Supporting Information

Brønsted Acid-Promoted Ring-opening and Annulation of 2,3-Diaryl-2*H*-azirines and Thiobenzamide to Synthesize 2,4,5-Trisubstituted Thiazoles.

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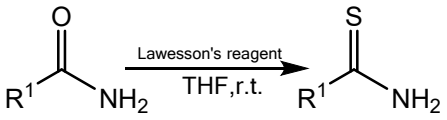
1. General information

^{1}H NMR, and ^{13}C NMR spectra were recorded on Mercury 400M in DMSO-d6. All ^{1}H NMR and ^{13}C NMR chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. Copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. Products were purified by flash chromatography on 200–300 mesh silica gels. All reactions were carried out in oven-dried glassware, unless otherwise noted. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

2. Experimental section

2.1 General procedure for the synthesis of 1k,1m,1n.



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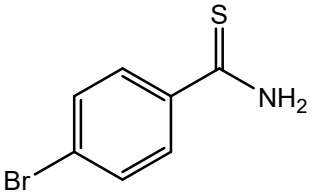
Substrates **1** were prepared according to reported method.[1] Add corresponding amide (10 mmol) and Lawesson's reagent (4.9 g, 12 mmol) to dry THF (150 mL). Stir the reaction mixture over night. Evaporate the solvent under reduced pressure. Add EtOAc (100 mL) and saturated $NaHCO_3$ (100 mL, aq) to the mixture. Combined organic phase was washed with saturated NaCl (aq) and dried over Na_2SO_4. Purify the crude product further by silica gel flash chromatography, using hexane/EtOAc, to obtain thiobenzamide 1.

4-bromobenzothioamide (1k)

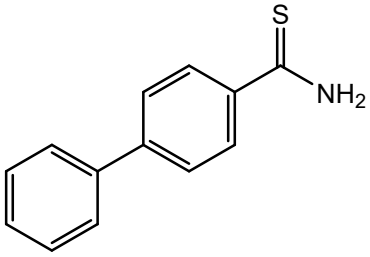


yellow solid.

^{1}H NMR (400 MHz, DMSO-d6): δ 9.93 (s, 1H), 9.55 (s, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.63 - 7.61 (m, 2H).

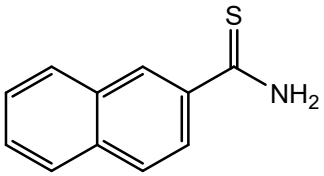
^{13}C NMR (101 MHz, DMSO-d6): δ 204.01, 143.73, 136.07, 134.55, 134.49, 130.17.

[1,1'-biphenyl]-4-carbothioamide (1m)



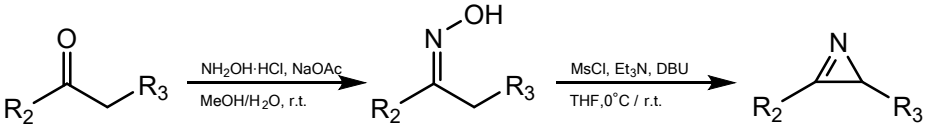
yellow solid.
^{1}H NMR (400 MHz, DMSO-d6): δ 9.90 (s, 1H), 9.55 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.3 Hz, 4H), 7.50 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-d6): δ 199.86, 143.14, 139.51, 138.55, 129.51, 128.57, 128.51, 127.29, 126.56.

naphthalene-2-carbothioamide (1n)



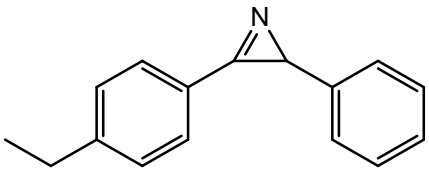
yellow solid.
^{1}H NMR (400 MHz, DMSO-d6): δ 9.99 (s, 1H), 9.67 (s, 1H), 8.45 (d, J = 1.3 Hz, 1H), 8.06-8.01 (m, 2H), 7.97-7.93 (m, 2H), 7.65-7.54 (m, 2H).
^{13}C NMR (101 MHz, DMSO-d6): δ 200.52, 137.22, 134.47, 132.28, 129.57, 128.17, 128.01, 127.80, 127.31, 127.11, 125.57.

2.2 General procedure for the synthesis of 2a-2m.



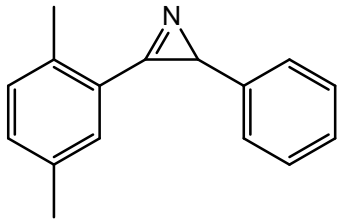
Substrates **2** were prepared according to reported method.[2] A solution of ketone (1 eq), $NH_2OH{\cdot}HCl$ (1.5 eq) and sodium acetate (1.5 eq) in a mixture solvent of MeOH/H_2O (20:1) was stirred at room temperature. When the reaction completed (indicated by TLC), the solvent was removed in vacuo and extracted by DCM. The combined organic phase was washed with sat. $NaHCO_3$(aq.), brine sequentially, and then dried over anhydrous Na_2SO_4. After removing the solvent, the crude oxime was used directly for the next step.
To a solution of the crude oxime (1 eq) in dry THF was added triethylamine (1.5 eq) and methanesulfonyl chloride (1.5 eq) sequentially at room temperature or 0°C. The solution got cloudy after the addition of methanesulfonyl chloride. The resulting mixture was stirred for 30 min, and DBU (1.5 eq) was then added over 10 min. After stirred for additional 30 min, the reaction mixture was passed through a pad of silica gel, washing with EtOAc. The mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel to give the 2*H*-azirine.

3-(4-ethylphenyl)-2-phenyl-2*H*-azirine (2d)



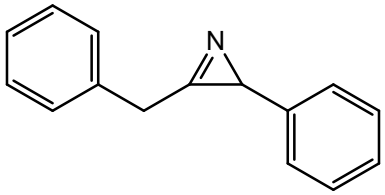
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J= 8.0 Hz, 2H), 7.37 (d, J= 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 7.15 (d, J= 6.8 Hz, 2H), 3.29 (s, 1H), 2.74 (q, J= 7.6 Hz, 2H), 1.28 (t, J= 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 150.2, 141.0, 130.0, 128.8, 128.2, 126.9, 126.0, 121.4, 34.2, 29.1, 15.2.
HRMS (ESI) calcd for $C_{16}H_{15}NH^+$: $[M+H]^+$ 222.1277, found: 222.1275.

3-(2,5-dimethylphenyl)-2-phenyl-2*H*-azirine (2e)



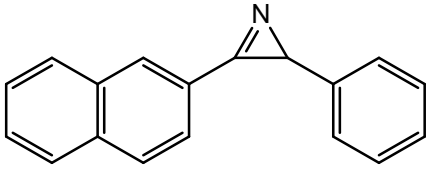
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.30-7.23 (m, 5H), 7.14 (d, J= 7.6 Hz, 2H), 3.20 (s, 1H), 2.64 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 141.4, 138.1, 135.9, 133.6, 132.1, 130.9, 128.2, 126.8, 125.9, 122.1, 32.7, 20.6, 19.4.
HRMS (ESI) calcd for $C_{16}H_{15}NH^+$: $[M+H]^+$ 222.1277, found: 222.1273.

3-benzyl-2-phenyl-2*H*-azirine (2f)



Yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.22 (m, 8H) , 7.05-7.03 (m, 2H) , 4.17 (dd, J1 = 35.2 Hz, J2 = 17.2 Hz, 2H) , 2.98 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 140.9, 132.7, 129.0, 128.9, 128.2, 127.5, 126.9, 125.7, 34.1, 33.4.
HRMS (ESI) calcd for $C_{15}H_{13}NH^+$: $[M+H]^+$ 208.1121, found: 208.1120.

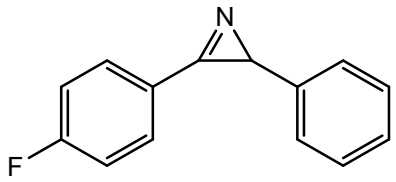
3-(naphthalen-2-yl)-2-phenyl-2*H*-azirine (2g)



White solid.

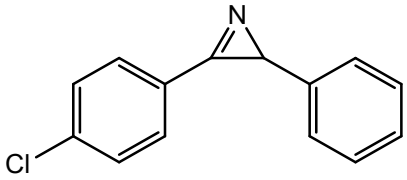
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.05 (d, J= 8.4 Hz, 1H), 8.00 (d, J= 8.4 Hz, 1H), 7.90 (d, J= 8.0 Hz, 2H), 7.61 (t, J= 7.2 Hz, 1H), 7.55 (t, J= 7.6 Hz, 1H), 7.30-7.24 (m, 3H), 7.21-7.19 (m, 2H), 3.41 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.4, 140.8, 135.5, 132.8, 132.1, 129.3, 129.0, 128.6, 128.3, 128.0, 127.1, 127.1, 126.1, 124.5, 121.3, 34.6.
HRMS (ESI) calcd for $C_{18}H_{13}NH^+$: $[M+H]^+$ 244.1121, found: 244.1123.

3-(4-fluorophenyl)-2-phenyl-2*H*-azirine (2h)



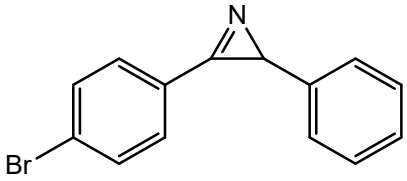
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, J= 5.6, 8.8 Hz, 2H), 7.30-7.22 (m, 5H), 7.14 (dd, J= 1.6, 8.0 Hz, 2H), 3.33 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.91, 164.37, 162.51, 140.64, 132.31, 132.21, 128.38, 127.23, 126.11, 116.90, 116.68, 34.60.
HRMS (ESI) calcd for $C_{14}H_{10}FNH^+$: $[M+H]^+$ 212.0870, found: 212.0869.

3-(4-chlorophenyl)-2-phenyl-2*H*-azirine (2i)



Yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.4 Hz, 2H) , 7.44 (d, J = 8.4 Hz, 2H) , 7.22-7.14 (m, 3H) , 7.06-7.04 (m, 2H) , 3.25 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 140.4, 139.5, 131.0, 129.7, 128.3, 127.2, 126.0, 122.6, 34.6.
HRMS (ESI) calcd for $C_{14}H_{10}ClNH^+$: $[M+H]^+$ 228.0575, found: 228.0573.

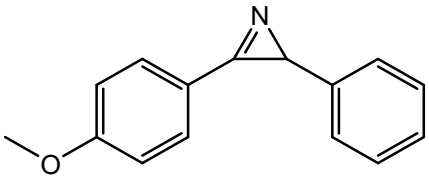
3-(4-bromophenyl)-2-phenyl-2*H*-azirine (2j)



Colorless oil
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J= 8.0 Hz, 2H), 7.70 (d, J= 8.0 Hz, 2H), 7.29-7.25 (m, 3H), 7.13 (d, J= 7.2 Hz, 2H), 3.34 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.0, 140.3, 132.7, 131.1, 128.3, 128.1, 127.2, 126.0, 122.9, 34.6.

HRMS (ESI) calcd for $C_{14}H_{10}BrNH^+$: $[M+H]^+$ 272.0069, found: 272.0067.

3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine (2k)



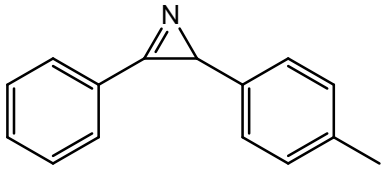
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J= 8.8 Hz, 2H), 7.27-7.22 (m, 3H), 7.15-7.13 (m, 2H), 7.04 (d, J= 8.4 Hz, 2H), 3.88 (s, 3H), 3.27 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.4, 162.0, 141.2, 131.8, 128.2, 126.8, 126.0, 116.3, 114.7, 55.5, 34.0.

HRMS (ESI) calcd for $C_{15}H_{13}NOH^+$: $[M+H]^+$ 224.1070, found: 224.1072.

3-phenyl-2-(p-tolyl)-2*H*-azirine (2l)



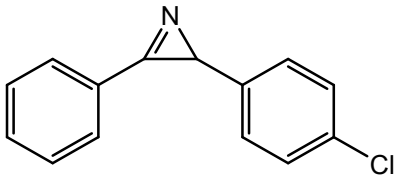
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.59-7.51 (m, 3H), 7.10-7.03 (m, 4H),3.30 (s, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.7, 137.8, 136.7, 133.0, 129.8, 129.2, 128.9, 126.0, 124.2, 34.3, 21.1.

HRMS (ESI) calcd for $C_{15}H_{13}NH^+$: $[M+H]^+$ 208.1121,found: 208.1119.

2-(4-chlorophenyl)-3-phenyl-2*H*-azirine (2m)



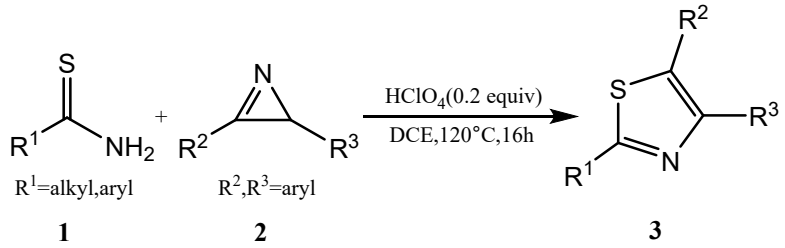
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J= 6.8 Hz, 2H), 7.61-7.53 (m, 3H), 7.24 (d, J= 8.0 Hz, 2H), 7.07 (d, J= 8.0 Hz, 2H), 3.29 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.2, 139.4, 133.3, 132.7, 129.9, 129.3, 128.4, 127.3, 123.6, 33.7.

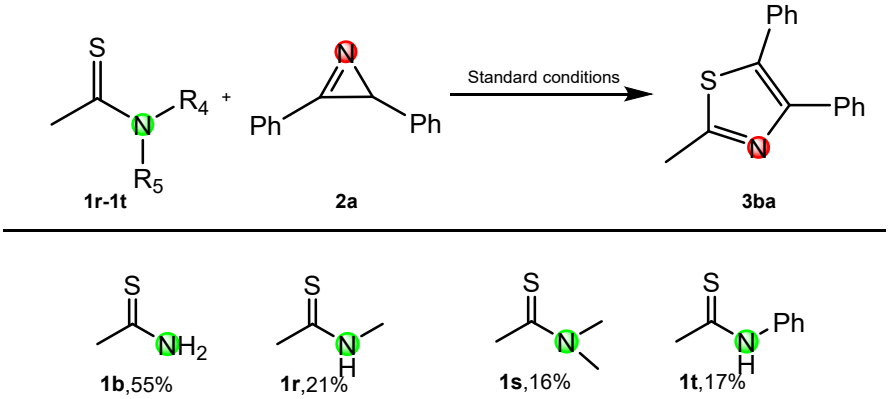
HRMS (ESI) calcd for $C_{14}H_{10}ClNH^+$: $[M+H]^+$ 228.0575,found: 228.0572.

2.3 General procedure for the synthesis of product 3



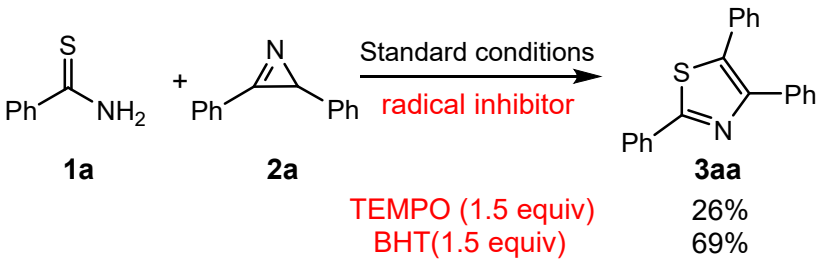
To a 15 mL sealed tube containing a magnetic stir bar were added thioamide (**1**, 0.3 mmol, 1.5 equiv.), 2*H*-azirine (**2**, 0.2 mmol, 1.0 equiv.). $HClO_4$ (2.3 μL, 0.04 mmol, 0.2 equiv.) was washed down by 1,2-dichloroethane (DCE, 2.0 mL) and the substrates were dissolved. After stirred for 16 h at 120 °C, the mixture was concentrated under reduced pressure and purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate (v/v) = 100:1) to afford product **3**.

2.4 Trace the nitrogen atom.



Under the standard conditions, add **2a** (0.2 mmol) and different thioamide **1r-1t** (0.3 mmol) to DCE (2mL). After the reaction, we got the same trithiazole as **3ba**, while there weren't new products.

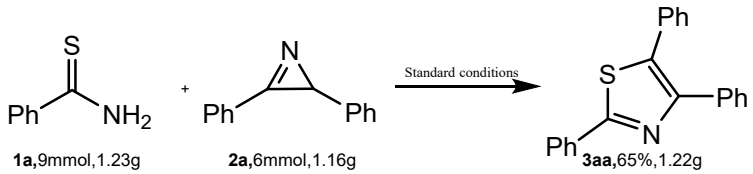
2.5 Mechanism study



To a 15 mL sealed tube containing a magnetic stir bar were added benzothioamide (**1a**, 0.3 mmol, 1.5 equiv.), 2,3-diphenyl-2*H*-azirine (**2a**, 0.2 mmol, 1.0 equiv.), radical inhibitor (1.5 equiv.). $HClO_4$ (2.3 μL, 0.04 mmol, 0.2 equiv.) was washed down by 1,2-dichloroethane (DCE, 2.0 mL) and the substrates were dissolved. After stirred for 16 h

at 120 °C, the mixture was concentrated under reduced pressure and purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate (v/v) = 100:1) to afford product **3aa**. The products were obtained with yields of 26% and 69% respectively.

2.6 Gram-scale reaction

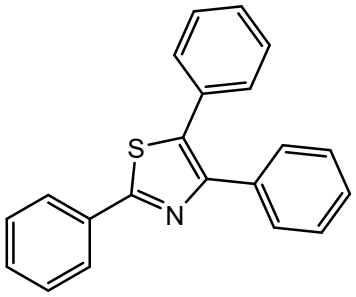


A gram-scale reaction was carried out by using thiobenzamide **1a** (9 mmol) and 2*H*-azirine **2a** (6 mmol) under the standard conditions, the corresponding product **3aa** was produced in 65% yield.

1. A. S. Mayhoub, L. Marler, T. P. Kondratyuk, E. J. Park, J. M. Pezzuto and M. Cushman, *Bioorg Med Chem*, 2012, **20**, 510-520.
2. J. Xuan, X. D. Xia, T. T. Zeng, Z. J. Feng, J. R. Chen, L. Q. Lu and W. J. Xiao, *Angew Chem Int Ed Engl*, 2014, **53**, 5653-5656.

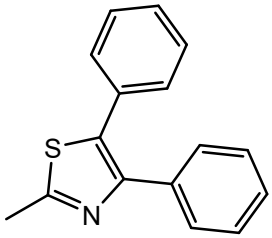
3. Characterization data of products

2,4,5-triphenylthiazole (3aa)



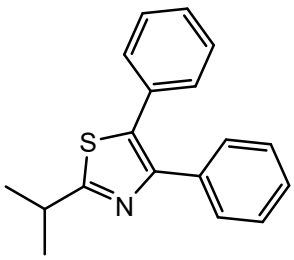
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 77% yield;
M.p. = 92-93°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.04 – 7.93 (m, 2H), 7.57 – 7.47 (m, 5H), 7.41 – 7.35 (m, 5H), 7.34 (d, J = 1.8 Hz, 1H), 7.33 (d, J = 2.0 Hz, 2H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.15, 150.60, 134.84, 133.30, 133.23, 131.66, 130.95, 129.78, 129.76, 129.49, 129.15, 129.08, 128.83, 128.53, 126.53.
HRMS (ESI) calcd for $C_{21}H_{15}NSH^+$: $[M+H]^+$ 314.0998, found: 314.0995.

2-methyl-4,5-diphenylthiazole (3ba)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 55% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 7.44 – 7.40 (m, 2H), 7.39 – 7.35 (m, 3H), 7.32 – 7.27 (m, 5H), 2.70 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.14, 148.98, 134.99, 132.37, 132.07, 129.75, 129.43, 128.99, 128.77, 128.75, 128.22, 19.30.
HRMS (ESI) calcd for $C_{16}H_{13}NSH^+$: $[M+H]^+$ 252.0841, found: 252.0839.

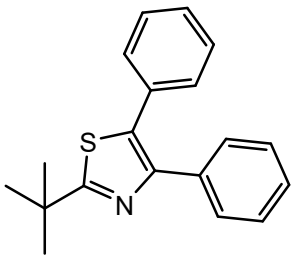
2-isopropyl-4,5-diphenylthiazole (3ca)



Following the general procedure the title compound was isolated by flash

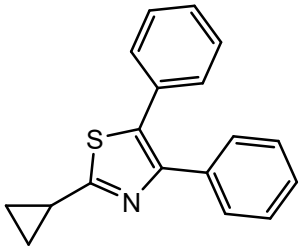
chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as light yellow oil in 67% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 7.45 – 7.40 (m, 2H), 7.39 – 7.33 (m, 3H), 7.33 – 7.25 (m, 5H), 3.35 – 3.27 (m, 1H), 1.38 (d, J = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, DMSO-d6): δ 175.32, 148.81, 135.11, 132.15, 131.63, 129.76, 129.40, 129.05, 128.73, 128.20, 33.07, 23.24.
HRMS (ESI) calcd for $C_{18}H_{17}NSH^+$: $[M+H]^+$ 280.1154, found: 280.1154.

2-(tert-butyl)-4,5-diphenylthiazole (3da)



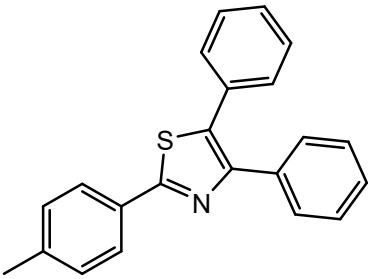
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 56% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 3H), 7.33 – 7.26 (m, 5H), 1.44 (s, 9H).
^{13}C NMR (101 MHz, DMSO-d6): δ 178.59, 148.70, 135.14, 132.12, 131.68, 129.78, 129.41, 129.06, 128.76, 128.75, 128.21, 37.91, 30.97.
HRMS (ESI) calcd for $C_{19}H_{19}NSH^+$: $[M+H]^+$ 294.1311, found: 294.1307.

2-cyclopropyl-4,5-diphenylthiazole (3ea)



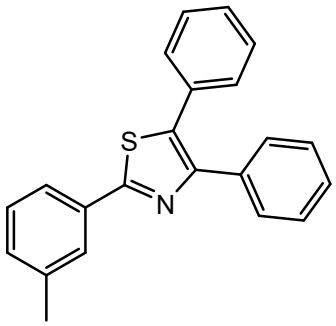
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 71% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 7.38 (ddd, J = 8.8, 3.9, 2.1 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.30 – 7.24 (m, 5H), 2.41 (tt, J = 8.2, 4.8 Hz, 1H), 1.17 – 1.10 (m, 2H), 1.05 – 1.00 (m, 2H).
^{13}C NMR (101 MHz, DMSO-d6): δ 171.13, 148.78, 135.06, 132.07, 130.44, 129.73, 129.38, 129.03, 128.71, 128.68, 128.22, 14.45, 11.39.
HRMS (ESI) calcd for $C_{18}H_{15}NSH^+$: $[M+H]^+$ 278.0998, found: 278.0996.

4,5-diphenyl-2-(p-tolyl)thiazole (3fa)



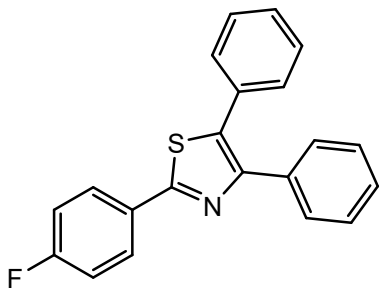
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless solid in 71% yield;
M.p. = 163-165°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 7.86 (d, J = 8.1 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.40 – 7.28 (m, 10H), 2.35 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.27, 150.43, 140.82, 134.91, 132.75, 131.74, 130.64, 130.28, 129.76, 129.46, 129.14, 129.00, 128.80, 128.48, 126.45, 21.44.
HRMS (ESI) calcd for $C_{22}H_{17}NSH^+$: $[M+H]^+$ 328.1154, found: 328.1152.

4,5-diphenyl-2-(m-tolyl)thiazole (3ga)



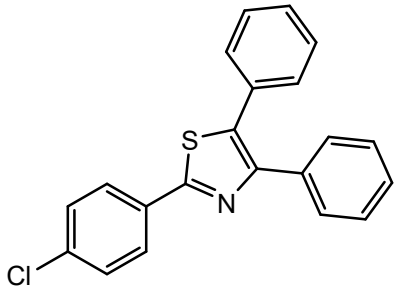
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 73% yield;
M.p. = 167-165°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 7.81 (s, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.50 (dt, J = 5.4, 3.3 Hz, 2H), 7.43 – 7.29 (m, 10H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.28, 150.55, 139.13, 134.88, 133.19, 133.14, 131.69, 131.64, 129.76, 129.65, 129.48, 129.16, 129.05, 128.82, 128.52, 126.86, 123.80, 21.38.
HRMS (ESI) calcd for $C_{22}H_{17}NSH^+$: $[M+H]^+$ 328.1154, found: 328.1152.

2-(4-fluorophenyl)-4,5-diphenylthiazole (3ha)



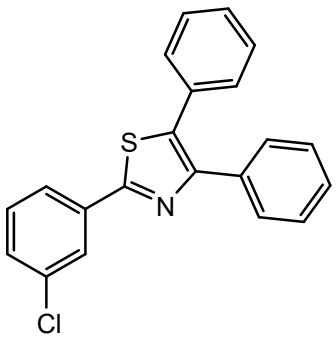
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as light yellow solid in 70% yield;
M.p. = 136-138°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.05 – 7.99 (m, 2H), 7.52 – 7.47 (m, 2H), 7.41 – 7.30 (m, 10H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.03, 163.96, 162.56, 150.56, 134.75, 133.35, 131.57, 129.76, 129.49, 129.13, 128.88, 128.83, 128.55, 116.89, 116.67.
^{19}F NMR (376 MHz, DMSO-d6) δ -110.20.
HRMS (ESI) calcd for $C_{21}H_{14}FNSH^{+}$: $[M+H]^{+}$ 332.0904, found: 332.0901.

2-(4-chlorophenyl)-4,5-diphenylthiazole (3ia)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 69% yield;
M.p. = 173-176°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.03 – 7.98 (m, 2H), 7.61 – 7.57 (m, 2H), 7.51 (ddd, J = 8.8, 3.9, 2.2 Hz, 2H), 7.43 – 7.32 (m, 8H).
^{13}C NMR (101 MHz, DMSO-d6): δ 163.78, 150.75, 135.50, 134.67, 133.76, 132.03, 131.49, 129.84, 129.79, 129.53, 129.21, 129.14, 128.87, 128.63, 128.22.
HRMS (ESI) calcd for $C_{21}H_{14}ClNSH^{+}$: $[M+H]^{+}$ 348.0608, found: 348.0608.

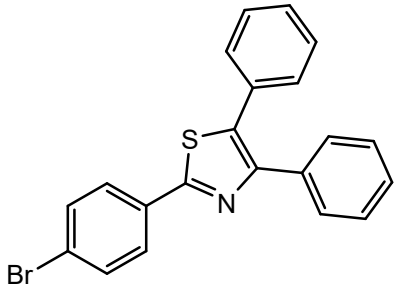
2-(3-chlorophenyl)-4,5-diphenylthiazole (3ja)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as light yellow solid in 68% yield;
M.p. = 179-182°C.

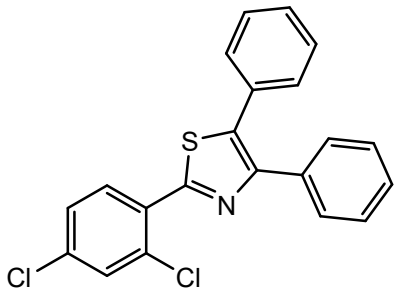
^{1}H NMR (400 MHz, DMSO-d6): δ 8.02 (d, J = 1.9 Hz, 1H), 7.93 (dt, J = 6.7, 1.8 Hz, 1H), 7.58 (ddd, J = 9.2, 5.6, 3.6 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.43 – 7.32 (m, 8H).
^{13}C NMR (101 MHz, DMSO-d6): δ 163.31, 150.79, 135.06, 134.60, 134.52, 134.14, 131.74, 131.41, 130.64, 129.79, 129.54, 129.27, 129.16, 128.88, 128.66, 125.77, 125.35.
HRMS (ESI) calcd for $C_{21}H_{14}ClNSH^+$: $[M+H]^+$ 348.0608, found: 348.0608.

2-(4-bromophenyl)-4,5-diphenylthiazole (3ka)



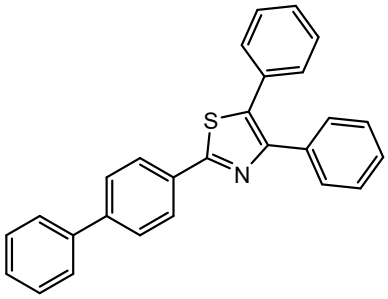
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 60% yield;
M.p. = 202-204°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 7.94 – 7.89 (m, 2H), 7.73 – 7.68 (m, 2H), 7.52 – 7.46 (m, 2H), 7.42 – 7.31 (m, 8H).
^{13}C NMR (101 MHz, DMSO-d6): δ 163.85, 150.76, 134.66, 133.76, 132.72, 132.35, 131.48, 129.77, 129.51, 129.19, 129.14, 128.85, 128.62, 128.38, 124.26.
HRMS (ESI) calcd for $C_{21}H_{14}BrNSH^+$: $[M+H]^+$ 392.0103, found: 392.0101.

2-(2,4-dichlorophenyl)-4,5-diphenylthiazole (3la)



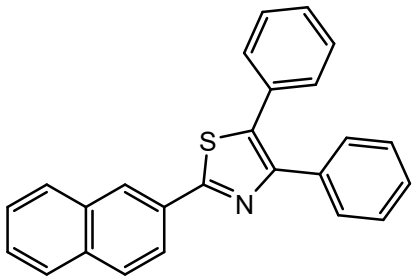
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 59% yield;
M.p. = 210-212°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.34 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.59 (dd, J = 8.6, 2.0 Hz, 1H), 7.51 (dd, J = 6.6, 2.9 Hz, 2H), 7.43 – 7.36 (m, 5H), 7.36 – 7.30 (m, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 159.18, 149.56, 135.47, 135.20, 134.46, 132.00, 131.92, 131.18, 130.64, 130.30, 129.81, 129.54, 129.29, 129.13, 128.87, 128.66, 128.56.
HRMS (ESI) calcd for $C_{21}H_{13}Cl_2NSH^+$: $[M+H]^+$ 382.0219, found: 382.0222.

2-([1,1'-biphenyl]-4-yl)-4,5-diphenylthiazole (3ma)



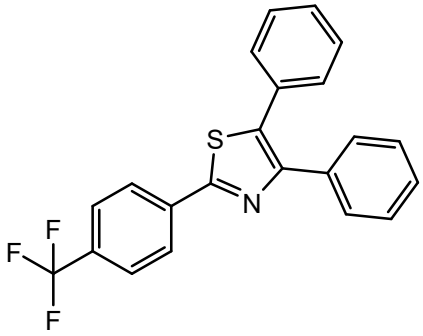
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 64% yield;
M.p. = 226-228°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.08 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.56 – 7.48 (m, 4H), 7.45 – 7.38 (m, 6H), 7.38 – 7.32 (m, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.75, 150.73, 142.42, 139.53, 134.83, 133.35, 132.23, 131.66, 129.81, 129.56, 129.53, 129.18, 129.14, 128.88, 128.60, 128.53, 127.95, 127.17, 127.13.
HRMS (ESI) calcd for $C_{27}H_{19}NSH^+$: $[M+H]^+$ 390.1311, found: 390.1307.

2-(naphthalen-2-yl)-4,5-diphenylthiazole (3na)



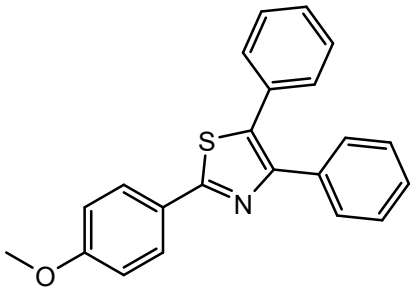
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 51% yield;
M.p. = 219-222°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.57 (s, 1H), 8.14 – 8.02 (m, 4H), 8.00 – 7.90 (m, 1H), 7.79 – 7.53 (m, 5H), 7.47 – 7.27 (m, 6H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.15, 150.80, 134.84, 134.24, 133.51, 133.37, 132.34, 131.67, 130.65, 129.80, 129.55, 129.45, 129.22, 129.13, 128.97, 128.88, 128.61, 128.49, 128.28, 128.24, 127.85, 127.57, 126.79, 125.97, 123.89.
HRMS (ESI) calcd for $C_{25}H_{17}NSH^+$: $[M+H]^+$ 364.1154, found: 364.1151.

4,5-diphenyl-2-(4-(trifluoromethyl)phenyl)thiazole (3oa)



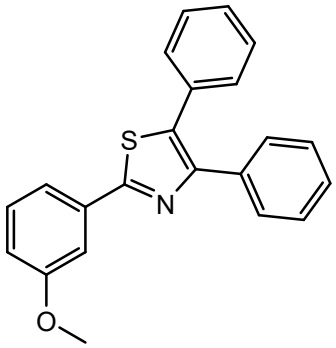
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 64% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 8.17 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.50 (ddd, J = 4.8, 3.5, 1.8 Hz, 2H), 7.44 – 7.29 (m, 8H).
^{13}C NMR (101 MHz, DMSO-d6): δ 163.24, 151.09, 136.69, 134.71, 134.54, 131.32, 129.80, 129.56, 129.34, 129.16, 128.90, 128.72, 127.20, 126.77, 126.73.
^{19}F NMR (376 MHz, DMSO-d6) δ -61.30.
HRMS (ESI) calcd for $C_{22}H_{14}F_3NSH^+$: $[M+H]^+$ 382.0872, found: 382.0869.

2-(4-methoxyphenyl)-4,5-diphenylthiazole (3pa)



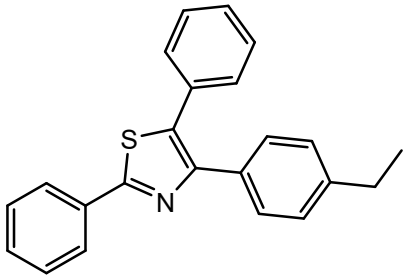
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 73% yield;
M.p. = 153-155°C
^{1}H NMR (400 MHz, DMSO-d6): δ 7.93 (d, J = 8.6 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.29 (m, 8H), 7.08 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.09, 161.54, 150.29, 134.97, 132.20, 131.82, 129.76, 129.48, 129.15, 128.96, 128.83, 128.47, 128.15, 126.02, 115.12, 55.88.
HRMS (ESI) calcd for $C_{22}H_{17}NOSH^+$: $[M+H]^+$ 344.1104, found: 344.1101.

2-(3-methoxyphenyl)-4,5-diphenylthiazole (3qa)



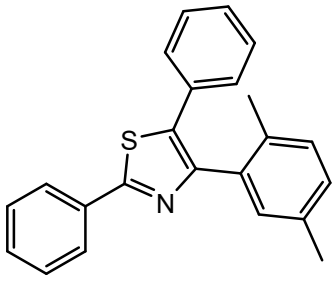
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 70% yield;
M.p. = 160-162°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 7.57 – 7.49 (m, 4H), 7.43 (dd, J = 12.9, 5.0 Hz, 1H), 7.41 – 7.31 (m, 8H), 7.11 – 7.07 (m, 1H), 3.84 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.92, 160.23, 150.58, 134.84, 134.52, 133.43, 131.62, 130.98, 129.78, 129.49, 129.18, 129.11, 128.85, 128.55, 119.07, 116.77, 111.33, 55.79.
HRMS (ESI) calcd for $C_{22}H_{17}NOSH^{+}$: $[M+H]^{+}$ 344.1104, found: 344.1101.

4-(4-ethylphenyl)-2,5-diphenylthiazole (3ad)



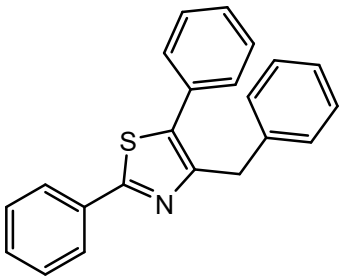
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 68% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 8.01 – 7.94 (m, 2H), 7.55 – 7.48 (m, 3H), 7.45 – 7.40 (m, 2H), 7.38 (d, J = 4.0 Hz, 5H), 7.15 (d, J = 8.3 Hz, 2H), 2.58 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.99, 150.64, 144.13, 133.27, 132.68, 132.26, 131.80, 130.89, 129.77, 129.74, 129.47, 129.08, 129.01, 128.18, 126.49, 28.35, 15.76.
HRMS (ESI) calcd for $C_{23}H_{19}NSH^{+}$: $[M+H]^{+}$ 342.1311, found: 342.1308.

4-(2,5-dimethylphenyl)-2,5-diphenylthiazole (3ae)



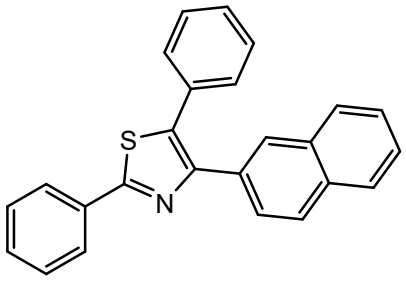
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 72% yield;
M.p. = 155-157°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 7.96 (dt, J = 5.0, 3.0 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.33 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.17 – 7.09 (m, 3H), 2.24 (s, 3H), 1.97 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.51, 151.44, 135.31, 135.21, 134.14, 133.66, 133.33, 131.70, 131.10, 130.89, 130.69, 129.76, 129.66, 129.36, 128.62, 128.51, 126.47, 20.93, 19.51
HRMS (ESI) calcd for $C_{23}H_{19}NSH^+$: $[M+H]^+$ 342.1311, found: 342.1308.

4-benzyl-2,5-diphenylthiazole (3af)



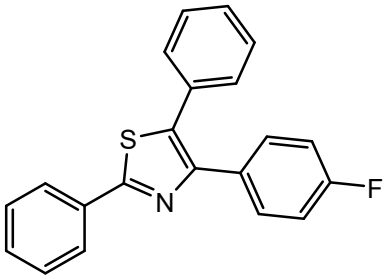
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as light yellow oil in 49% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 7.96 – 7.90 (m, 2H), 7.55 – 7.41 (m, 8H), 7.32 – 7.18 (m, 5H), 4.17 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.05, 151.18, 139.87, 133.67, 133.29, 131.39, 130.82, 129.75, 129.61, 129.47, 128.99, 128.95, 128.82, 126.64, 126.43, 35.28.
HRMS (ESI) calcd for $C_{22}H_{17}NSH^+$: $[M+H]^+$ 328.1154, found: 328.1151.

4-(naphthalen-2-yl)-2,5-diphenylthiazole (3ag)



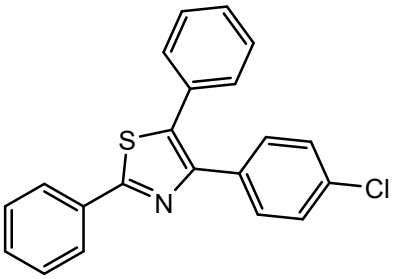
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 65% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 8.15 (s, 1H), 8.02 (dd, J = 7.3, 2.0 Hz, 2H), 7.90 – 7.86 (m, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.57 – 7.46 (m, 6H), 7.42 – 7.35 (m, 5H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.31, 150.50, 133.69, 133.29, 133.24, 132.89, 132.38, 131.65, 130.99, 129.81, 129.77, 129.51, 129.14, 128.57, 128.41, 128.13, 128.02, 126.99, 126.92, 126.89, 126.60.
HRMS (ESI) calcd for $C_{25}H_{17}NSH^+$: $[M+H]^+$ 364.1154, found: 364.1150.

4-(4-fluorophenyl)-2,5-diphenylthiazole (3ah)



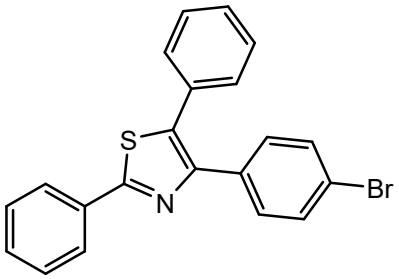
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 72% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 8.01 – 7.95 (m, 2H), 7.57 – 7.49 (m, 5H), 7.43 – 7.34 (m, 5H), 7.21 – 7.14 (m, 2H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.23, 163.47, 161.03, 149.53, 133.15, 131.48, 131.26, 131.18, 130.99, 129.77, 129.57, 129.18, 126.53, 115.90, 115.69.
^{19}F NMR (376 MHz, DMSO-d6) δ -113.43.
HRMS (ESI) calcd for $C_{21}H_{14}FNSH^+$: $[M+H]^+$ 332.0904, found: 332.0901.

4-(4-chlorophenyl)-2,5-diphenylthiazole (3ai)



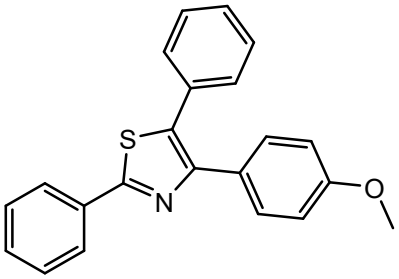
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as light yellow oil in 72% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 8.00 – 7.94 (m, 2H), 7.54 – 7.47 (m, 5H), 7.43 – 7.35 (m, 7H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.41, 149.20, 133.84, 133.62, 133.21, 133.08, 131.35, 131.03, 130.81, 130.07, 129.77, 129.61, 129.28, 128.91, 126.55.
HRMS (ESI) calcd for $C_{21}H_{14}ClNSH^+$: $[M+H]^+$ 348.0608, found: 348.0605.

4-(4-bromophenyl)-2,5-diphenylthiazole (3aj)



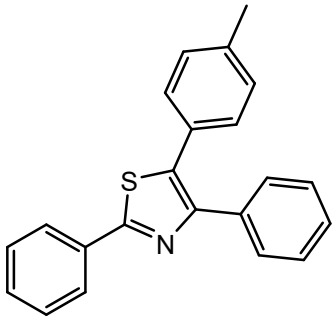
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 67% yield;
M.p. = 207-209°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.00 – 7.94 (m, 2H), 7.55 – 7.49 (m, 5H), 7.45 (q, J = 2.4 Hz, 1H), 7.44 – 7.34 (m, 6H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.44, 149.24, 133.98, 133.88, 133.07, 131.83, 131.35, 131.10, 131.04, 129.77, 129.62, 129.48, 129.29, 126.55, 121.89.
HRMS (ESI) calcd for $C_{21}H_{14}BrNSH^+$: $[M+H]^+$ 392.0103, found: 392.0102.

4-(4-methoxyphenyl)-2,5-diphenylthiazole (3ak)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 67% yield;
M.p. = 171-173°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.03 – 7.91 (m, 2H), 7.55 – 7.48 (m, 3H), 7.47 – 7.42 (m, 2H), 7.41 – 7.34 (m, 5H), 6.93 – 6.85 (m, 2H), 3.75 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.89, 159.49, 150.45, 133.31, 131.92, 131.83, 130.86, 130.43, 129.75, 129.73, 129.48, 128.94, 127.23, 126.48, 114.23, 55.57.
HRMS (ESI) calcd for $C_{22}H_{17}NOSH^+$: $[M+H]^+$ 344.1104, found: 344.1100.

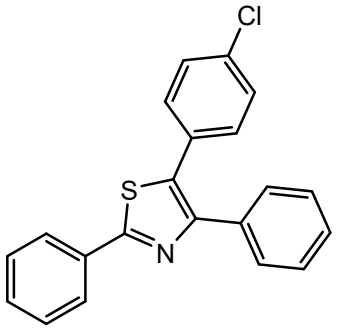
2,4-diphenyl-5-(p-tolyl)thiazole (3al)



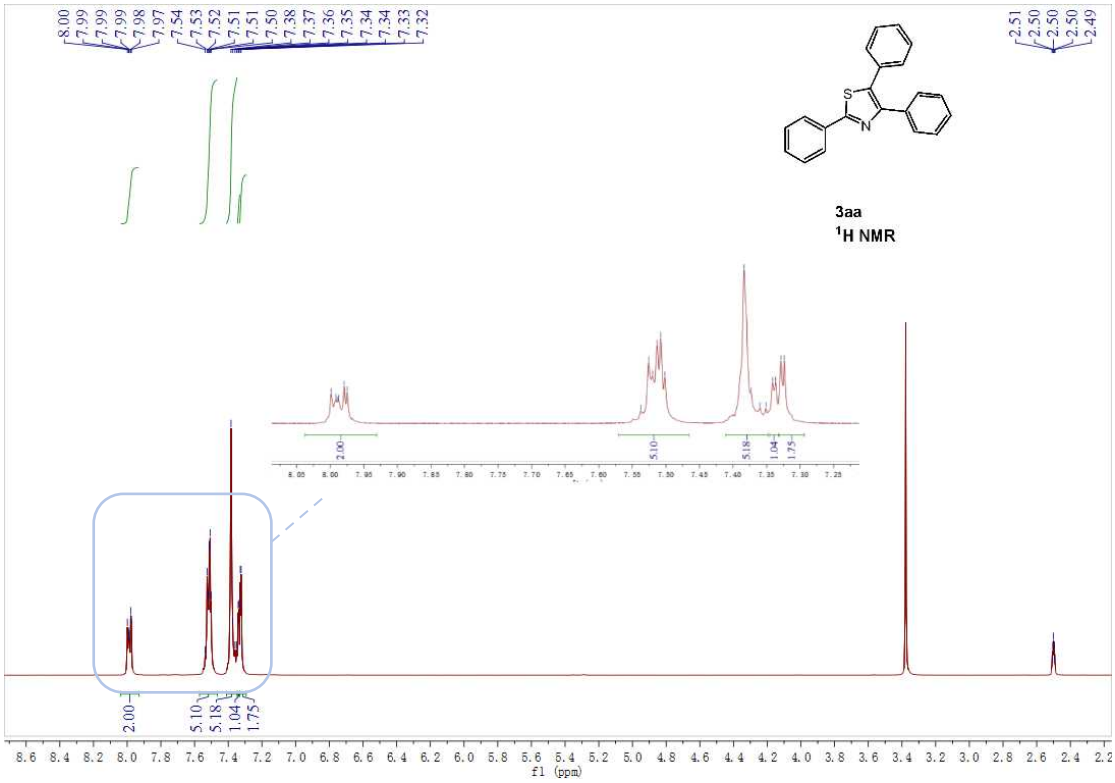
Following the general procedure the title compound was isolated by flash

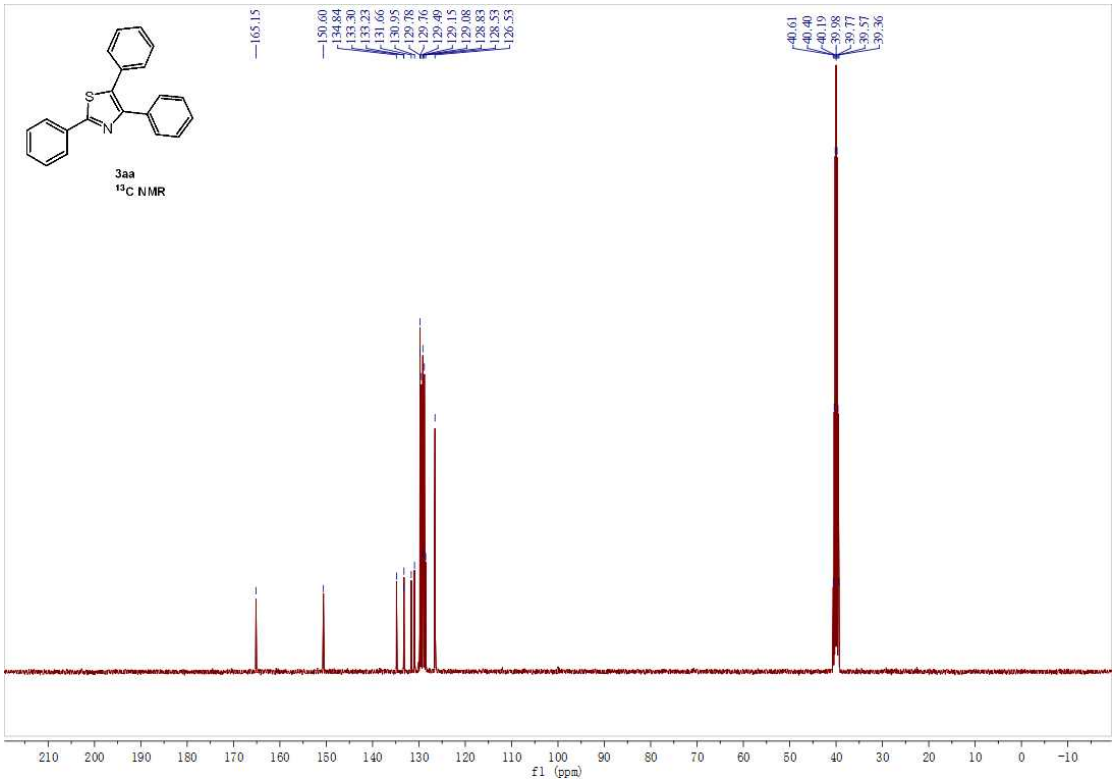
chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as colorless oil in 71% yield;
^{1}H NMR (400 MHz, DMSO-d6): δ 8.01 – 7.93 (m, 2H), 7.56 – 7.46 (m, 5H), 7.38 – 7.29 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.22 – 7.15 (m, 2H), 2.30 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d6): δ 164.83, 150.30, 138.63, 134.97, 133.47, 133.28, 130.86, 130.05, 129.73, 129.60, 129.11, 128.81, 128.67, 128.45, 126.48, 21.27.
HRMS (ESI) calcd for $C_{22}H_{17}NSH^+$: $[M+H]^+$ 328.1154, found: 328.1151.

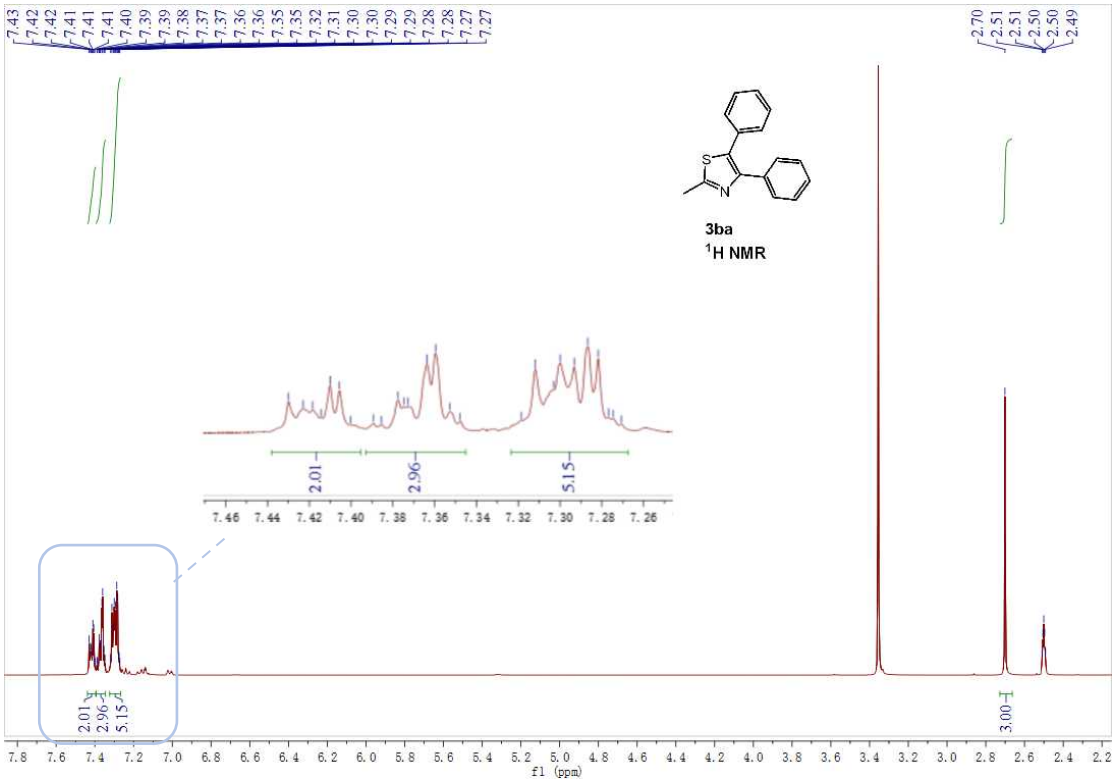
5-(4-chlorophenyl)-2,4-diphenylthiazole (3am)

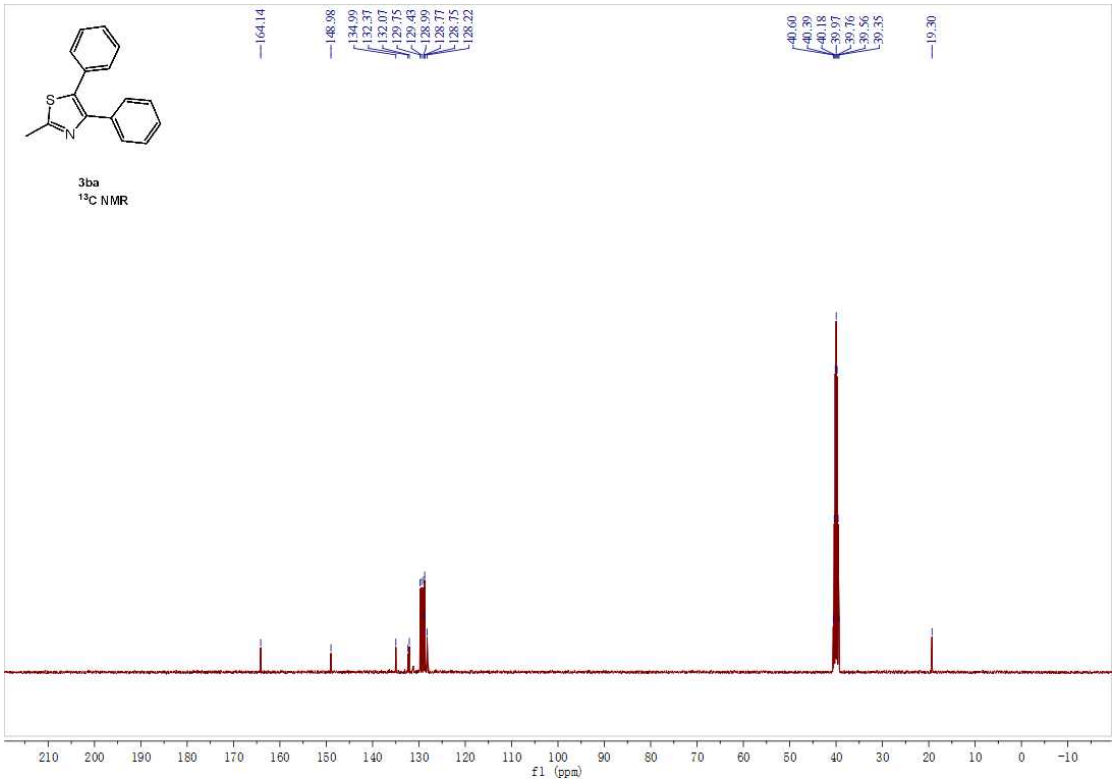


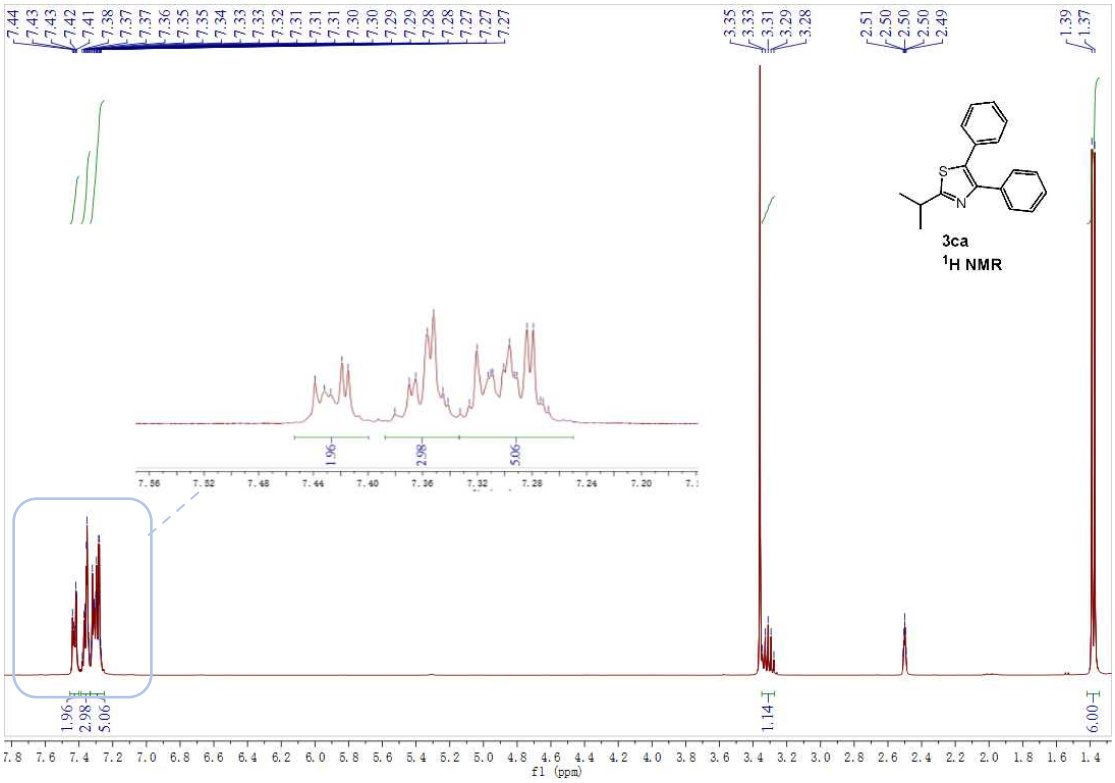
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/*n*-hexane =1/100) as white solid in 66% yield;
M.p. = 176-179°C.
^{1}H NMR (400 MHz, DMSO-d6): δ 8.00 – 7.93 (m, 2H), 7.54 – 7.47 (m, 5H), 7.46 – 7.41 (m, 2H), 7.38 – 7.32 (m, 5H).
^{13}C NMR (101 MHz, DMSO-d6): δ 165.49, 151.10, 134.58, 133.79, 133.11, 131.85, 131.52, 131.06, 130.57, 129.78, 129.54, 129.20, 128.95, 128.71, 126.56.
HRMS (ESI) calcd for $C_{21}H_{14}ClNSH^+$: $[M+H]^+$ 348.0608, found: 348.0608.

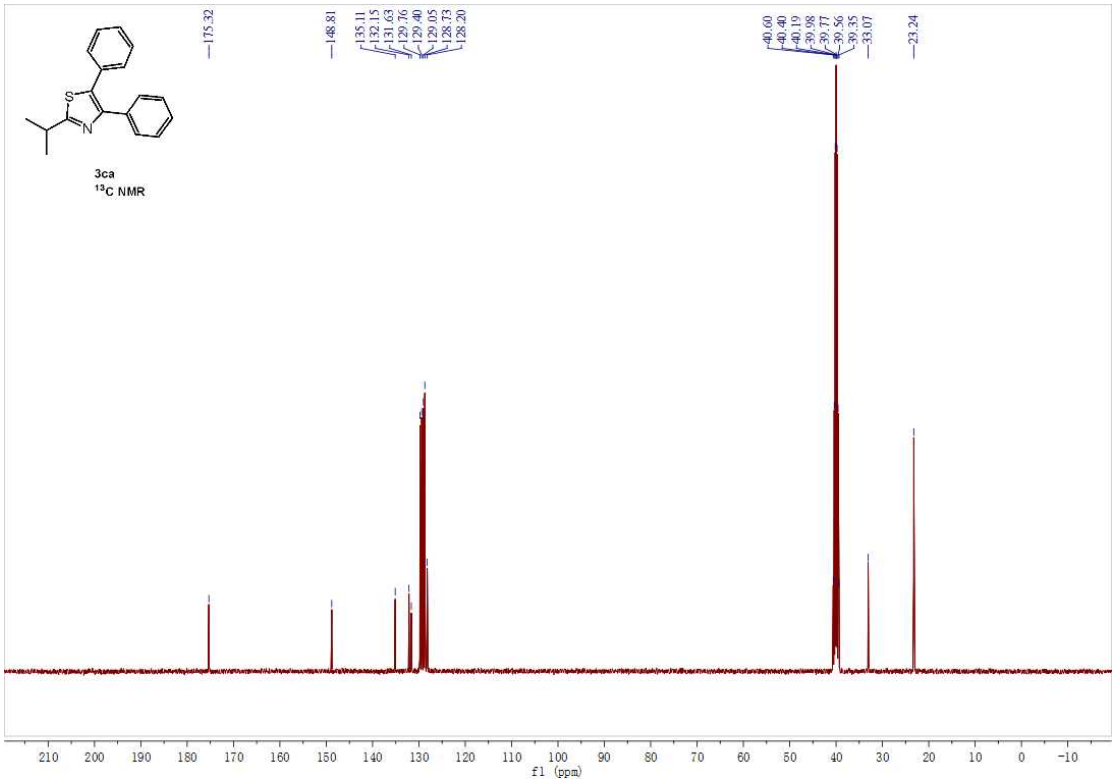

3aa
^{1}H NMR
f1 (ppm)

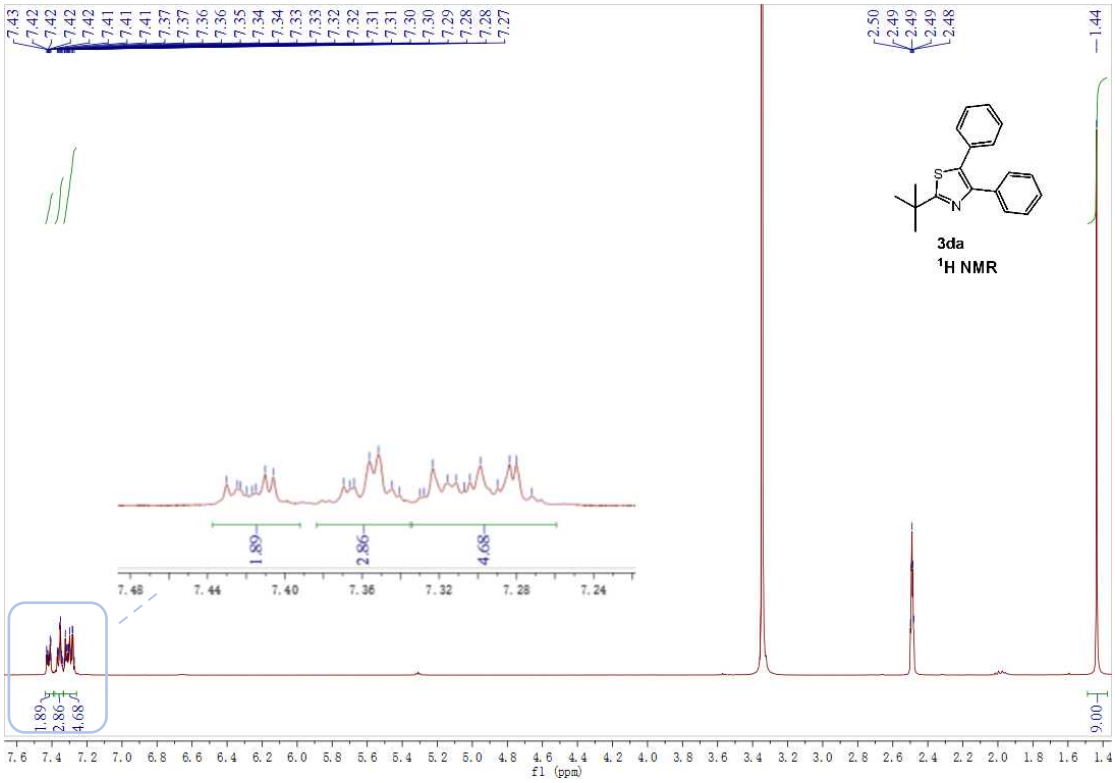

3aa
^{13}C NMR
f1 (ppm)

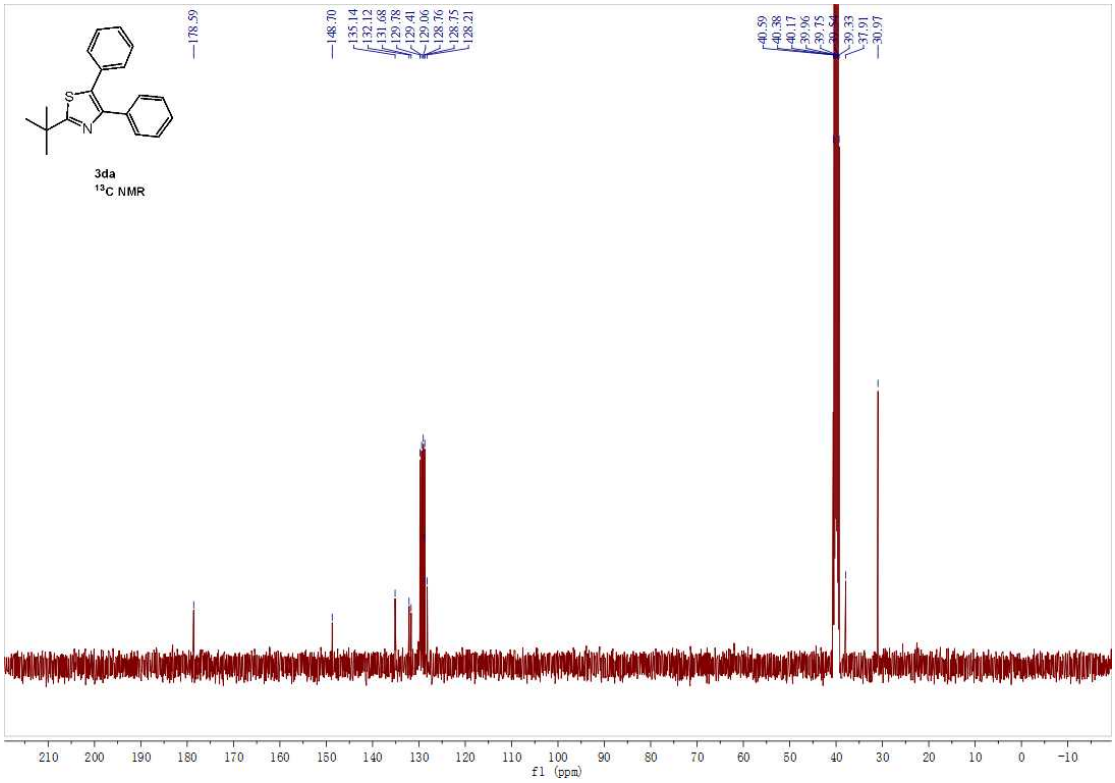

3ba
1H NMR
2.01
2.96
5.15
3.00
f1 (ppm)

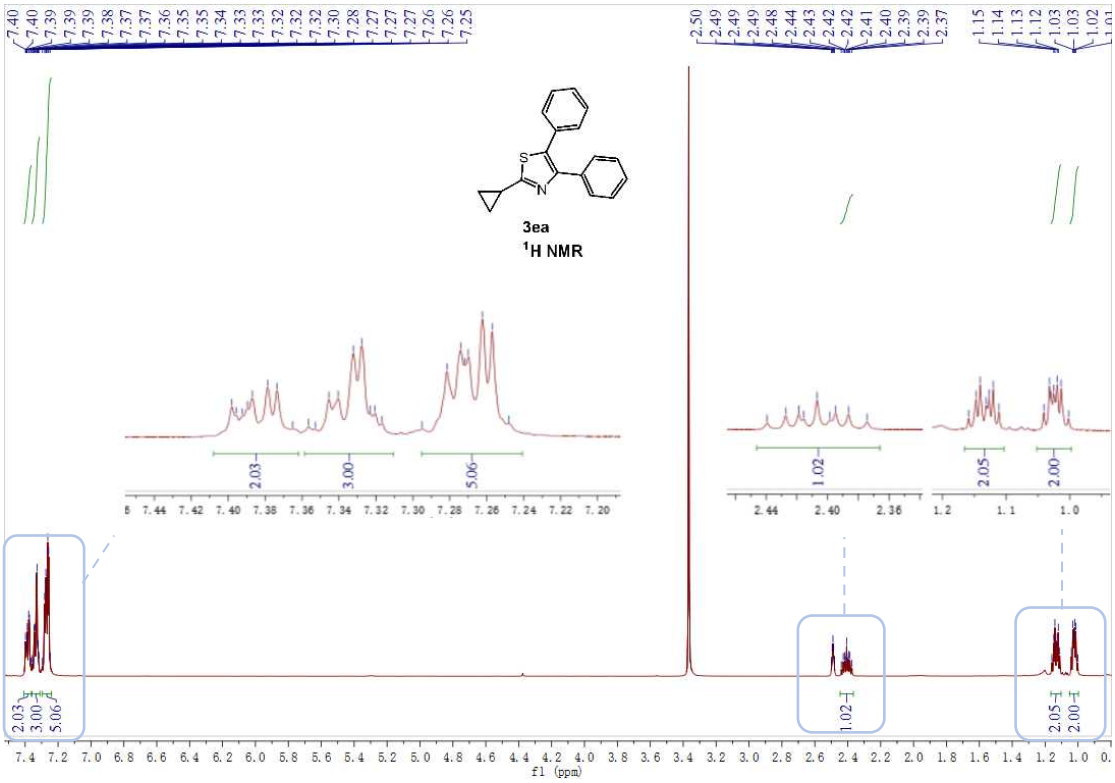

3ba
13C NMR
f1 (ppm)

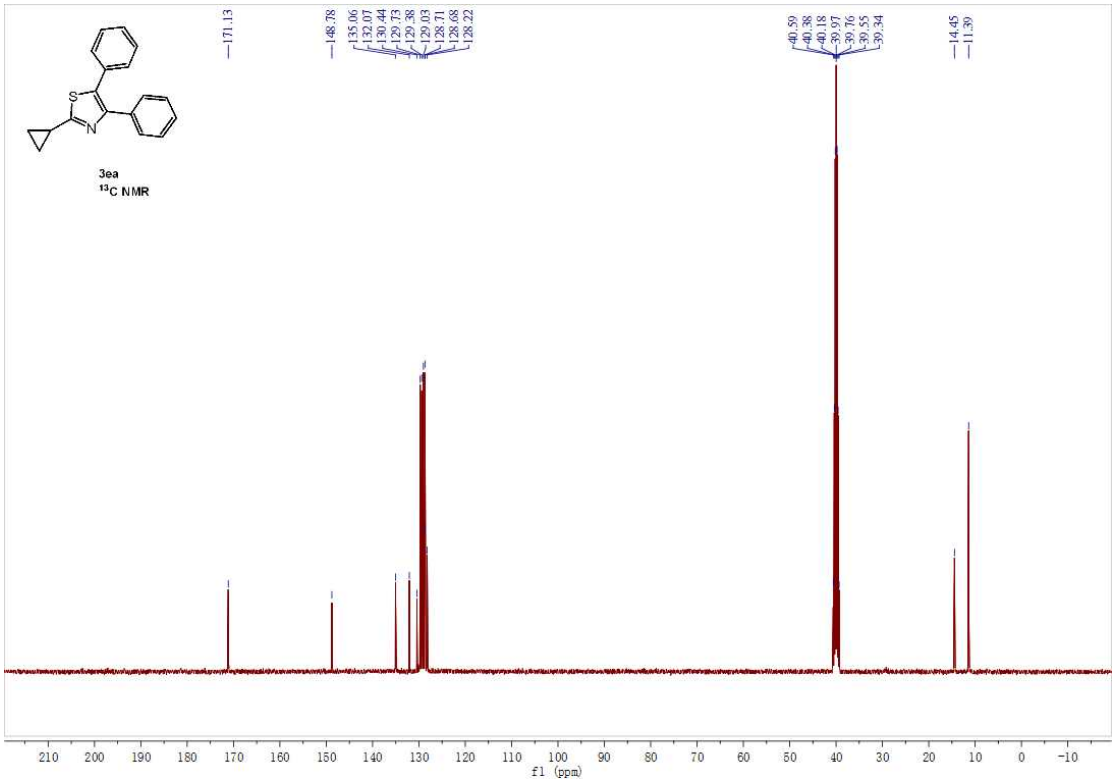

3ca
1H NMR
f1 (ppm)

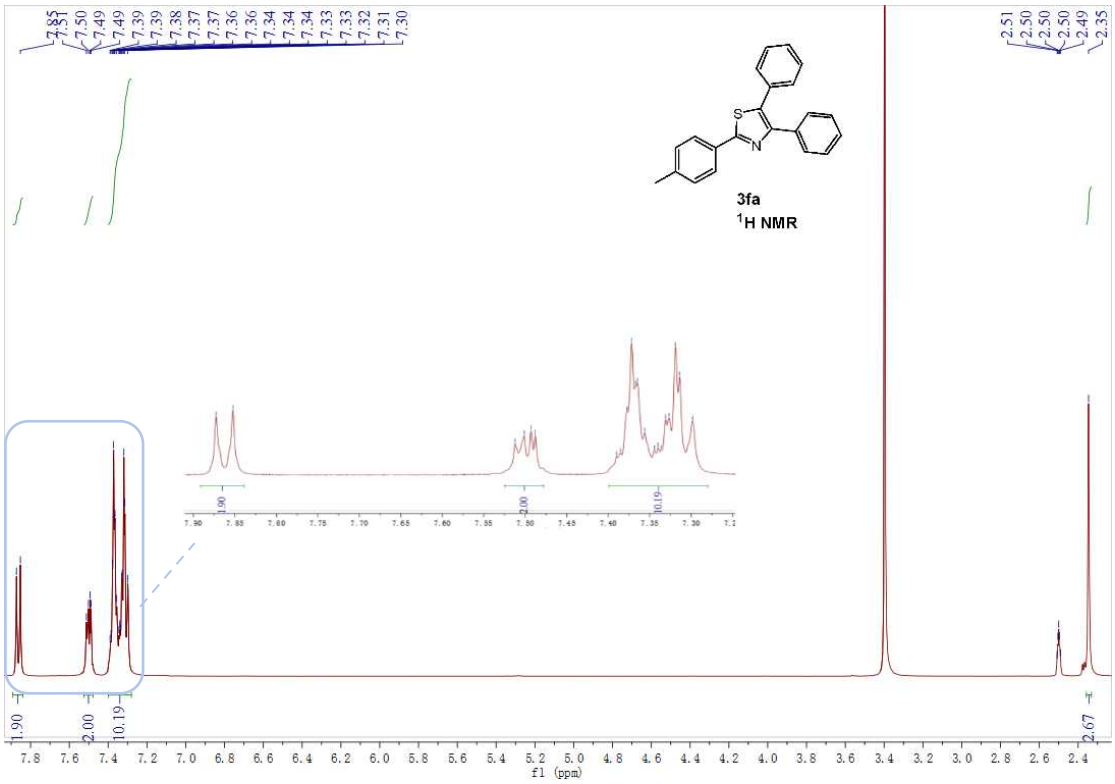

3ca
13C NMR
f1 (ppm)


3da
1H NMR
f1 (ppm)


3da
13C NMR
f1 (ppm)


3ea
^{1}H NMR
f1 (ppm)


3ea
^{13}C NMR
f1 (ppm)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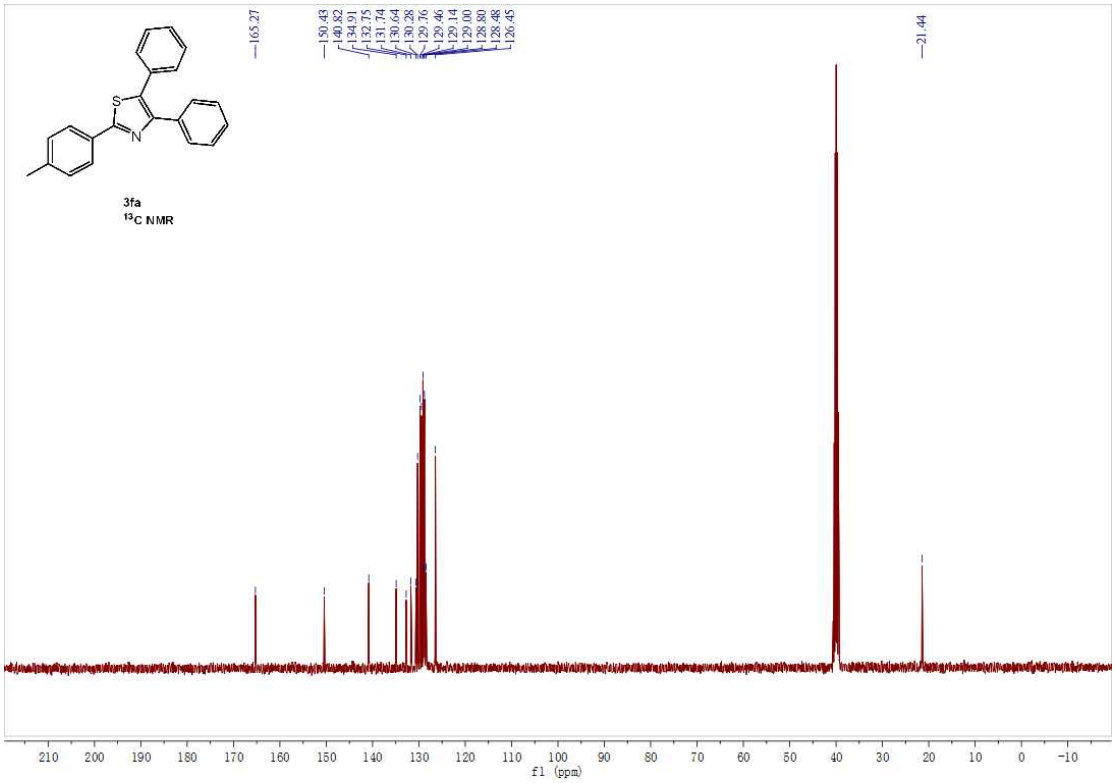
1H NMR
f1 (ppm)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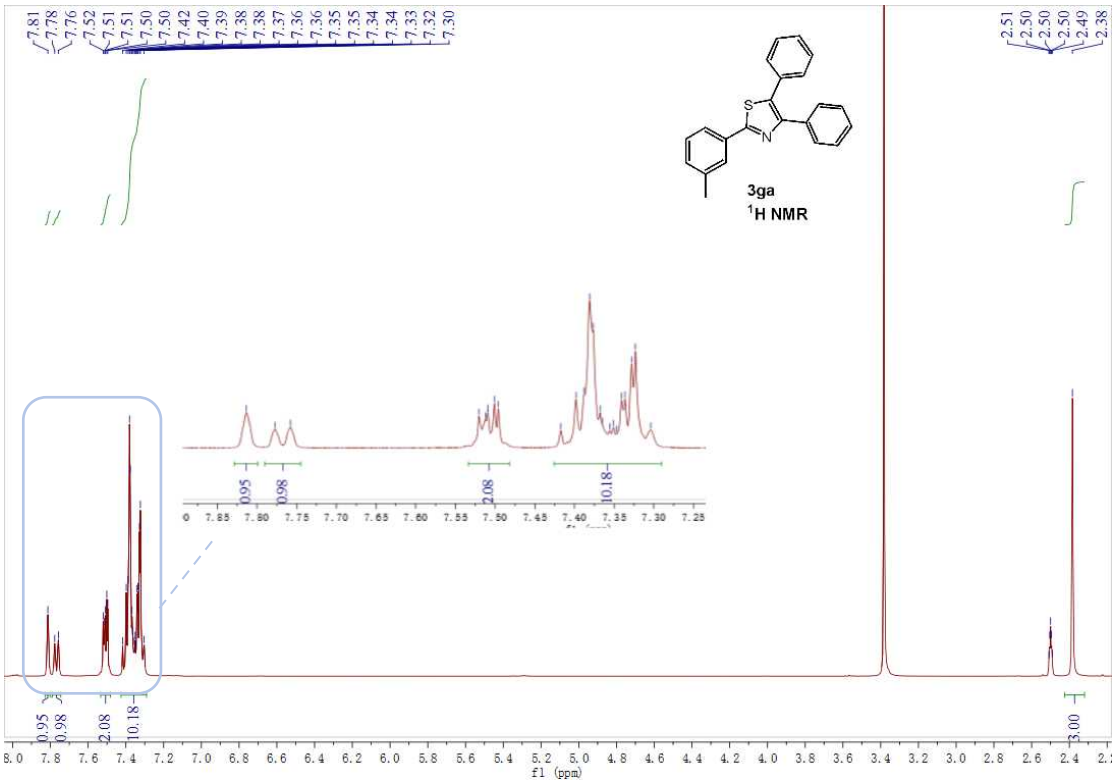
13C NMR
f1 (ppm)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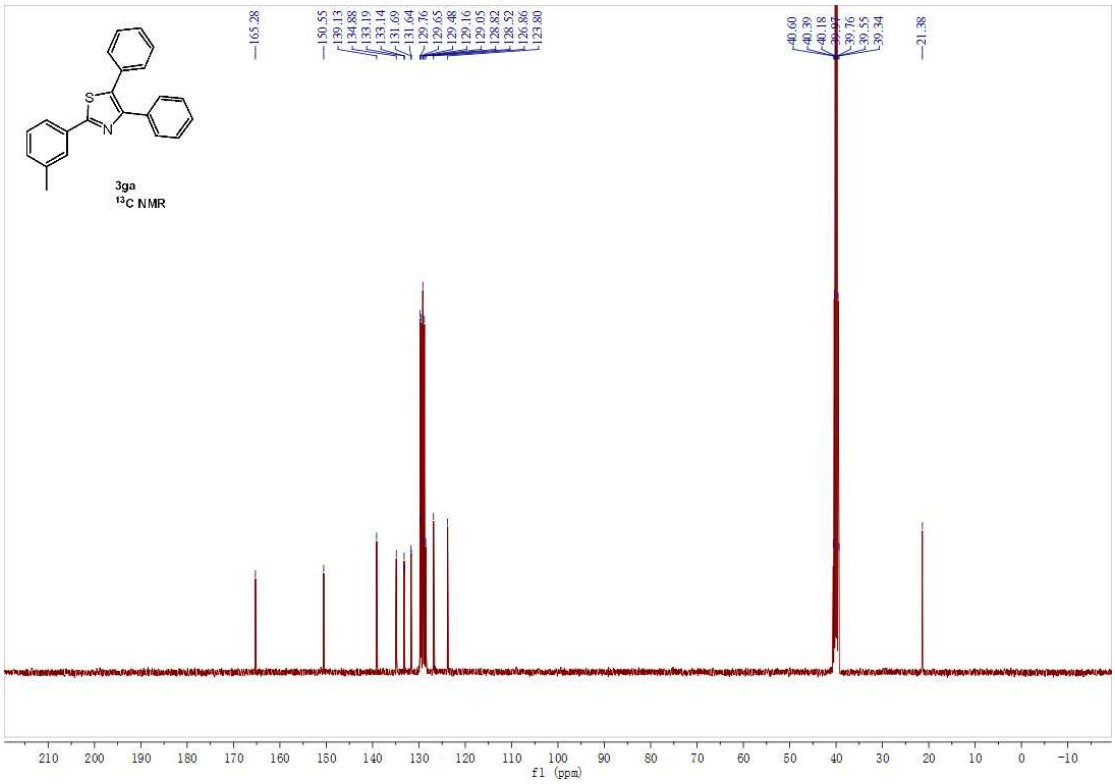
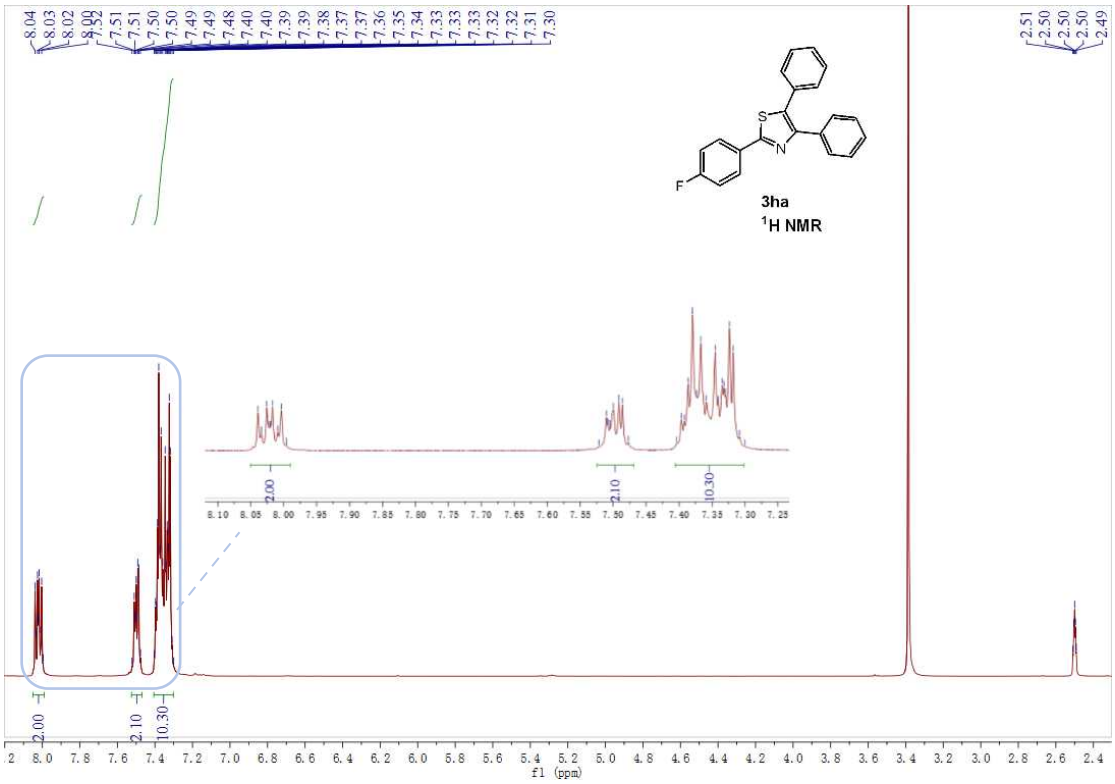
1H NMR
f1 (ppm)


3ga
13C NMR
f1 (ppm)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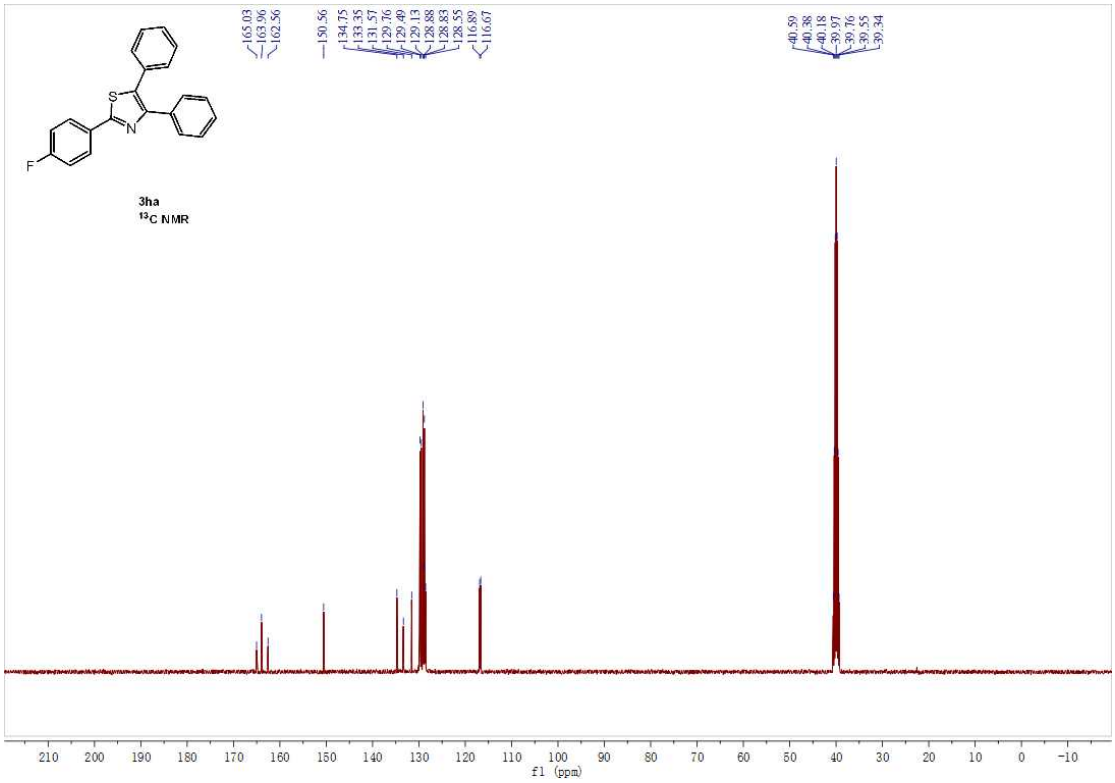
1H NMR
f1 (ppm)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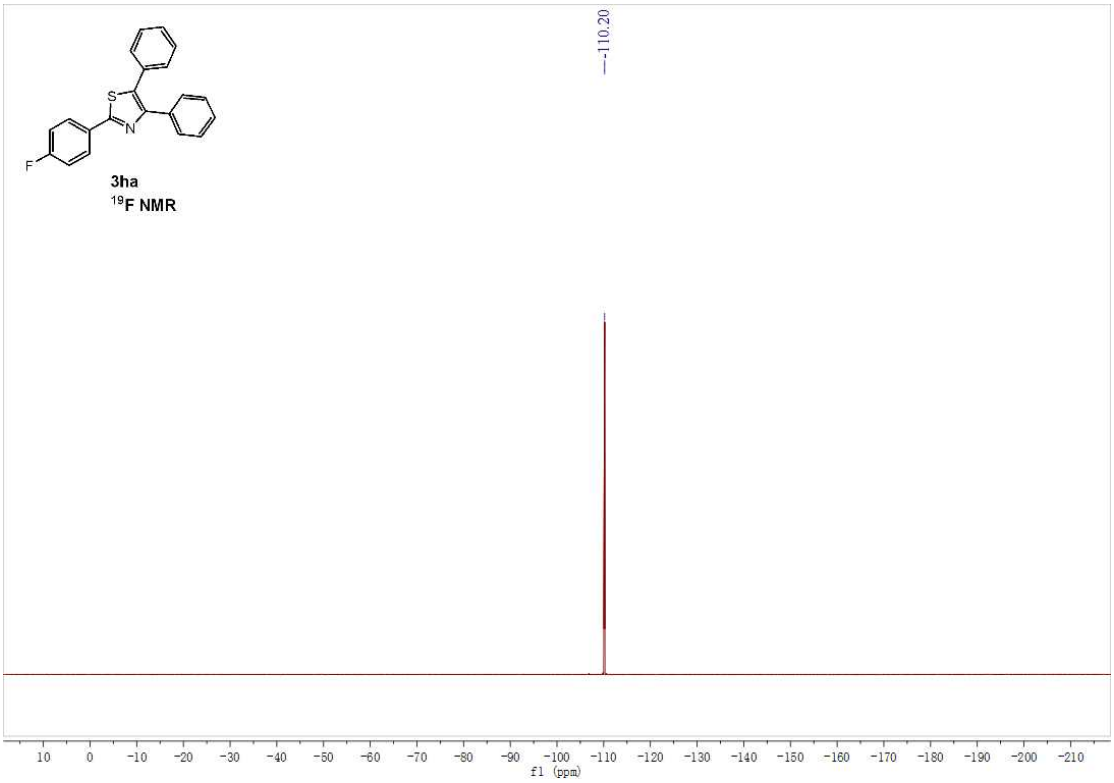
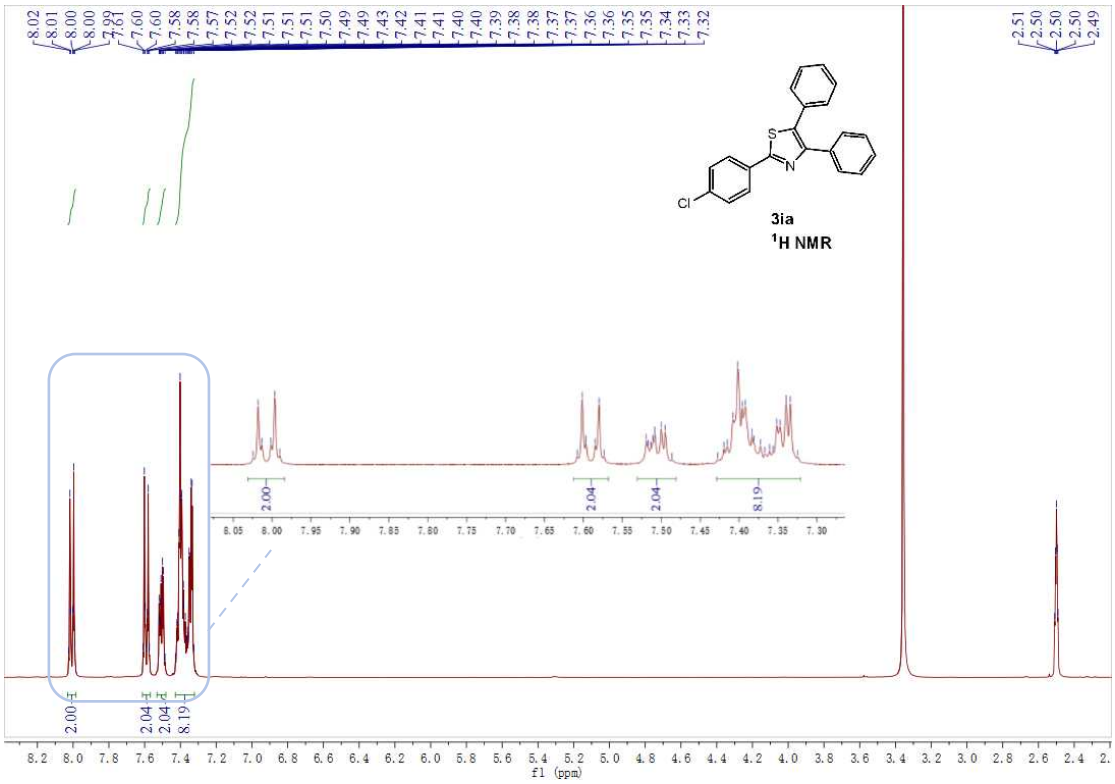
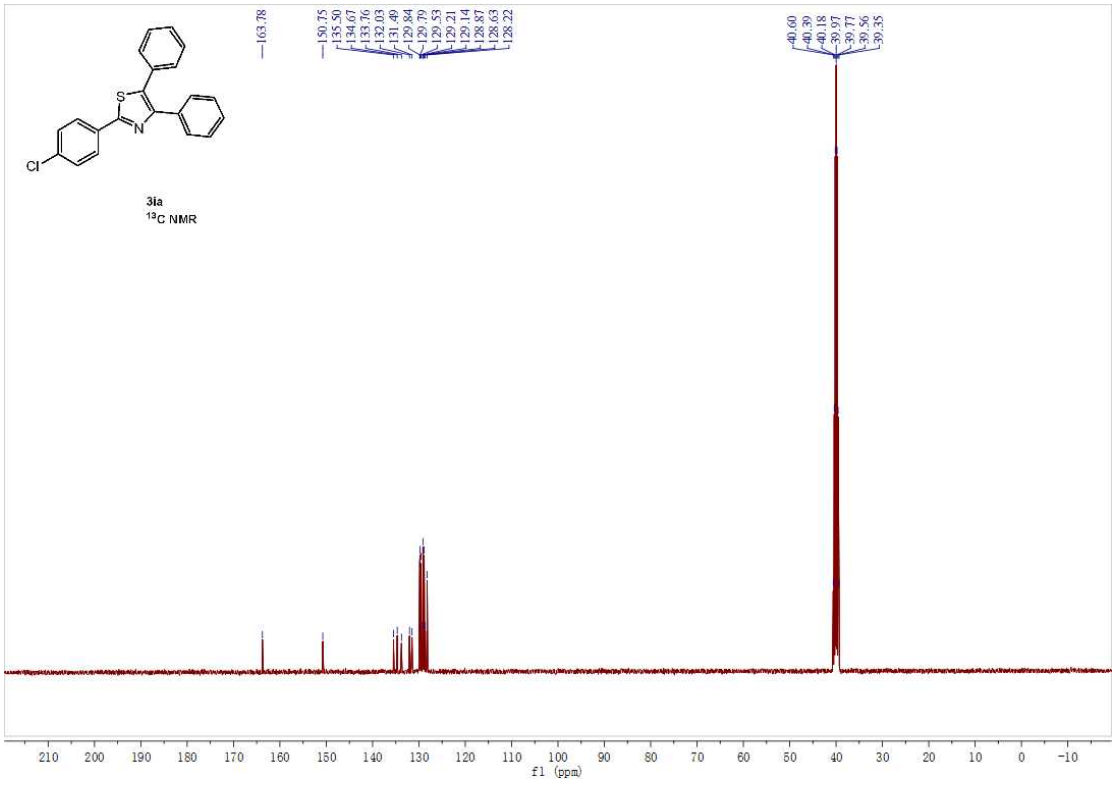
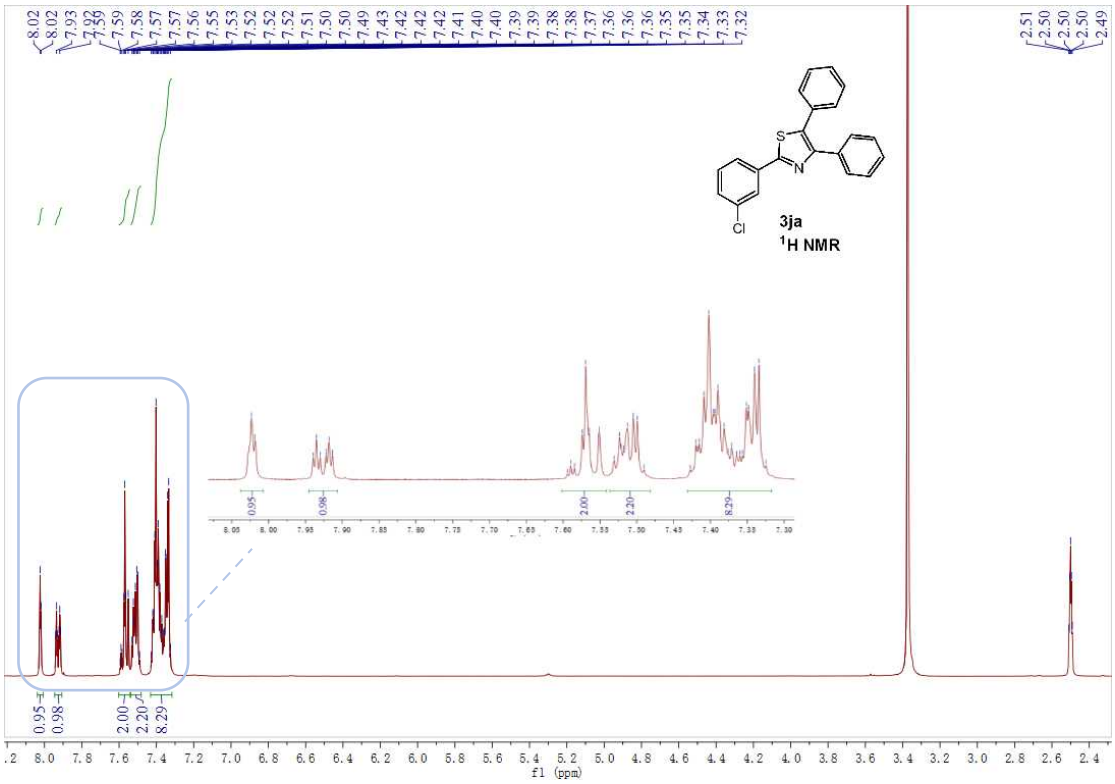
13C NMR
f1 (ppm)


-110.20
S
N
F
3ha
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


3ia
^{1}H NMR
f1 (ppm)


3ia
^{13}C NMR
f1 (ppm)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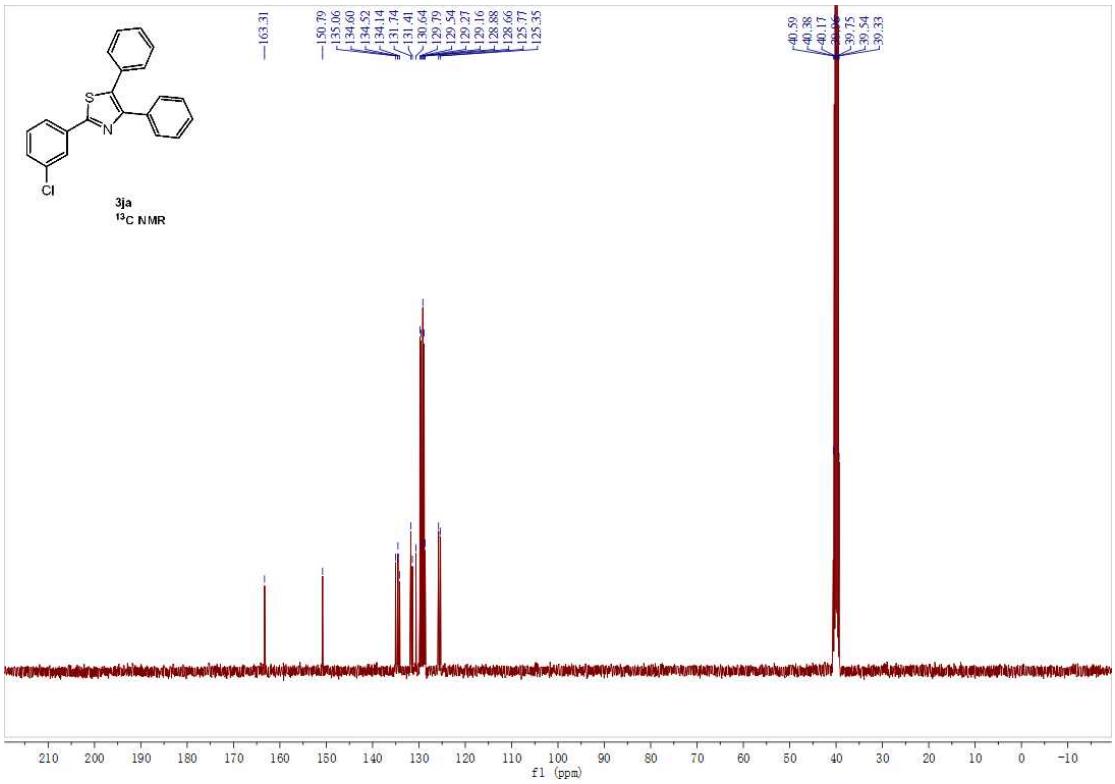
^{1}H NMR
f1 (ppm)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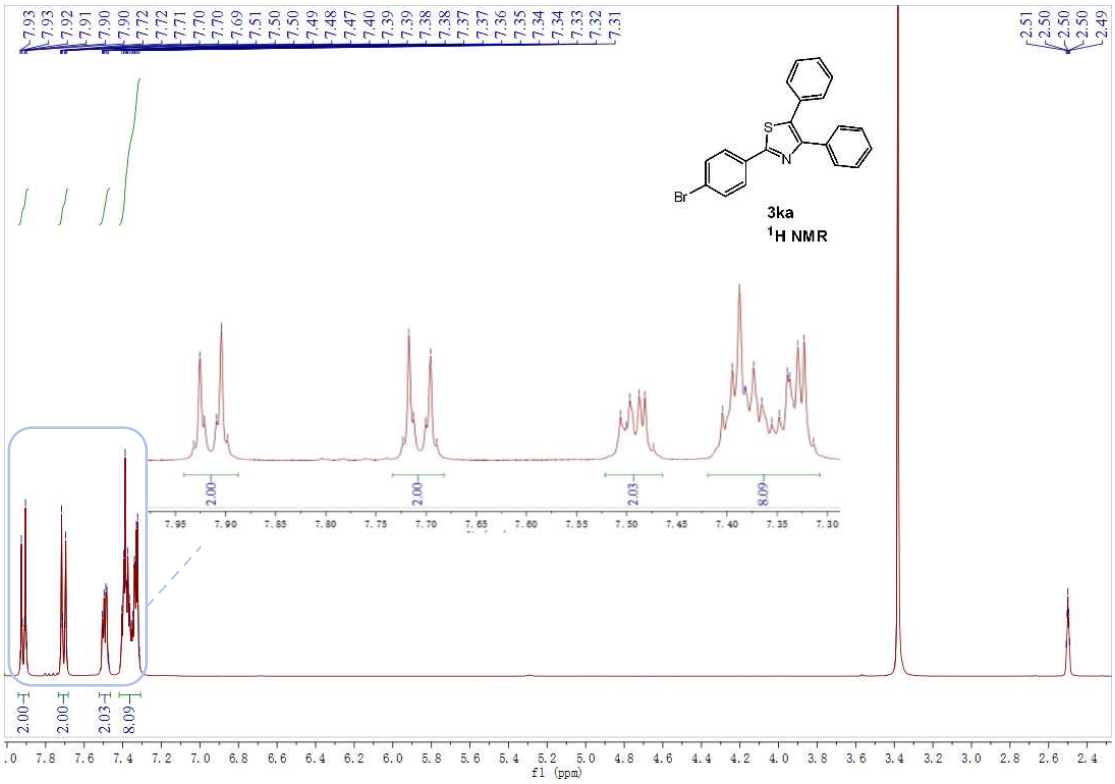
^{13}C NMR
f1 (ppm)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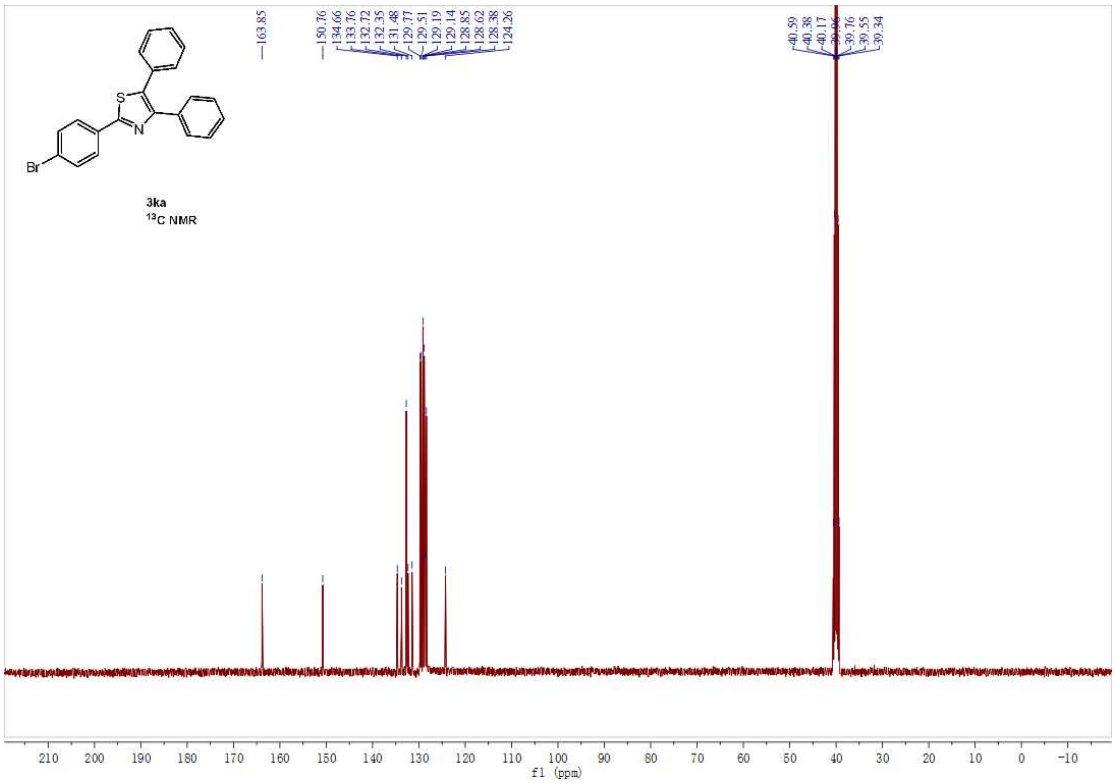
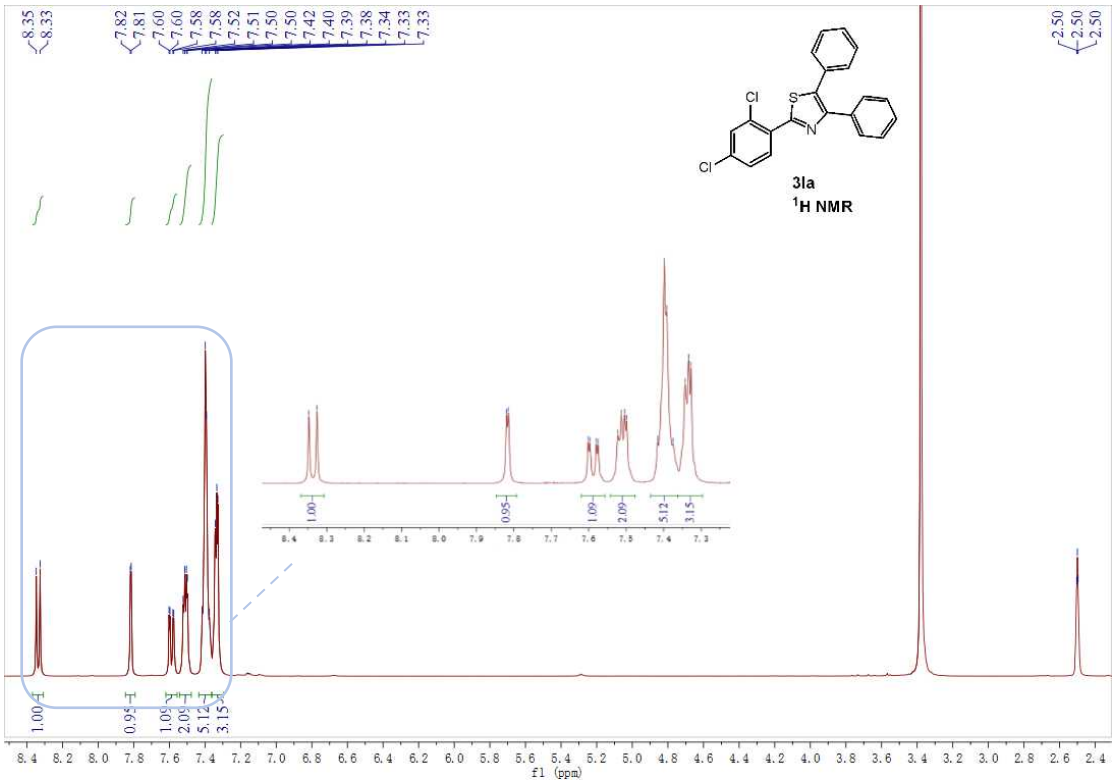
1H NMR
f1 (ppm)


3ka
13C NMR
f1 (ppm)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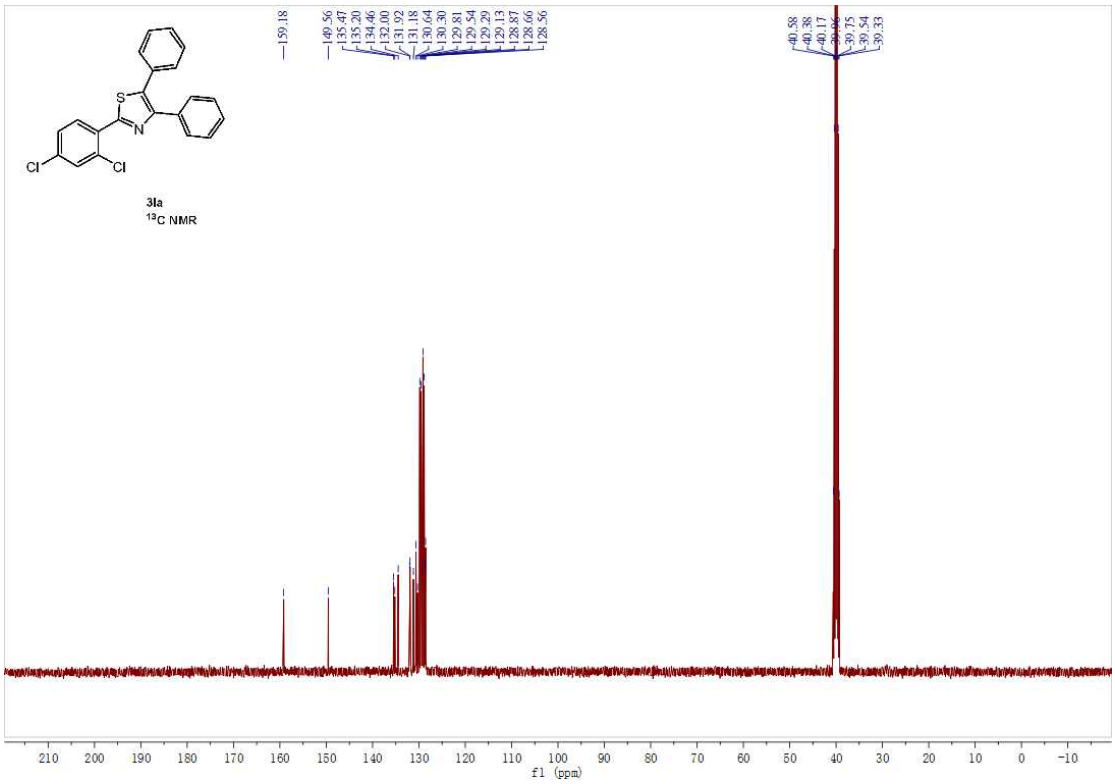
^{1}H NMR
f1 (ppm)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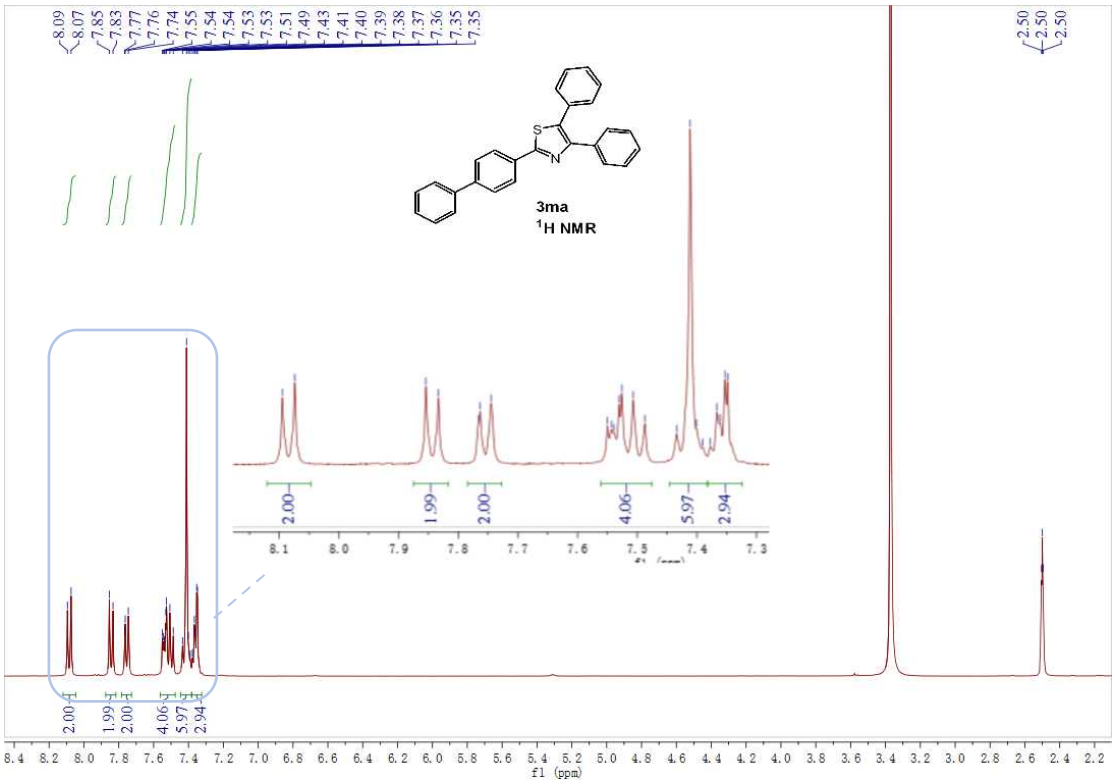
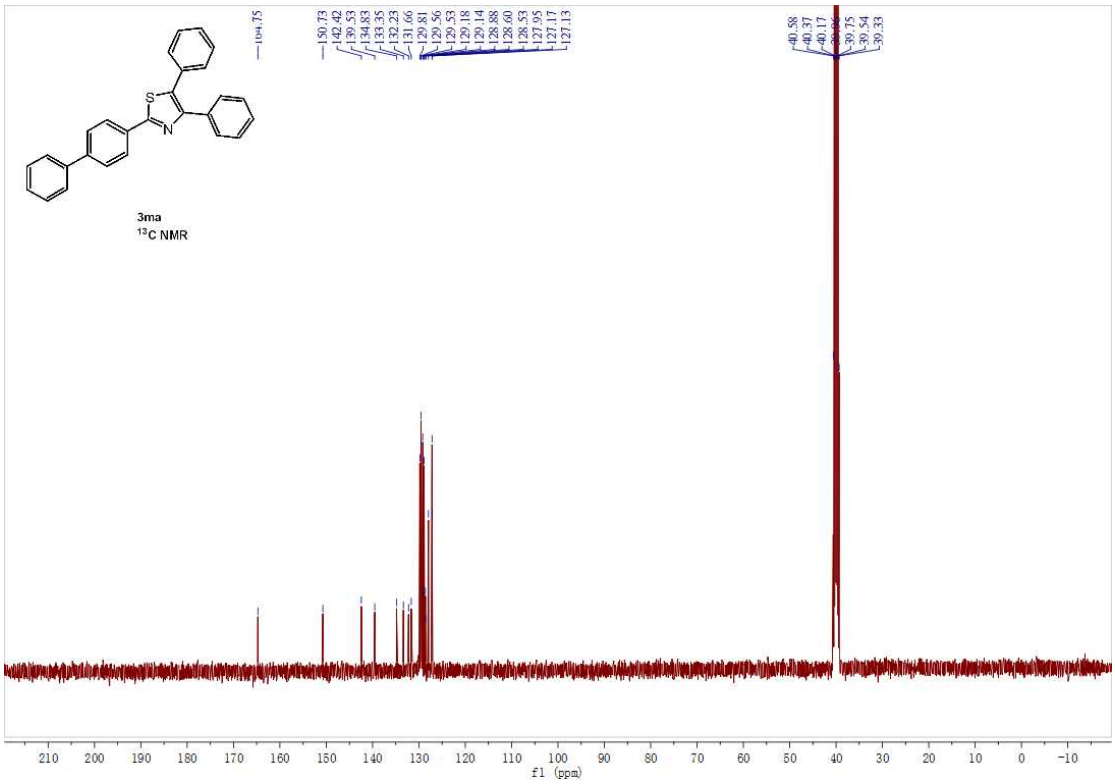
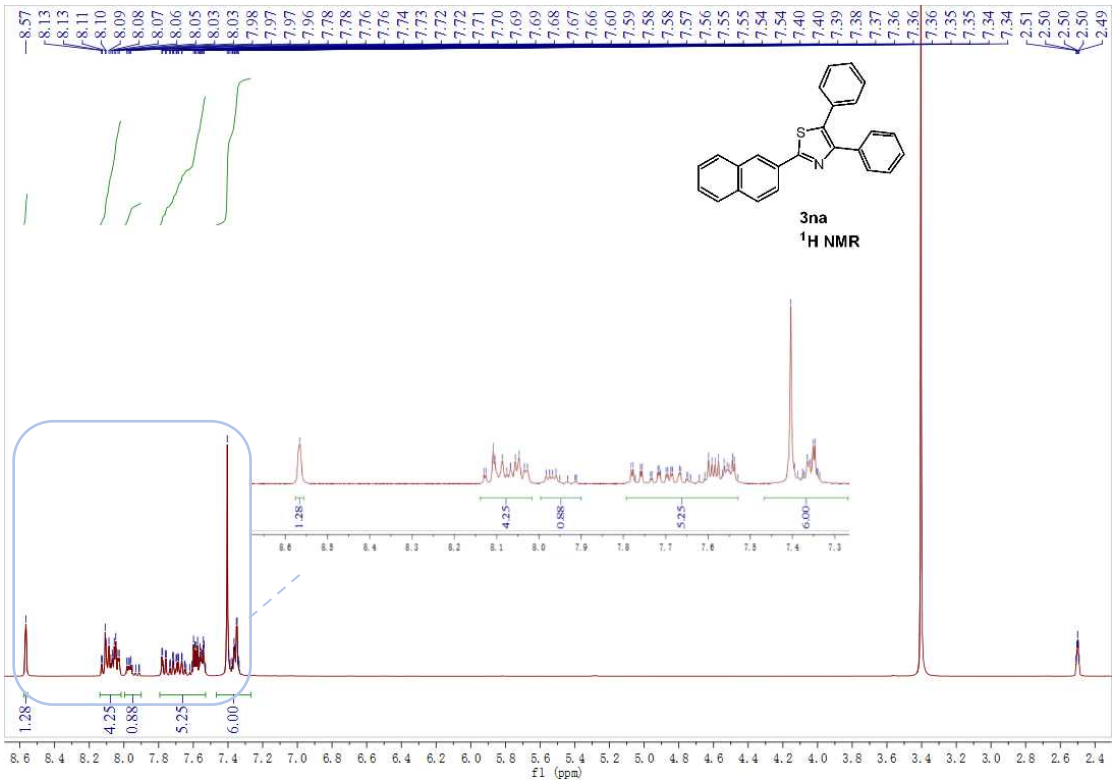
^{13}C NMR
f1 (ppm)


3ma
1H NMR
f1 (ppm)


3ma
13C NMR
f1 (ppm)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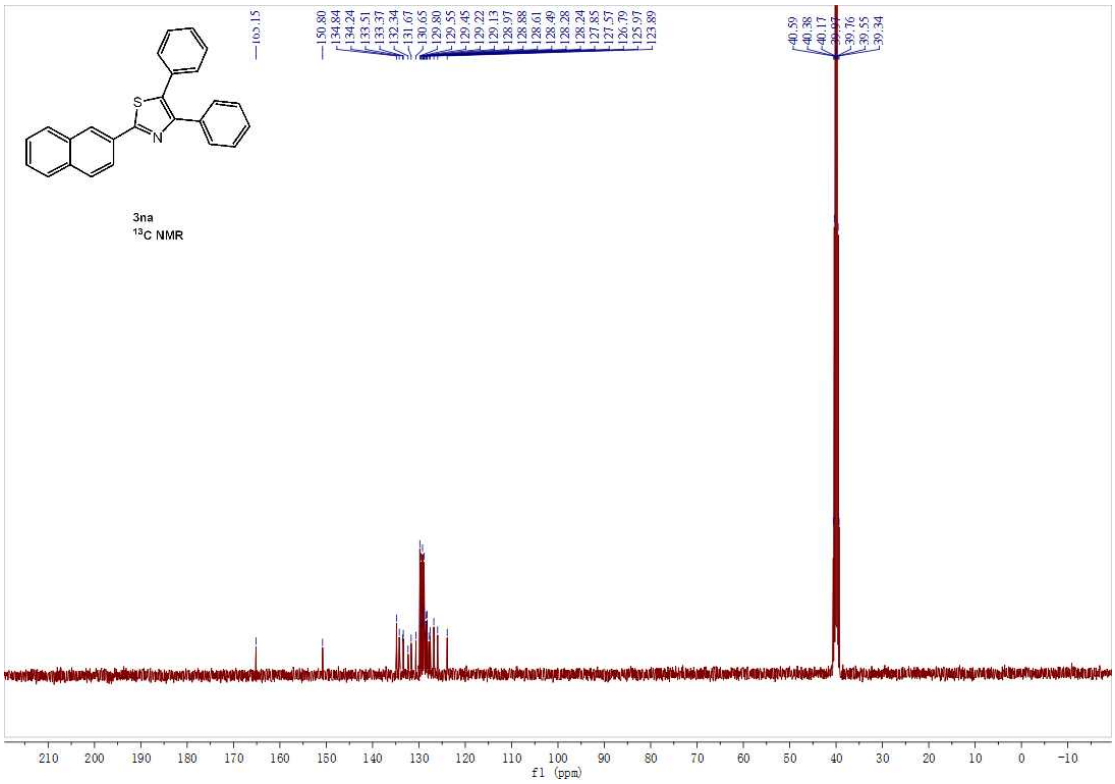
^{1}H NMR
f1 (ppm)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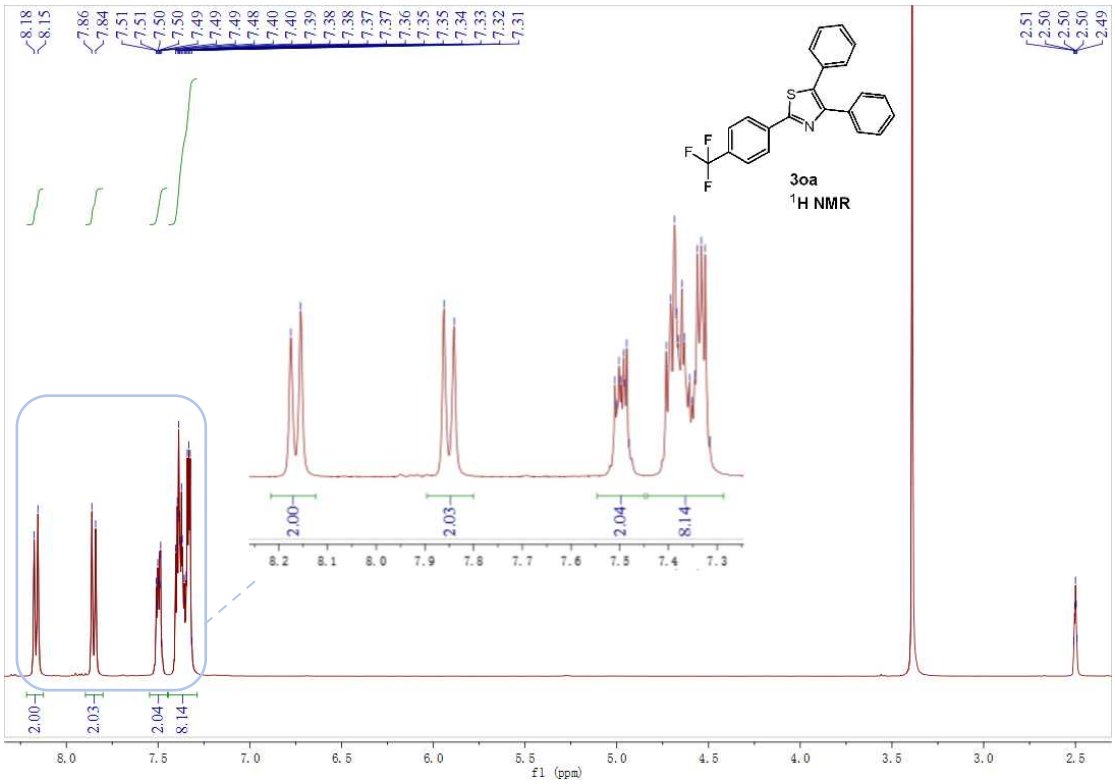
^{13}C NMR
f1 (ppm)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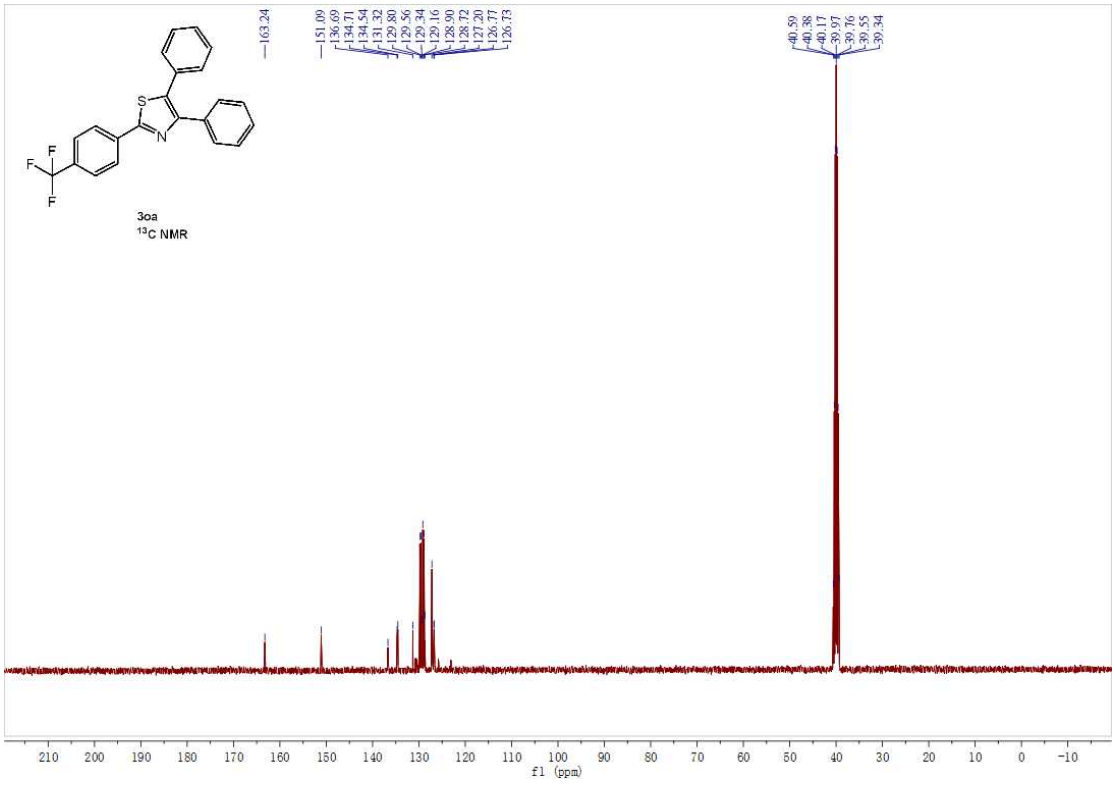
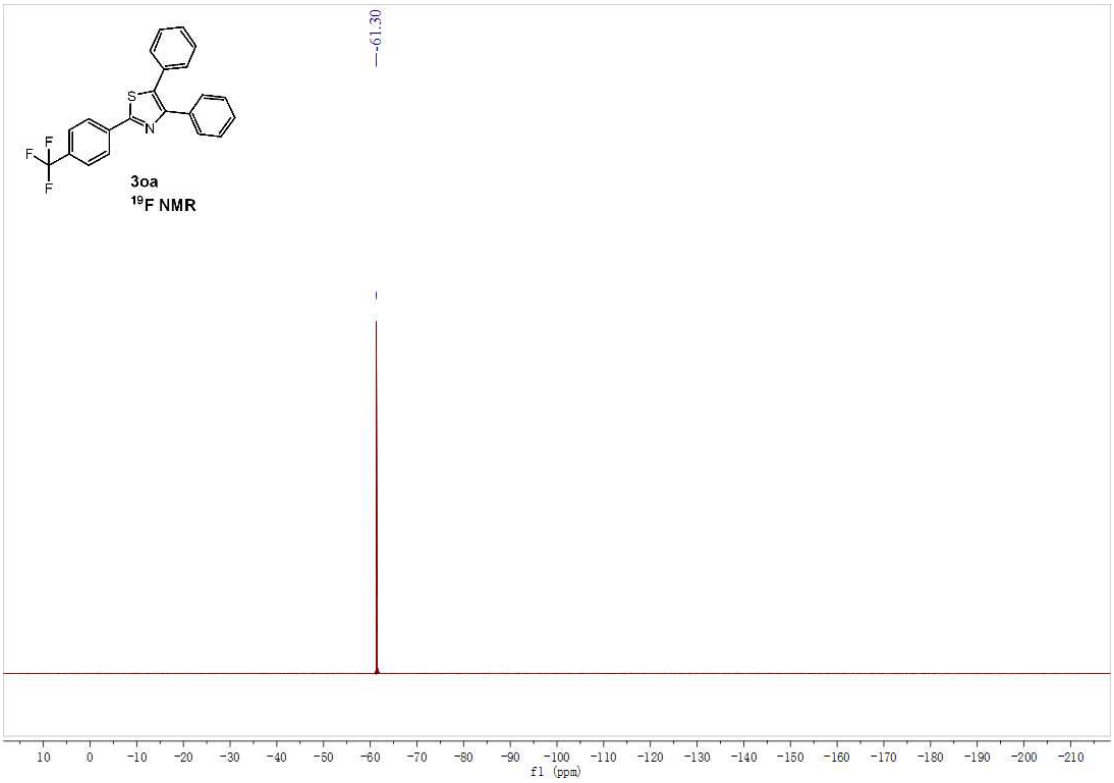
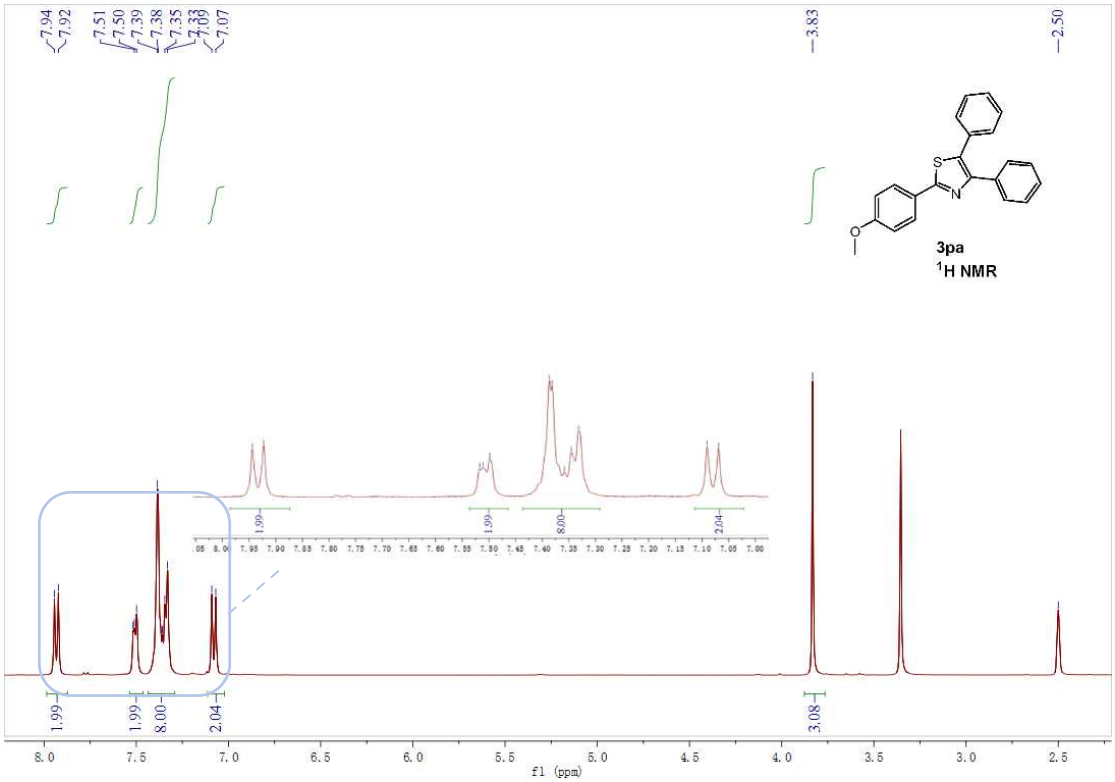
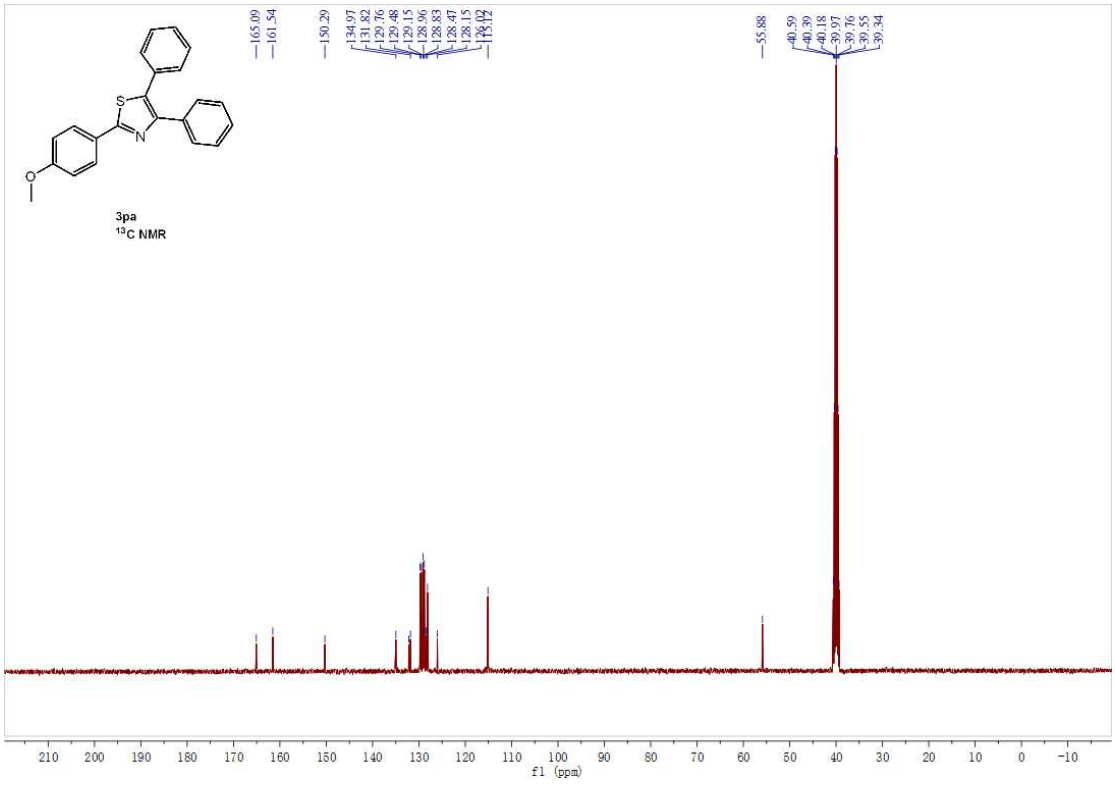
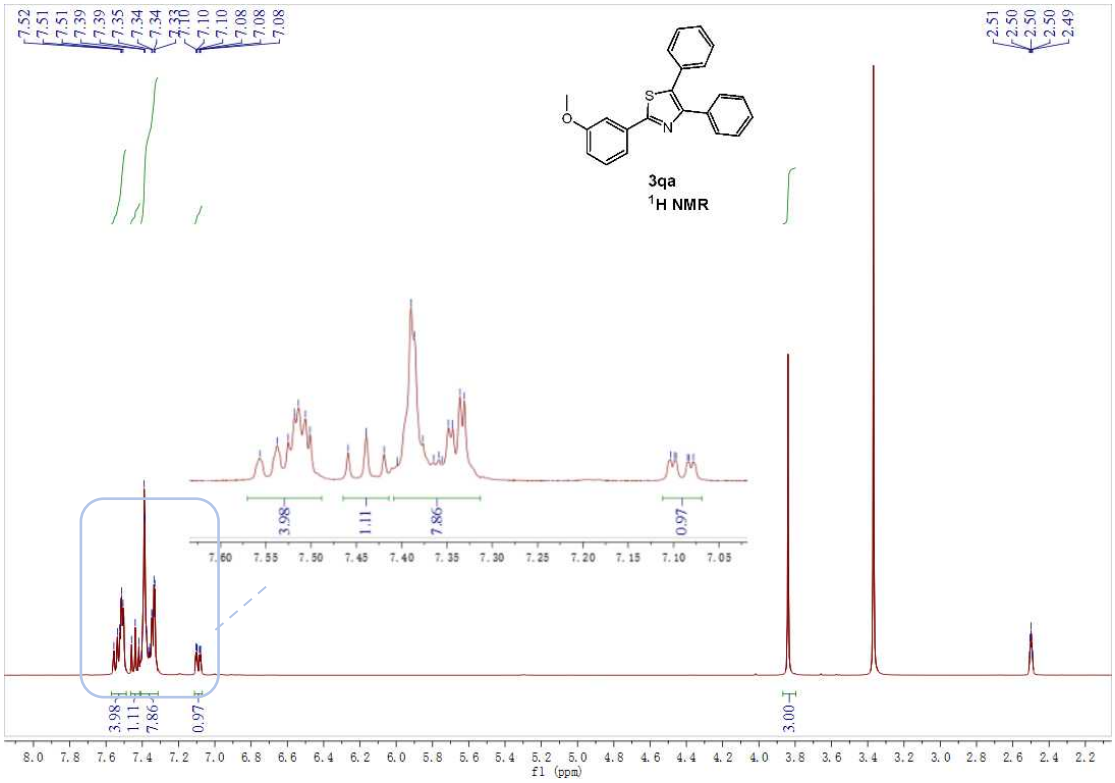
1H NMR
f1 (ppm)

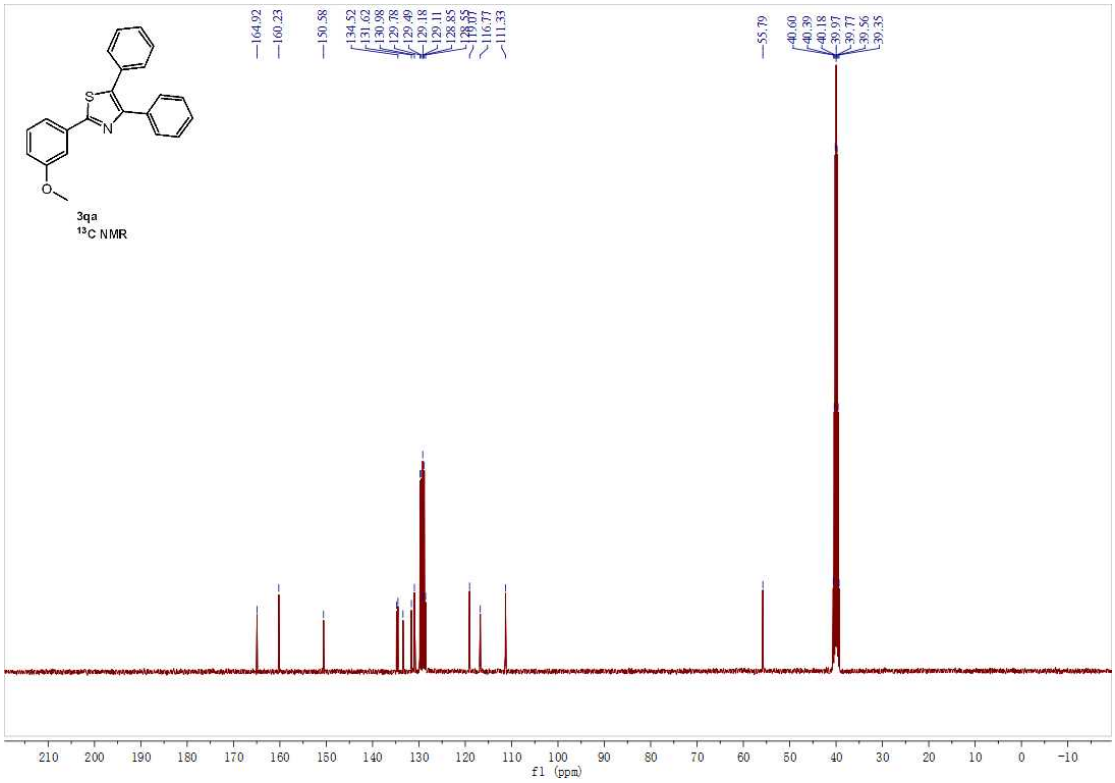

3oa
13C NMR
f1 (ppm)

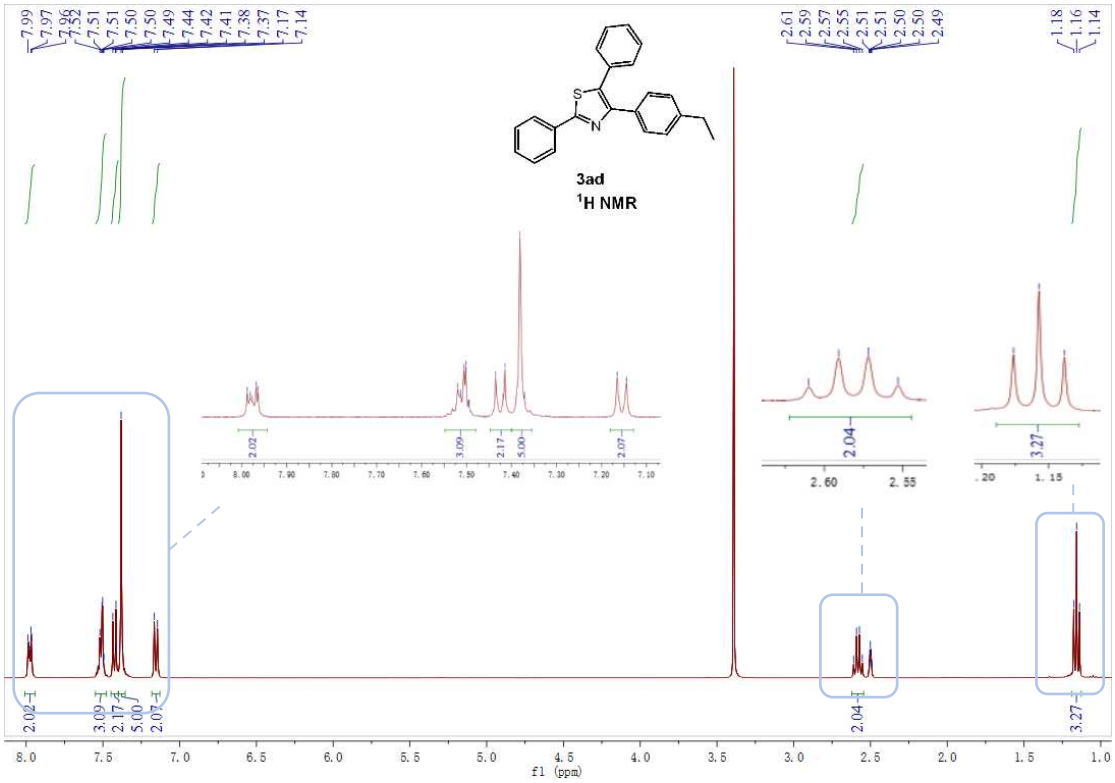

-61.30
S
N
F
F
F
3oa
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

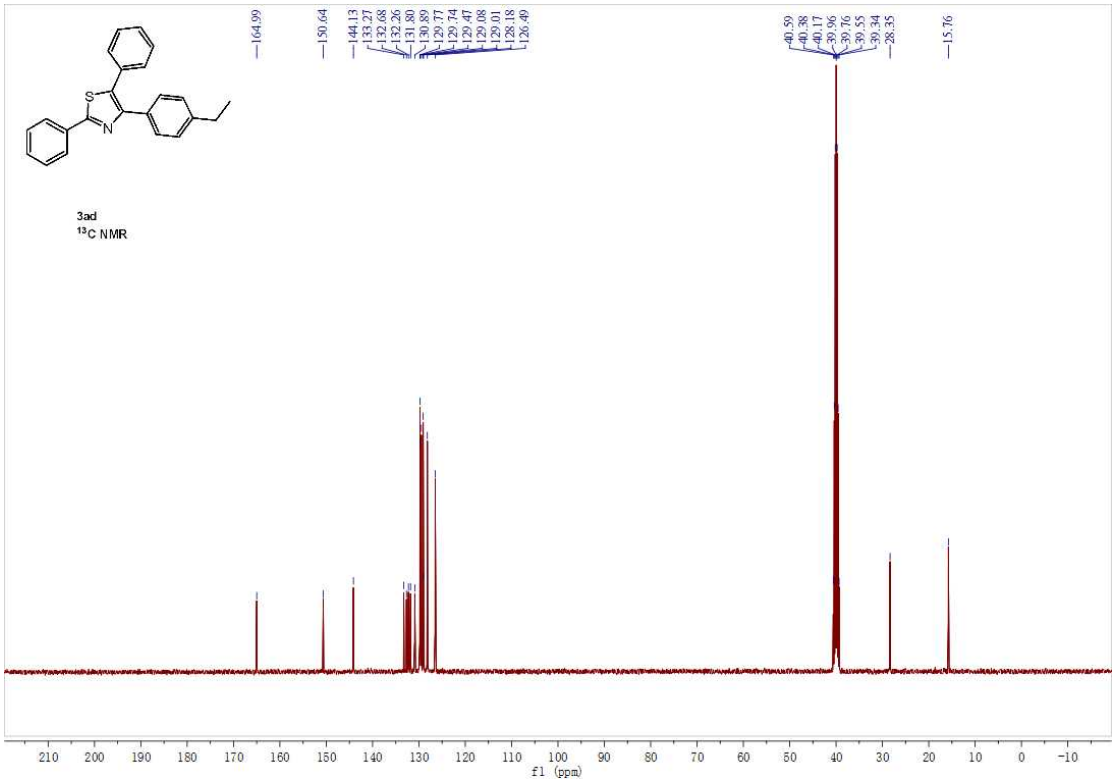

7.94
7.92
7.51
7.50
7.39
7.38
7.35
7.33
7.08
7.07
3.83
2.50
3pa
^{1}H NMR
1.99
1.99
8.00
2.04
3.08
f1 (ppm)


165.09
161.54
150.29
134.97
131.82
129.76
129.48
129.15
128.96
128.83
128.47
128.15
55.88
40.59
40.39
40.18
39.97
39.76
39.55
39.34
3pa
^{13}C NMR
f1 (ppm)


3qa
1H NMR
f1 (ppm)


3qa
13C NMR
f1 (ppm)


3ad
1H NMR
f1 (ppm)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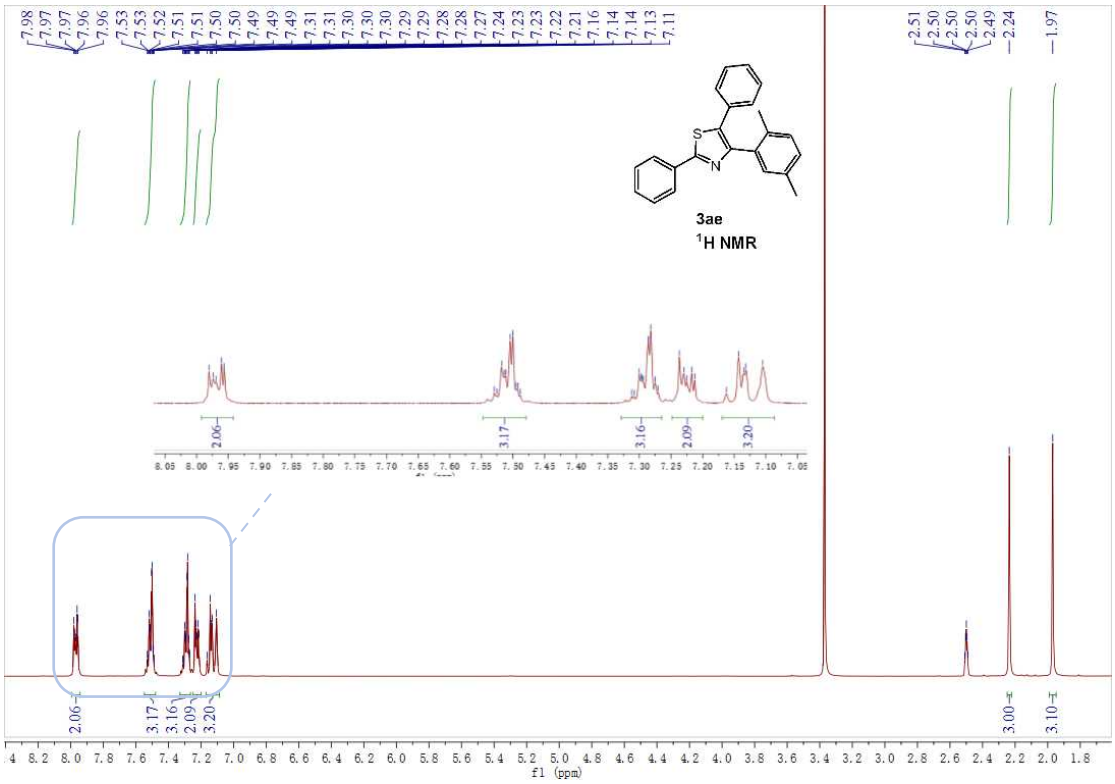
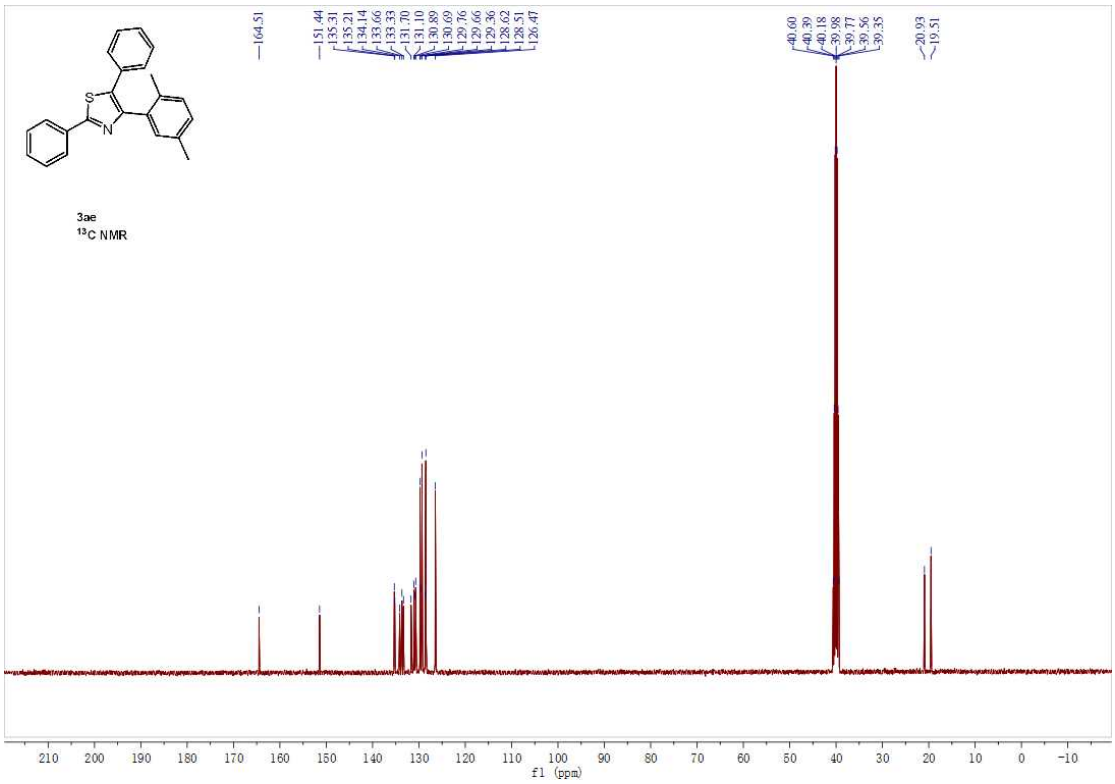
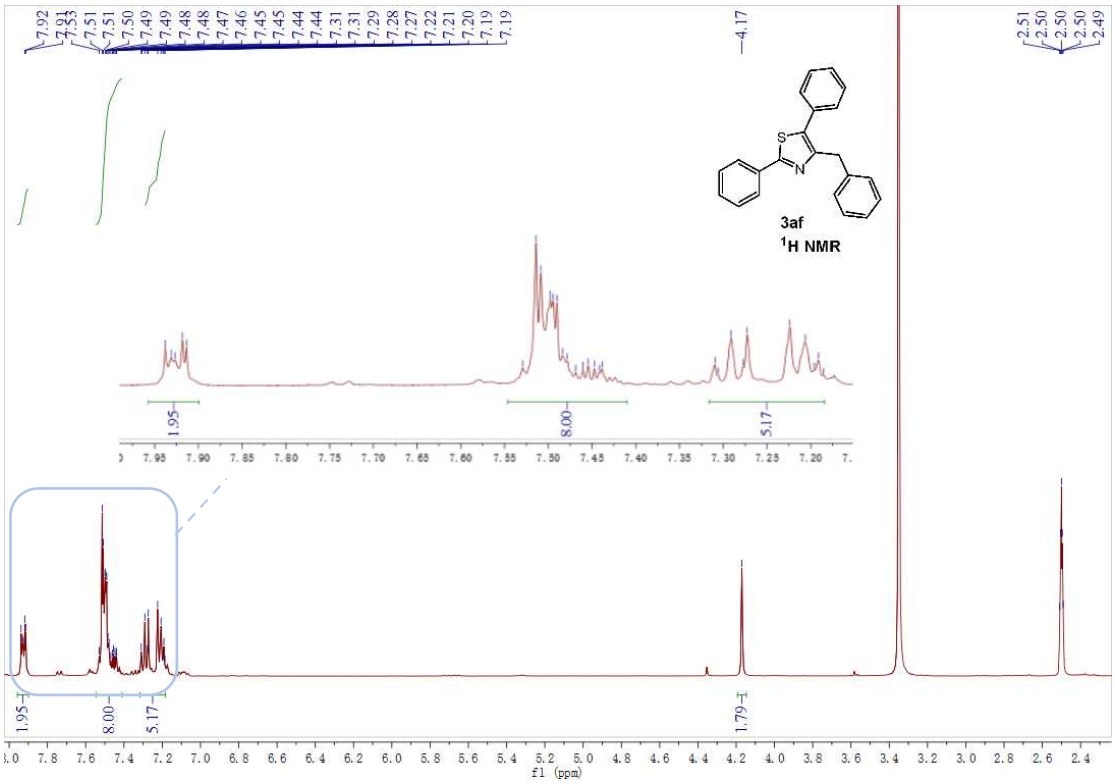
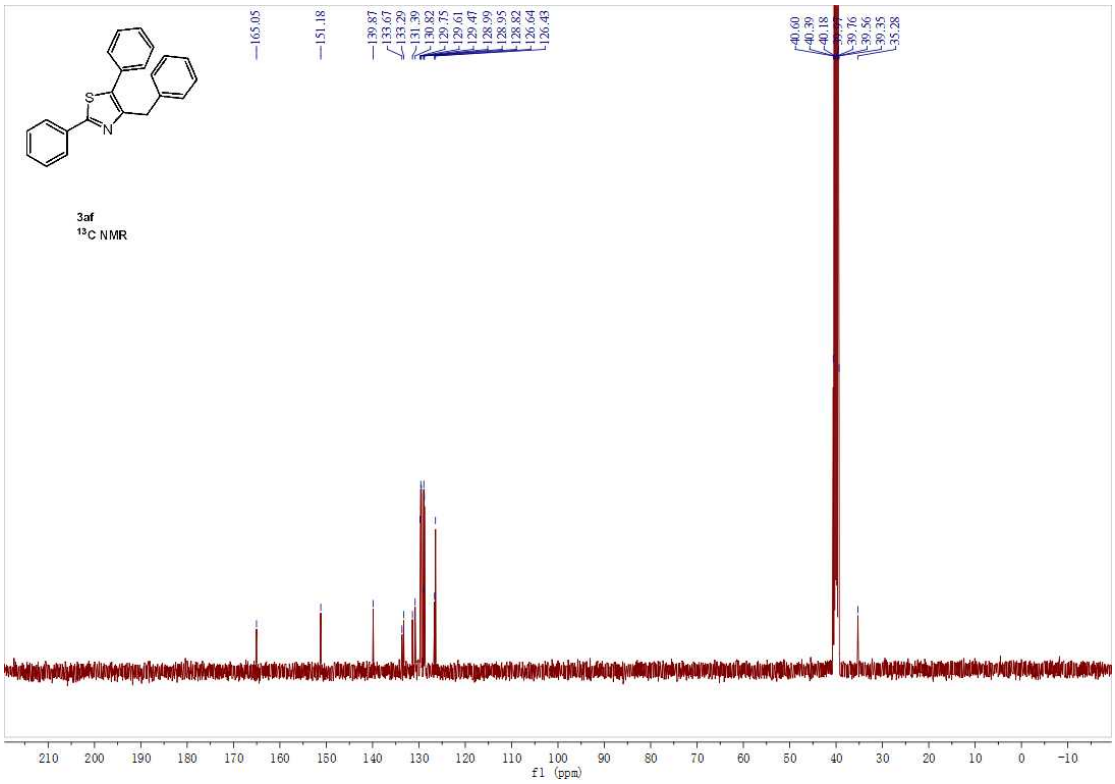
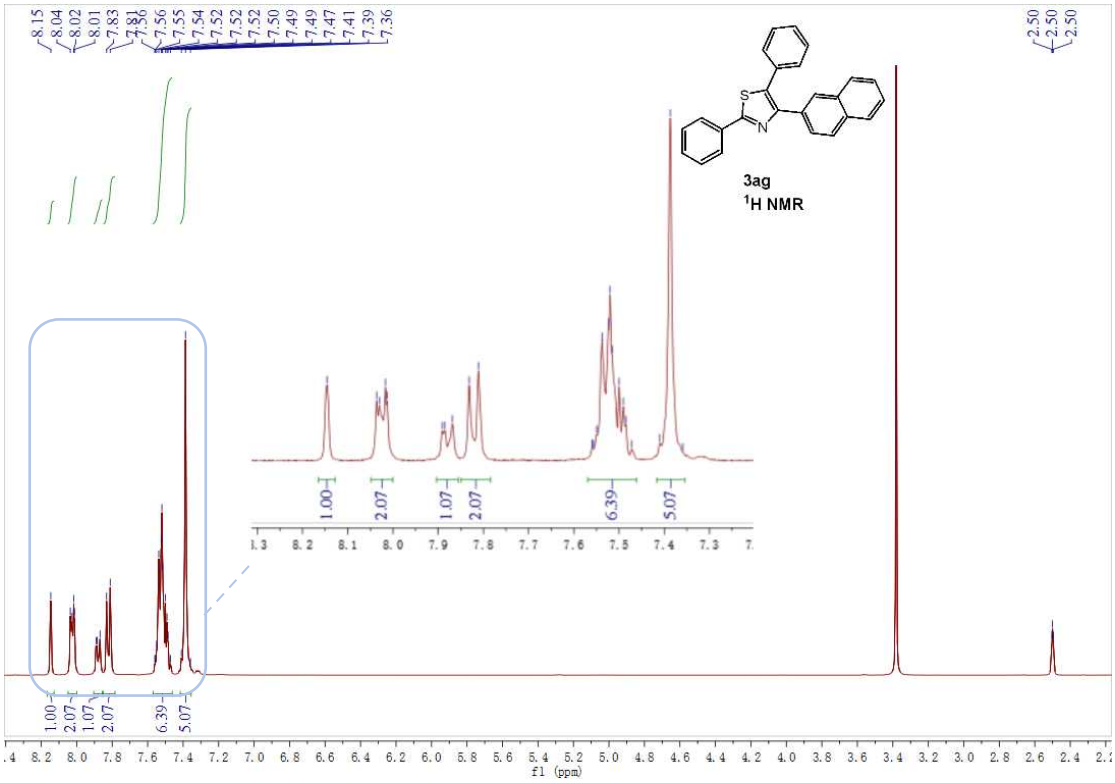
13C NMR
f1 (ppm)

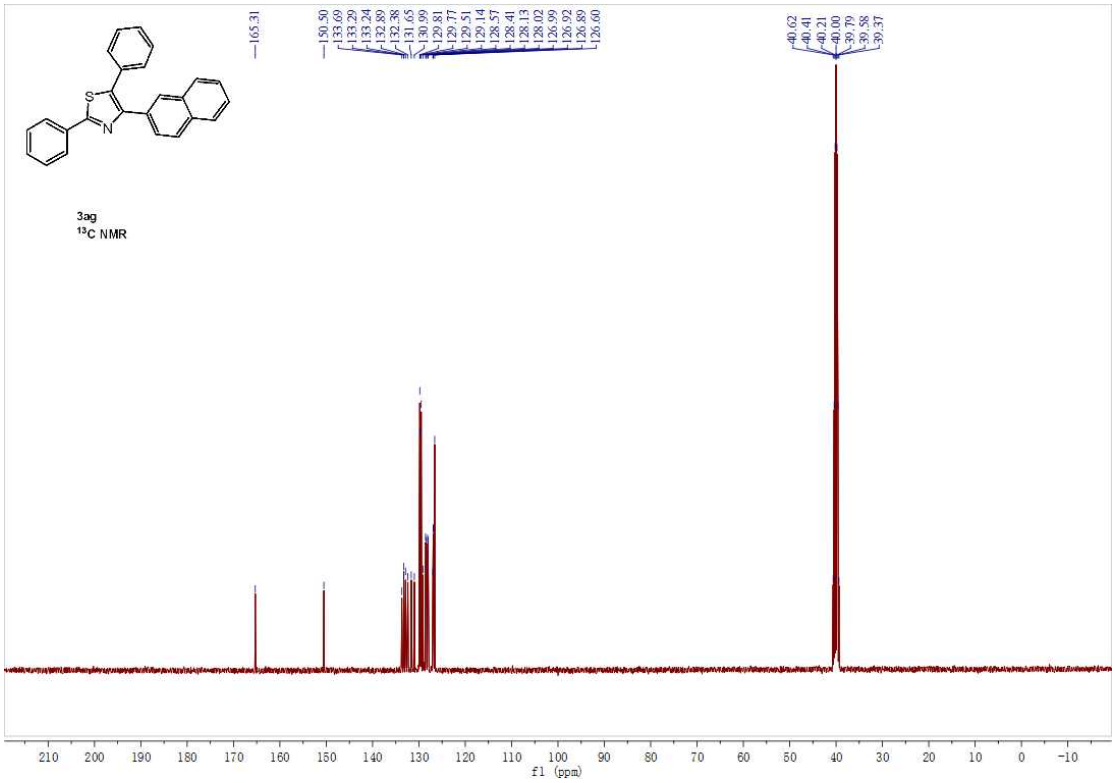

3ae
^{1}H NMR
f1 (ppm)


3ae
^{13}C NMR
f1 (ppm)


3af
^{1}H NMR
f1 (ppm)


3af
^{13}C NMR
f1 (ppm)


3ag
1H NMR
f1 (ppm)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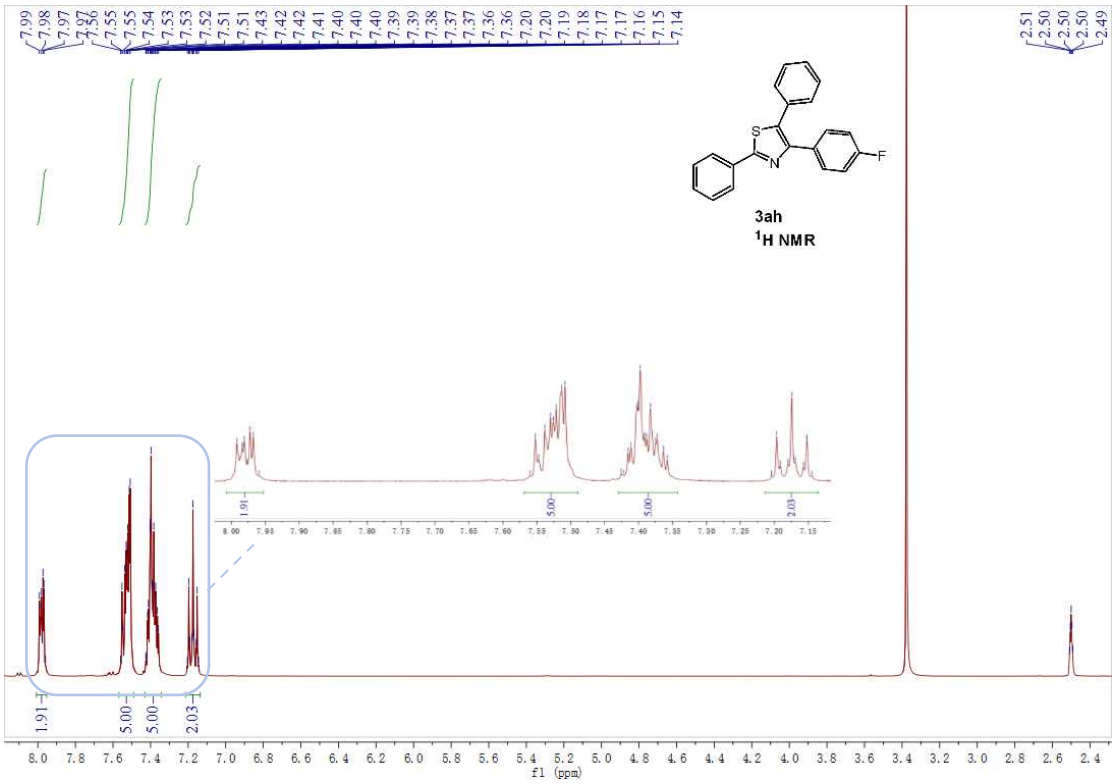
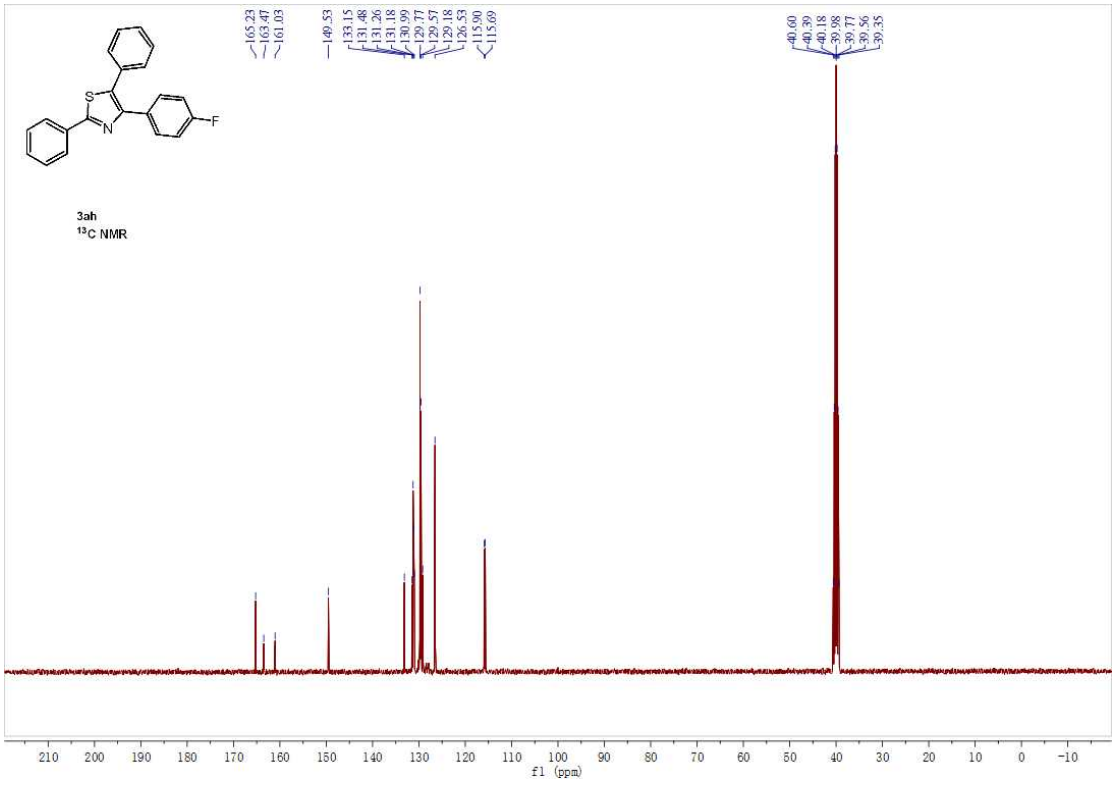
13C NMR
f1 (ppm)


3ah
1H NMR
f1 (ppm)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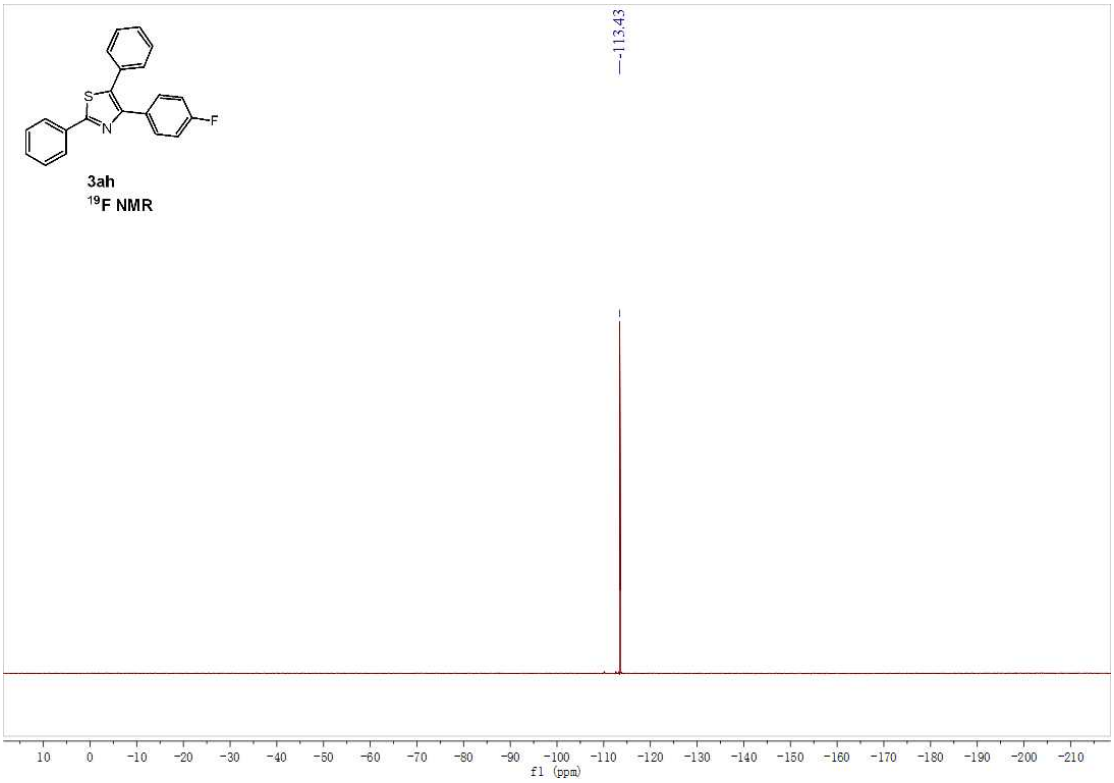
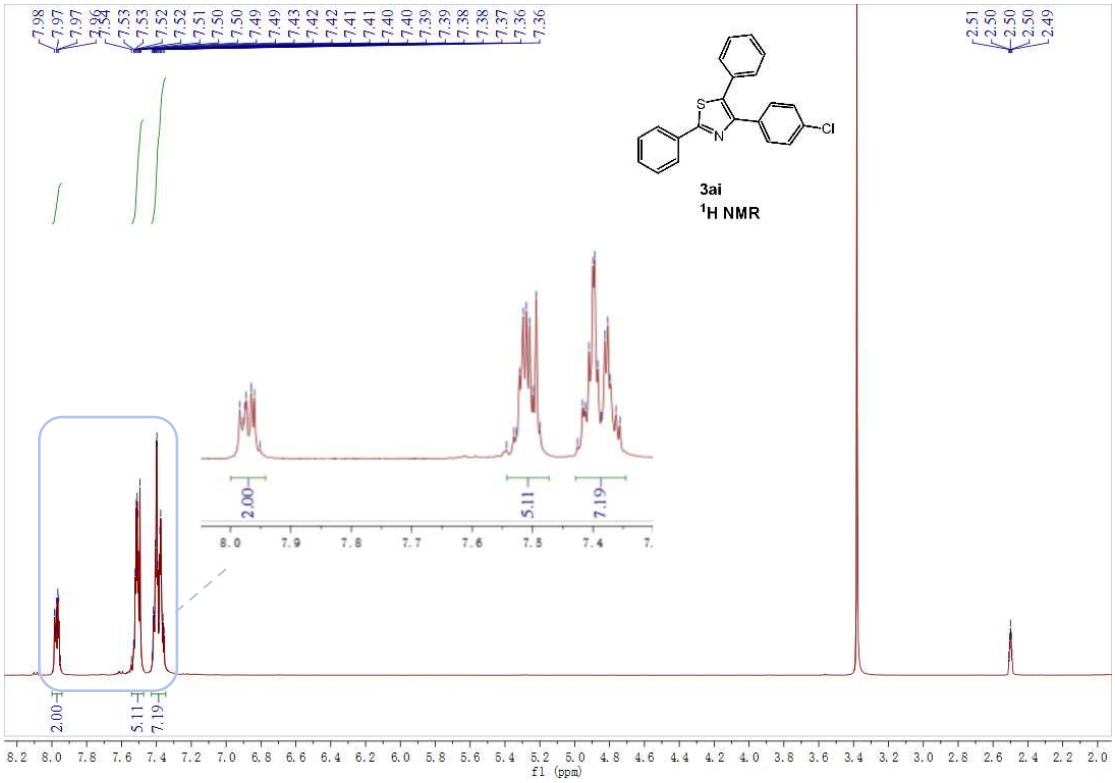
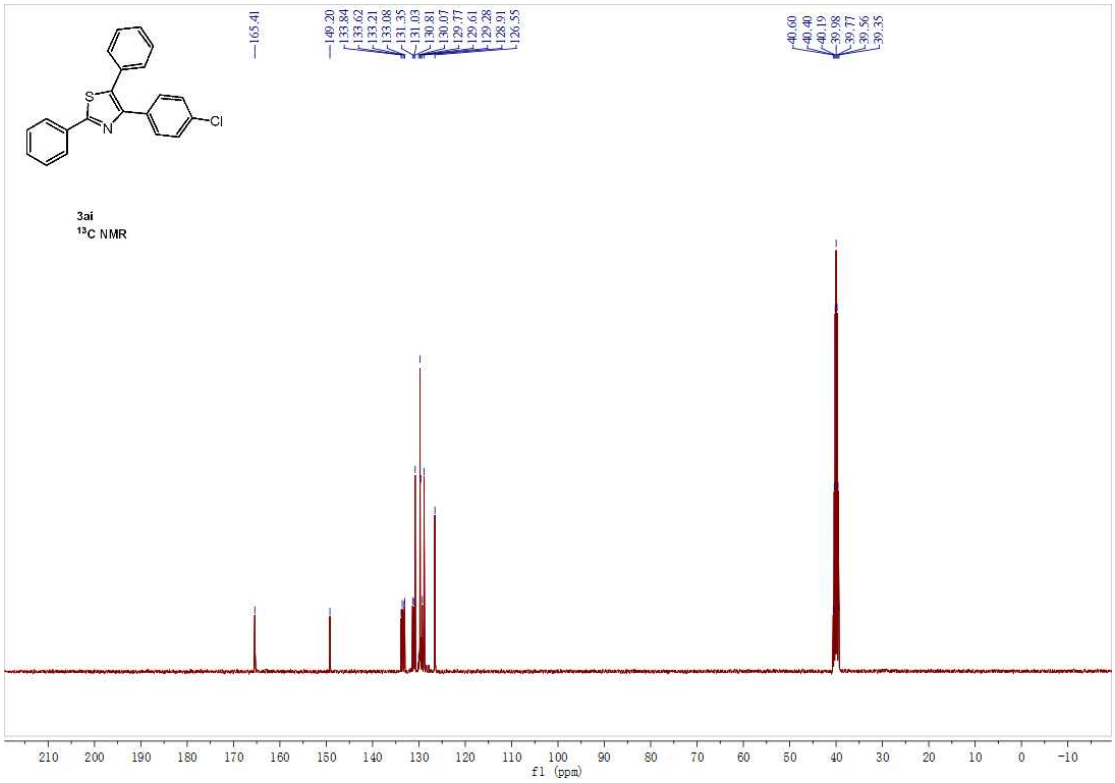
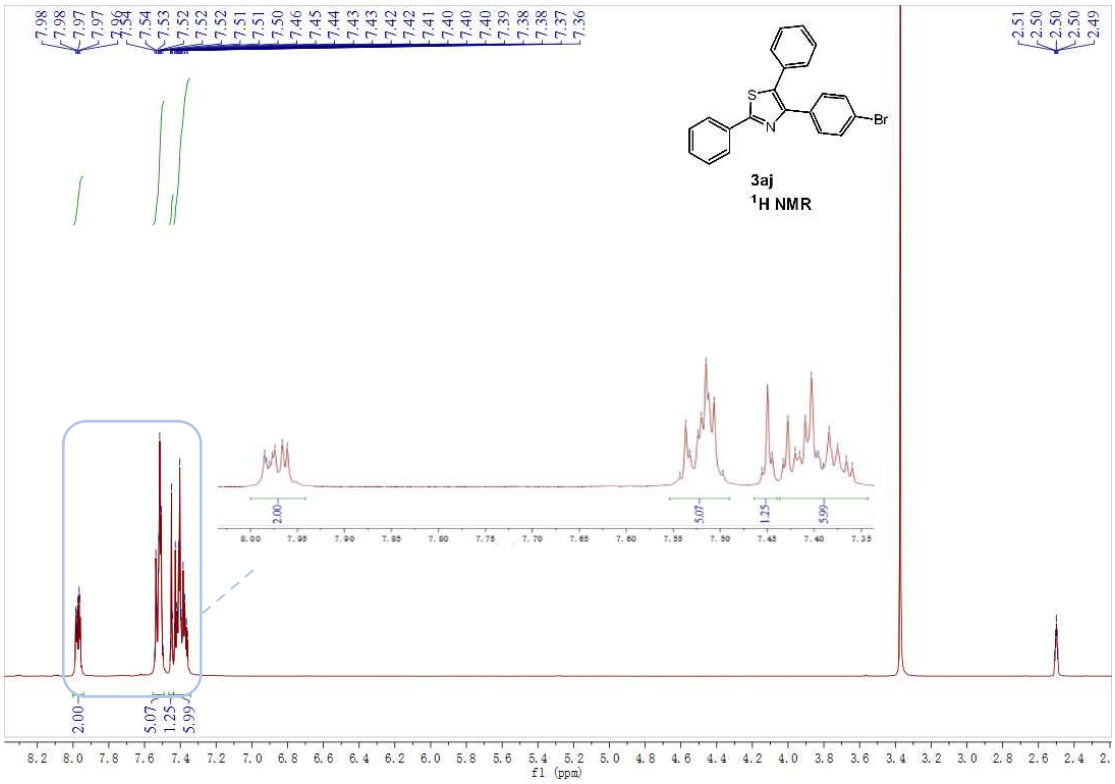
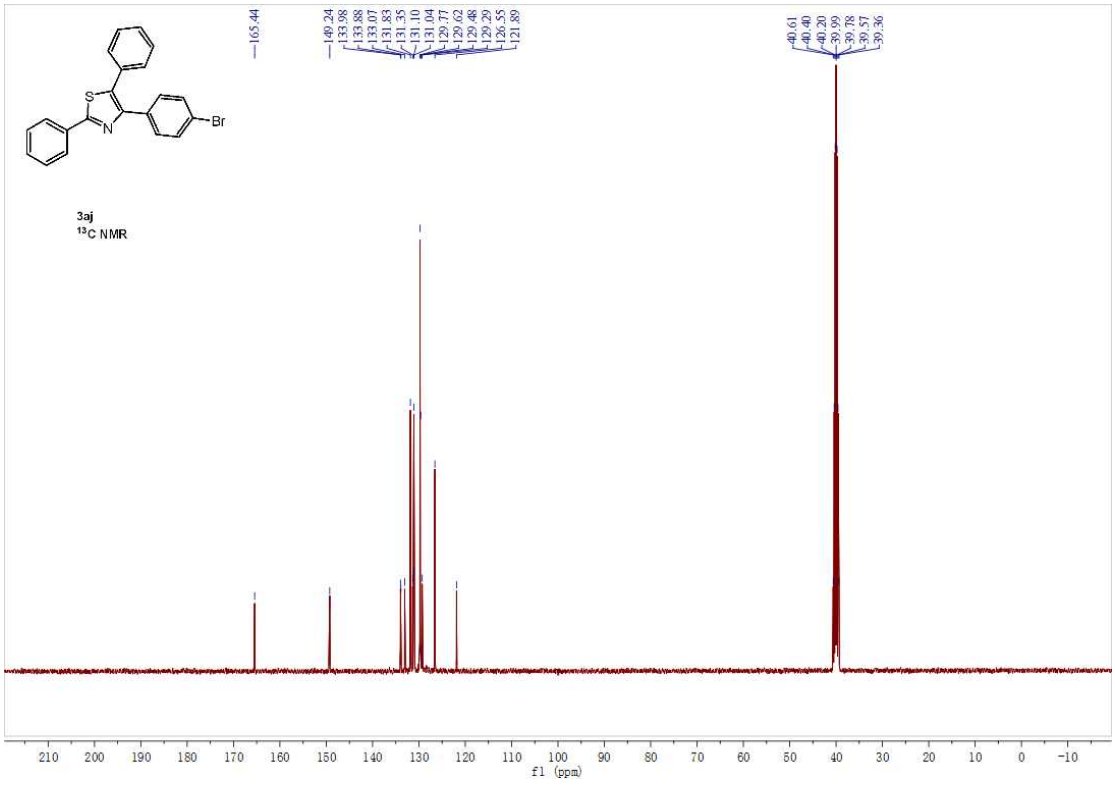
13C NMR
f1 (ppm)


-113.43
S
N
F
3ah
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


3ai
1H NMR
f1 (ppm)


3ai
13C NMR
f1 (ppm)


3aj
1H NMR
f1 (ppm)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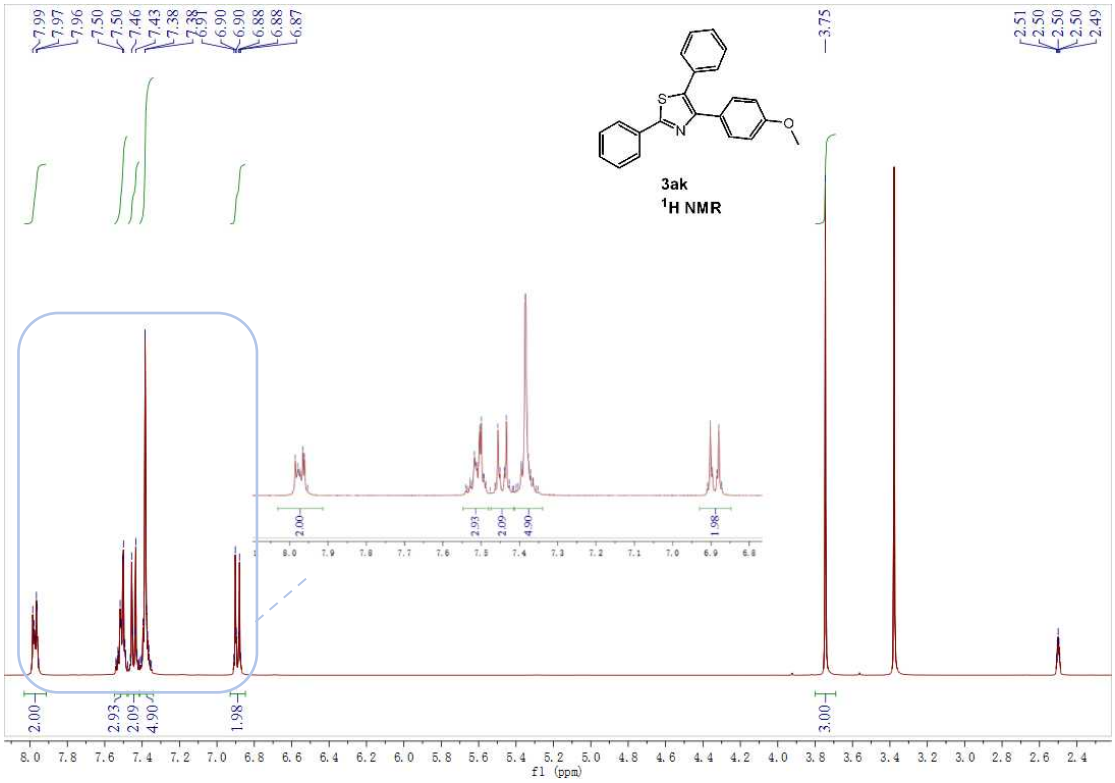
13C NMR
f1 (ppm)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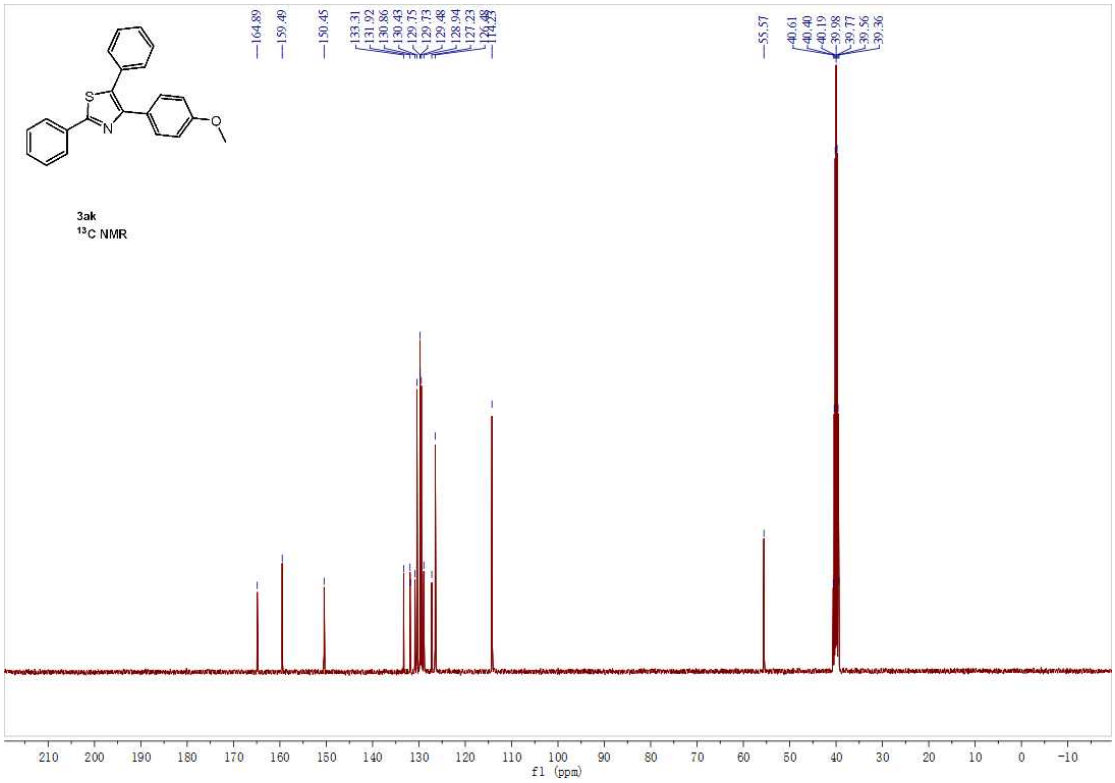
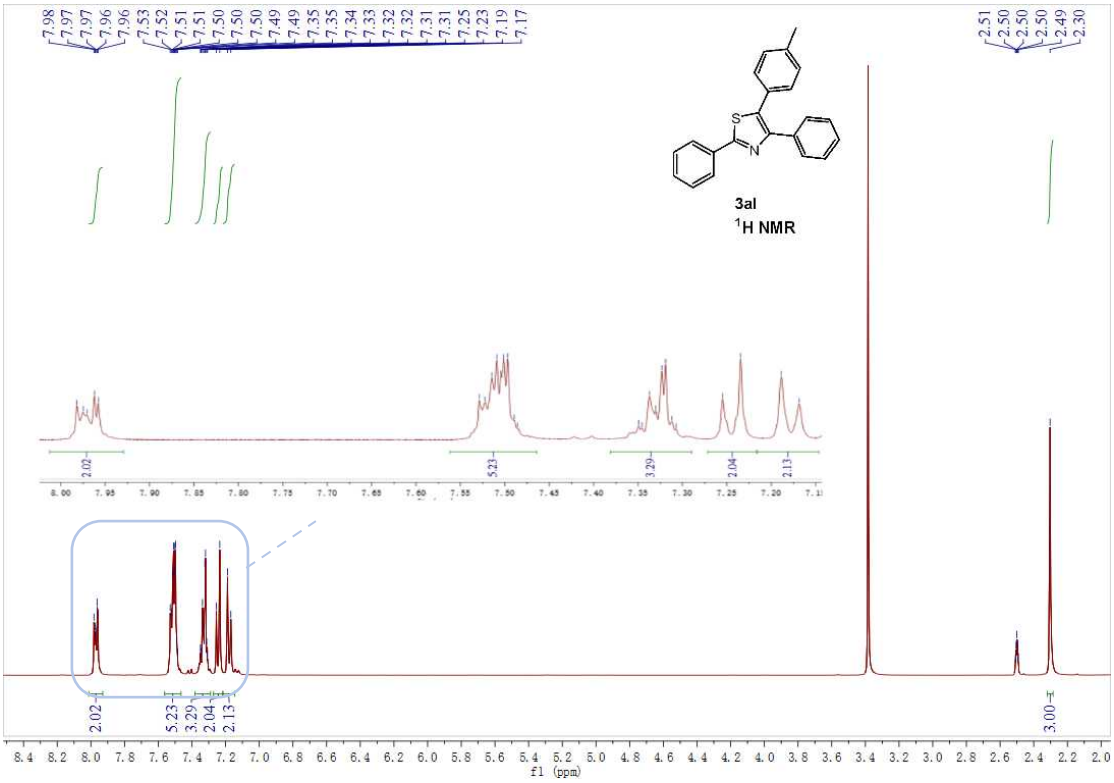
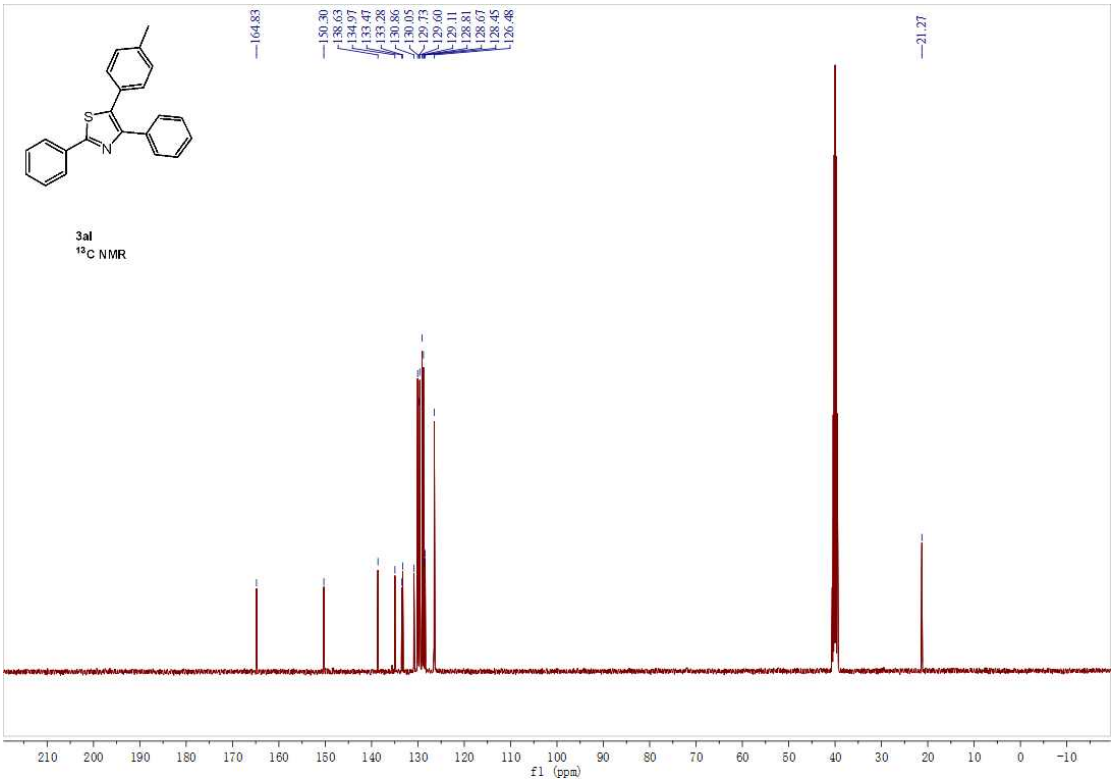
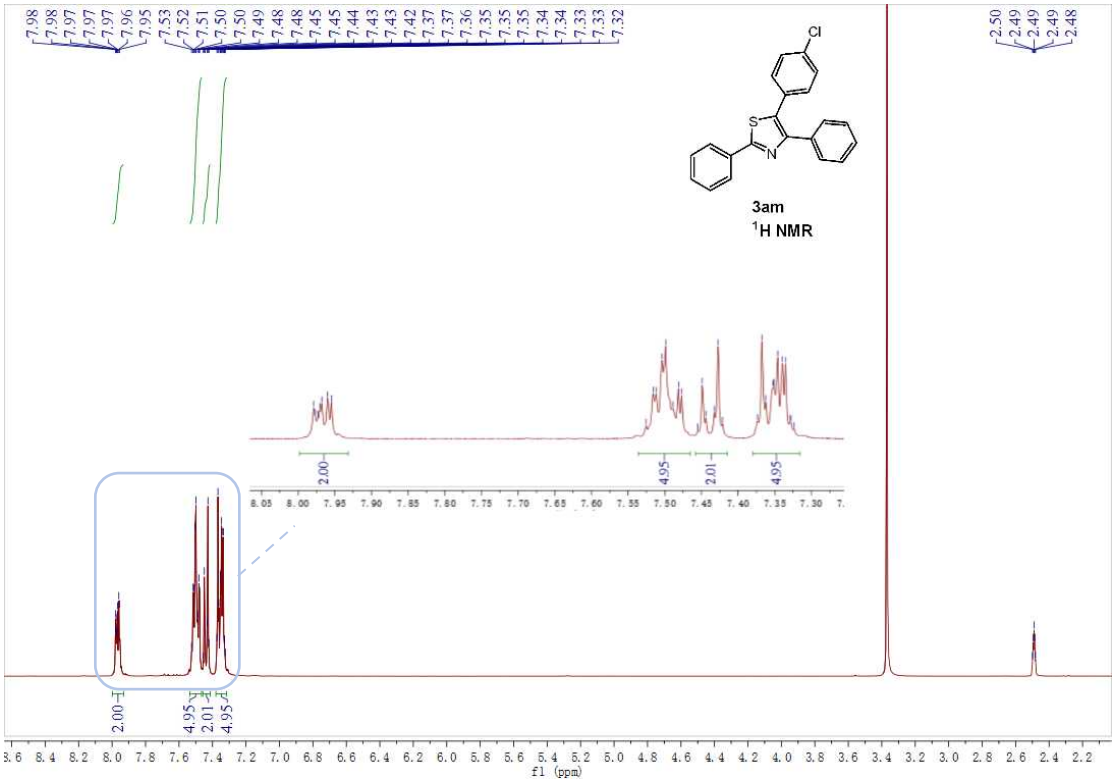
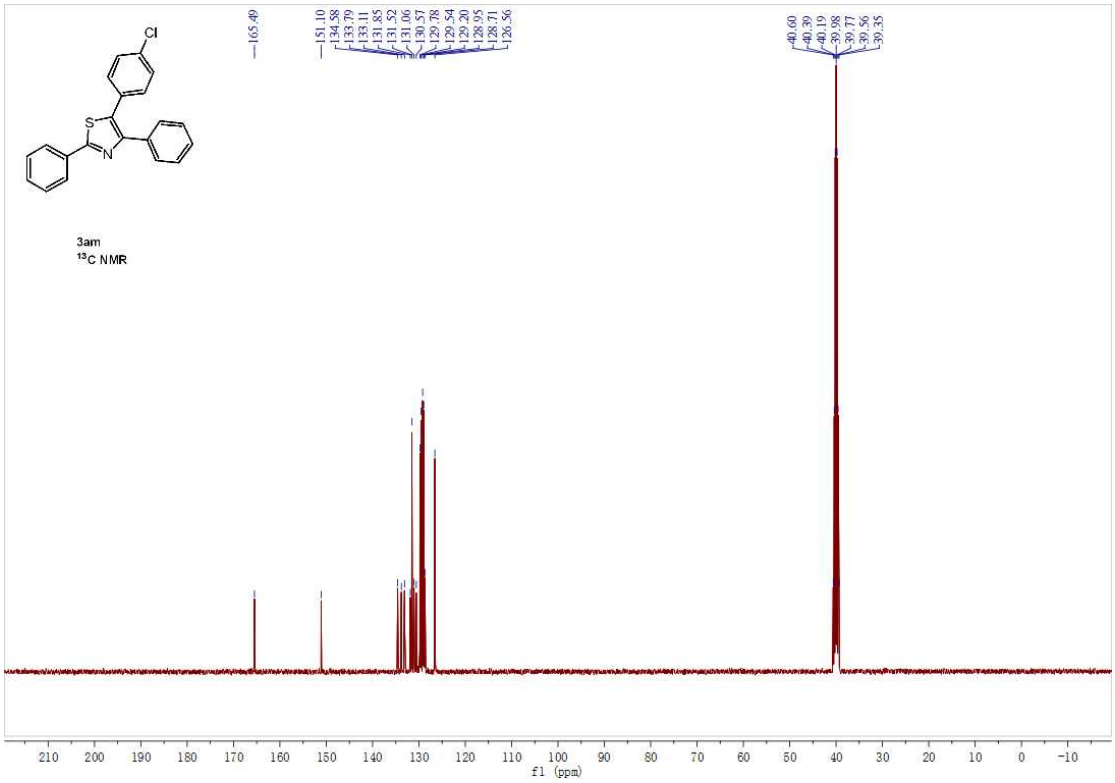
1H NMR
f1 (ppm)


3ak
13C NMR
f1 (ppm)


3al
^{1}H NMR
f1 (ppm)


3al
^{13}C NMR
f1 (ppm)


3am
^{1}H NMR
f1 (ppm)


3am
^{13}C NMR
f1 (ppm)