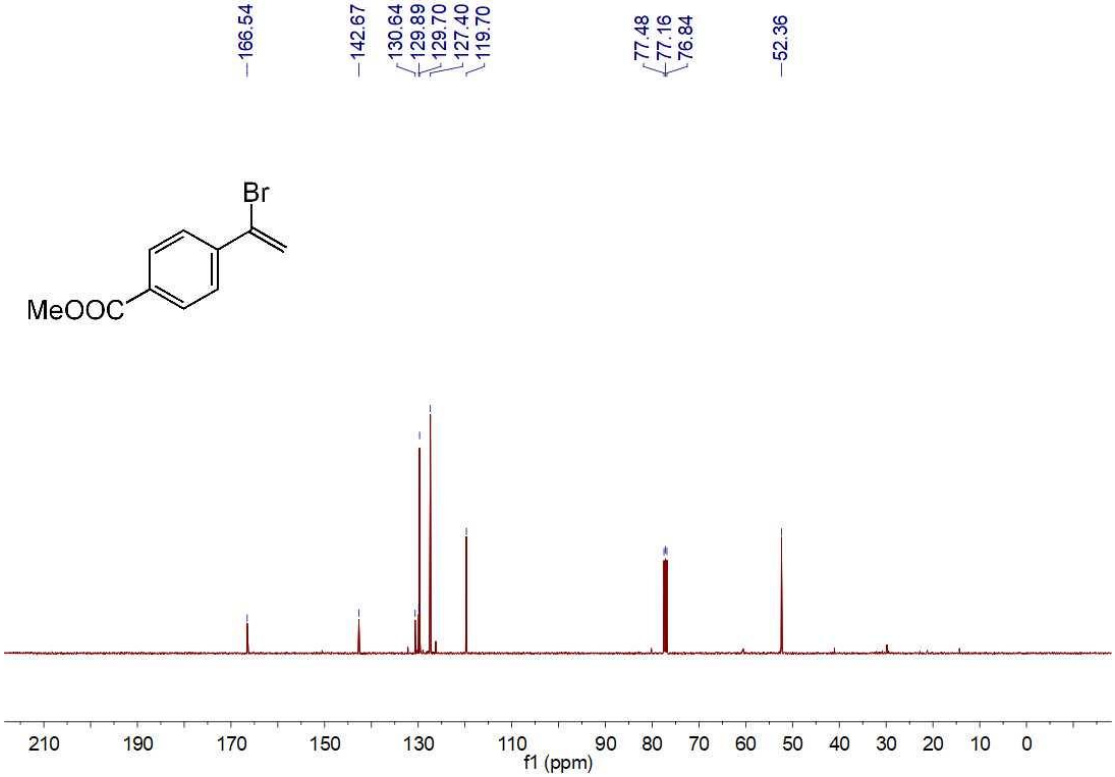

Figure S32 The ^{13}C NMR spectra of **2p** ($CDCl_3$, 101M)

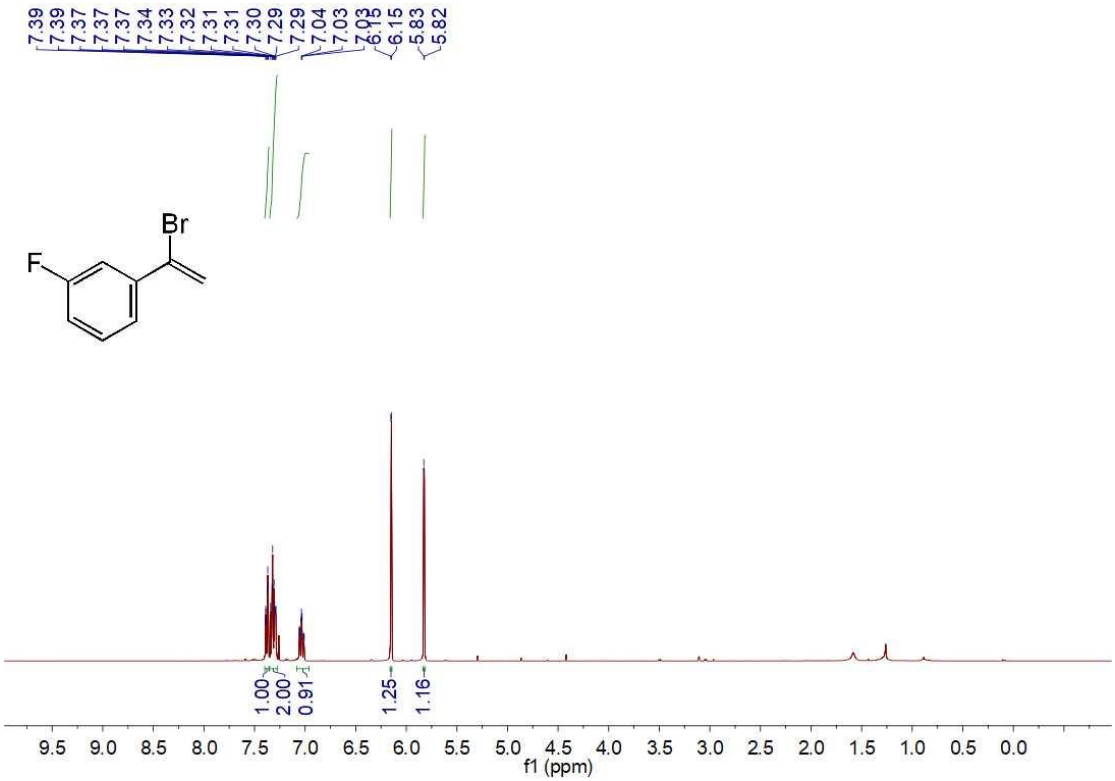

Figure S33 The ^{1}H NMR spectra of **2q** ($CDCl_3$, 400M)

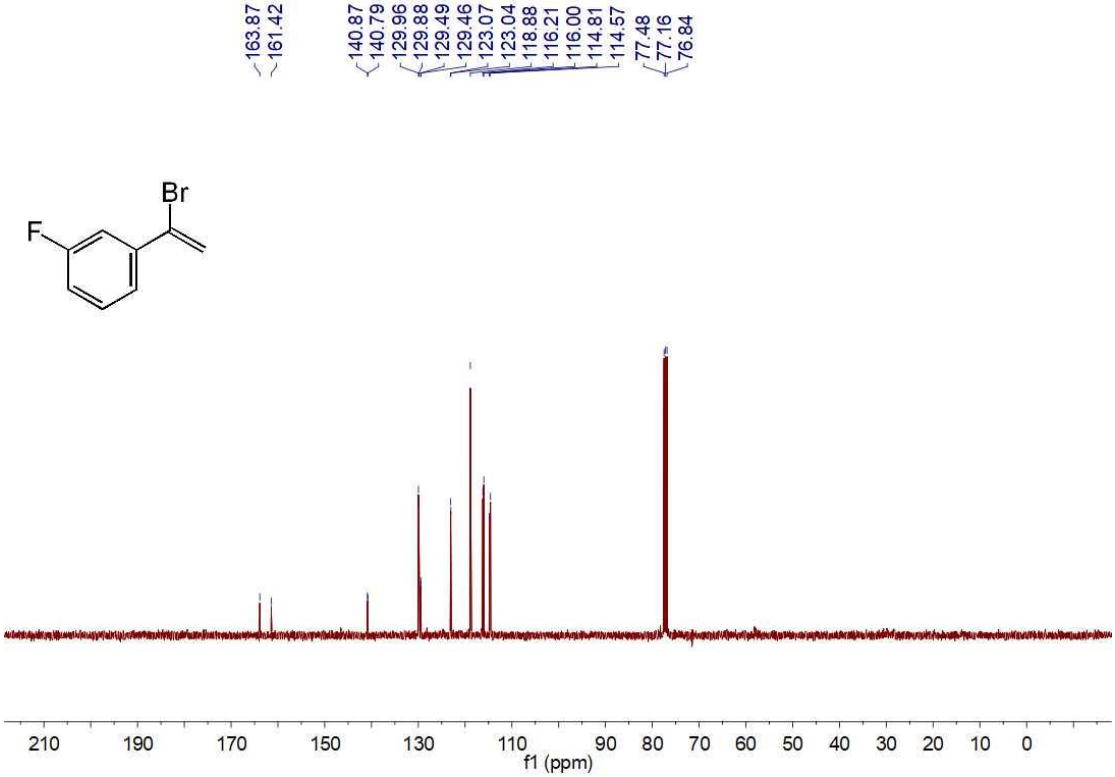

Figure S34 The ^{13}C NMR spectra of **2q** ($CDCl_3$, 101M)

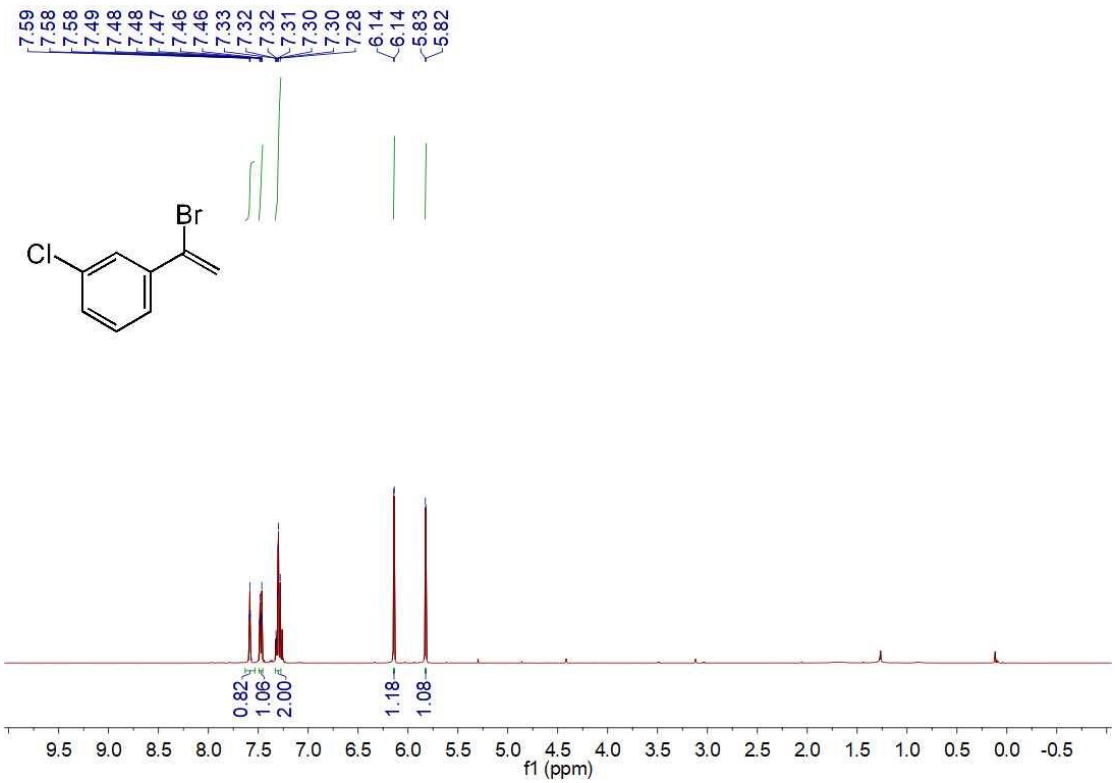

Figure S35 The ^{1}H NMR spectra of **2r** ($CDCl_3$, 400M)

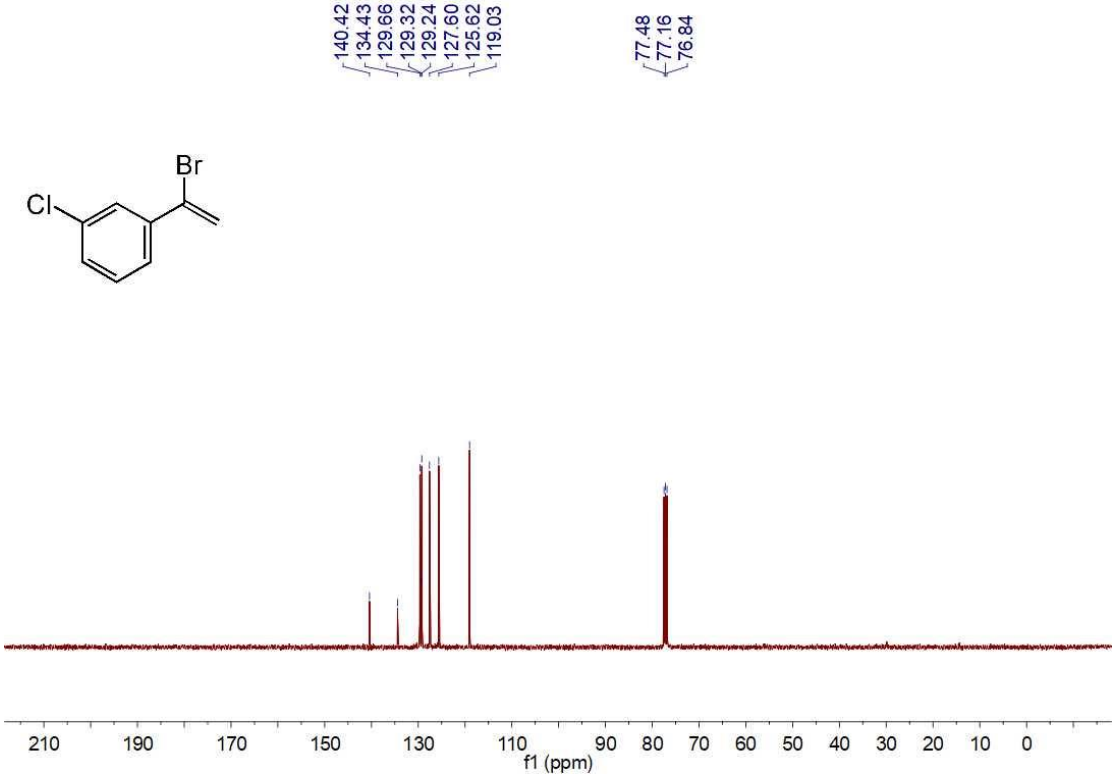

Figure S36 The ^{13}C NMR spectra of **2r** ($CDCl_3$, 101M)

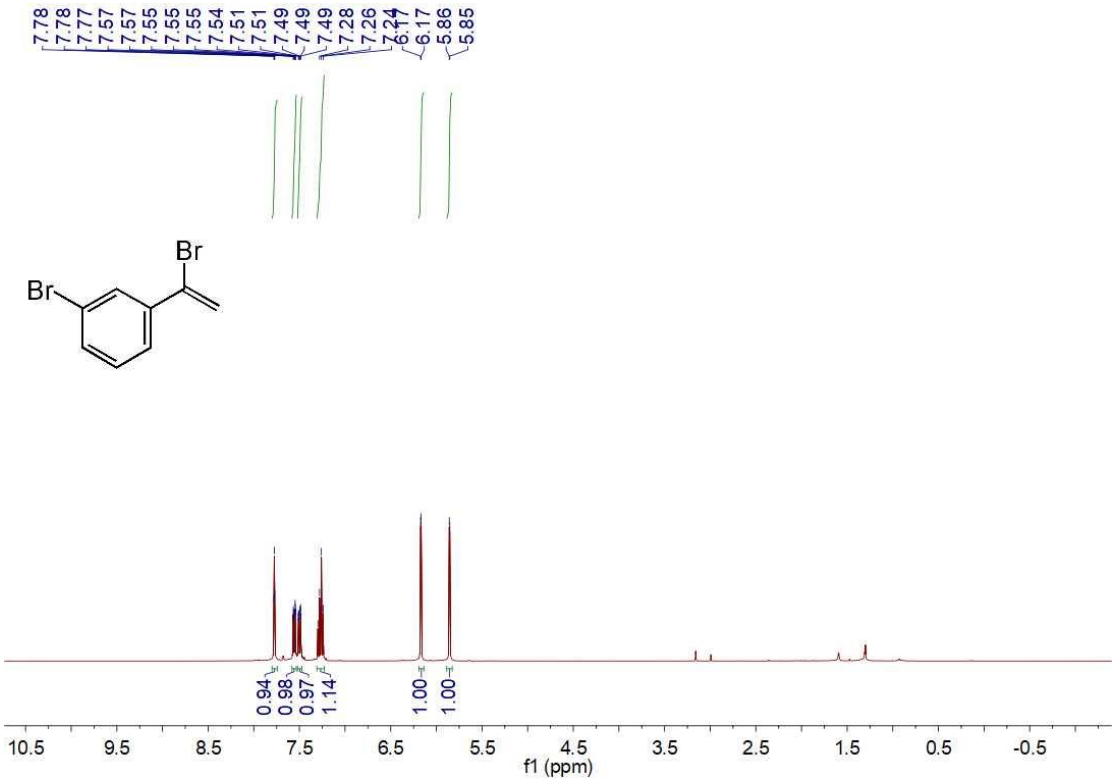

Figure S37 The ^{1}H NMR spectra of **2s** ($CDCl_3$, 400M)

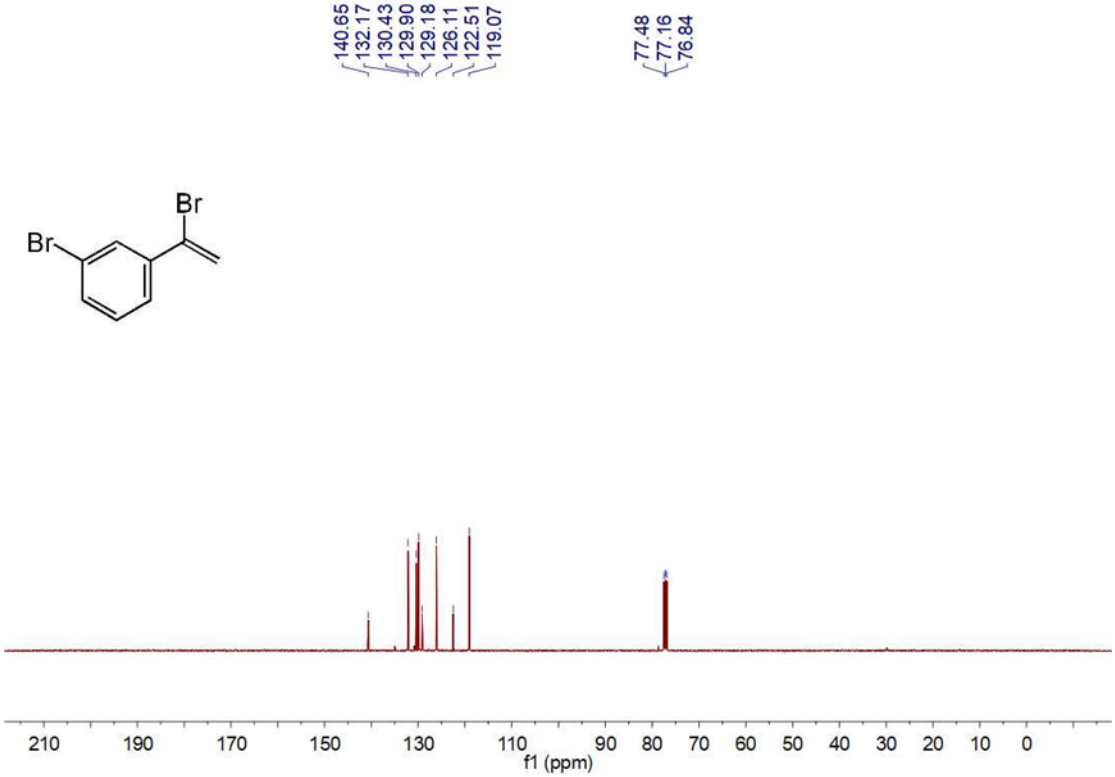

Figure S38 The ^{13}C NMR spectra of **2s** ($CDCl_3$, 101M)

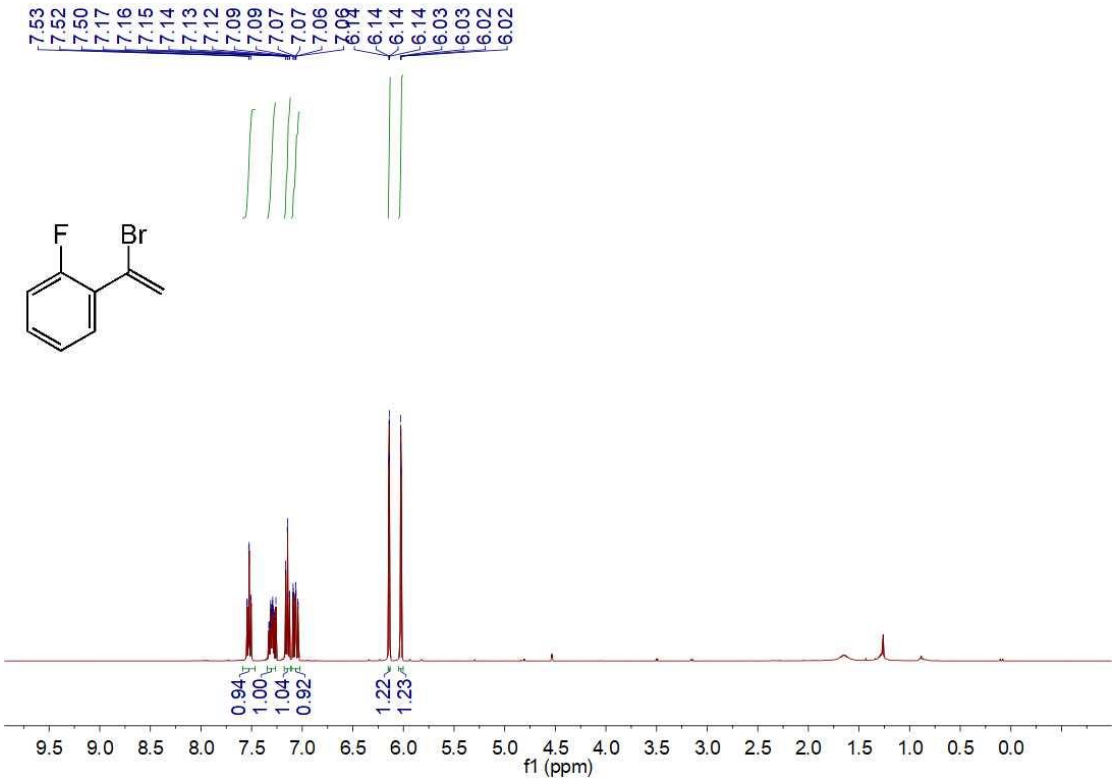

Figure S39 The ^{1}H NMR spectra of **2t** ($CDCl_3$, 400M)

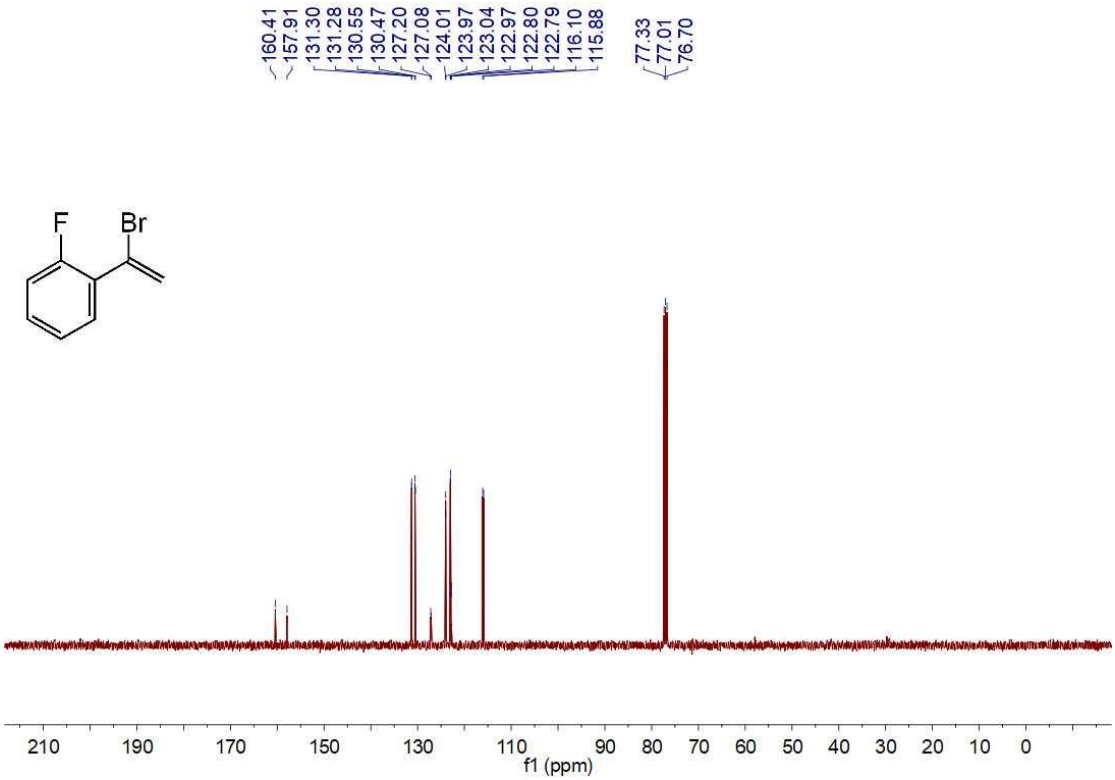

Figure S40 The ^{13}C NMR spectra of **2t** ($CDCl_3$, 101M)

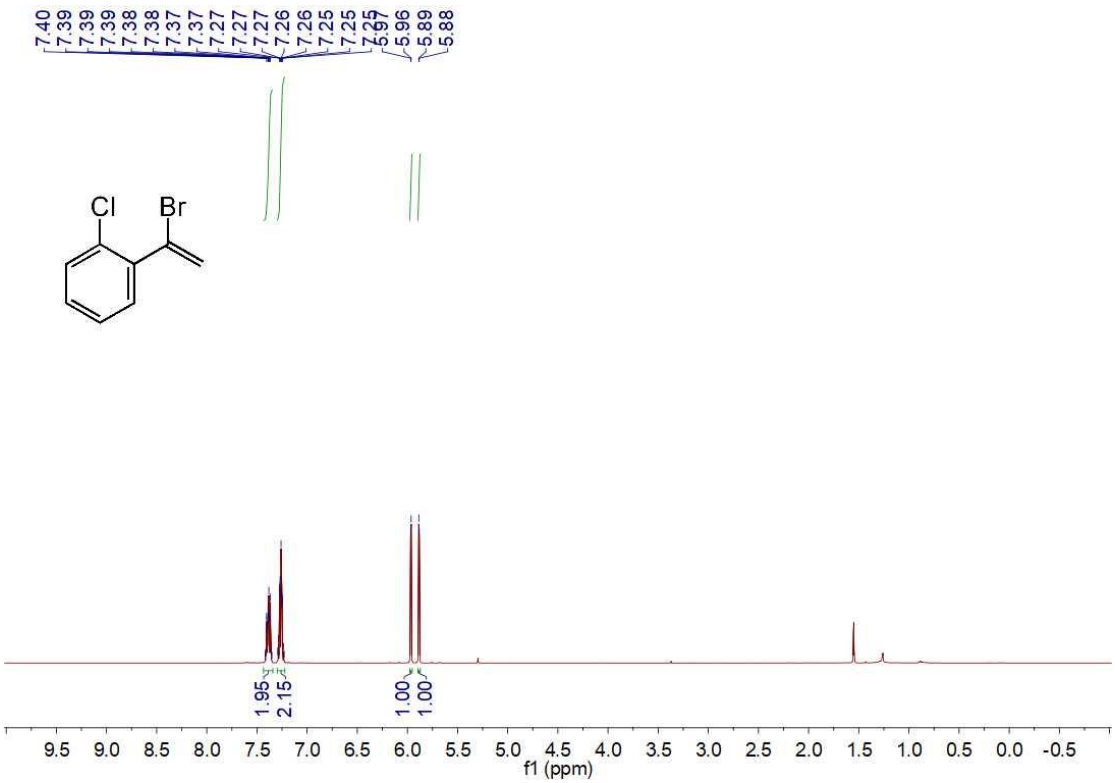

Figure S41 The ^{1}H NMR spectra of **2u** ($CDCl_3$, 400M)

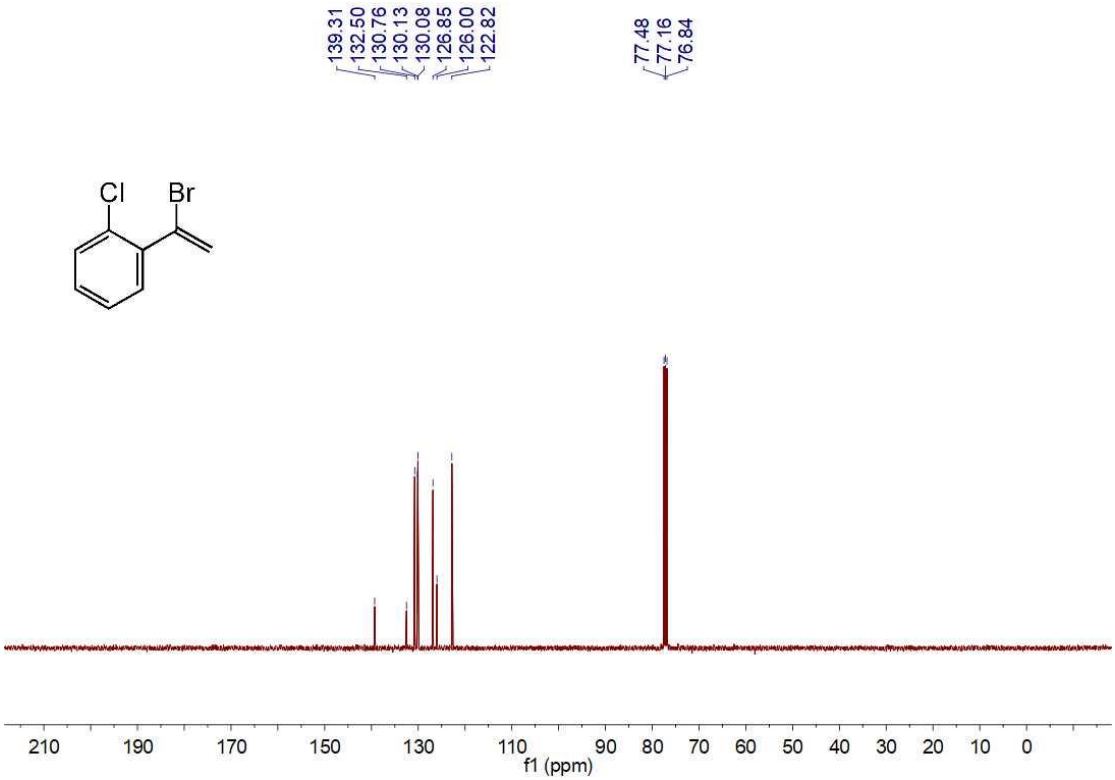

Figure S42 The ^{13}C NMR spectra of **2u** ($CDCl_3$, 101M)

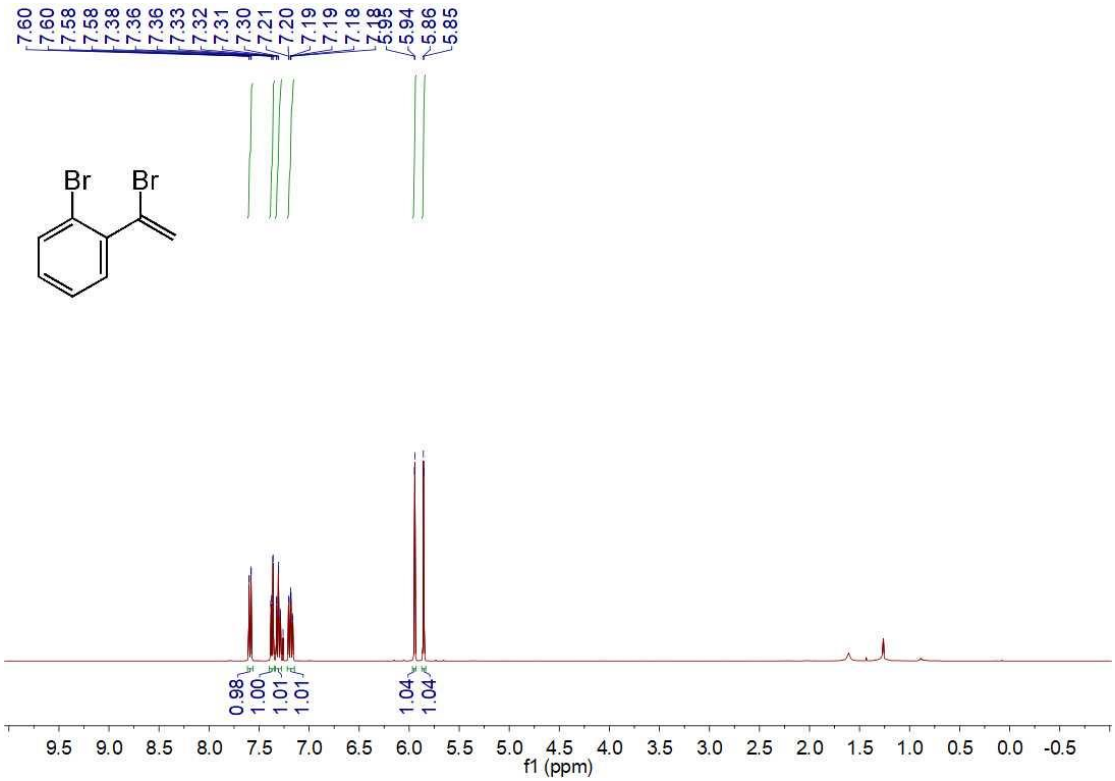

Figure S43 The ^{1}H NMR spectra of **2v** ($CDCl_3$, 400M)

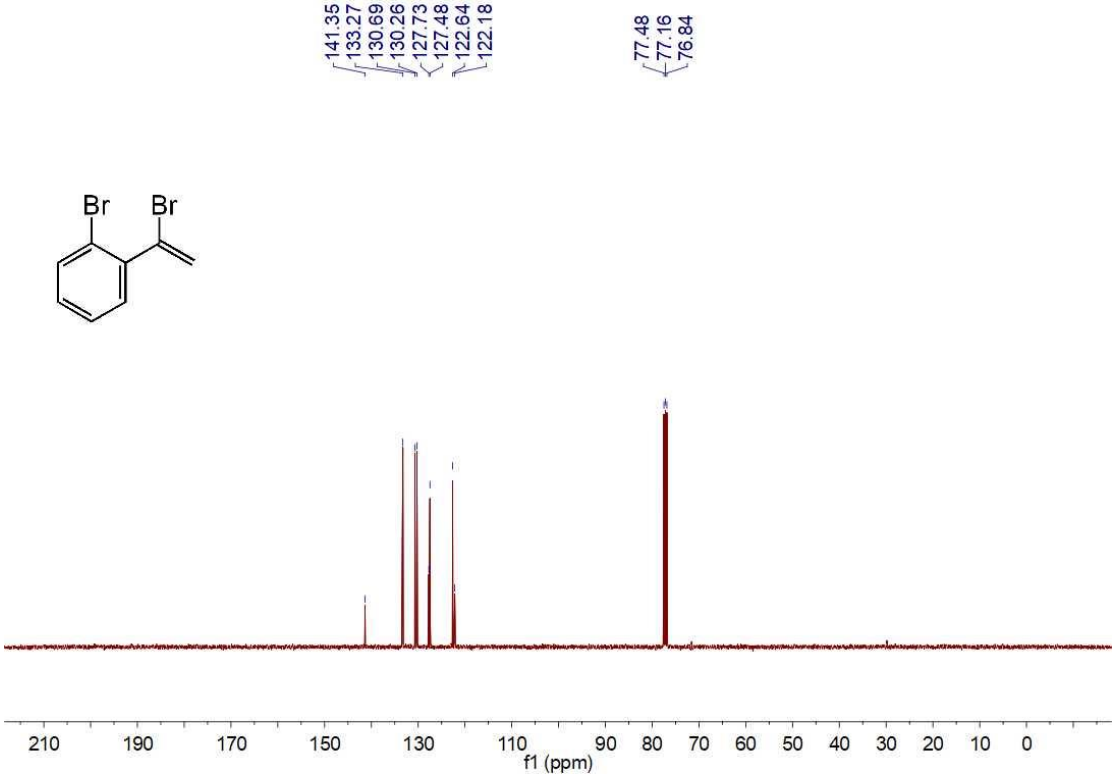

Figure S44 The ^{13}C NMR spectra of **2v** ($CDCl_3$, 101M)

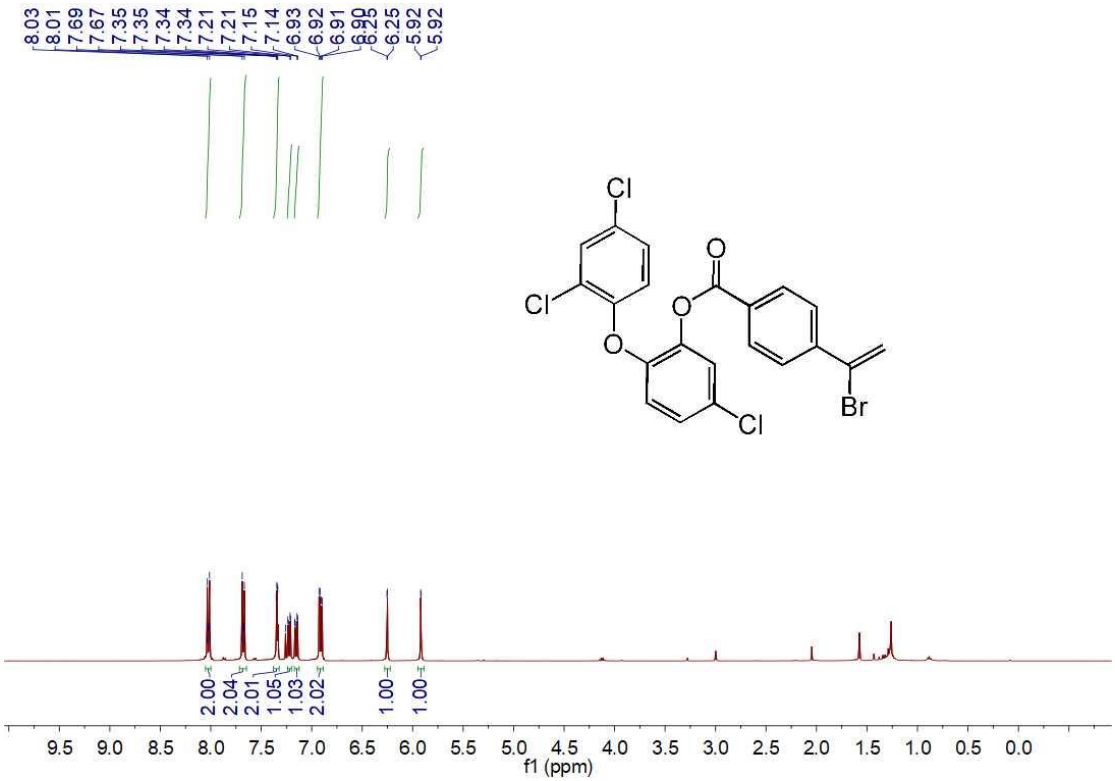

Figure S45 The ^{1}H NMR spectra of **2w** ($CDCl_3$, 400M)

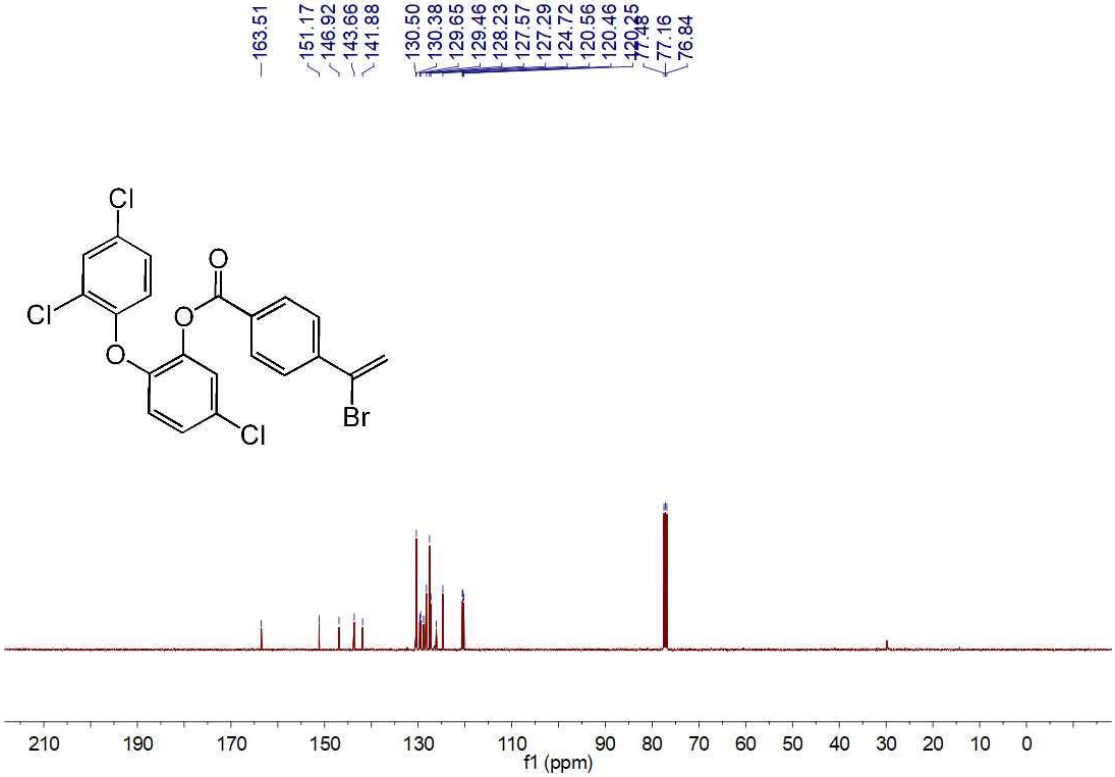

Figure S46 The ^{13}C NMR spectra of **2w** ($CDCl_3$, 101M)

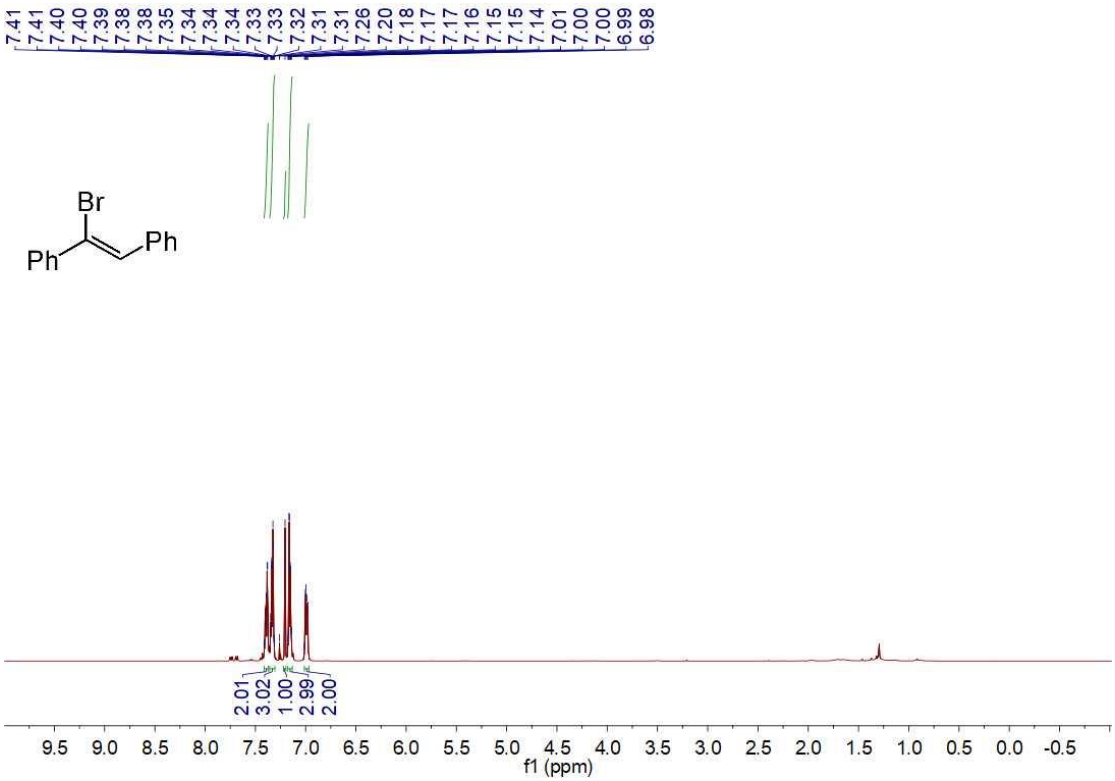

Figure S47 The ^{1}H NMR spectra of **2x** ($CDCl_3$, 400M)

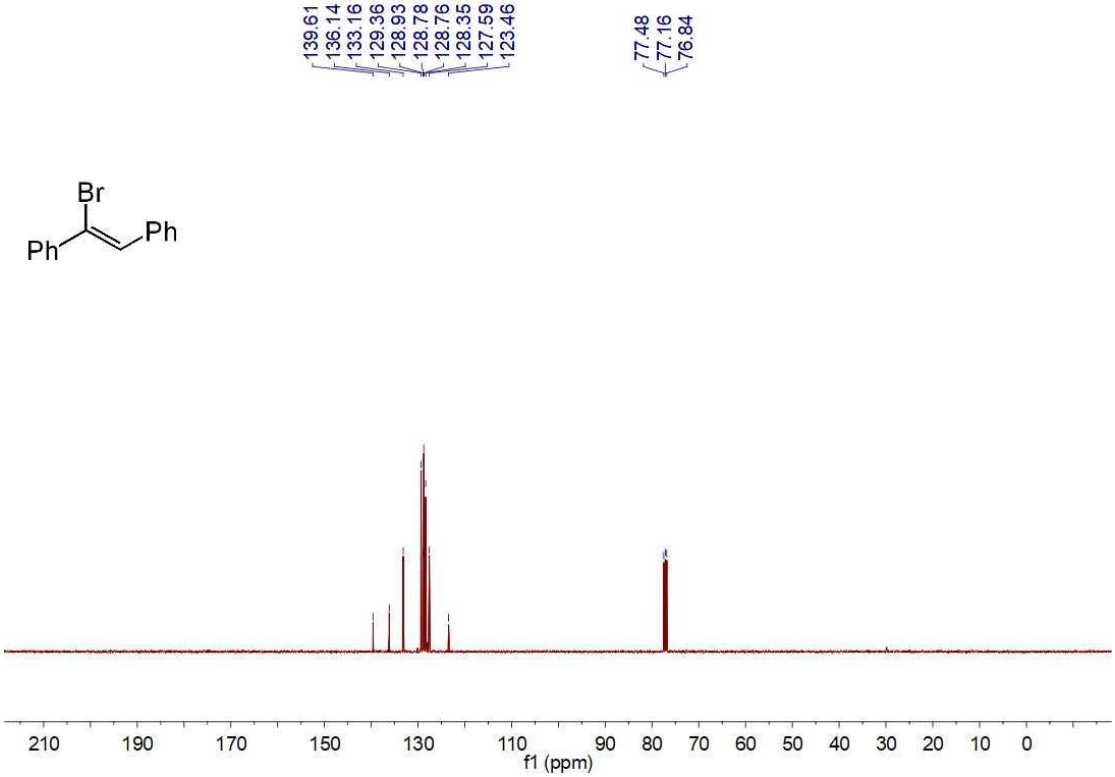

Figure S48 The ^{13}C NMR spectra of **2x** ($CDCl_3$, 101M)

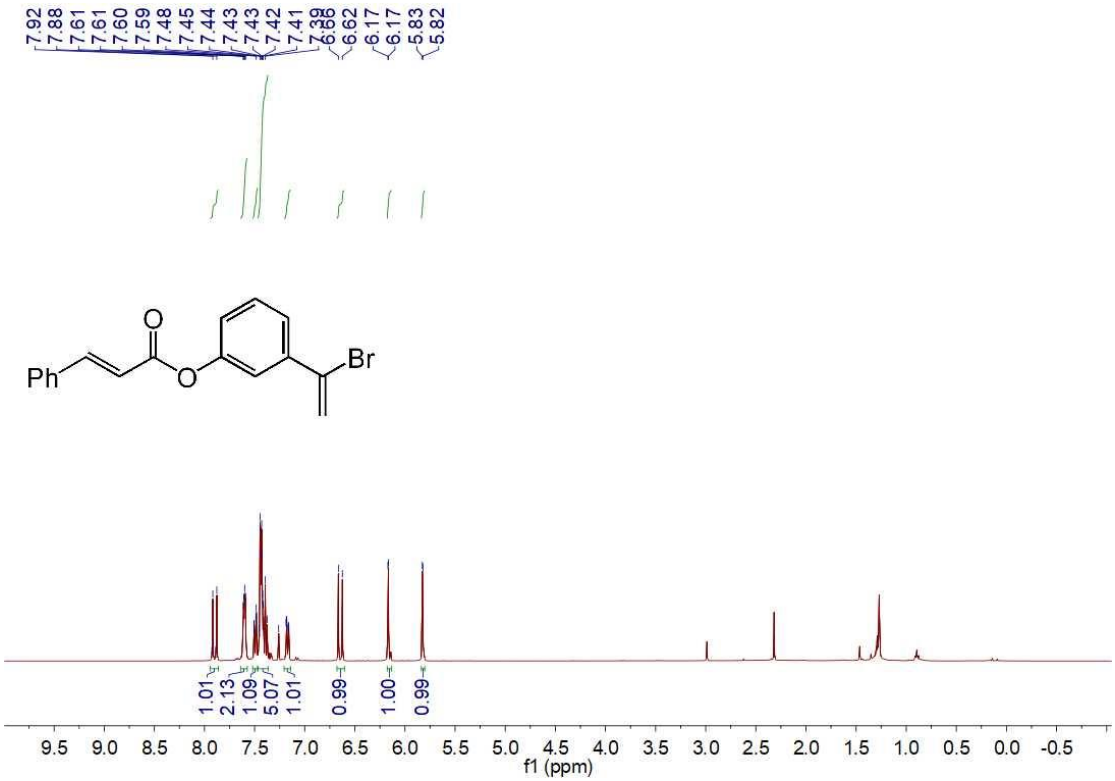

Figure S49 The ^{1}H NMR spectra of **2y** ($CDCl_3$, 400M)

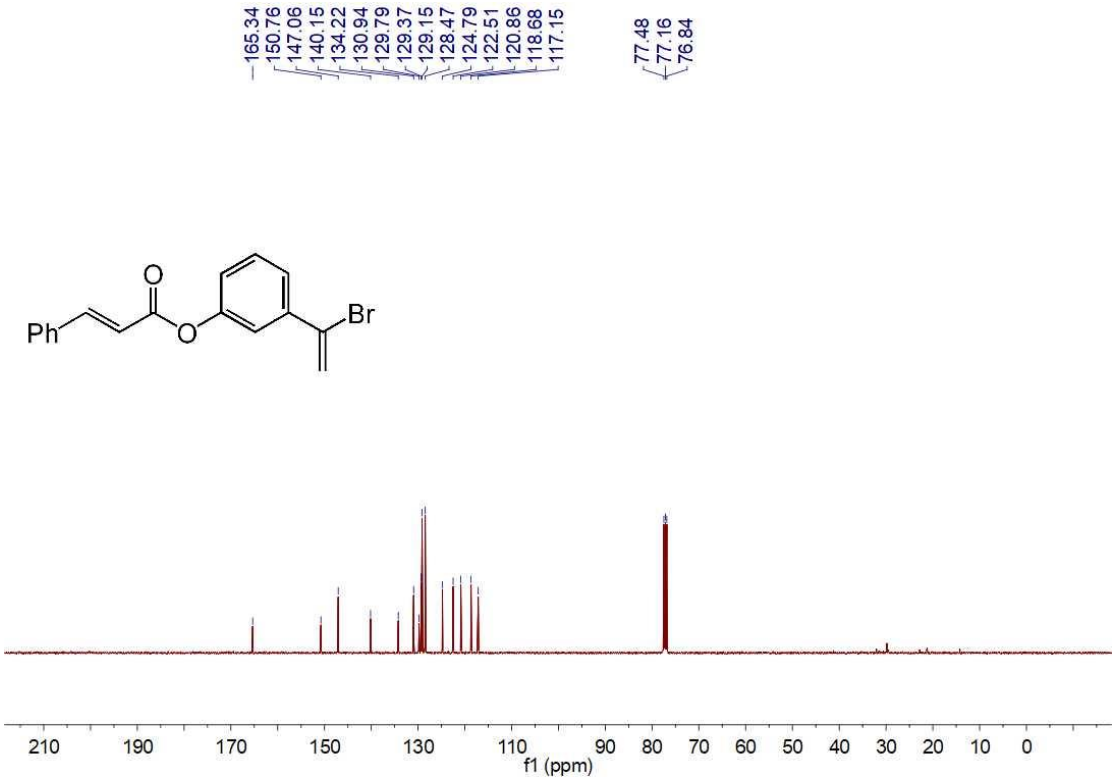

Figure S50 The ^{13}C NMR spectra of **2y** ($CDCl_3$, 101M)

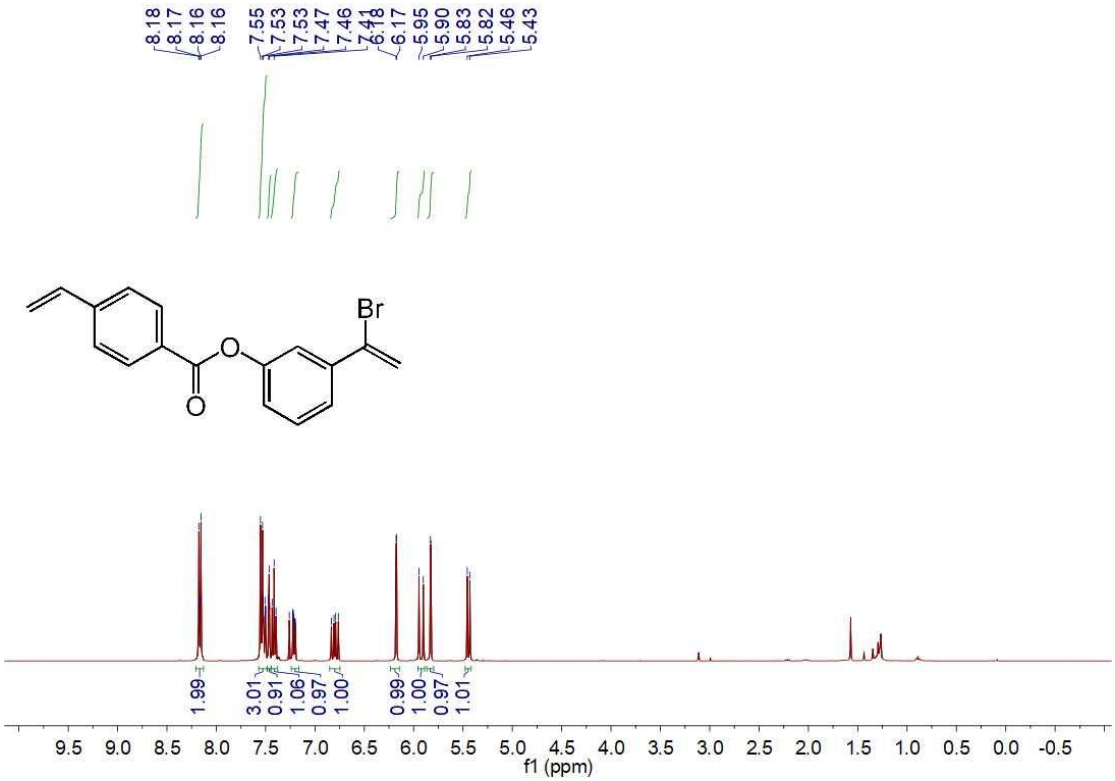

Figure S51 The ^{1}H NMR spectra of **2z** ($CDCl_3$, 400M)

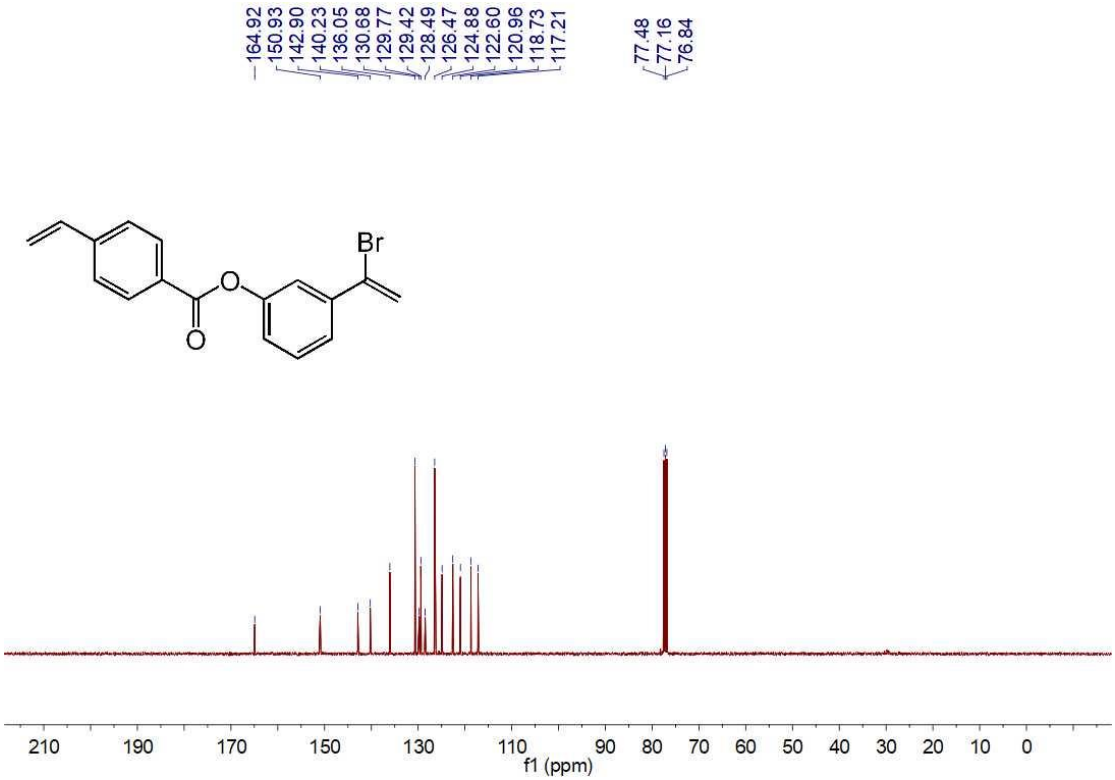

Figure S52 The ^{13}C NMR spectra of **2z** ($CDCl_3$, 101M)

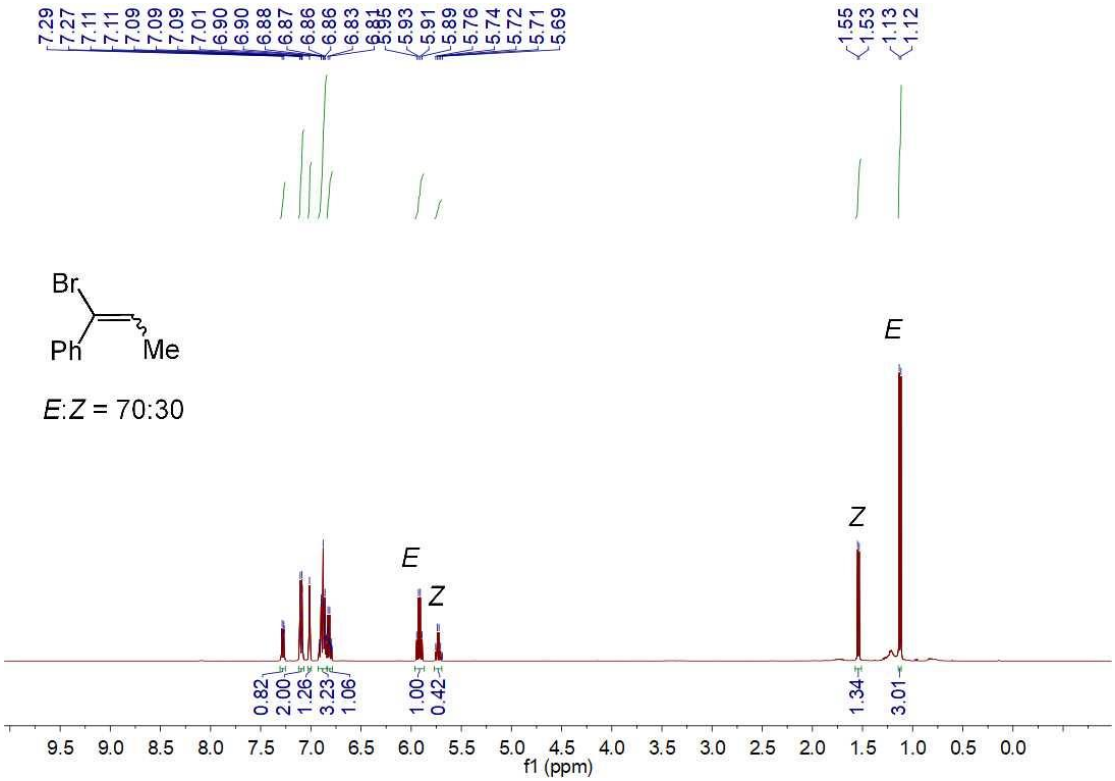

Figure S53 The ^{1}H NMR spectra of **2aa** (C_6D_6, 400M)

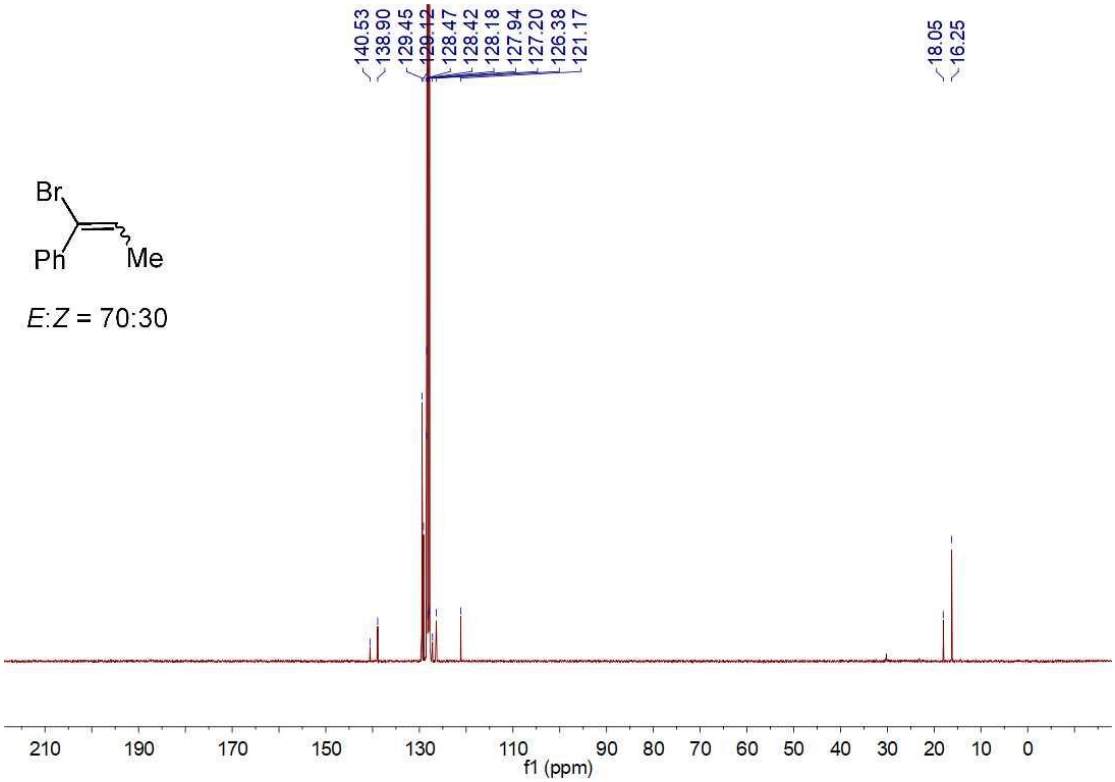

Figure S54 The ^{13}C NMR spectra of **2aa** (C_6D_6, 101M)

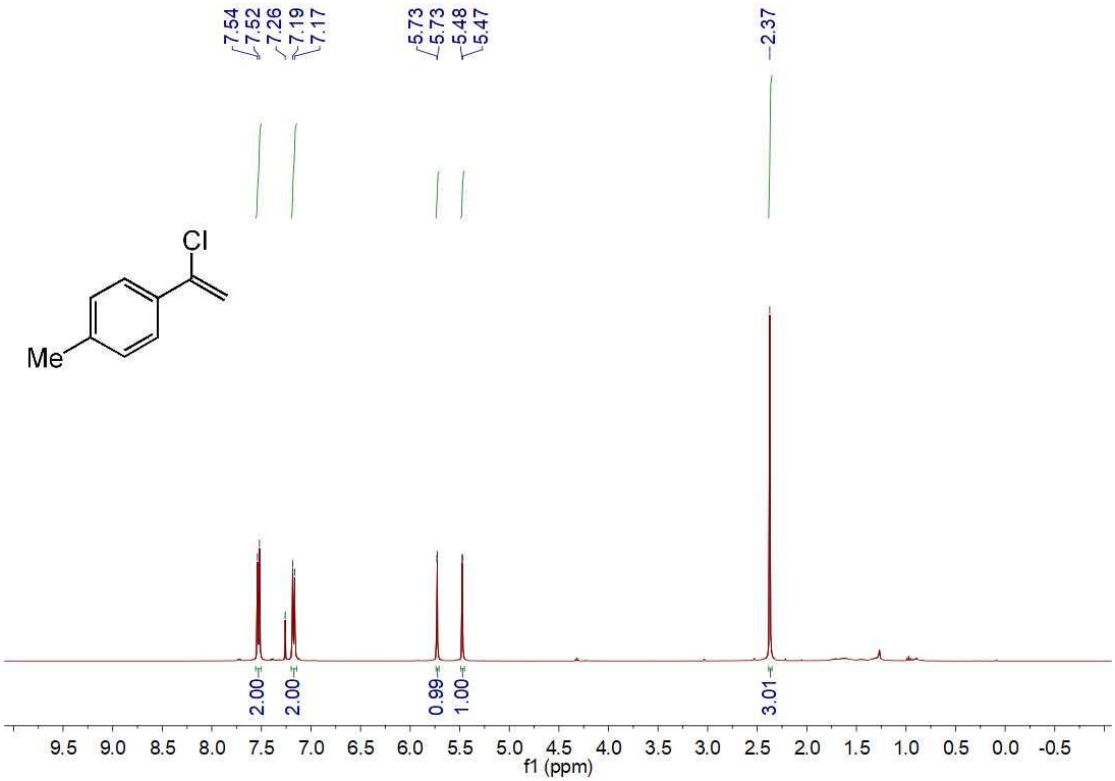

Figure S55 The ^{1}H NMR spectra of **3a** ($CDCl_3$, 400M)

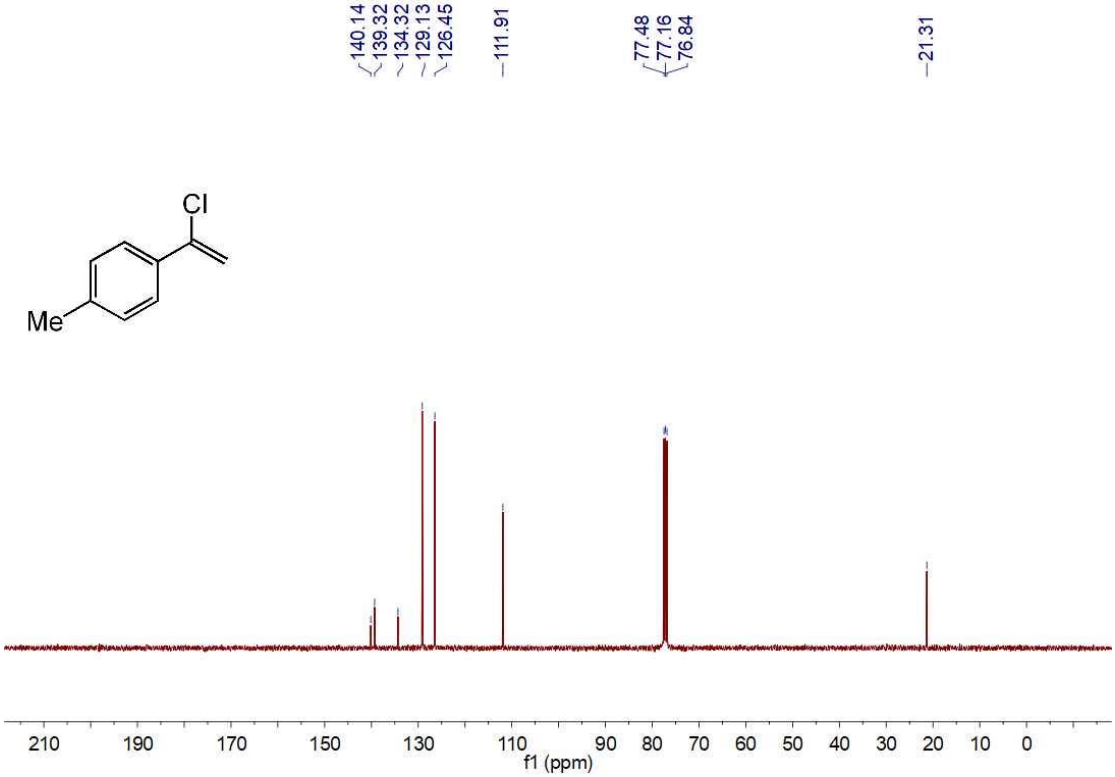

Figure S56 The ^{13}C NMR spectra of **3a** ($CDCl_3$, 101M)

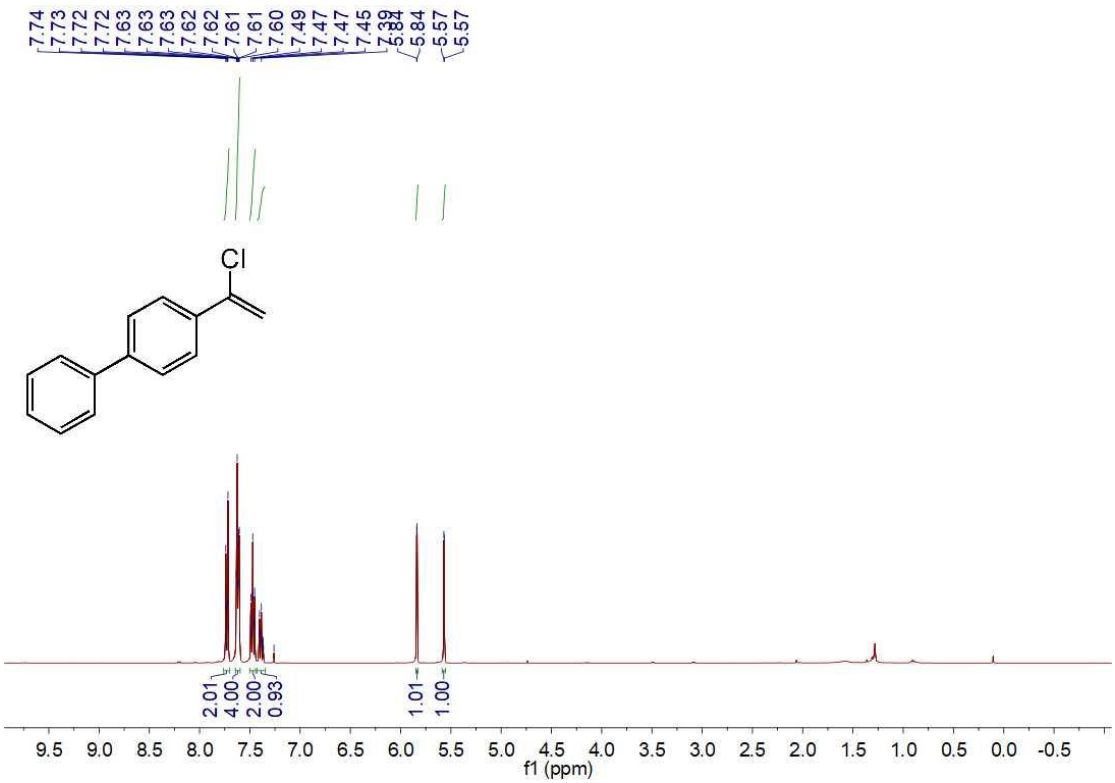

Figure S57 The ^{1}H NMR spectra of **3b** ($CDCl_3$, 400M)

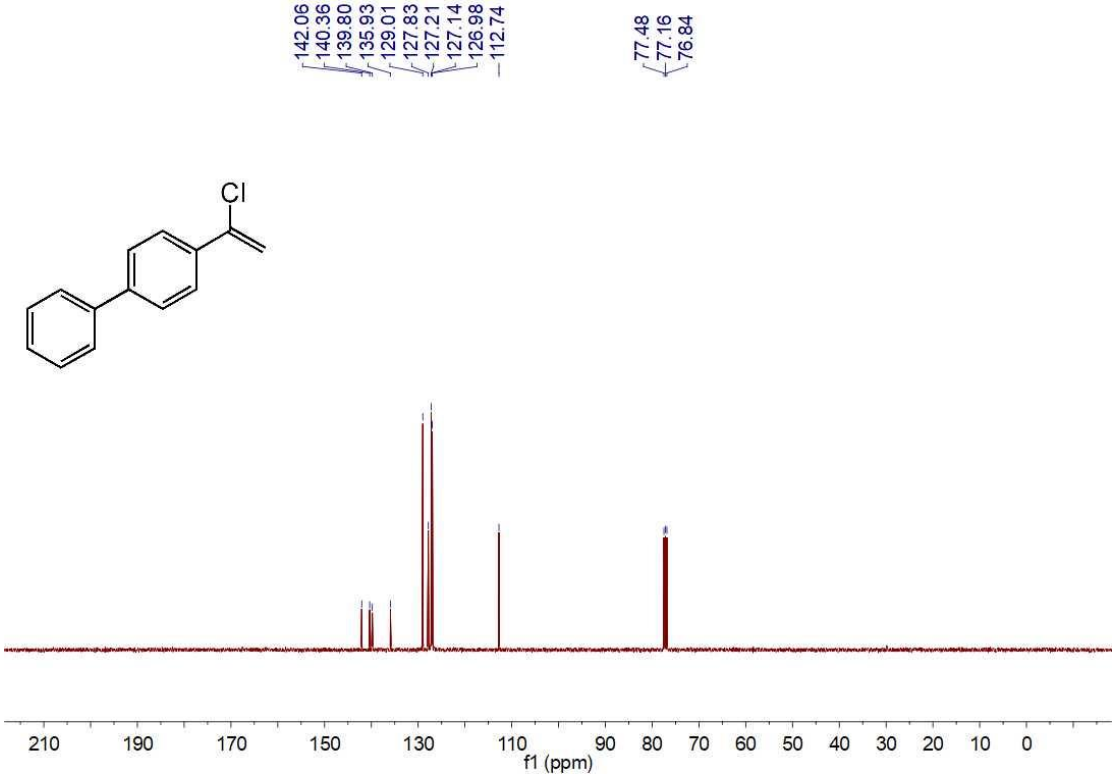

Figure S58 The ^{13}C NMR spectra of **3b** ($CDCl_3$, 101M)

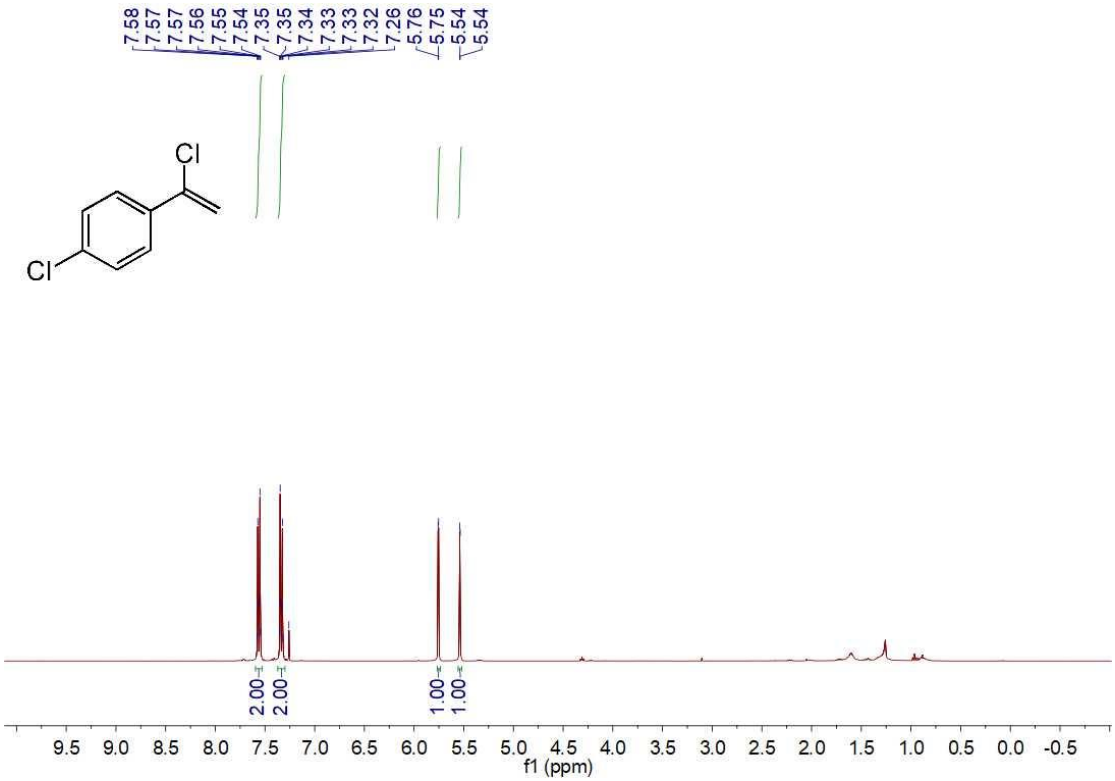

Figure S59 The ^{1}H NMR spectra of **3c** ($CDCl_3$, 400M)

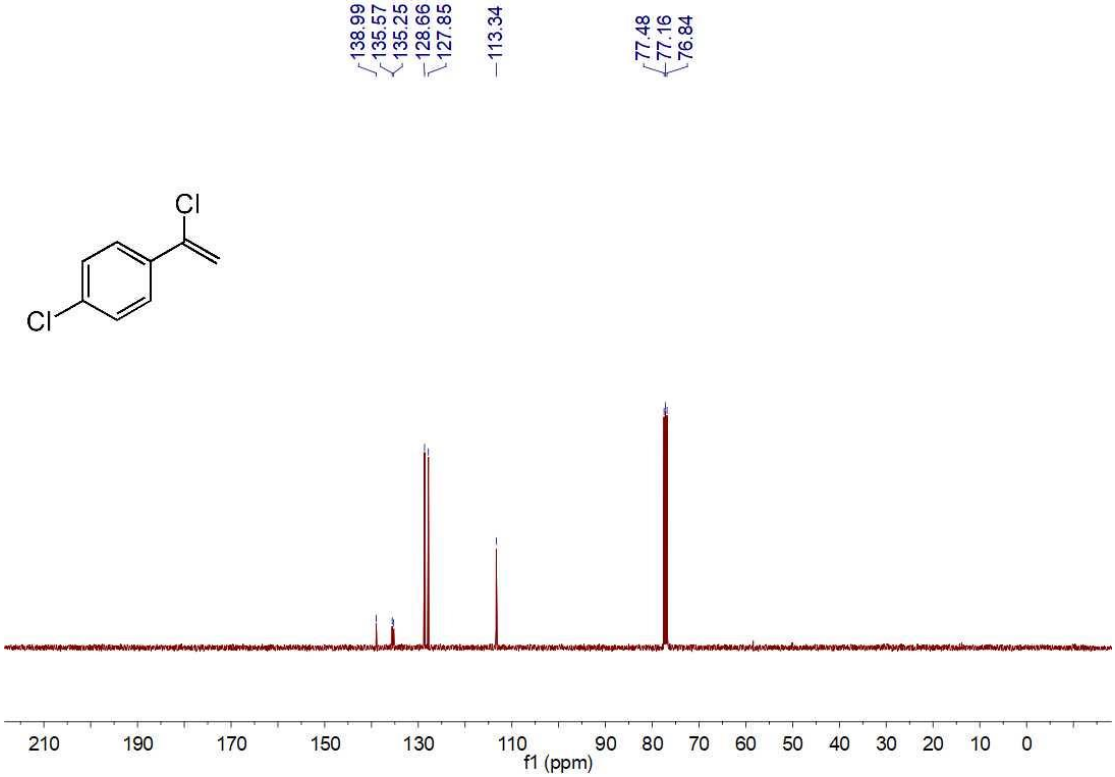

Figure S60 The ^{13}C NMR spectra of **3c** ($CDCl_3$, 101M)

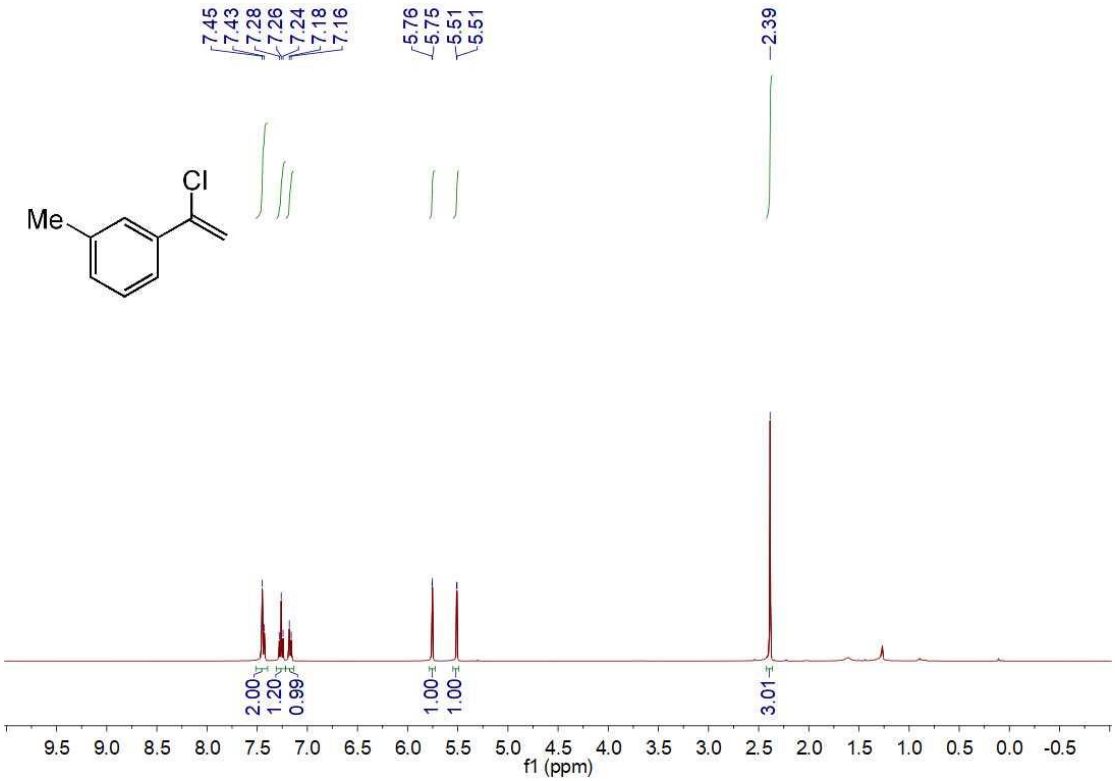

Figure S61 The ^{1}H NMR spectra of **3d** ($CDCl_3$, 400M)

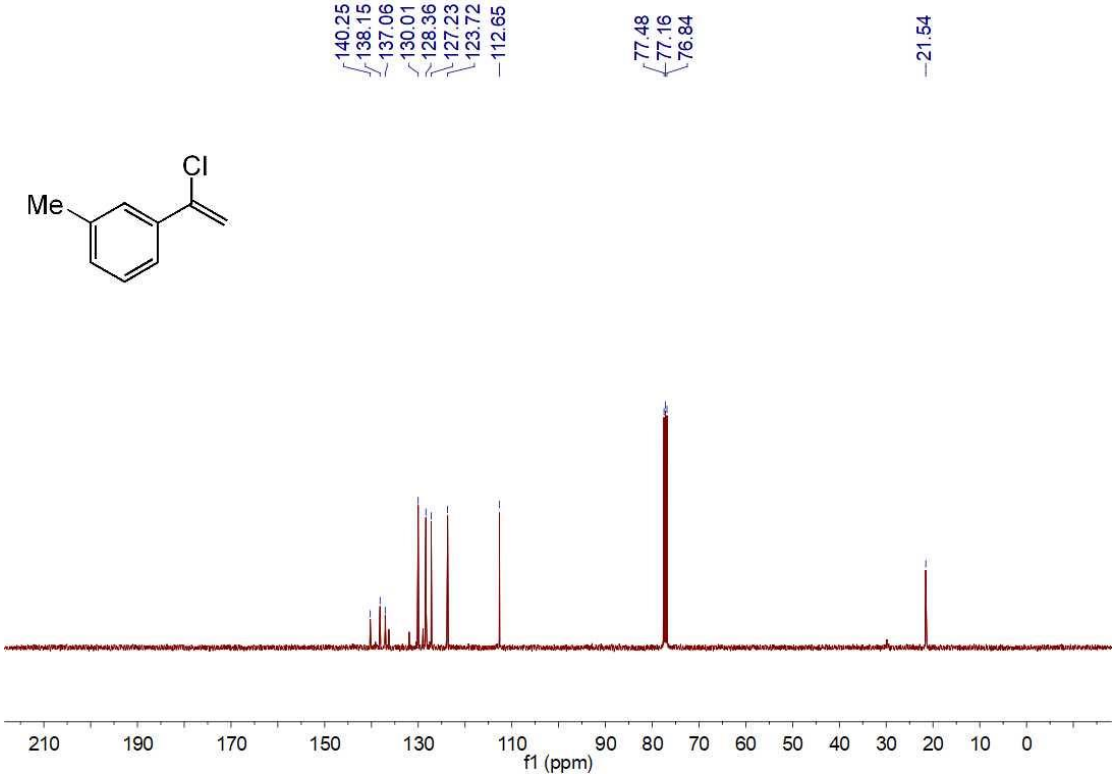

Figure S62 The ^{13}C NMR spectra of **3d** ($CDCl_3$, 101M)

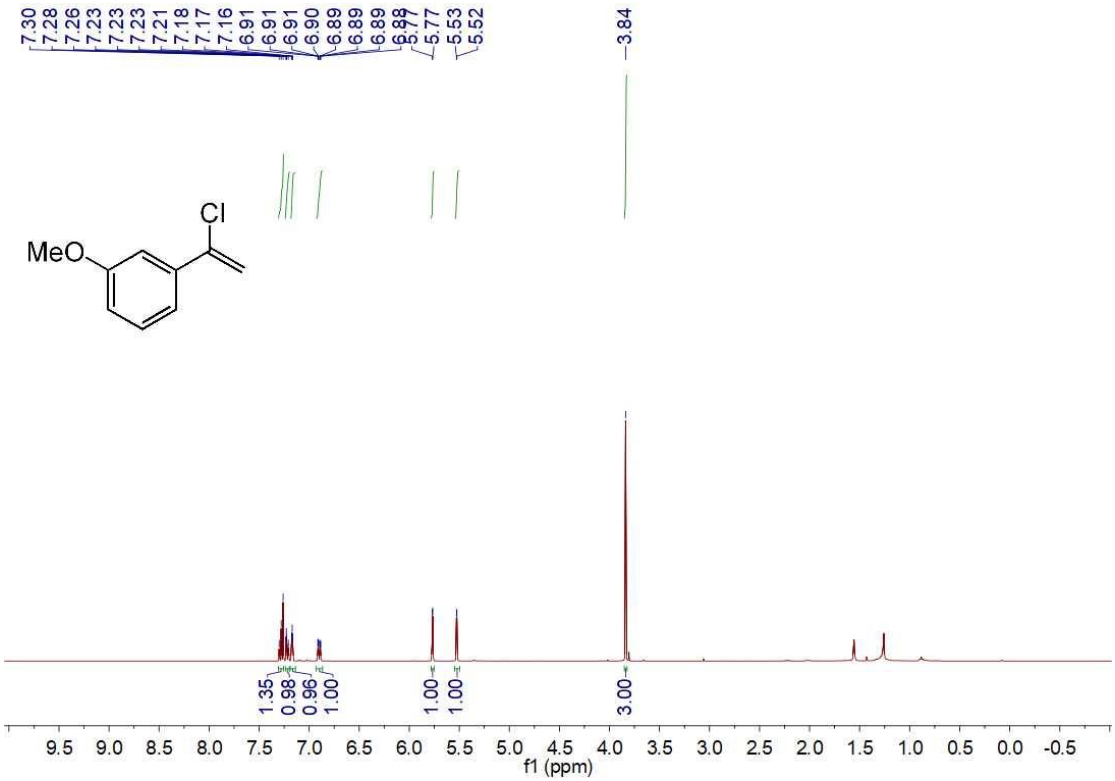

Figure S63 The ^{1}H NMR spectra of **3e** ($CDCl_3$, 400M)

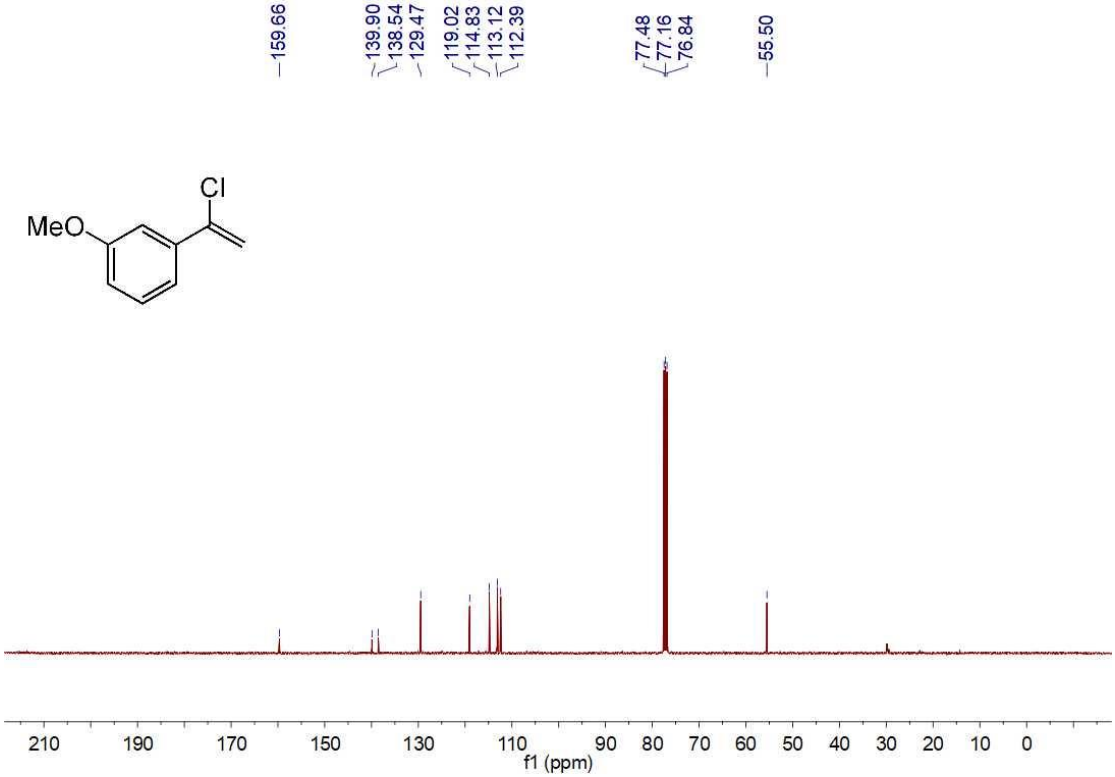

Figure S64 The ^{13}C NMR spectra of **3e** ($CDCl_3$, 101M)

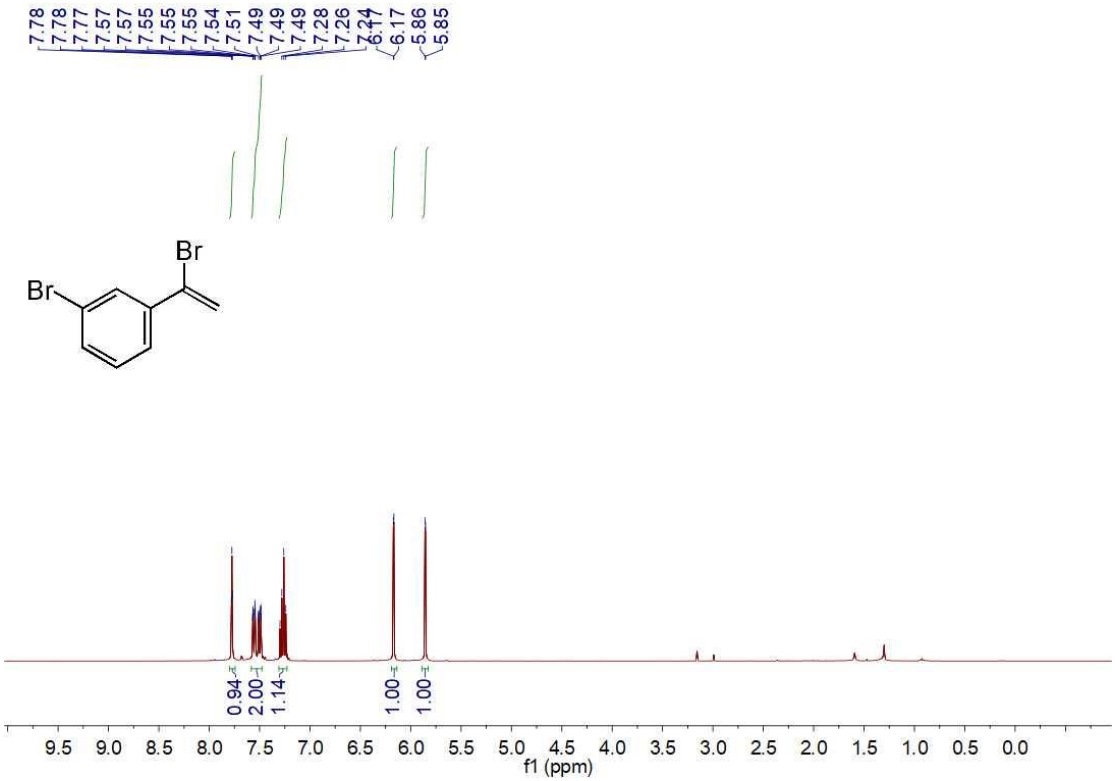

Figure S65 The ^{1}H NMR spectra of **3f** ($CDCl_3$, 400M)

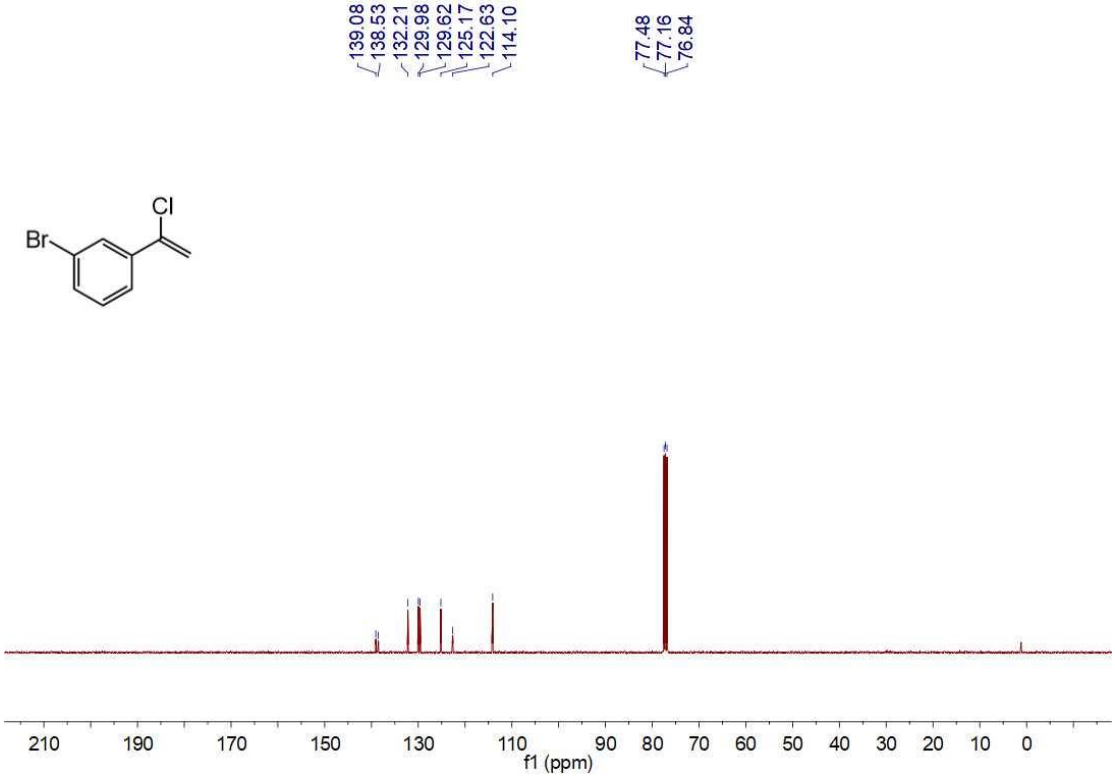

Figure S66 The ^{13}C NMR spectra of **3f** ($CDCl_3$, 101M)

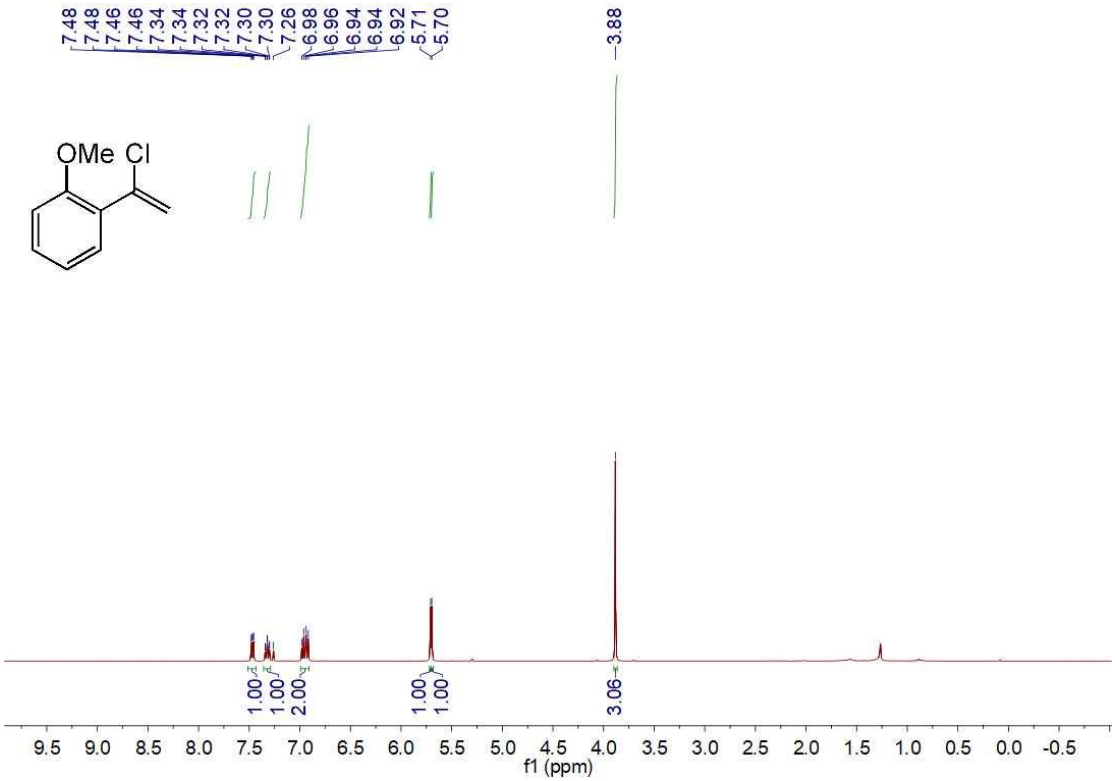

Figure S67 The ^{1}H NMR spectra of **3g** ($CDCl_3$, 400M)

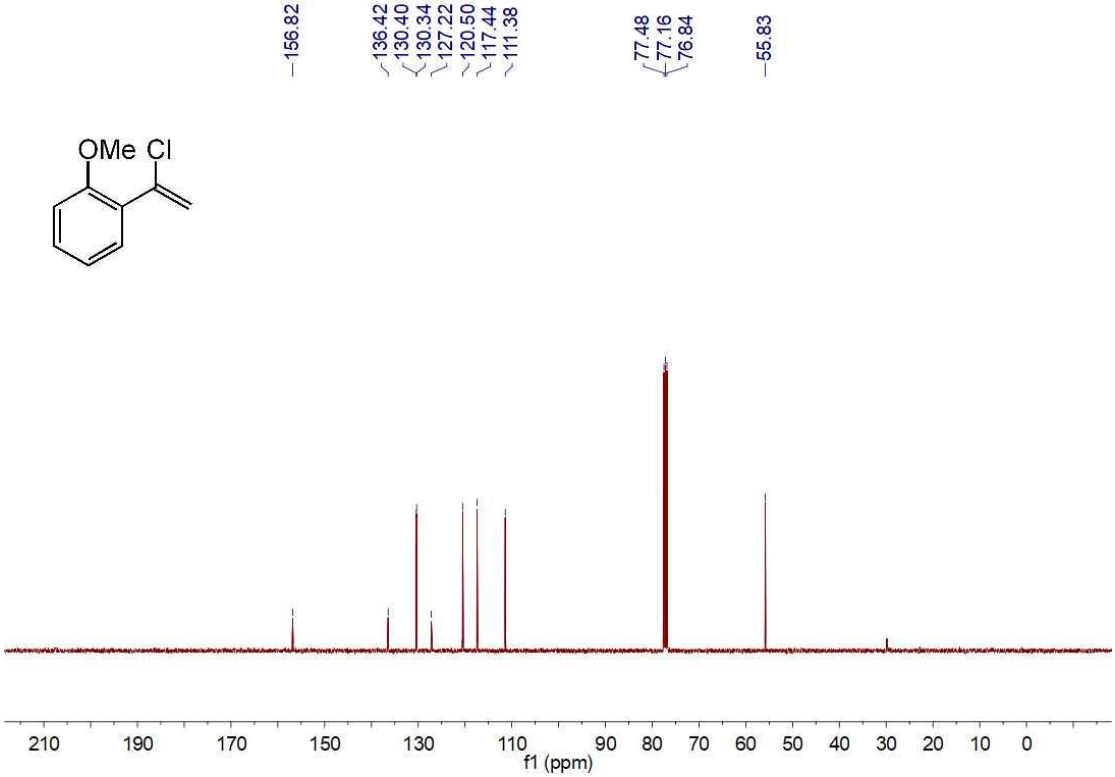

Figure S68 The ^{13}C NMR spectra of **3g** ($CDCl_3$, 101M)

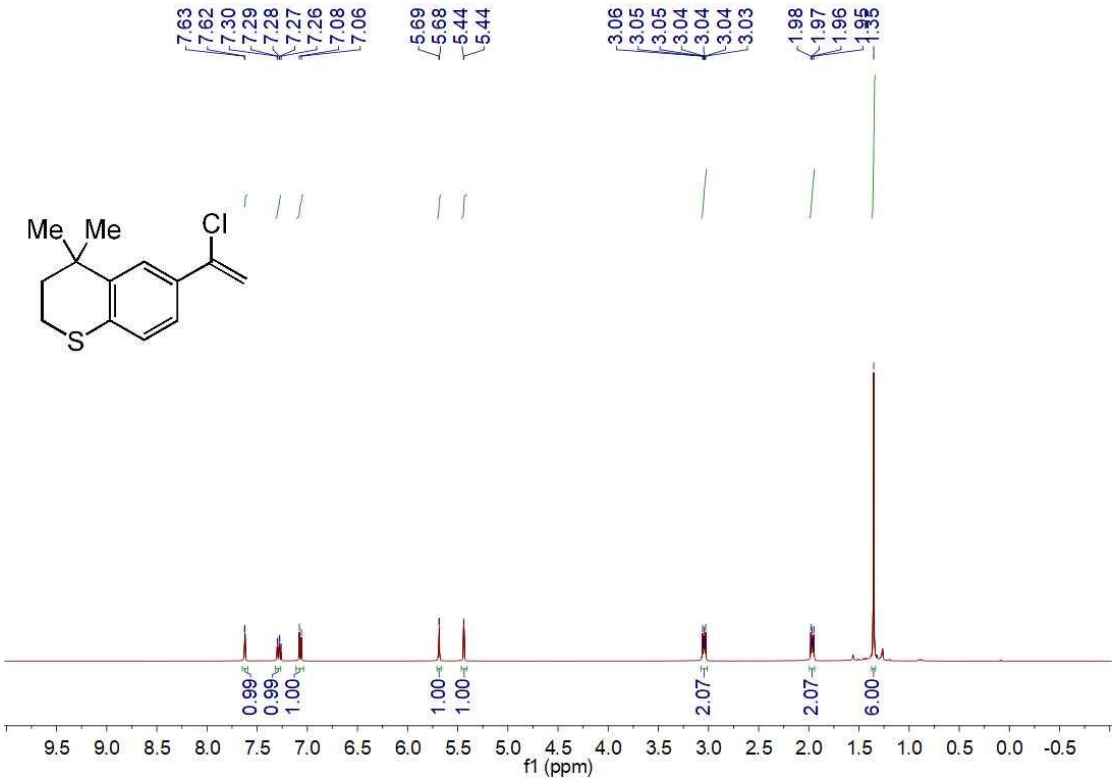

Figure S69 The ^{1}H NMR spectra of **3h** ($CDCl_3$, 400M)

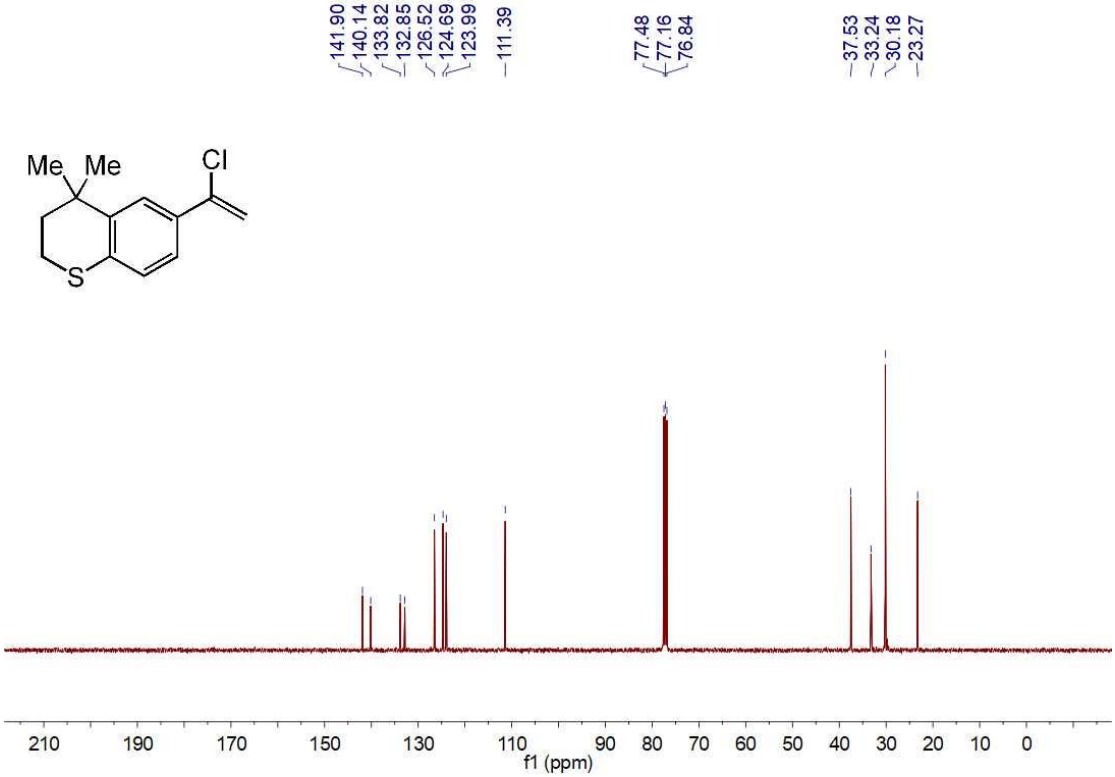

Figure S70 The ^{13}C NMR spectra of **3h** ($CDCl_3$, 101M)

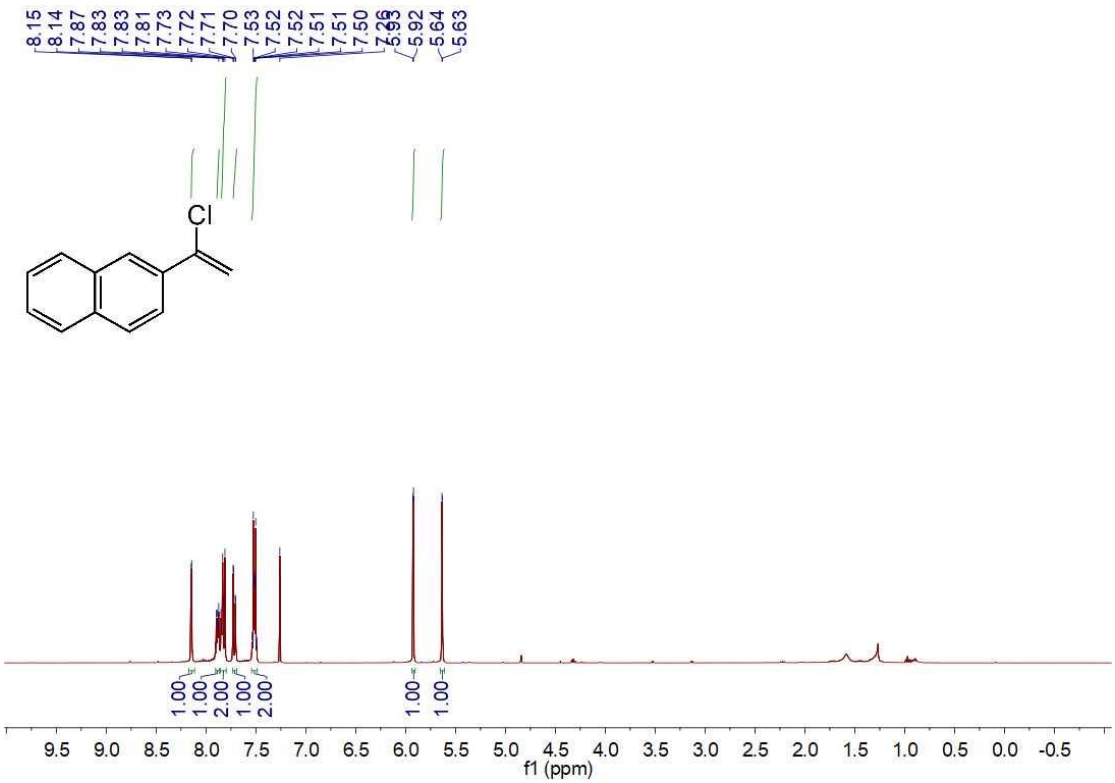

Figure S71 The ^{1}H NMR spectra of **3i** ($CDCl_3$, 400M)

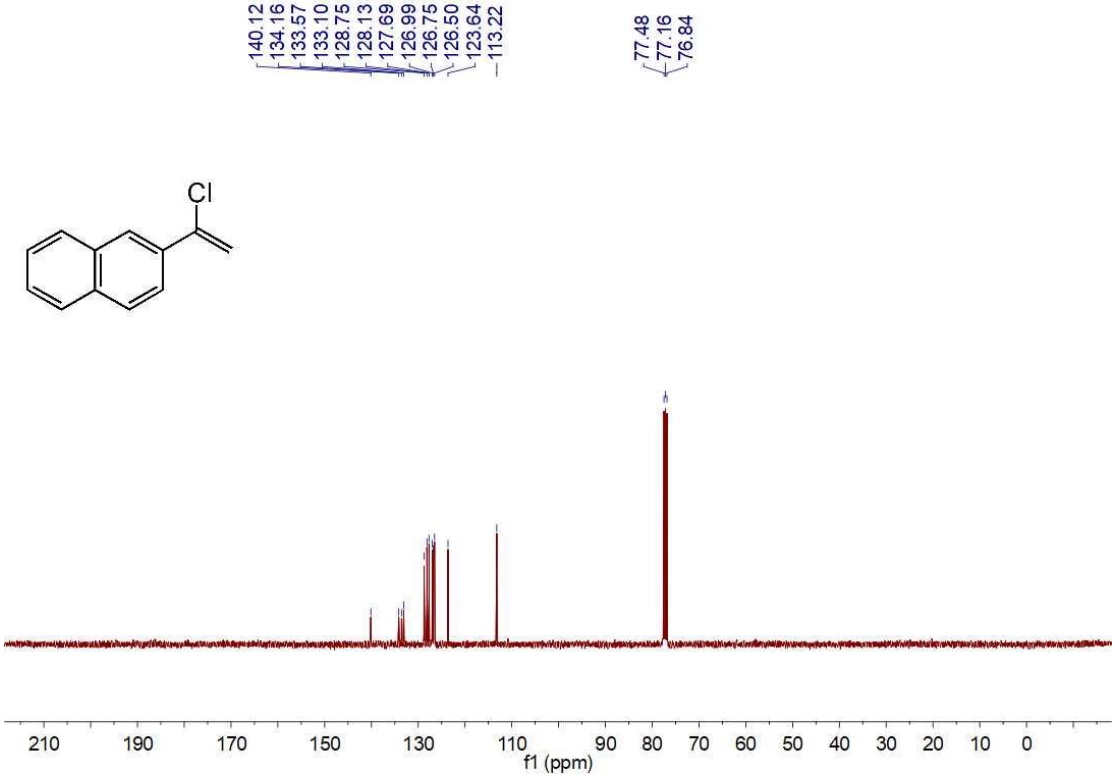

Figure S72 The ^{13}C NMR spectra of **3i** ($CDCl_3$, 101M)

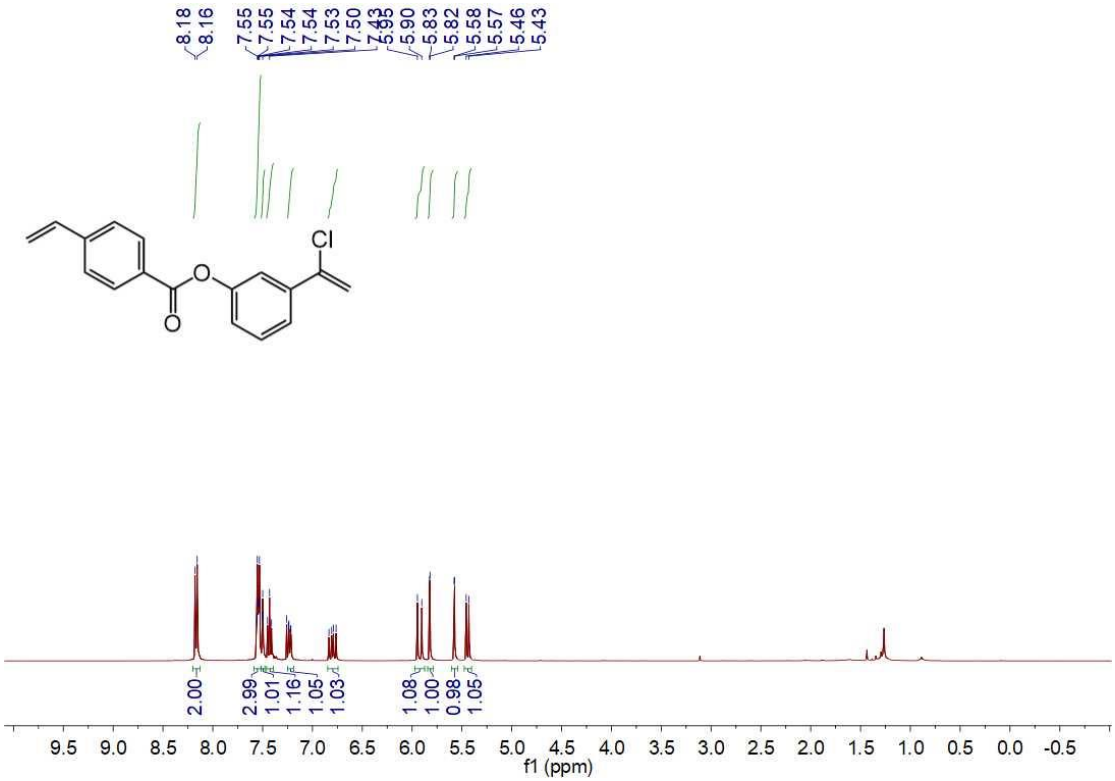

Figure S73 The ^{1}H NMR spectra of **3j** ($CDCl_3$, 400M)

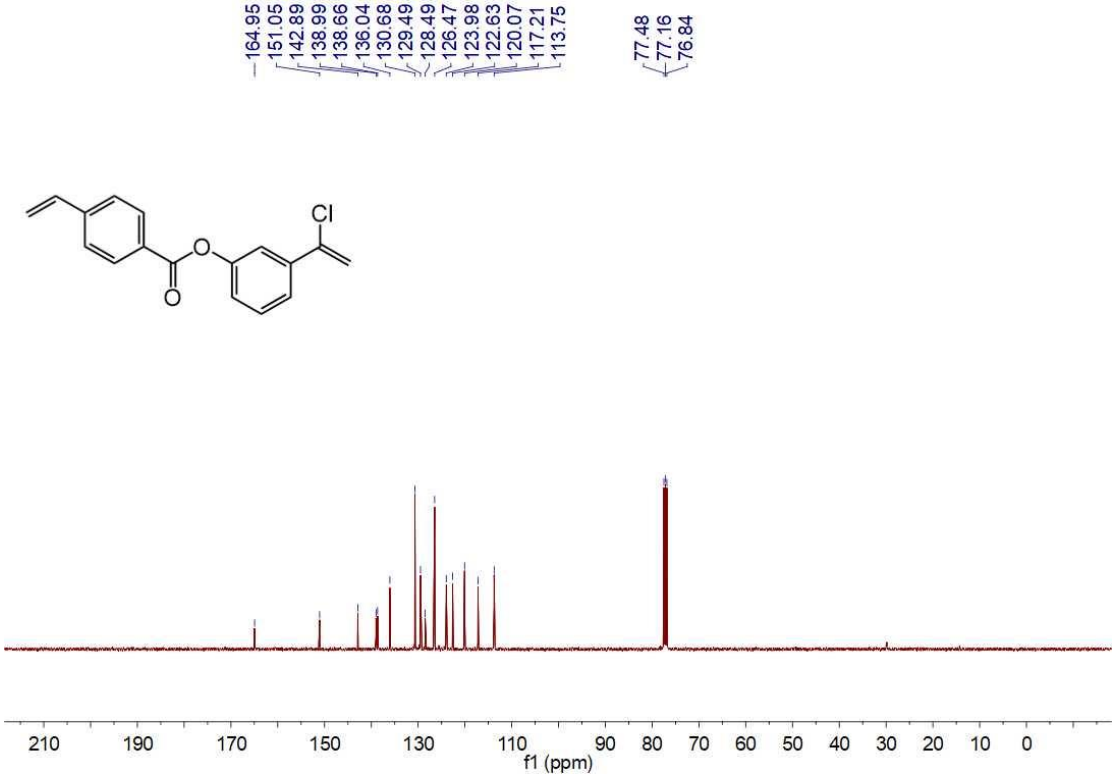

Figure S74 The ^{13}C NMR spectra of **3j** ($CDCl_3$, 101M)

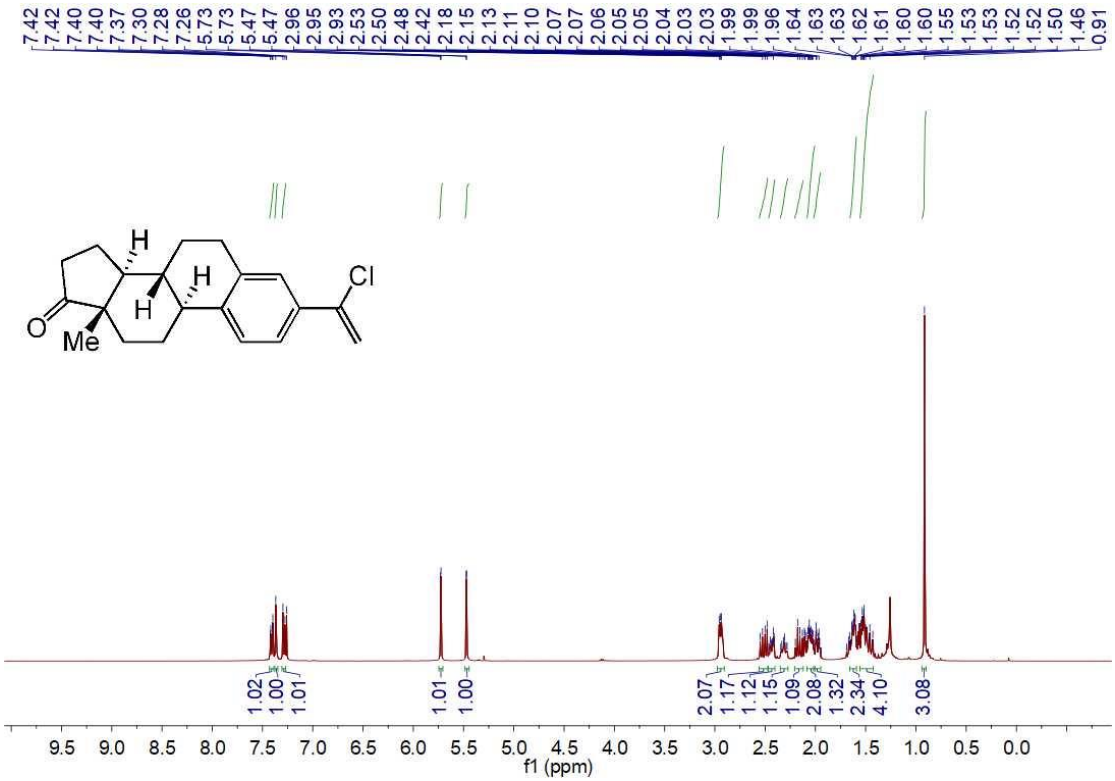

Figure S75 The ^{1}H NMR spectra of **3k** ($CDCl_3$, 400M)

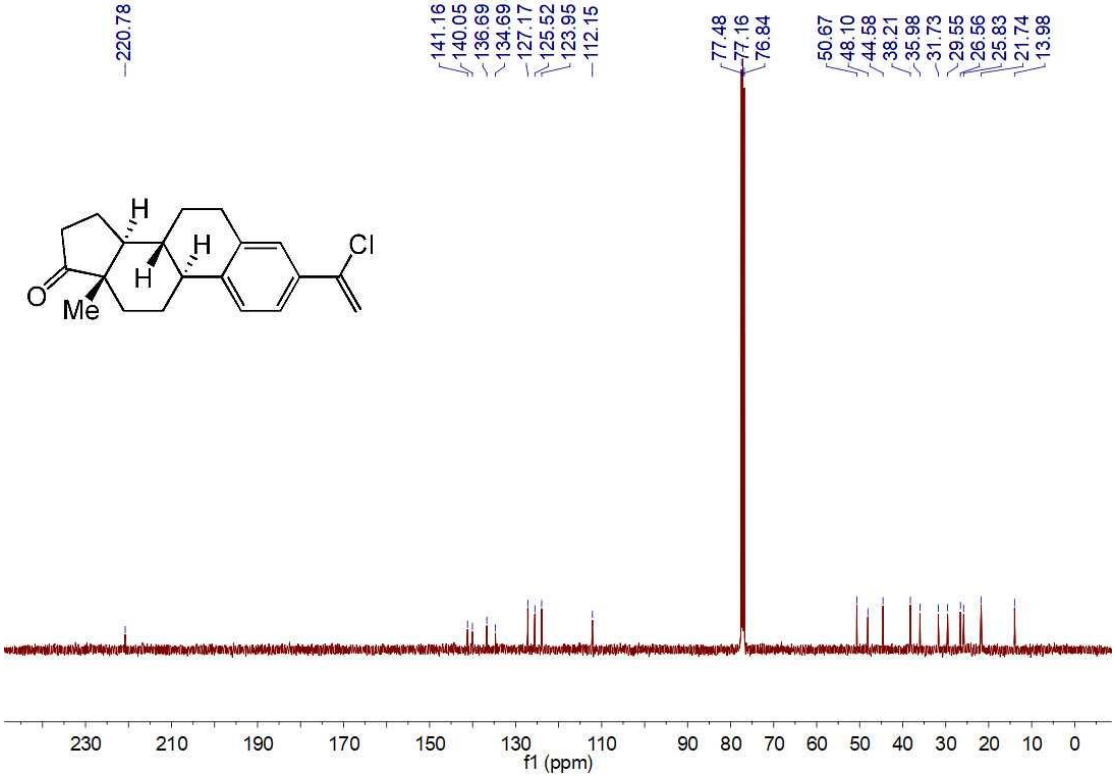

Figure S76 The ^{13}C NMR spectra of **3k** ($CDCl_3$, 101M)

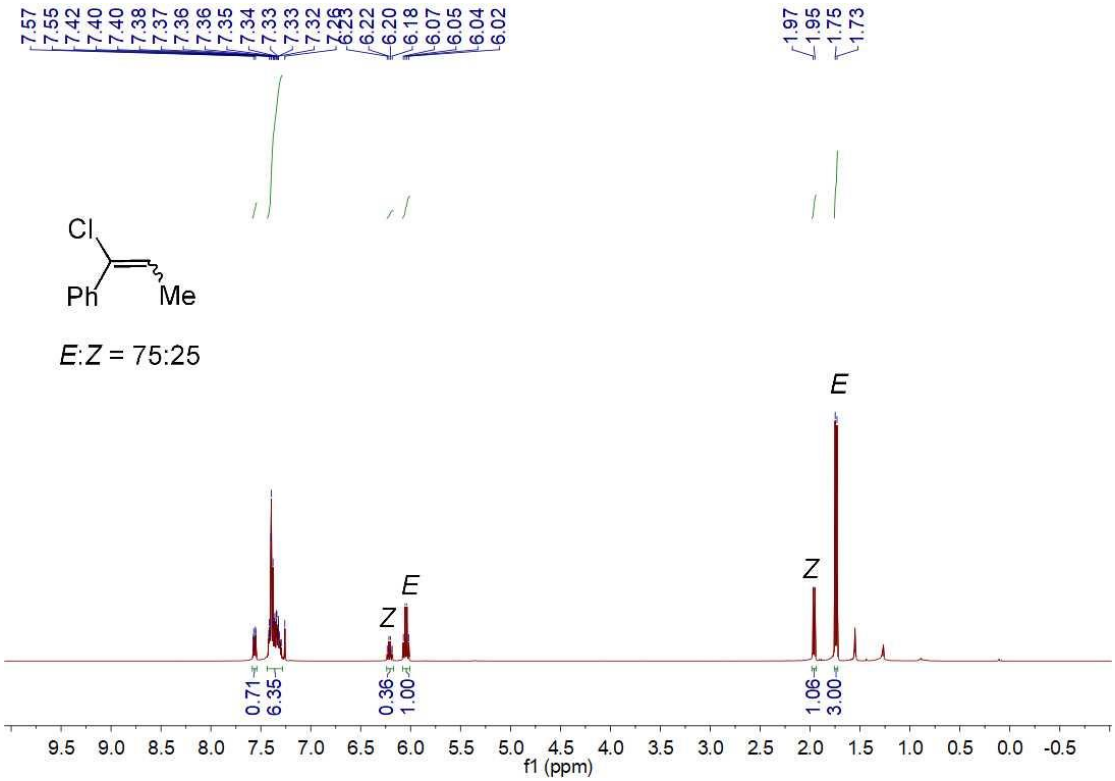

Figure S77 The ^{1}H NMR spectra of **3l** ($CDCl_3$, 400M)

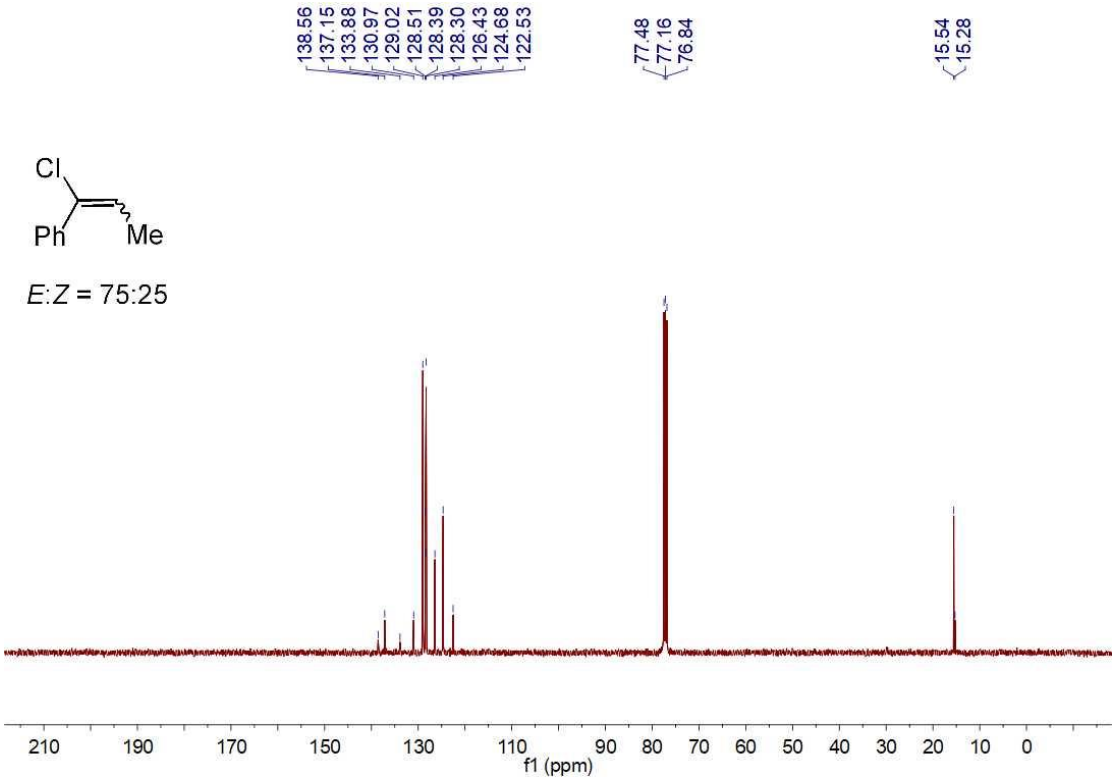

Figure S78 The ^{13}C NMR spectra of **3l** ($CDCl_3$, 101M)

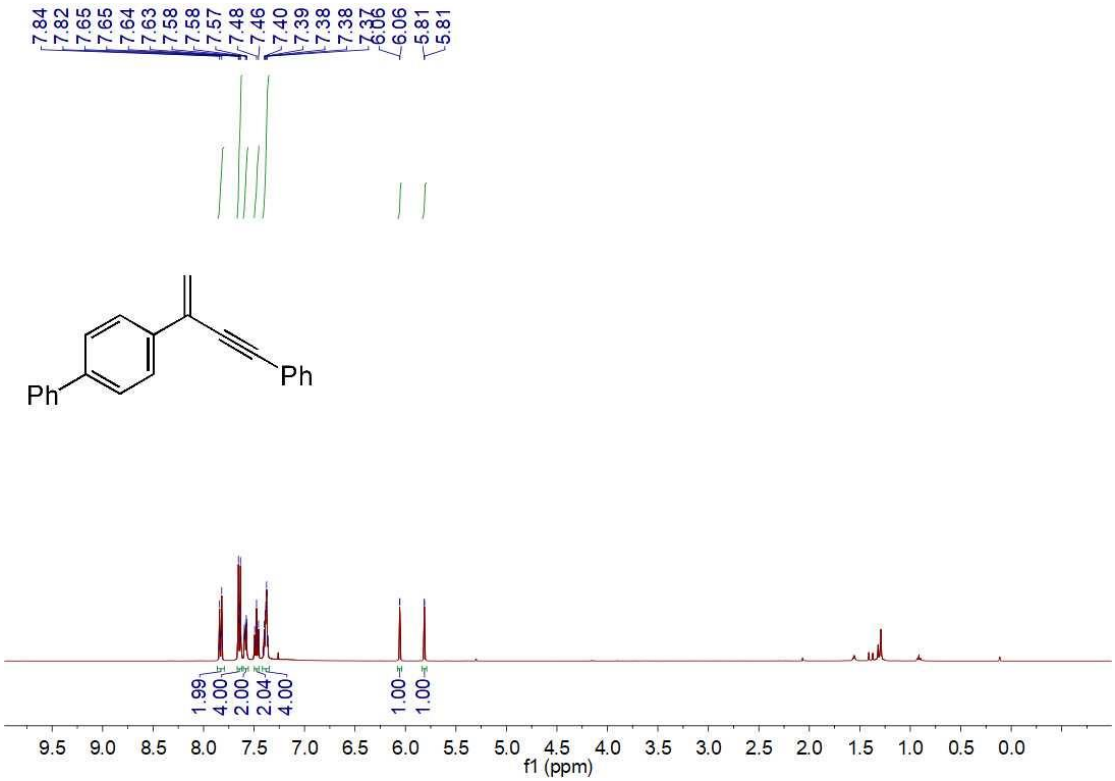

Figure S79 The ^{1}H NMR spectra of **4a** ($CDCl_3$, 400M)

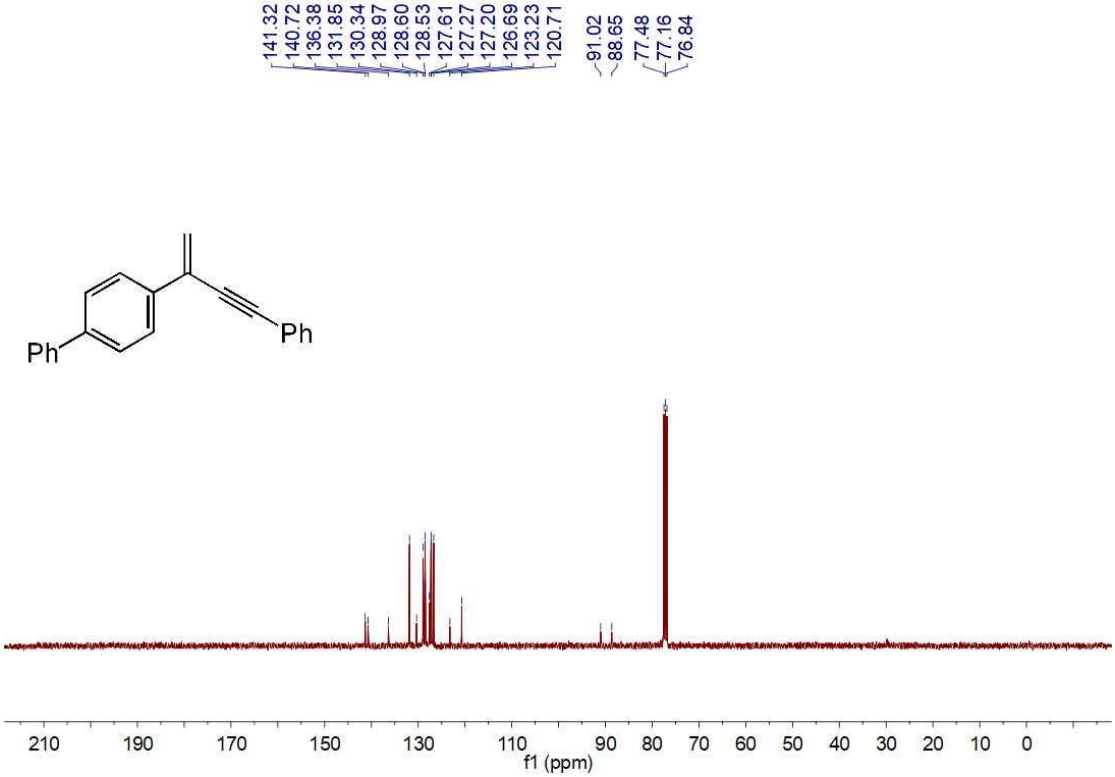

Figure S80 The ^{13}C NMR spectra of **4a** ($CDCl_3$, 101M)

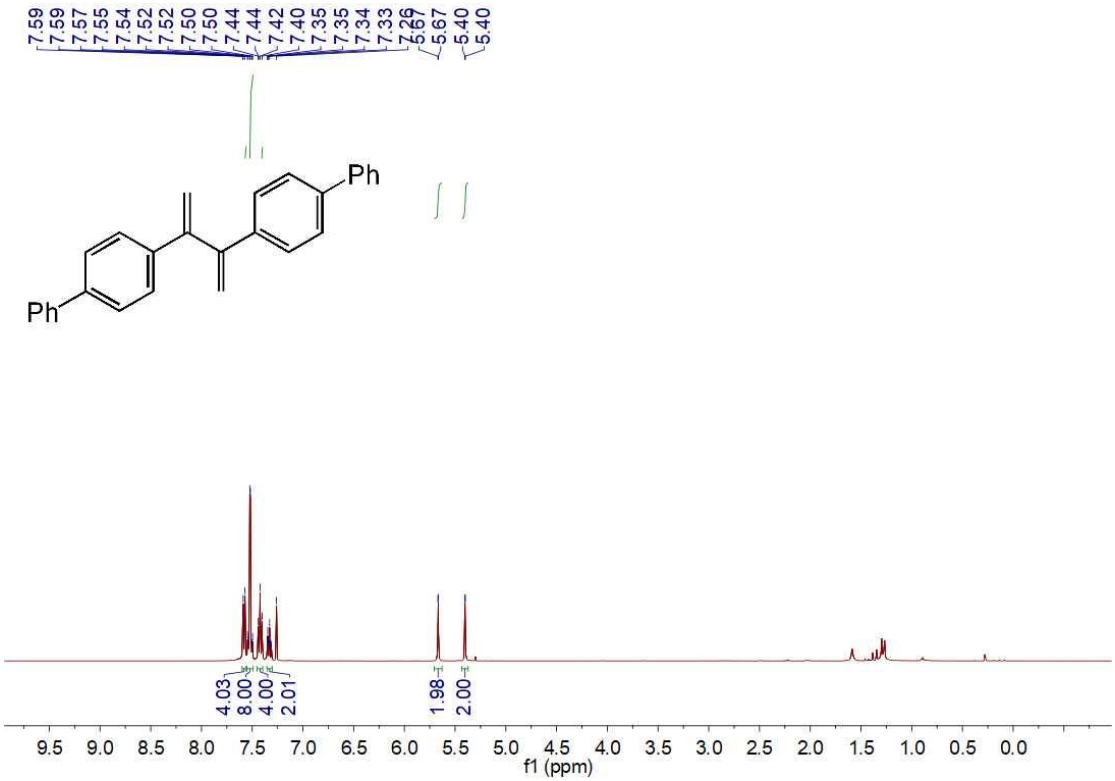

Figure S81 The ^{1}H NMR spectra of **4b** ($CDCl_3$, 400M)

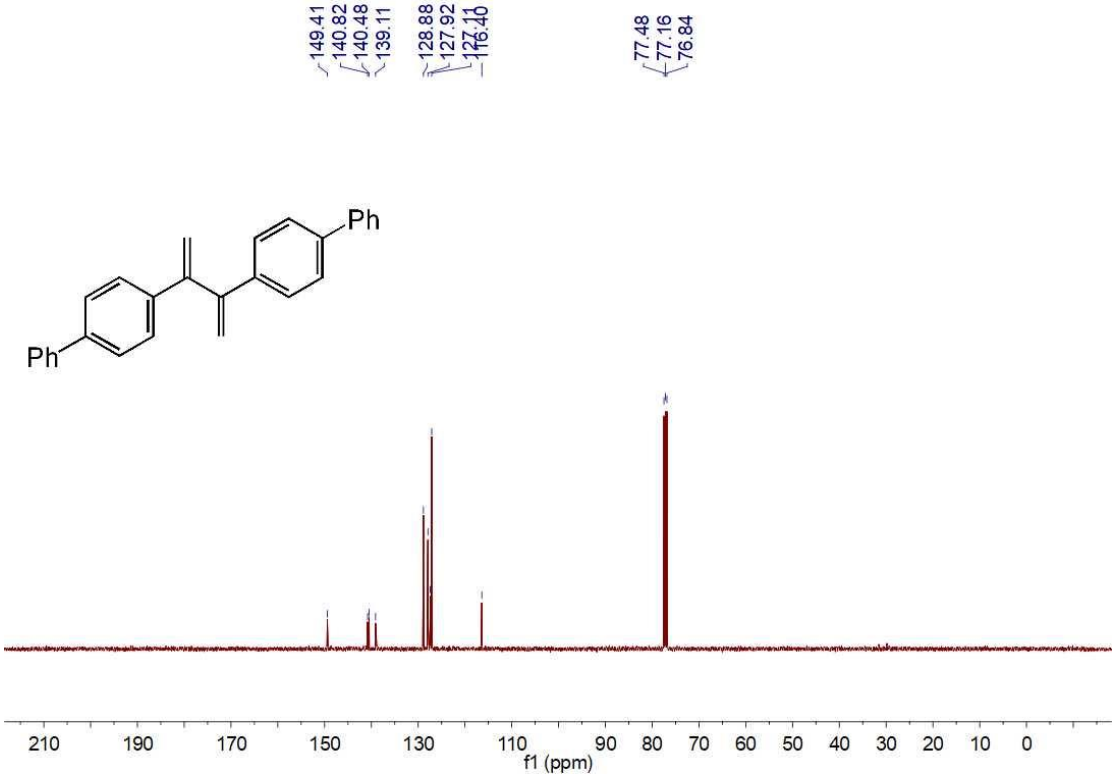

Figure S82 The ^{13}C NMR spectra of **4b** ($CDCl_3$, 101M)

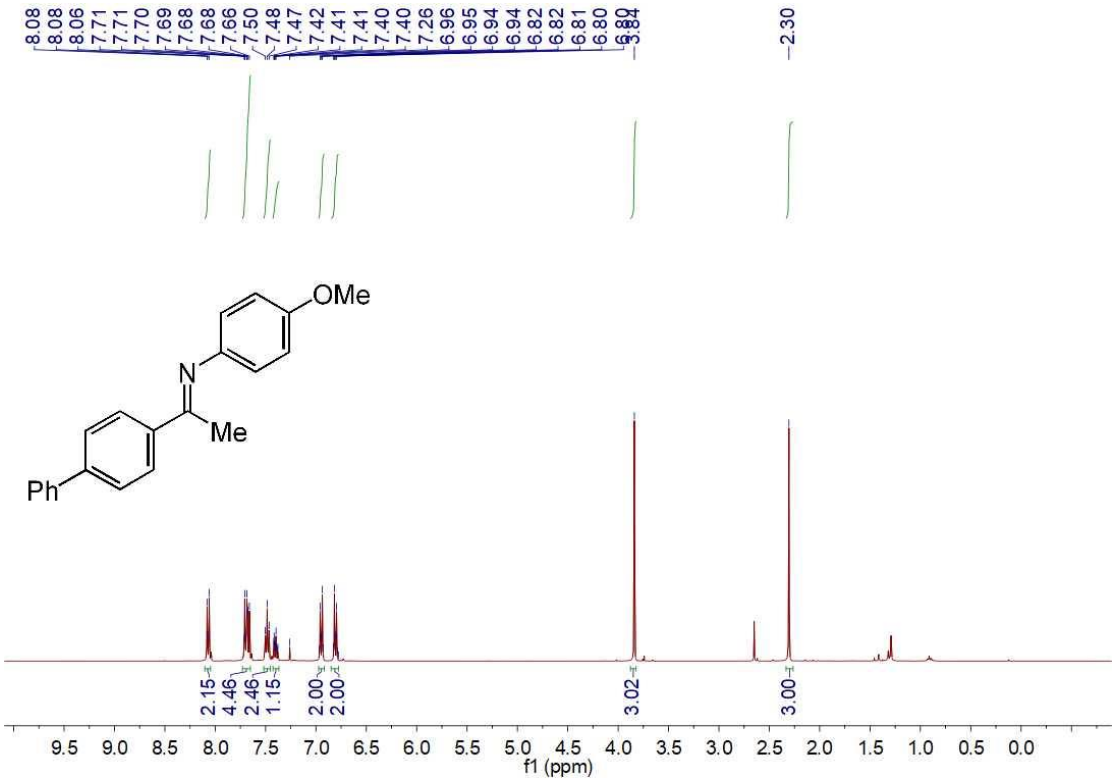

Figure S83 The ^{1}H NMR spectra of **4c** ($CDCl_3$, 400M)

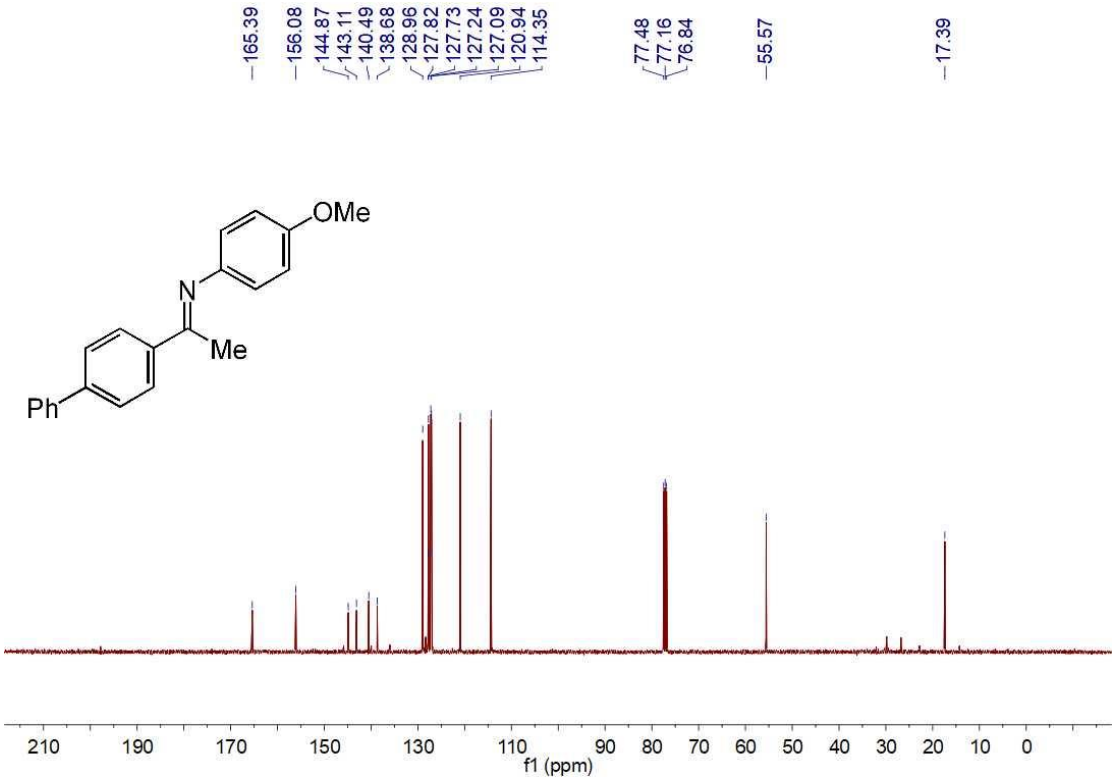

Figure S84 The ^{13}C NMR spectra of **4c** ($CDCl_3$, 101M)

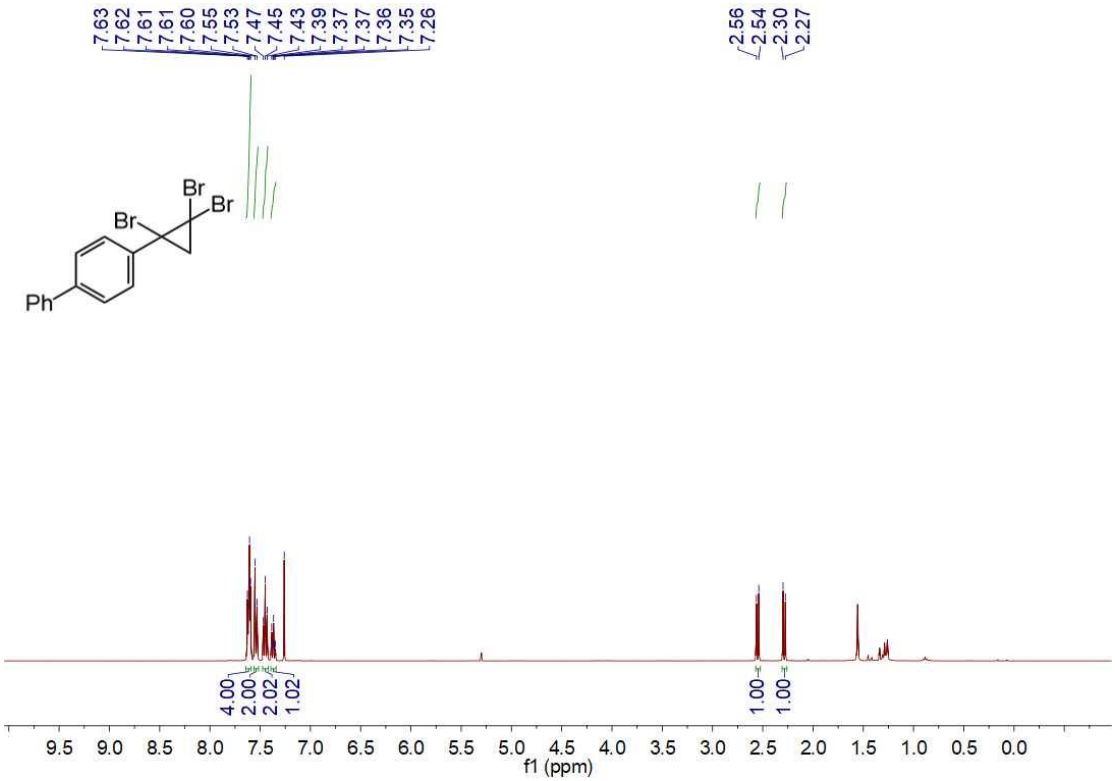

Figure S85 The ^{1}H NMR spectra of **4d** ($CDCl_3$, 400M)

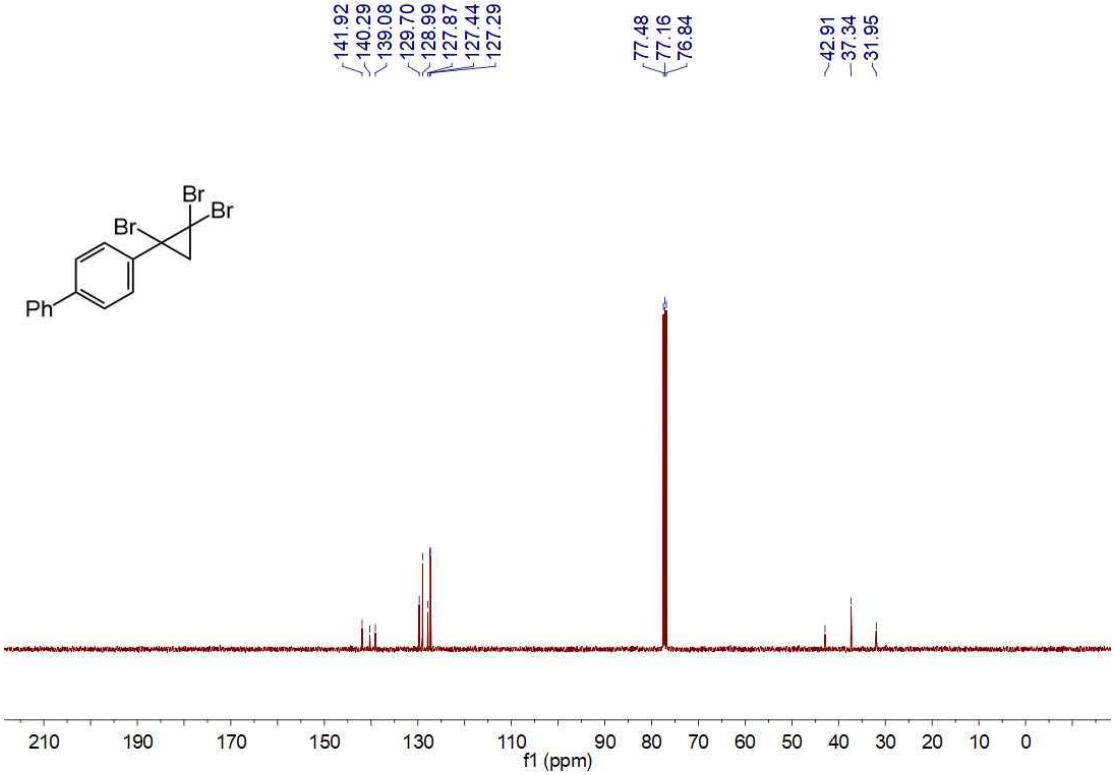

Figure S86 The ^{13}C NMR spectra of **4d** ($CDCl_3$, 101M)

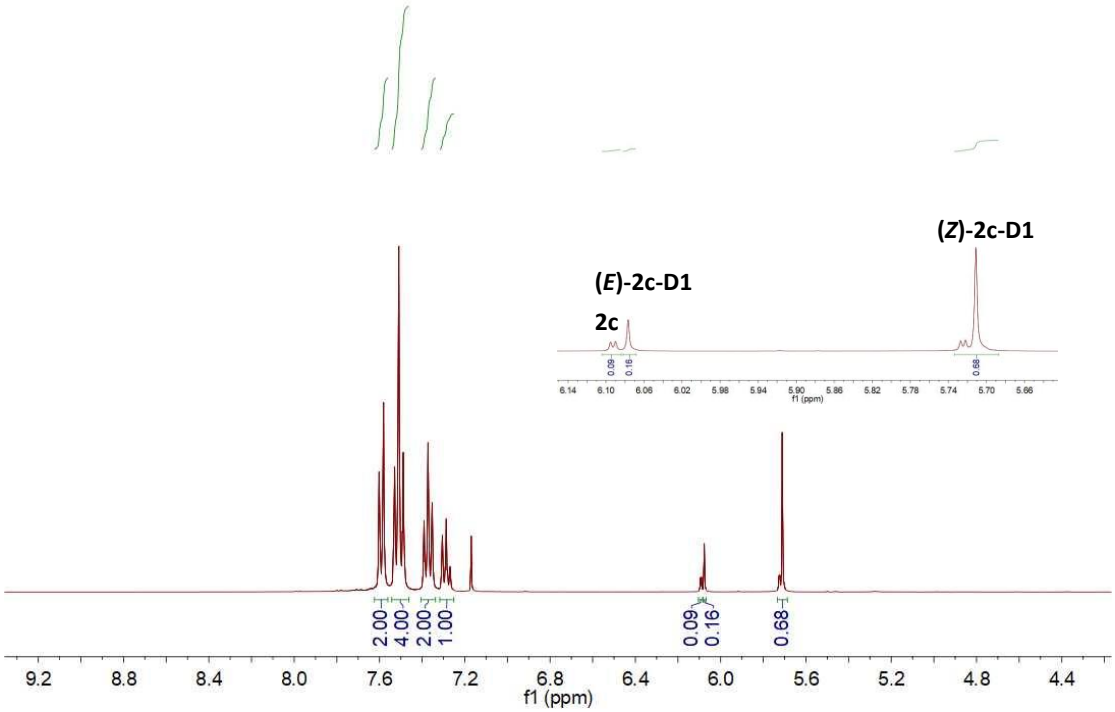

Figure S87 The ^{1}H NMR spectra of **1c-D--TMSBr** ($CDCl_3$, 400M)

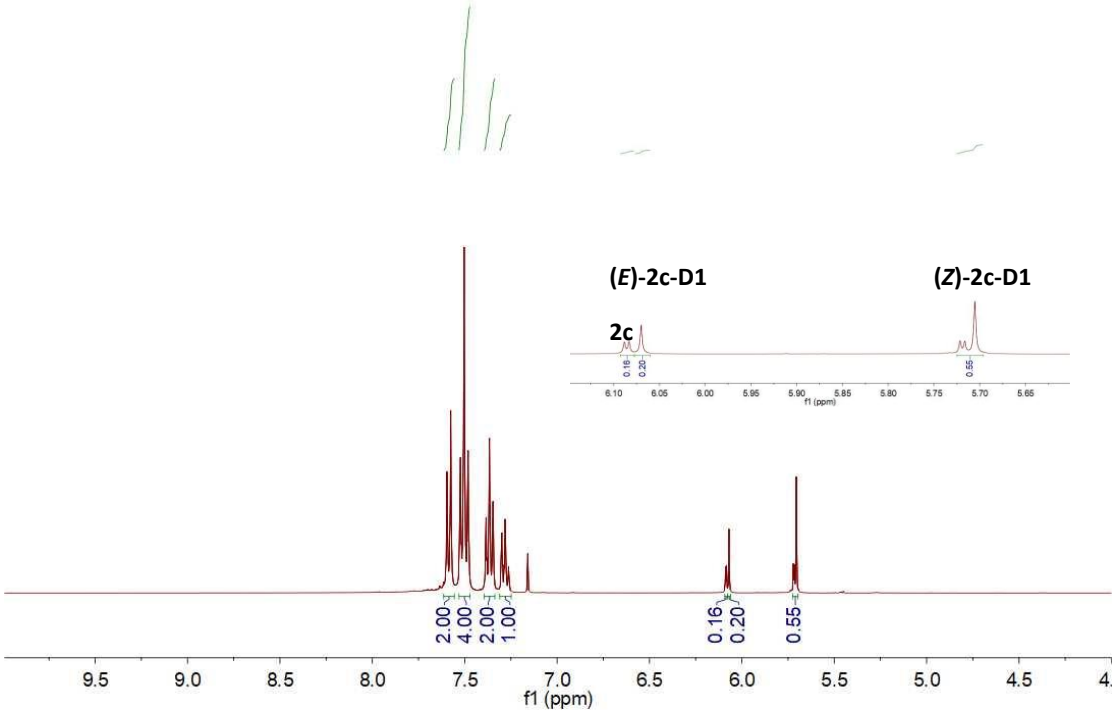

Figure S88 The ^{1}H NMR spectra of **1c-D—TMSBr+Mn(OAc)$_2$** ($CDCl_3$, 400M)

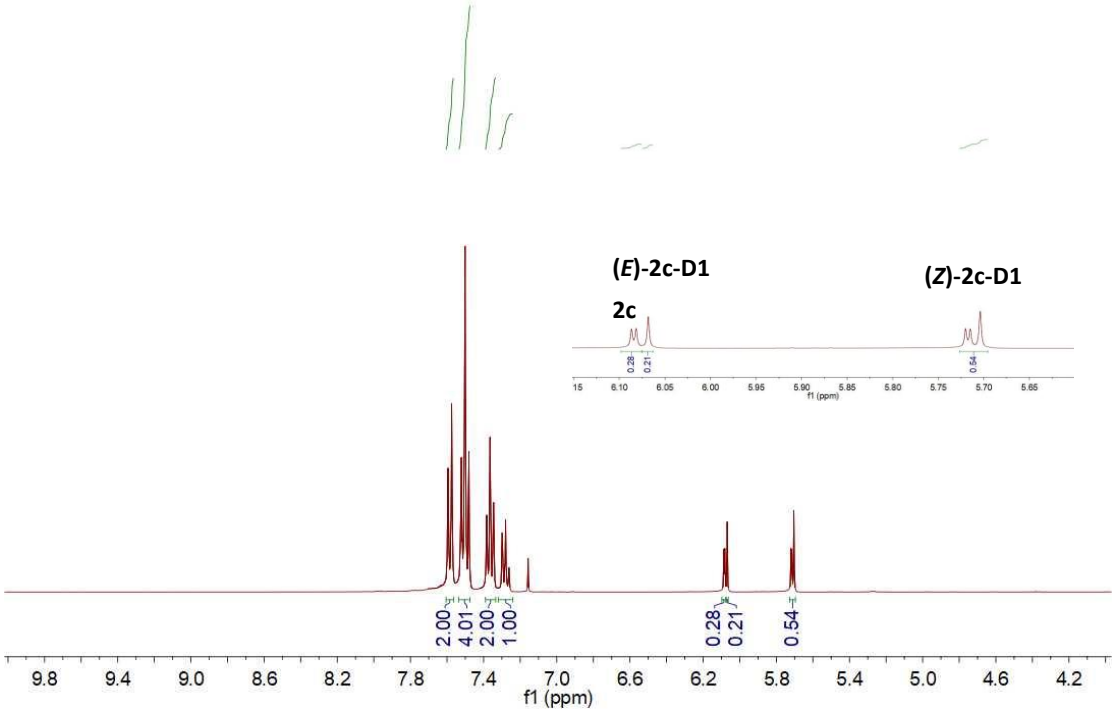

Figure S89 The ^{1}H NMR spectra of **1c-D—TMSBr+Mn(OAc)$_2$·4H$_2$O** ($CDCl_3$, 400M)