Electronic Supplementary Material (ESI) for RSC Advances.

Efficient Hydroarylation and Hydroalkenylation of Vinylarenes by Brønsted Acid Catalysis

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Supporting Information

Contents

1. General Information

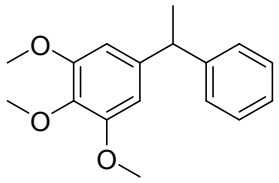
All chemical reagents used were brought from commerce source, and without further purification. Dioxane, tetrahydrofuran (THF), and cyclohexane were distilled from Na prior to use. All reactions were carried out under nitrogen with standard Schlenk techniques. Catalyst was kept and handled in glove box. All NMR data were collected by a Bruker 400 MHz NMR Spectrometer using $CDCl_3$ as solvent. All chemical shifts are reported in ppm and were referenced to residual solvent peaks (^1H NMR $CDCl_3$ δ = 7.26 ppm, ^{13}C NMR CDCl3 δ = 77.0 ppm).

2. General Procedures

General Procedure A for Vinylarenes for the Hydroarylation

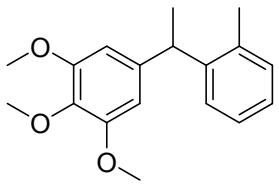
In a glovebox, the catalyst Tf_2NH (4 mol%, 4.7 mg) was added to a schlenk tube. Then 0.2 mmol of substrate, and 171.6 mg 1,2,3-Trimethoxybenzeney (5 eqvi., 1 mmol) and dioxane (2 mL) were added. After this, the reaction mixture was heated to 90 ℃ for 12 hours. When the reaction finished, the solvent was removed under vacuum. The residual was purified by silica gel column chromatography using petroleum ether as the eluant.

3a: Compound **3a** was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 75 % yield as colourless oil.



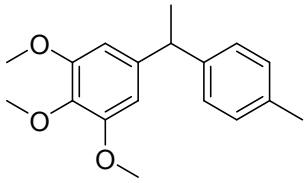
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.27 – 7.21 (m, 4H), 7.16 – 7.12 (m, 1H), 6.90 (d, *J* = 8.8, 1H), 6.64 (d, *J* = 8.8, 1H), 4.47 (q, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.61 (s, 3H), 1.57 (d, *J* = 7.2, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.10, 151.57, 146.99, 142.34, 132.55, 128.19, 127.57, 125.74, 121.84, 107.05, 60.66, 55.96, 37.92, 21.67; **HRMS** (ESI) calcd. for $C_{17}H_{20}O_3$ [M^+]: 272.1412, found: 272.1429.

3b: Compound 3b was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 86 % yield as colourless oil.



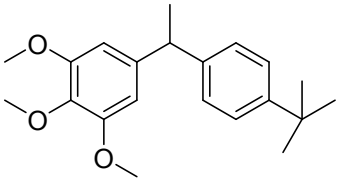
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.18 – 7.08 (m, 4H), 6.82 (d, *J* = 8.8, 1H), 6.63 (d, *J* = 8.8, 1H), 4.64 (q, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.64 (s, 3H), 2.34 (s, 3H), 1.55 (d, *J* = 7.2, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.05, 151.51, 144.91, 142.24, 135.79, 132.44, 130.18, 126.63, 125.75, 121.63, 106.83, 60.61, 60.37, 55.92, 34.18, 21.18, 19.52; **HRMS** (ESI) calcd. for $C_{18}H_{22}O_3$ [M^+]: 286.1569, found: 286.1586.

3c: Compound 3c was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 82 % yield as colourless oil.



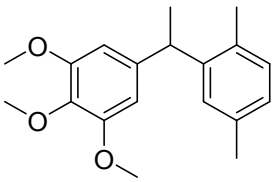
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.15 – 7.09 (m, 4H), 6.92 (d, *J* = 8.8, 1H), 6.67 (d, *J* = 8.4, 1H), 4.48 (q, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.68 (s, 3H), 2.32 (s, 3H), 1.58 (d, *J* = 7.2, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.01, 151.53, 143.93, 142.32, 135.13, 132.79, 128.89, 127.42, 121.81, 107.09, 60.75, 60.65, 55.96, 37.39, 21.79, 20.99; **HRMS** (ESI) calcd. for $C_{18}H_{22}O_3$ [M^+]: 286.1569, found: 286.1582.

3d: Compound 3d was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 88 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, *J* = 8.4, 2H), 7.20 (d, *J* = 8.4, 2H), 6.92 (d, *J* = 8.4, 1H), 6.67 (d, *J* = 8.4, 1H), 4.50 (q, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.70 (s, 3H), 1.60 (d, J = 7.6, 3H), 1.32 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.97, 151.50, 148.45, 143.67, 142.30, 132.93, 127.18, 125.05, 121.92, 107.16, 60.76, 60.66, 55.95, 37.19, 34.33, 31.45, 21.70; **HRMS** (ESI) calcd. for $C_{21}H_{28}O_3$ [M^+]: 328.2038, found: 328.2050.

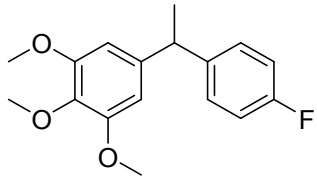
3e: Compound 3e was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 92 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.05 – 6.92 (m, 3H), 6.83 (d, J = 8.4, 1H), 6.64 (d, J = 8.4, 1H), 4.62 (q, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.66 (s, 3H), 2.30 (d, J = 6.4, 6H), 1.55 (d, J = 7.2, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 151.99, 151.52, 144.62, 142.22, 135.05, 132.66, 132.55, 130.09, 127.38, 126.42, 121.69, 106.85, 60.61, 60.39, 55.91, 34.14, 21.25, 19.07; **HRMS** (ESI) calcd. for $C_{19}H_{24}O_3$ [M^+]: 300.1725, found:

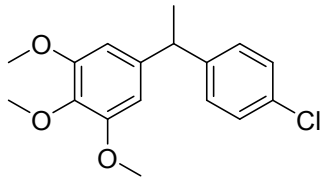
300.1742.

3f: Compound 3f was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 75 % yield as colourless oil.



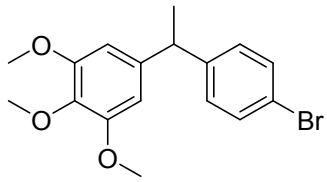
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.19 (m, 2H), 6.97 (t, 2H), 6.89 (d, *J* = 8.4, 1H), 6.66 (d, *J* = 8.8, 1H), 4.45 (q, 1H), 3.85 (d, *J* = 3.6, 6H), 3.64 (s, 3H), 1.56 (d, *J* = 7.6, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 162.30, 159.88, 152.22, 151.50, 142.71, 142.67, 142.35, 132.23, 128.90, 128.82, 121.63, 114.96, 114.75, 107.03, 77.37, 77.05, 76.74, 60.65, 55.94, 37.28, 21.74; **HRMS** (ESI) calcd. for $C_{17}H_{19}FO_3$ [M^+]: 290.1318, found: 290.1336.

3g: Compound 3g was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 62 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.24 – 7.21 (m, 2H), 7.16 – 7.14 (m, 2H), 6.88 (d, *J* = 8.4, 1H), 6.66 (d, *J* = 8.8, 1H), 4.44 (q, 1H), 3.85 (d, *J* = 1.6 Hz, 6H), 3.64 (s, 3H), 1.55 (d, *J* = 7.6, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.30, 151.50, 145.59, 142.35, 131.85, 131.36, 128.89, 128.26, 121.64, 107.03, 60.63, 55.96, 37.45, 21.53; **HRMS** (ESI) calcd. for $C_{17}H_{19}ClO_3$ [M^+]: 306.1023, found: 306.1046.

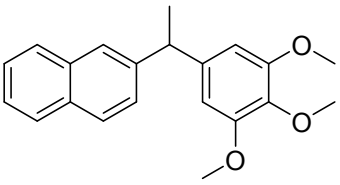
3h: Compound 3h was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 50 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 – 7.36 (m, 2H), 7.10 (d, *J* = 8.4, 2H), 6.88 (d, *J* = 8.8, 1H), 6.65 (d, *J* = 8.8, 1H), 4.42 (q, 1H), 3.85 (s, 6H), 3.63 (s, 3H), 1.55 (d, J = 7.2, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.31, 151.50, 146.12, 142.34, 131.74, 131.21, 129.31, 121.64, 119.41, 107.03, 60.64, 55.96, 37.51, 21.46; **HRMS** (ESI) calcd. for

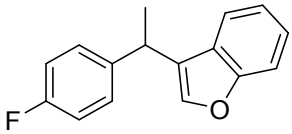
$C_{17}H_{19}BrO_3$ [M⁺]: 350.0518, found: 350.0526.

3i[1]: Compound 3i was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 80 % yield as colourless oil.



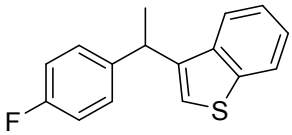
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 – 7.71 (m, 4H), 7.48 – 7.36 (m, 3H), 6.95 (d, *J* = 8.8, 1H), 6.68 (d, *J* = 8.8, 1H), 4.69 (q, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.68 (s, 3H), 1.71 (d, J = 7.2, 3H); MS (EI): m/z (rel. intensity) 322 (72, M⁺), 307, 291, 141.

3j: Compound 3j was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 80% % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49-7.36 (m, 2H), 7.23-7.09 (m, 4H), 7.00-6.93 (m, 2H), 6.41 (s, 1H), 4.24 (q, 1H), 1.66-1.63 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 162.96, 160.53, 154.88, 139.04, 129.03, 124.27, 123.61, 122.60, 122.33, 120.57, 120.43, 115.53, 115.32, 111.03, 39.06, 20.47; **HRMS** (ESI) calcd. for $C_{16}H_{13}FO$ [M⁺]: 240.0950, found: 240.0978.

3k[1]: Compound 3k was prepared according to the general procedure A and the reaction mixture was purified by flash column chromatograph (petroleum ether) in 84 % yield as colourless oil.



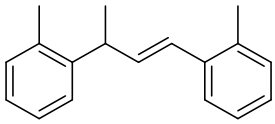
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45-7.40 (m, 4H),7.29 (s, 1H), 7.21-7.12 (m, 4H), 3.62-3.55 (m, 1H), 1.44 (d, *J* = 7.2, 3H); MS (EI): m/z (rel. intensity) 256 (75, M⁺), 241, 221, 196, 161, 128, 110, 88.

General Procedure B for Homo-Hydroalkenylation

In a glovebox, the catalyst Tf_2NH (4 mol%, 4.7 mg) was added to a Schlenk tube. Then 0.2 mmol of styrene was added by microsyringe, followed by addition of 1.5 mL THF, and 0.5 ml cyclohexane as solvent. After this, the Schlenk tube was sealed, and heated to 80 ℃ for 12 hours.

When the reaction finished, the solvent was removed under vacuum. Then he residual was purified by silica gel column chromatography using n-Pentane as the eluant.

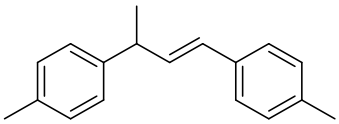
4b[2]: Compound 4b was prepared according to the general procedure



B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 82 % yield as colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.43-7.73 (m, 1H),7.29-7.12 (m, 7H), 6.62 (d, *J* = 16, 1H), 6.27 (q, 1H), 3.94-3.87 (m, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.49 (d, *J* = 6.8, 3H); MS (EI): m/z (rel. intensity) 236 (40, M^+), 221, 129, 105, 91.

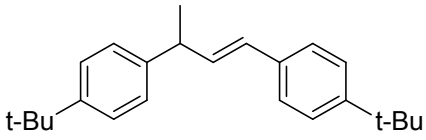
4c[2]: Compound 4c was prepared according to the general procedure B



and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 91 % yield as colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.24-7.06 (m, 8H), 6.39-6.28 (m, 2H), 3.61-3.54 (m, 1H), 2.31 (d, *J* = 5.6, 6H), 1.44 (d, *J* = 6.8, 3H); MS (EI): m/z (rel. intensity) 236 (53, M^+), 221, 129, 105, 91, 65.

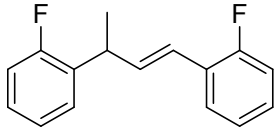
4d[3]: Compound 4d was prepared according to the general procedure



B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 82 % yield as colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35-7.32 (m, 6H), 7.22-7.20 (m, 2H), 6.45-6.32 (m, 2H), 3.65-3.58 (m, 1H), 1.47 (d, *J* = 6.8, 3H), 1.32 (s, 9H), 1.31 (s, 9H); MS (EI): m/z (rel. intensity) 320 (8, M^+), 263, 207, 145, 117, 91, 57.

4j[4]: Compound 4j was prepared according to the general procedure B

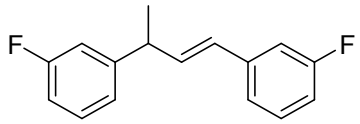


and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 78 % yield as colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) : δ = 7.46-7.42 (m, 1H), 7.15-6.98 (m, 7H), ,

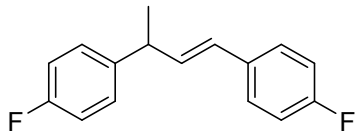
6.63-6.45 (m, 2H), 4.01-3.91 (m, 1H), 1.49 (d, *J* = 6.8, 3H); MS (EI): m/z (rel. intensity) 244 (73, M^+), 229, 214, 183, 148, 133, 109, 83.

4k[4]: Compound 4k was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 70 % yield as colourless oil.



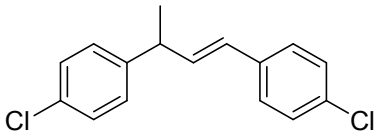
^{1}H NMR ($CDCl_3$, 400 MHz) : δ = 7.30-7.21 (m, 2H), 7.11-7.02 (m, 3H), 6.97-6.89 (m, 3H), 6.40-6.31 (q, 2H), 3.67-3.60 (m, 1H), 1.46 (d, *J* = 6.8, 3H); MS (EI): m/z (rel. intensity) 244 (76, M^+), 229, 214, 183, 148, 133, 109, 83.

4f[4]: Compound 4f was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 90 % yield as colourless oil.



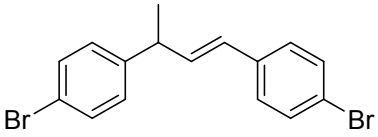
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83-7.28 (m, 2H), 7.23-7.19 (m, 2H), 7.03-6.96 (m, 4H), 6.37-6.22 (m, 2H), 3.65-3.58 (m, 1H), 1.45 (d, *J* = 7.2, 3H); MS (EI): m/z (rel. intensity) 244 (49, M^+), 229, 214, 183, 148, 133, 109, 83.

4g[5]: Compound 4g was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 60 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.20-7.07 (m, 8H), 6.27-6.17 (m, 2H), 3.54-3.48 (m, 1H), 1.35 (d, *J* = 6.8, 3H); MS (EI): m/z (rel. intensity) 276 (38, M^+), 261, 241, 206, 191, 149, 125, 101, 95.

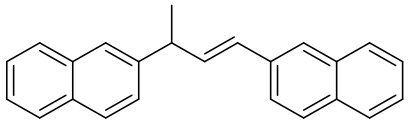
4h[6]: Compound 4h was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 85 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44-7.39 (m, 4H), 7.21 (d, *J* = 8.4, 2H), 7.14 (d, *J* = 8.0, 2H),

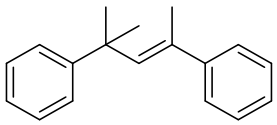
6.32 (d, *J* = 2.8, 2H), 3.61-3.56 (m, 1H), 1.44 (d, J=7.2, 3H); MS (EI): m/z (rel. intensity) 366 (12, M^+), 244, 229, 214, 133, 123, 109, 83.

4l[6]: Compound 4l was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 80 % yield as colourless oil.



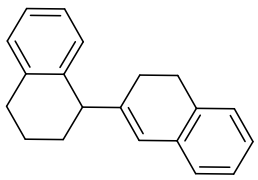
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86-7.74 (m, 8H), 7.64 (d, *J* = 8.4, 1H), 7.52-7.42 (m, 5H), 6.68-6.59 (m, 2H), 3.93-3.87 (m, 1H), 1.65 (d, *J* = 6.8, 3H); MS (EI): m/z (rel. intensity) 308 (100, M^+), 293, 265, 180, 165, 141, 134, 115.

4m[7]: Compound 4m was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 84 % yield as colourless oil.



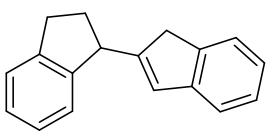
^{1}H NMR ($CDCl_3$, 400 MHz) : δ = 7.50-7.44 (m, 4H), 7.39-7.35 (m, 4H), 7.27-7.22 (m, 2H), 6.20 (s, 1H), 1.63 (s, 3H), 1.58 (s, 6H); MS (EI): m/z (rel. intensity) 236 (52, M^+), 221, 193, 143, 127, 105, 91.

4n[8]: Compound 4n was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 75 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz) : δ = 7.21-7.00 (m, 8H), 6.22 (s, 1H), 3.72 (t, 1H), 2.85-2.76 (m, 4H), 2.45-2.09 (m, 2H), 1.98-1.93 (m, 2H), 1.87-1.73 (m, 2H); MS (EI): m/z (rel. intensity) 260 (46, M^+), 232, 217, 130, 115, 97.

4o: Compound 4o was prepared according to the general procedure B and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 76 % yield as colourless oil.



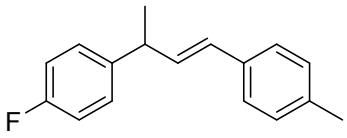
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.31-7.05 (m, 8H), 6.57 (s, 1H), 4.28 (t, 1H), 3.32 (q, 2H), 3.03-2.85 (m,

2H), 2.45-2.37 (m, 1H), 2.09-2.00 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.61, 146.03, 145.42, 144.08, 143.57, 127.55, 126.95, 126.59, 124.90, 124.78, 124.18, 123.84, 120.51, 47.60, 38.90, 34.04, 32.04; **HRMS** (ESI) calcd. for $C_{18}H_{16}$ [M^+]: 232.1252, found: 232.1266.

General Procedure C for Cross-Hydroalkenylation of Vinylarenes

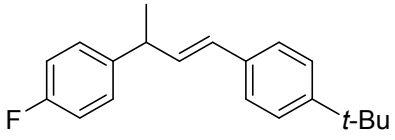
In a glovebox, the catalyst Tf_2NH (4 mol%, 4.7 mg) was added to a Schlenk tube. Then 0.2 mmol of substrate, and 122 μL of 4-Fluorostyrene (5 eqvi., 1 mmol) was added, followed by addition of 1.5 mL THF, and 0.5 ml cyclohexane as solvent. After this, the Schlenk tube was sealed, and heated to 80 ℃ for 12 hours. When the reaction finished, the solvent was removed under vacuum. Then he residual was purified by silica gel column chromatography using n-Pentane as the eluant.

5b: Compound 5b was prepared according to the general procedure C and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 86 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35-7.08 (m, 6H), 7.00-6.93 (m, 2H), 6.37-6.24 (m, 2H), 3.62-3.55 (m, 1H), 2.32 (s, 3H), 1.44 (d, *J* = 6.8, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 163.24, 160.80, 142.54, 136.91, 135.79, 135.30, 133.85, 129.22, 128.72, 127.61, 127.53, 127.16, 126.07, 115.42, 115.21, 42.16, 21.27, 21.00; **HRMS** (ESI) calcd. for $C_{17}H_{17}F$ [M^+]: 240.1314, found: 240.1328.

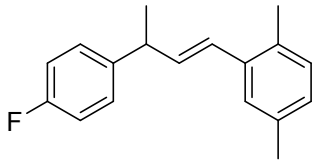
5c: Compound 5c was prepared according to the general procedure C and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 78 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36-7.27 (m, 2H), 7.07-6.92 (m, 6H), 6.34-6.20 (m, 2H), 3.84-3.77 (m, 1H), 2.37 (s, 9H), 1.45 (d, J=6.8, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 163.26, 160.82, 143.27, 135.67, 134.83, 134.80, 132.40, 130.40, 127.61, 127.53, 127.24, 127.06, 126.86, 115.45, 115.23, 77.37, 77.06, 76.74, 38.04, 31.56, 30.22, 29.76, 29.42, 19.03;

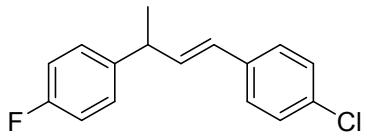
HRMS (ESI) calcd. for $C_{20}H_{23}F$ [M^+]: 282.1784, found: 282.1796.

5d: Compound 5d was prepared according to the general procedure C and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 89 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34-6.95 (m, 7H), 6.37-6.30 (m, 2H), 3.87-3.80 (m, 1H), 2.35 (d, *J* = 5.6, 6H), 1.45 (d, *J* = 6.8, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 163.25, 160.80, 143.28, 135.72, 134.79, 132.45, 130.41, 127.63, 127.55, 127.21, 127.08, 126.89, 115.48, 115.27, 77.42, 77.10, 76.78, 38.02, 21.24, 20.51, 19.10; **HRMS** (ESI) calcd. for $C_{18}H_{19}F$ [M^+]: 254.1471, found: 254.1486.

5e: Compound 5e was prepared according to the general procedure C and the reaction mixture was purified by flash column chromatograph (n-Pentane) in 55 % yield as colourless oil.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36-7.18 (m, 6H), 7.02-6.94 (m, 2H), 6.41-6.26 (m, 2H), 3.65-3.59 (m, 1H), 1.48-1.42 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 162.69, 160.27, 135.76, 134.40, 132.75, 128.68, 127.39, 115.40, 115.19, 77.38, 77.06, 76.74, 41.84, 21.27; **HRMS** (ESI) calcd. for $C_{16}H_{14}ClF$ [M^+]: 260.0768, found: 260.0784

Reference:

1, B. L. H. Taylor, E. C. Swift, J. D. Waetzig, E. R. Jarvo, *J. Am. Chem. Soc.* **2011**, *133*, 389.

2, H. Ma, Q. Sun, W. Li, J. Wang, Z. Zhang, Y. Yang, Z. Lei, T*etrahedron Lett.* **2011**, *52*, 1569.

3, J. H. Choi, J. K. Kwon, T. V. RajanBabu, H. J. Lim, *Adv. Synth. Catal,* **2013**, *355,* 3633.

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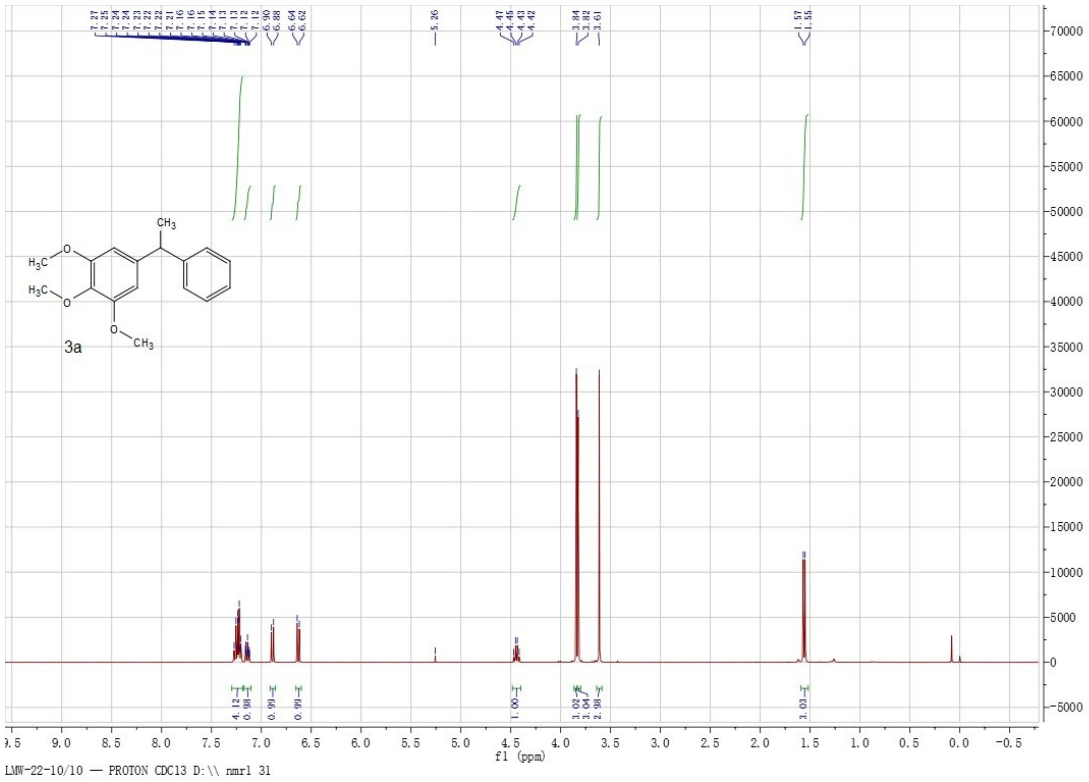
5, G. W. Kabalka, G. Dong, B, Venkataiah, *Tetrahedron Lett.* 2004, *45,* 2775.

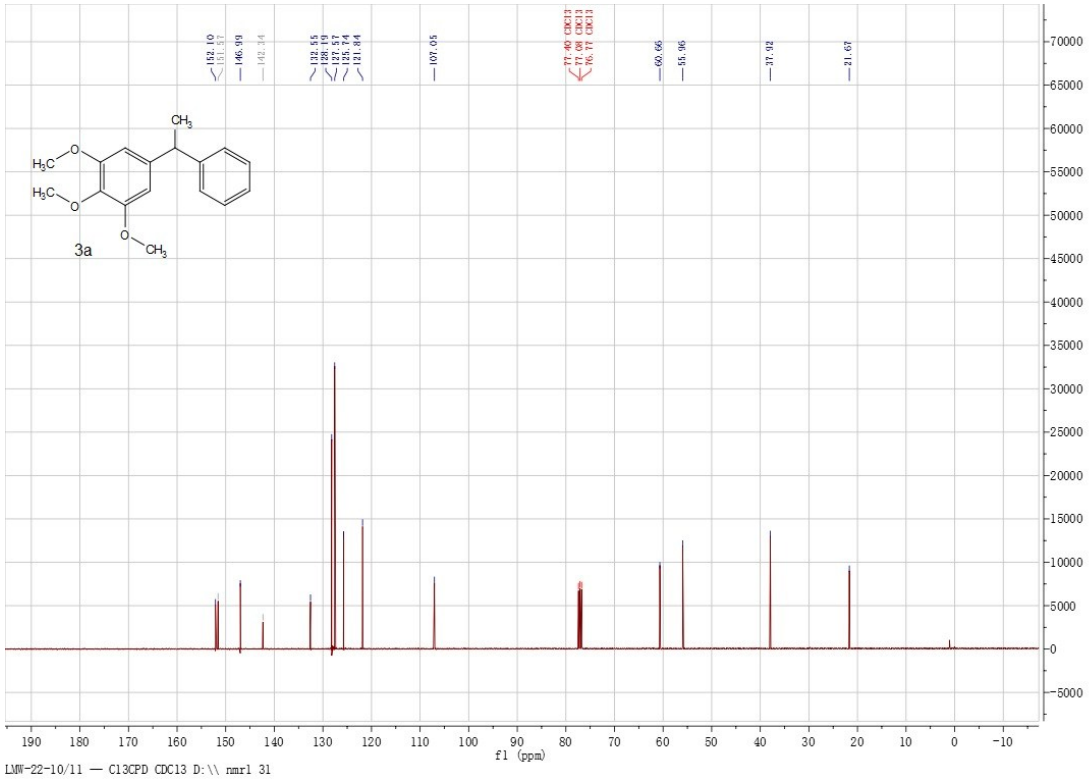
6, T. Tsuchimoto, S. Kamiyama, R. Negoro, E. Shirakawa, Y. Kawakami , *Chem. Commun.* , **2003**, 852.
7, C. Yi, R. Hua , H. Zeng, *Catal Commun,* **2008**, *9*, 85.
8, S. Lindner, S. Braese, *RSC Advances*, **2014**, *4*, 29439.

3. NMR spectra

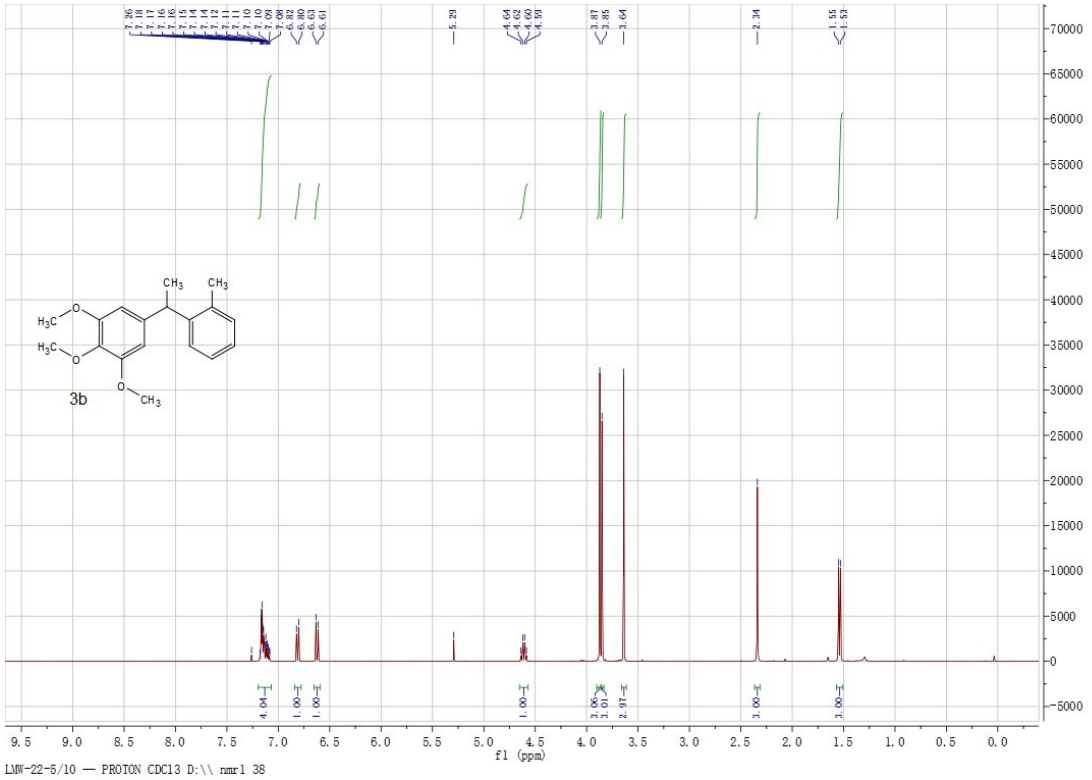
^{1}H NMR spectrum of **3a** recorded in $CDCl_3$



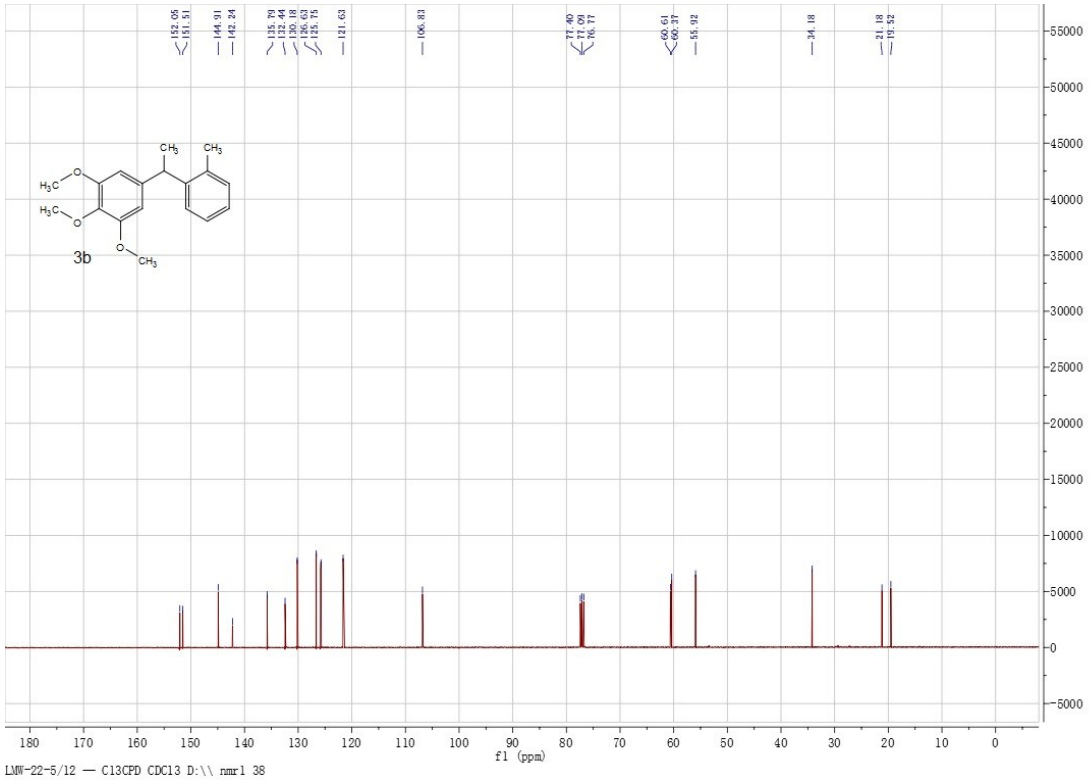
^{13}C NMR spectrum of **3a** recorded in $CDCl_3$



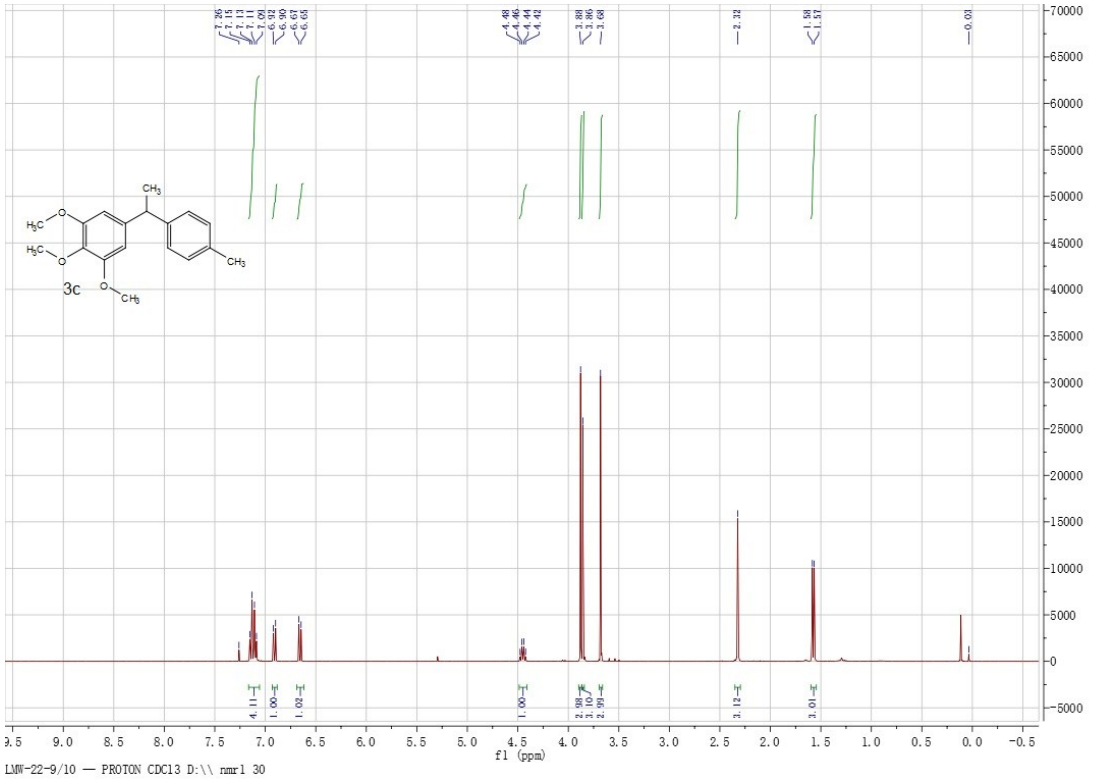
^{1}H NMR spectrum of **3b** recorded in $CDCl_3$



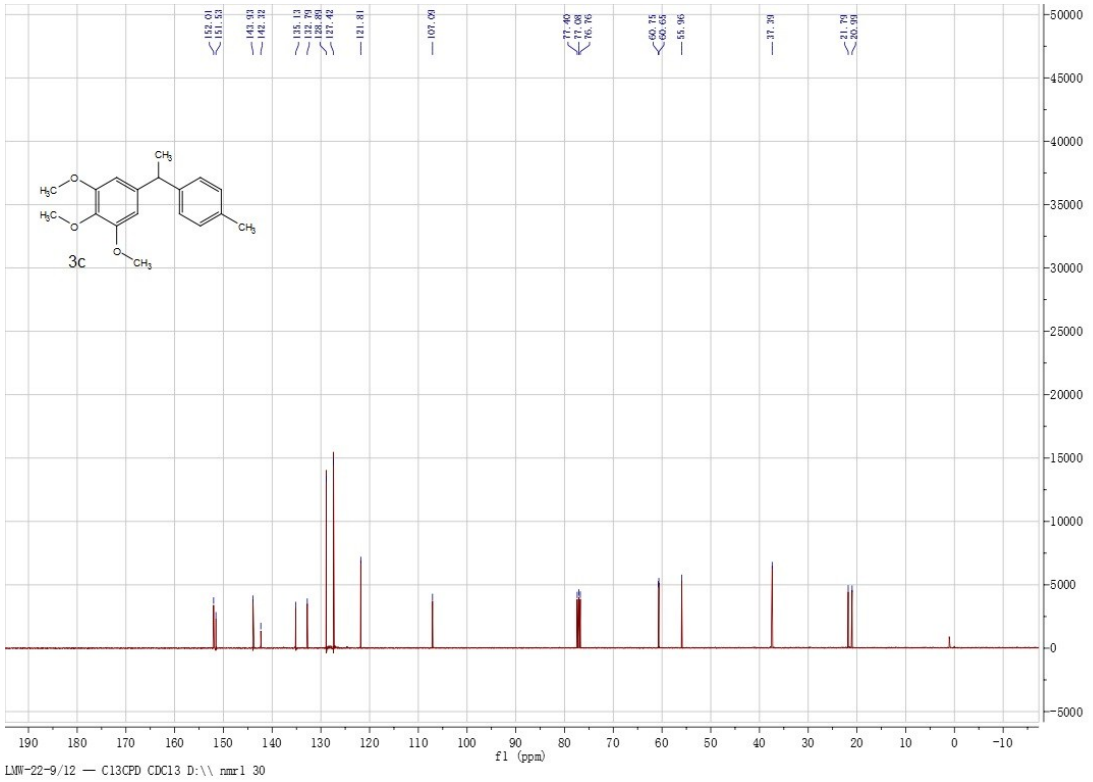
^{13}C NMR spectrum of **3b** recorded in $CDCl_3$



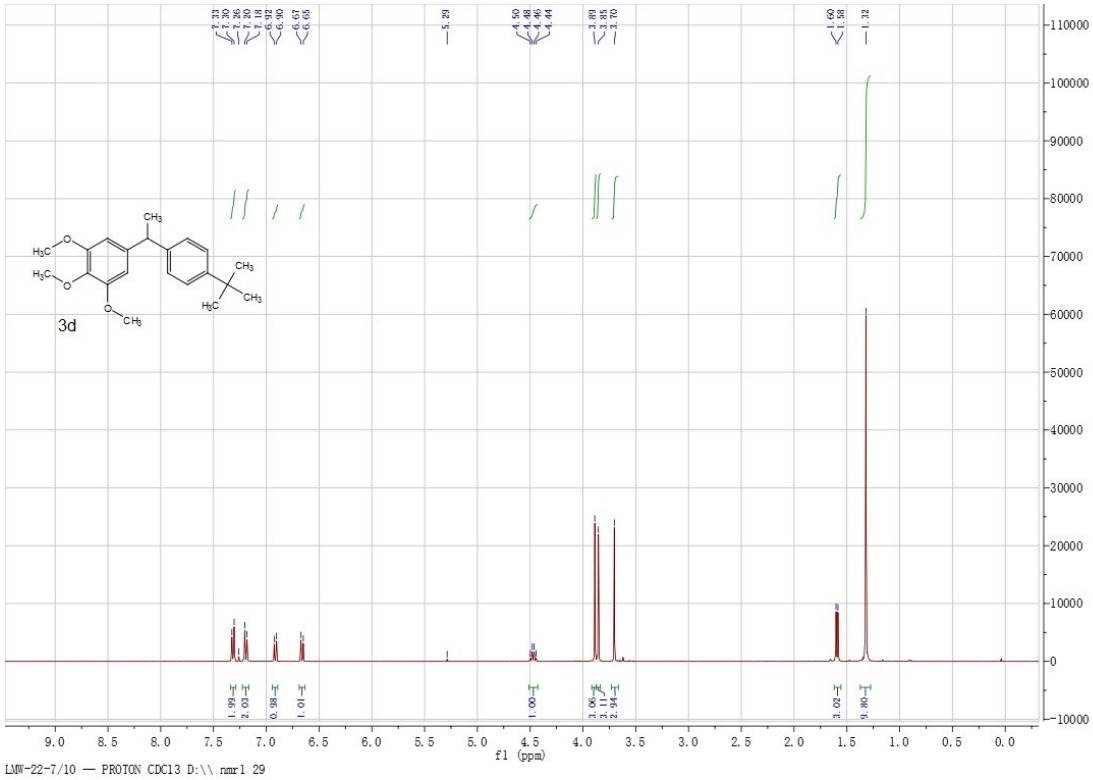
^{1}H NMR spectrum of **3c** recorded in $CDCl_3$



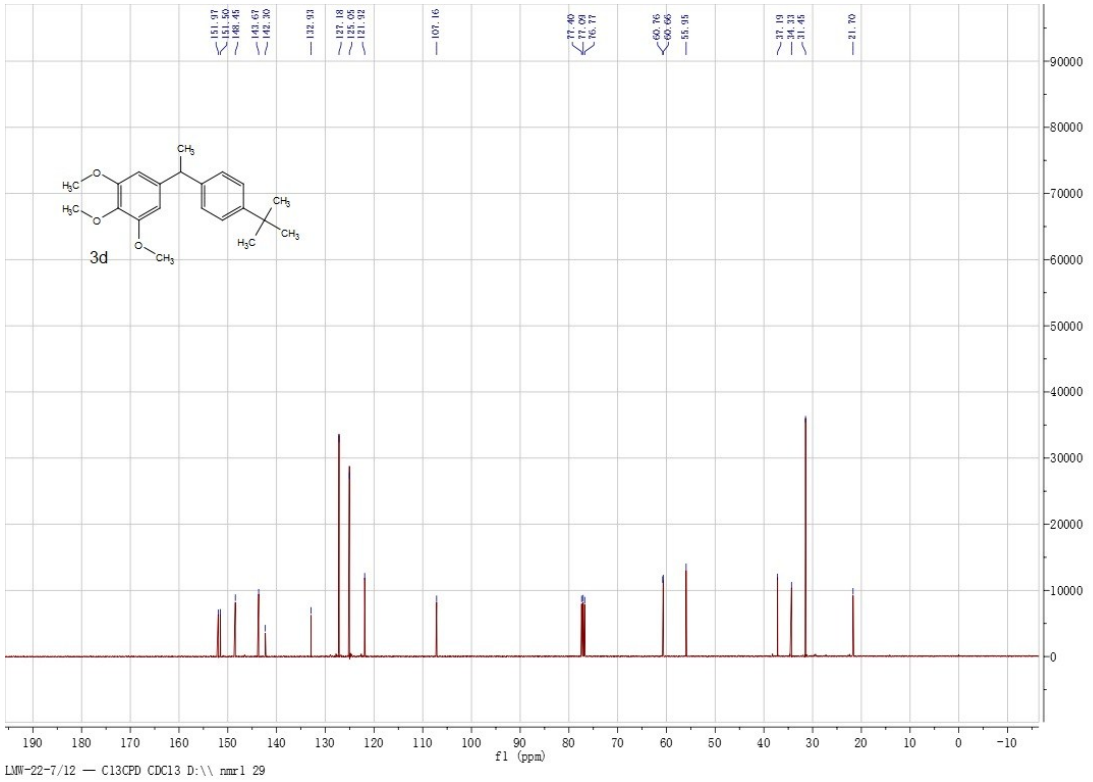
^{13}C NMR spectrum of **3c** recorded in $CDCl_3$



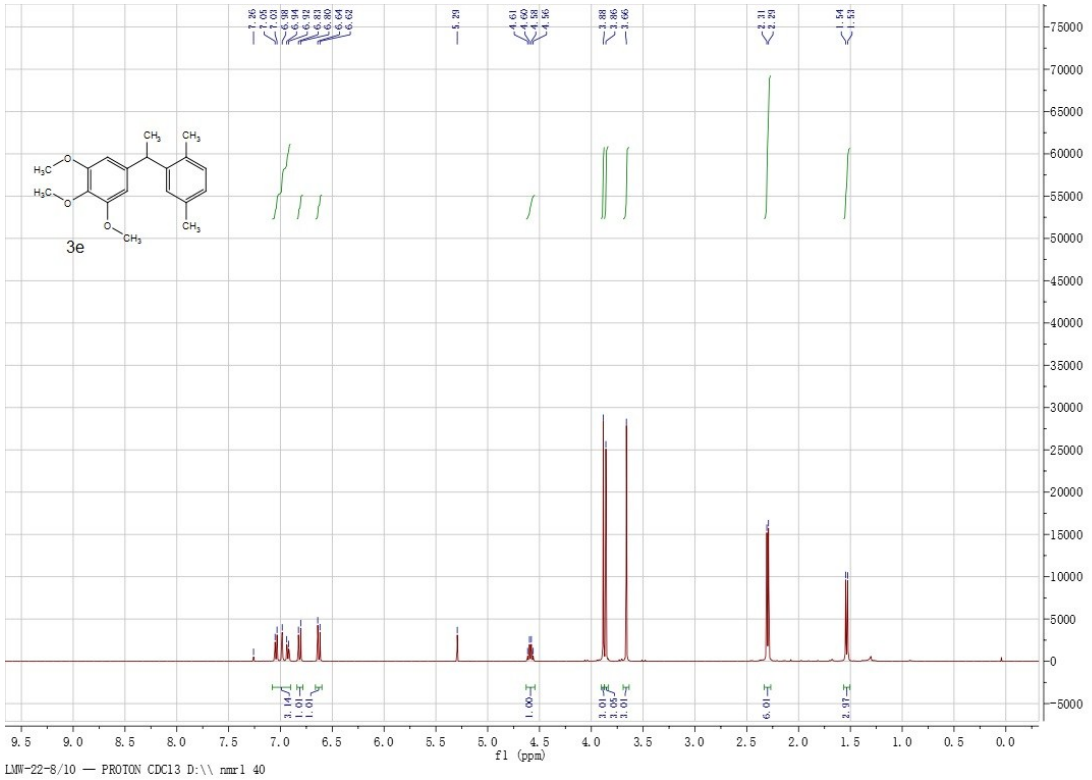
^{1}H NMR spectrum of **3d** recorded in $CDCl_3$



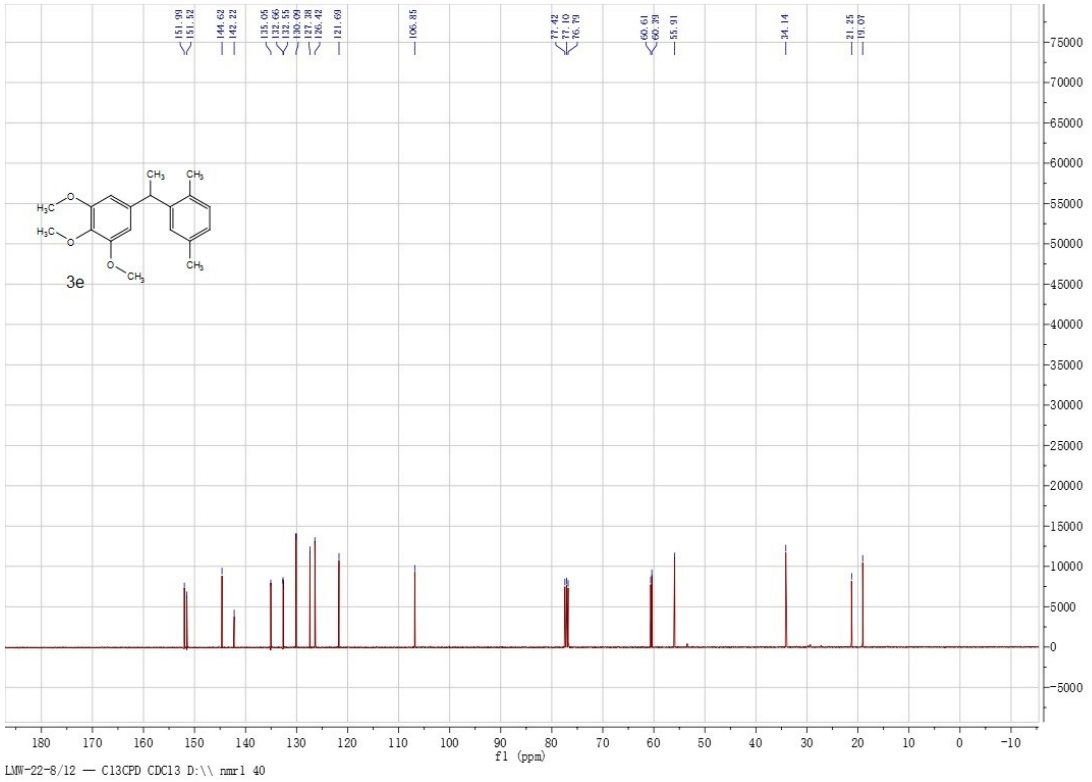
^{13}C NMR spectrum of **3d** recorded in $CDCl_3$



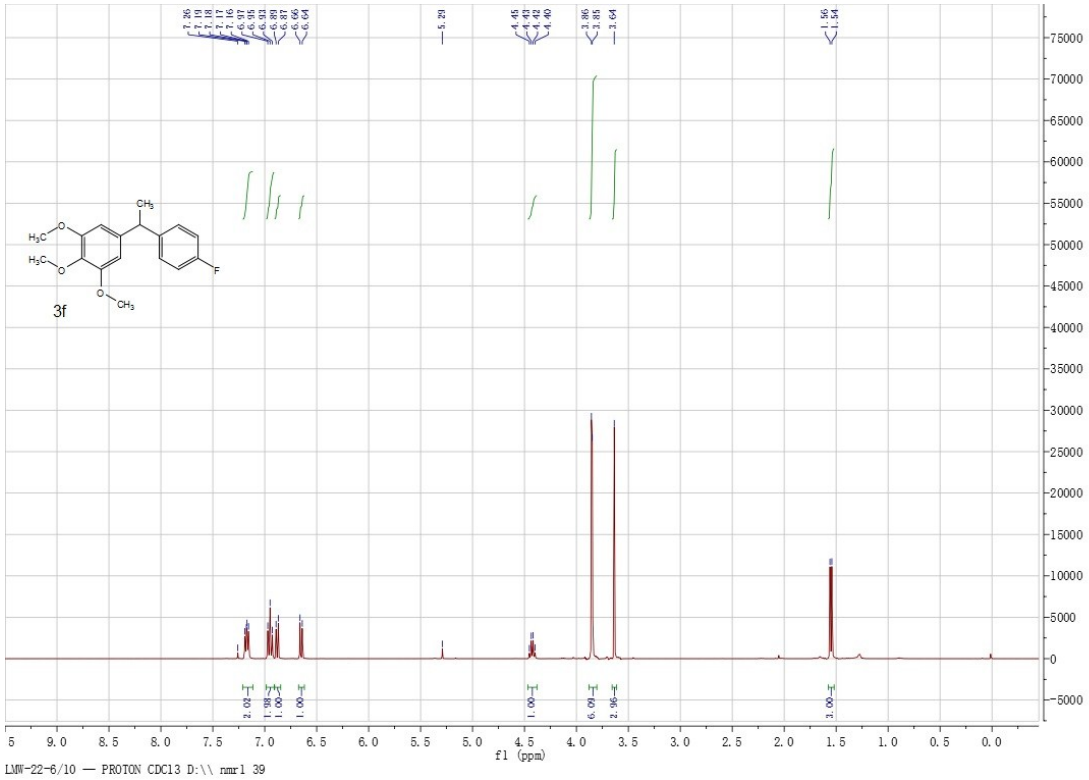
^{1}H NMR spectrum of **3e** recorded in $CDCl_3$



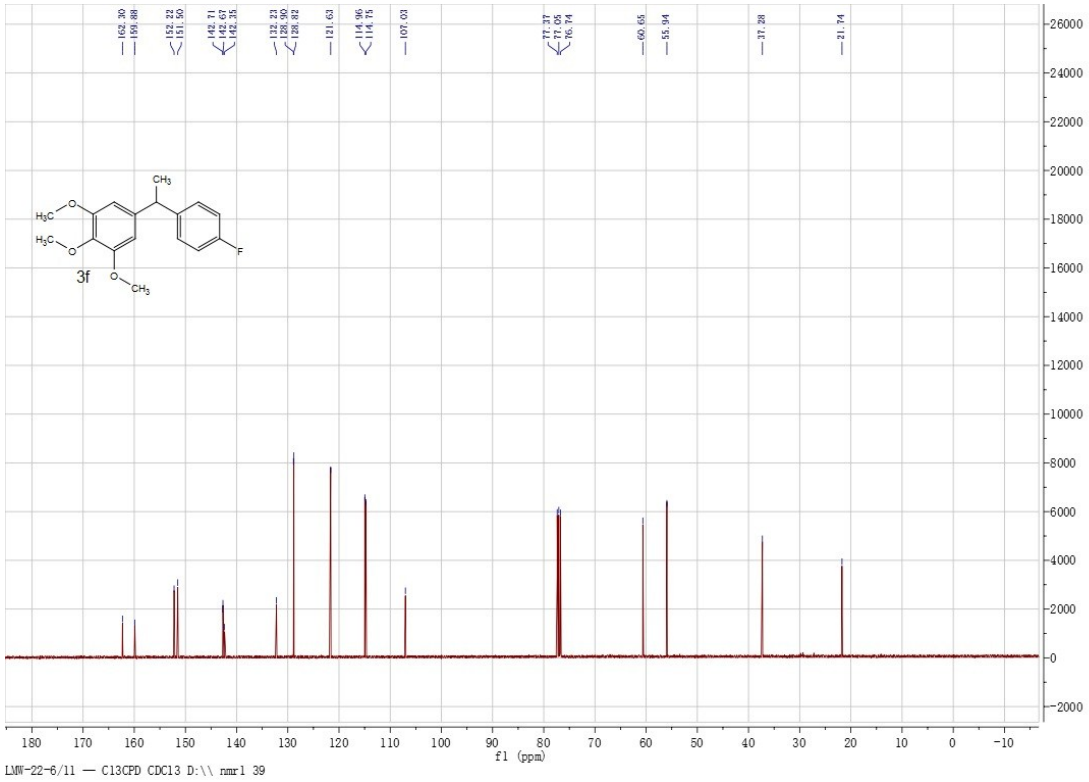
^{13}C NMR spectrum of **3e** recorded in $CDCl_3$



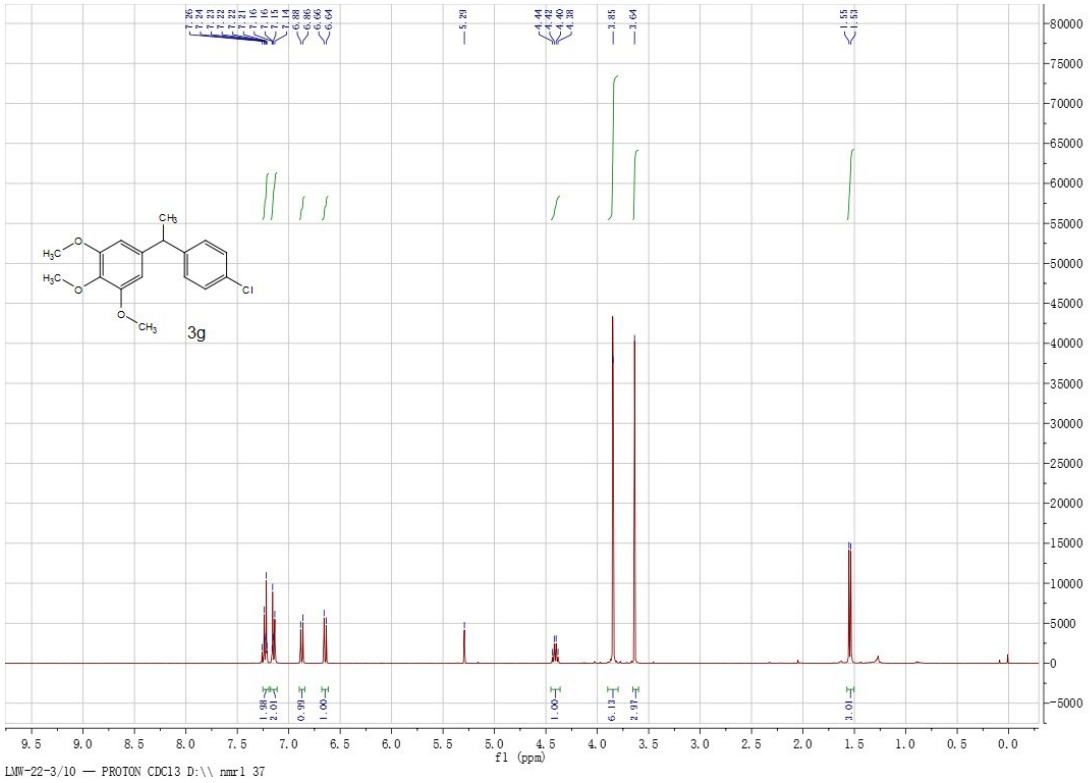
^{1}H NMR spectrum of **3f** recorded in $CDCl_3$



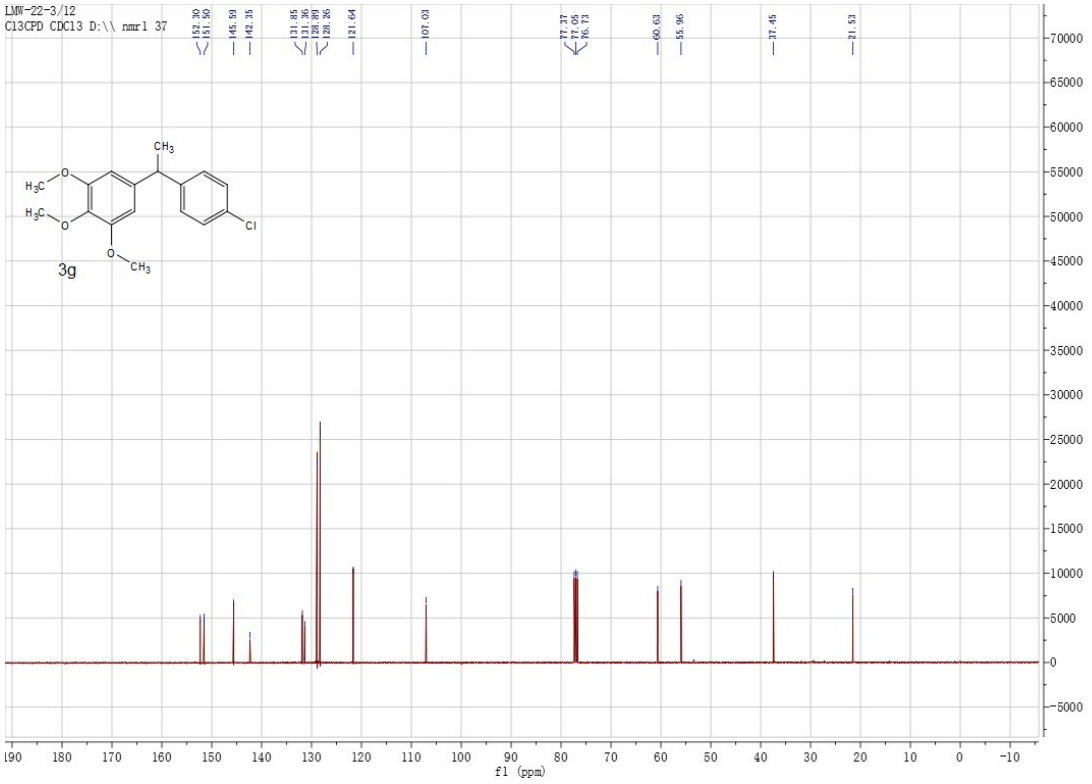
^{13}C NMR spectrum of **3f** recorded in $CDCl_3$



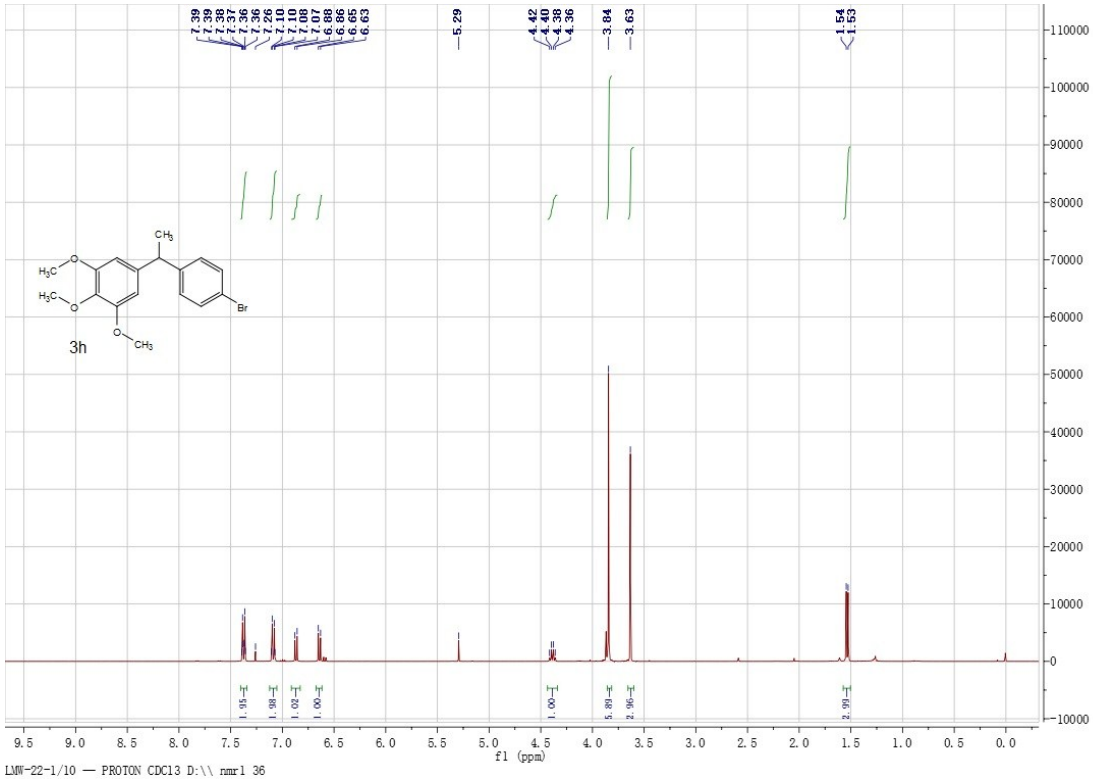
^{1}H NMR spectrum of **3g** recorded in $CDCl_3$



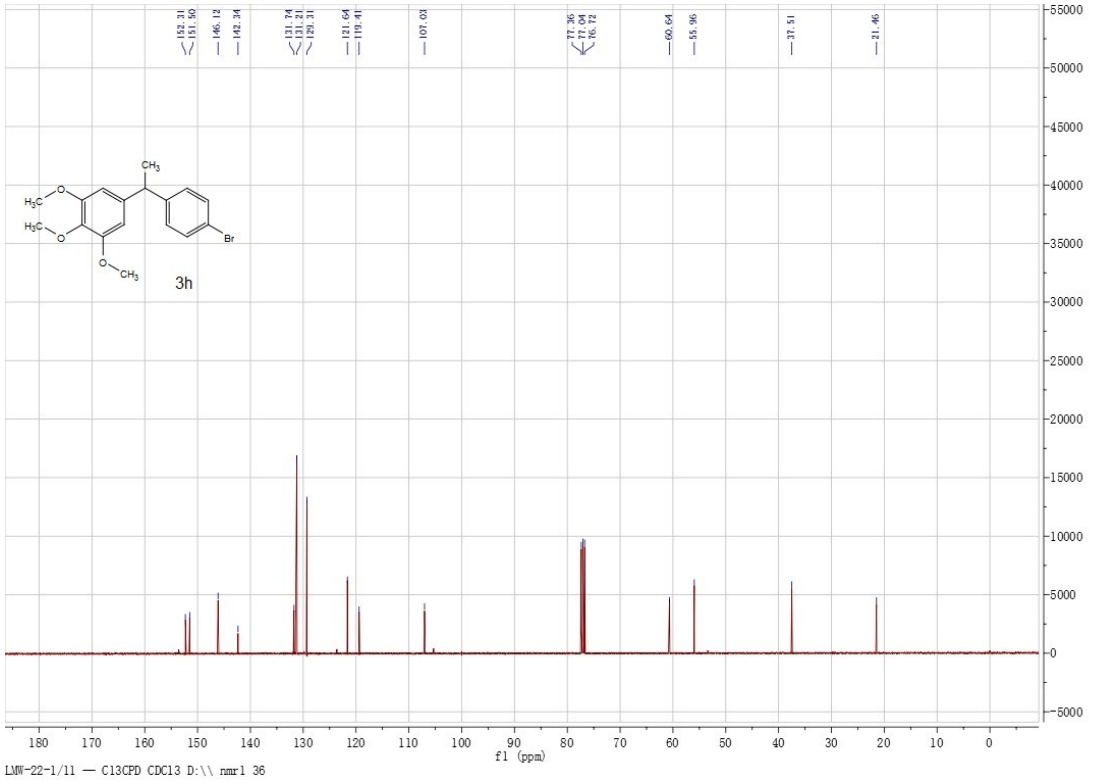
^{13}C NMR spectrum of **3g** recorded in $CDCl_3$



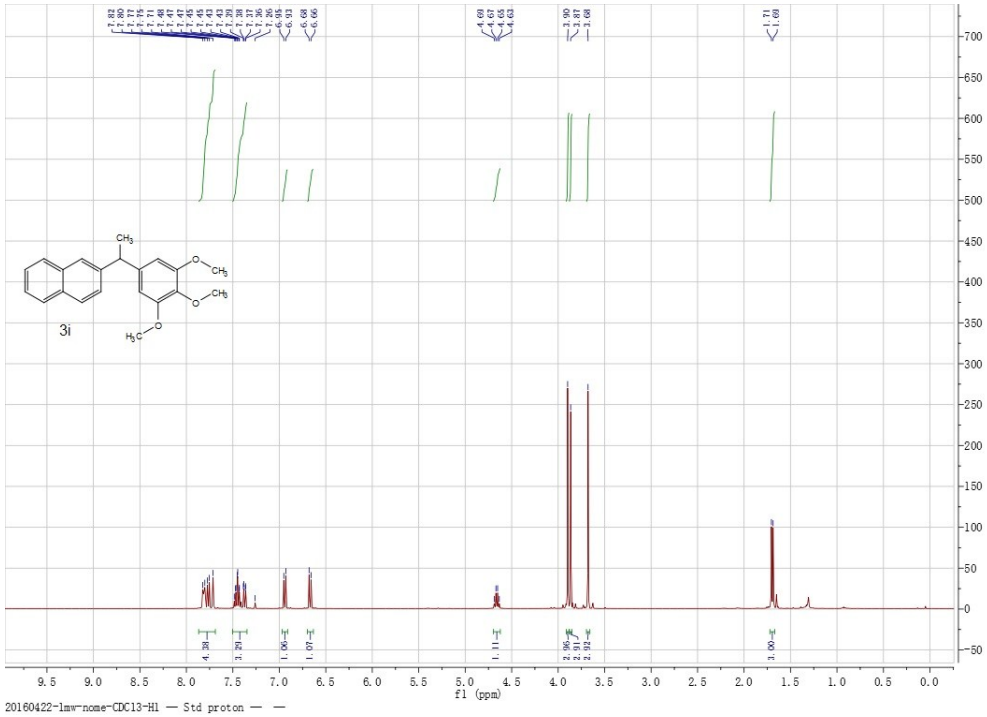
^{1}H NMR spectrum of **3h** recorded in $CDCl_3$



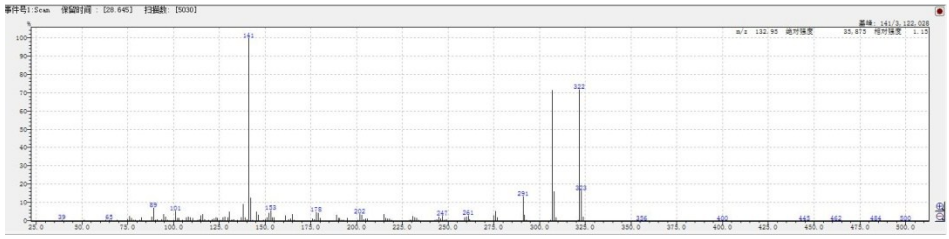
^{13}C NMR spectrum of **3h** recorded in $CDCl_3$



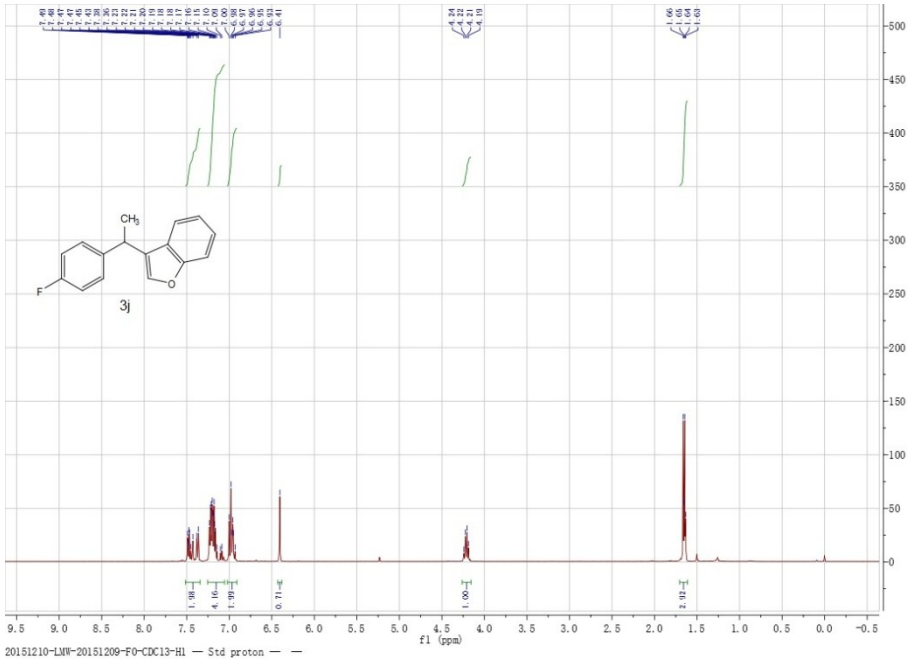
^{1}H NMR spectrum of **3i** recorded in $CDCl_3$



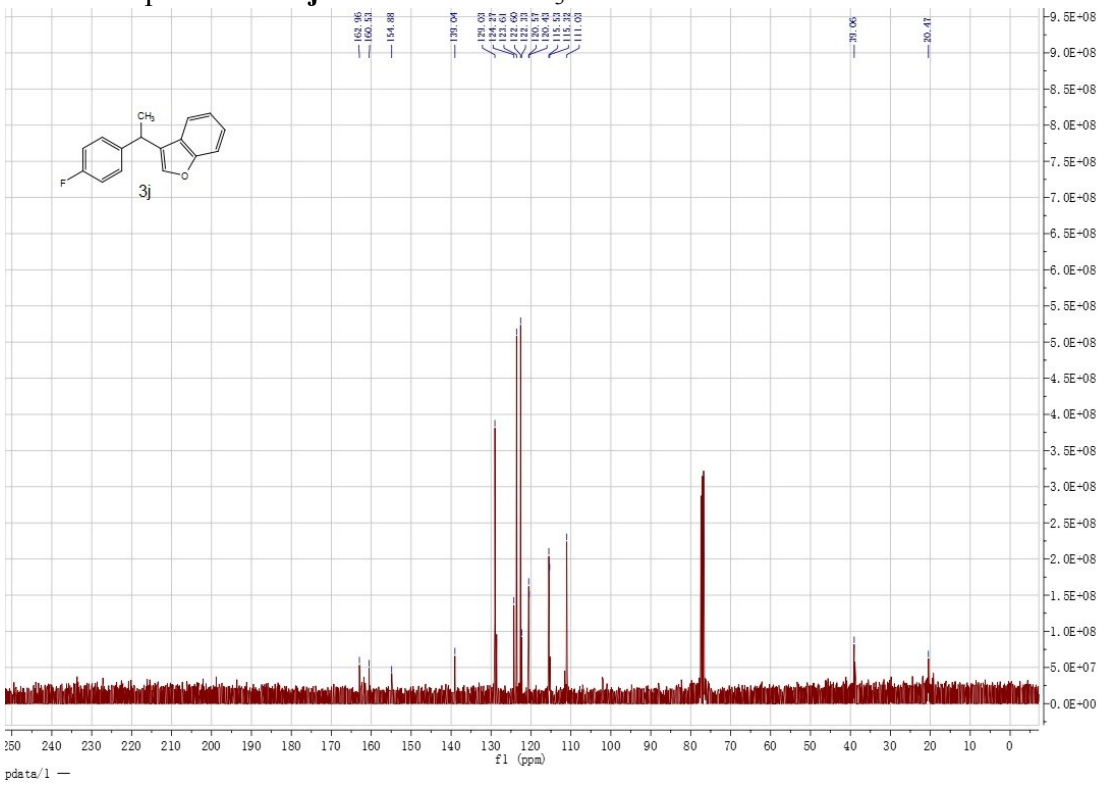
Low resolution mass spec for **3k**



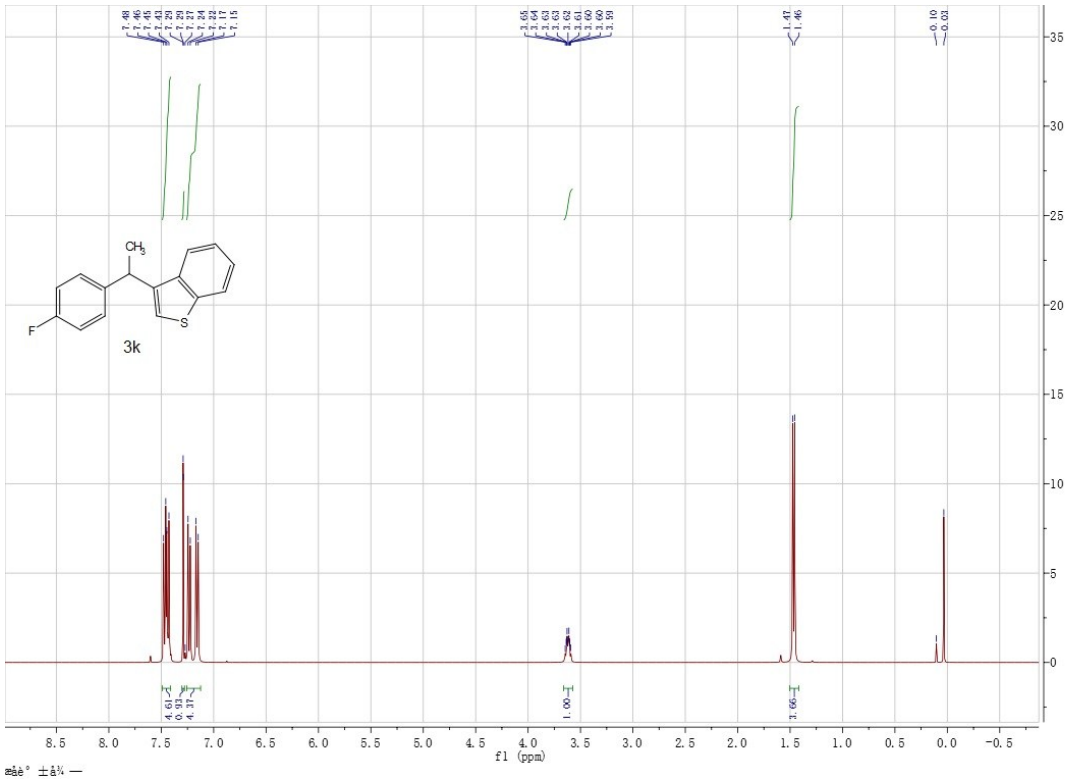
^{1}H NMR spectrum of **3j** recorded in $CDCl_3$



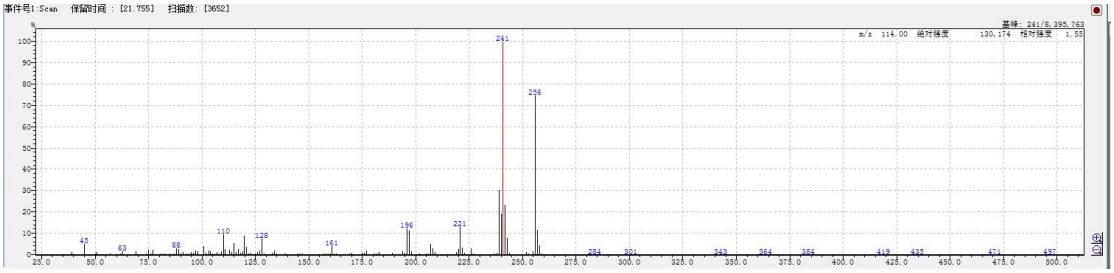
^{13}C NMR spectrum of **3j** recorded in $CDCl_3$



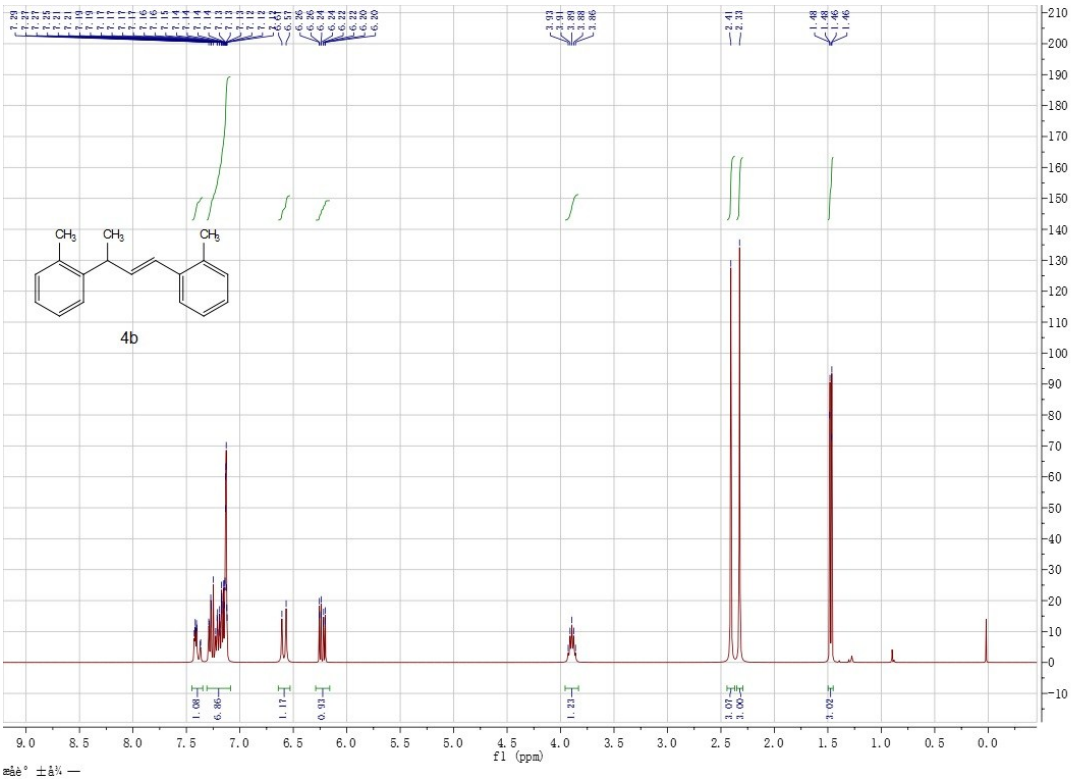
^{1}H NMR spectrum of **3k** recorded in $CDCl_3$



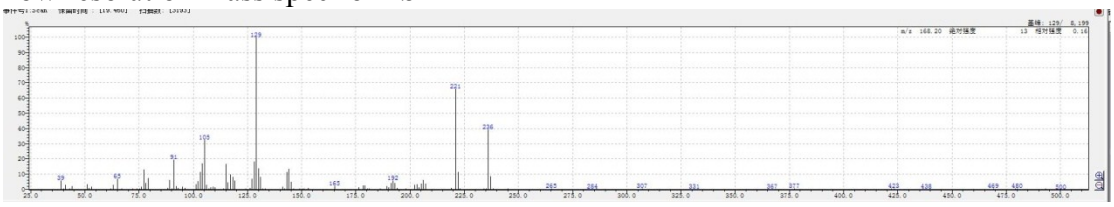
Low resolution mass spec for **3k**



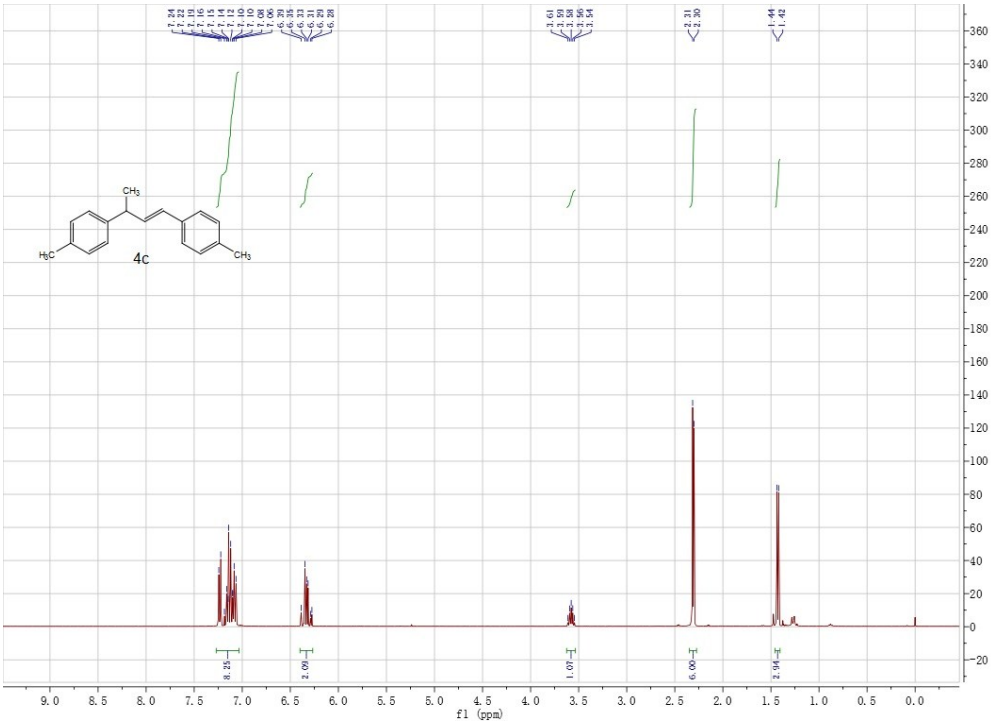
^{1}H NMR spectrum of **4b** recorded in $CDCl_3$



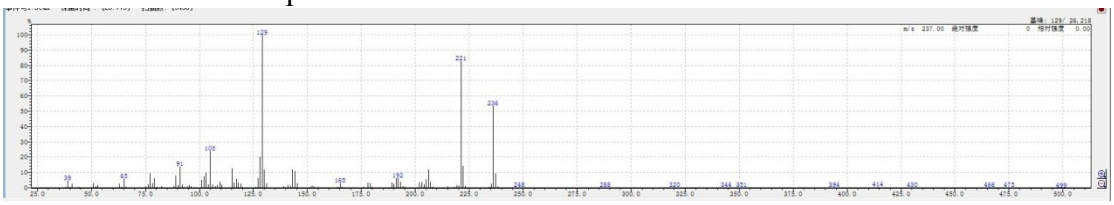
Low resolution mass spec for **4b**



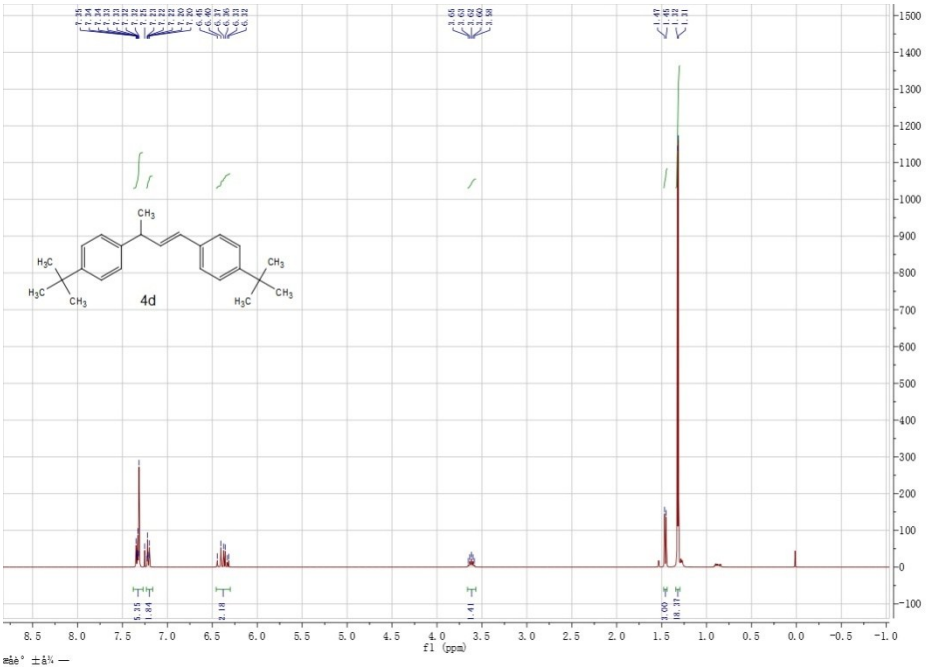
^{1}H NMR spectrum of **4c** recorded in $CDCl_3$



Low resolution mass spec for **4c**

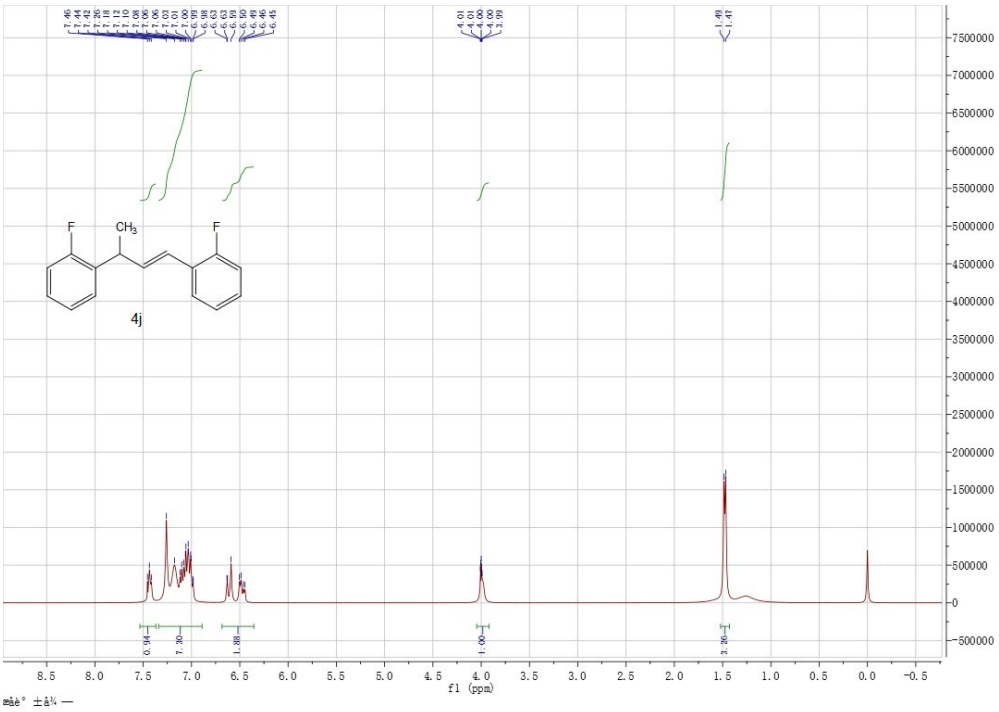


^{1}H NMR spectrum of **4d** recorded in $CDCl_3$

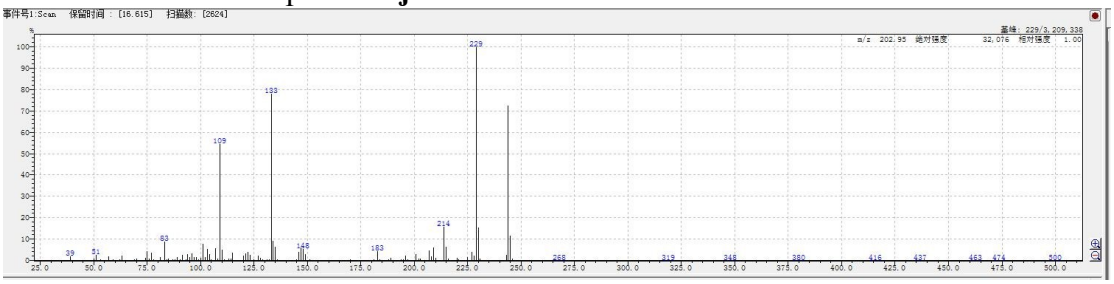


Low resolution mass spec for **4d**

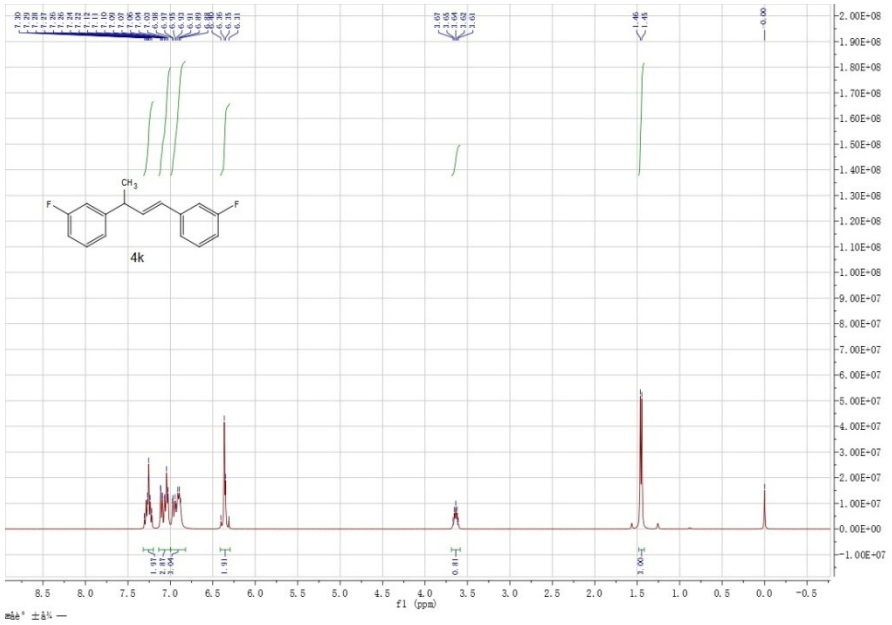
^{1}H NMR spectrum of **4j** recorded in $CDCl_3$



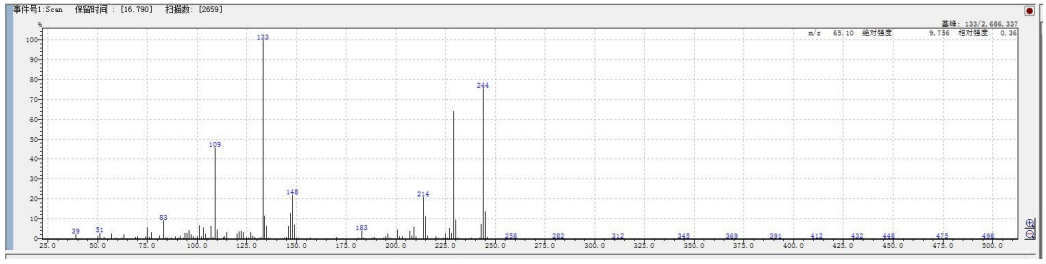
Low resolution mass spec for **4j**



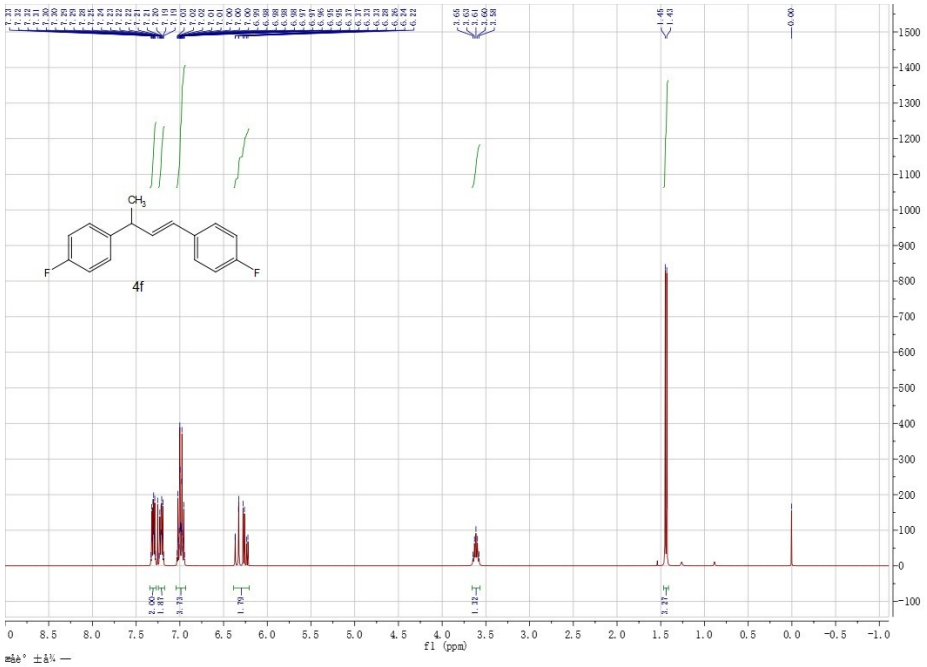
^{1}H NMR spectrum of **4k** recorded in $CDCl_3$



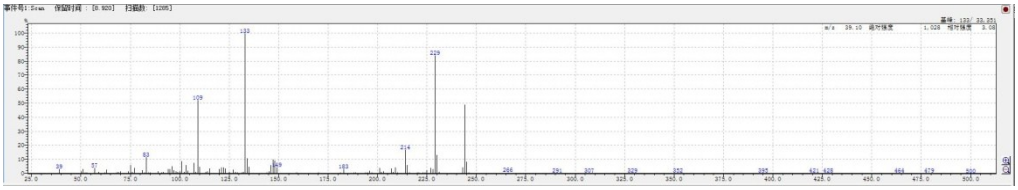
Low resolution mass spec for **4k**



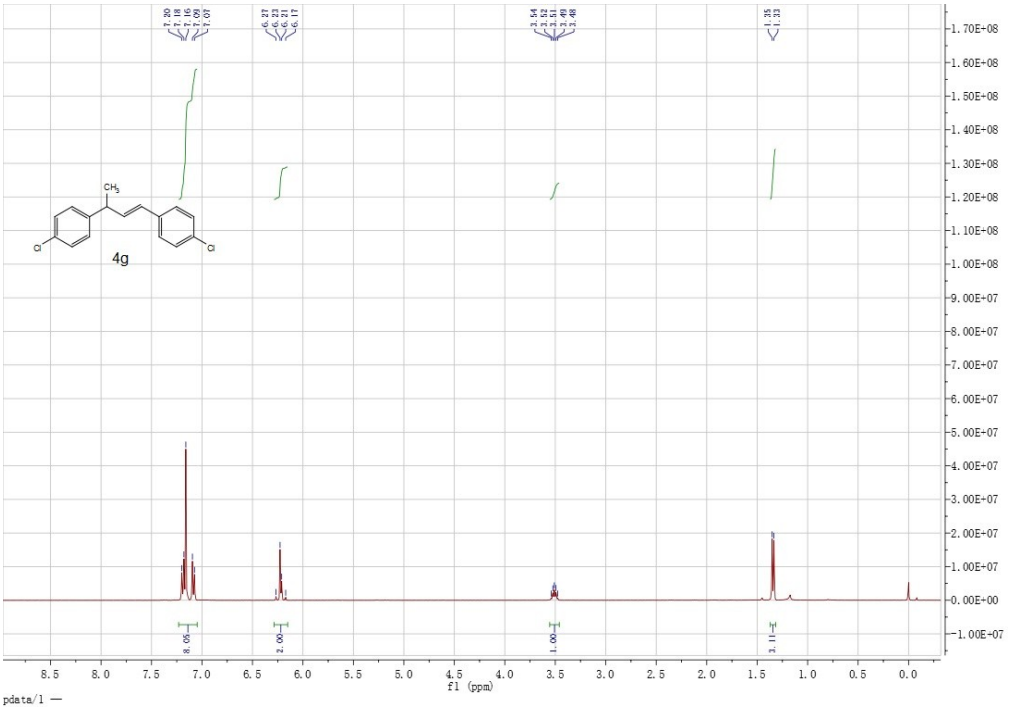
^{1}H NMR spectrum of **4f** recorded in $CDCl_3$



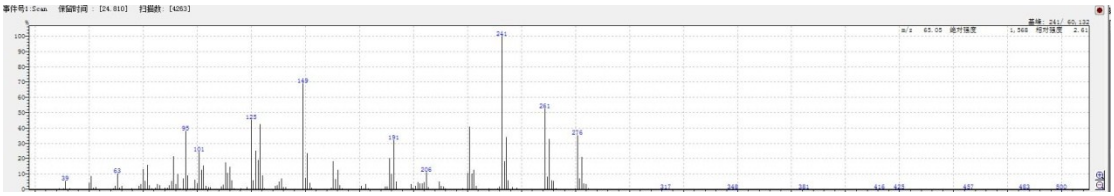
Low resolution mass spec for **4f**



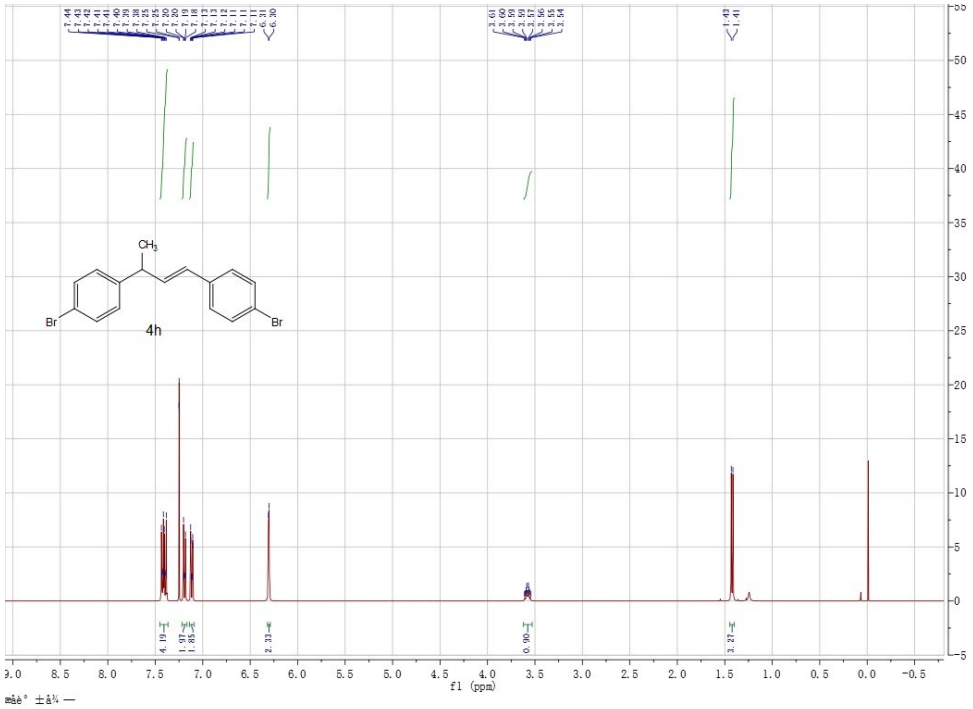
^{1}H NMR spectrum of **4g** recorded in $CDCl_3$



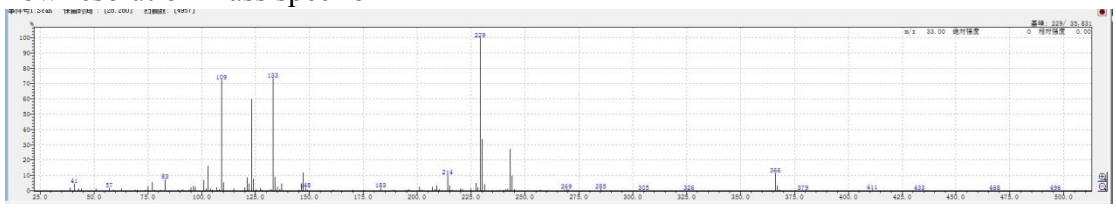
Low resolution mass spec for **4g**



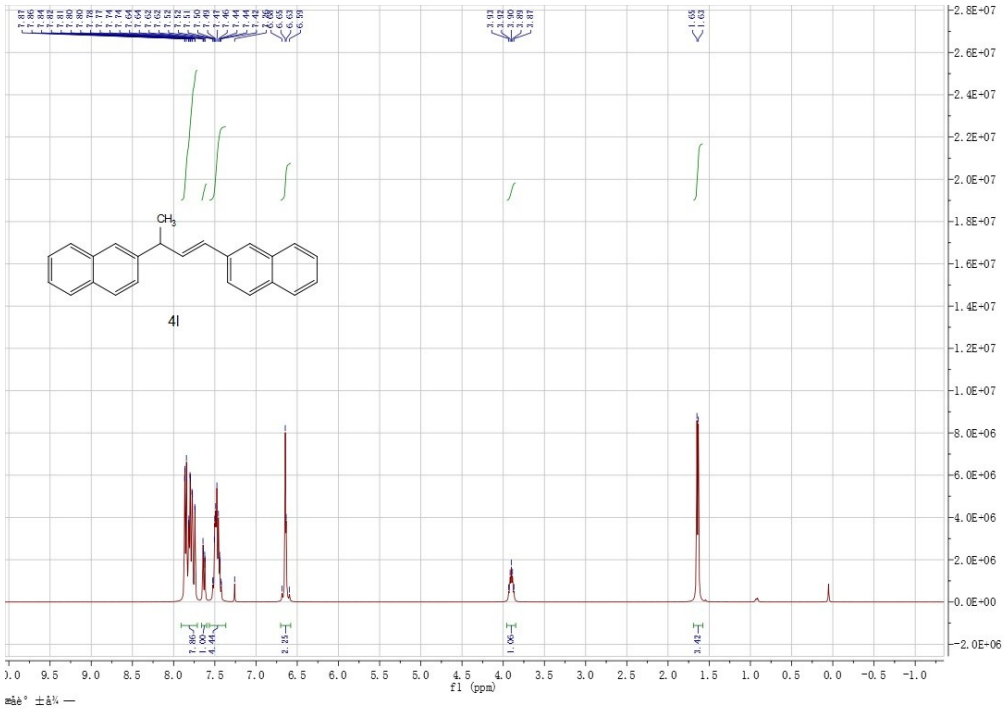
^{1}H NMR spectrum of **4h** recorded in $CDCl_3$



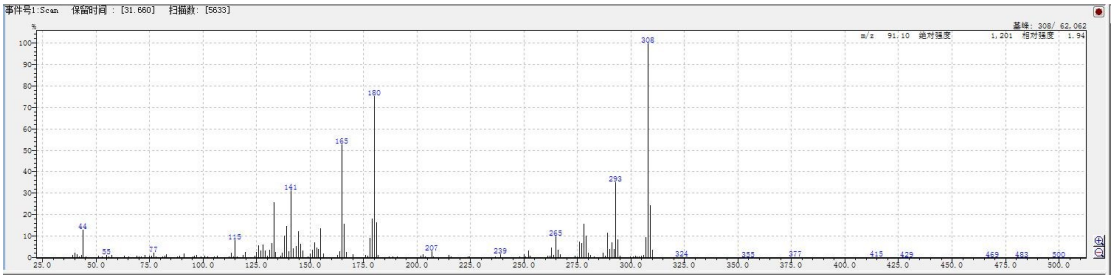
Low resolution mass spec for **4h**



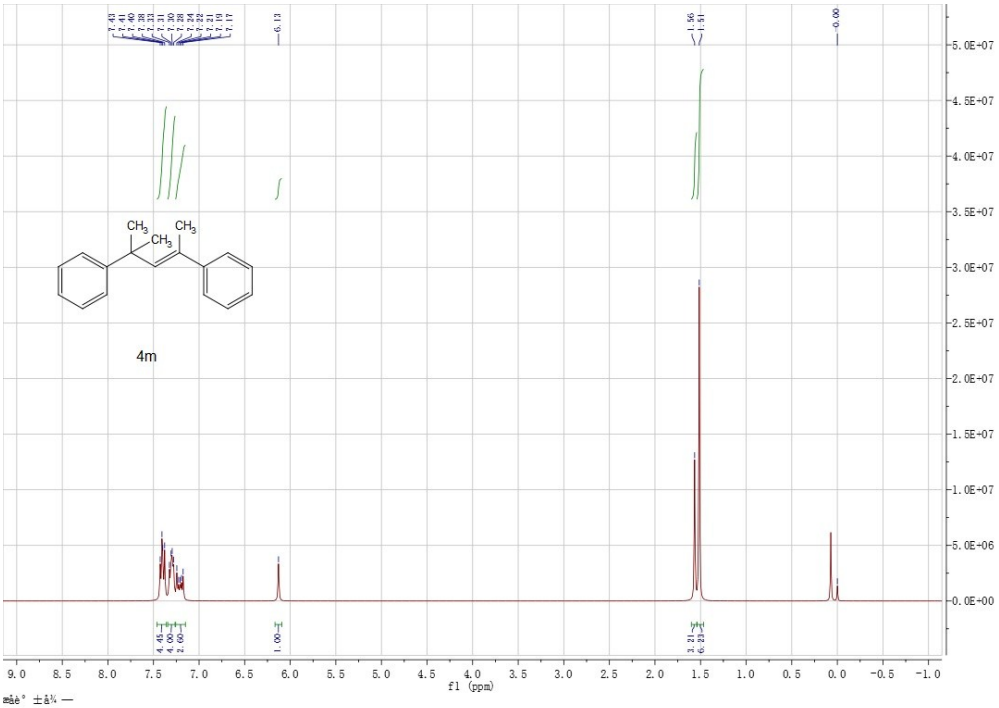
^{1}H NMR spectrum of **4l** recorded in $CDCl_3$



Low resolution mass spec for **4l**

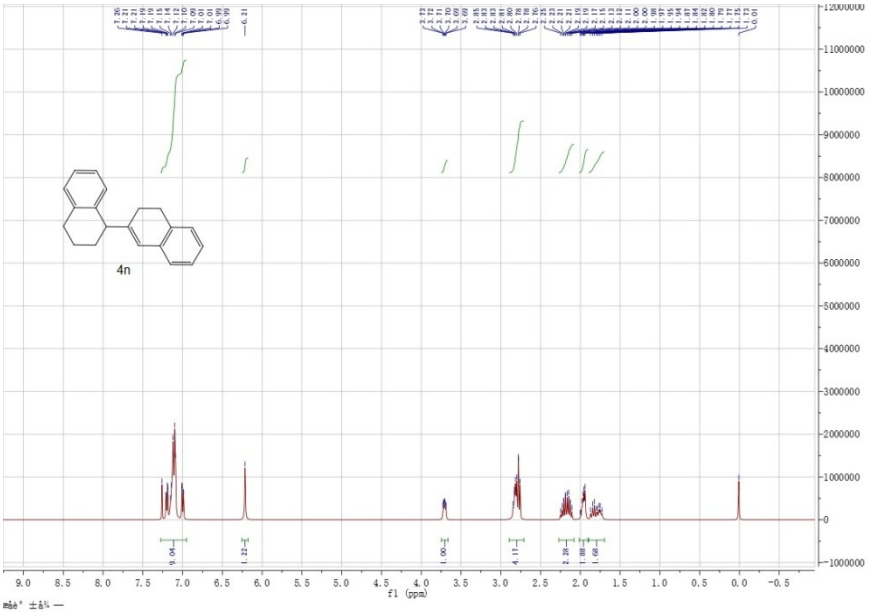


^{1}H NMR spectrum of **4m** recorded in $CDCl_3$

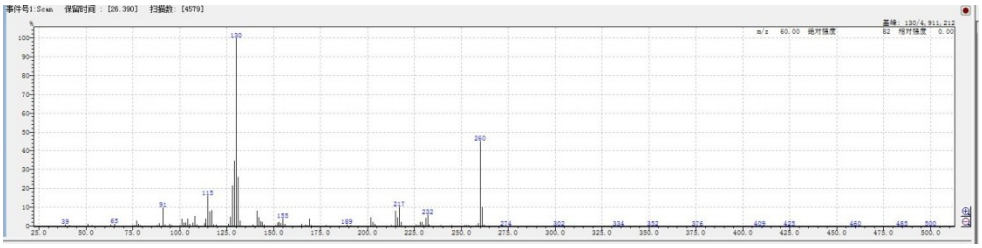


Low resolution mass spec for **4m**

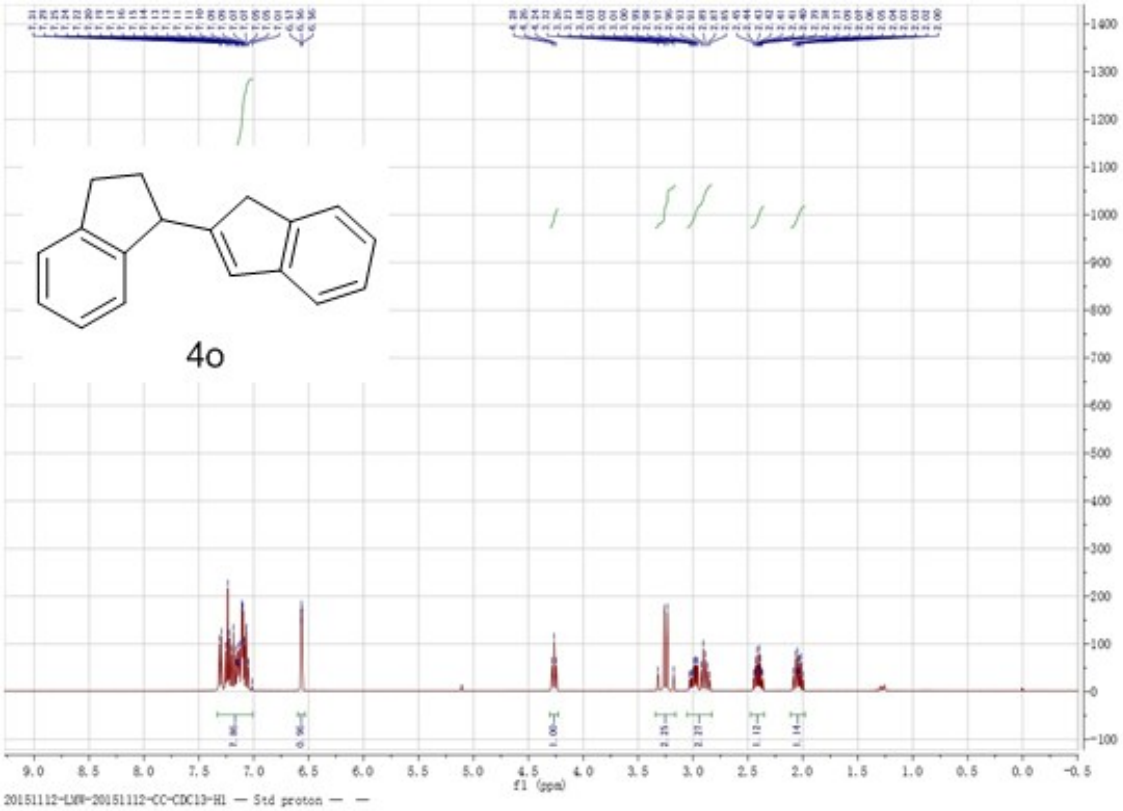
^{1}H NMR spectrum of **4n** recorded in $CDCl_3$



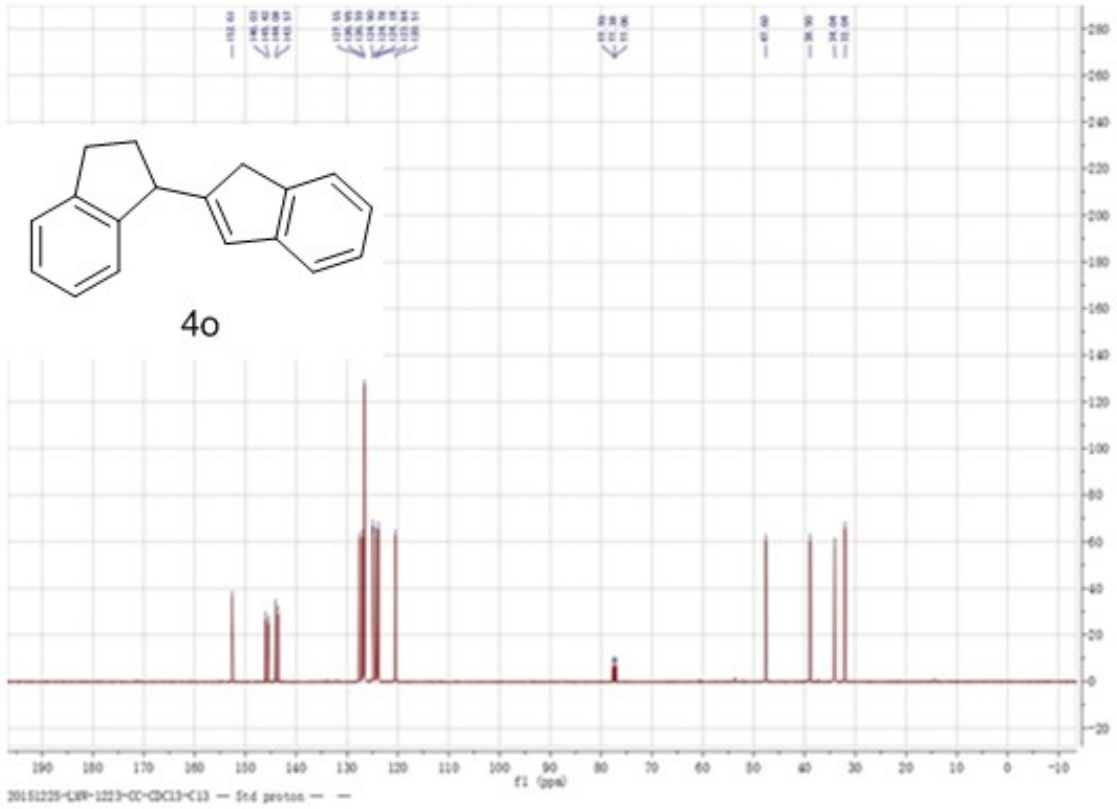
Low resolution mass spec for **4n**



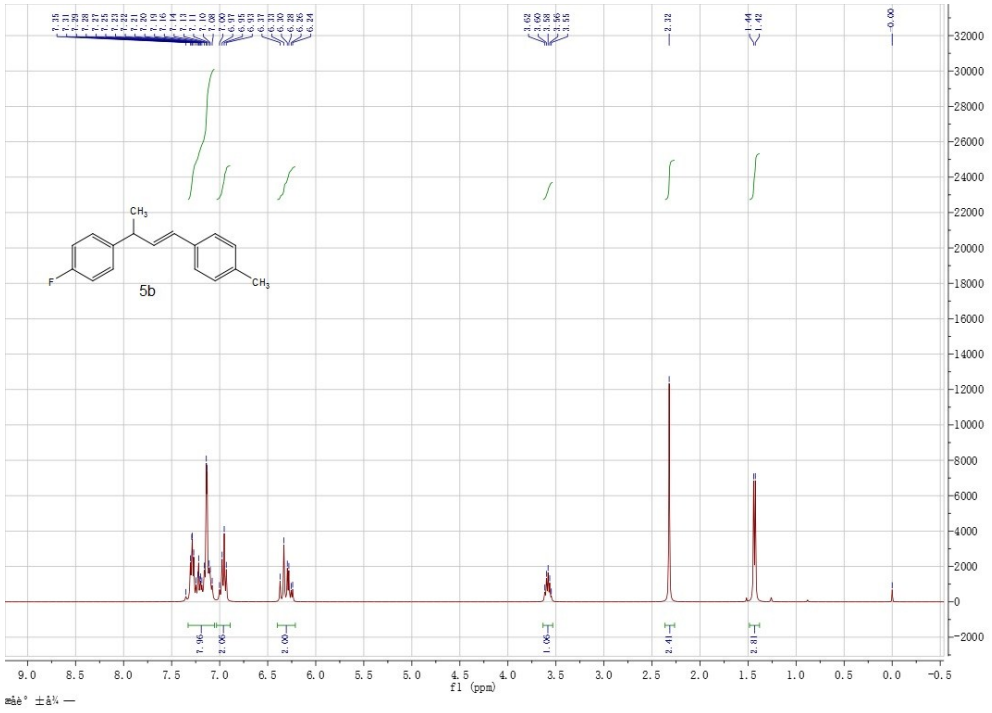
^{1}H NMR spectrum of **4o** recorded in $CDCl_3$



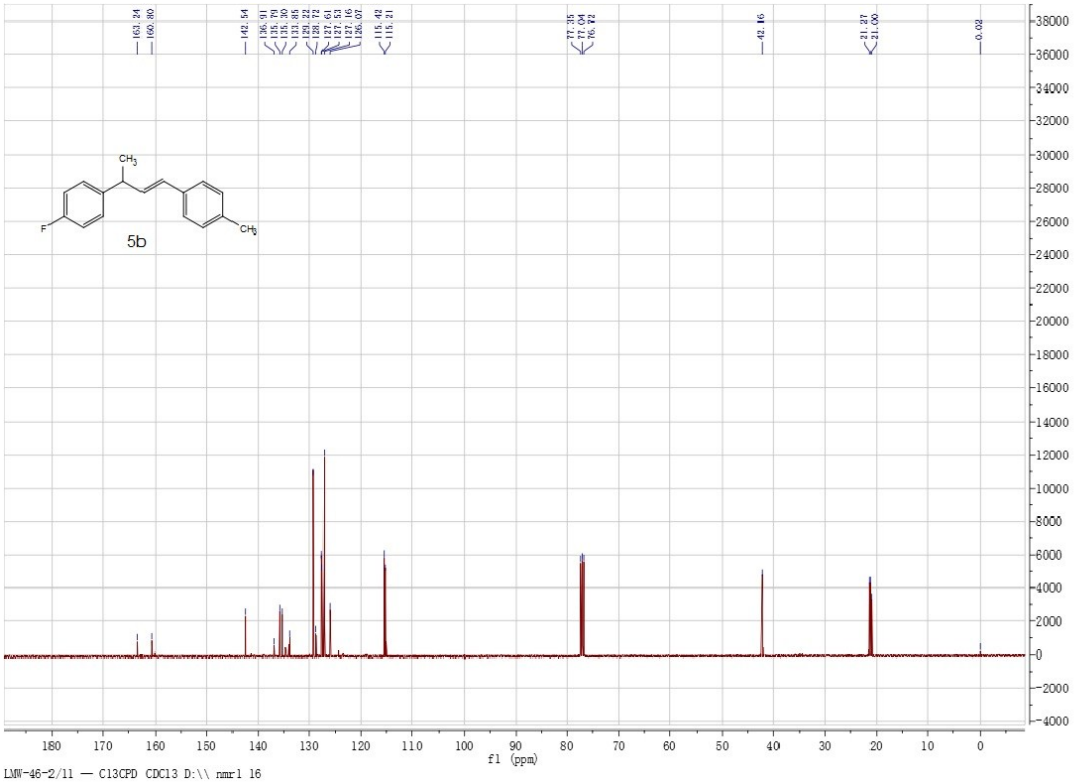
^{13}C NMR spectrum of **4o** recorded in $CDCl_3$



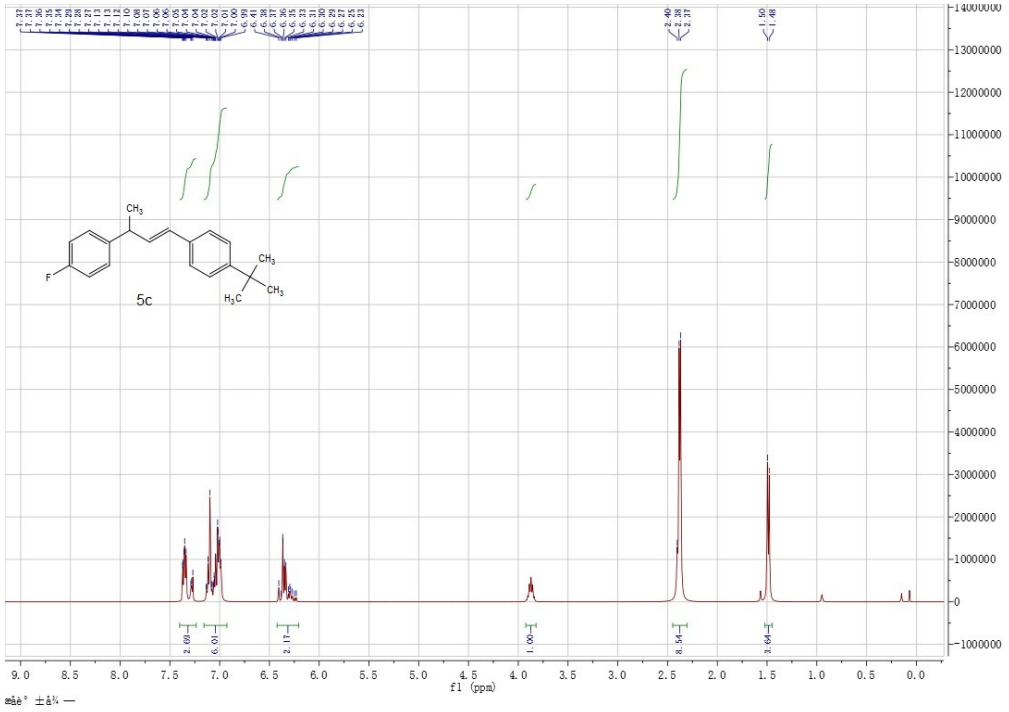
^{1}H NMR spectrum of **5b** recorded in $CDCl_3$



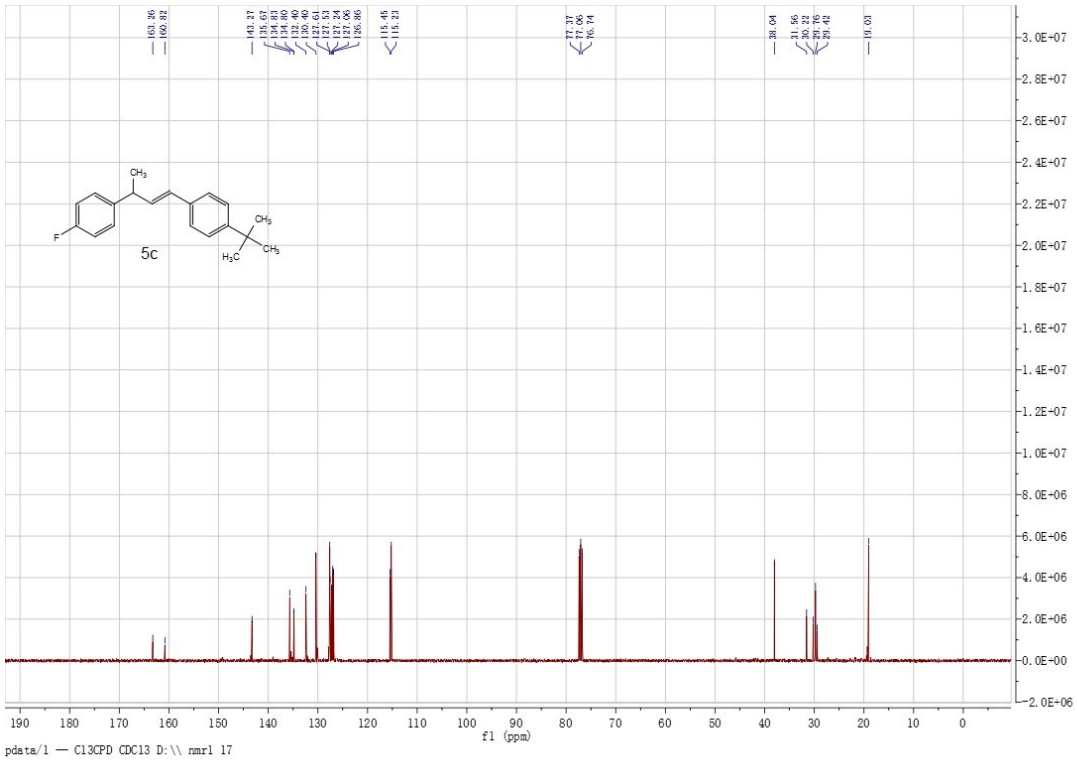
^{13}C NMR spectrum of **5b** recorded in $CDCl_3$



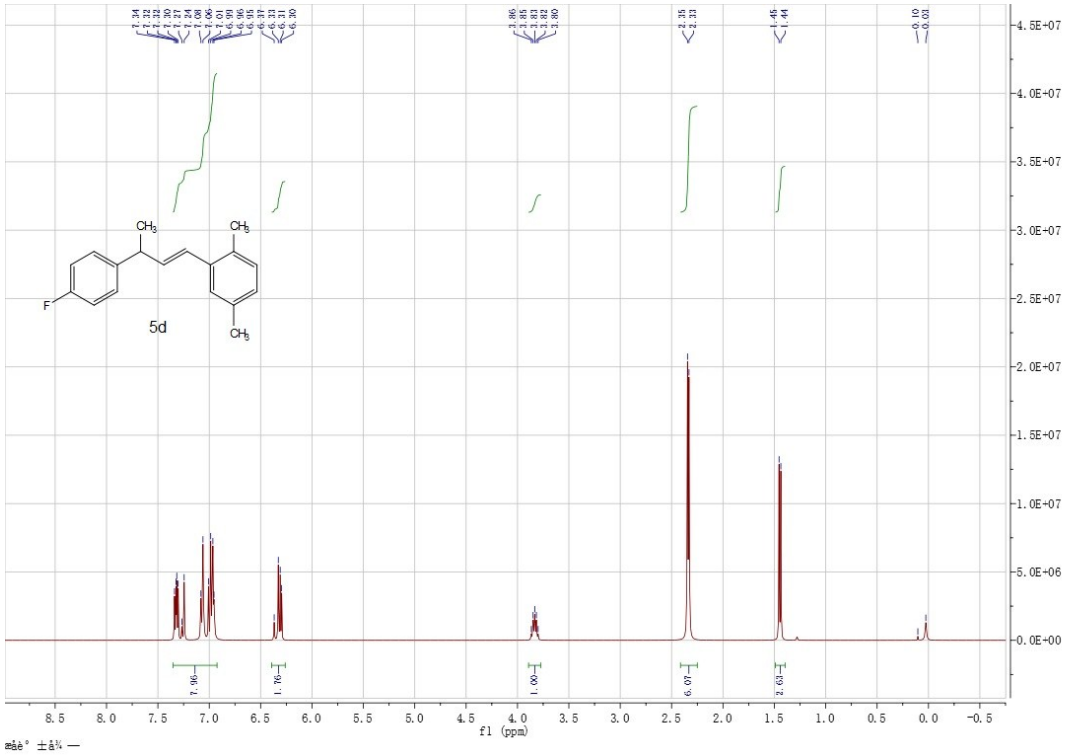
^{1}H NMR spectrum of **5c** recorded in $CDCl_3$



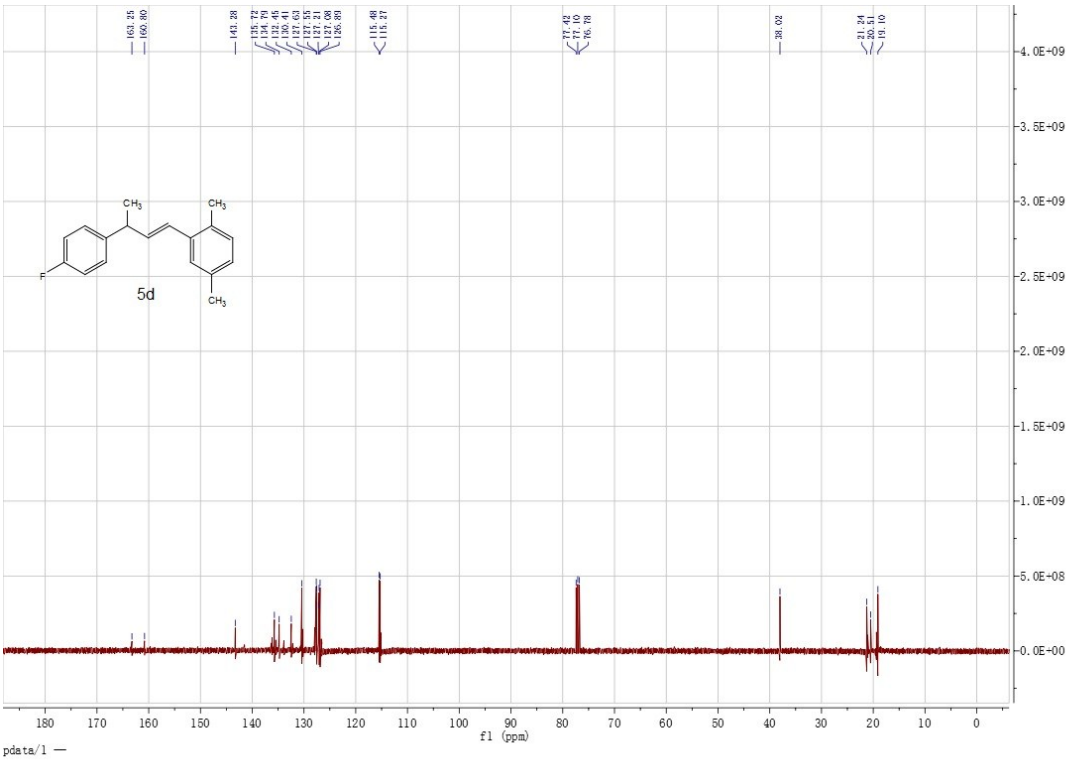
^{13}C NMR spectrum of **5c** recorded in $CDCl_3$



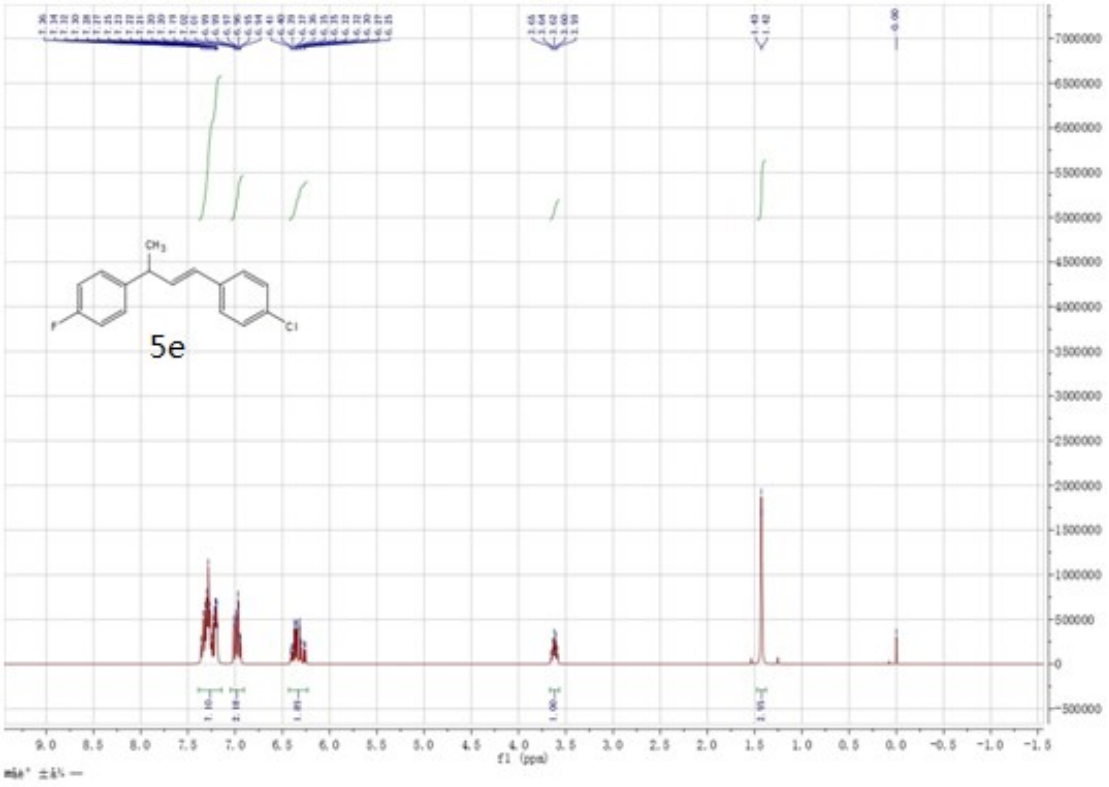
^{1}H NMR spectrum of **5d** recorded in $CDCl_3$



^{13}C NMR spectrum of **5d** recorded in $CDCl_3$



^{1}H NMR spectrum of **5e** recorded in $CDCl_3$



^{13}C NMR spectrum of **5e** recorded in $CDCl_3$