Supporting Information for

Direct access to thiomethyl/selenomethyl-substituted pyrazoles by combined isocyanide insertion into inert C(sp)-S bond and intermolecular cyclization

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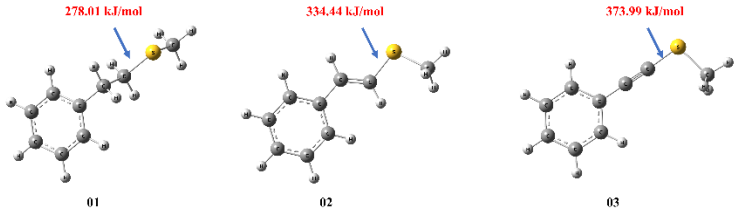
1. General information

Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 400 MHz and 100 MHz, using $CDCl_3$ as reference standard (δ 7.26 ppm) for ^{1}H NMR and (δ 77.16 ppm) for ^{13}C NMR. HRMS spectra were recorded with Agilent 6550 Q-TOF Quadrupole/Time-of-Flight Tandem mass spectrometer using ESI. Single Crystal X-ray diffraction data were collected using a Bruker D8 Quest diffractometer (Mo Kα, λ= 0.71073 Å). Melting points were uncorrected. Precoated silica gel plates GF-254 were used for thin-layer analytical chromatography. Column chromatography was performed on silica gel (200-300 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

2. Computational Details



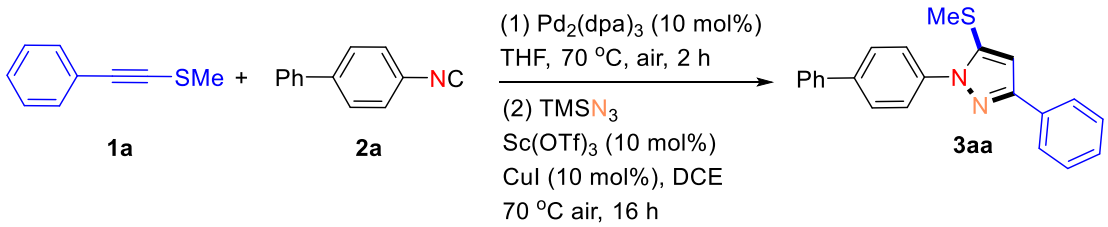
system	E/Hartree	Bond dissociation energies/hartree	Bond dissociation energies/kJ·mol^{-1}	Bond dissociation energies/kcal·mol^{-1}
01M1	-748.374319	-	-	-
01M1-A	-310.199424	-	-	-
01M1-B	-438.069005	0.10589	278.01	66.45
02M2	-747.169564	-	-	-
02M2-A	-308.973172	-	-	-
02M2-B	-438.06901	0.127382	334.44	79.93
03M3	-745.935714	-	-	-
03M3-A	-307.724261	-	-	-
03M3-B	-438.069006	0.142447	373.99	89.39

The theoretical calculations were performed via the Gaussian 16 suite of programs[1]. The structures of the studied compounds (denoted by M1, M2, and M3) were fully optimized at the B3LYP-D3BJ/TZVP level of theory. The solvent effect was included in the calculations using the solvation model based on the density (SMD) model. The vibrational frequencies of the optimized structures were carried out at the same level. The structures were characterized as a local energy minimum on the potential energy surface by verifying that all the vibrational frequencies were real. The bond dissociation energies of C-S bond in three molecules were estimated at the B3LYP-D3BJ/TZVP level of theory.

3. Synthesis of the substrates

The thioalkynes **1a-1m** and alkynyl selenides **4a** were synthesized according to the published procedures.[2,3] The isocyanobenzenes **2a-2o**, were synthesized according to the published procedures.[4,5]

4. General procedure for the synthesis of thiomethyl-substituted pyrazoles



A mixture of $Pd_2(dpa)_3$ (0.02 mmol, 19 mg), thioalkyne **1a** (0.2 mmol, 43 mg) and isocyanide **2a** (0.3 mmol, 54 mg) in THF (2 mL) was stirred at 70 °C (heating oil temperature) in a sealed tube under air atmosphere. After 2 h, the resulting mixture was cooled down to room temperature and then filtered to a round bottom flask by a short pad of silica gel (eluent: CH_2Cl_2). Volatiles were evaporated under reduced pressure. The crude products were directly used in the next reaction with without further purification.

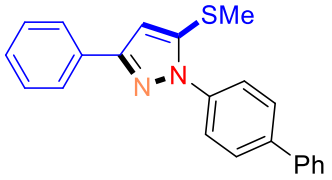
The above crude mixture was dissolved in DCE (2 mL) and then $Sc(OTf)_3$ (0.02 mmol, 10 mg), CuI (0.02 mmol, 4 mg) and $TMSN_3$ (0.3 mmol, 35 mg) was added. The reaction mixture was stired at 70 °C (heating mantle temperature). After 16 h, the resulting mixture is filtered by a short pad of silica gel (eluent: CH_2Cl_2) and

concentrated in vacuo then the crude product was purified by column chromatography using PE/EA (25:1-20:1) to provide the corresponding compounds **3aa**.

5. Detailed procedure for the 1 mmol scale thioalkyne 1a with isocyanide 2a

A mixture of $Pd_2(dpa)_3$ (0.1 mmol, 95 mg), thioalkyne **1a** (1.0 mmol, 148 mg) and isocyanide **2a** (1.5 mmol, 269 mg) in THF (8 mL) was stirred at 70 ^oC (heating oil temperature) in a sealed tube under air atmosphere. After 2 h, the resulting mixture was cooled down to room temperature and then filtered to a round bottom flask by a short pad of silica gel (eluent: CH_2Cl_2). Volatiles were evaporated under reduced pressure. The crude products were directly used in the next reaction with without further purification.

The above crude mixture was dissolved in DCE (8 mL) and then $Sc(OTf)_3$ (0.1 mmol, 50 mg), CuI (0.1 mmol, 20 mg) and $TMSN_3$ (1.5 mmol, 175 mg) was added. The reaction mixture was stired at 70 ^oC (heating mantle temperature). After 16 h, the resulting mixture is filtered by a short pad of silica gel (eluent: CH_2Cl_2) and concentrated in vacuo then the crude product was purified by column chromatography using PE/EA (25:1-20:1) to provide the corresponding compounds **3aa** (171 mg, 50%).



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3aa)

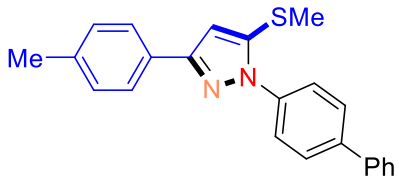
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 48 mg (70%) of the title compound **3aa**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.91-7.87 (m, 2H), 7.77-7.71 (m, 4H), 7.67-7.63 (m, 2H), 7.50-7.34 (m, 6H), 6.70 (s, 1H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ 152.3, 140.9, 140.3, 139.2, 138.9, 132.9, 129.0, 128.8, 128.3, 127.8, 127.8, 127.3, 125.8, 125.1, 105.7, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2S^+$ 343.1263; Found 343.1256.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-(p-tolyl)-1*H*-pyrazole (3ba)

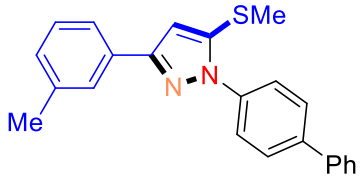
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl(*p*-tolylethynyl)sulfane (0.2 mmol, 32 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 51 mg (72%) of the title compound **3ba**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.79-7.67 (m, 6H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.34 (m, 1H), 7.24 (d, *J* = 8 Hz, 2H), 6.65 (s, 1H), 2.45 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.4, 140.8, 140.3, 139.0, 138.9, 138.1, 130.1, 129.5, 129.0, 127.8, 127.7, 127.3, 125.7, 125.1, 105.6, 21.5, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2S^+$ 357.1420; Found 357.1415.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-(m-tolyl)-1*H*-pyrazole (3ca)

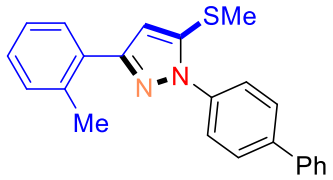
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl(*m*-tolylethynyl)sulfane (0.2 mmol, 32 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 51 mg (71%) of the title compound **3ca**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.76-7.71 (m, 5H), 7.67-7.63 (m, 3H), 7.50-7.46 (m, 2H), 7.41-7.37 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.17 (ddt, *J* = 7.6, 1.8, 0.8 Hz, 1H), 6.69 (s, 1H), 2.47 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.5, 140.9, 140.3, 139.1, 138.9, 138.4, 132.8, 129.1, 129.0, 128.7, 127.8, 127.8, 127.3, 126.4, 125.2, 123.0, 105.8, 21.6, 18.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2S^+$ 357.1420; Found 357.1417.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-(*o*-tolyl)-1*H*-pyrazole (3da)

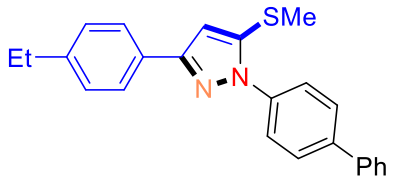
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl(*o*-tolylethynyl)sulfane (0.2 mmol, 32 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 50 mg (70%) of the title compound **3da**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.80-7.76 (m, 2H), 7.74-7.70 (m, 2H), 7.67-7.63 (m, 3H), 7.48 (ddd, *J* = 7.7, 6.9, 1.2 Hz, 2H), 7.42-7.36 (m, 1H), 7.30-7.25 (m, 3H), 6.55 (s, 1H), 2.58 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.9, 140.7, 140.3, 138.9, 138.0, 136.3, 132.7, 131.0, 129.4, 129.0, 128.1, 127.7, 127.3, 126.0, 124.9, 108.8, 21.5, 18.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2S^+$ 357.1420; Found 357.1416.



1-([1,1'-biphenyl]-4-yl)-3-(4-ethylphenyl)-5-(methylthio)-1*H*-pyrazole (3ea)

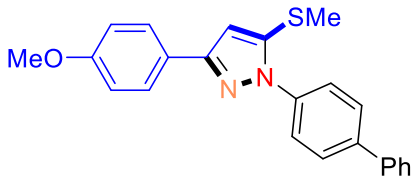
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and ((4-ethylphenyl)ethynyl)(methyl)sulfane (0.2 mmol, 35 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 55 mg (74%) of the title compound **3ea**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.71 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.68-7.60 (m, 4H), 7.55 (dt, *J* = 8.2, 1.1 Hz, 2H), 7.41-7.36 (m, 2H), 7.32-7.27 (m, 1H), 7.20-7.16 (m, 2H), 6.58 (s 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.19 (t, *J* = 7.6, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.4, 144.4, 140.8, 140.3, 139.0, 138.9, 130.3, 129.0, 128.3, 127.8, 127.7, 127.3, 125.8, 125.1, 105.6, 28.8, 18.3, 15.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2S^+$ 371.1576; Found 371.1573.



1-([1,1'-biphenyl]-4-yl)-3-(4-methoxyphenyl)-5-(methylthio)-1*H*-pyrazole (3fa)

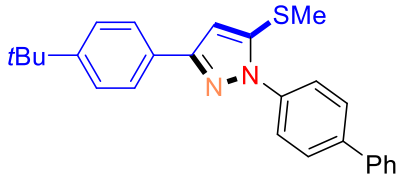
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and ((4-methoxyphenyl)ethynyl)(methyl)sulfane (0.2 mmol, 36 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 57 mg (76%) of the title compound **3fa**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.84-7.81 (m, 2H), 7.76-7.70 (m, 4H), 7.66-7.63 (m, 2H), 7.50-7.46 (m, 2H), 7.42-7.37 (m, 1H), 6.99-6.95 (m, 2H), 6.63 (s, 1H), 3.85 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 159.8, 152.2, 140.7, 140.3, 139.0, 138.9, 129.0, 127.8, 127.7, 127.3, 127.1, 125.7, 125.0, 114.2, 105.4, 55.4, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2OS^+$ 373.1369; Found 373.1361.



1-([1,1'-biphenyl]-4-yl)-3-(4-(tert-butyl)phenyl)-5-(methylthio)-1*H*-pyrazole (3ga)

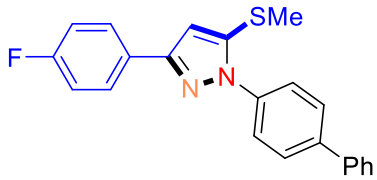
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and ((4-(*tert*-butyl)phenyl)ethynyl)(methyl)sulfane (0.2 mmol, 41 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 60 mg (75%) of the title compound **3ga**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.83-7.80 (m, 2H), 7.77-7.71 (m, 4H), 7.66-7.64 (m, 2H), 7.49-7.45 (m, 4H), 7.41-7.37 (m, 1H), 6.68 (s, 1H), 2.47 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.4, 151.3, 140.8, 140.4, 139.0, 138.9, 130.1, 129.0, 127.8, 127.7, 127.3, 125.7, 125.6, 125.1, 105.7, 34.8, 31.5, 18.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}N_2S^+$ 399.1889; Found 399.1885.



1-([1,1'-biphenyl]-4-yl)-3-(4-fluorophenyl)-5-(methylthio)-1*H*-pyrazole (3ha)

The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and ((4-fluorophenyl)ethynyl)(methyl)sulfane (0.2 mmol, 33 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 48 mg (67%) of the title compound **3ha**.

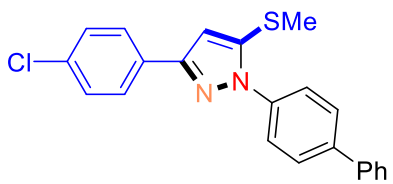
Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.88-7.82 (m, 2H), 7.72 (t, *J* = 1.2 Hz, 4H), 7.64 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.48 (td, *J* = 7.3, 6.6, 1.3 Hz, 2H), 7.42-7.36 (m, 1H), 7.14-7.08 (m, 2H), 6.63 (s, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 163.0 (*J* = 246 Hz), 151.5, 141.0, 140.3, 139.4, 138.8, 129.2 (J = 3 Hz), 129.0, 127.8, 127.6 (*J* = 8 Hz), 127.3, 125.1, 115.7 (*J* = 22 Hz), 105.6, 18.4.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ -114.83.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}FN_2S^+$ 361.1169; Found 361.1168.



1-([1,1'-biphenyl]-4-yl)-3-(4-chlorophenyl)-5-(methylthio)-1*H*-pyrazole (3ia)

The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and ((4-

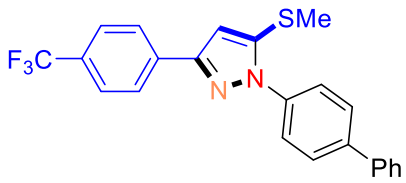
chlorophenyl)ethynyl)(methyl)sulfane (0.2 mmol, 36 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 49 mg (65%) of the title compound **3ia**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.84-7.79 (m, 2H), 7.72 (s, 4H), 7.66-7.60 (m, 2H), 7.50-7.45 (m, 2H), 7.41-7.36 (m, 3H), 6.65 (s, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 151.3, 141.1, 140.3, 139.5, 138.8, 134.0, 131.5, 129.0, 129.0, 127.8, 127.3, 127.1, 125.1, 105.6, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}ClN_2S^+$ 377.0874; Found 377.0862.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (3ja)

The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl((4-(trifluoromethyl)phenyl)ethynyl)sulfane (0.2 mmol, 43 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 51 mg (62%) of the title compound **3ja**.

Physical state: yellow solid.

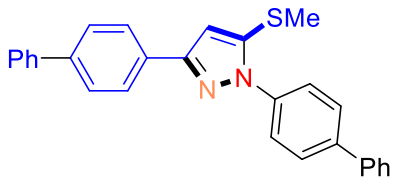
Mp: 137-139 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.73 (s, 4H), 7.69-7.63 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42-7.38 (m, 1H), 6.73 (s, 1H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.9, 141.2, 140.2, 139.9, 138.6, 136.4, 130.0 (J = 32 Hz), 129.1, 127.9, 127.3, 125.9, 125.8 (*J* = 4f Hz) 125.1, 124.4 (*J* = 274 Hz), 105.8, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ -62.86.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}F_3N_2S^+$ 411.1137; Found 411.1128.



1,3-di([1,1'-biphenyl]-4-yl)-5-(methylthio)-1*H*-pyrazole (3ka)

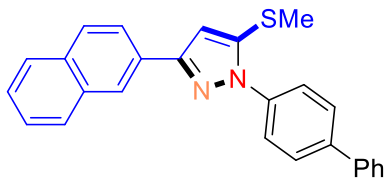
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and ([1,1'-biphenyl]-4-ylethynyl)(methyl)sulfane (0.2 mmol, 45 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 61 mg (73%) of the title compound **3ka**.

Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.98-7.95 (m, 2H), 7.78-7.71 (m, 4H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.66 (ddd, *J* = 8.0, 4.0, 1.5 Hz, 5H), 7.47 (dd, *J* = 8.1, 7.0 Hz, 4H), 7.38 (dtd, *J* = 9.8, 5.6, 2.6 Hz, 2H), 6.73 (s, 1H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.0, 140.9, 140.9, 140.9, 140.3, 139.3, 138.9, 131.9, 129.0, 128.9, 127.8, 127.8, 127.5, 127.3, 127.1, 126.2, 125.1, 105.8, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{23}N_2S^+$ 419.1576; Found 419.1563.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-(naphthalen-2-yl)-1*H*-pyrazole (3la)

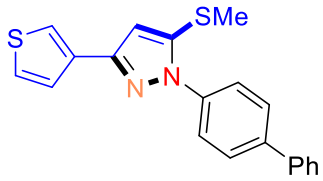
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl(naphthalen-2-ylethynyl)sulfane (0.2 mmol, 40 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 56 mg (71%) of the title compound **3la**.

Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.34 (dd, *J* = 1.6, 0.8 Hz, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.93-7.90 (m, 2H), 7.88-7.84 (m, 1H), 7.81-7.77 (m, 2H), 7.76-7.73 (m, 2H), 7.68-7.64 (m, 2H), 7.52-7.47 (m, 4H), 7.43-7.37 (m, 1H), 6.84 (s, 1H), 2.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.3, 140.9, 140.3, 139.4, 138.9, 133.7, 133.4, 130.3, 129.0, 128.5, 128.4, 127.9, 127.8, 127.8, 127.3, 126.4, 126.1, 125.2, 124.5, 124.1, 105.9, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}N_2S^+$ 393.1420; Found 393.1406.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-(thiophen-2-yl)-1*H*-pyrazole (3ma)

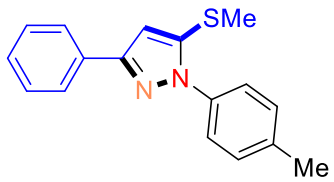
The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and 2-((methylthio)ethynyl)thiophene (0.2 mmol, 31 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 47 mg (68%) of the title compound **3ma**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.71 (s, 4H), 7.65 (d, *J* = 3.0 Hz, 2H), 7.63 (t, *J* = 1.3 Hz, 1H), 7.55-7.54 (m, 1H), 7.49-7.45 (m, 2H), 7.40-7.36 (m, 2H), 6.58 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.1, 141.7, 140.3, 139.0, 138.8, 134.8, 129.0, 127.8, 127.3, 126.1, 125.2, 121.2, 106.1, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_2S_2^+$ 349.0828; Found 349.0817.



5-(methylthio)-3-phenyl-1-(p-tolyl)-1*H*-pyrazole (3ab)

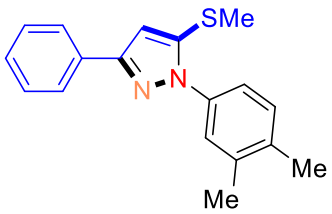
The compound was prepared from 1-isocyano-4-methylbenzene (0.3 mmol, 35 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 41 mg (73%) of the title compound **3ab**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.90-7.85 (m, 2H), 7.57-7.53 (m, 2H), 7.44-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.03-6.98 (m, 2H), 6.65 (s, 1H), 3.86 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 159.3, 151.9, 139.1, 133.0, 132.8, 128.7, 128.1, 126.5, 125.7, 114.2, 105.1, 55.6, 18.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2S^+$ 281.1107; Found 281.1109.



1-(3,4-dimethylphenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3ac)

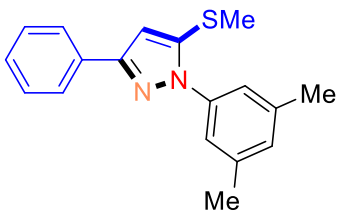
The compound was prepared from 4-isocyano-1,2-dimethylbenzene (0.3 mmol, 39 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 42 mg (71%) of the title compound **3ac**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.79-7.73 (m, 2H), 7.34-7.28 (m, 3H), 7.25-7.19 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.53 (s, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 151.9, 139.0, 137.6, 137.4, 136.8, 133.0, 130.0, 128.7, 128.0, 126.1, 125.7, 122.3, 105.0, 20.0, 19.6, 18.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2S^+$ 295.1263; Found 295.1262.



1-(3,5-dimethylphenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3ad)

The compound was prepared from 1-isocyano-4-methoxybenzene (0.3 mmol, 40 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 42 mg (72%) of

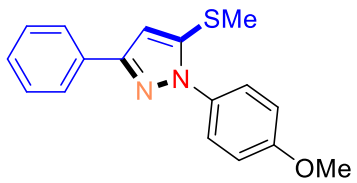
the title compound **3ad**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.87-7.82 (m, 2H), 7.40 (ddt, *J* = 7.2, 6.0, 1.0 Hz, 2H), 7.33-7.27 (m, 1H), 7.25-7.22 (m, 2H), 7.02 (dt, *J* = 1.9, 1.0 Hz, 1H), 6.61 (d, *J* = 0.8 Hz, 1H), 2.42 (d, *J* = 0.9 Hz, 3H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.0, 139.4, 139.2, 138.9, 133.0, 129.8, 128.7, 128.1, 125.8, 122.7, 104.9, 21.4, 18.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2S^+$ 295.1263; Found 295.1259.



1-(4-methoxyphenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3ae)

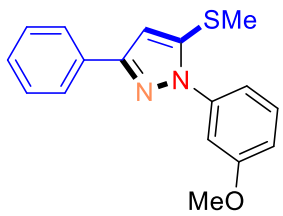
The compound was prepared from 1-isocyano-4-methoxybenzene (0.3 mmol, 40 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 44 mg (75%) of the title compound **3ae**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.90-7.85 (m, 2H), 7.57-7.53 (m, 2H), 7.44-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.03-6.98 (m, 2H), 6.65 (s, 1H), 3.86 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 159.3, 151.9, 139.1, 133.0, 132.8, 128.7, 128.1, 126.5, 125.7, 114.2, 105.1, 55.6, 18.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2OS^+$ 297.1056; Found 297.1052.



1-(3-methoxyphenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3af)

The compound was prepared from 1-isocyano-3-methoxybenzene (0.3 mmol, 40 mg)

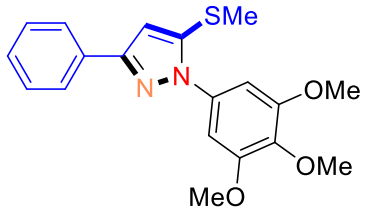
and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 43 mg (73%) of the title compound **3af**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.61 (d, *J* = 7.5 Hz, 2H), 6.15 (q, *J* = 7.2, 6.6 Hz, 4H), 5.97 (d, *J* = 7.1 Hz, 2H), 5.69 (d, *J* = 8.2 Hz, 1H), 5.39 (s, 1H), 2.60 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 160.2, 152.2, 140.7, 139.3, 132.9, 129.8, 128.8, 128.2, 125.8, 117.1, 114.2, 110.4, 105.4, 55.6, 18.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2OS^+$ 297.1056; Found 297.1052.



5-(methylthio)-3-phenyl-1-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole (3ag)

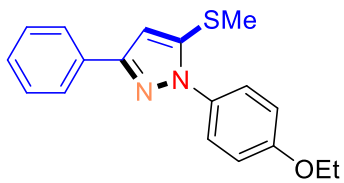
The compound was prepared from 5-isocyano-1,2,3-trimethoxybenzene (0.3 mmol, 58 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 53 mg (74%) of the title compound **3ag**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.88-7.84 (m, 2H), 7.44-7.39 (m, 2H), 7.36-7.31 (m, 1H), 6.87 (s, 2H), 6.62 (s, 1H), 3.91 (s, 6H), 3.89 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 153.4, 152.2, 139.5, 137.7, 135.3, 132.8, 128.8, 128.3, 125.8, 104.7, 102.5, 61.1, 56.4, 17.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_3S^+$ 357.1267; Found 357.1255.



1-(4-ethoxyphenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3ah)

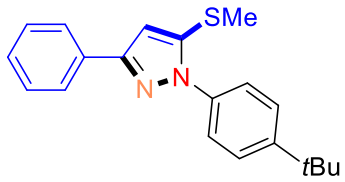
The compound was prepared from 1-ethoxy-4-isocyanobenzene (0.3 mmol, 44 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 47 mg (76%) of the title compound **3ah**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.88-7.84 (m, 2H), 7.55-7.50 (m, 2H), 7.41 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.35-7.31 (m, 1H), 7.01-6.96 (m, 2H), 6.65 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 158.8, 151.9, 139.1, 133.0, 132.6, 128.7, 128.1, 126.6, 125.7, 114.7, 105.1, 63.9, 18.2, 14.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2OS^+$ 311.1213; Found 311.1203.



1-(4-(*tert*-butyl)phenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3ai)

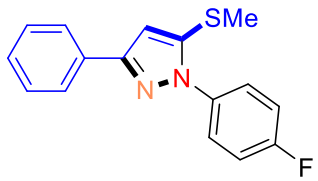
The compound was prepared from 1-(*tert*-butyl)-4-isocyanobenzene (0.3 mmol, 48 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 45 mg (70%) of the title compound **3ai**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.91-7.87 (m, 2H), 7.59 (d, *J* = 6.5 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 1H), 6.67 (s, 1H), 2.44 (s, 3H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.0, 151.2, 139.0, 137.1, 133.0, 128.7, 128.1, 126.0, 125.7, 124.5, 105.3, 34.8, 31.4, 18.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N_2S^+$ 323.1576; Found 323.1566.



1-(4-fluorophenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3aj)

The compound was prepared from 1-fluoro-4-isocyanobenzene (0.3 mmol, 36 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 36 mg (63%) of the title compound **3aj**.

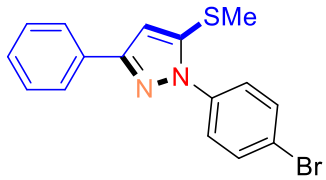
Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 4.0 Hz, 2H), 7.42 (s, 2H), 7.34 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 162.1 (d, J = 246), 152.4, 139.2, 135.8, 132.8, 128.8, 128.3, 126.9 (d, *J* = 8), 125.8, 116.0 (d, *J* = 23), 105.8, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ -114.26.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}FN_2S^+$ 285.0856; Found 285.0848.



1-(4-bromophenyl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (3ak)

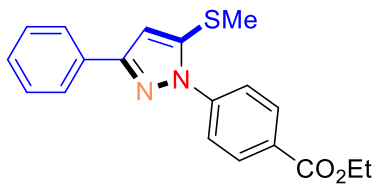
The compound was prepared from 1-bromo-4-isocyanobenzene (0.3 mmol, 54 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 42 mg (61%) of the title compound **3ak**.

Physical state: Brownish yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.82-7.73 (m, 2H), 7.50 (qd, *J* = 8.8, 1.7 Hz, 4H), 7.33 (ddd, *J* = 7.7, 6.6, 1.5 Hz, 2H), 7.28-7.23 (m, 1H), 6.58 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.6, 139.2, 138.7, 132.7, 132.2, 128.8, 128.4, 126.3, 125.8, 121.6, 106.1, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_2S^+$ 345.0056; Found 345.0036.



Ethyl 4-(5-(methylthio)-3-phenyl-1*H*-pyrazol-1-yl)benzoate (3al)

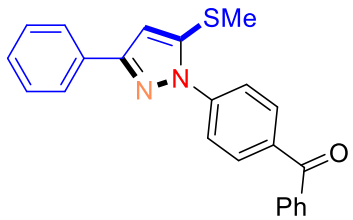
The compound was prepared from ethyl 4-isocyanobenzoate (0.3 mmol, 53 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 42 mg (62%) of the title compound **3al**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.19-8.16 (m, 2H), 7.86 (dt, *J* = 8.3, 1.2 Hz, 2H), 7.83-7.80 (m, 2H), 7.46-7.41 (m, 2H), 7.37-7.32 (m, 1H), 6.69 (s, 1H), 4.42 (q, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 1.44 (t, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 166.1, 152.9, 143.3, 139.5, 132.6, 130.6, 129.4, 128.9, 128.5, 125.9, 124.0, 106.5, 61.4, 18.4, 14.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O_2S^+$ 339.1162; Found 339.1155.



(4-(5-(methylthio)-3-phenyl-1*H*-pyrazol-1-yl)phenyl)(phenyl)methanone (3am)

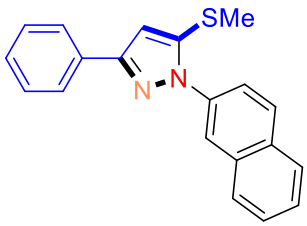
The compound was prepared from (4-isocyanophenyl)(phenyl)methanone (0.3 mmol, 62 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 51 mg (68%) of the title compound **3am**.

Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.95 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.91-7.81 (m, 6H), 7.66-7.59 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40-7.33 (m, 1H), 6.71 (s, 1H), 2.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 195.8, 153.0, 142.9, 139.6, 137.5, 136.3, 132.8, 132.5, 131.2, 130.2, 128.9, 128.5, 125.9, 123.9, 106.4, 18.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_2OS^+$ 371.1213; Found 371.1195.



5-(methylthio)-1-(naphthalen-2-yl)-3-phenyl-1*H*-pyrazole (3an)

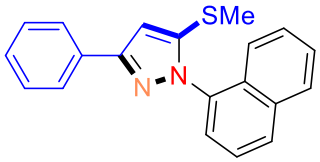
The compound was prepared from 2-isocyanonaphthalene (0.3 mmol, 46 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 46 mg (73%) of the title compound **3an**.

Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.14-8.12 (m, 1H), 7.99-7.95 (m, 1H), 7.94-7.89 (m, 4H), 7.84 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.58-7.52 (m, 2H), 7.47-7.42 (m, 2H), 7.38-7.33 (m, 1H), 6.72 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.5, 139.5, 137.2, 133.2, 132.9, 132.6, 129.1, 128.8, 128.4, 128.3, 127.9, 126.9, 126.7, 125.9, 123.3, 123.0, 105.7, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_2S^+$ 317.1107; Found 317.1101.



5-(methylthio)-1-(naphthalen-1-yl)-3-phenyl-1*H*-pyrazole (3ao)

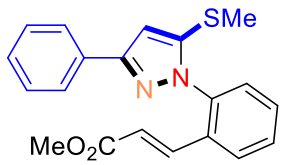
The compound was prepared from 1-isocyanonaphthalene (0.3 mmol, 46 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 47 mg (74%) of the title compound **3ao**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.02-7.99 (m, 1H), 7.95-7.92 (m, 2H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.58-7.49 (m, 5H), 7.44 (ddd, *J* = 7.7, 5.8, 1.6 Hz, 2H), 7.37 (dt, *J* = 8.3, 1.9 Hz, 1H), 6.81 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.5, 141.3, 135.9, 134.4, 133.0, 130.8, 130.0, 128.8, 128.2, 127.5, 126.8, 125.9, 125.8, 125.1, 123.4, 104.9, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_2S^+$ 317.1107; Found 317.1100.



Methyl (*E*)-3-(2-(5-(methylthio)-3-phenyl-1*H*-pyrazol-1-yl)phenyl)acrylate (3ap)

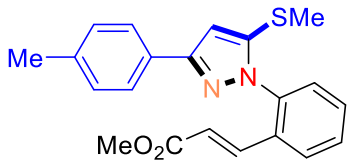
The compound was prepared from methyl (*E*)-3-(2-isocyanophenyl)acrylate (0.3 mmol, 56 mg) and methyl(phenylethynyl)sulfane (0.2 mmol, 30 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 43 mg (61%) of the title compound **3ap**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.81-7.75 (m, 1H), 7.55-7.49 (m, 2H), 7.48-7.37 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.33 (d, *J* = 16.1 Hz, 1H), 3.72 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.1, 152.9, 140.9, 139.7, 138.6, 132.8, 132.6, 130.7, 129.9, 129.0, 128.8, 128.3, 127.6, 126.0, 120.6, 105.7, 51.9, 29.9, 18.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2O_2S^+$ 351.1162; Found 351.1162.



Methyl (*E*)-3-(2-(5-(methylthio)-3-(*p*-tolyl)-1*H*-pyrazol-1-yl)phenyl)acrylate (3bp)

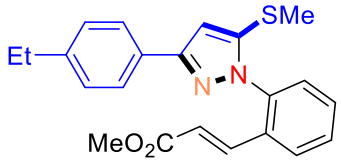
The compound was prepared from methyl (*E*)-3-(2-isocyanophenyl)acrylate (0.3 mmol, 56 mg) and methyl(*p*-tolylethynyl)sulfane (0.2 mmol, 32 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 46 mg (63%) of the title compound **3bp**.

Physical state: yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.79-7.75 (m, 1H), 7.75-7.71 (m, 2H), 7.54-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.42 (d, *J* = 16.1 Hz, 1H), 7.24-7.20 (m, 2H), 6.69 (s, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.0, 152.9, 140.7, 139.7, 138.6, 138.1, 132.5, 130.7, 130.0, 129.8, 129.5, 129.0, 127.5, 125.8, 120.5, 105.5, 51.9, 21.4, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}N_2O_2S^+$ 365.1318; Found 365.1314.



Methyl (*E*)-3-(2-(3-(4-ethylphenyl)-5-(methylthio)-1*H*-pyrazol-1-yl)phenyl)acrylate (3ep)

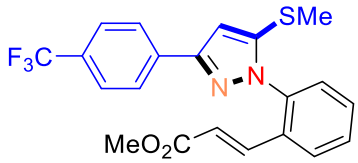
The compound was prepared from methyl (*E*)-3-(2-isocyanophenyl)acrylate (0.3 mmol, 56 mg) and ((4-ethylphenyl)ethynyl)(methyl)sulfane (0.2 mmol, 35 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 47 mg (62%) of the title compound **3ep**.

Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.35-7.31 (m, 3H), 7.10-7.06 (m, 2H), 7.04-7.01 (m, 1H), 6.98 (d, *J* = 16.1 Hz, 1H), 6.84-6.80 (m, 2H), 6.26 (s, 1H), 5.89 (d, *J* = 16.0 Hz, 1H), 3.28 (s, 3H), 2.25 (q, *J* = 7.6 Hz, 2H), 1.93 (s, 3H), 0.83 (t, *J* = 7.4, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.0, 152.9, 144.5, 140.7, 139.7, 138.6, 132.5, 130.6, 130.2, 129.8, 128.9, 128.3, 127.5, 125.9, 120.5, 105.5, 51.8, 28.8, 18.3, 15.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2O_2S^+$ 379.1475; Found 379.1469.



Methyl (*E*)-3-(2-(5-(methylthio)-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrazol-1-yl)phenyl)acrylate (3jp)

The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl((4-(trifluoromethyl)phenyl)ethynyl)sulfane (0.2 mmol, 43 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 47 mg (56%) of the title compound **3jp**.

Physical state: yellow amorphous solid.

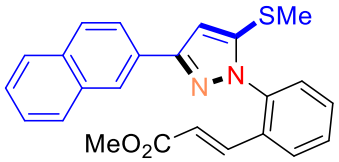
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.82-7.77 (m, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.57-7.50 (m, 2H), 7.48-7.44 (m, 1H), 7.39 (d, *J* = 16.1 Hz,

1H), 6.75 (s, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.0, 151.5, 141.6, 139.5, 138.4, 136.2, 132.5, 130.8, 130.1, 129.9, 128.8, 127.6, 126.1, 125.8, 120.7, 105.8, 51.9, 29.9, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ -62.75.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}F_3N_2O_2S^+$ 419.1036; Found 419.1025.



Methyl (*E*)-3-(2-(5-(methylthio)-3-(naphthalen-2-yl)-1*H*-pyrazol-1-yl)phenyl)acrylate (3lp)

The compound was prepared from methyl (*E*)-3-(2-isocyanophenyl)acrylate (0.3 mmol, 56 mg) and methyl(naphthalen-2-ylethynyl)sulfane (0.2 mmol, 40 mg) following the general procedure. purification by column chromatography (silica, PE:EA=25:1) afforded 50 mg (62%) of the title compound **3lp**.

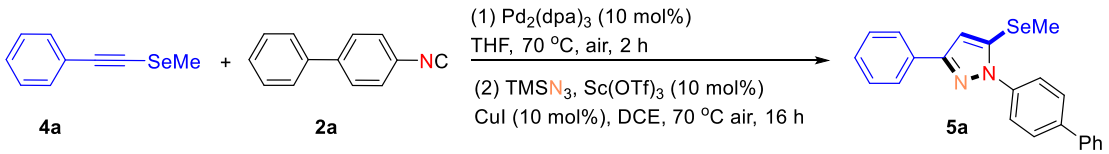
Physical state: yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.34-8.26 (m, 1H), 8.00 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.91-7.87 (m, 2H), 7.86-7.77 (m, 2H), 7.55-7.44 (m, 6H), 6.86 (s, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.0, 152.9, 141.2, 139.7, 138.6, 133.7, 133.4, 132.6, 130.7, 130.2, 129.9, 129.0, 128.5, 128.4, 127.9, 127.6, 126.4, 126.1, 124.6, 124.1, 120.6, 105.8, 51.9, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}N_2O_2S^+$ 419.1036; Found 419.1025.

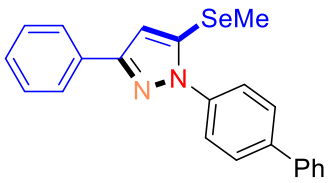
6. General procedure for the synthesis of selenomethyl-substituted pyrazoles



A mixture of $Pd_2(dpa)_3$ (0.02 mmol, 19 mg), alkynyl selenides **4a** (0.2 mmol, 39 mg) and isocyanide **2a** (0.3 mmol, 54 mg) in THF (2 mL) was stirred at 70 °C (heating oil temperature) in a sealed tube under air atmosphere. After 2 h, the resulting mixture was cooled down to room temperature and then filtered to a round bottom flask by a short

pad of silica gel (eluent: CH_2Cl_2). Volatiles were evaporated under reduced pressure. The crude products were directly used in the next reaction with without further purification.

The above crude mixture was dissolved in DCE (2 mL) and then $Sc(OTf)_3$ (0.02 mmol, 10 mg), CuI (0.02 mmol, 4 mg) and $TMSN_3$ (0.3 mmol, 35 mg) was added. The reaction mixture was stired at 70 °C (heating mantle temperature). After 16 h, the resulting mixture is filtered by a short pad of silica gel (eluent: CH_2Cl_2) and concentrated in vacuo then the crude product was purified by column chromatography using PE/EA (25:1-20:1) to provide the corresponding compounds **5a**.



1-([1,1'-biphenyl]-4-yl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (5a)

The compound was prepared from 4-isocyano-1,1'-biphenyl (0.3 mmol, 54 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 54 mg (69%) of the title compound **5a**.

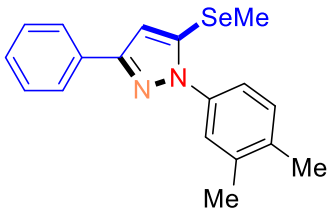
Physical state: yellow solid.

Mp: 183- 185 °C.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.92-7.87 (m, 2H), 7.72 (d, *J* = 1.0 Hz, 3H), 7.65 (dq, *J* = 7.3, 1.2 Hz, 2H), 7.51-7.33 (m, 7H), 6.76 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 152.9, 141.0, 140.3, 139.5, 132.9, 130.5, 129.0, 128.8, 128.2, 127.8, 127.3, 125.9, 125.3, 108.5, 9.5, 1.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_5Se$ 391.0708; Found 391.0694.



1-(3,4-dimethylphenyl)-5-(methylselanyl)-3-phenyl-1*H*-pyrazole (5b)

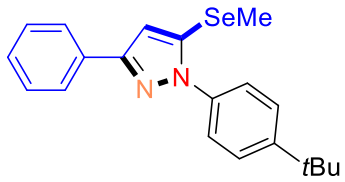
The compound was prepared from 4-isocyano-1,2-dimethylbenzene (0.3 mmol, 36 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 47 mg (68%) of the title compound **5b**.

Physical state: yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.14-8.11 (m, 2H), 7.70-7.65 (m, 3H), 7.61-7.56 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 2.60 (s, 3H), 2.59 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 152.5, 138.1, 137.8, 137.0, 133.1, 130.6, 130.0, 128.8, 128.1, 126.3, 125.8, 122.4, 107.8, 20.0, 19.7, 9.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2Se$ 343.0708; Found 343.0708.



1-(4-(tert-butyl)phenyl)-5-(methylselanyl)-3-phenyl-1*H*-pyrazole (5c)

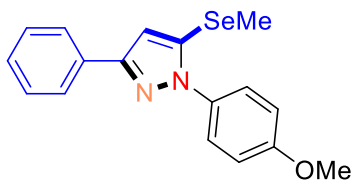
The compound was prepared from 1-(*tert*-butyl)-4-isocyanobenzene (0.3 mmol, 48 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 48 mg (65%) of the title compound **5c**.

Physical state: yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.90-7.85 (m, 2H), 7.56-7.49 (m, 4H), 7.44-7.39 (m, 2H), 7.35-7.31 (m, 1H), 6.72 (s, 1H), 2.30 (s, 3H), 1.38 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 152.6, 151.3, 137.8, 133.0, 130.4, 128.7, 128.1, 126.1, 125.8, 124.6, 108.0, 34.9, 31.5, 9.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N_2Se$ 371.1021; Found 371.1022.



1-(4-methoxyphenyl)-5-(methylselanyl)-3-phenyl-1*H*-pyrazole (5d)

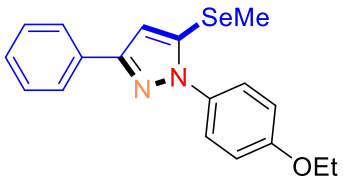
The compound was prepared from 1-isocyano-4-methoxybenzene (0.3 mmol, 40 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 47 mg (69%) of the title compound **5d**.

Physical state: yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 7.87-7.83 (m, 2H), 7.53-7.49 (m, 2H), 7.43-7.39 (m, 2H), 7.32 (q, *J* = 3.0, 2.3 Hz, 1H), 7.01-6.98 (m, 2H), 6.70 (s, 1H), 3.87 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC): δ 159.5, 152.5, 133.6, 130.7, 128.8, 128.1, 126.7, 125.8, 114.3, 108.0, 55.7, 9.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2OSe$ 345.0501; Found 345.0501.



1-(4-ethoxyphenyl)-5-(methylselanyl)-3-phenyl-1*H*-pyrazole (5e)

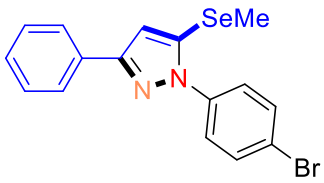
The compound was prepared from 1-ethoxy-4-isocyanobenzene (0.3 mmol, 44 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 48 mg (67%) of the title compound **5e**.

Physical state: yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 7.89-7.82 (m, 2H), 7.52-7.47 (m, 2H), 7.41 (tq, *J* = 7.0, 0.8 Hz, 2H), 7.34-7.30 (m, 1H), 7.02-6.95 (m, 2H), 6.69 (s, 1H), 4.09 (q, *J* = 7.0, 2H), 2.27 (s, 3H), 1.45 (t, *J* = 7.0, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC): δ 158.9, 152.4, 133.3, 133.1, 130.6, 128.8, 128.1, 126.7, 125.8, 114.8, 107.9, 63.9, 14.9, 9.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2OSe$ 359.0657; Found 359.0655.



1-(4-bromophenyl)-5-(methylselanyl)-3-phenyl-1*H*-pyrazole (5f)

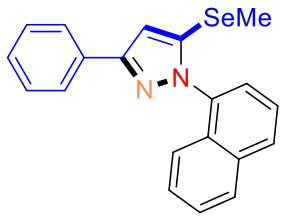
The compound was prepared from 1-bromo-4-isocyanobenzene (0.3 mmol, 54 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 47 mg (60%) of the title compound **5f**.

Physical state: yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.85-7.83 (m, 2H), 7.63-7.60 (m, 2H), 7.55-7.53 (m, 2H), 7.42-7.40 (m, 2H), 7.36-7.33 (m, 1H), 6.73 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 153.1, 139.3, 132.7, 132.3, 130.4, 128.8, 128.4, 126.5, 125.9, 121.8, 109.0, 9.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_5Se$ 392.9500; Found 392.9480.



5-(methylselanyl)-1-(naphthalen-1-yl)-3-phenyl-1*H*-pyrazole (5g)

The compound was prepared from 1-isocyanonaphthalene (0.3 mmol, 46 mg) and methyl(phenylethynyl)selane (0.2 mmol, 39 mg) following the general procedure. Purification was performed by a preparation plate with silica gel ((silica, 30:1 petroleum ether : EtOAc) to afford 49 mg (67%) of the title compound **5g**.

Physical state: yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.02-7.97 (m, 1H), 7.96-7.88 (m, 3H), 7.61-7.60 (m, 1H), 7.59-7.50 (m, 2H), 7.49-7.40 (m, 4H), 7.37-7.32 (m, 1H), 6.85 (s, 1H), 2.17 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 152.9, 136.6, 134.4, 133.0, 132.6, 130.8, 130.0, 128.8, 128.2, 127.5, 126.9, 125.9, 125.7, 125.1, 123.4, 107.8, 9.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_5Se$ 365.0551; Found 365.0547.

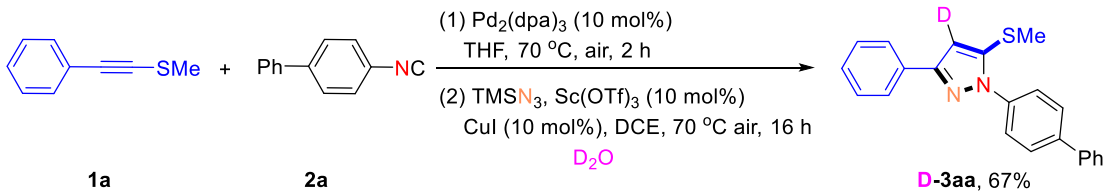
7. Control experiments

(1) Radical trapping reactions

To a solution of thioalkyne **1a** (0.2 mmol, 43 mg) isocyanide **2a** (0.3 mmol, 54 mg),

$Pd_2(dpa)_3$ (0.02 mmol, 19 mg) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 0.3 mmol, 47 mg) or butylated hydroxytoluene (BHT, 0.3 mmol, 66 mg) in THF (2 mL) was stirred at 70 °C (heating oil temperature) in a sealed tube under air atmosphere. After 2 h, the resulting mixture was cooled down to room temperature and then filtered to a round bottom flask by a short pad of silica gel (eluent: CH_2Cl_2). Volatiles were evaporated under reduced pressure. The crude products were directly used in the next reaction with without further purification. The above crude mixture was dissolved in DCE (2 mL) and then $Sc(OTf)_3$ (0.02 mmol, 10 mg), CuI (0.02 mmol, 4 mg) and $TMSN_3$ (0.3 mmol, 35 mg) was added. The reaction mixture was stired at 70 °C (heating mantle temperature). After 16 h, the resulting mixture is filtered by a short pad of silica gel (eluent: CH_2Cl_2) and concentrated in vacuo then the crude product was purified by column chromatography using PE/EA (25:1-20:1) to provide the corresponding compounds **3aa**. With TEMPO, the yield of **3aa** was 67%. And with BHT, the yield of **3aa** was 68%.

(2) Isotopic labeling experiments



1a **2a** **D-3aa**, 67%

A mixture of thioalkyne **1a** (0.2 mmol, 43 mg), isocyanide **2a** (0.3 mmol, 54 mg) and $Pd_2(dpa)_3$ (0.02 mmol, 19 mg) in THF (8 mL) was stirred at 70 °C (heating oil temperature) in a sealed tube under air atmosphere. After 2 h, the resulting mixture was cooled down to room temperature and then filtered to a round bottom flask by a short pad of silica gel (eluent: CH_2Cl_2). Volatiles were evaporated under reduced pressure. The crude products were directly used in the next reaction with without further purification. The above crude mixture was dissolved in DCE (2 mL) and then $Sc(OTf)_3$ (0.02 mmol, 10 mg), CuI (0.02 mmol, 4 mg), D_2O (0.4 mmol, 8 mg) and $TMSN_3$ (0.3 mmol, 35 mg) was added. The reaction mixture was stired at 70 °C (heating mantle temperature). After 16 h, the resulting mixture is filtered by a short pad of silica gel (eluent: CH_2Cl_2) and concentrated in vacuo then the crude product was purified by

column chromatography using PE/EA (25:1-20:1) to provide the corresponding compounds D-**3aa** (46 mg, 67%).

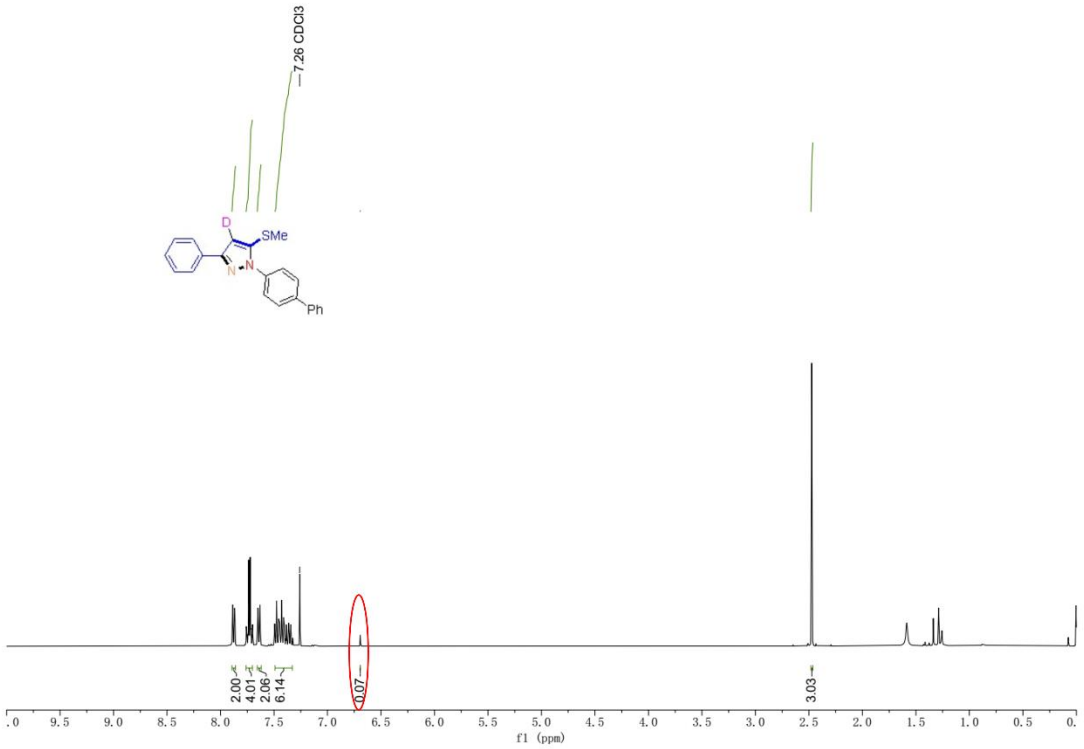
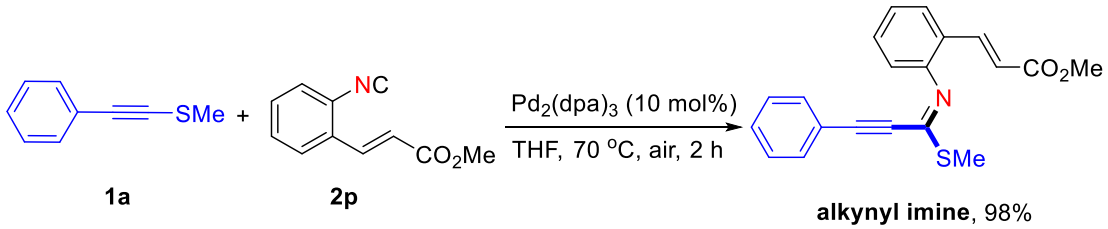


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D-**3aa**

(3) Capture the intermediate alkynyl imine



A mixture of thioalkyne **1a** (0.2 mmol, 43 mg), isocyanide **2p** (0.3 mmol, 54 mg) and $Pd_2(dpa)_3$ (0.02 mmol, 19 mg) in THF (8 mL) was stirred at 70 °C (heating oil temperature) in a sealed tube under air atmosphere. After 2 h, the resulting solution was cooled to room temperature and then filtered to a round bottom flask by a short pad of silica gel (eluent: CH_2Cl_2). The CH_2Cl_2 were removed in vacuo, then the crude product was purified by column chromatography using PE/EA (40:1) to provide the desired product **alkynyl imine** (66 mg) in 98% isolated yield.

Physical state: yellow solid.

Mp: 76- 78 °C.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.95 (d, *J* = 16.1 Hz, 1H), 7.64-7.58 (m, 1H), 7.35 (dd, *J* = 9.3, 5.2 Hz, 2H), 7.26 (q, *J* = 3.2, 2.8 Hz, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 3.77 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 167.8, 150.7, 150.1, 141.7, 132.4, 130.4, 130.2, 128.5, 127.4, 127.0, 125.1, 121.1, 120.6, 118.2, 96.8, 81.9, 51.7, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2S^+$ 336.1053; Found 336.1062.

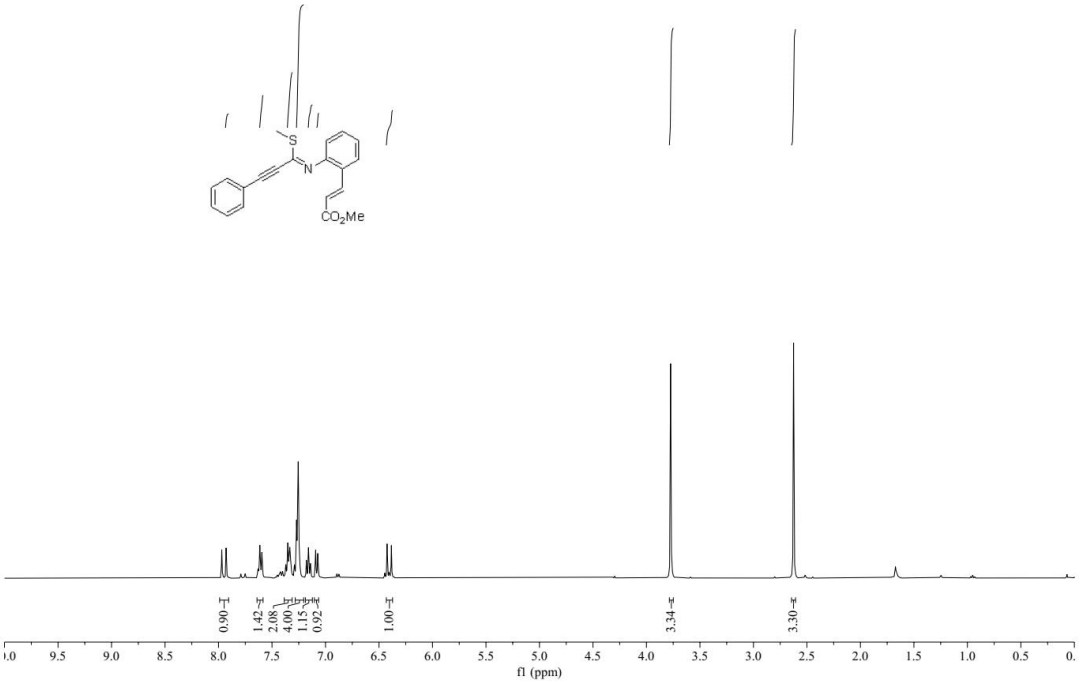


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of alkynyl imine

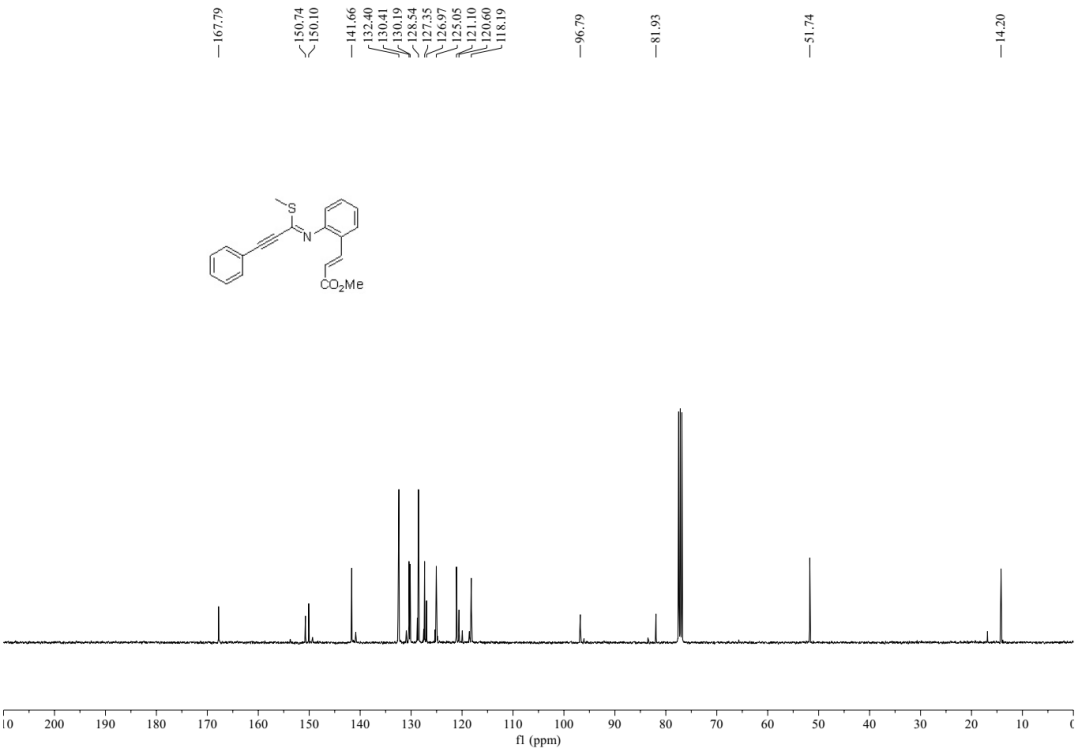
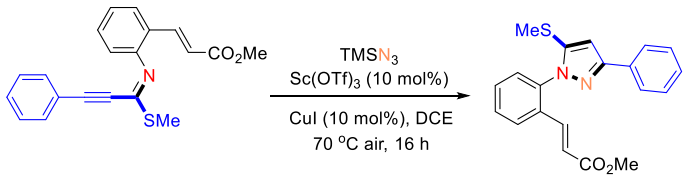


Figure S3. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of alkynyl imine



alkynyl imine **3ap**, 70%

The **alkynyl imine** (0.197 mmol, 66 mg) was dissolved in DCE (2 mL) and then $Sc(OTf)_3$ (0.02 mmol, 10 mg), CuI (0.02 mmol, 4 mg) and $TMSN_3$ (0.3 mmol, 35 mg) was added. The reaction mixture was stired at 70 ^oC (heating mantle temperature). After 16 h, the resulting mixture is filtered by a short pad of silica gel (eluent: CH_2Cl_2) and concentrated in vacuo then the crude product was purified by column chromatography using PE/EA (25:1-20:1) to provide the corresponding compounds **3ap** (48 mg, 70%).

8. Crystal data and structure refinement of product 3ja

Single crystal of compound **3ja** was obtained by slow evaporation from CH_2Cl_2 solution.

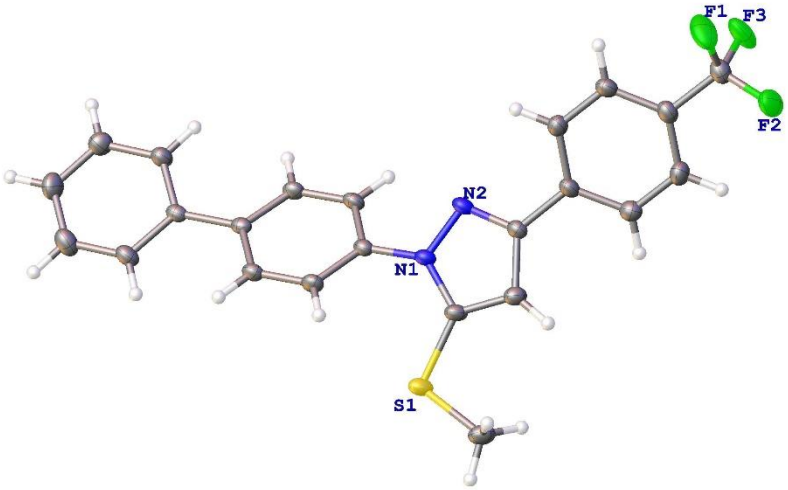


Figure S5. Crystal data and structure refinement of product **3ja** (with thermal ellipsoils shown at the 50% probability level)

Table S6. **Crystal data and structure refinement for 3ja.**

Identification code	4227
Empirical formula	$C_{23}H_{17}F_3N_2S$
Formula weight	410.44
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.4446(7)
b/Å	7.4929(4)
c/Å	22.0408(12)
α/°	90
β/°	92.240(5)
γ/°	90
Volume/Å^3	1888.63(18)
Z	4
ρ_{calc}g/cm^3	1.444
μ/mm^{-1}	1.883
F(000)	848.0
Crystal size/mm^3	0.16 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.012 to 148.068
Index ranges	$-14 \le h \le 13$, $-9 \le k \le 9$, $-21 \le l \le 27$
Reflections collected	13984
Independent reflections	7212 [R_{int} = 0.0552, R_{sigma} = 0.0484]
Data/restraints/parameters	7212/52/554

Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0576, wR_2 = 0.1695
Final R indexes [all data]	R_1 = 0.0619, wR_2 = 0.1781
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.30
Flack parameter	0.250(15)

Crystal structure determination of 3ja

Crystal Data for $C_{23}H_{17}F_3N_2S$ (*M* =410.44 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 11.4446(7) Å, *b* = 7.4929(4) Å, *c* = 22.0408(12) Å, *β* = 92.240(5)°, *V* = 1888.63(18) $Å^3$, *Z* = 4, *T* = 150.00(10) K, μ(Cu Kα) = 1.883 mm^{-1}, *Dcalc* = 1.444 g/cm^3, 13984 reflections measured (4.012° ≤ 2Θ ≤ 148.068°), 7212 unique (R_{int} = 0.0552, R_{sigma} = 0.0484) which were used in all calculations. The final R_1 was 0.0576 (I > 2σ(I)) and wR_2 was 0.1781 (all data).

Table S7. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3ja. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2152.7(10)	2184(2)	7334.8(6)	34.8(3)
F1	10111(4)	4927(6)	9305(2)	64.6(13)
F2	9298(3)	3407(7)	9992.6(15)	53.6(11)
F3	10331(3)	2107(7)	9340.7(17)	57.0(11)
N1	4429(3)	2373(6)	6998.1(18)	25.2(8)
N2	5566(3)	2446(6)	7213.8(19)	28.2(9)
C1	4213(4)	2309(7)	6360(2)	23.1(9)
C2	4953(4)	1330(7)	6001(2)	26.8(10)
C3	4759(4)	1287(7)	5380(2)	26.1(10)
C4	3820(4)	2192(7)	5092(2)	22.3(9)
C5	3085(4)	3151(7)	5466(2)	27.0(10)
C6	3270(4)	3218(7)	6088(2)	28.3(10)
C7	3628(4)	2173(7)	4423(2)	23.5(9)
C8	2577(4)	2780(8)	4151(2)	32.0(11)
C9	2424(5)	2837(9)	3527(3)	41.0(13)
C10	3314(5)	2326(9)	3155(2)	40.0(13)
C11	4354(5)	1719(8)	3412(2)	35.5(12)
C12	4509(4)	1647(8)	4040(2)	30.6(11)
C13	3665(4)	2333(8)	7464(2)	28.7(10)
C14	4330(4)	2389(8)	7993(2)	30.0(11)
C15	5499(4)	2457(7)	7813(2)	26.0(10)
C16	6553(4)	2637(8)	8211(2)	29.8(11)
C17	6540(4)	2093(8)	8813(2)	33.0(11)
C18	7502(5)	2361(9)	9203(2)	35.8(12)
C19	8491(4)	3185(8)	8993(2)	31.7(11)

C20	8529(4)	3711(8)	8389(2)	31.7(11)
C21	7559(4)	3442(8)	8001(2)	29.8(11)
C22	1709(5)	2387(9)	8103(2)	38.8(13)
C23	9534(5)	3421(8)	9409(2)	34.1(12)
S2	-277.1(11)	7951(2)	7705.0(6)	37.5(4)
F5	7547(10)	6044(11)	9968(8)	58(3)
F6	7190(20)	6330(30)	10275(11)	78(7)
F7	6792(10)	8050(40)	10481(4)	95(8)
F8	6979(12)	9130(20)	10292(10)	61(5)
F9	7876(13)	8670(30)	9725(10)	81(6)
F10	8026(16)	7990(40)	9660(10)	73(7)
N3	1989(3)	7271(6)	7451.7(17)	26.0(8)
N4	3107(3)	7174(6)	7691.6(18)	26.3(8)
C24	1221(4)	7184(7)	4873(2)	24.4(9)
C25	188(4)	6521(8)	4597(2)	31.4(11)
C26	22(5)	6468(9)	3972(3)	36.7(12)
C27	888(5)	7052(8)	3602(2)	34.0(11)
C28	1920(5)	7745(8)	3862(2)	35.4(12)
C29	2078(4)	7788(8)	4488(2)	32.7(12)
C30	1416(4)	7207(7)	5543(2)	23.8(9)
C31	2358(4)	8139(7)	5820(2)	25.7(10)
C32	2557(4)	8150(7)	6443(2)	26.5(10)
C33	1795(4)	7228(7)	6810(2)	23.8(9)
C34	853(4)	6301(7)	6549(2)	25.6(10)
C35	675(4)	6286(7)	5927(2)	25.5(10)
C36	1201(4)	7568(7)	7892(2)	26.7(10)
C37	1824(4)	7619(8)	8434(2)	29.9(11)
C38	3001(4)	7389(8)	8283(2)	27.6(10)
C39	4033(4)	7433(7)	8700(2)	28.4(11)
C40	3939(4)	8056(9)	9288(2)	35.9(12)
C41	4894(5)	8156(9)	9687(2)	36.3(12)
C42	5979(4)	7603(7)	9498(2)	29.6(11)
C43	5130(5)	6872(8)	8515(2)	34.5(12)
C44	6094(4)	6960(9)	8913(2)	35.7(12)
C45	-767(5)	8708(9)	8428(3)	41.3(14)
C46	7033(5)	7668(8)	9920(2)	33.4(9)

Table S8. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3ja. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	19.5(5)	51.1(8)	33.9(6)	-4.9(6)	3.5(4)	-2.5(5)

F1	60(3)	64(3)	68(3)	11(2)	-31(2)	-24(2)
F2	41.5(19)	87(3)	31.3(16)	-8.3(18)	-6.0(14)	3(2)
F3	37.0(18)	80(3)	53(2)	-17(2)	-17.0(15)	24(2)
N1	15.4(17)	31(2)	29.5(19)	0.1(17)	2.1(14)	0.4(17)
N2	15.2(17)	38(2)	32(2)	-1.4(18)	-1.1(14)	0.6(17)
C1	16.9(19)	25(2)	27(2)	1(2)	0.5(16)	0(2)
C2	16(2)	31(3)	33(2)	0(2)	0.0(18)	3.6(19)
C3	20(2)	28(3)	31(2)	0(2)	4.3(18)	5.6(19)
C4	17(2)	21(2)	29(2)	2(2)	2.4(16)	-0.4(19)
C5	19(2)	31(3)	31(2)	1(2)	1.7(17)	3.7(19)
C6	20(2)	32(3)	33(2)	1(2)	4.1(18)	7(2)
C7	18(2)	22(2)	31(2)	0(2)	0.4(16)	0.2(18)
C8	22(2)	38(3)	36(3)	-4(2)	-4.2(19)	3(2)
C9	37(3)	45(3)	40(3)	-4(3)	-9(2)	9(3)
C10	45(3)	48(3)	26(2)	-4(3)	-5(2)	-2(3)
C11	35(3)	40(3)	32(3)	-5(2)	4(2)	2(2)
C12	22(2)	40(3)	29(3)	-2(2)	-0.1(19)	4(2)
C13	18(2)	37(3)	31(2)	-3(2)	4.5(17)	-2(2)
C14	24(2)	37(3)	30(2)	-2(2)	4.6(18)	-2(2)
C15	20(2)	30(3)	28(2)	1.9(19)	0.1(17)	2.8(19)
C16	20(2)	42(3)	28(2)	0(2)	-0.9(17)	4(2)
C17	27(2)	38(3)	34(3)	3(2)	1.9(19)	1(2)
C18	36(3)	47(3)	24(2)	3(2)	0.5(19)	3(3)
C19	28(2)	38(3)	30(2)	-1(2)	-3.1(19)	7(2)
C20	21(2)	42(3)	32(3)	0(2)	1.6(19)	3(2)
C21	28(2)	37(3)	24(2)	0(2)	2.1(18)	3(2)
C22	29(3)	48(3)	40(3)	-3(3)	10(2)	0(3)
C23	33(3)	37(3)	32(3)	-2(2)	-5(2)	4(2)
S2	19.5(6)	60.0(9)	33.1(6)	-0.9(6)	1.2(4)	4.3(6)
F5	54(5)	46(3)	71(7)	-2(3)	-35(5)	12(3)
F6	94(13)	57(7)	80(12)	33(8)	-52(11)	-29(7)
F7	47(5)	200(20)	36(3)	-34(6)	-14(3)	37(9)
F8	46(6)	68(6)	66(8)	-32(6)	-24(6)	8(5)
F9	45(5)	97(10)	98(11)	54(9)	-38(5)	-40(6)
F10	33(4)	150(20)	35(6)	4(9)	0(4)	-12(8)
N3	15.8(17)	33(2)	28.9(19)	0.9(19)	-0.4(14)	-0.8(18)
N4	17.9(18)	30(2)	31(2)	-2.3(18)	-2.0(14)	0.6(18)
C24	19(2)	24(2)	30(2)	1(2)	1.7(17)	1.0(19)
C25	26(2)	36(3)	32(3)	3(2)	-0.1(19)	-2(2)
C26	30(3)	44(3)	36(3)	1(2)	-4(2)	-4(2)

C27	38(3)	39(3)	24(2)	2(2)	-3(2)	1(2)
C28	29(3)	45(3)	32(3)	5(2)	6(2)	0(2)
C29	22(2)	45(3)	31(2)	2(2)	2.1(18)	-3(2)
C30	18(2)	24(2)	29(2)	-3(2)	2.6(16)	0.8(19)
C31	22(2)	24(2)	32(2)	-1(2)	4.2(17)	-4.6(19)
C32	18(2)	27(2)	34(2)	0(2)	-0.3(17)	-4.8(19)
C33	19(2)	27(2)	24(2)	-2(2)	1.6(16)	0(2)
C34	22(2)	24(2)	31(2)	0.8(19)	2.1(18)	-1.9(19)
C35	18(2)	26(2)	32(3)	-3(2)	1.5(18)	-4.5(19)
C36	17(2)	32(3)	31(2)	2(2)	0.9(17)	2.4(18)
C37	25(2)	40(3)	26(2)	0(2)	2.6(18)	0(2)
C38	23(2)	30(3)	29(2)	-1(2)	0.0(17)	-1(2)
C39	25(2)	32(3)	28(2)	0(2)	0.7(18)	-2(2)
C40	26(2)	51(3)	31(3)	-2(2)	4.2(19)	3(2)
C41	32(3)	51(4)	26(2)	-3(2)	1.3(19)	4(3)
C42	28(2)	30(3)	31(2)	0.0(19)	-2.3(17)	-1.2(19)
C43	27(2)	47(3)	29(2)	-6(2)	0.3(19)	3(2)
C44	24(2)	50(4)	32(3)	-7(2)	0.0(19)	4(2)
C45	27(3)	53(4)	44(3)	-8(3)	10(2)	6(3)
C46	32(2)	37(2)	31(2)	0.8(16)	-4.5(15)	-2.1(17)

Table S9. Bond Lengths for 3ja.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C13	1.746(5)	F5	C46	1.354(9)
S1	C22	1.793(5)	F6	C46	1.278(12)
F1	C23	1.332(7)	F7	C46	1.310(9)
F2	C23	1.325(6)	F8	C46	1.372(11)
F3	C23	1.354(7)	F9	C46	1.308(11)
N1	N2	1.369(5)	F10	C46	1.316(13)
N1	C1	1.418(6)	N3	N4	1.367(5)
N1	C13	1.374(6)	N3	C33	1.424(6)
N2	C15	1.325(6)	N3	C36	1.368(6)
C1	C2	1.392(6)	N4	C38	1.324(6)
C1	C6	1.392(7)	C24	C25	1.400(7)
C2	C3	1.379(7)	C24	C29	1.398(6)
C3	C4	1.401(6)	C24	C30	1.484(6)
C4	C5	1.399(6)	C25	C26	1.384(7)
C4	C7	1.482(6)	C26	C27	1.379(8)
C5	C6	1.380(7)	C27	C28	1.394(8)
C7	C8	1.399(7)	C28	C29	1.385(7)
C7	C12	1.396(7)	C30	C31	1.404(7)

C8	C9	1.381(8)	C30	C35	1.403(6)
C9	C10	1.385(8)	C31	C32	1.383(7)
C10	C11	1.376(8)	C32	C33	1.395(7)
C11	C12	1.390(7)	C33	C34	1.388(7)
C13	C14	1.368(7)	C34	C35	1.378(7)
C14	C15	1.411(6)	C36	C37	1.369(7)
C15	C16	1.471(7)	C37	C38	1.411(6)
C16	C17	1.388(7)	C38	C39	1.467(7)
C16	C21	1.394(7)	C39	C40	1.386(7)
C17	C18	1.384(8)	C39	C43	1.399(7)
C18	C19	1.385(8)	C40	C41	1.378(7)
C19	C20	1.389(7)	C41	C42	1.388(7)
C19	C23	1.487(7)	C42	C44	1.389(7)
C20	C21	1.389(7)	C42	C46	1.496(7)
S2	C36	1.749(5)	C43	C44	1.384(7)
S2	C45	1.802(6)			

Table S10. **Bond Angles for 3ja.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	S1	C22	99.0(2)	C36	N3	C33	128.8(4)
N2	N1	C1	118.2(3)	C38	N4	N3	104.8(4)
N2	N1	C13	111.5(4)	C25	C24	C30	121.9(4)
C13	N1	C1	130.3(4)	C29	C24	C25	116.8(4)
C15	N2	N1	104.8(4)	C29	C24	C30	121.3(4)
C2	C1	N1	119.7(4)	C26	C25	C24	121.6(5)
C2	C1	C6	119.4(4)	C27	C26	C25	120.4(5)
C6	C1	N1	120.9(4)	C26	C27	C28	119.5(5)
C3	C2	C1	120.0(4)	C29	C28	C27	119.6(5)
C2	C3	C4	122.0(4)	C28	C29	C24	122.0(5)
C3	C4	C7	121.8(4)	C31	C30	C24	121.3(4)
C5	C4	C3	116.7(4)	C35	C30	C24	121.6(4)
C5	C4	C7	121.5(4)	C35	C30	C31	117.0(4)
C6	C5	C4	122.1(4)	C32	C31	C30	121.8(4)
C5	C6	C1	119.8(4)	C31	C32	C33	119.4(4)
C8	C7	C4	121.0(4)	C32	C33	N3	119.2(4)
C12	C7	C4	121.4(4)	C34	C33	N3	120.7(4)
C12	C7	C8	117.5(4)	C34	C33	C32	120.1(4)
C9	C8	C7	120.7(5)	C35	C34	C33	119.9(4)
C8	C9	C10	120.9(5)	C34	C35	C30	121.8(4)
C11	C10	C9	119.5(5)	N3	C36	S2	121.2(4)
C10	C11	C12	119.8(5)	N3	C36	C37	106.8(4)

C11	C12	C7	121.6(5)	C37	C36	S2	131.8(4)
N1	C13	S1	122.4(4)	C36	C37	C38	105.1(4)
C14	C13	S1	131.0(4)	N4	C38	C37	111.8(4)
C14	C13	N1	106.6(4)	N4	C38	C39	121.1(4)
C13	C14	C15	105.3(4)	C37	C38	C39	127.0(4)
N2	C15	C14	111.9(4)	C40	C39	C38	120.2(4)
N2	C15	C16	121.1(4)	C40	C39	C43	118.4(5)
C14	C15	C16	126.9(4)	C43	C39	C38	121.4(4)
C17	C16	C15	120.3(4)	C41	C40	C39	121.9(5)
C17	C16	C21	119.0(5)	C40	C41	C42	119.2(5)
C21	C16	C15	120.7(4)	C41	C42	C44	120.1(5)
C18	C17	C16	120.8(5)	C41	C42	C46	120.8(5)
C17	C18	C19	119.9(5)	C44	C42	C46	119.1(5)
C18	C19	C20	120.2(5)	C44	C43	C39	120.3(5)
C18	C19	C23	119.6(5)	C43	C44	C42	120.1(5)
C20	C19	C23	120.2(5)	F5	C46	C42	111.0(6)
C21	C20	C19	119.6(5)	F6	C46	F8	105.6(10)
C20	C21	C16	120.6(5)	F6	C46	F10	107.8(14)
F1	C23	F3	104.9(5)	F6	C46	C42	116.6(8)
F1	C23	C19	112.7(5)	F7	C46	F5	103.4(9)
F2	C23	F1	107.1(5)	F7	C46	C42	113.6(6)
F2	C23	F3	105.4(4)	F8	C46	C42	110.1(7)
F2	C23	C19	114.1(5)	F9	C46	F5	102.5(10)
F3	C23	C19	111.9(5)	F9	C46	F7	111.7(13)
C36	S2	C45	100.1(3)	F9	C46	C42	113.6(10)
N4	N3	C33	119.4(3)	F10	C46	F8	100.0(13)
N4	N3	C36	111.6(4)	F10	C46	C42	115.1(12)

Table S11. **Torsion Angles for 3ja.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C13	C14	C15	178.3(5)	N3	C33	C34	C35	179.6(4)
N1	N2	C15	C14	0.1(6)	N3	C36	C37	C38	1.6(6)
N1	N2	C15	C16	-176.4(5)	N4	N3	C33	C32	-39.7(7)
N1	C1	C2	C3	-178.9(5)	N4	N3	C33	C34	141.1(5)
N1	C1	C6	C5	179.3(4)	N4	N3	C36	S2	174.2(4)
N1	C13	C14	C15	-0.2(6)	N4	N3	C36	C37	-1.6(6)
N2	N1	C1	C2	37.6(7)	N4	C38	C39	C40	165.2(6)
N2	N1	C1	C6	-142.2(5)	N4	C38	C39	C43	-14.1(8)
N2	N1	C13	S1	-178.4(4)	C24	C25	C26	C27	0.9(9)
N2	N1	C13	C14	0.2(6)	C24	C30	C31	C32	-179.2(5)
N2	C15	C16	C17	-159.5(5)	C24	C30	C35	C34	179.9(4)

N2	C15	C16	C21	24.1(8)	C25	C24	C29	C28	0.3(9)
C1	N1	N2	C15	-178.8(4)	C25	C24	C30	C31	-169.1(5)
C1	N1	C13	S1	0.0(8)	C25	C24	C30	C35	11.5(8)
C1	N1	C13	C14	178.6(5)	C25	C26	C27	C28	-1.8(9)
C1	C2	C3	C4	-0.7(8)	C26	C27	C28	C29	2.0(9)
C2	C1	C6	C5	-0.5(8)	C27	C28	C29	C24	-1.2(9)
C2	C3	C4	C5	0.1(8)	C29	C24	C25	C26	-0.1(8)
C2	C3	C4	C7	178.7(5)	C29	C24	C30	C31	12.5(8)
C3	C4	C5	C6	0.3(8)	C29	C24	C30	C35	-166.9(5)
C3	C4	C7	C8	167.5(5)	C30	C24	C25	C26	-178.6(5)
C3	C4	C7	C12	-16.1(8)	C30	C24	C29	C28	178.8(5)
C4	C5	C6	C1	-0.1(8)	C30	C31	C32	C33	-0.7(8)
C4	C7	C8	C9	176.9(5)	C31	C30	C35	C34	0.6(7)
C4	C7	C12	C11	-176.5(5)	C31	C32	C33	N3	-178.8(4)
C5	C4	C7	C8	-14.0(7)	C31	C32	C33	C34	0.4(8)
C5	C4	C7	C12	162.4(5)	C32	C33	C34	C35	0.3(8)
C6	C1	C2	C3	0.9(7)	C33	N3	N4	C38	175.1(5)
C7	C4	C5	C6	-178.3(5)	C33	N3	C36	S2	0.5(8)
C7	C8	C9	C10	-1.2(9)	C33	N3	C36	C37	-175.2(5)
C8	C7	C12	C11	0.0(8)	C33	C34	C35	C30	-0.8(8)
C8	C9	C10	C11	1.4(10)	C35	C30	C31	C32	0.2(7)
C9	C10	C11	C12	-0.9(10)	C36	N3	N4	C38	0.9(6)
C10	C11	C12	C7	0.2(9)	C36	N3	C33	C32	133.5(6)
C12	C7	C8	C9	0.4(8)	C36	N3	C33	C34	-45.7(8)
C13	N1	N2	C15	-0.2(6)	C36	C37	C38	N4	-1.2(7)
C13	N1	C1	C2	-140.7(6)	C36	C37	C38	C39	176.6(5)
C13	N1	C1	C6	39.4(8)	C37	C38	C39	C40	-12.3(9)
C13	C14	C15	N2	0.0(6)	C37	C38	C39	C43	168.4(6)
C13	C14	C15	C16	176.3(5)	C38	C39	C40	C41	-178.5(6)
C14	C15	C16	C17	24.6(8)	C38	C39	C43	C44	178.7(5)
C14	C15	C16	C21	-151.8(6)	C39	C40	C41	C42	-0.5(10)
C15	C16	C17	C18	-175.8(5)	C39	C43	C44	C42	0.1(9)
C15	C16	C21	C20	176.0(5)	C40	C39	C43	C44	-0.6(9)
C16	C17	C18	C19	0.2(9)	C40	C41	C42	C44	0.0(9)
C17	C16	C21	C20	-0.5(8)	C40	C41	C42	C46	-179.2(6)
C17	C18	C19	C20	-1.3(9)	C41	C42	C44	C43	0.2(9)
C17	C18	C19	C23	-178.2(5)	C41	C42	C46	F5	124.3(10)
C18	C19	C20	C21	1.5(9)	C41	C42	C46	F6	84.7(19)
C18	C19	C23	F1	-145.6(6)	C41	C42	C46	F7	8.4(17)
C18	C19	C23	F2	-23.1(8)	C41	C42	C46	F8	-35.6(13)

C18	C19	C23	F3	96.5(6)	C41	C42	C46 F9	-120.7(13)
C19	C20	C21	C16	-0.6(8)	C41	C42	C46 F10	-147.6(16)
C20	C19	C23	F1	37.5(7)	C43	C39	C40 C41	0.8(9)
C20	C19	C23	F2	160.0(5)	C44	C42	C46 F5	-54.9(11)
C20	C19	C23	F3	-80.4(7)	C44	C42	C46 F6	-94.5(19)
C21	C16	C17	C18	0.7(9)	C44	C42	C46 F7	-170.8(16)
C22	S1	C13	N1	-175.3(5)	C44	C42	C46 F8	145.2(12)
C22	S1	C13	C14	6.4(6)	C44	C42	C46 F9	60.1(14)
C23	C19	C20	C21	178.4(5)	C44	C42	C46 F10	33.2(17)
S2	C36	C37	C38	-173.5(4)	C45	S2	C36 N3	-168.2(5)
N3	N4	C38	C37	0.2(6)	C45	S2	C36 C37	6.4(6)
N3	N4	C38	C39	-177.7(5)	C46	C42	C44 C43	179.4(5)

Table S12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3ja.

Atom	*x*	*y*	*z*	U(eq)
H2	5592.25	692.19	6183.23	32
H3	5276.47	624.37	5139.56	31
H5	2437.8	3776.2	5285.86	32
H6	2755.53	3882.19	6329.75	34
H8	1961.58	3156.85	4398.52	38
H9	1699.58	3232.59	3349.66	49
H10	3206.59	2395.23	2726.05	48
H11	4965.14	1348.86	3161.09	43
H12	5231.09	1228.92	4213.51	37
H14	4062.58	2383.77	8395.25	36
H17	5862.45	1530.27	8959.15	40
H18	7483.51	1980.07	9613.25	43
H20	9213.88	4250.5	8242.73	38
H21	7580.54	3811.23	7589.46	36
H22A	857.41	2259.43	8113.49	58
H22B	1939.74	3560.46	8262.75	58
H22C	2085.8	1451.47	8351.79	58
H25	-414	6097.44	4844.65	38
H26	-692.92	6027.24	3796.86	44
H27	781.11	6982.54	3172.8	41
H28	2512.28	8186.21	3611.34	42
H29	2791.56	8241.45	4661.01	39
H31	2874.06	8779.26	5571.92	31
H32	3205.31	8779.76	6619.17	32
H34	331.84	5679.05	6799.4	31

H35	33.3	5633.02	5754.06	31
H37	1528.24	7775.71	8827.27	36
H40	3196.52	8424.84	9419.07	43
H41	4810.8	8596.98	10087.49	44
H43	5212.29	6429.09	8115.57	41
H44	6837.24	6578.58	8784.55	43
H45A	-1575.8	9129.48	8381.36	62
H45B	-264.77	9686.43	8577.17	62
H45C	-725.82	7719.99	8719.7	62

Table S13. **Atomic Occupancy for 3ja.**

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
F5	0.57(3)	F6	0.43(3)	F7	0.57(3)
F8	0.43(3)	F9	0.57(3)	F10	0.43(3)

9. Crystal data and structure refinement of 5a

Single crystal of compound alkynyl imines was obtained by slow evaporation from CH_2Cl_2 solution.

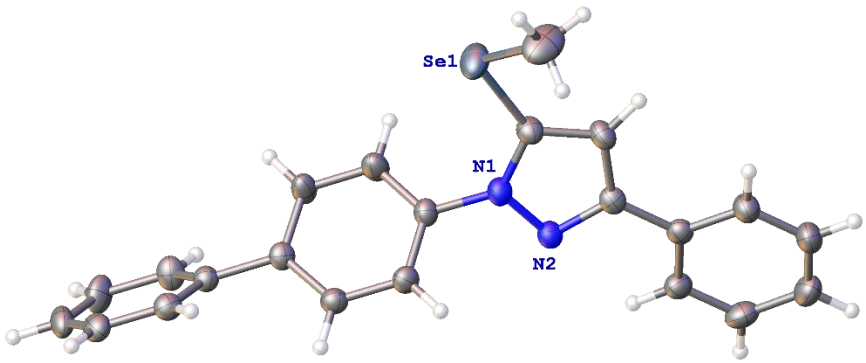


Figure S14. Crystal data and structure refinement of product **5a** (with thermal ellipsoils shown at the 50% probability level)

Table S15. **Crystal data and structure refinement for 5a.**

Identification code	**5a**
Empirical formula	$C_{22}H_{18}N_2Se$
Formula weight	389.34
Temperature/K	219.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.6690(4)
b/Å	13.8133(4)

c/Å	13.9111(4)
α/°	90
β/°	101.261(3)
γ/°	90
Volume/Å^3	1822.21(11)
Z	4
ρ_{calc}g/cm^3	1.419
μ/mm^{-1}	2.818
F(000)	792.0
Crystal size/mm^3	0.15 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.11 to 147.5
Index ranges	-12 ≤ h ≤ 5, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	7179
Independent reflections	3572 [R_{int} = 0.0434, R_{sigma} = 0.0536]
Data/restraints/parameters	3572/0/227
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1336
Final R indexes [all data]	R_1 = 0.0648, wR_2 = 0.1514
Largest diff. peak/hole / e Å^{-3}	0.44/-0.65

Crystal structure determination of 5a

Crystal Data for $C_{22}H_{18}N_2Se$ (*M* =389.34 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 9.6690(4) Å, *b* = 13.8133(4) Å, *c* = 13.9111(4) Å, *β* = 101.261(3)°, *V* = 1822.21(11) Å^3, *Z* = 4, *T* = 219.99(10) K, μ(Cu Kα) = 2.818 mm^{-1}, *Dcalc* = 1.419 g/cm^3, 7179 reflections measured (9.11° ≤ 2Θ ≤ 147.5°), 3572 unique (R_{int} = 0.0434, R_{sigma} = 0.0536) which were used in all calculations. The final R_1 was 0.0517 (I > 2σ(I)) and wR_2 was 0.1514 (all data).

Table S16. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Se1	3014.6(5)	4136.4(3)	5174.5(3)	57.20(19)
N1	4472(3)	3143.9(18)	6885.8(18)	33.0(5)
N2	4847(2)	2272.3(19)	7295.1(16)	32.2(5)
C1	6282(3)	6513(2)	9138(2)	31.6(6)
C2	5638(3)	6746(2)	9919(2)	41.6(7)
C3	6051(4)	7554(3)	10491(2)	47.8(8)
C4	7125(4)	8142(2)	10300(2)	44.2(8)
C5	7769(3)	7917(2)	9520(2)	39.6(7)
C6	7357(3)	7111(2)	8951(2)	34.9(6)
C7	5826(3)	5647(2)	8534(2)	31.0(6)

C8	6787(3)	4957(2)	8343(2)	34.0(6)
C9	6350(3)	4138(2)	7789(2)	33.9(6)
C10	4925(3)	4000(2)	7425(2)	32.2(6)
C11	3950(3)	4672(3)	7607(2)	40.9(7)
C12	4401(3)	5489(2)	8154(3)	41.0(7)
C13	3635(3)	3051(2)	5975(2)	35.6(6)
C14	3473(3)	2074(2)	5802(2)	36.9(6)
C15	4239(3)	1622(2)	6638(2)	32.0(6)
C16	4405(3)	581(2)	6848(2)	32.5(6)
C17	4855(3)	255(2)	7811(2)	38.4(7)
C18	4997(4)	-729(3)	8013(3)	48.7(8)
C19	4709(4)	-1396(3)	7257(3)	50.9(8)
C20	4279(4)	-1071(3)	6310(3)	50.5(9)
C21	4122(3)	-100(3)	6108(2)	40.9(7)
C22	3320(6)	3589(4)	3947(3)	75.6(14)

Table S17. Anisotropic Displacement Parameters ($Å^2×10^3$) for 5a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se1	87.9(4)	37.2(3)	42.1(3)	4.44(15)	1.7(2)	6.79(19)
N1	37.9(12)	31.4(13)	30.9(11)	-2.6(10)	9.4(10)	-1.1(10)
N2	36.5(12)	32.2(13)	28.4(11)	-2.2(10)	7.9(9)	-0.8(10)
C1	33.0(13)	31.4(15)	30.3(13)	-0.1(12)	5.9(11)	-0.3(11)
C2	46.7(16)	40.6(18)	42.4(16)	-3.2(14)	20.8(14)	-6.6(14)
C3	73(2)	37.8(18)	39.3(16)	-8.1(14)	26.4(16)	5.0(17)
C4	64(2)	26.6(15)	38.0(16)	-2.1(13)	-0.2(14)	-1.9(14)
C5	45.0(16)	32.4(16)	39.9(15)	5.3(13)	5.0(13)	-1.1(13)
C6	37.2(14)	38.7(16)	29.8(13)	1.2(12)	8.7(11)	1.5(13)
C7	34.9(13)	33.8(15)	26.8(12)	-1.7(11)	12.2(10)	-0.8(12)
C8	31.5(13)	37.2(16)	33.5(14)	-0.3(12)	6.5(11)	1.1(12)
C9	33.5(14)	36.0(16)	33.7(14)	-3.4(12)	10.2(11)	2.7(12)
C10	37.2(14)	30.2(15)	30.0(13)	-2.9(11)	8.8(11)	-1.5(12)
C11	28.4(13)	44.4(18)	50.4(17)	-12.1(15)	8.6(12)	-2.2(13)
C12	31.1(14)	40.3(17)	53.3(18)	-16.3(15)	12.9(13)	-0.9(13)
C13	41.7(15)	36.0(16)	28.8(13)	1.5(12)	6.1(11)	-2.6(13)
C14	41.8(15)	37.5(16)	30.5(13)	-3.8(12)	4.8(11)	-8.8(13)
C15	30.8(12)	36.9(15)	30.5(13)	-1.4(12)	11.5(10)	-3.6(12)
C16	27.5(12)	35.8(16)	34.6(14)	-1.2(12)	7.1(10)	0.2(11)
C17	38.5(14)	39.5(17)	35.9(14)	-3.0(13)	3.8(12)	5.5(13)
C18	44.4(17)	50(2)	49.2(19)	9.2(16)	2.3(14)	12.0(15)

C19	49.9(18)	33.4(17)	67(2)	0.6(16)	4.5(16)	3.4(15)
C20	51.1(18)	39.3(19)	56(2)	-11.4(16)	-0.8(16)	-1.5(15)
C21	45.2(16)	36.8(17)	38.8(15)	-3.0(13)	3.3(13)	-2.8(14)
C22	108(4)	83(3)	35.8(18)	12(2)	15(2)	28(3)

Table S18. Bond Lengths for 5a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Se1	C13	1.894(3)	C7	C12	1.393(4)
Se1	C22	1.942(4)	C8	C9	1.388(4)
N1	N2	1.351(3)	C9	C10	1.385(4)
N1	C10	1.423(4)	C10	C11	1.380(4)
N1	C13	1.369(4)	C11	C12	1.384(4)
N2	C15	1.333(4)	C13	C14	1.375(4)
C1	C2	1.392(4)	C14	C15	1.399(4)
C1	C6	1.392(4)	C15	C16	1.469(4)
C1	C7	1.478(4)	C16	C17	1.400(4)
C2	C3	1.384(5)	C16	C21	1.381(4)
C3	C4	1.384(5)	C17	C18	1.389(5)
C4	C5	1.388(5)	C18	C19	1.385(5)
C5	C6	1.380(4)	C19	C20	1.377(5)
C7	C8	1.393(4)	C20	C21	1.374(5)

Table S19. Bond Angles for 5a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	Se1	C22	97.12(17)	C11	C10	N1	120.3(3)
N2	N1	C10	119.3(2)	C11	C10	C9	120.4(3)
N2	N1	C13	111.6(2)	C10	C11	C12	119.7(3)
C13	N1	C10	129.1(3)	C11	C12	C7	121.3(3)
C15	N2	N1	105.4(2)	N1	C13	Se1	122.1(2)
C2	C1	C7	120.1(3)	N1	C13	C14	106.3(3)
C6	C1	C2	118.3(3)	C14	C13	Se1	131.4(2)
C6	C1	C7	121.7(3)	C13	C14	C15	105.6(3)
C3	C2	C1	120.8(3)	N2	C15	C14	111.1(3)
C2	C3	C4	120.4(3)	N2	C15	C16	120.5(3)
C3	C4	C5	119.1(3)	C14	C15	C16	128.4(3)
C6	C5	C4	120.4(3)	C17	C16	C15	120.4(3)
C5	C6	C1	120.9(3)	C21	C16	C15	121.3(3)
C8	C7	C1	121.7(3)	C21	C16	C17	118.3(3)
C12	C7	C1	120.4(3)	C18	C17	C16	120.5(3)
C12	C7	C8	117.8(3)	C19	C18	C17	120.0(3)

C9	C8	C7	121.5(3)	C20	C19	C18	119.2(4)
C10	C9	C8	119.2(3)	C21	C20	C19	120.9(3)
C9	C10	N1	119.2(3)	C20	C21	C16	121.0(3)

Table S20. Torsion Angles for 5a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Se1	C13	C14	C15	176.0(2)	C8	C7	C12	C11	0.2(5)
N1	N2	C15	C14	0.2(3)	C8	C9	C10	N1	-177.8(3)
N1	N2	C15	C16	-179.0(2)	C8	C9	C10	C11	0.3(4)
N1	C10	C11	C12	178.2(3)	C9	C10	C11	C12	0.2(5)
N1	C13	C14	C15	0.1(3)	C10	N1	N2	C15	178.1(2)
N2	N1	C10	C9	55.0(4)	C10	N1	C13	Se1	5.6(4)
N2	N1	C10	C11	-123.1(3)	C10	N1	C13	C14	-178.0(3)
N2	N1	C13	Se1	-176.40(19)	C10	C11	C12	C7	-0.4(5)
N2	N1	C13	C14	0.0(3)	C12	C7	C8	C9	0.2(4)
N2	C15	C16	C17	17.6(4)	C13	N1	N2	C15	-0.1(3)
N2	C15	C16	C21	-162.5(3)	C13	N1	C10	C9	-127.2(3)
C1	C2	C3	C4	-0.5(5)	C13	N1	C10	C11	54.7(4)
C1	C7	C8	C9	179.0(3)	C13	C14	C15	N2	-0.2(3)
C1	C7	C12	C11	-178.5(3)	C13	C14	C15	C16	179.0(3)
C2	C1	C6	C5	-0.4(4)	C14	C15	C16	C17	-161.5(3)
C2	C1	C7	C8	-128.8(3)	C14	C15	C16	C21	18.4(4)
C2	C1	C7	C12	49.9(4)	C15	C16	C17	C18	179.2(3)
C2	C3	C4	C5	0.8(5)	C15	C16	C21	C20	-180.0(3)
C3	C4	C5	C6	-0.8(5)	C16	C17	C18	C19	0.8(5)
C4	C5	C6	C1	0.6(5)	C17	C16	C21	C20	-0.1(5)
C6	C1	C2	C3	0.3(5)	C17	C18	C19	C20	-0.2(5)
C6	C1	C7	C8	50.9(4)	C18	C19	C20	C21	-0.5(6)
C6	C1	C7	C12	-130.4(3)	C19	C20	C21	C16	0.7(5)
C7	C1	C2	C3	-180.0(3)	C21	C16	C17	C18	-0.7(4)
C7	C1	C6	C5	179.9(3)	C22	Se1	C13	N1	137.5(3)
C7	C8	C9	C10	-0.5(4)	C22	Se1	C13	C14	-37.9(4)

Table S21. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5a.

Atom	*x*	*y*	*z*	U(eq)
H2	4904.89	6345.01	10061.48	50
H3	5595.75	7705.91	11018.27	57
H4	7416.29	8692.17	10697.62	53
H5	8498.56	8321.09	9377.7	47

Atom	*x*	*y*	*z*	U(eq)
H6	7813.6	6962.24	8422.86	42
H8	7763.81	5049.69	8596.84	41
H9	7020.25	3677.45	7660.23	41
H11	2973.49	4573.05	7356.99	49
H12	3726.52	5950.4	8273.58	49
H14	2951.3	1769.28	5232.47	44
H17	5065.29	710.37	8331.08	46
H18	5291.02	-944.03	8669.71	58
H19	4807.62	-2069.39	7390.45	61
H20	4088.82	-1525.95	5788.5	61
H21	3813.95	107.44	5450.11	49
H22A	3294.72	4106.87	3462.39	113
H22B	2578.08	3115.88	3706.4	113
H22C	4241.5	3268.51	4053.37	113

10. Crystal data and structure refinement of product alkynyl imine

Single crystal of compound **alkynyl imine** was obtained by slow evaporation from CH_2Cl_2 solution.

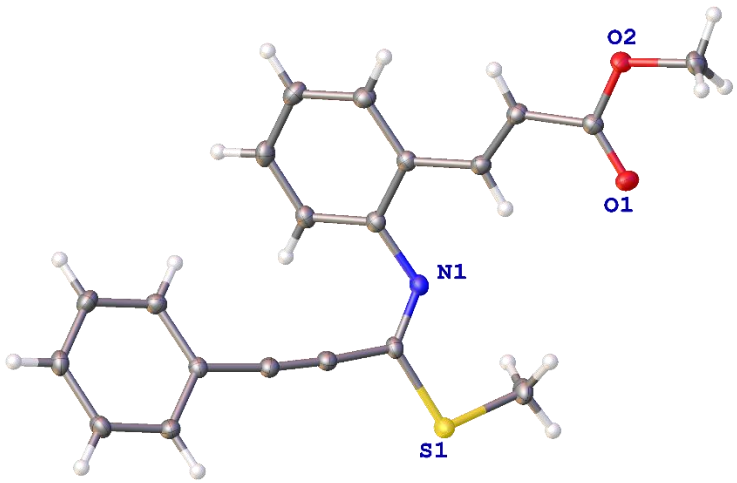


Figure S22. Crystal data and structure refinement of product alkynyl imines (with thermal ellipsoils shown at the 50% probability level)

Table S23. Crystal data and structure refinement for alkynyl imine.

Identification code	**alkynyl imine**
Empirical formula	$C_{20}H_{17}NO_2S$
Formula weight	335.40
Temperature/K	296.30

Crystal system	triclinic
Space group	P-1
a/Å	8.053(4)
b/Å	10.667(4)
c/Å	11.338(6)
α/°	111.696(14)
β/°	95.674(19)
γ/°	101.888(16)
Volume/Å^3	869.0(7)
Z	2
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.197
F(000)	352.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.94 to 57.414
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	22643
Independent reflections	4397 [R_{int} = 0.0957, R_{sigma} = 0.0717]
Data/restraints/parameters	4397/0/219
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0505, wR_2 = 0.1066
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.1236
Largest diff. peak/hole / e Å^{-3}	0.26/-0.31

Crystal structure determination of alkynyl imine

Crystal Data for $C_{20}H_{17}NO_2S$ (*M* =335.40 g/mol): triclinic, space group P-1 (no. 2), *a* = 8.053(4) Å, *b* = 10.667(4) Å, *c* = 11.338(6) Å, *α* = 111.696(14)°, *β* = 95.674(19)°, *γ* = 101.888(16)°, *V* = 869.0(7) Å^3, *Z* = 2, *T* = 296.30 K, μ(MoKα) = 0.197 mm^{-1}, *Dcalc* = 1.282 g/cm^3, 22643 reflections measured (3.94° ≤ 2Θ ≤ 57.414°), 4397 unique (R_{int} = 0.0957, R_{sigma} = 0.0717) which were used in all calculations. The final R_1 was 0.0505 (I > 2σ(I)) and wR_2 was 0.1236 (all data).

Table S24. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for alkynyl imine. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	672.6(7)	2032.5(5)	8298.3(5)	30.97(15)
O1	3107(2)	2176.0(14)	3402.3(13)	37.8(4)
O2	3766.7(18)	3607.0(13)	2378.0(12)	32.0(3)
N1	643(2)	3909.9(15)	7268.3(14)	25.9(3)
C1	4024(2)	6960.8(18)	11540.4(16)	24.0(4)
C2	4017(2)	8266.5(19)	11531.7(18)	28.2(4)

C3	4899(3)	9483.6(19)	12577.5(19)	31.9(4)
C4	5800(3)	9404(2)	13641.8(18)	31.3(4)
C5	5810(3)	8114(2)	13668.3(18)	31.7(4)
C6	4931(2)	6884.9(19)	12616.9(17)	28.2(4)
C7	3072(2)	5721.4(18)	10434.3(17)	26.6(4)
C8	2222(2)	4774.9(19)	9467.7(17)	27.1(4)
C9	1170(2)	3710.2(18)	8276.3(17)	24.9(4)
C10	970(2)	5287.0(18)	7308.5(17)	24.7(4)
C11	469(2)	6341.0(19)	8243.0(17)	28.3(4)
C12	704(2)	7657(2)	8233.2(18)	32.1(5)
C13	1434(3)	7947(2)	7270(2)	32.8(5)
C14	1918(2)	6905(2)	6326.1(19)	29.9(4)
C15	1695(2)	5558.5(18)	6315.6(17)	24.2(4)
C16	2179(2)	4446.5(19)	5313.0(17)	24.9(4)
C17	2901(2)	4537.1(19)	4334.3(17)	26.9(4)
C18	3259(2)	3314.5(19)	3361.1(17)	25.8(4)
C19	4085(3)	2483(2)	1319.9(19)	36.0(5)
C20	-606(3)	1008(2)	6704.7(19)	38.6(5)

Table S25. Anisotropic Displacement Parameters ($Å^2×10^3$) for alkynyl imine. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	38.3(3)	25.4(2)	26.2(3)	10.34(19)	5.7(2)	2.3(2)
O1	56.4(10)	32.4(8)	36.7(8)	19.4(6)	20.3(7)	21.2(7)
O2	42.6(8)	30.8(7)	29.6(7)	15.1(6)	18.5(6)	12.8(6)
N1	27.2(8)	25.4(8)	22.5(8)	7.9(6)	6.3(6)	3.8(6)
C1	21.9(9)	24.5(9)	22.8(9)	7.8(7)	5.6(7)	3.0(7)
C2	28.9(10)	30.2(10)	27.8(10)	13.2(8)	5.1(8)	9.4(8)
C3	34.8(11)	22.9(9)	37.7(11)	10.4(8)	9.3(9)	8.8(8)
C4	31.7(11)	27.2(10)	26.4(10)	3.2(8)	6.8(8)	3.6(8)
C5	34.2(11)	34.1(10)	22.7(9)	9.6(8)	2.2(8)	5.1(9)
C6	33.4(11)	24.6(9)	26.9(10)	11.7(8)	6.1(8)	5.6(8)
C7	29.8(10)	25.0(9)	25.2(9)	10.5(8)	8.2(8)	5.3(8)
C8	31.3(10)	25.3(9)	24.6(9)	11.0(8)	6.6(8)	4.9(8)
C9	24.9(9)	24.6(9)	20.7(9)	5.2(7)	6.7(7)	2.8(7)
C10	21.2(9)	25.2(9)	24.0(9)	8.3(7)	1.9(7)	2.8(7)
C11	27.8(10)	32.0(10)	23.6(9)	8.7(8)	5.8(8)	8.9(8)
C12	29.9(11)	31.1(10)	31.0(10)	5.2(8)	6.7(8)	12.2(8)
C13	30.4(11)	24.5(9)	43.2(12)	12.7(9)	6.7(9)	8.0(8)
C14	29.2(10)	29.7(10)	33.2(10)	15.1(8)	9.6(8)	6.6(8)

C15	20.9(9)	25.8(9)	24.5(9)	9.4(7)	3.2(7)	5.0(7)
C16	24.5(9)	25.1(9)	26.0(9)	11.4(7)	3.3(7)	6.5(7)
C17	26.3(10)	24.2(9)	31.0(10)	11.9(8)	8.2(8)	5.3(7)
C18	23.2(10)	29.6(10)	26.0(9)	11.9(8)	6.1(7)	7.4(8)
C19	42.7(12)	40.1(11)	27.7(10)	11.2(9)	14.7(9)	16.9(10)
C20	45.1(13)	28.0(10)	29.9(11)	4.4(8)	5.5(9)	-2.6(9)

Table S26. Bond Lengths for alkynyl imine.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C9	1.762(2)	C5	C6	1.392(3)
S1	C20	1.797(2)	C7	C8	1.199(3)
O1	C18	1.214(2)	C8	C9	1.440(3)
O2	C18	1.342(2)	C10	C11	1.393(2)
O2	C19	1.437(2)	C10	C15	1.412(3)
N1	C9	1.286(2)	C11	C12	1.381(3)
N1	C10	1.421(2)	C12	C13	1.391(3)
C1	C2	1.398(3)	C13	C14	1.383(3)
C1	C6	1.397(3)	C14	C15	1.406(3)
C1	C7	1.441(2)	C15	C16	1.460(2)
C2	C3	1.382(3)	C16	C17	1.328(3)
C3	C4	1.385(3)	C17	C18	1.468(3)
C4	C5	1.389(3)			

Table S27. Bond Angles for alkynyl imine.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	S1	C20	100.90(10)	C11	C10	N1	121.54(17)
C18	O2	C19	116.93(15)	C11	C10	C15	119.40(17)
C9	N1	C10	120.06(15)	C15	C10	N1	118.86(15)
C2	C1	C7	118.69(17)	C12	C11	C10	121.21(18)
C6	C1	C2	119.66(17)	C11	C12	C13	120.15(17)
C6	C1	C7	121.65(17)	C14	C13	C12	119.28(18)
C3	C2	C1	120.68(18)	C13	C14	C15	121.69(18)
C2	C3	C4	119.50(18)	C10	C15	C16	119.66(17)
C3	C4	C5	120.48(18)	C14	C15	C10	118.25(16)
C4	C5	C6	120.33(18)	C14	C15	C16	122.10(17)
C5	C6	C1	119.34(18)	C17	C16	C15	127.11(18)
C8	C7	C1	173.6(2)	C16	C17	C18	121.41(17)
C7	C8	C9	176.0(2)	O1	C18	O2	123.18(16)
N1	C9	S1	121.42(14)	O1	C18	C17	126.06(17)
N1	C9	C8	125.42(17)	O2	C18	C17	110.76(16)
C8	C9	S1	113.15(14)				

Table S28. Torsion Angles for alkynyl imine.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C10	C11	C12	-176.38(17)	C10	C15	C16	C17	-178.61(18)
N1	C10	C15	C14	176.35(16)	C11	C10	C15	C14	1.3(3)
N1	C10	C15	C16	-3.3(3)	C11	C10	C15	C16	-178.33(16)
C1	C2	C3	C4	0.1(3)	C11	C12	C13	C14	0.0(3)
C2	C1	C6	C5	0.2(3)	C12	C13	C14	C15	-0.2(3)
C2	C3	C4	C5	-0.6(3)	C13	C14	C15	C10	-0.5(3)
C3	C4	C5	C6	0.8(3)	C13	C14	C15	C16	179.12(18)
C4	C5	C6	C1	-0.7(3)	C14	C15	C16	C17	1.8(3)
C6	C1	C2	C3	0.0(3)	C15	C10	C11	C12	-1.5(3)
C7	C1	C2	C3	179.34(17)	C15	C16	C17	C18	-177.52(17)
C7	C1	C6	C5	-179.06(17)	C16	C17	C18	O1	-7.5(3)
C9	N1	C10	C11	-54.7(2)	C16	C17	C18	O2	171.62(17)
C9	N1	C10	C15	130.34(19)	C19	O2	C18	O1	1.9(3)
C10	N1	C9	S1	175.90(13)	C19	O2	C18	C17	-177.18(15)
C10	N1	C9	C8	-5.3(3)	C20	S1	C9	N1	-0.94(18)
C10	C11	C12	C13	0.8(3)	C20	S1	C9	C8	-179.85(14)

Table S29. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for alkynyl imine.

Atom	*x*	*y*	*z*	U(eq)
H2	3412.74	8317.06	10815.07	34
H3	4886.43	10349.01	12566.32	38
H4	6403.15	10220.79	14344.05	38
H5	6406.56	8072.2	14392.21	38
H6	4947.48	6021.35	12630.97	34
H11	-33.28	6155.63	8885.43	34
H12	374.37	8349.99	8871.85	39
H13	1595.17	8832.03	7261.32	39
H14	2402.58	7100.66	5681.78	36
H16	1957.56	3579.99	5365.93	30
H17	3186.45	5393.48	4263.66	32
H19A	4183.78	2746.23	601.09	54
H19B	3144.25	1662.39	1067.37	54
H19C	5140.97	2291.12	1584.57	54
H20A	103.16	1008.82	6072.34	58
H20B	-1542.05	1403.01	6574.25	58
H20C	-1063.52	66	6615.97	58

11. Copies of the NMR spectra

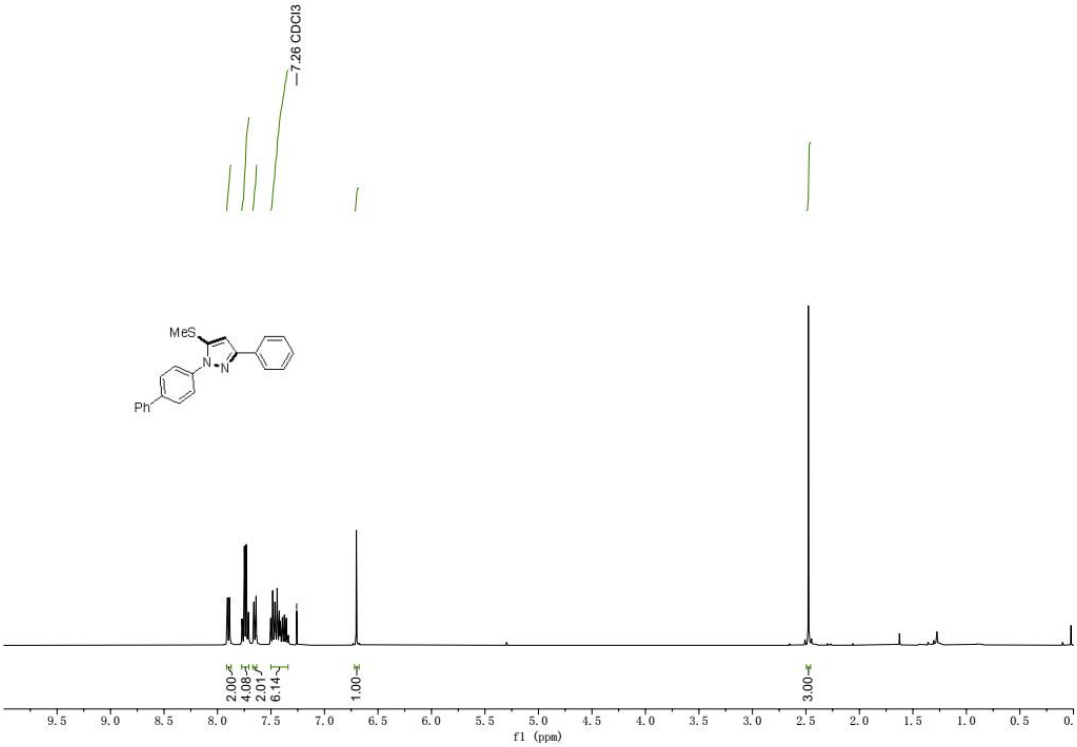


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aa

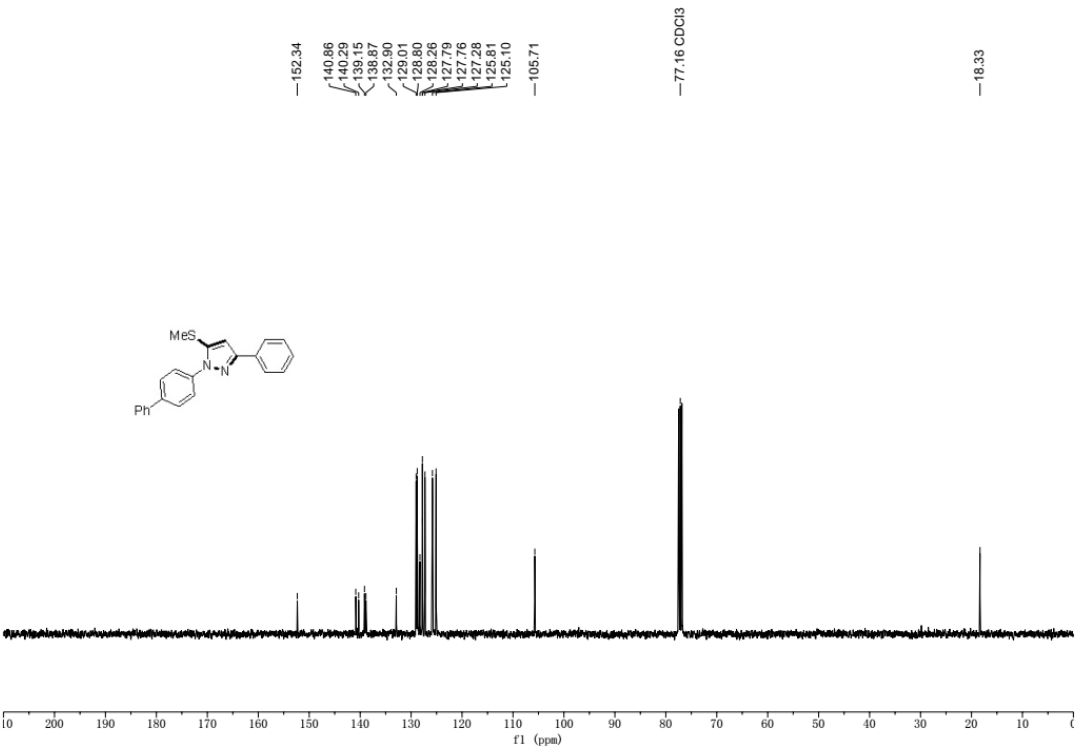


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aa

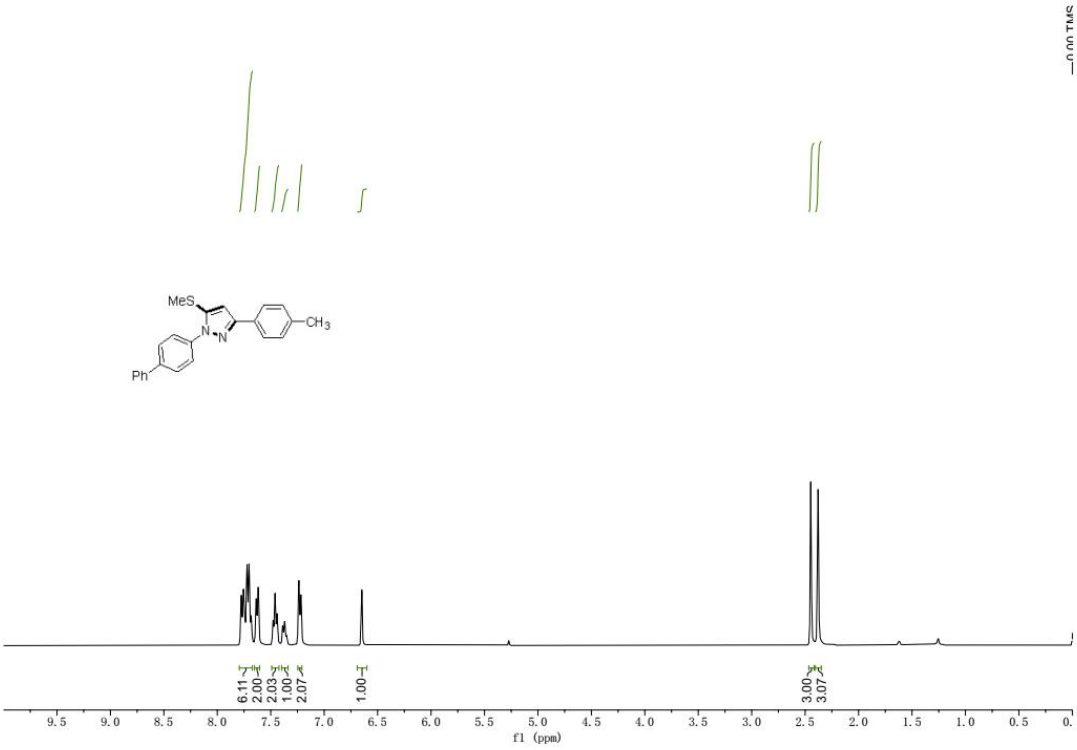


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ba

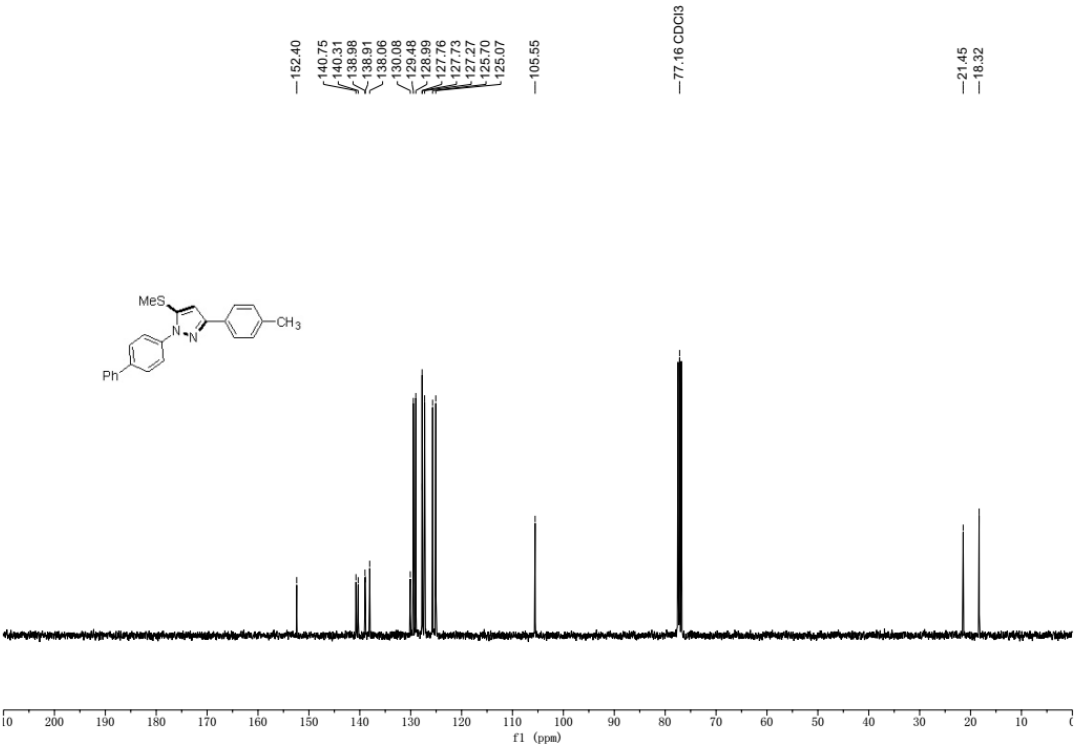


Figure S33. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ba

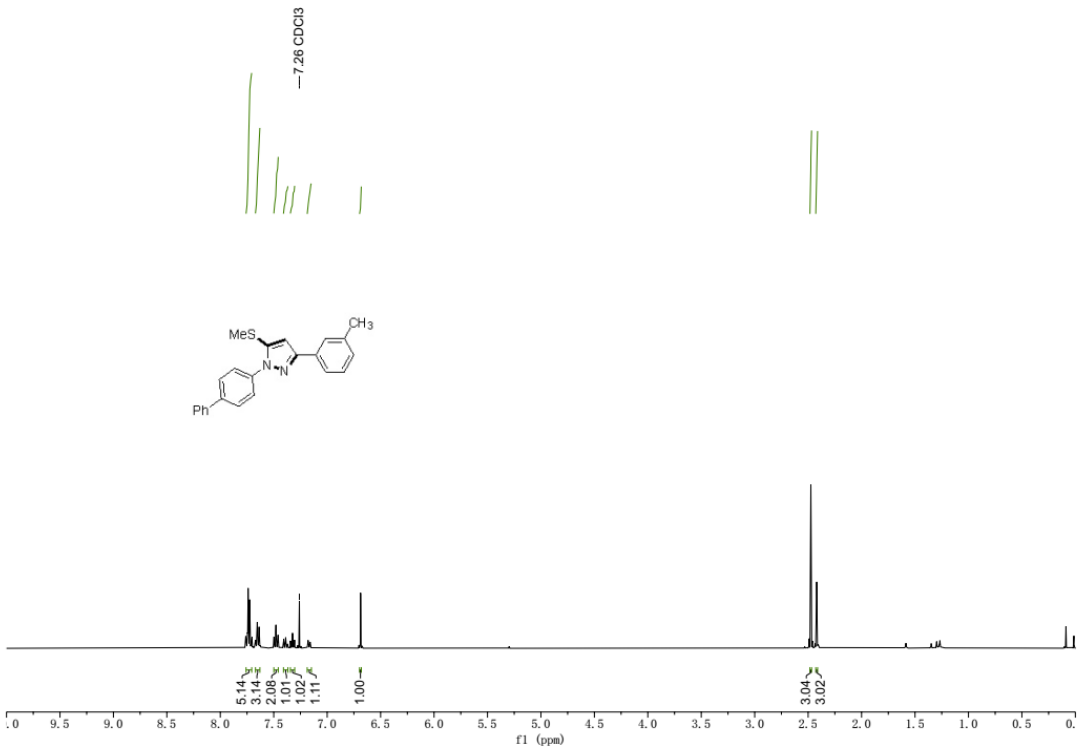


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ca

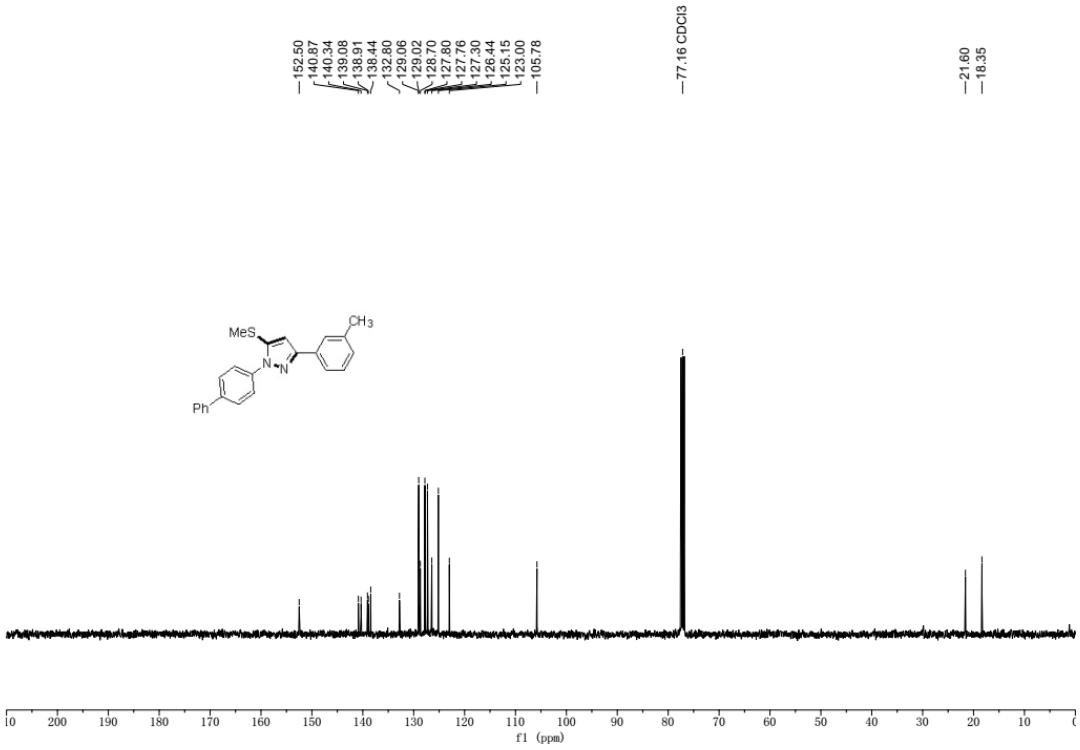


Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ca

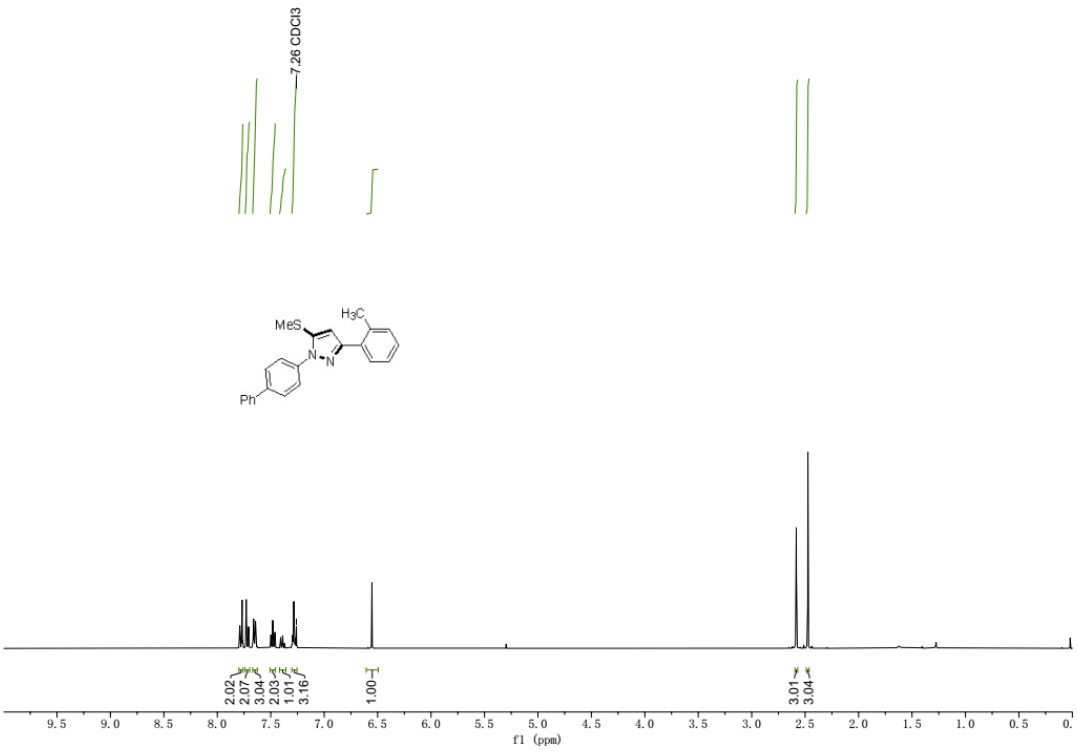


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3da

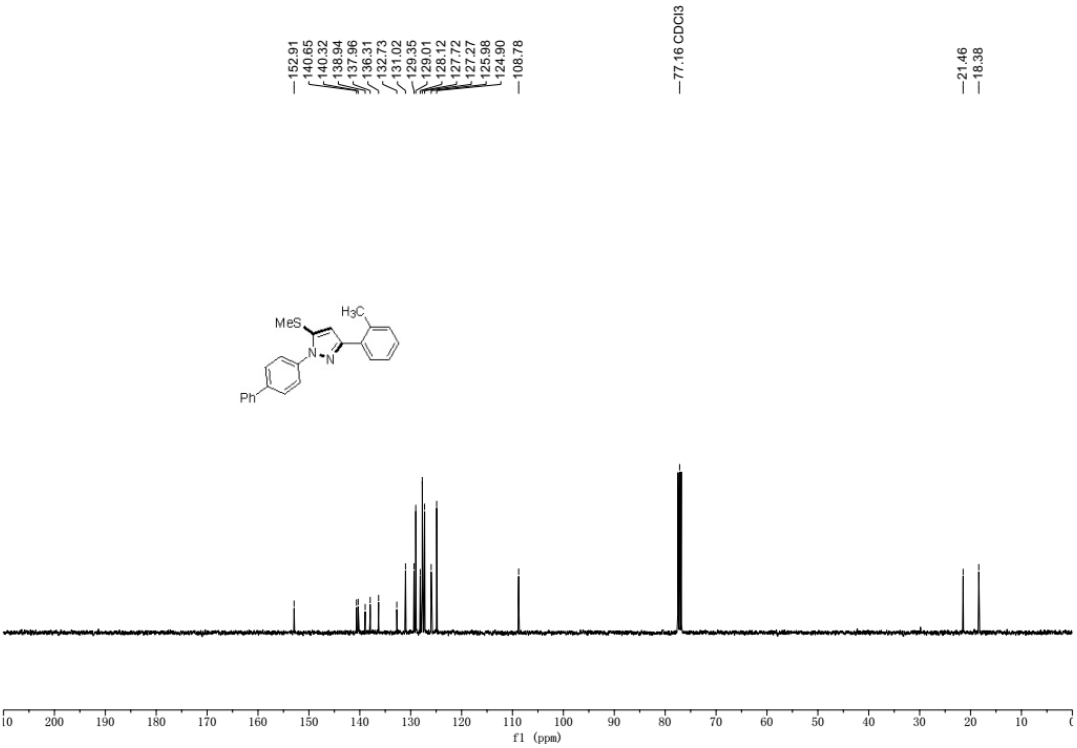


Figure S37. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3da

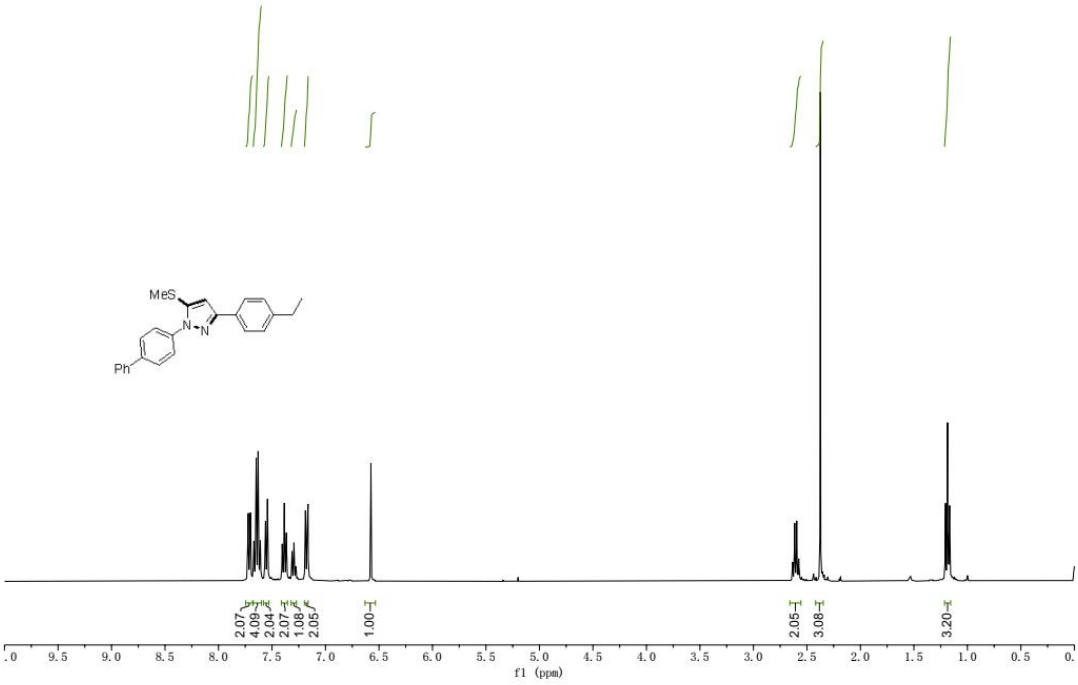


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ea

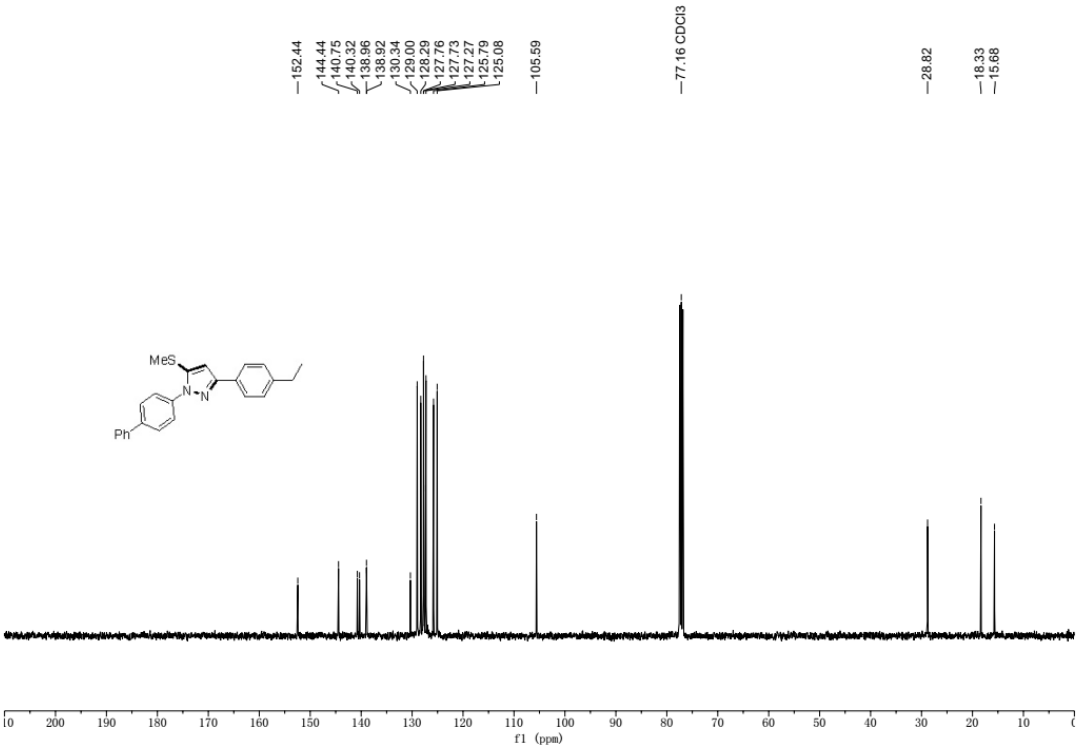


Figure S39. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ea

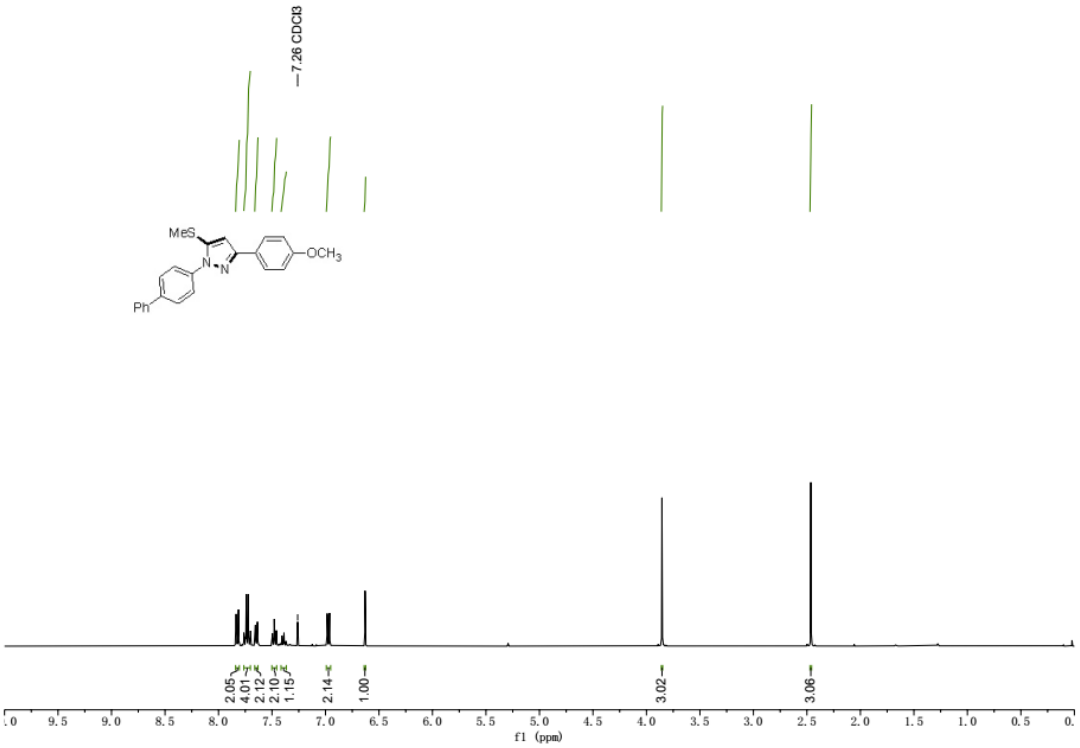


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3fa

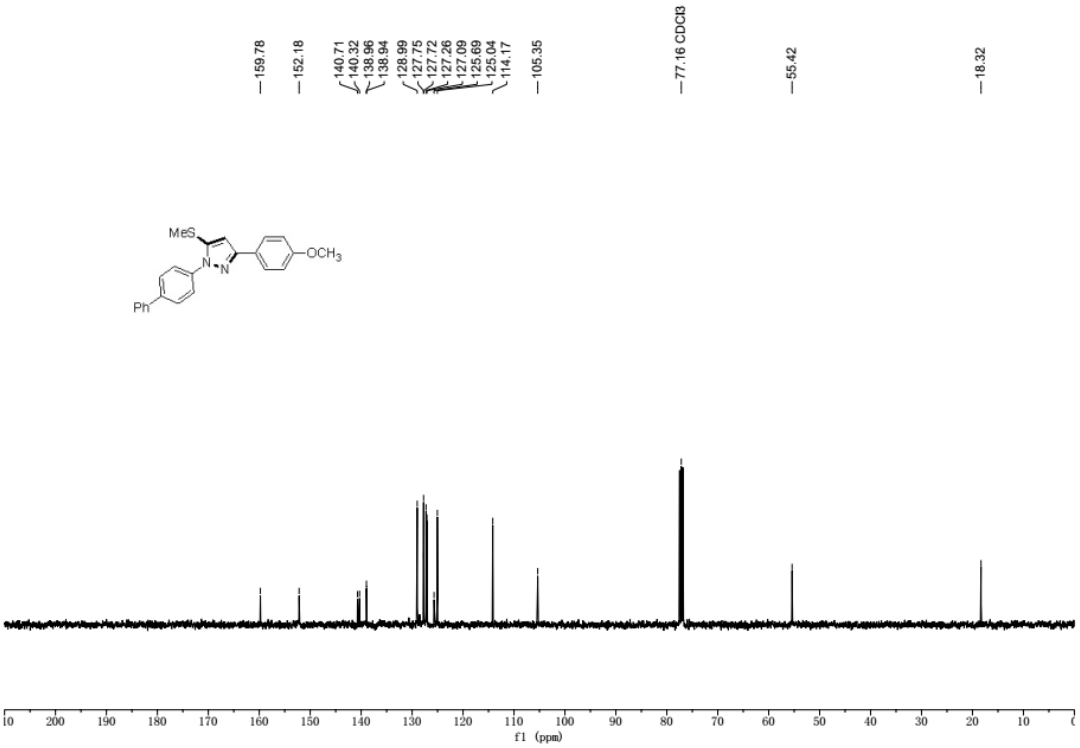


Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3fa

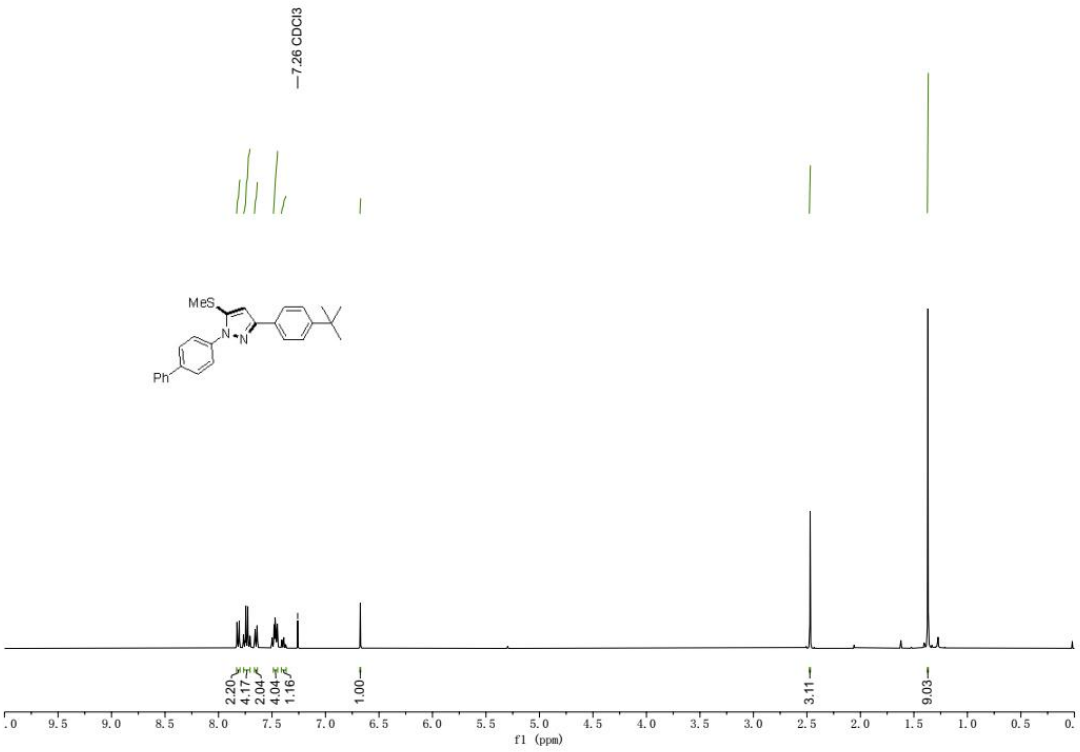


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ga

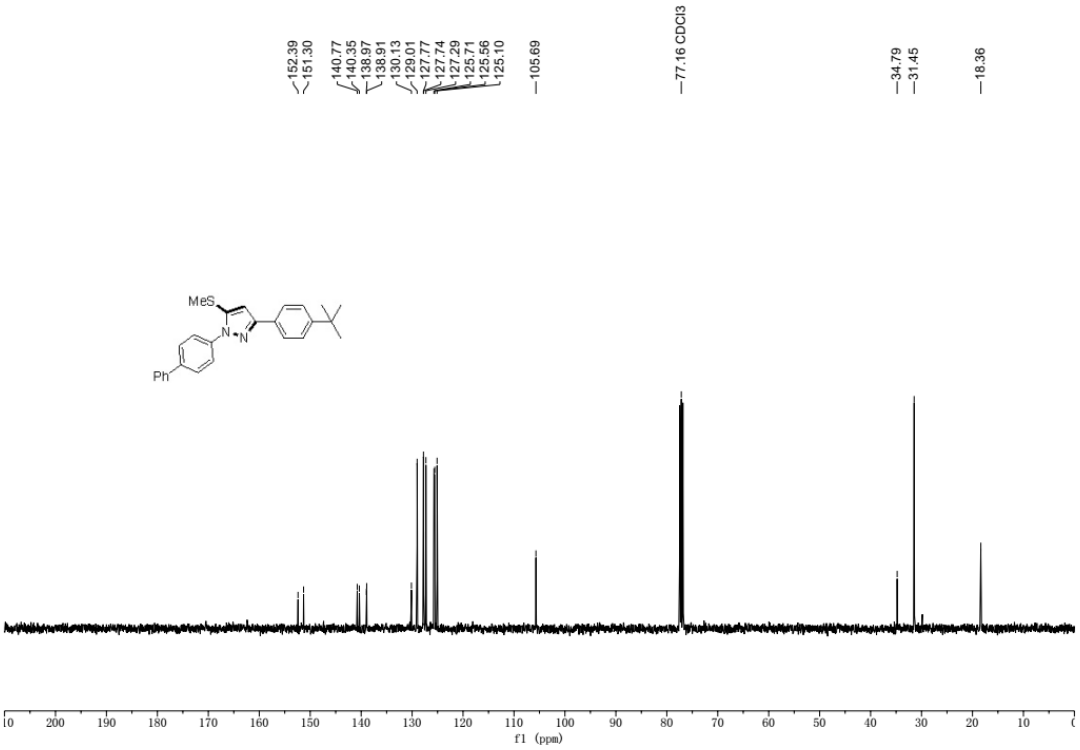


Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ga

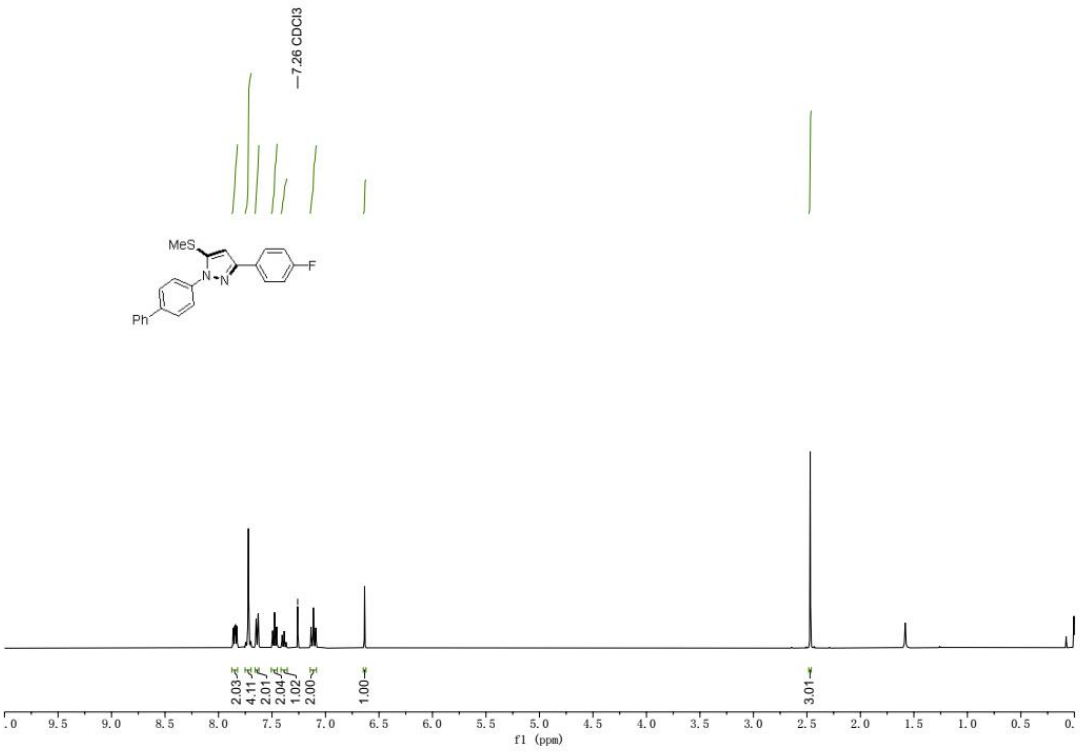


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ha

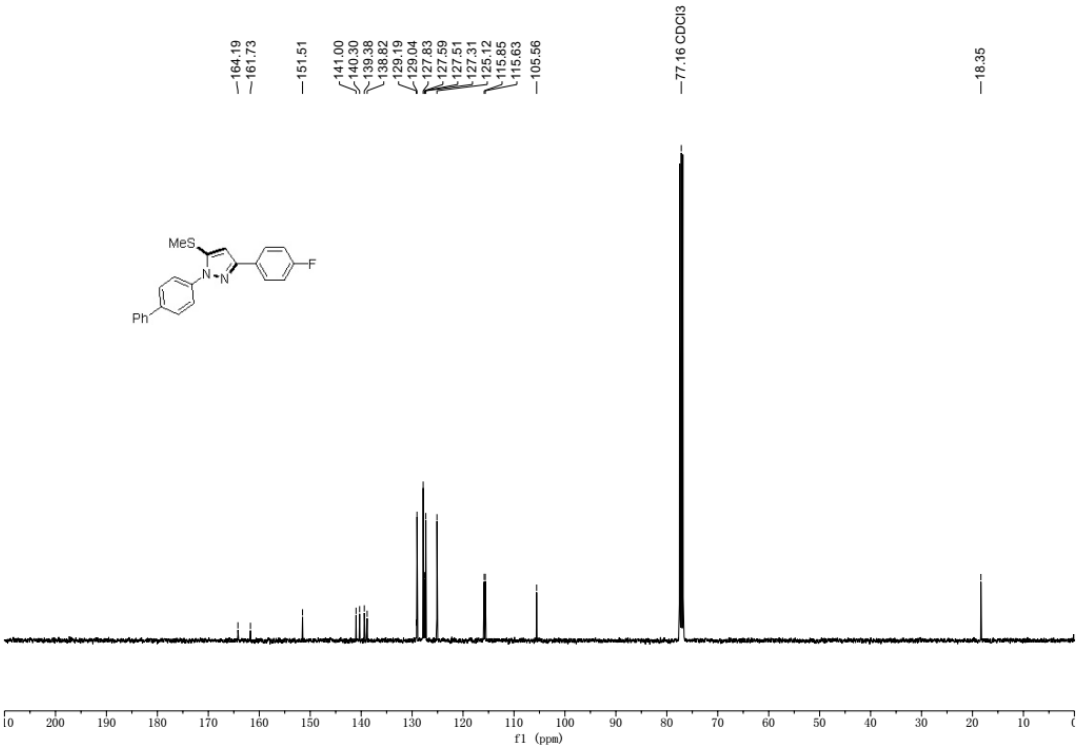


Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ha

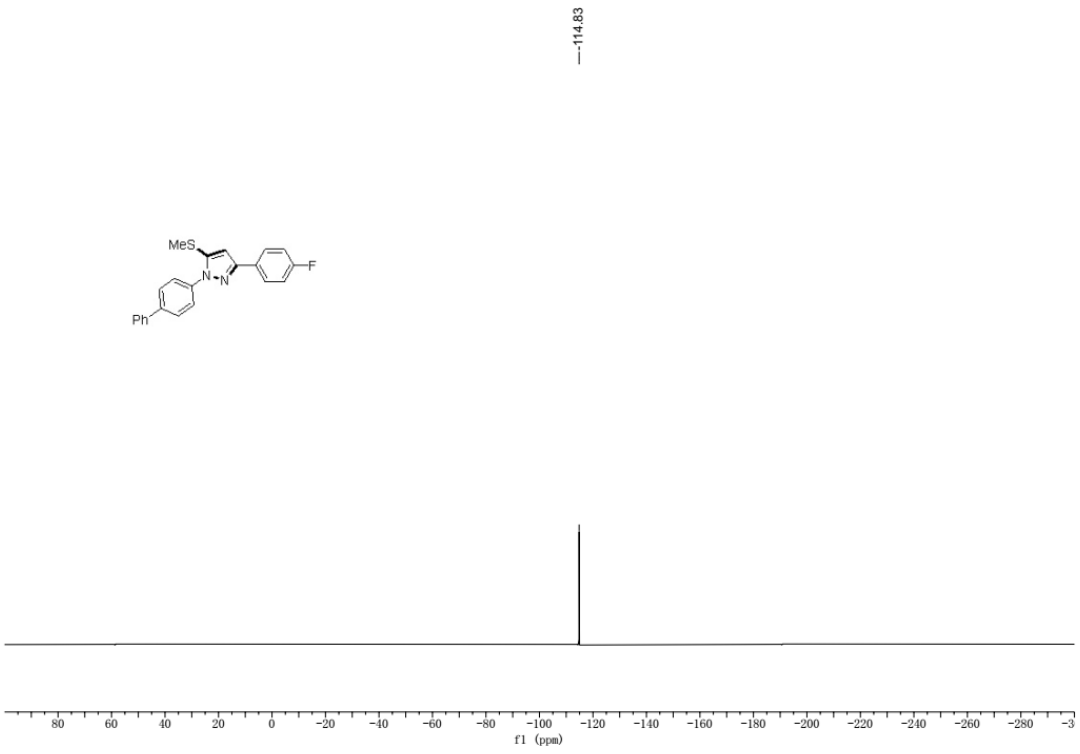


Figure S46. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (3ha)

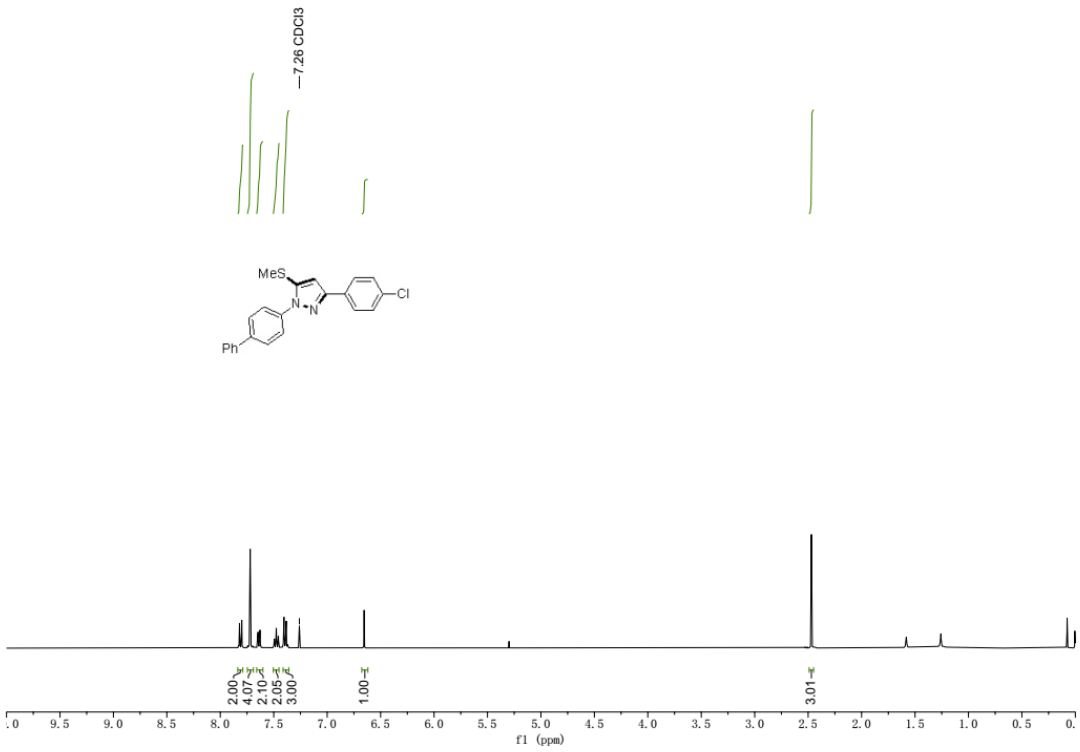


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ia

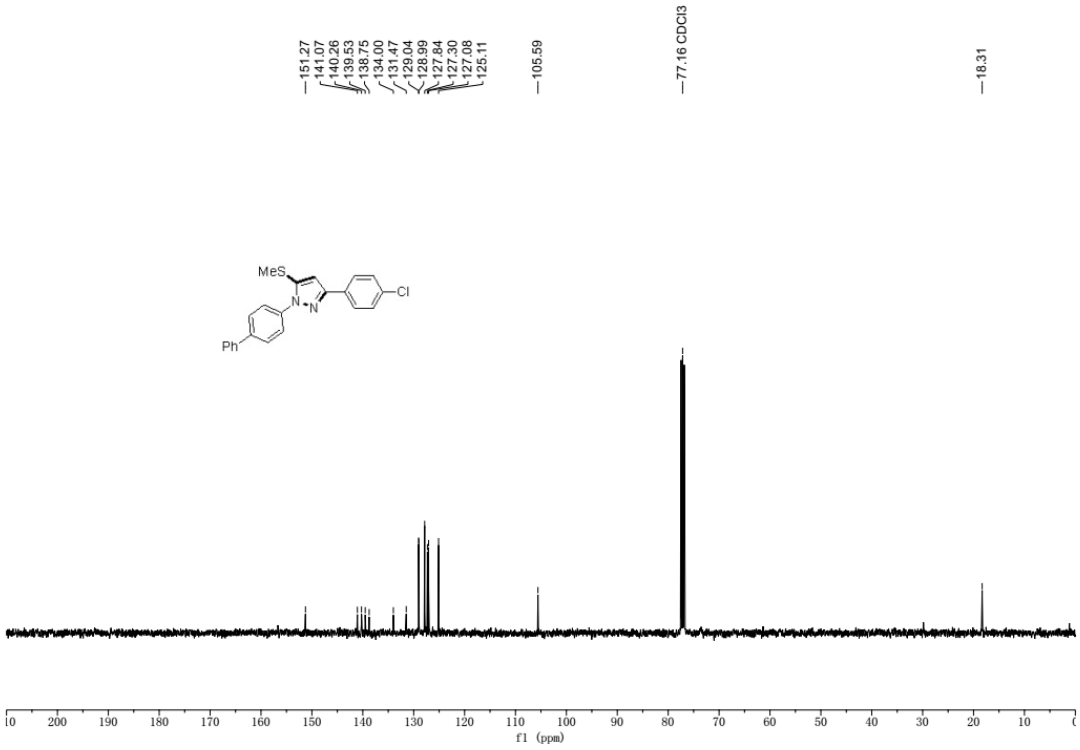


Figure S48. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ia

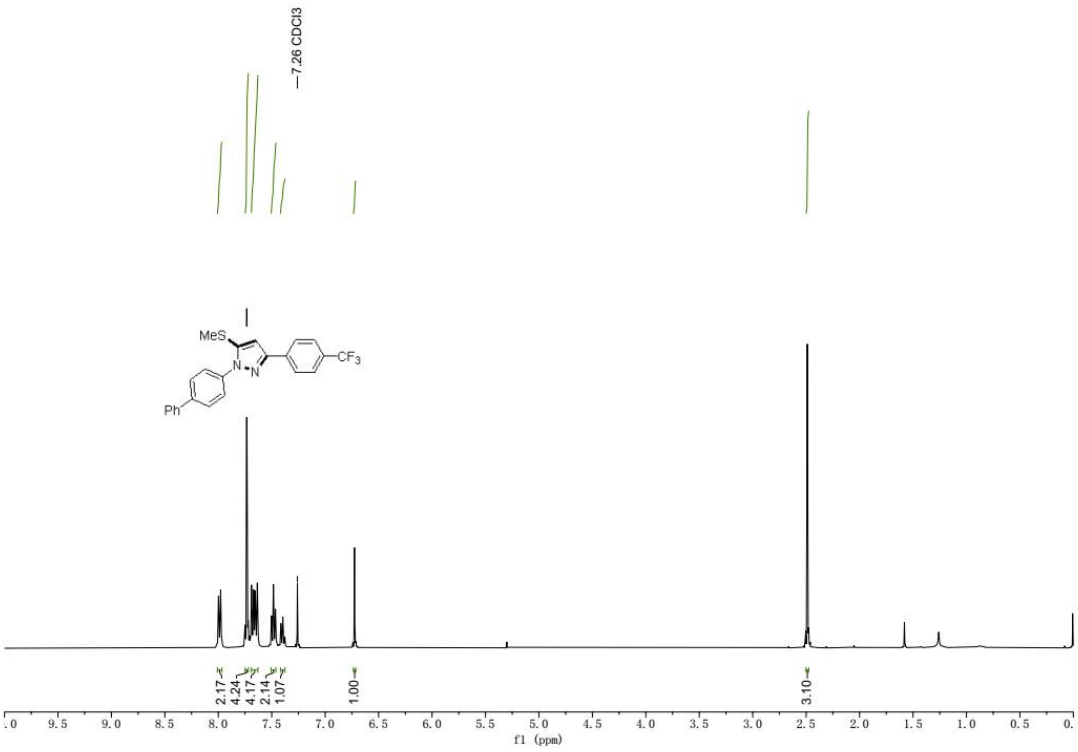


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ja

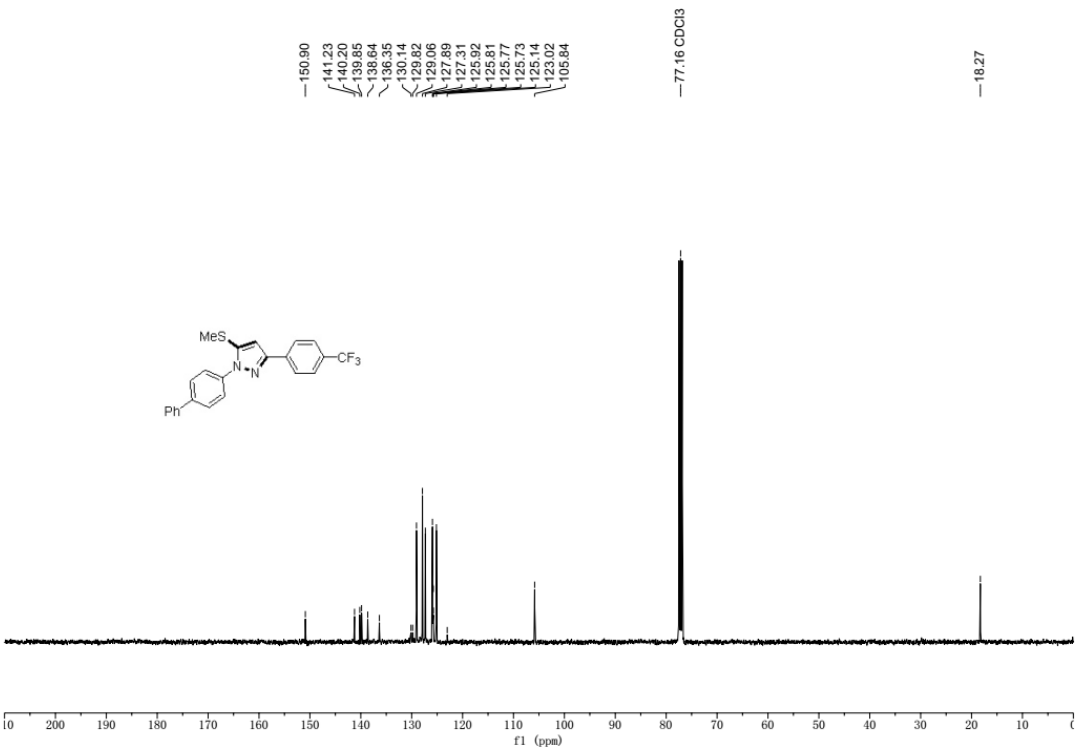


Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ja

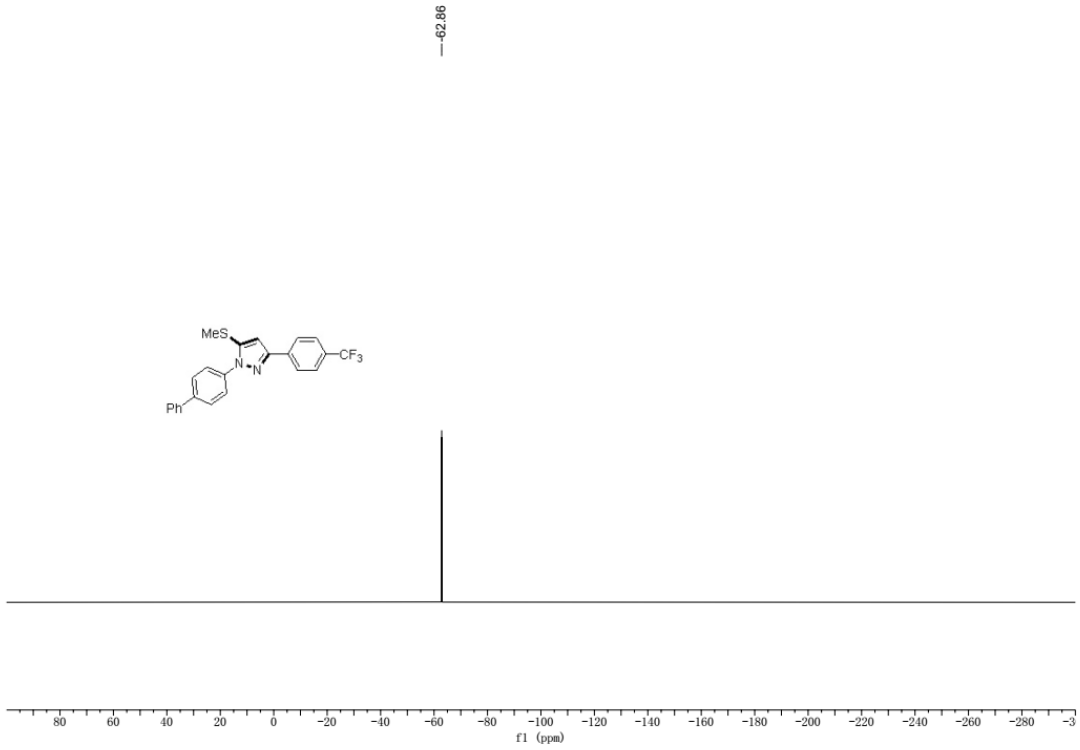


Figure S51. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (3ja)

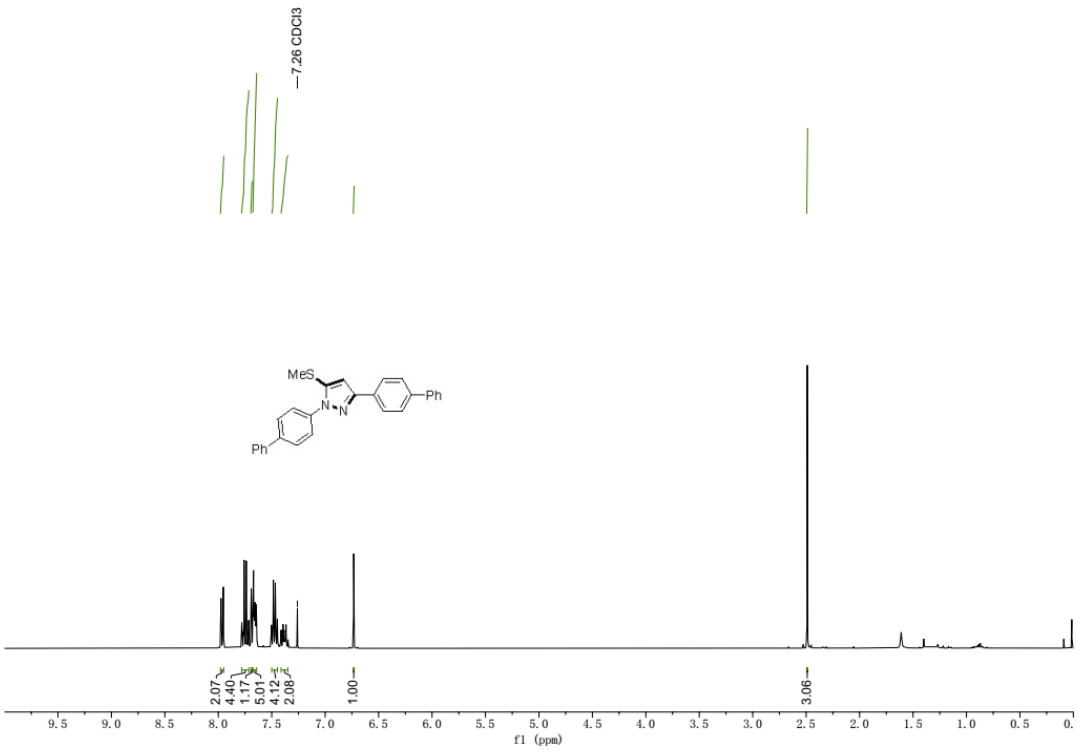


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ka

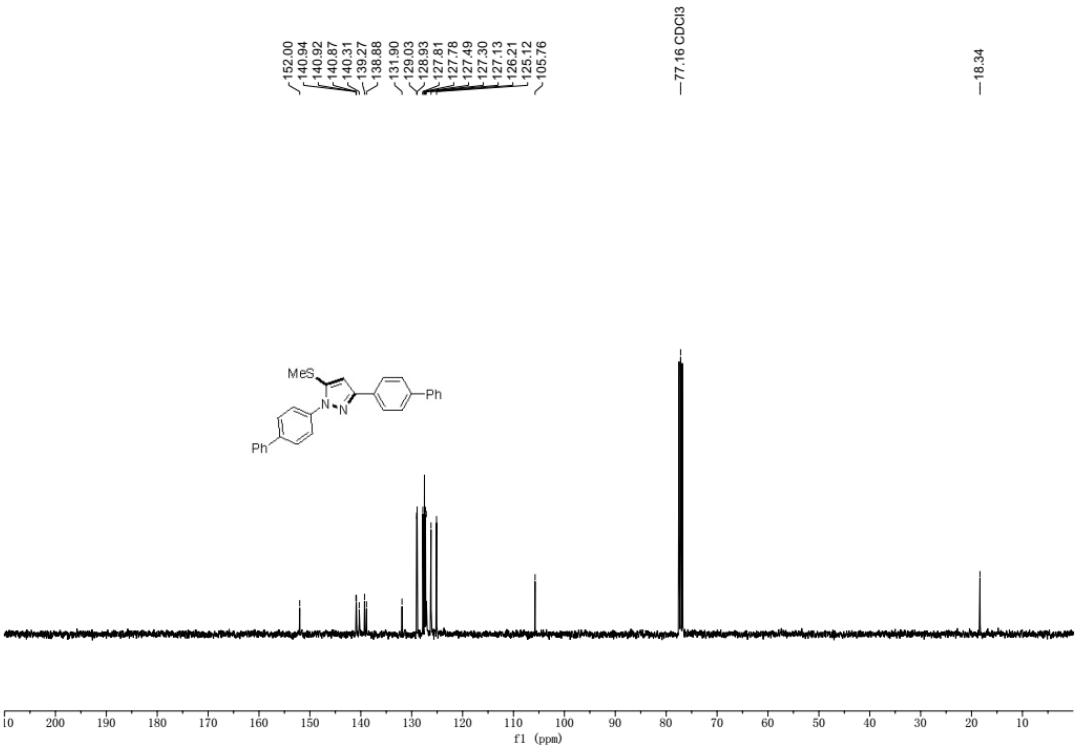


Figure S53. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ka

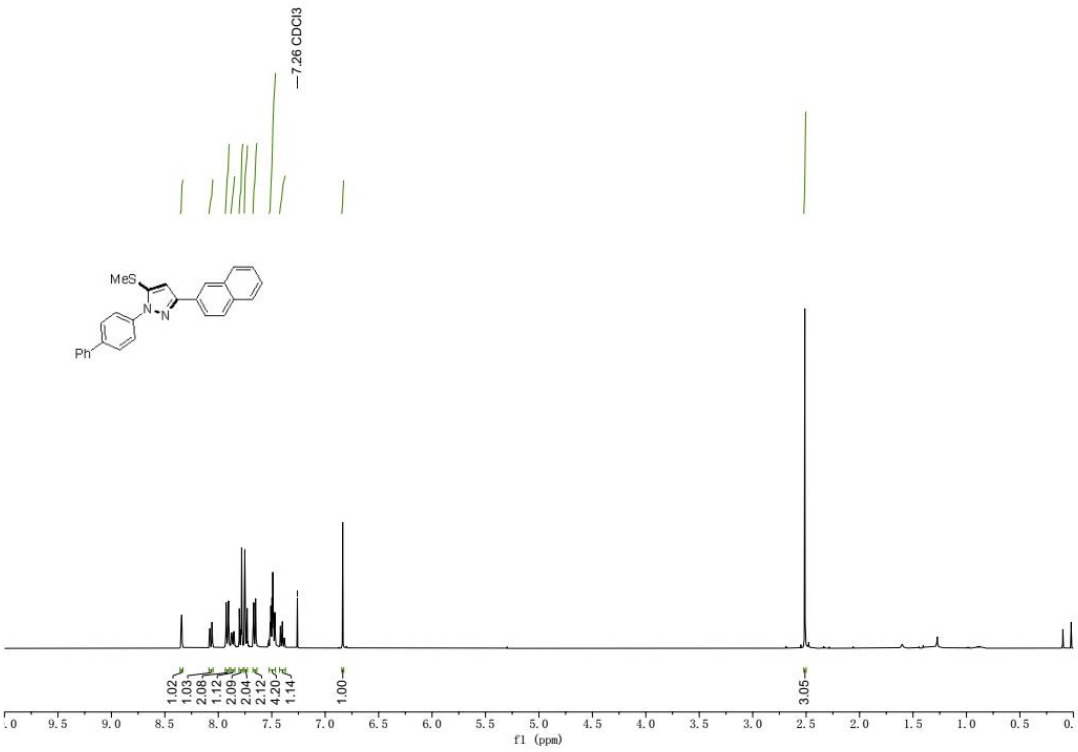


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3la

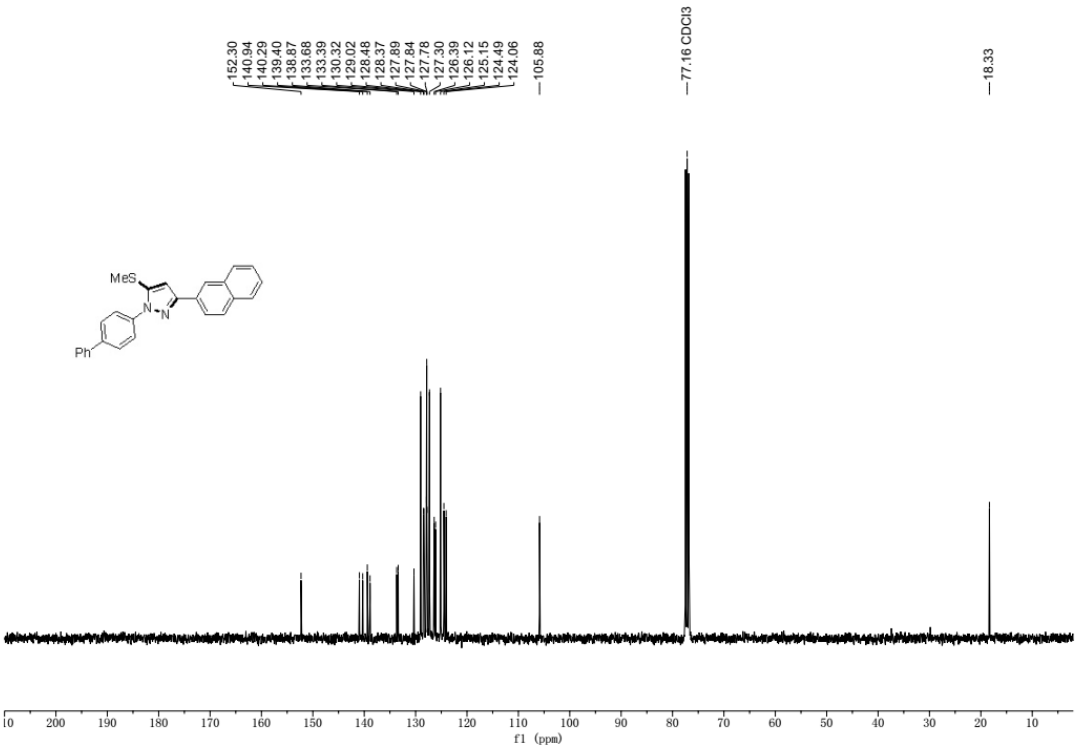


Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3la

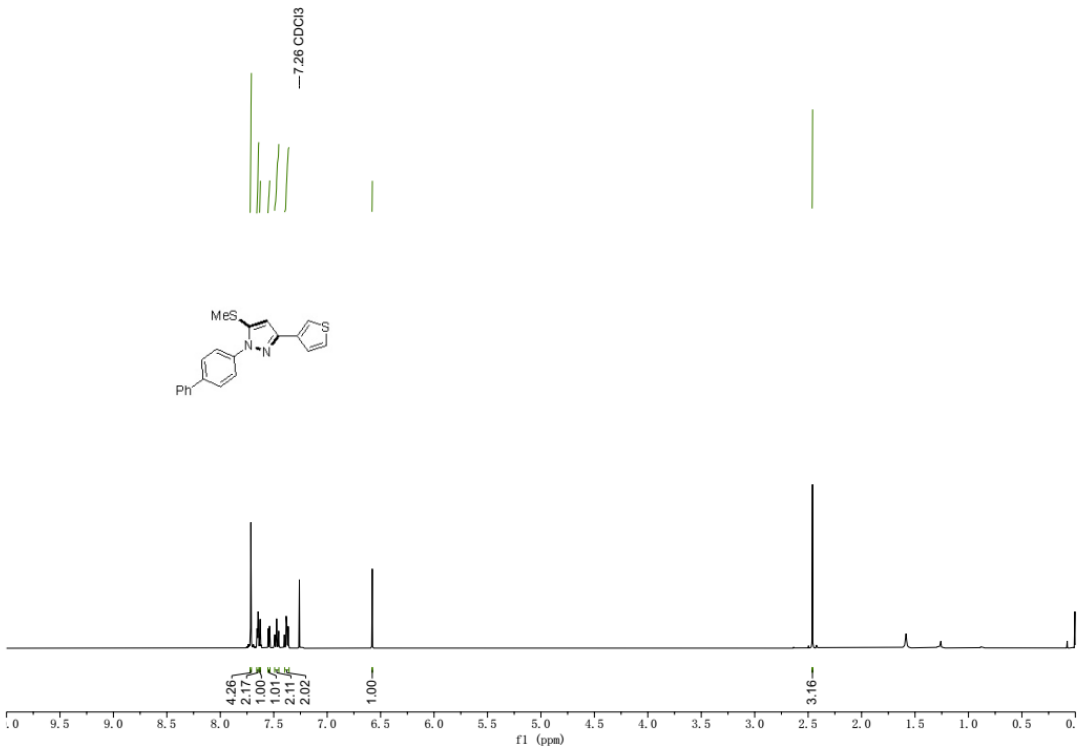


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ma

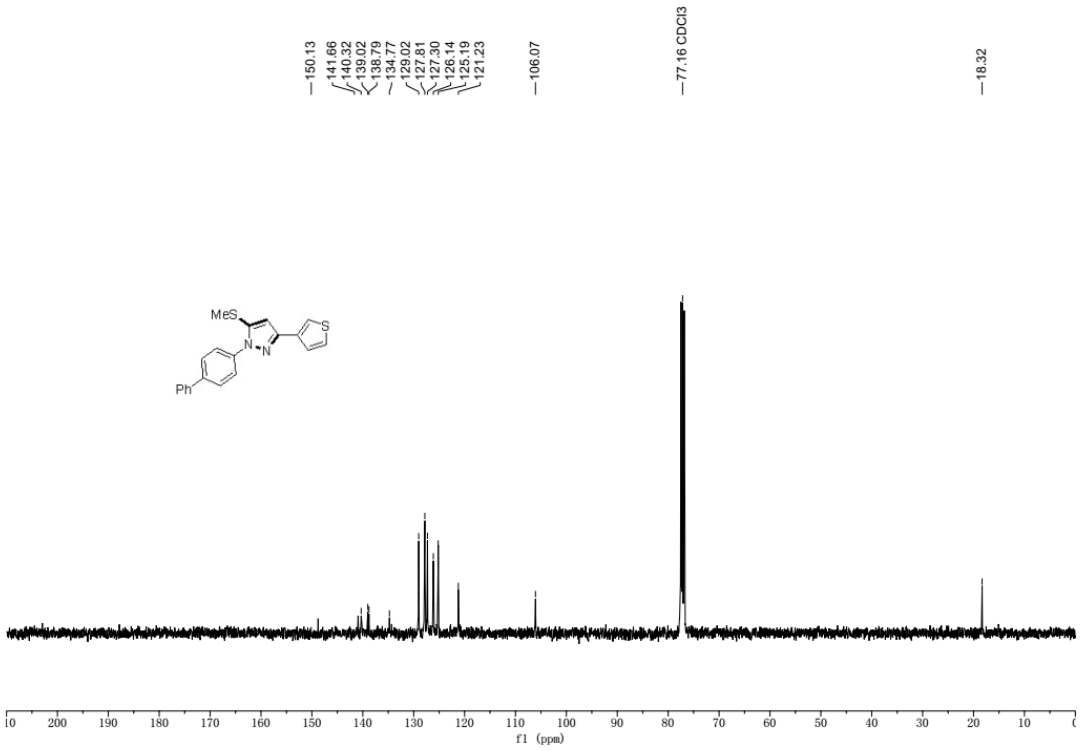


Figure S57. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ma

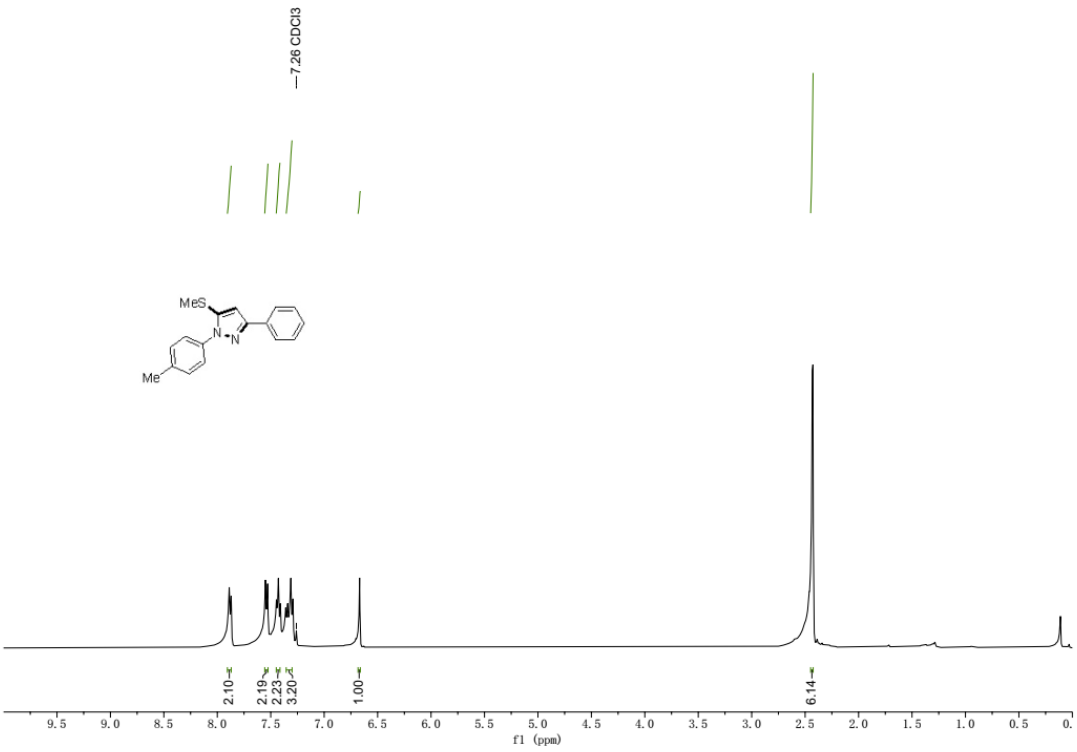


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ab

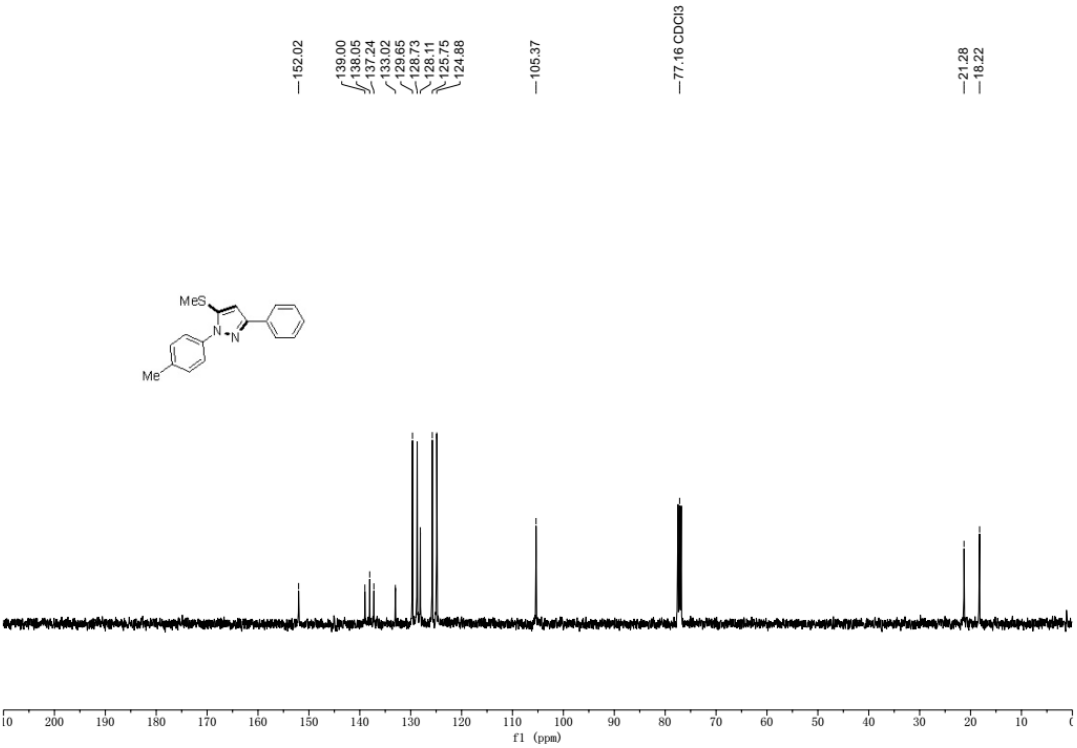


Figure S59. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ab

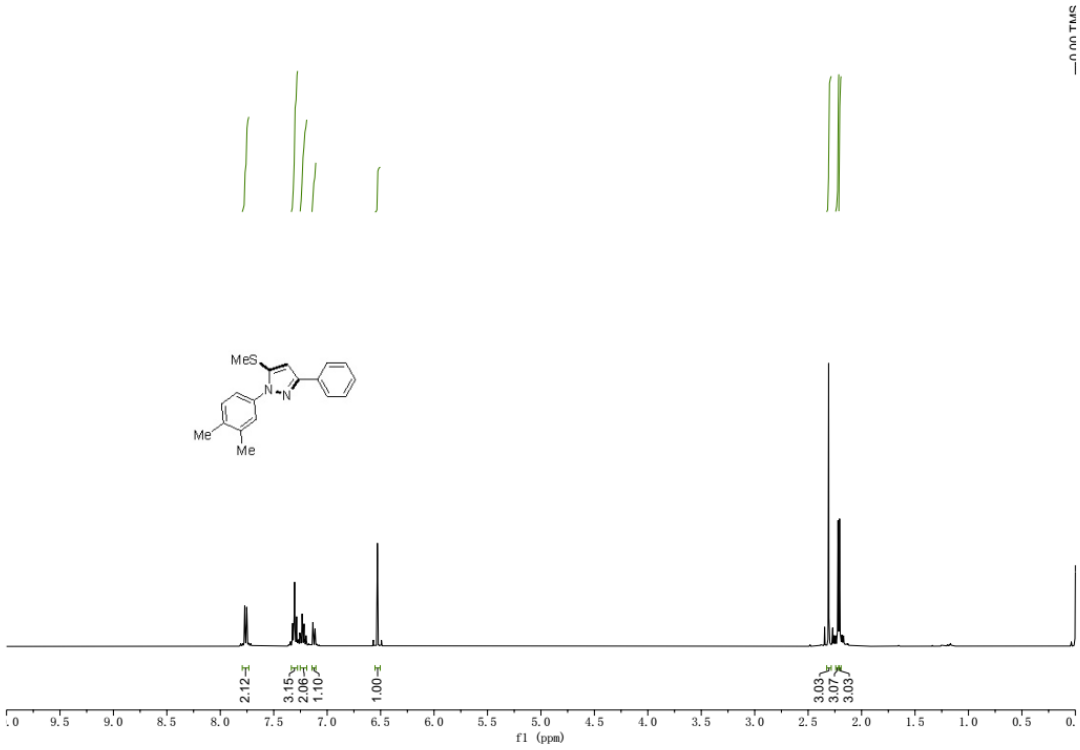


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ac

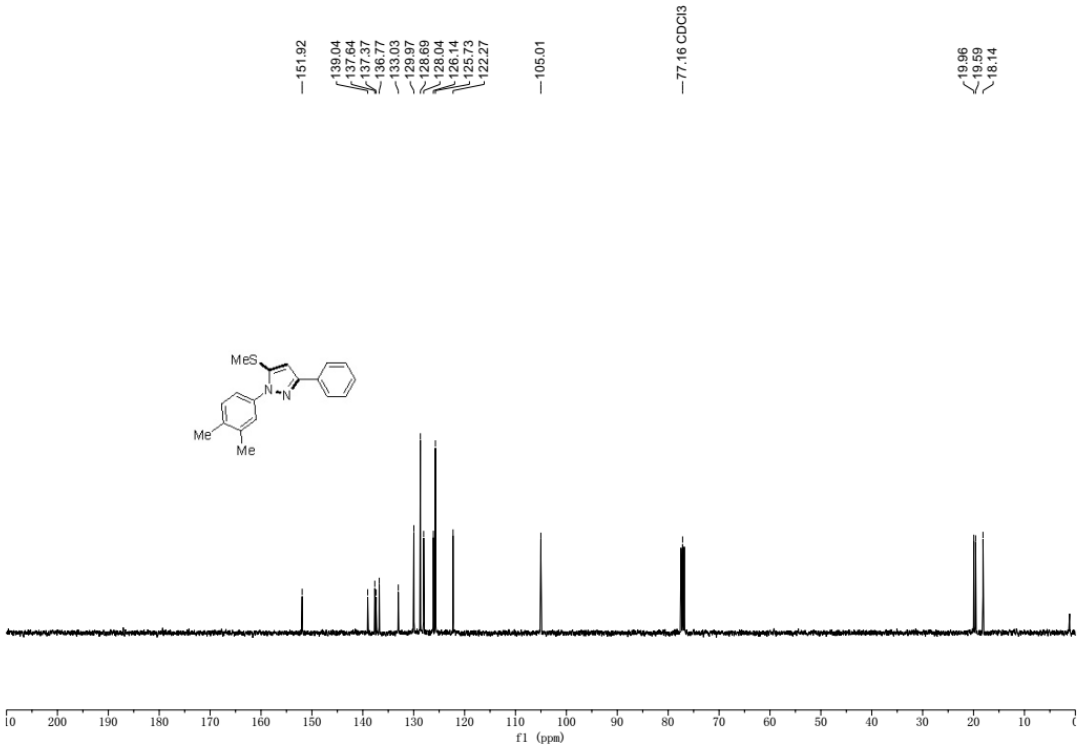


Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ac

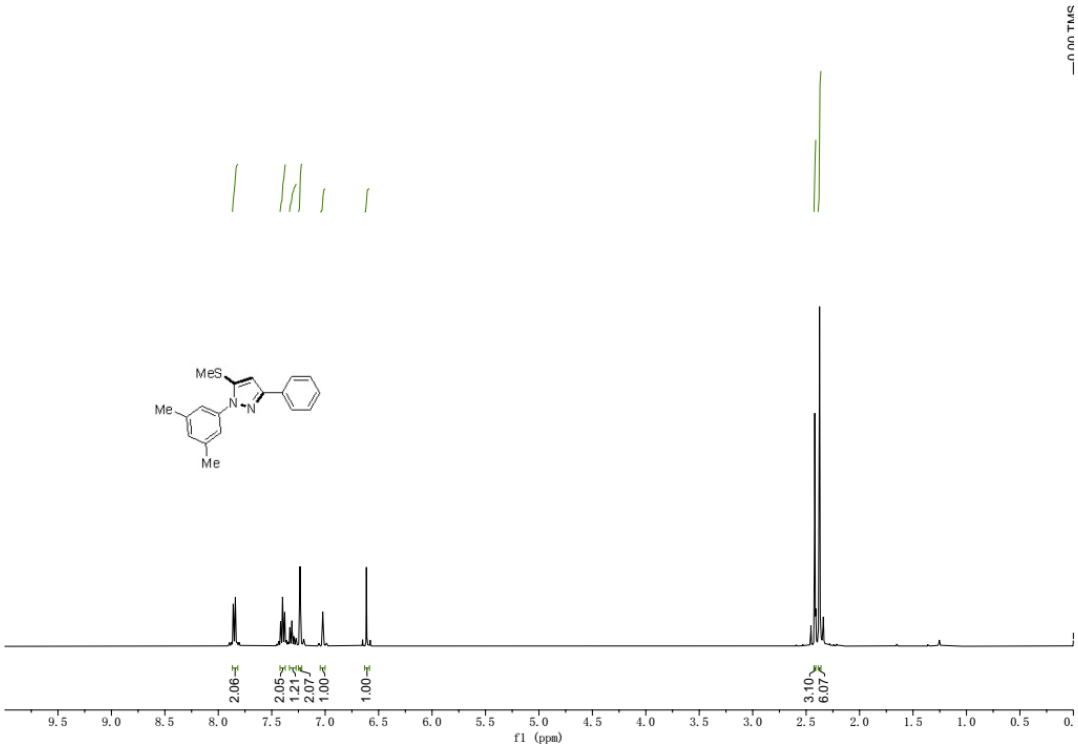


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ad

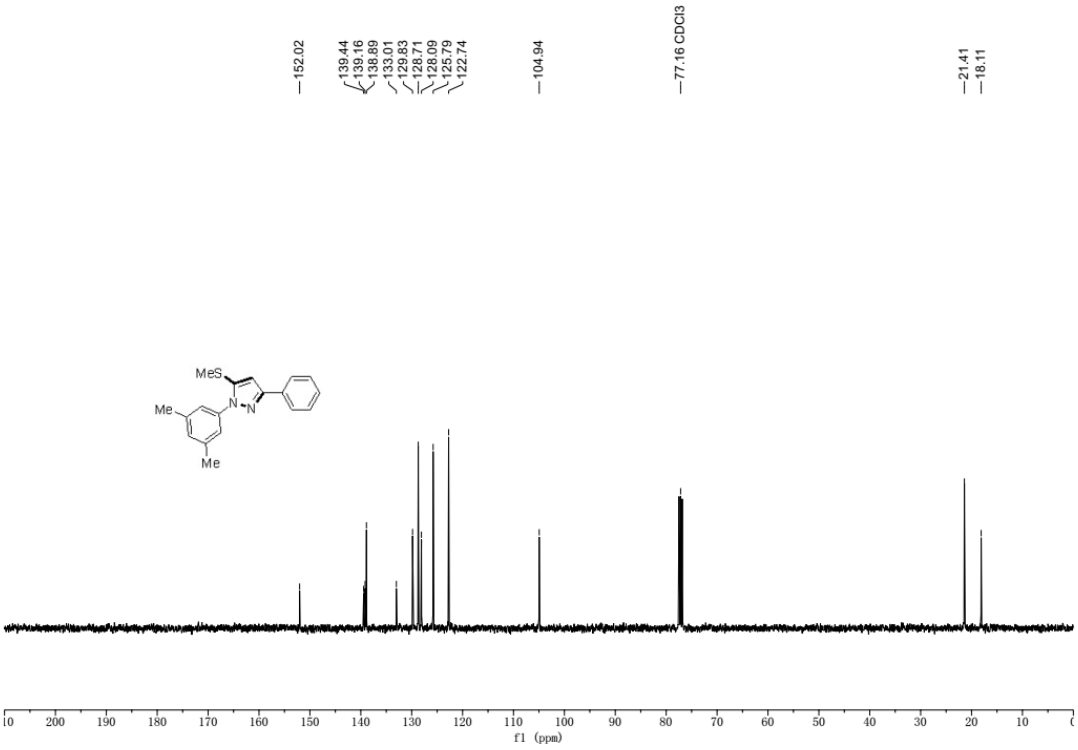


Figure S63. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ad

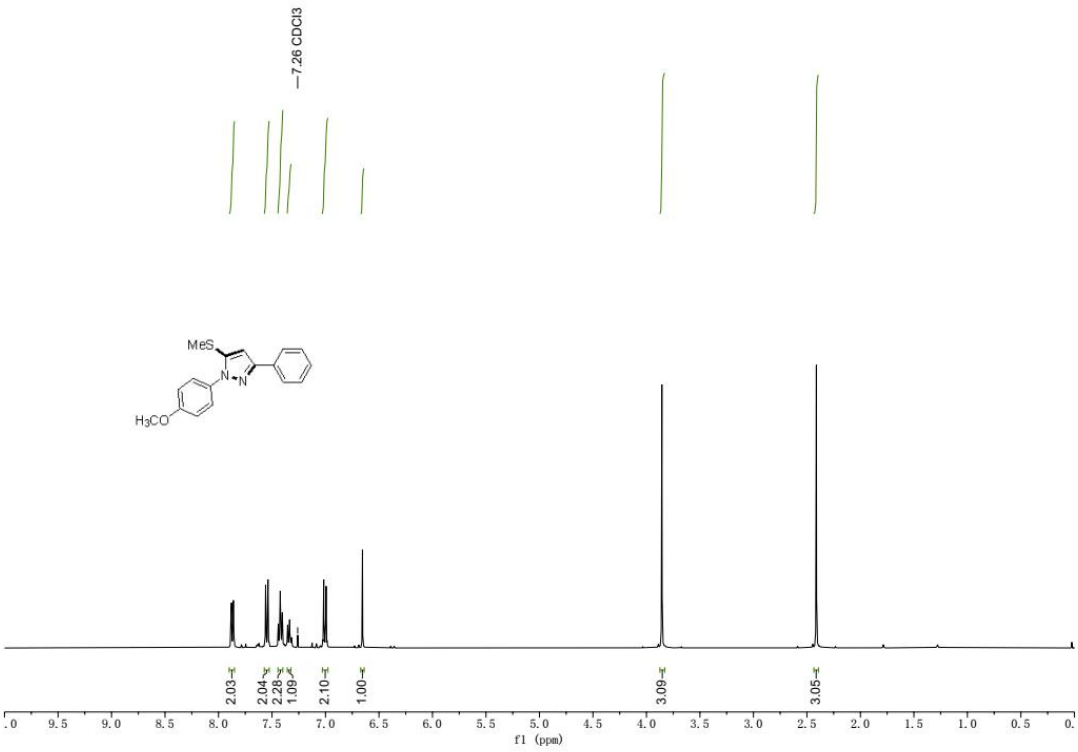


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ae

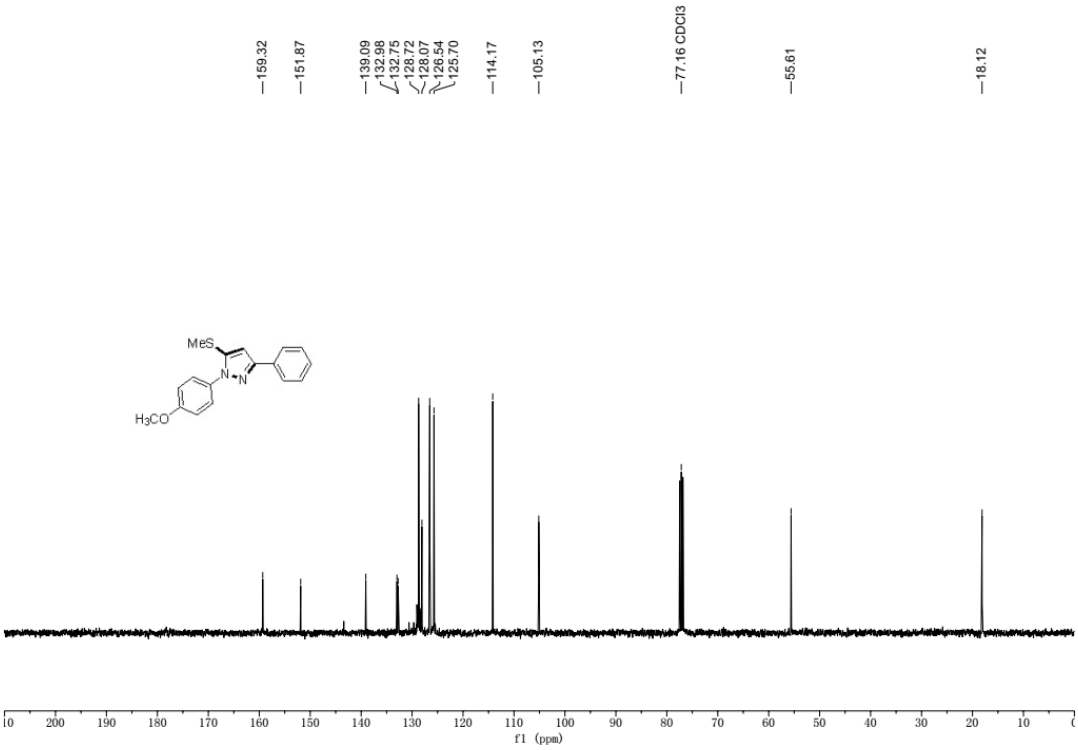


Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ae

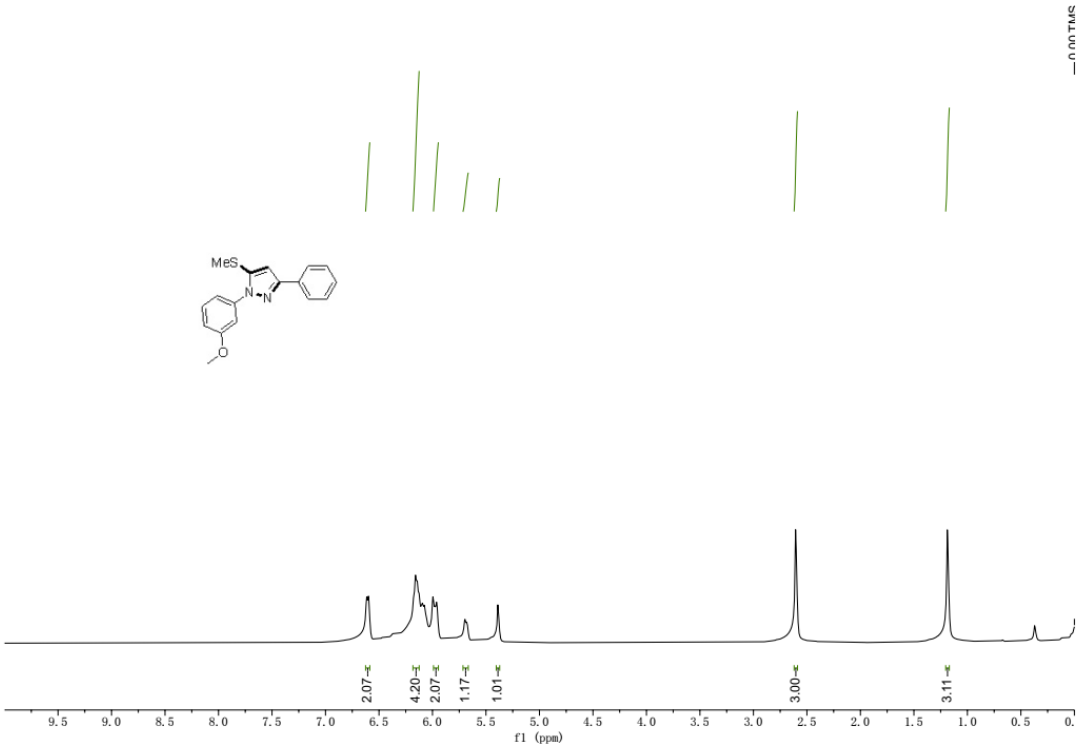


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3af

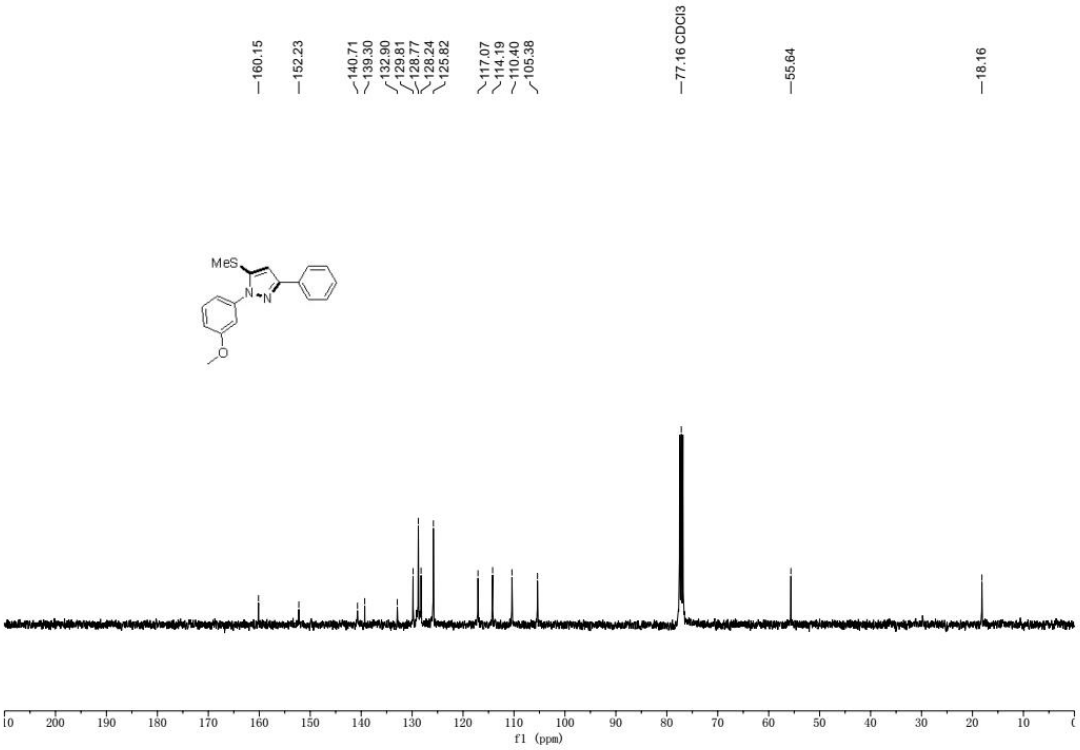


Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3af

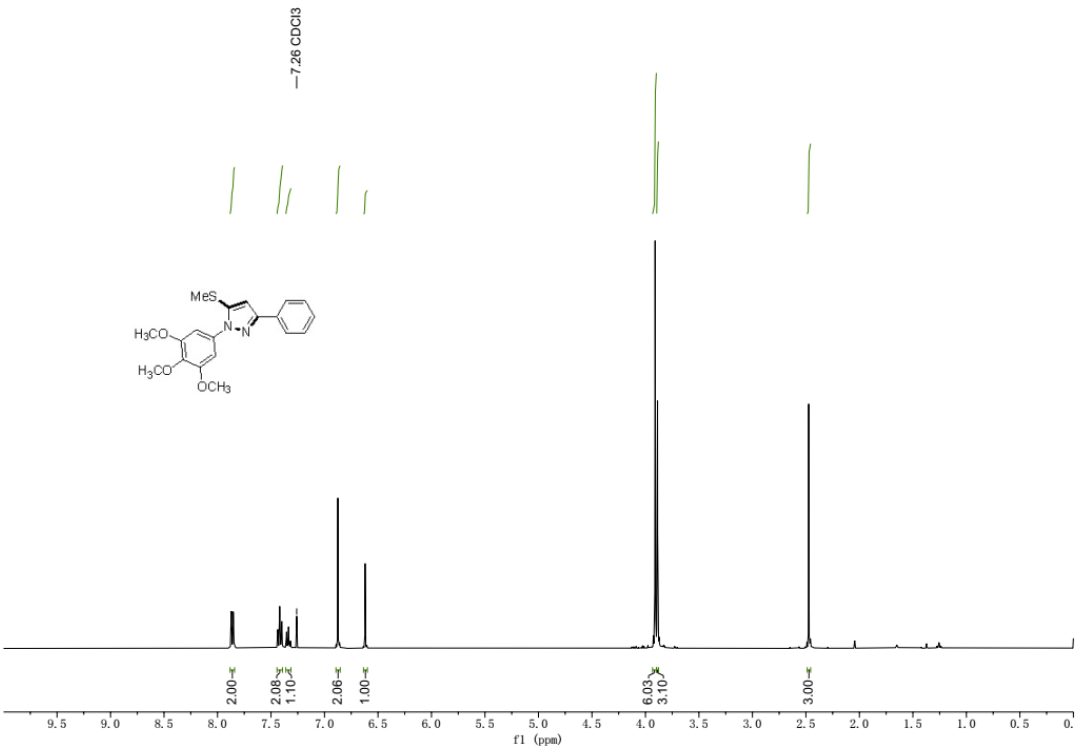


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ag

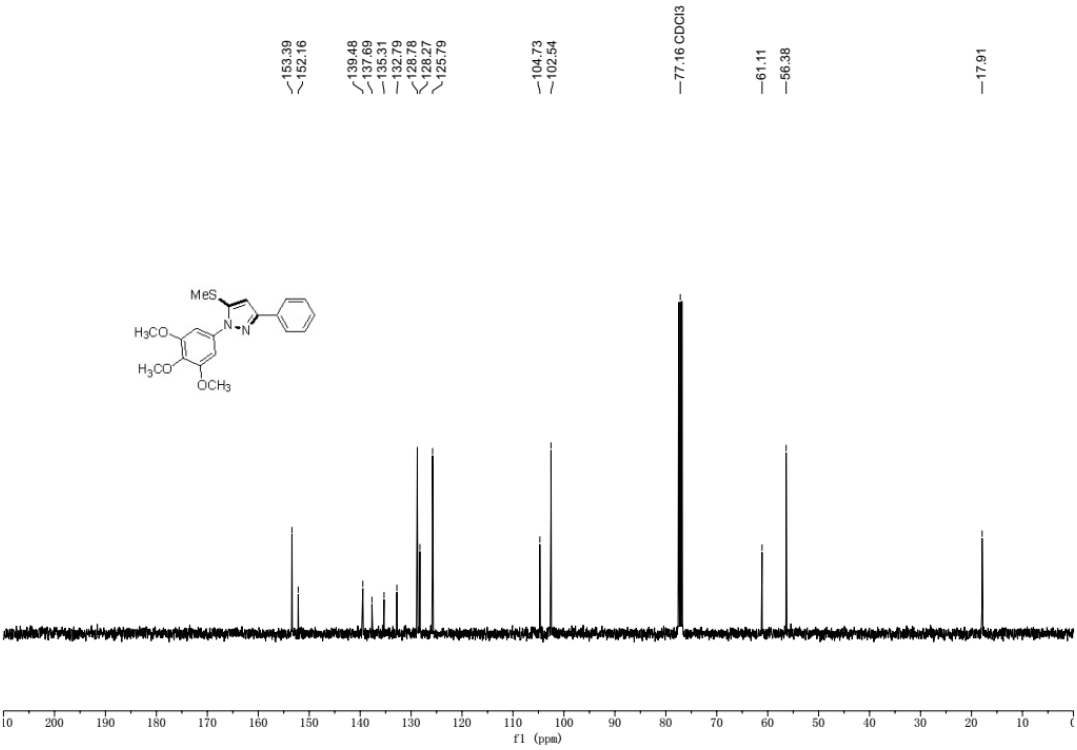


Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ag

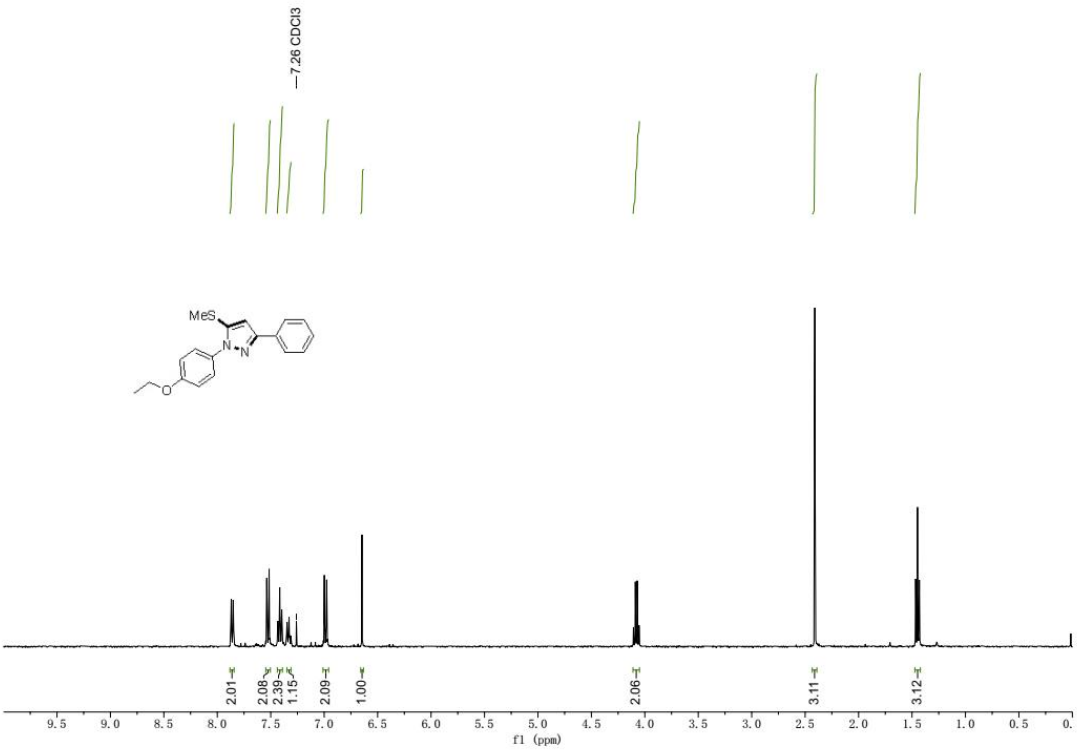


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ah

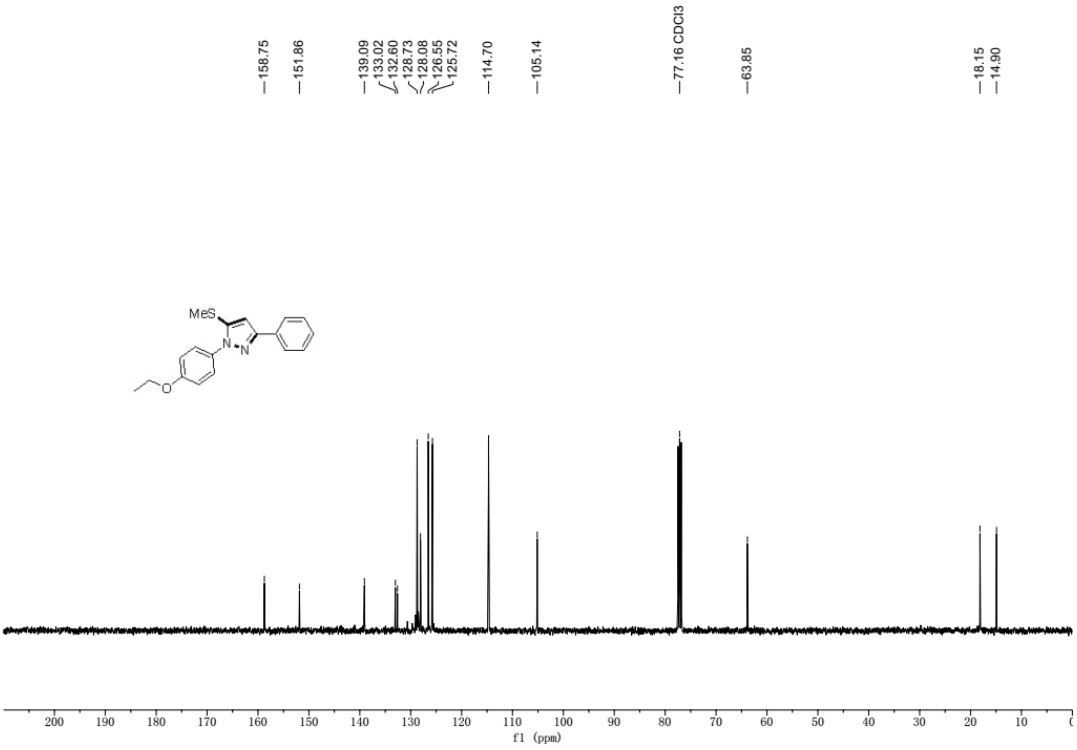


Figure S71. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ah

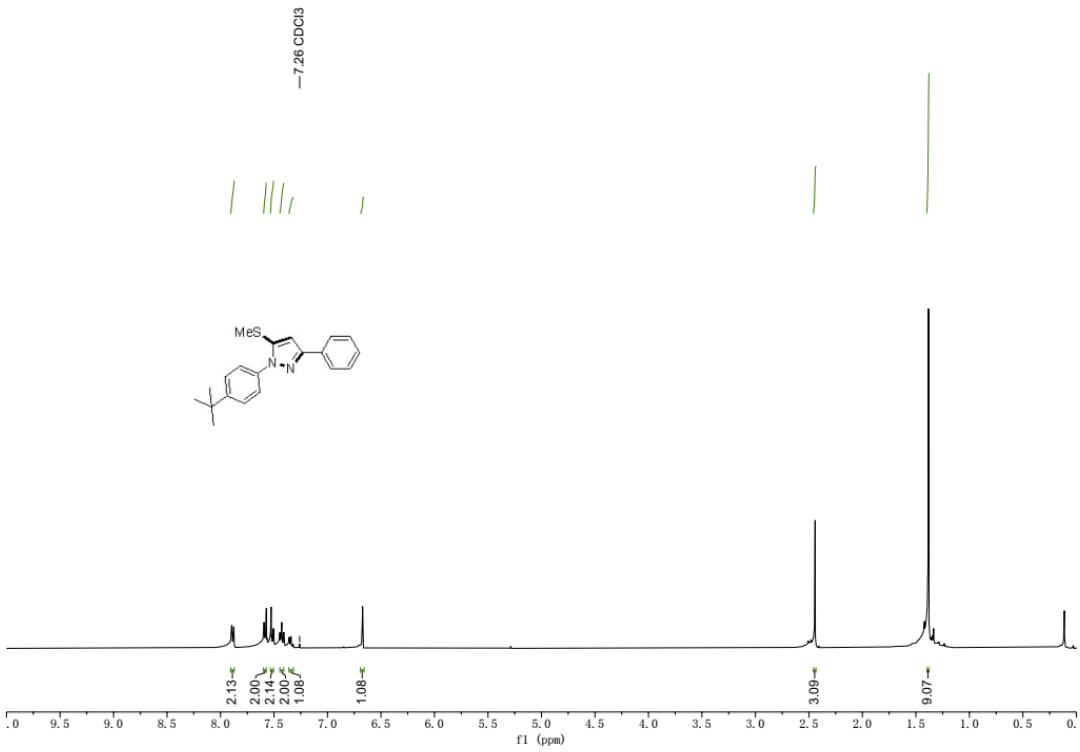


Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ai

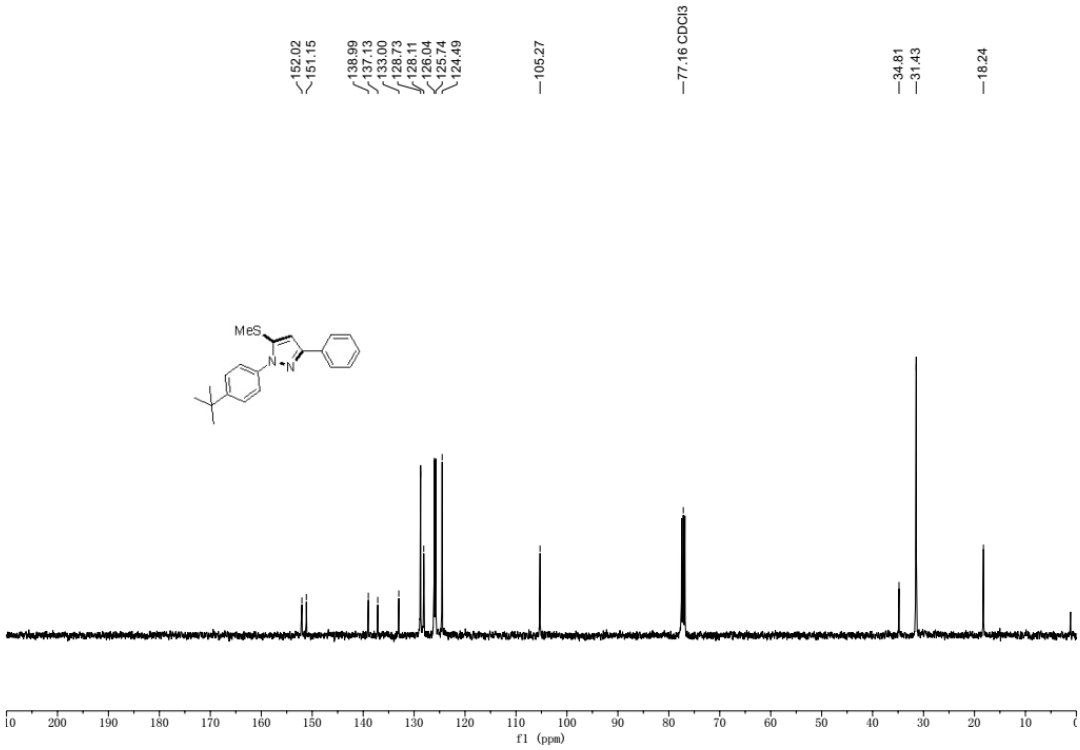


Figure S73. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ai

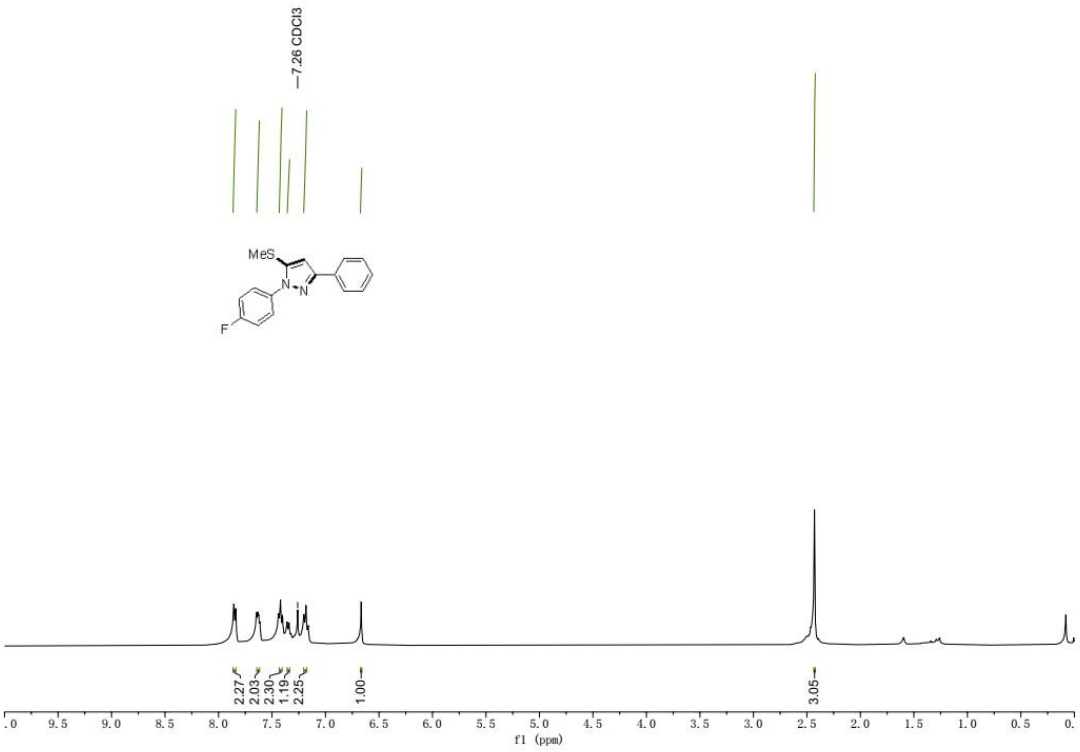


Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aj

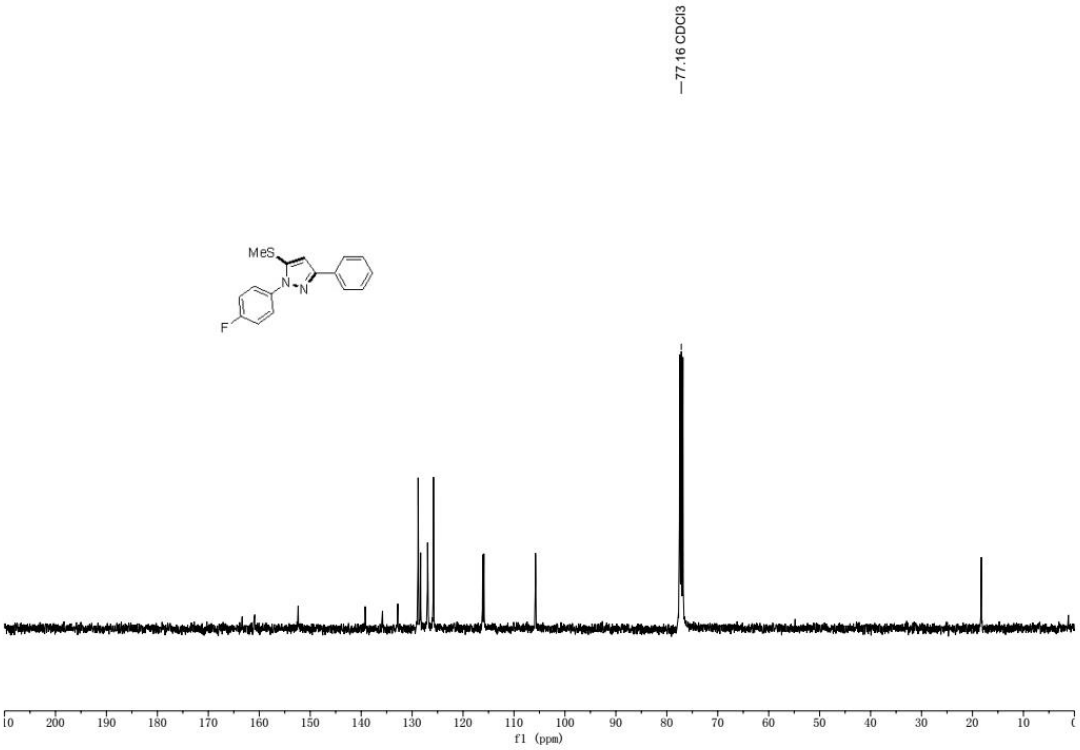


Figure S75. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aj

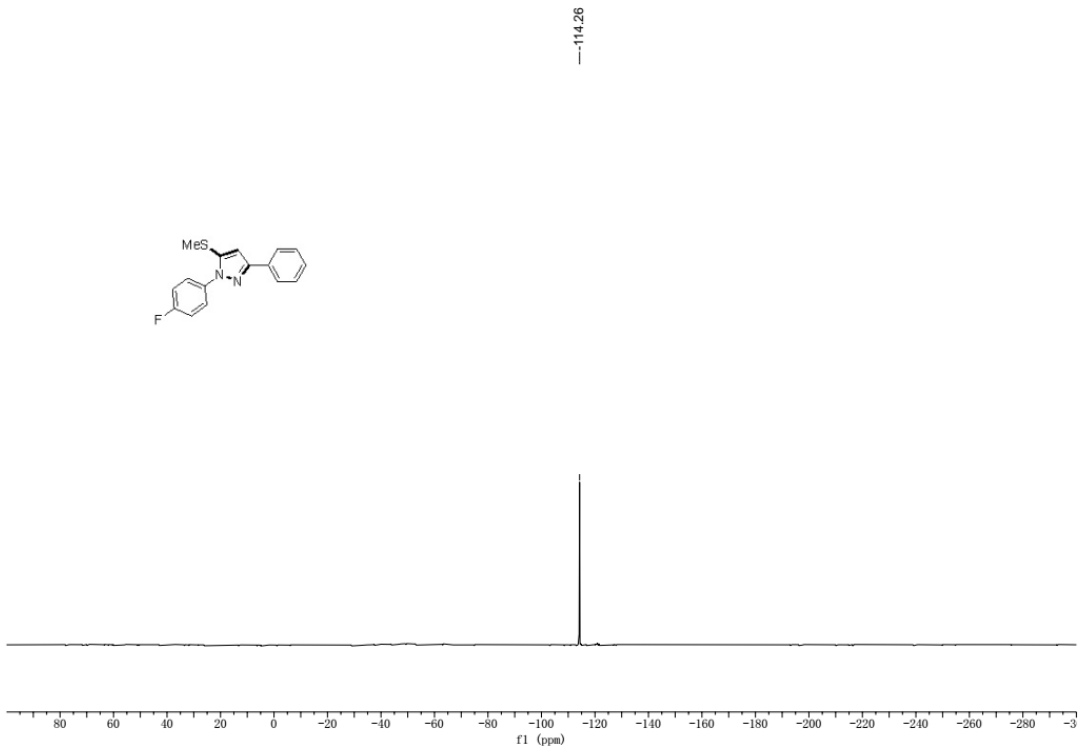


Figure S76. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (3aj)

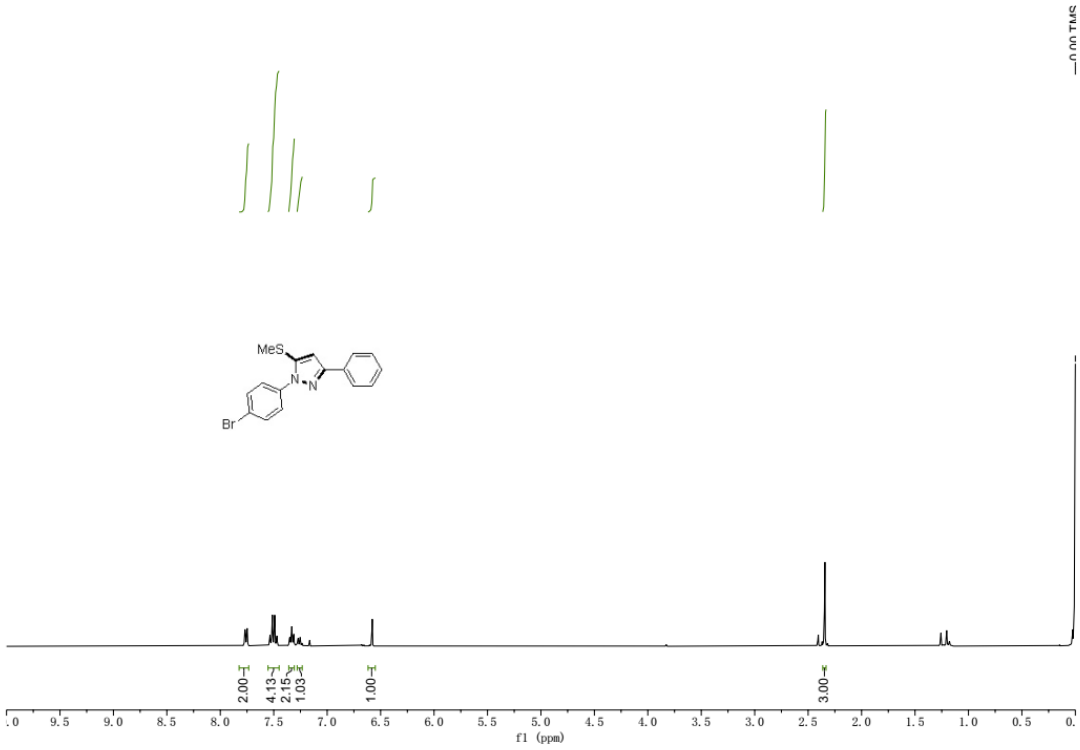


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ak

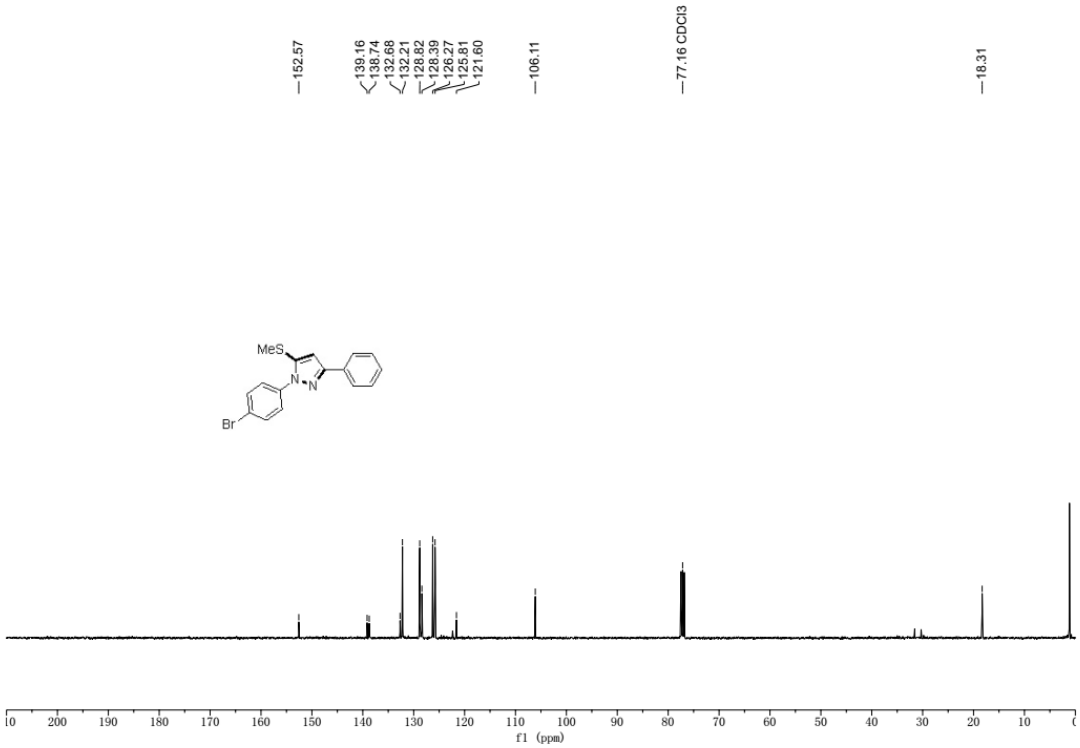


Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ak

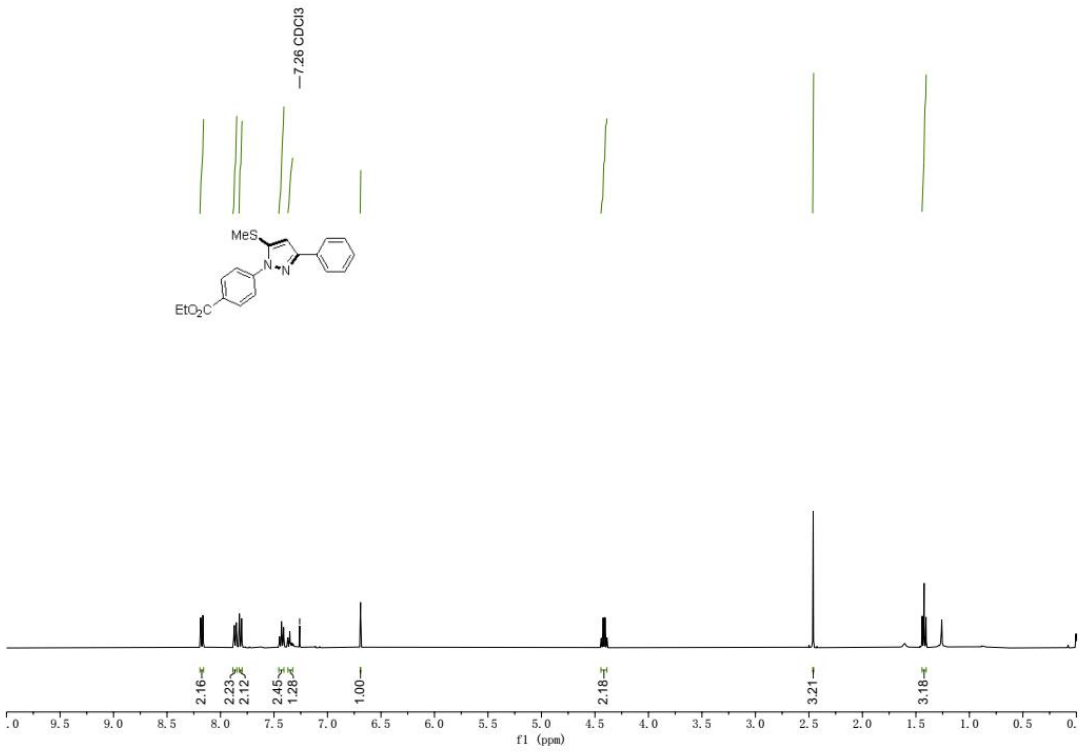


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3al

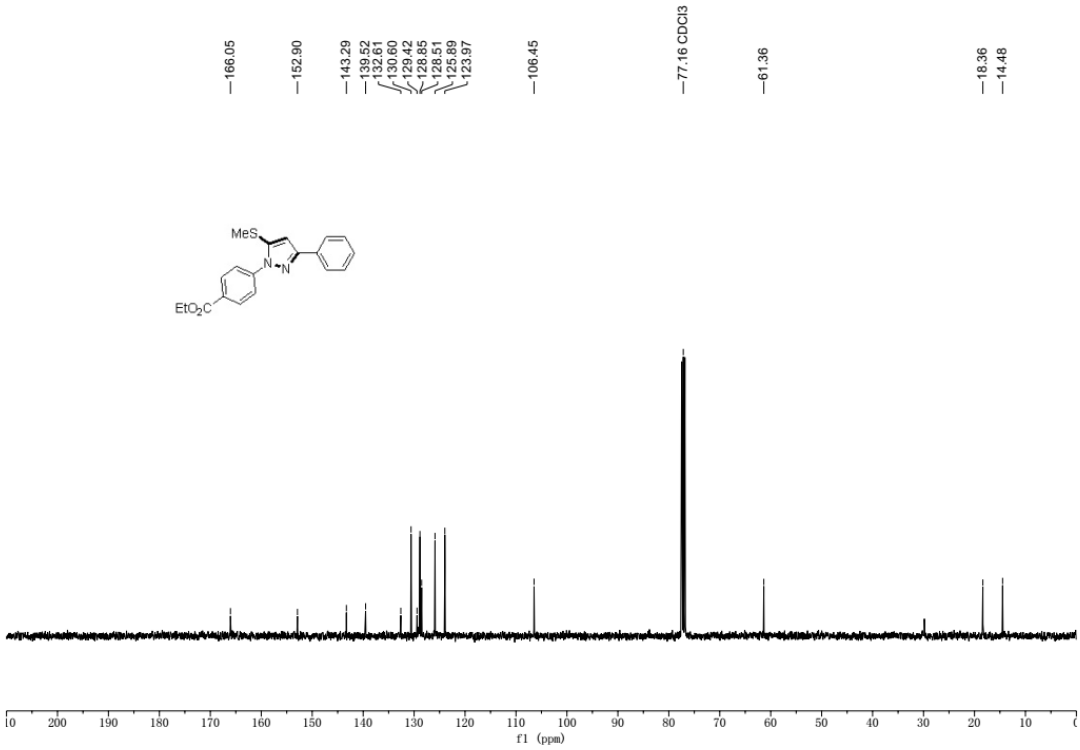


Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3al

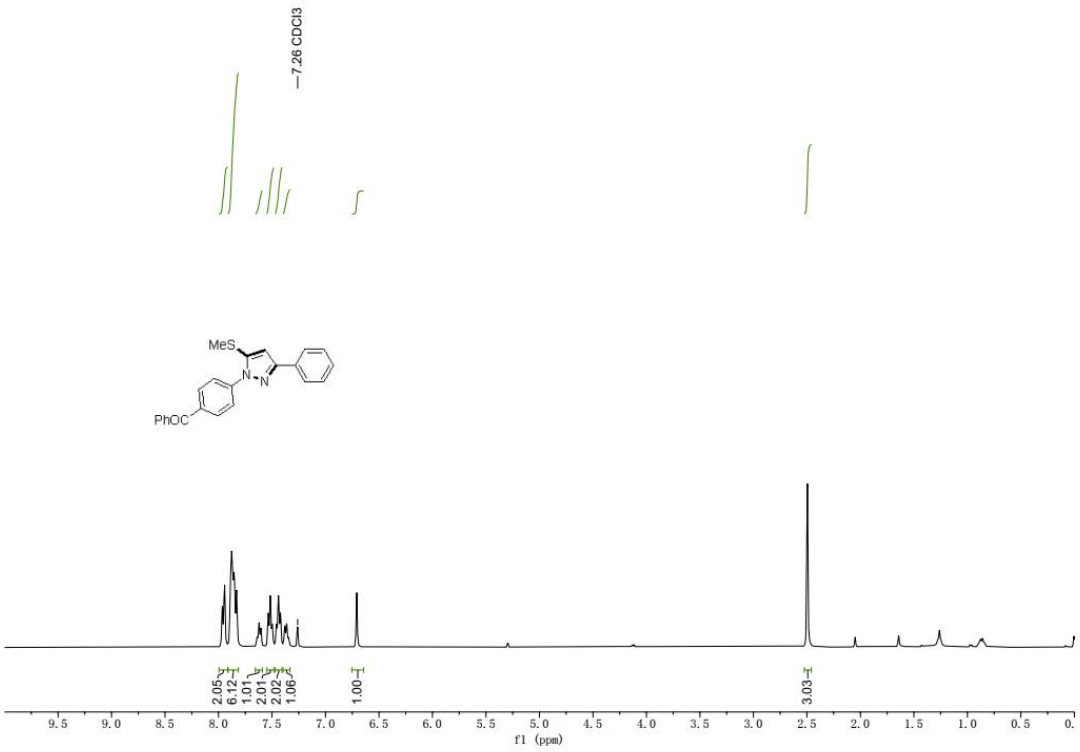


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3am

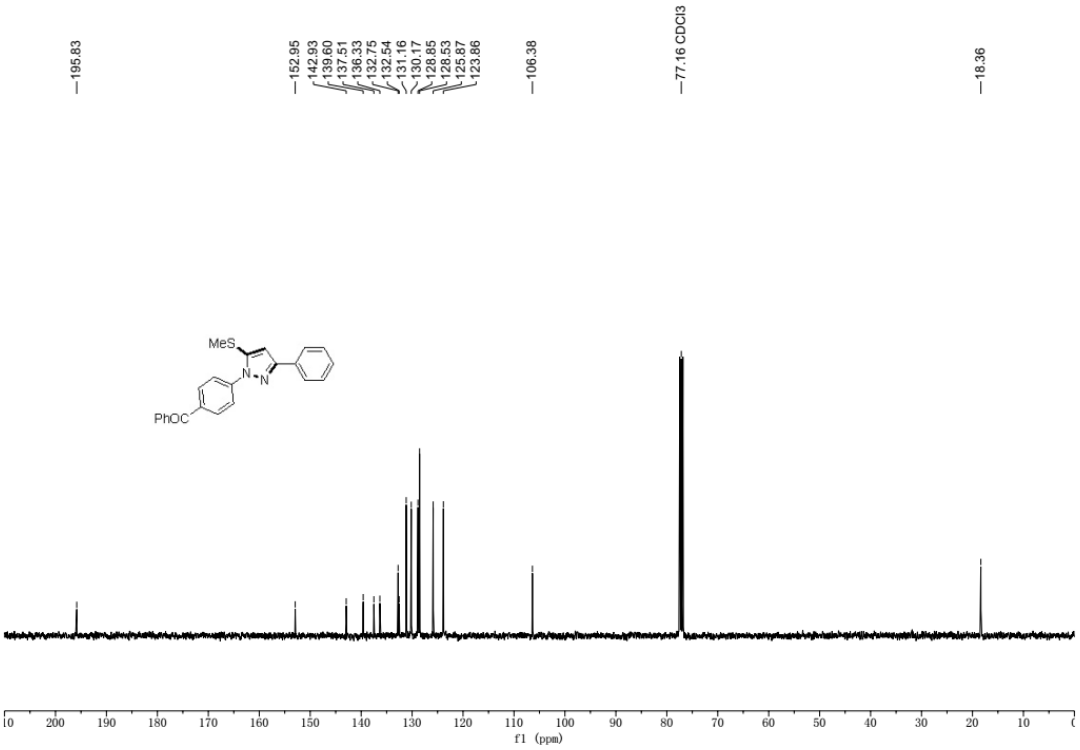


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3am

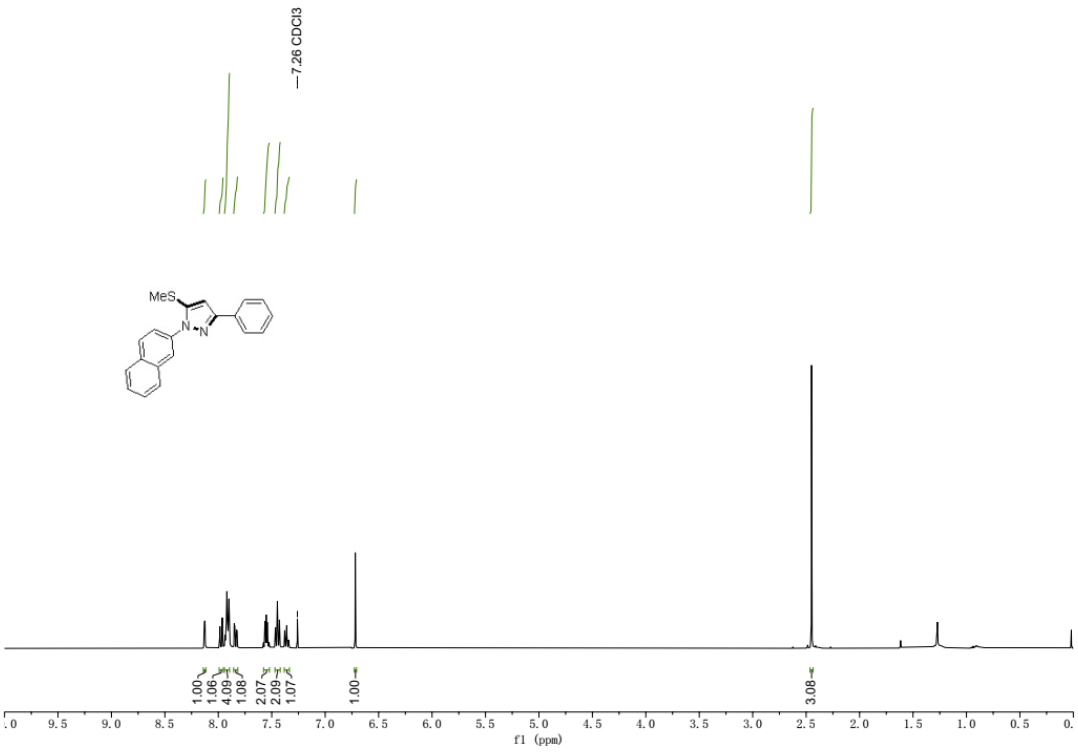


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3an

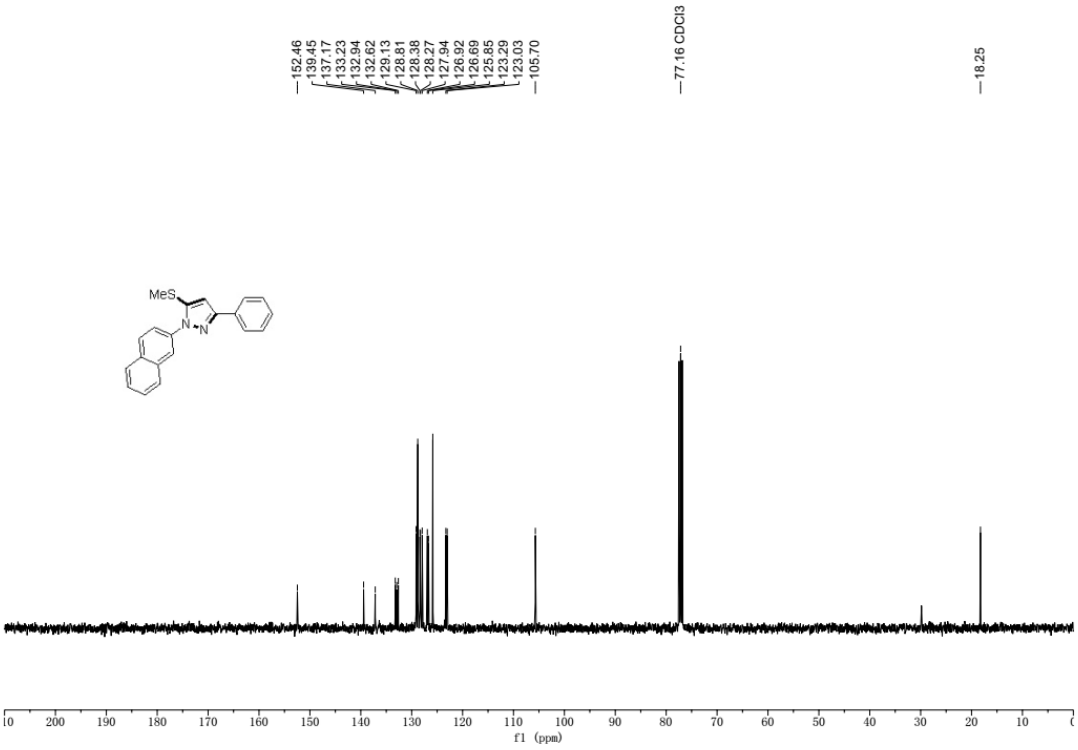


Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3an

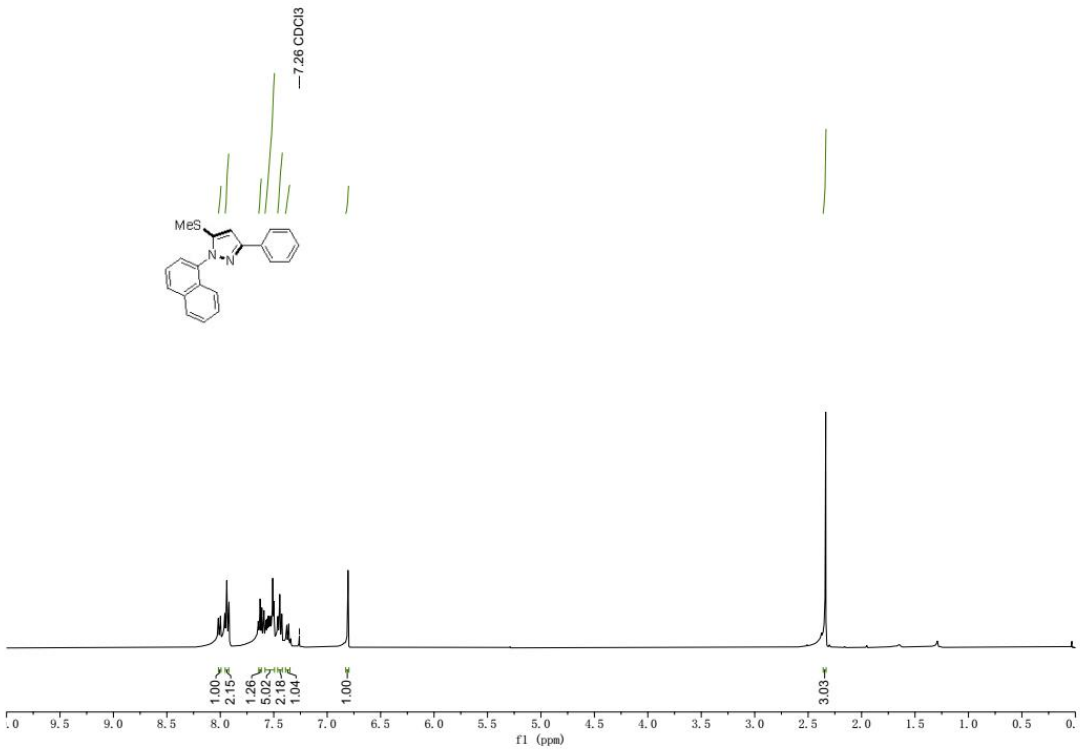


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ao

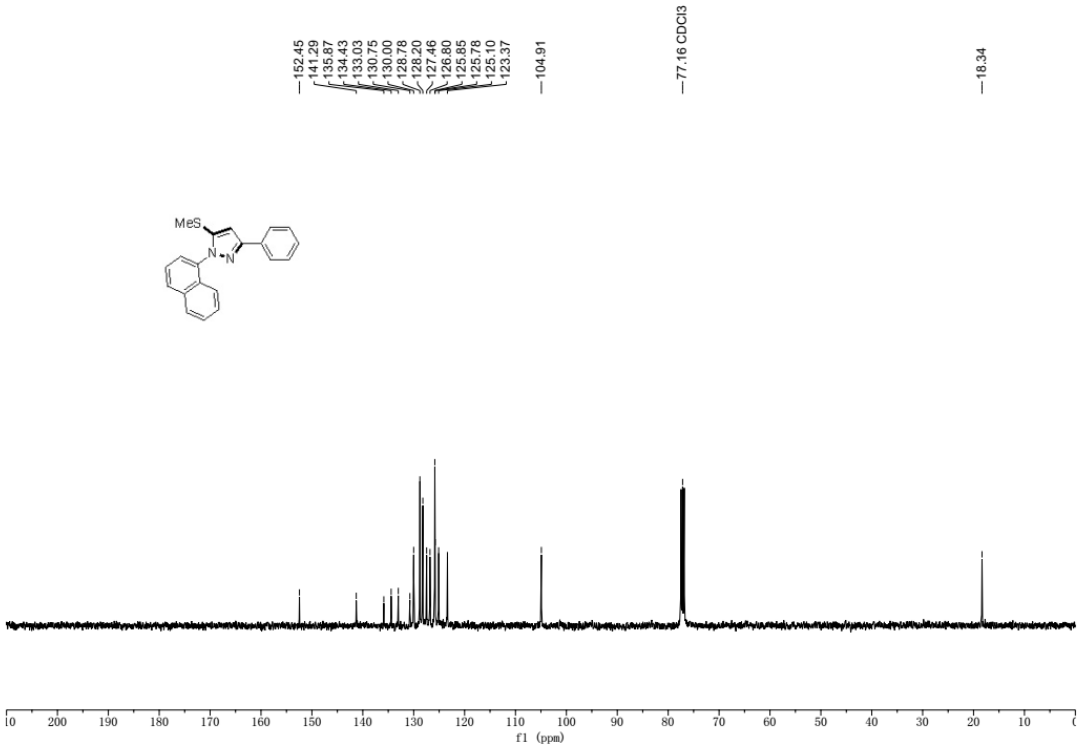


Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ao

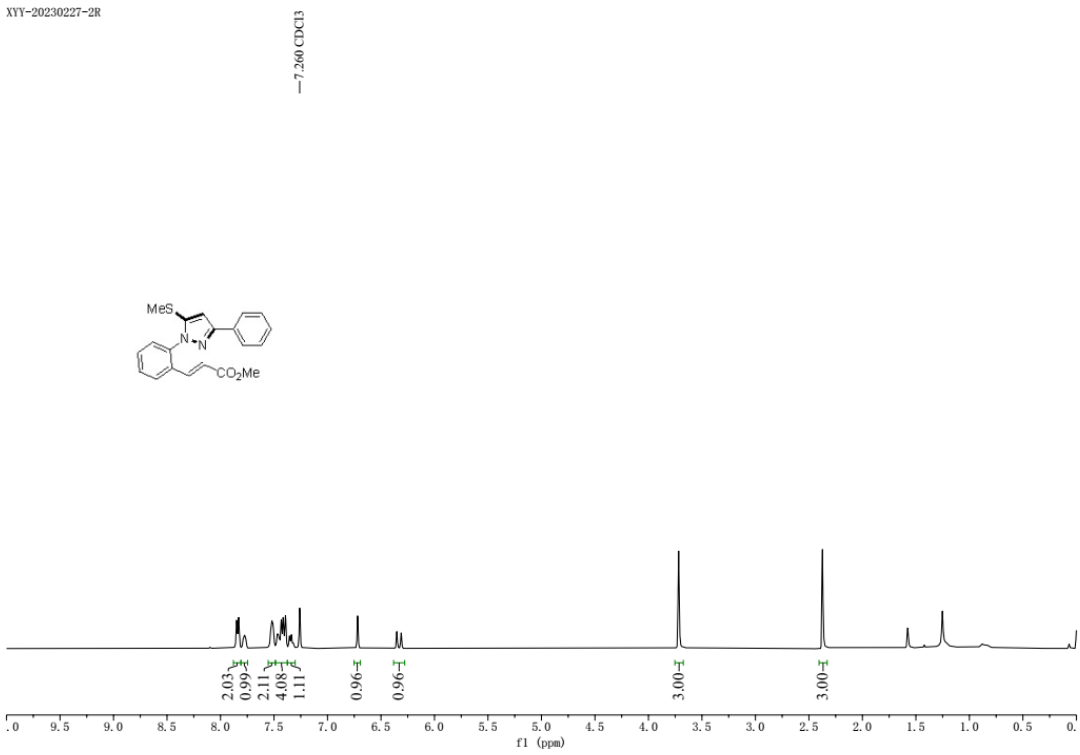


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ap

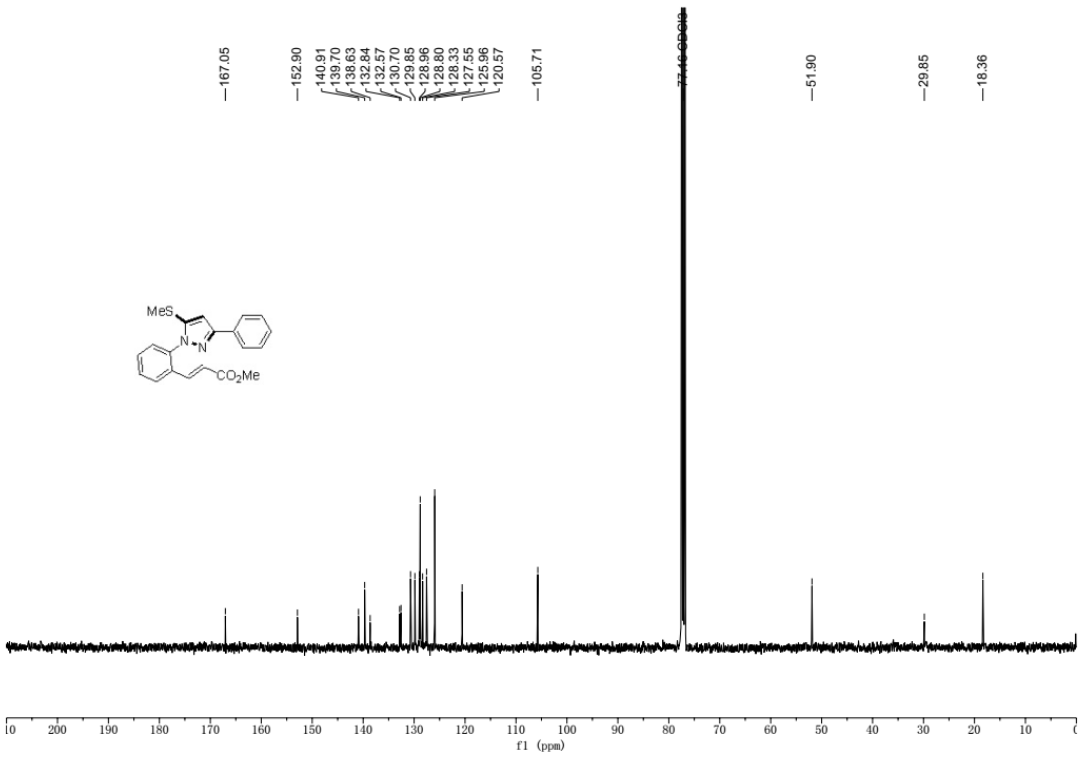


Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ap

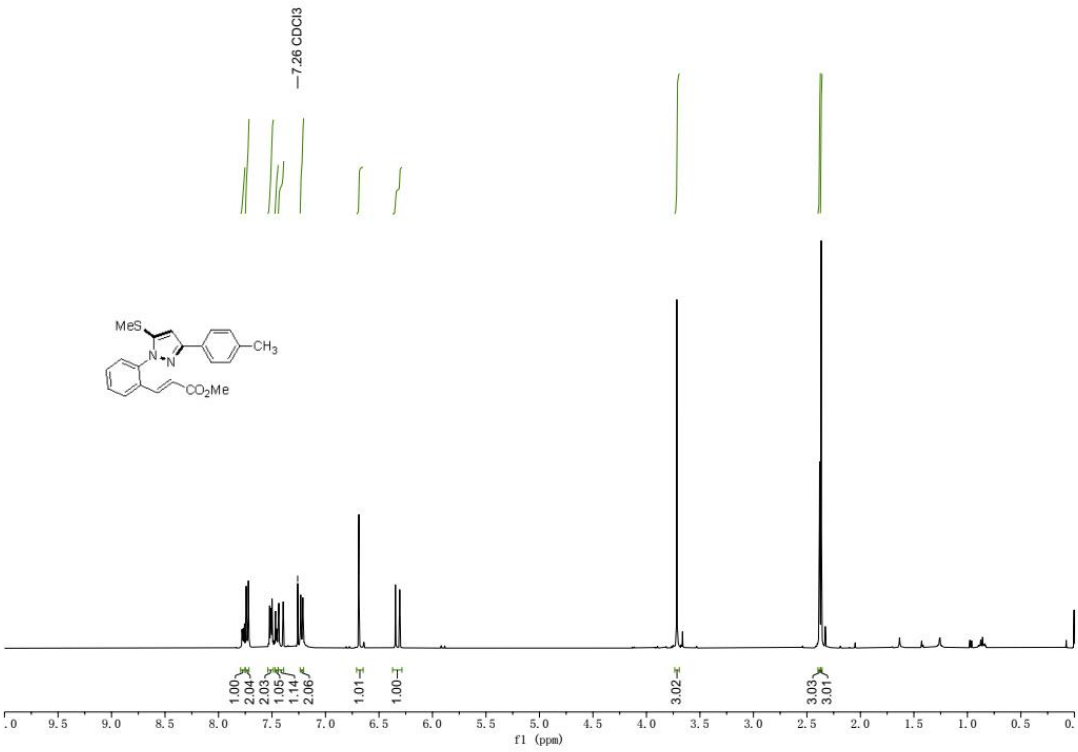


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3bp

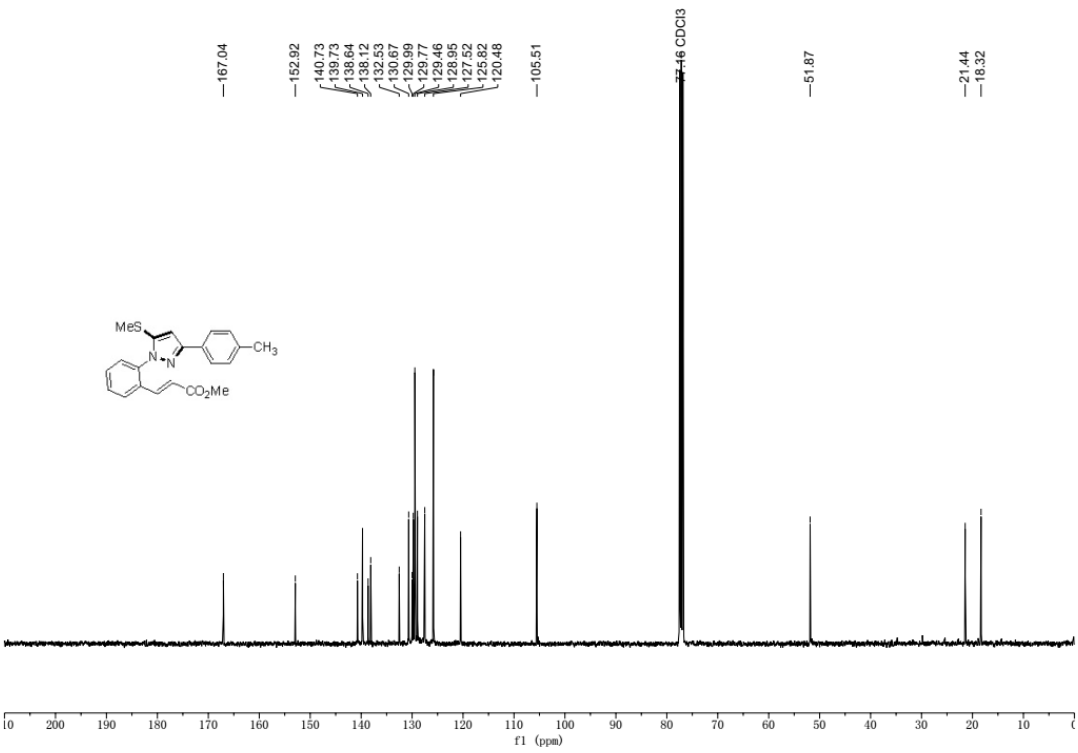


Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3bp

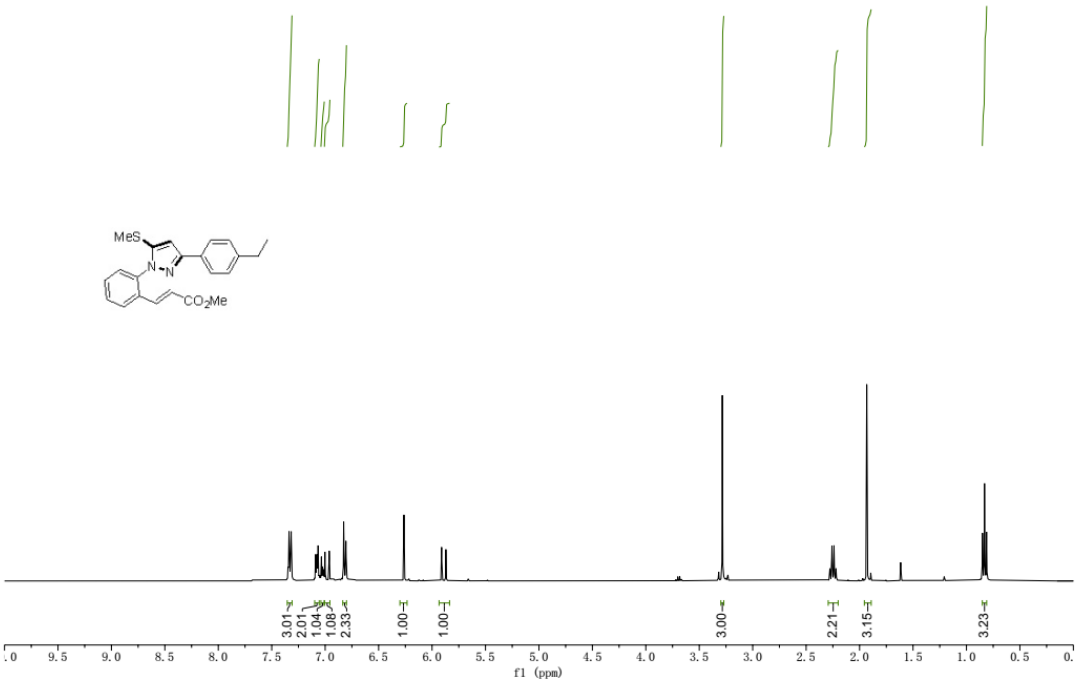


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ep

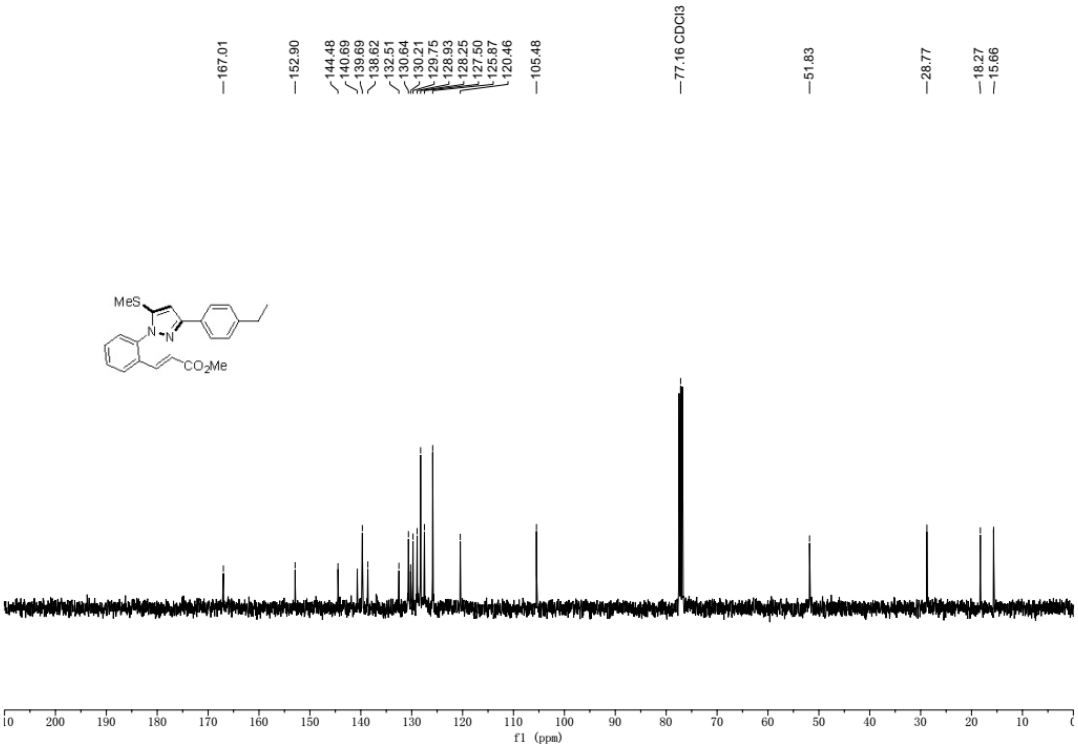


Figure S92. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ep

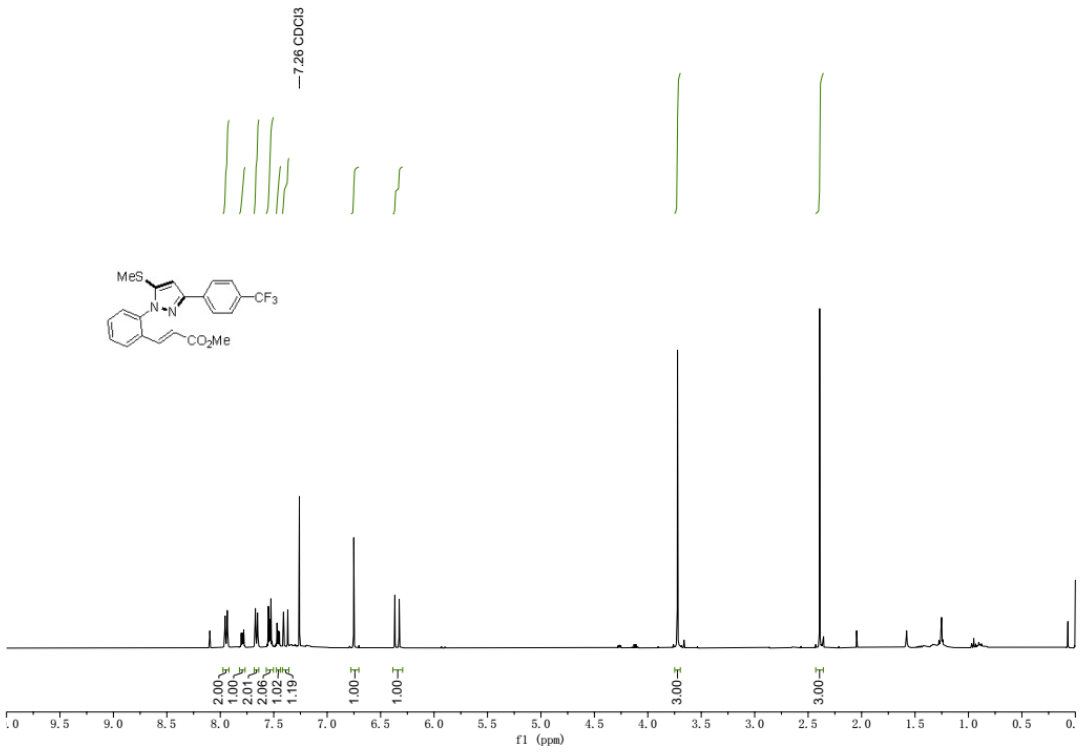


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3jp

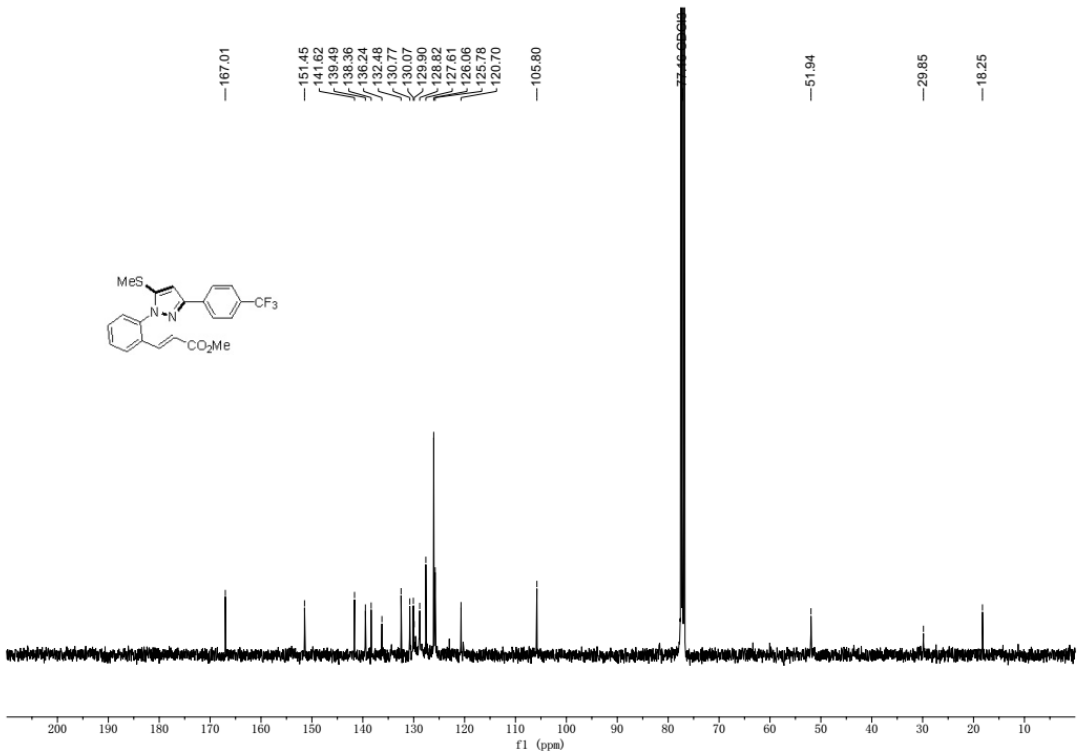


Figure S94. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3jp

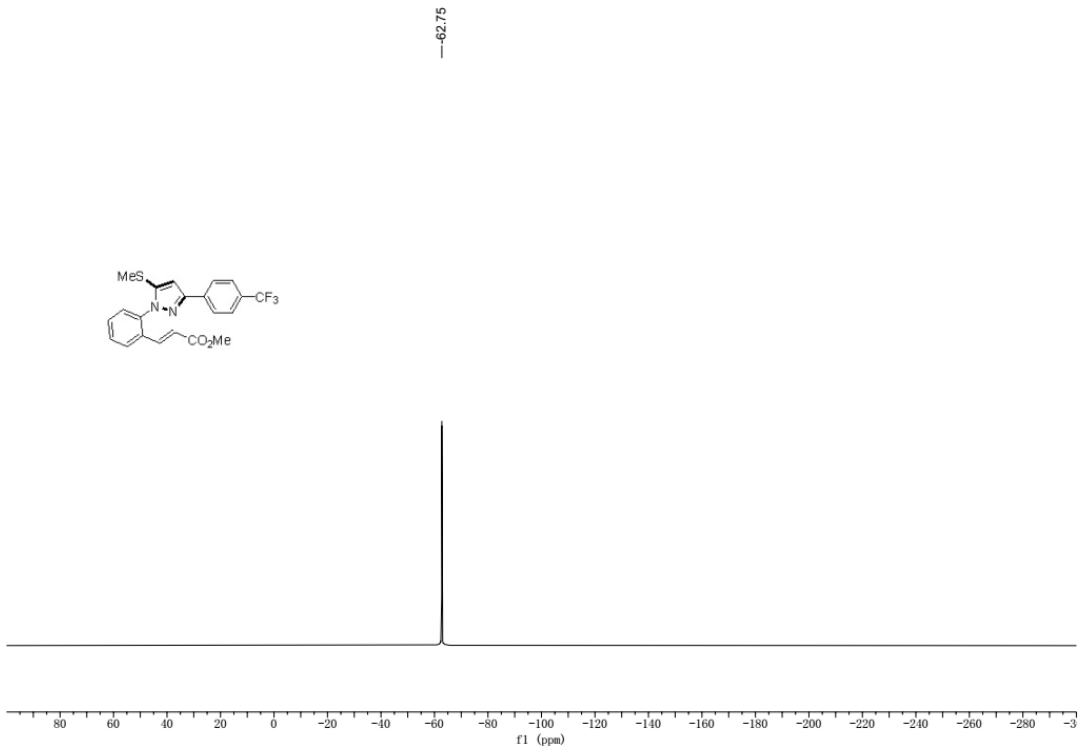


Figure S95. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (3jp)

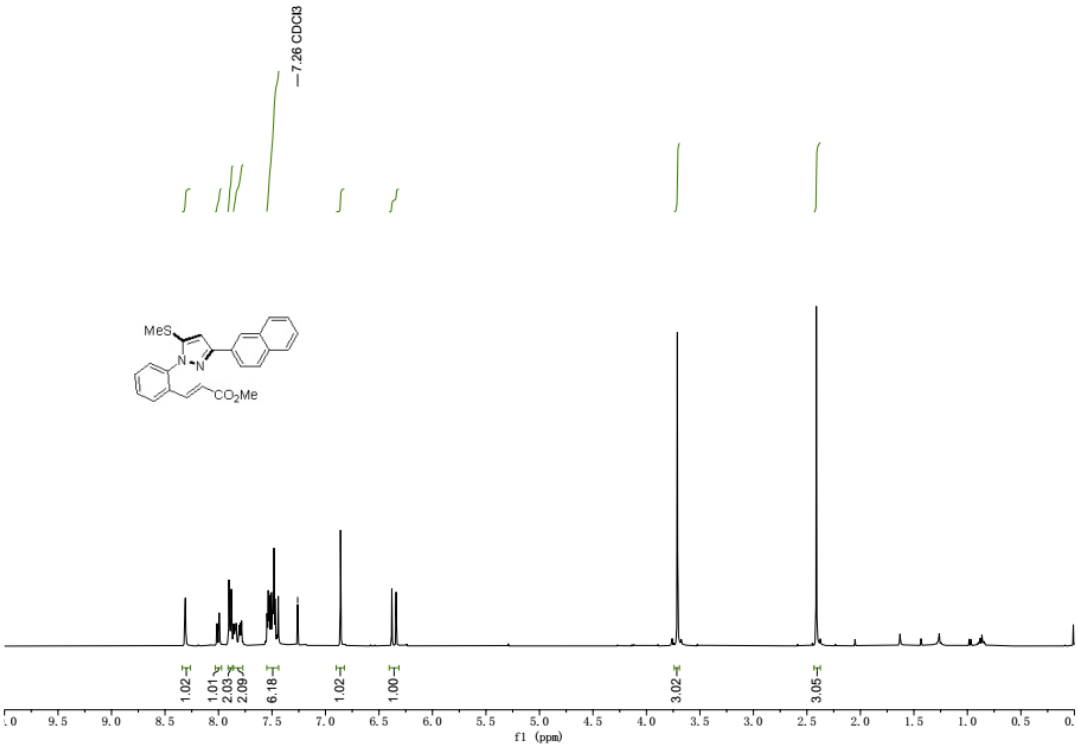


Figure S96. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3lp

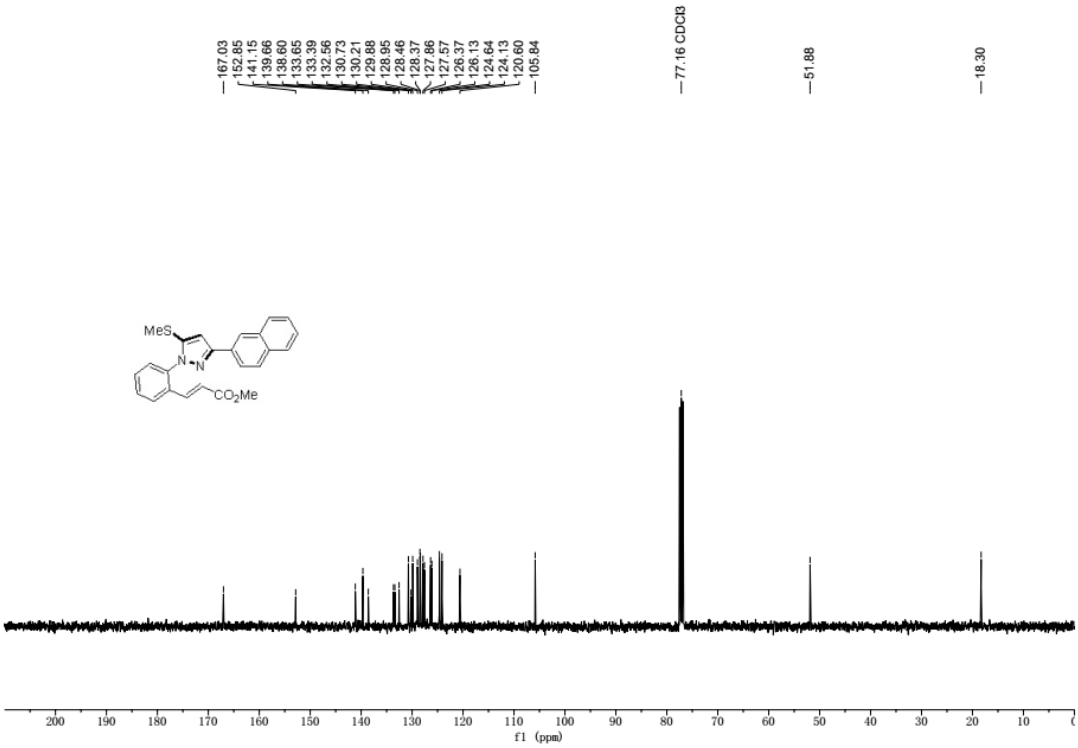


Figure S97. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3lp

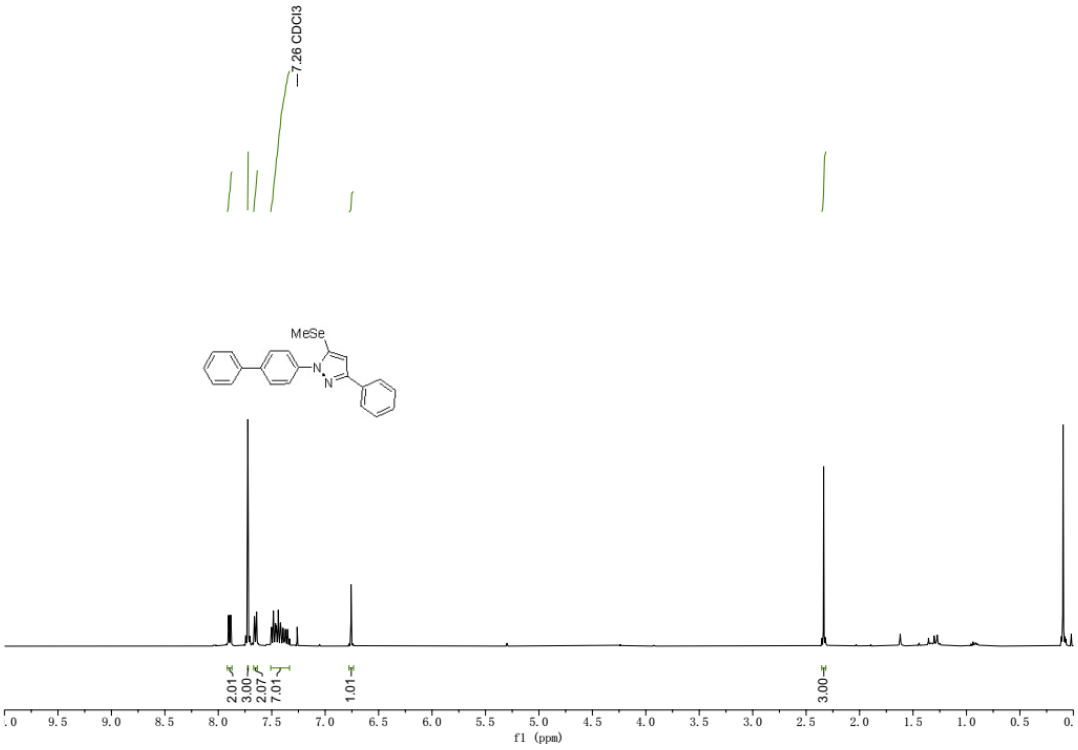


Figure S98. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5a

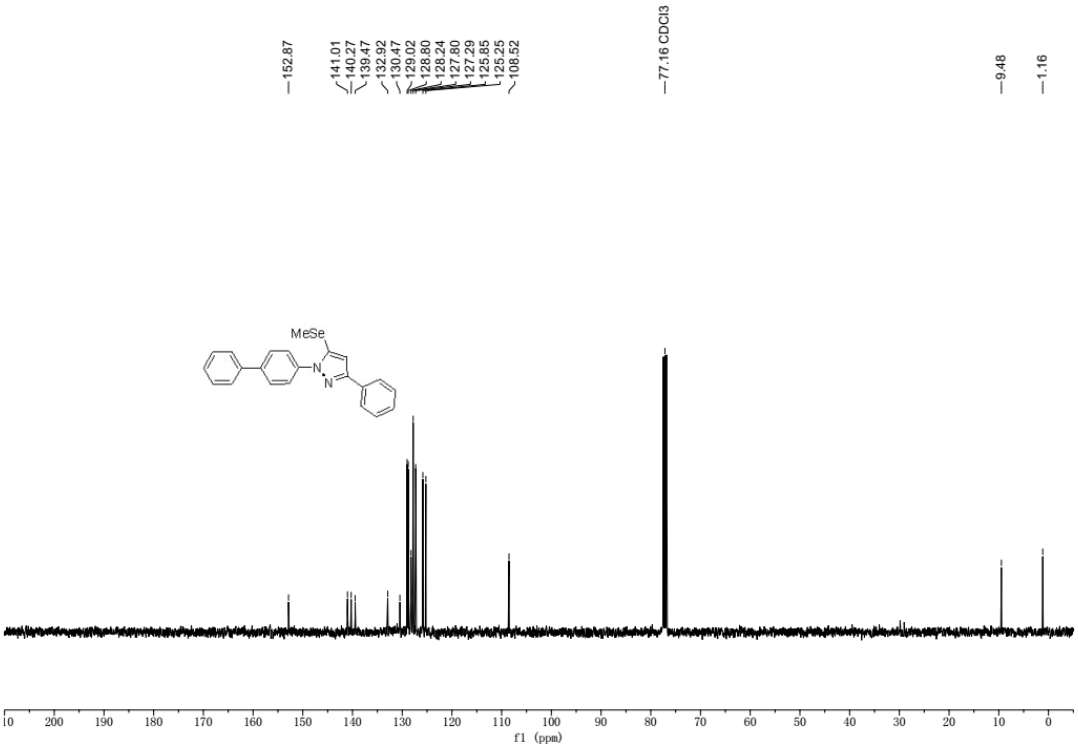


Figure S99. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5a

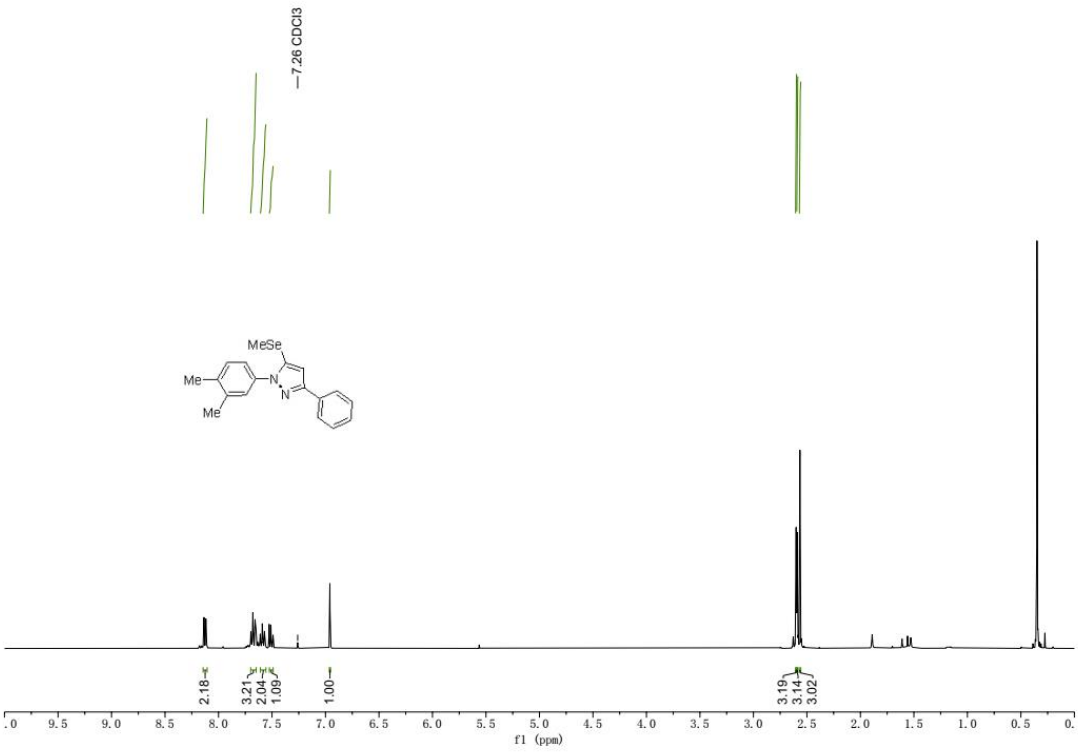


Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5b

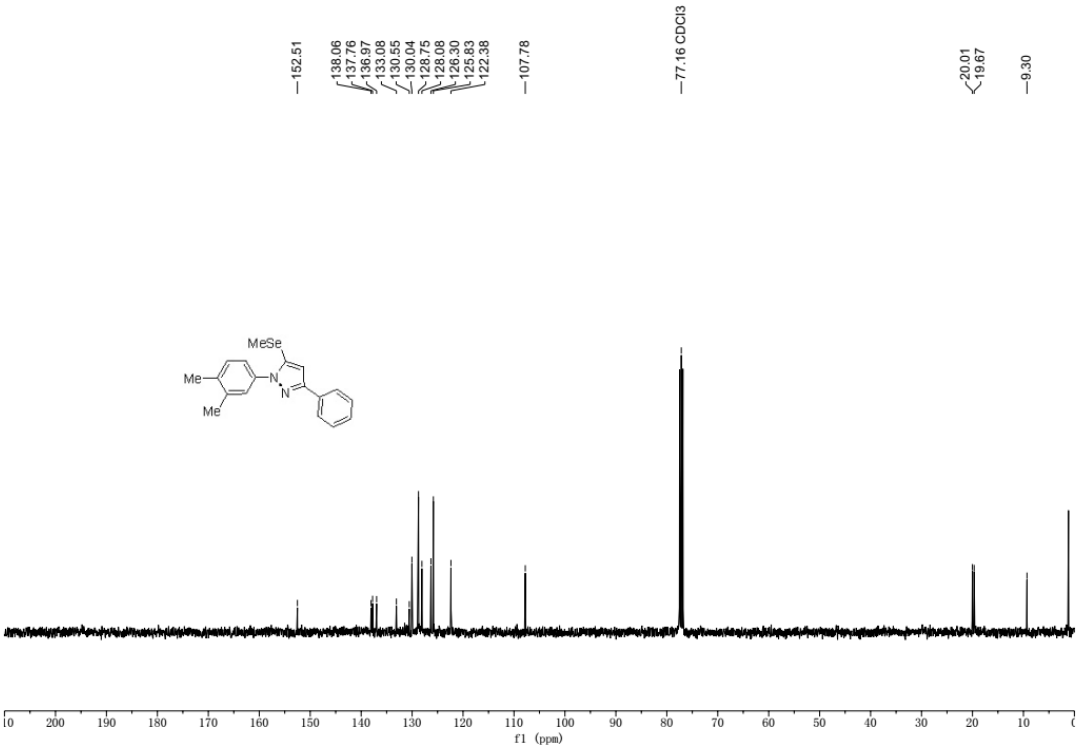


Figure S101. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5b

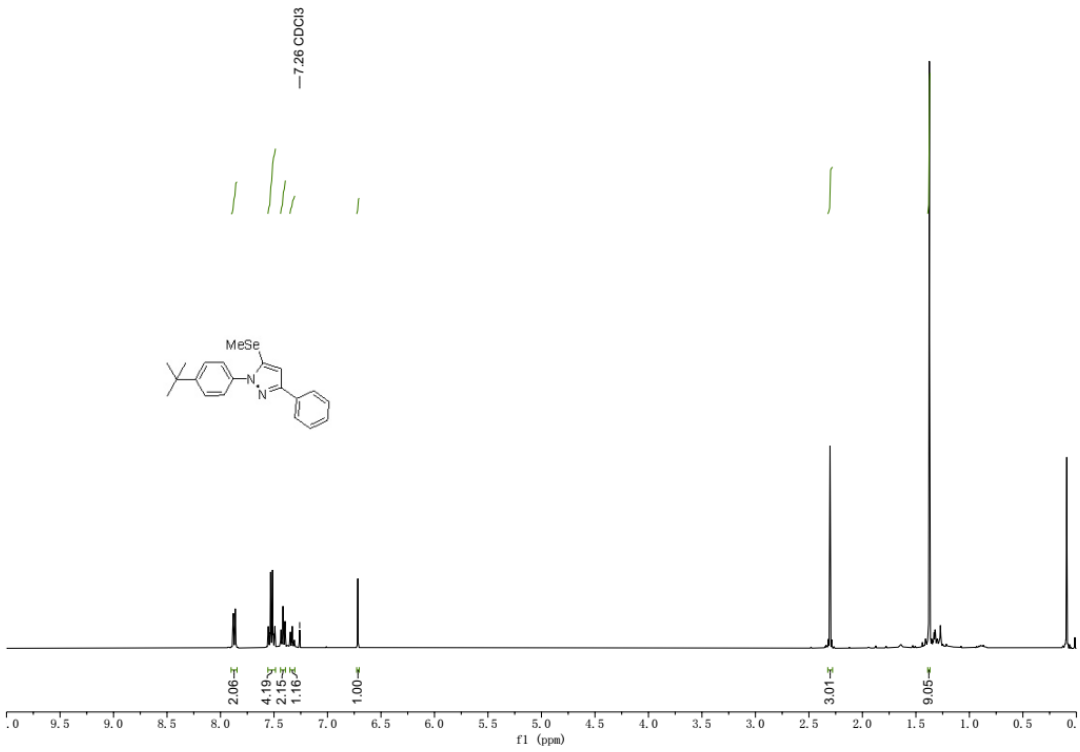


Figure S102. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5c

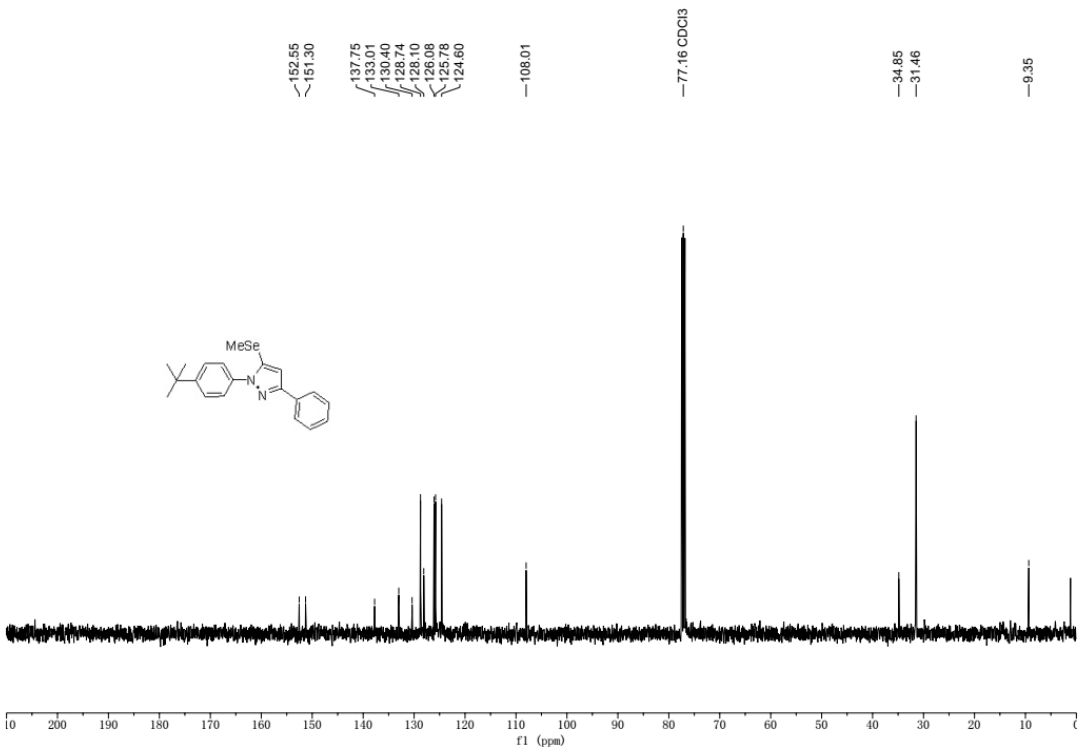


Figure S103. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5c

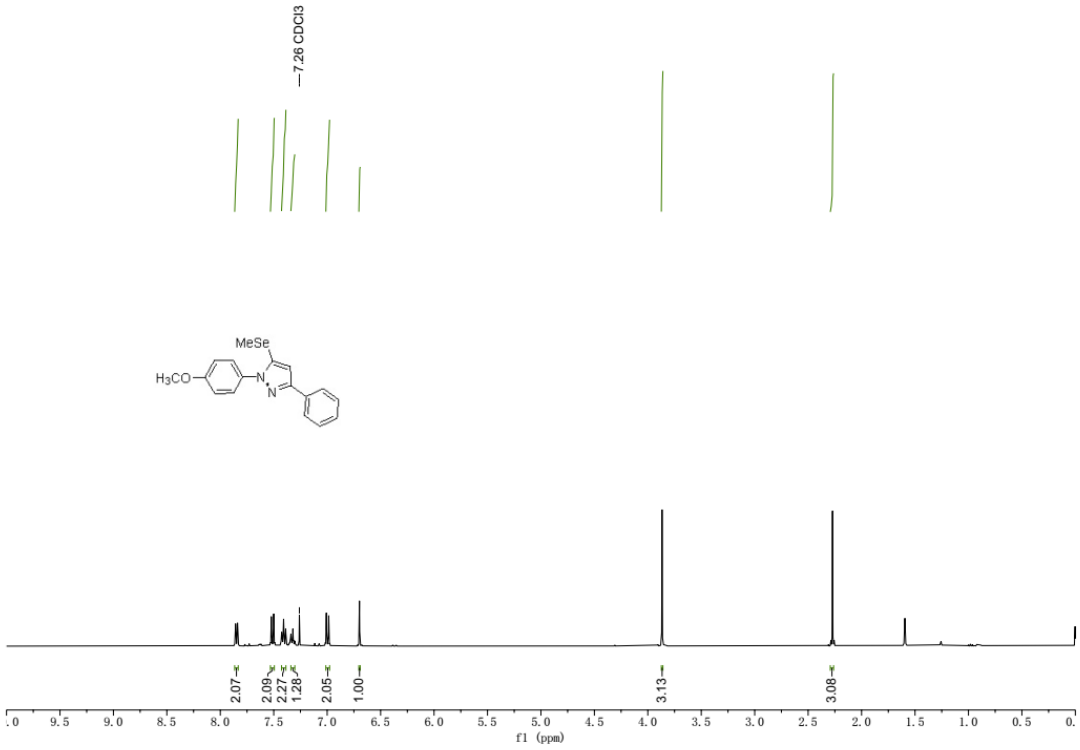


Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5d

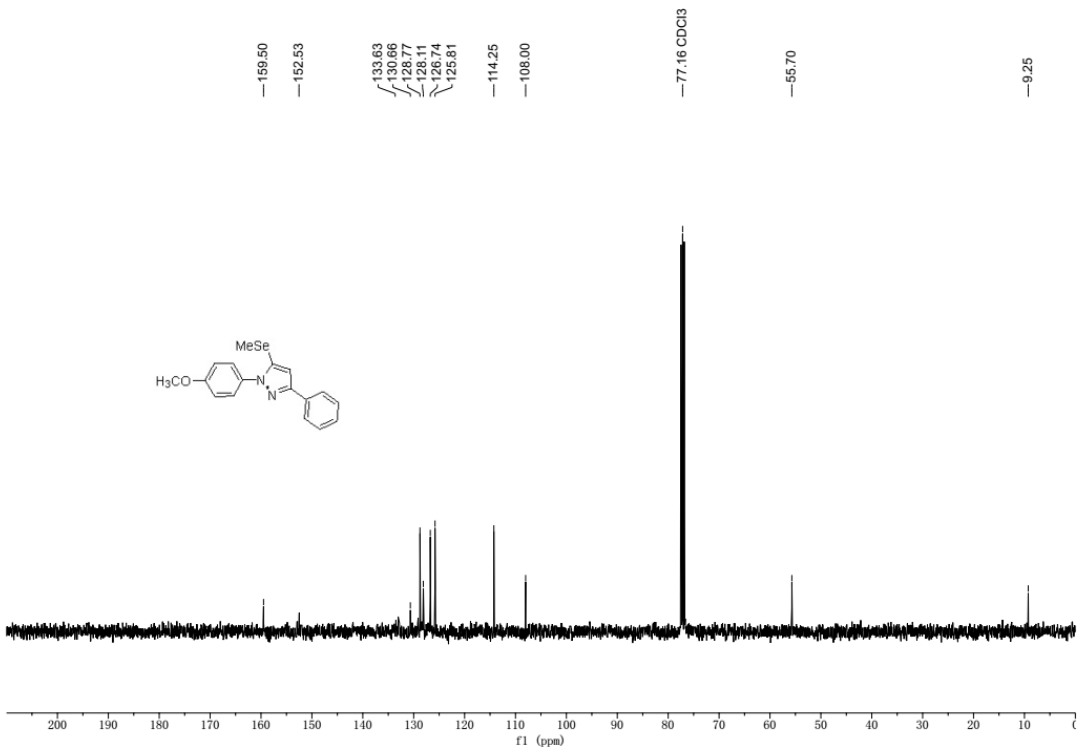


Figure S105. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5d

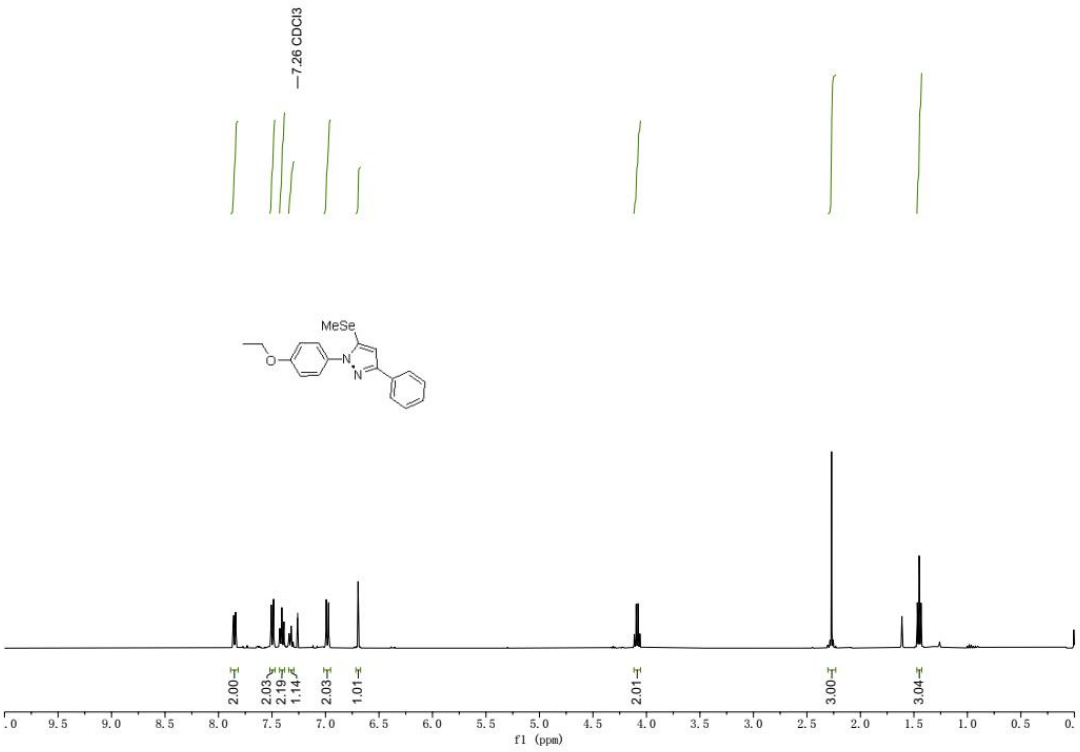


Figure S106. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5e

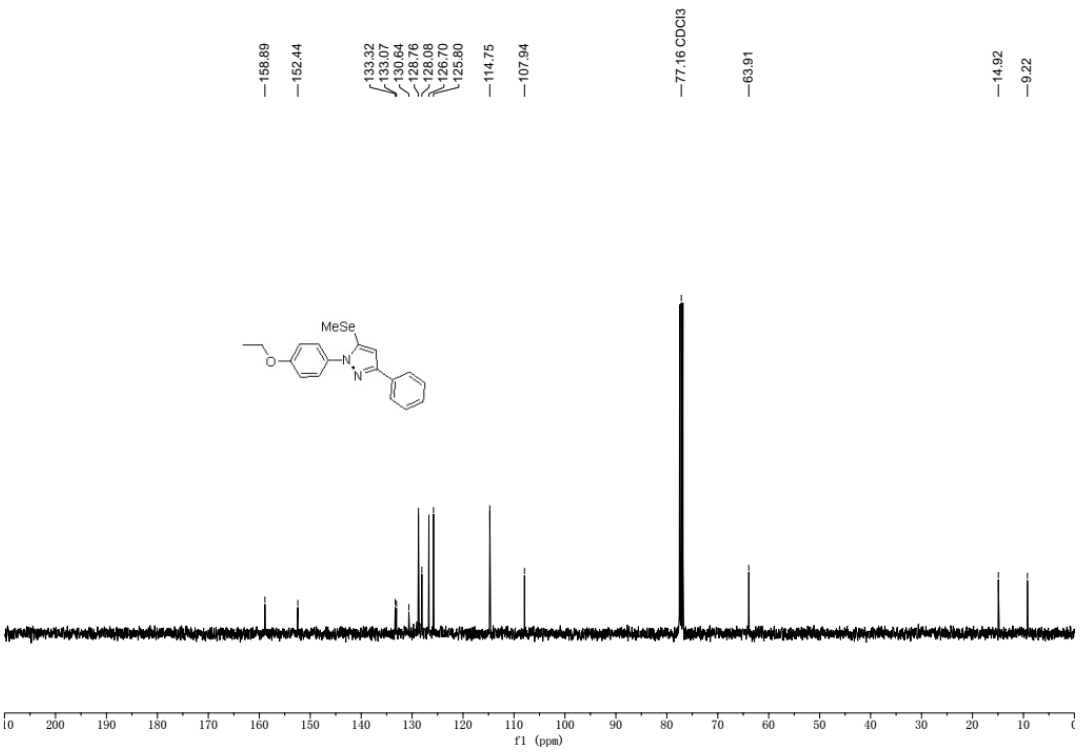


Figure S107. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5e

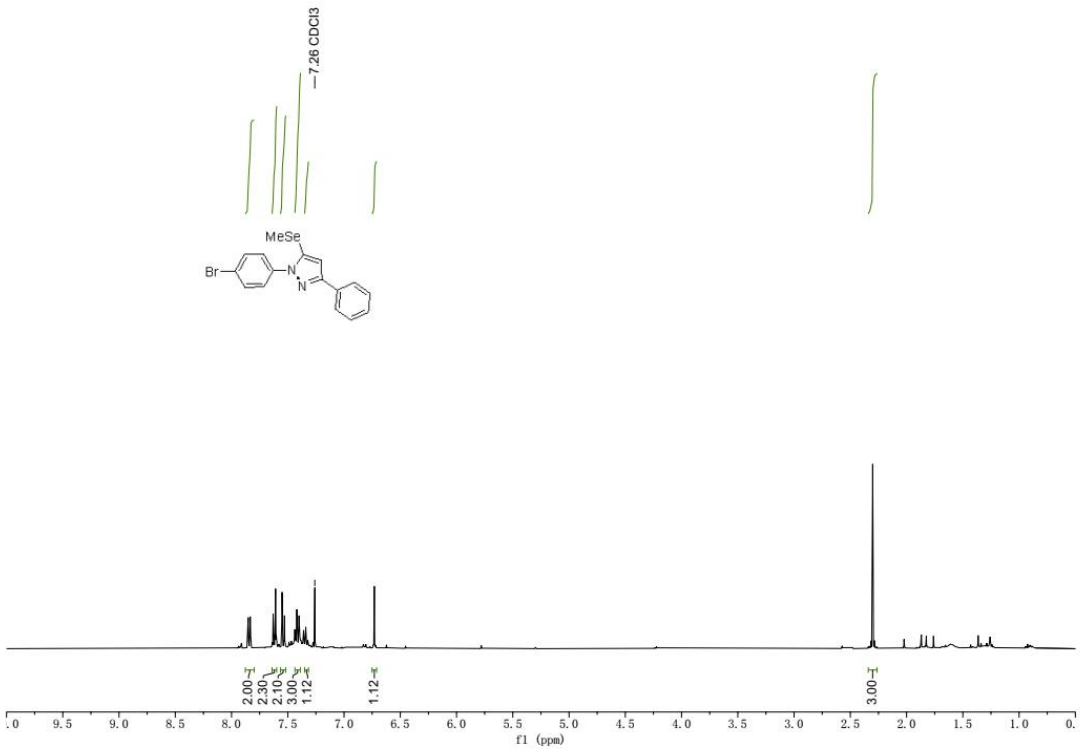


Figure S108. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5f

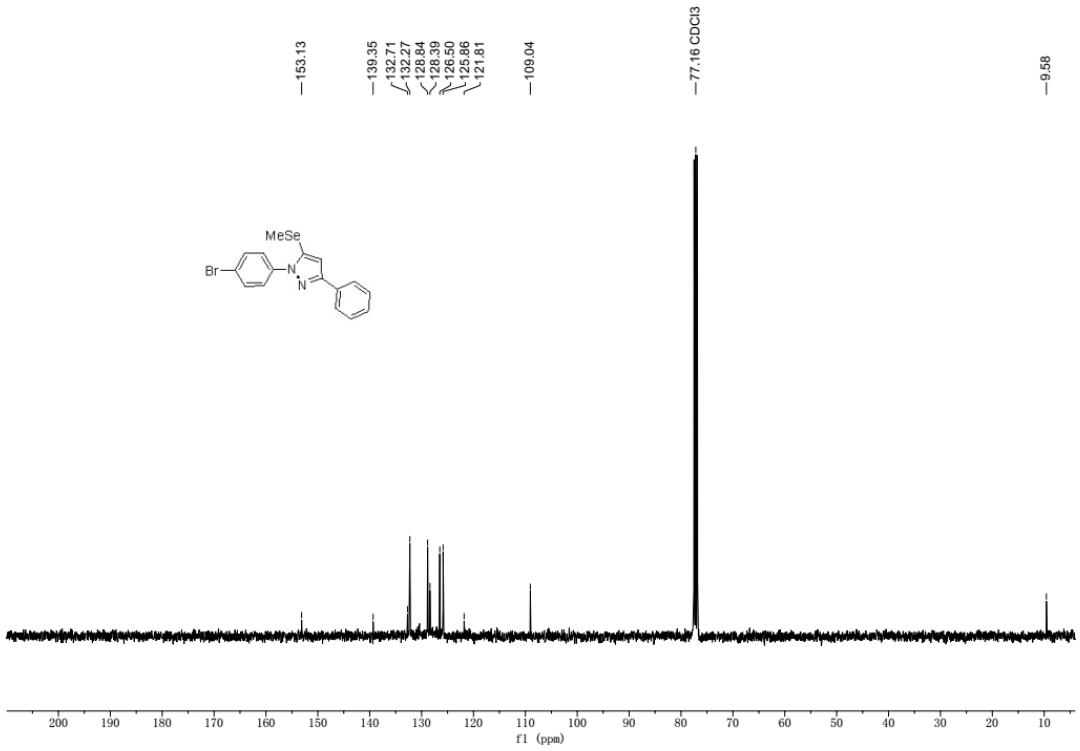


Figure S109. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5f

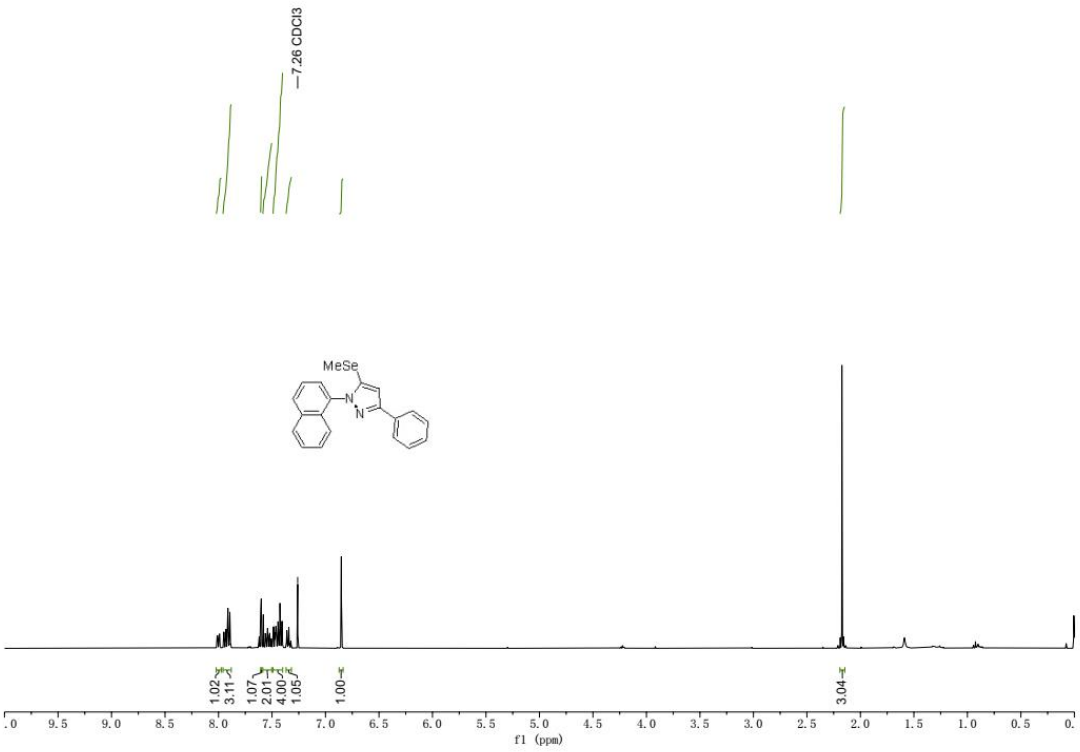


Figure S110. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5g

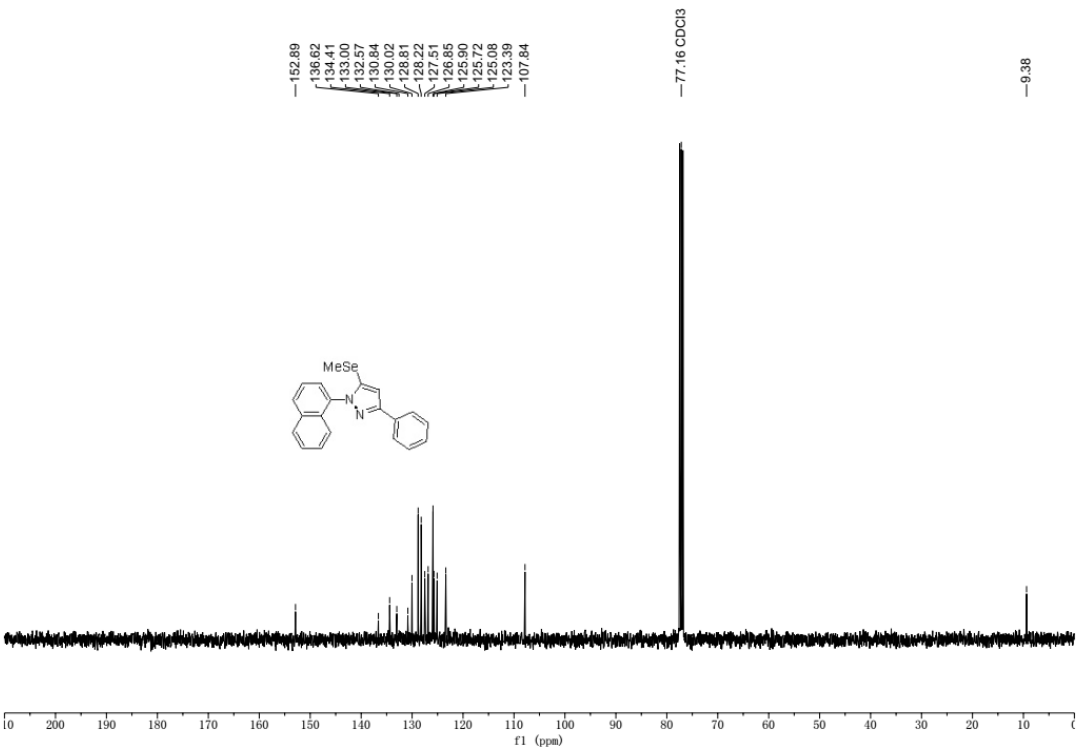


Figure S111. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5g

12. References

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