Visible Light Driven via Photoredox/Nickel-Catalyzed stereoselective Synthesis of Z- or E-Vinyl Thioethers from Thiosilane and Terminal Alkynes

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Supplementary Information

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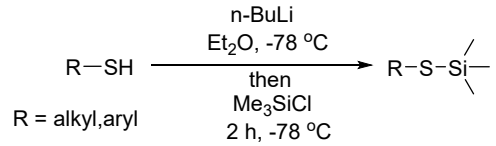
1. General information

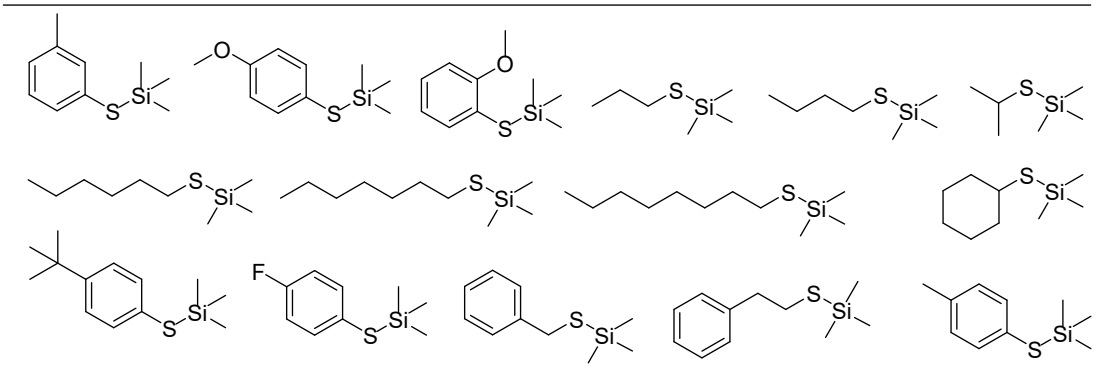
Commercial reagents were purchased from Aldrich, TCI, J&K chemical, and were used as received. All experiments were carried out under a nitrogen atmosphere, all solvents and reagents were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz Spectrometer (^{1}H 400 MHz, ^{13}C 101 MHz). All chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual $CDCl_3$ (7.26 ppm) as internal standards. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.00 ppm) as internal standards. ^{19}F NMR chemical shifts were externally referenced to CCl_3F (0 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, qd = quadruple doublet, dt = double triplet, and m = multiplet. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. All reactions were monitored by thin-layer chromatography (TLC) on gel F254 plates using UV light as the visualizing agent, and the products were purified by flash column chromatography on silica gel (200–300 meshes) from the Qingdao Marine Chemical Factory in China. All allylic carbonates were prepared using standard literature procedures or the preparation procedures descried in this supporting information. All vinyl triflates were prepared using standard literature procedures.

2. Preparation of substrates

General Procedure for Preparation of trimethylsilyl thioethers



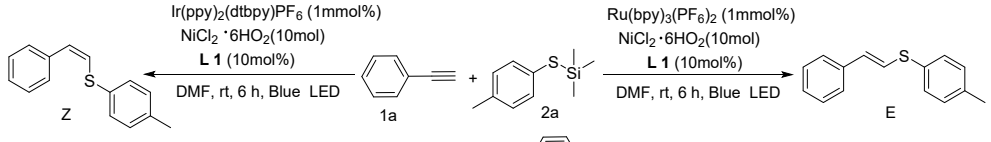
The compounds substrates were synthesized by a literature procedure. To a 100 mL round bottom flask equipped with a magnetic stir bar, the solution of thiol (20 mmol) in diethyl ether (21 mL) was added slowly 1.6 M n-butyl lithium in hexane (22 mmol) dropwise at -78 °C. Chlorotrimethylsilane (22 mmol) was added dropwise to the reaction mixture at -78 °C. Then, the reaction mixture was stirred at room temperature for 4 h， then was added hexane (13 mL). The mixture was evaporated and the precipitated solid was filtered off. The organic layer was evaporated and the residue was purified by distillation under reduced pressure to give the corresponding product.

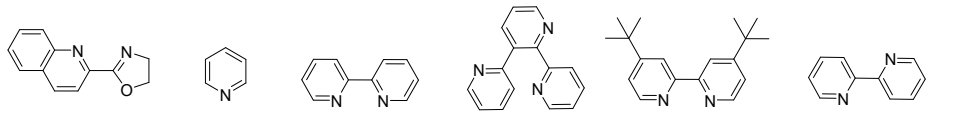


Compounds prepared according to literature.[a,b]

3. Determination of the optimal reaction conditions

Table S1. The effect of different ligand.[a]



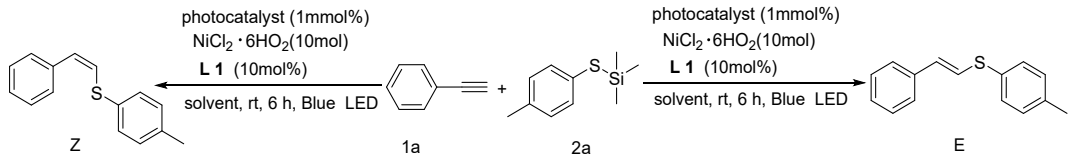


L 1 = 2-(4,5-Dihydro-2-oxazolyl)quinoline **L 2** = Py **L 3** = 1,10-phen **L 4** = terpyridine **L 5** = dtbbpy **L 6** = 2,2'-bipyridine

Entry	photocatalyst	phosphine	Yield %	E/Z
1	$Ru(bpy)_3(PF_6)_2$	2-(4,5-Dihydro-2-oxazolyl)quinoline	96	90/10
2	$Ru(bpy)_3(PF_6)_2$	Py	40	58/42
3	$Ru(bpy)_3(PF6)_2$	1,10-phen	48	60/40
4	$Ru(bpy)_3(PF6)_2$	terpyridine	55	58/42
5	$Ru(bpy)_3(PF6)_2$	dtbbpy	48	60/40
6	$Ru(bpy)_3(PF6)_2$	2,2'-bipyridine	72	65/35
7	$Ir(ppy)_2(dtppy)PF_6$	2-(4,5-Dihydro-2-oxazolyl)quinoline	92	88/12

Reaction conditions: 1a (0.1 mmol), 2a (0.15 mmol), photocatalyst (1 mol), $NiCl_2 \cdot 6H_2O$ (10 mol%), **L 1** (10 mol%), in dry solvent [0.1M] at room temperature with the irradiation of a blue LED for 6 h 90 W blue LEDs. Isolated yields. The Z/E ratios were determined by ^1H NMR spectroscopy.

Table S2. The effect of different solvent

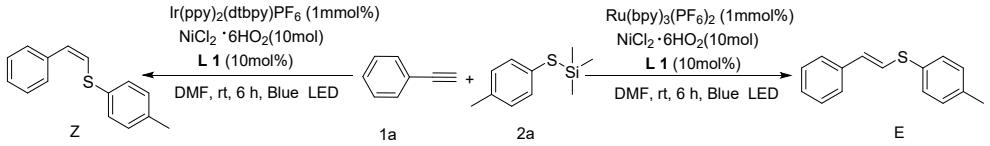


Entry	photocatalysts	solvent	Yield %	E/Z
1	$Ru(bpy)_3(PF_6)_2$	NMP	15	50/50
2	$Ru(bpy)_3(PF_6)_2$	2-Methyltetrahydrofuran	36	52/48
3	$Ru(bpy)_3(PF_6)_2$	THF	24	60/40
4	$Ru(bpy)_3(PF_6)_2$	EtOH	18	52/48
5	$Ir(ppy)_2(dtbpy)PF_6$	NMP	40	53/47
6	$Ir(ppy)_2(dtbpy)PF_6$	2-Methyltetrahydrofuran	35	60/40
7	$Ir(ppy)_2(dtbpy)PF_6$	THF	42	62/38
8	$Ir(ppy)_2(dtbpy)PF_6$	EtOH	20	70/30

Reaction conditions: 1a (0.1 mmol), 2a (0.15 mmol), photocatalyst (1 mol), $NiCl_2 \cdot 6H_2O$ (10 mol%), L 1 (10 mol%),

in dry solvent [0.01M] at room temperature with the irradiation of a blue LED for 6 h 90 W blue LEDs. Isolated yields. The Z/E ratios were determined by ^{1}H NMR spectroscopy.

Table S3. The effect of light sources



Entry	Light source	Yield %	E/Z
1	90 W blue LED	96	90/10
2	10 W 460-465 nm LED	36	45/55
3	10 W 365-367 nm LED	24	40/60
5	5 W CFL	18	50/50
6	Sun light	trace	--

Reaction conditions: 1a (0.1 mmol), 2a (0.15 mmol), photocatalyst (1 mol), $NiCl_2 \cdot 6H_2O$ (10 mol%), L 1 (10 mol%), in dry solvent [0.01M] at room temperature with the irradiation of a blue LED for 6 h 90 W blue LEDs. Isolated yields. The Z/E ratios were determined by ^{1}H NMR spectroscopy.

Supplementary Figure 1. The effect of light sources

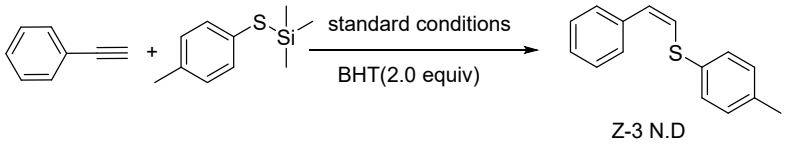
4. Reference

(a) J. R. Combs, Y.C. Lai, and D. L. V. Vranken, *Org. Lett*. **2021**, *23*, 284.

(b) M. Mesgar, J. N. Le, and O, Daugulis, *J. Am. Chem. Soc.* **2018**, *140*, 13703.

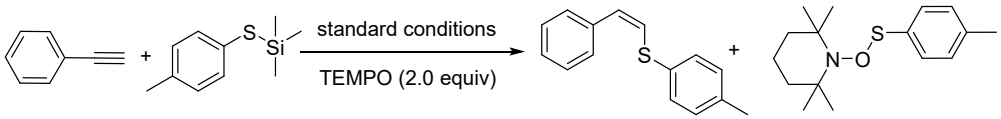
5. Mechanistic Studies

a) BHT-capture experiment



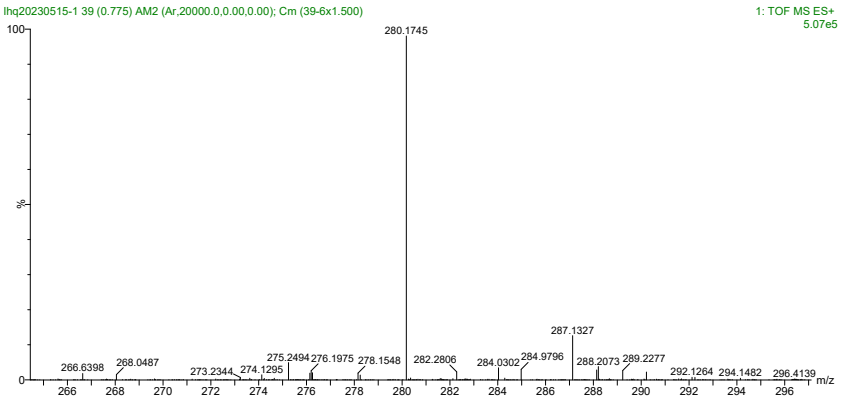
The reaction was conducted under the optimized standard conditions in the presence of 2.0 equiv of BHT as a radical scavenger. Under such conditions, the corresponding product Z-3 was not observed.

b) TEMPO Trapping Experiment



The reaction was conducted under the optimized reaction conditions in the presence of 2.0 equivalents of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as a radical scavenger. Under such conditions, the corresponding product Z-3 was not observed, while the TEMPO-trapping product was found by HRMS (ESI), which suggests a radical pathway.

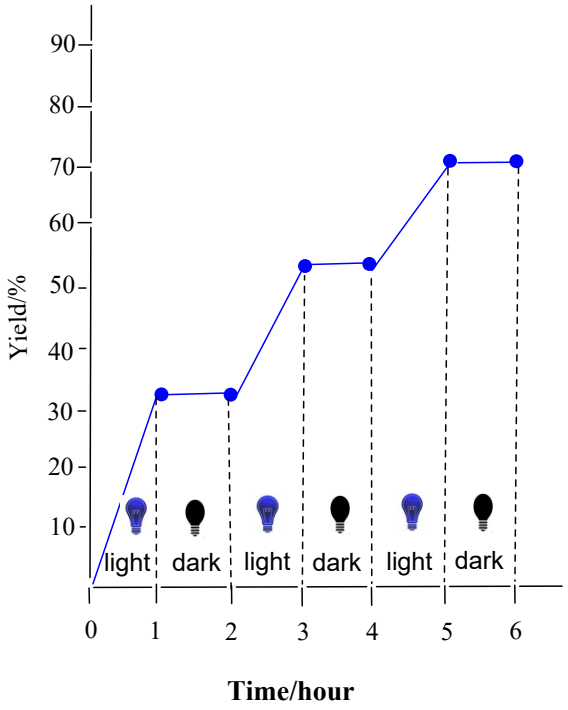
HRMS (ESI+): m/z: $[M + H]^+$ Calc. for $C_{16}H_{26}NOS^+$ 280.1730; Found 280.1745.



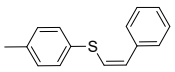
c) light on/off experiment

Five standard reaction mixtures of a flame-dried 8 mL reaction vial were charged with $Ru(bpy)_3(PF_6)_2$ (1 mol%), $NiCl_2 \cdot 6H_2O$ (10 mol%), **L 1** (10 mol%), and a magnetic stir bar. DMF (0.1 M) was added. The reaction mixture was degassed by nitrogen sparging for 30 min, followed by the addition of thiosilane (0.1 mmol, 1.0 equiv) and alkynes (0.15 mmol, 1.5 equiv). The reaction flask was placed in a 90 W blue LED constant low temperature water bath set at 25 °C. After 1 hour, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining four vials were stirred in the absence of light for an additional 30 min. Then, one vial was removed for analysis, and the lamps were turned back on to irradiate the remaining three reaction mixtures. After an additional 2 hours of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining two vials were stirred in the absence of light for an additional

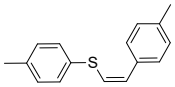
30 min. Then, a vial was removed for analysis, and the lamps were turned back on to irradiate the remaining one reaction mixture. After 3 hours, the lamps were turned off, and the last vial was removed for analysis, where yields were determined by n-octane as an internal standard.



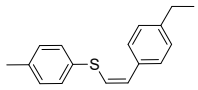
6. Characterization of Products



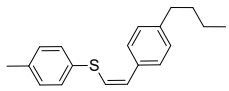
(Z)-styryl(p-tolyl)sulfane (Z-3). 20.7 mg, 92 %, Z/E = 88:12. yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 12.9, 7.8 Hz, 4H), 7.31 (dd, *J* = 12.1, 7.2 Hz, 1H), 7.23 (dd, *J* = 12.8, 5.3 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 0.12H), 6.66 (s, 0.12H), 6.53 (d, *J* = 10.8 Hz, 0.88H), 6.45 (d, *J* = 10.8 Hz, 0.88H), 2.33 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.36, 137.23, 136.61, 136.53, 132.64, 131.10, 130.56, 130.48, 129.93, 129.90, 128.68, 128.61, 128.26, 127.34, 127.02, 126.97, 126.45, 125.87, 124.41, 77.32, 77.00, 76.68, 21.05. HR-MS (ESI) m/z calcd for $C_{15}H_{15}S$ $[M + H]^+$ 227.0889; found: 227.0887.



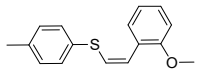
(Z)-(4-methylstyryl)(p-tolyl)sulfane (4). 21.0 mg, 89 %, Z/E = 95:5. white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 15.4 Hz,0.05H), 6.65 (d, *J* = 15.5 Hz, 0.05H), 6.51 (d, *J* = 10.7 Hz, 0.97H), 6.39 (d, *J* = 10.7 Hz, 0.95H), 2.34 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.23, 136.83, 133.75, 132.80, 131.03, 130.39, 130.27, 129.86, 129.32, 128.96, 128.64, 126.56, 125.84, 125.80, 122.87, 77.32, 77.00, 76.68, 21.24, 21.04. HR-MS (ESI) m/z calcd for $C_{16}H_{17}S$ $[M + H]^+$ 241.1045; found: 241.1047.



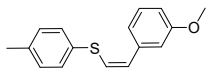
(Z)-(4-ethylstyryl)(p-tolyl)sulfane (5). 23.0 mg, 92%, Z/E > 99:1. white oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.45 (d, *J* = 10.7 Hz, 1H), 6.32 (d, *J* = 10.7 Hz, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.22, 137.24, 134.00, 132.82, 130.40, 129.87, 128.72, 127.78, 126.59, 125.82, 77.32, 77.00, 76.68, 28.64, 21.05, 15.50. HR-MS (ESI) m/z calcd for $C_{17}H_{19}S$ $[M + H]^+$ 255.1202; found 255.1203.



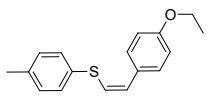
(Z)-(4-butylstyryl)(p-tolyl)sulfane (6). 25.0 mg, 90%, Z/E > 93:7. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.15 (dd, *J* = 14.1, 7.9 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 0.07H), 6.68 (d, *J* = 15.4 Hz, 0.07H), 6.54 (d, *J* = 10.7 Hz, 0.93H), 6.41 (d, *J* = 10.7 Hz, 0.93H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.36 (s, 3H), 1.67 – 1.57 (m, 2H), 1.38 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.91, 137.25, 133.96, 132.84, 131.19, 130.41, 130.24, 129.87, 128.70, 128.65, 128.35, 126.61, 125.86, 125.76, 122.85, 77.32, 77.00, 76.68, 35.42, 33.53, 22.33, 21.06, 13.94. HR-MS (ESI) m/z calcd for $C_{19}H_{23}S$ $[M + H]^+$ 283.1515; found 283.1513.



(Z)-(2-methoxystyryl)(p-tolyl)sulfane (7). 24.0 mg, 95%, Z/E > 99:1. yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 9.5, 5.2 Hz, 2H), 6.39 (d, *J* = 10.8 Hz, 1H), 3.73 (s, 3H), 2.22 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.50, 137.02, 132.79, 130.24, 129.87, 129.77, 129.16, 128.49, 126.59, 125.32, 121.62, 120.07, 110.28, 77.32, 77.00, 76.68, 55.37, 20.97. HR-MS (ESI) m/z calcd for $C_{16}H_{17}OS$ $[M + H]^+$ 257.0995; found 257.0997.

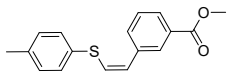


(Z)-(3-methoxystyryl)(p-tolyl)sulfane (8). 24.5 mg, 96%, Z/E = 83:17. light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.00 (m, 7H), 6.86 – 6.68 (m, 2H), 6.53 (d, *J* = 15.5 Hz, 0.17H), 6.44 (d, *J* = 10.8 Hz, 0.83H), 6.39 (d, *J* = 10.8 Hz, 0.83H), 3.77 (s, 2H), 3.72 (s, 1H), 2.28 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.50, 137.89, 137.46, 132.61, 130.68, 130.57, 130.16, 129.96, 129.92, 129.60, 129.25, 127.53, 126.24, 124.94, 121.38, 118.57, 113.72, 113.03, 112.97, 111.15, 77.32, 77.00, 76.68, 55.24, 21.07. HR-MS (ESI) m/z calcd for $C_{16}H_{17}OS$ $[M + H]^+$ 257.0995; found 257.0997.

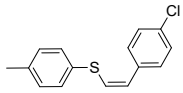


(Z)-(4-ethoxystyryl)(p-tolyl)sulfane (9). 26.6 mg, 93%, Z/E = 96:4. white solid.^{1}H NMR (400

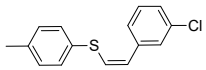
MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.97 – 6.89 (m, 2H), 6.85 (s, 0.04H), 6.71 (s, 0.04H), 6.53 (d, *J* = 10.7 Hz, 0.96H), 6.35 (dd, *J* = 10.7, 2.8 Hz, 0.96H), 4.07 (q, *J* = 6.9 Hz, 2H), 2.37 (s, 3H), 1.44 (td, *J* = 6.9, 1.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.54, 157.90, 137.11, 136.77, 132.83, 131.87, 131.48, 130.25, 130.05, 129.91, 129.84, 129.29, 129.22, 127.19, 126.42, 124.03, 120.89, 114.58, 114.21, 77.32, 77.00, 76.68, 63.38, 21.02, 14.79. HR-MS (ESI) calcd for $C_{17}H_{19}OS$ $[M + H]^+$ 271.1151; found 271.1157.



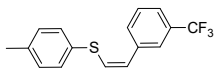
methyl (Z)-3-(2-(p-tolylthio)vinyl)benzoate (10). 21.8 mg, 23.1%, Z/E = 96:4. white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 9.4 Hz, 0.04H), 6.58 (s, 0.04H), 6.54 (d, *J* = 11.2 Hz, 1.92H), 3.94 (s, 3H), 3.91 (s, 1H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03, 137.64, 136.83, 132.74, 132.25, 131.24, 130.65, 130.22, 129.97, 129.88, 128.74, 128.38, 127.92, 125.30, 77.32, 77.00, 76.68, 52.19, 21.08; HR-MS (ESI) m/z calcd for $C_{17}H_{17}O_2S$ $[M+H]^+$ 285.0944, found 285.0948.



(Z)-(4-chlorostyryl)(p-tolyl)sulfane (11). 22.1 mg, 85%, Z/E = 94:6. white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.22 (m, 4H), 7.21 – 7.12 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 15.5 Hz, 0.06H), 6.48 (s, 0.06H), 6.43 – 6.35 (m, 1.88H), 2.27 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.62, 135.02, 132.53, 132.22, 130.96, 130.59, 130.02, 129.98, 129.90, 128.76, 128.42, 127.98, 126.98, 125.67, 125.10, 77.32, 77.00, 76.68, 21.07. HR-MS (ESI) m/z calcd for $C_{15}H_{14}ClS$ $[M + H]^+$ 261.0499; found 261.0496.

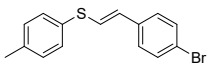


(Z)-(3-chlorostyryl)(p-tolyl)sulfane (12). 21.8 mg, 84%, Z/E = 95:5. light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.50 (t, J = 1.8 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.20 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 6.1 Hz, 3H), 6.89 (s, 0.09H), 6.51 (d, J = 10.8 Hz, 1.09H), 6.45 (d, J = 5.8 Hz,0.96H), 2.34 (d, J = 3.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.47, 138.29, 137.74, 137.67, 134.54, 134.16, 132.12, 131.18, 130.63, 130.21, 130.05, 129.98, 129.79, 129.75, 129.47, 129.09, 128.50, 128.47, 127.75, 127.04, 126.96, 126.88, 126.71, 125.61, 124.78, 123.95, 77.32, 77.00, 76.68, 21.06. HR-MS (ESI) m/z calcd for $C_{15}H_{14}ClS$ $[M+H]^+$ 261.0499; found 261.0494.

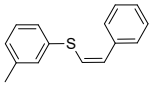


(Z)-p-tolyl(3-(trifluoromethyl)styryl)sulfane (13). 26.4 mg, 90%, Z/E = 90:10. white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 3H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 5.9 Hz, 3H), 7.20 (t, *J* = 6.8 Hz, 2H), 7.03 (s, 0.1H), 6.63 (d, *J* = 10.9 Hz, 0.9H), 6.55 (dd, *J* = 13.2, 6.5 Hz, 0.90H), 2.38 (s, 3H).^{13}C NMR (101 MHz, CDCl3) δ 140.06, 138.02, 131.46, 130.75, 130.46, 130.12, 129.85, 129.76, 128.72, 128.64, 128.50, 127.17, 125.78, 125.54, 125.21, 124.62, 77.32,

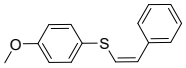
77.00, 76.68, 21.08. HR-MS (ESI) m/z calcd for $C_{16}H_{14}F_3SH$ $[M+H]^+$ 295.0763; found 295.0765.



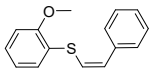
(Z)-(4-bromostyryl)(p-tolyl)sulfane (14). 26.1 mg, 86%, Z/E = 66:33. white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.16 (dd, *J* = 8.2, 2.9 Hz, 3H), 6.85 (d, *J* = 15.5 Hz, 0.33H), 6.52 (d, *J* = 8.5 Hz, 0.33H), 6.49 (d, *J* = 3.8 Hz, 0.66H), 6.44 (d, *J* = 10.8 Hz, 0.66H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.65, 135.60, 135.45, 132.20, 131.70, 131.38, 131.02, 130.61, 130.46, 130.20, 130.03, 129.98, 128.36, 128.21, 127.29, 125.91, 125.12, 120.93, 120.72, 77.32, 77.00, 76.68, 21.10, 21.07. HR-MS (ESI) m/z calcd for $C_{15}H_{14}BrS$ $[M+H]^+$ 304.9994; found 304.9997.



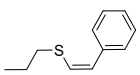
(Z)-Styryl(m-tolyl)sulfane (15). 20.0 mg, 88%, Z/E > 99:1. white oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.18 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 10.8 Hz, 1H), 6.49 (d, *J* = 10.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.97, 136.45, 135.88, 130.62, 128.94, 128.69, 128.24, 128.00, 127.05, 127.01, 126.93, 126.19, 77.32, 77.00, 76.68, 21.26. HR-MS (ESI) calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 227.0889; found 227.0889.



(Z)-(4-methoxyphenyl)(styryl)sulfane (16). 20.8 mg, 86%, Z/E > 99:1.white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 10.8 Hz, 1H), 6.40 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.47, 136.60, 132.92, 128.65, 128.33, 128.28, 126.91, 126.78, 125.71, 114.77, 77.32, 77.00, 76.68, 55.37. HR-MS (ESI) calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0838; found:243.0839.

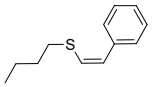


(Z)-(2-methoxyphenyl)(styryl)sulfane (17). 19.8 mg, 82%, Z/E > 99:1. pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 15.0, 7.6 Hz, 3H), 7.14 (dd, *J* = 12.6, 5.3 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 10.8 Hz, 1H), 6.36 (dd, *J* = 10.8, 2.3 Hz, 1H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.13, 136.41, 130.83, 128.79, 128.42, 128.17, 127.60, 126.94, 125.22, 124.07, 121.24, 110.81, 77.32, 77.00, 76.68, 55.80. HR-MS (ESI) calc for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0838; found: 243.0836

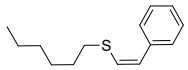


(Z)-propyl(styryl)sulfane (18). 16.0 mg, 90%, Z/E = 96:4. colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.23 – 7.14 (m, 1H), 6.76 (d, *J* = 15.6 Hz, 0.04H), 6.56 (d, *J* = 15.4 Hz, 0.04H), 6.42 (d, *J* = 11.0 Hz, 0.96H), 6.32 (d, *J* = 11.0 Hz, 0.96H), 2.87 (tt, *J* = 10.6, 3.7 Hz, 1H), 2.05 (dd, *J* = 9.5, 3.3 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.62 (dd, *J* = 11.3, 4.3 Hz, 1H), 1.51 – 1.41 (m, 2H), 1.40 – 1.23 (m, 3H).^{13}C NMR (101

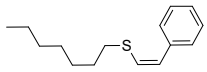
MHz, $CDCl_3$) δ 136.99, 128.51, 128.12, 127.62, 126.46, 125.36, 125.14, 77.32, 77.00, 76.68, 37.81, 23.48, 13.11. HR-MS (ESI) m/z calcd for $C_{11}H_{15}S$ $[M + H]^+$179.0889, found: 179.0884.



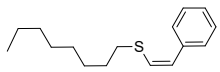
(Z)-butyl(styryl)sulfane (19). 17.7 mg, 92%, Z/E = 95:5. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 4.3 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.70 (s, 0.05H), 6.47 (s, 0.05H), 6.42 (d, J = 11.0 Hz, 0.95H), 6.23 (d, *J* = 10.9 Hz, 0.95H), 2.82 – 2.73 (m, 2H), 1.66 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.43 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.97 – 0.85 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.00, 128.53, 128.14, 127.65, 126.54, 126.48, 125.37, 125.14, 77.32, 77.00, 76.68, 35.53, 32.24, 21.63, 13.59. HR-MS (ESI) m/z calcd for $C_{12}H_{17}S$ $[M + H]^+$ 193.1051; found: 193.1054



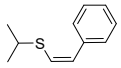
(Z)-hexyl(styryl)sulfane (20). 19.8.0 mg, 90%, Z/E = 94:6. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 4.3 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.70 (s, 0.06H), 6.47 (s, 0.06H), 6.42 (d, *J* = 10.9 Hz, 0.94H), 6.23 (d, *J* = 10.9 Hz, 0.94H), 2.77 (dd, *J* = 15.2, 7.8 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.40 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.35 – 1.24 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ136.99, 128.51, 128.11, 127.63, 126.48, 126.44, 125.34, 125.10, 77.32, 77.00, 76.68, 35.83, 31.31, 30.13, 28.19, 22.46, 13.96. HR-MS (ESI) m/z calcd for $C_{14}H_{21}S$ $[M + H]^+$ 221.1364; found: 221.1373.



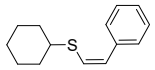
(Z) **-heptyl(styryl)sulfane (21).** 20.0 mg, 92%, Z/E = 94:6. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.35 (dd, *J* = 19.2, 11.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 0.06H), 6.50 (s, 0.06H), 6.44 (d, *J* = 10.9 Hz, 0.94H), 6.26 (d, *J* = 10.9 Hz, 0.94H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.75 – 1.66 (m, 2H), 1.42 (dd, *J* = 14.1, 6.6 Hz, 2H), 1.37 – 1.24 (m, 6H), 0.90 (t, *J* = 5.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.02, 128.55, 128.16, 127.67, 126.50, 125.16, 77.32, 77.00, 76.68, 35.88, 31.67, 30.22, 28.83, 28.52, 22.57, 14.05. HR-MS (ESI) m/z calcd for $C_{14}H_{23}S$ $[M + H]^+$ 235.1515; found 235.1513.



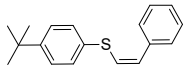
(Z)-octyl(styryl)sulfanea (22). 23.8 mg, 96%, Z/E = 94:6. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 4.2 Hz, 1H), 7.21 (dt, *J* = 13.7, 6.8 Hz, 1H), 6.72 (d, *J* = 15.6 Hz, 0.06H), 6.47 (s, 0.06H), 6.42 (dd, *J* = 10.6, 5.9 Hz, 0.94H), 6.23 (dd, *J* = 10.8, 5.5 Hz, 0.94H), 2.77 (t, *J* = 7.2 Hz, 2H), 1.74 – 1.61 (m, 2H), 1.47 – 1.35 (m, 2H), 1.28 (s, 9H), 0.88 (t, *J* = 6.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.02, 128.55, 128.16, 127.67, 126.50, 125.39, 125.16, 77.32, 77.00, 76.68, 35.88, 31.77, 30.21, 29.13, 28.56, 22.61, 14.16, 14.06. HR-MS (ESI) m/z calcd for $C_{16}H_{25}S$ $[M + H]^+$ 249.1671; found 249.1673.



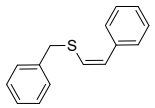
(Z)-isopropyl(styryl)sulfane (23). 16.7 mg, 94%, Z/E = 96:4. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 15.6 Hz, 0.04H), 6.55 (s, 0.04H), 6.45 (d, *J* = 11.0 Hz, 0.94H), 6.33 (d, *J* = 11.0 Hz, 0.94H), 3.15 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.38 (d, *J* = 6.8 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.06, 128.61, 128.17, 126.54, 125.85, 125.22, 77.32, 77.00, 76.68, 39.18, 23.50. HR-MS (ESI) m/z calcd for $C_{11}H_{15}S$ $[M + H]^+$ 179.0889; found 179.0889.



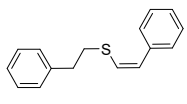
(Z)-cyclohexyl(styryl)sulfane (24). 19.6 mg, 90%, Z/E = 98:2. light yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 15.6 Hz, 1H), 6.54 (s, 1H), 6.42 (d, *J* = 11.0 Hz, 1H), 6.32 (d, *J* = 11.0 Hz, 1H), 2.86 (ddd, *J* = 10.6, 7.3, 3.8 Hz, 1H), 2.05 (dd, *J* = 9.5, 3.3 Hz, 2H), 1.79 (dd, *J* = 8.9, 3.9 Hz, 2H), 1.62 (dd, *J* = 11.3, 4.3 Hz, 1H), 1.46 (dd, *J* = 22.4, 11.7 Hz, 2H), 1.31 (dt, *J* = 34.0, 11.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.09, 128.55, 128.10, 126.40, 125.85, 125.50, 124.92, 77.32, 77.00, 76.68, 47.68, 33.60, 25.91, 25.54. HR-MS (ESI) m/z calcd for $C_{14}H_{19}S$ $[M + H]^+$ 219.1202; found 219.1206.



(Z)-(4-(tert-butyl)phenyl)(styryl)sulfane (25). 23.0 mg, 86%, Z/E > 99:1. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.33 (m, 6H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.50 (q, *J* = 10.8 Hz, 2H), 1.31 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.54, 136.54, 132.68, 130.19, 128.68, 128.26, 126.94, 126.90, 126.43, 126.19, 77.32, 77.00, 76.68, 34.51, 31.22.HR-MS (ESI) m/z calcd for $C_{18}H_{21}S$ $[M + H]^+$ 269.1358; found: 269.1339.

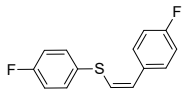


(Z)-benzyl(styryl)sulfane (26). 20.5 mg, 91%, Z/E = 97:3. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.7 Hz, 2H), 7.38 – 7.17 (m, 9H), 6.71 (d, *J* = 15.5 Hz, 1H), 6.50 (s, 1H), 6.41 (d, *J* = 10.9 Hz, 1H), 6.24 (d, *J* = 10.9 Hz, 1H), 3.99 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.35, 136.82, 128.96, 128.67, 128.64, 128.20, 127.38, 126.70, 125.96, 125.84, 77.32, 77.00, 76.68, 39.49. HR-MS (ESI) m/z calcd for $C_{15}H_{15}S$ $[M + H]^+$ 227.0889; found: 227.0888.

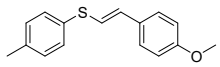


(Z)-phenethyl(styryl)sulfane (27). 21.3 mg, 89%, Z/E > 99:1. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.46 (d, *J* = 10.9 Hz, 1H), 6.25 (d, *J* = 10.9 Hz, 1H), 3.01 (td, *J* = 7.0, 2.5 Hz, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.83, 136.87, 128.63, 128.57, 128.54, 128.21, 126.97, 126.68, 126.51, 125.91, 77.32, 77.00, 76.68, 37.13, 36.79. HR-MS (ESI) m/z calcd for $C_{16}H_{17}S$ $[M + H]^+$ 241.1045;

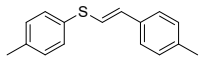
found: 241.1043.



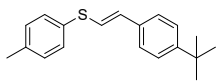
(Z)-(4-fluorophenyl)(4-fluorostyryl)sulfane (28). 19.3 mg, 78%, Z/E = 83:17. yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 4H), 7.31 – 7.25 (m, 1H), 7.10 – 6.97 (m, 4H), 6.70 (s, 0.17H), 6.61 (s, 0.17H), 6.52 (d, *J* = 10.7 Hz, 0.83H), 6.37 (d, *J* = 10.7 Hz, 0.83H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.59, 163.55, 163.48, 162.91, 161.13, 161.02, 160.45, 132.69, 132.64, 132.61, 132.55, 132.52, 132.49, 131.04, 131.00, 130.43, 130.35, 129.95, 129.65, 127.52, 127.44, 126.12, 125.99, 123.61, 116.47, 116.45, 116.23, 115.74, 115.52, 115.37, 115.16, 77.32, 77.00, 76.68.HR-MS (ESI) m/z calcd for $C_{14}H_{11}F_2S$ $[M + H]^+$ 259.0544; found: 259.0547.



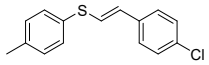
(E)-(4-methoxystyryl)(p-tolyl)sulfane (29). 24.3 mg, 95%, Z/E = 83:17. white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.20 (dd, *J* = 15.1, 8.4 Hz, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 0.83H), 6.75 (d, *J* = 8.7 Hz, 0.83H), 6.64 – 6.54 (m, 2H), 6.40 (s, 0.17H), 6.25 (d, *J* = 10.7 Hz, 0.17H), 3.72 (d, *J* = 10.0 Hz, 3H), 2.25 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.15, 158.52, 137.15, 136.82, 132.79, 131.81, 131.32, 130.28, 130.06, 129.97, 129.84, 129.46, 129.39, 127.19, 126.36, 124.23, 121.11, 114.05, 113.67, 77.32, 77.00, 76.68, 55.25, 21.02. HR-MS (ESI) m/z calcd for $C_{16}H_{17}OS$ $[M + H]^+$ 257.0995; found 257.0997.



(E)-(4-methylstyryl)(p-tolyl)sulfane (30). 22.8 mg, 92%, Z/E = 90:10. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 1H), 7.33 (dd, *J* = 16.7, 8.2 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.12 (dd, *J* = 15.2, 8.0 Hz, 4H), 6.79 (d, *J* = 15.4 Hz, 0.90H), 6.65 (d, *J* = 15.4 Hz, 0.90H), 6.52 (d, *J* = 10.7 Hz, 0.10H), 6.39 (d, *J* = 10.7 Hz, 0.10H), 2.33 (d, *J* = 7.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.31, 137.04, 136.86, 133.88, 132.83, 131.50, 131.05, 130.42, 130.29, 129.89, 129.33, 128.97, 128.65, 126.99, 126.59, 125.86, 125.82, 122.89, 77.32, 77.00, 76.68, 21.18, 21.06. HR-MS (ESI) m/z calcd for $C_{16}H_{17}S$ $[M + H]^+$ 241.1045; found: 241.1047

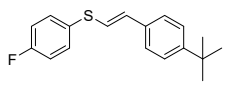


(E)-(4-(tert-butyl)styryl)(p-tolyl)sulfane (31). 25.3 mg, 90%, Z/E = 88:12.white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.37 (m, 1H), 7.37 – 7.27 (m, 6H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 15.4 Hz, 0.88H), 6.70 (d, *J* = 15.4 Hz, 0.88H), 6.55 (d, *J* = 10.7 Hz, 0.12H), 6.44 (s, 0.12H), 2.36 (s, 3H), 1.34 (d, *J* = 9.5 Hz, 10H).^{13}C NMR (101 MHz, $CDCl_3$) δ150.61, 136.99, 133.87, 131.58, 131.11, 130.41, 130.20, 129.88, 128.48, 126.49, 125.95, 125.69, 125.56, 125.20, 123.06, 77.32, 77.00, 76.68, 34.56, 31.24, 21.05.HR-MS (ESI) m/z calcd for $C_{19}H_{23}S$ $[M + H]^+$ 283.1515.; found: 283.1519.

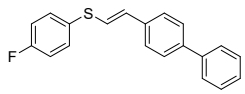


(E)-(4-chlorostyryl)(p-tolyl)sulfane (32). 21.3 mg, 82%, Z/E = 91:9. yellow oil.^{1}H NMR (400

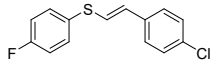
MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 10.9, 7.0 Hz, 4H), 7.29 – 7.11 (m, 2H), 6.83 (d, *J* = 15.5 Hz, 0.91H), 6.58 – 6.45 (m, 1.01H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.60, 135.17, 132.84, 130.97, 130.60, 130.56, 130.02, 129.99, 129.91, 128.77, 128.46, 127.98, 126.99, 125.68, 125.12, 77.32, 77.00, 76.68, 21.10. HR-MS (ESI) m/z calcd for $C_{15}H_{14}ClS$ [M + H] $^+$ 261.0499; found 261.0496.



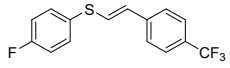
(E)-(4-(tert-butyl)styryl)(4-fluorophenyl)sulfane (33). 23.2 mg, 81%, Z/E = 93:7. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 4H), 7.30 – 7.23 (m, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 15.4 Hz, 0.93H), 6.67 (d, *J* = 15.4 Hz, 0.93H), 6.54 (s, 0.7H), 6.34 (d, *J* = 10.7 Hz, 0.7H), 1.32 (d, *J* = 9.6 Hz, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 160.93, 150.90, 133.63, 132.52, 132.44, 132.22, 132.14, 131.84, 130.29, 130.25, 128.51, 125.77, 125.62, 125.26, 122.51, 116.37, 116.15, 77.32, 77.00, 76.68, 34.60, 31.24. HR-MS (ESI) m/z calcd for $C_{18}H_{20}FS$ [M + H] $^+$ 287.1264; found: 287.1267.



(E)-(2-([1,1'-biphenyl]-4-yl)vinyl)(4 fluoropheny l) sulfane (34). 26.0 mg, 85%, Z/E =82:18. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 5H), 7.49 – 7.33 (m, 8H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 15.4 Hz, 0.82H), 6.68 (d, *J* = 15.4 Hz, 0.82H), 6.59 (s, 0.18H), 6.42 (s, 0.18H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.52, 140.32, 135.43, 132.71, 132.62, 130.63, 129.16, 128.80, 127.36, 127.00, 126.88, 126.72, 126.61, 126.38, 124.02, 116.48, 116.45, 116.26, 77.32, 77.00, 76.68. HR-MS (ESI) m/z calcd for $C_{20}H_{16}FS$ [M + H] $^+$ 307.0951; found: 307.0956.

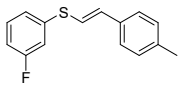


(E)-(4-chlorostyryl)(4-fluorophenyl)sulfane(35). 20.0 mg, 76%, Z/E = 90:10. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 3H), 7.24 (q, *J* = 8.6 Hz, 4H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 15.4 Hz,1.8H), 6.52 (dd, *J* = 16.5, 13.2 Hz, 0.1H), 6.42 (d, *J* = 10.7 Hz, 0.1H).^{13}C NMR (101 MHz, $CDCl_3$) δ163.67, 161.21, 134.92, 133.11, 133.05, 132.97, 132.77, 132.68, 129.92, 129.28, 129.25, 129.14, 128.84, 128.49, 127.46, 127.07, 125.71, 125.09, 116.54, 116.50, 116.33, 116.28, 77.32, 77.00, 76.68. HR-MS (ESI) m/z calcd for $C_{14}H_{11}ClFS$ [M + H] $^+$ 265.0249; found: 265.0246.

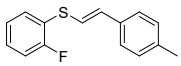


(E)-(4-fluorophenyl)(4-(trifluoromethyl)styryl)sulfane (36). 21.5 mg, 72%, Z/E > 99:1.
white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.48 –
7.42 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.08 (dd, *J* = 11.9, 5.3 Hz, 2H), 6.94 (d, *J* = 15.5 Hz, 1H), 6.54 (d, *J* = 15.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.90, 161.43, 139.81, 133.66, 133.57, 133.00, 132.91, 129.92, 129.21, 128.88, 128.76, 128.54, 128.06, 127.80, 125.89, 125.70, 125.66,

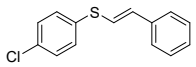
125.62, 125.58, 125.48, 125.22, 122.78, 116.68, 116.59, 116.46, 116.37, 77.32, 77.00, 76.68. HR-MS (ESI) m/z calcd for $C_{15}H_{11}F_4S$ [M + H] $^+$ 299.0512; found: 299.0516.



(E)-(3-fluorophenyl)(4-methylstyryl)sulfane (37). 19.0 mg, 72.0 mg, 78%, Z/E = 90:10. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.14 (dd, *J* = 24.0, 7.7 Hz, 3H), 7.06 (d, *J* = 9.1 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.84 – 6.70 (m, 1.82H), 6.62 (d, *J* = 10.6 Hz, 0.1H), 6.38 (d, *J* = 10.6 Hz, 0.1H), 2.33 (d, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.12, 161.65, 138.44, 137.97, 134.49, 133.37, 130.29, 130.20, 129.40, 128.99, 128.74, 126.13, 124.18, 124.15, 122.89, 119.86, 115.55, 115.31, 113.42, 113.21, 77.32, 77.00, 76.68, 21.18. HR-MS (ESI) m/z calcd for $C_{15}H_{14}FS$ [M + H] $^+$ 245.0795; found 245.0793.

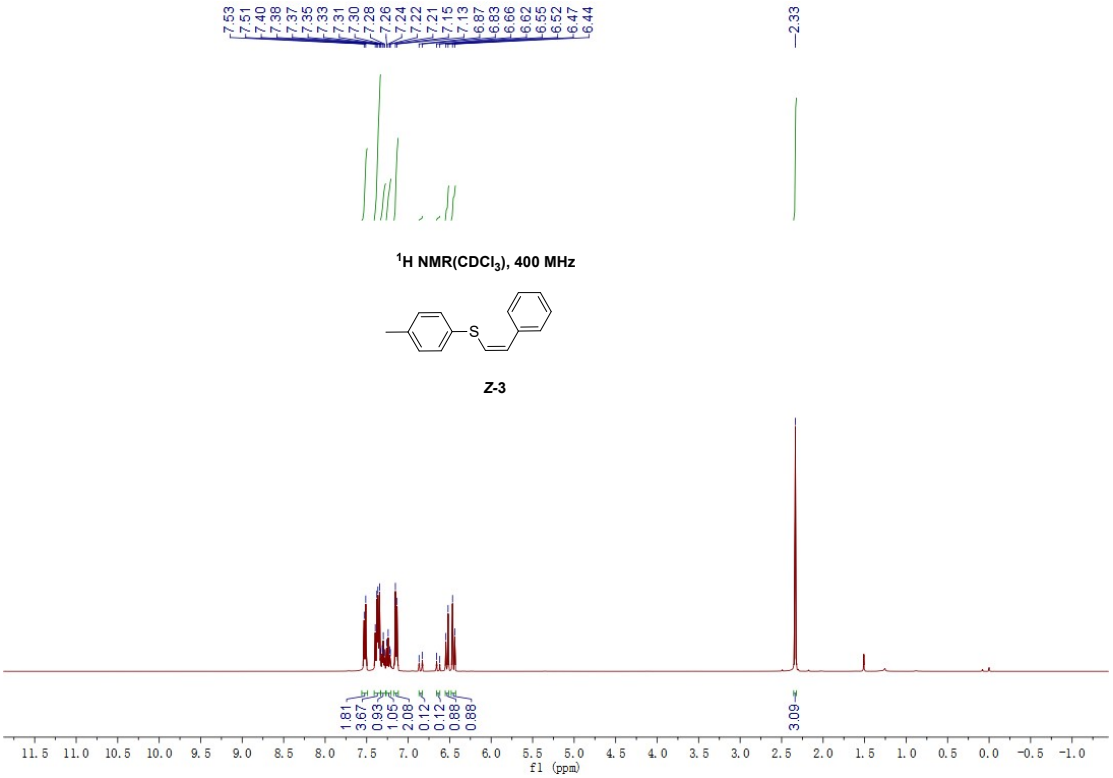


(E)-(2-fluorophenyl)(4-methylstyryl)sulfane (38). 20.0 mg, 83%, Z/E = 90:10. colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 15.0, 7.1 Hz, 1H), 7.29 – 7.17 (m, 3H), 7.16 – 7.03 (m, 4H), 6.79 – 6.66 (m,1.8H), 6.60 (d, *J* = 10.6 Hz, 0.1H), 6.31 (d, *J* = 10.6 Hz, 0.1H), 2.33 (d, *J* = 12.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 159.34, 137.74, 137.17, 133.50, 133.32, 132.95, 132.17, 131.61, 131.60, 129.35, 129.17, 129.09, 129.00, 128.75, 128.67, 128.54, 128.28, 126.76, 126.03, 124.68, 124.65, 123.25, 123.14, 122.65, 122.48, 119.89, 119.88, 115.95, 115.84, 115.73, 115.63, 77.32, 77.00, 76.68, 21.24, 21.17. HR-MS (ESI) m/z calcd for $C_{15}H_{14}FS$ [M + H] $^+$ 245.0795; found 245.0797.



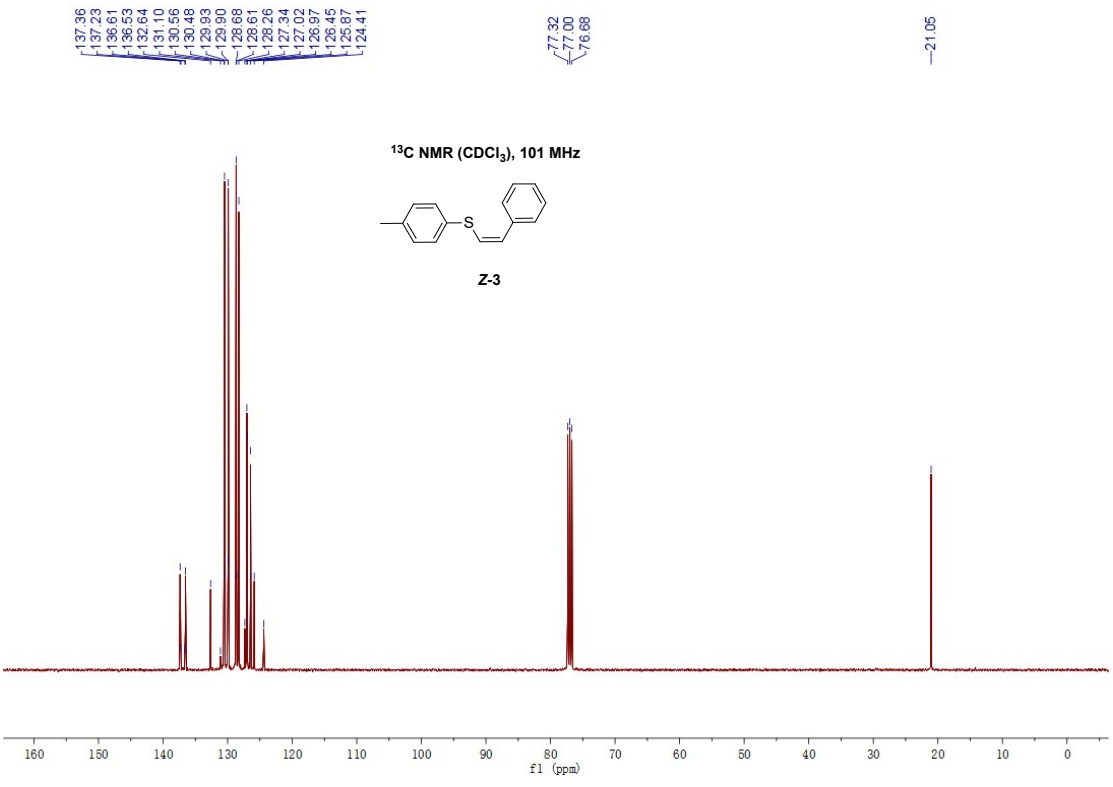
(E)-(4-chlorophenyl)(styryl)sulfane (39). 19.7 mg, 80%, Z/E = 92:8. yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.26 (m, 9H), 7.26 – 7.20 (m, 1H), 6.81 (d, *J* = 15.4 Hz, 0.92H), 6.73 (d, *J* = 15.4 Hz, 0.92H), 6.61 (d, *J* = 10.7 Hz, 0.08H), 6.42 (s, 0.08H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.23, 133.82, 132.94, 132.72, 131.21, 130.92, 129.26, 128.74, 128.70, 128.32, 128.01, 127.80, 127.31, 126.07, 125.12, 122.46, 77.32, 77.00, 76.68; HR-MS (ESI) m/z calcd for $C_{14}H_{12}ClS$ [M + H]$^+$ 247.0343; found: 247.0345.

7. Spectral Data



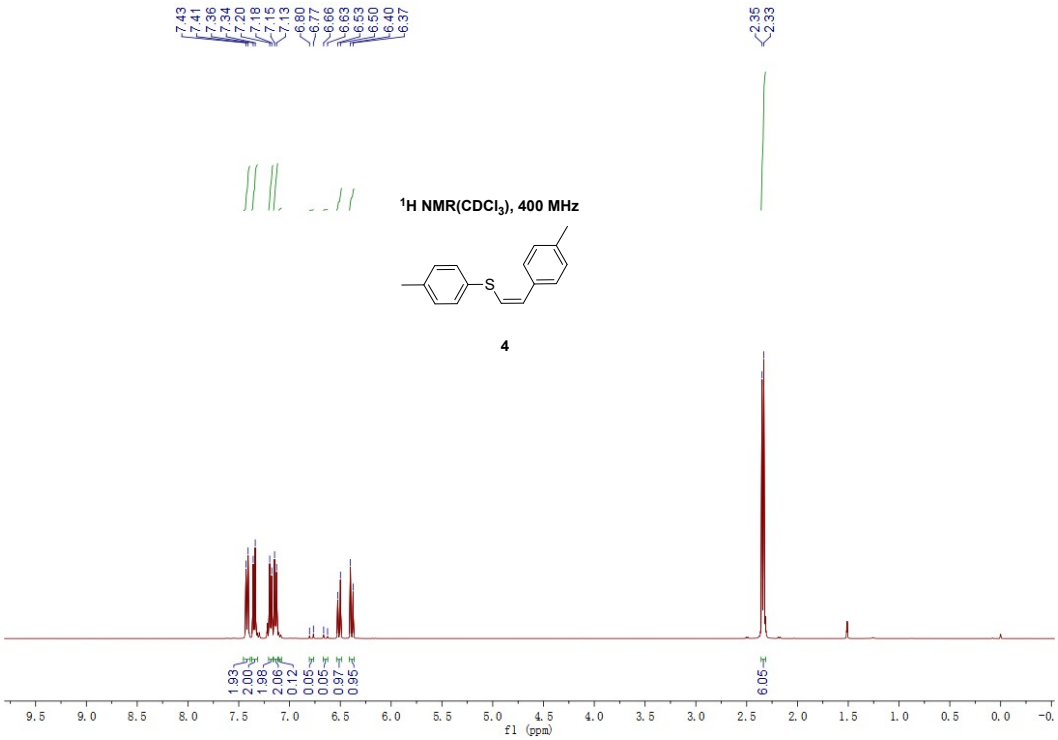
^{1}H NMR($CDCl_3$), 400 MHz

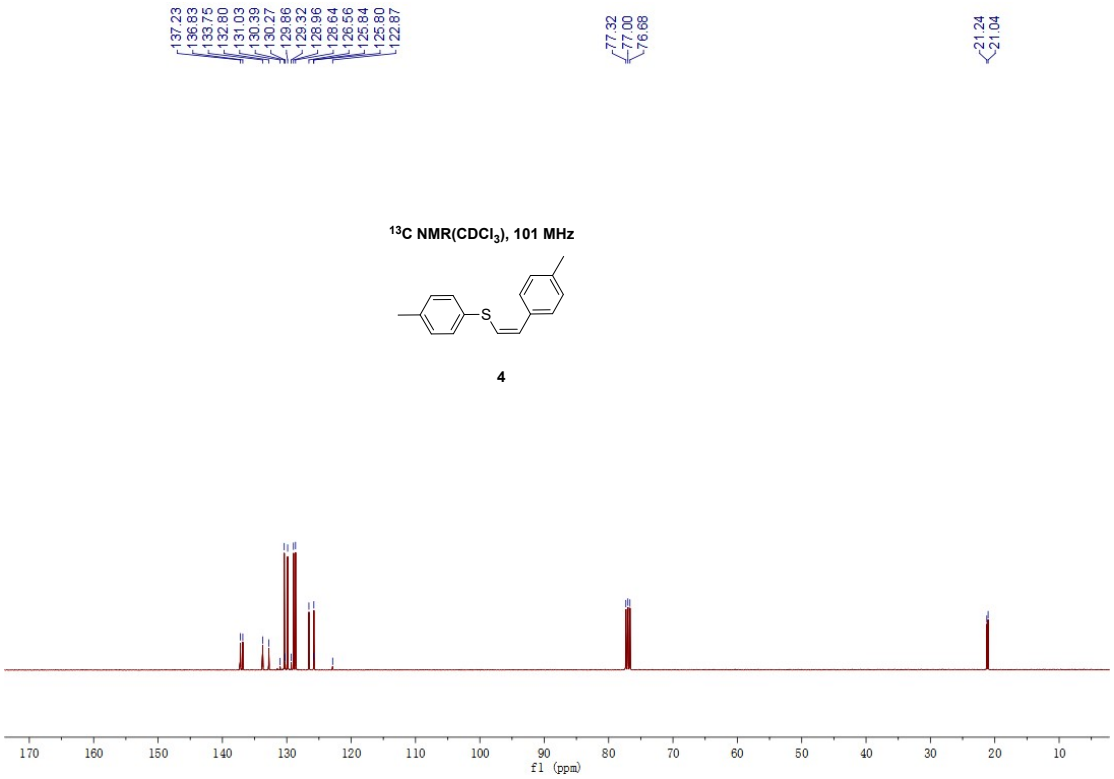
***Z*-3**

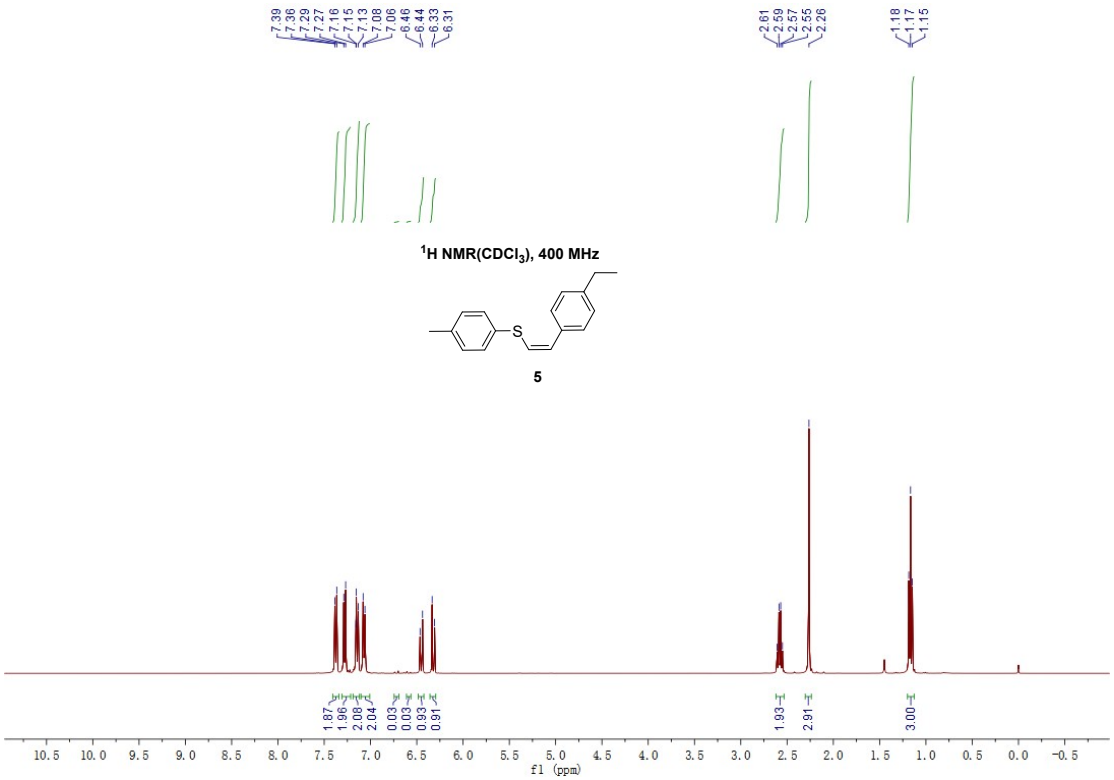


^{13}C NMR ($CDCl_3$), 101 MHz

***Z*-3**

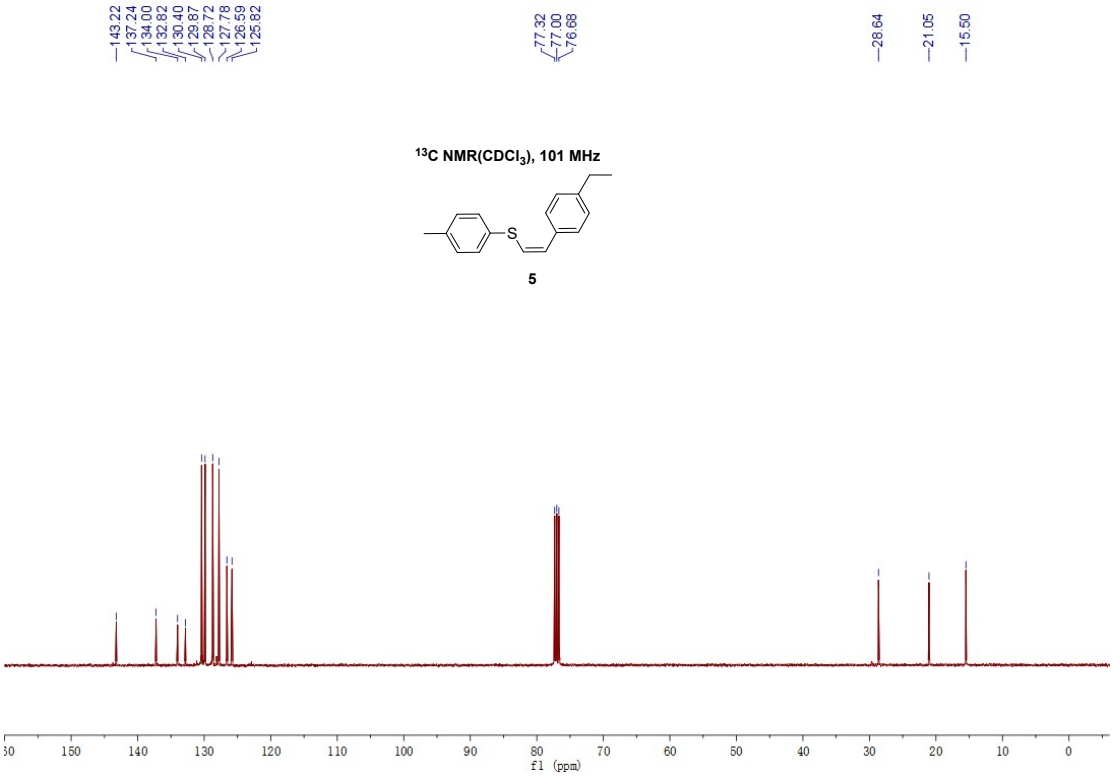

7.43
7.41
7.36
7.34
7.20
7.18
7.15
7.13
6.80
6.77
6.66
6.63
6.53
6.50
6.40
6.37
2.35
2.33
1H NMR(CDCl3), 400 MHz
S
4
1.93
2.00
1.98
2.06
0.12
0.05
0.05
0.97
0.95
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


137.23
136.83
133.75
132.80
131.03
130.39
130.27
129.86
129.32
128.96
128.64
126.56
125.84
125.80
122.87
77.32
77.00
76.68
21.24
21.04
13C NMR(CDCl3), 101 MHz
S
4
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



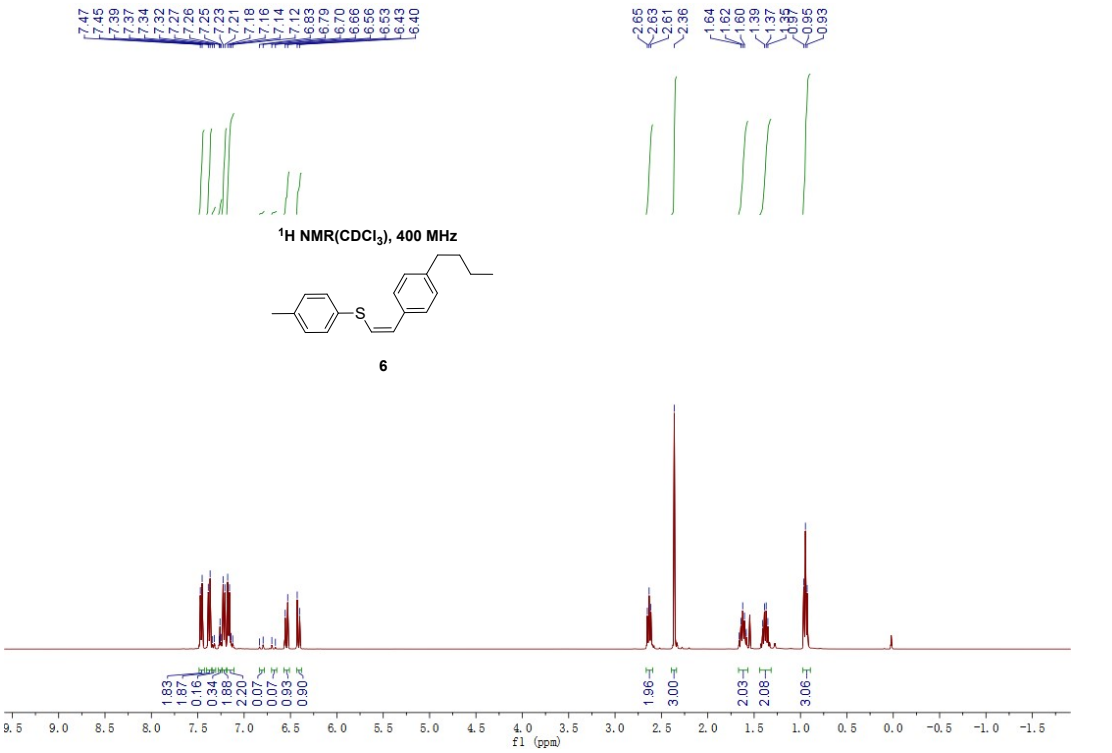
^{1}H NMR($CDCl_3$), 400 MHz

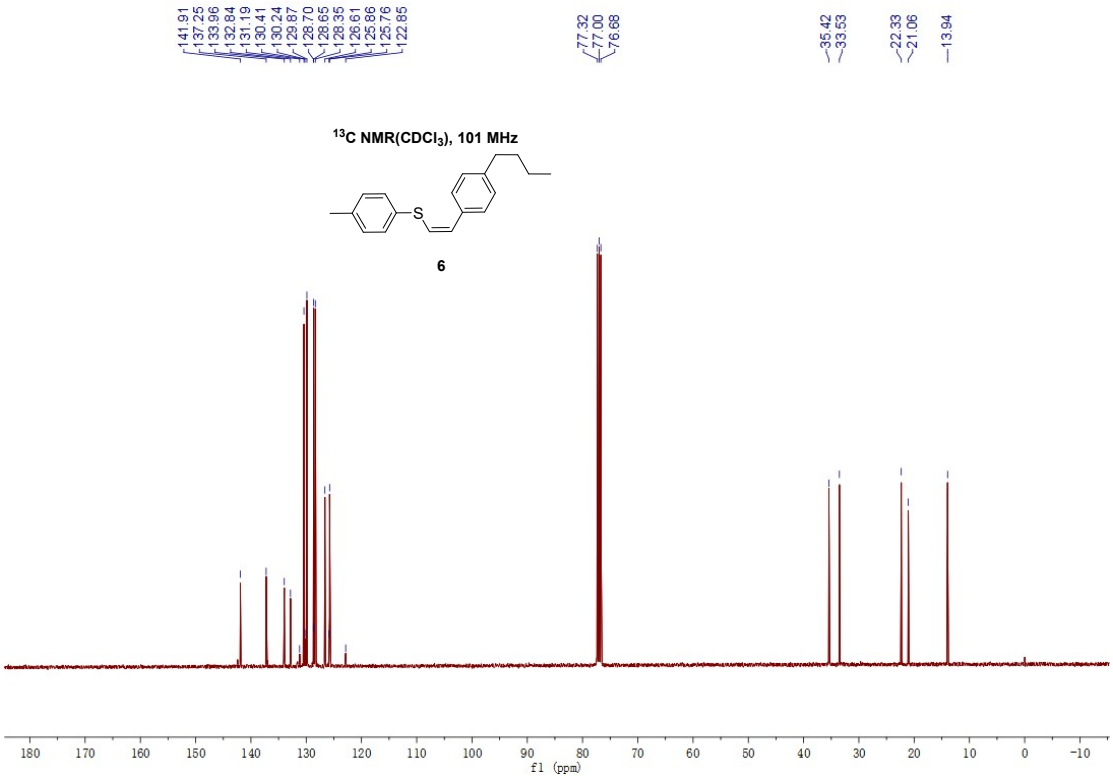
5

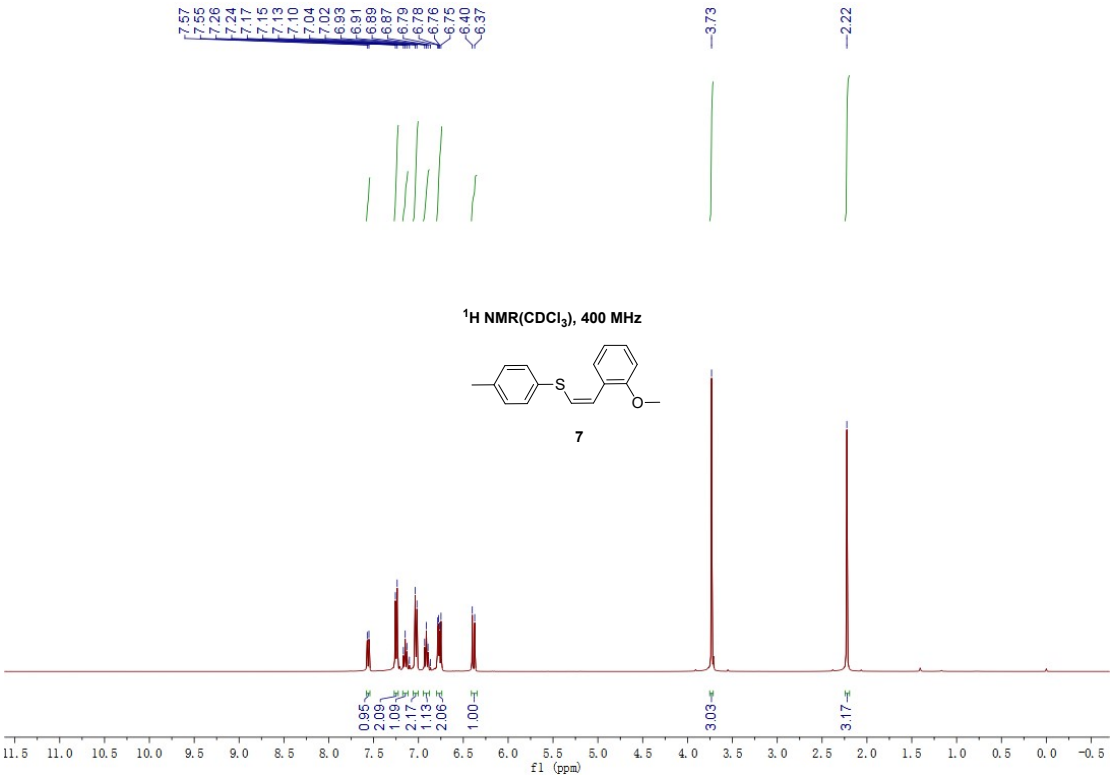


^{13}C NMR($CDCl_3$), 101 MHz

5

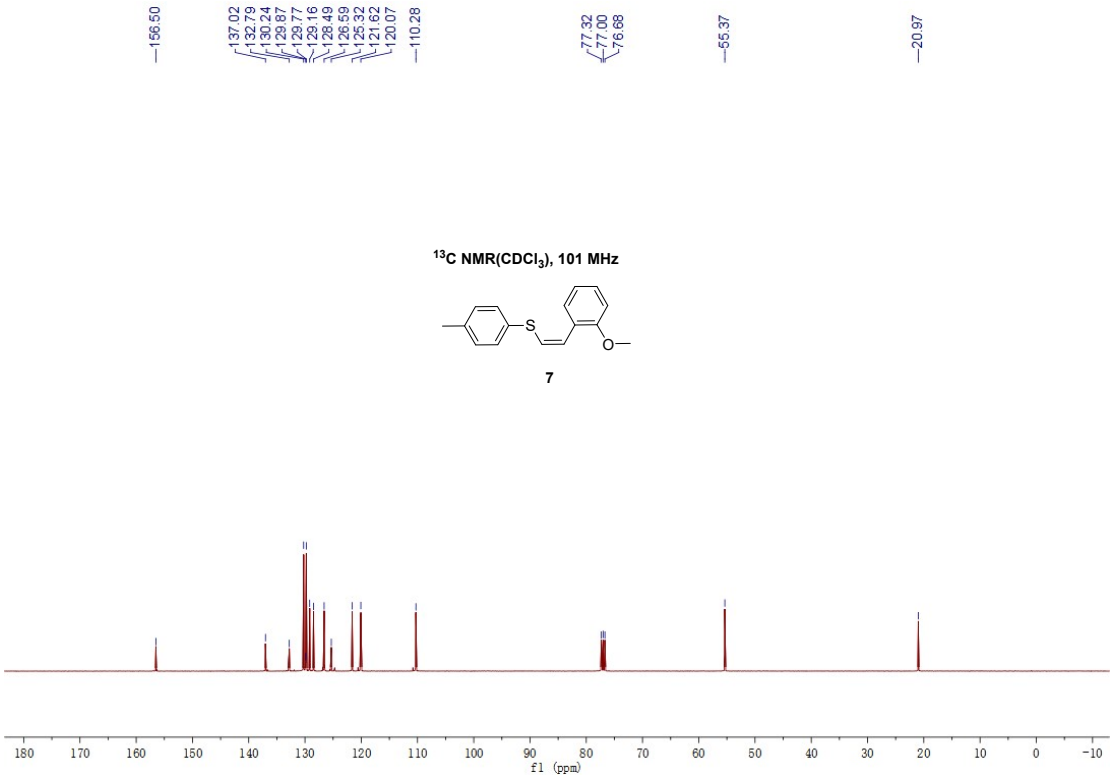

7.47
7.45
7.39
7.37
7.34
7.32
7.27
7.26
7.25
7.23
7.21
7.18
7.16
7.14
7.12
6.83
6.79
6.70
6.66
6.56
6.53
6.43
6.40
2.65
2.63
2.61
2.36
1.64
1.62
1.60
1.39
1.37
0.97
0.95
0.93
1H NMR(CDCl3), 400 MHz
S
6
1.83
1.87
0.16
0.34
1.88
2.20
0.07
0.07
0.93
0.90
1.96
3.00
2.03
2.08
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


141.91
137.25
133.96
132.84
131.19
130.41
130.24
129.87
128.70
128.65
128.35
126.81
125.86
125.76
122.85
77.32
77.00
76.68
35.42
33.53
22.33
21.06
13.94
13C NMR(CDCl3), 101 MHz
S
6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



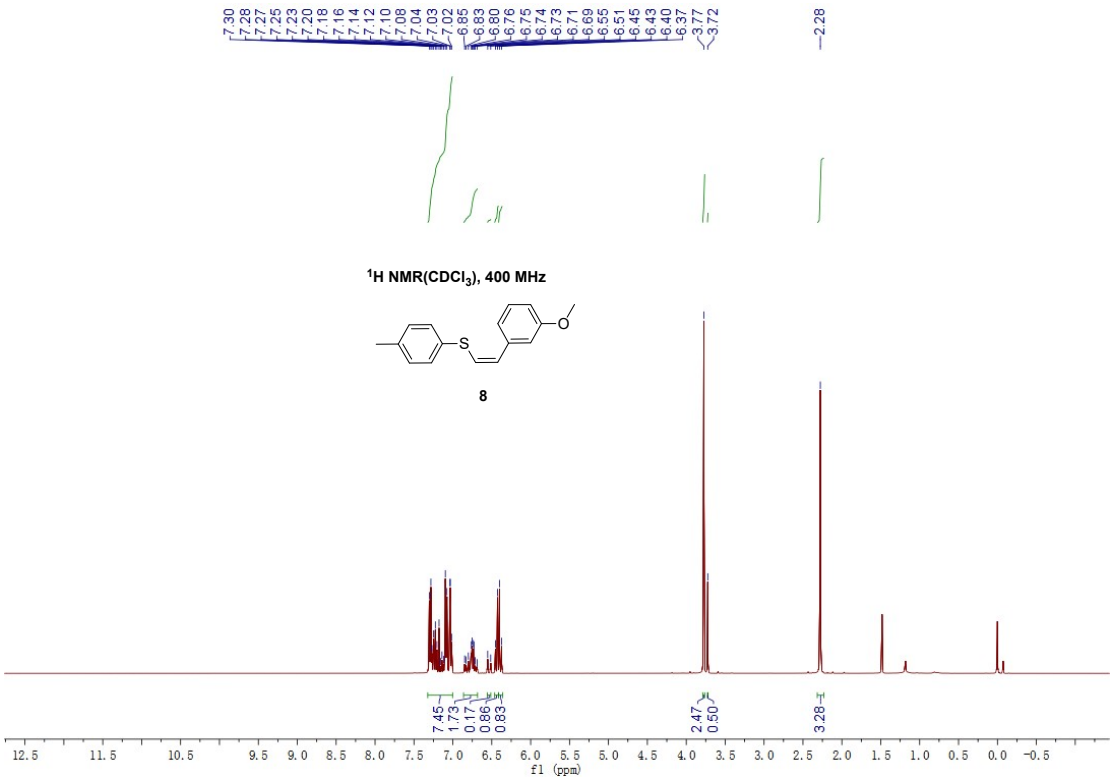
^{1}H NMR($CDCl_3$), 400 MHz

7



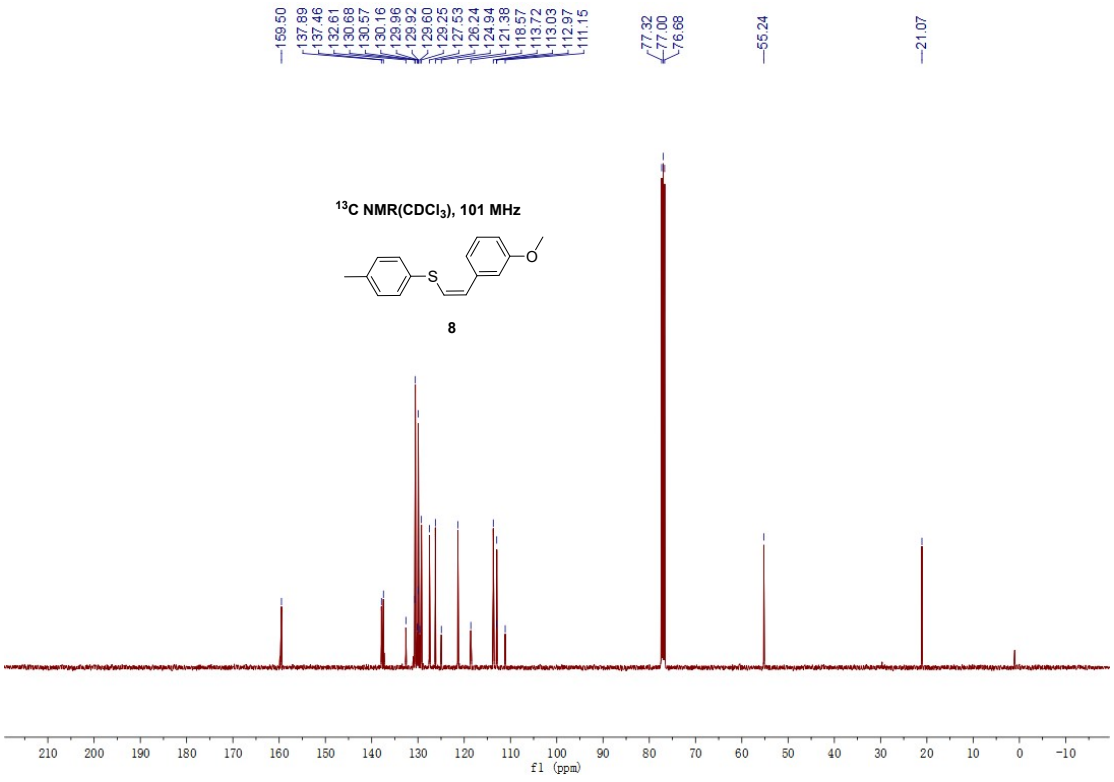
^{13}C NMR($CDCl_3$), 101 MHz

7



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

8



^{13}C NMR($CDCl_3$), 101 MHz

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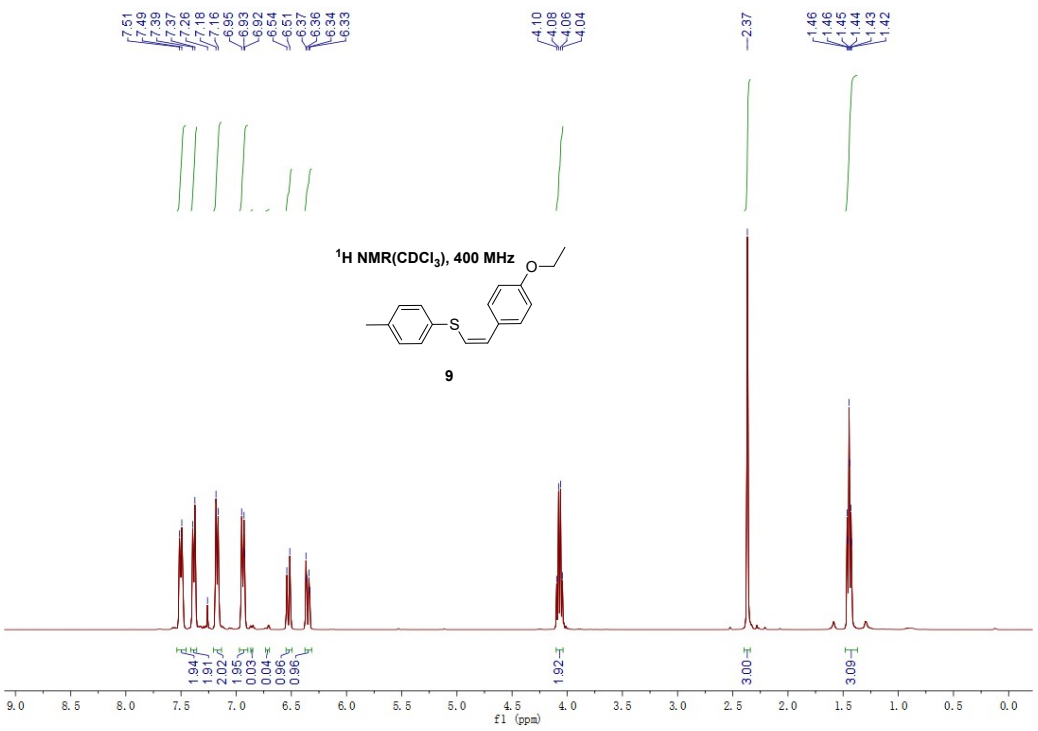
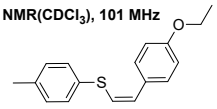


^{1}H NMR($CDCl_3$), 400 MHz

9

^{13}C NMR($CDCl_3$), 101 MHz



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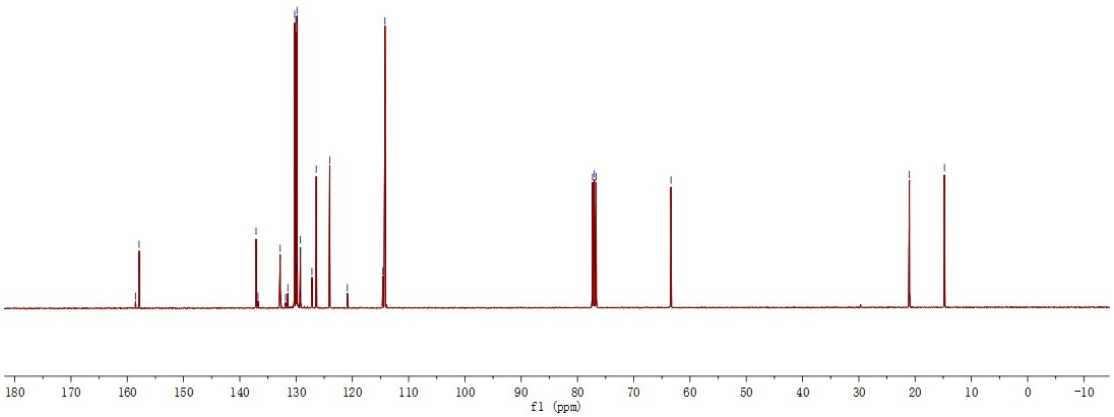

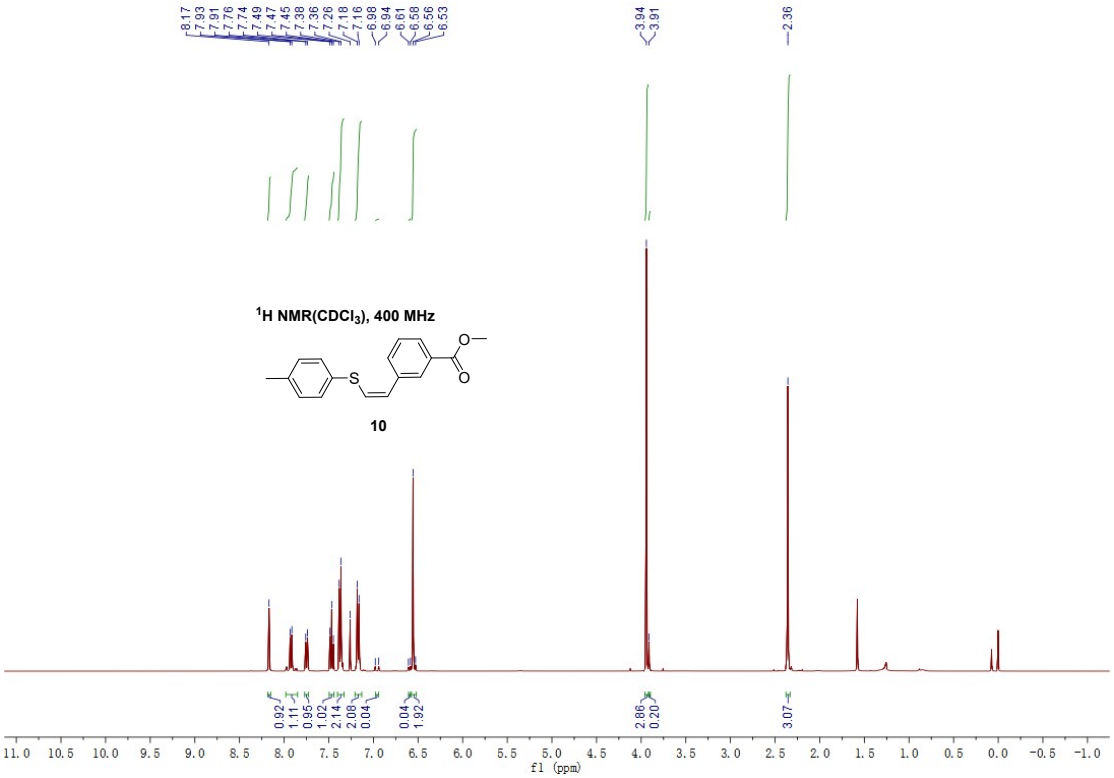

^{1}H NMR($CDCl_3$), 400 MHz

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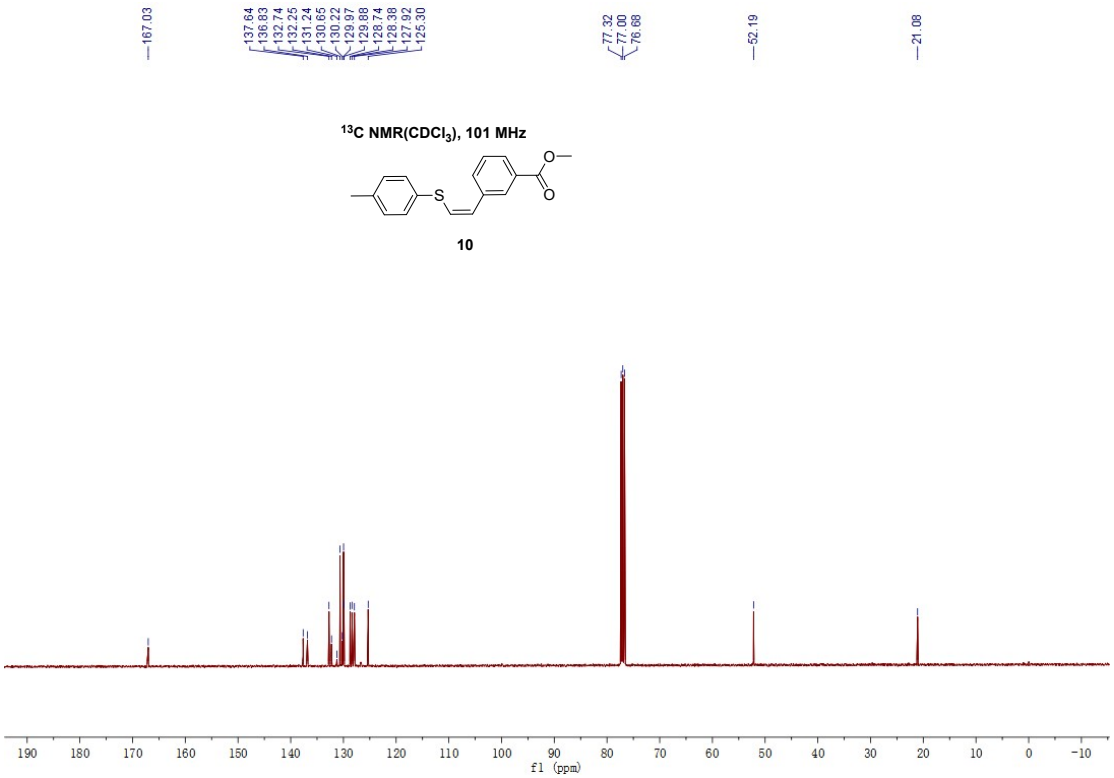

^{13}C NMR($CDCl_3$), 101 MHz

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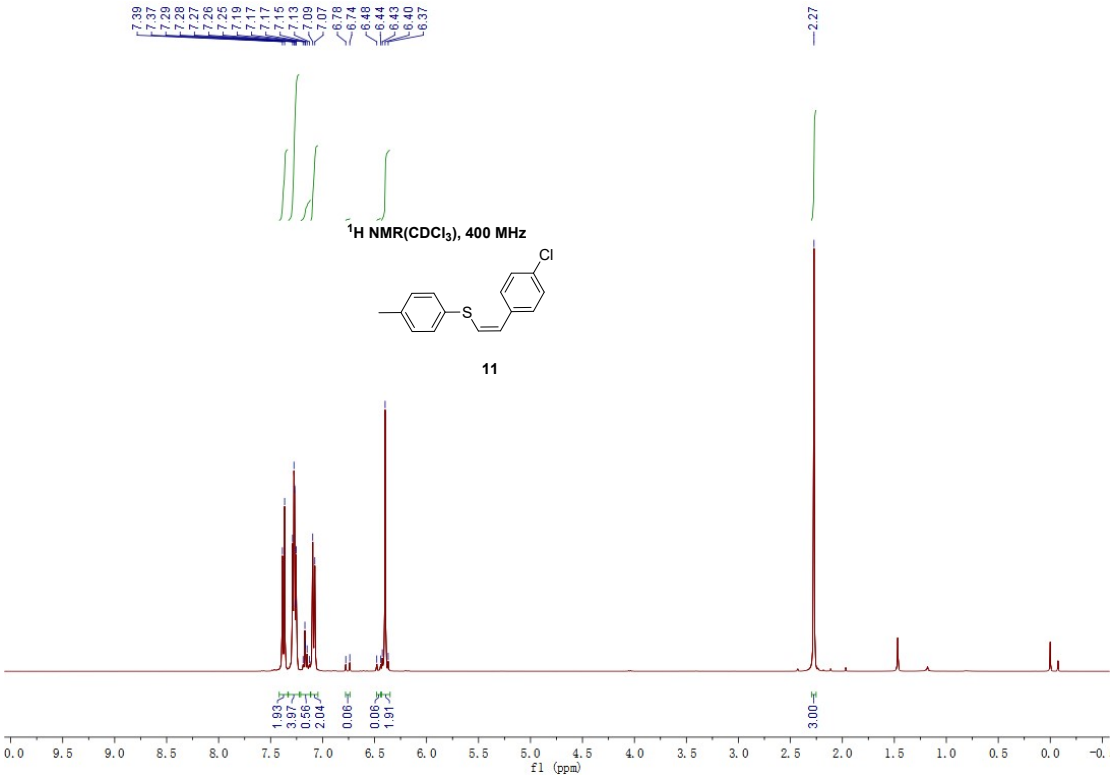

^{1}H NMR($CDCl_3$), 400 MHz

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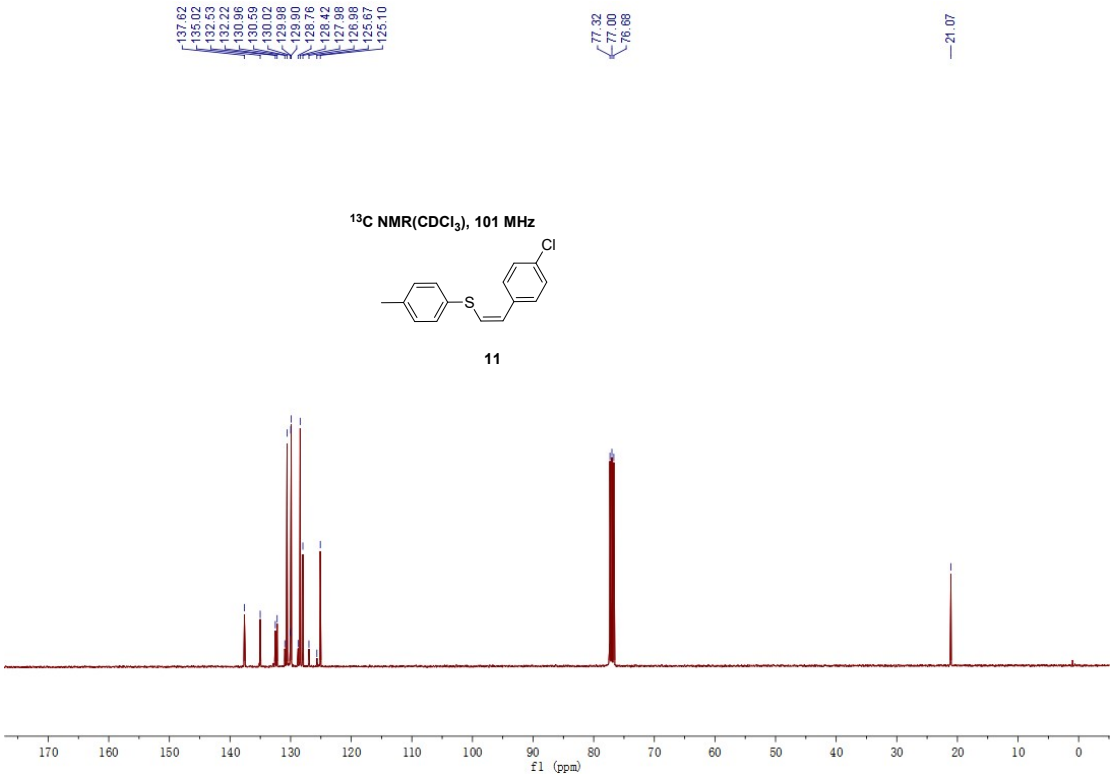

^{13}C NMR($CDCl_3$), 101 MHz

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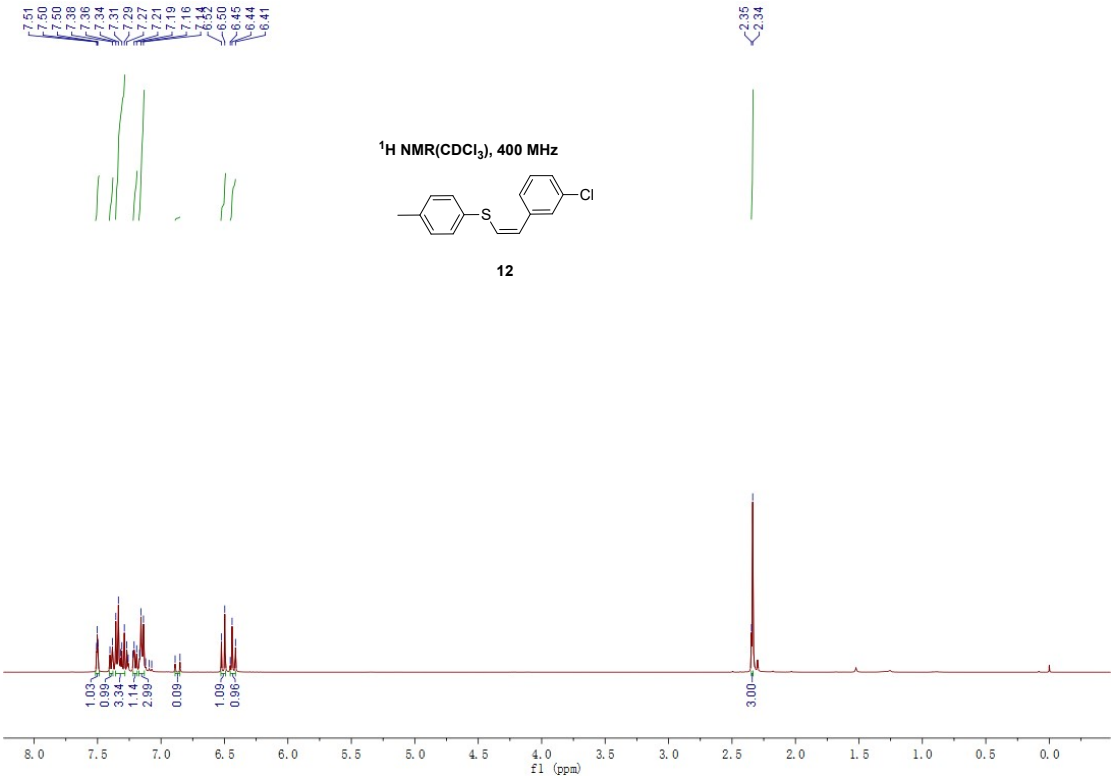
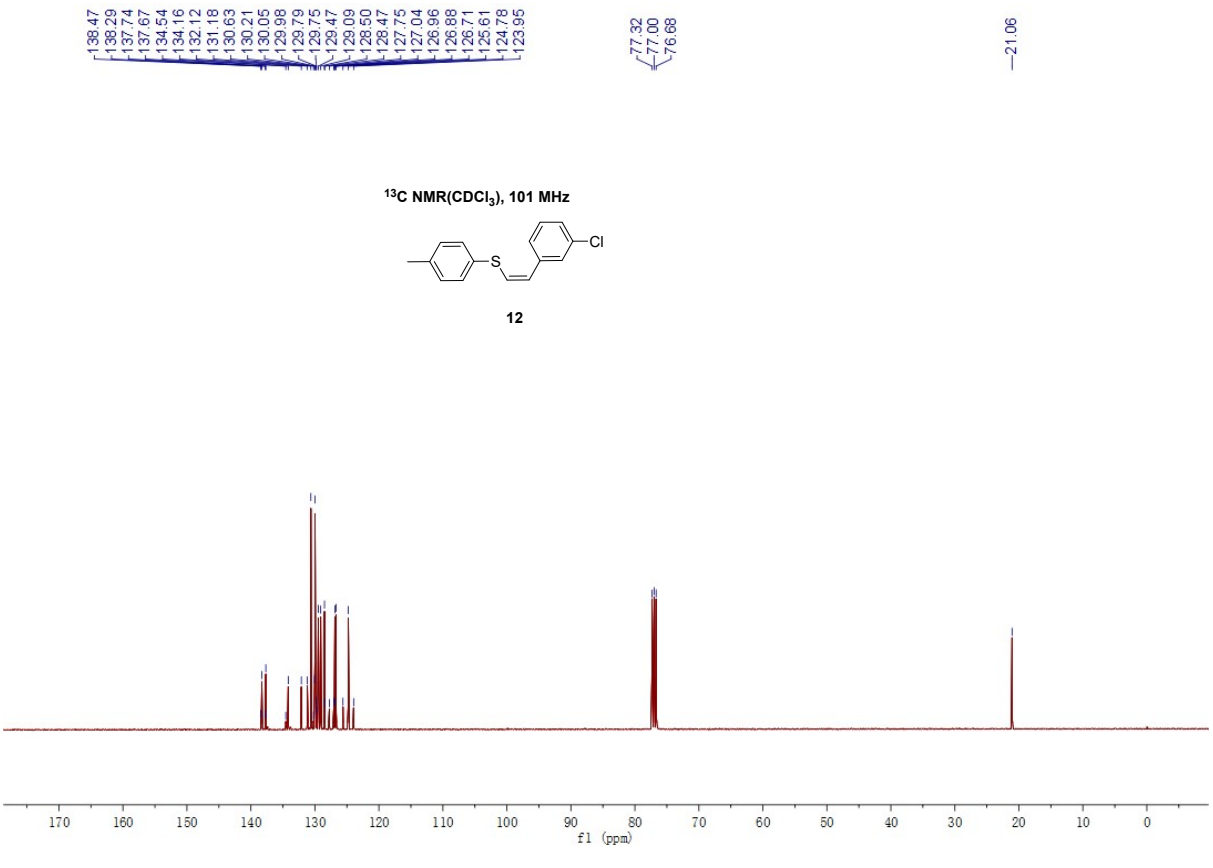


^{1}H NMR($CDCl_3$), 400 MHz

12



^{13}C NMR($CDCl_3$), 101 MHz

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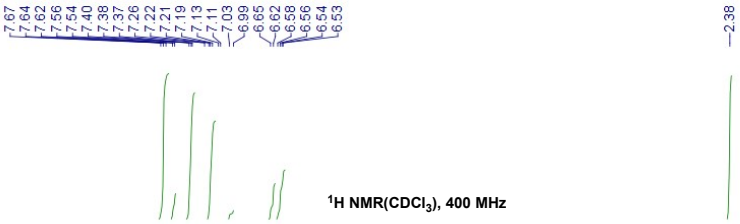
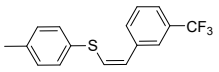


^{1}H NMR($CDCl_3$), 400 MHz



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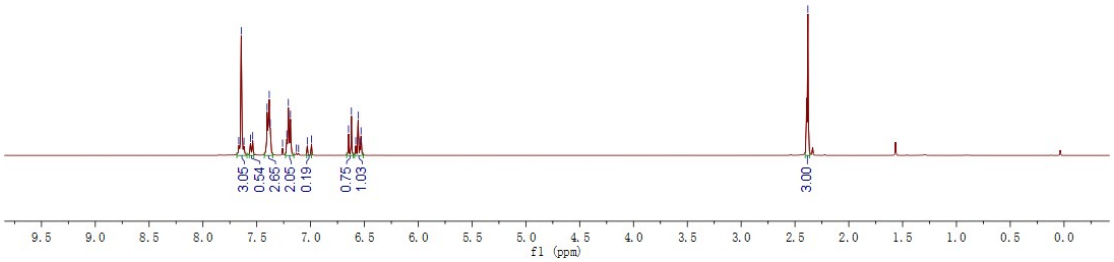
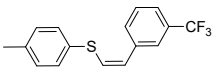


^{13}C NMR($CDCl_3$), 101 MHz



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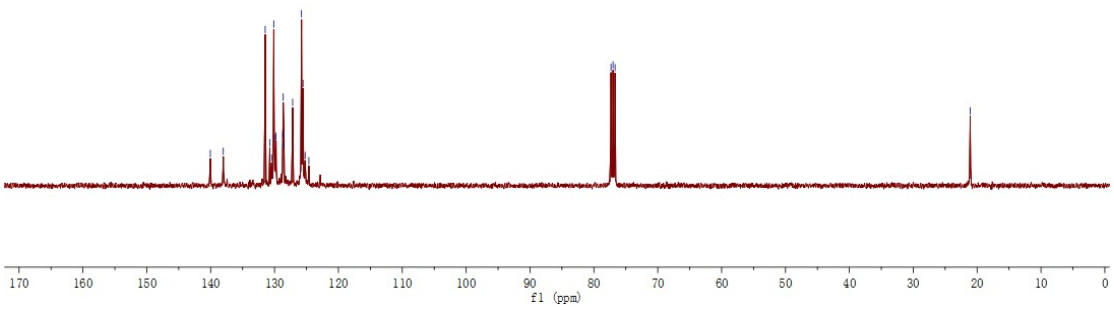
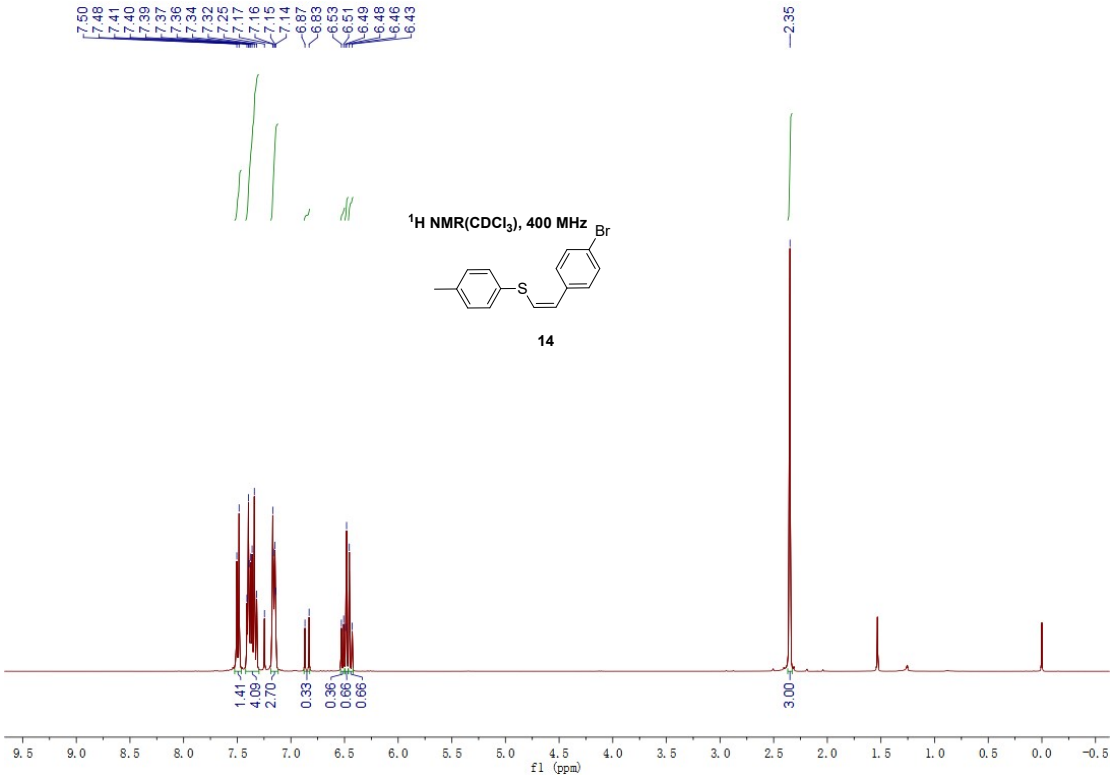
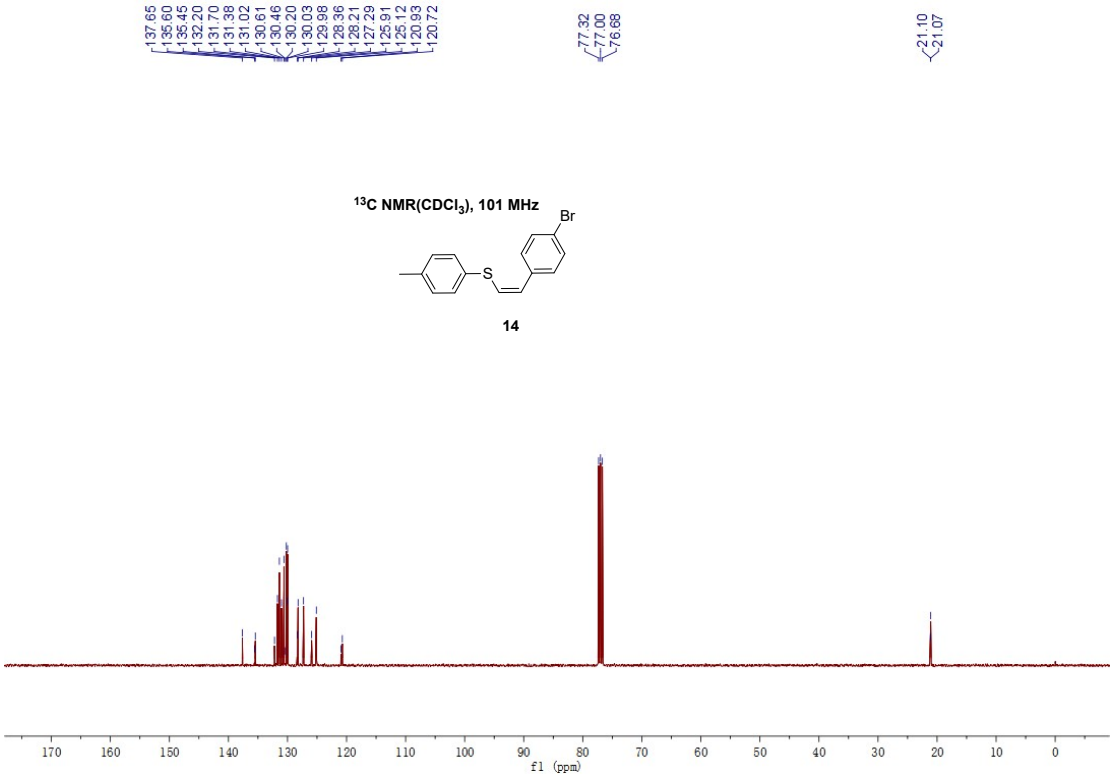




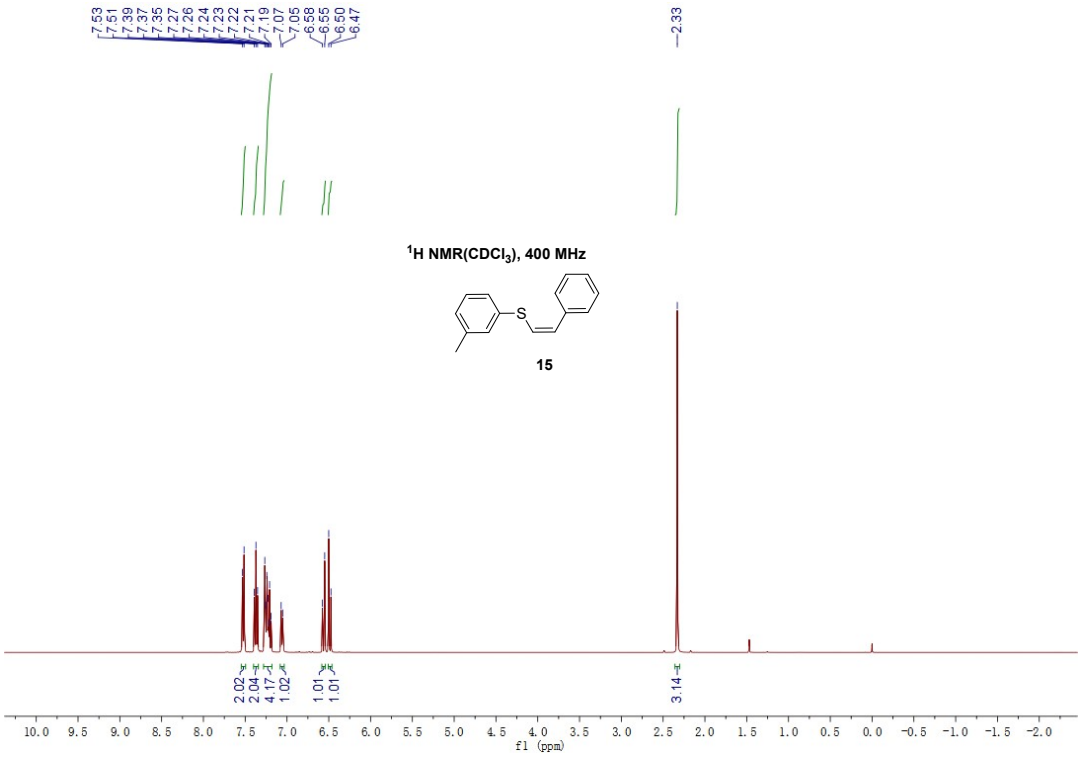
^{1}H NMR($CDCl_3$), 400 MHz

14



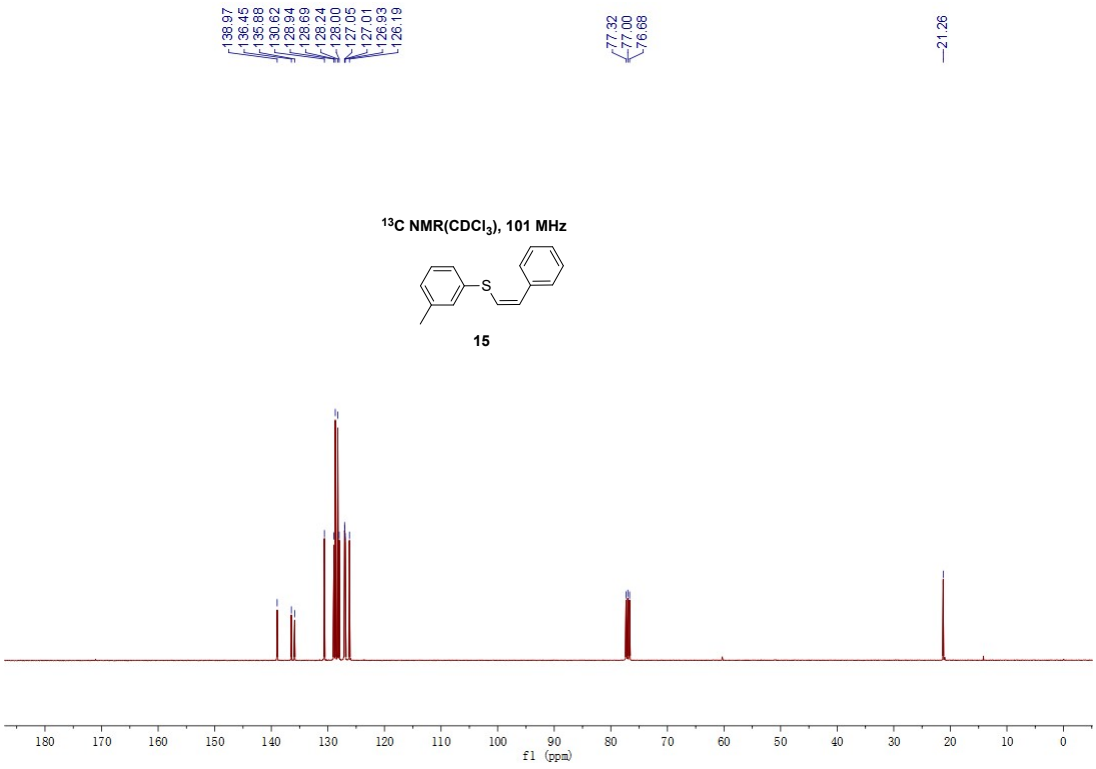
^{13}C NMR($CDCl_3$), 101 MHz

14



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

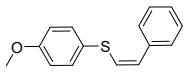
15



^{13}C NMR($CDCl_3$), 101 MHz

15

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



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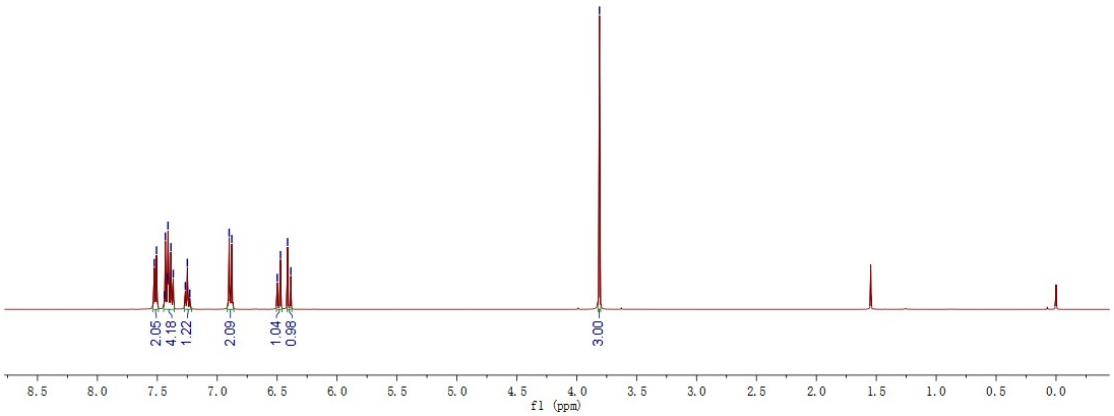
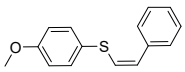


^{13}C NMR($CDCl_3$), 101 MHz



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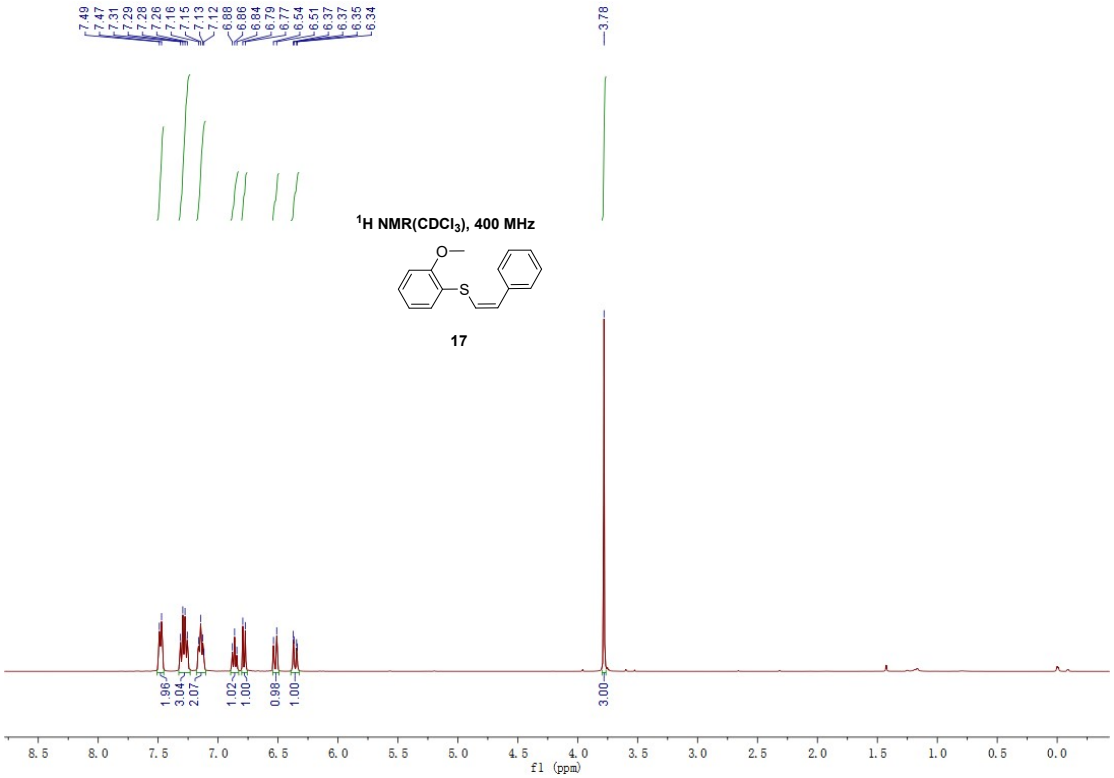

^{1}H NMR($CDCl_3$), 400 MHz

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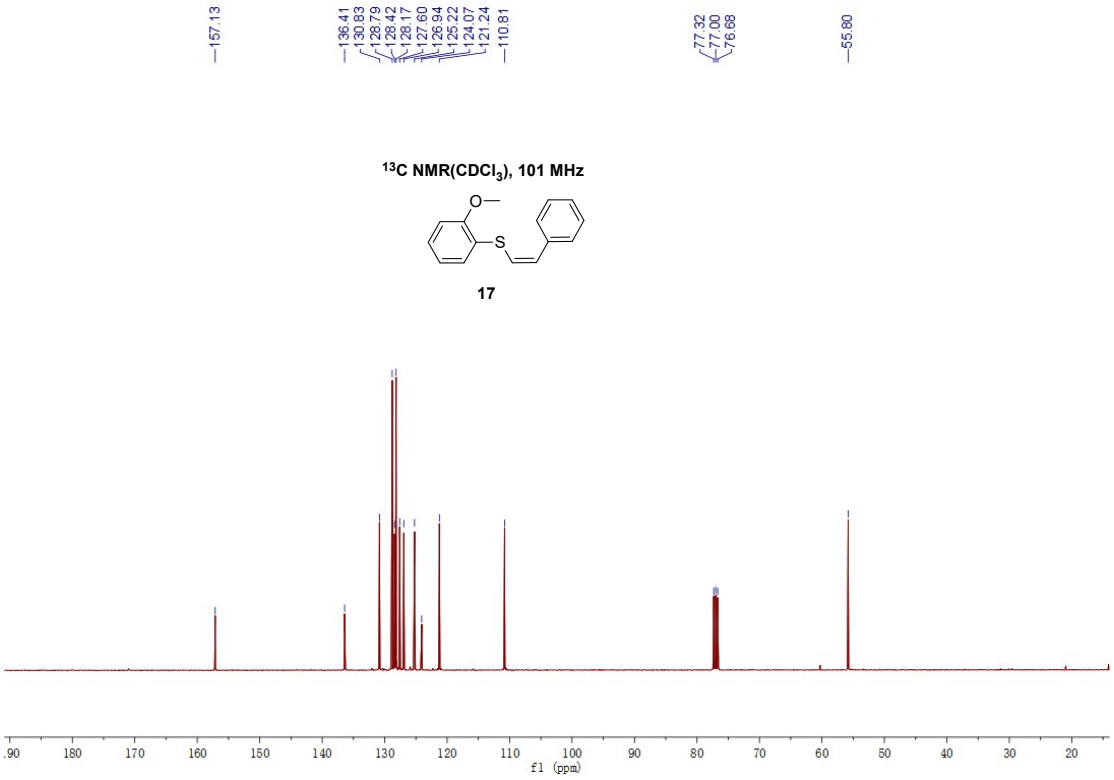

^{13}C NMR($CDCl_3$), 101 MHz

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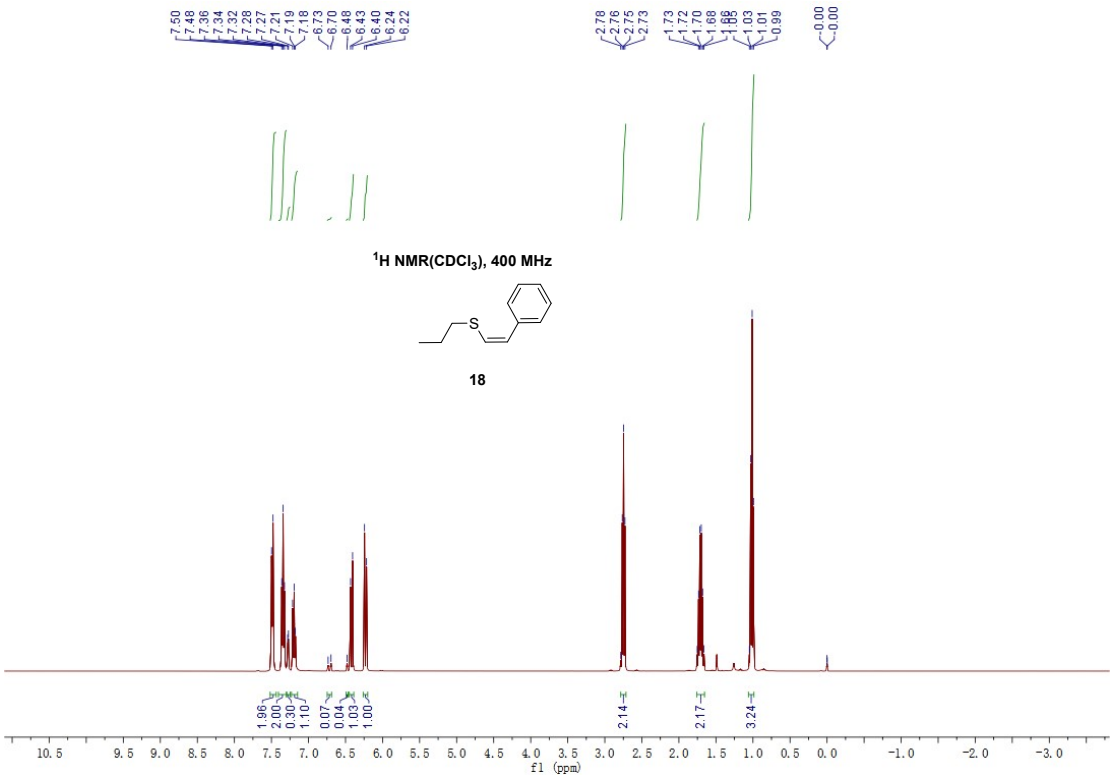

^{1}H NMR($CDCl_3$), 400 MHz

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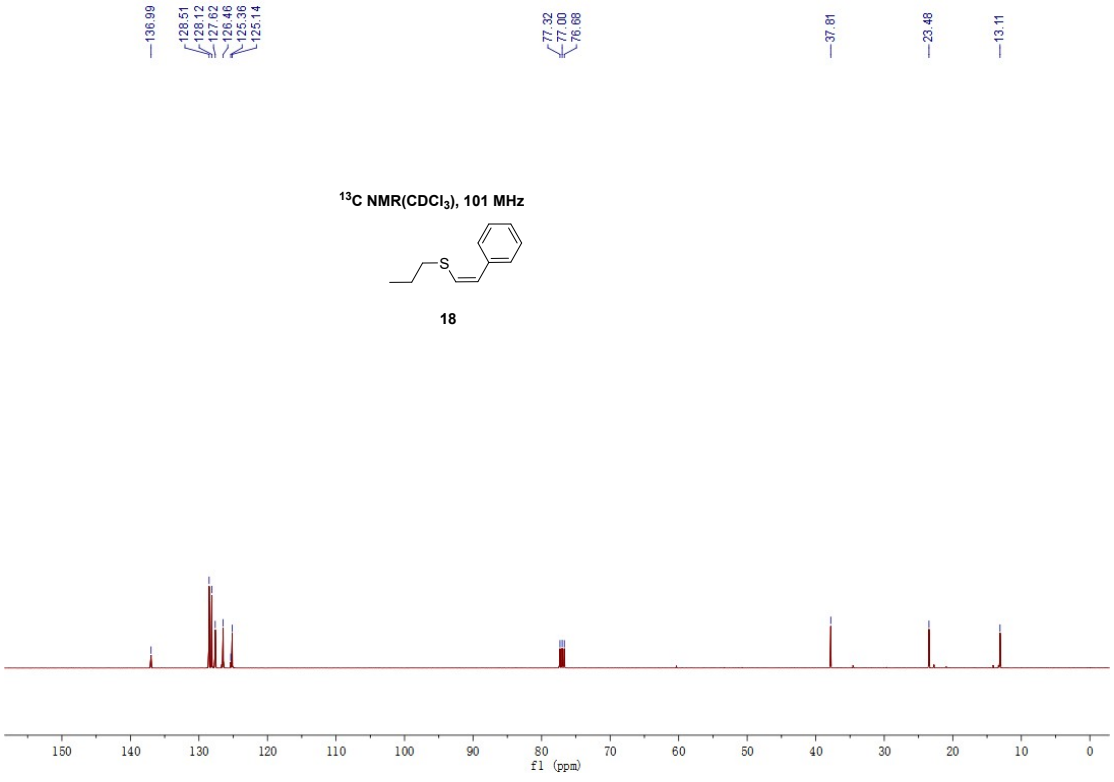

^{13}C NMR($CDCl_3$), 101 MHz

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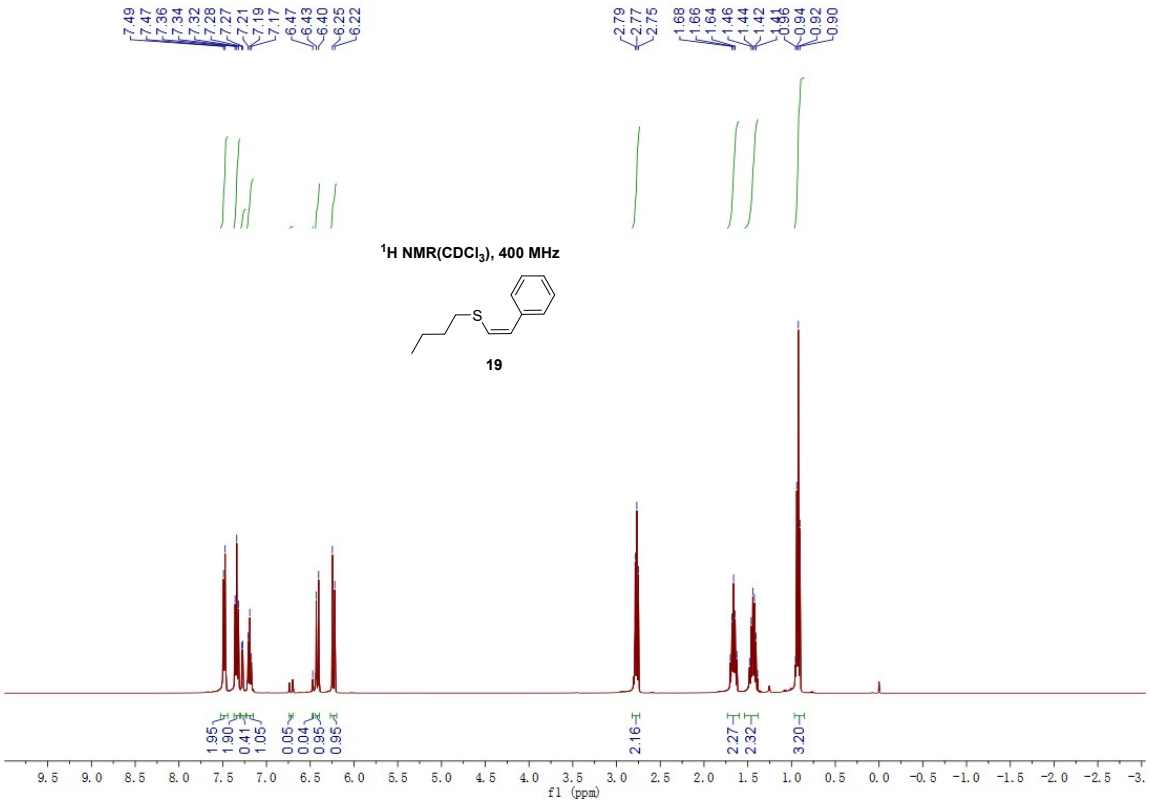
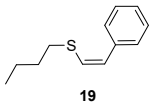


^{1}H NMR($CDCl_3$), 400 MHz

19

^{13}C NMR($CDCl_3$), 101 MHz



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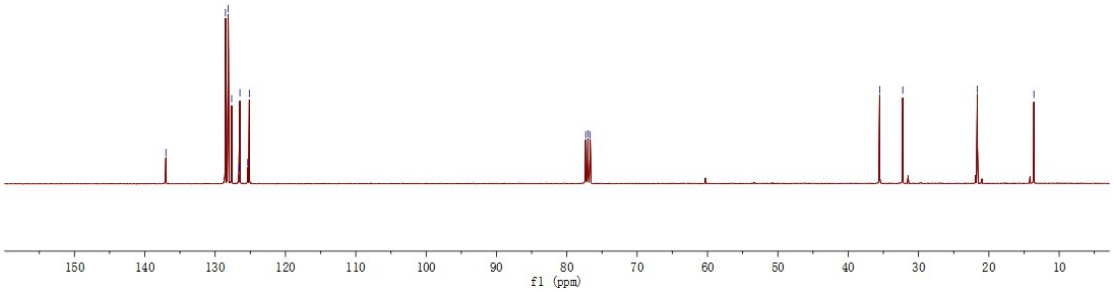
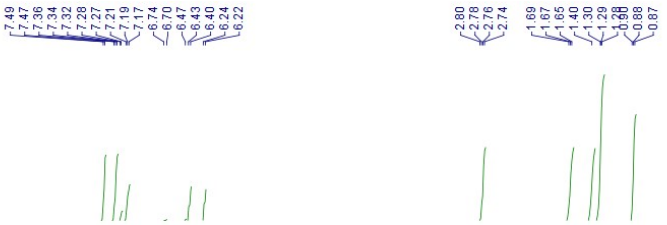
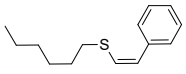




^{1}H NMR($CDCl_3$), 400 MHz



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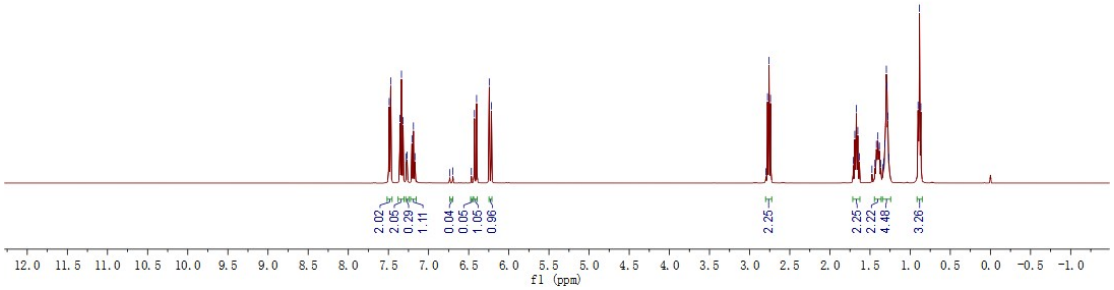
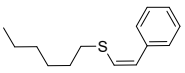


^{13}C NMR($CDCl_3$), 101 MHz



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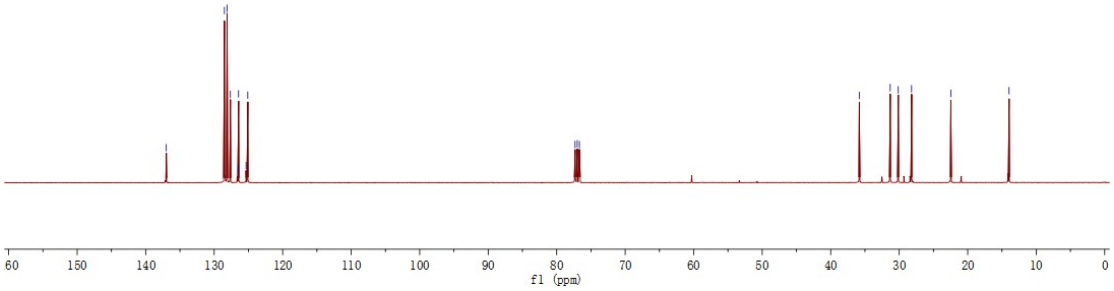
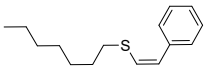


^{1}H NMR($CDCl_3$), 400 MHz



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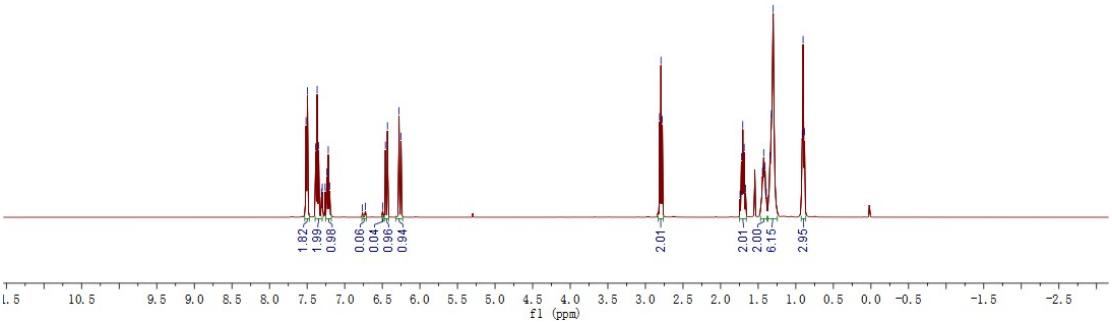
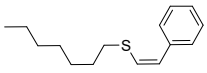


^{13}C NMR($CDCl_3$), 101 MHz



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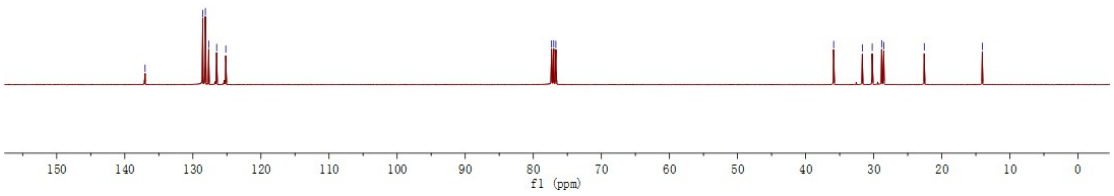
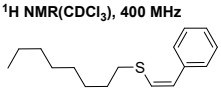


^{1}H NMR($CDCl_3$), 400 MHz



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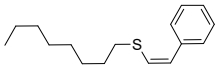
^{13}C NMR($CDCl_3$), 101 MHz



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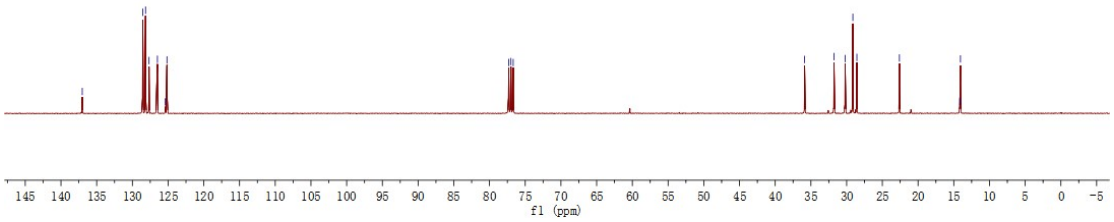

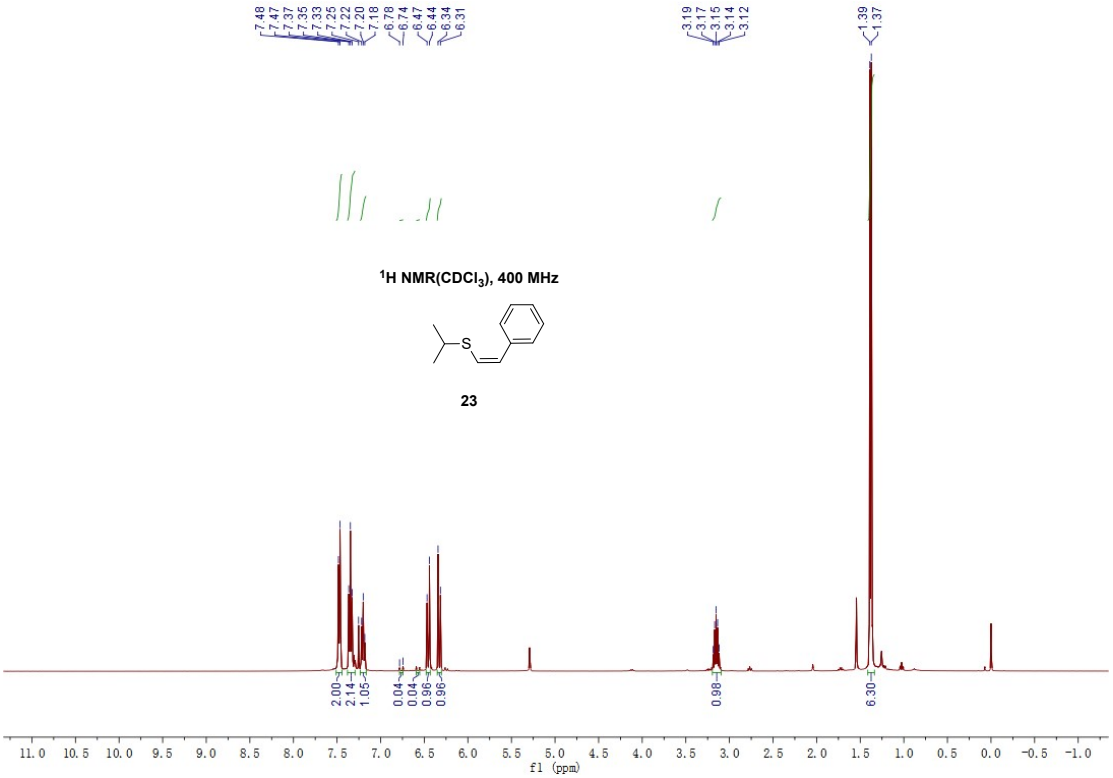

^{1}H NMR($CDCl_3$), 400 MHz

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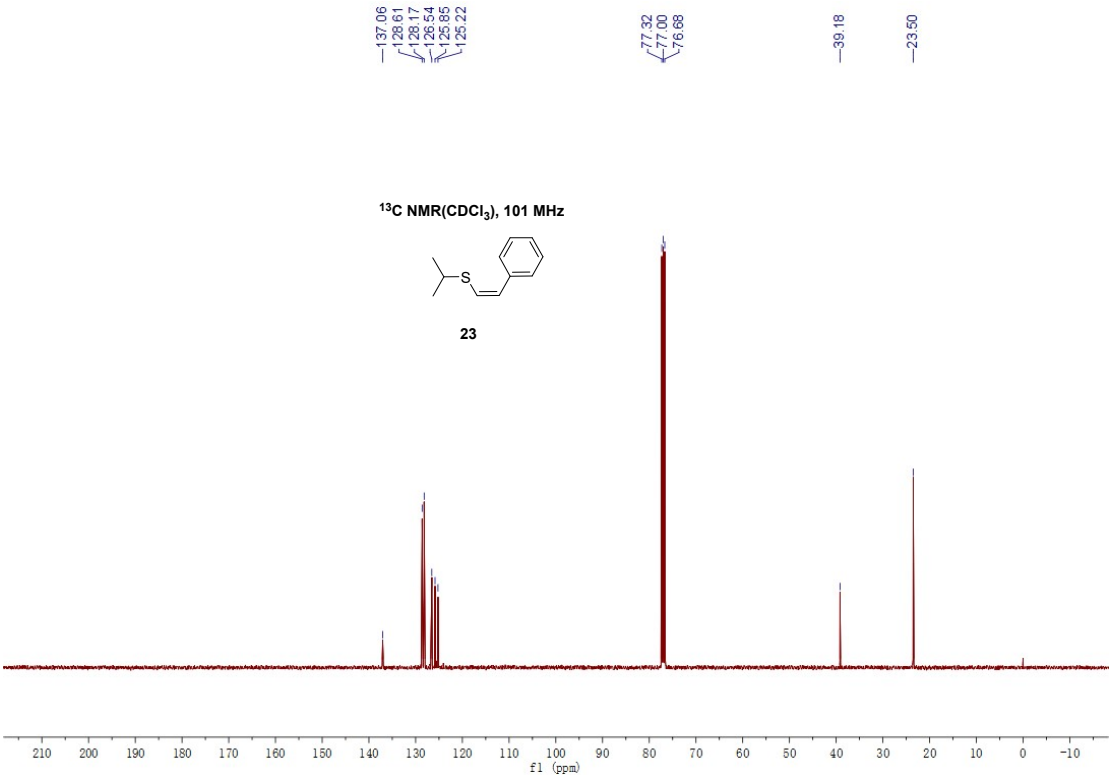

^{13}C NMR($CDCl_3$), 101 MHz

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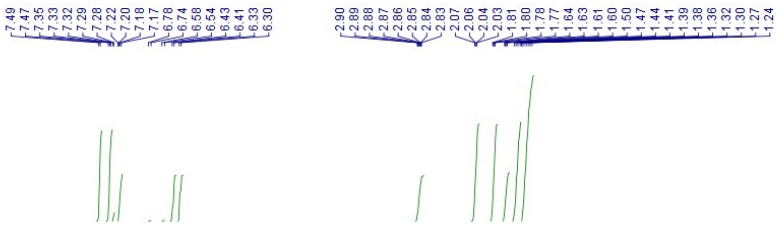
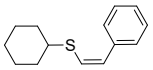


^{1}H NMR($CDCl_3$), 400 MHz



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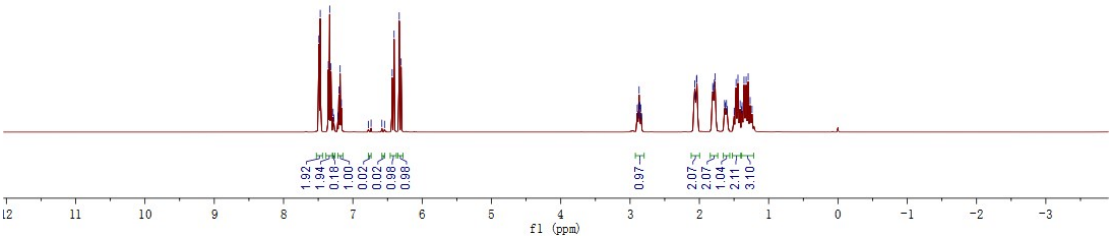
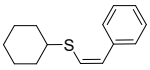


^{13}C NMR($CDCl_3$), 101 MHz



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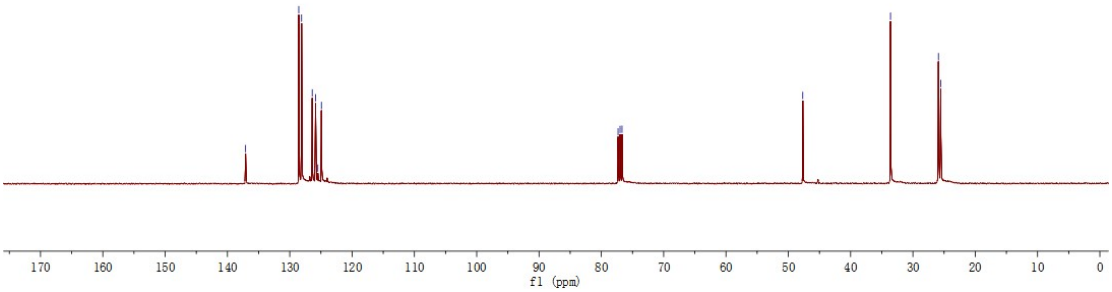

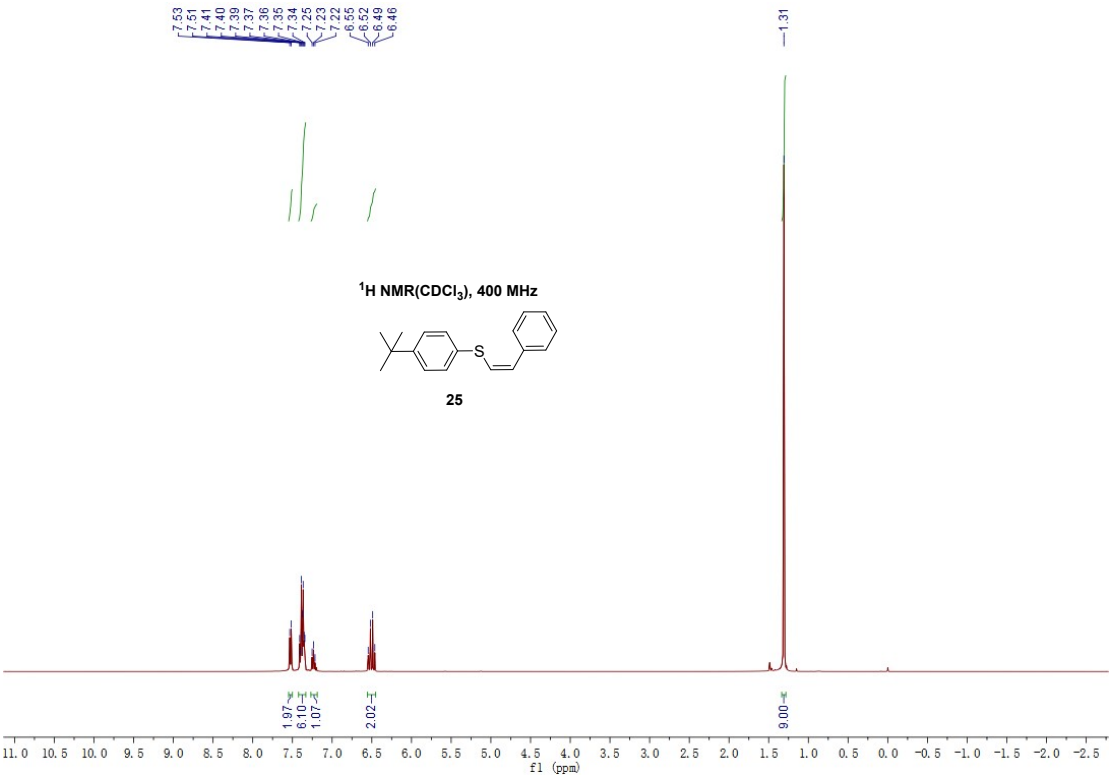

^{1}H NMR($CDCl_3$), 400 MHz

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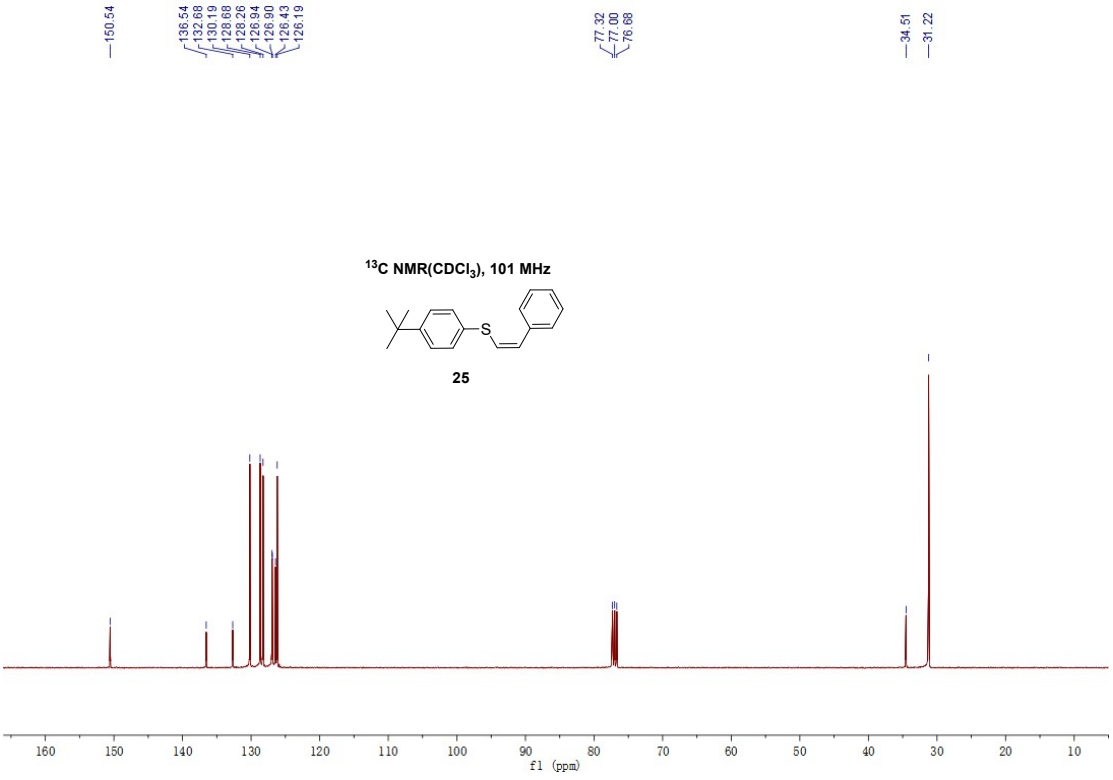

^{13}C NMR($CDCl_3$), 101 MHz

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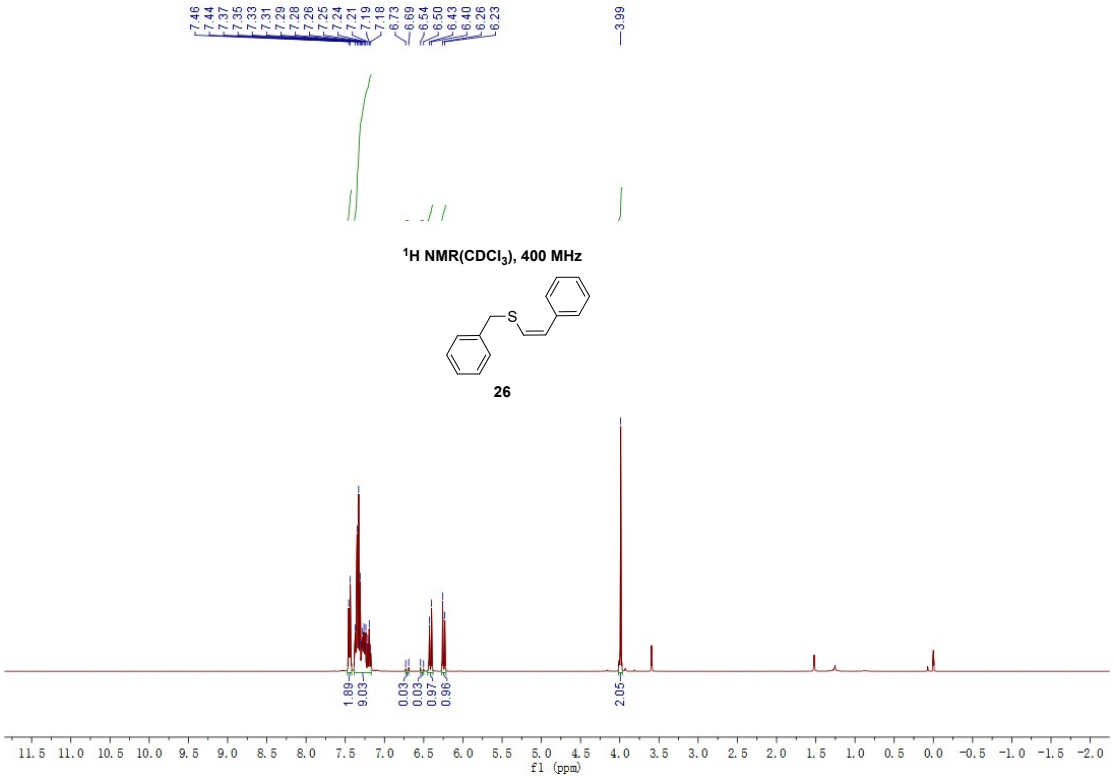

^{1}H NMR($CDCl_3$), 400 MHz

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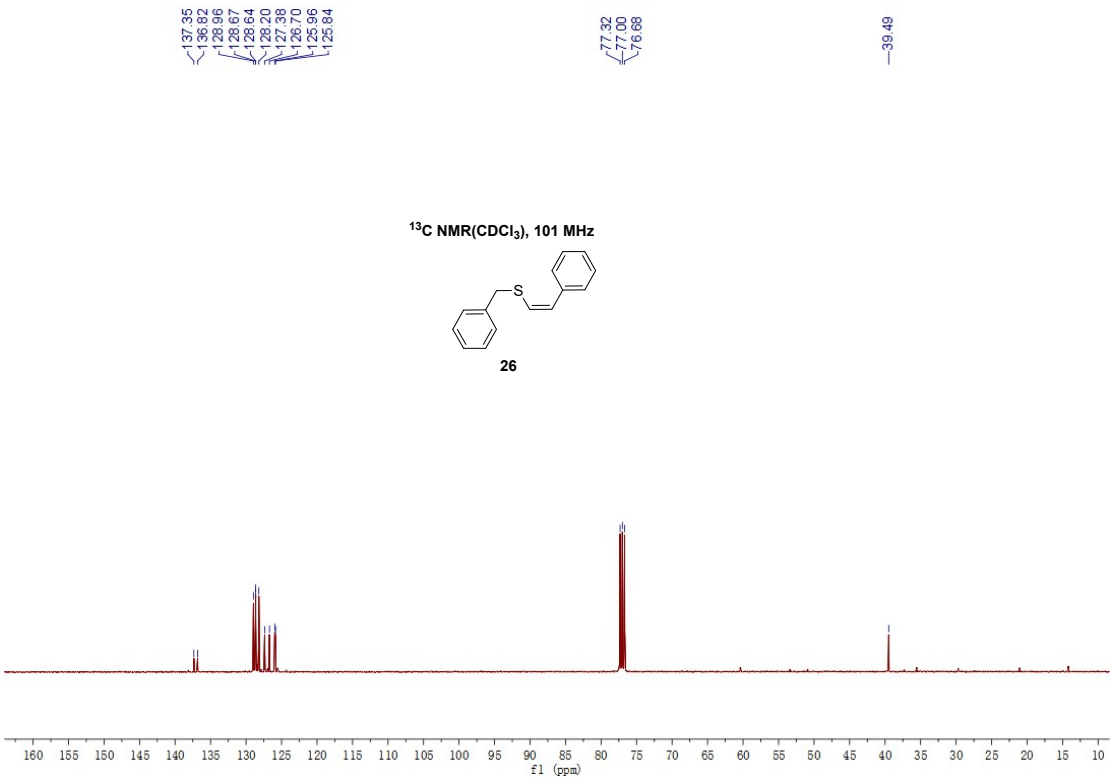

^{13}C NMR($CDCl_3$), 101 MHz

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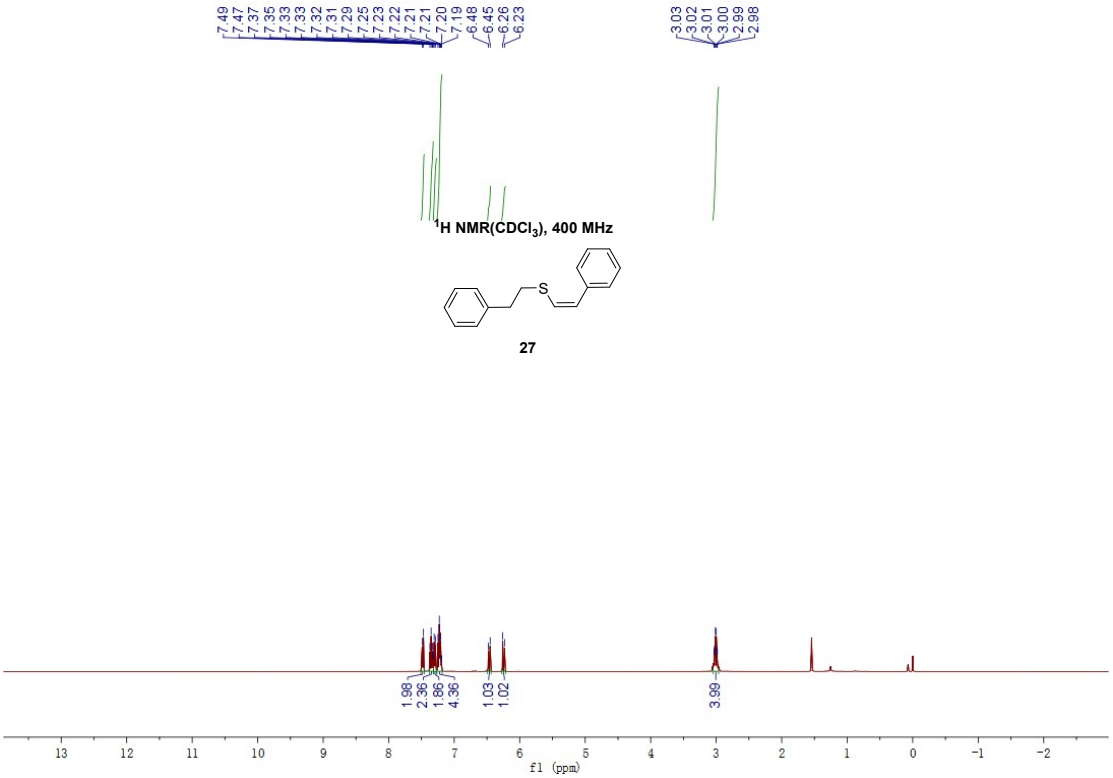

^{1}H NMR($CDCl_3$), 400 MHz

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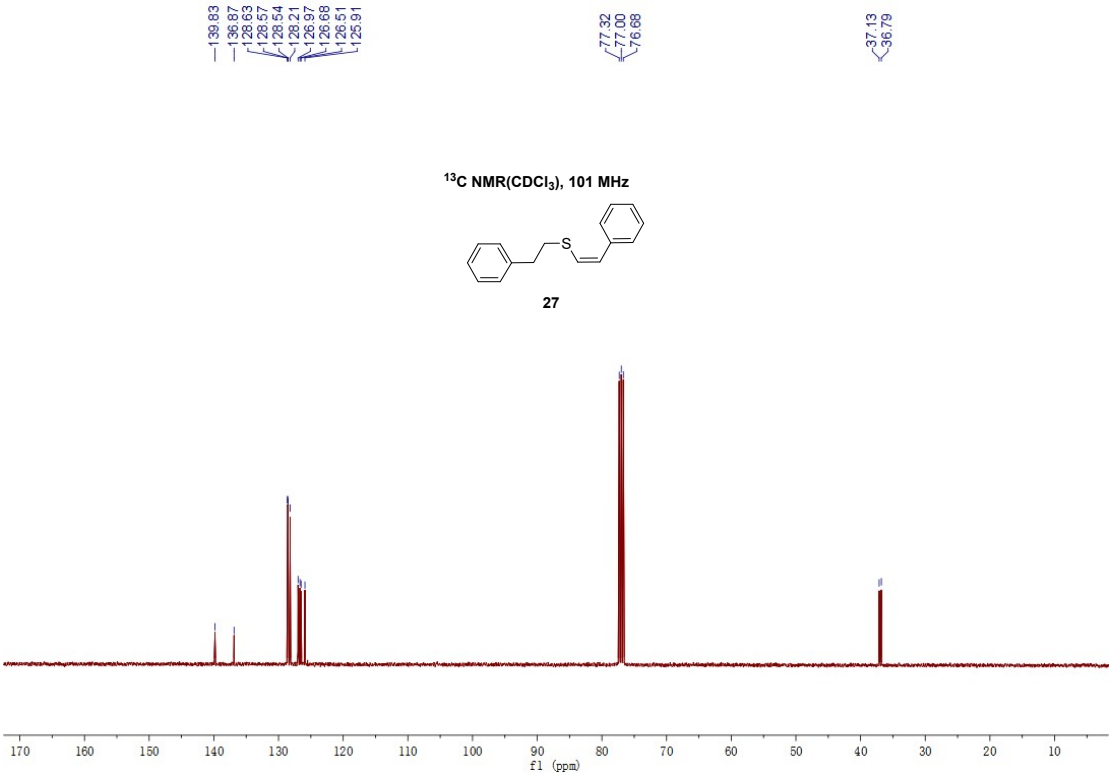
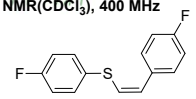


^{13}C NMR($CDCl_3$), 101 MHz

27

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



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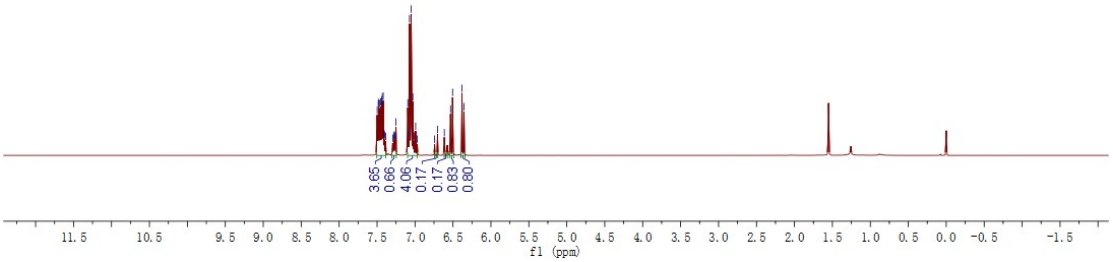
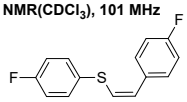


^{13}C NMR($CDCl_3$), 101 MHz



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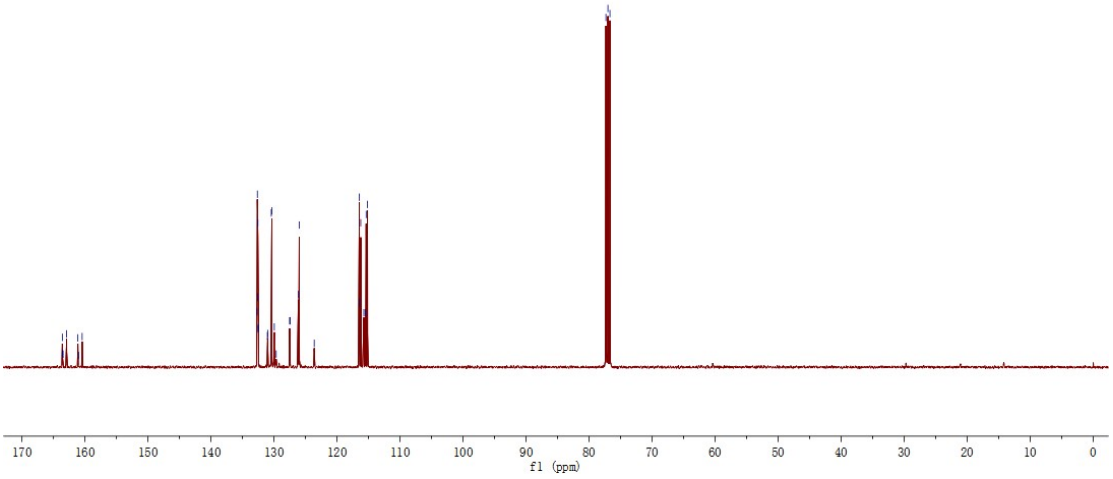
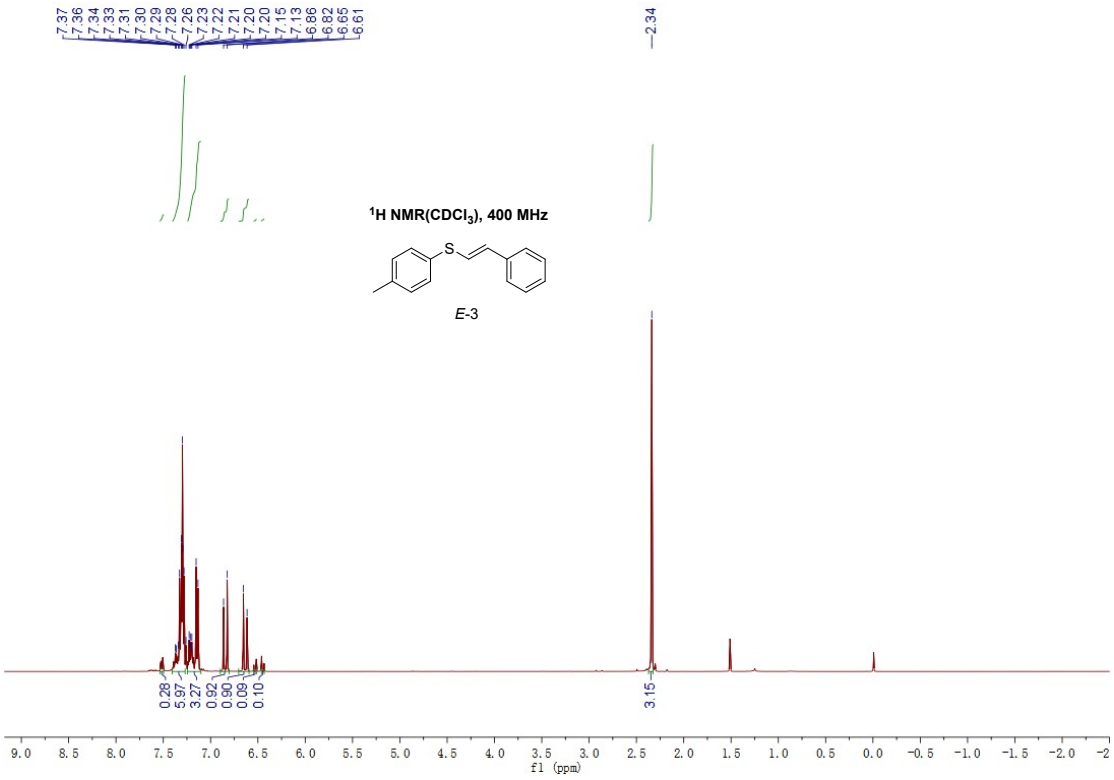
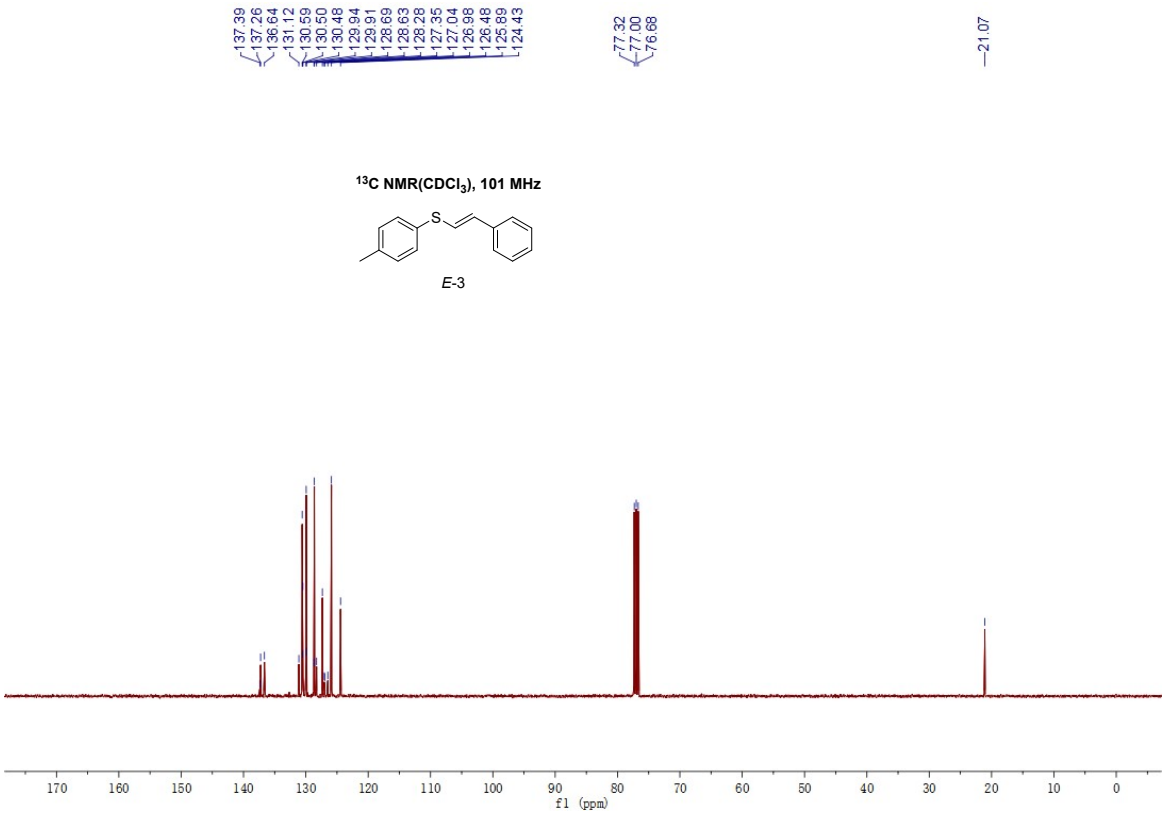




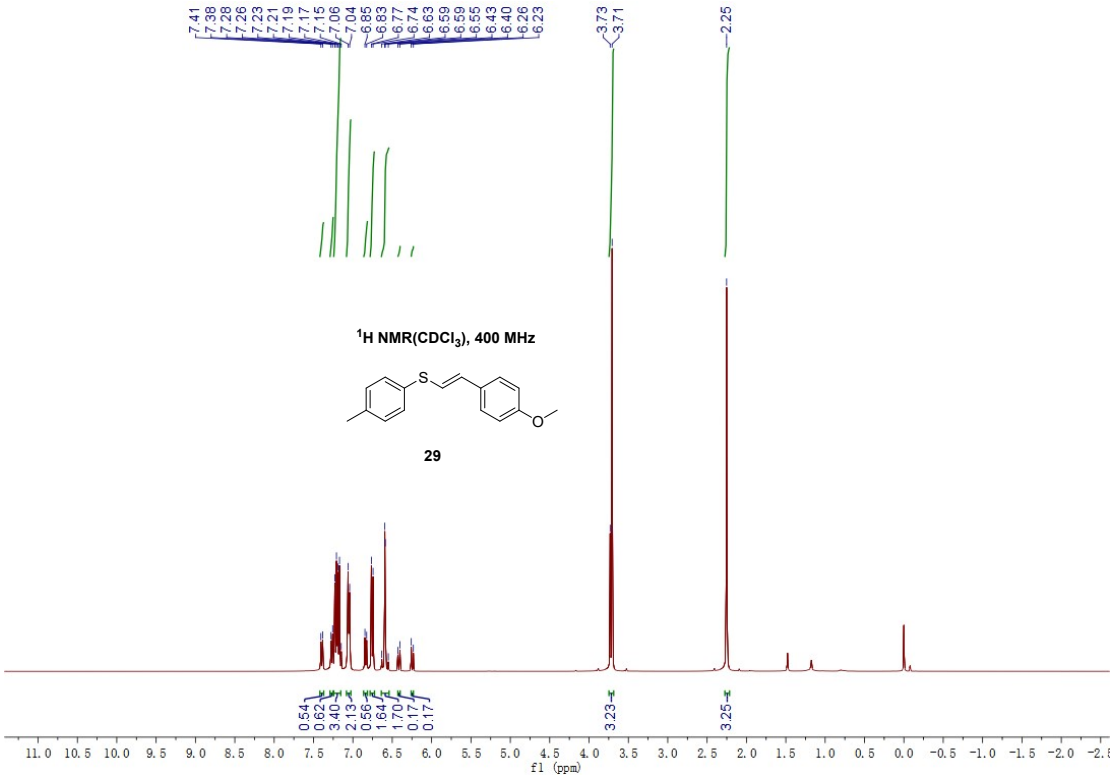
^{1}H NMR($CDCl_3$), 400 MHz

E-3



^{13}C NMR($CDCl_3$), 101 MHz

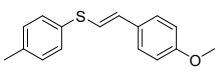
E-3



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

29

^{13}C NMR($CDCl_3$), 101 MHz



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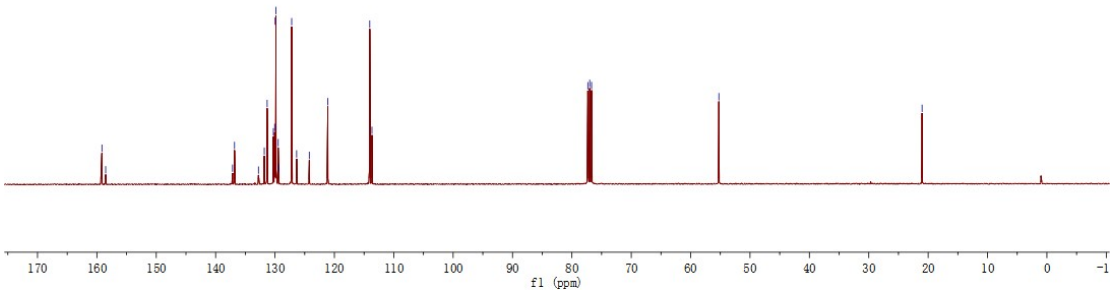
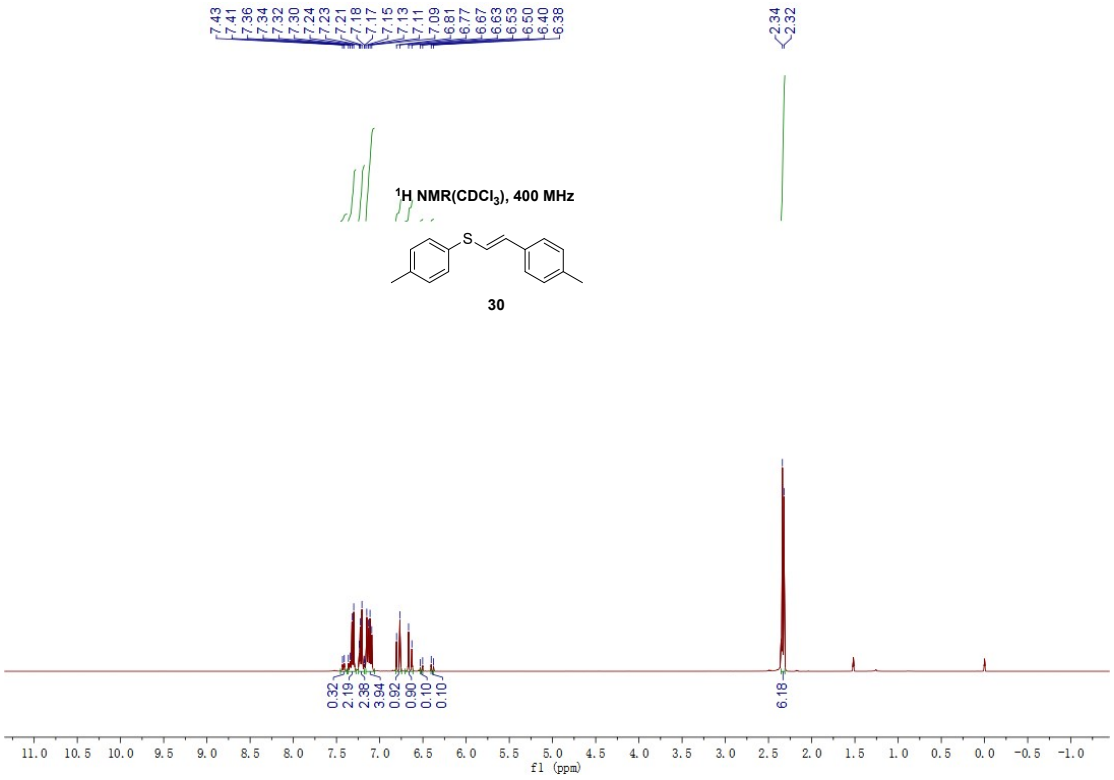
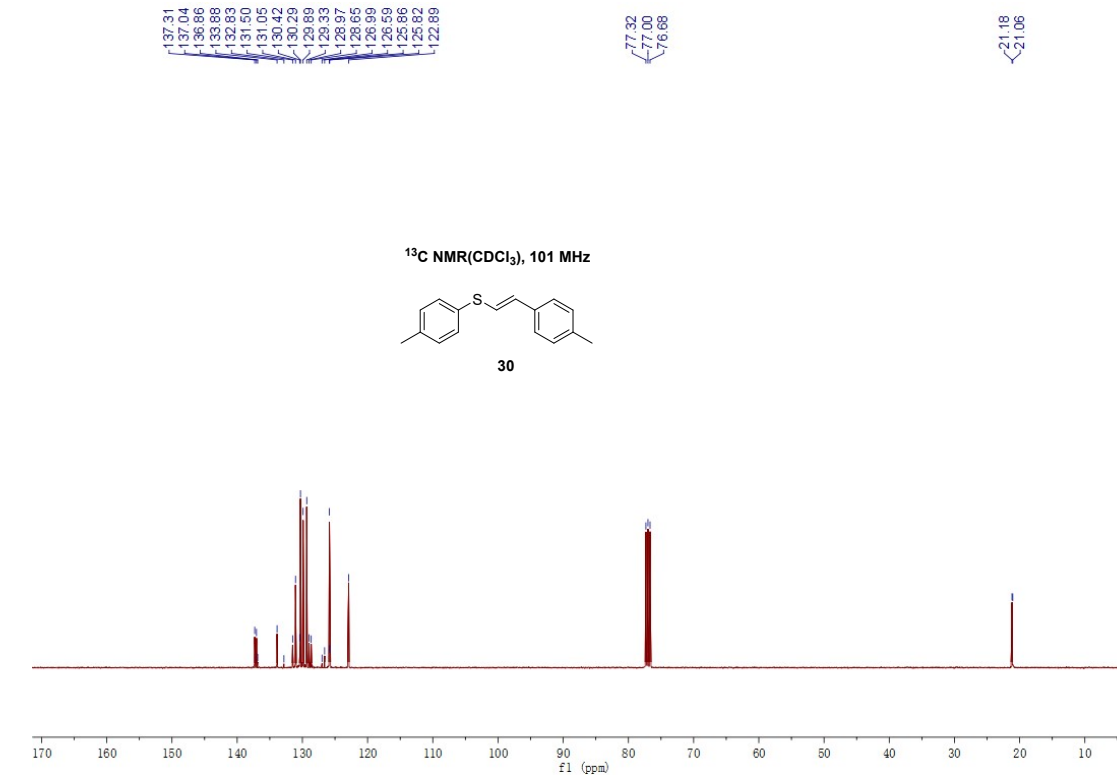




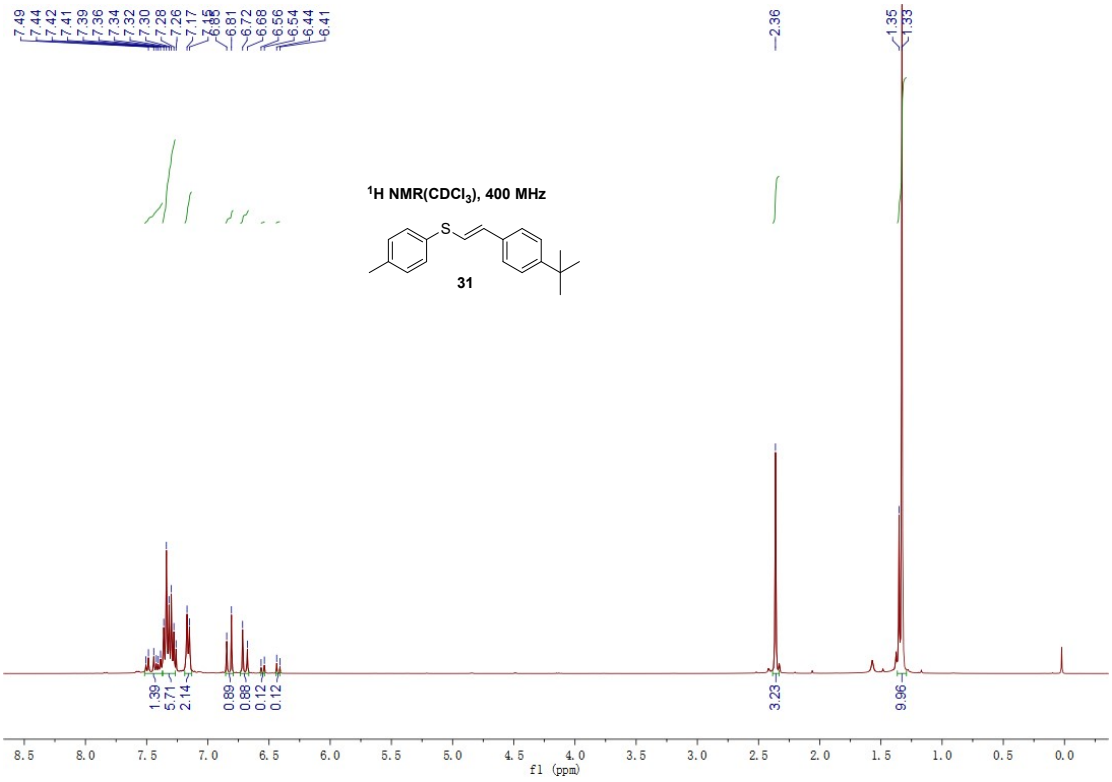
^{1}H NMR($CDCl_3$), 400 MHz

30



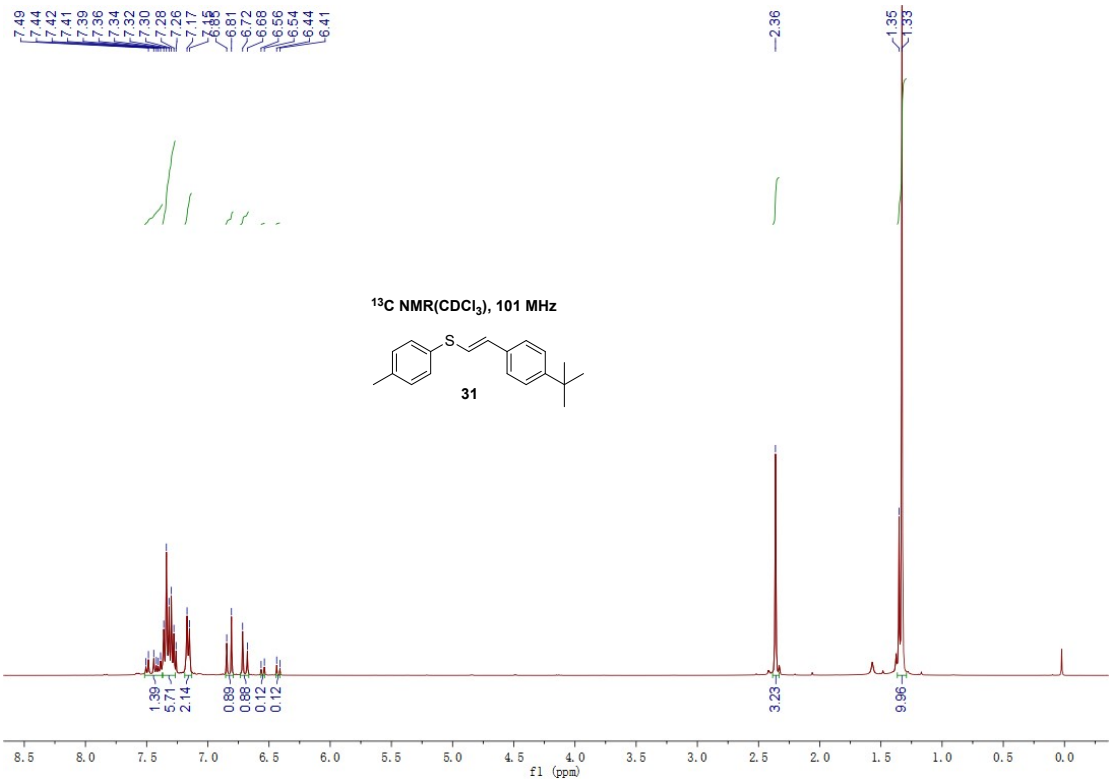
^{13}C NMR($CDCl_3$), 101 MHz

30



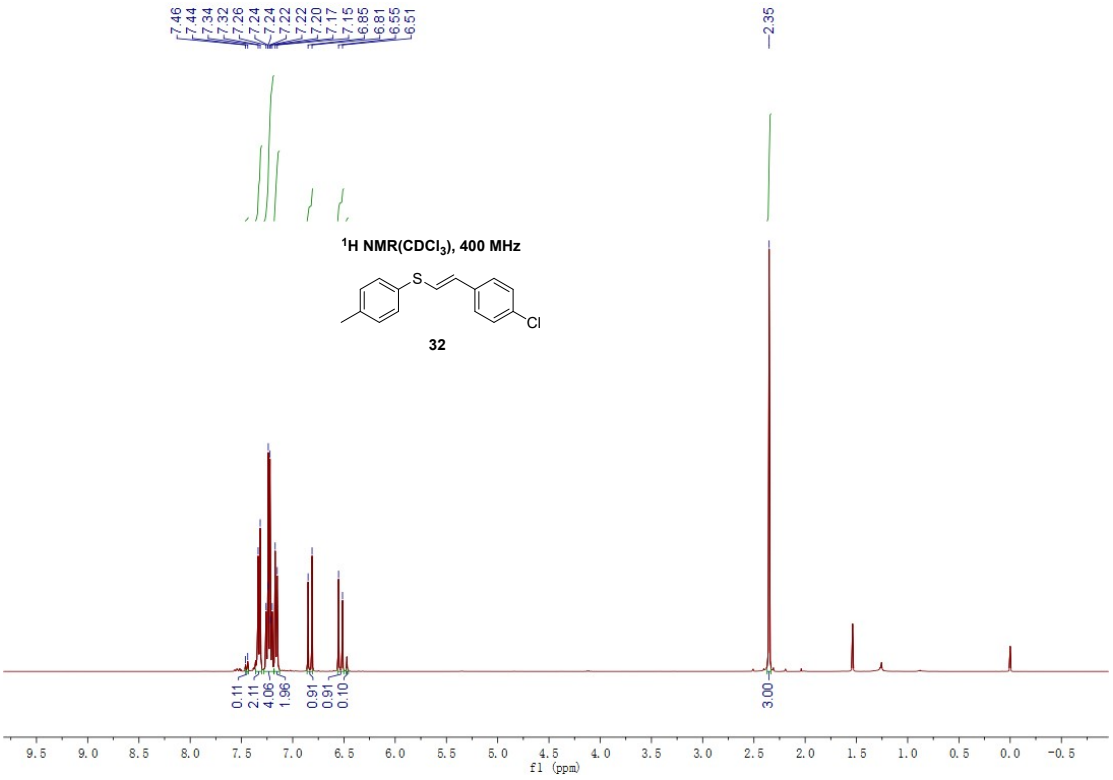
^{1}H NMR($CDCl_3$), 400 MHz

31



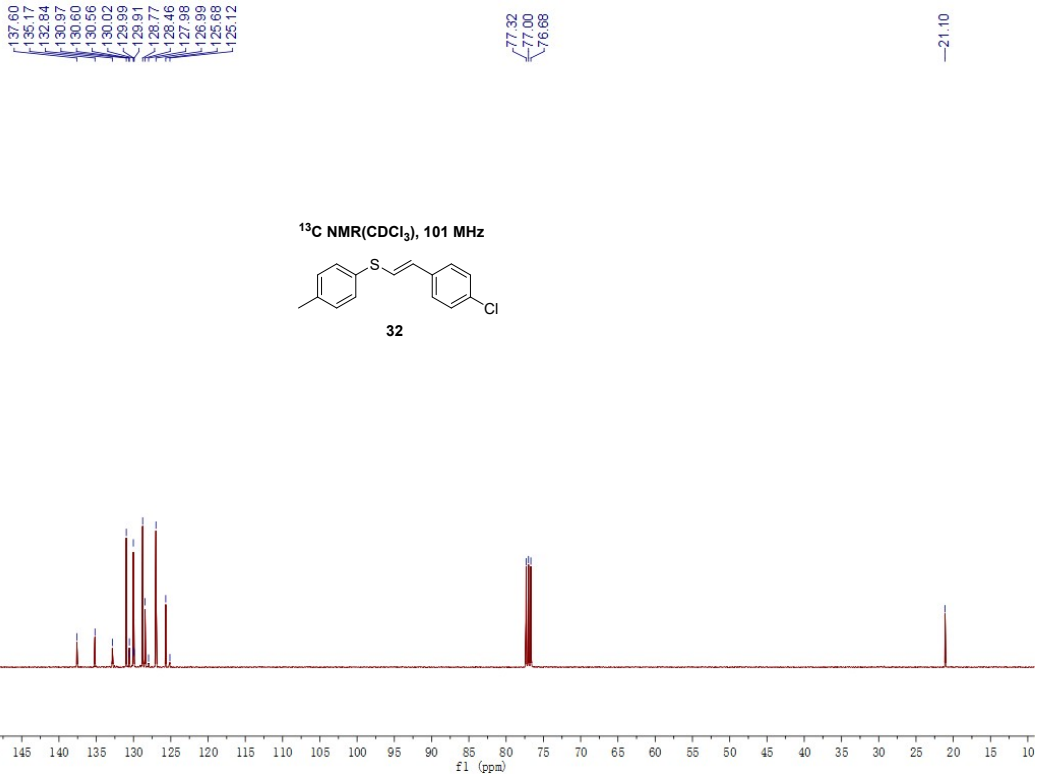
^{13}C NMR($CDCl_3$), 101 MHz

31



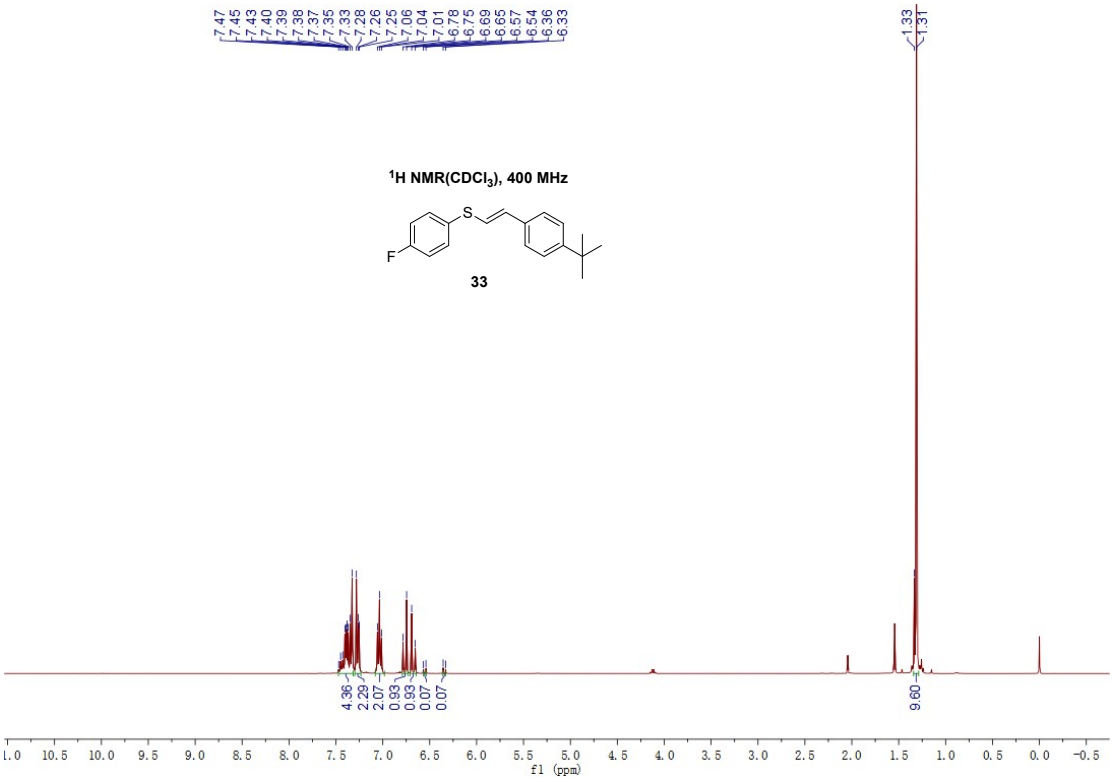
^{1}H NMR($CDCl_3$), 400 MHz

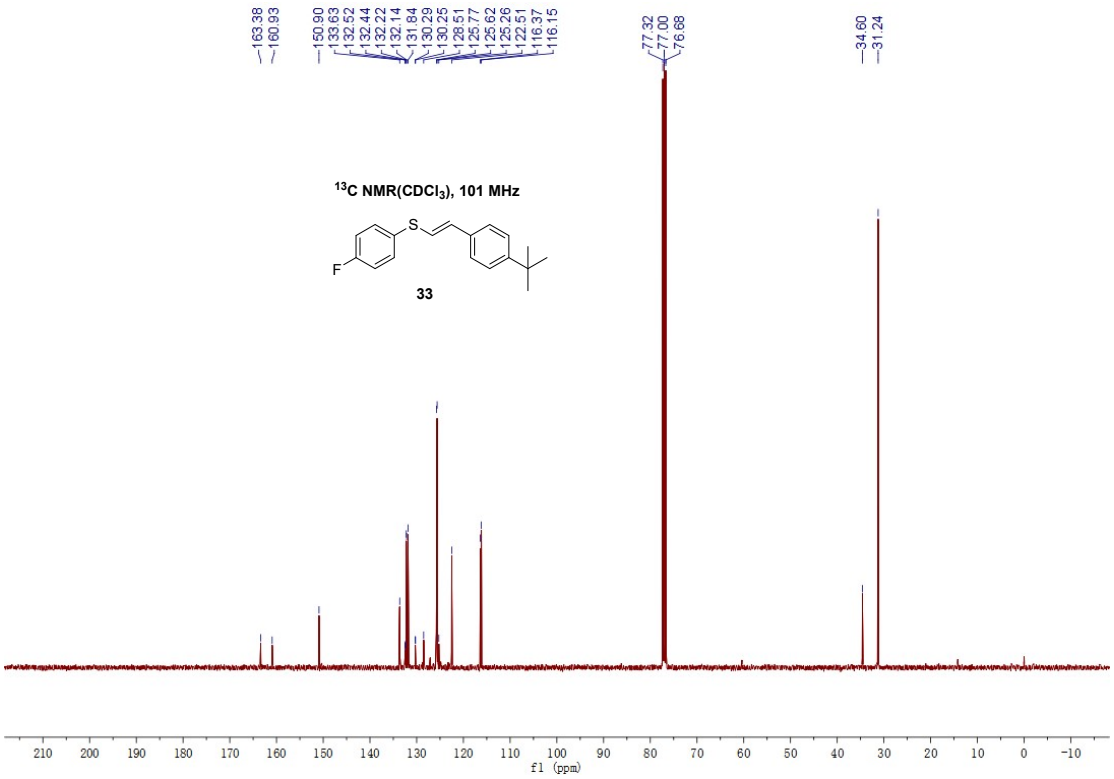
32

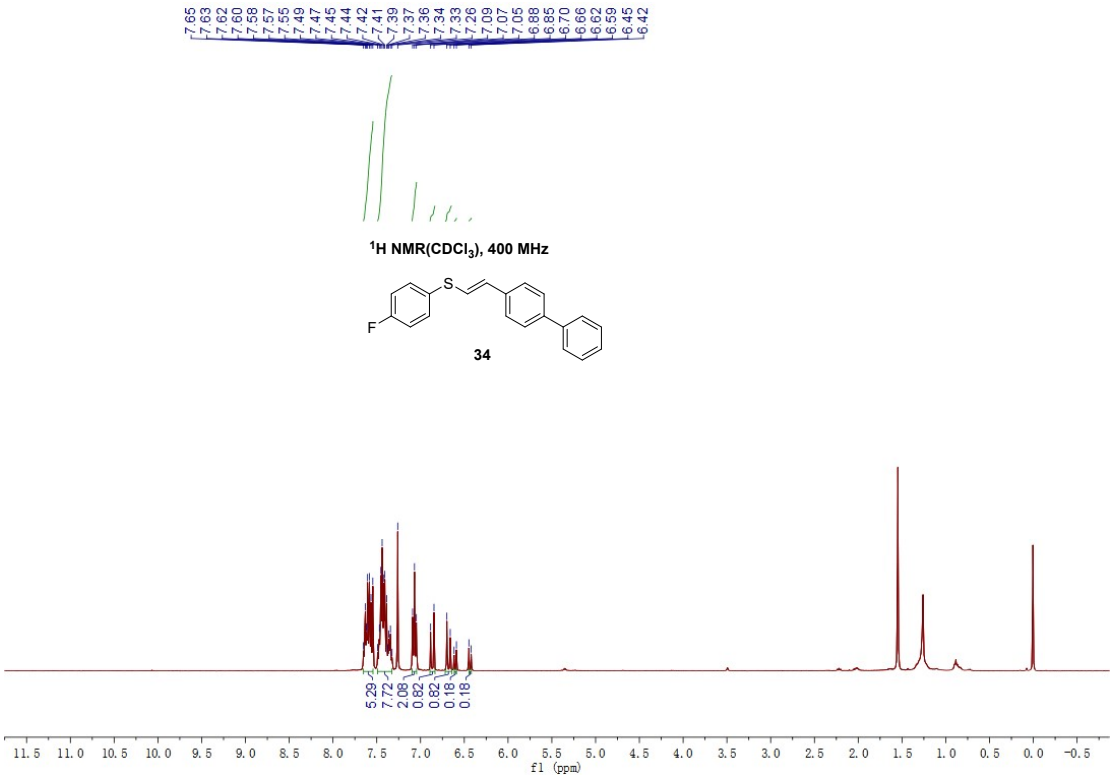


^{13}C NMR($CDCl_3$), 101 MHz

32

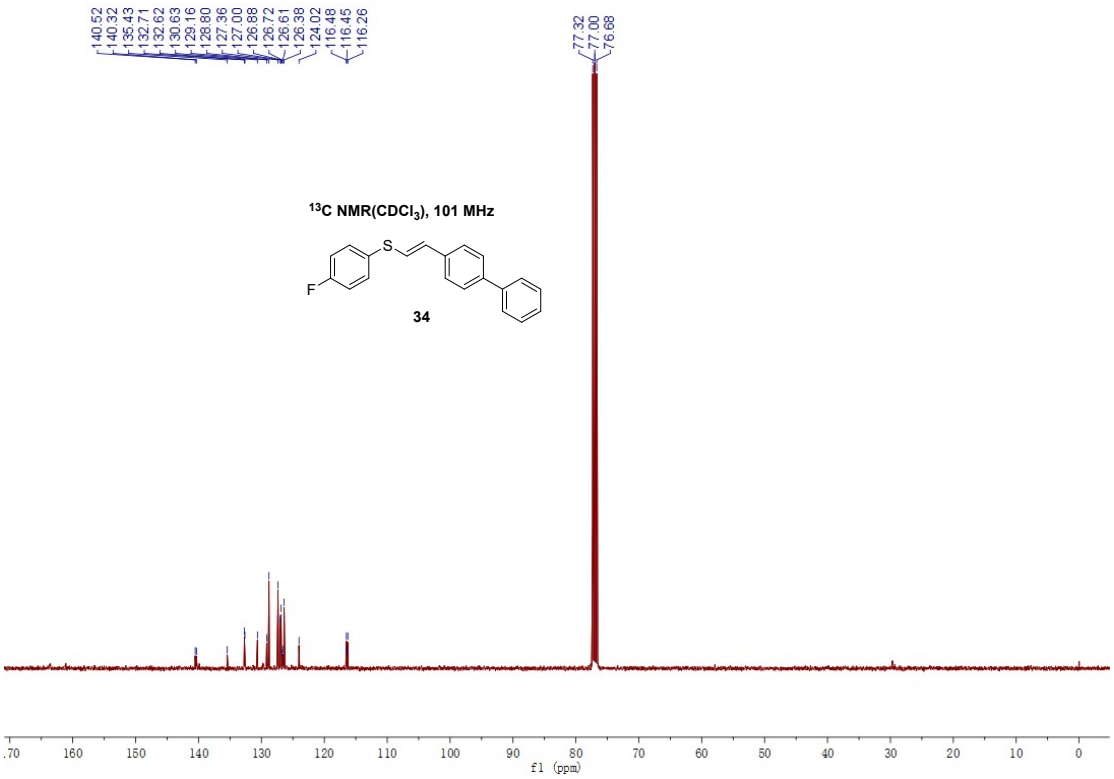

7.47
7.45
7.43
7.40
7.39
7.38
7.37
7.35
7.33
7.28
7.26
7.25
7.06
7.04
7.01
6.78
6.75
6.69
6.65
6.57
6.54
6.36
6.33
1.33
1.31
^{1}H NMR(CDCl$_3$), 400 MHz
S
F
33
4.36
2.29
2.07
0.93
0.93
0.07
0.07
9.60
f1 (ppm)


163.38
160.93
150.90
133.63
132.52
132.44
132.22
132.14
131.84
130.29
130.25
128.51
125.77
125.62
125.26
122.51
116.37
116.15
77.32
77.00
76.68
34.60
31.24
^{13}C NMR(CDCl$_3$), 101 MHz
S
F
33
f1 (ppm)



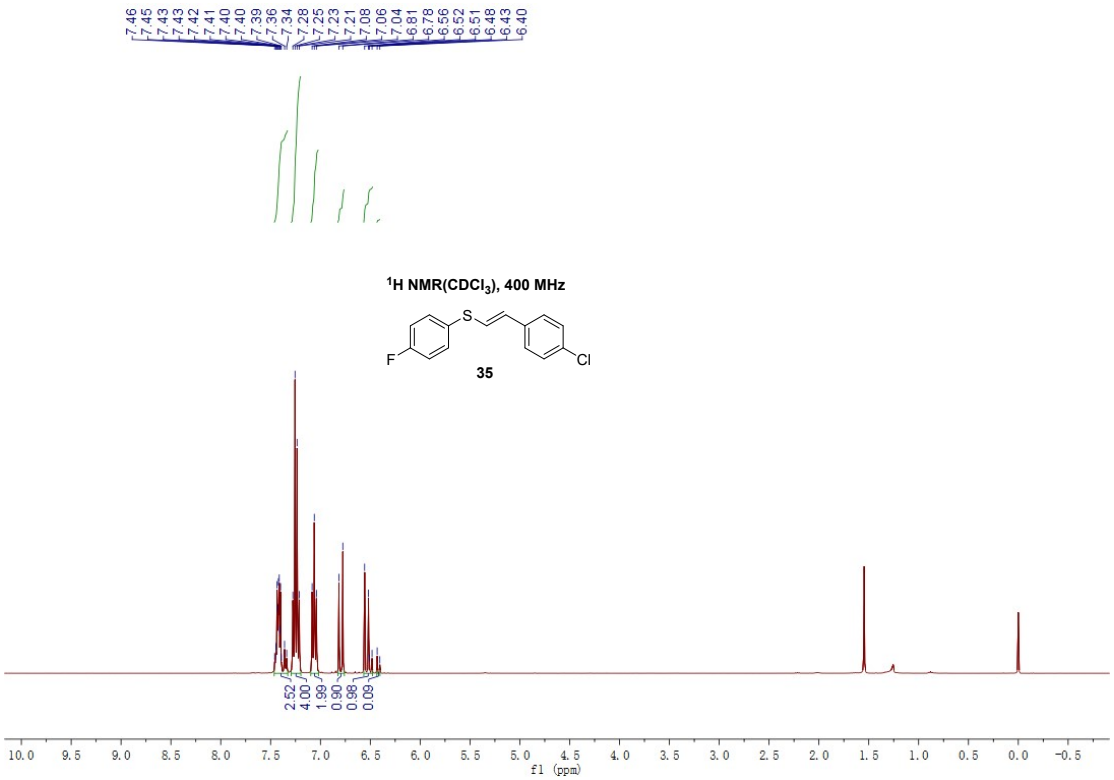
^{1}H NMR($CDCl_3$), 400 MHz

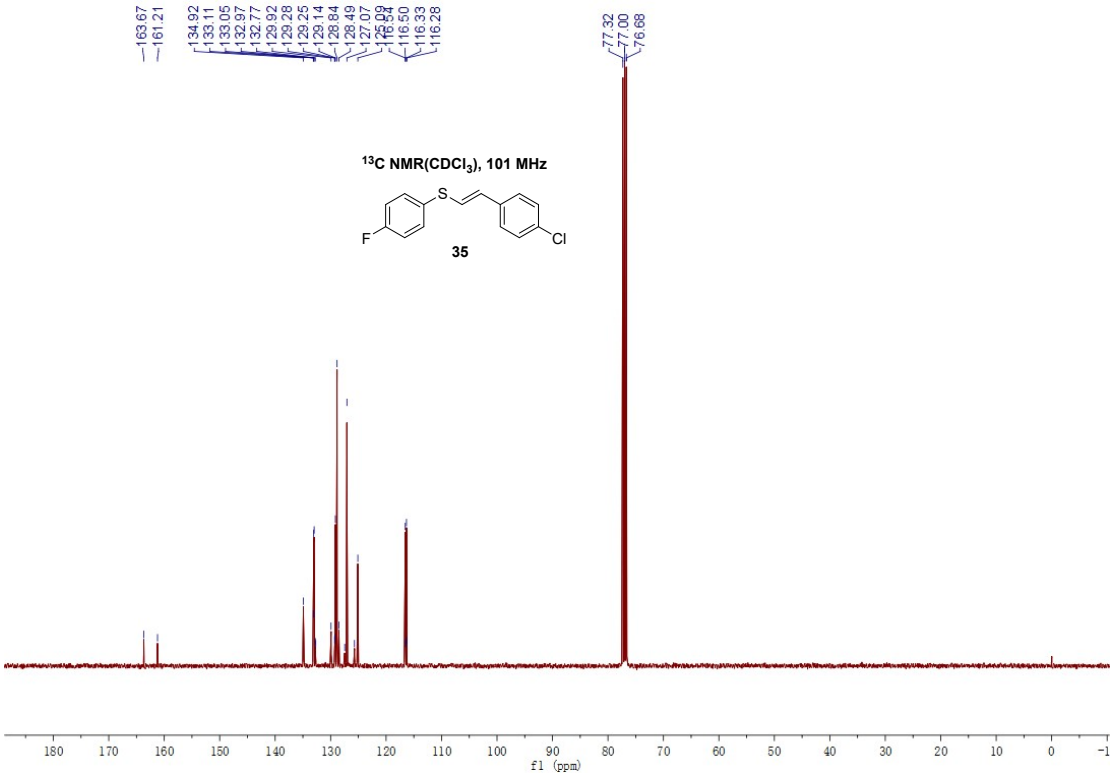
34

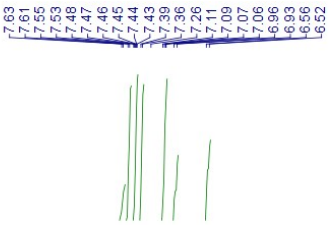


^{13}C NMR($CDCl_3$), 101 MHz

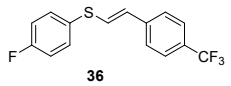
34


7.46
7.45
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.36
7.34
7.28
7.25
7.23
7.21
7.08
7.06
7.04
6.81
6.78
6.56
6.52
6.51
6.48
6.43
6.40
1H NMR(CDCl3), 400 MHz
S
F
Cl
35
2.52
4.00
1.99
0.90
0.98
0.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.67
161.21
134.92
133.11
133.05
132.97
132.77
129.92
129.28
129.25
129.14
128.84
128.49
127.07
116.50
116.33
116.28
77.32
77.00
76.68
13C NMR(CDCl3), 101 MHz
S
F
Cl
35
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



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



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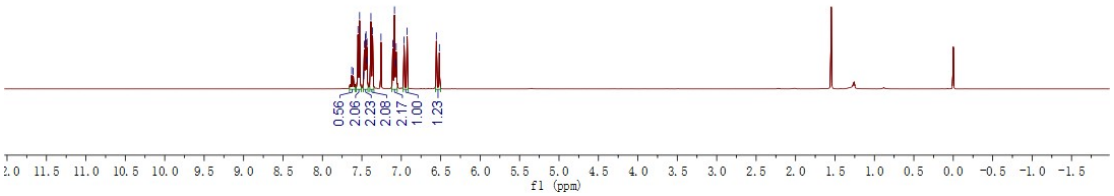
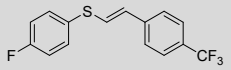


^{13}C NMR($CDCl_3$), 101 MHz



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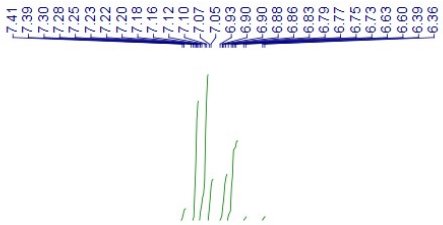
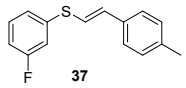


^{1}H NMR($CDCl_3$), 400 MHz



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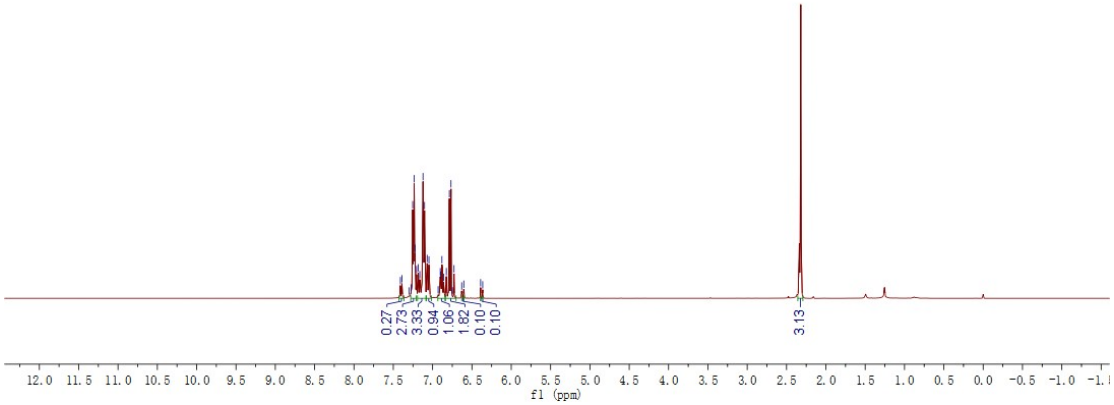
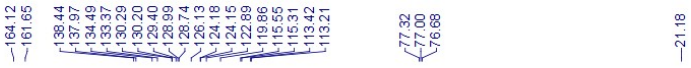
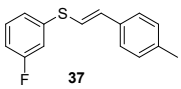




^{13}C NMR($CDCl_3$), 101 MHz



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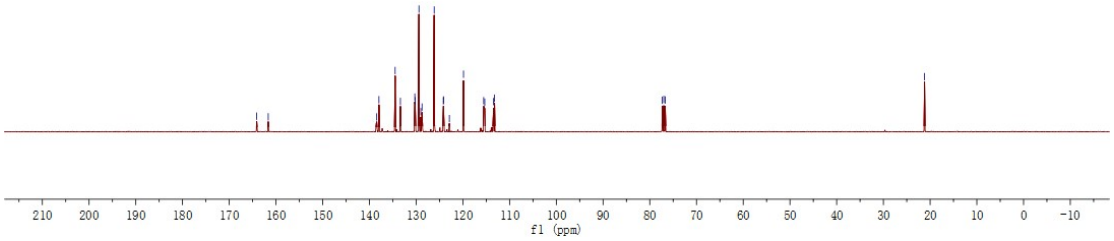
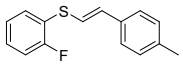


^{1}H NMR($CDCl_3$), 400 MHz



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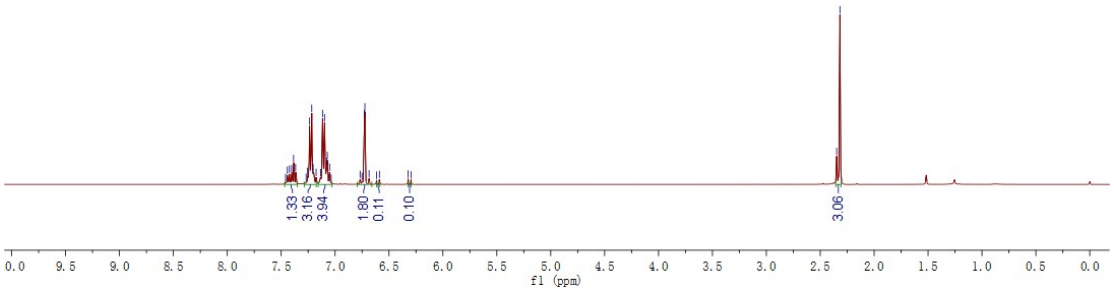
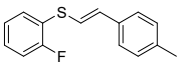


^{13}C NMR($CDCl_3$), 101 MHz



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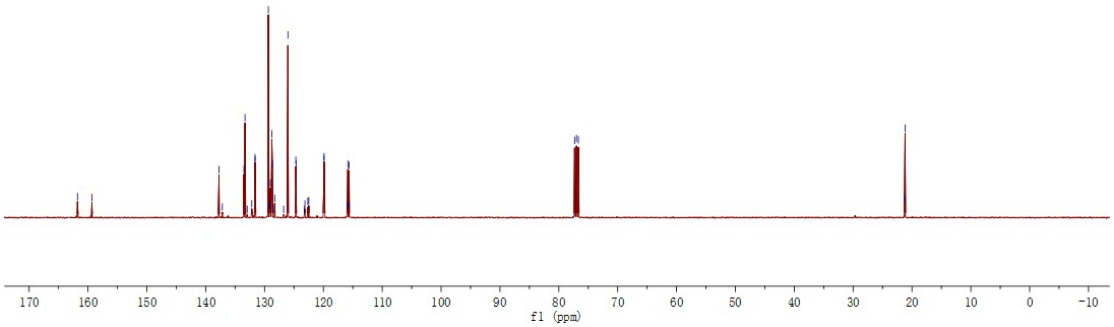
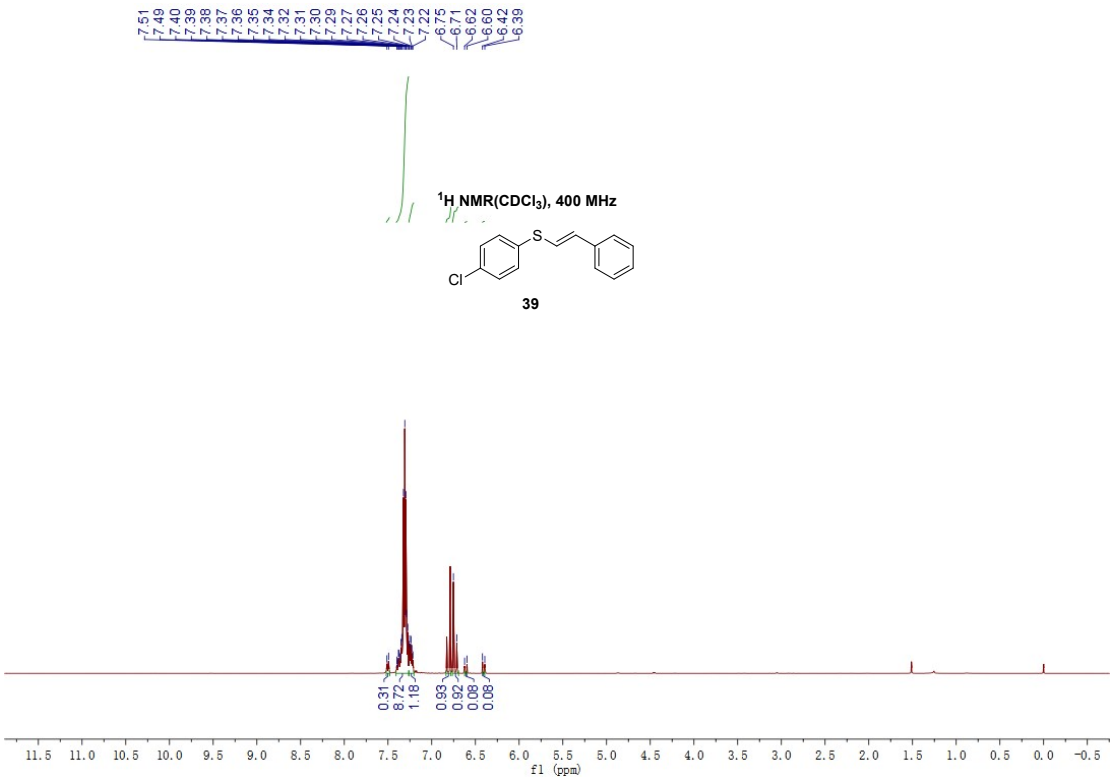
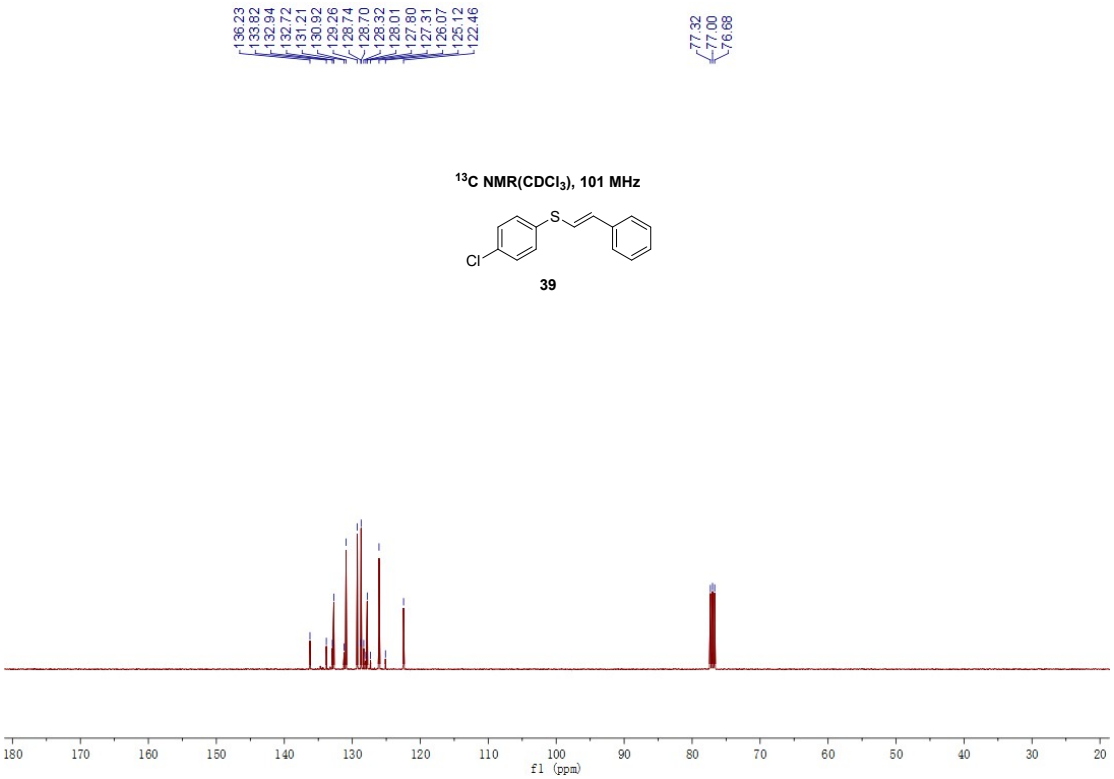




^{1}H NMR($CDCl_3$), 400 MHz

39



^{13}C NMR($CDCl_3$), 101 MHz

39